Fluorinated Phenanthrenes as Aryne Precursors: PAH Synthesis Based on Domino Ring Assembly Using 1,1-Difluoroallenes

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Abstract: On treatment with the catalyst, $InBr_3$, 1,1-difluoroallenes that bear a cyclopentene moiety and an aryl group underwent domino ring assembly in the presence or absence of *N*-bromosuccinimide or *N*-iodosuccinimide to afford aryne precursors such as three-ringed *ortho*-fluoro(halo)phenanthrenes, four-ringed *ortho*-fluoro(halo)tetraphenes, *ortho*-fluoro(halo)chrysenes and fluoro[4]helicenes. Metalation of the aryne precursors followed by elimination of the fluoride resulted in the unprecedented systematic generation of arynes bearing π-extended systems. Diels–Alder reactions of these arynes with isobenzofurans afforded the corresponding cycloadducts whose reductive aromatisation in an $SnCl_2$/HBr system furnished fully aromatised benzotriphenylenes. In addition, oxidative aryl–aryl coupling (the Scholl reaction) of these benzotriphenylenes facilitated the synthesis of 'half HBCs' (hexabenzocoronenes).

Introduction

Polycyclic aromatic hydrocarbons (PAHs), which are a family of compounds consisting of benzene rings fused in various configurations,[1] have attracted considerable attention recently because of their viability as organic electronic materials.[2] With their linear benzene ring configuration, acenes are one of the most representative types of PAHs (Figure 1) and are known to be excellent organic semiconducting materials.[3] Aphenes possess a bent configuration, which is one of core structures in PAHs. Known for their zig-zag configuration, phenacenes have experienced a resurgence in popularity as air-stable organic semiconductors[4] and their O_2-sensing properties are fascinating to research chemists.[5] Helicenes are optical and electronic materials[6] with unique chirality-derived characteristics.[7] In addition to these topologically one-dimensional molecules, both triphenylenes with their topologically two-dimensional configuration and circulenes, which possess a cyclic configuration, have been used for applications in materials and supramolecular chemistry,[8] particularly since they both contain discotic columnar structures in their crystals, which make them excellent materials for use as liquid crystals, in OFETs and for the construction of photovoltaic cells.

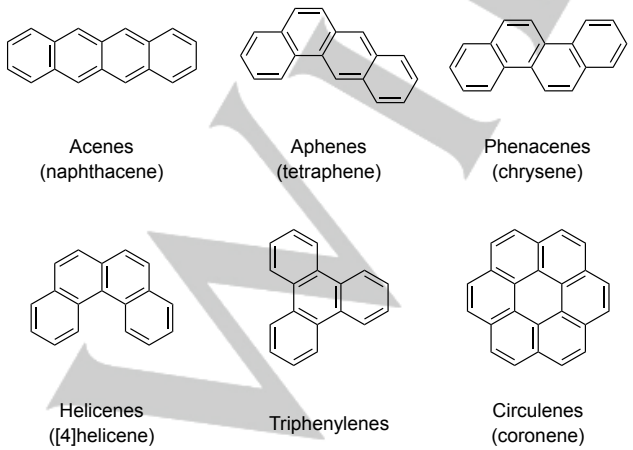


Figure 1. Major Families of PAHs.

Arynes have a formal triple bond within their six-membered ring, thus making them useful tools for the synthesis of fused benzene ring structures.[9] However, with the exception of didehydronaphthalenes and didehydrophenanthrenes,[9c] the synthetic uses of these types of π-extended arynes have been still limited.[9c,d][10]

One primary shortcoming of π-extended arynes lies in the preparation of their precursors. In order for arynes to be useful as starting materials for π-extended PAHs, the synthetic routes to their respective precursors must facilitate both the construction of π-systems and the introduction of functional groups (MG and LG in Figure 2).

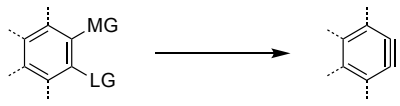
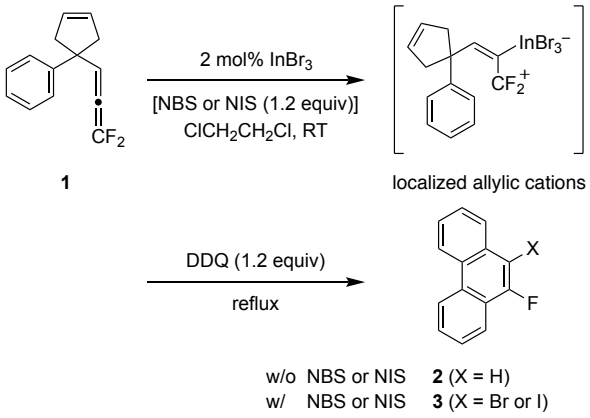


Figure 2. π-Extended Arynes and Their Precursors (MG = Metalation Group, LG = Leaving Group).

Previously, we reported on In-catalysed domino cyclisation/ring expansion sequences using 1,1-difluoroallenes **1** (Scheme 1).[11,12] Difluoroallenes bearing a cyclopentene moiety and an aryl group were treated with $InBr_3$ catalyst to generate the localized difluoroallylic cations in which stabilisation was achieved by the transfer of a lone pair of electrons from fluorine to a vacant carbon p orbital (i.e. the α-cation stabilising effect of fluorine substituents).[13,14] Here, the In-substituted allylic cations readily underwent a regioselective Friedel–Crafts-type cyclisation followed by ring expansion to afford pinpoint-

fluorinated PAHs **2**. Noteworthy is that when the reaction was performed in the presence of a halogenating agent such as NBS (*N*-bromosuccinimide) or NIS (*N*-iodosuccinimide), the carbon-indium bond facilitated halogenation, thus affording *ortho*-fluoro(halo)phenanthrene analogues of **3** that could be subsequently transformed into their respective arynes via dehalogenation.

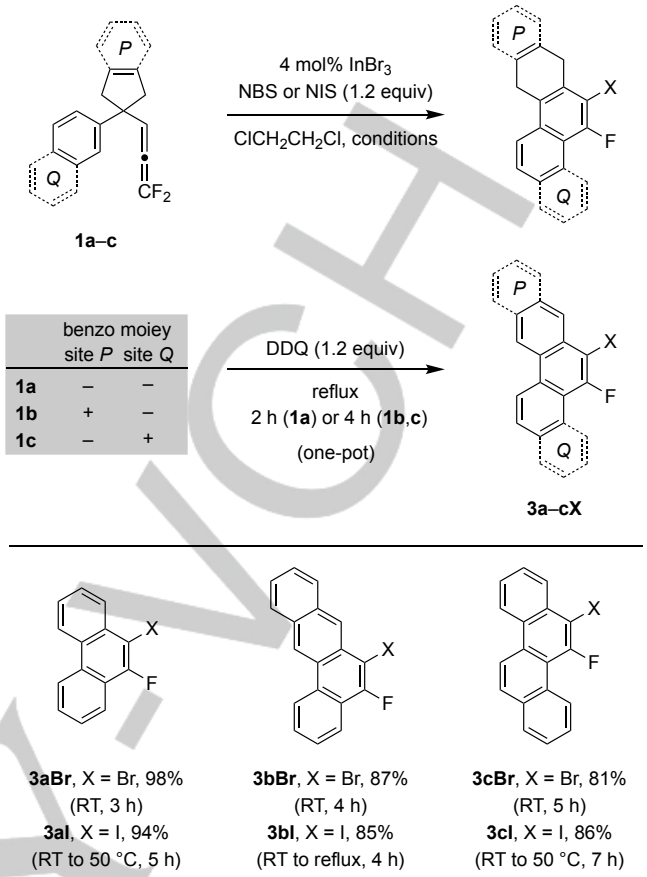


Scheme 1. Domino Cyclisation/Ring Expansion/Halogenation of 1,1-Difluoroallenes **1**.

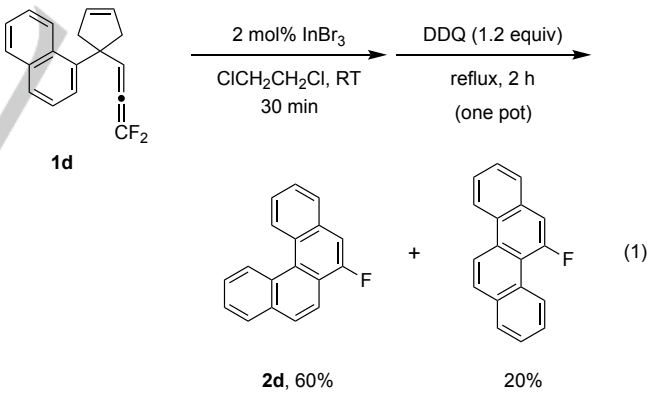
Thus, we envisioned that the domino cyclisation/ring expansion/halogenation sequence would open a route to the systematic synthesis of π-extended arynes. In this paper, the synthesis of *ortho*-bromo(fluoro)phenanthrenes, *ortho*-bromo(fluoro)chrysenes and *ortho*-bromo(fluoro)tetraphenes and their respective iodo analogues are described. Also discussed are Diels–Alder reactions of isobenzofurans with the *in situ*-generated didehydrophenanthrene, didehydrochrysene and didehydrotetraphene, two of which were composed of four benzene rings, as well as their subsequent reductive aromatisation to the respective benzotriphenylene derivatives.[15] Furthermore, arynes bearing a [4]helicene framework were generated from fluorohelicene via dehydrofluorination; this reaction resulted in the corresponding benzotriphenylenes. Finally, the most suitable products were subjected to oxidative aryl–aryl coupling (the Scholl reaction)[16] to facilitate the synthesis of half hexabenzocoronenes (HBCs).[17]

Results and Discussion

Preparation of *ortho*-fluoro(halo)arenes (phenanthrenes, tetraphenes and chrysenes) and fluoro[4]helicenes. *ortho*-Fluoro(halo)phenanthrenes, -tetraphenes and -chrysenes **3** were prepared via domino ring assembly of 1,1-difluoroallenes (Scheme 2). First, 1,1-difluoroallenes bearing a cyclopentene moiety and an aryl group (**1a**–**1c**) were prepared from arylacetonitriles via (i) an initial double allylation for the construction of the five-membered ring. (ii) A subsequent partial reduction was carried out, followed by (iii) difluorovinylidenation of the resulting aldehydes (not shown).[12b] Difluoroallenes, including **1b** and **1c**, with an additional benzo moiety on either the *P* or *Q* site (Scheme 2) were treated with 4 mol% of $InBr_3$ in the presence of NBS (1.2 equiv) or NIS (1.2 equiv) followed by a one-pot dehydrogenation using DDQ. Domino cyclisation/ring expansion/halogenation (via bromination or iodination) afforded

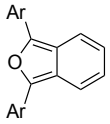


Scheme 2. Preparation of *ortho*-Fluoro(halo)arenes **3** (Aryne Precursors).



the desired *ortho*-fluoro(halo)phenanthrenes **3aBr** (98% yield) and **3al** (94% yield), fluoro(halo)tetraphenes **3bBr** (87% yield) and **3bl** (85% yield) and, lastly, fluoro(halo)chrysenes **3cBr** (81% yield) and **3cl** (86% yield). Fluoro[4]helicene, **2d**, was prepared as shown in Eq 1.[18]

Generation of Arynes A–D and Their Diels–Alder Reactions. To construct the benzene rings, the arynes underwent Diels–Alder reactions using isobenzofurans as the dienes. The isobenzofurans **4a–f** (Figure 3) were easily prepared from commercially available methyl *o*-formylbenzoate and the corresponding arylmagnesium bromides (2.3 equiv) via the method reported by Hamura.[19]



	Ar		
4a	Ph	**4d**	C_6H_4*p*-*t*-Bu
4b	C_6H_4*p*-OMe	**4e**	C_6H_4*p*-F
4c	C_6H_4*p*-*n*-Hex	**4f**	2-Thienyl

Figure 3. Analogues of Isobenzofurans **4**.

In the presence of isobenzofuran **4a**, bromo(fluoro)phenanthrene **3aBr** was treated with butyllithium (1.2 equiv) at −90°C, which allowed for Li–Br exchange to take place followed by LiF elimination to generate the desired aryne.[20] After warming to RT, the adduct **5aa** was obtained in 55% yield along with fluorophenanthrene **2a** in 24% yield (Entry 1, Table 1). Thus, it was clear that the intermediate 13,14-didehydrophenanthrene (phenanthryne) (**A**) was generated to undergo Diels–Alder reaction with **4a**. Deuterium labelling experiments (D_2O quench) performed under identical reaction conditions indicated that no deuterium had been incorporated into the structure of **2a** (as determined by ^{1}H NMR). This meant that protonation was a competitive process in the reaction medium, especially in the presence of THF.

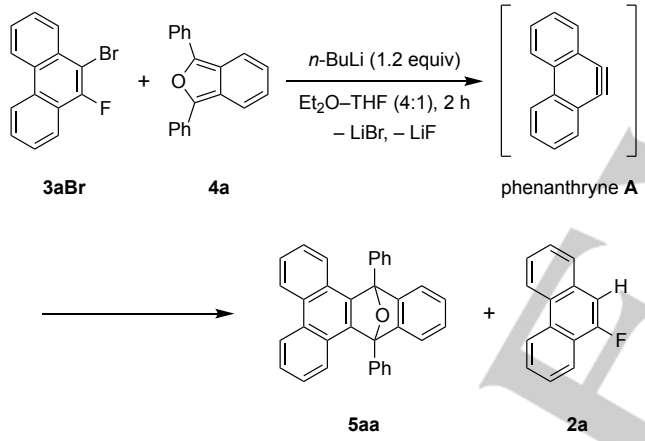


Table 1. Generation and Diels–Alder Reaction of Aryne **A**.

Entry	**4a** [equiv]	Temperature	**5aa** [%][a]	**2a** [%][a]
1	1.2	–90 °C to RT	55	24
2	1.2	RT	66	9
3	2.0	RT	84	8

[a] ^{1}H NMR yield based on an internal standard CH_2Br_2.

In order to boost the elimination of lithium fluoride from the intermediary fluoro(lithio)phenanthrene, the reaction was performed at room temperature (Entry 2). Here, the **5aa**/**2a** ratio increased significantly, and **5aa** was obtained in 66% yield. By using 2.0 equiv of **4a**, the yield of **5aa** was improved to 84% (Entry 3). Diels–Alder reactions of **3** with several other isobenzofurans were conducted under the aforementioned conditions (Table 2). Phenanthryne **A** underwent Diels–Alder reaction to afford the desired adducts **5aa**–**5af** in 67%–89% yields. Similar reactions were also conducted using π-extended **3bBr** and **3cBr** with **4a** in which the reactions proceeded via the intermediates 5,6-didehydrotetraphene **B** and 5,6-didehydrochrysene **C** (Figure 4) to afford the oxygenated benzotriphenylene analogues **5ba** and **5ca** in 88% and 94% yields, respectively (Eqs 2 and 3).

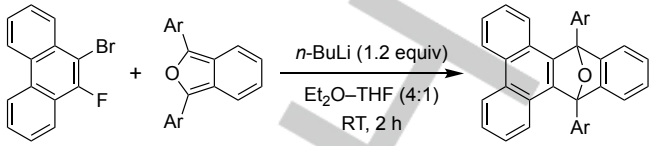
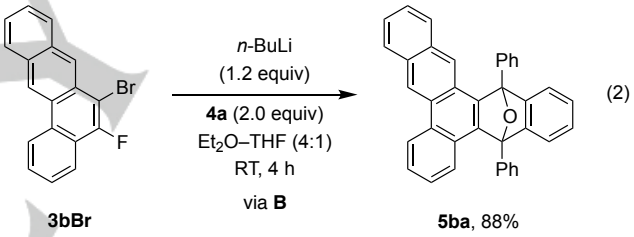
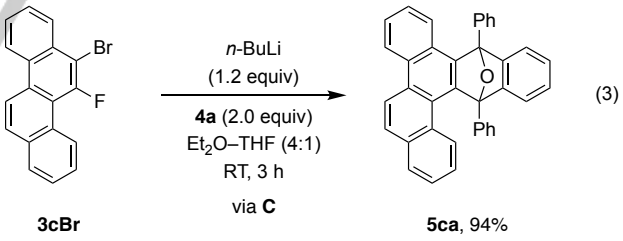


Table 2. Diels–Alder Reaction between Phenanthryne **A** and Isobenzofurans **4**.

Entry	**4**	Ar	**5**	Yield [%]
1	**4a**	Ph	**5aa**	89
2	**4b**	C_6H_4*p*-OMe	**5ab**	81
3	**4c**	C_6H_4*p*-*n*-Hex	**5ac**	82
4	**4d**	C_6H_4*p*-*t*-Bu	**5ad**	81
5	**4e**	C_6H_4*p*-F	**5ae**	80
6	**4f**	2-Thienyl	**5af**	67





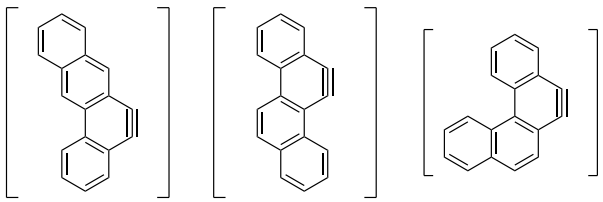
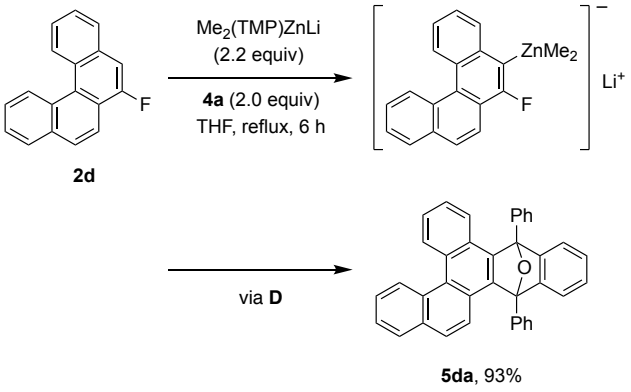


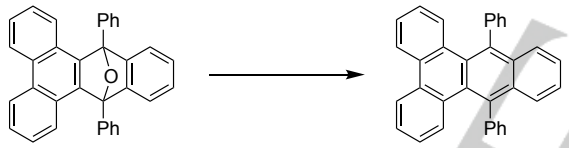
Figure 4. Generated π-Extended Arynes **B**–**D**.

Although deprotonation of fluorohelicene **2d** with butyllithium afforded the Diels–Alder adduct **5da** in low yield (56%), the use of Me_2(TMP)ZnLi dramatically improved the yield of **5da** (Scheme 3).[21] Treatment of **2d** with Me_2(TMP)ZnLi (4.0 equiv) in the presence of **4a** (THF, reflux, 1.5 h) afforded **5da** in 93% yield.



Scheme 3. Diels–Alder Reaction of Didehydrohelicene **D** and Isobenzofurans **4** (TMP = tetramethylpiperidino).

Reductive Aromatisation of the Diels–Alder Adducts 5. Reductive aromatisation of the adduct **5aa** to benzotriphenylene **6aa** proceeded under basic conditions (Scheme 4). Low-valent titanium species generated from $TiCl_3$ and butyllithium promoted aromatisation to afford **6aa** in 92% yield. The low-valent titanium species were also generated from Cp_2TiCl_2/butyllithium and from $TiCl_4$/Zn, both of which afforded **6aa** in 90% and 72% yields, respectively. Although successful with **5aa**, aromatisation using the latter two reagent systems was ineffective when applied to other π-extended analogues of **5,** whereas the former two reagent systems were strongly basic. Thus, further examination was carried out.



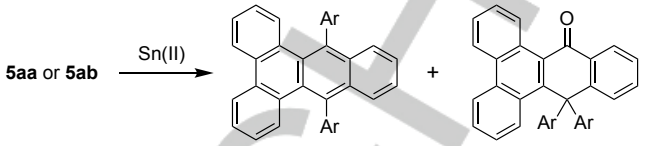
5aa **6aa**

$TiCl_3$ (15 equiv), *n*-BuLi (30 equiv) Et_2O, RT, 4 h	92%
Cp_2TiCl_2 (5 equiv), *n*-BuLi (10 equiv) THF, RT, 1 h	90%
$TiCl_4$ (15 equiv), Zn (30 equiv) THF, RT, 12 h	72%

Scheme 4. Reductive Aromatisation of **5** Under Basic Conditions (^{1}H NMR yield based on an internal standard CH_2Br_2).

Next, reductive aromatisation under acidic conditions was examined with commercially available tin(II) chloride (Table 3). Using $SnCl_2$ (10 equiv)/HCl (20 equiv) afforded **6aa** in 49% yield (Entry 1); however, decreasing the amounts of reagents raised the yield to 81% (Entry 2). The *p*-methoxy-bearing substrate **5ab** afforded **6ab** in 52% yield along with the migration product **7ab** in 45% yield (Entry 3). As shown in Scheme 5, the protonation of **5ab** generated the carbocation intermediate **8ab.** Thus, it was rationalized that the use of a group, such as a *p*-methoxyphenyl group**,** that is more nucleophilic than the phenyl group, caused 1,4-migration and led to the formation of **7ab** (Path a).

Nucleophilic components, such as alcohols and the counter anions of acids, also affected product selectivity (**6ab/7ab**)**.** The use of a methanol solution of HCl increased the selectivity to afford **6ab** in 76% yield and **7ab** in 11% yield (Entry 4, Table 3). In contrast, using an ether solution of HCl decreased product selectivity to afford **6ab** in 37% yield and **7ab** in 57% yield (Entry 5). The type of counter anions for the acid also decisively affected product selectivity; this could be best seen in the cases of HBr and HI. Whereas HBr afforded **6ab** and **7ab** in 98% and



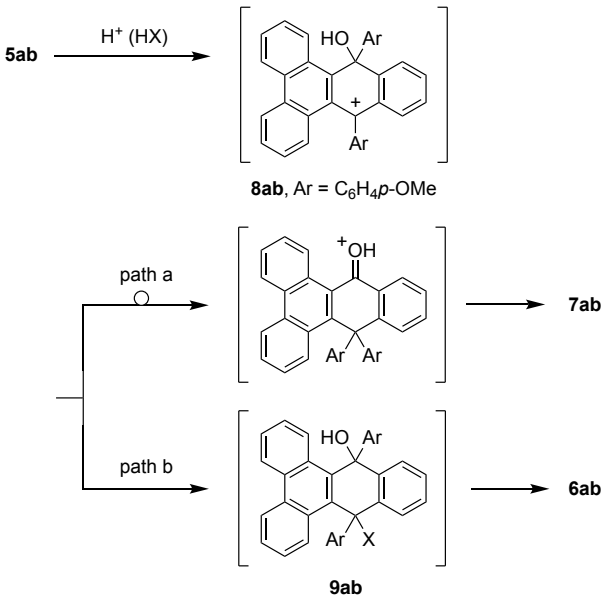
6aa, Ar = Ph
6ab, Ar = C_6H_4*p*-OMe

7aa, Ar = Ph
7ab, Ar = C_6H_4*p*-OMe

Table 3. Reductive Aromatisation of **5** Under Acidic Conditions.

Entry	5	Reagents and Conditions	Yield [%][a]	
			6	7
1	**5aa**	$SnCl_2$ (10 equiv), HCl (20 equiv) Et_2O, RT, overnight	49, **6aa**	–
2	**5aa**	$SnCl_2$ (5 equiv), HCl (10 equiv) THF, reflux, 9 h	(81), **6aa**	–
3	**5ab**	$SnCl_2$ (5 equiv), HCl (10 equiv) THF, 60 °C, 5 h	(52), **6ab**	(45), **7ab**
4	**5ab**	$SnCl_2$ (5 equiv), HCl (10 equiv in MeOH), THF, 60 °C, 5 h	76, **6ab**	11, **7ab**
5	**5ab**	$SnCl_2$ (5 equiv), HCl (10 equiv in Et_2O), THF, 60 °C, 5 h	37, **6ab**	57, **7ab**
6	**5ab**	$SnCl_2$ (5 equiv), HBr (10 equiv) THF, 60 °C, 5 h	(98), **6ab**	2, **7ab**
7	**5ab**	$SnCl_2$ (5 equiv), HI (10 equiv) THF, 60 °C, 5 h	97, **6ab**	–

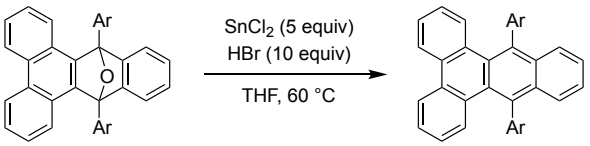
[a] ^{1}H NMR yield based on an internal standard CH_2Br_2 (isolated yield in parentheses).



Scheme 5. A Plausible Mechanism for the Formation of Benzotriphenylene **6ab** and Ketone **7ab**.

2% yields, respectively (Entry 6), HI afforded **6ab** as the sole product (97% yield, Entry 7). The effect of nucleophilic components (methanol in Entry 4, a bromide ion in Entry 6 and an iodide ion in Entry 7) is rationalised through their attack on the carbocation intermediate **8ab**, which suppresses rearrangement to **7ab** (Path a, Scheme 5). Thus, the generation of intermediate **9ab** is promoted and, ultimately, the formation of the desired benzotriphenylene **6ab** (Path b).

Using the optimised conditions, various benzotriphenylene analogues were synthesised (Table 4). The Diels–Alder adducts, **5aa**–**af**, which had aryl groups with a functionality and thienyl groups were successfully aromatised using the aforementioned

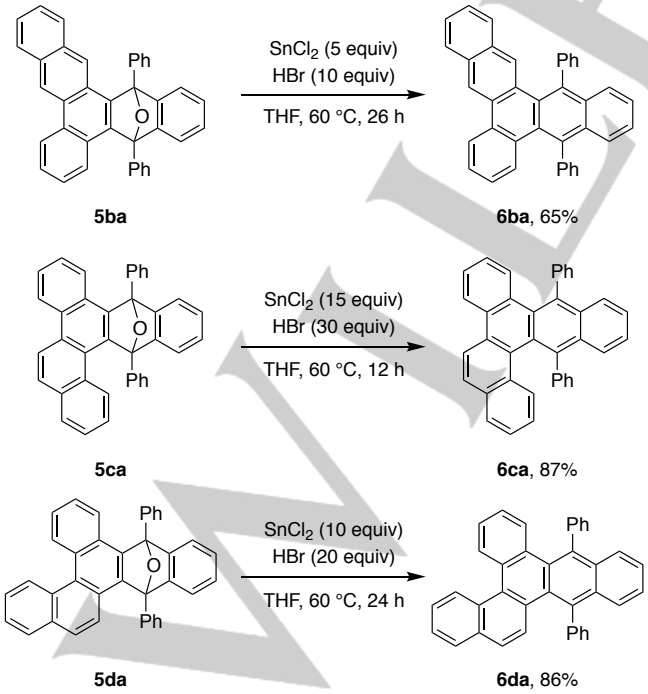


5 **6**

Table 4. Synthesis of Benzotriphenylenes **6** (1).

Entry	Ar	**5**	*t* [h]	**6**	Yield [%]
1[a]	Ph	**5aa**	10	**6aa**	93
2[b]	C_6H_4*p*-OMe	**5ab**	5	**6ab**	98
3	C_6H_4*p*-*n*-Hex	**5ac**	3	**6ac**	98
4	C_6H_4*p*-*t*-Bu	**5ad**	12	**6ad**	99
5	C_6H_4*p*-F	**5ae**	6	**6ae**	86
6[c]	2-Thienyl	**5af**	9	**6af**	62

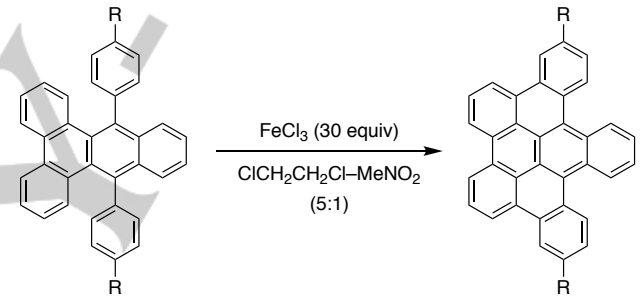
[a] $SnCl_2$ (15 equiv) and HBr (30 equiv). [b] Table 3, Entry 6. [c] $SnCl_2$ (5 equiv) and HCl (10 equiv).



Scheme 6. Synthesis of Benzotriphenylenes **6** (2).

acidic conditions to afford the benzotriphenylenes **6aa**–**af** in 62%–99% yields. The cycloadducts **5ba, 5ca** and **5da**, which possessed a tetraphene, a chrysene and a helicene substructure also gave **6ba, 6ca** and **6da** in 65%, 87% and 86% yields, respectively (Scheme 6). Thus, the generation of π-extended arynes based on domino ring assembly of 1,1-difluoroallenes has facilitated systematic entry to benzotriphenylenes with structural diversity.

Intramolecular Ary–Aryl Coupling of Benzotriphenylenes 6. Dehydrogenative coupling of the aromatic compounds (the Scholl reaction) is a powerful method for expanding π-systems. Since the synthesised diaryltriphenylenes **6** were structurally suitable for the Scholl reaction, we investigated the π extension of **6** to facilitate the synthesis of 'half HBCs' (hexabenzocoronenes). Thus, the triphenylene **6aa** was treated with excess iron(III) chloride in 1,2-dichloroethane–nitromethane (5:1) at 0°C. The desired product **10aa** (**'**half HBC') was obtained in 84% yield (Scheme 7). Primary and tertiary alkyl-bearing **6ac** and **6ad** underwent similar dehydrogenative coupling to give **10ac** and **10ad** in 98% and 94% yields, respectively.[22]



6aa (R = H)
6ac (R = *n*-Hex)
6ad (R = *t*-Bu)

10aa, 84%, 1 h
10ac, 98%, 1 h
10ad, 94%, 0.5 h

Scheme 7. Synthesis of 'Half HBCs' **10**.

Conclusion

Using o*rtho*-fluoro(halo)arenes (such as phenanthrenes, tetraphenes and chrysenes) and fluorohelicenes, benzotriphenylenes were synthesised via π-extended aryne intermediates. These aryne precursors were prepared through domino ring assembly of 1,1-difluoroallenes bearing a cyclopentene moiety and an aryl group; this reaction was initiated on treatment with the $InBr_3$ catalyst in the presence or absence of NBS or NIS. Metalation (*n*-BuLi or $Me_2TMPZnLi$) of the precursors and the subsequent elimination of a fluoride ion generated the corresponding arynes. This is an unprecedented means for the systematic generation of π-extended arynes and may prove beneficial in accessing synthetic routes to higher-order PAHs. Diels–Alder reactions with isobenzofurans afforded cycloadducts whose reductive aromatisation in an $SnCl_2$/HBr system furnished the fully aromatised benzotriphenylene analogues. In addition, further dehydrogenative aryl–aryl coupling (the Scholl reaction) provided a facile entry to 'half HBC' analogues.

Experimental Section

THF, diethyl ether and DMF were dried by passing through a column of activated alumina followed by a column of Q-5 scavenger (Engelhard). 1,2-Dichloroethane and nitromethane were distilled from CaH_2 and stored under MS 4A. Me_2Zn (a heptane solution), $TiCl_4$, $SnCl_2$ and $FeCl_3$ were purchased from Merck KGaA and used as received. Cp_2TiCl_2 and conc. HBr were purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and used as received. $TiCl_3$ and conc. HCl were purchased from Kishida Chemical Co., Ltd. and used as received.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography). Purification was also performed by preparative HPLC (GPC), using a JAI LC-908 instrument (Jaigel-2H, $CHCl_3$).

IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR method). NMR spectra were recorded on Bruker Avance 500 or Jeol JNM ECS-400 spectrometers in $CDCl_3$ at 500 or 400 MHz (^{1}H NMR), at 126 or 101 MHz (^{13}C NMR), and at 470 or 376 MHz (^{19}F NMR). Chemical shifts were given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00), $CDCl_3$ (for ^{13}C NMR: δ = 77.0) and C_6F_6 (for ^{19}F NMR: δ = 0.0; C_6F_6 exhibits a ^{19}F NMR signal at –162.9 ppm vs. $CFCl_3$). High-resolution mass spectroscopy (HRMS) was conducted with Jeol JMS-T100GCV (EI/TOF) and Jeol JMS-T100CS (ESI$^+$/TOF or APCI$^+$/TOF) spectrometers. Elemental analyses (EA) were performed with a Yanako MT-3 CHN Corder apparatus.

Isobenzofurans **4** were prepared by the reported method.[19a] Preparation and spectral data of *ortho*-fluoro(halo)phenanthrenes (**3aBr** and **3aI**) were described in the previous paper.[11a] *Ortho*-fluoro(halo)tetraphenes (**3bBr** and **3bI**) and *ortho*-fluoro(halo)chrysenes (**3cBr** and **3cI**) were prepared by the same method. Preparation and spectral data of fluorohelicene **2d** were described in the previous paper.[11a]

6-Bromo-5-fluorobenzo[*a*]anthracene **3bBr**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.60 (m, 2H), 7.64 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.71 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H), 8.01–8.06 (m, 2H), 8.07 (dd, *J* = 8.0, 0.5 Hz, 1H), 8.67 (s, 1H), 8.68 (d, *J* = 7.5 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 103.9 (d, J_{CF} = 21 Hz), 121.2 (d, J_{CF} = 6 Hz), 121.8 (d, J_{CF} = 1 Hz), 122.8 (d, J_{CF} = 3 Hz), 124.1 (d, J_{CF} = 21 Hz), 126.1 (d, J_{CF} = 8 Hz), 126.2, 126.4, 126.5, 127.5, 127.8, 128.0, 128.0, 128.2, 130.7 (d, J_{CF} = 6 Hz), 131.2 (d, J_{CF} = 1 Hz), 132.2, 153.9 (d, J_{CF} = 252 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ = 50.2 (s); IR (neat): $\nu^{\sim}$ =2960, 1358, 1219, 876, 771, 744 cm^{-1}; HRMS (EI): calcd. for $C_{18}H_{10}BrF$ [M]$^+$: 323.9950; found: 323.9951.

5-Fluoro-6-iodobenzo[*a*]anthracene **3bI**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57–7.66 (m, 2H), 7.68 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.78 (dd, *J* = 7.6, 7.6 Hz, 1H), 8.09–8.14 (m, 3H), 8.69 (s, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 81.4 (d, J_{CF} = 26 Hz), 121.5 (d, J_{CF} = 6 Hz), 122.0 (d, J_{CF} = 1 Hz), 123.0 (d, J_{CF} = 4 Hz), 124.0 (d, J_{CF} = 22 Hz), 129.9 (d, J_{CF} = 4 Hz), 131.2 (d, J_{CF} = 8 Hz), 131.6 (d, J_{CF} = 2 Hz), 131.7 (d, J_{CF} = 6 Hz), 157.5 (d, J_{CF} = 250 Hz), 126.3, 126.5, 126.6, 127.5, 127.8, 128.0, 128.6, 132.7; ^{19}F NMR (470 MHz, $CDCl_3$): δ = 68.9 (s). IR (neat): $\nu^{\sim}$ = 3055, 1616, 1495, 1356, 876, 771 cm^{-1}; Anal. calcd. for $C_{18}H_{10}FI$: C, 58.09; H, 2.71; found: C, 57.67; H, 2.55.

6-Bromo-5-fluorochrysene **3cBr**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.73 (m, 4H), 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 8.37 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.60 (dd, *J* = 9.5, 2.5 Hz, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 9.13 (br d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 107.3 (d, J_{CF} = 19 Hz), 119.6 (d, J_{CF} = 13 Hz), 120.5 (d, J_{CF} = 3 Hz), 123.3 (d, J_{CF} = 2 Hz), 126.4 (d, J_{CF} = 2 Hz), 126.9 (d, J_{CF} = 2 Hz), 127.0 (d, J_{CF} = 7 Hz), 127.5 (d, J_{CF} = 2 Hz), 127.5 (d, J_{CF} = 28 Hz), 127.96, 128.02, 128.1 (d, J_{CF} = 6 Hz), 128.5, 129.4, 130.1 (d, J_{CF} = 6 Hz), 130.5 (d, J_{CF} = 3 Hz), 132.7, 156.1 (d, J_{CF} = 253 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ = 63.5 (s); IR (neat): $\nu^{\sim}$ 3051, 1589, 1431, 1238, 912, 746 cm^{-1}; HRMS (EI): calcd. for $C_{18}H_{10}BrF$ [M]$^+$: 323.9950; found: 323.9946.

5-Fluoro-6-iodochrysene **3cI**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64–7.77 (m, 4H), 7.99 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 9.1 Hz, 1H), 8.33 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.67–8.72 (m, 2H), 9.17 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 85.3 (d, *J* = 29 Hz), 119.5 (d, *J* = 15 Hz), 120.7 (d, *J* = 3 Hz), 123.5 (d, *J* = 2 Hz), 126.5 (d, *J* = 3 Hz), 127.0 (d, *J* = 2 Hz), 127.6 (d, *J* = 3 Hz), 128.07 (d, *J* = 3 Hz), 128.09 (d, *J* = 10 Hz), 128.5 (d, *J* = 8 Hz), 131.3 (d, *J* = 6 Hz), 132.2 (d, *J* = 6 Hz), 132.7 (d, *J* = 5 Hz), 158.9 (d, *J* = 251 Hz), 127.7, 127.9, 129.8, 132.8; ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.4 (s); IR (neat): $\nu^{\sim}$ 3057, 1581, 1427, 1238, 816, 756 cm^{-1}; Anal. calcd. for $C_{18}H_{10}FI$: C, 58.09; H, 2.71; found: C, 57.84; H, 2.72.

Generation and Diels–Alder reaction of arynes (from *ortho*-fluoro(halo)arenes). Synthesis of adduct **5aa** is described as a typical procedure. To a mixed ether–THF solution (4:1, 4 mL) of bromo(fluoro)phenanthrene **3aBr** (36 mg, 0.13 mmol) and isobenzofuran **4a** (70 mg, 0.26 mmol) was added a hexane solution of butyllithium (1.6 mol/L, 0.10 mL, 0.16 mmol) at room temperature. The resulting solution was stirred for 2 h. Saturated. aq. NH_4Cl was added to quench the reaction and organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate 20:1) to give adduct **5aa** (52 mg, 89% yield) as a colorless solid.

9,14-Dihydro-9,14-diphenyl-9,14-epoxybenzo[*b*]triphenylene **5aa**: ^{1}H NMR: δ = 6.95–7.00 (m, 2H), 7.32 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.45–7.55 (m, 8H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.63–7.67 (m, 2H), 8.05 (br d, *J* = 5.0 Hz, 4H), 8.62 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ = 93.2, 122.0, 123.5, 124.5, 125.2, 126.1, 126.2, 127.2, 128.8, 129.4 130.2, 130.4, 135.1, 148.5, 151.2; IR (neat): $\nu^{\sim}$ 3064, 1456, 1218, 771, 752 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{34}H_{23}O$ [M+H]$^+$: 447.1749; found: 447.1750.

9,14-Dihydro-9,14-di(4-methoxyphenyl)-9,14-epoxybenzo[*b*]triphenylene **5ab**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.88 (s, 6H), 6.96–6.97 (m, 2H), 7.04 (dd, *J* = 7.7, 1.3 Hz, 4H), 7.37 (ddd, *J* = 8.3, 7.1, 1.0 Hz, 2H), 7.54 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 2H), 7.59–7.63 (m, 2H), 7.68 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.96 (br d, *J* = 6.5 Hz, 4H), 8.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 55.4, 92.6, 114.1, 121.9, 123.5, 124.5, 125.1, 126.05, 126.12, 127.2, 127.3, 130.4, 131.7 (br), 148.5, 151.5, 160.3; IR (neat): $\nu^{\sim}$ 2837, 1516, 1248, 1176, 904, 723 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{36}H_{27}O_3$ [M+H]$^+$: 507.1960; found: 507.1957.

9,14-Di(4-hexylphenyl)-9,14-dihydro-9,14-epoxybenzo[*b*]triphenylene **5ac**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 6H), 1.25–1.39 (m, 12H), 1.64 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.65 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 4H), 6.96–6.99 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 4H), 7.35 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 2H), 7.53 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 2H), 7.60–7.64 (m, 2H), 7.68 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.94 (br d, *J* = 6.7 Hz, 4H), 8.67 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.9, 31.3, 31.7, 35.8, 93.0, 122.0, 123.4, 124.6, 125.1, 126.0, 126.1, 127.3, 128.8, 130.2 (br s), 130.4, 132.3, 144.2, 148.6, 151.5; IR (neat): $\nu^{\sim}$ = 2925, 2856, 993, 746, 723 cm^{-1}; HRMS (APCI+): calcd. for $C_{46}H_{47}O$ [M+H]$^+$: 615.3627; found: 615.3632.

9,14-Di(4-*tert*-butylphenyl)-9,14-dihydro-9,14-epoxybenzo[*b*]triphenylene **5ad**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 18H), 6.96–6.97 (m, 2H), 7.38 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 2H), 7.48–7.56 (m, 6H), 7.58–7.64 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.95 (br d, *J* = 6.5 Hz, 4H), 8.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 31.4, 34.8, 93.0, 121.9, 123.5, 124.7, 125.0, 125.6, 126.0, 126.1, 127.4, 130.0 (br s), 130.5, 132.1, 148.6, 151.6, 152.4; IR (neat): $\nu^{\sim}$ = 2962, 1269, 906, 750, 723 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{42}H_{39}O$ [M+H]$^+$: 559.3001; found: 559.3000.

9,14-Di(4-fluorophenyl)-9,14-dihydro-9,14-epoxybenzo[*b*]triphenylene **5ae**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.93–6.97 (m, 2H), 7.20 (dd, *J* = 8.8, 8.8 Hz, 4H), 7.35 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.50 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 2H), 7.55–7.61 (m, 4H), 8.02 (br s, 4H), 8.61 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 92.5, 115.8 (d, J_{CF} = 22 Hz), 121.9, 123.6, 124.2, 125.4, 126.2, 126.4, 127.0, 130.5, 130.9 (d, J_{CF} = 2 Hz), 132.2 (br), 148.1, 150.9, 163.4 (d, J_{CF} = 249 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ = 49.9–50.0 (m); IR (neat): $\nu^{\sim}$ = 1512, 1227, 833, 750, 725 cm^{-}

[1]; HRMS (APCI+): Calcd. for $C_{34}H_{21}F_2O$ $[M+H]^+$: 483.1561; found: 483.1564.

9,14-Dihydro-9,14-di(2-thienyl)-9,14-epoxybenzo[*b*]triphenylene **5af**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.05 (dd, *J* = 9.0, 4.0 Hz, 2H), 7.22–7.28 (m, 2H), 7.43 (ddd, *J* = 10.0, 7.0, 1.0 Hz, 2H), 7.57 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 2H), 7.56–7.61 (m, 2H), 7.76–7.82 (m, 6H), 8.69 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 88.8, 121.2, 123.5, 124.0, 125.7, 126.2, 126.4, 126.8, 127.3, 127.8, 129.7, 130.5, 138.0, 147.1, 150.8; IR (neat): ν̃ = 1215, 771, 744, 723, 667 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{30}H_{19}OS_2$ $[M+H]^+$: 459.0877; found: 459.0876.

5,16-Dihydro-5,16-diphenyl-5,16-epoxybenzo[*h*]pentaphene **5ba**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.95–7.01 (m, 2H), 7.36 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 1H), 7.40 (ddd, *J* = 8.0, 6.5, 1.3 Hz, 1H), 7.45 (ddd, *J* = 8.0, 6.5, 1.4 Hz, 1H), 7.48–7.57 (m, 7H), 7.60 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.66–7.69 (m, 1H), 7.71–7.75 (m, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H), 8.08 (d, *J* = 6.0 Hz, 2H), 8.11 (br s, 2H), 8.81 (d, *J* = 8.0 Hz, 1H), 9.14 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 93.3, 121.9, 122.0, 122.5, 123.1, 123.7, 124.7, 125.16, 125.22, 125.7, 125.9, 126.49, 126.55, 127.5, 128.1, 128.3, 128.77, 128.79, 129.1, 129.39, 129.45, 130.3 (br s), 130.9, 131.2, 131.3, 135.0, 135.1, 148.8, 148.9, 151.07, 151.15; IR (neat): ν̃ = 3014, 1215, 746, 698, 667 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{38}H_{25}O$ $[M+H]^+$: 497.1905; found: 497.1920.

11,16-Dihydro-11,16-diphenyl-11,16-epoxynaphtho[2,3-*g*]chrysene **5ca**: ^{1}H NMR (500 MHz, $CDCl_3$, –40 °C): δ = 6.95 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.02 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.29 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.36–7.45 (m, 3H), 7.48–7.68 (m, 4H), 7.51 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.56 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.89–7.96 (m, 3H), 8.03 (d, *J* = 7.1 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 8.36 (br s, 1H), 8.72 (d, *J* = 9.1 Hz, 1H), 8.76 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, –40 °C): δ = 91.9, 94.7, 121.2, 122.4, 122.8, 123.2, 123.8, 124.4, 125.2, 125.4, 125.5, 125.6, 125.9, 126.0, 126.2, 126.9, 126.97, 127.04, 127.4, 127.7, 128.0 (br), 128.56, 128.59, 128.62 (br), 128.7, 128.8 (br), 129.3, 129.5, 129.6, 129.8, 132.0, 134.0, 135.0, 147.6, 147.9, 149.8, 151.2; IR (neat): ν̃ = 3055, 1454, 1300, 906, 727, 698 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{38}H_{25}O$ $[M+H]^+$: 497.1905; found: 497.1903.

Generation and Diels–Alder reaction of arynes (from fluorohelicenes). Synthesis of adduct **5da** is described as a typical procedure. To a THF solution (2 mL) of fluorohelicene **2d** (40 mg, 0.16 mmol) and isobenzofuran **4a** (87 mg, 0.32 mmol) was added a THF solution of Me_2(TMP)ZnLi (0.30 mol/L, 1.2 mL, 0.35 mmol)[21] at –78 °C. The resulting solution was heated to reflux and stirred for 6 h. Saturated. aq. NH_4Cl was added to quench the reaction and organic materials were extracted with dichloromethane three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate 20:1) to give adduct **5da** (74 mg, 93% yield) as a pale yellow solid.

9,14-Dihydro-9,14-diphenyl-9,14-epoxydibenzo[*b,p*]chrysene **5da**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.98–7.06 (m, 2H), 7.34 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.44–7.60 (m, 12H), 7.60–7.67 (m, 2H), 7.69 (d, *J* = 6.7 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 8.00–8.12 (m, 2H), 8.97 (d, *J* = 8.3 Hz, 1H), 9.03 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 93.28, 93.34, 122.0, 122.1, 122.5, 123.8, 125.29, 125.33, 125.5, 125.8, 125.9, 125.99, 126.04, 126.3, 127.6, 128.2, 128.3, 128.76, 128.80, 128.9, 129.1, 129.4, 129.5, 130.3, 130.4, 130.8, 132.9, 134.7, 134.9, 148.0, 149.1, 151.1, 151.2; IR (neat): ν̃ = 2925, 1454, 1259, 1090, 1020, 748, 698 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{38}H_{24}O$ $[M+H]^+$: 497,1900; found: 497.1904.

Reductive aromatisation of Diels–Alder adducts. Synthesis of benzotriphenylene **6aa** is described as a typical procedure. To a THF solution (3 mL) of Diels–Alder adduct **5aa** (28 mg, 0.055 mmol) and $SnCl_2$ (167 mg, 0.88 mmol) was added *c.* HBr (0.2 mL, 1.7 mmol) at room temperature. The resulting solution was heated to 60 °C and stirred for 10 h. A small amount of SiO_2 was added to the resulting mixture. After removal of the solvent under reduced pressure, the silica gel was charged to a small pad of SiO_2 and purification by column chromatography (hexane/ethyl acetate 10:1) gave benzotriphenylene **6aa** (27 mg, 93% yield) as a colorless solid.

9,14-Diphenylbenzo[*b*]triphenylene **6aa**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.97 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 2H), 7.33 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 2H), 7.42–7.46 (m, 2H), 7.46–7.57 (m, 12H), 7.91–7.95 (m, 2H), 8.26 (dd, *J* = 8.1, 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 123.3, 125.6, 125.8, 126.7, 126.8, 127.6, 128.9, 129.0, 130.5, 131.3, 131.7, 131.9, 132.6, 135.4, 141.7; IR (neat): ν̃ = 3062, 1487, 1439, 744, 702 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{34}H_{23}$ $[M+H]^+$: 431.1800; found: 431.1789.

9,14-Di(4-methoxyphenyl)benzo[*b*]triphenylene **6ab**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.91 (s, 6H), 7.00 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 2H), 7.05–7.08 (m, 4H), 7.33 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 2H), 7.42–7.47 (m, 6H), 7.54 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.96 (br d, *J* = 6.6 Hz, 2H), 8.25 (dd, *J* = 8.5, 1.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 55.4, 123.3, 125.5, 125.8, 126.6, 126.7, 129.0, 130.3, 131.6, 131.9, 132.1, 133.7 (2C), 133.9, 134.8, 159.2; IR (neat): ν̃ = 1217, 912, 771, 748, 731 cm^{-1}; HRMS (APCI+): calcd. for $C_{36}H_{27}O_2$ $[M+H]^+$: 491.2011; found: 491.2025.

9,14-Di(4-hexylphenyl)benzo[*b*]triphenylene **6ac**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.1 Hz, 6H), 1.32–1.46 (m, 12H), 1.73 (tt, *J* = 7.7, 7.6 Hz, 4H), 2.74 (t, *J* = 7.7 Hz, 4H), 6.95 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 2H), 7.30–7.34 (m, 6H), 7.42–7.46 (m, 6H), 7.50 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.96–8.00 (m, 2H), 8.25 (dd, *J* = 8.4, 1.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.9, 31.4, 31.8, 35.8, 123.2, 125.5, 125.6, 126.6, 126.8, 128.9, 129.0, 130.4, 131.5, 131.8, 131.9, 132.4, 135.3, 138.8, 142.3; IR (neat): ν̃ = 2925, 2854, 904, 752, 727 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{46}H_{47}$ $[M+H]^+$: 599.3678; found: 599.3667.

9,14-Di(4-*tert*-butylphenyl)benzo[*b*]triphenylene **6ad**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (s, 18H), 6.93 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.30 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.39–7.48 (m, 8H), 7.52 (d, *J* = 8.1 Hz, 4H), 7.99–8.02 (m, 2H), 8.23 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 31.5, 34.7, 123.2, 125.5, 125.6, 125.8, 126.6, 126.8, 129.0, 130.4, 131.6, 131.88, 131.92, 132.2, 135.3, 138.6, 150.7; IR (neat): ν̃ = 2962, 2925, 912, 748, 727 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{42}H_{39}$ $[M+H]^+$: 543.3052; found: 543.3046.

9,14-Di(4-fluorophenyl)benzo[*b*]triphenylene **6ae**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.23 (dd, *J* = 8.4, 8.4 Hz, 4H), 7.37 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.44–7.54 (m, 8H), 7.86–7.91 (m, 2H), 8.27 (dd, *J* = 8.4, 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 116.1 (d, J_{CF} = 21 Hz), 123.4, 125.9 (d, J_{CF} = 5 Hz), 126.4, 127.0, 129.1, 130.3, 131.0, 131.8, 132.0, 134.1, 134.2, 134.3, 137.4 (d, J_{CF} = 3 Hz), 162.5 (d, J_{CF} = 248 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ = 47.4–47.5 (m); IR (neat): ν̃ = 1506, 1223, 845, 750, 727 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{34}H_{21}F_2$ $[M+H]^+$: 467.1611; found: 467.1618.

9,14-Di(2-thienyl)benzo[*b*]triphenylene **6af**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (ddd, *J* = 7.5, 7.0, 1.0 Hz, 2H), 7.25–7.29 (m, 2H), 7.34–7.37 (m, 2H), 7.39 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.50–7.55 (m, 4H), 7.70 (dd, *J* = 8.5, 1.0 Hz, 2H), 8.23–8.27 (m, 2H), 8.27 (dd, *J* = 8.5, 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 123.4, 126.1, 126.28, 126.32, 127.2, 127.4, 127.7, 127.8, 129.0, 130.4, 130.4, 131.1, 131.8, 132.5, 142.7; IR (neat): ν̃ = 2922, 1259, 1095, 1024, 798 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{30}H_{19}S_2$ $[M+H]^+$: 443.0928; found: 443.0930.

5,16-Diphenylbenzo[*h*]pentaphene **6ba**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.98 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.31 (ddd, *J* = 7.6, 6.5, 1.1 Hz, 1H), 7.35 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.5, 6.7, 1.5 Hz, 1H), 7.44–7.60 (m, 11H), 7.62–7.66 (m, 2H), 7.90 (d, 8.2 Hz, 1H), 7.92–7.97 (m, 2H), 7.98 (s, 1H), 8.38 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.66 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 121.5, 123.9, 125.5, 125.67, 125.70, 126.1, 126.2, 126.6, 126.8, 126.9, 127.3, 127.5, 127.6, 128.3, 128.9, 129.1, 129.2, 129.3, 129.6, 130.7, 130.7, 130.9, 131.66, 131.69, 131.8, 132.0, 132.1, 132.3, 132.5, 132.6, 135.6, 135.6, 141.5, 141.7; IR (neat): ν̃ = 3053, 1489, 906, 737, 704 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{38}H_{25}$ $[M+H]^+$: 481.1956; found: 481.1956.

11,16-Diphenylnaphtho[2,3-*g*]chrysene **6ca**: ^{1}H NMR (500 MHz, $CDCl_3$, –40 °C): δ = 6.49 (d, *J* = 7.7 Hz, 1H), 6.79 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.01 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.08 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.10 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.21 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.34 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.41–7.65 (m, 8H), 7.75 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.99 (dd, *J* = 6.5, 2.7 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 8.48 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, –40 °C): δ = 120.1, 123.3, 124.9, 125.0, 125.4, 125.5, 125.9, 126.47, 126.55, 126.63, 126.7, 126.80, 126.82, 127.1, 127.56, 127.64, 127.9, 127.9, 128.3, 128.6, 128.7, 129.0, 129.2, 129.5, 129.5, 130.0, 131.1, 131.3, 131.4, 131.81, 131.84, 132.3, 133.0, 133.6, 134.4, 137.3, 139.8, 141.2; IR (neat): ν̃ = 3053, 2924, 1489, 906, 729, 702 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{38}H_{25}$ [M+H]$^+$: 481.1956; found: 481.1954.

9,14-Diphenyldibenzo[*b,p*]chrysene **6da**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.03 (ddd, *J* = 7.7, 7.7, 1,3 Hz, 1H), 7.33 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 7.44–7.64 (m, 16H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.96–8.02 (m, 2H), 8.39 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.83 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 125.51, 125.54, 125.6, 125.7, 125.8, 125.9, 126.3, 126.7, 126.8, 127.6, 127.8, 129.5, 129.6, 129.9, 130.0, 130.7, 131.8, 132.0, 132.7, 132.8, 132.9, 133.0, 134.6, 134.8, 141.2, 141.6; IR (neat): ν̃ = 3060, 3022, 1493, 752, 704 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{38}H_{24}$ [M+H]$^+$: 481.1951; found: 481.1965.

9,9-Di(4-methoxyphenyl)benzo[*b*]triphenylen-14(9*H*)-one **7ab**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.60 (s, 3H), 3.81 (s, 3H), 6.55 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 7.4 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.69 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.75 (ddd, *J* = 8.0, 8.0, 0.9 Hz, 1H), 6.84–6.88 (m, 2H), 6.99 (ddd, *J* = 8.5, 7.7, 1.1 Hz, 1H), 7.07 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.34 (ddd, *J* = 8.8, 7.5, 1.3 Hz, 1H), 7.38 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 7.43 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1H), 7.47 (ddd, *J* = 9.0, 7.7, 1.4 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 54.9, 55.2, 60.4, 113.3, 113.3, 113.7, 114.1, 123.2, 125.6, 126.8, 127.28, 127.28, 127.31, 127.4, 128.0, 128.06, 128.09, 128.12, 129.0, 129.0, 129.4, 130.0, 132.2, 132.4, 132.5, 134.1, 134.4, 134.5, 134.9, 135.3, 135.5, 139.9, 141.8, 158.1, 158.9, 197.6; IR (neat): ν̃ = 2925, 1670, 1506, 1244, 748 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{36}H_{27}O_3$ [M+H]$^+$: 507.1960; found: 507.1960.

Oxidative aryl–aryl coupling leading to half HBC. Synthesis of half HBC **10aa** is described as a typical procedure. To a mixed 1,2-dichloroethane–$MeNO_2$ solution (10:1, 11 mL) of $FeCl_3$ (523 mg, 3.22 mmol) was added benzotriphenylene **6aa** (46 mg, 0.11 mmol) at 0 °C. The resulting solution was stirred for 1 h. MeOH was added to quench the reaction and organic materials were extracted with dichloromethane three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (dichloromethane) to give half HBC **10aa** (38 mg, 84% yield) as a yellow solid.

Dibenzo[*fg,ij*]naphtho[1,2,3,4-*rst*]pentaphene **10aa:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.71–7.77 (m, 4H), 7.96 (dd, *J* = 7.9, 7.9 Hz, 2H), 8.80 (d, *J* = 7.5 Hz, 2H), 8.82 (d, *J* = 7.9 Hz, 4H), 8.94–9.00 (m, 2H), 9.11 (dd, *J* = 6.4, 3.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 121.7, 121.8, 122.1, 123.8, 124.5, 125.2, 125.7, 126.4, 126.8, 126.9, 128.4, 128.9, 129.5, 129.8, 129.9, 130.1, 131.2; IR (neat): ν̃ = 1261, 1092, 1018, 796, 741 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{34}H_{19}$ [M+H]$^+$: 427.1487; found: 427.1477.

7,16-Dihexyldibenzo[*fg,ij*]naphtho[1,2,3,4-*rst*]pentaphene **10ac**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 6.8 Hz, 6H), 1.32–1.42 (m, 8H), 1.47 (tt, *J* = 7.6, 7.2 Hz, 4H), 1.80 (tt, *J* = 7.8, 7.6 Hz, 4H), 2.85 (t, *J* = 7.8 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.60 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 7.8, 7.8 Hz, 2H), 8.41 (s, 2H), 8.53 (d, *J* = 8.0 Hz, 2H), 8.61 (d, *J* = 8.1 Hz, 2H), 8.74 (d, *J* = 8.3 Hz, 2H), 9.00 (dd, *J* = 6.4, 3.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2, 22.7, 29.2, 31.6, 31.8, 36.4, 121.2, 121.4, 121.6, 122.9, 124.4, 124.8, 125.4, 126.3, 127.1, 127.4, 128.4, 128.8, 129.6, 129.7, 129.8, 131.0, 141.3; IR (neat): ν̃ = 2924, 1466, 1441, 806, 750 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{46}H_{43}$ [M+H]$^+$: 595.3365; found: 595.3353.

7,16-Di-*tert*-butyldibenzo[*fg,ij*]naphtho[1,2,3,4-*rst*]pentaphene **10ad**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.51 (s, 18H), 7.62 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.73 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.89 (dd, *J* = 7.9, 7.9 Hz, 2H), 8.75 (d, *J* = 2.0 Hz, 2H), 8.76 (d, *J* = 7.9 Hz, 2H), 8.81 (d, *J* = 8.0 Hz, 2H), 8.86 (d, *J* = 8.6 Hz, 2H), 9.09 (dd, *J* = 6.4, 3.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 31.6, 35.2, 119.7, 121.5, 121.6, 121.9, 124.6, 124.7, 125.0, 125.6, 126.7, 127.4, 128.5, 128.9, 129.6, 130.0, 130.4, 130.8, 149.6; IR (neat): ν̃ = 2956, 2922, 1259, 1018, 796 cm^{-1}; HRMS (APCI$^+$): calcd. for $C_{42}H_{35}$ [M+H]$^+$: 539.2739; found: 539.2745.

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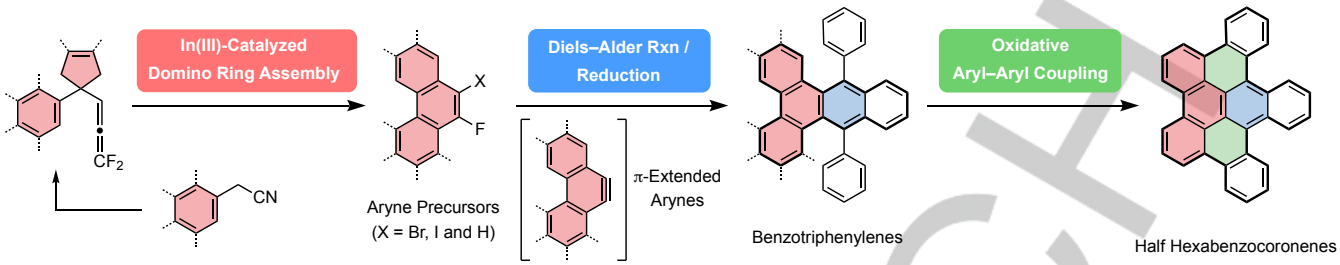

1,1-Difluoroallenes bearing a cyclopentene moiety and an aryl group underwent In-catalyzed domino ring assembly to afford aryne precursors such as *ortho*-fluoro(halo)phenanthrenes and fluoro[4]helicenes. Their elimination of XF generated π-extended arynes, whose Diels–Alder reactions with isobenzofurans followed by aromatisation furnished benzotriphenylenes. Their aryl–aryl coupling facilitated “half HBC” synthesis.