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Synthesis of a Five-Fold-Differentiated 1,3,5,7,9-Pentasubstituted Corannulene: A Maximal Labeling Problem in the Context of Corannulene

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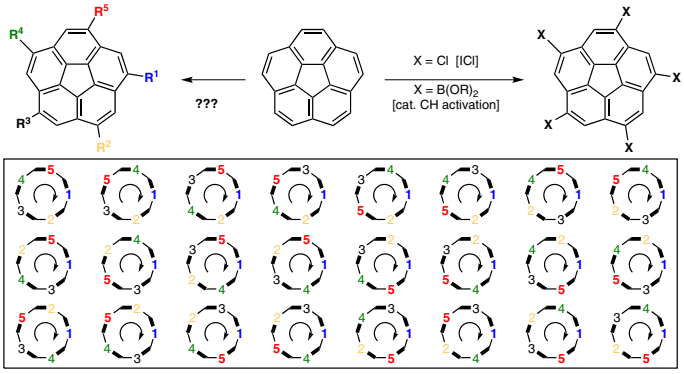

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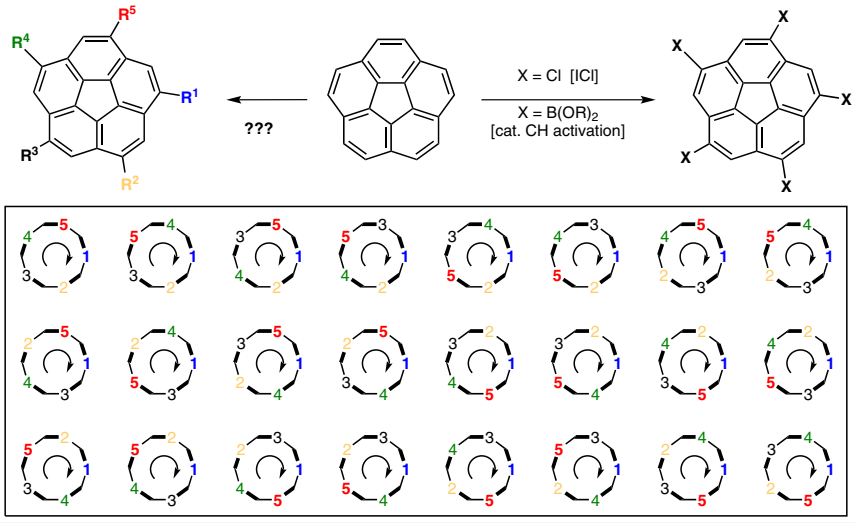
Abstract This work defines a maximally labeled isomer problem in the context of 1,3,5,7,9-pentasubstituted corannulenes and explores two new synthetic strategies for the construction of key C–C bonds in the corannulene nucleus: a) a Diels–Alder cycloaddition of thiophene dioxide and acenaphthene fragments; b) a manganese-mediated reductive coupling of benzylic halides, which tolerates carboxy ester functionality. It advances the area of curved aromatics based on corannulene by setting a new family of targets for chemical synthesis and providing additional general synthetic tools.

Key words 1,3,5,7,9-pentasubstituted corannulene, Diels–Alder cycloaddition, reductive coupling

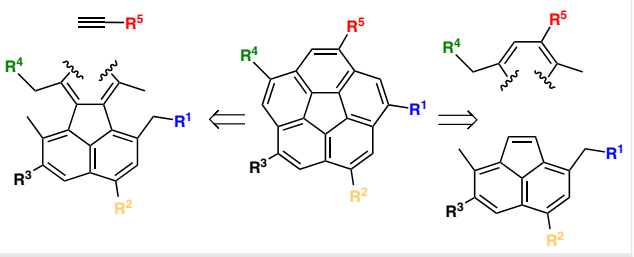
With access to corannulene on kilogram scale,[1] and the existence of convenient methods to make 1,3,5,7,9-pentaX-corannulene (X = Cl;[2] X = $B(OR)_2$[3]), a diverse spectrum of *sym*-pentasubstituted forms lie well within the grasp of even the avocational synthetic chemist.[4] In contrast, synthesis of a fivefold differentiated 1,3,5,7,9-pentasubstituted corannulene remains an open challenge. The issue of selectivity requires the ability to on one hand restrict substitution to all the *pro*-R (respectively all *pro*-S) hydrogen atom sites, yet replace each such hydrogen by a different ligand (R^1, R^2, R^3, R^4, R^5). Such problems in isomerism fall into the class of maximally labeled 'symmetric' scaffolds,[5] for example, the classic maximally labeled tetrahedra of van't Hoff,[6] and LeBel,[7] for which there are two permutational isomers,[8] or the maximally labeled octahedra of Werner, for which there are 30 permutational isomers.[9] In the present case, the five potential sites of substitution present a field of C_5-static symmetry, with the possibility of a dynamic mirror operation perpendicular to the five-fold axis upon bowl inversion. Thus, there are 48 maximally labeled isomers, each asymmetric (i.e., of C_1 symmetry) as static bowl structures, and inversion interconverts the enantiomeric pairs to yield 24 possible time-averaged C_s-symmetry isomers. In the present work, selective preparation of one such isomer serves as a *reduction to practice* of the idea; however, a future goal would be to address each isomer by a general synthetic methodology. Indeed, if five-fold chemical orthogonality could be achieved,[10] then in principle any one of these permutation isomers can serve as the key intermediate to prepare a library of derivatives comprising a full set of 24 pentafunctional derivatives selectively (Scheme 1); but how to reach that goal?

Starting from corannulene and step-by-step replacing CH bonds seems a Herculean task even with modern methods in selective directed multi-CH activation.[11] In contrast, an approach through a convergent synthesis of the corannulene nucleus would reduce the problem to the selective control of the substitution pattern on the converging fragments (Scheme 2). Following the most common disconnection, one would combine a tetrasubstituted diene with a monosubstituted dieneophile (Scheme 2, left). Alternatively, one could imagine combining a trisubstituted dieneophile with a disubstituted diene (Scheme 2, right).

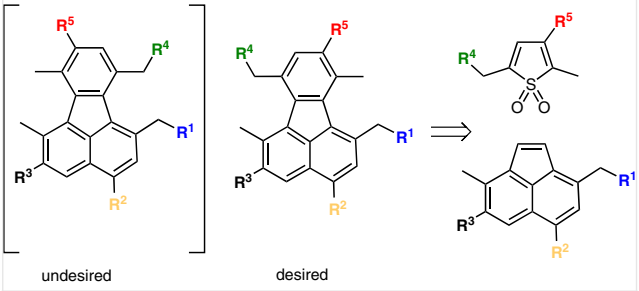
The latter strategy, which happens to balance the number of substituents in each fragment better, has been given much less attention in previous corannulene syntheses. Thus, Diels–Alder chemistry between a disubstituted thiophene dioxide and a trisubstituted acenaphthene would provide an opportunity to explore another general convergent method toward the corannulene nucleus as well as address the isomer selectivity problem,[12] even if it required separation of an undesired cycloaddition isomer (Scheme 3).



Scheme 1 Maximally labeled *sym*-pentasubstituted corannulene

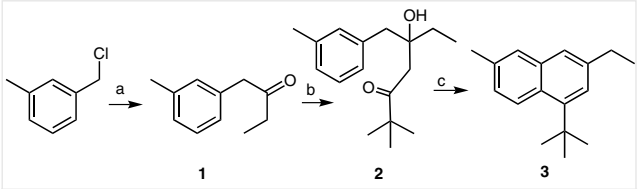


Scheme 2 Disconnection strategies



Scheme 3 Diels–Alder strategy from acenaphthene and thiophene-*S*,*S*-dioxide fragments

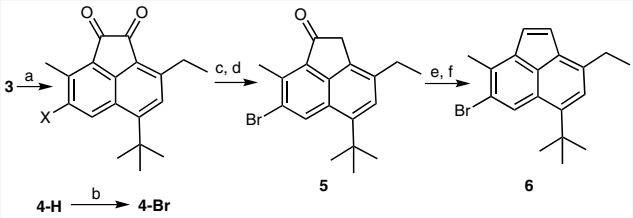
With a strategy in place, construction of the fragments could begin. Synthesis of the acenaphthene fragment followed a modification of the route developed during earlier corannulene syntheses for preparing acenaphthoquinones. The Grignard reagent of α-chloro-*m*-xylene reacted with propionitrile and after hydrolysis gave 1-(3-methylphenyl)-2-butanone **1** (Scheme 4).[13] Aldol reaction between **1** and the enolate of pinacolone, generated at –78 °C with LDA, produced carbinol **2**. Acidic treatment with HBr induced a cyclization rearomatization to form 1-*tert*-butyl-3-ethyl-6-methylnaphthylene (**3**) as a clean product.[14]



Scheme 4 Synthesis of **3**. *Reagents and conditions*: (a) Mg (Et_2O) ca. –10 °C, 3-methylbenzyl chloride (Et_2O), 2–3 h, ca. –10 °C, propionitrile (Et_2O), 48 h, –10 °C to r.t. (84%); (b) *i*-Pr_2NH (Et_2O), 0 °C, *n*-BuLi (*n*-hexane), 30 min at 0 °C, 3,3-dimethylbutan-2-one, 1.5 h, at –78 °C, **1**, 8 h at –78 °C (73%); (c) **2** (AcOH), 48% aq HBr, r.t., to 90 °C, 4 h (77%).

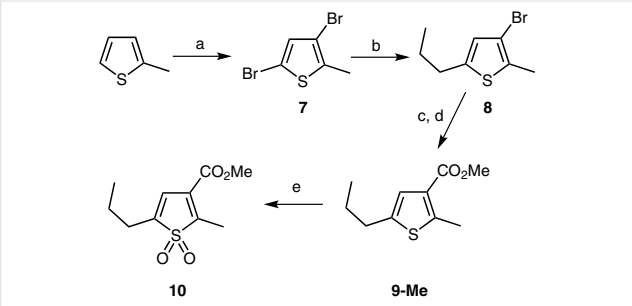
Elaboration of **3** to the acenaphthene took two circuitous routes; the shorter reported here and the longer is archived in the supplementary material as compounds **Alt-Ia/b – Alt-IVa/b**. Initially, diacylation of **3** with oxalyl chloride and $AlBr_3$ lead to the acenaphthoquinone **4**-H. Bromination of **4**-H occurred selectively at the desired position to form **4**-Br. Reduction of **4**-Br with sodium borohydride gave a mixture of diols, which upon treatment with *p*-toluenesulfonic acid produced acenaphthone **5**. After carbonyl reduction and dehydration of the ensuing alcohol one arrives at the acenaphthene **6** (Scheme 5).[15]

The thiophene dioxide fragment was prepared starting from 2-methylthiophene. Bromination with elemental bromine in acetic acid gave 2,4-dibromo-5-methylthiophene (**7**, Scheme 6). Selective lithiation of the 2-bromo group followed by coupling with 1-iodopropane produced 3-bromo-2-methyl-5-propylthiophene (**8**). Subsequent lithiation of **8**



Scheme 5 Synthesis of **6**. *Reagents and conditions*: (a) CH_2Cl_2 (N_2-degassed), $AlBr_3$, at –25 °C, oxalyl chloride (CH_2Cl_2), 30 min at –25 °C, to ca. –10 °C, 8 h (38%); (b) Br_2, r.t. to 60 °C, 1 h (98%); (c) CH_2Cl_2–EtOH (5:1), $NaBH_4$, r.t. to reflux, 2 h; (d) toluene, TsOH·H_2O, r.t. to reflux, 3 h (84%, 2 steps); (e) CH_2Cl_2–EtOH (5:3), $NaBH_4$, r.t. to reflux, 2 h; (f) toluene, TsOH·H_2O, r.t. to reflux, 2 h (69%, 2 steps).

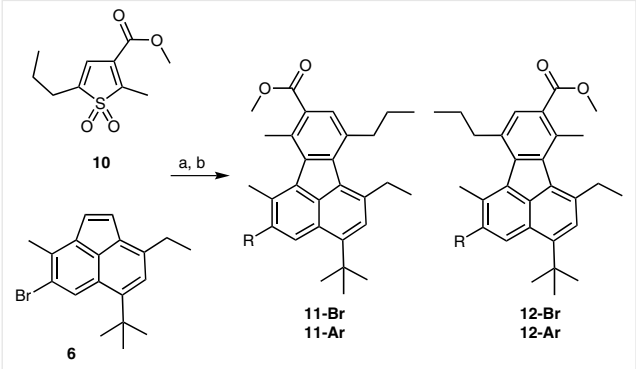
and quenching with CO_2 lead to the 2-methyl-5-propylthiophene-3-carboxylic acid, which could be esterified to the methyl ester **9**.[16] Methyl ester **9** was oxidized by peroxytrifluoroacetic acid to complete the thiophene dioxide fragment **10**.[17]



Scheme 6 Synthesis of **10**. *Reagents and conditions*: (a) AcOH, at 0 °C, Br_2 (AcOH), 0 °C to r.t., 12 h (90%); (b) THF, at –78 °C, *n*-BuLi (*n*-hexane) 45 min, at –78 °C, *n*-propyl iodide at –78 °C, 10 min to –15 °C 1 h to r.t., 1 h (72%); (c) THF, at –78 °C, *n*-BuLi (*n*-hexane) 45 min, at –78 °C, CO_2 at –78 °C to r.t., 1 h; (d) MeOH, $SOCl_2$, r.t. to reflux 20 h (40%, 2 steps); (e) H_2O_2 (35% in H_2O) at 0 °C, TFAA at 0 °C (slow addition, very exothermic; DANGER: do not exceed 10 °C), another 10 min at 0 °C, **9-Me** (MeCN; DANGER: do not exceed 30 °C; 36%).

Diels–Alder reaction between fragments **6** and **10** followed by rearomatization with DDQ proceeded smoothly but gave a mixture of two regioisomeric bromofluoranthenes **11**-Br/**12**-Br in roughly equal parts. The isomers could only be separated by preparative HPLC. Coupling the mixture of bromides with 4-methoxyphenylboronic acid led to arylfluoranthenes **11**-Ar/**12**-Ar, which could be separated by normal chromatographic methods. The desired isomer **12**-Ar was used moving forward (Scheme 7).[18]

Wohl–Ziegler bromination of the separated **12**-Ar delivered a mixture of brominated fluoranthenes, in which the major contribution came from a mixture of diastereomers of pentabromide **13**. In the course of this work, C_s-symmetrical fluoranthene derivatives with comparable substituents to **12**-Ar have shown similar bromination patterns.[19]



Scheme 7 Synthesis of **12-Ar**. *Reagents and conditions*: (a) reflux 24 h, benzene, DDQ, reflux 4 h (56%); (b) 4-methoxyphenylboronic acid, K_2CO_3 (toluene–EtOH–H_2O, 4:4:1), N_2, r.t., $Pd(PPh_3)_4$, r.t. to reflux 5 h (28% isolated **12-Ar**).

Despite there being several methods for reductive coupling of benzylic bromides to convert bromoalkylfluoranthenes into corannulenes, the manganese-based coupling of benzylic bromides had not been investigated.[20] This method promised to tolerate the carboxylic ester, as well as the *tert*-butyl group and offered an alternative to the nickel-mediated methods. Indeed, manganese-mediated reductive cyclization of pentabromide **13** produced a mixture of cyclized products **14**, which following rearomatization by DDQ yielded the target compound **15**, a 1,3,5,7,9-pentasubstituted corannulene where all substituents are different (Scheme 8).[21]

All signals for **15** in the proton NMR spectrum could be assigned (Figure 1). The proton signals for the five hydrogens on the corannulene nucleus all appear in the region δ = 7.5–8.8 ppm. Those proton signals for hydrogens adjacent to alkyl groups bearing benzylic hydrogens showed the expectedly small $J_{1,4}$ couplings (ca. 1 Hz); and therefore assignment could be made from the splitting patterns. Some baseline impurities notwithstanding, there is no doubt about the identity of the final product (see Supporting Information).

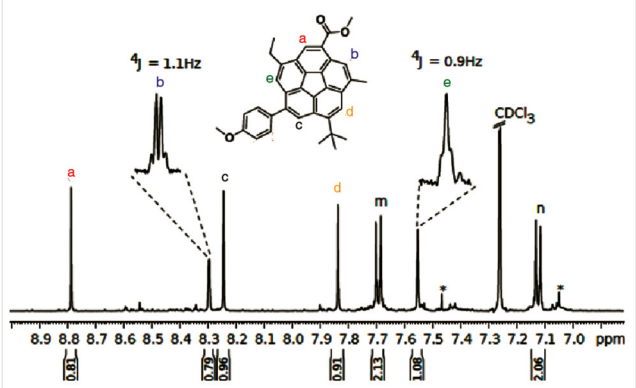
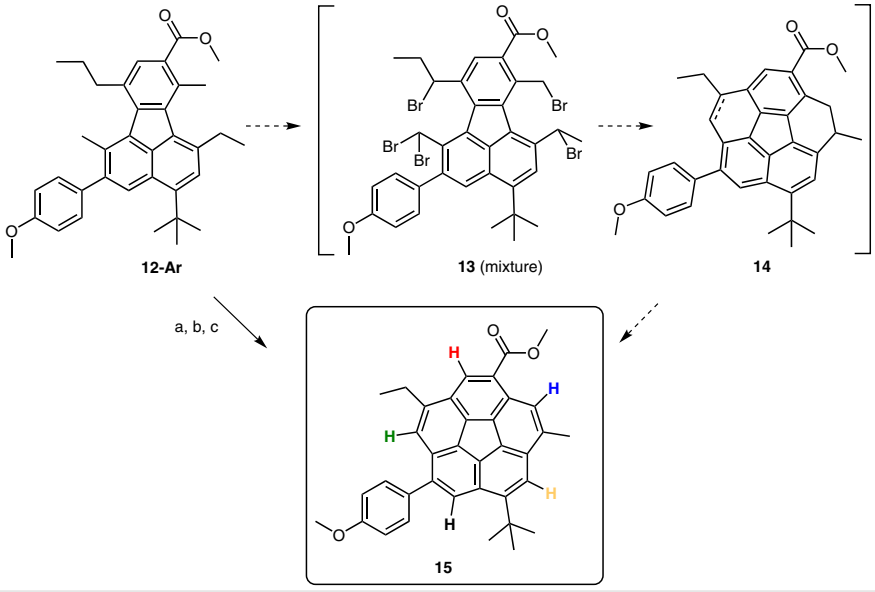


Figure 1 ^{1}H NMR support of structure



Scheme 8 Synthesis of **15**. *Reagents and conditions*: (a) NBS, BPO (CCl_4), r.t. to reflux, *hv* (Osram, 100 W), 7 h; (b) THF–H_2O (1.5:1), N_2, r.t., $CuCl_2$, r.t., 3 min, Mn powder, r.t., 24 h; (c) benzene, DDQ, r.t. to reflux, 5 h (11%, 3 steps).

The presence of the ethyl group allows the assessment of the barrier to bowl inversion by variable-temperature NMR (Figure 2). At the static limit the methylene protons are diastereotopic and give rise to a doublet of doublet quartets, which upon increasing rate of bowl inversion coalesce and then become a simple quartet at the dynamic limit. From the line shape or temperature of coalescence, the barrier can be estimated to be 8.9 kcal/mol, a value consistent with that seen for other pentasubstituted corannulenes (pentaethyl = 9.0 kcal/mol).

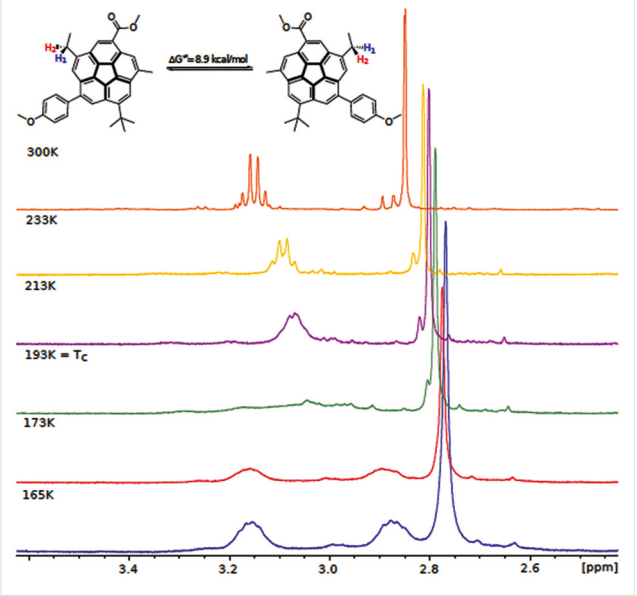


Figure 2 Variable-temperature ^1H NMR spectra of the methylene region of **15**

Having demonstrated the proof of principle regarding a single maximally labeled isomer, the task remains to tailor each of these substituents to a specific further reactivity. With an olefin, an electron-rich aromatic, an azide or a thiol, an ester, and an alkyl group, one could imagine exploiting metathesis, E_{Ar}, 'click', transesterification, and CH activation chemistry in selective ways. At that point one might be able to display in the 'second sphere' all 24 distributions of a set of five differentiable groups after reaction with appropriate reaction partners. At present this is fantasy and folly, but also fun!

Overall, this work defines a maximally labeled isomer problem in the context of 1,3,5,7,9-pentasubstituted corannulenes and explores two new synthetic strategies for the construction of key C–C bonds in the corannulene nucleus:

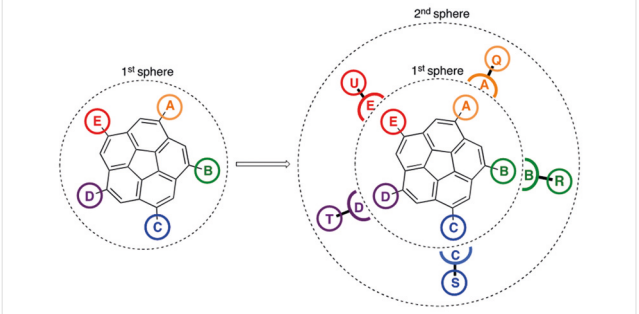


Figure 3 Star-growth by orthogonal reactivity

(a) a Diels–Alder cycloaddition of thiophene dioxide and acenaphthene fragments; b) a manganese-mediated reductive coupling of benzylic halides, which tolerates carboxyester functionality. It advances the area of curved aromatics based on corannulene by setting a new family of targets for chemical synthesis and providing additional general synthetic tools (Figure 3).

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1562845.

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(18) **Cycloaddition**
To an oven-dried 50 mL round-bottom flask, equipped with stir bar and reflux condenser with N_2 inlet, was added the acenaphthylene **6** (1.26 g, 3.83 mmol), thiophene-1,1-dioxide **10** (0.89 g, 3.86 mmol), and dry xylene (9 mL). The yellow solution was degassed three times by pulling vacuum and heated to reflux for 24 h. After cooling to r.t., the solvent was removed by rotary evaporation and the crude product was obtained as brown resin.
In an oven-dried 100 mL round-bottom flask, equipped with stir bar and reflux condenser with N_2 inlet, the crude dihydrofluoranthene (max. 3.83 mmol) was dissolved in dry benzene (65 mL). DDQ (1.3 g, 5.73 mmol) was added in one step, and the dark suspension was heated to reflux for 4 h. After cooling to r.t., the mixture was filtered through a plug of silica and thoroughly rinsed with CH_2Cl_2. The filtrate was evaporated giving a dark residue which was sonicated with *n*-hexane. The resulting suspension was filtered through Celite giving a yellow solution. The solution was washed with sat. aq $NaHCO_3$, the organic phase was dried over $MgSO_4$ and filtered. The solvent was evaporated, and the crude product was subjected to flash column chromatography on silica using *n*-hexane–EtOAc (50:1). The fluoranthenes **11-Br**/**12-Br** (mixture of regioisomers) were obtained as yellow resins (1.05 g, 56%, two steps). Analytical separation of the two isomers was achieved by HPLC (Waters Spherisorb S5, Nitrile, 250 × 20mm, 25 mL/min) with *n*-hexane–EtOAc (200:1). The solvent mixture was recycled through rotary evaporation.
Methyl 4-*tert*-Butyl-2-bromo-6-ethyl-1,7-dimethyl-10-propylfluoranthene-8-carboxylate (12-Br)
R_f = 0.3 (silica gel; *n*-hexane–EtOAc, 10:1). IR (film): 2958 (w), 2932 (w), 2872 (w), 1717 (s), 1585 (w), 1458 (m), 1433 (m), 1378 (w), 1364 (w), 1277 (m), 1255 (m), 1200 (s), 1168 (m), 1054 (m), 995 (w), 957 (w), 906 (m), 731 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (s, 1 H), 7.81 (s, 1 H), 7.42 (s, 1 H), 3.95 (s, 3 H), 3.05 (q, ^3J = 7.5 Hz, 2 H), 2.96 (t-like, ^3J = 7.5 Hz, 2 H), 2.81 (s, 3 H), 2.73 (s, 3 H), 1.69 (sext, ^3J = 7.5 Hz, 2 H), 1.64 (s, 9 H), 1.35 (t, ^3J = 7.5 Hz, 3 H), 0.90 (t, ^3J = 7.5 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 168.67, 146.31, 142.11, 141.64, 138.96, 136.95, 134.38, 132.05, 131.40, 131.07, 130.81, 130.07, 130.06, 127.25, 125.86, 125.49, 51.95, 37.32, 36.12, 32.45, 32.43, 29.22, 24.54, 24.35, 21.96, 15.15, 14.16. ESI-HRMS: *m/z* [M + Na]$^+$ calcd for $C_{29}H_{33}BrNaO_2^+$: 515.1556; found: 515.1551.
Methyl 3-*tert*-Butyl-5-bromo-1-ethyl-6,7-dimethyl-10-propylfluoranthene-8-carboxylate (11-Br)
R_f = 0.3 (silica gel; *n*-hexane–EtOAc, 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60 (s, 1 H), 7.85 (s, 1 H), 7.40 (s, 1 H), 3.95 (s, 3 H), 3.13–2.98 (m, 4 H), 2.74 (s, 3 H), 2.69 (s, 3 H), 1.71 (sext, ^3J = 7.5 Hz, 2 H), 1.65 (s, 9 H), 1.34 (t, ^3J = 7.5 Hz, 3 H), 0.96 (t, ^3J = 7.5 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 168.67, 147.17, 142.42, 141.83, 140.21, 137.89, 134.77, 134.59, 132.38, 131.79, 131.58, 131.06, 129.70, 129.54, 128.08, 126.13, 125.86, 52.13, 37.73, 36.34, 32.65, 31.96, 29.80, 25.15, 24.73, 22.59, 16.10, 14.21.
Aryl Coupling
The isomeric mixture of bromofluoranthenes **11-Br**/**12-Br** (378

mg, 0.766 mmol), 4-methoxyphenylboronic acid (151.5 mg, 0.996 mmol), and K_2CO_3 were dissolved in a thoroughly degassed solvent mixture of toluene (13 mL), EtOH (13 mL), and H_2O (3.3 mL). To the mixture was added $Pd(PPh_3)_4$, and the solution was heated to reflux for 5 h. After cooling to r.t., the mixture was washed with 10% aq HCl (3 × 50 mL) and brine (3 × 50 mL), and the organic phase was dried over $MgSO_4$. Filtering and evaporating the solvent gave the crude product **11-Ar**/**12-Ar** as a yellow solid which was purified by column chromatography on silica with *n*-hexane–EtOAc (100:1 to 50:1). The two isomers can be separated by normal gravity column chromatography, a first separation delivered the desired isomer as yellow solid (112 mg, 28%). Typically, collected mixed fractions were resubmitted.

Methyl 4-*tert*-Butyl-2-(4-methoxyphenyl)-6-ethyl-1,7-dimethyl-10-propylfluoranthene-8-carboxylate (12-Ar)

R_f = 0.3 (silica gel; *n*-hexane–EtOAc, 10:1). IR (film): 2955 (m), 2932 (w), 2871 (w), 2835 (w), 1714 (s), 1608 (m), 1513 (m), 1462 (m), 1433 (m), 1390 (m), 1364 (m), 1281 (m), 1264 (s), 1245 (s), 1200 (s), 1174 (s), 1160 (m), 1055 (m), 1036 (m), 994 (w), 958 (w), 894 (m), 835 (m), 737 (s), 705 (m), 580 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.83 (s, 1 H), 7.46 (s, 1 H), 7.43 (d, ^3J = 8.5 Hz, 2 H), 7.04 (d, ^3J = 8.5 Hz, 2 H), 3.96 (s, 3 H), 3.91 (s, 3 H), 3.11 (q, ^3J = 7.5 Hz, 2 H), 3.04 (t-like, ^3J = 7.5 Hz, 2 H), 2.85 (s, 3 H), 2.52 (s, 3 H), 1.74 (sext, ^3J = 7.5 Hz, 2 H), 1.66 (s, 9 H), 1.37 (t, ^3J = 7.5 Hz, 3 H), 0.94 (t, ^3J = 7.5 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 169.07, 159.06, 147.23, 143.00, 142.24, 142.16, 138.67, 136.76, 135.54, 135.16, 134.43, 132.15, 131.31, 131.25, 131.16, 130.99, 129.80, 128.09, 126.95, 125.12, 113.98, 55.58, 52.06, 37.81, 36.44, 32.73, 29.52, 24.39, 23.27, 22.26, 15.53, 14.44. ESI-HRMS: *m/z* [M$^{+\bullet}$] calcd for $C_{36}H_{40}NaO_3^+$: 543.2870; found: 543.2870.

Methyl 3-*tert*-Butyl-5-(4-methoxyphenyl)-1-ethyl-6,7-dimethyl-10-propylfluoranthene-8-carboxylate (11-Ar)

R_f = 0.3 (silica gel; *n*-hexane–EtOAc, 10:1). IR (film): 2959 (m), 2873 (w), 1718 (m), 1608 (w), 1513 (m), 1461 (m), 1437 (m), 1391 (w), 1378 (w), 1365 (w), 1319 (s), 1219 (m), 1175 (m), 1108 (w), 1088 (w), 1058 (w), 1034 (m), 908 (m), 836 (m), 729 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.85 (s, 1 H), 7.44 (d, ^3J = 8.5 Hz, 2 H), 7.04 (d, ^3J = 8.5 Hz, 2 H), 3.95 (s, 3 H), 3.90 (s, 3 H), 3.14 (q, ^3J = 7.5 Hz, 2 H), 3.05 (t-like, ^3J = 7.5 Hz, 2 H), 2.80 (s, 3 H), 2.46 (s, 3 H), 1.73 (sext, ^3J = 7.5 Hz, 2 H), 1.66 (s, 9 H), 1.35 (t, ^3J = 7.5 Hz, 3 H), 0.96 (t, ^3J = 7.5 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 168.80, 159.07, 147.92, 142.68, 142.40, 142.38, 139.75, 137.50, 135.46, 135.28, 134.44, 131.94, 131.64, 131.44, 131.20, 130.73, 129.30, 127.62, 127.45, 125.20, 113.97, 55.58, 52.04, 37.88, 36.45, 32.70, 29.90, 24.71, 23.72, 22.68, 16.27, 14.22.

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(21) **Bromination**

Fluoranthene **12-Ar** (112 mg, 0.215 mmol) was dissolved in CCl_4 (5 mL), and NBS (199 mg, 1.12 mmol) and BPO (2 mg) were added. The mixture was heated to reflux by irradiating with an incandescent light bulb (Osram, 100 W). After 7 h the suspension was cooled in an ice bath, and the succinimide was filtered with a frit. The filtrate was evaporated (recycling of CCl_4) and dissolved in CH_2Cl_2. The CH_2Cl_2 solution was thoroughly washed with H_2O, dried over $MgSO_4$, filtered, and evaporated to deliver a crude bromide mixture (185 mg).

Ring Closure

To an oven-dried two-necked 50 mL round-bottom flask, equipped with stir bar, was added the crude mixture of bromofluoranthenes (185 mg) in THF (16 mL), and H_2O (10 mL) was added. The solution was thoroughly degassed and $CuCl_2$ was added and the now yellow-greenish mixture was stirred at r.t. for 3 min, prior to the addition of Mn powder in one step. The reaction mixture was stirred at r.t. for 24 h, and was then quenched with 10% aq HCl and extracted with MTBE (3 × 60 mL). The organic phase was washed with brine (3 × 50 mL), dried over MgSO4, filtered, and evaporated to give a crude cyclized product as an orange-brownish resin (83 mg).

Dehydrogenation

The crude cyclized product (42 mg) was dissolved in dry benzene (4 mL), and DDQ (55.6 mg, 0.245 mmol) was added. The dark mixture was refluxed for 5 h and was diluted with *n*-hexane after cooling to r.t. The suspension was filtered through a plug of Al_2O_3, which was thoroughly rinsed with *n*-hexane–EtOAc (20:1). The filtrate was washed with sat. aq $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated to give the crude corannulene **15** as a yellow-brownish resin (18 mg). Preparative TLC with *n*-hexane–EtOAc (50:1) followed by *n*-hexane–EtOAc–toluene (50:1:1) afforded the pentasubstituted corannulene **15** as a yellowish resin (5.2 mg, 11%, 3 steps). R_f = 0.3 (silica gel; *n*-hexane–EtOAc, 10:1). IR (film): 2955 (w), 2930 (w), 2871 (w), 1715 (m), 1607 (w), 1514 (m), 1463 (m), 1438 (w), 1394 (w), 1365 (w), 1247s, 1207 (w), 1175 (m), 1137 (w), 1121 (w), 1094 (w), 1069 (w), 1035 (w), 988 (w), 882 (w), 835 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 8.30 (q, ^4J = 1.1 Hz, 1 H), 8.25 (s, 1 H), 7.84 (s, 1 H), 7.69 (d, ^3J = 8.7 Hz), 7.55 (t, ^4J = 0.9 Hz), 7.12 (d, ^3J = 8.7 Hz), 4.09 (s, 3 H), 3.93 (s, 3 H), 3.15 (dq, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 2 H), 2.85 (d, ^4J = 1.1 Hz, 3 H), 1.74 (s, 9 H), 1.46 (t, ^3J = 7.5 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 167.83, 159.44, 150.54, 144.25, 140.07, 138.26, 137.99, 135.70, 134.36, 134.32, 133.54, 132.57, 131.00, 130.35, 130.32, 130.21, 128.60, 128.57, 127.70, 127.63, 127.56, 126.19, 123.98, 119.74, 114.28, 55.44, 22.24, 37.29, 32.61, 26.43, 19.03, 16.90. ESI-HRMS: *m/z* [M$^{+\bullet}$] calcd for $C_{36}H_{32}NaO_3^+$: 535.2249; found: 535.2241.