Supporting Information

Tandem Cyclization of Alkynylmetals Bearing Remote Leaving Group via Cycloalkylidene Carbenes

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1-Iodo-5-(2-phenylethyl)-4-oxa-6-heptyne (7) **(Representative Procedure for the Preparation of Oxaalkynyl Iodides)**: To a solution of 2-(2-phenylethyl)-1,3-dioxane (2.77 g, 14.4 mmol) and bis(trimethylsilyl)acetylene (9.2 mL, 37 mmol) in CH_2Cl_2 (300 mL) at -85 °C was added $TiCl_4$ (2.2 mL, 20 mmol). The reaction mixture was stirred for 1 h at this temperature and was quenched by the addition of methanol (*ca*. 10 mL). The mixture was poured into 1N HCl and extracted three times with ether. The organic layers were washed with 1N HCl, dried ($MgSO_4$), and concentrated in *vacuo* . The residue was treated with KF (3.4 g) in methanol (56 mL) under reflux for 1.5 h. The mixture was poured into brine and extracted three times with ether. The organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by flash chromatography (SiO_2, 10-30% ethyl acetate in hexane) gave 2.75 g (87% yield) of 5-(2-phenylethyl)-4-oxa-6-heptyn-1-ol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.8-2.15 (5H, m), 2.48 (1H, d, *J* = 2.1 Hz), 2.79 (2H, t, *J* = 8.1 Hz), 3.51 (1H, m), 3.79 (2H, t, *J* = 5.7 Hz), 3.9-4.05 (2H, m), 7.15-7.35 (5H, m).

To a solution of the alcohol (1.07 g, 4.91 mmol) in THF (5 mL) at -78 °C was added BuLi (1.6 M in hexane) (3.1 mL, 4.9 mmol). After being stirred for 1 h, a THF (5 mL) solution of *p*-toluenesulfonyl chloride (1.03 g, 5.40 mmol) was added to the mixture at -78 °C. The reaction mixture was allowed to warm to 0 °C over *ca*. 4 h and poured into water. The mixture was extracted twice with ether. The combined extracts were washed with aq $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by flash chromatography (SiO_2, 6-20% ethyl acetate in hexane) gave 1.83 g (100% yield) of 5-(2-phenylethyl)-4-oxa-6-heptynyl *p*-toluenesulfonate; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.9-2.05 (4H, m), 2.40 (3H, s), 2.44 (1H, d, *J* = 2.1 Hz), 2.70 (2H, m), 3.38 (1H, td, *J* = 6.0 and 9.3 Hz), 3.97 (1H, td, *J* = 6.0 and 9.3 Hz), 3.91 (1H, dt, *J* = 2.1 and 6.6 Hz), 4.1-4.2 (2H, m), 7.15-7.35 (7H, m), 7.8 (2H, m).

A mixture of the tosylate (1.83 g, 4.91 mmol) and NaI (1.47 g, 7.35 mmol) in acetone (12 mL) was heated under reflux for 12 h. The mixture was poured into water and extracted three times with ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by flash chromatography (SiO_2, 3% ethyl acetate in hexane) gave 1.39 g (86% yield) of iodide **7**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.0-2.15 (2H, m), 2.47 (1H, d, *J* = 2.1

Hz), 2.79 (2H, t), 3.25-3.35 (2H, m), 3.43 (1H, td, *J* = 9.3 and 9.6 Hz), 3.80 (1H, td, *J* = 5.7 and 9.6 Hz), 4.00 (1H, dt, *J* = 2.1 and 6.0 Hz), 7.2-7.3 (5H, m).

1-Iodo-4-(2-phenylethyl)-5-hexyne (**13**) **(Representative Procedure for the Preparation of Alkynyl Iodides)**: To a THF (110 mL) solution of BuLi (1.6 M in hexane) (109 mL, 174 mmol) at -30 °C was added dropwise a THF (70 mL) solution of 5-hexyn-1-ol (4.91 g, 50.0 mmol). The cooling bath was removed and the mixture was stirred at room temperature for 2 h. To the resulting suspension at -40 °C was added a THF (10 mL) solution of 2-phenylethyl bromide (9.25 g, 50.0 mmol). The mixture was stirred at room temperature for 1 h and then at 40 °C for 1 h. The resulting mixture was poured into water and extracted three times with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Unreacted alcohol and bromide were removed by Kugelrohr distillation (55 °C/3 mmHg) and the residue was purified by flash chromatography (SiO_2, 10% ethyl acetate in hexane) to give 5.08 g (50% yield) of 4-(2-phenylethyl)-5-hexyn-1-ol; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45-1.9 (7H, m), 2.14 (1H, d, *J* = 2.4 Hz), 2.37 (1H, m), 2.72 (1H, m), 2.86 (1H, m), 3.66 (2H, t, *J* = 6.0 Hz), 7.0-7.4 (5H, m).

Tosylation of the alcohol by a procedure similar to that described above gave 4-(2-phenylethyl)-5-hexyn-1-yl *p*-toluenesulfonate (76% yield); ^1H NMR (300 MHz, $CDCl_3$) δ 1.35-2.0 (6H, m), 2.10 (1H, d, *J* = 2.1 Hz), 2.28 (1H, m), 2.44 (3H, s), 2.67 (1H, m), 2.82 (1H, m), 4.05 (2H, m), 7.15-7.4 (7H, m), 7.8 (2H, m).

Treatment of the tosylate with NaI in acetone by a procedure similar to that described above gave iodide **13** (92% yield); ^1H NMR (300 MHz, $CDCl_3$) δ 1.5-1.7 (2H, m), 1.7-1.8 (2H, m), 1.85-2.15 (2H, m), 2.14 (1H, d, *J* = 2.4 Hz), 2.36 (1H, m), 2.72 (1H, m), 2.86 (1H, m), 3.20 (2H, m), 7.2-7.3 (5H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 6.57, 30.12, 31.07, 33.40, 35.60, 36.69, 70.43, 86.65, 125.90, 128.38, 128.47, 141.68. IR (liquid film) 3280, 750, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{17}I$: C, 53.86; H, 5.49. Found: C, 53.79; H, 5.41.

10-Oxatricyclo[7.3.0.0^{3,8}]dodeca-1-ene (**10**): (A 58:38:4 mixture of diastereomers) ^1H NMR (300 MHz, $CDCl_3$) δ 1.0-2.05 (6H, m), 2.35-2.5 (3H, m), 3.07 (1H for the major isomer, m), 4.0-4.25 (2H, m), 4.35 (1H for the second major isomer, br, d, *J* = *ca*. 8 Hz), 4.72 (1H for the major isomer, m), 5.30 (1H for the major isomer, br s), 5.48 (1H for the second major isomer, br s), 5.67 (1H for the minor isomer, br s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.03, 26.14, 26.24, 28.21, 30.95, 53.22, 59.26, 71.71, 90.92, 124.99, 148.28 [the second major isomer resonated at 21.16, 22.36, 23.89, 26.19, 27.81, 45.97, 46.94, 72.24, 91.07, 124.24, 146.59]; IR (liquid film) 1065, 1050, 1025, 970 cm^{-1};

10-Oxatricyclo[7.4.0.0^{3,8}]trideca-1-ene (**12**). Purification of the crude products by flash chromatography (SiO_2, Et_2O in pentane) gave, in the order of elution, the second major diastereomer of **12b** (17%) and a 86:14 mixture of the major and minor diastereomers (**12a** and **12c**) in 45% combined yield. **12b**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.0-1.75 (10H, m), 2.16 (1H, m), 2.39 (1H, m), 2.45-2.65 (2H, m), 3.48 (1H, dt, *J* = 3.0 and 11.1 Hz), 3.96 (1H, br d, *J* = 11.1 Hz), 4.27 (1H, br d, *J* = *ca*. 6 Hz), 5.21 (1H, br s); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 22.28, 22.42, 23.99, 25.84, 26.23, 27.69, 40.43, 41.88, 67.07, 85.14, 127.36, 139.66; IR (liquid film) 1100, 1095 cm^{-1}; MS, (relative intensity) 178 (M$^+$, 100); 149 (19), 135 (26); HRMS calcd for $C_{12}H_{18}O$: 178.1358, found 178.1363. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.78; H, 9.97. **12a** and **12c** (86:14); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0-2.05 (10H, m), 2.14 (1H for **112a**, m), 2.35 (1H for **12c**, m), 2.46 (1H, br d, *J* = *ca*. 14 Hz), 3.48 (1H, m), 3.9-4.0 (2H, m), 4.12 (1H for **12c**, br d, *J* = *ca*. 8 Hz), 5.40 (1H for **12a**, br s), 5.51 (1H for **12c**, br s); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 25.96, 26.39, 26.45, 26.60, 27.96, 31.02, 46.41, 55.60, 67.07, 84.85, 127.23, 141.43 [the minor isomer resonated at 22.24, 24.14, 25.05, 26.19, 26.74, 31.56, 40.99, 44.67, 67.35, 83.62, 129.58, 141.53]; IR (liquid film) 1100, 1090 cm^{-1}; MS, (relative intensity) 178 (M$^+$, 100); 149 (20), 135 (27); HRMS calcd for $C_{12}H_{18}O$: 178.1358, found 178.1361. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.61; H, 10.12.

3-Phenylbicyclo[3.3.0]oct-1-ene (**14**) (A 91:9 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (1H, quint, *J* = *ca*. 11 Hz), 1.37 (1H, td, *J* = 9.7 and 12.1 Hz), 1.95-2.15 (3H, m), 2.20-2.35 (2H, m), 2.58 (1H, td, *J* = 6.8 and 12.0 Hz), 2.96 (1H, m), 4.22 (1H, m), 5.32 (1H, br s), 7.2-7.35 (5H, m) [the minor isomer resonated at 3.08 (1H, m), 4.18 (1H, br d, *J* = *ca*. 9 Hz), 5.41 (1H, br s)]; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 23.87, 28.39, 32.13, 43.69, 52.43, 57.19, 121.39, 125.94, 127.26, 128.28, 146.79, 155.97; IR (liquid film) 1600, 750, 700 cm^{-1}; MS, (relative intensity) 184 (M$^+$, 80); 155 (100); HRMS calcd for $C_{14}H_{16}$: 184.1252, found 184.1258. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.25; H, 8.41.

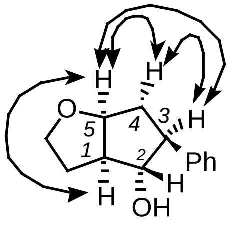
8-Phenylbicyclo[4.3.0]nona-1(9)-ene (**17**) (A 67:33 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$) δ 095-1.1 (1H, m), 1.20-1.45 (3H, m), 1.7-1.9 (2H, m), 1.95-2.1 (2H, m), 2.4-2.65 (3H, m), 3.85 (1H, m), 5.28 (1H, br s, J = 2.1 Hz), 7.24-7.33 (5H, m) [minor diastereomer resonated at 5.33 (1H, br s)]; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 25.94, 27.13, 28.80, 35.98, 42.29, 45.57, 50.26, 124.18, 125.78, 127.30, 128.25, 147.50, 147.63 [the minor isomer resonated at 26.07, 27.38, 28.95, 35.84, 40.80, 45.12, 49.86, 123.71, 125.71, 127.03, 128.28, 147.55, 147.72]; IR (liquid film) 1600, 760, 700 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C,90.59; H, 9.15.

3-Phenyloxybicyclo[3.3.0]oct-1-ene (**19**). The diastereomers were separated by a recycling preparative HPLC, equipped with a GPC column (JAIGEL-1H column, Japan Analytical Industry) using $CHCl_3$ as an eluent. ^{1}H NMR for the major isomer (500 MHz, $CDCl_3$) δ 1.21 (1H, quint, *J* = 9.6 Hz), 1.59 (1H, m), 1.9-2.1 (3H, m), 2.15-2.4 (2H, m), 2.75-2.85 (2H, m), 5.51 (1H, br s), 5.60 (1H, m), 6.9-6.95 (3H, m), 7.30 (2H, m); ^{1}H NMR for the minor isomer (500 MHz, $CDCl_3$) δ 1.03 (1H, dq, *J* = 7.5 and 11.1 Hz), 1.77 (1H, td, *J* = 6.6 and 12.2 Hz), 1.95-2.15 (3H, m), 2.2-2.45 (3H, m), 3.21 (1H, m), 5.44 (1H, br d, J = 6.2 Hz), 5.61 (1H, br s), 6.9-7.0 (3H, m), 7.30 (2H, m); ^{13}C NMR for the major isomer (125.8 MHz, $CDCl_3$) δ

24.07, 27.11, 32.15, 39.87, 49.74, 88.15, 115.35, 118.23, 120.36, 129.42, 157.94, 158.26. ^{13}C NMR for the minor isomer (125.8 MHz, CDCl$_3$) δ 23.88, 28.39, 31.93, 37.29, 50.11, 87.91, 115.36, 116.87, 120.21, 129.37, 158.35, 164.61; IR (liquid film) 1595, 1230, 745, 690. cm^{-1}; MS, (relative intensity) 200 (M$^+$, 8); 171 (10), 107 (100); HRMS calcd for C$_{14}$H$_{16}$O: 200.1201, found 200.1198.

Bicyclo[3.3.0]oct-1-en-3-one Ethylene Acetal (**21**): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.02 (1H, dq, *J* = 8.7 and 11.1 Hz), 1.69 (1H, dd, *J* = 6.9 and 13.2 Hz), 1.8-2.0 (3H, m), 2.24 (2H, m), 2.29 (1H, dd, *J* = 6.9 and 13.2 Hz), 2.82 (1H, m), 3.8-4.05 (4H, m), 5.31 (1H, q, *J* = 2.1 Hz); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 24.16, 26.88, 32.00, 42.96, 48.00, 64.41, 64.83, 118.45, 161.32; IR (liquid film) 1665, 1060, 890, 790 cm^{-1}; MS, (relative intensity) 166 (M$^+$, 100); 138 (75), 79 (30); HRMS calcd for C$_{10}$H$_{14}$O$_2$: 166.0994, found 166.0977.

(1R*,2S*,3S*,5S*)-3-phenyl-6-oxabicyclo[3.3.0]octan-2-ol (**i**). Treatment of **2** with Me$_2$CHC(Me)$_2$BH$_2$•DMS (1.1 equiv) in THF at -10–0 °C for 3 h and subsequent oxidative work-up (6N NaOH, 30% H$_2$O$_2$, EtOH, 50 °C, 24 h) gave alcohol **i** in 41% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.80 (1H, dt, *J* = 5.7 and 13.3 Hz, H-4β), 1.91 (1H, m, H-8β), 2.03 (1H, qd, *J* = 8.5 and 12.6 Hz, H-8α), 2.14 (1H, br s, OH), 2.46 (1H, td, *J* = 7.4 and 13.7 Hz, H-4α), 2.58 (1H, dq, *J* = 2.1 and 8.1 Hz, H-1), 2.91 (1H, ddd, *J* = 7.3, 9.9, and 12.9 Hz, H-3), 3.78 (1H, dd, *J* = 8.4 and 9.2 Hz, H-2), 3.86 (1H, dt, *J* = 6.0 and 8.8 Hz, H-7), 3.92 (1H, dt, J = 4.0 and 8.8 Hz, H-7), 4.54 (1H, dt, *J* = 5.9 and 7.8 Hz, H-5), 7.25-7.35 (5H, m); NOESY experiment showed cross-peaks between H-1 and H-5, between H-3 and H4-α, between H-3 and H-5, and between H-4α and H-5. ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 30.76, 37.33, 50.32, 53.26, 67.54, 80.54, 83.41, 126.88, 127.34, 128.65, 140.72; IR (liquid film) 3400 (br), 1060, 760, 705 cm^{-1}; MS, (relative intensity) 204 (M$^+$, 83); 186 (93), 142 (100); HRMS calcd for C$_{13}$H$_{16}$O$_2$: 204.1150, found 204.1154.



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