Lactone Synthesis Based on Atom Transfer Carbonylation

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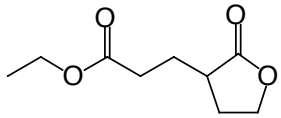
Supporting Information

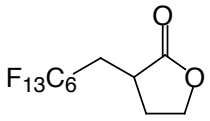
General Methods. ^{1}H NMR spectra were recorded with a JEOL FT-NMR JNM-EX 270 (270 MHz) spectrometer and/or a Bruker AM600 (600 MHz) spectrometer. ^{13}C NMR spectra were recorded with a JEOL JNM-EX 270 (68 MHz) spectrometer. Chemical shifts are reported in parts per million (δ), relative to internal TMS at 0.00 for ^{1}H NMR and chloroform at 77.0 for ^{13}C NMR. Infrared spectra were recorded with a JASCO FT/IR-410 spectrometer. GC analyses were performed with a Shimadzu GC-17A gas chromatography equipped with Supelco fused silica capillary column DB-1. GC-MS analyses were performed with a Shimadzu GCMS QP-5000 mass spectrometer. High-resolution mass spectra (HRMS) were recorded with a JEOL JMS-DX303HF spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. The products were purified by flash chromatography on silica gel (Fuji Silysia BW-300) and, if necessary, were further purified by recycling preparative HPLC (JAI, LC-908) equipped with a GPC column (JAIGEL 1H-2H) using chloroform as an eluent. Organic solvents were dried and distilled prior to use.

2-(2'-Ethoxycarbonyl)ethyl-γ-butyrolactone (2a).



^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.27 (t, J = 7.1 Hz, 3H), 1.83 (tdd, J = 7.4, 7.1 and 14.3 Hz, 1 H), δ 1.96 (dddd, J = 8.5, 9.9, 10.4 and 12.3 Hz, 1H), 2.16 (tdd, J = 7.1, 7.4 and 14.3 Hz, 1 H), 2.42 (dddd, J = 2.7, 6.5, 8.7 and 12.3 Hz, 1H), 2.51 (t, J = 7.4 Hz, 2H), 2.61 (tdd, J = 7.1, 8.7 and 10.4 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.20 (ddd, J = 6.5, 9.2 and 9.9 Hz, 1H),4.35 (ddd, J = 2.7, 8.5 and 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 14.09, 25.38, 28.65, 31.61, 38.31, 60.47, 66.31, 172.63, 178.65; IR (neat, cm^{-1}) 1768, 1731; EIMS (relative intensity) m/z 141 (M^+-OCH_2CH_3,100), 113 (32), 99 (29), 86 (51), 68 (21); HRMS calcd for $C_9H_{14}O_2$ m/z 186.0892, found: 186.0878.

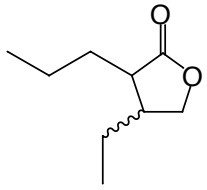
2-(Perfluorohexylmethyl)-γ-butyrolactone (2b).



^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.08-2.18 (m, 2H), δ 2.65 (quintet like, $J\approx$ 6.5 Hz, 1H),

δ 2.88 (dd-like, $J \approx 6.7$ and 15.8 Hz, 1H), 2.91-2.96 (m, 1H)4.25 (ddd, J = 6.1, 9.0 and 11.2 Hz,, 1H), δ 4.45 (td, J = 9.0 Hz and 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 29.83, 32.11 (t, J = 21.5 Hz), 33.40, 66.70, 107.58-119.77 (m, CF_2, CF_3), 176.85; IR (KBr, cm^{-1}) 1781, 1767, 1241, 1184, 1027; EIMS (relative intensity) *m/z* 419 (M^+,2), 417 (2), 374 (26), 360 (5), 327 (2), 295 (4), 105 (11), 91 (13), 77 (9), 55 (100); HRMS calcd for $C_{11}H_7F_{12}O_2$ (M^+-F) *m/z* 399.0255, found: 399.0260; Anal. Calcd for $C_{11}H_7F_{13}O_2$: C, 31.60; H, 1.69, found: C, 31.31; H, 1.74.

3-Ethyl-2-propyl-γ-butyrolactone (2c).



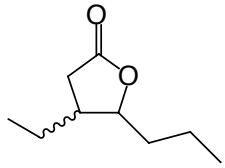
Obtained as a *cis/trans*-isomer mixture in a 64/36 ratio, a colorless liquid.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.94 (t, 3H, J = 7.1 Hz, cis), 0.94 (t, J = 7.1 Hz, trans 3H), 0.95 (t, J = 7.1 Hz, cis 3H), 0.95 (t, J = 7.1 Hz, trans 3H), 1.22-1.30 (m, cis 1H), 1.40-1.61 (m, cis 5H and trans 5H), 1.66-1.74 (m, cis 2H and trans 1H), 2.17-2.21 (m, trans 2H), 2.38-2.43 (m, cis 1H),

2.56 (quartet-like, $J \approx 7.3$ Hz , cis 1H), 3.84 (dd, J = 8.2 and 8.6 Hz, trans 1H), 4.09 (dd, J = 9.3 and 3.4 Hz, cis 1H), 4.22 (dd, J = 9.1, and 5.9 Hz, cis 1H), 4.39 (dd, J = 8.6 and 7.1 Hz, trans 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 11.32 (trans), 11.50 (cis), 13.91 (cis), 13.98 (trans), 19.63 (cis), 19.99 (trans), 20.70 (cis), 25.73 (trans), 26.89 (cis), 31.59 (trans), 40.13 (cis), 42.31 (trans), 42.83 (cis), 44.81 (trans), 70.15 (cis), 71.33 (trans), 179.06 (cis), 179.57 (trans);
IR (neat, cm^{-1}) 1774, 2931, 2962; EIMS (relative intensity) m/z, cis: 127 (M^+-CH_2CH_3,7), 114 (35), 85 (100), 55 (27), trans: 127 (M^+-CH_2CH_3,6), 114 (31), 85 (100), 55 (21); HRMS calcd for $C_9H_{17}O_2$ ($[M+H]^+$), m/z 157.1229, found, cis : 157.1224, trans: 157.1225.

Cis/trans stereoisomers were assigned by comparison of NMR data with those of reported lactones having a similar structure, see: Daub, G. W.; Edwards, J. P.; Okada, C. R.; Allen, J. W.; Maxey, C. T.; Wells, M. S.; Goldstein, A. S.; Dibley, M. J.; Wang, C. J.; Ostercamp, D. P.; Chung, S.; Cunningham, P. S.; Berliner, M. A. *J. Org. Chem.* **1997**, *62*, 1976.

3-Ethyl-4-propyl-γ-butyrolactone (2d).



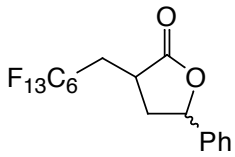
Obtained as a *cis/trans*-isomer mixture in a 53/47 ratio, a colorless liquid.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.94 (t, J = 7.4 Hz, cis 3H), δ 0.95 (t, J = 7.4 Hz, trans 3H), δ 0.96 (t, J = 7.4 Hz, cis 3H), δ 0.96 (t, J = 7.4 Hz, trans 3H), 1.04-1.74 (m, cis 6H and trans 6H), 2.03-2.09 (m, trans 1H), 2.21 (dd, J = 8.7and 17.6 Hz, trans 1H), 2.29 (dd, J = 7.1and 17.1 Hz, cis 1H), 2.38-2.44 (m, cis 1H), 2.58 (dd, J = 7.9 and 17.1 Hz, cis 1H),2.68 (dd, J = 8.5 and 17.6 Hz, trans 1H),4.11 (td,

J = 7.4 and 4.6 Hz, trans 1H), 4.51 (ddd, J = 3.8, 6.4 and 10.0 Hz, cis 1H), ^{13}C NMR ($CDCl_3$, 68 MHz) δ 11.83 (trans), 11.98 (cis), 13.79 (two superimposed lines), 18.91 (trans), 19.14 (cis), 21.16 (cis), 25.95 (trans), 31.81 (cis), 34.03 (cis), 34.77 (trans), 36.81 (trans), 40.37 (cis), 42.64 (trans), 83.20 (cis), 85.57 (trans), 176.68 (trans), 176.89 (cis); IR (neat, cm^{-1}) 1775; EIMS (relative intensity) *m/z* cis 156 (M^+,1), 138 (3), 128 (3), 113 (100), 85 (23), 73 (13), 67 (14), 56 (67); trans 156 (M^+,1), 138 (2), 128 (2), 113 (100), 85 (22), 73 (7), 67 (13), 56 (37) ; HRMS calcd for $C_9H_{16}O_2$ *m/z* 156.1150, found, cis: 156.1134; trans:156.1162.

Cis/trans stereoisomers were assigned by comparison of NMR data with those of reported lactones having a similar structure, see: Reissig, H.-U.; Angert, H. *J. Org. Chem.* **1993**, *58*, 6280.

2-(Perfluorohexylmethyl)-4-phenyl-γ-butyrolactone (2e).

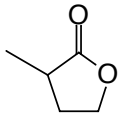


Obtained as a *cis/trans*-isomer mixture in a 49/51 ratio, a colorless solid.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.06 (q-like, $J \approx$ 12.0 Hz, 1H), 2.18-2.28 (m, 2H), 2.61 (ddd, J = 8.5, 11.5 and 12.9 Hz, 1H), 2.71-2.75 (m, 1H), 2.89-3.06 (m, 4H), 5.48 (dd, J = 5.3 and 11.0 Hz, cis 1H), 5.71 (dd, J = 0.9 and 7.9 Hz, trans 1H), 7.32-7.48 (m, 10H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 31.94, 32.12 (J = 22.0 Hz), 35.56, 36.72, 38.96, 78.42, 79.97, 109.71-121.96 (m, CF_2, CF_3), 124.61, 125.36, 128.38, 128.78, 128.79, 128.88, 137.80, 138.74, 175.85, 176.63; IR (KBr, cm^{-1}) 1763, 1234, 1193, 1145; EIMS (relative intensity) *m/z* cis: 494 (M^+,100), 450 (41), 429 (6), 388 (7), 360 (9), 117 (87), 105 (54), 91 (37); trans: 494 (M^+,100), 471 (4), 450 (47), 429 (6), 388 (7), 360 (10), 117 (100), 105 (59), 91 (41); HRMS calcd for $C_{17}H_{11}F_{13}O_2$ *m/z* 494.0551; found cis: 494.0554 trans: 494.055.

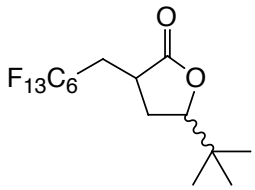
Cis/trans stereoisomers were assigned by comparison of NMR data with those of reported lactones having a similar structure, see: Reineke, N.; Zaidi, N. A.; Mitra, M.; O'Hagans, D.; Batsanov, A. S.; Howard, J. A. K.; Naumov, D. Y. *J. Chem. Soc., Perkin Trans. 1* **1996**, *2*, 147.

2-Methyl-γ-butyrolactone (2f).



This compound is already known and commercially available, the properties (^{1}H and ^{13}C NMR) were consistent with those previously reported. See: "The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra", Pouchert, C. J.; Behnke, J. 1993, Edition I, Vol. 1 Page 1127.

2-(Perfluorohexylmethyl)-4-tert**-butyl-γ-butyrolactone (2g).**

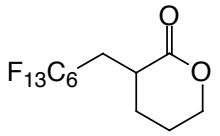


Obtained as a *cis*/*trans*-isomer mixture in a 37/63 ratio, a colorless solid.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.97 (s, trans 9H), 0.98 (s, cis 9H), 1.76 (q-like, $J \approx 12.1$ Hz, cis 1H), 2.07-2.20 (m, trans 2H and cis 1H), 2.43-2.51 (m, trans 1H and cis 1H), 2.77-3.03 (m, trans 2H and cis 2H), 4.16 (dd, J = 11.1 and 5.3 Hz, cis 1H), 4.26 (dd, J = 9.1 and 3.7 Hz, trans 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 24.90, 24.92, 29.06 (trans), 31.16 (cis), 32.00 1 (t, J = 21.3Hz, cis), 32.98 (t, J = 21.5 Hz, trans), 33.19 (cis), 33.43 (trans), 34.74 (cis), 35.28 (cis), 86.30 (trans), 86.63 (cis), 110.79-119.28 (m, CF_2, CF_3), 176.49 (cis), 177.17 (trans); IR (KBr, cm^{-1}) 1772, 1235, 1191, 1144; EIMS (relative intensity) *m*/*z* 475 (M^+,2), 459 (32), 417 (46), 387 (4), 341 (6), 295 (8), 83 (15), 70 (13), 57 (100); HRMS calcd for $C_{14}H_{12}F_{13}O_2$ (M^+-CH_3) *m*/*z* 459.0630 , found: 459.0625.

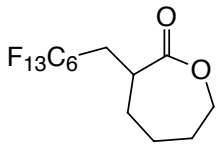
Cis/*trans* stereoisomers were assigned by comparison of NMR data with those of reported lactones having a similar structure, see: Reissig, H-U.; Angert, H. *J. Org. Chem.* **1993**, *58*, 6280.

2-(Perfluorohexylmethyl)-δ-valerolactone (2h).



^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.67-1.77 (m, 1H), 1.97-2.02 (m, 2H), 2.11-2.22 (m, 1H)2.40 (tdd, , J = 6.8, 7.1 and 15.5 Hz 1H),2.90-2.96 (m, 2H), 3.07 (dd-like, $J \approx 15.6$ Hz, 35.3 Hz, 1H)4.35-4.42 (m, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 21.85, 25.33,31.75 (t, J = 20.8 Hz), 33.63, 68.20, 110.11-119.19 (m, CF_2, CF_3), 172.40 IR (KBr, cm^{-1}) 1729, 1239, 1191, 1140; EIMS (relative intensity) *m*/*z* 432 (M^+,2), 413 (13), 388 (100), 374 (7), 327 (3), 83 (10), 69 (46); HRMS calcd for $C_{12}H_9F_{13}O_2$ *m*/*z* 432.0395, found: 432.0374.

2-(Perfluorohexylmethyl)-ε-caprolactone (2I).



^{1}H NMR ($CDCl_3$, 270 MHz) 1.50-2.30 (m, 7H), 2.91-3.13 (m, 2H), 4.28-4.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 27.84, 28.45, 30.80, 33.37 (t, J = 20.8 Hz), 35.91 , 68.68, 108.00-119.64 (m,, CF_2, CF_3), 175.36; IR (KBr, cm^{-1}) 1733, 1237, 1191, 1147; EIMS (relative intensity) *m*/*z* 446 (M^+,33),

427 (4), 416 (23), 402 (47), 387 (17), 127 (4), 69 (10), 55 (73), 42 (100); HRMS calcd for $C_{13}H_{11}F_{13}O_2$ *m/z* 446.0551, found: 446.0546.