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Solution-phase synthesis of bowl- and basket-shaped fullerene fragments via benzannulated enyne–allenes*

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Abstract: Benzannulated enyne–allenes bearing an aryl substituent at both the alkynyl and allenyl termini are excellent precursors of 5-aryl-11*H*-benzo[*b*]fluorenyl derivatives having the carbon frameworks of fullerene fragments. The mildness of the reaction conditions and the availability of several synthetic methods for benzannulated enyne–allenes allow the design of new synthetic pathways leading to bowl- and basket-shaped fullerene fragments. Specifically, a bowl-shaped $C_{28}H_{18}$ hydrocarbon bearing a 27-carbon framework of C_{60} and a basket-shaped $C_{56}H_{40}$ hydrocarbon bearing a 54-carbon framework of C_{60} were synthesized. The interior 30-carbon core of the $C_{56}H_{40}$ hydrocarbon can be regarded as a partially hydrogenated [5,5]circulene, a $C_{30}H_{12}$ semibuckminsterfullerene. In addition, a basket-shaped $C_{56}H_{38}$ hydrocarbon was also constructed to serve as a precursor toward an end-cap template for (6,6) carbon nanotubes.

Keywords: allenes; buckybaskets; buckybowls; fullerene fragments; organic synthesis; polycyclic aromatics.

INTRODUCTION

Development of new synthetic pathways for bowl- and basket-shaped fullerene fragments (buckybowls and buckybaskets) is an area of intense current interest [1]. This is due in part to the possibility of using these nonplanar polycyclic aromatic hydrocarbons as building blocks for the construction of fullerenes [2]. These curved hydrocarbons could also serve as precursors of carbon nanotube end-caps [3]. The use of these end-caps as "seeds" for growing carbon nanotubes is an attractive strategy for producing carbon nanotubes of uniform diameter and chirality. The exposed concave surfaces of the fullerene fragments are more accessible, allowing the investigation of their chemical reactivities that could mimic the endohedral chemistry of fullerenes. Reports of complexation with transition metals on both the concave and convex surfaces have appeared in the literature [1a,4]. In addition, these nonplanar polycyclic aromatic hydrocarbons provide a platform for the study of the effect of pyramidalization of sp^2-hybridized carbons on aromaticity [5]. The effect of the structural architecture on the bowl-to-bowl inversion rate is being actively investigated [6].

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FULLERENE FRAGMENTS

Corannulene (**1**), a $C_{20}H_{10}$ buckybowl, is the smallest fullerene fragment bearing a significant curvature (Fig. 1). It was first synthesized in a 17-step sequence by Barth and Lawton in 1966 [7]. A variety of other synthetic pathways involving flash vacuum pyrolysis (FVP) or solution-phase synthesis are now available, allowing the large-scale production of corannulene [1]. Diindeno[1,2,3,4-*defg*;1',2',3',4'-*mnop*]chrysene (**2**), a $C_{26}H_{12}$ buckybowl, was first synthesized by FVP [8] and more recently by the palladium-catalyzed intramolecular arylation reactions [6m]. Attaching an ethenyl piece to the top and to the bottom sides of the structure shown for **2** will lead to [5,5]circulene (**3**), a $C_{30}H_{12}$ semibuckminsterfullerene [9]. Alternatively, connecting an ethenyl piece to the left- and right-hand sides of **2** will produce an isomeric difluorenonaphthacene **4** [9c]. The carbon framework of **3** can be mapped onto the surface of C_{60}, whereas that of **4** does not map onto the ring system of any known fullerenes smaller than C_{78}. Both **3** and **4** have been prepared by FVP and/or by solution-phase synthesis. Tetraindeno[5,5]circulene **5**, a $C_{54}H_{16}$ buckybasket bearing 90 % of the carbon framework of C_{60}, is hitherto unknown. The isomeric tetraindenodifluorenonaphthacene **6** also has not yet been synthesized.

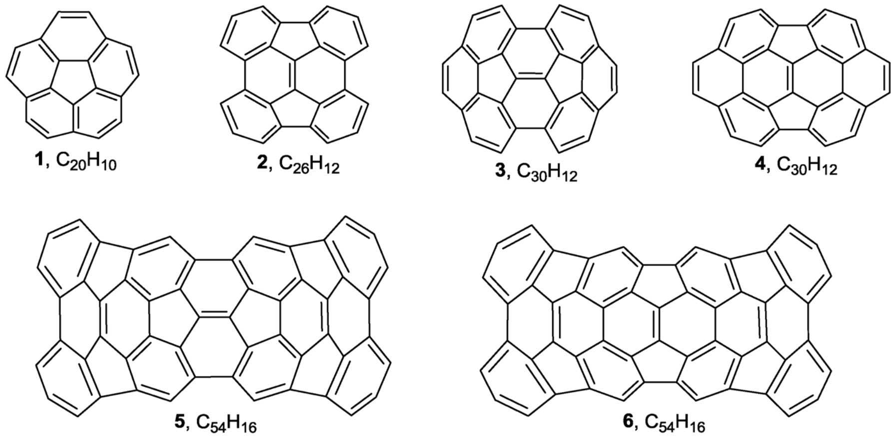


Fig. 1 Bowl- and basket-shaped fullerene fragments.

We have developed synthetic pathways leading toward curved polycyclic aromatic hydrocarbons, including the bowl-shaped $C_{28}H_{18}$ **7** [10] and the basket-shaped $C_{56}H_{40}$ **8** [11] and $C_{56}H_{38}$ **9** [3f] (Fig. 2). It is worth noting that compared to **2**, buckybowl **7** can be regarded as a partially hydrogenated diindenochrysene derivative with an additional CH_2 bridge. Buckybasket **8** has a structural motif resembling that of **5** but requires the formation of five additional C–C bonds to connect the peripheral carbon atoms. On the other hand, buckybasket **9** could serve as a precursor for **6**, needing the connectivity of four additional C–C bonds.

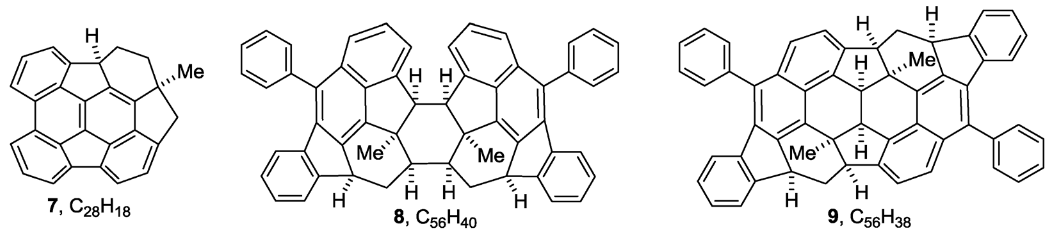
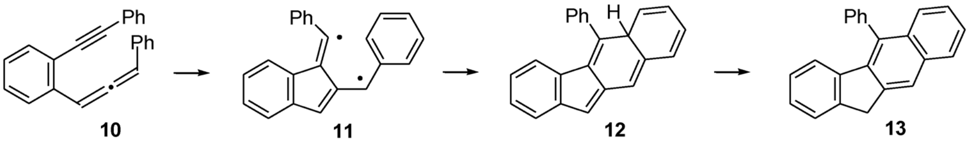


Fig. 2 Fullerene fragments prepared from benzannulated enyne–allenes.

THE SCHMITTEL CYCLIZATION REACTION

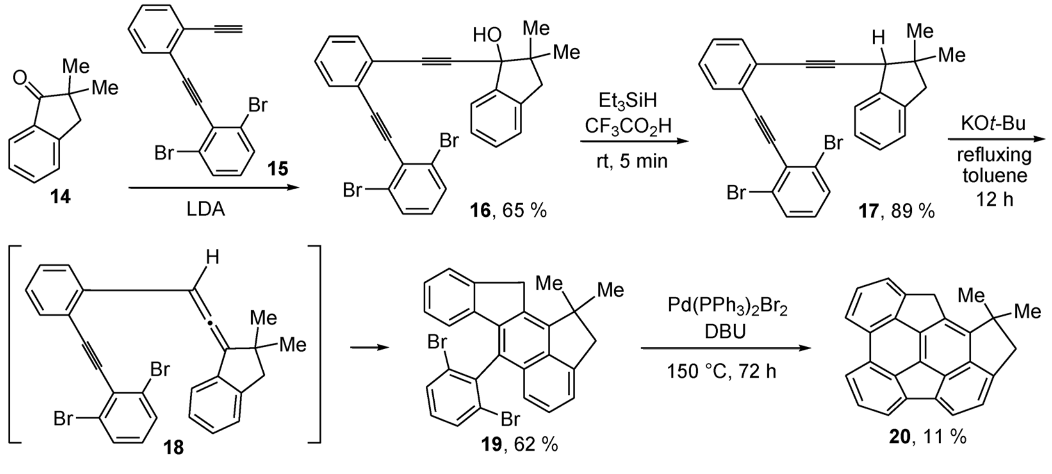
One of the key reactions of our synthetic schemes is the Schmittel cyclization reaction [12]. It involves the transformation of a benzannulated enyne–allene bearing an aryl substituent at the alkynyl and at the allenyl termini, such as **10**, to a 5-aryl-11*H*-benzo[*b*]fluorenyl derivative, as depicted in **13**, under mild thermal conditions (Scheme 1). The reaction can be regarded as a stepwise Diels–Alder reaction. The initial formation of biradical **11** followed by an intramolecular radical–radical coupling through a C–C double bond of the aryl substituent at the allenyl terminus produces the Diels–Alder adduct **12**. A subsequent prototropic rearrangement to regain aromaticity then furnishes a 5-aryl-11*H*-benzo[*b*]fluorenyl derivative as shown in **13**. It is worth noting that 5-phenyl-11*H*-benzo[*b*]fluorene (**13**) represents a small planar fragment of the C_{60} and other fullerene surfaces.



Scheme 1

SYNTHESIS OF THE $C_{28}H_{18}$ BUCKYBOWL 7 AND STEPS TOWARD THE $C_{27}H_{12}$ MONOMETHANO-BRIDGED DIINDENOCHRYSENE 33

A successful synthetic sequence leading to indenochrysene **20** bearing a significant curvature was developed as outlined in Scheme 2 [13]. The benzannulated enediyne **17**, serving as a precursor for the benzannulated enyne–allene **18**, was prepared in two steps from 2,2-dimethyl-1-indanone (**14**). Condensation between **14** and the benzannulated enediyne **15** bearing two bromo substituents furnished the benzannulated enediynyl alcohol **16**. Reduction of **16** with triethylsilane in the presence of trifluoroacetic acid produced **17** in excellent yield. Treatment of **17** with potassium *tert*-butoxide in refluxing toluene then promoted a 1,3-prototropic rearrangement to form, in situ, the benzannulated enyne–allene **18**. The subsequent Schmittel cyclization reaction then produced benzofluorene **19**. The presence of the two bromo substituents in **19** provided the opportunity for the Pd-catalyzed intramolecular arylation reactions. Using the protocol reported by Scott et al. [14], indenochrysene **20** was obtained in 11 % yield.



Scheme 2

The X-ray structure of **20** indicates the presence of a significant curvature. The pyramidalization angle, defined as $\Theta_{\sigma\pi} - 90$ using the π-orbital axis vector analysis (POAV) [15], of one of the central ethylene carbon atoms of **20** was found to be 10.3º (Fig. 3), which is larger than those of **2** at 9.0º [8b] and corresponds to 88 % of the POAV angle of C_{60} at 11.64º. In addition, one of the four carbon atoms attached to the central double bond of **20** has a POAV angle of 9.2º, which is also larger than those of the corresponding carbon atoms of **2**. Apparently, the presence of an extra five-membered ring in **20** causes the additional strain of its structure and is responsible for the low efficiency of the transformation from **19** to **20**. The dynamic NMR studies of **20** suggest a relatively fast bowl-to-bowl inversion on the NMR time scale even at −40 °C, reminiscent of what was observed for **2** [6m].

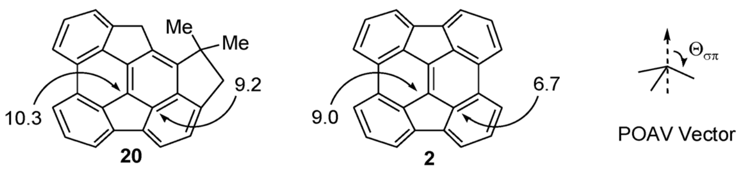
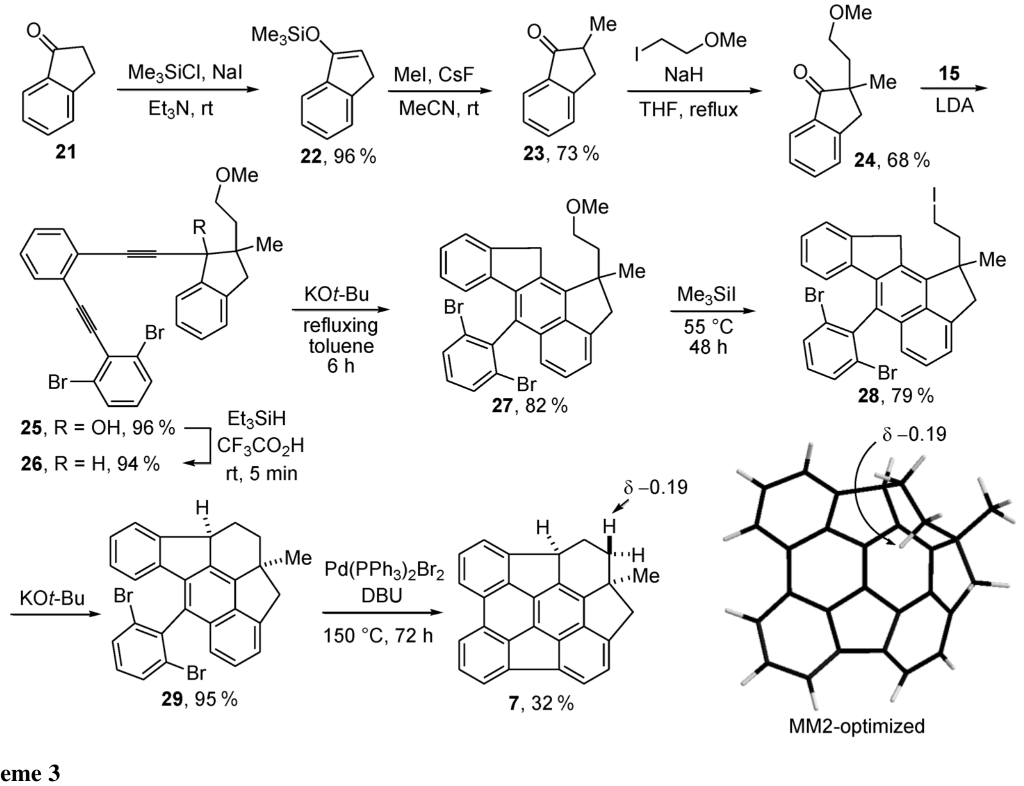


Fig. 3 POAV pyramidalization angles ($\Theta_{\sigma\pi} - 90$) of **2** and **20**.

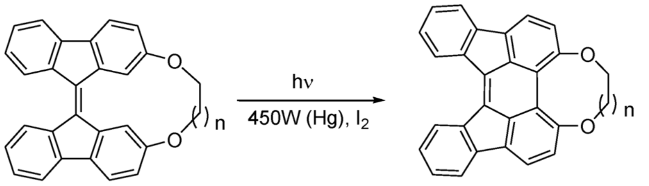
Compared to **2**, the structure of **20** has one less ring on the upper right-hand corner. The 1-indanone derivative **24** having a 2-(2-methoxyethyl) substituent was prepared to allow the formation of this ring (Scheme 3) [10]. A synthetic sequence similar to the one described for **20** was employed to reach benzofluorene **27**. Treatment of **27** with trimethylsilyl iodide furnished iodide **28**. An efficient intramolecular alkylation reaction promoted by potassium *tert*-butoxide then gave dibromide **29**. The



Scheme 3

subsequent Pd-catalyzed intramolecular arylation reactions, again using the Scott's protocol, produced the $C_{28}H_{18}$ buckybowl **7** in 32 % yield.

The first indication of the successful formation of **7** came from the appearance of a significantly upfield-shifted ^{1}H NMR signal as a doublet of a triple at δ –0.19. This signal could be attributed to one of the hydrogens on the sp^3-hybridized carbons pointing toward the endohedral (concave) side of **7** depicted in the MM-2 optimized structure. It is located in the magnetically shielded region of the aromatic system. It is also worth noting that the transformation from **29** to **7** is more efficient than the transformation from **19** to **20**. This is perhaps due to the presence of an extra tether in **29**, forcing the carbons to be connected to move closer to each other so that the C–C bond formation can readily occur. The effect of a tight tether in enhancing the efficiency of the reaction was demonstrated in the oxidative photocyclization of tethered bifluorenylidene derivative **30** to give the mono-cyclized product **31** (Scheme 4) [16].



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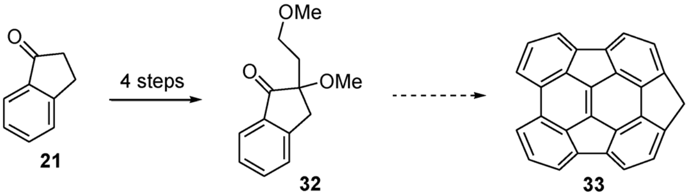
31: n = 1, 50%; n = 2, 6%; n = 3, 0%

Scheme 4

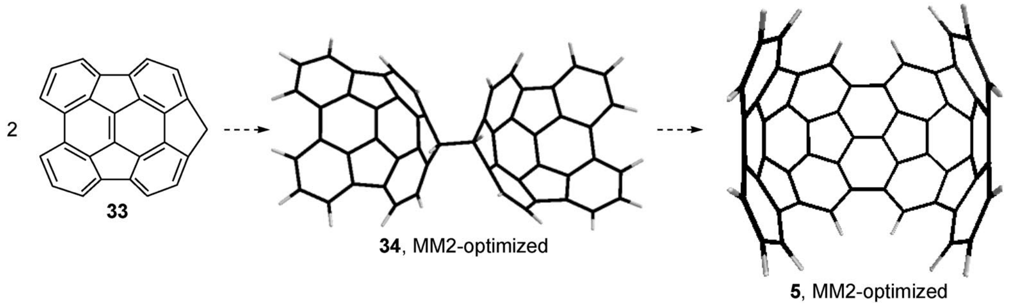
The presence of the methyl substituent in **7** prevented the formation of the full aromatized, monomethano-bridged diindenochrysene **33** by treatment of **7** with dichlorodicyanobenzoquinone (DDQ). As a possible alternative route leading to **33**, a synthetic pathway has been developed to produce 1-indanone **32** bearing a more easily removable 2-methoxy substituent as a potential precursor for **33** (Scheme 5) [17]. A synthetic pathway similar to the one outlined in Scheme 3 is being actively pursued to reach **33**.



21 **32** **33**

Scheme 5

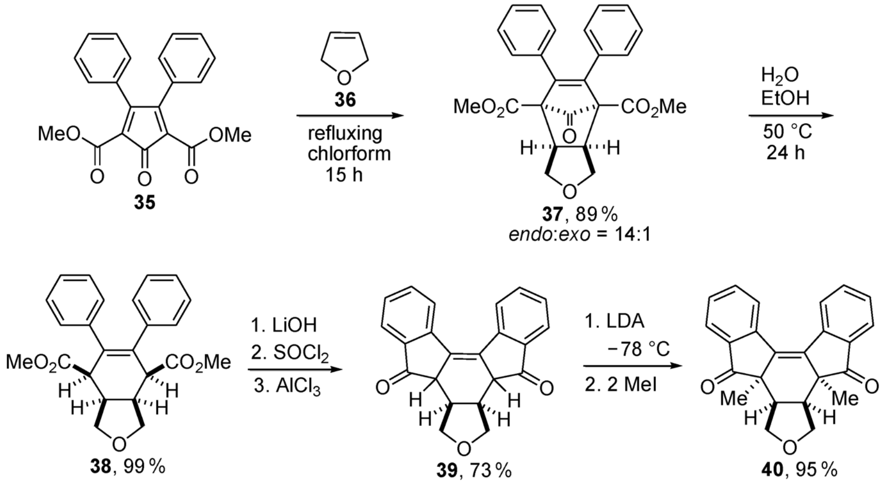
We envision the possibility of using **33** as a building block for the construction of larger fullerene fragments. Dimerization of **33** could lead to **34** and/or its isomers (Scheme 6). By using 4-chloro-1-indanone or 4-methoxy-1-indanone to start the synthetic sequence, functional groups could be attached to **34** at the desired positions for the formation of two additional C–C bonds leading to **5**.



Scheme 6

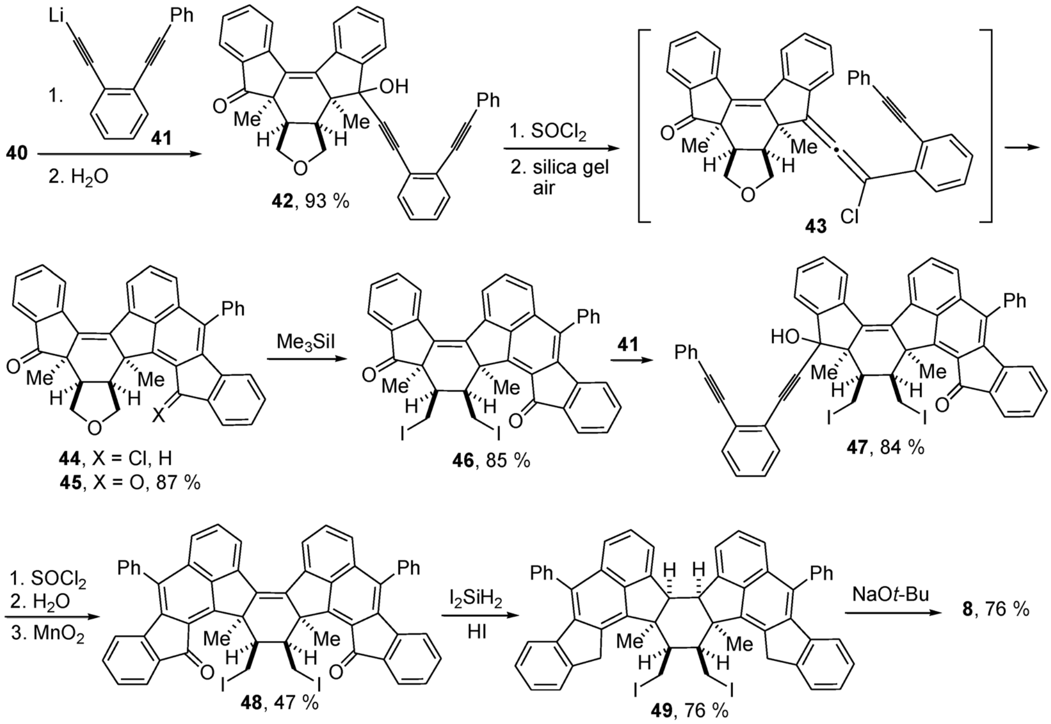
SYNTHESIS OF THE $C_{56}H_{40}$ BUCKYBASKET 8

The synthetic sequence for buckybasket **8** began with the Diels–Alder reaction between cyclopentadienone **35** and 2,5-dihydrofuran (**36**) to form **37** leading to diketone **40** as a key synthetic intermediate (Scheme 7) [11]. Decarbonylation of **37** to form **38** followed by saponification, diacid chloride formation, and two intramolecular Friedel–Crafts reactions then furnished diketone **39**. Dimethylation from the less hindered side opposite to the tetrahydrofuran ring produced diketone **40** in six steps from **35**. It is worth noting that diketone **40** contains two units of 1-indanone substructure, and the methyl groups and hydrogen atoms on the central cyclohexenyl ring are *cis* to one another.



Scheme 7

Condensation between **40** and 1 equiv of lithium acetylide **41** produced propargylic alcohol **42** (Scheme 8). Treatment of **42** with thionyl chloride produced, in situ, the benzannulated enyne–allene **43** bearing a chloro substituent. The subsequent Schmittel cyclization reaction furnished the chlorinated benzofluorene **44**, which was oxidized by air oxidation to furnish diketone **45**. Cleavage of the tetrahydrofuran ring in **45** with trimethylsilyl iodide then produced diiodide **46**. Condensation of **46** with 1 equiv of lithium acetylide **41** was selective in attacking the less hindered keto group to give propargylic alcohol **47**, which on exposure to thionyl chloride followed by oxidation with manganese dioxide furnished diketone **48**. The structure of **48** was established by X-ray structure analysis. Interestingly, treatment of **48** with diiodosilane [18] in the presence of hydrogen iodide reduced the two keto groups



Scheme 8

with concomitant reduction of the central C–C double bond to give **49**. It is worth noting that the newly formed C–H bonds on the central cyclohexyl ring in **49** are *cis* to the methyl groups as indicated by the measurements of the nuclear Overhauser effect (NOE). The presence of multiple sp^3-hybridized carbons in **49** with the hydrogen atoms and the methyl groups of the central cyclohexyl ring all *cis* to one another makes it possible to place the carbons bearing an iodo substituent in close proximity to the neighboring methylene carbons of the benzofluorenyl substructures. As a result, the intramolecular alkylation reactions, promoted by treatment with potassium *tert*-butoxide, were successful in producing the $C_{56}H_{40}$ buckybasket **8** bearing the 54-carbon framework of **5**.

The ^{1}H NMR spectrum of **8** indicates that it is unsymmetrical and adopts a basket-shaped skewed conformation, which places several of its hydrogens in the magnetically shielded region of the aromatic system (Fig. 4). The ^{1}H NMR signal of an aromatic hydrogen appears significantly upfield at δ 3.98 and the signals of the *endo* and *exo* hydrogens of a methylene group also appear significantly upfield at δ –3.32 and 0.29, respectively.

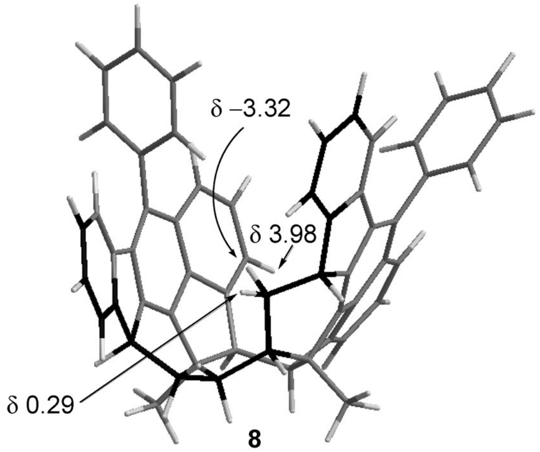
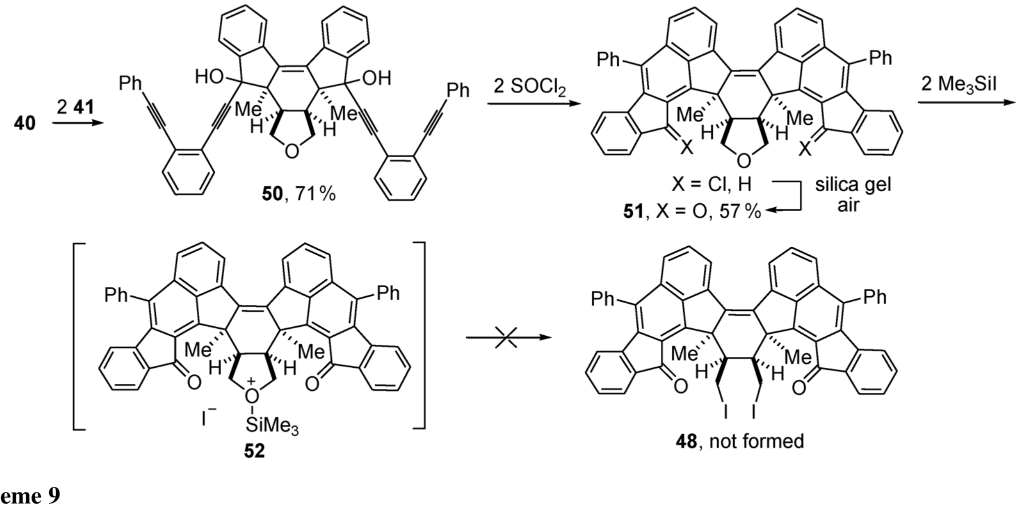


Fig. 4 MM-2 optimized structure of buckybasket **8**.

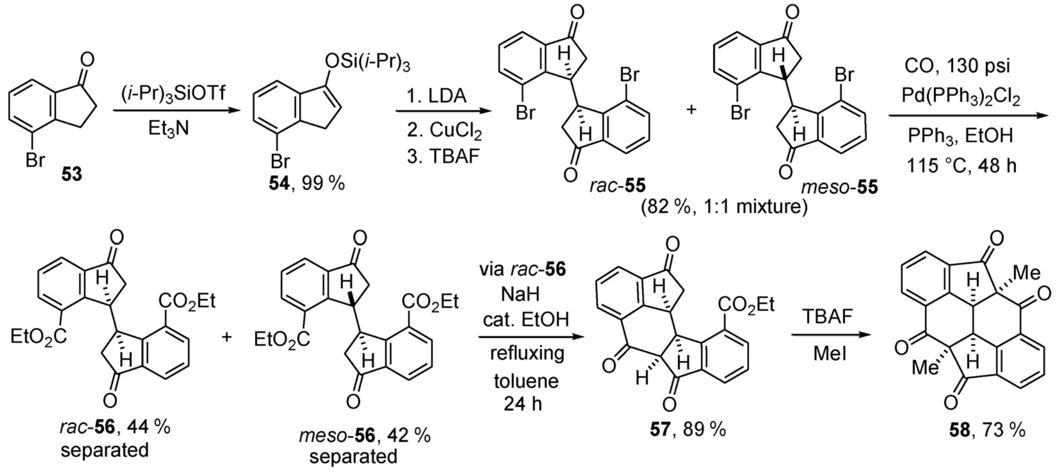
The presence of two 1-indanone substructures in **40** also allows condensation with 2 equiv of lithium acetylide **41** in a mixed solvent system of diethyl ether and benzene to produce propargylic diol **50** (Scheme 9) [19]. Treatment of **50** with thionyl chloride followed by air oxidation furnished diketone **51**. The structure of **51** was established by X-ray structure analysis. However, unlike **45**, repeated attempts to try to cleave the tetrahydrofuran ring in **51** with trimethylsilyl iodide were unsuccessful. The root cause of the failure became apparent after examination of the X-ray structure of **51**. The X-ray structure shows that the tetrahydrofuran ring in **51** is folded inside the two benzofluorenyl moieties, blocking the backsides of the *α* carbons of the silyloxonium ion **52** from an S_N2 attack by an iodide ion.



Scheme 9

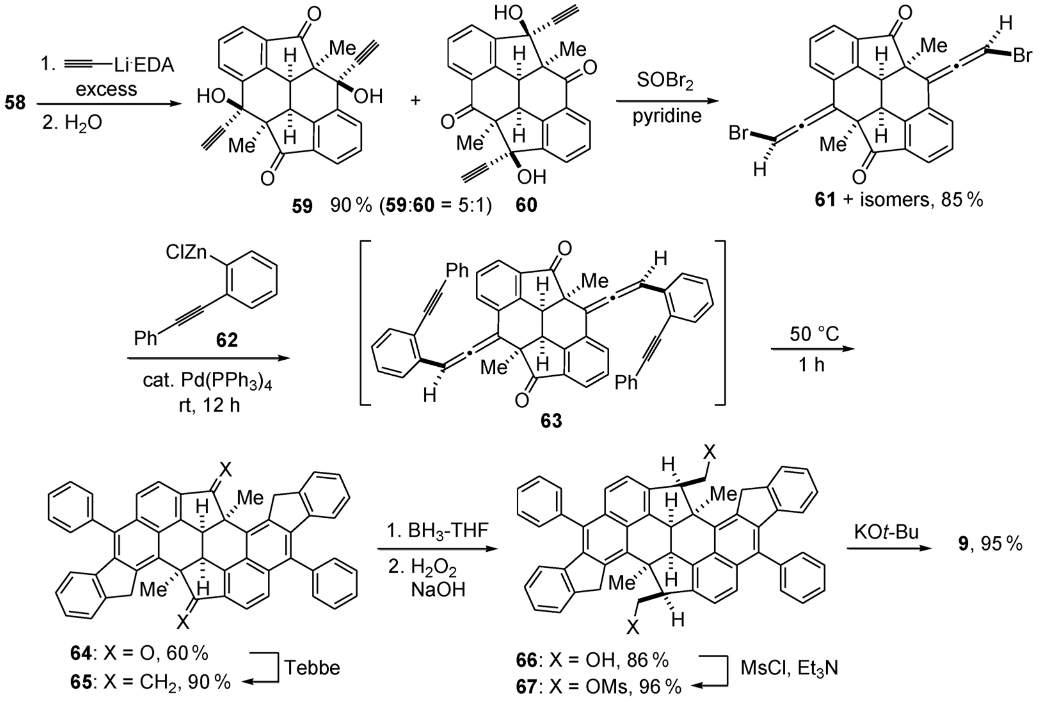
SYNTHESIS OF THE $C_{56}H_{38}$ BUCKYBASKET 9

Tetraketone **58** was prepared to serve as a key intermediate leading to buckybaskets **9** [3f]. Starting from 4-bromo-1-indanone (**53**), the synthetic scheme involved a five-step sequence (Scheme 10). As in the case of diketone **40**, tetraketone **58** also contains two units of 1-indanone or α-tetralone substructure, and the methyl groups and hydrogen atoms on the sp^3-hybridized carbons are *cis* to one another.



Scheme 10

Treatment of **58** with an excess of lithium acetylide-ethylenediamine complex furnished propargylic diol **59** as the major product (**59**:**60** = 5:1) (Scheme 11). The X-ray structure of **59** indicated that the attacks occurred from the sterically less hindered convex side. On exposure of the mixture of **59** and **60** to thionyl bromide, allenic dibromide **61** was produced as the major isomer and its isomers as minor products. The X-ray structure of **61** showed that the two bromo substituents pointed toward the concave side of the molecule. The benzannulated enyne–allene **63** was produced in situ by the Pd-catalyzed Negishi coupling reactions between **61** and 2 equiv of arylzinc chloride **62**. Rearrangement to benzofluorenyl diketone **64** was complete after 12 h at room temperature followed by heating at 50 °C for 1 h. The remaining tasks involved methylenations with the Tebbe reagent to form **65** having two exocyclic C–C double bonds followed by the hydroboration-oxidation sequence to furnish diol **66**. The hydroboration reactions occurred from the sterically less hindered convex side. As a result, the two hydroxymethyl groups in **66** were oriented toward the concave side, placing them in close proximity to the neighboring methylene carbons of the benzofluorenyl substructures. Transformation to the corresponding methanesulfonate **67** followed by potassium *tert*-butoxide-promoted intramolecular alkylation reactions then successfully concluded the 12-step synthetic sequence from 4-bromo-1-indanone (**53**) to the $C_{56}H_{38}$ buckybasket **9** having the same 54-carbon framework of **6**.



Scheme 11

The presence of multiple sp^3-hybridized carbons with the methine hydrogens and the methyl groups all *cis* to one another is primarily responsible for a basket-like shape of **9** as depicted in the MM-2 optimized structure (Fig. 5). These sp^3-hybridized carbons also greatly relieve the strain energy that exists in **6** having the fully aromatized 30-carbon difluorenonaphthacenyl structure. They also place several carbons on the periphery in close proximity to one another for potential C–C bond formations.

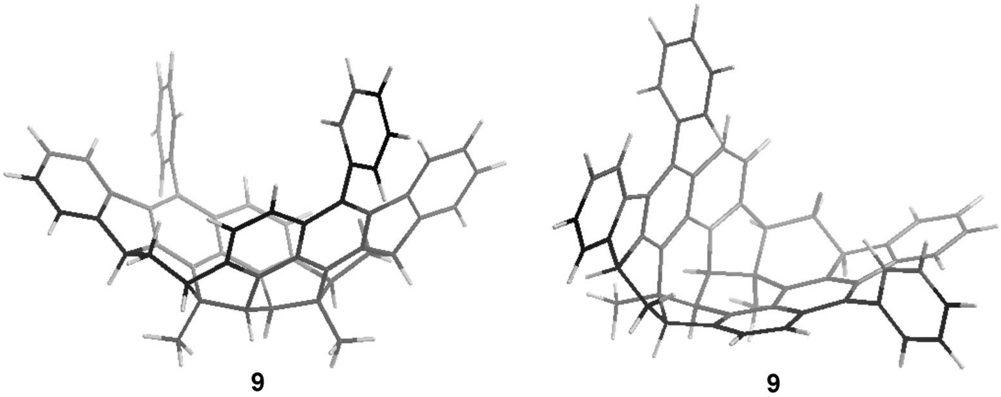

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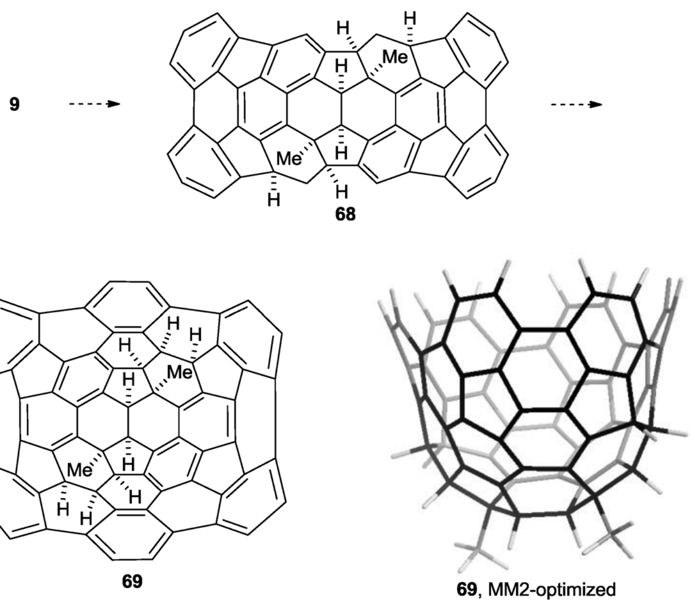
Fig. 5 MM2-optimized structure of buckybasket **9** viewed from two different perspectives.

The remaining steps in the quest to transform **9** to the $C_{66}H_{26}$ buckybasket **69** will involve forming four additional C–C bonds to produce the corresponding tetraindeno-fused derivative **68** (Scheme 12). Introducing two more phenyl substituents to the partially hydrogenated 30-carbon difluor-



Scheme 12

enonaphthacenyl core of **68** and connecting them to the four indeno groups at the periphery could then lead to **69** having a hitherto unknown [6]cycloparaphenylene unit at the rim. Hexacycloparaphenylene represents a nanohoop segment of (6,6) carbon nanotubes. The use of cycloparaphenylenes as "seeds" for growing armchair carbon nanotubes of uniform diameter is an area of intense current interest [20].

CONCLUSION AND OUTLOOK

Development of efficient synthetic routes for bowl- and basket-shaped fullerene fragments by rational design and implementation of a sequence of classical solution-phase reactions remains a challenge to synthetic organic chemists. However, such an approach offers the advantage of allowing delicate functional groups and structural features to be present along the journey to the final destination. The Schmittel cyclization reactions of benzannulated enyne–allenes have found useful applications in this regard by allowing easy assembly of various functionalized fragments for transformation to carbon frameworks that can be mapped onto the surfaces of fullerenes. The mildness of the reaction conditions and the availability of several synthetic methods for benzannulated enyne–allenes provide ample opportunities for designing and developing new synthetic pathways leading to nonplanar polycyclic aromatic compounds possessing significant curvature.

ACKNOWLEDGMENTS

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