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Synthesis of Fluoranthenes and Indenocorannulenes: Elucidation of Chiral Stereoisomers on the Basis of Static Molecular Bowls

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Abstract: Cycloaromatization of a *peri* diyne with an external alkyne provides a general route to indeno-fused polynuclear aromatics. Fluoranthenes **9** (or **13**) are easily accessible in good to excellent yields (75−99%; 18 examples) from the reaction of symmetric (or asymmetric) diynes **4** and alkynes **5** (or norbornadiene) in the presence of Wilkinson's catalyst. This formal [(2+2)+2] cycloaddition can also be applied to generate various indenocorannulenes **28** from 2,3-diethynylcorannulene derivatives **27** and alkynes **5**. The indenocorannulenes **28** exist in a static bowl form at room temperature with bowl-to-bowl inversion barriers higher than 24 kcal/mol. This barrier renders the rate of inversion slow enough at room temperature to establish a class of chiral, bowl-shaped stereoiomers containing no tetrahedrally ligated atoms. The crystal structure of **28g** provides insight into the bowl-shaped geometry of these compounds. This new synthetic method occurs under neutral conditions and tolerates various functional groups (e.g., alkyl, aryl, alcohols, and esters).

Introduction

Following Euler's rule, a planar sheet of hexagons can be converted into a curved surface by the inclusion of pentagons, twelve being a "magic" number for the creation of closed surfaces.[1] In a chemical context, methods for the synthesis of sp[2] carbon sheets with five-membered rings among networks of six-membered rings allow the synthesis of chemical Eulerean surfaces, like corannulene, fullerenes, and capped carbon tubes.[2] Although the indenyl radical could be argued to be the simplest 6/5 ring system of this ilk, the simplest curved surface is corannulene, within which fluoranthene is the simplest all-benzenoid fragment. Indenocorannulene is a higher order curved surface with two five-membered rings, and is to corannulene what fluoranthene is to naphthalene. The transition from a bowl to a capped-carbon tube occurs at $C_{50}H_{10}$, which is effectively per-indeno fused corannulene.[3] As such, methods for synthesizing fluoranthene from naphthalene or indenocorannulene from corannulene provide routes to higher-order bowls and tubes.

In addition to being excellent model targets for developing 6/5 ring systems, fluoranthenes are also important synthetic intermediates en route to corannulene and derivatives.[4] The Diels−Alder reaction of cyclopentadienone derivatives **3**, and an alkyne **5** or equivalent (e.g., norbornadiene, $R^3 = R^4 = H$ in **9**, Scheme 1) with the subsequent elimination of carbon monoxide inter alia, is a commonly used method to access fluoranthene-based corannulene precursors. Cyclopentadienone derivatives **3** or direct precursors are often generated by the Knoevenagel condensation from a diketone **1** and a ketone **2**.[5] Direct carbonylation of diynes **4** has been used in some cases where the product cyclopentadienone is stable.[6] Knoevenagel condensation is not suitable for acid- or base-sensitive functional

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(2) (a) Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1−65. (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (c) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (d) Terrones, H.; Mackay, A. L. In *The Fullerenes*; Kroto, H. W., Fischer, J. E., Cox, D. E., Eds.; Pergamon: Oxford, 1993, pp 113−122. (e) Seiders, T. J.; Siegel, J. S. *Chem. Britain* **1995**, *31*, 307−312.

(3) Baldridge, K. K.; Siegel, J. S. *Theor. Chim. Acta* **1997**, *97*, 67−71.

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(6) Catalytic carbonylation in the presence of iridium complexes and carbon monoxide, see: (a) Shibata, T.; Yamashita, K.; Katayama, E.; Takagi, K. *Tetrahedron* **2002**, *58*, 8661−8667. (b) Shibata, T.; Yamashita, K.; Ishida, H.; Takagi, K. *Org. Lett.* **2001**, *3*, 1217−1219. Carbonylation with stoichiometric amount of metal carbonyl, see: (c) Shibata, T.; Yamashita, K.; Takagi, K.; Ohta, T.; Soai, K. *Tetrahedron* **2000**, *56*, 9259−9267. (d) Knölker, H.-J.; Braier, A.; Bröcher, D. J.; Jones, P. G.; Piotrowski, H. *Tetrahedron Lett.* **1999**, *40*, 8075−8078. Reaction of 1,8-bis(phenylethynyl)naphthalene gave the corresponding complexed cyclopentadienone in a 5% yield, see ref 13.

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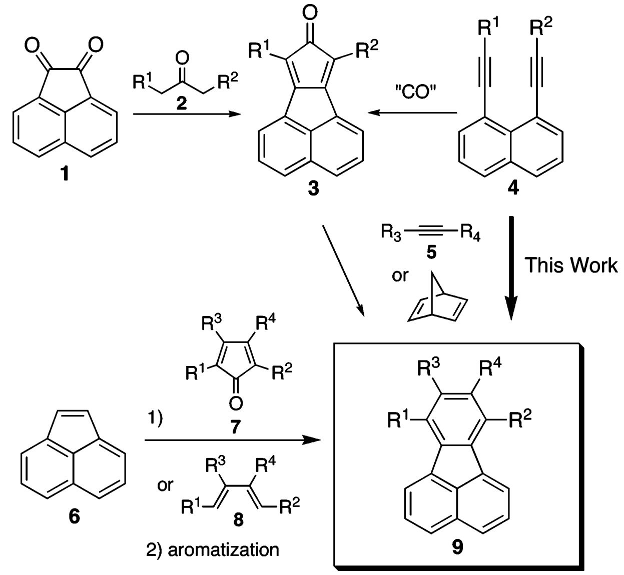
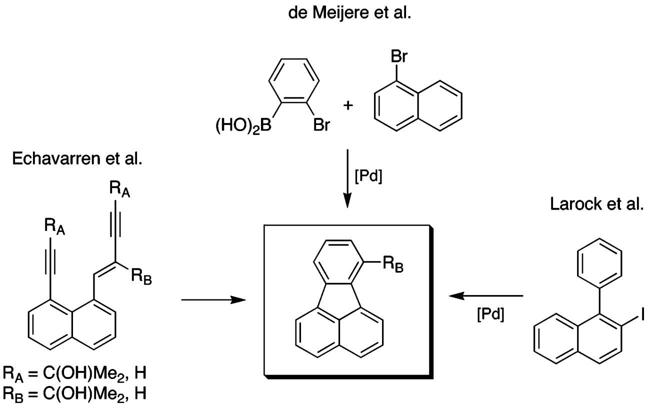
Scheme 1. Traditional Methods for the Preparation of Fluoranthenes **9**



Scheme 2. Recently Developed Methods for the Preparation of Fluoranthenes.

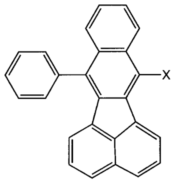


groups.[7] Other dienophiles, such as acenaphthalene **6**, react with cyclopentadienones **7**[8] or dienes **8**[9] under the formal [(2+2)+2] cycloaddition to generate di- or tetra-hydrofluoranthenes, which aromatize to fluoranthenes **9** in the presence of DDQ or potassium permanganate. In light of this mix of pluses and minuses, new routes to fluoranthene that avoid the preparation of asymmetric cyclopentadienones **7** would facilitate the synthesis of some key target compounds.[8]

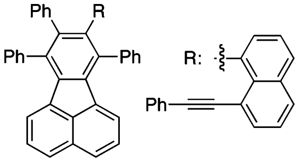
Recently, Echavarren et al. reported an intramolecular cyclization of an enyne and an alkyne moiety at the *peri* (1,8) positions of naphthalene leading to fluoranthene (Scheme 2).[10] This formal [4+2] cycloaddition is suitable only for the terminal enynes and alkynes. De Meijere et al. found fluoranthene to be accessible from 1-bromonaphthalene and 2-bromophenyl boronic acid by a one-pot Suzuki−Heck reaction with a yield of up to 97%.[11] Larock et al. discovered 1,4-palladium migration from 2-iodo-1-phenylnaphthalene to afford fluoranthene in an 81% yield.[12] Each of these methods enriches our repertoire of synthetic transformations.

The reaction of two triple bonds in 1,8-bis(phenylethynyl)-naphthalene (**4a**) under thermal or photochemical conditions[13] or in the presence of metal catalysts[14] has been well studied. Most of the research focuses on intramolecular cyclizations to form 7-phenylbenzo[*k*]fluoranthene (**10a**) and its derivative **10b**. Wilkinson's catalyst appears to reduce the amount of **10a**.

Over 40 years ago, fluoranthene derivatives were accessible by a two-step synthesis from 1,8-bis(phenylethynyl)naphthalene and alkynes with 1 equiv. of Wilkinson's catalyst;[15,16] however, such a stoichiometric method is not suitable for larger scale syntheses. Badrieh et al. reported that when **4a** was heated with a catalytic amount of $RhCl_3$-Aliquat 336, besides two cyclization adducts (**10a** and **10b**), a new cycloaddition product **11** was also obtained;[17] the 1-rhodacyclopentadiene being a likely intermediate en route to **11**.



10a (X = H)
10b (X = Cl)



11

These results indicate that formal [(2+2)+2] cycloaddition (or dimerization) of diyne **4** is competitive with intramolecular cyclization in Badrieh's protocol. If an excess of an additional alkyne were used in this reaction, then it should be reasonable to prepare fluoranthenes as major products.

Synthesis of benzene derivatives via transition-metal catalyzed alkyne trimerization is well-known,[18] but in general, fluoranthenes have not been synthesized by the catalytic [(2+2)+2] cycloaddition of diynes and alkynes. Here we report an efficient method to prepared (a)symmetric 7,8,9,10-substituted fluoranthenes from the reaction of *peri*-diynes and alkynes catalyzed

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(7) The Knoevenagel reaction of diketone **1** and ketones **2** would not directly afford cyclopentadienone **3** but the Aldol product, namely carbinols, can be transferred to **3** under acidic conditions, see: (a) Sygula, A.; Sygula, R.; Ellern, A.; Rabideau, P. W. *Org. Lett.* **2003**, *5*, 2595−2597. (b) Allen, C. F. H.; van Allan, J. A. *J. Org. Chem.* **1952**, *17*, 845−854.

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(9) (a) Fabrizio, E. F.; Payne, A.; Westlund, N. E.; Bard, A. J.; Magnus, P. P. *J Phys. Chem. A* **2002**, *106*, 1961−1968. (b) Rice, J. E.; LaVoie, E. J.; Hoffmann, D., *J. Org. Chem.* **1983**, *48*, 2360−2363.

(10) Gonzalez, J. J.; Francesch, A.; Cardenas, D. J.; Echavarren, A. M. *J. Org. Chem.* **1998**, *63*, 2854−2857.

(11) This synthetic method was also applied to prepare indenocorannulene (**IC**, Figure 3), see: Wegner, H. A.; Scott, L. T.; de Meijere, A. *J. Org. Chem.* **2003**, *68*, 883−887.

(12) Campo, M. A.; Huang, Q.; Yao, T.; Tian, Q.; Larock, R. C., *J. Am. Chem. Soc.* **2003**, *125*, 11506−11507.

(13) Bossenbroek, B.; Sanders, D. C.; Curry, H. M.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 371−379.

(14) (a) Dyker, G. *J. Org. Chem.* **1993**, *58*, 234−238. (b) Blum, J.; Baidossi, W.; Badrieh, Y.; Hoffman, R. E.; Schumann, H. *J. Org. Chem.* **1995**, *60*, 4738−4742.

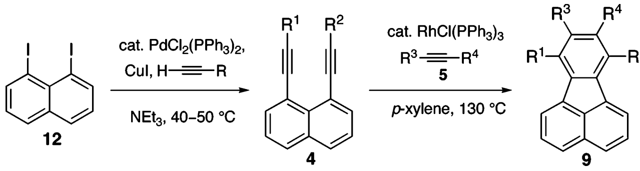
(15) Müller, von E.; Thomas, R.; Zountsas, G. *Liebigs Ann. Chem.* **1972**, *758*, 16−28.

(16) A similar procedure was used to prepare an 5-iminocyclopentadiene derivative from diyne **4a** and an isocyanide, see: Neidlein, R.; Kux, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1324−1326.

(17) Badrieh, Y.; Blum, J.; Amer, I.; Vollhardt, K. P. C., *J. Mol. Catal.* **1991**, *66*, 295−312. Although the authors mentioned **11** as the major product in the *abstract* and *discussion*, the data in the Experimental Section shows it is the minor product.

(18) Reviews: (a) Fujiwara, M.; Ojima, I. in *Modern Rhodium-Catalyzed Organic Reactions* (Ed.: Evans, P. A.), Wiley-VCH: Weinheim, **2005**, pp 129−149. (b) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901−2916. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (d) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (e) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−556. (f) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1−8.

Scheme 3. Preparation of 7,8,9,10-Tetrasubstituted Fluoranthenes **9** from Diynes **4** and Alkynes **5**



by Wilkinson's complex.[19,20] The experience acquired from the fluoranthene studies is applied to the synthesis of a series of indenocorannulenes.

Results and Discussions

A mixture of 1,8-diiodonaphthalene (**12**) and a variety of terminal alkynes (3 eq.) under Sonogashira conditions[21] (2.5 mol % of $PdCl_2(PPh_3)_2$ and 10 mol % of CuI in NEt_3 at 40−50 °C) afforded diynes **4** in good to excellent yields (Scheme 3; Table 1). Due to the higher reactivity of aryl iodides than aryl bromides, *o*-bromophenylethyne can also be used in this reaction without loss of product specificity. Diyne **4d** (R^1 = Ph, R^2 = PhF_5) was prepared via successive Sonogashira reactions. The bulky 4-*tert*-butylphenylethyne did not give a satisfactory yield (34%) under the same conditions. When this reaction was carried out at 80 °C, the chemical yield was increased to 66%.[22]

Heating diyne **4a**−**e** and 5 eq. of the alkyne **5a**−**i** in the presence of Wilkinson's catalyst (5 mol %), produces fluoranthenes **9a**−**o** in good to excellent yields (Scheme 3; Table 1).[23] Generally, terminal alkynes (or less bulky internal ones) afforded better yields than the diaryl internal acetylenes. Bis(trimethylsilyl)ethyne (**5h**) gave complicated results in *p*-xylene as described above, as well as when **5h** was used as the solvent at 150 °C (entry 8 in Table 1). The reaction conditions were tolerant of many functional groups, as is known from normal Rh-catalyzed [2+2+2] alkyne trimerization reactions.[20] In comparison with the Knoevenagel condensation, base-sensitive functional group tolerance is an obvious advantage of this procedure (e.g., pentafluorophenyl).[24]

Preparation of 7,10-disubstitued fluoranthenes **13** should be possible from the diyne **4** and acetylene gas; however, the safety problems of using acetylene gas at high temperature/pressure make norbornadiene (NBD) a preferred acetylene equivalent. Caveats to this reagent substitution are the well-known reactions of NBD with alkynes[25] in the presence of transition-metal catalysts to give (a) formal [2+2],[26] (b) homo Diels−Alder,[27] or (c) [(2+2)+2+2] cycloadducts.[28] NBD also generates various homo-coupling products in the presence of the different rhodium catalysts.[29] Despite a manifold of possibilities, diynes **4** and NBD react to form mainly 7,10-disubstituted fluoranthenes **13** and byproducts **14** (Scheme 4).[30,31] To our knowledge, heptacycles **14** are the first examples of formal [(2+2)+(2+2)] cycloaddition of alkynes and NBD.[32,33] Rare are reactions wherein four new bonds form in a one-pot transformation and in this case a three-, a five- and a seven-membered ring are constructed.

A limited survey of rhodium catalysts, such as $RhCl(PPh_3)_3$, $[RhCl(COD)]_2$, and $Rh_2(OAc)_4{\cdot}2H_2O$, displayed generally efficient catalysis and from good to excellent product yields and ratios (Table 2). Catalysts $[RhCl(COD)]_2$ or $Rh_2(OAc)_4{\cdot}2H_2O$ selectively form **13** in yields above 90%, to the exclusion **14**. Typical reaction conditions were 5 mol % catalyst in *p*-xylene, at 80−90 °C for 48−60 h. Addition of ligands, e.g., Py, PCy_3, and PPh_3 to $[RhCl(COD)]_2$ also affected the product ratio, usually disfavoring **13**. Comparison of Wilkinson's catalyst with the combination of $[RhCl(COD)]_2$ and 4 equiv. of PPh_3 gave almost the same chemoselectivity between **13** and **14**, but the former complex generated cleaner products. The substituents R^1 and R^2 in diynes **4** also play an important role in adjusting the ratio between **13** and **14**. Electron-deficient and less bulky substituents enhance the formation of **14**. Other transition-metal catalysts, such as $Ni(CO)_2(PPh_3)_2$, $PdCl_2(COD)$, $Pd(PPh_3)_4$, $PtCl_2$ and $[RuCl_2(NBD)]_n$, either did not give the expected cycloadducts **13** (or **14**) or afforded complicated mixtures.

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(19) Although the Rh complexes proved easier to handle here, the cobalt complex, $CoCp(CO)_2$, is the most widely used, see: (a) Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3227−3230. (b) Dosa, P. I.; Whitener, G. D.; Vollhardt, K. P. C.; Bond, A. D.; Teat, S. J. *Org. Lett.* **2002**, *4*, 2075−2078.

(20) Alkyne trimerization with Wilkinson's catalyst, see: (a) Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3281−3284. (b) Witulski, B.; Stengel, T.; Fernandez-Hernandez, J. M. *Chem. Commun.* **2000**, 1965−1966. (c) Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2426−2430.

(21) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *6*, 4467−4470. Reviews: (b) Sonogashira, K.; in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: Diederich, F., Stang, P. J.), Wiley-VCH: Weinheim, **1998**, pp 203−229. (c) Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of Transition Metal Catalysts in Organic Synthesis*; Springer: Berlin, 1999; pp 179−225.

(22) Preparation of 1,8-bis(trimethylsilylethynyl)naphthalene with 0.2 equiv. of $PdCl_2(PPh_3)_2$ at greater than 80 °C gave a quantitative yield, see ref 6d. However, synthesis of 1,8-bis(allyldiphenylsilylethynyl)naphthalene was reported in a 60% yield, see ref 6c.

(23) Only the reaction products from **4** are isolated and characterized. Yields are based on **4** as the limiting reagent. Trimers coming from alkynes **5** were also formed but neglected.

(24) It is known that pentafluorophenyl moiety is base sensitive, especially at the *para*-position for examples: (a) Buscemi, S.; Pace, A.; Calabrese, R.; Vivona, N.; Metrangolo, P. *Tetrahedron* **2001**, *57*, 5865−5871. (b) Allen, D. M.; Batsanov, A. S.; Brooke, G. M.; Lockett, S. J. *J. Fluorine Chem.* **2001**, *108*, 57−67. (c) Zhang, Y.; Wen, J. *Synthesis* **1990**, *8*, 727−728.

(25) Review of reactions of NBD and alkynes. (a) Lautens, M.; Tam W. *Adv. Metal-Org. Chem.* **1998**, *6*, 49−101. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92.

(26) [2+2] Cycloadducts, namely *exo*-3,4-disubstituted tricyclo[$4.2.1.0^{2,5}$]non-3-enes, for example, see: (a) Villeneuve, K.; Jordan, R. W.; Tam, W. *Synlett* **2003**, 2123-2128. (b) Jordan, R. W.; Tam, W. *Org. Lett.* **2001**, *3*, 2367−2370. (c) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580−581.

(27) Homo Diels−Alder cycloadducts, for example, see: (a) Pardigon, O.; Tenaglia, A.; Buono, G. *J. Mol. Catal. A: Chemical* **2003**, *196*, 157−164. (b) Hilt, G.; Smolko, K. I. *Synthesis* **2002**, 686−692. (c) Hilt, G.; du Mesnil, F.-X. *Tetrahedron Lett.* **2000**, *41*, 6757−6761. (d) Lautens, M.; Tam, W.; Lautens, J. C.; Edwards, L. G.; Crudden, C. M.; Smith, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 6863−6879. (e) Pardigon, O.; Tenaglia, A.; Buono, G. *J. Org. Chem.* **1995**, *60*, 1868−1871. (f) Binger, P.; Albus, S. *J. Organomet. Chem.* **1995**, *493*, C6−C8. (g) Lautens, M.; Tam, W.; Edwards, L. G. *J. Org. Chem.* **1992**, *57*, 8−9.

(28) The reaction of acetylene gas in neat NBD with a catalytic amount of $Ni(CN)_2(PPh_3)_2$ or $Ni(CO)_2(PPh_3)_2$ gave a [(2+2)+2+2] cycloadduct, namely tetracyclo[$5.4.0.0.^{2,9}0^{8,10}$]undeca-3,5-diene. The same conditions with an internal alkyne, instead of acetylene gas, afforded a [2+2] cycloadduct or homo Diels−Alder product, see: Schrauzer, G. N.; Glockner, P. *Chem. Ber.* **1964**, *97*, 2451−2462.

(29) Neat NBD used as the solvent, see: Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446−5456.

(30) It was also observed that NBD as an acetylene unit participates in the [2+2+2] cycloaddition with two alkynes to generate 1,3-disubstituted benzenes as byproducts under the catalysis of the ruthenium complexes, see ref 26c.

(31) Only the reaction products from **4** are isolated and characterized. Yields are based on **4** as the limiting reagent. Dimers coming from NBD were also formed but neglected.

(32) Primary communication: Wu, Y.-T.; Linden, A.; Siegel, J. S. *Org. Lett.* **2005**, *7*, 4353−4355.

(33) Other examples of [(2+2)+4] cycloadducts, namely tetracyclo[$5.4.0.0.^{2,9}0^{8,10}$]-undeca-3-enes, from NBD and 1,3-butadienes, see: (a) Lautens, M.; Tam, W.; Sood; C. *J. Org. Chem.* **1993**, *58*, 4513−4515. (b) Chen, Y.; Snyder, J. K. *J. Org. Chem.* **1998**, *63*, 2060−2061.

Table 1. Preparation of 7,8,9,10-Tetrasubstituted Fluoranthenes **9**[d]

entry	R^1	R^2	diyne (yield %)	alkyne	R^3	R^4	product (yield %)
1	Ph	Ph	**4a** (89)	5a	Ph	Ph	**9a** (83)
2			**4a**	5b	4-*n*Bu-Ph	4-*n*Bu-Ph	**9b** (86)
3			**4a**	5c	*n*Pr	*n*Pr	**9c** (99)
4			**4a**	5d	CMe_2OH	H	**9d** (99)
5			**4a**	5e	CO_2Me	CO_2Me	**9e** (99)
6			**4a**	5f	Ph	H	**9f** (96)
7			**4a**	5 g	4-*n*Bu-Ph	4-*t*Bu-Ph	**9 g** (85)
8			**4a**	5h	TMS	TMS	**9h** (trace)
9	4-*n*Bu-Ph	4-*n*Bu-Ph	**4b** (78)	5a	Ph	Ph	**9i** (85)
10			**4b**	5b	4-*n*Bu-Ph	4-*n*Bu-Ph	**9j** (75)
11			**4b**	5i	TMS	H	**9k** (99)
12	4-*t*Bu-Ph	4-*t*Bu-Ph	**4c** (66)[a]	5a	Ph	Ph	**9l** (83)
13			**4c**	5 g	4-*n*Bu-Ph	4-*t*Bu-Ph	**9m** (86)
14	Ph	F_5Ph	**4d** (95)[b]	5a	Ph	Ph	**9n** (77)
15	2-Br−Ph	2-Br−Ph	**4e** (91)	5c	*n*Pr	*n*Pr	**9o** (83)[c]

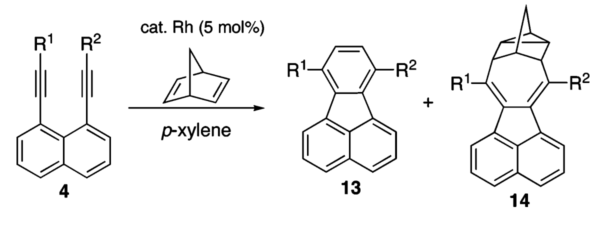
[a] The reaction was carried out at 80 °C instead of 40 °C. [b] The chemical yield was calculated from the mono Sonogashira reaction of 1-iodo-8-(phenylethynyl)naphthalene and pentafluorophenylethyne. [c] This is an average chemical yield. The reaction was carried out at 110 °C instead of 130 °C. **9o** and two cyclization adducts were isolated as an inseparable mixture (ratio range from 97:3:0 to 89:7:4 over several runs). [d] Details, see Scheme 3.

Table 2. Survey of Reaction Conditions that Form **13**/**14** from **4** and NBD

entry	R^1	R^2	catalyst [mol %]	*T* (°C)	time (h)	product (ratio)[a]	conversion (isolated yield)
1	Ph	Ph	$RhCl(PPh_3)_3$ [5%]	130	48	**13a**:**14a** (77:23)	100 (99)
2	Ph	Ph	$RhCl(PPh_3)_3$ [5%]	80	60	**13a**:**14a** (73:27)	100 (—)[b]
3	Ph	Ph	$RhCl(PPh_3)_3$ [5%]	50	60	**13a**:**14a** (77:23)	31 (—)[b]
4	Ph	Ph	$Rh_2(OAc)_4$·$2H_2O$ [2.5%]	80	48	**13a**:**14a** (100:0)	100 (96)[c]
5	Ph	Ph	$[RhCl(COD)]_2$ [2.5%]	80	48	**13a**:**14a** (100:0)	100 (96)[c]
6	Ph	Ph	$[RhCl(COD)]_2$ [2.5%][d]	70	48	**13a**:**14a** (100:0)	100 (96)[c]
7	Ph	Ph	$[RhCl(COD)]_2$ [2.5%] + MeCN	80	60	**13a**:**14a** (100:0)	100 (96)[c]
8	Ph	Ph	$[RhCl(COD)]_2$ [2.5%] + Py	80	60	**13a**:**14a** (67:33)	100 (—)[b]
9	Ph	Ph	$[RhCl(COD)]_2$ [2.5%] + PPh_3	80	60	**13a**:**14a** **(**75:25)	100 (—)[b]
10	Ph	Ph	$[RhCl(COD)]_2$ [2.5%] + PCy_3	80	24	**13a**:**14a** (100:0)	56 (—)
11	Ph	Ph	$RhH((PPh_3)_4$ [5%]	80	60	**13a**:**14a** (100:0)	58 (—)
12	4-*t*Bu-Ph	4-*t*Bu-Ph	$RhCl(PPh_3)_3$ [5%]	130	60	**13b**:**14b** (81:19)	100 (95)
13	4-*t*Bu-Ph	4-*t*Bu-Ph	$[RhCl(COD)]_2$ [2.5%]	90	60	**13b**:**14b** (100:0)	100 (92)
14	Ph	F_5Ph	$RhCl(PPh_3)_3$ [5%]	130	60	**13c**:**14c** (51:49)	100 (83)
15	2-Br−Ph	2-Br−Ph	$RhCl(PPh_3)_3$ [5%]	110	60	**13d**:**14d** (=98:2)	100 (78)[e]
16	4-E-Ph[f]	4-E-Ph	$RhCl(PPh_3)_3$ [5%]	80	45	**13e**:**14e** (63:37)	100 (95)
17	4-E-Ph	4-E-Ph	$[RhCl(COD)]_2$ [2.5%]	90	60	**13e**:**14e** (100:0)	100 (99)

[a] The ratio was determined by ^1H NMR. [b] Starting material was consumed but product was not isolated. [c] Purification of the combined crude products from entries 4−7 gave 96% yield. [d] MeCN was used, instead of *p*-xylene. [e] An intramolecular cyclization product (ca. 2%) was also observed. [f] E = CO_2Me.

Scheme 4. Preparation of 7,10-Substituted Fluoranthenes **13** from Diynes **4** and NBD



Acenaphthylene (**6**),[34] reacts with diyne **4a** to produce 6a,14a-dihydro-7,14-diphenylacenaphtho[*1*,*2*-*k*]fluoranthene (**15**) and its fully aromatized product **16**[35] in ca. 75% yield. In this reaction, a trace (ca. 4%) of the intramolecular cyclization product **10a** was also observed. The formation of **16** probably happened during the workup by the oxidation of **15** with air.

To highlight the key role of the proximal diyne in this reaction, a mixture of 1,2-diphenylethyne, NBD and Wilkinson's catalyst was heated at 130 °C and shown to produce only starting materials, according to the HPLC and GC analysis. Formation of the 1-rhodacyclopentadiene derivatives **19** appears to be determinant.[36] Assuming this intermediate, a working mechanism for the formation of **13** and **14** can be formulated by analogy with related literature processes (Scheme 6).[37] Initially, 1-rhodacyclopentadiene **19** is formed, and subsequent coordination of NBD partitions between an η^4-complex **18** or an η^2-complex **20**. Complex **18** can easily rearrange to the deltacyclane derivative **17**. Heptacycle **14** is produced from the intermediate **17** after a reductive elimination of the Rh complex. In contrast, complex **20** inserts NBD from its ligand sphere to afford σ-complex **22**. A reductive elimination of the Rh catalyst gives a transient dihydrofluoranthene **21** that thermally eliminates cyclopentadiene to produce fluoranthene **13**.

Scott and co-workers reported that dibenzo[*a*,*g*]corannulene

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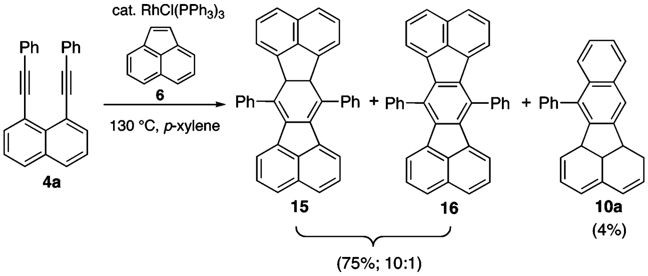
(34) Commercially available acenaphthylene (with 75% purity and 20% of acenaphthene) was purchased from Aldrich.

(35) It is known that $KMnO_4$ can oxidize **15** to 7, 14-diphenylacenaphtho[*1*,*2*-*k*]fluoranthene (**16**) directly after the Diels−Alder reaction, see ref 8b.

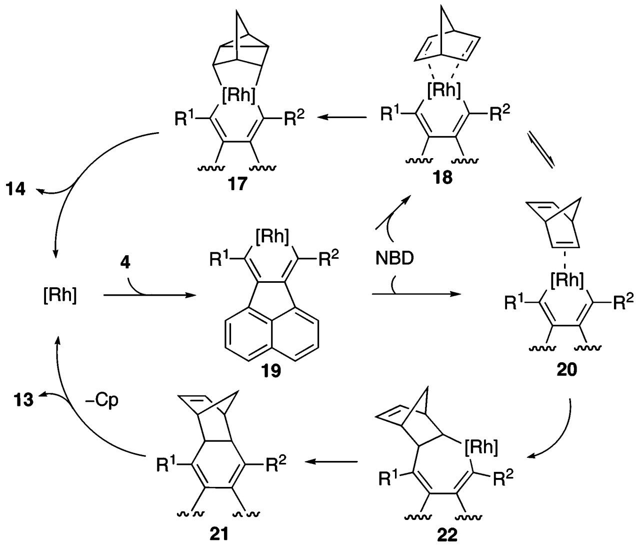
(36) The crystal structure of a similar cobalt complex see: (a) Diercks, R.; Eaton, B. E.; Guertzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248. (b) Rh complex: Adams, R. D.; Qu, B. *J. Clust. Sci.* **2000**, *11*, 55−65.

(37) The detailed mechanism of formation of a [2+2] cycloadduct or a homo Diels−Alder product remains open, see ref 25a, p 94.

Scheme 5. Synthesis of 6a,14a-Dihydro-7,14-diphenylacenaphtho[*1,2-k*]fluoranthene (**15**)

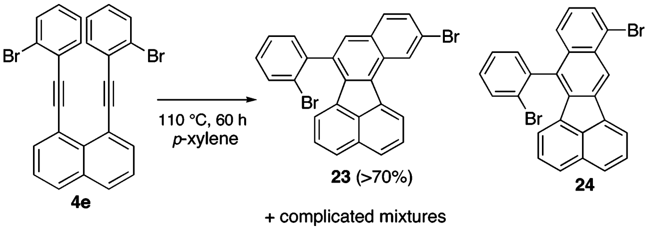


Scheme 6. Proposed Mechanism of the Reaction of Diynes **4** and NBD



[Rh] = LRhCl (L = PPh$_3$, η^2-NBD)

Scheme 7. Unusual Intramolecular Cyclization Adduct **23** from Diyne **4e**



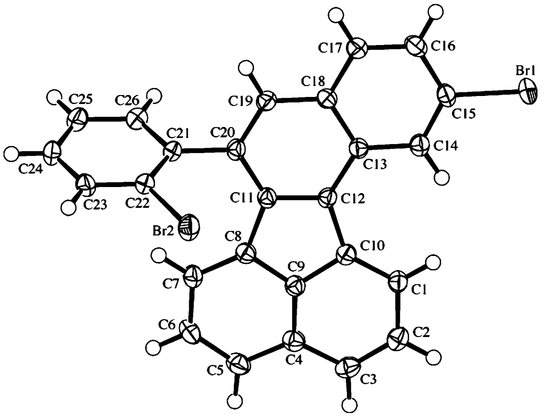


Figure 1. Molecular structure of **23** in the crystal.[41]

is accessible by a 7,10-bis(2-bromophenyl)fluoranthene (**13d**) using a Heck-type intramolecular arylation.[38] The same strategy was applied by Rabideau et al. to synthesize 1,2-dihydrocyclopenta[*b*,*c*]dibenzo[*g*,*m*]corannulene.[39] These leading works inspired us to prepare 7,10-bis(2-bromophenyl) substituted fluoranthenes using our formal [(2+2)+2] protocol. Products of this type can be regarded as potential precursors of 1,2-disubstituted dibenzo[*d*,*m*]corannulene. Fluoranthene derivatives **9o** or **13d** are generated from 1,8-bis(2-bromophenylethynyl)naphthalene **4e** and 4-octyne or NBD, respectively; however, a lower reaction temperature (110 °C instead of 130 °C) was necessary in order to reduce the amount of the byproduct(s).[40] To probe the structure of this side product further, diyne **4e** alone was heated at 110 °C for 60 h and afforded a complicated mixture, which after washing with hexane, yielded a clean yellow solid **23**. X-ray crystal analysis revealed an unusual structure for **23** (Scheme 7 and Figure 1), instead of the expected structure of **24**. Notably, compound **23** was observed as a minor byproduct in the [(2+2)+2] cycloaddition reaction.

This successful method for the synthesis of fluoranthene derivatives was applied to the preparation of indenocorannulenes from 2,3-diethynylcoranulene **27**. The key starting materials for the [(2+2)+2] cycloadditions are accessible from the corresponding 2,3-dichlorocorannulene derivatives **25**. To circumvent the well-known problems of cross coupling reactions involving aryl chlorides and alkynes,[42] we implemented a modification of Nolan's protocol[43,44] to prepare the 2,3-diethynylcorannulenes **27**. From **25** and trimethyltin-substituted alkynes **26**, several derivatives could be synthesized (Scheme 8).[45] In some cases, diynes **27** were isolated with small impurities; however, the level of purity did not inhibit carrying the material on to the next step.[46]

Indenocorannulenes **28** are accessible from the reaction of diynes **27** and alkynes **5** (Table 3). Comparing the yields for indenocorannulenes **28** with analogous fluoranthenes **9**, the latter are always superior; however, the reaction conditions were not optimized to increase the yield of the more highly strained indenocorannulene products. It has been observed that the substituents R^7 in diynes **27** and R^3 and R^4 in alkynes **5** play important roles in this formal [(2+2)+2] cycloaddition. Initial studies suggest that alkyl functional groups at the R^7 position give lower chemical yields than aryl moieties.

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(38) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430.

(39) Marcinow, Z.; Sygula, A.; Ellern, A.; Rabideau, P. W. *Org. Lett.* **2001**, *3*, 3527−3529.

(40) In contrast to other diynes, **4e** easily undergoes the intramolecular cyclization.

(41) Compound **23**: $C_{26}H_{14}Br_2$, triclinic crystals of space group $P\bar{1}$, unit cell dimensions: $a = 7.9066(2)$, $b = 9.3760(2)$, $c = 13.4358(3)$ Å, $\alpha = 105.214(2)$, $\beta = 98.189(2)$, $\gamma = 101.572(2)$ °, $V = 921.32(4)$ Å^3.

(42) Sonogashira type, see: (a) Méry, D.; Heuzé, K.; Astruc, D. *Chem. Commun.* **2003**, 1934−1935. (b) Remmele, H.; Köllhofer, A.; Plenio, H. *Organometallics* **2003**, *22*, 4098−4103. (c) Köllhofer, A.; Pullmann, T.; Plenio, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1056−1058. (d) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127−14136. (e) Eberhard, M. R.; Wang, Z.; Jensen, C. M. *Chem. Commun.* **2002**, 818−819. Suzuki type: (f) Fürstner, A.; Leitner, A. *Synlett* **2001**, 290−292. (g) Stille type: Shirakawa, E.; Yamasaki, K.; Hiyama, T. *J. Chem. Soc., Perkin Trans 1* **1997**, 2449−2450. Other Method: (h) Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.-i.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 1780−1787.

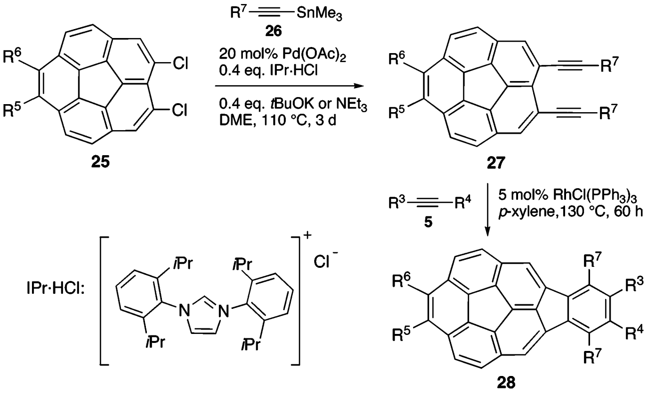
(43) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119−122.

(44) The coupling reaction of **25c** and trimethyl(phenylethynyl)stannane in THF under the same conditions did not afford diyne **27e**, but only complicated products.

(45) This procedure has been applied to prepare pentaethynylcorannulenes and decaethynyl-corannulenes, with isolated yields up to 91%, see: Wu, Y.-T.; Bandera, D.; Linden, A.; Siegel, J. S. unpublished results.

(46) The electron-deficient diester derivative of **25** provides the optimal yield for the coupling reaction.

Scheme 8. Preparation of Indenocorannulenes **28** from Diynes **27** and Alkynes **5**



Single crystals of **28g** were grown from CH$_2$Cl$_2$/MeOH, and the crystal structure determination shows that two symmetry-independent molecules of **28g** crystallize with one disordered molecule of CH$_2$Cl$_2$. Some of the ester groups in the molecules of **28g** are slightly disordered. The disorder of the solvent molecule could not be modeled adequately, so the contribution of the solvent molecule to the intensity data was removed by using the *SQUEEZE*[47] routine of the *PLATON*[48] program. The molecules pack in the crystal lattice such that columns are formed where the bowls are stacked pointing in approximately the same direction, but the adjacent columns have the bowls facing in the opposite direction (Figure 2). Within each column, the bowls are slightly slipped sideways with respect to the molecules immediately above and below. To our knowledge, the crystal structure of **28g** is the first example within the indenocorannulene family.

Quantitative aspects of the structure show the degree of strain and distortion in **28g** (Figure 3). There are two molecules in the asymmetric unit (mol A and mol B) and a potential of bilateral symmetry over which the molecular geometry can be averaged. The experimental and computational results are compared by averaging of the crystal structure values over mol A and mol B as well as over the expected symmetry equivalent positions, assuming bilateral symmetry. The experimental geometry of the bowl is overall well represented by the computations insofar as the trends of the bond lengths as a function of bond type correlate. The computations predict a slightly longer bond length on average and specifically longer bonds for all spoke, flank β, γ, and rim β sites. Despite this general elongation, the computations still predict key features such as the fact that the spoke γ bond is the anomalously short bond in the molecule, consistent with that found in each of the molecules in the asymmetric unit of the crystal structure. Overall, the bond lengths are common to other bowl structures.

Curvature and bowl depth are two characteristic features of molecular bowls. The bowl depth in **28g** as gauged from the distance between hub and rim planes is 1.02/1.05 Å (mol A/mol B) and 1.07 Å (cacld), respectively. The analogous experimental bowl depth for corannulene is 0.87 Å. The π-orbital axis vector (POAV)[49] pyramidalization angles in the crystal structure calculated for the carbon atoms of the hub ring are 8.8°, 9.8°, and 10.8° (averaged over mol A and B and bilateral symmetry) vs 9.0° and 9.9° and 11.0° (calcd), respectively;[50] however, the “ace-“ ring adopts a more flat conformation (POAV = 0.7°, 4.9°, and 6.7°; 4.6° (C7), 6.4° (C8), 4.8° (C9), 0.2 (C21), and 0.0 (C26)). For reference corannulene and C$_{60}$ have hub POAV angles of 8.7 and 11.6, respectively.

The curvature imparts special reactivity to molecular bowls. We predicted a shift of electron density to the base of the bowl with greater curvature.[3] We also demonstrated the binding of metals via η^6 ligation to favor sites of lower curvature.[51] In contrast, η^2 ligation should be enhanced and therefore the spoke γ bond with calculated POAV angles of 11.0° and 6.7° should be especially receptive to metal complexation and other addition chemistry. Position C6/C10 in nonsubstituted indenocorannulene **IC** (Figure 3) in the presence of potassium undergoes the reductive dimerization.[52] The arene of the indeno fusion is relatively normal; it presents a more or less flat geometry with bond lengths as expected from indene or fluoranthene.

Derivatives of **28** allow us to test our previous quartic correlation of bowl depth with inversion barrier.[54] On the basis of corannulene’s predicted barrier of 11.5 kcal/mol and a bowl depth of 0.87 Å, we would expect a barrier of between 22 and 27 kcal/mol for the bowl depths of 1.02−1.07 Å found above (equation). This prediction leads to the expectation that new stereoisomers can be created based on the restricted bowl-inversion properties in indenocorannulenes. Motivated by this hypothesis, we undertook dynamic NMR studies of a subset of derivatives of **28**.

$$[E_a = (\text{bowl depth}_{\,\text{IC}}/\text{bowl depth}_{\text{corannulene}})^4 * 11.5\ \text{kcal/mol}]$$

The ^{13}C NMR spectrum of tetraphenylindenocorannulene **28a** displayed a greater number of signals than would be expected from a planar, or rapidly inverting bowl structure (cf. **9a**). This result indicates that indenocorannulenes **28** exist as static bowl forms at room temperature on the NMR time scale. This finding is also consistent with earlier findings on the relationship between annelated corannulene structure and bowl-inversion barrier height.[54] The predicted barrier for **28a** was higher than the expected barrier to rotation around the aryl-substituent to indenocorannulene bond.[55] As such, **28a** could only give a lower limit to the barrier, which would not suffice to establish the steroisomeric phenomena. Thus, the alcohol **28b** was synthesized and used to obtain an accurate assessment of the inversion barrier.

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(47) van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194−201.

(48) Spek, A. L. *PLATON, Program for the Analysis of Molecular Geometry*, University of Utrecht, The Netherlands, **2005**.

(49) (a) Haddon, R. C. *Science* **1993**, *261*, 1545−1550. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389. (c) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243−249. (d) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137−142.

(50) POAV pyramidalizaion angles of the crystal structure were analyzed by *mol2mol* software.

(51) Seiders, T. J.; Baldridge, K. K.; O’Connor, J. M.; Siegel, J. S. *J. Chem. Soc., Chem. Commun.* **2004**, 950−951. (b) Seiders, T. J.; Baldridge, K. K.; O′Connor, J. M.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 4781−4782.

(52) Aprahamian, I.; Hoffman, R. E.; Sheradsky, T.; Preda, D. V.; Bancu, M.; Scott, L. T.; Rabinovitz, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1712−1715.

(53) Compound **28g**: C$_{46}$H$_{28}$O$_8$·0.5CH$_2$Cl$_2$, monoclinic crystals of space group $P2_1/n$, unit cell dimensions: a = 17.2204(4), b = 14.7197(3), c = 28.2615(7) Å, β = 95.9558(9), V = 7125.0(3) Å^3.

(54) Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517−525.

(55) Gust, D. *J. Am. Chem. Soc.* **1977**, *99*, 6980−6982.

Table 3. Preparation of Indenocorannulenes **28**

entry	S. M.	R^5	R^6	R^7	diyne (yield %)	alkyne	R^3	R^4	product (yield %)
1	**25a**	H	H	Ph	**27a** (33)	**5a**	Ph	Ph	**28a** (54)
2	**25a**	H	H	Ph	**27a**	**5d**	CMe_2OH	H	**28b** (60)
3	**25a**	H	H	*n*Pr	**27b** (34)	**5k**	$CH(OEt)_2$	H	**28c** (14)[a]
4	**25a**	H	H	*n*Pr	**27b**	**5l**	CO_2Me	H	**28d** (trace)[b]
5	**25a**	H	H	*n*Pr	**27b**	**5a**	Ph	Ph	**28e** (42)
6	**25b**	CO_2Me	CO_2Me	Ph	**27c** (65)	**5a**	Ph	Ph	**28f** (64)
7	**25b**	CO_2Me	CO_2Me	Ph	**27c**	**5e**	CO_2Me	CO_2Me	**28g** (19)
8	**25b**	CO_2Me	CO_2Me	Ph	**27c**	**5c**	*n*Pr	*n*Pr	**28h** (57)
9	**25b**	CO_2Me	CO_2Me	*n*Pr	**27d** (51)	**5a**	Ph	Ph	**28i** (47)
10	**25c**	Ph	CO_2Me	Ph	**27e** (42)	**5a**	Ph	Ph	**28j** (81)

[a] **28c** was isolated as an aldehyde and **27b** (69%) was recovered. [b] **27b** (65%) was recovered.

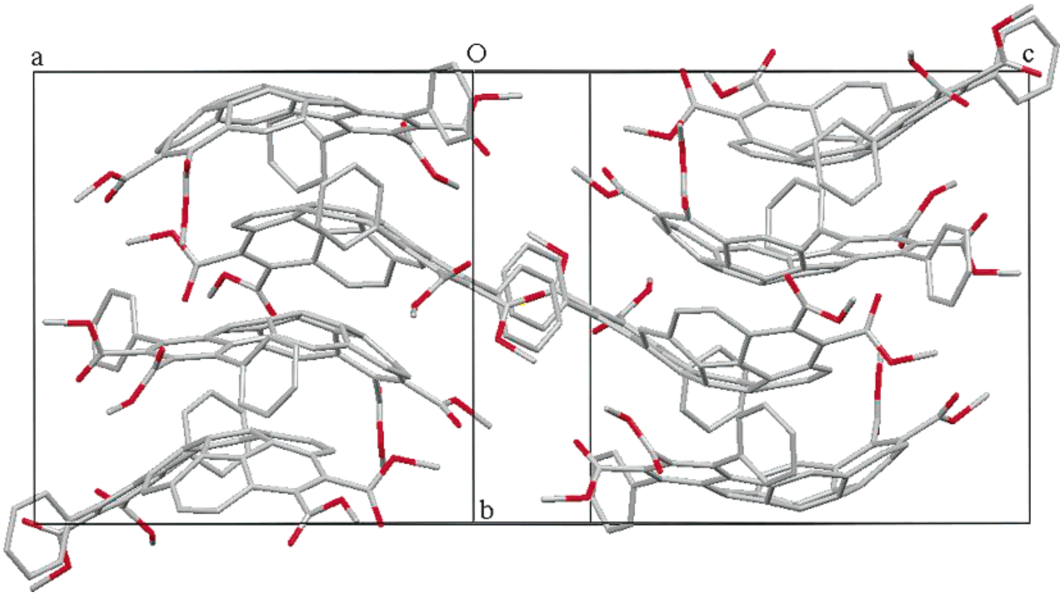
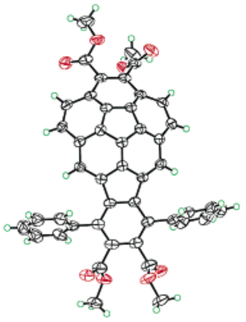
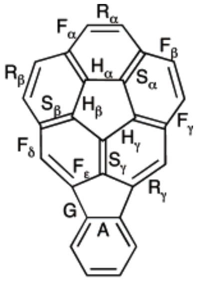


Figure 2. Crystal packing of **28g**.

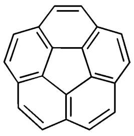




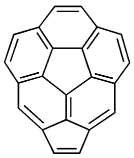
IC

Figure 3. Molecular structure of **28g** in the crystal.[53]

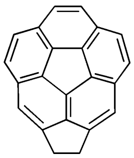
Determination of the coalescence temperature was limited by temperature specifications on the NMR instrument. Even at 172 °C, two separate signals of methyl groups are observed.[56] Therefore, it can be concluded that the bowl-to-bowl inversion barrier of indenocorannulenes must be higher than 24 kcal/mol, which is consistent with the estimates from structure correlation studies. Indeed, the determination of this barrier limit and the substitution pattern of **28b** meet the criteria necessary to demonstrate stereogenicity due to slow bowl inversion character. Energetic computations of the nonsubstituted indenocorannulene (**IC**) via MP2/cc-pVDZ//B3LYP/cc-pVDZ predict a bowl-to-bowl inversion barrier of 29.8 kcal/mol (Table 5). Bowl-inversion barriers above 25 kcal/mol imply inversion half-lives on the order of weeks in solution at room temperature. As such, **28b** represents a chiral buckybowl with persistent stereochemistry on the laboratory time scale. This result now opens the way for the development of new chiral stereoisomers based on annelated corannulenes. The chiroptical properties of pure enantiomeric forms of buckybowls are being investigated.



A



B



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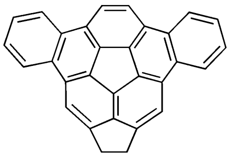

D

Conclusion and Outlook

This formal [(2+2)+2] cycloaddition from *peri*-diynes and alkynes provides an easy way to prepare highly substituted fluoranthenes **9** and **13** and indenocorannulenes **28**. Furthermore the general idea that *peri* dialkynyl aromatics can serve as general synthetic precursors for the introduction of five-membered rings into higher order curved aromatic surfaces is established. Noting that every site in corannulene has a *peri* partner, implies that the conversion of per-substituted coran-

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(56) The separation of two methyl signals at room temperature depends on the solvents and also on the concentration in $CDCl_3$. The temperature-dependent separation of two methyl signals of **28b** in [D_6]-DMSO: 22.5 Hz (300 K), 12.6 Hz (422 K) and 11.4 Hz (455 K).

Table 4. Bond Distances (Å) by Bond Type for **28g** (X-ray) and Indenocorannulene (**IC**, calcd.)

bond[a]	**28g** mol A		**28g** mol B		**28g** avg	IC[b]	Δ(28–IC)[c]
Rim$_\alpha$ (R$_\alpha$)	1.394	×	1.389	×	1.391_5	1.3872	0.4_3
R$_\beta$	1.371	1.383	1.388	1.373	1.378_3	1.3905	$\mathbf{1.2_2}$
R$_\gamma$	1.394	1.384	1.375	1.397	1.398_8	1.3948	0.4_0
Flank$_\alpha$ (F$_\alpha$)	1.465	1.439	1.457	1.460	1.455_3	1.4500	0.5_3
F$_\beta$	1.449	1.437	1.449	1.440	1.443_8	1.4471	$\mathbf{0.3_3}$
F$_\gamma$	1.440	1.441	1.447	1.429	1.439_3	1.4493	$\mathbf{1.0_0}$
F$_\delta$	1.439	1.457	1.452	1.448	1.449_0	1.4596	$\mathbf{1.0_6}$
F$_\epsilon$	1.430	1.427	1.426	1.427	1.427_5	1.4319	$\mathbf{0.4_4}$
Hub$_\alpha$ (H$_\alpha$)	1.419	×	1.437	×	1.428_0	1.4310	$\mathbf{0.3_0}$
H$_\beta$	1.409	1.426	1.425	1.429	1.422_3	1.4257	$\mathbf{0.3_4}$
H$_\gamma$	1.410	1.419	1.420	1.411	1.415_0	1.4189	$\mathbf{0.3_9}$
Spoke$_\alpha$ (S$_\alpha$)	1.369	1.381	1.375	1.363	1.372_0	1.3898	$\mathbf{1.7_8}$
S$_\beta$	1.392	1.381	1.391	1.388	1.388_0	1.3996	$\mathbf{1.1_6}$
S$_\gamma$	1.348	×	1.357	×	1.352_5	1.3632	$\mathbf{1.0_7}$
G	1.480	1.501	1.496	1.485	1.490_5	1.4895	0.1_0
A	1.425	×	1.443	×	1.434_0	1.4389	$\mathbf{0.4_9}$

[a] Bond Type: R = Rim; F = Flank; H = Hub; S = Spoke; G = Gable; A = Ace-. [b] calcd indenocorannulene (**IC**) at B3LYP/cc-pVDZ. [c] Unit:pm.

Table 5. Bowl-to-Bowl Inversion Barriers of Corannulene Derivatives[a]

	A	B	C	D	IC[b]
B3LYP/cc-pVDZ	9.2[57]	27.7[54]	25.6[54]		26.4
MP2/cc-pVDZ//B3LYP/cc-pVDZ	11.0[54]	30.9[54]	28.9[54]		29.8
B3LYP/6-31G**//RHF or B3LYP/3-21G			24.1[39]	19.3[39]	
RHF/cc-pVDZ	9.2[54]	29.2[54]	26.6[54]		
Exp.	11.5[58]		27.7[59]	ca. 23.1[39]	> 24

[a] unit: kcal/mol. [b] IC = Indenocorannulene.

nulenes to capped carbon tubes is presaged by the results presented here. Given the great advances that have come in the preparative scale syntheses of corannulene derivatives, it is reasonable to expect a solution phase synthesis of carbon tubes with homogeneous molecular weight distributions.

With the synthetic technology to prepare indenocorannulenes at hand, the study of the physical properties with the use of florescence, UV−Visible and cyclic voltammety spectroscopy is in progress. Preliminary observations in this area betray an interesting transition of material properties from planar aromatics, to bowls and beyond.

Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AMX 300 (300 and 75.5 MHz). IR: Bruker IFS 66 (FT-IR). EI−MS: Finnegan MAT 95 spectrometer (70 eV). High-resolution mass data (HRMS) were obtained by preselected-ion peak matching at $R \approx 10\,000$ to be within ± 3 ppm of the exact mass. Elemental analyses: Mikroanalytisches Laboratorium des Organisch-Chemisches Institut der Universität Zürich. Chromatography: Merck silica gel 60 (230−400 mesh) or Fluka neutral alumina (Brockmann I, Activity II). Solvents for chromatography were technical grade and freshly distilled before use. 1,8-Diiodonaphthalene (**12**),[13] 7,10-diphenylfluoranthene (**13b**),[32] 3,6-diphenyltetracyclo$[5.4.0.0.^{2,9}0^{8,10}]$-undec-3,5-dieno[4,5-*d*]acenaphthylene (**14b**),[32] ethynylpentafluorobenzene,[60] 2-bromophenylethyne,[21c] 2,3-dichlorocorannulene **25a**,[4h] 1,3-bis[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene monohydrochloride (IPr•HCl),[61] trimethyl(phenylethynyl)stannane (**26a**),[62] trimethyl(1-pentynyl)stannane (**26b**)[63] were prepared according to the literature procedures. Other compounds, which are not mentioned in the Experimental Section and Supporting Information, are commercially available.

General Procedure for Preparation of Diynes **4** by the Sonogashira Coupling (**GP1**): To a solution of the respective terminal alkyne (15.9 mmol) and diiodide **12** (5.26 mmol) in NEt_3 (10 mL) in a screw-capped Pyrex bottle $Pd(PPh_3)_2Cl_2$ (100 mg), CuI (100 mg) and PPh_3 (100 mg) are added at ambient temperature. The reaction mixture is purged with nitrogen for 5 min. The sealed bottle is heated at 40−50 °C overnight (ca. 16−24 h). After cooling to room temperature, the suspension is filtered through a 3 cm thick layer of diatomaceous earth, and the diatomaceous earth is rinsed well with Et_2O (150 mL). The solvent of the filtrate is removed under reduced pressure, and the residue is subjected to chromatography on silica gel. Elution with hexane/CH_2Cl_2 affords the coupling product **4**.

1,8-Bis(phenylethynyl)naphthalene (4a): According to **GP1**, a mixture of **12** (2.00 g, 5.26 mmol), phenylethyne (1.62 g, 15.9 mmol), $PdCl_2(PPh_3)_2$ (100 mg), CuI (100 mg), PPh_3 (100 mg) and NEt_3 (15 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 40 °C for 11 h. After filtration and removal of the solvent, the residue was subjected to chromatography on silica gel. Elution with hexane/CH_2Cl_2 (from 1:0 to 10:1) gave 1.53 g (89%) of **4a** [$R_f = 0.44$ (SiO_2, hexane/CH_2Cl_2 5:1)] as a pale yellow solid (mp 98−99 °C), which was directly used without any further purification. Further crystallization from CH_2Cl_2/hexane afforded a pale yellow crystals, mp 99−100 °C.

1,8-Bis(4-*s*-butylphenylethynyl)naphthalene (4b): According to **GP1**, a mixture of **12** (2.00 g, 5.26 mmol), 4-*n*-butylphenylethyne (2.50 g, 15.8 mmol), $PdCl_2(PPh_3)_2$ (100 mg), CuI (100 mg), PPh_3 (100 mg), and NEt_3 (15 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 50 °C for 21 h. After filtration and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 10:1 to 5:1) gave 1.81 g (78%) of **4b** [$R_f = 0.53$ (Al_2O_3, hexane/CH_2Cl_2 5:1)] as a pale green solid, mp 80−81 °C. IR (KBr): ν cm^{-1} = 2958,

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2924, 2868, 2206 (C≡C), 1567, 1509, 1375, 825, 767. − ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.93 (t, J = 7.2 Hz, 6 H), 1.34 (sext, J = 7.8 Hz, 4 H), 1.51−1.61 (m, 4 H), 2.54 (t, J = 7.8 Hz, 4 H), 6.91−6.94 (m, 4 H), 7.24−7.27 (m, 4 H), 7.43 (dd, J = 7.5, J = 8.4 Hz, 2 H), 7.80 (dd, J = 1.5, J = 8.4 Hz, 2 H), 7.84 (dd, J = 1.5, J = 7.5 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 13.8 (+), 22.2, 33.4, 35.5 (all −), 89.0, 96.9, 120.9, 121.1, 134.1, 142.7 (C$_{\text{quat}}$), 125.4, 127.9, 129.3, 131.5 × 2, 134.7 (all +). MS (70 eV), m/z (%): 440 (100) [M$^+$], 397 (60), 339 (30), 326 (17). Elemental analysis calcd (%) for $C_{34}H_{32}$ (440.6): C 92.68, H 7.32; found: C 92.65, H 7.44. HRMS (EI) calcd. for $C_{34}H_{32}$: 440.2504; found: 440.2496.

1,8-Bis[(4-*tert*-butylphenyl)ethynyl]naphthalene (4c): According to **GP1**, a mixture of **12** (0.50 g, 1.32 mmol), 4-*tert*-butylphenylethyne (627 mg, 3.96 mmol), PdCl$_2$(PPh$_3$)$_2$ (25 mg), CuI (25 mg), PPh$_3$ (25 mg) and NEt$_3$ (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 80 °C for 20 h. After filtration and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane gave 384 mg (66%) of **4c** [R_f = 0.20 (Al$_2$O$_3$, hexane)] as a pale yellow solid, mp 188−189 °C, R_f = 0.53 (SiO$_2$, hexane/CH$_2$Cl$_2$ 3:1). IR (KBr): ν cm−^{1} = 2194 (C≡C), 1930, 1565, 1502, 1375, 1361, 1266, 828, 765, 563. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 1.28 (s, 18 H), 7.13−7.17 (m, 4 H), 7.24−7.29 (m, 4 H), 7.44 (dd, J = 7.2, 8.4 Hz, 2 H), 7.80 (dd, J = 1.2, 8.4 Hz, 2 H), 7.85 (dd, J = 1.2, 7.2 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 31.1 (+), 34.6, 89.1, 96.9, 120.8, 121.1, 134.8, 151.0 (all C$_{\text{quat}}$), 124.8, 125.5, 129.3, 131.4, 134.0 (all +). One C$_{\text{quat}}$ cannot be observed due to the signals overlap. MS (70 eV), m/z (%): 440 (100) [M$^+$], 425 (41), 384 (47), 369 (38), 327 (21), 326 (20), 56 (23). Elemental analysis calcd. (%) for $C_{34}H_{32}$ (440.6): C 92.68, H 7.32; found: C 92.70, H 7.45. HRMS (EI) calcd. for $C_{34}H_{32}$: 440.2504; found: 440.2498.

1-(Pentafluorophenylethynyl)-8-(phenylethynyl)naphthalene (4d): A mixture of 1-iodo-8-(phenyl-ethyl)naphthalene (683 mg, 1.93 mmol), pentafluorophenylethyne (481 mg, 2.50 mmol), PdCl$_2$(PPh$_3$)$_2$ (25 mg), CuI (20 mg), PPh$_3$ (20 mg) and NEt$_3$ (7 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 40 °C for 21 h. After filtration and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH$_2$Cl$_2$ (from 1:0 to 10:1) gave 770 mg (95%) of **4d** [R_f = 0.65 (Al$_2$O$_3$, hexane/CH$_2$Cl$_2$ 3:1)] as pale yellow needles, mp 155 °C. IR (KBr): ν cm^{-1} = 2220 (C≡C), 1517, 1497, 1565, 1096, 986, 922, 824, 754, 689. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 7.11−7.23 (m, 3 H), 7.35−7.39 (m, 2 H), 7.47 (d, J = 7.8 Hz, 1 H), 7.50 (d, J = 7.5 Hz, 1 H), 7.82−7.93 (m, 4 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 79.5 (d, J = 3.8 Hz), 89.3, 96.7, 101.3 (d, J = 3.7 Hz), 119.1, 120.7, 131.2, 134.1, 135.6 (m), 139.7 (m), 142.6 (m), 145.0 (m), 148.4 (m) (all C$_{\text{quat}}$), 125.3, 125.8, 127.6, 127.8, 129.6, 130.8, 131.0, 134.4, 135.1 (all +). ^{19}F (282.4 MHz, CDCl$_3$): δ ppm = −163.2 (td, J = 7.2, J = 22.3 Hz, 2 F), −154.5 (t, J = 20.9 Hz, 1 F), −136.1 (dd, J = 7.2, J = 21.7 Hz, 2 F). − MS (70 eV), m/z (%): 420/419/418/417/416 (5/29/100/17/10) [M$^+$], 398 (65), 378 (16), 367 (11), 199 (12). HRMS (EI) calcd for $C_{26}H_{11}F_5$: 418.0781; found: 418.0770.

1,8-Bis[(2-bromophenyl)ethynyl]naphthalene (4e): According to **GP1**, a mixture of **12** (2.00 g, 5.26 mmol), 2-bromophenylethyne (2.86 g, 15.8 mmol), PdCl$_2$(PPh$_3$)$_2$ (100 mg), CuI (100 mg), PPh$_3$ (100 mg) and NEt$_3$ (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 50 °C for 12 h. After filtration and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH$_2$Cl$_2$ (from 10:1 to 5:1) gave a pale yellow oil. Crystallization from hexane afforded 2.33 g (91%) of **4e** [R_f = 0.30 (Al$_2$O$_3$, hexane/CH$_2$Cl$_2$ 10:1)] as pale yellow needles, mp 111−112 °C. IR (KBr): ν cm^{-1} = 2203 (C≡C), 1554, 1467, 1432, 1376, 1044, 1024, 824, 765, 750. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 6.90−7.04 (m, 4 H), 7.21−7.27 (m, 2 H), 7.43−7.53 (m, 4 H), 7.85 (d, J = 8.4 Hz, 2 H), 7.94 (d, J = 7.2 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 94.1, 95.2, 120.4, 125.4, 125.8, 131.2, 134.0 (all C$_{\text{quat}}$), 125.6, 126.4, 128.9, 129.9, 131.9, 133.1, 135.0 (all +). MS (70 eV), m/z (%): 489/488/487/486/485/484 (4/15/8/28/4/15) [M$^+$], 408/407/406/405 (4/10/7/9) [M$^+$ − Br], 326 (100) [M$^+$ − Br$_2$], 162 (28). Elemental analysis calcd. (%) for $C_{26}H_{14}Br_2$ (486.2): C 64.23, H 2.90; found: C 63.99, H 3.02. HRMS (EI) calcd for $C_{26}H_{14}Br_2$: 483.9462; found: 483.9455.

1,8-Bis[(4-methoxycarbonylphenyl)ethynyl]naphthalene (4f): According to **GP1**, a mixture of **12** (0.80 g, 2.11 mmol), 4-ethynylbenzoic acid methyl ester (1.01 g, 6.31 mmol), PdCl$_2$(PPh$_3$)$_2$ (50 mg), CuI (50 mg), PPh$_3$ (50 mg) and NEt$_3$ (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was heated at 80 °C for 18 h. Due to the lower solubility of **4f** in Et$_2$O, the reaction mixture was dissolved in CH$_2$Cl$_2$ (200 mL) after removal of NEt$_3$, and washed with water (3 × 100 mL). The solution was dried over MgSO$_4$ and the solvent of the filtrate was removed. The residue was subjected to chromatography on alumina. The yellow fraction was collected and crystallization from hexane/CH$_2$Cl$_2$ (1:1) gave 690 mg (74%) of **4f** [R_f = 0.67 (alumina, CH$_2$Cl$_2$)] as a white solid, mp 203−204 °C. IR (KBr): ν cm^{-1} = 2205 (C≡C), 1720 (C=O), 1603, 1434, 1270, 1108, 828, 766, 695. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 3.90 (s, 6 H), 7.35−7.39 (m, 4 H), 7.47 (dd, J = 7.2, J = 8.4 Hz, 2 H), 7.73−7.78 (m, 4 H), 7.85 (dd, J = 1.2, J = 8.4 Hz, 2 H), 7.94 (dd, J = 1.2, J = 7.2 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 52.0 (+), 92.6, 95.7, 120.1, 128.2, 129.03, 131.3, 134.0, 166.3 (all C$_{\text{quat}}$), 125.6, 129.01, 130.1, 131.1, 135.0 (all +). MS (70 eV), m/z (%): 444 (100) [M$^+$], 413 (17) [M$^+$ − OCH$_3$], 385 (14), 326 (55), 162 (19). Elemental analysis calcd. (%) for $C_{30}H_{20}O_4$ (444.5): C 81.07, H 4.54; found: C 81.07, H 4.61. HRMS (EI) calcd. for $C_{30}H_{20}O_4$: 444.1362; found: 444.1350.

General Procedure for the Formal [(2+2)+2] Cycloaddition of Diynes **4** (or **27**) with Alkynes **5** (**GP2**): A thick-walled screw-capped Pyrex bottle (or Schlenk tube) equipped with a magnetic stirring bar is charged with 0.50 mmol of the diyne **4** (or **27**), 23.0 mg (25.0 μmol) of the Wilkinson's catalyst, 2.50 mmol of the respective alkyne **5** and 20 mL of *p*-xylene. Dry nitrogen is bubbled through the solution for 5 min. The sealed bottle (or Schlenk tube with a reflux condenser under nitrogen) is kept in an oil bath at 130 (or 110) °C for 60 h. After cooling to room temperature, the solvent is removed under reduced pressure and the residue is subjected to chromatography. Elution with hexane/CH$_2$Cl$_2$ affords the cycloadduct **9** (or **28**).

7,8,9,10-Tetraphenylfluoranthene (9a): According to **GP2**, a mixture of diyne **4a** (164 mg, 0.50 mmol), alkyne **5a** (446 mg, 2.50 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (50 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 60 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane/CH$_2$Cl$_2$ (5:1) afforded 210 mg (83%) of **9a** [R_f = 0.63 (SiO$_2$, hexane/CH$_2$Cl$_2$ 3:1)] as a bright yellow solid. ^{1}H NMR spectrum is identical to the reference.[8b] ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 123.1, 125.3, 126.4, 126.5, 126.8, 127.5, 128.1, 130.0, 131.2 (all +), 129.5, 133.2, 136.41, 136.43, 137.1, 139.77, 139.79, 140.6 (all C$_{\text{quat}}$).

8,9-Bis(4-*n*-butylphenyl)-7,10-diphenylfluoranthene (9b): According to **GP2**, a mixture of diyne **4a** (164 mg, 0.50 mmol), alkyne **5b** (726 mg, 2.50 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 52 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane/CH$_2$Cl$_2$ (10:1) afforded 267 mg (86%) of **9b** [R_f = 0.26 (SiO$_2$, hexane/CH$_2$Cl$_2$ 10:1)] as a bright yellow solid, mp 190−191 °C. IR (KBr): ν cm^{-1} = 2954, 2855, 1425, 1021, 826, 775, 700. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.82 (t, J = 7.2 Hz, 6 H), 1.06−1.18 (m, 4 H), 1.33−1.43 (m, 4 H), 2.35 (t, J = 7.2 Hz, 4 H), 6.61 (d, J = 6.9 Hz, 2 H), 6.66 (d, J = 7.8 Hz, 4 H), 6.76 (d, $J = 7.8$ Hz, 4 H), 7.24−7.34 (m, 12 H), 7.69 (d, $J = 8.4$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 13.8 (+), 21.7, 33.2, 34.9 (all −), 123.0, 126.3, 126.5, 126.6, 127.5, 128.0, 130.1, 131.0 (all +), 129.5, 133.0, 136.2, 136.6, 137.0, 139.4, 140.0, 140.9 (all C$_{\text{quat}}$). One C$_{\text{quat}}$ cannot be observed due to signal overlap. − MS (70 eV), *m/z* (%): 618 (100) [M$^+$]. Elemental analysis calcd (%) for $C_{48}H_{42}$ (618.9): C 93.16, H 6.84; found: C 93.10, H 6.93. HRMS (EI) calcd for $C_{48}H_{42}$: 618.3287; found: 618.3278.

7,10-Diphenyl-8,9-di-*n*-propylfluoranthene (9c): According to **GP2**, a mixture of diyne **4a** (164 mg, 0.50 mmol), alkyne **5c** (276 mg, 2.50 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 110 °C for 36 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane/CH$_2$Cl$_2$ (5:1) afforded 218 mg (99%) of **9c** [$R_f = 0.53$ (SiO$_2$, hexane/CH$_2$Cl$_2$ 3:1)] as a pale yellow solid, mp 240−242 °C. IR (KBr): ν cm^{-1} = 3055 (C−H), 2957, 2868, 1424, 1025, 773, 732, 701. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.81 (t, $J = 7.5$ Hz, 6 H), 1.45−1.56 (m, 4 H), 2.49−2.55 (m, 4 H), 6.24 (d, $J = 7.2$ Hz, 2 H), 7.19 (d, $J = 7.2$ Hz, 2 H), 7.21 (d, $J = 7.2$ Hz, 2 H), 7.44 (d, $J = 7.5$ Hz, 2 H), 7.45 (d, $J = 8.1$ Hz, 2 H), 7.52−7.77 (m, 4 H), 7.56 (d, $J = 8.1$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 14.6 (+), 24.8, 32.4 (all −), 122.3, 125.7, 127.2, 127.4, 128.7, 129.3 (all +), 135.2, 136.9, 137.8, 138.7, 140.7 (all C$_{\text{quat}}$). Two C$_{\text{quat}}$ cannot be observed due to signal overlap. MS (70 eV), *m/z* (%): 438 (100) [M$^+$], 409 (31), 367 (100), 289 (17), 181 (11). Elemental analysis calcd (%) for $C_{34}H_{30}$ (438.6): C 93.11, H 6.89; found: C 92.97, H 6.86. HRMS (EI) calcd for $C_{34}H_{30}$: 438.2348; found: 438.2345.

8-(1-Hydroxy-1-methylethyl)-7,10-diphenylfluoranthene (9d): According to **GP2**, a mixture of diyne **4a** (164 mg, 0.50 mmol), alkyne **5d** (210 mg, 2.50 mmol), Wilkinson's catalyst (23.0 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 60 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane/CH$_2$Cl$_2$ (1:1) afforded 204 mg (99%) of **9d** [$R_f = 0.50$ (SiO$_2$, hexane/Et$_2$O 1:1)] as a colorless solid, mp 186 °C. IR (KBr): ν cm^{-1} = 3452 (O−H), 3055 (C−H), 1425, 1362, 1162, 824, 722, 699. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 1.55 (s, 6 H), 1.95 (br. s, 1 H), 5.88 (d, $J = 7.2$ Hz, 1 H), 7.14−7.33 (m, 3 H), 7.45−7.70 (m, 13 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 32.7 (+), 74.4 (C$_{\text{quat}}$), 122.7, 123.3, 126.4, 126.5, 127.0, 127.4, 127.6, 127.7, 127.9, 128.6, 128.9, 129.1, 130.3 (all +), 129.5, 133.0, 135.0, 135.2, 135.6, 136.8, 137.6, 139.7, 141.0, 141.1, 145.6 (all C$_{\text{quat}}$). MS (70 eV), *m/z* (%): 412 (34) [M$^+$], 397 (53) [M$^+$ − CH$_3$], 394 (100) [M$^+$ − H$_2$O], 379 (86) [M$^+$ − H$_2$O − CH$_3$], 355 (24), 302 (16), 188 (16). Elemental analysis calcd. (%) for $C_{31}H_{24}O$ (412.5): C 90.26, H 5.86; found: C 89.99, H 5.85. HRMS (EI) calcd for $C_{31}H_{24}O$: 412.1827; found: 412.1836.

8,9-Dimethoxycarbonyl-7,10-diphenylfluoranthene (9e): According to **GP2**, a mixture of diyne **4a** (164 mg, 0.50 mmol), alkyne **5e** (355 mg, 2.50 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 60 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on Al$_2$O$_3$. Elution with hexane/CH$_2$Cl$_2$ (1:1) afforded 233 mg (99%) of **9e** [$R_f = 0.19$ (Al$_2$O$_3$, hexane/CH$_2$Cl$_2$ 1:1)] as a colorless solid, mp 248 °C. IR (KBr): ν cm^{-1} = 2952 (C−H), 1743 (C=O), 1715 (C=O), 1440, 1426, 1251, 1220, 1174, 771. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 3.59 (s, 6 H), 6.74 (d, $J = 7.2$ Hz, 2 H), 7.34 (dd, $J = 7.2$, $J = 8.1$ Hz, 2 H), 7.52−7.77 (m, 10 H), 7.78 (d, $J = 8.1$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 52.1, 124.4, 127.6, 127.7, 128.1, 128.5, 129.0 (all +), 129.5, 131.6, 133.2, 134.9, 136.0, 137.8, 139.1, 168.2 (all C$_{\text{quat}}$). MS (70 eV), *m/z* (%): 470 (100) [M$^+$], 439 (54) [M$^{+\,-}$ OCH$_3$], 350 (13), 219 (13), 175 (17). Elemental analysis calcd (%) for $C_{32}H_{22}O_4$ (470.5): C 81.69, H 4.71; found: C 81.79, H 4.62. HRMS (EI) calcd for $C_{32}H_{22}O_4$: 470.1518; found: 470.1527.

7,8,10-Triphenylfluoranthene (9f): According to **GP2**, a mixture of diyne **4a** (82 mg, 0.25 mmol), alkyne **5f** (128 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 13.0 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 61 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane/CH$_2$Cl$_2$ (20:1) afforded 103 mg (96%) of **9f** [$R_f = 0.24$ (SiO$_2$, hexane/CH$_2$Cl$_2$ 10:1)] as a pale green solid, mp 198 °C. IR (KBr): ν cm^{-1} = 1427, 776, 759, 701. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 6.69 (d, $J = 7.2$ Hz, 1 H), 7.13−7.26 (m, 5 H), 7.28−7.41 (m, 9 H), 7.48−7.58 (m, 3 H), 7.68−7.76 (m, 4 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 122.8, 123.3, 126.3, 126.6, 127.2, 127.5, 127.6, 127.8, 128.4, 128.6, 129.1, 129.9, 130.3, 131.1 (all +), 129.7, 133.1, 135.7, 135.9, 136.1, 136.6, 137.9, 138.2, 139.3, 140.7, 140.9 (all C$_{\text{quat}}$). One C$_{\text{quat}}$ and two CH cannot be observed due to the signals overlap. MS (70 eV), *m/z* (%): 430 (100) [M$^+$], 353 (8) [M$^+$ − C$_6$H$_5$], 352 (13). Elemental analysis calcd. (%) for $C_{34}H_{22}$ (430.5): C 94.85, H 5.15; found: C 94.83, H 5.37. HRMS (EI) calcd. for $C_{34}H_{22}$: 430.1722; found: 430.1716.

8-(4-*n*-Butylphenyl)-9-(4-*tert*-butylphenyl)-7,10-diphenylfluoranthene (9g): According to **GP2**, a mixture of diyne **4a** (82 mg, 0.25 mmol), alkyne **5g** (363 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 13.0 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 53 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane and hexane/CH$_2$Cl$_2$ (20:1) afforded 132 mg (85%) of **9g** [$R_f = 0.29$ (SiO$_2$, hexane/CH$_2$Cl$_2$ 10:1)] as a yellow solid, mp 242 °C. IR (KBr): ν cm^{-1} = 2956 (C−H), 2859, 1426, 775, 765, 700. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.80 (t, $J = 7.2$ Hz, 3 H), 1.04−1.16 (m, 2 H), 1.11 (s, 9 H), 1.34−1.41 (m, 2 H), 2.34 (t, $J = 7.5$ Hz, 2 H), 6.59−6.67 (m, 4 H), 6.74−6.78 (m, 4 H), 6.84−6.87 (m, 2 H), 7.24−7.34 (m, 12 H), 7.68 (d, $J = 8.1$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 13.9, 31.2 (all +), 21.7, 33.4, 34.1 (all -), 35.0 (C$_{\text{quat}}$), 123.1, 123.3, 126.3, 126.6, 126.7, 127.6, 128.1 × 2, 130.2, 130.9, 131.1 (all +), 129.6, 133.3, 136.3, 136.7, 136.8, 137.2 × 2, 139.4, 140.0, 140.1, 141.0, 141.1, 147.9 (all C$_{\text{quat}}$). Three C$_{\text{quat}}$ and five CH cannot be observed due to signal overlap or too weak. MS (70 eV), *m/z* (%): 618 (100) [M$^+$], 603 (13), 561 (18) [M$^+$ − C$_4$H$_9$]. Elemental analysis calcd. (%) for $C_{48}H_{42}$ (618.9): C 93.16, H 6.84; found: C 93.19, H 7.05. HRMS (EI) calcd. for $C_{48}H_{42}$: 618.3287; found: 618.3281.

7,10-Bis(4-*n*-butylphenyl)-8,9-diphenylfluoranthene (9i): According to **GP2**, a mixture of diyne **4b** (110 mg, 0.25 mmol), alkyne **5a** (223 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 13.0 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 58 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO$_2$. Elution with hexane and hexane/CH$_2$Cl$_2$ (10:1) afforded 119 mg (85%) of **9i** [$R_f = 0.21$ (SiO$_2$, hexane/CH$_2$Cl$_2$ 10:1)] as a pale green solid, mp 209−210 °C. IR (KBr): ν cm^{-1} = 2955 (C−H), 2928, 1426, 826, 775, 700. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.94 (t, $J = 7.2$ Hz, 6 H), 1.33 (sext, $J = 7.5$ Hz, 4 H), 1.57−1.67 (m, 4 H), 2.62 (t, $J = 8.1$ Hz, 4 H), 6.63 (d, $J = 7.8$ Hz, 2 H), 6.81−6.92 (m, 10 H), 7.09−7.12 (m, 4 H), 7.18−7.21 (m, 4 H), 7.27−7.30 (m, 2 H), 7.69 (d, $J = 7.8$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 13.9 (+), 22.0, 33.4, 35.2 (all −), 123.1, 125.1, 126.2, 126.4, 127.5, 128.1, 129.8, 131.3 (all +), 129.5, 133.2, 136.5, 136.6, 136.9, 137.1, 140.0, 140.6, 141.2 (all C$_{\text{quat}}$). MS (70 eV), *m/z* (%): 618 (100) [M$^+$], 561 (6) [M$^+$ − C$_4$H$_9$]. Elemental analysis calcd.

(%) for $C_{48}H_{42}$ (618.9): C 93.16, H 6.84; found: C 93.09, H 7.03. HRMS (EI) calcd for $C_{48}H_{42}$: 618.3287; found: 618.3273.

7,8,9,10-Tetrakis(4-*n*-butylphenyl)fluoranthene (9j): According to **GP2**, a mixture of diyne **4b** (110 mg, 0.25 mmol), alkyne **5b** (363 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 12.5 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 57 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (10:1) afforded 136 mg (75%) of **9j** [$R_f = 0.32$ (SiO_2, hexane/CH_2Cl_2 10:1)] as a yellow solid, mp 92−93 °C. IR (KBr): ν cm^{-1} = 2955, 2926, 2855, 1515, 1457, 1426, 1377, 826, 776, 554. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.82 (t, J = 7.2 Hz, 6 H), 0.93 (t, J = 7.5 Hz, 6 H), 1.12 (sext, J = 7.5 Hz, 4 H), 1.25−1.42 (m, 8 H), 1.54−1.64 (m, 4 H), 2.34 (t, J = 7.5 Hz, 4 H), 2.60 (t, J = 7.8 Hz, 4 H), 6.62−6.68 (m, 6 H), 6.72−6.75 (m, 4 H), 7.06 (d, J = 8.1 Hz, 4 H), 7.15−7.19 (m, 4 H), 7.21−7.26 (m, 2 H), 7.63 (d, J = 7.8 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 13.9, 14.0 (all +), 21.8, 22.1, 33.3, 33.5, 35.1, 35.4 (all −), 123.1, 126.2, 126.5, 127.5, 128.1, 129.6, 131.2 (all +), 130.0, 133.3, 136.4, 136.9, 137.3, 137.4, 139.2, 141.0 (all C_{quat}). Two C_{quat} cannot be observed due to signal overlap. MS (70 eV), m/z (%): 730 (100) [M$^+$], 673 (6) [M$^+$ − C_4H_9]. Elemental analysis calcd. (%) for $C_{56}H_{58}$ (731.1): C 92.00, H 8.00; found: C 92.02, H 8.16. HRMS (EI) calcd. for $C_{56}H_{58}$: 730.4539; found: 730.4544.

7,10-Bis(4-*n*-butylphenyl)-8-trimethylsilylfluoranthene (9k): According to **GP2**, a mixture of diyne **4b** (397 mg, 0.90 mmol), alkyne **5i** (442 mg, 4.50 mmol), Wilkinson's catalyst (42 mg, 45.0 μmol) and *p*-xylene (40 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 84 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (10:1) afforded 485 mg (99%) of **9k** [$R_f = 0.58$ (SiO_2, hexane/CH_2Cl_2 10:1)] as a yellow solid, mp 137−138 °C. IR (KBr): ν cm^{-1} = 2956, 2929, 2857, 1428, 1247, 865, 835, 776. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.05 (s, 9 H), 1.01 (t, J = 7.2 Hz, 6 H), 1.39−1.53 (m, 4 H), 1.70−1.80 (m, 4 H), 2.74−2.81 (m, 4 H), 6.40 (d, J = 7.2 Hz, 1 H), 7.20−7.37 (m, 9 H), 7.46 (s, 1 H), 7.57 (d, J = 7.8 Hz, 2 H), 7.65 (d, J = 8.1 Hz, 1 H), 7.70 (dd, J = 0.9, J = 7.5 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 0.7, 14.0 × 2 (all +), 22.2, 22.5, 33.7, 33.8, 35.5, 35.6 (all −), 123.0, 123.2, 126.1, 126.6, 127.3, 127.6, 128.5, 128.6, 129.0, 129.8, 135.5 (all +), 129.6, 132.9, 136.3, 137.0 × 2, 137.1, 137.4, 138.6, 138.7, 138.9, 142.3, 142.4, 143.6 (all C_{quat}). MS (70 eV), m/z (%): 538 (100) [M$^+$], 523 (85) [M$^+$ − CH_3], 507 (10), 451 (17). Elemental analysis calcd (%) for $C_{39}H_{42}Si$ (538.8): C 86.93, H 7.86; found: C 87.09, H 7.97. HRMS (EI) calcd for $C_{39}H_{42}Si$: 538.3056; found: 538.3056.

7,10-Bis(4-*tert*-butylphenyl)-8,9-diphenylfluoranthene (9l): According to **GP2**, a mixture of diyne **4c** (110 mg, 0.25 mmol), alkyne **5a** (223 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 13.0 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 54 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane and hexane/CH_2Cl_2 (10:1) afforded 128 mg (83%) of **9l** [$R_f = 0.21$ (SiO_2, hexane/CH_2Cl_2 10:1)] as a pale green solid, mp 347−348 °C. IR (KBr): ν cm^{-1} = 2958 (C−H), 2865, 1116, 827, 776, 704. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 1.33 (s, 18 H), 6.61 (d, J = 7.2 Hz, 2 H), 6.81−6.90 (m, 10 H), 7.20−7.32 (m, 10 H), 7.68 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 31.3 (+), 34.4 (C_{quat}), 123.1, 124.8, 125.1, 126.2, 126.4, 127.5, 129.6, 131.3 (all +), 133.2, 136.6 × 2, 136.7, 137.1, 140.0, 140.7, 149.6 (all C_{quat}). One C_{quat} cannot be observed due to signal overlap. MS (70 eV), m/z (%): 618 (100) [M$^+$], 294 (17). Elemental analysis calcd. (%) for $C_{48}H_{42}$ (618.9): C 93.16, H 6.84; found: C 93.19, H 6.84. HRMS (EI) calcd. for $C_{48}H_{42}$: 618.3287; found: 618.3296.

8-(4-*n*-Butylphenyl)-7,9,10-tris(4-*tert*-butylphenyl)fluoranthene (9m): According to **GP2**, a mixture of diyne **4c** (110 mg, 0.25 mmol), alkyne **5g** (363 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 13.0 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 56 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (20:1) afforded 157 mg (86%) of **9m** [$R_f = 0.22$ (SiO_2, hexane/CH_2Cl_2 10:1)] as a pale green solid, mp 197−198 °C. IR (KBr): ν cm^{-1} = 2959 (C−H), 826, 774. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.80 (t, J = 7.5 Hz, 3 H), 1.04−1.16 (m, 2 H), 1.10 (s, 9 H), 1.31−1.42 (m, 2 H), 1.31 (s, 9 H), 1.33 (s, 9 H), 2.36 (t, J = 7.2 Hz, 2 H), 6.64−6.67 (m, 3 H), 6.73−6.78 (m, 5 H), 6.83−6.86 (m, 2 H), 7.17−7.32 (m, 10 H), 7.68 (d, J = 8.1 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 13.8 (+), 21.5, 33.4, 34.9 (all −), 31.1, 31.3 × 2 (all +), 34.0, 34.4 (all C_{quat}), 122.97, 123.01 × 2, 124.6, 124.7, 126.1, 126.4, 127.5, 129.6 × 2, 130.9, 131.1 (all +), 129.5, 133.2, 136.1, 136.3, 136.8, 136.9, 137.0, 137.2, 137.3, 139.1, 140.9, 141.1, 147.5, 149.4 × 2 (all C_{quat}). Four C_{quat} and two CH cannot be observed due to signal overlap. MS (70 eV), m/z (%): 730 (100) [M$^+$]. Elemental analysis calcd. (%) for $C_{56}H_{58}$ (731.1): C 92.00, H 8.00; found: C 92.16, H 8.15. HRMS (EI) calcd. for $C_{56}H_{58}$: 730.4539; found: 730.4537.

7-Pentafluorophenyl-8,9,10-triphenylfluoranthene (9n): According to **GP2**, a mixture of diyne **4d** (105 mg, 0.25 mmol), alkyne **5a** (223 mg, 1.25 mmol), Wilkinson's catalyst (12 mg, 13.0 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 130 °C for 72 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (20:1) afforded 116 mg (77%) of **9n** [$R_f = 0.27$ (SiO_2, hexane/CH_2Cl_2 10:1)] as a pale orange solid, mp 304 °C. IR (KBr): ν cm^{-1} = 1522, 1494, 988, 700. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.64 (d, J = 6.9 Hz, 1 H), 6.80 (d, J = 6.9 Hz, 1 H), 6.82−6.92 (m, 5 H), 6.96−7.02 (m, 5 H), 7.27−7.34 (m, 6 H), 7.44 (dd, J = 6.9, 8.1 Hz, 1 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ = 114.5 (C_{quat}, dd, J = 3.1, 20.6 Hz), 121.0, 123.7, 125.7, 126.6, 126.7, 126.9, 127.1, 127.2, 127.5, 127.7, 128.0, 128.2, 129.5, 129.8, 130.9 (all +), 120.2, 133.1, 135.2, 136.0, 137.1, 137.3, 138.9, 139.1, 141.2, 141.8, 142.4 (m), 145.6 (m) (all C_{quat}). Four C_{quat} cannot be observed due to signal overlap or too weak. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ ppm = −162.8 (m, 2 F), −155.2 (t, J = 20.9 Hz, 1 F), −139.0 (dd, J = 8.2, 23.4 Hz, 2 F). MS (70 eV), m/z (%): 596 (100) [M$^+$]. HRMS (EI) calcd for $C_{40}H_{21}F_5$: 596.1563; found: 596.1558.

7,10-Bis(2-bromophenyl)-8,9-di-*n*-propylfluoranthene (9o) and two cyclization adducts: According to **GP2**, a mixture of diyne **4d** (243 mg, 0.50 mmol), alkyne **5c** (276 mg, 2.50 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 110 °C for 60 h. After cooling to room temperature, the solvent is removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (10:1) afforded 247 mg (ca. 83%) of **9o** and two cyclization adducts [ratio range from 97:3:0 to 89:7:4 over several runs; $R_f = 0.65$ (Al_2O_3, hexane/CH_2Cl_2 3:1)] as a pale yellow solid, mp 227−230 °C. MS (70 eV), m/z (%): 599/598/597/596/595/594 (18/54/37/100/20/51) [M$^+$ of **9o**], 516 (11) [M$^+$ − Br], 489/488/487/486 (20/57/23/54) [M$^+$ of two cyclization products], 460 (26), 377 (31), 365 (18), 188 (14), 182 (13). **9o**: ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.82 (t, J = 7.2 Hz, 6 H), 1.38−1.65 (m, 4 H), 2.32−2.45 (m, 2 H), 2.54−2.67 (m, 2 H), 6.25 (s, 1 H), 6.27 (s, 1 H), 7.21−7.27 (m, 2 H), 7.38−7.44 (m, 2 H), 7.50−7.54 (m, 4 H), 7.64 (d, J = 8.1 Hz, 2 H), 7.84 (d,

J = 8.1 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 14.6, 14.7 (all +), 24.1, 24.3, 32.4, 32.6 (all −), 121.6, 125.9, 126.0, 127.62, 127.66, 129.11, 129.13, 131.2, 131.6, 133.0, 133.2 (all +), 124.3, 124.6, 129.6, 132.7, 135.1, 135.3, 136.62, 136.65, 138.8, 141.2 (all C$_{quat}$). Six C$_{quat}$ and three CH cannot be observed due to signal overlap. HRMS (EI) calcd for $C_{34}H_{28}Br_2$: 594.0558; found: 594.0563.

7,10-Bis(4-*tert*-butylphenyl)fluoranthene (13b) and 3,6-Bis(4-*tert*-butylphenyl)tetracyclo-[5.4.0.0^{2,9}.0^{8,10}]undec-3,5-dieno[4,5-*d*]acenaphthylene (14b): Variant A: According to **GP2**, a mixture of diyne **4b** (221 mg, 0.50 mmol), NBD (1 mL, 9.22 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The mixture was kept in an oil bath under nitrogen at 130 °C for 60 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane afforded 87 mg of pure **13b**, a mixture (168 mg) of **13b** and **14b** and 21 mg of pure **14b**.

Variant B: Analogous to **GP2**, a mixture of diyne **4b** (110 mg, 0.25 mmol), NBD (0.5 mL, 4.61 mmol), [Rh(COD)Cl]$_2$ (3.10 mg, 6.29 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The sealed bottle was kept in an oil bath at 90 °C for 60 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on alumina (II). Elution with hexane/CH$_2$Cl$_2$ (10:1) afforded 107 mg (92%) of **13b**.

13b: a pale yellow crystal, mp 275−278 °C, R_f = 0.80 (alumina, hexane/CH$_2$Cl$_2$ 3:1). IR (KBr): ν cm^{-1} = 3049 (C−H), 2960, 1479, 1361, 1266, 1112, 824, 773, 563. − ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 1.44 (s, 18 H), 7.24 (s, 2 H), 7.28 (dd, J = 0.8, J = 7.2 Hz, 2 H), 7.34 (t, J = 7.2 Hz, 2 H), 7.53 (d, J = 8.8 Hz, 4 H), 7.57 (d, J = 8.8 Hz, 4 H), 7.70 (dd, J = 0.8, J = 7.2 Hz, 2 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 31.5 (+), 34.7 (C$_{quat}$), 122.9, 125.4, 126.5, 127.4, 128.6, 129.2, (all +), 129.7, 132.7, 136.4, 136.8, 137.7, 137.9, 150.6 (all C$_{quat}$). MS (70 eV), *m/z* (%): 466 (100) [M$^+$], 451 (34) [M$^+$ − CH$_3$], 218 (19), 190 (12), 86 (11), 84 (17). Elemental analysis calcd. (%) for $C_{36}H_{34}$ (466.7): C 92.66, H 7.34; found: C 92.24, H 7.23. HRMS (EI) calcd. for $C_{36}H_{34}$: 466.2700; found: 466.2656.

14b: a pale yellow crystal, mp 318−320 °C, R_f = 0.75 (alumina, hexane/CH$_2$Cl$_2$ 3:1). IR (KBr): ν cm^{-1} = 2960 (C−H), 1505, 1362, 1268, 802, 776. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.92 (t, J = 5.4 Hz, 1 H), 1.47 (s, 18 H), 1.55 (s, 2 H), 1.86 (d, J = 5.4 Hz, 2 H), 2.60 (s, 3 H), 5.18 (d, J = 7.2 Hz, 2 H), 7.00 (t, J = 7.8 Hz, 2 H), 7.23 (dd, J = 1.8, J = 7.2 Hz, 2 H), 7.33 (dd, J = 1.8, J = 8.1 Hz, 2 H), 7.38 (d, J = 8.1 Hz, 2 H), 7.48 (dd, J = 2.1, J = 8.1 Hz, 2 H), 7.55 (dd, J = 2.1, J = 8.1 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 8.8, 20.6, 31.5, 33.2, 55.5 (all +), 35.1 (C$_{quat}$), 35.8 (−), 119.4, 123.4, 126.7, 126.9, 127.3, 127.5, 127.9 (all +), 131.2, 133.4, 139.8, 143.2, 144.0, 150.5 (all C$_{quat}$). One C$_{quat}$ cannot be observed due to signal overlap. MS (70 eV), *m/z* (%): 532 (100) [M$^+$], 440 (21), 57 (14) [C$_4$H$_9$$^+$]. HRMS (EI) calcd. for $C_{41}H_{40}$: 532.3130; found: 532.3119.

7-Phenyl-10-pentafluorophenylfluoranthene (13c) and 3-Phenyl-6-pentafluorophenyltetracyclo-[5.4.0.0^{2,9}.0^{8,10}]undec-3,5-dieno[4,5-*d*]acenaphthylene (14c): According to **GP2**, a mixture of diyne **4d** (209 mg, 0.50 mmol), NBD (1 mL, 9.22 mmol), Wilkinson's catalyst (23 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The mixture was kept in an oil bath at 130 °C under nitrogen for 60 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane afforded 37 mg of pure **13c**, a mixture of **13c** and **14c** (123 mg; ratio ca. 1:1) and a mixture of **13c** and **14c** (38 mg; ratio ca. 1: 10).

13c: a pale yellow crystal, mp > 350 °C, R_f = 0.70 (alumina, hexane/CH$_2$Cl$_2$ 3:1). IR (KBr): ν cm^{-1} = 3058 (C−H), 1649, 1521, 1491, 1080, 990, 774, 706. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.09 (d, J = 7.2 Hz, 1 H), 7.42 (d, J = 7.2 Hz, 1 H), 7.25 (d, J = 7.8 Hz, 1 H), 7.34 (d, J = 7.8 Hz, 1 H), 7.37 (dd, J = 7.2, J = 8.1 Hz, 1 H), 7.47 (dd, J = 7.2, J = 8.1 Hz, 1 H), 7.51−7.59 (m, 3 H), 7.61−7.66 (m, 2 H), 7.77 (d, J = 8.1 Hz, 1 H), 7.82 (d, J = 8.1 Hz, 1 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ = 121.2, 123.5, 127.0, 127.5, 127.7, 127.8, 128.0, 128.6, 128.9, 129.36, 129.39 (all +), 120.0, 129.8, 132.5, 135.1, 135.7, 137.4, 138.3, 139.9, 140.2 (all C$_{quat}$). ^{19}F NMR (282.4 MHz, CDCl$_3$): δ ppm = −162.3 (dt, J = 8.5, J = 22.9 Hz, 2 F), −155.3 (t, J = 22.2 Hz, 1 F), −140.3 (dd, J = 8.5, 23.2 Hz, 2 F). Four C$_{quat}$ cannot be observed due to signal overlap or too weak. MS (70 eV), *m/z* (%): 445/444/443 (11/100/15) [M$^+$]. HRMS (EI) calcd. for $C_{28}H_{13}F_5$: 444.0937; found: 444.0923.

14c: ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 0.96 (t, J = 5.4 Hz, 1 H), 1.58 (s, 2 H), 1.87−1.97 (m, 2 H), 2.37 (s, 1 H), 2.62 (s, 2 H), 5.84 (d, J = 7.5 Hz, 1 H), 6.11 (d, J = 7.5 Hz, 1 H), 7.05 (dd, J = 7.5, J = 8.1 Hz, 1 H), 7.20 (t, J = 7.5, J = 8.1 Hz, 1 H), 7.27−7.31 (m, 1 H), 7.41−7.50 (m, 4 H), 7.51−7.57 (m, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 8.2, 19.9, 20.8, 32.7 (all +), 35.3 (−), 53.7, 55.0, 117.7, 120.3, 123.3, 124.7, 127.1, 127.29, 127.33, 127.5, 127.6, 129.4, 129.7 (all +), 130.8, 132.3, 137.5, 137.9, 138.6, 145.1, 145.8 (all C$_{quat}$). ^{19}F NMR (282.4 MHz, CDCl$_3$): δ ppm = −161.6 (m, 2 F), −156.7 (t, J = 20.9 Hz, 1 F), −141.9 (m, 2 F). Eight C$_{quat}$ cannot be observed due to signal overlap or too weak. MS (70 eV), *m/z* (%): 510 (100) [M$^+$ of **14c**], 444 (24) [M$^+$ of **13c**]. HRMS (EI) calcd. for $C_{33}H_{19}F_5$: 510.1407; found: 510.1379.

7,10-Bis(2-bromophenyl)fluoranthene (13d) and 3,6-Bis(2-bromophenyl)tetracyclo[5.4.0.0^{2,9}.0^{8,10}]-undec-3,5-dieno[4,5-*d*]acenaphthylene (14d): Variant A: According to **GP2**, a mixture of diyne **4e** (243 mg, 0.50 mmol), NBD (1.0 mL, 9.22 mmol), Wilkinson's catalyst (23.0 mg, 25.0 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The mixture was kept in an oil bath at 110 °C under nitrogen for 60 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH$_2$Cl$_2$ (from 1:1 to 1:2) afforded 201 mg (ca. 78%) of **13d**, **14d** and intramolecular cyclization adduct (ratio ca. 100:2:2) as an inseparable mixture. The ^{1}H NMR spectrum of **13d** is identical to ref 38.

7,10-Bis(4-methoxylcarbonylphenyl)fluoranthene (13e) and 3,6-Bis(4-methoxylcarbonylphenyl)-tetracyclo[5.4.0.0^{2,9}.0^{8,10}]undec-3,5-dieno[4,5-*d*]acenaphthylene (14e): Variant A: According to **GP2**, a mixture of diyne **4f** (111 mg, 0.25 mmol), NBD (0.5 mL, 4.61 mmol), Wilkinson's catalyst (11.5 mg, 12.5 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The mixture was kept in an oil bath at 80 °C under nitrogen for 60 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH$_2$Cl$_2$ (from 1:1 to 1:2) afforded 115 mg (95%) of **13e** and **14e** as an inseparable mixture (ratio 63:37).

Variant B: According to **GP2**, a mixture of diyne **4f** (111 mg, 0.25 mmol), NBD (0.5 mL, 4.61 mmol), [RhCl(COD)]$_2$ (3.1 mg, 6.25 μmol) and *p*-xylene (10 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The mixture was kept in an oil bath at 80 °C under nitrogen for 60 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH$_2$Cl$_2$ (1:2) afforded 116 mg (99%) of **13e**.

13e: a white solid, mp 259−260 °C, R_f = 0.30 (alumina, hexane/CH$_2$Cl$_2$ 1:2). IR (KBr): ν cm^{-1} = 2952 (C−H), 1720 (C═O), 1607, 1437, 1276, 1115, 829, 780, 769, 707. ^{1}H NMR (300 MHz, CDCl$_3$): δ ppm = 4.02 (s, 6 H), 7.21 (d, J = 7.2 Hz, 2 H), 7.27 (s, 2 H), 7.36 (t, J = 7.2 Hz, 2 H), 7.73−7.79 (m, 6 H), 8.24 (d, J = 8.1 Hz, 4 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, plus DEPT): δ ppm = 52.1, 123.1, 127.1, 127.5, 128.7, 129.1, 129.9 (all +), 129.6, 129.8, 132.6, 135.5, 136.7, 137.2, 145.5, 166.9 (all C$_{quat}$). MS (70 eV), *m/z* (%): 470 (100) [M$^+$], 352 (10). Elemental analysis calcd (%) for $C_{32}H_{22}O_4$ (470.5): C 81.69, H 4.71; found: C 81.46, H 4.75. HRMS (EI) calcd for $C_{32}H_{22}O_4$: 470.1518; found: 470.1528.

14e: A mixture of **13e** and **14e** was obtained as a yellow solid. **14e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.96 (t, J = 5.4 Hz, 1 H), 1.57 (s, 2 H), 1.85 (d, J = 5.4 Hz, 2 H), 2.55 (s, 2 H), 2.61 (s, 1 H), 4.00 (s, 6 H), 5.88 (d, J = 7.5 Hz, 2 H), 7.02 (t, J = 7.5 Hz, 2 H), 7.42 (dd, J = 2.7, J = 7.5 Hz, 4 H), 7.53 (dd, J = 1.5, J = 7.8 Hz, 2 H), 8.16 (dd, J = 1.5, J = 7.8 Hz, 2 H), 8.24 (dd, J = 2.7, J = 7.5 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 8.4, 20.2, 33.2, 52.0, 54.7 (all +), 35.2 (−), 120.1, 123.5, 127.1, 127.76, 128.1, 130.8, 131.1 (all +), 128.9, 130.75, 133.1, 137.5, 138.4, 141.7, 151.1, 166.9 (all C_{quat}). MS (70 eV), m/z (%): 536 (22) [M^+ of **14e**], 470 (100) [M^+ of **13e**]. HRMS (EI) calcd. for $C_{37}H_{28}O_4$: 536.1988; found: 536.1996.

6a,14a-dihydro-7,14-diphenylacenaphtho[*1,2-k*]fluoranthene (15) and 7,14-diphenylacenaphtho-[*1,2-k*]fluoranthene (16): Similar to **GP2**, a mixture of diyne **4a** (164 mg, 0.50 mmol), **6** [381 mg (75% purity), 2.50 mmol], Wilkinson's catalyst (23.0 mg, 5.00 μmol) and *p*-xylene (20 mL) in a Pyrex bottle at ambient temperature was purged with nitrogen for 5 min. The mixture was kept in an oil bath at 130 °C under nitrogen for 46 h. After cooling to room temperature and removal of the solvent, the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (from 7:1 to 4:1) afforded an inseparable mixture (ratio ca. 10:1) of **15** and **16** [182 mg (ca. 75%); R_f = 0.24 (SiO_2, hexane/CH_2Cl_2 3:1)] as a yellow solid. **15**: ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 5.28 (s, 2 H), 6.31 (d, J = 6.9 Hz, 2 H), 6.70 (d, J = 7.2 Hz, 2 H), 7.17 (dd, J = 7.2, J = 8.1 Hz, 2 H), 7.22 (dd, J = 6.9, J = 8.1 Hz, 2 H), 7.47−7.65 (m, 10 H), 7.51 (d, J = 8.1 Hz, 2 H), 7.57 (d, J = 8.1 Hz, 2 H). Due to the lower solubility and stability of **15**, the ^{13}C NMR spectrum could not be recorded. MS (70 eV), m/z (%): 480 (100) [M^+ of **15**], 478 (70) [M^+ of **16**], 403 (37), 326 (12), 206 (19). HRMS (EI) calcd. for $C_{38}H_{24}$: 480.1878; found: 480.1851. ^{1}H NMR spectra of **16** is identical to the reference,[8b] but the integration of the signal at 6.67 ppm should be 4 H, instead of 2 H.

3-Bromo-11-(2-bromophenyl)benzo[*j*]fluoranthene (23): A mixture of **4e** (243 mg, 0.50 mmol) and *p*-xylene (20 mL) in a screw-capped Pyrex bottle was purged with nitrogen for 5 min and the sealed bottle was kept in an oil bath at 110 °C for 60 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was washed with hexane (5 × 5 mL) to give **23** (170 mg, = 70%) as a yellow-brown solid, mp 249−252 °C. IR (KBr): ν cm^{-1} = 3053 (C−H), 1567, 1471, 1432, 1026, 876, 760, 728. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 6.77 (d, J = 6.9 Hz, 1 H), 7.32−7.92 (m, 11 H), 8.49 (d, J = 7.2 Hz, 1 H), 8.94 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 121.4, 123.8, 129.4, 131.0, 131.77, 131.81, 133.2, 135.7, 135.8, 136.3, 136.6, 141.1 (all C_{quat}), 123.7, 124.2, 126.5, 127.4, 127.56, 127.6, 127.90, 127.94, 128.6, 128.9, 129.6, 130.8, 131.0, 132.9 (all +). MS (70 eV), m/z (%): 489/488/487/486/485/484 (12/44/24/85/12/ 41) [M^+], 406 (11) [$M^+ - Br$], 326 (100) [$M^+ - Br_2$], 163 (57). HRMS (EI) calcd. for $C_{26}H_{14}Br_2$: 483.9462; found: 483.9459.

General Procedure for Preparation Diynes **27** (**GP3**): A solution of dichloride **25** (0.50 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), IPr•HCl (85 mg, 0.20 mmol) and *t*BuOK (22.4 mg, 0.20 mmol) or NEt_3 (1 mL, in the case of ester) in DME (10 mL) in a Schlenk tube is heated at 50 °C under nitrogen for 30 min. Then, trimethyltin substituted alkyne **26** is added to the above solution and the mixture is refluxed at 110 °C under nitrogen for 3 d. After cooling to room temperature, the solvent is removed under reduced pressure. The residue is subjected to chromatography on silica gel (or alumina). Elution with hexane/CH_2Cl_2 affords the coupling product **27** in an acceptable purity.

2,3-Bis(phenylethynyl)corannulene (27a): According to **GP3**, a solution of dichloride **25a** (159 mg, 0.50 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), IPr•HCl (85.0 mg, 0.20 mmol) and *t*BuOK (22.4 mg, 0.20 mmol) in DME (10 mL) was heated at 50 °C under nitrogen for 30 min. Then, alkyne **26a** was added to the above solution and the mixture was refluxed at 110 °C for 3 d. After removal of the solvent, the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (from 15:1 to 5:1) afforded 75.0 mg (33%) of **27a** [R_f = 0.32 (SiO_2, hexane/ CH_2Cl_2 3:1] as a brown semisolid. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 7.08−7.21 (m, 6 H), 7.38−7.41 (m, 4 H), 7.60 (d, J = 8.7 Hz, 2 H), 7.65 (s, 2 H), 7.66 (d, J = 8.7 Hz, 2 H), 8.05 (s, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 89.5, 94.3, 121.1, 123.5, 129.8, 130.9, 134.3, 134.5, 135.4 (all C_{quat}), 126.2, 127.2, 127.6, 127.96, 127.98, 131.8, 133.9 (all +). One C_{quat} was not observed due to signal overlap. MS (70 eV), m/z (%): 450 (100) [M^+], 338 (34), 224 (30). HRMS (EI) calcd. for $C_{36}H_{18}$: 450.1409; found: 450.1392.

2,3-Bis(1-pentynyl)corannulene (27b): According to **GP3**, a solution of dichloride **25a** (450 mg, 1.42 mmol), $Pd(OAc)_2$ (64.0 mg, 0.29 mmol), IPr•HCl (241 mg, 0.57 mmol) and *t*BuOK (64.0 mg, 0.57 mmol) in DME (15 mL) was heated at 50 °C under nitrogen for 30 min. Then, alkyne **26b** was added to the above solution and the mixture was refluxed at 110 °C for 3 d. After removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 8:1 to 3:1) afforded 183 mg (34%) of **27b** as a pale yellow oil, R_f = 0.15 (Al_2O_3, hexane/CH_2Cl_2 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 1.13 (t, J = 7.2 Hz, 6 H), 1.74 (sext, J = 7.2 Hz, 4 H), 2.55 (t, J = 7.2 Hz, 4 H), 7.65 (d, J = 8.7 Hz, 2 H), 7.70 (s, 2 H), 7.72 (d, J = 8.7 Hz, 2 H), 7.95 (s, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 13.7 (+), 22.2, 22.3 (all −), 80.5, 95.1, 122.1, 128.3, 129.9, 130.8, 134.3, 135.5 (all C_{quat}), 126.2, 127.0, 127.4, 133.2 (all +). One C_{quat} cannot be observed due to signal overlap. MS (70 eV), m/z (%): 382 (100) [M^+], 353 (62) [$M^+ - C_2H_5$], 337 (57), 322 (16), 162 (14), 149 (10), 60 (12). HRMS (EI) calcd for $C_{30}H_{22}$: 382.1722; found: 382.1709.

1,2-Dimethoxycarbonyl-6,7-bis(phenylethynyl)corannulene (27c): According to **GP3**, a solution of dichloride **25b** (217 mg, 0.50 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), IPr·HCl (85.0 mg, 0.20 mmol) and NEt_3 (1 mL) in DME (10 mL) was heated at 50 °C under nitrogen for 30 min. Then, alkyne **26a** was added to the above solution and the mixture was refluxed at 110 °C for 62 h. After removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 1:1 to 1:2) afforded 185 mg (65%) of **27c** **[**R_f = 0.54 (Al_2O_3, hexane/CH_2Cl_2 1:2] as a brown oil in an acceptable purity. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 4.05 (s, 6 H), 7.12−7.28 (m, 6 H), 7.38−7.45 (m, 4 H), 7.78 (d, J = 8.7 Hz, 2 H), 8.06 (d, J = 8.7 Hz, 2 H), 8.10 (s, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 52.9 (+), 89.0, 95.3, 122.7, 123.3, 127.2, 130.7, 131.8, 133.7, 167.5 (all C_{quat}), 127.4, 127.8, 128.0, 128.3, 131.9, 133.9 (all +). Three C_{quat} cannot be observed due to signal overlap. MS (70 eV), m/z (%): 566 (100) [M^+], 520 (12), 448 (29), 224 (13). HRMS (EI) calcd for $C_{40}H_{22}O_4$: 566.1518; found: 556.1502.

1,2-Dimethoxycarbonyl-6,7-bis(1-pentynyl)corannulene (27d): According to **GP3**, a solution of dichloride **25b** (217 mg, 0.50 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), IPr•HCl (85.0 mg, 0.20 mmol) and NEt_3 (1 mL) in DME (10 mL) was heated at 50 °C under nitrogen for 30 min. Then, alkyne **26b** was added to the above solution and the mixture was refluxed at 110 °C for 2.5 d. After removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 3:1 to 3:2) afforded 141 mg (57%) of **27d** [R_f = 0.31 (Al_2O_3, hexane/CH_2Cl_2 2:1)] as a yellow-brown semisolid. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 1.14 (t, J = 7.2 Hz, 6 H), 1.75 (sext, J = 7.2 Hz, 4 H), 2.56 (t, J = 7.2 Hz, 4 H), 4.07 (s, 6 H), 7.73 (d, J = 9.0 Hz, 2 H), 7.94 (s, 2 H), 8.02 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 14.2 (+), 22.65, 24.74 (all −), 53.3 (+), 80.7, 96.8, 123.9, 127.3, 129.0, 131.2, 132.0, 133.8, 135.5, 136.0, 167.9 (all C_{quat}), 127.5, 128.0, 133.7 (all +). MS (70 eV), m/z (%): 498 (100) [M^+], 469 (37), 437 (42), 350 (39), 337 (56), 322 (59), 205 (38), 168 (53), 162 (76), 155 (64).

1-Methoxycarbonyl-2-phenyl-6,7-bis(1-phenylethynyl)corannulene (27e): According to **GP3**, a solution of dichloride **25c** (160 mg, 0.35 mmol), $Pd(OAc)_2$ (16.0 mg, 71.3 μmol), IPr•HCl (60.0 mg, 0.14 mmol) and NEt_3 (1 mL) in DME (10 mL) was heated at 50 °C under nitrogen for 30 min. Then, alkyne **26a** was added to the above solution and the mixture was refluxed at 110 °C for 3 d. After removal of the solvent, the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (1:2) afforded 87.0 mg (42%) of **27e** [R_f = 0.56 (Al_2O_3, hexane/CH_2Cl_2 1:2] as a yellow-brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 3.69 (s, 3 H), 7.12−7.18 (m, 4 H), 7.22−7.28 (m, 2 H), 7.39−7.46 (m, 4 H), 7.48−7.58 (m, 6 H), 7.67 (d, J = 8.7 Hz, 1 H), 7.79 (d, J = 8.7 Hz, 1 H), 8.06 (d, J = 9.0 Hz, 1 H), 8.01 (s, 1 H), 8.14 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 52.0 (+), 89.2, 94.6, 94.7, 121.6, 122.2, 123.2, 123.3, 128.7, 129.2, 129.4, 129.7, 130.5, 134.1, 134.2, 134.3, 135.0, 135.7, 137.8, 141.9, 168.7 (all C_{quat}), 126.9, 127.0, 127.1, 127.9, 128.0, 128.1, 129.8, 131.8, 133.7, 133.9 (all +). Two C_{quat} and two CH signals cannot be observed due to signal overlap. MS (70 eV), m/z (%): 584 (100) [M^+], 524 (36), 275 (13), 261 (42), 149 (29). HRMS (EI) calcd. for $C_{44}H_{24}O_2$: 584.1776; found: 584.1788.

9,10,11,12-Tetraphenylindenocorannulene (28a): According to **GP2**, a mixture of diyne **27a** (65.0 mg, 144 μmol), alkyne **5a** (128 mg, 718 μmol), Wilkinson's catalyst (7.0 mg, 7.56 μmol) and *p*-xylene (10 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction mixture was heated at 130 °C under nitrogen for 39 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2 (from 10:0 to 5:1) afforded 49.0 mg (54%) of **28a** [R_f = 0.15 (SiO_2, cyclohexane/CH_2Cl_2 8:1)] as a yellow solid, mp 274−277 °C. IR (KBr): ν cm^{-1} = 3053, 3025, 1601, 1496, 1441, 1377, 1070, 1025, 885, 826, 742, 698. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 6.27 (s, 2 H), 6.65−6.90 (m, 12 H), 7.05−7.15 (m, 4 H), 7.18−7.25 (m, 6 H), 7.34 (t, J = 7.5 Hz, 2 H), 7.55 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 123.3, 124.5, 125.27, 125.29, 125.9, 126.0, 126.7, 127.2, 127.5, 129.1, 129.2, 129.7, 130.5 (all +), 128.9, 135.9, 136.3, 136.5, 137.1, 137.5, 138.3, 138.5, 139.6, 140.5, 143.7 (all C_{quat}). One C_{quat} and one CH cannot be observed due to signal overlap. MS (70 eV), m/z (%): 628 (100) [M^+], 548 (10). HRMS (EI) calcd. for $C_{50}H_{28}$: 628.2191; found: 628.2212.

10-(1-Methyl-1-hydroxyethanyl)-9,12-diphenylindenocorannulene (28b): According to **GP2**, a mixture of diyne **27a** (68.0 mg, 151 μmol), alkyne **5b** (110 mg, 1.30 mmol), Wilkinson's catalyst (7.0 mg, 7.57 μmol) and *p*-xylene (10 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction was heated at 130 °C under nitrogen for 46 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on SiO_2. Elution with hexane/CH_2Cl_2/Et_2O (from 1:5:0 to 10:3:10) afforded 48.0 mg (60%) of **28b** [R_f = 0.36 (SiO_2, hexane/Et_2O 1:1)] as a yellow solid, mp 248−250 °C. IR (KBr): ν cm^{-1} = 3409 (O−H), 2967 (C−H), 1724, 1599, 1440, 1361, 1150, 1071, 885, 827, 705. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm = 1.504 (s, 3 H), 1.508 (s, 3 H), 1.81 (s, 1 H), 5.79 (s, 1 H), 6.97 (s, 1 H), 7.22 (d, J = 9.0 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 1 H), 7.41 (d, J = 8.4 Hz, 1 H), 7.42 (d, J = 9.0 Hz, 1 H), 7.43 (s, 2 H), 7.46 (s, 1 H), 7.49−7.63 (m, 5 H), 7.67−7.80 (m, 5 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 32.4, 32.6 (all +), 74.2 (C_{quat}), 123.3, 124.5, 126.29, 126.33, 126.8, 126.9, 127.7, 127.9, 128.02, 128.09, 128.14, 128.7, 128.9, 129.5, 130.2, 130.5 (all +), 129.9, 135.4, 135.7, 136.6, 136.8, 137.3, 137.4, 138.0, 138.1, 138.3, 139.1, 140.4, 140.55, 140.59, 144.4, 146.7 (all C_{quat}). Three C_{quat} and one CH cannot be observed due to the signals overlap. MS (70 eV), m/z (%): 534 (7) [M^+], 516 (100) [M^+ − H_2O], 501 (42), 250 (13). HRMS (EI) calcd for $C_{41}H_{26}O$: 534.1984; found: 534.1988.

10-Formyl-9,12-di-*n*-propylindenocorannulene (28c): According to **GP2**, a mixture of diyne **27b** (157 mg, 0.41 mmol), alkyne **5k** (263 mg, 2.05 mmol), Wilkinson's catalyst (19.0 mg, 20.5 μmol) and *p*-xylene (16 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The solution was maintained at 130 °C under nitrogen atmosphere for 60 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 1:0 to 2:1) afforded 108 mg of **27b** and an inseparable mixture (ca. 120 mg) of **28c** and trimerization adducts of **5k**. The mixture was diluted with THF (50 mL) and treated with concentrated hydrochloric acid (1 mL). The solution was stirred at room temperature for 1 h. After aqueous workup and removal of the solvent, the residue was subjected to chromatography on alumina, eluting with hexane/CH_2Cl_2 (2:1) to afford 25 mg (14%) of **28c** [R_f = 0.23 (Al_2O_3, hexane/CH_2Cl_2 2:1)] as a yellow semisolid. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 1.12 (t, J = 7.4 Hz, 3 H), 1.18 (t, J = 7.4 Hz, 3 H), 1.73−1.89 (m, 4 H), 2.98−3.11 (m, 2 H), 3.27−3.39 (m, 1 H), 3.44−3.58 (m, 1 H), 7.49 (s, 2 H), 7.537 (s, 1 H), 7.538 (d, J = 9.0 Hz, 2 H), 7.61 (d, J = 9.0 Hz, 2 H), 7.69 (s, 1 H), 7.76 (s, 1 H), 10.26 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 14.1, 14.2 (all +), 22.6, 24.1, 30.4, 35.2 (all −), 124.3, 124.8, 126.89, 126.93, 127.2, 127.4, 128.2, 128.3, 133.9, 191.8 (all +), 130.3, 130.4, 133.7, 136.5, 136.7, 137.0, 137.6, 138.13, 138.15, 138.30, 138.5, 139.0, 139.6, 140.0, 140.1, 143.2, 144.7 (all C_{quat}). MS (70 eV), m/z (%): 436 (100) [M^+], 407 (M^+ − CHO), 350 (20), 149 (27). HRMS (EI) calcd. for $C_{33}H_{24}O$: 436.1827; found: 536.1811.

10,11-Diphenyl-9,12-di-*n*-propylindenocorannulene (28e): According to **GP2**, a mixture of diyne **27b** (28.1 mg, 73.0 μmol), alkyne **5a** (62 mg, 0.35 mmol), Wilkinson's catalyst (3.5 mg, 3.78 μmol) and *p*-xylene (10 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction was maintained at 130 °C under nitrogen for 3 d. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 1:0 to 10:1) afforded 17.0 mg (42%) of **28e** [R_f = 0.40 (Al_2O_3, hexane/CH_2Cl_2 5:1)] as a yellow solid, mp 242−243 °C. IR (KBr): ν cm^{-1} = 3048 (C−H), 2957, 2924, 2869, 1598, 1465, 1378, 1069, 867, 819, 700, 565. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.90 (s, 6 H), 1.40−1.57 (m, 2 H), 1.57−1.74 (m, 2 H), 2.67−2.81 (m, 4 H), 6.89−6.97 (m, 2 H), 6.98−7.17 (m, 8 H), 7.52 (s, 2 H), 7.64 (d, J = 9.0 Hz, 2 H), 7.63 (d, J = 9.0 Hz, 2 H), 7.68 (s, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 14.4 (+), 23.0, 33.2 (all -), 123.1, 125.9, 126.7, 126.91, 126.94, 127.1, 128.2, 130.0, 130.4 (all +), 130.1, 135.6, 137.0, 137.6, 137.9, 140.3, 141.2, 142.6 (all C_{quat}). Two C_{quat} cannot be observed due to signal overlap. MS (70 eV), m/z (%): 560 (100) [M^+], 489 (41), 356 (20), 243 (11). HRMS (EI) calcd. for $C_{44}H_{32}$: 560.2504; found: 560.2496.

4,5-Di(methoxycarbonyl)-9,10,11,12-tetraphenylindenocorannulene (28f): According to **GP2**, a mixture of diyne **27c** (85 mg, 0.15 mmol), alkyne **5a** (134 mg, 0.75 mmol), Wilkinson's catalyst (7.0 mg, 7.57 μmol) and *p*-xylene (8 mL) in a Schlenk tube at ambient temperature purged with nitrogen for 5 min. The reaction was maintained at 130 °C under nitrogen for 3 d. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 3:1 to 1:1) afforded 70.0 mg (64%) of **28f** [R_f = 0.55 (Al_2O_3, hexane/CH_2Cl_2 1:2)] as a yellow solid, mp 315−320 °C. IR (KBr): ν cm^{-1} = 2953 (C−H), 2925, 1727 (C=O), 1440, 1264, 1071, 744, 698. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 4.00 (s, 6 H), 6.36 (s, 2 H), 6.72−7.00 (m, 12 H), 7.23 (t, J = 7.5 Hz, 2 H), 7.28−7.35 (m, 4 H), 7.43 (t, J = 7.5 Hz, 2 H), 7.61 (d, J = 7.8 Hz, 2 H), 7.69 (s, J = 7.8 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 52.6, 124.1, 125.2, 125.7, 126.3, 126.8, 127.1, 128.4, 129.4, 129.9, 130.0, 130.6 131.4 (all +), 136.9, 137.1, 137.3, 137.5, 139.0, 139.2, 141.7, 141.9, 167.3 (all C_{quat}). Five C_{quat} and one CH cannot be observed due to signal overlap. MS (70 eV), m/z (%): 744 (100) [M^+], 322 (14), 293 (17), 167 (16), 149 (66), 71 (18), 57 (19). HRMS (EI) calcd. for $C_{54}H_{32}O_4$: 744.2301; found: 744.2290.

4,5,10,11-Tetra(methoxycarbonyl)-9,12-diphenylindenocorannulene (28g): According to **GP2**, a mixture of diyne **27c** (87.0 mg, 0.15 mmol), alkyne **5e** (109 mg, 0.77 mmol), Wilkinson's catalyst (7.0 mg, 7.57 μmol) and *p*-xylene (10 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction was maintained at 130 °C under nitrogen for 60 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 1:3 to 3:1) afforded 17.6 mg (17%) of **28g** [R_f = 0.45 (alumina, CH_2Cl_2)] as a yellow solid, mp 324−326 °C. IR (KBr): ν cm^{-1} = 2949 (C−H), 1728 (C=O), 1436, 1223, 1083, 701. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 3.53 (s, 6 H), 3.99 (s, 6 H), 6.46 (s, 2 H), 7.24−7.29 (m, 2 H), 7.38 (d, J = 9.0 Hz, 2 H), 7.47−7.63 (m, 6 H), 7.70−7.77 (m, 2 H), 7.73 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 52.6, 53.2, 126.0, 126.6, 128.9, 129.0, 129.43, 129.47, 129.8, 130.0 (all +), 131.8, 132.8, 136.3, 137.2, 137.3, 137.4, 137.6, 139.3, 139.9, 140.1, 144.7, 167.2, 167.8 (all C_{quat}). One C_{quat} cannot be observed due to signal overlap. MS (70 eV), *m/z* (%): 708 (100) [M$^+$], 677 (25) [M$^+$ − OCH_3], 322 (23), 206 (10), 149 (48), 91 (15), 57 (12). HRMS (EI) calcd. for $C_{46}H_{28}O_8$: 708.1784; found: 708.1766.

4,5-Di(methoxycarbonyl)-9,12-diphenyl-10,11-di-*n*-propylindenocorannulene (28h): According to **GP2**, a mixture of diyne **27c** (53.0 mg, 93.5 μmol), alkyne **5c** (52.0 mg, 0.47 mmol), Wilkinson's catalyst (4.3 mg, 4.65 μmol) and *p*-xylene (5 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction was maintained at 110 °C under nitrogen for 3 d. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 3:1 to 1:1) afforded 36.1 mg (57%) of **28h** [R_f = 0.34 (alumina, hexane/CH_2Cl_2 1:1)] as a yellow solid. IR (KBr): ν cm^{-1} = 2955 (C−H), 2870, 1727 (C=O), 1439, 1263, 1172, 703. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.72 (t, J = 7.2 Hz, 6 H), 1.43 (sext, J = 7.2 Hz, 4 H), 2.32−2.54 (m, 4 H), 3.98 (s, 6 H), 6.04 (s, 2 H), 7.31 (d, J = 9.0 Hz, 2 H), 7.48−7.60 (m, 6 H), 7.63−7.67 (m, 4 H), 7.68 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 14.6 (+), 24.6, 32.3 (all −), 52.6, 123.4, 125.5, 127.5, 128.3, 129.0, 129.1, 129.3, 129.6 (all +), 125.6, 131.3, 135.9, 136.7, 137.5, 137.7, 138.4, 140.0, 140.3, 142.3, 167.4 (all C_{quat}). Two C_{quat} cannot be observed due to signal overlap. MS (70 eV), *m/z* (%): 676 (100) [M$^+$], 615 (13), 573 (14), 466 (25), 149 (21), 91 (11). HRMS (EI) calcd. for $C_{48}H_{36}O_4$: 676.2614; found: 676.2637.

4,5-Di(methoxycarbonyl)-10,11-diphenyl-7,12-di-*n*-propylindenocorannulene (28i): According to **GP2**, a mixture of diyne **27c** (85.0 mg, 0.17 mmol), alkyne **5a** (152 mg, 0.85 mmol), Wilkinson's catalyst (8.0 mg, 8.65 μmol) and *p*-xylene (5 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction was maintained at 110 °C under nitrogen for 3 d. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 3:1 to 1:1) afforded 42.6 mg (42%) of **28i** [R_f = 0.34 (alumina, hexane/CH_2Cl_2 1:1)] as a yellow solid, mp 158−161 °C. IR (KBr): ν cm^{-1} = 2953 (C−H), 2869, 1725 (C=O), 1436, 1261, 1171, 701. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 0.90 (t, J = 7.5 Hz, 6 H), 1.48 (m, 2 H), 1.64 (m, 2 H), 2.72 (t, J = 8.3 Hz, 4 H), 4.05 (s, 6 H), 6.93−7.17 (m, 10 H), 7.64 (s, 2 H), 7.66 (d, J = 9.0 Hz, 2 H), 7.84 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 14.5 (+), 23.2, 33.3 (all −), 52.8, 123.1, 126.1, 126.2, 127.1, 127.3, 129.6, 130.1, 130.4 (all +), 125.9, 131.6, 136.1, 136.9, 137.6, 137.7, 137.8, 138.8, 140.1, 142.4, 143.2, 144.9, 167.5 (all C_{quat}). MS (70 eV), *m/z* (%): 676 (100) [M$^+$], 573 (13), 558 (14), 466 (15), 149 (15). HRMS (EI) calcd. for $C_{48}H_{36}O_4$: 676.2614; found: 676.2604.

4-(Methoxycarbonyl)-5,9,10,11,12-pentaphenylindenocorannulene (28j): According to **GP2**, a mixture of diyne **27e** (80.0 mg, 0.14 mmol), alkyne **5a** (122 mg, 0.68 mmol), Wilkinson's catalyst (6.3 mg, 6.81 μmol) and *p*-xylene (10 mL) in a Schlenk tube at ambient temperature was purged with nitrogen for 5 min. The reaction was maintained at 130 °C under nitrogen for 46 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on alumina. Elution with hexane/CH_2Cl_2 (from 10:0 to 2:1) afforded 85.0 mg (81%) of **28j** [R_f = 0.43 (alumina, hexane/CH_2Cl_2 1:1)] as a yellow solid, mp 246−247 °C. IR (KBr): ν cm^{-1} = 3055 (C−H), 2926, 1721 (C=O), 1601, 1442, 1232, 1075, 886, 745, 699. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 3.58 (s, 3 H), 6.33 (s, 1 H), 6.36 (s, 1 H), 6.72−7.60 (m, 29 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): δ ppm = 51.8, 124.0, 124.3, 125.3, 128.5, 126.3, 126.6, 126.8, 127.0, 127.65, 127.70, 127.8, 128.1, 128.39, 128.42, 128.8, 128.9, 129.6, 130.0, 130.1, 130.6, 131.4 (all +), 127.2, 128.2, 128.7, 135.9, 136.6, 137.0, 137.28, 137.35, 137.41, 137.47, 137.6, 137.7, 138.9, 139.2, 139.4, 140.9, 141.4, 141.5, 141.6, 141.7, 144.7, 168.7 (all C_{quat}). Four C_{quat} and eight CH cannot be observed due to signal overlap. MS (70 eV), *m/z* (%): 762 (100) [M$^+$], 279 (13), 167 (22), 149 (55), 71 (13), 57 (16). HRMS (EI) calcd for $C_{58}H_{34}O_4$: 762.2559; found: 762.2582.

Computational Section

The conformational analyses of structure **IC** described in this study, including structural and orbital arrangements as well as property calculations, were carried out using the Gaussian98[64] and GAMESS[65] software packages. Structural computations were performed using hybrid density functional methods (HDFT). The HDFT method employed Becke's 3 parameter functional[66] in combination with nonlocal correlation provided by the Lee−Yang−Parr expression[67,68] that contains both local and nonlocal terms, B3LYP. Dunning's correlation consistent basis set, cc-pVDZ,[69] a [3s2p1d] contraction of a (9s4p1d) primitive set, was employed. Full geometry optimizations were performed and uniquely characterized by calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies (0 = minima; 1 = transition state). From the fully optimized structures, single point energy computations were performed using the MP2[70] dynamic correlation treatment for the analysis of chemical and physical properties such as bond localization, and bowl depth. These levels of theory have been previously shown to be reliable for structural and energetic determinations in these types of compounds.[54,57] We note a nontrivial sensitivity of predicted structure (esp. bowl depth) and barrier with the inclusion of polarization functionality and with the extent and manner of including dynamic correlation. For example, in the case of corannulene, dynamic correlation via HDFT predicts a barrier of 9.2 kcal/mol, whereas MP2 predicts 11.0 kcal/mol at the same basis set. A more complete analysis of this effect is currently being written.

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Supporting Information Available: The procedures for the preparation of 2,3-dichlororcorannulenes derivatives **26b** and **26c**, the crystal structure data of **23** and **28g** and computational data of **IC** are presented on the World Wide Web at http://pubs.acs.org. This material is available free of charge via the Internet at http://pubs.acs.org.

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