DOI: 10.1002/ejoc.200700291

Synthesis of Cyclic and Macrocyclic Ethers Using Metathesis Reactions of Alkenes and Alkynes

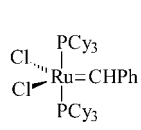
Elisabetta Groaz,[a] Donatella Banti,[a,b] and Michael North*[a,c]

Keywords: Oxygen heterocycles / Medium-ring compounds / Macrocycles / Metathesis / Ruthenium

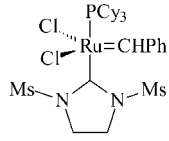
The metathesis transformations of cyclohexanes and cyclohexenes bearing allylic and/or propargylic ether substituents has been investigated. A range of products containing fused 6,8-bicyclic ring systems resulting from alkene and/or enyne metatheses were obtained using first and second generation, well defined alkylidene ruthenium catalysts. However, the unstrained cyclohexene unit did not participate in any of these metathesis processes, even though doing so would have led to a thermodynamically more stable product. This contrasts with previous results on similar compounds and on the corresponding amino-substituted cyclohexenes. The synthesis of dienes and dihydrofurans by metathesis processes involving the side chains of suitable cyclohexene ethers is also reported. When the unstrained cyclohexene unit was replaced by a norbornene group, the strained alkene did participate in a cascade of alkene and enyne metatheses. This chemistry was extended to alkyne metatheses of cyclohexene and norbornene esters, leading to 6,12-fused cycloalkynes which would subsequently undergo further enyne and/or alkene metatheses. This culminated in the development of the first one-pot metathesis process in which alkyne, enyne and alkene metathesis reactions initiated by two different catalysts all occur sequentially to form a 5,12-fused bicyclic diene product.

Introduction

Ring-closing metathesis (RCM) of alkenes is now well established as a highly versatile method for the synthesis of cyclic compounds, especially those containing normal or large rings. Progress in this area received a major boost through the development of well-defined ruthenium based metathesis initiators[1] such as compounds **1**[2] and **2**.[3] Compounds **1** and **2** not only induce metathesis processes at synthetically useful rates, they do so at ambient or near ambient temperature, tolerate many functional groups and do not require strictly anhydrous or anaerobic conditions. The related process of ring-closing enyne metathesis leading to cyclic dienes is also induced by well-defined ruthenium based catalysts such as **1** and **2**, and leads to synthetically useful cyclic dienes. Enyne metathesis has not been as widely exploited as alkene metathesis, but is of growing synthetic importance.[4]



1



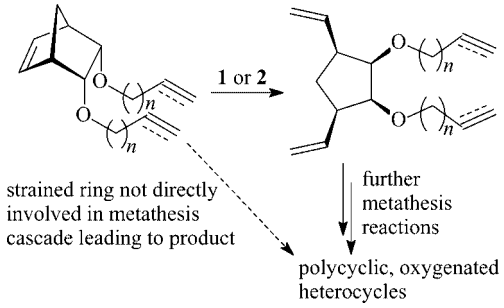
Ms = 2,4,6-trimethylphenyl

2

In a series of publications,[5] we have reported the use of catalysts **1** and **2** to initiate a cascade of alkene and enyne metathesis reactions of readily available norbornene derivatives. This chemistry provided a facile approach to the preparation of polycyclic oxygenated heterocycles in a one-pot process where in the metathesis transformations could be combined with Diels–Alder reactions. The driving force for the metathesis cascade in these reactions was initially assumed to be the release of ring-strain during the ring-opening metathesis (ROM) of the norbornene ring. However, the results obtained indicated that the norbornene unit first underwent ring-opening metathesis and cross metathesis to give an unstrained cyclopentane derivative which subsequently underwent the metathesis cascade leading to the final products as shown in Scheme 1. Hence it appeared that a strained starting material was not needed for this metathesis chemistry, and indeed we have reported that suitably functionalised 1,2-diaminocyclohexenes do undergo a metathesis cascade in which the cyclohexene unit participates.[6] To further investigate this area, we initiated a project to investigate alkene, enyne and alkyne metatheses of suitably substituted cyclohexane and cyclohexene deriva-

[a] Department of Chemistry, King's College, Strand, London, WC2R 2LS, UK
[b] School of Pharmacy and Chemistry, Kingston University, Penrhyn Road, Kingston-upon-Thames, Surrey, KT1 2EE, UK
[c] School of Natural Sciences, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
Fax: +44-870-131-3783
E-mail michael.north@ncl.ac.uk
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

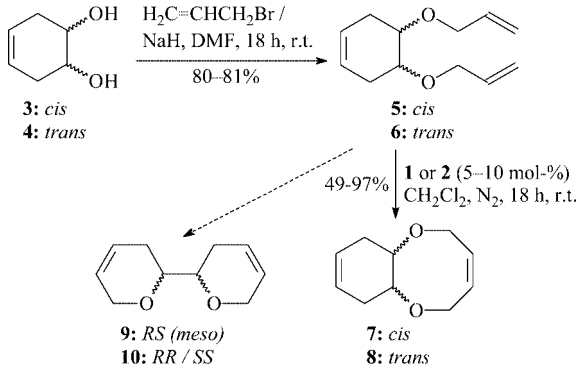
tives.[7,8] In this manuscript we give full details of this work, present additional results on the metathesis of norbornene derivatives for comparison, and show that alkyne,[9] enyne and alkene metatheses can all be combined into a one-pot process with a suitable substrate.



Scheme 1. Ring-closing metathesis of norbornene derivatives.

Results and Discussion

The first substrates investigated in this project were the *cis*- and *trans*-cyclohexene derivatives **5** and **6**, which were prepared from the known diols **3**[10] and **4**[11] as shown in Scheme 2. The metathesis of these compounds could proceed in two ways: a simple RCM leading to 6,8-fused bicyclic bis-ethers **7** and **8**, or a RCM-ROM-RCM cascade involving the cyclohexene unit and leading to bis-dihydropyrans **9** and **10** (Scheme 2). It was anticipated that bis-dihydropyrans **9** and **10** would be the thermodynamically most stable metathesis products, and literature precedent for the formation of compound **10** in a metathesis reaction existed in the work of Mioskowski et al.[12] These authors showed that treatment of compound **11** with catalyst **1** at 60 °C in benzene led initially to the formation of a mixture of compounds **6** and **10**, but that prolonged reaction (6 h) resulted in the formation of only compound **10**.



Scheme 2. Synthesis and metathesis of cyclohexene derivatives **5** and **6**.

However, when the compounds **5** or **6** were treated with catalysts **1** or **2** in dichloromethane, the only monomeric products obtained were 6,8-fused bicycles **7** and **8**. In both cases, the dimers **12**–**13** were also isolated, and in the case of the *trans*-substrate **6**, small amounts of macrocyclic dimer **14** were obtained. Compound **14** was obtained as a single C_2-symmetrical stereoisomer, but the relative configuration of the stereocentres and the stereochemistry of the alkene units could not be determined. For reactions involving the *cis*-substrate **5**, use of 5 mol-% of catalyst **1** at 25 °C under nitrogen gave a 49% yield of compound **7** (Table 1). Increasing the reaction temperature to 35 °C only slightly increased the yield, whilst an attempt to raise the temperature further by changing the solvent to toluene was detrimental. Changing the atmosphere to ethene resulted only in the quantitative recovery of unreacted starting material. However, increasing the amount of catalyst **1** to 10 mol-% did slightly increase the yield of compound **7**, though the

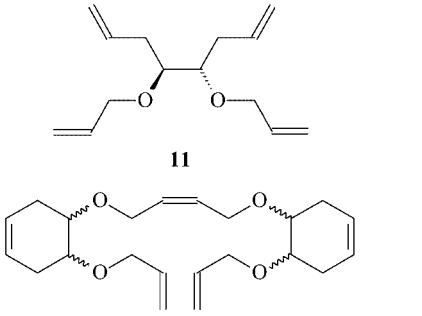
Table 1. Metathesis of **5** to **7** and **12**.

Catalyst	Solvent	Temp. [°C]	Atmosphere	Time [h]	**7** (% yield)	**12** (% yield)
1, 5 mol-%	CH_2Cl_2	25	N_2	20	49	5
1, 5 mol-%	CH_2Cl_2	25	ethene	48	0	0
1, 5 mol-%	CH_2Cl_2	35	N_2	20	51	6
1, 5 mol-%	toluene	55	N_2	20	38	13
1, 10 mol-%	CH_2Cl_2	25	N_2	20	54	9
2, 5 mol-%	CH_2Cl_2	25	N_2	20	71	7

Table 2. Metathesis of **6** to **8**, **13** and **14**.

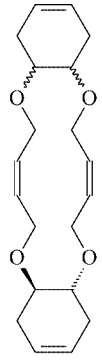
Catalyst	Solvent	Temp. [°C]	Atmosphere	Time [h]	**8** (% yield)	**13** (% yield)	**14** (% yield)
1, 5 mol-%	CH_2Cl_2	25	N_2	20	82	9	5
1, 5 mol-%	CH_2Cl_2	25	ethene	48	0	0	0
1, 5 mol-%	CH_2Cl_2	35	N_2	20	92	6	2
1, 10 mol-%	CH_2Cl_2	25	N_2	20	86	9	5
2, 5 mol-%	CH_2Cl_2	25	N_2	20	97	0	0

highest yield was obtained by the use of 5 mol-% of the second generation catalyst **2**. Under these conditions, compound **7** could be isolated in 71% yield along with 7% of dimer **12**. The *trans*-fused substrate **6** was generally more reactive and only 5 mol-% of catalyst **1** was required to form compound **8** in 82% yield (Table 2). This yield could be increased to 92% by carrying out the reaction at 35 °C, though again the highest yield (97%) was obtained using catalyst **2**, and in this case no dimeric products were isolated. The ^{1}H and ^{13}C NMR spectroscopic data for compound **8** were totally different to those given by Mioskowski et al. for compound **10**,[12] thus confirming that the products were different species.



11

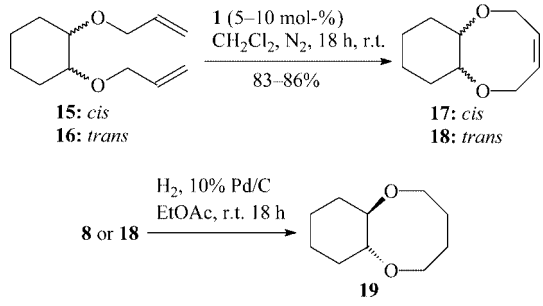
12: *cis*-stereochemistry on each cyclohexene ring
13: *trans*-stereochemistry on each cyclohexene ring



14

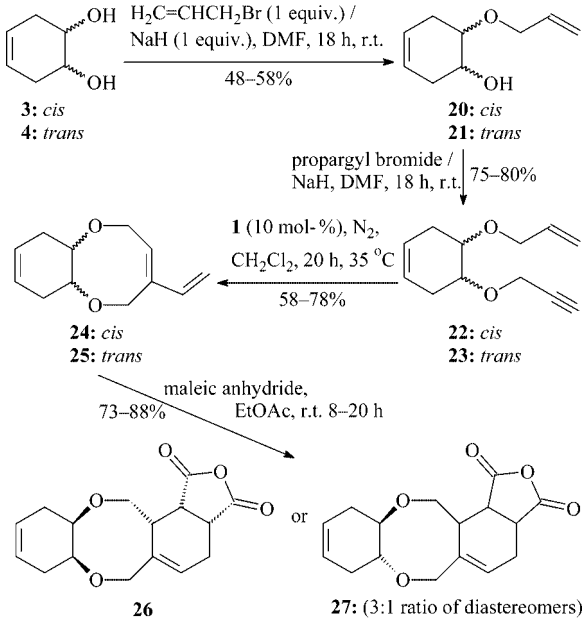
A partial explanation for the difference between our results and those of Mioskowski et al. may be the different reaction temperatures employed. All of the metathesis reactions conducted by Mioskowski et al. were carried out at 60 °C in benzene, whilst we chose to work in dichloromethane at 25–35 °C. It may be that the 6,8-bicyclic compounds **7** and **8** are the kinetic products of metathesis reactions starting from compounds **5**, **6** and **11** whilst the bis-dihydropyrans **9**, **10** are the thermodynamic products. However, this cannot be the whole explanation because it does not explain why metathesis of compound **5** at 55 °C in toluene (Table 1) gave product **7** and not compound **9**; nor does it explain why Mioskowski et al. were able to isolate cyclohexene **6** rather than compound **8** from their reactions. The course of the metathesis reactions on these substrates may also be very sensitive to other factors such as solvent and concentration. Attempts to explore the further metathesis of compounds **7** and **8** by re-exposing them to catalyst **1** or **2** under a range of reaction conditions resulted only in the re-isolation of compounds **7** and **8**.

To confirm the structures of compounds **7** and **8**, the metathesis of the corresponding cyclohexane derivatives **15** and **16** was undertaken (Scheme 3). Compounds **15** and **16** can only undergo RCM to give 6,8-fused bicyclic ethers **17** and **18** respectively, and the metathesis of these compounds has previously been reported by Grubbs et al.[13] using $RuCl_2(PCy_3)_2$=CH–CH=CPh_2 as the metathesis initiator. When compounds **15** and **16** were treated with first generation Grubbs' catalyst **1** at room temperature in dichloromethane, they were both converted into 6,8-fused bicyclic products **17** and **18** in 83–86% yield. Consistent with the results of Grubbs' et al.,[13] the *cis*-isomer **15** was less reactive towards RCM than *trans*-isomer **16** as the former required 10 mol-% of catalyst **1** to consume all the starting material, whilst the metathesis of compound **16** proceeded under identical conditions with only 5 mol-% of catalyst **1**. Final proof of the structure of compound **8** was obtained by hydrogenating each of compounds **8** and **18** to give compound **19** (Scheme 3). Compound **19** was analysed by GC-MS, and the product obtained from compounds **8** and **18** had identical retention times and mass spectra.



Scheme 3. Synthesis of compounds **17**–**19**.

On the basis of the above results, it was apparent that at temperatures below 60 °C, metathesis cascades involving a cyclohexene unit could not compete with RCM of terminal alkenes even when the latter process generates the thermodynamically less stable product. Because enyne metatheses generally proceed less readily than alkene metatheses,[4] the ability of a cyclohexene unit to intervene in a ring-closing enyne metathesis (RCEM) process was investigated.[14] For this study, allyl propargyl bis-ethers **22** and **23** were prepared from the diols **3** and **4**, respectively, as shown in



Scheme 4. Synthesis and enyne metathesis of compounds **22** and **23**.

Scheme 4. Thus, mono-allylation of the diols **3** and **4** gave a moderate yield of the alcohols **20** and **21** which could be propargylated to give the desired bis-ethers **22** and **23**.

Tables 3 and 4 detail the results obtained when the bis-ethers **22** and **23** were treated with first- or second-generation Grubbs' catalyst. In every case, the only isolated product was the 6,8-fused diene **24** or **25** resulting from a single RCEM event, and no evidence for involvement of the cyclohexene unit in the metathesis process was ever observed.[15] However, the results do confirm that RCEM is a less favourable process than RCM since under identical reaction conditions, dienes **24** and **25** were obtained in significantly lower yields than compounds **7** and **8**. Thus, whereas treatment of compound **5** with 5 mol-% of catalyst **1** at 25 °C gave a 49% yield of the *cis*-6,8-fused bicycle **7**, treatment of compound **22** with the same catalyst under identical conditions gave only a 26% yield of the *cis*-6,8-fused bicycle **24**. A similar trend was apparent for the *trans*-fused products **8** and **25** which were formed in 82 and 47% yield, respectively. The optimal conditions for the formation of the dienes **24** and **25** involved the use of 10 mol-% of catalyst **1** at 35 °C in dichloromethane, and the *trans*-diene **25** was formed in higher yield than *cis*-diene **24**, again consistent with the results obtained for the RCM of substrates **5** and **6** (Table 1 and Table 2).

Table 3. Metathesis of **22** to **24**.

Catalyst	Solvent	Temp. [°C]	Atm.	Time [h]	% Yield
1 (5 mol-%)	CH_2Cl_2	25	N_2	20	26
1 (10 mol-%)	CH_2Cl_2	25	N_2	24	46
1 (10 mol-%)	CH_2Cl_2	35	N_2	24	58
1 (10 mol-%)	CH_2Cl_2	25	ethene	20	12
2 (5 mol-%)	CH_2Cl_2	25	N_2	20	15

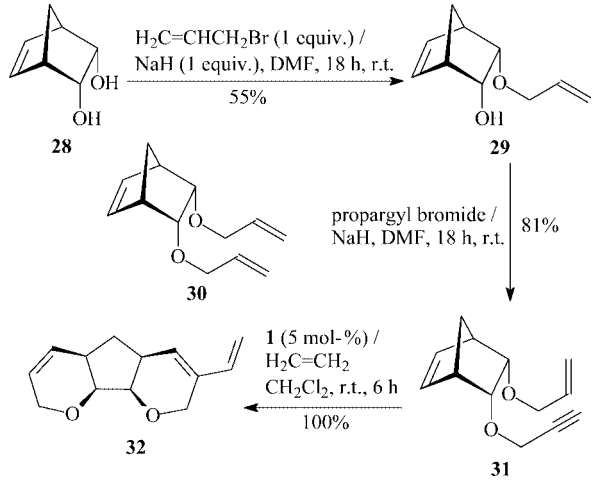
Table 4. Metathesis of **23** to **25**.

Catalyst	Solvent	Temp. [°C]	Atm.	Time [h]	% Yield
1 (5 mol-%)	CH_2Cl_2	25	N_2	1.5	(38)[a]
1 (5 mol-%)	CH_2Cl_2	25	N_2	3	(43)[a]
1 (5 mol-%)	CH_2Cl_2	25	N_2	20	47
1 (10 mol-%)	CH_2Cl_2	25	N_2	20	72
1 (10 mol-%)	CH_2Cl_2	35	N_2	20	78
1 (5 mol-%)	CH_2Cl_2	25	ethene	20	11
1 (10 mol-%)	CH_2Cl_2	25	ethene	24	25
2 (5 mol-%)	toluene	60	N_2	20	32
2 (5 mol-%)	CH_2Cl_2	25	N_2	24	32

[a] Brackets indicate conversion from NMR rather than isolated yield.

Enyne metatheses are often accelerated by conducting the reactions under ethene[16] (to prepare a more reactive methylidene ruthenium complex[17] in situ), but in the case of substrates **22** and **23**, this was detrimental to the product yield. This is consistent with previous observations on the synthesis of eight-membered dienes by RCEM catalysed by complex **1**.[15] Interestingly, use of the second generation metathesis catalyst **2** also resulted in decreased yields of compounds **24** and **25**, in marked contrast to the metathesis of compounds **5** and **6**, where use of the second generation catalyst gave a higher yield of product than was obtained by use of the first generation catalyst **1**. Both dienes **24** and **25** readily underwent a Diels–Alder reaction with maleic anhydride to give the tetracyclic anhydrides **26** and **27**, respectively. In the case of the *cis*-diene **24**, the anhydride was formed as a single diastereomer, whilst the anhydride derived from the *trans*-diene **25** was formed as a 3:1 ratio of diastereomers. Neither anhydride was crystalline, and their NMR spectra (including 2D correlations and NOESY) did not allow the stereochemistry of the anhydrides to be defined.

For comparison, the metathesis of the norbornene derivative **31** was also investigated. Compound **31** was prepared from the known[18] diol **28** as shown in Scheme 5. Treatment of diol **28** with allyl bromide gave a mixture of the alcohol **29** and the bis-allyl ether **30**.[19] Compound **29** could then be readily converted into allylpropargyl ether **31** by treatment with propargyl bromide. Treatment of compound **31** with either catalyst **1** or **2** in the presence of ethene gave the tricyclic diene **32**, with optimal results being obtained by the use of catalyst **1** at 25 °C in dichloromethane (Table 5). Thus, in contrast to substrates **22** and **23**, the strained alkene within compound **31** readily participates in a RCM−ROM−RCEM cascade.



Scheme 5. Synthesis and enyne metathesis of compound **31**.

Table 5. Metathesis of **31** to **32**.

Catalyst	Solvent	Temp. [°C]	Atm.	Time [h]	% Yield
1 (5 mol-%)	CH_2Cl_2	25	ethene	6	100
1 (5 mol-%)	CH_2Cl_2	35	ethene	20	82
1 (5 mol-%)	CH_2Cl_2	25	N_2	24	0
2 (5 mol-%)	toluene	60	ethene	24	54

It was apparent from the results presented in Table 3 and Table 4, that ring-opening of a cyclohexene unit could not compete with RCEM to form the eight-membered ring in compounds **22** and **23**. Therefore, a different class of substrates was investigated: the bis-propargyl ethers **35**–**38**. Compounds **35**–**38** were readily prepared by propargylation of diols **3**,**4**,**33**,**34**, respectively, as shown in Scheme 6. Me-

Table 6. Metathesis of **35** to **39**, **40** and **41**.

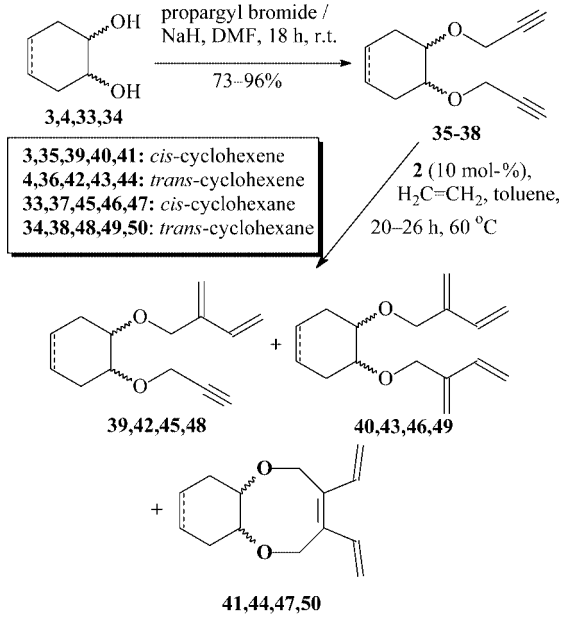
Catalyst	Solvent	Temp. [°C]	Atmosphere	Time [h]	**39** (%)	**40** (%)	**41** (%)
1 (5 mol-%)	CH_2Cl_2	25	N_2	48	0	0	0
1 (5 mol-%)	CH_2Cl_2	25	ethene	48	0	0	0
1 (5 mol-%)	CH_2Cl_2	35	ethene	24	0	0	0
2 (5 mol-%)	toluene	60	ethene	48	11	7	6
2 (10 mol-%)	toluene	60	ethene	24	31	15	13
2 (10 mol-%)	toluene	60	ethene	48	17	16	14

Table 7. Metathesis of **36** to **42**, **43** and **44**.

Catalyst	Solvent	Temp. [°C]	Atmosphere	Time [h]	**42** (%)	**43** (%)	**44** (%)
1 (5 mol-%)	CH_2Cl_2	25	N_2	48	0	0	0
1 (5 mol-%)	CH_2Cl_2	25	ethene	24	0	0	0
1 (10 mol-%)	CH_2Cl_2	35	ethene	19	0	0	0
2 (5 mol-%)	CH_2Cl_2	25	ethene	24	0	0	0
2 (5 mol-%)	toluene	60	ethene	16	11	7	5
2 (10 mol-%)	toluene	60	ethene	20	28	18	14
2 (5 mol-%)	toluene	80	ethene	24	7	3	3
2 (10 mol-%)	toluene	80	ethene	24	20	14	11
2(10 mol-%)[a]	toluene	60	ethene	24	27	13	10

[a] Added as two 5 mol-% portions.

tathesis reactions on substrates **35** and **36** were carried out with catalysts **1** and **2** under various reaction conditions (Table 6 and Table 7). Both substrates were inert to catalyst **1** under all reaction conditions investigated, and underwent metathesis reactions initiated by catalyst **2** only at elevated temperatures in the presence of ethene.[20] In both cases, the optimal reaction reactions involved the use of 10 mol-% of catalyst **2** at 60 °C in toluene for 20–24 h, and under these conditions a mixture of three metathesis products (**39**–**41** and **42**–**44**, respectively) was obtained from both substrates (Scheme 6). The cyclohexane derivatives **37** and **38** reacted analogously under the optimised reaction conditions (catalyst **2** 10 mol-%, 60 °C in toluene for 24 h) to give mixtures of compounds **45**–**47** and **48**–**50**, respectively.



Scheme 6. Synthesis and enyne metathesis of compounds **35**–**38**.

The formation of the compounds **39**–**50** can be accounted for by an initial reaction between catalyst **2** and ethene to generate the corresponding methylidene complex, followed by an enyne metathesis between this species and one of the terminal alkyne units of compounds **35**–**38**. The resulting vinylidene can then either undergo cross metathesis with another molecule of ethene to form dienes **39**, **42**, **45** or **48** (and the process can be repeated at the other alkyne to give the bis-dienes **40**, **43**, **46** or **49**), or can undergo RCEM to form an eight-membered ring and produce trienes **41**, **44**, **47** or **50** after a subsequent cross metathesis with ethene. Interestingly, whilst the diene and bis-diene containing products can be accounted for by a mechanism in which the initial metathesis occurs to attach the large ruthenium unit at the terminus of the alkyne, formation of the eight-membered ring trienes requires the opposite regiochemistry for the initial metathesis reaction, thus placing the large ruthenium unit at the internal end of the alkyne.

To further investigate the enyne metathesis potential of the substrates **35** and **36**, a series of reactions was carried out in which the ethene atmosphere was replaced by a fivefold excess of 1-hexene. Under these conditions, both catalysts **1** and **2** reacted with the substrates **35** and **36** (Table 8 and Table 9) and did so to produce a mixture of dienes (**51**, **52**) and bis-dienes (**53**, **54**) as shown in Scheme 7. The

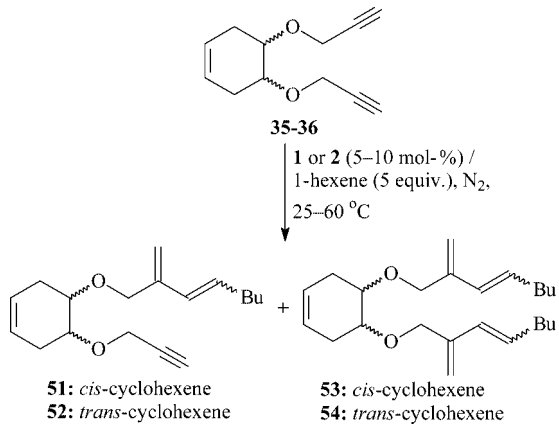
Table 8. Metathesis of **35** to **51** and **53**.

Catalyst	Solvent	Temp. [°C]	Time [h]	**51** (%)	**53** (%)
1 (5 mol-%)	CH_2Cl_2	25	24	27	16
1 (5 mol-%)	CH_2Cl_2	35	24	53	27
1 (10 mol-%)	CH_2Cl_2	25	24	60	40
2 (5 mol-%)	toluene	60	24	18	10

dienes **51** and **52** were formed as a 1:1 ratio of *E*- and *Z*-isomers, whilst bis-dienes **53** and **54** were each formed as a 1:1 ratio of *EE*- and *ZZ*-isomers.

Table 9. Metathesis of **36** to **52** and **54**.

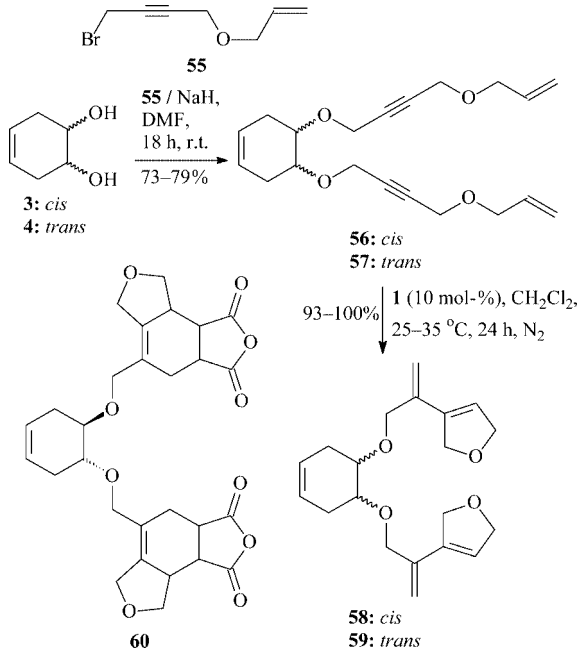
Catalyst	Solvent	Temp. [°C]	Time [h]	**52** (%)	**54** (%)
1 (5 mol-%)	CH_2Cl_2	25	24	19	12
1 (5 mol-%)	CH_2Cl_2	35	24	32	16
1 (10 mol-%)	CH_2Cl_2	25	24	50	26
2 (5 mol-%)	toluene	60	24	22	14



Scheme 7. Cross metathesis between compounds **35**, **36** and 1-hexene.

Comparison of the results obtained for the metathesis of compounds **35**–**36** in the presence of ethene and 1-hexene reveals some interesting differences. Most notably, catalyst **1** was more active than catalyst **2** for reactions carried out with 1-hexene, whilst catalyst **1** was totally inactive in the presence of ethene. It is known that catalyst **1** reacts with ethene to form the analogous methylidene complex which subsequently decomposes relatively rapidly compared to other alkylidenes ruthenium compounds.[21] Given that the metathesis reactions involving substrates **35**–**36** are relatively slow, it is likely that the rate of decomposition of the methylidene complex is greater than the rate of initiation of metathesis, thus accounting for the lack of reactivity observed using catalyst **1** with substrates **35**–**36**. In contrast, the methylidene complex derived from catalyst **2** is known to be much more stable (its half life is 8.5 times longer[22]), so that it is able to initiate the metathesis of substrates **35**–**36** faster than it decomposes. However, in the presence of 1-hexene the methylidene complex will be in equilibrium with the pentylidene complex which will have a similar stability to complex **1** and which serves to protect the more reactive methylidene complex when it is not involved in productive metatheses.[23] The other interesting contrast between the use of ethene and 1-hexene is the total lack of any cyclic triene formation in the latter case which may be due to steric hindrance caused by the butyl groups since the formation of compounds **51**–**54** indicates that the regiochemistry of the enyne metathesis is such that the ruthenium unit is located at the internal end of the alkyne.

The effect of setting up an intramolecular enyne cascade was investigated through the reaction of diols **3** and **4** with bromide **55**[24] to give compounds **56** and **57**, respectively, as shown in Scheme 8. Compounds **56** and **57** underwent enyne metathesis reactions to give bis-dienes **58** and **59**, respectively, only when treated with first-generation Grubb's catalyst **1**, and only in the absence of ethene (Table 10 and Table 11). In the case of the *cis*-substrate **56**, a high yield of compound **58** was obtained by use of 10 mol-% of the catalyst **1** at 25 °C, whilst for the corresponding *trans*-substrate **57**, a temperature of 35 °C was necessary to obtain complete conversion to product **59**. Compounds **58** and **59** decomposed over a period of a few hours at room temperature, presumably as a result of double-bond migrations. As a result, it was not possible to carry out Diels–Alder reactions on the isolated dienes.



Scheme 8. Synthesis and metathesis of substrates **56** and **57**.

Table 10. Metathesis of **56** to **58**.

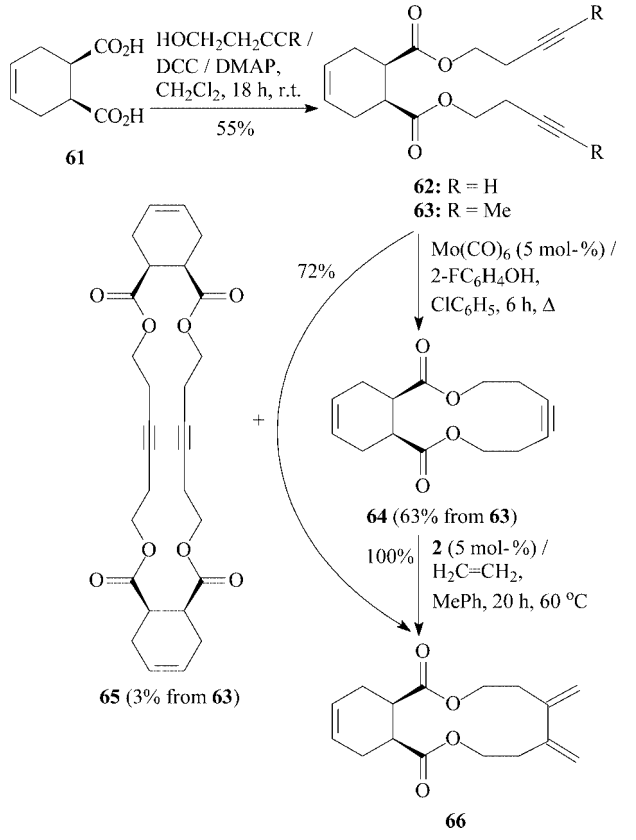
Catalyst	Solvent	Temp. [°C]	Atm.	Time [h]	% Yield
1 (5 mol-%)	CH_2Cl_2	25	N_2	15	7
1 (5 mol-%)	CH_2Cl_2	25	ethene	24	0
1 (10 mol-%)	CH_2Cl_2	25	N_2	24	93
2 (5 mol-%)	CH_2Cl_2	25	N_2	24	0
2 (5 mol-%)	toluene	60	N_2	24	0

Table 11. Metathesis of **57** to **59**.

Catalyst	Solvent	Temp. [°C]	Atm.	Time [h]	% Yield
1 (5 mol-%)	CH_2Cl_2	25	N_2	22	28
1 (5 mol-%)	CH_2Cl_2	25	ethene	24	0
1 (5 mol-%)	CH_2Cl_2	35	N_2	22	32
1 (10 mol-%)	CH_2Cl_2	25	N_2	21	68
1 (10 mol-%)	CH_2Cl_2	35	N_2	24	100
2 (5 mol-%)	CH_2Cl_2	25	N_2	48	0
2 (5 mol-%)	toluene	60	N_2	24	0

However, the bis-anhydride **60** could be accessed as a 1:1:1 ratio of diastereomers in 75% yield from the *trans*-substrate **57** by carrying out the enyne metathesis and Diels–Alder reactions sequentially without purifying the intermediate bis-dihydrofuran **59**.

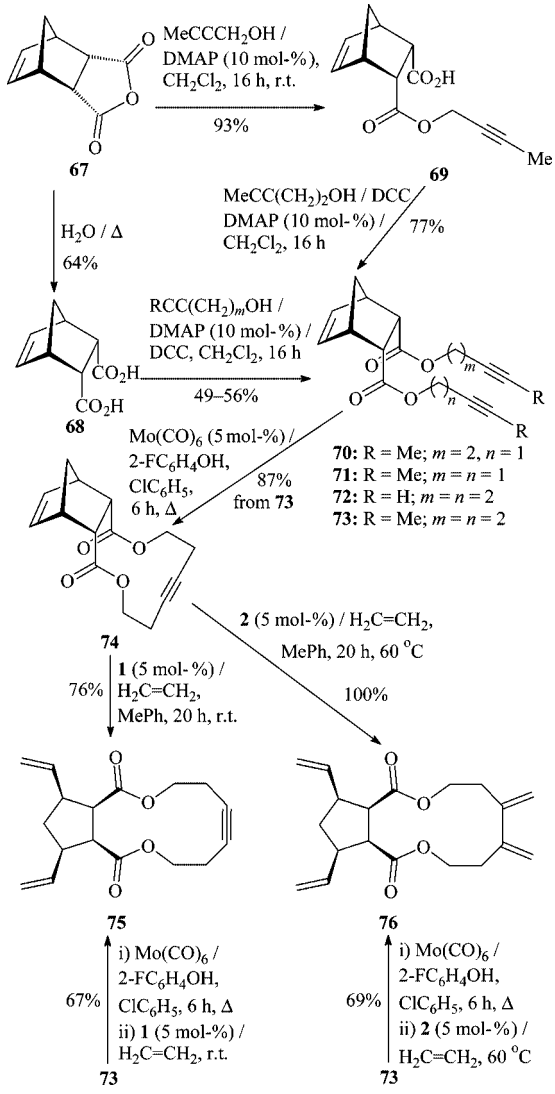
Compounds such as **35**–**38** which contain two alkyne units could in principle also undergo alkyne metathesis reactions; so we decided to investigate if reaction conditions could be found, under which a suitable substrate could undergo sequential alkyne and enyne or alkene metatheses. Alkylideneruthenium compounds such as catalysts **1** and **2** do not initiate alkyne metatheses, and of the various catalytic systems available for alkyne metathesis,[9] the (hexacarbonyl)molybdenum/2-fluorophenol system developed by Grela[25] appeared to be experimentally convenient. Ring-closing alkyne metathesis (RCAM) usually requires that the cycloalkyne being formed contains at least 12 carbon atoms,[25–27] so compounds **35**–**38** would not be expected to undergo RCAM. Hence, substrates **62** and **63** were prepared because RCAM would provide a 12-membered ring and they contain an additional alkene unit which might be involved in subsequent enyne metathesis reactions. Compounds **62** and **63** were readily available by esterification of diacid **61**[28] as shown in Scheme 9.



Scheme 9. Synthesis and alkyne metathesis of substrates **62** and **63**.

Treatment of compound **62** with (hexacarbonyl)molybdenum/2-fluorophenol in refluxing chlorobenzene gave only intractable polymeric materials, in line with previous reports of the failure of terminal alkynes to undergo alkyne metathesis reactions.[25,29] In contrast, treatment of substrate **63** bearing two internal alkynes under identical conditions gave the expected cyclic alkyne **64** in 63% yield, along with 3% of the dimeric bis-alkyne **65**. Compound **64** could not be induced to undergo alkene or enyne metatheses in the presence of catalyst **1**, but in the presence of catalyst **2** and ethene, it did undergo enyne cross-metathesis to give diene **66** in quantitative yield.[20b] No products arising from metatheses involving the cyclohexene unit could be detected. Compound **66** could also be prepared directly from bis-alkyne **63** by sequential addition of the alkyne and enyne metathesis catalysts to a solution of compound **63** in chlorobenzene. This one-pot process gave a higher chemical yield of diene **66** (72%) and demonstrated that catalyst **2** was stable to the (hexacarbonyl)molybdenum, 2-fluorophenol and their decomposition products formed during the initial alkyne metathesis.

To extend this combination of alkyne and enyne metatheses to substrates containing an alkene unit which would participate in metathesis reactions, the norbornene diesters **70**–**73** were prepared. The starting material for the synthesis



Scheme 10. Synthesis and metathesis reactions of substrates **70**–**73**.

of these diesters was *endo*-norborn-5-ene-2,3-dicarboxylic anhydride (**67**) which underwent ring-opening with water to give the diacid **68**.[30] DCC-induced diesterification of the diacid **68** gave the symmetrical diesters **71**–**73** (Scheme 10). For the synthesis of unsymmetrical diester **70**, anhydride **67** was first ring-opened with but-2-yn-1-ol to give acid **69**, then esterified to give the desired diester **70**.

Diesters **70**–**71** failed to undergo alkyne metathesis when treated with (hexacarbonyl)molybdenum/2-fluorophenol under the conditions used for diester **63**. RCAM in these cases would have given 10- to 11-membered ring-containing alkynes for which there is only very limited precedent in alkyne metathesis chemistry.[27] However, no dimeric products (analogous to **65**) were detected either. The terminal diyne **72** did react under these conditions, but produced an insoluble polymeric material.[25,29] Compound **73**, however, was an excellent substrate for RCAM induced by the Grela catalyst system,[25] giving cyclic alkyne **74** in 87% yield (Scheme 10). Treatment of compound **74** with first-generation Grubbs metathesis catalyst **1** in the presence of ethene resulted only in the ROM of the strained norbornene ring, giving the bis-alkene **75**. In contrast, use of the second-generation catalyst **2** resulted in both ROM of the norbornene unit and enyne cross metathesis, leading to diene **76**.[20b]

The synthesis of compounds **75** and **76** could also be carried out directly from bis-yne **73** in a one-pot process by sequential addition of the two metathesis catalysts. In the case of the synthesis of the compound **76**, this involves all three classes of metathesis reactions (alkyne, enyne and alkene) occurring sequentially in a one-pot process. Such a combination of metathesis transformations has not previously been reported.

Conclusions

Treatment of allyl or propargyl ethers of cyclohexenes with ruthenium-based metathesis initiators at temperatures of up to 60 °C results in metathesis occurring exclusively at alkene or alkyne units within the side-chains to give 6,8-fused bicyclic bis-ethers as a result of a kinetically controlled reaction rather than the thermodynamically more stable bis-dihydropyran derivatives that could have been formed by participation of the cyclohexene unit in the metathesis cascade. This contrasts with previous work on the metathesis of cyclohexene ethers at elevated temperatures,[12] and with previous work on diamino cyclohexene derivatives.[6] These metathesis sequences were also extended to cross-metatheses leading to bis-dienes, and to intramolecular enyne metatheses leading to dihydrofurans. These results illustrate some significant differences in reactivity between the first- and second-generation Grubbs' catalysts **1** and **2**, and show that for enyne metatheses, the first-generation catalyst **1** sometimes gives better results than the second-generation catalyst **2**, a result which can be explained on the basis of the stability of the various alkylidene ruthenium compounds formed during the metathesis cascades. In contrast, a norbornene derivative bearing allylic and propargylic ether substituents did undergo a cascade of enyne and alkene metatheses involving the norbornene unit, leading to the formation of a 6,5,6-tricyclic diene. This is consistent with previous work on the metathesis of norbornene derivatives.[5]

Alkyne metathesis of cyclohexene and norbornene esters was also investigated using (hexacarbonyl)molybdenum/2-fluorophenol as the metathesis initiator. 6,12-Fused bicyclic alkynes could be formed in good yield, and the products were substrates for further alkene or enyne metatheses initiated by catalysts **1** and **2**. Although the conditions required for alkyne metatheses are very different to those employed for alkene or enyne metatheses, it has been shown that the two processes can also be carried out sequentially in a one-pot process using molybdenum hexacarbonyl/2-fluorophenol followed by either catalyst **1** or **2**. The culmination of this work was the illustration that all three types of metathesis: alkyne, enyne and alkene could be carried out sequentially on a substrate in a one-pot process. This opens up new potential for sequential and cascade metathesis processes involving multiple catalysts and reaction types as well as non-metathesis transformations.

Experimental Section

Dichloromethane was dried by distillation over calcium hydride. Toluene was dried by distillation from metallic sodium prior to use. All reactions were carried out under an inert atmosphere. Chromatographic separations were performed using silica gel 60 (230–400 mesh) supplied by Merck. Analytical thin layer chromatography (TLC) was carried out on Merck polyester backed sheets coated with silica gel 60 F254, using short wavelength (254 nm) ultraviolet light, or basic potassium permanganate ($KMnO_4$) stains to visualise components.

Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded with a Perkin–Elmer Paragon 1000 Fourier transform IR spectrometer using sodium chloride plates. Characteristic absorptions are reported in wavenumbers (cm^{-1}) with the following abbreviations: strong (s), medium (m) or weak (w).

^1H and ^{13}C NMR spectra were recorded with Bruker Avance digital NMR spectrometers operating at 360, 400 or 500 MHz for protons and 90, 100 or 125 MHz for carbon atoms. All spectra were recorded at room temperature in $CDCl_3$ (unless otherwise stated) and referenced to tetramethylsilane. Chemical shifts are expressed in parts per million. Coupling constants are given in Hertz. The multiplicity of signals is reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br) or a combination of any of these. Determination of structures was achieved with the aid of DEPT spectra and two-dimensional NMR techniques including COSY, long-range COSY, NOESY, one-bond heteronuclear correlation and multiple bond heteronuclear correlation as appropriate.

Low- and high-resolution mass spectra were recorded at the EPSRC national service at the University of Wales, Swansea, or with a Bruker Apex III FTMS or Jeol AX505W spectrometer within the chemistry department at King's College London. The sample was ionized by electron ionisation (EI), chemical ionisation (CI) or electrospray ionisation (ESI). The major fragment ions are reported and only the molecular ions are assigned. GCMS was

performed with the Jeol AX505W spectrometer using a 0.25-μm BP1 column (25 m × 0.25 mm) with helium as the carrier gas at 12 psi. The temperature was held at 60 °C for 2 min, then increased at 8 °C/min to 280 °C.

All metathesis products were purified by flash chromatography so that the concentration of residual ruthenium species and/or phosphane was below the detection limits of ^{1}H and ^{13}C NMR spectroscopy.

***cis*-1,2-Bis(allyloxy)cyclohex-4-ene (5):** To a stirring solution of *cis*-1,2-dihydroxycyclohex-4-ene[10] (**3**, 0.50 g, 4.4 mmol) in DMF (25 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.53 g, 13.2 mmol). After stirring for 1 h at 0 °C, allyl bromide (2.65 g, 21.9 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (10 mL), the mixture was extracted with Et_2O (4 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **5** as a colourless oil (0.68 g, 80%). IR (neat): $\tilde{\nu}_{max}$ = 3078 (w), 3028 (m), 2908 (s), 2983 (m), 2907 (s), 1646 (m) cm^{-1}. ^{1}H NMR: δ = 6.01–5.90 (m, 1 H, C*H*=CH$_2$), 5.60 (t, *J* = 1.5 Hz, 1 H, C*H*=CH), 5.30 (dq, *J* = 17.2, 1.7 Hz, 1 H, =CH$_2$), 5.17 (ddd, *J* = 10.4, 3.1, 1.4 Hz, 1 H, =CH$_2$), 4.20–4.09 (m, 2 H, CH$_2$O), 3.78–3.75 (m, 1 H, OCH), 2.42–2.36 (m, 1 H, CH$_2$), 2.26 (ddd, *J* = 16.4, 4.5, 1.8 Hz, 1 H, CH$_2$) ppm. ^{13}C NMR: δ = 135.9 (=CH), 124.6 (=CH), 116.9 (=CH$_2$), 75.0 (OCH), 70.5 (CH$_2$O), 29.7 (CH$_2$) ppm. MS (EI): *m*/*z* (%) = 194 (5) [M$^+$], 153 (2), 167 (11), 137 (100); found (ESI) 217.1196 [M + Na$^+$], $C_{12}H_{18}O_2Na$ requires 217.1199.

***trans*-1,2-Bis(allyloxy)cyclohex-4-ene (6):**[12] To a stirring solution of *trans*-1,2-dihydroxycyclohex-4-ene[11] (**4**, 1.0 g, 8.8 mmol) in DMF (60 mL) at 0 °C was slowly added NaH (60% in mineral oil, 1.05 g, 26.3 mmol). After stirring for 1 h at 0 °C, allyl bromide (5.3 g, 43.8 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (20 mL) the mixture was extracted with Et_2O (4 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **6** (1.4 g, 81%) as a colourless oil with identical spectroscopic properties to those previously reported.[12] Found (ESI) 217.1197 [M + Na$^+$], $C_{12}H_{18}O_2Na$ requires 217.1199.

Metathesis of 5 to 7 and 12. Method A: To a stirring solution of compound **5** (0.1 g, 0.5 mmol) in dry CH_2Cl_2 (46 mL) was added a solution of catalyst **1** (0.04 g, 0.05 mmol, 10 mol-%) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 h at room temperature under N_2, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **7** (0.05 g, 54%) and compound **12** (0.02 g, 9%) as transparent oils. **Data for 7:** IR (neat): $\tilde{\nu}_{max}$ = 3025 (m), 2898 (s), 2828 (m), 1718 (w), 1656 (m) cm^{-1}. ^{1}H NMR: δ = 6.07–5.99 (m, 2 H, OCH$_2$C*H*=), 5.84 (t, *J* = 1.6 Hz, 2 H, CHCH$_2$C*H*=), 5.14 (d, *J* = 2.4 Hz, 1 H, CH), 5.10 (d, *J* = 2.4 Hz, 1 H, CH), 4.28–4.23 (m, 4 H, 2 OCH$_2$), 2.56–2.54 (m, 4 H, 2 CH$_2$) ppm. ^{13}C NMR: δ = 129.5 (=CH), 124.4 (=CH), 73.1 (OCH), 66.0 (OCH$_2$), 30.2 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 184 (100) [M + NH$_4^+$], 167 (8) [MH$^+$]; found (ESI) 189.0884 [M + Na$^+$], $C_{10}H_{14}O_2Na$ requires 189.0886. **Data for 12:** IR (neat): $\tilde{\nu}_{max}$ = 3017 (w), 2932 (s), 2959 (m), 1657 (w) cm^{-1}. ^{1}H NMR: δ = 5.87 (ddd, *J* = 17.2, 10.5, 5.6 Hz, 1 H, C*H*=CH$_2$), 5.76 (t, *J* = 2.9 Hz, 1 H, OCH$_2$C*H*=CH), 5.50 (s, 2 H, CHCH$_2$C*H*=C*H*), 5.21 (dq, *J* = 17.2, 1.7 Hz, 1 H, CH=C*H*$_2$), 5.09 (ddd, *J* = 10.4, 3.1, 1.4 Hz, 1 H, CH=C*H*$_2$), 4.10–4.01 (m, 4 H, 2 OCH$_2$), 3.67 (t, *J* = 5.8 Hz, 2 H, 2 OCH), 2.32–2.26 (m, 2 H, CH$_2$), 2.19–2.15 (m, 2 H, CH$_2$) ppm. ^{13}C NMR: δ = 135.5 (=CH), 129.6 (=CH), 124.2 (2 =CH), 116.4 (=CH$_2$), 77.1 (2 OCH), 71.1 (OCH$_2$), 70.3 (OCH$_2$), 30.7 (2 CH$_2$) ppm. MS (CI): *m*/*z* (%) = 378 (100) [M + NH$_4^+$]; found (ESI) 378.2642 (M + NH$_4^+$), $C_{22}H_{36}NO_4$ requires 378.2639.

Metathesis of 5 to 7 and 12. Method B: To a stirring solution of compound **5** (0.1 g, 0.5 mmol) in dry CH_2Cl_2 (46 mL) was added a solution of catalyst **2** (0.023 g, 0.026 mmol, 5 mol-%) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 h at room temperature under N_2, then the solvent was evaporated in vacuo, and the residue subjected to flash chromatography (hexane/EtOAc, 90:10) to give compound **7** (0.06 g, 71%) and compound **12** (0.013 g, 7%) as colourless oils.

Metathesis of 6 to 8, 13 and 14: To a stirring solution of compound **6** (0.1 g, 0.51 mmol) in dry CH_2Cl_2 (46 mL) was added a solution of catalyst **1** (0.021 g, 0.03 mmol, 5 mol-%) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 h at 35 °C under N_2, then the solvent was evaporated in vacuo and the residue subjected to flash chromatography (hexane/EtOAc, 90:10) to give compound **8** (0.08 g, 92%), compound **13** (0.013 g, 6%) and compound **14** (0.005 g, 2%) as transparent oils. **Data for 8:** IR (neat): $\tilde{\nu}_{max}$ = 3027 (m), 2904 (s), 2845 (m), 1656 (w) cm^{-1}. ^{1}H NMR: δ = 5.71–5.63 (m, 1 H, OCH$_2$C*H*=), 5.48–5.41 (m, 1 H, CHCH$_2$C*H*=), 4.41–4.26 (m, 2 H, OCH$_2$), 3.42–3.34 (m, 1 H, OCH), 2.45–2.37 (m, 1 H, C*H*$_2$CH=), 2.06–1.98 (m, 1 H, C*H*$_2$CH=) ppm. ^{13}C NMR: δ = 129.8 (=CH), 124.8 (=CH), 82.1 (OCH), 69.4 (OCH$_2$), 33.2 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 184 (100) [M + NH$_4^+$], 167 (4) [MH$^+$]; found (ESI) 184.1332 (M + NH$_4^+$), $C_{10}H_{18}NO_2$ requires 184.1332. **Data for 13:** IR (neat): $\tilde{\nu}_{max}$ = 3015 (w), 2931 (s), 2959 (m), 1653 (w) cm^{-1}. ^{1}H NMR: δ = 5.92–5.81 (m, 1 H, C*H*=CH$_2$), 5.76 (t, *J* = 2.9 Hz, 1 H, OCH$_2$C*H*=CH), 5.47 (s, 2 H, CHCH$_2$C*H*=C*H*), 5.22 (dd, *J* = 17.2, 1.7 Hz, 1 H, =CH$_2$), 5.09 (dd, *J* = 10.3, 1.5 Hz, 1 H, =CH$_2$), 4.11–4.05 (m, 4 H, 2 OC*H*$_2$CH=), 3.51 (t, *J* = 3.7 Hz, 2 H, 2 OCH), 2.41–2.37 (m, 2 H, CH$_2$), 2.03–1.98 (m, 2 H, CH$_2$) ppm. ^{13}C NMR: δ = 135.5 (=CH), 129.6 (=CH), 124.2 (2 CH=), 116.4 (=CH$_2$), 77.2 (2 OCH), 71.1 (OCH$_2$), 70.2 (OCH$_2$), 30.7 (2 CH$_2$) ppm. MS (CI): *m*/*z* (%) = 378 (6) [M + NH$_4^+$], 108 (100); found (ESI) 378.2641 (M + NH$_4^+$), $C_{22}H_{36}NO_4$ requires 378.2639. **Data for 14:** IR (neat): $\tilde{\nu}_{max}$ = 3026 (w), 2921 (s), 2850 (m), 1655 (m), 1632 (m) cm^{-1}. ^{1}H NMR: δ = 5.84–5.82 (m, 1 H, OCH$_2$C*H*=), 5.50–5.48 (m, 1 H, CHCH$_2$C*H*=), 4.18–4.15 (m, 1 H, OCH$_2$), 4.02–3.95 (m, 1 H, OCH$_2$), 3.55–3.53 (m, 1 H, OCH), 2.44–2.39 (m, 1 H, CH$_2$), 2.04–1.98 (m, 1 H, CH$_2$) ppm. ^{13}C NMR: δ = 128.4 (=CH), 128.2 (=CH), 123.2 (=CH), 108.6 (=CH), 75.5 (OCH), 75.3 (OCH), 68.8 (OCH$_2$), 68.6 (OCH$_2$), 29.3 (CH$_2$), 29.2 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 350 (100) [M + NH$_4^+$], 167 (10); found (ESI) 355.1869 [M + Na$^+$], $C_{20}H_{28}O_4Na$ requires 355.1879.

Metathesis of 6 to 8: To a stirring solution of compound **6** (0.1 g, 0.51 mmol) in dry CH_2Cl_2 (46 mL) was added a solution of catalyst **2** (0.02 g, 0.026 mmol, 5 mol-%) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 h at room temperature under N_2, then the solvent was evaporated in vacuo and the residue subjected to flash chromatography (hexane/EtOAc, 90:10) to give compound **8** (0.083 g, 97%) as a colourless oil.

***cis*-1,2-Bis(allyloxy)cyclohexane (15):**[13] To a stirring solution of *cis*-cyclohexane-1,2-diol[31] (**33**, 1.0 g, 8.6 mmol) in DMF (15 mL) at 0 °C was slowly added NaH (60% in mineral oil, 1.0 g, 25.9 mmol). After stirring for 1 h at 0 °C, allyl bromide (5.2 g, 43.1 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (15 mL), the mixture was extracted with Et_2O (4 × 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, evapo-

rated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **15** (1.3 g, 75%) as a colourless oil with identical spectroscopic properties to those previously reported.[13] MS (CI): *m*/*z* (%) = 197 (17) [MH^+], 155 (5), 139 (100).

***trans*-1,2-Bis(allyloxy)cyclohexane (16):**[13,32] To a stirring solution of *trans*-1,2-dihydroxycyclohexane[33] (**34**, 0.50 g, 4.3 mmol) in DMF (15 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.52 g, 12.9 mmol). After stirring for 1 h at 0 °C, allyl bromide (2.6 g, 21.5 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (10 mL), the mixture was extracted with Et_2O (4 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **16** (0.68 g, 80%) as a colourless oil with identical spectroscopic properties to those previously reported.[13,32] IR (neat): $\tilde{\nu}_{max}$ = 3078 (w), 2929 (s), 2859 (s), 1647 (m) cm^{-1}.

Metathesis of 15 to 17:[13] To a stirring solution of compound **15** (0.10 g, 0.51 mmol) in dry CH_2Cl_2 (46 mL) was added a solution of catalyst **1** (0.04 g, 0.05 mmol, 10 mol-%) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 h at 35 °C under N_2, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give product **17** (0.07 g, 86%) as a transparent oil with identical spectroscopic properties to those previously reported.[13] MS (CI): *m*/*z* (%) = 186 (100) [M + NH_4^+], 169 (32) [MH^+].

Metathesis of 16 to 18:[13] To a stirring solution of compound **16** (0.1 g, 0.5 mmol) in dry CH_2Cl_2 (46 mL) was added a solution of catalyst **1** (0.02 g, 0.03 mmol, 5 mol-%) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 20 h at room temperature under N_2, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give product **18** (0.071 g, 83%) as a transparent oil with identical spectroscopic properties to those previously reported.[13] MS (CI): *m*/*z* (%) = 186 (100) [M + NH_4^+], 169 (17) [MH^+].

Synthesis of Compound 19. Method A Hydrogenation of Compound 8: Compound **8** (0.05 g, 0.30 mmol) was dissolved in EtOAc (10 mL) and hydrogenated at 1 atmosphere pressure overnight using 10% Pd on activated carbon (0.005 g) as catalyst. The suspension was then filtered through a pad of Celite and the filtrate was evaporated in vacuo to give compound **19** (0.05 g, 98%) as a colourless oil which was analysed by GC-MS without further purification. GCMS: retention time 13.453 min. MS (EI): *m*/*z* (%) = 170 (35) [M^+], 71 (100).

Synthesis of Compound 19. Method B Hydrogenation of Compound 18: Compound **18** (0.05 g, 0.30 mmol) was dissolved in EtOAc (10 mL) and hydrogenated at 1 atmosphere pressure overnight using 10% Pd on activated carbon (0.005 g) as catalyst. The suspension was then filtered through a pad of Celite and the filtrate was evaporated in vacuo to give compound **19** (0.05 g, 99%) as a colourless oil which was analysed by GC-MS without further purification. GCMS: retention time 13.461 min. MS (EI): *m*/*z* (%) = 170 (35) [M^+], 71 (100).

***cis*-2-Allyloxy-1-hydroxycyclohex-4-ene (20):** To a stirring solution of *cis*-1,2-dihydroxycyclohex-4-ene[10] (**3**, 1.0 g, 8.8 mmol) in DMF (20 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.35 g, 8.8 mmol). After stirring for 1 h at 0 °C, allyl bromide (1.1 g, 8.8 mmol) was added, the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (15 mL) the mixture was extracted with Et_2O (4 × 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 70:30) to give compound **20** (0.65 g, 48%) as a colourless oil. Compound **5** (0.23 g, 15%) was also obtained. IR (neat): $\tilde{\nu}_{max}$ = 3441 (br), 3028 (m), 2907 (s), 1646 (m) cm^{-1}. ^1H NMR: δ = 5.95 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1 H, C*H*=CH_2), 5.60 (d, *J* = 1.5 Hz, 2 H, CH=CH), 5.31 (dq, *J* = 17.2, 1.5 Hz, 1 H, =CH_2), 5.20 (dq, *J* = 10.2, 1.2 Hz, 1 H, =CH_2), 4.15–4.04 (m, 3 H, OCH_2, C*H*OH), 3.65 (td, *J* = 6.5, 2.2 Hz, 1 H, C*H*OCH_2), 2.33–2.27 (m, 4 H, 2 CH_2), 2.19–2.17 (br. s, 1 H, OH) ppm. ^{13}C NMR: δ = 135.4 (CH=), 124.2 (CH=), 124.1 (CH=), 117.4 (=CH_2), 76.2 (OCH), 69.9 (OCH_2), 67.1 (OCH), 32.0 (CH_2), 27.7 (CH_2) ppm. MS (CI): *m*/*z* (%) = 172 (100) [M + NH_4^+], 155 (6) [MH^+]; found (ESI) 172.1333 (M + NH_4^+), $C_9H_{18}NO_2$ requires 172.1332.

***trans*-2-Allyloxy-1-hydroxycyclohex-4-ene (21):** To a stirring solution of *trans*-1,2-dihydroxycyclohex-4-ene[11] (**4**, 3.2 g, 27.7 mmol) in DMF (50 mL) at 0 °C was slowly added NaH (60 % in mineral oil, 1.1 g, 27.7 mmol). After stirring for 1 h at 0 °C, allyl bromide (3.4 g, 27.7 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (30 mL) the mixture was extracted with Et_2O (4 × 30 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 70:30) to give compound **21** (2.5 g, 58%) as a colourless oil. Compound **6** (1.5 g, 27%) was also obtained. IR (neat): $\tilde{\nu}_{max}$ = 3440 (br), 3030 (m), 2904 (s), 1646 (m) cm^{-1}. ^1H NMR: δ = 6.02–5.91 (m, 1 H, C*H*=CH_2), 5.61–5.52 (m, 2 H, CH=CH), 5.31 (dq, *J* = 17.1, 1.6 Hz, 1 H, =CH_2), 5.21 (dq, *J* = 10.1, 1.3 Hz, 1 H, =CH_2), 4.22–4.17 (m, 1 H, OCH_2), 4.06–4.00 (m, 1 H, OCH_2), 3.84–3.77 (m, 1 H, C*H*OH), 3.48–3.42 (m, 1 H, OCH), 2.85 (br. s, 1 H, OH), 2.60–2.49 (m, 2 H, CH_2), 2.15–1.96 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 135.3 (CH=), 125.0 (CH=), 124.4 (CH=), 117.6 (=CH_2), 79.6 (OCH), 70.6 (OCH), 70.5 (OCH_2), 33.0 (CH_2), 30.8 (CH_2) ppm. MS (CI): *m*/*z* (%) = 172 (100) [M + NH_4^+]; found (ESI) 172.1332 (M + NH_4^+), $C_9H_{18}NO_2$ requires 172.1332.

***cis*-2-Allyloxy-1-(prop-2-ynyloxy)cyclohex-4-ene (22):** To a stirring solution of compound **20** (0.36 g, 2.3 mmol) in DMF (15 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.28 g, 7.0 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% solution in toluene, 0.7 g, 0.5 mL, 4.7 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (10 mL), the mixture was extracted with Et_2O (4 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 80:20) to give compound **22** (0.34 g, 75%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3296 (s), 3029 (m), 2908 (s), 2857 (m), 2113 (w), 1652 (w) cm^{-1}. ^1H NMR: δ = 5.96 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1 H, C*H*=CH_2), 5.64–5.57 (m, 2 H, CH=CH), 5.31 (dq, *J* = 17.2, 1.7 Hz, 1 H, =CH_2), 5.18 (dq, *J* = 10.4, 1.4 Hz, 1 H, =CH_2), 4.41–4.30 (m, 2 H, OCH_2), 4.20–4.09 (m, 2 H, OCH_2), 4.05 (td, *J* = 5.3, 1.6 Hz, 1 H, C*H*$OCH_2C{\equiv}$), 3.78–3.74 (m, 1 H, $CHOCH_2CH$=), 2.42 (t, *J* = 2.5 Hz, 1 H, ≡CH), 2.40–2.27 (m, 4 H, 2 CH_2) ppm. ^{13}C NMR: δ = 136.4 (=CH), 125.4 (=CH), 124.9 (=CH), 117.7 (=CH_2), 81.4 (≡C), 75.8 (OCH), 75.0 (≡CH), 74.7 (OCH), 71.0 (OCH_2), 57.5 (OCH_2), 30.3 (CH_2), 29.9 (CH_2) ppm. MS (CI): *m*/*z* (%) = 210 (100) [M + NH_4^+], 193 (11) [MH^+], 154 (7); found (ESI) 215.1044 [M + Na^+], $C_{12}H_{16}O_2Na$ requires 215.1043.

***trans*-2-Allyloxy-1-(prop-2-ynyloxy)cyclohex-4-ene (23):** To a stirring solution of compound **21** (0.9 g, 5.8 mmol) in DMF (30 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.7 g,

17.5 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% solution in toluene, 1.7 g, 1.3 mL, 11.7 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (10 mL), the mixture was extracted with Et_2O (4 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 70:30) to give compound **23** (0.9 g, 80%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3293 (s), 3031 (m), 2908 (s), 2855 (m), 2117 (w), 1657 (m) cm^{-1}. ^1H NMR: δ = 6.01–5.91 (m, 1 H, C*H*=CH_2), 5.57 (t, *J* = 1.2 Hz, 2 H, CH=CH), 5.31 (dq, *J* = 17.2, 1.7 Hz, 1 H, =CH_2), 5.18 (dq, *J* = 10.4, 1.3 Hz, 1 H, =CH_2), 4.43–4.32 (m, 2 H, $OCH_2C{\equiv}$), 4.16 (dt, *J* = 5.7, 1.5 Hz, 2 H, OCH_2CH=), 3.79–3.73 (m, 1 H, C*H*$OCH_2C{\equiv}$), 3.66–3.60 (m, 1 H, C*H*OCH_2CH=), 2.55–2.47 (m, 2 H, CH_2), 2.43 (t, *J* = 2.3 Hz, 1 H, ≡CH), 2.17–2.07 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 135.3 (=CH), 124.2 (=CH), 124.1 (=CH), 116.5 (=CH_2), 80.5 (≡C), 77.3 (OCH), 76.8 (OCH), 73.7 (≡CH), 70.9 (OCH_2), 57.7 (OCH_2), 30.8 (CH_2), 30.7 (CH_2) ppm. MS (CI): *m*/*z* (%) = 210 (22) [M + NH_4^+], 193 (100) [MH^+], 151 (3), 135 (23); found (ESI) 210.1484 (M + NH_4^+), $C_{12}H_{20}NO_2$ requires 210.1489.

Metathesis of 22 to Diene 24: To a stirring solution of compound **22** (0.05 g, 0.26 mmol) in dry CH_2Cl_2 (22 mL) was added a solution of catalyst **1** (0.02 g, 0.03 mmol, 10 mol-%) in dry CH_2Cl_2 (4 mL). The reaction mixture was stirred for 20 h at 35 °C under N_2, then the solvent was evaporated in vacuo and the residue subjected to flash chromatography (CH_2Cl_2) to give compound **24** (0.03 g, 58%) as a transparent oil. IR (neat): $\tilde{\nu}_{max}$ = 3292 (w), 3028 (m), 2900 (s), 2844 (m), 1656 (w), 1605 (w) cm^{-1}. ^1H NMR: δ = 6.25 (dd, *J* = 17.8, 11.1 Hz, 1 H, C*H*=CH_2), 5.75 (t, *J* = 6.2 Hz, 1 H, CH=C), 5.60–5.52 (m, 2 H, CH=CH), 5.10 (d, *J* = 17.8 Hz, 1 H, =CH_2), 5.02 (dd, *J* = 14.5, 6.1 Hz, 1 H, OCH_2CH=), 4.99 (d, *J* = 11.1 Hz, 1 H, =CH_2), 4.91 (dd, *J* = 15.3, 1.6 Hz, 1 H, OCH_2C=), 4.24 (d, *J* = 15.3 Hz, 1 H, OCH_2C=), 4.05–4.01 (m, 1 H, OCH_2CH=), 3.99 (t, *J* = 3.3 Hz, 1 H, C*H*OCH_2C=), 3.88–3.84 (m, 1 H, C*H*OCH_2CH=), 2.35–2.20 (m, 4 H, 2 CH_2) ppm. ^{13}C NMR: δ = 139.4 (=C), 138.2 (=CH), 128.3 (=CH), 124.0 (=CH), 123.8 (=CH), 112.6 (=CH_2), 75.0 (OCH), 70.6 (OCH), 65.6 (OCH_2), 64.2 (OCH_2), 30.0 (CH_2), 29.3 (CH_2) ppm. MS (CI): *m*/*z* (%) = 210 (100) [M + NH_4^+], 193 (52) [MH^+]; found (ESI) 193.1224 [MH^+], $C_{12}H_{17}O_2$ requires 193.1223.

Metathesis of 23 to Diene 25: To a stirring solution compound **23** (0.05 g, 0.26 mmol) in dry CH_2Cl_2 (22 mL) was added a solution of catalyst **1** (0.02 g, 0.03 mmol, 10 mol-%) in dry CH_2Cl_2 (4 mL). The reaction mixture was stirred for 20 h at 35 °C under N_2, then the solvent was evaporated in vacuo and the residue subjected to flash chromatography (CH_2Cl_2) to give compound **25** (0.04 g, 78%) as a transparent oil. Unreacted starting material (0.008 g, 16%) was also recovered. IR (neat): $\tilde{\nu}_{max}$ = 3029 (m), 2904 (s), 2847 (m), 1653 (w), 1606 (m) cm^{-1}. ^1H NMR: δ = 6.23 (dd, *J* = 17.8, 11.1 Hz, 1 H, C*H*=CH_2), 5.74 (t, *J* = 5.6 Hz, 1 H, CH=C), 5.48–5.41 (m, 2 H, CH=CH), 5.07 (d, *J* = 17.8 Hz, 1 H, =CH_2), 4.94 (d, *J* = 11.1 Hz, 1 H, =CH_2), 4.67 (d, *J* = 15.6 Hz, 1 H, OCH_2CH=), 4.51–4.35 (m, 3 H, OCH_2), 3.48–3.37 (m, 2 H, 2 OCH), 2.46–2.38 (m, 2 H, CH_2), 2.08–1.96 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 140.3 (=CH), 140.0 (=C), 131.7 (=CH), 126.0 (=CH), 125.9 (=CH), 113.5 (=CH_2), 83.9 (OCH), 81.9 (OCH), 70.3 (OCH_2), 69.2 (OCH_2), 34.3 (CH_2), 34.2 (CH_2) ppm. MS (CI): *m*/*z* (%) = 210 (100) [M + NH_4^+], 193 (80) [MH^+]; found (ESI) 193.1225 [MH^+], $C_{12}H_{17}O_2$ requires 193.1223.

Diels–Alder Adduct 26: To a solution of diene **24** (0.006 g, 0.03 mmol) in EtOAc (2 mL) at room temperature was added maleic anhydride (0.009 g, 0.09 mmol). The mixture was stirred for 8 h at room temperature, then the solvent was evaporated under reduced pressure and the residue dissolved in CH_2Cl_2 and filtered twice through a pad of Celite, leaving product **26** (0.008 g, 88%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3027 (w), 2918 (m), 2859 (w), 1848 (m), 1778 (s) cm^{-1}. ^1H NMR: δ = 5.82 (t, *J* = 5.0 Hz, 1 H, =CH), 5.55–5.48 (m, 2 H, CH=CH), 4.39 (d, *J* = 15.0 Hz, 1 H, OCH_2C=), 4.14 (dd, *J* = 14.9, 1.3 Hz, 1 H, OCH_2C=), 4.08–4.02 (m, 1 H, OCH_2CH), 3.87 (t, *J* = 6.2 Hz, 1 H, C*H*OCH_2C=), 3.76–3.71 (m, 2 H, $CHOCH_2$), 3.33–3.27 (m, 2 H, O =CCHCHC=O), 3.24–3.19 (m, 1 H, OCH_2C*H*), 2.51–2.39 (m, 3 H, 2 =CHCH_2), 2.31–2.14 (m, 3 H, CH_2CH=CHCH_2) ppm. ^{13}C NMR: δ = 173.6 (C=O), 171.7 (C=O), 141.1 (=C), 124.1 (=CH), 123.7 (=CH), 122.2 (=CH), 74.9 (OCH), 74.7 (OCH), 69.5 (OCH_2), 65.3 (OCH_2), 43.6 (CHC=O), 39.5 (CHC=O), 37.4 (CH), 30.3 (CH_2), 28.0 (CH_2), 23.1 (CH_2) ppm. MS (CI): *m*/*z* (%) = 308 (100) [M + NH_4^+]; found (ESI) 313.1048 [M + Na^+], $C_{16}H_{18}O_5Na$ requires 313.1046.

Diels–Alder Adduct 27: To a solution of diene **25** (0.01 g, 0.05 mmol) in EtOAc (2 mL) at room temperature was added maleic anhydride (0.025 g, 0.26 mmol). The mixture was stirred overnight at room temperature, then the solvent was evaporated under reduced pressure and the residue dissolved in CH_2Cl_2 and filtered twice through a pad of Celite, leaving product **27** (0.011 g, 73%) as a 3:1 mixture of diastereomers. IR (neat): $\tilde{\nu}_{max}$ = 3032 (w), 2919 (m), 2859 (w), 1852 (m), 1777 (s) cm^{-1}. ^1H NMR: δ = (major diastereomer) 5.74 (t, *J* = 4.5 Hz, 1 H, C=CH), 5.44–5.41 (m, 2 H, CH=CH), 4.45 (d, *J* = 14.1 Hz, 1 H, OCH_2C=), 4.24–4.21 (m, 2 H, OCH_2CH), 4.12 (d, *J* = 14.9 Hz, 1 H, OCH_2C=), 3.66–3.40 (m, 2 H, OCHCHO), 3.36–3.23 (m, 2 H, O=CCHCHC=O), 2.92 (m, 1 H, OCH_2C*H*), 2.58–2.49 (m, 1 H, C=CHCH_2), 2.42–2.29 (m, 2 H, =CHCH_2), 2.21–2.17 (m, 1 H, =CHCH_2), 2.12–1.90 (m, 2 H, =CHCH_2) ppm. (minor diastereomer): δ = 5.68 (ddd, *J* 5.1, 3.2, 1.5 Hz, 1 H, C=CH), 5.44–5.41 (m, 2 H, CH=CH), 4.24–4.21 (m, 2 H, OCH_2CH), 3.77 (dd, *J* 11.1, 5.5 Hz, 1 H, OCH_2C=), 3.66–3.40 (m, 1 H, OCH_2C=), 3.36–3.23 (m, 5 H, OCHCHO, CHCHCH), 2.58–2.49 (m, 1 H, C=CHCH_2), 2.42–2.29 (m, 3 H, 3 = CHCH_2), 2.12–1.90 (m, 2 H, 2 =CHCH_2) ppm. ^{13}C NMR (major diastereomer): δ = 173.5 (C=O), 171.8 (C=O), 140.7 (=C), 124.9 (=CH), 124.6 (=CH), 123.2 (=CH), 83.2 (OCH), 81.1 (OCH), 74.3 (OCH_2), 73.7 (OCH_2), 42.9 (*C*HC=O), 41.8 (*C*HC=O), 38.4 (CH), 33.4 (CH_2), 32.8 (CH_2), 23.7 (CH_2) ppm. (minor diastereomer) δ = 173.5 (C=O), 171.8 (C=O), 139.3 (=C), 124.5 (=CH), 124.4 (=CH), 119.6 (=CH), 82.7 (OCH), 80.9 (OCH), 72.6 (OCH_2), 68.3 (OCH_2), 42.9 (*C*HC=O), 39.7 (*C*HC=O), 38.1 (CH), 33.1 (CH_2), 31.8 (CH_2), 21.5 (CH_2) ppm. MS (CI): *m*/*z* (%) = 308 (100) [M + NH_4^+], 226 (34), 212 (38); found (ESI) 313.1049 [M + Na^+], $C_{16}H_{18}O_5Na$ requires 313.1046.

***endo*,*endo*-3-Allyloxy-2-hydroxy-5-norbornene (29):** To a stirring solution of diol **28**[18] (1.0 g, 7.9 mmol) in DMF (15 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.32 g, 7.9 mmol). After stirring for 1 h at 0 °C, allyl bromide (0.96 g, 7.9 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (15 mL) the mixture was extracted with Et_2O (4 × 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/Et_2O, 70:30) to give compound **29** as a colourless oil (0.73 g, 55%). Bis-ether **30**[19] (0.47 g, 29%) and unreacted diol **28** (0.16 g, 16%) were also isolated. IR (neat): $\tilde{\nu}_{max}$ = 3361 (br), 3074 (m), 2974 (s), 2870 (s), 1724 (m), 1646 (s) cm^{-1}. ^1H NMR: δ = 6.23–6.18 (m, 2 H, CH=CH), 5.92 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1 H, C*H*=CH_2), 5.29 (dq, *J* = 17.2, 1.6 Hz, 1 H, =CH_2), 5.20 (dq, *J* = 10.4, 1.3 Hz, 1 H, =CH_2), 4.21 (dt, *J* = 7.8, 3.9 Hz, 1 H, C*H*OH), 4.12–4.01 (m, 2 H, OCH_2),

3.95 (dd, J = 7.5, 3.7 Hz, 1 H, C*H*OCH$_2$), 3.05–3.02 (m, 2 H, C*H*CH=CHC*H*), 2.48 (d, J = 8.0 Hz, 1 H, OH), 1.48 (dt, J = 9.6, 2.2 Hz, 1 H, CHC*H*$_2$CH), 1.16 (d, J = 9.6 Hz, 1 H, CHC*H*$_2$CH) ppm. ^{13}C NMR: δ = 135.2 (=CH), 135.0 (=CH), 134.9 (=CH), 117.5 (=CH$_2$), 78.5 (OCH), 71.5 (OCH$_2$), 71.3 (OCH), 48.3 (CH), 46.2 (CH), 41.9 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 184 (46) [M + NH$_4^+$], 167 (45) [MH$^+$], 150 (20), 90 (100); found (ESI) 167.1067 [MH$^+$], $C_{10}H_{15}O_2$ requires 167.1067.

***endo*,*endo*-3-Allyloxy-2-(prop-2-ynyloxy)-5-norbornene (31):** To a stirring solution of compound **29** (0.32 g, 1.9 mmol) in DMF (12 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.23 g, 5.8 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% in toluene, 0.57 g, 0.43 mL, 3.85 mmol) was added and the reaction mixture was warmed to room temperature. The reaction was stirred overnight, hydrolysed with water (10 mL) and extracted with Et$_2$O (4 × 10 mL). The combined organic phases were dried (MgSO$_4$), filtered and evaporated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc, 70:30) to give compound **31** (0.32 g, 81%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3294 (m), 3246 (m), 3073 (w), 2975 (s), 2934 (m), 2870 (m), 2112 (w), 1737 cm^{-1}. (s). ^{1}H NMR: δ = 6.28 (br. s, 2 H, CH=CH), 5.96 (ddt, J = 17.1, 10.3, 5.9 Hz, 1 H, C*H*=CH$_2$), 5.28 (dq, J = 17.3, 1.5 Hz, 1 H, =CH$_2$), 5.19 (dq, J = 10.3, 1.2 Hz, 1 H, =CH$_2$), 4.30–4.25 (m, 3 H, CHOCH$_2$C≡), 4.09–4.04 (m, 3 H, C*H*OC*H*$_2$CH=), 3.13–3.12 (m, 1 H, CH$_2$C*H*CHOCH$_2$C≡), 3.09–3.08 (m, 1 H, CH$_2$C*H*CHOCH$_2$CH=), 2.43 (t, J = 2.4 Hz, 1 H, ≡CH), 1.49 (dt, J = 9.6, 2.3 Hz, 1 H, CHC*H*$_2$CH), 1.19 (d, J = 9.6 Hz, 1 H, CHC*H*$_2$CH) ppm. ^{13}C NMR: δ = 135.6 (=CH), 134.8 (2 =CH), 117.6 (=CH$_2$), 81.2 (≡C), 79.1 (≡CH), 78.4 (OCH), 74.6 (OCH), 71.7 (OCH$_2$), 57.5 (OCH$_2$), 46.3 (2 CH), 42.2 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 222 (100) [M + NH$_4^+$], 205 (17) [MH$^+$]; found (CI) 222.1491 (M + NH$_4^+$), $C_{13}H_{20}NO_2$ requires 222.1489.

Metathesis of 31 to Tricyclic Diene 32: Norbornene derivative **31** (0.10 g, 0.49 mmol) was dissolved in dry CH$_2$Cl$_2$ (45 mL) and ethene was passed through the stirred solution for 10 min. A solution of catalyst **1** (0.02 g, 0.024 mmol, 5 mol-%) in dry CH$_2$Cl$_2$ (4 mL) was added and the reaction mixture was stirred at 35 °C for 20 h under ethene. The solvent was evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 80:20) to afford tricyclic diene **32** (0.10 g, 100%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3345 (s), 2931 (s), 2874 (s), 1736 (s), 1646 (s) cm^{-1}. ^{1}H NMR: δ = 6.19 (dd, J = 17.8, 11.1 Hz, 1 H, C*H*=CH$_2$), 5.81–5.73 (m, 3 H, CH=CH, C=CH), 4.94–4.89 (m, 2 H, =CH$_2$), 4.51 (d, J = 15.1 Hz, 1 H, OC*H*$_2$CH=), 4.26–4.13 (m, 3 H, OC*H*$_2$CH=, OC*H*$_2$C=), 4.09–4.01 (m, 2 H, OCHCHO), 2.29–2.27 (m, 1 H, C*H*CH=CH), 2.20–2.17 (m, 1 H, C*H*-CH=C), 1.95 (dt, J = 12.3, 6.3 Hz, 1 H, CHC*H*$_2$CH), 1.56–1.44 (m, 1 H, CHC*H*$_2$CH) ppm. ^{13}C NMR: δ = 136.3 (=CH), 135.7 (=C), 127.3 (=CH), 126.7 (=CH), 126.4 (=CH), 111.8 (=CH$_2$), 77.5 (OCH), 77.0 (OCH), 65.4 (CH$_2$O), 65.0 (CH$_2$O), 40.0 (CH), 39.5 (CH), 36.3 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 222 (100) [M + NH$_4^+$], 205 (72) [MH$^+$]; found (ESI) 205.1226 [MH$^+$], $C_{13}H_{17}O_2$ requires 205.1223.

***cis*-1,2-Bis(prop-2-ynyloxy)cyclohex-4-ene (35):** To a stirring solution of *cis*-1,2-dihydroxycyclohex-4-ene[10] (**3**, 0.9 g, 7.8 mmol) in DMF (20 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.94 g, 23.5 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% solution in toluene, 3.5 g, 2.6 mL, 23.5 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (15 mL), the mixture was extracted with Et$_2$O (4 × 15 mL). The combined organic phases were dried (MgSO$_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to afford compound **35** (1.3 g, 89%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3290 (s), 3029 (w), 2910 (m), 2114 (w), 1653 (w) cm^{-1}. ^{1}H NMR: δ = 5.53 (t, J = 1.5 Hz, 1 H, =CH), 4.31–4.20 (m, 2 H, OCH$_2$), 3.97–3.93 (m, 1 H, OCH), 2.35 (t, J = 2.4 Hz, 1 H, ≡CH), 2.31–2.20 (m, 2 H, CHC*H*$_2$) ppm. ^{13}C NMR: δ = 124.4 (=CH), 80.6 (≡C), 74.6 (≡CH), 74.2 (OCH), 56.6 (OCH$_2$), 29.2 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 208 (100) [M + NH$_4^+$], 179 (2), 151 (1), 135 (8); found (ESI) 213.0887 [M + Na$^+$], $C_{12}H_{14}O_2Na$ requires 213.0886.

***trans*-1,2-Bis(prop-2-ynyloxy)cyclohex-4-ene (36):** To a stirring solution of *trans*-1,2-dihydroxycyclohex-4-ene[11] (**4**, 1.0 g, 8.8 mmol) in DMF (60 mL) at 0 °C was slowly added NaH (60% in mineral oil, 1.1 g, 26.3 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% solution in toluene, 6.5 g, 4.9 mL, 43.8 mmol) was added and the reaction mixture was warmed to room temperature and stirred overnight. After hydrolysis with water (20 mL), the mixture was extracted with Et$_2$O (4 × 20 mL). The combined organic phases were dried (MgSO$_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **36** (1.6 g, 96%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3292 (s), 3030 (m), 2906 (s), 2854 (m), 2115 (w), 1656 (w) cm^{-1}. ^{1}H NMR: δ = 5.58–5.51 (m, 1 H, =CH), 4.33 (d, J = 2.4 Hz, 2 H, OCH$_2$), 3.81–3.73 (m, 1 H, OCH), 2.50 (ddd, J = 17.5, 5.0, 3.1 Hz, 1 H, CH$_2$), 2.43 (t, J = 2.4 Hz, 1 H, ≡CH), 2.12 (ddd, J = 15.6, 4.9, 2.6 Hz, 1 H, CH$_2$) ppm. ^{13}C NMR: δ = 123.3 (=CH), 79.6 (≡C), 76.2 (≡CH), 73.2 (OCH), 56.7 (OCH$_2$), 29.8 (CH$_2$) ppm. MS (CI): *m*/*z* (%) = 191 (4) [MH$^+$], 154 (51), 136 (69), 122 (39), 95 (48), 79 (100); found (ESI) 191.1069 [MH$^+$], $C_{12}H_{15}O_2$ requires 191.1067.

***cis*-1,2-Bis(prop-2-ynyloxy)cyclohexane (37):** To a stirring solution of *cis*-1,2-dihydroxycyclohexane[13] (**33**, 1.0 g, 8.6 mmol) in DMF (15 mL) at 0 °C was slowly added NaH (60% in mineral oil, 1.0 g, 25.9 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% solution in toluene, 6.4 g, 4.8 mL, 43.1 mmol) was added and the reaction mixture was warmed up to room temperature and stirred overnight. After hydrolysis with water (15 mL) the mixture was extracted with Et$_2$O (4 × 15 mL). The combined organic phases were dried (MgSO$_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to afford compound **37** as a colourless oil (1.25 g, 76%). IR (neat): $\tilde{\nu}_{max}$ = 3288 (s), 2939 (s), 2861 (m), 2117 (m), 1715 (w) cm^{-1}. ^{1}H NMR: δ = 4.26–4.16 (m, 2 H, OCH$_2$), 3.73 (dd, J = 6.1, 2.5 Hz, 1 H, OCH), 2.33 (t, J = 2.5 Hz, 1 H, ≡CH), 1.84–1.76 (m, 1 H, C*H*$_2$CH), 1.58–1.42 (m, 2 H, C*H*$_2$CH$_2$CH), 1.30–1.21 (m, 1 H, C*H*$_2$CH) ppm. ^{13}C NMR: δ = 80.4 (≡C), 75.7 (≡CH), 73.9 (OCH), 55.6 (OCH$_2$), 27.2 (CH$_2$), 21.9 (CH$_2$) ppm. MS (EI): *m*/*z* (%) = 191 (M–H$^+$, 2), 153 (21), 137 (20), 97 (35); found (ESI) 215.1046 [M + Na], $C_{12}H_{16}O_2Na$ requires 215.1042.

***trans*-1,2-Bis(prop-2-ynyloxy)cyclohexane (38):** To a stirring solution of *trans*-1,2-dihydroxycyclohexane[13,32] (**34**, 1.0 g, 8.6 mmol) in DMF (15 mL) at 0 °C was slowly added NaH (60% in mineral oil, 1.0 g, 25.9 mmol). After stirring for 1 h at 0 °C, propargyl bromide (80% solution in toluene, 6.4 g, 4.8 mL, 43.1 mmol) was added and the reaction mixture was warmed to room temperature and then stirred overnight. After hydrolysis with water (20 mL), the mixture was extracted with Et$_2$O (4 × 20 mL). The combined organic phases were dried (MgSO$_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **38** (1.2 g, 73%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3290 (s), 2934 (s), 2861 (m), 2116 (w), 1716 (w) cm^{-1}. ^{1}H NMR: δ = 4.37–4.27 (m, 2 H, OCH$_2$), 3.45–3.39 (m, 1 H, OCH), 2.42 (t, J = 2.3 Hz, 1 H, ≡CH), 2.06–2.03 (m, 1 H, C*H*$_2$CH), 1.69–1.67 (m, 1 H, C*H*$_2$CH$_2$CH), 1.33–1.21 (m, 2 H,

CH_2CH_2) ppm. ^{13}C NMR: δ = 80.8 (OCH), 80.6 (≡C), 73.7 (≡CH), 57.2 (OCH_2), 30.1 (CH_2), 23.5 (CH_2) ppm. MS (CI): *m*/*z* (%) = 210 (100) [M + NH_4^+]; found (ESI) 215.1041 [M + Na^+], $C_{12}H_{16}O_2Na$ requires 215.1042.

Metathesis of 35 to 39, 40 and 41: Compound **35** (0.1 g, 0.53 mmol) was dissolved in dry toluene (48 mL) and ethene was passed through the stirred solution for 20 min. A solution of catalyst **2** (0.05 g, 0.05 mmol, 10 mol-%) in dry toluene (5 mL) was then added and the reaction mixture was stirred at 60 °C for 24 h under ethene. The solvent was evaporated in vacuo and the residue subjected to flash chromatography (CH_2Cl_2) to afford three products, **39** (0.04 g, 31%), **40** (0.02 g, 15%) and **41** (0.015 g, 13%) as colourless oils. **Data for 39:** IR (neat): $\tilde{\nu}_{max}$ = 3295 (s), 3029 (m), 2907 (s), 2114 (w), 1721 (m), 1596 (m) cm^{-1}. ^1H NMR: δ = 6.31 (dd, *J* = 17.7, 11.0 Hz, 1 H, C*H*=CH_2), 5.55–5.49 (m, 2 H, CH=CH), 5.26 (d, *J* = 18.0 Hz, 1 H, CH=C*H*$_2$), 5.24 (s, 1 H, C=CH_2), 5.10 (s, 1 H, C=CH_2), 5.03 (d, *J* = 11.0 Hz, 1 H, CH=C*H*$_2$), 4.31–4.26 (m, 2 H, OCH_2C≡), 4.26–4.19 (m, 2 H, OCH_2C=), 3.98–3.96 (m, 1 H, C*H*OCH_2C≡), 3.70–3.67 (m, 1 H, C*H*OCH_2C=), 2.34 (t, *J* = 2.4 Hz, 1 H, ≡CH), 2.32–2.19 (m, 4 H, 2 CH_2) ppm. ^{13}C NMR: δ = 142.6 (=C), 136.5 (=CH), 124.2 (=CH), 123.7 (=CH), 116.9 (=CH_2), 114.1 (=CH_2), 80.3 (≡C), 77.0 (≡CH), 74.8 (OCH), 73.8 (OCH), 68.4 (OCH_2), 56.4 (OCH_2), 29.3 (CH_2), 28.5 (CH_2) ppm. MS (CI): *m*/*z* (%) = 236 (100) [M + NH_4^+], 219 (17) [MH^+]; found (ESI) 219.1380 [MH^+], $C_{14}H_{19}O_2$ requires 219.1380. **Data for 40:** IR (neat): $\tilde{\nu}_{max}$ = 3027 (m), 2919 (s), 2114 (w), 1652 (w), 1596 (m) cm^{-1}. ^1H NMR: δ = 6.31 (dd, *J* = 17.8, 11.1 Hz, 1 H, C*H*=CH_2), 5.52 (t, *J* = 1.5 Hz, 1 H, =CH), 5.51 (s, 1 H, C=C*H*$_2$), 5.25 (d, *J* = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.09 (s, 1 H, C=C*H*$_2$), 5.02 (d, *J* = 11.1 Hz, 1 H, CH=C*H*$_2$), 4.28–4.20 (m, 2 H, OCH_2), 3.72–3.70 (m, 1 H, OCH), 2.36–2.17 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 141.0 (=C), 134.7 (=CH), 122.3 (=CH), 114.9 (=CH_2), 112.2 (=CH_2), 73.0 (OCH), 66.7 (OCH_2), 27.3 (CH_2) ppm. MS (CI): *m*/*z* (%) = 264 (100) [M + NH_4^+], 247 (7) [MH^+], 194 (29), 163 (26), 135 (77); found (ESI) 264.1959 (M + NH_4^+), $C_{16}H_{26}NO_2$ requires 264.1958. **Data for 41:** IR (neat): $\tilde{\nu}_{max}$ = 3027 (m), 2918 (s), 2845 (m), 1652 (w), 1606 (m) cm^{-1}. ^1H NMR: δ = 6.81 (dd, *J* = 17.6, 11.4 Hz, 1 H, C*H*=CH_2), 5.56 (s, 1 H, =CH), 5.28 (d, *J* = 17.6 Hz, 1 H, =CH_2), 5.15 (d, *J* = 11.3 Hz, 1 H, =CH_2), 5.14 (d, *J* = 14.7 Hz, 1 H, OCH_2), 4.29 (d, *J* = 14.9 Hz, 1 H, OCH_2), 3.91 (t, *J* = 4.7 Hz, 1 H, OCH), 2.34–2.22 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 132.7 (=C), 132.6 (=CH), 122.9 (=CH), 114.4 (=CH_2), 71.9 (OCH), 64.8 (OCH_2), 28.6 (CH_2) ppm. MS (CI): *m*/*z* (%) = 236 (100) [M + NH_4^+], 219 (13) [MH^+]; found (ESI) 236.1645 (M + NH_4^+), $C_{14}H_{22}NO_2$ requires 236.1645.

Metathesis of 36 to 42, 43 and 44: Diyne **36** (0.10 g, 0.53 mmol) was dissolved in dry toluene (48 mL) and ethene was passed through the stirred solution for 20 min. A solution of catalyst **2** (0.05 g, 0.05 mmol, 10 mol-%) in dry toluene (5 mL) was then added and the reaction mixture was stirred at 60 °C for 24 h under ethene. The solvent was evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to afford three products, **42** (0.03 g, 28%), **43** (0.02 g, 18%) and **44** (0.02 g, 14%). **Data for 42:** IR (neat): $\tilde{\nu}_{max}$ = 3296 (m), 3029 (w), 2904 (s), 2115 (w), 1596 (m) cm^{-1}. ^1H NMR: δ = 6.32 (dd, *J* = 17.7, 11.0 Hz, 1 H, C*H*=CH_2), 5.48–5.45 (m, 2 H, CH=CH), 5.26 (d, *J* = 18.2 Hz, 1 H, CH=C*H*$_2$), 5.23 (s, 1 H, C=CH_2), 5.10 (s, 1 H, C=CH_2), 5.05 (d, *J* = 11.0 Hz, 1 H, CH=C*H*$_2$), 4.32–4.27 (m, 2 H, OCH_2C≡), 4.24–4.23 (m, 2 H, OCH_2C=), 3.71–3.66 (m, 1 H, OCH), 3.59–3.54 (m, 1 H, OCH), 2.46–2.41 (m, 2 H, 2 CH_2), 2.34 (t, *J* = 2.4 Hz, 1 H, ≡CH), 2.05 (dd, *J* = 15.4, 7.5 Hz, 2 H, 2 CH_2) ppm. ^{13}C NMR: δ = 143.0 (=C), 136.6 (=CH), 124.2 (=CH), 124.1 (=CH), 117.2 (=CH_2), 114.4 (=CH_2), 80.6 (≡C), 77.4 (≡CH), 76.8 (OCH), 73.8 (OCH), 69.5 (OCH_2), 57.8 (OCH_2), 30.7 (CH_2), 30.5 (CH_2) ppm. MS (CI): *m*/*z* (%) = 236 (88) [M + NH_4^+], 219 (22) [MH^+], 152 (38), 126 (39), 112 (62); found (ESI) 219.1380 [MH^+], $C_{14}H_{19}O_2$ requires 219.1380. **Data for 43:** IR (neat): $\tilde{\nu}_{max}$ = 3029 (m), 2903 (s), 1653 (w), 1596 (s) cm^{-1}. ^1H NMR: δ = 6.31 (dd, *J* = 17.8, 11.0 Hz, 1 H, C*H*=CH_2), 5.51–5.45 (m, 1 H, =CH), 5.24 (d, *J* = 17.5 Hz, 1 H, CH=C*H*$_2$), 5.23 (s, 1 H, C=C*H*$_2$), 5.09 (s, 1 H, C=C*H*$_2$), 5.02 (d, *J* = 11.0 Hz, 1 H, CH=C*H*$_2$), 4.30–4.22 (m, 2 H, OCH_2), 3.59–3.53 (m, 1 H, OCH), 2.44–2.40 (m, 1 H, CH_2), 2.05 (ddd, *J* = 15.6, 4.6, 2.6 Hz, 1 H, CH_2) ppm. ^{13}C NMR: δ = 143.9 (=C), 134.4 (=CH), 125.0 (=CH), 117.7 (=CH_2), 115.0 (=CH_2), 78.0 (OCH), 70.5 (OCH_2), 31.3 (CH_2) ppm. MS (CI): *m*/*z* (%) = 264 (100) [M + NH_4^+], 247 (37) [MH^+], 180 (32), 135 (23); found (ESI) 247.1692 [MH^+], $C_{16}H_{23}O_2$ requires 247.1693. **Data for 44:** IR (neat): $\tilde{\nu}_{max}$ = 3029 (m), 2908 (s), 2847 (m), 1656 (w), 1604 (m) cm^{-1}. ^1H NMR: δ = 6.74 (dd, *J* = 17.6, 11.4 Hz, 1 H, C*H*=CH_2), 5.44 (s, 1 H, =CH), 5.24 (d, *J* = 17.7 Hz, 1 H, =CH_2), 5.13 (d, *J* = 11.5 Hz, 1 H, =CH_2), 4.71–4.63 (m, 2 H, OCH_2), 3.49–3.47 (m, 1 H, OCH), 2.44–2.40 (m, 1 H, CH_2), 2.06–2.02 (m, 1 H, CH_2) ppm. ^{13}C NMR: δ = 133.3 (CH=), 133.1 (=C), 123.3 (=CH), 114.2 (=CH_2), 79.5 (OCH), 67.8 (OCH_2), 31.6 (CH_2) ppm. MS (CI): *m*/*z* (%) = 236 (100) [M + NH_4^+], 219 (41) [MH^+], 125 (62), 107 (74); found (ESI) 236.1646 (M + NH_4^+), $C_{14}H_{22}NO_2$ requires 236.1645.

Metathesis of 37 to 45, 46 and 47: Diyne **37** (0.1 g, 0.5 mmol) was dissolved in dry toluene (48 mL) and ethene was passed through the stirred solution for 20 min. A solution of catalyst **2** (0.04 g, 0.05 mmol, 10 mol-%) in dry toluene (4 mL) was then added and the reaction mixture was stirred at 60 °C for 24 h under ethene. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (CH_2Cl_2) to afford three products, **45** (0.04 g, 36%), **46** (0.03 g, 22%) and **47** (0.02 g, 19%). **Data for 45:** IR (neat): $\tilde{\nu}_{max}$ = 3302 (m), 2934 (s), 2858 (m), 2114 (w), 1596 (m) cm^{-1}. ^1H NMR: δ = 6.31 (dd, *J* = 17.8, 11.1 Hz, 1 H, C*H*=CH_2), 5.27 (d, *J* = 17.3 Hz, 1 H, CH=C*H*$_2$), 5.25 (s, 1 H, C=CH_2), 5.09 (s, 1 H, C=CH_2), 5.02 (d, *J* = 10.9 Hz, 1 H, CH=C*H*$_2$), 4.22–4.21 (m, 2 H, OCH_2C≡), 4.19–4.18 (m, 2 H, OCH_2C=), 3.75–3.73 (m, 1 H, OCH), 3.47–3.45 (m, 1 H, OCH), 2.31 (t, *J* = 2.3 Hz, 1 H, ≡CH), 1.82–1.73 (m, 2 H, C*H*$_2$CHO), 1.56–1.52 (m, 2 H, C*H*$_2$CH$_2$CHO), 1.44–1.38 (m, 2 H, C*H*$_2$CH$_2$CHO), 1.28–1.18 (m, 2 H, C*H*$_2$CHO) ppm. ^{13}C NMR: δ = 142.0 (=C), 135.7 (=CH), 115.8 (=CH_2), 113.2 (=CH_2), 79.7 (OCH), 76.2 (OCH), 74.8 (≡C), 72.6 (≡CH), 67.2 (OCH_2), 54.9 (OCH_2), 26.7 (CH_2), 26.4 (CH_2), 21.3 (CH_2), 20.7 (CH_2) ppm. MS (EI): *m*/*z* (%) = 220 (1) [M^+], 153 (7), 137 (79), 67 (100); found (ESI) 243.1359 [M + Na^+], $C_{14}H_{20}O_2Na$ requires 241.1356. **Data for 46:** IR (neat): $\tilde{\nu}_{max}$ = 3086 (w), 2936 (s), 2859 (m), 1653 (w), 1596 (m) cm^{-1}. ^1H NMR: δ = 6.40 (dd, *J* = 17.8, 11.0 Hz, 1 H, C*H*=CH_2), 5.34 (s, 1 H, C=CH_2), 5.34 (d, *J* = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.17 (s, 1 H, C=CH_2), 5.10 (d, *J* = 11.0 Hz, 1 H, CH=C*H*$_2$), 4.32–4.23 (m, 2 H, OCH_2), 3.58 (dd, *J* = 6.0, 2.4 Hz, 1 H, OCH), 1.91–1.89 (m, 1 H, C*H*$_2$CHO), 1.69–1.62 (m, 1 H, C*H*$_2$CH$_2$CHO), 1.57–1.48 (m, 1 H, C*H*$_2$CHO), 1.35–1.29 (m, 1 H, C*H*$_2$CH$_2$CHO) ppm. ^{13}C NMR: δ = 143.2 (=C), 136.8 (=CH), 115.6 (=CH_2), 113.0 (=CH_2), 76.2 (OCH), 67.3 (OCH_2), 26.8 (CH_2), 21.1 (CH_2) ppm. MS (CI): *m*/*z* (%) = 266 (100) [M + NH_4^+], 249 (34) [MH^+], 182 (20), 165 (8); found (ESI) 249.1848 [MH^+], $C_{16}H_{25}O_2$ requires 249.1849. **Data for 47:** IR (neat): $\tilde{\nu}_{max}$ = 3089 (w), 2936 (s), 2859 (m), 1605 (w) cm^{-1}. ^1H NMR: δ = 6.77 (dd, *J* = 17.6, 11.4 Hz, 1 H, =CH), 5.25 (d, *J* = 17.6 Hz, 1 H, =CH_2), 5.17–5.11 (m, 2 H, =CH_2, OCH_2), 4.23 (d, *J* = 14.8 Hz, 1 H, OCH_2), 3.65 (d, *J* = 8.1 Hz, 1 H, OCH), 1.98–1.73 (m, 1 H, C*H*$_2$CHO), 1.64–1.57 (m, 1 H, C*H*$_2$CH$_2$CHO), 1.50–1.47 (m, 1 H, C*H*$_2$CHO), 1.31–1.19 (m, 1 H, C*H*$_2$CH$_2$CHO) ppm. ^{13}C NMR: δ = 132.6 (=C and =CH), 114.2 (=CH_2), 76.2 (OCH),

65.3 (OCH_2), 27.9 (CH_2), 21.3 (CH_2) ppm. MS (CI): *m/z* (%) = 238 (100) [M + NH_4^+], 221 (11) [MH^+]; found (ESI) 243.1360 [M + Na^+], $C_{14}H_{20}O_2Na$ requires 243.1361.

Metathesis of 38 to 48, 49 and 50: Diyne **38** (0.1 g, 0.52 mmol) was dissolved in dry toluene (48 mL) and ethene was passed through the stirred solution for 20 min. A solution of catalyst **2** (0.04 g, 0.05 mmol, 10 mol-%) in dry toluene (4 mL) was then added and the reaction mixture was stirred at 60 °C for 24 h under ethene. The solvent was then evaporated in vacuo and the residue was purified by flash chromatography (CH_2Cl_2 then hexane/EtOAc, 90:10) to afford three products, **48** (0.04 g, 36%), **49** (0.03 g, 24%) and **50** (0.02 g, 20%). **Data for 48:** IR (neat): $\tilde{\nu}_{max}$ = 3300 (m), 2934 (s), 2860 (m), 2115 (w), 1596 (w) cm^{-1}. ^1H NMR: δ = 6.31 (dd, *J* = 17.8, 11.0 Hz, 1 H, =CH), 5.25 (d, *J* = 17.6 Hz, 1 H, CH=CH_2), 5.24 (s, 1 H, C=CH_2), 5.09 (s, 1 H, C=CH_2), 5.04 (d, *J* = 11.0 Hz, 1 H, CH=CH_2), 4.25 (t, *J* = 4.7 Hz, 2 H, $OCH_2C\equiv$), 4.21–4.17 (m, 2 H, OCH_2), 3.36–3.30 (m, 1 H, OCH), 3.25–3.19 (m, 1 H, OCH), 2.33 (t, *J* = 2.5 Hz, 1 H, ≡CH), 1.98–1.94 (m, 2 H, CH_2CHO), 1.61–1.59 (m, 2 H, CH_2CH_2CHO), 1.25–1.14 (m, 4 H, CH_2CH_2) ppm. ^{13}C NMR: δ = 143.2 (=C), 136.7 (=CH), 117.0 (=CH_2), 114.2 (=CH_2), 81.4 (≡C), 80.7 (≡CH), 76.3 (OCH), 73.5 (OCH), 69.3 (OCH_2), 57.6 (OCH_2), 30.4 (CH_2), 30.0 (CH_2), 23.6 (CH_2), 23.5 (CH_2) ppm. MS (CI): *m/z* (%) = 221 (2) [MH^+], 153 (7), 137 (79), 67 (100); found (ESI) 243.1359 [M + Na^+], $C_{14}H_{20}O_2Na$ requires 241.1356. **Data for 49:** IR (neat): $\tilde{\nu}_{max}$ = 3087 (w), 2932 (s), 2860 (m), 1596 (m) cm^{-1}. ^1H NMR: δ = 6.30 (dd, *J* = 17.8, 11.0 Hz, 1 H, =CH), 5.25 (s, 1 H, C=CH_2), 5.23 (d, *J* = 17.4 Hz, 1 H, CH=CH_2), 5.08 (s, 1 H, C=CH_2), 5.01 (d, *J* = 11.0 Hz, 1 H, CH=CH_2), 4.23 (s, 2 H, OCH_2), 3.27–3.21 (m, 1 H, OCH), 1.95 (dd, *J* = 10.4, 2.6 Hz, 1 H, CH_2CHO), 1.61–1.58 (m, 1 H, CH_2CH_2CHO), 1.26–1.12 (m, 2 H, CH_2CH_2) ppm. ^{13}C NMR: δ = 143.3 (=C), 136.8 (=CH), 116.8 (=CH_2), 114.1 (=CH_2), 81.2 (OCH), 69.5 (OCH_2), 30.1 (CH_2), 23.6 (CH_2) ppm. MS (CI): *m/z* (%) = 266 (100) [M + NH_4^+], 249 (34) [MH^+], 182 (20), 165 (8); found (ESI) 271.1671 [M + Na^+], $C_{16}H_{24}O_2Na$ requires 271.1668. **Data for 50:** IR (neat): $\tilde{\nu}_{max}$ = 3089 (w), 2938 (s), 2863 (m), 1605 (w) cm^{-1}. ^1H NMR: δ = 6.76 (dd, *J* = 17.6, 11.3 Hz, 1 H, =CH), 5.25 (d, *J* = 17.7 Hz, 1 H, =CH_2), 5.13 (d, *J* = 11.5 Hz, 1 H, =CH_2), 4.69 (d, *J* = 14.8 Hz, 1 H, OCH_2), 4.54 (d, *J* = 14.8 Hz, 1 H, OCH_2), 3.18–3.15 (m, 1 H, OCH), 1.93–1.90 (m, 1 H, CH_2CHO), 1.61–1.60 (m, 1 H, CH_2CH_2CHO), 1.19–1.10 (m, 2 H, CH_2CH_2) ppm. ^{13}C NMR: δ = 133.3 (=C and =CH), 114.2 (=CH_2), 81.4 (OCH), 65.6 (OCH_2), 31.6 (CH_2), 30.7 (CH_2), 28.7 (CH_2), 23.3 (CH_2) ppm. MS (CI): *m/z* (%) = 238 (100) [M + NH_4^+], 221 (11) [MH^+]; found (ESI) 243.1357 [M + Na^+], $C_{14}H_{20}O_2Na$ requires 243.1356.

Metathesis of 35 to 51 and 53: To a stirring solution of compound **35** (0.05 g, 0.26 mmol) and 1-hexene (0.11 g, 1.3 mmol) in dry CH_2Cl_2 (22 mL) under N_2 was added a solution of catalyst **1** (0.02 g, 0.026 mmol, 10 mol-%) in dry CH_2Cl_2 (4 mL). The reaction mixture was stirred for 24 h at room temperature under N_2, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (CH_2Cl_2) to afford mono-cross metathesis product **51** (0.04 g, 60%) and bis-cross metathesis product **53** (0.04 g, 40%) as transparent oils. Each compound was isolated as a 1:1 ratio of *E*- and *Z*-isomers. **Data for 51:** IR (neat): $\tilde{\nu}_{max}$ = 3282 (m), 3028 (w), 2953 (s), 2930 (s), 2872 (m), 2117 (w), 1720 (m), 1696 (m) cm^{-1}. ^1H NMR: δ = 5.99 (d, *J* = 16.0 Hz, 1 H, =C-CH=$_{trans}$), 5.76 (dt, *J* = 15.9, 6.9 Hz, 2 H, =C-CH=C$H_{cis+trans}$), 5.52–5.47 (m, 5 H, CH=$CH_{cis+trans}$, =C-CH=$_{cis}$), 5.07 (br. s, 2 H, =$CH_{2cis+trans}$), 4.97 (br. s, 2 H, =$CH_{2cis+trans}$), 4.27 (t, *J* = 2.2 Hz, 4 H, $OCH_2C\equiv_{cis+trans}$), 4.20 (s, 2 H, $OCH_2C=_{trans}$), 4.19 (s, 2 H, $OCH_2C=_{cis}$), 3.97–3.96 (m, 2 H, $OCH_{cis+trans}$), 3.68–3.64 (m, 2 H, $OCH_{cis+trans}$), 2.32 (t, *J* = 2.3 Hz, 2 H, ≡$CH_{cis+trans}$), 2.31–2.18 (m, 8 H, CH_2CH=CHC$H_{2cis+trans}$), 2.02 (q, *J* = 6.1 Hz, 4 H, =CHC$H_2CH_{2cis+trans}$), 1.35–1.24 (m, 8 H, MeCH_2C$H_{2cis+trans}$), 0.83 (t, *J* = 7.1 Hz, 6 H, $CH_{3cis+trans}$) ppm. ^{13}C NMR: δ = 142.7 (C=), 134.0 and 129.6 (=CH), 131.6 and 126.9 (=CH), 124.5 (=CH), 123.8 (=CH), 114.8 and 114.6 (=CH_2), 80.5 (≡C), 74.7 (OCH), 74.6 (≡CH), 73.9 and 73.7 (OCH), 71.8 and 69.2 (OCH_2), 56.6 (OCH_2), 32.8 and 32.2 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 28.7 and 28.6 (CH_2), 22.4 and 22.2 (CH_2), 14.0 and 13.4 (CH_3) ppm. MS (CI): *m/z* (%) = 292 (100) [M + NH_4^+], 135 (13); found (ESI) 297.1816 [M + Na^+], $C_{18}H_{26}O_2Na$ requires 297.1825. **Data for 53:** IR (neat): $\tilde{\nu}_{max}$ = 3030 (w), 2958 (s), 2927 (s), 2854 (s), 1728 (m), 1680 (m), 1635 (w) cm^{-1}. ^1H NMR: δ = 5.99 (d, *J* = 16.0 Hz, 1 H, =C-CH=$_{trans}$), 5.78–5.70 (m, 2 H, =C-CH=C$H_{cis+trans}$), 5.51–5.43 (m, 3 H, =C-CH=$_{cis}$, $CHCH_2CH=_{cis+trans}$), 5.22 (br. s, 1 H, =CH_{2trans}), 5.08 (br. s, 1 H, =CH_{2cis}), 4.96 (br. s, 2 H, =$CH_{2cis+trans}$), 4.25 (d, *J* = 13.0 Hz, 1 H, OCH_{2trans}), 4.18 (d, *J* = 13.0 Hz, 1 H, OCH_{2cis}), 4.08 (d, *J* = 13.4 Hz, 1 H, OCH_{2trans}), 4.04 (d, *J* = 13.4 Hz, 1 H, OCH_{2cis}), 3.69 (t, *J* = 4.6 Hz, 2 H, $CH_{cis+trans}$), 2.34–2.28 (m, 2 H, CHC$H_{2cis+trans}$CH=), 2.19–2.14 (m, 4 H, CHC$H_{2cis+trans}$CH=, =CHC$H_{2cis+trans}CH_2$), 2.01 (q, *J* = 6.8 Hz, 2 H, =CHC$H_{2cis+trans}CH_2$), 1.34–1.23 (m, 8 H, MeCH_2C$H_{2cis+trans}$), 0.82 (t, *J* = 7.0 Hz, 6 H, C$H_{3cis+trans}$) ppm. ^{13}C NMR: δ = 142.9 and 142.6 (C=), 133.9 and 129.7 (=CH), 131.4 and 127.0 (=CH), 124.3 and 124.2 (=CH), 114.5 and 114.3 (=CH_2), 74.7 and 74.5 (OCH), 72.0 and 69.4 (OCH_2), 32.8 and 32.2 (CH_2), 31.4 and 29.4 (CH_2), 29.3 and 28.7 (CH_2), 22.4 and 22.3 (CH_2), 14.0 and 13.9 (CH_3) ppm. MS (CI): *m/z* (%) = 376 (100) [M + NH_4^+], 359 (23) [MH^+], 247 (51); found (ESI) 381.2753 [M + Na^+], $C_{24}H_{38}O_2Na$ requires 381.2764.

Metathesis of 36 to 52 and 54: To a stirring solution of compound **36** (0.05 g, 0.26 mmol) and 1-hexene (0.11 g, 1.3 mmol) in dry CH_2Cl_2 (22 mL) under N_2 was added a solution of catalyst **1** (0.02 g, 0.026 mmol, 10 mol-%) in dry CH_2Cl_2 (4 mL). The reaction mixture was stirred for 24 h at room temperature under N_2, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (CH_2Cl_2) to afford mono-cross metathesis product **52** (0.05 g, 50%) and bis-cross metathesis product **54** (0.02 g, 26%) as transparent oils. Each compound was isolated as a 1:1 ratio of *E*- and *Z*-isomers. **Data for 52:** IR (neat): $\tilde{\nu}_{max}$ = 3284 (m), 3030 (w), 2955 (s), 2929 (s), 2871 (m), 2117 (w), 1719 (m), 1698 (m) cm^{-1}. ^1H NMR: δ = 6.00 (d, *J* = 16.0 Hz, 1 H, =C-CH_{trans}=), 5.78–5.72 (m, 2 H, =C-CH=C$H_{cis+trans}$), 5.52–5.48 (m, 5 H, =C-CH_{cis}=, CH_2CH =C$HCH_{2cis+trans}$), 5.21 (br. s, 1 H, =CH_{2trans}), 5.07 (br. s, 1 H, =CH_{2cis}), 4.97 (br. s, 2 H, =$CH_{2cis+trans}$), 4.32–4.23 (m, 4 H, $OCH_{2cis+trans}C\equiv$), 4.20 (s, 2 H, $OCH_{2trans}C=$), 4.06 (s, 2 H, $OCH_{2cis}C=$), 3.70–3.66 (m, 2 H, $OCH_{cis+trans}$), 3.58–3.52 (m, 2 H, $OCH_{cis+trans}$), 2.44–2.41 (m, 4 H, =CHC$H_{2cis+trans}$CHO), 2.34–2.33 (m, 2 H, ≡$CH_{cis+trans}$), 2.17 (q, *J* = 6.9 Hz, 2 H, CH=CHCH_{2trans}), 2.03 (q, *J* = 6.9 Hz, 6 H, CH=CHCH_{2cis}, =CHC$H_{2cis+trans}$CHO), 1.33–1.23 (m, 8 H, $MeCH_2CH_{2cis+trans}$), 0.83 (t, *J* = 7.2 Hz, 6 H, $CH_{3cis+trans}$) ppm. ^{13}C NMR: δ = 143.3 and 142.9 (=C), 134.5 and 130.0 (=CH), 132.0 and 127.4 (=CH), 124.6 (CH=CH), 115.2 and 115.1 (=CH_2), 81.0 (≡C), 77.6 (OCH), 77.5 (OCH), 74.1 (≡CH), 73.4 and 70.6 (OCH_2), 58.2 (OCH_2), 33.2 and 29.1 (CH_2), 32.6 and 31.8 (CH_2), 31.1 (CH_2), 30.9 and 30.8 (CH_2), 22.8 and 22.7 (CH_2), 14.4 and 14.3 (CH_3) ppm. MS (EI): *m/z* (%) = 274 (3) [M^+], 217 (5), 151 (11), 135 (16), 124 (24), 95 (37), 79 (100); found (ESI) 297.1834 [M + Na^+], $C_{18}H_{26}O_2Na$ requires 297.1825. **Data for 54:** IR (neat): $\tilde{\nu}_{max}$ = 3029 (w), 2958 (s), 2926 (s), 2857 (s), 1732 (m), 1682 (m), 1645 (w) cm^{-1}. ^1H NMR: δ = 5.99 (d, *J* = 15.9 Hz, 1 H, =C-CH=$_{trans}$), 5.76–5.71 (m, 2 H, =C-CH=$CH_{cis+trans}$), 5.50–5.45 (m,

3 H, =C-CH=$_{cis}$, $CHCH_2CH{=}_{cis+trans}$), 5.22 (br. s, 1 H, $=CH_{2trans}$), 5.08 (br. s, 1 H, $=CH_{2cis}$), 4.96 (br. s, 2 H, $=CH_{2cis+trans}$), 4.26–4.19 (m, 2 H, $OCH_{2cis+trans}$), 4.08–4.05 (m, 2 H, $OCH_{2cis+trans}$), 3.54 (br. s, 2 H, $OCH_{cis+trans}$), 2.40 (d, J = 17.0 Hz, 2 H, $=CHCH_{2cis+trans}CH$), 2.18–2.15 (m, 2 H, $=CHCH_{2cis+trans}CH_2$), 2.03–2.01 (m, 4 H, $=CHCH_{2cis+trans}CH_2$, $=CHCH_{2cis+trans}CH$), 1.30–1.24 (m, 8 H, $MeCH_2CH_{2cis+trans}$), 0.83 (t, J = 7.1 Hz, 6 H, $CH_{3cis+trans}$) ppm. ^{13}C NMR: δ = 143.1 and 142.7 (=C), 133.9 and 129.7 (=CH), 131.4 and 127.0 (=CH), 124.2 (=CH), 114.6 and 114.4 ($=CH_2$), 76.8 (OCH), 73.2 and 70.3 (OCH_2), 32.7 and 28.7 (CH_2), 32.2 and 31.4 (CH_2), 30.5 and 30.4 (CH_2), 22.4 and 22.3 (CH_2), 14.0 and 13.9 (CH_3) ppm. MS (CI): m/z (%) = 376 (100) [M + NH_4^+], 359 (34) [MH^+], 247 (39); found (ESI) 359.2944 [MH^+], $C_{24}H_{39}O_2$ requires 359.2945.

***cis*-1,2-Bis[4-(allyloxy)but-2-ynyloxy]cyclohex-4-ene (56):** To a stirring solution of *cis*-1,2-dihydroxycyclohex-4-ene[10] (**3**, 0.35 g, 3.1 mmol) in DMF (25 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.37 g, 9.2 mmol). After stirring for 1 h at 0 °C, bromide **55**[24] (1.45 g, 7.7 mmol) was added and the reaction mixture warmed to room temperature. The reaction was stirred overnight, hydrolysed with water (10 mL) and extracted with Et_2O (4 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 70:30) to give compound **56** (0.74 g, 73%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3079 (w), 3029 (m), 2908 (s), 2854 (s), 2239 (w), 1670 (m), 1648 (m) cm^{-1}. ^{1}H NMR: δ = 5.84 (ddt, J = 17.1, 10.4, 5.8 Hz, 1 H, CH=CH_2), 5.52 (br. s, 1 H, CH=CH), 5.24 (ddd, J = 17.2, 3.1, 1.5 Hz, 1 H, $=CH_2$), 5.16 (dd, J = 10.3, 1.4 Hz, 1 H, $=CH_2$), 4.30 (dd, J = 3.3, 1.6 Hz, 2 H, CHOCH_2), 4.13 (t, J = 1.7 Hz, 2 H, CH_2OCH_2CH=), 3.99 (dt, J = 5.7, 1.3 Hz, 2 H, OCH_2CH=), 3.93 (t, J = 5.8 Hz, 1 H, OCH), 2.32 (dd, J = 15.5, 5.8 Hz, 1 H, CH_2), 2.25–2.20 (m, 1 H, CH_2) ppm. ^{13}C NMR: δ = 134.3 (CH=), 124.5 (CH=), 118.3 ($=CH_2$), 83.2 (≡C), 82.4 (≡C), 74.1 (OCH), 71.1 (OCH_2), 57.9 (OCH_2), 56.9 (OCH_2), 29.2 (CH_2) ppm. MS (CI): m/z (%) = 348 (100) [M + NH_4^+], 331 (4) [MH^+]; found (ESI) 348.2169 (M + NH_4^+), $C_{20}H_{30}NO_4$ requires 348.2169.

***trans*-1,2-Bis[4-(allyloxy)but-2-ynyloxy]cyclohex-4-ene (57):** To a stirring solution of *trans*-1,2.dihydroxycyclohex-4-ene[11] (**4**, 0.4 g, 3.5 mmol) in DMF (25 mL) at 0 °C was slowly added NaH (60% in mineral oil, 0.42 g, 10.5 mmol). After stirring for 1 h at 0 °C, bromide **55**[24] (2.0 g, 10.5 mmol) was added. The reaction mixture was warmed to room temperature, stirred overnight, hydrolysed with water (10 mL) and extracted with Et_2O (4 × 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 70:30) to give compound **57** (0.92 g, 79%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3079 (w), 3029 (w), 2904 (s), 2852 (s), 2243 (w), 1647 cm^{-1} (w). ^{1}H NMR: δ = 5.93 (ddt, J = 17.1, 11.5, 5.8 Hz, 1 H, CH=CH_2), 5.60–5.53 (m, 1 H, CH=CH), 5.33 (dq, J = 17.2, 1.6 Hz, 1 H, $=CH_2$), 5.23 (dq, J = 10.4, 1.3 Hz, 1 H, $=CH_2$), 4.44–4.34 (m, 2 H, CHOCH_2), 4.22 (t, J = 1.8 Hz, 2 H, $CH_2OCH_2C{\equiv}$), 4.08 (dt, J = 5.5, 1.1 Hz, 2 H, OCH_2CH=), 3.80–3.73 (m, 1 H, OCH), 2.53 (d, J = 16.2 Hz, 1 H, CH_2), 2.12 (ddd, J = 15.6, 4.8, 2.6 Hz, 1 H, CH_2) ppm. ^{13}C NMR: δ = 134.4 (=CH), 124.5 (=CH), 118.3 ($=CH_2$), 83.4 (≡C), 82.2 (≡C), 77.3 (OCH), 71.0 (OCH_2), 58.1 (OCH_2), 57.9 (OCH_2), 31.0 (CH_2) ppm. MS (CI): m/z (%) = 348 (100) [M + NH_4^+]; found (ESI) 348.2168 (M + NH_4^+), $C_{20}H_{30}NO_4$ requires 348.2169.

Metathesis of Compound 56 to 58: To a stirring solution of compound **56** (0.05 g, 0.15 mmol) in dry CH_2Cl_2 (12 mL) was added a solution of catalyst **1** (0.012 g, 0.015 mmol, 10 mol-%) in dry CH_2Cl_2 (3 mL). The reaction mixture was stirred for 24 h at room temperature under N_2, then the solvent was evaporated in vacuo and the residue subjected to flash chromatography (hexane/EtOAc, 70:30) to give bis-diene **58** (0.046 g, 93%) as a transparent oil. IR (neat): $\tilde{\nu}_{max}$ = 3429 (br), 3027 (w), 2847 (s), 1641 (m), 1603 (w) cm^{-1}. ^{1}H NMR: δ = 5.93 (br. s, 1 H, CH=C), 5.52 (br. s, 1 H, CH=CH), 5.25 (br. s, 1 H, $=CH_2$), 4.84 (br. s, 1 H, $=CH_2$), 4.72–4.68 (m, 4 H, CH_2OCH_2), 4.24 (s, 2 H, OCH_2C=), 3.72 (t, J = 5.6 Hz, 1 H, OCH), 2.34 (dd, J = 15.1, 5.1 Hz, 1 H, CH_2), 2.19 (dd, J = 13.9, 1.7 Hz, 1 H, CH_2) ppm. ^{13}C NMR: δ = 137.9 (=C), 137.4 (=C), 124.6 (=CH), 122.8 (=CH), 115.0 ($=CH_2$), 77.2 (OCH_2), 75.6 (OCH_2), 75.3 (OCH), 70.5 (OCH_2), 29.5 (CH_2) ppm. MS (CI): m/z (%) = 348 (100) [M + NH_4^+], 331 (26) [MH^+], 315 (15), 262 (9); found (ESI) 353.1721 [M + Na^+], $C_{20}H_{26}O_4Na$ requires 353.1723.

Metathesis of 57 to 59: To a stirring solution of compound **57** (0.05 g, 0.15 mmol) in dry CH_2Cl_2 (12 mL) was added a solution of catalyst **1** (0.012 g, 0.015 mmol, 10 mol-%) in dry CH_2Cl_2 (3 mL). The reaction mixture was stirred for 24 h at 35 °C under N_2, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 80:20) to give bis-diene **59** (0.05 g, 100%) as a transparent oil. IR (neat): $\tilde{\nu}_{max}$ = 3028 (w), 2845 (s), 1645 (m), 1602 (w) cm^{-1}. ^{1}H NMR: δ = 5.91 (t, J = 1.8 Hz, 1 H, CH=), 5.49 (br. s, 1 H, CH=CH), 5.24 (br. s, 1 H, $=CH_2$), 4.84 (br. s, 1 H, $=CH_2$), 4.72–4.66 (m, 4 H, CH_2OCH_2), 4.27 (s, 2 H, OCH_2C=), 3.58–3.53 (m, 1 H, OCH), 2.46–2.40 (m, 1 H, CH_2), 2.05 (ddd, J = 15.5, 4.8, 2.7 Hz, 1 H, CH_2) ppm. ^{13}C NMR: δ = 138.0 (=C), 137.5 (=C), 124.6 (=CH), 122.9 (=CH), 115.1 ($=CH_2$), 77.8 (OCH), 77.1 (OCH_2), 75.6 (OCH_2), 71.6 (OCH_2), 31.1 (CH_2) ppm. MS (CI): m/z (%) = 348 (100) [M + NH_4^+], 331 (29) [MH^+]; found (ESI) 353.1698 [M + Na^+], $C_{20}H_{26}O_4Na$ requires 353.1723.

Diels–Alder Adduct 60: To a stirring solution of compound **57** (0.05 g, 0.15 mmol) in dry CH_2Cl_2 (12 mL) was added a solution of catalyst **1** (0.012 g, 0.015 mmol, 10 mol-%) in dry CH_2Cl_2 (3 mL). The reaction mixture was stirred for 20 h at room temperature under N_2. The solvent was then evaporated in vacuo and the residue was redissolved in EtOAc (6 mL). Maleic anhydride (0.074 g, 0.76 mmol) was added and the mixture was stirred for a further 20 h. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (CH_2Cl_2) to yield a 1:1:1 ratio of diastereomeric Diels–Alder adducts **60** (0.061 g, 75%) as a transparent oil. IR (neat): $\tilde{\nu}_{max}$ = 3030 (w), 2853 (s), 1847 (m), 1775 (s) cm^{-1}. ^{1}H NMR: δ = 5.46 (br. s, 1 H, =CH), 4.37–4.28 (m, 2 H, CHOCH_2), 4.26–4.17 (m, 1 H, C=CCH_2O), 4.13–4.04 (m, 1 H, C=CCH_2O), 4.00–3.93 (m, 2 H, CHCH_2O), 3.52–3.44 (m, 2 H, COCHCHCO), 3.40 (br. s, 1 H, OCH), 2.76–2.65 (m, 2 H, CH_2C=CCH), 2.37 (d, J = 17.6 Hz, 1 H, =CHCH_2), 2.17 (br. s, 1 H, CH_2C=CCH), 1.98–1.95 (m, 1 H, =CHCH_2) ppm. ^{13}C NMR: δ = 173.8, 173.7 and 173.6 (C=O), 171.1 (C=O), 138.0, 137.7, and 137.6 (=C), 137.4 (=C), 124.1, 124.0, and 123.9 (=CH), 77.8, 77.7, and 77.4 (OCH), 70.2, 70.1, and 70.0 (OCH_2), 68.9, 68.8, and 68.7 (OCH_2), 68.6, 68.5, and 68.4 (OCH_2), 41.5 (CH), 41.4 (CH), 41.3 (CH), 30.2, 30.1, and 29.7 (CH_2), 26.9, 26.8, and 26.7 (CH_2) ppm. MS (CI): m/z (%) = 544 (100) [M + NH_4^+], 338 (66); found (ESI) 549.1736 [M + Na^+], $C_{28}H_{30}O_{10}Na$ requires 549.1731.

***cis*-Dibut-3-ynyl Cyclohex-4-ene-1,2-dicarboxylate (62):** To a suspension of *cis*-cyclohex-4-ene-1,2-dicarboxylic acid[28] (**61**, 1.0 g, 5.9 mmol) in CH_2Cl_2 (30 mL) were added *N*,*N*′-dicyclohexylcarbodiimide (3.0 g, 14.7 mmol), 3-butyn-1-ol (1.0 g, 1.11 mL, 14.7 mmol) and 4-(dimethylamino)pyridine (0.07 g, 0.59 mmol). The reaction mixture was stirred overnight at room temperature,

filtered, washed with 1 M HCl (2 × 10 mL), 20% aqueous $NaHCO_3$ (2 × 10 mL) and water (2 × 10 mL). The organic layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **62** (0.9 g, 55%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3291 (s), 3029 (w), 2963 (m), 2920 (m), 2851 (w), 2121 (w) and 1735 (s) cm^{-1}. ^1H NMR: δ = 5.72 (t, J = 1.5 Hz, 1 H, =CH), 4.29–4.20 (m, 2 H, OCH_2), 3.14–3.10 (m, 1 H, CHCO), 2.62 (ddd, J = 17.8, 4.0, 1.9 Hz, 1 H, CH_2CH), 2.56 (dt, J = 6.8, 2.7 Hz, 2 H, $CH_2C{\equiv}$), 2.41 (ddd, J = 16.0, 4.5, 1.3 Hz, 1 H, CH_2CH), 2.04 (t, J = 2.7 Hz, 1 H, ≡CH) ppm. ^{13}C NMR: δ = 172.9 (C=O), 125.1 (=CH), 80.1 (≡C), 69.8 (≡CH), 62.3 (OCH_2), 39.6 (CH), 25.7 (CH_2), 18.9 (CH_2) ppm. MS (CI): m/z (%) = 292 (100) [M + NH_4^+], 275 (27) [MH^+], 222 (11); found (ESI) 297.1100 [M + Na^+], $C_{16}H_{18}O_4Na$ requires 297.1097.

***cis*-Dipent-3-ynyl Cyclohex-4-ene-1,2-dicarboxylate (63):** To a suspension of *cis*-cyclohex-4-ene-1,2-dicarboxylic acid[28] (**61**, 1.0 g, 5.9 mmol) in CH_2Cl_2 were added *N*,*N*′-dicyclohexylcarbodiimide (3.0 g, 14.7 mmol), 3-pentyn-1-ol (1.2 g, 14.7 mmol) and 4-(dimethylamino)pyridine (0.07 g, 0.6 mmol). The reaction mixture was stirred overnight at room temperature, filtered, washed with 1 M HCl (2 × 10 mL), 20% aqueous $NaHCO_3$ (2 × 10 mL) and water (2 × 10 mL). The organic layer was then dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc, 90:10) to give compound **63** (1.0 g, 55%) as colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3029 (w), 2960 (m), 2920 (m), 2854 (w), 2195 (w), 1739 (s) cm^{-1}. ^1H NMR: δ = 5.69 (t, J = 1.4 Hz, 1 H, =CH), 4.22–4.11 (m, 2 H, OCH_2), 3.10–3.07 (m, 1 H, CHC=O), 2.59 (dd, J = 16.1, 4.8 Hz, 1 H, CH_2CH=), 2.49–2.43 (m, 2 H, $CH_2C{\equiv}$), 2.37 (dd, J = 16.5, 5.0 Hz, 1 H, CH_2CH=), 1.79 (t, J = 2.6 Hz, 3 H, ≡CCH_3) ppm. ^1H NMR: δ = 172.9 (C=O), 125.1 (CH=), 77.2 (≡C), 74.7 (≡C), 63.0 (OCH_2), 39.7 (CH), 25.7 (CH_2), 19.1 (CH_2), 3.5 (CH_3) ppm. MS (EI): m/z (%) = 302 (4) [M^+], 218 (46), 188 (54), 79 (28), 67 (100); found (ESI) 303.1597 [MH^+], $C_{18}H_{23}O_4$ requires 303.1591.

Metathesis of *cis*-Dipent-3-ynyl Cyclohex-4-ene-1,2-dicarboxylate 63 to 64 and 65: A solution of *cis*-dipent-3-ynyl cyclohex-4-ene-1,2-dicarboxylate (**63**, 0.3 g, 1.0 mmol), $Mo(CO)_6$ (0.013 g, 0.05 mmol, 5 mol-%) and 2-fluorophenol (0.1 g, 1.00 mmol) in chlorobenzene (20 mL) was refluxed for 6 h, then the solvent was evaporated in vacuo and the residue subjected to flash chromatography (cyclohexane/EtOAc, 80:20) to give compounds **64** (0.16 g, 63%) and **65** (0.01 g, 3%) as white solids. Starting material **63** (0.006 g, 2%) was also recovered. **Data for 64:** M.p. 69–72 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3028 (m), 2915 (s), 2848 (m), 1740 (s), 1657 cm^{-1} (m). ^1H NMR: δ = 5.63 (t, J = 1.5 Hz, 1 H, =CH), 4.33 (ddd, J = 10.5, 8.2, 4.3 Hz, 1 H, OCH_2), 4.07 (dt, J = 10.3, 5.0 Hz, 1 H, OCH_2), 3.10–3.06 (m, 1 H, CHC=O), 2.56 (dd, J = 16.3, 4.5 Hz, 1 H, CH_2CH=), 2.49–2.32 (m, 3 H, CH_2CH=, $CH_2C{\equiv}$) ppm. ^{13}C NMR: δ = 173.2 (C=O), 124.9 (CH=), 78.9 (≡C), 61.4 (OCH_2), 39.4 (CH), 25.8 (CH_2), 19.6 (CH_2) ppm. MS (EI): m/z (%) = 248 (17) [M^+], 220 (41), 106 (90), 79 (100); found (ESI) 271.0941 [M + Na^+], $C_{14}H_{16}O_4Na$ requires 271.0941. **Data for 65:** M.p. 122–125 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3030 (w), 2961 (m), 2919 (m), 2851 (w), 1734 cm^{-1} (s). ^1H NMR: δ = 5.61 (s, 1 H, =CH), 4.19–4.11 (m, 1 H, OCH_2), 4.09–4.02 (m, 1 H, OCH_2), 3.03 (t, J = 4.9 Hz, 1 H, CHC=O), 2.45 (t, J = 6.6 Hz, 3 H, CH_2CH=, $CH_2C{\equiv}$), 2.27 (dd, J = 16.7, 4.8 Hz, 1 H, CH_2CH=) ppm. ^{13}C NMR: δ = 172.8 (C=O), 125.1 (=CH), 77.6 (≡C), 63.0 (OCH_2), 39.9 (CH), 25.7 (CH_2), 19.1 (CH_2) ppm. MS (EI): m/z (%) = 496 (79) [M^+], 354 (8), 326 (10), 249 (30), 79 (100); found (ESI) 519.1978 [M + Na^+], $C_{28}H_{32}O_8Na$ requires 271.1989.

Diene 66 from 6,12-Fused Bicycle 64: The 6,12-fused bicycle **64** (0.06 g, 0.22 mmol) was dissolved in dry toluene (20 mL) and ethene was passed through the solution for 10 min. A solution of catalyst **2** (0.009 g, 0.01 mmol, 5 mol-%) in dry toluene (2 mL) was added and the reaction mixture was stirred at 60 °C for 20 h. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (CH_2Cl_2/EtOAc, 95:5) to give compound **66** (0.06 g, 100%) as a colourless oil. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3028 (w), 2957 (m), 1735 (s), 1638 cm^{-1} (m). ^1H NMR: δ = 5.58 (s, 1 H, =CH), 5.03 (s, 2 H, $=CH_2$), 4.29–4.24 (m, 1 H, OCH_2), 4.20–4.13 (m, 1 H, OCH_2), 2.97–2.93 (m, 1 H, CHC=O), 2.68 (ddd, J = 14.5, 9.8, 4.6 Hz, 1 H, CH_2C=), 2.53 (dt, J = 14.6, 4.2 Hz, 1 H, CH_2C=), 2.41 (dd, J = 16.0, 4.8 Hz, 1 H, CH_2CH=), 2.21 (dd, J = 16.4, 4.8 Hz, 1 H, CH_2CH=) ppm. ^{13}C NMR: δ = 173.1 (C=O), 144.3 (=C), 125.2 (=CH), 114.6 ($=CH_2$), 63.6 (OCH_2), 40.2 (CH), 33.7 (CH_2), 25.6 (CH_2) ppm. MS (CI): m/z (%) = 294 (100) [M + NH_4^+], 277 (13) [MH^+]; found (ESI) 294.1698 (M + NH_4^+), $C_{16}H_{24}O_4N$ requires 294.1700.

Diene 66 from Diyne 63: A solution of *cis*-dipent-3-ynyl cyclohex-4-ene-1,2-dicarboxylate (**63**, 0.10 g, 0.33 mmol), $Mo(CO)_6$ (0.004 g, 0.016 mmol, 5 mol-%) and 2-fluorophenol (0.04 g, 0.33 mmol) in chlorobenzene (5 mL) was refluxed for 20 h. The reaction mixture was cooled to room temperature and ethene was passed through the stirred solution for 10 min. A solution of catalyst **2** (0.014 g, 0.016 mmol, 5 mol-%) in chlorobenzene (2 mL) was then added and the mixture was stirred at 60 °C for 20 h under ethene. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (CH_2Cl_2/EtOAc, 95:5) to give compound **66** (0.07 g, 72%) as a colourless oil. Data as reported above.

3-[(But-2-ynyloxy)carbonyl]norborn-5-ene-*endo*,*cis*-2-carboxylic Acid (69): Norborn-5-ene-2,3-*endo*,*cis*-dicarboxylic anhydride (**67**, 3.0 g, 18.3 mmol) was dissolved in CH_2Cl_2 (60 mL) and but-2-yn-1-ol (1.35 g, 19.2 mmol) was added, followed by 4-(dimethylamino)-pyridine (0.223 g, 1.83 mmol). The reaction was stirred for 16 h, then the solvent was evaporated in vacuo and the residue purified by flash chromatography (CH_2Cl_2/EtOAc, 90:10) to provide compound **69** (4.0 g, 93%) as a white solid. M.p. 127–130 °C. IR (neat): $\tilde{\nu}_{max}$ = 3077 (w), 2978 (m), 2874 (w), 2242 (w), 1743 (s) and 1710 (s) cm^{-1}. ^1H NMR: δ = 12.0 (br. s, 1 H, OH), 6.35 (dd, J = 5.6, 2.9 Hz, 1 H, =CH), 6.24 (dd, J = 5.6, 2.9 Hz, 1 H, =CH), 4.69 (dq, J = 15.2, 2.3 Hz, 1 H, OCH_2), 4.49 (dq, J = 15.3, 2.4 Hz, 1 H, OCH_2), 3.39–3.30 (m, 2 H, COCHCHCO), 3.22 (br. s, 2 H, CHCH_2CH), 1.87 (t, J = 2.4 Hz, 3 H, ≡CCH_3), 1.52 (dt, J = 8.7, 1.7 Hz, 1 H, CHCH_2), 1.36 (d, J = 8.7 Hz, 1 H, CHCH_2) ppm. ^{13}C NMR ([D_6]DMSO): δ = 173.4 (C=O), 171.9 (C=O), 135.5 (=CH), 134.7 (=CH), 83.2 (≡C), 74.4 (≡C), 52.3 (OCH_2), 48.4 (CH_2), 48.2 (CH), 47.2 (CH), 46.4 (CH), 45.9 (CH), 3.4 (CH_3) ppm. MS (CI): m/z (%) = 252 (100) [M + NH_4^+], 235 (37) [MH^+], 182 (41); found (ESI) 257.0781 [M + Na^+], $C_{13}H_{14}O_4Na$ requires 257.0784.

But-2-ynyl Pent-3-ynyl *endo*,*cis*-Norborn-5-ene-2,3-dicarboxylate (70): To a suspension of compound **69** (2.0 g, 5.6 mmol) in CH_2Cl_2 (40 mL) were added *N*,*N*′-dicyclohexylcarbodiimide (1.9 g, 9.4 mmol), pent-3-yn-1-ol (0.8 g, 9.4 mmol) and 4-(dimethylamino)pyridine (0.1 g, 0.9 mmol). The reaction was stirred overnight at room temperature, filtered, washed with 1 M HCl (2 × 20 mL), 20% aqueous $NaHCO_3$ (2 × 20 mL) and water (2 × 20 mL). The organic layer was then dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc, 80:20) to provide compound **70** (1.97 g, 77%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 2977 (s), 2920 (m), 2872 (w), 2242 (w) and 1742 (s) cm^{-1}. ^1H NMR: δ = 6.31–6.26 (m, 2 H, CH=CH), 4.66 (dq, J = 15.3, 2.4 Hz, 1 H, $OCH_2C{\equiv}$),

4.53 (dq, J = 15.3, 2.4 Hz, 1 H, $OCH_2C\equiv$), 4.13–4.04 (m, 2 H, OCH_2CH_2), 3.34–3.33 (m, 2 H, COCHCHCO), 3.20 (t, J = 1.5 Hz, 2 H, $CHCH_2CH$), 2.46–2.41 (m, 2 H, $CH_2CH_2C\equiv$), 1.87 (t, J = 2.4 Hz, 3 H, $\equiv CCH_3$), 1.80 (t, J = 2.5 Hz, 3 H, $\equiv CCH_3$), 1.49 (dt, J = 8.6, 1.8 Hz, 1 H, $CHCH_2CH$), 1.34 (d, J = 8.6 Hz, 1 H, $CHCH_2CH$) ppm. ^{13}C NMR: δ = 172.5 (C=O), 172.2 (C=O), 135.3 (2 =CH), 83.4 (≡C), 77.5 (≡C), 75.3 (≡C), 73.7 (≡C), 63.2 (OCH_2), 53.2 (OCH_2), 49.7 (CH), 49.0 (CH_2), 48.6 (CH), 48.4 (CH), 46.8 (CH), 19.5 (CH_2), 4.1 (CH_3), 3.9 (CH_3) ppm. MS (CI): m/z (%) = 318 (100) [M + NH_4^+], 301 (45) [MH^+], 234 (12); found (ESI) 323.1252 [M + Na^+], $C_{18}H_{20}O_4Na$ requires 323.1254.

Dibut-2-ynyl *endo*,*cis*-Norborn-5-ene-2,3-dicarboxylate (71): To a suspension of *endo*,*cis*-norborn-5-ene-2,3-dicarboxylic acid[30] (**68**, 1.0 g, 5.5 mmol) in CH_2Cl_2 (30 mL) were added *N*,*N*′-dicyclohexylcarbodiimide (2.8 g, 13.7 mmol), 2-butyn-1-ol (1.0 g, 1.03 mL, 13.7 mmol) and 4-(dimethylamino)pyridine (0.07 g, 0.549 mmol). The reaction mixture was stirred overnight at room temperature, then filtered, washed with 1 M HCl (2 × 10 mL), 20% aqueous $NaHCO_3$ (2 × 10 mL) and water (2 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to provide diester **71** (0.89 g, 56%) as a white solid. M.p. 67–70 °C. IR (neat): $\tilde{\nu}_{max}$ = 3075 (w), 2978 (m), 2942 (w), 2873 (w), 2241 (w) and 1745 (s) cm^{-1}. ^{1}H NMR: δ = 6.21 (t, J = 1.8 Hz, 2 H, CH=CH), 4.59 (dq, J = 15.2, 2.3 Hz, 2 H, 2 OCH_2), 4.43 (dq, J = 15.3, 2.4 Hz, 2 H, 2 OCH_2), 3.27 (t, J = 1.5 Hz, 2 H, 2 CHCO), 3.13 (t, J = 1.6 Hz, 2 H, 2 CHCHCO), 1.79 (t, J = 2.5 Hz, 6 H, 2 CH_3), 1.42 (dt, J = 8.6, 1.8 Hz, 1 H, $CHCH_2$), 1.25 (d, J = 8.6 Hz, 1 H, $CHCH_2$) ppm. ^{13}C NMR: δ = 172.1 (C=O), 135.3 (=CH), 83.5 (≡C), 73.6 (≡C), 53.3 (OCH_2), 49.0 (CH_2), 48.5 (CH), 46.7 (CH), 4.1 (CH_3) ppm. MS (CI): m/z (%) = 304 (100) [M + NH_4^+], 287 (31) [MH^+]; found (ESI) 309.1111 [M + Na^+], $C_{17}H_{18}O_4Na$ requires 309.1097.

Dibut-3-ynyl *endo*,*cis*-Norborn-5-ene-2,3-dicarboxylate (72): To a suspension of *endo*,*cis*-norborn-5-ene-2,3-dicarboxylic acid[30] (**68**, 1.0 g, 5.5 mmol) in CH_2Cl_2 (30 mL) were added *N*,*N*′-dicyclohexylcarbodiimide (2.8 g, 13.7 mmol), but-3-yn-1-ol (1.0 g, 13.7 mmol) and 4-(dimethylamino)pyridine (0.07 g, 0.55 mmol). The reaction mixture was stirred overnight at room temperature, filtered, washed with 1 M HCl (2 × 10 mL), 20% aqueous $NaHCO_3$ (2 × 10 mL) and water (2 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to provide diester **72** (0.80 g, 51%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 3291 (s), 2972 (s), 2121 (w) and 1743 (s) cm^{-1}. ^{1}H NMR: δ = 6.29 (d, J = 1.6 Hz, 2 H, CH=CH), 4.20–4.07 (m, 4 H, 2 OCH_2), 3.33 (br. s, 2 H, 2 CHCO), 3.20 (br. s, 2 H, 2 CHCHCO), 2.53–2.48 (m, 4 H, 2 $CH_2C\equiv$), 2.01 (t, J = 2.7 Hz, 2 H, 2 ≡CH), 1.50 (dt, J = 8.6, 1.7 Hz, 1 H, $CHCH_2$), 1.35 (d, J = 8.6 Hz, 1 H, $CHCH_2$) ppm. ^{13}C NMR: δ = 172.1 (C=O), 134.9 (=CH), 80.3 (≡C), 69.7 (≡CH), 62.1 (OCH_2), 48.6 (CH_2), 47.9 (CH), 46.4 (CH), 18.9 (CH_2) ppm. MS (CI): m/z (%) = 304 (100) [M + NH_4^+], 287 (52) [MH^+], 234 (24); found (ESI) 287.1279 [MH^+], $C_{17}H_{19}O_4$ requires 287.1278.

Dipent-3-ynyl *endo*,*cis*-Norborn-5-ene-2,3-dicarboxylate (73): To a suspension of *endo*,*cis*-norborn-5-ene-2,3-dicarboxylic acid[30] (**68**, 1.0 g, 5.5 mmol) in CH_2Cl_2 (30 mL) were added *N*-*N*′-dicyclohexylcarbodiimide (2.8 g, 13.7 mmol), 3-pentyn-1-ol (1.15 g, 13.7 mmol) and 4-(dimethylamino)pyridine (0.07 g, 0.55 mmol). The reaction mixture was stirred overnight at room temperature, then filtered, washed with 1 M HCl (2 × 10 mL), 20% aqueous $NaHCO_3$ (2 × 10 mL) and water (2 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, evaporated in vacuo and the residue purified by flash chromatography (hexane/EtOAc, 90:10) to provide diester **73** (0.84 g, 49%) as a colourless oil. IR (neat): $\tilde{\nu}_{max}$ = 2963 (s), 2919 (m), 2871 (w), 1742 (s), 1716 (m) cm^{-1}. ^{1}H NMR: δ = 6.21 (t, J = 1.7 Hz, 2 H, CH=CH), 4.07–3.93 (m, 4 H, 2 OCH_2), 3.24 (t, J = 1.5 Hz, 2 H, 2 CHCO), 3.11 (s, 2 H, 2 CHCHCO), 2.37–2.33 (m, 4 H, 2 $CH_2C\equiv$), 1.71 (t, J = 2.5 Hz, 6 H, 2 CH_3), 1.42–1.39 (m, 1 H, $CHCH_2$), 1.26 (d, J = 8.6 Hz, 1 H, $CHCH_2$) ppm. ^{13}C NMR: δ = 172.1 (C=O), 134.9 (=CH), 77.1 (≡C), 74.9 (≡C), 62.8 (OCH_2), 48.6 (CH_2), 48.0 (CH), 46.4 (CH), 19.1 (CH_2), 3.5 (CH_3) ppm. MS (EI): m/z (%) = 314 [M^+, 4], 249 (40), 203 (19), 165 (24), 157 (10), 67 (100); found (ESI) 337.1404 [M + Na^+], $C_{19}H_{22}O_4Na$ requires 303.1410.

Cyclic Alkyne 74: A solution of compound **73** (0.3 g, 1.0 mmol), $Mo(CO)_6$ (0.013 g, 0.05 mmol, 5 mol-%) and 2-fluorophenol (0.1 g, 1.0 mmol) in chlorobenzene (20 mL) was refluxed for 6 h, then the solvent was evaporated in vacuo and the residue was subjected to flash chromatography (cyclohexane/EtOAc, 80:20) to give product **74** (0.23 g, 87%) as a white solid. M.p. 134–136 °C. IR (neat): $\tilde{\nu}_{max}$ = 3075 (w), 2970 (m), 2909 (w), 1744 (s) cm^{-1}. ^{1}H NMR: δ = 6.21 (t, J = 1.7 Hz, 2 H, =CH), 4.45–4.38 (m, 2 H, OCH_2), 3.74 (ddd, J = 10.4, 4.6, 1.8 Hz, 2 H, OCH_2), 3.31 (t, J = 1.4 Hz, 2 H, CHCO), 3.08 (t, J = 1.5 Hz, 2 H, CHCHCO), 2.51–2.42 (m, 2 H, $CH_2C\equiv$), 2.22 (d, J = 15.1 Hz, 2 H, $CH_2C\equiv$), 1.45 (dt, J = 8.6, 1.8 Hz, 1 H, $CHCH_2$), 1.29 (d, J = 8.6 Hz, 1 H, $CHCH_2$) ppm. ^{13}C NMR: δ = 172.3 (C=O), 134.7 (=CH), 78.9 (≡C), 61.6 (OCH_2), 48.7 (CH), 48.1 (CH_2), 46.0 (CH), 19.7 (CH_2) ppm. MS (EI): m/z (%) = 260 [M^+, 14], 193 (15), 182 (32), 164 (12), 66 (100); found (ESI) 283.0938 [M + Na^+], $C_{15}H_{16}O_4Na$ requires 283.0940.

Diene 75 from 74: Compound **74** (0.05 g, 0.19 mmol) was dissolved in dry toluene (16 mL) and ethene was passed through the stirred solution for 10 min. A solution of catalyst **1** (0.008 g, 0.01 mmol, 5 mol-%) in dry toluene (3 mL) was added and the reaction mixture was stirred at room temperature for 20 h under ethene. The solvent was evaporated in vacuo and the residue subjected to flash chromatography (CH_2Cl_2/EtOAc, 98:2) to give compound **75** (0.04 g, 76%) as a white solid. Unreacted starting material **74** (0.011 g, 22%) was also recovered. M.p. 68–71 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3074 (w), 2957 (m), 2911 (w), 1738 (s), 1639 cm^{-1} (m). ^{1}H NMR: δ = 5.99 (ddd, J = 17.1, 10.1, 8.4 Hz, 2 H, =CH), 4.99 (ddd, J = 17.1, 1.8, 1.0 Hz, 2 H, $=CH_2$), 4.94 (ddd, J = 10.2, 1.8, 0.6 Hz, 2 H, $=CH_2$), 4.41 (dt, J = 10.3, 3.7 Hz, 2 H, OCH_2), 3.88 (dt, J = 10.4, 4.5 Hz, 2 H, OCH_2), 3.31–3.27 (m, 2 H, CHCO), 2.91–2.83 (m, 2 H, $CHCH_2$), 2.48–2.40 (m, 2 H, $CH_2C\equiv$), 2.31 (dt, J = 15.2, 2.9 Hz, 2 H, $CH_2C\equiv$), 1.97 (dt, J = 13.1, 7.3 Hz, 1 H, $CHCH_2$), 1.76 (dt, J = 13.0, 10.9 Hz, 1 H, $CHCH_2$) ppm. ^{13}C NMR: δ = 171.4 (C=O), 139.0 (=CH), 114.6 ($=CH_2$), 79.2 (≡C), 61.4 (OCH_2), 51.1 (CH), 45.0 (CH), 37.7 (CH_2), 19.5 (CH_2) ppm. MS (CI): m/z (%) = 306 (100) [M + NH_4^+], 289 (65) [MH^+]; found (ESI) 289.1436 [MH^+], $C_{17}H_{21}O_4$ requires 289.1434.

Diene 75 from 73: A solution of compound **73** (0.1 g, 0.32 mmol), $Mo(CO)_6$ (0.004 g, 0.016 mmol, 5 mol-%) and 2-fluorophenol (0.036 g, 0.32 mmol) in chlorobenzene (5 mL) was refluxed for 20 h. The reaction mixture was cooled to room temperature and ethene was passed through the stirred solution for 10 min. A solution of catalyst **1** (0.013 g, 0.016 mmol, 5 mol-%) in chlorobenzene (2 mL) was then added and the mixture was stirred at room temperature for 20 h under ethene. The solvent was then evaporated in vacuo and the residue was purified by flash chromatography (CH_2Cl_2/EtOAc, 98:2) to give compound **75** (0.061 g, 67%) as a white solid. Data as reported above.

Diene 76 from 74: Compound **74** (0.05 g, 0.19 mmol) was dissolved in dry toluene (16 mL) and ethene was passed through the stirred solution for 10 min. A solution of catalyst **2** (0.008 g, 0.01 mmol,

5 mol-%) in dry toluene (3 mL) was added and the reaction mixture was stirred at 60 °C for 20 h under ethene. The solvent was evaporated in vacuo and the residue purified by flash chromatography (CH_2Cl_2/EtOAc, 95:5) to give compound **76** (0.06 g, 100%) as a white solid. M.p. 55–57 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3076 (w), 2954 (m), 1749 (s), 1638 (w), 1595 cm^{-1} (w). ^1H NMR: δ = 5.89 (ddd, J = 17.1, 10.1, 8.5 Hz, 1 H, =CH), 5.07 (s, 1 H, C=CH_2), 5.03 (s, 1 H, C=CH_2), 4.97 (ddd, J = 17.1, 1.7, 0.9 Hz, 1 H, CH=CH_2), 4.91 (dd, J = 10.1, 1.4 Hz, 1 H, CH=CH_2), 4.31–4.25 (m, 1 H, OCH_2), 3.99 (ddd, J = 10.8, 4.3, 3.4 Hz, 1 H, OCH_2), 3.15–3.10 (m, 1 H, CHCO), 2.85–2.74 (m, 1 H, C*H*CHCO), 2.65 (ddd, J = 14.8, 11.8, 4.4 Hz, 1 H, CH_2C=), 2.49 (dt, J = 14.5, 3.1 Hz, 1 H, CH_2C=), 1.95–1.86 (m, 1 H, CHCH_2) ppm. ^{13}C NMR: δ = 173.2 (C=O), 145.4 (=C), 140.4 (=CH), 116.6 (=CH_2), 116.5 (=CH_2), 65.0 (OCH_2), 53.0 (CH), 47.0 (CH), 39.0 (CH_2), 35.2 (CH_2) ppm. MS (CI): *m*/*z* (%) = 334 (100) [M + NH_4^+], 317 (83) [MH^+]; found (ESI) 317.1747 [MH^+], $C_{19}H_{25}O_4$ requires 317.1747.

Diene 76 from 73: A solution of *cis*-dipent-3-ynyl-5-norbornene-*endo*-2,3-dicarboxylate (**73**, 0.1 g, 0.3 mmol), $Mo(CO)_6$ (0.004 g, 0.016 mmol, 5 mol-%) and 2-fluorophenol (0.036 g, 0.32 mmol) in chlorobenzene (5 mL) was refluxed for 20 h. The reaction mixture was cooled to room temperature and ethene was passed through the stirred solution for 10 min. A solution of catalyst **2** (0.013 g, 0.016 mmol, 5 mol-%) in chlorobenzene (2 mL) was then added and the mixture was stirred at 60 °C for 20 h under ethene. The solvent was evaporated in vacuo and the residue purified by flash chromatography (CH_2Cl_2/EtOAc, 95:5) to give compound **76** (0.07 g, 69%) as a white solid. Data as reported above.

Supporting Information (see footnote on the first page of this article): Copies of the ^{13}C NMR spectra of all new compounds and the ^1H NMR spectrum of compound **8**.

Acknowledgments

The authors thank the EPSRC national mass spectrometry service at the University of Wales, Swansea for recording mass spectra.

[1] For recent reviews of the development and applications of ruthenium based metathesis initiators see: a) R. H. Grubbs, *Adv. Synth. Catal.* **2007**, *349*, 34–40; b) R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760–3765; c) T. J. Donohoe, A. J. Orr, *Angew. Chem. Int. Ed.* **2006**, *45*, 2664–2670; d) D. J. Wallace, *Angew. Chem. Int. Ed.* **2005**, *44*, 1912–1915; e) R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140; f) M. D. McReynolds, J. M. Dougherty, P. R. Hanson, *Chem. Rev.* **2004**, *104*, 2239–2258; g) D. S. Blechert, S. J. Connon, *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923.

[2] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

[3] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[4] For recent reviews of enyne metathesis see:a) M. Mori, *Adv. Synth. Catal.* **2007**, *349*, 121–135; b) S. V. Maifeld, D. Lee, *Chem. Eur. J.* **2005**, *11*, 6118–6126; c) S. T. Diver, A. J. Giessert, *Chem. Rev.* **2004**, *104*, 1317–1382; d) C. S. Poulsen, R. Madsen, *Synthesis* **2003**, 1–18.

[5] a) D. Banti, E. Groaz, M. North, *Tetrahedron* **2004**, *60*, 8043–8052; b) D. Banti, M. North, *Tetrahedron Lett.* **2003**, *44*, 8157–8160; c) D. Banti, M. North, *Adv. Synth. Catal.* **2002**, *344*, 694–704; d) D. Banti, M. North, *Tetrahedron Lett.* **2002**, *43*, 1561–1564.

[6] E. Groaz, D. Banti, M. North, *Tetrahedron Lett.* **2007**, *48*, 1927–1930.

[7] For a preliminary account of some of the work reported in this manuscript see: E. Groaz, D. Banti, M. North, *Adv. Synth. Catal.* **2007**, *349*, 142–146.

[8] For a previous report of cyclohexene ring opening during cross metathesis see: S. Randl, S. J. Connon, S. Blechert, *Chem. Commun.* **2001**, 1796–1797.

[9] For reviews of alkyne metathesis see:a) W. Zhang, J. S. Moore, *Adv. Synth. Catal.* **2007**, *349*, 93–120; b) A. Fürstner, P. W. Davies, *Chem. Commun.* **2002**, 2307–2320; c) U. H. F. Bunz, *Acc. Chem. Res.* **2001**, *34*, 998–1010.

[10] T. J. Donohoe, L. Mitchell, M. J. Waring, M. Helliwell, A. Bell, N. J. Newcombe, *Org. Biomol. Chem.* **2003**, *1*, 2173–2186.

[11] S. Michaud, J. Viala, *Tetrahedron* **1999**, *55*, 3019–3024.

[12] C. Baylon, M.-P. Heck, C. Mioskowski, *J. Org. Chem.* **1999**, *64*, 3354–3360. The ^1H and ^{13}C NMR spectra of compound **10** are given in the supplementary information to this paper.

[13] S. J. Miller, S.-H. Kim, Z.-R. Chen, R. H. Grubbs, *J. Am. Chem. Soc.* **1995**, *117*, 2108–2109.

[14] For previous reports of enyne metathesis involving ring-opening of a cyclohexene unit see: a) T. Kitamura, M. Mori, *Org. Lett.* **2001**, *3*, 1161–1163; b) T. Kitamura, Y. Kuzuba, Y. Sato, H. Wakamatsu, R. Fujita, M. Mori, *Tetrahedron* **2004**, *60*, 7375–7389. See also ref.[6].

[15] For a related use of catalyst **1** to form eight-membered rings by enyne metathesis see: a) M. Mori, T. Kitamura, N. Sakakibara, Y. Sato, *Org. Lett.* **2000**, *2*, 543–545; b) M. Mori, T. Kitamura, Y. Sato, *Synthesis* **2001**, 654–664.

[16] a) M. Mori, N. Sakakibara, A. Kinoshita, *J. Org. Chem.* **1998**, *63*, 6082–6083; b) A. J. Giessert, N. J. Brazis, S. T. Diver, *Org. Lett.* **2003**, *5*, 3819–3822.

[17] A. Kinoshita, N. Sakakibara, M. Mori, *Tetrahedron* **1999**, *55*, 8155–8167.

[18] a) A. Newman, *J. Am. Chem. Soc.* **1955**, *77*, 3789; b) G. A. Russell, K. D. Schmitt, J. Mattox, *J. Am. Chem. Soc.* **1975**, *97*, 1882.

[19] G. S. Weatherhead, J. G. Ford, E. J. Alexanian, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 1828–1829.

[20] For previous reports on the higher activity of catalyst **2** than catalyst **1** in enyne metathesis see: a) R. Stragies, U. Voigtmann, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 5465–5468; b) K. Tonogaki, M. Mori, *Tetrahedron Lett.* **2002**, *43*, 2235–2238.

[21] M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

[22] S. H. Hong, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, *126*, 7414–7415.

[23] Decomposition of ruthenium alkylidenes is known to be a second order process in contrast to the first order decomposition of methylidene complexes: M. Ulman, R. H. Grubbs, *J. Org. Chem.* **1999**, *64*, 7202–7207.

[24] a) A. G. M. Barrett, S. P. D. Baugh, D. C. Braddock, K. Flack, V. C. Gibson, M. R. Giles, E. L. Marshall, P. A. Procopiou, A. J. P. White, D. J. Williams, *J. Org. Chem.* **1998**, *63*, 7893; b) L. J. van-Boxtel, S. Koerbe, M. Noltemeyer, A. de Meijere, *Eur. J. Org. Chem.* **2001**, 2283.

[25] a) K. Grela, J. Ignatowska, *Org. Lett.* **2002**, *4*, 3747–3749; b) V. Sashuk, J. Ignatowska, K. Grela, *J. Org. Chem.* **2004**, *69*, 7748–7751.

[26] A. Fürstner, G. Seidel, *Angew. Chem. Int. Ed.* **1998**, *37*, 1734–1736.

[27] For examples of the formation of eleven-membered rings in low yields see: a) A. Fürstner, C. Mathes, C. W. Lehmann, *Chem. Eur. J.* **2001**, *7*, 5299–5317; b) G. Brizius, U. H. F. Bunz, *Org. Lett.* **2002**, *4*, 2829–2831.

[28] a) P. Mohr, N. Waespesarcevic, C. Tamm, K. Gawronska, J. K. Gawronski, *Helv. Chim. Acta* **1983**, *66*, 2501–2511; b) M. Gay, Á. M. Montaña, V. Moreno, M. Font-Bardia, X. Solans, *J. Organomet. Chem.* **2005**, *690*, 4856–4866.

[29] a) A. Mortreux, F. Petit, M. Petit, T. Szymanska-Buzar, *J. Mol. Catal. A* **1995**, *96*, 95–105; b) R. R. Schrock, in *Handbook of Metathesis*, vol. 1, *Catalyst Development* (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, Germany, **2003**, pp. 173–189.
[30] D. N. Ford, W. Kitching, P. R. Wells, *Aust. J. Chem.* **1969**, *22*, 1157–1168.
[31] S. Y. Jonsson, K. Färnegårdh, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2001**, *123*, 1365–1371.
[32] A. Dahlén, A. Sundgren, M. Lahmann, S. Oscarson, G. Hilmersson, *Org. Lett.* **2003**, *5*, 4085–4088.
[33] S. Göksu, H. Seçen, Y. Sütbeyaz, *Synthesis* **2002**, 2373–2378.
Received: April 2, 2007
Published Online: June 12, 2007

