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Supporting Information

Selective Synthesis of Chiral Bicyclic [6.6.0] and [5.7.0] Ethers From 3,4-bisallyloxy-but-1-yne Derivatives via Ruthenium-Catalysed En-yn-ene Metathesis

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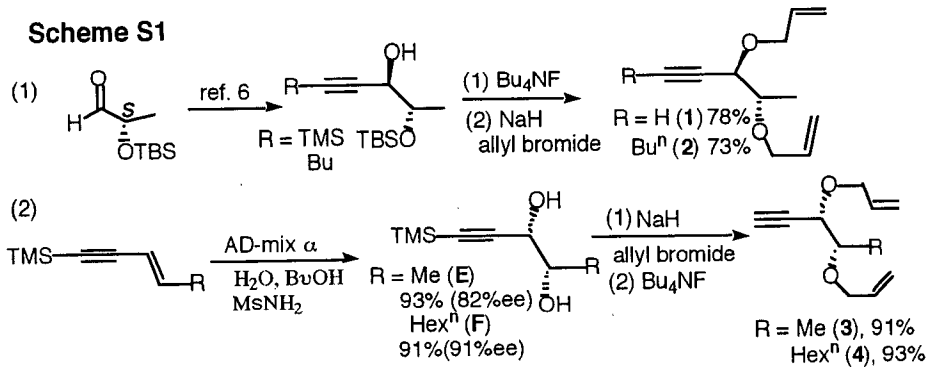
(I) Experimental Procedures for Synthesis of the Substrates

Scheme S1



(1) Synthesis of *(3R,4S)*-3,4-bisallyloxy-but-1-yne (1). To a THF solution (15 ml) of (*3R.4S*)-(t-butyl-dimethylsilyloxy)-2-trimethylsilyl-pent-1-yne-3-ol (2.00 g, 6.98 mmol)[7] was added Bu_4NF (1M in THF, 10.4 ml, 10.4 mmol) at 28 ^{0}C, and the mixture was stirred for 4 h. The reaction was quenched by aqueous $NH_4Cl_{(aq)}$ solution, followed by extraction with diethyl ether and drying over $MgSO_4$. Elution of the residues through a silica column using hexane/ether (1:1, R_f = 0.2) gave a diol (1.00 g,10.0 mmol) in 96 % yield. To a THF solution (30 ml) of NaH (0.60 g, 25.0 mmol) was slowly added this diol (1.0 g, 10.0 mmol) at 0 ^{0}C, and the mixture was stirred for 1 h before addition of allyl bromide (2.41 g, 20.0 mmol). The solution was stirred at RT for 10 h before addition of aqueous NH_4Cl solution. The solution was concentrated, and the organic layer was extracted with ether. Elution of the residues through a silica column using hexane/ether (4:1, R_f = 0.8), gave the dienyne **1** (0.95 g, 5.28 mmol) in 78 % yield.

Synthesis of (*3S, 4S*)-3,4-bisallyloxy-but-1-yne (3). To a mixture of *t*-BuOH (43 ml) and water (43 ml) was added AD-mix α (12.25 g), methanesulfonamide (1.05 g, 11 mmol) and enyne (1.52 g, 11 mmol) at 0 °C. The reaction was stirred at 0 °C without light for 27 hours. The mixtures were quenched by $Na_2SO_{3(s)}$ (13.24 g) at 0 °C for 45 minutes and warmed to RT for 1 h. The organic solvent was removed in vacuo, the organic layer was extracted with EtOAc and dred over $MgSO_4$. Elution of the residue through a silica column using hexane/ether (1:1, R_f = 0.2), gave the diol **E** (1.76 g, 10.2 mmol) in 91 % yield

To a THF solution (30 ml) of NaH (0.60 g, 25.0 mmol) was added diol **E** (1.0 g, 10.0 mmol) at 0 °C, and the mixture was stirred for 1 hour before addition of allyl bromide (2.41 g, 20.0 mmol). The mixture was stirred at room temperature for 10 hours before quenching with aqueous $NH_4Cl_{(aq)}$ solution. The organic layer was extracted with diethyl ether and dried over $MgSO_4$. The crude product was dissolved in THF (30 mL) and added with Bu_4NF (1M, THF, 12 ml, 12.0 mmol). The mixture were stirred for 4 hours at 23 °C. The solution was concentrated and the residues was eluted through a silica column (hexane/ether 4:1, R_f = 0.8) to give the dienyne **3** (0.94 g, 5.20 mmol, 82% ee) in 87 % yield. Crystallization of this sample from ether/hexane gave pure diol **3** (0.78 g, 4.37 mmol, 73%) in 96% ee.

Synthesis of (*3S, 4S*)-3,4-bisallyloxy-hexa-1,5-diyne) (5). To a THF solution (20 mL) of (*4S,5S*)-diethynyl-2,2-dimethyl-[1,3]-dioxolane (0.68 g, 7.0 mmol) was added concentrated HCl (10 mL), the mixture was stirred at 28 °C for 12 h. The

reaction was added with a saturated $NaHCO_3$ solution, followed by extraction with EtOAc. The extract was dried over $MgSO_4$ and concentrated to give a diol as an oil (0.53 g, 4.7 mmol, 67 % yield). To a THF solution (30 mL) containing NaH (0.30 g, 12.4 mmol), diol (0.63 g, 5.6 mmol) in THF (5.0 mL) was slowly added at 0 °C. The mixture was stirred for 1.5 h before addition of ally bromide (1.37 g, 11.2 mmol) and the resulting mixture was stirred at 23 °C for 10 hr. To the solution was added aqueous NH_4Cl solution, and concentrated in vacuo. The solution was extracted with diethyl ether and dried over $MgSO_4$. Elution of the residues through a short silica column using hexane/ether (3:1; R_f = 0.68), gave compound **5** as a dark oil (0.94 g, 4.9 mmol) in 84 %yield.

General Procedure for the Catalytic En-yn-ene Metathesis:

To a 25 ml round bottom flask was added ruthenium catalyst $(PCy_3)_2Cl_2Ru$=CHPh **A** (18.1 mg, 0.022 mmol, 2.0 mol %) in CH_2Cl_2 (7.39 mL, 0.15 M) via a syringe, and a CH_2Cl_2 solution (0.50 mL) of *anti*-diol derivative **1** (200 mg, 1.10 mmol) under an atmosphere of ethylene gas (1.0 atm). The resulting light brown solution was allowed to stir at 23 °C for 48 h. The solution was filtered over a short silica bed and purified by a preparative TLC plate (diethylether/hexane = 1/5) to afford fused dioxabicyclo[4.4.0]decane **8a** (100 mg, 0.65 mmol, 60 %), dioxabicyclo-[5.2.0]decane **8b** (13.3 mg, 0.087 mmol, 8 %) and furan derivative **8c** (31.0 mg, 0.172 mmol, 16.0 %), respectively.

(II) Spectral Data of the Compounds:

Spectral data for *(3R,4S)*-3,4-bisallyloxy-but-1-yne (1)

$[\alpha]^{23}_{D}$ – 69.9 (c =1.0, $CHCl_3$); IR (neat, cm^{-1}): 2218 (w), 1631 (s); ^1H NMR: δ 5.94-5.87 (m, 2 H), 5.29 (dd, *J* = 14.4, 2.0 Hz, 1H), 5.25 (dd, *J* = 14.4, 2.0 Hz, 1H), 5.17 (dd, *J* = 10.4, 2.0 Hz, 1H), 5.14 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.26 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.10-4.07 (m, 3 H), 3.99 (dd, *J* = 12.8, 6.8 Hz, 1H), 3.63 (m, 1 H), 2.42 (d, *J* = 2.0 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR: δ 135.3, 134.4, 117.7, 117.0, 80.8, 76.6, 74.9, 71.9, 70.9, 70.1, 16.2; HRMS calcd for $C_{11}H_{16}O_2$: 180.2473, Found 180.2472.

Spectral data for (*2S, 3R*)-2,3-bis-allyloxy-non-4-yne (2)

$[\alpha]^{23}_{D}$ – 65.7 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2230 (w), 1631 (s); ^1H NMR: δ 5.93-5.84 (m, 2 H), 5.26 (dd, *J* = 11.6, 1.6 Hz, 1 H), 5.23 (dd, *J* = 11.6, 1.6 Hz, 1 H), 5.14 (dd, *J* = 10.0, 1.6 Hz, 1 H), 5.11 (dd, *J* = 10.0, 1.6 Hz, 1 H), 4.24 (dd, *J* = 12.8, 4.8 Hz, 1 H), 4.11-4.06 (m, 3 H), 3.96 (dd, *J* = 12.8, 6.4 Hz, 1 H), 3.60-3.54 (m, 1 H), 2.22 (t, *J* = 6.8 Hz, 2 H), 1.50-1.41 (m, 2 H), 1.40-1.37 (m, 2 H), 1.21 (d, *J* = 6.4 Hz, 3 H), 0.838 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR: δ 135.2, 134.6, 117.1, 116.6, 87.3, 76.8, 71.7, 70.5, 69.6, 30.6, 21.8, 18.4, 15.8, 13.5; HRMS calcd for $C_{15}H_{24}O_2$: 236.3562, Found 236.3560.

Spectral data for (*3S, 4S*)-3,4-bisallyloxy-but-1-yne (3).

$[\alpha]^{23}_{D}$ + 34.7 (c =1.0, $CHCl_3$); IR (neat, cm^{-1}): 2145; ^1H NMR: δ 5.83-5.90 (m, 2 H), 5.27 (dd, *J* = 15.8, 2.0, 1H); 5.22 (dd, 1H, *J* = 16.4, 2.0 Hz, 1 H), 5.16 (dd, *J* = 10.4, 2.0 Hz, 1H), 5.13 (dd. *J* = 10.8, 2.0 Hz, 1 H), 4.23 (dd, *J* = 13.0, 1.2 Hz, 1

H), 4.10 (m, 3 H), 3.96 (dd, *J* = 12.8, 1.2 Hz, 1 H), 3.60 (m, 1 H), 2.41 (s, 1 H), 1.24 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR: δ 134.9, 133.9, 117.2, 116.6, 80.2, 74.8, 73.8, 72.2, 70.8, 69.9, 15.9; MS (75 eV, m/z): 180 (M^+); HRMS calcd for $C_{11}H_{16}O_2$: 180.1296, Found 180.1295.

Spectral data for (*3S, 4S*)-bis-allyloxy-dec-1-yne (4): $[\alpha]^{23}_D$ + 14.7 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2145 (w); ^{1}H NMR: δ 5.82-5.93 (m, 2 H), 5.22 (dd, J = 16.4, 1.6 Hz, 1 H), 5.19 (dd, J = 16.6, 2.0 Hz, 1 H), 5.14 (dd, J = 10.4, 1.6 Hz, 1 H), 5.12 (dd, J = 10.2, 2.0 Hz, 1 H), 4.24 (m, 2 H), 4.13 (dd, J = 6.0, 2.0 Hz, 1 H), 3.99 (m, 2 H), 3.39-3.42 (m, 1 H), 2.42 (s, 1 H), 1.61-1.75 (m, 4 H), 1.22-1.38 (m, 6 H), 0.85 (t, J = 6.8 Hz, 3 H); ^{13}C NMR: δ 135.2, 134.2, 117.4, 116.9, 80.7, 80.4, 75.0, 72.6, 71.8, 70.1, 34.9, 31.8, 29.7, 25.5, 22.6, 14.0; HRMS calcd for $C_{16}H_{26}O_2$: 250.1956, Found 250.1953.

Spectral data for (*3S, 4S*)-3,4-bisallyloxy-hexa-1,5-diyne) (5).

$[\alpha]^{23}_D$ + 80.7 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2218 (w), 1630 (s); ^{1}H NMR: δ 5.94-5.84 (m, 2 H), 5.33 (dd, *J* = 17.2, 1.6 Hz, 2 H), 5.20 (dd, *J* = 10.4, 1.6 Hz, 2 H), 4.32-4.27 (m, 4 H), 4.07 (dd, *J* = 12.8, 6.0 Hz, 2 H), 2.51 (s, 2 H); ^{13}C NMR: δ 133.6, 118.0, 79.2, 75.4, 70.5, 70.1; HRMS calcd for $C_{12}H_{14}O_2$: 190.2490, Found 190.2493.

Spectral data for (*3R, 4S*)-3-(allyloxy)-4-[(E)-but-2-enyloxy]-pent-1-yne (6):

$[\alpha]^{23}_D$ – 15.1 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2218 (w), 1629 (s); ^{1}H NMR: δ 5.97-

5.82 (m, 1 H), 5.65-5.62 (m, 1 H), 5.60-5.50 (m, 1 H), 5.26 (d, J = 17.2 Hz, 1 H), 5.20 (d, J = 10.4 Hz, 1 H), 4.30 (dd, J = 16.0, 8.0 Hz, 1 H), 4.21-3.96 (m, 4 H), 3.63-3.60 (m, 1 H), 2.42 (d, J = 2.0 Hz, 1 H), 1.68 (d, J = 4.4 Hz, 3 H) 1.21 (d, J = 5.6 Hz, 3 H); ^{13}C NMR: δ 134.1, 129.2, 127.8, 117.5, 80.7, 76.0, 74.6, 71.7, 70.4, 69.9, 17.6, 16.0; HRMS calcd for $C_{12}H_{18}O_2$: 194.1342, Found 194.1346.

Spectral data for (*3S, 4S*)-3-allyloxy-4-but-2-enyloxy-oct-1-yne (7): $[\alpha]^{23}_D$ + 9.9 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2107 (w), 1631 (s); ^{1}H NMR: δ 5.84-5.93 (m, 1 H), 5.61-5.70 (m, 1H), 5.56-5.61 (m, 1H), 5.31 (dd, J = 16.6, 2.0 Hz, 1 H), 5.19 (dd, J = 10.2, 2.0 Hz, 1 H), 4.28 (dd, J = 12.8, 4.4 Hz, 1 H), 4.15 (m, 2 H), 3.94 (dd, J = 13.0, 4.4 Hz, 2 H), 3.38-3.41 (m, 1 H), 2.41 (s, 1 H), 1.68 (d, J = 1.8 Hz, 3 H), 1.42-1.58 (m, 2 H), 1.33-1.41 (m, 4 H), 0.82 (t, J = 6.6 Hz, 3 H); ^{13}C NMR: δ 134.2, 129.3, 128.0, 117.3, 80.1, 79.9, 74.9, 72.2, 71.8, 70.1, 30.7, 27.7, 22.7, 17.7, 14.0; HRMS calcd for $C_{15}H_{24}O_2$: 236.1943, Found 236.1841.

Spectral data for (*8S, 8aR*)-8-Methyl-2,6,8,8a-tetrahyro-pyrano[3,4-b]-pyran (8a): $[\alpha]^{23}_D$ + 46.2 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 6.14 (d, *J* = 10.4 Hz, 1 H), 5.79 (d, *J* = 12.4 Hz, 1 H), 5.42 (s, 1 H), 4.30-4.18 (m, 4 H), 3.72 (d, *J* = 8.8 Hz, 1 H), 3.44-3.40 (m, 1 H), 1.20 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR: δ 130.5, 127.2, 124.3, 121.1, 74.4, 72.5, 65.9, 65.5, 18.4; HRMS calcd for $C_9H_{12}O_2$: 152.0854, Found 152.0859.

Spectral data for (*8S, 8aR*)-8-Methyl-2,6,8,8a-tetrahydro-furo[2,3-c]o oxepine (8b): $[\alpha]^{23}_{D}$ + 10.2 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 6.28 (d, *J* = 11.6 Hz, 1 H), 5.82 (s, 1 H), 5.63 (dd, *J* = 12.0, 4.4 Hz, 1 H), 4.62-4.58 (m, 2 H), 4.35 (dd, *J* = 14.0, 5.2 Hz, 1 H), 4.32-4.31 (m, 1 H), 4.26 (d, *J* = 17.6 Hz, 1 H), 3.34-3.31 (m, 1 H), 1.32 (d, *J* = 3.8 Hz, 3 H); ^{13}C NMR: δ 139.5, 130.5, 125.9, 120.6, 88.6, 79.1, 74.0, 69.4, 19.1; HRMS calcd for $C_9H_{12}O_2$: 152.0164, Found 152.0167.

Spectral data for (*2R*)-2-[(*1S*)-1-(-Allyloxy-ethyl)-3-vinyl-2,5-dihydro-furan (8c): $[\alpha]^{23}_{D}$ - 12.6 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 6.41 (dd, *J* = 18.0, 11.2 Hz, 1 H), 5.99-5.95 (m, 1 H), 5.90 (s, 1 H), 5.31 (dd, *J* = 16.0, 1.6 Hz, 1 H), 5.20-5.14 (m, 4 H), 4.74-4.69 (m, 2 H), 4.12 (dd, *J* = 12.8, 2.8 Hz, 1 H), 4.05 (dd, *J* = 12.8, 2.8 Hz, 1 H), 3.80-3.77 (m, 1 H), 1.04 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR: δ 139.1, 135.4, 129.4, 126.7, 116.7, 116.2, 86.2, 75.7, 75.6, 69.7, 12.7; HRMS calcd for $C_{11}H_{16}O_2$: 180.1257, Found 180.1252.

Spectral data for (*8S, 8aR*)-4-butyl-8-methyl-2,6,8,8a-tetrahydro-pyrano [3,4-b]pyran (9a): $[\alpha]^{23}_{D}$ + 8.4 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 5.63 (s, 1 H), 5.58 (s, 1 H), 4.31-4.22 (m, 4 H), 3.65 (d, J = 8.8 Hz, 1 H), 3.46-3.40 (m, 1 H), 2.18-2.10 (m, 2 H), 1.46-1.38 (m, 2 H), 1.30- 1.20 (m, 5 H), 0.890 (t, J = 6.8 Hz, 3 H); ^{13}C NMR: δ 133.2, 131.8, 122.9, 117.9, 74.6, 72.7, 66.2, 65.5, 30.9, 30.1, 18.6, 13.9; HRMS calcd for $C_{13}H_{20}O_2$: 208.1530, Found 208.1534.

Spectral data for (*8S, 8aR*)-4-butyl-8-methyl-2,6,8,8a-tetrahydrofuro[2,3-c]

oxepine (9b): $[\alpha]^{23}_{D}$ – 13.6 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 5.86 (s, 1 H), 5.59 (t, J = 2.8 Hz, 1 H), 4.63 (m, 2 H), 4.33-4.22 (m, 2 H), 4.03 (d, J = 16.4 Hz, 1 H), 3.38-3.34 (m, 1 H), 2.78-2.64 (m, 1 H), 2.42-2.22 (m, 2 H), 1.40-1.21 (m, 6 H), 0.886 (t, J = 7.6 Hz, 3 H); ^{13}C NMR: δ 140.5, 132.0, 127.2, 123.2, 88.8, 80.2, 74.0, 68.0, 36.7, 30.8, 22.4, 19.5, 13.8; HRMS calcd for $C_{13}H_{20}O_2$: 208.1463, Found 208.1460.

Spectral data for (*2R*)-2-[(*1S*)-1-allyloxy-ethyl]-3-(1-butyl-vinyl)-2,5-dihydro-furan (9c): $[\alpha]^{23}_{D}$ – 19.0 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 6.0-5.87 (m, 1 H), 5.86 (s, 1 H), 5.29-5.28 (m, 2 H), 5.17 (d, J = 3.2 Hz, 1 H), 4.98 (s, 1 H), 4.88 (s, 1 H), 4.72-4.70 (m , 2 H), 4.13 (dd, J = 12.8, 2.8 Hz, 1 H), 4.03 (dd, J = 12.8, 2.8 Hz, 1 H), 3.78-3.70 (m, 1 H), 2.33-2.20 (m, 2 H), 1.50-1.23 (m, 4 H), 1.01 (d, J = 6.4 Hz, 3 H), 0.895 (t, J = 7.2 Hz, 3 H); ^{13}C NMR: δ 141.1, 140.0, 135.4, 123.6, 116.6, 113.2, 86.7, 76.3, 75.6, 69.6, 34.5, 30.5, 22.4, 13.8, 12.5; HRMS calcd for $C_{15}H_{24}O_2$: 236.1854, Found 236.1852.

Spectral data for (*8S, 8aS*)-8-methyl-2,6,8,8a-tetrahydropyrano[3,4-b]pyran (10a): $[\alpha]^{23}_{D}$ – 38.5 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 6.18 (d, J = 10.0 Hz, 1 H), 5.82 (d, J = 2.8 Hz, 1 H), 5.48 (s, 1 H), 4.12-4.27 (m, 6 H), 1.24 (d, J = 6.8 Hz, 3 H); ^{13}C NMR: δ 129.09, 127.06, 124.97, 120.28, 70.26, 68.83, 65.42, 60.69, 11.52; HRMS calcd for $C_9H_{12}O_2$: 152.0856, Found 152.0855.

Spectral data for (*8S, 8aS*)-8-methyl-2,6,8,8a-tetrahydrofuro[2,3-c]oxepine (10b): $[\alpha]^{23}_{D}$ - 9.8 (c 0.1, $CHCl_3$); ^{1}H NMR: δ 6.21 (d, *J* = 12.0 Hz, 1 H), 5.81 (s, 1 H), 5.60 (td, *J* = 12.0, 3.4 Hz, 1 H), 4.95 (dd, *J* = 4.6, 2.0 Hz, 1 H), 4.64 (d, *J* = 5.2 Hz, 2 H), 4.28 (s, 2 H), 4.20-4.24 (m, 1 H), 1.16 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR: δ 140.31, 131.84, 125.70, 120.30, 88.08, 75.21, 73.54, 63.83, 15.08; HRMS calcd for $C_9H_{12}O_2$: 152.0156, Found 152.0155.

Spectral data for (*8S, 8aS*)-8-hexyl-2,6,8,8a-tetrahydropyrano[3,4-b]pyran (11a): $[\alpha]^{23}_{D}$ – 37.9 (c 1.0, $CHCl_3$); ^{1}H NMR: δ 6.16 (d, *J* = 10 Hz, 1 H), 5.79 (d, *J* = 10 Hz, 1 H), 5.49 (s, 1 H), 4.05-4.31 (m, 5 H), 3.93-3.98 (m, 1 H), 1.48-1.55 (m, 4 H) , 1.22-1.40 (m, 6 H) , 0.85 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR: δ 129.6, 127.1, 125.0, 120.7, 73.2, 70.3, 65.6, 60.8, 31.6, 29.2 25.5, 24.7, 22.5 13.9; HRMS calcd for $C_{14}H_{22}O_2$: 222.1628, Found 222.1629.

Spectral data for (*8S, 8aS*)-8-hexyl-2,6,8,8a-tetrahydrofuro[2,3-c]oxepine (11b): $[\alpha]^{23}_{D}$ – 10.6 (c 0.5, $CHCl_3$); ^{1}H NMR: δ 6.21 (d, *J* = 12 Hz, 1 H), 5.76 (s, 1 H), 5.58 (td, *J* = 12.0, 3.4, Hz, 1 H), 4.94 (dd, *J* = 4.6, 2.0 Hz, 1 H), 4.64 (d, *J* = 5.2 Hz, 2 H), 4.27 (s, 2 H), 3.96 (m, 1 H), 1.41-1.54 (m, 4 H), 1.17-1.39 (m, 6 H), 0.85 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR: δ 141.21, 131.84, 125.70, 120.3, 88.1 75.2, 73.5, 63.8, 31.7, 31.0, 29.7 25.5, 22..5, 1.8; HRMS calcd for $C_{14}H_{22}O_2$: 222.1623, Found 222.1622.

Spectral data for (*8R, 8aR*)-8-(1-ethynyl-2,6,8,8a-tetrahydro-pyrano[3,4-b]pyran (12a): $[\alpha]^{23}_D$ – 162.0 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 6.19 (d, J = 10.4 Hz, 1 H), 5.83 (d, J = 8.0 Hz, 1 H), 5.49 (s, 1 H), 4.89 (dd, J = 6.0, 2.0 Hz, 1 H), 4.52 (d, J = 18.0 Hz, 1 H), 4.31 (m, 3 H), 4.16 (d, J = 18.0 Hz, 1 H), 2.43 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.0, 127.3, 124.5, 120.2, 78.2, 74.7, 69.4, 65.5, 64.3, 62.0; HRMS calcd for $C_{10}H_{10}O_2$: 162.1711, Found 162.1715.

Spectral data for 3,3-divinyl-2,5,2,5-tetrahydro-[2,2]bifuranyl (12b): $[\alpha]^{23}_D$ – 143.0 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 6.56 (dd, J = 18.0, 11.2 Hz, 2 H), 6.00 (s, 2 H), 5.30 (t, J = 2.8 Hz, 2 H), 5.24 (d, J = 10.0 Hz, 2 H), 5.20 (d, J = 18.0 Hz, 2 H), 4.67 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 129.5, 127.1, 115.7, 84.3, 75.9; HRMS calcd for $C_{12}H_{14}O_2$: 190.2404, Found 190.2407.

Spectral data for *2R*-2-[(*1R*)-(1-allyloxy-prop-2-ynyl)-3-vinyl-2,5-dihydro-furan (12c): $[\alpha]^{23}_D$ – 15.4 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 6.44 (dd, J = 18.0, 11.2 Hz, 1 H), 6.1 (s, 1 H), 5.85-5.80 (m, 1 H), 5.28 (dd, J = 14.0, 2.0 Hz, 1 H), 5.17 (dd, J = 7.2, 1.6 Hz, 1 H), 5.10 (m, 1 H), 4.82 (dd, J = 14.0, 1.6 Hz, 1 H), 4.62 (d, J = 14.4 Hz, 1 H), 4.00 (s, 1 H), 4.23 (dd, J = 12.8, 4.0 Hz, 1 H), 3.97 (dd, J = 12.8, 6.8 Hz, 1 H), 2.45 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1,

134.0, 129.0, 127.5, 117.4, 116.3, 86.4, 80.6, 57.5, 74.6, 69.9, 69.7; HRMS calcd for $C_{10}H_{10}O_2$: 190.1069, Found 190.1071.

Spectral data for (*2S, 3R*)-3-allyloxy-2-[(E)-2-butenyloxy]-4-nonyne (13): $[\alpha]^{23}_D$ – 4.6 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2216 (w), 1630 (s).; ^1H NMR (400 MHz, $CDCl_3$): δ 5.94-5.86 (m, 1 H), 5.71-5.64 (m, 1 H), 5.60-5.50 (m, 1 H), 5.29 (d, J = 17.2 Hz, 1 H), 5.16 (d, J = 10.8 Hz, 1 H), 4.25 (dd, J = 12.8, 4.0 Hz, 1 H), 4.11-3.97 (m, 4 H), 3.62-3.52 (m, 1 H), 2.22 (t, J = 6.8 Hz, 2 H), 1.69 (d, J = 6.4 Hz, 3 H), 1.53-1.38 (m, 4 H), 1.22 (d, J = 6.4 Hz, 3 H), 0.902 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 129.2, 128.2, 117.3, 87.5, 76.7, 73.3, 72.0, 70.5, 69.9, 30.9, 22.1, 18.6, 17.9, 16.1, 13.7; HRMS calcd for $C_{16}H_{26}O_2$: 250.1933, Found 250.1937.

Spectral data for *(4S, 5S)*-4-allyloxy-5-but-2-enyloxy-undec-2-yne (14): $[\alpha]^{23}_D$ + 14.9 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2218 (w), 1631 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 5.84-5.89 (m, 1 H), 5.60-5.66 (m, 1 H), 5.51-5.58 (m, 1 H), 5.26 (dd, J = 16.6, 2.0 Hz, 1 H), 5.13 (dd, J = 10.4, 2.0 Hz, 1 H), 4.17 (dd, J = 12.8, 4.4 Hz, 1 H), 4.06 (m, 2 H), 3.96 (dd, J = 13.0, 4.4 Hz, 2 H), 3.31-3.33 (m, 1 H), 1.82 (s, 3 H), 1.66 (d, J = 6.6 Hz, 3 H), 1.61-1.66 (m, 2H), 1.48-1.50 (m, 2H), 1.22-1.38 (m, 6H), 0.84 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 129.1, 128.2, 116.7, 82.9, 80.4, 76.0, 72.4, 72.1, 69.8, 31.7, 31.2, 29.3, 25.5, 22.6, 17.6, 13.9, 3.6; HRMS calcd for $C_{18}H_{30}O_2$: 278.5385, Found 278.5284.

Spectral data for *(3R, 4S)*-4-(allyloxy)-3-[(E)-butenyloxy]-pent-1-yne (15): $[\alpha]^{23}{}_{D}$ – 106.4 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2220 (w), 1628 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 5.93-5.86 (m, 1 H), 5.74-5.70 (m, 1 H), 5.55-5.50 (m, 1 H), 5.25 (d, J = 17.2 Hz, 1 H), 5.20 (d, J = 9.6 Hz, 1 H), 4.19 (dd, J = 11.6, 6.4 Hz, 1 H), 4.09-4.05 (m, 3H), 3.92 (dd, J = 11.6, 7.2 Hz, 1 H), 3.63-3.60 (m, 1 H), 2.41 (d, J = 2.0 Hz, 1 H), 1.68 (d, J = 7.2 Hz, 3 H) 1.23 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 130.4, 127.1, 117.0, 81.0, 76.6, 74.7, 71.4, 70.9, 69.9, 17.9, 16.2; HRMS calcd for $C_{12}H_{18}O_2$: 194.1342, Found 194.1344.

Spectral data for *(4S, 5S)*-5-allyloxy-4-but-2-enyloxy-undec-2-yne (16): $[\alpha]^{23}{}_{D}$ + 31.0 (c 1.0, $CHCl_3$); IR (neat, cm^{-1}): 2218 (w), 1630 (s) ^1H NMR (400 MHz, $CDCl_3$): δ 5.83-5.93 (m, 1 H), 5.60-5.72 (m, 1 H), 5.49-5.60 (m, 1 H), 5.22 (d, J = 17.6 Hz, 1 H), 5.10 (d, J = 10.4 Hz, 1 H), 4.20 (dd, J = 14.6, 6.6 Hz, 2 H), 4.06 (m, 2 H), 3.95 (dd, J = 16.2, 6.8 Hz, 1 H), 3.30-3.34 (m, 1 H), 1.85 (s, 3 H), 1.68 (d, J = 4.4 Hz, 3 H), 1.61-1.64 (m, 2H), 1.46-1.52 (m, 2H), 1.23-1.40 (m, 6H), 0.84 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 129.5, 127.3, 116.7, 82.8, 80.8, 76.1, 72.4, 71.8, 69.6, 31.8, 31.1, 29.3, 25.5, 22.6, 17.7, 14.0, 3.6; HRMS calcd for $C_{18}H_{30}O_2$: 278.2259, Found 278.2158.

Spectral data for *(8S, 8aS)*-8-butyl-2,6,8,8a-tetrahydrofuro[2,3-c] oxepine (17b): $[\alpha]^{23}{}_{D}$ – 6.9 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 6.21 (d,

J = 12 Hz, 1 H), 5.76 (s, 1 H), 5.58 (td, J = 12.0, 3.4 Hz, 1 H), 4.94 (dd, J = 4.6, 2.0 Hz, 1 H), 4.64 (d, J = 5.2 Hz, 2 H), 4.27 (s, 2 H), 3.93-3.97 (m, 1 H), 1.43-1.46 (m, 2 H), 1.17-1.39 (m, 4 H), 0.85 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 132.0, 125.2, 120.0, 88.2, 78.1, 75.3, 64.5, 28.3, 24.6, 22.7, 14.0; HRMS calcd for $C_{12}H_{18}O_2$: 194.1356, Found 194.1255.

Spectral data for (*8S, 8aS*)-8-hexyl-4-methyl-2,6,8,8a-tetrahydropyrano[3,4-b] pyran (18a): $[\alpha]^{23}_D$ – 69.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.59 (s, 1 H), 5.57 (s, 1 H), 4.07-4.27 (m, 5 H), 3.89-3.94 (m, 1 H), 1.89 (s, 3H), 1.56-1.60 (m, 2 H), 1.42-1.56 (m, 2 H), 1.22-1.39 (m, 6 H), 0.84 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.4, 129.9, 124.1, 118.2, 73.6, 70.4, 65.6, 61.6, 31.8, 29.4, 26.0, 25.7, 22.6, 17.6, 14.0; HRMS calcd for $C_{15}H_{24}O_2$: 236.1661, Found 236.1660.

Spectral data for (*8S, 8aS*)-8-hexyl-4-methyl-2,6,8,8a-tetrahydrofuro[2,3-c] oxepine (18 b): $[\alpha]^{23}_D$ – 16.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (s, 1 H), 5.45 (s, 1 H), 5.03 (m, 1 H), 4.63 (d, J = 4.4 Hz, 2 H), 4.19 (s, 2 H), 3.88-3.93 (m, 1 H), 1.90 (s, 3 H), 1.40-1.51 (m, 4 H), 1.24-1.33 (m, 6 H), 0.83 (t, J = 6.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 129.1, 127.7, 123.0, 87.9, 78.9, 75.1, 64.7, 31.8, 29.4, 26.4, 25.9, 22.6, 22.6, 14.0; HRMS calcd for $C_{15}H_{24}O_2$: 236.1823, Found 236.1822.