Supporting Information

Stereoselective synthesis of cyclic ethers by intramolecular trapping of dicobalt hexacarbonyl- stabilized propargylic cations

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Preparation of 9-(*tert*-Butyl-diphenyl-silanyloxy)-7-nonyne-1,6-diol (2b). To a solution of the 6-(tetrahydro-pyran-2-yloxy)-hexan-1-ol (1 g, 4.94 mmol) in dry CH₂Cl₂ (25 mL) under argon was added Et₃N (4.8 mL, 35 mmol) and DMSO (3.2 mL) at 0 °C. After 15 min of stirring, SO₃·Py (2.34 g, 14.8 mmol) was added. The reaction was allowed to warm to room temperature and monitored for TLC until complete conversion (2 h). The reaction was diluted with CH₂Cl₂ and washed with HCl aqueous solution (5% w/v), a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄ and concentrated. The crude obtained was filtered through a pad of silica gel and the aldehyde was used in the next reaction.

n-BuLi (5 mL of a 1.5 M solution in hexane, 7.44 mmol) was added dropwise via syringe to a cooled (−78 °C) solution of *tert*-butyl-diphenyl-2-propynyloxy-silane (2.35 g, 8 mmol) in anhydrous THF (45 mL) under argon. After 15 min, the crude aldehyde dissolved in THF (5 mL) was added. The resulting mixture was stirred for 2 h and then quenched with saturated aqueous NH₄Cl and diluted with Et₂O. The aqueous layer was extracted with Et₂O and the combined organic layers were dried, filtered and concentrated to yield the crude propargylic alcohol as oil which was used without further purification.

To a stirred solution of the crude propargylic alcohol in MeOH (30 mL) was added Dowex 50Wx8 (500 mg, 30% (w)) at room temperature. The reaction mixture was vigorously stirred for 15 h, until TLC showed complete conversion. After filtration, the solution was concentrated and purified by silica gel flash-chromatography, yielding **2b** (1.46 g, 72 % overall yield). ¹H NMR (CDCl₃) 1.06 (s, 9H), 1.30-1.64 (m, 8H), 3.62 (t, *J* = 6.5 Hz, 2H), 4.30 (m, 1H), 4.36 (s, 2H), 7.41 (m, 6H), 7.71 (m, 4H); ¹³C NMR (CDCl₃) δ 19.1 (s), 24.8 (t), 25.4 (t), 25.9 (q), 32.5 (t), 37.4 (t), 52.7 (t), 62.2 (d), 62.7 (t), 83.1 (s), 86.3 (s), 127.7 (d), 129.8 (d), 133.2 (s), 135.6 (d); IR (film) (cm^{−1}) 3372, 2931, 2862, 1425, 1050; MS *m/z* (relative intensity) 353 (M – Bu-*t*)⁺ (0.7), 335 (M – H₂O – Bu-*t*) (31), 199 (100), 139 (34); HRMS calcd for C₂₁H₂₅O₃Si [M – Bu-*t*]⁺: 353.15730, found: 353.15786.

Preparation of 10-(*tert*-Butyl-diphenyl-silanyloxy)-8-decyne-1,7-diol (2c). The procedure used above to obtain **2b** was applied to 7-(tetrahydro-pyran-2-yloxy)-heptan-1-ol (1 g, 4.6 mmol) yielding **2c** (1.45 g, 74 % overall yield). ¹H NMR (CDCl₃) 1.07 (s, 9H), 1.25-1.64 (m, 10H), 3.61 (t, *J* = 6.6 Hz, 2H), 4.29 (t, *J* = 6.5 Hz, 1H), 4.37 (s, 2H), 7.41 (m, 6H), 7.71 (m, 4H); ¹³C NMR (CDCl₃) δ 19.1 (s), 25.0 (t), 25.6 (t), 26.7 (q), 29.0 (t), 32.5 (t), 37.4 (t), 52.7 (t), 62.2 (d), 62.8 (t), 83.0 (s), 86.5 (s), 127.7 (d), 129.8 (d), 133.2 (s), 135.6 (d); IR (film) (cm^{−1}) 3375, 2932, 2858, 1422, 1053; MS *m/z* (relative intensity) 367 (M – Bu-*t*)⁺ (0.7), 349 (M – H₂O – Bu-*t*) (36), 199 (100), 139 (42); HRMS calcd for C₂₂H₂₇O₃Si [M – Bu-*t*]⁺: 367.17295, found: 367.17112.

Preparation of 11-(*tert*-Butyl-diphenyl-silanyloxy)-9-undecyne-1,8-diol (2d). The procedure used above to obtain **2b** was applied to 8-(Tetrahydro-pyran-2-yloxy)-octan-1-ol (1 g, 4.3 mmol) yielding **2d** (1.35 g, 71 % overall yield). ¹H NMR (CDCl₃) 1.07 (s, 9H), 1.23-1.65 (m, 12H), 3.61 (t, *J* = 6.6 Hz, 2H), 4.29 (m, 1H), 4.37 (s, 2H), 7.41 (m, 6H), 7.71 (m, 4H); ¹³C NMR (CDCl₃) δ 19.1 (s), 25.0 (t), 25.6 (t), 26.7 (q), 29.2 (t), 29.3 (t), 32.6 (t), 37.5 (t), 52.7 (t), 62.2 (d), 62.8 (t), 83.0 (s), 86.5 (s), 127.7 (d), 129.8 (d), 133.2 (s), 135.6 (d); IR (film) (cm^{−1}) 3373, 2933, 2859, 1421, 1053; MS *m/z* (relative intensity) 381 (M – Bu-*t*)⁺ (0.7), 363 (M – H₂O – Bu-*t*) (56), 199 (100), 139 (50); HRMS calcd for C₂₃H₂₉O₃Si [M – Bu-*t*]⁺: 381.18860, found: 381.19106.

Preparation of *tert*-Butyl-(3-oxepan-2-yl-2-propynyloxy)-diphenyl-silane (4b). Solid Co₂(CO)₈ (376 mg, 1.1 mmol) was added to a solution of the alkyne **2b** (438 mg, 1 mmol) in anhydrous CH₂Cl₂ (5 mL) under argon atmosphere. The dark solution was stirred at room temperature until TLC showed the formation of the complex to be completed (ca. 4 h). The solvent of the resulting reaction mixture was then removed under vacuum, and the residue was purified by silica gel column chromatography to yield the Co₂(CO)₈-alkyne complex **3b** (673 mg, 93 % yield) as a dark red oil.

To a solution of cobalt complex **3b** (200 mg, 0.29 mmol) in CH₂Cl₂ (3 mL) under argon atmosphere was added dropwise BF₃·Et₂O (45 µL, 0.35 mmol) at –30 °C. After 50 min, TLC shows complete conversion to a less polar complex. The mixture was poured into saturated aqueous NaHCO₃ (5 mL) with vigorous stirring. The aqueous layer was extracted with CH₂Cl₂ and the combined organic layers were dried (MgSO₄), filtered and concentrated to yield the crude cobalt complex as an oil which was used without further purification.

The cobalt complex previously obtained was dissolved under argon atmosphere in 3 mL of reagent grade acetone at 0 °C. Ceric ammonium nitrate (643 mg, 1.17 mmol) was added in portions with stirring until evolution of CO ceased and the CAN color persisted (10 min). Solvent was removed under vacuum and the pink solid residue was then partitioned between Et₂O and distilled H₂O. The aqueous phase was extracted additionally twice with Et₂O. The combined organic extracts were dried, filtered, concentrated and subjected to silica gel flash chromatography yielding **4b** (88 mg, 78 % yield) as an oil. ¹H NMR (CDCl₃) 1.06 (s, 9H), 1.42–1.82 (m, 7H), 1.98 (m, 1H), 3.60 (m, 1H), 3.76 (m, 1H), 4.35 (m, 1H), 4.37 (s, 2H), 7.41 (m, 6H), 7.71 (m, 4H); ¹³C NMR (CDCl₃) δ 19.2 (s), 24.8 (t), 26.7 (q), 27.5 (t), 30.7 (t), 36.7 (t), 52.8 (t), 66.6 (t), 68.6 (d), 82.8 (s), 85.5 (s), 127.7 (d), 129.7 (d), 133.2 (s), 135.6 (d); IR (film) (cm^{–1}) 2934, 2856, 1422, 1110; MS m/z (relative intensity) 335 (M – Bu-*t*)⁺ (100), 256 (18), 199 (88), 139 (34); HRMS calcd for C₂₁H₂₃O₂Si [M – Bu-*t*]⁺: 335.14673, found: 335.14709; Anal. Calcd for C₂₅H₃₂O₂Si: C, 76.48; H, 8.22. Found: C, 76.48; H, 8.29.

Preparation of *tert*-Butyl-(3-oxocan-2-yl-2-propynyloxy)-diphenyl-silane (4c). The procedure used above to obtain **4b** applied to **3c** on a 200 mg (0.28 mmol) scale, yielding **4c** (82 mg, 72% yield). ¹H NMR (CDCl₃) 1.06 (s, 9H), 1.34–1.85 (m, 10H), 3.31 (m, 1H), 3.69 (m, 1H), 4.04 (m, 1H), 4.37 (s, 2H), 7.41 (m, 6H), 7.71 (m, 4H); ¹³C NMR (CDCl₃) δ 19.2 (s), 24.9 (t), 25.5 (t), 26.7 (q), 26.8 (t), 28.6 (t), 35.3 (t), 52.8 (t), 66.8 (t), 67.0 (d), 83.1 (s), 85.1 (s), 127.7 (d), 129.7 (d), 133.3 (s), 135.6 (d); IR (film) (cm^{–1}) 2930, 2857, 1462, 1421, 1110; MS m/z (relative intensity) 349 (M – Bu-*t*)⁺ (40), 300 (19), 199 (100), 139 (33); HRMS calcd for C₂₆H₃₄O₂Si [M]⁺: 406.23281, found: 406.23159; Anal. Calcd for C₂₆H₃₄O₂Si: C, 76.80; H, 8.43. Found: C, 76.85; H, 8.76.

Preparation of *tert*-Butyl-(3-oxonan-2-yl-2-propynyloxy)-diphenyl-silane (4d).

The procedure used above to obtain **4b** was applied to **3d** on a 200 mg (0.28 mmol) scale, yielding **4d** (64 mg, 55% yield). ¹H NMR (CDCl₃) 1.07 (s, 9H), 1.22–1.75 (m, 12H), 3.21 (m, 1H), 3.74 (m, 1H), 3.95 (m, 1H), 4.37 (s, 2H), 7.41 (m, 6H), 7.71 (m, 4H); ¹³C-NMR (CDCl₃) δ 19.2 (s), 25.0 (t), 25.8 (t), 26.7 (q), 28.6 (t), 29.1 (t), 29.2 (t), 29.7 (t), 29.8 (t), 36.4 (t), 52.8 (t), 68.3 (t), 68.8 (d), 83.2 (s), 85.2 (s), 127.7 (d), 129.7 (d), 133.3 (s), 135.6 (d); IR (film) (cm^{–1}) 2931, 2855, 1461, 1420, 1110; MS m/z (relative intensity) 363 (M – Bu-*t*)⁺ (18), 263 (16), 199 (100), 135 (55); HRMS calcd for C₂₇H₃₆O₂Si [M]⁺: 420.24846, found: 420.24851; Anal. Calcd for C₂₇H₃₆O₂Si: C, 77.09; H, 8.63. Found: C, 77.07; H, 9.02.

Preparation of (4*R*,5*R*)- and (4*R*,5*S*)-4-Benzoyloxy-7-[(1*S*,3*S*)-3-methoxymethyl-1,2,2-trimethyl-cyclopentyl]-6-heptyne-1,5-diol (7d). To a stirred solution of **6a** (300 mg, 0.63 mmol) in THF : H₂O (5 : 1, 6 mL) was added NaIO₄ (536 mg, 2.5 mmol) at rt. After 30 min, the mixture was diluted with ether (10 mL) and the organic layer separated. The organic phase was washed with water and brine, dried, filtered, and concentrated, yielding the crude aldehyde as an oil, which was used without further purification.

n-BuLi (0.8 mL of a 1.5 M solution in hexane, 1.1 mmol) was added dropwise via syringe to a cooled (–78 °C) solution of (1*S*,3*S*)-1-ethynyl-3-methoxymethyl-1,2,2-trimethyl-cyclopentane (230 mg, 1.3 mmol) in anhydrous THF (10 mL) under argon. After 15 min, the crude aldehyde dissolved in THF (5 mL) was added. The resulting mixture was stirred for 2 h and then quenched with saturated aqueous NH₄Cl and diluted with Et₂O. The aqueous layer was extracted with Et₂O and the combined organic

layers were dried, filtered and concentrated to yield the crude propargylic alcohol as an oil which was used without further purification.

To a stirred solution of the crude propargylic alcohol in dry THF (7 mL) under argon was added TBAF (0.9 mL 1M solution in THF, 0.8 mmol) at room temperature. After 12 h, water and Et₂O were added. The separated aqueous layer was extracted with Et₂O, and the combined organic layers were dried, filtered and concentrated. Silica gel column chromatography of the residue gave **7d** (173 mg, 71% yield) as an oil: ¹H NMR (CDCl₃) δ 0.91 (s, 3H), 0.92 (s, 3H), 0.96 (s, 3H), 0.97 (s, 3H), 1.14 (s, 3H), 1.15 (s, 3H), 1.36 (m, 2H), 1.63 (m, 4H), 1.72 (m, 4H), 1.83 (m, 2H), 1.89 (m, 2H), 1.99 (m, 4H), 3.23 (dd, *J* = 8.7, 8.7 Hz, 2H), 3.30 (s, 3H), 3.42 (dd, *J* = 8.7, 5.9 Hz, 2H), 3.50 (m, 2H), 3.57 (m, 4H), 3.72 (dd, *J* = 6.3, 6.3 Hz, 2H), 4.38 (d, *J* = 5.6 Hz, 1H), 4.54 (d, *J* = 3.9 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 11.3 Hz, 1H), 7.27 (m, 2H), 7.33 (m, 8H); ¹³C NMR (CDCl₃) δ 20.7 (q), 23.0 (q), 23.9 (q), 25.5 (t), 26.0 (t), 26.3 (t), 27.4 (t), 28.3 (t), 28.8 (t), 37.5 (t), 45.4 (d), 45.5 (d), 58.8 (q), 62.6 (t), 63.8 (d), 64.7 (d), 67.9 (t), 72.2 (t), 73.2 (t), 75.5 (t), 80.1 (s), 80.6 (s), 82.0 (d), 82.4 (d), 91.8 (s), 92.1 (s), 127.6 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 138.2 (s); IR (CHCl₃) (cm⁻¹) 3438, 2969, 2877, 2201, 1672, 1454, 1108, 941; MS *m/z* (relative intensity) 355 (*M* – 32), 303 (4), 241 (6), 199 (100), 163 (7), 105 (55), 91 (45), 77 (24); Anal. Calcd for C₂₄H₃₆O₄: C, 74.19; H, 9.34. Found: C, 74.06; H, 9.43.

Preparation of [4*R*,5(*R*+*S*),8(*R*+*S*)]-4-Benzoyloxy-6-nonyne-1,5,8-triol (7f**).** The procedure used above to obtain **7d** was applied to **6a** on a 400 mg (0.84 mmol) scale, using *tert*-Butyl-[1(*R*+*S*)-1-methyl-prop-2-ynoxy]-diphenyl-silane (376 mg, 1.3 mmol) as alkyne, yielding **7f** (165 mg, 69% yield) as an oil: ¹H NMR (CDCl₃) δ 1.39 (d, *J* = 3.0 Hz, 3H), 1.41 (d, *J* = 3.0 Hz, 3H), 1.59 (m, 2H), 1.69 (m, 4H), 1.79 (m, 2H), 3.51 (m, 2H), 3.75 (ddd, *J* = 5.8, 5.8, 1.1 Hz, 4H), 4.43 (dd, *J* = 5.7, 1.1 Hz, 1H), 4.48 (dddd, *J* = 3.0, 3.0, 3.0, 1.4 Hz, 2H), 4.52 (dd, *J* = 3.9, 1.2 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 7.28 (m, 2H), 7.34 (m, 8H); ¹³C NMR (CDCl₃) δ 24.0 (q), 24.0 (q), 26.5 (t), 27.04 (t), 28.2 (t), 28.4 (t), 57.8 (d), 57.9 (d), 62.3 (t), 63.7 (d), 64.3 (d), 72.6 (t), 73.0 (t), 81.5 (d), 81.7 (d), 82.0 (s), 82.2 (s), 88.3 (s), 88.5 (s), 127.9 (d), 128.1 (d), 128.1 (d), 128.5 (d), 137.9 (s), 137.9 (s); IR (CHCl₃) (cm⁻¹) 3601, 3396, 3012, 2935, 2878, 1454, 1213, 1055, 883; MS *m/z* (relative intensity) 279 (*M* + 1)⁺ (2), 241 (8), 199 (10), 149 (22), 142 (100), 100 (30), 91 (53); HRMS calcd for C₁₆H₁₈O₂ [*M* – 2H₂O]: 242.1307, found: 242.1319.

Preparation of (5*R*,6*R*)- and (5*R*,6*S*)-5-Benzoyloxy-7-tridecyne-1,6-diol. (7b**).** The procedure used above to obtain **7d** was applied to **6b** on a 260 mg (0.53 mmol) scale, using 1-heptyne (0.14 mL, 1.1 mmol) as alkyne, yielding **7b** (158 mg, 65% yield) as an oil: ¹H NMR (CDCl₃) δ 0.89 (dd, *J* = 6.5, 6.5 Hz, 6H), 1.33 (m, 7H), 1.53 (m, 9H), 1.69 (m, 3H), 1.79 (m, 1H), 2.21 (m, 4H), 2.31 (m, 2H), 2.38 (m, 2H), 3.49 (m, 2H), 3.61 (dd, *J* = 5.6, 5.6 Hz, 4H), 4.32 (m, 1H), 4.52 (bs, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.66 (m, 2H), 4.73 (d, *J* = 11.4 Hz, 1H), 7.35 (m, 8H), 7.49 (m, 2H); ¹³C NMR (CDCl₃) δ 13.9 (q), 18.7 (t), 21.4 (t), 21.8 (t), 22.1 (t), 28.2 (t), 28.2 (t), 29.5 (t), 30.7 (t), 32.6 (t), 32.7 (t), 62.6 (t), 63.9 (d), 64.8 (d), 72.4 (t), 73.3 (t), 78.0 (s), 78.8 (s), 81.8 (d), 82.4 (d), 86.8 (s), 87.2 (s), 127.8 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.4 (d), 128.5 (d), 138.2 (s); IR (CHCl₃) (cm⁻¹) 3570, 3020, 2936, 2873, 2211, 1273, 1210, 1114, 742; MS *m/z* (relative intensity) 283 (*M* – 35)⁺ (1), 235 (8), 199 (73), 181 (11), 139 (17), 105 (57), 91 (100), 77 (37); Anal. Calcd for C₂₀H₃₀O₃: C, 75.43; H, 9.50. Found: C, 75.49; H, 9.39.

Preparation of (5*R*,6*R*)- and (5*R*,6*S*)-5-Benzoyloxy-8-[(1*S*,3*S*)-3-methoxymethyl-1,2,2-trimethyl-cyclopentyl]-6-octyne-1,5-diol. (7e**).** The procedure used above to obtain **7d** was applied to **6b** on a 300 mg (0.61 mmol) scale, using (1*S*,3*S*)-1-ethynyl-3-methoxymethyl-1,2,2-trimethyl-cyclopentane (215 mg, 1.2 mmol) as alkyne, yielding **7e** (165 mg, 65% yield) as an oil: ¹H NMR (CDCl₃) δ 0.92 (s, 3H), 0.93 (s, 3H), 0.96 (s, 3H), 0.97 (s, 3H), 1.14 (s, 3H), 1.15 (s, 3H), 1.37 (m, 4H), 1.51 (m, 6H), 1.66

(m, 6H), 1.88 (m, 2H), 1.97 (m, 2H), 2.02 (m, 2H), 3.23 (dd, $J = 8.7, 8.7$ Hz, 2H), 3.30 (s, 3H), 3.31 (s, 3H), 3.42 (dd, $J = 8.7, 5.8$ Hz, 2H), 3.46 (m, 2H), 3.56 (dd, $J = 6.2, 6.2$ Hz, 4H), 4.34 (d, $J = 5.7$ Hz, 1H), 4.53 (d, $J = 3.7$ Hz, 1H), 4.56 (d, $J = 11.6$ Hz, 1H), 4.64 (d, $J = 11.3$ Hz, 1H), 4.66 (d, $J = 11.6$ Hz, 1H), 4.73 (d, $J = 11.3$ Hz, 1H), 7.27 (m, 3H), 7.32 (m, 7H); ^{13}C NMR (CDCl_3) δ 20.6 (q), 20.7 (q), 21.4 (t), 21.8 (t), 23.0 (q), 23.1 (q), 23.9 (q), 26.0 (t), 29.5 (t), 30.8 (t), 32.6 (t), 32.7 (t), 37.5 (t), 45.4 (d), 45.5 (d), 58.8 (q), 62.4 (t), 63.8 (d), 64.8 (d), 72.2 (t), 73.3 (t), 75.5 (t), 80.0 (s), 80.8 (s), 82.1 (d), 82.6 (d), 91.6 (s), 92.0 (s), 127.7 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 138.3 (s); IR (CHCl_3) (cm^{-1}) 3556, 3016, 2970, 2940, 2200, 1455, 1205, 1108; MS m/z (relative intensity) 384 ($\text{M} - 18$) $^+$ (1), 293 (2), 276 (2), 231 (4), 207 (5), 193 (8), 175 (11), 147 (13), 105 (81), 91 (100); Anal. Calcd for $\text{C}_{25}\text{H}_{38}\text{O}_4$: C, 74.59; H, 9.51. Found: C, 74.40; H, 9.87.

Preparation of [5*R*,6(*R*+*S*),9(*R*+*S*)]-5-Benzoyloxy-7-decyne-1,6,9-triol. (7g). The procedure used above to obtain **7d** was applied to **6b** on a 400 mg (0.81 mmol) scale, using *tert*-Butyl-[1(*R*+*S*)-1-methyl-prop-2-ynoxy]-diphenyl-silane (350 mg, 1.2 mmol) as alkyne, yielding **7g** (161 mg, 68% yield) as an oil: ^1H NMR (CDCl_3) δ 1.40 (d, $J = 6.6$ Hz, 3H), 1.41 (d, $J = 6.5$ Hz, 3H), 1.52 (m, 7H), 1.68 (m, 5H), 2.6 (bs, 3H), 3.49 (ddd, $J = 5.5, 5.5, 5.5$ Hz, 2H), 3.57 (dd, $J = 5.3, 5.3$ Hz, 4H), 4.39 (dd, $J = 5.6, 1.2$ Hz, 1H), 4.49 (m, 3H), 4.58 (d, $J = 11.6$ Hz, 1H), 4.63 (d, $J = 11.4$ Hz, 1H), 4.66 (d, $J = 11.6$ Hz, 1H), 4.68 (d, $J = 11.4$ Hz, 1H), 7.29 (m, 2H), 7.34 (m, 8H); ^{13}C NMR (CDCl_3) δ 21.4 (t), 21.6 (t), 24.0 (q), 29.7 (t), 30.2 (t), 32.3 (t), 32.4 (t), 57.8 (d), 57.9 (d), 62.1 (t), 63.9 (d), 64.4 (d), 72.6 (t), 73.1 (t), 81.5 (d), 81.9 (d), 81.9 (s), 82.4 (s), 88.1 (s), 88.4 (s), 127.9 (d), 128.0 (d), 128.1 (d), 128.5 (d), 137.9 (s), 138.0 (s); IR (CHCl_3) (cm^{-1}) 3610, 3418, 3014, 2937, 1455, 1232, 1072, 728; MS m/z (relative intensity) 274 ($\text{M} - 18$) $^+$ (2), 267 (5), 207 (43), 199 (15), 149 (22), 129 (11), 115 (15), 105 (49), 91 (100); Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: C, 69.84; H, 8.27. Found: C, 69.46; H, 8.63.

Preparation of (2*S*,3*R*)-3-Benzoyloxy-2-hept-1-ynyl-tetrahydro-pyran (9a) and (2*R*,3*R*)-3-Benzoyloxy-2-hept-1-ynyl-tetrahydro-pyran (10a). The general procedure for the preparation of the dicobalt hexacarbonyl complexes described in the paper was applied to **7a** on a 172 mg (0.6 mmol) scale, yielding **8a** (306 mg, 92% yield) as a dark red oil.

The general procedure of cyclization (room temperature) and decomplexation was successively applied to **8a** on a 44 mg (0.07 mmol) scale, yielding **9a** : **10a** in 94% yield (19 mg) as a 10 : 1 epimeric mixture. **9a**: colorless oil; $[\alpha]_D^{25} = -18.2$ (c 2, CHCl_3); ^1H NMR (CDCl_3) δ 0.89 (dd, $J = 7.16, 7.16$ Hz, 3H), 1.32 (m, 2H), 1.38 (m, 2H), 1.55 (m, 4H), 1.79 (m, 1H), 2.10 (m, 1H), 2.25 (ddd, $J = 7.1, 7.1, 1.9$ Hz, 1H), 3.39 (ddd, $J = 7.8, 6.8, 4.0$ Hz, 1H), 3.46 (ddd, $J = 11.4, 8.7, 3.0$ Hz, 1H), 3.93 (ddd, $J = 11.4, 4.3, 4.3$ Hz, 1H), 4.15 (ddd, $J = 6.8, 1.9, 1.9$ Hz, 1H), 4.66 (d, $J = 11.9$ Hz, 1H), 4.74 (d, $J = 11.9$ Hz, 1H), 7.28 (m, 1H), 7.35 (m, 4H); ^{13}C NMR (CDCl_3) δ 13.9 (q), 18.7 (t), 22.1 (t), 23.5 (t), 27.9 (t), 28.2 (t), 31.1 (t), 65.8 (t), 70.5 (d), 71.6 (t), 76.4 (d), 77.6 (s), 87.2 (s), 127.5 (d), 127.7 (d), 128.3 (d), 138.5 (s); IR (CHCl_3) (cm^{-1}) 3019, 2933, 2859, 2239, 1455, 1219, 1083; MS m/z (relative intensity) 285 ($\text{M} + 1$) $^+$ (1), 230 (2), 178 (12), 123 (6), 105 (63), 91 (3), 77 (24), 71 (100); Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 79.61; H, 9.30. **10a**: colorless oil; $[\alpha]_D^{25} = +84.8$ (c 2.1, CHCl_3); ^1H NMR (CDCl_3) δ 0.90 (dd, $J = 7.2, 7.2$ Hz, 3H), 1.33 (m, 2H), 1.41 (m, 2H), 1.56 (m, 3H), 1.82 (m, 3H), 2.29 (ddd, $J = 7.1, 7.1, 2.0$ Hz, 2H), 3.51 (ddd, $J = 9.1, 4.1, 4.1$ Hz, 1H), 3.58 (ddd, $J = 11.4, 3.9, 3.9$ Hz, 1H), 3.89 (ddd, $J = 11.4, 10.2, 2.8$ Hz, 1H), 4.60 (d, $J = 12.2$ Hz, 1H), 4.66 (d, $J = 12.2, 1\text{H}$), 4.67 (m, 1H), 7.28 (m, 1H), 7.33 (m, 4H); ^1H NMR (CDCl_3) δ 13.9 (q), 18.8 (t), 22.1 (t), 23.8 (t), 25.9 (t), 28.3 (t), 31.0 (t), 62.9 (t), 68.4 (d), 70.6 (t), 74.1 (d), 75.4 (s), 88.8 (s), 127.5 (d), 127.6 (d), 128.2 (d), 138.4 (s); IR (CHCl_3) (cm^{-1}) 3011, 2933, 2862, 2237, 1454, 1270, 1075; MS m/z (relative intensity) 285 ($\text{M} + 1$) $^+$ (1), 195 (M) $^+$ (1), 178 (7), 123 (13), 105 (77), 91 (16), 71 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 79.69; H, 9.16.

Preparation of (2*S*,3*R*)-3-Benzoyloxy-2-hept-1-ynyl-oxepane (9b) and (2*R*,3*R*)-3-Benzoyloxy-2-hept-1-ynyl-oxepane (10b). The procedure used above to obtain **9a** and **10a** was applied to **8b** on a 44 mg (0.07 mmol) scale, yielding **9b** and **10b** (16 mg, 75% yield) as a 4 : 1 epimeric mixture. **9b**: colorless oil; $[\alpha]_D^{25} = -30.77$ (c 4.9, CHCl₃); ¹H NMR (CDCl₃) δ 0.88 (dd, *J* = 6.9, 6.9 Hz, 3H), 1.33 (m, 4H), 1.52 (m, 2H), 1.69 (m, 2H), 1.89 (m, 4H), 2.22 (ddd, *J* = 7.0, 7.0, 1.9 Hz, 2H), 3.64 (m, 1H), 3.70 (m, 1H), 3.94 (ddd, *J* = 12.4, 5.4, 5.4 Hz, 1H), 4.29 (ddd, *J* = 6.4, 1.9, 1.9 Hz, 1H), 4.61 (s, 1H), 4.62 (s, 1H), 7.29 (m, 1H), 7.33 (m, 4H); ¹³C NMR (CDCl₃) δ 13.9 (q), 18.8 (t), 21.5 (t), 22.5 (t), 28.3 (t), 30.4 (t), 30.7 (t), 31.1 (t), 69.1 (t), 71.7 (t), 73.9 (d), 79.3 (s), 84.1 (d), 86.1 (s), 127.5 (d), 127.7 (d), 128.3 (d), 138.6 (s); IR (CHCl₃) (cm⁻¹) 2932, 2861, 2235, 1454, 1269, 1112, 1071, 755.; MS *m/z* (relative intensity) 244 (*M* – 56)⁺ (1), 230 (3), 192 (9), 153 (4), 123 (12), 105 (87), 85 (100), 77 (30); Anal. Calcd for C₂₀H₂₈O₂: C, 79.96; H, 9.39. Found: C, 79.75; H, 9.69. **10b**: a colorless oil; $[\alpha]_D^{25} = +36.61$ (c 1.3, CHCl₃); ¹H NMR (CDCl₃) δ 0.89 (dd, *J* = 7.1, 7.1 Hz, 3H), 1.36 (m, 4H), 1.54 (m, 2H), 1.71 (m, 2H), 1.84 (m, 4H), 2.27 (ddd, *J* = 7.1, 7.1, 2.05 Hz, 2H), 3.62 (m, 2H), 4.03 (ddd, *J* = 12.0, 5.6, 5.6 Hz, 1H), 4.59 (ddd, *J* = 3.8, 2.0, 2.0 Hz, 1H), 4.64 (s, 2H), 7.33 (m, 5H); ¹³C NMR (CDCl₃) δ 13.9 (q), 18.9 (q), 20.5 (t), 22.2 (t), 28.3 (t), 29.9 (t), 30.7 (t), 31.7 (t), 67.1 (t), 71.5 (t), 71.6 (d), 76.3 (s), 80.0 (d), 88.5 (s), 127.4 (d), 127.6 (d), 128.2 (d), 138.7 (s); IR (CHCl₃) (cm⁻¹) 3020, 2935, 2863, 2236, 1605, 1454, 1093, 1071; MS *m/z* (relative intensity) 244 (*M* – 56)⁺ (2), 210 (1), 192 (3), 149 (7), 123 (19), 105 (100), 85 (55); Anal. Calcd for C₂₀H₂₈O₂: C, 79.96; H, 9.39. Found: C, 79.99; H, 9.38.

Preparation of (2*S*,3*R*)-3-Benzoyloxy-[(1*S*,3*S*)-3-methoxymethyl-1,2,2-trimethyl-cyclopentylethynyl]-tetrahydro-pyran (9d) and (2*R*,3*R*)-3-Benzoyloxy-[(1*S*,3*S*)-3-methoxymethyl-1,2,2-trimethyl-cyclopentylethynyl]-tetrahydro-pyran (10d). The general procedures for the preparation of the dicobalt hexacarbonyl complexes, cyclization (rt.) and decomplexation used above to obtain **4b** was applied to **8d** on a 42 mg (0.06 mmol) scale, yielding **9d** and **10d** (19 mg, 80% yield) as a 8 : 1 epimeric mixture. **9d**: colorless oil; $[\alpha]_D^{25} = -11.8$ (c 6.9, CHCl₃); ¹H-NMR (CDCl₃) δ 0.96 (s, 3H), 1 (s, 3H), 1.19 (s, 3H), 1.39 (m, 1H), 1.54 (m, 1H), 1.65 (m, 1H), 1.82 (m, 1H), 1.92 (m, 1H), 2.08 (m, 3H), 3.24 (dd, *J* = 8.7, 8.7 Hz, 2H), 3.33 (s, 3H), 3.40 (m, 1H), 3.44 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.48 (ddd, *J* = 11.2, 8.2, 3.2 Hz, 1H), 3.95 (ddd, *J* = 11.2, 6.4, 4.1 Hz, 1H), 4.24 (d, *J* = 6.4 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.73 (d, *J* = 11.8 Hz, 1H), 7.27 (m, 1H), 7.35 (m, 4H); ¹³C NMR (CDCl₃) δ 20.8 (q), 23.0 (q), 23.3 (t), 24.0 (q), 26.0 (t), 27.5 (t), 37.6 (t), 45.4 (s), 45.6 (d), 45.7 (d), 58.8 (q), 65.4 (t), 70.3 (d), 71.5 (t), 75.5 (t), 76.5 (d), 79.4 (s), 92.3 (s), 127.5 (d), 127.6 (d), 128.3 (d), 138.5 (s); IR (CHCl₃) (cm⁻¹) 3010, 2970, 2875, 2229, 1454, 1266, 1087, 946; MS *m/z* (relative intensity) 370 (*M* – 16)⁺ (1), 279 (3), 247 (3), 217 (4), 177 (7), 133 (4), 119 (6), 105 (32), 71 (100); Anal. Calcd for C₂₄H₃₄O₃: C, 77.80; H, 9.25. Found: C, 77.80; H, 9.56. **10d**: colorless oil; $[\alpha]_D^{25} = +92.2$ (c 1.6, CHCl₃); ¹H-NMR (CDCl₃) δ 0.99 (s, 3H), 1.01 (s, 3H), 1.21 (s, 3H), 1.41 (m, 1H), 1.56 (m, 1H), 1.70 (m, 2H), 1.83 (m, 2H), 1.92 (m, 1H), 2.07 (m, 2H), 3.26 (dd, *J* = 8.9, 8.9 Hz, 1H), 3.32 (s, 3H), 3.45 (dd, *J* = 8.9, 5.6 Hz, 1H), 3.55 (m, 2H), 3.88 (ddd, *J* = 10.8, 10.8, 3.0 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 4.1 Hz, 1H), 7.32 (m, 5H); ¹³C-NMR (CDCl₃) δ 20.8 (q), 23.1 (q), 24.0 (t), 24.1 (q), 26.1 (t), 26.2 (t), 37.7 (t), 45.5 (s), 45.7 (s), 45.8 (d), 58.8 (q), 62.9 (t), 68.4 (d), 70.5 (t), 74.5 (d), 75.6 (t), 77.2 (s), 94.1 (s), 127.5 (d), 127.6 (d), 128.2 (d), 138.6 (s); IR (CHCl₃) (cm⁻¹) 3009, 2969, 2873, 2360, 2236, 1455, 1219, 1074; MS *m/z* (relative intensity) 370 (*M* – 16)⁺ (1), 279 (3), 177 (8), 159 (4), 123 (4), 105 (8), 91 (49), (100); Anal. Calcd for C₂₄H₃₄O₃: C, 77.80; H, 9.25. Found: C, 77.79; H, 9.50.

Preparation of (2*S*,3*R*)-3-Benzoyloxy-2-[(1*S*,3*S*)-3-methoxymethyl-1,2,2-trimethyl-cyclopentylethynyl]-oxepane (9e) and (2*R*,3*R*)-3-Benzoyloxy-2-[(1*S*,3*S*)-3-methoxymethyl-1,2,2-trimethyl-cyclopentylethynyl]-oxepane (10e). The procedure used above to obtain **9a** and **10a** was applied to **8e** on a 75 mg (0.11 mmol) scale, yielding **9e** and **10e** (26 mg, 63% yield) as a 21 : 1 epimeric mixture.

Data for the 3 : 1 mixture: ^1H NMR (CDCl_3) δ 0.93 (s, 9H), 0.99 (s, 15H), 1.17 (s, 12H), 1.20 (m, 1H), 1.39 (m, 4H), 1.48 (m, 4H), 1.70 (m, 17H), 1.70 (m, 2H), 1.87 (m, 10H), 2.05 (m, 8H), 3.24 (m, 4H), 3.32 (s, 12H), 3.43 (m, 4H), 3.66 (m, 8H), 3.94 (ddd, $J = 12.2, 5.5, 5.5$ Hz, 3H), 4.20 (m, 1H), 4.35 (d, $J = 6.1$ Hz, 3H), 4.68 (s, 8H), 4.69 (d, $J = 3.72$ Hz, 1H), 7.29 (m, 4H), 7.35 (m, 16H); ^{13}C NMR (CDCl_3) δ 20.4 (t), 20.7 (q), 20.8 (q), 21.6 (t), 23.0 (q), 23.1 (q), 26.0 (t), 26.1 (t), 29.8 (t), 30.4 (t), 30.6 (t), 30.8 (t), 37.6 (t), 45.4 (s), 45.6 (d), 45.7 (d), 58.8 (q), 66.6 (t), 68.6 (t), 71.1 (d), 71.4 (t), 71.7 (t), 73.6 (d), 75.6 (t), 77.9 (s), 80.4 (d), 81.0 (s), 84.5 (d), 91.4 (s), 93.9 (s), 127.4 (d), 127.5 (d), 127.6 (d), 128.2 (d), 128.3 (d), 138.5 (s), 138.9 (s); IR (CHCl_3) (cm^{-1}) 2969, 2936, 2876, 2223, 1453, 1271, 1108, 942; MS m/z (relative intensity) 384 (M^+) (1), 246 (1), 191 (3), 177 (7), 105 (24), 91 (38), 85 (100); Anal. Calcd for $\text{C}_{25}\text{H}_{36}\text{O}_3$: C, 78.08; H, 9.44. Found: C, 78.03; H, 9.59.

Preparation of (2R)- and (2S)-4-[(2S,3R)-3-Benzoyloxy-tetrahydro-pyran-2-yl]-3-butyn-2-ol (9f), (2R)- and (2S)-4-[(2R,3R)-3-Benzoyloxy-tetrahydro-pyran-2-yl]-3-butyn-2-ol (10f) and [5R,6(R+S),9(R+S)]-5-Benzoyloxy-9-Methyl-2H,3H,4H,5H,6H,9H-oxonin-6-ol (11). The general procedure for the preparation of the dicobalt hexacarbonyl complexes described in the paper was applied to **7f** on a 254 mg (0.9 mmol) scale, yielding **8f** (443 mg, 86% yield) as a dark red oil.

The general procedure of cyclization (room temperature) was applied to **8f** on a 135 mg (0.24 mmol) scale and the resulting mixture of cyclized products submitted to an alternative method of decomplexation.

Iodine (548 mg, 2.16 mmol) was added to a solution of the previous crude oil in THF (20 mL) under argon atmosphere at room temperature. The stirring was continued for 1 h, and the mixture was then poured into a cold saturated aqueous solution of Na_2SO_3 (20 mL) and extracted with Et_2O . The combined organic extracts were dried, filtered, reduced and subjected to silica gel flash chromatography to yield the epimeric mixture **9f** and **10f** (33 mg, 53% yield, **9f** : **10f**, 1 : 1.7) and **11** (9.5 mg, 15% yield). **9f**: colorless oil; ^1H NMR (C_6D_6) δ 1.47 (d, $J = 6.6$ Hz, 3H), 1.57 (m, 2H), 1.80 (m, 1H), 2.11 (m, 1H), 3.43 (m, 1H), 3.47 (m, 1H), 3.93 (ddd, $J = 11.5, 3.9, 3.9$ Hz, 1H), 4.18 (d, $J = 7.0$ Hz, 1H), 4.58 (m, 1H), 4.67 (d, $J = 11.9$ Hz, 1H), 4.71 (d, $J = 11.9$ Hz, 1H), 7.30 (m, 1H), 7.36 (m, 4H); ^{13}C NMR (C_6D_6) δ 23.5 (t), 24.1 (q), 24.2 (q), 27.9 (t), 58.4 (d), 66.1 (t), 70.3 (d), 71.6 (t), 76.0 (d), 81.6 (s), 88.1 (s), 127.7 (d), 127.8 (d), 128.4 (d), 138.3 (s); IR (CHCl_3) (cm^{-1}) 3429, 3012, 2932, 2869, 1454, 1250, 1078; MS m/z (relative intensity) 242 ($\text{M} - 18$) $^+$ (1), 199 (4), 172 (30), 149 (5), 129 (9), 105 (9), 91 (100); HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ [$\text{M}^+ - \text{H}_2\text{O}$] 242.1307, found 242.1304. **10f**: colorless oil; ^1H -NMR (CDCl_3) δ 1.49 (d, $J = 6.6$ Hz, 3H), 1.54 (m, 1H), 1.76 (m, 1H), 1.83 (m, 2H), 3.54 (m, 1H), 3.59 (ddd, $J = 11.4, 4.2, 4.2$ Hz, 1H), 3.87 (m, 1H), 4.61 (m, 1H), 4.62 (s, 2H), 4.68 (m, 1H), 7.29 (m, 1H), 7.37 (m, 4H); ^{13}C -NMR (CDCl_3) δ 23.6 (t), 24.2 (q), 26.0 (t), 58.3 (d), 63.4 (t), 68.3 (d), 70.8 (t), 73.9 (d), 79.6 (s), 90.1 (s), 127.7 (d), 127.8 (d), 128.4 (d), 138.0 (s); IR (CHCl_3) (cm^{-1}) 3020, 2951, 2928, 2857, 2225, 2206, 1679, 1360, 1081; MS m/z (relative intensity) 258 ($\text{M} - 2$) $^+$ (2), 202 (2), 188 (5), 145 (4), 105 (28), 91 (99), 71 (100); HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$ [$\text{M}^+ - 2\text{H}$] 258.1256, found 258.1256. **11**: colorless oil; ^1H NMR (C_6D_6) δ 1.22 (d, $J = 6.8$ Hz, 3H), 1.46 (m, 1H), 1.84 (m, 2H), 1.96 (m, 1H), 2.30 (bs, 1H), 3.45 (ddd, $J = 12.4, 3.8, 3.8$ Hz, 1H), 3.52 (ddd, $J = 6.9, 6.9, 1.9$ Hz, 1H), 3.87 (m, 1H), 4.28 (ddd, $J = 6.8, 6.8, 6.8$ Hz, 1H), 4.34 (d, $J = 11.7$ Hz, 1H), 4.46 (d, $J = 11.7$ Hz, 1H), 4.47 (m, 1H), 7.20 (m, 5H); ^{13}C NMR (C_6D_6) δ 20.0 (q), 29.0 (t), 30.0 (t), 65.6 (t), 65.8 (d), 67.4 (d), 71.6 (t), 86.1 (d), 89.6 (s), 92.4 (s), 127.5 (d), 127.6 (d), 128.0 (d), 128.4 (d), 138.6 (s); IR (CHCl_3) (cm^{-1}) 3597, 3454, 3013, 2934, 2871, 1454, 1217, 109; MS m/z (relative intensity) 261 ($\text{M} + 1$) $^+$ (1), 260 (M^+) (2), 218 (7), 149 (4), 121 (6), 97 (16), 91 (100). HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3$ [$\text{M}^+ + \text{H}$] 261.1491, found 261.1505.

Preparation of (2R)- and (2S)-4-[(2S,3R)-3-Benzoyloxy-oxepan-2-yl]-3-butyn-2-ol (9g), (2R)- and (2S)-4-[(2R,3R)-3-Benzoyloxy-oxepan-2-yl]-3-butyn-2-ol (10g) and [6R,7(R+S),8(R+S)]-6-Benzoyloxy-10-Methyl-2H,3H,4H,5H,6H,7H,10H-oxecin-7-ol (12). The procedure used above to obtain **9a** and **10a** was applied to **8g** on a 185 mg (0.3 mmol) scale, yielding the epimeric mixture **9g** and **10g** (38 mg, 43% yield, **9g** : **10g**, 1 : 2.5) and **12** (13 mg, 15% yield). **9g**: a colorless oil; $^1\text{H-NMR}$ (CDCl_3) δ 1.45 (d, $J = 1.6$ Hz, 3H), 1.52 (m, 1H), 1.70 (m, 2H), 1.80 (m, 1H), 1.91 (m, 2H), 3.64 (ddd, $J = 12.2, 6.8, 5.2$ Hz, 1H), 3.71 (ddd, $J = 9.7, 6.7, 3.0$ Hz, 1H), 3.92 (ddd, $J = 12.2, 5.4, 5.4$ Hz, 1H), 4.30 (dd, $J = 6.7, 0.9$ Hz, 1H), 4.55 (m, 1H), 4.56 (d, $J = 11.9$ Hz, 1H), 4.64 (d, $J = 11.9$ Hz, 1H), 7.29 (m, 2H), 7.36 (m, 3H); $^{13}\text{C-NMR}$ (CDCl_3) δ 21.5 (t), 24.1 (q), 24.2 (q), 30.4 (t), 30.6 (t), 58.4 (d), 69.7 (t), 71.7 (t), 73.7 (d), 83.3 (s), 83.6 (d), 87.1 (s), 127.6 (d), 127.8 (d), 128.3 (d), 138.3 (s); IR (CHCl_3) (cm^{-1}) 3415, 3014, 2933, 2859, 1454, 1211, 1105, 765, 724; MS m/z (relative intensity) 256 ($M - 18$)⁺ (3), 214 (5), 172 (12), 135 (41), 105 (100), 77 (20); Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$: C, 74.42; H, 8.08. Found: C, 74.24; H, 8.42. **10g**: colorless oil; $^1\text{H-NMR}$ (C_6D_6) δ 1.32 (d, $J = 6.6$ Hz, 3H), 1.35 (m, 1H), 1.52 (m, 1H), 1.66 (m, 2H), 1.77 (m, 1H), 1.91 (m, 1H), 3.56 (ddd, $J = 9.0, 4.0, 4.0$ Hz, 1H), 3.61 (ddd, $J = 12.1, 7.1, 5.0$ Hz, 1H), 4.09 (m, 1H), 4.35 (dddd, $J = 6.6, 6.6, 6.6, 1.3$ Hz, 1H), 4.43 (d, $J = 12.4$ Hz, 1H), 4.44 (d, $J = 12.4$ Hz, 1H), 4.77 (dd, $J = 4.0, 1.3$ Hz, 1H), 7.14 (dd, $J = 7.3, 7.3$ Hz, 1H), 7.23 (m, 2H), 7.39 (d, $J = 7.6$ Hz, 2H); $^{13}\text{C-NMR}$ (C_6D_6) δ 20.6 (t), 24.2 (q), 30.2 (t), 30.5 (t), 58.1 (d), 66.6 (t), 71.3 (t), 71.5 (d), 80.5 (d), 80.6 (s), 90.4 (s), 127.4 (d), 127.8 (d), 128.1 (d), 128.3 (d), 139.0 (s); IR (CHCl_3) (cm^{-1}) 3473, 3011, 2933, 2866, 1454, 1210, 1071, 728; MS m/z (relative intensity) 256 ($M - 18$)⁺ (1), 244 (2), 149 (3), 105 (32), 91 (70), 85 (100), 77 (13). **12**: colorless oil; $^1\text{H NMR}$ (CDCl_3) δ 1.42 (d, $J = 6.4$ Hz, 3H), 1.49 (m, 1H), 1.59 (m, 2H), 1.66 (m, 2H), 1.72 (m, 1H), 2.87 (bs, 1H), 3.36 (ddd, $J = 8.7, 6.4, 6.4$ Hz, 1H), 3.51 (m, 1H), 3.70 (m, 1H), 4.17 (ddd, $J = 6.4, 6.4, 6.4$ Hz, 1H), 4.39 (d, $J = 4.9$ Hz, 1H), 4.65 (d, $J = 11.7$ Hz, 1H), 4.67 (d, $J = 11.7$ Hz, 1H), 7.30 (m, 1H), 7.35 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3) δ 21.7 (t), 22.1 (q), 29.6 (t), 30.3 (t), 64.4 (d), 65.4 (d), 68.4 (t), 73.0 (t), 82.0 (d), 83.5 (s), 86.1 (s), 127.8 (d), 127.9 (d), 128.4 (d), 138.1 (s); IR (CHCl_3) (cm^{-1}) 3023, 3005, 2940, 2213, 1602, 1103, 1017; MS m/z (relative intensity) 273 ($M - 1$)⁺ (1), 257 (2), 183 (1), 167 (2), 149 (4), 105 (6), 91 (100); HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2$ [$M^+ - \text{OH}$] 257.1542, found 257.1538.

Preparation of 2-But-3-ynyloxy-tetrahydro-pyran. To a stirred solution of commercially available 3-butyn-1-ol (4 g, 57.1) in dry CH_2Cl_2 (250 mL) were added 3,4-dihydro-2H-pyran (6.2 mL, 62.8 mmol) and a catalytic amount of PPTS (1.3 g, 5.7 mmol). The reaction was stirred at rt until starting material was not detected by TLC. Then, Et_3N was added until pH ~ 7 and the reaction mixture was poured into brine (200 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic phases were dried over MgSO_4 , concentrated, and purified by silica gel column chromatography to yield THP-protected 3-butyn-1-ol (8.3 g, 94% yield) as an oil: $^1\text{H NMR}$ (CDCl_3) δ 1.53 (m, 4H), 1.69 (m, 1H), 1.79 (m, 1H), 1.94 (dd, $J = 2.6, 2.6$ Hz, 1H), 2.46 (ddd, 7.0, 7.0, 2.6 Hz, 2H), 3.48 (m, 1H), 3.54 (ddd, $J = 9.7, 7.1, 7.1$ Hz, 1H), 3.82 (m, 2H), 4.61 (dd, $J = 3.4, 3.4$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3) δ 19.3 (t), 19.9 (t), 25.3 (t), 30.4 (t), 62.1 (t), 65.4 (t), 69.1 (s), 81.3 (d), 98.7 (d); IR (CHCl_3) (cm^{-1}) 3308, 3010, 2947, 2878, 2121, 1441, 1122, 1032, 981; MS m/z (relative intensity) 155 ($M + 1$)⁺ (1), 149 (56), 113 (8), 104 (5), 85 (14), 83 (21), 71 (20); Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 70.03; H, 8.97.

Preparation of (3Z)-6-Benzoyloxy-tetradec-3-en-8-yne-1,7-diol. (17). The procedure used above to obtain **2b** was applied to **16** on a 400 mg 1.2 mmol scale, yielding **17** (235 mg, 57% overall yield) as an oil: $^1\text{H NMR}$ (CDCl_3) δ 0.89 (dd, $J = 6.86, 6.86$ Hz, 6H), 1.33 (m, 8H), 1.52 (m, 4H), 2.22 (m, 4H), 2.31 (m, 4H), 2.52 (m, 4H), 3.51 (m, 2H), 3.60 (m, 4H), 4.33 (bs, 1H), 4.5 (bs, 1H), 4.65 (s, 4H), 5.50 (m, 2H), 5.62 (m, 2H), 7.29 (m, 2H), 7.35 (m, 8H); $^{13}\text{C NMR}$ (CDCl_3) δ 13.9 (q), 18.8 (t), 22.16 (t), 28.1 (t), 28.3 (t), 30.8 (t), 31.1 (t), 62.1 (t), 63.8 (d), 72.4 (t), 78.2 (s), 81.5 (d), 81.9 (d), 87.2 (s), 127.7

(d), 127.8 (d), 127.9 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.4 (d), 138.1 (s); IR (CHCl₃) (cm⁻¹) 3565, 3449, 3011, 2933, 2873, 2360, 1455, 1071, 749, 510; MS *m/z* (relative intensity) 245 (M – 85)⁺ (2), 205 (6), 169 (3), 124 (9), 115 (4), 91 (100). Anal. Calcd for C₂₁H₃₀O₃: C, 76.33; H, 9.15. Found: C, 76.32; H, 9.38.

Preparation of (2*R,3*S**)-3-Benzoyloxy-2-hept-1-ynyl-3,4,7,8-tetrahydro-2*H*-oxocine (19) and (2*S**,3*S**)-3-Benzoyloxy-2-hept-1-ynyl-3,4,7,8-tetrahydro-2*H*-oxocine. (20).** The procedure used above to obtain **4b** was applied to **17** on a 72 mg (0.12 mmol) scale, yielding **19** and **20** (22 mg, 61% yield) as a 1 : 1.5 epimeric mixture. **19**: colorless oil; ¹H NMR (CDCl₃) δ 0.88 (dd, *J* = 7.2, 7.2 Hz, 3H), 1.31 (m, 2H), 1.37 (m, 2H), 1.52 (dddd, *J* = 7.3, 7.3, 7.3, 7.3 Hz, 2H), 2.04 (m, 1H), 2.24 (ddd, *J* = 7.3, 7.3, 1.9 Hz, 2H), 2.39 (m, 1H), 2.50 (m, 1H), 2.68 (m, 1H), 3.52 (ddd, *J* = 12.2, 12.2, 1.7 Hz, 1H), 3.72 (m, 1H), 4.03 (ddd, *J* = 12.2, 3.8, 3.8 Hz, 1H), 4.11 (ddd, *J* = 8.9, 1.9, 1.9 Hz, 1H), 4.69 (s, 2H), 5.78 (m, 1H), 5.90 (ddd, *J* = 10.6, 6.1, 6.1 Hz, 1H), 7.28 (m, 1H), 7.34 (m, 2H), 7.39 (m, 2H); ¹³C NMR (CDCl₃) δ 13.9 (q), 18.9 (t), 22.2 (t), 28.3 (t), 28.4 (t), 29.5 (t), 31.1 (t), 71.7 (t), 72.5 (t), 72.8 (d), 79.4 (s), 83.4 (d), 86.3 (s), 127.5 (d), 127.7 (d), 128.2 (d), 128.5 (d), 129.9 (d), 138.5 (s); IR (CHCl₃) (cm⁻¹) 2932, 2860, 2357, 1221, 1086, 804, 696, 525; MS *m/z* (relative intensity) 312 (M + 1)⁺ (4), 236 (8), 222 (1), 207 (1), 167 (10), 149 (34), 122 (15), 105 (70), 57 (100); Anal. Calcd for C₂₁H₂₈O₂: C, 80.73; H, 9.03. Found: C, 80.63; H, 9.39. **20**: colorless oil; ¹H NMR (CDCl₃) δ 0.87 (dd, *J* = 7.2, 7.2 Hz, 3H), 1.31 (m, 2H), 1.37 (m, 2H), 1.53 (dddd, *J* = 7.3, 7.3, 7.3, 7.3 Hz, 2H), 2.02 (dddd, *J* = 14.5, 8.1, 3.6, 1.9 Hz, 1H), 2.25 (ddd, *J* = 7.3, 7.3, 2.4 Hz, 2H), 2.27 (m, 1H), 2.64 (m, 1H), 2.72 (ddd, *J* = 12.3, 10.4, 10.4 Hz, 1H), 3.44 (ddd, *J* = 12.0, 12.0, 1.9 Hz, 1H), 3.59 (ddd, *J* = 10.4, 4.6, 2.4 Hz, 1H), 4.11 (ddd, *J* = 12.0, 3.6, 3.6 Hz, 1H), 4.44 (ddd, *J* = 2.4, 2.4, 2.4 Hz, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 5.71 (dddd, *J* = 10.4, 10.4, 7.0, 1.7 Hz, 1H), 5.82 (ddd, *J* = 10.4, 8.1, 8.1 Hz, 1H), 7.27 (m, 1H), 7.33 (m, 2H), 7.43 (m, 2H); ¹³C NMR (CDCl₃) δ 13.9 (q), 19.0 (t), 22.2 (t), 28.3 (t), 29.5 (t), 29.6 (t), 31.1 (t), 70.7 (t), 72.3 (t), 72.8 (d), 77.4 (s), 81.6 (d), 87.7 (s), 127.4 (d), 127.8 (d), 128.1 (d), 128.9 (d), 130.4 (d), 138.8 (s); IR (CHCl₃) (cm⁻¹) 3017, 2931, 2864, 2363, 2340, 1455, 1271, 1071, 1027, 667; MS *m/z* (relative intensity) 236 (M – 76)⁺ (8), 222 (2), 199 (13), 149 (17), 123 (19), 111 (14), 105 (100). Anal. Calcd for C₂₁H₂₈O₂: C, 80.73; H, 9.03. Found: C, 80.74; H, 9.37.

Preparation of (4*R* and 4*S*)-7-[(2*R*,3*S*)-3-Hydroxy-tetrahydro-pyran-2-yl]-2-heptyne-1,4-diol (23a). The procedure used above to obtain **2b** using the *tert*-butyl-diphenyl-2-propynyloxy-silane as alkyne was applied to **22** on a 200 mg (0.77 mmol) scale, yielding **23a** (253 mg, 70% overall yield). ¹H NMR (CDCl₃) δ 1.05 (s, 18H), 1.38-1.78 (m, 16H), 1.83 (m, 2H), 2.08 (m, 2H), 2.73 (br s, 4H), 2.99 (m, 2H), 3.27 (m, 4H), 3.86 (m, 2H), 4.35 (m, 2H), 4.38 (s, 4H), 7.40 (m, 12H), 7.71 (m, 8H); ¹³C NMR (CDCl₃) δ 19.1 (s), 20.9 (t), 21.0 (t), 25.6 (t), 26.7 (q), 31.3 (t), 31.5 (t), 32.9 (t), 37.5 (t), 52.7 (t), 62.0 (d), 62.2 (d), 67.5 (t), 70.1 (d), 70.2 (d), 82.3 (d), 82.9 (s), 86.4 (s), 127.7 (d), 129.8 (d), 133.1 (s), 135.6 (d); IR (CHCl₃) (cm⁻¹) 3374, 3071, 2933, 2858, 1428, 1373, 1112; MS *m/z* (relative intensity) 467 (M + 1)⁺ (7), 449 (21), 307 (19), 285 (16), 199 (100). HRMS calcd for C₂₈H₃₈O₄Si [M]⁺ 466.25394, found 466.25088.

Preparation of (5*R* and 5*S*)-8-[(2*R*,3*S*)-3-Hydroxy-tetrahydro-pyran-2-yl]-3-octyne-2,5-diol (23b). The procedure employed above to obtain **2b** using the *tert*-butyl-(1-methyl-prop-2-ynyloxy)-diphenyl-silane as alkyne was applied to **22** on a 200 mg (0.77 mmol) scale, yielding **23b** (249 mg, 67 % overall yield). ¹H NMR (CDCl₃) δ 1.08 (s, 9H), 1.33-1.78 (m, 12H), 1.82 (m, 1H), 2.06 (m, 1H), 2.88 (br s, 2H), 2.96 (m, 1H), 3.25 (m, 2H), 3.86 (d, *J* = 10.7 Hz, 1H), 4.24 (s, 1H), 4.52 (dd, *J* = 6.2, 6.2 Hz, 1H), 7.40 (m, 6H), 7.69 (d, *J* = 6.9 Hz, 2H), 7.76 (d, *J* = 7.3 Hz, 2H); ¹³C NMR (CDCl₃) δ 19.1 (s), 20.8 (t), 21.1 (t), 25.2 (q), 25.7 (t), 26.9 (q), 31.4 (t), 31.5 (t), 32.9 (t), 37.5 (t), 60.0 (d), 61.9 (d), 62.0 (d), 67.5 (t), 70.0 (d), 70.1 (d), 82.3 (d), 85.0 (s), 86.8 (s), 127.5 (d), 127.6 (d), 129.7 (d), 133.7 (s), 133.8 (s), 135.7 (d), 136.0 (d); IR (CHCl₃) (cm⁻¹) 3373, 3071, 2933, 2858, 1428, 1340, 1098; MS

m/z (relative intensity) 482 ($M + 1$)⁺ (18), 463 (100), 307 (50), 267 (22). Anal. Calcd for C₂₉H₄₀O₄Si: C, 72.46; H, 8.39. Found: C, 72.46; H, 8.72.

Preparation of 3-[(4a*S*,6*R*,9a*R*)-octahydro-2*H*-pyrano[3,2-*b*]oxepin-6-yl]-2-propyn-1-ol (24a). The procedure used above to obtain **4b** was applied to **23a** on a 200 mg (0.43 mmol) scale, yielding **24a** (65 mg, 72% overall yield). $[\alpha]_D^{25} = +26.2$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) δ 1.06 (s, 9H), 1.26–1.70 (m, 7H), 1.97–2.15 (m, 3H), 3.05 (m, 1H), 3.30 (m, 1H), 3.40 (ddd, $J = 10.6, 9.4, 5.0$ Hz, 1H), 3.84 (d, $J = 10.3$ Hz, 1H), 4.37 (m, 3H), 7.41 (m, 6H), 7.71 (d, $J = 7.3$ Hz, 4H); ¹³C NMR (CDCl₃) δ 19.1 (s), 19.7 (t), 25.5 (t), 26.7 (q), 31.6 (t), 35.8 (t), 36.3 (t), 52.7 (t), 66.7 (d), 67.3 (t), 71.2 (d), 81.0 (d), 82.6 (s), 85.3 (s), 127.7 (d), 129.8 (d), 133.2 (s), 135.6 (d); IR (CHCl₃) (cm⁻¹) 3071, 2934, 2858, 1461, 1428, 1113, 1092, 1064; MS m/z (relative intensity) 391 ($M - \text{Bu-}t$)⁺ (4), 233 (12), 199 (100), 105 (54). HRMS calcd for C₂₄H₂₇O₃Si [$M - \text{Bu-}t$]⁺ 391.17295, found 391.17328.

Preparation of (2*R* and 2*S*)-4-[(4a*S*,6*S*,9a*R*)-octahydro-2*H*-pyrano[3,2-*b*]oxepin-6-yl]-3-butyn-2-ol (24b). The procedure used above to obtain **4b** was applied to **23b** on a 200 mg (0.42 mmol) scale, yielding **24b** (65 mg, 70 % overall yield). ¹H NMR (CDCl₃) δ 1.42 (d, $J = 6.5$ Hz, 6H), 1.59–1.74 (m, 6H), 1.92–2.10 (m, 8H), 3.09 (m, 4H), 3.28 (ddd, $J = 10.6, 10.6, 4.0$ Hz, 2H), 3.83 (d, $J = 10.6$ Hz, 2H), 4.47 (dd, $J = 6.0, 6.0$ Hz, 2H), 4.55 (q, $J = 6.6$ Hz, 2H); ¹³C NMR (CDCl₃) δ 19.1 (t), 24.1 (q), 25.7 (t), 31.4 (t), 34.4 (t), 35.9 (t), 58.3 (d), 67.5 (t), 68.9 (d), 78.4 (d), 82.2 (d), 84.3 (s), 86.0 (s); IR (CHCl₃) (cm⁻¹) 3346, 2937, 2862, 1715, 1680, 1453, 1279, 1081; MS m/z (relative intensity) 209 (2), 179 (8), 136 (49), 91 (56), 71 (100). HRMS calcd for C₁₃H₂₀O₃ [M]⁺ 224.14124, found 224.14090.

Preparation of (*E*)-5-[(2*R*,3*S*)-3-(*tert*-Butyl-dimethyl-silanyloxy)-tetrahydro-pyran-2-yl]-2-penten-1-ol (27). The sequence used to obtain the allylic alcohol precursor of **26** was applied to **26** on a 5 g (18.2 mmol) scale, yielding **27** (3.9 g, 71% overall yield) as an oil: $[\alpha]_D^{25} = +48.5$ (c 4.1, CHCl₃); ¹H NMR (CDCl₃) δ 0.05 (s, 6H), 0.87 (s, 9H), 1.40 (m, 2H), 1.62 (m, 2H), 1.88 (m, 1H), 1.98 (m, 1H), 2.08 (m, 1H), 2.22 (m, 1H), 2.96 (ddd, $J = 9.2, 9.2, 2.4$ Hz, 1H), 3.27 (m, 2H), 3.85 (m, 1H), 4.06 (d, $J = 4.8$ Hz, 2H), 5.66 (m, 2H); ¹³C-NMR (CDCl₃) -4.7 (q), -4.0 (q), 17.9 (s), 25.7 (t), 25.8 (q), 28.0 (t), 31.6 (t), 33.6 (t), 63.8 (t), 67.7 (t), 71.3 (d), 82.0 (d), 129.0 (d), 133.1 (d); IR (CHCl₃) (cm⁻¹) 3445, 2954, 2857, 1463, 1257, 1097, 838; MS m/z (relative intensity) 300 (M)⁺ (4), 283 (2), 243 (8), 225 (21), 171 (30), 151 (68), 101 (51), 67 (100). Anal. Calcd for C₁₆H₃₂O₃Si: C, 63.95; H, 10.73. Found: C, 63.75; H, 10.83.

Preparation of (2*R*,3*S*)-2-[(3*S*,4*R*)- and (2*R*,3*S*)-2-[(3*S*,4*S*)-3-Benzoyloxy-4-hydroxy-undec-5-ynyl]-tetrahydro-pyran-3-ol (29). The procedure described above to obtain **7d** using 1-heptyne (0.2 mL, 1.6 mmol) as alkyne was applied to **28** on a (340 mg, 0.8 mmol) scale, yielding **29** (219 mg, 73% overall yield) as an oil: ¹H NMR (CDCl₃) δ 0.89 (m, 6H), 1.33 (m, 12H), 1.52 (m, 4H), 1.65 (m, 4H), 1.96 (m, 4H), 2.08 (m, 2H), 2.21 (m, 4H), 2.21 (m, 4H), 2.35 (d, $J = 5.6$ Hz, 1H), 2.54 (d, $J = 5.6$ Hz, 1H), 2.97 (m, 2H), 3.28 (m, 4H), 3.52 (m, 2H), 3.87 (m, 2H), 4.33 (m, 1H), 4.51 (m, 1H), 4.64 (s, 2H), 4.70 (s, 2H); ¹³C-NMR (CDCl₃) δ 13.9 (q), 18.7 (t), 22.1 (t), 25.6 (t), 25.8 (t), 26.7 (t), 27.5 (t), 28.0 (t), 28.2 (t), 31.0 (t), 32.8 (t), 64.2 (d), 64.8 (d), 67.5 (t), 70.5 (d), 72.4 (t), 73.1 (t), 78.0 (s), 78.9 (s), 82.0 (d), 82.5 (d), 86.7 (s), 87.1 (s), 127.7 (d), 127.9 (d), 128.0 (d), 128.4 (d), 138.3 (s); IR (CHCl₃) (cm⁻¹) 3603, 3011, 2935, 2860, 2230, 1602, 1454, 1090; MS m/z (relative intensity) 356 ($M - 18$)⁺ (1), 249 (14), 216 (1), 157 (3), 141 (37), 97 (13), 91 (100). HRMS calcd for C₂₃H₃₂O₃ [$M - \text{H}_2\text{O}$] 356.2351, found 356.2304.

Preparation of (6*R*,7*S*,10*R*,11*S*)-7-Benzoyloxy-6-hept-1-ynyl-octahydro-1,5-dioxabenzocycloheptene (31) and of (6*S*,7*S*,10*R*,11*S*)-7-Benzoyloxy-6-hept-1-ynyl-octahydro-1,5-dioxabenzocycloheptene (32). The procedure used above to obtain **4b** was applied to **29** (at -20 °C) on a 57 mg (0.09 mmol) scale, yielding **31** and **32** (19 mg, 65% overall yield) as a 1 : 2 epimeric mixture. **31**: colorless oil; $[\alpha]_D^{25} = +35.8$ (c 0.6, CHCl₃); ¹H NMR (C₆D₆) δ 0.87 (dd, $J = 7.1, 7.1$ Hz, 3H), 1.25 (m,

6H), 1.43 (m, 4H), 1.95 (m, 2H), 2.02 (m, 1H), 2.13 (ddd, $J = 7.0, 7.0, 2.0$ Hz, 2H), 2.15 (m, 1H), 3.10 (m, 2H), 3.37 (ddd, $J = 9.7, 9.7, 4.0$ Hz, 1H), 3.74 (m, 1H), 4.05 (m, 1H), 4.39 (d, $J = 11.9$ Hz, 1H), 4.48 (d, $J = 11.9$ Hz, 1H), 4.67 (m, 1H), 7.22 (m, 3H), 7.51 (m, 2H); ^{13}C NMR (C_6D_6) δ 13.8 (q), 18.8 (t), 22.2 (t), 24.2 (t), 25.8 (t), 27.2 (t), 28.4 (t), 31.0 (t), 31.8 (t), 67.1 (t), 71.1 (t), 75.1 (d), 80.3 (d), 80.4 (s), 82.5 (d), 83.5 (d), 85.1 (s), 127.4 (d), 127.5 (d), 128.2 (d), 138.8 (s); IR (CHCl_3) (cm^{-1}) 3010, 2935, 2860, 2236, 1602, 1257, 1093; MS m/z (relative intensity) 265 ($\text{M} - 91$)⁺ (1), 209 (1), 157 (5), 141 (39), 123 (23), 112 (33), 97 (50), 71 (100); HRMS calcd for $\text{C}_{23}\text{H}_{32}\text{O}_3$ 356.2351, found 356.2357.

32: colorless oil; $[\alpha]_{\text{D}}^{25} = -26.9$ (c 1.1, CHCl_3); ^1H NMR (CDCl_3) δ 0.89 (dd, $J = 7.1, 7.1$ Hz, 3H), 1.33 (m, 6H), 1.54 (m, 2H), 1.63 (m, 1H), 1.72 (m, 1H), 1.87 (m, 2H), 2.00 (m, 2H), 2.27 (ddd, $J = 7.0, 7.0, 2.1$ Hz, 2H), 3.06 (ddd, $J = 6.8, 6.8, 4.6$ Hz, 1H), 3.28 (ddd, $J = 8.5, 8.5, 2.3$ Hz, 1H), 3.66 (ddd, $J = 5.8, 4.1, 1.6$ Hz, 1H), 3.75 (ddd, $J = 8., 6.8, 3.5$ Hz, 1H), 3.85 (m, 1H), 4.59 (m, 1H), 4.60 (s, 1H), 4.61 (s, 1H), 7.28 (m, 1H), 7.33 (m, 2H), 7.38 (m, 2H); ^{13}C NMR (CDCl_3) δ 13.9 (q), 18.9 (t), 22.2 (t), 24.5 (t), 25.6 (t), 27.8 (t), 28.3 (t), 31.0 (t), 31.6 (t), 67.4 (t), 71.2 (d), 71.6 (t), 72.7 (d), 76.4 (s), 78.6 (d), 80.8 (d), 88.2 (s), 127.4 (d), 128.2 (d), 138.6 (s); IR (CHCl_3) (cm^{-1}) 3013, 2956, 2933, 2860, 2234, 1271, 1093; MS m/z (relative intensity) 265 ($\text{M} - 91$)⁺ (4), 209 (2), 157 (3), 141 (94), 122 (12), 105 (34), 97 (100), 91 (67). HRMS calcd for $\text{C}_{23}\text{H}_{32}\text{O}_3$ 356.2351, found 356.2348.

Preparation of 7-[(2*R*,3*S*)-3-(*tert*-Butyl-dimethyl-silyloxy)-tetrahydro-pyran-2-yl]-1-heptyn-4-one Dicobalt Hexacarbonyl Complex (39). The general procedure for the preparation of the dicobalt hexacarbonyl complexes and the general cyclization procedure (room temperature) described above were applied to **38** on a 90 mg (0.28 mmol) scale, yielding **39** (50 mg, 36% yield) as a dark red oil: ^1H NMR (CDCl_3) δ 1.38 (m, 2H), 1.69 (m, 3H), 1.86 (m, 2H), 2.09 (m, 1H), 2.58 (t, $J = 7.0$ Hz, 2H), 2.99 (dd, $J = 8.5, 7.0$ Hz, 2H), 3.29 (m, 2H), 3.85 (d, $J = 9.9$ Hz, 2H), 3.96 (s, 2H), 6.16 (s, 1H); ^{13}C NMR (CDCl_3) δ 19.5 (t), 25.5 (t), 31.1 (t), 32.8 (t), 42.6 (t), 46.6 (t), 67.4 (t), 70.1 (d), 74.6 (d), 82.1 (d), 205.0 (s).

Preparation of (4*Z*,2*R* and 2*S*)-2-Benzyloxy-5-[(2*R*,3*S*)-3-(*tert*-butyl-dimethyl-silyloxy)-tetrahydro-pyran-2-yl]-4-penten-1-ol (41). The same sequence used in the paper to obtain **37** from **36** was applied to **40** on a 0.5 g (1.58 mmol) scale yielding **41** (463 mg, 72% overall yield) as a colorless oil: ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 0.05 (s, 6H), 0.86 (s, 18H), 1.45 (m, 2H), 1.64 (m, 4H), 2.04 (m, 2H), 2.26 (br s, 2H), 2.45 (m, 2H), 2.57 (m, 2H), 3.33-3.91 (m, 14H), 4.57 (m, 2H), 4.66 (m, 2H), 5.53 (m, 2H), 5.65 (m, 2H); ^{13}C -NMR (CDCl_3) δ -4.7 (q), -4.6 (q), 18.0 (s), 25.4 (t), 25.8 (q), 29.3 (t), 29.7 (t), 33.5 (t), 63.2 (t), 63.3 (t), 67.4 (t), 71.3 (d), 71.3 (t), 77.9 (d), 78.3 (d), 78.7 (d), 78.9 (d), 127.7 (d), 128.4 (d), 130.1 (d), 130.2 (d), 130.7 (d), 131.9 (d), 138.4 (s); IR (film) (cm^{-1}) 3445, 2930, 2857, 1252, 1098; MS m/z (relative intensity) 406 (M)⁺ (0.2), 241 (10), 179 (19), 145 (20), 122 (35), 91 (99), 75 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{38}\text{O}_4\text{Si}$: C, 67.94; H, 9.42. Found: C, 67.91; H, 9.58.

Preparation of (3*R* and 3*S*,4*R* and 4*S*)-4-Benzyloxy-7-[(2*R*,3*S*)-3-(*tert*-butyl-dimethyl-silyloxy)-tetrahydro-pyran-2-yl]-hept-6-en-1-yn-3-ol (42). The same sequence used in the paper to obtain **38** was applied to **41** on a 0.4 g (0.98 mmol) scale, yielding **42** (214 mg, 69% overall yield) as a colorless oil: ^1H NMR (CDCl_3) δ 1.43 (m, 4H), 1.68 (m, 8H), 2.13 (m, 4H), 2.26-2.72 (m, 12H), 3.35 (m, 8H), 3.63 (dd, $J = 10.9, 5.5$ Hz, 4H), 3.83 (m, 8H), 4.41 (ddd, $J = 5.2, 5.2, 2.1$ Hz, 4H), 4.68 (m, 8H), 5.47-5.90 (m, 8H), 7.25-7.39 (m, 20H); ^{13}C NMR (CDCl_3) δ 25.2 (t), 25.3 (t), 25.4 (t), 25.5 (t), 28.9 (t), 29.2 (t), 29.8 (t), 30.5 (t), 31.4 (t), 31.6 (t), 31.7 (t), 32.1 (t), 32.8 (t), 63.5 (d), 63.6 (d), 67.3 (t), 67.4 (t), 70.0 (d), 70.2 (d), 72.5 (t), 72.6 (t), 73.1 (t), 73.7 (d), 73.8 (d), 74.0 (d), 74.3 (d), 78.0 (d), 78.3 (d), 78.4 (d), 80.6 (d), 80.7 (d), 80.8 (d), 82.7 (s), 82.8 (s), 127.8 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.3 (d), 128.4 (d), 128.5 (d), 130.1 (d), 130.3 (d), 130.6 (d), 130.7 (d), 131.8 (d), 137.5 (s), 137.8 (s), 137.9 (s); IR (film) (cm^{-1}) 3393, 3290, 3029, 2933, 2859, 1638, 1455, 1090. Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4$: C, 72.13; H, 7.65. Found: C, 72.16; H, 8.13.

Preparation of (1*S*,4*S*,3*R*,6*Z*,8*R*)-3-Etynyl-2,9-dioxa-4-(phenylmethoxy)bicyclo[6.4.0]dodec-6-ene (43) and (1*S*,4*R*,3*R*,6*Z*,8*R*)-3-ethynyl-2,9-dioxa-4-(phenylmethoxy)bicyclo[6.4.0]dodec-6-ene (44). The procedure used above to obtain **4b** was applied to **42** on a 69 mg (0.12 mmol) scale, yielding **43** and **44** (23 mg, 65% overall yield) as a 1 : 1 epimeric mixture. **43**: colorless oil; $[\alpha]_D^{25} = +147.0$ (c 1.0, CHCl₃); ¹H NMR (C₆D₆) δ 1.40 (m, 3H), 2.09 (m, 1H), 2.22 (d, *J* = 2.0 Hz, 1H), 2.31 (m, 1H), 2.59 (m, 1H), 2.99 (dd, *J* = 11.4, 11.4 Hz, 1H), 3.16 (m, 1H), 3.70 (dd, *J* = 11.0, 3.9 Hz, 1H), 3.82 (m, 2H), 4.41 (dd, *J* = 9.3, 1.6 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 5.69 (m, 1H), 5.96 (dd, *J* = 11.1, 4.9 Hz, 1H), 7.25 (m, 3H), 7.42 (m, 2H); ¹³C NMR (C₆D₆) δ 25.4 (t), 28.9 (t), 31.6 (t), 66.7 (t), 71.3 (d), 72.3 (t), 72.9 (d), 79.9 (d), 80.6 (d), 82.6 (d), 84.3 (s), 124.8 (d), 127.9 (d), 128.0 (d), 128.2 (d), 135.5 (d), 138.8 (s); IR (film) (cm⁻¹) 3286, 2939, 2858, 1455, 1217, 1099; Anal. Calcd for C₁₉H₂₂O₃: C, 76.48; H, 7.43. Found: C, 76.46; H, 7.24. **44**: white solid; mp. 105 – 107 °C; $[\alpha]_D^{25} = +21.6$ (c 0.75, CHCl₃); ¹H NMR (CDCl₃) δ 1.63 (m, 3H), 2.22 (m, 1H), 2.30 (m, 1H), 2.53 (d, *J* = 2.3 Hz, 1H), 2.60 (m, 1H), 3.19 (m, 1H), 3.29 (m, 1H), 3.60 (m, 1H), 3.87 (dd, *J* = 12.1, 3.1 Hz, 1H), 3.95 (dd, *J* = 9.1, 2.6 Hz, 1H), 4.53 (dd, *J* = 2.4, 2.4 Hz, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.76 (d, *J* = 12.3 Hz, 1H), 5.58 (m, 2H), 7.24-7.42 (m, 5H); ¹³C NMR (CDCl₃) δ 25.5 (t), 30.5 (t), 31.4 (t), 67.2 (t), 71.9 (d), 72.6 (t), 74.6 (d), 79.7 (d), 80.2 (d), 80.8 (d), 81.8 (s), 125.9 (d), 127.6 (d), 128.0 (d), 128.2 (d), 135.7 (d), 138.4 (s); IR (film) (cm⁻¹) 3255, 2932, 2866, 1456, 1085, 960; MS *m/z* (relative intensity) 298 (M)⁺ (1), 207 (10), 123 (10), 91 (100), 71 (88); HRMS calcd for C₁₉H₂₂O₃ 298.15690, found 298.15785.

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