

REVIEW ARTICLE

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Synthesis of corannulene-based nanographenes

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Corannulene (C₂₀H₁₀) is a polycyclic hydrocarbon in which five six-membered rings surround a central five-membered ring to construct a bowl-like aromatic structure. Here we examine the development of synthetic strategies that allow for the growth of the peripheral aromatic rings as a means to extend the aromatic area of the central corannulene nucleus and provide access to unique nanocarbon molecules.

S *p*²-hybridised structures of carbon have fascinated the research community for a very long time. In 1985, buckminsterfullerene, otherwise known as C₆₀, was discovered (Fig. 1a)¹. In this ball-shaped molecule, the curvature in the structure stems from the presence of five-membered rings. In 1991, carbon nanotubes arrived on the scene². Here, the structure is cylindrical and composed of only rolled-up six-membered rings. In 2004, a sheet-like single layer from graphite—graphene—was isolated³. All of these materials were shown to have extraordinary electronic and mechanical properties due to their unique curved or planar *sp*²-hybridised aromatic structures.

Inspired by these discoveries, chemists have been developing strategies to access such aromatic hydrocarbons through rational (*'bottom-up'*) synthetic approaches. Scott's 12-step chemical synthesis of fullerene C₆₀ from a rationally designed precursor is a testament to the ingenuity and resourcefulness of organic chemists⁴. In planar structures, nanographenes (well-defined cutouts of graphene with nano-scale dimensions) can now be prepared on a regular basis with a very diverse portfolio⁵. It is expected that combining the planar structure of graphene with the curvature of fullerenes may produce hybrid materials with interesting properties^{6–8}.

To induce non-planarity into nanographenes, a practical approach would be to introduce a five-membered ring such as in the case of fullerene, C₆₀. A perfect building block that allows for such a structural arrangement to happen is corannulene (**1**)—a molecule in which five six-membered rings surround a central five-membered ring to give a bowl-like structure (Fig. 1b)^{9–20}. Corannulene also offers many beneficial features as a molecular building block. It has high solubility in common organic solvents. It can be derivatized in a well-defined manner. Due to synthetic ease, the derivatives can be prepared on a multigram scale. These attributes are important as they allow for the scalable preparation of carefully designed corannulene-based building blocks and the subsequent synthesis, purification and structural analysis of the larger (fused) aromatic systems.

Recently, therefore, there has been a surge in employment of corannulene as a core molecule in the synthesis of extended aromatic structures. Our aim in this review article is to discuss

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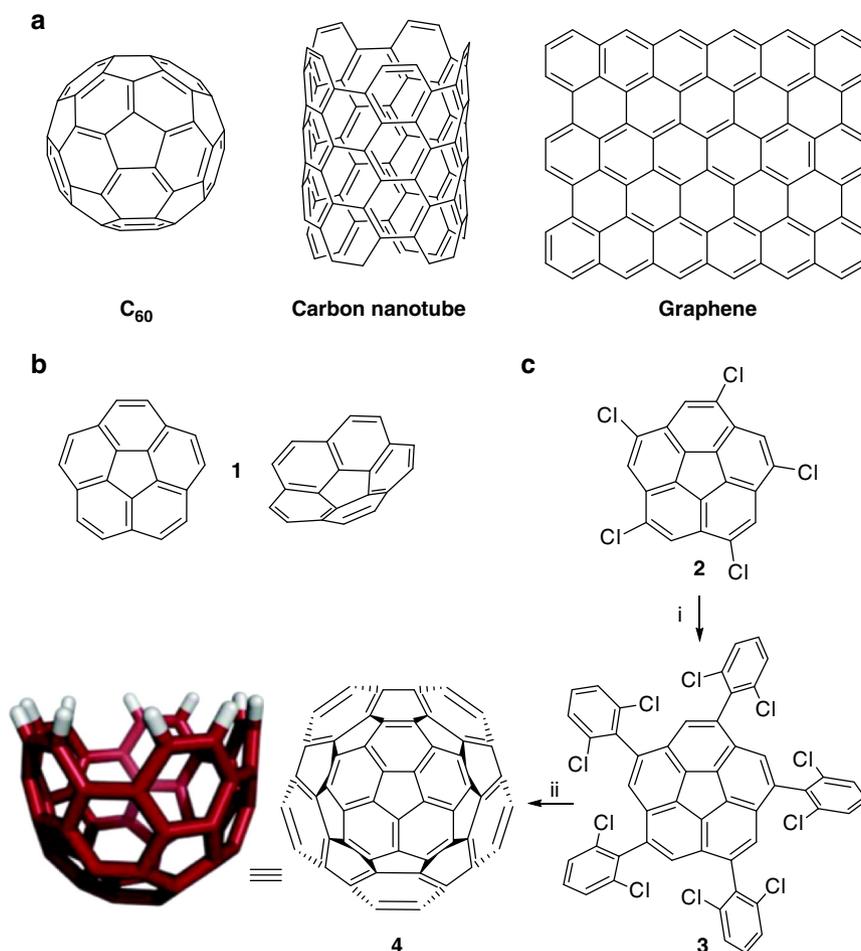


Fig. 1 Curved and planar polycyclic aromatic hydrocarbons. **a** Chemical structures of fullerene, carbon nanotube and graphene. **b** Chemical structure of corannulene **1**. **c** Synthesis of carbon nanotube end-cap. (i) $C_{38}H_{53}ClNO_2PPd-CH_3OC_4H_9$, 2,6-dichlorophenyl zinc chloride, THF, 100 °C, 5 h; 52%. (ii) Flash vacuum pyrolysis, 1100 °C, 0.25 Torr; 3%. **c** is partially reprinted with permission from ref. ²³. Copyright 2012 American Chemical Society

recent advances in this fascinating area of research. In light of the two comprehensive review articles written by the pioneers of the field, Scott⁹ and Siegel¹⁰, we limit our discussion to examples published after 2006. The discussion is categorised on the basis of synthetic method and a chronological order is maintained in each section.

Pyrolytic method

Barth and Lawton's first synthesis of corannulene was a true feat of organic synthesis. It comprised 17 synthetic steps and allowed access to this beautiful molecule in a <1% overall yield²¹. Following this elegant work, the field remained dormant for the next quarter of a century until Scott's group demonstrated flash vacuum pyrolysis (FVP) as an alternative to Barth and Lawton's solution-phase method. Scott's method allowed access to corannulene in a remarkably practical fashion (3-step synthesis with an overall yield of 26%)²². This work breathed new life into the research area of non-planar aromatics and rejuvenated the field of corannulene.

In FVP, high temperatures are employed to overcome the energy barrier of introducing the necessary strain onto the molecular structure. Conversion of the precursor to the desired product depends on both the heating time and temperature. The power of this synthetic tool can be appreciated in the final synthetic step of a hemispherical polyarene ($C_{50}H_{10}$) that could serve as a carbon nanotube end-cap (Fig. 1c)²³. The first step of the synthesis is a five-fold chlorination of corannulene with iodine monochloride. The pentachloro product **2** follows a Negishi

coupling with 2,6-dichlorophenylzinc chloride to present precursor **3**. The C–Cl bonds are cleaved during the pyrolysis of **3** to generate aryl radicals that join to form a web of five-membered rings in polyarene **4**. X-ray analysis of crystals of **4** confirm the structure and measure a bowl depth of 5.16 Å. A CS_2 molecule was read in the crystal structure in the 'basket' of the polyarene—a sulfur atom hovering above the centre of the structure and the carbon atom hovering below the plane of the rim carbons. This work demonstrates that the FVP method originally developed for the preparation of corannulene and fullerene C_{60} is still relevant and can be a valuable synthetic tool in the preparation of carbon-based nano-tubular architectures through rational synthesis pathways. The reader is referred to a recent conference paper by Scott for an insightful discussion on this approach to carbon nanotubes and its prospects for the future²⁴.

While FVP has been critical in rejuvenating the field, the high temperatures limit the range of functionalities on the corannulene scaffold. Solution-phase methods alleviate this situation by employing milder reaction conditions. In this regard, the reactions may be aided by metal catalysis. Alternatively, metal-free conditions can be employed to achieve the same purpose. In the following sections, we examine both pathways for the extension of the corannulene nucleus.

Reactions involving metal catalysis

Pd-catalysed coupling. Scott's group in 2007 reported the synthesis of extended corannulene structures; pentaindenocorannulene

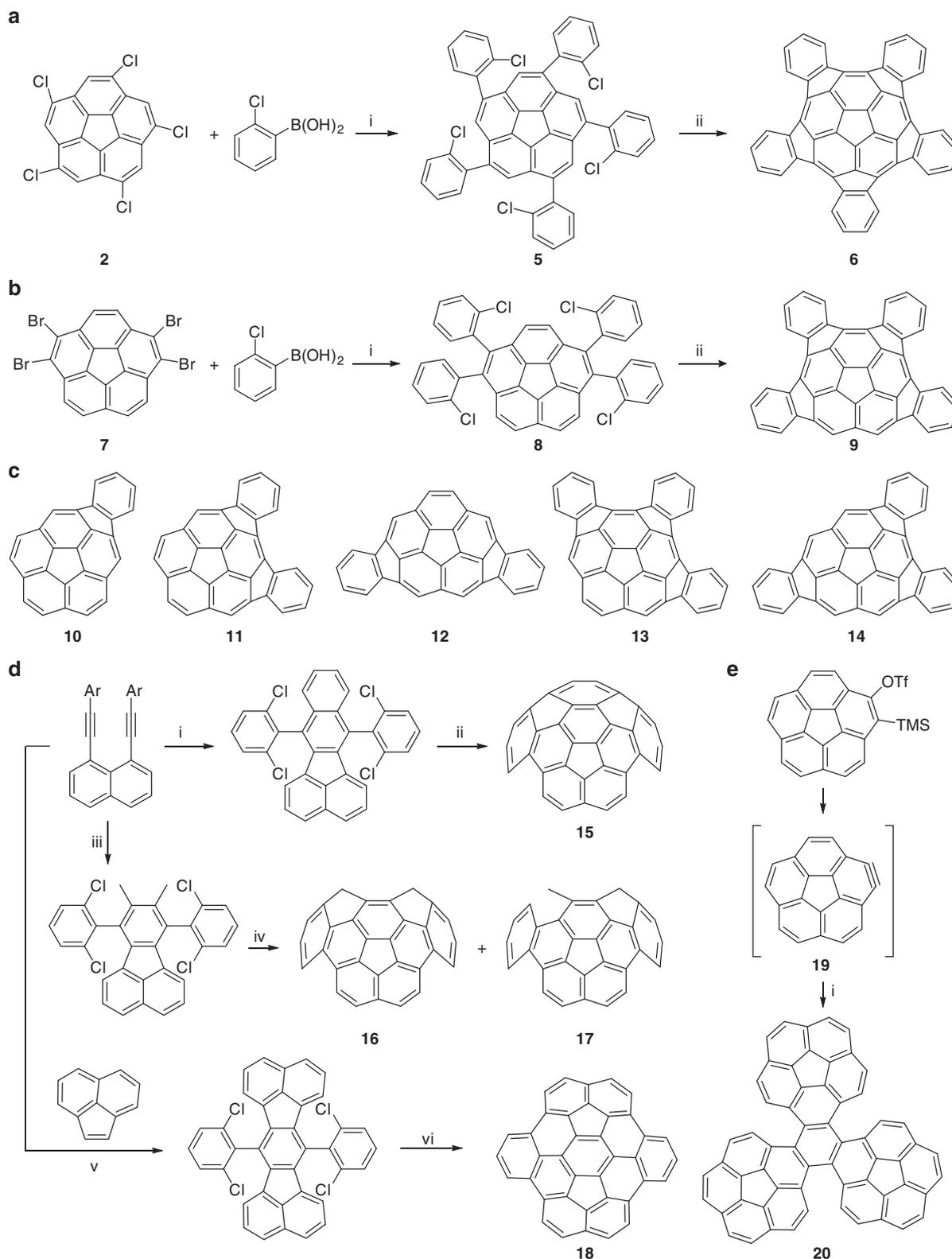


Fig. 2 Corannulene extension pathways involving palladium catalysis. **a** Synthesis of pentaindenocorannulene. (i) $\text{Pd}_2(\text{dba})_3$, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, Cs_2CO_3 , dioxane, 80 °C, 48 h; 48%. (ii) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU, DMAc, 180 °C (microwave), 45 min; 35%. **b** Synthesis of tetraindenocorannulene. (i) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , toluene/EtOH/ H_2O , 85 °C, 24 h; 91%. (ii) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU, DMAc, 170 °C (microwave), 40 min; 13%. **c** Mono, di, and triindenocorannulenes prepared by palladium-catalysed coupling reaction. **d** Wu's synthesis of buckybowls **15–18**. (i) $\text{Pd}(\text{OAc})_2$, $\text{C}_6\text{H}_5\text{I}$, AgOAc , *p*-xylene, 110 °C, 36 h; 60% (Ar = 2,6- $\text{C}_6\text{H}_3\text{Cl}_2$). (ii) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU, DMF, 160 °C, 36 h; 31%. (iii) 2-butyne, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, *p*-xylene, 110 °C, 60 h; 99%. (iv) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU, NMP, 160 °C, 36 h; 28% (**16:17**, 71:29). (v) $\text{RhCl}(\text{PPh}_3)_3$, DDQ; 90%. (vi) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU; > 10%. **e** Corannulene trimer synthesis. (i) $\text{Pd}_2(\text{dba})_3$, CsF, MeCN, rt, 12 h; 40%

and tetraindenocorannulene (Fig. 2a)²⁵. The synthesis of the former starts with a Suzuki–Miyaura coupling of penta-chlorinated **2** with 2-chlorophenyl-boronic acid to give **5** which undergoes Pd-catalysed intramolecular arylation assisted with microwave heating for the conversion to **6**. A similar pathway is used to afford **9** with the difference being the starting material. As for **9**, starting point tetrabromocorannulene **7** undergoes the Suzuki–Miyaura coupling to form **8** where the same Pd-catalysed conditions are used (including microwave heating) to achieve tetra-indenoannulated **9** (Fig. 2b). Both polyindenoannulated corannulenes show multiple peaks in the UV-Vis spectra with absorption tails in the visible region. A pyrolysis route was explored and tetraindenocorannulene was formed with low yields of 1.3% and no amount of pentaindenocorannulene could be isolated. In these indenocorannulene structures the carbon atoms at the core of corannulene experience greater pyramidalisation than C₆₀ as a result of connecting the peri carbons of corannulene as per the POAV analysis of the crystal structures of **6** and **9**.

The class of indenocorannulenes established by Scott was expanded to a total of seven members by Scott's group in 2009 by reporting the palladium-catalysed synthesis of 5 more indenoannulated corannulenes: **10**, **11**, **12**, **13** and **14** (Fig. 2c)²⁶. A general route follows as (1) Suzuki–Miyaura coupling of polyhalogenated corannulene with 2-chlorophenyl-boronic acid and; (2) subsequent intramolecular cyclisation to stitch one or more 5-membered rings in a palladium-catalysed reaction subjected to microwave heating. ¹H, ¹³C NMR and UV-VIS spectroscopic studies were performed on all seven indenocorannulenes and X-ray analysis of the crystals were carried out with POAV analysis of Hadon to quantify the pyramidalisation angles.

Wu's group in 2011 reported a palladium-catalysed synthesis of buckybowls **15**, **16** and **17** (Fig. 2d)²⁷. The synthesis of **15** starts from a cycloaddition of 1,8-bis(aryl-ethynyl)naphthalene and iodobenzene to give a tetrachloro compound where a quadruple ring-closure is assisted with catalyst Pd(PCy₃)Cl₂ in the presence of DBU to afford **15**. The same starting material is cocyclotrimerised with 2-butyne followed by being subjected to the same palladium catalysis to give a mixture of products **16** and **17**. Later, the authors utilized a similar strategy to obtain **18** using acenaphthalene as a reactant, an aromatization step, and a palladium-catalysed ring-closing sequence²⁸. The solubility of **18** was found to be low in common organic solvents. X-ray crystallography analysis showed that the bowl was deep (ca. 2.30 Å). In terms of the molecular structure, **18** represent a subunit of C₇₀ and higher fullerenes.

A palladium-catalysed cyclotrimerization of corannulyne **19** to furnish hydrocarbon C₆₀H₂₄ (**20**) was reported by Sygula's group in 2011 (Fig. 2e)²⁹. Aryne **19** was generated from 2-trimethylsilylcorannulenyl triflate that can cyclotrimerise to **20** in the presence of catalyst Pd₂(dba)₃. The presence of the three bulky corannulene moieties bound to an axis of a benzene ring produces substantial steric hindrance forcing **20** to assume a propeller-like twisted structure. The most stable conformation is that of an 'up-up, down-down, up-down' structure as observed in its crystal structure. The conformational conversion was studied with variable temperature NMR spectroscopy of **20** which reveal a high activation barrier as the signals of the protons are broadened at 140 °C and sharpened at 0 °C. The bowl inversion studies show that the corannulenes are distinct from one another in terms of bowl inversion as a result of their unsymmetrical environments.

Itami and Scott in 2013 reported the synthesis of warped nanographenes³⁰ **25/26** which begins from a corannulene core that expands with aromatic six-membered rings and seven-membered ring webbings in between (Fig. 3). Three different routes to expand the molecule were outlined. One of the methods

is a complete C–H phenylation of all the hydrogens on corannulene (**21**) in the presence of catalyst Pd(OAc)₂. The second is a five-fold C–H biphenylation (**22**) with the same catalyst and the last, corannulene undergoes a five-fold C–H borylation (**23**) that proceeds into a Suzuki–Miyaura coupling (**24**)³¹. These extended corannulene structures can undergo cyclodehydrogenation to form carbon-rich warped nanographenes. The crystal of the nanographene endows a negative curvature geometry to the lattice due to the introduction of odd-numbered ring defects. **26** has a double concave structure due to the C–C–C bonds moving away from the natural angle of 120° to angles of within a range of 106° to 138°. **25** and **26** are soluble in several organic solvents—a distinct difference from graphite—because of the absence of large-area van der Waal's interactions between its adjacent molecules. The absorption spectra show the longest maximum wavelength of **26** to be at 418 nm and its fluorescence at 504 nm and 535 nm with a quantum yield of 0.26. Cyclic voltammetry measurements of **25** present two reversible oxidation at oxidation potentials +0.63 V and +0.97 V versus the ferrocene/ferrocenium couple (Fc/Fc⁺) for the first and second potentials, respectively.

Along similar lines, Segawa and Itami demonstrated preparation of the first example of a fused five-helicene system **28** where each helicene comprises six repeating units (Fig. 3). The synthesis employs selective reactivity of aryl bromides over aryl chlorides to first achieve C–Br coupling through Suzuki–Miyaura reaction on pentaborylcorannulene scaffold to access chlorinated **27** which upon direct arylation conditions, again under palladium catalysis, generates **28**³². **28** is different from **25** and **26** as the phenanthrene units are separate from each other and forms a unique π-system with a propeller-like structure with regular twists and turns throughout the molecule. Very recently the authors extended their elegant work by incorporating thiophene heterocycles into the warped nanographene structure³³.

Dibenzocorannulene-fused porphyrin was reported by Osuka as one of the few large hybrid planar-non-planar aromatic structures (Fig. 4a)³⁴. The synthesis begins from a cross-coupling of brominated porphyrin **29** with corannulene-containing **30** giving linked product **31**. A β-brominated porphyrin **32** was cross-coupled with **30** producing a β-linked corannulene on porphyrin **33**. Both **31** and **33** were subjected to oxidation with FeCl₃ to form five-membered fused ring in **34** and six-membered fused ring **35** thus extending the π-conjugation between porphyrin and corannulene. The dibenzocorannulene bowl depths in **34** and **35** are found to be 0.71 Å and 0.83 Å, respectively.

Cao et al. reported a method to extend the π-conjugation of corannulene with heterocyclic thiophenes by first coupling four thiophene fragments followed by an oxidative cyclisation to bridge the attached aromatic systems (Fig. 4b)³⁵. Initially, tetrabromocorannulene **7** is linked with thiophenes 2-(tributylstannyl)-5-hexylthiophene **36** and 3-(tributylstannyl)-5-hexylthiophene **37** with a Stille coupling catalysed by Pd(PPh₃)₂Cl₂. The coupled products **38** and **39** are then cyclised oxidatively with DDQ and FeCl₃ respectively to afford fused isomers **40** and **41**. The products exhibit exceptional thermal stability where decomposition occurs at 447 °C for **40** and 452 °C for **41**. Incorporating thiophene units to corannulene can improve the charge transport properties (for instance hole mobility of 0.06 cm² V⁻¹ s⁻¹) and its arrangement making it a suitable candidate for applications in organic field-effect transistors (OFETs).

A one-pot, two-step synthesis of methylene-bridged arenes was reported by Wu in 2015 (Fig. 4c)³⁶. Among the arenes used was corannulene. Specifically, bromocorannulene **42** is cross-coupled with alkyne **43** following a base-facilitated retro Diels–Alder condensation that arrives at **44**. Crystal structure of **44** was

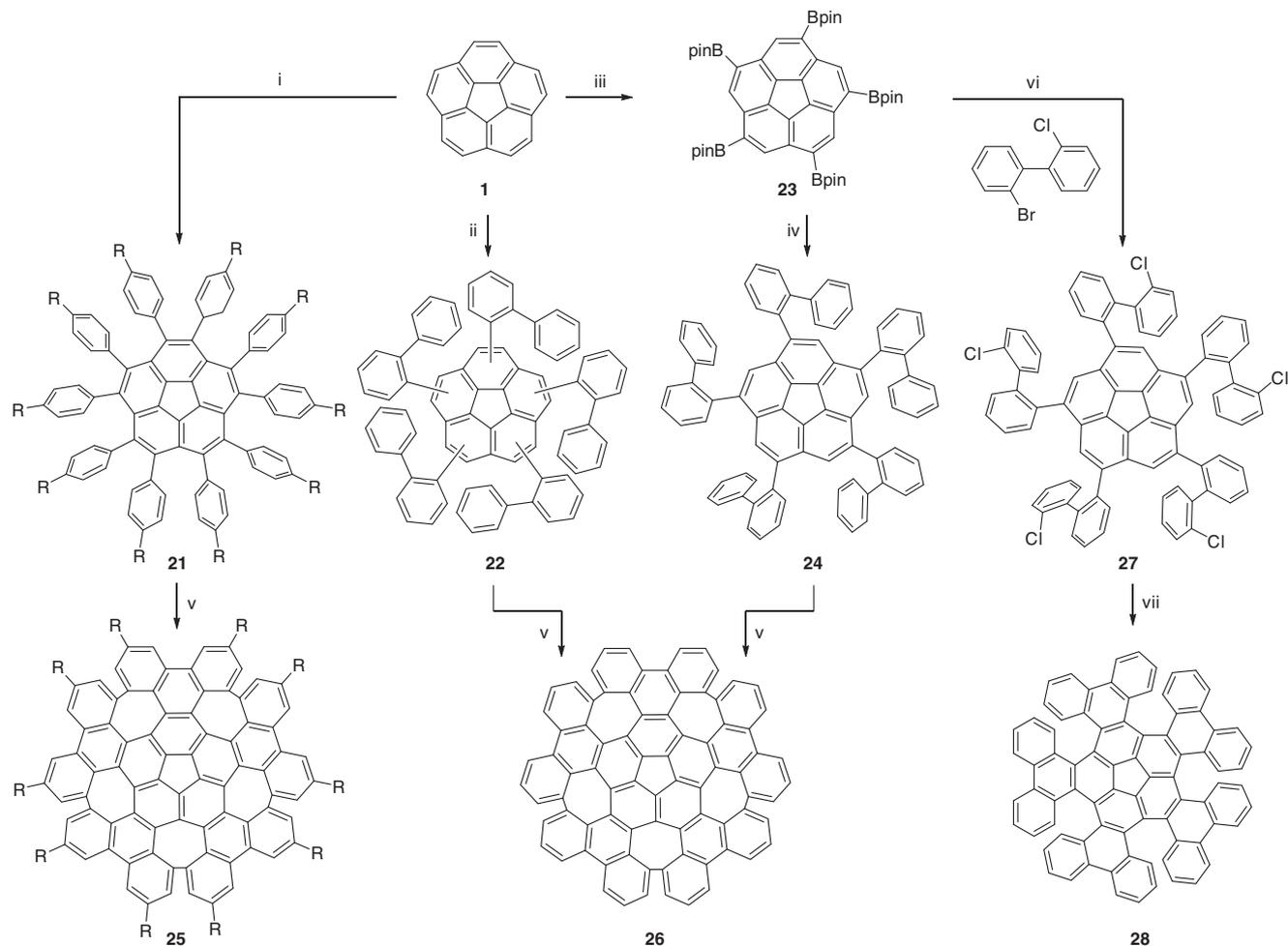


Fig. 3 Corannulene extension into warped nanographenes. (i) Pd(OAc)₂, tris(*p*-(*t*-butyl)phenyl)boroxine, *o*-chloranil, DCE, 80 °C, 23% (R = *t*-butyl). (ii) Pd(OAc)₂, tris(*o*-biphenyl)boroxin, *o*-chloroanil, DCE, 80 °C, 16 h; 21%. (iii) Ir(OMe)(cod)₂, B₂(pin)₂, 4,4'-dimethylbipyridyl, *t*-BuOK, THF, 85 °C, 4 days; 95%. (iv) Pd₂(dba)₃·CHCl₃, 2-bromobiphenyl, SPhos, Cs₂CO₃, toluene/water, 80 °C, 24 h; 88%. (v) DDQ, TfOH/CH₂Cl₂ (5:95), 0 °C, 30 min; 50% (from **22**), 40% (from **24**). (vi) Pd₂(dba)₃·CHCl₃, SPhos, Cs₂CO₃, toluene/water, 80 °C, 24 h; 76%. (vii) PdCl₂(PCy₃)₂, DBU, DMAc, 140 °C, 3 days; 10%

analysed and the bowl structure is slightly deepened compared to corannulene but has a similar bowl-inversion barrier of approximately 11 kcal/mol. The packing of extended **44** occurs in a highly ordered manner with unidirectional bowl-in-bowl columns with a distance of 15 Å between bowls.

In 2016, Segawa and Itami presented a practically simple method to access thiophene-based extended aromatics in a general fashion (Fig. 4d, e)³⁷. In their synthesis, phenyleneethylene derivatives **45** and **47** and elemental sulfur were combined to give thiophene-fused corannulenes **46** and **48**. The yield for the mono-thienannulation was nearly quantitative and the synthesis is found to be practical and scalable.

Recently, Smith and Scott described the first palladium-catalysed synthesis of tribenzocorannulene on a half-gram scale (Fig. 5a)³⁸. In this synthesis, the precursor **49** is obtained in three steps from commercially available compounds. Intramolecular arylation strategy is then used to fuse the aromatic scaffold and obtain **50** in an isolated yield of 56%. The X-ray crystal structure of this molecule along with the computational data of other benzannulated corannulene structures helped in establishing that sequential benzannulation of the corannulene scaffold leads to a progressive decrease in the bowl depth.

A Pd-catalysed cascade developed by Würthner group in 2016^{39,40} was modified for the Suzuki–Miyaura cross-coupling of **51** and **52a** (X = Br) (Fig. 5b)⁴¹. Boronic ester **51** was coupled

with dicarboximide **52a** to form **53** and **54**. The competing intramolecular Suzuki–Miyaura coupling could be inhibited by substituting the dicarboximide with a chloro-bromo **52b** (X = Cl). Crystal structures of **53** exhibit columnar stacks with adjacent column alternating in the orientation of the curvature of corannulene. After optimising the conditions of the monoannulated **53**, similar conditions of the Pd-catalysis together with the Heck additive, the diannulated bowl **57** with two bulky imide groups was formed from diboron diester **55** and **56**. The diboron ester was isolated from the chromatographic purification of a mixture of regioisomers derived from altering equivalents of the diboron reagent. Unlike **53**, the crystal arrangement of **57** displays two **57** molecules sandwiching two toluene solvate molecules. The sandwich molecules were positioned such that an imide substituent is placed towards the interior of the opposing corannulene fragment.

Baldrige and Siegel reported a trio of annulated corannulenes (Fig. 5c)⁴². 1,6-dibromo-2,5-dimethylcorannulene **58** is coupled with 2-fluoro-phenyl boronic acid and 2-chloro-phenyl boronic acid to give **59a** (X = Cl) and **59b** (X = F) respectively. **59a** was converted to **60** via a palladium-catalysed C–H insertion with Pd(OAc)₂, it can also be converted to another indenoannulated **61** that forms through a C–C coupling with Pd(PCy₃)₂Cl₂. As for fluorinated **59b**, reacting it with silyl cation with microwave heating gave a mixture of products **60–62**. Packing behaviour of

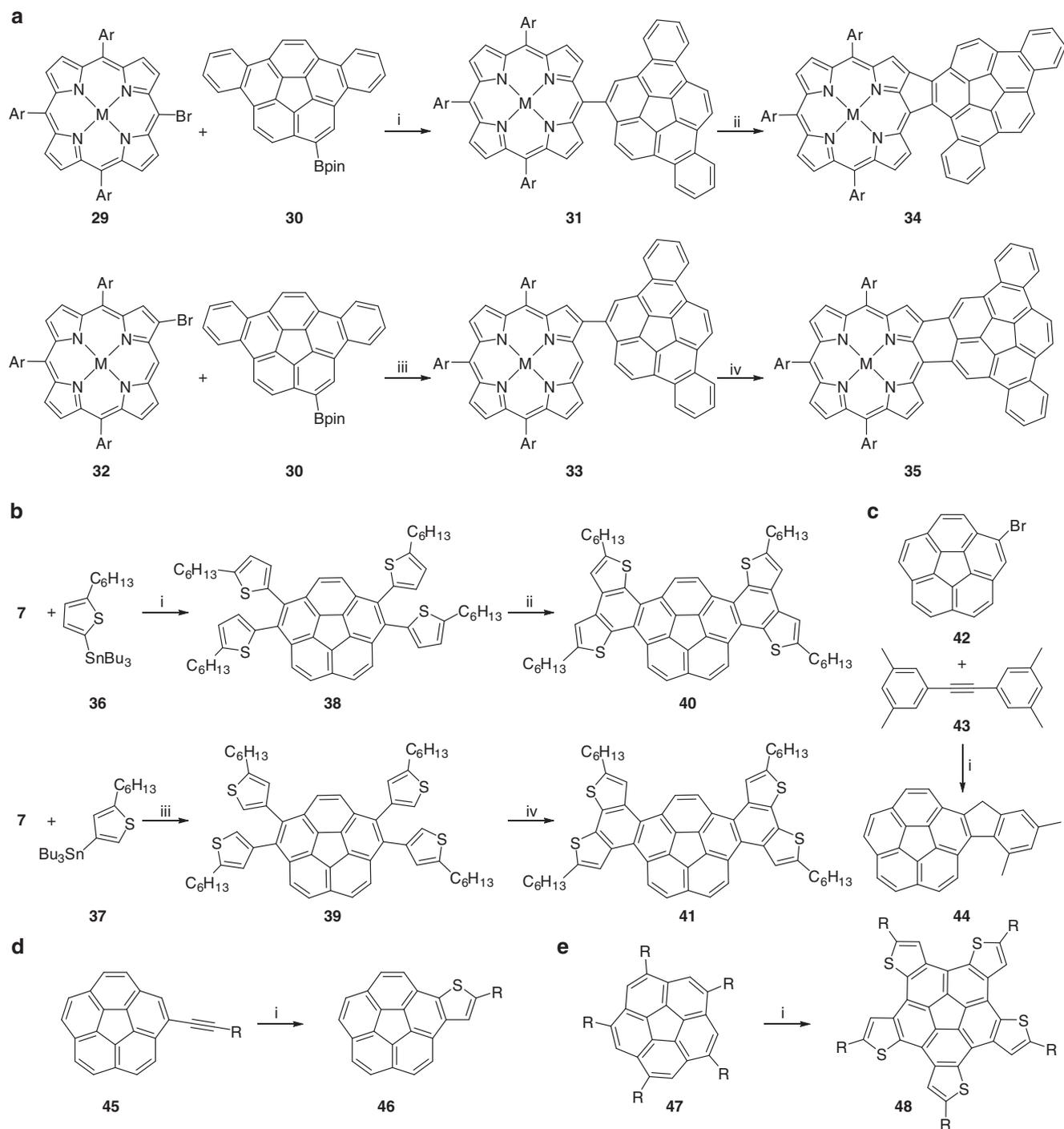


Fig. 4 Heteroatom inclusion in the extended corannulene scaffold. **a** Porphyrin-corannulene hybrids. (i) Pd cat., K_3PO_4 , THF/ H_2O , 40 °C; 65% (M = Zn), 75% (M = Ni). (ii) $FeCl_3$, $CH_2Cl_2/MeNO_2$, rt, 10–40 min; 70% (M = Zn), 88% (M = Ni). (iii) Pd cat., K_3PO_4 , THF/ H_2O , 40 °C; 69% (M = Zn), 59% (M = Ni). (iv) $FeCl_3$, $CH_2Cl_2/MeNO_2$, rt, 10 min; 45% (M = Zn), 29% (M = Ni). **b** Thiophene-corannulene hybrids. (i) $Pd(PPh_3)_2Cl_2$, DMF, 130 °C, 48 h, 95%. (ii) DDQ, CH_3SO_3H , DCM, 0 °C, 10 min, 60%. (iii) $Pd(PPh_3)_2Cl_2$, DMF, 130 °C, 48 h, 82%; (iv) $FeCl_3$, Et_2O , DCM, rt, 30 min, 27%. **c** Synthesis of **44**. (i) $PdCl_2$, DPPE, DBU, CsOPiv, dioxane, 110 °C, 24 h; 63%. **d** Elemental sulfur for monothiophene-extended corannulene. (i) S_8 , DMF, 140 °C, 48 h (R = 4-*tert*-butylphenyl). **e** Elemental sulfur for pentathiophene-extended corannulene. (i) S_8 , DMF, 140 °C, 48 h (R = 3,5-di-*tert*-butylphenylacetylene)

the structures follow rough columns where symmetrical **60** and **61** follows a unidirectional form while racemic mixture of **62** exhibits a slip-stacked arrangement with enantiomeric columns following either direction.

In 2018, the preparation of nitrogen-containing benzocorannulenes were described (Fig. 6). Here, the synthesis starts with the

oxidative dimerization of 9-aminophenanthrene **63** to tetrabenzocorannulene **64**^{43–46}. A single fusion of the aromatic scaffold through palladium-catalysed C–Cl/C–H coupling reaction furnished **65**. Bromination of the twisted **65** then yields a triply brominated compound **66**. A double C–Br/C–H coupling reaction then affords aza-buckybowl **67**. Under iridium-catalysed

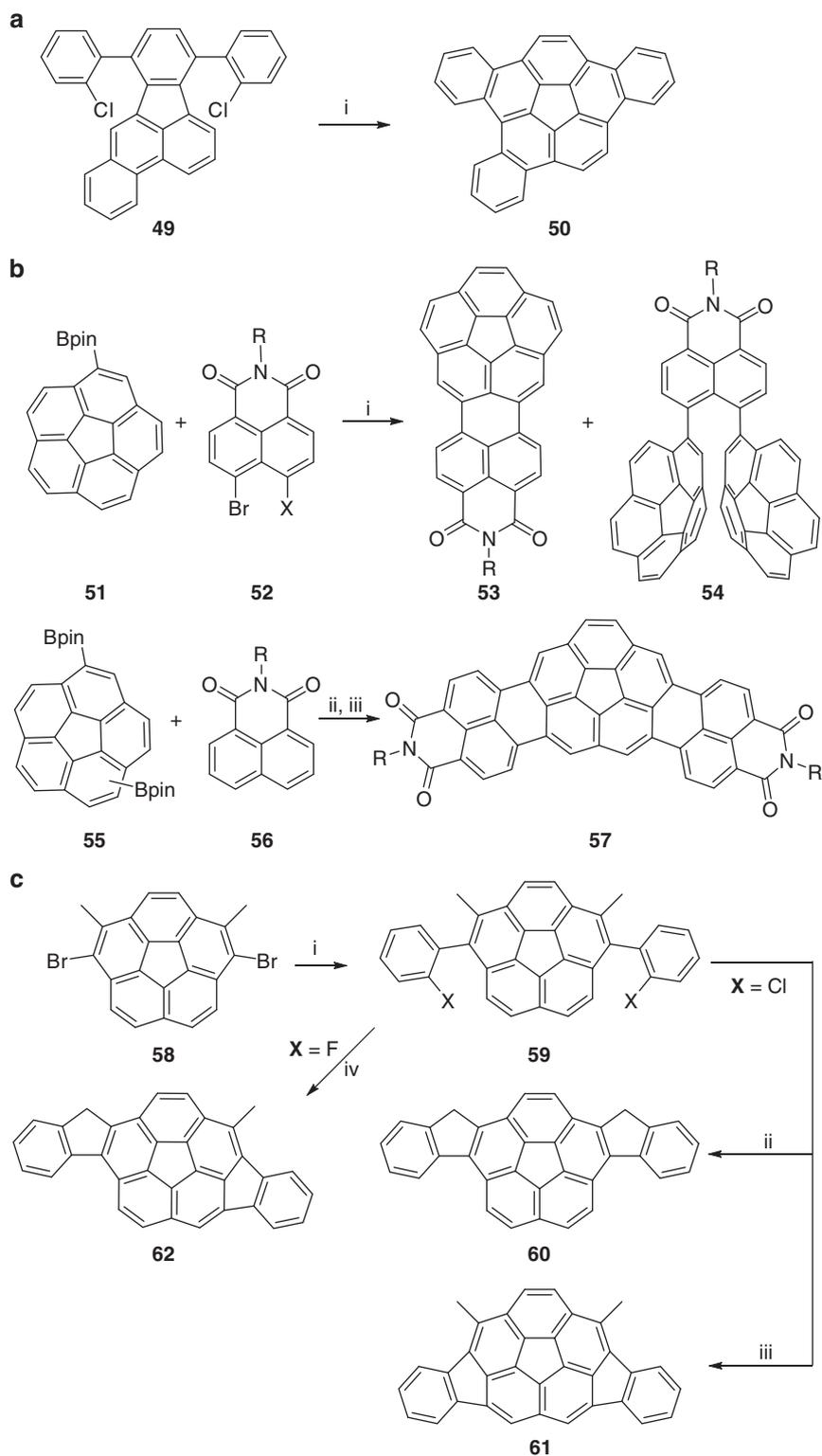


Fig. 5 Palladium-catalysed extension of the corannulene nucleus. **a** Synthesis of tribenzocorannulene. (i) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU, DMAc, 150 °C, 3 days, 56%. **b** Corannulene-diimide conjugates. (i) $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $\text{P}(\text{o-tolyl})_3$, Cs_2CO_3 , Bu_4NCl , toluene/water (2:1), 90 °C, 12 h; 15% (**53**), 28% (**54**). (ii) $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $\text{P}(\text{o-tolyl})_3$, Cs_2CO_3 , H_2O , *o*-DCB, 90 °C, 2 h. (iii) Bu_4NCl , 160 °C, 24 h ($\text{R} = 2,6$ -diisopropylbenzene); 31%. **c** Trio of five-membered ring-fusion with corannulene. (i) $\text{Pd}(\text{PPh}_3)_4$, (2-fluorophenyl)boronic acid, K_2CO_3 , THF, H_2O , 70 °C, 15 h; 80%. (ii) $\text{Pd}(\text{OAc})_2$, [1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride], NMP, K_2CO_3 , 125 °C, 20 min; 32%. (iii) $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$, DBU, DMA, 160 °C (microwave), 30 min; 31%. (iv) $[\text{Pr}_3\text{Si}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$, DMDMS, PhCl, 120 °C (microwave), 30 h; 6.2:1:4.5 of **60**, **61** and **62**, respectively

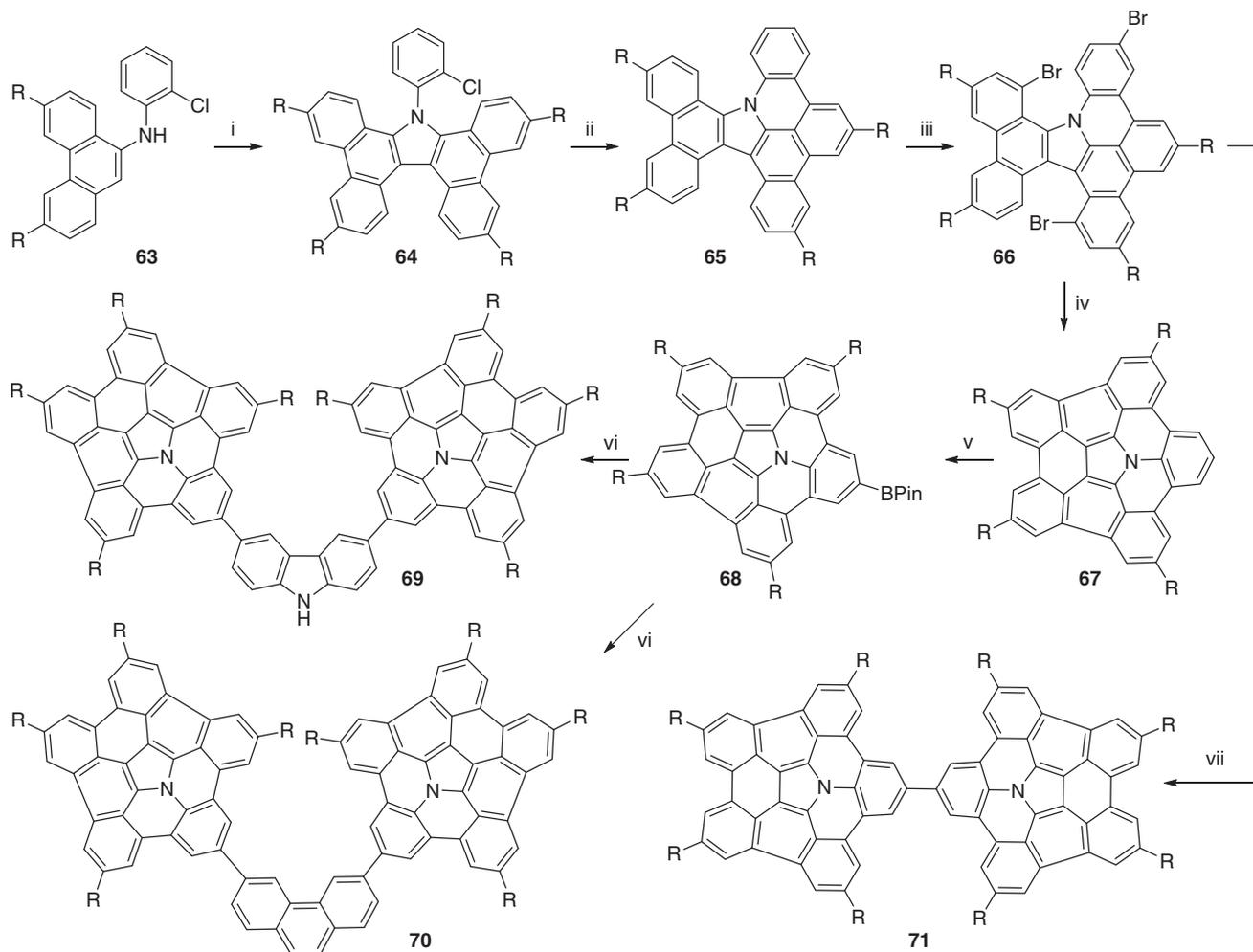


Fig. 6 Nitrogen-doped extended corannulenes. (i) 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), TFA, toluene, rt, 1 h, 94%, (R = *t*-butyl). (ii) Pd(OAc)₂, PCy₃ *HBF₄, K₂CO₃, DMA, 130 °C, 43 h, 63%. (iii) Br₂, CCl₄, 70 °C, 12.5 h, 56%. (iv) Pd(OAc)₂, PCy₃ *HBF₄, K₂CO₃, DMA, 130 °C, 16 h, 46%. (v) bis (pinacolato)diboron, [Ir(OMe)cod]₂, 4,4'-di-*tert*-butyl-2,2'-bipyridyl, octane, 10.5 h, 110 °C, 80%. (vi) Pd(PPh₃)₄, Cs₂CO₃, THF/H₂O, reflux, 4 h for **69** (50%); Pd(PPh₃)₄, Cs₂CO₃, 1,4-dioxane/H₂O, 80 °C, 1 h for **70** (68%). (vii) Pd(OAc)₂, HPCy₃ *HBF₄, K₂CO₃, DMA, 130 °C, 31%

reaction, **67** allows for the installation of a pinacole ester moiety (**68**). This functional group can be used to dimerize the azabuckybowl with aromatic spacers such as carbazole (**69**) or phenanthrene (**70**). Alternatively, a directly linked dimer **71** can be formed through tri-brominated **66** again under palladium catalysis. All of these extended azacorannulene systems show the capability of strongly interacting with fullerenes and forming supramolecular complexes.

Rh-catalysed coupling. A group of indenocorannulenes with a variety of functional groups using a [(2 + 2) + 2] cycloaddition route was developed by Siegel's group in 2006⁴⁷. Diyne **74** was prepared from **73** and dichlorinated corannulene derivative **72** via a modified version of a procedure reported by Nolan (Fig. 7a)⁴⁸. The diyne is reacted with second alkyne **75** in another cycloaddition step mediated by a rhodium catalyst to afford indenocorannulene **76**. R¹ and R² groups on alkyne facilitate this step whereas aromatic substituents at R⁵ promote higher yields as compared to alkyl groups.

In 2015, Baldrige and Siegel used the rhodium-mediated reaction between **77** and **78** to yield tetraarylindenocorannulene **79**⁴⁹. The tetraaryl groups in **79** were then fused through silylation-induced intramolecular Friedel-Crafts arylation⁵⁰ also developed by the Siegel group and discussed below. A net result

of this fusion was preparation of a corannulene-graphene hybrid structure linked through a five-membered cycle (Fig. 7b).

Friedel-Crafts reactions

Overview. Siegel's group reported a Friedel-Crafts arylation of fluorinated arenes in 2011 assisted by silyl cations through a dehydrofluorination reaction (Fig. 7c)⁵⁰. A corannulene-based substrate **81** was shown to undergo an intramolecular aryl coupling catalysed by silyl cation ¹Pr₃Si⁺ through elimination of HF to form indenoannulated **82**. Earlier examples of the synthesis of compounds **60**, **61**, **62** and **80** also utilised this method.

In 2018, Wu, Siegel and Chi described corannulene dimer diradicaloids via multi-step synthesis (Fig. 7d). The key step of connecting the corannulene scaffolds was achieved through intramolecular Friedel-Crafts alkylations on di-aldehyde substrates **83**. Oxidative dehydrogenation with the help of DDQ provided the fully aromatic extended structures **84**⁵¹.

Cycloaddition reactions

Diels-Alder cycloaddition. Sygula's group in 2005 reported the synthesis of corannulyne **19**⁵². **19** could be accessed through the *ortho*-deprotonation of bromocorannulene **42** in the presence of excess sodium amide and a catalytic amount of potassium *tert*-butoxide (Fig. 8a). **19** is highly valuable as it can take part in

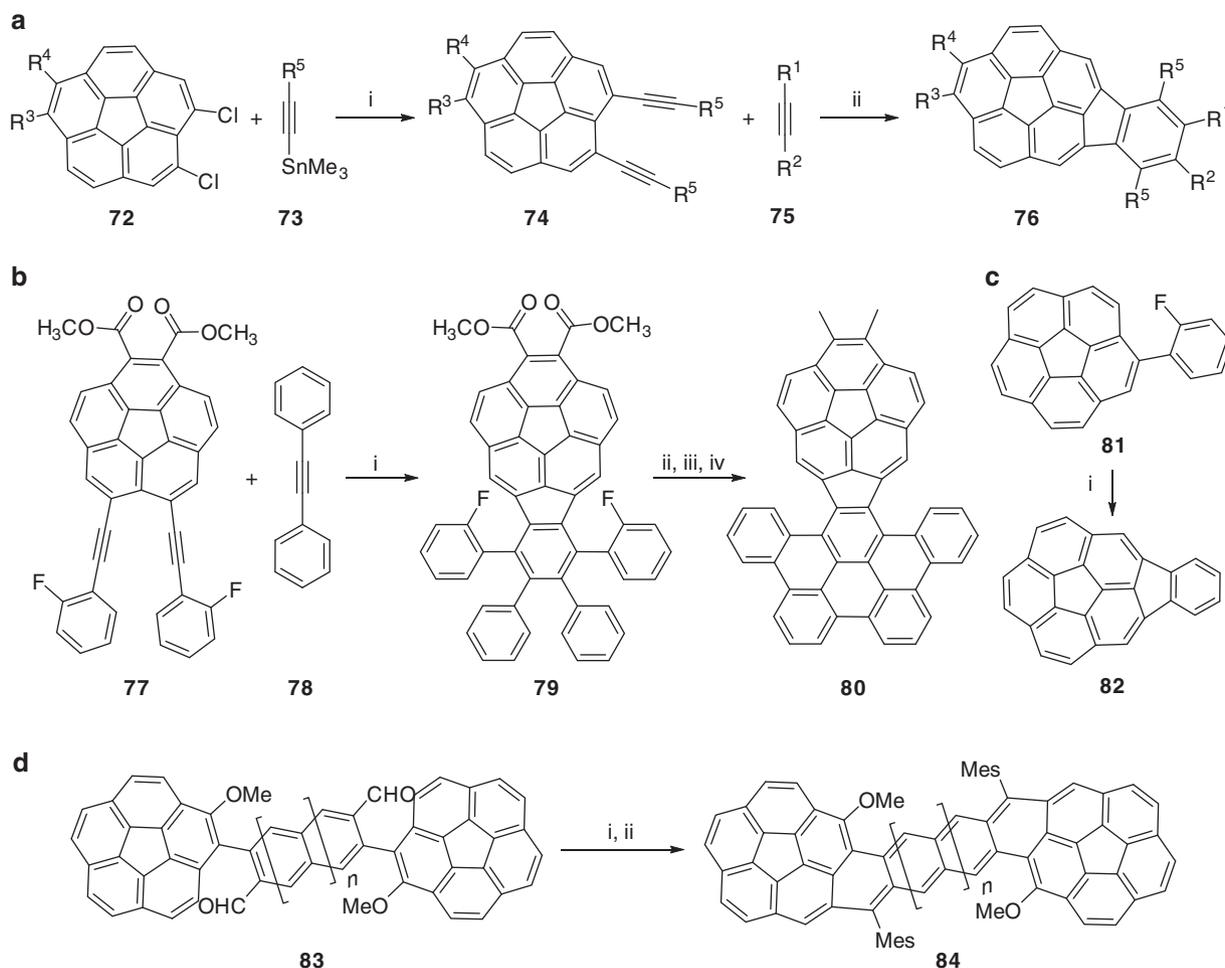


Fig. 7 Corannulene extension pathways involving rhodium catalysis and Friedel-Crafts reactions. **a** Synthesis of indenocorannulenes. (i) Pd(OAc)₂, IPr⁺HCl, *t*-BuOK, DME, 110 °C, 3 days; (ii) RhCl(PPh₃)₃, *p*-xylene, 130 °C, 60 h. **76a**: R¹ = R² = R⁵ = Ph, R³ = R⁴ = H; 54% **76b**: R¹ = R² = Ph, R³ = R⁴ = H, R⁵ = *n*Pr; 42%. **76c**: R¹ = R² = R⁵ = Ph, R³ = R⁴ = CO₂Me; 64%. **76d**: R¹ = R² = R³ = R⁴ = CO₂Me, R⁵ = Ph; 19%. **76e**: R¹ = R² = *n*Pr, R³ = R⁴ = CO₂Me, R⁵ = Ph; 57%. **76f**: R¹ = R² = Ph, R³ = R⁴ = CO₂Me, R⁵ = *n*Pr; 47%. **76g**: R¹ = R² = R³ = R⁵ = Ph, R⁴ = CO₂Me; 81%. **76h**: R¹ = CMe₂OH, R² = R³ = R⁴ = H, R⁵ = Ph; 60%. **76i**: R¹ = CH(OEt)₂, R² = R³ = R⁴ = H, R⁵ = *n*Pr; 14%. **76j**: R¹ = CO₂Me, R² = R³ = R⁴ = H, R⁵ = *n*Pr, traces. **b** Corannulene-graphene hybrid. (i) [(Ph₃P)₃RhCl], *p*-xylene, 130 °C, 3 days; 65–73%. (ii) DIBAL-H, dry toluene, –78 °C, 1 h. (iii) Et₃SiH, TFA, CH₂Cl₂, 0 °C, 3 h; 25% (over two steps). (iv) [Pr₃Si]⁺[CB₁₁H₆Cl₆][–], PhCl, (MeS)₂Si(CH₃)₂, 90 °C (MW), 1 h; 40%. **c** Friedel-Craft arylation. (i) [Pr₃Si]⁺[CB₁₁H₆Cl₆][–], Me₂Si(Mes)₂, PhCl, 110 °C, 8 h; 79%. **d** Corannulene diradicaloids synthesis. (i) Mesitylmagnesium bromide, BF₃·OEt₂, rt. (ii) DDQ, Toluene, 80 °C (*n* = 0, 1)

cycloaddition reactions with various dienes to give Diels-Alder adducts that can finally be aromatised to give extended aromatics. In this initial study furan was used as a diene to give **85** which was later treated with Fe₂(CO)₉ to cleave the oxygen bridge and to give benzocorannulene **90** in quantitative yields.

In 2006, the generation of isocorannulenofuran **86** from the elimination of ethylene in **85** was reported (Fig. 8a)⁵³. Unlike isobenzofuran, **86** is stable enough to be isolated for a full characterisation study. In the synthetic aspect, **86** can carry out Diels-Alder reactions with **87–89** (Fig. 8b). Their corresponding hydrocarbons **93–95** (Fig. 8c) can be furnished by deoxygenation of the corresponding Diels-Alder adducts using Fe₂(CO)₉ or a low-valent titanium catalyst. Despite the low solubilities of **94** and **95**, ¹H NMR spectra could be obtained with HRMS to confirm their structures with their expected molecular ions.

Bis-corannulene molecular tweezer C₆₀H₂₄ was synthesised in 2007 beginning with isocorannulenofuran **86** (Fig. 8c)⁵⁴. A Diels-Alder reaction of **86** and **90** gives *syn* and *anti* Diels-Alder adducts with a total yield of 92% with *anti* isomer being the major product. The endoxide bridges in the adducts can be removed

with low-valent titanium to produce hydrocarbon buckycatcher **96**. Dark red crystals of **96**-fullerene complexes reveal the position of fullerene within the concavity of the corannulenes. The complexes form as well in solution in an NMR titration experiment. Isocorannulenofuran **86** was further used by Sygula to create better receptors of fullerenes⁵⁵.

Recently, isocorannulenofuran **86** allowed for reaction with a bis-benzynes precursor **91** in a double Diels-Alder cycloaddition to *syn* and *anti* adducts⁵⁶. The endoxide bridges were removed in the presence of trimethylsilyl chloride and sodium iodide to afford **97** in which an anthracene bridges the two terminal corannulenes (Fig. 8c).

In the context of Diels-Alder chemistry as illustrated by the work of Sygula, the Stuparu group showed that bis-corannulyne can be generated and trapped with furan while using tetra-bromocorannulene as the precursor⁵⁷.

1,3-Dipolar cycloaddition. Nozaki's group introduced 1,3-dipolar cycloaddition between azomethine ylide and corannulene as a viable synthetic method to access nitrogen-doped corannulenes

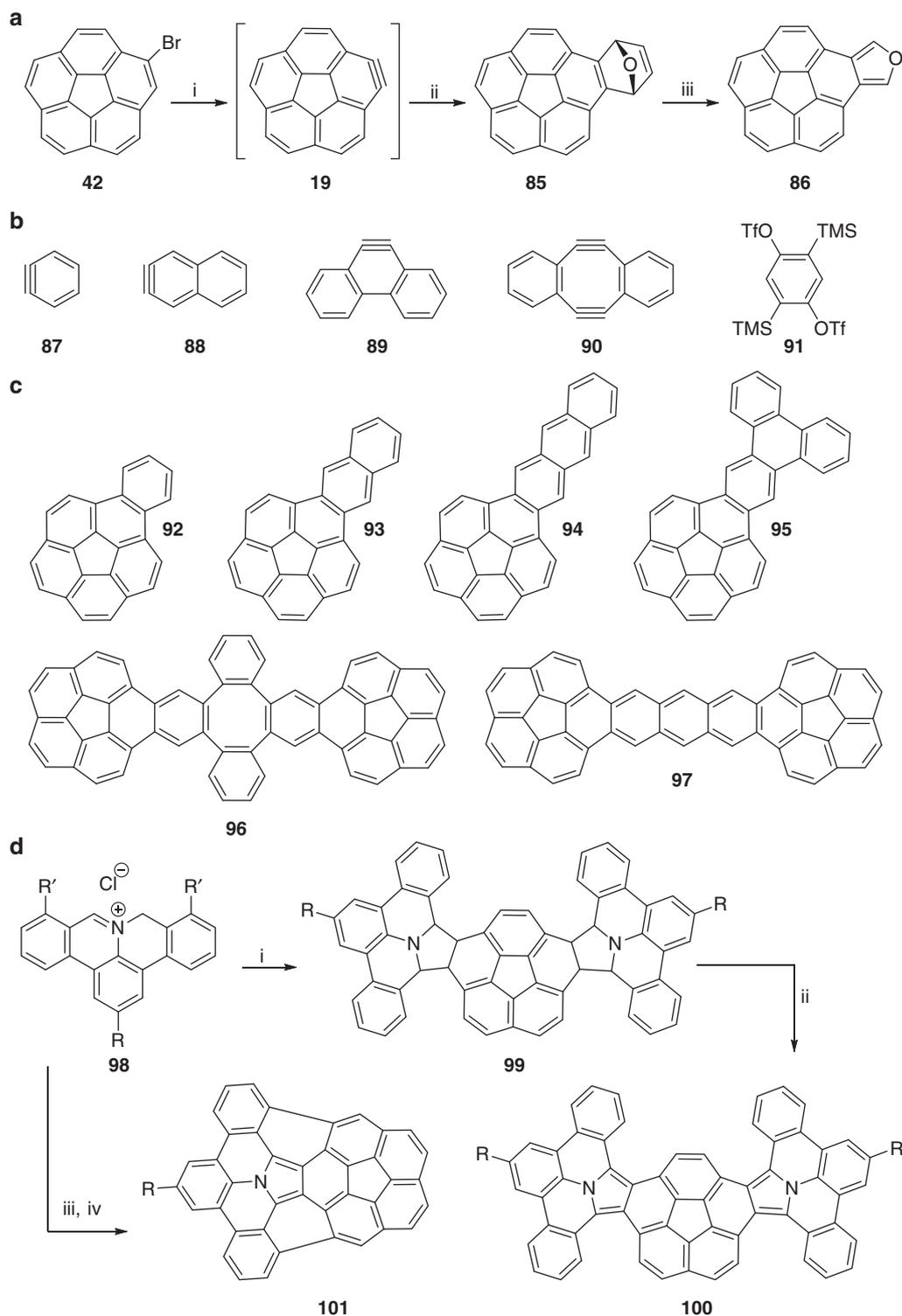


Fig. 8 Cycloaddition pathways for extension of corannulene. **a** Synthesis of corannulyne and isocorannulenofuran. (i) NaNH_2 , $t\text{-BuOK}$, THF, rt. (ii) Furan (excess); 80%. (iii) 2,6-bis-2-pyridyl-1,2,4,5-tetrazine, CHCl_3 , 55 °C, 15 min; 94%. **b** Various arynes useful in reaction with isocorannulenofuran. **c** Extended aromatic structures. **d** 1,3-Dipolar cycloaddition. (i) corannulene **1**, $i\text{Pr}_2\text{NEt}$, DMSO, 120 °C, 1 h; 29%. (ii) DDQ, CH_2Cl_2 , rt, 14 h; 80% ($\text{R} = t\text{-Bu}$, $\text{R}' = \text{H}$). (iii) corannulene **1**, DMSO, 140 °C, 20 h; DDQ, rt, 2 h; 22%. (iv) $\text{Pd}(\text{OAc})_2$, 150 °C, 24 h; 46% ($\text{R} = t\text{-Bu}$, $\text{R}' = \text{Cl}$)

(Fig. 8d)^{58–60}. The synthesis begins with iminium chloride salt **98** which gives rise to the ylide in situ upon treatment with diisopropyl ethylamine at 120 °C for a period of an hour. The cycloaddition between the ylide and corannulene occurs at the rim double bond and produces mono- and bis-adducts in 46 and 29% (**99**) yields, respectively. These adducts can be subjected to

aromatization through dehydrogenation reactions to give fully aromatic and extended corannulenes having nitrogen atom(s) in the scaffold (**100**). A subsequent study utilized bis-chloro-based salt that allows for an intramolecular cyclization to further stitch the aromatic scaffold into a larger and highly curved aromatic system (**101**).

Photochemistry

Photochemical pathway. The synthesis of corannulene carbaldehyde **102** at a 15 g scale and in an isolated yield of >90% made it possible to explore its application in synthesis of corannulene-based vinylenes **103** through a Wittig olefination reaction with a variety of commercially available phosphonium ylides (Fig. 9a)^{61,62}. In subsequent studies, these stilbene-like precursors were shown to undergo a photocyclisation-induced oxidation reaction to yield extended corannulenes **104**^{62,63}. The modularity of this process was further demonstrated through switching of the coupling partners such that commercially available aldehydes were used and corannulene was transformed into a ylide compound. Lastly, corannulene ketone was also shown to be applicable in this synthetic scheme. Initial results show that the mild nature of the reaction allowed for the incorporation of reactive sites or heteroatoms in the final compounds. Recently, this method was used to combine benzo-pyrene⁶⁴ or helicene⁶⁵ with corannulene.

Wang, Siegel and Li recently accomplished synthesis of a highly complex and beautiful planar-non-planar hybrid structure named as ‘corannurylene pentapetalae’ (Fig. 9a)⁶⁶. In their design, perylene diimide was used as the planar fragment and

corannulene was used as the curved core. The perylene diimide chromophore is arranged around this core in a 5-fold symmetric fashion to give a flower-like molecule. The final step of the synthesis involved an oxidative photocyclization reaction of **105** to afford **106**.

Scholl reactions

Overview. In 2018, Martín and coworkers presented an elegant molecular hybrid of coronene and corannulene⁶⁷. The final step of the synthesis involved precursor **107** that upon treatment with FeCl₃ formed **108** with a positively curved helical structure. All the ring closures here led to six-membered rings. Under different oxidative conditions (DDQ, TfOH), however, one more ring formed and it was composed of seven members. In this molecule (**109**) both curvatures could be observed in the crystal structure. **109** could also be obtained in a two-step process through **108**.

Outlook

Aromatic scaffold extension of corannulene is a viable synthetic route to access non-planar nanocarbons. This chemistry offers a

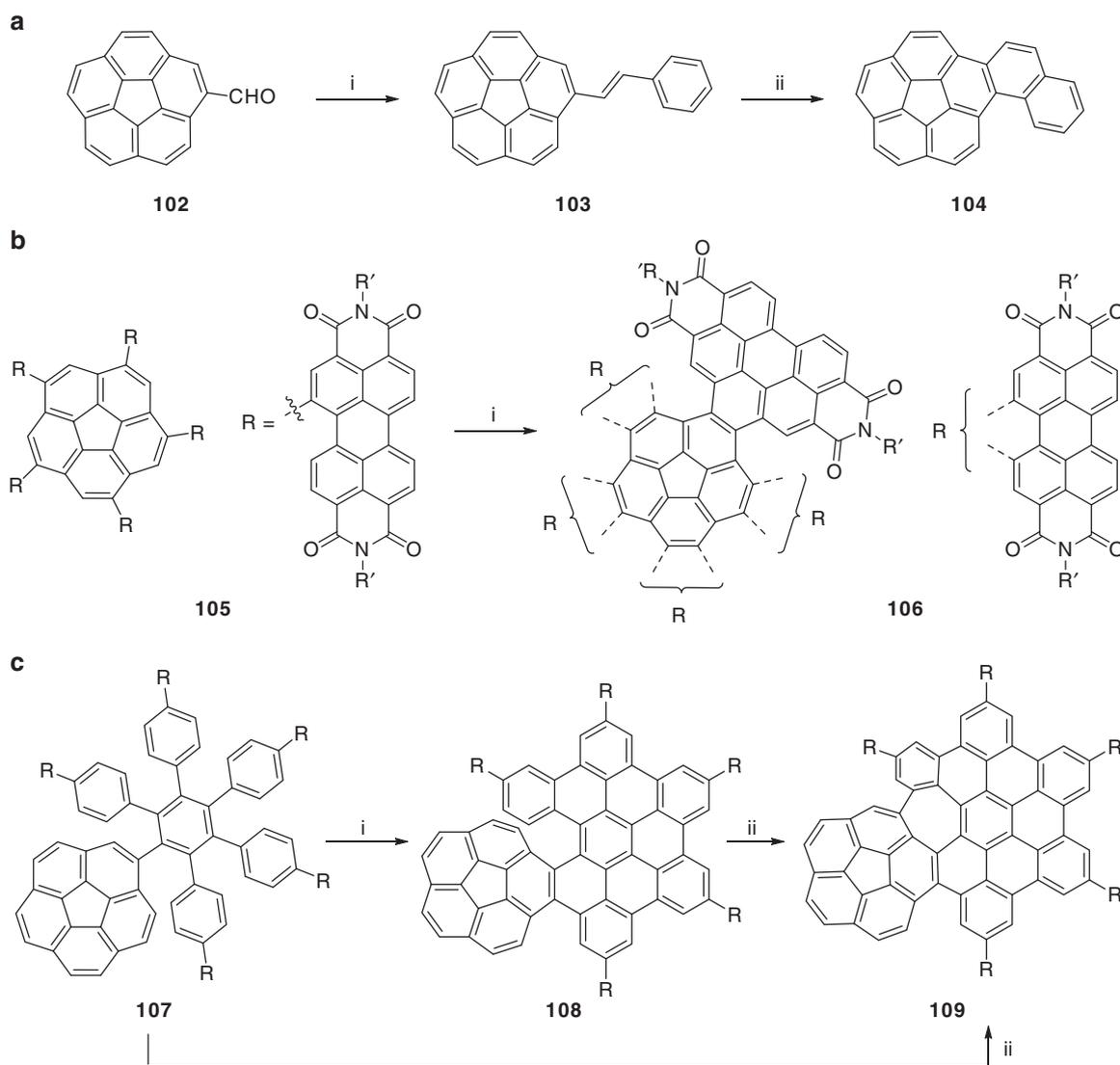


Fig. 9 Light-induced and Scholl-based cyclisations for extension of corannulene. **a** Photochemical synthesis via stilbenes. (i) $\text{RCH}_2\text{PPh}_3^+\text{Br}^-$, $n\text{-BuLi}$, THF. (ii) $h\nu$, propylene oxide, I_2 , toluene (typically quantitative yields). **b** Corannurylene pentapetalae synthesis. (i) Iodine, LED (40 W), toluene, 62% ($\text{R}' = \text{C}_{11}\text{H}_{23}$). **c** Corannulene-coronene hybrid synthesis. (i) FeCl_3 , MeNO_2 , -50°C , 15 min 69%. (ii) DDQ, TfOH, 0°C , 15 min, 48% (from **107**), 100% (from **108**) ($\text{R} = t\text{-Bu}$)

synthetic challenge to those interested in the intrinsic beauty of the chemical structures and motivated to develop rational synthetic pathways. To others, new material properties arising from the non-planarity may be of significant attraction. It is interesting to note that to some five-membered rings represents defects in graphene and offers a completely different perspective to the importance of such curved structures. As such, the approach discussed here is not the only one to induce non-planarity into graphene-like structures. Larger seven or eight-membered rings can also achieve this goal⁶. Moreover, multiple five-membered rings as a core as shown by the elegant work of Chow and Kuck⁶⁸ can be used to render the structure non-planar. However, continued improvement in access to large quantities of corannulene as well as its functionalized derivatives that serve as precursors to the extended structures makes this approach particularly appealing towards the synthesis of curved nanocarbons. Nonetheless, multistep nature of most of the current synthetic protocols with associated time-consuming chromatographic purifications and low-to-moderate overall yields all seem to restrict the appeal of this chemistry to experts. Therefore, one-pot procedures involving cascade or multicomponent reactions need to be considered and developed in the present context. Such efforts can be combined with the concept of mechanochemistry^{69,70}. The motivation for exploring the applicability of such unconventional processes and their combination is not only to enhance practicality of non-planar nanocarbon synthesis but also to improve sustainability metrics of such endeavours.

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Author contributions

E.M.M., D.H. and M.C.S. discussed pertinent literature examples, composed the text, and reviewed the manuscript. E.M.M. and D.H. contributed equally to this manuscript.

Additional information

Competing interests: The authors declare no competing interests.

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