

Supporting Information

Hydroruthenation Triggered Catalytic Conversion of Dialdehydes and Keto Aldehydes to Lactones

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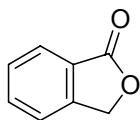
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General Information. ^1H NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer in CDCl_3 or acetone- d_6 and are referenced at 0.00 ppm for TMS. Chemical shifts are reported in parts per million (δ). ^{13}C NMR spectra were recorded 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. $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ 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 ^1H 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 ^1H NMR using tetrachloroethane as an internal standard.

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

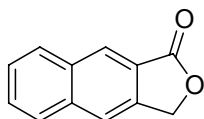
A mixture of phthalaldehyde (**1a**, 67.1 mg, 0.50 mmol), and carbonyl chlorohydride tris(triphenylphosphine) ruthenium (47.6 mg, 0.05 mmol) in toluene (3 mL) was stirred at 90 °C for 5 h under argon. After the reaction, the solvent was removed under reduced pressure. The residue was purified by flash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

1(3*H*)-isobenzofuranone (2a)



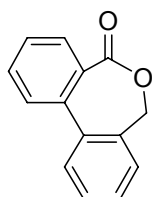
(R_f = 0.35, Hexane : EtOAc = 3 : 1), ^1H NMR (500 MHz, CDCl_3) δ 5.33 (s, 2H), 7.51 (m, 1H), 7.54 (m, 1H), 7.69 (dd, J = 7.4, 7.8 Hz 1H), 7.94 (d, J = 7.4 Hz, 1H). This spectrum was identical to those of commercially available **2a**.⁵

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

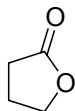


This compound was purified by preparative HPLC. ^1H NMR (500 MHz, acetone- d_6) δ 5.55 (s, 2H), 7.62-7.68 (m, 1H), 7.68-7.74 (m, 1H), 8.07 (d, J = 8.3 Hz, 1H), 8.12 (s, 1H), 8.19 (d, J = 8.3 Hz, 1H), 8.50 (s, 1H).⁶

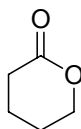
Dibenz[*c,e*]oxepin-5(7*H*)-one (2c)



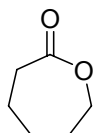
(R_f = 0.25, Hexane : EtOAc = 5 : 1), ^1H NMR (500 MHz, CDCl_3) δ 5.03 (br, 2H), 7.41-7.49 (m, 2H), 7.50-7.57 (m, 2H), 7.61 (dd, J = 7.8, 1.4 Hz, 1H), 7.63-7.71 (m, 2H), 7.99 (dd, J = 7.8, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 69.28, 128.53, 128.66, 128.76, 130.22, 130.79, 132.04, 132.64, 134.94, 170.31.^{5,7}

 γ -Butyrolactone (2f)

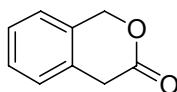
^1H NMR (500 MHz, CDCl_3) δ 2.20-2.30 (m, 2H), 2.49 (t, J = 7.8 Hz, 2H), 4.35 (t, J = 7.3 Hz, 2H). This spectrum was identical to those of commercially available **2f**.

 δ -Valerolactone (2g)

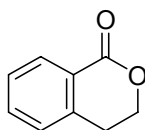
^1H NMR (500 MHz, CDCl_3) δ 1.82-1.96 (m, 4H), 2.56 (t, J = 6.9 Hz, 2H), 4.35 (t, J = 5.5 Hz, 2H). This spectrum was identical to those of commercially available **2g**.

 ϵ -Caprolactone (2h)

(R_f = 0.25, Hexane : EtOAc = 3 : 1), ^1H NMR (500 MHz, CDCl_3) δ 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**.

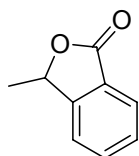
3-Isochromanone (2d)

3-Isochromanone (**2d**) and 1-isochromanone (**2d'**) are an inseparable mixture. (R_f = 0.21, hexane:EtOAc = 5:1), ^1H NMR (500 MHz, CDCl_3) δ 3.72 (s, 2H), 5.32 (s, 2H), 7.21-7.45 (m, 4H).⁸

1-Isochromanone (2d')

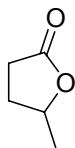
(R_f = 0.21, hexane:EtOAc = 5:1), ^1H NMR (500 MHz, CDCl_3) δ 3.07 (t, J = 6.0 Hz, 2H), 4.54 (t, J = 6.0 Hz, 2H), 7.28-7.45 (m, 2H), 7.50-7.58 (m, 1H), 8.11 (d, J = 7.3 Hz, 1H).⁹

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



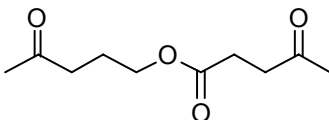
(R_f = 0.23, Hexane : EtOAc = 5 : 1), ^1H NMR (500 MHz, CDCl_3) δ 1.64 (d, J = 6.9 Hz, 3H), 5.57 (q, J = 6.9 Hz, 3H), 7.45 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.63-7.70 (m, 1H), 7.90 (d, J = 7.3 Hz, 1H).⁵

γ -Valerolactone (2i)



(R_f = 0.45, Hexane : EtOAc = 2 : 1), ^1H 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')

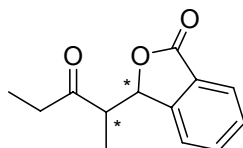


Yellow oil; (R_f = 0.11, Hexane : EtOAc = 2 : 1), ^1H NMR (500 MHz, CDCl_3) δ 1.88-1.94 (m, 2H), 2.16 (s, 3H), 2.19 (s, 3H), 2.52 (t, J = 6.9 Hz, 2H), 2.56 (t, J = 6.4 Hz, 2H), 2.75 (t, J = 6.4 Hz, 2H), 4.09 (t, J = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 22.83, 27.96, 29.99, 37.98, 39.83, 63.81, 172.74, 206.62, 207.71; IR (neat) 1714, 1651 cm^{-1} ; EIMS m/z (relative intensity) 143 (M^+ - $\text{CH}_3\text{C}(\text{O})\text{CH}_2$, 16), 99 (100), 85(33), 71(17); HRMS (CI) m/z calcd for $\text{C}_{10}\text{H}_{16}\text{O}_4$ (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 chlorohydrate 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%).

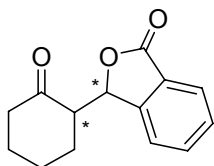
3-(1-methyl-2-oxobutyl)-1(3*H*)-isobenzofuranone (4a)



Obtained as an inseparable diastereomer mixture (2:1). Pale yellow oil; (R_f = 0.35, Hexane : EtOAc = 3 : 1), major diastereomer: ^1H 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 = 5.1 Hz, 1H), 7.51-7.58 (m, 2H), 7.63-7.70 (m, 1H), 7.88-7.93 (m, 1H); ^{13}C NMR (125 MHz, S4

CDCl₃) δ 7.59, 11.37, 35.15, 49.47, 81.17, 123.72, 125.82, 126.88, 129.45, 133.99, 147.53, 170.14, 211.40. minor diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 1.08-1.14 (m, 3H), 1.23 (d, J = 6.9 Hz, 3H), 2.40-2.72 (m, 2H), 2.85-2.93 (m, 1H), 5.82 (d, J = 6.5 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.51-7.58 (m, 1H), 7.63-7.70 (m, 1H), 7.88-7.93 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 12.59, 50.77, 81.30, 122.41, 125.90, 126.24, 129.45, 134.32, 148.57, 211.52; IR (neat) 2978, 1763, 1714, 1595 cm⁻¹; EIMS m/z (relative intensity) 218 (M⁺, 3), 203 (5), 189 (22), 161 (16), 133 (100), 115 (9), 105 (18), 85 (3), 77 (19), 57 (17); HRMS (EI) m/z calcd. for C₁₃H₁₄O₃ (M⁺): 218.0943, found: 218.0952.

3-(2-Oxocyclohexyl)-1(3H)-isobenzofuranone (4b)

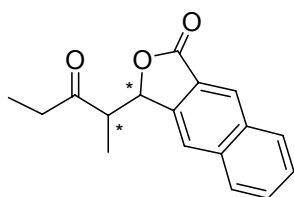


Diastereomers were separated by chromatography on silica gel.

major diastereomer: white solid (mp = 106-109 °C); (R_f = 0.28, Hexane : Ether = 1 : 1), ¹H 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, 1H), 7.43-7.47 (m, 2H), 7.56-7.59 (m, 1H), 7.79-7.83 (m, 1H); ¹³C 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(16), 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 :230.0936.

minor diastereomer: colorless oil; ¹H 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); ¹³C 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, 27), 201 (17), 134 (15), 133 (100), 105 (44), 77 (46), 55 (22), 51 (20); HRMS (EI) m/z calcd. for C₁₄H₁₄O₃ (M⁺): 230.0943, found: 230.0941.

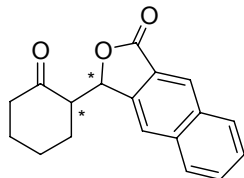
3-(1-Methyl-2-oxobutyl)-3H-naphtho[2,3-c]furan-1-one (4c)



Obtained as an inseparable diastereomer mixture. Yello oil; (R_f = 0.3, Hexane : Ether = 1 : 1), major diastereomer: ¹H 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); ¹³C NMR (125 MHz, CDCl₃) δ 7.51, 11.26, 35.05, 49.71, 81.09, 122.69, 124.30, 127.09, 128.45, 128.96, 129.68, 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 = 6.8 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); ¹³C 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

(EI) m/z calcd. for $C_{17}H_{16}O_3$ (M^+): 268.3071, found: 268.1104.

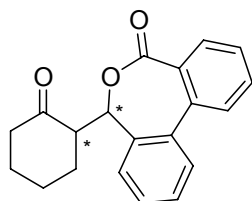
3-(2-Oxocyclohexyl)-3*H*-naphtho[2,3-*c*]furan-1-one (4d)



Diastereomers were separated by chromatography on silica gel.

major diastereomer: white solid (mp = 174-175 °C); (R_f = 0.25, Hexane : Ether = 3 : 2), 1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.24, 26.47, 26.98, 42.25, 53.83, 79.86, 123.18, 124.57, 126.74, 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 $C_{18}H_{16}O_3$ (M^+): 280.1099, found :280.1093, minor diastereomer: White solid (mp = 148-150 °C); (R_f = 0.18, Hexane : Ether = 3 : 2), 1H NMR (500 MHz, $CDCl_3$) δ 1.59-1.82 (m, 3H), 1.90-1.97 (m, 1H), 2.10-2.18 (m, 2H), 2.39 (td, J = 13.8, 5.5 Hz, 1H), 2.55-2.62 (m, 1H), 2.78-2.86 (m, 1H), 6.12(d, J = 6.0 Hz, 1H), 7.56-7.62 (m, 1H), 7.63-7.68 (m, 1H), 7.92-7.98 (m, 2H), 8.03 (d, J = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.61, 27.46, 28.89, 29.69, 42.45, 55.63, 79.16, 116.15, 121.91, 126.88, 127.03, 128.43, 128.96, 129.80, 136.34, 142.72, 170.30, 209.84; IR (KBr) 2923, 1762, 1699 cm^{-1} ; EIMS m/z (relative intensity) 280 (M^+ , 34), 251 (20), 183 (100), 155 (29), 127 (37); HRMS (EI) m/z calcd. for $C_{18}H_{16}O_3$ (M^+): 280.1099, found: 280.1097.

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



Diastereomers were separated by chromatography on silica gel.

major diastereomer: white solid (mp = 179-181 °C); (R_f = 0.10, Hexane : Ether = 2 : 1), 1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{20}H_{18}O_3$ (M^+): 306.1256, found: 306.1263. minor diastereomer: white solid (mp = 180-182 °C); (R_f = 0.13, Hexane : Ether = 3 : 2), 1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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,

Supplementary Material (ESI) for Chemical Communications

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132.67, 136.31, 137.61, 138.71, 169.83, 210.11; IR (KBr) 2925, 1715, 1701 cm^{-1} ; EIMS 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) m/z calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_3$ (M^+): 306.1256, found: 306.1256.

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