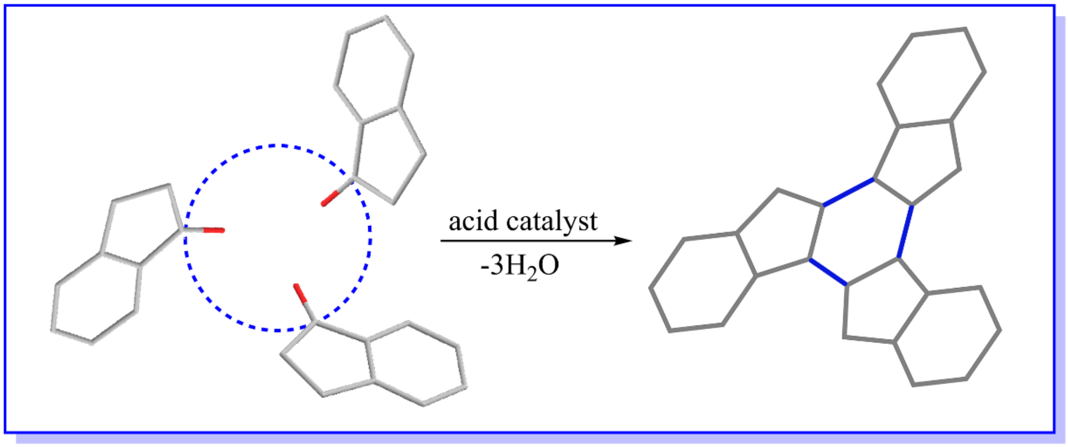
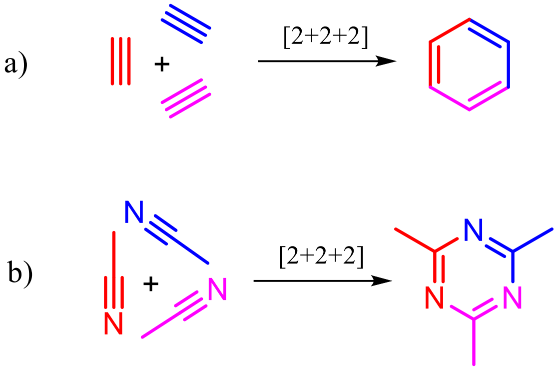
CHAPTER 1

Introduction



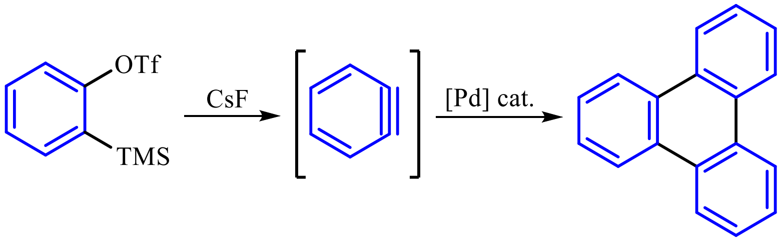
1.1 General Introduction

The French scientist Marcelin Berthelot reported the first example of [2+2+2] cyclotrimerization of acetylene into benzene in 1866.[1] Similarly, McKusick *et al.* in 1952 demonstrated that nitriles were also trimerized to convert into 1,3,5-triazines.[2] (**Scheme 1.1**)



Scheme 1.1 [2+2+2] cyclotrimerizations

Benzocyclotrimers (BCTs) are a class of compounds formed by the annulation of three cyclic alkenes. The most typical method for the synthesis of these polycyclic hydrocarbons, is cross–coupling cyclotrimerization reaction by using a single monomer to build the whole structure.[3] (**Scheme 1.2**)



Triphenylene **1**

Scheme 1.2 Cyclotrimerization to obtained triphenylene **1**

BCTs have attracted growing interest, since they have potential for building host molecules that act as tweezers, baskets, cages, bowls, and others that allow incoming molecular species to enter into their cavities.[4-6] BCTs have been greatly exploited as significant precursors for developing curved molecular architectures.[7, 8] Beginning in the latter half of the 20th century, bowl-shaped hydrocarbons with curved connections of trigonal carbons have drawn attention as precursors and intermediates of more complex compounds with curved surfaces like fullerene and its higher polyhedra.[9-11]

Considering the presence of peculiar angular strains, bowl-shaped π-conjugated compounds can be difficult to synthesize.[12] The flexible hetero-BCTs **2-4** were synthesized, which has three non-planar branches adorning the core of the aromatic ring.[13-15] (**Fig. 1.1**)

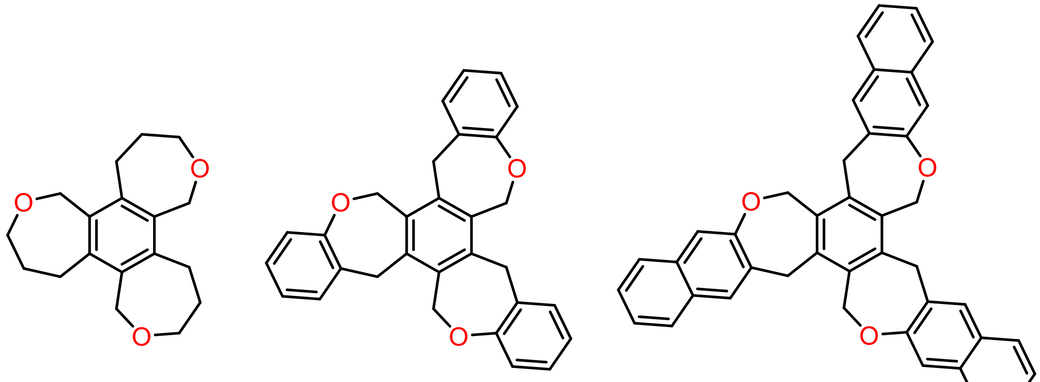
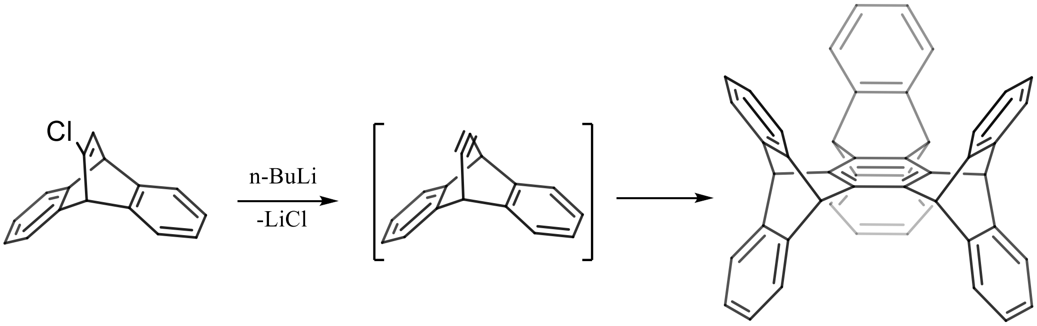


Figure 1.1 Flexible BCTs **2-4**

Several different coupling strategies, along with different monomers, have been used over the years in attempts to synthesize BCTs. Initially, the transient formation of strained and highly reactive alkynes were thought to be of interest for the cyclotrimerization of polycyclic alkenes. Heptiptycene **6**, produced by Huebner *et al.* as a byproduct of the reaction of 11-chloro-9,10-dihydro-9,10-

ethenoanthracene **5** with butyllithium (BuLi), was the first bridged–BCT to be reported.[16] (**Scheme 1.3**)

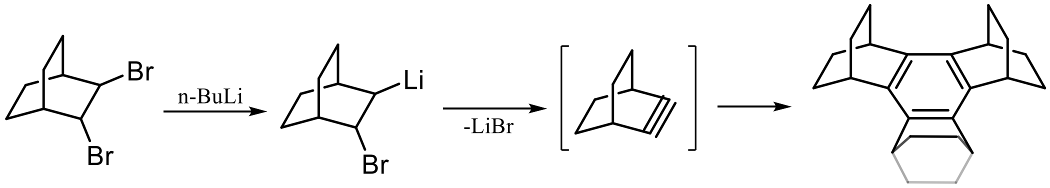


5

Heptiptycene **6**

Scheme 1.3 Stepwise cyclotrimerization route to heptiptycene **6**

Following this, Komatsu *et al.* discovered in the 1980s that trimerization of strained transient alkyne **8** produced D_{3h} benzocyclotrimer **9** in excellent yield (80 %) when 2,3-dibromobicyclo[2.2.2]oct-2-ene **7** was treated with n-BuLi. Researchers were able to obtain numerous C_{3v} symmetrical BCTs due to this approach.[17] (**Scheme 1.4**)



7

8

tris(bicyclooocteno)
benzene **9**

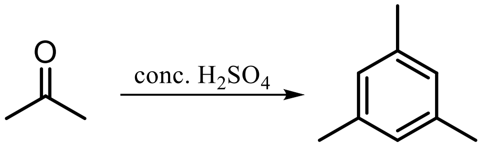
Scheme 1.4 Synthesis of BCT **9 via** alkyne **8**

Bowl-shaped hydrocarbons derivatives are employed to develop open and close geodesic polyarenes. Numerous researchers have developed several methods for constructing BCTs with varying branches and terminals. These methods includes triple aldol reaction, cyclotrimerizations of arynes, and cyclotrimerization catalyzed by Lewis acid, nickel, palladium, or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

1.2 General methods for the synthesis of BCTs

1.2.1 *Triple Aldol Condensation*

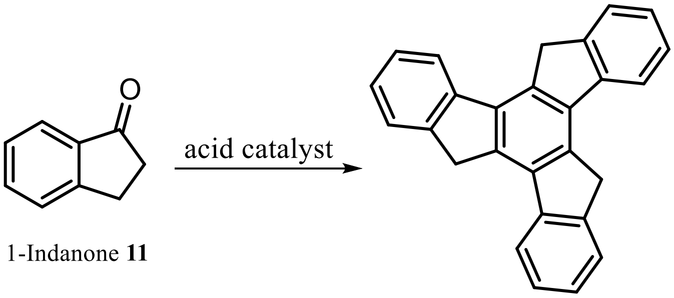
Acetone is one such classical example since it often produces mesityelene **10** *via* acid-catalyzed aldol condensation.[18] (**Scheme 1.5**)



mesityelene **10**

Scheme 1.5 Aldol condensation of acetone

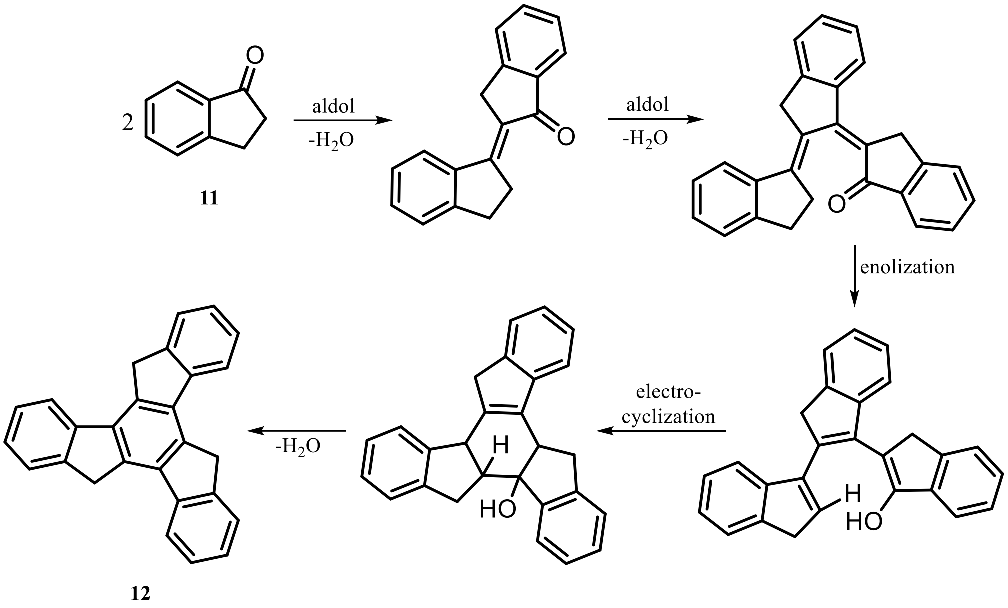
The first triple aldol condensation was discovered in 1800s.[19] In which, acid catalyzed triple aldol condensation of 1-indanone **11** led to form truxene **12**. (**Scheme 1.6**) The mechanism of the cyclocondensation follows as displayed in below **Scheme 1.7**.[20]



1-Indanone **11**

Truxene **12**

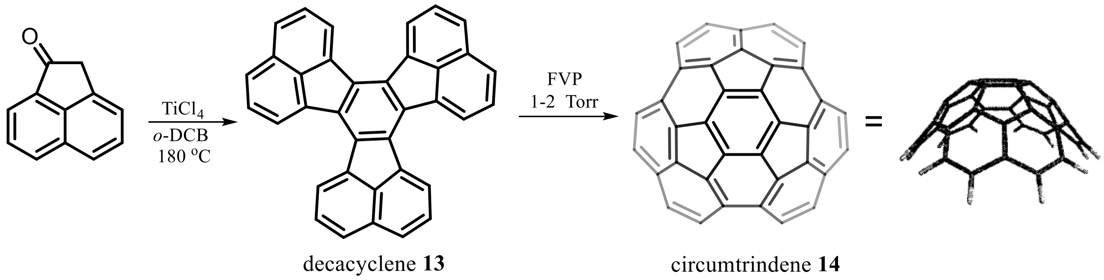
Scheme 1.6 Synthesis of truxene **12** *via* cyclotrimerization



Scheme 1.**7** Steps in triple aldol condensation

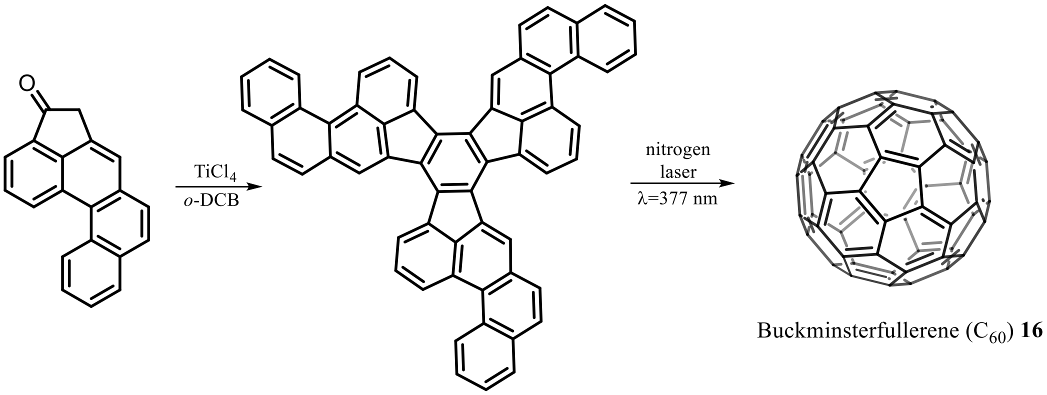
Then the era of curved PAHs came into being. Chemists have synthesized a large number of curved PAHs containing five and six membered rings. Specifically selective ketone transformation led into various synthetic elaborations towards graphene, buckminsterfullerene and other higher polyhedra.[8]

In 1996, Scott *et al.* prepared decacyclene trimer **13** which led to the synthesis of fullerene fragment circumtrindene **14** comprising 60% of the C_{60} ball *via* flash vacuum pyrolysis (FVP).[21] (**Scheme 1.8**)



Scheme 1.8 Synthetic route of circumtrindene **14** from decacyclene **13**

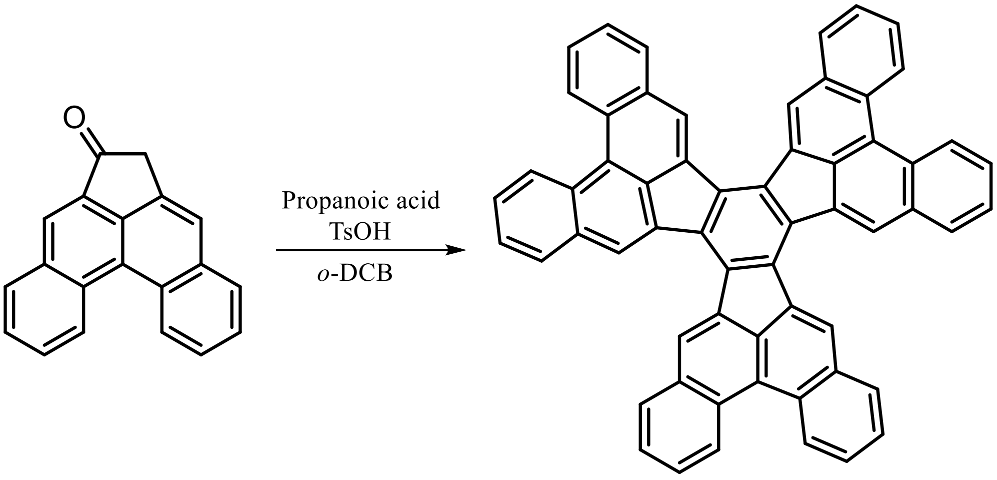
In 2001, the same group reported research towards the rational [60]fullerene **15**. They have synthesized the C_{60} polyarene **15** using titanium tetrachloride in *o*-dichlorobenzene at 100 °C for 2 h. Then they have closed it using a nitrogen laser and by loss of hydrogens afforded C_{60}–fullerene **16**.[22] (**Scheme 1.9**) Later, in 2010, Mueller *et al.* have synthesized two similar BCTs **17** and **18** using a different catalyst.[23] (**Scheme 1.10**)



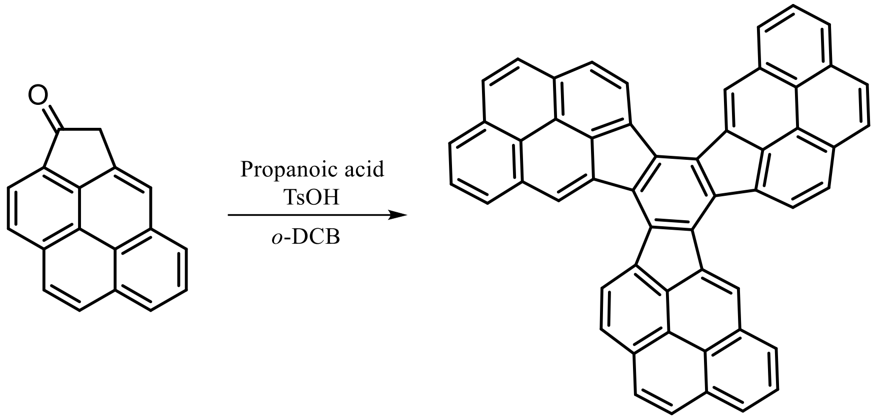
$C_{60}H_{30}$ Polyarene **15**

Buckminsterfullerene (C_{60}) **16**

Scheme 1.9 Synthetic route of rational C_{60}–fullerene **16**



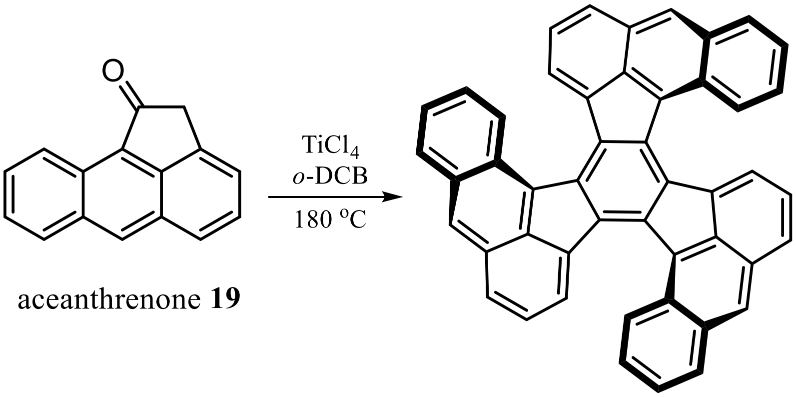
$C_{60}H_{30}$ **17**



$C_{54}H_{24}$ **18**

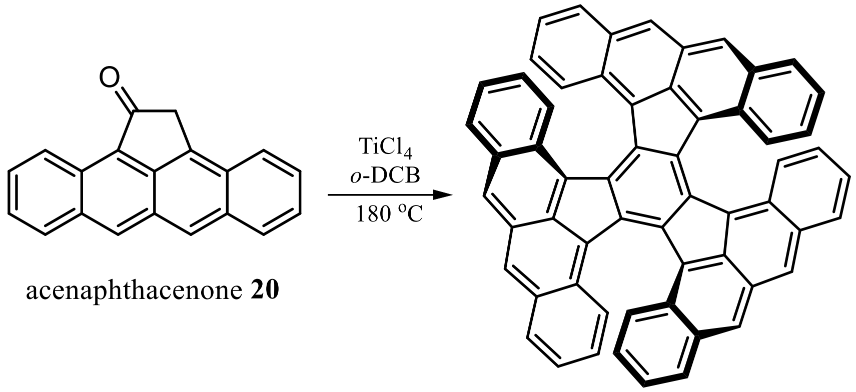
Scheme 1.10 Synthetic route to $C_{60}H_{30}$ **17** and $C_{54}H_{24}$ **18** BCTs

In 2015, Xin Geng *et al.* utilized triple aldol condensation catalyzed by $TiCl_4$ to transform the compounds aceanthrenone **19** and acenaphthacenone **20** into tribenzodecacyclene **21** and hexabenzodecacyclene **22** in low yields of 16 % and 0.8 %, respectively. (**Scheme 1.11**) In terms of stability, highly strained hexabenzodecacyclene **22** was sensitive to light and air, but tribenzodecacyclene **21** was fairly stable under normal conditions. Additionally, the color of these two compounds varied significantly with the increase in effective conjugation length.[24]



aceanthrenone **19**

tribenzodecacyclene **21**



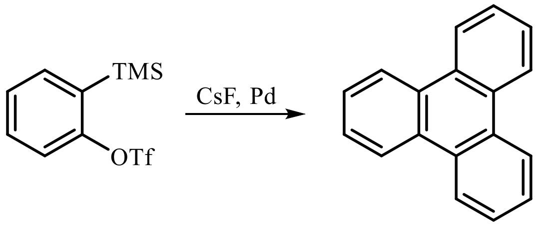
acenaphthacenone **20**

hexabenzodecacyclene **22**

Scheme 1.11 Synthesis of benzannulated decacyclenes **21** and **22**

1.2.2 *Cyclotrimerizations of Aryne*

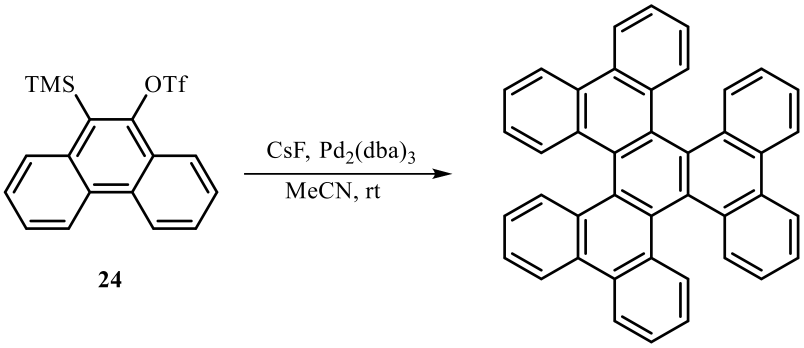
In 1998, Diego and coworkers performed a systematic study and achieved significant advancements in the synthetic field of aryl-aryl coupling using CsF and Pd catalyst. This was the first example of metal-mediated cyclotrimerization of arynes, in which 2-trimethylsilylphenyl trifluoromethanesulfonate **23** was converted into triphenylene **1** using anhydrous CsF and (tetrakis(triphenylphosphine) palladium (0) ($[Pd(PPh_3)_4]$) as catalysts.[3] (**Scheme 1.12**)



23 **1**

Scheme 1.12 Pd-Catalyzed Cyclotrimerization of **22**

In 1999, again the same group has synthesized a symmetric three-branchphene **25** using the palladium-catalyzed trimerization of *o*-trimethylsilylaryl triflate **24**. This milder reaction condition enabled to obtain a D_3-symmetric molecular propeller that was highly twisted and strained.[25] (**Scheme 1.13**)

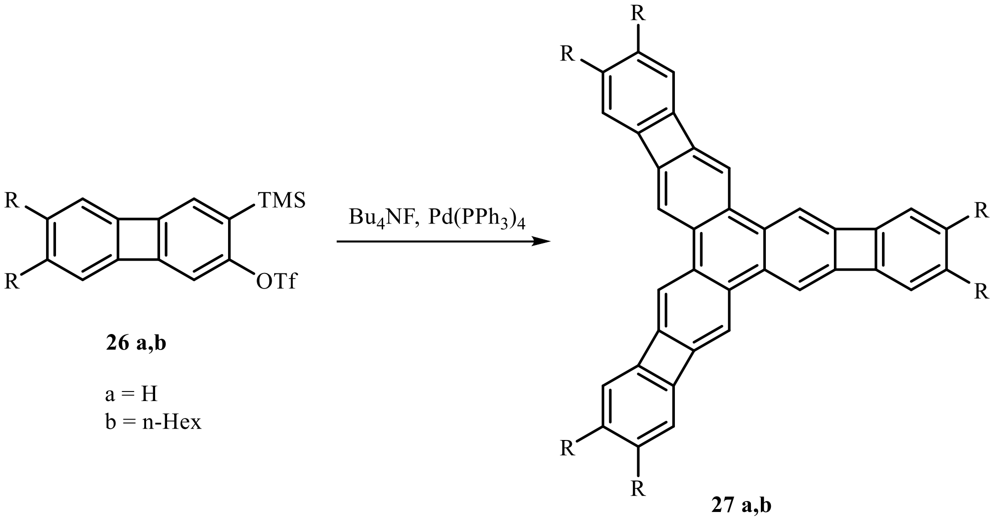


24

hexabenzotriphenylene **25**

Scheme 1.13 Synthesis of hexabenzotriphenylene **25**

A combination of $Pd(PPh_3)_4$ with tetrabutylammonium fluoride (TBAF) was used by Lglesias *et al.* in 2004 to synthesize tris(benzocyclobutadieno)triphenylenes **27**. (**Scheme 1.14**)



26 a,b

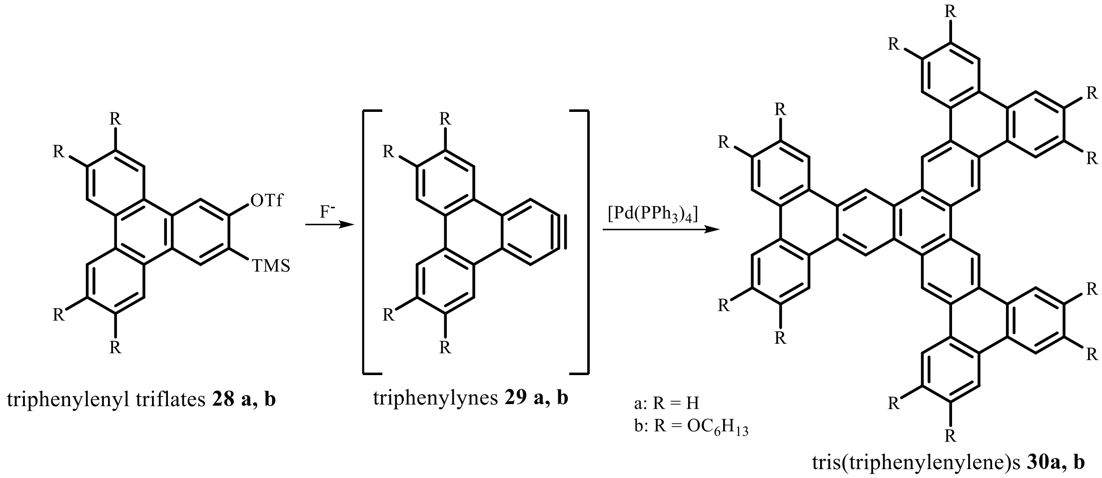
a = H
b = n-Hex

27 a,b

Scheme 1.14 Synthesis of tris(benzocyclobutadieno)triphenylenes **26**

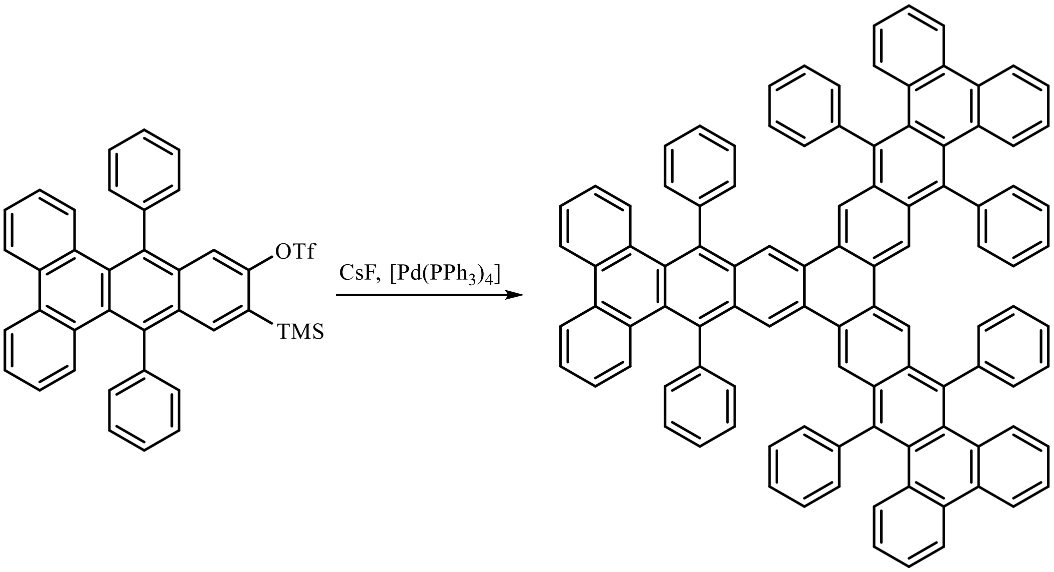
When the R = H atom in **26a**, compound **27a** was formed in total yield of 58%. Nevertheless, the resulting compound was very insoluble, which made it hard to get its NMR analysis. Then, R was substituted with n-Hex group in **26b**, to obtain compound **27b** in 65% yield under identical reaction conditions.[26] As they anticipated, the solubility was improved considerably by replacement with peripheral alkyl chains, allowing it to be purified by column chromatography and thoroughly characterized. They also suggested that compound 2**7b** with a newly extended conjugated frame could be advantageous in materials science.

In 2006, Carmen Romero *et al.* synthesized extended triphenylenes **30** *via* fluoride-induced generation of triphenylynes **29** from triphenylenyl triflates **28**, enabled their palladium-catalyzed cyclotrimerization to form polycyclic arenes.[27] (**Scheme 1.15**)



Scheme 1.15 Cyclotrimerization of **29** to afford tris(triphenylenylene)s **30**

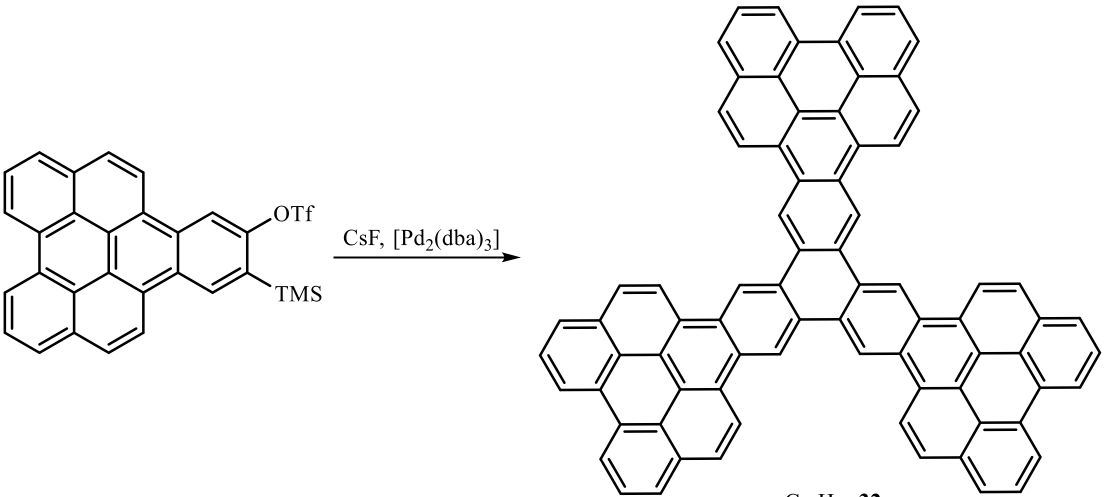
[16]Cloverphene **31**, a large cata-condensed molecule with 102 sp^2 carbons and unique molecular geometries. Such clover and arch-like structures were synthesized by Diego *et al.* in 2012. The resulting molecule **31** was obtained in 22% of yellow-colored having C_3-symmetric conformation.[28] (**Scheme 1.16**)



[16]cloverphene **31**

Scheme 1.16 Synthesis of clover-shaped cyclotrimer **31**

The same group then developed a very straightforward method for the synthesis of a threefold symmetric clover-shaped $C_{78}H_{36}$ molecule **32** with 22 fused benzene rings from perylene. (**Scheme 1.17**)



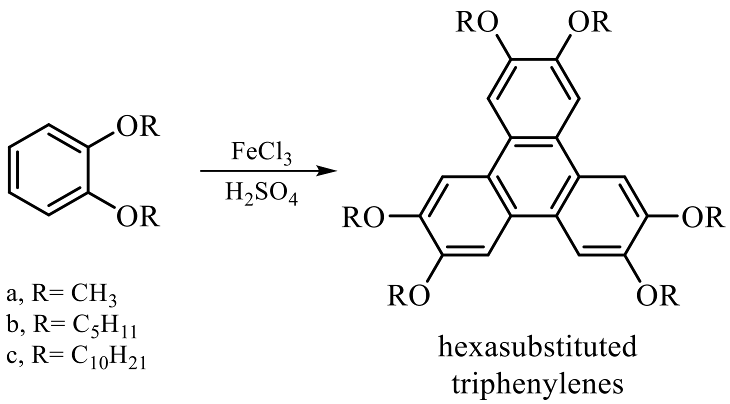
$C_{78}H_{36}$ **32**

Scheme 1.17 Synthesis of cyclotrimer **32**

One-pot synthesis produced the cyclotrimer **32** with a yield of 46%, as a very insoluble grey solid. Despite the extreme insolubility of the solid, the geometry of the clover-shaped molecule was confirmed by using non-contact atomic force microscopy.[29]

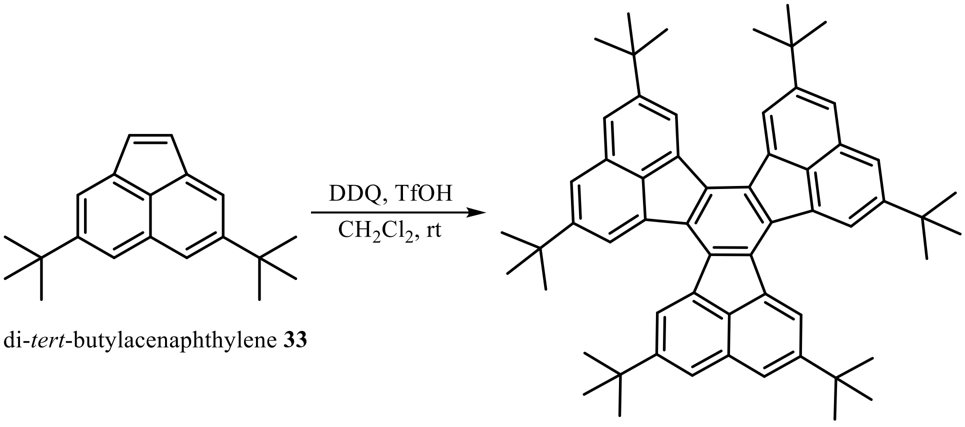
1.2.3 *Other Cyclotrimerization Methods*

In addition to the primary approaches mentioned above, a number of alternative methods have been used to construct cyclotrimers. Iron (III) chloride is one of the most often utilized and well-known Lewis acid catalyst for cyclotrimerization, as shown in **scheme 1.18**.[30]



Scheme 1.18 Synthesis of triphenylenes

In 2015, Hee Yeon Cho and Lawrence T. Scott discovered an effective method for constructing fused three-branchphene **34** (48% yield) using the oxidative cyclotrimerization of unsaturated compound **33** with triflic acid and 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ).[31] (**Scheme 1.19**) This was totally surprising reaction that hadn't been published before. Additionally, this was the first example of intermolecular oxidative cyclotrimerization reactions of aromatic compounds and alkenes with a metal-free reagent system that had been reported.



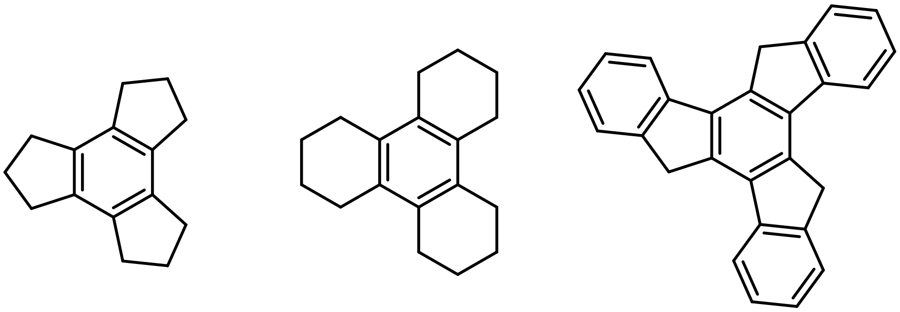
di-*tert*-butylacenaphthylene **33**

hexa-*tert*-butyldecacyclene **34**

Scheme 1.19 DDQ catalyzed cyclization of di-*tert*-butylacenaphthylene **33**

These methods have been widely used to synthesize plane, curved and twisted carbocycles which could lead to build graphene or fullerene fragments. BCTs have also paved the way for their application in the design and preparation of molecular containers, baskets, cages, and bowls.

Similar to other polycyclic aromatics, BCTs like trindane **35**, dodecahydrotriphenylene (DDHTP) **36**, and truxene **12** are potential precursors to construct more complex structures and cane be a good candidates for organic emitters and semiconductors. (**Fig. 1.2**) The presence of C_3-symmetry in these molecules makes them architecturally beautiful.



Trindane **35**

Dodecahydrotriphenylene **36**

Truxene **12**

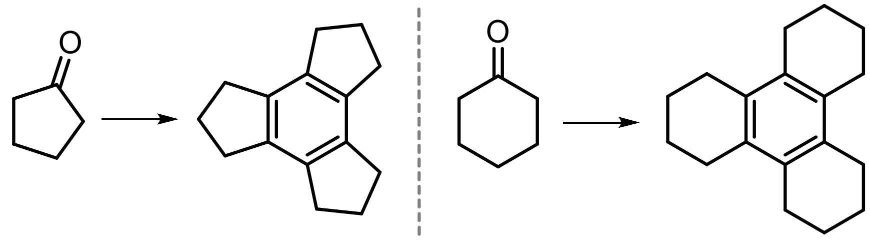
Figure 1.2 structures of BCTs **35**, **36** and **11**

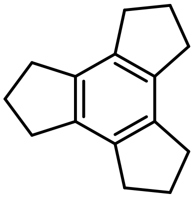
Truxene **12** along with its heteroanalogues have been the focus of extensive research to develop OLEDs, OFETs, small molecule storage materials, sensors, DSSCs, and many other devices. However, there are only a handful reports for the functionalization and/or modification on trindane **35** and DDHTP **36** molecules which seems to be a formidable task for synthetic chemists.

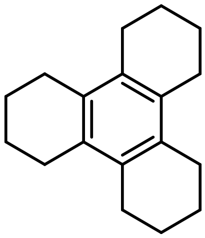
1.3 Trindane and Dodecahydrotriphenylene: Synthesis and Reactivity

The spectroscopic characteristics of the tethered systems trindane **35** and DDHTP **36** reveal no sign of any significant perturbation of aromaticity.[32] Despite being readily available and possessing three-fold symmetry, these systems have struggled hitherto arouse the curiosity of synthetic chemists so far. These trisannelated benzene derivatives **35** and **36** can be prepared easily *via* acid-catalyzed cyclocondensation of cyclopentanone and cyclohexanone respectively. Numerous acid catalysts have been incorporated to improve the yield of the products. (**Table 1.1**)

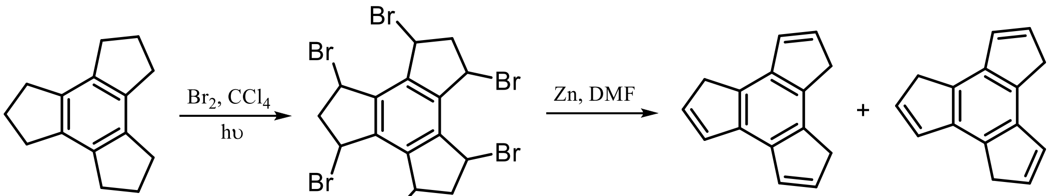
Table 1.1 *Improved yields in cyclotrimerization of cyclopentanone and cyclohexanone*



Product	Reaction condition	% yield	Reference
	$B(HSO_4)_3$, 100 °C, Solvent-free	85 %	[33-37]
	$SiCl_4$, EtOH, reflux	65 %	
	$SOCl_2$, EtOH, reflux	52 %	

	$ZrCl_4$, Solvent-free, MW	40 %	
	H_2SO_4, EtOH, reflux	33 %	
	$B(HSO_4)_3$, 100 °C, Solvent-free	85 %	[36-40]
	$SiCl_4$, EtOH, reflux	77 %	
	$ZrCl_4$, Solvent-free, MW	71 %	
	$SOCl_2$, EtOH, reflux	60 %	
	$TiCl_4$, Toluene, reflux	44 %	

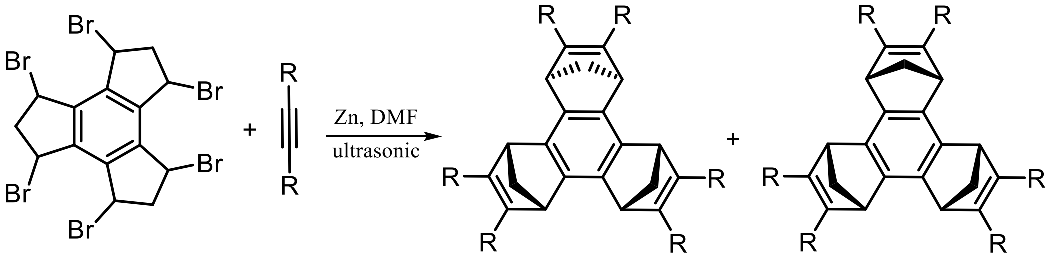
Katz *et al.* have prepared 1,3,4,6,7,9-hexabromotrindane **38** in 82% yield by the photobromination of trindane **35** using liquid bromine. Then hexabromotrindane **37** was subjected to debromination using zinc in DMF to give a mixture of dihydro-1H-trindenes **38a** and **38b** isomers in 43% yield.[41] (**Scheme 1.20**)



35 hexabromotrindane **37** **38a** **38b**

Scheme 1.20 Synthesis of trindenes **38a, b**

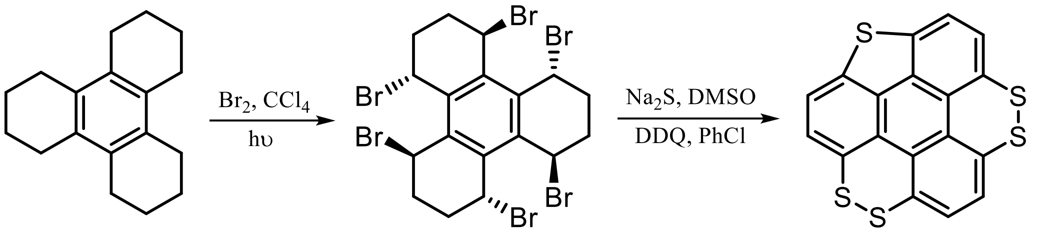
Wei *et al.* have utilized the Diels–Alder reaction with dimethyl but-2-ynedioate **39** as a dienophile, with *in situ* generated two isomers of tri-diene intermediates **38a** and **38b**. Initially, compound **37** eliminates six bromine atoms using 8 *equiv.* of zinc powder and *in situ* generated isomers **39a** and **39b** readily reacted with a large excess of dimethyl but-2-ynedioate **39** (20 *equiv.*) in DMF under ultrasonic irradiation to give a corresponding mixture of cycloadducts **40-*trans*** and **40-*cis*** in 32% yield.[33] (**Scheme 1.21**) Moreover, in a mixture of these tris(bicyclo[2.2.1]hexeno)benzene derivatives **41**, only trans isomer was found to be crystalized and they confirmed its structure by SCXRD analysis.



38 **39** R = COOMe **40-*trans*** **40-*cis***

Scheme 1.21 Diels–Alder reaction of hexabromotrindane **38** with **40**

Same group has also reported the polycyclic pentathioaromatic carbocycle **42** using DDHTP **36** as scaffold. They have prepared the **36** by the $ZrCl_4$–catalyzed trimerization of cyclohexanone under solvent-free condition. Consequently, DDHTP **36** was illuminated with a 300 W incandescent bulb for the bromination in a water–ice bath to afford hexabromododecahydrotriphenylene **41** in 87 % yield.

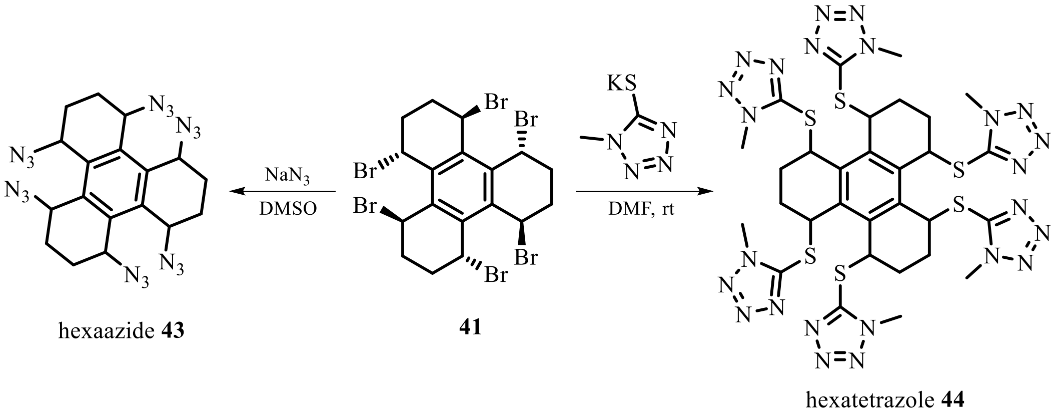


DDHTP **36** hexabromide **41** tristhiasumanene **42**

Scheme 1.22 Synthesis of pentathioaromatic carbocycle **42**

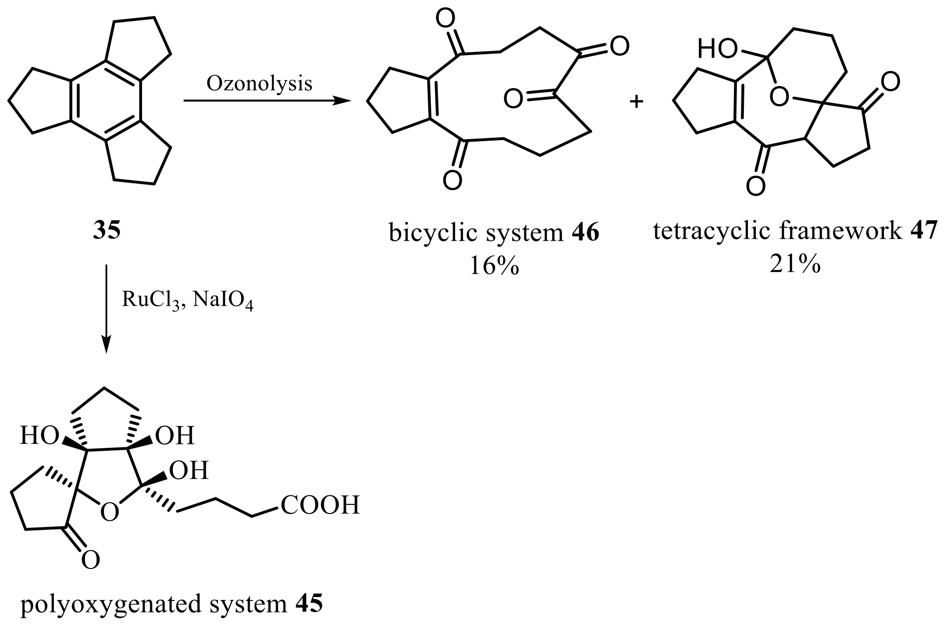
The hexabromide **41** was added to a stirred mixture of Na_2S in DMSO–water at 0°C for 10 hours at room temperature to give tristhiasumanene **42**. This structure has a bowl-shaped molecule.[38] (**Scheme 1.22**) Similarly, selenium and tellurium polycyclic heteroaromatic derivatives have been prepared using hexabromide **41**.[42]

This hexabromide **41** served as a useful precursor for numerous polycyclic heteroarenes due to the excellent reactivity of benzylic halides and peculiar structure. Same group has used the synthetic feature of **41** to develop several derivatives having univalent groups by employing the nucleophilic substitution reaction. In addition to swapping out the six bromines for azides, they used inorganic azide i.e. NaN_3, and produced a hexa-substituted azide derivative **43** of **41**. They also introduced heteroaromatic thiolates in order to obtain the six-fold C_{3d} symmetrical derivative **44**.[43] (**Scheme 1.23**)



Scheme 1.23 Nucleophilic substitution of **41** to afford heteroarenes **43** and **44**

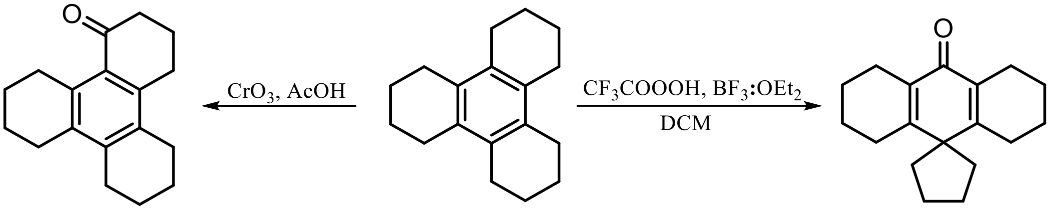
The oxidation of trindane **35** molecule has been investigated by Subramania Ranganathan and his research group using various oxidants. Ru (VIII) mediated oxidation of **35** gave highly functionalized complex condensed systems **45** in one step *via* $C_{(sp2)}$–$C_{(sp2)}$ oxidation. The sequential oxidation of each carbon centre of the aromatic ring gave highly oxygenated system **45** in 15 % yield.[34] Similarly, the *endo* π oxidation afforded product **46** and **47** without the aromatic framework observed when they ozonized the trindane **35** for 3 h in dichloromethane.[44] Here, interestingly bicyclic system **46** folds to produce the intricate tetracyclic species **47**. It was observed that the attack of either RuO_4 or ozone produced typically or solely, the compounds resulting from the attack on the *endo* π-bonds in trindane **35**. All three π-bonds of **35** were oxidized by Ru species, while two of the three double bonds of **35** were cleaved in ozonolysis. (**Scheme 1.24**)



Scheme 1.24 Oxidation of **35** under two different conditions

These reactions of trindane **35** indicate that properly tethered benzene rings can be anticipated to exhibit an affinity for *endo* π-activity offering an objective in synthetic study to achieve various condensed systems.

The oxidation of DDHTP **36** on treatment with CrO_3 in acetic acid gave only benzylic oxo-product decahydrotryphenylen-1-one **48** *via* sp^3 C–H oxidation.[45] However when **36** reacts with excess of peroxytrifluoroacetic acid and boron trifluoride etherate in dichloromethane, a cross-conjugated cyclohexadienone **49** in 45% yield was obtained.[46] Surprisingly the DDHTP **36** produced a fused ring spirodienone **49** and lost its core benzene framework during the course of reaction. (**Scheme 1.25**)



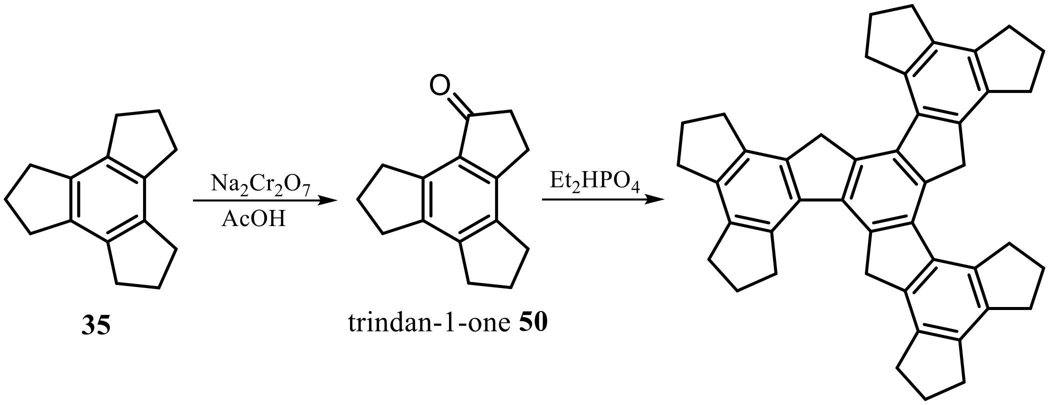
decahydro
triphenylen-1-one **48**

36

dienone **49**

Scheme 1.25 Oxidation of DDHTP **36** using different reagents

In 1989, French workers converted trindane **35** into trindan-1-one **50** and when performing its aldol condensation, they encountered an insoluble substance. They classified it as a rational trimer **51** of trindan-1-one **50** based on the molecular weight obtained using mass spectrometry. It is interesting to note that the BCT **51** contains three quarters of the carbon framework of fullerene.[47] (**Scheme 1.26**)



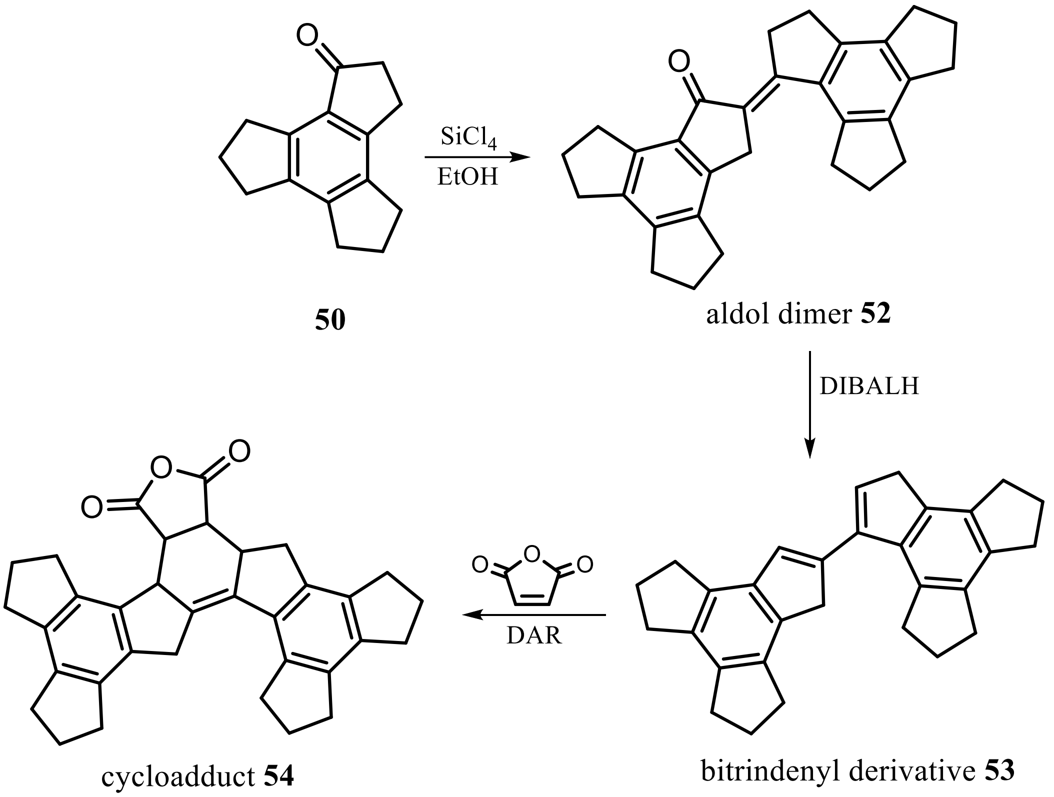
35

trindan-1-one **50**

BCT **51**

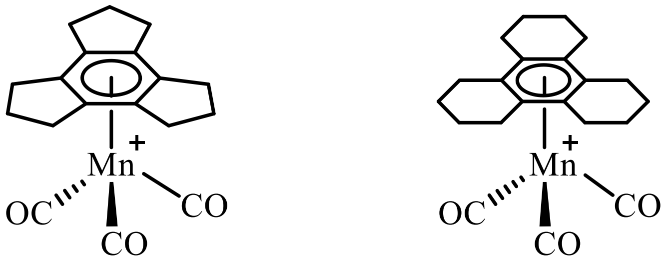
Scheme 1.26 Cyclotrimerization of compound **50**

This work encouraged Ferrier *et al.* to develop the tennis-ball route to synthesize spherical architecture by using the trindan-1-one **50**. Initially, the aldol dimer **52** has been prepared using $SiCl_4$ as a catalyst in dry EtOH. The carbonyl group of enone **52** was consequently reduced using diisobutylaluminium hydride (DIBALH), resulting in bitrindenyl derivative **53**. To this diene **53** they performed Diels–Alder reaction using maleic anhydride as dienophile, and obtained corresponding architecturally beautiful cycloadduct **54**.[48] (**Scheme 1.27**)



Scheme 1.27 Synthetic route towards the construction of aesthetic molecule **54**

Trindane **35** and DDHTP **36** have also been exploited in organometallic chemistry to prepare (arene)ML_n complexes **55** and **56** as shown in **Fig. 1.3**.[49, 50] Arenes **35** and **36** were coordinated to a $Mn(CO)_3^+$ fragment, and it was found that both the complexes were air-stable.



(η^6-trindane)Mn(CO)$_3$ **55** (η^6-DDHTP)Mn(CO)$_3$ **56**

Figure 1.3 (arene)ML$_n$ complexes of **35** and **36**

The scarce reports on carbocycles **35** and **36** clearly reveal the formidable task for synthetic chemists to functionalize these carbocycles. We embarked upon this challenge and applied some simple synthetic methodologies for the incorporation of versatile strategic functionalities and construction of targeted molecules. In the upcoming chapters, we shall disclose a series of our laboratory findings on these aesthetically appealing carbocycles.

1.4 References

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