SUPPORTING INFORMATION

Oxovanadium-catalysed domino reactions of hydroxy enynes for the construction of Cashmeran-like odorants

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I. General Information

All reactions were performed under argon using solvents and reagents from commercial suppliers without further purification. Unless otherwise noted all solvents for extraction and chromatography were technical grade and used without further purification. Flash chromatography was performed using *Brunschwig silica gel 100726* (particle size 32–63 μ m, 60 Å) and *Santai Technologies, Inc.* silica gel columns (120 g or 320 g, 60 Å), and a mixture of pentane: MTBE as eluent.

NMR spectra were recorded with AV-II 300, AV 400 or AV 500 MHz Bruker spectrometer *instruments*. The chemical shifts for ¹H NMR spectra are reported in δ (ppm) referenced to the residual proton signal of the deuterated solvent; coupling constants are expressed in Hertz (Hz). ¹³C NMR spectra were referenced to the carbon signals of the deuterated solvent; the nature of the carbons (C, CH, CH₂, or CH₃) was determined by recording the DEPT 90 and DEPT 135 experiments, and is given in parentheses. For complete assignments of ¹H NMR signals, COSY, NOESY, and ROESY 2D- or 1D-NMR methods were applied; for complete assignments of ¹³C NMR signals, HMBC and HSQC 2D NMR methods were employed. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet, dd = double doublet, bs = broad singlet. IR spectra were recorded with a *Bruker* Tensor 27 or a Bruker Alpha Platinum instrument with integrated diamond ATR. Melting points were determined using a SGW X-4 micro hot-stage apparatus or Büchi melting point apparatus B 545 and are uncorrected. GC/MS spectral data were obtained from an Agilent 6890 N and MSD 5975 using a column HP-5 MS (30 m \times 0.25 mm, 0.25 μ m). High resolution mass spectra were determined on a Thermo Fisher Scientific Q-Exactive Orbitrap (ESI-MS), Bruker micrOTOF II spectrometer (ESI-MS) and Waters Micromass GCT Premier (EI-MS).

II. Preparation of Substrates Vinyl Propargyl Alcohols 9

General procedure I: At -78 °C, *n*-butyllithium (1.2–1.5 eq.) was added to a solution of vinyl acetylene or substituted vinyl acetylenes (1.5–2.0 eq., 50% *w/w* in xylenes) in tetrahydrofuran (0.5–1.0 M), and the solution was stirred for 30 min. Ketone or aldehyde (1.0 eq.) was added dropwise over 1 h at -78 °C, the resulting mixture was stirred for 2 h before it was allowed to warm to room temperature and stirred further for 2 h. The reaction was quenched by addition of saturated aqueous NH₄Cl. The organic layer was separated and the aqueous phase was well extracted with MTBE (3 × 100 mL). The combined organic extracts were washed with brine (30 mL), dried over MgSO₄, filtered and then concentrated under reduced pressure. The resulting residue was purified by flash chromatography (PE : MTBE = 90 : 10 to 30 : 70) followed by bulb-to-bulb distillation to yield the corresponding propargyl alcohols **9**.

6,6,9-Trimethyldeca-1,8-dien-3-yn-5-ol (**90**) and 6,6,7,7-tetramethylnona-1,8-dien-3-yn-5-ol (**9q**) are known compounds, ¹ which were prepared from aldehydes according to the general procedure I.



5,9-Dimethyldeca-1,8-dien-3-yn-5-ol (9a)

Following the general procedure I, a solution of vinyl acetylene (1.50 eq., 18.6 g, 357 mmol) in THF (300 mL) was treated with *n*-butyllithium (1.30 eq., 309 mmol, 193 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 6-methylhept-5-en-2-one (30.0 g, 238 mmol), and purified by distillation to afford 5,9-dimethyldeca-1,8-dien-3-yn-5-ol (**9a**, 39.0 g, 92% yield, b.p.: 167 °C/0.24 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ = 5.81 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.61 (dd, *J* = 17.6, 2.3 Hz, 1H), 5.45 (dd, *J* = 10.9, 2.3 Hz, 1H), 5.17 (t, *J* = 7.3 Hz, 1H), 2.38–2.07 (m, 3H), 1.75–1.62 (m, 8H), 1.49 (s, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 132.5 (s), 126.9 (t), 123.8 (d), 116.8 (d), 93.4 (s), 82.2 (s), 68.7 (s), 43.4 (t), 29.8 (q), 25.7 (q), 23.7 (t), 17.7 (q) ppm. GC/MS (EI): *m/z* (%): 177 (1) [*M*⁺ – H], 163 (11), 145 (46), 135 (24), 117 (24), 105 (66), 95 (70), 79 (26), 69 (29), 55 (49), 43 (100). IR (neat): 3347, 2972, 2929, 1609, 1449, 1375, 1096, 919 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₂H₁₈O + Na]⁺: 201.1250, found: 201.1248. Odor description: fatty, fruity, green, floral, apricot jam, violet, pear, cucumber, mint leaf.



5-Isobutyl-9-methyldeca-1,8-dien-3-yn-5-ol (9b)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 3.09 g, 59.4 mmol) in THF (60.0 mL) was treated with *n*-butyllithium (1.30 eq., 38.6 mmol, 16.0 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with 2,8-dimethylnon-7-en-4-one² (5.0 g, 29.7 mmol), and purified by distillation to afford 5-isobutyl-9-methyldeca-1,8-dien-3-yn-5-ol (**9b**, 4.60 g, 70.3% yield, b.p.: 110 °C/0.07 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.82$ (dd, J = 17.6, 11.1 Hz, 1H), 5.61 (dd, J = 17.6, 2.2 Hz, 1H), 5.45 (dd, J = 11.1, 2.2 Hz, 1H), 5.18 (t, J = 7.2 Hz, 1H), 2.36–2.12 (m, 3H), 2.04–1.92 (m, 1H), 1.72–1.66 (m, 5H), 1.65 (s, 3H, Me), 1.60–1.57 (m, 2H), 1.02 (d, J = 2.6 Hz, 3H, Me), 1.01 (d, J = 2.6 Hz, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 132.4$ (s), 126.7 (t), 124.0 (d), 116.9 (d), 92.9 (s), 83.6 (s), 71.7 (s), 50.5 (t), 42.8 (t), 25.7 (s), 24.8 (d), 24.3 (q), 24.2 (q), 23.3 (t), 17.7 (q) ppm. GC/MS (EI): m/z (%): 219 (1) [M^+ – H], 205 (2), 187 (4), 177 (13), 159 (48), 145 (14), 137 (26), 121 (34), 105 (48), 95 (37), 79 (28), 69 (60), 55 (64), 41 (100). IR (neat): 2954, 2927, 2869, 1609, 1466, 1450, 1376, 1366, 1152, 1044, 1000, 971, 917cm⁻¹. HRMS (ESI): m/z calcd for [C₁₅H₂₄O–H₂O+H]⁺: 203.1794, found: 203.1796. Odor description: metallic, green, fatty, oily.



6-(But-3-en-1-yn-1-yl)-2,10-dimethylundeca-2,9-dien-6-ol (9c)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 10.7 g, 206 mmol) in THF (200 mL) was treated with *n*-butyllithium (1.3 eq., 134 mmol, 54.0 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with 2,10-dimethylundeca-2,9-dien-6-one³ (20.0 g, 103 mmol), and purified by distillation to afford 6-(but-3-en-1-yn-1-yl)-2,10-dimethylundeca-2,9-dien-6-ol (**9c**, 20.6 g, 81% yield, b.p.: 148 °C/ 0.14 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.83$ (dd, J = 17.6, 11.1 Hz, 1H), 5.62 (dd, J = 17.6, 2.2 Hz, 1H), 5.46 (dd, J = 11.1, 2.2 Hz, 1H), 5.21–5.14 (m, 2H), 2.36–2.12 (m, 5H), 1.73–1.62 (m, 16H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 132.5$ (s), 126.9 (t), 124.0 (d), 116.8 (d), 92.4 (s), 83.5 (s), 72.0 (s),

41.9 (t), 25.8 (q), 23.3 (t), 17.7 (q) ppm. GC/MS (EI): m/z (%): 231 (1) $[M^+ - CH_3]$, 213 (4), 203 (2), 185 (6), 173 (8), 159 (31), 145 (18), 131 (24), 121 (31), 105 (34), 91 (25), 79 (23), 69 (100), 55 (60), 41 (91). IR (neat): 3413, 2967, 2916, 2857, 1715, 1609, 1447, 1376, 1069, 971, 918, 834 cm⁻¹. HRMS (ESI): m/z calcd for $[C_{17}H_{26}O + Na]^+$: 269.1876, found: 269.1872. Odor description: green, plastic, metallic, waxy, candle wax.



1-Cyclopentylidene-4-methyloct-7-en-5-yn-4-ol (9d)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 17.1 g, 328 mmol) in THF (160 mL) was treated with *n*-butyllithium (1.3 eq., 213 mmol, 86.0 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with 5-cyclopentylidenepentan-2-one (25.0 g, 164 mmol), and purified by distillation to afford 1-cyclopentylidene-4-methyloct-7-en-5-yn-4-ol (**9d**, 31.0 g, 92% yield, b.p.: 119 °C/0.1 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.82$ (dd, J = 17.6, 11.1 Hz, 1H), 5.61 (dd, J = 17.6, 2.2 Hz, 1H), 5.46 (dd, J = 11.1, 2.2 Hz, 1H), 5.33–5.26 (m, 1H), 2.33–2.12 (m, 7H), 1.79–1.54 (m, 6H), 1.50 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 144.4$ (s), 126.9 (t), 119.3 (d), 116.8 (d), 93.5 (s), 82.2 (s), 68.8 (s), 43.2 (t), 33.6 (t), 29.8 (q), 28.6 (t), 26.4 (t), 26.3 (t), 25.3 (t) ppm. GC/MS (EI): m/z (%): 189 (11) [M^+ – CH₃], 171 (17), 157 (13), 143 (33), 131 (56), 117 (62), 109 (11), 105 (60), 95 (86), 91 (68), 79 (81), 67 (91), 55 (47), 51 (33), 43 (100). IR (neat): 3356, 2939, 2865, 1450, 1369, 1159, 1129, 1094, 971, 917 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₄H₂₀O + Na]⁺: 227.1406, found: 227.1404. Odor description: fishy, green, metallic, galbanum.



(E)-5,8-Dimethyldeca-1,8-dien-3-yn-5-ol (9e)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 8.25 g, 158 mmol) in THF (80 mL) was treated with *n*-butyllithium (1.3 eq., 103 mmol, 42.0 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with (*E*)-5-methylhept-5-en-2-one (10.0 g, 79 mmol), and purified by distillation to afford (*E*)-5,8-dimethyldeca-1,8-dien-3-yn-5-ol (**9e**, 12.6 g, 89% yield, b.p.: 97 °C/0.07 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.82$ (dd, J = 17.6, 11.1 Hz, 1H), 5.61 (dd, J = 17.6, 2.2 Hz, 1H), 5.46 (dd, J = 11.1, 2.2 Hz, 1H), 5.30

(q, J = 6.7 Hz, 1H), 2.34–2.11 (m, 3H), 1.87–1.69 (m, 2H), 1.64 (s, 3H, Me), 1.58 (d, J = 6.7 Hz, 3H, Me), 1.50 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 135.7$ (s), 126.9 (t), 118.9 (d), 116.8 (d), 93.4 (s), 82.2 (s), 68.7 (s), 41.7 (t), 34.9 (t), 29.8 (q), 15.7 (q), 13.4 (q) ppm. GC/MS (EI): m/z (%): 177 (1) [M^+ – H], 163 (16), 145 (78), 131 (20), 117 (20), 105 (51), 95 (92), 91 (43), 79 (28), 55 (52), 43 (100). IR (neat): 3357, 2979, 2919, 2860, 1448, 1370, 1132, 971, 920, 871 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₂H₁₈O + Na]⁺: 201.1250, found: 201.1252. Odor description: green, rubbery, methyl octyne carbonate.



1-(Benzofuran-2-yl)-3-methylhept-6-en-4-yn-3-ol (9f)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 1.38 g, 26.6 mmol) in THF (50 mL) was treated with *n*-butyllithium (1.3 eq., 17.3 mmol, 11.0 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 4-(benzofuran-2-yl)butan-2-one⁴ (2.50 g, 13.3 mmol), and purified by flash chromatography followed by distillation to afford 1-(benzofuran-2-yl)-3-methylhept-6-en-4-yn-3-ol (**9f**, 2.8 g, 88% yield, b.p.: 212 °C/0.12 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.51-7.36$ (m, 2H), 7.26–7.12 (m, 2H), 6.42 (s, 1H), 5.79 (dd, J = 17.6, 10.9 Hz, 1H), 5.61 (dd, J = 17.6, 2.3 Hz, 1H), 5.48 (dd, J = 10.9, 2.3 Hz, 1H), 3.13–2.93 (m, 2H), 2.19–2.07 (m, 3H), 1.58 (s, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 158.8$ (s), 154.7 (s), 128.9 (s), 127.4 (t), 123.2 (d), 122.5 (d), 120.3 (d), 116.5 (d), 110.8 (d), 102.1 (d), 92.5 (s), 82.7 (s), 68.1 (s), 41.2 (t), 30.2 (q), 24.2 (t) ppm. GC/MS (EI): m/z (%): 240 (16) [M^+], 221 (43), 207 (93), 197 (18), 179 (49), 169 (28), 152 (8), 145 (25), 131 (100), 115 (41), 107 (18), 95 (42), 77 (39), 63 (10), 51 (13). IR (neat): 3387, 2978, 1600, 1455, 1253, 1139, 1103, 927, 798, 740 cm⁻¹. HRMS (EI): m/z calcd for [C₁₆H₁₆O₂]⁺: 240.1150, found: 240.1153. Odor description: odorless.



3-Methyl-1-(1-methyl-1*H*-indol-3-yl)hept-6-en-4-yn-3-ol (9g)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 7.76 g, 149 mmol) in THF (100 mL) was treated with *n*-butyllithium (1.30 eq., 97 mmol, 60.0 mL, 1.6 M in hexane)

at -78 °C for 1 h; then reacted with 4-(1-methyl-1H-indol-3-yl)butan-2-one⁴ (15.0 g, 74.5 mmol), and purified by flash chromatography (PE: MTBE = 3 : 1) to yield 3-methyl-1-(1-methyl-1*H*-indol-3-yl)hept-6-en-4-yn-3-ol (**9**g, 13.8 g, 73% yield) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 7.9 Hz, 1H), 7.30–7.18 (m, 2H), 7.13–7.06 (m, 1H), 6.85 (s, 1H), 5.85 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.66 (dd, *J* = 17.6, 2.3 Hz, 1H), 5.49 (dd, *J* = 10.9, 2.3 Hz, 1H), 3.71 (s, 3H, Me), 3.07–2.91 (m, 2H), 2.19 (s, 1H), 2.15–2.02 (m, 2H), 1.57 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 137.2 (s), 127.8 (s), 127.2 (t), 126.1 (d), 121.7 (d), 119.1 (d), 118.7 (d), 116.9 (d), 114.5 (s), 109.3 (t), 93.5 (s), 82.5 (s), 68.8 (s), 44.1 (t), 32.6 (q), 30.0 (q), 20.6 (t) ppm. GC/MS (EI): *m/z* (%): 253 (9) [*M*⁺], 238 (32), 220 (20), 205 (5), 194 (38), 182 (28), 167 (5), 158 (29), 144 (100), 131 (11), 115 (18), 102 (7), 95 (5), 77 (11), 63 (3), 55 (3). IR (neat): 3376, 2930, 1613, 1472, 1424, 1373, 1130, 1012, 973, 736 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₇H₁₉NO + H]⁺: 254.1539, found: 254.1545. Odor description: odorless.



1-(1H-Indol-3-yl)-3-methylhept-6-en-4-yn-3-ol (9h)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 8.34 g, 160 mmol) in THF (100 mL) was treated with *n*-butyllithium (1.3 eq., 104 mmol, 65.0 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 4-(1*H*-indol-3-yl)butan-2-one⁴ (15.0 g, 80.0 mmol), and purified by flash chromatography (PE : MTBE = 3 : 1) to afford 1-(1*H*-indol-3-yl)-3-methylhept-6-en-4-yn-3-ol (**9h**, 14.9 g, 78% yield) as a yellow liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.95$ (bs, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.25–7.07 (m, 2H), 6.99 (s, 1H), 5.86 (dd, J = 17.6, 10.9 Hz, 1H), 5.66 (dd, J = 17.6, 2.3 Hz, 1H), 5.49 (dd, J = 10.9, 2.3 Hz, 1H), 3.11–2.91 (m, 2H), 2.21–2.02 (m, 3H), 1.59 (s, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 136.4$ (s), 127.4 (s), 127.2 (t), 122.1 (d), 121.1 (d), 119.3 (d), 118.9 (d), 116.8 (d), 116.0 (s), 111.2 (d), 93.3 (s), 82.5 (s), 68.8 (s), 43.8 (t), 30.0 (q), 20.6 (t) ppm. GC/MS (EI): m/z (%): 239 (18) [M^+], 221 (26), 206 (32), 194 (11), 180 (56), 168 (73), 144 (40), 130 (100), 117 (20), 103 (13), 95 (10), 89 (6), 77 (21), 63 (5), 51 (5). IR (neat): 3411, 2929, 1599, 1456, 1337, 1225, 1092, 1010, 972, 739 cm⁻¹. HRMS (EI): m/z calcd for [$C_{16}H_{17}NO$]⁺: 239.1310, found: 239.1309. Odor description: odorless.



5-Isopropyldeca-1,8-dien-3-yn-5-ol (9i)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 5.94 g, 114 mmol) in THF (60 mL) was treated with *n*-butyllithium (1.3 eq., 74.2 mmol, 30.0 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with 2-methyloct-6-en-3-one (8.0 g, 57.1 mmol), and purified by distillation to afford 5-isopropyldeca-1,8-dien-3-yn-5-ol (**9i**, 7.6 g, 69.3% yield, *Z/E* = 19:81, b.p.: 95 °C/0.09 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 5.87–5.77 (m, 1H), 5.65–5.58 (m, 1H), 5.54–5.41 (m, 3H), 2.43–2.17 (m, 2H), 2.16–2.01 (m, 1H), 1.90–1.59 (m, 6H), 1.06–0.98 (m, 6H, 2Me) ppm. ¹³C NMR (100 MHz, CDCl₃): major isomer: δ = 131.2 (d), 126.8(0) (t), 125.5 (d), 116.8 (d), 91.6 (s), 84.0 (s), 75.0 (s), 38.8 (t), 37.7(5) (d), 27.6 (t), 17.9 (q), 17.8 (q), 17.0 (q) ppm; minor isomer: δ = 130.2 (d), 126.8(3) (t), 124.6 (d), 116.8 (d), 91.6 (s), 84.0 (s), 75.1 (s), 38.7 (t), 37.7(0) (d), 22.1 (t), 17.9 (q), 17.8 (q), 12.8 (q) ppm. GC/MS (EI): *m/z* (%): 191 (1) [*M*⁺ − H], 177 (3) [*M*⁺ − CH₃], 159 (6), 149 (70), 131 (16), 123 (14), 107 (29), 91 (26), 79 (100), 67 (10), 55 (82), 51 (14), 43 (45). IR (neat): 3447, 2963, 2918, 1609, 1411, 1368, 1138, 1036, 964, 917 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₃H₂₀O + Na]⁺: 215.1406, found: 215.1408. Odor description: fatty, mushroom, green, earthy.



5-Isobutylnona-1,8-dien-3-yn-5-ol (9j)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 5.20 g, 100 mmol) in THF (100 mL) was treated with *n*-butyllithium (1.3 eq., 64.9 mmol, 26.0 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with 2-methyloct-7-en-4-one⁵ (7.0 g, 49.9 mmol), and purified by distillation to afford 5-isobutylnona-1,8-dien-3-yn-5-ol (**9**j, 7.40 g, 77% yield, b.p.: 105 °C/0.07 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 5.94–5.77 (m, 2H), 5.61 (dd, *J* = 17.6, 2.2 Hz, 1H), 5.46 (dd, *J* = 11.1, 2.2 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.01–4.94 (m, 1H), 2.39–2.22 (m, 2H), 2.06–1.90 (m, 2H), 1.79–1.70 (m, 2H), 1.66–1.53 (m, 2H), 1.03 (d, *J* = 3.1 Hz, 3H, Me), 1.01 (d, *J* = 3.1 Hz, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 138.5 (d), 126.9 (t), 116.8 (s), 114.8 (t), 92.7 (s), 83.7 (s), 71.4 (s), 50.5 (t),

42.0 (t), 28.9 (t), 24.9 (d), 24.3 (q), 24.2 (q) ppm. GC/MS (EI): m/z (%): 191 (1) [M^+ – H], 177 (2), 159 (4), 149 (6), 137 (83), 135 (50), 131 (9), 121 (8), 117 (12), 107 (12), 95 (26), 91 (25), 79 (100), 57 (19), 55 (34), 51 (17), 43 (36). IR (neat): 2953, 1712, 1365, 1140, 995, 971, 911, 677 cm⁻¹. HRMS (ESI): m/z calcd for [$C_{13}H_{20}O + Na$]⁺: 215.1406, found: 215.1408. Odor description: green, earthy, fatty, chamomile herbal.



5,7,7-trimethylnona-1,8-dien-3-yn-5-ol (9k)

Following the general procedure I, a solution of vinyl acetylene (1.50 eq., 18.6 g, 357 mmol) in THF (300 mL) was treated with *n*-butyllithium (1.30 eq., 309 mmol, 193 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 4,4-dimethylhex-5-en-2-one (30.0 g, 238 mmol), and purified by distillation to afford 5,7,7-trimethylnona-1,8-dien-3-yn-5-ol (**9k**, 33.7 g, 79% yield, b.p.: 122 °C/0.33 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.08$ (dd, J = 17.6, 10.7 Hz, 1H), 5.79 (dd, J = 17.6, 10.9 Hz, 1H), 5.58 (dd, J = 17.6, 2.3 Hz, 1H), 5.44 (dd, J = 10.9, 2.3 Hz, 1H), 5.14–4.99 (m, 2H), 2.57 (s, 1H), 1.83 (dd, J = 16.9, 14.5 Hz, 2H), 1.47 (s, 3H, Me), 1.28 (s, 3H, Me), 1.10 (s, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 148.9$ (d), 126.4 (t), 116.9 (d), 111.5 (s), 94.5 (s), 82.9 (s), 67.7 (s), 54.7 (t), 37.0 (s), 32.6 (q), 30.2 (q), 26.5 (q) ppm. GC/MS (EI): m/z (%): 177 (1) [$M^+ -$ H], 163 (4), 145 (23), 135 (5), 121 (5), 105 (17), 95 (100), 91 (16), 79 (16), 69 (23), 55 (18), 43 (62). IR (neat): 3421, 2962, 1638, 1609, 1457, 1363, 1009, 972 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₂H₁₈O + Na]⁺: 201.1250, found: 201.1249. Odor description: green, fatty, undecavertol, vegetable, cucumber, nonadienol, slightly mushroom myrth.



5,6,7,7-tetramethylnona-1,8-dien-3-yn-5-ol (9l)

Following the general procedure I, a solution of vinyl acetylene (1.5 eq., 5.57 g, 107 mmol) in THF (200 mL) was treated with *n*-butyllithium (1.40 eq., 100 mmol, 70 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 3,4,4-trimethylhex-5-en-2-one (10.0 g, 71.3 mmol), and purified by distillation to afford diastereomeric mixture of 5,6,7,7-tetramethylnona-1,8-dien-3-yn-5-ol (**9l**, 7.1 g, 52 % yield, dr = 7:3, b.p.: 92 °C/0.1 mbar) as a colorless liquid. These

two isomers could be separated by silica gel chromatography (PE: MTBE = 95:5, major isomer $R_f = 0.35$, minor isomer $R_f = 0.30$).

Major isomer: ¹H NMR (300 MHz, CDCl₃): $\delta = 6.22$ (dd, J = 17.7, 10.7 Hz, 1H), 5.81 (dd, J = 17.6, 11.0 Hz, 1H), 5.58 (dd, J = 17.6, 2.1 Hz, 1H), 5.43 (dd, J = 11.0, 2.1 Hz, 1H), 5.11 (d, J = 17.7 Hz, 1H), 5.03 (d, J = 10.7 Hz, 1H), 3.02 (s, 1H), 1.79–1.68 (m, 1H), 1.49 (s, 3H, Me), 1.23 (s, 3H, Me), 1.05 (s, 3H, Me), 1.03 (d, J = 6.1 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 150.9$ (d), 126.3 (t), 117.0 (d), 110.6 (t), 93.3 (s), 83.8 (s), 72.3 (s), 52.6 (d), 40.2 (s), 31.5 (q), 29.6 (q), 20.9 (q), 13.1 (t) ppm. GC/MS (EI): m/z (%): 191 (1) [M^+ – H], 177 (3), 159 (13), 149 (3), 121 (3), 105 (10), 95 (100), 91 (14), 83 (13), 79 (13), 69 (21), 55 (29). IR (neat): 2974, 1377, 1115, 1031, 972, 913 cm⁻¹. HRMS (EI): m/z calcd for [$C_{13}H_{20}O$]⁺: 192.1514, found: 192.1519.

Minor isomer: ¹H NMR (300 MHz, CDCl₃): $\delta = 6.11$ (dd, J = 17.6, 10.8 Hz, 1H), 5.80 (dd, J = 17.6, 11.0 Hz, 1H), 5.58 (dd, J = 17.6, 2.2 Hz, 1H), 5.43 (dd, J = 11.0, 2.2 Hz, 1H), 5.05– 4.91 (m, 2H), 2.21 (s, 1H), 1.87–1.75 (m, 1H), 1.52 (s, 3H, Me), 1.15 (s, 3H, Me), 1.14 (s, 3H, Me), 1.09 (d, J = 7.1 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 149.6$ (d), 126.4 (t), 117.0 (d), 110.3 (t), 95.4 (s), 82.9 (s), 72.1 (s), 51.6 (d), 40.0 (s), 29.8 (q), 28.5 (q), 24.4 (q), 12.4 (q) ppm. GC/MS (EI): m/z (%): 191 (1) [M^+ – H], 177 (4), 159 (5), 149 (4), 135 (4), 121 (5), 105 (8), 95 (100), 79 (14), 69 (20), 55 (31). IR (neat): 2977, 1376, 1033, 972, 677 cm⁻¹. HRMS (EI): m/z calcd for [C₁₃H₂₀O]⁺: 192.1514, found: 192.1513.



2,5,9-Trimethyldeca-1,8-dien-3-yn-5-ol (9m)

Following the general procedure I, a solution of 2-methylbut-1-en-3-yne (1.20 eq., 9.43 g, 143 mmol) in THF (200 mL) was treated with *n*-butyllithium (1.20 eq., 143 mmol, 89.4 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 6-methylhept-5-en-2-one (15.0 g, 119 mmol), and purified by distillation to afford 2,5,9-trimethyldeca-1,8-dien-3-yn-5-ol (**9m**, 20.8 g, 90% yield, b.p.: 121 °C/0.18 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 5.29-5.11$ (m, 3H), 2.37–2.05 (m, 3H), 1.87 (s, 3H, Me), 1.75–1.61 (m, 8H), 1.48 (s, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 132.4$ (s), 126.4 (s), 123.9 (d), 121.8 (t), 91.8 (s), 84.7 (s), 68.7 (s), 43.4 (t), 29.9 (q), 25.7 (q), 23.8 (t), 23.5 (q), 17.7 (q) ppm. GC/MS (EI): *m/z* (%): 191 (1) [*M*⁺ – H], 177 (11), 159 (24), 149 (16), 134 (16), 119 (47), 109 (56), 91 (35), 79 (17),

69 (28), 55 (37), 43 (100). IR (neat): 3381, 2973, 2926, 2858, 1614, 1449, 1373, 1286, 1120, 1183, 895 cm⁻¹. HRMS (ESI): m/z calcd for $[C_{13}H_{20}O + Na]^+$: 215.1406, found: 215.1408. Odor description: floral, fruity, saugescloree.



1-(1-(3-Methylbut-2-en-1-yl)cyclopentyl)pent-4-en-2-yn-1-ol (9p)

Following the general procedure I, a solution of vinyl acetylene (1.50 eq., 15.6 g, 300 mmol) in THF (300 mL) was treated with *n*-butyllithium (1.40 eq., 280 mmol, 175 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with 1-(3-methylbut-2-en-1-yl)cyclopentane-1-carbaldehyde (33.3 g, 200 mmol), and purified by distillation to afford 1-(1-(3-methylbut-2-en-1-yl)cyclopentyl)pent-4-en-2-yn-1-ol (**9p**, 39.0 g, 89% yield, b.p.: 158 °C/0.18 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 5.82$ (ddd, J = 17.6, 10.9, 1.4 Hz, 1H), 5.61 (dd, J = 17.6, 2.2 Hz, 1H), 5.46 (dd, J = 10.9, 2.2 Hz, 1H), 5.25 (t, J = 7.7 Hz, 1H), 4.32 (s, 1H), 2.36 (dd, J = 14.4, 8.4 Hz, 1H), 2.07 (dd, J = 14.4, 6.8 Hz, 2H), 1.77–1.56 (m, 11H), 1.54–1.35 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 134.1$ (s), 126.9 (t), 121.2 (d), 116.9 (d), 90.5 (s), 84.0 (s), 69.6 (d), 51.2 (s), 35.4 (t), 34.5 (t), 33.4 (t), 26.2 (q), 25.9 (t), 18.1 (q) ppm. GC/MS (EI): m/z (%): 217 (1) [M^+ – H], 203 (3), 185 (9), 175 (8), 157 (8), 137 (17), 121 (14), 107 (16), 98 (24), 81 (41), 69 (100), 55 (23), 41 (43). IR (neat): 3388, 2950, 2867, 1609, 1449, 1377, 1157, 1020, 972, 917 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₅H₂₂O + Na]⁺: 241.1563, found: 241.1561.



(Z)-1-Phenylhept-4-en-1-one

To a solution of Weinreb amide N-methoxy-N-methylbenzamide (5.93 g, 35.9 mmol) in THF (100 mL), freshly prepared Grignard reagent (*Z*)-hex-3-en-1-ylmagnesium bromide (1.5 eq., 53.9 mmol, 54 mL, 1.0 M in THF) was added dropwise over 1 h at 0 °C. The reaction was

monitored by GC and TLC. After complete conversion, the reaction mixture was quenched with saturated aqueous NH₄Cl (30 mL). The organic phase was separated, and the aqueous layer was extracted with MTBE (2 × 10 mL). The combined organic layers were washed with brine (20 mL), and dried (MgSO₄), and the solvents were evaporated in *vacuo*. The residue was purified by column chromatography on silica gel followed by kugelrohr distillation to give (*Z*)-1-phenylhept-4-en-1-one (5.2 g, 59%, *Z/E* = 95:5, b.p.: 158 °C/0.15 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.98 (s, 1H), 7.59 (s, 1H), 7.61–7.41 (m, 3H), 5.49–5.31 (m, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.54–2.42 (m, 2H), 2.14–2.01 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 199.8 (s), 137.0 (s), 133.0 (d), 132.9 (d), 128.6 (d), 128.1 (d), 127.3 (d), 38.7 (t), 22.0 (t), 20.5 (t), 14.3 (q) ppm. GC/MS (EI): *m/z* (%): 188 (5) [*M*⁺], 159 (7), 145 (2), 120 (28), 105 (100), 91 (5), 77 (46), 67 (2). IR (neat): 2963, 1684, 1598, 1449, 1359, 1237, 1202, 957, 744, 689 cm⁻¹. HRMS (EI): *m/z* calcd for [C₁₃H₁₆O]⁺: 188.1201, found: 188.1209.

(Z)-5-Phenylundeca-1,8-dien-3-yn-5-ol (cis-9r)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 2.08 g, 40.0 mmol) in THF (60 mL) was treated with *n*-butyllithium (1.3 eq., 26.0 mmol, 16.5 mL, 1.6 M in hexane) at -78 °C for 0.5 h; then reacted with (*Z*)-1-phenylhept-4-en-1-one (3.77 g, 20.0 mmol), and purified by silica gel chromatography (PE/MTBE = 95:5 \rightarrow 85:15) to afford (*Z*)-5-phenylundeca-1,8-dien-3-yn-5-ol (*cis-*9r, 3.9 g, 81% yield, b.p.: 198 °C/0.12 mbar) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.63 (s, 1H), 7.61 (s, 1H), 7.41–7.24 (m, 3H), 5.91 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.70 (dd, *J* = 17.6, 2.1 Hz, 1H), 5.53 (dd, *J* = 11.0, 2.1 Hz, 1H), 5.44–5.26 (m, 2H), 2.49 (s, 1H), 2.37–2.21 (m, 1H), 2.19–1.86 (m, 5H), 0.93 (t, *J* = 7.5 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 144.5 (s), 132.6 (d), 128.2 (d), 128.1 (d), 127.7 (d), 127.6 (t), 125.4 (d), 116.6 (d), 91.9 (s), 84.9 (s), 73.7 (s), 45.2 (t), 22.9 (t), 20.5 (t), 14.3 (q) ppm. GC/MS (EI): *m/z* (%): 239 (1) [*M*⁺ – H], 211 (3), 193 (8), 178 (3), 167 (7), 157 (100), 141 (5), 128 (11), 115 (7), 105 (20), 91 (6), 79 (57). IR (neat): 2962, 1448, 1055, 971, 920, 763, 698 cm⁻¹. HRMS (EI): *m/z* calcd for [C₁₇H₂₀O]⁺: 240.1514, found: 240.1517.



(E)-1-Phenylhept-4-en-1-one

Following the procedure of (*Z*)-1-phenylhept-4-en-1-one, a solution of Weinreb amide *N*-methoxy-*N*-methylbenzamide (7.70 g, 46.6 mmol) in THF (100 mL) was treated with freshly prepared Grinard reagent (*Z*)-hex-3-en-1-ylmagnesium bromide (1.5 eq., 70.0 mmol, 70 mL, 1.0 M in THF) at 0 °C for 2 h and purified by silica gel chromatography (PE/MTBE = 95:5 \rightarrow 90:10) to afford (*E*)-1-phenylhept-4-en-1-one (4.6 g, 62% yield, *Z*/*E* = 5:95, b.p.: 146 °C/0.16 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ = 8.01–7.91 (m, 2H), 7.60–7.40 (m, 3H), 5.60–5.38 (m, 2H), 3.07–2.99 (m, 2H), 2.49–2.36 (m, 2H), 2.07–1.93 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 199.8 (s), 137.1 (s), 133.1 (d), 132.9 (d), 128.6 (d), 128.1 (d), 127.5 (d), 38.6 (t), 27.2 (t), 25.5 (t), 13.8 (q) ppm. GC/MS (EI): *m*/*z* (%): 188 (6) [*M*⁺], 159 (7), 145 (3), 131 (3), 120 (26), 105 (100), 91 (6), 77 (48), 67 (3). IR (neat): 2962, 1684, 1597, 1448, 1202, 966, 742, 689 cm⁻¹. HRMS (ESI): *m*/*z* calcd for [C₁₃H₁₆O + H]⁺: 189.1274, found: 189.1276.

(E)-5-Phenylundeca-1,8-dien-3-yn-5-ol (trans-9r)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 2.38 g, 45.7 mmol) in THF (60 mL) was treated with *n*-butyllithium (1.3 eq., 29.7 mmol, 18.5 mL, 1.6 M in hexane) at -78 °C for 0.5 h; then reacted with (*E*)-1-phenylhept-4-en-1-one (4.30 g, 22.8 mmol), and purified by silica gel chromatography (PE/MTBE = 95:5 \rightarrow 85:15) to afford (*E*)-5-phenylundeca-1,8-dien-3-yn-5-ol (*trans-9r*, 4.8 g, 87% yield, b.p.: 206 °C/0.2 mbar) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.66-7.56$ (m, 2H), 7.41–7.22 (m, 3H), 5.90 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.69 (dd, *J* = 17.6, 2.1 Hz, 1H), 5.53 (dd, *J* = 11.0, 2.1 Hz, 1H), 5.49–5.30 (m, 2H), 2.51 (s, 0.05H, *Z*-isomer-Me), 2.50 (s, 0.95H, *E*-isomer-Me), 2.29–1.86 (m, 6H), 0.93 (t, *J* = 7.5 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 144.6$ (s), 132.7 (d), 128.2(4) (d), 128.2(0) (d), 127.7 (d), 127.5 (t), 125.4 (d), 116.7 (d), 92.0 (s), 84.9 (s), 73.6 (s), 45.1 (t), 28.0 (t), 25.6 (t), 13.8 (q) ppm. GC/MS (EI): *m/z* (%): 239 (2) [*M*⁺ – H], 222 (2), 211 (4), 193 (11), 178 (4), 167 (7), 157 (100), 141 (6), 128 (14), 115 (9), 105 (24), 91 (7), 79 (78), 67 (3). IR (neat): 2960, 1600, 1448, 966, 920, 761, 699 cm⁻¹. HRMS (EI): *m/z* calcd for [C₁₇H₂₀O]⁺: 240.1514, found: 240.1521.



(1*R**,2*R**)-1-(But-3-en-1-yn-1-yl)-2-(2-methylbut-3-en-2-yl)cyclohexan-1-ol (*cis*-9s)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 15.7 g, 301 mmol) in THF (200 mL) was treated with *n*-butyllithium (1.30 eq., 195 mmol, 78 mL, 2.5 M in hexane) at -78 °C for 1 h; then reacted with 2-(2-methylbut-3-en-2-yl)cyclohexan-1-one (25 g, 150 mmol), and purified by distillation to afford diastereomer mixture of 1-(but-3-en-1-yn-1-yl)-2-(2-methylbut-3-en-2-yl)cyclohexan-1-ol (**9s**, 27.5 g, 84%, dr = 68:32, b.p.: 127 °C/0.14 mbar) as a colorless liquid. Odor description: green metallic, fruity, MOC.

(1*R**,2*R**)-1-(But-3-en-1-yn-1-yl)-2-(2-methylbut-3-en-2-yl)cyclohexan-1-ol (*cis*-9s)

Cis-9s (3.2g) was separated from the diastereomers mixture (6 g) by silica gel chromatography (the less polar isomer, PE : MTBE = 10:1, $R_f = 0.55$) and purified by distillation (132 °C/0.15 mbar). Its relative configuration was confirmed by 2D NMR. ¹H NMR (400 MHz, CDCl₃): $\delta = 6.17$ (dd, J = 17.6, 10.7 Hz, 1H), 5.81 (dd, J = 17.6, 11.1 Hz, 1H), 5.56 (dd, J = 17.6, 2.2 Hz, 1H), 5.41 (dd, J = 11.1, 2.2 Hz, 1H), 5.05 (dd, J = 17.6, 1.5 Hz, 1H), 5.01 (dd, J = 10.7, 1.5 Hz, 1H), 2.21 (d, J = 1.2 Hz, 1H), 2.04–1.95 (m, 1H), 1.80–1.41 (m, 8H), 1.36 (s, 3H, Me), 1.26 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 148.6$ (d), 125.9 (t), 117.2 (d), 111.2 (t), 97.0 (s), 84.2 (s), 69.8 (s), 54.3 (d), 43.8 (t), 40.6 (s), 28.4 (q), 27.0 (q), 26.4 (t), 23.3 (t), 21.1 (t) ppm. GC/MS (EI): m/z (%): 217 (1) [M^+ – H], 203 (11), 185 (23), 175 (17), 157 (15), 147 (23), 131 (34), 119 (34), 107 (63), 91 (65), 79 (80), 69 (47), 55 (95), 41 (100). IR (neat): 3553, 2932, 2863, 1607, 1446, 1363, 1174, 968, 906 cm⁻¹. HRMS (ESI): m/z calcd for [$C_{15}H_{22}O + Na$]⁺: 241.1563, found: 241.1564.



(Z)-2-(Cyclooct-3-en-1-yl)hex-5-en-3-yn-2-ol (9t)

Following the general procedure I, a solution of vinyl acetylene (2.0 eq., 6.16 g, 118 mmol) in THF (100 mL) was treated with *n*-butyllithium (1.3 eq., 77 mmol, 48.2 mL, 1.6 M in hexane) at -78 °C for 1 h; then reacted with (*Z*)-1-(cyclooct-3-en-1-yl)ethan-1-one (Tanaisone,⁶ 9.0 g, 59.1 mmol), and purified by distillation to afford (*Z*)-2-(cyclooct-3-en-1-yl)hex-5-en-3-yn-2-ol (**9t**, 8.6 g, 71% yield, dr = 69:31, b.p.: 162 °C/0.17 mbar) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ = 6.03–5.53 (m, 4H), 5.46 (dd, *J* = 10.9, 2.3 Hz, 1H), 2.53–2.17 (m, 3H), 2.12–1.91 (m, 3H), 1.89–1.70 (m, 1H), 1.69–1.22 (m, 7H) ppm. ¹³C NMR (75 MHz, CDCl₃): major isomer: δ = 130.2 (d), 129.1 (d), 126.9 (t), 116.8 (d), 93.9 (s), 82.6 (s), 71.8 (s), 50.9 (d), 28.8 (t), 27.7 (t), 26.9 (q), 25.1 (t), 24.8 (t) ppm. minor isomer: δ = 130.0 (d), 129.2

(d), 126.9 (t), 116.8 (d), 93.8 (s), 82.6 (s), 71.7 (s), 50.9 (d), 28.9 (t), 27.6 (t), 27.3 (q), 25.1 (t), 24.7 (t) ppm. GC/MS (EI): m/z (%): 203 (3) $[M^+ - H]$, 189 (6), 171 (4), 161 (9), 147 (8), 133 (5), 119 (5), 109 (34), 95 (100), 79 (18), 67 (56), 55 (15). IR (neat): 3390, 2928, 2856, 1609, 1469, 1370, 1200, 1111, 1062, 971, 919, 755 cm⁻¹. HRMS (EI): m/z calcd for $[C_{14}H_{20}O]^+$: 204.1514, found: 204.1511.

III. Oxovanadium-Catalyzed Cycloisomerization of 5-Hydroxy-enynes 9

General procedure II: [Ph₃SiO]₃VO (5 mol %, 447 mg) and xylenes (40.0 mL) were charged into a 100 mL three-necked reaction flask equipped with a thermometer, a slow-addition inlet, a *Dean-Stark* with a condenser and a nitrogen inlet. Unless otherwise specified, the solution was heated under reflux for 30 min, then a solution of freshly prepared **9** (10.0 mmol) in xylenes (10.0 mL) was added dropwise into this refluxing catalyst system by a syringe pump over 10 h. The refluxing was continued till the total reaction time reached 15 h. The reaction was monitored by GC and TLC. After cooled to room temperature, the reaction mixture was diluted with MTBE (100 mL), washed with aqueous NaHCO₃ and brine, dried over MgSO₄, filtered and then concentrated under reduced pressure to give the crude product. The residue was purified by flash chromatography followed by bulb-to-bulb (kugelrohr) distillation to yield the corresponding **19** or **20**.



3,7,7-Trimethyl-1,2,5,6,7,7a-hexahydro-4*H***-inden-4-one** (19a)⁷

Following the general procedure II, 1.2 g, 67% yield, b.p.: 92 °C/0.1 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.82-2.71$ (m, 1H), 2.49–2.23 (m, 4H), 2.10 (s, 3H, Me), 1.95–1.83 (m, 1H), 1.75–1.46 (m, 3H), 0.98 (s, 3H, Me), 0.83 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 200.4$ (s), 154.7 (s), 133.5 (s), 56.5 (d), 38.9 (t), 38.5 (t), 37.4 (t), 32.7 (s), 29.0 (q), 24.3 (t), 19.0 (q), 16.3 (q) ppm. GC/MS (EI): m/z (%): 178 (56) [M^+], 163 (19), 150 (8), 145 (7), 135 (19), 122 (75), 109 (100), 107 (26), 91 (18), 79 (52), 65 (10), 55 (16), 41 (17). IR (neat): 2952, 2864, 2831, 1675, 1615, 1430, 1385, 1276, 1157, 987, 818 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₂H₁₈O + H]⁺: 179.1430, found: 179.1429. Spectral data obtained matched with literature values.⁷ Odor description: woody fruity sweet, honey resinous.



3-Isobutyl-7,7-dimethyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19b)

Following the general procedure II, 1.16 g, 53% yield, b.p.: 126 °C/0.11 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 2.78 (t, *J* = 8.4 Hz, 1H), 2.56 (dd, *J* = 13.0, 8.0 Hz, 1H), 2.42 (dd, *J* = 13.0, 8.0 Hz, 1H), 2.38–2.32 (m, 4H), 1.96–1.77 (m, 2H), 1.75–1.46 (m, 3H), 0.98 (s, 3H, Me), 0.91 (d, *J* = 6.6 Hz, 3H, Me), 0.87–0.83 (m, 6H, 2Me) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 200.4 (s), 157.9 (s), 134.4 (s), 56.6 (d), 39.0 (t), 38.6 (t), 37.8 (t), 36.2 (t), 32.8 (s), 29.0 (q), 27.5 (d), 24.3 (t), 22.7 (q), 22.4 (q), 19.1 (q) ppm. GC/MS (EI): *m/z* (%): 220 (63) [*M*⁺], 205 (77), 192 (3), 187 (6), 177 (50), 164 (78), 149 (99), 131 (52), 121 (100), 107 (79), 91 (80), 77 (70), 65 (20), 55 (47), 43 (38). IR (neat): 2953, 2866, 2835, 1674, 1608, 1461, 1365, 1275, 1202, 1157, 883 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₅H₂₄O + H]⁺: 221.1900, found: 221.1899. Odor description: green, plastic, anisic, ivy, minty.



7,7-Dimethyl-3-(4-methylpent-3-en-1-yl)-1,2,5,6,7,7a-hexahydro-4*H***-inden-4-one (19c) Following the general procedure II, 1.39 g, 56% yield, b.p.: 156 °C/0.14 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): \delta = 5.08 (t,** *J* **= 7.2 Hz, 1H), 2.76 (t,** *J* **= 9.2 Hz, 1H), 2.70–2.50 (m, 2H), 2.42–2.29 (m, 4H), 2.21–2.04 (m, 2H), 1.94–1.84 (m, 1H), 1.75–1.61 (m, 5H), 1.60 (s, 3H, Me), 1.57–1.44 (m, 1H), 0.98 (s, 3H, Me), 0.83 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): \delta = 200.3 (s), 158.4 (s), 133.7 (s), 131.9 (s), 123.9 (d), 56.6 (d), 39.0 (t), 37.7 (t), 36.0 (t), 32.8 (s), 29.9 (t), 29.0 (q), 26.5 (t), 25.7 (q), 24.3 (t), 19.0 (q), 17.6 (q) ppm. GC/MS (EI):** *m/z* **(%): 246 (18) [***M***⁺], 231 (3), 213 (1), 203 (4), 190 (32), 178 (41), 165 (25), 147 (18), 134 (31), 122 (100), 109 (37), 91 (28), 77 (26), 69 (52), 55 (20), 41 (57). IR (neat): 2954, 2914, 2862, 1673, 1609, 1453, 1275, 1200, 1157, 1099, 1001, 882 cm⁻¹. HRMS (ESI):** *m/z* **calcd for [C₁₇H₂₆O + H]⁺: 247.2056, found: 247.2058. Odor description: woody tobacco, sweet, honey, giner bread.**



1'-Methyl-3',3a',5',6'-tetrahydrospiro[cyclopentane-1,4'-inden]-7'(2'H)-one (19d)

Following the general procedure II, 1.32 g, 65% yield, b.p.: 135 °C/0.09 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 3.04–2.93 (m, 1H), 2.48–2.23 (m, 4H), 2.09 (s, 3H, Me), 2.00–1.89 (m, 1H), 1.83–1.47 (m, 9H), 1.46–1.25 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 200.7 (s), 154.4 (s), 134.2 (s), 55.3 (d), 44.9 (s), 38.7 (t), 38.3 (t), 38.0 (t), 37.6 (t), 29.2 (t), 27.0 (t), 25.4 (t), 25.0 (t), 16.4 (q) ppm. GC/MS (EI): *m/z* (%): 204 (25) [*M*⁺], 189 (3), 176 (4), 171 (5), 161 (7), 148 (10), 135 (6), 123 (31), 109 (100), 95 (10), 91 (15), 79 (29), 67 (8), 53 (10), 41 (10). IR (neat): 2938, 2860, 1675, 1615, 1450, 1430, 1339, 1276, 1190, 953, 816 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₄H₂₀O + H]⁺: 205.1587, found: 205.1586. Odor description: woody, warm fruity, tobacco, slightly sweet honey like.



(6aR*,11aS*)-3-Methyl-1,2,6,6a-tetrahydroindeno[3a,4-b]benzofuran-4(5H)-one (19f)

Following the general procedure II, the crude product was purified by flash chromatography to afford **19f**. 1.31 g, 54 % yield, m.p.: 132 °C, a white solid. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.24-7.07$ (m, 2H), 6.88 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 3.56 (s, 1H), 2.84 (dt, J = 18.8, 7.7 Hz, 1H), 2.51–2.34 (m, 2H), 2.29 (s, 3H, Me), 2.22–1.92 (m, 5H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 199.2$ (s), 162.9 (s), 158.8 (s), 131.5 (s), 129.6 (s), 128.8 (d), 124.6 (d), 120.6 (d), 109.1 (d), 100.7 (s), 46.3 (d), 39.5 (t), 37.3 (t), 36.3 (t), 28.0 (t), 17.0 (q) ppm. GC/MS (EI): m/z (%): 240 (100) $[M^+]$, 225 (45), 207 (12), 197 (23), 183 (20), 165 (10), 152 (7), 141 (4), 133 (14), 120 (21), 107 (13), 91 (11), 77 (10), 63 (3), 51 (3). IR (neat): 2933, 1683, 1627, 1478, 1311, 1244, 1147, 956, 875, 761 cm⁻¹. HRMS (EI): m/z calcd for $[C_{16}H_{16}O_2]^+$: 240.1150, found: 240.1152. Odor description: odorless.



(6aS*,11bR*)-3,7-Dimethyl-1,2,5,6,6a,7-hexahydro-4*H*-cyclopenta[*d*]carbazol-4-one (19g)

Following the general procedure II, the crude product was purified by flash chromatography to afford **19g**. 1.06 g, 42 % yield, a yellow solid, m.p.: 128–129 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.04 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.52 (t, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 3.60 (bs, 1H), 2.92–2.80 (m, 4H), 2.44–2.31 (m, 2H), 2.26–1.99 (m, 7H), 1.76 (tt, *J* = 13.9, 3.9 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 201.0 (s), 153.9 (s), 150.9 (s), 136.0 (s), 135.1 (s), 128.4 (d), 122.9 (d), 117.0 (d), 105.3 (d), 71.0 (d), 59.5 (s), 43.5 (t), 37.7 (t), 35.7 (t), 32.5 (q), 24.3 (t), 16.5 (q) ppm. GC/MS (EI): *m/z* (%): 253 (67) [*M*⁺], 224 (7), 196 (100), 169 (13), 144 (15), 115 (6), 97 (4), 77 (5). IR (neat): 2916, 1676, 1622, 1603, 1498, 1427, 1284, 1161, 935, 860, 739 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₇H₁₉ON + H]⁺: 254.1539, found: 254.1542. Odor description: odorless.



(6a*S**,11b*R**)-3-Methyl-1,2,5,6,6a,7-hexahydro-4*H*-cyclopenta[*d*]carbazol-4-one (19h) Following the general procedure II, the crude product was purified by flash chromatography to afford 19h. 460 mg, 38 % yield, a yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.00 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.65–6.52 (m, 2H), 3.93 (t, *J* = 2.8 Hz, 1H), 2.94– 2.73 (m, 1H), 2.50–2.02 (m, 8H), 1.99–1.75 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 200.7 (s), 154.6 (s), 149.5 (s), 135.5 (s), 134.9 (s), 128.2 (d), 123.3 (d), 118.6 (d), 108.5 (d), 64.4 (d), 60.7 (s), 42.8 (t), 37.8 (t), 35.8 (t), 29.6 (t), 16.5 (q) ppm. GC/MS (EI): *m/z* (%): 239 (100) [*M*⁺], 224 (17), 211 (11), 196 (13), 182 (86), 167 (26), 155 (22), 143 (6), 130 (16), 115 (6), 103 (3), 90 (7), 77 (8), 63 (3), 51 (3). IR (neat): 2919, 1709, 1680, 1604, 1483, 1360, 1246, 1221, 852, 740 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₆H₁₇ON +H]⁺: 240.1383, found: 240.1386. Odor description: odorless.

3-Isopropyl-7-methyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19i)



Following the general procedure II, 1.09 g, 56 % yield, dr = 19:81, as a colorless liquid. These two isomers were separated by silica gel chromatography.

anti-19i, major isomer, the less polar one (petane : MTBE = 95 : 5, $R_f = 0.45$), b.p.: 116 °C/0.19 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 3.68-3.55$ (m, 1H), 2.50– 2.39 (m, 3H), 2.36–2.23 (m, 2H), 2.21–2.11 (m, 1H), 1.91–1.79 (m, 1H), 1.58–1.27 (m, 3H), 1.05–0.98 (m, 9H, 3Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 200.6$ (s), 163.1 (s), 133.2 (s), 54.1 (d), 41.7 (t), 38.5 (d), 33.0 (t), 30.6 (t), 30.2 (t), 27.4 (d), 21.2 (q), 21.1 (q), 19.5 (q) ppm. GC/MS (EI): m/z (%): 192 (91) $[M^+]$, 177 (34), 164 (25), 159 (21), 149 (61), 135 (100), 121 (76), 107 (72), 91 (74), 77 (47), 65 (31), 55 (47), 41 (40). IR (neat): 2952, 2927, 2868, 1673, 1608, 1456, 1327, 1257, 1203, 820 cm⁻¹. HRMS (ESI): m/z calcd for $[C_{13}H_{20}O + H]^+$: 193.1587, found: 193.1588. Odor description: green, metallic, aromatic, weak.

syn-19i, minor isomer, the more polar one (petane : MTBE = 95 : 5, $R_f = 0.43$), b.p.: 102 °C/0.13 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 4.16-4.05$ (m, 1H), 2.91–2.83 (m, 1H), 2.37–2.25 (m, 3H), 2.22–2.12 (m, 1H), 1.85–1.76 (m, 1H), 1.74–1.61 (m, 2H), 1.54–1.37 (m, 2H), 1.13 (d, J = 5.5 Hz, 3H, Me), 1.04 (d, J = 5.5 Hz, 3H, Me), 0.76 (d, J = 5.6 Hz, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 198.0$ (s), 162.2 (s), 131.7 (s), 50.4 (d), 36.2 (t), 30.7 (t), 30.4 (t), 29.7 (d), 27.5 (d), 25.8 (t), 20.9 (q), 20.8 (q), 11.9 (q) ppm. GC/MS (EI): m/z (%):192 (82) [M^+], 177 (27), 164 (18), 159 (20), 150 (56), 135 (100), 121 (74), 107 (67), 91 (71), 77 (45), 65 (32), 55 (43), 41 (40). IR (neat): 2956, 2868, 1671, 1606, 1456, 1340, 1254, 1171, 1024 cm⁻¹. HRMS (ESI): m/z calcd for [$C_{13}H_{20}O + H$]⁺: 193.1587, found: 193.1584. Odor description: dusty, mouldy, herbal, green, amylic.

3-Isobutyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19j)

Following the general procedure II, 1.20 g, 62% yield, b.p.: 112 °C/0.1 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.94-2.79$ (m, 1H), 2.50–2.10 (m, 7H), 2.09–1.92 (m, 2H), 1.89–1.67 (m, 2H), 1.52–1.37 (m, 1H), 1.33–1.19 (m, 1H), 0.90 (d, J = 6.6 Hz, 3H, Me) pom. ¹³C NMR (100 MHz, CDCl₃): $\delta = 200.5$ (s), 156.1 (s), 136.7 (s), 47.3 (d), 41.8 (t), 38.6 (t), 36.2 (t), 32.5 (t), 31.6 (t), 27.5 (d), 24.3 (t), 22.6 (q), 22.5 (q) ppm. GC/MS (EI): m/z (%): 192 (43) $[M^+]$, 177 (100), 164 (7), 159 (14), 149 (19), 137 (59), 121 (16), 107 (44), 91 (39), 79 (42), 65 (12), 55 (28), 41 (25). IR (neat): 2952, 2925, 2865, 1675, 1612, 1458, 1319, 1260, 1177, 1094, 929 cm⁻¹. HRMS (ESI): m/z calcd for $[C_{13}H_{20}O + H]^+$: 193.1587, found: 193.1588. Odor description: green, leathery, slightly fatty anisic.



1,1,3-Trimethyl-1,2,5,6,7,7a-hexahydro-4*H***-inden-4-one** (19k)⁸

Following the general procedure II, 0.81 g, 45% yield, b.p.: 102 °C/0.21 mbar, a colorless liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 2.66-2.51$ (m, 1H), 2.49–2.32 (m, 2H), 2.27–2.14 (m, 1H), 2.10 (s, 3H, Me), 2.06–1.95 (m, 2H), 1.81–1.58 (m, 3H), 1.41–1.23 (m, 1H), 1.13 (s, 3H, Me), 0.87 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 200.6$ (s), 153.1 (s), 133.6 (s), 56.3 (d), 54.9 (t), 41.4 (s), 40.9 (t), 27.4 (q), 24.3 (t), 23.7(3) (q), 23.7(2) (t), 16.7 (q) ppm. GC/MS (EI): m/z (%): 178 (54) $[M^+]$, 163 (100), 149 (4), 145 (7), 135 (52), 122 (74), 107 (65), 91 (34), 79 (22), 65 (14), 55 (26), 41 (20). IR (neat): 2930, 2864, 1674, 1613, 1427, 1364, 1340, 1325, 1218, 925, 830 cm⁻¹. HRMS (ESI): m/z calcd for $[C_{12}H_{18}O + H]^+$: 179.1430, found: 179.1430. Odor description: green, woody fruity, ionone beta, cedarwood.



1,1,2,3-Tetramethyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19l)

Following the general procedure II, 950 mg, 49% yield, dr = 62:38, b.p.: 145 °C/0.16 mbar, a colorless liquid. ¹H NMR (300 MHz, CDCl₃, mixture of isomers): δ = 2.65–1.91 (m, 8H), 1.81–1.56 (m, 2H), 1.42–1.21 (m, 1H), 1.08 (s, 1.1H, minor-Me), 1.01 (s, 1.9H, major-Me),

0.97–0.89 (m, 3H, Me), 0.86 (s, 1.9H, major-Me), 0.64 (s, 1.1H, minor-Me) ppm. ¹³C NMR (75 MHz, CDCl₃): major isomer: $\delta = 201.2$ (s), 158.5 (s), 131.9 (s), 56.5 (d), 53.5 (d), 42.8 (s), 41.0 (d), 25.2 (q), 23.7 (t), 23.6 (t), 22.6 (q), 15.6 (q), 13.1 (q) ppm; minor isomer: $\delta = 200.6$ (s), 157.0 (s), 133.0 (s), 55.6 (d), 53.6 (d), 45.9 (s), 41.1 (d), 25.4 (q), 24.0 (t), 23.4 (t), 16.7 (q), 14.1 (q), 9.9 (q) ppm. GC/MS (EI): m/z (%): 192 (53) [M^+], 177 (100), 159 (10), 149 (58), 135 (20), 121 (64), 107 (22), 91 (26), 79 (17), 65 (8). IR (neat): 2934, 1673, 1613, 1455, 1369, 1322, 1264, 952, 815 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₃H₂₀O + H]⁺: 193.1587, found: 193.1589. Odor description: coniferous, musky, fruity.



syn:anti = 14:86

3,5,7,7-Tetramethyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19m)

Following the general procedure II, 1.04 g, 54 % yield, dr = 14:86, b.p.: 112 °C/0.13 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 2.98–2.75 (m, 1H), 2.54–2.26 (m, 3H), 2.15 (s, 0.42H, minor-Me), 2.05 (s, 2.53H, major-Me), 1.94–1.81 (m, 1H), 1.78–1.66 (m, 1H), 1.63–1.44 (m, 2H), 1.12–1.08 (m, 3H, Me), 1.00 (s, 0.43H, minor-Me), 0.96 (s, 2.56H, major-Me), 0.88 (s, 2.57H, major-Me), 0.75 (s, 0.41H, minor-Me) ppm. ¹³C NMR (100 MHz, CDCl₃): major isomer: δ = 202.8 (s), 153.0 (s), 133.8 (s), 57.3 (d), 48.7 (t), 41.0 (d), 38.7 (t), 33.2 (s), 29.1 (q), 24.1 (t), 19.8 (q), 16.1 (q), 15.5 (q) ppm; minor isomer: δ = 202.9 (s), 154.5 (s), 133.6 (s), 54.8 (d), 46.2 (t), 41.3 (d), 39.4 (t), 33.1 (s), 29.8 (q), 24.1 (t), 23.6 (q), 23.3 (t), 16.3 (q) ppm. GC/MS (EI): *m/z* (%): 192 (35) [*M*⁺], 177 (9), 163 (3), 149 (20), 136 (45), 121 (20), 109 (100), 93 (20), 79 (29), 65 (7), 55 (14), 41 (16). IR (neat): 2955, 2928, 2903, 2867, 1674, 1615, 1456, 1385, 1366, 1246, 1201, 985 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₃H₂₀O + H]⁺: 193.1587, found: 193.1586. Odor description: eucalyptus.

6,6,9-Trimethyldeca-1,4,8-trien-3-one (20o)



Following the general procedure II, 1.17 g, 61 % yield, Z/E = 60:40, as a pale yellow liquid. These two isomers were separated by silica gel chromatography.

(Z)-6,6,9-Trimethyldeca-1,4,8-trien-3-one (Z-20o)

0.60 g, 31% yield, b.p.: 108 °C/0.20 mbar, a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 6.39$ (dd, J = 17.6, 10.4 Hz, 1H), 6.22 (dd, J = 17.6, 1.3 Hz, 1H), 6.05 (d, J = 13.3 Hz, 1H), 5.95 (dd, J = 10.4, 1.3 Hz, 1H), 5.87 (d, J = 13.3 Hz, 1H), 5.13 (t, J = 7.5 Hz, 1H), 2.13 (d, J = 7.5 Hz, 1H), 1.70 (s, 3H, Me), 1.59 (s, 3H, Me), 1.08 (s, 6H, 2Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 195.2$ (s), 151.5 (d), 138.2 (d), 133.5 (s), 129.8 (t), 124.9 (d), 120.9 (d), 41.2 (t), 38.4 (s), 27.1 (q), 26.0 (q), 17.9 (q) ppm. GC/MS (EI): m/z (%): 192 (1) $[M^+]$, 177 (6), 159 (2), 149 (7), 137 (17), 124 (25), 109 (100), 95 (29), 81 (16), 69 (54), 55 (59), 41 (71). IR (neat): 2962, 2926, 2871, 1665, 1613, 1451, 1378, 1360, 1208, 1092, 987 cm⁻¹. HRMS (ESI): m/z calcd for $[C_{13}H_{20}O + H]^+$: 193.1587, found: 193.1586. Odor description: weak, herbal, fruity, chamomile.

(*E*)-6,6,9-Trimethyldeca-1,4,8-trien-3-one (*E*-20o)

0.41 g, 21% yield, b.p.: 114 °C/0.21 mbar, a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 6.92$ (d, J = 16.0 Hz, 1H), 6.63 (dd, J = 17.4, 10.6 Hz, 1H), 6.28 (dd, J = 17.4, 1.4 Hz, 1H), 6.25 (d, J = 16.0 Hz, 1H), 5.81 (dd, J = 10.6, 1.4 Hz, 1H), 5.08 (t, J = 7.6 Hz, 1H), 2.07 (d, J = 7.6 Hz, 1H), 1.70 (s, 3H, Me), 1.59 (s, 3H, Me), 1.07 (s, 6H, 2Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 190.2$ (s), 157.9 (d), 135.0 (d), 134.0 (s), 128.2 (t), 124.4 (d), 119.9 (d), 40.3 (t), 37.9 (s), 26.1 (q), 26.0 (q), 17.9 (q) ppm. GC/MS (EI): m/z (%): 192 (1) [M^+], 177 (1), 159 (1), 137 (3), 124 (57), 109 (100), 95 (7), 81 (7), 69 (39), 55 (31), 41 (41). IR (neat): 2963, 2927, 1684, 1664, 1627, 1611, 1402, 1324, 1213, 1104, 986 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₃H₂₀O + H]⁺: 193.1587, found: 193.1588. Odor description: herbal, earthy, carrots, plastic.

2,2,7,7-Tetramethyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19o)



Modified Conditions



was added dropwise into this refluxing catalyst system by a syringe pump over 48 h. The refluxing was continued till the total reaction time reached 50 h. The crude product was purified by flash chromatography to afford **190** (0.79 g, 41 % yield, b.p.: 108 °C/0.18 mbar) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): $\delta = 6.42$ (d, J = 2.7 Hz, 1H), 2.91–2.83 (m, 1H), 2.44–2.30 (m, 2H), 1.87–1.63 (m, 3H), 1.52 (dd, J = 12.6, 9.5 Hz, 1H), 1.15 (s, 3H, Me), 1.07 (s, 3H, Me), 0.98 (s, 3H, Me), 0.84 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 199.7$ (s), 148.8 (d), 139.5 (s), 53.8 (d), 44.0 (s), 41.6 (t), 38.7 (t), 36.5 (t), 32.3 (s), 29.1 (q), 28.8 (q), 26.4 (q), 19.1 (q) ppm. GC/MS (EI): m/z (%): 192 (54) [M^+], 177 (100), 164 (4), 159 (9), 149 (15), 136 (50), 123 (54), 107 (66), 91 (33), 79 (54), 69 (23), 55 (32), 41 (35). IR (neat): 2952, 2863, 1682, 1614, 1461, 1334, 1289, 1255, 1200, 1151, 860 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₃H₂₀O + H]⁺: 193.1587, found: 193.1588. Odor description: weak, green fatty aromatic.



7',7'-Dimethyl-5',6',7',7a'-tetrahydrospiro[cyclopentane-1,2'-inden]-4'(1'*H***)-one (19p) Following the general procedure III, 19p** (0.91 g, 42% yield, b.p.: 158 °C/ 0.2 mbar) was obtained as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.51$ (d, J = 3.4 Hz, 1H), 2.80 (t, J = 11.2 Hz, 1H), 2.43–2.24 (m, 2H), 1.98–1.84 (m, 1H), 1.81–1.37 (m, 11H), 0.96 (s, 3H, Me), 0.81 (s, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 199.5$ (s), 147.8 (d), 140.0 (s), 55.3 (s), 53.9 (d), 40.4 (t), 39.9 (t), 38.7 (t), 37.3 (t), 36.5 (t), 32.3 (s), 29.1 (q), 24.7(4) (t), 24.7(0) (t), 19.1 (q) ppm. GC/MS (EI): m/z (%): 218 (62) [M^+], 203 (11), 189 (7), 175 (24), 162 (100), 149 (24), 133 (16), 119 (21), 105 (30), 91 (42), 77 (17), 65 (9), 55 (10). IR (neat): 2947, 1682, 1612, 1253, 860 cm⁻¹. HRMS (EI): m/z calcd for [C₁₅H₂₂O]⁺: 218.1671, found: 218.1666. Odor description: fatty, green, soapy.



1,1,2,2-Tetramethyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (19q)

Following the general procedure III, **19q** (3.7 g, 37%, b.p.: 120 °C/0.12mbar, m.p.: 54–55 °C) was obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 6.49$ (d, J = 2.9 Hz, 1H),

2.78–2.69 (m, 1H), 2.53–2.44 (m, 1H), 2.25–2.13 (m, 1H), 2.09–2.00 (m, 1H), 1.80–1.62 (m, 2H), 1.42–1.27 (m, 1H), 0.98 (s, 3H, Me), 0.96 (s, 3H, Me), 0.92 (s, 3H, Me), 0.77 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.7 (s), 148.7 (d), 138.9 (s), 53.3 (d), 48.5 (s), 47.9 (s), 40.1 (t), 23.7 (t), 23.4 (t), 22.4 (q), 21.1 (q), 20.9 (q), 20.3 (q) ppm. GC/MS (EI): *m/z* (%): 192 (32) [*M*⁺], 177 (100), 163 (8), 159 (21), 149 (86), 135 (49), 121 (71), 107 (33), 91 (43), 79 (28), 65 (14), 55 (41), 41 (37). IR (neat): 2966, 2936, 2866, 1680, 1613, 1452, 1375, 1268, 1201, 1157, 891, 839 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₃H₂₀O + H]⁺: 193.1587, found: 193.1587. Odor description: fruity green, damascone, honey.



syn:anti = 95:5

(7*R**,7a*R**)-7-Ethyl-3-phenyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (*syn*-19r)

Following the general procedure II, 1.10 g, 46% yield, b.p.: 206 °C/0.12 mbar, *syn/anti* = 95:5, as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.50–7.23 (m, 5H), 3.46–3.30 (m, 1H), 2.95–2.64 (m, 2H), 2.48–2.28 (m, 2H), 2.12–1.98 (m, 2H), 1.94–1.78 (m, 2H), 1.72–1.47 (m, 2H), 1.41–1.21 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 201.1 (s), 149.2 (s), 136.1 (s), 136.0 (s), 128.3 (d), 128.1 (d), 127.8 (d), 53.4 (d), 38.5 (d), 37.9 (t), 37.6 (t), 27.1 (t), 25.4 (t), 18.4 (t), 12.1 (q) ppm. GC/MS (EI): *m/z* (%): 240 (80) [*M*⁺], 225 (2), 212 (15), 197 (7), 184 (74), 169 (66), 156 (47), 141 (100), 128 (46), 115 (77), 105 (10), 91 (29), 77 (17), 65 (8), 55 (21). IR (neat): 2955, 2874, 1680, 1595, 1493, 1445, 1227, 1161, 906, 757, 693 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₇H₂₀O + H]⁺: 241.1587, found: 241.1585.



syn:anti = 4: 96

(7*S**,7a*R**)-7-Ethyl-3-phenyl-1,2,5,6,7,7a-hexahydro-4*H*-inden-4-one (*anti*-19r)

Following the general procedure II, 0.93 g, 39% yield, b.p.: 202 °C/0.09 mbar, *syn/anti* = 4:96, as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.48–7.22 (m, 5H), 2.96–2.61 (m, 3H), 2.60–2.22 (m, 3H), 2.18–1.98 (m, 1H), 1.75–1.39 (m, 4H), 1.34–1.10 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 201.0 (s), 149.0 (s), 136.5 (s), 136.2 (s), 128.2 (d), 128.0 (d), 127.8 (d), 54.5 (d), 45.3 (d), 42.5 (t), 37.6 (t), 30.2 (t), 29.8 (t), 26.1 (t), 11.2 (q) ppm. GC/MS (EI): *m/z* (%): 240 (100) [*M*⁺], 225 (2), 212 (11), 197 (7), 184 (75), 169 (71), 156 (51), 141 (98), 128 (48), 115 (82), 105 (9), 91 (33), 77 (19), 65 (10), 55 (21). IR (neat): 2957, 1681, 1493, 1445, 1183, 928, 758, 693 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₇H₂₀O + H]⁺: 241.1587, found: 241.1588.

9,9-Dimethyl-1,2,3,5,6,7,8,8a,9,9a-decahydro-4*H*-fluoren-4-one (19s)



Following the general procedure II, **19s** was obtained as a mixture of two diasteromers. 1.0 g, 46% yield, *syn-19s/anti-19s* = 45:55, as a pale yellow liquid. The two isomers could be separated by silica gel chromatography. Their relative configurations were determined by 2D-NMR.

(8aS*,9aR*)-9,9-Dimethyl-1,2,3,5,6,7,8,8a,9,9a-decahydro-4*H*-fluoren-4-one (*syn*-19s)

The minor isomer, the more polar one (petane : MTBE = 10 : 1, R_f = 0.43), b.p.: 152 °C/0.11 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 3.43 (dd, J = 17.7, 3.2 Hz, 1H), 2.52–2.37 (m, 2H), 2.27–2.15 (m, 2H), 2.09–1.95 (m, 2H), 1.87–1.58 (m, 5H), 1.40–1.12 (m, 4H), 1.10 (s, 3H, Me), 0.73 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 200.5 (s), 157.1 (s), 131.3 (s), 56.3 (d), 55.9 (d), 44.0 (s), 41.2 (t), 28.0 (t), 26.6 (q), 25.2 (t), 24.9 (t), 24.8 (t), 24.4 (t), 23.7 (t), 18.6 (q) ppm. GC/MS (EI): m/z (%): 218 (74) [M^+], 203 (100), 185 (42), 175 (62), 161 (23), 147 (46), 133 (24), 119 (30), 105 (45), 91 (55), 79 (26), 65 (15), 55 (34), 41 (28). IR (neat): 2927, 2859, 1671, 1609, 1448, 1290, 1226, 1120, 967, 827 cm⁻¹. HRMS (ESI): m/z calcd for [C₁₅H₂₂O + H]⁺: 219.1743, found: 219.1742. Odor description: fatty, oily, sl. musky.

(8a*R**,9a*R**)-9,9-Dimethyl-1,2,3,5,6,7,8,8a,9,9a-decahydro-4*H*-fluoren-4-one (*anti*-19s) The major isomer, the less polar one (petane : MTBE = 10 : 1, R_f = 0.45), b.p.: 148 °C/0.16 mbar, a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 3.59–3.50 (m, 1H), 2.57–2.37 (m, 2H), 2.26–2.12 (m, 2H), 2.08–1.98 (m, 1H), 1.96–1.61 (m, 8H), 1.43–1.12 (m, 4H), 0.98 (s, 3H, Me), 0.88 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 201.4 (s), 159.5 (s), 128.6 (s), 60.5 (d), 55.8 (d), 41.3 (t), 40.9 (s), 30.6 (t), 29.2 (t), 28.8 (t), 26.3 (t), 26.0 (q), 24.5 (t), 24.0 (t), 23.0 (q) ppm. GC/MS (EI): *m/z* (%): 218 (68) [*M*⁺], 203 (100), 185 (42), 175 (68), 161 (25), 147 (48), 133 (25), 119 (34), 105 (45), 91 (54), 77 (26), 65 (15), 55 (30), 41 (28). IR (neat): 2925, 2854, 1675, 1621, 1443, 1268, 1226, 1131, 883 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₅H₂₂O + H]⁺: 219.1743, found: 219.1741. Odor description: fatty, oily, very weak.



(4a*R**,9*R**,10a*R**)-11-Methyl-3,4,4a,5,6,7,8,9,10,10a-decahydro-2*H*-1,9-(metheno)benzo [8]annulen-2-one (*syn*-19t)

Following the general procedure II, 0.48 g, 23 % yield, b.p.: 158 °C/0.13 mbar, a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ = 3.06 (d, *J* = 7.4 Hz, 1H), 2.82 (d, *J* = 10.4 Hz, 1H), 2.39–2.31 (m, 2H), 2.21 (dt, *J* = 14.1, 10.9 Hz, 1H), 2.09–1.86 (m, 6H), 1.85–1.67 (m, 4H), 1.66–1.47 (m, 2H), 1.46–1.21 (m, 2H), 1.08–0.89 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 201.9 (s), 152.2 (s), 136.5 (s), 49.4 (d), 48.1 (d), 38.5 (d), 36.4 (t), 33.4 (t), 32.8 (t), 32.2 (t), 31.1 (t), 28.7 (t), 24.3 (t), 13.7 (q) ppm. GC/MS (EI): *m/z* (%): 204 (100) [*M*⁺], 189 (86), 171 (15), 161 (41), 147 (70), 133 (36), 119 (47), 105 (48), 91 (65), 77 (50), 65 (14), 55 (19). IR (neat): 2913, 1677, 1627, 1438, 1289, 1261, 1210, 1169, 999, 930, 886, 718 cm⁻¹. HRMS (ESI): *m/z* calcd for [C₁₄H₂₀O + H]⁺: 205.1587, found: 205.1590. Odor description: fruity, green, straw, damascone, honey, wood fiber.

IV. References

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V. NMR Spectra of New Compounds Synthesized

¹H NMR spectrum of compound **9a**



¹³C NMR spectrum of compound **9a**



¹H NMR spectrum of compound **9b**



¹³C NMR spectrum of compound **9b**



¹H NMR spectrum of compound **9c**



¹³C NMR spectrum of compound **9c**



¹H NMR spectrum of compound **9d**



¹³C NMR spectrum of compound **9d**



¹H NMR spectrum of compound **9e**



¹³C NMR spectrum of compound **9e**



¹H NMR spectrum of compound **9f**



¹³C NMR spectrum of compound **9f**



¹H NMR spectrum of compound 9g



¹³C NMR spectrum of compound **9**g



¹H NMR spectrum of compound **9h**



¹³C NMR spectrum of compound **9h**


¹H NMR spectrum of compound **9i**



¹³C NMR spectrum of compound **9i**



¹H NMR spectrum of compound **9**j



¹³C NMR spectrum of compound **9**j



¹H NMR spectrum of compound **9**k



¹³C NMR spectrum of compound **9**k



¹H NMR spectrum of compound **91-major**



¹³C NMR spectrum of compound **91-major**



¹H NMR spectrum of compound **91-minor**



¹³C NMR spectrum of compound **91-minor**



¹H NMR spectrum of compound **9m**



¹³C NMR spectrum of compound **9m**



¹H NMR spectrum of compound **9p**



¹³C NMR spectrum of compound **9p**





¹H NMR spectrum of compound (*Z*)-1-Phenylhept-4-en-1-one

¹³C NMR spectrum of compound (Z)-1-Phenylhept-4-en-1-one



¹H NMR spectrum of compound *cis-9*r



¹³C NMR spectrum of compound *cis*-9r





¹H NMR spectrum of compound (*E*)-1-Phenylhept-4-en-1-one

¹³C NMR spectrum of compound (*E*)-1-Phenylhept-4-en-1-one



¹H NMR spectrum of compound *trans-*9r



¹³C NMR spectrum of compound *trans*-9r



¹H NMR spectrum of compound *cis*-9s



¹³C NMR spectrum of compound *cis*-9s



HSQC spectrum of compound cis-9s



HMBC spectrum of compound *cis-9s*



COSY spectrum of compound *cis*-9s



NOE spectrum of compound *cis*-9s



¹H NMR spectrum of compound **9t**



¹³C NMR spectrum of compound 9t



¹H NMR spectrum of compound **19a**





52

¹H NMR spectrum of compound **19b**



80 70 60 50 40 30 20

220 210 200 190 180 170 160 150 140 130 120 110 100 90

10 ppm



¹³C NMR spectrum of compound **19c**



¹H NMR spectrum of compound **19d**



¹³C NMR spectrum of compound **19d**



¹H NMR spectrum of compound **19f**



¹³C NMR spectrum of compound **19f**



¹H NMR spectrum of compound **19g**



 ^{13}C NMR spectrum of compound 19g



HSQC spectrum of compound 19g



HMBC spectrum of compound 19g



COSY spectrum of compound 19g



NOE spectrum of compound 19g



¹H NMR spectrum of compound **19h**



¹³C NMR spectrum of compound **19h**



¹H NMR spectrum of compound *anti*-19i



¹³C NMR spectrum of compound *anti*-19i



HSQC spectrum of compound anti-19i



HMBC spectrum of compound anti-19i







NOE spectrum of compound anti-19i



¹H NMR spectrum of compound *syn*-19i





HSQC spectrum of compound syn-19i

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HMBC spectrum of compound syn-19i

199773 Liu GLN01584-038-02 bs 0021



COSY spectrum of compound syn-19i

199773 Liu GLN01584-038-02 bs 0021



NOE spectrum of compound syn-19i

199773 Liu GLN01584-038-02 bs 0021





¹³C NMR spectrum of compound **19j**



¹H NMR spectrum of compound **19k**





¹H NMR spectrum of compound **19**



¹³C NMR spectrum of compound **19**



¹H NMR spectrum of compound **19m**



¹³C NMR spectrum of compound **19m**



¹H NMR spectrum of compound **Z-200**



¹³C NMR spectrum of compound **Z-20o**



¹H NMR spectrum of compound *E*-200



¹³C NMR spectrum of compound *E*-200


¹H NMR spectrum of compound **190**



¹³C NMR spectrum of compound **190**





¹³C NMR spectrum of compound **19p**





¹³C NMR spectrum of compound **19**q



¹H NMR spectrum of compound *syn*-19r



¹³C NMR spectrum of compound *syn*-19r



HSQC spectrum of compound syn-19r



HMBC spectrum of compound syn-19r



COSY spectrum of compound syn-19r



NOE spectrum of compound syn-19r



¹H NMR spectrum of compound *anti-19*r



¹³C NMR spectrum of compound *anti*-19r



HSQC spectrum of compound anti-19r



HMBC spectrum of compound anti-19r



COSY spectrum of compound anti-19r



NOE spectrum of compound *anti*-19r



¹H NMR spectrum of compound *anti-19s*



¹³C NMR spectrum of compound *anti-19s*



HSQC spectrum of compound anti-19s



HMBC spectrum of compound anti-19s



COSY spectrum of compound *anti-19s*



NOE spectrum of compound anti-19s



¹H NMR spectrum of compound *syn-*19s



¹³C NMR spectrum of compound *syn-*19s





HSQC spectrum of compound syn-19s

HMBC spectrum of compound syn-19s





COSY spectrum of compound syn-19s



¹H NMR spectrum of compound *syn*-19t



¹³C NMR spectrum of compound *syn*-19t



HSQC spectrum of compound *syn*-19t



HMBC spectrum of compound *syn*-19t



COSY spectrum of compound *syn*-19t



NOE spectrum of compound syn-19t

