1
Synthesis of Dendralenes

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1.1
Introduction

The synthesis and study of conjugated polyenes has been at the heart of the chemical sciences ever since an appreciation of their structure began to develop. Of the five classes of conjugated alkenes that arise from the different possible modes of connectivity (Figure 1.1), some have received significantly more attention than others. The linear and cyclic classes featuring vicinal connections between alkene units – the linear polyenes **1** and annulenes **2** – are common structural motifs in naturally occurring compounds and contrived structures of industrial, commercial, and academic importance, and have hence been extensively synthesized and studied. Oligoalkenes with geminal connections between alkenes – cyclic radialenes **4** and acyclic dendralenes **5** – are yet to receive such attention, nor are "hybrid" structures featuring both geminal and vicinal connections, the fulvenes **3**. There is, however, undoubtedly a growing interest in the subject of this chapter: the synthesis of dendralenes.

Dendralenes have been the subject of two comprehensive reviews [1, 2]. The first covers research in the area until 1984; and the second covers the period between 1984 and 2011. While it would be impossible to summarize the evolution of dendralene synthesis without some repetition of the key strategies found in each of these reviews, we seek to present the subject differently herein, by summarizing the best methods from both reviews, and placing emphasis on the significant work that has appeared between 2011 and the present. We also present the synthetic strategies in a new way, based on which carbon–carbon bonds of the dendralene are formed in the approach. Newly formed bonds are highlighted in bold, and should not be confused with wedged bonds, used to indicate stereochemistry. A broad measure of the synthetic power of a strategy is the number of bonds formed in the process, and we have therefore first highlighted strategies that form more than one bond per step [3]. This has allowed us insight into the strengths, weaknesses, and gaps present amongst current approaches. Our review covers examples in the literature up until April 2015, and we exclusively deal with the synthesis of the parent and substituted

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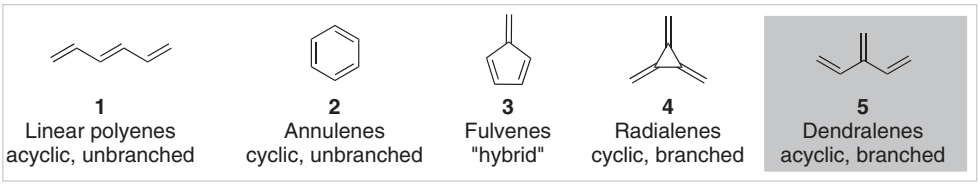


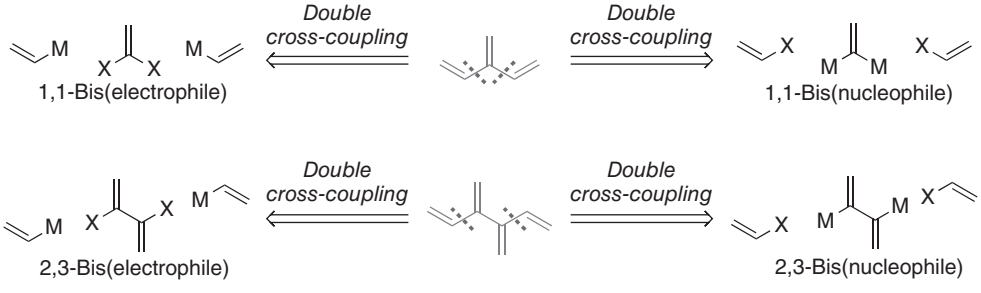
Figure 1.1 Fundamental conjugated hydrocarbons.

dendralenes, directing readers to other reviews or chapters of this book dealing with their closely related, cross-conjugated relatives (fulvenes [4], radialenes [5, 6], quinomethanes [7], etc.). We have not included related compounds that may be generated by substituting a carbon atom in the dendralene backbone with a similar unsaturated moiety, such as an alkyne or aromatic ring. We have also limited our survey to exclude cross-conjugated polymers, which have been reviewed elsewhere [8].

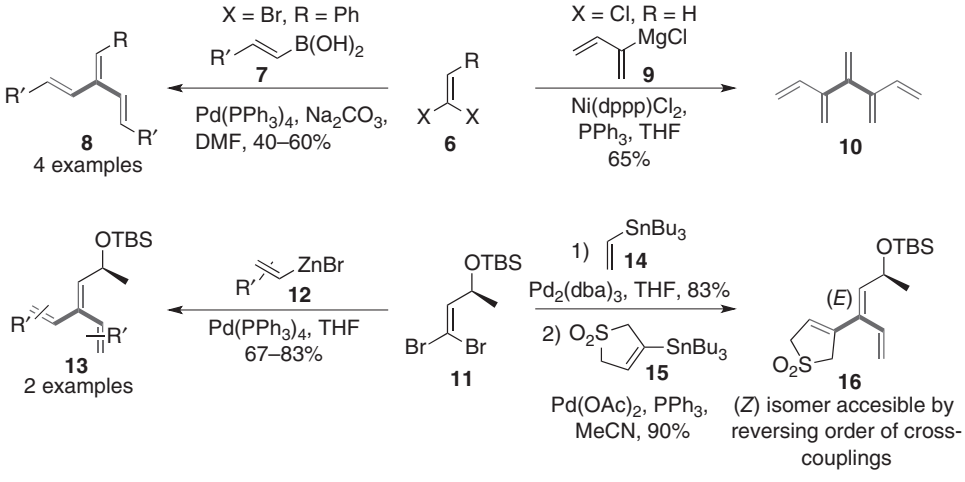
1.2 Multibond Forming Processes

1.2.1 Double Alkenylation Reactions

The double alkenylation approach (Scheme 1.1) has only been exploited relatively recently, most probably because of the rise to prominence of cross-coupling methodologies in recent times. The first double cross-couplings between 1,1-dihaloalkenes and metalloalkenes were isolated examples appearing in 1998 [9] and 2000 [10]. In 2002, Oh and Lim [11] reported a series of double Suzuki–Miyaura reactions between a 1,1-dibromoalkene **6** and alkenyl boronic acids **7** (Scheme 1.2). In 2007 and 2008, the Sherburn research group reported syntheses of substituted [3]dendralenes [12] and the state-of-the-art synthesis of [5]dendralene [13] respectively, transforming a 1,1-dihaloalkene via double



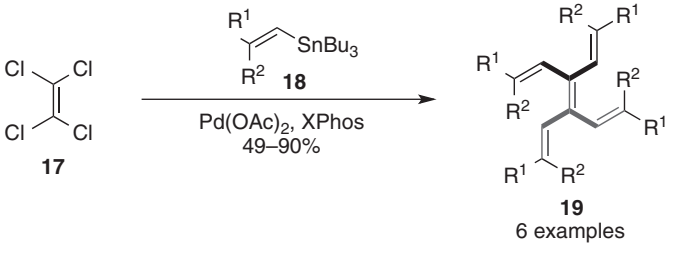
Scheme 1.1 Double alkenylation approaches to [3]- and [4]dendralene, via sp^2–sp^2 cross-coupling.



Scheme 1.2 Examples of double cross-coupling approaches to dendralenes by Oh and Lim [11] and Sherburn and coworkers [12, 13].

Negishi or Kumada cross-couplings to incorporate one alkenyl substituent (**9** or **12**) twice, and also, in the former case, the related stepwise, stereoselective Stille couplings to form unsymmetrically substituted, chiral [3]dendralenes **16** (Scheme 1.2). An application of this stepwise approach *en route* to the natural product triptolide [14] highlighted that when using two different metalloalkene cross-coupling partners, complete control of the stereochemistry of the resulting alkene is sometimes unattainable. Thus, most successful applications of this method incorporate two identical alkenes, so no issues of stereochemistry arise. A recent example is the synthesis by Ichikawa and coworkers [15] of a single tetrafluoro[3]dendralene via double Negishi cross-coupling of 2,2-difluorovinylzinc bromide to a dibromoolefin.

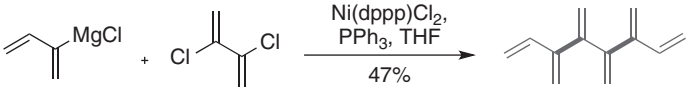
Recently, a new benchmark in alkenyl cross-coupling syntheses was set by the Sherburn group, using an extension of this double cross-coupling strategy. Tetravinylethylene (TVE) and substituted analogs **19**, previously only accessible by longer, lower yielding, sequences [16–18], were generated via a fourfold Stille cross-coupling of alkenyl stannanes **18** and tetrachloroethylene (**17**), a cheap



Scheme 1.3 Synthesis of TVEs via fourfold sp^2–sp^2 cross-coupling reactions [19, 20].

and readily available starting material produced annually on a kiloton scale (Scheme 1.3) [19–21]. TVEs possess an interesting carbon framework composed of two [3]dendralene subunits sharing the same central, tetrasubstituted alkene. The bold, one-step approach was used to generate six different symmetrically substituted TVEs, is unique in its use of a tetrachloroalkene, and cannot be surpassed in terms of step economy [22].

Higher dendralenes are accessible by double cross-coupling by including branched alkenes into the electrophile unit. For example, in their state-of-the-art synthesis of the parent dendralenes [23], Sherburn and coworkers prepared [6]dendralene (**21**) by the reaction between 2,3-dichloro-1,3-butadiene (**20**), and the Grignard reagent (**9**) prepared from chloroprene, another readily available unsaturated halide produced annually on a megaton scale (Scheme 1.4) [24]. The scope of this reaction in the synthesis of substituted higher dendralenes remains unexplored.



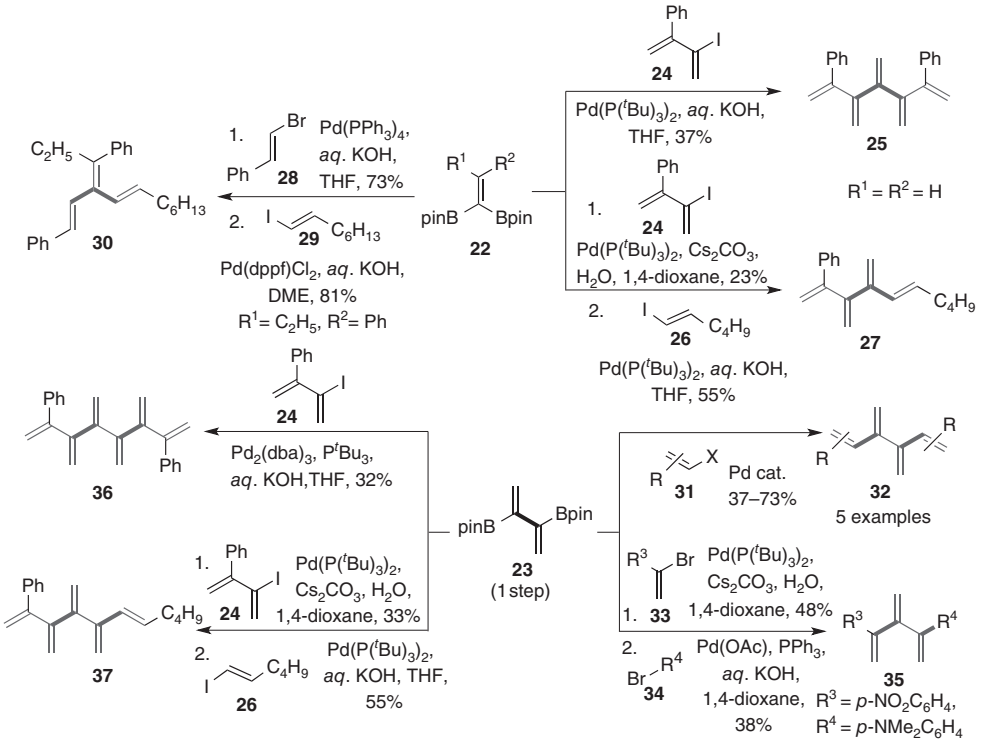
9 **20** **21**

Scheme 1.4 Synthesis of [6]dendralene via a double sp^2–sp^2 cross-coupling reaction [23].

The same double cross-couplings are feasible by swapping the reactivity of components, that is, using a double nucleophilic ethylene or 1,3-butadiene and two alkenyl electrophiles. So far, apart from an isolated example by the Sherburn group using 2,3-bis(trimethylstannyl)-1,3-butadiene [10], the Shimizu group is presently the only one to explore this avenue of dendralene synthesis, and have published a series of papers detailing the use of 1,1-bis(pinacolatoboryl)ethylene (**22**) and 2,3-bis(pinacolatoboryl)-1,3-butadiene (**23**) as nucleophilic components in Suzuki–Miyaura cross-coupling reactions (Scheme 1.5) [25–27]. A double cross-coupling reaction leads to symmetrically substituted [4]-, [5]-, and [6]dendralenes (**32**, **25**, **36**), and a two-step process leads to unsymmetrically substituted [3]-, [4]-, and [5]dendralenes (**30**, **35**, **27**, **37**). While the yields for many of these reactions remain quite low, the potential scope is broad. The two strategies are complementary, and many interesting substituted dendralene frameworks are within rapid, step-economic reach from some very readily available starting materials.

1.2.2
Double Alkenation Reactions

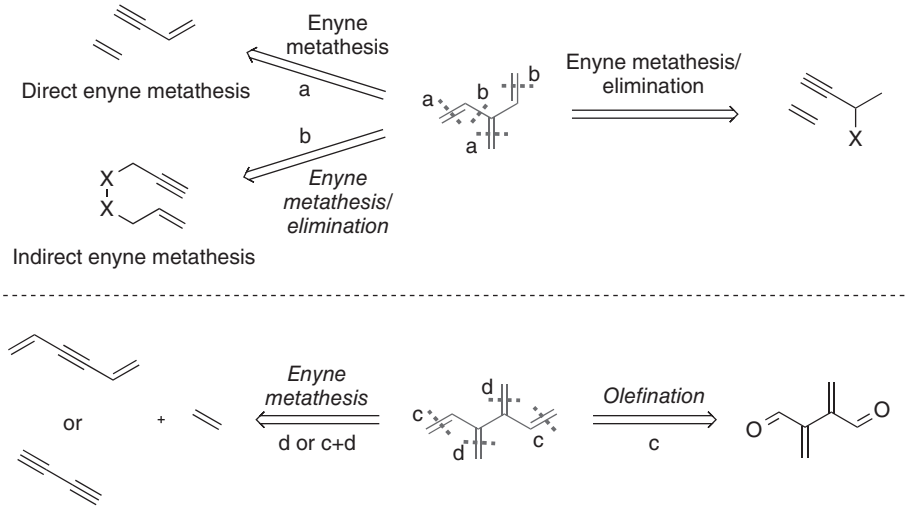
Various approaches that synthesize butadienes by the installation of methylene groups on two adjacent carbon atoms can be classified as the same overall transformation as the enyne metathesis reaction (Scheme 1.6). Unsurprisingly, metal-catalyzed enyne metathesis has proved versatile in this regard, as have



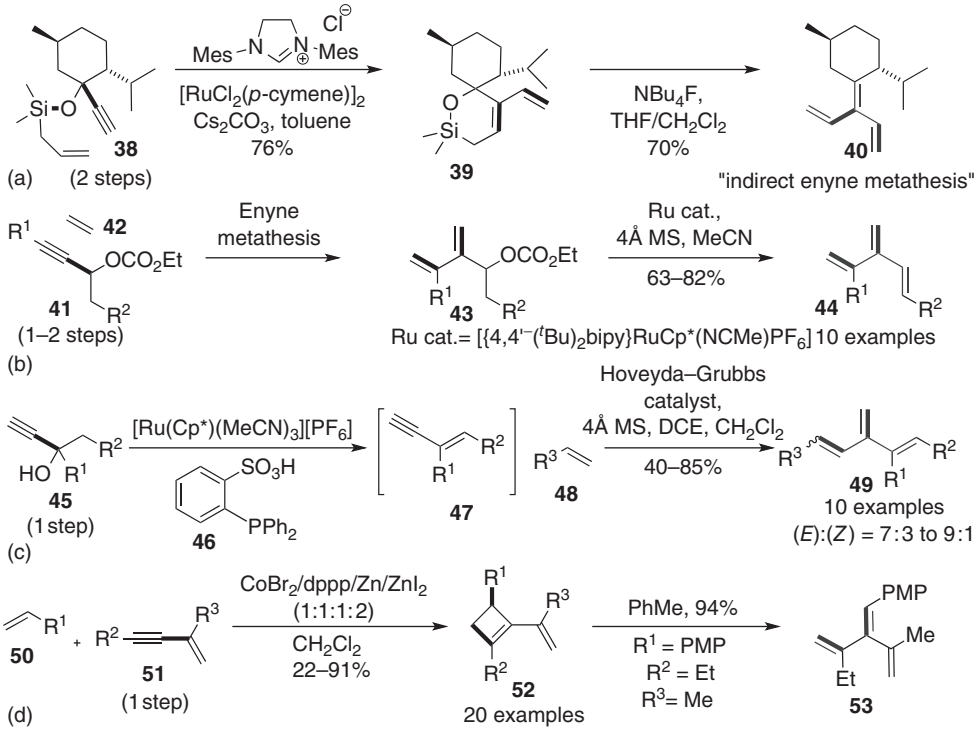
Scheme 1.5 Syntheses of dendralenes utilizing a double nucleophilic cross-coupling building block, from the Shimizu group [25–27].

[2+2] cycloaddition/4π electrocyclic ring-opening sequences (referred to herein as *uncatalyzed enyne metathesis reactions*), but other complementary examples of multibond forming processes that effect the same bond formations have also been developed.

In 2003, Bruneau and coworkers reported the first use of enyne metathesis to synthesize masked dendralenes **39** (Scheme 1.7 (a)) [28]. This work paved the way for a series of related syntheses of dendralenes with a variety of substitution patterns [29, 30], including a remarkable synthesis of a [4]dendralene via a double intramolecular enyne metathesis/double elimination sequence by Park and Lee [29]; however, because the products are masked dendralenes, the carbon–carbon bond disconnections for this strategy are different from the direct metathesis approach, in which the newly formed butadiene unit stays intact (Scheme 1.6). It was Bruneau again who first developed this route, using metathesis between ethylene (**42**) and propargylic carbonates **41** to synthesize 1,3-butadiene **43**, revealing the third alkene via subsequent elimination (Scheme 1.7 (b)) [31]. The same group has now published metathesis reactions that directly furnish intact [3]dendralenes **49** by conducting the elimination first and then performing metathesis on an alkyne **47** already bearing the third alkene (Scheme 1.7 (c)) [32].



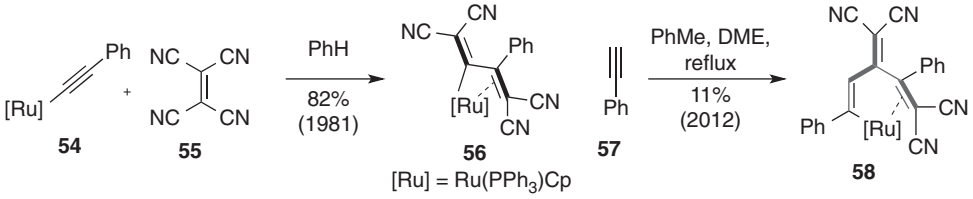
Scheme 1.6 Possibilities for the synthesis of dendralenes via reactions forming two or more alkene groups.



Scheme 1.7 Representative examples of substituted [3]dendralene syntheses involving enyne metathesis or an equivalent transformation [28, 31–33].

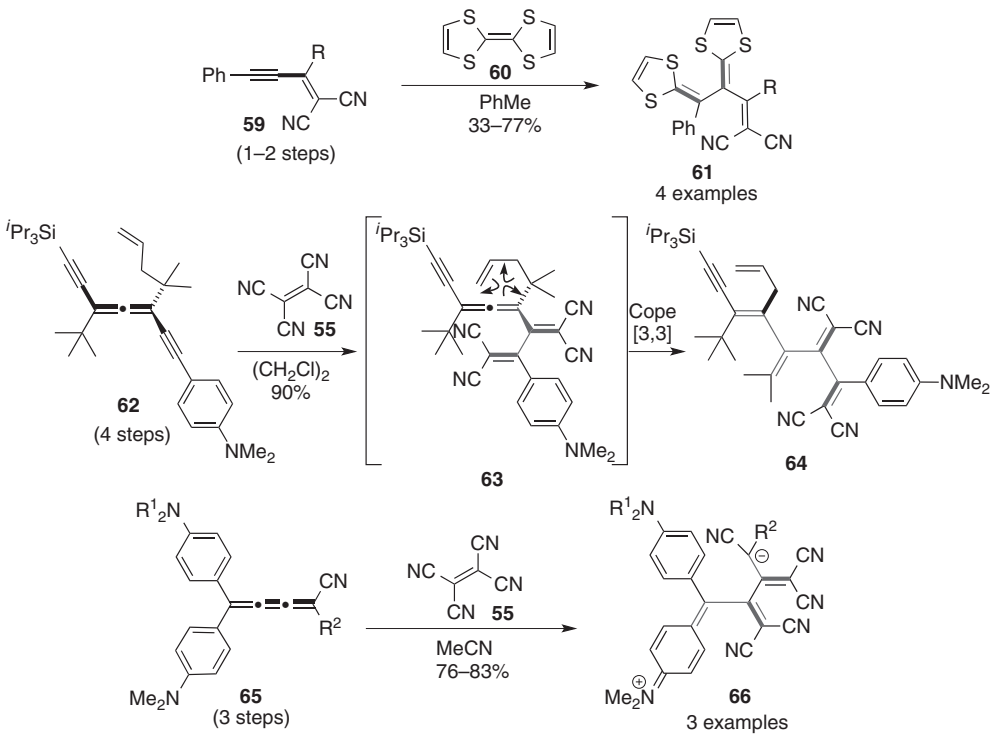
The related, intramolecular ring-closing enyne metathesis had been reported by Chang and coworkers [34]. A promising, if isolated, example of a related metal-catalyzed synthesis of a [3]dendralene **53** was reported by the Ogoshi group in 2014 (Scheme 1.7 (d)) [33]. A cobalt catalyst was used to generate a variety of alkenyl cyclobutenes **52** from the reaction of an alkene **50** and alkyne **51**. One of the cyclobutenes **52** was converted by thermal electrocyclic ring-opening to a substituted [3]dendralene **53**. If this ring-opening proves general, the methodology provides a modern, step-efficient incarnation of older methods that unmasked dendralenes from alkenyl cyclobutenes, derived from lengthy sequences [1]. A couple of isolated examples of dendralene synthesis via Ru(II)-catalyzed double carbene addition to alkynes have also been reported, albeit with only moderate (*E*)/(*Z*) selectivity [35]; and a coupling of an organozirconium reagent and vinyl bromide, equivalent to an enyne metathesis, has also been used to prepare a [3]dendralene [36].

In the 1970s and 1980s, it was discovered that electron-deficient alkenes, such as tetracyanoethylene (TCNE, **55**) reacted with metallated alkynes **54** to furnish a metallated hexasubstituted 1,3-diene unit **56**, an overall transformation akin to enyne metathesis (Scheme 1.8) [37, 39]. In a recent (2012) addition to this work, the Bruce group reported the synthesis of a ruthenated [3]dendralene **58** via insertion of phenylacetylene (**57**) into **56** (Scheme 1.8) [38]. The metallated dendralene synthesis is low yielding and, as yet, an isolated example, but presents an interesting avenue for future investigations.

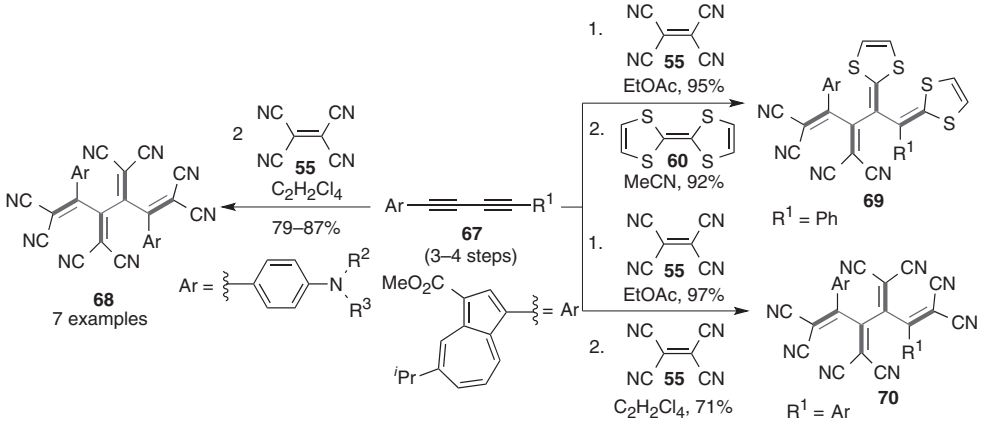


Scheme 1.8 Synthesis of a ruthenated [3]dendralene [37, 38].

Uncatalyzed metathesis has also been performed on systems without metal components. Hopf was the first to show that highly electron-rich olefins such as tetrathiafulvalene (TTF, **60**) undergo a sequence of [2+2] cycloaddition and 4π electrocyclic ring-opening with electron-deficient alkynes **59** to generate a new butadiene unit, which may be part of a dendralene (e.g., **61**) if a neighboring alkene is already in place (Scheme 1.9) [40]. The group of Diederich has made extensive use of the cycloaddition/4π electrocyclic ring-opening pathway to generate butadienes, some of which appear in dendralene frameworks [43–45]. Examples from recent papers demonstrate the versatility of this approach. TCNE (**55**) undergoes the cycloaddition/ring-opening process with alkyne **62** [41]. A preexisting alkene in the alkyne starting material (akin to Hopf's strategy) allows the generation of the [3]dendralene framework in **63**. Finally, the presence of the requisite functionality for a Cope rearrangement allows further downstream functionalization, and the *in situ* generation of [4]dendralene **64**. A similar



Scheme 1.9 Representative dendralene syntheses featuring uncatalyzed metathesis reactions [40–42].

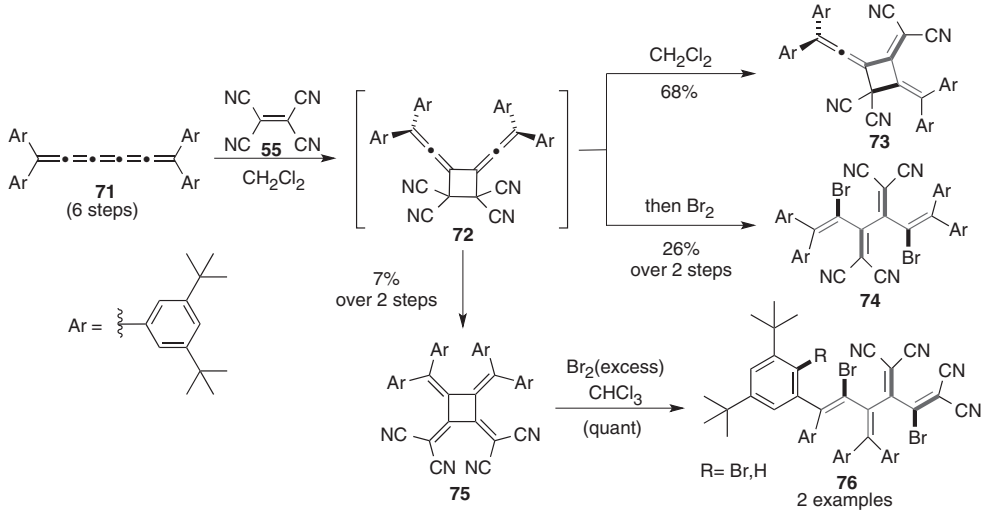


Scheme 1.10 Stepwise or double [2+2]cycloaddition/retro-4π-electrocyclization cascades to synthesize [4]dendralenes [46, 47].

strategy from the same group has also led to interesting zwitterionic dendralene structures **66** derived from the cycloaddition/4π electrocyclic ring-opening sequence between cumulenes **65** and TCNE (**55**) [42].

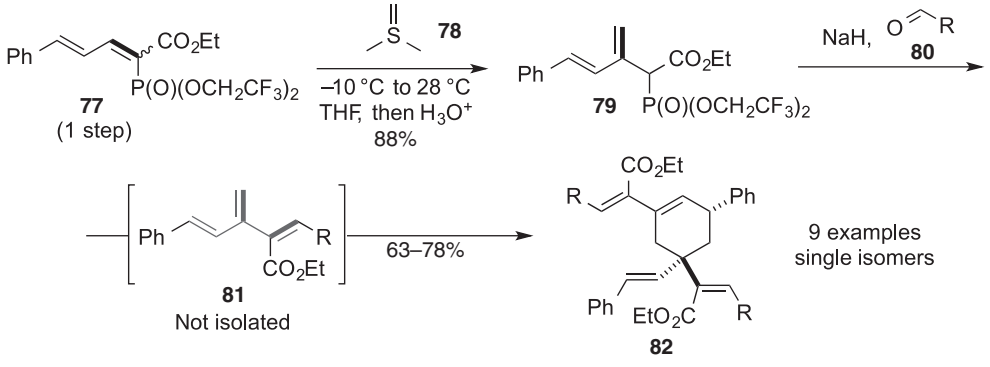
Uncatalyzed metathesis can also be performed on substrates that contain two reactive alkyne sites, for the rapid synthesis of highly substituted [4]dendralenes. Diederich and coworkers recently reported double [2+2] cycloaddition/retro-4π-electrocyclization cascades to yield a number of fully substituted [4]dendralenes **68** featuring push–pull chromophores (Scheme 1.10) [46, 48]. Using a similar double alkyne substrate **67**, Diederich has also used different alkenes to incorporate varied functional groups into the product dendralene, a strategy recently also adopted by Morita and coworkers [47], who in 2012 reported stepwise or one-pot reactions to incorporate both TCNE (**55**) and TTF (**60**) into the structure of [4]dendralenes **69**, via double uncatalyzed metathesis.

Further varied examples of the [2+2] cycloaddition/ring-opening sequence, this time promoted by the addition of bromine, were reported by the group of Tykwinski (Scheme 1.11) [49]. By using a [5]cumulene **71** as starting material, the group generated unsaturated cyclobutanes **72** which formed highly substituted [4]dendralenes **74** when a ring opening was triggered by bromination, or underwent thermal, radical isomerization to yield cyclic [3]dendralene **73**, or [4]radialene **75**. [4]Radialene **75** could itself undergo bromination and ring opening to furnish [4]dendralene **76**.



Scheme 1.11 Cycloaddition/ring-opening sequences by Tykwinski and coworkers to synthesize various dendralenes [49].

A new, complementary approach to enyne metathesis has also emerged in the work of Singh and Ghosh (Scheme 1.12) [50, 51]. A stepwise methylenation (using dimethyl sulfonium methylide ylide **78**) and Stille–Gennari olefination sequence



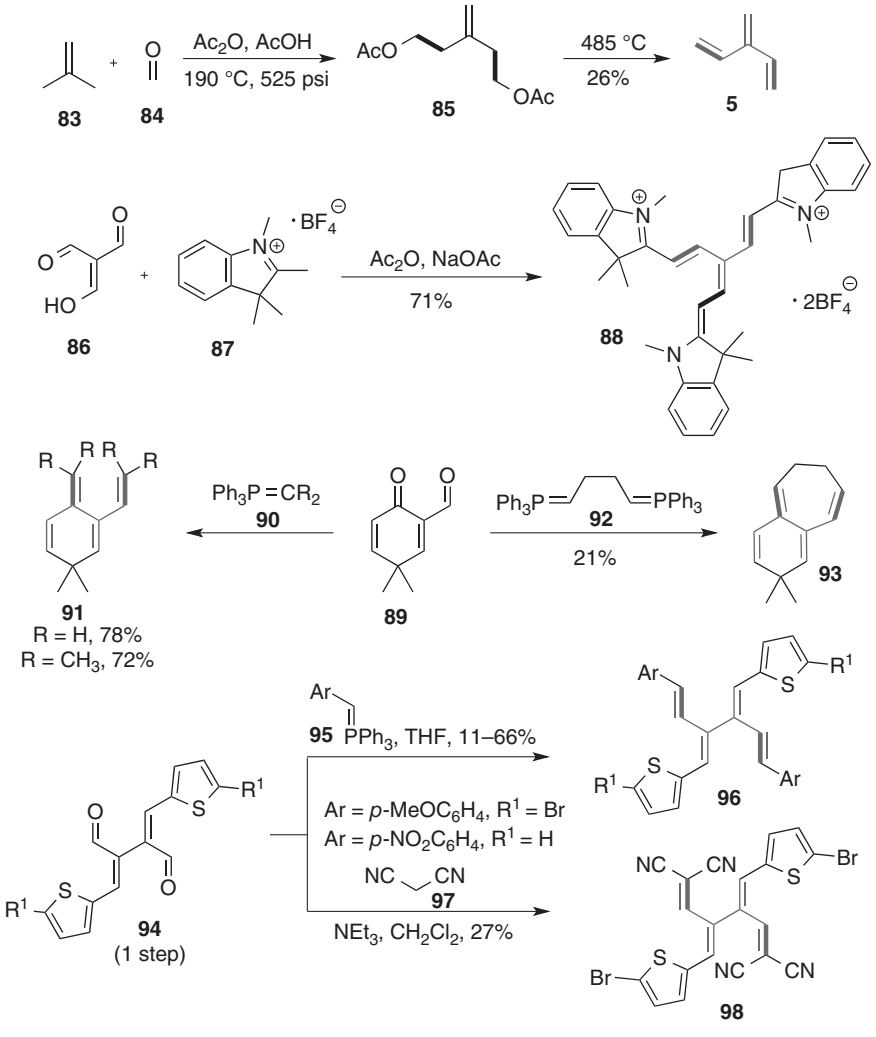
Scheme 1.12 The methylenation/olefination sequence of Singh and Ghosh that forms [3]dendralene prior to *in situ* dimerization [50, 51].

was used to furnish a variety of 1,2,5-trisubstituted [3]dendralenes **81**, which rapidly underwent Diels–Alder (DA) dimerization to yield the isolated DA dimer products **82**. The sequence can be performed in one pot, via the intermediacy of the ylide adduct of **77** and **78**, but was highest yielding when proceeding after quenching this intermediate with water and isolating dienyl phosphonate **79**.

Olefination-type reactions (including addition/elimination sequences) are a reliable method of generating alkenes, and have therefore seen many applications in dendralene synthesis. Their use in multibond forming approaches to dendralenes has also been documented. The landmark first synthesis of [3]dendralene (**5**) by Blomquist in 1955 employed a double Alder–ene reaction between 2-methylpropene (**83**) and two molecules of formaldehyde (**84**), followed by acetylation and elimination to furnish the target hydrocarbon **5** (Scheme 1.13) [52]. Double addition/elimination strategies have also been employed on 1,1-dicarbonylalkenes and 2,3-dicarbonylbutadienes to form [3]- and [4]dendralenes, respectively [56–61]. Another notable and very early example of this approach was used by Reichardt and Mormann to synthesize tri-substituted [3]dendralene **88**, via a triple condensation reaction (Scheme 1.13) [53]. This strategy has found application in a number of related examples [62–65]. Cassens and Lüttke used double Wittig olefinations to form cyclic and bicyclic [4]dendralene structures from 1,3-diketones **89** (Scheme 1.13) [1, 54]. Bryce and coworkers also used the double olefination approach to install the terminal alkenes of a [3]dendralene [66]. Talpur and coworkers [55] have recently used the same double Wittig reaction, and also a double Knoevenagel condensation, to form functionalized [4]dendralenes **96** and **98** (Scheme 1.13).

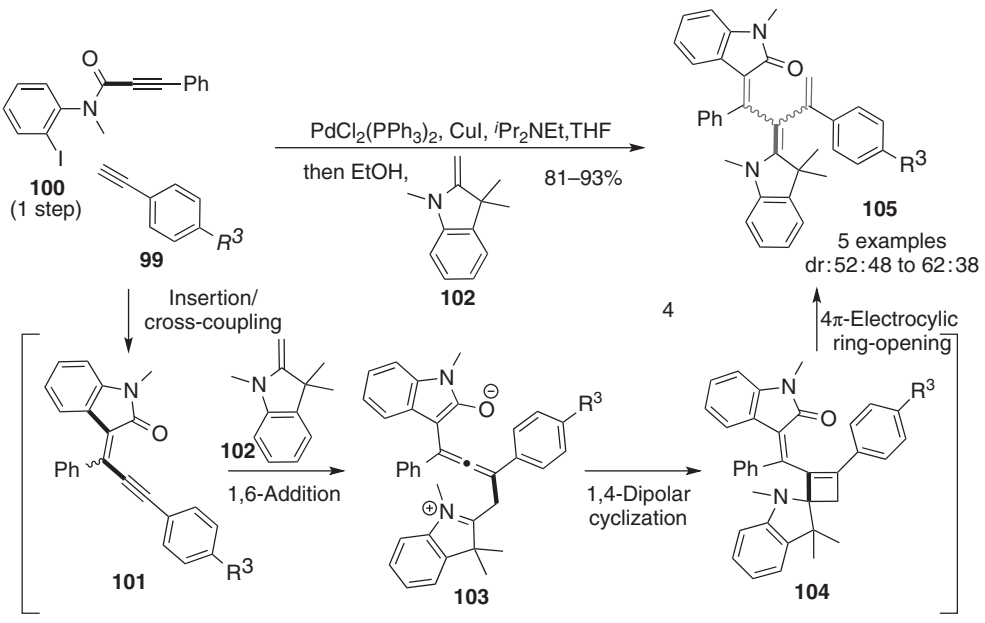
1.2.3
Other Multibond Forming Processes

The Müller group has reported a rapid approach to highly substituted [3]dendralenes via a remarkable, consecutive one-pot palladium(0)-catalyzed sequence

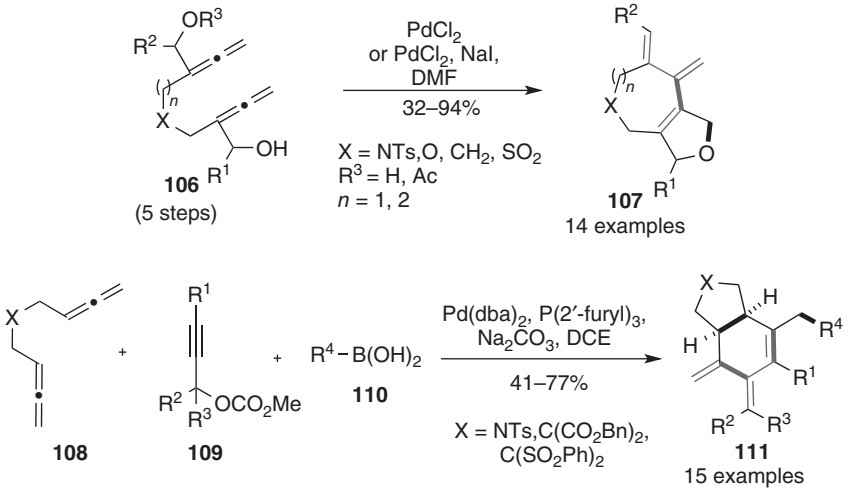


Scheme 1.13 Representative examples of double alkenation syntheses of dendralenes, featuring double addition/elimination sequences or double olefination reactions [1, 52–55].

(Scheme 1.14) [67]. Pd(0)-mediated 5-*exo-dig* cyclization followed by Sonogashira cross-coupling between alkyne **99** and the alkenyl palladium(II) species generated from cyclization yielded intermediate **101**, which underwent 1,6-addition from Fischer's base **102**, followed by Mannich-type 1,4-dipolar cyclization to form cyclobutene intermediate **104**. Ultimately a 4π electrocyclic ring opening furnished [3]dendralenes **105** as the product of this complex mechanism. The methyl substituent on the nitrogen of anilide **100** was found to be crucial to enforce the mechanistic pathway that generates dendralenes, as opposed to other structures. While five examples were cataloged, only the substituent on one aryl



Scheme 1.14 The Pd-catalyzed cascade synthesis of substituted [3]dendralenes by Müller and coworkers [67].

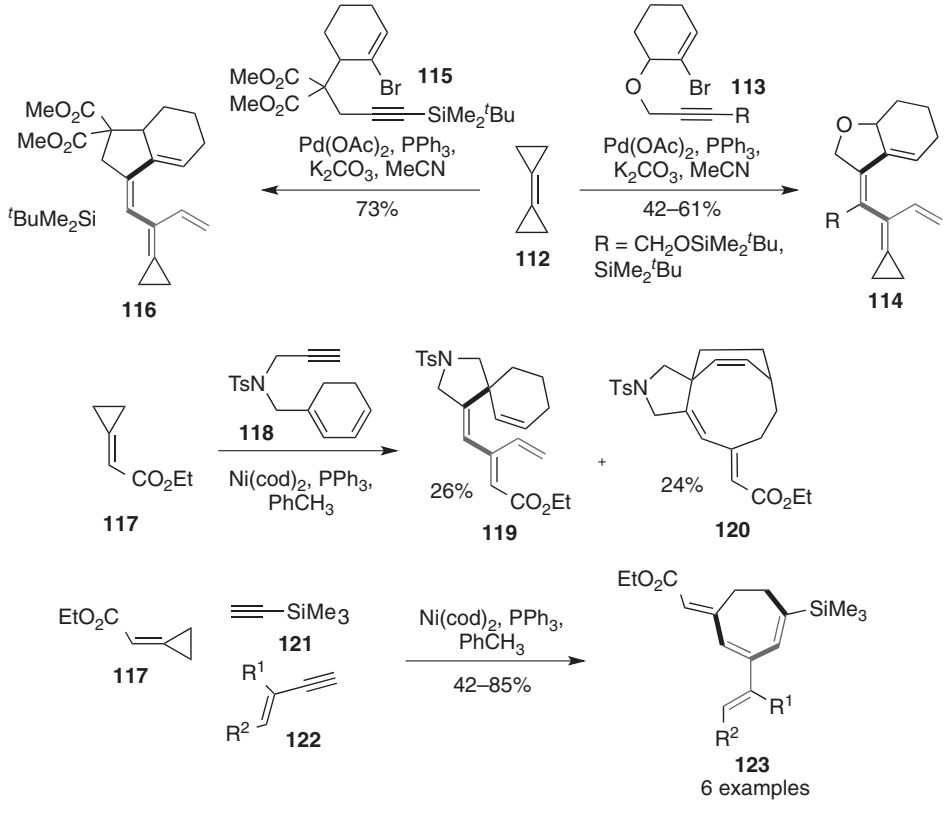


Scheme 1.15 Multi-bond-forming syntheses of [3]dendralenes from the Ma group [68–70].

group was varied; and the dendralenes were formed as mixtures of (*E*) and (*Z*) isomers about the central alkene. Evidently, increased scope and selectivity is worth pursuing in this impressive sequence.

The Ma group has reported some very elegant multibond forming processes to synthesize dendralenes, including both palladium(II)- and rhodium(I)-catalyzed cycloisomerizations of di-allenes **106** to form cyclic dendralenes **107** (Scheme 1.15) [68, 69, 71], and also the remarkable palladium(0)-catalyzed three-component reaction of di-allenes **108**, propargylic carbonates **109**, and boronic acids **110** to form bicyclic [3]dendralenes **111** (Scheme 1.15) [70]. Similar, intermolecular transformations to those used to form dendralenes **107** had been reported earlier by Alcaide, to synthesize dihydrofuran-containing dendralenes [72, 73].

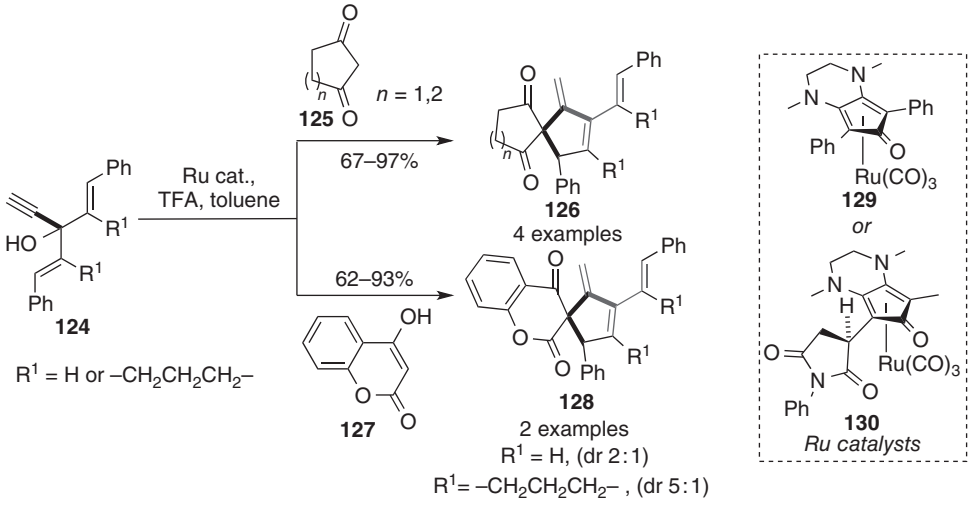
Alkynes are also versatile starting materials to couple with alkenes or allenes in transition-metal-catalyzed processes to form dendralenes. In 2014, building



Scheme 1.16 Transition-metal-catalyzed reactions of alkynes and cyclopropylidenes to form [3]dendralenes [75–77].

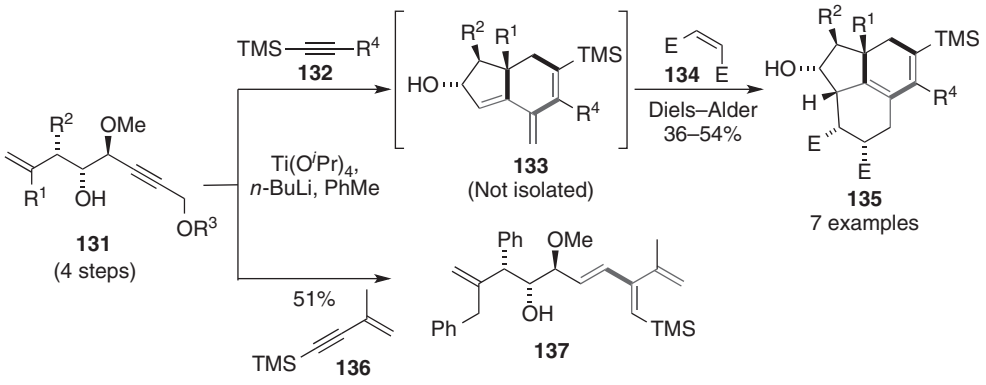
on earlier work from Schelper and de Meijere [74], Demircan reported [75] the synthesis of 3-cyclopropylidene-containing dendralenes using Pd(0)-catalyzed cascade reactions of alkynes and 1,1′-bi(cyclopropylidene) (**112**) (Scheme 1.16). In 2013, Saito and coworkers [76] had reported a related, isolated synthesis of [3]dendralene **119** employing a Ni(0) catalyst, building on their earlier, more general work employing alkynes **121**, ene–ynes **122**, and ethyl cyclopropylideneacetate (**117**) in Ni(0)-catalyzed three-component cycloaddition reactions (Scheme 1.16) [77].

Haak and coworkers in 2015 [78] and 2012 [79] reported monocyclic and bicyclic [3]dendralenes, which were generated via ruthenium-catalyzed cascade transformations. The complex mechanism involves ruthenium(0)-mediated dehydration of the alkyne **124**, addition of the nucleophile to an alkenyl ruthenium allenylidene, and cyclization at a ruthenated alkyne to furnish unusual spirocyclic [3]dendralenes **126** and **128** (Scheme 1.17).



Scheme 1.17 Ru(0)-catalyzed synthesis of cyclic [3]dendralenes by Haak and coworkers [78, 79].

In a very nice titanium-mediated annulation cascade, Cheng and Micalizio [80] synthesized functionalized, bicyclic [3]dendralenes **133** *in situ* as intermediates that were trapped via a subsequent DA reaction (Scheme 1.18). The report includes one example of a DA dimerization product, seven examples of intermolecular metallocycle-mediated annulation followed by intermolecular [4+2]cycloaddition reaction to afford (**135**), and one example of an isolated, acyclic substituted [3]dendralene **137**.

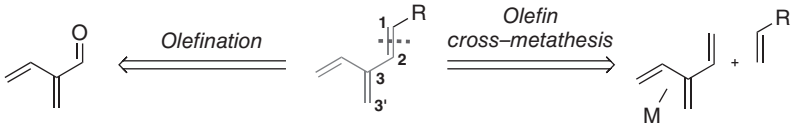


Scheme 1.18 Ti(IV)-mediated cascade syntheses of [3]dendralenes by Cheng and Micalizio [80].

1.3
Solo-Bond-Forming Reactions

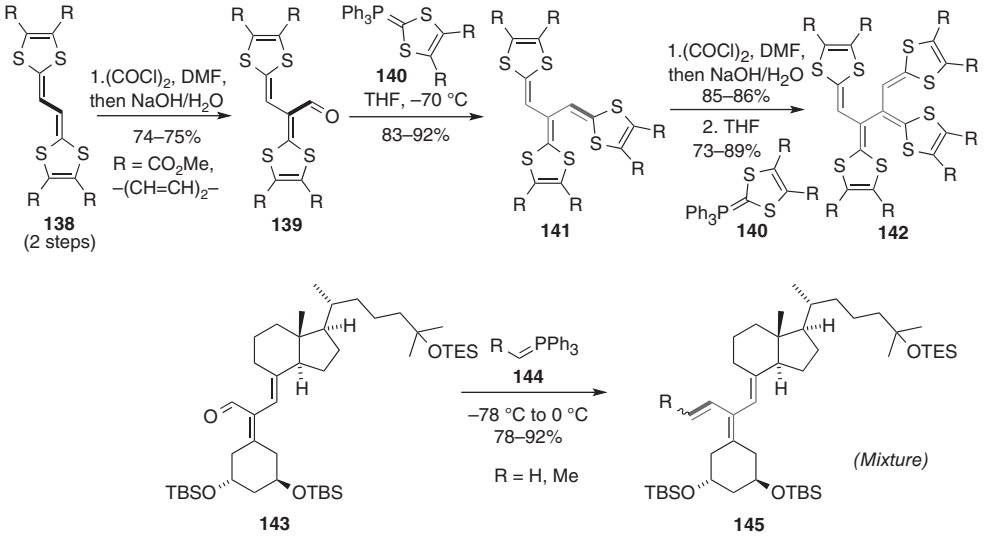
1.3.1
C1–C2 Alkenation Reactions

The most obvious method to install the C1–C2 alkene of a dendralene is an olefination reaction (Scheme 1.19), but it has seen very little use, because of the propensity of 2-carbonyl-1,3-butadiene derivatives to undergo rapid Diels–Alder dimerization [81]. In fact, the only successful uses of 2-carbonyl-1,3-butadienes in such processes feature substrates stabilized by 1,1-disubstitution and a 4*Z* substituent. Such an example is the iterative formylation/olefination sequence reported by Yoshida and coworkers (Scheme 1.20) [82]. A selective, single electrophilic formylation followed by a Wittig reaction gave hexa-substituted [3]dendralenes **141**, which could be further homologated to octa-substituted [4]dendralenes **142** using the same sequence. Related examples have also been reported [84, 85]. A similar iterative formylation/Horner–Wadsworth–Emmons (HWE) sequence was used by Bryce *et al.* to synthesize [3]- and [4]dendralenes containing dithiole and ferrocene functionalities [66]. DeLuca and coworkers [83] recently reported the synthesis of two [3]dendralenes **145** using a Wittig reaction;, however, the stereoselectivities of the reactions were not reported (Scheme 1.20).

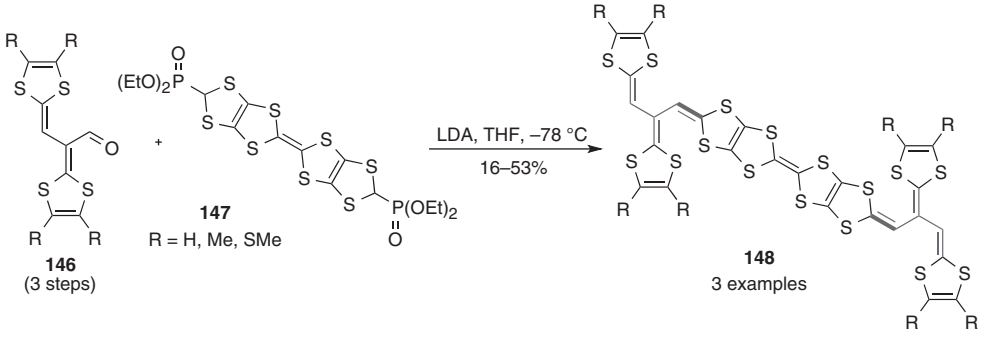


Scheme 1.19 Single alkene (C1–C2) bond disconnections of [3]dendralenes.

In 2012, Misaki and coworkers [86] prepared three examples of compounds containing two hexa-substituted [3]dendralene subunits **148** using a double HWE



Scheme 1.20 Syntheses of dendralenes using Wittig reactions [82, 83].

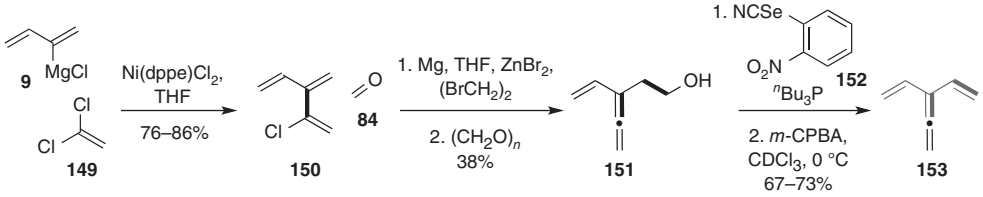


Scheme 1.21 Syntheses of dendralenes using double HWE reactions, by Misaki and coworkers [86].

reaction (Scheme 1.21). The starting materials were synthesized using Yoshida's method via a single electrophilic formylation to give the cross-conjugated diene aldehyde **146**.

Recently, Sherburn and coworkers [87] attempted to use Wittig olefination to synthesize 1-substituted [3]dendralenes, only to determine that [3]dendralenes featuring a 1*E*-conjugating substituent underwent rapid DA dimerization and could not be isolated. The Wittig reaction furnished only an isolated example of a 1*Z*-phenyl substituted [3]dendralene in low yield (20%), along with a mixture of three Diels–Alder dimerization products. This led to the development of a cross-metathesis approach involving tricarbonyl-iron complexed dendralenes, which is discussed in Section 1.4.

1,1-Divinylallene (**153**) is a dendralene prone to decomposition, but it could be isolated and characterized through a cautious approach [88]. The extreme sensitivity of this compound to dimerization and decomposition dictated that a mild elimination method be used to reveal the last alkene, after the C3–C3′ bond was established by Kumada cross-coupling (Scheme 1.22). The isolation of this compound (with a half-life of 43 h at 0.02 M) via this method suggests that similar strategies could be used to obtain and characterize highly reactive dendralenes.

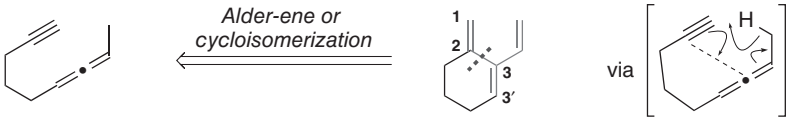


Scheme 1.22 Synthesis of 1,1-divinylallene, by Sherburn and coworkers, using a mild elimination method [88].

Finally, we note the absence of general cross-metathesis routes to functionalize preexisting dendralene frameworks. This is no doubt due to the reduced reactivity of conjugated alkenes in cross-metathesis reactions [87, 89]. A solution to this problem is addressed below, in Section 1.4.

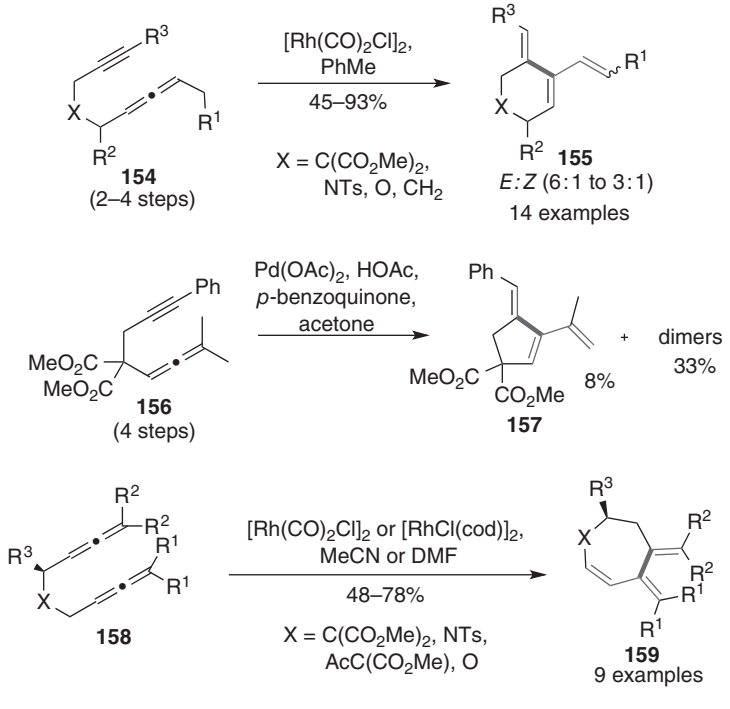
1.3.2
C2–C3 Alkenylation Reactions

Reactions that incorporate a new alkene onto an existing carbon framework, forming the C2–C3 bond, are very common (Scheme 1.23). From the 1970s onwards, a few examples of thermal rearrangements, Alder–ene reactions [90–93], and isomerizations that generally require harsh conditions and show limited scope were published. Hullio and Mastoi also reported an isolated example of a substituted [3]dendralene, prepared by pyridine-catalyzed addition of dimethylacetylene dicarboxylate to *trans*-cinnamyl aldehyde [94]. Developments in transition-metal catalysis have allowed much milder transformations with significantly enhanced scope. Foremost among these are the transition metal-catalyzed cycloisomerizations, which are formal Alder–ene reactions, that provide robust access to a wide variety of cyclic dendralenes, most especially 2,3′-cyclodendralenes [95–105]. For example, Brummond and coworkers reported



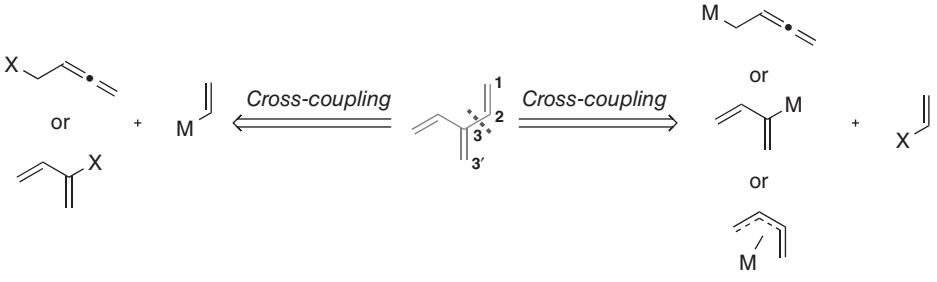
Scheme 1.23 Formation of dendralene via Alder–ene or metal catalyzed cycloisomerization reaction.

the rhodium(I)-catalyzed synthesis of 14 different cyclic [3]dendralenes **155** featuring a variety of different functional groups and heterocycles (Scheme 1.24) [99]. In many cases, mixtures of alkene isomers are observed. Iridium(I) [105], platinum(II) [107, 108], cobalt/rhodium nanoparticles [109], palladium(II) [68], rhodium(I) [69, 110], and gold(I) catalysts [108, 111, 112] have also been used to perform these and related cycloisomerizations, with the mechanism, scope, and limitations varying among catalysts. Recently, Deng and Bäckvall [106] reported another palladium(II)-catalyzed example, but it only formed dendralenes **157** as the unwanted by-products of acetoxylation reactions (Scheme 1.24). Aside from developments in the metal-catalyzed formal Alder–ene reaction, Malacria *et al.* and Mukai and coworkers have revisited the thermal variant, with some promising results [108, 113, 114]. A related reaction, the intermolecular ruthenium(II)-catalyzed coupling of cyclic allenes and alkynes, has also been used to synthesize a variety of 2,4-cyclo-[3]dendralenes [115]. Di-allenes are also useful substrates for similar transition-metal-catalyzed processes [71]. Lu and Ma reported Rh(I)-catalyzed cycloisomerizations of 1,5-diallenes **158**, to provide seven-membered heterocycle-containing [3]dendralenes **159** (Scheme 1.24) [69]. Where chiral, enantioenriched substrates were used, no significant racemization was observed under the reaction conditions.



Scheme 1.24 Representative examples of transition-metal-catalyzed cycloisomerization reactions forming the C2–C3 bond of cyclic [3]dendralenes [69, 99, 106].

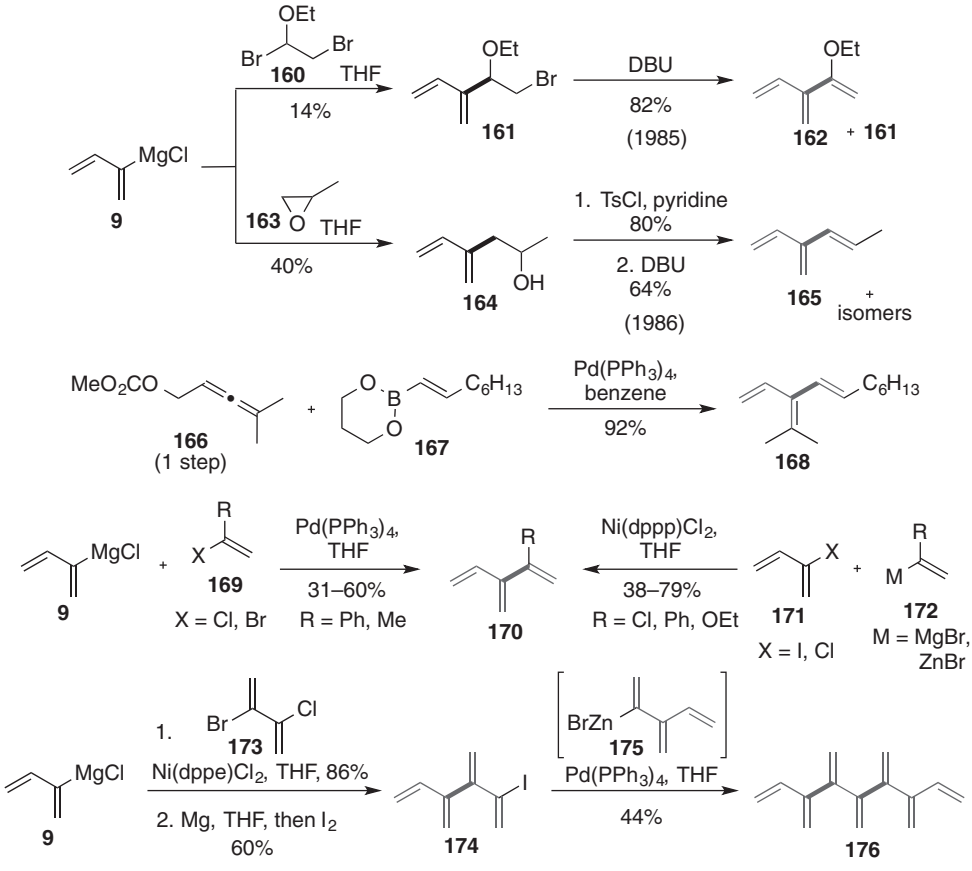
The first syntheses of dendralenes by C2–C3 bond formation (Scheme 1.25) were reported by Tsuge and coworkers in 1985 and 1986, and proceed via substitution at either a bromide **160** or an epoxide **163**, followed by elimination (Scheme 1.26) [116, 117]. Similar addition/elimination sequences to carbonyl groups or epoxides [120], and substitution reactions [121], followed. Such methods have been superseded by cross-coupling techniques that take place between a 2-functionalized 1,3-butadiene and an alkene (each can be either electrophilic or nucleophilic); or a 4-functionalized 1,2-butadiene and alkene, and occur with allylic transposition (Scheme 1.25). No doubt due to the ready availability of alkenyl halides and allenes, and the variety of increasingly mild and selective reaction variants, cross-coupling has provided access to a large number of diversely substituted dendralenes over the past 20 years, some of which have even been part of natural product syntheses [14, 122, 123].



Scheme 1.25 Alkenylation approaches to [3]dendralene via cross-coupling C2–C3 bond formation.

The first reports of cross-coupling routes to dendralenes were isolated examples in 1994 by Suzuki *et al.* (Scheme 1.26, **166** + **167** → **168**) [118] and 1998 by Allain *et al.* [124]. This early work paved the way for a more general approach featuring Kumada, Stille, and Negishi reactions to synthesize mono-substituted [3]dendralenes **170** and the parent dendralenes, developed by the Sherburn group (Scheme 1.26) [119]. Aside from cross-couplings with readily available alkenyl and butadienyl units, including the use of 3-sulfolene building blocks as "masked butadienes" to synthesize higher dendralenes [10, 125], the group also reported bond formations between higher dendralene cross-coupling partners, such as the Negishi cross-coupling of 2-iodo[4]dendralene (**174**) and the organozinc derivative of 2-chloro[3]dendralene (**175**) (Scheme 1.26) [23]. Double cross-coupling reactions that furnish the C2–C3 bond in addition to another bond, have already been discussed (Section 1.2.1).

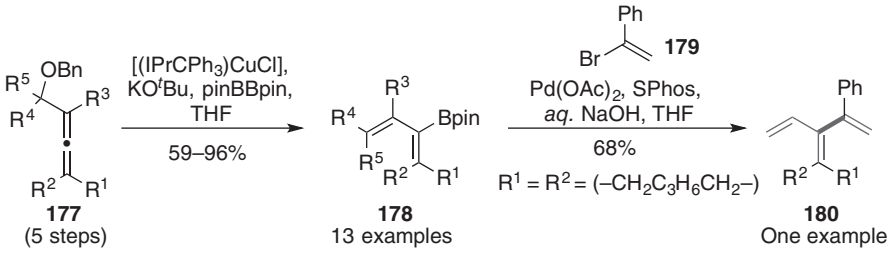
Recently, Tsuji and coworkers reported an isolated synthesis of a [3]dendralene **180** via a Suzuki–Miyaura cross-coupling reaction (Scheme 1.27) [126]. A variety of different 2-boryl-1,3-butadienes **178** were synthesized. While only one was coupled with an alkenyl halide **179**, these butadien-2-yl coupling partners **178**, in



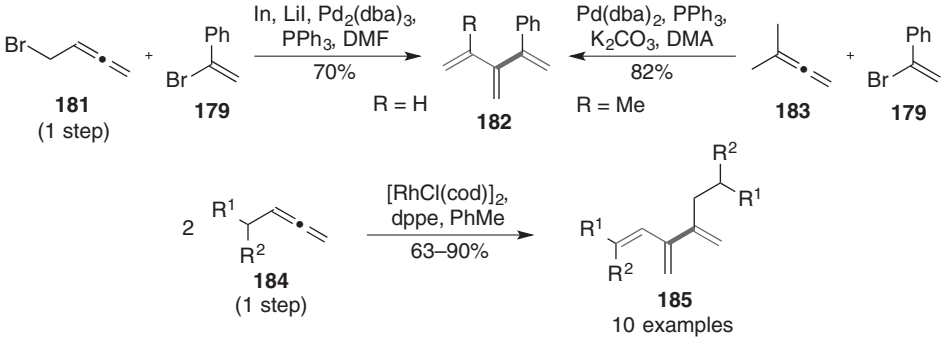
Scheme 1.26 Representative syntheses of dendralenes via C2–C3 bond formation, featuring either classical approaches or transition-metal-catalyzed sp^2–sp^2 cross-coupling [23, 116–119].

principle, offer a variety of building blocks to add to those already available for simple cross-coupling routes to dendralenes. 1,3-Butadien-2-yl cross-coupling partners have also been used in other Stille and Negishi cross-couplings [127–130].

Despite being a less obvious starting material than a 1,3-butadiene-2-yl coupling partner, 1,2-butadien-4-yl precursors (such as **166** in Suzuki's pioneering example in Scheme 1.26) have seen the most use in dendralene synthesis [118, 131–136]. A couple of more recent examples include the palladium-catalyzed cross-coupling reaction of alkenyl bromides **179** with, for example, the organoindium derived from allenyl bromide **181**, or 1,1-dimethyl allene (**183**) (via a Mizoroki–Heck reaction) (Scheme 1.28) [132, 135]. Palladium(0)-catalyzed dimerizations or homocouplings can also furnish the C2–C3 bond [138–142], as can nickel(0)- [143, 144] and rhodium(I)-catalyzed ones [137].

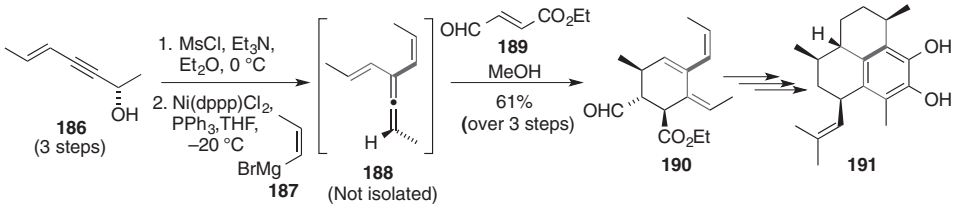


Scheme 1.27 Recent [3]dendralene synthesis by Tsuji and coworkers using a metallated butadiene [126].



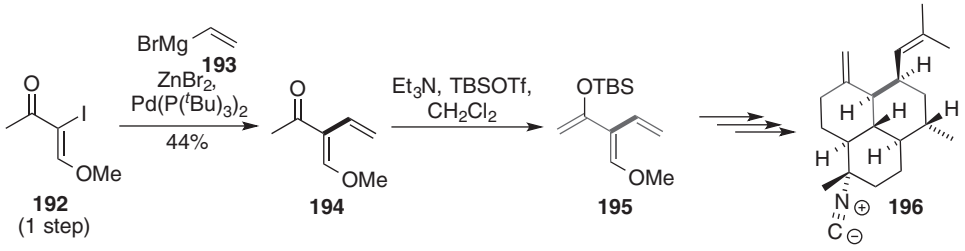
Scheme 1.28 Cross-coupling syntheses of [3]dendralenes using allene starting materials [132, 135, 137].

Two final examples of cross-coupling to furnish [3]dendralenes via C2–C3 bond formation are part of very short and efficient total syntheses, and highlight the versatility and attractiveness of the approach. As an extension of their work on 1,1-divinylallene (**153**) (Scheme 1.22), Sherburn *et al.* [123] synthesized allenic [3]dendralene **188** via Kumada cross-coupling of a metallated alkene **187** and a chiral, propargyl mesylate. A subsequent Diels–Alder reaction produced cyclic [3]dendralene **190** *en route* to a pseudopterosin aglycone **191** (Scheme 1.29). Allenic [3]dendralenes are prone to decomposition [136], so the subsequent DA reaction was carried out *in situ*.



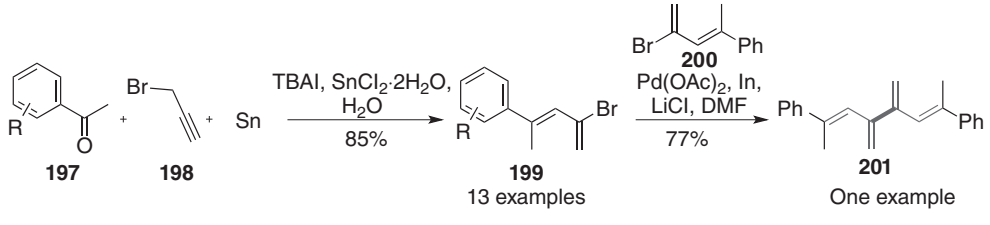
Scheme 1.29 Chiral [3]dendralene synthesis via sp^2–sp cross-coupling as part of a total synthesis by Sherburn and coworkers [123].

In another total synthesis involving a [3]dendralene, Pronin and Shenvi [122] synthesized a "Danishefsky dendralene" **195** using a Negishi cross-coupling reaction with a functionalized alkenyl iodide **192** followed by silyl enol ether formation to generate the dendralene (Scheme 1.30). A subsequent series of transformations, including two DA reactions, led to the total synthesis of amphilectene natural product **196**.



Scheme 1.30 [3]Dendralene synthesis via sp^2-sp^2 cross-coupling as part of a total synthesis by Pronin and Shenvi [122].

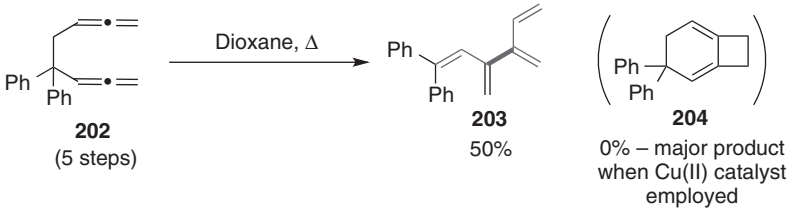
[4]Dendralenes have also been assembled by solo sp^2-sp^2 bond-forming reactions. The most prominently targeted C–C bond has been the central one. This approach is maximally convergent, and especially well suited to symmetrical targets. Li and coworkers [145] recently synthesized a symmetrical, 1,1,6,6-tetrasubstituted [4]dendralene **201** by a palladium(0)-catalyzed homocoupling reaction (Scheme 1.31). While only an isolated example of a [4]dendralene **201** was synthesized in this study, in principle, many different butadienyl halide-coupling partners **199** could be employed in this way. Other palladium-catalyzed homocouplings of functionalized 1,3-butadienes [146], and thermal oxidative homocoupling of highly electron-rich butadienes [147] have also been reported. In fact, the first practical synthesis of the parent [4]dendralene was an oxidative homocoupling of the chloroprene Grignard reagent [148].



Scheme 1.31 Synthesis of 2-bromo-1,3-butadienes and subsequent homocoupling to form a [4]dendralene, by Li and coworkers [145].

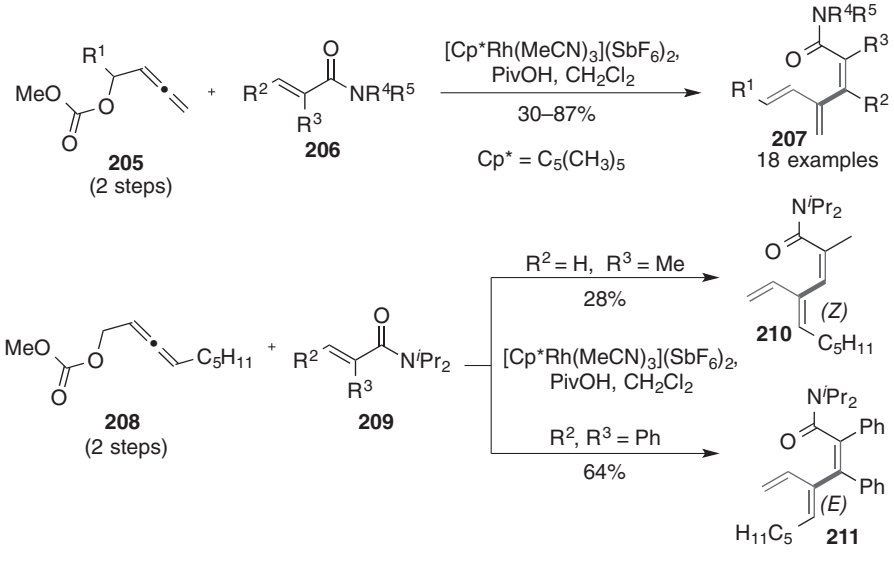
Isomerizations and rearrangements featured heavily in early approaches to [4]dendralene and derivatives [17, 149–155]. An interesting, recent case of unsymmetrical [4]dendralene formation was reported by Mukai and coworkers in

2012 (Scheme 1.32) [156]. Cu(II)-promoted intramolecular [2+2] cycloaddition of 1,4-diallenes **202** yielded bicyclooctadienes **204**; however, under uncatalyzed thermal conditions, the authors noted that the formal [3,3]-sigmatropic rearrangement product, [4]dendralene **203**, was formed in 50% yield. If optimized, this presents a nice method to form unsymmetrical [4]dendralenes, but relies on a lengthy synthesis of starting materials.



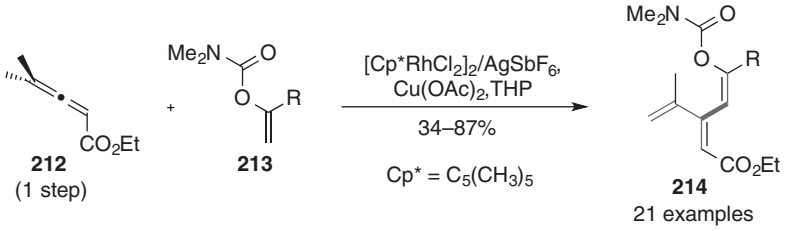
Scheme 1.32 Thermal isomerization synthesis of an unsymmetrical [4]dendralene by Mukai and coworkers [156].

C–H activation is an important and rapidly developing area of dendralene synthesis. In very recent years, several C2–C3 bond forming approaches to dendralenes involving C–H activation have been reported. In 2013, Glorius and coworkers developed a Rh(III)-catalyzed, Heck-type alkenyl C–H activation and coupling reaction with allenyl carbinol carbonates **205** and acrylamides **206** (Scheme 1.33) [157]. This new reaction performs well for the synthesis of highly substituted [3]dendralenes.



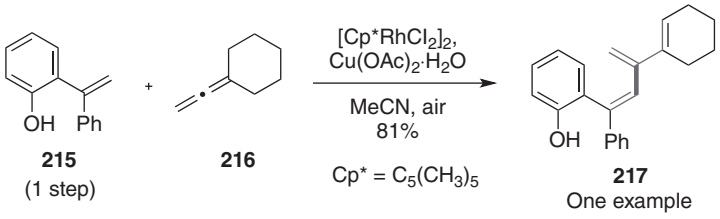
Scheme 1.33 Rh(III)-catalyzed Heck-type C–H activation of carbonates by Glorius and coworkers [157].

A similar transformation was subsequently reported in 2014 by Fu and coworkers, who used allene and carbamate precursors to generate [3]dendralenes via rhodium(III) catalysis (Scheme 1.34) [158]. A variety of different carbamates **213** successfully underwent Rh(III)-catalyzed C–H activation and coupling to generate cyclic and acyclic substituted [3]dendralenes **214**. While the general route works quite well between the tri-substituted allene and acyclic carbamates, the reaction is not high yielding if the enol ester is cyclic or the allene is mono- or tetra-substituted.



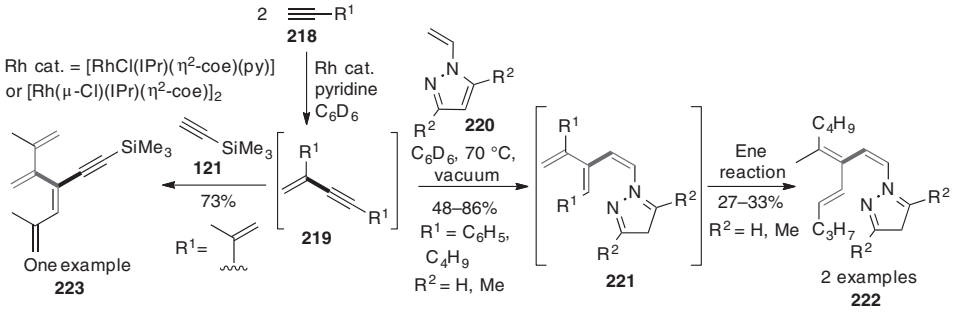
Scheme 1.34 Rh(III)-catalyzed C–H activations of carbamates by Fu and coworkers [158].

Another C–H activation method that has potential in the synthesis of dendralenes was reported by Gulías and coworkers in 2015 (Scheme 1.35) [159]. A stable dendralene intermediate **217** was prepared from substituted phenol **215** and allene **216**, as an intermediate in the Rh(III)-catalyzed synthesis of 2*H*-chromenes. In principle, this method could be adapted to target substituted dendralenes.



Scheme 1.35 Rh(III)-catalyzed allene alkenylation by Gulías and coworkers [159].

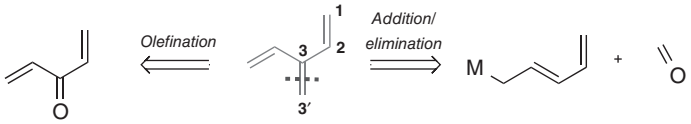
A final recent contribution to C–H activation-based methods is the work by Oro and coworkers, who reported the Rh(I)-catalyzed hydrovinylation of alkynes **218** with *N*-vinylpyrazoles **220** to form pyrazole-containing [3]dendralenes **221** (Scheme 1.36) [160, 161]. Some of these dendralenes could also be subjected to thermal Alder–ene reactions to alter the substitution pattern on the dendralene products.



Scheme 1.36 Rh(I)-catalyzed hydrovinylation of alkynes by Oro and coworkers, and a subsequent ene reaction, to synthesize [3]dendralenes [160, 161].

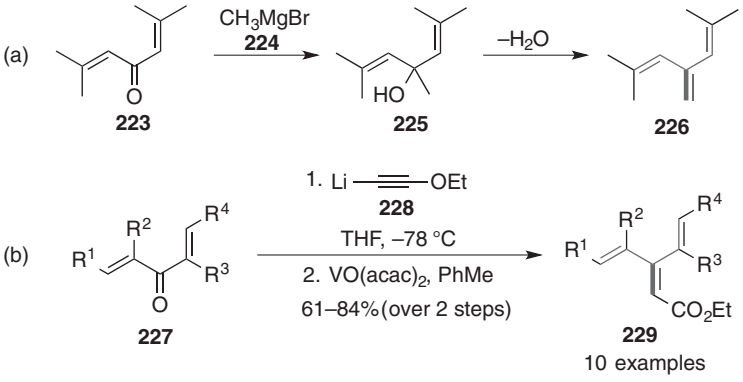
1.3.3
C3–C3′ Alkenation Reactions

The first example of a dendralene synthesis via C3–C3′ bond formation (Scheme 1.37) dates back to 1904, when Fellenberg reported an addition/elimination sequence between methyl magnesium bromide (**224**) and phorone (**223**) (Scheme 1.38 (a)) [162]. Since then, a number of variations leading to different substituents have been reported. In fact, early syntheses of dendralenes prominently feature the C3–C3′ bond disconnection, utilizing classical reactions such as Wittig reactions [165–175], HWE olefination [176–178], ketene additions/decarboxylation sequences [179–183], and Grignard addition/dehydration sequences [162, 184, 185] to transform readily available 1,4-dien-3-ones into dendralenes. Recently, West and coworkers made several cyclic and acyclic derivatives of substituted [3]dendralenes **229** through catalytic Meyer–Schuster rearrangements of propargyl alcohols derived from alkyne **228** addition to dienones **227** (Scheme 1.38 (b)) [163, 164]. It was found for these highly substituted dendralenes that if the dienone **227** was not symmetrical, mixtures of (*E*) and (*Z*) alkene isomers were formed. Despite this limitation, a very noteworthy feature of the work is the use of a less substituted dienone **227** starting material – prior to this, only highly substituted variants had been employed.

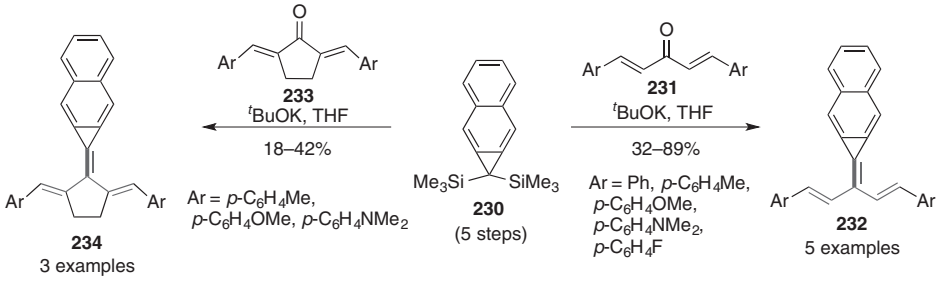


Scheme 1.37 Single alkenation (C3–C3′) bond disconnections of [3]dendralene.

Other variants of olefination have also been applied to dendralene synthesis [186–188]. In 2004, Dixon and Halton [189] prepared a variety of cyclic [3]dendralenes using Peterson-type olefination reactions (Scheme 1.39). These



Scheme 1.38 (a) Addition/elimination sequence by von Fellenberg [162] and (b) Meyer–Schuster rearrangement by West and coworkers [163, 164].

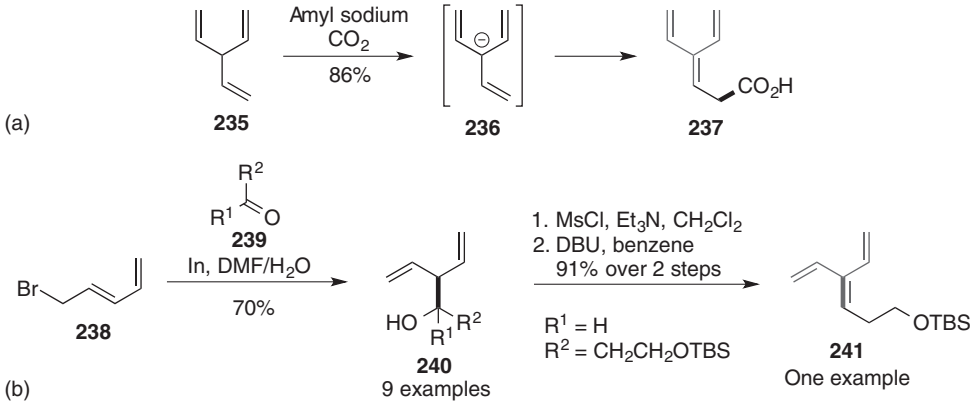


Scheme 1.39 Peterson-type olefination approach to [3]dendralenes by Dixon and Halton [189].

examples feature symmetrical dienone starting materials, so the stereoselectivity of the Peterson olefination approach to dendralenes is yet to be tested.

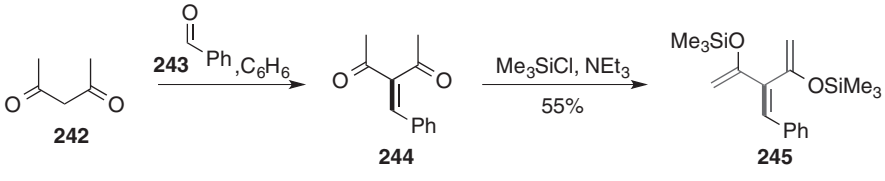
Another way to circumvent the stereoselectivity issues that may arise from olefination or addition/elimination sequences to 1,4-dien-3-ones is to switch the polarity of components and olefinate a carbonyl compound with a symmetrical nucleophilic pentadienyl anion equivalent. A seminal contribution was reported by Paul and Tchelitcheff in 1951, who combined trivinylmethane (**235**) and carbon dioxide to form a [3]dendralene **237** (Scheme 1.40 (a)) [190]. In this instance, the anion of trivinyl methane **236** is indeed a pentadienyl anion, but bond formation occurs with allylic transposition through a vinyl unit.

Fallis and coworkers [191, 192] have synthesized substituted [3]dendralenes using a similar approach, by reacting indium metal with bromodiene **238**, and using the resulting indium pentadienyl species in addition/elimination sequences with a number of functionalized aldehydes or ketones **239** (Scheme 1.40 (b)). This strategy builds on work by the Miginiacs in 1964 [193], and has also seen subsequent use [12, 194–196].



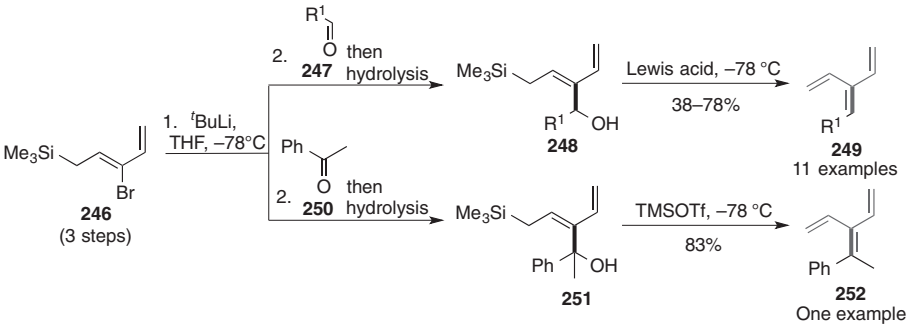
Scheme 1.40 [3]Dendralene synthesis using (a) a trivinyl methide anion [190] and (b) an indium pentadienyl nucleophile [191, 192].

A separate approach to this bond formation is the Knoevenagel condensation of a 1,3-diketone with a carbonyl compound, followed by conversion of the carbonyl groups to alkenes. For example, in 1983 Tsuge and coworkers reported condensation between diketone **242** and benzaldehyde (**243**), followed by double silyl enol ether formation to generate a [3]dendralene **245** (Scheme 1.41) [197–199]. The ready availability of the carbonyl compounds involved suggests that this method could be useful for other substituted dendralenes. Silyl enol ether formation to generate a [3]dendralene was subsequently used to great effect in total synthesis by Pronin and Shenvi (Scheme 1.30, [122]). The Knoevenagel condensation can also be performed with different electrophiles, followed by chlorinative dehydration to reveal a dihalodendralene [200, 201], or hydride reduction/elimination to reveal a terminally unsubstituted [3]dendralene [202].



Scheme 1.41 A Knoevenagel condensation/silyl enol ether formation approach to a [3]dendralene [197].

Recently, a Peterson-type olefination variant of this strategy was explored by Parrain and coworkers [203]. By incorporating a trimethylsilyl group in the pentadienyl anion equivalent **246**, alcohols **248** that readily undergo Lewis-acid-catalyzed γ-elimination were formed as addition products of aldehydes **247** (Scheme 1.42). The one-step, facile elimination is an improvement on the mesylation/elimination approach of Fallis. Interestingly, while alcohols of the type **248** and **251** bearing different, substituted alkenyl substituents have been



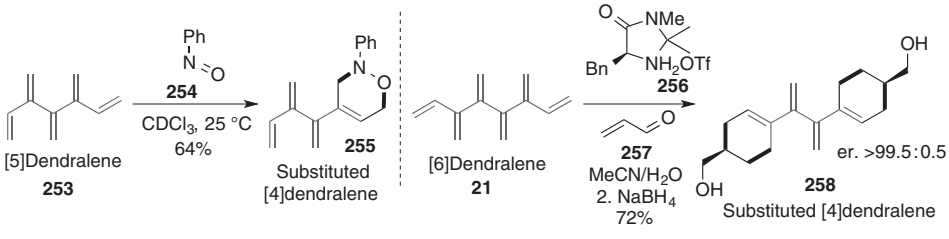
Scheme 1.42 Syntheses of dendralenes via Peterson-type olefination by Parrain and coworkers [203].

prepared [204], the corresponding elimination reactions (now with the possibility of forming mixtures of (*E*) and (*Z*) isomers), do not appear to have been reported. This presents an avenue worthy of further investigation.

1.4 Dendralenes from Dendralenes

Aside from the synthesis of dendralenes from nondendralenic materials, there also exist a variety of transformations that can be applied to a preexisting dendralene framework to add further functionality. Most of these examples form part of exploratory studies to test the reactivity of dendralenes; nevertheless, they show potential for the synthesis of a variety of functionalized dendralenes. Broadly, these can be divided into transformations that reduce the length of the [*n*]dendralene framework (e.g., $n \rightarrow n-1$), ones that functionalize and preserve an existing [*n*]dendralene framework (i.e., $n \rightarrow n$), or ones that add extra branched alkenes to form a higher [*n*]dendralene (e.g., $n \rightarrow n+1$).

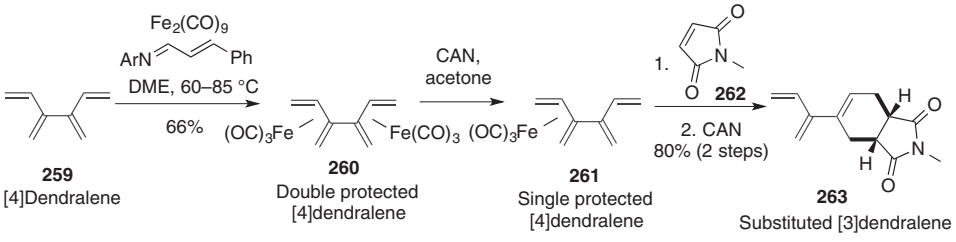
In the first category, the Sherburn group, the first to synthesize the parent family of dendralenes, have documented a number of transformations that result in the conversion of a higher dendralene into a lower one. [5]Dendralene (**253**) and



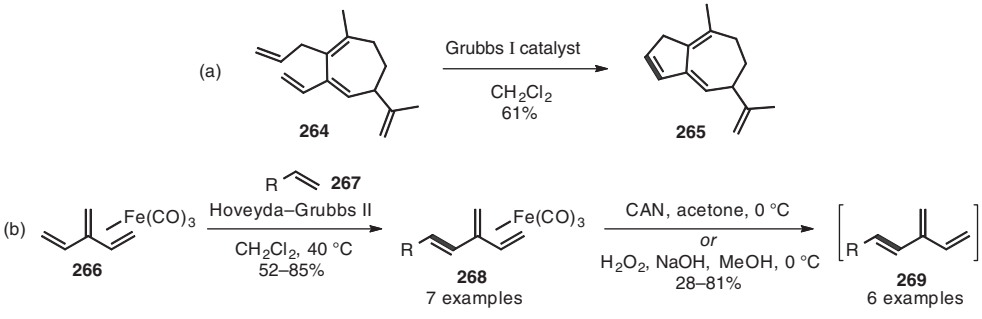
Scheme 1.43 Hetero-DA and enantioselective DA reactions of dendralenes from the Sherburn group [205, 206].

higher [*n*]dendralenes undergo DA reactions to furnish [*n* – 1]dendralenes. Aside from reactions with *N*-methylmaleimide (NMM) (**262**) [19, 20, 23, 89, 148] and SO_2 [10], these include hetero-DA reactions to form heterocycle-containing dendralenes **255** [205], and enantioselective DA reactions to form chiral, enantioenriched dendralenes **258** [206] (Scheme 1.43).

Singly complexed tricarbonyliron-[4]dendralene **261** (prepared from [4]dendralene (**259**)) [89, 207] can be reacted with NMM (**262**) to undergo a single DA reaction at a terminal diene site to produce, after decomplexation, a reactive [3]dendralene **263** (Scheme 1.44), which cannot be isolated by reacting uncomplexed [4]dendralene (**259**) and dienophiles (see Chapter 12). Complexation and reaction, therefore, provides a viable avenue toward dendralenes not isolable from other reaction conditions.



Scheme 1.44 Tricarbonyl iron-complexed dendralenes enabling the synthesis of a formal terminal single DA-adduct of [4]dendralene [89].

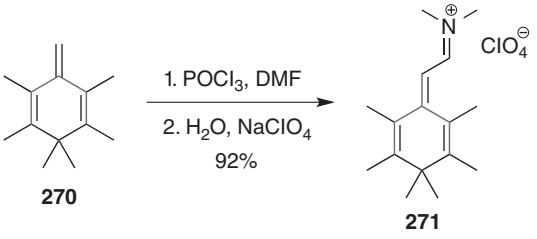


Scheme 1.45 Examples of (a) RCM [120] and (b) cross-metathesis using dendralene precursors [87, 89].

Dendralenes may also be functionalized at one of the alkene positions without destroying the alkene. An interesting case is the ring-closing metathesis (RCM) reaction of cyclic dendralene **264**, using Grubbs I catalyst, to form a bicyclic dendralene **265**, maintaining the [3]dendralene framework (Scheme 1.45 (a)) [120]. In contrast to the "naked" parent dendralene, tricarbonyliron-complexed [3]dendralene (**266**) undergoes smooth cross- and homometathesis reactions to furnish

a variety of highly reactive, 1*E*-substituted [3]dendralenes **269** (Scheme 1.45 (b)) [87, 89].

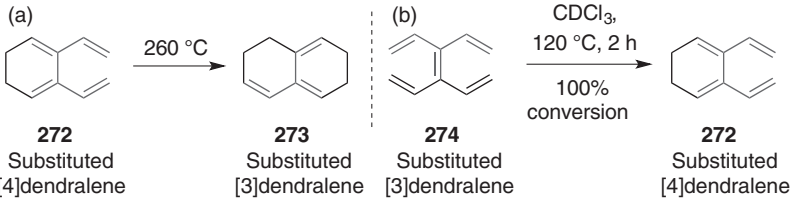
Instances where a dendralenic alkene participates as a nucleophile in an addition or substitution, and the alkene is regenerated by elimination, appear surprisingly rare. One such example is the preparation of the Vilsmeier salt **271** of cyclic [3]dendralene **270** (Scheme 1.46) [208]. Formylation of very electron-rich dendralenes has also been reported, such as part of the iterative formylation/olefination sequence to build higher dendralenes reported by Yoshida *et al.* (Scheme 1.20) [82].



Scheme 1.46 Synthesis of the Vilsmeier salt of a cyclic [3]dendralene [208].

Halodendralenes are valuable substrates for dendralene to dendralene transformations that preserve or extend the dendralene framework. They are intermediates in the synthesis of [7]- and [8]dendralene (Scheme 1.26) [23], as are their nucleophilic relatives, pinacolatoboryldendralenes, in the synthesis of substituted [4]-, [5]-, and [6]dendralenes [25, 27]. (Pseudo)halodendralenes have also been used in Stille [209] and Sonagashira cross-couplings [178, 210]. Dendralene dimers can be obtained via homocoupling of halodendralenes [211]. Dendralene frameworks can also be extended by uncatalyzed metathesis reactions on alkyne-containing dendralenes, and olefination reactions on carbonyl-containing ones [1, 211–214], each of which has been discussed.

Rearrangements and isomerizations can lead to either an extension or a reduction of an existing dendralene framework. For example, the Cope rearrangement shown in Scheme 1.9 converted a [3]dendralene **63** to a [4]dendralene



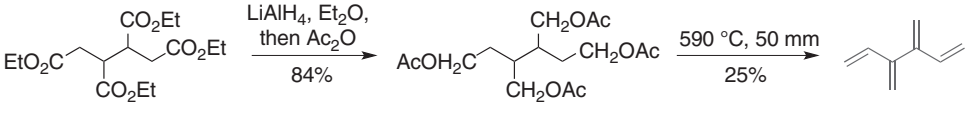
Scheme 1.47 Isomerization reactions that either reduce [215] or extend the dendralene framework [19].

64, while changing the path of the dendralene backbone. In contrast, rearrangement and electrocyclic ring closure of [4]dendralene **272** leads to bicyclic [3]dendralene **273** (Scheme 1.47 (a)) [215]. **272** is itself the product of thermally or photochemically promoted electrocyclic ring closure of TVE (**274**) (a [3]dendralene), (Scheme 1.47 (b)) [19]. The intramolecular Alder–ene reaction of a [3]dendralene reported by Oro and coworkers in Scheme 1.36 provides an example of an isomerization that neither reduces or extends the dendralene framework, but does alter the connectivity [160, 161].

Elimination reactions to reveal masked dendralenes featured prominently in early attempts to synthesize cross-conjugated compounds [1]. Cheletropic extrusion of sulfur dioxide was used to convert lower dendralenes to [5], [6], and [8]dendralene [10], and to make substituted chiral [4]dendralenes [12].

1.5
Functional Group Interconversion Reactions

Our review has focused on syntheses of dendralenes that construct the carbon framework via carbon–carbon bond formation. While almost all strategies ultimately rely on carbon–carbon bond formation, some are better considered as distinct isomerization or functional group interconversion strategies that unmask a hidden dendralene. For example, one of the earliest syntheses of [3]dendralene (**5**) [216], and the very first synthesis of [4]dendralene (**259**) (Scheme 1.48) [217], proceed from commercially available starting materials without any carbon–carbon bond formations. Therefore, while we have taken note in each section of strategies that, while ultimately relying on an elimination or isomerization, have included an earlier key carbon–carbon bond-forming reaction, there are a number of somewhat esoteric strategies that we have not mentioned in this review. These approaches, which typically feature long sequences of steps to form synthetic intermediates primed for a key thermal elimination and/or isomerization, and are therefore limited in their preparative utility, are more prevalent in the early literature, and are very well summarized by Hopf's earliest review [1], with more recent variations being covered by the 2012 review of Hopf and Sherburn [2].



275 **276** **259**

Scheme 1.48 The first synthesis of [4]dendralene, by Bailey and Nielsen, has no C–C bond forming events [217].

1.6 Concluding Remarks

By categorizing syntheses of dendralenes based on the carbon–carbon bonds formed in their approach, it is clear that over the past few decades there has been a massive shift away from lengthy and scope-limited isomerization and elimination-based strategies to unmask dendralenes, toward direct formation of functionalized dendralene frameworks via carbon–carbon bond-forming reactions. A plethora of techniques to directly and rapidly access dendralenes with a wide variety of substitution levels and functionality now exist. Some of these reactions, the most notable example being C–H activation, have only very recently enjoyed intense research focus. Given the number of short and practical preparative methods that now exist for the preparation of dendralenic structures, selective "dendralene to dendralene" functionalization reactions are also likely to see significant growth in the near future. It is therefore likely that the current trend of rapid expansion in synthetic means to dendralenes will continue strongly, driven by research in these areas, and in other reactions that are yet to be realized.

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