

Synthesis of Corannulene and Alkyl Derivatives of Corannulene

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Abstract: Synthesis of corannulene and alkyl corannulene derivatives has been accomplished using solution-phase chemistry. The key step in the synthesis is the coupling of benzylic bromides of 1,6,7,10-tetraalkylfluoranthene derivatives by low-valent titanium to construct the corannulene nucleus. The use of low-valent titanium represents a viable alternative to flash vacuum pyrolysis methods previously developed. Corannulene (**1**), methylcorannulene (**8**), three different dimethylcorannulenes (**2**, **3**, **5**), two different tetramethylcorannulenes (**4**, **6**), acecorannulene (**7**), C_{5h} symmetric pentamethylcorannulene (**9**), and decamethylcorannulene (**10**) have been prepared using low-valent titanium carbon–carbon coupling chemistry and halogen for alkyl exchange chemistry mediated by trimethylaluminum and catalytic nickel salts.

Corannulene (**1**), first synthesized in 1966 by Lawton and Barth,^{1,2} has received renewed attention since the discovery of macroscopic quantities of fullerenes.³ To replace the original 17-step synthesis, Scott^{4–6} and our lab^{7,8} have developed two different strategies for the synthesis of the corannulene nucleus, using flash vacuum pyrolysis (FVP) and solution-phase chemistry, respectively. Modifications to the original FVP method have been reported from various laboratories.^{9–11} Although FVP methods provide rapid access to fullerene fragments, they lack the ability to construct simple alkyl derivatives of corannulene in a regioselective manner. In contrast, solution-phase chemistry highlighted by organometallic C–C coupling methods allows controlled synthesis of corannulene and numerous alkyl derivatives (Figure 1).

Retrosynthetic Analysis. An obvious retrosynthetic disconnection of corannulene is at the flanking bonds, suggesting a dialkylfluoranthene precursor. Such a strategy might employ Friedel–Crafts or other π -mediated carbon–carbon bond-forming methodology; however, attempts using these methodologies have been uniformly unsuccessful.^{12,13} The likely downfall of such strategies is the severe distortion required to reach the transition state, leading to unreasonably high activation

energies. In contrast to Friedel–Crafts chemistry, syntheses using FVP methods have succeeded in making these flanking bonds; presumably, the activation energy is overcome by use of high temperatures (900–1100 °C).

An alternative disconnection, the rim bonds,¹⁴ suggests 1,6,7,10-tetramethylfluoranthene (**11**) as a precursor. In fluoranthene **11** the methyl groups are within van der Waals contacts of one another, and the crystal structure reveals a molecular distortion to a twisted C_2 symmetric conformation.¹⁵ Initial preparation of **1**, by way of fluoranthene **11**, utilized a relatively low-temperature pyrolysis,⁷ and this fact motivated a reinvestigation of solution-phase methods.

The key reaction in the solution-phase synthesis is the coupling of the methyl carbons to form the rim bond. A variety of methods have been developed to couple functionalized benzylic carbons. Homocoupling of benzylic and allylic halides with a low-valent titanium reagent¹⁶ proved to be our method of choice, and has led to a useful solution-phase synthesis of **1**. Further retrosynthetic analysis from fluoranthene **11** reveals 3,8-dimethylacenaphthaquinone (**12**) as a precursor¹² that would be readily available from 2,7-dimethylnaphthalene. Substituted acenaphthaquinones with appropriate functionality in the 3 and 8 positions represent the keystones for the syntheses of alkyl corannulenes in general, of which corannulene (**1**), methylcorannulene (**8**), three different dimethylcorannulenes (**2**, **3**, **5**), two different tetramethylcorannulenes (**4**, **6**), acecorannulene (**7**), C_{5h} symmetric pentamethylcorannulene (**9**), and decamethylcorannulene (**10**) have been prepared.

Corannulene and 2,5-Dimethylcorannulene. Synthesis of **1** (Scheme 1) follows a route similar to our previous work.^{7,15} Formaldehyde and HCl in acetic acid accomplish a chloromethylation in the 1 position of 2,7-dimethylnaphthalene (**13**). The chlorine is displaced by cyanide, hydrolyzed to the carboxylic acid, and cyclized by way of the acid chloride in three steps to yield 3,8-dimethyl-1-acenaphthenone (**17**).¹⁷ Ketone **17**

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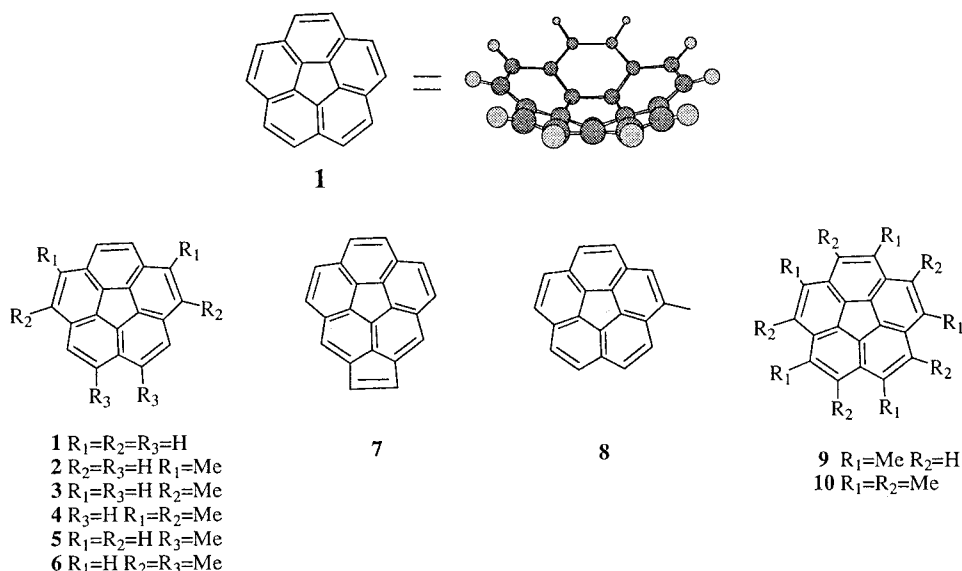


Figure 1. Derivatives of corannulene (1).

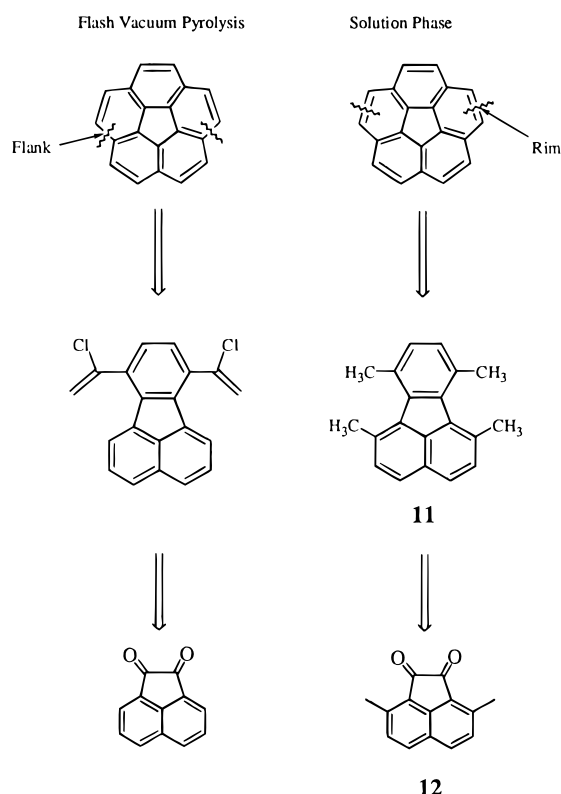


Figure 2. Retrosynthetic disconnections of corannulene.

is oxidized with selenium dioxide in dioxane/water to yield diketone **12**. Diketone **12** is condensed with 3-pentanone in methanolic potassium hydroxide to construct the cyclopentadienone precursor. The cyclopentadienone is generated in acetic anhydride and trapped by a Diels–Alder reaction with norbornadiene, an acetylene equivalent. A cascade of retrocycloadditions follows to release cyclopentadiene and carbon monoxide, and affords fluoranthene **11**. Fluoranthene **11** is brominated with *N*-bromosuccinimide (NBS) under irradiation with light to yield 1,6,7,10-tetrakis(dibromomethyl)fluoranthene (**18**). In early work, octabromide **18** was reacted with the low-valent titanium reagent generated from TiCl₃ and LiAlH₄ to afford **1** in 33% yield. Later procedures, using TiCl₄ and Zn–Cu couple, increase the yield of **1** to 80%.

A slightly modified method of this corannulene synthesis leads to 2,5-dimethylcorannulene (**2**) (Scheme 1).⁸ At the cyclopentadienone precursor stage, 4-heptanone is used instead of 3-pentanone. In addition, because the resulting 7,10-diethyl-1,6-dimethylfluoranthene (**19**) does not form an octabromide, the reductive coupling (TiCl₃–LiAlH₄) is performed on the tetrabromide **20** followed by a 2,3-dichloro-5,6-dicyanoquinone (DDQ) oxidation to yield corannulene **2**.

1,6-Dimethylcorannulene (3) and 1,2,5,6-Tetramethylcorannulene (4). The synthesis of 1,6-dimethylcorannulene (**3**) (Scheme 2) starts from 2,7-dibromonaphthalene (**21**).^{18,19} Nickel-catalyzed Kumada coupling²⁰ of the aryl bromides with ethylmagnesium chloride yields 2,7-diethylnaphthalene. Synthesis of 1,6-diethyl-7,10-dimethylfluoranthene (**27**) from naphthalene **21** proceeds in a manner analogous to the synthesis of fluoranthenes **11** and **19** shown in Scheme 1. As with fluoranthene **19**, fluoranthene **27** is brominated with NBS under irradiation with light to yield the tetrabromide **28**, which is coupled by the improved low-valent titanium reagent (TiCl₄/Zn–Cu) to yield 1,6-dimethyltetrahydrocorannulene. Dehydrogenation with DDQ yields corannulene **3**.

Synthesis of 1,2,5,6-tetramethylcorannulene (**4**) (Scheme 2) draws from the syntheses of corannulenes **2** and **3**. 4-Heptanone is used in the two-step conversion of 3,8-diethylacenaphthaquinone (**26**) to 1,6,7,10-tetraethylfluoranthene (**29**). Bromination of fluoranthene **29** with NBS under irradiation with light yields the tetrabromide **30**, which is coupled by the low-valent titanium reagent followed by dehydrogenation with DDQ to yield corannulene **4**. Although only run once, the yield of this dehydrogenation (6%) is notably lower than that seen in previous dehydrogenations, and deserves further investigation.

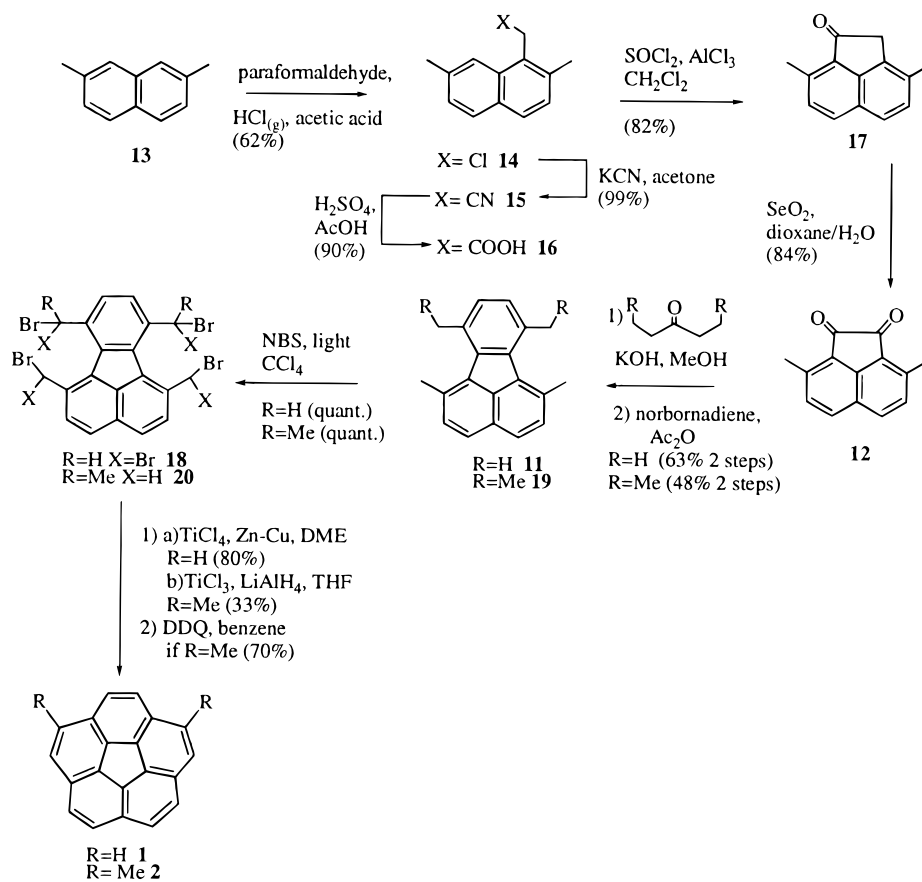
2,3-Dichlorocorannulene, 2,7-Dimethyl-4,5-dichlorocorannulene, and Accorannulylene. Whereas the methods described above give relatively fast and efficient access to several corannulene derivatives, synthesis of derivatives with substituents in the peri positions would not be possible. An alternative route was therefore developed.

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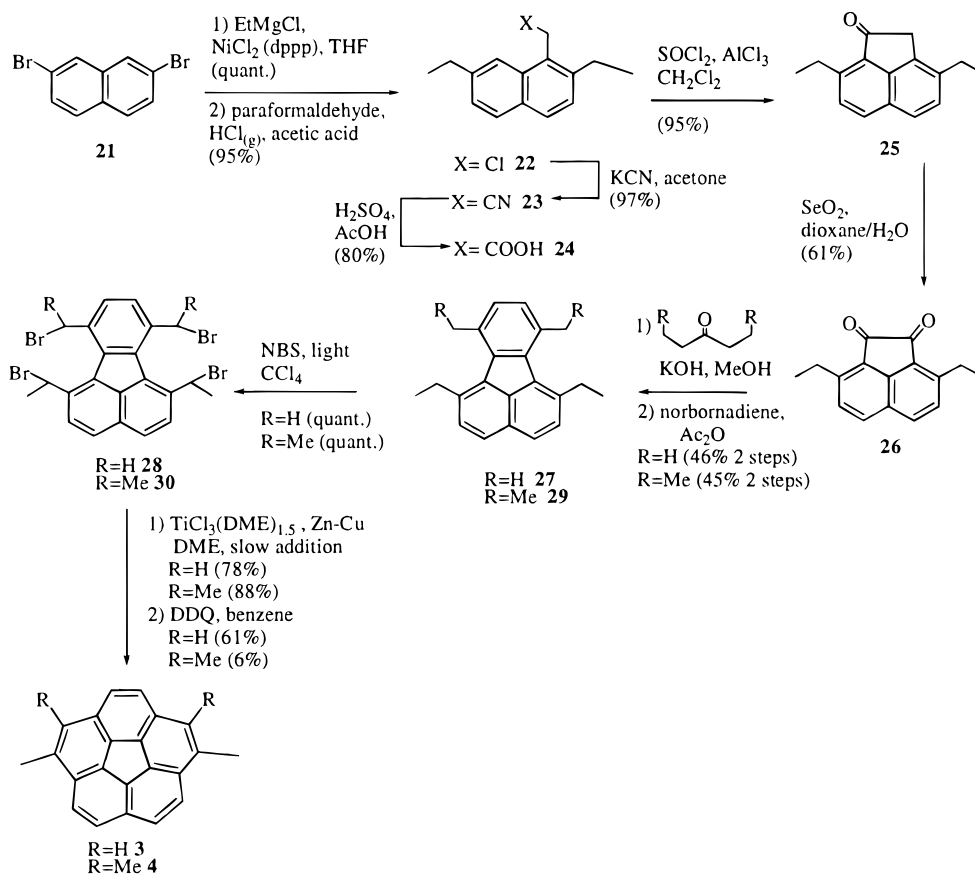
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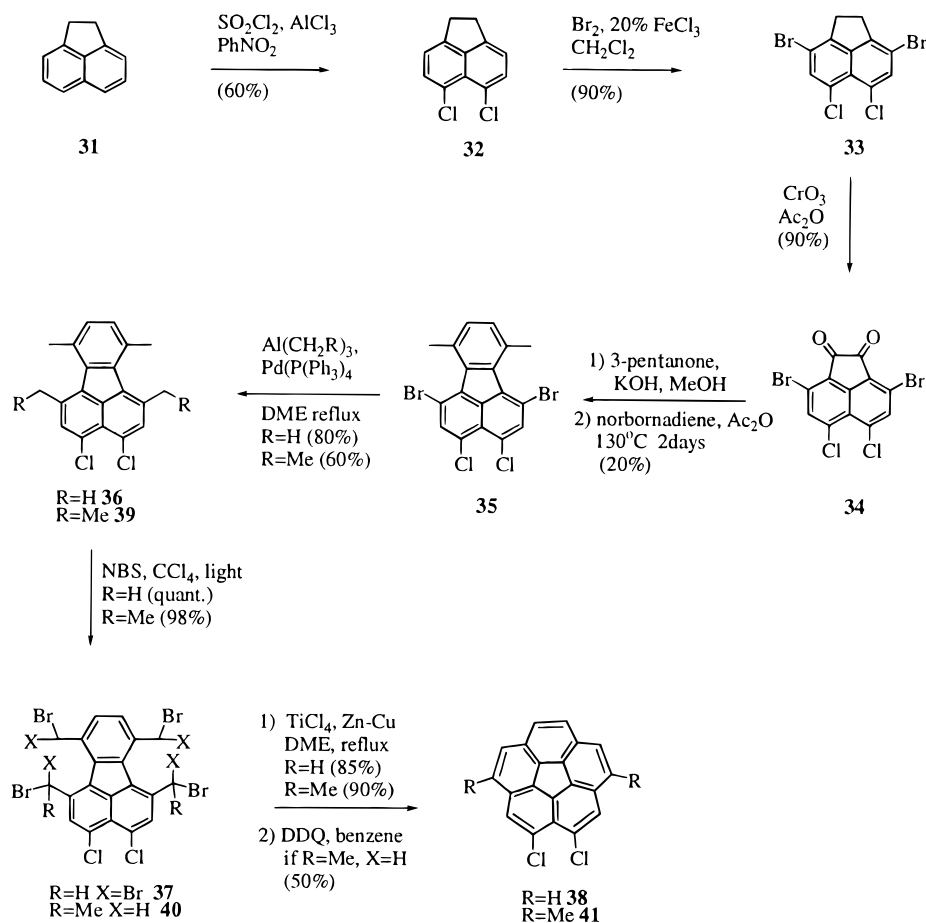
Scheme 1



Scheme 2



Scheme 3



The synthesis of derivatives with substitution in the peri positions (Scheme 3) begins with chlorination of acenaphthene (**31**) by sulfonyl chloride in nitrobenzene with a catalytic amount of aluminum chloride,²¹ followed by electrophilic bromination with bromine and ferric chloride or ferric bromide in methylene chloride. The oxidation of 5,6-dichloro-3,8-dibromoacenaphthene (**33**) is achieved by chromium trioxide in acetic anhydride²² to yield a synthetically versatile acenaphthaquinone derivative (**34**). The standard procedure for converting acenaphthaquinones to fluoranthenes (vida supra) is effected with 3-pentanone to yield 1,6-dibromo-3,4-dichloro-7,10-dimethylfluoranthene (**35**). Palladium-catalyzed reaction of trimethylaluminum with the bromides of fluoranthene **35** yields 3,4-dichloro-1,6,7,10-tetramethylfluoranthene (**36**).²³ Bromination with NBS gives the octabromide **37** as a sparingly soluble material, which is coupled by the improved low-valent titanium reagent to afford 2,3-dichlorocorannulene (**38**).

2,7-Dimethyl-4,5-dichlorocorannulene (**41**) is synthesized (Scheme 3) by palladium-catalyzed replacement of the bromides of fluoranthene **35** with triethyl aluminum to yield 1,6-diethyl-7,10-dimethyl-3,4-dichlorofluoranthene (**39**). By analogy to corannulene **3**, corannulene **41** is synthesized by bromination of fluoranthene **39** with NBS under irradiation of light to the tetrabromide **40**, followed by low-valent titanium coupling and DDQ dehydrogenation.

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Acecorannulylene (**7**), previously synthesized by a FVP route,^{24,25} is significantly more curved than **1**.²⁶ A slight modification of the route to corannulenes **38** and **41** allowed for the synthesis of corannulene **7**. The synthesis from **7** (Scheme 4) involves exhaustive methylation of fluoranthene **35** with trimethylaluminum and a nickel(0) catalyst to afford 1,3,4,6,7,10-hexamethylfluoranthene (**42**). Fluoranthene **42** is brominated with excess NBS under irradiation with light to yield the dodecabromide **43**, which is coupled by the improved low-valent titanium reagent ($\text{TiCl}_4/\text{Zn-Cu}$) to yield **7** in somewhat low yield (20%).

Alkylcorannulenes from Halocorannulenes. A variety of halocorannulenes are now available, for example compounds **38** and **41**, as well as bromocorannulene (**44**),²⁷ pentachlorocorannulene (**45**),^{27,28} and decachlorocorannulene (**46**).^{27–29} Each of these can be conveniently converted to their corresponding alkyl corannulene derivatives (**5**, **6**, **8**, **9**, **10**) by a general coupling procedure that uses alkyl aluminum reagents in the presence of a catalytic amount of nickel(0) (Scheme 5). An important variable in this methodology is the solvent. Whereas this method works well with most halocorannulenes in THF or

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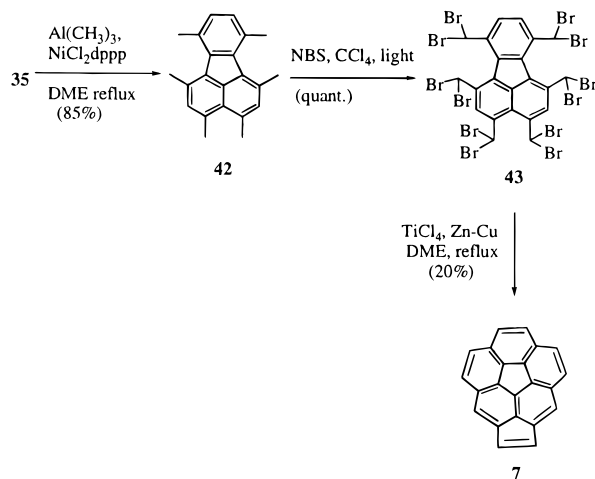
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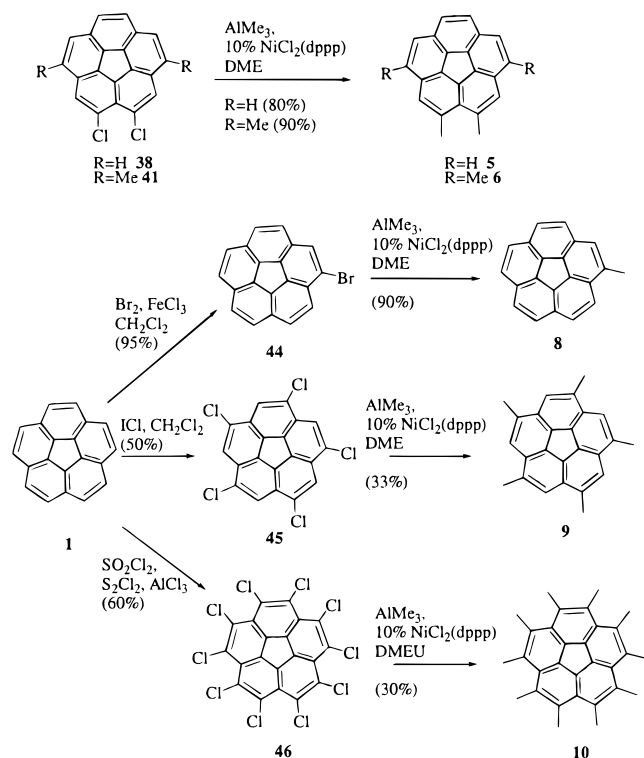
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Scheme 4



Scheme 5



DME, the sparingly soluble corannulene **46** reacts only in dimethylethylene urea (DMEU).

Physical Properties. Having access to corannulene derivatives with controlled substitution allows a systematic investigation of the effects of substitution on the spectroscopic and electrochemical properties of the corannulene nucleus (Table 1). The addition of methyl groups to the corannulene nucleus shifts the UV spectra to longer wavelengths for each of the four peaks. With red shifts of only 8, 14, 21, and 18 nm between **1** and **10** for the individual peaks, the UV spectra seem relatively insensitive to methyl substitution. Fluorescence spectra also reflect relative wavelength insensitivity to methyl substitution. The shifts in the UV and fluorescence spectra, although small, are in the expected direction for methyl acting as a weak electron donor.

Originally, Lawton observed the electrochemical reduction of **1** to the anion and dianion.³⁰ Subsequent studies have found the reduction of **1** with lithium to proceed through each discrete

Table 1. Ultraviolet, Fluorescence, Electrochemical Reduction Potentials, and Ionization Potentials for Corannulene Derivatives

compd	UV ^a		fluorescence (λ) ^a		$E_{1/2}^c$ (V)	IP ^f (eV)
	λ_{\max}	ϵ ($\times 10^4$)	excitation	emission		
1	196	7.8	247, 286	421	-2.23	8.05
	220	5.4			-2.84	
	251	7.8			-1.87 ^d	
	286	4.2			-2.47 ^d	
3	198	5.1	258, 290	425	-2.29	7.72
	222	3.9			-2.94	
	256	4.6				
	289	3.0				
4	199	2.9	264, 294	429	-2.32	7.56
	226	2.3			-2.86	
	262	2.3				
	293	2.1				
5	198	5.4	256, 290	420	-2.30	7.79
	222	4.0			-2.90	
	254	5.7				
	289	3.1				
6	200	1.1	260, 294	426	-2.35	7.62
	225	0.8			-2.87	
	258	1.2				
	292	0.7				
9	200	2.3	261, 297	431	-2.38	7.71
	226	1.6			-2.93	
	260	2.3				
	295	1.4				
10	204 ^b	0.7			-2.48 ^e	7.19
	234 ^b	0.5			> -3.00 ^e	
	272 ^b	0.6				
	304 ^b	0.4				

^a In acetonitrile. ^b In cyclohexane. ^c 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile vs Ag/AgNO₃ in acetonitrile. ^d 0.1 M tetrabutylammonium perchlorate in acetonitrile vs aqueous Ag/AgCl (literature values under the same conditions -1.88 and -2.46 V, ref 29). ^e 0.1 M tetrabutylammonium hexafluorophosphate in *N,N*-dimethylformamide vs Ag/AgNO₃. ^f Calculated (RHF/DZV(2d,p)/B3LYP/cc-pVDZ) using Koopmans' theorem.³⁴

reduction state up to the tetraanion, which forms a sandwich complex of $(1^{4-})_2Li^+$.³¹⁻³³ No evidence for aggregation has been observed for 1^- , 1^{2-} , or 1^{3-} . The relative ease of reduction of **1** piqued our interest in the sensitivity of the reduction potential to alkyl substitution. The addition of methyl groups to the corannulene nucleus shifted the electrochemical reduction for the monoanion and dianion to a more negative potential and is consistent with an increasing electron density in the corannulene nucleus. Comparing **1** and **10**, a difference of 250 mV for the monoanion and at least 160 mV for the dianion is measured.

Whereas the electrochemical reduction, an estimate of the electron affinity, was reversible, the oxidation was irreversible. To obtain estimates for the oxidation, the ionization potentials were calculated using Koopmans' theorem at the RHF/DZV(2d,p)/B3LYP/cc-pVDZ level of theory.³⁴ Upon addition of methyl groups to the corannulene nucleus, the ionization potentials diminished from 8.05 eV for **1** to 7.19 eV for **10**. Like the electrochemical reduction, the shift to lower ionization potential is consistent with an increase in electron density in the corannulene nucleus as the number of methyl substituents increases.

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Substitution of the rim of corannulene expands the scope of this class of compounds. In particular, alkyl substitution can effect bowl depth, crystal packing, HOMO-LUMO gap, and inversion dynamics. Alkyl corannulenes can be used as building blocks for larger structures, such as cyclophanes, dendrimers, and liquid crystals. Such constructs hold the promise of developing selective fullerene hosts, electron-transport materials, and novel polymers.

Experimental Section

General Data. ^1H - and ^{13}C NMR spectra were recorded on Varian (Mercury 300 MHz/400 MHz; Unity 500 MHz) or General Electric (QE 300 MHz) spectrometers with tetramethylsilane as the internal standard. Low-resolution mass spectral analyses were performed in the EI-mode on a HP GC/MS 59970 spectrometer. High-resolution mass spectra were obtained from the University of California Riverside mass spectrometry facility in the FAB or DEI mode. UV/vis spectra were recorded on a Perkin-Elmer Lambda 6 UV/vis spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1420 IR spectrophotometer. Fluorescence spectra were recorded on a Photon Technology International fluorimeter. Cyclic voltammograms were recorded on a Bioanalytical Systems CV-50W electrochemical apparatus. Melting points were obtained on a Mel-Temp melting point apparatus and are reported uncorrected.

Techniques and Materials. All experiments were carried out under argon in freshly distilled solvents under anhydrous conditions unless otherwise noted. Commercial chemicals were used as supplied. Tetrahydrofuran (THF), toluene, and dimethoxyethane (DME) were distilled from sodium/benzophenone; dichloromethane was distilled from calcium hydride; carbon tetrachloride was distilled from phosphorus pentoxide; nitrobenzene was dried with calcium chloride; and dimethylethyleneurea (DMEU) was dried with 4 Å molecular sieves. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Characterization of all new compounds was done by ^1H and ^{13}C NMR as well as by mass spectroscopy. Fluoranthenes containing benzylic bromides were often obtained as mixtures of diastereomers and not purified because of their poor solubility. All tetrahydrocorannulenes were obtained as mixtures of cis and trans isomers; in addition, they already contained the corresponding corannulenes and dihydrocorannulenes and were used as crude materials for further oxidation. When such compounds were isolated and used as mixtures, characterization was restricted to ^1H NMR spectroscopy. All compounds mentioned in Scheme 1 toward the synthesis of **18** have been reported previously.⁷

Preparative column chromatography was performed with silica gel (230–425 mesh) from Fisher Scientific Company. Thin-layer chromatography (TLC) was performed on aluminum backed silica gel 60 F₂₅₄ plates from Alltech.

1,6,7,10-Tetrakis(dibromomethyl)fluoranthene (18). 1,6,7,10-Tetramethylfluoranthene (3.97 g, 15.4 mmol), *N*-bromosuccinimide (27.4 g, 154 mmol), and benzoyl peroxide (10 mg) in dry carbon tetrachloride (250 mL) were irradiated with incandescent light and refluxed for 15 h. The solvent was distilled off and the solid dissolved in dichloromethane (100 mL), washed 3 times with water (100 mL), dried over magnesium sulfate, filtered, and evaporated to yield a golden solid (13.65 g, quantitative). Mp >300 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.10 (s, 2H), 7.22 (s, 2H), 7.99 (d, $^3J = 8.5$ Hz, 2H), 8.22 (s, 2H), 8.28 (d, $^3J = 8.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 38.5, 39.0, 127.6, 129.1, 130.1, 130.2, 131.5, 131.8, 132.3, 136.5, 137.9. HRMS *m/z*: found 889.4202; calcd ($\text{C}_{20}\text{H}_{10}\text{Br}_8$) 889.4168.

Corannulene (1). Zinc-copper couple (28.7 g, 442 mmol) and titanium tetrachloride (12.2 mL, 110 mmol) in DME (250 mL) were refluxed for 2 h yielding a black suspension. A solution of 1,6,7,10-tetrakis(dibromomethyl)fluoranthene (**18**) (6.73 g, 7.56 mmol) in DME (100 mL) was added to the refluxing suspension over a period of 2 days. The mixture was refluxed an additional 3 h, diluted with cyclohexane (250 mL), and filtered through a plug of silica gel; the plug was washed with additional benzene (500 mL). The solvent was evaporated to yield a pale yellow solid (1.50 g, 80%). Mp 264–265 °C (lit. mp 268–269 °C).² ^1H NMR (500 MHz, CDCl_3): δ 7.82 (s,

10H). ^{13}C NMR (125 MHz, CDCl_3): δ 127.2, 130.8, 135.8. HRMS *m/z*: found 250.0779; calcd ($\text{C}_{20}\text{H}_{10}$) 250.0783.

1,6-Dimethyl-7,10-diethylfluoranthene (19). A 20% solution of potassium hydroxide in methanol (100 mL) was added to a solution of 3,8-dimethylacenaphthenequinone (**12**) (9.25 g, 44 mmol) and 4-heptanone (25 mL) in methanol (250 mL). The solution was stirred at ambient temperature for 1 h, diluted with water (250 mL), and extracted with dichloromethane (300 mL). The organic layer was washed once with 10% aqueous hydrochloric acid (100 mL) and three times with water (250 mL), dried with magnesium sulfate, filtered, and evaporated. The crude oil was transferred to a 200 mL sealable reaction vessel and 2,5-norbornadiene (30 mL) and acetic anhydride (100 mL) were added. The vessel was sealed and placed in an oil bath at 140 °C for 3 days. The reaction was cooled to ambient temperature, diluted with benzene (100 mL), neutralized with 10% aqueous sodium hydroxide (100 mL), and extracted 3 times with water (100 mL). The organic layer was dried with magnesium sulfate, filtered, and evaporated to yield a dark brown oil. The oil was purified by column chromatography on silica gel with cyclohexane as the eluent to yield a golden yellow oil that solidifies upon standing (6.00 g, 48% 2 steps). Mp 46–47 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 1.30 (t, $^3J = 7.0$ Hz, 3H), 2.79 (s, 3H), 3.11 (q, $^3J = 7.0$ Hz, 2H), 7.26 (s, 2H), 7.35 (d, $^3J = 8.0$ Hz, 2H), 7.66 (d, $^3J = 8.0$, 2H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 15.49, 24.54, 28.41, 125.98, 126.62, 128.51, 131.82, 131.93, 133.61, 135.10, 136.49, 139.19. HRMS *m/z*: found 286.1718; calcd ($\text{C}_{22}\text{H}_{22}$) 286.1722.

1,6-Bis(bromomethyl)-7,10-bis(1-bromoethyl)fluoranthene (20) (Mixture of Diastereomers). 1,6-Dimethyl-7,10-diethylfluoranthene (**19**) (0.81 g, 2.83 mmol), *N*-bromosuccinimide (4.04 g, 22.68 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (250 mL) were irradiated with incandescent light and refluxed for 6 h. The solution was extracted 3 times with water (200 mL), dried with magnesium sulfate, filtered, and evaporated to yield a golden solid (2.15 g, quantitative). ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 2.0–2.2 (m, 6H), 4.6–5.2 (m, 4H), 5.8–6.1 (m, 2H), 7.7–8.0 (m, 6H).

2,5-Dimethyl-1,2,5,6-tetrahydrocorannulene (Mixture of Cis and Trans Isomers). Titanium trichloride (1.54 g, 9.97 mmol) and lithium aluminum hydride (0.190 g, 4.98 mmol) in THF (200 mL) were refluxed for 30 min yielding a black suspension. A solution of 1,6-bis(bromomethyl)-7,10-bis(1-bromoethyl)fluoranthene (**20**) (3.00 g, 4.98 mmol) in THF (100 mL) was added to the refluxing black suspension over a period of 12 h and refluxed an additional 3 h after the addition was complete. The reaction was diluted with benzene (100 mL), extracted 3 times with water (250 mL), dried with magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography (cyclohexane/benzene 9:1) to yield a pale yellow solid (0.45 g, 33%). ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 1.49 (d, $^3J = 6.9$ Hz, 6H), 1.57 (d, $^3J = 6.3$ Hz, 6H), 2.49–3.85 (m, 12H), 7.0–7.2 (m, 2H), 7.00 (s, 2H), 7.02 (s, 2H), 7.14 (d, $^3J = 8.4$ Hz, 2H), 7.15 (d, $^3J = 8.4$ Hz, 2H), 7.57 (d, $^3J = 8.4$ Hz, 4H).

2,5-Dimethylcorannulene (2). 2,5-Dimethyl-1,2,5,6-tetrahydrocorannulene (0.40 g, 1.42 mmol) and 2,3-dichloro-5,6-dicyanoquinone (0.81 g, 3.55 mmol) in benzene (125 mL) were refluxed for 1 h. The solution was diluted with cyclohexane (125 mL) and filtered through a plug of silica gel, then the plug was washed with additional cyclohexane (125 mL). The solvent was evaporated to yield a pale yellow solid (0.28 g, 70%). Mp 189–193 °C. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 2.83 (s, 6H), 7.55 (s, 2H), 7.68 (d, $^3J = 8.5$ Hz, 2H), 7.74 (d, $^3J = 8.5$, 2H), 7.94 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 18.74, 124.83, 125.79, 126.31, 127.12, 129.97, 130.66, 131.56, 134.93, 135.50, 136.04, 136.66. HRMS-FAB⁺ [M + Cs]⁺: found 411.0150, calcd ($\text{C}_{22}\text{H}_{14}$) 411.0166.

2,7-Diethylnaphthalene. Ethylmagnesium chloride 25% in THF (58.7 h, 228 mL, 660 mmol) was added dropwise to a solution of 2,7-dibromonaphthalene¹⁸ (90.0 g, 315 mmol) and 1,3-bis(diphenylphosphino)nickel(II) chloride (1.71 g, 3.15 mmol) in THF (350 mL) at 0 °C. The mixture was refluxed for 30 min, cooled to ambient temperature, and quenched carefully by slow addition of water (50 mL). Benzene (100 mL) was added and the organic layer was washed 3 times with water (500 mL), dried with magnesium sulfate, filtered, and evaporated to yield a tan solid (58.0 g, quantitative). Mp 38–40 °C. ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 1.30 (t, $^3J = 7.5$ Hz, 6H), 2.78

(q, $^3J = 7.5$ Hz, 4H), 7.26 (d, $^3J = 8.4$ Hz, 2H), 7.55 (s, 2H), 7.71 (d, $^3J = 8.4$ Hz, 2H). ^{13}C NMR (CDCl_3 , 300 MHz): δ (ppm) 15.7, 29.1, 125.0, 126.1, 127.4, 130.3, 133.8, 141.6. HRMS m/z : found 184.1256; calcd ($\text{C}_{14}\text{H}_{16}$) 184.1252.

1-(Chloromethyl)-2,7-diethylnaphthalene (22). 2,7-Diethylnaphthalene (41.6 g, 226 mmol), paraformaldehyde (8.1 g, 270 mmol), and a solution of hydrogen chloride (16 g, 450 mmol) in acetic acid (125 mL) (prepared by bubbling hydrogen chloride through acetic acid) in a sealable reaction vessel were heated and stirred in an oil bath at 50 °C for 20 h. The reaction was neutralized with an aqueous solution of sodium bicarbonate, extracted with benzene (100 mL), washed 3 times with water (125 mL), dried with magnesium sulfate, filtered, and evaporated to yield a brown oil (49.9 g, 95%). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 1.29 (t, $^3J = 7.5$ Hz, 3H), 1.33 (t, $^3J = 7.5$ Hz, 3H), 2.83 (q, $^3J = 7.5$ Hz, 2H), 2.87 (q, $^3J = 7.5$ Hz, 2H), 5.07 (s, 2H), 7.23 (d, $^3J = 8.4$ Hz, 1H), 7.29 (d, $^3J = 7.4$ Hz, 1H), 7.69 (d, $^3J = 8.1$ Hz, 1H), 7.70 (d, $^3J = 8.1$ Hz, 1H), 7.87 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 15.6, 15.8, 26.6, 29.8, 39.6, 121.3, 126.3, 126.8, 128.6, 128.7, 129.3, 131.0, 132.1, 141.6, 142.9. MS m/z (rel intensity): 234 (15, M + 2), 232 (40, M⁺), 197 (100, M - Cl⁺).

1-(Cyanomethyl)-2,7-diethylnaphthalene (23). 1-(Chloromethyl)-2,7-diethylnaphthalene (22) (49.9 g, 214 mmol) and potassium cyanide (28.0 g, 429 mmol) in a mixture of water (25 mL) and acetone (250 mL) were refluxed for 18 h. The solution was diluted with benzene (100 mL), washed 3 times with water (100 mL), dried with magnesium sulfate, filtered, and evaporated to yield a brown oil (46.6 g, 97%). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 1.27 (t, $^3J = 7.5$ Hz, 3H), 1.33 (t, $^3J = 7.5$ Hz, 3H), 2.82 (q, $^3J = 7.5$ Hz, 2H), 2.84 (q, $^3J = 7.5$ Hz, 2H), 4.02 (s, 2H), 7.24 (d, $^3J = 8.4$ Hz, 1H), 7.33 (d, $^3J = 8.1$ Hz, 1H), 7.70 (s, 1H), 7.71 (d, $^3J = 8.1$ Hz, 1H), 7.73 (d, $^3J = 8.4$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 15.3, 15.5, 16.2, 27.1, 29.4, 118.0, 120.6, 121.9, 126.5, 126.7, 128.7, 128.8, 130.9, 131.8, 140.6, 143.3. MS m/z (rel intensity): 223 (100, M⁺), 208 (95, M - CH₃⁺).

1-(Carboxymethyl)-2,7-diethylnaphthalene (24). 1-(Cyanomethyl)-2,7-diethylnaphthalene (23) (46.6 g, 208 mmol), concentrated sulfuric acid (80 mL), acetic acid (150 mL), and water (150 mL) were refluxed for 1 day. The solution was neutralized with 10% aqueous sodium hydroxide, extracted with dichloromethane (500 mL), washed 3 times with water (100 mL), dried with magnesium sulfate, filtered, and evaporated to yield a light yellow solid (41.0 g, 80%). Mp 78–80 °C. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 1.24 (t, $^3J = 7.5$ Hz, 3H), 1.28 (t, $^3J = 7.5$ Hz, 3H), 2.79 (q, $^3J = 7.5$ Hz, 2H), 2.83 (q, $^3J = 7.5$ Hz, 2H), 4.13 (s, 2H), 7.27 (d, $^3J = 8.4$ Hz, 1H), 7.28 (d, $^3J = 8.4$ Hz, 1H), 7.68 (d, $^3J = 7.8$ Hz, 1H), 7.71 (d, $^3J = 7.8$ Hz, 1H), 7.72 (s, 1H), 10.53 (bs, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 15.4, 15.6, 27.0, 29.5, 33.7, 121.5, 125.7, 126.1, 126.8, 128.0, 128.6, 130.9, 132.9, 141.0, 142.6, 178.1. HRMS m/z : found 242.1301; calcd ($\text{C}_{16}\text{H}_{18}\text{O}_2$) 242.1307.

3,8-Diethylacenaphthene (25). 1-(Carboxymethyl)-2,7-diethylnaphthalene (24) (30.5 g, 126 mmol) and thionyl chloride (15.8 g, 133 mmol) in dichloromethane (600 mL) were refluxed for 45 min. Aluminum chloride (16.8 g, 126 mmol) was added slowly and the resulting mixture was stirred for an additional 30 min. The solution was carefully quenched by slow addition of water (100 mL), washed 3 times with water (500 mL), dried with magnesium sulfate, filtered, and evaporated to yield a light brown solid (26.8 g, 95%). Mp 71–73 °C. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 1.30 (t, $^3J = 7.5$ Hz, 3H), 1.31 (t, $^3J = 7.5$ Hz, 3H), 2.78 (q, $^3J = 7.5$ Hz, 2H), 3.24 (q, $^3J = 7.5$ Hz, 2H), 3.70 (s, 2H), 7.39 (d, $^3J = 8.5$ Hz, 1H), 7.45 (d, $^3J = 8.5$ Hz, 1H), 7.72 (d, $^3J = 8.5$ Hz, 1H), 7.93 (d, $^3J = 8.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 14.9, 15.1, 24.7, 26.4, 41.0, 124.3, 127.9, 128.5, 128.8, 130.3, 131.0, 131.2, 136.7, 143.8, 143.9, 203.9. MS m/z (rel intensity): 224 (100, M⁺), 209 (80, M - CH₃⁺).

3,8-Diethylacenaphthenequinone (26). 3,8-Diethylacenaphthene (25) (26.8 g, 120 mmol) and selenium dioxide (27.9 g, 251 mmol) in a mixture of 1,4-dioxane (500 mL) and water (20 mL) were heated to 70 °C for 5 h. The solution was cooled to ambient temperature, filtered, and diluted with benzene (200 mL). The organic layer was washed 3 times with water (250 mL), dried with magnesium sulfate, filtered, evaporated, and filtered through a plug of silica gel with dichloromethane as the eluent to yield an orange solid (17.0 g, 61%) Mp

131–133 °C. ^1H NMR (300 MHz, CDCl_3): δ 1.35 (t, $^3J = 7.5$ Hz, 6H), 3.29 (q, $^3J = 7.5$ Hz, 4H), 7.56 (d, $^3J = 8.4$ Hz, 2H), 8.08 (d, $^3J = 8.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 15.1, 25.1, 124.0, 127.9, 129.2, 132.3, 144.3, 147.7, 188.8. IR (KBr): 1710 cm^{-1} (C=O). HRMS m/z : found 238.0993; calcd ($\text{C}_{16}\text{H}_{14}\text{O}_2$) 238.0994.

1,6-Diethyl-7,10-dimethylfluoranthene (27). A 20% solution of potassium hydroxide in methanol (100 mL) was added to a solution of 3,8-diethylacenaphthenequinone (26) (18.0 g, 75.6 mmol) and 3-pentanone (50 mL) in methanol (500 mL). The mixture was stirred at ambient temperature for 1 h, diluted with water (500 mL), and extracted with dichloromethane (400 mL). The organic layer was washed once with 10% aqueous hydrochloric acid (100 mL) and 3 times with water (250 mL), dried with magnesium sulfate, filtered, and evaporated. The crude oil was transferred to a 200 mL sealable reaction vessel and 2,5-norbornadiene (50 mL) and acetic anhydride (100 mL) were added. The vessel was sealed and placed in an oil bath at 130 °C for 4 days. The reaction was cooled to ambient temperature, diluted with benzene (100 mL), and extracted 3 times with 10% sodium hydroxide (100 mL) and then water (100 mL). The organic layer was dried with magnesium sulfate, filtered, and evaporated to yield a dark brown oil. The oil was purified by flash chromatography with cyclohexane as the eluent to yield a golden yellow oil that solidifies upon standing (9.7 g, 46%, 2 steps). Mp 36–38 °C. ^1H NMR (500 MHz, CDCl_3): δ 1.28 (t, $^3J = 7.5$ Hz, 6H), 2.67 (s, 6H), 3.12 (q, $^3J = 7.5$ Hz, 4H), 7.06 (s, 2H), 7.39 (d, $^3J = 7.5$ Hz, 2H), 7.66 (d, $^3J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 15.9, 23.7, 29.3, 126.5, 126.7, 129.8, 129.9, 130.5, 133.8, 134.0, 138.8, 140.1. HRMS m/z : found 286.1713; calcd ($\text{C}_{22}\text{H}_{22}$) 286.1722.

1,6-Bis(1-bromoethyl)-7,10-bis(bromomethyl)fluoranthene (28) (Mixture of Diastereomers). 1,6-Diethyl-7,10-dimethylfluoranthene (27) (3.27 g, 11.4 mmol), *N*-bromosuccinimide (8.14 g, 45.7 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (250 mL) were irradiated with incandescent light and refluxed for 3 h. The solution was extracted 3 times with water (200 mL), dried over magnesium sulfate, filtered, and evaporated to yield a golden solid (6.89 g, quantitative). ^1H NMR (300 MHz, CDCl_3): δ 2.04 (d, $^3J = 6.6$ Hz, 6H), 2.13 (d, $^3J = 6.6$ Hz, 6H), 4.73 (d, $^3J = 11.1$ Hz, 2H), 4.86 (d, $^3J = 11.1$ Hz, 2H), 4.96 (d, $^3J = 11.4$ Hz, 2H), 5.00 (d, $^3J = 11.1$ Hz, 2H), 5.87 (q, $^3J = 6.6$ Hz, 2H), 6.02 (q, $^3J = 6.9$ Hz, 2H), 7.64 (s, 2H), 7.66 (s, 2H), 7.88 (d, $^3J = 8.4$ Hz, 2H), 7.89 (d, $^3J = 8.7$ Hz, 2H), 7.97 (d, $^3J = 8.7$ Hz, 4H).

1,6-Dimethyl-1,2,5,6-tetrahydrocorannulene (Mixture of Cis/Trans Isomers). Titanium trichloride(DME)_{1.5} (8.79 g, 30.4 mmol) and zinc-copper couple (6.26 g, 96.3 mmol) in DME (400 mL) were refluxed for 2 h yielding a black suspension. A solution of 1,6-bis(1-bromoethyl)-7,10-bis(bromomethyl)fluoranthene (28) (3.00 g, 4.98 mmol) in 1,2-dimethoxyethane (150 mL) was added to the refluxing black suspension over a period of 3 days and the solution was refluxed an additional 3 h after the addition was complete. The reaction was diluted with cyclohexane (400 mL) and filtered through a plug of silica gel, then the plug was washed with additional cyclohexane (500 mL). The solvent was evaporated to yield a yellow solid (1.58 g, 78%). ^1H NMR (300 MHz, CDCl_3): δ 1.42 (d, $^3J = 6.9$ Hz, 6H), 1.57 (d, $^3J = 6.9$ Hz, 6H), 2.7–3.6 (m, 12H), 6.9 (s, 4H), 7.27 (d, $J = 8.7$ Hz, 4H), 7.61 (d, $J = 8.7$ Hz, 4H).

1,6-Dimethylcorannulene (3). 1,6-Dimethyl-1,2,5,6-tetrahydrocorannulene (2.13 g, 7.55 mmol) and 2,3-dichloro-5,6-dicyanoquinone (3.43 g, 15.1 mmol) in benzene (250 mL) were stirred at ambient temperature for 8 h. The solution was diluted with cyclohexane (250 mL) and filtered through a plug of silica gel, then the plug was washed with additional cyclohexane (250 mL). The solvent was evaporated to yield a pale yellow solid (1.30 g, 61%). Mp 206–208 °C. ^1H NMR (500 MHz, CDCl_3): δ 2.81 (s, 6H), 7.54 (s, 2H), 7.68 (s, 2H), 7.83 (d, $^3J = 9.0$ Hz, 2H), 7.91 (d, $^3J = 9.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 18.7, 124.9, 125.8, 126.8, 126.9, 130.2, 131.0, 131.1, 134.9, 135.4, 135.9, 136.3. HRMS m/z : found 278.1094; calcd ($\text{C}_{22}\text{H}_{14}$) 278.1096.

1,6,7,10-Tetraethylfluoranthene (29). A 20% solution of potassium hydroxide in methanol (100 mL) was added to a solution of 3,8-diethylacenaphthenequinone (26) (5.0 g, 21 mmol) and 4-heptanone (20 mL) in methanol (250 mL). The solution was stirred at ambient

temperature for 1 h, diluted with water (250 mL), and extracted with dichloromethane. The organic layer was washed once with 10% aqueous hydrochloric acid (100 mL) and 3 times with water (250 mL), dried with magnesium sulfate, filtered, and evaporated. The crude oil was transferred to a 200 mL sealable reaction vessel and 2,5-norbornadiene (30 mL) and acetic anhydride (60 mL) were added. The vessel was sealed and placed in an oil bath at 140 °C for 3 days. The reaction was cooled to ambient temperature, diluted with benzene (100 mL), and extracted 3 times with 10% aqueous sodium hydroxide (100 mL) and then water (100 mL). The organic layer was dried with magnesium sulfate, filtered, and evaporated to yield a dark brown oil. The oil was purified by flash chromatography with cyclohexane as the eluent to yield a golden yellow solid (2.8 g, 45% 2 steps). Mp 60–61 °C. ¹H NMR (CDCl₃, 300 MHz): δ 1.32 (t, ³J = 7.5 Hz, 6H), 1.35 (t, ³J = 7.5 Hz, 6H), 3.06 (q, ³J = 7.5 Hz, 4H), 3.11 (q, ³J = 7.5 Hz, 4H), 7.27 (s, 2H), 7.46 (d, ³J = 8.4 Hz, 2H), 7.72 (d, ³J = 8.4, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 15.7, 15.8, 28.3, 29.2, 126.0, 126.4, 128.0, 129.4, 133.3, 133.9, 136.2, 138.3, 139.0. HRMS *m/z*: found 314.2034; calcd (C₂₄H₂₆) 314.2035.

1,6,7,10-Tetrakis(bromoethyl)fluoranthene (30) (Mixture of Diastereomers), 1,6,7,10-Tetraethylfluoranthene (**29**) (2.76 g, 8.78 mmol), *N*-bromosuccinimide (6.22 g, 34.90 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (125 mL) were irradiated with incandescent light and refluxed for 3 h. The solution was cooled to ambient temperature, extracted 3 times with water (200 mL), dried over magnesium sulfate, and evaporated to yield a golden solid (5.40 g, 98%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.9–2.3 (m, 12H), 5.7–5.9 (m, 4H), 7.7–8.0 (m, 6H).

1,2,5,6-Tetramethylcorannulene (4). Titanium trichloride(DME)_{1.5} (18.3 g, 63.4 mmol) and zinc–copper couple (13.1 g, 201 mmol) in DME (400 mL) were refluxed for 2 h to yield a black suspension. A solution of 1,6,7,10-tetrakis(bromoethyl)fluoranthene (**30**) (6.68 g, 10.6 mmol) in DME (100 mL) was added to the refluxing black suspension over a period of 3 days and the mixture was refluxed an additional 3 h. The solution was diluted with cyclohexane (400 mL) and filtered through a plug of silica gel, then the plug was washed with additional cyclohexane (500 mL). The solvent was evaporated to yield a yellow solid. The yellow solid and 2,3-dichloro-5,6-dicyanoquinone (4.13 g, 18.2 mmol) in benzene (100 mL) were stirred at ambient temperature for 8 h, diluted with cyclohexane (250 mL), and filtered through a plug of silica gel, then the plug was washed with additional cyclohexane (250 mL). The solvent was evaporated to yield a pale yellow solid (0.16 g, 6%, 2 steps). Mp 168–171 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.71 (s, 12H), 7.76 (d, ³J = 8.6 Hz, 2H), 7.85 (d, ³J = 8.6, 2H), 7.90 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 15.11, 15.13, 124.3, 124.6, 126.5, 129.0, 130.5, 131.3, 132.0, 132.3, 133.4, 133.8, 135.3. HRMS *m/z*: found 306.1414; calcd (C₂₄H₁₈) 306.1409.

5,6-Dichloroacenaphthene (32). Sulfuryl chloride (110 g, 66 mL, 815 mmol) was added dropwise over a period of 2 h to a solution of acenaphthene (**31**) (60 g, 390 mmol) and aluminum chloride (10.4 g, 78 mmol) in nitrobenzene (250 mL). The solution was stirred an additional 2 h and then poured into 600 mL of a 5:1 mixture of methanol and water. The precipitate was collected, washed with methanol thoroughly, and dried to yield a tan solid (52 g, 60%). Mp 167–169 °C (lit. mp 166–168 °C).²¹ ¹H NMR (500 MHz, CDCl₃): δ 3.27 (s, 4H), 7.09 (d, ³J = 7.5 Hz, 2H), 7.44 (d, ³J = 7.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 30.0, 120.3, 125.7, 126.0, 131.4, 142.1, 145.9. MS *m/z* (rel intensity): 226 (10, M + 4), 224 (66, M + 2), 222 (60, M⁺), 187 (80, M – Cl⁺), 152 (100, M – 2Cl⁺).

3,8-Dibromo-5,6-dichloroacenaphthene (33). Bromine (35.9 g, 224 mmol) was added in five portions (every 30 min) to a refluxing solution of 5,6-dichloroacenaphthene (**32**) (25.0 g, 112 mmol) and ferric chloride (1.82 g, 11.2 mmol) in dichloromethane (500 mL). The solution was stirred at reflux for an additional 2 h after the last addition, cooled to ambient temperature, extracted 2 times with water (500 mL), and evaporated. The brownish solid was triturated with methanol (250 mL) thoroughly to yield of a light brown solid (40.0 g, 90%). Mp 201–203 °C (lit. mp 201–202 °C).³⁵ ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.28 (s, 4H), 7.62 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 31.3, 115.2, 123.8, 127.6, 133.6, 141.9, 145.5. MS *m/z* (rel intensity):

378 (30, M⁺), 380 (65, M + 2), 382 (60, M + 4), 384 (25, M + 6), 220 (100, M – 2Br⁺).

3,8-Dibromo-5,6-dichloroacenaphthenequinone (34). Chromium trioxide (45.9 g, 460 mmol) was added in 3 portions over 2 h to the vigorously stirred solution of 3,8-dibromo-5,6-dichloroacenaphthene (**33**) (35.0 g, 91.9 mmol) and acetic anhydride (500 mL) at 0 °C. Between the additions the solution was allowed to warm to room temperature for 45 min. *Note: Care must be given to avoid a highly exothermic reaction if the temperature is not moderated or the solution is not stirred well.* After the additions were complete, the reaction was carefully heated to 80 °C for 30 min. The solution was poured into 1.5 L of water and stirred for 30 min, and the precipitate was collected and washed thoroughly with water to yield golden yellow solid (35.5 g, 90%). Mp 208 °C dec (lit. mp 286–287 °C).³⁵ ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.25 (s, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 118.1, 123.0, 126.1, 135.0, 136.0, 148.4, 182.9. IR (KBr) 1725 cm⁻¹ (C=O). HRMS *m/z*: found 405.7807; calcd (C₁₂H₂Br₂Cl₂O₂) 405.7799.

1,6-Dibromo-3,4-dichloro-7,10-dimethylfluoranthene (35). A 20% solution of potassium hydroxide in methanol (50 mL) was added to a solution of 3,8-dibromo-5,6-dichloroacenaphthenequinone (**34**) (35.2 g, 86.0 mmol) and 3-pentanone (15 mL) in methanol (500 mL). The solution was stirred at ambient temperature for 1 h, diluted with water (500 mL), and neutralized with a 10% aqueous hydrochloric acid solution. The precipitate formed was collected by filtration, washed with water, dried in air, split into two roughly equal portions, and transferred to two 200 mL sealable reaction vessels. 2,5-Norbornadiene (50 mL) and acetic anhydride (100 mL) were added to each vessel. The vessels were sealed and placed in an oil bath at 130 °C for 4 days, cooled to ambient temperature, combined, diluted with benzene (100 mL), neutralized slowly with 10% aqueous sodium hydroxide (100 mL), and extracted 3 times with water (100 mL). The organic layer was dried with magnesium sulfate, filtered and evaporated to yield a dark brown oil. The oil was purified by column chromatography with 2:1 cyclohexane/benzene as the eluent to yield a golden yellow solid (9.5 g, 20% for 2 steps). Mp 148–151 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.83 (s, 6 H), 7.17 (s, 2 H), 7.96 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 25.7, 116.3, 122.7, 130.6, 131.4, 133.0, 136.9, 137.0, 137.3, 138.6. HRMS *m/z*: found 453.8530; calcd (C₁₈H₁₀Br₂Cl₂) 453.8526.

3,4-Dichloro-1,6,7,10-tetramethylfluoranthene (36). Trimethylaluminum (2.7 mL, 2 M in hexanes, 5.43 mmol) was added dropwise to a solution of 1,6-dibromo-3,4-dichloro-7,10-dimethylfluoranthene (**35**) (1.13 g, 2.47 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.074 g, 0.064 mmol) in DME (50 mL). The solution was warmed to 60 °C for 30 min, quenched slowly with ethanol, extracted with dichloromethane (50 mL), and washed 3 times with water (100 mL). The organic layer was dried with magnesium sulfate, filtered, and evaporated. The crude product was purified by filtration through a plug of silica gel with benzene as the eluent to yield a golden yellow solid (0.65 g, 80%). Mp 162–164 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.67 (s, 6H), 2.73 (s, 6H), 7.11 (s, 2H), 7.44 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 23.9, 24.2, 121.4, 129.2, 129.6, 131.2, 132.8, 134.8, 134.9, 136.8, 138.8. HRMS *m/z*: found 326.0617; calcd (C₂₀H₁₆Cl₂) 326.0629.

1,6,7,10-Tetrakis(dibromomethyl)-3,4-dichlorofluoranthene (37), 3,4-Dichloro-1,6,7,10-tetramethylfluoranthene (**36**) (2.00 g, 6.12 mmol), *N*-bromosuccinimide (13.1 g, 73.4 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (250 mL) were irradiated with incandescent light and refluxed for 12 h. The solvent was evaporated and the solid was triturated 3 times with methanol (50 mL) to yield a golden solid (5.90 g, quantitative). Mp >300 °C. ¹H NMR (400 MHz, C₂D₂Cl₄ at 80 °C): δ (ppm) 6.98 (s, 2H), 7.05 (s, 2H), 8.20 (s, 2H), 8.29 (s, 2H). ¹³C NMR (100 MHz, C₂D₂Cl₄ at 80 °C): δ (ppm) 39.7, 40.5, 128.0, 129.8, 133.2, 135.3, 136.1, 136.4, 137.0, 139.7, 140.5.

2,3-Dichlorocorannulene (38). Zinc–copper couple (28.7 g, 442 mmol) and titanium tetrachloride (12.2 mL, 110 mmol) in DME (250 mL) were refluxed for 2 h to yield a black suspension. In 10 portions, solid 1,6,7,10-tetrakis(dibromomethyl)-3,4-dichlorofluoranthene (**37**)

(35) Our reported melting point of acenaphthenequinone (**34**) is considerably different than the literature value. The only other characterization provided in the original work is the bromine elemental analysis. Krivoshapko, N. G.; Karishin, A. P.; Samusenko, Y. V.; Dryanitsa, T. F.; Lykko, V. P. *Ukr. Khim. Zh.* **1973**, *39*, 49–52.

(5.92 g, 6.13 mmol) was added to the refluxing black suspension over a period of 2 days. The mixture was refluxed an additional 3 h after the last addition, diluted with cyclohexane (250 mL), and filtered through a plug of silica gel, then the plug was washed with additional benzene (500 mL). The solvent was evaporated to yield a pale yellow solid (1.65 g, 85%). Mp 210–213 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.82 (s, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.92 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 124.2, 125.9, 127.4, 128.6, 128.8, 130.8, 131.0, 133.4, 135.4, 135.8. HRMS *m/z*: found 318.0006; calcd (C₂₀H₈Cl₂) 318.0003.

3,4-Dichloro-1,6,diethyl-7,10-dimethylfluoranthene (39). Triethylaluminum (70 mL, 1 M in hexanes, 70 mmol) was added dropwise to a solution of 1,6-dibromo-3,4-dichloro-7,10-dimethylfluoranthene (**35**) (14.8 g, 32.4 mmol) and tetrakis(triphenylphosphine)palladium(0) (2.0 g, 1.7 mmol) in DME (1 L). The solution was warmed to 70 °C for 15 h, slowly quenched with methanol, neutralized with 10% aqueous hydrochloric acid, and extracted with ether (250 mL). The organic layers were combined, washed 3 times with water (250 mL), dried with magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography with cyclohexane as the eluent to yield a golden yellow solid (5.73 g, 50%). Mp 70–72 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.30 (t, ³*J* = 7.6 Hz, 6H), 2.64 (s, 6H), 3.06 (q, ³*J* = 7.6 Hz, 4H), 7.10 (s, 2H), 7.52 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 15.5, 23.7, 28.8, 121.4, 129.5, 129.7, 130.8, 132.6, 133.9, 136.8, 138.8, 139.1. HRMS *m/z*: found 354.0958; calcd (C₂₂H₂₀Cl₂) 354.0942.

1,6-Bis(1-bromoethyl)-7,10-bis(bromomethyl)-3,4-dichlorofluoranthene (40) (Mixture of Diastereomers). 3,4-Dichloro-1,6,diethyl-7,10-dimethylfluoranthene (**39**) (5.69 g, 16.1 mmol), *N*-bromosuccinimide (11.4 g, 64.1 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (250 mL) were irradiated with incandescent light and refluxed for 2 h. The solution was cooled to ambient temperature and filtered through a plug of silica, then the plug was washed with additional 1:1 dichloromethane/cyclohexane mixture (250 mL). The solvent was evaporated to yield a golden solid (10.5 g, 98%). ¹H NMR (400 MHz, CDCl₃): δ 2.01 (d, ³*J* = 6.8 Hz, 6H), 2.09 (d, ³*J* = 6.8 Hz, 6H), 4.67 (d, ³*J* = 11.6 Hz, 2H), 4.80 (d, ³*J* = 11.6 Hz, 2H), 4.86 (d, ³*J* = 8.0 Hz, 2H), 4.89 (d, ³*J* = 8.0 Hz, 2H), 5.70 (q, ³*J* = 6.8 Hz, 2H), 5.83 (q, ³*J* = 6.8 Hz, 2H), 7.64 (s, 2H), 7.66 (s, 2H), 7.99 (s, 2H).

2,7-Dimethyl-1,2,6,7-tetrahydro-4,5-dichlorocorannulene (Mixture of Cis/Trans Isomers). Zinc–copper couple (35.7 g, 548 mmol) and titanium tetrachloride (15 mL, 137 mmol) in DME (1.2 L) were refluxed for 2 h yielding a black suspension. A solution of 1,6-bis(1-bromoethyl)-7,10-bis(bromomethyl)-3,4-dichlorofluoranthene (**40**) (10.5 g, 15.7 mmol) in toluene (30 mL) was added to the refluxing black suspension over a period of 3 days and the solution was refluxed an additional 3 h after the addition was complete. The reaction was diluted with cyclohexane (400 mL) and filtered through a plug of silica gel, then the plug was washed with additional cyclohexane (500 mL). The solvent was evaporated to yield a yellow solid (4.9 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ 1.42 (d, ³*J* = 7.2 Hz, 6H), 1.50 (d, ³*J* = 6.8, 6H), 2.79–3.32 (m, 8H), 3.39 (q, ³*J* = 7.6 Hz, 2H), 3.48 (q, ³*J* = 7.6 Hz, 2H), 6.91 (s, 2H), 7.35 (s, 2H).

4,5-Dichloro-2,7-dimethylcorannulene (41). 2,7-Dimethyl-1,2,6,7-tetrahydro-4,5-dichlorocorannulene (4.8 g, 14 mmol) and 2,3-dichloro-5,6-dicyanoquinone (7.5 g, 33 mmol) in benzene (500 mL) were stirred at ambient temperature for 2 days. The solution was diluted with cyclohexane (250 mL) and passed through a plug of silica gel, then the plug was washed with additional cyclohexane (250 mL). The solvent was evaporated to yield a pale yellow solid (2.36 g, 50%). ¹H NMR (400 MHz, CDCl₃): δ 2.76 (d, ⁴*J* = 1 Hz, 6H), 7.54 (d, ⁴*J* = 1 Hz, 2H), 7.66 (s, 2H), 7.96 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 18.7, 123.5, 126.5, 126.7, 126.8, 130.1, 130.7, 130.9, 133.1, 134.1, 135.1, 135.2. HRMS *m/z*: found 346.0309; calcd (C₂₂H₁₂Cl₂) 346.0316.

1,3,4,6,7,10-Hexamethylfluoranthene (42). Trimethylaluminum (23.0 mL, 2 M in hexanes, 46.0 mmol) was added dropwise to a solution of 1,6-dibromo-3,4-dichloro-7,10-dimethylfluoranthene (**35**) (3.50 g, 7.7 mmol) and 1,3-bis(diphenylphosphino)propane nickel(II) chloride (0.21 g, 0.38 mmol) in DME (125 mL). The solution was warmed to reflux for 24 h, quenched slowly with ethanol, extracted with dichloromethane (50 mL), and washed 3 times with water (100 mL). The organic layer was dried with magnesium sulfate, filtered, and evapo-

rated. The crude product was purified by column chromatography on silica gel with cyclohexane as the eluent to yield a golden yellow solid (1.85 g, 85%). Mp 113–116 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.69 (s, 6H), 2.73 (s, 6H), 2.85 (s, 2H), 7.07 (s, 2H), 7.11 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 24.3, 24.4, 24.7, 126.2, 128.8, 130.0, 131.3, 133.5, 134.2, 135.1, 135.4, 139.3. HRMS *m/z*: found 286.1730; calcd (C₂₂H₂₂) 286.1716.

1,3,4,6,7,10-Hexakis(dibromomethyl)fluoranthene (43). 1,3,4,6,7,10-Hexamethylfluoranthene (**42**) (0.40 g, 1.4 mmol), *N*-bromosuccinimide (5.97 g, 33.6 mmol), and benzoyl peroxide (22 mg) in carbon tetrachloride (225 mL) were irradiated with incandescent light and refluxed for 70 h. The solvent was evaporated and the solid was triturated 3 times with methanol (50 mL), to yield a golden solid (1.75 g, quantitative). Mp >300 °C. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.99 (s, 2H), 7.06 (s, 2H), 7.58 (s, 2H), 8.21 (s, 2H), 9.91 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 36.9, 37.2, 37.3, 120.8, 129.8, 131.2, 131.4, 133.3, 136.9, 138.6, 138.7, 140.0.

Accorannulene (7). Zinc–copper couple (7.82 g, 120 mmol) and titanium tetrachloride (3.3 mL, 30 mmol) in DME (200 mL) were refluxed for 2 h to yield a black suspension. 1,3,4,6,7,10-Hexakis(dibromomethyl)-3,4-dichlorofluoranthene (**43**) (1.15 g, 0.93 mmol) in toluene (25 mL) was added to the refluxing black suspension over a period of 12 h. The mixture was refluxed an additional 3 h after the last addition, diluted with cyclohexane (250 mL), and filtered through a plug of silica gel, then the plug was washed with additional benzene (500 mL). The product was further purified by column chromatography on silica gel with 30:1 cyclohexane/benzene as the eluent. The solvent was evaporated to yield a pale yellow solid (0.020 g, 20%). ¹H NMR (300 MHz, CDCl₃): δ 6.49 (s, 2H), 7.32 (s, 2H), 7.38 (s, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H).

2,3-Dimethylcorannulene (5). Trimethylaluminum (2.0 mL, 2.0 M in hexanes, 4.0 mmol) was added dropwise to a solution of 2,3-dichlorocorannulene (**38**) (0.50 g, 1.57 mmol) and 1,3-bis(diphenylphosphino)nickel(II) chloride (0.017 g, 0.031 mmol) in DME (50 mL) and the solution was heated to reflux for 12 h. The solution was quenched slowly with ethanol, diluted with dichloromethane (50 mL), washed 3 times with water (100 mL), dried with magnesium sulfate, filtered, and evaporated. The product was purified by passage through a plug of silica gel with benzene as the eluent to yield a white solid (0.41 g, 95%). Mp 130–132 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.99 (s, 6H), 7.59 (s, 2H), 7.72 (d, ³*J* = 8.7 Hz, 2H), 7.78 (s, 2H), 7.79 (d, ³*J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 24.2, 126.2, 126.5, 127.1, 127.2, 130.0, 130.3, 130.6, 134.3, 135.62, 135.64, 137.5. HRMS *m/z*: found 278.1093; calcd (C₂₂H₁₄) 278.1095.

2,4,5,7-Tetramethylcorannulene (6). Trimethylaluminum (0.15 mL, 2.0 M in hexane, 0.3 mmol) was added dropwise to a solution of 4,5-dichloro-2,7-dimethylcorannulene (**41**) (0.041 g, 0.144 mmol) and 1,3-bis(diphenylphosphino)nickel(II) chloride (0.008 g, 0.014 mmol) in DME (15 mL) and the solution was heated to 60 °C for 15 h. The solution was quenched with methanol slowly, diluted with benzene (10 mL), washed 3 times with water (25 mL), dried over magnesium sulfate, and evaporated. The product was purified by passage through a plug of silica with a 1:1 mixture of benzene/hexanes as the eluent to yield as a pale yellow solid (0.035 g, 95%). Mp 188–190 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.79 (d, ⁴*J* = 1 Hz, 6H), 2.79 (d, ⁴*J* = 1 Hz, 6H), 7.51 (d, ⁴*J* = 1 Hz, 2H), 7.64 (s, 2H), 7.66 (d, ⁴*J* = 1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 18.9, 24.6, 124.9, 125.7, 126.1, 129.3, 130.3, 130.5, 134.2, 134.5, 135.1, 135.3, 137.1. HRMS *m/z*: found 306.1398; calcd (C₂₄H₁₈) 306.1409.

Bromocorannulene (44). Bromine (0.35 g, 2.2 mmol) was added dropwise over 5 min to a solution of corannulene (**1**) (0.52 g, 2.1 mmol) and ferric bromide (0.062 g, 0.21 mmol) in dichloromethane (50 mL) at –80 °C. The solution was allowed to warm to ambient temperature over 4 h, quenched with a saturated solution of sodium bisulfite, washed 3 times with water, dried over magnesium sulfate, filtered, and evaporated. The crude product was purified by passage through a plug of silica gel with benzene as the eluent to yield a pale yellow solid (0.65 g, 95%). This material was used as isolated; however, a spectroscopically pure sample can be obtained by column chromatography with cyclohexane as the eluent. Mp 174–176 °C (lit. mp 180–182 °C).²⁷ ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71 (d, ³*J* = 8.8

Hz, 1H), 7.78–7.82 (m, 5H), 7.87 (d, $^3J = 8.8$ Hz, 1H), 7.93 (d, $^3J = 8.8$ Hz, 1H), 8.03 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 121.1, 125.7, 126.2, 126.7, 126.9₅, 126.9₆, 127.5 (127.5), 127.8, 129.1, 129.9, 130.5, 130.7, 130.8, 131.6, 134.4, 134.7, 135.3₇, 135.4, 135.5. HRMS m/z : found 327.9886; calcd ($\text{C}_{20}\text{H}_9\text{Br}$) 327.9888.

Methylcorannulene (8). Trimethylaluminum (0.15 mL 2.0 M in hexanes, 0.30 mmol) was added dropwise to a solution of bromocorannulene (**44**) (0.05 g, 0.15 mmol) and 1,3-bis(diphenylphosphino)nickel(II) chloride (0.004 g, 0.007 mmol) in DME (15 mL). The solution was heated to reflux for 2 h, quenched slowly with ethanol, diluted with dichloromethane (50 mL), washed 3 times with water (100 mL), dried with magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography on silica gel with hexane as the eluent to yield of a white solid (0.035 g, 90%). Mp 123–129 °C. ^1H NMR (400 MHz, CDCl_3): δ 2.92 (d, $J = 0.8$ Hz, 3H), 7.64 (d, $J = 0.8$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.83–7.92 (m, 6H), 7.99 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 19.0, 124.7, 125.6, 126.4, 126.5, 126.7, 126.8, 126.88, 126.90, 130.2, 130.3, 130.7, 130.8, 131.3, 134.6, 135.4, 135.5, 135.6, 135.7, 135.8, 136.6. HRMS m/z : found 264.0926; calcd ($\text{C}_{21}\text{H}_{12}$) 264.0939.

1,3,5,7,9-Pentachlorocorannulene (45). Iodine monochloride (25 mL, 25 mmol, 1 M in dichloromethane) was cooled to -78 °C and corannulene (**1**) (0.480 g, 1.92 mmol) was added. The mixture was allowed to warm to room temperature over 10 h and stirred an additional 3 days at ambient temperature. The solution was poured into 50 mL of chloroform and washed 2 times with 5% aqueous sodium thiosulfate (20 mL) and 2 times with water (20 mL). The resulting yellow suspension was evaporated to dryness and triturated 2 times with hexanes (20 mL) and 3 times with dichloromethane (10 mL). The resulting yellowish solid was recrystallized from 1,1,2,2-tetrachloroethane to yield a pale yellow solid (0.420 g, 52%). Mp >300 °C. ^1H NMR (400 MHz, 1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$, 80 °C): δ 8.02 (s, 5H). MS m/z (rel intensity): 419.7 (63, M^+), 0.421.7 (100, $\text{M} + 2$), 423.7 (70, $\text{M} + 4$), 425.7 (23, $\text{M} + 6$).

Decachlorocorannulene (46). A solution of 2,3-dichlorocorannulene (**38**) (0.100 g, 0.314 mmol), sulfuryl chloride (2.5 mL), and sulfur monochloride (0.100 g, 0.735 mmol) was added over 5 min to a solution of aluminum chloride (0.025 g, 0.188 mmol) in sulfuryl chloride (7.5 mL). The solution was heated to a gentle reflux for 12 h. After all of the liquid evaporates, additional sulfuryl chloride (5 mL) was added and the solution was reflux for and an additional 5 h. The solution was cooled then poured onto water and neutralized with potassium carbonate and the solid collected by filtration. The solid was dried in air for 1 h,

dissolved in DME (10 mL), and heated to reflux for 12 h. The solution was cooled to ambient temperature and filtered to yield a yellow solid (0.110 g, 60%). Mp >300 °C. Due to the extremely poor solubility the product has not yet been characterized by ^{13}C NMR. Our experience is in contrast to the literature report;²⁹ however, no solvent for the NMR was reported therein. HRMS m/z : found 589.6884; calcd ($\text{C}_{20}\text{Cl}_{10}$) 589.6885

1,3,5,7,9-Pentamethylcorannulene (9). Trimethylaluminum (0.71 mL, 1.42 mmol, 2 M solution in hexanes) was added to a solution of 1,3,5,7,9-pentachlorocorannulene (**45**) (0.050 g, 0.118 mmol) and 1,3-bis(diphenylphosphino)nickel(II) chloride (0.020 g, 0.037 mmol) in DME (50 mL). The solution was refluxed for 24 h, quenched slowly with methanol then 10% aqueous hydrochloric acid, diluted with benzene (20 mL), washed 2 times with water (20 mL), dried with magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography with cyclohexane as the eluent to yield a pale yellow solid (0.012 g, 33%). Mp 179–182 °C. ^1H NMR (400 MHz, CDCl_3): δ 2.78 (d, $^4J = 0.8$ Hz, 15H), 7.55 (d, $^4J = 0.8$ Hz, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ 19.1, 122.8, 130.5, 134.4, 136.1. HRMS m/z : found 320.1560; calcd ($\text{C}_{25}\text{H}_{20}$) 320.1565.

Decamethylcorannulene (10). Trimethylaluminum (2.73 mL, 2 M in hexanes, 5.46 mmol) was added dropwise to a solution of decachlorocorannulene (**46**) (0.130 g, 0.219 mmol) and 1,3-bis(diphenylphosphino)nickel(II) chloride (0.020 g, 0.037 mmol) in DMEU (25 mL). The solution was heated to 90 °C for 18 h, quenched with ethanol slowly, diluted with benzene, washed 5 times with water, dried over magnesium sulfate, filtered, and evaporated. The product was purified by passage through a plug of silica with benzene as the eluent. The solvent was evaporated to yield a yellow solid (0.025 g, 30%). Mp 310–312 °C. ^1H NMR (500 MHz, CDCl_3): δ 2.89 (s, 30H). ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 20.5, 129.6, 130.5, 133.7. HRMS m/z : found 390.2347; calcd 390.2348.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **22**, **23**, and **24** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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