Supplementary Information supplied for the following compounds;

3,4-Dimethyl-1-[3-(3-oxo-cyclopent-1-enyl)-propyl]-pyrrole-2,5-dione (**8**)
5,6 Dimethyl-2,3,9,10-tetrahydro-1*H*-3a-aza-cyclopenta[*d*]azulene-4,7,8-trione (**9**)
(3-Bromo-cyclopent-2-enyloxy)-*tert*-butyl-diphenyl-silane (**11c**)
3-[3-(*tert*-Butyl-diphenyl-silanyloxy)-cyclopent-1-enyl]-propan-1-ol (**12c**)
1-{3-[3-(*tert*-Butyl-diphenyl-silanyloxy)-cyclopent-1-enyl]-propyl}-3,4-dimethyl-pyrrole-2,5-dione (**13c**)
8-(*tert*-Butyl-diphenyl-silanyloxy)-5,6-dimethyl-2,3,7a,8,9,10-hexahydro-1*H*-3a-aza-cyclopenta[*d*]azulene-4,7-dione (**14c**, **both isomers**)
1-[3-(3-Hydroxy-cyclopent-1-enyl)-propyl]-3,4-dimethyl-pyrrole-2,5-dione (**15**)
8-Hydroxy-5,6-dimethyl-2,3,7a,8,9,10-hexahydro-1*H*-3a-aza-cyclopenta[*d*]azulene-4,7-dione (**16 & 17**)

General Procedure for the Mitsunobu Reaction: DEAD (1.6 equiv.) was added dropwise to a stirred solution of the imide (1-1.1 equiv.), the alcohol (1 equiv.) and triphenylphosphine (1.6 equiv.) in anhydrous THF (0.2 M/equiv.) under nitrogen at 0ºC. The solution was allowed to warm to room temp. and stirred for 17-24h (TLC control). After this time, the reaction was evapourated onto silica gel and purified by flash chromatography (1-40% EtOAc/ *n*-hexane).

3,4-Dimethyl-1-[3-(3-oxo-cyclopent-1-enyl)-propyl]-pyrrole-2,5-dione (8): 3,4-Dimethyl maleimide (0.14 g, 1.09 mmol) and 3-(3'-hydroxypropyl)-2-cyclopenten-1-one (0.90 g, 6.44 mmol) were reacted according to the general Mitunobu procedure above to give the title product as a colourless oil (1.04 g, 66%). – IR (film): ν = 1705, 1617 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.96 (t, J = 1.5 Hz, 1 H), 3.55 (t, J = 7.0 Hz, 2 H), 2.58 (m, 2 H), 2.44-2.38 (m, 4 H), 1.97 (s, 6 H), 1.89 (quin, J = 7.0 Hz, 2 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.8 (C=O), 181.3 (C), 172.2 (C=O), 137.2 (C), 129.6 (CH), 37.1 (CH_2), 35.0 (CH_2), 31.2 (CH_2), 30.5 (CH_2), 25.8 (CH_2), 8.4 (CH_3). – $C_{14}H_{17}NO_3$ (247.30): calcd. C 68.00, H 6.93, N 5.66; found C 68.10, H 6.99, N 6.13. – LRMS (EI): *m/z* 247 [M^+], 138, 109, 96, 86, 84. – HRMS (EI): $C_{14}H_{17}NO_3$ [M^+] calcd. 247.1208; found 247.1207.

General Photolysis Procedure: A solution of the alkenylimide in solvent (110mL) was placed in a 150 mL pyrex immersion-well photoreactor and degassed for 10min by bubbling nitrogen through the solution with a long syringe needle. The solution was irradiated under an atmosphere of nitrogen for the appropriate period of time using a 125W medium pressure Hg-lamp. After the reaction was complete (TLC and ^{1}H NMR control) the solvent was removed under reduced pressure and the resultant crude photocycloadduct purified by flash column chromatography in the solvent system stated.

5,6 Dimethyl-2,3,9,10-tetrahydro-1*H*-3a-aza-cyclopenta[*d*]azulene-4,7,8-trione (9): The maleimide **8** (157 mg, 0.64 mmol) in acetonitrile (110 mL) was subjected to the general photolysis procedure (29 h) after which purification by flash column chromatography (50% EtOAc/ petroleum ether) gave the title compound as a white solid (26 mg, 16 %). – IR ($CDCl_3$): ν = 1752, 1700, 1609 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92-3.82 (m, 1 H), 3.72-3.65 (m, 1 H), 3.62 (s, 1 H), 2.64-2.57 (m, 2 H), 2.25-1.87 (m, 12 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.9 (C=O), 195.4 (C=O), 167.4 (C=O), 139.1 (C), 136.8 (C), 79.0 (CH), 65.7 (C), 48.5 (CH_2), 43.4 (CH_2), 39.4 (CH_2), 35.4 (CH_2), 21.6 (CH_2), 17.2 (CH_3), 16.2 (CH_3). – $C_{14}H_{17}NO_3$ (247.30): calcd. C 68.00, H 6.93, N 5.66; found C 68.31, H 6.91, N 5.75. – LRMS (EI): *m/z* 247 [M^+], 163, 138, 124, 109, 84. – HRMS (EI): $C_{14}H_{17}NO_3$ [M^+] calcd. 247.1208; found 247.1210.

(3-Bromo-cyclopent-2-enyloxy)-*tert*-butyl-diphenyl-silane (11c): *tert*-Butyldiphenylsilyl chloride (10.6 mL, 40.89 mmol) was added to a solution of **10** (5.55 g, 34.07 mmol), imidazole (3.02 g, 44.30 mmol) and 4-DMAP (0.83 g, 6.81 mmol) in DCM (130 mL) and stirred for 17 h. The solution was diluted with DCM (250 mL) and washed with sat. NH_4Cl (200 mL) and brine (200 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Flash chromatography (1% Et_2O/ *n*-hexane) yielded the title compound as a colourless oil (13.22 g, 97%). – b.p. 223^{0}C / 0.1mbar. – IR (film): ν = 3071, 2932, 2894, 2857, 1621, 1591 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (dd, J = 1.7, 7.6 Hz, 4 H), 7.45-7.34 (m, 6 H), 5.68 (dd, *J* = 2.0, 4.3 Hz, 1 H), 4.82-4.77 (m, 1 H), 2.77-2.64 (m, 1 H), 2.46-2.35 (m, 1 H), 2.23-2.11 (m, 1 H), 1.98-1.86 (m, 1 H), 1.05 (s, 9 H). – ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 135.8 (CH), 134.0 (C), 133.9 (CH), 129.8 (CH), 127.8 (CH), 125.8 (C), 77.4 (CH), 38.4 (CH_2), 34.5 (CH_2), 27.0 (CH_3), 19.2 (C). – LRMS (EI): *m/z* 402 [M^+], 400 [M^+], 381, 345, 199, 84. – HRMS (CI): $C_{21}H_{24}OBrSi$ [M^+-H] calcd. 399.0780; found 399.0789.

3-[3-(*tert*-Butyl-diphenyl-silanyloxy)-cyclopent-1-enyl]-propan-1-ol (12c): *t*-BuLi (10.65 mL, 18.10 mmol) was added dropwise to a solution of **11c** (3.63 g, 9.05 mmol) in THF (20 mL) at –78ºC and stirred for 45min. Trimethylene oxide (0.50 mL, 7.69 mmol) and $BF_3.Et_2O$ (1.15 mL, 9.07 mmol) were added dropwise and stirring continued for a further 20 min. The reaction mixture was quenched with sat. $NaHCO_3$ solution (20 mL), allowed to warm to room temperature and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (2 x 100 mL), dried (Na_2SO_4) and concentrated. Flash chromatography (30% Et_2O/ *n*-hexane) yielded the title compound as a pale yellow oil (2.17 g, 74%). – IR (film): ν = 3340, 3070, 3050, 2932, 2891, 2857, 1652, 1589 cm^{-1}. – ^1H NMR (270 MHz, $CDCl_3$): δ = 7.71-7.67 (m, 4 H), 7.44-7.33 (m, 6 H), 5.33-5.31 (m, 1 H), 4.90-4.85 (m, 1 H), 3.60 (t, *J* = 6.5 Hz, 2 H), 2.38-2.33 (m, 1 H), 2.01-2.14(m, 4 H), 1.87-1.79 (m, 1 H), 1.77-1.62 (m, 2 H), 1.49 (s, OH), 1.05 (s, 9 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7 (C), 135.9 (CH), 134.9 (C), 129.5 (CH), 127.6 (CH), 127.5 (CH), 79.3 (CH), 62.9 (CH_2), 34.3 (CH_2), 33.6 (CH_2), 30.7 (CH_2), 27.7 (CH_2), 27.2 (CH_3), 19.3 (C). – LRMS (EI): *m/z* 379 [M^+-H], 323, 245, 199, 181. – HRMS (EI): $C_{24}H_{31}O_2Si$ [M^+-H] calcd. 379.2093; found 379.2084.

1-{3-[3-(*tert*-Butyl-diphenyl-silanyloxy)-cyclopent-1-enyl]-propyl}-3,4-dimethyl-pyrrole-2,5-dione (13c): 3,4-Dimethyl maleimide (0.60 g, 4.78 mmol) and **12c** (1.52 g, 3.99 mmol) were reacted according to the general Mitunobu procedure above to give the title compound as a colourless oil (1.51 g, 78%). – IR (film): ν = 3071, 2931, 2858, 1703 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.64 (m, 4 H), 7.43-7.34 (m, 6 H), 5.32-5.31 (m, 1 H), 4.86-4.83 (m, 1 H), 7.14 (t, *J* = 7.1 Hz, 2 H), 2.35-2.30 (m, 1 H), 2.10-1.88 (m, 12 H), 1.82-1.76 (m, 1 H), 1.04 (s, 9 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3 (C=O), 146.7 (C), 137.0 (C), 135.8 (CH), 135.7 (CH), 134.8 (CH), 134.7 (C), 134.6 (C), 129.6 (CH), 129.4 (CH), 127.7 (CH), 127.5 (CH), 79.1 (CH), 37.7 (CH_2), 34.1 (CH_2), 33.6 (CH_2), 28.6 (CH_2), 27.0 (CH_3), 26.5 (CH_2), 19.1

(C), 8.7 (CH_3). – $C_{30}H_{37}NO_3Si$ (487.7): calcd. C 73.88, H 7.65, N 2.87; found C 74.22, H 8.02, N 2.47. – LRMS (CI): *m/z* 486 [M^+-H], 470, 430, 410, 306, 199, 107. – HRMS (CI): $C_{30}H_{36}NO_3Si$ [M^+-H] calcd. 486.2464; found 486.2460.

8-(*tert*-Butyl-diphenyl-silanyloxy)-5,6-dimethyl-2,3,7a,8,9,10-hexahydro-1*H*-3a-aza-cyclopenta[*d*]azulene-4,7-dione (14c): The maleimide **13c** (0.20g, 0.42 mmol) in acetonitrile (110 mL) was subjected to the general photolysis procedure (4 h) after which purification by flash column chromatography (25% EtOAc/ *n*-hexane) gave a white solid as a 1:1 mixture of diastereoisomers (0.13 g, 66%). Further chromatography allowed isolation of pure samples of each isomer: **Isomer A** – mp 189°C. – IR ($CDCl_3$): ν = 2956, 2857, 1685, 1641, 1617 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.79-7.65 (m, 4 H), 7.50-7.37 (m, 6 H), 4.22-4.11 (m, 1 H), 3.59-3.43 (m, 1 H), 2.90 (d, *J* = 7.5 Hz, 1 H), 2.27-2.17 (m, 1 H), 2.10 (unresol. q, 3 H), 2.00 (unresol. q, 3 H), 1.95-1.60 (m, 8 H), 1.03 (s, 9 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ =204.1 (C), 167.9 (C), 140.0 (C), 136.0 (CH), 135.7 (CH), 133.9 (C), 133.4 (C), 132.7 (C), 130.0 (CH), 129.9 (CH), 127.7 (CH), 127.7 (CH), 75.7 (CH), 74.6 (CH), 66.1 (C), 47.6 (CH_2), 45.6 (CH_2), 38.5 (CH_2), 33.4 (CH_2), 26.7 (CH_3), 22.5 (CH_2), 19.0 (C), 16.0 (CH_3), 15.8 (CH_3). – LRMS (CI): *m/z* 488 [MH^+], 430, 410, 232, 199, 107, 85. – HRMS (CI): $C_{30}H_{38}NO_3Si$ [MH^+] calcd. 488.2621; found 488.2632. **Isomer B** – m.p 129°C. – IR ($CDCl_3$): ν = 2959, 2858, 1688, 1642, 1615cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ =7.69-7.58 (m, 4 H), 7.49-7.36 (m, 6 H), 4.23 (dt, *J* = 6.2, 4.0 Hz, 1 H), 3.71 (dt, *J* = 12.1, 6.6 Hz, 1 H), 3.53 (dt, *J* = 12.1, 6.6 Hz, 1 H), 3.18 (d, J = 4 Hz, 1 H), 2.37-2.31 (m, 1 H), 2.20-2.13 (m, 1 H), 2.05-1.65 (m, 9 H), 1.50 (unresol. q, 3 H), 1.06 (s, 9 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.4 (C=O), 167.8 (C=O), 138.5 (C), 135.9 (CH), 135.7 (CH), 134.1 (C), 133.7 (C), 132.6 (C), 130.0 (CH), 129.9 (CH), 127.8 (CH), 127.7 (CH), 77.8 (CH), 76.9 (CH), 68.4 (C), 48.1 (CH_2), 45.0 (CH_2), 38.7 (CH_2), 35.4 (CH_2), 26.9 (CH_3), 21.8 (CH_2), 19.0 (C), 16.9 (CH_3), 15.7 (CH_3). – $C_{30}H_{37}NO_3Si$ (487.70): calcd. C 73.88, H 7.65, N 2.87; found C 74.08, H 7.49, N 2.73. – LRMS (CI): *m/z* 488 [MH^+], 430, 410, 402, 382, 232, 199, 107. – HRMS (CI): $C_{30}H_{38}NO_3Si$ [MH^+] calcd. 488.2621; found 488.2634.

1-[3-(3-Hydroxy-cyclopent-1-enyl)-propyl]-3,4-dimethyl-pyrrole-2,5-dione (15): TBAF (5 mL, 5 mmol) was added to a solution of **13c** (201 mg, 0.41 mmol) and

glacial acetic acid (0.15 mL) in THF (1 mL) and heated at 40°C for 7 h and stirred at room temperature for 17 h. The reaction mixture was diluted with EtOAc (10 mL), quenched with water (20 mL) and extracted with EtOAc (2 x 20 mL). The organic layers were washed with sat. $NaHCO_3$ solution (2 x 20 mL), water (20 mL), brine (20 mL), dried and concentrated. Flash chromatography (50% EtOAc/ *n*-hexane) yielded the title compound as a colourless oil (93 mg, 91%). – IR (film): ν = 3449, 2942, 1704 cm^{-1}. – ^1H NMR (270 MHz, $CDCl_3$): δ = 5.50-5.49 (m, 1 H), 4.82-4.78 (m, 1 H), 3.5 (t, *J* = 7.10 Hz, 2 H), 2.47-2.37 (m, 1 H), 2.33-1.99 (m, 4 H), 1.96 (s, 6 H), 1.82-1.67 (m, 4 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3 (C=O), 148.5 (C), 137.1 (C), 127.2 (CH), 77.7 (CH), 37.6 (CH_2), 34.0 (CH_2), 33.4 (CH_2), 28.4 (CH_2), 26.5 (CH_2), 8.6 (CH_3). – $C_{14}H_{19}NO_3$ (249.30): calcd. C 67.45, H 7.68, N 5.62; found C 67.05, H 7.81, N 5.29. – LRMS (CI) *m/z* 248 [M^+-H], 232, 138, 126, 107. – HRMS (EI): $C_{14}H_{18}NO_3$ [M^+-H] calcd. 248.1287, found 248.1278.

8-Hydroxy-5,6-dimethyl-2,3,7a,8,9,10-hexahydro-1*H*-3a-aza-cyclopenta[*d*]azulene-4,7-dione (16 & 17): The maleimide **15** (180 mg, 0.72 mmol) in toluene (100 mL) was subjected to the general photolysis procedure (9 h) after which purification by flash column chromatography (75% EtOAc/ *n*-hexane) gave a white solid as a 3.5:1 mixture of diastereoisomers (132 mg, 73%). Further chromatography allowed isolation of pure samples of each isomer: **Major isomer (16)** – IR ($CDCl_3$): ν = 3375, 2954, 2878, 1688, 1641, 1595 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 4.52-4.45 (m, 1 H), 3.67-3.57 (m, 2 H), 3.12 (d, *J* = 7.8 Hz, 1 H), 2.42 (ddd, *J* = 4.4, 11.7, 16.1 Hz, 1 H), 2.26-2.17 (m, 2 H), 2.04-1.71 (m, 12 H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.2 (C=O), 167.5 (C=O), 139.3 (C), 135.8 (C), 74.4 (CH), 74.2 (CH), 67.0 (C), 47.9 (CH_2), 45.2 (CH_2), 37.9 (CH_2), 32.6 (CH_2), 22.3 (CH_2), 16.4 (CH_3), 15.9 (CH_3). – LRMS (CI): *m/z* 250 [MH^+], 232, 138, 126, 107, 85. – HRMS (CI): $C_{14}H_{20}NO_3$ [MH^+] calcd. 250.1443; found 250.1437. **Minor isomer (17)** – IR ($CDCl_3$): ν = 3341, 2956, 2878, 1681, 1642, 1591 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 4.37-4.32 (m, 1 H), 3.78-3.72 (m, 1 H), 3.59-3.52 (m, 1 H), 3.05 (d, *J* = 4.0 Hz, 1 H), 2.29-2.10 (m, 4 H), 2.04-1.94 (m, 8 H), 1.87-1.71 (m, 3 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8 (C=O), 167.6 (C=O), 138.1 (C), 135.3 (C), 77.9 (CH), 76.2 (CH), 68.4 (C), 48.2 (CH_2), 44.9 (CH_2), 38.7 (CH_2), 34.3 (CH_2), 21.8

(CH_2), 17.5 (CH_3), 16.1 (CH_3). – LRMS (CI): *m/z* 250 [MH^+], 232, 192, 138, 126, 107. – HRMS (CI): $C_{14}H_{20}NO_3$ [MH^+] calcd. 250.1443; found 250.1449.