Supporting Information

Hydoruthenation Triggered Catalytic Conversion of Dialdehydes and Keto Aldehydes to Lactones
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General Information. $^1$H NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer in CDCl$_3$ or acetone-d$_6$ and are referenced at 0.00 ppm for TMS. Chemical shifts are reported in parts per million (δ). $^{13}$C NMR spectra were recorded with a JEOL JMN-500 (125 MHz) spectrometer in CDCl$_3$ and are referenced at 77 ppm for CDCl$_3$. Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. RuHCl(CO)(PPh$_3$)$_3$ was purchased from Wako Pure Chemical Industries, Ltd. Solvents were distilled prior to use. The products were purified by flash chromatography on silica gel (Nacalai Tesque Inc., Silica Gel 60, 230-400 mesh), and/or by preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) with GPC columns using CHCl$_3$ as an eluent.

2,2'-Diphenyldicarboxaldehyde (1c),$^1$ Homophthalaldehyde (1d),$^2$ butanedialdehyde (1f),$^3$ adipaldehyde (1h),$^1$ and 4-oxopentanal (1i)$^4$ were prepared by literature procedures. Substrate 1d is 65% purity which based on $^1$H NMR analysis relative to tetrachloroethane as an internal standard. Substrate 1f is 62% purity which based on GC analysis. Yield of γ-butyrolactone (2f), δ-valerolactone (2g), and ε-caprolactone (2h) were determined by $^1$H NMR using tetrachloroethane as an internal standard.

Typical Procedure for the Ruthenium Hydride-Catalyzed Lactonization of Dialdehydes and Keto Aldehydes:

A mixture of phthalaldehyde (1a, 67.1 mg, 0.50 mmol), and carbonyl chlorohydride tris(triphenylphosphine) ruthenium (47.6 mg, 0.05 mmol) in toluene (3 mL) was stirred at 90 °C for 5 h under argon. After the reaction, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane: EtOAc = 5 : 1) to give 3a (67.0 mg, 99%).

1(3H)-isobenzofuranone (2a)

(R$_f$ = 0.35, Hexane : EtOAc = 3 : 1). $^1$H NMR (500 MHz, CDCl$_3$) δ 5.33 (s, 2H), 7.51 (m, 1H), 7.54 (m, 1H), 7.69 (dd, $J$ = 7.4, 7.8 Hz 1H), 7.94 (d, $J$ = 7.4 Hz, 1H). This spectrum was identical to those of commercially available 2a.$^5$

Naphtho[2,3-c]furan-1(3H)-one (2b)

This compound was purified by preparative HPLC. $^1$H NMR (500 MHz, acetone-d$_6$) δ 5.55 (s, 2H), 7.62-7.68 (m, 1H), 7.68-7.74 (m, 1H), 8.07 (d, $J$ = 8.3 Hz, 1H), 8.12 (s, 1H), 8.19 (d, $J$ = 8.3 Hz, 1H), 8.50 (s, 1H).$^6$

Dibenz[c,e]oxepin-5(7H)-one (2c)

S2
γ-Butyrolactone (2f)

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\text{O} \\
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\[^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \delta 2.20-2.30 (m, 2H), 2.49 (t, } J = 7.8 \text{ Hz, 2H), 4.35 (t, } J = 7.3 \text{ Hz, 2H). This spectrum was identical to those of commercially available 2f.}

δ-Valerolactone (2g)

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\text{O} \quad \begin{array}{c}
\text{O} \\
\end{array}
\]

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \delta 1.82-1.96 (m, 4H), 2.56 (t, } J = 6.9 \text{ Hz, 2H), 4.35 (t, } J = 5.5 \text{ Hz, 2H). This spectrum was identical to those of commercially available 2g.}

ε-Caprolactone (2h)

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\text{O} \\
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(R\(_f\) = 0.25, Hexane : EtOAc = 3 : 1), \[^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \delta 1.73-1.81 (m, 4H), 1.83-1.91 (m, 2H), 2.61-2.67 (m, 2H), 4.21-4.25 (m, 2H). This spectrum was identical to those of commercially available 2h.

3-Isochromanone (2d)

3-Isochromanone (2d) and 1-isochromanone (2d') are an inseparable mixture. (R\(_f\) = 0.21, hexane:EtOAc = 5:1), \[^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \delta 3.72 (s, 2H), 5.32 (s, 2H), 7.21-7.45 (m, 4H).^8

1-Isochromanone (2d’)

\[
\text{O} \quad \begin{array}{c}
\text{O} \\
\end{array}
\]

(R\(_f\) = 0.21, hexane:EtOAc = 5:1), \[^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \delta 3.07 (t, } J = 6.0 \text{ Hz, 2H), 4.54 (t, } J = 6.0 \text{ Hz, 2H), 7.28-7.45 (m, 2H), 7.50-7.58 (m, 1H), 8.11 (d, } J = 7.3 \text{ Hz, 1H).^9}

S3
3-Methyl-1(3H)-isobenzofuranone (2e)

![3-Methyl-1(3H)-isobenzofuranone](image)

(R_f = 0.23, Hexane : EtOAc = 5 : 1), ^1^H NMR (500 MHz, CDCl_3) δ 1.64 (d, J = 6.9 Hz, 3H), 5.57 (q, J = 6.9 Hz, 3H), 7.45 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.63-7.70 (m, 1H), 7.90 (d, J = 7.3 Hz, 1H).

γ-Valerolactone (2i)

![γ-Valerolactone](image)

(R_f = 0.45, Hexane : EtOAc = 2 : 1), ^1^H NMR (500 MHz, CDCl_3) δ 1.42 (d, J = 6.0 Hz, 3H), 1.79-1.88 (m, 1H), 2.32-2.41 (m, 1H), 2.49-2.61 (m, 2H), 4.61-4.67 (m, 1H). This spectrum was identical to those of commercially available 2i.

4-Oxopropanoic acid 4-oxopentyl ester (2i')

![4-Oxopropanoic acid 4-oxopentyl ester](image)

Yellow oil; (R_f = 0.11, Hexane : EtOAc = 2 : 1), ^1^H NMR (500 MHz, CDCl_3) δ 1.88-1.94 (m, 2H), 2.16 (s, 3H), 2.19 (s, 3H), 2.52 (t, J = 6.9 Hz, 2H), 2.56 (t, J = 6.4 Hz, 2H), 2.75 (t, J = 6.4 Hz, 2H), 4.09 (t, J = 6.9 Hz, 2H); ^1^C NMR (125 MHz, CDCl_3) δ 22.83, 27.96, 29.99, 37.98, 39.83, 63.81, 172.74, 206.62, 207.71; IR (neat) 1714, 1651 cm\(^{-1}\); EIMS m/z (relative intensity) 143 (M^+\_CH_3C(O)CH_2, 16), 99 (100), 85(33), 71(17); HRMS (CI) m/z calcd for C_{10}H_{16}O_4 (M^++H): 200.1127, found: 201.1133.

Typical Procedure for the Ruthenium Hydride-Catalyzed Cross-Coupling Reaction:

A mixture of phthalaldehyde (1a, 67.2 mg, 0.50 mmol), ethyl vinyl ketone (3a, 209.1 mg, 2.49 mmol), and carbonyl chlorohydride tris(triphenylphosphine) ruthenium (48.2 mg, 0.05 mmol) in toluene (2 mL) was stirred at 90 °C for 5 h under argon. After the reaction, the solvent was removed under reduced pressure. The residue was purified by a preparative HPLC with GPC columns using CHCl_3 as an eluent to give 4a (86.9 mg, 79%).

3-(1-methyl-2-oxobutyl)-1(3H)-isobenzofuranone (4a)

![3-(1-methyl-2-oxobutyl)-1(3H)-isobenzofuranone](image)

Obtained as an inseparable diastereomer mixture (2:1). Pale yellow oil; (R_f = 0.35, Hexane : EtOAc = 3 : 1), major diastereomer: ^1^H NMR (500 MHz, CDCl_3) δ 1.05 (d, J = 8.3 Hz, 3H), 1.12 (t, J = 7.4 Hz, 3H), 2.59 (q, J = 7.4 Hz, 2H), 3.11-3.19 (m, 1H), 5.83 (d, J = 5.1Hz, 1H), 7.51-7.58 (m, 2H), 7.63-7.70 (m, 1H), 7.88-7.93 (m, 1H); ^1^C NMR (125 MHz, CDCl_3) δ 22.83, 27.96, 29.99, 37.98, 39.83, 63.81, 172.74, 206.62, 207.71; IR (neat) 1714, 1651 cm\(^{-1}\); EIMS m/z (relative intensity) 143 (M^+\_CH_3C(O)CH_2, 16), 99 (100), 85(33), 71(17); HRMS (CI) m/z calcd for C_{10}H_{16}O_4 (M^++H): 200.1127, found: 201.1133.
Diastereromers were separated by chromatography on silica gel.

major diastereomer: white solid (mp = 106-109 °C); (Rf = 0.28, Hexane : Ether = 1 : 1), $^1$H NMR (500 MHz, CDCl₃) δ 0.87-0.87 (m, 1H), 1.43-1.62 (m, 2H), 1.72-1.81 (m, 2H), 1.99-2.07 (m, 1H), 2.32-2.41 (m, 1H), 2.41-2.47 (m, 1H), 3.16-3.21 (m, 1H), 6.03 (d, $J = 3.3$ Hz, 1H), 7.43-7.47 (m, 2H), 7.56-7.59 (m, 1H), 7.79-7.83 (m, 1H); $^{13}$C NMR (125 MHz, CDCl₃) δ 24.19, 26.52, 26.96, 42.12, 53.21, 79.73, 124.09, 125.47, 126.81, 129.12, 133.98, 147.63, 170.49, 210.03; IR (KBr) 2939, 1762, 1707 cm⁻¹; EIMS $m/z$ (relative intensity) 212 (M⁻+18, 26), 201 (18), 134 (15), 133 (100), 115 (12), 105 (49), 104 (14), 77 (48), 76 (15), 55 (23), 51 (22); HRMS (EI) $m/z$ calcd. for C₁₄H₁₄O₃ (M⁺): 230.0943, found: 230.0941.

minor diastereomer: colorless oil; $^1$H NMR (500 MHz, CDCl₃) δ 0.84-0.94 (m, 1H), 1.49-1.70 (m, 2H), 1.77-1.89 (m, 2H), 2.06-2.14 (m, 1H), 2.39-2.48 (m, 1H), 2.48-2.55 (m, 1H), 6.11 (d, $J = 3.3$ Hz, 1H), 7.50-7.56 (m, 2H), 7.62-7.67 (m, 1H), 7.86-7.90 (m, 1H); $^{13}$C NMR (125 MHz, CDCl₃) δ 24.15, 26.50, 26.93, 42.08, 53.16, 79.69, 124.05, 125.41, 126.82, 129.10, 129.32, 133.96, 147.59, 170.52, 210.04; IR (KBr) 2937, 1760, 1710 cm⁻¹; EIMS $m/z$ (relative intensity) 212 (M⁻+18, 26), 201 (18), 134 (15), 133 (100), 115 (12), 105 (49), 104 (14), 77 (46), 55 (22), 51 (20); HRMS (EI) $m/z$ calcd. for C₁₄H₁₄O₃ (M⁺): 230.0943, found: 230.0941.

3-(1-Methyl-2-oxobutyl)-3H-naphtho[2,3-c]furan-1-one (4c)

Obtained as an inseparable diastereomer mixture. Yello oil; (Rf = 0.3, Hexane : Ether = 1 : 1), major diastereomer: $^1$H NMR (500 MHz, CDCl₃) δ 1.09-1.17 (m, 6H), 2.63 (q, $J = 6.9$ Hz, 2H), 3.19-3.25 (m, 1H), 5.96-6.05 (m, 1H), 7.58-7.63 (m, 1H), 7.64-7.69 (m, 1H), 7.95-7.97 (m, 2H), 8.03 (d, $J = 8.3$ Hz, 1H), 8.47 (s, 1H); $^{13}$C NMR (125 MHz, CDCl₃) δ 7.51, 11.26, 35.05, 49.71, 81.09, 122.69, 124.30, 127.09, 128.45, 128.69, 133.09, 136.02, 140.78, 170.00, 211.56.

minor diastereomer: δ 1.09-1.17 (m, 3H), 1.27 (d, $J = 6.9$ Hz, 3H), 2.45-2.74 (m, 2H), 2.98 (quint, $J = 8.8$ Hz, 1H), 5.97 (m, 1H), 7.58-7.63 (m, 1H), 7.76 (s, 1H), 7.92 (d, $J = 8.3$ Hz, 1H), 7.94-7.97 (m, 1H), 8.03 (d, $J = 8.3$ Hz, 1H), 8.47 (s, 1H); $^{13}$C NMR (125 MHz, CDCl₃) δ 7.51, 12.58, 35.05, 51.26, 81.24, 121.33, 123.67, 126.94, 128.34, 129.04, 129.76, 133.09, 136.18, 142.04, 170.00, 211.71; IR (KBr) 2935, 1760, 1710 cm⁻¹; EIMS $m/z$ (relative intensity) 268 (M⁺, 14), 239 (30), 212 (51), 211 (21), 197 (23), 184 (15), 183 (100), 165 (11), 155 (25), 127 (55), 126 (25), 77 (15), 57 (41); HRMS S5
Diastereromers were separated by chromatography on silica gel.

major diastereomer: white solid (mp = 174-175 °C); (R_t = 0.25, Hexane : Ether = 3 : 2), ^1H NMR (500 MHz, CDCl₃) δ 0.97 (qd, J = 12.7, 3.7 Hz, 1H), 1.51-1.70 (m, 2H), 1.76-1.84 (m, 1H), 1.86-1.94 (m, 1H), 2.05-2.13 (m, 1H), 2.46 (td, J = 13.3, 6.5 Hz, 1H), 2.51-2.57 (m, 1H), 3.28-3.34 (m, 1H), 6.25 (d, J = 3.2 Hz, 1H), 7.56-7.62 (m, 1H), 7.62-7.68 (m, 1H), 7.93-7.97 (m, 2H), 8.02 (d, J = 8.3 Hz, 1H), 8.46 (s, 1H); ^13C NMR (125 MHz, CDCl₃) δ 24.24, 26.47, 26.98, 42.25, 53.83, 79.86, 123.18, 124.57, 127.00, 128.57, 128.87, 129.71, 133.13, 136.26, 141.09, 170.45, 210.34.; IR (KBr) 2939, 1707, 1757 cm⁻¹; EIMS m/z (relative intensity) 280 (M⁺, 22), 262 (25), 251 (21), 183 (100), 155 (32), 127 (66), 126 (28); HRMS (EI) m/z calcd. for C₁₇H₁₆O₃ (M⁺): 268.3071, found: 268.1104.

7-(2-Oxocyclohexyl)-7H-dibenzo[c,e]oxepin-5-one (4e)

Diastereromers were separated by chromatography on silica gel.

major diastereomer: white solid (mp = 179-181 °C); (R_t = 0.10, Hexane : Ether = 2 : 1), ^1H NMR (500 MHz, CDCl₃) δ 1.42 (qd, J = 12.8, 3.7 Hz, 1H), 1.68-1.78 (m, 1H), 1.81-1.92 (m, 2H), 2.14-2.20 (m, 1H), 2.33-2.38 (m, 1H), 2.47-2.58 (m, 2H), 3.52 (td, J = 10.6, 4.1 Hz, 1H), 5.40 (d, J = 9.6 Hz, 1H), 7.43-7.48 (m, 2H), 7.50 (td, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.62 (d, J = 7.3 Hz, 2H), 7.69 (t, J = 6.9 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H); ^13C NMR (125 MHz, CDCl₃) δ 24.91, 29.20 , 32.00, 42.79, 51.00, 75.00, 124.80, 128.27, 128.45, 128.69, 129.40, 129.69, 131.47, 131.47, 132.48, 134.46, 137.17, 139.77, 169.50, 209.18; IR (KBr) 2957, 1701 cm⁻¹; EIMS m/z (relative intensity) 306 (M⁺, 5), 210 (25), 209 (78), 181 (100), 178 (21), 165 (40), 153 (23), 152 (45), 81 (31), 69 (61), 57 (33), 55 (38); HRMS (EI) m/z calcd. for C₂₀H₁₈O₃ (M⁺): 306.1256, found: 306.1263. minor diastereomer: white solid (mp = 180-182 °C); (R_t = 0.13, Hexane : Ether = 3 : 2), ^1H NMR (500 MHz, CDCl₃) δ 1.62-1.78 (m, 2H), 1.80-1.91 (m, 1H), 2.00-2.08 (m, 1H), 2.18-2.28 (m, 1H), 2.40-2.48 (m, 1H), 2.52 (td, J = 12.9, 6.0 Hz, 1H), 2.77-2.85 (m, 1H), 3.48-3.56 (m, 1H), 5.32 (d, J = 9.2 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.36-7.42 (m, 1H), 7.45-7.51 (m, 1H), 7.51-7.56 (m, 1H), 7.59-7.72 (m, 3H), 7.95-7.99 (m, 1H); ^13C NMR (125 MHz, CDCl₃) δ 24.95, 28.78, 31.73, 42.81, 51.11, 75.49, 116.14, 123.76, 128.28, 128.41, 129.07, 129.24, 129.41, 131.16, S6
132.67, 136.31, 137.61, 138.71, 169.83, 210.11; IR (KBr) 2925, 1715, 1701 cm\(^{-1}\); EIMS \textit{m/z} (relative intensity) 306 (M\(^+\), 5), 210 (29), 209 (100), 181 (96), 178 (24), 165 (42), 153 (23), 152 (52), 69 (32), 55 (22); HRMS (EI) \textit{m/z} calcd. for C\textsubscript{20}H\textsubscript{18}O\textsubscript{3} (M\(^+\)): 306.1256, found: 306.1256.

References