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Stereoselective Intermolecular [2+2] Photocycloaddition Reactions of Tetrahydrophthalic Anhydride and Derivatives with Alkenols and Alkynols

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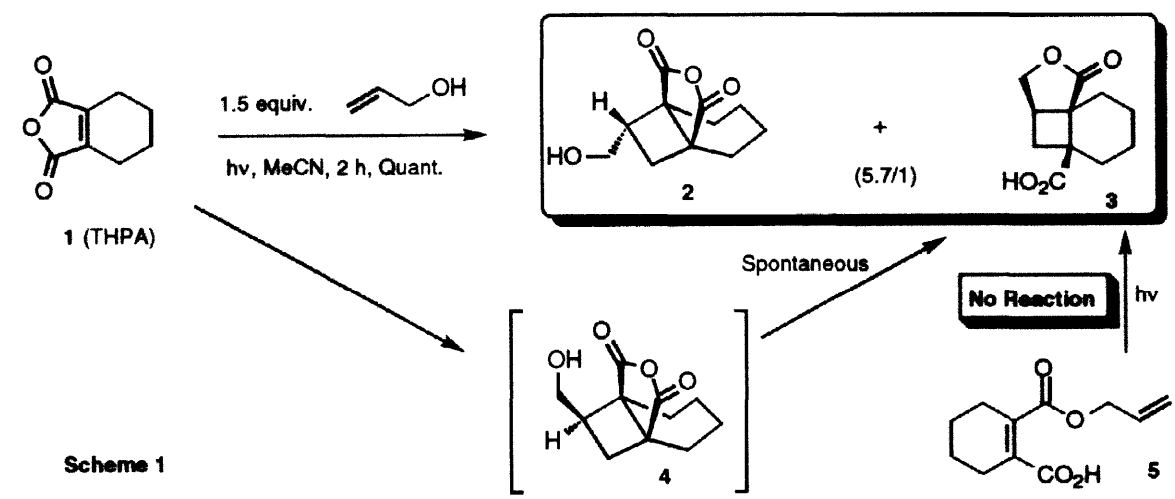
Abstract: Intermolecular [2+2] photocycloaddition of a variety of alken- and alkyn-3-ols with 3,4,5,6-tetrahydrophthalic anhydride (THPA) and the related imide (THPI) gave the corresponding cyclobutanes and cyclobutenes in high yield. Irradiation times were relatively short and stereoselectivities as high as 10/1 for the cyclobutane examples. © 1999 Elsevier Science Ltd. All rights reserved.

As part of a program directed towards the total synthesis of cyclooctane containing natural products we have been investigating a variety of [2+2] photocycloaddition reactions.[1-5] Of particular interest was the observation that the intermolecular [2+2] photocycloaddition between 3,4,5,6-tetrahydrophthalic anhydride (THPA) **1** and allyl alcohol proceeded smoothly to give a mixture of hydroxy-anhydride **2** and acid-lactone **3** (5.7/1) in essentially quantitative yield (Scheme 1).[1] The lactone **3** is formed as a result of the initial *endo* adduct **4** undergoing spontaneous ring closure. Conversely, the proposed intramolecular [2+2] photocycloaddition of acid-ester **5** to form **3** failed under a variety of conditions. The formation of **2/3** represents an unexpectedly efficient, intermolecular photochemical process in terms of yield and stereoselectivity. The failure of **5** to undergo intramolecular cycloaddition, coupled with the fact that there is no formation (tlc) of **5** *in situ* when THPA and allyl alcohol are mixed in acetonitrile prior to irradiation, confirms the intermolecular nature of the photocycloaddition.



Scheme 1

Alkenes and Alkenols: Intrigued by these results we set out to explore the generality of the intermolecular [2+2] photocycloaddition of THPA with a variety of alkenols, the results of which are summarised in Table 1. In general the cycloadditions were both efficient and rapid giving the corresponding cyclobutanes in high yield, with excellent stereoselectivity, using only 1.5 equivalents of the alkenols in all cases. In most examples *exo*-addition, with respect to the alkenol substituent and the anhydride moiety, was favoured resulting in the

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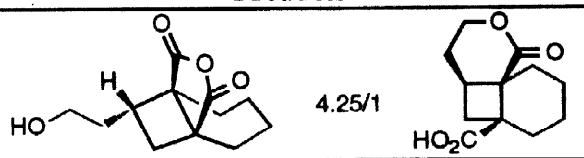
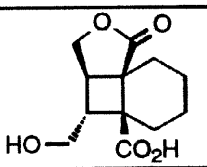
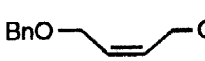
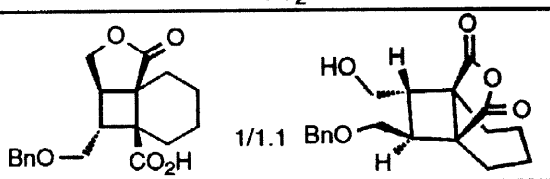
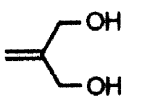
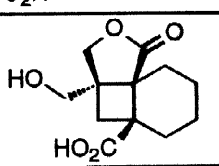
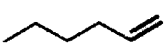
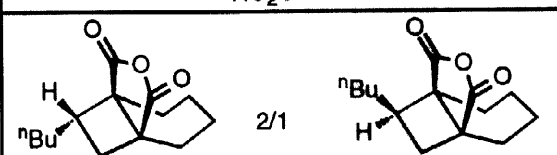
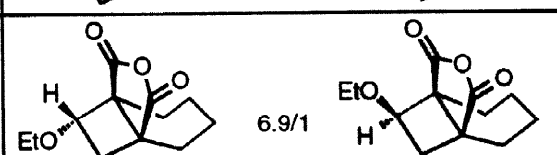
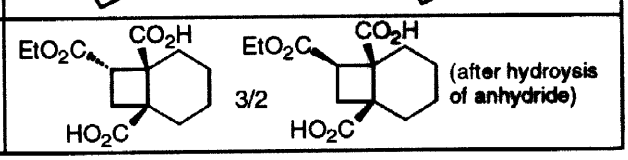
predominant formation of cyclobutane-anhydrides. In the alkenol examples the initially formed *endo* adducts underwent spontaneous cyclisation to give lactone products. Particularly noteworthy is the reaction of THPA with (Z)-2-butene-1,4-diol (entry **b**) which gave the cyclobutane-lactone **6** as the sole product, in excellent yield, after only 4 h irradiation. Similarly, reaction of THPA with the isomeric 2-hydroxymethyl-2-propen-1-ol gave an almost quantitative yield of the lactone **7** (entry **d**), but (Z)-4-benzyloxy-2-buten-1-ol (entry **c**) gave, as expected, a 1/1 mixture of the lactone and anhydride. Excellent results were also obtained with simple alkenes such as 1-hexene, although a relatively moderate 2/1 stereoselectivity was observed (*vide infra*). Interestingly, the photocycloaddition also proceeded well with both ethyl acrylate and ethyl vinyl ether, indicating a complete indifference to electronic extremes (entries **f** and **g**). Irradiation of a mixture of allyl alcohol and maleic anhydride gave only unidentified polymeric material, a result which we attributed to the instability of the resulting photoadduct although we have been unable to prove this.

Table 1: Photocycloaddition of various alkenes with THPA

Entry	Alkene	Time	Yield	Products
a		4 h	88%	 4.25/1
b		4 h	87%	 **6**
c		6 h	74%	 1/1.1
d		6 h	97%	 **7**
e		5 h	90%	 2/1
f		6 h	86%	 6.9/1
g		8 h	78%	 3/2 (after hydroysis of anhydride)

We then turned our attention to the study of similar reactions using 3,4,5,6-tetrahydrophthalimide **8** (THPI) and the *N*-methyl derivative **9** as substrates. The results of these experiments proved to be particularly interesting with respect to the nature of the alkenol derivative used as reaction partner. For example, irradiation of **8** in the presence of allyl alcohol or the corresponding ethyl ether (entries **a** and **b**) gave the expected products in similar, high yields and in almost identical reaction times with almost complete selectivity for the *exo* isomer **10a**. When **9** was employed, longer reaction times were required (for the same scale) but the yields and degree of stereoselectivity were again very similar for both the free alcohol and the ether. Given that the ratio of stereoisomers obtained from reaction of **8** and **9** were broadly the same for both alkenols and the corresponding ethers, it is unlikely that the high stereoselectivity of these photocycloadditions is controlled by hydrogen bonding of either the alkenol OH or the imide NH (*vide infra*). Reaction of maleimide with allyl alcohol proceeded well to give a good yield of the corresponding cycloadduct with reasonably high stereoselectivity. The relative stereochemistry present in a number of the cycloadducts of THPA and THPI was confirmed through various nOe experiments as detailed in *Fig.* 1.

Table 2: Photocycloaddition of alkenes with Imides

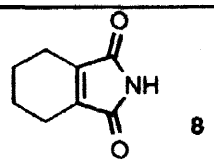
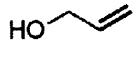
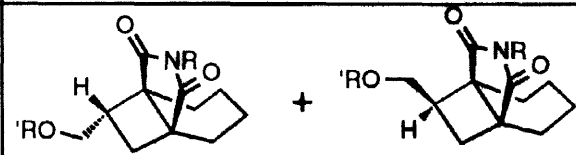
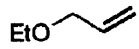
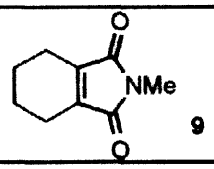
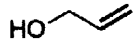
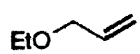
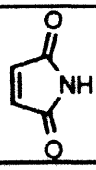
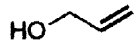
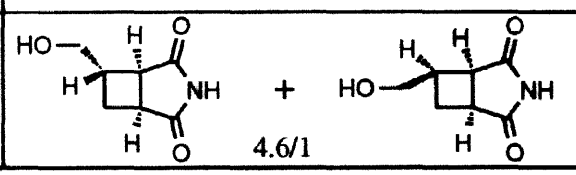
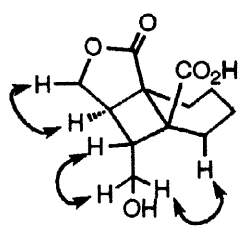
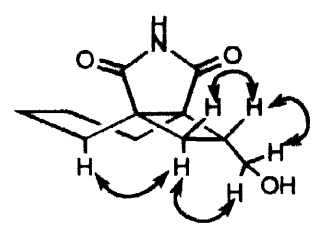
Entry	Imide	Alkene	Time	Yield	Products
a	 **8**		70 min	89%	 **10a** 10/1 R, R' = H **10b**
b	**8**		75 min	92%	**10a + 10b** 8.2/1 R = H, R' = Et
c	 **9**		4.5 h	77%	**10a + 10b** 7/1 R = Me, R' = H
d	**9**		5.5 h	80%	**10a + 10b** 6.3/1 R = Me, R' = Et
e			2 h	72%	 4.6/1

Fig. 1: Selected NOESY enhancements of 6 and 10a

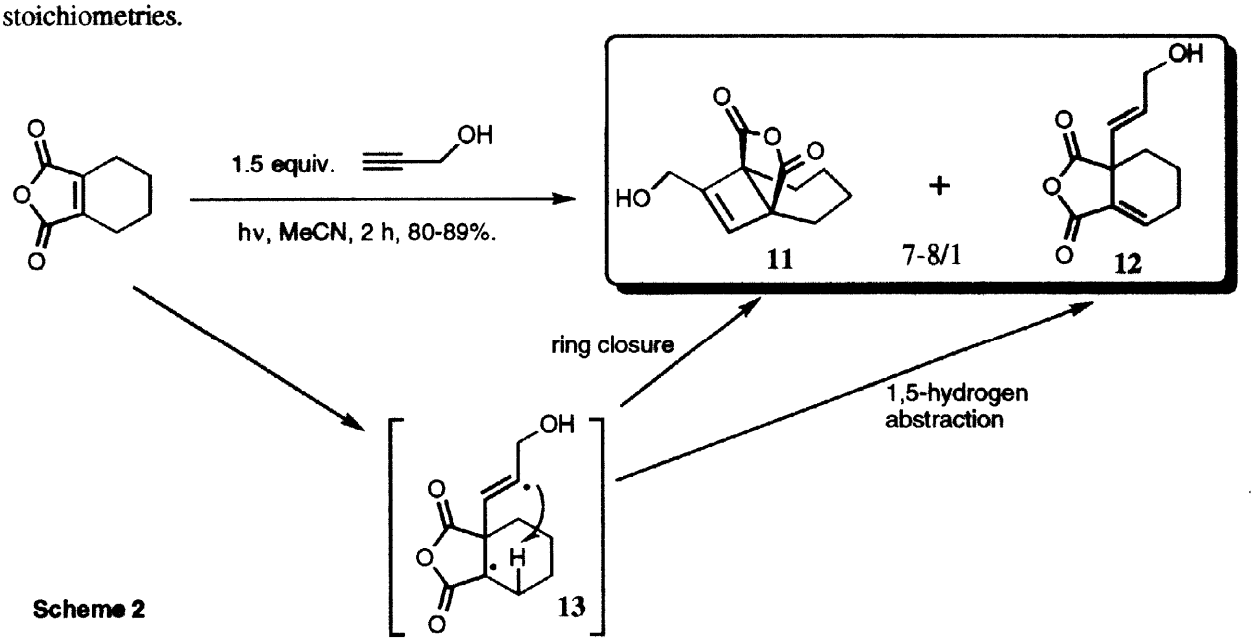




The efficiency of THPA and the corresponding imides as chromophores in [2+2] photocycloadditions can be explained by the fact that the UV spectrum of THPA shows a λ_{max}(MeCN) = 301 nm (ε = 84), which

coincides with a strong emission at 302 nm from the 125 W medium-pressure mercury vapour lamp used in this study. The fact that **5** failed to give any cycloaddition products with either allyl or propargyl alcohol even after prolonged irradiation is consistent with the finding that **5** shows a λ_{max} at approximately 220 nm which is beyond the cut off point for the pyrex filtered UV source used in this study.

Alkynes and Alkynols: We also found that THPA underwent very efficient [2+2] photocycloaddition with propargyl alcohol, under the same conditions, to give the cyclobutene-anhydride **11** in good yield.[1,3] In addition to this, a minor by-product was formed which we initially did not characterise. When we repeated the reaction on a larger scale, we found that the minor component could be isolated and analysis showed it to be the cyclohexene-anhydride **12**, which we propose is formed from the triplet-biradical **13** *via* a transannular 1,5-hydrogen abstraction[6] (Scheme 2). We are confident that formation of **12** signifies a distinct, minor reaction pathway and is not a secondary photo-product derived from **11**, because a separate experiment showed that there was no formation of **12** upon prolonged irradiation (24 h) of **11**. Furthermore, there was no significant change in product ratio when the reaction was run with different starting material stoichiometries.

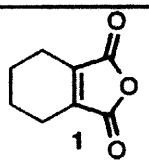
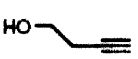
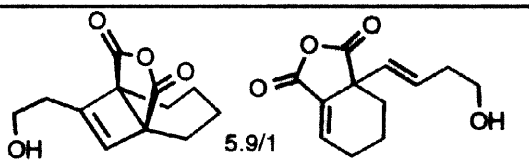
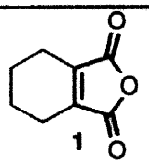
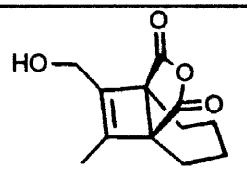
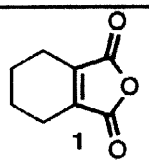
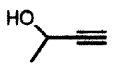
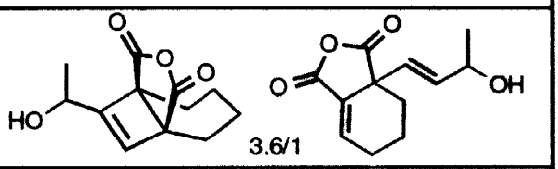
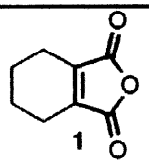
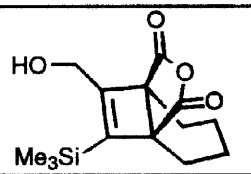
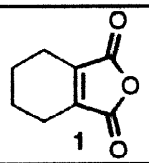
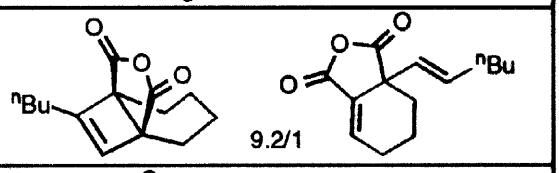
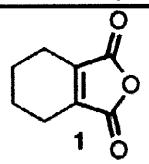
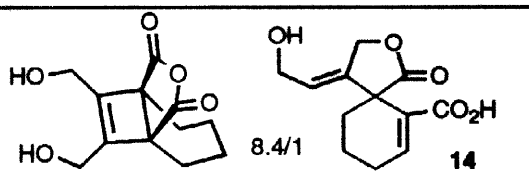
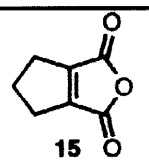
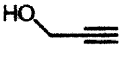
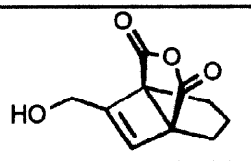
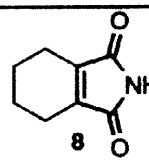
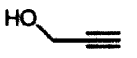
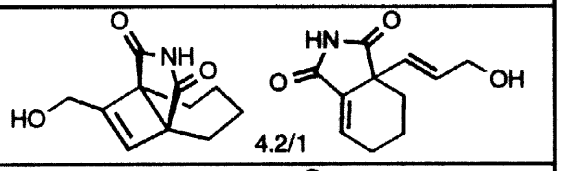
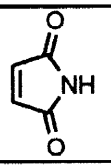
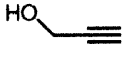
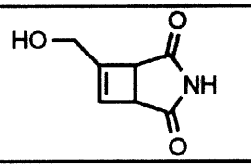


Scheme 2

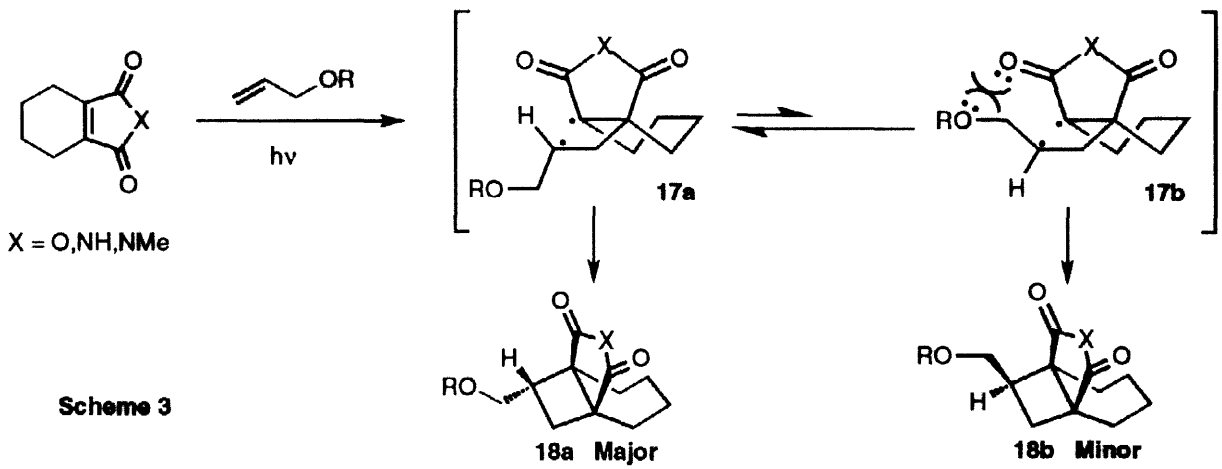
Table 3 summarises the results of [2+2] photocycloadditions using a variety of alkynes and alkynols as reaction partners. The cyclobutenes were formed rapidly and in good to excellent yield in all cases. With both THPA and THPI the cyclobutenes predominated and the 1,5-hydrogen abstraction products were formed only as minor components (10-15%). The interesting spirocyclic lactone **14**, formed by irradiation of 2-butyne-1,4-diol with THPA (entry **f**), is a result of the corresponding minor product undergoing lactonisation. Substitution at both the 1- and 3-positions of the alkynol did not appear to affect the course of the reaction and proved useful in the synthesis of substituted cyclobutenes. In some cases it appeared (tlc) that minor, 1,5-abstraction, products were formed, but it was not possible to purify and characterise them (entries **b** and **d**). Not surprisingly, maleimide (entry **i**) gave only the cyclobutene adduct because, 1,5-hydrogen abstraction would be impossible. The lower homologue of THPA, 1-cyclopentene-1,2-dicarboxylic anhydride, **15** gave only the [2+2] photocycloadduct **16** when irradiated with propargyl alcohol. Although, in all cases, the

cyclobutene-anhydrides formed were stable to column chromatography, they were found to be labile with respect to polymerisation upon standing at room temperature for extended periods of time. They could, however, be stored indefinitely in the freezer without significant decomposition.

Table 3: Photocycloaddition of various alkynes with anhydride and imide chromophores

Entry	THPA/Imide	Alkyne	Time	Yield	Products
a			4 h	83%	 5.9/1
b			3 h	72%	
c			2 h	74%	 3.6/1
d			3 h	68%	
e			3 h	85%	 9.2/1
f			6 h	75%	 8.4/1 14
g	 15		6 h	78%	 16
h	 8		2 h	72%	 4.2/1
i			1 h	79%	

Stereoselectivity: As illustrated earlier, the cycloaddition of THPA or THPI with alkenols proceeds with high stereoselectivity in favour of the *exo*-isomer. Obviously this is not a result of hydrogen bonding as this would favour the *endo*-isomer and ultimately the lactone in the case of THPA. Furthermore, use of alkenyl ethers, where hydrogen bonding would be impossible, does not significantly alter the *exo/endo* ratios. A plausible explanation centres around the argument that photocycloaddition of THPA (or THPI) with an alkenol forms an initial 1,4-biradical adduct which could exist as two conformers **17a** and **17b**. On the reaction timescale it would be reasonable to expect that **17a** and **17b** would be interconvertible by free rotation prior to ring closure to the cyclobutane. Electrostatic repulsion of the oxygen lone pairs in **17b** would favour equilibration to conformer **17a** and hence formation of the major *exo*-isomer **18a**. This is partially substantiated by the fact that the [2+2] photocycloaddition between 1-hexene and THPA (entry **e**, Table 1) gives a lower degree of selectivity (2/1). This can be explained by assuming that in the analogous 1,4-biradical adduct that would be formed with 1-hexene the butyl side chain does not suffer any electrostatic repulsion and therefore the *exo/endo* ratio is governed by steric effects and tends towards unity as observed. Further evidence of the stepwise nature of these cycloadditions, and the indermediacy of a 1,4-biradical, is also clearly demonstrated in the reaction of THPA with (Z)-2-butene-1,4-diol (entry **b**, Table 1) in which the *cis*-hydroxymethylene groups of the starting diol end up mutually *trans* in the product.



Scheme 3

In summary, THPA and the corresponding imide have proved to be exceptionally efficient partners in intermolecular [2+2] photocycloaddition reactions with alkenols and alkynols, giving high yields of cycloadducts with levels of stereoselection almost unprecedented in classical intermolecular cycloadditions.[7] Present studies are involved with the use of these cycloadducts for natural product synthesis.

Acknowledgements: We thank the EPSRC (GR/K15985) for financial support of this work.

EXPERIMENTAL SECTION: Photochemical reactions were carried out in a 100 mL pyrex immersion well photoreactor. The reaction mixture was initially degassed by passage of oxygen free nitrogen through the solution for 15 min and then irradiated under an atmosphere of nitrogen for the time stated. The UV source was a water cooled, 125 W medium pressure mercury discharge lamp with a 30 mm arc length. These lamps were obtained from 125 W Osram HQL (MBF-U) bulbs by puncturing the outer glass envelope with a heated

glass rod and removing the mercury lamp from inside by cutting the two copper electrodes as close to the screw thread as possible. These were then used as normal with a standard 125 W power supply obtained from Photochemical Reactors Ltd, Reading. Lamps prepared in this way were inexpensive and, on average, had a lifetime in excess of 200 h. NMR spectra were obtained in deuterochloroform (unless otherwise stated), with chemical shifts measured down-field from TMS (^{1}H) or referenced to the residual solvent resonance (^{13}C) using a Jeol EX 270 FT or a Bruker AC 300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1720 X FT spectrometer using sodium chloride plates. Low resolution, electron impact mass spectra (Kratos MS25) and elemental microanalyses (Carlo Erba EA 1108) were carried out at the University of East Anglia. High resolution mass spectra were run at the University of Manchester on a Kratos Concept 1-S instrument. Flash chromatography was carried out using either Matrex silica 60 (70-200 μm) or Merck silica 60 (40-63 μm) eluting with the solvents stated. Tlc analyses were performed using Camlab polygram® SIL G/UV$_{254}$ plastic backed plates (0.25 mm layer of silica) and were visualised using UV (254 nm), alkaline potassium manganate(VII) solution or acidic cerium(IV) sulfate solution. Melting points were obtained using a Köpfler hot stage apparatus and are uncorrected. Acetonitrile was distilled from calcium hydride. Petroleum ether (PE) refers to the fraction boiling between 40-60 °C.

10-Hydroxymethyl-8-oxatricyclo[4.3.2.0^{1,6}]undecane-7,9-dione 2:

A solution of THPA **1** (1.0 g, 6.58 mmol) and allyl alcohol (0.57 g, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 2 h after which time all the THPA had been consumed. The solvent was removed under reduced pressure to give a mixture of the title compound and 4a-carboxy-2-oxatricyclo[4.3.1]undecan-1-one **3** as a white crystalline solid (1.38 g, ~100%). ^{1}H NMR showed the ratio of **2/3** to be 5.7/1. Recrystallisation from diethylether gave the pure title compound as a moisture sensitive colourless solid (1.11 g, 80%); (Found: C, 62.63; H, 6.79; $C_{11}H_{14}O_4$ requires: C, 62.85; H, 6.71%); ν_{max}/cm^{-1} 3397 (OH), 1849 (C=O) and 1778 (C=O), δH: 3.65-3.83 (2H, m, unresolved ABX, -CH_2OH), 2.66-2.78 (1H, m, cyclobutane CH), 2.32-2.43 (1H, dd, *J* 8.3 Hz , *J* 12.1 Hz, 1H of cyclobutane CH_2), 2.04-2.22 (2H, m), 1.79-1.96 (2H,m), 1.48-1.77 (3H,m), 1.28-1.47 (1H, m), 0.98-1.21 (1H, m); δC: 177.46 (Q), 175.98 (Q), 61.53 (CH_2), 48.42 (Q), 44.15 (Q), 41.31 (CH), 28.56 (CH_2), 27.50 (CH_2), 20.98 (CH_2), 20.61 (CH_2), 20.01 (CH_2). Evaporation of the remaining mother liquors gave a mixture of **2/3** as a pale yellow viscous oil. Full experimental details for the preparation of pure **3** by an alternative method can be found in Ref.1.

10-Hydroxyethyl-8-oxatricyclo[4.3.2.0^{1,6}]undecane-7,9-dione:

A solution of THPA (1.0 g, 6.58 mmol) and 3-buten-1-ol (0.85 mL, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 7 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (40-60% EtOAc/PE) to yield an inseparable mixture of title compound and 1-oxo-octahydro-2-oxa-cyclobuta[1,2:1,4]dibenzene-5a-carboxylic acid as a colourless oil (1.25g, 85%) in a ratio of 4.25/1. (R_f 0.16, 40% EtOAc/PE); MS: *m/z* 224 (M^+, 13%), 206 (30%), 178 (17%), 153 (100%), 91 (25%), 79 (49%). Concentration of the first few fractions gave semi-pure title compound: ν_{max}/cm^{-1} 3407, 1852 and 1776; δH: 0.85-2.89 (13H, m), 3.61 (2H, t, *J* 6.3Hz); δC: 20.34 (CH_2), 20.79 (CH_2), 21.12 (CH_2), 27.73 (CH_2), 31.66 (CH_2), 33.41 (CH_2), 38.06 (CH), 44.35 (Q), 49.22 (Q), 59.98 (CH_2), 175.18 (Q), 177.05 (Q). Concentration of the end fractions gave semi-pure 1-oxo-octahydro-2-oxa-cyclobuta[1,2:1,4]dibenzene-5a-carboxylic acid; ν_{max}/cm^{-1} 1731; δH: 0.85-2.89 (13H, m), 4.26 (1H, ddd, *J* 5.0Hz, *J* 7.3Hz, *J* 11.9Hz),

4.52 (1H, ddd, *J* 4.3Hz, *J* 5.9Hz, *J* 11.2Hz); δC: 18.28 (CH_2), 18.76 (CH_2), 26.29 (CH_2), 29.63 (CH_2), 30.10 (CH_2), 31.07 (CH_2), 31.86 (CH), 46.76 (Q), 48.27 (Q), 67.21 (CH_2), 175.51 (Q), 178.20 (Q).

4-Hydroxymethyl-1-oxo-hexahydro-2-oxa-cyclopenta[1,4]cyclobuta[1,2]benzene-4a-carboxylic acid 6:

A solution of THPA (1.0 g, 6.58 mmol) and 2-butene-1,4-diol (0.81 mL, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 4 h. Concentration under reduced pressure and washing with hot diethyl ether (3 x 20 mL) afforded the pure title compound as a colourless solid (1.2 g, 87%); (R_f 0.13, 40% EtOAc / PE); mp 183-186°C; (Found: C, 59.84; H, 6.76. $C_{12}H_{16}O_5$ requires: C, 59.98; H, 6.72%); ν_{max}/cm^{-1} 3359, 1757 and 1695; δH (CD_3OD): 1.35-1.48 (1H, m), 1.63-1.87 (6H, m), 2.00-2.09 (1H, m), 2.78-2.92 (2H, m), 3.64 (1H, dd, *J* 11.6Hz, *J* 7.3Hz), 3.72 (1H, dd, *J* 11.2Hz, *J* 6.9Hz), 4.23 (1H, dd, *J* 9.6Hz, *J* 1.0Hz), 4.27 (1H, dd, *J* 9.6Hz, *J* 3.6Hz); δC (CD_3OD): 22.06 (CH_2), 22.95 (CH_2), 27.35 (CH_2), 27.90 (CH_2), 39.26 (CH), 44.51 (CH), 47.78 (Q), 50.62 (Q), 61.26 (CH_2), 71.91 (CH_2), 176.69 (Q), 182.64 (Q); MS: *m/z* 240 (M^+, 14%), 222 (25%), 153 (13%), 125 (14%), 91 (15%), 74 (56%), 58 (100%), 45 (51%), 31 (75%).

4-Benzyloxymethyl-1-oxo-hexahydro-2-oxa-cyclopenta[1,4]cyclobuta[1,2]benzene-4a-carboxylic acid:

A solution of THPA (1.0 g, 6.58 mmol) and (Z)-4-benzyloxy-2-butene-1-ol (1.2 g, 6.58 mmol) in acetonitrile (100 mL) was irradiated for 6 h. The solvent was removed under reduced pressure and the residue was stirred in THF/water (30 mL/20 mL) for 18 h. The solvents were again removed under reduced pressure and the residue subjected to flash chromatography (20-99% EtOAc/PE). Recrystallisation (EtOAc/PE) of the first fraction furnished the title compound as a colourless solid (0.75 g, 35%); (R_f 0.32, 40% EtOAc/PE); mp 160-163°C; (Found: C, 68.88; H, 6.72. $C_{19}H_{21}O_5$ requires: C, 69.06; H, 6.72%); ν_{max}/cm^{-1} 3000, 1756 and 1694; δH: 1.23-1.31 (1H, m), 1.61-1.89 (6H, m), 2.05-2.12 (1H, m), 2.84 (1H, dd, *J* 3.3Hz, *J* 8.3Hz), 3.02 (1H, ddd, *J* 6.9Hz, *J* 6.9Hz, *J* 6.9Hz), 3.54 (1H, dd, *J* 6.9Hz, *J* 9.9Hz), 3.63 (1H, dd, *J* 6.9Hz, *J* 9.9Hz), 4.16-4.25 (2H, m) ; 4.51 (2H, s), 7.27-7.39 (5H, m); δC: 20.66 (CH_2), 22.01 (CH_2), 26.25 (CH_2), 26.99 (CH_2), 38.18 (CH), 40.63 (CH), 46.50 (Q), 49.49 (Q), 68.10 (CH_2), 70.13 (CH_2), 73.10 (CH_2), 127.64 (2 x CH), 127.74 (CH), 128.44 (2 x CH), 137.91 (Q), 177.75 (Q), 179.87 (Q); MS: *m/z* 330 (M^+, 2%), 206 (8%), 178 (8%), 154 (8%), 133 (8%), 91 (100%), 44 (39%). Further elution gave 1-benzyloxymethyl-2-hydroxymethyl-2a,6a-dicarboxybicyclo[4.2.0.]oct-1-ene as a colourless solid (0.89g, 39%); (R_f 0.10, 40% EtOAc/PE); mp 79-82°C; ν_{max}/cm^{-1} 3200 and 1697; δH: 1.37-2.04 (8H, m), 2.46-2.55 (1H, m), 3.13-3.22 (1H, m), 3.41 (1H, dd, *J* 8.7Hz, *J* 8.7Hz), 3.52 (1H, dd, *J* 8.9Hz, *J* 5.5Hz), 3.65 (1H, dd, *J* 10.9Hz, *J* 6.9Hz), 3.75 (1H, dd, *J* 10.6Hz, *J* 7.9Hz), 4.40 (1H, d, *J* 12.2Hz), 4.47 (1H, d, *J* 11.5Hz), 7.24-7.40 (5H, m); δC: 21.24 (CH_2), 22.48 (CH_2), 28.43 (CH_2), 28.93 (CH_2), 39.89 (CH), 45.33 (CH), 49.16 (Q), 52.38 (Q), 62.03 (CH_2), 71.80 (CH_2), 74.37 (CH_2), 128.66 (CH), 128.78 (2 x CH), 129.36 (2 x CH), 139.51 (Q), 177.64 (Q), 180.37 (Q); MS: *m/z* 330 ($\{M-18\}^+$, 7%), 302 (8%), 232 (1%), 196 (4%), 153 (15%), 91 (100%).

3a-Hydroxymethyl-1-oxo-hexahydro-2-oxa-cyclopenta[1,4]cyclobuta[1,2]benzene-4a-carboxylic acid 7:

A solution of 2-(hydroxymethyl)-2-propen-1-ol (0.89 g, 10.0mmol) and THPA (1.01 g, 6.60 mmol) in acetonitrile (100 mL) was irradiated for 4 h. The solvent was removed under reduced pressure to give a sticky solid, which was washed with diethyl ether (30 mL) and dried to yield the title compound as a colourless solid (1.54 g, 97%); mp 160-162°C; (Found C, 59.85; H, 6.77. $C_{12}H_{16}O_5$ requires: C, 59.99; H, 6.71%);

ν_{max}/cm^{-1} (nujol) 3306 (br. OH), 1749 (C=O lactone), 1695 (C=O acid); δH (CD_3OD): 4.27 (1H, d, *J* 9.2Hz), 4.14 (1H, d, *J* 9.2Hz), 4.01-3.92 (2H, dd, *J* 11.3, 14.0Hz), 2.66 (1H, d, *J* 12.5Hz), 1.89 (1H, d, *J* 12.5Hz), 1.78-1.49 (8H, m); δC (CD_3OD): 183.1 (Q), 177.2 (Q), 75.9 (CH_2), 64.2 (CH_2), 52.4 (Q), 47.3 (Q), 45.1 (Q), 38.0 (CH_2), 34.2 (CH_2), 30.7 (CH_2), 25.9 (CH_2), 21.9 (CH_2); MS: *m/z* 222 (M^+, 2.2%), 57 (100%).

10-Butyl-8-oxatricyclo[4.3.2.0^{1,6}]undecane-7,9-dione:

A solution of THPA (1.0 g, 6.58 mmol) and hex-1-ene (1.2 mL, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 5 h. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (10% EtOAc/PE) to give the title compound (inseparable diastereomers, 2/1) as a colourless oil (1.4 g, 90%); (R_f 0.55, 20% EtOAc/PE); (Found: C, 70.89; H, 8.49. $C_{14}H_{20}O_3$ requires: C, 71.14, H, 8.54%); ν_{max}/cm^{-1} 1849 and 1780; δH: 0.88 (3H, t, *J* 6.9Hz), 1.00-1.60 (12H, m), 1.63-2.04 (2H, m), 2.16-2.62 (3H, m); δC (Major diastereomer): 13.84 (CH_3), 20.38 (CH_2), 20.45 (CH_2), 21.17 (CH_2), 22.39 (CH_2), 27.78 (CH_2), 28.84 (CH_2), 30.73 (CH_2), 31.93 (CH_2), 41.09 (CH), 44.05 (Q), 49.26 (Q), 175.22 (Q), 177.25 (Q); (Minor diastereomer): 13.84 (CH_3), 20.38 (CH_2), 21.37 (CH_2), 22.46 (CH_2), 27.57 (CH_2), 28.12 (CH_2), 28.99 (CH_2), 31.75 (CH_2), 36.66 (CH_2), 37.23 (CH), 42.95 (Q), 49.58 (Q), 174.68 (Q), 175.54 (Q); MS: *m/z* 236 (M^+, 8%), 208 (6%), 191 (8%), 164 (19%), 153 (100%), 135 (23%), 121 (51%), 79 (29%).

***Exo*-10-Ethoxy-8-oxatricyclo[4.3.2.0^{1,6}]undecane-7,9-dione:**

A solution of THPA (1.0 g, 6.58 mmol) and ethoxyethene (0.95 mL, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 6 h. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (5-10% EtOAc/PE) furnishing the title compound as a cream solid (0.16 g, 11%); (R_f=0.49, 20% EtOAc/PE); mp 87-92°C; (Found: C, 64.51; H, 7.20. $C_{12}H_{16}O_4$ requires: C, 64.26; H, 7.20%); ν_{max}/cm^{-1} 1847 and 1785; δH: 0.96-1.11 (1H, m), 1.20 (3H, t, *J* 7.3Hz), 1.25-1.51 (2H, m), 1.71-2.03 (2H, m), 2.15-2.22 (1H, m), 2.36 (1H, dd, *J* 8.6Hz, *J* 12.2Hz), 2.62 (1H, dd, *J* 7.3Hz, *J* 12.2Hz), 3.40 (2H, dq, *J* 1.7Hz, *J* 7.3Hz), 3.99 (1H, dd, *J* 7.3Hz, *J* 8.6Hz); δC: 14.84 (CH_3), 18.20 (CH_2), 19.96 (CH_2), 21.13 (CH_2), 27.24 (CH_2), 33.28 (CH_2), 40.20 (Q), 53.57 (Q), 65.86 (CH_2), 74.59 (CH), 174.06 (Q), 176.30 (Q); MS: *m/z* 196 ({M-28}$^+$, 3%), 168 (19%), 150 (7%), 136 (13%), 122 (4%), 108 (5%), 95 (7%), 72 (100%). Further elution gave *endo*-10-ethoxy-8-oxatricyclo[4.3.2.0^{1,6}]undecane-7,9-dione as a yellow oil (1.1 g, 75%); (R_f 0.37, 20% EtOAc/PE); (Found: C, 64.03; H, 7.27. $C_{12}H_{16}O_4$ requires: C, 64.26; H, 7.20%); ν_{max}/cm^{-1} 1838 and 1781; δH: 1.19 (3H, t, *J* 6.9Hz), 1.20-1.35 (1H, m), 1.47-1.68 (4H, m), 1.91-2.08 (2H, m), 2.16-2.25 (1H, m), 2.36 (1H, dd, *J* 5.6Hz, *J* 13.2Hz), 2.62 (1H, dd, *J* 7.6Hz, *J* 13.2Hz), 3.47 (1H, dq, *J* 6.9Hz, *J* 8.9Hz), 3.67 (1H, dq, *J* 6.9Hz, *J* 8.9Hz), 4.10 (1H, dd, *J* 5.6Hz, *J* 7.6Hz); δC: 15.06 (CH_3), 20.86 (CH_2), 20.92 (CH_2), 27.35 (CH_2), 27.49 (CH_2), 37.63 (CH_2), 40.47 (Q), 52.83 (Q), 65.55 (CH_2), 74.45 (CH), 172.50 (Q), 175.58 (Q); MS: *m/z* 196 ({M - 28}$^+$, 3%), 168 (20%), 153 (9%), 136 (8%), 122 (6%), 108 (4%), 95 (7%), 72 (100%).

***Exo/endo*-7-ethoxycarbonylbicyclo[4.2.0.]octane-1,6-dicarboxylic acid:**

A solution of THPA (1.0 g, 6.58 mmol) and ethyl acrylate (1.1 mL, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 8 h. The solvent was removed under reduced pressure and the resulting residue was stirred in THF/water (15 mL/10 mL) for 18 h. The solvents were removed under reduced pressure and the residue was subjected to flash chromatography (50% EtOAc/PE) affording the title compound (inseparable 3/2 mixture of *exo/endo* isomers) as a colourless solid, (1.4 g, 78%); (R_f 0.28, EtOAc); mp 46-50°C; (Found: C, 57.40; H,

6.75. $C_{13}H_{18}O_6$ requires: C, 57.75; H, 6.72%); ν_{max}/cm^{-1} 2925, 1735 and 1701; δH: 1.19, 1.26 (3H, t, *J* 7.1Hz), 1.39-2.31 (8H, m), 2.18-2.35 (1.4H, m), 2.48 (0.4H, dd, *J* 10.8Hz, *J* 8.6Hz), 3.11-3.28 (1H, m), 3.90-4.24 (3H, m); δC: 13.89 (CH_3), 14.27 (CH_3), 19.73 (CH_2), 20.25 (CH_2), 20.51 (CH_2), 20.79 (CH_2), 26.22 (CH_2), 26.63 (CH_2), 27.33 (CH_2), 28.52 (CH_2), 33.55 (CH), 34.97 (CH), 37.56 (CH), 41.80 (CH), 44.31 (Q), 47.35 (Q), 50.12 (Q), 53.73 (Q), 60.67 (2 x CH_2), 171.97 (Q), 172.06 (Q), 181.62 (Q), 181.67 (Q), 182.49 (Q), 183.27 (Q); MS: *m/z* 270 (M^+, 2%), 252 (8%), 225 (15%), 207 (17%), 180 (78%), 152 (100%), 134 (39%), 107 (43%), 79 (47%).

***Exo*-7-hydroxymethylbicyclo[4.2.0]octane-1,6-dicarboximide 10a** (R, R' = H):

A solution of THPI (**8**) (1.0 g, 6.62 mmol) and allyl alcohol (0.68 mL, 9.93 mmol) in acetonitrile (100 mL) was irradiated for 70 min after which the solvent was removed under reduced pressure and the residue purified by flash chromatography (50% EtOAc/PE). The first product eluted was the title compound as a colourless oil which slowly solidified to a colourless solid (1.07 g, 77%); (R_f 0.11, 50% EtOAc/PE); mp (EtOAc) 113.5-115 °C; (Found: C, 62.92; H, 7.12; N, 6.56. $C_{11}H_{15}NO_3$ requires: C, 63.16; H, 7.18; N, 6.70%); ν_{max}/cm^{-1} (neat): 3458 (br. OH), 3229 (NH), 1768 and 1700 (CONHCO); δH: 9.30 (1H, s, br., NH), 3.83-3.52 (2H, m, CH_2OH), 2.72 (1H, br., OH), 2.61 (1H, m, $CHCH_2OH$), 2.30 (1H, m), 2.10 (1H, m), 1.92 (1H, m), 1.85-1.30 (7H, m); δC: 183.56 (Q), 182.96 (Q), 62.36 (CH_2), 49.08 (Q), 44.17 (Q), 41.66 (CH), 28.59 (CH_2), 27.91 (CH_2), 20.83 (CH_2), 20.34 (CH_2), 20.29 (CH_2); MS: *m/z* 209 (M^+, 1.07%), 152 (100%). Further elution gave a colourless oil (0.17 g) which was shown by analysis to be a mixture of the title compound and the *endo*-isomer (**10b**; R, R' = H). Integration of the appropriate signals in the ^1H NMR showed the total yield of the title compound was 1.13 g (81%) and the *endo* -isomer 0.11 g (8%).

***Exo*--7-ethoxymethylbicyclo[4.2.0]octane-1,6-dicarboximide 10a** (R = OEt, R' = H):

A solution of THPI (**8**) (1.0 g, 6.62 mmol) and 1-ethoxyprop-2-ene (1.12 mL, 9.93 mmol) in acetonitrile (100 mL) was irradiated for 75 min after which the solvent was removed under reduced pressure and the residue purified by flash chromatography (50% EtOAc/PE) to give the title compound as a colourless oil (0.94 g, 60%); (R_f 0.39, 50% EtOAc/PE); ν_{max}/cm^{-1} (neat): 3218 (NH), 1770 and 1704 (CONHCO); δH: 9.71 (1H, br., NH), 3.61-3.44 (4H, m, $CH_3CH_2OCH_2$), 2.70 (1H, m, $CHCH_2OEt$), 2.35 (1H, dd, *J* 3.6Hz, *J* 8.6Hz), 2.06 (2H, m), 1.89-1.44 (7H, m), 1.19 (3H, t, *J* 6.9Hz, CH_3); δC: 183.6 (Q), 182.7 (Q), 69.65 (CH_2), 66.02 (CH_2), 48.72 (Q), 44.19 (Q), 38.78 (CH), 29.20 (CH_2), 27.57 (CH_2), 20.58 (CH_2), 20.32 (CH_2), 20.07 (CH_2), 14.77 (CH_3); MS: *m/z* 237 (M^+, 0.5%), 152 (100%); HRMS: *m/z* (CI, NH_3) Found: 238.1444; $C_{13}H_{19}NO_3$ (M + H^+) requires: 238.1443. Further elution gave a colourless oil (0.50 g)which was shown by analysis to be a mixture of the title compound and the *endo*-isomer (**10b**; R = OEt, R' = H). Integration of the appropriate signals in the ^1H NMR showed the total yield of the title compound was 1.28 g (82%) and the *endo* -isomer 0.16 g (10%).

***Exo*-7-hydroxymethylbicyclo[4.2.0]octane-1,6-(*N*-methyl)dicarboximide 10a** (R =H,R' = Me)

A solution of *N*-methyl-3,4,5,6-tetrahydrophthalimide (**9**) (1.0 g, 6.06 mmol) and allyl alcohol (0.62 mL, 9.09 mmol) in acetonitrile (100 mL) was irradiated for 4.5 h after which the solvent was removed under reduced pressure and the residue purified by flash chromatography (50-80% EtOAc/PE) to give the title compound as a colourless oil (0.86 g, 64%); (R_f 0.11, 50% EtOAc/PE); ν_{max}/cm^{-1} (neat): 3450 (OH), 1767 and 1698 ($CON(CH_3)CO$); δH: 3.87-3.70 (2H, m, CH_2OH), 3.39 (1H, br., OH), 3.07 (3H, s, NCH_3), 2.50 (1H, m, $CHCH_2OH$), 2.29 (1H, dd, *J* 3.6Hz, *J* 8.6Hz), 2.15-1.64 (7H, m), 1.49 (2H, m); δC: 182.5 (Q), 182.0 (Q), 61.94 (CH_2), 47.33 (Q), 42.62 (Q), 41.06 (CH), 28.74 (CH_2), 27.68 (CH_2), 24.89 (CH_3),

20.42 (CH_2), 20.18 (CH_2), 19.91 (CH_2); MS: *m/z* 223 (M^+, 3.0%), 166 (100%); HRMS: *m/z* (CI, NH_3) Found: 224.1288, $C_{12}H_{17}NO_3$ (M + H^+) requires: 224.1287. Further elution gave a colourless oil (0.18 g) which was shown by analysis to be a mixture of the title compound and the *endo* isomer (**10b**; R = H, R' = Me). Integration of the appropriate signals in the ^1H NMR spectrum showed the total yield of the title compound was 0.91 g (67%) and the *endo* -isomer 0.13 g (10%).

***Exo*-7-ethoxymethylbicyclo[4.2.0]octane-1,6-(*N*-methyl)dicarboximide 10a** (R = OEt, R' = Me): A solution of *N*-methyl-3,4,5,6-tetrahydrophthalimide (**9**) (0.84 g, 5.09 mmol) and 1-ethoxyprop-2-ene (0.86 mL, 7.64 mmol) in acetonitrile (85 mL) was irradiated for 5.5 h after which the solvent was removed under reduced pressure and the residue purified by flash chromatography (50% EtOAc/PE) to give the title compound as a colourless oil (0.74 g, 58%); (R_f 0.49, 50% EtOAc/PE); ν_{max}/cm^{-1} (neat): 1770 and 1704 ($CON(CH_3)CO$); δH: 3.58-3.43 (4H, m), 3.01 (3H, s, NCH_3), 2.51 (1H, m), 2.25 (1H, m), 2.11-1.99 (2H, m), 1.97-1.56 (5H, m), 1.44 (2H, m), 1.19 (3H, t, *J* 6.9Hz, CH_3); δC: 181.8 (Q), 181.1 (Q), 69. 29 (CH_2), 65.55 (CH_2), 47.05 (Q), 42.52 (Q), 38.49 (CH), 28.86 (CH_2), 27.32 (CH_2), 24.44 (CH_3), 20.16 (CH_2), 20.06 (CH_2), 19.70 (CH_2), 14.48 (CH_3); MS: *m/z* 251 (M^+, 0.82%), 166 (100%); HRMS: *m/z* (CI, NH_3) Found: 252.1595, $C_{14}H_{21}NO_3$ (M + H^+) requires: 252.1599. Further elution gave a colourless oil (0.28 g) which was shown to be a mixture of the title compound and the *endo* isomer (**10b**; R = OEt, R' = Me). Integration of the appropriate signals in the ^1H NMR spectrum showed the total yield of the title compound to be 0.88 g (69%) and the *endo* -isomer 0.14 g (11%).

6-Hydroxymethyl-3-azabicyclo[3.2.0]heptane-2,4-dione:

A solution of maleimide (0.5 g, 5.15 mmol) and allyl alcohol (0.53 mL, 7.73 mmol) in acetonitrile (100 mL) was irradiated for 2 h. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (EtOAc) affording the title compound as an inseparable mixture of *exo/endo* isomers (82/18) (0.57 g, 72%); (R_f 0.27, EtOAc); (Found: C, 54.49; H, 5.91; N, 9.09. $C_7H_9NO_3$ requires: C, 54.19; H, 5.81; N, 9.03%); ν_{max}/cm^{-1} 3429(OH), 3246 (NH), 1765 (C=O) and 1700 (C=O); δH (d^6DMSO): 11.82 (1H, br, NH), 4.86 (0.82H, br. t, *exo*-OH), 4.58 (0.18H, br. t, *endo*-OH), 3.56- 3.41 (2H, *exo/endo* -CH_2OH), 3.30-2.92 (2H, m, *exo/endo* cyclobutane CHs), 2.51-2.38 (1H, m, *exo/endo* cyclobutane CH), 2.32-1.80 (2H, m, *exo/endo* cyclobutane -CH_2-); MS: *m/z* 155.1 (M^+, 30.47%).

2-(3'-Hydroxy-1'-propenyl)-2,3,4,5-tetrahydrophthalic anhydride 12:

A solution of THPA (3.0 g, 19.7 mmol) and propargyl alcohol (1.7 mL, 29.6 mmol) in acetonitrile (100 mL) was irradiated for 6 h. The solvent was removed under reduced pressure and flash chromatography of the residue (20-60% EtOAc/PE) afforded pure 2a,6a-anhydro-1-hydroxymethylbicyclo[4.2.0]oct-1-ene **11** as a yellow oil (2.8 g, 68%) which was identical to the same material reported in Ref 1. Further elution gave the title compound **12** as a colourless solid (0.6 g, 15%); (R_f=0.17, 40% EtOAc/PE); mp 59-62°C; (Found: C, 63.06; H, 5.75. $C_{11}H_{12}O_4$ requires: C, 63.44; H, 5.81%); ν_{max}/cm^{-1} 3430, 1854, 1776 and 1676; δH: 1.60-1.91 (3H, m), 2.15-2.20 (1H, m), 2.22-2.52 (2H, m), 4.21 (2H, d, *J* 3.0Hz), 5.71 (1H, dd, *J* 15.5Hz, *J* 3.6Hz), 5.78 (1H, d, *J* 15.8Hz), 7.15 (1H, t, *J* 3.6Hz); δC: 16.33 (CH_2), 25.21 (CH_2), 27.24 (CH_2), 50.03 (Q), 62.25 (CH_2), 128.12 (CH), 128.35 (Q), 135.51 (CH), 142.10 (CH), 163.32 (Q), 171.88 (Q).

10-(2-Hydroxyethyl)-8-oxatricyclo[4.3.2.$0^{1,6}$]undec-10-ene-7,9-dione:

A solution of THPA (2.0 g, 13.2 mmol) and 3-butyn-1-ol (1.5 mL, 19.7 mmol) in acetonitrile (100 mL) was irradiated for 4 h. The solvent was removed under reduced pressure and flash chromatography of the residue (20-99% EtOAc/PE) afforded the title compound as a pale yellow oil (2.1 g, 71%); (R_f 0.34, 40% EtOAc/PE);

ν_{max}/cm^{-1} 3402, 1844, 1772 and 1634; δH: 1.44-1.70 (4H, m), 1.92-2.35 (4H, m), 2.42 (2H, tt, *J* 6.2Hz, *J* 2.0Hz), 3.80 (2H, dt, *J* 6.3Hz, *J* 2.0Hz), 6.21 (1H, t, *J* 1.7Hz); δC: 19.25 (CH_2), 19.41 (CH_2), 24.06 (CH_2), 25.11 (CH_2), 31.32 (CH_2), 51.05 (Q), 54.65 (Q), 58.96 (CH_2), 134.91 (CH), 153.62 (Q), 172.42 (Q), 172.54 (Q); MS: *m/z* 222 (M^+, 1%), 192 (45%), 164 (20%), 150 (100%), 119 (64%), 91 (72%). Further elution gave 2-(3'-hydroxy-1'-butenyl)-2,3,4,5-tetrahydrophthalic anhydride as a yellow oil (0.35 g, 12%); (R_f 0.20, 40% EtOAc/PE); ν_{max}/cm^{-1} 3388, 1854, 1775 and 1675; MS: *m/z* 222 (M^+, 8%), 192 (30%), 178 (53%), 160 (76%), 147 (66%), 117 (52%), 91 (100%), 79 (59%).

10-Hydroxymethyl-11-methyl-8-oxatricyclo[4.3.2.0^{1,6}]undec-10-ene-7,9-dione:

A solution of THPA (2.0 g, 13.2 mmol) and 2-butyn-1-ol (1.5 mL, 19.7 mmol) in acetonitrile (100 mL) was irradiated for 6 h. The solvent was removed under reduced pressure and flash chromatography of the residue (20-60% EtOAc/PE) afforded the title compound as a colourless solid (2.1 g, 72%); (R_f 0.33, 40% EtOAc/PE); mp 66-70°C; (Found: C, 64.91; H, 6.32. $C_{12}H_{14}O_4$ requires: C, 64.84; H, 6.35%); ν_{max}/cm^{-1} 3435, 1843 and 1760; δH: 1.46-1.68 (4H, m), 1.83 (3H, t, *J* 1.2Hz), 1.86-2.09 (4H, m), 4.25 (2H, d, *J* 1.0Hz); δC 11.07 (CH_3), 19.53 (CH_2), 19.59 (CH_2), 23.49 (CH_2), 24.28 (CH_2), 52.00 (Q), 52.97 (Q), 56.73 (CH_2), 144.18 (Q), 145.19 (Q), 172.09 (Q), 172.94 (Q); MS: *m/z* 222 (M^+, 4%), 178 (10%), 150 (100%), 135 (31%), 122 (63%), 107 (43%), 91 (26%), 79 (23%).

10-(1-Hydroxyethyl)-8-oxatricyclo[4.3.2.0^{1,6}]undec-10-ene-7,9-dione:

A solution of THPA (2.0 g, 13.2 mmol) and 3-butyn-2-ol (1.4 mL, 19.7 mmol) in acetonitrile (100 mL) was irradiated for 4 h. The solvent was removed under reduced pressure and flash chromatography of the residue (20-80% EtOAc/PE) afforded the title compound (as a mixture of diastereomers) as a yellow oil (1.7 g, 58%); (R_f 0.33, 40% EtOAc/PE); (Found: C, 64.42; H, 6.36. $C_{12}H_{14}O_4$ requires: C, 64.84; H, 6.35%); ν_{max}/cm^{-1} 3430, 1847 and 1775; δH: 1.36 (1.5H, d, *J* 6.6Hz), 1.38 (1.5H, d, *J* 6.6Hz), 1.40-1.74 (4H, m), 1.81-2.18 (5H, m), 4.40-4.48 (1H, m), 6.26-6.27 (1H, m); δC: 18.76 (CH_2), 19.01 (CH_2), 19.08 (CH_2), 19.17 (CH_2), 20.68 (CH_3), 20.81 (CH_3), 24.65 (CH_2), 24.71 (CH_2), 24.96 (CH_2), 25.00 (CH_2), 50.75 (Q), 50.85 (Q), 54.21 (Q), 54.36 (Q), 64.47 (CH), 64.76 (CH), 132.72 (CH), 132.97 (CH), 157.61 (Q), 157.77 (Q), 172.02 (Q), 172.11 (Q), 172.11 (Q), 172.22(Q); MS: *m/z* 222 (M^+, 1%), 194 (3%), 178 (19%), 149 (42%), 135 (56%), 122 (100%), 107 (69%), 91 (38%), 79 (73%). Further elution gave 2-(3'-hydroxy-1'-butenyl)-2,3,4,5-tetrahydrophthalic anhydride (as a mixture of diastereomers) as a yellow oil (0.46 g, 16%); (R_f 0.22, 40% EtOAc/PE); ν_{max}/cm^{-1} 3415, 1850, 1778 and 1674; δH: 1.26 (1.5H, d, *J* 6.6Hz), 1.27 (1.5H, d, *J* 6.6Hz), 1.50-1.90 (3H, m), 2.05-2.52 (4H, m), 4.32-4.41 (1H, m), 5.62 (0.5H, dd, *J* 2.0Hz, *J* 15.5Hz), 5.64 (0.5H, dd, *J* 2.0Hz, *J* 15.5Hz), 5.72 (1H, d, *J* 15.8Hz), 7.14 (1H, t, *J* 3.6Hz); δC: 16.24 (CH_2), 23.29 (CH_3), 25.18 (CH_2), 27.22 (CH_2), 49.85 (Q), 67.56 (CH_2), 67.60 (CH_2), 127.01 (CH), 128.21 (Q), 128.25 (Q), 140.27 (CH), 140.36 (CH), 142.24 (CH), 142.28 (CH), 163.36 (Q), 172.02 (Q); MS: *m/z* 220 ({M-2}$^+$, 1%), 178 (1%), 163 (2%), 149 (2%), 134 (100%), 117 (9%), 105 (8%), 91 (17%), 79 (10%).

10-Hydroxymethyl-11-trimethylsilyl-8-oxatricyclo[4.3.2.0^{1,6}]undec-10-ene-7,9-dione:

A solution of THPA (1.2 g, 7.89 mmol) and 3-trimethylsilyl-2-butyn-1-ol (1.5 g, 11.8 mmol) in acetonitrile (100 mL) was irradiated for 3 h. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (10-20% EtOAc/PE) affording the title compound as a yellow oil (1.5 g, 68%); (R_f 0.40, 40% EtOAc/PE); (Found: C, 59.64; H, 7.23. $C_{14}H_{20}O_4Si$ requires: C, 59.98; H, 7.20%); ν_{max}/cm^{-1} 3539, 1845, 1773, 1615 and 846; δH: 0.20 (9H, s), 1.45-1.76 (4H, m), 1.88-2.23 (4H, m), 4.30 (2H, s); δC: 1.00 (3 x CH_3), 19.18 (CH_2), 19.45 (CH_2), 24.50 (CH_2), 25.76 (CH_2), 52.66 (Q), 55.06 (Q),

59.05 (CH_2), 154.16 (Q), 162.38 (Q), 172.76 (Q), 172.83 (Q); MS: *m/z* 265 ({M–CH_3}$^+$, 39%) 208 (47%), 193 (37%), 164 (13%) 134 (29%), 117 (16%), 91 (12%), 73 (100%).

10-Butyl-8-oxatricyclo[4.3.2.0^{1,6}]undec-10-ene-7,9-dione:

A solution of THPA (1.0 g, 6.58 mmol) and 1-hexyne (1.1 mL, 9.87 mmol) in acetonitrile (100 mL) was irradiated for 3 h. The solvent was removed under reduced pressure and the residue subjected to flash chromatography (5% EtOAc/PE) affording the title compound as a yellow solid (1.1 g, 71%); (R_f 0.61, 20% EtOAc/PE); (Found: C, 72.05; H, 7.69. $C_{12}H_{18}O_3$ requires: C, 71.76; H, 7.75%); ν_{max}/cm^{-1} 1844, 1773 and 1635; δH: 0.91 (3H, t, *J* 6.9Hz), 1.30-1.70 (8H, m), 1.90-2.15 (6H, m), 6.07 (1H, t, *J* 1.6Hz); δC: 13.66 (CH_3), 19.45 (CH_2), 19.54 (CH_2), 22.32 (CH_2), 24.12 (CH_2), 25.25 (CH_2), 27.39 (CH_2), 27.68 (CH_2), 50.68 (Q) 54.56 (Q), 132.72 (CH), 156.95 (Q), 172.06 (Q), 172.81 (Q); MS: *m/z* 234 (M$^+$, 1%) , 190 (6%) , 162 (100%) , 133 (21%) , 91 (40%). Further elution gave 2-(1'-hexenyl)-2,3,4,5-tetrahydrophthalic anhydride as a colourless oil (0.11 g, 7%); (R_f 0.51, 20% EtOAc/PE); (Found: C, 71.56; H, 7.65. $C_{12}H_{18}O_3$ requires: C, 71.76; H, 7.75%); ν_{max}/cm^{-1} 1856, 1780 and 1676; δH: 0.88 (3H, t, *J* 6.9Hz), 1.20-1.88 (7H, m), 2.00-2.20 (3H, m), 2.20-2.50 (2H, m), 5.44 (1H, d, *J* 15.5Hz), 5.55 (1H, dt, *J* 15.5Hz, *J* 6.3Hz), 7.10 (1H, t, *J* 3.6Hz); δC: 13.77 (CH_3), 16.26 (CH_2), 22.09 (CH_2), 25.12 (CH_2), 27.26 (CH_2), 30.86 (CH_2), 31.88 (CH_2), 50.19 (Q) ,127.48 (CH), 128.72 (Q), 137.41 (CH), 141.35 (CH), 163.53 (Q), 172.22 (Q); MS: *m/z* 190 ({M–44}$^+$, 17%), 162 (15%), 134 (100%), 119 (14%), 105 (21%), 91 (40%).

10,11-Bis(hydroxymethyl)-8-oxatricyclo[4.3.2.0^{1,6}]undec-10-ene-7,9-dione:

A solution of THPA (1.2 g, 7.89 mmol) and 2-butyne-1,4-diol (0.54 g, 6.25 mmol) in acetonitrile (100 mL) was irradiated for 5 h. The solvent was removed under reduced pressure and flash chromatography of the residue (20-99% EtOAc/PE) afforded the title compound as a colourless solid (1.0 g, 67%); (R_f 0.51, EtOAc); mp 109-112°C; (Found: C, 60.41; H, 5.94. $C_{12}H_{14}O_5$ requires: C, 60.48; H, 5.93%); ν_{max}/cm^{-1} 3568, 1831 and 1765; δH: 1.49-1.68 (4H, m), 1.93-2.12 (4H, m), 4.28 (4H, s); δC: 20.08 (CH_2), 24.74 (CH_2), 53.40 (Q), 57.16 (CH_2), 147.33 (Q), 173.53 (Q); MS: *m/z* 220 ({M–H_2O}$^+$, 13%), 192 (25%), 166 (27%), 148 (66%), 120 (94%), 105 (53%), 91 (100%), 79 (45%). Further elution gave 3-carboxy-8-(2'-hydroxyethyl)-2-oxo-5,6,7,9-tetrahydro-1-oxa-2a-spirobicyclodecatriene as a colourless solid (0.13 g, 8%); (R_f 0.19, EtOAc); mp 145-151°C; ν_{max}/cm^{-1} 3342, 1747 and 1703; δH: 1.51-1.91 (4H, m), 2.30-2.38 (2H, m), 4.07 (2H, d, *J* 6.3Hz), 5.01-5.16 (2H, m), 5.34 (1H, tt, *J* 2.3Hz, *J* 5.9Hz), 7.39 (1H, dd, *J* 3.3Hz, *J* 4.6Hz); δC: 16.96 (CH_2), 25.91 (CH_2), 34.05 (CH_2), 49.22 (Q), 59.49 (CH_2), 70.19 (CH_2), 123.64 (CH), 130.94 (Q), 142.03 (Q), 145.87 (CH), 168.33 (Q), 182.71 (Q); MS: *m/z* 220 ({M–H_2O}$^+$, 4%), 192 (3%), 148 (5%), 120 (5%), 105 (6%), 84 (100%), 49 (75%).

9-Hydroxymethyl-7-oxatricyclo[3.3.2.0^{1,5}]dec-9-ene-6,8-dione 16:

A solution of 1-cyclopentene-1,2-dicarboxylic anhydride (1.0 g, 7.24 mmol) and propargyl alcohol (0.63 mL, 10.9 mmol) in acetonitrile (100 mL) was irradiated for 6 h. The solvent was removed under reduced pressure and flash chromatography of the residue (20-40% EtOAc/PE) afforded the title compound as a colourless solid (1.1 g, 78%); (R_f 0.25, 40% EtOAc/PE); mp 96-100°C; Found: C, 61.56; H, 5.08. $C_{10}H_{10}O_4$ requires: C, 61.84; H, 5.19%; ν_{max}/cm^{-1} 3316, 1851, 1789 and 1646; δH: 1.72-2.26 (7H, m), 4.28 (2H, d, *J* 1.7Hz), 6.28 (1H, t, *J* 1.7Hz); δC: 24.62 (CH_2), 25.18 (CH_2), 28.32 (CH_2), 58.40 (CH_2), 60.99 (Q), 63.81 (Q), 130.35 (CH), 150.67 (Q), 169.70 (Q), 170.01 (Q); MS: *m/z* 194 (M$^+$, 1%), 150 (34%), 122 (51%), 107 (28%), 94 (100%), 79 (25%).

7-(Hydroxymethyl)bicyclo[4.2.0]oct-7-ene-1,6-dicarboximide:

A solution of THPI (**8**) (1.0 g, 6.62 mmol) and propargyl alcohol (0.38 g, 6.62 mmol) in acetonitrile (100 mL) was irradiated for 2 h, after which time all the THPI had been consumed (tlc control). The lamp was switched off and the solvent removed under reduced pressure to leave an oily solid (1.37 g). This was subjected to flash chromatography (60% EtOAc/PE) and two components were eluted. The first was the title compound as a colourless solid (0.74 g, 58%); (R_f 0.18, 50% EtOAc/PE); mp (EtOAc) 137-139 °C; (Found: C, 63.61; H, 6.28; N, 6.74. $C_{11}H_{13}NO_3$ requires: C, 63.77; H, 6.28; N, 6.76%); ν_{max}/cm^{-1} (DCM thin film): 3419 (br. OH), 3192 (NH), 1764 and 1700 (CONHCO); δH ($CDCl_3/d^6DMSO$): 10.77 (1H, br. NH), 6.18 (1H, t, *J* 1.8Hz), 4.89 (1H, t, *J* 5.6Hz, OH), 3.99 (2H, m), 1.91-1.82 (4H, m), 1.59-1.51 (2H, m), 1.50-1.37 (2H, m); δC: 179.5 (Q), 178.3 (Q), 155.2 (Q), 132.0 (CH), 57.07 (CH), 54.30 (Q), 51.36 (Q), 24.58 (CH_2), 23.70 (CH_2), 19.21 (CH_2), 19.10 (CH_2); MS: *m/z* 207 (M^+, 100%), 208 (13.6%), 152 (99%). Further elution afforded the 1,5-abstraction product as a colourless oil (0.19 g, 14%); (R_f 0.13, 50% EtOAc/PE).

6-Hydroxymethyl-3-azabicyclo[3.2.0]hept-6-ene-2,4-dione:

A solution of maleimide (0.5 g, 5.15 mmol) and propargyl alcohol (0.45 mL, 7.73 mmol) in acetonitrile (100 mL) was irradiated for 1 h. The solvent was removed under reduced pressure and flash chromatography of the residue (EtOAc) afforded the title compound as a colourless solid (0.63 g, 79%); mp 106-108°C (EtOAc); (Found: C, 54.91; H, 4.45; N, 9.01. $C_7H_7NO_3$ requires: C, 54.90; H, 4.61 ; N, 9.15%); ν_{max}/cm^{-1} 3418 (OH), 3256 (NH), 1762 (C=O) and 1717 (C=O); δH (d^6DMSO): 10.86 (1H, br., NH), 6.21 (1H, s, vinyl), 5.02 (1H, br, OH), 3.95 (2H, br., CH_2OH), 3.66 (1H, d, *J* 3.0Hz, cyclobutene CH), 3.56 (1H, br, cyclobutene CH); δC: 176.82 (Q), 175.65 (Q), 152.89 (Q), 129.04 (CH), 57.95 (CH_2), 48.54 (CH), 45.41 (CH); MS: *m/z* 153.1 (M^+, 57.16%).

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