SUPPORTING INFORMATION

On the Scope of Catalytic Enantioselective Tandem Carbonyl Ylide

Formation - Intramolecular [3+2] Cycloadditions

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Experimental Section

Synthesis of 2-diazo-3,6-diketoester (**25**)

See main paper for the detailed synthesis of **25**.

Synthesis of 2-diazo-3,6-diketoester (26)

6-Iodohept-2-yne^{S1}

n-Butyllithium (1.43 M in hexanes, 26.3 mL, 37.5 mmol) was added dropwise to a stirred solution of 5-chloropent-1-yne (3.50 g, 34.1 mmol) in THF (100 mL) at -78°C . The temperature was allowed to reach slowly 25°C and MeI (5.33 g, 37.5 mmol) was added dropwise. The mixture was heated to reflux for 2 h,^{S1} cooled to room temperature, poured into water (50 mL) and extracted with petrol (3x50 mL). The combined organic extracts were washed with water (50 mL), dried (MgSO_4), filtered and concentrated *in vacuo*. The crude residue was dissolved in a solution of NaI (13.65 g, 91.1 mmol) in acetone (75 mL) and heated to reflux for 22 h, cooled to room temperature, diluted with petrol, washed with water, dried (MgSO_4) and filtered. The solvent was evaporated *in vacuo* to give a yellow liquid, which was purified by filtration over a short path of silica to give a colourless liquid (4.78 g, 68%). ^1H NMR (200 MHz, CDCl_3) δ 3.28 (2H, t, $J = 6.9$ Hz), 2.29–2.20 (2H, m), 1.94 (2H, quint, $J = 6.7$ Hz), 1.76 (3H, t, $J = 2.5$ Hz).

4-Oxodec-8-ynoic acid (12)

General procedure as for **8**. The pale yellow solid, obtained from 2,3-dihydrofuran (3.62 mL, 47.8 mmol) and 6-iodohex-2-yne (7.11 g, 34.2 mmol), was recrystallised (petrol/ CH_2Cl_2) to give 4-oxodec-8-ynoic acid (2.87 g, 46%). IR (KBr disc) 3052, 2954, 1698, 1410, 1246, 1191, 1099 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 11.30 (1H, bs), 2.77–2.53 (6H, m), 2.19–2.11 (2H, m), 1.81–1.70 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 208.4, 178.8, 41.3, 36.9, 27.7, 22.8, 18.1, 3.4; MS (CI+) m/z 200 ($\text{M}+\text{NH}_4^+$, 100), 184 (52), 167 (18), 139 (10), 128 (69), 111 (15); HRMS (ES, $[\text{M}+\text{NH}_4]^+$) calc. 200.1287, measured 200.1293.

^{S1} Buck, M.; Chong, J. M. *Tetrahedron Lett.* **2001**, 42, 5825-5827.

***tert*-Butyl 3,6-dioxododec-10-ynoate (20)**

General procedure as for **15**. The crude product, obtained from **12** (2.86 g, 15.7 mmol), was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2, R_f = 0.14) to afford *tert*-butyl 3,6-dioxododec-10-ynoate as a pale yellow oil (2.32 g, 53%). IR (neat) 2977, 2922, 1740, 1713, 1368 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.33 (2H, s), 2.74–2.65 (4H, m), 2.51 (2H, t, J = 7.4 Hz), 2.08–2.06 (2H, m), 1.70–1.62 (5H, m), 1.39 (9H, s); ¹³C NMR (50 MHz, CDCl₃) δ 208.4, 202.0, 166.3, 81.8, 78.1, 76.2, 50.5, 41.3, 36.2, 36.0, 27.8, 22.8, 18.0, 3.3; MS (CI⁺) m/z 298 (M+NH₄⁺, 65), 281 (M+H⁺, 4), 242 (100), 198 (37); HRMS (ES, [M+NH₄]⁺) calc. 298.2018, measured 298.2032.

***tert*-Butyl (Z)-3,6-dioxododec-10-enoate (16)**

tert-Butyl 3,6-dioxododec-10-ynoate **20** (1.0 g, 3.57 mmol) was dissolved in dry petrol (50 mL) in a 100 mL-conical flask, then Lindlar's catalyst (Aldrich, 0.20 g, 20% w/w) and quinoline (0.1 mL) were added. The reaction mixture was degassed (10–15 min) by bubbling argon through it. The flask was purged with H₂ (vacuum / hydrogen flow, 4 times) and the mixture was stirred vigorously for 5h30 (TLC monitoring) under H₂ (1 atm). The reaction mixture was filtered on a short path of silica and the solvent was evaporated *in vacuo*. The crude residue was purified by flash silica gel chromatography (petrol-Et₂O 8:2; R_f = 0.33) to afford *tert*-butyl 3,6-dioxododec-10-enoate as a pale yellow oil, mixture of (Z) and (E) isomers (Z:E $\approx$ 90:10 by ¹H NMR and GC) (0.93 g, 93% yield). ¹H NMR (200 MHz, CDCl₃) δ 5.49–5.20 (2H, m), 3.34 (2H, s), 2.75–2.63 (4H, m), 2.40 (2H, m, J = 7.4 Hz), 2.05–1.92 (2H, m), 1.62–1.50 (5H, m), 1.41 (9H, s).

***tert*-Butyl (Z)-2-diazo-3,6-dioxododec-10-enoate (26)**

General procedure as for **25**. The crude yellow oil, obtained from **16** (0.93 g, 3.3 mmol), was purified by flash chromatography (SiO₂, petrol-Et₂O 9:1, R_f = 0.12) to afford (Z)-*tert*-butyl 2-diazo-3,6-dioxododec-10-enoate as a yellow oil, mixture of (Z) and (E) isomers (Z:E $\approx$ 9:1 by ¹H NMR) (0.90 g, 88%). IR (neat) 2978, 2934, 2131, 1713, 1654, 1369, 1313, 1131 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.53–5.24 (2H, m), 3.10–3.04 (2H, m), 2.73–2.66 (2H, m), 2.46 (2H, t, J = 7.4 Hz), 2.10–1.97 (2H, m), 1.66–1.53

(5H, m), 1.50 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 209.2, 191.6, 160.5, 130.7+125.7 (C=C, (*E*)-isomer), 129.7+124.7 (C=C, (*Z*)-isomer), 83.1, 42.1, 36.1, 34.2, 31.9 ((*E*)-isomer), 28.3, 26.1, 23.5, 22.5 ((*E*)-isomer), 17.9 ((*E*)-isomer), 12.8; MS (ES+) m/z 639 ($2^*\text{M}+\text{Na}^+$, 100), 611 (38), 583 (12), 482 (5), 431 (4), 331 ($\text{M}+\text{Na}^+$, 67), 326 ($\text{M}+\text{NH}_4^+$, 8), 309 ($\text{M}+\text{H}^+$, 7), 253 (9); HRMS (ES, $[\text{M}+\text{H}]^+$) calc. 309.1814, measured 309.1815.

Synthesis of 2-diazo-3,6-diketoester (27)

6-Iodo-1-hexene ^{S2}

A stirred solution of 6-bromo-1-hexene (14.7 mL, 90.3 mmol) and NaI (40.6 g, 270.8 mmol) in acetone (150 mL) was heated to reflux for 5 h. The reaction mixture was concentrated *in vacuo* until the volume was reduced to *ca.* 50 mL. The mixture was diluted with water (150 mL), extracted with Et_2O (3 x 50 mL) and the combined organic extracts dried (MgSO_4). The solution was passed through a pad of basic alumina before removal of the solvent to give 6-iodo-1-hexene as a colourless oil (18.1 g, 95%).

4-Oxo-9-decenoic acid (9)

General procedure as for **8**. 4-Oxo-9-decenoic acid (10.4 g, 66%) was obtained from 2,3-dihydrofuran (6.45 mL, 85.7 mmol) and 6-iodo-1-hexene (18.0 g, 85.7 mmol) as a white solid. Mp 45-46 °C; IR (KBr disc) 3060, 2932, 1733, 1702, 1418, 1243 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.80 (1H, ddt, J = 17.0, 10.0 and 6.5 Hz), 5.06-4.93 (2H, m), 2.77-2.60 (4H, m), 2.47 (2H, t, J = 7.0 Hz), 2.12-2.01 (2H, m), 1.69-1.52 (2H, m), 1.49-1.31 (2H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 209.3, 178.3, 138.2, 114.4, 42.2,

^{S2} (a) Iyer, R. S.; Kuo, G.-H.; Helquist, P. *J. Org. Chem.* **1985**, *50*, 5898-5900. (b) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098-2107.

36.5, 33.3, 28.1, 27.6, 23.0; MS (APCI-) m/z 183 ($M-H^+$, 100), 165 (17), 149 (15), 117 (13); HRMS ($M+NH_4^+$) calc. 202.1443, measured 202.1447.

***tert*-Butyl 3,6-dioxododec-11-enoate (17)**

General procedure as for **15**. The crude product, obtained from **9** (2.58 g, 14.0 mmol), was purified by column chromatography (SiO_2 , petrol- Et_2O 8:1 to 3:1; R_f = 0.41 petrol- Et_2O 1:1) to give *tert*-butyl -3,6-dioxododec-11-enoate as a colourless oil (2.67 g, 68%). IR (neat) 2978, 2932, 1737, 1713, 1369, 1319, 1257, 1152 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 5.79 (1H, ddt, J = 17.0, 10.2 and 6.7 Hz), 5.01 (1H, dq, J = 17.0 and 1.7 Hz), 4.96-4.94 (1H, m), 3.41 (2H, s), 2.83-2.80 (2H, m), 2.72-2.70 (2H, m), 2.46 (2H, t, J = 7.4 Hz), 2.06 (2H, q, J = 7.2 Hz), 1.63-1.57 (2H, m), 1.47 (9H, s), 1.41-1.34 (2H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.8, 201.9, 166.2, 138.3, 114.5, 81.8, 50.5, 42.4, 36.1, 35.9, 33.3, 28.2, 23.1; MS (CI+) m/z 300 ($M+NH_4^+$, 100), 244 (61); HRMS ($M+NH_4^+$) calc. 300.2175, measured 300.2175.

***tert*-Butyl 2-diazo-3,6-dioxododec-11-enoate (27)**

General procedure as for **25**. The crude yellow oil, obtained from **17** (1.50 g, 5.32 mmol), was purified by flash chromatography (SiO_2 , petrol- Et_2O 5:1; R_f = 0.62 petrol- Et_2O 1:1) to afford *tert*-butyl 2-diazo-3,6-dioxododec-11-enoate as a yellow oil (1.55 g, 95%). IR (neat) 2979, 2934, 2133, 1717, 1655, 1370, 1314, 1133 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 5.79 (1H, ddt, J = 17.0, 10.2 and 7.0 Hz), 5.02-4.98 (1H, m), 4.94 (1H, ddt, J = 10.2, 2.2 and 1.3 Hz), 3.11-3.09 (2H, m), 2.74-2.72 (2H, m), 2.49 (2H, t, J = 7.5 Hz), 2.06 (2H, app. qt, J = 7.0 and 1.3 Hz), 1.64-1.57 (2H, m), 1.53 (9H, s), 1.48-1.36 (2H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.5, 191.9, 160.7, 138.6, 114.7, 83.1, 65.8, 42.4, 35.9, 34.1, 33.4, 28.2, 28.1, 23.0; MS (CI+) m/z 326 ($M+NH_4^+$, 41), 309 ($M+H^+$, 40), 300 (49), 270 (100), 253 (19), 244 (22), 226 (12), 200 (20); HRMS ($M+H^+$) calc. 309.1814, measured 309.1814.

Synthesis of 2-diazo-3,6-diketoester (28)

(E)-4-Oxoundec-9-enoic acid (10)

General procedure as for **8**. (E)-4-Oxoundec-9-enoic acid (9.1 g, 85%) was obtained from 2,3-dihydrofuran (5.67 mL, 75.0 mmol) and (E)-7-iodohept-2-ene^{S3} (12.0 g, 53.6 mmol) as a white solid. Mp 49-50 °C. IR (KBr disc) 3396, 3022, 2929, 2854, 1701, 1465, 1381 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.47-5.35 (2H, m), 2.78-2.57 (4H, m), 2.45 (2H, t, *J* = 7.4 Hz), 2.06-1.90 (2H, m), 1.76-1.56 (5H, m), 1.34 (2H, app. quint, *J* = 7.5 Hz); ¹³C NMR (50 MHz, CDCl₃) δ 209.5, 179.0, 131.1, 125.3, 42.5, 36.7, 32.1, 28.9, 27.7, 23.1, 17.7; MS (CI+) *m/z* 216 (M+NH₄⁺, 100), 199 (30); HRMS (CI, [M+H]⁺) calc. 199.1334, measured 199.1340.

tert-Butyl (E)-3,6-dioxotridec-11-enoate (18)

General procedure as for **15**. The crude product, obtained from **10** (5.96 g, 30.1 mmol), was purified by column chromatography (SiO₂, petrol-Et₂O 8:2; *R*_f = 0.41 petrol-Et₂O 1:1) to give *tert*-butyl (E)-3,6-dioxotridec-11-enoate as a colourless oil (8.60 g, 97%). IR (neat) 2978, 2932, 2858, 1716, 1456, 1368 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.35-5.25 (2H, m), 3.30 (2H, s), 2.75-2.54 (4H, m), 2.41-2.29 (2H, m), 1.93-1.80 (2H, m), 1.62-1.48 (3H, m), 1.48-1.30 (4H, m), 1.36 (9H, s), 1.41-1.34 (2H, m); ¹³C NMR (50 MHz, CDCl₃) δ 209.2, 202.2, 166.5, 131.0, 125.0, 81.7, 50.4, 42.3, 36.0, 35.7, 32.0, 28.8, 27.7, 23.0, 17.6; MS (CI+) *m/z* 314 (M+NH₄⁺, 81), 297 (M+H⁺, 5), 258 (100), 214 (40), 176 (25), 158 (18), 120 (13); HRMS (M+H⁺) calc. 297.2066, measured 297.2066.

tert-Butyl (E)-2-diazo-3,6-dioxotridec-11-enoate (28)

General procedure as for **25**. The crude yellow oil, obtained from **18** (8.11 g, 27.7 mmol), was purified by flash chromatography (SiO₂, petrol-Et₂O 9:1; *R*_f = 0.49 petrol-Et₂O 1:1) to afford *tert*-butyl (E)-2-diazo-3,6-dioxotridec-11-enoate as a yellow oil (4.04 g, 50%). IR (neat) 2975, 2932, 2855, 2130, 1713, 1653, 1456, 1393 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.37-5.29 (2H, m), 3.08-2.97 (2H, m), 2.71-2.61 (2H, m), 2.46-2.35 (2H, m), 1.98-1.84 (2H, m), 1.59-1.52 (3H, m), 1.36 (9H, s), 1.41-1.05 (4H, m); ¹³C

^{S3} Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720-5727.

NMR (50 MHz, CDCl₃) δ 209.5, 191.9, 160.7, 131.0, 125.0, 83.2, 83.0, 42.4, 35.9, 34.0, 32.1, 28.9, 28.0, 23.0, 17.6; MS (CI+) m/z 340 (M+NH₄⁺, 40), 323 (M+H⁺, 28), 314 (50), 284 (100), 258 (47), 214 (36), 170 (23); HRMS (M+H⁺) calc. 323.1971, measured 323.1976.

Synthesis of 2-diazo-3,6-diketoester (29)

5-Iodo-1-trimethylsilylpent-1-yne ^{S4}

A solution of 5-chloropent-1-yne (3.5 g, 34.1 mmol) in THF (35 mL) was cooled to -78 °C and *n*-butyllithium (2.3 M in hexanes, 19.3 mL, 44.4 mmol) was added dropwise. After 10 minutes at -78 °C, chlorotrimethylsilane (6.5 mL, 51.2 mmol) was added dropwise and the mixture was allowed to warm slowly to 25 °C. The solution was stirred overnight then poured into water (25 mL). The layers were separated and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine (25 mL), dried (MgSO₄), filtered and the solvent evaporated *in vacuo*. A solution of NaI (12.8 g, 85.3 mmol) in acetone (70 mL) was added to the crude silane and heated to reflux for 24 h. The reaction mixture was diluted with petrol, washed with water, dried (MgSO₄), filtered and the solvent was evaporated *in vacuo*. The pale yellow liquid obtained was pure by ¹H NMR (8.35 g, 92% yield). ¹H NMR (200 MHz, CDCl₃) δ 3.28 (2H, t, J = 6.8 Hz), 2.36 (2H, t, J = 6.8 Hz), 1.99 (2H, quint, J = 6.7 Hz), 0.14 (9H, s).

4-Oxonon-8-ynoic acid (11)

General procedure as for **8**. The pale brown solid, obtained from 2,3-dihydrofuran (3.32 mL, 43.9 mmol) and 5-iodo-1-trimethylsilylpent-1-yne (8.35 g, 31.4 mmol), was recrystallised (petrol/CH₂Cl₂) to give 4-oxonon-8-ynoic acid (3.11 g, 59%). IR (KBr disc) 3294, 2939, 1712, 1404, 1372, 1186,

^{S4} Cochrane, J. S.; Hanson, J. R. *J. Chem. Soc., Perkin Trans. I* **1972**, 361-366.

1102 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 10.32 (1H, bs), 2.72–2.41 (6H, m), 2.17 (2H, dt, $J = 6.9$ and 2.5 Hz), 1.94 (1H, t, $J = 2.5$ Hz), 1.78 (2H, quint, $J = 7.0$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 208.3, 178.6, 83.4, 69.1, 40.9, 36.9, 27.8, 22.1, 17.4 ; MS (CI+) m/z 188 (23), 186 ($\text{M}+\text{NH}_4^+$, 80), 174 (28), 172 (100), 170 (57), 169 ($\text{M}+\text{H}^+$, 17), 52 (56) ; HRMS (ES, $[\text{M}+\text{NH}_4]^+$) calc. 186.1130, measured 186.1136.

***tert*-Butyl 3,6-dioxoundec-10-ynoate (19)**

General procedure as for **15**. The crude product, obtained from **11** (3.11 g, 18.5 mmol), was purified by column chromatography (SiO_2 , petrol- Et_2O 8:2, $R_f = 0.1$) to give *tert*-butyl 3,6-dioxoundec-10-ynoate as a pale yellow oil (2.43 g, 49%). IR (neat) 3290, 2976, 2941, 1735, 1713, 1369, 1152 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 3.31 (2H, s), 2.76–2.59 (4H, m), 2.52 (2H, t, $J = 7.2$ Hz), 2.13 (2H, dt, $J = 7.0$ Hz and 2.6 Hz), 1.89 (1H, t, $J = 2.7$ Hz), 1.69 (2H, quint, $J = 6.9$ Hz), 1.39 (9H, s); ^{13}C NMR (50 MHz, CDCl_3) 208.1, 201.9, 166.2, 83.4, 81.8, 69.1, 50.5, 41.2, 36.2, 36.0, 27.8, 22.2, 17.6; MS (CI+) m/z 284 ($\text{M}+\text{NH}_4^+$, 30), 230 (51), 228 (100), 186 (55), 120 (44), 52 (59) ; HRMS (ES, $[\text{M}+\text{NH}_4]^+$) calc. 284.1862, measured 284.1862.

***tert*-Butyl 2-diazo-3,6-dioxoundec-10-ynoate (29)**

General procedure as for **25**. The crude residue, obtained from **19** (2.43 g, 9.12 mmol), was purified by flash chromatography (SiO_2 , petrol- Et_2O 8:2, $R_f = 0.29$) to afford *tert*-butyl 2-diazo-3,6-dioxoundec-10-ynoate as a yellow solid (2.44 g, 92%). Mp 44–46 $^{\circ}\text{C}$; IR (KBr disc) 3281, 2976, 2933, 2132, 1710, 1651, 1368, 1313, 1129 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 3.03 (2H, m), 2.68 (2H, m), 2.57 (2H, t, $J = 7.2$ Hz), 2.16 (2H, dt, $J = 6.9$ Hz, $J = 2.7$ Hz), 1.91 (1H, t, $J = 2.7$ Hz), 1.74 (2H, quint, $J = 6.9$ Hz), 1.46 (9H, s) ; ^{13}C NMR (50 MHz, CDCl_3) δ 208.5, 191.5, 160.4, 83.5, 83.1, 69.0, 41.3, 36.1, 34.2, 28.2, 22.2, 17.7; MS (CI+) m/z 324 ($\text{M}+\text{NH}_4^+$, 41), 293 ($\text{M}+\text{H}^+$, 21), 284 (20), 254 (100), 228 (52), 186 (80), 172 (78) ; HRMS (ES, $[\text{M}+\text{H}]^+$) calc. 293.1501, measured 293.1491.

Synthesis of 2-diazo-3,6-diketoester (30)

tert-Butyl 2-diazo-3,6-dioxododec-10-ynoate (30)

General procedure as for **25**. The crude yellow oil, obtained from **20** (1.51 g, 5.39 mmol), was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2, *R*_f = 0.31) to afford *tert*-butyl 2-diazo-3,6-dioxododec-10-ynoate as a yellow oil (1.47 g, 89%). IR (neat) 2978, 2935, 2132, 1714, 1652, 1369, 1313, 1132, 1024 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.10–3.00 (2H, m), 2.75–2.68 (2H, m), 2.57 (2H, t, *J* = 7.4 Hz), 2.13–2.10 (2H, m), 1.75–1.68 (5H, m), 1.49 (9H, s); ¹³C NMR (50 MHz, CDCl₃) δ 208.8, 191.6, 160.5, 83.1, 78.2, 76.2, 41.4, 36.2, 34.2, 28.2, 22.9, 18.1, 3.4; MS (CI⁺) *m/z* 324 (M+NH₄⁺, 41), 307 (M+H⁺, 26), 298 (66), 268 (100), 242 (76), 198 (41); HRMS (ES, [M+H]⁺) calc. 307.1658, measured 307.1662.

Synthesis of 2-diazo-3,6-diketoester (31)

6-Iodo-1-trimethylsilylhex-1-yne^{S5}

A solution of 6-trimethylsilyl-5-hexyn-1-ol^{S6} (1.66 g, 9.75 mmol) and Et₃N (2.03 mL, 14.6 mmol) in CH₂Cl₂ (25 mL) was cooled to 0 °C under argon. MsCl (0.83 mL, 10.7 mmol) was added dropwise and the solution was stirred for 15 min at 0 °C, then 15 min at 20 °C. The mixture was hydrolysed with ice–

^{S5} Kita, Y.; Okunaka, R.; Honda, T.; Shindo, M.; Taniguchi, M.; Kondo, M.; Sasho, M. *J. Org. Chem.* **1991**, *56*, 119-125.

^{S6} Witulski, B.; Bergsträßer, U.; Gößmann, M. *Tetrahedron* **2000**, *56*, 4747-4752.

water (20 mL), the solution was diluted with CH_2Cl_2 (25 mL), washed with 10% HCl (20 mL), sat. aq. NaHCO_3 (20 mL) and water (20 mL), dried (MgSO_4), filtered and the solvent was evaporated *in vacuo* to give the mesylate as a yellow liquid (2.31 g, 96% yield). ^1H NMR (200 MHz, CDCl_3) δ 4.27 (2H, m), 3.02 (3H, s), 2.30 (2H, m), 1.95–1.80 (2H, m), 1.71–1.60 (2H, m), 0.16–0.10 (9H, m). The crude mesylate (2.31 g, 9.30 mmol) was dissolved in a solution of NaI (3.48 g, 23.2 mmol) in acetone (25 mL) and heated to reflux for 22 h. The mixture was cooled to room temperature, diluted with petroleum ether, washed with water, dried (MgSO_4), filtered and the solvent was evaporated *in vacuo* to give a pale yellow liquid (2.35 g, 90% yield). IR (neat) 2960, 2175, 1260, 1097–1021 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 3.26–3.18 (2H, m), 2.31–2.21 (2H, m), 2.0–1.86 (2H, m), 1.70–1.55 (2H, m), 0.15–0.09 (9H, m).

4-Oxodec-9-ynoic acid (**13**)

General procedure as for **8**. 4-Oxodec-9-ynoic acid (2.20 g, 41%) was obtained as a pale brown solid from 2,3-dihydrofuran (3.12 mL, 41.2 mmol) and 6-iodo-1-trimethylsilylhex-1-yne (8.25 g, 29.4 mmol). IR (KBr disc) 3401, 3276, 2943, 1700, 1457, 1242 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 10.32 (1H, bs), 2.75–2.57 (4H, m), 2.50 (2H, m), 2.20 (2H, dt, $J = 6.9$ Hz and 2.5 Hz), 1.94 (1H, t, $J = 2.6$ Hz), 1.78–1.44 (4H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 208.5, 178.8, 84.0, 68.6, 42.0, 36.8, 27.8, 22.8, 18.2 ; MS (CI+) m/z 200 ($\text{M}+\text{NH}_4^+$, 100), 183 ($\text{M}+\text{H}^+$, 11) ; HRMS (ES, $[\text{M}+\text{NH}_4]^+$) calc. 200.1287, measured 200.1283.

tert-Butyl 3,6-dioxododec-11-ynoate (**21**)

General procedure as for **15**. The crude product, obtained from **13** (2.12 g, 11.6 mmol), was purified by flash chromatography (SiO_2 , petrol- Et_2O 7:3, $R_f = 0.11$) to afford *tert*-butyl 3,6-dioxododec-11-ynoate as a yellow oil (1.22 g, 37%). IR (neat) 3284, 2975, 2939, 1732, 1713, 1369, 1154 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 3.30 (2H, s), 2.74–2.56 (4H, m), 2.39 (2H, t, $J = 7.2$ Hz), 2.10 (2H, dt, $J = 7.0$ Hz and 2.7 Hz), 1.86 (1H, t, $J = 2.7$ Hz), 1.68–1.38 (4H, m), 1.36 (9H, s); ^{13}C NMR (50 MHz, CDCl_3) δ 208.5,

202.0, 166.3, 83.9, 81.8, 68.6, 50.5, 41.9, 36.2, 35.9, 27.7, 22.7, 18.1 ; MS (CI+) m/z 298 ($M+NH_4^+$, 75), 281 ($M+H^+$, 9), 242 (100), 224 (26) ; HRMS (ES, $[M+H]^+$) calc. 281.1753, measured 281.1745.

***tert*-Butyl 2-diazo-3,6-dioxododec-11-ynoate (31)**

General procedure as for **25**. The crude yellow oil, obtained from **21** (1.22 g, 4.35 mmol), was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2, R_f = 0.3) to afford *tert*-butyl 2-diazo-3,6-dioxododec-11-ynoate as a yellow oil (1.07 g, 80%). IR (neat) 3282, 2979, 2937, 2133, 1712, 1651, 1370, 1314, 1133, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.09 (2H, m), 2.72 (2H, m), 2.51 (2H, t, J = 7.4 Hz), 2.19 (2H, dt, J = 7.0 Hz, J = 2.6 Hz), 1.94 (1H, t, J = 2.6 Hz), 1.74–1.67 (2H, m), 1.52 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 208.9, 191.6, 160.5, 84.1, 83.2, 68.5, 42.1, 36.0, 34.2, 28.3, 27.8, 22.8, 18.2 ; MS (CI+) m/z 324 ($M+NH_4^+$, 19), 307 ($M+H^+$, 22), 298 (29), 268 (100), 251 (40), 242 (46) ; HRMS (ES, $[M+H]^+$) calc. 307.1658, measured 307.1655.

Synthesis of 2-diazo-3,6-diketoester (32)

4-Oxoundec-9-ynoic acid (14)

General procedure as for **8**. 4-Oxoundec-9-ynoic acid (11.91 g, 96%) was obtained from 2,3-dihydrofuran (6.67 mL, 88.3 mmol) and 7-iodohept-2-yne^{S7} (14.0 g, 63.0 mmol) as a brown solid (96%). Mp 45 °C. IR (KBr disc) 3396, 3037, 2938, 1701, 1465, 1382 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 2.78–2.58 (4H, m), 2.48 (2H, t, J = 7.3 Hz), 2.22–2.08 (2H, m), 1.82–1.60 (5H, m), 1.60–1.38 (2H, m); ¹³C NMR (50 MHz, CDCl₃) δ 209.1, 178.8, 78.6, 75.8, 42.0, 36.5, 28.2, 27.5, 22.7, 18.2, 3.2; MS

^{S7} Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806-7807.

(CI+) m/z 214 ($M+NH_4^+$, 100), 197 ($M+H^+$, 20); HRMS (CI, $[M+H]^+$) calc. 197.1177, measured 197.1179.

***tert*-Butyl 3,6-dioxotridec-11-ynoate (22)**

General procedure as for **15**. The crude product, obtained from **14** (5.87 g, 29.9 mmol), was purified by flash chromatography (SiO_2 , petrol-Et₂O 8:2, R_f = 0.32 in petrol-Et₂O 1:1) to afford *tert*-butyl 2-diazo-3,6-dioxododec-11-ynoate as a yellow oil (3.58 g, 41%). IR (neat) 3420, 2979, 2934, 2875, 1714, 1456, 1369, 1320, 1258, 1152 cm^{-1} ; ¹H NMR (200 MHz, CDCl₃) δ 3.33 (2H, s), 2.78-2.59 (4H, m), 2.40 (2H, t, J = 7.0 Hz), 2.10-1.99 (2H, m), 1.68 (3H, t, J = 2.6 Hz), 1.64–1.31 (4H, m), 1.39 (9H, s); ¹³C NMR (50 MHz, CDCl₃) δ 209.0, 202.3, 166.5, 81.8, 78.6, 75.7, 50.5, 42.0, 36.1, 35.8, 28.2, 27.7, 22.7, 18.2, 3.1; MS (CI+) m/z 312 ($M+NH_4^+$, 100), 256 (84), 212 (38), 176 (17), 156 (15); HRMS (ES, $[M+NH_4]^+$) calc. 312.2175, measured 312.2178.

***tert*-Butyl 2-diazo-3,6-dioxotridec-11-ynoate (32)**

General procedure as for **25**. The crude yellow oil, obtained from **22** (3.44 g, 11.7 mmol), was purified by flash chromatography (SiO_2 , petrol-Et₂O 8:2, R_f = 0.32) to afford *tert*-butyl 2-diazo-3,6-dioxododec-11-ynoate as a yellow oil (3.23 g, 86%). IR (neat) 2978, 2935, 2864, 2133, 1713, 1654, 1370, 1314, 1134, 1027 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 3.10-3.03 (2H, m), 2.73-2.66 (2H, m), 2.47 (2H, t, J = 7.2 Hz), 2.14-2.05 (2H, m), 1.73 (3H, t, J = 2.6 Hz), 1.69–1.57 (2H, m), 1.49 (9H, s), 1.47-1.39 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 209.4, 191.9, 160.7, 83.1, 78.7, 75.7, 42.1, 35.9, 34.1, 28.3, 28.1, 22.8, 18.3, 3.2; MS (CI+) m/z 338 ($M+NH_4^+$, 91), 321 ($M+H^+$, 38), 312 (47), 282 (100), 265 (14), 256 (20); HRMS (ES, $[M+H]^+$) calc. 321.1814, measured 321.1820.

Synthesis of 2-diazo-3,6-diketodiester (33) by cross-metathesis

See main paper for the detailed synthesis of **33**.

Synthesis of 2-diazo-3,6-diketoester (**34**) by cross-metathesis

(*E*)-8, 11-Dioxo-tridec-2-enedioic acid 13-*tert*-butyl ester 1-methyl ester (**24**)

General procedure as for **23**. The crude mixture, obtained from **17**, was purified by column chromatography (SiO₂, petrol-ethyl acetate 8:2, *R*_f = 0.15) to give a purple liquid (35 mg, 87%, *E*:*Z* 97:3 by ¹H NMR). ¹H NMR (200 MHz, CDCl₃) δ 6.93 (1H, dt, *J*_{trans} = 15.7 Hz, *J* = 6.9 Hz), 6.21 (1H, dt, *J*_{cis} = 11.5 Hz, *J* = 7.5 Hz), 5.83 (1H, dt, *J*_{trans} = 15.6 Hz, *J* = 1.6 Hz), 5.78 (1H, dt, *J*_{cis} = 11.5 Hz, *J* = 1.7 Hz), 3.73 (3H, s, (*E*)-isomer), 3.71 (3H, s, (*Z*)-isomer), 3.41 (2H, s), 2.85-2.64 (4H, m), 2.46 (2H, app. t, *J* = 7.0 Hz), 2.21 (2H, q), 1.65-1.25 (4H, m), 1.47 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 208.6, 202.0, 167.0, 166.3, 148.9, 121.2, 82.0, 51.4, 50.6, 42.3, 36.3, 36.0, 31.9, 27.9, 27.4, 23.1; MS (CI + NH₃) *m/z* 358 (M + NH₄⁺, 100), 340 (M, 5), 302 (62) 285 (32), 258 (18), 241 (14); HRMS (ES, [M + NH₄]⁺) calc. 358.2230, measured 358.2227.

(*E*)-12-Diazo-8, 11-dioxo-tridec-2-enedioic acid 13-*tert*-butyl ester 1-methyl ester (**34**)

General procedure as for **25**. The residue, obtained from **24** (35 mg, 0.10 mmol), was purified by column chromatography (SiO₂, petrol-ethyl acetate 8:2, *R*_f = 0.20) to give a yellow liquid (31 mg, 82%, *E*:*Z* 97:3 by ¹H NMR). IR (neat) 2980, 2936, 2133, 1714, 1652, 1370, 1313, 1030 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.05 (1H, dt, *J*_{trans} = 15.6 Hz, *J* = 7.0 Hz), 5.92 (1H, dt, *J*_{trans} = 15.6 Hz, *J* = 1.5 Hz), 3.54 (3H, s), 3.21 (2H, t, *J* = 6.1 Hz), 2.45 (2H, t, *J* = 6.1 Hz), 2.09 (2H, t, *J* = 7.3 Hz), 1.85 (2H, q, *J* = 7.1 Hz), 1.48-1.41 (2H, m), 1.36 (9H, s), 1.19-1.11 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 207.4, 191.2, 166.7, 160.7, 149.2, 121.7, 82.5, 76.3, 42.3, 36.2, 34.9, 32.2, 28.2, 27.8, 23.6; MS (CI+) *m/z* 384

($M+NH_4^+$, 5), 359 (18), 358 (100), 356 (20), 328 (11), 302 (46), 211 (24), 258 (26); HRMS (ES, $[M+NH_4]^+$) calc. 384.2135, measured 384.2133.

Synthesis of *tert*-butyl 2-oxo-6-heptenyl diazomalonate (47)

1-Hydroxy-6-hepten-2-one (45)

In a 100 mL three-necked flask equipped with a condenser and under Ar, previously ground Mg turnings (584 mg, 24 mmol) were suspended in dry Et₂O (30 mL). To this was added a small portion of the 5-bromo-1-pentene needed. After ca. 5 min the reaction started and the remaining bromide solution was slowly added. The mixture was then heated to reflux for 15 min, cooled to 25 °C and a solution of glycolonitrile^{S8} (428 mg, 7.5 mmol) in Et₂O (5 mL) was added quickly. A grey solid formed immediately, and the reaction mixture was heated to reflux for 3 days. Ice was carefully added, followed by addition of a solution of H₂SO₄ (0.75 mL) in H₂O (2.25 mL). The mixture was extracted with Et₂O (3x20 mL) and the combined organic extracts were washed with sat. aq. Na₂CO₃ (20 mL) and H₂O (20 mL). The combined aqueous layers were neutralized to pH 6 then extracted with Et₂O (10x10 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated *in vacuo*. The crude yellow liquid was distilled *in vacuo* (b.p. 64-68 °C / 0.5 mmHg) to afford a colorless oil (384 mg, 40%). *R*_f = 0.20 (petrol-Et₂O 2:1); IR (neat) 3429, 3068, 2920, 1715, 1636, 1405 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.75-5.68 (1H, m), 5.01-4.95 (2H, m), 4.20 (2H, s), 3.21 (1H, bs), 2.39 (2H, t, *J* = 7.4 Hz), 2.05 (2H, q, *J* = 7.3 Hz), 1.71 (2H, quint, *J* = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 209.7, 137.4, 115.6, 68.1,

^{S8} (a) Pfeil, E.; Barth, H. *Liebigs Ann. Chem.* **1955**, 593, 81-90. (b) Gaudry, R. *Org. Synth., Coll. Vol. III* **1955**, 436-437.

37.4, 32.9, 22.5; MS (CI+) m/z 146 ($M+NH_4^+$, 100), 130 (22), 126 (19), 97 (40); HRMS (ES, $[M+NH_4]^+$) calc. 146.1181, measured 146.1178.

***tert*-Butyl 2-oxo-6-heptenyl malonate (46)**

A solution of alcohol **45** (3.27 g, 25.6 mmol) and *tert*-butyl hydrogen malonate (4.34 mL, 28.2 mmol) in dry CH_2Cl_2 (100 mL) under Ar was cooled to 0 °C, then treated with DCC (5.8 g, 28.2 mmol) and DMAP (314 mg, 2.6 mmol). The solution was allowed to warm to 25 °C and stirred for 15 h. The reaction mixture was filtered and the filtrate concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2 , petrol-Et₂O 10:1, R_f = 0.05) to give **46** as a pale yellow oil (6.05 g, 88%). IR (neat) 3485, 2972, 1718, 1639 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 5.75-5.65 (1H, m), 4.99-4.92 (2H, m), 4.65 (2H, s), 3.36 (2H, s), 2.40 (2H, t, J = 7.4 Hz), 2.03 (2H, q, J = 6.9 Hz), 1.67 (2H, quint, J = 7.3 Hz), 1.43 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 166.2, 165.2, 137.5, 115.5, 82.2, 68.5, 42.3, 37.7, 32.8, 27.8, 22.0; MS (CI+) m/z 288 ($M+NH_4^+$, 100), 270 ($M+H^+$, 3), 232 (51); HRMS (ES, $[M+NH_4]^+$) calc. 288.1805, measured 288.1811.

***tert*-Butyl 2-oxo-6-heptenyl diazomalonate (47)**

To a solution of **46** (1.35 g, 5.0 mmol) in dry CH_3CN (10 mL) was added a solution of tosyl azide^{S9} (3.08 g, 12.5 mmol) in dry CH_3CN (10 mL) and solid anhydrous K_2CO_3 .^{S10} The reaction mixture was stirred at 25 °C for 24 h, the solvent was then removed under reduced pressure and the resulting slurry was taken up into Et₂O. The organic phase was washed with 10% aq. K_2CO_3 (2x15 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2 , petrol-Et₂O 5:1, R_f = 0.17) to afford **47** as a yellow oil (1.10 g, 74%). IR (neat) 3435, 2980, 2137, 1728, 1682, 1642 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 5.80-5.69 (1H, m), 5.04-4.97 (2H, m), 4.77 (2H, s), 2.43 (2H, t, J = 7.3 Hz), 2.08 (2H, q, J = 7.1 Hz), 1.72 (2H, quint, J = 7.3 Hz), 1.52 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 160.8, 159.3, 137.5, 115.6, 83.3, 68.2, 37.7, 32.8, 28.2, 22.1; MS

^{S9} Regitz, M.; Hocker, J.; Liedhegener, A. *Org. Synth., Coll. Vol. V* **1973**, 179-183.

^{S10} Muñoz, L.; Koskinen, A. *J. Org. Chem.* **1993**, 58, 879-886.

(CI+) m/z 314 ($M+NH_4^+$, 21), 288 (100), 258 (100), 232 (52), 146 (30); HRMS (ES, $[M+NH_4]^+$) calc. 314.1710, measured 314.1714.

Cycloaddition Reactions

7-Carbo *tert*-butoxy-*endo*-6-methyl-11-oxatricyclo[5.3.1.0^{1,5}]undecan-8-one (35)

See main paper for the detailed synthesis of **35**.

7-Carbo *tert*-butoxy-*exo*-6-methyl-11-oxatricyclo[5.3.1.0^{1,5}]undecan-8-one (36)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2, R_f = 0.20 in petrol-Et₂O 7:3) to afford a white solid. $[\alpha]_D^{27}$ -28.4 (c = 1.0 in CHCl₃) (Scheme 4, using **6** in hexane at 0 °C); Mp 65-67 °C; IR (KBr disc) 2954, 2927, 2867, 1743, 1722, 1367, 1304, 1083 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 2.44–2.39 (1H, m), 2.34–2.28 (1H, m), 2.09-2.02 (1H, m), 1.96-1.89 (3H, m), 1.60–1.54 (1H, m), 1.49–1.43 (1H, m), 1.45 (9H, s), 1.40–1.29 (1H, m), 1.18-1.05 (3H, m), 1.04 (3H, d, J = 7.3 Hz) ; ¹³C NMR (125 MHz, C₆D₆) δ 203.7, 165.6, 95.8, 92.4, 81.8, 49.8, 42.8, 37.1, 35.3, 35.2, 28.4, 28.0, 27.4, 12.8 ; MS (CI+) m/z 298 ($M+NH_4^+$, 12), 281 ($M+H^+$, 4), 242 (100) ; HRMS (ES, $[M+H]^+$) calc. 281.1753, measured 281.1757.

8-Carbo *tert*-butoxy-12-oxatricyclo[5.4.1.0^{1,6}]dodecan-9-one (37)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 10:1, R_f = 0.38 in petrol-Et₂O 1:1) to afford a colourless oil. $[\alpha]_D^{25}$ –8.2 (c = 1.0 in CHCl₃) (Scheme 4, using **6** in hexane at 0 °C); IR (neat) 2933, 1743, 1728, 1368, 1169, 1155, 1080 cm^{–1}; ¹H NMR (500 MHz, CDCl₃) δ 2.55–2.52 (2H, m), 2.39 (1H, dd, J = 14.2 Hz and 8.0 Hz), 2.16–2.12 (1H, m), 2.09 (1H, dd, J = 14.2 Hz and 2.2 Hz), 2.05 (1H, dt, J = 13.8 Hz and 8.3 Hz), 2.02–1.97 (1H, m), 1.80 (1H, ddd, J = 13.6 Hz, 6.8 Hz and 6.7 Hz), 1.78–1.73 (1H, m), 1.69–1.50 (4H, m), 1.51 (9H, s), 1.22–1.17 (2H, m); ¹³C NMR (50 MHz, CDCl₃) δ 204.8, 167.5, 87.4, 82.4, 81.8, 41.2, 40.2, 36.7, 33.5, 32.8, 31.8, 27.9, 23.7, 20.8; MS (CI+) m/z 298 (M+NH₄⁺, 43), 281 (M+H⁺, 8), 242 (100); HRMS (ES, [M+H]⁺) calc. 281.1753, measured 281.1753.

8-Carbo *tert*-butoxy-*endo*-7-methyl-12-oxatricyclo[5.4.1.0^{1,6}]dodecan-9-one (38)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2, R_f = 0.22) to afford a pale–yellow oil. $[\alpha]_D^{24}$ +23.2 (c = 1.0 in CHCl₃) (Scheme 4, using **6** in hexane at 0 °C); IR (neat) 2936, 1740, 1720, 1458 cm^{–1}; ¹H NMR (200 MHz, CDCl₃) δ 2.69–2.54 (1H, m), 2.43–2.26 (2H, m), 2.12–2.0 (1H, m), 2.0–1.88 (2H, m), 1.82–1.74 (1H, m), 1.73–1.57 (5H, m), 1.50 (9H, s), 1.45–1.22 (2H, m), 1.14 (3H, d, J = 7.1 Hz); ¹³C NMR (50 MHz, CDCl₃) δ 203.9, 167.0, 91.1, 82.2,

80.7, 48.6, 47.1, 35.9, 34.4, 31.5, 27.9, 27.5, 19.7, 18.0, 14.5; MS (CI+) m/z 312 ($M+NH_4^+$, 20), 295 ($M+H^+$, 5), 256 (100); HRMS (ES, $[M+H]^+$) calc. 295.1909, measured 295.1906.

7-Carbo *tert*-butoxy-11-oxatricyclo[5.3.1.0^{1,5}]undec-5-en-8-one (39)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2 ; R_f = 0.11) to afford a white solid. $[\alpha]_D^{25}$ +340.0 (c = 1.0 in CHCl₃) (Scheme 6, using **6** in hexane at -15 °C); Mp 65-67 °C; IR (KBr disc) 2974, 2923, 1743, 1720, 1368, 1306, 1158, 1057 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.86 (1H, t, J = 2.0 Hz), 2.89–2.80 (1H, m), 2.52–2.24 (4H, m), 2.16–2.00 (3H, m), 1.97–1.90 (1H, m), 1.77–1.69 (1H, m), 1.50 (9H, s) ; ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 165.1, 157.4, 119.2, 100.2, 96.5, 82.8, 33.0, 32.8, 29.6, 28.0, 26.2, 22.6 ; MS (CI+) m/z 546 (2xM+NH₄⁺, 24), 490 ($M+226$, 7), 282 ($M+NH_4^+$, 46), 265 ($M+H^+$, 10), 226 (100) ; HRMS (ES, $[M+H]^+$) calc. 265.1440, measured 265.1449.

7-Carbo *tert*-butoxy-6-methyl-11-oxatricyclo[5.3.1.0^{1,5}]undec-5-en-8-one (40)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2 ; R_f = 0.13) to afford a white solid. $[\alpha]_D^{27}$ +266.2 (c = 1.0 in CHCl₃) (Scheme 6, using **6** in hexane at 25 °C); Mp 82-83 °C; IR (KBr disc) 2974, 2923, 1743, 1720, 1368, 1306, 1158, 1057 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.81–2.72 (1H, m), 2.61–2.54 (1H, m), 2.40–2.32 (2H, m), 2.21–2.01 (4H, m), 1.97–1.90 (1H, m), 1.81 (3H, s), 1.76–1.72 (1H, m), 1.52 (9H, s) ; ¹³C NMR (100 MHz, CDCl₃) δ 198.6,

164.3, 150.5, 127.7, 101.7, 94.0, 82.7, 33.7, 33.1, 30.4, 28.0, 26.1, 21.1, 11.8 ; MS (CI+) m/z 296 ($M+NH_4^+$, 9), 279 ($M+H^+$, 4), 240 (100), 192 (26), 163 (27), 108 (49) ; HRMS (ES, $[M+H]^+$) calc. 279.1596, measured 279.1595.

8-Carbo *tert*-butoxy-12-oxatricyclo[5.4.1.0^{1,6}]dodec-6-en-9-one (41)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2, R_f = 0.12) to afford a colourless oil. $[\alpha]_D^{25}$ +283.9 (c = 1.0 in CHCl₃) (Scheme 6, using **6** in hexane at 0 °C); IR (neat) 2979, 2937, 2863, 1748, 1732, 1369, 1308, 1161, 1069 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.84 (1H, t, J = 2.6 Hz), 2.74–2.62 (2H, m), 2.41 (1H, ddd, J = 1.9 Hz, J = 7.5 Hz, J = 17.7 Hz), 2.17–2.02 (4H, m), 1.89–1.82 (3H, m), 1.50 (9H, s), 1.41–1.30 (2H, m) ; ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 165.2, 148.6, 120.5, 92.9, 86.6, 82.7, 36.4, 32.8, 29.3, 28.0, 26.4, 25.5, 22.9 ; MS (CI+) m/z 574 ($2^*M+NH_4^+$, 5), 518 ($M+240$, 5), 296 ($M+NH_4^+$, 32), 279 ($M+H^+$, 8), 240 (100) 223 (6), 183 (4) ; HRMS (ES, $[M+H]^+$) calc. 279.1596, measured 279.1592.

8-Carbo *tert*-butoxy-7-methyl-12-oxatricyclo[5.4.1.0^{1,6}]dodec-6-en-9-one (42)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 8:2) to afford a pale–yellow oil. $[\alpha]_D^{24}$ +231.2 (c = 1.0 in CHCl₃) (Scheme 6, using **6** in hexane at 0 °C); IR (neat) 2970, 2936, 1740, 1450 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 2.63–2.45 (3H, m), 2.16–2.0 (3H, m), 1.94–1.81 (3H, m), 1.77 (3H, s), 1.65 (1H, m), 1.52 (9H, s), 1.49–1.12 (2H, m); ¹³C NMR (50 MHz,

CDCl₃) δ 199.1, 164.7, 141.2, 128.0, 94.5, 85.2, 83.7, 36.5, 33.3, 30.4, 28.0, 25.2, 24.3, 23.1, 10.1; MS (CI⁺) m/z 254 (100), 237 (60), 180 (43), 163 (28), 148 (91), 131 (14) ; HRMS (CI⁺, [M+NH₄]⁺) calc. 310.2018, measured 310.2004.

8-Oxo-11-oxatricyclo[5.3.1.0^{1,5}]undecan-6, 7-dicarboxylic acid 7-*tert*-butyl ester 6-methyl ester (43)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 7:3, R_f = 0.20) to afford a white solid. $[\alpha]_D^{24}$ -11.4 (c = 1.0 in CHCl₃) (Scheme 5, using **6** in hexane at 0 °C); Mp 53-54 °C; IR (KBr disc) 2975, 2951, 2873, 1750, 1438, 1368, 1264, 1167, 1083, 840 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.69 (3H, s), 2.98 (1H, d, J = 7.5 Hz), 2.98-2.89 (1H, m), 2.59 (1H, ddd, J = 17.2 Hz, 7.6 Hz and 1.0 Hz), 2.48-2.39 (1H, m), 2.11-2.05 (1H, m), 1.98-1.82 (3H, m), 1.74-1.48 (2H, m), 1.46 (9H, s), 1.50-1.42 (1H, m); ¹³C NMR (100 MHz; CDCl₃) δ 200.8, 171.9, 165.9, 93.9, 91.9, 83.0, 59.5, 52.1, 50.4, 36.7, 35.7, 34.1, 33.0, 27.8, 24.7; MS (CI⁺) m/z 342 (M+NH₄⁺, 58), 325 (M+H⁺, 3), 286 (100), 166 (13); HRMS (EI, M⁺) calc. 324.1567, measured 324.1574.

9-Oxo-12-oxatricyclo[6.3.1.0^{1,6}]dodecan-7, 8-dicarboxylic acid 8-*tert*-butyl ester 7-methyl ester (44)

General procedure as for **35**. The residue was purified by flash chromatography (SiO₂, petrol-Et₂O 7:3, R_f = 0.20) to afford a white solid. $[\alpha]_D^{24}$ -7.4 (c = 1.0 in CHCl₃) (Scheme 5, using **6** in hexane at 0 °C); Mp 87-88 °C; IR (KBr disc) 2951, 2871, 1746, 1458, 1442, 1367, 1263, 1170, 1087, 841 cm⁻¹; ¹H NMR

(400 MHz; CDCl₃) δ 3.68 (3H, s), 3.12 (1H, d, J = 6.1 Hz), 2.81 (1H, dt, J = 17.2 Hz and 8.9 Hz), 2.55 (1H, dt, J = 17.2 Hz and 5.7 Hz), 2.41-2.36 (1H, m), 2.05 (2H, dd, J = 8.9 Hz and 5.8 Hz), 2.00-1.94 (1H, m), 1.88-1.83 (1H, m), 1.69-1.49 (3H, m), 1.48 (9H, s), 1.46-1.31 (3H, m); ¹³C NMR (100 MHz; CDCl₃) δ 202.0, 172.0, 166.1, 89.3, 83.0, 82.4, 57.7, 52.2, 45.9, 36.4, 33.9, 31.6, 28.2, 27.9, 19.5, 17.9; MS (CI+) m/z 356 (M+NH₄⁺, 58), 339 (M+H⁺, 4), 300 (100); HRMS (EI, M⁺) calc. 338.1724, measured 338.1723.

***tert*-Butyl decahydro-1H-7-carboxy-3a,7-epoxy-5-oxaazulene-one (48a)**

To a stirred, degassed solution of *tert*-Butyl 2-oxo-6-heptenyl diazomalonate **47** (150 mg, 0.51 mmol) in dry CH₂Cl₂ was added Rh₂(*R*-BNP)₄ (8.0 mg, 0.005 mmol). The reaction mixture was put in an oil bath preheated at 55 °C. When the reaction was complete (TLC monitoring), the solvent was removed in vacuo and the residue purified by flash column chromatography (petrol-AcOEt 5:1, R_f = 0.20) to afford a white solid (33 mg, 24%). [α]_D²⁷ +5.1 (c = 0.018 in CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 4.67 (1H, d, J = 10.4 Hz), 4.14 (1H, d, J = 10.6 Hz), 2.73-2.68 (2H, m), 2.10-1.92 (4H, m), 1.77-1.67 (1H, m), 1.59 (1H, bs), 1.52 (10H, s); ¹³C NMR (100 MHz; CDCl₃) δ 166.6, 164.8, 91.0, 87.5, 83.4, 42.9, 42.2, 33.2, 32.4, 27.8, 24.9; MS (CI+) m/z 286 (M+NH₄⁺, 42), 269 (M+H⁺, 9), 230 (100); HRMS (ES, [M+NH₄]⁺) calc. 286.1649, measured 286.1649.

5,5-Dimethyl-2-oxo-tetrahydrofuran-3-carboxylic acid 2-oxo-hept-6-enyl ester (48b)

To a stirred, degassed solution of *tert*-Butyl 2-oxo-6-heptenyl diazomalonate **47** (150 mg, 0.51 mmol) in dry CH₂Cl₂ was added Rh₂(*R*-BNP)₄ (8.0 mg, 0.005 mmol). The reaction mixture was put in an oil bath preheated at 55 °C. When the reaction was complete (TLC monitoring), the solvent was removed in vacuo and the residue purified by flash column chromatography (petrol-AcOEt 5:1, R_f = 0.02) to afford

a light yellow oil (35 mg, 25%). IR (neat) 3461, 2979, 1775, 1731, 1642, 1373 cm^{-1} ; ^1H NMR (400 MHz; CDCl_3) δ 5.79-5.69 (1H, m), 5.04-4.97 (2H, m), 4.81 (1H, d, $J = 16.7$ Hz), 4.71 (1H, d, $J = 16.7$ Hz), 3.88 (1H, t, $J = 9.7$ Hz), 2.58 (1H, dd, $J = 13.1$ Hz and 9.6 Hz), 2.46-2.38 (3H, m), 2.07 (2H, q, $J = 6.9$ Hz), 1.71 (2H, quint, $J = 7.3$ Hz), 1.53 (3H, s), 1.43 (3H, s); ^{13}C NMR (100 MHz; CDCl_3) δ 202.8, 170.8, 167.4, 137.5, 115.6, 84.0, 68.9, 47.4, 38.5, 37.7, 32.8, 28.3, 27.7, 22.1; MS (CI+) m/z 286 ($\text{M}+\text{NH}_4^+$, 100), 269 ($\text{M}+\text{H}^+$, 4), 132 (12); HRMS (ES, $[\text{M}+\text{NH}_4]^+$) calc. 286.1649, measured 286.1652.

Hydrogenation reactions on cycloadducts

7-Carbo *tert*-butoxy -11-oxatricyclo[5.3.1.0^{1,5}]undecan-8-one (3)

Pd/C (6.5 g, 10% w/w) was added to a solution of 7-carbo *tert*-butoxy-11-oxatricyclo[5.3.1.0^{1,5}]undec-5-en-8-one **39** (61.6 mg, 0.23 mmol, obtained from **29** using **6** in hexane at 25 °C) in dry hexane (7 mL), in a 25 mL-conical flask. The reaction mixture was degassed (10-15 min) by bubbling argon through it. The flask was purged with H_2 (vacuum / hydrogen flow, 4 times) and the mixture was stirred vigorously for 30 min (TLC monitoring) under H_2 (1 atm). The reaction mixture was filtered on a short path of silica and the filtrate concentrated *in vacuo*. The crude 7-carbo *tert*-butoxy-11-oxatricyclo[5.3.1.0^{1,5}]undecan-8-one **C1** was obtained pure by ^1H N.M.R. (petrol- Et_2O 7:3; $R_f = 0.24$) (59.0 mg, 95%). $[\alpha]_{\text{D}}^{27} +9.9$ ($c = 1.0$ in CHCl_3); ee = 80%; IR (neat) 2956, 1744, 1724, 1369, 1320, 1151, 1137, 1066 cm^{-1} ; ^1H NMR (500 MHz; CDCl_3) δ 2.59–2.47 (4H, m), 2.44 (1H, app. dt, $J = 12.9$ Hz and 8.5 Hz), 2.18–2.10 (1H, m), 2.02-1.83 (4H, m), 1.72–1.67 (1H, m), 1.57–1.50 (2H, m), 1.50 (9H, s); ^{13}C NMR (100 MHz; CDCl_3) δ 205.2, 167.1, 93.8, 91.5, 82.5, 45.1, 41.7, 36.7, 34.3, 33.6, 27.9, 25.1;

MS (CI⁺) m/z 284 (M+NH₄⁺, 20), 267 (M+H⁺, 4), 242 (3), 228 (100), 96 (12); HRMS (ES, [M+NH₄]⁺)
calc. 284.1862, measured 284.1858.

7-Carbo *tert*-butoxy-*exo*-6-methyl-11-oxatricyclo[5.3.1.0^{1,5}]undecan-8-one (36)

Pd/C (6.5 g, 10% w/w) was added to a solution of 7-carbo *tert*-butoxy-6-methyl-11-oxatricyclo[5.3.1.0^{1,5}]undec-5-en-8-one **40** (64.6 mg, 0.23 mmol, obtained from **30** using **6** in hexane at 25 °C) in dry hexane (7 mL), in a 25 mL-conical flask. The reaction mixture was degassed (10-15 min) by bubbling argon through it. The flask was purged with H₂ (vacuum / hydrogen flow, 4 times) and the mixture was stirred vigorously for 24 h (TLC monitoring) under H₂ (1 atm). The reaction mixture was filtered on a short path of silica and the filtrate concentrated *in vacuo*. The crude 7-carbo *tert*-butoxy-*exo*-6-methyl-11-oxatricyclo[5.3.1.0^{1,5}]undecan-8-one **36** was purified by flash silica gel chromatography (petrol-Et₂O 8:2; R_f = 0.20 in petrol-Et₂O 7:3) to afford a white solid (48.5 mg, 75%). [α]_D²⁷ −15.3 (c = 1.0 in CHCl₃); ee = 63% ; Characterisation : same as for **36** above.

Key nOes for cycloadduct (36)

Chiral GC Conditions

All cycloadducts were resolved using a Chirasil Dex-CD capillary column.

Cycloadduct	Elution conditions (°C)	Flow (cm ³ min ⁻¹)	Retention Times (min)
(+)-3	140 (isotherm)	0.5	32.5 35.0
(+)-35	140 (isotherm)	0.5	28.0 29.9
(-)-36	170 (isotherm)	0.5	28.5 30.2
(+)-37	140 (isotherm)	0.5	65.6 69.1
(+)-38	140 (isotherm)	0.5	55.8 60.5
(+)-39	80 °C / 1 min / 5 °C.min ⁻¹ / 170 °C/ 100 min	0.5	27.2 27.9

<p>(+)-40</p>	80 °C / 1 min / 5 °C.min ⁻¹ / 170 °C/ 100 min	0.5	26.6 27.6
<p>(+)-41</p>	80 °C / 1 min / 5 °C.min ⁻¹ / 170 °C/ 100 min	0.5	33.8 34.7
<p>(+)-42</p>	80 °C / 1 min / 5 °C.min ⁻¹ / 170 °C/ 100 min	0.5	32.7 34.5
<p>(-)-43</p>	140 (isotherm)	1.0	114.7 118.6
<p>(-)-44</p>	155 (isotherm)	1.0	73.9 76.6
<p>(+)-48</p>	160 (isotherm)	1.0	23.3 24.3

Supporting information for

On the Scope of Catalytic Enantioselective Tandem Carbonyl Ylide Formation - Intramolecular [3+2] Cycloadditions

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All new compounds described were fully characterised by ^1H NMR, ^{13}C NMR, IR and mass spectroscopy.

^1H and ^{13}C NMR spectra for previously unreported 2-diazo-3,6-diketoesters (**25-47**) and cycloadducts (**35-48**) are included in the following pages. All spectra were recorded in CDCl_3 , except for compounds **33** and **34**, which were recorded in C_6D_6 . APT ^{13}C spectra have CH_3 and CH signals above the baseline and CH_2 and quaternary C below the baseline.