Stereoselective aldol-type cyclization reaction mediated by Dibutylboron triflate/Diisopropylethyl amine.

Sanjib Das, Lian-Sheng Li, and Subhash C. Sinha*

The Skaggs Institute for Chemical Biology and the Department of Molecular Biology,
The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA.

subhash@scripps.edu

Supporting Information

Synthesis of substrates.

Scheme 1. Synthesis of compound **1a** (racemic).

Compound **14**: ^1H NMR (500 MHz, CDCl_3): δ 7.78-7.65 (m, 4H), 7.45-7.37 (m, 6H), 4.84 (s, 1H), 4.77 (s, 1H), 4.06 (m, 1H), 3.91-3.81 (m, 2H), 3.01 (d, $J = 2.2$ Hz, 1H), 2.25 (dd, $J = 13.9$, 8.1 Hz, 1H), 2.16 (dd, $J = 13.9$, 5.5 Hz, 1H), 1.77 (s, 3H), 1.73-1.69 (m, 2H), 1.05 (s, 9H).

Compound **15**: ^1H NMR (500 MHz, CDCl_3): δ 4.90 (d, $J = 1.5$ Hz, 1H), 4.81 (d, $J = 1.5$ Hz, 1H), 4.01 (m, 1H), 3.91-3.83 (m, 2H), 2.47 (dd, $J = 6.1$, 4.0 Hz, 1H), 2.3 (d, $J = 2.2$ Hz, 1H), 2.21 (d, $J = 7.0$ Hz, 2H), 1.77 (s, 3H), 1.76 – 1.61 (m, 2H).

Compound **16**: ^1H NMR (500 MHz, CDCl_3): δ 7.56-7.3 (m, 5H), 5.52 (s, 1H), 4.83 (d, $J = 2.2$ Hz, 1H), 4.79 (d, $J = 2.2$ Hz, 1H), 4.26 (ddd, $J = 6.6$, 5.1, 1.5 Hz, 1H), 4.02-3.93 (m, 2H), 2.45 (dd, $J = 14.3$, 7.0 Hz, 1H), 2.25 (dd, $J = 13.9$, 6.2 Hz, 1H), 1.8 (s, 3H), 1.78 (m, 1H), 1.55 (m, 1H).

Compound **1a**: ^1H NMR (500 MHz, CDCl_3): δ 7.45-7.29 (m, 5H), 5.51 (s, 1H), 4.32 (m, 1H), 4.22 (dd, $J = 11.3$, 5.1 Hz, 1H), 3.95 (dt, $J = 11.8$, 2.5 Hz, 1H), 2.82 (dd, $J = 16.3$, 6.9 Hz, 1H), 2.54 (dd, $J = 16.5$, 5.1 Hz, 1H), 2.16 (s, 3H), 1.78 (dddd, $J = 11.3$, 11.1, 5.1, 1.1 Hz, 1H), 1.57 (dt, $J = 11.7$, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 206.4, 138.4, 128.7, 128.1, 125.9, 101.0, 73.2, 66.7, 49.4, 31.1, 30.9. ESI-MS: m/z 221 $[\text{MH}^+]$.

Scheme 2. Synthesis of compound **1b** (racemic).

Compound **17**: ^1H NMR (500 MHz, CDCl_3): δ 7.42 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.47 (s, 1H), 4.82 (d, $J = 1.1$ Hz, 1H), 4.78 (d, $J = 1.1$ Hz, 1H), 4.26 (ddd, $J = 6.2$, 5.1, 1.5 Hz, 1H), 4.0-3.91 (m, 2H), 3.79 (s, 3H), 2.44 (dd, $J = 14.0$, 6.6 Hz, 1H), 2.24 (dd, $J = 14.0$, 6.3 Hz, 1H), 1.79 (s, 3H), 1.76 (m, 1H), 1.52 (m, 1H).

Compound **1b**: ^1H NMR (500 MHz, CDCl_3): δ 7.3 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.49 (s, 1H), 4.33 (m, 1H), 4.25 (dd, $J = 11.7$, 5.1 Hz, 1H), 3.98 (dt, $J = 11.8$, 2.6 Hz, 1H), 3.79 (s, 3H), 2.87 (dd, $J = 16.5$, 6.9 Hz, 1H), 2.58 (dd, $J = 16.5$, 5.9 Hz, 1H), 2.2 (s, 3H), 1.80

(ddt, $J = 12.5, 5.1, 5.1$ Hz, 1H), 1.62 (dt, $J = 13.2, 1.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 206.4, 159.8, 130.9, 127.2, 113.4, 100.9, 73.1, 66.6, 55.2, 49.4, 31.0, 30.9. ESI-MS: m/z 251 $[\text{MH}^+]$, 273 $[\text{MNa}^+]$.

Scheme 3. Synthesis of compound **1c**.

Compound 18: ^1H NMR (500 MHz, CDCl_3): δ 7.34 (d, $J = 8.8$ Hz, 2H), 7.24-7.02 (m, 5H), 6.79 (d, $J = 8.8$ Hz, 2H), 5.43 (s, 1H), 4.65 (m, 1H), 4.29 (ddd, $J = 11.7, 5.1, 1.5$ Hz, 1H), 4.19-4.07 (m, 3H), 3.99 (dd, $J = 9.1, 3.6$ Hz, 1H), 3.94 (dt, $J = 11.7, 2.6$ Hz, 1H), 3.73 (s, 3H), 3.15 (dd, $J = 13.9, 3.7$ Hz, 1H), 2.35 (dd, $J = 13.6, 9.6$ Hz, 1H), 1.91 (m, 1H), 1.65 (m, 1H), 1.18 (d, $J = 6.2$ Hz, 3H), ESI-MS: m/z 426 $[\text{MH}^+]$, 448 $[\text{MNa}^+]$.

Compound 19: ^1H NMR (500 MHz, CDCl_3): δ 7.37 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 5.45 (s, 1H), 4.26 (ddd, $J = 6.3, 5.2, 1.5$ Hz, 1H), 3.93 (dt, $J = 12.1, 2.6$ Hz, 1H), 3.79 (m, 1H), 3.78 (s, 3H), 3.67 (apparent t, $J = 4.2$ Hz, 2H), 2.24 (t, $J = 4.8$ Hz, 1H), 1.91-1.83 (m, 2H), 1.65 (dq, $J = 13.8, 2.2$ Hz, 1H), 0.94 (d, $J = 7$ Hz, 3H).

Compound 1c: ^1H NMR: (500 MHz, CDCl_3): δ 7.35 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.44 (s, 1H), 4.28 (ddd, $J = 6.3, 5.2, 1.5$ Hz, 1H), 4.02 (ddd, $J = 10.6, 8.5, 2.2$ Hz, 1H), 3.95 (dt, $J = 12.1, 2.6$ Hz, 1H), 3.79 (s, 3H), 2.82 (dq, $J = 7.4, 2.5$ Hz, 1H), 2.21 (s, 3H), 1.79 (dddd, $J = 11.2, 7.2, 5.2, 2.2$ Hz, 1H), 1.58 (m, 1H), 1.07 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 211.8, 160.0, 131.1, 127.3, 113.6, 100.9, 79.0, 66.9, 55.4, 51.6, 30.8, 28.7, 12.2. ESI-MS: m/z 265 $[\text{MH}^+]$, 263 $[\text{M-H}]^-$, 287 $[\text{MNa}^+]$, 299 $[\text{M+Cl}]^-$.

Compound **1d**: ^1H NMR (500 MHz, CDCl_3): δ 7.4–7.24 (m, 5H), 6.71 (d, J = 16.0 Hz, 1H), 6.12 (dd, J = 16.0, 4.4 Hz, 1H), 5.11 (dd, J = 4.4, 1.2 Hz, 1H), 4.21 (m, 1H), 3.94 (ddd, J = 11.2, 8.5, 2.4 Hz, 1H), 3.88 (dt, J = 11.8, 2.6 Hz, 1H), 2.79 (m, 1H), 1.75 (m, 1H), 1.54 (dq, J = 12.9, 2.3 Hz, 1H), 1.04 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 211.5, 136.0, 133.0, 128.5, 128.1, 126.8, 125.5, 100.2, 78.5, 66.5, 51.4, 30.6, 28.6, 12.0. ESI-MS: m/z 260 $[\text{MH}^+]$.

Scheme 4. Synthesis of compound **1e**.

Compound **21**: ^1H NMR: (500 MHz, CDCl_3): δ 7.02–7.16 (m, 5H), 5.86 (m, 1H), 5.06–5.03 (m, 2H), 4.46 (t, J = 5.1 Hz, 1H), 4.09 (ddd, J = 6.6, 5.1, 1.5 Hz, 1H), 3.68 (dt, J = 2.5, 6.6 Hz, 1H), 3.43 (ddd, J = 8.0, 5.8, 2.2 Hz, 1H), 2.72 (t, J = 8.1 Hz, 2H), 2.3 (dq, J = 5.8, 7.0 Hz, 1H), 1.94–1.9 (m, 2H), 1.44–1.31 (m, 2H), 1.04 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 141.8, 140.2, 128.4, 128.2, 125.7, 114.6, 101.0, 79.8, 66.5, 42.3, 36.3, 30.2, 28.2, 15.2.

Compound **1e**: ^1H NMR: (500 MHz, CDCl_3): δ 7.3–7.14 (m, 5H), 4.45 (t, J = 5.5 Hz, 1H), 4.13 (ddd, J = 6.2, 4.8, 1.1 Hz, 1H), 3.77–3.68 (m, 2H), 2.72 (dq, J = 7.4, 6.9 Hz, 1H), 2.66 (t, J = 7.3 Hz, 2H), 2.2 (s, 3H), 1.9–1.85 (m, 2H), 1.63 (ddt, J = 12.5, 4.8, 1.1 Hz, 1H), 1.49 (dq, J = 15.0, 1.8 Hz, 1H), 1.01 (d, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 211.6, 141.5, 128.3, 128.2, 125.7, 100.8, 78.4, 66.2, 51.4, 36.2, 30.6, 30.0, 28.7, 11.9. ESI-MS: m/z 263 $[\text{MH}^+]$, 285 $[\text{MNa}^+]$, 297 $[\text{M}+\text{Cl}]^-$.

Scheme 5. Synthesis of compound **1f**.

Compound **22**: ^1H NMR: (500 MHz, CDCl_3): δ 7.4-7.22 (m, 5H), 5.82 (ddd, $J = 17.2, 10.6, 7.7$ Hz, 1H), 5.04-5.0 (m, 1H), 4.67 (t, $J = 5.2$ Hz, 1H), 4.49 (ABq, $J = 12.1$ Hz, 2H), 4.08 (ddd, $J = 11.4, 5.2, 1.1$ Hz, 1H), 3.7 (dt, $J = 2.6, 11.4$ Hz, 1H), 3.59-3.57 (m, 2H), 3.45 (ddd, $J = 8.8, 5.8, 2.2$ Hz, 1H), 2.28 (dq, $J = 5.9, 7.0$ Hz, 1H), 1.94-1.9 (m, 2H), 1.42-1.31 (m, 2H), 1.03 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 140.2, 128.2, 127.5, 114.6, 99.5, 79.8, 72.8, 66.5, 65.6, 42.3, 35.3, 31.4, 27.1, 15.1.

Compound **1f**: ^1H NMR: (500 MHz, CDCl_3): δ 7.4-7.22 (m, 5H), 4.67 (t, $J = 5.5$ Hz, 1H), 4.46 (s, 2H), 4.11 (ddd, $J = 12.8, 3.6, 1.1$ Hz, 1H), 3.78-3.71 (m, 2H), 3.52 (dt, $J = 6.2, 3.3$ Hz, 2H), 2.67 (dq, $J = 7.0, 6.9$ Hz, 1H), 2.15 (s, 3H), 1.93-1.84 (m, 2H), 1.63 (dq, $J = 13.2, 5.1$ Hz, 1H), 1.49 (dq, $J = 13.2, 1.45$ Hz, 1H), 1.01 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 211.3, 138.3, 128.2, 127.5, 127.4, 99.4, 78.3, 72.8, 66.2, 65.4, 51.5, 35.1, 30.1, 28.7, 11.9. ESI-MS: m/z 293 $[\text{MH}^+]$, 315 $[\text{MNa}^+]$.

Scheme 6. Synthesis of compound **1g**.

Compound **24**: ^1H NMR (500 MHz, CDCl_3): δ 7.38 (dd, $J = 6.6, 1.8$ Hz, 2H), 6.87 (d, $J = 6.6, 1.8$ Hz, 2H), 5.43 (s, 1H), 4.25 (ddd, $J = 11.4, 5.2, 1.1$ Hz, 1H), 3.97 (ddd, $J = 11.3, 4.1, 2.2$ Hz, 1H), 3.92 (dt, $J = 12.1, 2.6$ Hz, 1H), 3.76 (s, 3H), 3.67 (t, $J = 8.1$ Hz, 1H), 3.56 (m, 1H), 2.65 (bs, 1H), 1.99 – 1.86 (m, 2H), 1.4 (dq, $J = 6.9, 1.5$ Hz, 1H), 0.97 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.7, 131.1, 127.1, 113.4, 101.1, 79.1, 66.8, 64.9, 55.1, 39.4, 27.2, 11.6.

Compound **1g**: ^1H NMR (500 MHz, CDCl_3): δ 7.38 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.47 (s, 1H), 4.42 (m, 1H), 4.24 (ddd, J = 11.1, 4.2, 1.2 Hz, 1H), 4.03 (m, 1H), 3.81 (s, 3H), 2.79 (m, 1H), 2.22 (s, 3H), 1.8 (m, 1H), 1.51 (ddt, J = 11.7, 3.6, 1.5 Hz, 1H), 1.21 (d, J = 7 Hz, 3H). ESI-MS: m/z 265 [MH^+], 287 [MNa^+], 299 [$\text{M}+\text{Cl}^-$]

Compound **1h**: See reference 6.

Scheme 7. Synthesis of compound **1i**

Compound **1i**: ^1H NMR (500 MHz, CDCl_3): δ 7.36 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.50 (s, 1H), 4.28 (ddd, J = 11.4, 4.8, 1.1 Hz, 1H), 4.01 (dd, J = 11.3, 2.2 Hz, 1H), 3.95 (dt, J = 11.3, 2.2 Hz, 1H), 3.81 (s, 3H), 2.2 (s, 3H), 1.82 (m, 1H), 1.45 (dq, J = 13.2, 2.2 Hz, 1H), 1.22 (s, 3H), 1.16 (s, 3H).

Scheme 8. Synthesis of compound **1j**

Compound **26**: ^1H NMR (400 MHz, CDCl_3): δ 7.66 (m, 4H), 7.4-7.26 (m, 11H), 4.7 (m, 1H), 4.19 (m, 3H), 3.85 (m, 3H), 3.46 (d, J = 2.4 Hz, 1H), 3.27 (dd, J = 13.5, 3.5 Hz, 1H), 2.78 (dd, J = 13.5, 9.7 Hz, 1H), 1.8 (m, 1H), 1.68 (m, 1H), 1.28 (d, J = 7.0 Hz, 3H), 1.04 (s, 9H).

Compound **27**: ^1H NMR (500 MHz, CDCl_3): δ 7.65 (m, 4H), 7.38 (m, 6H), 4.42 (t, $J = 5.2$ Hz, 1H), 3.97 (m, 1H), 3.87 (m, 2H), 3.82 (m, 1H), 3.72 (m, 1H), 1.78 (m, 1H), 1.6 (m, 3H), 1.41 (m, 1H), 1.07 (d, $J = 7.0$ Hz, 3H), 1.05 (s, 9H), 0.91 (t, $J = 7.4$ Hz, 3H).

Compound **1j**: ^1H NMR (600 MHz, CDCl_3): δ 4.49 (t, $J = 5.3$ Hz, 1H), 4.23 (m, 1H), 3.92 (dd, $J = 11.0, 2.2$ Hz, 1H), 3.86 (dd, $J = 11.0, 1.3$ Hz, 1H), 2.74 (dd, $J = 16.2, 8.3$ Hz, 1H), 2.36 (dd, $J = 16.2, 4.8$ Hz, 1H), 2.2 (s, 3H), 1.61 (dd, $J = 7.4, 4.8$ Hz, 1H), 1.6 (dd, $J = 7.4, 5.3$ Hz, 1H), 1.53 (m, 1H), 1.08 (d, $J = 7.0$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 207.0, 103.4, 75.1, 73.0, 46.6, 31.6, 31.0, 27.9, 11.3, 8.1.

Scheme 9. Synthesis of compound **1k**

Compound **28**: ^1H NMR (500 MHz, CDCl_3): δ 7.65 (m, 4H), 7.37 (m, 6H), 5.8 (m, 1H), 5.08 (m, 2H), 4.52 (t, $J = 5.5$ Hz, 1H), 3.98 (m, 1H), 3.85 (d, $J = 1.85$ Hz, 2H), (m, 2H), 3.8 (m, 1H), 3.72 (m, 1H), 2.36 (t, $J = 5.9$ Hz, 2H), 1.78 (m, 1H), 1.63 (m, 1H), 1.42 (m, 1H), 1.06 (d, $J = 6.5$ Hz, 3H), 1.05 (s, 9H).

Compound **1k**: ^1H NMR (600 MHz, CDCl_3): δ 5.8 (m, 1H), 5.1 (m, 2H), 4.61 (t, $J = 5.2$ Hz, 1H), 4.24 (ddd, $J = 8.3, 4.4, 2.2$ Hz, 1H), 3.91 (dd, $J = 11.4, 2.6$ Hz, 1H), 3.86 (dd, $J = 11.0, 1.3$ Hz, 1H), 2.75 (dd, $J = 15.8, 8.3$ Hz, 1H), 2.36 (m, 3H), 2.19 (s, 3H), 1.1 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 206.9, 132.5, 117.5, 101.6, 75.2, 73.0, 46.5, 39.4, 31.5, 31.1, 11.3. ESI-MS: m/z 197 $[\text{M}-\text{H}]^-$, 233 $[\text{M}+\text{Cl}]^-$.

Scheme 10. Synthesis of compound **1l**:

Compound **29**: ^1H NMR (500 MHz, CDCl_3): δ 7.36 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 7.8 Hz, 2H), 5.46 (s, 1H), 4.09 (dd, J = 11.4, 4.8 Hz, 1H), 3.78 (s, 3H), 3.69-3.67 (m, 3H), 3.5 (t, J = 11.0 Hz, 1H), 2.1 (m, 1H), 1.92 (m, 1H), 1.02 (d, J = 7.4 Hz, 3H), 0.75 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.7, 131.1, 127.2, 113.9, 100.9, 84.3, 73.0, 66.4, 55.2, 35.6, 30.3, 11.8, 9.6. ESI-MS: m/z 267 $[\text{MH}^+]$, 289 $[\text{MNa}^+]$, 301 $[\text{M}+\text{Cl}]^-$.

Compound **11**: ^1H NMR (500 MHz, CDCl_3): δ 7.34 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.43 (s, 1H), 4.11 (dd, J = 11.2, 4.8 Hz, 1H), 3.93 (dd, J = 10.2, 3.3 Hz, 1H), 3.78 (s, 3H), 3.53 (t, J = 11.0 Hz, 1H), 2.68 (dq, J = 2.9, 7.0 Hz, 1H), 2.21 (s, 3H), 2.02 (m, 1H), 1.23 (d, J = 7.0 Hz, 3H), 0.79 (d, J = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 210.4, 159.7, 130.8, 127.1, 113.4, 100.7, 83.0, 72.7, 55.2, 48.5, 30.9, 28.3, 11.9, 9.3. ESI-MS: m/z 279 $[\text{MH}^+]$, 301 $[\text{MNa}^+]$.

Scheme 11. Synthesis of compound **1m** (racemic):

Compound **1m**: ^1H NMR (500 MHz, CDCl_3): δ 7.36 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.48 (s, 1H), 4.34 (m, 1H), 4.23 (ddd, J = 11.4, 4.8, 1.1 Hz, 1H), 3.98 (dt, J = 11.75, 2.6 Hz, 1H), 3.79 (s, 3H), 2.84 (dd, J = 16.1, 7.35 Hz, 1H), 2.53 (dd, J = 16.1, 5.5 Hz, 1H), 2.48 (dq, J = 7.3, 4.0 Hz, 2H), 1.8 (m, 1H), 1.62 (m, 1H), 1.05 (t, J = 7.3 Hz, 3H). ESI-MS: m/z 265 $[\text{MH}^+]$, 287 $[\text{MNa}^+]$.

Scheme 12. Synthesis of compound **1n** (racemic).

Compound 31: ^1H NMR (500 MHz, CDCl_3): δ 7.28 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 4.44 (s, 2H), 4.06 (m, 1H), 3.81 (s, 3H), 3.68 (ddd, $J = 9.2, 6.3, 4.8$ Hz, 1H), 3.61 (ddd, $J = 9.2, 7.8, 4.5$ Hz, 1H), 3.30 (d, $J = 2.2$ Hz, 1H), 2.62 (dq, $J = 6.9, 4.2$ Hz, 1H), 2.54-2.48 (m, 2H), 1.75 and 1.62 (two sets of m, 2H), 1.12 (d, $J = 7.4$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H).

Compound 1n: ^1H NMR (500 MHz, CDCl_3): δ 7.38 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.47 (s, 1H), 4.22 (ddd, $J = 11.4, 5.2, 1.5$ Hz, 1H), 4.01 (ddd, $J = 13.6, 7.4, 2.6$ Hz, 1H), 3.93 (dt, $J = 11.7, 2.6$ Hz, 1H), 3.8 (s, 3H), 2.82 (dq, $J = 7, 7$ Hz, 1H), 2.53 (dq, $J = 7.3, 1.5$ Hz, 2H), 1.76 (m, 1H), 1.49 (dq, $J = 15.4, 2.6$ Hz, 1H), 1.20 (d, $J = 7.4$ Hz, 3H), 1.05 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 213.4, 159.9, 131.2, 127.3, 113.6, 101.25, 78.2, 66.8, 55.3, 50.9, 36.4, 28.7, 13.1, 7.6.

Compound 5a: See reference **11**.

Scheme 13. Synthesis of compound **5b** (racemic).

Compound 32: ^1H NMR (500 MHz, CDCl_3): δ 4.79 (s, 1H), 4.75 (s, 1H), 4.03-3.96 (m, 2H), 3.81 (ddd, $J = 11.7, 5.5, 1.5$ Hz, 1H), 2.76 (dd, $J = 13.9, 7.0$ Hz, 1H), 2.1 (dd, $J = 13.9, 5.8$ Hz, 1H), 1.96 (bm, 1H), 1.85 (bm, 1H), 1.76 (s, 3H), 1.67-1.54 (m, 10H).

Compound 5b: ^1H NMR (500 MHz, CDCl_3): δ 4.32 (m, 1H), 3.99 (dt, $J = 12.1, 2.9$ Hz, 1H), 3.75 (ddd, $J = 11.7, 5.5, 1.5$ Hz, 1H), 2.16 (s, 3H), 2.04 (bm, 1H), 1.73 (bm, 1H), 1.67-1.31 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3): δ 207.4, 98.7, 65.0, 59.1, 50.2, 38.8, 31.6, 31.4, 28.1, 25.8, 22.6, 22.5. ESI-MS: m/z 213 [MH^+], 235 [MNa^+].

Scheme 14. Synthesis of compound **7a** (racemic).

Compound 34: ^1H NMR (500 MHz, CDCl_3): δ 7.25 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 4.7 (d, J = 6.6 Hz, 1H), 4.45 (s, 2H), 3.82 (m, 1H), 3.81 (s, 3H), 3.71-3.61 (m, 2H), 2.94 (d, J = 3.5 Hz, 1H), 2.18-2.02 (m, 2H), 1.76-1.74 (m, 2H), 1.73 (s, 3H), 1.66-1.58 (m, 2H).

Compound 35: ^1H NMR (500 MHz, CDCl_3): δ 7.42 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.45 (s, 1H), 4.73 (bs, 1H), 4.70 (bs, 1H), 4.25 (ddd, J = 11.3, 5.2, 1.5 Hz, 1H), 3.94 (dt, J = 12.4, 2.6 Hz, 1H), 3.83 (m, 1H), 3.79 (s, 3H), 2.22-2.07 (m, 2H), 1.85-1.76 (m, 2H), 1.73 (s, 3H), 1.69-1.63 (m, 2H).

Compound 7a: ^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.43 (s, 1H), 4.24 (ddd, J = 11.4, 4.8, 1.1 Hz, 1H), 3.93 (dt, J = 11.7, 2.6 Hz, 1H), 3.82 (m, 1H), 3.80 (s, 3H), 2.67-2.58 (m, 2H), 2.14 (s, 3H), 1.93-1.76 (m, 3H), 1.50 (dq, J = 11.0, 2.6 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 208.8, 163.3, 127.4, 113.7, 101.2, 76.1, 67.0, 55.4, 39.1, 31.4, 30.2, 29.9, 29.8.

Scheme 15. Synthesis of compound **7b** (racemic).

Compound 36: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.25 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 5.38 (q, $J = 7.0$ Hz, 1H), 4.45 (s, 2H), 3.94 (m, 1H), 3.80 (s, 3H), 3.71-3.6 (m, 2H), 2.75 (d, $J = 2.2$ Hz, 1H), 2.32 (dd, $J = 13.2, 8.1$ Hz, 1H), 2.12 (dd, $J = 12.7, 5.5$ Hz, 1H), 1.76 (m, 1H), 1.71 (d, $J = 1.1$ Hz, 3H), 1.6 (m, 1H), 1.56 (s, 3H).

Compound 37: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.42 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.46 (s, 1H), 5.36 (q, $J = 6.25$ Hz, 1H), 4.24 (ddd, $J = 11.7, 5.2, 1.0$ Hz, 1H), 3.95-3.89 (m, 2H), 3.79 (s, 3H), 1.76 (t, $J = 1.5$ Hz, 3H), 1.60 (m, 1H), 1.62-1.58 (m, 3H), 1.54 (s, 3H).

Compound 7b: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.42 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.39 (s, 1H), 4.23 (ddd, $J = 11.4, 4.8, 1.1$ Hz, 1H), 3.91 (td, $J = 11.7, 2.6$ Hz, 1H), 3.81 (s, 3H), 3.77 (m, 1H), 2.92 (dq, $J = 9.5, 6.9, 3.0$ Hz, 1H), 2.15 (s, 3H), 1.93 (ddd, $J = 13.9, 9.5, 3.3$ Hz, 1H), 1.76 (ddt, $J = 12.8, 4.8, 1.1$ Hz, 1H), 1.63 (ddd, $J = 14.0, 9.6, 4.4$ Hz, 1H), 1.51 (dq, $J = 13.2, 1.5$ Hz, 1H), 1.13 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 212.7, 159.9, 131.4, 127.3, 113.69, 101.1, 75.2, 67.0, 55.4, 42.6, 39.1, 31.7, 29.1, 17.6.

Scheme 16. Synthesis of compound **10a-10b**.

Compound 10a: ^1H NMR (400 MHz, CDCl_3): δ 4.52 (t, $J = 5.0$ Hz, 1H), 4.06 (ddd, $J = 11.4$, 5.0, 1.5 Hz, 1H), 3.71 (m, 2H), 2.46 (t, $J = 7.4$ Hz, 2H), 2.13 (s, 3H), 1.7-1.59 (m, 5H), 1.43 (m, 1H), 1.21 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 101.6, 72.7, 66.5, 43.4, 34.3, 33.0, 29.8, 21.7, 18.4.

Compound 10b: ^1H NMR (400 MHz, CDCl_3): δ 7.35 (m, 2H), 7.28 (m, 1H), 4.74 (t, $J = 5.0$ Hz, 1H), 4.66 (dd, $J = 11.4$, 2.6 Hz, 1H), 4.18 (dd, $J = 11.4$, 5.0 Hz, 1H), 3.88 (td, $J = 12.0$, 2.6 Hz, 1H), 2.47 (t, $J = 7.3$ Hz, 2H), 2.11 (s, 3H), 1.97 (m, 1H), 1.70 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 141.7, 128.4, 127.6, 125.8, 101.9, 78.5, 66.7, 43.3, 34.3, 33.3, 29.8, 18.3.

Dibutylborontriflate/*i*-Pr₂NEt-mediated aldol-type cyclization reaction.

Procedure A: To a solution of the substrate (1mmol) in CH_2Cl_2 (10 mL) at -78°C , was added *i*-Pr₂NEt (1.2 mmol), followed by rapid addition of Bu_2BOTf (1 M in CH_2Cl_2 , 1.2 mmol). The resulting reaction mixture was stirred at -78°C for 10-15 min, then PBS buffer (pH = 7.4, 1.2 mL), methanol (1.2 mL), and H_2O_2 (0.4 mL) were added. The stirring was continued for 1h at 0°C and 1 h at room temperature. The clear solution was extracted with ether, washed with

aqueous NaHCO₃ solution and then with brine, and dried over Na₂SO₄. Solvents were removed under vacuum and residue was purified by column chromatography.

Procedure B: 1.2 equivalents of *i*-Pr₂NEt and 1.5 equivalents of Bu₂BOTf were used.

4a

Compound **4a**: ¹H NMR (500 MHz, CDCl₃): δ 7.35-7.31 (m, 5H), 4.69 (dd, *J* = 11.0, 3.0 Hz, 1H), 4.04 (m, 1H), 3.90-3.82 (m, 2H), 2.67-2.55 (m, 2H), 2.47 (dd, *J* = 6.6, 0.8 Hz, 2H), 2.31 (bs, 1H), 2.02 and 1.87 (two sets of m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 206.2, 140.6, 128.8, 128.3, 125.7, 79.1, 76.7, 60.4, 49.6, 47.8, 38.6. ESI-MS: *m/z* 221 [MH⁺], 243 [MNa⁺].

4b

Compound **4b**: ¹H NMR (500 MHz, CDCl₃): δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.64 (t, *J* = 7.3 Hz, 1H), 4.03 (m, 1H), 3.88-3.83 (m, 2H), 3.81 (s, 3H), 2.6 (d, *J* = 7.7 Hz, 2H), 2.47 (d, *J* = 7.7 Hz, 2H), 2.23 (bs, 1H), 2.02 and 1.87 (two sets of m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 206.4, 159.6, 132.7, 127.1, 114.2, 78.8, 76.7, 60.5, 55.5, 49.6, 47.8, 38.5. ESI-MS: *m/z* 221 [MH⁺], 249 [M-H]⁻, 273 [MNa⁺], 285 [M+Cl]⁻

Compound **4c**: ^1H NMR: (500 MHz, CDCl_3): δ 7.26 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 4.64 (dd, $J = 10.6, 3.5$ Hz, 1H), 3.87-3.85 (m, 2H), 3.81 (s, 3H), 3.65 (dt, $J = 2.8, 1.0$ Hz, 1H), 2.71-2.65 (m, 2H), 2.54-2.45 (m, 2H), 2.06 (m, 1H), 1.93 (m, 1H), 1.06 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 207.7, 159.6, 132.8, 127.0, 114.2, 82.9, 79.2, 60.8, 55.4, 50.1, 49.7, 36.3, 9.4. ESI-MS: m/z 265 [MH^+], 287 [MNa^+].

Compound **4d**: ^1H NMR (600 MHz, CDCl_3): δ 7.38 (m, 2H), 7.32 (m, 2H), 7.27 (m, 1H), 6.6 (d, $J = 16.2$ Hz, 1H), 6.21 (dd, $J = 16.2, 6.1$ Hz, 1H), 4.34 (m, 1H), 3.88 (m, 2H), 3.59 (dt, $J = 9.2, 2.2$ Hz, 1H), 2.57 (m, 2H), 2.51 (bs, 1H), 2.45 (m, 1H), 2.05 (m, 1H), 2.04 (m, 1H), 1.04 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 207.2, 163.1, 135.9, 131.6, 128.6, 128.1, 127.8, 126.6, 82.5, 78.0, 60.6, 49.9, 47.9, 36.1, 9.2. GC-MS: m/z 260 [M^+].

Compound **4e**: ^1H NMR (500 MHz, CDCl_3): δ 7.48-7.05 (m, 5H), 3.87 (t, $J = 5.1$ Hz, 2H), 3.58 (ddd, $J = 11.3, 7.7, 3.6$ Hz, 1H), 3.44 (dt, $J = 2.6, 9.6$ Hz, 1H), 2.81-2.66 (m, 2H), 2.62 (bs, 1H), 2.42-2.33 (m, 3H), 2.02-1.77 (m, 4H), 0.99 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 207.7, 140.9, 128.4, 128.2, 125.9, 82.11, 76.4, 60.5, 49.9, 47.7, 37.8, 36.1, 31.4, 9.1. ESI-MS: m/z 263 $[\text{MH}^+]$, 285 $[\text{MNa}^+]$, 261 $[\text{M-H}]^-$, 297 $[\text{M+Cl}]^-$. $[\alpha]_{\text{D}}^{20} -7.8$ (c 2.29, CHCl_3).

Compound **4f**: ^1H NMR (500 MHz, CDCl_3): δ 7.41-7.24 (m, 5H), 4.51 (Abq, $J = 11.7, 12.1$ Hz, 2H), 3.86-3.79 (m, 3H), (t, $J = 5.1$ Hz, 2H), 3.44 (dt, $J = 2.6, 9.9$ Hz, 1H), 2.78 (bs, 1H), 2.45-2.31 (m, 3H), 1.99-1.77 (m, 4H), 1.0 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 207.7, 138.0, 128.3, 127.7, 127.0, 82.4, 75.0, 73.0, 66.1, 60.6, 49.9, 47.8, 36.3, 36.0, 9.1. ESI-MS: m/z 293 $[\text{MH}^+]$, 315 $[\text{MNa}^+]$, 291 $[\text{M-H}]^-$, 327 $[\text{M+Cl}]^-$. $[\alpha]_{\text{D}}^{20} -10.04$ (c 2.65, CHCl_3).

Compound **4g**: ^1H NMR (500 MHz, CDCl_3): δ 7.29 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 4.62 (dd, $J = 11.7, 2.6$ Hz, 1H), 3.99 (m, 1H), 3.81 (s, 3H), 3.89-3.79 (m, 2H), 2.76 (dd, $J = 14.3, 11.7$ Hz, 1H), 2.23 (m, 1H), 2.52 (dd, $J = 13.9, 2.6$ Hz, 1H), 2.08 (m, 1H), 1.71 (bs, 1H), 1.59 (m, 1H), 1.27 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 210.6, 159.6, 132.9,

128.3, 114.3, 79.1, 78.7, 61.0, 55.4, 51.2, 49.38, 34.4, 11.3. ESI-MS: m/z 265 $[MH^+]$, 287 $[MNa^+]$.

Compound **4h**: 1H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, $J = 6.9$ Hz, 2H), 6.8 (d, $J = 6.9$ Hz, 2H), 4.64 (dd, $J = 9.1, 2.9$ Hz, 1H), 3.8 (s, 3H), 3.76-3.71 (m, 2H), 3.67 (dd, $J = 8.7, 1.8$ Hz, 1H), 2.64-2.57 (m, 3H), 2.2 (bs, 1H), 1.96 (m, 1H), 1.12 (d, $J = 5.9$ Hz, 3H), 1.03 (d, $J = 5.5$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.4, 163.1, 159.2, 133.1, 126.7, 113.9, 84.1, 78.9, 66.8, 55.2, 49.9, 47.1, 36.4, 8.8, 8.7. ESI-MS: m/z 279 $[MH^+]$, 301 $[MNa^+]$, 313 $[M+Cl]^-$.

$[\alpha]_D^{20} +101.6$ (c 1.15, $CHCl_3$).

Compound **4i**: 1H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 4.64 (dd, $J = 12.1, 2.9$ Hz, 1H), 3.85-3.77 (m, 2H), 3.8 (s, 3H), 3.66 (dd, $J = 10.6, 1.8$ Hz, 1H), 2.86 (dd, $J = 14.3, 12.1$ Hz, 1H), 2.50 (dd, $J = 14.3, 3.0$ Hz, 1H), 1.95 (m, 1H), 1.75 (m, 1H), 1.23 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.9, 159.5, 132.9, 126.9, 114.1, 84.1, 79.2, 61.5, 55.4, 49.2, 46.2, 31.5, 19.5, 18.9. ESI-MS: m/z 279 $[MH^+]$, 301 $[MNa^+]$.

4j

Compound **4j**: ¹H NMR (600 MHz, CDCl₃): δ 3.80 (m, 1H), 3.71 (m, 2H), 3.52 (m, 1H), 2.47-2.37 (m, 3H), 2.30 (m, 1H), 2.24 (m, 1H), 1.95 (m, 1H), 1.65 (m, 1H), 1.59 (m, 1H), 0.99 (d, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 207.7, 79.5, 78.7, 65.7, 47.5, 44.2, 39.2, 29.3, 11.2, 9.6. GC-MS: *m/z* 185 [M⁺].

4k

Compound **4k**: ¹H NMR (600 MHz, CDCl₃): δ 5.82 (m, 1H), 5.12 (m, 2H), 3.80 (dt, *J* = 12.3, 3.1 Hz, 1H), 3.69 (m, 3H), 2.48-2.27 (m, 7H), 1.19 (m, 1H), 1.0 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 207.3, 133.2, 118.3, 79.5, 76.7, 65.8, 47.2, 44.2, 40.4, 39.1, 11.0. GC-MS: *m/z* 198 [M⁺], ESI-MS: *m/z* 221 [MNa⁺], 233 [M-Cl]⁻.

4l

Compound **4l**: ¹H NMR (500 MHz, CDCl₃): δ 7.28 (d, *J* = 7.3 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 4.6 (dd, *J* = 9.1, 2.1 Hz, 1H), 3.8 (s, 3H), 3.69 (dd, *J* = 9.5, 6.6 Hz, 1H), 3.63 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.6 (m, 1H), 2.96 (bd, *J* = 6.6 Hz, 1H), 2.78 (dd, *J* = 12.0, 10.2 Hz, 1H), 2.56 (dq, *J* = 1.6, 5.9 Hz, 1H), 2.46 (dd, *J* = 12.0, 2.1 Hz, 1H), 1.24 (d, *J* = 5.9 Hz, 3H), 0.82 (d, *J* = 5.8 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 210.2, 159.4, 132.5, 126.8, 113.9, 84.2, 79.1, 67.5, 55.2,

46.9, 45.7, 36.0, 12.2, 10.6. ESI-MS: m/z 279 $[MH^+]$, 301 $[MNa^+]$, 317 $[MK^+]$, 277 $[M-H]^-$. $[\alpha]_D^{20} -111.8$ (c 2.5, $CHCl_3$).

4m

Compound **4m**: 1H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 4.16 (d, $J = 10.7$ Hz, 1H), 4.01 (m, 1H), 3.81 (s, 3H), 3.83-3.78 (m, 2H), 2.64 – 2.59 (m, 2H), 2.34 (dq, $J = 10.6, 6.6$ Hz, 1H), 2.11 and 1.96 (two sets of m, 2H), 0.80 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.8, 159.7, 131.8, 127.1, 114.1, 85.7, 77.6, 60.6, 55.4, 51.6, 48.2, 38.5, 9.6. ESI-MS: m/z 265 $[MH^+]$, 287 $[MNa^+]$.

4n

Compound **4n**: 1H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 4.13 (d, $J = 10.7$ Hz, 1H), 4.01 (dt, $J = 9.9, 2.6$ Hz, 1H), 3.81 (s, 3H), 3.78-3.75 (m, 2H), 2.79 (dq, $J = 10.3, 6.6$ Hz, 1H), 2.51 (dq, $J = 7.4, 2.6$ Hz, 1H), 2.08 (m, 1H), 1.57 (m, 1H), 1.31 (d, $J = 7.4$ Hz, 3H), 0.80 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.3, 160.0, 132.4, 128.6, 114.3, 86.4, 79.7, 61.5, 55.7, 50.1, 47.6, 34.6, 11.8, 9.8. ESI-MS: m/z 279 $[MH^+]$, 301 $[MNa^+]$.

6a

Compound **6a**: ^1H NMR (400 MHz, CDCl_3): δ 3.95 (m, 1H), 3.76 (m, 1H), 3.58 (m, 1H), 2.43 (dd, $J = 14.1, 11.4$ Hz, 1H), 2.32 (s, 2H), 2.24 (ddd, $J = 14.1, 2.9, 0.9$ Hz, 1H), 2.22 (bs, 1H), 1.77-1.72 (m, 3H), 1.57 (m, 1H), 1.51-1.42 (m, 4H), 1.29 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 207.7, 76.4, 69.9, 65.6, 52.5, 42.9, 39.1, 31.7, 25.2, 21.7, 21.1. ESI-MS: m/z 197 [MNa^+].

6b

Compound **6b**: ^1H NMR (500 MHz, CDCl_3): δ 4.06 (tt, $J = 8.4, 3.3$ Hz, 1H), 3.85 (t, $J = 5.8$ Hz, 2H), 2.80 (bs, 1H), 2.36-2.27 (m, 4H), 1.93-1.74 (m, 4H), 1.66 – 1.23 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3): δ 207.5, 76.7, 69.8, 60.9, 52.8, 47.6, 39.2, 38.6, 31.7, 25.3, 21.9, 21.1. ESI-MS: m/z 213 [MH^+], 235 [MNa^+].

8a

Compound **8a**: ^1H NMR (500 MHz, CDCl_3): δ 7.36 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 4.86 (dd, $J = 11, 2.2$ Hz, 1H), 3.98 (tt, $J = 9.55, 2.6$ Hz, 1H), 3.79 (s, 3H), 3.75 (dt, $J = 5.1, 4.4$ Hz, 2H), 2.98 (dd, $J = 17.2, 11.3$ Hz, 1H), 2.90 (ddd, $J = 16.1, 12.5, 3.7$ Hz, 1H), 2.79 (dd, $J = 16.9, 2.6$ Hz, 1H), 2.66 (ddd, $J = 14.3, 6.3, 3.0$ Hz, 1H), 2.28 (t, $J = 2.3$ Hz, 1H), 1.94-1.69 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 210.6, 159.3, 134.0, 126.8, 114.2, 83.1, 78.4, 61.0, 55.4, 53.6, 42.2, 36.7, 32.6. ESI-MS: m/z 265 [MH^+], 287 [MNa^+], 299 [$\text{M}+\text{Cl}^-$].

Compound **9a**: ^1H NMR (500 MHz, CDCl_3): δ 7.17 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.12 (d, J = 8.4 Hz, 1H), 4.15 (m, 1H), 3.91-3.86 (m, 2H), 3.78 (s, 3H), 3.52 (apparent q, J = 8.4 Hz, 1H), 2.41 (bs, 1H), 2.23 (m, 1H), 2.16-2.00 (m, 3H), 1.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 208.2, 159.8, 130.4, 128.4, 114.2, 82.7, 78.9, 61.5, 57.4, 55.6, 37.1, 34.2, 31.2. ESI-MS: m/z 265 [MH^+], 287 [MNa^+].

Compound **8b**: ^1H NMR (500 MHz, CDCl_3): δ 7.38 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 4.56 (dd, J = 10.6, 2.6 Hz, 1H), 3.82 (m, 1H), 3.81 (s, 3H), 3.80 (q, J = 5.5 Hz, 2H), 3.05 (dd, J = 12.9, 10.7 Hz, 1H), 2.95 (m, 1H), 2.74 (dd, J = 12.8, 2.6 Hz, 1H), 2.23 (t, J = 5.5 Hz, 1H), 2.12 (ddd, J = 14.6, 8.0, 6.2 Hz, 1H), 1.91 (dq, J = 9.5, 7.0, 5.8 Hz, 1H), 1.70 (m, 2H), 1.18 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 211.8, 159.3, 134.2, 127.0, 114.1, 78.9, 78.3, 61.1, 55.4, 53.9, 43.2, 39.3, 37.6, 16.2. ESI-MS: m/z 279 [MH^+].

Compound **11a** and **12a** (1:1 mixture of two diastereomers): ^1H NMR (400 MHz, CDCl_3): δ 3.96 (m, 1H), 3.86 (m, 1H), 3.83-3.61 (m, 6H), 2.63-2.54 (m, 3H), 2.45-2.3 (m, 5H), 2.11-1.91 (m, 4H), 1.86-1.57 (m, 8H), 1.18 (d, $J = 6.2$ Hz, 3H), 1.13 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 210.9, 209.5, 74.6, 73.9, 72.6, 70.3, 60.5, 59.5, 48.9, 46.8, 41.3, 40.9, 39.1, 38.9, 31.4, 30.1, 21.5, 20.7, 20.1, 19.9. ESI-MS: m/z 185 $[\text{M} - \text{H}]^-$, 209 $[\text{MNa}^+]$.

11b

Compound **11b**: ^1H NMR (500 MHz, CDCl_3): δ 7.30 (m, 5H), 4.65 (dd, $J = 9.7, 4.1$ Hz, 1H), 3.77 (m, 2H), 3.67 (m, 1H), 2.46 (m, 1H), 2.38-2.22 (m, 3H), 2.18 (m, 1H), 2.04-1.98 (m, 3H), 1.86 (m, 2H), 1.66 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 209.3, 141.8, 128.6, 127.8, 126.4, 78.4, 74.1, 60.6, 48.7, 40.9, 40.8, 28.6, 20.5. ESI-MS: m/z 271 $[\text{MNa}^+]$, 283 $[\text{M} + \text{Cl}]^-$.

12b

Compound **12b**: ^1H NMR (500 MHz, CDCl_3): δ 7.33 (m, 5H), 4.67 (dd, $J = 7.0, 6.6$ Hz, 1H), 3.81 (m, 1H), 3.75 (m, 1H), 3.67 (m, 1H), 2.66 (m, 1H), 2.57 (m, 1H), 2.55 (dd, $J = 14.0, 3.3$ Hz, 1H), 2.36 (m, 2H), 1.87-1.8 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3): δ 211.4, 142.3, 128.5, 127.6, 126.3, 76.3, 74.1, 59.4, 45.8, 40.9, 31.2, 21.9. ESI-MS: m/z 271 $[\text{MNa}^+]$, 283 $[\text{M} + \text{Cl}]^-$.

GC-MS Analysis of pure **1b** and crude residue from the reaction of **1b** with Bu₂BOTf/*i*-Pr₂NEt
(See pages S-24 to S-26).

The reaction was quenched before completion. In the crude residue from the reaction of **1b** with Bu₂BOTf/*i*-Pr₂NEt, two major peaks were noticed. They are: **1b**, R_T = 19.72 min and product **4b**, R_T = 20.49 min. Three minor peaks appeared at 15.06, 19.76, and 19.87, which did not correspond to a diastereomer of **4b** from an inspection of their MS data.

LC-MS Analysis of pure **11b** and **12b**, and crude residue from the reaction of **11b** with Bu₂BOTf/*i*-Pr₂NEt.

(See pages S-27 to S-29).

References for supporting information:

1. Paquette, L. A.; Peng, X.; Bondar, D. *Org. Lett.* **2002**, *4*, 937-940.
2. Penning, T.D.; Djuric, S. W.; Haack, R. A.; Kalish, V. J.; Miyashiro, J. M.; Rowell, B. W.; Yu, S. S. *Synth. Commun.* **1990**, *20*, 307-312.
3. Drouet, K. E.; Theodorakis, E. A. *Chem. Eur. J.* **2000**, *6*, 1987-2001.
4. Nishimura, T.; Kakiuchi, N.; Onoue, T.; Ohe, K.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1915-1918.
5. Chakraborty, T. K.; Das, S. *Tetrahedron Lett.* **2001**, *42*, 3387-3390.
6. Arefolov, A.; Panek, J. S. *Org. Lett.* **2002**, *4*, 2397-2400.
7. Claus, E.; Pahl, A.; Jones, P. G.; Meyer, H. M.; Kalesse, M. *Tetrahedron. Lett.* **1997**, *38*, 1359-1362
8. Paterson, I.; Delgado, O.; Florence, G. J.; Lyothier, I.; Scott, J. P.; Sereinig, N. *Org. Lett.* **2003**, *5*, 35-38.
9. Inoue, T.; Mukaiyama, T. *Bull.Chem. Soc. Jpn.* **1980**, *53*, 174-178.
10. Evans D.A.; Rieger, D. L.; Bilodeau, M. T.; Urpi, F. *J. Am. Chem. Soc.* **1991**, *113*, 1047-1049.
11. Ohi, K.; Nishiyama, S. *Synlett* **1999**, 573-575.