SUPPORTING INFORMATION

Platinum- and Gold-Catalyzed Cycloisomerization Reactions of Hydroxylated Enynes

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General: All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O (Mg-anthracene), CH₂Cl₂ (P₄O₁₀), MeCN, Et₃N (CaH₂), MeOH (Mg), DMF, DMA (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_C \equiv 77.0$ ppm; residual CHCl₃ in CDCl₃: $\delta_H \equiv 7.24$ ppm; CD₂Cl₂: $\delta_C \equiv 53.8$ ppm; residual CH₂Cl₂ in CD₂Cl₂: $\delta_H \equiv 5.32$ ppm). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Gallenkamp melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

Starting Materials

Method A: General Procedure for the PtCl₂-Catalyzed Allylation of Alkynals. A suspension of PtCl₂ (5%), the alkynal (1 equiv.), and allylchlorodimethylsilane **4** (1.2 eq.) in MeCN (5 mL/mmol) was stirred for 15-20 h at ambient temperature. Saturated aq. NaHCO₃ was added, the aqueous phase was repeatedly extracted with methyl *tert*-butyl ether, the combined organic layers were dried over Na₂SO₄, filtered and evaporated. The residue was dissolved in THF (25 mL/mmol) and treated with Bu₄NF·3H₂O (300 mg/mmol) for 30 min. Evaporation of the solvent and subsequent flash chromatography of the crude product

(hexanes/EtOAc mixture) afforded the corresponding homoallyl alcohols in analytically pure form.

Method B: General procedure for Allylation of Alkynals via Grignard Reaction. A solution of the alkynal (1 eq.) in THF was added to a solution of allylmagnesium bromide (1M in Et₂O, 1.5 eq.) at 0°C and stirring was continued for 1 h. The reaction was carefully quenched with water at 0°C and the aqueous layer was extracted with methyl *tert*-butyl ether. The combined organic phases were dried over Na₂SO₄ before they were filtered and evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc mixture) afforded the corresponding homoallylic alcohol in analytically pure form.

The physical data of the products formed by method **A** or method **B** are compiled below.

1-(Phenylethynyl)-but-3-en-1-ol (2a).¹ Yield = 81% (method **A**). IR (KAP): 3353, 3079, 3034, 2980, 2940, 2912, 2231, 1642, 1599, 1490, 1443, 1029, 993, 918, 756, 691 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 1.75 (bs, OH), 2.59 (t, *J* = 6.2 Hz, 2H), 4.67 (t, *J* = 6 Hz, 1H), 5.26 (m, 2H), 5.97 (m, 1H), 7.31 (m, 3H), 7.44 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 42.2, 62.0, 85.2, 91.1, 119.1, 122.5, 128.3, 128.4, 131.7, 133.0. MS (EI): *m/z* (rel intensity): 172 ([M⁺], 2), 131 (100), 103 (20), 77 (18). HR-MS (CI) *calcd.* for C₁₂H₁₂O+H: 173.0966; *found*: 173.0966.

Undec-1-en-5-yn-4-ol (2b).² Yield = 45% (method **A**). IR (KAP): 3357, 3078, 3006, 2957, 2933, 2860, 2229, 1642, 1036, 996, 915 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.91 (t, *J* = 7 Hz, 3H), 1.35 (m, 2H), 1.52 (m, 2H), 1.70 (bs, OH), 2.21 (dt, *J* = 7.2, 2 Hz, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 4.42 (t, *J* = 6 Hz, 1H), 5.19 (m, 2H), 5.90 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.0, 18.7, 22.2, 28.3, 31.0, 42.6, 61.6, 80.5, 86.1, 118.7, 133.4. MS (EI): *m/z* (rel intensity): 125 (100), 91 (20), 81 (57), 79 (28), 67 (20), 55 (88), 41 (45), 29 (30).

Tridec-1-en-5-yn-4-ol (2c).³ Yield = 58% (method **A**). IR (KAP): 3357, 3078, 3003, 2956, 2929, 2857, 2228, 1642, 1379, 1036, 995, 914 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.89 (t, *J* = 6.7 Hz, 3H), 1.10-1.50 (m, 8H), 1.70 (bs, OH), 2.21 (dt, *J* = 7, 2 Hz, 2H), 2.46 (dt, *J* = 6.1, 1.2 Hz, 2H), 4.41 (dt, *J* = 6, 2 Hz, 1H), 5.17 (t, *J* = 1.2 Hz, 1H), 5.21 (m, 1H), 5.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 18.7, 22.6, 28.7, 28.8, 31.8, 80.5, 86.1, 118.7, 133.4. MS (EI): *m/z* (rel intensity): 153 (100), 109 (37), 93 (39), 79 (29), 67 (48), 55 (59), 41 (45). Anal. *calcd.* for C₁₃H₂₂O (194.32): C, 80.35; H, 11.41.

7,7'-Diethoxy-hept-1-en-5-yn-4-ol (5). Yield = 79% (method **B**). IR (KAP): 3432, 3079, 2978, 2932, 2888, 2242, 1643, 1144, 1119, 1054, 1007, 917 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 1.23 (m, 6H), 2.50 (dt, *J* = 7.4, 0.7 Hz, 2H), 3.59 (m, 2H), 3.74 (m, 2H), 4.50 (t, *J* = 7 Hz, 1H), 5.18 (t, *J* = 1.1 Hz, 1H), 5.22 (m, 1H), 5.30 (d, *J* = 1.3 Hz, 1H), 5.88 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 14.9, 41.7, 60.8, 60.85, 61.3, 80.4, 85.5, 91.1, 119.1, 132.6. MS (EI): *m/z* (rel intensity): 197 ([M⁺-H], 3), 157 (6), 153 (33), 111 (100), 103 (49), 83 (55),

¹ Padwa, A.; Dean, D. C.; Fairfax, D. J.; Xu, S. L. *J. Org. Chem.* **1993**, 58, 4646

² Journet, M.; Malacria, M. *J. Org. Chem.* **1992**, 57, 3085

³ Roush, W. R.; Park, J. C. *J. Org. Chem.* **1990**, 55, 1143

79 (37), 55 (33). Anal. *calcd.* for $C_{11}H_{18}O_3$ (198.26): C, 66.64; H, 9.15; *found*: C, 66.52; H, 9.07.

4,4-Dimethyl-1-phenyl-hex-5-en-1-yn-3-ol (7). Yield = 77% (method B). IR (film): 3426, 3082, 3062, 2968, 2930, 2871, 2198, 1639, 1598, 1573, 1490, 1443, 1056, 1032, 1000, 980, 916, 756, 691 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.31 (m, 3H), 6.01 (dd, J = 11.1, 17.2 Hz, 1H), 5.17 (m, 2H), 4.29 (s, 1H), 1.88 (bs, OH), 1.19 (d, J = 6.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 131.7, 128.4, 128.3, 122.7, 114.6, 88.2, 86.0, 70.5, 42.4, 23.1, 22.5. MS (EI): m/z (rel intensity): 200 ($[M^+]$, 3), 185 (9), 131 (100), 103 (22), 77 (25), 70 (46), 51 (7), 41 (18). HR-MS (ESI) *calcd.* for $C_{14}H_{16}O$ + Na: 223.1099; *found*: 223.1097. Anal. *calcd.* for $C_{14}H_{16}O$ (200.28): C 83.96, H 8.05; *found*: C 84.11, H 8.11.

1-Cyclohex-2-enyl-3-phenyl-prop-2-yn-1-ol (9). Yield = 69% (method A). IR (film): 3353, 3059, 3080, 3022, 2927, 2861, 2836, 2228, 1649, 1598, 1572, 1489, 1444, 1029, 756, 691 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.31 (m, 3H), 5.90 (m, 1H), 5.78 (dd, J = 1.8, J = 10.3 Hz, 1H), 4.47 (d, J = 6.5 Hz, 1H), 2.50 (m, 1H), 2.03 (bs, OH), 1.95 (m, 1H), 1.83 (m, 3 H), 1.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.8, 130.4, 128.4, 128.3, 126.9, 122.7, 89.1, 85.7, 66.5, 42.4, 25.2, 24.6, 21.1. MS (EI): m/z (rel intensity): 212 ($[M^+]$, 4), 131 (100), 103 (13), 77 (13), 53 (3), 41 (3). HR-MS (EI) *calcd.* for $C_{15}H_{16}O$: 212.1201; *found*: 212.1204. Anal. *calcd.* for $C_{15}H_{16}O$ (212.29): C 84.87, H 7.60; *found*: C 85.06, H 7.68.

7-(tert-Butyl-dimethyl-silanoxy)-oct-1-en-5-yn-4-ol (11). Yield = 82 % (method B). IR (KAP): 3359, 3080, 2982, 2956, 2931, 2887, 2858, 2217, 1643, 1473, 1464, 1255, 1102, 1030, 1004, 917, 836, 779 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ 0.13 (d, J = 3.8 Hz, 6H), 0.91 (s, 9H), 1.41 (d, J = 6.6 Hz, 3H), 2.47 (t, J = 6.5 Hz, 2H), 4.45 (t, J = 7 Hz, 1H), 4.57 (q, J = 7 Hz, 1H), 5.18 (s, 1H), 5.21 (d, J = 5.3 Hz, 1H), 5.90 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -3.7, -3.8, 18.1, 25.2, 25.7, 41.9, 58.8, 61.4, 83.2, 89.1, 118.8, 132.9. MS (EI): m/z (rel intensity): 254 (1), 213 (8), 197 (7), 75 (100). Anal. *calcd.* for $C_{14}H_{26}O_2Si$ (254.45): C, 66.09; H, 10.30; *found*: C, 66.14; H, 10.18.

Non-8-en-3-yn-2-ol (13a).⁴ A solution of *n*-BuLi (1.6 M in hexanes, 12.5 mL, 20 mmol) was added to a solution of but-3-yn-2-ol (0.8 mL, 10 mmol) in THF (10 mL) at $-78^\circ C$. After stirring for 15 min, a solution of 5-bromo-1-pentene (1.5 g, 10 mmol) and HMPA (5.2 mL, 30 mmol) in THF (10 mL) was introduced and the resulting mixture was stirred at $-78^\circ C$ for 1 h before it was allowed to reach ambient temperature overnight. The reaction was quenched with aq. HCl (1M), the aqueous layer was extracted with methyl *tert*-butyl ether, the combined organic phases were dried over Na_2SO_4 , filtered and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc 9/1) to give alcohol **13a** as a colorless oil (590 mg, 43%). IR (KAP): 3341, 3078, 2980, 2934, 2863, 2843, 2247, 1641, 1076, 999, 913 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ 1.43 (d, J = 6.6 Hz, 3H), 1.63 (quint, J = 7.4 Hz, 2H), 1.73 (bs, OH), 2.20 (m, 4H), 4.51 (q, J = 6.6 Hz, 1H), 4.99 (ddd, J = 10.4, 2.2, 1 Hz, 1H), 5.04 (dt, J = 19.9, 1.6 Hz, 1H), 5.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.9, 24.6, 26.9, 27.7, 32.6, 58.5, 82.4, 84.2, 115.1, 137.7. MS (EI): m/z (rel intensity): 137 ($[M^+]$, 3), 123

⁴ Roush, W. R.; Spada, A. P. *Tetrahedron Lett.* **1982**, 23, 3773.

(21), 109 (21), 105 (45), 95 (44), 91 (29), 81 (31), 79 (69), 77 (29), 67 (62), 55 (56), 43 (100), 27 (28). Anal. *calcd.* for C₉H₁₄O (138.21): C, 78.21; H, 10.21; *found*: C, 78.11; H, 10.09.

1-Phenyl-oct-7-en-2-yn-1-ol (13b). Prepared analogously (57%). IR (KAP): 3365, 3064, 3031, 2976, 2935, 2861, 2226, 1641, 1602, 1493, 1453, 1030, 993, 915, 760, 698 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 1.67 (quint, *J* = 7.3 Hz, 2H), 1.86 (bs, OH), 2.18 (m, 2H), 2.32 (dt, *J* = 7.2, 2 Hz, 2H), 4.99 (dd, *J* = 9.3, 0.9 Hz, 1H), 5.06 (dd, *J* = 17.2, 1.8 Hz, 1H), 5.81 (m, 1H), 7.40 (m, 3H), 7.57 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 18.1, 27.6, 32.7, 64.8, 80.1, 87.2, 115.2, 126.5, 128.1, 128.4, 137.6, 141.1. MS (EI): *m/z* (rel intensity): 200 ([M⁺], 8), 199 (27), 171 (38), 167 (27), 157 (52), 141 (37), 129 (68), 115 (66), 105 (100), 91 (77), 77 (89), 51 (27), 39 (28). Anal. *calcd.* for C₁₄H₁₆O (200.28): C, 83.96; H, 8.05; *found*: C, 83.84; H, 8.12.

Buta-2,3-dienyl-trimethyl-silane (16). To a solution of propargyl alcohol (2.9 mL, 50 mmol) and tosyl chloride (11.4 g, 60 mmol) at -5°C was added powdered KOH (0.5 mol, 28 g) in several portions while maintaining the internal temperature between -5°C and 0°C. After stirring for 30 min at 0°C, the reaction mixture was poured into 100 mL of ice-water and the product was extracted with methyl *tert*-butyl ether (2x100 mL) and the combined organic layers were dried over Na₂SO₄. Evaporation of the solvent provides propargyl tosylate as a pale-brown oil which was used in the next step without purification (9.1 g, 87%). Characteristic data: ¹H NMR (300 MHz, CDCl₃): δ 2.46 (s, 3H), 2.49 (d, *J* = 2.6 Hz, 1H), 4.70 (d, *J* = 2.6 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H). To a suspension of LiCl (3.7 g, 86.7 mmol) in diethyl ether was added CuCN (44.9 mmol, 4 g) and the mixture was cooled to 0°C. A solution of TMSCH₂MgCl (1 M in Et₂O, 44 mL, 44 mmol,) was slowly added and stirring was continued for 40 min. The mixture was then cooled to -78°C before the crude propargyl tosylate prepared above (9.1 g, 43.33 mmol) was slowly added. The mixture was allowed to reach ambient temperature over 17 h. For work-up, the precipitate was filtered off, the filtrate was concentrated and the residue was distilled at atmospheric pressure (bp ≈ 100°C) to give the title compound as a colorless liquid (3.6 g, 66%). ¹H NMR (300 MHz, CDCl₃): δ 0.04 (s, 9H), 1.32 (dt, *J* = 8.6, 2.7 Hz, 2H), 4.63 (dt, *J* = 6.7, 2.7 Hz, 2H), 5.08 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ -2.0, 17.1, 73.9, 86.3, 208.9.

Compound 17. BF₃·Et₂O (1.2 g, 8.7 mmol) was added to a solution of aldehyde **15** (384 mg, 4 mmol)⁵ and 2,3-butadienyl-trimethylsilane **16** (1.10 g, 8.7 mmol) in CH₂Cl₂ (60 mL) at -78°C and the resulting mixture was stirred for 5.5 h at that temperature. The reaction was quenched with aq. sat. NaHCO₃ while cold, the aqueous phase was extracted with CH₂Cl₂, the combined organic layers were dried over Na₂SO₄, the solvent was slowly distilled off at 550 Torr (bath temperature ca. 30°C), and the residue was purified by flash chromatography (pentane/Et₂O, 40:1) to give alcohol **17** as a colorless liquid (300 mg, 50%). ¹H NMR (300 MHz, CDCl₃): δ 1.14 (s, 1H), 1.19 (s, 3H), 1.81 (br., 1H), 2.59 (m, 1H), 5.08 (s, 1H), 5.18 (d, *J* = 11.5 Hz, 1H), 5.19 (s, 1H), 5.49 (d, *J* = 1 Hz, 1H), 5.50 (d, *J* = 17.3 Hz, 1H), 6.36 (dd, *J* = 17.7, 11.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 20.5, 22.7, 62.7, 78.3, 92.6, 115.5, 116.0, 135.0, 145.5; MS (EI): *m/z* (rel intensity): 149 (7), 135 (100), 117 (30), 107 (89), 91 (97), 79 (90), 67 (41), 53 (46).

⁵ Aoyagi, S.; Wang, T.-C.; Kibayashi, C. *J. Am. Chem. Soc.* **1993**, 115, 11393.

Products

General Procedure for the PtCl₂-Catalyzed Cycloisomerization Reaction. PtCl₂ (5%) was added to a solution of the enyne in toluene (5 mL/mmol) and the resulting mixture was stirred at 60-80°C until the reaction was complete (GC/MS and TLC). The solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc mixture) to give the bicyclo[3.1.0]hexanone derivative in analytically pure form. The physical data of the compounds thus formed are compiled below.

‘One-Pot’ Allylation/Cycloisomerization Cascade. PtCl₂ (13.3 mg, 15%) was added to a solution of aldehyde **1** (65 mg, 0.5 mmol) in MeCN (2.5 mL) followed by allylchlorodimethylsilane **4** (151 mg, 0.6 mmol) and the resulting mixture was stirred at 80°C for 24 h. After cooling to room temperature, TBAF·3H₂O (160 mg) was introduced and the mixture was stirred for 30 min at room temperature. Saturated aq. NaHCO₃ was then added, the aqueous phase was repeatedly extracted with methyl *tert*-butyl ether, the combined organic layers were dried over Na₂SO₄, filtered and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc mixture) to give product **3a** in analytically pure form (47 mg, 55 %). For the analytical and spectroscopic data, see below.

1-Phenyl-bicyclo[3.1.0]hexan-3-one (3a). IR (KAP): 3466, 3060, 3035, 2982, 2942, 2905, 2804, 1743, 1602, 1578, 1499, 1445, 755, 698 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.66 (dd, *J* = 5.7, 4.6 Hz, 1H), 1.33 (dd, *J* = 8, 5.9 Hz, 1H), 2.00 (m, 1H), 2.39 (d, *J* = 18.9 Hz, 1H), 2.66 (d, *J* = 18.6 Hz, 1H), 2.85 (ddd, *J* = 17.7, 5.8, 1.1 Hz, 1H), 2.95 (ddd, *J* = 17.4, 3.4, 2 Hz, 1H), 7.10-7.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 21.8, 23.1, 27.6, 42.2, 45.6, 125.7, 126.0, 128.4, 143.0, 216.5. MS (EI): *m/z* (rel intensity): 172 ([M⁺], 42), 144 (91), 129 (100), 115 (29), 103 (46), 77 (23). Anal. *calcd.* for C₁₂H₁₂O (172.23): C, 83.69; H, 7.02; *found*: C, 83.59; H, 7.11. HR-MS (EI) *calcd.* for C₁₂H₁₂O: 172.0888; *found*: 172.0890.

2-Deutero-1-phenyl-bicyclo[3.1.0]hexan-3-one (3a-D₁). IR (KAP): 3460, 3060, 3035, 2983, 2941, 2905, 2804, 2180, 1743, 1602, 1499, 1446, 755, 698 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂): δ 0.66 (dd, *J* = 5.6, 4.7 Hz, 1H), 1.31 (m, 1H), 2.01 (m, 1H), 2.35 (d, *J* = 18.8 Hz, 1H), 2.64 (d, *J* = 18.8 Hz, 1H), 2.84 (ddd, *J* = 18.7, 5.7, 1.9 Hz, 1H), 2.91 (d, *J* = 1.3 Hz, 1H), 7.20-7.40 (m, 5H); ¹³C NMR (100 MHz, CD₂Cl₂): δ 21.9, 23.4, 27.9, 42.5, 45.5 (m, J_{C-D}), 126.1, 126.2, 128.7, 143.7, 216.3. MS (EI): *m/z* (rel intensity): 173 ([M⁺], 44), 145 (100), 130 (82), 116 (18), 104 (43).

1-Pentyl-bicyclo[3.1.0]hexan-3-one (3b). IR (KAP): 3056, 3033, 2956, 2926, 2856, 2872, 1746 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.10 (t, *J* = 4.7 Hz, 1H), 0.75 (ddd, *J* = 8, 4.9, 2 Hz, 1H), 0.91 (t, *J* = 6.9 Hz, 3H), 1.20-1.50 (m, 8H), 1.62 (m, 1H), 2.21 (d, *J* = 19 Hz, 1H), 2.24 (d, *J* = 18.7 Hz, 1H), 2.46 (d, *J* = 17.7 Hz, 1H), 2.63 (dd, *J* = 17.4, 4.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.0, 18.7, 19.0, 22.6, 24.7, 27.3, 31.9, 36.0, 42.4, 45.0, 218.5. MS (EI): *m/z* (rel intensity): 166 ([M⁺], 8), 124 (23), 110 (15), 95 (47), 82 (41), 67 (100), 55 (29), 41 (35). Anal. *calcd.* for C₁₁H₁₈O (166.27): C, 79.46; H, 10.91; *found*: C, 79.60; H, 10.96.

1-Heptyl-bicyclo[3.1.0]hexan-3-one (3c). IR (KAP): 3470, 3056, 3033, 2956, 2925, 2854, 1746 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.10 (t, $J = 4.7$ Hz, 1H), 0.75 (ddd, $J = 8, 4.9, 2$ Hz, 1H), 0.90 (t, $J = 6.9$ Hz, 3H), 1.20-1.40 (m, 12H), 1.61 (m, 1H), 2.21 (d, $J = 19$ Hz, 1H), 2.24 (d, $J = 18.8$ Hz, 1H), 2.46 (dd, $J = 17.7, 1.1$ Hz, 1H), 2.64 (dd, $J = 17.4, 4.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 18.7, 19.1, 22.7, 24.7, 29.3, 27.7, 31.9, 36.1, 42.5, 45.1, 218.5. MS (EI): m/z (rel intensity): 194 ($[\text{M}^+]$, 8), 152 (23), 110 (24), 95 (57), 82 (53), 67 (100), 55 (28), 41 (39). Anal. *calcd.* for $\text{C}_{13}\text{H}_{22}\text{O}$ (194.32): C, 80.35; H, 11.41; *found*: C, 80.18; H, 11.30.

4,4-Dimethyl-1-phenyl-bicyclo[3.1.0]hexan-3-one (8). IR (film): 3060, 3026, 2966, 2929, 2868, 1742, 1603, 1580, 1501, 758, 698 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.33 (m, 2H), 7.22 (m, 3H), 3.09 (dd, $J = 2.5, 18.4$ Hz, 1H), 2.61 (d, $J = 18.3$ Hz, 1H), 1.80 (dd, $J = 4.6, 8.2$ Hz, 1H), 1.24 (s, 3H), 1.19 (m, 1H), 1.13 (s, 3H), 0.54 (dd, $J = 4.6, 5.9$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 219.7, 143.1, 128.5, 126.2, 125.8, 48.7, 44.4, 34.8, 26.6, 24.9, 20.9, 20.4. MS (EI): m/z (rel intensity): 200 ($[\text{M}^+]$, 31), 172 (56), 157 (100), 143 (32), 129 (55), 115 (21), 103 (37), 91 (16), 83 (53), 77 (23), 70 (6), 51 (10), 41 (15). HR-MS (ESI) *calcd.* for $\text{C}_{14}\text{H}_{16}\text{O} + \text{Na}$: 223.1099; *found*: 223.1098. Anal. *calcd.* for $\text{C}_{14}\text{H}_{16}\text{O}$: C 83.96, H 8.05; *found*: C 83.88, H 7.97.

2a-Phenyl-octahydro-cyclopropa[cd]inden-1-one (10). IR (film): 3058, 3029, 2938, 2870, 1739, 1602, 1498, 1446, 747, 698 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.30 (m, 2H), 7.17 (m, 3H), 2.96 (ddd, $J = 1.0, 2.5, 19.6$ Hz, 1H), 2.73 (dd, $J = 1.0, 19.6$ Hz, 1H), 2.75 (m, 1H), 2.15 (dd, $J = 6.6, 8.6$ Hz, 1H), 1.93 (m, 2H), 1.73 (m, 1H), 1.45 (m, 3H), 1.22 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 222.3, 144.7, 128.5, 125.8, 43.8, 43.0, 28.9, 27.1, 24.5, 24.1, 18.9, 17.5. MS (EI): m/z (rel intensity): 212 ($[\text{M}^+]$, 30), 184 (100), 169 (34), 155 (35), 141 (52), 128 (27), 115 (19), 103 (27), 91 (21), 77 (22), 51 (7), 39 (6). HR-MS (EI) *calcd.* for $\text{C}_{15}\text{H}_{16}\text{O}$: 212.1201; *found*: 212.1204. Anal. *calcd.* for $\text{C}_{15}\text{H}_{16}\text{O}$: C 84.87, H 7.60; *found*: C 84.86, H 7.57.

1-(tert-Butyl-dimethyl-silanoxy)-bicyclo[3.1.0]hexan-3-one (12). Mixture of two diastereomers as shown in the insert (d.r. = 3:1); the assignment of the isomers is

unambiguous (based on 1D and 2D spectra) and follows the numbering scheme shown in the insert. Spectroscopic data of the **major isomer**: ^1H NMR (400 MHz, CDCl_3): δ 3.35 (q, $J = 6.2$ Hz, 1H, H-7), 2.81 (ddt, $J = 1.3, 2.2, 18.8$ Hz, 1H, H-2a), 2.58 (ddd, $J = 1.7, 5.8, 19.0$ Hz, 1H, H-4a), 2.16 (dd, $J = 1.2, 19.0$ Hz, 1H, H-4b), 2.10 (dd, $J = 1.2, 18.8$

Hz, 1H, H-2b), 1.36 (ddd, $J = 4.2, 5.8, 8.3$ Hz, 1H, H-5), 1.17 (d, $J = 6.3$ Hz, 3H, H-12), 0.86 (s, 9H, H-9), 0.78 (ddt, $J = 2.0, 6.0, 8.0$ Hz, 1H, H-6a), 0.16 (dd, $J = 4.2, 5.8$ Hz, 1H, H-6b), 0.02 (s, 3H, H-10), 0.01 (s, 3H, H-11); ^{13}C NMR (100 MHz, CDCl_3): δ 217.9 (C-3), 72.1 (C-7), 42.1 (C-4), 40.1 (C-2), 31.3 (C-1), 25.7 (C-9), 22.2 (C-12), 18.8 (C-5), 18.0 (C-8), 17.0 (C-6), -4.5 (C-10), -4.6 (C-11). Spectroscopic data of the **minor isomer**: ^1H NMR (400 MHz, CDCl_3): δ 3.81 (q, $J = 6.1$ Hz, 1H, H-7), 2.57 (ddd, $J = 2, 5.8, 19.1$ Hz, 1H, H-4a), 2.49 (ddt, $J = 1.2, 2.2, 18.9$ Hz, 1H, H-2a), 2.18 (dd, $J = 1.2, 19.0$ Hz, 1H, H-4b), 2.15 (dd, $J =$

1.2, 19.2 Hz, 1H, H-2b), 1.46 (ddd, $J = 4.1, 5.8, 8.3$ Hz, 1H, H-5), 1.15 (d, $J = 6.1$ Hz, 3H, H-12), 1.00 (ddt, $J = 2.0, 5.4, 8.0$ Hz, 1H, H-6a), 0.85 (s, 9H, H-9), 0.04 (dd, $J = 4.6, 5.8$ Hz, 1H, H-6b), 0.02 (s, 3H, H-10), 0.01 (s, 3H, H-11); ^{13}C NMR (100 MHz, CDCl_3): δ 217.7 (C-3), 69.5 (C-7), 42.8 (C-2), 42.1 (C-4), 30.8 (C-1), 25.7 (C-9), 22.1 (C-12), 18.1 (C-8), 16.2 (C-5), 15.9 (C-6), -4.4 (C-10), -4.8 (C-11). Anal. *calcd.* for $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}$ (254.45): C, 66.09; H, 10.30; *found*: C, 66.02; H, 10.29.

1-Bicyclo[3.1.0]hex-1-yl-propan-2-one (14a).⁶ IR (KAP) 3061, 3020, 2997, 2939, 2939, 2881, 2861, 1711, 1356 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 0.38 (dd, $J = 8.1, 4.6$ Hz, 1H), 0.52 (t, $J = 4.6$ Hz, 1.07 (m, 1H), 1.20 (m, 1H), 1.40-1.80 (m, 5H), 2.17 (s, 3H), 2.43 (d, $J = 15.2$ Hz, 1H), 2.59 (d, $J = 15.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 12.3, 21.3, 23.5, 24.9, 27.3, 29.9, 31.5, 50.5, 209.0. MS (EI): m/z (rel intensity): 138 ($[\text{M}^+]$, 2), 123 (5), 95 (45), 80 (53), 67 (26), 43 (100). Anal. *calcd.* for $\text{C}_9\text{H}_{14}\text{O}$ (138.21): C, 78.21; H, 10.21; *found*: C, 78.33; H, 10.06.

2-Bicyclo[3.1.0]hex-1-yl-1-phenyl-ethanone (14b). IR (KAP) 3060, 3025, 2997, 2943, 2881, 2860, 1690, 1597, 1580, 1448, 752, 690 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.37 (dd, $J = 8.1, 5.2$ Hz, 1H), 0.51 (t, $J = 4.8$ Hz, 1.13 (m, 1H), 1.20 (m, 1H), 1.50-1.90 (m, 5H), 3.07 (d, $J = 15.8$ Hz, 1H), 3.23 (d, $J = 15.8$ Hz, 1H), 7.45 (m, 2H), 7.54 (m, 1H), 8.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 12.4, 21.4, 23.5, 25.1, 27.5, 32.1, 128.2, 128.5, 132.8, 137.6, 199.9. MS (EI): m/z (rel intensity): 200 ($[\text{M}^+]$, 10), 105 (100), 77 (33). Anal. *calcd.* for $\text{C}_{14}\text{H}_{16}\text{O}$ (200.28): C, 83.96; H, 8.05; *found*: C, 84.08; H, 8.00.

Sabinone (18). A suspension of PtCl_2 (32 mg, 0.12 mmol) and diene **17** (300 mg, 2.0 mmol) in benzene (15 mL) was stirred for 40 h at 60°C . For work up, the solvent was evaporated and the product was purified by flash chromatography (pentane/ Et_2O , 50:1) to give sabinone **18** as a colorless oil (233 mg, 78%). The physical data are in agreement with those reported in the literature.⁷ ^1H NMR (300 MHz, CDCl_3): δ 0.41 (dd, $J = 3.6, 5.1$ Hz, 1H), 0.91 (d, $J = 6.7$ Hz, 3H), 0.94 (d, $J = 6.7$ Hz, 3H), 1.04 (ddd, $J = 2.9, 5.5, 8.1$ Hz, 1H), 1.46 (m, 1H), 2.03 (dd, $J = 3.4, 8.3$ Hz, 1H), 2.28 (d, $J = 19.1$ Hz, 1H), 2.48 (dd, $J = 2.6, 19.1$ Hz, 1H), 5.24 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 19.5, 19.6, 21.8, 26.4, 30.4, 32.7, 41.5, 113.5, 148.0, 206.1; MS (EI): m/z (rel intensity): 150 ($[\text{M}^+]$, 17), 135 (29), 122 (16), 108 (100), 91 (17), 79 (55), 67 (5), 53 (36), 41 (24).

Sabinol (19). NaBH_4 (65 mg, 1.74 mmol) was added to a stirred solution of ketone **18** (200 mg, 1.3 mmol) and CeCl_3 (426 mg, 1.74 mmol) in MeOH (15 mL) at 0°C . After stirring for 10 min at that temperature, the reaction was quenched with water, the aqueous phase was extracted with CH_2Cl_2 , the combined organic phases were dried over Na_2SO_4 , the solvent was evaporated, and the residue was purified by flash chromatography (pentane/ Et_2O , 25:1) to afford alcohol **19** as a colorless oil (135 mg, 65%, d.r. = 1:1). Analytically pure samples of the individual isomers were obtained by preparative GC which showed the following

⁶ Katz, T. J.; Yang, G. X-Q. *Tetrahedron Lett* **1991**, 5895

⁷ Sirisoma, N. S.; Höld, K. M.; Casida, J. E. *J. Agric. Food Chem.* **2001**, 49, 1915.

spectroscopic data:⁸ IR (KAP): 3341, 2957, 2872, 1660, 1464, 1364, 1090, 1068, 1040, 879, 828, 785 cm⁻¹. MS (EI): *m/z* (rel intensity): 151 (2), 134 (21), 119 (25), 109 (26), 91 (100), 81 (57), 67 (13), 55 (26). **trans-19**: ¹H NMR (300 MHz, CDCl₃): δ 0.79 (ddd, *J* = 2.1, 4.2, 6.3 Hz, 1H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 1.03 (t, *J* = 4.0 Hz, 1H), 1.34 (br, 1H), 1.42 (hept., *J* = 6.8 Hz, 1H), 1.63 (dd, *J* = 3.3, 8.7 Hz, 1H), 1.70 (d, *J* = 13.9 Hz, 1H), 2.04 (ddd, *J* = 2.1, 7.4, 13.9 Hz, 1H), 4.43 (d, *J* = 7.4 Hz, 1H), 4.92 (s, 1H), 4.98 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 19.5, 19.7, 20.0, 28.9, 32.5, 37.2, 37.7, 75.1, 106.7, 157.2; **cis-19**: ¹H NMR (300 MHz, CDCl₃): δ 0.54 (dd, *J* = 3.4, 4.7 Hz, 1H), 0.62 (m, 1H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 1.32 (d, *J* = 8.6 Hz, 1H), 1.38 (hept., *J* = 6.8 Hz, 1H), 1.55 (t, *J* = 10.7 Hz, 1H), 1.67 (dd, *J* = 3.3, 8.3 Hz, 1H), 2.24 (dd, *J* = 7.6, 12.2 Hz, 1H), 4.17 (q, *J* = 7.7 Hz, 1H), 4.84 (s, 1H), 4.95 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 17.8, 19.4, 19.6, 27.8, 32.9, 33.4, 37.6, 71.4, 101.9, 156.1.

Acetic acid 1-phenylethynyl-but-3-enyl ester (20). Acetic anhydride (1.3 mL, 13.3 mmol) and 4-dimethylaminopyridine (0.162 g, 1.33 mmol) were added to a solution of alcohol **2a** (0.450 g, 2.61 mmol) in triethylamine (4 mL). After stirring for 1 h, the mixture was poured on chilled water, the aqueous phase was extracted with *tert*-butyl methyl ether, the combined organic layers were dried (MgSO₄), filtered and evaporated, and the crude product was purified by flash chromatography (hexane/ethyl acetate, 15:1) to give acetate **20** as a yellow liquid (0.475 g, 85%). IR (film): 3081, 3021, 2981, 2937, 2233, 1745, 1643, 1599, 1573, 1491, 1443, 1230, 1021, 990, 922, 758, 692 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.44 (m, 2H), 7.31 (m, 3H), 5.89 (m, 1H), 5.65 (t, *J* = 6.4 Hz, 1H), 5.20 (m, 2H), 2.62 (t, *J* = 6.7 Hz, 2H), 2.11 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 169.3, 132.3, 131.9, 128.7, 128.3, 122.2, 118.8, 86.0, 85.8, 63.7, 39.4, 21.0. MS (EI): *m/z* (rel intensity): 214 ([M⁺], 1), 172 (81), 154 (21), 131 (99), 115 (11), 105 (26), 91 (3), 77 (15), 63 (6), 51 (7), 43 (100), 39 (5). HR-MS (ESI) *calcd.* for C₁₄H₁₄O₂ + Na: 237.0891; *found*: 237.0894. Anal. *calcd.* for C₁₄H₁₄O₂: C 78.48, H 6.59; *found*: C 78.36, H 6.65.

1-Phenyl-bicyclo[3.1.0]hexan-2-one (22). A solution of acetate **20** (0.200 g, 0.933 mmol) in CH₂Cl₂ (2.4 mL) was added to a suspension of (Ph₃P)AuCl (9.25 mg, 18.7 μmol) and AgSbF₆ (6.43 mg, 18.7 μmol) in CH₂Cl₂ (21 mL). After stirring at ambient temperature for 15 min, the solvent was evaporated and the crude product was dissolved in methanol (8 mL). K₂CO₃ (12.9 mg) was added and the suspension was stirred for 1 h before the reaction was quenched with water and the aqueous phase was extracted with *tert*-butyl methyl ether. The combined organic layers were dried (MgSO₄), filtered and evaporated, and the residue was purified by flash chromatography (hexane/ethyl acetate, 4:1 + 1 % triethylamine, *v/v*) to give ketone **22** as a yellow liquid (0.119 g, 74%). IR (film): 3059, 3029, 3000, 2944, 2877, 1722, 1603, 1500, 1446, 753, 698 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.31 (m, 4H), 7.25 (m, 1H), 2.40 (m, 1H), 2.28 (m, 3H), 2.09 (m, 1H), 1.57 (m, 1H), 1.41 (dd, *J* = 4.4, 4.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 213.0, 136.3, 129.1, 128.4, 127.1, 41.3, 32.7, 29.5, 21.8, 20.9. MS (EI): *m/z* (rel. intensity): 172 ([M⁺], 99), 157 (3), 144 (100), 129 (91), 116 (99), 103(81), 89 (17), 77

⁸ (a) Cooper, M. A.; Holden, C. M.; Laftus, P.; Whittaker, D. J. *Chem. Soc. Perkin Trans. II* **1973**, 665; (b) Ohloff, G.; Uhde, G.; Thomas, A. F.; Kovats, E. S. *Tetrahedron* **1966**, 22, 309.

(30), 63 (19), 51 (23), 39 (22), 27 (9). HR-MS (EI) *calcd.* for $C_{12}H_{12}O$: 172.0888; *found*: 172.0891. Anal. *calcd.* for $C_{12}H_{12}O$: C 83.69, H 7.02; *found*: C 83.58, H 6.96.

Although the enol-acetate **21** is labile and is therefore best processed in situ, it can be isolated in analytically pure form by chromatography on Alox. It shows the following analytical and spectroscopic properties: IR (film): 3061, 3029, 2995, 2909, 2844, 1759, 1650, 1603, 1580, 1498, 1207, 755, 699 cm^{-1} . 1H NMR (600 MHz, $CDCl_3$): δ 7.27 (m, 2H), 7.25 (m, 2H), 7.19

21

(m, 1H), 5.21 (dt, $J = 1.9, 2.3$ Hz, 1H), 2.75 (ddd, $J = 2.2, 7.0, 17.3$ Hz, 1H), 2.38 (dd, $J = 2.4, 17.3$ Hz, 1H), 1.96 (s, 3H), 1.73 (dddd, $J = 1.9, 4.6, 8.3, 7.0$ Hz, 1H), 1.59 (dd, $J = 4.4, 8.3$ Hz, 1H), 0.89 (t, $J = 4.6$ Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.4, 153.9, 138.7, 128.6, 128.2, 126.4, 109.9, 36.8, 30.9, 25.0, 20.8, 20.6. MS (EI): m/z (rel intensity): 214 ($[M]^+$, 5), 172 (100), 157 (11), 143 (9), 129 (25), 115 (18), 105 (6), 91 (17), 77 (9), 66 (7), 51 (6), 43 (28), 39 (7). HR-MS (EI) *calcd.* for $C_{14}H_{14}O_2$: 214.0994; *found*: 214.0996. Anal. *calcd.* for $C_{14}H_{14}O_2$: C 78.48, H 6.59; *found*: C 78.34, H 6.65.

4-Methyl-1-phenyl-bicyclo[3.1.0]hexan-3-one (24). The assignment is unambiguous (based on 1D and 2D spectra), following the numbering scheme shown in the insert.

IR (KAP): 3461, 3060, 3027, 2967, 2931, 2872, 1741, 1603, 1499, 1452, 760, 698 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.33 (m, 2H), 7.16-7.22 (m, 2H), 2.98 (ddd, $J = 1.4, 2.4, 18.8$ Hz, 1H, H-2a), 2.60 (d, $J = 18.8$ Hz, 1H, H-2b), 2.39 (dq, $J = 1.4, 7.6$ Hz, 1H, H-4), 1.71 (dd, $J = 4.5, 8.2$ Hz, 1H, H-5), 1.29 (ddd, $J = 2.5, 5.8, 8.3$ Hz, 1H, H-6a), 1.26 (d, $J = 7.6$ Hz, 3H, H-7), 0.64 (dd, $J = 4.6, 5.9$ Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.8 (C-3), 143.1 (Ph), 128.5 (Ph), 126.2 (Ph), 125.7 (Ph), 47.6 (C-4), 44.4 (C-2), 28.9 (C-5), 27.3 (C-1), 22.8 (C-6), 18.2 (C-7). MS (EI): m/z (rel intensity): 186 ($[M]^+$, 28), 158 (88), 143 (100), 129 (72), 115 (25), 103 (47), 77 (26). Anal. *calcd.* for $C_{13}H_{22}O$ (186.26): C, 83.83; H, 7.58; *found*: C, 83.75; H, 7.54.

4-Methyl-1-phenyl-bicyclo[3.1.0]hexan-3-one (25). 1H NMR (400 MHz, $CDCl_3$): δ 7.28-

7.33 (m, 2H), 7.16-7.22 (m, 2H), 2.99 (dt, $J = 2.0, 18.0$ Hz, 1H, H-2a), 2.90 (m, 1H, H-4), 2.63 (d, $J = 18.2$ Hz, 1H, H-2b), 2.08 (ddd, $J = 4.6, 5.6, 8.2$ Hz, 1H, H-5), 1.13 (m, 1H, H-6a), 1.12 (d, $J = 6.9$ Hz, 3H, H-7), 0.52 (dd, $J = 4.6, 5.9$ Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$): δ 216.8 (C-3), 143.0 (Ph), 128.5 (Ph), 126.1 (Ph), 126.0 (Ph), 45.5 (C-2), 45.3 (C-4), 28.5 (C-5), 25.1 (C-1), 19.9 (C-6), 12.3 (C-7). MS (EI): m/z (rel intensity): 186 ($[M]^+$, 28), 158 (88), 143 (100), 129 (72), 115 (25), 103 (47), 77 (26).