Exploiting Domino Enyne Metathesis Mechanisms For Skeletal Diversity Generation

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Table of Contents

1 Experimental: Procedures and Data

1.1 General Procedures

Experimental techniques were performed using oven dried glassware apparatus unless otherwise indicated. Reactions were performed under nitrogen with dry, freshly distilled solvents.

Dichloromethane, ethyl acetate, methanol and acetonitrile were distilled from calcium hydride. Tetrahydrofuran and diethyl ether were distilled over a mixture of lithium aluminium hydride and calcium hydride in the presence of triphenyl methane. Petrol was distilled before use and refers to the 30-40 °C fraction. Anhydrous DMF and pyridine were used as supplied by Fluka in sureseal™ bottles. *n*-BuLi in hexane (Aldrich) was titrated with benzyl-biphenyl-4-ylmethylene-amine and anhydrous menthol before use. Cyclopentadiene was prepared by cracking dicyclopentadiene (Aldrich) at atmospheric pressure and collecting the monomer at 0 °C. All other reagents were purified in accordance with the instructions in 'Purification of Laboratory Chemicals'[1] or used as obtained from commercial sources.

Room temperature (RT) refers to ambient temperature. Temperatures of 0 °C were maintained using an ice-water bath and temperature of -78 °C were maintained using an acetone-cardice bath. Reactions involving microwave irradiation were performed in 10 ml or 30 ml microwave tubes with clip lids using CEM Discover® microwave apparatus.

Yields refer to chromatographically and spectroscopically pure compounds. All reactions were monitored by thin layer chromatography (TLC) using glass plates precoated with Merck silica gel 60 F254. Visualisation was by the quenching of UV fluorescence (ν_{max} = 254 nm) or by staining with either: ceric ammonium molybdate; potassium permanganate; or, Dragendorff's reagent (0.08 % w/v bismuth subnitrate and 2 % w/v KI in 3M aq. AcOH). Retention factors (R_f) are quoted to 0.01. All flash column chromatography was performed using Merck 9385 Kieselgel 60 silica gel.

Melting points were obtained using a Reichert hot plate microscope with a digital thermometer attachment and are uncorrected.

Infrared spectra were recorded neat on a Perkin-Elmer Spectrum One spectrometer with internal referencing. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}).

Proton magnetic resonance spectra were recorded on Bruker Ultrashield 400 or 500. Proton assignments are supported by ^1H-^1H correlation (COSY) spectra where necessary. Chemical shifts (δ_H) are quoted in ppm to the nearest 0.01 ppm and are referenced to the residual non-deuterated solvent peak (7.26 ppm for $CHCl_3$ of $CDCl_3$, 2.54 ppm for DMSO of d_6-DMSO). Coupling constants (*J*) are reported in Hertz to the nearest 0.5 Hz. Data are reported as follows: chemical shift; integration; multiplicity [app, apparent; br, broad; s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet; or as a combination of these (e.g. app s, br d, dd, dt, ddd.)]; coupling constant(s); and, assignment. Diastereotopic protons are assigned as H_a and H_b, where the H_a indicates the lower field proton.

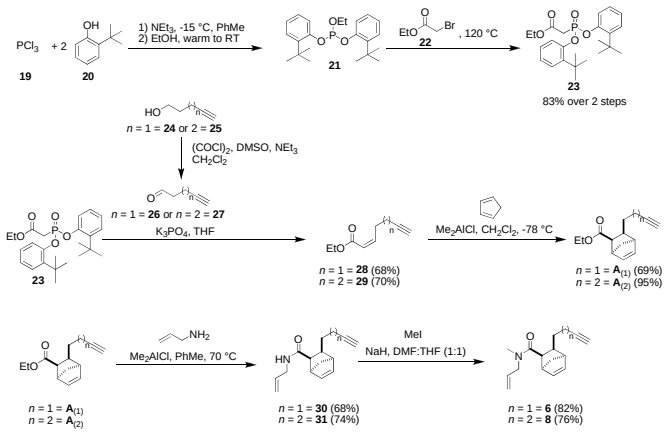
Carbon magnetic resonance spectra were recorded on Bruker 400 or 500 spectrometers operating at 100 and 125 MHz respectively. Carbon spectra assignments are supported by DEPT editing and, where necessary, ^{13}C-^1H correlation (HMQC) spectra and ^{13}C-^1H long range correlation (HMBC) spectra. Chemical shifts (δ_C) are quoted in ppm to the nearest 0.1 ppm, and are referenced to the deuterated solvent peak (77.0 ppm for ^{13}C of $CDCl_3$, 40.45 ppm for ^{13}C of d_6-DMSO). Coupling constants (*J*) are reported in Hertz to the nearest 1 Hz. Data are reported as follows: chemical shift; multiplicity (singlet unless otherwise stated; d, doublet); coupling constant; and, assignment.

LCMS spectra were recorded on an HP/Agilent MSD LC-MS APCI+ 120-1000 full gradient ACq T = 1 min 1μl. High resolution mass measurements were made by the EPSRC mass spectrometry service (Swansea) or using a Waters LCT Premier Mass Spectrometer (University of Cambridge, Department of Chemistry). Electrospray ionisation (ESI) was used in both cases.

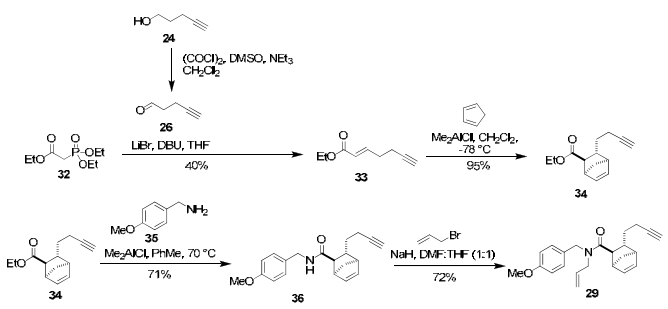
The numbering/lettering on the structures does not follow the IUPAC naming system and is used for the assignment of the ^1H-NMR and ^{13}C-NMR spectra. Most nuclei are denoted by a superscript lowercase letter, where x is 1-3 *e.g.* C^aH_x (NB a capital J is used for clarity *i.e.* C^JH_x). For groups such as OCH_2CH_3, NCH_2CH_3, $C(CH_3)_3$, $Si(CH_3)_3$ and $Si(CH(CH_3)_2)_3$ the nuclei described is denoted by H for ^1H-NMR spectra and C for ^{13}C-NMR spectra *e.g.* OCH_2CH_3 or OCH_2CH_3.

1.2 Preparation of the Metathesis Substrates $A_{(1)}$, $A_{(2)}$, 6, 8, and 16

The *cis* norbornene substrates $\mathbf{A}_{(1)}$, $\mathbf{A}_{(2)}$, **6**, and **8** were synthesized from the 'Ando-like' phosphonate **23** (Supporting Information Scheme 1). The *trans* norbornene amide **16** could be accessed from triethyl phosphonoacetate **32** (Supporting Information Scheme 2).



Supporting Information Scheme 1

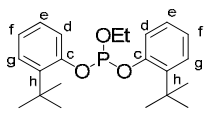


Supporting Information Scheme 2

[1] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Butterworth-Heinmann, **2003**.

1.2.1 Synthesis of the 'Ando-like' Phosphonate 23

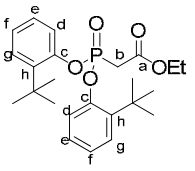
1.2.1.1 Di-(2-tert-butyl-phenyl) ethyl phosphite 21



Using the procedure reported by Touchard *et al.*,[2] a round bottom flask, equipped with an overhead stirrer, containing phosphorus trichloride **19** (6.35 ml, 72.8 mmol) and PhMe (160 ml) at -25 °C was charged dropwise sequentially with 2-*t*-butylphenol **20** (21.8 ml, 141.9 mmol) over 10 minutes followed by NEt_3 (30.6 ml, 219.9 mmol) over 45 minutes. The reaction mixture was stirred at -15 °C to -20 °C for 3 hours before being charged with EtOH (4.08 ml, 69.9 mmol) and allowed to warm to room temperature overnight. The reaction mixture was quenched by the addition of H_2O, the organic layers washed with H_2O (x 2), dried ($MgSO_4$), filtered through a pad of basic alumina and the solvent removed *in vacuo* to give the phosphite **21** as pale yellow oil (26.95 g, 98%) that was used in the next step without further purification.

δ_H (400 MHz; $CDCl_3$) 7.35 (2H, d, *J* 7.5 1.5, C^gH), 7.22 (2H, dt, *J* 8.0 1.5, C^eH), 7.14-7.09 (2H, m, C^fH), 7.03-6.98 (2H, m C^dH), 4.20 (2H, quin, *J* 7.0, $C\underline{H}_2CH_3$), 1.42 (18H, s, 2 x $C(C\underline{H}_3)_3$), 1.29 (3H, t, *J* 7.0 $OCH_2C\underline{H}_3$).

1.2.1.2 Di-(2-tert-butyl-phenyl) ethyl phosphonoacetate 23



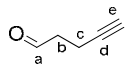
Using the procedure reported by Touchard *et al.*,[2] a round bottom flask, equipped with a magnetic stirrer, containing ethyl bromoacetate **22** (16.2 ml, 145.6 mmol) and the phosphite **21** was heated at 130 °C overnight. The reaction mixture was cooled and excess ethyl bromoacetate was removed by distillation *in vacuo*. The resulting crude yellow solid was purified by recrystallisation (*n*-heptane) to give the title compound **23** as a white crystalline solid (21.45 g, 68%).

ν_{max} (neat)/cm^{-1} 2959w, 2912w, 2978w, 1740s (C=O), 1487m, 1441m, 1299m, 1277m, 1257m, 177m, 1116w, 933s; δ_H (400 MHz; $CDCl_3$) 7.68 (2H, dt, *J* 8.0 1.0, 2 x C^gH), 7.36 (2H, dt, *J* 7.7 1.7, 2 x C^eH), 7.18-7.06 (4H, m, 4 x C^dH and C^fH), 4.12 (2H, q, *J* 7.3, $OC\underline{H}_2CH_3$), 3.36 (2H, d, *J* 21.6, C^bH_2), 1.37 (18H, s, 2 x $C(C\underline{H}_3)_3$), 1.15 (3H, t, *J* 7.3, $OCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 164.4 (d, *J* 6.1, C^a), 150.1 and 150.0 (d, *J* 8.4, C^c), 139.2 and 139.1 (d, *J* 8.4, C^h), 127.6 (C^gH), 127.4 (C^eH), 124.6 (C^fH), 119.6 (C^dH), 62.0 ($O\underline{C}H_2CH_3$), 36.4 and 34.7 (d, *J* 138.7, C^bH_2), 34.9 ($C(\underline{C}H_3)_3$), 30.1 ($\underline{C}(CH_3)_3$), 13.8 ($OCH_2C\underline{H}_3$); mp 91-93 °C (*n*-heptane) (Lit. 90 °C (*n*-heptane)).[3] The data obtained was consistent with that reported previously.[3]

1.2.2 General Procedure for the Swern Oxidation

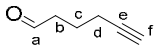
A round-bottom flask, equipped with a magnetic stirrer, containing oxalyl chloride (1.15 equiv.) and CH_2Cl_2 (3.0 ml/mmol alcohol) at -78 °C was charged dropwise with anhydrous dimethyl sulfoxide (2.4 equiv.) and stirred for 15 minutes. The resulting mixture was charged dropwise with a solution of the alcohol (1 equiv.) and CH_2Cl_2 (0.5 ml/mmol alcohol) and stirred for 15 minutes before being charged dropwise with NEt_3 (5 equiv.). The now thick grey/yellow reaction mixture was stirred for 1 hour at -78 °C before being allowed to slowly warm to room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 and quenched by the addition of H_2O. The aqueous layer was acidified with aqueous 2N HCl solution, extracted with CH_2Cl_2 (x 2) and the combined organic layers washed sequentially with 1% aqueous HCl solution in saturated aqueous NaCl solution, followed by 5% aqueous $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2 (x 1), the combined organic layers washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and the solvent removed (with care) *in vacuo* to give the (volatile) crude aldehyde which was immediately used in the next step without further purification:

1.2.2.1 Pent-4-ynal 26 (crude)



An orange oil/paste. δ_H (400 MHz; $CDCl_3$) 9.82 (1H, s, C^aH), 2.74-2.66 (2H, m, C^bH_2), 2.54-2.48 (2H, m, C^cH_2), 2.17 (1H, s, C^eH). The data obtained was consistent with that previously reported by Kulkarni *et al.*[4]

1.2.2.2 Hex-5-ynal 27 (crude)



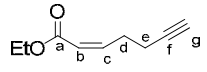
An orange oil/paste. δ_H (400 MHz; $CDCl_3$) 9.77 (1H, s, C^aH), 2.59-2.48 (2H, m, C^bH_2), 2.24-2.20 (2H, m, C^dH_2), 1.95 (1H, t, *J* 2.6, C^fH), 1.82 (2H, quin, *J* 7.0, C^cH_2). The data obtained was consistent with that previously reported by Dupuy and Surzur.[5]

1.2.3 General Procedure for the Modified Horner-Wadsworth-Emmons Reaction

Using an adapted procedure similar to that reported by Touchard *et al.*,[2] a round-bottom flask, equipped with a magnetic stirrer, containing K_3PO_4 (2 equiv.), the phosphonate **23** (1.3 equiv.) and THF (15 ml/mmol alcohol) at room temperature was charged with a solution of the crude aldehyde (1 equiv.) and THF (0.5 ml/mmol alcohol) and stirred at room temperature overnight. The reaction mixture was filtered through a pad of silica, the silica washed with PhMe (x 3) and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

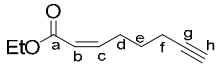
[2] F. P. Touchard, N. Capelle, M. Mercier, *Adv. Synth. Catal.* **2005**, 347, 707.
[3] F. P. Touchard, *Eur. J. Org. Chem.* **2005**, 1790.
[4] B. A. Kulkarni, A. Sharma, S. Gamre, S. Chattopadhyay, *Synthesis* **2004**, 4, 595.
[5] C. Dupuy, J.-M. Surzur, *Bull. Soc. Chim. Fr.* **1980**, Part 2, 374

1.2.3.1 (*Z*)-Hept-2-en-6-ynoic acid ethyl ester 28



A yellow oil (3.11 g, 68%). R_f 0.29 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3297w (C≡H), 2982w, 2117w (C≡C), 1715s (C=O), 1646m, 1415m, 1217m, 1189s, 1165s, 1030m; δ_H (400 MHz; $CDCl_3$) 6.30 (1H, dt, *J* 11.7 6.9, C^cH), 5.83 (1H, app dt, *J* 11.7 1.7, C^bH), 4.12 (2H, q, *J* 7.3, $OC\underline{H}_2CH_3$), 2.87 (2H, ddd, *J* 9.1 6.9 1.7, C^dH_2), 2.33 (2H, app td, *J* 7.3 2.7, C^eH_2), 2.96 (1H, t, *J* 2.8, C^gH), 1.28 (3H, t, *J* 7.3, $OCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 166.1 (C^a), 147.4 (CH^c), 121.0 (C^bH), 82.3 (C^f), 69.0 (C^gH), 59.9 ($O\underline{C}H_2CH_3$), 27.7 (C^dH_2), 18.0 (C^eH_2), 14.2 ($OCH_2\underline{C}H_3$); LCMS (APCI+) 153 ($M+H^+$).

1.2.3.2 (*Z*)-Oct-2-en-7-ynoic acid ethyl ester 29

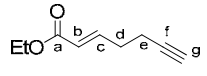


A pale yellow oil (70%). R_f 0.40 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3300w (C≡H), 2882w, 2937w, 2118w (C≡C), 1715s (C=O), 1644m, 1416m,1184s, 1156s, 1031m; δ_H (400 MHz; $CDCl_3$) 6.17 (1H, dt, *J* 11.3 7.6, C^cH), 5.75 (1H, dt, *J* 11.3 1.7, C^bH), 4.13 (2H, q, *J* 7.1, $OC\underline{H}_2CH_3$), 2.72 (2H, ddd, *J* 9.1 7.6 1.7, C^dH_2), 2.19 (2H, app td, *J* 7.1 2.6, C^fH_2), 1.93 (1H, t, *J* 2.9, C^hH), 1.65 (2H, quin, *J* 7.3, C^eH_2), 1.25 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 166.2 (C^a), 148.7 (C^cH), 120.5 (C^bH), 83.8 (C^g), 68.6 (C^hH), 59.8 ($O\underline{C}H_2CH_3$), 28.1 (C^dH_2), 27.9 (C^eH_2), 18.1 (C^fH_2), 14.2 ($OCH_2\underline{C}H_3$); HRMS (ESI, $M+H^+$) found 167.1074, $C_{10}H_{15}O_2^+$ required 167.1078, Δppm +2.3.

1.2.4 General Procedure for the Horner-Wadsworth-Emmons Reaction

A round-bottom flask, equipped with a magnetic stirrer, containing lithium bromide (1 equiv.) and THF (3 ml/mmol aldehyde) at room temperature was charged sequentially with a solution of the crude aldehyde and THF (1.5 ml/mmol aldehyde), triethyl phosphonoacetate **32** (1 equiv.) and DBU (1 equiv.) and stirred at room temperature for 16 hours. The reaction mixture was quenched by the addition of water and stirred for 1 hour. The reaction mixture was extracted with CH_2Cl_2 (x 3), the combined organic layers washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.2.4.1 (*E*)-Hept-2-en-6-ynoic acid ethyl ester 33

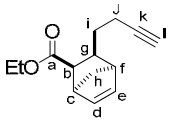


A pale yellow oil (1.46 g, 40%). R_f 0.41 (SiO_2; 1:9 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3293w (C≡H), 2983w, 2119w (C≡C), 1716s (C=O), 1656m, 1435w, 1367m, 1267s, 1203s, 1156s, 973m; δ_H (400 MHz; $CDCl_3$) 6.95 (1H, dt, *J* 15.6 6.6, C^cH), 5.86 (1H, dt, *J* 15.6 1.3, C^bH), 4.16 (2H, q, *J* 7.0, $OC\underline{H}_2CH_3$), 2.44-2.36 (2H, m, C^dH_2), 2.35-2.30 (2H, m, C^eH_2), 1.98 (1H, t, *J* 2.4, C^gH), 1.26 (3H, t, *J* 7.0, $OCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 166.3 (C^a), 146.2 (C^cH), 122.5 (C^bH), 82.6 (C^f), 69.3 (C^gH), 60.2 ($O\underline{C}H_2CH_3$), 30.9 (C^dH_2), 17.3 (C^eH_2), 14.2 ($OCH_2\underline{C}H_3$); LCMS (APCI+) 153 ($M+H^+$). The data obtained was consistent with that reported previously.[6]

1.2.5 General Procedure for the Diels Alder Reaction

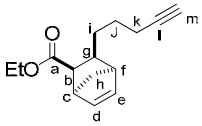
A round-bottomed flask, equipped with a magnetic stirrer, containing the alkene (1 equiv.), cyclopentadiene (10 equiv.) and CH_2Cl_2 (5.5 ml/mmol alkene) at -78 °C was slowly charged with dimethylaluminium chloride (1 M solution in hexane, 1.4 equiv.) over 15 minutes. The clear yellow solution was stirred at -78 °C for 1 hour and then allowed to warm to room temperature overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl solution, the aqueous layer extracted with CH_2Cl_2 (x 3), the combined organic layers dried ($MgSO_4$) and solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.2.5.1 (1*S**, 2*R**, 3*S**, 4*R**)-ethyl 3-(but-3-ynyl) bicyclo[2.2.1]hept-5-ene-2-carboxylate $A_{(1)}$



A colourless oil (0.98 g, 69%). R_f 0.30 (SiO_2; 2.5:97.5 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3298w (C≡H), 2971w, 2938w, 2871w, 2117w (C≡C), 1737s (C=O), 1454w, 1374w, 1339w, 1246w, 1179s, 1149s, 1040m; δ_H (400 MHz; $CDCl_3$) 6.36-6.32 (1H, dd, *J* 5.6 2.7, C^eH), 6.08-6.04 (1H, dd, *J* 5.6 2.8, C^dH), 4.09-3.02 (2H, q, *J* 7.3, $OC\underline{H}_2CH_3$), 3.08-3.00 (2H, m, C^bH and C^fH), 2.89 (1H, app s, C^cH), 2.65-2.56 (1H, m, C^gH), 2.26-2.08 (2H, m, C^JH_2), 1.95-1.92 (1H, t, *J* 2.8, C^lH), 1.64-1.54 (1H, m, $C^i\underline{H}_aH_b$), 1.48-1.44 (1H, br d, *J* 8.3, $C^h\underline{H}_aH_b$), 1.31-1.27 (1H, br d, *J* 8.3, $C^hH_a\underline{H}_b$), 1.26-1.10 (3H, t, *J* 7.3, $OCH_2C\underline{H}_3$), 1.16-1.05 (1H, m, $C^iH_a\underline{H}_b$); δ_C (100 MHz; $CDCl_3$) 173.6 (C^a), 137.0 (C^eH), 132.9 (C^dH), 84.1 (C^k), 68.4 (C^lH), 59.9 ($O\underline{C}H_2CH_3$), 48.7 (C^hH_2), 48.1 (C^bH), 45.9 (C^cH or C^fH), 45.2 (C^cH or C^fH), 42.9 (C^gH), 28.8 (C^iH_2), 17.3 (C^JH_2), 14.3 ($OCH_2\underline{C}H_3$); HRMS (ESI, $M+Na^+$) found 241.1206, $C_{14}H_{18}O_2Na^+$ required 241.1209, Δppm +1.8.

1.2.5.2 (1*S**, 2*R**, 3*S**, 4*R**)-ethyl 3-(pent-4-ynyl) bicyclo[2.2.1]hept-5-ene-2-carboxylate $A_{(2)}$

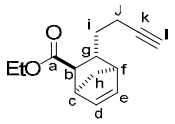


A colourless oil (1.18 g, 95%). R_f 0.17 (SiO_2; 1:9 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3297w (C≡H), 2970w, 2937w, 2868w, 2117w (C≡C), 1731s (C=O), 1459w, 1373w, 1338m, 1253m, 1179s, 1147s, 1040m; δ_H (400 MHz; $CDCl_3$) 6.33 (1H, dd, *J* 5.6 2.8, C^eH), 6.05 (1H, dd, *J* 5.6 2.9, C^dH), 4.13-3.97 (2H, m, $OC\underline{H}_2CH_3$), 3.06-2.95 (2H, m, C^bH and C^fH), 2.84 (1H, app s, C^cH), 2.48-2.37 (1H, m, C^gH), 2.13 (2H, app td, J 2.8, 2.7, C^kH_2), 1.91 (1H, t, *J* 2.6, C^mH), 1.64-1.36 (4H,

[6] H.-L. Huang, R.-S. Liu, *J. Org. Chem.* **2003**, 68, 805.

m, $C^iH_aH_b$, C^JH_2 and $C^hH_aH_b$) 1.29-1.16 (4H, m, $C^hH_aH_b$ and OCH_2CH_3), 1.00-0.85 (1H, m, $C^iH_aH_b$); δ_C (100 MHz; $CDCl_3$) 173.8 (C^a), 136.8 (C^eH), 132.9 (C^dH), 84.4 (C^l), 68.2 (C^mH), 59.8 (OCH_2CH_3), 48.6 (C^hH_2), 48.2 (C^bH), 45.8 (C^cH or C^fH), 45.5 (C^cH or C^fH), 43.7 (C^gH), 29.3 (C^iH_2), 27.4 (C^JH_2) 18.5 (C^kH_2), 14.3 (OCH_2CH_3); HRMS (ESI, $M+H^+$) found 233.1537, $C_{15}H_{21}O_2^+$ required 233.1547, Δppm +4.29.

1.2.5.3 (1*S**, 2*R**, 3*R**, 4*R**)-ethyl 3-(but-3-ynyl) bicyclo[2.2.1]hept-5-ene-2-carboxylate 34

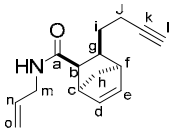


A colourless oil (1.12 g, 95%). R_f 0.39 (SiO_2; 1:9 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3301w (C≡H), 2975w, 2114w (C≡C), 1727s (C=O), 1447w, 1271w, 1333m, 1267m, 1194s, 1173s, 1115m, 1034s; δ_H (400 MHz; $CDCl_3$) 6.46 (1H, dd, *J* 5.6 3.1, C^eH), 5.97 (1H, dd, *J* 5.6 3.1, C^dH), 4.08-3.98 (2H, m, OCH_2CH_3), 3.08 (1H, app s, C^cH), 2.57 (1H, app s, C^fH), 2.40 (1H, t, *J* 4.1, C^bH), 2.27-2.22 (2H, m, C^JH_2), 1.90 (1H, t, *J* 2.7, C^lH), 1.89-1.73 (1H, m, C^gH), 1.74-1.62 (2H, m, C^iH_2), 1.45-1.38 (2H, m, C^hH_2), 1.18 (3H, t, *J* 7.2, OCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 174.1 (C^a), 138.1 (C^eH), 133.8 (C^dH), 84.3 (C^k), 68.3 (C^lH), 60.1 (OCH_2CH_3), 51.1 (C^bH), 46.9 (C^fH), 46.3 (C^hH_2), 45.6 (C^cH), 43.1 (C^gH), 34.9 (C^iH_2), 17.7 (C^JH_2), 14.2 (OCH_2CH_3); HRMS (ESI, $M+H^+$) found 219.1384, $C_{14}H_{19}O_2$ required 219.1385, Δppm -0.5

1.2.6 General Procedure for Amide Formation

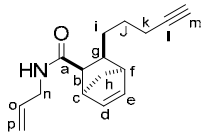
A round bottom flask, equipped with a magnetic stirrer, containing the ester (1 equiv.) and PhMe (40 ml/mmol ester) at room temperature was charged with a solution of the amine (3 equiv.), dimethyl aluminium chloride (1 M solution in hexanes, 3 eqiuv.) and PhMe (10 ml/mmol ester) that had been pre-stirred for 30 minutes at room temperature. The reaction mixture was heated at 65 °C overnight. The reaction mixture was diluted with PhMe, quenched with saturated aqueous NH_4Cl solution, the aqueous layer extracted with PhMe (x 3), the combined organic layers washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.2.6.1 (1*S**, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(but-3-ynyl) bicyclo[2.2.1]hept-5-ene-2-carbox-amide 30



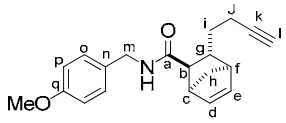
A pale yellow oil (0.18 g, 68%). R_f 0.42 (SiO_2; 6:4 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3304m br, 3076w br, 2965m, 2869w, 2118w (C≡C), 1643s (C=O), 1537s br, 1342w, 1254m, 1224m, 912m; δ_H (400 MHz; $CDCl_3$) 6.40 (1H, dd, *J* 5.6 2.8, C^eH), 6.13 (1H, dd, *J* 5.6 2.8, C^dH), 5.87-5.75 (1H, m, C^nH), 5.55-5.45 (1H, app s, NH), 5.32 (1H, dd, *J* 17.2 1.0, $C^oH_{trans}H_{cis}$), 5.13 (1H, dd, *J* 10.5 1.0, $C^oH_{trans}H_{cis}$), 3.87-3.80 (2H, m, C^mH_2), 3.03-2.99 (1H, app s, C^fH), 2.94-2.86 (2H, m, C^bH and C^cH), 2.66-2.56 (1H, m, C^gH), 2.27-2.08 (2H, m, C^JH_2), 1.95 (1H, t, *J* 2.4, C^lH), 1.57-1.45 (2H, m, $C^hH_aH_b$ and $C^lH_aH_b$), 1.32 (1H, br d, *J* 8.3, $C^hH_aH_b$), 1.26-1.15 (1H, m, $C^lH_aH_b$); δ_C (100 MHz; $CDCl_3$) 172.7 (C^a), 136.4 (C^eH), 134.5 (C^nH), 133.7 (C^dH), 116.5 (C^oH_2), 84.2 (C^k), 68.5 (C^lH), 50.1 (C^bH), 49.6 (C^hH_2), 46.6 (C^cH or C^fH), 46.5 (C^cH or C^fH), 43.1 (C^gH), 41.9 (C^mH_2), 28.7 (C^iH_2), 17.3 (C^JH_2); HRMS (ESI, $M+H^+$) found 230.1548 $C_{15}H_{20}NO$, required 230.1545, Δppm 1.3.

1.2.6.2 (1*S**, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(pent-4-ynyl) bicyclo[2.2.1]hept-5-ene-2-carbox- amide 31



A pale yellow oil (0.37 g, 74%). R_f 0.25 (SiO_2; 6:4 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3305m br, 3061w br, 2964m, 2835w, 2866m, 2118w (C≡C), 1642s (C=O), 1536s br, 11429w, 1255m, 1223m, 990w, 910s; δ_H (400 MHz; $CDCl_3$) 6.38 (1H, dd, *J* 5.6 2.8, C^eH), 6.13 (1H, dd, *J* 5.6 3.1, C^dH), 5.86-5.74 (1H, m, C^oH), 5.58-5.45 (1H, app s, NH), 5.20-5.05 (2H, m, C^pH_2), 3.89-3.76 (2H, m, C^nH_2), 3.01-2.97 (1H, app s, C^fH), 2.91-2.83 (2H, m, C^bH and C^cH), 2.46-2.35 (1H, m, C^gH), 2.16-2.08 (2H, m, C^kH_2), 1.91 (1H, t, *J* 2.4, C^mH), 1.63-1.25 (5H, m, C^hH_2, $C^iH_aH_b$ and C^JH_2), 1.08-0.97 (1H, m, $C^iH_aH_b$); δ_C (100 MHz; $CDCl_3$) 172.9 (C^a), 136.2 (C^eH), 134.5 (C^oH), 133.9 (C^dH), 116.4 (C^pH_2), 84.5 (C^l), 68.2 (C^mH), 50.3 (C^bH), 49.6 (C^hH_2), 46.4 (C^cH or C^fH), 45.8 (C^cH or C^fH), 43.9 (C^gH), 41.8 (C^nH_2), 29.3 (C^iH_2), 27.5 (C^JH_2), 18.5 (C^kH_2); HRMS (ESI, $M+Na^+$) found 266.1523, $C_{16}H_{21}NONa$ required 266.1521, Δppm 0.8.

1.2.6.3 (1*S**, 2*R**, 3*R**, 4*R**)-3-(but-3-ynyl)-*N*-(4-methoxy benzyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide 36



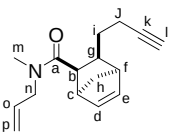
A white solid (1.79 g, 71%). R_f 0.23 (SiO_2; 1:1 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 3294w, 3061w (C≡H), 2964w, 2113w (C≡C), 1645s (C=O), 1631w, 1513s, 1458w, 1334w, 1300w, 1247s, 1175m, 1034m; δ_H (400 MHz; $CDCl_3$) 7.16 (2H, d, *J* 8.7, 2 x C^oH), 6.75 (2H, d, *J* 8.7, 2 x C^pH), 6.29 (1H, dd, *J* 5.6 3.1, C^eH), 6.04 (1H, dd, *J* 5.6 2.8, C^dH), 5.77 (1H, app s, NH), 4.33 (2H, d, *J* 5.6, C^mH_2), 3.79 (3H, s, OCH_3), 3.11 (1H, s, C^cH), 2.62 (1H, s, C^fH), 2.40 (1H, t, *J* 4.5, C^bH), 2.32-2.36 (2H, m, C^JH_2), 1.85 (1H, t, *J* 2.4, C^lH), 1.83-1.78 (1H, m, C^gH), 1.75-1.67 (2H, m, C^iH_2), 1.53-1.45 (2H, m, C^hH_2); δ_C (100 MHz; $CDCl_3$) 173.6 (C^a), 158.9 (C^q), 138.3 (C^eH), 133.7 (C^dH), 130.6 (C^n), 129.1 (C^oH), 114.0 (C^pH), 84.3 (C^k), 68.9 (C^lH), 55.3 (OCH_3), 52.9 (C^bH), 47.3 (C^fH), 46.8 (C^hH_2), 46.4 (C^cH), 43.1 (C^mH_2), 43.1 (C^gH), 34.9 (C^iH_2), 17.6 (C^JH_2); HRMS (ESI, $M+H^+$) found 310.1802, $C_{20}H_{24}NO_2$ required 310.1802, Δppm +0.9; mp 88-89 °C.

1.2.7 General Procedure for the Alkylation Reaction

A round bottom flask, equipped with a magnetic stirrer, containing the amide (1 equiv.), THF (7 ml/mmol) and DMF (7 ml/mmol) at 0 °C was charged with sodium hydride (60% in mineral oil, 3 equiv.) and stirred for 1 hour. The reaction mixture warmed to room temperature, charged with the alkyl halide (3 equiv.) and stirred at 40 °C overnight. The reaction mixture was quenched by the addition

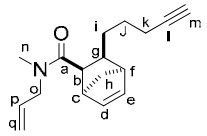
of saturated aqueous NH_4Cl solution, the aqueous layer extracted with EtOAc (x 3), the combined organic layers washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.2.7.1 (1*S**, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(but-3-ynyl)-*N*-methylbicyclo[2.2.1]hept-5-ene-2-carboxamide 6



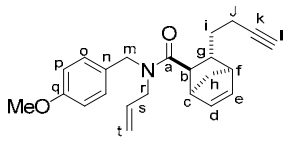
A white solid (0.12 g, 82%). R_f 0.27 (SiO_2; 4:6 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 23297w, 3080w, 2964m, 2115w (C≡H), 1637s (C=O), 1452m, 1433m, 1403s, 1346m, 1263m, 1211m, 1141m, 944m; δ_H (500 MHz; d_6-DMSO, 393K) 6.37 (1H, dd, *J* 5.6 3.1, C^eH), 5.95 (1H, dd, *J* 5.6 3.1, C^dH), 5.85-5.73 (1H, app s, C^oH), 5.20-5.13 (2H, m, C^pH_2), 4.07-3.97 (1H, app s, $C^n\underline{H_a}H_b$), 3.62 (1H, dd, *J* 15.7 5.9, $C^nH_a\underline{H_b}$), 3.23 (1H, d, *J* 8.2, C^cH), 2.92-2.80 (5H, m, C^bH, C^fH, C^mH_3 and H_2O), 2.64-2.47 (2H, m, C^gH, C^lH and DMSO), 2.22-2.07 (2H, m, C^JH_2), 3.25 (2H, t, *J* 1.6, C^iH_2), 1.30-3.33 (1H, m, $C^h\underline{H_a}H_b$), 1.10-1.01 (1H, m, $C^hH_a\underline{H_b}$); HRMS (ESI, M+H^+) found 244.1693, $C_{16}H_{22}NO$ required 244.1701, Δppm -3.3; mp 72-75 °C (Et_2O: Petrol).

1.2.7.2 (1*S**, 2*R**, 3*S**, 4*R**)-*N*-allyl-*N*-methyl-3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide 8



A pale yellow oil (0.32 g, 76%). R_f 0.26 (SiO_2; 3:7 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 3298w, 2938m, 2113w (C≡H), 1642s (C=O), 1405m, 1256w, 1212w, 1142w, 994w; δ_H (500 MHz; d_6-DMSO; 393K) 6.37 (1H, dd, *J* 5.6 3.4, C^eH), 5.94 (1H, dd, *J* 5.6 2.8, C^dH), 5.85-5.72 (1H, app s, C^pH), 5.20-5.13 (2H, m, C^qH_2), 4.12-3.99 (1H, app s, $C^o\underline{H_a}H_b$), 3.78 (1H, dd, *J* 15.4 5.6, $C^oH_a\underline{H_b}$), 3.21 (1H, br d, *J* 8.5, C^cH), 2.93-2.81 (5H, m, C^bH, C^fH, C^nH_3 and H_2O), 2.51-2.44 (2H, m, C^gH, C^mH and DMSO), 2.14 (2H, ddd *J* 9.4 6.9 5.2, C^kH_2), 1.56-1.31 (4H, m, C^iH_2 and C^JH_2), 1.21-1.14 (1H, m $C^h\underline{H_a}H_b$), 0.96-0.88 (1H, m, $C^hH_a\underline{H_b}$); HRMS (ESI, M+Na)$^+$ found 280.1675, $C_{17}H_{23}NONa$ required 0.96-280.1677, Δppm -0.7.

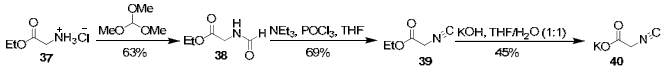
1.2.7.3 (1*S**, 2*R**, 3*R**, 4*R**)-*N*-allyl-3-(but-3-ynyl)-*N*-(4-methoxybenzyl)bicycle[2.2.1] hept-5-ene-2-carboxamide 16



A white solid (0.22 g, 72%). R_f 0.45 (SiO_2; 4:6 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3300w, 2964m, 2116w (C≡H), 1636s (C=O), 1612s, 1585w, 1511s, 1475m, 1439s, 1413s, 3101m, 1245s, 1215s, 1173s, 1033s, 921m; δ_H (400 MHz; d_6-DMSO; 373 K) 7.11 (2H, d, *J* 8.6, 2 x C^oH), 6.89 (2H, d, *J* 8.6, 2 x C^pH), 6.23-6.16 (1H, m, C^eH), 5.86-5.70 (2H, m, C^dH and C^sH), 5.18-5.02 (2H, m, C^tH_2), 4.59 (1H, d, *J* 14.5, $C^m\underline{H_a}H_b$), 4.35 (1H, d, *J* 14.5, $C^mH_a\underline{H_b}$), 4.37-4.08 (2H, m, C^rH_2), 3.75 (3H, s, OCH_3), 3.03-2.89 (2H, m, C^cH and C^fH), 2.73-2.68 (1H, app s, C^gH or C^bH), 2.62-2.56 (1H, br, s, C^gH or C^bH), 2.15-1.99 (3H, m, C^lH and C^JH_2), 1.64-1.49 (3H, m, C^iH_2 and $C^h\underline{H_a}H_b$), 1.29 (1H, d, *J* 8.3, $C^hH_a\underline{H_b}$); HRMS (ESI, M+H^+) found 350.2114, $C_{23}H_{28}NO_2$ required 3510.2115, Δppm -0.1; mp 59-62 °C (Et_2O: Petrol).

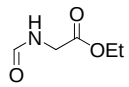
1.3 Preparation of the Isocyanide 40

The isocyante **40** could be synthesised in three steps from glycine ethyl ester hydrogen chloride **37** (Supporting Information Scheme 3).[7]



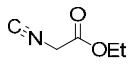
Supporting Information Scheme 3

1.3.1.1 Ethyl 2-formamidoacetate 38



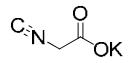
Using the procedure reported by Diver and co-workers,[7] a round bottom flask, equipped with a magnetic stirrer, containing a suspension of gycine ethyl ester hydrochloride **37** (5 g, 35.8 mmol) and trimethylorthoformate (47.0 ml, 429.6 mmol) was heated at 110 °C for 2 hours. The volatiles were removed and the resulting crude yellow oil was purified by distillation *in vacuo* to give the title compound **38** as a pale yellow oil (2.99 g, 63%).

1.3.1.2 Ethyl ester isocyanide 39



Using the procedure reported by Diver and co-workers,[7] a round bottom flask, equipped with a magnetic stirrer, containing **38** (2.99 g, 22.8 mmol), NEt_3 (15.89 ml, 114.1 mmol) and THF (30 ml) at -78 °C was charged dropwise with a solution of phosphoryl chloride (2.50 ml, 27.4 mmol) and THF (16.7 ml) over 30 minutes. The reaction mixture was stirred at -78 °C for 30 minutes before being warmed to 0 °C and stirred for a further 1 hour. The reaction mixture was quenched by the addition of ice water, stirred for 15 minutes, extracted with Et_2O (x 3), the combined organic layers dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by distillation *in vacuo* to give the title compound **39** as a pale yellow oil (1.8 g, 69%). Compound **39** was used immediately in the next step to prevent decomposition.

1.3.1.3 Polar isocyanide 40



Using the procedure reproted by Diver and co-workers,[7] a round bottom flask, equipped with a magnetic stirrer, containing **39** (1.8 g, 12.5 mmol), KOH (0.69 g, 12.3 mmol), THF (7.0 ml) and H_2O (1.75 ml) at room temperature was stirred for 5 hours. The volatiles were removed and the crude compound dried *in vacuo* overnight. The

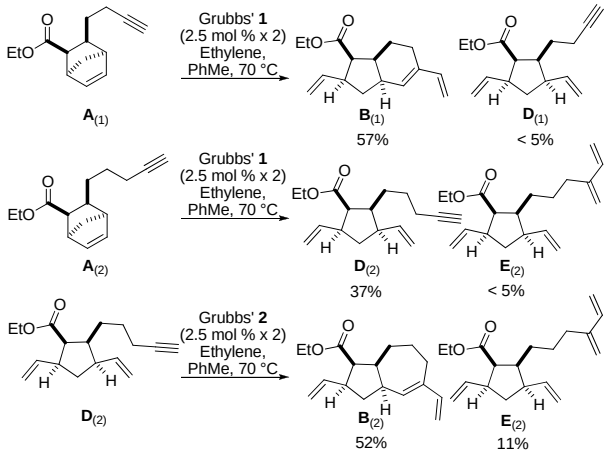
[7] B. R. Galan, K. P. Kalbarczyk, S. Szczepankiewicz, J. B. Keister, S. T. Diver, *Org. Lett.* **2007**, 9, 1203.

grey/yellow solid was washed with Et_2O, pulverised, stirred with Et_2O for 30 minutes and isolated by filtration to give the title compound **40** as a grey/yellow solid (0.95 g, 45%).

ν_{max} (neat)/cm^{-1} 2156m (C≡N), 1615s (C=O), 1570w, 1432m, 1400s, 1378s; δ_H (500 MHz; d_6-DMSO) 3.65 (2H, app s, CH_2). δ_H (125 MHz; d_6-DMSO) 178.2 (C=O), 164.5 (C≡N), 46.8 (CH_2). The data obtained was consistent with that reported previously.[7]

1.4 Scheme 3: Metathesis Reactions of $A_{(1)}$, $A_{(2)}$, and $D_{(2)}$

The metathesis reactions of $\mathbf{A}_{(1)}$, $\mathbf{A}_{(2)}$, and $\mathbf{D}_{(2)}$were performed using Grubbs' 1st generation catalyst **1** and Grubbs' 2nd generation catalyst **2** (Supporting Information Scheme 4).

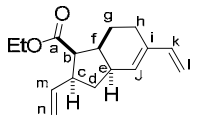


Supporting Information Scheme 4

1.4.1 General Procedure for the Metathesis Reaction with either Grubbs' 1 or Grubbs' 2

A round bottom flask, equipped with a magnetic stirrer, containing the norbornene (1 equiv.) and degassed PhMe (0.01 M) at -78 °C was saturated with ethylene (the gas was bubbled though the reaction mixture *via* a balloon and long needle for 10 minutes), placed under an ethylene atmosphere and charged with a solution the Grubbs' catalyst **1** or **2** (2.5 mol %) and degassed PhMe (0.3 ml/mg catalyst). The reaction mixture was stirred for a further 15 minutes at -78 °C before being warmed to room temperature and heated at 70 °C. After 3 hours, the reaction mixture was charged with a further portion of the Grubbs' catalyst **1** or **2** (2.5 mol %) and degassed PhMe (0.3 ml/mg catalyst) and heated at 70 °C for a further 3 hours. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude products were purified by column chromatography to give:

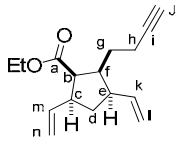
1.4.1.1 (1*R**, 2*S**, 3a*S**, 7a*S**)-ethyl 2,5-divinyl-2,3,3a,6,7,7a-hexahydro-1H-indene-1-carboxylate $B_{(1)}$



A colourless oil (138 mg, 57%). R_f 0.33 (SiO_2; 2.5:97.5 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2978w, 2938w, 2868w, 1730s (C=O), 1640w, 1376m, 1180s, 1155s, 990m; δ_H (500 MHz; $CDCl_3$) 6.33 (1H, dd, *J* 17.3 10.6, C^{k}H), 5.94 (1H, ddd, *J* 17.1 10.1 8.3, C^{m}H), 5.84 (1H, br dd, *J* 3.9 2.3, C^{J}H), 5.11-4.89 (4H, m, C^{l}H$_2$ and C^{n}H$_2$), 4.10-4.02 (2H, m, OC$\underline{H}_2$CH$_3$), 3.16 (1H, t, *J* 8.8, C^{b}H), 2.87-2.74 (1H, m, C^{c}H), 2.59-2.50 (1H, m, C^{e}H), 2.49-2.40 (1H, m, C^{f}H), 2.26 (1H, dt, *J* 16.3 4.2, C$^h\underline{H}_a$H$_b$), 2.05-1.98 (1H, m, C$^d\underline{H}_a$H$_b$), 1.97-1.87 (1H, m, C^{h}H$_a\underline{H}_b$), 1.79-1.73 (1H, m, C$^g\underline{H}_a$H$_b$), 1.67 (1H, q, *J* 11.9, C^{d}H$_a\underline{H}_b$), 1.52-1.41 (1H, m, C^{g}H$_a\underline{H}_b$), 1.22 (3H, t, *J* 7.3, OCH$_2$C$\underline{H}_3$); δ_C (125 MHz; $CDCl_3$) 173.6 (C^a), 139.8 (C^{m}H), 139.5 (C^{k}H), 136.2 (C^i), 130.9 (C^{J}H), 114.8 (C^{n}H$_2$), 110.7 (C^{l}H$_2$), 59.7 (O$\underline{C}$H$_2$CH$_3$), 51.7 (C^{b}H), 46.2 (C^{c}H), 40.5 (C^{e}H), 40.0 (C^{f}H), 37.8 (C^{d}H$_2$), 23.4 (C^{h}H$_2$), 22.5 (C^{g}H$_2$), 14.3 (OCH$_2\underline{C}$H$_3$); HRMS (ESI, M+H$^+$) found 247.1703, $C_{16}H_{23}O_2$ required 247.1698, Δppm 2.0.

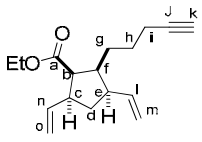
The ring-opened enyne $\mathbf{D}_{(1)}$ was also isolated:

1.4.1.2 (1*R**, 2*S**, 3*R**, 5*S**)-ethyl 2-(but-3-ynyl)-3,5-divinylcyclopentanecarboxylate $D_{(1)}$



A colourless oil (8 mg, 5%). R_f 0.37 (SiO_2; 2.5:97.5 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3310w (C≡H), 2979w, 2935w, 1728s (C=O), 1639w, 1449w, 1382w, 1158s; δ_H (500 MHz; $CDCl_3$) 5.99 (1H, app dt, *J* 16.6 6.4, C^{k}H), 5.80 (1H, ddd, *J* 17.4 10.1 7.2, C^{m}H), 5.12-4.88 (4H, m, C^{l}H$_2$ and C^{n}H$_2$), 4.16-4.03 (2H, m, OC$\underline{H}_2$CH$_3$), 2.95 (1H, t, *J* 6.7, C^{b}H), 2.88-2.97 (1H, m, C^{e}H), 2.77-2.66 (1H, m, C^{c}H), 2.54-2.46 (1H, m, C^{f}H), 2.27-2.13 (2H, m, C^{h}H$_2$), 2.10-2.02 (1H, m, C$^d\underline{H}_a$H$_b$), 1.96-1.88 (2H, m, C^{d}H$_a\underline{H}_b$ and C^{J}H), 1.64-1.44 (2H, m, C^{g}H$_2$), 1.23 (3H, t, *J* 7.0, OCH$_2$C$\underline{H}_3$); δ_C (125 MHz; $CDCl_3$) 173.2 (C^a), 141.5 (C^{k}H), 137.9 (C^{m}H), 115.6 (C^{n}H$_2$), 114.7 (C^{l}H$_2$), 84.1 (C^i), 68.4 (C^{J}H), 59.8 (O$\underline{C}$H$_2$CH$_3$), 51.7 (C^{b}H), 47.1 (C^{e}H), 45.2 (C^{c}H), 44.8 (C^{f}H), 37.8 (C^{d}H$_2$), 27.1 (C^{g}H$_2$), 17.2 (C^{h}H$_2$), 14.4 (OCH$_2\underline{C}$H$_3$); HRMS (ESI, M+H$^+$) found 247.1689, $C_{16}H_{23}O_2$ required 247.1698, Δppm -3.6.

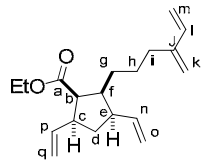
1.4.1.3 (1*R**, 2*S**, 3*R**, 5*S**)-ethyl 2-(pent-4-ynyl)-3,5-divinylcyclopentanecarboxylate $D_{(2)}$



A colourless oil (31 mg, 37%). R_f 0.48 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 3305w (C≡H), 2979w, 2937w, 2867w, 2118w (C≡C), 1727s (C=O), 1639w, 1448w, 1381m, 1190m, 1157s, 913m; δ_H (400 MHz; $CDCl_3$) 6.01 (1H, m, C^{l}H), 5.79 (1H, ddd, *J* 17.4 10.5 7.3, C^{n}H), 5.11-4.87 (4H, m, C^{m}H$_2$ and C^{o}H$_2$), 4.17-4.02 (2H, m, OC$\underline{H}_2$CH$_3$), 2.93 (1H, t, *J* 6.6, C^{b}H), 2.88-2.75 (1H, m, C^{e}H), 2.76-2.64 (1H, m, C^{c}H), 2.35-2.23 (1H, m, C^{f}H), 2.17-1.99 (3H, m, C^{d}H$_2$ and C$^i\underline{H}_a$H$_b$), 1.98-1.85 (2H, C^{i}H$_a\underline{H}_b$ and C^{k}H), 1.58-1.30 (4H, m, C^{g}H$_2$ and C^{h}H$_2$), 1.23 (3H, t, *J* 7.3, OCH$_2$C$\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 173.2 (C^a), 141.8 (C^{l}H), 138.0 (C^{n}H), 115.6 (C^{o}H$_2$), 114.4 (C^{m}H$_2$), 84.4 (C^J), 68.2 (C^{k}H), 59.8 (O$\underline{C}$H$_2$CH$_3$), 53.4 (C^{b}H), 47.2 (C^{e}H), 46.0 (C^{c}H), 45.5 (C^{f}H), 37.6 (C^{d}H$_2$), 27.7 (C^{g}H$_2$ or C^{h}H$_2$), 27.6 (C^{g}H$_2$ or C^{h}H$_2$), 18.6 (C^{i}H$_2$), 14.4 (OCH$_2\underline{C}$H$_3$); HRMS (ESI, M+H$^+$) found 261.1862, $C_{17}H_{25}O_2$ required 261.1855, Δppm 2.7.

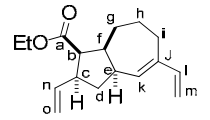
The tetra-ene compound $\mathbf{E}_{(2)}$ was also isolated:

1.4.1.4 (1*R**, 2*S**, 3*R**, 5*S**)-ethyl 2-(4-methylenehex-5-enyl)-3,5-divinylcyclopentane carboxylate $E_{(2)}$



A colourless oil (1.5 mg, 5%). R_f 0.71 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2933m br, 1728s (C=O), 1447w, 1381w, 1189m, 1158s, 909s; δ_H (400 MHz; $CDCl_3$) 6.35 (1H, dd, *J* 17.4 10.8, C^lH), 6.08-5.97 (1H, m, C^nH), 5.82 (1H, ddd, *J* 17.0 10.1 6.9, C^pH), 5.23-4.87 (8H, m, C^kH_2, C^mH_2, C^oH_2 and C^qH), 4.16-4.03 (2H, m, $OC\underline{H}_2CH_3$), 2.5 (1H, t, *J* 6.7, C^bH), 2.87-2.77 (1H, m, C^eH), 2.76-2.65 (1H, m, C^cH), 2.35-2.26 (1H, m, C^fH), 2.21-2.10 (2H, m, C^iH_2), 2.10-1.99 (1H, m, $C^d\underline{H}_aH_b$), 1.98-1.86 (1H, m, $C^dH_a\underline{H}_b$), 1.49 (2H, quin, *J* 7.3, C^hH_2), 1.40-1.17 (5H, m, C^gH_2 and $OCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 173.3 (C^a), 146.4 (C^J), 141.9 (C^nH), 138.9 (C^lH), 138.1 (C^pH), 115.6 (C^kH_2 or C^mH_2 or C^oH_2 or C^qH_2) , 115.4 (C^kH_2 or C^mH_2 or C^oH_2 or C^qH_2), 114.1 (C^kH_2 or C^mH_2 or C^oH_2 or C^qH_2), 113.1 (C^kH_2 or C^mH_2 or C^oH_2 or C^qH_2), 59.7 ($O\underline{C}H_2CH_3$), 53.5 (C^bH), 47.2 (C^cH), 46.4 (C^fH), 45.6 (C^eH), 37.6 (C^dH_2), 31.6 (C^iH_2), 28.4 (C^gH_2), 27.4 (C^hH_2), 14.4 ($OCH_2\underline{C}H_3$); HRMS (ESI, $M+H^+$) found 289.2164, $C_{19}H_{29}O_2$ required 289.2168, Δppm -1.4.

1.4.1.5 (1*R**, 2*S**, 3a*S**, 8a*S**, *E*)-ethyl 2,5-divinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $B_{(2)}$

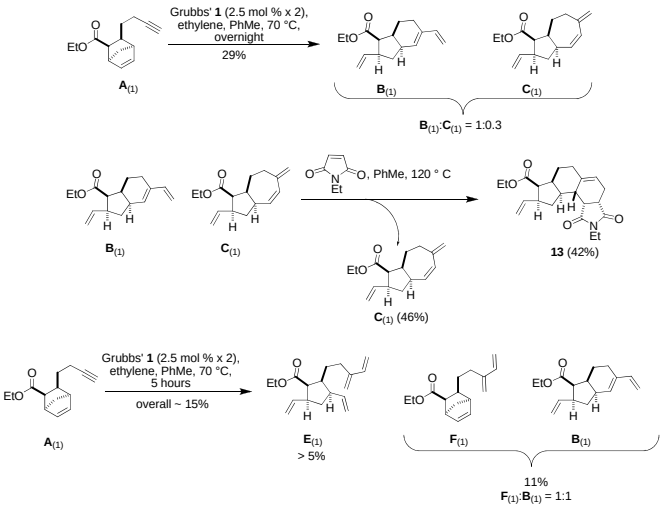


A colourless oil (40.0 mg, 52%).R_f 0.48 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2935w, 2860w, 1729s (C=O), 1640w, 1379m, 1153s; δ_H (400 MHz; $CDCl_3$) 6.36 (1H, dd, *J* 17.1 10.5, C^lH), 5.82 (1H, ddd, *J* 17.4 10.5 7.3, C^nH), 2.77 (1H, br d, *J* 4.1, C^kH), 5.14-4.83 (4H, m, C^mH_2 and C^oH_2), 4.08-4.02 (2H, q, *J* 6.9, $OC\underline{H}_2CH_3$), 3.22-3.10 (1H, m, C^eH), 2.89 (1H, t, *J* 6.9, C^bH), 2.76-2.63 (1H, m, C^cH), 2.49-2.40 (1H, m, $C^i\underline{H}_aH_b$), 2.30-2.08 (4H, m, C^fH, $C^iH_a\underline{H}_b$ and C^dH_2), 1.51-1.40 (4H, m, C^gH_2 and C^hH_2), 1.22 (3H, t, *J* 6.9, $OCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 173.1 (C^a), 138.9 (C^lH), 138.2 (C^nH), 136.1 (C^J or C^kH), 136.0 (C^J or C^kH), 115.6 (C^oH_2), 109.6 (C^mH_2), 59.6 ($O\underline{C}H_2CH_3$), 54.7 (C^bH), 47.1 (C^cH), 42.9 (C^fH), 39.9 (C^eH), 38.1 (C^dH_2), 24.5 (C^gH_2), 23.7 (C^iH_2), 21.3 (C^hH_2), 14.4 ($OCH_2\underline{C}H_3$); HRMS (ESI, $M+H^+$) found 261.1858, $C_{17}H_{25}O_2$ required 261.1855, Δppm 1.1.

The tetra-ene compound $\mathbf{E}_{(2)}$ was also isolated as a colourless oil (4.8 mg, 11%).

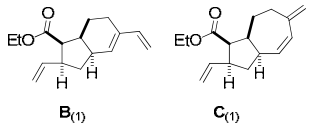
1.5 Scheme 4: a) The Metathesis Reactions of $A_{(1)}$ with Grubbs' 2

Key reactions are shown below (Supporting Information Scheme 5).



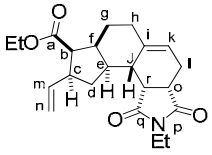
Supporting Information Scheme 5

1.5.1.1 (1*R**, 2*S**, 3a*S**, 7a*S**)-ethyl 2,5-divinyl-2,3,3a,6,7,7a-hexahydro-1H-indene-1-carboxylate $B_{(1)}$ and (1*R**, 2*S**, 3a*R**, 8a*S**, *Z*)-ethyl 6-methylene-2-vinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $C_{(1)}$



A round bottom flask, equipped with a magnetic stirrer, containing the ester $\mathbf{A}_{(1)}$ (100 mg, 0.46 mmol) and degassed PhMe (46 ml) at -78 °C was saturated with ethylene (the gas was bubbled though the reaction mixture *via* a balloon and long needle for 10 minutes), placed under an ethylene atmosphere and charged with a solution Grubbs' **2** (2.5 mol %, 9.7 mg, 11.4 μmmol) and degassed PhMe (3 ml). The reaction mixture was stirred for a further 15 minutes at -78 °C before being warmed to room temperature and heated at 70 °C. After 2 hours, the reaction mixture was charged with a further portion of Grubbs' **2** (2.5 mol %, 9.7 mg, 11.4 μmmol) and degassed PhMe (3 ml) and heated at 70 °C overnight. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude products were purified by column chromatography to give a 1:0.3 inseparable mixture of the *exo*- and *endo*- ring isomers $\mathbf{B}_{(1)}$ and $\mathbf{C}_{(1)}$ as a colourless oil (33 mg, 29%).

1.5.1.2 (3a*S**, 7a*S**, 8*R**, 9*S**, 10a*S**, 10b*S**, 10c*R**)-ethyl 2-ethyl-1,3-dioxo-9-vinyl-1,2,3,3a,4,6,7,7a,8, 9,10,10a, 10b,10c-tetradecahydroindeno[4,5-e]isoindole-8-carboxylate 13



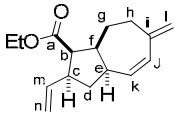
A round bottom flask, equipped with a magnetic stirrer, containing a mixture of $\mathbf{B}_{(1)}$ and $\mathbf{B}_{(2)}$ (24 mg, 97 μmol), *N*-ethylmaleimide (18.2 mg, 0.15 mmol) and PhMe (1.5 ml) was heated at 120 °C overnight. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude products were purified by

column chromatography to give the title compound **13** as colourless oil (11.4 mg, 42%).

R_f 0.31 (SiO_2; 1:9 Et_2OAc: Petrol); ν_{max} (neat)/cm^{-1} 2939w br, 1725m, (C=O), 1695 (C=O), 1443w, 1403m, 1228m, 1159m; δ_H (400 MHz; $CDCl_3$) 5.82 (1H, ddd, *J* 17.1 10.1 7.0, C^mH), 5.49-5.44 (1H, br m, C^kH), 5.11 (1H, app dt, *J* 17.2 1.5, $C^nH_{trans}H_{cis}$), 5.00 (1H, app dt, *J* 10.1 1.5, $C^nH_{trans}H_{cis}$), 4.11-3.98 (2H, m, OCH_2CH_3), 3.46 (2H, q, *J* 7.2, NCH_2CH_3), 3.16-3.09 (1H, m, C^eH), 3.08-3.00 (2H, m, C^rH and C^oH), 2.96 (1H, t, *J* 6.7, C^bH), 2.87-2.78 (1H, m, C^cH), 2.66-2.56 (2H, m, $C^lH_aH_b$ and C^fH), 2.57-2.49 (1H, m, C^JH), 2.45-2.38 (1H, m, $C^dH_aH_b$), 2.17-2.10 (2H, m, $C^lH_aH_b$ and $C^hH_aH_b$), 1.98-1.89 (1H, m, $C^hH_aH_b$), 1.89-1.78 (2H, m, $C^dH_aH_b$ and $C^gH_aH_b$), 1.21 (3H, t, *J* 7.7, OCH_2CH_3), 1.08-1.04 (4H, m, NCH_2CH_3 and $C^gH_aH_b$); δ_C (100 MHz; $CDCl_3$) 179.9 (C^q), 178.2 (C^p), 173.8 (C^a), 143.1 (C^i), 137.9 (C^mH), 117.4 (C^kH), 115.6 (C^nH_2), 59.7 (OCH_2CH_3), 53.9 (C^bH), 47.4 (C^cH), 42.6 (C^fH), 41.6 (C^oH or C^rH), 40.6 (C^JH), 40.0 (C^oH or C^rH), 36.9 (C^dH_2), 34.3 (C^eH), 33.5 (NCH_2CH_3), 31.1 (C^hH_2), 24.8 (C^gH_2), 24.3 (C^lH_2), 14.4 (OCH_2CH_3), 13.0 (NCH_2CH_3); HRMS (ESI, $M+H^+$) found 372.2187, $C_{22}H_{30}NO_4$ required 372.2175, Δppm 3.2.

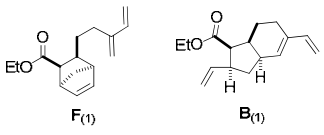
The *endo*- ring isomer $\mathbf{C}_{(1)}$ was also isolated:

1.5.1.3 (1*R**, 2*S**, 3a*R**, 8a*S**, *Z*)-ethyl 6-methylene-2-vinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $\mathbf{C}_{(1)}$



A colourless oil (2.6 mg, 46%). R_f 0.38 (SiO_2; 4% Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2935m br, 1731s (C=O), 1446w, 1379w, 1154m; δ_H (500 MHz; $CDCl_3$) 5.89 (1H, br d, *J* 11.6, C^JH), 5.81 (1H, ddd, *J* 17.6 10.3 7.5, C^mH), 5.36 (1H, dd, *J* 11.6 2.8, C^kH), 5.07 (1H, dt, *J* 1.8 1.76, $C^nH_{trans}H_{cis}$), 4.98 (1H, dt, *J* 10.3 1.0, $C^nH_{trans}H_{cis}$), 4.77-4.74 (2H, br m, C^lH_2), 4.06 (2H, q, *J* 7.3, OCH_2CH_3), 3.27-3.18 (1H, m, C^eH), 2.86 (1H, t, *J* 7.0, C^bH), 2.73-2.58 (2H, m, C^cH and C^fH), 2.47 (1H, dd, *J* 15.0 7.6, $C^hH_aH_b$), 2.37-2.29 (1H, m, $C^hH_aH_b$), 2.28-2.21 (1H, m, $C^dH_aH_b$), 2.04-1.94 (1H, m, $C^dH_aH_b$), 1.91-1.84 (1H, m, $C^gH_aH_b$), 1.47-1.39 (1H, m, $C^gH_aH_b$), 1.19 (3H, t, *J* 7.3, OCH_2CH_3); δ_C (125 MHz; $CDCl_3$) 172.9 (C^a), 148.2 (C^i), 138.2 (C^mH), 135.3 (C^kH), 128.8 (C^JH), 115.5 (C^nH_2), 113.7 (C^lH_2), 59.7 (OCH_2CH_3), 54.3 (C^bH), 49.3 (C^cH), 46.7 (C^eH), 39.7 (C^dH_2), 39.1 (C^fH), 33.4 (C^hH_2), 26.2 (C^gH_2), 15.3 (OCH_2CH_3); HRMS (ESI, $M+H^+$) found 247.1695, $C_{16}H_{23}O_2$ required 247.1698, Δppm -1.2.

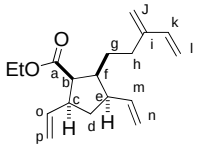
1.5.1.4 (1*S**, 2*R**, 3*S**, 4*R**)-ethyl 3-(3-methylenepent-4-enyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $\mathbf{F}_{(1)}$ and (1*R**, 2*S**, 3a*S**, 7a*S**)-ethyl 2,5-divinyl-2,3,3a,6,7,7a-hexahydro-1H-indene-1-carboxylate $\mathbf{B}_{(1)}$



A round bottom flask, equipped with a magnetic stirrer, containing the norbornene **6** (100 mg, 0.46 mmol) and degassed PhMe (46 ml) at -78 °C was saturated with ethylene (the gas was bubbled though the reaction mixture *via* a balloon and long needle for 10 minutes), placed under an ethylene atmosphere and charged with a solution Grubbs' **2** (2.5 mol %, 9.7 mg, 11.4 μmmol) and degassed PhMe (3 ml). The reaction mixture was stirred for a further 15 minutes at -78 °C before being warmed to room temperature and heated at 70 °C. After 2 hours, the reaction mixture was charged with a further portion of Grubbs' **2** (2.5 mol %, 9.7 mg, 11.4 μmmol) and degassed PhMe (3 ml) and heated at 70 °C for a further 3 hours. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude products were purified by column chromatography to give a 1:1 mixture of the *exo* ring isomers $\mathbf{B}_{(1)}$ and the cross-metathesised norbornene $\mathbf{F}_{(1)}$ as a colourless oil (13 mg, 11%).

The all-ene compound $\mathbf{E}_{(1)}$ was also isolated:

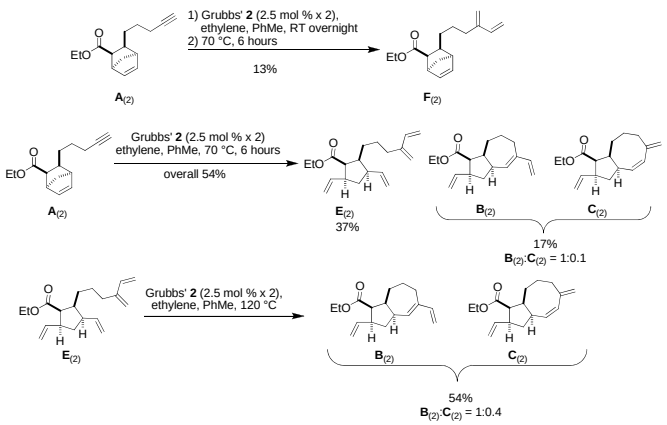
1.5.1.5 (1*R**, 2*S**, 3*R**, 5*S**)-ethyl 2-(3-methylenepent-4-enyl)-3,5-divinylcyclopentane carboxylate $\mathbf{E}_{(1)}$



A white paste (5 mg, 4%). R_f 0.46 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2931m br, 1729s (C=O), 1447w, 1381w, 1158s, 1027w, 911s; δ_H (400 MHz; $CDCl_3$) 6.31 (1H, dd, *J* 17.6 10.9, C^kH), 6.01 (1H, app dt, *J* 16.8 9.8, C^mH), 5.79 (1H, ddd, *J* 17.4 10.4 7.3, C^oH), 5.19 (1H, d, *J* 17.6, $C^lH_{trans}H_{cis}$), 5.11-4.48 (7H, m, $C^lH_{trans}H_{cis}$, C^JH_2, C^nH_2 and C^pH_2), 4.14-4.03 (2H, m, OCH_2CH_3), 2.96 (1H, t, *J* 6.7, C^bH), 2.86-2.77 (1H, m, C^eH), 2.74-2.64 (1H, m, C^cH), 2.36-2.27 (1H, m, C^fH), 2.19 (2H, br t, *J* 7.5, C^hH_2), 2.08-2.00 (1H, m, $C^dH_aH_b$), 1.95-1.86 (1H, m, $C^dH_aH_b$), 1.58-1.39 (2H, m, C^gH_2), 1.23 (3H, t, *J* 7.3, OCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 173.3 (C^a), 146.3 (C^i), 141.8 (C^mH), 138.7 (C^kH), 138.0 (C^oH), 115.7 (C^JH_2 or C^lH_2 or C^nH_2 or C^pH_2), 115.2 (C^JH_2 or C^lH_2 or C^nH_2 or C^pH_2), 114.3 (C^JH_2 or C^lH_2 or C^nH_2 or C^pH_2), 113.3 (C^JH_2 or C^lH_2 or C^nH_2 or C^pH_2), 59.7 (OCH_2CH_3), 53.4 (C^bH), 47.1 (C^cH), 46.1 (C^fH), 45.4 (C^eH), 37.6 (C^dH_2), 30.3 (C^hH_2), 27.0 (C^gH), 14.4 (OCH_2CH_3); HRMS (ESI, $M+H^+$) found 275.2006, $C_{18}H_{27}O_2$ required 257.2011, Δppm -1.8.

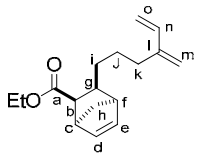
1.6 Scheme 4: b) The Metathesis Reactions of $\mathbf{A}_{(2)}$ with Grubbs' 2

Key reactions are shown below (Supporting Information Scheme 6).



Supporting Information Scheme 6

1.6.1.1 (1*S**, 2*R**, 3*S**, 4*R**)-ethyl 3-(4-methylenehex-5-enyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $\mathbf{F}_{(2)}$

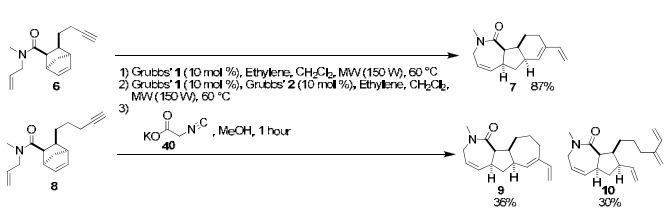


A round bottom flask, equipped with a magnetic stirrer, containing the norbornene $\mathbf{A}_{(2)}$ (100 mg, 0.43 mmol) and degassed PhMe (43 ml) at -78 °C was saturated with ethylene (the gas was bubbled though the reaction mixture *via* a balloon and long needle for 10 minutes), placed under an ethylene atmosphere and charged with a solution Grubbs' **2** (2.5 mol %, 9.3 mg, 10.9 μmmol) and degassed PhMe (2.75 ml). The reaction mixture was stirred for a further 15 minutes at -78 °C before being warmed to room temperature and stirred overnight. TLC analysis showed that $\mathbf{A}_{(2)}$ remained. The reaction mixture was saturated with ethylene and heated at 70 °C for 6 hours. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give the title compound $\mathbf{F}_{(2)}$ as a colourless oil (15 mg, 13%).

R_f 0.30 (SiO_2; 5:95 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2972m, 2936m, 1733s (C=O), 1595w, 1462w, 1373w, 1338w, 1252w, 1178s, 1147s; δ_H (400 MHz; $CDCl_3$) 6.40-6.30 (2H, m, C^eH and C^nH), 6.05 (1H, dd, *J* 5.6 3.1, C^dH), 5.23 (1H, dd, *J* 17.0 0.7, $C^o\underline{H}_{trans}H_{cis}$), 5.17 (1H, dd, *J* 10.8 0.7, $C^oH_{trans}\underline{H}_{cis}$), 5.00-5.49 (2H, 2 x app s, C^mH_2), 4.06 (2H, q, *J* 8.0, $OC\underline{H}_2CH_3$), 3.05-2.99 (2H, m, C^bH and C^fH), 2.88-2.85 (1H, app s, C^cH), 2.51-2.41 (1H, m, C^gH), 2.22-2.11 (2H, m, C^kH_2), 1.59-1.18 (8H, m, C^hH_2, $C^i\underline{H}_a\underline{H}_b$, C^JH_2 and $OCH_2C\underline{H}_3$), 0.95-0.82 (1H, m, $C^i\underline{H}_a\underline{H}_b$); δ_C (100 MHz; $CDCl_3$) 173.9 (C^a), 146.4 (C^l), 138.9 (C^nH), 136.7 (C^eH), 133.1 (C^dH), 115.5 (C^mH_2 or C^oH_2), 113.1 (C^mH_2 or C^oH_2), 59.8 ($O\underline{C}H_2CH_3$), 48.7 (C^hH_2), 48.3 (C^bH), 45.7 (C^cH or C^fH), 45.5 (C^cH or C^fH), 44.0 (C^gH), 31.5 (C^iH_2), 30.0 (C^JH_2), 27.0 (C^kH_2), 14.3 ($OCH_2\underline{C}H_3$); HRMS (ESI, M+H$^+$) found 261.1829, $C_{17}H_{25}O2^+$ required 261.1855, Δppm -0.49.

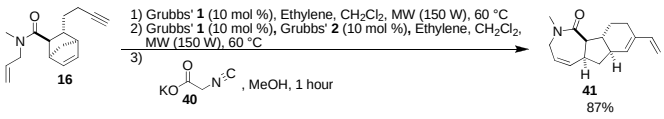
1.7 Scheme 5: Optimised Domino Metathesis of 6 and 8

An optimised procedure for the domino metathesis reactions of **6** and **8** was developed (Supporting Information Scheme 7).



Supporting Information Scheme 7

The 1,3-diene **41** was also synthesised from the *trans* norbornene **16** (Supporting Information Scheme 8).

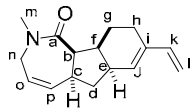


Supporting Information Scheme 8

1.7.1 General Procedure

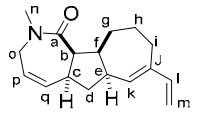
A microwave tube, equipped with magnetic stirrer, containing the norbornene (1 equiv.) and degassed CH_2Cl_2 (0.01M) at -78 °C was saturated with ethylene (the gas was bubbled though the reaction mixture *via* a balloon and long needle for 10 minutes), placed under an ethylene atmosphere and charged with a solution Grubbs' **1** (10 mol %) in degassed CH_2Cl_2 (2.6 ml). The reaction mixture was stirred for a further 15 minutes at -78 °C before being warmed to room temperature. The reaction mixture was heated by microwave irradiation (150 W) at 60 °C for 1 hour. After cooling to room temperature the reaction mixture was cooled to -78 °C, saturated with ethylene and placed under an ethylene atmosphere. The reaction mixture was charged with a solution Grubbs' **1** (10 mol %), Grubbs' **2** (10 mol %) and degassed CH_2Cl_2 (1.0 ml), stirred for 15 minutes at -78 °C before being warmed to room temperature and then heated by microwave irradiation (150 W) at 60 °C for 2 hours. The reaction mixture was cooled to room temperature and quenched *via* the addition of the isocyanate **40** (7 equiv. wrt to catalyst) in MeOH (1 ml) and stirred for 1 hour. The solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2, filtered through a plug of silica to remove the isocyanate **40**, the silica washed with Et_2O and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.7.1.1 (5a*S**, 6a*S**, 10a*S**, 10b*R**, *Z*)-2-methyl-8-vinyl-2,3,6,6a,9,10,10a,10b-octahydroindeno[1,2-c]azepin-1(5aH)-one 7



A white solid (23 mg, 87%). R_f 0.16 (SiO_2; 6:4 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2939m, 2871m, 1622s (C=O), 1485w, 1434w, 1394w, 1337w, 1225w, 991w; δ_H (400 MHz; $CDCl_3$) 6.33 (1H, dd, *J* 17.6 10.9, C^kH), 6.05-5.99 (1H, m, C^oH), 5.82 (1H, br dd, *J* 9.8 4.5, C^pH), 5.78-5.75 (1H, m, C^JH), 5.09 (1H, d, *J* 17.4, $C^l\underline{H}_{trans}H_{cis}$), 4.93 (1H, d, *J* 10.6, $C^lH_{trans}\underline{H}_{cis}$), 4.09 (1H, dd, *J* 14.8 7.3, $C^n\underline{H}_a\underline{H}_b$), 3.37 (1H, dd, *J* 14.8 7.3, $C^nH_a\underline{H}_b$), 3.28 (1H, dd, *J* 10.4 6.2, C^bH), 3.22-3.14 (1H, m, C^cH), 3.04 (3H, s, C^mH_3), 2.63-2.56 (1H, m, C^fH), 2.54-2.40 (2H, m, C^eH and $C^d\underline{H}_a\underline{H}_b$), 2.28-2.22 (1H, m, $C^h\underline{H}_a\underline{H}_b$), 2.02-1.93 (1H, m, $C^hH_a\underline{H}_b$), 1.90-1.83 (1H, m, $C^g\underline{H}_a\underline{H}_b$), 1.61-1.54 (1H, m, $C^dH_a\underline{H}_b$), 1.15-1.06 (1H, m, $C^gH_a\underline{H}_b$); δ_C (100 MHz; $CDCl_3$) 172.2 (C^a), 143.2 (C^pH), 139.6 (C^kH), 135.9 (C^i), 131.5 (C^JH), 127.5 (C^oH), 110.8 (C^lH_2), 55.6 (C^bH), 46.1 (C^nH_2) 42.6 (C^fH), 40.1 (C^dH_2), 37.9 (C^eH), 37.0 (C^mH_3), 36.2 (C^cH), 23.6 (C^hH_2), 22.4 (C^gH_2); HRMS (ESI, M+H$^+$) found 244.1699, $C_{16}H_{22}NO$ required 244.1701, Δppm -0.8; mp 110-113 °C (Et_2O: Petrol).

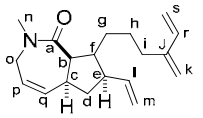
1.7.1.2 (4*Z*, 5a*S, 6a*S**, 7*E*, 11a*S**, 11b*R**)-2-methyl-8-vinyl-2,3,5a,6,6a,9,10,11,11a, 11b-decahydro-1H-azuleno [1,2-c]azepin-1-one 9**



A white paste (11 mg, 36%). R_f 0.34 (SiO_2; 4:6 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2931m, 2863m, 1655 (C=O), 1476m, 1397m, 1208m, 1104w, 990w, 855w; δ_H (400 MHz; $CDCl_3$) 6.41 (1H, dd, *J* 17.4 10.6, C^lH), 5.94-5.86 (1H, m, C^pH), 5.78-5.73 (1H, m, C^qH), 5.54 (1H, d, *J* 4.7, C^kH), 5.09 (1H, d, *J* 17.4, $C^mH_{trans}H_{cis}$), 4.85 (1H, d, *J* 10.6, $C^mH_{trans}H_{cis}$), 4.43-4.34 (1H, m, $C^oH_aH_b$), 3.43 (1H, t, *J* 6.2, C^bH), 3.15 (1H, dd, *J* 16.1 7.5, $C^oH_aH_b$), 3.07-2.96 (1H, m, C^eH), 2.89 (3H, s, C^nH_3), 2.66-2.57 (1H, m, C^cH), 2.45 (1H, dd, *J* 14.0 7.5, $C^iH_aH_b$), 2.33-2.06 (4H, m, C^fH, $C^iH_aH_b$, $C^dH_aH_b$ and $C^gH_aH_b$), 1.59-1.30 (4H, m, $C^dH_aH_b$, $C^gH_aH_b$, C^hH_2); δ_C (125 MHz; $CDCl_3$) 172.8 (C^a), 139.4 (C^lH), 136.2 (C^J), 136.1 (C^kH), 135.2 (C^qH), 124.8 (C^pH), 109.0 (C^mH_2), 48.4 (C^bH), 46.3 (C^oH_2) 44.1 (C^fH), 42.2 (C^cH), 39.2 (C^dH_2), 37.2 (C^eH), 35.0 (C^nH_3), 24.1 (C^gH_2), 23.8 (C^iH_2), 22.2 (C^hH_2); HRMS (ESI, M+H^+) found 258.1841, $C_{17}H_{25}NO$ required 258.1834, Δppm 2.7.

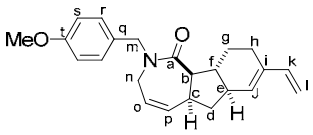
The all-ene compound **10** was also isolated:

1.7.1.3 (5a*S, 7*R**, 8a*R**, *Z*)-2-methyl-8-(4-methylene hex-5-enyl)-7-vinyl-2,3,6,7,8,8a-hexahydrocyclopenta[c] azepin-1(5aH)-one 10**



A colourless oil (10 mg, 30%). R_f 0.61 (SiO_2; 4:6 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2925m, 2861m, 1647s (C=O), 1450w, 1399m, 1213m, 1011w, 910m; δ_H (400 MHz; $CDCl_3$) 6.41-6.18 (2H, m, C^rH and C^lH), 5.96-5.85 (1H, m, C^pH), 5.78-5.70 (1H, m, C^qH), 5.21 (1H, d, *J* 17.8, $C^sH_{trans}H_{cis}$), 5.05-4.84 (5H, m, $C^sH_{trans}H_{cis}$, C^kH_2 and C^mH_2), 4.45-4.34 (1H, br, m, $C^oH_aH_b$), 3.46 (1H, t, *J* 6.3, C^bH), 3.16 (1H, dd, *J* 16.4 8.0, $C^oH_aH_b$), 2.94 (3H, s, C^nH_3), 2.73-2.54 (2H, m, C^cH and C^eH), 2.22-2.08 (3H, m, C^fH and C^iH_2), 1.90-1.21 (6H, m, C^dH_2, C^gH_2, C^hH_2); δ_C (125 MHz; $CDCl_3$) 172.8 (C^a), 146.8 (C^J), 143.4 (C^lH), 138.9 (C^rH), 135.1 (C^qH), 124.5 (C^pH), 115.3 (C^kH_2 or C^sH_2), 113.5 (C^mH_2), 113.1 (C^kH_2 or C^sH_2), 47.5 (C^bH), 47.1 (C^fH), 46.2 (C^oH_2), 42.4 (C^cH or C^eH), 42.3 (C^cH or C^eH), 39.5 (C^dH_2), 35.1 (C^nH_3), 31.7 (C^iH_2), 28.0 (C^gH_2 or C^hH_2), 27.8 (C^gH_2 or C^hH_2); HRMS (ESI, M+H^+) 286.2166, $C_{19}H_{28}NO$ required 286.2171, Δppm -1.7.

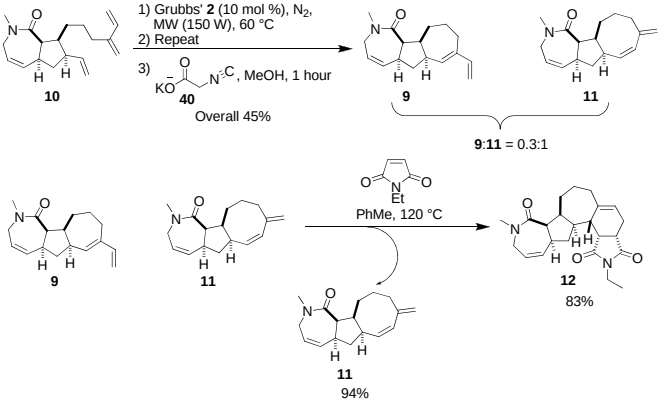
1.7.1.4 (5aS*, 6aS*, 10aR*, 10bR*, Z)-2-(4-methoxybenzyl)-8-vinyl-2,3,6,6a,9,10,10a, 10b-octahydroindeno[1,2-c]azepin-1(5aH)-one 41



A pale brown solid (20.4 mg, 55%). R_f 0.42 (SiO_2; 30:70 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2921m br, 2860w, 1633s (C=O), 1612s, 1511s, 1465m, 1439m, 1416m, 1302m, 1246s, 1174m, 1109w, 1034m, 990w; δ_H (400 MHz; $CDCl_3$) 7.16 (2H, d, *J* 8.8, 2 x C^rH), 6.82 (2H, d, *J* 8.8, 2 x C^sH), 6.31 (1H, dd, *J* 17.4 10.9, C^kH), 5.85 (1H, s, C^JH), 5.79-5.69 (2H, m, C^oH and C^pH), 5.09 (1H, d, *J* 17.4, $C^lH_{trans}H_{cis}$), 4.92 (1H, d, *J* 10.9, $C^lH_{trans}H_{cis}$), 4.53 (2H, app q, *J* 14.5, C^mH_2), 3.77 (3H, s, OCH_3), 3.72-3.66 (1H, m, $C^nH_aH_b$), 3.43-3.36 (1H, m, $C^nH_aH_b$), 3.13-3.04 (1H, m, C^cH), 2.84 (1H, t, *J* 11.2, C^bH), 2.39-2.32 (2H, m, C^hH_2), 2.28-2.21 (1H, m, $C^gH_aH_b$), 2.17-2.10 (1H, m, $C^dH_aH_b$), 2.10-2.03 (2H, m, C^eH and C^fH), 1.49-1.39 (1H, m, $C^gH_aH_b$), 1.21-1.12 (1H, m, $C^dH_aH_b$); δ_C (100 MHz; $CDCl_3$) 172.9 (C^a) 158.8 (C^t), 139.7 (C^kH), 137.4 (C^pH), 137.1 (C^i), 130.9 (C^JH), 130.1 (C^q), 129.7 (C^rH), 127.9 (C^oH), 113.8 (C^sH), 111.1 (C^lH_2), 55.2 (OCH_3), 52.1 (C^bH), 50.3 (C^mH), 46.4 (C^fH), 42.9 (C^eH), 42.6 (C^nH_2), 38.8 (C^cH), 37.9 (C^dH_2), 27.3 (C^gH_2), 25.3 (C^hH_2); HRMS (ESI, M+H^+) found 250.2091 $C_{23}H_{28}NO_2$ required 250.2120, Δppm +4.1; mp 79-81 °C

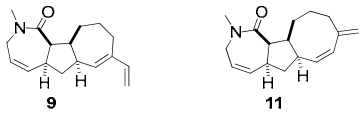
1.8 Scheme 6: Metathesis of the tetra-ene 10

The tetra-ene **10** could be converted, *via* a mixture of **9** and **11**, to the *endo* ring isomer **11** and the Diels Alder adduct **12** (Supporting Information Scheme 9).



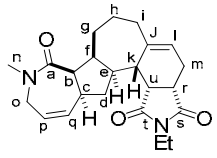
Supporting Information Scheme 9

1.8.1.1 (4*Z*, 5a*S, 6a*S**, 7*E*, 11a*S**, 11b*R**)-2-methyl-8-vinyl-2,3,5a,6,6a,9,10,11, 11a,11b-decahydro-1H-azuleno [1,2-c]azepin-1-one 9 and 4-Methyl-13-methylene-4-aza-tricyclo[8.6.0.0^{2,8}] hexadeca-6,11-dien-3-one 11**



A microwave tube, equipped with magnetic stirrer, containing the tetra-ene **10** (19 mg, 0.066 mmol) and degassed CH_2Cl_2 (15 ml) at room temperature was placed under and nitrogen atmosphere and charged with a solution Grubbs' **2** (10 mol %, 5.8 mg, 6.9 μmol) and degassed CH_2Cl_2 (1.0 ml) and heated by microwave irradiation (150 W) at 60 °C for 2 hours. The reaction mixture was quenched *via* the addition of the isocyanate **40** (6 mg, 0.48 mmol) in MeOH (1 ml) and stirred for 1 hour. The solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2, filtered through a plug of silica to remove the isocyanate **40**, the silica washed with Et_2O and the solvent removed *in vacuo*. The crude products were purified by column chromatography to give a 0.3:1 inseparable mixture of the *exo*- and *endo*- ring isomers **9** and **11** as a colourless oil (7.7 mg, 45%).

1.8.1.2 Diels Alder Adduct 12

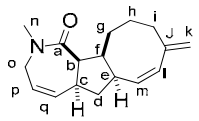


A microwave tube, equipped with a magnetic stirrer, containing *N*-ethylmaleimide (7 mg, 0.056 mmol) at room temperature was charged with a solution of the 1:0.3 mixture of **9** and **11** (7.7 mg, 0.03 mmol) and PhMe (1.0 ml) and heated under microwave irradiation (300 W) at 160 °C for 6 hours. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude products were purified by column chromatography to give the title compound **12** as a white paste (2.2 mg, 83%).

R_f 0.16 (SiO_2; 4:6 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 2929w, 2860w, 1692s (C=O), 1645m (C=O), 1403m, 1443w, 1403m, 1349m, 1227m, 916w br; δ_H (400 MHz; $CDCl_3$) 5.93-5.84 (1H, m, C^pH), 5.79-5.71 (1H, m, C^qH), 5.48-5.44 (1H, m, C^lH), 4.43-4.36 (1H, m, $C^o\underline{H}_a H_b$), 3.40 (1H, t, *J* 5.5, C^bH), 3.40 (2H, q, *J* 7.0, $NC\underline{H}_2CH_3$), 3.13 (1H, dd, *J* 16.3 7.5, $C^oH_a\underline{H}_b$), 3.03-2.18 (7H, m, C^eH, C^kH, C^nH_3, C^rH and C^uH), 2.75-2.53 (1H, m, C^cH), 2.57 (1H, dd, *J* 14.8 7.3, $C^m\underline{H}_a H_b$), 2.48-2.38 (1H, m, $C^d\underline{H}_a H_b$), 2.35-2.10 (3H, m, C^fH, $C^i\underline{H}_a H_b$ and $C^mH_a\underline{H}_b$), 2.09-2.00 (1H, m, $C^iH_a\underline{H}_b$), 1.66-1.16 (5H, m, $C^dH_a\underline{H}_b$ C^gH_2 and C^hH_2), 1.01 (3H, t, *J* 7.0, $NCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 180.3 (C^s), 178.5 (C^t), 173.4 (C^a), 144.5 (C^J), 135.0 (C^qH), 124.6 (C^pH), 119.0 (C^lH), 49.8 (C^bH), 46.4 (C^oH_2), 45.2 (C^fH), 42.2 (C^rH or C^uH), 41.8 (C^cH), 41.3 (C^kH), 40.6 (C^rH or C^uH), 38.6 (C^dH_2), 35.1 (C^eH or C^nH_3), 34.9 (C^eH or C^nH_3), 33.3 ($N\underline{C}H_2CH_3$), 31.2 (C^iH_2), 28.1 (C^gH_2), 24.8 (C^mH_2), 24.0 (C^hH_2), 13.0 ($NCH_2\underline{C}H_3$); HRMS (ESI, M+Na)$^+$ found 405.2154, $C_{23}H_{30}N_2O_3Na$ required 405.2154, Δppm 4.9.

The *endo*- ring isomer **11** was also isolated:

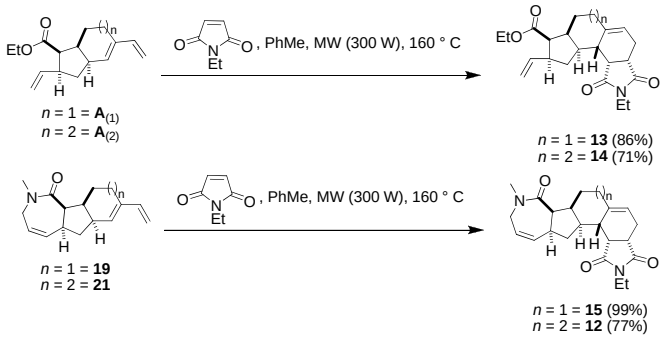
1.8.1.3 4-Methyl-13-methylene-4-aza-tricyclo[8.6.0.0^{2,8}] hexadeca-6,11-dien-3-one 11



A colourless oil (5.6 mg, 94%). R_f 0.23 (SiO_2; 4:6 Et_2O: Petrol); ν_{max} (neat)/cm^{-1} 2923m, 2860m, 1654s (C=O), 1478m, 1453m, 1397m, 1323w, 1209m, 1106w, 911w, 731m; δ_H (500 MHz; $CDCl_3$) 6.18 (1H, br d, *J* 13.9, C^lH), 5.94-5.85 (1H, m, C^pH), 5.79-5.71 (1H, m, C^qH), 5.18 (1H, dd, *J* 11.8 5.2, $C^m\underline{H}$), 4.82 (1H, d, *J* 2.0, $C^k\underline{H}_a H_b$), 4.81-4.78 (1H, app s, $C^kH_a\underline{H}_b$), 4.42-4.33 (1H, m, $C^o\underline{H}_a H_b$), 3.46 (1H, t, *J* 5.6, C^bH), 3.42-3.31 (1H, m, C^eH), 3.10 (1H, dd, *J* 16.3 7.6, $C^oH_a\underline{H}_b$), 2.91 (3H, s, C^nH_3), 2.74-2.33 (4H, m, C^cH, $C^d\underline{H}_a H_b$, $C^g\underline{H}_a H_b$ and $C^i\underline{H}_a H_b$), 2.30-2.23 (1H, m, $C^iH_a\underline{H}_b$), 2.14-2.05 (1H, m, C^fH), 1.64-1.53 (2H, m, C^hH_2), 1.50-1.40 (1H, m, $C^gH_a\underline{H}_b$), 1.39-1.27 (1H, m, $C^dH_a\underline{H}_b$); δ_C (125 MHz; $CDCl_3$) 172.5 (C^a), 147.9 (C^J), 135.8 (C^mH), 134.9 (C^qH), 131.9 (C^lH), 124.5 (C^pH), 116.2 (C^kH_2), 49.7 (C^bH), 46.9 (C^fH), 46.1 (C^oH_2), 42.7 (C^dH_2), 42.0 (C^cH), 37.0 (C^eH), 35.0 (C^nH_3), 33.1 (C^iH_2), 31.9 (C^hH_2), 24.8 (C^gH_2); HRMS (ESI, M+H$^+$) found 258.1877, $C_{17}H_{24}NO$ required 258.1858, Δppm 3.6.

1.9 Scheme 7: Diels Alder Reactions

The 1,3-diene containing compound **8**, **11**, **19**, and **21** could be converted to the corresponding Diels Alder adduct (Supporting Information Scheme 10).



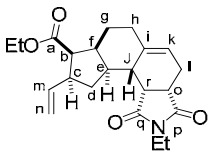
Supporting Information Scheme 10

1.9.1 General Procedure

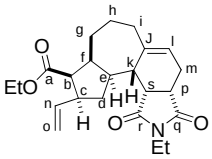
A microwave tube, equipped with a magnetic stirrer, containing *N*-ethylmaleimide (2.5 equiv.) at room temperature was charged with a solution of the diene (1 equiv.) and PhMe (1 ml/mmol *N*-ethylmaleimide) and heated under microwave irradiation (300 W) at 160 °C for 6 hours. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.9.1.1 (3a*S**, 7a*S**, 8*R**, 9*S**, 10a*S**, 10b*S**, 10c*R**)-ethyl 2-ethyl-1,3-dioxo-9-vinyl-1,2,3,3a,4,6,7,7a,8,9, 10,10a, 10b,10c-tetradecahydroindeno[4,5-e]isoindole-8-carboxylate 13

A colourless oil (24 mg, 86%).The data obtained was consistent with that reported for compound **26** above.



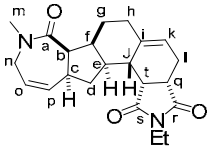
1.9.1.2 (3a*S**, 8a*S**, 9*R**, 10*S**, 11a*S**, 11b*S**, 11c*R**)-ethyl 2-ethyl-1,3-dioxo-10-vinyl-2,3,3a,4,6,7,8,8a, 9,10,11,11a,11b,11c-tetradecahydro-1H-azuleno[4,5-e] isoindole-9-carboxylate 14



A colourless oil (18 mg, 71%). R_f 0.19 (SiO_2; 1:9 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 2928w br, 2857w, 1724m, (C=O), 1695 (C=O), 1444w, 1403m, 1351m, 1228m, 1157m; δ_H (400 MHz; $CDCl_3$) 5.81 (1H, ddd, *J* 17.4 10.5 6.9, C^nH), 5.52-5.44 (1H, m, C^lH), 5.13 (1H, dt, *J* 17.1 1.7, $C^o\underline{H}_{tans}H_{cis}$), 5.04-4.99 (1H, m, $C^oH_{trans}\underline{H}_{cis}$), 4.11-4.02 (2H, m, $OC\underline{H}_2CH_3$), 3.44 (2H, q, *J* 7.3, $NC\underline{H}_2CH_3$), 3.30-3.81 (1H, m, C^eH), 3.11 (1H, dd, *J* 8.7 5.2, C^sH), 3.06-3.01 (1H, m, C^pH), 2.96

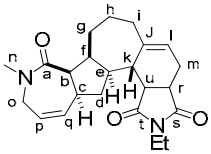
(1H, t, *J* 6.9, C^bH), 2.87-2.76 (1H, m, C^cH), 2.67-2.52 (2H, m, $C^i\underline{H}_a\underline{H}_b$ and C^kH), 2.49-2.24 (2H, m, C^fH and $C^d\underline{H}_a\underline{H}_b$), 2.22-1.94 (4H, m, $C^i\underline{H}_a\underline{H}_b$, C^mH_2 and $C^d\underline{H}_a\underline{H}_b$), 1.62-1.30 (4H, m, C^gH_2 and C^hH_2), 1.24 (3H, t, *J* 6.9, $OCH_2C\underline{H}_3$), 1.04 (3H, t, *J* 7.3, $NCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 180.1 (C^r), 178.2 (C^q), 173.8 (C^a), 144.3 (C^J), 137.7 (C^nH), 119.5 (C^lH), 115.6 (C^oH_2), 59.7 ($O\underline{C}H_2CH_3$), 55.3 (C^bH), 46.6 (C^cH), 43.8 (C^fH), 42.3 (C^sH), 41.9 (C^kH), 40.5 (C^pH), 37.3 (C^eH), 37.1 (C^dH_2), 33.4 ($N\underline{C}H_2CH_3$), 31.1 (C^mH_2), 27.6 (C^hH_2), 24.8 (C^iH_2), 23.7 (C^gH_2), 14.4 ($OCH_2\underline{C}H_3$), 13.0 ($NCH_2\underline{C}H_3$); HRMS (ESI, $M+H^+$) found 386.2335, $C_{23}H_{32}NO_4$ required 386.2331, Δppm 1.0.

1.9.1.3 Diels Alder Adduct 15



A colourless oil (15 mg, 99%). R_f 0.42 (SiO_2; 1:1 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 2937w, 2875w, 1691s (C=O), 1645m (C=O), 1441m, 1403m, 1350m, 1228m, 917w; δ_H (400 MHz; $CDCl_3$) 5.95-5.87 (881H, m, C^oH), 5.83-5.76 (1H, m, C^pH), 5.52-5.47 (1H, m, C^kH), 4.48-4.39 (1H, m, $C^n\underline{H}_a\underline{H}_b$), 3.54 (1H, t, *J* 5.9, C^bH), 3.46 (2H, q, *J* 7.3, $NC\underline{H}_2CH_3$), 3.15 (1H, dd, *J* 16.3 7.6, $C^n\underline{H}_a\underline{H}_b$), 3.00-2.83 (6H, C^eH, C^mH_3, C^qH and C^tH), 2.79-2.69 (2H, m, C^cH and C^JH), 2.63 (1H, dd, *J* 15.3 6.9, $C^l\underline{H}_a\underline{H}_b$), 2.56-2.43 (2H, m, C^fH and $C^d\underline{H}_a\underline{H}_b$), 2.29-2.19 (1H, m, $C^l\underline{H}_a\underline{H}_b$), 2.19-1.95 (3H, m, C^hH_2 and $C^g\underline{H}_a\underline{H}_b$), 1.76-1.68 (1H, m, $C^g\underline{H}_a\underline{H}_b$), 1.27-1.16 (1H, m, $C^d\underline{H}_a\underline{H}_b$), 1.06 (3H, t, *J* 7.3, $NCH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 180.2 (C^r), 178.6 (C^s), 173.0 (C^a), 143.5 (C^i), 135.3 (C^pH), 124.4 (C^oH), 117.0 (C^kH), 47.3 (C^bH), 46.4 (C^nH_2), 43.0 (C^cH or C^fH), 42.9 (C^cH or C^fH), 41.6 (C^qH or C^tH), 40.9 (C^JH), 40.2 (C^qH or C^tH), 38.1 (C^dH_2), 35.1 (C^mH_3), 33.5 ($N\underline{C}H_2CH_3$), 31.6 (C^eH), 31.2 (C^hH_2), 24.2 (C^lH_2), 23.3 (C^gH_2), 13.1 ($NCH_2\underline{C}H_3$); HRMS (ESI, $M+Na)^+$ found 391.2002, $C_{22}H_{28}N_2O_3Na$ required 391.1998, Δppm 1.0.

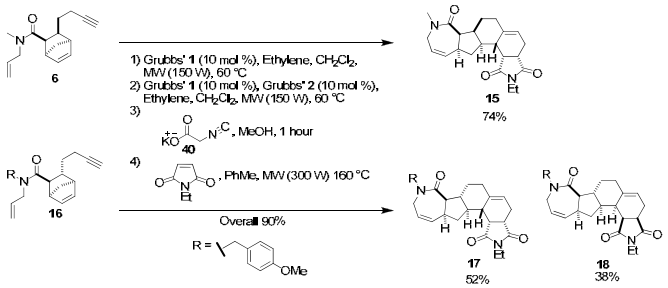
1.9.1.4 Diels Alder Adduct 12



A white paste (11 mg, 77%). The data obtained was consistent with that reported for compound **25** above.

1.10 Scheme 8: Tandem Metathesis-Diels Alder Reaction

An optimised procedure was developed to convert the norbornene substrates in to the polycyclic target compounds (Supporting Information Scheme 11).

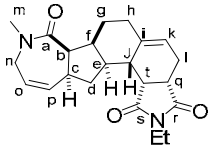


Supporting Information Scheme 11

1.10.1 General Procedure

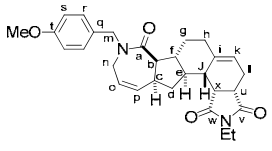
A microwave tube, equipped with magnetic stirrer, containing the norbornene (1 equiv.) and degassed CH_2Cl_2 (0.01M) at -78 °C was saturated with ethylene (the gas was bubbled though the reaction mixture *via* a balloon and long needle for 10 minutes), placed under an ethylene atmosphere and charged with a solution Grubbs' **1** (10 mol %) in degassed CH_2Cl_2 (1.0 ml). The reaction mixture was stirred for a further 15 minutes at -78 °C before being warmed to room temperature. The reaction mixture was heated by microwave irradiation (150 W) at 60 °C for 1 hour. After cooling to room temperature the reaction mixture was cooled to -78 °C, saturated with ethylene and placed under an ethylene atmosphere. The reaction mixture was charged with a solution Grubbs' **1** (10 mol %), Grubbs' **2** (10 mol%) and degassed CH_2Cl_2 (1.0 ml), stirred for 15 minutes at -78 °C before being warmed to room temperature and then heated by microwave irradiation (150 W) at 60 °C for 2 hours. The reaction mixture was cooled to room temperature and quenched *via* the addition of the isocyanate **40** (7 equiv. wrt catalyst) in MeOH (1 ml) and stirred for 1 hour. The solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2, filtered through a plug of silica to remove the isocyanate **40**, the silica washed with Et_2O and the solvent removed *in vacuo*. The residue was taken up in PhMe (1 ml/mmol *N*-ethylmaleimide) and transferred to a microwave tube containing *N*-ethylmaleimide (2.5 equiv.). The reaction vessel was purged with nitrogen and heated under microwave irradiation (300 W) at 160 °C for 6 hours. The reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by column chromatography to give:

1.10.1.1 Diels Alder Adduct 15



An off white paste (20 mg, 74%). The data obtained was consistent with that reported for **15** described above.

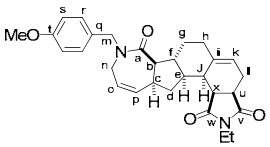
1.10.1.2 Diels Alder Adduct 17



An off white paste (14.8 mg, 52%). An off white paste (6.4 mg, 26%). R_f 0.31 (SiO_2; 3:7 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 2934m, 1767w, 1962s (C=O), 1637m, 1512m, 1441m, 1404m, 1350m,

1247m, 1227m, 1175w; δ_H (400 MHz; $CDCl_3$) 7.17 (2H, d, *J* 8.5, 2 x C^rH), 6.81 (2H, d, *J* 8.5, 2 x C^sH), 5.76-5.69 (2H, m, C^oH and C^pH), 5.54 (1H, app s, C^kH), 4.51 (H, q, *J* 14.5, C^mH_2), 3.91-3.85 (1H, m, $C^nH_aH_b$), 3.77 (3H, s, OCH_3), 3.45 (2H, q, *J* 7.0, NCH_2CH_3), 3.29-3.15 (2H, m, $C^nH_aH_b$ and C^cH), 3.10-3.05 (1H, m, C^xH), 3.04-2.99 (1H, m, C^uH), 2.91 (1H, t, *J* 9.3, C^bH), 2.63-2.55 (1H, m, $C^lH_aH_b$), 2.46-2.32 (2H, m, $C^dH_aH_b$ and C^eH), 2.30-2.16 (3H, m, C^hH_2 and C^fH), 2.12-1.97 (3H, $C^lH_aH_b$, $C^dH_aH_b$ and C^JH), 1.46-1.36 (1H, m, $C^gH_aH_b$), 1.13-0.98 (4H, m, $C^gH_aH_b$ and NCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 179.8 (C^v), 177.9 (C^w), 17.7 (C^a), 158.9 (C^t), 141.6 (C^i), 137.1 (C^pH), 130.0 (C^q), 129.8 (C^rH), 127.8 (C^oH), 118.9 (C^kH), 113.8 (C^sH), 55.2 (OCH_3), 54.2 (C^bH), 50.6 (C^mH_2), 45.4 (C^fH), 43.5 (C^JH), 42.8 (C^nH_2), 41.9 (C^uH), 40.4 (C^xH), 39.8 (C^cH or C^eH), 39.7 (C^cH or C^eH), 38.0 (C^dH_2), 33.5 (NCH_2CH_3), 28.6 (C^hH_2), 27.8 (C^gH_2), 24.6 (C^lH_2), 13.0 (NCH_2CH_3); HRMS (ESI, M+H)$^+$ found 475.2609, $C_{29}H_{35}N_2O_4$ required 475.2597, Δppm 2.5.

1.10.1.3 Diels Alder Adduct 18

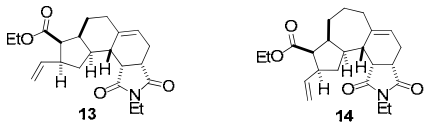


An off white paste (10.7 mg, 38%). An off white paste (7.8 mg, 31%). R_f 0.16 (SiO_2; 3:7 EtOAc: Petrol); ν_{max} (neat)/cm^{-1} 2937w, 1694s (C=O), 1629w, 1512m, 1443m, 1404m, 1350m, 1246m, 1227m, 1126w; δ_H (400 MHz; $CDCl_3$) 7.17 (2H, d, *J* 8.6, 2 x C^rH), 6.82 (2H, d, *J* 8.6, 2 x C^sH), 5.97 (1H, dd, *J* 6.2 10.1, C^pH), 5.81-5.72 (1H, m, C^oH), 5.60 (1H, br d, *J* 4.9, C^kH), 4.81 (1H, d, *J* 14.7, $C^mH_aH_b$), 4.39 (1H, d, *J* 14.7, $C^mH_aH_b$), 4.15 (1H, dd, *J* 6.4 15.6, $C^nH_aH_b$), 3.77 (3H, s, OCH_3), 3.60-3.35 (3H, m, NCH_2CH_3, $C^nH_aH_b$), 3.14 (1H, dd, *J* 4.4 8.3, C^xH), 3.05-2.99 (2H, m, C^uH and C^cH), 2.78 (1H, t, *J* 11.4, C^bH), 2.71-2.52 (5H, m, $C^lH_aH_b$, C^fH, C^hH_2, C^JH), 2.19-2.03 (4H, m, $C^lH_aH_b$, C^dH_2 and $C^gH_aH_b$), 1.83-1.73 (1H, m, C^eH), 1.09-0.99 (4H, m, $C^gH_aH_b$ and NCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 179.7 (C^v), 178.4 (C^w), 173.6 (C^a), 158.8 (C^t), 140.8 (C^i), 137.8 (C^pH), 130.1 (C^q), 129.6 (C^rH), 127.6 (C^oH), 120.8 (C^kH), 113.8 (C^sH), 55.2 (OCH_3), 54.4 (C^bH), 50.9 (C^mH_2), 43.5 (C^eH or C^fH or C^JH), 43.2 (C^eH or C^fH or C^JH), 42.5 (C^xH), 41.2 (C^nH_2), 41.6 (C^uH), 37.3 (C^cH or C^fH or C^JH), 37.3 (C^cH or C^fH or C^JH), 36.7 (C^dH_2), 33.5 (NCH_2CH_3), 29.9 (C^hH_2), 29.0 (C^gH_2), 25.4 (C^lH_2), 13.0 (NCH_2CH_3); HRMS (ESI, M+Na)$^+$ found 475.2599, $C_{29}H_{35}N_2O_4$ required 475.2597, Δppm 0.4.

2 nOe Studies

The adducts produced in the Diels Alder reactions, *i.e.* **12-15**, **17**, and **18** (Supporting Information Scheme 10), were not crystalline and hence no crystal structures could be obtained. The facial selectivity of the reaction (*i.e.* the diastereoisomer produced) was determined using NOESY spectra analysis. The nOe cross peaks present in the NOESY spectra were compared to those expected after examination of the calculated 3D structures of the compounds. These structures were calculated at the MM2 level using the *Chem 3D Ultra* package supplied by CambridgeSoft.

2.1 *Cis* Ethyl Ester Adducts 13 and 14



For **13** and **14**, the pattern of cross peaks observed in the NOESY best represented the *endo* isomer resulting from bottom-face attack (Figure 1). On similar systems investigated by North and co-workers, the Diels Alder adducts produced were also the result of *endo*, bottom face attack by the dieneophile on the diene.[8] As here, these compounds were identified based on analysis of the nOe cross peaks.

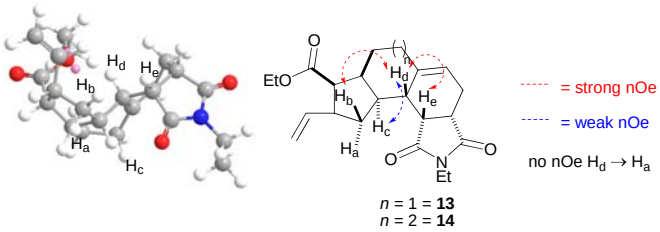
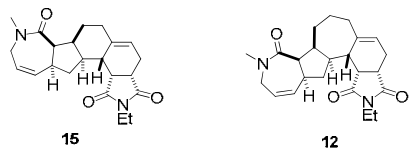


Figure 1

Using **13** an example, the following demonstrates how the structures generated by *Chem 3D Ultra* were used in combination with analysis the NOSEY spectra obtained:

- In the *endo* isomer, H_e and H_d are on the same side of the molecule and in close proximity ($H_e \rightarrow H_d$ in *endo* calculated to be 2.4 Å) and hence would give rise to a strong nOe cross peak. This is what was observed and hence **13** is identified as the *endo* isomer. Were the *exo* isomer formed, this distance between H_e and H_d would be greater and a weaker cross peak, or no cross peak at all, would be expected ($H_e \rightarrow H_d$ in *exo* calculated to be 3.1 Å).
- Although bottom-face attack by the dieneophile would result in H_d and H_c being on opposite sides of the molecule, a weak cross peak is still observed in the NOESY spectrum ($H_d \rightarrow H_c$ from bottom-face attack calculated to be 3.0 Å). This cross peak would however be expected to be stronger if top-face attack had occurred ($H_d \rightarrow H_c$ from top-face attack calculated to be 2.1 Å). The cross peak in the NOESY that confirms **13** results from bottom-face attack is that observed between H_d and H_b ($H_d \rightarrow H_b$ from bottom-face attack calculated to be 2.8 Å compared with $H_d \rightarrow H_c$ from top-face attack calculated to be 3.6 Å). Furthermore, the lack of cross peak between H_d and H_a ($H_d \rightarrow H_a$ from bottom-face attack calculated to be 3.8 Å compared with $H_d \rightarrow H_a$ from top-face attack calculated to be 3.2 Å) confirms this hypothesis.

2.2 *Cis* Amide adducts 15 and 12

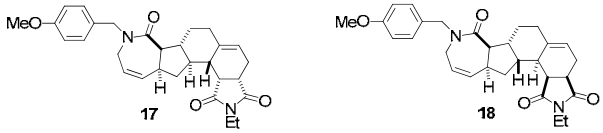


Using the same rationale as used above for **14** and **14**, **15** was confirmed as resulting from *endo*, bottom-face attack.

[8] D. Banti, M. North, *Adv. Synth. Catal.* **2002**, 344, 694.

Unfortunately, with **12**, the peaks of interest overlapped in the ^{1}H NMR spectrum and it was not possible to confirm the stereochemical nature of the product formed. It is however likely that the diastereoisomer shown (again resulting from *endo*, bottom face attack) is correct as this diastereoisomer was observed not only for the equivalent 5,7,6,5 ethyl ester adduct **14** but also for the similar 7,5,6,6,5 fused polycyclic amide **15**.

2.3 *Trans* Amide adducts 17 and 18



The Diels Alder reaction of **41** gave a mixture of diastereoisomers **17** and **18** that were separable by column chromatography. The structures of the diastereoisomers **17** and **18** were confirmed by analysis of the NOESY spectra.

Compound **17**, resulting from *endo* and bottom-face attack, displayed similar nOe cross peaks to those observed for **13** and **15**. For compound **18**, a cross peak between H_d and H_e suggests its structure best represents the *endo* isomer, and a cross peak between H_d and H_c suggests the product is formed as a result of a top-face attack by *N*-ethylmaleimide (Figure 2).

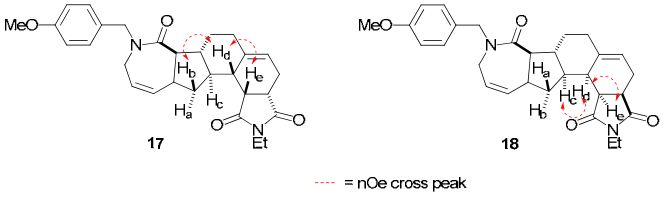


Figure 2

Thus, assuming the different nitrogen substitution of the 1,3-dienes *cis*-**7** and *trans*-**41** (*i.e.* methyl compared to 4-methyoxy benzyl) does not influence the stereochemical outcome of the Diels Alder reaction, the *cis* or *trans* relationship about the cyclopentane controls the reaction selectivity. An explanation can be given on steric grounds.

In the *cis* 1,3-diene **7**, where bottom-face attack is observed, the top face must be shielded in a way that it is not in the *trans* 1,3-diene **41**, where both top- and bottom-face attack occur. This may result from the orientation of the cycloheptene portion of the molecule preventing top face attack. The examination of 3D models of **7** (MM2, *MacroModel*, Schrödinger) supports this. In comparison, the conformation of **41** is flatter when compared to **7**. There is, therefore, less (or no) steric bias favouring bottom face attack and, as a result, both top- and bottom- face attack are observed (Figure 3).

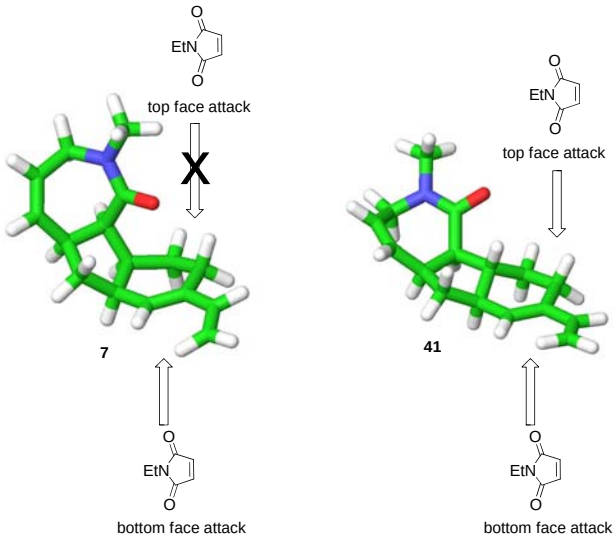


Figure 3

3 The Reaction Mechanism

With reference to Scheme 2: Pathway 1 is discussed in the text. For pathway 2, in addition to ***MC-2a*** or ***MC-2b*** potentially forming $\mathbf{B}_{(n)}$ and $\mathbf{C}_{(n)}$ directly, a reaction with ethylene could furnish the cross-metathesized norbornene $\mathbf{F}_{(n)}$. From this compound, the tetra-ene $\mathbf{E}_{(n)}$ (*via* either ***MC-3a*** or ***MC-3b***) could be accessed. From $\mathbf{E}_{(n)}$, depending on the site of ruthenium carbene insertion, both ring isomers $\mathbf{B}_{(n)}$ and $\mathbf{C}_{(n)}$ could be formed. Insertion into the isolated olefin of $\mathbf{E}_{(n)}$ (to give ***MC-3b***) is predicted to lead to $\mathbf{C}_{(n)}$ exclusively, *via* an intramolecular olefin RCM.[10c] Insertion into either the internal or terminal position of the diene of $\mathbf{E}_{(n)}$ (to give ***MC-4a*** or ***MC-4b***) could yield both $\mathbf{B}_{(n)}$ and $\mathbf{C}_{(n)}$. This latter processes formally represents the first step in the *yne-then-ene* RCEYM pathway from $\mathbf{D}_{(n)}$.

4 NMR Spectra

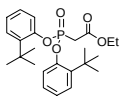
^{1}H and ^{13}C NMR spectra can be found below.

4.1 NMR Spectra: Preparation of Substrates

The compounds below are listed in the same order as they appear in the experimental section above.

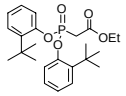
[BLANK PAGE]

^{1}H NMR: Di-(2-tert-butyl-phenyl) ethyl phosphonoacetate 23



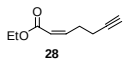
23

^{13}C NMR: Di-(2-tert-butyl-phenyl) ethyl phosphonoacetate 23



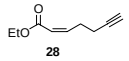
23

^{1}H NMR: (*Z*)-Hept-2-en-6-ynoic acid ethyl ester 28



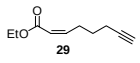
28

^{13}C NMR: (*Z*)-Hept-2-en-6-ynoic acid ethyl ester 28



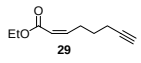
28

^{1}H NMR: (Z)-Oct-2-en-7-ynoic acid ethyl ester 29



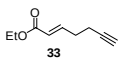
29

^{13}C NMR: (Z)-Oct-2-en-7-ynoic acid ethyl ester 29



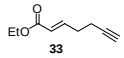
29

^{1}H NMR: (*E*)-Hept-2-en-6-ynoic acid ethyl ester 33



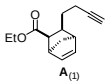
33

^{13}C NMR: (*E*)-Hept-2-en-6-ynoic acid ethyl ester 33



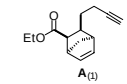
33

^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-ethyl 3-(but-3-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $A_{(1)}$**



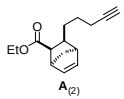
$A_{(1)}$

^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-ethyl 3-(but-3-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $A_{(1)}$**



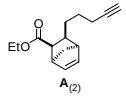
$A_{(1)}$

^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-ethyl 3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $A_{(2)}$**



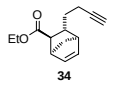
$A_{(2)}$

^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-ethyl 3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $A_{(2)}$**



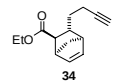
$A_{(2)}$

^{1}H NMR: (1*S, 2*R**, 3*R**, 4*R**)-ethyl 3-(but-3-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate 34**



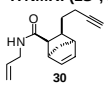
34

^{13}C NMR: (1*S, 2*R**, 3*R**, 4*R**)-ethyl 3-(but-3-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate 34**



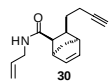
34

^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(but-3-ynyl)bicyclo[2.2.1]hept-5-ene-2-carbox-amide 30**



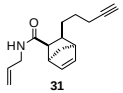
30

^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(but-3-ynyl)bicyclo[2.2.1]hept-5-ene-2-carbox-amide 30**



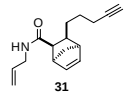
30

^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carbox- amide 31**



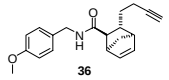
31

^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carbox-amide 31**



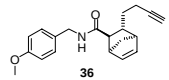
31

^{1}H NMR: (1*S, 2*R**, 3*R**, 4*R**)-3-(but-3-ynyl)-*N*-(4-methoxybenzyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide 36**



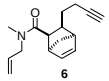
36

^{13}C NMR: (1*S, 2*R**, 3*R**, 4*R**)-3-(but-3-ynyl)-*N*-(4-methoxybenzyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide 36**



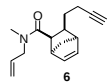
36

^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(but-3-ynyl)-*N*-methylbicyclo[2.2.1]hept-5-ene-2-carboxamide 6**



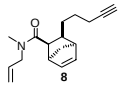
6

^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-3-(but-3-ynyl)-*N*-methylbicyclo[2.2.1]hept-5-ene-2-carboxamide 6**



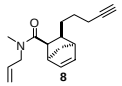
6

^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-*N*-methyl-3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide 8**



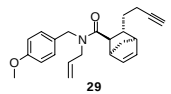
40

^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-*N*-allyl-*N*-methyl-3-(pent-4-ynyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide 8**



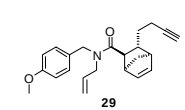
41

^{1}H NMR: (1*S, 2*R**, 3*R**, 4*R**)-*N*-allyl-3-(but-3-ynyl)-*N*-(4-methoxybenzyl)bicycle[2.2.1] hept-5-ene-2-carboxamide 29**



42

^{13}C NMR: (1*S, 2*R**, 3*R**, 4*R**)-*N*-allyl-3-(but-3-ynyl)-*N*-(4-methoxybenzyl)bicycle[2.2.1] hept-5-ene-2-carboxamide 29**



43

4.2 NMR Spectra: Metathesis Products

The compounds below are given in alphabetical order.

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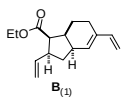
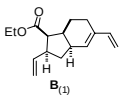
^{1}H NMR: (1*R, 2*S**, 3a*S**, 7a*S**)-ethyl 2,5-divinyl-2,3,3a,6,7,7a-hexahydro-1H-indene-1-carboxylate $B_{(1)}$**



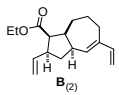
$B_{(1)}$

^{13}C NMR: (1*R, 2*S**, 3a*S**, 7a*S**)-ethyl 2,5-divinyl-2,3,3a,6,7,7a-hexahydro-1H-indene-1-carboxylate $B_{(1)}$**



$B_{(1)}$

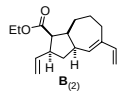
^{1}H NMR: (1*R, 2*S**, 3a*S**, 8a*S**, *E*)-ethyl 2,5-divinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $B_{(2)}$**



$B_{(2)}$

48

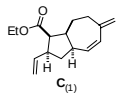
^{13}C NMR: (1*R, 2*S**, 3a*S**, 8a*S**, *E*)-ethyl 2,5-divinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $B_{(2)}$**



$B_{(2)}$

49

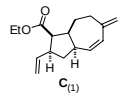
^{1}H NMR: (1*R, 2*S**, 3a*R**, 8a*S**, *Z*)-ethyl 6-methylene-2-vinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $C_{(1)}$**



$C_{(1)}$

50

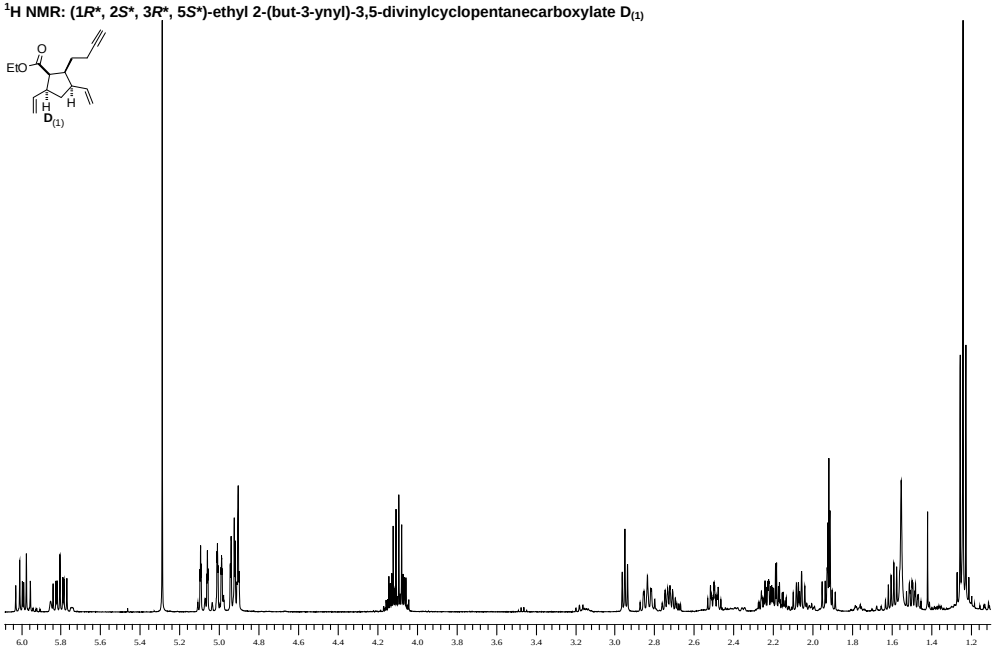
^{13}C NMR: (1*R, 2*S**, 3a*R**, 8a*S**, *Z*)-ethyl 6-methylene-2-vinyl-1,2,3,3a,6,7,8,8a-octahydroazulene-1-carboxylate $C_{(1)}$**



$C_{(1)}$

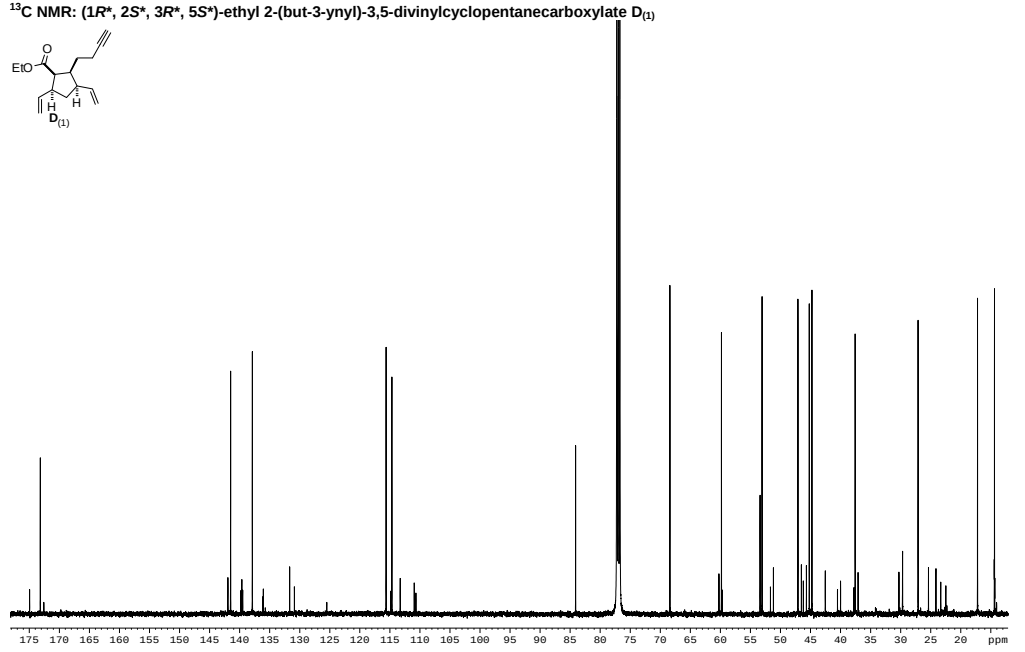
51

^{1}H NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(but-3-ynyl)-3,5-divinylcyclopentanecarboxylate $D_{(1)}$**



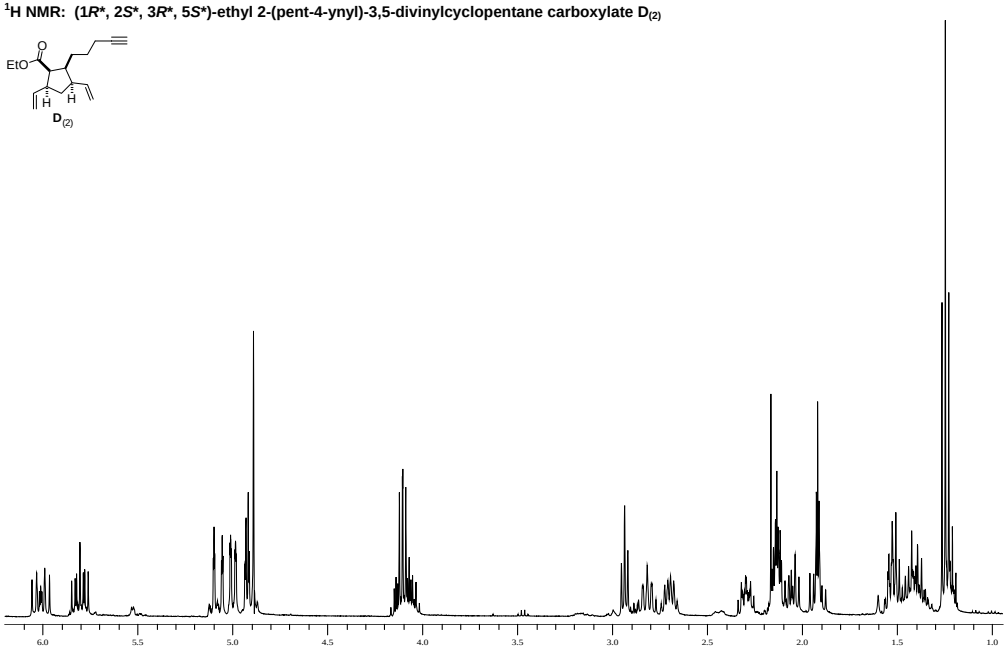
52

^{13}C NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(but-3-ynyl)-3,5-divinylcyclopentanecarboxylate $D_{(1)}$**



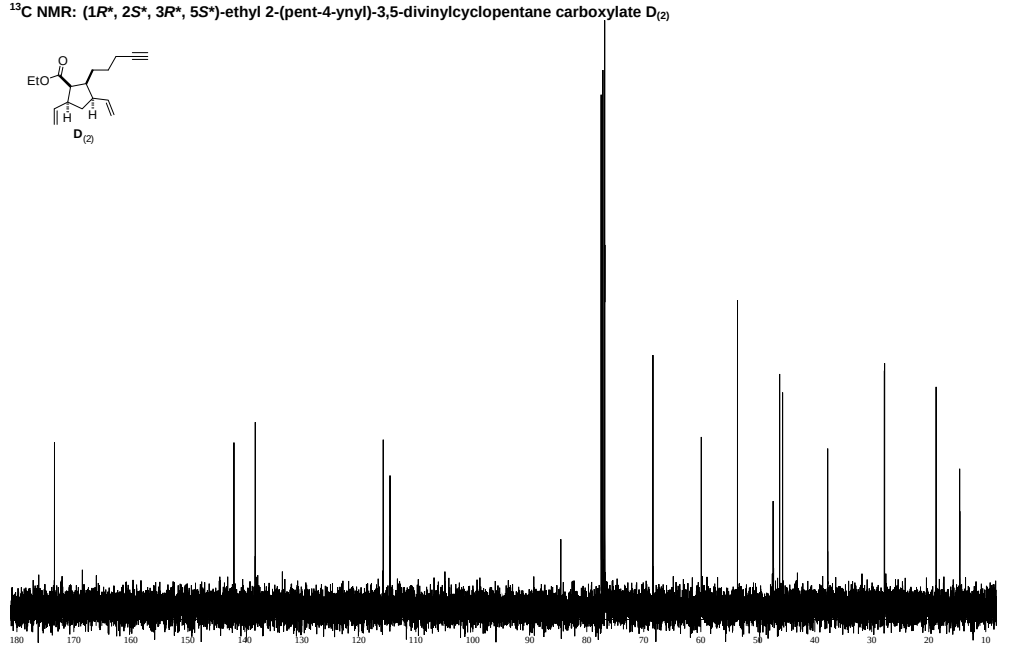
53

^{1}H NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(pent-4-ynyl)-3,5-divinylcyclopentane carboxylate $D_{(2)}$**



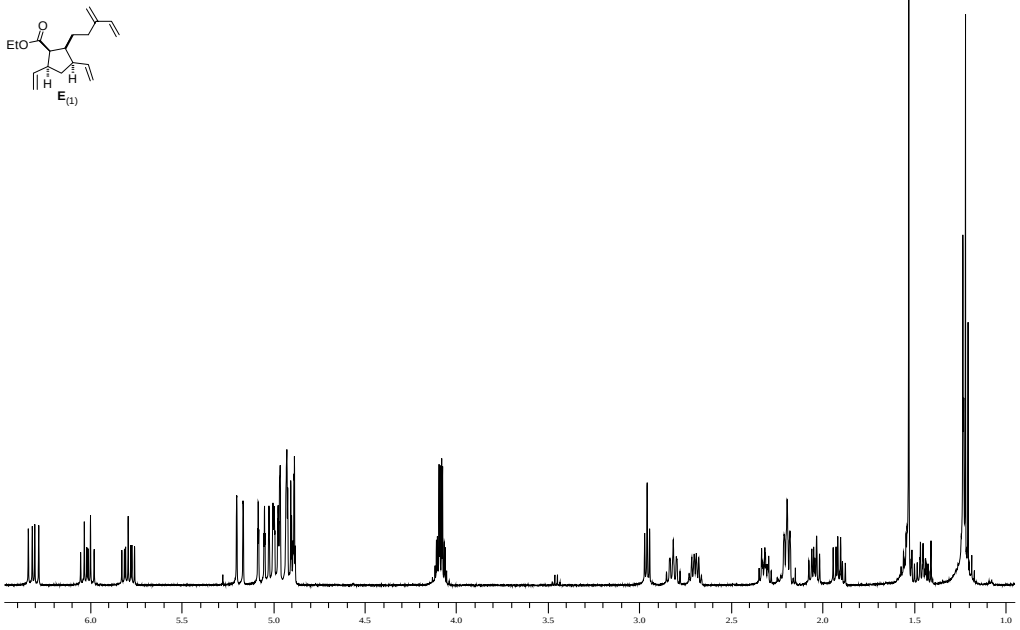
54

^{13}C NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(pent-4-ynyl)-3,5-divinylcyclopentane carboxylate $D_{(2)}$**



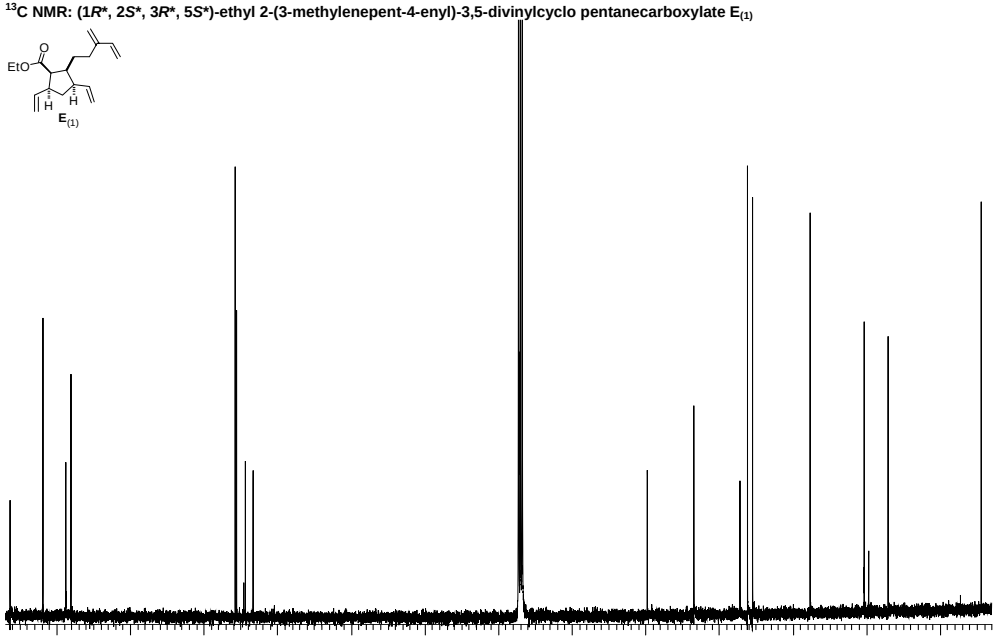
55

^{1}H NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(3-methylenepent-4-enyl)-3,5-divinylcyclo pentanecarboxylate $E_{(1)}$**



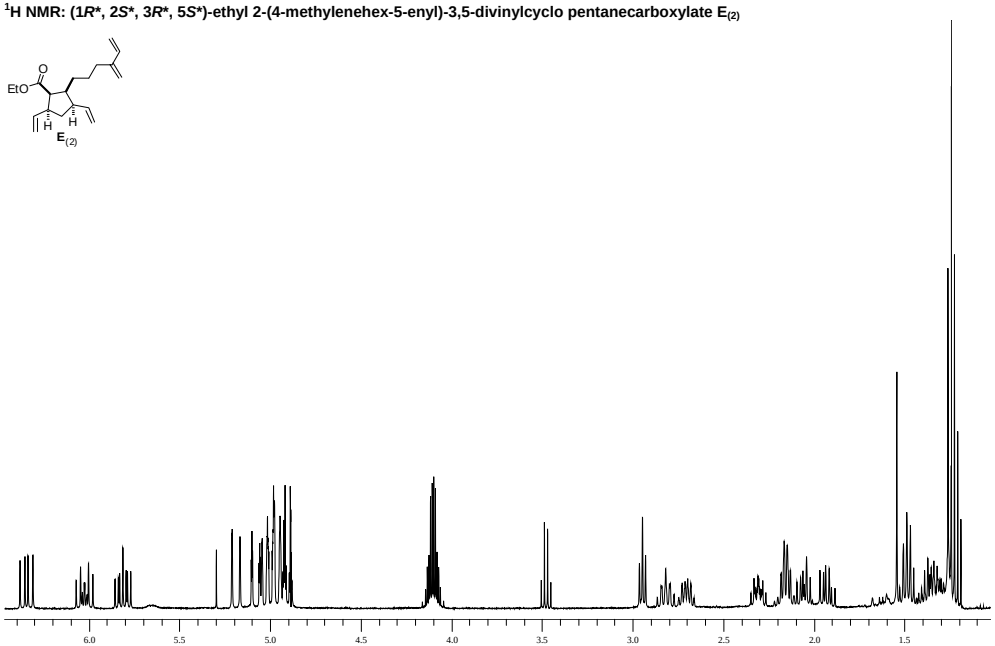
56

^{13}C NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(3-methylenepent-4-enyl)-3,5-divinylcyclo pentanecarboxylate $E_{(1)}$**



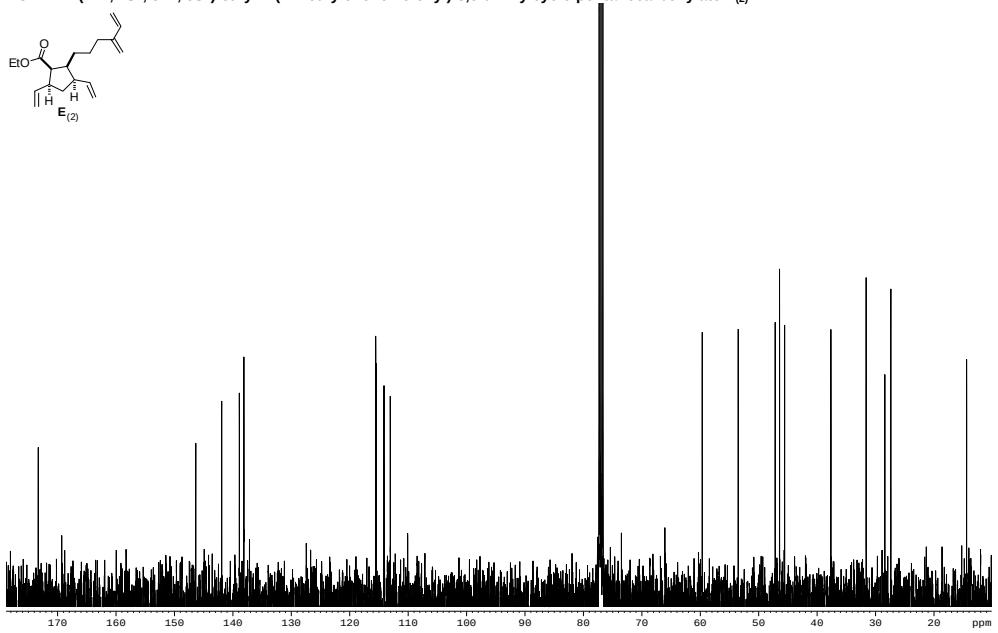
57

^{1}H NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(4-methylenehex-5-enyl)-3,5-divinylcyclo pentanecarboxylate $E_{(2)}$**



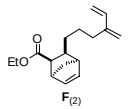
58

^{13}C NMR: (1*R, 2*S**, 3*R**, 5*S**)-ethyl 2-(4-methylenehex-5-enyl)-3,5-divinylcyclo pentanecarboxylate $E_{(2)}$**



59

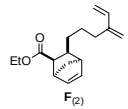
^{1}H NMR: (1*S, 2*R**, 3*S**, 4*R**)-ethyl 3-(4-methylenehex-5-enyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $F_{(2)}$**



$F_{(2)}$

60

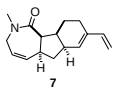
^{13}C NMR: (1*S, 2*R**, 3*S**, 4*R**)-ethyl 3-(4-methylenehex-5-enyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate $F_{(2)}$**



$F_{(2)}$

61

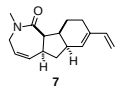
^{1}H NMR: (5a*S, 6a*S**, 10a*S**, 10b*R**, *Z*)-2-methyl-8-vinyl-2,3,6,6a,9,10,10a,10b-octahydroindeno[1,2-c]azepin-1(5aH)-one 7**



7

62

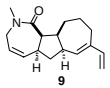
^{13}C NMR: (5a*S, 6a*S**, 10a*S**, 10b*R**, *Z*)-2-methyl-8-vinyl-2,3,6,6a,9,10,10a,10b-octahydroindeno[1,2-c]azepin-1(5aH)-one 7**



7

63

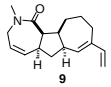
^{1}H NMR: (4*Z*, 5a*S, 6a*S**, 7*E*, 11a*S**, 11b*R**)-2-methyl-8-vinyl-2,3,5a,6,6a,9,10,11,11a, 11b-decahydro-1H-azuleno[1,2-c]azepin-1-one 9**



9

64

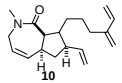
^{13}C NMR: (4*Z*, 5a*S, 6a*S**, 7*E*, 11a*S**, 11b*R**)-2-methyl-8-vinyl-2,3,5a,6,6a,9,10,11,11a, 11b-decahydro-1H-azuleno[1,2-c]azepin-1-one 9**



9

65

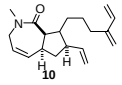
^{1}H NMR: (5a*S, 7*R**, 8a*R**, *Z*)-2-methyl-8-(4-methylenehex-5-enyl)-7-vinyl-2,3,6,7,8,8a-hexahydrocyclopenta[c]azepin-1(5aH)-one 10**



10

66

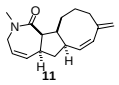
^{13}C NMR: (5a*S, 7*R**, 8a*R**, *Z*)-2-methyl-8-(4-methylenehex-5-enyl)-7-vinyl-2,3,6,7,8,8a-hexahydrocyclopenta[c]azepin-1(5aH)-one 10**



10

67

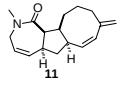
^{1}H NMR: 4-Methyl-13-methylene-4-aza-tricyclo[8.6.0.0^{2,8}]hexadeca-6,11-dien-3-one 11



11

68

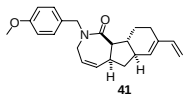
^{13}C NMR: 4-Methyl-13-methylene-4-aza-tricyclo[8.6.0.0^{2,8}]hexadeca-6,11-dien-3-one 11



11

69

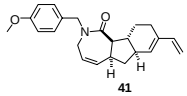
^{1}H NMR: (5a*S, 6a*S**, 10a*R**, 10b*R**, *Z*)-2-(4-methoxybenzyl)-8-vinyl-2,3,6,6a,9,10,10a, 10b-octahydroindeno[1,2-c]azepin-1(5aH)-one 41**



41

70

^{13}C NMR: (5a*S, 6a*S**, 10a*R**, 10b*R**, *Z*)-2-(4-methoxybenzyl)-8-vinyl-2,3,6,6a,9,10,10a, 10b-octahydroindeno[1,2-c]azepin-1(5aH)-one 41**



41

71

4.3 NMR Spectra: Diels Alder Adducts

The compounds below are listed in the same order as they appear in the experimental section above.

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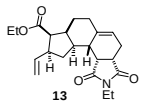
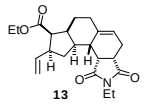
^{1}H: The Diels Alder Adduct 13



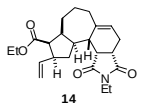
13

^{13}C NMR: The Diels Alder Adduct 13



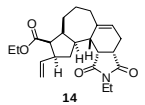
13

^{1}H NMR: Diels Alder Adduct 14



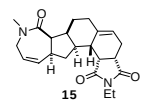
14

^{13}C NMR: Diels Alder Adduct 14



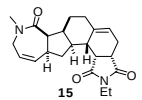
14

^{1}H NMR: Diels Alder Adduct 15



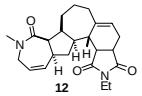
15

^{13}C NMR: Diels Alder Adduct 15



15

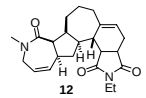
^{1}H NMR: Diels Alder Adduct 12



12

80

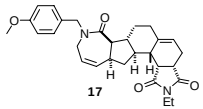
^{13}C NMR: Diels Alder Adduct 12



12

81

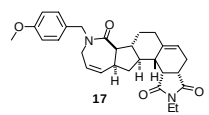
^{1}H NMR: Diels Alder Adduct 17



17

82

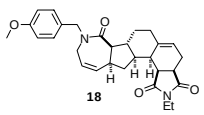
^{13}C NMR: Diels Alder Adduct 17



17

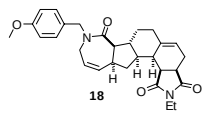
83

^{1}H NMR: Diels Alder Adduct 18



18

^{13}C NMR: Diels Alder Adduct 18



18