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Ring-Closing Metathesis: Novel Routes to Aromatic Heterocycles

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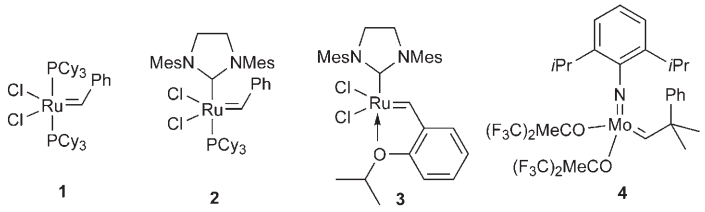
Abstract: Olefin metathesis has been established as an important and general reaction in synthetic organic chemistry. Recently, it has attracted interest as a powerful tool for the construction of aromatic heterocycles. The importance of heteroaromatic motifs in medicinal chemistry and biology, as well as the efficiency and wealth of metathesis transformations, have resulted in significant success in this rapidly developing area.

Keywords: furans · heterocycles · indoles · metathesis · pyridine · pyrroles

Introduction

Alkene metathesis, in all its various guises, has had a profound impact on the formation of carbon–carbon double bonds and upon the area of total synthesis in recent years.[1–6] The wealth of synthetic transformations that can be accomplished is astonishing and there are countless applications of metathesis to form complex molecules. The intramolecular variant of this reaction (ring-closing metathesis, RCM) has received a significant amount of attention as it provides efficient access to numerous carbo- and heterocycles.[7–11] The popularity of this powerful transformation can be largely attributed to the rational design of air-stable and well-defined catalysts which are tolerant of a range of functional groups. In particular, the commercially available ruthenium carbene catalysts **1**,[12,13] **2**,[14] and **3**,[15] as well as the molybdenum alkylidene complex **4** developed by the Schrock group,[16] have achieved widespread use to promote a range of cyclisations (Figure 1).



1 2 3 4

Figure 1. Commercially available ruthenium- and molybdenum-based catalysts.

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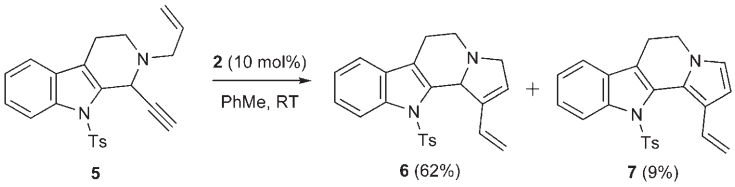
An interesting application which has recently captured the attention of organic chemists is the use of RCM to form aromatic carbocycles[17–28] and heterocycles. The development of flexible routes to aromatic motifs continues to be of significant interest to synthetic chemists given the importance of these structures in biology and in the pharmaceutical industry. As a result of this interest, this area has advanced rapidly over the past few years; there are several established methods to construct furans and pyrroles, as well as benzofurans and indoles. More recently, syntheses of six-membered heteroaromatic structures have been reported using this strategy. A selection of these approaches is highlighted herein.

Construction of Furans and Pyrroles

An early strategy employed to gain access to aromatic compounds using the RCM transformation was to perform an allylic oxidation on the newly formed cyclic olefin. This oxidation has been observed by a number of research groups; recently, Pérez-Castells and co-workers reported that the ring-closing enyne metathesis of compound **5** resulted in the formation of the pyrrole **7** in addition to the desired diene **6** (Scheme 1).[29]

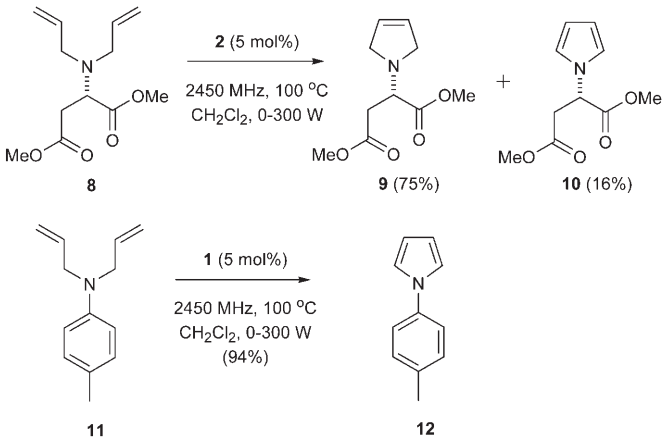


5 6 (62%) 7 (9%)

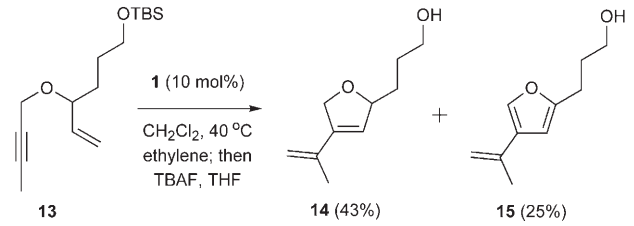
Scheme 1. Ring-closing enyne metathesis for the formation of pyrroles.

Similarly, Xiao and co-workers reported the isolation of significant amounts of the corresponding aromatic pyrroles whilst attempting to synthesise a series of 3-pyrrolines under microwave conditions (Scheme 2).[30] The group explored this microwave assisted strategy further and discovered that the extent of aromatisation could be controlled by varying the substituent on nitrogen. In the case of chiral diallylamines such as **8**, the 3-pyrroline **9** was obtained as the major product; however, when substituted aromatic amines were subjected to the same conditions the aromatic pyrrole was isolated as the sole product in excellent yield.

Nay and co-workers reported a similar unexpected dehydrogenation arising from the ring-closing enyne metathesis of 4-oxo-1,6-enynes (Scheme 3).[31] The enyne metathesis and deprotection provided a mixture of the desired dihydrofuran **14**, as well as a significant amount of the aromatised furan **15**. The group examined the origin of the oxidation and established that neither spontaneous oxidation of dihydrofuran **14** in refluxing dichloromethane (air atmosphere)



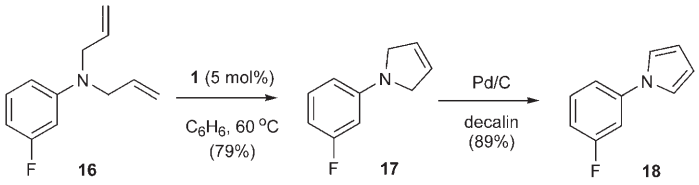
Scheme 2. Formation of pyrroles under microwave conditions.



Scheme 3. Unexpected dehydrogenation to form furans.

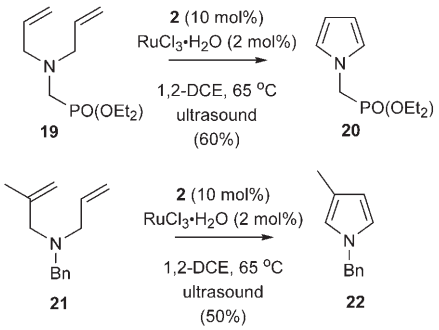
or dehydrogenation in the presence of fresh catalyst **1** were possible. It was therefore proposed that the dehydrogenation was catalysed by a product of decomposition of the catalyst resulting from excessive heating.

Pujol and co-workers adopted a sequential RCM and oxidation procedure to assemble the core of *N*-arylpyrrole **18** (Scheme 4).[32] The RCM with Grubbs first generation catalyst **1** provided the dihydropyrrole **17**, and the dehydrogenation was accomplished with palladium on carbon to provide the pyrrole **18** in excellent yield.



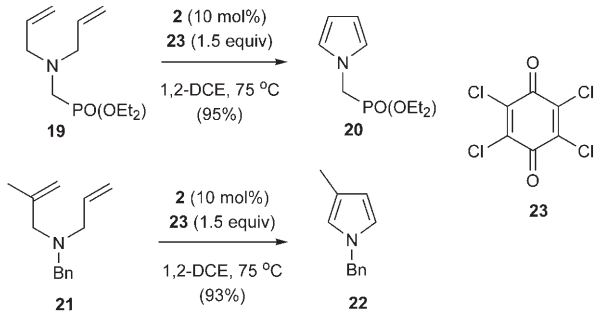
Scheme 4. RCM/oxidation strategy for the synthesis of pyrrole **18**.

The potential of this coupled RCM and oxidation strategy drew the attention of the Stevens group, and in 2004 they developed a more general method for preparing pyrroles using a tandem Grubbs carbene/$RuCl_3$ catalytic system.[33] This combination of ring closure and dehydrogenation promoted by $RuCl_3$ provided the corresponding pyrroles in moderate yields (Scheme 5). It was found that the basicity of the *N*-atom also played a crucial role in the dehydrogenation mediated by $RuCl_3$; unfortunately, when amines with electron-withdrawing protecting groups (e.g., Tosyl, Boc, Ac) were subjected to these conditions the oxidation was suppressed and only the corresponding pyrrolines were recovered.



Scheme 5. Tandem Grubbs carbene/$RuCl_3$ catalytic system for the formation of pyrroles.

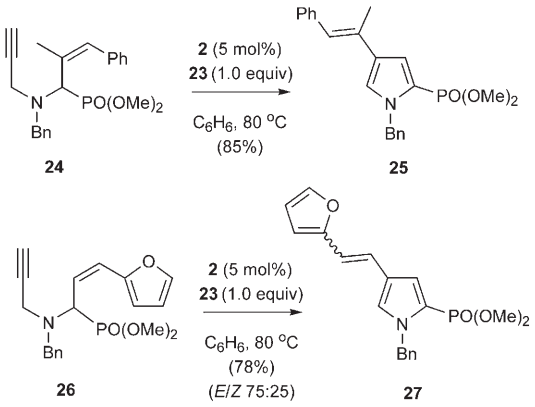
A marked improvement to this procedure was realised by employing the potent hydrogen acceptor tetrachloro-1,4-benzoquinone (**23**) as the oxidant in place of $RuCl_3$.[34] Now the desired aromatic heterocycles could be obtained efficiently and in excellent yield (Scheme 6).



Scheme 6. Stevens tetrachloro-1,4-benzoquinone (**23**) oxidising system for the formation of pyrroles.

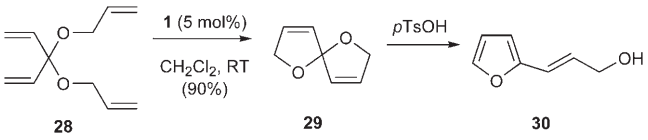
In 2007, the Stevens group expanded this strategy further to allow access to 2-phosphono pyrroles using a tandem ring-closing enyne metathesis/oxidation approach (Scheme 7).[35] The sequence consisted of ring-closing enyne metathesis of a substituted aminophosphonate using pre-catalyst **2**, in combination with in situ oxidation using tetrachloro-1,4-benzoquinone (**23**). Pyrrole **25** was formed in excellent yield and exclusively as the *E* isomer; however, all the other pyrroles examined were formed as a mixture of *E*/*Z* isomers.

Whilst the oxidation strategy has provided some promising results for the formation of certain aromatic compounds, there is no general approach to the formation of these systems which has the flexibility to readily install a range of substituent patterns and functional groups. Thus, alternative aromatisation tactics have been explored to accomplish efficient and adaptable routes to aromatic heterocycles.



Scheme 7. Ring-closing enyne metathesis/oxidation strategy for the formation of 2-phosphono pyrroles.

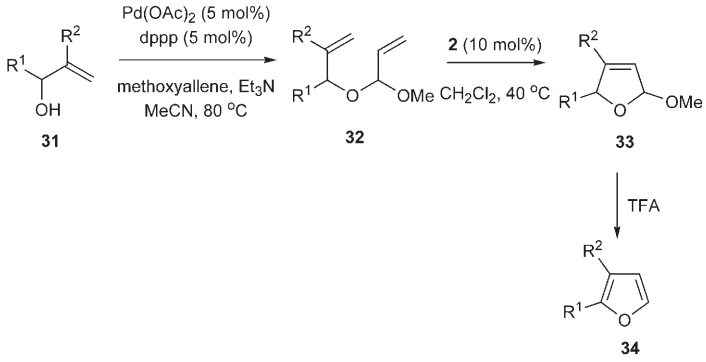
Another strategy to access aromatic compounds following RCM is to equip the acyclic precursor with a leaving group so that a subsequent elimination will reveal the aromatic core. In 1999, Harrity and co-workers were investigating the efficacy of using RCM to form spirocycles by the execution of two tandem metatheses on the alkene **28** (Scheme 8).[36] This elegant approach provided spirocycle **29** in excellent yield under mild conditions, and without competing formation of the seven-membered ring system. In order to illustrate that these systems could not have been forged under acidic conditions, the spirocycle **29** was treated with *p*-TsOH and indeed was found to decompose to the furan **30**. However, this novel strategy for the formation of furans was not investigated any further.



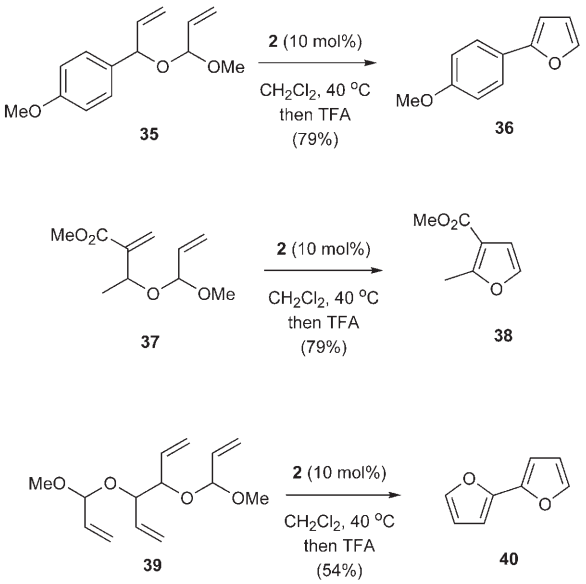
Scheme 8. Decomposition of spirocycle **29** under acidic conditions to provide furan **30**.

This approach captured the attention of the Donohoe group in 2005, who strived to expand the scope of this single reaction to form a general and mild strategy to synthesise substituted aromatic heterocycles. A successful protocol was developed to access a range of substituted furans by synthesising the corresponding unsymmetrical acetals **32** (Scheme 9).[37,38] These acetals were readily produced from the allylic alcohols **31** by coupling with methoxyallene under palladium catalysis conditions.[39–41] The RCM reactions proceeded in excellent yields using catalyst **2** and the dihydrofuran **33** collapsed to reveal the aromatic compound upon treatment with TFA.

This mild and flexible approach was employed to form a series of 2,3-substituted furans containing aryl, alkyl and carbonyl functional groups (Scheme 10). The strategy was also extended to the synthesis of some linked biaryl compounds;



Scheme 9. Synthesis of 2,3-disubstituted furans by elimination of a suitable leaving group.



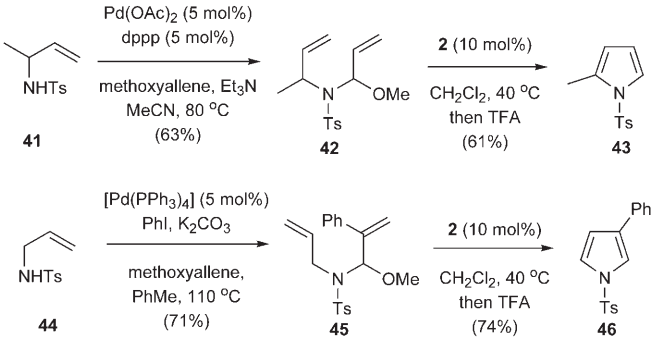
Scheme 10. Donohoe synthesis of substituted furans.

this was achieved in the case of the bisfuran **40** by executing two tandem couplings and metathesis/aromatisation processes.

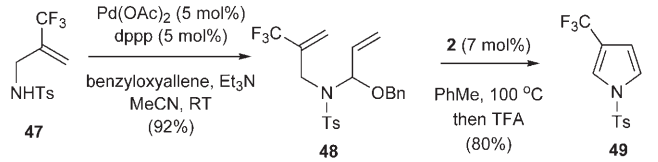
The feasibility of expanding the scope of this method to include the synthesis of protected pyrroles was investigated and resulted in the successful formation of a number of derivatives (Scheme 11). Furthermore, an additional substituent could also be incorporated at the 4-position of the aromatic compound by carrying out the palladium(0) coupling of amine **44** with methoxyallene in the presence of iodobenzene.

In 2007, Rutjes and co-workers demonstrated that this procedure was also applicable to the synthesis of trifluoromethyl-substituted pyrroles (Scheme 12).[42] Such derivatives represent a class of compounds of interest in the pharmaceutical industry and can be difficult to access using other methods.

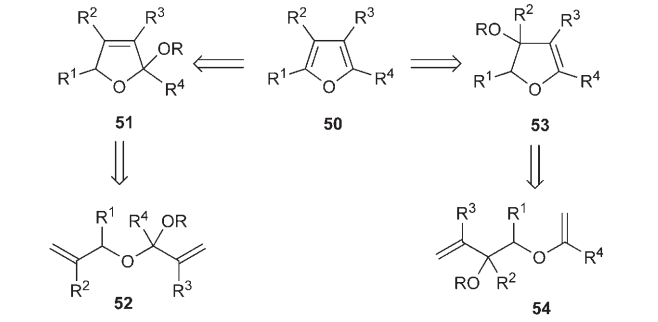
In the same year, the Donohoe group explored an alternative disconnection of the furan core (Scheme 13).[43] This approach utilised RCM to forge the 2,3-carbon bond of the



Scheme 11. Synthesis of substituted pyrroles.



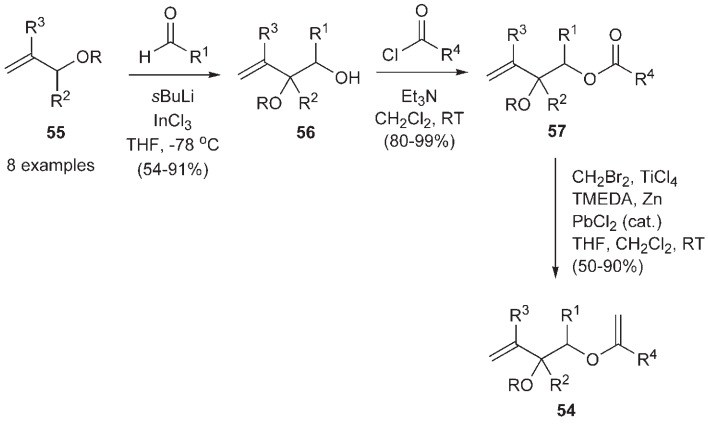
Scheme 12. Rutjes synthesis of a trifluoromethyl-substituted pyrrole.



Scheme 13. Possible disconnections of the furan core.

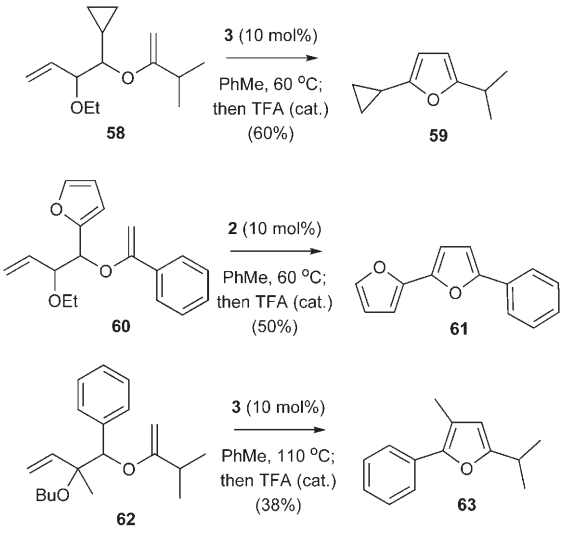
heterocycle and required efficient access to a range of acyclic enol ethers **54**.

Diol mono-ethers **56** were constructed using the indium-mediated addition of allyl ethyl ether **55** to a range of aldehydes (Scheme 14).[44] These alcohols were then transformed into esters using the corresponding acid chloride and a subsequent olefination under Takai–Utimoto conditions provided the desired enol ether **54**.[45,46]



Scheme 14. Formation of enol ethers.

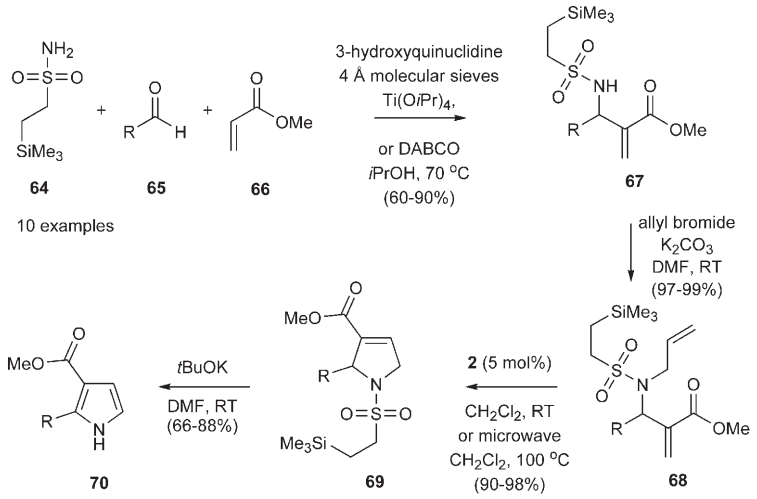
The enol ether–olefin RCM was then executed using catalyst **2** and **3** and the elimination was carried out in situ to provide the functionalised furans in reasonable yields (Scheme 15). Considering the final furan product, it is noteworthy that the R^1 substituent is derived from an aldehyde and R^4 originates from an acid chloride; thus, this powerful strategy allows the installation of groups at the 2- and 5-positions with great flexibility. The procedure was also extended to the synthesis of trisubstituted furan **63**, albeit in lower yield.



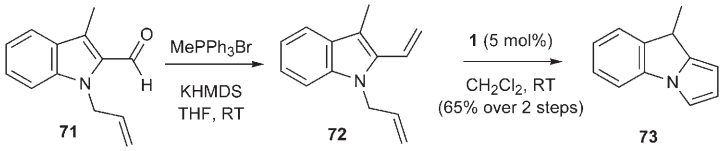
Scheme 15. Donohoe synthesis of substituted furans from enol ethers.

Another interesting strategy to effect the aromatisation is the base induced elimination of sulfonyl leaving groups. Lamaty and co-workers utilised this strategy in 2004 and developed a new route to 2-substituted 3-methoxycarbonyl pyrroles **70** (Scheme 16).[47] The group employed a three component aza version of the Baylis–Hillman reaction to produce β-aminoesters **67**. Treatment of these amines with allyl bromide and a subsequent RCM provided the dihydropyrrole **69** in good yield. It was found that the aromatisation of **69** provided optimum yields with *t*BuOK in DMF and this process delivered a range of substituted pyrroles **70**.

An additional strategy to impart aromaticity is to have an adjacent π system, so that reorganisation of the double bonds by isomerisation provides the new aromatic ring. This process was observed by Pérez-Castells and co-workers in 2002 when the group were attempting to synthesise pyrrolo-[1,2-*a*]indoles (Scheme 17).[48] In the case of diene **72**, the product isolated from the RCM reaction was the pyrrole **73** whereby the indole olefin had shifted to form a new aromatic heterocycle. Interestingly, this was the only example reported to isomerise in this fashion.



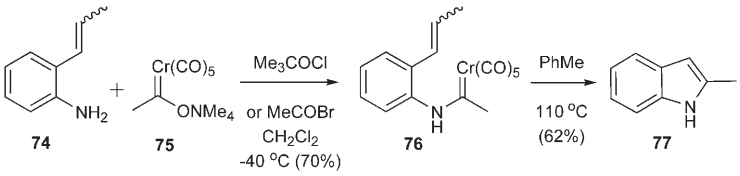
Scheme 16. Lamaty synthesis of substituted pyrroles.



Scheme 17. Formation of pyrrole by isomerisation of an existing π-framework.

Construction of Benzofurans and Indoles

The use of RCM to form a new ring that is fused to an existing unsaturated framework can result in the formation of a new aromatic ring as a consequence of the structure of the metathesis product. In 1993, Söderberg and co-workers discovered that, upon heating, the *N*-arylamino-substituted chromium carbene **76** was converted into the corresponding indole **77** in a formal metathesis reaction (Scheme 18).[49] This represented one of only a few complexes which were shown to cyclise in this manner.

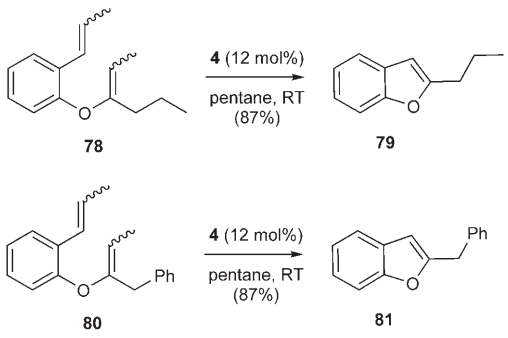


Scheme 18. Söderberg synthesis of indoles using chromium carbenes.

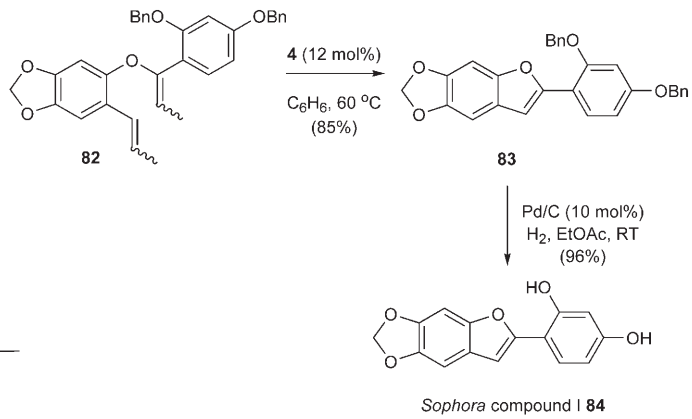
In 1994, the Grubbs group utilised this principle to generate benzofurans by performing RCM on a series of acyclic enol ethers (Scheme 19).[50] The enol ethers were generated by olefination of the corresponding esters, and the RCM was carried out using the molybdenum alkylidene catalyst **4**. This protocol provided access to a variety of 2-substituted benzofurans from readily available 2-propenylphenols.

The synthetic utility of this approach was illustrated by the rapid synthesis of the naturally occurring antifungal phytoalexine known as *Sophora* compound I (Scheme 20).[50] The Grubbs group constructed the acyclic enol ether **82** by olefination of the corresponding ester and RCM provided the protected precursor of the natural product in 85% yield. With the advanced intermediate **83** in hand, the remaining synthesis was completed smoothly to furnish the natural product.

Nishida and co-workers

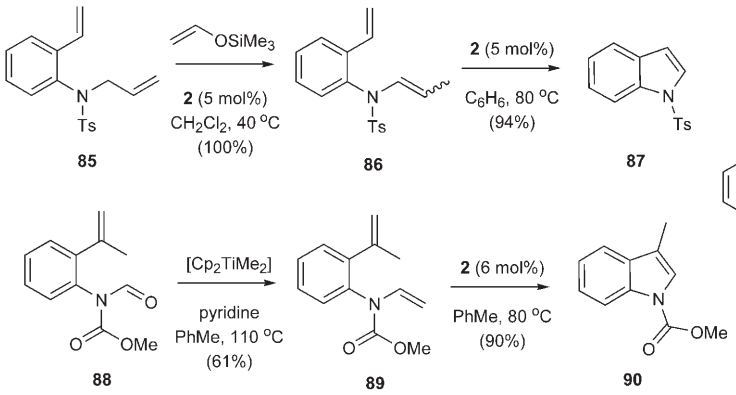


Scheme 19. Grubbs synthesis of benzofurans.

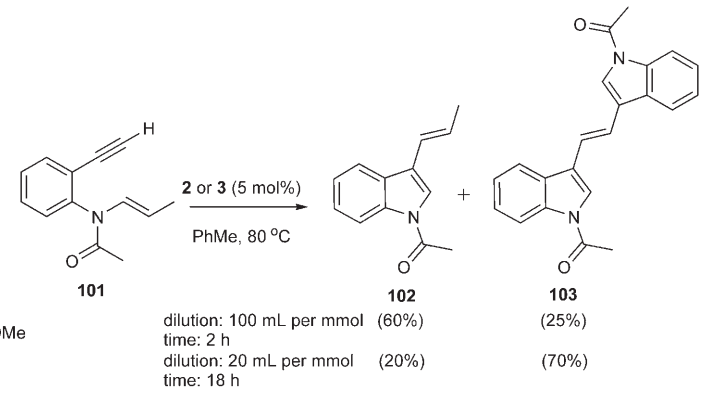


Scheme 20. Grubbs synthesis of *Sophora* compound I.

modified this protocol to provide a series of protected indoles; the group used Grubbs second generation catalyst **2** in combination with vinyloxytrimethylsilane to effect the isomerisation of the allylic amine **85** to the required enamine **86** (Scheme 21).[51,52] The RCM of enamine **86** provided the corresponding indole **87** in excellent overall yield. In 2006, Bennassar and co-workers also employed a similar strategy to generate indoles.[53,54] Their approach involved



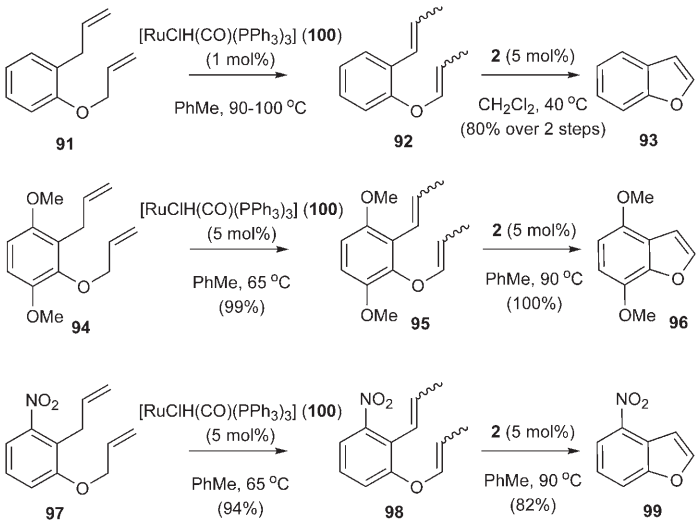
Scheme 21. Nishida and Bennassar syntheses of protected indoles from enamides.



Scheme 23. Ring-closing enyne metathesis to form indoles.

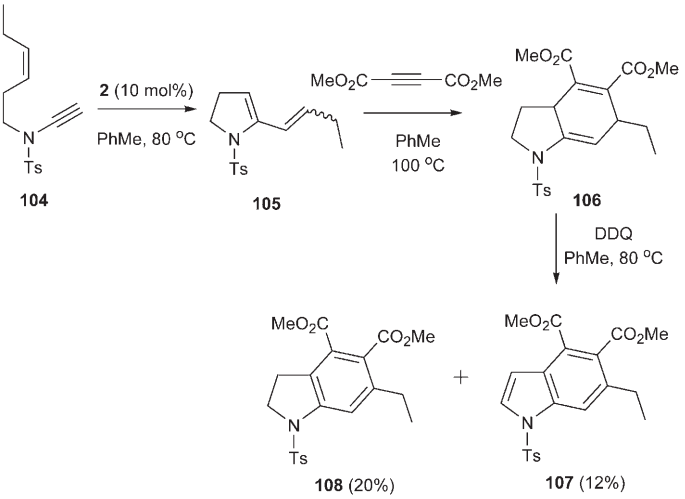
the synthesis of a range of acyclic enamides by olefination of the corresponding methoxycarbonyl-protected amide under Petasis conditions. An enamide–ene RCM of the acylic precursor provided the desired indoles in good yields.

van Otterlo and co-workers also utilised this isomerisation/RCM procedure to assemble a series of benzofurans (Scheme 22).[55,56] Ruthenium complex **100** was used to perform the isomerisation of two allyl groups to form the corresponding aryl enol ether; RCM with precatalyst **2** then provided the desired benzofuran in excellent yield. The RCM was successful for both electron rich and deficient arene substituents; furthermore, bulky *ortho*-groups could be incorporated without hampering the metathesis reaction.



Scheme 22. Double isomerisation/RCM strategy to form benzofurans.

In 2004, the Pérez-Castells group attempted to apply the ring-closing enyne metathesis transformation to the synthesis of protected indoles (Scheme 23).[57] In fact, they obtained a mixture of the desired vinylindole **102**, as well as the dimer **103**. The vinylindole **102** could be obtained as the major product (60%) by adopting high dilution (100 mL per mmol) and short reaction times (2 h); conversely, the dimer **103** could be formed preferentially (70%) by using low dilution (20 mL per mmol) and longer reaction times (18 h).

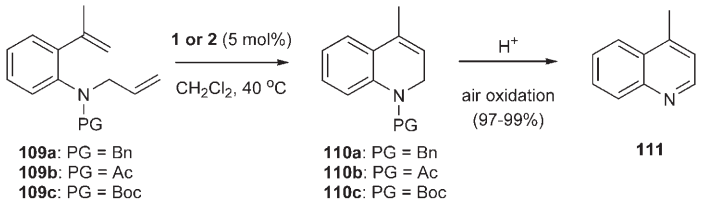


Scheme 24. Mori synthesis of indoles using a tandem enyne metathesis/Diels-Alder sequence.

An innovative approach to assemble aromatic heterocycles is to functionalise the RCM products prior to the aromatisation procedure. As these precursors are not aromatic they may exhibit reactivity that may be different to the desired final product. Mori and co-workers demonstrated this elegantly in the synthesis of indole **107** (Scheme 24).[58] The group postulated that since the enyne metathesis product **105** contained a diene moiety, it may be possible to perform a tandem enyne metathesis/Diels–Alder procedure. Thus, the metathesis of enyne **104** was carried with Grubbs second generation catalyst **2**, before addition of dimethyl but-2-ynedioate to the reaction mixture. After oxidation with DDQ, both indoline **108** and the fully aromatic indole **107** were obtained. This approach to aromatic heterocycles represents a rapid route to complex structures which bodes well for future studies.

Construction of Six-Membered Aromatic Heterocycles

In 2001, Nishida, Nakagawa and co-workers were investigating the formation of a series of protected 1,2-dihydroquinolines **110** by RCM of the corresponding acyclic diene **109** (Scheme 25).[59] It was found that the dihydroquinoline **110** was isolated in good yield following RCM, but that the protecting groups on nitrogen were removed during silica gel column chromatography and the resulting dihydroquinoline was spontaneously auto-oxidised to give 4-methylquinoline **111** directly.



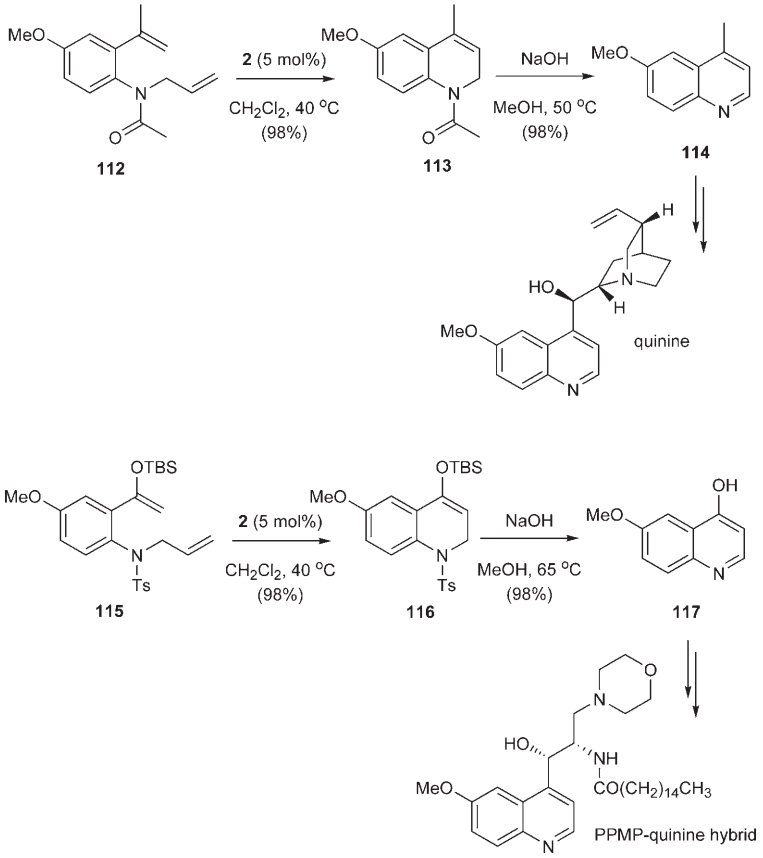
Scheme 25. Synthesis of quinoline **111** by RCM/oxidation.

The group also applied this procedure to the synthesis of quinolines **114** and **117**, which are intermediates in the synthesis of the anti-malarial agents quinine[60] and phenyl-2-palmitoylamino-3-morpholino-1-propanol (PPMP)–quinine hybrid,[61] respectively (Scheme 26).[61,62]

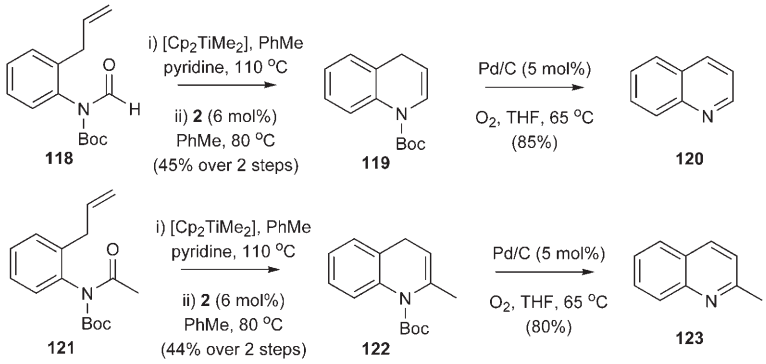
The Bennasar group used a similar strategy to construct quinolines with the elegant use of the enamide–ene RCM reaction (Scheme 27).[53] The formation of two quinolines **120** and **123** was reported, whereby the oxidation of the 1,4-dihydroquinoline system was effected using catalytic palladium on carbon under an atmosphere of oxygen.

Nan and co-workers revealed the potential of this RCM/oxidation strategy for the formation of six-membered aromatics in 2004, with the synthesis of a library of 6-substituted 3-amino-2-pyridones (Scheme 28).[63] The group utilised a novel α-amino acrylamide RCM to form a variety of α-amino α,β-unsaturated lactams which were oxidised in situ with DDQ. The 6-position could be substituted with electron-rich or electron-deficient aromatic rings using this approach, in addition to long chain and hindered alkyl groups.

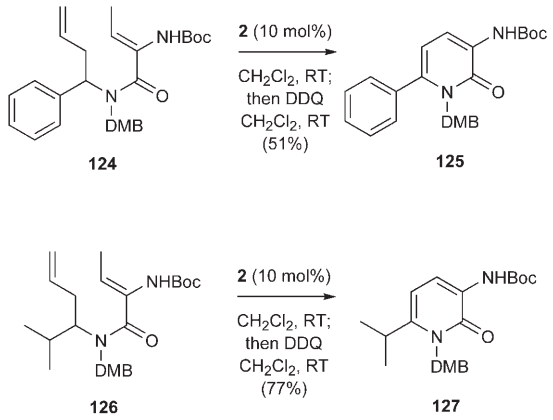
In the same year, the O'Brien group employed this technique to construct the 2-pyridone core in the final stages of the synthe-



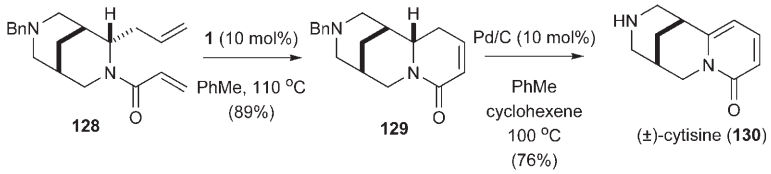
Scheme 26. Access to key intermediates in the syntheses of quinine and PPMP–quinine hybrid.



Scheme 27. Bennasar synthesis of quinolines by RCM/oxidation with Pd/C.



Scheme 28. Synthesis of a library of 3-amino-2-pyridones using a RCM/oxidation strategy.



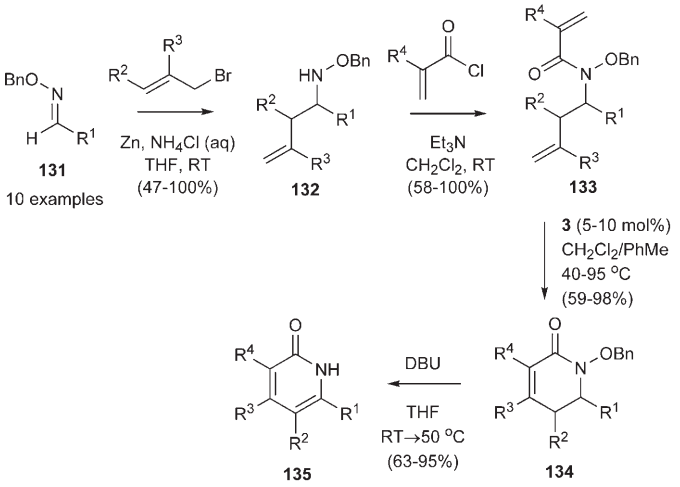
Scheme 29. O'Brien synthesis of (±)-cytisine.

sis of the naturally occurring lupin alkaloid cytisine **130** (Scheme 29).[64] The RCM of diene **128** proceeded smoothly using Grubbs first generation catalyst **1** to provide the dihydropyridone **129** in 89% yield. The key oxidation–*N*-deprotection sequence was executed using palladium on carbon to reveal the aromatic core and complete an efficient six-step approach to the natural product.

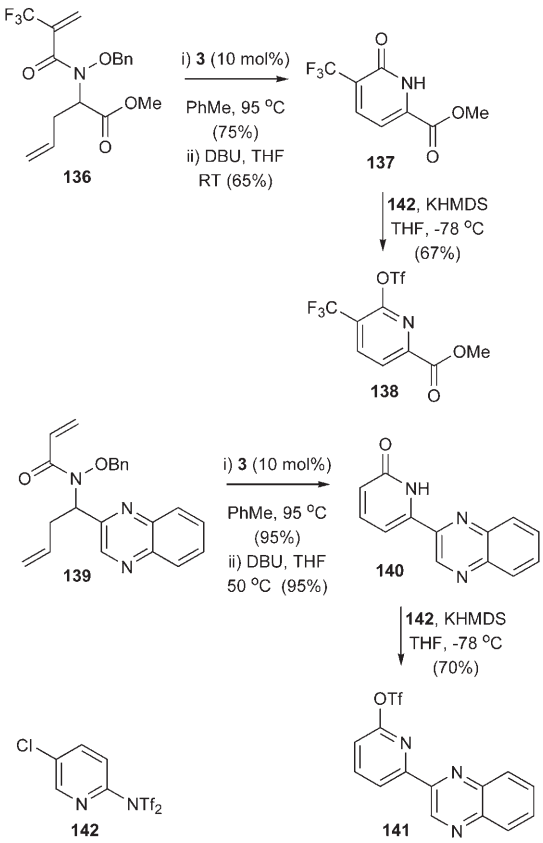
In 2007, the Donohoe group developed a novel route to a variety of 2-pyridones and pyridines *via* the key dihydropyridone **134**, which was constructed by RCM of the acyclic acrylamide **133** (Scheme 30).[65] The elimination of benzyl alcohol from the dihydropyridone **134** was accomplished using DBU to provide the functionalised pyridones in excellent yields.

With all the substituents originating from readily available components, Donohoe and co-workers were able to construct a large number of pyridones with varying substituent patterns (Scheme 31). The pyridones were readily transformed into the corresponding pyridines using the pyridine derived triflating reagent **142** developed by Comins and co-workers These intermediates are set for further substitution by utilising a wealth of reported procedures.

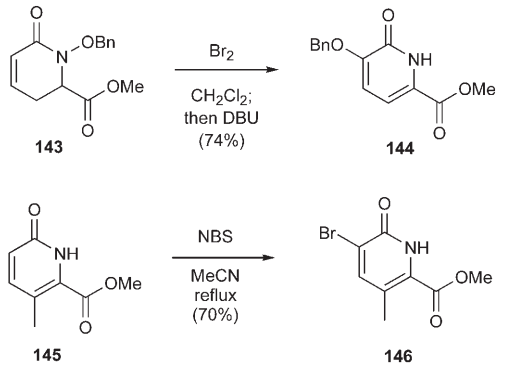
One advantage of this approach to aromatic compounds is that the intermediates formed after metathesis are not aromatic and therefore can be derivatised using chemistry that would not usually be successful on aromatic compounds. Of course, after functionalisation, aromaticity can then be bestowed upon the system. For example, alternative aromatisation conditions have been developed whereby bromine was added to **143**, prior to reaction with DBU (Scheme 32). It was expected that the corresponding 3-bromopyridone would be the product; however, this pyridone was trapped in situ with the benzyloxy leaving group to give the interesting 3-benzyloxy aro-



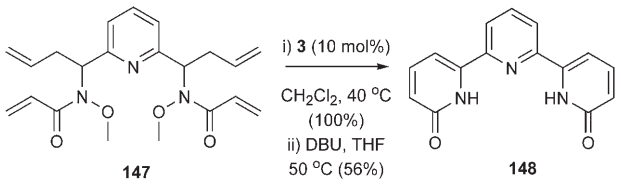
Scheme 30. Donohoe synthesis of 2-pyridones.



Scheme 31. Synthesis of 2-pyridones and the corresponding pyridines.



Scheme 32. Alternative conditions for the formation of 2-pyridones.



Scheme 33. Formation of dipyridone **148** using a double RCM/elimination strategy.

matic **144** in good yield. To extend this idea further, pyridone **145** was brominated selectively at C-3 to give **146**, which could be manipulated with ease.

The same approach was successfully applied to the synthesis of dipyridone **148** by employing a double RCM and aromatisation strategy (Scheme 33). The bis(methoxyacrylamide) **147** was formed using the protocol outlined previously (Scheme 30); the double RCM and double elimination proceeded in excellent yield to produce the pyridine-2,6-dipyridone **148**.

Conclusion

It is clear from this summary that metathesis-based approaches to the synthesis of aromatic heterocycles have displayed prominent success. Several strategies have been established which are capable of constructing aromatic motifs with the incorporation of varying substituent patterns and synthetic points of flexibility. The versatility of such approaches bodes well for future research in this area.

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