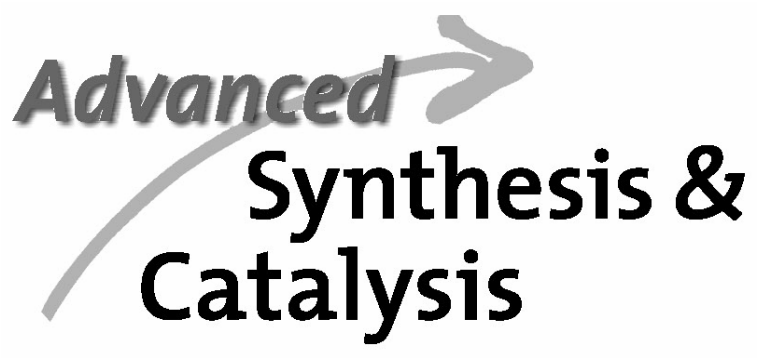


Supporting Information

# A New Method for Constructing Quaternary Carbon Centres: Tandem Rhodium-Catalysed 1,4-Addition/Intramolecular Cyclization.

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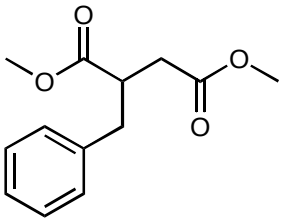
## Supporting Information

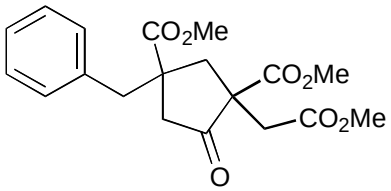
### Characterisation of products

**Dimethyl 2-benzylsuccinate (3):**[1]



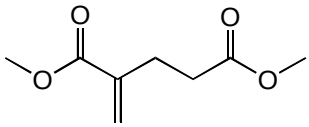
The reaction was performed following the general procedure with TMSCl on 1 mmol scale. After purification, the 1,1'-alkene (**3**) was obtained as a white solid (222 mg, 94% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.24-7.03 (m, 5 H), 3.59 (s, 3 H), 3.56 (s, 3 H), 3.11-2.94 (m, 2 H), 2.70-2.55 (m, 2 H), 2.32 (dd, *J* = 16.9, 4.8 Hz, 1 H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.4, 172.0, 137.9, 128.7, 128.3, 126.4, 51.6, 51.5, 42.9, 37.5, 34.6; **MS** (EI): *m/z* 236 ([$M^+$], 5), 176 (50), 163 (25), 145 (25), 131 (50), 117 (95), 115 (40), 103 (15), 91 (100), 77 (15), 65 (35), 59 (25); **HRMS** (EI): calculated for $C_{13}H_{16}O_4$ $[M+H]^+$ 237.1121, found 237.1122.

**Dimethyl 1-benzyl-3-(2-methoxy-2-oxoethyl)-4-oxocyclopentane-1,3-dicarboxylate (4):**



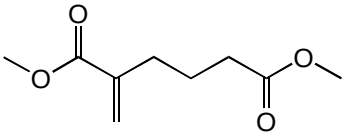

The reaction was performed following the general procedure without TMSCl on 0.5 mmol scale. After purification, the cyclic ketone (**4**) was obtained as a pale yellow oil (10.1 mg, 10% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.28-7.13 (m, 3 H), 7.11-6.98 (m, 2 H), 3.69 (s, 3 H), 3.68 (s, 3 H), 3.66 (s, 3 H), 3.55-3.32 (m, 1 H), 3.21-2.76 (m, 5 H), 2.61-2.36 (m, 2 H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 209.0, 175.7, 170.8, 170.1, 136.3, 129.4, 128.2, 126.9, 58.0, 52.6, 52.0, 51.7, 48.9, 46.2, 44.2, 41.0, 37.1; **MS** (EI): *m/z* 362 ([$M^+$], 3), 330 (5), 271 (10), 204 (10), 176 (20), 144 (10), 127 (20), 117 (20), 116 (25), 115 (30), 91 (100), 77 (10), 65 (15), 59 (30).

**Dimethyl 2-methylenepentanedioate (8):**[2]




The reaction was performed following either the method **A** on 5 mmol scale, or the method **B** on 20 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-alkene (**8**) was obtained as a colourless oil (Method **A**: 362 mg, 42% yield; Method **B**: 992 mg, 29% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 6.12 (br s, 1H), 5.53 (br s, 1H), 3.70 (s, 3H), 3.60 (s, 3H), 2.63-2.51 (m, 2H), 2.50-2.39 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.9, 166.9, 138.6, 125.8, 51.7, 51.4, 32.7, 27.2. **MS** (EI): *m/z* 172 ([$M^+$], 1), 140 (20), 112 (40), 81 (20), 71 (10), 59 (100), 53 (80); **HRMS** (EI): calculated for $C_8H_{12}O_4$ $[M+H]^+$ 173.0808, found 173.0810.

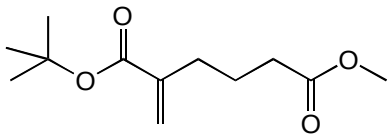
**Dimethyl 2-methylenehexanedioate (9):**[3]




The reaction was performed following either the method **A** on 50 mmol scale, or the method **B** on 20 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-

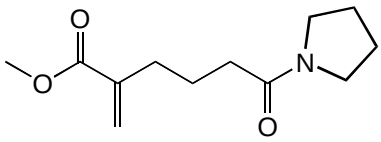
alkene (**9**) was obtained as a colourless oil (Method **A**: 4.7 g, 50% yield; Method **B**: 710 mg, 25% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.13 (br s, 1H), 5.50 (br s, 1H), 3.71 (s, 3H), 3.61 (s, 3H), 2.28 (t, *J* = 6.9 Hz, 4H), 1.77 (quintet, *J* = 6.9 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 173.6, 167.3, 139.5, 125.2, 51.7, 51.3, 33.2, 31.1, 23.4; **MS** (EI): *m/z* 186 ([$M^+$], 1), 154 (90), 126 (100), 111 (50), 95 (75), 84 (60), 74 (25), 67 (80), 59 (80), 55 (55); **HRMS** (EI): calculated for $C_9H_{14}O_4$ $[M+NH_4]^+$ 204.1230, found 204.1231.

**1-*tert*-Butyl 6-methyl 2-methylenehexanedioate (10):**



The reaction was performed following the method **A** on 17 mmol scale. After purification, the 1,1'-alkene (**10**) was obtained as a colourless oil (1.7 g, 43% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.00 (br s, 1H), 5.40 (br s, 1H), 3.60 (s, 3H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.23 (t, *J* = 7.5 Hz, 2H), 1.74 (quintet, *J* = 7.5 Hz, 2H), 1.42 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 173.8, 166.2, 141.3, 124.2, 80.5, 51.8, 51.4, 33.4, 31.2, 28.8, 28.4, 28.0, 23.6; **MS** (EI): *m/z* 228 ([$M^+$], 10), 172 (10), 154 (15), 141 (10), 123 (10), 95 (10), 67 (10), 57 (100); **HRMS** (EI): calculated for $C_{12}H_{20}O_4$ $[M+NH_4]^+$ 246.1700, found 246.1700.

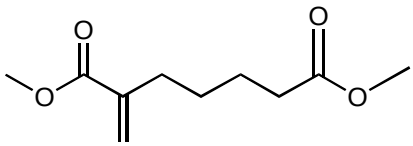
**Methyl 2-methylene-6-oxo-6-(pyrrolidin-1-yl)hexanoate (11):**



The reaction was performed following the method **A** on 50 mmol scale. After purification by flash column chromatography eluting ethyl acetate/petroleum ether (2/1), the 1,1'-alkene (**11**) was obtained as a colourless oil (6.6 g, 59% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.14 (br s, 1H), 5.56 (br s, 1H), 3.72 (s, 3H), 3.43 (t, *J* = 6.9 Hz, 2H), 3.37 (t, *J* = 6.9 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.92 (app t, *J* = 6.6 Hz, 2H), 1.89-1.69 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.0, 167.6, 140.0, 125.0, 51.7, 46.4, 45.5, 33.9, 31.3, 26.0, 24.3, 23.3; **MS** (EI): *m/z* 225

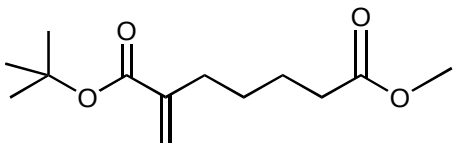
([$M^+$], 10), 225 (10), 194 (10), 166 (10), 126 (10), 113 (100), 98 (30), 70 (60), 55 (40); **HRMS** (EI): calculated for $C_{12}H_{19}NO_3$ $[M+H]^+$ 226.1438, found 226.1437.

**Dimethyl 2-methyleneheptanedioate (12):**[4]



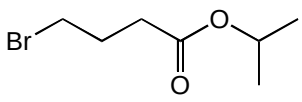
The reaction was performed following the method **A** on 25 mmol scale. After purification, the 1,1'-alkene (**12**) was obtained as a colourless oil (1.9 g, 38% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.14 (br s, 1H), 5.54 (br s, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 2.33 (t, *J* = 7.8 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.65 (quintet, *J* = 7.8 Hz, 2H), 1.49 (quintet, *J* = 7.8 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.0, 167.6, 140.1, 124.9, 51.8, 51.5, 33.8, 31.5, 27.7, 24.4; **MS** (EI): *m/z* 200 ([$M^+$], 10), 200 ([M]$^+$ <1), 169 (10), 140 (20), 136 (10), 127 (10), 108 (30), 98 (10), 95 (30), 81 (80), 74 (20), 67 (50), 59 (100), 55 (30); **HRMS** (EI): calculated for $C_{10}H_{16}O_4$ $[M+NH_4]^+$ 218.1387, found 218.1389.

**1-*tert*-Butyl 7-methyl 2-methyleneheptanedioate (13):**



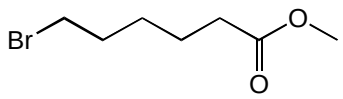
The reaction was performed following the method **A** on 25 mmol scale. After purification, the 1,1'-alkene (**13**) was obtained as a colourless oil (2.3 g, 36% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.02 (br s, 1H,), 5.42 (br s, 1H,), 3.64 (s, 3H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.64 (quintet, *J* = 7.5 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.47 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 173.9, 166.4, 141.9, 123.6, 80.4, 51.4, 33.8, 31.5, 28.0, 27.9, 24.5; **MS** (EI): *m/z* 242 ([$M^+$], 10), 168 (10), 155 (10), 140 (10), 109 (10), 81 (20), 67 (20), 57 (100); **HRMS** (EI): calculated for $C_{13}H_{22}O_4$ $[M+H]^+$ 243.1591, found 243.1593.

**Isopropyl 4-bromobutanoate (15a):**[5]



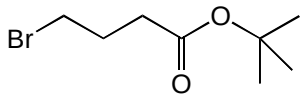
The esterification of 4-bromobutyric acid was performed following classical experimental procedure. 4-bromobutyric acid (4.18 g, 25 mmol) was stirred at room temperature for 48 h in dry isopropanol (25 mL) in the presence of a catalytic amount of concentrated sulfuric acid (0.1 mL). After evaporation of the solvent, the crude was extracted with ethyl acetate, washed twice with a saturated sodium hydrogenocarbonate solution, then with water and finally with brine. The solution was dried over $MgSO_4$, filtered and evaporated under vacuum to afford the isopropyl 4-bromobutanoate (**15a**) (3.55 g, 68% yield) as colourless oil which was use without any further purification. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.98 (heptet, *J* = 6.0 Hz, 1H), 3.40 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 6.9 Hz, 2H), 2.10 (quintet, *J* = 6.9 Hz, 2H), 1.15 (d, *J* = 6.0 Hz, 6H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.9, 67.8, 32.8, 27.8, 21.7.

**Methyl 6-bromohexanoate (15b):**[6]




The reaction was performed following the procedure described above with 6-bromohexanoic acid (9.75 g, 50 mmol) in 50 mL of dry methanol. Methyl 6-bromohexanoate (**15b**) (8.59 g, 82 % yield) was then obtained as a colourless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.65, (s, 3H), 3.39 (t, *J* = 6.0 Hz, 2H), 2.30 (t, *J* = 6.9 Hz, 2H), 2.85 (quintet, *J* = 6.7 Hz, 2H), 2.60 (quintet, *J* = 6.7 Hz, 2H), 2.45 (quintet, *J* = 6.7 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 173.8, 51.4, 33.7, 33.3, 32.6, 27.5, 23.9.

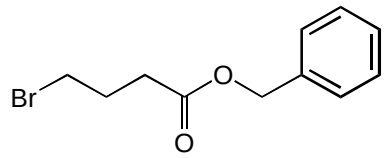
***tert*-Butyl 4-bromobutanoate (15c):**[7]




Concentrated sulfuric acid (0.2 mL) was added to a solution of 4-bromobutyric acid (3.34 g, 20 mmol), *tert*-butanol (9.2 mL, 0.1 mol), magnesium sulfate (9.6 g, 80 mmol) in dry dichloromethane (80 mL). The reaction mixture was vigorously stirred for 48 h at room temperature. The reaction was then quenched with a saturated sodium bicarbonate solution. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated to dryness. The crude was then purified by column chromatography using dichloromethane as eluent to afford *tert*-butyl 4-bromobutanoate (**15c**) (1.3 g, 30% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.40 (t, *J* =

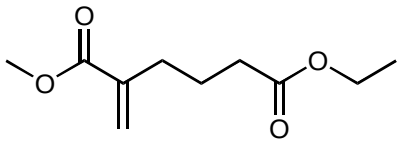
6.7 Hz, 2H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.10 (quintet, *J* = 6.7 Hz, 2H), 1.35 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.8, 80.4, 33.6, 32.6, 27.9, 27.8.

**Benzyl 4-bromobutanoate (15d):**[8]



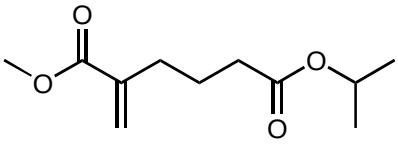

The reaction was performed following the procedure described above using 4-bromobutyric acid (3.34 g, 20 mmol), concentrated sulfuric acid (0.2 mL), magnesium sulfate (9.6 g, 80 mmol) and benzyl alcohol (10.4 mL, 0.1 mol) in 80 mL of dry dichloromethane. After purification by column chromatography ($CH_2Cl_2$), benzyl 4-bromobutanoate (**15d**) (4.89 g, 95% yield) was obtained as a colourless oil. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.46-7.30 (m, 5H), 5.14 (s, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.20 (quintet, *J* = 7.0 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.2, 135.7, 128.5, 128.3, 128.2, 66.3, 32.6, 32.4, 27.6.

**6-Ethyl 1-methyl 2-methylenehexanedioate (17):**



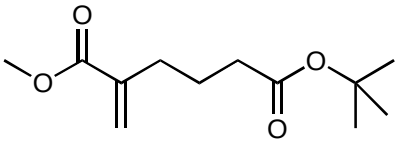

The reaction was performed following the method **B** on 5 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-alkene (**17**) was obtained as a colourless oil (264 mg, 26% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 6.13 (br s, 1H), 5.51 (br s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 2.29 (t, *J* = 6.9 Hz, 4H), 1.79 (quintet, *J* = 6.9 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 173.2, 167.3, 139.5, 125.3, 60.2, 51.7, 33.4, 31.1, 23.4, 14.1; **MS** (EI): *m/z* 200 ([$M^+$], 1), 168 (15), 155 (20), 154 (20), 140 (25), 126 (30), 112 (20), 95 (30), 81 (10), 67 (40), 59 (100); **HRMS** (EI): calculated for $C_{10}H_{16}O_4$ $[M+H]^+$ 201.1121, found 201.1122.

**6-Isopropyl 1-methyl 2-methylenehexanedioate (18):**



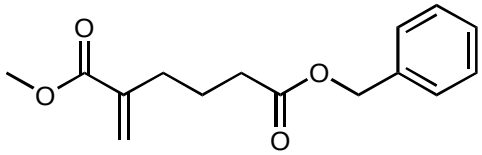
The reaction was performed following the method **B** on 5 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-alkene (**18**) was obtained as a colourless oil (310 mg, 29% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.12 (br s, 1H), 5.50 (br s, 1H), 4.93 (heptet, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 2.30 (t, *J* = 6.0 Hz, 2H), 2.21 (t, *J* = 6.9 Hz, 2H), 1.73 (quintet, *J* = 6.9 Hz, 2H), 1.14 (d, *J* = 6.0 Hz, 6H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.8, 167.4, 139.7, 125.4, 67.6, 51.8, 33.9, 31.2, 23.6, 21.8; **MS** (EI): *m/z* 214 ([$M^+$], 1), 155 (10), 154 (10), 140 (10), 126 (10), 112 (10), 95 (15), 67 (25), 59 (100); **HRMS** (EI): calculated for $C_{11}H_{18}O_4$ $[M+H]^+$ 215.1278, found 215.1279.

**6-*tert*-Butyl 1-methyl 2-methylenehexanedioate (19):**



The reaction was performed following the method **B** on 2 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-alkene (**19**) was obtained as a colourless oil (222 mg, 48% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.12 (br s, 1H), 5.50 (br s, 1H), 3.70 (s, 3H), 2.25 (t, *J* = 6.7 Hz, 2H), 2.15 (t, *J* = 7.1 Hz, 2H), 1.70 (quintet, *J* = 7.1 Hz, 2H), 1.37 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.7, 167.5, 139.8, 125.3, 80.1, 51.8, 34.8, 31.1, 28.1, 23.7; **MS** (EI): *m/z* 228 ([$M^+$], 1), 155 (15), 154 (10), 123 (15), 112 (10), 95 (10), 67 (20), 59 (60), 57 (100); **HRMS** (EI): calculated for $C_{12}H_{20}O_4$ $[M+H]^+$ 229.1434, found 229.1435.

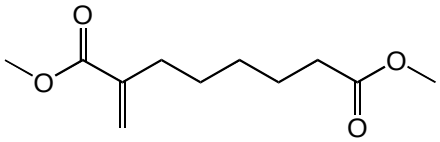
**6-Benzyl 1-methyl 2-methylenehexanedioate (20):**



The reaction was performed following the method **B** on 10 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-alkene (**20**) was obtained as a colourless oil (1.29 g, 49% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.40-7.24 (m, 5H),

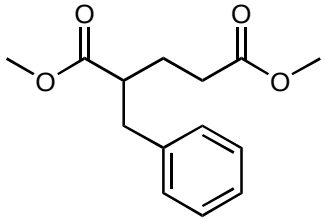
6.11 (br s, 1H), 5.48 (br s, 1H), 5.06 (s, 2H), 3.68 (s, 3H), 2.35-2.20 (m, 4H), 1.73 (quintet, $J$ = 6.9 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 173.0, 167.3, 139.4, 135.9, 128.4, 128.3, 128.2, 128.1, 125.4, 66.1, 51.7, 33.4, 31.1, 23.4; **MS** (EI): *m/z* 262 ([$M^+$], 1), 155 (10), 124 (10), 107 (10), 91 (100), 77 (15), 65 (20), 59 (15), 51 (10); **HRMS** (EI): calculated for $C_{15}H_{18}O_4$ $[M+H]^+$ 263.1278, found 263.1279.

**Dimethyl 2-methyleneoctanedioate (21):**



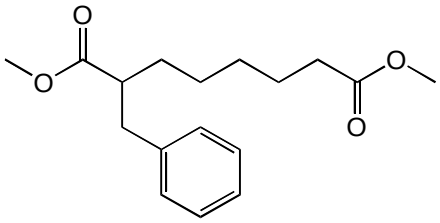
The reaction was performed following the method **B** on 5 mmol of trimethyl phosphonoacetate. After purification, the 1,1'-alkene (**21**) was obtained as a colourless oil (271 mg, 24% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 6.12 (br s, 1H), 5.50 (br s, 1H), 3.71 (s, 3H), 3.62 (s, 3H), 2.29-2.19 (m, 4H), 1.60 (quintet, $J$ = 6.9 Hz, 2H), 1.40 (quintet, $J$ = 6.9 Hz, 2H), 1.27 (quintet, $J$ = 6.9 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.1, 167.7, 140.5, 124.6, 51.7, 51.4, 33.9, 31.6, 28.6, 28.0, 24.6; **MS** (EI): *m/z* 214 ([$M^+$], 1), 154 (20), 150 (30), 122 (30), 109 (10), 95 (35), 81 (25), 74 (10), 67 (30), 59 (100); **HRMS** (EI): calculated for $C_{11}H_{18}O_4$ $[M+NH_4]^+$ 232.1543, found 232.1542.

**Dimethyl 2-benzylpentanedioate (22a):[9]**



The reaction was performed following the general procedure on 0.5 mmol of 1,1'-alkene. After purification, the 1,4-addition product (**22a**) was obtained as a pale yellow oil (116 mg, 93% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.14-6.92 (m, 5H), 3.45 (s, 3H), 3.40 (s, 3H), 2.81-2.70 (m, 1H), 2.60-2.47 (m, 2H), 2.21-2.05 (m, 2H), 1.81-1.62 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 175.1, 173.1, 138.6, 128.7, 128.3, 126.4, 51.5, 46.5, 38.2, 31.6, 26.6; **MS** (EI): m/z 250 ([$M^+$], 5), 190 (60), 187 (25), 159 (20), 131(30), 130 (100), 117 (60), 115 (20), 103 (10), 91 (95), 77 (10), 65 (25), 59 (15); **HRMS** (EI): calculated for $C_{17}H_{24}O_4$ $[M+NH_4]^+$ 268.1543, found 268.1541.

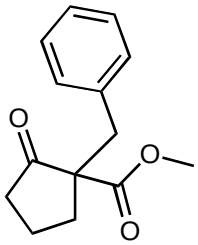
**Dimethyl 2-benzyloctanedioate (25a):**



The reaction was performed following the general procedure on 0.5 mmol of 1,1'-alkene. After purification, the 1,4-addition product (**25a**) was obtained as a colourless oil (132 mg, 90% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.18-6.95 (m, 5H), 3.51 (s, 3H), 3.44 (s, 3H), 2.81-2.75 (m, 1H), 2.60-2.40 (m, 2H), 2.12 (t, *J* = 6.9 Hz, 2H), 1.59-1.30 (m, 4H), 1.22-1.08 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 176.0, 174.1, 139.3, 128.7, 128.3, 126.3, 51.4, 51.3, 38.5, 33.9, 31.8, 28.9, 28.0, 27.0, 24.7; **MS** (EI): *m/z* 292 ([$M^+$], 3), 232 (20), 200 (10), 131 (25), 117 (30), 104 (20), 91 (100), 77 (10), 65 (15), 59 (35); **HRMS** (EI): calculated for $C_{17}H_{24}O_4$ $[M+NH_4]^+$ 310.2013, found 310.2014.

**Reaction using dimethyl 2-methylenehexanedioate (9) (93 mg, 0.5 mmol) as starting 1,1'-alkene:**

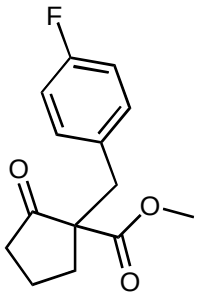
**Methyl 1-benzyl-2-oxocyclopentanecarboxylate (23a):[10]**



The reaction was performed following the general procedure. After purification, the cyclic product (**23a**) was obtained as a colourless oil (89 mg, 77% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.23-7.11 (m, 3H), 7.08-6.99 (m, 2H), 3.64 (s, 3H), 3.14, 3.02 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.41-2.22 (m, 2H), 2.0 (t, 1H, *J* = 6.7 Hz), 1.95-1.72 (m, 2H), 1.60-1.45 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 214.8, 171.3, 136.4, 130.0, 128.7, 128.3, 126.8, 61.4, 52.6, 39.0, 38.3, 31.6, 19.4; **MS** (EI): *m/z* 232 ([$M^+$], 15), 214 (20), 173 (30), 172 (25), 155 (15), 145 (30), 144 (25), 131 (20), 130 (55),

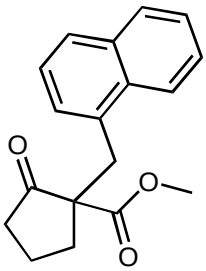
129 (35), 128 (20), 117 (50), 116 (40), 115 (70), 91 (100), 77 (25), 65 (50), 59 (30); **HRMS** (EI): calculated for $C_{14}H_{16}O_3$ $[M+NH_4]^+$ 250.1438, found 250.1439.

**Methyl 1-(4-fluorobenzyl)-2-oxocyclopentanecarboxylate (23b):**[11]




The reaction was performed following the general procedure. After purification, the cyclic product (**23b**) was obtained as a colourless oil (113 mg, 90% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.11-7.02 (m, 2H), 6.92 (tm, *J* = 9.0 Hz, 2H), 3.68 (s, 3H), 3.10, 3.00 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.45-2.30 (m, 2H), 2.11-1.80 (m, 3H), 1.66-1.55 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.5, 172.1, 162.7 (d, *J* = 245.4 Hz), 133.1 (d, *J* = 3.0 Hz), 132.5 (d, *J* = 6.8 Hz), 116.1 (d, *J* = 21.1 Hz), 61.4, 52.7, 38.3, 38.2, 31.7, 19.4; **MS** (EI): *m/z* 250 ($[M^+]$, 15), 222 (10), 191 (20), 190 (15), 189 (10), 163 (10), 149 (10), 148 (40), 147 (20), 146 (10), 135 (30), 134 (25), 133 (50), 115 (20), 110 (10), 109 (100), 96 (10), 84 (10), 83 (20), 59 (10); **HRMS** (EI): calculated for $C_{15}H_{14}FO_3$ $[M+NH_4]^+$ 268.1343, found 268.1345.

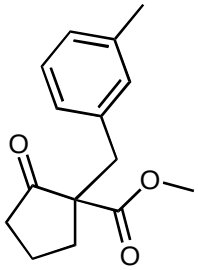
**Methyl 1-( naphthalen-1-ylmethyl)-2-oxocyclopentanecarboxylate (23c):**




The reaction was performed following the general procedure. After purification, the cyclic product (**23c**) was obtained as a colourless oil (123 mg, 87% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.42 (quintet x m, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 8.4 Hz, 1H), 7.19 (d, , *J* = 8.4 Hz, 1H), 3.79, 3.50 (2 x d(AB), *J* = 14.0 Hz, 2H), 3.65 (s, 3H), 2.40-2.21 (m, 2H), 1.90-1.59 (m, 3H), 1.44-1.34 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.2, 171.8,

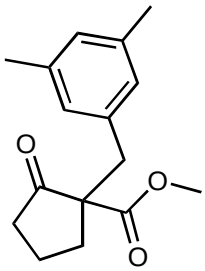
133.7, 133.0, 132.9, 128.7, 128.4, 128.0, 127.6, 126.0, 125.3, 124.0, 61.8, 52.7, 38.1, 33.3, 32.1, 19.4; **MS** (EI): *m/z* 282 ([$M^+$], 10), 205 (15), 165 (40), 152 (20), 141 (100), 128 (30), 115 (35), 59 (20); **HRMS** (EI): calculated for $C_{18}H_{18}O_3$ $[M+NH_4]^+$ 300.1594, found 300.1595.

**Methyl 1-(3-methylbenzyl)-2-oxocyclopentanecarboxylate (23d):**[12]




The reaction was performed following the general procedure. After purification, the cyclic product (**23d**) was obtained as a colourless oil (113 mg, 92% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.11-7.04 (m, 1H), 6.99-6.92 (m, 1H), 6.89-6.80 (m, 2H), 3.65 (s, 3H), 3.10, 2.99 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.40-2.20 (m, 2H), 2.23 (s, 3H), 2.03-1.72 (m, 3H), 1.61-1.48 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 214.9, 171.4, 137.9, 136.4, 130.9, 128.3, 127.6, 127.1, 61.5, 52.6, 39.0, 38.4, 31.6, 21.4, 19.4; **MS** (EI): *m/z* 246 ([$M^+$], 10), 228 (50), 187 (35), 186 (20), 171 (55), 169 (20), 159 (35), 158 (25), 145 (20), 144 (45), 143 (35), 131 (50), 130 (45), 129 (60), 128 (45), 127 (20), 116 (35), 115 (70), 106 (15), 105 (100), 92 (20), 91 (50), 77 (30), 59 (20); **HRMS** (EI): calculated for $C_{15}H_{18}O_3$ $[M+NH_4]^+$ 264.1594, found 264.1593.

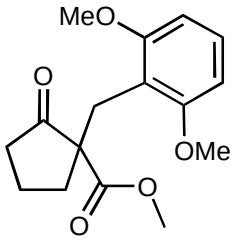
**Methyl 1-(3,5-dimethylbenzyl)-2-oxocyclopentanecarboxylate (23e):**




The reaction was performed following the general procedure. After purification, the cyclic product (**23e**) was obtained as a colourless oil (111 mg, 85% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.79 (br s, 1H), 6.64 (br s, 2H), 3.62 (s, 3H), 3.05, 2.95 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.40-2.22 (m, 2H), 2.18 (s, 6H), 2.04-1.72 (m, 3H), 1.61-1.41 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 214.9, 171.4, 137.7, 136.3, 128.4,

127.9, 61.4, 53.4, 52.5, 38.9, 38.3, 31.5, 21.2, 19.4; **MS** (EI): *m/z* 260 ([$M^+$], 5), 242 (30), 185 (30), 173 (20), 144 (20), 143 (20), 130 (10), 129 (30), 128 (30), 120 (10), 119 (100), 106 (15), 105 (20), 91 (30), 77 (20), 59 (10); **HRMS** (EI): calculated for $C_{16}H_{20}O_3$ $[M+NH_4]^+$ 278.1751, found 278.1752.

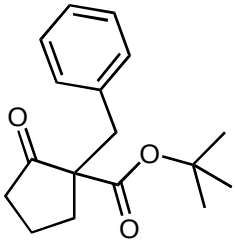
**Methyl 1-(2,6-dimethoxybenzyl)-2-oxocyclopentanecarboxylate (23f):**




The reaction was performed following the general procedure. After purification, the cyclic product (**23f**) was obtained as a colourless oil (110 mg, 75% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.10 (t, *J* = 8.5 Hz, 1H), 6.42 (d, *J* = 8.5 Hz, 2H), 3.65 (s, 6H), 3.63 (s, 3H), 3.37, 3.03 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.35-2.05 (m, 3H), 1.82-1.52 (m, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.0, 171.7, 158.8, 128.0, 113.6, 103.3, 60.1, 55.3, 52.4, 37.7, 31.7, 27.2, 19.4; **HRMS** (ESI): calculated for $C_{16}H_{20}O_5$ $[M+H]^+$ 293.1384, found 293.1379.

**Reaction using 1-*tert*-butyl 6-methyl 2-methylenehexanedioate (10) (114 mg, 0.5 mmol) as starting 1,1'-alkene:**

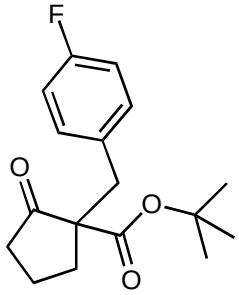
***tert*-Butyl 1-benzyl-2-oxocyclopentanecarboxylate (26a):**[10, 13]




The reaction was performed following the general procedure. After purification, the cyclic product (**26a**) was obtained as a colourless oil (119 mg, 87% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.11 (m, 3H), 7.08-7.04 (m, 2H), 3.04 (s, 2H), 2.33-2.20 (m, 2H), 1.94-1.72 (m, 3H), 1.57-1.41 (m, 1H), 1.35 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.5, 170.3, 136.9, 129.0, 128.3, 126.6, 82.0, 61.9, 38.7, 38.3, 31.9, 27.8,

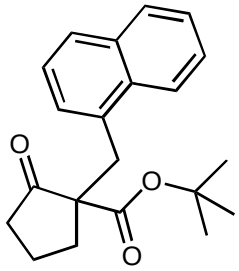
19.5; **MS** (EI): *m/z* 274 ([$M^+$], 1), 218 (15), 200 (20), 173 (15), 172 (30), 171 (15), 155 (20), 145 (25), 130 (40), 129 (20), 128 (10), 117 (30), 116 (20), 115 (55), 91 (100), 78 (10), 65 (15), 57 (95); **HRMS** (EI): calculated for $C_{17}H_{22}O_3$ $[M+NH_4]^+$ 292.1907, found 292.1908.

***tert*-Butyl 1-(4-fluorobenzyl)-2-oxocyclopentanecarboxylate (26b):**




The reaction was performed following the general procedure. After purification, the cyclic product (**26b**) was obtained as a colourless oil (120 mg, 82% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.08-7.00 (m, 2H), 6.86 (tm, 2H, *J* = 9.0 Hz), 3.00 (s, 2H), 2.37-2.21 (m, 2H), 1.96-1.75 (m, 3H), 1.60-1.48 (m, 1H), 1.35 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.3, 170.2, 161.7 (d, *J* = 245.4 Hz), 132.6, 131.8 (d, *J* = 6.8 Hz), 115.0 (d, *J* = 21.1 Hz), 81.1, 61.9, 38.2, 37.7, 31.9, 27.8, 19.4; **MS** (EI): *m/z* 292 ([$M^+$], 3), 236 (25), 219 (10), 191 (10), 190 (25), 173 (10), 148 (20), 147 (10), 135 (20), 134 (15), 133 (30), 115 (10), 109 (100), 96 (10), 83 (10), 57 (90); **HRMS** (EI): calculated for $C_{17}H_{21}FO_3$ $[M+NH_4]^+$ 310.1813, found 310.1816.

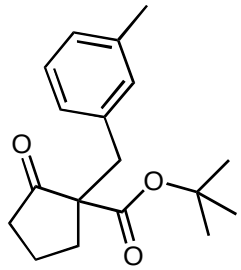
***tert*-Butyl 1-(naphthalen-1-ylmethyl)-2-oxocyclopentanecarboxylate (26c):[10]**




The reaction was performed following the general procedure. After purification, the cyclic product (**26c**) was obtained as a colourless oil (133 mg, 82% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.40 (quintet x m, *J* = 8.4 Hz, 2H), 7.30-7.18 (m, 2H), 3.72, 3.49 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.34-2.19 (m, 2H), 1.83-1.52 (m, 3H), 1.42-1.30 (m, 1H),

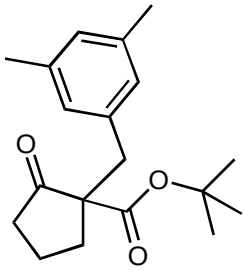
1.36 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.6, 170.8, 133.7, 133.5, 133.1, 128.7, 128.1, 127.4, 125.9, 125.5, 125.4, 124.2, 82.1, 62.4, 38.0, 33.7, 32.3, 27.8, 19.5; **MS** (EI): *m/z* 324 ([$M^+$], 5), 268 (10), 251 (10), 250 (25), 205 (25), 178 (10), 166 (10), 165 (55), 153 (10), 152 (25), 142 (25), 141 (80), 128 (60), 115 (30), 96 (10), 57 (100); **HRMS** (EI): calculated for $C_{21}H_{24}O_3$ $[M+NH_4]^+$ 342.2064, found 342.2063.

***tert*-Butyl 1-(3-methylbenzyl)-2-oxocyclopentanecarboxylate (26d):**



The reaction was performed following the general procedure. After purification, the cyclic product (**26d**) was obtained as a colourless oil (128 mg, 89% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.09-7.03 (m, 1H), 6.95-6.91 (m, 1H), 6.88-6.82 (m, 2H), 3.01 (s, 2H), 2.43-2.20 (m, 2H), 2.24 (s, 3H), 1.98-1.72 (m, 3H), 1.60-1.45 (m, 1H), 1.35 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.3, 170.3, 137.7, 136.8, 131.0, 128.1, 127.3, 127.0, 81.9, 61.9, 38.6, 38.3, 31.9, 27.8, 21.3, 19.5; **MS** (EI): *m/z* 288 ([$M^+$], 1), 215 (25), 214 (55), 187 (20), 186 (20), 171 (35), 168 (20), 159 (40), 144 (15), 143 (10), 131 (25), 130 (15), 129 (30), 128 (20), 116 (15), 115 (40), 105 (100), 92 (20), 91 (30), 84 (20), 77 (20), 57 (95); **HRMS** (EI): calculated for $C_{18}H_{24}O_3$ $[M+NH_4]^+$ 306.2064, found 306.2064.

***tert*-Butyl 1-(3,5-dimethylbenzyl)-2-oxocyclopentanecarboxylate (26e):**

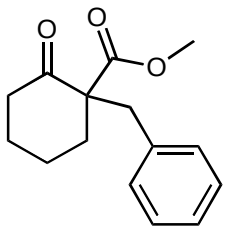


The reaction was performed following the general procedure. After purification, the cyclic product (**26e**) was obtained as a colourless oil (119 mg, 79% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.76 (br s, 1H), 6.67 (br s, 2H), 3.01, 2.91 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.32-2.16 (m, 2H), 2.20 (s, 6H), 1.98-1.71 (m, 3H), 1.59-1.47 (m, 1H), 1.35

(s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 215.3, 170.3, 137.6, 136.8, 128.3, 128.0, 81.9, 62.0, 38.6, 38.3, 31.9, 27.9, 21.1, 19.5; **MS** (EI): *m/z* 302 ([$M^+$], 1), 229 (15), 228 (40), 185 (20), 173 (20), 157 (10), 130 (10), 129 (20), 128 (20), 127 (10), 120 (15), 119 (100), 115 (20), 106 (20), 105 (15), 84 (10), 77 (10), 57 (60); **HRMS** (EI): calculated for $C_{19}H_{26}O_3$ [M+$NH_4$]$^+$ 320.2220, found 320.2217.

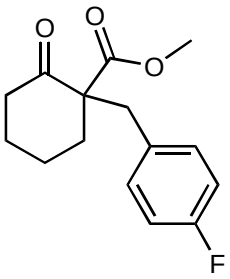
**Reaction using dimethyl 2-methyleneheptanedioate (12) (100 mg, 0.5 mmol) as starting 1,1'-alkene:**

**Methyl 1-benzyl-2-oxocyclohexanecarboxylate (24a):[14]**



The reaction was performed following the general procedure. After purification, the cyclic product (**24a**) was obtained as a colourless oil (107 mg, 87% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.10 (m, 3H), 7.04-6.98 (m, 2H), 3.56 (s, 3H), 3.24, 2.79 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.48-2.26 (m, 3H), 1.99-1.88 (m, 1H), 1.70-1.50 (m, 3H), 1.42-1.33 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 207.1, 171.3, 136.4, 130.2, 128.0, 126.6, 62.2, 52.2, 41.3, 40.4, 35.7, 27.5, 22.4; **MS** (EI): *m/z* 246 ([$M^+$], 3), 228 (20), 186 (20), 185 (25), 169 (10), 158 (10), 129 (10), 117 (20), 115 (35), 91 (100), 77 (10), 69 (10), 65 (25), 59 (10); **HRMS** (EI): calculated for $C_{15}H_{18}O_3$ [M+H]$^+$ 247.1329, found 247.1329.

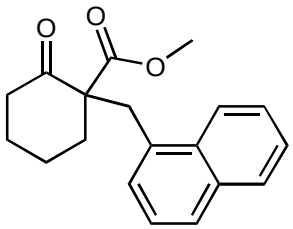
**Methyl 1-(4-fluorobenzyl)-2-oxocyclohexanecarboxylate (24b):**



The reaction was performed following the general procedure. After purification, the cyclic product (**24b**) was obtained as a colourless oil (98 mg, 74% yield). **$^1$H NMR**

(300 MHz, $CDCl_3$): δ 7.09-7.02 (m, 2H), 6.90 (tm, *J* = 9.0 Hz, 2H), 3.61 (s, 3H), 3.20, 2.80 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.52-2.26 (m, 3H), 2.05-1.95 (m, 1H), 1.77-1.36 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 207.1, 171.4, 161.8 (d, *J* = 244.6 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 6.8 Hz), 114.8 (d, *J* = 21.1 Hz), 62.3, 52.2, 41.3, 39.6, 36.0, 22.5; **MS** (EI): *m/z* 264 ([$M^+$], 5) 246 (10), 204 (10), 176 (10), 135 (10), 133 (20), 109 (100), 83 (15), 67 (10), 59 (25); **HRMS** (EI): calculated for $C_{15}H_{17}FO_3$ $[M+NH_4]^+$ 282.1505, found 282.1499.

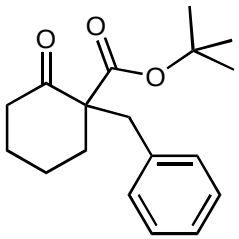
**Methyl 1-(naphthalen-1-ylmethyl)-2-oxocyclohexanecarboxylate (24c):**



The reaction was performed following the general procedure. After purification, the cyclic product (**24c**) was obtained as a colourless oil (129 mg, 93% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.91-7.85 (m, 1H), 7.77-7.71 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.41-7.28 (m, 3H), 7.21-7.17 (m, 1H), 3.81, 3.31 (2 x d(AB), *J* = 14.0 Hz, 2H), 3.39 (s, 3H), 2.50-2.29 (m, 3H), 1.99-1.88 (m, 1H), 1.66-1.40 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 207.1, 171.4, 133.7, 132.9, 132.8, 128.7, 128.5, 127.5, 125.6, 125.3, 125.0, 123.9, 62.0, 52.1, 41.2, 36.2, 35.5, 27.5, 22.6; **MS** (EI): *m/z* 296 ([$M^+$], 1), 278 (10), 219 (10), 165 (25), 152 (15), 142 (15), 141 (100), 128 (15), 115 (40), 55 (25); **HRMS** (EI): calculated for $C_{21}H_{24}O_3$ $[M+NH_4]^+$ 314.1751, found 314.1752.

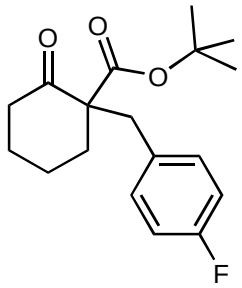
**Reaction using 1-*tert*-butyl 7-methyl 2-methyleneheptanedioate (13) (121 mg, 0.5 mmol) as starting 1,1'-alkene:**

***tert*-Butyl 1-benzyl-2-oxocyclohexanecarboxylate (27a):[13,15]**



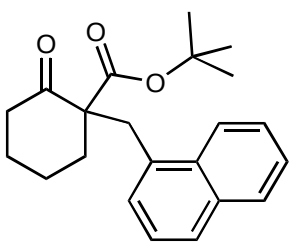
The reaction was performed following the general procedure. After purification, the cyclic product (**27a**) was obtained as a colourless oil (128 mg, 89% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.05 (m, 5H), 3.18, 2.80 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.45-2.36 (m, 2H), 2.30-2.23 (m, 1H), 1.99-1.88 (m, 1H), 1.70-1.44 (m, 3H), 1.40-1.20 (m, 1H), 1.20 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 207.5, 170.1, 136.8, 130.6, 127.8, 126.5, 81.9, 62.4, 41.2, 40.3, 36.3, 27.8, 27.5, 22.6; **MS** (EI): *m/z* 288 ([$M^+$], 1), 214 (10), 186 (10), 169 (10), 115 (15), 91 (40), 77 (10), 65 (10), 57 (100); **HRMS** (EI): calculated for $C_{21}H_{24}O_3$ $[M+NH_4]^+$ 306.2064, found 306.2063.

***tert*-Butyl 1-(4-fluorobenzyl)-2-oxocyclohexanecarboxylate (27b):**



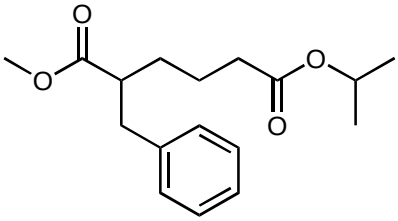

The reaction was performed following the general procedure. After purification, the cyclic product (**27b**) was obtained as a colourless oil (82 mg, 62% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.10-7.04 (m, 2H), 6.85 (tm, *J* = 9.0 Hz, 2H), 3.14, 2.76 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.48-2.39 (m, 2H), 2.35-2.23 (m, 1H), 2.00-1.89 (m, 1H), 1.70-1.23 (m, 4H), 1.26 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 207.7, 170.1, 161.7 (d, *J* = 244.6 Hz), 132.5 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 6.8 Hz), 114.6 (d, *J* = 21.1 Hz), 82.2, 62.5, 41.3, 39.5, 36.5, 27.8, 22.6; **MS** (EI): m/z 306 ([$M^+$], 1), 250 (20), 233 (10), 232 (20), 205 (10), 204 (40), 187 (20), 176 (10), 147 (10), 135 (20), 133 (25), 109 (90), 83 (20), 67 (10), 57 (100); **HRMS** (EI): calculated for $C_{18}H_{23}FO_3$ $[M+H]^+$ 307.1704, found 307.1704.

***tert*-Butyl 1-(naphthalen-1-ylmethyl)-2-oxocyclohexanecarboxylate (27c):**



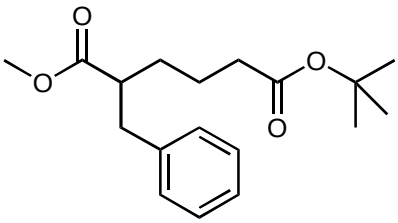
The reaction was performed following the general procedure. After purification, the cyclic product (**27c**) was obtained as a colourless oil (107 mg, 63% yield). **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.41-7.28 (m, 4H), 3.70, 3.40 (2 x d(AB), *J* = 14.0 Hz, 2H), 2.49-2.39 (m, 2H), 2.34-2.25 (m, 1H), 1.98-1.88 (m, 1H), 1.62-1.30 (m, 4H), 1.15 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 207.5, 170.3, 133.7, 133.5, 133.1, 128.8, 128.6, 127.2, 125.6, 125.2, 125.1, 124.6, 82.0, 62.9, 41.3, 36.7, 34.6, 27.6, 27.5, 22.7; **MS** (EI): *m/z* 338 ([$M^+$], 3), 264 (15), 219 (15), 165 (25), 152 (10), 142 (10), 141 (100), 128 (20), 115 (15), 57 (75); **HRMS** (EI): calculated for $C_{22}H_{26}O_3$ $[M+Na]^+$ 361.1774, found 361.1772.

**6-Isopropyl 1-methyl 2-benzylhexanedioate (28):**



The reaction was performed following the general procedure on 0.5 mmol of 1,1'-alkene. The 1,4-addition product (**28**) was obtained as a mixture with the cyclopentanone (**23a**) (30/70) and the products could not be separated by column chromatography. Interpretation of the NMR spectra of the mixture afforded: **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.18-6.94 (m, 5H), 4.81 (heptet, *J* = 6.0 Hz, 1H), 3.43 (s, 3H), 2.85-2.75 (m, 1H), 2.61-2.43 (m, 2H), 2.16 (t, *J* = 7.1 Hz, 2H), 1.95-1.73 (m, 4H), 1.08 (d, *J* = 6.0 Hz, 6H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 175.7, 172.8, 139.1, 128.8, 126.9, 126.4, 67.5, 51.5, 47.3, 38.5, 34.4, 31.3, 22.8, 21.8.

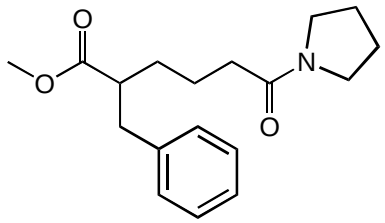
**6-*tert*-Butyl 1-methyl 2-benzylhexanedioate (29):**



The reaction was performed following the general procedure on 0.5 mmol of 1,1'-alkene. After purification, the 1,4-addition product (**29**) was obtained as a colourless

oil (100 mg, 88% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.22-7.05 (m, 5H), 3.51 (s, 3H), 2.90-2.80 (m, 1H), 2.70-2.50 (m, 2H), 2.11 (t, *J* = 7.1 Hz, 2H), 1.60-1.35 (m, 4H), 1.32 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 175.8, 172.6, 139.1, 128.8, 128.4, 126.4, 80.2, 51.5, 47.4, 38.5, 35.3, 31.3, 28.0, 22.9; **MS** (EI): *m/z* 306 ([$M^+$], <1), 250 (20), 232 (10), 201 (30), 190 (50), 173 (70), 155 (10), 131 (20), 130 (40), 117 (20), 91 (100), 77 (10), 65 (15), 57 (85), 55 (15); **HRMS** (EI): calculated for $C_{18}H_{26}O_4$ $[M+NH_4]^+$ 324.2169, found 324.2169.

**Methyl 2-benzyl-6-oxo-6-(pyrrolidin-1-yl)hexanoate (30):**




The reaction was performed following the general procedure on 0.5 mmol of 1,1'-alkene. After purification, the 1,4-addition product (**30**) was obtained as a colourless oil (137 mg, 90% yield). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.13-6.92 (m, 5H), 3.40 (s, 3H), 3.25 (t, *J* = 6.9 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 2.80-2.70 (m, 1H), 2.62-2.45 (m, 2H), 2.09-2.01 (m, 2H), 1.80-1.59 (m, 4H), 1.57-1.35 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 175.8, 170.9, 139.1, 128.7, 128.2, 126.2, 51.3, 47.4, 46.4, 45.5, 38.4, 34.3, 31.7, 26.0, 24.3, 22.6; **MS** (EI): *m/z* 303 ([$M^+$], 15), 166 (10), 140 (20), 126 (50), 113 (100), 98 (45), 91 (70), 85 (20), 70 (70), 55 (65); **HRMS** (EI): calculated for $C_{18}H_{25}NO_3$ $[M+H]^+$ 304.1907, found 304.1906.

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