

Supporting Information

Titanium-mediated Alkylative Cyclizations of 1,3-Diene-Tethered Esters

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Typical experimental procedure for the formation of 3a and 4a: A 3.0 M solution of methylmagnesium chloride (0.2 mL) in THF was added at 0 °C over a period of 5 min to a solution of Ti(O-*i*-Pr)₄ (0.16 mL, 0.55 mmol) in anhydrous THF (5 mL). After the mixture had been stirred for an additional 5 min, **1** (77 mg, 0.5 mmol) was added, followed by slow addition (over a period of 1 h) of a 2.0 M solution of cyclopentylmagnesium chloride (0.45 mL) in THF. The reaction mixture was then stirred for 10 min and quenched with addition of water (0.5 mL). The resulting mixture was stirred for an additional 1 h, dried over sodium sulfate, and filtered. The filter cake was washed with CH₂Cl₂ (10 mL), and the combined filtrates were concentrated under vacuum. Purification by column chromatography on silica gel afforded 38.5 mg (62%) of **3a** and 20.4 mg (21%) of **4a**.

Typical experimental procedure for the formation of 6: A 3.0 M solution of methylmagnesium chloride (0.2 mL) in THF was added at 0 °C over a period of 5 min to a solution of Ti(O-*i*-Pr)₄ (0.16 mL, 0.55 mmol) in anhydrous THF (5 mL). After the mixture had been stirred for an additional 5 min, **2** (84 mg, 0.5 mmol) was added, followed by slow addition (over a period of 1 h) of a 2.0 M solution of cyclopentylmagnesium chloride (0.75 mL) in THF. The reaction mixture was then stirred for 10 min and quenched with addition of water (0.5 mL). The resulting mixture was stirred for an additional 1 h, dried over sodium sulfate, and filtered. The filter cake was washed with CH₂Cl₂ (10 mL), and the combined

filtrates were concentrated under vacuum. Purification by column chromatography on silica gel afforded 84.3 mg (81%) of 6.

3a: IR (neat) 1739 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.72 (ddq, $J = 10.8, 1.1, 6.8$ Hz, 1H), 5.24 (ddq, $J = 10.8, 8.6, 1.7$ Hz, 1H), 3.11–3.03 (apparent q, 1H), 2.38–2.02 (m, 4H), 1.90–1.81 (m, 1H), 1.73–1.62 (m, 1H), 1.67 (dd, $J = 6.8, 1.7$ Hz, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 219.3, 128.2, 126.6, 48.4, 37.6, 30.8, 21.0, 13.4.

4a: IR (neat) 3325 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.51 (dt, $J = 15.1, 6.8$ Hz, 1H), 5.31 (dd, $J = 15.1, 8.0$ Hz, 1H), 3.84–3.78 (apparent q, 1H), 2.29–2.20 (apparent qn, 1H), 2.03–1.26 (m, 16H), 1.15–1.09 (m, 2H); ^{13}C NMR (90 MHz, CDCl_3) δ 132.4, 130.9, 78.7, 52.0, 40.0, 39.0, 33.3, 32.2, 30.0, 25.1, 21.1.

3b: IR (neat) 1740 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.72 (ddt, $J = 10.6, 1.0, 6.8$ Hz, 1H), 5.24 (ddt, $J = 10.6, 8.6, 1.7$ Hz, 1H), 3.10–3.02 (apparent q, 1H), 2.33–2.02 (m, 4H), 1.89–1.85 (m, 1H), 1.73–1.63 (m, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 219.3, 128.1, 126.6, 48.4, 37.6, 30.8, 21.0, 13.3, 13.1, 12.9.

4b: IR (neat) 3345 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.51 (dt, $J = 15.4, 6.8$ Hz, 1H), 5.31 (dd, $J = 15.4, 8.0$ Hz, 1H), 2.28–2.21 (apparent q, 1H), 2.02–1.25 (m, 16H), 1.14–1.09 (m, 1H); ^{13}C NMR (90 MHz, CDCl_3) δ 132.3, 130.9, 78.4, 78.2, 78.0, 51.9, 39.9, 39.0, 33.2, 32.2, 32.0, 31.8, 31.6, 30.0, 25.1, 25.0, 21.1.

5: IR (neat) 1711 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.62 (dq, $J = 10.9, 6.6$ Hz, 1H), 5.53 (ddq, $J = 10.9, 8.5, 1.5$ Hz, 1H), 3.32–3.25 (m, 1H), 2.48–2.42 (m, 1H), 2.35–2.27 (m, 1H), 2.05–2.00 (m, 2H), 1.91–1.65 (m, 4H), 1.58 (dd, $J = 6.6, 1.5$ Hz, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ __.2, 127.5, 126.2, 49.0, 41.7, 34.5, 27.7, 24.3, 13.0.

6a: IR (neat) 3390 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.58 (dt, $J = 15.2, 7.0$ Hz, 1H), 5.23 (dd, $J = 15.2, 8.7$ Hz, 1H), 3.17 (ddd, $J = 9.9, 9.9, 4.0$ Hz, 1H), 2.05–1.09

(m, 21H); ^{13}C NMR (90 MHz, CDCl_3) δ 132.9, 132.5, 73.0, 50.3, 39.9, 39.0, 33.5, 32.2, 31.6, 25.3, 25.1, 24.8.

6b: IR (neat) 3397 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.58 (dt, 15.4, 6.7 Hz, 1H), 5.25 (ddt, $J = 15.4, 8.7, 1.1$ Hz, 1H), 3.18 (ddd, $J = 9.8, 9.8, 4.1$ Hz, 1H), 2.04–1.63 (m, 8H), 1.39 (tq, $J = 7.4, 7.4$ Hz, 2H), 1.30–1.16 (m, 4H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 133.3, 132.2, 73.0, 50.3, 34.7, 33.6, 31.6, 25.3, 24.8, 22.6, 13.6.

6c: IR (neat) 3407 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.63–5.52 (m, 1H), 5.22 (dd, $J = 15.4, 8.7$ Hz, 1H), 3.19–3.16 (m, 1H), 2.05–0.84 (m, 21H); ^{13}C NMR (90 MHz, CDCl_3) δ 133.7, 133.2, 132.1, 131.9, 73.0, 50.3, 50.2, 39.7, 34.7, 33.6, 32.6, 31.6, 31.4, 29.2, 29.0, 25.3, 24.8, 22.5, 19.1, 14.0, 11.4.

6d: IR (neat) 3390 cm^{-1} ; ^1H NMR (360 MHz, CDCl_3) δ 5.57 (dt, $J = 15.4, 7.1$ Hz, 1H), 5.23 (dd, $J = 15.4, 8.9$ Hz, 1H), 3.19 (ddd, $J = 9.8, 9.8, 4.1$ Hz, 1H), 2.04–1.59 (m, 8H), 1.34–1.17 (m, 5H), 0.88 (d, $J = 6.6$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 133.2, 132.2, 73.0, 50.3, 42.0, 33.6, 31.6, 28.3, 25.3, 24.8, 22.3, 22.2.



































