

**Stereoselective Synthesis of (*E*)-4-Alkylidene-cyclopent-2-en-1-ones by a
Tandem Ring Closure-Michael addition-Elimination**

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Supplementary Informations

4a: yield 84%, bp 105°C/6 torr, IR (cm⁻¹, neat) 1575. ¹H NMR (200 MHz, CDCl₃) δ : 2.26 (s, 3H), 3.93 (s, 2H), 5.88 (s, 2H), 7.20-7.42 (m, 5H). Anal. Calcd for C₁₂H₁₂O (172.2) C, 83.69; H, 7.02. Found: C, 83.75; H, 7.06.

5a: yield 88%, oil, IR (cm⁻¹, neat) 1695, 1590, ¹H NMR (200 MHz, CDCl₃) δ : 2.29 (s, 3H), 3.86 (s, 2H), 6.31 (s, 2H), 7.25-7.45 (m, 5H). Anal. Calcd for C₁₂H₁₂O₂ (188.2) C, 76.57; H, 6.43. Found: C, 76.50; H, 6.46.

6a: yield 77%, oil, IR (cm⁻¹, neat) 1690, 1595. ¹H NMR (200 MHz, CDCl₃) δ : 1.91 (s, 3H), 2.14 (s, 3H), 2.37 (s, 3H), 3.10 (s, 2H), 7.24-7.48 (m, 5H). MS *m/e* (relative intensity) : 213 (M+1, 12), 212 (M, 73), 197 (14), 184 (19), 169 (100), 154 (28), 141 (39), 128 (23), 115 (55). Anal. Calcd for C₁₅H₁₆O (212.3) C, 84.87; H, 7.60. Found: C, 84.95; H, 7.56.

6b: yield 63%, mp: 59°C, IR (cm⁻¹, KBr) 1695, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 1.10 (d, 6H, *J* = 6.7 Hz), 2.22 (s, 3H), 2.48-2.66 (m, 1H), 3.09 (s, 2H), 5.70-5.77 (m, 1H), 7.26-7.47 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ : 12.9, 22.6, 29.8, 37.5, 127.8, 128.2, 129.4, 131.7, 134.0, 134.8, 141.5, 164.0, 203.1. MS *m/z* (relative intensity) : 227 (M+1, 10), 226 (M, 67), 211 (31), 198 (11), 184 (100), 155 (32), 141 (26), 115, 32). Anal. Calcd for C₁₆H₁₈O (226.31) C, 84.91; H, 8.02. Found: C, 84.95; H, 7.96.

6c : yield 81%, oil, IR (cm⁻¹, neat) 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 0.92 (t, 3H, *J* = 6.7 Hz), 1.26-1.57 (m, 6H), 2.21 (s, 3H), 2.22-2.26 (m, 2H), 3.08 (s, 2H), 5.88-5.96 (m, 1H), 7.26-7.49 (m, 5H). Anal. Calcd for C₁₈H₂₂O (254.37) C, 84.99; H, 8.72. Found: C, 84.96; H, 8.68.

6d : yield 76%, oil, IR (cm⁻¹, neat) 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 0.92 (t, 3H, *J* = 6.7 Hz), 1.26-1.57 (m, 6H), 2.21 (s, 3H), 2.22-2.26 (m, 2H), 3.08 (s, 2H), 5.88-5.96 (m, 1H), 7.26-7.49 (m, 5H). 0.90 (t, 3H, *J* = 6.7 Hz), 1.18-1.54 (m, 14H), 2.21 (s, 3H),

2.22-2.25 (m, 2H), 3.07 (s, 2H), 5.86-5.97 (m, 1H), 7.20-7.47 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ : 13.4, 14.6, 23.2, 26.7, 27.9, 29.5, 29.7, 30.0, 30.7, 32.4, 38.2, 127.8, 128.2, 128.8, 129.9, 132.3, 137.5, 141.9, 164.3, 203.4. MS m/z (relative intensity) : 310 (M, 10), 197 (20), 184 (100), 169 (8), 154 (13), 141 (16), 115 (11). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}$ (310.48) C, 85.11; H, 9.74. Found: C, 85.02; H, 9.78.

6e : yield 68%, oil, IR (cm^{-1} , neat) 1690, 1600. ^1H NMR (200 MHz, CDCl_3) δ : 1.52-1.73 (m, 2H), 2.08-2.16 (m, 2H), 2.21 (s, 3H), 2.22-2.27 (m, 2H), 3.07 (s, 2H), 4.98-5.10 (m, 2H), 5.73-5.95 (m, 2H), 7.28-7.47 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ : 13.4, 28.9, 30.0, 33.8, 38.2, 115.5, 127.2, 128.3, 128.7, 129.9, 132.20, 137.8, 138.7, 142.0, 164.1, 203.3. MS m/z (relative intensity) : 252 (M, 16), 210 (17), 197 (62), 184 (100), 167 (22), 153 (33), 141 (42), 128 (25), 115 (47). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ (252.35) C, 85.67; H, 7.99. Found: C, 85.73; H, 8.05.

6f : yield 73%, oil, IR (cm^{-1} , neat) 1690, 1600. ^1H NMR (200 MHz, CDCl_3) δ : 1.36 (s, 3H), 1.78-1.90 (m, 2H), 2.21 (s, 3H), 2.28-2.43 (m, 2H), 3.10 (s, 2H), 3.93-4.10 (m, 4H), 5.88-5.97 (m, 1H), 7.27-7.47 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ : 12.9, 24.1, 25.3, 37.9, 38.4, 64.8, 109.8, 126.3, 127.8, 128.3, 129.5, 131.8, 137.1, 141.8, 163.5, 220.8. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_3$ (298.38) C, 76.48; H, 7.43. Found: C, 76.44; H, 7.40.

6g : yield 73%, mp : 51°C , IR (cm^{-1} , KBr) 3300, 1690, 1600. ^1H NMR (200 MHz, CDCl_3) δ : 1.37-1.67 (m, 6H), 1.71 (bs, 1H), 2.20 (s, 3H), 2.21-2.28 (m, 2H), 3.07 (s, 2H), 3.65 (t, 2H, $J = 6.4\text{Hz}$), 5.86-5.96 (m, 1H), 7.26-7.47 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ : 13.4, 26.1, 29.5, 30.7, 38.2, 63.2, 127.5, 128.3, 128.7, 129.9, 132.2, 137.7, 142.0, 164.3, 203.5. MS m/z (relative intensity) : 271 (M+1, 5), 270 (M, 31), 211 (8), 197 (19), 184 (100), 153 (25), 141 (37), 128 (21), 115 (36). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$ (270.37) C, 79.96; H, 8.20. Found: C, 80.01; H, 8.23.

6h : yield 84%, mp : 80°C, IR (cm⁻¹, KBr) 1715, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 2.15 (s, 3H), 2.17 (s, 3H), 2.39-2.53 (m, 2H), 2.56-2.71 (m, 2H), 3.09 (s, 2H), 3.79-3.88 (m, 1H), 7.24-7.44 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ : 13.3, 24.7, 30.5, 38.1, 43.1, 128.3, 128.5, 128.7, 129.9, 132.1, 138.5, 142.3, 163.8, 203.0, 207.88. MS *m/z* (relative intensity) : 255 (M+1, 11), 254 (M, 60), 236 (14), 211 (50), 197 (100), 184 (55), 153 (26), 141 (31), 128 (21), 115 (47). Anal. Calcd for C₁₇H₁₉O₂ (255.33) C, 79.97; H, 7.50. Found: C, 79.94; H, 7.53.

6i : yield 80%, mp : 87°C, IR (cm⁻¹, KBr) 1730, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 2.19 (s, 3H), 2.51-2.56 (m, 4H), 3.10 (s, 2H), 3.69 (s, 3H), 3.83-3.90 (m, 1H), 7.25-7.47 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ : 12.9, 25.5, 33.3, 37.5, 51.8, 127.9, 128.2, 128.4, 129.4, 131.5, 138.4, 142.1, 163.2, 173.1, 202.5. MS *m/z* (relative intensity) : 271 (M+1, 14), 270 (M, 81), 238 (28), 210 (58), 197 (100), 184 (24), 167 (38), 153 (38), 141 (37), 128 (24), 115 (55). Anal. Calcd for C₁₇H₁₈O₃ (270.33) C, 75.53; H, 6.71. Found: C, 75.48; H, 6.74.

6j : yield 67%, oil, IR (cm⁻¹, neat) 1730, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 1.37-1.87 (m, 4H), 1.94-2.11 (m, 2H), 2.19 (s, 3H), 2.23-2.39 (m, 2H), 3.06 (s, 2H), 3.66 (s, 3H), 5.83-5.93 (m, 1H), 7.23-7.48 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ : 13.4, 25.1, 29.2, 30.3, 34.4, 38.2, 52.1, 126.9, 128.3, 128.7, 129.6, 132.2, 138.0, 142.1, 164.1, 174.4, 203.2. MS *m/z* (relative intensity) : 299 (M+1, 18), 298 (M, 94), 267 (13), 211 (100), 184 (82), 172 (29), 141 (39), 128 (23), 115 (39). Anal. Calcd for C₁₉H₂₂O₃ (298.38) C, 76.48; H, 7.43. Found: C, 76.55; H, 7.40.

6k: yield 65%, mp 168°C, IR (cm⁻¹, neat) 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 3.36 (s, 3H), 3.45 (s, 2H), 6.81 (s, 1H), 7.21-7.55 (m, 10H). Anal. Calcd for C₁₉H₁₆O (260.3) C, 87.66; H, 6.19. Found: C, 87.63; H, 6.22.

6l: yield 79%, oil, IR (cm⁻¹, neat) 1730, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 1.19 (t, 3H, *J* = 7.7 Hz), 2.51-2.62 (m, 4H), 2.61 (q, 2H, *J* = 7.7 Hz), 3.10 (s, 2H), 3.70 (s, 3H), 5.82-5.93 (m, 1H), 7.27-7.46 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ : 14.7, 20.2, 26.0, 33.9, 38.13, 52.2, 128.4, 128.8, 129.5, 129.7, 132.2, 137.3, 142.1, 169.2, 173.5, 203.3. MS *m/z* (relative intensity) : 286 (M+2, 2), 285 (M+1, 22), 284 (M, 96), 252 (25), 237 (10), 224 (44), 211 (100), 167 (26), 115 (25). Anal. Calcd for C₁₈H₂₀O₃ (284.3) C, 76.03; H, 7.09. Found: C, 76.09; H, 7.01.

6m: yield 87%, oil, IR (cm⁻¹, neat) 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 0.92 (t, 3H, *J* = 6.6 Hz), 1.24-1.54 (m, 6H), 2.14-2.18 (m, 2H), 2.21 (s, 3H), 3.82 (s, 3H), 5.86-5.97 (m, 1H), 6.89-6.92 (m, 3H), 7.26-7.38 (m, 1H); MS *m/z* (relative intensity) : 285 (M+1, 9), 284 (M, 43), 269 (16), 255 (30), 241 (14), 227 (21), 214 (100), 199 (9), 115 (9); . Anal. Calcd for C₁₉H₂₄O₂ (284.4) C, 80.24; H, 8.51. Found: C, 80.19; H, 8.47.

6n: yield 68%, mp: 82°C, IR (cm⁻¹, KBr) 1730, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 2.19 (s, 3H), 2.52-2.57 (m, 4H), 3.10 (s, 2H), 3.70 (s, 3H), 3.82 (s, 3H), 5.81-5.92 (m, 1h), 6.86-6.91 (m, 3H), 7.26-7.36 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ : 12.9, 25.5, 33.3, 37.6, 51.8, 55.2, 113.6, 114.9, 121.8, 124.4, 129.2, 132.8, 138.4, 142.0, 159.4, 163.3, 173.0, 202.3. MS *m/z* (relative intensity) : 301 (M+1, 17), 300 (M, 79), 268 (22), 240 (40), 227 (100), 214 (20), 115 (18). Anal. Calcd for C₁₈H₂₀O₃ (284.3) C, 76.03; H, 7.09. Found: C, 75.97; H, 7.13.

6o: yield 73%, oil, IR (cm⁻¹, neat) 1730, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 1.16 (t, 3H, *J* = 7.6 Hz), 1.47-1.72 (m, 4H), 2.18-2.35 (m, 4H), 2.57 (q, 2H, *J* = 7.6 Hz), 3.01 (s, 2H), 3.64 (s, 3H), 5.86-5.91 (m, 1H), 7.05-7.10 (m, 2H), 7.22-7.29 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ : 14.7, 20.2, 25.1, 29.1, 30.4, 34.3, 38.2, 52.0, 115.6, 116.1, 127.1, 131.1, 131.4, 136.2, 140.6, 160.4, 165.3, 169.6, 174.4, 293.5; MS *m/z* (relative intensity) : 331 (M+1, 24), 330 (M, 98), 298 (13), 243 (100), 216 (56), 201 (44), 159 (45), 133 (51), 109 (66). Anal. Calcd for C₂₀H₂₃FO₃ (330.4) C, 72.71; H, 7.02. Found: C, 72.76; H, 6.96.

6p: yield 73%, oil, IR (cm⁻¹, neat) 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 0.88-0.95 (m, 3H), 1.25-1.55 (m, 6H), 2.21 (s, 3H), 3.07 (s, 3H), 5.91-5.99 (m, 1H), 7.17-7.40 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ : 13.4, 14.5, 23.0, 29.3, 30.7, 32.0, 38.2, 126.8, 128.1, 128.4, 128.7, 129.9, 130.0, 134.6, 137.3, 140.6, 164.9, 202.19. MS *m/z* (relative intensity) : 290 (M+2, 9), 289 (M+1, 6), 288 (M, 27), 218 (100), 183 (14), 165 (20), 153 (27), 115 (20). Anal. Calcd for C₁₈H₂₁ClO (288.8) C, 74.86; H, 7.33. Found: C, 74.90; H, 7.29.

6q: yield 67%, mp: 75°C, IR (cm⁻¹, KBr) 1730, 1690, 1600. ¹H NMR (200 MHz, CDCl₃) δ : 1.49-1.77 (m, 4H), 2.19 (s, 3H), 2.24-2.39 (m, 4H), 3.06 (s, 3H), 3.68 (s, 3H), 5.89-5.96 (m, 1H), 7.17-7.40 (m, 4H); MS *m/z* (relative intensity) : 334 (M+2, 30), 333 (M+1, 18), 332 (M, 84), 301 (10), 245 (100), 218 (64), 165 (58), 153 (62), 115 (44). Anal. Calcd for C₁₉H₂₁ClO₃ (332.8) C, 68.57; H, 6.36. Found: C, 68.53; H, 6.32.