All reactions requiring anhydrous conditions were conducted in flame-dried glass apparatus under an atmosphere of Ar. DME, THF and Et_2O were freshly distilled from sodium benzophenone ketyl prior to use. DMSO was distilled from CaH_2 at 15 mmHg. CH_2Cl_2 was freshly distilled from CaH_2. Anhydrous ethanol was obtained by distillation from its magnesium alkoxide and stored under Ar over activated 4Å molecular sieves. Preparative chromatographic separations were performed on EM Science silica gel 60 (35-75 μm) and reactions followed by TLC analysis using EM Science silica plates with fluorescent indicator (254 nm) and visualized with UV, phosphomolybdic acid or potassium permanganate. All commercially available reagents were purchased from Aldrich and were typically used as supplied. Melting points were recorded using open capillary tubes on a Büchi melting point apparatus and are uncorrected. Specific optical rotations were measured at ambient temperature (23 °C) from $CHCl_3$ solutions on a Perkin-Elmer 243 polarimeter using a 1 mL cell with 1 dm path length. Infra-red spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer using a thin film supported between NaCl plates or KBr discs where stated. ^1H and ^{13}C NMR spectra were recorded in Fourier transform mode at the field strength specified either on a Bruker AC300 or AM400 spectrometer. Spectra were obtained from $CDCl_3$ solutions in 5 mm diameter tubes, and the chemical shift in ppm is quoted relative to the residual signals of chloroform (δ_H = 7.25 ppm, or δ_C = 77.0 ppm). Multiplicities in the ^1H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet, br = broad; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were run on a Kratos MS-50 spectrometer. Ion mass/charge (*m/z*) ratios are reported as values in atomic mass units.

Allyl (*E*)-7-oxo-2,11-dodecadienoate (8). A solution of allyl (triphenylphosphoranylidene)acetate (**7**, 4.13 g, 11.5 mmol) in CH_2Cl_2 (80 mL) at rt under Ar, was treated with freshly prepared 5-oxo-9-decenal (0.91 g, 5.42 mmol) in CH_2Cl_2 (20 mL). After stirring for 1 h the reaction mixture was concentrated *in vacuo* and the crude residue further purified *via* column chromatography (eluting with 30% Et_2O in hexanes) to yield the enoate **8** (1.13 g, 4.52 mmol, 83%) as a colorless oil. ^1H NMR analysis indicated only the *trans* isomer: IR (neat) 2935, 1718, 1649, 1365, 1262, 1174, 992, 904, 712, 634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.55 (quintet, J = 7 Hz, 2H), 1.64 (quintet, J = 7 Hz, 2H), 1.93 (qm, J = 7 Hz, 2H), 2.11 (qm, J = 7 Hz, 2H), 2.29 (t, J = 7 Hz, 2H), 2.32 (t, J = 7 Hz, 2H), 4.51 (dt, J = 6, 1 Hz, 2H), 4.85 (ddt, J = 10, 2, 1 Hz, 1H), 4.89 (dq, J = 17, 2 Hz, 1H), 5.12 (dq, J = 10, 1 Hz, 1H), 5.21 (dq, J = 17, 2 Hz, 1H), 5.64 (ddt, J = 17, 10, 7 Hz, 1H), 5.74 (dt, J = 16, 2 Hz, 1H), 5.83 (ddt, J = 17, 10, 6 Hz, 1H), 6.84 (dt, J = 16, 7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 22.5, 31.2, 32.8, 41.4, 41.6, 64.6, 114.9, 117.7, 121.4, 132.1, 137.6, 148.4, 165.7; MS (CI) *m/z* 251, 192, 175, 165, 147, 97; HRMS (CI) *m/z* 251.1648 (calcd for $C_{15}H_{23}O_3$: 251.1647).

Allyl Azido-7-oxo-11-dodecenoate (9). The enoate **8** (250 mg, 1.0 mmol) was treated with a freshly prepared solution of hydrazoic acid (6.5 mL, 1.58 M in PhH, 10.3 mmol) followed by triethylamine (0.28 mL, $\rho = 0.726$, 203 mg, 2.0 mmol). The resulting solution was then heated to a gentle reflux and stirred under Ar for 27 h. After this time the mixture was allowed to cool and then concentrated *in vacuo*. The residue was further purified *via* column chromatography (eluting with 20% Et_2O in hexanes) to afford the alkyl azide **9** (249 mg, 0.85 mmol, 85%) as a colorless oil: IR (neat) 2934, 2103, 1732, 1713, 1371, 1271, 989, 920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.40-1.80 (m, 6H), 2.05 (qm, $J = 7$ Hz, 2H), 2.40 (t, $J = 7$ Hz, 2H), 2.43 (t, $J = 7$ Hz, 2H), 2.53 (d, $J = 7$ Hz, 2H), 3.80 (quintet, $J = 7$ Hz, 1H), 4.62 (dt, $J = 6$, 1 Hz, 2H), 4.97 (dq, $J = 10$, 2 Hz, 1H), 5.00 (dq, $J = 17$, 2 Hz, 1H), 5.25 (dq, $J = 10$, 1 Hz, 1H), 5.33 (dq, $J = 17$, 1 Hz, 1H), 5.75 (ddt, $J = 17$, 10, 7 Hz, 1H), 5.91 (ddt, $J = 17$, 10, 6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 22.8, 33.1, 33.8, 39.4, 42.0 (2C), 58.9, 65.6, 115.3, 118.7, 131.8, 137.9, 170.3; MS (CI) *m/z* 294, 266, 208, 168, 154; HRMS (CI) *m/z* 294.1818 (calcd for $C_{15}H_{24}N_3O_3$: 294.1818).

Allyl Azido-6-(2-pent-4-enyl[1,3]dioxolan-2-yl)hexanoate (13). A solution of the ketone **9** (564 mg, 1.92 mmol) and bis(trimethylsilyl)ethylene glycol (0.94 mL, $\rho = 0.842$, 791 mg, 3.83 mmol) in anhydrous CH_2Cl_2 (2 mL) at –78°C under Ar, was treated with trimethylsilyltriflate (35 μL, $\rho = 1.23$, 43 mg, 0.19 mmol). After stirring for 20 min the solution was allowed to warm to rt and then quenched 35 min later by the addition of pyridine (1 mL). The mixture was then diluted with CH_2Cl_2 (20 mL) and shaken with sat. aq. $NaHCO_3$ (20 mL). The layers were separated and the aqueous phase extracted (2x10 mL CH_2Cl_2). The combined organic extracts were then washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was further purified *via* column chromatography (eluting with 25% Et_2O in hexane) to yield the ketal **13** (640 mg, 1.90 mmol, 99%) as a colorless oil: IR (neat) 2945, 2100, 1736, 1639, 1462, 1375, 1272, 1166, 1069, 992, 911 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30-1.70 (m, 10H), 2.04 (qt, $J = 7$, 1 Hz, 2H), 2.51 (d, $J = 7$ Hz, 2H), 3.78 (q, $J = 7$ Hz, 1H), 3.91 (s, 4H), 4.60 (dt, $J = 6$, 1 Hz, 2H), 4.93 (ddt, $J = 10$, 2, 1 Hz, 1H), 4.99 (dq, $J = 17$, 2 Hz, 1H), 5.24 (dq, $J = 10$, 1 Hz, 1H), 5.32 (dq, $J = 17$, 1 Hz, 1H), 5.78 (ddt, $J = 17$, 10, 7 Hz, 1H), 5.91 (ddt, $J = 17$, 10, 6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 23.1, 33.8, 34.5, 36.6, 36.6, 39.5, 59.1, 64.9 (2C), 65.5, 111.3, 114.7, 118.6, 131.8, 138.5, 170.3; MS (FAB) *m/z* 338, 336, 310, 268, 240, 141; HRMS (FAB) *m/z* 338.2074 (calcd for $C_{17}H_{28}N_3O_4$: 338.2080).

(*E*)-9-Azido-1,4,12-trioxaspiro[4.13]octadec-14-en-11-one (11). A stirred solution of the diene **13** (27 mg, 80 μmol) in anhydrous CH_2Cl_2 (8 mL) at rt under Ar, was treated with a portion of bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (**10**, 7 mg, 8.5 μmol)

followed by another such addition after 4 h. After stirring for an additional 19 h the solvent was removed *in vacuo*. The resulting black residue was further purified *via* column chromatography (eluting with CH_2Cl_2) to yield, in order of elution, unreacted starting material (11.0 mg, 33 μmol, 41%) and the desired lactone **11** as an inseparable mixture of isomers (5.2 mg, 17 μmol, 21%, colorless oil, *E:Z* = 80:20 by ^{1}H NMR analysis): IR (neat) 2924, 2092, 1733, 1462, 1376, 1260, 1168, 1063, 971 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3) δ 1.20-1.70 (m, $10H_{E+Z}$), 2.00-2.20 (m, $2H_{E+Z}$), 2.43 (dd, *J* = 15, 11 Hz, $1H_E$), 2.46 (dd, *J* = 14, 11 Hz, $1H_Z$), 2.70 (dd, *J* = 15, 4 Hz, $1H_E$), 2.71 (dd, *J* = 14, 4 Hz, H_Z), 3.78 (dtd, *J* = 10, 6, 4 Hz, $1H_{E+Z}$), 3.88 (s, $4H_{E+Z}$), 4.44 (ddd, *J* = 12, 6, 1 Hz, $1H_E$), 4.45-4.53 (m, $1H_Z$), 4.59-4.66 (m, $1H_Z$), 4.68 (dd, *J* = 12, 7 Hz, $1H_E$), 5.64 (dddt, *J* = 15, 7, 6, 1 Hz, $1H_E$), 5.72-5.86 (m, $1H_E+2H_Z$); ^{13}C NMR (75 MHz, CDCl3) *E*-isomer δ 20.8, 21.9, 30.6, 32.9, 33.1, 35.2, 38.8, 58.9, 64.1, 64.5, 64.6, 111.7, 125.8, 138.3, 169.6, *Z*-isomer δ 19.7, 21.8, 26.7, 33.0, 34.4, 35.0, 39.5, 58.3, 59.9, 64.7, 64.8, 111.9, 122.9, 138.2, 170.0; MS (CI) *m/z* 267 $(M-N_3)^+$, 141, 99; HRMS (CI) *m/z* 308.1608 (calcd for $C_{15}H_{22}N_3O_4$: 308.1610).

(*E*)-9-[3-(4-Methoxyphenyl)oxaziridin-2-yl]-1,4,12-trioxaspiro[4.13]octadec-14-en-11-one (12). A solution of the azide **11** (10.7 mg, 34.6 μmol, *E:Z* ~ 4:1) in anhydrous THF (0.5 mL) at rt under Ar, was treated with triphenylphosphine (9.2 mg, 35.1 μmol) and the resulting mixture heated to reflux and stirred for 23 h. After this time *p*-anisaldehyde (4.3 μL, ρ = 1.12, 4.8 mg, 35.4 μmol) was added and reflux continued for 35 h. The reaction mixture was then allowed to cool to rt and stirred for 14 h before being further cooled to –78°C and treated with a solution of dried 3-chloroperoxybenzoic acid (9.3 mg, 85 wt% rest 3-chlorobenzoic acid, 46 μmol) in anhydrous CH_2Cl_2 (0.5 mL). The mixture was allowed to warm to rt over 1.5 h and then quenched by the addition of sat. aq. $Na_2S_2O_3$ (3 mL) and stirred vigorously for 10 min. After dilution with CH_2Cl_2 (5 mL), 10% w/v aq. Na_2CO_3 (5 mL) was added and the layers well shaken and then separated. The aqueous phase was then extracted (2x5 mL CH_2Cl_2) and the combined organic extracts dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was then further purified *via* column chromatography (eluting with 30% EtOAc in hexanes) to yield the oxaziridine product **12** (11.4 mg, 27.3 μmol, 79%, colorless oil) as a mixture of isomers (dr (oxaziridine) = 59:41, *E:Z* ~ 4:1). Diastereoisomers resulting from oxaziridine stereogenicity could be separated by careful column chromatography (eluting with 50% Et_2O in hexanes) but olefinic mixtures could not be resolved (*E:Z* ~ 4:1).

Minor oxaziridine isomers **12** (less polar): IR (neat) 2919, 1738, 1620, 1516, 1459, 1376, 1254, 1167, 1036 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3) *E*-isomer δ 1.30-1.90 (m, 10H), 2.00-2.10 (m, 2H), 2.42-2.56 (m, 2H), 2.57-2.67 (m, 1H), 3.80 (s, 3H), 3.89-3.91 (m, 4H), 4.29 (ddm, *J* = 12, 6 Hz, 1H), 4.53 (s, 1H), 4.85 (dd, *J* = 12, 7 Hz, 1H), 5.65 (dddt, *J* = 15, 7, 6, 1 Hz, 1H), 5.75-5.88 (m, 1H), 6.89 (d, *J* = 9 Hz, 2H), 7.33 (d, *J* = 9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) *E*-isomer δ 20.8, 22.4, 30.5, 32.6, 33.6, 35.5, 36.9, 55.3, 64.0, 64.4 (2C), 68.3, 79.7, 111.9, 114.0 (2C), 125.8, 126.7,

128.9 (2C), 138.1, 161.1, 170.0; MS (FAB) *m/z* 418 $(M+H)^+$, 282, 217, 136; HRMS (FAB) *m/z* 418.2225 (calcd for $C_{23}H_{32}NO_6$: 418.2230).

Major oxaziridine isomers **12** (more polar): IR (neat) 2949, 1739, 1614, 1515, 1459, 1373, 1304, 1248, 1170, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *E*-isomer δ 1.30-1.70 (m, 10H), 2.00-2.20 (m, 2H), 2.55-2.67 (m, 2H), 2.87-2.97 (m, 1H), 3.81 (s, 3H), 3.85-3.90 (m, 4H), 4.42 (dd, *J* = 12, 5 Hz, 1H), 4.56 (s, 1H), 4.73 (dd, *J* = 12, 7 Hz, 1H), 5.67 (dddm, *J* = 16, 7, 6 Hz, 1H), 5.74-5.85 (m, 1H), 6.89 (d, *J* = 9 Hz, 2H), 7.33 (d, *J* = 9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) *E*-isomer δ 21.6, 22.3, 30.6, 31.9, 33.0, 35.6, 39.1, 55.3, 63.8, 64.5 (2C), 68.7, 81.4, 111.8, 114.0 (2C), 126.1, 126.6, 129.0 (2C), 137.8, 161.1, 170.7; MS (FAB) *m/z* 418 $(M+H)^+$, 282, 154; HRMS (FAB) *m/z* 418.2232 (calcd for $C_{23}H_{32}NO_6$: 418.2230).

Allyl 3-[3-(4-Methoxyphenyl)oxaziridin-2-yl]-6-(2-pent-4-enyl[1,3]dioxolan-2-yl)hexanoate (14). A stirred solution of the azide **13** (50 mg, 0.15 mmol) in anhydrous THF (2 mL) at rt under Ar, was treated with triphenylphosphine (39 mg, 0.15 mmol) and the resulting solution heated to reflux and stirred for 24 h. After this time *p*-anisaldehyde (18 μL, ρ = 1.12, 20 mg, 0.15 mmol) was added and heating continued for 32 h. The mixture was then allowed to cool and allowed to stir for 18 h at rt. Following this period the reaction was further cooled to –78 °C and then treated with a solution of dried 3-chloroperoxybenzoic acid (36 mg, 85 wt.%, 0.18 mmol) in anhydrous CH_2Cl_2 (1 mL). After 30 min the cooling bath was removed and the reaction allowed to warm to rt over a further 30 min. Sat. aq. $Na_2S_2O_3$ (5 mL) was added and the mixture stirred vigorously for 5 min. Et_2O (10 mL) and 10% w/v aq. Na_2CO_3 (5 mL) were then added and the layers shaken well and separated. The aqueous phase was then extracted (5 mL, Et_2O) and the combined organic extracts washed with brine (5 mL), dried (Na_2SO_4) and then concentrated *in vacuo*. The residue was then further purified *via* column chromatography (eluting with 40-50% Et_2O in hexanes) to yield the oxaziridine isomers **14** (29 mg, 65 μmol, 43%, dr = 1:1) as a colorless oil. Diastereoisomers could be separated if desired by careful column chromatography (eluting with 30% Et_2O in hexanes).

Less polar isomer **14**: IR (neat) 2927, 1739, 1615, 1521, 1459, 1306, 1249, 1174, 1030, 910 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.40-1.70 (m, 9H), 1.75-1.90 (m, 1H), 2.05 (qt, *J* = 7, 1 Hz, 2H), 2.57-2.70 (m, 3H), 3.80 (s, 3H), 3.93 (s, 4H), 4.44 (ddt, *J* = 13, 6, 1 Hz, 1H), 4.52 (ddt, *J* = 13, 6, 1 Hz, 1H), 4.72 (s, 1H), 4.95 (ddt, *J* = 10, 2, 1 Hz, 1H), 5.00 (dq, *J* = 17, 2 Hz, 1H), 5.16 (dq, *J* = 9, 1 Hz, 1H), 5.21 (dq, *J* = 17, 2 Hz, 1H), 5.70-5.87 (m, 2H), 6.87 (d, *J* = 9 Hz, 2H), 7.32 (d, *J* = 9 Hz, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 23.1, 33.9, 34.3, 36.6, 36.7, 37.1, 55.3, 65.0, 65.5 (2C), 66.7, 80.5, 111.5, 113.8 (2C), 114.6, 118.6, 126.9, 128.9 (2C), 131.7, 138.7, 160.9, 171.0; MS (FAB) *m/z* 446 $(M+H)^+$, 402, 307, 273, 250, 154; HRMS (FAB) *m/z* 446.2537 (calcd for $C_{25}H_{36}NO_6$: 446.2543).

More polar isomer **14**: IR (neat) 2945, 1733, 1613, 1511, 1463, 1378, 1305, 1245, 1168, 1035, 907 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30-1.64 (m, 10H), 1.96 (q, *J* = 7, 2H), 2.58 (dd, *J* = 14, 8 Hz, 1H), 2.59-2.70 (m, 1H), 2.87 (dd, *J* = 14, 4 Hz, 1H), 3.80 (s, 3H), 3.80-3.90 (m, 4H), 4.56 (s, 1H), 4.61 (dm, *J* = 6 Hz, 2H), 4.91 (ddt, *J* = 9, 2, 1 Hz, 1H), 4.96 (dq, *J* = 16, 2 Hz, 1H), 5.24 (dq, *J* = 10, 1 Hz, 1H), 5.34 (dq, *J* = 17, 1 Hz, 1H), 5.73 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.94 (ddt, *J* = 17, 11, 6 Hz, 1H), 6.88 (d, *J* = 9 Hz, 2H), 7.33 (d, *J* = 9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 23.1, 32.5, 33.8, 36.7, 36.9, 39.3, 55.3, 64.9 (2C), 65.3, 67.6, 81.3, 111.3, 113.9 (2C), 114.6, 118.3, 126.4, 128.9 (2C), 132.1, 138.5, 161.1, 171.2; MS (FAB) *m/z* 446 $(M+H)^+$, 402, 310, 250; HRMS (FAB) *m/z* 446.2539 (calcd for $C_{25}H_{36}NO_6$: 446.2543).

***N*-(11-Oxo-1,4,12-trioxaoxospiro[4.13]octadec-14-en-9-yl)-4-methoxybenzamide (16).** Bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (**10**, 3 mg, 3.6 μmol) was added to a stirred solution of the diene **14** (16 mg, 36 μmol, dr = 77:23) in CH_2Cl_2 (7 mL) at rt under Ar. The initially purple mixture gradually turned a muddy brown and then black. After 22 h the solvent was removed *in vacuo* and the residue further purified *via* column chromatography (eluting with 40-60% EtOAc in hexanes) to yield in order of elution: *p*-anisaldehyde (2.1 mg, 15 μmol, 43%), the uncyclized amide **15** (1.1 mg, 2.5 μmol, 7%) and then the amidolactone **16** (5.4 mg, 13 μmol, 36%) as an inseparable mixture of olefin isomers (^1H NMR analysis indicated *E*:*Z* = 80:20).

Amidodiene **15**: IR (neat) 3314, 2945, 1735, 1629, 1609, 1539, 1502, 1303, 1256, 1180, 1034, 914, 844 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35-1.50 (m, 4H), 1.52-1.80 (m, 6H), 2.02 (qt, *J* = 7, 1 Hz, 2H), 2.63 (dd, *J* = 16, 5 Hz, 1H), 2.71 (dd, *J* = 16, 5 Hz, 1H), 3.84 (s, 3H), 3.88-3.90 (m, 4H), 4.38-4.48 (m, 1H), 4.59 (dq, *J* = 6, 1 Hz, 2H), 4.92 (ddt, *J* = 10, 2, 1 Hz, 1H), 4.97 (dq, *J* = 17, 2 Hz, 1H), 5.24 (dq, *J* = 10, 1 Hz, 1H), 5.31 (dq, *J* = 17, 1 Hz, 1H), 5.76 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.90 (ddt, *J* = 17, 10, 6 Hz, 1H), 6.77 (d, *J* = 9 Hz, 1H), 6.91 (d, *J* = 9 Hz, 2H), 7.73 (d, *J* = 9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 23.1, 33.8, 34.2, 36.5, 36.7, 38.2, 46.2, 55.4, 64.9 (2C), 65.3, 111.4, 113.7 (2C), 114.6, 118.7, 126.9, 128.7 (2C), 131.8, 138.6, 162.1, 166.2, 171.9; MS (CI) *m/z* 446 $(M+H)^+$, 400, 376, 277, 141.

Amidolactone **16**: IR (neat) 3338, 2920, 1731, 1633, 1604, 1541, 1505, 1455, 1308, 1255, 1176, 1027, 974, 842 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *E*-isomer δ 1.30-1.80 (m, 9H), 1.93-2.40 (m, 3H), 2.59 (dd, *J* = 16, 5 Hz, 1H), 2.69 (dd, *J* = 16, 4 Hz, 1H), 3.84 (s, 3H), 3.86-3.90 (m, 4H), 4.18 (dd, *J* = 12, 6 Hz, 1H), 4.35-4.45 (m, 1H), 5.02 (dd, *J* = 12, 7 Hz, 1H), 5.69 (dtm, *J* = 15, 7 Hz, 1H), 5.85 (dt, *J* = 15, 7 Hz, 1H), 6.91 (d, *J* = 9 Hz, 2H), 7.15-7.30 (obscured, 1H), 7.76 (d, *J* = 9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) *E*-isomer δ 21.3, 22.2, 30.5, 32.6, 33.3, 35.3, 36.6, 46.3, 55.4, 63.8, 64.4, 64.6, 111.8, 113.7 (2C), 126.0, 126.8, 128.7 (2C), 138.3, 162.1, 165.8, 172.2; MS

(FAB) *m/z* 418 $(M+H)^+$, 307, 289, 135; HRMS (FAB) *m/z* 418.2221 (calcd for $C_{23}H_{32}NO_6$: 418.2230).

Conversion of 15 to 16. Bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (**10**, 1 mg, 1.2 μmol) was added to a stirred solution of the amidodiene **15** (8.0 mg, 18 μmol) in CH_2Cl_2 (4 mL) at rt under Ar. After stirring for 6 h the mixture was concentrated *in vacuo* and the resulting residue further purified *via* column chromatography (eluting with 60% EtOAc in hexanes) to yield the amidolactone **16** (7.1 mg, 17 μmol, 95%) as an inseparable mixture of olefin isomers. ^{1}H NMR analysis indicated *E:Z* = 86:14 and that the product was identical to that previously obtained from oxaziridinyldiene **14** (see above).

(*E*)-15-Oxy-4-oxa-15-azabicyclo[9.3.1]pentadeca-6,11(15)-dien-3-one (18). A stirred solution of the oxaziridine **12** (3.5 mg, 8.4 μmol, *E:Z* ~ 4:1) in MeOH-H_2O (5:1, 1.2 mL) was treated with 4-methylphenylsulfonic acid monohydrate (0.6 mg, 3 μmol) and then heated to a gentle reflux and stirred for 6 h. After this time the mixture was allowed to cool, diluted with CH_2Cl_2 (5 mL) and shaken with sat. aq. $NaHCO_3$ (5 mL). The layers were separated and then the aqueous phase extracted (2x5 mL CH_2Cl_2). The combined organic extracts were then dried (Na_2SO_4) and concentrated *in vacuo*. The residue was further purified *via* column chromatography (eluting with 5-10% MeOH in CH_2Cl_2) to yield the nitrone **18** (1.4 mg, 5.9 μmol, 70%, *E:Z* ~ 4:1) as a colorless oil. Repeated careful chromatography (5% MeOH in CH_2Cl_2) yields pure *trans* isomer: IR (neat) 2921, 1729, 1591, 1462, 1370, 1250, 1195, 1144, 969 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44-1.63 (m, 2H), 1.82-1.95 (m, 2H), 1.96-2.08 (m, 4H), 2.19-2.30 (m, 1H), 2.25 (dd, *J* = 14, 2 Hz, 1H), 2.32-2.44 (m, 1H), 2.57 (tdd, *J* = 14, 11, 4 Hz, 1H), 3.44 (ddd, *J* = 16, 12, 1 Hz, 1H), 3.54 (dd, *J* = 14, 6 Hz, 1H), 4.03-4.14 (m, 1H), 4.43 (dd, *J* = 12, 7 Hz, 1H), 4.60 (dd, *J* = 11, 3 Hz, 1H), 5.72-5.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6, 23.3, 28.4, 28.9, 30.3, 33.1, 35.9, 63.0, 64.3, 125.2, 135.6, 151.2, 170.4; MS (FAB) *m/z* 238 $(M+H)^+$, 154, 136; HRMS (FAB) *m/z* 238.1439 (calcd for $C_{13}H_{20}NO_3$: 238.1443).

Transannular Cycloadduct (19). A solution of the nitrone **18** (9.6 mg, 40 μmol) in PhMe (2 mL) under Ar was heated to reflux and stirred for 2 h. After this time the mixture was allowed to cool and concentrated *in vacuo*. The residue was then further purified *via* column chromatography (eluting with 90% EtOAc in hexanes) to yield the isomerically pure cycloadduct **19** (6.1 mg, 26 μmol, 64%) as colorless crystalline solid: mp 105-108 °C (CH_2Cl_2); IR (neat) 2914, 1732, 1453, 1294, 1143, 1091 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40-2.10 (m, 12H), 2.44 (dm, *J* = 13 Hz, 1H), 2.52 (ddd, *J* = 6, 4, 2 Hz, 1H), 2.64 (dd, *J* = 13, 10 Hz, 1H), 4.05 (ddd, *J* = 7, 6, 4 Hz, 1H), 4.19-4.25 (obscured, 1H), 4.21 (dd, *J* = 13, 7 Hz, 1H), 4.55 (dd, *J* = 13, 6 Hz, 1H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 15.3, 22.8, 27.8, 31.2, 33.2, 35.9, 42.8, 55.8, 60.5, 70.6, 75.1, 84.9, 175.9; MS (FAB) *m/z* 238 $(M+H)^+$, 217, 139; HRMS (FAB) *m/z* 238.1440 (calcd for $C_{13}H_{20}NO_3$: 238.1443).

Methyl (4-Hydroxymethyloctahydrocyclopenta[3,4]isoxazolo[2,3-*a*]pyrindin-7-yl)acetate. A solution of the ester **19** (3.4 mg, 14.3 μmol) in MeOH (2 mL) was treated with potassium carbonate (2 mg, 14.4 μmol) and the resulting suspension heated to a gentle reflux and stirred for 3 h. After this time the mixture was allowed to cool to rt and partitioned between CH_2Cl_2 (10 mL) and H_2O (10 mL). The layers were separated and then the aqueous phase extracted (2x5 mL CH_2Cl_2). The combined organic extracts were washed with brine (5 mL), dried (Na_2SO_4) and then concentrated *in vacuo*. The residue was then further purified *via* column chromatography (eluting with 5% MeOH in CH_2Cl_2) to yield the hydroxyester (3.4 mg, 12.6 μmol, 88%) as a colorless oil: IR (neat) 3441, 2935, 2862, 1731, 1442, 1290, 1175, 1040, 879 cm^{-1}; ^1H NMR (300 MHz, d_6-DMSO, T = 60°C, one signal obscured by H_2O resonance) δ 1.20-1.50 (m, 6H), 1.50-1.90 (m, 6H), 2.10-2.17 (m, 1H), 2.37 (dd, *J* = 15, 8 Hz, 1H), 2.61 (dd, *J* = 15, 6 Hz, 1H), 3.40-3.50 (m, 3H), 3.59 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO, T = 60°C, four signals obscured by DMSO septet) δ 20.9, 25.5, 29.9, 50.8, 54.3, 57.0, 61.9, 73.5, 84.5, 171.5; MS (FAB) *m/z* 270 $(M+H)^+$, 196, 154, 136; HRMS (FAB) *m/z* 270.1707 (calcd for $C_{14}H_{24}NO_4$: 270.1705).

Methyl [(1*S,5*S**,7*R**)-1-[(1*S**)-1,2-dihydroxyethyl]-6-azaspiro[4.5]dec-7-yl]acetate (20).** The isoxazolidine (3.4 mg, 12.6 μmol) was treated with samarium (II) diiodide (4 mL, 0.1 M in THF, 0.4 mmol) and the resulting solution stirred at rt under Ar for 48 h. After this time the mixture was quenched with 5% w/v aq. $Na_2S_2O_3$ (5 mL) and stirred vigorously for 10 min. CH_2Cl_2 (10 mL) and sat. aq. $NaHCO_3$ (10 mL) were then added and the layers shaken and then separated. The aqueous phase was then extracted (3x5 mL CH_2Cl_2) and the combined organic extracts washed with brine (5 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was then further purified *via* column chromatography (eluting with 20-25% MeOH in CH_2Cl_2) to yield the dihydroxy amino ester **20** (2.2 mg, 8.1 μmol, 64%) as a colorless oil: IR (neat) 3315, 2939, 2860, 1729, 1602, 1440, 1381, 1290, 1215, 1171, 1072, 867, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35-2.00 (m, 13H), 2.71 (dd, *J* = 17, 6 Hz, 1H), 2.94 (ddm, *J* = 17, 5 Hz, 1H), 3.21-3.31 (m, 1H), 3.46 (dd, *J* = 11, 6 Hz, 1H), 3.70 (s, 3H), 3.76 (dd, *J* = 11, 3 Hz, 1H), 3.98 (ddd, *J* = 9, 6, 3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 24.4, 28.9, 29.4, 35.3, 36.4, 38.3, 49.6, 51.7, 52.0, 65.9, 66.4, 72.9, 172.1.

Crystallographic Supplementary Materials

Structure Solution and Refinement Results for **19**.

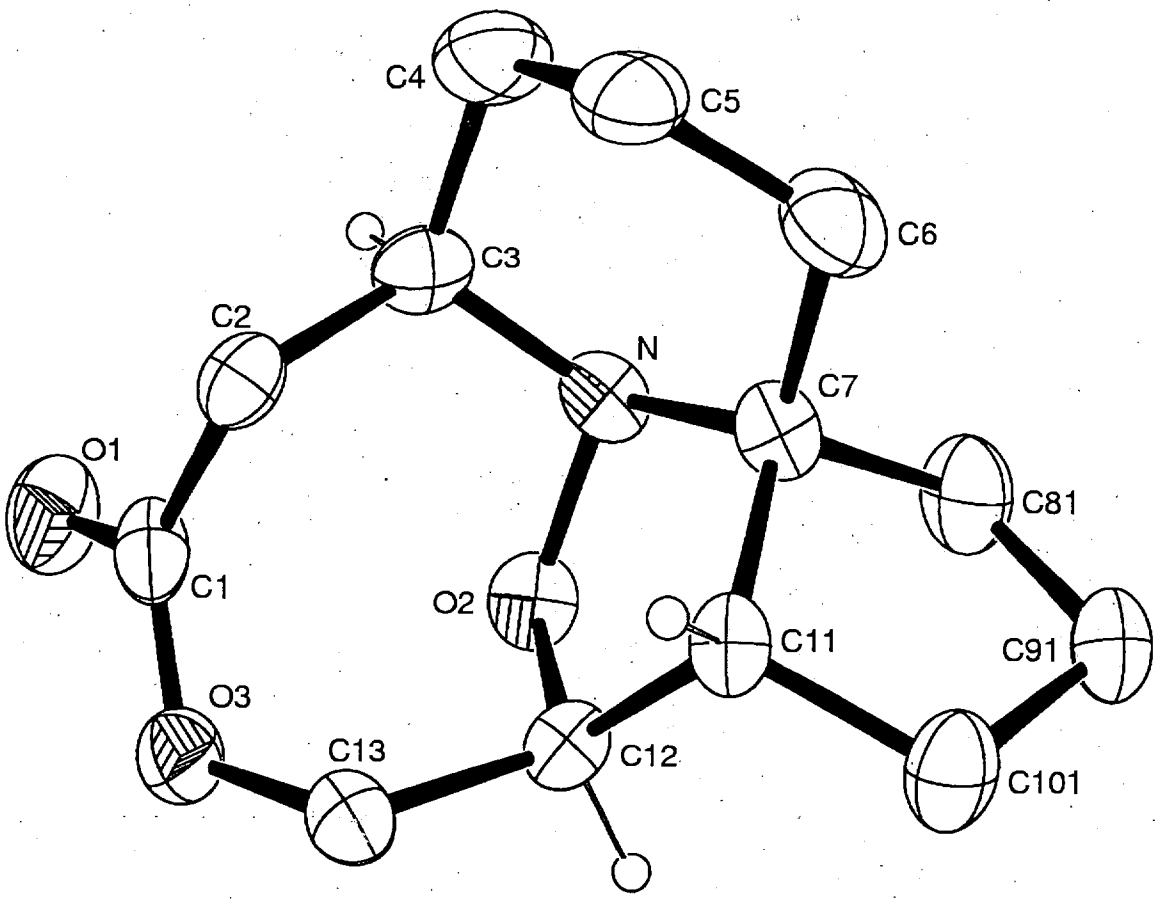

Figure 1. Fully labeled ORTEP for **19**. Thermal displacement ellipsoids at the 30% probability level.

Table 1. Crystal data and structure refinement for **19**.

Identification code	PA092000	
Empirical formula	$C_{13}H_{19}NO_3$	
Formula weight	237.29	
Temperature	288(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.798(3) Å	α= 90°.
	b = 12.687(6) Å	β= 90°.
	c = 15.244(8) Å	γ = 90°.
Volume	1121.3(10) $Å^3$	
Z	4	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	0.808 mm^{-1}	
F(000)	512	
Crystal size	0.30 x 0.05 x 0.05 mm^3	
Theta range for data collection	4.53 to 69.94°.	
Index ranges	-1<=h<=3, -15<=k<=1, -18<=l<=1	
Reflections collected	1239	
Independent reflections	1092 [R(int) = 0.0283]	
Completeness to theta = 69.94°	96.7 %	
Absorption correction	Psi-scans	
Max. and min. transmission	0.9607 and 0.7935	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1092 / 12 / 163	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0753	
R indices (all data)	R1 = 0.0704, wR2 = 0.0874	
Absolute structure parameter	0.4(5)	
Largest diff. peak and hole	0.100 and -0.103 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **19**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5346(8)	1857(3)	6923(2)	82(2)
O(2)	2806(6)	488(2)	5426(2)	57(1)
O(3)	2626(6)	2364(2)	6067(2)	66(1)
N	2142(8)	-417(2)	5927(2)	52(1)
C(1)	3418(12)	1735(4)	6694(3)	60(2)
C(2)	1833(8)	970(3)	7102(2)	52(2)
C(3)	2426(8)	-138(3)	6845(2)	59(1)
C(4)	1124(12)	-920(4)	7397(3)	80(2)
C(5)	-1325(12)	-952(4)	7132(3)	76(2)
C(6)	-1507(10)	-1322(3)	6216(2)	74(2)
C(7)	-101(10)	-688(3)	5576(3)	49(2)
C(81)	255(10)	-1303(3)	4731(3)	74(2)
C(91)	-1910(30)	-1044(10)	4184(9)	74(5)
C(101)	-2424(9)	43(3)	4425(3)	68(1)
C(82)	255(10)	-1303(3)	4731(3)	74(2)
C(92)	-830(30)	-737(11)	4058(9)	73(5)
C(102)	-2424(9)	43(3)	4425(3)	68(1)
C(11)	-1187(8)	317(3)	5262(2)	47(1)
C(12)	788(11)	1046(3)	5156(2)	50(1)
C(13)	577(9)	2085(3)	5638(3)	60(2)

Table 3. Bond lengths [Å] and angles [°] for **19**.

O(1)-C(1)	1.182(5)
O(2)-C(12)	1.428(5)
O(2)-N	1.432(3)
O(3)-C(1)	1.326(5)
O(3)-C(13)	1.402(5)
N-C(7)	1.448(5)
N-C(3)	1.453(5)
C(1)-C(2)	1.475(6)
C(2)-C(3)	1.499(5)
C(3)-C(4)	1.504(6)
C(4)-C(5)	1.477(6)
C(5)-C(6)	1.477(5)
C(6)-C(7)	1.504(5)
C(7)-C(11)	1.501(5)
C(7)-C(81)	1.521(5)
C(81)-C(91)	1.541(15)
C(91)-C(101)	1.458(14)
C(101)-C(11)	1.503(5)
C(11)-C(12)	1.481(5)
C(12)-C(13)	1.514(5)
C(12)-O(2)-N	109.3(3)
C(1)-O(3)-C(13)	118.5(4)
O(2)-N-C(7)	103.6(3)
O(2)-N-C(3)	106.8(3)
C(7)-N-C(3)	121.0(3)
O(1)-C(1)-O(3)	117.4(5)
O(1)-C(1)-C(2)	123.5(5)
O(3)-C(1)-C(2)	119.0(5)
C(1)-C(2)-C(3)	111.3(4)
N-C(3)-C(2)	117.0(3)
N-C(3)-C(4)	108.8(4)
C(2)-C(3)-C(4)	110.9(4)
C(5)-C(4)-C(3)	110.4(4)

C(4)-C(5)-C(6)	109.7(5)
C(5)-C(6)-C(7)	113.9(4)
N-C(7)-C(11)	107.0(4)
N-C(7)-C(6)	112.0(4)
C(11)-C(7)-C(6)	115.7(4)
N-C(7)-C(81)	108.3(4)
C(11)-C(7)-C(81)	102.8(3)
C(6)-C(7)-C(81)	110.5(3)
C(7)-C(81)-C(91)	103.8(6)
C(101)-C(91)-C(81)	103.5(9)
C(91)-C(101)-C(11)	109.5(7)
C(12)-C(11)-C(7)	103.9(4)
C(12)-C(11)-C(101)	114.9(3)
C(7)-C(11)-C(101)	106.0(3)
O(2)-C(12)-C(11)	107.0(3)
O(2)-C(12)-C(13)	111.0(4)
C(11)-C(12)-C(13)	115.3(4)
O(3)-C(13)-C(12)	112.2(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **19**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	55(4)	101(3)	90(2)	-15(2)	-10(3)	-30(3)
O(2)	39(3)	68(2)	63(2)	-7(2)	11(2)	-1(2)
O(3)	74(3)	60(2)	64(2)	1(2)	-5(2)	-22(2)
N	39(4)	48(2)	70(2)	0(2)	10(2)	0(2)
C(1)	62(7)	61(3)	57(3)	-17(2)	9(3)	-18(4)
C(2)	46(5)	65(2)	45(2)	-4(2)	1(2)	0(3)
C(3)	41(4)	68(3)	67(2)	11(2)	-15(3)	8(3)
C(4)	79(6)	78(3)	82(3)	26(3)	-20(4)	5(3)
C(5)	79(7)	81(3)	68(3)	24(3)	3(3)	-25(3)
C(6)	73(5)	66(3)	85(3)	3(2)	11(3)	-21(3)
C(7)	35(5)	46(2)	66(2)	-6(2)	6(3)	1(3)
C(81)	77(5)	66(3)	80(3)	-29(3)	5(3)	11(3)
C(91)	87(10)	66(6)	69(6)	-21(5)	-13(7)	-12(7)
C(101)	49(4)	77(3)	79(3)	-17(2)	-13(3)	3(3)
C(82)	77(5)	66(3)	80(3)	-29(3)	5(3)	11(3)
C(92)	69(10)	90(8)	59(6)	-24(6)	-1(7)	-1(7)
C(102)	49(4)	77(3)	79(3)	-17(2)	-13(3)	3(3)
C(11)	32(4)	56(2)	53(2)	-13(2)	10(2)	-1(3)
C(12)	42(5)	64(3)	45(2)	0(2)	3(3)	0(3)
C(13)	66(5)	48(2)	66(2)	-3(2)	-10(3)	1(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **19**.

	x	y	z	U(eq)
H(2A)	264	1125	6923	62
H(2B)	1915	1038	7735	62
H(3)	4064	-235	6982	71
H(4A)	1802	-1614	7329	95
H(4B)	1235	-722	8011	95
H(5A)	-1996	-255	7184	91
H(5B)	-2169	-1425	7516	91
H(6A)	-3113	-1297	6039	89
H(6B)	-1012	-2051	6189	89
H(81A)	360	-2053	4846	89
H(81B)	1645	-1075	4431	89
H(91A)	-1593	-1104	3561	89
H(91B)	-3175	-1509	4335	89
H(10A)	-4074	127	4505	82
H(10B)	-1935	514	3960	82
H(82A)	1889	-1376	4607	89
H(82B)	-412	-2001	4781	89
H(92A)	-1679	-1220	3683	87
H(92B)	317	-384	3702	87
H(10C)	-3933	-258	4539	82
H(10D)	-2586	651	4045	82
H(11)	-2274	589	5699	56
H(12)	946	1202	4529	60
H(13A)	172	2634	5223	72
H(13B)	-658	2034	6065	72