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SUPPORTING INFORMATION

Title: An Efficient Synthesis of Bicyclo[3.3.0]oct-2-en-4-ones and 2-Azabicyclo[3.3.0]oct-7-en-6-ones via β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complexes
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Electronic Supporting Information

An Efficient Synthesis of Bicyclo[3.3.0]oct-2-en-4-ones and 2-Azabicyclo[3.3.0]oct-7-en-6-ones via β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complexes

Heiko Schirmer, Frank J. Funke, Stephan Müller, Mathias Noltemeyer, Bernhard Flynn, and Armin de Meijere*

Pentacarbonyl[(2E)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]-chromium (**2a**): 2-(But-3'-ynyl)-1,3-dioxolane (**1a**) (1.52 g, 12.0 mmol) in 80 ml of THF was treated with *n*-butyllithium (5.1 ml, 12 mmol), hexacarbonylchromium (2.64 g, 12.0 mmol), triethyloxonium tetrafluoroborate (2.66 g, 14.0 mmol) and dimethylamine (1 equiv. as a gas) according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 3 : 1, column 40 × 4 cm) 3.42 g (68%) of **2a** (R_f = 0.23, diethyl ether) was obtained as yellow crystals, m.p. 78 °C. – IR (KBr): ν = 2889 cm^{-1} (C–H), 2045 (C=O), 1916 (C=O), 1892 (C=O), 1537, 1477, 1434, 1268, 1203, 1123, 1059, 927, 879, 823, 666. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.21 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.59–1.71 (m, 2 H, 5-H), 2.10 [s, 6 H, $N(CH_3)_2$], 2.53 (t, ^3J = 7.8 Hz, 2 H, 4-H), 3.34 (m_c, 4 H, OCH_2CH_2O), 4.62 (t, ^3J = 4.5 Hz, 1 H, 2'-H), 4.71 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.39 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.50 (+, OCH_2CH_3), 25.36 (–, C-5), 31.29 (–, C-4), 39.97, 41.72 [+, $N(CH_3)_2$], 65.10 (–, OCH_2CH_2O), 74.06 (–, OCH_2CH_3), 103.17 (+, C-2'), 117.85 (+, C-2), 158.05 (C_{quat}, C-3), 219.32, 224.41 (C_{quat}, C=O), 286.86 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 419 (3) [M^+], 391 (8) [M^+ – CO], 335 (22) [M^+ – 3 CO], 307 (9) [M^+ – 4 CO], 279 (69) [M^+ – 5 CO], 247 (4), 219 (100) [M^+ – 5 CO – $(OCH_2)_2$], 207 (24), 188 (22), 173 (20), 166 (23), 154 (10), 138 (15), 122 (17), 110 (48), 95 (19), 80 (7), 52 (35) [Cr^+], 45 (5).

Pentacarbonyl{(2E)-3-[(1',3'-dioxolan-2'-ylmethyl)methylamino]-1-ethoxy-2-hexen-1-ylidene}chromium (**2d**): 1-Pentyne (**1d**) (681 mg, 10.0 mmol) in 150 ml of THF was treated with *n*-butyllithium (4.23 ml, 10.0 mmol), hexacarbonylchromium (2.20 g, 10.0 mmol), triethyloxonium tetrafluoroborate (2.00 g, 10.5 mmol) and (1,3-dioxolan-2-ylmethyl)methylamine (1.29 g, 11.0 mmol) according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 3 : 1, column 40 × 4 cm) 3.65 g (84%) of **2d** (R_f = 0.17, diethyl ether)

was obtained as yellow crystals, m.p. 93 °C. – IR (KBr): ν = 2921 cm^{-1} (C–H), 2065, 1965, 1906 (C=O), 1878, 1531, 1419, 1268, 1119, 1031, 901, 669. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.00 (t, ^{3}J = 7.0 Hz, 3 H, 6-H), 1.48 (t, ^{3}J = 7.1 Hz, 3 H, OCH_2CH_3), 1.54 (m_c, 2 H, 5-H), 2.68 (m_c, 2 H, 4-H), 2.92 (m_c, 2 H, NCH_2), 3.17 (s, 3 H, NCH_3), 3.89 (m_c, 4 H, OCH_2CH_2O), 4.02 (m_c, 1 H, 2'-H), 4.71 (q, ^{3}J = 7.0 Hz, 2 H, OCH_2CH_3), 6.11 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 13.11 (+, C-6), 14.37 (+, OCH_2CH_3), 26.16 (–, C-5), 40.45 (–, C-4), 45.98 (–, NCH_2), 49.81 (+, NCH_3), 63.98 (–, OCH_2CH_2O), 73.35 (–, OCH_2CH_3), 101.03 (+, C-2'), 117.83 (+, C-2), 156.21 (C_{quat}, C-3), 219.08, 223.71 (C_{quat}, C=O), 286.13 (C_{quat}, C-1). – $C_{18}H_{23}CrNO_8$ (433.4): calcd. C 49.89, H 5.35; found C 50.08, H 5.42.

5-Dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1,2-dimethyl-1,3-cyclopenta-diene (**4a**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2a**) (839 mg, 2.00 mmol) in 40 ml pyridine was treated with 2-butyne (**3a**) (324 mg, 6.00 mmol), and the mixture was heated at 80 °C for 3 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 30 × 2.0 cm) 487 mg (87%) of **4a** (R_f = 0.65 on alumina, diethyl ether) was obtained as a colorless oil. – IR (film): ν = 2939 cm^{-1} (C–H), 2865 (C–H), 2819, 2776, 1666 (C=C), 1592 (C=C), 1442, 1379, 1343, 1268, 1237, 1201, 1137, 1063, 1040, 1008, 964, 943, 891, 742. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (m_c, 2 H, 2'-H), 1.30 (t, ^{3}J = 7.0 Hz, 3 H, OCH_2CH_3), 1.54 (m_c, 1 H, 1'-H), 1.58 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 1.95 (m_c, 1 H, 1'-H), 2.13 [s, 6 H, $N(CH_3)_2$], 3.75–3.93 (m, 6 H, OCH_2CH_2O, OCH_2CH_3) 4.63 (s, 1 H, 4-H), 4.73 (t, ^{3}J = 4.8 Hz, 1 H, 2''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.64, 9.99 (+, CH_3), 14.42 (+, OCH_2CH_3), 27.97 (–, C-1', C-2'), 39.87 [+, $N(CH_3)_2$], 64.36, 64.74, 64.77

(–, OCH_2CH_2O, OCH_2CH_3), 74.33 (C_{quat}, C-5), 92.98 (+, C-4), 105.00 (+, C-2''), 131.01 (C_{quat}, C-1), 141.75 (C_{quat}, C-2), 161.18 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 281 (33) [M^+], 252 (41) [$M^+ - C_2H_5$], 236 (18), 205 (13), 180 (47), 164 (10), 152 (28), 122 (10), 99 (100), 84 (16), 73 (37) [$CH(OCH_2)_2^+$], 45 (9). – $C_{16}H_{27}NO_3$ (281.4): calcd. C 68.29, H 9.67; found C 68.14, H 9.62.

5-Dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1,2-diethyl-1,3-cyclopentadiene (**4b**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-yl-idene]chromium (**2a**) (1.05 g, 2.50 mmol) in 50 ml of pyridine was treated with 3-hexyne (**3b**) (410 mg, 5.00 mmol) and heated at 80 °C for 4 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 40 × 2.0 cm) 603 mg (78%) of **4b** (R_f = 0.72 on alumina, diethyl ether) was obtained as a colorless oil. – IR (film): ν = 2964 cm^{-1} (C–H), 2873 (C–H), 2820, 2778, 1653 (C=C), 1591 (C=C), 1462, 1408, 1375, 1329, 1259, 1197, 1135, 1035, 970, 938, 889, 748. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.01 (t, ^3J = 7.8 Hz, 3 H, CH_2CH_3), 1.09 (t, ^3J = 7.8 Hz, 3 H, CH_2CH_3), 1.29 (m_c, 2 H, 2'-H), 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.67 (m_c, 1 H, 1'-H), 1.98 (m_c, 1 H, 1'-H), 2.01–2.21 (m, 4 H, CH_2CH_3), 2.13 [s, 6 H, $N(CH_3)_2$], 3.75–3.94 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.60 (s, 1 H, 4-H), 4.74 (t, ^3J = 4.8 Hz, 1 H, 2''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.06, 13.86 (+, CH_2CH_3), 14.47 (+, OCH_2CH_3), 17.58, 18.15 (–, CH_2CH_3), 27.77, 28.05 (–, C-1', C-2'), 40.21 [+, $N(CH_3)_2$], 64.25, 64.75 (–, OCH_2CH_2O, OCH_2CH_3), 75.07 (C_{quat}, C-5), 93.51 (+, C-4), 105.11 (+, C-2''), 137.92 (C_{quat}, C-1), 145.76 (C_{quat}, C-2), 160.74 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 309 (53) [M^+], 280 (63) [$M^+ - C_2H_5$], 265 (22), 235 (10), 208 (41), 178 (30), 150 (10), 99 (100), 73 (36) [$CH(OCH_2)_2^+$], 45 (7).

1,2-Dicyclopropyl-5-dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1,3-cyclo-pentadiene (**4d**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2a**) (839 mg, 2.00 mmol) in 40 ml of pyridine was treated with dicyclopropylethyne (**3d**) (424 mg, 4.00 mmol) and heated at 80 °C for 4 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 30 × 2.0 cm) 436 mg (65%) of **4d** (R_f = 0.63 on alumina, diethyl ether) was obtained as a colorless oil. – IR (film): ν = 2976 cm^{-1} (C–H), 2873 (C–H), 2820, 2777, 1637 (C=C), 1586 (C=C), 1451, 1403, 1343, 1322, 1195, 1144, 1042, 982, 942, 900, 816, 748. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.58 (m_c, 1 H, *c*Pr-H), 0.63 (m_c, 1 H, *c*Pr-H), 0.72 (m_c, 1 H, *c*Pr-H), 0.77 (m_c, 1 H, *c*Pr-H), 0.79–0.88 (m, 2 H, *c*Pr-H), 0.92 (m_c, 1 H, *c*Pr-H), 1.07 (m_c, 1 H, *c*Pr-H), 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.32–1.43 (m, 3 H, 2'-H, *c*Pr-H), 1.49 (m_c, 1 H, *c*Pr-H), 1.79 (m_c, 1 H, 1'-H), 1.94 (m_c, 1 H, 1'-H), 2.20 [s, 6 H, $N(CH_3)_2$], 3.75 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 3.88 (m_c, 4 H, OCH_2CH_2O) 4.60 (s, 1 H, 4-H), 4.77 (t, ^3J = 4.8 Hz, 1 H, 2''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 4.50, 4.66, 5.50, 5.58 (–, *c*Pr-C), 7.58, 8.73 (+, *c*Pr-C), 14.44 (+, OCH_2CH_3), 28.23, 28.47 (–, C-1', C-2'), 40.07 [+, $N(CH_3)_2$], 64.27, 64.78 (–, OCH_2CH_2O, OCH_2CH_3), 74.99 (C_{quat}, C-5), 94.53 (+, C-4), 105.18 (+, C-2''), 135.65 (C_{quat}, C-1), 145.80 (C_{quat}, C-2), 161.06 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 333 (24) [M^+], 305 (18) [$M^+ – C_2H_4$], 289 (19) [$M^+ – N(CH_3)_2$], 232 (19), 202 (18), 175 (10), 129 (11), 99 (49), 84 (100), 73 (46) [$CH(OCH_2)_2^+$], 58 (32), 47 (16).

1-tert-Butyl-5-dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1,3-cyclo-pentadiene (**4e**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-

penten-1-ylidene]chromium (**2a**) (839 mg, 2.00 mmol) in 40 ml of pyridine was treated with 3,3-dimethylbutyne (**3e**) (492 mg, 6.00 mmol) and heated at 80 °C for 3 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 30 × 2.0 cm) 355 mg (57%) of **4e** (R_f = 0.55 on alumina, pentane/diethyl ether, 1 : 1) was obtained as a colorless oil. – IR (film): ν = 2960 cm^{-1} (C–H), 2865 (C–H), 2820, 2776, 1627 (C=C), 1571 (C=C), 1468, 1401, 1340, 1260, 1197, 1144, 1027, 966, 944, 902, 852, 734, 648. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19 [s, 9 H, $C(CH_3)_3$], 1.30 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.46 (m_c, 2 H, 2'-H), 1.90 (m_c, 1 H, 1'-H), 2.01 (m_c, 1 H, 1'-H), 2.18 [s, 6 H, $N(CH_3)_2$], 3.75–3.94 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.61 (d, ^4J = 1.9 Hz, 1 H, 4-H), 4.76 (t, ^3J = 4.8 Hz, 1 H, 2"-H), 5.80 (d, ^4J = 1.9 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.46 (+, OCH_2CH_3), 27.93, 28.50 (–, C-1', C-2'), 30.72 [+, $C(CH_3)_3$], 34.67 [C_{quat}, $C(CH_3)_3$], 40.76 [+, $N(CH_3)_2$], 64.24, 64.76 (–, OCH_2CH_2O, OCH_2CH_3), 78.94 (C_{quat}, C-5), 95.81 (+, C-4), 105.13 (+, C-2"), 124.96 (+, C-2), 158.54 (C_{quat}, C-1), 161.09 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 309 (43) [M^+], 280 (31) [$M^+ - C_2H_5$], 252 (40), 208 (14), 177 (21), 166 (10), 99 (57), 84 (100), 73 (21) [$CH(OCH_2)_2^+$], 47 (17).

5-Dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1-trimethylsilyl-1,3-cyclo-pentadiene (**4f-A**) *and 5-Dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-2-trimethylsilyl-1,3-cyclopentadiene* (**4f-B**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2a**) (1.05 g, 2.50 mmol) in 50 ml of pyridine was treated with trimethylsilylethyne (**3f**) (737 mg, 7.50 mmol) and heated at 80 °C for 4 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 40 × 2.0 cm) 325 mg (40%) of **4f-A** (R_f = 0.51 on alumina,

pentane/diethyl ether, 1 : 1) and 76 mg (9%) of **4f-B** (R_f = 0.17 on alumina, pentane/diethyl ether, 1 : 1) were obtained as colorless oils. **4f-A**: IR (film): ν = 2952 cm^{-1} (C–H), 2819 (C–H), 2776, 1611 (C=C), 1535 (C=C), 1444, 1403, 1368, 1324, 1246, 1191, 1143, 1074, 1018, 969, 943, 886, 833, 761, 631. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.14 [s, 9 H, $Si(CH_3)_3$], 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.39 (m_c, 2 H, 2'-H), 1.80 (m_c, 1 H, 1'-H), 2.01 (m_c, 1 H, 1'-H), 2.18 [s, 6 H, $N(CH_3)_2$], 3.77–3.94 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.75 (t, ^3J = 4.8 Hz, 1 H, 2''-H), 4.95 (d, ^4J = 1.2 Hz, 1 H, 4-H), 6.24 (d, ^4J = 1.2 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.75 [+, $Si(CH_3)_3$], 14.46 (+, OCH_2CH_3), 28.18, 28.64 (–, C-1', C-2'), 40.53 [+, $N(CH_3)_2$], 64.74, 64.79 (–, OCH_2CH_2O, OCH_2CH_3), 80.34 (C_{quat}, C-5), 102.08 (+, C-4), 105.11 (+, C-2''), 139.11 (+, C-2), 156.81 (C_{quat}, C-1), 159.60 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 325 (45) [M^+], 296 (86) [$M^+ - C_2H_5$], 252 (18) [$M^+ - Si(CH_3)_3$], 238 (21), 222 (44), 210 (53), 196 (37), 167 (11), 135 (28), 99 (58), 73 (100) [$CH(OCH_2)_2^+$, $Si(CH_3)_3^+$], 47 (14).

4f-B: IR (film): ν = 2954 cm^{-1} (C–H), 2879 (C–H), 2778, 1606 (C=C), 1549 (C=C), 1449, 1401, 1331, 1246, 1219, 1142, 1040, 840, 765, 696, 627. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.10 [s, 9 H, $Si(CH_3)_3$], 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.58–1.80 (m, 4 H, 2'-H, 1'-H), 2.25 [s, 6 H, $N(CH_3)_2$], 3.73–3.94 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.71 (d, ^5J = 1.2 Hz, 1 H, 4-H), 4.79 (t, ^3J = 4.8 Hz, 1 H, 2''-H), 6.29 (d, ^5J = 1.2 Hz, 1 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –1.37 [+, $Si(CH_3)_3$], 14.45 (+, OCH_2CH_3), 28.12, 29.12 (–, C-1', C-2'), 40.22 [+, $N(CH_3)_2$], 64.40, 64.75 (–, OCH_2CH_2O, OCH_2CH_3), 76.33 (C_{quat}, C-5), 98.95 (+, C-4), 104.87 (+, C-2''), 143.21 (C_{quat}, C-2), 150.47 (+, C-1), 162.68 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 325 (35) [M^+], 296 (100) [$M^+ - C_2H_5$], 252 (5) [$M^+ - Si(CH_3)_3$], 224 (44), 210 (10), 180 (13), 99 (48), 73 (39) [$CH(OCH_2)_2^+$, $Si(CH_3)_3^+$], 45 (8).

1-tert-Butyldimethylsilyl-5-dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1,3-cyclopentadiene (**4g-A**) *and 2-tert-Butyldimethylsilyl-5-dimethylamino-5-[2'-(1'',3''-dioxolan-2''-yl)ethyl]-3-ethoxy-1,3-cyclopentadiene* (**4g-B**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2a**) (1.05 g, 2.50 mmol) in 50 ml of pyridine was treated with *tert*-butyldimethylsilylethyne (**3g**) (841 mg, 6.00 mmol) and heated at 80 °C for 4 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 40 × 2.0 cm) 385 mg (42%) of **4g-A** (R_f = 0.78 on alumina, pentane/diethyl ether, 1 : 1) and 59 mg (6%) of **4g-B** (R_f = 0.15 on alumina, pentane/diethyl ether, 1 : 1) were obtained as colorless oils. **4g-A**: IR (film): ν = 2954 cm^{-1} (C–H), 2854 (C–H), 2775, 1611 (C=C), 1532 (C=C), 1471, 1402, 1361, 1325, 1246, 1192, 1144, 1074, 1014, 884, 833, 807, 770, 671. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.13 [s, 6 H, $Si(CH_3)_2$], 0.93 [s, 9 H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.42 (m_c, 2 H, 2'-H), 1.84 (m_c, 1 H, 1'-H), 1.97 (m_c, 1 H, 1'-H), 2.17 [s, 6 H, $N(CH_3)_2$], 3.77–3.92 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.75 (t, ^3J = 4.8 Hz, 1 H, 2''-H), 4.95 (d, ^4J = 1.2 Hz, 1 H, 4-H), 6.37 (d, ^4J = 1.2 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –4.52 [+, $Si(CH_3)_2$], 14.48 (+, OCH_2CH_3), 17.69 [C_{quat}, $SiC(CH_3)_3$], 27.24 [+, $SiC(CH_3)_3$], 28.07, 28.23 (–, C-1', C-2'), 40.69 [+, $N(CH_3)_2$], 64.79 (–, OCH_2CH_2O, OCH_2CH_3), 81.60 (C_{quat}, C-5), 101.83 (+, C-4), 105.15 (+, C-2''), 139.97 (+, C-2), 154.84 (C_{quat}, C-1), 159.27 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 367 (73) [M^+], 238 (100) [$M^+ - C_2H_5$], 309 (19), 251 (68), 237 (27), 195 (50), 177 (24), 166 (21), 99 (62), 73 (37) [$CH(OCH_2)_2^+$], 59 (14).

4g-B: IR (film): ν = 2927 cm^{-1} (C–H), 2854 (C–H), 2776, 1604 (C=C), 1559 (C=C), 1469, 1408, 1391, 1361, 1248, 1221, 1141, 1040, 941, 825, 773, 674, 578. – ^{1}H NMR (250 MHz,

$CDCl_3$): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 0.86 [s, 9 H, $SiC(CH_3)_3$], 1.24 (m_c, 2 H, 2'-H), 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.67 (m_c, 1 H, 1'-H), 1.75 (m_c, 1 H, 1'-H), 2.26 [s, 6 H, $N(CH_3)_2$], 3.74–3.92 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.73 (d, ^5J = 1.2 Hz, 1 H, 4-H), 4.81 (t, ^3J = 4.8 Hz, 1 H, 2"-H), 6.36 (d, ^5J = 1.2 Hz, 1 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –4.59 [+, $Si(CH_3)_2$], 14.42 (+, OCH_2CH_3), 16.61 [C_{quat}, $SiC(CH_3)_3$], 26.83 [+, $SiC(CH_3)_3$], 28.48, 29.33 (–, C-1', C-2'), 40.34 [+, $N(CH_3)_2$], 64.42, 64.80 (–, OCH_2CH_2O, OCH_2CH_3), 77.51 (C_{quat}, C-5), 98.92 (+, C-4), 104.90 (+, C-2"), 141.087 (C_{quat}, C-2), 152.76 (+, C-1), 162.76 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 367 (27) [M^+], 238 (100) [$M^+ – C_2H_5$], 265 (54), 251 (11), 180 (21), 99 (50), 73 (35) [$CH(OCH_2)_2^+$], 57 (14).

1-[2',2'-Bis(ethoxycarbonyl)-4'-bromopent-4'-enyl]-5-dimethylamino-5-[2''-(1''',3'''-dioxolan-2'''-yl)ethyl]-3-ethoxycyclopenta-1,3-diene (**4h**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2a**) (1.00 g, 2.38 mmol) in 48 ml of pyridine was treated with diethyl 6-bromo-6-hepten-1-yne-4,4-dicarboxylate (**3h**) (1.59 g, 5.01 mmol) and heated at 80 °C for 2 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 30 × 2.0 cm) 623 mg (48%) of **4h** (R_f = 0.31 on alumina, pentane/diethyl ether, 1 : 1) was obtained as a colorless oil. – IR (film): ν = 2980 cm^{-1}, 2875, 2782 (C–H), 1734 (C=O), 1637 (C=C), 1587, 1446, 1335, 1297, 1042, 905, 735. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.17 (t, ^3J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.30 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.42–1.60 (m, 3 H, 1"-H, 2"-H), 1.98 (dt, ^2J = 12.6, ^3J = 7.7 Hz, 1 H, 1"-H), 2.17 [s, 6 H, $N(CH_3)_2$], 2.62 (d, ^2J = 9.8 Hz, 1 H, 1'-H), 2.90 (d, ^2J = 9.8 Hz, 1 H, 1'-H), 3.35 (s, 2 H, 3'-H), 3.72–4.01 (m, 6 H, OCH_2CH_3, OCH_2CH_2O),

4.16 (m_c, 4 H, $CO_2CH_2CH_3$), 4.72 (m_c, 1 H, 2'''-H), 5.50 (s, 1 H, 4-H), 5.68 (s, 1 H, 5'-H), 5.92 (s, 1 H, 2-H), 5.74 (s, 1 H, 5'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): 13.82 (+, OCH_2CH_3), 14.38 (+, 2 × $CO_2CH_2CH_3$), 28.22, 29.53 (–, C-1", C-2"), 39.76 (+, NCH_3), 43.50 (–, C-1'), 45.72 (–, C-3'), 55.74 (C_{quat}, C-2'), 61.68 (–, OCH_2CH_3), 64.55, 64.75 (–, 2 × $CO_2CH_2CH_3$, OCH_2CH_2O), 76.94 (C_{quat}, C-5), 95.39 (+, C-4), 104.81 (+, C-2'''), 121.89 (–, C-5'), 123.56 (+, C-2), 127.35 (C_{quat}, C-4'), 149.44 (C_{quat}, C-1), 159.67 (C_{quat}, C-3), 170.10 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m*/*z* (%): 545/543 (20/19) [M^+], 516/514 (11/10) [$M^+ - C_2H_5$], 464 (70) [M^+ – Br], 266 (100), 157 (38), 99 (42), 57 (40), 43 (26). – $C_{25}H_{38}NO_7Br$: 543.1831 (correct HRMS).

5-Dimethylamino-3-ethoxy-1,2-dimethyl-5-[2'-(2''-methyl-1'',3''-dioxolan-2''-yl)ethyl]-1,3-cyclopentadiene (**4i**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(2'-methyl-1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2b**) (1.08 g, 2.49 mmol) in 50 ml of pyridine was treated with 2-butyne (**3a**) (406 mg, 7.51 mmol) and heated at 80 °C for 3 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 30 × 2.0 cm) 554 mg (75%) of **4i** (R_f = 0.69 on alumina, diethyl ether) was obtained as a colorless oil. – IR (film): ν = 2972 cm^{-1} (C–H), 2818 (C–H), 2775, 1665 (C=C), 1589 (C=C), 1442, 1372, 1342, 1200, 1115, 947, 887, 860, 817, 732, 634, 536. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19 (m_c, 2 H, 2'-H), 1.24 (s, 3 H, CH_3), 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.53 (m_c, 1 H, 1'-H), 1.58 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 1.94 (m_c, 1 H, 1'-H), 2.14 [s, 6 H, $N(CH_3)_2$], 3.78–3.93 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.63 (s, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.68, 10.09 (+, CH_3), 14.44 (+, OCH_2CH_3), 23.78 (+, CH_3), 28.09, 32.66 (–, C-1', C-2'), 39.91 [+, $N(CH_3)_2$], 64.40, 64.52 (–, OCH_2CH_2O, OCH_2CH_3), 74.26 (C_{quat}, C-5), 93.13 (+, C-4), 110.29 (C_{quat}, C-2"),

130.88 (C_{quat}, C-1), 141.89 (C_{quat}, C-2), 161.09 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 295 (41) [M^+], 266 (66) [$M^+ - C_2H_5$], 250 (10), 180 (43), 165 (17), 152 (17), 87 (100) [$CH_3C(OCH_2)_2^+$], 43 (16).

5-Dimethylamino-3-ethoxy-5-[2'-(2''-methyl-1'',3''-dioxolan-2''-yl)ethyl]-1,2-diphenyl-1,3-cyclopentadiene (**4j**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(2'-methyl-1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]chromium (**2b**) (1.08 g, 2.49 mmol) in 50 ml of pyridine was treated with diphenylethyne (**3c**) (891 mg, 5.00 mmol) and heated at 80 °C for 4 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 1 : 1, column 30 × 2.0 cm) 528 mg (51%) of **4j** (R_f = 0.47 on alumina, pentane/diethyl ether, 1 : 1) was obtained as colorless crystals, m.p. 76 °C. – IR (KBr): ν = 2980 cm^{-1} (C–H), 2880 (C–H), 2781, 1579 (C=C), 1447, 1376, 1348, 1302, 1212, 1053, 948, 863, 761, 702. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 (s, 3 H, CH_3), 1.25 (m_c, 2 H, 2'-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.73 (m_c, 1 H, 1'-H), 2.10 (m_c, 1 H, 1'-H), 2.37 [s, 6 H, $N(CH_3)_2$], 3.70–4.01 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 5.03 (s, 1 H, 4-H), 7.11–7.27 (m, 8 H, Ph-H), 7.44–7.48 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.33 (+, OCH_2CH_3), 23.29 (+, CH_3), 28.50, 32.22 (–, C-1', C-2'), 40.13 [+, $N(CH_3)_2$], 64.17, 64.33, 64.80 (–, OCH_2CH_2O, OCH_2CH_3), 75.69 (C_{quat}, C-5), 96.93 (+, C-4), 110.17 (C_{quat}, C-2''), 126.69, 127.02, 127.72, 127.79, 129.40, 130.02 (+, Ph-C), 133.88, 135.55 (C_{quat}, Ph-C), 137.95 (C_{quat}, C-1), 145.85 (C_{quat}, C-2), 159.16 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 419 (3) [M^+], 390 (3) [$M^+ - C_2H_5$], 257 (4), 170 (8), 143 (18), 99 (16), 87 (100) [$CH_3C(OCH_2)_2^+$], 43 (16).

5-Dimethylamino-3-ethoxy-5-[2'-(2''-methyl-1'',3''-dioxolan-2''-yl)ethyl]-1-trimethylsilyl-1,3-cyclopentadiene (**4l-A**) *and 5-Dimethylamino-3-ethoxy-5-[2'-(2''-methyl-1'',3''-dioxolan-2''-yl)ethyl]-2-trimethylsilyl-1,3-cyclopentadiene* (**4l-B**): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(2'-methyl-1',3'-dioxolan-2'-yl)-2-penten-1-ylidene]–chromium (**2b**) (1.08 g, 2.49 mmol) in 50 ml of pyridine was treated with trimethylsilylethyne (**3f**) (735 mg, 7.50 mmol) and heated at 80 °C for 4 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 1 : 1, column 30×2.0 cm) 383 mg (45%) of **4l-A** (R_f = 0.55 on alumina, pentane/diethyl ether, 1 : 1) and 77 mg (9%) of **4l-B** (R_f = 0.19 on alumina, pentane/diethyl ether, 1 : 1) were obtained as colorless oils. **4l-A**: IR (film): ν = 2952 cm^{-1} (C–H), 2876 (C–H), 2779, 1614 (C=C), 1538 (C=C), 1446, 1373, 1327, 1292, 1247, 1193, 1150, 1113, 1063, 988, 885, 873, 762, 734. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.14 [s, 9 H, $Si(CH_3)_3$], 1.24 (s, 3 H, CH_3), 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.37 (m_c, 2 H, 2'-H), 1.76 (m_c, 1 H, 1'-H), 2.96 (m_c, 1 H, 1'-H), 2.19 [s, 6 H, $N(CH_3)_2$], 3.78–3.95 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.95 (d, ^4J = 1.4 Hz, 1 H, 4-H), 6.24 (d, ^4J = 1.4 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.68 [+, $Si(CH_3)_3$], 14.46 (+, OCH_2CH_3), 23.85 (+, CH_3), 28.81, 32.93 (–, C-1', C-2'), 40.53 [+, $N(CH_3)_2$], 64.54, 64.56, 64.81 (–, OCH_2CH_2O, OCH_2CH_3), 80.83 (C_{quat}, C-5), 102.41 (+, C-4), 110.31 (C_{quat}, C-2''), 139.00 (+, C-2), 156.93 (C_{quat}, C-1), 159.46 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 339 (27) [M^+], 310 (78) [$M^+ - C_2H_5$], 266 (6) [$M^+ - Si(CH_3)_3$], 238 (8), 208 (7), 84 (100), 87 (63) [$CH_3C(OCH_2)_2^+$], 73 (16) [$Si(CH_3)_3^+$], 47 (14). – $C_{18}H_{33}NO_3Si$ (339.6): calcd. C 63.67, H 9.80; found C 63.92, H 9.69.

4l-B: IR (film): ν = 2954 cm^{-1} (C–H), 2873 (C–H), 2776, 1605 (C=C), 1547 (C=C), 1449, 1374, 1320, 1246, 1218, 1149, 1064, 946, 898, 837, 765, 734, 696, 627. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.10 [s, 9 H, $Si(CH_3)_3$], 1.26 (s, 3 H, CH_3), 1.28 (t, ^3J = 7.0 Hz, 3 H,

OCH_2CH_3), 1.61–1.75 (m, 4 H, 2'-H, 1'-H), 2.24 [s, 6 H, $N(CH_3)_2$], 3.78 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 3.88 (m_c, 4 H, OCH_2CH_2O), 4.72 (d, ^5J = 2.0 Hz, 1 H, 4-H), 6.29 (d, ^5J = 2.0 Hz, 1 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –1.34 [+, $Si(CH_3)_3$], 14.47 (+, OCH_2CH_3), 23.90 (+, CH_3), 28.45, 34.15 (–, C-1', C-2'), 40.15 [+, $N(CH_3)_2$], 64.40, 64.55 (–, OCH_2CH_2O, OCH_2CH_3), 76.30 (C_{quat}, C-5), 99.32 (+, C-4), 110.17 (C_{quat}, C-2''), 142.93 (C_{quat}, C-2), 150.67 (+, C-1), 162.51 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 339 (27) [M^+], 310 (100) [$M^+ - C_2H_5$], 224 (37), 180 (10), 87 (52) [$CH_3C(OCH_2)_2^+$], 73 (11) [$Si(CH_3)_3^+$], 43 (8).

5-[(1'',3''-Dioxolan-2''-ylmethyl)methylamino]-3-ethoxy-5-propyl-1-trimethylsilyl-1,3-cyclo-pentadiene (**4p**): Pentacarbonyl{(2*E*)-3-[(1',3'-dioxolan-2'-ylmethyl)methylamino]-1-ethoxy-2-hexen-1-ylidene}chromium (**2d**) (530 mg, 1.22 mmol) in 40 ml of pyridine was treated with trimethylsilylethyne (**3f**) (361 mg, 3.68 mmol) and was heated at 80 °C for 40 h according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20 : 1 to 0 : 1, column 20 × 1 cm) 232 mg (56%) of **4p** was obtained as a colorless oil. – ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 0.78 (t, ^3J = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 1.11 (m_c, 2 H, $CH_2CH_2CH_3$), 1.32 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.63 (m_c, 1 H, $CH_2CH_2CH_3$), 1.84 (m_c, 1 H, $CH_2CH_2CH_3$), 2.32 (s, 3 H, NCH_3), 2.47 (dd, ^2J = 13.5, ^3J = 4.0 Hz, 1 H, 1'-H), 2.65 (dd, ^2J = 13.5, ^3J = 4.7 Hz, 1 H, 1'-H), 3.75–4.06 (m, 6 H, OCH_2CH_3, OCH_2CH_2O), 4.89 (t, ^3J = 4.7 Hz, 1 H, 2''-H), 4.96 (d, ^4J = 1.6 Hz, 1 H, 4-H), 6.27 (d, ^4J = 1.6 Hz, 1 H, 2-H).

1-Dimethylamino-(exo/endo)-4-hydroxy-7-methylbicyclo[4.3.0]non-6-en-8-one (*endo/exo*-**9a**), *1-Dimethylamino-exo-6-hydroxy-2,3-dimethylbicyclo[3.3.0]oct-2-en-4-one* (*exo*-**8a**) *and 1-*

Dimethylamino-endo-6-hydroxy-2,3-dimethylbicyclo[3.3.0]oct-2-en-4-one (*endo*-**8a**): 5-Dimethylamino-5-[2'-(1",3"-dioxolan-2"-yl)ethyl]-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (**4a**) (296 mg, 1.05 mmol) in 50 ml of THF was treated with conc. HCl (3.1 ml, 31 mmol) at room temp. for 18 h according to GP 3. After column chromatography on silica gel (diethyl ether/methanol, 8 : 1 to 1 : 1, column 40 × 4 cm) 35 mg (16%) of *endo/exo*-**9a** (1.4 : 1), (R_f = 0.79, 0.75, methanol) was obtained as a colorless oil, 115 mg (52%) of *exo*-**8a** (R_f = 0.59, methanol) as colorless crystals, m.p. 101 °C, and 38 mg (17%) of *endo*-**8a** (R_f = 0.51, methanol) as a colorless oil. *endo/exo*-**9a**: IR (film): ν = 3442 cm^{-1} (OH), 2953 (C–H), 2868 (C–H), 2827, 2780, 1690 (C=O), 1648 (C=C), 1462, 1382, 1320, 1259, 1213, 1157, 1100, 1026, 919, 732, 645. – Major diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84–1.18 (m, 1 H, 2-H), 1.51–1.61 (m, 1 H, 2-H), 1.69 (s, 3 H, CH_3), 1.74 (AB, d, ^2J = 18.7 Hz, 1 H, 9-H), 2.07 [s, 6 H, $N(CH_3)_2$], 2.09–2.26 (m, 3 H, 3-H, 5-H), 2.55 (AB, d, ^2J = 18.7 Hz, 1 H, 9-H), 2.64 (br. s, 1 H, OH), 2.72 (m_c, 1 H, 5 H), 4.32 (m_c, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.61 (+, CH_3), 27.82, 31.61, 33.25, 37.34 (–, C-5, C-3, C-2, C-9), 38.70 [+, $N(CH_3)_2$], 65.34 (C_{quat}, C-1), 67.90 (+, C-4), 136.89 (C_{quat}, C-7), 173.08 (C_{quat}, C-6), 207.00 (C_{quat}, C-8). – MS (70 eV), *m/z* (%): 209 (9) [M^+], 194 (12) [$M^+ – CH_3$], 180 (40), 165 (10), 152 (19), 84 (100), 74 (39), 44 (5) [$N(CH_3)_2^+$].

exo-**8a**: IR (KBr): ν = 3119 cm^{-1} (OH), 2949 (C–H), 2802 (C–H), 1692 (C=O), 1645 (C=C), 1439, 1388, 1326, 1301, 1223, 1165, 1125, 1097, 1078, 1053, 1010, 963, 938, 880, 597. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (m_c, 1 H, 8-H), 1.60 (m_c, 2 H, 7-H), 1.62 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 2.17 [s, 6 H, $N(CH_3)_2$], 2.28 (m_c, 1 H, 8-H), 2.61 (s, 1 H, 5-H), 3.61 (br. s, 1 H, OH), 4.15 (m_c, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.86, 13.09 (+, CH_3), 28.26, 32.07 (–, C-8, C-7), 40.63 [+, $N(CH_3)_2$], 55.58 (+, C-5), 74.31 (+, C-6), 79.15 (C_{quat}, C-1), 137.41 (C_{quat}, C-3), 172.32 (C_{quat}, C-2), 207.02 (C_{quat}, C-4). –

MS (70 eV), *m/z* (%): 209 (42) [M^+], 192 (5) [M^+ – OH], 180 (11), 165 (9), 152 (100), 137 (15), 126 (13), 110 (8), 44 (5) [$N(CH_3)_2^+$].

endo-**8a**: IR (film): ν = 3473 cm^{-1} (OH), 2944 (C–H), 2861 (C–H), 2822, 2775, 1688 (C=O), 1642 (C=C), 1456, 1382, 1312, 1259, 1215, 1167, 1117, 1076, 1005, 965, 918, 732. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (m_c, 1 H, 8-H), 1.66 (m_c, 1 H, 8-H), 1.70 (s, 3 H, CH_3), 1.95 (m_c, 2 H, 7-H), 2.01 (s, 3 H, CH_3), 2.15 [s, 6 H, $N(CH_3)_2$], 2.73 (d, $^3J_{cis}$ = 8.9 Hz, 1 H, 5-H), 3.40 (br. s, 1 H, OH), 4.26 (m_c, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.76, 12.83 (+, CH_3), 28.48, 32.21 (–, C-8, C-7), 40.33 [+, $N(CH_3)_2$], 47.43 (+, C-5), 73.03 (+, C-6), 77.70 (C_{quat}, C-1), 139.00 (C_{quat}, C-3), 173.77 (C_{quat}, C-2), 208.59 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 209 (25) [M^+], 192 (6) [M^+ – OH], 180 (21), 166 (11), 153 (100), 138 (31), 122 (10), 110 (11), 91 (10), 77 (10), 44 (5) [$N(CH_3)_2^+$].

1-Dimethylamino-endo-6-hydroxy-2,3-diphenylbicyclo[3.3.0]oct-2-en-4-one (*endo*-**8c**) *and 1-Dimethylamino-exo-6-hydroxy-2,3-diphenylbicyclo[3.3.0]oct-2-en-4-one* (*exo*-**8c)**: 5-Dimethylamino-5-[2'-(1",3"-dioxolan-2"-yl)ethyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**4c**) (759 mg, 1.87 mmol) in 50 ml of THF was treated with conc. HCl (5.0 ml, 50 mmol) at room temp. for 3 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2 : 1 to 0 : 1, column 40 × 4 cm) 233 mg (37%) of *endo/exo*-**8c** (10 : 1) (R_f = 0.44, diethyl ether) was obtained as a colorless oil and 306 mg (49%) of *endo*-**8c** as colorless crystals, m.p. 131 °C. *endo*-**8c**: IR (KBr): ν = 3401 cm^{-1} (OH), 2968 (C–H), 2788 (C–H), 1685 (C=O), 1618 (C=C), 1487, 1443, 1349, 1203, 1175, 1096, 1024, 768, 740, 636, 589. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 (m_c, 1 H, 8-H), 1.91 (m_c, 1 H, 8-H), 2.04 (m_c, 2 H, 7-H), 2.36 [s, 6 H, $N(CH_3)_2$], 3.04 (d, ^3J = 4.6 Hz, 1 H, OH), 3.13 (d, ^3J = 9.0 Hz, 1 H, 5-H), 4.47 (dddd, $^3J_{cis}$ = 9.0, $^3J_{trans}$ = 5.2, ^3J = 7.8, ^3J = 4.6 Hz, 1 H, 6-H), 7.12–7.31 (m,

8 H, Ph-H), 7.53–7.62 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 29.57, 33.13 (–, C-8, C-7), 40.47 [+, $N(CH_3)_2$], 49.30 (+, C-5), 73.18 (+, C-6), 79.22 (C_{quat}, C-1), 128.11, 128.31 (twofold intensity), 129.52, 129.69, 129.95 (+, Ph-C), 131.46, 133.90 (C_{quat}, Ph-C), 142.15 (C_{quat}, C-3), 171.85 (C_{quat}, C-2), 206.71 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 333 (53) [M^+], 316 (9) [M^+ – OH], 305 (17), 289 (20), 277 (100), 261 (10), 202 (12), 178 (21), 154 (28), 126 (14), 110 (32), 59 (25), 44 (47) [$N(CH_3)_2^+$]. – $C_{22}H_{23}NO_2$ (333.4): calcd. C 79.25, H 6.95; found C 79.15, H 6.88.

exo-**8c**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.63–1.81 (m, 3 H, 8-H, 7-H), 2.34 (m_c, 1 H, 8-H), 2.41 [s, 6 H, $N(CH_3)_2$], 2.95 (br. s, 1 H, OH), 3.00 (s, 1 H, 5-H), 4.38 (m_c, 1 H, 6-H), 7.13–7.33 (m, 8 H, Ph-H), 7.56–7.67 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 29.17, 33.17 (–, C-8, C-7), 40.74 [+, $N(CH_3)_2$], 56.28 (+, C-5), 75.01 (+, C-6), 79.91 (C_{quat}, C-1), 127.99, 128.10, 128.25, 129.39, 129.64, 129.90 (+, Ph-C), 131.62, 134.38 (C_{quat}, Ph-C), 140.72 (C_{quat}, C-3), 171.22 (C_{quat}, C-2), 205.59 (C_{quat}, C-4).

2,3-Dicyclopropyl-1-dimethylamino-endo-6-hydroxybicyclo[3.3.0]oct-2-en-4-one (*endo*-**8d**) *and 2,3-Dicyclopropyl-1-dimethylamino-exo-6-hydroxybicyclo[3.3.0]oct-2-en-4-one* (*exo*-**8d**): 1,2-Dicyclopropyl-5-dimethylamino-5-[2'-(1",3"-dioxolan-2"-yl)ethyl]-3-ethoxy-1,3-cyclopentadiene (**4d**) (302 mg, 0.906 mmol) in 50 ml of THF was treated with conc. HCl (2.7 ml, 27 mmol) at room temp. for 2 d according to GP 3. After column chromatography on silica gel (diethyl ether, column 40 × 4 cm) 29 mg (12%) of *endo*-**8d** (R_f = 0.32, diethyl ether) and 62 mg (26%) of *exo/endo*-**8d** (1 : 1.4) (R_f = 0.28, diethyl ether) were obtained as a colorless oil. *endo*-**8d**: IR (film): ν = 3456 cm^{-1} (OH), 2950 (C–H), 2867 (C–H), 2823, 2779, 1686 (C=O), 1611 (C=C), 1463, 1397, 1315, 1214, 1157, 1107, 1023, 983, 920, 856, 818, 732. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.67 (m_c, 1 H, *c*Pr-H), 0.71 (m_c, 1 H, *c*Pr-H), 0.98

(m_c, 1 H, *c*Pr-H), 1.04–1.11 (m, 4 H, *c*Pr-H), 1.21–1.37 (m, 3 H, *c*Pr-H), 1.44 (m_c, 1 H, 8-H), 1.81–1.96 (m, 3 H, 8-H, 7-H), 2.14 [s, 6 H, $N(CH_3)_2$], 2.63 (d, $^3J_{cis}$ = 8.7 Hz, 1 H, 5-H), 3.53 (d, ^3J = 5.9 Hz, 1 H, OH), 4.18 (m_c, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 5.18, 5.21 (–, *c*Pr-C), 6.19 (+, *c*Pr-C), 8.21, 9.21 (–, *c*Pr-C), 12.04 (+, *c*Pr-C), 29.55, 32.69 (–, C-8, C-7), 40.43 [+, $N(CH_3)_2$], 47.29 (+, C-5), 73.23 (+, C-6), 77.59 (C_{quat}, C-1), 139.48 (C_{quat}, C-3), 179.89 (C_{quat}, C-2), 208.02 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 261 (100) [M^+], 246 (22), 232 (30), 217 (26), 204 (33), 188 (52), 176 (36), 145 (20), 129 (29), 110 (90), 91 (93), 79 (40), 65 (23), 44 (40) [$N(CH_3)_2^+$]. – $C_{16}H_{23}NO_2$ (261.4): 261.1728 (correct HRMS).

exo-**8d**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.62–0.73 (m, 2 H, *c*Pr-H), 0.93–1.11 (m, 4 H, *c*Pr-H), 1.18–1.50 (m, 4 H, *c*Pr-H), 1.65 (m_c, 1 H, 8-H), 1.79–1.98 (m, 3 H, 8-H, 7-H), 2.16 [s, 6 H, $N(CH_3)_2$], 2.50 (s, 1 H, 5-H), 3.65 (br. s, 1 H, OH), 4.08 (m_c, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 5.03, 5.19 (–, *c*Pr-C), 6.30 (+, *c*Pr-C), 7.88, 8.95 (–, *c*Pr-C), 12.01 (+, *c*Pr-C), 29.29, 32.59 (–, C-8, C-7), 40.65 [+, $N(CH_3)_2$], 55.14 (+, C-5), 73.67 (+, C-6), 78.92 (C_{quat}, C-1), 137.83 (C_{quat}, C-3), 178.13 (C_{quat}, C-2), 206.45 (C_{quat}, C-4).

2-tert-Butyl-1-dimethylamino-endo-6-hydroxybicyclo[3.3.0]oct-2-en-4-one (*endo*-**8e**): 1-tert-Butyl-5-dimethylamino-5-[2'-(1",3"-dioxolan-2"-yl)ethyl]-3-ethoxy-1,3-cyclopentadiene (**4e**) (270 mg, 0.872 mmol) in 45 ml of THF was treated with conc. HCl (2.5 ml, 25 mmol) at room temp. for 2 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2 : 1 to 0 : 1, column 40 × 4 cm) 138 mg (67%) of *endo*-**8e** (R_f = 0.40 in diethyl ether) was obtained as colorless crystals, m.p. 106 °C. – IR (KBr): ν = 3481 cm^{-1} (OH), 2968 (C–H), 2778 (C–H), 1675 (C=O), 1580 (C=C), 1466, 1399, 1372, 1340, 1305, 1274, 1229, 1192, 1160, 1101, 1041, 983, 963, 923. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 [s, 9 H, $C(CH_3)_3$],

1.60 (m_c, 1 H, 8-H), 1.96 (m_c, 1 H, 8-H), 2.09 (m_c, 2 H, 7-H), 2.12 [s, 6 H, $N(CH_3)_2$], 2.85 (d, ^3J = 7.9 Hz, 1 H, 5-H), 3.15 (br. s, 1 H, OH), 4.47 (m_c, 1 H, 6-H), 6.02 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 30.00 (–, C-8), 31.33 [+, $C(CH_3)_3$], 34.86 (–, C-7), 36.18 [C_{quat}, $C(CH_3)_3$], 40.50 [+, $N(CH_3)_2$], 50.03 (+, C-5), 72.39 (+, C-6), 81.73 (C_{quat}, C-1), 131.48 (+, C-3), 193.97 (C_{quat}, C-2), 208.28 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 237 (22) [M^+], 220 (24) [M^+ – OH], 204 (15), 180 (10) [M^+ – $C(CH_3)_3$], 162 (100) [M^+ – $C(CH_3)_3$ – H_2O], 126 (12), 44 (6) [$N(CH_3)_2^+$]. – $C_{14}H_{23}NO_2$ (237.3): calcd. C 70.85, H 9.77; found. C 70.91, H 9.77.

1-Dimethylamino-exo-6-hydroxy-2-trimethylsilylbicyclo[3.3.0]oct-2-ene-4-one (*exo*-**8f**) *and 1-Dimethylamino-endo-6-hydroxy-2-trimethylsilylbicyclo[3.3.0]oct-2-en-4-one* (*endo*-**8f**): 5-Dimethylamino-5-[2'-(1",3"-dioxolan-2"-yl)ethyl]-3-ethoxy-1-trimethylsilyl-1,3-cyclopentadiene (**4f**-A) (261 mg, 0.802 mmol) in 40 ml of THF was treated with conc. HCl (2.5 ml, 25 mmol) at room temp. for 2 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2 : 1 to 0 : 1, column 40 × 4 cm) 152 mg (75%) of *exo*-**8f** (R_f = 0.40, diethyl ether) was obtained as colorless crystals, m.p. 79 °C, and 25 mg (12%) of *exo/endo*-**8f** (1 : 1) (R_f = 0.27, diethyl ether) as a colorless oil. *exo*-**8f**: IR (KBr): ν = 3492 cm^{-1} (OH), 2999 (C–H), 2898 (C–H), 1698 (C=O), 1468, 1344, 1310, 1250, 1098, 1034, 1017, 906, 891, 869, 841, 769, 633. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.23 [s, 9 H, $Si(CH_3)_3$], 1.51 (m_c, 2 H, 7-H), 1.71 (m_c, 1 H, 8-H), 2.16 [s, 6 H, $N(CH_3)_2$], 2.36 (m_c, 1 H, 8-H), 2.62 (d, ^3J = 1.7 Hz, 1 H, 5-H), 3.41 (br. s, 1 H, OH), 4.16 (m_c, 1 H, 6-H), 6.20 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.45 [+, $Si(CH_3)_3$], 30.07, 32.87 (–, C-8, C-7), 41.03 [+, $N(CH_3)_2$], 55.31 (+, C-5), 74.79 (+, C-6), 83.72 (C_{quat}, C-1), 140.20 (+, C-3), 189.74 (C_{quat}, C-2), 209.34 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 253 (37) [M^+], 234

(22), 225 (9), 180 (10) [$M^+ - Si(CH_3)_3$], 162 (41), 126 (100), 110 (31), 73 (12) [$Si(CH_3)_3^+$], 44 (5) [$N(CH_3)_2^+$].

endo-**8f**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.26 [s, 9 H, $Si(CH_3)_3$], 1.60–1.78 (m, 3 H, 8-H, 7-H), 2.18 [s, 6 H, $N(CH_3)_2$], 2.37 (m_c, 1 H, 8-H), 2.76 (d, ^3J = 8.6 Hz, 1 H, 5-H), 3.21 (br. s, 1 H, OH), 4.27 (m_c, 1 H, 6-H), 6.30 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.40 [+, $Si(CH_3)_3$], 30.31, 33.04 (–, C-8, C-7), 40.88 [+, $N(CH_3)_2$], 48.16 (+, C-5), 73.49 (+, C-6), 82.75 (C_{quat}, C-1), 141.48 (+, C-3), 190.86 (C_{quat}, C-2), 210.65 (C_{quat}, C-4).

2-tert-Butyldimethylsilyl-1-dimethylamino-exo-6-hydroxybicyclo[3.3.0]oct-2-en-4-one (*exo*-**8g**) *and 2-tert-Butyldimethylsilyl-1-dimethylamino-endo-6-hydroxybicyclo[3.3.0]oct-2-en-4-one* (*endo*-**8g**): 1-tert-Butyldimethylsilyl-5-dimethylamino-5-[2'-(1",3"-dioxolan-2"-yl)ethyl]-3-ethoxy-1,3-cyclopentadiene (**4g-A**) (308 mg, 0.838 mmol) in 40 ml of THF was treated with conc. HCl (3.0 ml, 30 mmol) at room temp. for 3 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2 : 1 to 0 : 1, column 40 × 4 cm) 71 mg (29%) of *exo*-**8g** (R_f = 0.55, diethyl ether) was obtained as colorless crystals, m.p. 120 °C, and 116 mg (47%) of *exo/endo*-**8g** (3.2 : 1) (R_f = 0.50, diethyl ether) as a colorless oil. *exo*-**8g**: IR (KBr): ν = 3426 cm^{-1} (OH), 2957 (C–H), 2860 (C–H), 1698 (C=O), 1467, 1313, 1293, 1256, 1222, 1203, 1151, 1102, 1033, 1017, 967, 833, 806, 773. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.18 [s, 3 H, $Si(CH_3)_2$], 0.27 [s, 3 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.40 (m_c, 1 H, 7-H), 1.54 (m_c, 1 H, 8-H), 1.72 (m_c, 1 H, 7-H), 2.16 [s, 6 H, $N(CH_3)_2$], 2.40 (m_c, 1 H, 8-H), 2.61 (s, 1 H, 5-H), 3.15 (br. s, 1 H, OH), 4.18 (m_c, 1 H, 6-H), 6.31 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –5.22 [+, $Si(CH_3)_2$], –3.93 [+, $Si(CH_3)_2$], 17.40 [C_{quat}, $SiC(CH_3)_3$], 26.94 [+, $SiC(CH_3)_3$], 29.28, 32.62 (–, C-8, C-7), 40.90 [+, $N(CH_3)_2$],

54.29 (+, C-5), 74.78 (+, C-6), 84.05 (C_{quat}, C-1), 141.16 (+, C-3), 188.25 (C_{quat}, C-2), 209.51 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 295 (19) [M^+], 278 (11) [$M^+ - OH$], 238 (58), 220 (14), 196 (32), 180 (12) [$M^+ - Si(CH_3)_2C(CH_3)_3$], 162 (55), 126 (100), 110 (32), 73 (18), 44 (12) [$N(CH_3)_2^+$]. – $C_{16}H_{29}NO_2Si$ (295.5): calcd. C 65.03, H 9.89; found C 64.85, H 9.79.

endo-**8g**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.17 [s, 3 H, $Si(CH_3)_2$], 0.25 [s, 3 H, $Si(CH_3)_2$], 0.92 [s, 9 H, $SiC(CH_3)_3$], 1.38 (m_c, 2 H, 7-H), 1.59 (m_c, 1 H, 8-H), 1.95 (m_c, 1 H, 8-H), 2.11 [s, 6 H, $N(CH_3)_2$], 2.71 (d, ^3J = 8.9 Hz, 1 H, 5-H), 3.42 (br. s, 1 H, OH), 4.24 (m_c, 1 H, 6-H), 6.39 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –5.24 [+, $Si(CH_3)_2$], –3.96 [+, $Si(CH_3)_2$], 17.36 [C_{quat}, $SiC(CH_3)_3$], 26.91 [+, $SiC(CH_3)_3$], 29.44, 32.65 (–, C-8, C-7), 40.65 [+, $N(CH_3)_2$], 47.07 (+, C-5), 73.37 (+, C-6), 83.09 (C_{quat}, C-1), 142.66 (+, C-3), 188.66 (C_{quat}, C-2), 210.49 (C_{quat}, C-4).

1-Dimethylamino-(endo/exo)-4-hydroxy-4,7-dimethylbicyclo[4.3.0]non-6-en-8-one (*endo/exo*-**9i**), *1-Dimethylamino-exo-6-hydroxy-2,3,6-trimethylbicyclo[3.3.0]oct-2-en-4-one* (*exo*-**8i**) *and 1-Dimethylamino-endo-6-hydroxy-2,3,6-trimethylbicyclo[3.3.0]oct-2-ene-4-one* (*endo*-**8i**): 5-Dimethylamino-3-ethoxy-1,2-dimethyl-5-[2'-(2"-methyl-1",3"-dioxolan-2"-yl)ethyl]-1,3-cyclopentadiene (**4i**) (420 mg, 1.42 mmol) in 60 ml of THF was treated with conc. HCl (4.5 ml, 45 mmol) at room temp. for 18 h according to GP 3. After column chromatography on silica gel (diethyl ether/methanol, 40 : 1 to 1 : 1, column 40 × 4 cm) 50 mg (16%) of *endo/exo*-**9i** (2.9 : 1) (R_f = 0.80, diethyl ether/methanol, 2 : 1) was obtained as a colorless oil and 239 mg (76%) of *exo/endo*-**8i** (3.2 : 1) (R_f = 0.55, diethyl ether/methanol, 2 : 1) as a colorless oil. *endo/exo*-**9i**: IR (film): ν = 3444 cm^{-1} (OH), 2948 (C–H), 2863 (C–H), 2821, 2776, 1685 (C=O), 1652 (C=C), 1456, 1381, 1333, 1304, 1266, 1198, 1174, 1156, 1130,

1096, 1049, 1018, 997. – Major diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40 (s, 3 H, CH_3), 1.51–1.61 (m, 3 H, 2-H, 3-H), 1.73 (s, 3 H, CH_3), 1.76 (AB, d, ^{2}J = 18.7 Hz, 1 H, 9-H), 2.00 (m_c, 1 H, 2-H), 2.12–2.22 [m, 7 H, $N(CH_3)_2$, 5-H], 2.54 (AB, d, ^{2}J = 18.7 Hz, 1 H, 9-H), 2.59–2.67 (m, 2 H, 5-H, OH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.61 (+, CH_3), 30.85 (+, CH_3), 32.82, 33.75, 37.07, 38.83 (–, C-5, C-3, C-2, C-9), 38.68 [+, $N(CH_3)_2$], 64.70 (C_{quat}, C-1), 72.34 (C_{quat}, C-4), 136.42 (C_{quat}, C-7), 173.69 (C_{quat}, C-6), 207.14 (C_{quat}, C-8). – MS (70 eV), *m/z* (%): 223 (8) [M^+], 208 (2) [$M^+ - CH_3$], 151 (28), 73 (100), 53 (7), 44 (15) [$N(CH_3)_2^+$].

exo/endo-**8i**: IR (film) ν = 3446 cm^{-1} (OH), 2955 (C–H), 2872 (C–H), 2784, 1694 (C=O), 1649 (C=C), 1456, 1382, 1323, 1284, 1245, 1213, 1141, 1101, 1072, 1039, 911, 734, 646. – *exo*-**9i** (major diastereomer): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 (s, 3 H, CH_3), 1.21 (m_c, 1 H, 8-H), 1.59 (s, 3 H, CH_3), 1.62 (m_c, 2 H, 7-H), 1.90 (s, 3 H, CH_3), 2.13 [s, 6 H, $N(CH_3)_2$], 2.23 (m_c, 1 H, 8-H), 2.44 (s, 1 H, 5-H), 3.38 (br. s, 1 H, OH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.86, 13.09, 25.30 (+, CH_3), 28.74, 38.30 (–, C-8, C-7), 40.43 [+, $N(CH_3)_2$], 57.82 (+, C-5), 78.28, 79.51 (C_{quat}, C-6, C-1), 137.91 (C_{quat}, C-3), 170.58 (C_{quat}, C-2), 206.48 (C_{quat}, C-4). – *endo*-**9i** (minor diastereomer): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12 (m_c, 1 H, 8-H), 1.38 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.85 (m_c, 2 H, 7-H), 1.89 (s, 3 H, CH_3), 2.06 [s, 6 H, $N(CH_3)_2$], 2.19 (m_c, 1 H, 8-H), 2.42 (s, 1 H, 5-H), 3.38 (br. s, 1 H, OH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.60, 12.85, 28.92 (+, CH_3), 30.49, 40.54 (–, C-8, C-7), 40.01 [+, $N(CH_3)_2$], 55.17 (+, C-5), 78.00, 79.92 (C_{quat}, C-6, C-1), 136.92 (C_{quat}, C-3), 172.47 (C_{quat}, C-2), 207.61 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 223 (48) [M^+], 208 (50) [$M^+ - CH_3$], 179 (44), 161 (100), 152 (35), 133 (20), 105 (10), 84 (16), 53 (10), 44 (29 [$N(CH_3)_2^+$].

2-tert-Butyl-1-dimethylamino-endo-6-hydroxy-6-methylbicyclo[3.3.0]oct-2-en-4-one (*endo*-**8k**) *and 2-tert-Butyl-1-dimethylamino-exo-6-hydroxy-6-methylbicyclo[3.3.0]oct-2-en-4-one* (*exo*-**8k**): 1-*tert*-Butyl-5-dimethylamino-3-ethoxy-5-[2'-(2"-methyl-1",3"-dioxolan-2"-yl)ethyl]-1,3-cyclopentadiene (**4k)** (291 mg, 0.90 mmol) in 45 ml of THF was treated with conc. HCl (2.5 ml, 25 mmol) at room temp. for 3 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2 : 1 to 0 : 1, column 40 × 4 cm) 113 mg (50%) of *endo*-**8k** (R_f = 0.58, diethyl ether) was obtained as colorless crystals, m.p. 101 °C, and 71 mg (31%) of *exo*-**8k** (R_f = 0.52, diethyl ether) as colorless crystals, m.p. 93 °C. *endo*-**8k**: IR (KBr): ν = 3414 cm^{-1} (OH), 2952 (C–H), 2784 (C–H), 1683 (C=O), 1594 (C=C), 1460, 1397, 1377, 1304, 1280, 1250, 1217, 1178, 1161, 1110, 1039, 933, 850. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 [s, 9 H, $C(CH_3)_3$], 1.49 (s, 3 H, CH_3), 1.88 (m_c, 2 H, 7-H), 2.09 (m_c, 1 H, 8-H), 2.11–2.18 [m, 7 H, $N(CH_3)_2$, OH], 2.24 (m_c, 1 H, 8-H), 2.67 (s, 1 H, 5-H), 5.90 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 28.42 (+, CH_3), 31.06 [+, $C(CH_3)_3$], 32.69 (–, C-8), 36.03 [C_{quat}, $C(CH_3)_3$], 40.22 [+, $N(CH_3)_2$], 43.62 (–, C-7), 56.03 (+, C-5), 78.14 (C_{quat}, C-6), 82.62 (C_{quat}, C-1), 129.79 (+, C-3), 192.92 (C_{quat}, C-2), 207.60 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 251 (63) [M^+], 234 (97) [M^+ – OH], 208 (46), 194 (19) [M^+ – $C(CH_3)_3$], 176 (100), 152 (99), 124 (35), 91 (10), 44 (8) [$N(CH_3)_2^+$]. – $C_{15}H_{25}NO_2$ (251.4): calcd. C 71.67, H 10.02; found C 71.86, H 10.14.

exo-**8k**: IR (KBr): ν = 3486 cm^{-1} (OH), 2979 (C–H), 2788 (C–H), 1681 (C=O), 1582 (C=C), 1451, 1374, 1305, 1281, 1242, 1206, 1122, 1038, 933, 911, 891, 544. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, CH_3), 1.27 [s, 9 H, $C(CH_3)_3$], 1.55 (m_c, 1 H, 8-H), 1.88 (m_c, 2 H, 7-H), 2.15 [s, 6 H, $N(CH_3)_2$], 2.32 (m_c, 1 H, 8-H), 2.66 (s, 1 H, 5-H), 2.96 (br. s, 1 H, OH), 5.98 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 25.23 (+, CH_3), 29.58 (–, C-8, C-7), 31.25 [+, $C(CH_3)_3$], 36.05 [C_{quat}, $C(CH_3)_3$], 40.59 [+, $N(CH_3)_2$], 57.45 (+,

C-5), 77.99 (C_{quat}, C-6), 82.79 (C_{quat}, C-1), 130.98 (+, C-3), 191.57 (C_{quat}, C-2), 207.52 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 251 (50) [M^+], 234 (91) [$M^+ – OH$], 208 (51), 194 (25) [$M^+ – C(CH_3)_3$], 176 (94), 152 (100), 126 (32), 91 (10), 44 (8) [$N(CH_3)_2^+$].

1-Dimethylamino-endo-6-hydroxy-6-methyl-2-trimethylsilylbicyclo[3.3.0]oct-2-en-4-one (*endo*-**8l**) *and 1-Dimethylamino-exo-6-hydroxy-6-methyl-2-trimethylsilylbicyclo[3.3.0]oct-2-en-4-one* (*exo*-**8l**): 5-Dimethylamino-3-ethoxy-5-[2'-(2''-methyl-1'',3''-dioxolan-2''-yl)ethyl]-1-trimethylsilyl-1,3-cyclopentadiene (**4l-A**) (312 mg, 0.919 mmol) in 45 ml of THF was treated with conc. HCl (2.7 ml, 27 mmol) at room temp. for 2 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2 : 1 to 0 : 1, column 40 × 4 cm) 104 mg (42%) of *endo*-**8l** (R_f = 0.70, diethyl ether) was obtained as colorless crystals, m.p. 80 °C, and 93 mg (38%) of *exo/endo*-**8l** (1.4 : 1) (R_f = 0.45, diethyl ether) as a colorless oil. *endo*-**8l**: IR (KBr): ν = 3453 cm^{-1} (OH), 2964 (C–H), 2819 (C–H), 1698 (C=O), 1448, 1383, 1275, 1242, 1212, 1179, 1152, 1031, 980, 904, 835, 759. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.21 [s, 9 H, $Si(CH_3)_3$], 1.45 (s, 3 H, CH_3), 1.79 (m_c, 2 H, 7-H), 1.87–2.07 (m, 2 H, 8-H), 2.10 [s, 6 H, $N(CH_3)_2$], 2.23 (br. s, 1 H, OH), 2.51 (s, 1 H, 5-H), 6.12 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.67 [+, $Si(CH_3)_3$], 28.83 (+, CH_3), 33.01 (–, C-8), 40.48 [+, $N(CH_3)_2$], 42.34 (–, C-7), 55.09 (+, C-5), 78.64 (C_{quat}, C-6), 84.06 (C_{quat}, C-1), 140.05 (+, C-3), 188.77 (C_{quat}, C-2), 209.47 (C_{quat}, C-4). – MS (70 eV), *m/z* (%): 267 (35) [M^+], 252 (100) [$M^+ – CH_3$], 250 (48) [$M^+ – OH$], 225 (10), 210 (11), 197 (17), 176 (30), 124 (31), 73 (26) [$Si(CH_3)_3^+$], 44 (7) [$N(CH_3)_2^+$].

exo-**8l**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 1.26 (s, 3 H, CH_3), 1.33 (m_c, 1 H, 8-H), 1.63 (m_c, 2 H, 7-H), 2.01 (m_c, 1 H, 8-H), 2.15 [s, 6 H, $N(CH_3)_2$], 2.48 (s, 1 H, 5-H), 2.63 (br. s, 1 H, OH), 6.22 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus

DEPT): δ = –0.42 [+, $Si(CH_3)_3$], 25.35 (+, CH_3), 30.48, 38.83 (–, C-8, C-7), 40.83 [+, $N(CH_3)_2$], 57.31 (+, C-5), 78.71 (C_{quat}, C-6), 84.21 (C_{quat}, C-1), 141.31 (+, C-3), 187.90 (C_{quat}, C-2), 208.77 (C_{quat}, C-4).

endo-6-Hydroxy-1,2,3,8-tetramethyl-8-azabicyclo[3.3.0]oct-2-en-4-one (**12a**): Pentacarbonyl-{(2*E*)-3-[(1',3'-dioxolan-2'-ylmethyl)methylamino]-1-ethoxy-2-buten-1-ylidene}chromium (**2c**) (500 mg, 1.23 mmol) and 2-butyne (**3a**) (202 mg, 3.73 mmol) were reacted for 6 d in anhydrous pyridine (25 ml) and then for 14 h in DME/HCl according to GP 4. After column chromatography on silica gel (diethyl ether/methanol, 1 : 0 to 10 : 1, column 15 × 1.5 cm) 86 mg (36%) of **12a** (R_f = 0.07, diethyl ether) was obtained as a colorless oil. – IR (film): 3389 cm^{-1} (OH), 2924, 2787 (C–H), 1696 (C=O), 1641 (C=C), 1444, 1338, 1095, 802. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.30 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.42 (s, 3 H, NCH_3), 2.58–2.70 (m, 3 H, 5-H, 7-H, OH), 2.99 (dd, ^2J = 9.8, ^3J = 5.0 Hz, 1 H, 7-H), 4.40 (m_c 1 H, 6-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, plus APT): δ = 7.82, 14.06, 18.86 (+, CH_3), 36.58 (+, NCH_3), 61.09 (+, C-5), 62.33 (–, C-7), 68.73 (+, C-6), 70.11 (–, C-1), 137.74 (–, C-3), 171.69 (–, C-2), 206.75 (–, C-4). – MS (70 eV), *m*/*z* (%): 195 (23) [M^+], 180 (100) [$M^+ – CH_3$], 152 (14) [$M^+ – C_2H_5N$], 109 (18), 83 (10), 44 (18) [$C_2H_5N^+$]. – $C_{11}H_{17}NO_2$ (195.3): 195.1259 (correct HRMS).

endo-6-Hydroxy-8-methyl-2,3-diphenyl-1-propyl-8-azabicyclo[3.3.0]oct-2-en-4-one (**12c**): Pentacarbonyl{(*2E*)-3-[(1',3'-dioxolan-2'-ylmethyl)methylamino]-1-ethoxy-2-hexen-1-ylidene}chromium (**2d**) (800 mg, 1.85 mmol) and diphenylethyne (**3c**) (987 mg, 5.54 mmol) were reacted for 3 d in anhydrous pyridine (37 ml) and then for 20 h in DME/HCl according to GP 4. After column chromatography on silica gel (diethyl ether/methanol, 1 : 0 to 10 : 1,

column 20 × 1 cm) 269 mg (42%) of **12c** (R_f = 0.16, diethyl ether) was obtained as colorless crystals, m.p. 124 °C. – IR (KBr): ν = 3441 cm^{-1} (OH), 2924 (C–H), 1694 (C=O), 1617 (C=C), 1439, 1385, 1033, 739. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.3 Hz, 3 H, 3'-H), 1.35 (m_c, 2 H, 2'-H), 1.74 (m_c, 1 H, 1'-H), 2.00 (m_c, 1 H, 1'-H), 2.01 (s, 3 H, NCH_3), 2.68 (br. s, 1 H, OH), 2.86 (dd, ^2J = 9.8, ^3J = 5.3 Hz, 1 H, 7-H), 2.99 (d, ^3J = 8.4 Hz, 1 H, 5-H), 3.07 (dd, ^2J = 9.8, ^3J = 5.5 Hz, 1 H, 7-H), 4.49 (m_c 1 H, 6-H), 7.01–7.38 (m, 10 H, Ph-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, plus APT): δ = 14.45 (+, C-3'), 18.52 (–, C-2'), 33.94 (–, C-1'), 35.55 (+, NCH_3), 60.16 (+, C-5), 61.73 (–, C-7), 69.82 (+, C-6), 70.14 (–, C-1), 127.63, 127.80, 128.19, 128.38, 128.48, 129.74 (+, Ph-C), 130.57, 130.60 (–, Ph-C), 142.25 (–, C-3), 170.45 (–, C-2), 204.58 (–, C-4). – MS (70 eV), *m*/*z* (%): 347 (5) [M^+], 304 (100) [M^+ – C_3H_7], 262 (10), 230 (8), 168 (13), 123 (8), 57 (15), 43 (11) [$C_3H_7^+$]. – $C_{23}H_{25}NO_2$ (347.5): calcd. C 79.51, H 7.25; found C 79.68, H 7.53.

endo-6-Hydroxy-8-methyl-1-propyl-2-trimethylsilyl-8-azabicyclo[3.3.0]oct-2-en-4-one (**12d**): 5-[(1",3"-Dioxolan-2"-ylmethyl)methylamino]-3-ethoxy-5-propyl-1-trimethylsilyl-1,3-cyclopentadiene (**4p**) (120 mg, 0.353 mmol) in 8 ml DME was treated with conc. HCl (10 ml, 0.10 mol) at 80 °C for 20 h according to GP 3. After column chromatography on silica gel (diethyl ether/methanol, 1 : 0 to 10 : 1, column 20 × 1.5 cm) 67 mg (71%) of **12d** (R_f = 0.16 in diethyl ether) was obtained as a colorless oil. – IR (film): ν = 3373 cm^{-1} (OH), 2953, 2790 (C–H), 1686 (C=O), 1626 (C=C), 1456, 1244, 1092, 837. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.24 [s, 9 H, $Si(CH_3)_3$], 0.89 (t, ^3J = 6.4 Hz, 3 H, 3'-H), 0.90–1.23 (m, 2 H, 2'-H), 1.52–1.80 (m, 3 H, 1'-H, OH), 2.43 (s, 3 H, NCH_3), 2.50 (d, ^3J = 9.9 Hz, 1 H, 5-H), 2.62 (dd, ^2J = 9.9, ^3J = 7.5 Hz, 1 H, 7-H), 3.11 (dd, ^2J = 9.9, ^3J = 5.5 Hz, 1 H, 7-H), 4.43 (m_c, 1 H, 6-H), 6.39 (s, 1 H, 3-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, plus APT): δ = 0.09 [+, $Si(CH_3)_3$],

14.67 (+, C-3'), 19.53 (–, C-2'), 35.96 (–, C-1'), 36.32 (+, NCH_3), 58.96 (+, C-5), 61.39 (–, C-7), 68.68 (+, C-6), 80.07 (–, C-1), 144.16 (+, C-3), 185.09 (–, C-2), 206.83 (–, C-4). – MS (70 eV), *m*/*z* (%): 267 (44) [M^+], 224 (100) [$M^+ – C_3H_7$], 168 (53), 140 (80), 124 (61), 73 (60) [$SiMe_3^+$], 44 (80). – $C_{14}H_{25}NO_2Si$ (267.4): 267.1654 (correct HRMS).