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Focus Review

Metathesis Reactions

Small-Ring Metathesis: Delights and Difficulties

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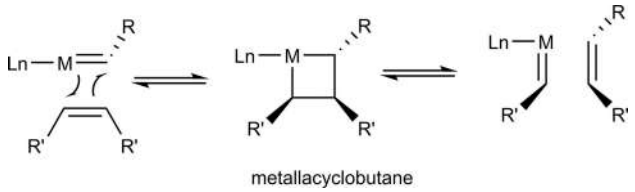
Abstract: The metathetical opening of strained cyclopropene and cyclobutene rings is a well-established conversion, successfully used in several total syntheses and in the preparation of polymers. Concurrently, it is generally considered that small cyclic products cannot be easily made by ring-closing metathesis (RCM). The current reports on the preparation of substituted cyclobutenes via 1,5-enyne RCM changed this scenario. In recent years, there have been significant pieces of work on metathesis of strained three- and four-membered rings reported, which required a thorough review.

Introduction

Among the many types of transition-metal-catalyzed carbon-carbon bond forming reactions, olefin metathesis has come to the front in recent years owing to the wide range of transformations that are possible using metal carbene complexes of W, Mo and Ru as catalysts (Scheme 1). Many examples are



Scheme 1. Olefin metathesis.

known in the literature wherein natural products, drugs, polymers, pharmaceuticals, and other important molecules prepared via synthetic pathways with at least one olefin metathesis step.[1] Olefin metathesis ('metathesis' from the Greek meaning 'change of position, transposition') rearranges the carbon atoms of two C=C bonds, generating two new ones; it promotes unique skeletal rearrangements and is significant for several reasons: first, the process is catalytic and typically 1–5 mol% of the catalyst is required to get an efficient conversion; the high yield and mild reaction conditions make it user friendly; a range of functional group tolerance and in some cases minimal substrate protection is necessary; fourthly, the reversible nature of the reaction, relative atom economy, and gaseous ethylene is usually the only by-product, which can be removed by evaporation; the olefin substrates are easy to prepare, and others need more effort to get access to. Although preparations of terminal and some disubstituted alkenes are relatively easier than tri- or tetra-substituted olefins, owing to higher level of steric hindrance and controlling *E* and *Z* selectivity. Thus, olefin metathesis allows facile access from easily available olefins to those that are cumbersome to access. Lastly, the olefins are useful because of their stability and as well as reactivity. Olefins are typically stored for a long time without decomposition. And yet, olefins contain a π-bond that is sufficiently reactive for further structural elaboration (e.g. hydrogenation, epoxidation, halogenations, cycloaddition, oxidation etc). Most commonly used catalysts for metathesis reactions are Ru based catalysts, e.g. Grubbs 1st generation catalyst (G-1), Grubbs second generation catalyst (G-2) and Hoveda-Grubbs second generation catalyst HG-2 (Figure 1).

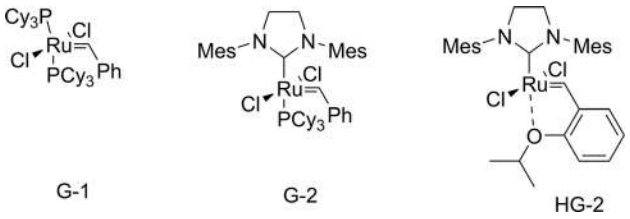


Figure 1. Commonly used catalysts in metathesis reactions.

Although olefin metathesis can be classified in three main variations (a) ring closing metathesis (RCM), (b) enyne metathesis (EM), and (c) cross-metathesis (CM), but (d) ring-opening metathesis polymerization (ROMP), (e) ring opening cross metathesis (ROM/CM), and (f) ring-opening metathesis/ring-closing metathesis (ROM/RCM) also gained popularity in synthesis of complex molecules and polymers (Scheme 2).[2]

The well accepted mechanism for olefin metathesis proposed by Chauvin[3] involves [2+2] cycloadditions and retro-additions sequentially, and the key intermediate is a metallacyclobutane species. Each step of the catalytic cycle is in principle reversible (Scheme 3), normally resulting in an equilibrium mixture of olefins. The rate of the reaction and product selectivity are determined by the interaction of the catalyst and

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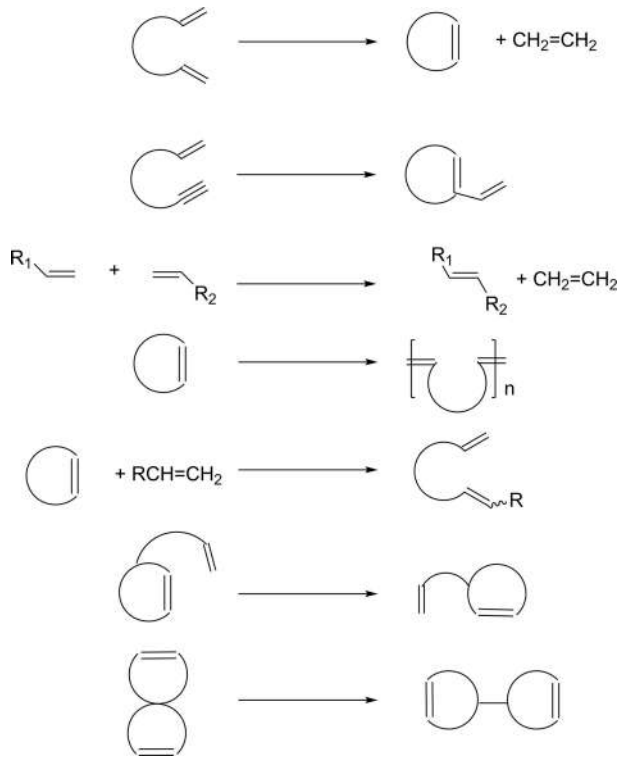
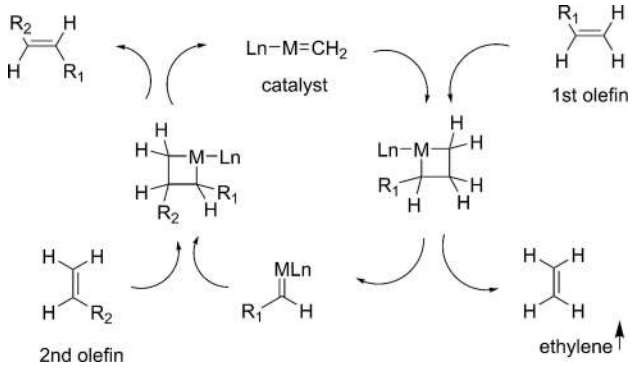


Scheme 2. General representation of various metathesis processes.



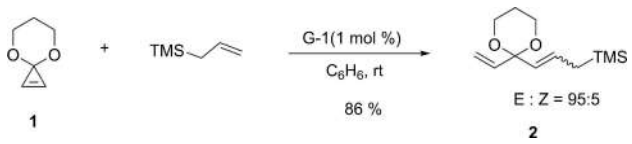
Scheme 3. Mechanism of olefin metathesis.

substrate properties: the structure-activity relationships are very complex and remain poorly understood.

In 2008, Grela reported a highlight article about the joy and challenges of the metathesis of strained cyclopropene and cyclobutene.[4] In recent years, there have been significant pieces of work in the literature, which required a thorough review on this topic.

ROM with Cyclopropene

The ring opening metathesis process is thermodynamically controlled and driven by the release of strain associated with cyclic olefins. Strain energies have been exploited to promote ring-opening metathesis reactions. The first example of selective ring-opening cross-metathesis of cyclopropenone ketals for the one-step synthesis of protected 1,4-divinyl ketones was reported by Michaut, Parrain, and Santelli (Scheme 4).[5]



Scheme 4. ROM/CM of cyclopropenone ketal with allyl silane.

In a total synthesis of cytotoxic agent bistramide A (**9**), Kozmin and co-workers developed a nice and efficient route using ring-opening cross metathesis (ROM/CM) of cyclopropene **4** with acyclic olefin **3** to yield **5**. In a following cross transformation, alkene **5** react with another acyclic olefin (**6**) to get **7** and gaseous ethylene as by-product. Compound **24** was used for the synthesis of bistramide A (**9**) (Scheme 5).[6]

Kozmin and co-workers also used similar cascades of metathesis reaction involving opening of the strained cyclopropene using ruthenium catalyst G-2 for the synthesis of spiroketal-containing natural products spirofugin A(**10**)[7] and routiennocin (**11**)[8] (Scheme 6).

Giudici and Hoveyda reported a novel asymmetric ring-opening/cross-metathesis (AROM/CM) reaction of cyclopropenes **12a–c** and allyl ester **13** using chiral ruthenium catalyst.[9] They revealed that a nonreacting ester containing alkenes or alkynes takes part in this reaction (ee up to 98%). In that article, Hoveda et al. also reported another asymmetric ring-opening cross metathesis(AROM/CM) reaction of cyclopropenes with styrene catalyzed by chiral ruthenium catalyst **15** and yielded desired diene in high yield (90%) and good enantioselectivity (93% ee) (Scheme 7).

In another report by Hoveyda et al., it has been found that Ru-catalysed cross-metathesis of cyclopropenes with allyl alcohol derivatives proceeds stereoselectively. In this case, H-bonding interactions have dominated extensively in the design of catalyst for stereoselective synthesis. Using allyl alcohols as the cross-partner, instead of allyl esters, a significant improvement in both conversion and diastereoselectivity was found. Here the H-bonding interactions can considerably control Ru-catalyzed olefin metathesis reactions. The reaction rate was very

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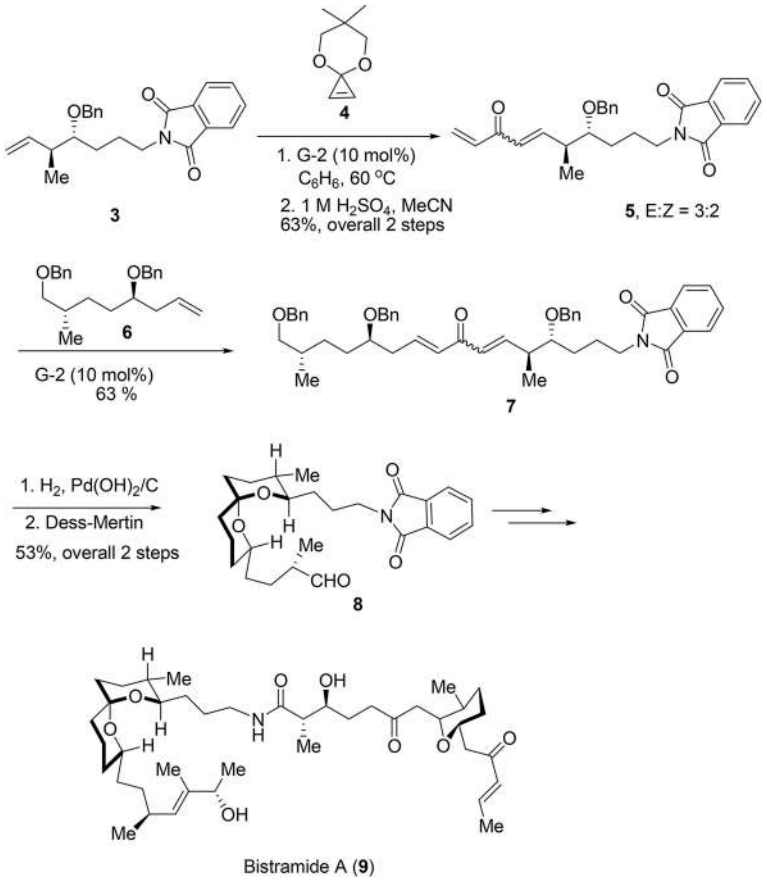
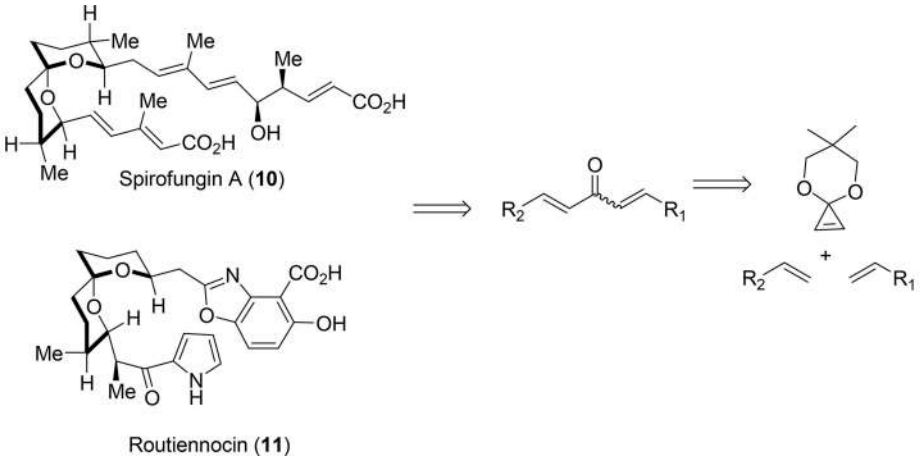


Scheme 5. ROM/CM reaction of cyclopropenone ketal in the total synthesis of bistramide A (**9**).

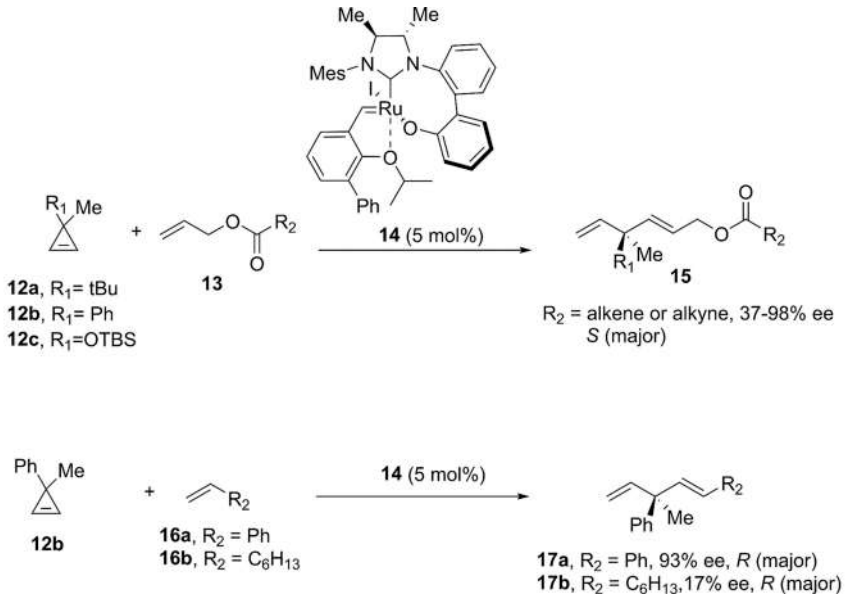


Scheme 6. ROM/CM reaction of cyclopropenone ketal in the total synthesis of spirofungin A (**10**) and routiennocin (**11**).

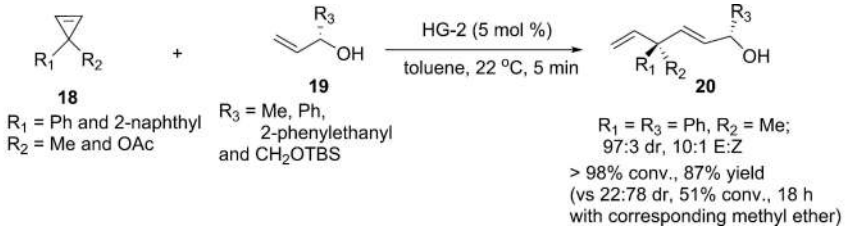
high (>98% conversion, up to 87% yield), (often within minutes) in the presence of ≤2 mol% of an achiral ruthenium catalyst to get various hexa-2,5-dien-1-ols with high stereochemical purity (up to >98:2 dr and 1:1 E:Z)[10] (Scheme 8).

Hoveyda et al. have demonstrated a synthetically useful transformation in the first step of their quebrachamine synthesis, which gives a sufficient amount of starting material for a multi-step total synthesis. Cyclopropene **23** has been prepared from the diazo compound **21**, which is in turn available from a 1,3-dicarbonyl compound, via a Rh-catalyzed [2+1] cycloaddition to TMS acetylene. The removal of the TMS group in **22** through a base-catalyzed pathway furnished the cyclopropene **23**, which reacts with ethylene at 1 bar in the presence of HG-2 catalyst (Scheme 9).[11]

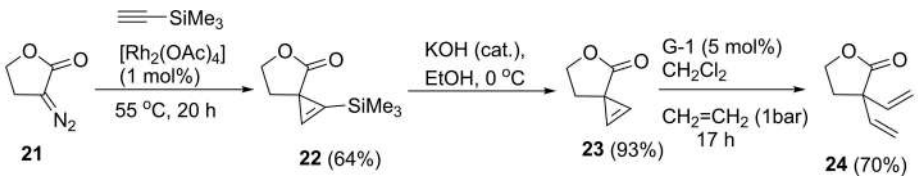
One of the important processes for strained systems like cyclopropenes and cyclobutenes is the ring opening meta-



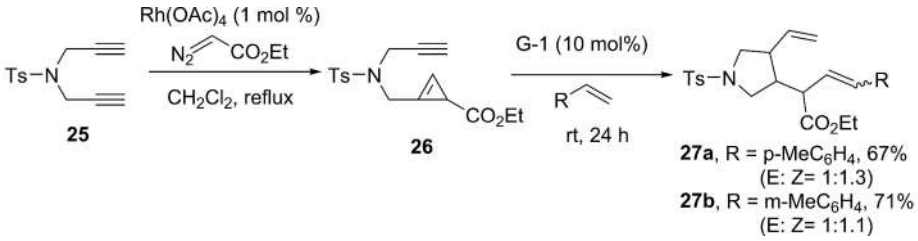
Scheme 7. ROM/CM reaction of strained cyclopropenes.



Scheme 8. ROM/CM reaction of cyclopropenes with allyl alcohols.



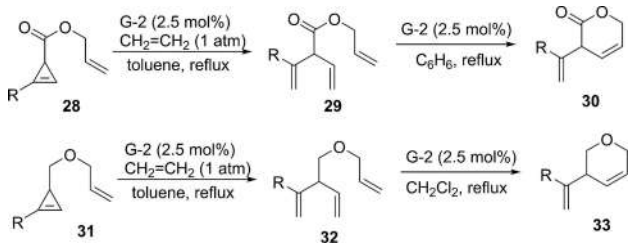
Scheme 9. Synthesis of quebrachamine precursor **24** via ROM/CM.



Scheme 10. ROM-RCM of cyclopropene systems for the synthesis of pyrrolines.

thesis-ring closing metathesis (ROM-RCM). Employing the G-1 catalyst, Zhu and Shi have reported a ring-closing enyne metathesis (RCEM) of small-rings such as cyclopropenes. They have reported a new tandem ROM-RCM-CM sequence starting with 1,6-cyclopropenes **26** with a wide variety of substituted olefins. The cyclopropane **26** was prepared with the aid of a carbene insertion reaction using Rh-catalyst. The ROM-RCM reaction of that cyclopropene using G-1 catalyst provided 3-pyrroline derivatives in good yields.[12] (Scheme 10).

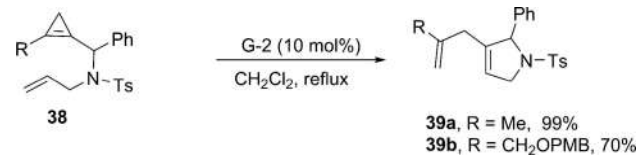
A wide range of oxygen-heterocycles have been assembled by ring rearrangement metathesis. When the allyl ester of cyclopropene carboxylic acid **28** is treated with G-2 in presence of ethylene gas it provides lactone **30**. Similarly, cyclopropene derivatives such as **31** provide pyran derivatives **33** by treatment with G-2 in the presence of ethylene (Scheme 11).[13]



Scheme 11. ROM-RCM of cyclopropene systems for the synthesis of six member lactone and ether.

Reaction of allyl ethers **34** with catalyst G-2 deliver the corresponding dihydrofurans **35** in excellent yield (Scheme 12). Using acrylates **36** as starting materials, lactones **37** are the products in moderate yields (Scheme 13). The yields of lactones increase by changing the catalyst from G-2 to Grela's catalyst **14**.

ROM-RCM of allyl sulphonamides **38** using G-2 under dichloromethane reflux conditions produced pyrrolines **39** in excellent yields (Scheme 14). ROM-RCM of cyclopropenyl carbonyl ether **40** with G-2 provided five-membered heterocycles **41** along with a seven membered heterocycle **42** in a 40:60 ratio (97%) (Scheme 15). Allyldimethylsilyl ethers **43a** and **43b** underwent efficient ROM-RCM, and the corresponding sensitive cyclic siloxanes were immediately treated with MeLi to give the allylic silanes **44a** and **44b** in 73% and 62% yields, respectively (Scheme 16).



Scheme 14. ROM-RCM of cyclopropene systems for the synthesis of dihydropyrroles.

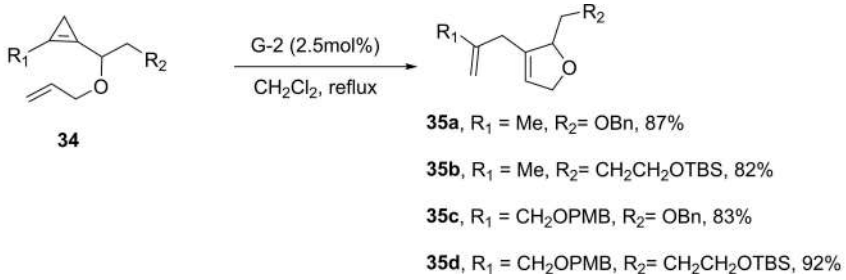
ROM with Cyclobutene

Like cyclopropene, cyclobutene is also strained and carry out ROM-RCM very easily. Maougal and co-workers reported an elegant route to the synthesis of bipiperidine derivative **46** from compound **45** using G-2 (Scheme 17).[14]

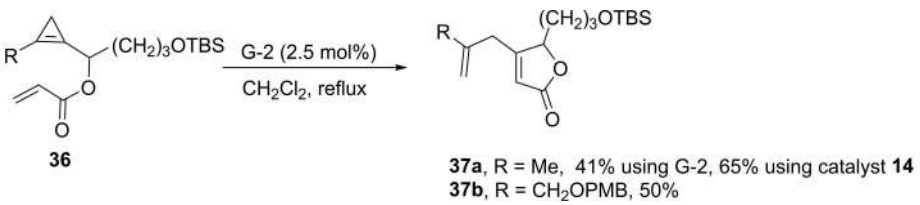
Grubbs et al. reported a route to synthesize of bidihydropyran derivative **48** from compound **47** using G-2 (Scheme 18).[15]

Four- and five-membered ring fused cyclobutene derivatives **49** and **51** are opened by an alkene moiety in a tether by ROM to produce cyclopentane derivatives **50** and **52** having furan and pyran rings (Scheme 19).[16] The ring size of the heterocycle formed in this reaction corresponds to the length of the side chain on cyclobutene.

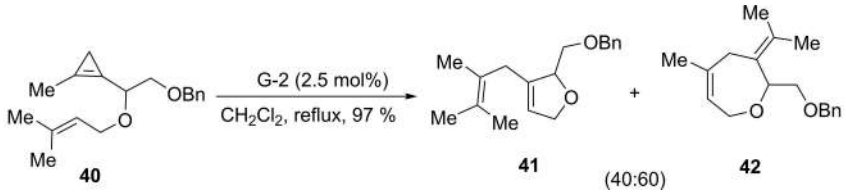
Snapper and co-workers reported the regio- and stereoselective ring opening cross-metathesis (ROCM) of cyclobutene derivatives with unhindered, relatively electron-rich terminal alkenes as cross partners using G-1 catalyst. They noted that substituents near the strained ring strongly influence the outcome of the reaction. The cycloadducts with a hydroxyl group (**53**) projecting from the *exo*-face of the cyclobutene provide reasonable levels of regioselectivity. Moreover, the newly formed olefins in the major regioisomers are exclusively *E*-olefins (>20:1) (Scheme 20)..[17] Thus, the substrate structure plays crucial role in the reactivity profile of ruthenium alkylidene catalyzed olefin metatheses.



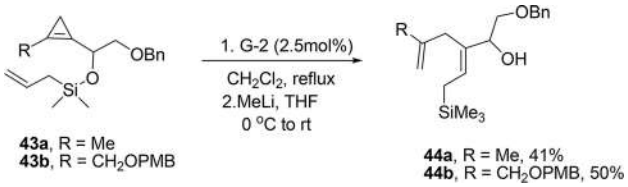
Scheme 12. ROM-RCM of cyclopropene systems for the synthesis of dihydrofurans.



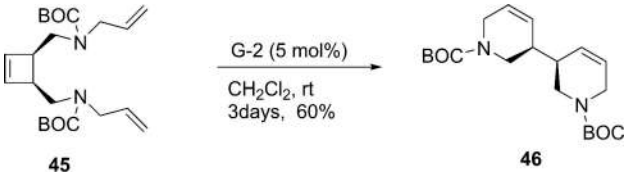
Scheme 13. ROM-RCM of cyclopropene systems for the synthesis of butyro-lactone.



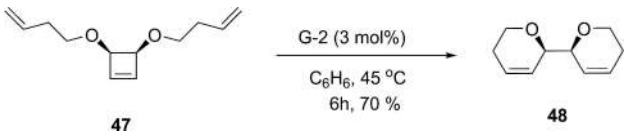
Scheme 15. ROM-RCM of substituted cyclopropene system with catalyst G-2.



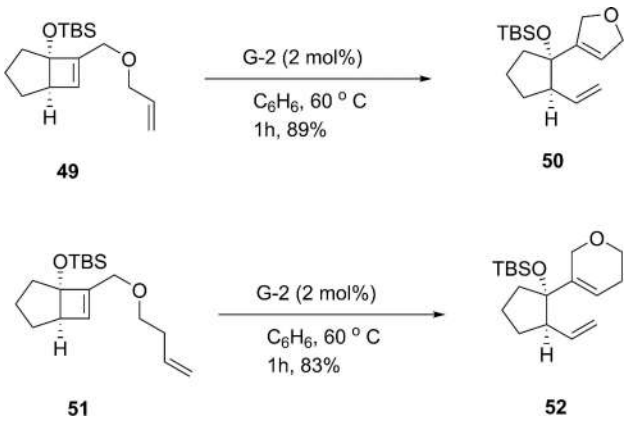
Scheme 16. ROM-RCM of cyclopropene systems for the synthesis of allyl silanes.



Scheme 17. ROM-RCM of cyclobutene system for the synthesis of 3,3′-bis (1,2,3,6-tetrahydropyridine).



Scheme 18. Synthesis of bidihydropyran derivatives using ROM-RCM



Scheme 19. Synthesis of dihydrofuran and dihydropyran derivatives using ROM-RCM

A novel method for the synthesis of various medium size bicyclic systems using ROM-RCM strategy of cyclobutene derivatives was reported by Snapper and Limanto.[18] In this strategy, G-2 catalyzed ROM-RCM of various cyclobutene systems containing an alkene tether give bicyclic systems. This approach is also used for the synthesis of natural product (+)-asteriscanolide (**59**) (Scheme 21). Harrity et al. used a similar type of reaction for the synthesis of (±) sporochnol A (**62**) (Scheme 22).[19]

Snapper et al. also described an ROM/CM protocol for the synthesis of series of isoprostane analogue via the reaction of substituted cyclobutene **63** with gaseous ethylene using G-1 catalyst (Scheme 23).[20]

Simpkins and co-workers have applied the ROM-RCM strategy to synthesize of the tetracyclic spiroamine framework of a highly biologically active erythrina alkaloid (Scheme 24).[21] It is known that erythrina alkaloids exhibit sedative hypertensive and neuromuscular activity. In that synthesis, a cyclobutene derivative is used as synthon for ROM-RCM reaction.

Pandya and Snapper reported that, cyclobutane derivative **70** using catalyst G-1 provided lactone **71** as a mixture of isomers (3:1) in 37% isolated yield (Scheme 25).[22] This strategy is found to be useful for the synthesis of lipid oxidation metabolites 5-F2-isoprostanes **72**.

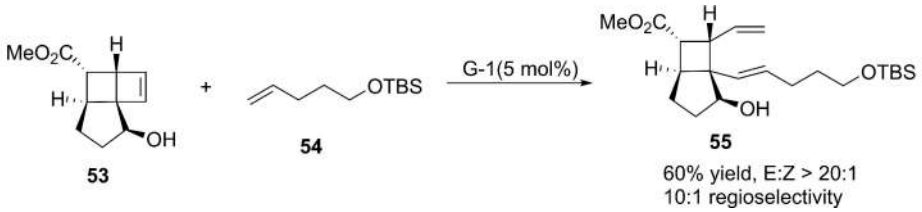
Using the ROM-RCM and CM protocol Pattenden et al. have reported an elegant synthesis of (+) *Z*-deoxypukalide. In this strategy, the cyclobutene ester **75** subjected to a ROM-RCM and CM protocol in presence of another olefin compound 2-methylpropinol using G-2 catalyst gave butenolide derivative **76** in 57% isolated yield (Scheme 26).[23]

Li and co-workers described an asymmetric synthesis of humulanolides using ROM-RCM protocol. In this synthesis, the cyclobutene derivative **78** subjected to catalyst **14** to afford the ROM-RCM cascades product Asteriscunolide D(**79**) (36% yield) admixed with the dimer **80** as minor product (7%) (Scheme 27).[24] Asteriscunolide was found to be a required synthon for the synthesis of asteriscunolides A–C.

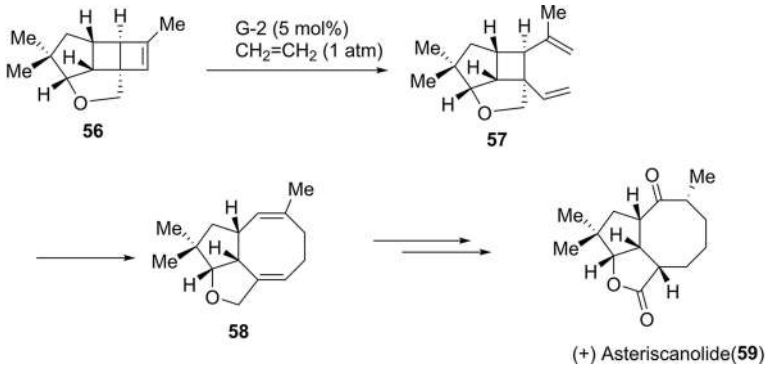
Hoveyda and co-workers reported asymmetric ring opening/ ring closing metathesis (AROM/RCM) of a cyclobutene derivative containing two olefin pendent when subjected to a chiral Mo-catalyst **83** to provide optically enriched dihydrofuran **82** (Scheme 28).[25]

A similar ROM/CM reaction of cyclobutene-1,2-diol derivative **84** with G-2 catalyst provides tetracyclic oxygen heterocycles **85**, with complete transfer of chirality (Scheme 29).[26]

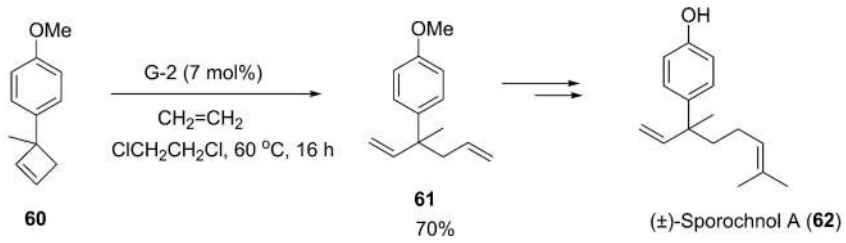
One elegant use of ROM/RCM protocol for the alkyne-substituted cyclobutenes is described by Mori and co-workers. In this enyene ROM/RCM cascade protocol, several isoquinoline derivatives were prepared from cyclobutene derivatives under ethylene atmosphere using G-2 catalyst (Scheme 30).[27]



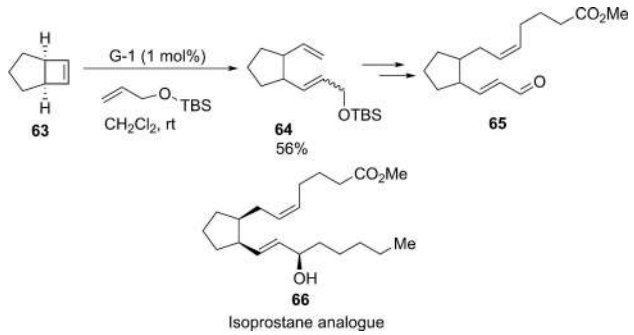
Scheme 20. ROM/CM of a cyclobutene with electron-rich terminal alkene.



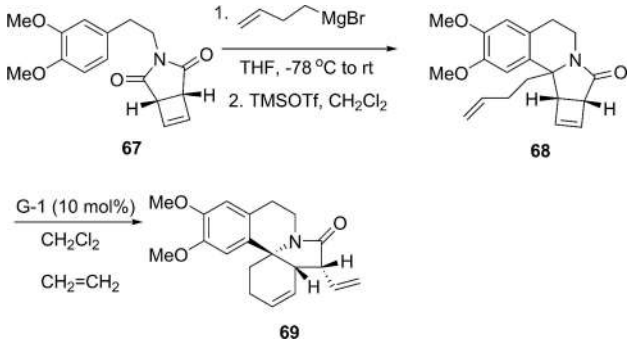
Scheme 21. ROM/CM of a cyclobutene in the total synthesis of (+)-asteriscanolide (**59**).



Scheme 22. ROM/CM protocol for the synthesis of sporochnol A (**62**) from precursor **61**.



Scheme 23. ROM/CM protocol for the synthesis of isoprostane analogue **66**.

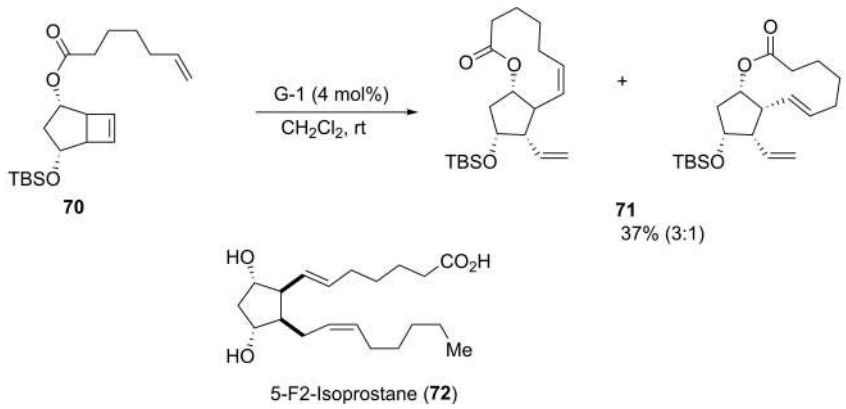


Scheme 24. ROM-RCM approach to erythrina alkaloid framework.

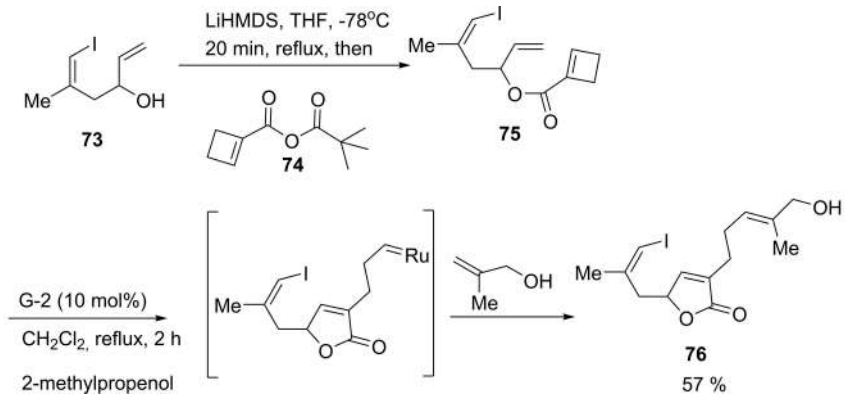
Not only for the synthesis of small ring compounds from cyclobutene derivatives, several examples of ROM-RCM reaction of cyclobutene derivatives proved to be useful strategy for the construction of 12- to 16- membered macrolides (Scheme 31).[28] Cyclobutene esters containing added olefin pendent group provides the macrolide-butenolids in good yield upon treatment of the substrate with catalyst G-2. The orientation of double bond was found as E-selective at the macrocyclic double bond.

Small Ring Synthesis by Ring Closing Metathesis

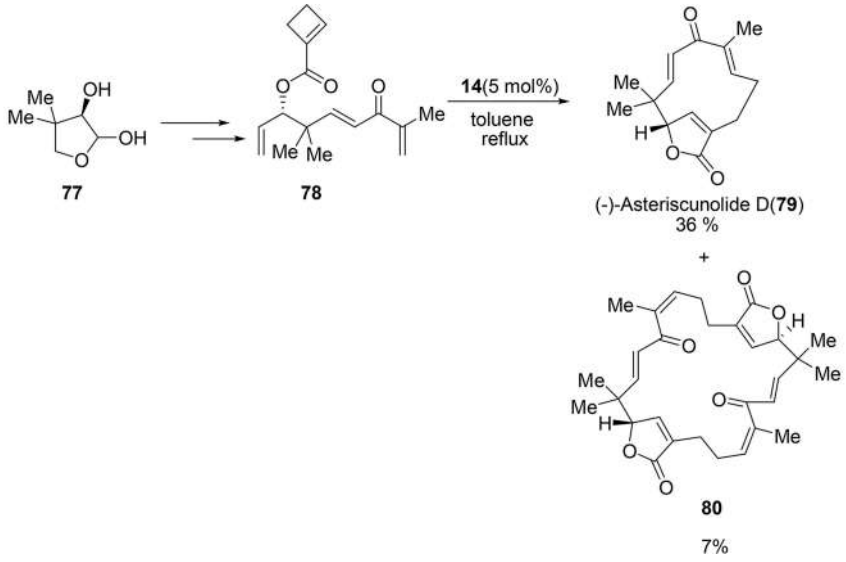
We have already discussed in the above section that ring opening metathesis of strained three- and four-membered ring



Scheme 25. ROM–RCM sequence to lactone derivatives.

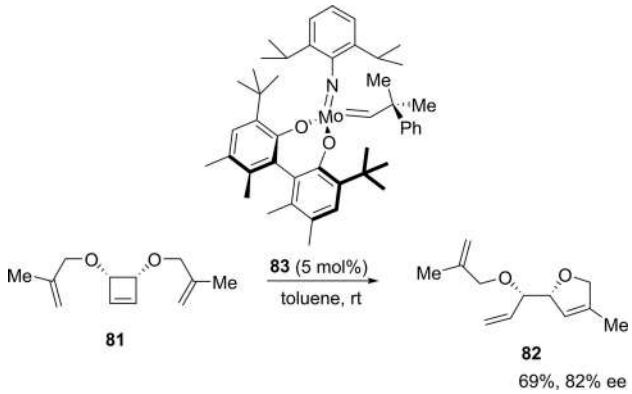


Scheme 26. ROM-RCM protocol towards the synthesis of lactone derivative **76**.

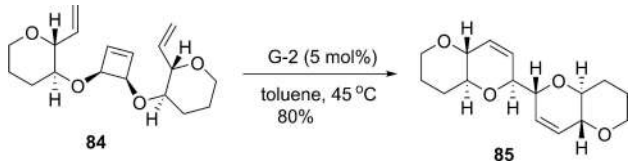


Scheme 27. ROM-RCM procedure towards the asymmetric synthesis of asteriscunolide D (**79**).

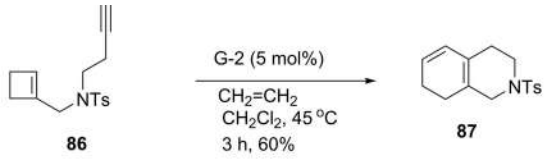
is a very useful transformation, nicely proved its superiority in large number of stereocontrolled total synthesis of biologically active natural products and for the synthesis of various polymeric materials. Simultaneously, there are no reports on the metathetical formation of three- membered carbocycles or heterocycles. Only two reports are available on the formation of four-membered carbocycles. Although, it is generally considered that smaller ring (less than 5 membered) cyclic products cannot be formed via ring closing metathesis reaction.

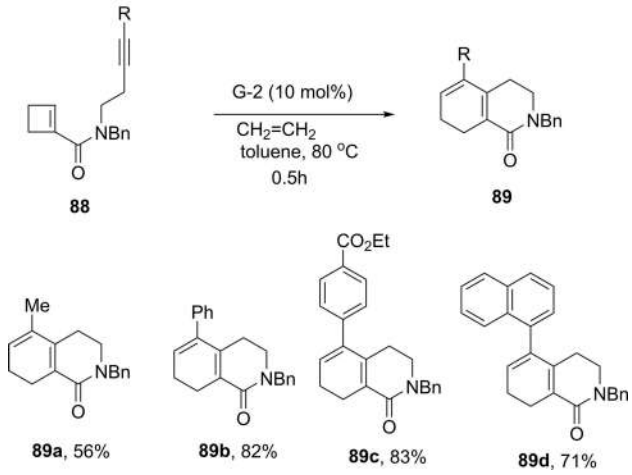


Scheme 28. An asymmetric ROM/RCM of *meso* cyclobutene **81.**



Scheme 29. ROM/RCM of cyclobutene **84**.



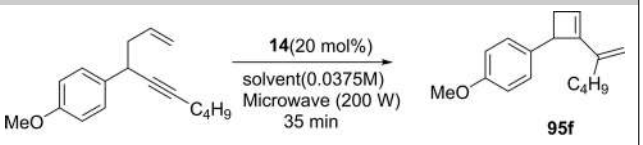


Scheme 30. ROM/RCM of cyclobutene-yne **86** and **88**.

In the year of 2008, Debleds and Campagne reported that vinyl-cyclobutenes may be prepared via enyne RCM . They found that both G-2 and HG-2 catalysts shows catalytic activity to promote enyene metathesis on 1,5-enyne substrates to obtain vinyl cyclobutenes (Scheme 32).[29] From the optimisation study, it was found that G-1 catalyst and carbophilic Lewis acid $PtCl_2$ proved to be ineffective for this transformation, as desired product was not obtained even in trace.[30] Whereas, G-2 and HG-2 led to the desired cyclobutene product in moderate yield. Interestingly, they found that yield was increased by the use of microwave irradiation.[31] Also by decreasing the catalyst loading from 20% to 10%, the yield was also found to decrease as in case of product **95a** yield was decreased from 58% to 20%. Several 1,5-enyne substrates provided the cyclobutene products **95a**–**95l** in yields up to 58%, as shown in Figure 2. It was established that while the cyclobutene ring contains various substituents (R_1, R_2), only alkyl substituents are well-tolerated on the alkynyl part (R_3). A bis-cyclobutene **95l** was obtained in 19% yield through double cyclisation of a bis-enyne substrate (Figure 2).

A recent report by Grela et al. on the enyne RCM found that yield of the cyclobutene product increased simply by changing the solvent dichloromethane (53%) to hexafluorobenzene (73%) (Table 1).[32]

Table 1. Effect of solvents and temperature in 1,5-enyne RCM.

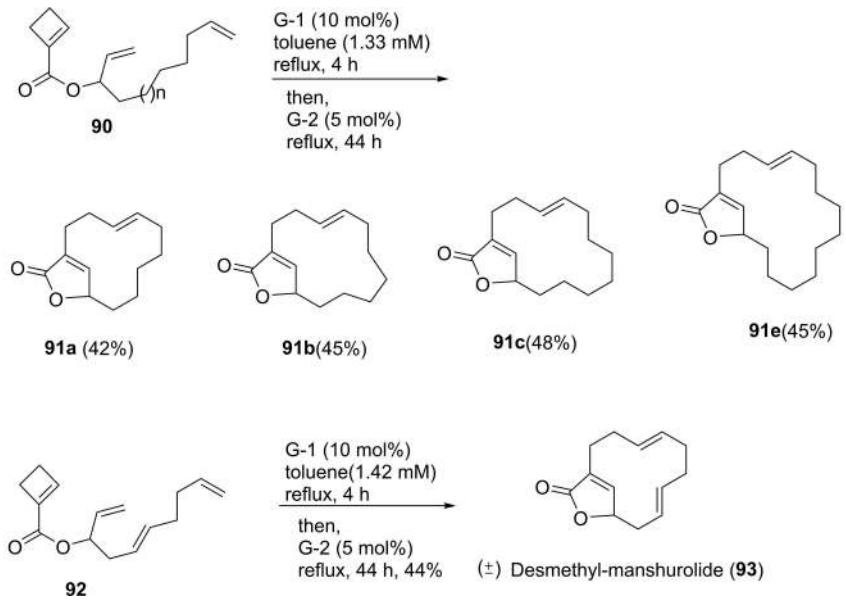


Entry	Solvent	Temperature	Yield
1	CH_2Cl_2	70 °C	53%
2	C_6F_6	100 °C	76%

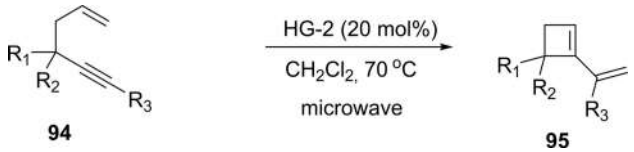
Outlook and Perspectives

The development of highly active and functional group tolerant ruthenium-based metathesis catalysts has led to a rapidly growing use of this transformation in many fields of chemical synthesis. The fact that these catalysts may be handled without rigorous air and moisture exclusion, sometimes even in the open air, made them extremely popular and allowed for the synthesis of new pharmaceutical compounds, polymeric materials, and fine chemicals. Apart from its commendable usefulness and applicability, metathesis is still facing some limitations and these areas still need further research. Some of the unresolved difficulties are: the troublesome formation of selected functionalized or crowded C–C double bonds; the instability of metathesis catalysts and irreversible deactivation; sometimes low activity of existing catalysts; the need of high catalyst loading; problems with catalyst removal after the reaction and finally, often the need of a large excess of alkene reactant.

It is not the right choice to heat the reactions unless we need to. Like many chemical reactions, temperature may be both friend and foe. The lower the temperature, the longer the catalyst will survive. Particularly troublesome metathesis catalyst decomposition products are ruthenium hydrides, which may be excellent olefin isomerization catalysts. Sometimes we need to heat the reaction to overcome an entropic barrier. This



Scheme 31. ROM-RCM strategy towards the synthesis of various macrolide rings.



Scheme 32. 1,5-Enyne RCM.

is often in the case for large ring formation and to compensate for dilution. It is the right choice to run RCM reactions in dilute conditions to avoid intermolecular reactions, since dilution will slow the reaction rate. If the reaction does not proceed at room temperature, then heating is necessary.

Addition of Lewis acids facilitated access to highly active and selective in situ metathesis catalysts. Addition of Lewis acids such as $Fe(acac)_3$ (acac = acetyl acetone) or $AlCl_3$ successfully inhibited the formation of undesired side product.[33] The beneficial effect of microwave irradiation instead of classical thermal conditions in olefin metathesis reactions is well documented in literature.[34] Modified reaction conditions and new techniques are coming up to obtain better results in metathesis reactions.

Aliphatic as well as aromatic fluorinated solvents show a great use in olefin metathesis reactions. Ruthenium (pre) catalysts bearing fluorinated tag in benzylidene, NHC, as well as in anionic ligands part have been successfully obtained. Utilization of fluorous phases allow for easy separation of the metathesis product. On the other hand, olefin metathesis reactions performed in fluorinated aromatic hydrocarbons give higher yields of the desired product as compared with reactions conducted in "classical" solvents.

The recent years have witnessed tremendous improvements in olefin metathesis in ionic liquids. The early reports involving

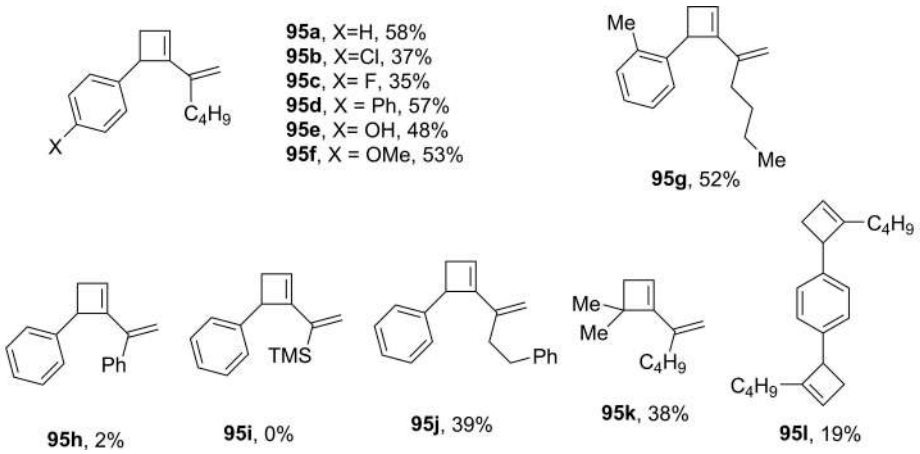


Figure 2. Products of 1,5-enyne RCM

existing neutral and cationic ruthenium complexes provided limited benefits with poor recyclability and high catalyst leaching. Subsequent evolutions incorporating ionic-tag motifs afforded efficient and highly recyclable catalysts, while minimizing the contamination of the product by metal residues. It is hoped that possible future developments may involve more robust ruthenium catalysts containing ionic tags covalently attached to the strongly coordinated NHC-ligand.

The data reported in the literature demonstrate that great care must be taken when choosing an appropriate catalyst for a given metathesis reaction. New metathesis methodologies are being developed, including sustainable production of valuable chemicals from renewable sources. These advancements create even new challenges, such as conducting metathesis under air with ppm amounts of the catalysts, gaining truly full control on *E/Z* geometry of the newly formed C–C double bond or preparing an iron-based catalyst are also highly important in olefin metathesis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Alkenes · cyclopropenes · cyclobutenes · metathesis · strained molecules

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