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SUPPORTING INFORMATION

Title: One-Pot Synthesis of Heterocycles Initiated by Chemoselective Reduction of Bifunctional Carbonyl Compounds
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Ref. No.: O200500927

Experimental

Analysis. IR spectra were recorded on a Horiba FT-720 spectrometer. For a tin hydride ate complex, ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded with a JEOL JNM-GSX-270 (270, 67.9 and 100 MHz, respectively) in ethyl acetate-d_8. Tetramethyltin was used as the internal standard in ^{119}Sn NMR. All the ^{1}H and ^{13}C spectra of the products were recorded with a JEOL JNM-GSX-270 (270 and 67.9 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303. Column chromatography was performed by using Fuji Davison gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel. Yields were determined by 1H NMR using internal standards.

General. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a JEOL JNM-GSX-270 (270 and 67.9 MHz) spectrometer, respectively, with TMS as internal or external standard. Mass spectra were recorded on a JEOL JMS-DS303 spectrometer. GLC analyses were performed on a Shimadzu GC-8A with FID using a 2 m ∞ 3 mm column packed with SE-52. Column chromatography was performed on silica gel (Wakogel C-300). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated.

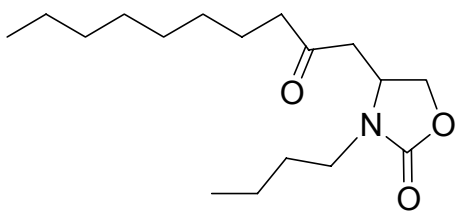
Materials. THF was distilled from sodium and benzophenone. Tri-*n*-butyltin hydride (nBu$_3$SnH) was prepared by the reduction of tri-*n*-butyltin chloride (nBu$_3$SnCl) with $LiAlH_4$.[1] All reactions were carried out under dry nitrogen. A commercial available epoxides was used as a substrate. Substrate **1** was prepared according to reported methods.[2]

1. Finholt, A. E.; Bond, Jr. A. C.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692-2696.
2. H-J, Wu; C-C, Lin, *J. Org. Chem.*, **1996**, *61*, 3820-3828; Bonete, P.; Najera, C. *Tetrahedron*, **1995**, *51*, 2763-2776.

Representative procedure for the preparation of 2-oxazolidinone initiated by chemoselective reduction.

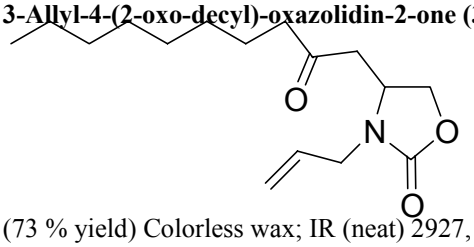
To a dry nitrogen-filled 10-mL round-bottomed flask containing Trii-*n*-butyltin hydride (0.291 g, 1 mmol) in THF (1 mL) was added and HMPA (0.180 g, 1 mmol) at rt. To the resulting solution was added carbonyl substrate (**1a**) (0.196 g, 1 mmol), and stirred at 60 ºC for 2 h. The reaction mixture was cooled to 0 ºC. To this mixture was added butyl isocyanate (0.0975 g, 0.8 mmol) and stirred for 0.5 h. The IR absorption band of NCO (2200 cm^{-1}) disappeared, which indicated the formation of stannylcarbamate adduct (II). The mixture was heated to 60 ºC and stirred for 1 h. The reaction was quenched by MeOH (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). By-products such as organotin compounds were removed by eluting with hexane. Subsequent elution with EtOAc gave 2-oxazolidonone **3a** (0.199 g, 84% based on BuN=C=O).

3-Butyl-4-(2-oxo-decyl)-oxazolidin-2-one (3a)



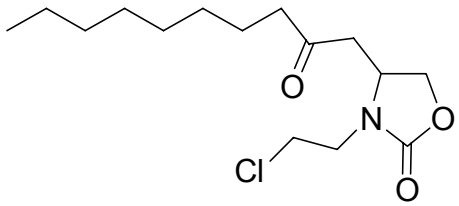
(84 % yield) Colorless wax; IR (neat) 2927, 1751, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.85-0.96 (m, 6H, $2CH_3$), 1.21-1.60 （m, 16H, CH_2）, 2.45 (t, 2H, *J*= 7.3 Hz, C=OCH_2), 2.61 (dd, 1H, *J*= 9.3 and 18.1 Hz, one of C=OCH_2), 2.88-2.96 (m, 1H, one of NCH_2), 3.01 (dd, 1H, *J*= 3.9 and 18.1 Hz, one of C=OCH_2), 3.37-3.50 (m, 1H, one of NCH_2), 3.84 (dd, 1H, *J*= 5.9 and 8.8 Hz, one of OCH_2), 4.12-4.22 (m, 1H, CHN), 4.52 (dd, 1H, *J*= 8.3 and 8.8 Hz, one of CH_2O); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.45, 13.83, 19.66, 22.38, 22.39, 28.85, 28.90, 29.08, 29.19, 31.56, 41.61, 43.02, 45.22, 50.64, 67.89, 157.73, 207.93; HRMS calcd for $C_{17}H_{31}NO_3$ 297.2304, found 297.2298.

3-Allyl-4-(2-oxo-decyl)-oxazolidin-2-one (3b)



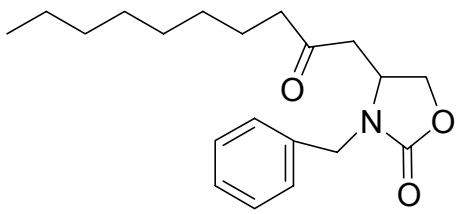
(73 % yield) Colorless wax; IR (neat) 2927, 1751, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.88 (t, 3H, *J*= 6.8 Hz, CH_3), 1.11-1.56 （m, 12H, CH_2）, 2.42 (t, 2H, *J*= 7.3 Hz, C=OCH_2), 2.58 (dd, 1H, *J*= 9.8 and 18.1 Hz, one of C=OCH_2), 3.01 (dd, 1H, *J*= 3.9 and 18.1 Hz, one of C=OCH_2), 3.63 (dd, 1H, *J*= 6.8 and 15.6 Hz, one of C=CCH_2), 3.87 (dd, 1H, *J*= 6.3 and 8.8 Hz, one of CH_2O), 4.06 (dd, 1H, *J*= 5.4 and 15.6 Hz, one of C=CCH_2), 4.12-4.33 (m, 1H, one of CH_2N), 4.57 (t, 1H, *J*= 8.8 Hz, one of CH_2O), 5.08-5.29 (m, 2H, C=CH_2), 5.68-5.85 (m, 1H, C*H*=CH_2); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.78, 22.30, 23.25, 28.77, 28.78, 28.99, 31.47, 42.79, 44.82, 45.10, 50.78, 67.96, 118.12, 132.04, 157.58, 207.79; HRMS calcd for $C_{16}H_{27}NO_3$ 281.1991, found 281.1988.

3-(2-Chloro-ethyl)-4-(2-oxo-decyl)-oxazolidin-2-one (3c)



(75 % yield) Colorless wax; IR (neat) 2931, 1754, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.88 (t, 3H, *J*= 6.4 Hz, CH_3), 1.22-1.58 （m, 12H, CH_2）, 2.47 (t, 2H, *J*= 7.3 Hz, C=OCH_2), 2.69 (dd, 1H, *J*= 8.8 and 18.1 Hz, one of C=OCH_2), 3.13 (dd, 1H, *J*= 4.4 and 18.1 Hz, one of C=OCH_2), 3.30-3.44 (m, 1H, one of CH_2N), 3.64-3.76 (m, 3H, CH_2Cl and one of CH_2N), 3.91 (dd, 1H, *J*= 6.3 and 8.8 Hz, one of CH_2O), 4.26-4.39 (m, 1H, CHN), 4.58 (t, 1H, *J*= 8.8 Hz, one of CH_2O); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.91, 22.45, 23.46, 28.92, 28.96, 29.13, 31.62, 41.31, 43.05, 44.15, 45.59, 51.64, 68.31, 157.47, 207.91; HRMS calcd for $C_{15}H_{26}ClNO_3$ 303.1601, found 303.1609.

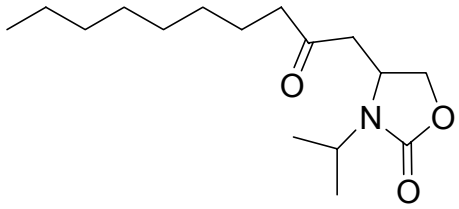
3-Benzyl-4-(2-oxo-decyl)-oxazolidin-2-one (3d)



(70 % yield) Colorless wax; IR (neat) 2927, 1758, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.88 (t, 3H, *J*= 6.8 Hz, CH_3), 1.08-1.48 （m, 12H, CH_2）, 2.24 (t, 2H, *J*= 8.3 Hz, C=OCH_2), 2.50 (dd, 1H, *J*= 9.3 and 18.1 Hz, one of C=OCH_2), 2.87 (dd, 1H, *J*= 3.9 and 18.1 Hz, one of C=OCH_2), 3.87 (dd, 1H, *J*= 6.6 and 8.6 Hz, one of CH_2O), 3.97-4.11 (m, 1H, CHN), 4.21 (d, 1H, *J*= 15.7 Hz, one of CH_2Ph), 4.54 (t, 1H, *J*= 8.6 Hz, one of

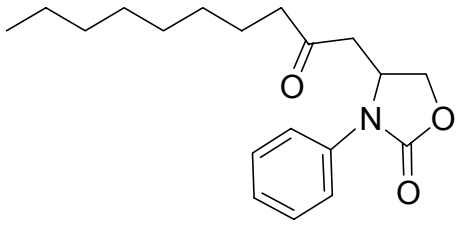
CH_2O), 4.21 (d, 1H, *J*= 15.7 Hz, one of CH_2Ph), 7.20-7.83 (m, 5H, Ph); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.99, 22.53, 23.41, 28.94, 29.18, 29.29, 31.67, 42.97, 45.33, 46.49, 50.82, 68.16, 127.77, 127.92, 127.77, 128.78, 158.31, 207.84; HRMS calcd for $C_{20}H_{29}NO_3$ 331.2147, found 331.2136.

3-Isopropyl-4-(2-oxo-decyl)-oxazolidin-2-one (3e)



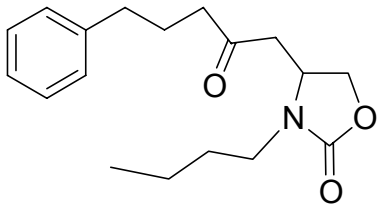
(87 % yield) Colorless wax; IR (neat) 2927, 1751, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.81 (t, 3H, *J*= 6.8 Hz, CH_3), 1.03-1.29 （m, 18H, CH_2 and $CH(C\underline{H}_3)_2$）, 2.37 (t, 2H, *J*= 7.3 Hz, $C=OCH_2$), 2.65 (dd, 1H, *J*= 10.3 and 18.6 Hz, one of $C=OCH_2$), 2.92 (dd, 1H, *J*= 3.4 and 18.6 Hz, one of $C=OCH_2$), 3.71-3.85 (m, 2H, one of CH_2O and $CHMe_2$), 4.10-4.19 (m, 1H, CHN), 4.41 (t, 1H, *J*= 8.8 Hz, one of CH_2O); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.99, 19.19, 21.32, 22.52, 23.51, 28.98, 29.01, 29.19, 31.67, 43.21, 45.85, 47.31, 50.32, 68.35, 157.29, 208.33; HRMS calcd for $C_{16}H_{29}NO_3$ 283.2147, found. 283.2136.

3-(4-Phenyl)-4-(2-oxo-decyl)-oxazolidin-2-one (3f)



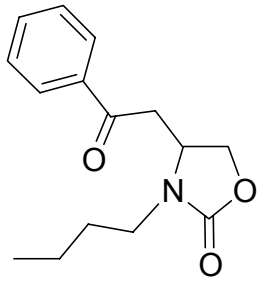
(85 % yield) Colorless wax; IR (neat) 2927, 1758, 1709, 755 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.87 (t, 3H, *J*= 6.8 Hz, CH_3), 1.17-1.55 （m, 12H, CH_2）, 2.32 (t, 2H, *J*= 7.3 Hz, $C=OCH_2$), 2.65 (dd, 1H, *J*= 9.8 and 18.1Hz, one of $C=OCH_2$), 2.97 (dd, 1H, *J*= 2.9 and 18.1 Hz, one of $C=OCH_2$), 4.01 (dd, 1H, *J*= 5.4 and 8.8 Hz, one of CH_2O), 4.67 (dd, 1H, *J*= 8.3 and 8.8 Hz, one of CH_2O), 4.75-4.85 (m, 1H, CHN), 7.14-7.41 (m, 5H, arom); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.81, 22.34, 23.26, 28.80(d), 28.99, 31.50, 42.87, 44.68, 52.16, 67.67, 121.68, 125.22, 129.06, 136.05, 155.29, 208.13; HRMS calcd for $C_{21}H_{27}NO_3$ 317.1991, found 317.1991.

3-Butyl-4-(2-oxo-5-phenylpentyl)-oxazolidin-2-one (3g)



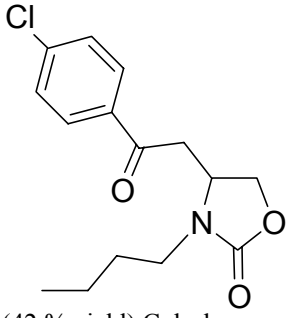
(56 % yield) Colorless wax; IR (neat) 2931, 1751, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.92 (t, 3H, *J*= 7.2 Hz, CH_3), 1.24-1.38 (m, 2H, CH_2), 1.41-1.54 (m, 2H, CH_2), 1.91 （tt, 2H, *J*= 7.3 and 7.4 Hz, $C\underline{H}_2CH_2Ph$）, 2.43 (t, 2H, *J*= 7.3 Hz, $C=OC\underline{H}_2CH_2$), 2.53 (dd, 1H, *J*= 9.4 and 18.8 Hz, one of $C=OCH_2$), 2.61 (t, 2H, *J*= 7.4 Hz, $PhCH_2$), 2.88 (m, 1H, one of NCH_2), 2.90 (dd, 1H, *J*= 3.9 and 18.8 Hz, one of $C=OCH_2$), 3.37-3.45 (m, 1H, one of NCH_2), 3.78 (dd, 1H, *J*= 6.0 and 8.9 Hz, one of OCH_2), 4.06-4.16 (m, 1H, CHN), 4.48 (t, 1H, *J*= 8.9 and 8.9 Hz, one of CH_2O); 7.12-7.31 (m, 5H, Ph); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.50, 19.62, 24.60, 29.14, 34.70, 41.56, 42.02, 45.21, 50.52, 67.87, 125.76, 128.45, 128.58, 140.90, 157.75, 207.48; HRMS calcd for $C_{18}H_{25}NO_3$ 303.1834, found 303.1834.

3-Butyl-4-(2-oxo-2-phenyl-ethyl)-oxazolidin-2-one (3h)



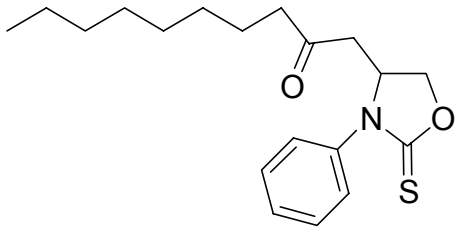
(38 % yield) Colorless wax; IR (neat) 2958, 1747, 1678 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.93 (t, 3H, *J*= 7.3 Hz, CH_3), 1.26-1.61 (m, 4H, CH_2), 2.96-3.06 （m, 1H, one of NCH_2）, 3.14 (dd, 1H, *J*= 9.3 and 17.6 Hz, one of $C=OCH_2$), 3.45-3.55 (m, 1H, one of NCH_2), 3.55 (dd, 1H, *J*= 3.9 and 17.6 Hz, one of $C=OCH_2$), , 3.95 (dd, 1H, *J*= 5.9 and 8.8 Hz, one of OCH_2), 4.32-4.43 (m, 1H, CHN), 4.63 (t, 1H, *J*= 8.8 Hz, one of OCH_2), 7.49-7.94 (m, 5H, Ph); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.64, 19.80, 29.34, 41.51, 41.81, 51.22, 68.23, 127.91, 128.81, 133.93, 137.22, 157.95, 196.93; HRMS calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1368.

3-Butyl-4-[2-(4-chloro-phenyl)-2-oxo-ethyl]-oxazolidin-2-one (3i)



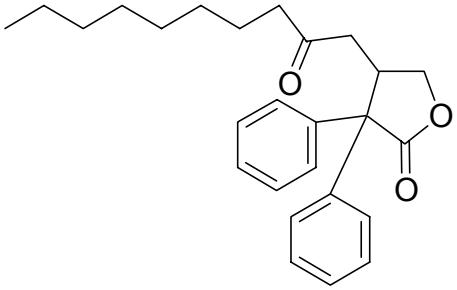
(42 % yield) Colorless wax; IR (neat) 2958, 1747, 1681 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.94 (t, 3H, *J*= 7.3 Hz, CH_3), 1.22-1.61 (m, 4H, $2CH_2$), 2.94-3.05 （m, 1H, one of NCH_2）, 3.13 (dd, 1H, *J*= 9.3 and 18.1 Hz, one of $C=OCH_2$), 3.46-3.57 (m, 1H, one of NCH_2), 3.52 (dd, 1H, *J*= 3.4 and 18.1 Hz, one of $C=OCH_2$), , 3.95 (dd, 1H, *J*= 5.4 and 8.8 Hz, one of OCH_2), 4.33-4.42 (m, 1H, CHN), 4.63 (t, 1H, *J*= 8.8 Hz, one of OCH_2), 7.47 (d, 2H, *J*= 8.3 Hz, arom), 7.90 (d, 2H, *J*= 8.3 Hz, arom); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.63, 19.81, 29.34, 41.47, 41.81, 51.13, 68.14, 129.17, 129.33, 134.21, 140.47, 157.89, 195.74; HRMS calcd for $C_{15}H_{18}ClNO_3$ 295.0975, found 295.0976.

1-(3-Phenyl-2-thioxo-oxazolidin-4-yl)-decan-2-one (5)



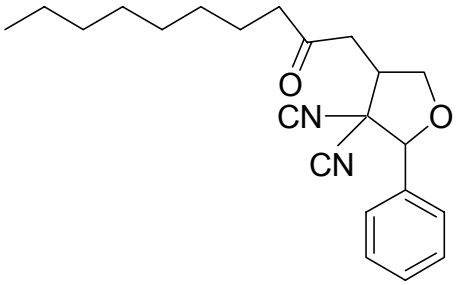
(76 % yield) Colorless wax; mp 80°C; IR (neat) 2927, 1743, 1700 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.87 (t, 3H, *J*= 7.3 Hz, CH_3), 1.16-1.53 （m, 12H, CH_2）, 2.20-2.40 (m, 2H, $C=OCH_2$), 2.71 (dd, 1H, *J*= 9.8 and 18.1Hz, one of $C=OCH_2$), 2.85 (dd, 1H, *J*= 3.4 and 18.1 Hz, one of $C=OCH_2$), 4.24 (dd, 1H, *J*= 6.8 and 9.3 Hz, one of CH_2O), 4.73-4.85 (m, 1H, CHN), 5.01 (t, 1H, *J*= 9.3 Hz, one of CH_2O), 7.14-7.55 (m, 5H, arom); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ14.05, 22.56, 23.41, 28.99(d), 29.19, 31.71, 43.00, 45.51, 58.56, 72.91, 121.91, 128.54, 129.62, 136.85, 187.70, 207.51; HRMS calcd for $C_{19}H_{27}NO_sS$ 333.1762, found 333.1755. calcd for $C_{19}H_{27}NO_sS$ C 68.43, H 8.16, N 4.20; found C 68.20, H 7.96, N 4.14.

4-(2-Oxo-decyl)-3,3-diphenyl-dihydro-furan-2-one (6)



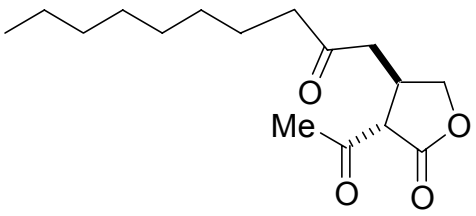
(47 % yield) Colorless wax; bp 190°C/0.1 mmHg; IR (neat) 2923, 1778, 1712 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.87 (t, 3H, *J*= 6.9 Hz, CH_3), 1.16-1.52 （m, 12H, CH_2）, 2.04 (dd, 1H, *J*= 10.4 and 18.3 Hz, one of $C=OCH_2$), 2.24 (t, 2H, *J*= 7.4 Hz, $C=OCH_2$), 2.48 (dd, 1H, *J*= 3.5 and 18.3 Hz, one of $C=OCH_2$), 3.84-3.92 (m, 2H, one of CH_2O and CHN), 4.66 (dd, 1H, *J*= 5.9 and 8.4 Hz, one of CH_2O), 7.05-7.50 (m, 10H, Ph); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ14.07, 22.60, 23.53, 29.03, 29.11, 29.24, 31.78, 38.44, 42.58, 43.14, 58.59, 69.83, 127.42, 127.90, 128.10, 128.45, 128.56, 128.62, 138.72, 139.18, 177.11, 208.63; HRMS calcd for $C_{26}H_{32}O_3$ 392.2351, found 392.2356.

4-(2-Oxo-decyl)-2-phenyl-dihydrofuran-3,3-dicarbonitrile (7)



(78 % yield, dr = 40 : 60) (Major isomer) Colorless wax; IR (neat) 2923, 1708 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.88 (t, 3H, *J*= 6.8 Hz, CH_3), 1.18-1.62 （m, 12H, CH_2）, 2.45-2.53 (m, 2H, $C=OCH_2$), 2.87 (dd, 1H, *J*= 9.3 and 18.1 Hz, one of $C=OCH_2$), 3.15 (dd, 1H, *J*= 3.5 and 18.1 Hz, one of $C=OCH_2$), 3.39-3.48 (m, 1H, CCH), 3.85 (dd, 1H, *J*= 8.3 and 9.3 Hz, one of CH_2O), 4.54 (t, 1H, *J*= 9.3 Hz, one of CH_2O), 5.18 (s, 1H, CH), 7.38-7.54 (m, 5H, Ph); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ14.00, 22.53, 23.57, 29.01(d), 29.19, 31.68, 42.67, 43.13, 45.29, 46.91, 71.68, 86.55, 113.21, 126.06, 128.72, 129.98, 132.79, 206.95; HRMS calcd for $C_{22}H_{28}N_2O_2$ 352.2151, found 352.2145.

3-Acetyl-4-(2-oxo-decyl)-dihydro-furan-2-one (8)



(72 % yield) Colorless wax; IR (neat) 1774, 1716, 1643 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$, 25 ºC) δ0.88 (t, 3H, *J*= 6.8 Hz, CH_3), 1.18-1.60 （m, 12H, CH_2）, 2.28 (s, 3H, $C=OCH_3$), 2.34-2.79 (m, 4H, , $C=OCH_2$), 3.26-3.40 (m, 1H, ring CH), 3.48 (d, 1H, *J*= 7.8 Hz, CHAc), 3.91 (t, 1H, *J*= 8.5 Hz, one of CH_2O), 4.61 (t, 1H, *J*= 8.5 Hz, one of CH_2O); ^{13}C NMR(67.9 MHz, $CDCl_3$, 25 ºC) δ13.91, 22.47, 23.51, 28.93, 28.98, 29.14, 29.48, 31.62, 32.77, 42.73, 44.32, 58.08. 71.59, 171.89, 200.05, 208.51; HRMS calcd for $C_{16}H_{26}O_4$ 282.1831, found 282.1823.