Supporting Information

For

A Rh(I)-Catalyzed Cycloisomerization of Homo- and Bis-homopropargylic Alcohols

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1. General Procedures

1) Method A

The synthesis of **2-Nonyl-2,3-dihydro-furan** (compound 5) is typical.

A mixture of **1-tridecyn-4-ol** (100mg, 0.509mmol), [Rh(COD)Cl]₂ (6.3mg, 0.013mmol, 2.5 mol%) and ligand **2e** (104mg, 0.280mmol, 55 mol%) in DMF (2.6mL, 0.2M) was placed in a pre-heated oil bath at 85°C and stirred for 2 h. The reaction mixture was cooled to rt, diluted with ether (30mL), and washed water (2 x 10mL). The aqueous layer was extracted with ether (2 x 20mL). The organic phases were combined, dried over anh. MgSO₄ and concentrated. The residual oil was purified by column chromatography (deactivated silica gel with 1% triethylamine, pet-ether:EtOAc=20:1) to give the title compound (69mg, 0.352mmol) as clear oil (69% yield).

2) Method B

The synthesis of **2-(3,4-dimethoxy-phenyl)-2,3-dihydrofuran** (compound 16) is typical.

A mixture of alcohol **8** (109mg, 0.528mmol), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0079mmol, 3.9mg, 1.5mol%), ligand **2e** (64mg, 0.174mmol, 33mol%) in DMF (2.6mL, 0.2M) was reacted for 3 h at 85°C. After work-up, the reaction mixture was purified by column chromatography (deactivated silica gel, eluted with pet-ether:EtOAc=9:1) to give the title compound (73mg, 0.353mmol) as clear oil (67% yield). Along with this compound, starting material (2mg, 0.01mmol, ~2% yield) was recovered.

3) Method C

The synthesis of **2,2-dimethyl-propionic acid 2,3-dihydro-furan-2-ylmethyl ester** (Compound 15) is typical.

A mixture of alcohol **7** (65mg, 0.36mmol), catalyst **3d** (22mg, 0.0177mmol, 5 mol%) and ligand **2e** (39mg, 0.0107mmol, 30 mol%) in DMF (1.8mL) was reacted at 85°C for 1 h. After work-up, the crude mixture was purified by column chromatography (deactivated silica gel, pet-ether:EtOAc=15:1) to give the title compound (44mg, 0.24mmol) as clear oil (68% yield).

4) Method D

The synthesis of compound 20 is typical.

A solution of alcohol **12** (109mg, 0.342mmol), catalyst **3c** (32mg, 0.0257mmol, 7.5 mol%), ligand **2d** (56mg, 0.154mmol, 45 mol%) in DMF (1.7mL) was placed in a pre-heated oil bath at 85°C and the solution was stirred for 2 h. After work-up, the crude mixture was purified by column chromatography (deactivated silica gel, pet-ether:EtOAc=7:1) to give the title compound (73mg, 0.229mmol) as clear oil (67% yield). Along with this compound, starting material (5mg, 0.02mmol, ~5% yield) was recovered.

2. Spectral data for compounds **5**, **14**~**22**.

Compound **5**

R_f 0.80 (pet-ether:EtOAc=20:1). IR (neat film): ν 2927, 2855, 1605, 1459, 1421, 1285, 1141, 1056 cm⁻¹. ¹H NMR (CDCl₃, 300MHz): δ 6.26(m, 1H), 4.83(m, 1H), 4.53(m, 1H), 2.65(m, 1H), 2.25(m, 1H), 1.20~2.00(m, 16H), 0.88(t, J=6.1Hz, 3H). ¹³C NMR (CDCl₃, 75MHz): δ 144.9, 98.9, 81.6, 36.1, 34.7, 31.9, 29.6, 29.5, 29.4, 29.2, 25.4, 22.6, 14.1. Anal. Calcd for C₁₃H₂₄O: C, 79.53; H, 12.32. Found: C, 79.30; H, 12.34.

2-Methyl-2-octyl-2,3-dihydro-furan :Compound **14**

R_f 0.80 (pet-ether:EtOAc=20:1). IR (neat film): ν 2929, 2856, 1605, 1587, 1421, 1285, 1123, 1056, 985 cm⁻¹. ¹H NMR (CDCl₃, 300MHz): δ 6.20(d, J=2.5Hz, 1H), 4.75(m, 1H),

2.45(m, 1H), 2.30(m, 1H), 1.60(m, 2H), 1.27(s, 3H), 1.20~1.25(m, 12H), 0.88(t, J=6.1Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz): δ 144.1, 98.3, 86.7, 41.3, 40.4, 31.9, 30.1, 29.6, 29.3, 26.4, 24.0, 22.6, 14.1. Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}$: C, 79.53; H, 12.32. Found: C, 79.43; H, 12.20.

2,2-dimethyl-propionic acid 2,3-dihydro-furan-2-ylmethyl ester : Compound 15¹

R_f 0.40 (pet-ether:EtOAc =10:1). $[\alpha]_D$ 81.4 (CHCl_3 , c 1.6). IR (neat film): ν 2972, 2878, 1731, 1622, 1478, 1460, 1280, 1038, 951, 901, cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 6.28 (dd, J = 2.3, 5.0 Hz, 1 H), 4.89 (dd, J = 2.6, 5.1 Hz, 1H), 4.74 (m, 1H), 4.19-4.09 (m, 2H), 2.73 (ddt, J = 15.3, 10.6, 2.4 Hz, 1H), 2.38 (ddt, J = 15.3, 7.3, 2.4 Hz, 1H), 1.21 (9 H, s). ^{13}C NMR (75 MHz, CDCl_3): δ 178.4, 145.1, 98.9, 78.3, 65.8, 38.9, 31.4, 27.2.

2-(3,4-dimethoxy-phenyl)-2,3-dihydrofuran :compound 16²

R_f 0.40 (pet-ether:EtOAc=4:1). IR (neat film): ν 3084, 2937, 2837, 1611, 1592, 1517, 1425, 1294, 1262, 1028 cm^{-1} . ^1H NMR (CDCl_3 , 300MHz): δ 7.18(m, 2H), 7.12(s, 1H), 6.43(m, 1H), 5.46(m, 1H), 4.97(m, 1H), 3.89(s, 3H), 3.87(s, 3H), 3.04(m, 1H), 2.62(m, 1H). ^{13}C NMR (CDCl_3 , 75MHz): δ 149.1, 148.5, 145.2, 135.4, 118.1, 114.8, 110.9, 99.2, 82.4, 55.9, 55.8, 37.6.

2-Heptyl-3,4-dihydro-2H-pyran (compound 17)³

R_f 0.80 (pet-ether:EtOAc=20:1). IR (neat film): ν 2928, 2856, 1730, 1461, 1260, 1121, 1033 cm⁻¹. ¹H NMR (CDCl₃, 300MHz): δ 6.36(d, J=5.7Hz, 1H), 4.65(m, 1H), 3.84(m, 1H), 1.85~2.10(m, 2H), 1.15~1.80(m, 14H), 0.88(t, J=6.5Hz, 3H). ¹³C NMR (CDCl₃, 75MHz): δ 143.8, 100.3, 75.2, 35.3, 31.8, 29.6, 29.3, 27.8, 25.3, 22.7, 19.9, 14.1.

2-Heptyl-2-methyl-3,4-dihydro-2H-pyran (compound 18)³

IR (neat film): ν 3060, 2928, 2854, 1919, 1649, 1589, 1495, 1233, 1259, 1067 cm⁻¹. ¹H NMR (CDCl₃, 300MHz): 6.26(m, 1H), 4.60(m, 1H), 1.95(m, 2H), 1.25~1.65(m, 14H), 1.22(s, 3H), 0.94(t, J=6.3Hz, 3H). ¹³C NMR (CDCl₃, 75MHz): δ 142.3, 98.8, 75.4, 39.5, 31.8, 31.3, 30.2, 29.3, 23.5, 23.4, 22.7, 17.6, 14.1.

Compound 19

R_f 0.25 (pet-ether:EtOAc=7:1) IR (neat film): ν 3062, 2974, 2862, 1882, 1639, 1613, 1514, 1463, 1385, 1302, 1245, 1077, 1035 cm⁻¹. ¹H NMR (CDCl₃, 300MHz): δ 7.19 (d, J=10.2Hz, 2H), 6.80(d, J=10.2Hz, 2H), 6.42(d, J=6.3Hz, for the major diastereomer), 6.29(d, J=5.8Hz, for the minor diastereomer), 4.89(td, J=5.8, 1.7Hz, for the major diastereomer), 4.74(dt, J=6.3, 2.0Hz, for the minor diastereomer), 3.80~4.20(m, 2H), 3.71(s, 3H), 1.80~2.10(m, 1H), 1.46~1.61(m, 1H), 1.22(d, J=6.3Hz, 3H). ¹³C NMR (CDCl₃,

75MHz): δ 159.1, 147.4, 145.4, 130.9, 130.6, 129.2, 129.1, 113.7, 102.5, 100.1, 71.0, 69.4, 69.1, 69.0, 68.0, 66.1, 55.2, 36.2, 35.8, 21.0, 20.8. HRMS: Clcd for $C_{14}H_{18}O_3$ (M^+): 234.1256. Found 234.1263.

compound 20

R_f 0.50 (pet-ether:EtOAc=9:1). $[\alpha]_D$ 11.5 (c 0.16 $CHCl_3$). IR (neat film): ν 3446, 2979, 2921, 1715, 1645, 1500, 1455, 1366, 1231, 1167, 1100 cm^{-1} . 1H NMR ($CDCl_3$, 300MHz): δ 7.26~7.40 (m, 5H), 6.36 (dd, $J=6.4, 1.7$ Hz, 1H), 4.82(d, $J=9.8$ Hz, 1H), 4.69(dt, $J=6.4, 1.7$ Hz, 1H), 4.68(d, $J=11.4$ Hz, 1H), 4.45(d, $J=11.4$ Hz, 1H), 4.29(dt, $J=5.4, 1.7$ Hz, 1H), 4.19(ddd, $J=9.8, 5.3, 1.7$ Hz, 1H), 4.09(q, $J=6.4$ Hz, 1H), 1.45(s, 9H), 1.30(d, $J=6.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 75MHz): δ 156.7, 145.2, 137.9, 128.3, 122.9, 127.7, 101.5, 79.4, 73.0, 70.5, 70.3, 47.5, 28.3, 17.0. HRMS: Clcd for $C_{18}H_{25}NO_4$ (M^+): 319.1783. Found 319.1792.

compound 21³

R_f 0.55 (pet-ether:EtOAc=9:1). $[\alpha]_D$ -13.0 (c 0.11, $CHCl_3$) IR (neat film): ν 3261, 2971, 1641, 1445, 1326, 1236, 1155, 1005 cm^{-1} . 1H NMR ($CDCl_3$, 300MHz): δ 7.75(d, $J=8.1$ Hz, 2H), 7.31(d, $J=8.1$ Hz, 2H), 6.28(dd, $J=6.4, 1.8$ Hz, 1H), 4.42(d, $J=9.0$ Hz, 1H), 4.28(dt, $J=6.4, 2.0$ Hz, 1H), 3.94~4.07(m, 2H), 2.43(s, 3H), 2.10(m, 1H), 1.44(m, 1H), 1.23(d, $J=6.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 75MHz): δ 146.4, 143.5, 138.0, 129.8, 127.0, 101.6, 71.6, 46.5, 38.0, 21.5, 20.8.

compound 22

R_f 0.65 (pet-ether:EtOAc=9:1). $[\alpha]_D$ 13.8 (c 0.20 CHCl_3). IR (neat film): ν 2975, 2932, 1690, 1454, 1366, 1329, 1147, 1108, 1027, 968 cm^{-1} . ^1H NMR (CDCl_3 , 500MHz): δ 7.28~7.40 (m, 5H), 5.09(d, $J=4.0\text{Hz}$, 1H), 4.76(d, $J=11.4\text{Hz}$, 1H), 4.65(dd, $J=5.8$, 3.2Hz, 1H), 4.41(d, $J=11.4\text{Hz}$, 1H), 4.17(m, 1H), 4.04(m, 1H), 3.84(m, 1H), 3.10(s, 3H), 1.90~2.12(m, 2H), 1.45(s, 9H), 1.20(d, $J=6.7\text{Hz}$, 3H), 1.19(d, $J=6.3\text{Hz}$, 3H), 1.13(d, $J=6.1\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 125MHz): δ 157.2, 138.7, 128.4, 128.2, 127.8, 95.5, 79.3, 71.3, 70.6, 68.5, 65.2, 51.9, 33.6, 28.4, 23.3, 21.4, 16.9. HRMS: Clcd for $\text{C}_{22}\text{H}_{35}\text{NO}_5$ (M^+): 393.2515. Found (submitted).

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