Supporting Information.

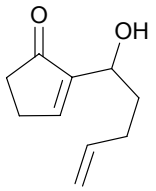
Experimental details.

All reagents were purchased from commercial sources and used without further purification. All reactions were carried out in flame-dried glassware under an atmosphere of dry argon unless otherwise stated. All solvents were routinely distilled prior to use. Dry solvents were obtained by standard procedures according to D. D. Perrin and D. R. Perrin, *Purification of Laboratory Chemicals*. Thin layer chromatographies (TLC) were performed on Merck precoated plates (silica gel 60 F_{254}). The plates were visualised using ultra-violet light (254 nm) and developed using $KMnO_4$ and/or vanillin stains. Flash column chromatography was performed using MERCK silica gel 60 (230-400 mesh) under pressure with the indicated solvents.

Routine nuclear magnetic resonance (NMR) spectra were recorded on a VARIAN GEMINI-200 VXR-200 (^{1}H : 200 MHz and ^{13}C : 50 MHz), a BRUCKER AC-250 (^{1}H : 250 MHz and ^{13}C : 62.5 MHz) and a VARIAN GEMINI-2000 (^{1}H : 300 MHz and ^{13}C : 75 MHz). High field spectra were recorded on a BRUCKER AM-500 (^{1}H : 500 MHz and ^{13}C : 125 MHz). Chemical shifts are expressed in parts per million (ppm) calibrated from $CHCl_3$ and coupling constants (*J*) are given in Hertz (Hz). Splitting partners are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; m, multiplet.

Low resolution mass spectra were recorded using VARIAN MATT-44 and FINNIGAN MAT-TSQ 70 spectrometers. Infra-red spectra (IR) were recorded, as thin films, on a PERKIN ELMER 681 and Shimadzu spectrometers and recorded in cm^{-1}. Elemental analyses were carried out at the University of Stuttgart, Germany. HRMS were carried out at the University of Mons (Pr R. Flammang)

Typical experimental procedure for Morita-Baylis-Hillman reaction.



Chemical Formula: $C_{10}H_{14}O_2$
Molecular Weight: 166,22

7a

In a schlenk tube, 2-cyclopentenone **5a** (4.49 ml, 52.57 mmol, 3 eq., 98%) and 4-pentenal **6a** (1.784 ml, 17.52 mmol, 1 eqv., 97%) were added to a solution of binol (1.267 g, 5.26 mmol, 0.25 eq., 99%) in THF (26 ml). The solution was then degassed, *n*-Bu_3P (2.298 ml, 8.76 mmol, 0.5 eq., 95%) was added and the reaction mixture was stirred at room temperature, under inert atmosphere, for 18 hours (monitoring by TLC).
The reaction mixture was cooled to -5 °C and 30 ml of an aqueous HCl solution (1N) were slowly added. The resulting solution was diluted with ether (30ml). The aqueous layer was extracted with Et_2O (2x30 ml) and the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 5/2, Rf = 0.18) affording the Morita-Baylis-Hillman product **7a** (2.764 g, 95%) as a colourless oil.

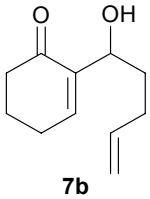
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.47 (td, 1H, *J* = 2.9, 1.0 Hz), 5.84 (ddt, 1H, *J* = 16.8, 10.3, 6.7 Hz), 5.05 (dd, 1H, *J* = 17.2, 1.9 Hz), 4.98 (dd, 1H, *J* = 10.2, 1.9 Hz), 4.47 (td, 1H, *J* = 6.3, 5.7 Hz), 2.95 (d, 1H, *J* = 5.7 Hz), 2.66-2.59 (m, 2H), 2.48-2.42 (m, 2H), 2.30-2.07 (m, 2H), 1.87-1.68 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 210.1, 158.1, 147.7, 138.1, 115.2, 67.5, 35.5, 35.1, 29.9, 26.9.

IR ν (cm^{-1}): 3433, 3076, 2976, 2920, 2859, 1693, 1639.

MS (CI) *m*/*z* (%): 167 (80), 149 (100), 111 (13).

HRMS *m*/*z* calculated for $C_{10}H_{14}O_2Na$: 189.0891. Found: 189.0887.



Chemical Formula: $C_{11}H_{16}O_2$
Molecular Weight: 180,24

7b

Yield = 95%

Aspect: colourless oil

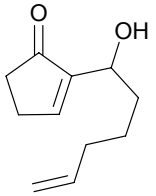
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 6.87 (t, 1H, *J* = 4.0 Hz), 5.80 (ddt, 1H, *J* = 17.0, 10.2, 6.6 Hz), 5.01 (dq, 1H, *J* = 17.0, 1.5 Hz), 4.95 (dd, 1H, *J* = 10.1, 1.5 Hz), 4.30 (t, 1H, *J* = 5.8 Hz), 2.98 (bs, 1H), 2.45-2.36 (m, 4H), 2.22-2.03 (m, 2H), 2.01-1.94 (m, 2H), 1.77-1.63 (m, 2H).

^{13}C NMR ($CDCl_3$, 125MHz) δ (ppm): 200.8, 146.2, 140.9, 138.4, 115.0, 71.3, 38.9, 35.5, 30.4, 25.9, 22.7.

IR ν (cm^{-1}): 3438, 3076, 2924, 2870, 1670.

MS (EI) *m*/*z* (%): 180 (4), 162 (8), 125 (100).

Elementary analysis calculated for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.98; H, 9.13.



Chemical Formula: $C_{11}H_{16}O_2$
Molecular Weight: 180,24

12

Yield = 81%

Aspect: colourless oil

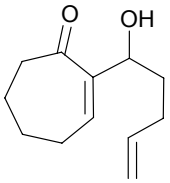
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.43 (bs, 1H), 5.83-5.67 (m, 1H), 5.01-4.85 (m, 2H), 4.40 (t, 1H, *J* = 6.0 Hz), 3.20 (bs, 1H), 2.68 (m, 2H), 2.40 (m, 2H), 2.05 (m, 2H), 1.70-1.30 (m, 4H).

^{13}C NMR ($CDCl_3$, 75MHz) δ (ppm): 210.0, 158.1, 147.9, 138.6, 114.8, 67.7, 35.5, 35.4, 33.7, 26.8, 24.9.

IR ν (cm^{-1}): 3429, 3075, 2921, 2860, 1684, 1639, 1000.

MS (APCI) *m*/*z* (%): 181 (5%); 163(100%).

Typical procedure for the Et_2AlI mediated coupling.



7c

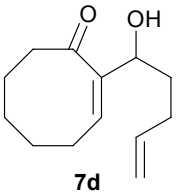
Chemical Formula: $C_{12}H_{18}O_2$
Molecular Weight: 194,27

In a round-bottomed flask, maintained under a positive pressure of argon, 2- cycloheptenone **5c** (1.96 g, 14.26 mmol, 1.2 eq., 80%) and 2-pentenal **6a** were diluted in DCM (40 ml). The resulting mixture was cooled to 0 °C and a solution of diethylaluminium iodide (14.1 g, 16.63mmol, 1.4 eq., 25 wt% in toluene) was added dropwise (~ 1ml/min). The yellow reaction mixture was stirred at 0 °C for 24 h. The reaction was finally quenched by the addition of a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM (3x20 ml) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (Et_2O/petroleum ether = 1/1, Rf= 0.23) affording the desired hydroxyenone **7c** (1.24 g, 54%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.10 (t, 1H, *J* = 5.9 Hz), 5.78 (ddt, 1H, *J* = 16.9, 11.2, 6.3 Hz), 4.98 (d, 1H, *J* = 16.9 Hz), 4.92 (d, 1H, *J* = 11.2 Hz), 4.22 (t, 1H, *J* = 6.8 Hz), 3.20 (bs, 1H), 2.57 (m, 2H), 2.40 (m, 2H), 2.20-2.00 (m, 2H), 1.90-1.50 (m, 6H).

^{13}C NMR ($CDCl_3$, 75MHz) δ (ppm): 206.3, 144.0, 143.1, 138.0, 114.7, 73.8, 43.1, 35.6, 30.4, 27.5, 24.9, 21.5.

IR ν (cm^{-1}): 3427, 3057, 2922, 2882, 1676.



7d

Chemical Formula: $C_{13}H_{20}O_2$
Molecular Weight: 208,3

Yield: 74%

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.10 (t, 1H, *J* = 5.7 Hz), 5.76 (ddt, 1H, *J* = 17.1, 10.5, 5.7 Hz), 4.98 (dd, 1H, *J* = 17.1, 1.8 Hz), 4.91 (d, 1H, *J* = 10.5 Hz), 4.13 (t, 1H, *J* = 6.6 Hz), 2.91 (bs, 1H), 2.56-2.46 (m, 2H), 2.34-2.30 (m, 2H), 2.20-1.90 (m, 2H), 1.90-1.80 (m, 2H), 1.70-1.50 (m, 6H).

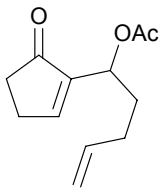
^{13}C NMR ($CDCl_3$, 75MHz) δ (ppm): 211.8, 140.9, 138.1, 136.1, 115.1, 75.7, 45.2, 35.6, 30.5, 29.4, 27.8, 22.9, 22.3.

IR ν (cm^{-1}): 3427, 3057, 2922, 2882, 1676.

MS (CI) *m*/*z* (%): 209 (14%), 191 (100%), 153 (17%).

HRMS *m*/*z* calculated for $C_{14}H_{21}O_2$: 209.154155. Found: 209.154146.

Typical procedure for acylation reaction.



Chemical Formula: $C_{12}H_{16}O_3$
Molecular Weight: 208,25

8a

Acetic anhydride (1.338 ml, 13.54 mmol, 1.5 eq., 95%) and $Sc(OTf)_3$ (90 mg, 0.18 mmol, 0.02 eq., 99%) were added to a solution of **7a** (1.5 g, 9.02 mmol, 1 eq.) in CH_3CN (90 ml). The reaction mixture was stirred at room temperature for 2h. The reaction mixture was diluted with ether (70 ml) and treated with a saturated aqueous solution of $NaHCO_3$ (3x 60 ml). The aqueous layer was extracted with Et_2O (3x50 ml) and the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 4/1, Rf = 0.32) affording the acylated product **8a** (1.855 g, 99%) as a colourless oil.

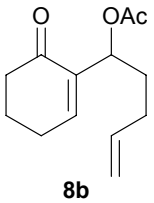
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.40 (td, 1H, *J* = 2.7, 1.1 Hz), 5.73 (ddt, 1H, *J* = 17.0, 10.5, 6.6 Hz), 5.49 (ddd, 1H, *J* = 7.5, 4.8, 1.2 Hz), 5.00-4.80 (m, 2H), 2.59-2.51 (m, 2H), 2.41-2.34 (m, 2H), 2.08-1.92 (m, 2H), 2.03 (s, 3H), 1.90-1.70 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 207.2, 170.1, 158.8, 145.3, 137.5, 115.3, 69.3, 35.4, 32.4, 29.7, 26.8, 21.3.

IR ν (cm^{-1}) 3077, 2997, 2977, 2925, 2856, 1747, 1702, 1640, 1245.

MS (CI) *m*/*z* (%): 209 (35), 149 (100)

Elementary analysis calculated for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.14; H, 7.83.



Chemical Formula: $C_{13}H_{18}O_3$
Molecular Weight: 222,28

8b

Yield = 97%

Aspect: colourless oil

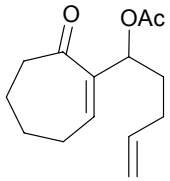
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.88 (t, 1H, *J* = 4.3 Hz), 5.78 (ddt, 1H, *J* = 16.9, 10.1, 6.5 Hz), 5.64 (dd, 1H, *J* = 8.1, 4.8 Hz), 5.05-4.91 (m, 2H), 2.47-2.36 (m, 4H), 2.12-1.92 (m, 4H), 2.07 (s, 3H), 1.86-1.63 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 197.4, 169.8, 145.1, 138.7, 137.6, 114.9, 70.5, 38.5, 33.6, 29.8, 25.8, 22.7, 21.3.

IR ν (cm^{-1}) 3076, 2932, 2850, 1742, 1672, 1641.

MS (EI) *m*/*z* (%): 222 (15), 179 (60), 168 (50), 162 (100), 125 (65).

Elementary analysis calculated for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16. Found: C, 70.07; H, 8.29.



Chemical Formula: $C_{14}H_{20}O_3$
Molecular Weight: 236,31

8c

Yield = 68%

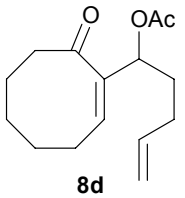
Aspect: colourless oil

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.61 (t, 1H, *J* = 5.9 Hz), 5.78 (ddt, 1H, *J* = 18.0, 9.6, 6.9 Hz), 5.48 (dd, 1H, *J* = 7.5, 4.8 Hz), 4.99 (d, 1H, *J* = 18 Hz), 4.94 (d, 1H, *J* = 9.6 Hz), 2.58 (m, 2H), 2.41 (m, 2H, *J* = 5.7 Hz), 2.12-2.02 (m, 2H), 2.05 (s, 3H), 1.90-1.60 (m, 6H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 203.6, 170.3, 143.1, 141.9, 138.0, 115.3, 73.1, 43.2, 34.6, 30.4, 27.9, 25.5, 21.9, 21.7.

IR ν (cm^{-1}): 3077, 2934, 2867, 1741, 1665, 1233.

MS (CI) *m*/*z* (%): 237 (11), 177 (100).



Chemical Formula: $C_{15}H_{22}O_3$
Molecular Weight: 250,33

8d

Yield = 84%

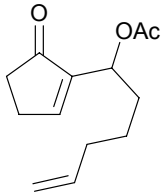
Aspect: colourless oil

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.10 (t, 1H, *J* = 6.0 Hz), 5.77 (ddt, 1H, *J* = 16.5, 9.6, 5.9 Hz), 5.25 (t, 1H, *J* = 6.9 Hz), 4.98 (d, 1H, *J* = 16.5 Hz), 4.94 (d, 1H, *J* = 9.6 Hz), 2.66-2.26 (m, 4H), 2.10-2.00 (m, 2H), 2.02 (s, 3H), 1.90-1.70 (m, 4H), 1.70-1.50 (m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 208.2, 167.2, 137.0, 136.4, 133.7, 114.0, 74.3, 43.9, 32.3, 28.9, 28.1, 26.8, 21.6, 21.1, 20.2.

IR ν (cm^{-1}): 3079, 2937, 2862, 1743, 1668, 1229.

MS (EI) *m*/*z* (%): 250 (7), 191 (100).



Chemical Formula: $C_{13}H_{18}O_3$
Molecular Weight: 222,28

13

Yield = 85%

Aspect: colourless oil

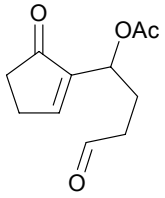
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.40 (t, 1H, *J* = 2.7 Hz), 5.80-5.66 (m, 1H), 5.44-5.42 (m, 1H), 4.99-4.86 (m, 2H), 2.60-2.52 (m, 2H), 2.42-2.38 (m, 2H), 2.06-1.96 (m, 2H), 2.02 (s, 3H), 1.80-1.60 (m, 2H), 1.41-1.30 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 207.1, 170.1, 158.6, 145.3, 138.2, 114.9, 69.5, 35.3, 33.5, 32.8, 26.2, 24.6, 21.2.

IR ν (cm^{-1}): 3076, 2976, 2930, 2862, 1742, 1703, 1238.

MS (CI) *m*/*z* (%): 223 (6), 163 (100).

Typical procedure for ozonolysis.



Chemical Formula: $C_{11}H_{14}O_4$
Molecular Weight: 210,23

9a

In a 500 ml 3-necked flask, a tiny amount of Sudan red 7B was added to a solution of acetate **8a** (2.310 g, 11.09 mmol, 1 eq.) in DCM (300 ml) until the solution became slightly pink. The resulting reaction mixture was cooled to -78 °C and ozone was bubbled through the solution until it became colourless. After the excess ozone was removed using a flow of argon, Ph_3P (4.408 g, 16.64 mmol, 1.5 eq., 99%) was added and the solution was let to warm up overnight.
Then, the reaction mixture was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ EtOAc: 1/1, Rf = 0.20) affording the desired aldehyde **9a** (1.935 g, 83%) as a colourless oil.

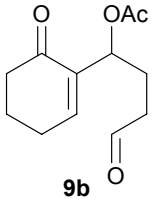
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.74 (t, 1H, *J* = 1.4 Hz), 7.47 (td, 1H, *J* = 2.8, 1.3 Hz), 5.57 (ddd, 1H, *J* = 5.9, 3.0, 1.5 Hz), 2.66-2.59 (m, 2H), 2.52-2.40 (m, 4H), 2.24-2.04 (m, 2H), 2.08 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 207.1, 201.1, 169.9, 159.3, 144.5, 68.9, 39.9, 35.4, 26.8, 25.8, 21.2.

IR ν (cm^{-1}) 2934, 2854, 2728, 1741, 1702, 1238.

MS (CI) *m*/*z* (%): 211 (3), 151 (100).

HRMS *m*/*z* calculated for $C_{11}H_{14}O_4Na$: 233.0790. Found: 233.0792.



9b

Chemical Formula: $C_{12}H_{16}O_4$
Molecular Weight: 224,25

Yield = 95%

Aspect: oil

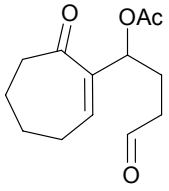
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.73 (t, 1H, *J* = 1.5 Hz), 6.89 (t, 1H, *J* = 4.1 Hz), 5.66 (ddd, 1H, *J* = 7.3, 4.8, 1.2 Hz), 2.51-2.37 (m, 6H), 2.15-1.89 (m, 4H), 2.06 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 201.4, 197.4, 169.7, 145.6, 138.1, 70.0, 40.1, 38.5, 27.0, 25.8, 22.7, 21.2.

IR ν (cm^{-1}) 2948, 2895, 2831, 1741, 1671, 1236.

MS (CI) *m*/*z* (%): 223 (7%), 164 (100).

HRMS *m*/*z* calculated for $C_{12}H_{17}O_4$: 225.112684. Found: 225.112358.



9c

Chemical Formula: $C_{13}H_{18}O_4$
Molecular Weight: 238,28

Yield = 75%

Aspect: colourless oil

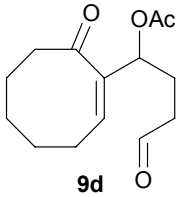
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.69 (s, 1H), 6.61 (t, 1H, *J* = 6.6 Hz), 5.42 (t, 1H, *J* = 5.7 Hz), 2.70-2.50 (m, 2H), 2.48-2.30 (m, 4H), 2.10-1.80 (m, 2H), 2.00 (s, 3H), 1.80-1.60 (m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 201.9, 200.3, 168.6, 141.1, 140.9, 70.9, 41.6, 39.1, 26.43, 26.40, 23.9, 20.3, 20.1.

IR ν (cm^{-1}): 2937, 2867, 2850, 2720, 1742, 1725, 1275.

MS (CI) *m*/*z* (%): 239 (17), 179 (100).

HRMS *m*/*z* calculated for $C_{13}H_{19}O_4$: 239.128334. Found: 239.127317.



9d

Chemical Formula: $C_{14}H_{20}O_4$
Molecular Weight: 252,31

Yield = 87%

Aspect: colourless oil

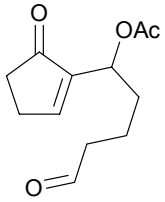
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.68 (s, 1H), 6.07 (t, 1H, *J* = 6.9 Hz), 5.21 (t, 1H, *J* = 6.6 Hz), 2.62-2.34 (m, 4H), 2.34-2.24 (m, 2H), 2.02-1.96 (m, 2H), 1.97 (s, 3H), 1.90-1.70 (m, 2H), 1.60-1.40 (m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 208.8, 201.3, 169.8, 137.8, 135.7, 74.8, 44.8, 40.2, 29.2, 27.6, 27.0, 22.7, 22.2, 21.2.

IR ν (cm^{-1}): 3035, 2930, 2856, 2823, 2724, 1742, 1727, 1683, 1229.

MS (EI) *m*/*z* (%): 253 (3), 193 (100).

HRMS *m*/*z* calculated for $C_{14}H_{21}O_4$: 253.143984. Found: 253.144340.



14

Chemical Formula: $C_{12}H_{16}O_4$
Molecular Weight: 224,25

Yield = 75%

Aspect: colourless oil

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.68 (s, 1H), 7.40 (bs, 1H), 5.48 (t, 1H, *J* = 4.8 Hz), 2.58-2.52 (m, 2H), 2.46-2.34 (m, 4H), 2.08 (s, 3H), 1.80-1.68 (m, 2H), 1.64-1.50 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 207.1, 201.8, 170.0, 159.0, 144.7, 69.1, 43.4, 35.2, 32.4, 26.7, 21.2, 17.7.

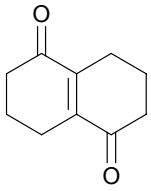
IR ν (cm^{-1}): 3075, 2931, 2919, 2727, 1742, 1742, 1727, 1701, 1239.

MS (CI) *m*/*z* (%): 225 (12), 165 (100).

HRMS *m*/*z* calculated for $C_{12}H_{17}O_4$: 225.112684. Found: 225.112085.

Typical procedure for Stetter reaction.

In a schlenck tube, thiazolium chloride **10a** (176 mg, 0.65 mmol, 1 eq., 99%) and Et_3N (95 µl, 0.78 mmol, 1.2 eq.) were added to a solution of aldehyde **9b** (145 mg, 0.65 mmol, 1 eq.) in EtOH (1 ml). The reaction mixture was heated at reflux for 2.5 h. After cooling to room temperature, the crude product was diluted with DCM and washed with water. The water layer was extracted with DCM and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (DCM, Rf: 0.19) affording enedione **11b** (70 mg, 66%) as a slightly yellow solid.



Chemical Formula: $C_{10}H_{12}O_2$
Molecular Weight: 164,2

11b

Yield: 66%

Aspect: slightly yellow solid

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.48 (t, 8H, *J* = 6.3 Hz), 1.98 (quint, 4H, *J* = 6.3 Hz).

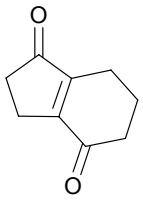
^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 201.5, 145.9, 38.4, 22.5, 21.8.

IR ν (cm^{-1}): 2944, 2894, 2872, 1671.

MS (APCI) *m/z* (%): 165 (3), 149 (15), 74 (100).

mp: 109-110 °C

RN: 42245-86-3



Chemical Formula: $C_9H_{10}O_2$
Molecular Weight: 150,17

11a

Yield = 50%

Aspect: white solid

^{1}H NMR ($CDCl_3$, (500 MHz) δ (ppm): 2.68-2.63 (m, 2H), 2.55-2.50 (m, 2H), 2.50-2.46 (m, 2H), 2.41-2.36 (m, 2H), 2.12-2.04 (m, 2H).

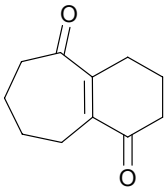
^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 210.2, 199.6, 159.6, 154.1, 39.1, 35.2, 23.2, 23.1, 20.6.

IR ν (cm^{-1}): 2934, 2871, 1706, 1681, 1194.

MS (APCI) *m*/*z* (%): 151 (100), 123 (14).

mp: < 30 °C

HRMS *m*/*z* calculated for $C_9H_{10}O_2$: 150.0681. Found: 150.0678.



Chemical Formula: $C_{11}H_{14}O_2$
Molecular Weight: 178,23

11c

Yield: 80%

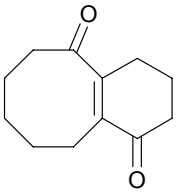
Aspect: yellow liquid

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.62-2.40 (m, 8H), 1.96 (quint, 2H, *J* = 6.6 Hz), 1.77 (quint, 2H, *J* = 6.7 Hz), 1.64 (quint, 2H, J = 6.6 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 206.3, 198.9, 150.5, 140.2, 40.4, 37.0, 24.7, 22.9, 21.8, 21.1, 20.8.

IR ν (cm^{-1}): 2942, 2865, 1681.

MS (APCI) *m*/*z* (%): 179 (100).



Chemical Formula: $C_{12}H_{16}O_2$
Molecular Weight: 192,25

11d

Yield: 80%

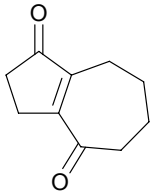
Aspect: yellow liquid

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.52 (m, 2H), 2.44-2.26 (m, 6H), 2.06-1.94 (m, 2H), 1.80-1.70 (m, 2H), 1.60-1.50 (m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 211.4, 198.8, 152.7, 134.6, 44.2, 38.1, 28.3, 27.7, 25.7, 24.3, 22.9, 22.8.

IR ν (cm^{-1}): 2931, 2861, 1670.

MS (APCI) *m*/*z* (%): 193 (100).



15

Chemical Formula: $C_{10}H_{12}O_2$
Molecular Weight: 164,2

Yield: 46%

Aspect: yellow liquid

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.80-2.60 (m, 4H), 2.48 (m, 2H), 2.43 (t, 2H, *J* = 4.8 Hz), 1.92-1.72 (m, 4H).

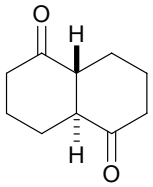
^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 210.3, 202.5, 162.0, 149.2, 44.0, 34.0, 25.3, 25.2, 24.2, 22.6.

IR ν (cm^{-1}): 2930, 2866, 1708, 1671.

MS (CI) *m*/*z* (%): 165 (100).

Typical procedure for enedione reduction.

In a round-bottomed flask, $TiCl_3$ (237 µl, 0.609 mmol, 4 eq., 30 wt% aqueous HCl 2N) was added dropwise to a solution of enedione **11b** (25 mg, 0.152 mmol, 1 eq.) in acetone (2.25 ml). The resulting solution was stirred for 1h15 at room temperature. Then, a solution of brine (10 ml) was added to the reaction mixture and the organic layer was extracted with DCM (3x10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (5% Et_2O/DCM, Rf = 0.40) affording *trans*-diketone **16b** (25mg, 97%) as a white solid.



16b

Chemical Formula: $C_{10}H_{14}O_2$
Molecular Weight: 166,22

Yield: 97%

Aspect: white solid

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 2.42-2.34 (M, 4H), 2.27 (td, 2H, *J* = 13.5, 6.0 Hz), 2.16-2.07 (m, 4H), 1.75-1.64 (m, 2H), 1.60 (qt, 2H, *J* = 13.5, 4.0).

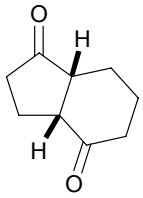
^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 210.1, 55.7, 41.4, 25.1, 24.6.

IR ν (cm^{-1}): 2951, 2908, 2879, 2857, 1703.

MS (CI) *m*/*z* (%): 167 (100), 149 (35), 131 (23).

mp: 158-159 °C

RN: 42245-85-2



Chemical Formula: $C_9H_{12}O_2$
Molecular Weight: 152,19

16a

Yield = 85%

Aspect: colourless oil

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 3.06 (ddd, 1H, *J* = 9.4, 6.7, 2.9 Hz), 2.78-2.72 (m, 1H), 2.61 (ddt, 1H, *J* = 12.6, 9.2, 3.1 Hz), 2.42-2.31 (m, 2H), 2.26 (dddt, 1H, *J* = 19.2, 9.4, 3.0, 1.5 Hz), 2.16-2.03 (m, 2H), 1.95-1.83 (m, 2H), 1.79 (dddd, 1H, *J* = 12.8, 9.7, 9.0, 6.8 Hz), 1.62-1.51 (m, 1H).

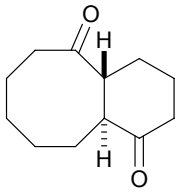
^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 218.0, 210.9, 51.9, 49.9, 41.0, 36.9, 24.3, 23.0, 21.6.

IR ν (cm^{-1}): 2943, 2867, 1741, 1708.

MS (CI) *m*/*z* (%): 153 (100), 152 (70), 135 (70), 93 (57).

HRMS *m*/*z* calculated for $C_9H_{12}O_2$: 152.0837. Found: 152.0833.

RN: 61154-29-8



Chemical Formula: $C_{12}H_{18}O_2$
Molecular Weight: 194,27

16d

Yield = 86%

Aspect: white solid

^{1}H NMR ($CDCl_3$, (500 MHz) δ (ppm): 2.78 (td, 1H, *J* = 12.0, 3.5 Hz), 2.53 (tdd, 1H, *J* = 12.0, 3.7, 1.0 Hz), 2.49-2.32 (m, 4H), 2.18-2.10 (m, 1H), 2.04-1.91 (m, 3H), 1.86-1.72 (m, 2H), 1.71-1.61 (m, 2H), 1.51-1.28 (m, 4H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 216.3, 211.2, 54.3, 53.2, 42.2, 42.0, 28.8, 28.1, 26.2, 25.7, 24.1, 22.5.

IR ν (cm^{-1}): 2936, 2862, 1715, 1699.

MS (CI) *m*/*z* (%): 195 (100), 177 (11).

HRMS *m*/*z* calculated for $C_{12}H_{18}O_2$: 194.1307. Found: 194.1314.

mp: 63-64 °C