Supporting Information (SI)

The Clerodane Ring System: Investigating the Viability of a Direct Diels-Alder Approach

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General experimental: Melting points for solid products were determined using a Kofler hot stage apparatus and are uncorrected; products without melting points were colourless oils unless otherwise stated. Infra-red spectra were recorded on a Perkin-Elmer 983G grating infra-red spectrophotometer using thin film, solution in $CHCl_3$, or as pressed KBr discs. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ with Me_4Si as internal standard, and were recorded on a Varian EM-360A (60 MHz), Bruker WM-250 (250 MHz), Varian XL-300 (300 MHz), Bruker WM-400 (400 MHz), or Bruker AM-500 (500 MHz) machines. Mass spectra were determined with a VG micromass 7070B instrument. Elemental microanalyses were performed in the Imperial College Chemistry Department microanalytical laboratory. Analytical thin layer chromatography (TLC) was performed on Merck precoated silica gel F 254 plates, and preparative chromatography was carried out on columns of Merck Kieselgel 60 (230-400 mesh) under low pressure; silica gel refers to the above grade of silica. Medium pressure liquid chromatography was carried out on silica gel using a Gilson 303 pump on a glass column (6.5 cm internal diameter, 94 cm length). Analytical and preparative high pressure liquid chromatography was performed using a Gilson 303 pump and a Gilson Holochrome ultra-violet detector, with Dynamax 250mm x 41.4 mm (internal diameter) or 250mm x 21mm (internal diameter) Si (ordinary) or (-18 (reverse phase) Macro-HPLC columns. Analytical gas chromatography was performed on a Perkin-Elmer Sigma 3 gas chromatograph using a 30m x 0.25mm bonded FSOT Superox column. Ultrasonication was carried out in a Semat ultrasound cleaning bath (BOW, 55 kHz). Petrol refers to light petroleum ether with boiling range 40-60 ˚C unless otherwise stated, and was redistilled before use. Ether refers to diethyl ether, and was distilled from sodium-benzophenone ketyl under argon before use, as was tetrahydrofuran (THF). Anhydrous dimethylformamide (DMF) and high pressure liquid chromatography grade 2-propanol (isopropanol) were purchased from Aldrich chemical Co. Ltd., glass distilled hexane was purchased from BDH Ltd., and were all used without further purification. Toluene and benzene were dried over sodium wire under argon, and toluene was distilled from sodium under argon before use. Dichloromethane (DCM) was distilled from phosphorus pentoxide under argon before use, and acetonitrile was distilled from calcium hydride under argon. All other solvents and reagents were purified by standard techniques. Saturated refers to aqueous solutions, and brine is saturated NaCl. Solutions were dried over anhydrous magnesium or sodium sulfate and evaporated with a rotary evaporator, followed by static evaporation with an oil pump.

5-(3'-Furyl)-3-methylidenetetrahydrofuran-2-one 13

To a suspension of zinc metal powder (0.82 g, 11.8 mmol), freshly activated by sequential treatment with dilute hydrochloric acid, water, acetone and drying at 50°C, in THF (5 mL) under argon at RT was added furan-3-carboxaldehyde (1.05 g, 10.5 mmol) in THF (5 mL) and bromomethyl acrylate (2.10 g, 11.7 mmol) in THF (5 mL), and the reaction mixture was subjected to sonication for 2 min. The reaction mixture was poured into 3 N HCl (30 mL) containing crushed ice (30 g) and extracted with ether (3 x 50 mL). The combined ethereal extracts were washed with saturated $NaHCO_3$ (30 mL), water (30 mL), brine (20 mL) and dried. Concentration at reduced pressure and column chromatography (30 to 50% ether - petrol) gave the title compound (1.55g, 90%). m.p. 27 ˚C; IR ($CHCl_3$) ν_{max} 2925, 1763, 1665 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.93 (ddt, *J* = 17.0, 6.5, 3.0 Hz, 1H), 3.32 (ddt, *J* = 17.0, 8.0, 3.0 Hz, 1H), 5.51 (dd, *J* = 8.0, 6.5 Hz, 1H), 5.70 (t, *J* = 3.0 Hz, 1H), 6.29 (t, *J* =3.0 Hz, 1H), 6.39 (dd, *J* = 2.0, 1.5 Hz 1H), 7.44 (m, 1H), 7.48 (m, 1H) ppm; *m/z* 164 (M^+); Found: C, 65.77; H, 5.00. $C_9H_8O_3$ requires: C, 65.85; H, 4.91%.

3-Trimethylsilyl-2-trimethylsilyloxydihydro-4,5H-furan 16

To a stirred solution of triethylamine (2.24g, 22 mmol) in ether (17 mL) under argon at RT was added dropwise trimethylsilyltrifluoromethane sulfonate (4.92 g, 22 mmol), and the reaction mixture cooled to 0˚C. γ-Butyrolactone (0.86 g, 10 mmol) was added dropwise in ether (3 mL), the reaction was allowed to warm to RT, and stirring was continued for 30 min. The ethereal phase was separated, the aqueous phase was washed with ether (2 x 10 mL), and the combined ethereal solutions were concentrated at reduced pressure. Bulb to bulb distillation gave the title compound (2.00 g, 87%) as a pale yellow oil. b.p. 110 ˚C at 4 mm; IR ($CHCl_3$) ν_{max} 2957, 1646, 1076, 756 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.23 (s, 9H), 2.57 (t, *J* = 9.0 Hz, 2H), 4.45 (t, *J* =9.0 Hz, 2H) ppm.

3-(1'-Hydroxyethyl)-3-trimethylsilyltetrahydrofuran- 2-one 15

To a stirred solution of redistilled acetaldehyde (4.21 mL, 75.3 mmol) in DCM (20 mL) under argon at -78 ˚C was added titanium tetrachloride (4.14 mL. 37.7 mmol) dropwise over 10 min, giving a yellow precipitate. Freshly prepared silyl enol ether **16** (8.69 g, 37.7 mmol) was added dropwise in DCM (30 mL) over 30 min, and the resultant mixture was stirred for a further 90 min at -78 ˚C, giving a yellow solution. Methanol (40 mL) was added at -78 ˚C, the reaction mixture was poured into water (100 mL), and the solution was extracted with ether (3 x 150 mL). The combined ethereal extracts were washed with water (50 mL) and brine (50 mL), dried, and concentrated at reduced pressure. Column chromatography (30 to 50% ether – petrol) gave the title compound (4.10 g, 68%). m.p. 48-50 ˚C; IR ($CHCl_3$) ν_{max} 3496, 2929, 1717, 1186 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.21 (s, 9H), 1.26 (d, *J* = 7.0 Hz, 3H), 2.25 (ddd, *J* = 13.5, 8.0, 4.0 Hz, 1H), 2.41 (ddd, *J* = 13.5, 9.5, 8.5 Hz, 1H), 2.83 (br s, 1H), 4.17 (ddd, *J* = 9.0, 8.5, 8.0 Hz, 1H), 4.32 (ddd, *J* = 9.5, 9.0, 4.0 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 1H) ppm; *m/z* 201 (M^+ - H), 187 (M^+ - Me), 143 (M^+ - Me – CO_2).

Z-3-Ethylidenetetrahydrofuran-2-one 14

To a stirred solution of lactone **15** (0.90 g, 4.5 mmol) in DCM (50 mL) under argon at -30 ˚C was added boron trifluoride diethyl etherate (5.61 mL, 45 mmol) dropwise over 5 min. The reaction mixture was then stirred for 16 h at -30˚C. The reaction mixture was poured into saturated NH_4Cl (50 mL), and extracted with DCM (3 x 50 mL). The combined organic extracts were washed with water (50 mL), dried, and concentrated at reduced pressure. Column chromatography (15 to 30% ether – petrol) gave firstly the titled compound **14** (0.28g, 55%) IR (film) ν_{max} 2859, 1748, 1672 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.15 (dt, *J* = 7.0, 2.5 Hz, 3H), 2.88 (tquint., *J* = 7.0, 2.5 Hz, 2H), 4.29 (t, *J* = 7.3 Hz, 2H), 6.30 (qt, *J* = 7.0, 2.5 Hz, 1H) ppm; followed by the *E*-isomer (0.20 g, 40%) IR (film) ν_{max} 2916, 1746, 1669 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.83 (dt, *J* = 7.0, 2.0 Hz, 3H), 2.84 (tdq, *J* = 7.3, 3.0, 2.0 Hz, 2H), 4.34 (t, *J* = 7.3 Hz, 2H), 6.77 (qt, *J* = 7.0, 3.0 Hz 1H) ppm.

Compound 18 derived from Diels-Alder adduct 19

Diene **17** (1.70 g, 4 mmol) and **13** (1.18 g, 7.2 mmol) were placed in a base washed, presilylated pressure vessel and hydroquinone (2 mg) added. The reaction mixture was degassed by evacuation and flushing with argon 3 times, then sealed under vacuum, and heated at 130˚C for 15 h. The resultant material was dissolved in THF (10 mL) and a solution of 3 N HCl (0.2 mL) in THF (10 mL) was added. The reaction was stirred for 3 h, then poured into saturated $NaHC0_3$ (10 mL). The solution was extracted with ether (4 x 20 mL), and the combined ethereal extracts were washed with saturated $NaHC0_3$ (2 x 10 mL), saturated NH_4Cl (10 mL), water (2 x 10 mL), and brine (10 mL). The ethereal solution was dried, concentrated at reduced pressure, and subjected to column chromatography (20 to 60% ether - petrol) to give firstly 1-acetylcyclohexene (0.5g), followed by starting lactone **13** (0.12g, 10%) and finally a mixture of apparent cycloaddition products (0.70 g). High pressure liquid chromatography (21 mm Si column, 5% isopropyl alcohol - hexane, uv detection 235 nm) gave a diastereomeric mixture of the title compound (0.58 g, 28%, 31% brsm) m.p. 152-153˚C; IR (KBr disc) ν_{max} 2940, 1758, 1714, 1160 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.10-1.40 (m, 4H), 1.42-1.55 (m, 1), 1.71-1.87 (m, 3H), 1.89-2.01 (m, 1H), 2.04-2.15 (m, 1H), 2.15-2.62 (m, 5H), 2.98 (m, 1H), 5.48 (t, *J* = 7.0 Hz, 0.5 H), 5.57 (dd, *J* = 10.8, 5.5 Hz, 0.5H), 6.41 (br s, 0.5H), 6.46 (br s, 0.5H), 7.47 (br s, 1H), 7.49 (br s, 0.5H), 7.54 (br s, 0.5 H) ppm; *m/z* 288 (M^+), 260 (M^+ - CO), 194 (M^+ - furanCO), 95 ($furanCO^+$); Found: C, 71.04; H, 7.12. $C_{17}H_{20}O_4$ requires: C, 70.81; H, 6.99%.

Compound 20

Diene **8** (1.07 g, 4.5 mmol) and lactone **14** (0.16 g, 1.5 mmol) were placed in a base washed, presilylated pressure vessel and hydroquinone (2mg) added. The reaction mixture was degassed by evacuation and flushing with argon 3 times, then sealed under vacuum, and heated at 160˚C for 16 h. The resultant mixture was dissolved in THF (15 mL) and tetrabutylammonium fluoride (5 mL of a 1 M solution in THF, 5 mmol) was added with stirring. After 2 h, the reaction mixture was poured into 1 N HCI (10 mL) and extracted with ether (3 x 20 mL). The combined ethereal extracts were washed with saturated $NaHC0_3$ (2 x 15 mL), water (15 mL), and brine (20 mL), and the solution was dried and concentrated at reduced pressure, Column chromatography (10 to 70%, ether - petrol) gave a diastereomeric mixture of the title compounds (105 mg, 30%). IR (film) ν_{max} 2934, 1754, 1709, 1189 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.90 (m, 3H), 1.05-1.27 (m, 4H), 1.65-1.85 (m, 4H), 1.90-2.08 (m, 2H), 2.15-2.38 (m, 3H), 2.40-2.70 (m, 1H), 3.34-3.60 (m, 1H), 4.15-4.38 (m, 2H) ppm; *m/z* 236 (M^+), 221 (M^+ - Me), 208 (M^+ - CO), 194 (M^+ - CO_2); Found: M^+ 236.1417. $C_{14}H_{20}O_3$ requires: M^+ 236.1412.

Preparation of 5-(3'-furyl)tetrahydrofuran 2-one 21

To a stirred solution of 3-bromopropionic acid (0.92 g. 6.0 mmol) in THF (25 mL) under argon at -78˚C was added n-butyllithium (4.0 mL of a 1.5 M solution in hexanes, 6.0 mmol) dropwise over 30 min. The resultant white dispersion was added dropwise to a stirred solution of lithium naphthalenide (46 mL of a 0.22 M solution in THF, 10.0 mmol) under argon at -78˚C, giving a brown solution. Furan-3-carboxaldehyde (0.32 g, 3.3 mmol) was added in THF (5 mL) and the reaction mixture was stirred for 60 min, giving a cloudy yellow solution. The reaction was then warmed to 0˚C over 3 h, giving a clear yellow solution, and poured into cold 5% NaOH (40 mL). The aqueous phase was separated, washed with ether (2 x 20 mL), and acidified with 1 N HCl (80 mL), then extracted with ether (3 x 100 mL). The combined ethereal solutions were washed with saturated $NaHCO_3$ (2 x 50 mL), water (2 x 50 mL), and brine (50 mL), and dried. Solvent removal at reduced pressure, and column chromatography (50% ether – petrol) gave the title compound (0.62 g, 41%) IR (film) ν_{max} 1771, 1598, 1160 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.23 (m, 1H), 2.50-2.67 (m, 3H), 5.48 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.41 (dd, *J* = 1.5, 1.0 Hz, 1H), 7.43 (t, *J* = 1.5 Hz, 1H), 7.48 (m, 1H) ppm; *m/z* 152 (M^+), 124 (M^+ - CO), 108 (M^+ - CO_2), 95 (furanCO$^+$); Found: C, 63.42; H, 5.54. $C_8H_8O_3$ requires: C, 63.17; H, 5.31%.

5-(3'-Furyl)-3-trimethylsilyl-2-trimethylsilyloxydihydro-4,5H-furan

To a stirred solution of triethylamine (2.23 g, 22 mmol) in ether (20 mL) under argon at RT was added dropwise trimethylsilyltrifluoromethanesulfonate (4.93 g, 22 mmol), and the reaction mixture cooled to 0˚C. Furyl lactone **21** (1.52 g, 10 mmol) was added dropwise in ether (5 mL), the reaction was allowed to warm to RT, and stirring was continued for 30 min. The ethereal phase was separated, the aqueous phase was washed with ether (2 x 10 mL), and the combined ethereal solutions were concentrated at reduced pressure to give the title compound (2.80 g, 95%) as a pale orange oil, utilised without any further purification. IR (film) ν_{max} 2952, 1643, 1595, 845 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.25 (s, 9H), 2.83 (br d, *J* = 8.0 Hz, 2H), 5.38 (br t, *J* = 8.0 Hz, 1H), 6.43 (m, 1H), 7.44 (m, 2H) ppm.

Compound 22

To a stirred solution of redistilled acetaldehyde (3.69 mL, 66.0 mmol) in DCM (70 mL) under argon at -78˚C was added titanium tetrachloride (3.62 mL, 33.0 mmol) dropwise over 10 min, giving a yellow precipitate. Freshly prepared silyl enol ether above (9.78 g, 33.0 mmol) was added dropwise in DCM (30 mL) over 30 min, and the resultant mixture was stirred for a further 90 min at -78˚C, giving a yellow solution. Methanol (40 mL) was added at -78˚C, the reaction mixture was poured into water (100 mL), and the solution was extracted with ether (3 x 150 mL). The combined ethereal extracts were washed with water (50 mL) and brine (50 mL), dried, and concentrated at reduced pressure. Column chromatography (40 to 70% ether - petrol) gave the title compounds as a mixture of isomers (4.60 g, 52%). m.p. 89-90˚C; IR (film) ν_{max} 3480, 2927, 1747, 1597, 1185 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.29 (d, *J* = 6.0 Hz, 0.3H), 1.33 (d, *J* = 6.0 Hz, 2.7H), 2.15 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.23 (br s, 1H), 2.72 (dd, *J* = 14.0, 8.3 Hz, 1H), 4.35 (br q, *J* = 6.0 Hz, 1H), 5.41 (br t, *J* = 8.5 Hz, 1H), 6.40 (br s, 1H), 7.44 (m, 2H) ppm; *m/z* 268 (M^+), 253 (M^+ - Me), 250 (M^+ - H_2O). (Found: C, 58.32: H, 7.46. $C_{13}H_{20}O_4Si$ requires: C, 58.17: H, 7.51%.).

Z-3-Ethylidene-5-(3'-furyl)tetrahydrofuran-2-one 11

To a stirred solution of **22** (138 mg, 0.51 mmol) in DCM (10 mL) under argon at -30˚C was added borontrifluoride diethyl etherate (0.64 mL, 5.1 mmol), and the reaction mixture was stirred for 16 h. The mixture was poured into saturated NH_4Cl (10 mL) and extracted with DCM (3 x 15 mL). The combined organic extracts were washed with water (2 x 15 mL), dried, and concentrated at reduced pressure. Column chromatography (20 – 50% ether - petrol) gave a mixture of **11** and the *E*-isomer (90 mg, 99%) in a 92:8 ratio (GC analysis). High pressure liquid chromatography (21 mm Si column, 10% isopropyl alcohol - hexane, uv detection 254 nm) gave firstly **11** (78 mg, 86%), IR (film) ν_{max} 2920, 1755, 1670, 1020 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.17 (dt, *J* = 7.3, 2.3 Hz, 3H), 2.83 (ddquint, *J* = 15.5, 6.5, 2.3 Hz, 1H), 3.18 (ddquint, *J* = 15.5, 7.5, 2.3 Hz, 1H), 5.39 (dd, *J* = 7.5, 6.5 Hz, 1H), 6.31 (qt, *J* = 7.3, 2.3 Hz, 1H), 6.36 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.38 (t, *J* = 2.0 Hz, 1H), 7.42 (dt, *J* = 2.0, 1.0 Hz, 1H) ppm; *m/z* 178 (M$^+$), 163 (M$^+$ - Me), 135 (M$^+$ - Me – CO); (Found: C, 67.20; H, 5.89. $C_{10}H_{10}O_3$ requires: C, 67.40; H, 5.66%); followed by the *E*-isomer (8.0mg, 8%). IR (film) ν_{max} 2920, 1757, 1668, 1023 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.84 (dt, *J* = 6.8, 2.0 Hz, 3H), 2.85 (dddq, *J* = 16.0, 5.5, 3.2, 2.0 Hz, 1H), 3.20 (dddq, *J* = 16.0. 8.3, 3.2, 2.0 Hz, 1H), 5.47 (dd, *J* = 8.3, 5.5 Hz, 1H), 6.35 (dd, *J* = 2.0, 1.0 Hz, 1H), 6.81 (qt, *J* = 6.8, 3.2 Hz, 1H), 7.40 (t, *J* = 2.0 Hz, 1H), 7.43 (dt, *J* = 2.0, 1.0 Hz, 1H) ppm; *m/z* 178 (M$^+$), 163 (M$^+$ - Me), 135 (M$^+$ - Me – CO); (Found: M$^+$, 178.0636. $C_{10}H_{10}O_3$ requires: M$^+$, 178.0629).

Diels-Alder adduct 24

Lactone **11** (0.89 g, 5.0 mmol) and diene **8** (3.58 g, 15 mmol) were placed in a base washed, pre-silylated pressure vessel, and hydroquinone (2 mg) added. The reaction mixture was degassed by evacuation and flushing with argon 3 times, then sealed under vacuum and heated to 135˚C. The reaction was monitored by TLC (50% ether – petrol), indicating loss of the dienophile after 91 h. The reaction mixture was dissolved in DCM (40 mL), and pre-adsorbed onto silica gel (9 g). Solvent removal at reduced pressure gave an adsorbed sample which was subjected to column chromatography (0 to 15% ether - petrol) to give a mixture of cycloaddition products and 1-acetylcyclohexene. High pressure liquid chromatography (42 mm Si column, 1% isopropyl alcohol - hexane, uv detection 240 nm) gave a diastereomeric mixture of the title compound (0.96 g, 46%), in a 6:3:1 ratio (GC analysis), IR (film) ν_{max} 2930, 1763, 1655, 1181 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.85 – 0.97 (m, 9H), 1.03 (d, *J* = 7.0 Hz, 0.9H), 1.12 (d, *J* = 7.0 Hz, 1.8H), 1.21 (d, *J* = 7.0 Hz, 0.3H), 1.23 – 2.55 (m, 12H), 2.67 – 3.04 (m, 2H), 5.28 – 5.45 (m, 1H), 6.40 (m, 1H), 7.42 (m, 2H) ppm; *m/z* 416 (M$^+$), 401 (M$^+$ - Me), 322 (M$^+$ - furanCO); (Found: M$^+$, 416.2376. $C_{24}H_{36}O_4Si$ requires: M$^+$, 416.2382).

Compound 25

To a stirred solution of cycloaddition products **24** (0.208 g, 0.5 mmol) in DCM (9 mL) under argon at -78˚C was added phenylselenyl chloride (96 mg, 0.5 mmol) dropwise in DCM (1 mL). The reaction was stirred for 5 min, then saturated $NaHCO_3$ (5 mL) was added at -78˚C with vigorous stirring. The reaction mixture was poured into saturated $NaHCO_3$ (10 mL), and extracted with DCM (3 x 15 mL). The combined organic extracts were washed with water (2 x 15 mL), dried, concentrated at reduced pressure and subjected to column chromatography (10 to 60% ether – petrol) to yield firstly **25** (102 mg, 44%), m.p. 178˚C; IR (film) ν_{max} 2934, 1762, 1690, 796 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.04 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.30 (m, 1H), 1.49 (m, 3H), 1.78 (m, 2H), 2.11 (m, 1H), 2.41 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.50 (m, 1H), 2.64 (m, 2H), 2.79 (dd, *J* = 13.5, 5.5 Hz, 1H), 3.22 (m, 1H), 5.49 (dd, *J* = 10.0, 5.5 Hz, 1H), 6.46 (dd, *J* = 1.5, 1.0 Hz, 1H), 7.36 (m, 2H), 7.44 (m, 4H), 7.55 (t, *J* = 1.5 Hz, 1H) ppm; *m/z* 458 (M^+), 301 (M^+ - SePh), 273 (M^+ - SePh – CO); (Found: C, 63.10; H. 5.72. $C_{24}H_{26}O_4Se$ requires: C, 63.02; H, 5.73%); followed by a diastereomeric mixture (61mg, 26%), m.p. 187˚C; IR ($CHCl_3$) ν_{max} 2934, 1757, 1708, 1689, 797 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.95 (m, 1H), 1.12 (dd, *J* = 7.0, 1.5 Hz, 1H), 1.19 (d, *J* = 7.0 Hz, 2H), 1.20 – 1.51 (m, 3H), 1.55 – 1.99 (m, 3H), 2.15 – 2.38 (m, 2H), 2.40 – 2.57 (m, 2H), 2.65 – 2.95 (m, 2H), 3.08 (m, 1H), 5.48 (m, 1H), 6.41 (m, 1H), 7.28 – 7.40 (m, 7H) ppm; *m/z* 458 (M^+), 301 (M^+ - SePh); (Found: (M^+ - PhSeH), 300.137. $C_{24}H_{26}O_4Se$ requires: (M^+ - PhSeH), 300.136).

Compounds 26 and 27

To a stirred solution of selenide **25** (220 mg, 0.48 mmol) in DCM (6 mL) under argon at 0˚C was added dropwise *m*-chloroperbenzoic acid (69 mg of an 80% mixture, 0.49 mmol) in DCM (4 mL). The reaction was stirred for 10 min at 0˚C, then saturated Na_2SO_3 (5 mL) was added, and the reaction mixture was poured into saturated $NaHCO_3$ (15 mL). The solution was extracted with DCM (3 x 20 mL), the combined organic extracts were washed with water (2 x 15 mL), dried, concentrated under reduced pressure, and subjected to column chromatography (50 to 70% ether - petrol) to yield a mixture of enones **26** and **27** (90 mg, 62%) in a 1:3 ratio (GC analysis). High pressure liquid chromatography (42mm C18 column, 40% water - methanol, uv detection 254nm) gave firstly **27** (58 mg, 40%), m,p. 145˚C; IR ($CHCl_3$) ν_{max} 2935, 1747, 1664, 1163 cm^{-1}; ^1H

NMR (300 MHz, $CDCl_3$) δ 1.14 (d, *J* = 6.3 Hz, 3H), 1.50 – 1.68 (m, 2H), 1.78 (m, 1H), 2.16 – 2.29 (m, 3H), 2.34 - 2.48 (m, 2H), 2.37 (dd, *J* = 16.3, 4.3 Hz, 1H), 2.41 (dd, *J* = 14.1, 8.4 Hz, 1H), 2.61 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.70 (dd, *J* = 16.3, 11.2 Hz, 1H), 3.84 (tt, *J* = 11.0, 6.2 Hz, 1H), 5.55 (t, *J* = 8.4 Hz, 1H), 6.43 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.47 (br t, *J* = 1.0 Hz, 1H), 7.54 (m, 1H) ppm; *m/z* 300 (M^+), 272 (M^+ - CO), 256 (M^+ - CO_2); (Found: M^+ 300.137, $C_{18}H_{20}O_4$ requires: M+ 300.136; followed by **26** (19 mg, 13%) m.p. 132˚C; IR ($CHCl_3$) ν_{max} 2936, 1760, 1685, 1610, 1183 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, *J* = 7.0 Hz, 3H), 1.43 (br q, *J* = 11.0 Hz, 1H), 1.57 – 1.69 (m, 2H), 1.84 – 1.97 (m, 2H), 2.12 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.25 (m, 1H), 2.28 – 2.36 (m, 1H), 2.39 (dd, *J* = 17.5, 2.5 Hz, 1H), 2.52 (dd, *J* = 17.5, 5.8 Hz, 1H), 2.76 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.12 (m, 1H), 5.40 (t, *J* = 8.0 Hz, 1H), 6.40 (m, 1H), 7.03 (m, 1H), 7.46 (t, *J* = 1.5 Hz, 1H), 7.48 (m, 1H) ppm; *m/z* 300 (M^+), 272 (M^+ - CO), 255 (M^+ - CO_2H); (Found: M^+ 300.137. $C_{18}H_{20}O_4$ requires: M^+ 300.136).

The X-ray crystal structure of 18

Crystal data for **18**: $C_{17}H_{20}O_4$, *M* = 288.33, triclinic, *P*–1 (no. 2), *a* = 6.246(2), *b* = 10.219(3), *c* = 12.572(5) Å, α = 110.08(3), β = 93.86(3), γ = 95.48(3)°, *V* = 745.9(4) $Å^3$, *Z* = 2, D_c = 1.284 g cm^{-3}, µ(Cu-Kα) = 0.739 mm^{-1}, *T* = 298 K, Nicolet R3m diffractometer; 1537 independent measured reflections (R_{int} = 0.00), F^2 refinement, R_1(obs) = 0.0540, wR_2(all) = 0.1370, 1093 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 100°], 190 parameters. CCDC 814882.

The data for this structure were collected in June 1992 using technology that was already very old for its time, and was far inferior to that available now, *ca*. 20 years later. As such, the data collection is not one that would be reproduced now; for example, data were only collected to a resolution of *ca*. 1 Å. Additionally, some of the data card entries in the CIF file have been left blank because we have been unable to locate the required information; this specifically applies to the crystal dimensions and the reflections used to determine the unit cell. These are issues of fine detail however; the important point is that there is little doubt as to the nature of the compound present.

Figures

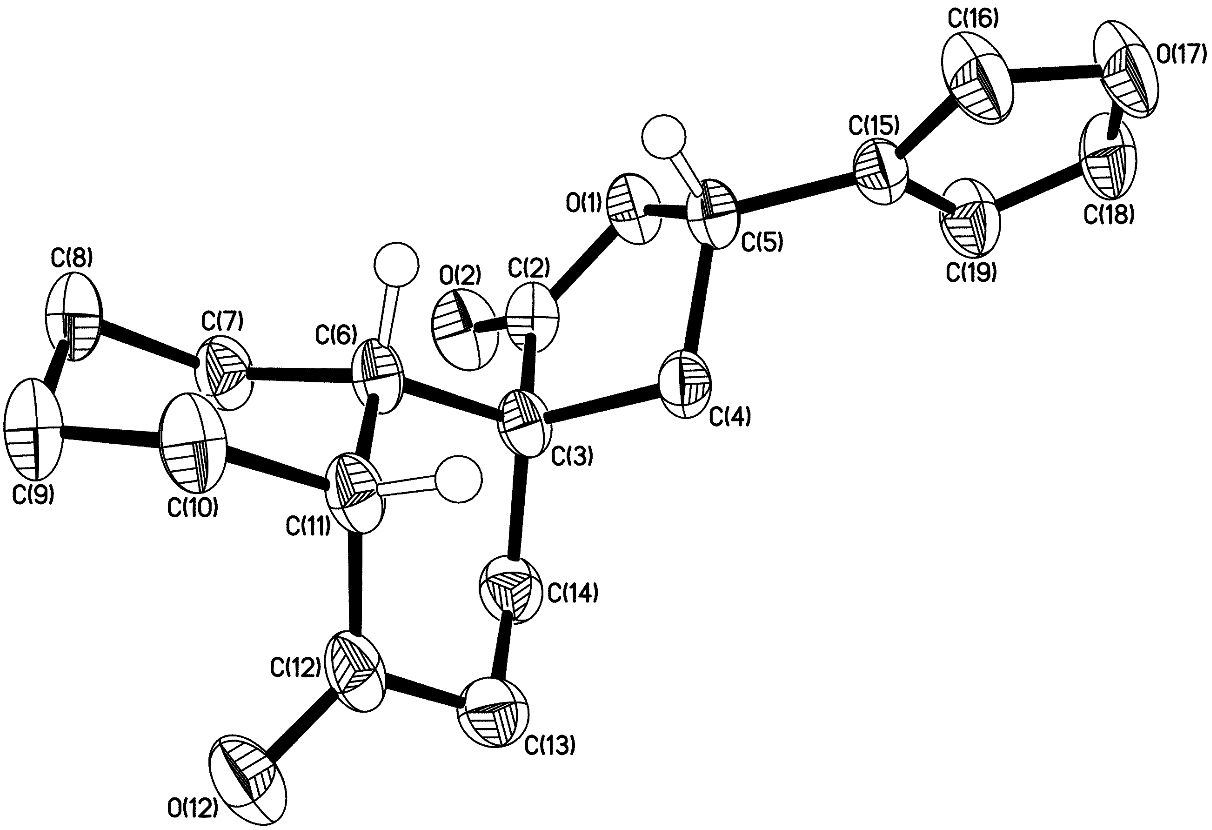

Fig. S1 The molecular structure of **18** (30% probability ellipsoids).