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Diverse strategic approaches *en route* to Taxol total synthesis

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ABSTRACT

Taxol is one of the most famous diterpenoid natural products used in clinical cancer therapy. Taxol and its analogues are popular synthetic targets and have attracted worldwide attention over the past decades. Tremendous research efforts have already been made and ten groups have achieved the total synthesis of Taxol since 1994. This mini-review summarized the recent highlights of divergent strategic approaches towards the chemical synthesis of Taxol's carbocyclic framework bearing a bridged eight-membered ring.

1. Introduction

Taxol (**1**) is a complex polyoxygenated diterpenoid natural product which was originally isolated from the bark of *Taxus brevifolia* by Wall and co-workers [1]. Taxol is a well-known anticancer drug with a unique molecular mechanism for various human cancers [2–4], which has promoted significant interests from chemical and biological communities. The source of Taxol has always been a primary concern since its discovery due to the extremely low content in the natural plant [5]. Considerable efforts have been devoted to find alternative sources to natural harvesting of Taxol, including: (1) total synthesis, (2) semi-synthesis, (3) microbial systems, and (4) plant cell fermentation. Among them, the chemical semi-synthesis and plant cell fermentation of the *Taxus* species are documented as the clinical supply of Taxol.

Accordingly, no natural product discovered in the last decades has stimulated as much public interests as Taxol. Structurally, Taxol has a highly strained 6–8–6 tricyclic carbocyclic core with two all-carbon quaternary stereocenters and a bridgehead double bond (Fig. 1). The potent bioactivity and intriguing chemical complexity of this oxygenated polycyclic diterpenoid has attracted considerable interests from the synthetic communities. Indeed, more than hundreds of reports presenting synthetic studies have been documented since the landmark total synthesis of Taxol achieved by Holton and Nicolaou groups in 1994, including ten total syntheses of Taxol (Fig. 2) [6–20]. It has been noted that the nature of substituents plays an important role in the construction of conformationally flexible central eight-membered ring. Various synthetic strategies including coupling reaction, ring-closing metathesis, oxy-Cope rearrangement, Diels–Alder reaction, radical cyclization, and ring expansion have been well developed to construct the eight-membered core ring. To maintain the coherence and focus of this review, the well-known success total syntheses of Taxol (Fig. 2) will not discuss further herein. Therefore, this mini-review mainly highlights on the diverse strategic approaches *en route* to Taxol's total synthesis, covering mainly the literature reports since 1995 [21–24].

2. Biomimetic approaches to Taxol

Early in 1966, Lythgoe and co-workers proposed a biosynthetic pathway, which suggested that the tricyclic carbon framework of the taxoids was envisioned to derive from geranylgeranyl pyrophosphate (GGPP) through intramolecular cyclization [25,26]. Based on feeding studies by Croteau and co-workers, the proton at C11 of intermediate **3** shifted to C7 to generate carbocation intermediate **4**, followed by transannular cyclization to afford the taxa-4(5),11-(12)-diene **5** as the final product of the cyclase phase [27–29]. Notably, several research groups including Croteau, Coates, Floss, Pattenden and Williams have also proposed that biosynthetic pathway of Taxol can be conceptually divided into several discrete stages, namely: cyclization, stereospecific oxidation, acylation, benzoylation, and assembly of C13-side chain (Scheme 1) [30–35].

In 1985, Pattenden and co-workers reported the total synthesis of verticillene (**8**), an assumed biosynthetic precursor of Taxol, by

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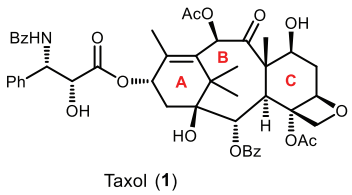
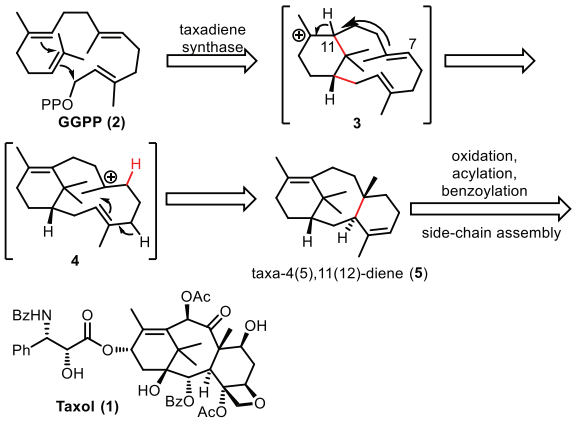
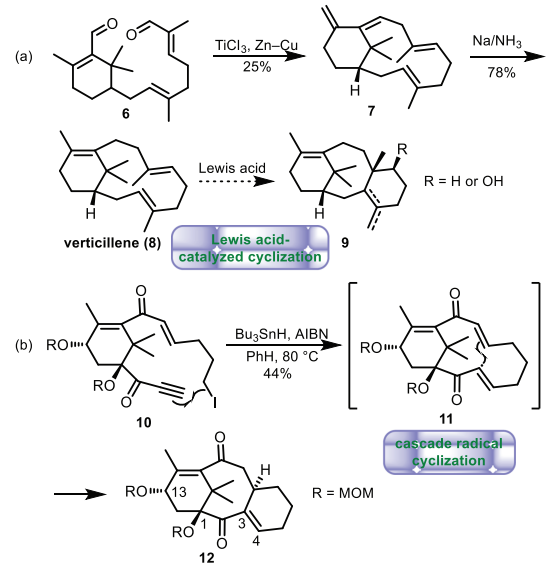


Fig. 1. The structure of Taxol.



Scheme 1. Proposed biosynthetic pathway of Taxol.

an intramolecular reductive carbonyl coupling as key step [34,36]. Treatment of dialdehyde **6** with titanium trichloride and Zn–Cu couple, followed by 1,4-reduction gave verticillene **8**. However, various Lewis acid-catalyzed biomimetic transannular cyclization of **8** or its isomers failed to yield the desired tricyclic products **9** (Scheme 2a) [37]. In 2009, the same group developed a cascade radical cyclization strategy leading to the 6–8–6 tricyclic core of Taxol [38–40]. Treatment of the radical precursor **10** with Bu_3SnH and AIBN in PhH at 80 °C afforded the desired tricycle **12** *via* presumably the intermediate **11** through the radical transannular cyclization. It is worthy to note that **12** contains oxidative substitutions at C1, C13 with desired stereochemistry and an unsaturated bond at C3–C4 (Scheme 2b).



Scheme 2. Pattenden's biomimetic approaches through Lewis acid-catalyzed and cascade radical cyclization (1985–2009).

In 1997, Takahashi and co-workers reported their biomimetic approach [41]. The aldol condensation of citral derivative **13** with γ-butyrolactone **14** generated compound **15** with three stereogenic centers at positions C1, C2 and C11 respectively, which corresponds to Taxol. A seven-step sequence of reduction of lactone, cyanoaddition, and protection of hydroxyl groups afforded cyanohydrin

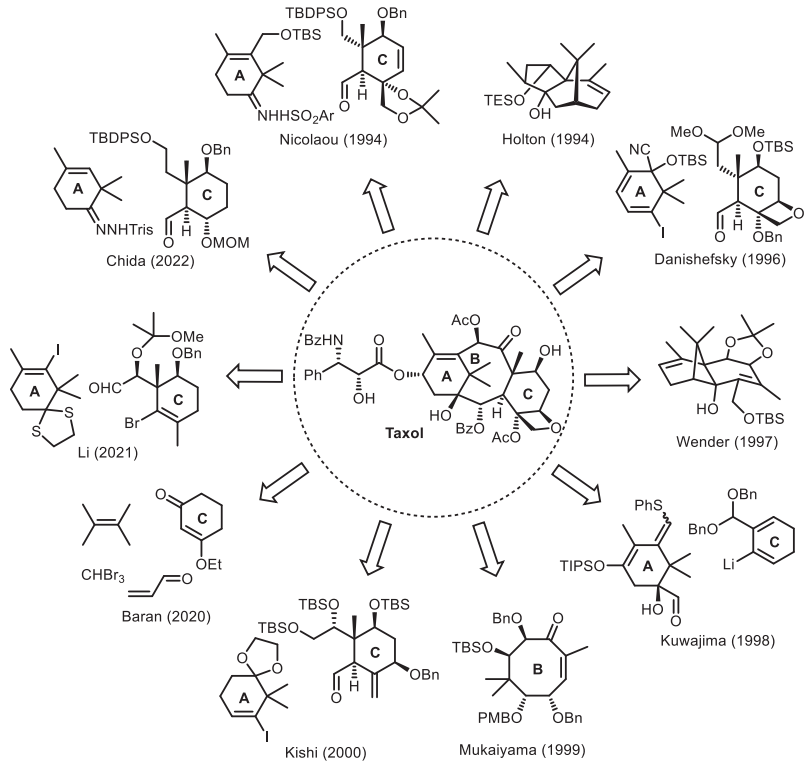
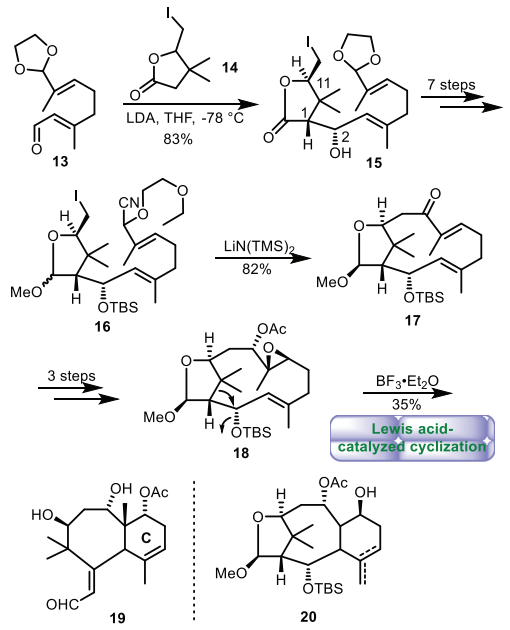
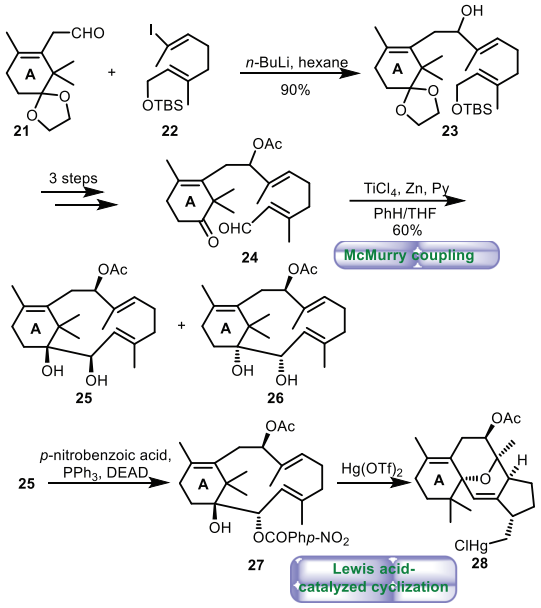


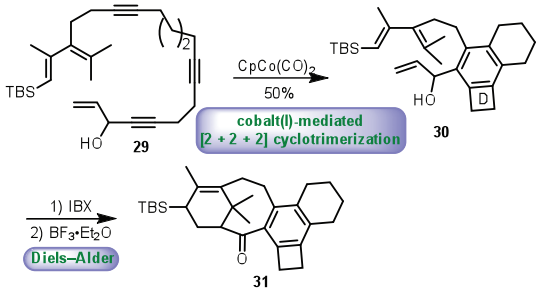
Fig. 2. The ten-total synthesis of Taxol.



Scheme 3. Takahashi's biomimetic approach through Lewis acid-catalyzed cyclization (1997).



Scheme 4. Nishizawa's biomimetic approach through McMurry coupling and Lewis acid catalyzed cyclization (1998).



Scheme 5. Malacria's approach to the tricyclic ring system through cobalt(I)-mediated [2+2+2] cyclotrimerization and intramolecular Diels–Alder reaction (2002).

ether **16**. Then intramolecular alkylation of **16** efficiently formed the 12-membered ring intermediate **17** in 82% yield. A three-step sequence of reduction, epoxidation, and acetylation gave acetate **18** in 87% yield. However, all attempts of acid-catalyzed cyclization to the formation of B/C ring of Taxol failed, instead rearrangement product bicyclo[5.4.0]undecene **19** bearing the desired six membered C-ring was obtained (Scheme 3).

In 1998, Nishizawa and co-workers reported synthetic efforts toward biomimetic construction of the taxane skeleton *via* transannular cyclization [42,43]. The aldol reaction of acetal aldehyde **21** with vinyl iodide **22** gave alcohol **23** in 90% yield. A three-step sequence of protection of hydroxyl group, cleavage of acetal and TBS groups, and Swern oxidation provided ketoaldehyde **24**. $TiCl_4$–Zn promoted McMurry coupling yielded diols **25** and **26** with bicyclo[9.3.1]pentadecatriene skeleton in 60% yield. However, all attempts to achieve the biomimetic transannular cyclization leading to the B/C ring system of Taxol failed and an unexpected rearrangement product **28** was obtained (Scheme 4). Although the biomimetic synthesis of Taxol has not yet achieved to date, the studies along this direction have enriched our understanding of the unique role of Taxol synthases in the plant biosynthesis assembly. Future research would be much needed to simulate the delicate conformational control of the GGPP precursor for a smooth tandem cationic C–C bond-forming and transannular cyclization to the core ring system with proper stereochemical control.

3. Linear strategies toward A/B/C ring core

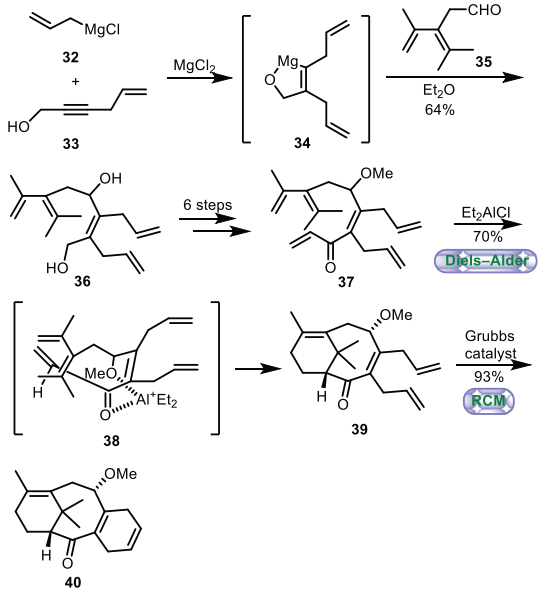
Among the strategies applied to the construction of the A/B/C ring core of Taxol, linear strategy is widely developed to the synthesis of challenging taxane framework, including Diels–Alder strategy, A to A/B/C strategy, and C to A/B/C strategy.

3.1. Diels–Alder strategy

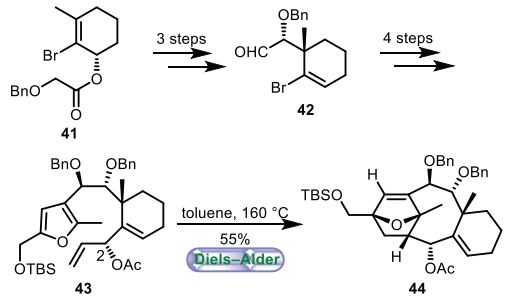
In 2002, Malacria and co-workers described the combination of cobalt(I)-mediated [2+2+2] cyclotrimerization and intramolecular Diels–Alder reaction to construct the 6–8–6 tricyclic core of Taxol [44]. Exposure of polyunsaturated precursor **29** to $CpCo(CO)_2$ afforded alcohol **30** with all carbon D ring in 50% yield. Next, oxidation of the secondary alcohol with IBX, followed by $BF_3{\cdot}Et_2O$ mediated intramolecular Diels–Alder reaction afforded the desired pentacyclic framework **31** as only one diastereomer (Scheme 5).

In 2003, Fallis and co-workers also applied intramolecular Diels–Alder reaction coupled with the ring-closing metathesis to the synthesis of 6–8–6 tricyclic core of Taxol [45,46]. The sequential combination of Grignard reagent **32** with alcohol **33** generated the magnesium chelate **34** *in situ*, followed by condensation with aldehyde **35** to afford the diol **36** in 64% yield. A six-step sequence of selective protection the secondary alcohol, oxidation the primary alcohol, Grignard addition, and oxidation of the resulting secondary alcohol was preformed, thus converting **36** to the Diels–Alder precursor **37**. With the key intermediate **37** in hand, the desired Diels–Alder cycloaddition was smoothly performed, thus affording the adduct **39** as a single diastereomer *via* chelation control model **38**. Lastly, the bicycle **39** annulated to give 6–8–6 tricyclic ring-system **40** by ring-closing metathesis (Scheme 6).

In 2018, Li and co-workers documented a highly concise and elegant enantioselective synthesis of the 6–8–6 tricyclic core of taxezopidine A and B [47]. The aldehyde **42** was prepared from **41** based on Shea's work [48,49], which includes glycolate Ireland–Claisen rearrangement, reduction, and Swern oxidation. Next, treatment of **42** with bromofuran and subsequent transformations of functional groups gave **43**. Then the type II intramolec-



Scheme 6. Fallis's approach to the tricyclic ring system through Diels–Alder reaction and ring-closing metathesis (2003).



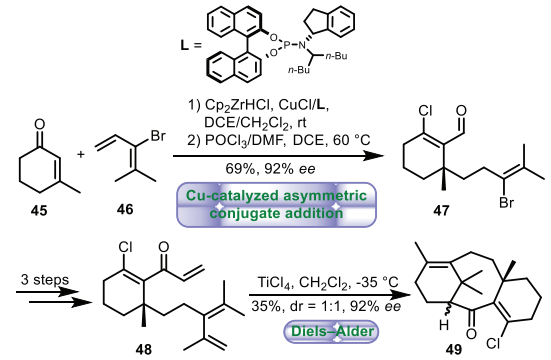
Scheme 7. Li's approach to the tricyclic ring system through type II intramolecular Diels–Alder furan reaction (2018).

ular Diels–Alder furan reaction of **43** was carried out, thus giving 6–8–6 tricyclic core of Taxol **44** as a single diastereomer in 55% yield. It is worthy note that the acetoxy group at the allylic position of **43** is crucial for high diastereoselectivity (Scheme 7).

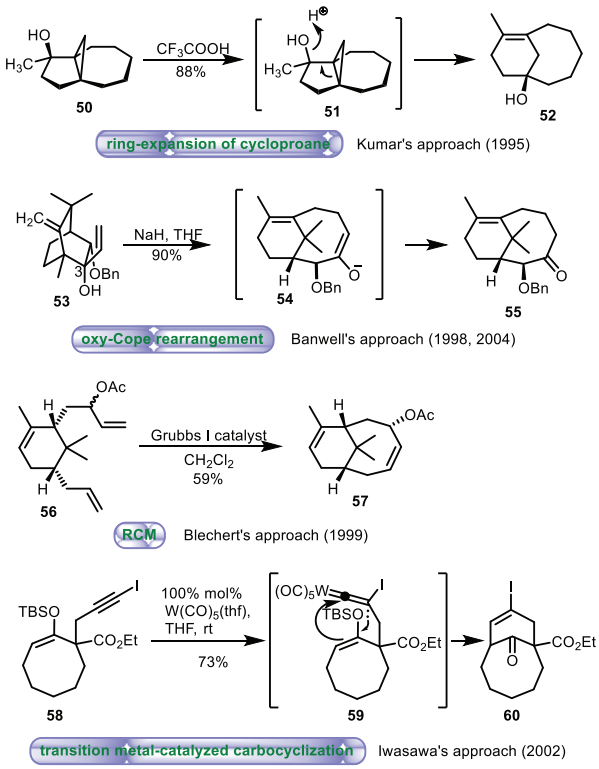
In 2020, Fletcher and co-workers described the concise procedure to prepare the Taxol core by type II intramolecular Diels–Alder reaction and Cu(I)-catalyzed asymmetric conjugate addition [50]. The addition reaction of cyclohexanone **45** and alkyl zirconocene (generated from bromodiene **46** and Cp_2ZrHCl) with copper-phosphoramidite complexes as catalyst followed by Vilsmeier–Haack reaction generated β-chloroaldehyde **47** in 69% yield with 92% *ee*. A three-step sequence of Grignard addition, Suzuki–Miyaura reaction, and oxidation of the resulting secondary alcohol afforded the intermediate **48**. Finally, treatment of **48** with $TiCl_4$ in CH_2Cl_2, the Diels–Alder reaction proceeded smoothly to give tricyclic ring core **49** in 35% yield with 1:1 *dr* and 92% *ee* (Scheme 8).

3.2. A to A/B/C strategy

The A/B ring system of Taxol contains bicyclo[5.3.1]undecane, which has attracted considerable attention since Taxol's discovery. Significant efforts have been made regarding to synthesis of A/B ring, such as ring-expansion of cyclopropane [51–53], oxy-Cope rearrangement [54–57], ring-closing metathesis [58–60], transition metal-catalyzed carbocyclization [61,62] and so on (Scheme 9).



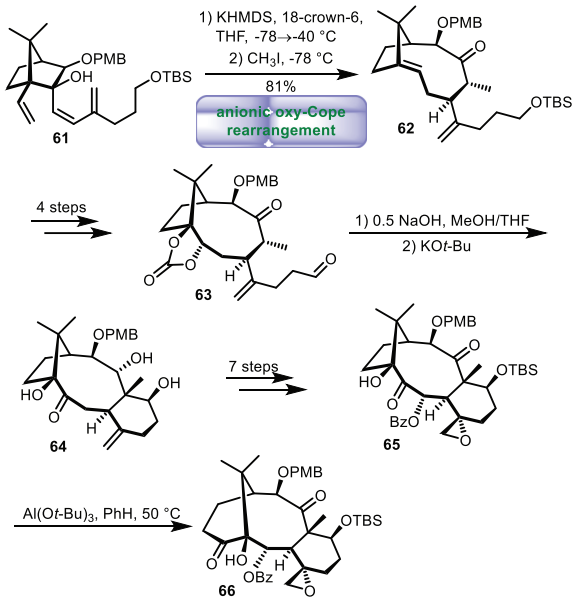
Scheme 8. Fletcher's approach to the tricyclic ring system through type II intramolecular Diels–Alder reaction and Cu(I)-catalyzed asymmetric conjugate addition (2020).



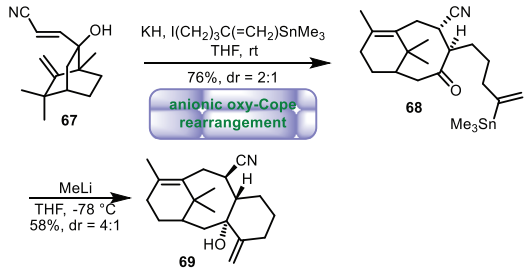
Scheme 9. Selected strategies to the A/B ring system.

During the past decades, Paquette and co-workers made remarkable efforts to pursue Taxol by using an anionic oxy-Cope rearrangement as the key strategic reaction [63–65]. Treatment of **61** with KHMDS and 18-crown-6 *via* the crucial anionic oxy-Cope rearrangement smoothly generated nine-membered ring, followed by methylation *in situ*, thus affording **62** in 81% overall yield. A four-step sequence of dihydroxylation, protection, desilylation, and Swern oxidation afforded keto aldehyde **63**. Intramolecular aldol reaction of **63** generated the C-ring stereoselectively, then transannular hydride shift of the resulting alcohol with KO*t*-Bu gave **64**. A seven-step sequence was carried out to generate **65**. Finally, **65** underwent α-ketol rearrangement with $Al(Ot\text{-}Bu)_3$ to provide highly functionalized taxane system **66** (Scheme 10).

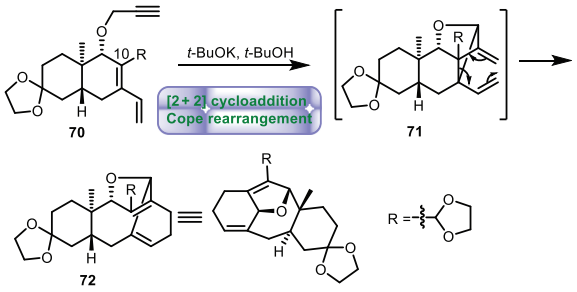
In 1995, Martin and co-workers achieved the 6–8–6 tricyclic ring of taxane *via* an anionic oxy-Cope rearrangement protocol [66]. The crucial anionic oxy-Cope rearrangement reaction of alcohol **67**, followed by alkylation *in situ*, furnished the bicyclo[5.3.1]undecenone **68** in 76% yield with 2:1 ratio of diastereose-



Scheme 10. Paquette's approach to the tricyclic ring system through anionic oxy-Cope rearrangement (1989–2003).



Scheme 11. Martin's approach to the tricyclic ring system through anionic oxy-Cope rearrangement (1995).

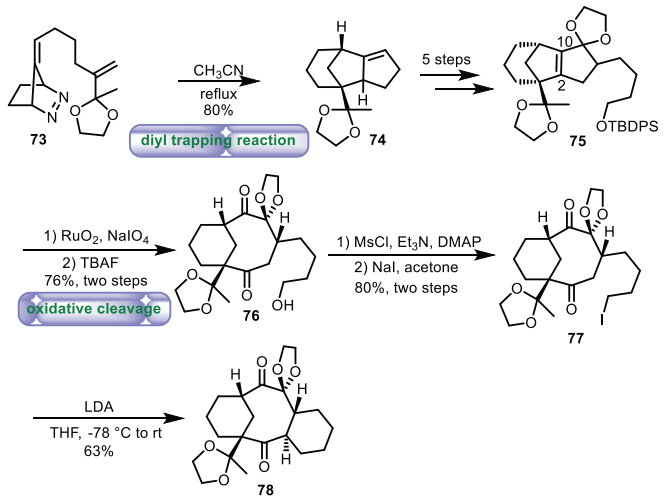


Scheme 12. Kanematsu's approach to the tricyclic ring system through tandem intramolecular [2 + 2] cycloaddition and Cope rearrangement reaction (1995).

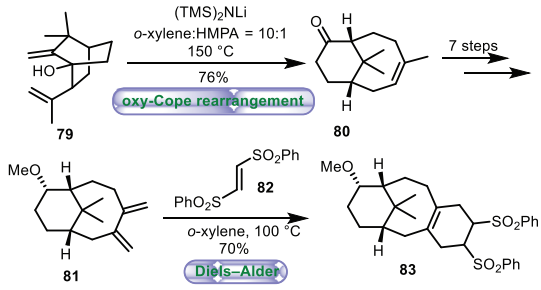
lectivity. Finally, exposure of excess MeLi by a vinyllithium reagent generated tricyclic compound **69** in 58% yield (Scheme 11).

In 1995, Kanematsu and co-workers applied tandem intramolecular [2 + 2] cycloaddition and Cope rearrangement strategy to the enantioselective synthesis of 6–8–6 tricyclic core of Taxol [67]. Treatment of enyne **70** with *t*-BuOK in *t*-BuOH, generated intermediate **71** *in situ via* a [2 + 2] cycloaddition, followed by Cope rearrangement affording product **72** bearing 6–8–6 tricyclic skeleton of taxane (Scheme 12).

In 1997, Little and co-workers reported the synthesis of 6–8–6 tricyclic ring of the taxane *via* intramolecular diyl trapping and oxidation of cleavage of olefin strategy [68]. The intramolecular diyl trapping reaction of bicyclic diazene **73** formed compound **74** in 80% yield. A five-step sequence of the addition of phenylselenyl



Scheme 13. Little's approach to the tricyclic ring system through intramolecular diyl trapping and oxidation of cleavage (1997).

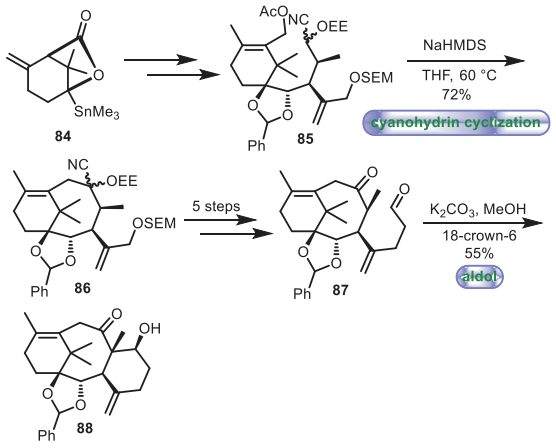


Scheme 14. Nagaoka's approach to the tricyclic ring system through oxy-Cope rearrangement and intermolecular Diels–Alder cycloaddition (1998).

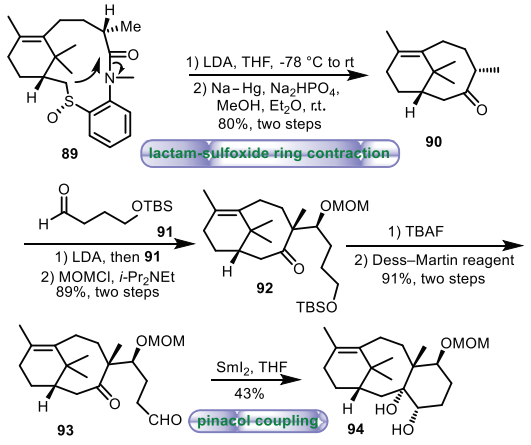
trifluoroacetate, Swern oxidation, elimation, alkylation, and ketalization was carried out, thus affording **75**. Oxidation of cleavage of olefin by using sodium periodate and ruthenium dioxide, followed by removing the silyl ether gave **76** with eight-membered ring in 76% yield over two steps. Then mesylation and iodization of **76** afforded **77**. Lastly, treatment of **77** with excess of LDA afford 6–8–6 tricyclic scaffold **78** with highly functionalized eight membered ring in 63% yield (Scheme 13).

In 1998, Nagaoka and co-workers described the synthesis of 6–8–6 tricyclic core of Taxol *via* oxy-Cope rearrangement and intermolecular Diels–Alder cycloaddition [69]. Treatment of **79** with $(TMS)_2NLi$ in a mixture of *o*-xylene and HMPA (10:1) at 150 °C gave bicyclo[5.3.1]undecane **80** in 76% yield through oxy-Cope rearrangement. Then a seven-step sequence of stereoselective reduction, methyl etherification, epoxidation, ring-opening, oxidation, and olefination was carried out to give diene **81**. Lastly, intermolecular Diels–Alder reaction of diene **81** with *trans*-1,2-bis(phenylsulfony)ethylene **82** was carried out in *o*-xylene at 100 °C to afford the tricyclic product **83** in 70% yield (Scheme 14).

In 1998, Stork and co-workers applied cyanohydrin cyclization and aldol reaction to the synthesis of the 6–8–6 tricyclic core of Taxol [70,71]. The compound **85** containing A ring was prepared from stannylactone **84**. Then the cyanohydrin cyclization of **85** was easily conducted with NaHMDS as base, thus resulting in the desired closure of the cyclooctane ring B to afford **86** in 72% yield. Next, a five-step sequence of desilylation, hydrolysis of cyanohydrin, Johnson–Claisen elongation, reduction, and oxidation was carried out to give dicarbonyl compound **87**. Finally, **87** underwent a smoothly intramolecular facile aldol reaction with K_2CO_3 in



Scheme 15. Stork's approach to the tricyclic ring system through cyanohydrin cyclization and aldol reaction (1998).

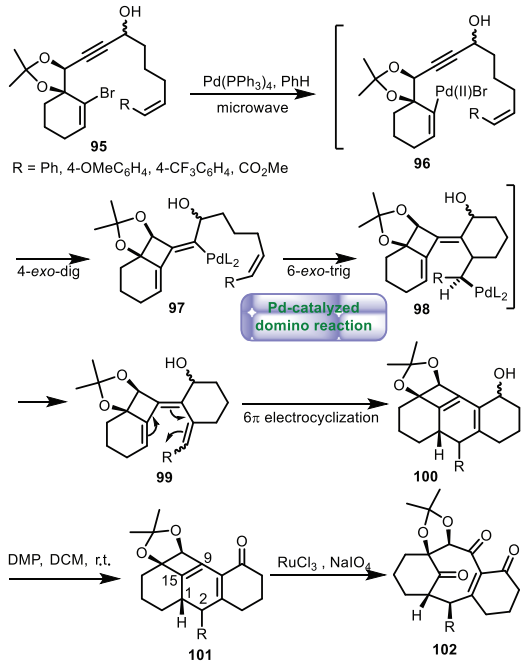


Scheme 16. Kajiwara's approach to the tricyclic ring system through lactam-sulfoxide ring contraction and pinacol coupling (1999).

MeOH and 18-crown-6 to provide the desired 6–8–6 tricyclic core **88** (Scheme 15).

In 1999, Kajiwara and co-workers described the synthesis of the 6–8–6 tricyclic core of Taxol by lactam-sulfoxide ring contraction and intramolecular pinacol coupling [72–76]. Ring contraction of lactam-sulfoxide **89** was achieved with LDA, followed by reductive removal of the spacer moiety with Na–Hg to afford A/B ring system **90**. Treatment of **90** with aldehyde **91**, followed by MOM protection afforded ether **92** in 89% yield. Removal of the TBS group of **92** with TBAF and Dess–Martin oxidation of the resulting primary alcohol gave aldehyde **93** in 91% yield. Lastly, upon treatment of aldehyde with SmI_2 in THF, the pinacol-type reaction proceeded smoothly to yield 6–8–6 tricyclic ring system **94** in 43% yield (Scheme 16).

In 2011, Suffert and co-workers completed the synthesis of 6–8–6 tricyclic core of Taxol through a palladium catalyzed domino reaction [77]. Reaction of alkenylbromide **95** with a catalytic amount of $Pd(PPh_3)_4$ produced the desired tetracyclic ring **100**, in which a tandem cyclization process including 4-*exo*-*dig*, 6-*exo*-*trig* cyclizations and a disrotatory 6π electrocyclization were performed. Subsequent oxidation of the secondary alcohol with Dess–Martin periodinane generated enone **101**. Finally, regioselective oxidation cleavage of **101** delivered taxane skeleton **102** (Scheme 17).



Scheme 17. Suffert's approach to the tricyclic ring system through palladium catalyzed domino reaction (2011).

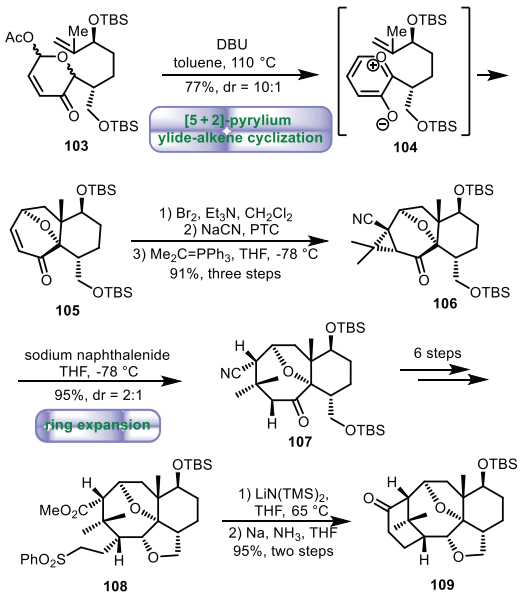
3.3. C to A/B/C strategy

In 1995, Magnus and co-workers provided the synthesis of 6–8–6 tricyclic core of Taxol *via* [5+2]-pyrylium ylide-alkene cyclization and ring expansion [78,79]. Treatment of pyrylium-ylide precursor **103** with DBU generated pyrylium-ylide intermate **104** *in situ*, followed by stereoselective [5+2] cycloaddition to give bicyclo[5.4.0]undecenone **105** in 77% yield with 10:1 *dr*. Then a three-step sequence of bromination, cyanation, and asymmetric cyclopropanation was performed, giving cyclopropane **106** in 91% yield over three steps. Subsequent, taxane **107** with B/C ring of Taxol was obtained in 95% yield with 2:1 *dr* through the cleavage of the internal cyclopropane bond. A six-step sequence of addition and reduction was carried out to give methyl ester **108**. Lastly, intramolecular nucleophilic addition and desulfonylation were carried out to obtain the desired tricyclic product **109** in 95% yield (Scheme 18).

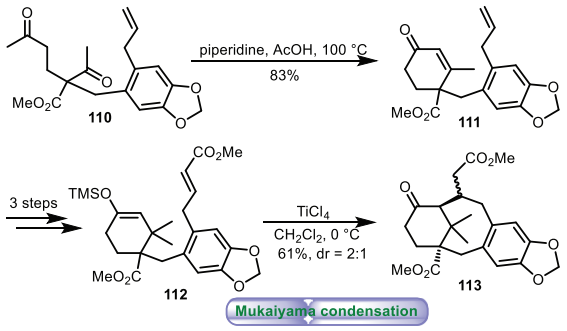
In 1998, d'Angelo and co-workers described the synthesis of 6–8–6 tricyclic core of Taxol *via* a Mukaiyama-type condensation [80,81]. Regioselective annulation diketone **110** with piperidine and acetic acid provided cyclohexanone **111** in 83% yield. Then a three-step sequence of oxidation, Wittig olefination, methylation, and silylation was carried out, thus affording silyl enol **112**. Then intramolecular Mukaiyama-type condensation of **112** was performed with $TiCl_4$ as catalyst, affording the expected tricyclic product **113** in 61% yield with 2:1 *dr* (Scheme 19).

In 2000, Shair and co-workers disclosed an elegant synthesis of 6–8–6 tricyclic core of Taxol by a tandem alkylation, oxy-Cope rearrangement, and transannular Dieckmann cyclization procedure [82]. The triple-domino cyclization was initiated by treating of **114** with the vinyl Grignard reagent, affording the C-aromatic taxane framework **117** directly in 63% yield. The elegant transformation underwent a tandem anion-accelerated oxy-Cope rearrangement (**115**) followed by spontaneous transannular Dieckmann cyclization (**116**) (Scheme 20).

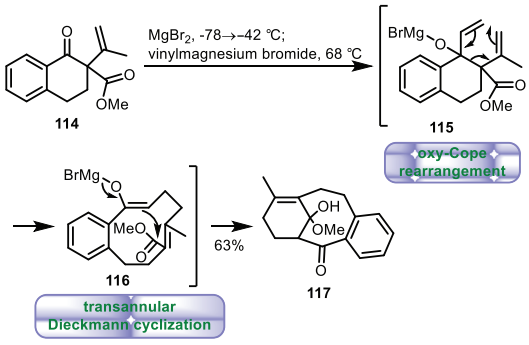
In 2005, Arseniyadis and co-workers applied Grob fragmentation and SmI_2-mediated intramolecular aldol reaction to the syn-



Scheme 18. Magnus's approach to the tricyclic ring system through [5 + 2]-pyrylium ylide-alkene cyclization and ring expansion (1995).

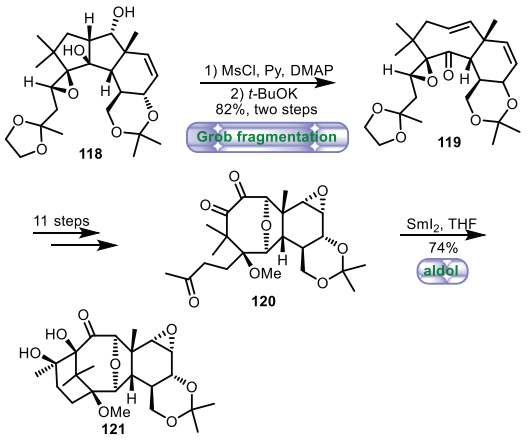


Scheme 19. d'Angelo's approach to the tricyclic ring system through Mukaiyama condensation (1998).

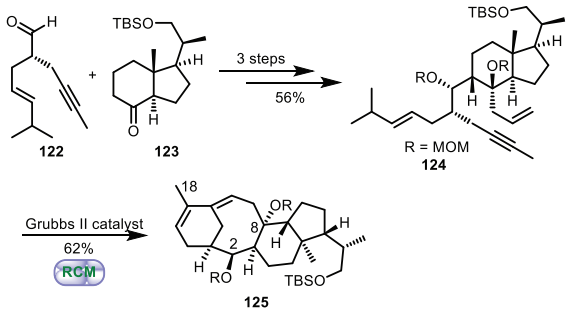


Scheme 20. Shair's approach to the tricyclic ring system through a tandem alkylation, oxy-Cope rearrangement, and transannular Dieckmann cyclization (2000).

thesis of 6–8–6 tricyclic core of Taxol [83–85]. Methylsulfonylation of acetonide **118** set the stage for the crucial B-ring formation through a Grob-type fragmentation, thus affording bicyclo[6.4.0]-system **119** in 82% yield over two steps, which corresponded to the taxoid B/C subunit. An eleven-step sequence including epoxide-opening, methylation, reduction, and oxidation was carried out, thus affording seco-taxane **120**. Finally, SmI_2-mediated intramolecular aldol reaction of **120** resulted in the desired product **121** in 74% yield (Scheme 21).



Scheme 21. Arseniyadis's approach to the tricyclic ring system through Grob fragmentation and SmI_2-mediated intramolecular aldol reaction (2005).

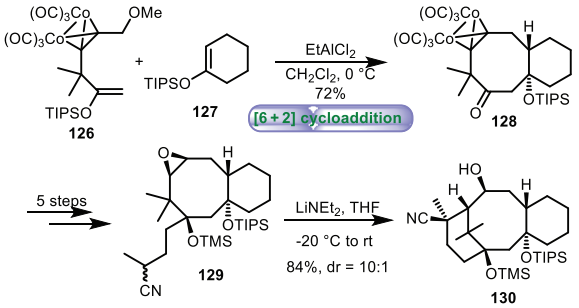


Scheme 22. Granja's approach to the tricyclic ring system through cascade dienyne ring-closing metathesis (2007).

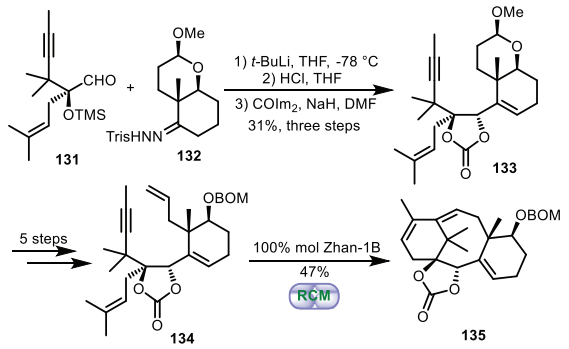
In 2007, Granja and co-workers documented a cascade dienyne ring-closing metathesis approach to the construction of 6–8–6 tricyclic core of Taxol [86–89]. The RCM precursor **124** was obtained from aldehyde **122** and ketone **123** through a three-step sequence of addition, carbonyl allylation and protection. Lastly, in the presence of Grubbs II catalyst, the tandem ring-closing reaction of readily available enyne **124** was performed, thus affording tricycle **125** in 62% yield bearing with C2, C8-hydroxy groups and the methyl of C18 in a single-step (Scheme 22).

In 2014, Tanino and co-workers applied [6 + 2] cycloaddition reaction to the synthesis of the 6–8–6 tricyclic core of Taxol [90]. Initially, the coupling reaction of dicobalt acetylene complex **126** with enol ether **127** was induced with $EtAlCl_2$ as Lewis acid, affording B/C ring intermediate **128**. Then a five-step sequence of transformations was carried out, affording nitrile **129** as a mixture of diastereomers. Finally, treatment of nitrile **129** with $LiNEt_2$ afforded the tricyclic skeleton **130** in 84% yield with 10:1 *dr via* epoxy nitrile cyclization (Scheme 23).

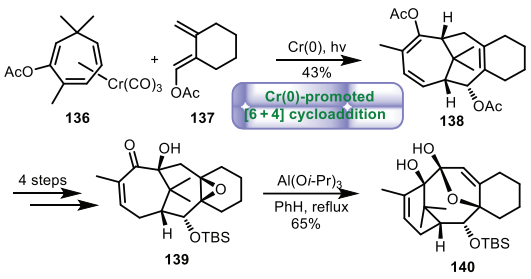
In 2016, Prunet and co-workers applied a ring-closing dienyne metathesis reaction to the synthesis of 6–8–6 tricyclic core of Taxol [91–98]. The Shapiro coupling reaction of aldehyde **131** with trisylhydrazone **132**, hydrolysis of the trimethylsilyl ether and protection of the diols gave the carbonate **133**. Then a five-step sequence of hydrolyzation, reduction, and elimination using the Grieco protocol was carried out to furnish the metathesis precursor **134**. With enyne **134** as cyclic precursor, the desired tricycle product **135** with A/B/C ring was obtained in 47% yield through tandem metathesis reaction (Scheme 24).



Scheme 23. Tanino's approach to the tricyclic ring system through [6 + 2] cycloaddition reaction (2014).



Scheme 24. Prunet's approach to the tricyclic ring system through ring-closing dienyne metathesis (2016).



Scheme 25. Rigby's approach to the tricyclic ring system through Cr(0)-promoted [6 + 4] cycloaddition (1995).

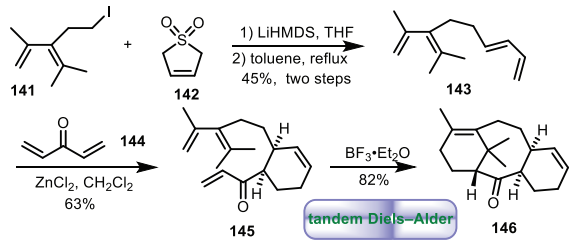
4. Convergent strategies toward A/B/C ring core

The construction of taxane framework *via* convergent strategies has also attracted great attention from synthetic communities with different strategies, including pericyclic reaction, transition metal-catalyzed cyclization and miscellaneous cyclization.

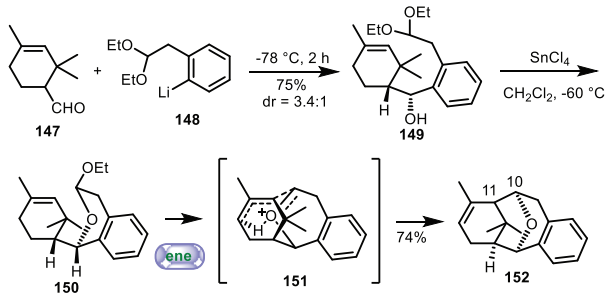
4.1. Pericyclic reaction

In 1995, Rigby and co-workers reported Cr(0)-promoted [6 + 4] cycloaddition for the synthesis of 6–8–6 tricyclic core of Taxol [99]. The tricyclic product **138** was prepared from Cr(0)-promoted [6 + 4] cycloaddition of **136** with diene **137**. Then a four-step sequence of transformations of protecting group, epoxidation, and enolate oxidation was carried out, thus giving epoxide **139**. Finally, α-ketol rearrangement of **139** with Al(O*i*-Pr)$_3$ gave the required tricyclic product **140** in 65% yield (Scheme 25).

In 1995, Winkler and co-workers reported the synthesis of the 6–8–6 tricyclic core of Taxol by tandem Diels–Alder strategy [100]. The condensation of iodide **141** with butadiene sulfone **142**, followed by extrusion of SO_2, resulted in the formation of tetraene compound **143**. The $ZnCl_2$ catalytic intermolecular Diels–Alder reaction of **143** with **144** give cyclohexene **145** bearing C-ring core in 63% yield. Lastly, the desired tricyclic enone **146** was obtained as a single diastereomer *via* $BF_3{\cdot}Et_2O$ mediated intramolecular Diels–Alder reaction (Scheme 26). Later then, Winkler and co-workers disclosed the synthesis of tricyclic ring system through the intramolecular Diels–Alder reaction starting from A-ring synthon [101,102].



Scheme 26. Winkler's approach to the tricyclic ring system through tandem Diels–Alder reaction (1995).



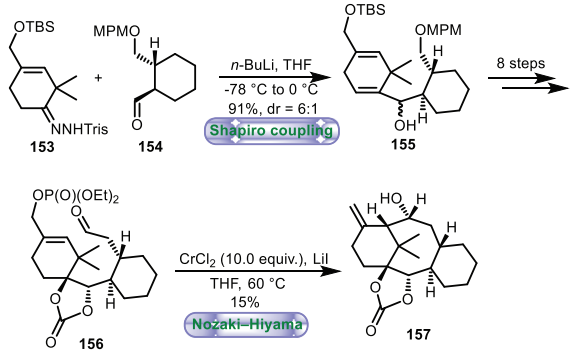
Scheme 27. Sonawane's approach to the tricyclic ring system through sequential transacetalation oxonium ene reaction (1998).

In 1998, Sonawane and co-workers applied novel sequential transacetalation oxonium ene reaction to the synthesis of 6–8–6 tricyclic core of Taxol [103]. The B-seco-taxane **149** was prepared from the coupling reaction of **147** with aryllithium **148** in 75% yield with 3.4:1 *dr*. In the presence of $SnCl_4$, the intramolecular nucleophilic substituted reaction and ene reaction were carried out to the assemble of the C-aromatic taxane skeleton **152** in 74% yield (Scheme 27).

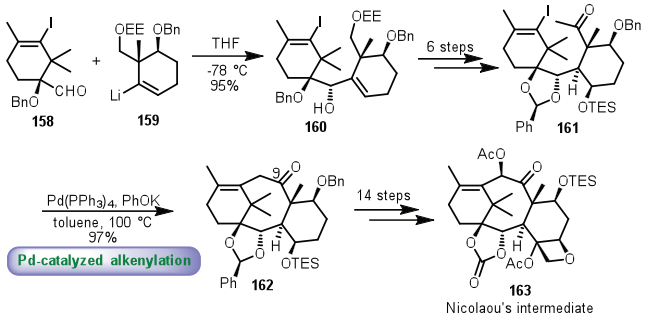
4.2. Transition metal-catalyzed cyclization

In 2004, Nakada and co-workers described the synthesis of 6–8–6 tricyclic core of Taxol by using Nozaki–Hiyama reaction [104]. Trisyl hydrazone **153** was converted to the corresponding alkenyllithium with *n*-butyllithium, followed by reaction of aldehyde **154** to produce **155** in 91% yield with 6:1 *dr*. Then, an eight-step sequence of oxidation, reduction, Witting reaction, and hydrolysis was carried out, producing the allylic phosphate **156**. Pleasingly, the cyclization reaction could be achieved under the condition of excessive $CrCl_2$ and LiI in THF, which gave the secure 6–8–6 tricyclic target **157** in only 15% yield (Scheme 28).

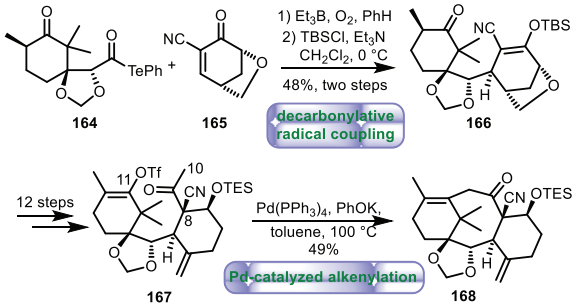
In 2015, the same group described the formal synthesis of Taxol *via* a palladium-catalyzed alkenylation of methyl ketone to furnish the eight-membered ring [105,106]. Firstly, treatment of the A-ring precursor **158** with alkenyllithium **159** in THF at −78 °C afforded **160** as a single isomer in 95% yield. Then the key precursor **161** was obtained through a six-step sequence of transformations. Palladium-catalyzed alkenylation of methyl ketone **161** was smoothly taken place, thus producing the tricyclic compound **162** with the oxygen atom at C9 in 97% yield. Finally, **162** transformed



Scheme 28. Nakada's approach to the tricyclic ring system through Nozaki–Hiyama reaction (2004).



Scheme 29. Nakada's approach to the tricyclic ring system through Pd-catalyzed alkenylation (2015).



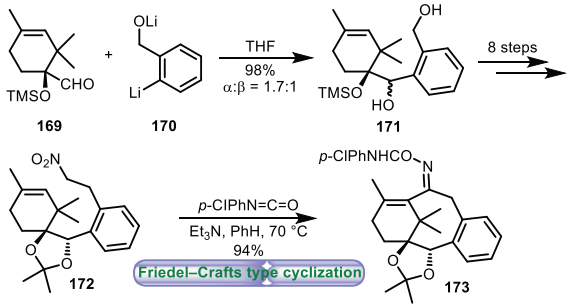
Scheme 30. Inoue's approach to the tricyclic ring system through decarbonylative radical coupling and Pd-catalyzed alkenylation (2018).

to Nicolaou's intermediate **163** *via* a fourteen-step sequence to complete the challenging work (Scheme 29).

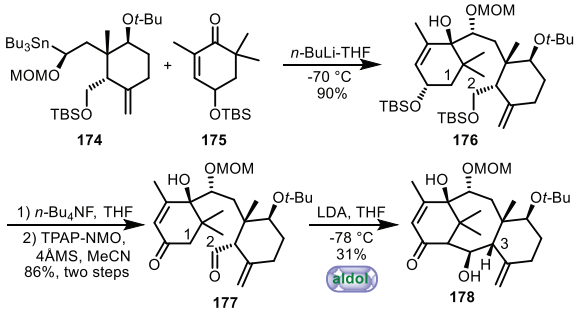
In 2018, Inoue and co-workers applied decarbonylative radical coupling and Pd-catalyzed intramolecular alkenylation to assemble the eight-member ring [107]. Treatment of **164** and **165** with Et_3B and O_2 in benzene at room temperature, followed by regioselectively protecting with TBSCl, afforded **166** in 48% yield over two steps. Then C10–C11 seco-taxane **167**, bearing the C8-quaternary carbon was achieved *via* the linear twelve-step sequence of transformations from **166**. Finally, subjecting with $Pd(PPh_3)_4$ and PhOK at 100 °C in toluene, the eight-member ring was cyclized to deliver the tricyclic product **168** in 49% yield (Scheme 30).

4.3. Miscellaneous cyclization

In 1997, Nagaoka and co-workers described the synthesis of 6–8–6 tricyclic core of Taxol *via* Friedel–Crafts type cyclization [108]. Initially, the coupling of ring A precursor **169** with aryllithium reagent **170** gave alcohol **171** as a mixture. Then the major



Scheme 31. Nagaoka's approach to the tricyclic ring system through Friedel–Crafts type cyclization (1997).



Scheme 32. Arseniyadis's approach to the tricyclic ring system through intramolecular Aldol reaction (1999).

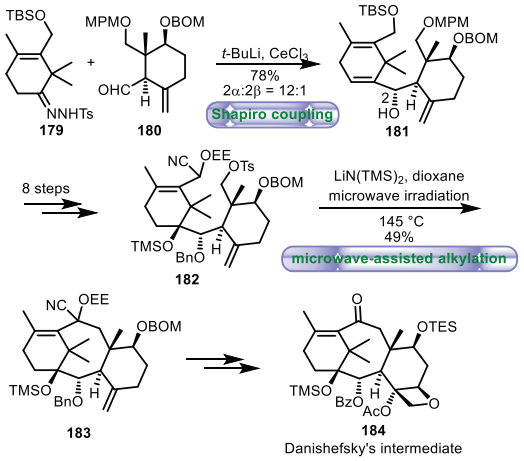
isomer of **171** was transformed into nitro compound **172** through an eight-step sequence. Treatment of precursor **172** with excess *p*-chlorophenyl isocyanate afforded tricyclic product **173** in 94% yield (Scheme 31).

In 1999, Arseniyadis and co-workers applied intramolecular aldol reaction to assemble of taxoid A/B/C ring system [109–111]. The addition of organostannane **174** to A-ring building block **175** generated **176**. Then desilylation and oxidation afforded B-seco-taxoids **177**. Finally, the A/B/C tricycle **178** was accomplished by intramolecular aldol reaction in 31% yield, in which only the C3-α substituted precursor could be cyclized smoothly (Scheme 32).

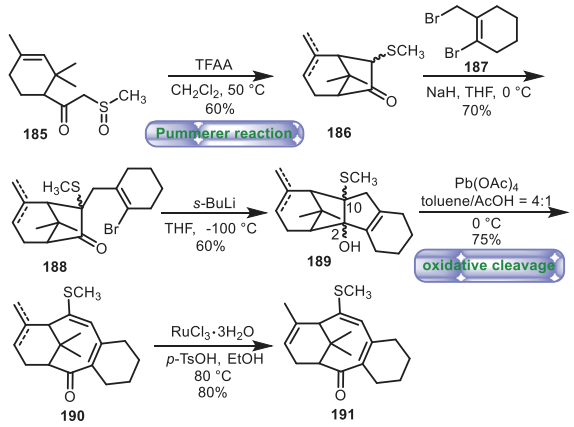
In 2006, Takahashi and co-workers documented their efforts toward the formal synthesis of Taxol by using microwave-assisted alkylation reaction as a novel step [112,113]. The Shapiro coupling reaction of A ring hydrazone **179** with aldehyde **180** provided the desired product **181** in 54% yield with $2\alpha/2\beta = 12{:}1$. Then they achieved the ideal intermediate **182** *via* an eight-step sequence of transformations from **181**. Upon treatment of **182** with $LiN(TMS)_2$ in refluxing dioxane under microwave irradiation triggered the intramolecular alkylation reaction, thus affording cyclization product **183** in 49% yield. Further transformations were carried out to complete the synthesis of Danishefsky's intermediate **184** (Scheme 33).

In 2007, Chavan and co-workers employed the strategy of Pummerer reaction and oxidative cleavage to the synthesis of 6–8–6 tricyclic core of Taxol [114]. The bicyclic system **186** was generated from β-oxo sulfoxide **185** through Pummerer reaction, followed by coupling with bromo-2-(bromomethyl)cyclohex-1-ene **187** to obtain **188** in 70% yield. The addition of *s*-BuLi to **188** delightfully afforded the tetracyclic compound **189** in 60% yield. Upon treatment of **189** with $Pb(OAc)_4$ broke C2–C10 bond, thus affording the A/B/C ring system **190** in 75% yield. Lastly, **190** was isomerized to **191** with catalytic amount of rhodium trichloride (Scheme 34).

In 2019, Inoue and co-workers applied decarbonylative radical coupling protocol and pinacol coupling reaction to build tricyclic core [115]. Vinyl iodide **192** bearing A ring framework was transformed into telluride **193** *via* a five-step sequence. Then coupling



Scheme 33. Takahashi's approach to the tricyclic ring system through microwave-assisted alkylation (2006).

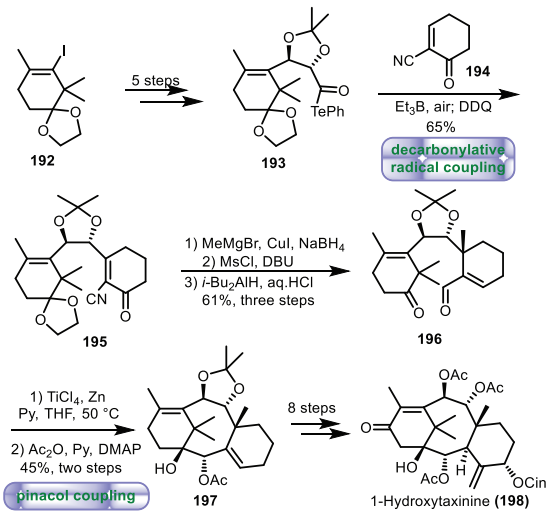


Scheme 34. Chavan's approach to the tricyclic ring system through sulfur-assisted synthetic protocol (2007).

of **193** with C ring fragment **194** was carried out under the previous decarbonylative radical condition [107], followed by oxidation of the resulting borane enolate by DDQ, thus affording the adduct **195**. Then **195** was converted to the key precursor ketoaldehyde **196** *via* a three-step sequence of methylation, reduction, elimination, reduction of the nitrile, and deprotection. Treatment of **196** with $TiCl_4$, Zn, and pyridine in THF at 50 °C, followed by acetylation furnished the tricyclic compound **197** in 45% yield over two steps. Finally, 1-hydroxytaxinine **198** was synthesized *via* an eight-step sequence of transformations (Scheme 35).

5. Summary and outlook

Taxol has attracted considerable attention from the synthetic communities due to its intriguing structure and important anticancer bioactivity. Since the pioneering total synthesis of Holton and Nicolaou groups, ten total syntheses of Taxol have been achieved up to the present. Nevertheless, development of efficient synthetic methods to construct the eight-membered B-ring remains a challenging task for organic synthesis in general. This mini-review has summarized the synthetic approaches toward eight-membered B-ring formation. Tremendous efforts made by a number of research groups worldwide have resulted in a range of diverse creative and elegant strategic approaches



Scheme 35. Inoue's approach to the tricyclic ring system through decarbonylative radical coupling and pinacol coupling reaction (2019).

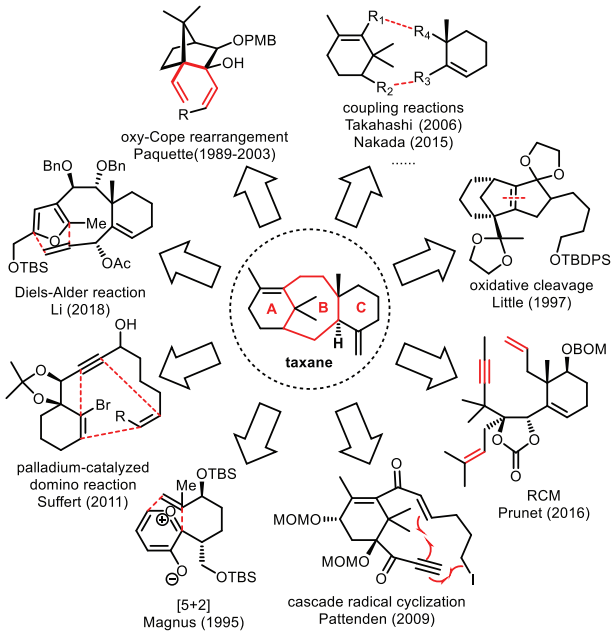


Fig. 3. Highlights of diverse approaches *en route* to the taxane core ring.

and methodologies. For example, oxy-Cope rearrangement, Diels–Alder reaction, Pd-catalyzed domino reaction, [5 + 2]-pyrylium ylide-alkene cyclization, cascade radical cyclization, ring-closing metathesis, oxidative cleavage, and diverse coupling reactions (Pd-catalyzed intramolecular alkenylation, decarbonylative radical coupling, acid/base/SmI_2-mediated aldol condensation, intramolecular Michael addition of sulfonyl carbanion, Nozaki–Hiyama reaction, and so on) have been successfully employed to construct these eight-membered B-rings (Fig. 3). These novel approaches could provide inspiration to synthetic communities. The further possible approach may be the combination of synthetic convergency and biomimetic conciseness, which could address the overall efficiency of total synthesis. Taxol will still stand for an ideal target molecule in total synthesis for many years to come. We believe that novel synthetic strategies and tactics would be well developed further and could be successfully applied to the total synthesis of Taxol in future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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