Supporting Information

Formation of Organomagnesium Compounds via EtMgBr-Mediated Radical Cyclization of Allyl β-Iodoacetals (ol991403a)

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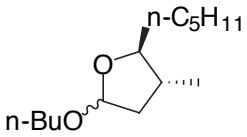
Instrumentation and Materials

^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica gel 60F_{254}. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Dichloromethane was dried with molecular sieves 4A. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. DME was distilled from sodium benzophenone ketyl and stocked under argon. Grignard reagents were prepared from the corresponding alkyl halide and Mg turning (Nacalai tesque, INC). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The starting allyl β-iodoacetals were prepared according to the reported procedure.[1]

(1) Stork, G.; Sher, P. M. *J. Am. Chem. Soc*. **1986**, *108*, 303.

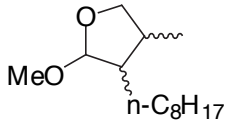
Experimental

General Procedure for Radical Cyclization of Allyl β-iodoacetals in THF



Reductive cyclization of iodoethanal butyl 1-vinylhexyl acetal (Table 1, Entry 2) is representative. To a solution of iodoethanal butyl 1-vinylhexyl acetal (354 mg, 1.0 mmol) in THF (5 mL) was added a THF solution of EtMgBr (2.0 mL, 1.0 M, 2.0 mmol) dropwise at room temperature. After being stirred for 20 min, white precipitates were formed. The reaction mixture was stirred for 2 h. The reaction mixture was poured into saturated aqueous NH_4Cl (20 mL) and extracted with hexane (20 mL × 3). The organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the residual oil afforded 2-butoxy-4-methyl-5-pentyltetrahydrofuran (194 mg, 0.85 mmol) in 85% yield as a 50/50 isomeric mixture. Spectral data for this compound was identical with those reported in the literature.[2]

2-Methoxy-4-methyl-3-octyltetrahydrofuran (41/40/14/5 Isomeric Mixture):

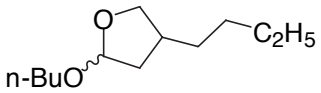


This isomeric mixture was converted into the corresponding lactone via Jones oxidation for data collection. 4-Methyl-3-octyltetrahydro-2-furanone (46/54): Faster moving band, R_f = 0.45 (hexane/ethyl acetate = 5/1) IR (neat) 3525, 2924, 2852, 1776, 1466, 1381, 1336, 1165, 1132, 1019 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.5 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H), 1.16-1.60 (m, 13H), 1.61-1.78 (m, 1H), 2.05 (dt, *J* = 9.6, 6.0 Hz, 1H), 2.28 (dddq, *J* = 8.1, 9.0, 9.6, 6.6 Hz, 1H), 3.68 (dd, *J* = 8.4, 9.0 Hz, 1H), 4.31 (dd, *J* = 8.1, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.87, 16.68, 22.44, 26.58,

(2) Inoue, R.; Nakao, J.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2039-2049.

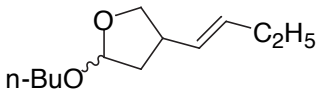
28.78, 29.04, 29.18, 29.45, 31.65, 35.93, 46.55, 72.42, 179.48. Found: C, 73.57; H, 11.47%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%. Slower moving band, R_f = 0.40 (hexane/ethyl acetate = 5/1) IR (neat) 2922, 2852, 1775, 1458, 1370, 1181, 1151, 1126, 1021, 987 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (t, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 7.2 Hz, 3H), 1.14-1.42 (m, 13H), 1.60-1.78 (m, 1H), 2.47 (dt, *J* = 5.7, 7.5 Hz, 1H), 2.57 (dddq, *J* = 1.8, 5.4, 5.7, 7.2 Hz, 1H), 3.89 (dd, *J* = 1.8, 8.7 Hz, 1H), 4.21 (dd, *J* = 5.4, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.16, 13.81, 22.39, 24.63, 27.30, 29.00, 29.13, 29.28, 31.60, 32.84, 43.51, 73.05, 178.94. Found: C, 73.59; H, 11.56%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

2-Butoxy-4-butyltetrahydrofuran (50/50 Isomeric Mixture):



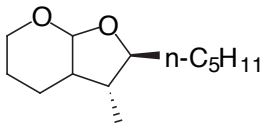
Spectral data for this compound was identical with those reported in the literature.[3]

2-Butoxy-4-(1-butenyl)tetrahydrofuran (50/50 Isomeric Mixture):



Spectral data for this compound was identical with those reported in the literature.[2]

7-Methyl-2,9-dioxa-8-pentylbicyclo[4.3.0]nonane (44/56 Isomeric Mixture)

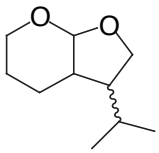


Faster moving band, R_f = 0.56 (hexane/ethyl acetate = 5/1): IR (neat) 3440, 2928, 2870, 1648, 1459, 1402, 1380, 1251, 1146, 1114, 1073, 994, 965, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 1.18-1.70 (m, 12H), 1.86-2.02 (m, 2H), 3.59 (ddt, *J* = 3.6, 11.1, 1.5 Hz,

(3) Tang, J.; Shinokubo, H.; Oshima, K. *Tetrahedron* **1999**, *55*, 1893-1904.

1H), 3.68-3.79 (m, 2H), 5.25 (d, J = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.48, 13.90, 20.06, 22.49, 23.16, 25.84, 31.94, 35.02, 39.02, 40.70, 61.00, 82.70, 100.90. Found: C, 73.33; H, 11.58%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%. **Slower moving band, R_f = 0.47 (hexane/ethyl acetate = 5/1)**: IR (neat) 3500, 2926, 1458, 1377, 1340, 1221, 1156, 1128, 1097, 1043, 980, 943, 900, 864, 810, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 6.6 Hz, 3H), 0.97 (d, J = 6.3 Hz, 3H), 1.21-1.40 (m, 6H), 1.46-1.73 (m, 5H), 1.74-1.83 (m, 2H), 1.92 (ddq, J = 8.1, 11.9, 6.3 Hz, 1H), 3.36 (ddd, J = 2.1, 11.7, 11.7 Hz, 1H), 3.54 (dt, J = 8.9, 6.0 Hz, 1H), 3.85 (ddd, J = 2.1, 2.1, 11.7 Hz, 1H), 4.92 (d, J = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 15.11, 20.59, 21.72, 22.52, 26.13, 31.83, 36.09, 37.58, 46.21, 64.45, 87.84, 101.52. Found: C, 73.68; H, 11.35%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

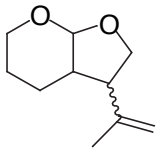
7-Isopropyl-2,9-dioxabicyclo[4.3.0]nonane (67/33 Isomeric Mixture)



Faster moving band, R_f = 0.53 (hexane/ethyl acetate = 3/1): IR (neat) 2936, 1467, 1402, 1253, 1142, 1114, 1087, 1031, 1000, 950, 898 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H), 1.27-1.43 (m, 1H), 1.50-1.74 (m, 4H), 1.85-1.95 (m, 2H), 3.64-3.79 (m, 3H), 3.92 (dd, J = 7.8, 7.8 Hz, 1H), 5.27 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.74, 20.88, 21.65, 23.21, 26.22, 35.67, 48.90, 60.70, 68.99, 102.11. Found: C, 70.52; H, 10.39%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%. **Slower moving band, R_f = 0.47 (hexane/ethyl acetate = 3/1)**: IR (neat) 3510, 2876, 1468, 1387, 1369, 1221, 1149, 1115, 1089, 1061, 1029, 949, 894, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H), 1.29-1.39 (m, 1H), 1.58-1.75 (m, 2H), 1.75-1.92 (m, 3H), 2.08 (dddd, J = 7.2, 8.1, 8.1, 8.7 Hz, 1H), 3.41 (ddd, J = 2.4, 11.4, 11.4 Hz, 1H), 3.66 (dd, J = 8.1, 8.4 Hz, 1H), 3.86 (ddd, J = 3.3, 3.9, 11.4 Hz, 1H), 4.16 (dd, J = 8.4, 8.7 Hz, 1H), 4.97 (d, J = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.37, 20.65, 21.36, 23.43, 29.98, 41.27, 44.31, 64.26, 71.03, 102.50. Found: C,

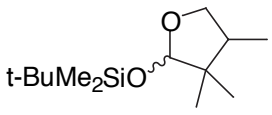
70.32; H, 10.39%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

7-Isopropenyl-2,9-dioxabicyclo[4.3.0]nonane (65/35 Isomeric Mixture)



Faster moving band, R_f = 0.50 (hexane/ethyl acetate = 3/1): IR (neat) 2934, 2880, 1649, 1451, 1401, 1145, 1072, 1048, 949, 889 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16-1.35 (m, 1H), 1.40-1.66 (m, 3H), 1.72 (s, 3H), 2.08 (dddd, *J* = 4.2, 6.0, 6.0, 12.0 Hz, 1H), 2.89 (ddd, *J* = 6.0, 7.5, 10.5 Hz, 1H), 3.58-3.76 (m, 2H), 3.91 (dd, *J* = 7.5, 8.1 Hz, 1H), 4.07 (dd, *J* = 8.1, 10.5 Hz, 1H), 4.55 (s, 1H), 4.86 (s, 1H), 5.36 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.96, 22.84, 23.05, 35.66, 47.12, 60.52, 66.80, 102.02, 111.05, 140.99. Found: C, 71.26; H, 9.39%. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. **Slower moving band, R_f = 0.45 (hexane/ethyl acetate = 3/1)**: IR (neat) 3072, 2930, 1640, 1458, 1380, 1227, 1120, 1025, 951, 888, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22-1.40 (m, 1H), 1.60-1.84 (m, 3H), 1.68 (s, 3H), 2.05 (dddd, *J* = 3.6, 3.6, 3.9, 11.1 Hz, 1H), 3.06 (ddd, *J* = 9.0, 9.0, 11.1 Hz, 1H), 3.41 (ddd, *J* = 2.4, 11.4, 11.7 Hz, 1H), 3.72 (dd, *J* = 8.4, 8.7 Hz, 1H), 3.89 (ddd, *J* = 3.0, 3.0, 11.7 Hz, 1H), 4.21 (dd, *J* = 8.7, 8.7 Hz, 1H), 4.81 (s, 1H), 4.84 (s, 1H), 5.02 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.99, 20.21, 21.64, 41.35, 45.52, 64.66, 71.86, 102.12, 113.17, 142.66. Found: C, 71,24; H, 9.35%. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%.

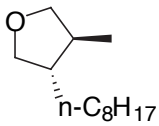
2-*t*-Butyldimethylsiloxy-3,3,4-trimethyltetrahydrofuran (35/65 Isomeric Mixture)



Faster moving band, R_f = 0.66 (hexane/ethyl acetate = 10/1): IR (neat) 2956, 2878, 1466, 1252, 1100, 1021, 994, 935, 861, 836, 777, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 6H), 0.78 (s, 3H), 0.85

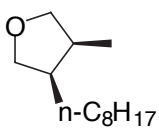
(d, J = 6.9 Hz, 3H), 0.87 (s, 9H), 0.93 (s, 3H), 2.18 (ddq, J = 8.4, 9.9, 6.9 Hz, 1H), 3.39 (dd, J = 8.1, 9.9 Hz, 1H), 4.04 (dd, J = 8.1, 8.4 Hz, 1H), 4.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –5.49, –4.39, 9.87, 17.86, 18.89, 20.65, 25.63, 38.61, 45.11, 73.28, 106.02. Found: C, 64.09; H, 11.64%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%. **Slower moving band, R_f = 0.62 (hexane/ethyl acetate = 10/1)**: IR (neat) 3450, 2950, 2856, 1459, 1252, 1101, 1074, 1052, 1022, 993, 938, 860, 837, 777, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.87 (s, 3H), 0.89 (s, 9H), 0.93 (s, 3H), 0.95 (d, J = 6.9 Hz, 3H), 1.86 (ddq, J = 6.9, 6.9, 8.1 Hz, 1H), 3.55 (dd, J = 6.9, 8.1 Hz, 1H), 4.03 (dd, J = 8.1, 8.1 Hz, 1H), 4.87 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –5.58, –4.37, 14.40, 16.57, 17.83, 25.63, 26.23, 41.41, 44.52, 73.24, 106.09. Found: C, 64.14; H, 11.63%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%.

***trans*-3-Methyl-4-octyltetrahydrofuran (R_f = 0.69 (hexane/ethyl acetate = 5/1))**:



IR (neat) 3450, 2954, 2920, 2850, 1638, 1459, 1379, 1044, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 1.16-1.40 (m, 13H), 1.44-1.55 (m, 1H), 1.58-1.72 (m, 1H), 1.73-1.89 (m, 1H), 3.28 (dd, J = 8.1, 8.1 Hz, 1H), 3.63 (dd, J = 8.1, 8.1 Hz, 1H), 3.93 (dd, J = 7.8, 7.8 Hz, 1H), 3.98 (dd, J = 7.8, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.96, 16.43, 22.55, 28.43, 29.18, 29.42, 29.81, 31.77, 32.40, 39.99, 47.09, 74.06, 75.28. Found: C, 78.44; H, 12.97%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.

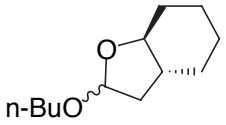
***cis*-3-Methyl-4-octyltetrahydrofuran (R_f = 0.63 (hexane/ethyl acetate = 5/1))**:



IR (neat) 3440, 2956, 2914, 2850, 1646, 1458, 1380, 1259, 1049, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H), 1.18-1.42 (m, 14H), 2.07-2.31 (m, 2H), 3.41 (dd, J = 8.4,

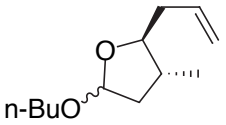
8.4 Hz, 1H), 3.45 (dd, *J* = 8.4, 3.9 Hz, 1H), 3.87 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.88 (dd, *J* = 7.5, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.82, 13.96, 22.55, 27.19, 28.56, 29.19, 29.44, 29.83, 31.77, 35.64, 42.41, 71.98, 75.29. Found: C, 78.59; H, 13.27%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.

8-Butoxy-7-oxabicyclo[4.3.0]nonane (5, Isomeric Mixture):



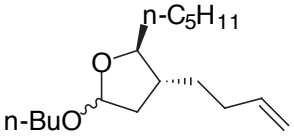
This isomeric mixture was converted into *trans*-7-oxabicyclo[4.3.0]nonan-8-one whose spectral data was identical with those reported in the literature.[3]

2-Butoxy-4-metyl-5-(2-propenyl)tetrahydrofuran (6, Isomeric Mixture):



This isomeric mixture was also converted into *trans*-4-methyl-5-(2-propenyl)tetrahydro-2-furanone whose spectral data was identical with those reported in the literature.[3]

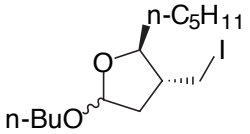
EtMgBr-Mediated Cyclization and Subsequent Functionalization



Cyclization of **7a** and trapping with allyl bromide is representative. Under reduced pressure, solvent was removed from an ethereal solution of EtMgBr (3.0 mL, 1.0 M, 3.0 mmol). The residual solid was dissolved in 5 mL of DME. To the mixture was added a solution of **7a** (354 mg, 1.0 mmol) in DME (2 mL) at room temperature. After being stirred for 30 min, allyl bromide (0.26 mL, 3.0 mmol) and a THF solution of CuCN•2LiCl (0.3 mL, 1.0 M, 0.3 mmol) were successively added. The

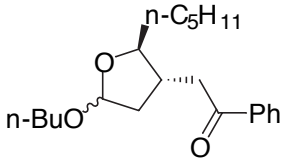
reaction mixture was stirred for 1h at room temperature. The reaction mixture was poured into saturated aqueous NH_4Cl (20 mL) and extracted with hexane (20 mL × 3). The organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the residual oil afforded 4-(3-butenyl)-2-butoxy-5-pentyltetrahydrofuran (196 mg, 0.73 mmol) in 73% yield as a 47/53 isomeric mixture. Spectral data for this compound was identical with those reported in the literature.[2]

2-Butoxy-4-iodomethyl-5-pentyltetrahydrofuran (51/49 Isomeric Mixture)



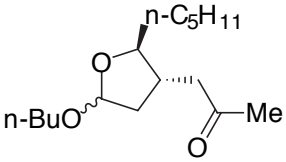
Faster moving band, R_f = 0.49 (hexane/ethyl acetate = 10/1): IR (neat) 2926, 2860, 1459, 1379, 1342, 1180, 1097, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.20-1.64 (m, 12H), 1.67-1.79 (m, 1H), 2.12-2.29 (m, 2H), 3.23 (dd, *J* = 7.8, 9.6 Hz, 1H), 3.31 (dd, *J* = 6.3, 9.6 Hz, 1H), 3.34 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.63 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.65-3.74 (m, 1H), 5.09 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.69, 13.73, 13.94, 19.30, 22.49, 25.44, 31.75, 31.76, 34.85, 40.42, 46.11, 66.92, 82.96, 102.94. Found: C, 47.41; H, 7.38%. Calcd for $C_{14}H_{27}IO_2$: C, 47.46; H, 7.68%. **Slower moving band, R_f = 0.46 (hexane/ethyl acetate = 10/1)**: IR (neat) 2926, 2858, 1459, 1378, 1350, 1181, 1090, 1029, 976 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.20-1.42 (m, 7H), 1.42-1.66 (m, 5H), 1.75 (ddd, *J* = 5.1, 9.9, 12.9 Hz, 1H), 2.16 (dd, *J* = 7.2, 12.9 Hz, 1H), 2.25-2.39 (m, 1H), 3.12 (dd, *J* = 7.5, 9.9 Hz, 1H), 3.27 (dd, *J* = 5.4, 9.9 Hz, 1H), 3.32 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.61-3.71 (m, 2H), 5.03 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.15, 13.77, 13.91, 19.31, 22.49, 25.88, 31.69, 31.69, 36.70, 41.32, 45.02, 66.85, 84.78, 103.19. Found: C, 47.50; H, 7.38%. Calcd for $C_{14}H_{27}IO_2$: C, 47.46; H, 7.68%.

4-Benzoylmethyl-2-butoxy-5-pentyltetrahydrofuran (50/50 Isomeric Mixture)



Faster moving band, R_f = 0.64 (hexane/ethyl acetate = 5/1): IR (neat) 2926, 2860, 1689, 1449, 1346, 1097, 982, 749, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.20-1.68 (m, 13H), 2.30-2.48 (m, 2H), 3.17 (d, *J* = 6.6 Hz, 2H), 3.36 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.67 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.76 (dt, *J* = 4.5, 6.6 Hz, 1H), 5.09 (dd, *J* = 1.5, 5.4 Hz, 1H), 7.40-7.49 (m, 2H), 7.50-7.58 (m, 1H), 7.91-7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.70, 13.91, 19.29, 22.48, 25.66, 31.77, 31.83, 34.44, 38.26, 39.07, 42.88, 66.92, 82.84, 103.61, 128.06, 128.62, 133.11, 137.11, 199.52. Found: C, 75.72; H, 9.44%. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70%. **Slower moving band, R_f = 0.51 (hexane/ethyl acetate = 5/1)**: IR (neat) 2926, 2858, 1686, 1599, 1449, 1350, 1216, 1181, 1092, 1002, 750, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.20-1.74 (m, 13H), 2.25 (dd, *J* = 6.9, 12.9 Hz, 1H), 2.56-2.72 (m, 1H), 2.92 (dd, *J* = 8.1, 15.9 Hz, 1H), 3.13 (dd, *J* = 5.4, 15.9 Hz, 1H), 3.33 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.67 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.73 (dt, *J* = 4.8, 7.5 Hz, 1H), 5.05 (d, *J* = 5.1 Hz, 1H), 7.46 (dt, *J* = 7.2, 7.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.74, 13.90, 19.28, 22.49, 26.01, 31.70, 31.76, 36.27, 38.50, 39.74, 42.38, 66.80, 85.17, 103.53, 128.12, 128.70, 133.20, 136.93, 199.06. Found: C, 75.58; H, 9.67%. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70%.

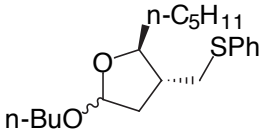
4-Acetylmethyl-2-butoxy-5-pentyltetrahydrofuran (50/50 Isomeric Mixture)



Faster moving band, R_f = 0.68 (hexane/ethyl acetate = 3/1): IR (neat) 2918, 2856, 1720, 1459, 1408, 1356, 1238, 1163, 1071, 997 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H), 1.20-1.60 (m, 13H), 2.12 (s, 3H), 2.09-2.23 (m, 1H), 2.28-2.40 (m, 1H), 2.58-2.64 (m, 2H), 3.34 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.56-3.68 (m, 2H), 5.05 (dd, *J* = 1.5, 5.7 Hz, 1H); ^{13}C NMR

($CDCl_3$) δ 13.68, 13.90, 19.25, 22.46, 25.66, 30.14, 31.74, 31.80, 34.25, 37.91, 39.00, 47.79, 66.94, 82.49, 103.48, 208.00. Found: C, 71.13; H, 11.05%. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18%. **Slower moving band, R_f = 0.51 (hexane/ethyl acetate = 3/1)**: IR (neat) 2928, 2863, 1720, 1461, 1357, 1164, 1096, 1069, 1032, 1002 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H), 1.20-1.62 (m, 13H), 2.13 (s, 3H), 2.18 (dd, *J* = 6.9, 12.9 Hz, 1H), 2.36 (dd, *J* = 8.4, 15.3 Hz, 1H), 2.40-2.53 (m, 1H), 2.58 (dd, *J* = 4.5, 15.3 Hz, 1H), 3.31 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.53-3.62 (m, 1H), 3.65 (dt, *J* = 9.3, 6.6 Hz, 1H), 5.01 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.73, 13.87, 19.27, 22.46, 25.96, 30.03, 31.68, 31.74, 36.18, 37.99, 39.57, 47.41, 66.76, 84.98, 103.41, 207.61. Found: C, 70.83; H, 10.94%. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18%.

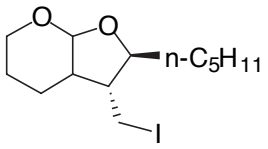
2-Butoxy-5-pentyl-4-(phenylthiomethyl)tetrahydrofuran (42/58 Isomeric Mixture)



Faster moving band, R_f = 0.48 (hexane/ethyl acetate = 10/1): IR (neat) 2922, 1585, 1480, 1461, 1439, 1378, 1342, 1265, 1090, 1026, 981, 735, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.20-1.64 (m, 12H), 1.77 (ddd, *J* = 1.5, 4.5, 13.5 Hz, 1H), 1.95-2.08 (m, 1H) 2.24 (ddd, *J* = 5.1, 9.9, 13.5 Hz, 1H), 3.02 (dd, *J* = 8.1, 12.6 Hz, 1H), 3.11 (dd, *J* = 6.9, 12.6 Hz, 1H), 3.35 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.65 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.81 (dt, *J* = 4.8, 6.8 Hz, 1H), 5.07 (dd, *J* = 1.5, 5.1 Hz, 1H), 7.13-7.21 (m, 1H), 7.24-7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.73, 13.92, 19.31, 22.49, 25.56, 31.77, 31.77, 34.89, 37.88, 38.69, 42.24, 66.88, 82.71, 103.46, 125.98, 128.95, 129.16, 136.56. Found: C, 71.12; H, 9.33%. Calcd for $C_{20}H_{32}O_2S$: C, 71.38; H, 9.58%. **Slower moving band, R_f = 0.41 (hexane/ethyl acetate = 10/1)**: IR (neat) 2928, 2856, 1585, 1480, 1439, 1378, 1290, 1236, 1091, 1026, 736, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.20-1.68 (m, 12H), 1.78 (ddd, *J* = 5.1, 9.6, 12.9 Hz, 1H), 2.17 (dd, *J* =7.2, 12.9 Hz, 1H), 2.30-2.44 (m, 1H), 2.90 (dd, *J* = 8.1, 12.6 Hz, 1H), 3.04 (dd, *J* = 6.3, 12.6 Hz, 1H),

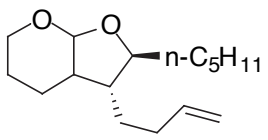
3.32 (dt, J = 9.6, 6.6 Hz, 1H), 3.66 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.77 (dt, *J* = 4.8, 7.5 Hz, 1H), 5.03 (d, *J* = 5.1 Hz, 1H), 7.14-7.21 (m, 1H), 7.23-7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.75, 13.90, 19.28, 22.49, 25.97, 31.67, 31.70, 36.84, 37.54, 39.59, 42.25, 66.81, 84.74, 103.54, 126.06, 128.99, 129.13, 136.60. Found: C, 71.12; H, 9.55%. Calcd for $C_{20}H_{32}O_2S$: C, 71.38; H, 9.58%.

7-Iodomethyl-2,9-dioxa-8-pentylbicyclo[4.3.0]nonane (60/40 Isomeric Mixture)



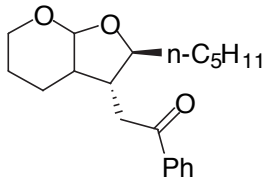
Faster moving band, R_f = 0.54 (hexane/ethyl acetate = 5/1): IR (neat) 2924, 2854, 1467, 1405, 1252, 1181, 1150, 1113, 1071, 962 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.20-1.64 (m, 11H), 1.78-1.94 (m, 1H), 2.07-2.18 (m, 1H), 2.31-2.44 (m, 1H), 3.08 (dd, *J* = 9.6, 10.5 Hz, 1H), 3.18 (dd, *J* = 6.0, 9.6 Hz, 1H), 3.61 (ddt, *J* = 1.5, 13.5, 3.9 Hz, 1H), 3.72-3.83 (m, 2H), 5.27 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 2.19, 13.90, 18.92, 22.45, 22.73, 25.58, 31.74, 35.60, 38.93, 49.99, 61.27, 80.56, 100.22. Found: C, 46.19; H, 7.04%. Calcd for $C_{13}H_{23}IO_2$: C, 46.16; H, 6.85%. **Slower moving band, R_f = 0.40 (hexane/ethyl acetate = 5/1)**: IR (neat) 2924, 2854, 1451, 1272, 1226, 1195, 1093, 1056, 1037, 897 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.20-1.46 (m, 6H), 1.46-1.74 (m, 4H), 1.75-1.86 (m, 3H), 1.91-2.01 (m, 1H), 3.24 (dd, *J* = 5.4, 10.5 Hz, 1H), 3.30 (dd, *J* = 4.5, 10.5 Hz, 1H), 3.38 (ddd, *J* = 2.7, 11.4, 11.4 Hz, 1H), 3.74 (dt, *J* = 4.8, 7.5 Hz, 1H), 3.87 (ddd, *J* = 2.7, 3.0, 11.4 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.31, 13.93, 20.65, 22.15, 22.50, 25.99, 31.66, 36.73, 44.05, 45.05, 64.26, 85.73, 101.28. Found: C, 46.20; H, 7.09%. Calcd for $C_{13}H_{23}IO_2$: C, 46.16; H, 6.85%.

7-(3-Butenyl)-2,9-dioxa-8-pentylbicyclo[4.3.0]nonane (61/39 Isomeric Mixture)



Faster moving band, R_f = 0.58 (hexane/ethyl acetate = 5/1): IR (neat) 2924, 2858, 1642, 1467, 1403, 1254, 1147, 1117, 1076, 996, 963, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.16-1.72 (m, 14H), 1.81-1.93 (m, 1H), 1.93-2.16 (m, 3H), 3.58-3.67 (m, 1H), 3.71-3.82 (m, 2H), 4.96 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 5.26 (d, *J* = 3.6 Hz, 1H), 5.79 (ddt, *J* = 10.2, 17.1, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.92, 19.75, 22.50, 23.26, 25.88, 25.92, 31.95, 32.35, 35.43, 36.94, 45.95, 60.91, 81.02, 100.78, 114.87, 138.32. Found: C, 75.86; H, 11.18%. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18%. **Slower moving band, R_f = 0.46 (hexane/ethyl acetate = 5/1)**: IR (neat) 2924, 2856, 1642, 1454, 1378, 1218, 1094, 1061, 1038, 994, 904 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.20-1.74 (m, 12H), 1.74-1.94 (m, 4H), 2.00-2.16 (m, 2H), 3.38 (ddd, *J* = 2.4, 11.1, 11.1 Hz, 1H), 3.68 (dt, *J* = 4.1, 7.7 Hz, 1H), 3.86 (ddd, *J* = 3.3, 3.3, 11.1 Hz, 1H), 4.92 (d, *J* = 2.7 Hz, 1H), 4.94-5.01 (m, 1H), 5.02 (ddt, *J* = 1.8, 17.1, 1.5 Hz, 1H), 5.79 (ddt, *J* = 10.2, 17.1, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.93, 20.85, 22.57, 22.88, 26.40, 31.64, 31.79, 31.89, 37.50, 42.70, 44.87, 64.26, 86.36, 101.61, 114.86, 138.50. Found: C, 76.12; H, 11.36%. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18%.

7-Benzoylmethyl-2,9-dioxa-8-pentylbicyclo[4.3.0]nonane (42/58 Isomeric Mixture)



Faster moving band, R_f = 0.48 (hexane/ethyl acetate = 3/1): IR (neat) 2928, 2862, 1686, 1598, 1449, 1379, 1275, 1149, 1098, 1003, 960, 902, 754, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.6 Hz, 3H), 1.20-1.64 (m, 12H), 2.21-2.33 (m, 1H), 2.48-2.61 (m, 1H), 2.95 (dd, *J* = 4.8, 17.4 Hz, 1H), 3.09 (dd, *J* = 9.9, 17.4 Hz, 1H), 3.56-3.65 (m, 1H), 3.70-3.81 (m, 1H), 3.86-3.95 (m, 1H), 5.31 (d, *J* = 3.9 Hz, 1H), 7.45 (dd, *J* = 7.5, 8.1 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.86, 20.16, 22.43, 22.97, 25.71, 31.82, 35.10, 36.02, 36,89, 41.65, 60.98, 80.79, 100.87, 127.95,

128.70, 133.30, 136.69, 198.86. **Slower moving band, R_f = 0.38 (hexane/ethyl acetate = 3/1)**: IR (neat) 2924, 2856, 1687, 1598, 1449, 1364, 1228, 1097, 1057, 1036, 897, 750, 689, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.6 Hz, 3H), 1.14-1.42 (m, 6H), 1.45-1.67 (m, 3H), 1.67-1.84 (m, 3H), 1.84-1.94 (m, 1H), 2.59-2.72 (m, 1H), 2.98 (dd, *J* = 6.0, 16.5 Hz, 1H), 3.07 (dd, *J* = 6.9, 16.5 Hz, 1H), 3.40 (ddd, *J* = 2.4, 11.1, 11.1 Hz, 1H), 3.75 (dt, *J* = 5.1, 7.7 Hz, 1H), 3.89 (ddd, *J* = 2.4, 3.9, 11.1 Hz, 1H), 4.96 (d, *J* = 3.6 Hz, 1H), 7.47 (dd, *J* = 7.2, 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.84, 20.57, 22.41, 22.54, 26.07, 31.61, 36.24, 38.95, 41.00, 45.26, 64.30, 85.88, 101.27, 128.06, 128.72, 133.27, 136.89, 199.19. Found: C, 75.77; H, 9.16%. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92%.