CNT Segments

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Design and Synthesis of Carbon Nanotube Segments

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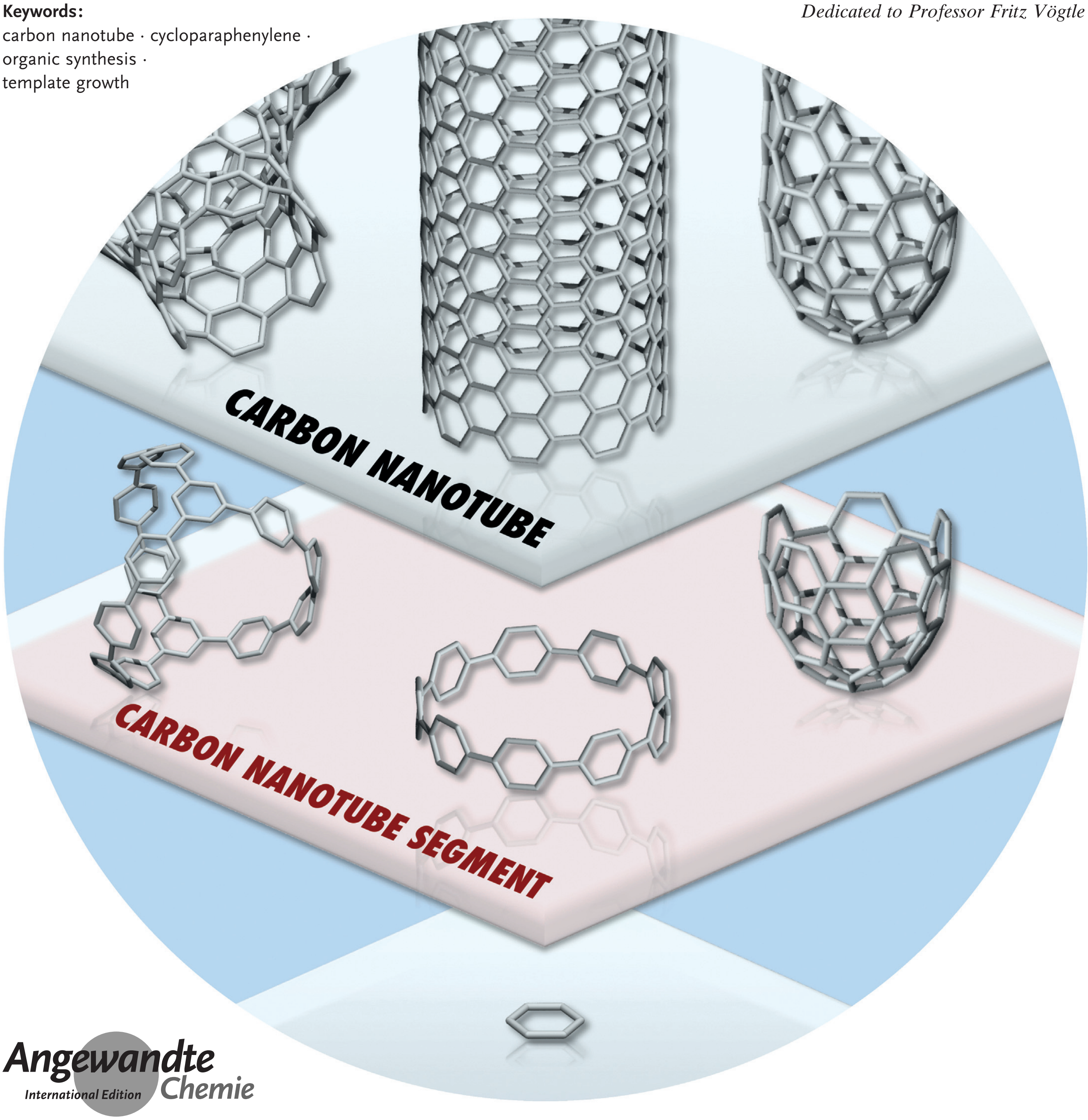
template growth

Dedicated to Professor Fritz Vögtle



The selective and predictable synthesis of structurally uniform carbon nanotubes (CNTs) represents a long-standing goal in both nano-carbon science and synthetic organic chemistry. This Review focuses on synthetic studies toward the controlled synthesis of CNTs with single chirality through the organic synthesis of CNT segments and the organic template assisted growth of CNTs.

From the Contents

1. Introduction

Since the first observation and detailed structural analysis of carbon nanotubes (CNTs) in 1991 by Iijima,[1] their synthesis has been the focus of much scientific interest due to their outstanding physical and chemical properties, as well as their wealth of potential applications in technology.[2,3] Single-walled CNTs can be considered as rolled-up structures of two-dimensional graphene sheets. The way in which the graphene is wrapped along the sheet is given by the chiral index, which is represented by a pair of numbers (n,m; Figure 1). The structure for $m = 0$ is called “zigzag”, the structure for $n = m$ is called “armchair”, and the structure for $n > m > 0$ is called “chiral”. The chiral index (n,m) can be used to deduce a variety of electrical, optical, magnetic, and mechanical properties of the CNTs. For example, (n,m)CNTs are metallic where $n-m$ is a multiple integer of three, whereas other CNTs are semiconducting.[4] Therefore, the controlled chirality-specific synthesis of CNTs is of utmost importance to induce defined macroscopic material properties.

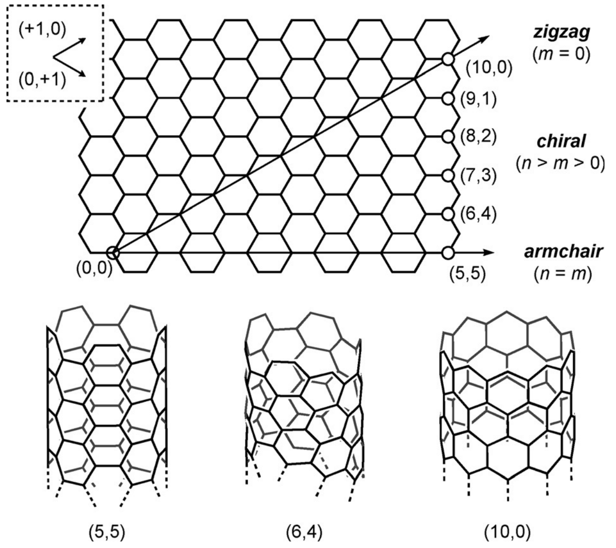


Figure 1. Chiral index (n,m) for CNTs.

A wide range of methods such as arc evaporation, laser ablation, and chemical vapor deposition (CVD) has been reported for the synthesis of CNTs.[5] As the electronic properties of CNTs depend on their inherent chirality, the lack of synthetic control over chirality has long been recognized as a fundamental impediment to the systematic development of CNTs and their subsequent applications. Although the separation of CNTs with single chirality has been partially accomplished by the use of DNA or polymer as dispersers,[6] these separation processes are limited by their small scale and high cost as well as the short length and the imperfect purity of the resulting CNTs. Moreover, the chirality-selective synthesis of CNTs still remains an unsolved issue. In this Review, we discuss strategies that aim to control the synthesis of CNTs with single chirality: The organic synthesis of CNT segments (Sections 2 and 3) and the growth of CNTs from organic templates (Section 4).

2. Segments of CNT sidewalls

Ring-shaped structures are obtained by “slicing” CNTs perpendicularly to the main axis. These ring-shaped aromatic molecules (Figure 2) are called “carbon nanorings” and represent the sidewall segment of CNTs with a specific chirality. Thus, these carbon nanorings are ideal templates or building blocks for the construction of uniform CNTs.

2.1. Segments of Armchair CNTs

Prior to the discovery of CNTs in 1991 by Iijima, molecules that corresponded to the segments of armchair CNTs were investigated by several chemists as a result of their intriguing and highly symmetric structures.[7] In 1983, Vögtle described the belt-shaped molecule shown in Figure 3 and embarked on its synthetic study.[8a] This belt-shaped molecule

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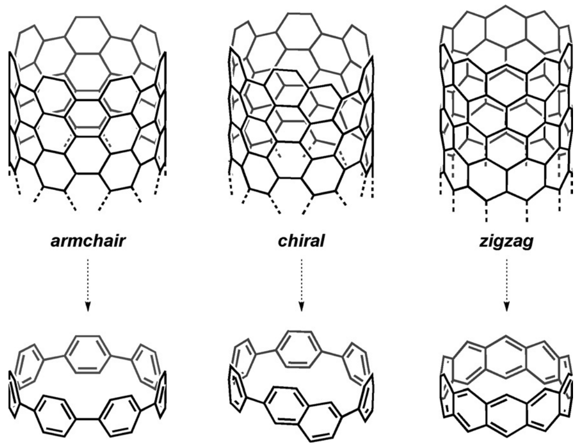

Figure 2. Carbon nanorings as segments of CNT sidewalls.

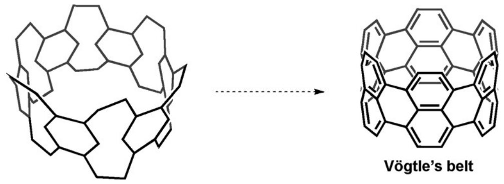

Figure 3. Structure of Vögtle's belt.

became known as "Vögtle's belt",[8b] but despite the synthetic efforts of various research groups, its synthesis has not yet been accomplished.

So far, various types of armchair CNT segments have been synthesized. In this section, we describe the chronological development and the synthetic strategies applied for the development of armchair CNT segments, including tetradehydrodianthracenes, all-Z-benzannulenes, cycloparaphenylenes, and π-extended carbon nanorings. A selection of representative armchair CNT segments is shown in Figure 4.

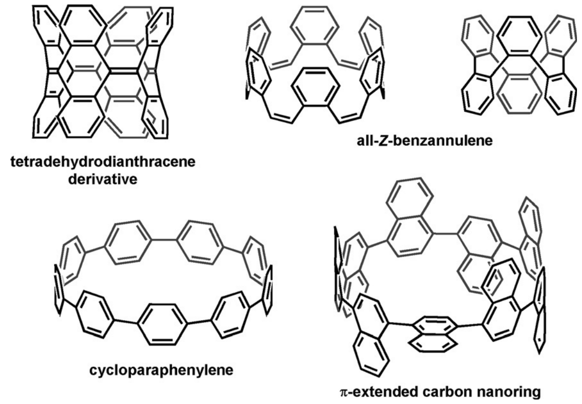

Figure 4. Selected representative armchair CNT segments.

2.1.1. *Tetradehydrodianthracene Derivatives*

The smallest possible armchair CNT is (2,2)CNT. It is, due to its small size, extremely strained, and has accordingly never been observed during the high-temperature synthesis of CNTs. To date, only one (2,2)CNT segment has been

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Kenichiro Itami was born in Pittsburgh, USA (1971) and raised in Tokyo. He studied chemistry at Kyoto University, Japan, and completed his PhD in 1998 with Prof. Yoshihiko Ito. After being Assistant Professor (with Prof. Jun-ichi Yoshida) at Kyoto University, he moved to Nagoya University as an Associate Professor (with Prof. Ryoji Noyori) in 2005, where he was promoted to Full Professor in 2008. Since 2012 he has also been Director of the Institute of Transformative Bio-Molecules (WPI-ITbM) and since 2013 Research Director of JST-ERATO Itami Molecular Nanocarbon Project. His research focuses on the development of new synthetic methods to realize ideal chemical synthesis.

reported. Despite the high levels of strain energy, the synthesis of the (2,2)CNT segment tetradehydrodianthracene (TDDA) was achieved in 1974. Furthermore, several TDDA derivatives have since been synthesized by the ring-expansion metathesis of TDDA, using its high levels of intrinsic strain as a thermodynamic driving force. All the TDDA derivatives discussed here are shown in Figure 5.

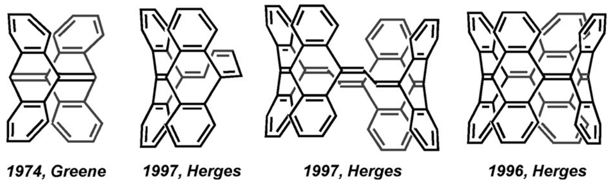
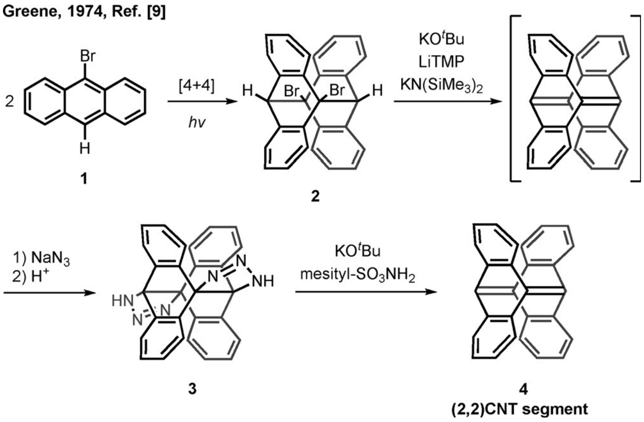


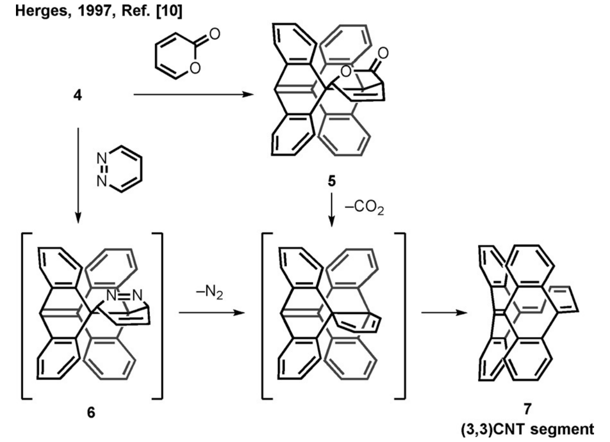
Figure 5. Tetradehydrodianthracene (TDDA) derivatives.

In 1974, Greene and co-workers reported the synthesis of TDDA **4** (Scheme 1)[9] by the [4+4] photocyclization of 9-bromoantharacene (**1**), which afforded dimer **2**. A subsequent dehydrobromination of **2** with KO^tBu/LiTMP/$KN(SiMe_3)_2$, followed by reaction with sodium azide led to precursor **3**. Treatment of **3** with KO^tBu and Carpino's reagent (mesityl-SO_3NH_2, mesityl = 2,4,6-trimethylphenyl) afforded **4**, which represents a (2,2)CNT segment.

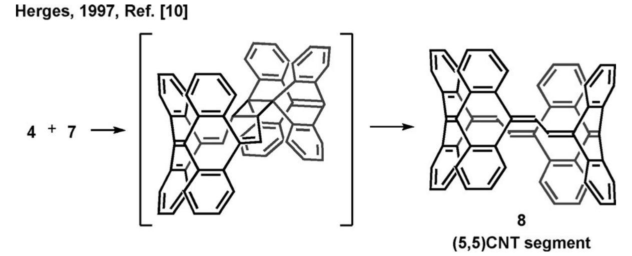


Scheme 1. Synthesis of TDDA (**4**).

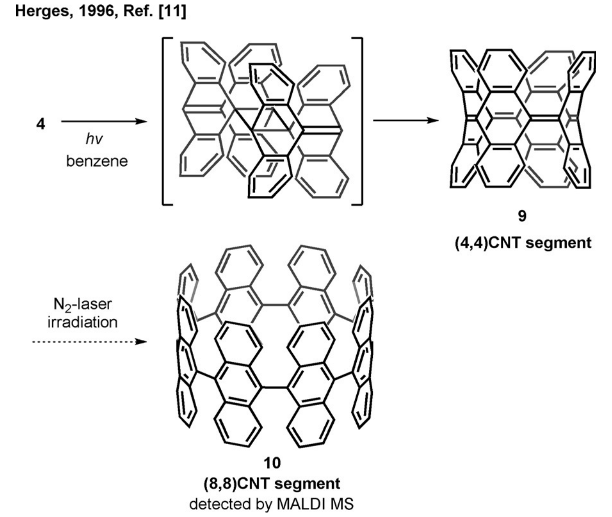
Twenty years after the achievement by Greene and co-workers, several TDDA derivatives were synthesized starting from **4**. For example, Herges and co-workers were able to synthesize the (3,3)CNT segment **7** from **4** by a strain-releasing photoreaction route (Scheme 2).[10] The Diels–Alder reaction of **4** with α-pyrone or 1,2-diazine resulted in the intermediate formation of **5** and **6**, respectively. Ensuing elimination of CO_2 from **5** or N_2 from **6** afforded macrocycle **7**, which represents a (3,3)CNT segment. In subsequent reports, Herges and co-workers reported the synthesis of several types of CNT segments, taking advantage of the high reactivity of **4** in photochemically induced cycloadditions. A photochemically induced metathesis of **4** with **7** furnished **8**, which is a (5,5)CNT segment (Scheme 3).[10] In addition, **4** was found to dimerize in benzene under photoirradiation conditions, thereby affording **9**, which is a (4,4)CNT segment with a paracyclophane structure (Scheme 4).[11] Herges and co-workers, furthermore, mentioned that irradiation of **9** with a nitrogen laser induced intermolecular metathesis, and the generation of **10** was suggested by MALDI TOF-MS.[7]



Scheme 2. Synthesis of TDDA derivative **7**.



Scheme 3. Synthesis of TDDA derivative **8**.



Scheme 4. Synthesis of TDDA derivative **9**.

2.1.2. ***All-Z-Benzannulenes***

Annulenes are fully conjugated cyclic polyenes.[12] All-*Z*-benzannulenes can be considered as sidewall segments of

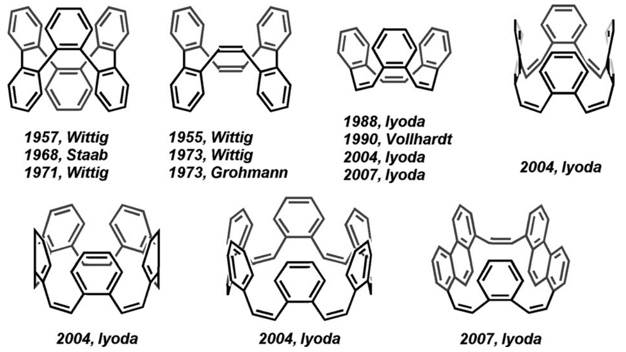
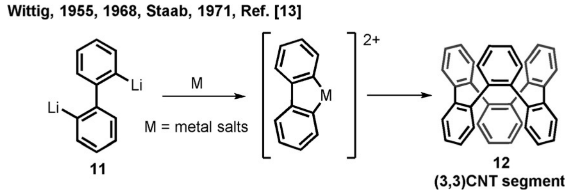
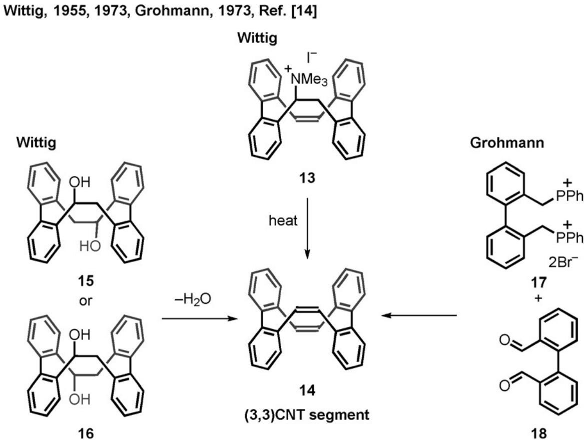


Figure 6. All-*Z*-benzannulenes.

armchair CNTs (Figure 6). Benzannulenes in which all the ethylene moieties are benzannulated are also called [*n*]cyclo-orthophenylenes. The first synthesis of all-*Z*-benzannulenes dates back to 1955 and their synthetic studies were intensified in the 1970s. Since the late 1990s, it has been predominantly the Iyoda research group who has been avidly investigating the synthesis of all-*Z*-benzannulenes.

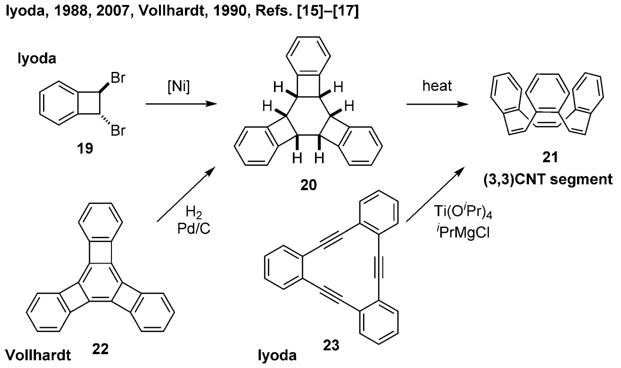


Scheme 5. Synthesis of hexabenz[12]annulene.



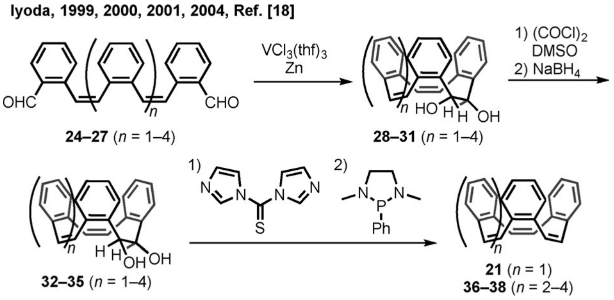
Scheme 6. Syntheses of tetrabenz[12]annulene.

The synthesis of hexabenz[12]annulene **12** and tetrabenz[12]annulene **14** was first published in the 1950s. Wittig et al. in 1957 and 1971, as well as Staab and Wünsche in 1968 accomplished the generation of **12** by the reaction of 2,2′-dilithiobiphenyl (**11**) with metal salts (Scheme 5).[13] The first synthesis of tetrabenz[12]annulene **14** was reported by Wittig et al. in 1955 by using the Hoffmann degradation of **13** (Scheme 6).[14] In 1973, an alternative synthetic route for the generation of **14** by dehydration of **15** and **16** was reported. In 1973, Grohmann et al. also synthesized **14** by using a Wittig reaction between 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**17**) and 2,2′-biphenyldicarboxaldehyde (**18**). Both **12** and **14** represent segments of (3,3)CNTs.

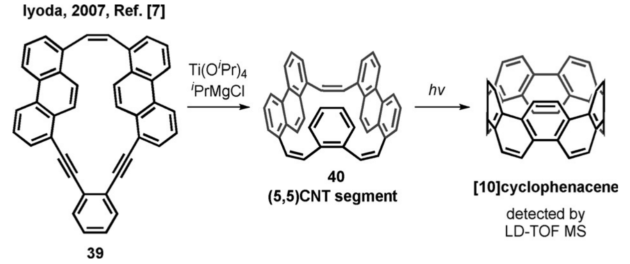


Scheme 7. Syntheses of tribenz[12]annulene.

In the 1990s, several types of benzannulenes were synthesized. Initially, tribenz[12]annulene **21**, which is a segment of (3,3)CNTs, was synthesized by the research groups of Iyoda and Vollhardt (Scheme 7). Iyoda et al. generated **21** by trimerization of 1,2-dibromo-1,2-dihydrobenzocyclobutene (**19**) in the presence of a nickel complex.[15] The configuration of intermediate **20** was all *syn*, and so a thermal ring-opening reaction of the cyclobutane moieties of **20** afforded tribenz[12]annulene **21**. In 1990, Vollhardt and co-workers succeeded in synthesizing **21** by hydrogenation of biphenylene derivative **22**, followed by a ring-opening reaction of the cyclobutane moieties.[16] A substantial limitation of the initial synthesis of **21** by Iyoda et al. is the low yield of the last step. To circumvent the shortcoming of this route, Iyoda and co-workers developed a new method for the synthesis of **21**,[17] in which tribenzohexadehydroannulene **23** was hydrogenated by $Ti(O^{i}Pr)_4$/$^{i}PrMgCl$, thus providing direct access to **21** in higher yield. The synthesis of benzannulenes of various size was also accomplished (Scheme 8).[18] Initially, oligo-*cis*-stilbene dialdehydes **24**–**27** were prepared. A subsequent McMurry coupling of **24**–**27** with $VCl_3(thf)_3$ and zinc led to the formation of the corresponding macrocycles **28**–**31**. Consecutive oxidation and reduction changed the configuration of the diol from *anti* to *syn* and furnished **32**–**35**. Benzannulenes **21** and **36**–**38** were obtained by a Corey–Winter reaction of **32**–**35**. Phenanthrene-containing benz[12]annulene **40**,



Scheme 8. Synthesis of benzannulenes.



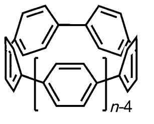
Scheme 9. Observation of [10]cyclophenacene.

a (5,5)CNT segment, was synthesized by the reduction of **39** (Scheme 9).[7] Compound **40** is expected to be converted into [10]cyclophenacene by oxidative cyclization, and Iyoda and co-workers mentioned the detection by LD-TOF MS of [10]cyclophenacene among the products of a photocyclization reaction of **40**.

2.1.3. *Cycloparaphenylenes*

Cyclic molecules consisting of *n* benzene rings connected through *para* linkages are called [*n*]cycloparaphenylenes ([*n*]CPPs). Each [*n*]CPP represents a corresponding (*n*,*n*)CNT segment. Although synthetic studies of CPPs already began in the 1930s,[19] their synthesis was not accomplished for almost 80 years, because of the difficulty in overcoming the substantial levels of intrinsic ring strain. In 2008, Bertozzi, Jasti, and co-workers reported the first synthesis of a CPP.[20] A few months later, the Itami group reported the first size-selective synthesis of a CPP,[21] and in 2010 Yamago et al. reported an alternative synthesis of CPPs.[22] These three research groups have since developed synthetic methods for the selective formation of CPPs, and [*n*]CPPs (*n* = 5–16, 18) have now been generated.[23] Table 1 summarizes the chronological development in the isolation of CPPs. The synthesis of CPPs has undoubtedly experienced dramatic advancements in recent years.

Table 1: Years of publication of the random (normal) and size-selective synthesis (bold) of [*n*]CPPs.



[*n*]cycloparaphenylene ([*n*]CPP)

n	Bertozzi/Jasti	Itami	Yamago
5	**2014**		**2014**
6	**2012**, **2015**		**2013**, **2015**
7	**2012**	**2014**	**2015**
8	**2012**	**2014**	**2010**, 2011, 2012, **2013**, **2015**
9	2008, **2012**	2011, **2012**	2011, **2015**
10	**2012**	**2012**, **2015**	2011, **2012**, **2013**, **2015**
11	**2012**	**2012**	2011, **2015**
12	2008, **2011**	**2009**, 2011	2011, **2011**, 2012, **2015**
13		**2012**	2011
14		**2010**	
15		**2010**	
16		**2010**	2012
18	2008		

The introduction of size-selective synthetic methods for the generation of CPPs has provided access to the size-dependent photophysical and redox properties of specific CPPs[24] as well as their host–guest behavior.[25] Characteristic photophysical properties of CPPs are that the longest-wavelength absorption maxima and the emission maxima are blue-shifted as the ring size increases. These counterintuitive optical properties of CPPs could mainly be ascribed to the ring-size effect in frontier molecular orbitals (in particular, the increase in the HOMO–LUMO gap as the number of benzene rings increases).[24b] Another size-dependent property of CPPs is their complexation with fullerenes. Depending on the size, $C_{60}\subset$[10]CPP,[25a] $Li^+@C_{60}\subset$[10]CPP,[25k] $C_{70}\subset$[10]CPP,[25b] $C_{70}\subset$[11]CPP,[25b] and $M@C_{82}\subset$[11]CPP (M = La, Gd)[25c,h] were formed. The interactions between CPPs and fullerenes are mainly through van der Waals interactions, whereas charge-transfer interactions are also observed in the case of $Li^+@C_{60}\subset$[10]CPP and $La@C_{82}\subset$[11]CPP as a consequence of the strong electron-acceptor properties of the metallofullerenes $Li^+@C_{60}$ and $La@C_{82}$.

Synthetically, the biggest challenge for the generation of [*n*]CPPs is the formation of a macrocycle which usually contains high levels of intrinsic ring strain, mostly resulting from the connection of benzene rings in *para* positions. The Jasti/Bertozzi, Itami, and Yamago research groups addressed this problem with the initial formation of unstrained macrocyclic CPP precursors. Three of their synthetic strategies are outlined in Figure 7. The method employed by Jasti, Bertozzi et al. uses L-shaped building blocks consisting of phenyl-substituted cyclohexadienes. Since cyclohexadiene moieties can be converted with relative ease into benzene rings by reductive aromatization, these L-shaped units can be regarded as terphenylene precursors. Coupling of these L-shaped units afforded macrocycles with cyclohexadiene

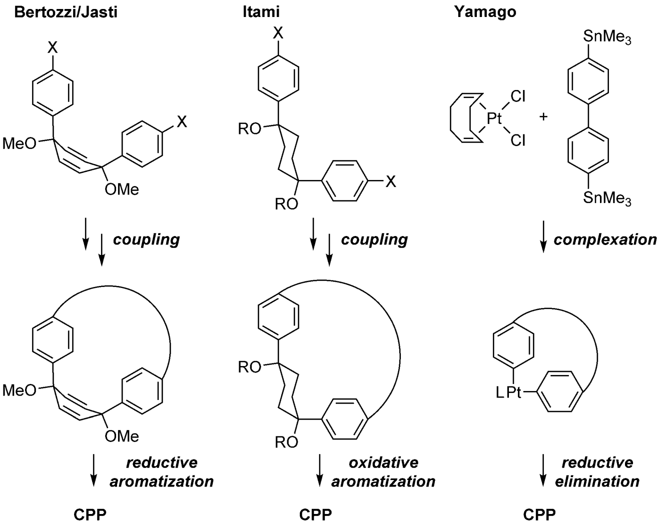
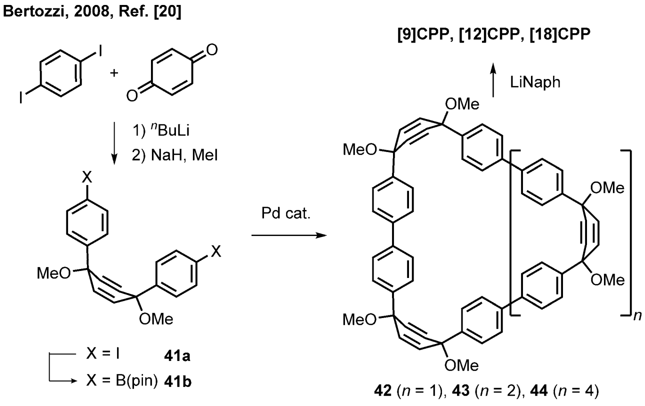


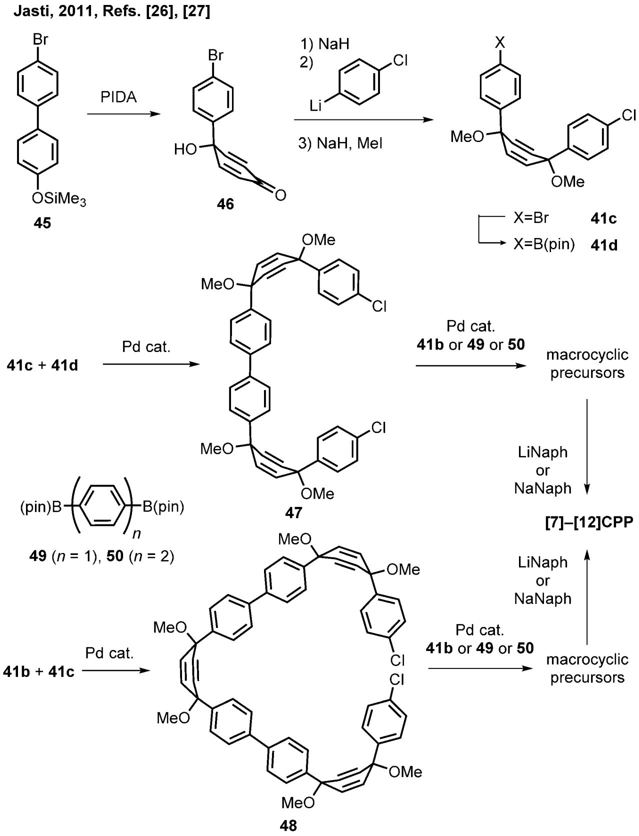
Figure 7. Strategies for the synthesis of CPPs.

moieties occupying the corners, thus generating unstrained CPP precursors. In the final step, these cyclohexadiene moieties were subjected to reductive aromatization to furnish the corresponding CPPs. Itami and co-workers, on the other hand, used 1,4-diphenylcyclohexanes as terphenylene precursors. The macrocycles obtained by coupling the L-shaped units were subsequently transformed into CPPs by oxidative aromatization. Yamago et al. used *cis*-platinum complexes as unstrained CPP precursors. Initially, macrocyclic platinum-bridged biphenyl moieties were synthesized, before an ensuing reductive elimination between the biphenyl ligands generated the CPPs. Each method was further developed by the three research groups and applied to the synthesis of a series of CPPs. We will now describe the synthesis of CPPs, arranging them according to the research groups who accomplished the synthesis.

The first synthesis of a CPP was achieved by Bertozzi, Jasti et al. in 2008 (Scheme 10).[20] For the synthesis of a strain-free macrocyclic CPP precursor, L-shaped unit **41a** was prepared from 1,4-diiodobenzene and *p*-benzoquinone, before a subsequent borylation of **41a** led to **41b** (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl). The palladium-catalyzed cross-coupling of **41a** with **41b** afforded three different macrocycles **42**–**44**. Finally, reductive aromatization of the isolated macrocycles **42**–**44** with lithium naphthalenide (LiNaph) provided [9]CPP, [12]CPP, and [18]CPP.

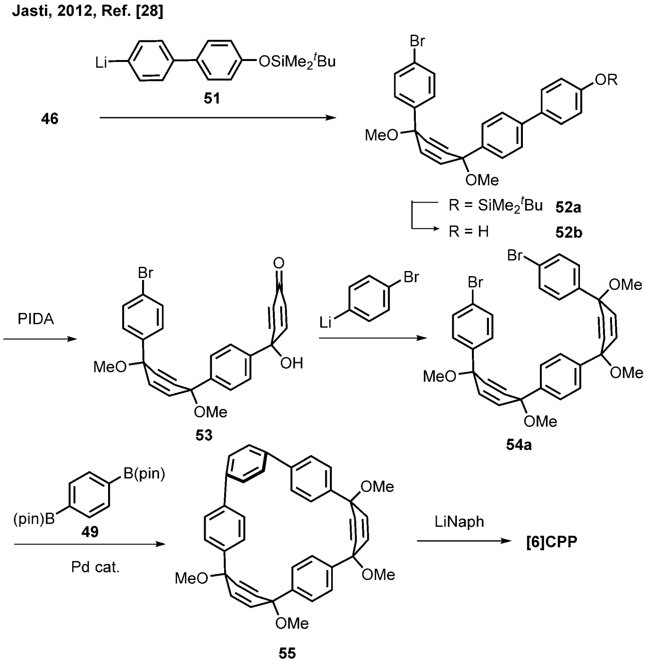


Scheme 10. The first synthesis of CPPs.



Scheme 11. Selective synthesis of [7]–[12]CPPs.

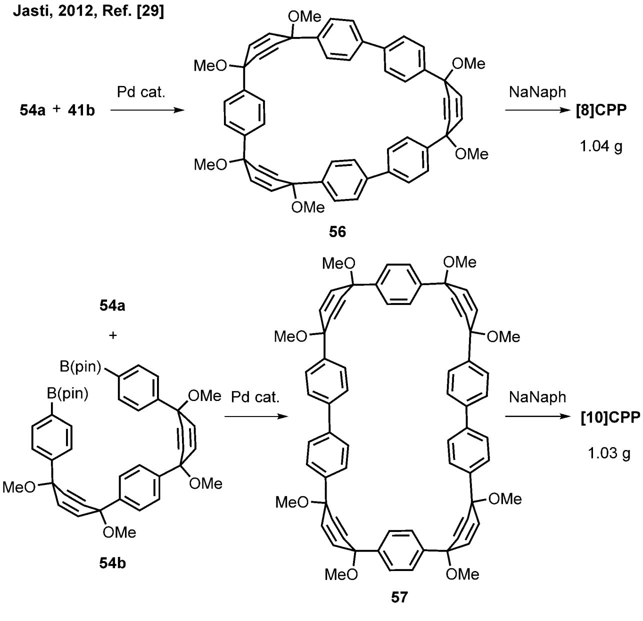
Later, Jasti and co-workers succeeded in the selective synthesis of [6]–[12]CPPs. The strategy for [7]–[12]CPPs relied on orthogonal Suzuki–Miyaura cross-coupling reactions involving three different types of L-shaped units **41b–d** (Scheme 11).[26,27] Thus, oxidative dearomatization of silyl-protected bromophenol **45** with iodobenzene diacetate (PIDA) resulted in the formation of ketone **46**. Subsequently, **46** was treated with 4-chlorophenyllithium to yield the unsymmetric L-shaped unit **41c**, which was then borylated to give **41d**. With these two L-shaped units **41c,d** in hand, the corresponding macrocyclic precursors for CPPs were built by orthogonal Suzuki–Miyaura cross-coupling reactions. Combining L-shaped units **41b–d** with linear units (**44** and **45**) afforded macrocycles, which were transformed into the corresponding CPPs by reductive aromatization using either LiNaph or sodium naphthalenide (NaNaph). The synthesis of [6]CPP was accomplished in 2012 (Scheme 12).[28] For that purpose, ketone **46** was combined with silyl-protected



Scheme 12. Selective synthesis of [6]CPP.

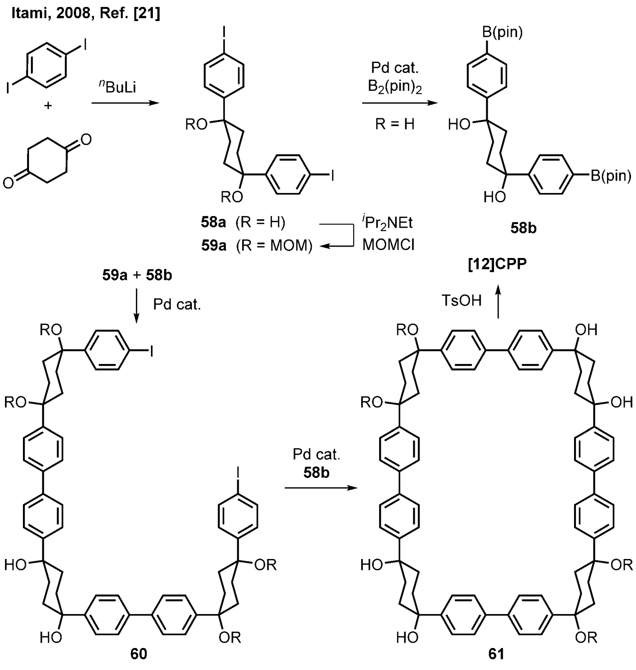
biphenyl unit **51** to afford **52a**. The *tert*-butyldimethylsilyl group on **52a** was cleaved to form **52b**, before oxidation of the phenol group with PIDA provided **53**. Nucleophilic addition of 4-bromophenyllithium led to the generation of U-shaped unit **54a**, and a subsequent coupling with 1,4-diborylbenzene **49** afforded **55**, which in turn furnished [6]CPP after reductive aromatization.

Jasti and co-workers were able to establish a gram-scale synthesis of [8]CPP and [10]CPP (Scheme 13).[29] The relatively straightforward synthesis of macrocycle **56** was achieved by a cross-coupling reaction of L-shaped unit **54a** with U-shaped unit **41b**, followed by a reductive aromatization reaction, which provided 1.04 g of [8]CPP. Similarly, the cross-coupling of **54a** with **54b** afforded 1.03 g of [10]CPP via macrocycle **57**.

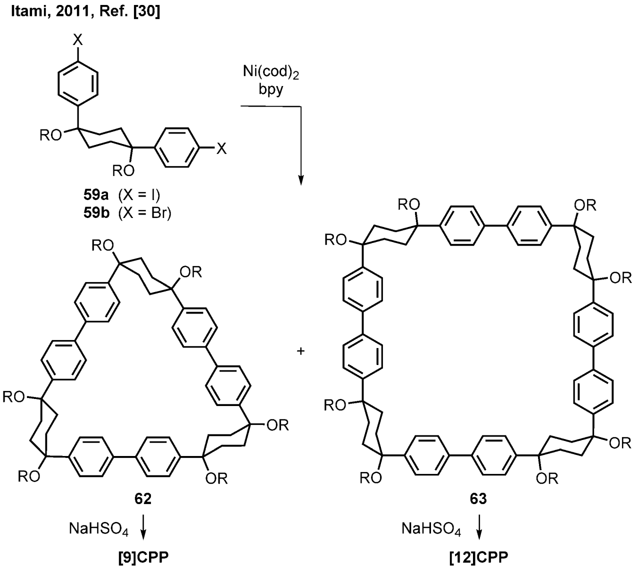


Scheme 13. Gram-scale synthesis of [8]- and [10]CPP.

In 2009, Itami and co-workers reported the first size-selective synthesis of [12]CPP (Scheme 14).[21] For the synthesis of [12]CPP, L-shaped unit **58a** was synthesized from 1,4-diiodobenzene and cyclohexane-1,4-dione. Next, **58a** was converted into **59a** and **58b** as a MOM-protected (MOM = methoxymethyl) L-shaped unit and as a borylated L-shaped unit, respectively, for the subsequent Suzuki–Miyaura coupling. Palladium-catalyzed cross-coupling of **58b** with an excess of **59a** afforded selectively acyclic C-shaped unit **60**, which was subsequently coupled with **58b** to exclusively furnish the macrocycle **61**. The cyclohexane units of **61** were deprotected, dehydrated, and dehydrogenated in a one-pot reaction mediated by *p*-toluenesulfonic acid (TsOH) and microwave irradiation to produce [12]CPP.



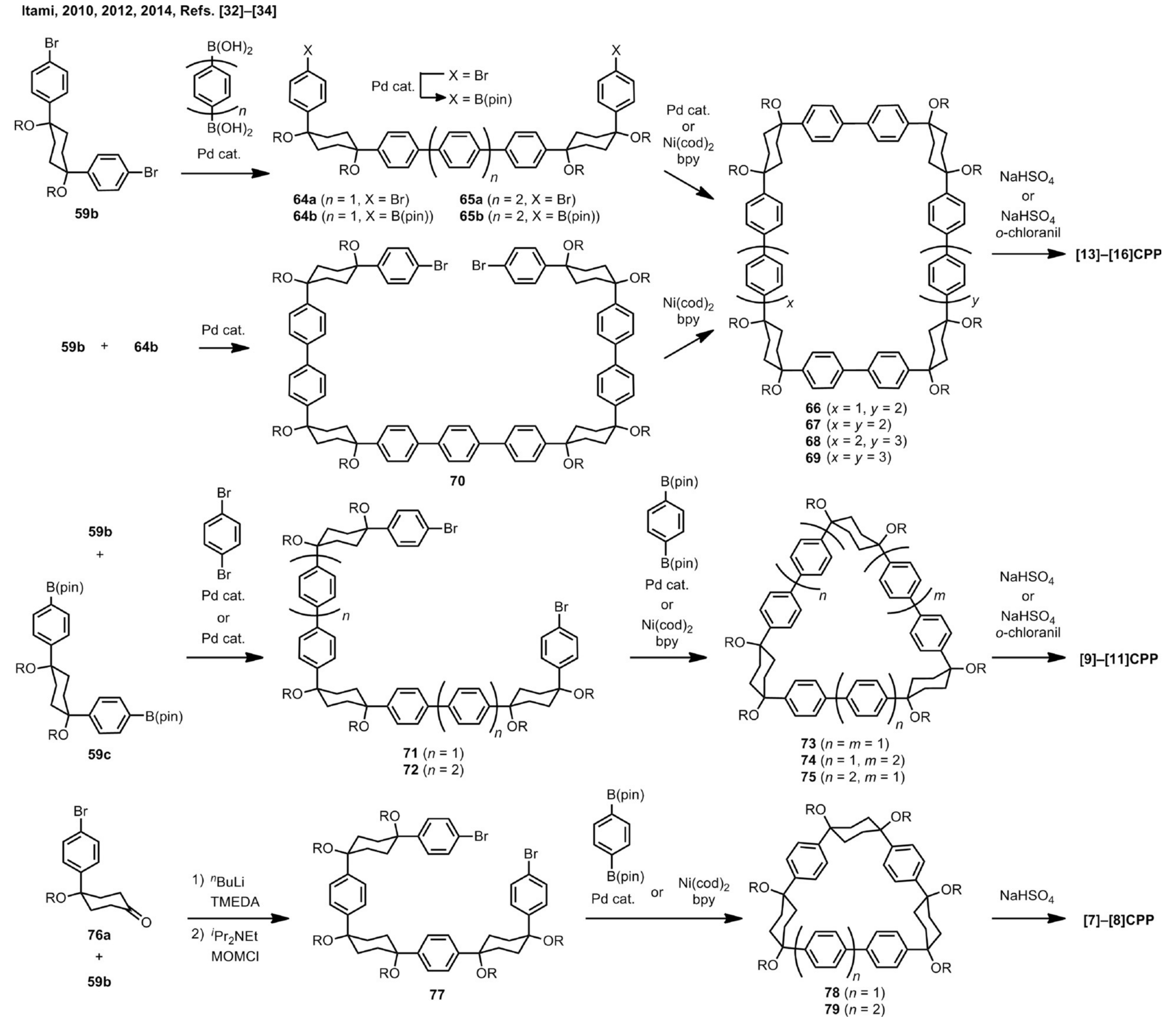
Scheme 14. Selective synthesis of [12]CPP (R = MOM unless otherwise noted).



Scheme 15. Concise synthesis of [9]CPP and [12]CPP (R = MOM).

While this synthetic route to [12]CPP has the advantage of being selective, several reaction steps are still required. Therefore, Itami and co-workers developed a more concise method for the synthesis of [9]CPP and [12]CPP in 2011 (Scheme 15).[30] The homocoupling reaction of L-shaped units **59a** or brominated derivative **59b** promoted by Ni(cod)$_2$/bpy (cod = 1,5-cyclooctadiene, bpy = 2,2′-bipyridyl) furnished macrocycles **62** and **63**, which are easily separated by column chromatography. The final aromatization step was also improved by using sodium hydrogen sulfate as the acid and *m*-xylene/water as the solvent, thus foregoing the necessity for microwave heating. As a result, [9]CPP and [12]CPP were synthesized in merely four steps from commercially available starting materials. This concise method can also be easily scaled up and, accordingly, large amounts (ca. 10 g) of [9]CPP and [12]CPP are now commercially available.[31]

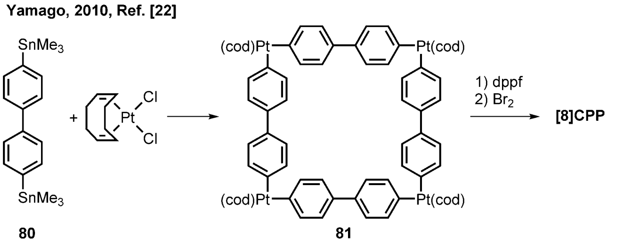
The Itami group furthermore established a size-selective synthesis for [7]–[16]CPPs (Scheme 16) through a combination of L-shaped building blocks **59b**,**c** and **76a** with linear units. Initially, the size-selective synthesis of large CPPs, [14]–[16]CPPs, was accomplished by assembling an L-shaped unit **59b** with 1,4-diborylbenzene and 4,4′-diborylbiphenyl to yield U-shaped units **64a** and **65a**, respectively.[32] The bromo substituents in U-shaped units **64a** and **65a** were converted into a boryl group by a palladium-catalyzed Miyaura borylation reaction, which resulted in the formation of **64b** and **65b**, respectively. Cross-coupling reactions between suitable pairs of **64a**–**65b** afforded the corresponding macrocycles **67**–**69** (**67**: **64a** + **64b**, **68**: **64b** + **65a**, **69**: **65a** + **65b**). Alternatively, macrocycles **67** and **69** can also be obtained by nickel-mediated homocoupling reactions of **64a** and **65a**, respectively.[33] A final oxidative aromatization of **67**–**69** with sodium hydrogen sulfate afforded [14]–[16]CPPs. In addition to these larger CPPs, the size-selective synthesis of [9]–[11]CPPs and [13]CPP were also accomplished in 2012.[33] Combining **64b** with **59b** yielded C-shaped unit **70**, the terminal moieties of which were linked using Ni(cod)$_2$/bpy to yield **66** as a precursor to [13]CPP. C-Shaped units **71** and **72** were obtained from **59b**,**c** and 1,4-dibromobenzene, and served as precursors for [9]–[11]CPPs. Connecting the terminals of **71** furnished **73**, and a subsequent aromatization led to [9]CPP, while cross-coupling of **71** with 1,4-diborylbenzene afforded **74**, which was converted into [10]CPP. Meanwhile, combining **59b**,**c** and 1,4-dibromobenzene afforded **75** through macrocyclization of **72**, which was transformed into [11]CPP. In 2014, the size-selective synthesis of smaller CPPs, [7]CPP and [8]CPP, was achieved.[34] Since CPPs smaller than [9]CPP cannot be synthesized by assembling the previously described L-shaped units, Itami and co-workers introduced a new smaller L-shaped unit **76a**, which can be converted into a biphenyl unit after aromatization. The twofold addition of dilithiated L-shaped unit **59b** to **76a** afforded C-shaped unit **77**, and a subsequent homocoupling of the terminal groups in **77** provided macrocycle **78**, which was used as the precursor for



Scheme 16. Size-selective synthesis of [7]–[16]CPPs (R = MOM).

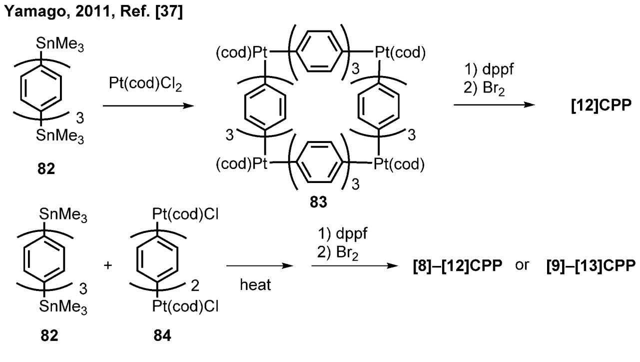
[7]CPP. Cross-coupling of **77** with 1,4-diborylbenzene yielded **79**, which was subsequently converted into [8]CPP. With this study, Itami and co-workers completed the comprehensive size-selective synthesis of [7]–[16]CPPs. The selective synthesis of [10]CPP was later improved by using the small L-shaped unit **76a**.[35]

The Yamago research group reported an alternative synthesis of [8]CPP by applying the platinum-mediated synthesis of cycloarenes developed by Bäuerle and co-workers[36] (Scheme 17).[22] The complexation of 4,4′-bis(trimethylstannyl)biphenyl (**80**) and Pt(cod)Cl_2 afforded macrocycle **81**. Since the ligand exchange on platinum is reversible, tetraplatinum complex **81** was formed selectively as it represents the least strained isomer. Reductive elimination of the aryl groups from the platinum center promoted by a ligand exchange from cod to dppf (dppf = 1,1′-bis(diphenylphosphino)ferrocene), followed by an oxidation with bromine resulted in the formation of [8]CPP.

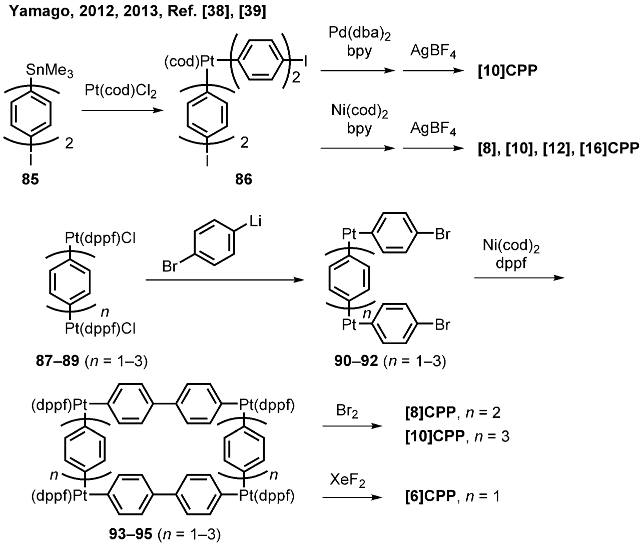


Scheme 17. Synthesis of [8]CPP.

In 2011, Yamago and co-workers reported both the random and selective synthesis of CPPs by the platinum complexation method (Scheme 18). For example, [12]CPP was synthesized selectively from bis(trimethylstannyl)terphenyl **82** via the macrocyclic platinum complex **83**.[37] The attempted reaction of **82** and a diplatinum unit **84** was expected to accomplish a selective synthesis of [10]CPP. However, [8]–[13]CPPs were obtained randomly at elevated temperatures, depending on the reaction time. Yamago and co-workers achieved an unexpected size-selective synthesis of [10]CPP (Scheme 19).[38] The homocoupling reaction of L-shaped platinum complex **86** was attempted to obtain cyclic dimer, trimer, and tetramer as precursors for [8]CPP, [12]CPP, and [16]CPP, respectively. When Ni(cod)$_2$/bpy and silver tetrafluoroborate was used for the homocoupling and the reductive elimination, respectively, [8]CPP, [10]CPP, [12]CPP, and [16]CPP were generated randomly. Surprisingly, [10]CPP was obtained selectively when Pd(dba)$_2$ (dba = dibenzylideneacetone) was used instead of Ni(cod)$_2$. In 2013, the selective synthesis of [6]CPP and [8]CPP was achieved and the method for the preparation of [10]CPP was improved.[39] The reaction of diplatinum complexes **87–89** with 4-bromophenyllithium afforded U-shaped diplatinum complexes **90–92**, and a subsequent homocoupling reaction of **90–92** provided macrocycles **93–95**. [6]CPP, [8]CPP, and [10]CPP were obtained by reductive elimination promoted by bromine (for [8]CPP and [10]CPPs) or by xenon difluoride (for [6]CPP).

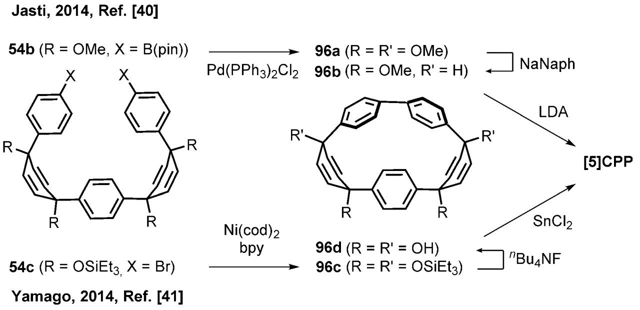


Scheme 18. Selective and random synthesis of [8]–[13]CPPs.



Scheme 19. Selective and random synthesis of CPPs.

The groups of Jasti and Yamago independently reported almost simultaneously the synthesis of [5]CPP, which is the smallest isolated [*n*]CPP to date. In the synthesis of [5]CPP by Jasti and co-workers (Scheme 20),[40] a homocoupling reaction between the C–B bonds of **54b** provided macrocycle **96a**. Treatment of **96a** with NaNaph promoted partial demethoxylation to form **96b**. Further reductive aromatization of **96b**



Scheme 20. Synthesis of [5]CPP.

needed additional treatment with lithium diisopropylamide (LDA) to obtain [5]CPP. Yamago and co-workers also achieved the synthesis of [5]CPP.[41] Nickel-mediated homocoupling reaction of **54c** afforded macrocycle **96c**. Cleavage of the triethylsilyl groups and reduction of **96c** with tin(II) chloride furnished [5]CPP. Unlike the larger [*n*]CPPs, both methods required additional steps, which reflects the high strain energy of [5]CPP. Yamago and co-workers subsequently synthesized [7]–[12]CPPs selectively by applying the synthetic method for [5]CPP.[42] [6]CPP was also synthesized by a Jasti–Yamago hybrid method.[43]

2.1.4. Armchair Carbon Nanorings

The previously presented synthetic strategies for the generation of [*n*]CPPs can also be applied for the synthesis of a variety of other strained ring-shaped compounds. When substituted benzene rings (e.g. tetraphenylbenzene), polycyclic aromatic hydrocarbons (e.g. naphthalene, pyrene, or chrysene), or heteroarenes (e.g. pyridine,[44] thiophene,[45] anthraquinone,[46] carbazole,[47] or perylene diimide[48]) are used in addition to benzene rings, CPP derivatives called "carbon nanorings" are obtained. Soon after the development of suitable synthetic methods for the generation of [*n*]CPPs by the groups of Jasti, Itami, and Yamago (Figure 7), a variety of carbon nanorings were synthesized by these and other groups. In this section, carbon nanorings, which represent segments of armchair CNTs, are described (Figure 8). Armchair carbon nanorings can be subdivided into multiaryl-CPPs, CPP dimers, and π-extended carbon nanorings.

Jasti and co-workers synthesized tetraphenylated [12]CPP in 2012 (Scheme 21),[49] whereby an L-shaped unit with four 4-*n*-butylphenyl groups (**97**) was prepared, and macrocycle **98** was obtained by stepwise cross-coupling of **97** with L-shaped

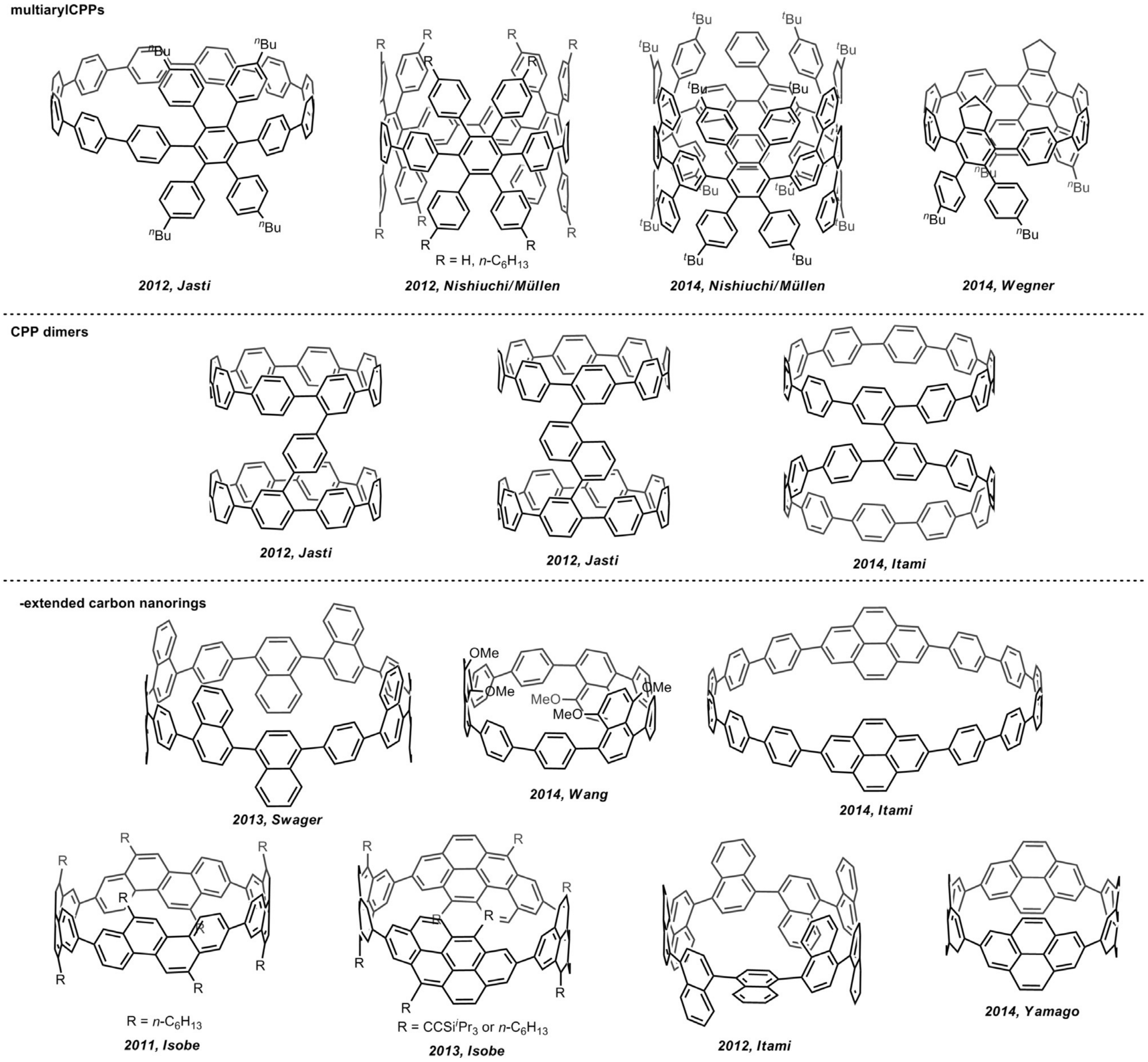
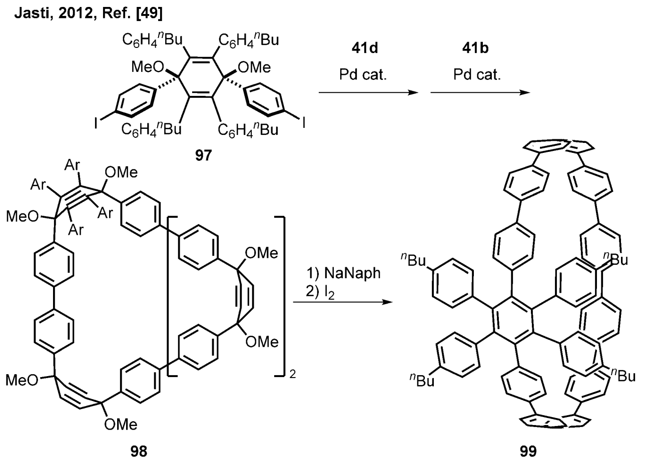


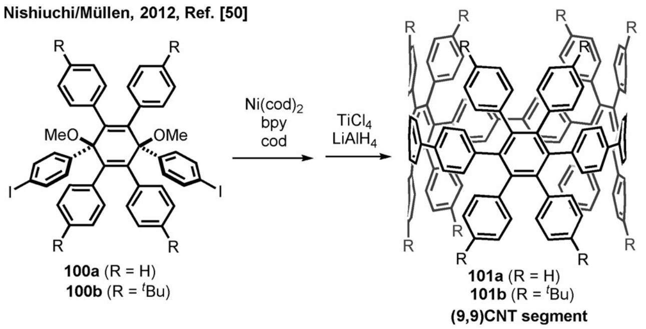
Figure 8. Armchair carbon nanorings.



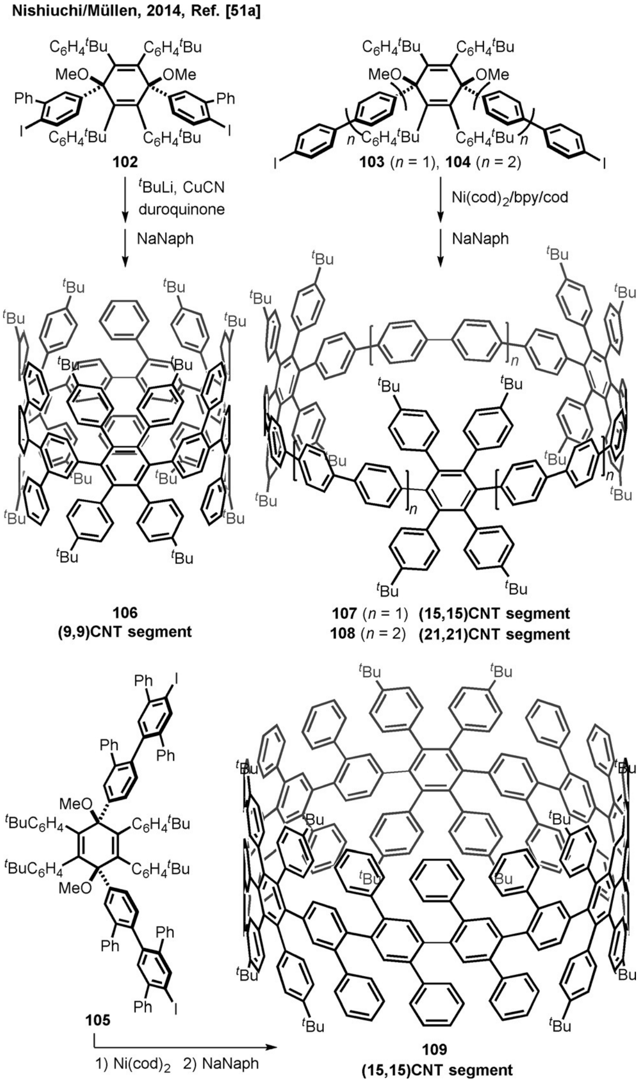
Scheme 21. Synthesis of tetraaryl[12]CPP (Ar = 4-C_6H_4nBu).

units bearing boryl and chloro groups (**41d**) and with a diboryl L-shaped unit **41b**. Finally, the reductive aromatization of **98** mediated by NaNaph, followed by quenching with iodine furnished tetraphenylated [12]CPP **99**.

After the report by Jasti and co-workers, several multi-aryl-CPPs were synthesized by Nishiuchi, Müllen et al. and used as potential precursors for belt-shaped molecules. In 2012, dodecaaryl[9]CPP was synthesized by using the Jasti method (Scheme 22).[50] Initially, L-shaped units with four phenyl or 4-*tert*-butylphenyl groups **100a**,**b** were prepared. Nickel(0)-mediated homocoupling reactions of **100a**,**b** furnished a macrocycle, which was converted into dodecaaryl-[9]CPPs **101a**,**b** by reductive aromatization with $TiCl_4$/$LiAlH_4$. In 2014, a series of multiaryl-CPPs **106–109** were prepared (Scheme 23).[51a] Nishiuchi, Müllen, and co-workers synthesized multiphenyl-substituted L-shaped units **102–105** and subsequent coupling reaction and aromatization afforded carbon nanorings **106–109**. The carbon nanorings **106–109** are the segments of (9,9), (15,15), (21,21), and (15,15)CNT, respectively. Conversion of the carbon nanorings **106–109** or alkylated derivatives[51b] into belt-shaped molecules under Scholl reaction conditions was unsuccessful.



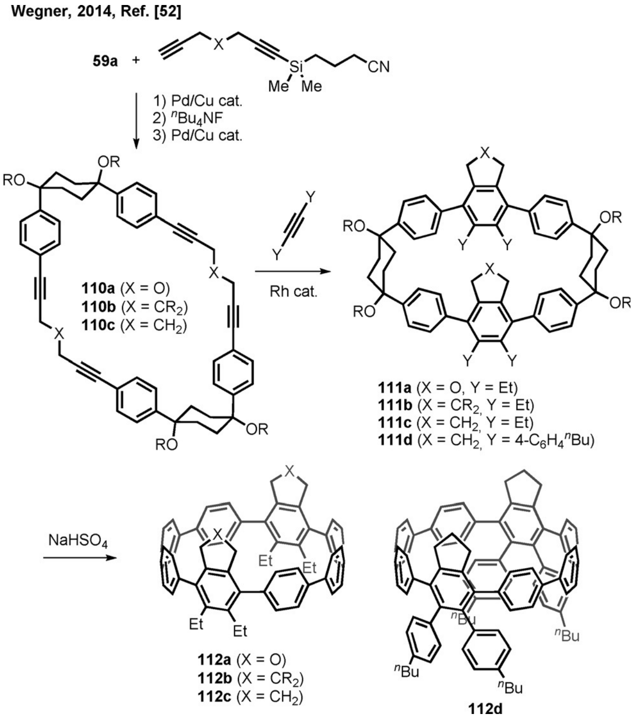
Scheme 22. Synthesis of dodecaaryl[9]CPP.



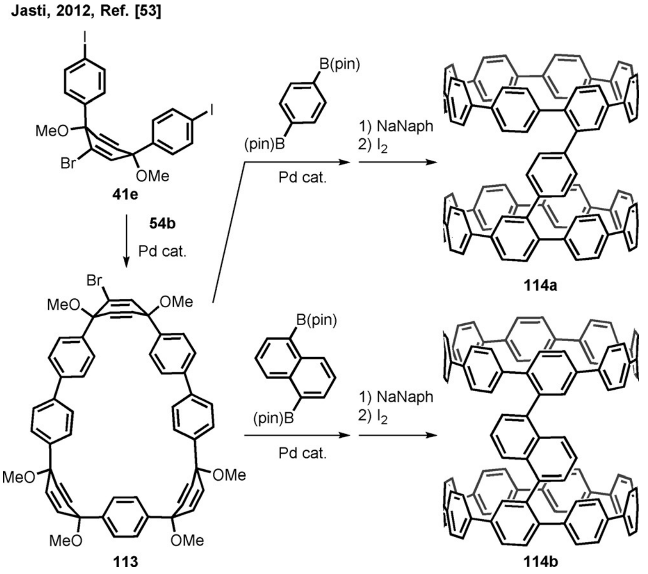
Scheme 23. Synthesis of multiaryl-CPPs.

In 2014, Wegner and co-workers reported the synthesis of [8]CPP derivatives **112a–d**, including tetraaryl[8]CPP derivative **112d** (Scheme 24).[52] Itami's L-shaped unit **59a** and monoprotected diynes were connected by sequential Sonogashira coupling and deprotection to furnish unstrained macrocycles **110a–c**. The diyne moieties of **110a–c** were converted into benzene rings by rhodium-catalyzed [2+2+2] cycloaddition with 3-hexyne or di(4-*n*-butylphenyl)acetylene. The resulting macrocycles **111a–d** were then subjected to acid-mediated aromatization to obtain [8]CPP derivatives **112a–d**.

When two CPPs are connected, potential precursors to belt-shaped molecules, that is carbon nanobelts, can be obtained. As a first step towards the synthesis of such carbon nanobelts, the synthesis of CPP dimers was examined. In 2012, Jasti and co-workers succeeded in synthesizing *p*-phenylene- and 1,5-naphthylene-bridged [8]CPP dimers **114a**,**b** (Scheme 25).[53] The bromine-containing macrocycle **113** was prepared by using a bromine-containing L-shaped unit **41e** in combination with the previously reported L-

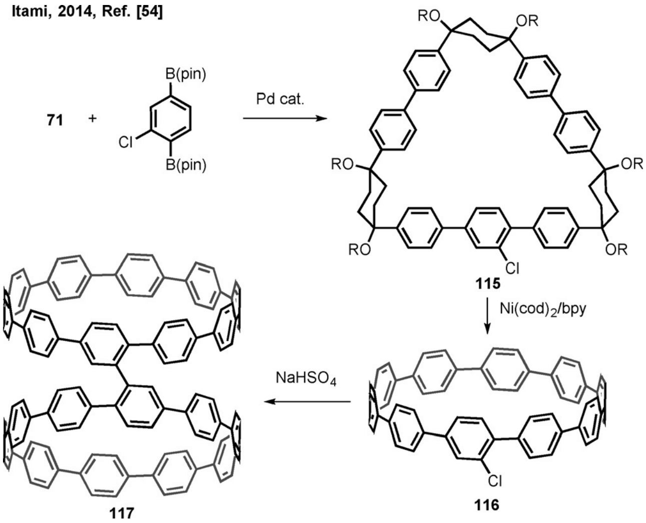


Scheme 24. Synthesis of [8]CPP derivatives (R = MOM).



Scheme 25. Synthesis of arylene-bridged [8]CPP dimers.

shaped unit **54b**. Subsequently, two **113** macrocycles were bridged with 1,4-diborylbenzene or 1,5-diborylnaphthalene and then subjected to reductive aromatization to afford [8]CPP dimers **114a**,**b**. Jasti and co-workers reported that a directly connected [8]CPP dimer could not be obtained from **113**.

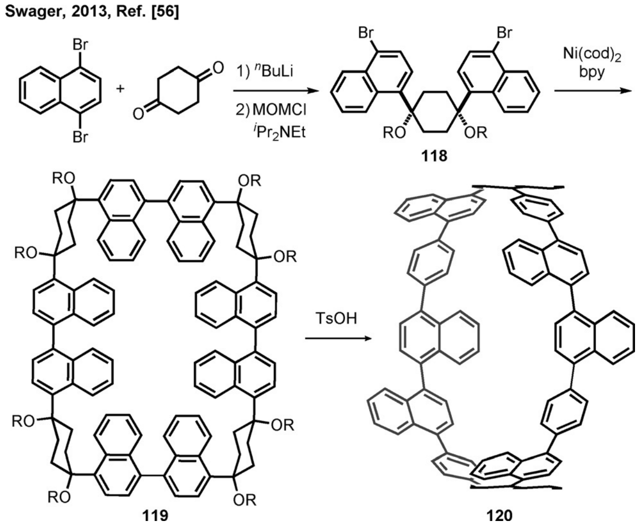


Scheme 26. Synthesis of directly connected [10]CPP dimers (R = MOM).

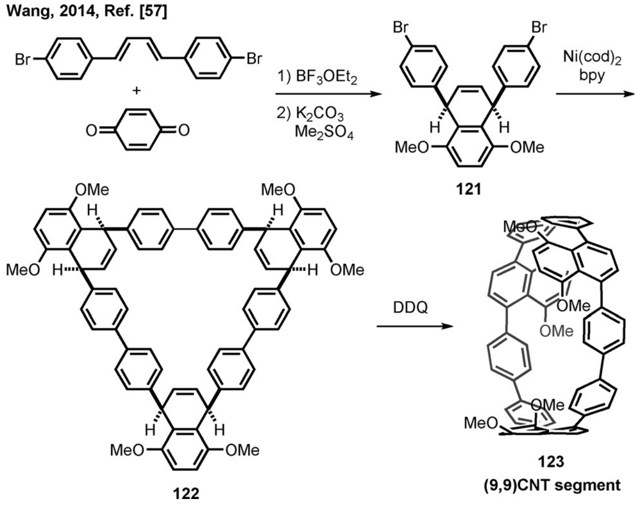
In 2014, Itami and co-workers accomplished the synthesis of a directly connected CPP dimer through the bottom-up synthesis of chloro-CPP.[54] Considering the required tolerance toward the reaction conditions of the CPP synthesis, such as palladium-catalyzed cross-coupling and acid-mediated aromatization, the chloro group is expected to be an efficient handle for further synthetic manipulation. The preparation of chloro[10]CPP was achieved by a simple modification of a previously reported route for [10]CPP (Scheme 26). Instead of 1,4-diborylbenzene, which was used for the synthesis of [10]CPP, 1,4-diboryl-2-chlorobenzene was used as the chloro-containing linear unit. A cross-coupling reaction of 1,4-diboryl-2-chlorobenzene with C-shaped unit **71** provided the chloro-containing macrocycle **115**. The subsequent aromatization of **115** furnished chloro[10]CPP **116**, which is the first example of a monosubstituted CPP. Finally, a homocoupling reaction of **116** with Ni(cod)$_2$/bpy afforded the directly connected [10]CPP dimer **117**. The synthetic route to the directly connected CPP dimers can be improved to the one-pot selective monofunctionalization of CPPs by using a Cr-CPP complex, which was reported by the Itami group in 2015.[55]

In the following section, π-extended carbon nanorings are described, and we present three examples of *p*-phenylene-polycyclic aromatic hydrocarbon (PAH) hybrid rings and four examples of all-PAH rings. In 2013, the first hybrid ring was reported by the Swager group, who applied Itami's "cyclohexane" method to the synthesis of carbon nanoring **120**, which bears naphthalene and benzene rings (Scheme 27).[56] Naphthalene-containing L-shaped unit **118** was prepared from 1,4-dibromonaphthalene and 1,4-cyclohexanedione. Subsequently, the macrocycle **119** was obtained by the nickel-mediated homocoupling of **118**. Oxidative aromatization of cyclic tetramer **119** with TsOH yielded carbon nanoring **120**, which is a segment of (12,12)CNT. It was also mentioned that a transformation of the 1,1′-binaphthyl units of **120** into perylene units should provide the perylene-containing carbon nanoring.

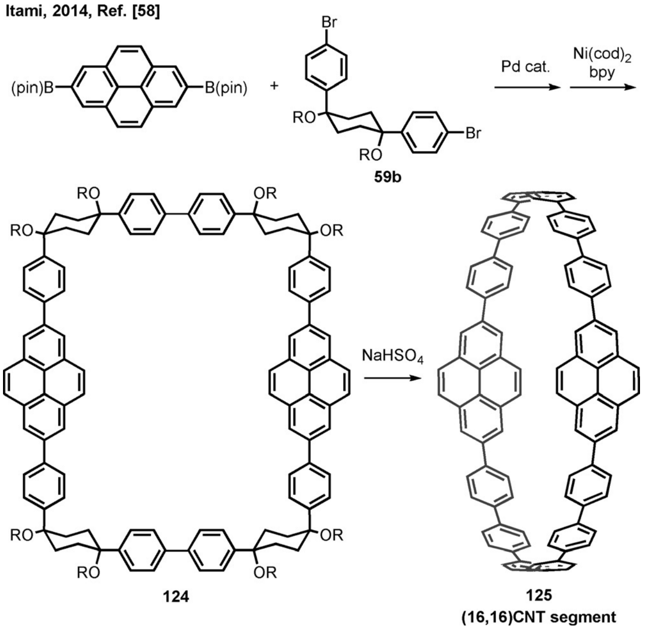
In 2014, Wang and co-workers used an alternative route to synthesize a carbon nanoring consisting of naphthalene and benzene rings (Scheme 28).[57] The *cis*-configurated L-shaped



Scheme 27. Synthesis of naphthalene-containing carbon nanorings (R = MOM).



Scheme 28. Synthesis of dimethoxynaphthalene-containing carbon nanorings.



Scheme 29. Synthesis of pyrene-containing carbon nanorings (R = MOM).

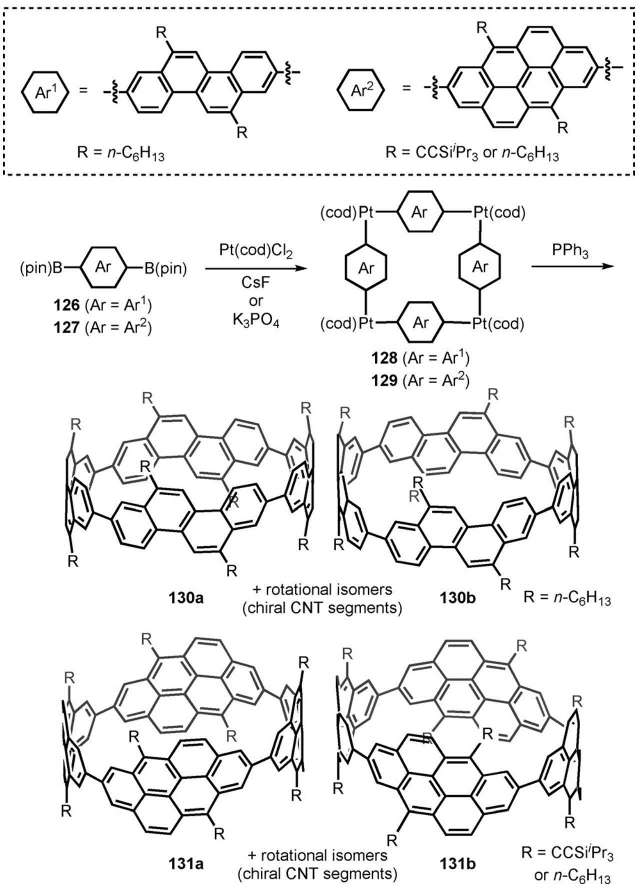
unit **121** was obtained selectively by the Diels–Alder reaction of 1,4-bis(4-bromophenyl)butadiene and *p*-benzoquinone. Homocoupling reaction of **121** afforded macrocycle **122**, and carbon nanoring **123** was obtained by oxidative aromatization of the cyclohexadiene moiety by using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). The dimethoxynaphthalene-containing carbon nanoring **123** represents a (9,9)CNT segment.

The synthesis of the pyrene-containing carbon nanoring cycloparaphenylene-2,7-pyrenylene (**125**) was reported by Itami and co-workers in 2014 (Scheme 29).[58] The synthetic route was based on the synthesis of [16]CPP. Macrocycle **124** was obtained by the homocoupling reaction of pyrene-containing U-shaped units, which were generated by the cross-coupling reaction of 1,4-diborylpyrene with the L-shaped unit **59b**. As the oxidative aromatization of **124** required high temperatures, 1,2,4-trichlorobenzene was used as the solvent. The obtained carbon nanoring **124** is a representative segment of (16,16)CNT.

The following discusses four examples of all-PAH carbon nanorings. In 2011 and 2013, Isobe and co-workers synthesized carbon nanorings solely consisting of chrysenes ([4]cyclo-2,8-chrysenylene, **130**) and anthanthrylenes ([4]cyclo-2,8-anthanthrylene, **131**) as shown in Scheme 30.[59, 60] By using Yamago's method for the synthesis of CPPs, macrocyclic platinum complexes **128** and **129** were prepared by the complexation of Pt(cod)Cl$_2$ with diborylated PAHs **126** and **127**, which can be synthesized from chrysene and pigment red, respectively. In contrast to Yamago's original macrocyclization using Pt(cod)Cl$_2$ and distannylarenes, the modification by Isobe and co-workers employs bases such as CsF and K$_3$PO$_4$ as promoters for the transmetalation of the diborylarenes. Treatment of macrocycles **128** and **129** with triphenylphosphine at elevated temperatures provided a mixture of rotational isomers of carbon nanorings, **130** and **131**, respectively. The rotational isomers of [4]cyclo-2,8-chrysenylene (**130a**,**b**) as well as rotational isomers of [4]cyclo-2,8-anthanthrylene (**131a**,**b**) represent armchair CNT segments. The other two types of rotational isomers, which correspond to chiral CNT segments, are described in Section 2.2.2.

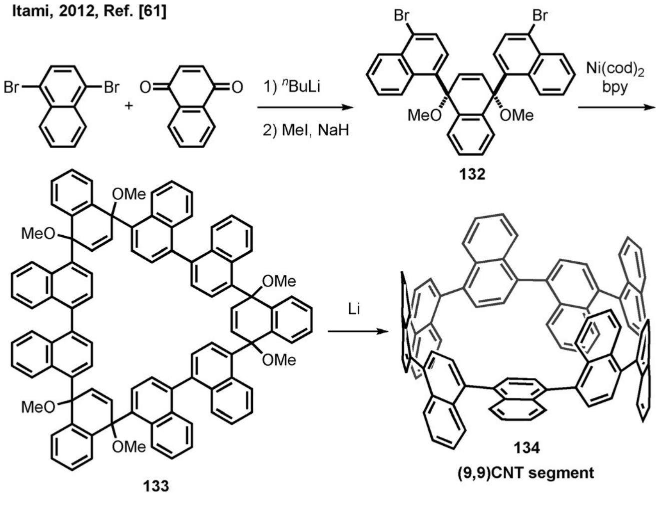
In 2012, Itami and co-workers reported the synthesis of [9]cyclo-1,4-naphthylene (**134**), which consists exclusively of naphthalene rings (Scheme 31).[61] A synthesis based on a reductive aromatization pathway was selected for the generation of **134**. Firstly, L-shaped unit **132** was prepared from 1,4-dibromobenzene and 1,4-naphthoquinone. A nickel-mediated macrocyclization of **132** yielded cyclic trimer **133**, which was subsequently converted into **134** by reductive aromatization with lithium metal. Interestingly, previously

Isobe, 2011, 2013, Refs. [59], [60]



Scheme 30. Synthesis of [4]cyclo-2,8-chrysenylene and [4]cyclo-2,8-anthanthrylene.

Itami, 2012, Ref. [61]

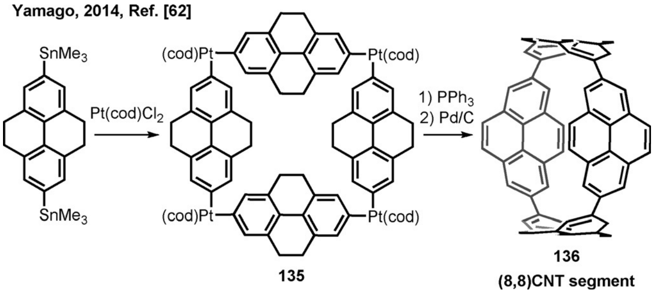


Scheme 31. Synthesis of cyclo-1,4-naphthylene.

reported aromatization conditions, using for example, LiNaph, were found to be unsuitable for this reaction.

In 2014, Yamago and co-workers reported the synthesis of [4]cyclo-2,7-pyrenylene **136** (Scheme 32).[62] To increase the solubility of the synthetic intermediates, 4,5,9,10-tetrahydropyrene was used instead of pyrene. The macrocyclic platinum complex **135**, which consists of four tetrahydropyrene rings, was synthesized using Yamago's original macrocyclization method. Reductive elimination of **135** provided a ring-shaped structure, which was subsequently dehydrogenated using palladium on carbon to afford [4]cyclo-2,7-pyrenylene (**136**), which represents a (8,8)CNT segment.

Yamago, 2014, Ref. [62]

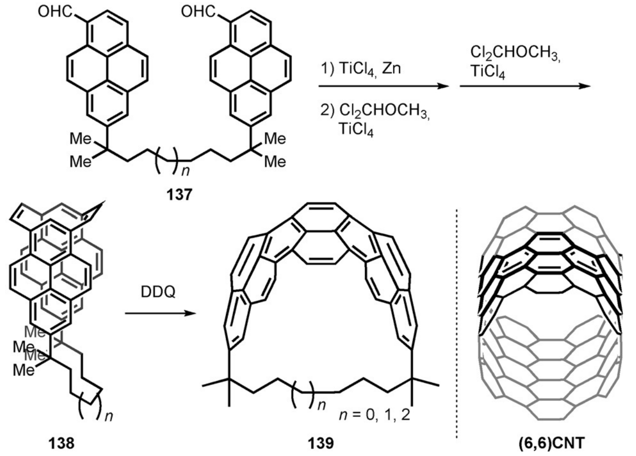


Scheme 32. Synthesis of [4]cyclo-2,7-pyrenylene.

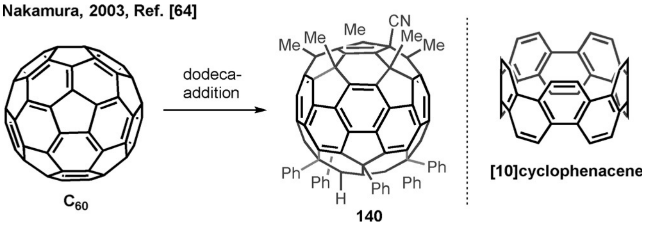
2.1.5. *Related Compounds*

The previous sections describe armchair CNT segments as the structures obtained by slicing armchair CNTs. On the other hand, it should be worth noting that the following two types of ring compounds with curved π-conjugation represent partial sidewall segments of armchair CNTs. An example of the compounds is teropyrenophane **139**, synthesized in 2008 by Bodwell and co-workers (Scheme 33).[63] They obtained macrocycle **138** through formylation and a subsequent intramolecular McMurry coupling of the formyl groups in **137**. An ensuing oxidation of macrocycle **138** with DDQ provided **139**, which is characterized by a curved π-conjugated structure that corresponds to that of (8,8)CNT (in the case of $n = 8$). In 2003, Nakamura et al. reported the synthesis of **140**, which represents a π-conjugated system of [10]cyclophenacene, after a multiple substitution of C_{60} (Scheme 34).[64]

Bodwell, 2009, 2013, Ref. [63]



Scheme 33. Synthesis of teropyrenophanes.



Scheme 34. Multisubstitution of C_{60}.

2.2. Segments of Chiral CNTs

In this section, the synthesis of chiral CNT segments is summarized. Figure 9 shows the reported chiral CNT segments. A possible explanation for the low number of reported examples of chiral carbon nanorings relative to that of armchair carbon nanorings could be the inherently lower symmetry of the former with respect to the latter.

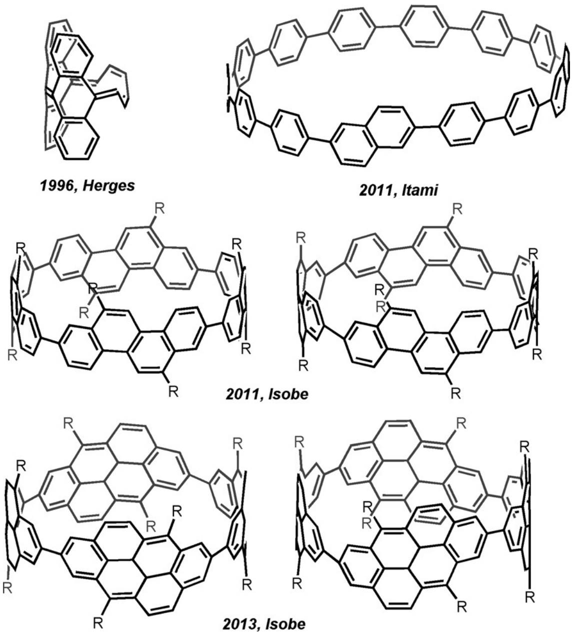
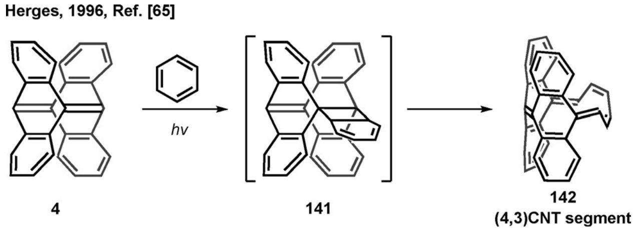


Figure 9. Chiral carbon nanorings.

2.2.1. Picotubes

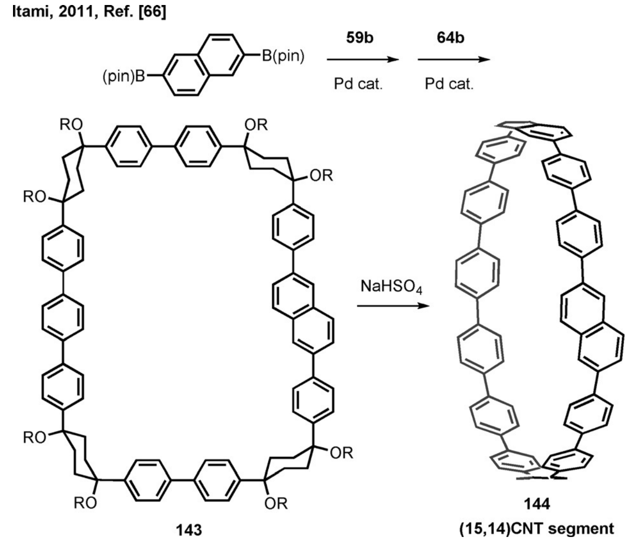
As previously shown, most TDDA derivatives reported to date represent segments of armchair CNTs. The TDDA derivative **142** was reported as the only chiral CNT segment among the TDDA derivatives to date. A ring-opening reaction of the cyclobutadiene moiety in **141**, generated by [2+2] photocyclization of TDDA (**4**) with benzene, resulted in the formation of **142** (Scheme 35).[65] Compound **142** can be considered to be a (4,3)CNT segment.



Scheme 35. Ring expansion of TDDA.

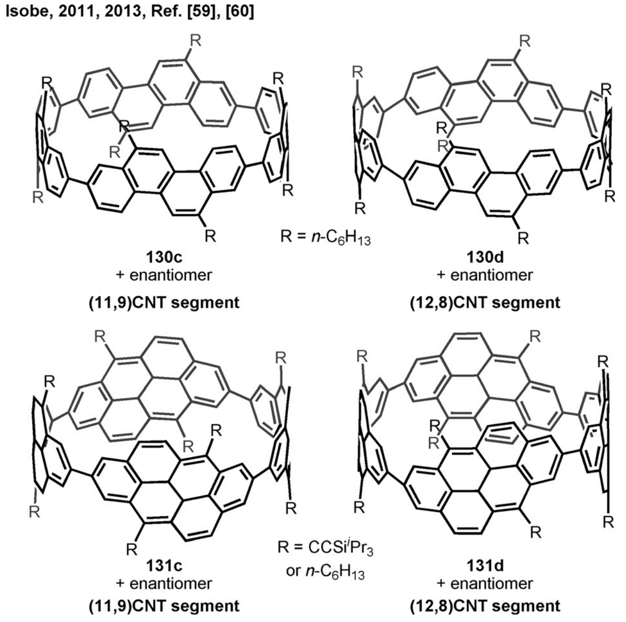
2.2.2. Chiral Carbon Nanorings

In 2011, Itami and co-workers reported the first synthesis of a chiral carbon nanoring, which represents a (15,14)CNT segment (Scheme 36).[66] A modular method for the synthesis of CPPs was used to synthesize the macrocycle **143**, which was based on the L-shaped unit **59b**, the U-shaped unit **64b**, and 2,6-diborylnaphthalene as the chirality-inducing unit. Cycloparaphenylene-2,6-naphthylene **144** was obtained by a subsequent oxidative aromatization of **143**. Itami and co-workers mentioned that many possible segments of chiral CNTs can be obtained by varying the acene unit and/or the number of paraphenylene moieties. For example, segments of $(n+2, n+1)$, $(n+3, n+1)$, and $(n+4, n+1)$CNTs can be obtained by inserting a 2,6-naphthylene, 2,6-anthrylene, or 2,8-tetracenylene unit, respectively, into the [*n*]CPP ring. As the 2,6-naphthylene moiety in **144** can easily rotate at ambient temperature, a separation of the **144** enantiomer was not possible.



Scheme 36. Synthesis of chiral carbon nanorings.

As discussed in Section 2.1.4, Isobe and co-workers were able to synthesize the chiral CNT segments [4]cyclo-2,8-chrysenylene **130c,d** and [4]cyclo-2,8-anthanthrylene **131c,d**, together with armchair CNT segments by using Yamago's method (Scheme 37).[59,60] These two types of rotational isomers represent (11,9)CNT and (12,8)CNT segments, respectively. In addition, each isomer consists of two enan-



Scheme 37. Chiral [4]cyclo-2,8-chrysene and [4]cyclo-2,8-anthanthracenylene.

tiomers, the separation of which was also accomplished successfully.

2.3. Segments of Zigzag CNTs

From a synthetic and structural perspective, segments of zigzag CNTs are also highly fascinating molecules. Cyclacene, the shortest conceivable zigzag CNT, had been the target of synthetic efforts even before the discovery of CNT structures. However, cyclacenes have not been synthesized to date, which is partly due to the instability of cyclacenes. In this section, studies towards the synthesis of cyclacenes and of one zigzag nanoring are described (Figure 10).

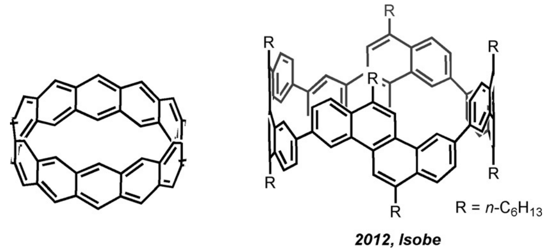
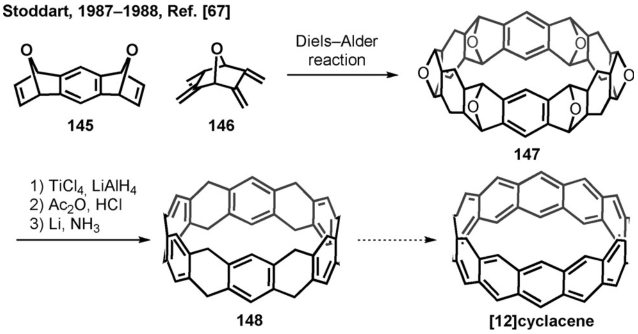


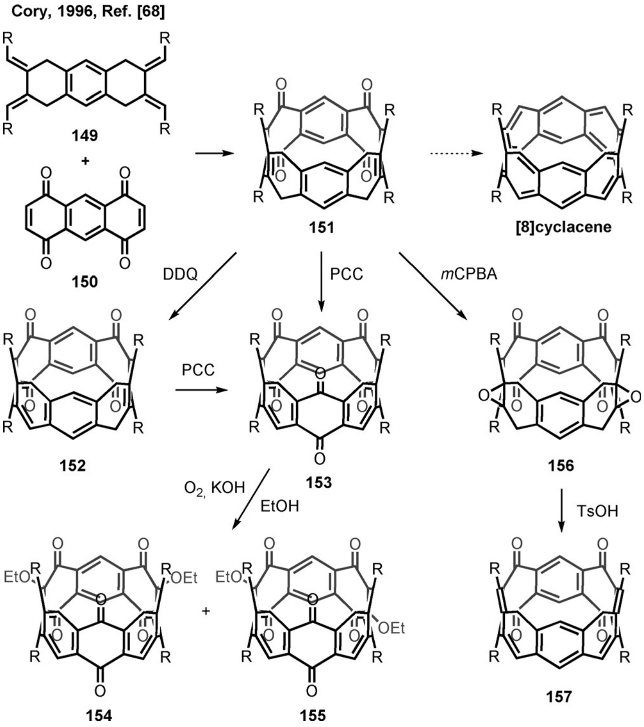
Figure 10. Representative zigzag carbon nanorings.

2.3.1. Cyclacenes



Scheme 38. Attempted synthesis of [12]cyclacene.

The first attempt to synthesize cyclacene was reported by Stoddart and co-workers in 1987 (Scheme 38).[67] Sequential Diels–Alder reactions between bisdienophile **145** and bisdiene **146** provided macrocycle **147**, which was subsequently deoxygenated, dehydrated, and reduced to afford octahydro[12]cyclacene **148**, which contains six alternating benzene rings. Although the transformation of **148** into [12]cyclacene by using various dehydrogenation reagents such as palladium on carbon, DDQ, and chloranil were attempted, all these efforts were unsuccessful.



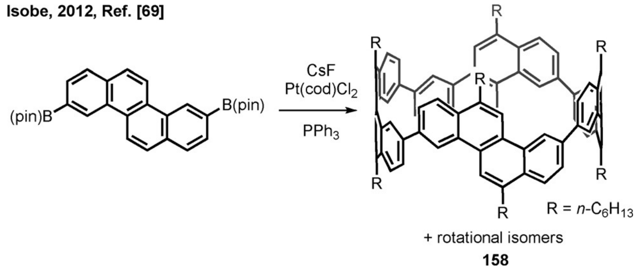
Scheme 39. Synthetic study towards [8]cyclacene.

In 1996, Cory et al. reported a synthetic study aimed at [8]cyclacene (Scheme 39).[68] They also employed Diels–Alder reactions of bisdiene **149** and bisquinone **150** to construct a carbon skeleton of [8]cyclacene. With macrocycle **151** in hand, a variety of transformations towards [8]cyclacene were attempted. For example, the dehydrogenation of **151** with DDQ furnished partially oxidized naphthalene **152**, but no anthracene. Further treatment of **152** with pyridinium chlorochromate (PCC) provided anthraquinone **153**, which implied that **152** was initially oxidized to anthracene, and subsequently into the corresponding anthraquinone. Similarly, **153** was also obtained by direct treatment of **151** with

PCC. Ensuing attempts to induce aromatization of the saturated rings in **153** in an oxygen atmosphere with potassium ethoxide merely produced a mixture of α-ethoxy-ketones **154** and **155** in a ratio of 1.1:1–1.3:1. The formation of an anthracene ring through consecutive epoxidation and dehydroxylation was also tested, but treatment with *m*-chloroperoxybenzoic acid (*m*CPBA) followed by treatment with TsOH provided bisdiene **157**.

2.3.2. Zigzag Carbon Nanorings

In 2012, Isobe and co-workers reported the synthesis of [4]cyclo-3,9-chrysenylene (**158**), which can be regarded as a sidewall segment of zigzag CNTs (Scheme 40).[69] They used 3,9-diborylchrysene as a monomer in the Isobe-modified Yamago platinum complexation method. Carbon nanoring **158** represents a model for (16,0)CNTs.



Scheme 40. Synthesis of [4]cyclo-3,9-chrysenylene.

3. Segments Representing CNT Terminals

Apart from sidewall segments of CNTs, structures representing CNT terminals are also important and potentially useful templates for the controlled synthesis of CNTs. In Figure 11, end-cap and junction units are shown, which represent terminal structures for end-capped and branched CNTs, respectively. The tubular structures of CNTs are thereby modified by incorporating non-hexagonal rings. This section describes the synthesis of structures that represent CNT end caps and junctions.

3.1. CNT End Caps

Bowl-shaped aromatic molecules, such as corannulene[70] and sumanene[71] have been previously studied, as they can be considered constitutional parts of fullerenes. After the discovery of CNTs, these bowl-shaped structures again received attention, as they can serve as model compounds for end caps of CNTs. The presence of at least one five-membered ring in all the bowl-shaped molecules shown in Figure 12 demonstrates the importance of a pentagon to construct these curved structures. Twelve pentagons are required to construct a closed sphere, as for example, in fullerenes, and, accordingly, six pentagons are necessary for the construction of hemispherical end-cap molecules. Here, an example of the successful synthesis of an end-cap molecule for a (5,5)CNT is described.

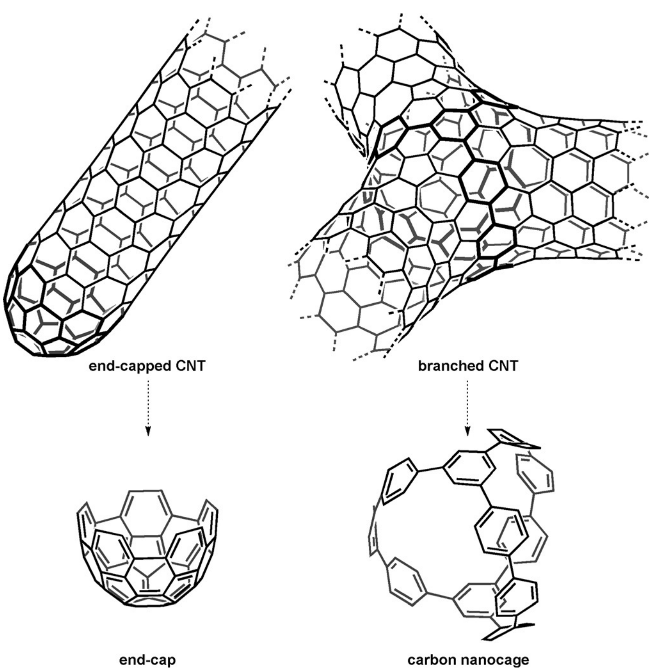


Figure 11. End cap (left) and junction (right) as terminal structures of CNTs.

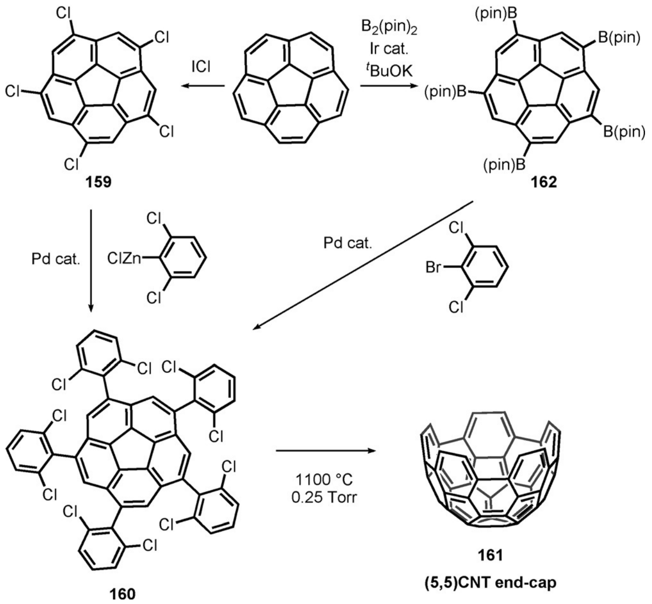
Figure 12. Bowl-shaped molecules.

In 2012, Scott et al. reported the synthesis of a (5,5)CNT end cap (Scheme 41).[72] Chlorination of corannulene with iodine monochloride provided 1,3,5,7,9-hexachlorocorannulene (**159**) with C_5 symmetry. This compound was transformed by a fivefold Negishi coupling reaction with 2,6-dichlorophenylzinc chloride to form compound **160**. A subsequent tenfold C−C bond formation was induced by flash vacuum pyrolysis (1100 °C, 0.25 Torr, gas phase) to afford hemispherical end-cap **161**. In the same year, Eliseeva and Scott also demonstrated an alternative synthesis of the (5,5)CNT end cap **161** by employing a regioselective C−H borylation reaction of corannulene.[73] A stereoselective borylation, induced by a base-assisted iridium-catalyzed borylation, furnished 1,3,5,7,9-pentaborylcorranulene **162**. An ensuing Suzuki–Miyaura coupling reaction between **162** and 2-bromo-1,3-dichlorobenzene provided the precursor **160**.

3.2. CNT Junctions

One possible junction unit for three-way-branched CNTs is the carbon nanocage illustrated in Scheme 42. These [*n.n.n*]carbon nanocages (**163**–**165**) with C_3 symmetry consist

Scott, 2012, Refs. [72], [73]



Scheme 41. Synthesis of a (5,5)CNT end cap.

of a pair of trisubstituted benzene rings and three [*n*]paraphenylene moieties, each linking two benzene rings. In 2013, Itami, Segawa, Kamada, and co-workers reported the first synthesis of the [6.6.6]carbon nanocage **163**.[74] Similar to Itami's synthesis of U-shaped units for [14]–[16]CPPs from diborylbenzene and L-shaped units, trifurcated unit **166** was obtained by a threefold Suzuki–Miyaura coupling of 1,3,5-triborylbenzene with L-shaped unit **59b**. Nickel-mediated dimerization of **166** provided an unstrained bicyclic precursor **167**, whose six cyclohexane moieties were subsequently aromatized to afford the [6.6.6]carbon nanocage **163**. Matsui, Segawa, and Itami then expanded this synthetic method to make carbon nanocages of various sizes available: the use of appropriately modified starting materials resulted in the synthesis of the [4.4.4]carbon nanocage and [5.5.5]carbon nanocage (**164** and **165**).[75] Based on Itami's synthesis of [7]CPP and [8]CPP, the smaller trifurcated unit **168** was prepared in several steps from 1,3,5-tribromobenzene and the smaller L-shaped unit **76b**. After transforming the chloro groups on **168** into boryl groups (**169**), two bicyclic macrocycles **170** and **171** were synthesized in the presence of Ni(cod)$_2$/phen (phen = 1,10-phenanthroline) or a palladium catalyst depending on the reaction conditions and starting materials used. Precursors **170** and **171** were subsequently subjected to acid-mediated aromatization reactions, thus affording the corresponding carbon nanocages (**164** and **165**).

4. Controlling the Synthesis of CNTs

In the previous sections, the systematic synthesis of CNT segments was reviewed. So far, absolute control over the synthesis of CNTs has not been achieved. In this section, several seminal studies, which aim to increase the control over the synthesis of CNTs by using modified typical synthetic methods, are described. Figure 13 shows four molecules, which have been employed as precursors for the synthesis of CNTs.

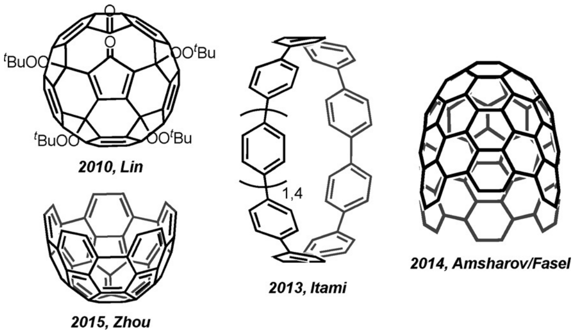


Figure 13. Molecular precursors used in the controlled synthesis of CNTs.

4.1. Simulations and Model Reactions

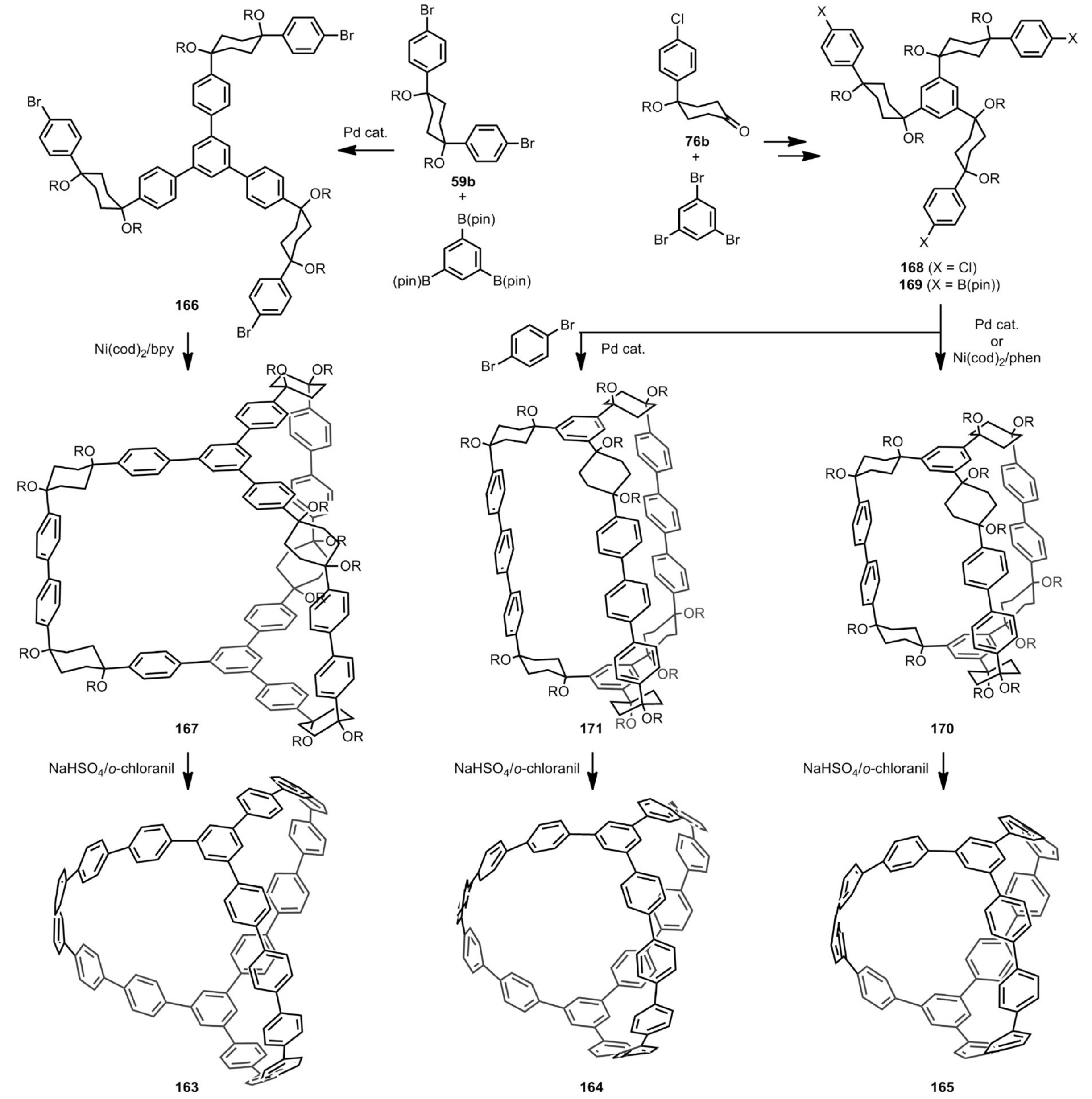
The metal-free growth of CNTs by using organic molecules as templates has been reported.[76] Simulations and model reactions were conducted to explain the mechanism of CNT growth in the absent of a metal catalyst. Fort and Scott reported a DFT study and some model Diels–Alder reactions to describe the growth of CNTs from carbon nanorings and end-cap molecules.[77] It was mentioned that suitable dienophiles such as nitroethylene or acetylene can react at the bay regions of CNT segments. Morokuma, Irle, and co-workers investigated and simulated CNT growth from carbon nanorings through radical mechanisms.[78]

4.2. CNT Growth from Mixtures of Segment Structures

The "cloning" of CNTs, where cut and dispersed CNTs are used as templates for CVD methods, has been studied.[79] Liu, Wang et al. applied this "cloning" method to the chirality-selective growth of CNTs from chirality-pure CNTs (Scheme 43).[80] For that purpose, CNTs (up to 90% purity) were dispersed on quartz or Si/SiO$_2$ and annealed, before being subjected to a CVD procedure (ethanol or methane, 900 °C). Raman spectroscopy as well as electrical measurements on the resulting CNTs suggested that the original chirality of the seeds was preserved.

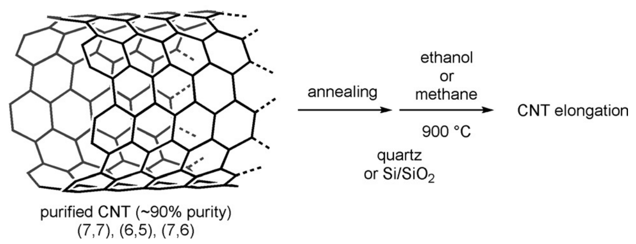
Liu and co-workers reported a metal-free synthesis of CNTs by using a fullerene cap (Scheme 44),[81] whereby fullerenedione **172**, synthesized in three steps from C$_{60}$,[82] was thermally decomposed and subsequently used as a template for CNT growth without purification. The diameter distribution of the resulting CNTs was found to be affected by the temperature of the thermal decomposition step (300–500 °C in air), which was explained by the conversion of the fullerenedione **172** into end-cap structures of various sizes, whereby the size was argued to depend on the reaction conditions. Accordingly, not only the theoretically expected (5,5)CNT was formed, but also CNTs with other diameters.

Itami/Segawa/Kamada, 2013, Itami/Segawa, 2014, Ref. [74], [75]



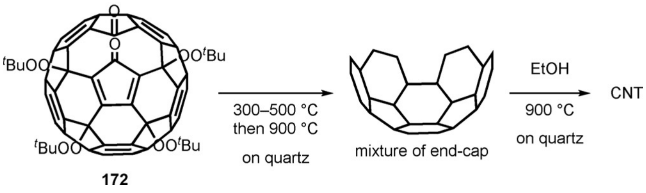
Scheme 42. Synthesis of carbon nanocages (R = MOM).

Liu/Wang, 2012, Ref. [80]



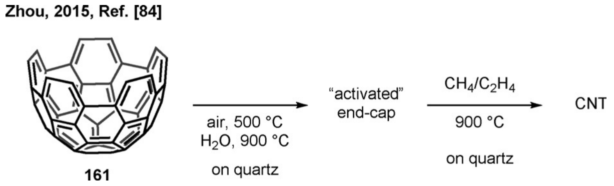
Scheme 43. CNT growth from purified CNTs.

Liu, 2010, Ref. [81]



Scheme 44. CNT growth from thermally decomposed fullerenediones.

Independently, the groups of Rümmeli and Shinohara reported the CVD growth of CNTs using activated C_{60}, and discussed the formation of cap structures in the initial stages of the CNT growth.[83] Zhou reported CNT growth from Scott's (5,5)CNT end-cap **161** (Scheme 45).[84] CNTs were generated from end cap **161**, which was activated by treatment with air and water at high temperatures. End cap **161**

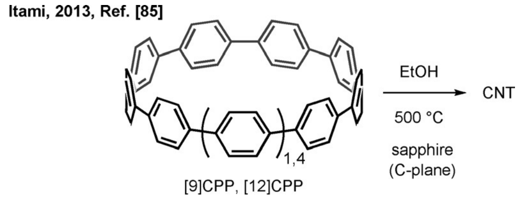


Scheme 45. CNT growth from (5,5)CNT end cap **161**.

was inert to CNT growth reactions without activation. Electrical transport measurements as well as Raman spectroscopy indicated that the resulting CNTs were mainly semiconducting.

4.3. CNT Growth from Pure Segment Structure Molecules

Itami and co-workers succeeded in the synthesis of CNTs by using CPP seeds in CVD methods (Scheme 46).[85] Solutions of [9]CPP or [12]CPP in toluene were spin-coated on the C-plane of a sapphire wafer, before being inserted for 15 min into a temperature chamber (500 °C) under a flow of ethanol to obtain CNTs. This method represents, compared to the common CVD approaches, a low-temperature alternative for the synthesis of CNTs. Transmission electron microscopy (TEM) analysis of the resulting CNTs suggested that their average diameter is close to that of the CPP seeds, which supports the assumption of a "growth-from-template" mechanism. The lack of absolute control over the chirality may be due to the partial thermal decomposition of CPPs at 500 °C.

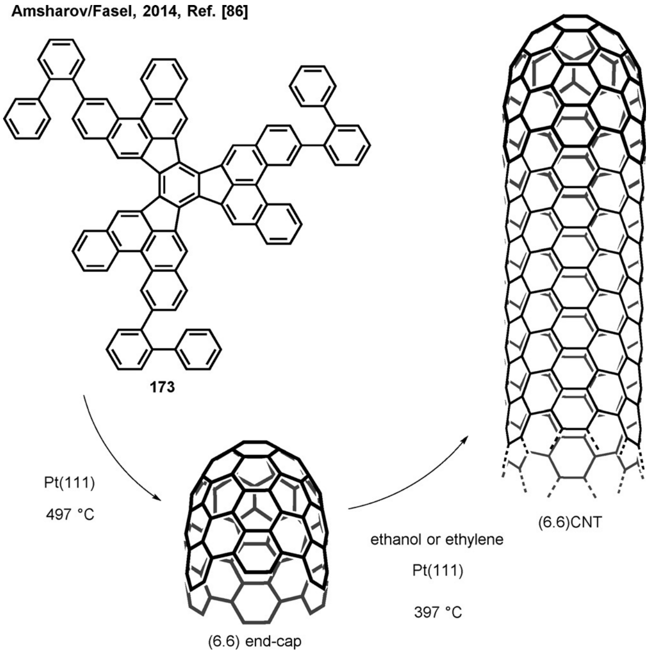


Scheme 46. Growth of CNTs from CPPs as templates.

In 2014, Amsharov, Fasel, and co-workers reported the first chirality-controlled synthesis of CNTs (Scheme 47).[86] They applied the selective formation of an end-cap structure from an "opened-up" structure deposited on a metal surface[87] as the first step. The molecule **173**, the "opened-up" precursor for (6,6)CNT end cap, was deposited on a platinum-(111) surface and heated to 497 °C to afford the (6,6)CNT end cap. Moderate flows of ethylene or ethanol gas at 497 or 397 °C resulted in the formation of (6,6)CNTs, as indicated by Raman spectroscopy and scanning tunneling microscopy (STM) images.

5. Summary

In this Review, the molecular design and the organic synthesis of CNT segment structures is summarized, and recent efforts in the controlled growth of CNTs by using template molecules are presented. For armchair CNTs, many types of ring-shaped molecules such as picotubes, all-*Z*-benzannulenes, cycloparaphenylenes, and related armchair carbon nanorings have been synthesized. Examples of chiral and zigzag CNT segments so far remain limited, probably because of the low symmetry of their chiral rings and the synthetic difficulty associated with the generation of cyclacenes. The next synthetic target would be belt-shaped molecules called "carbon nanobelts", including the Vögtle belt. We believe that carbon nanobelts will be synthesized in the near future by using suitable carbon nanorings as precursors. The pioneering reports using cycloparaphenylenes and CNT end caps to control the CNT growth have demonstrated a substantial impact on nanocarbon science in general. This field of research is the subject of continuous intensive research efforts, and we are looking forward to witnessing new discoveries and progress in the controlled synthesis of CNTs, which will undoubtedly contribute significantly to the development of materials science.



Scheme 47. Controlled synthesis of (6,6)CNTs from "opened-up" precursors for end-cap molecules on a Pt(111) surface.

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