Supporting Information for:

Selective Palladium-catalysed Synthesis of Diesters:
Alkoxy carbonylation of a CO$_2$-butadiene derived $\delta$-lactone

Francesco Ferretti,[a,b] Muhammad Sharif,[a,c] Sarim Dastgir,*[d,e] Fabio Ragaini,[b] Ralf Jackstell*[a] and Matthias Beller*[a]

[a] Dr. Francesco Ferretti, Dr. Muhammad Sharif, Dr. Ralf Jackstell and Prof. Dr. Matthias Beller
Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, Rostock, 18059, Germany.

[b] Dr. Francesco Ferretti, Prof. Dr. Fabio Ragaini
Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano, Italy.

[c] Dr. Muhammad Sharif
Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, 31261, Saudi Arabia.

[d] Dr. Sarim Dastgir
Qatar Environment and Energy Research Institute (QEERI), Hamad bin Khalifa University (HBKU), Qatar Foundation, Doha, Qatar.

[e] Dr. Sarim Dastgir
College of Science and Engineering, Hamad bin Khalifa University (HBKU), Doha, Qatar.

*To whom the correspondence should be addressed: matthias.beller@catalysis.de; sdastgir@hbku.edu.qa
1. Hydrogenation of dimethyl 7-ethylideneoct-3-enedioate (2a) to 2-ethyloctane-1,8-diol (5) with homogeneous catalysts.

**General procedure for hydrogenation of 2-ethyloctane-1,8-diol 5.** Metal complex or catalyst precursor and ligand were quickly weighed in a 4 mL vial in the air. The vial was then sealed, connected to the atmosphere with a needle and evacuated and refilled with argon for three times. 2a (0.5 mmol) and a stock solution of the solvent containing the appropriate additive were added. The vial was placed inside a 300 mL stainless steel Parr autoclave and the autoclave was flushed three times with nitrogen, pressurized with hydrogen and heated. After the reaction time, the autoclave was cooled with ice water and vented. The crude was analyzed by gas-chromatography.

**Table S1. Hydrogenation of 2a to 5.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Additive (mol%)</th>
<th>CO (bar)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>5 Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>c1</td>
<td>THF</td>
<td>MeONa (10)</td>
<td>50</td>
<td>120</td>
<td>22</td>
<td>traces</td>
</tr>
<tr>
<td>2</td>
<td>c2</td>
<td>THF</td>
<td>-</td>
<td>50</td>
<td>120</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>c3</td>
<td>THF</td>
<td>-</td>
<td>70</td>
<td>150</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>c4</td>
<td>MeOH</td>
<td>MSA (10)</td>
<td>70</td>
<td>150</td>
<td>22</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>c4</td>
<td>MeOH</td>
<td>HNTf₂ (10)</td>
<td>70</td>
<td>150</td>
<td>22</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>c4</td>
<td>MeOH</td>
<td>MSA (5)/Zn (5)</td>
<td>70</td>
<td>150</td>
<td>24</td>
<td>42</td>
</tr>
<tr>
<td>7</td>
<td>c4</td>
<td>MeOH</td>
<td>HNTf₂ (5)/Zn (5)</td>
<td>70</td>
<td>150</td>
<td>24</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>c4</td>
<td>MeOH</td>
<td>MeONa</td>
<td>70</td>
<td>150</td>
<td>22</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>c4</td>
<td>dioxane</td>
<td>HNTf₂ (5)</td>
<td>70</td>
<td>150</td>
<td>22</td>
<td>24</td>
</tr>
</tbody>
</table>

*Reactions conditions: 2a (0.5 mmol), metal complex (0.01mmol), ligand when added (0.02 mmol), solvent (2 mL). Conversion of 2a was complete in all cases. Yields were determined by GC analysis using hexadecane as the internal standard.

2. Characterization of products and NMR spectra

Dimethyl 7-ethylideneoct-3-enedioate (2a): 1H NMR (300 MHz, CDCl₃) δ 6.79 (q, J = 7.1 Hz, 1H, E/Z isomers), 5.56 – 5.38 (m, 2H, E/Z isomers), 3.65 (s, 3H, OCH₃, Z isomer), 3.64 (s, 3H, OCH₃, E isomer), 3.60 (s, 3H, OCH₃, Z isomer), 3.59 (s, 3H, OCH₃, E/Z isomers), 3.00 (d, J = 5.9 Hz, 2H, Z isomer), 2.94 (d, J = 5.1 Hz, 2H, E isomer), 2.35 – 2.24 (m, 2H, E/Z isomers), 2.12 – 1.97 (m, 2H, E/Z isomers), 1.73 (d, 3H, CH₃, Z isomer overlapped with the CHCH₃ signal of E isomer), 1.71 ppm (d, J = 7.1 Hz, 3H, CH₃, E isomer).
13C NMR (75 MHz, CDCl3) δ 172.4, 172.3 (Z isomer), 168.15, 168.11 (Z isomer), 138.2 (Z isomer), 138.0, 133.8, 132.3, 132.3 (Z isomer), 132.2 (Z isomer), 122.2, 121.6 (Z isomer), 51.82 (Z isomer), 51.76, 51.6, 37.91, 32.7 (Z isomer), 31.8, 26.7 (Z isomer), 26.15, 26.09 (Z isomer), 14.4 (Z isomer), 14.3 ppm.

GCMS-EI m/z (%) = 226 (M⁺, 1), 194 (13), 179 (7), 162 (100), 147 (10), 134 (67), 120 (20), 107 (29), 93 (16), 91 (20), 81 (22), 71 (26), 59 (30).


Dibutyl 7-ethylideneoct-3-enedioate (2b): 1H NMR (300 MHz, CDCl3) δ 6.79 (q, J = 7.1 Hz, 1H, E/Z isomers), 5.11 – 3.92 (m, 4H, E/Z isomers), 2.99 (d, J = 5.4 Hz, 2H, Z isomer), 2.93 (d, J = 5.1 Hz, 2H, E isomer), 2.31 (t, J = 7.6 Hz, 2H, E/Z isomers), 2.16 – 1.90 (m, 2H, E/Z isomers), 1.73 (d, 3H, CH3, Z isomer overlapped with the CH3 signal of E isomer), 1.70 (d, J = 7.2 Hz, 3H, CH3, E isomer), 1.63 – 1.45 (m, 4H, E/Z isomers), 1.43 – 1.15 (m, 4H, E/Z isomers), 0.86 ppm (m, 6H, E/Z isomers).

13C NMR (75 MHz, CDCl3) δ 171.9, 171.8 (Z isomer), 167.6, 137.6 (Z isomer), 137.4, 133.5, 132.6, 132.5 (Z isomer), 132.0 (Z isomer), 122.3, 121.7 (Z isomer), 64.3, 64.1, 38.1, 32.8 (Z isomer), 31.8, 30.7, 30.6, 26.7 (Z isomer), 26.1, 26.0 (Z isomer), 19.2, 19.1, 14.2, 13.7, 13.6 ppm.

GCMS-EI m/z (%) = 310 (M⁺, 1), 236 (7), 208 (6), 179 (11), 162 (100), 147 (8), 134 (50), 120 (11), 107 (22), 99 (13), 93 (12), 81 (13), 67 (5), 57 (27), 54 (26), 41 (39).


Bis(2-ethylhexyl) 7-ethylideneoct-3-enedioate (2c): 1H NMR (300 MHz, CDCl3) δ 6.84 (q, J = 7.1 Hz, 1H, E/Z isomers), 5.63 – 3.92 (m, 4H, E/Z isomers), 3.07 (d, J = 5.2 Hz, 2H, Z isomer), 3.03 (d, J = 4.2 Hz, 2H, E isomer), 2.50 – 2.30 (m, 2H E/Z isomers), 2.21 – 2.08 (m, 2H E/Z isomers), 1.75 (d, J = 7.1 Hz, 3H, CH3, Z isomer overlapped with the CH3 signal of E isomer), 1.74 ppm (d, J = 7.2 Hz, 3H, CH3, E isomer), 1.65 – 1.44 (m, 2H, E/Z isomers), 1.43 – 1.12 (m, 16H, E/Z isomers), 0.98 – 0.77 ppm (m, 12H, E/Z isomers).

13C NMR (75 MHz, CDCl3) δ 172.2, 167.8, 137.8 (Z isomer), 137.6, 133.6, 132.6, 132.1 (Z isomer), 122.4, 121.7 (Z isomer), 67.0, 66.6, 38.9, 38.7, 38.2, 33.0 (Z isomer), 31.9, 30.6, 30.4, 28.98, 28.91, 26.8 (Z isomer), 26.3, 26.1 (Z isomer), 24.0, 23.8, 23.0, 14.4 (Z isomer), 14.3, 14.0, 11.1, 11.0 ppm.

GCMS-EI m/z (%) = 422 (M⁺, 0.3), 292 (4), 264 (4), 198 (4), 180 (44), 162 (100), 152 (12), 134 (29), 107 (15), 81 (8), 71 (44), 57 (69), 43 (41).


Dibenzyl 7-ethylideneoct-3-enedioate (2d): 1H NMR (300 MHz, CDCl3) δ 7.39 – 7.21 (m, 10H, E/Z isomers), 6.92 (q, J = 7.1 Hz, 1H, E/Z isomers), 5.67 – 5.43 (m, 2H, E/Z isomers), 5.16 (s, 2H, E/Z isomers), 3.07 (d, J = 5.2 Hz, 2H, Z isomer), 3.03 (d, J = 4.2 Hz, 2H, E isomer), 2.50 – 2.30 (m, 2H E/Z isomers), 2.21 – 2.08 (m, 2H E/Z isomers), 1.75 (d, J = 7.1 Hz, 3H, CH3, Z isomer overlapped with the CH3 signal of E isomer), 1.74 ppm (d, J = 7.2 Hz, 3H, CH3, E isomer, Z isomer overlapped with the CH3 signal of E isomer).

13C NMR (75 MHz, CDCl3) δ 171.7, 171.6 (Z isomer), 167.3, 138.5 (Z isomer), 138.4, 136.4, 135.9, 133.8, 132.3, 132.2 (Z isomer), 128.5, 128.2, 128.0, 127.9, 122.2, 121.6 (Z isomer), 66.3, 66.1, 38.0, 32.8 (Z isomer), 31.8, 26.8 (Z isomer), 26.1, 26.0 (Z isomer), 14.3 ppm.

GCMS-EI m/z (%) = 287 (2), 269 (3), 251 (3), 223 (2), 181 (2), 163 (4), 107 (2), 91 (100), 65 (7).

Diisopropyl 7-ethylideneoct-3-enedioate (2e): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.81 (q, \(J = 7.1\) Hz, 1H, E/Z isomers), 5.67 – 5.33 (m, 2H, E/Z isomers), 5.07 – 4.86 (m, 2H, E/Z isomers), 3.01 (d, \(J = 5.2\) Hz, 2H, E isomer), 2.94 – 2.28 (m, 2H, E/Z isomers), 2.20 – 2.02 (m, 2H, E/Z isomers), 1.76 (d, 3H, CHC\(_2\)H\(_3\), Z isomer overlapped with the CHCH\(_3\) signal of E isomer), 1.74 (d, \(J = 7.1\) Hz, 3H, CHCH\(_3\), E isomer), 1.30 – 0.81 ppm (m, 12H, E/Z isomers).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.5, 167.2, 137.4 (Z isomer), 137.2, 133.6, 132.9, 132.0 (Z isomer), 122.4, 121.9 (Z isomer), 67.8, 67.8, 67.5, 67.4, 38.4, 33.2 (Z isomer), 31.8, 26.8 (Z isomer), 26.2, 26.1 (Z isomer), 21.9, 21.8, 14.3 (Z isomer), 14.3 ppm.

GCMS-EI m/z (%) = 285 (M\(^+\), 0.3), 240 (2), 222 (5), 198 (4), 194 (4), 180 (25), 162 (67), 153 (11), 134 (46), 107 (27), 93 (16), 81 (16), 67 (7), 54 (35), 43 (100).

ESI-HRMS calcd for C\(_{16}\)H\(_{26}\)O\(_4\)Na \[M+Na\]^+: 305.17233; found: 305.17229.

Dimethyl 2-ethylideneoctanedioate (3): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.82 (q, \(J = 7.1\) Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 2.38 – 2.18 (m, 4H), 1.76 (d, \(J = 7.1\) Hz, 3H), 1.67 – 1.55 (m, 2H), 1.45 – 1.20 ppm (m, 4H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 174.3, 168.4, 137.5, 133.2, 51.7, 51.5, 34.1, 29.1, 28.7, 26.3, 24.9, 14.3 ppm.

GCMS-EI m/z (%) = 228 (M\(^+\), 1), 196 (81), 181 (9), 164 (55), 153 (8), 137 (43), 122 (15), 109 (39), 94 (51), 81 (49), 67 (45), 59 (100), 55 (59), 41 (41).


Dimethyl 2-ethyloctanedioate (4): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.61 (s, 3H), 3.60 (s, 3H), 2.32 – 2.14 (m, 3H), 1.49 (m, 6H), 1.32 – 1.12 (m, 4H), 0.82 ppm (t, \(J = 7.4\) Hz, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 176.7, 174.1, 51.5, 51.3, 47.2, 34.0, 31.9, 29.1, 27.1, 25.5, 24.8, 11.8 ppm.

GCMS-EI m/z (%) = 199 (8), 171 (25), 166 (34), 157 (13), 138 (29), 129 (22), 114 (11), 102 (97), 97 (45), 87 (100), 69 (56), 59 (93), 55 (97), 41 (57).


2-Ethyloctane-1,8-diol (5): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.63 (t, \(J = 6.6\) Hz, 2H), 3.53 (d, \(J = 5.0\) Hz, 2H), 2.42 (br s, 2H), 1.70 – 1.47 (m, 2H), 1.44 – 1.15 (m, 11H), 0.88 ppm (t, \(J = 7.3\) Hz, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 65.0, 62.7, 41.9, 32.7, 30.3, 29.8, 26.8, 25.7, 23.3, 11.1.

GCMS-EI m/z (%) = 172 (M\(^+\), 0.3), 144 (2), 126 (16), 109 (24), 97 (52), 83 (61), 69 (88), 55 (100).

ESI-HRMS calcd for C\(_{10}\)H\(_{22}\)O\(_{2}\) [M+H]^+: 175.16926; found: 175.16928.
$^1$H NMR (300 MHz, CDCl$_3$) dimethyl 7-ethylideneoct-3-enedioate, 2a.

$^{13}$C NMR (75 MHz, CDCl$_3$) dimethyl 7-ethylideneoct-3-enedioate, 2a.
\(^1\)H NMR (300 MHz, CDCl\(_3\)) dibutyl 7-ethylideneoct-3-enedioate, 2b.

\(^1^3\)C NMR (75 MHz, CDCl\(_3\)) dibutyl 7-ethylideneoct-3-enedioate, 2b.
\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \text{bis(2-ethylhexyl) 7-ethylideneoct-3-enedioate, 2c.} \]

\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \text{bis(2-ethylhexyl) 7-ethylideneoct-3-enedioate, 2c.} \]
$^1$H NMR (300 MHz, CDCl$_3$) dibenzyl 7-ethylideneoct-3-enedioate, 2d.

$^{13}$C NMR (75 MHz, CDCl$_3$) dibenzyl 7-ethylideneoct-3-enedioate, 2d.
$^1$H NMR (300 MHz, CDCl$_3$) diisopropyl 7-ethylideneoct-3-enedioate, 2e.

$^{13}$C NMR (75 MHz, CDCl$_3$) diisopropyl 7-ethylideneoct-3-enedioate, 2e.
\(^1\)H NMR (300 MHz, CDCl\(_3\)) dimethyl 2-ethylideneoctanedioate, 3.

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) dimethyl 2-ethylideneoctanedioate, 3.
$^1$H NMR (300 MHz, CDCl$_3$) dimethyl 2-ethylhexanedioate, 4.

$^{13}$C NMR (75 MHz, CDCl$_3$) dimethyl 2-ethylhexanedioate, 4
\[ f_1 \, (ppm) \]

**1H NMR (300 MHz, CDCl\textsubscript{3})** 2-ethyl octane-1,8-diol, 5.

\[ f_1 \, (ppm) \]

**13C NMR (75 MHz, CDCl\textsubscript{3})** 2-ethyl octane-1,8-diol, 5.