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Structurally Characterized Hetero-Oligopolyphenylenes: Synthetic Advances Toward Next-Generation Heterosuperbenzenes

Daniel J. Gregg, Cecile M. A. Ollagnier, Christopher M. Fitchett, and Sylvia M. Draper*[a]

Abstract: The successful Diels–Alder [2+4] cycloaddition[1] of dipyrimidyl acetylene and suitably substituted 2,3,4,5-tetraarylcyclopenta-2,4-dien-1-ones (**3–7**) generates a series of selectively functionalized hexaarylbenzenes. Each has two pairs of peripheral functional groups (R′ and R = *tert*-butyl **8** and R = methyl **9**, methoxy **10**, bromo **11**, triisopropylsilylethynyl **12**) and four *ortho*-imine nitrogen atoms. The dibromo derivative **11** is a useful precursor for the formation of a mono ethynyl **13** and diethynyl **14** substituted polyphenylene. Changing the dienophile to di(2-thienyl)acetylene gives an S-heteroatom polyphenylene **15**. The compounds were fully characterized by using ^{1}H, ^{13}C and a range of 2D NMR spectroscopic techniques, elemental analysis, and mass spectrometry. Oxidative cyclodehydrogenation of dimethoxy hexaphenylbenzene **10** by using iron(III) chloride results in the formation of a spirocyclic dienone **16**, which in a separate reaction undergoes dienone/phenol rearrangement to give the first 4-fused-ring, N-heterosuperbenzene (HSB) **17.** Six single crystal molecular structures reveal the commonality of unidirectional twisting of the external aromatic rings in these heteroatom polyphenylenes. The twist angles and any H-bonding or interdigitation in these structures are discussed.

Keywords: cyclodehydrogenation · dendrimers · nitrogen-heterosuperbenzene · polycycles · rotamers

Introduction

Monodispersed, polyaromatic dendrimers are of considerable interest in the design of nanostructures.[2] Dendrimer research has undergone a shift of emphasis from the construction of new skeletons and higher-generation architectures to the fabrication of functional systems incorporating dyes, catalysts and biologically-active molecules.[3,4] The dense intramolecular packing, thermal and chemical stability, and postulated rigidity of dendrimers compare in a superior way to aliphatic systems and give rise to their potential applications. In particular, a polyphenylene framework offers a large-surface support structure for the generation of a multichromophore array with attendant increases in the potential for light-harvesting[5,6] and in the efficiency of energy transfer.[7]

[a] Dr. D. J. Gregg, Dr. C. M. A. Ollagnier, Dr. C. M. Fitchett, Prof. S. M. Draper
Department of Chemistry, University of Dublin
Trinity College, Dublin 2 (Ireland)
Fax: (+353) 1-671-2826
E-mail: smdraper@tcd.ie

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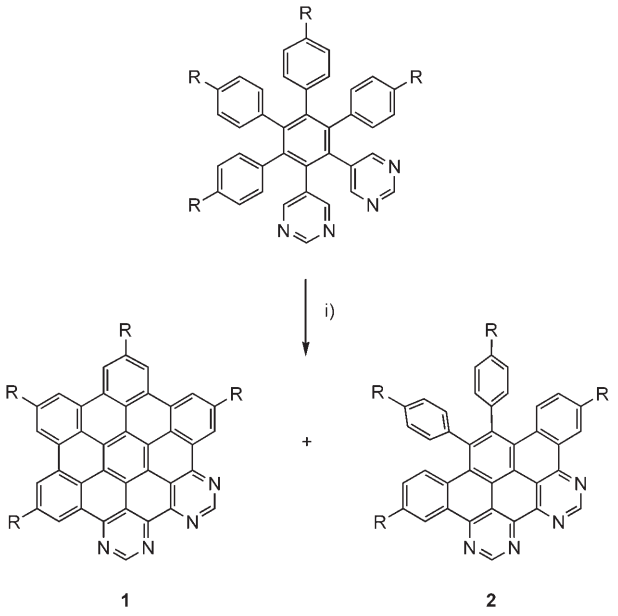
Sterically-crowded polyphenylene molecules of the type $C_nAr_n^{x\pm}$ warrant attention as molecular propellers.[8] Literature examples of propeller architectures include polyphenylated systems incorporating a ferrocenyl moiety that can exhibit restricted rotation and in some cases chirality.[9] Our interest in polyphenylenes stems from their potential role as precursors to a class of molecule, known collectively as the nitrogen-heterosuperbenzene family.

Until now, this family consisted of just two molecules: the founding member **1**[10,11] (comprising 13 fused aromatic rings) and its daughter **2**[12] (comprising 8 fused aromatic rings). Each has the same sequence of four peripheral N-atoms (Scheme 1). These N-doped graphenes are formed following a mild, oxidative cyclodehydrogenation reaction of 1,2-dipyrimidyl-3,4,5,6-tetra-(4-*tert*-butylphenyl)benzene in a manner similar to that developed for the formation of Clar-type hexabenzocoronenes.[13] The current members of the N-heterosuperbenzene family exhibit a range of notable chemical, physical, and photophysical properties as a function of their degree of aromaticity and rigidity.[10–12] Our aim is to instigate a systematic investigation of other factors, such as polarity, geometry, functionality, and type of heteroatom, in determining the fundamental properties of heterosuperbenzenes. In this context the generation of a new set

of 3-dimensional oligopolyphenylenes is a necessary first step.

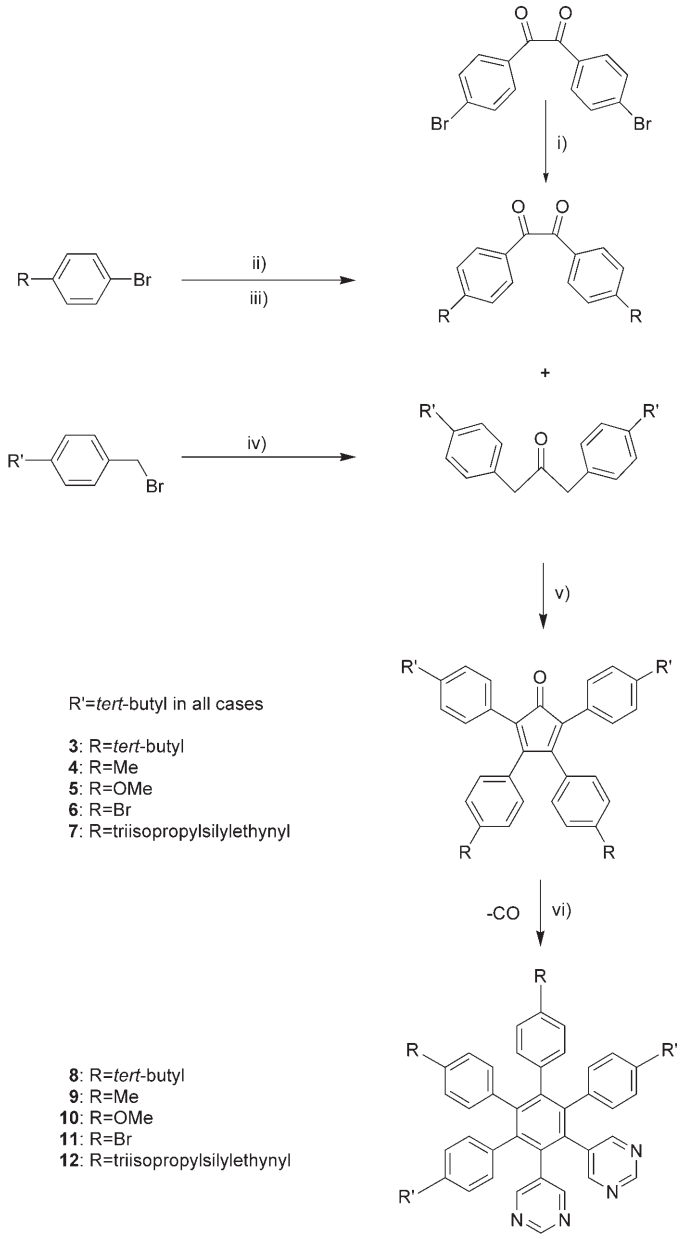


Scheme 1. The oxidative cyclodehydrogenation of N-doped oligophenylene to form N-HSB **1** and N-1/2HSB **2**. R = *tert*-butyl. Reaction conditions: i) $FeCl_3$.[12]

Results and Discussion

The functionalization of hexaaryl benzene: The [2+4] Diels–Alder cycloaddition[1] reaction of dipyrimidyl acetylene and suitably substituted 2,3,4,5-tetraarylcyclopenta-2,4-dien-1-ones **3**, **4**, **5**, **6**, and **7** was the method of choice for generating a series of selectively functionalized hexaarylbenzene precursors **8**, **9**, **10**, **11**, and **12**. Each retains the same arrangement of four peripheral functional groups and four *ortho*-imine nitrogen atoms, characteristic of the known nitrogen-heterosuperbenzenes (Scheme 2). Alkyl, ethynyl and bromo-substituted tetraphenylcyclopentadienones of the type required were accessed by a two-fold Knoevenagel condensation[14] of the appropriate 1,2-diketone (from the synthesis by Mueller-Westerhoff)[15] and the 1,3-diarylacetone (from the modified synthesis of des Abbayes).[16] In this manner the functionality achieved can be uniform throughout; or can consist of two pairs of substituents depending on whether they are of diketone or propanone origin.

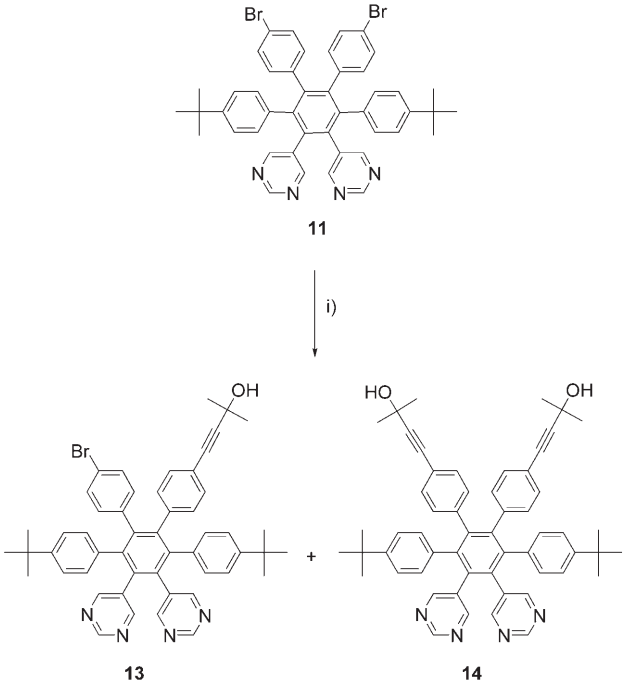
For **12**, the triisopropylsilylethynyl units were incorporated into the 1,2-diketone by coupling triisopropylsilylacetylene with dibromobenzil by using the method of Sonogashira et al.[17] and condensing the resulting 1,2-diketone with 1,3-diarylacetone in the presence of KOH. Derivative **7**, which is afforded in 81% yield, contains one diene and two dienophile functions, but the bulky triisopropylsilyl groups protect the C–C triple bonds from undergoing further Diels–Alder reaction.[14] Deprotection of the diethynyl functions for subsequent Diels–Alder reaction or functionalization is possible.[14]



Scheme 2. The synthesis of substituted N-doped hexaarylbenzenes **8, 9**, **10**, **11**, and **12**. Reaction conditions: i) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, toluene, triisopropylsilylacetylene; ii) *n*BuLi, THF, 195 K; iii) DMPD, THF, 195 K; iv) $Fe(CO)_5$, $Ca(OH)_2$, nBu_4NHSO_4; v) KOH, EtOH, reflux; vi) benzophenone, dipyrimidyl acetylene, 578 K. DMPD = 1,6-dimethylpiperazine-2,3-dione

Unfortunately the dibromo cyclopentadienone **6** is not a candidate for the direct coupling of triisopropylsilylacetylene due to the possibility of hydrogenation of the double bonds in the cyclopentadienone.[14] The dibromo hexaaryl benzene **11**, however, is a useful building block for accessing both di and mono-substituted polyphenylenes. Here Sonogashira coupling with 2-methyl-3-butyn-2-ol yields both the mono-substituted derivative **13** (as the major product, 38%)

along with di-substituted **14** (30%) (Scheme 3). Interestingly, even in the presence of a four-fold excess of alcohol significant amounts of the polyarylbenzene starting material **11** were recovered (30%). This and the high temperatures

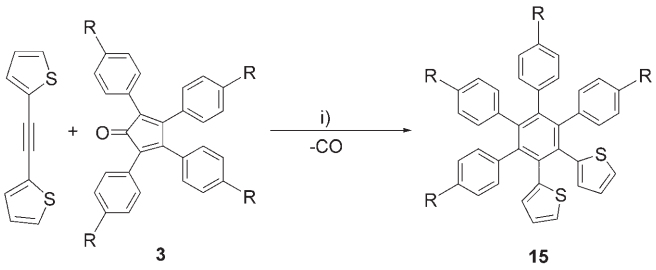


Scheme 3. The synthesis of ethynyl-substituted polyarylbenzenes by Pd-mediated cross-coupling reactions. Reaction conditions: i) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, DMF, 2-methyl-3-butyn-2-ol, 343 K, 24 h.

(343 K) and long reaction times (24 h) needed to progress the reaction suggests that **11** is somewhat deactivated toward the Pd-mediated cross-coupling process. This might be the result of a decrease in the lability of bromine substituents attached to such an electron-rich, aromatic core or because **11** is functioning as an effective Pd^{II} ligand.

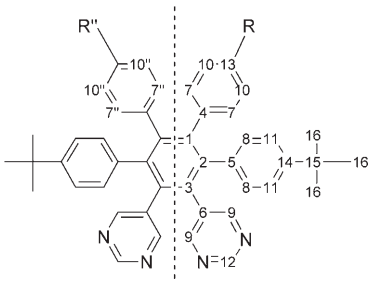
Altering the heteroatom: Acetylenic functions are interesting additions to conjugated arenes as they effect significant changes in the excited state emissions.[18] Thiophenes also mediate the electronic properties of species to which they are attached and have been shown to allow electronic communication over long distances more effectively than *p*-phenylene, ethenyl, azo, or ethynyl spacers.[19] To this end, although various heteroatoms could be incorporated into the polyphenylene in a step-wise manner by means of the synthetic strategy outlined, **15** was generated from di(2-thienyl)acetylene[20] and **3** as an example of an alternative heteroatom hexaarylbenzene (Scheme 4).

Spectroscopic characterization: All eight colorless heteroatom-doped polyphenylenes were fully characterized by using NMR spectroscopy, mass spectrometry, and elemental analysis. Molecules **8**, **10**, **11**, **12**, and **15** were structurally characterized by single crystal X-ray diffraction. As expected they



Scheme 4. The synthesis of substituted S-doped hexaarylbenzene **15**. R = *tert*-butyl. Reaction conditions: i) benzophenone, 578 K.

generally exhibit high melting points: compounds **9**, **10**, **13**, **14**, and **15** melt between 250–300 °C, whereas compounds **8**, **11**, and **12** melt above 300 °C. ESI-MS gave single signals at masses in agreement with the theoretically expected values and with isotopic distributions corresponding to $[M+H]^+$. The analyses of the NMR spectra were simplified by the presence of a C_2 symmetry axis in every polyphenylene (except **13** for which the substituents R and R″ differ, Figure 1).



8: R=R"=*tert*-butyl
9: R=R"=methyl
10: R=R"=methoxy
11: R=R"=bromo
12: R=R"=triisopropylsilylacetylene
13: R=Br, R"=3-methyl-3-hydroxy-butynyl
14: R=R"=3-methyl-3-hydroxy-butynyl

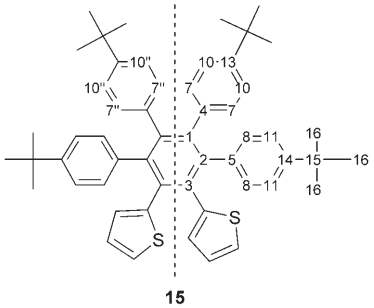


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Figure 1. The atom labeling scheme for the N- and S-doped polyphenylenes.

The aliphatic signals for the alkyl substituents in the R and R″ positions are characteristic of the particular alkyl substituent and in all cases the H16 protons are rendered equivalent by the free rotation of the *tert*-butyls. In all the

polyphenylenes the H16 protons resonate in the range $\delta =$ 1.13 –1.16 ppm.

The ^{1}H NMR spectra of **8**–**14** exhibit two sets of aromatic signals. One of these sets is assigned to the hydrogen atoms of the pyrimidine ring and consists of two low-field singlets at $\delta = 8.75$–8.77 ppm (H12) and $\delta = 8.20$–8.26 ppm (H9) integrating for two and four hydrogen atoms, respectively. The second is assigned to the aromatic protons of the phenyl carbons C7, C8, C10, and C11 and appears upfield at $\delta = 6.5$–7.1 ppm. As might be expected, the chemical shifts of the latter show considerable variation depending on the electronic properties of the substituents at R and R″ (see Table 1). The electron-donating methoxy groups in **10** result in an upfield shift of H7/H10 compared to **8** whereas the bromo or acetylene groups of **11**–**14**, respectively, cause a slight downfield shift in these signals compared to **8**. In this context it should be noted that hexaphenyl benzene displays only a single multiplet in its ^{1}H NMR spectrum at $\delta =$ 6.83 ppm.[21]

Table 1. Assignment of ^{13}C and ^{1}H NMR signals from TOCSY, HMQC, and HMBC COSY experiments on compounds **8**–**15**.

Compound	HH COSY (TOCSY) H7 and H10 [δ, ppm]	CH COSY (HMBC) C13 [δ, ppm]	HH COSY (TOCSY) H8 and H11 [δ, ppm]	CH COSY (HMBC) C15 [δ, ppm]	C14 [δ, ppm]
8	6.86, 6.69	147.9 or 148.6	6.93, 6.71	33.7	147.9 or 148.6
9	6.70	134.5	6.95, 6.70	33.8	148.7
10	6.71, 6.45	156.8	6.96, 6.70	33.8	148.7
11	7.06, 6.68	119.9	6.98, 6.69	33.9	149.3
12	7.04, 6.77	120.5	6.97, 6.70	33.8	149.2
13	6.70, 6.78, 6.99, 7.05		6.99, 6.70	33.8	
14	6.98, 6.77		6.98, 6.71	33.8	
15	6.66, 6.83	147.2	6.81, 6.92	33.6	147.6

The assignments made here for the new derivatives **8**–**15** were aided by heteronuclear CH COSY (HMQC) spectra and the clear observation of vicinal coupling in homonuclear HH COSY (TOCSY) experiments between H7 and H10 and between H8 and H11. HMBC NMR experiments were used to determine the ^{13}C NMR signals of the quaternary carbons C13, C14, and C15 and the aromatic protons H8 and H11 by virtue of their coupling (see Table 1).

The 135° DEPT NMR spectra of polyphenylenes **8**–**12** and **14** comprises of six aromatic CH signals. The two low-field signals at $\delta = 157$ and 155 ppm are due to the deshielded aromatic carbon atoms of the pyrimidine ring. The remaining four signals (eight signals for **13**) in the range $\delta =$ 110–130 ppm, are assigned to the phenyl carbons C7, C8, C10, and C11. The chemical shifts of these carbons mirror the substituent effects of their associated protons, for example, the most pronounced shift is observed in the methoxy derivative **10** and is predictably upfield ($\delta = 111.9$ ppm). These results are summarized in Table 2.

Table 2. The ^{13}C NMR spectroscopic chemical shifts of the aromatic CH carbons for the various heteroatom-doped polyphenylene derivatives ($CDCl_3$, RT, 100 MHz).

Compound	C12 [δ, ppm]	C9 [δ, ppm]	C7, C8, C10, C11 [δ, ppm]
8	155.4	157.6	130.4, 130.1, 123.7, 122.9
9	155.3	157.5	130.4, 130.3, 127.0, 123.8
10	156.8	157.5	131.6, 130.3, 123.9, 111.9
11	155.6	157.4	132.0, 130.1, 129.8, 124.1
12	155.6	157.4	130.3, 130.3, 130.2, 124.1
13	155.6, 155.5	157.4, 157.3	132.0, 130.3, 130.1, 130.1, 130.0, 129.7, 124.1, 124.1
14	155.5	157.4	130.4, 130.2, 130.0, 124.1
15	–	–	130.4, 130.0, 122.7, 122.9

Molecular structure determinations: As propeller-like molecules, sterically crowded polyphenylenes form the core of discotic liquid crystals and dendrimers. An interesting phenomenon of organometallic polyphenylated systems is their ability to exhibit correlated rotation, depending on the steric hindrance of the phenyl rings. The degree of ring-tilting is a delicate balance of steric and electronic factors: a perpendicular arrangement minimizing steric interactions; coplanarity maximizing π-orbital overlap.

Single crystal X-ray structure determinations of **8**, **10**, **11**, **12**, and **15** were performed and their molecular structures determined.[22] These contribute significantly to the current literature which reports only one existing single crystal structural determination of a heteroaryl polyphenylene.[23] The compounds all crystallized with one molecule in the asymmetric unit and the perspective views of the structures of **10** and **11** are presented in Figures 2 and 3, respectively.

The crystals of **11** were twinned and the two reciprocal-lattices were combined by using SAINT for solution and refinement. The structures of **8** and **10** exhibit positional disorder of one *tert*-butyl group each. Crystals of **15** were also

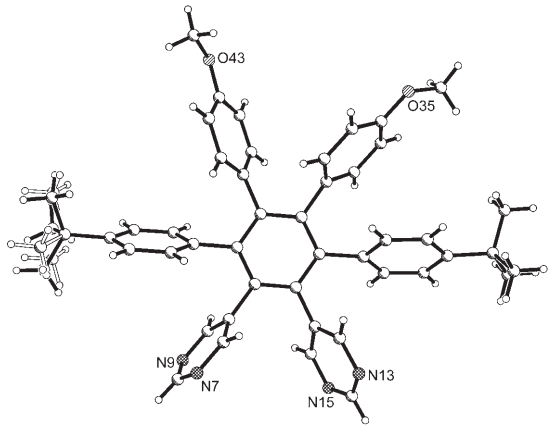


Figure 2. A perspective view of one enantiomer from the molecular structure of **10**, showing the positional disorder in one *tert*-butyl substituent.

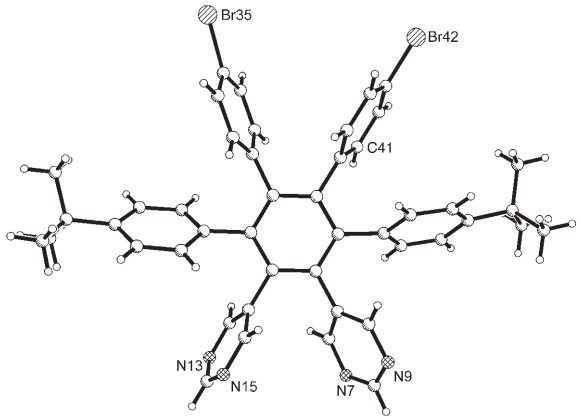


Figure 3. A perspective view of the molecular structure obtained from the twinned crystals of **11.**

disordered, with one thiophene occupying two coplanar orientations; the major having 80% occupancy. The result is an averaging of the bond lengths in this thiophene ring.

The molecular structures all exhibit significant and unidirectional twisting of the aryl and heteroaryl rings such that individual molecules are chiral, although the crystallographic space group in each case is achiral. The tilt angles between the mean planes of each terminal ring and the central core benzene are given in Table 3. These are similar to

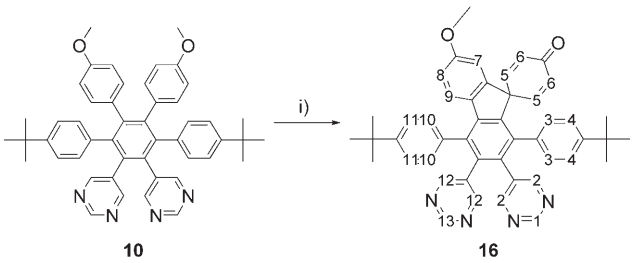
Table 3. The tilt angles between the mean planes of each terminal ring and the central core benzene for **8**, **10**, **11**, **12**, and **15**.

Compound	Ring type and tilt angles [°]					
	tert-butyl	*tert*-butyl	R	R	Heterocycle	Heterocycle
8	61.4	71.3	59.0	60.4	59.2	78.3
10	61.9	71.6	64.0	68.3	64.8	70.3
11	64.0	70.2	64.6	68.3	61.9	71.6
12	57.2	65.6	60.5	67.3	62.6	71.1
15	65.7	66.4	64.7	66.8	59.7	68.4

those of hexaphenylbenzene (approx. 65°)[24] and are relatively uniform throughout with the exception of **8**. Here one pyrimidyl ring is markedly more perpendicular, a result of the interdigitation of this pyrimidyl ring with that of an adjacent molecule, as shown in Figure 4. This comprises two C–H···π interactions (2.63(1) Å) and a slight π–π face-to-face interaction (3.16(1) Å).

Peripherally functionalized hexaphenylbenzenes have generated supramolecular networks through H-bonding.[25] However, despite the excellent H-bonding capability of heterocyclic nitrogen atoms, only **11** displays any hydrogen bonding (C41···N13 3.370(4) and C41–H···N13 175(1)°). This is perhaps typical of the weak aryl hydrogen donor atoms present.[26]

Cyclodehydrogenation of 10: Previous work undertaken by the authors has shown the choice of oxidative cyclodehydrogenation reagent to be key to the outcome of the ring-fusion process necessary for the formation of planar graphenes.[12] In general the milder iron(III) chloride gives greater variation in the extent of cyclodehydrogenation and for compound **8** gives products resulting from half or all of the possible ring fusions taking place. Polyphenylene **10** which differs from **8** only by the presence of two electron-donating methoxy substituents was chosen as a target compound to begin to explore substituent effects on this intriguing reaction. The result was the near quantitative conversion of **10** to the spirocyclic dienone **16**, shown in Scheme 5.



Scheme 5. The synthesis and NMR atom labeling of the N-doped spirocyclic dienone **16**. Reaction conditions: i) $FeCl_3$,[13] HCl is removed from the reaction mixture by a steady flow of argon.

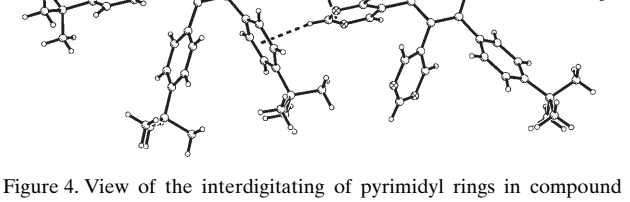


Figure 4. View of the interdigitating of pyrimidyl rings in compound **8**. The dashed lines indicate π–π and C–H···π interactions.

Asymmetric **16** was characterized by NMR spectroscopy, mass spectrometry, and accurate mass analyses. ^{1}H NMR spectroscopy immediately indicated the loss of the C_2 symmetry axis with two peaks each emerging for the now chemically distinct aromatic protons of the pyrimidine rings (H1 and H13 centered around $\delta = 8.8$, H2 and H12 centered around $\delta = 8.3$ ppm, see Figure 5 and atom labeling in Scheme 5).

The three proton system of H7, H8, and H9 showed well-resolved coupling information in the ^{1}H NMR spectrum. Vicinal coupling (^3J(H,H) = 8.52 Hz) between signals $\delta = 6.62$ and 6.32 ppm allows their assignment to H8 and H9, respectively, and long-range coupling (^4J(H,H) = 2.52 Hz) between signals $\delta = 6.62$ and 6.57 ppm confirms their assignment to H8 and H7. All other aromatic protons (H3, H4 and H10, H11) as well as the quinone type resonances (H5, H6) appear as doublets integrating for two in the $\delta = 6.0$–7.5 ppm region.

The formation of spirocyclic dienones from methoxy-substituted aromatic compounds has literature precedence. In

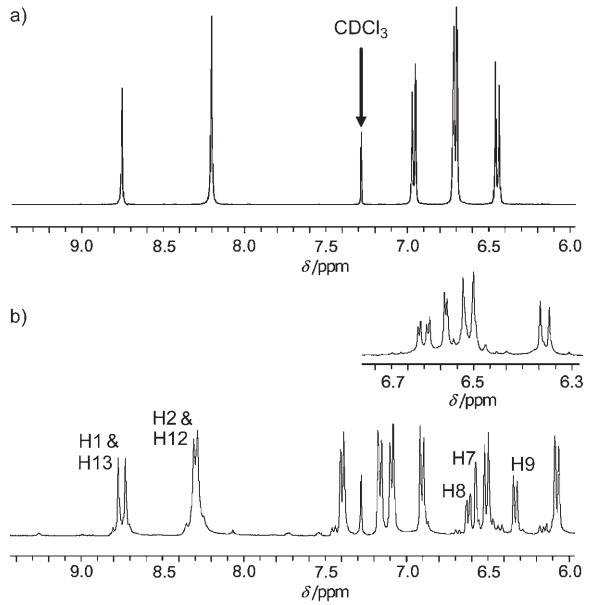


Figure 5. The aromatic region of the ^{1}H NMR spectra for polyphenylenes: a) **10**; b) **16** ($CDCl_3$, RT, 400 MHz).

the presence of Lewis acids the latter have been shown to undergo ether cleavage, oxidation to quinonoid structures, and C–C bond formation between phenyl rings.[27] The oxidative cationic mechanism, previously proposed for Lewis acid catalyzed cyclodehydrogenation also sheds some light on the generation of spirocyclic **16** reported here. It may arise from the methoxy-directed activation at the para-position of arenium ions generated during the cyclodehydrogenation of **10**. The methoxy substituents would activate attack at both *ortho*- or *para*-positions through resonance stabilization, but conformational requirements would ensure that the former is less likely.

Molecular structure determination: Slow evaporation of **16** in a 1:1 mixture of ethyl acetate and hexane produced crystals suitable for single crystal X-ray analysis. The crystals lost crystallinity quickly on solvent evaporation; however, a sample was mounted and the molecular structure determined. The asymmetric unit was found to contain two molecules of **16** and two molecules of ethyl acetate, one of which was disordered. The bond lengths and angles of both molecules of **16** are similar, the asymmetry in this case being generated by the position of the solvent molecules in the lattice.

The newly formed spirocyclic dienone causes only small changes in the twisting of the adjacent *tert*-butyl substituted rings (Figure 6). These have twist angles of between 73.9(5) and 79.7(5)° in relation to the central ring. One of these is orientated such that it interacts with a hydrogen atom of the planar fluorene moiety of the spirocycle giving C–H···π distances of 2.58(1) and 2.59(1) Å, for the two molecules in the asymmetric unit. The twists associated with the pyrimidyl rings differ significantly between the two molecules of **16** in the asymmetric unit. One set being more twisted than the other (83.1(5) and 88.3(5)° versus 68.1(5) and 75.1(5)°). The

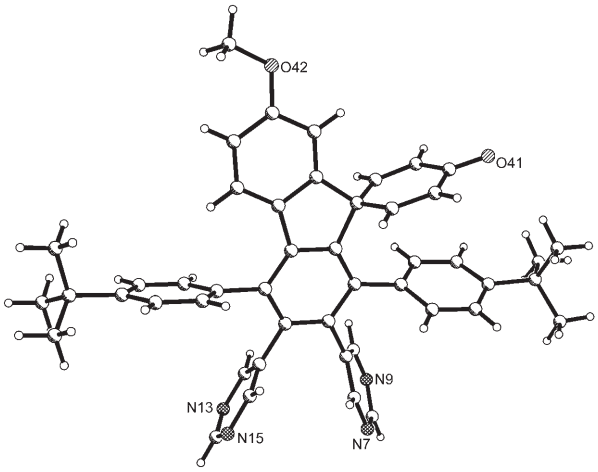
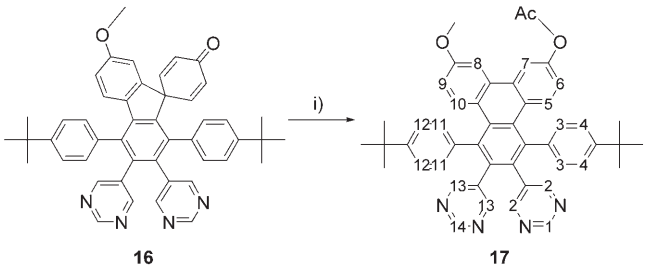


Figure 6. The perspective view of the molecular structure of **16**, showing one of the two molecules in the asymmetric unit. The second molecule and solvated molecules have been omitted for clarity.

molecules pack in a similar manner to those of **8**, with one molecule interdigitating another.

The formation of **16** immediately suggested the possibility of generating partially cyclized **17** by a dienone/phenol rearrangement reaction[28] in acetic anhydride and sulfuric acid (Scheme 6). Such a product would be the third isolated member of the N-heterosuperbenzene family and the least aromatic.



Scheme 6. The synthesis of **17** by the dienone/phenol rearrangement reaction. Reaction conditions: i) heat, acetic anhydride, H_2SO_4.

Data obtained from NMR spectroscopy, ESI-MS and accurate mass analyses were consistent with the formation of **17**. The absence of a C_2-symmetry axis in **17** renders the pyrimidine protons H1 and H14 chemically distinct ($\delta = 8.84$ and 8.85 ppm) (see Figure 7 and atom labeling in Scheme 6). The resonances due to H2 and H13, however, appear as a broad signal at $\delta = 8.09$ ppm superimposed on that of H7. There are two sets of three proton systems: H5, H6, and H7 on the acetyl substituted ring, and H8, H9, and H10 on the methoxy substituted ring. Well-resolved coupling information in the ^{1}H NMR spectrum and HH COSY (TOCSY) NMR spectroscopy aided the assignment of these protons. Protons H5 and H6 are assigned to the signals at $\delta = 7.64$ and 6.81 ppm, respectively, and exhibit vicinal coupling ($^3J(H,H) = 9$ Hz). The associated long-range coupling

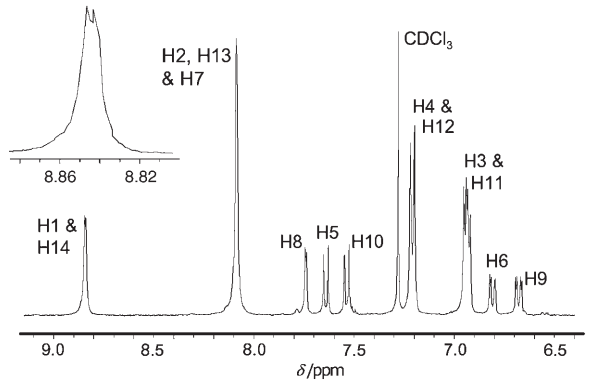


Figure 7. The aromatic region of the ^{1}H NMR spectra for the partially cyclized **17** ($CDCl_3$, RT, 400 MHz).

(^4J(H,H) = 2.52 Hz) between H6 and H7 was evident in the signals at $\delta = 6.81$ and 8.09 ppm.

Similarly vicinal coupling (^3J(H,H) = 9 Hz) between the signals at $\delta = 6.68$ and 7.54 ppm and long-range coupling (^4J(H,H) = 2 Hz) between the signals at $\delta = 6.68$ and 7.74 ppm allows unambiguous assignment of these signals to H9, H10, and H8 (with increasing chemical shift). These assignments were confirmed by NOE correlation experiments. The H3 and H11 signals appear as overlaid doublets at $\delta = 6.94$ (2H) and 6.93 ppm (2H), while those of H4 and H12 appear as a single doublet at $\delta = 7.21$ ppm (4H).

Conclusion

In the current work a set of structurally characterized heteroatom-oligophenylenes has been produced. Common to these are a benzoid-core, supporting phenyl, pyrimidyl, or thienyl termini. The species are accessed synthetically by the [2+4] Diels–Alder cycloaddition reaction of diarylacetylenes with appropriately functionalized tetraarylcyclopentadienones followed by in situ decarbonylation. The successful Sonagashira coupling of a dibromo polyphenylene suggests it to be a versatile synthon for the generation of an even greater range of functionalized heteropolyphenylenes. Those described are topologically designed so as to avoid the possibility of structural isomers and to allow for subsequent intramolecular cyclodehydrogenation to give flattened aromatic platforms. Here the electron-donor characteristics of peripheral substituents are expected to influence fundamental properties, such as the photophysics or supramolecular chemistry.

The formation of the third member of the nitrogen heterosuperbenzene family represents an important step forward in the synthesis of such molecules. Generated indirectly from the methoxy-substituted polyphenylene, its arrival anticipates that substituent control of the cyclodehydrogenation mechanism can be attained.

Experimental Section

1,3-bis-(4-*tert*-butylphenyl)propan-2-one,[10] **3**,[10] dipyrimidine acetylene,[10] **8**,[10] and 1,2-bis(4-triisopropylsilylethynylphenyl)ethane-1,2-dione,[14] were synthesized according to literature procedures. Flash chromatography was performed by using silica gel (Brockman I, Aldrich Chemical) or activated alumina (Type 507 C neutral alumina, Fluka Chemical) as the stationary phase.

Physical measurements and instrumentation: IR spectra were recorded from KBr disks on a Perkin–Elmer Paragon 1000 Fourier transform spectrophotometer. NMR spectra were recorded on a DPX 400 spectrometer operating at 400.13 MHz for ^{1}H, and 100.62 MHz for ^{13}C, and were standardized with respect to TMS. ESI-MS were recorded on a micromass LCT electrospray mass spectrometer. Accurate MS were referenced against leucine enkephalin (555.6 $gmol^{-1}$), and were reported within 5 ppm.

CCDC-285545 (**15**), CCDC-285546 (**16**), CCDC-285547 (**8**), CCDC-285548 (**12**), CCDC-285549 (**11**), and CCDC-285550 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Single-crystal analyses were made with a Bruker SMART APEX CCD area detector by using graphite monochromized $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation at 153(2) K (**8**, **15**, **16**) and 298(2) K (**10**, **11**, **12**). The data reduction was performed by using SAINT.[29] Intensities were corrected for Lorentz and polarization effects and for absorption by using SADABS[30] or TWINABS.[31] Space groups were determined from systematic absences and checked for higher symmetry. A full sphere of data was obtained for each by using the omega scan method. The structures were solved by direct methods with SHELXS,[32] and refined on F^2 by using all data by full-matrix least-squares procedures with SHELXL-97.[33] All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons. Absolute structure determinations were based on the Flack parameter. The functions minimized were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ in which $P = [\max(F_o)^2 + 2F_c^2]/3$. In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions.

2,5-bis-(4-*tert*-butylphenyl)-3,4-bis-(4-methyl-phenyl)cyclopenta-2,4-dienone (4): 4,4′-Dimethylbenzil, 1,3-bis-(4-*tert*-butylphenyl)propan-2-one (541 mg; 1.68 mmol), and KOH (100 mg) were refluxed in ethanol (100 mL) for 4 h. After this time, the red/brown solution was reduced and chromatographed (SiO_2, hexane:dichloromethane 1:1) to produce **4** as a deep red crystalline product. Yield: 0.353 g, 40 %; m.p. 240–241 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta = 7.28$ (d, ^3J(H,H) = 8.5 Hz, 4H; H_{aryl}), 7.20 (d, ^3J(H,H) = 8.5 Hz, 4H; H_{aryl}), 7.01 (d, ^3J(H,H) = 8.0 Hz, 4H; H_{aryl}), 6.86 (d, ^3J(H,H) = 8.0 Hz, 4H; H_{aryl}), 2.35 (s, 6H; $-CH_3$), 1.32 ppm (s, 18H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta = 200.7$ (1C; C=O), 153.6 (2C; $C_{quat/Cp}$), 149.6 (2C; $C_{quat/aryl}$), 137.7 (2C; $C_{quat/aryl}$), 130.0 (2C; $C_{quat/aryl}$), 129.2 (4C; C_{aryl}), 128.9 (4C; C_{aryl}), 128.1 (4C; C_{aryl}), 127.6 (2C; $C_{quat/aryl}$), 124.4 (4C; C_{aryl}), 124.2 (2C; $C_{quat/Cp}$), 34.1 (2C; $C_{quat/alkyl}$), 30.8 (6C; $-CH_3$), 21.0 ppm (2C; $-CH_3$); IR (KBr disk,): $\tilde{\nu} = 3033$ ($CH_{aromatic}$), 2961, 2902, 2867 (CH_3), 1710 (C=O), 1609, 1504 (C=C), 1461 cm^{-1} (CH_3); ESI-MS (CH_3CN): *m/z* (%): calcd: 525.7; found: 525.3 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{39}H_{40}O$ (524.7): C 89.27, H 7.68; found: C 88.76, H 7.73.

2,5-bis-(4-*tert*-butylphenyl)-3,4-bis-(4-methoxyphenyl)cyclopenta-2,4-dienone (5): 4,4′-Dimethoxybenzil (536 mg; 1.98 mmol), 1,3-bis-(4-*tert*-butylphenyl)propan-2-one (639 mg; 1.98 mmol), and KOH (110 mg) were refluxed in ethanol (100 mL) for 14 h. After this time, the red/brown solution was reduced and chromatographed (SiO_2, hexane:dichloromethane 1:1) to produce **5** as a deep red crystalline product. Yield: 0.305 g, 28 %; m.p. 210–212 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta = 7.28$ (d, ^3J(H,H) = 8.5 Hz, 4H; H_{aryl}), 7.20 (d, ^3J(H,H) = 8.5 Hz, 4H; H_{aryl}), 6.91 (d, ^3J(H,H) = 9 Hz, 4H; H_{aryl}), 6.75 (d, ^3J(H,H) = 8.5 Hz, 4H; H_{aryl}), 3.82 (s, 6H; $-CH_3$), 1.32 ppm (s, 18H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta = 200.6$ (1C; C=O), 159.2 (2C; $C_{quat/aryl}$), 153.1 (2C; $C_{quat/aryl}$), 149.6 (2C; $C_{quat/aryl}$), 130.7 (4C; C_{aryl}), 129.2 (4C; C_{aryl}), 127.7 (2C; $C_{quat/aryl}$),

125.2 (2C; $C_{quat/aryl}$), 124.5 (4C; C_{aryl}), 123.9 (2C; $C_{quat/aryl}$), 112.9 (4C; C_{aryl}), 54.7 (2C; $-CH_3$), 34.1 (2C; $C_{quat/alkyl}$), 30.8 ppm (6C; $-CH_3$); IR (KBr disk): $\tilde{\nu}=3036$ ($CH_{aromatic}$), 2961, 2903, 2865 (CH_3), 2837 ($O-CH_3$), 1706 (C=O), 1604 (C=C), 1462 (CH_3), 1405 (CH_3), 1250 cm^{-1} ($O-CH_3$); ESI-MS (CH_3CN): *m/z* (%): calcd: 557.5; found: 557.6 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{39}H_{40}O_3$ (556.7): C 84.13, H 7.24; found: C 83.56, H 7.56.

2,5-bis-(4-*tert*-butylphenyl)-3,4-bis-(4-bromo-phenyl)cyclopenta-2,4-dienone (6): 4,4′-Dibromobenzil (1.211 g; 3.29 mmol), 1,3-bis-(4-*tert*-butylphenyl)propan-2-one (1.056 g; 3.27 mmol), and KOH (177 mg) were refluxed in ethanol (400 mL) for 2 h. After this time, the red/brown solution was allowed to cool to RT, and was then kept at 0 °C for 3 h. The purple black solid was filtered off and purified by column chromatography (SiO_2, hexane:dichloromethane 1:1), to produce **6** as a deep red crystalline product. Yield: 1.250 g, 60 %; m.p. 289–290 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta=7.37$ (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 7.30 (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 7.17 (d, $^3J(H,H)=8.0$ Hz, 4H; H_{aryl}), 6.85 (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 1.33 ppm (s, 18H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta=199.8$ (1C; C=O), 151.5 (2C; $C_{quat/aryl}$), 150.4 (2C; $C_{quat/aryl}$), 131.6 (2C; $C_{quat/aryl}$), 131.0 (4C; C_{aryl}), 130.5 (4C; C_{aryl}), 129.2 (4C; C_{aryl}), 126.8 (2C; $C_{quat/aryl}$), 125.1 (2C; $C_{quat/aryl}$), 124.7 (4C; C_{aryl}), 122.4 (2C; $C_{quat/aryl}$), 34.2 (2C; $C_{quat/alkyl}$), 30.8 ppm (6C; $-CH_3$); IR (KBr disk): $\tilde{\nu}=3035$ ($CH_{aromatic}$), 2961, 2902, 2866 (CH_3), 1713 (C=O), 1586 (C=C), 1484 (CH_3), 1392 cm^{-1} (CH_3); ESI-MS (CH_3CN): *m/z* (%): calcd: 655.5; found: 655.3 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{37}H_{34}OBr_2$ (654.4): C 67.90, H 5.24; found: C 67.83, H 5.44.

2,5-bis-(4-*tert*-butylphenyl)-3,4-bis-(4-triisopropylsilylethynylphenyl)cyclopenta-2,4-dienone (7): 1,2-bis(4-triisopropylsilylethynylphenyl)ethane-1,2-dione (790 mg; 1.38 mmol), 1,3-bis-(4-*tert*-butylphenyl)propan-2-one (446 mg; 1.38 mmol), and KOH (125 mg) were refluxed in ethanol (20 mL) for 2 h. After this time, the red/brown solution was allowed to cool to RT, and was kept at 0 °C for 3 h. The purple black solid was filtered off as **7**. Yield: 0.960 g, 81 %; m.p. 281–283 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta=7.33$ (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 7.30 (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 7.18 (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 6.93 (d, $^3J(H,H)=8.0$ Hz, 4H; H_{aryl}), 1.33 (s, 18H; $-CH_3$), 1.17 ppm (s, 42H; CH; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta=200.0$ (1C; C=O), 152.2 (2C; $C_{quat/aryl}$), 150.2 (2C; $C_{quat/aryl}$), 132.8 (2C; $C_{quat/aryl}$), 131.3 (4C; C_{aryl}), 129.3 (4C; C_{aryl}), 128.8 (4C; C_{aryl}), 127.0 (2C; $C_{quat/aryl}$), 125.1 (2C; $C_{quat/aryl}$), 124.7 (4C; C_{aryl}), 123.0 (2C; $C_{quat/aryl}$), 106.4 (2C; $-C\equiv C-$), 91.7 (2C; $-C\equiv C-$), 34.2 (2C; $C_{quat/alkyl}$), 30.8 (6C; $-CH_3$), 18.2 (12C; $-CH_3$), 10.9 ppm (6C; $-CH$); IR (KBr disk): 3082, 3038 ($CH_{aromatic}$), 2954, 2893, 2865 (CH_3), 2152 (C≡C), 1711 ν(C=O), 1602 (C=C), 1462 cm^{-1} (CH_3); ESI-MS (CH_3CN) *m/z* (%): calcd: 857.5; found: 857.3 (100) $[M+H]^+$.

1,2-dipyrimidyl-3,6-bis-(4-*tert*-butylphenyl)-4,5-bis-(4-methyl-phenyl)benzene (9): Benzophenone (2 g), dipyrimidyl acetylene (115 mg; 0.631 mmol), and **4** (328 mg; 0.625 mmol) were mixed in a round-bottomed flask attached to an air condenser. The reaction mixture was heated over a microburner to reflux for 1 h. Carbon monoxide was evolved and the color changed from purple to red/brown. After cooling and chromatography (SiO_2, diethyl ether), recrystallization from EtOAc/petroleum ether produced colorless crystals of **9**. Yield: 0.305 g, 72 %; m.p. 293–295 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta=8.76$ (s, 2H; H12), 8.23 (s, 4H; H9), 6.95 (d, $^3J(H,H)=8.5$ Hz, 4H; H_{aryl}), 6.70 (m, 12H; H_{aryl}), 2.12 (s, 6H; $-CH_3$), 1.14 ppm (s, 18H; H16); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta=157.5$ (4C; C9), 155.3 (2C; C12), 148.7, 142.3, 141.2, 136.0, 135.2, 134.5, 133.6, 132.5 (2C; $C_{quat/aryl}$), 130.4, 130.3, 127.0, 123.8 (4C; C_{aryl}), 33.8 (2C; C15), 30.6 (6C; C16), 20.6 ppm (2C; $-CH_3$); IR (KBr disk): $\tilde{\nu}$3046, 3028 ($CH_{aromatic}$), 2961, 2925, 2865 (CH_3), 1548, 1513 (C=N), 1389 cm^{-1} (CH_3); ESI-MS (CH_3CN): *m/z* (%): calcd: 679.9; found: 679.4 (100) $[M+H]^+$; ESI-MS (CH_3CN): *m/z*: calcd for $C_{48}H_{47}N_4$: 679.3801 $[M+H]^+$; found: 679.3803; elemental analysis calcd (%) for $C_{48}H_{46}N_4$ (678.9): C 84.92, H 6.83, N 8.25; found: C 84.78, H 7.29, N 7.70.

1,2-dipyrimidyl-3,6-bis-(4-*tert*-butylphenyl)-4,5-bis-(4-methoxyphenyl)-benzene (10): Benzophenone (3 g), dipyrimidine acetylene (106 mg; 0.582 mmol), and **5** (324 mg; 0.582 mmol) were mixed in a round-bottomed flask attached to an air condenser. The reaction mixture was heated over a microburner to reflux for 1 h. Carbon monoxide was evolved and the color changed from purple to red/brown. After cooling, chromatography (SiO_2, diethyl ether) and recrystallization from acetone/water produced colorless crystals of **10**. Yield: 0.320 g, 77 %; m.p. 277–278 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta=8.75$ (s, 2H; H12), 8.21 (s, 4H; H9), 6.96 (d, $^3J(H,H)=8.0$ Hz, 4H; H8 or H11), 6.709 (d, $^3J(H,H)=8.5$ Hz, 4H; H7 or H10), 6.705 (d, $^3J(H,H)=8.0$ Hz, 4H; H8 or H11), 6.45 (d, $^3J(H,H)=8.5$ Hz, 4H; H7 or H10), 3.63 (s, 6H; $-OCH_3$), 1.15 ppm (s, 18H; H16); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta=157.5$ (4C; C9), 156.8 (2C; C13), 155.4 (2C; C12), 148.7 (2C; C14), 142.0, 141.3, 135.3, 133.7, 132.5 (2C; $C_{quat/aryl}$), 131.6 (4C; C_{aryl}), 131.5 (2C; $C_{quat/aryl}$), 130.3, 123.9, 111.9 (4C; C_{aryl}), 54.5 (2C; $-OCH_3$), 33.8 (2C; C15), 30.6 ppm (6C; C16); IR (KBr disk): $\tilde{\nu}=3039$ ($CH_{aromatic}$), 2962, 2905, 2868 (CH_3), 2838 ($O-CH_3$), 1611 (C=C), 1549, 1514 (C=N), 1248 cm^{-1} ($O-CH_3$); ESI-MS (CH_3CN): *m/z* (%): calcd 711.9; found: 711.5 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{48}H_{46}N_4O_2$ (710.9): C 81.09, H 6.52, N 7.88; found: C 81.40, H 6.58, N 7.64.

1,2-dipyrimidyl-3,6-bis-(4-*tert*-butylphenyl)-4,5-bis-(4-bromo-phenyl)benzene (11): Benzophenone (5 g), dipyrimidine acetylene (223 mg; 1.22 mmol) and **6** (800 mg; 1.22 mmol) were mixed in a round-bottomed flask attached to an air condenser. The reaction mixture was heated over a microburner to reflux for 1 h. Carbon monoxide was evolved and the color changed from purple to red/brown. After cooling and chromatography (SiO_2, diethyl ether), recrystallization from EtOAc/petroleum ether produced colorless crystals of **11**. Yield: 0.840 g, 85 %; m.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta=8.77$ (s, 2H; H12), 8.21 (s, 4H; H9), 7.06 (d, $^3J(H,H)=8.0$ Hz, 4H; H7 or H10), 6.98 (d, $^3J(H,H)=8.0$ Hz, 4H; H8 or H11), 6.69 (d, $^3J(H,H)=8.0$ Hz, 4H; H8 or H11), 6.68 (d, $^3J(H,H)=8.0$ Hz, 4H; H7 or H10), 1.15 ppm (s, 18H; H16); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta=157.4$ (4C; C9), 155.6 (2C; C12), 149.3 (2C; C14), 141.2, 140.7, 137.7, 134.4, 133.3, 133.2 (2C; $C_{quat/aryl}$), 132.0, 130.1, 129.8, 124.1 (4C; C_{aryl}), 119.9 (2C; C13), 33.9 (2C; C15), 30.6 ppm (6C; C16); IR (KBr disk): $\tilde{\nu}=3034$ ($CH_{aromatic}$), 2959, 2902, 2867 (CH_3), 1549, 1490 (C=N), 1400 cm^{-1} (CH_3); ESI-MS (CH_3CN): *m/z* (%): calcd: 809.6; found: 809.2 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{46}H_{40}N_4Br_2$ (808.6): C 68.32, H 4.99, N 6.93; found: C 67.77, H 5.03, N 6.74.

1,2-dipyrimidyl-3,6-bis-(4-*tert*-butylphenyl)-4,5-bis-(4-triisopropylsilylethynylphenyl)benzene (12): Dipyrimidine acetylene (130 mg; 0.714 mmol) and **7** (612 mg; 0.714 mmol) were sealed under vacuum in a glass tube and heated at 200 °C for 48 h. The reaction mixture was subsequently cooled to RT, the tube broken carefully, the residue extracted into dichloromethane (50 mL), and filtered. After removal of the solvent the recovered material was purified by flash chromatography (SiO_2, diethyl ether). Recrystallization from acetone/water produced colorless crystals of **12**. Yield: 0.470 g, 65 %; m.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta=8.76$ (s, 2H; H12), 8.22 (s, 4H; H9), 7.04 (d, $^3J(H,H)=8.0$ Hz, 4H; H7 or H10), 6.97 (d, $^3J(H,H)=8.0$ Hz, 4H; H8 or H11), 6.77 (d, $^3J(H,H)=8.0$ Hz, 4H; H7 or H10), 6.70 (d, $^3J(H,H)=8.0$ Hz, 4H; H8 or H11), 1.15 (s, 18H; H16), 1.08 ppm (s, 42H; $-CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): $\delta=157.4$ (4C; C9), 155.6 (2C; C12), 149.2 (2C; C14), 141.4, 141.3, 139.0, 134.6, 133.3, 133.1 (2C; $C_{quat/aryl}$), 130.3 (8C), 130.2 (4C), 124.1 (4C) (C_{aryl}), 120.5 (2C; C13), 106.6, 89.9 (1C; $-C\equiv C-$), 33.8 (2C; C15), 30.6 (6C; C16), 18.1 (12C; $-CH_3$), 10.8 ppm (6C; $-CH$); IR (KBr disk): $\tilde{\nu}=3034$ ($CH_{aromatic}$), 2945, 2893, 2865 (CH_3), 2153 (C≡C), 1549, 1510 (C=N); ESI-MS (CH_3CN) *m/z* (%): calcd: 1012.6; found: 1012.6 cm^{-1} (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{68}H_{82}N_4Si_2$ (1011.5): C 80.74, H 8.17, N 5.54; found: C 80.46, H 8.23, N 5.51.

1,2-dipyrimidyl-3,6-bis-(4-*tert*-butylphenyl)-4,5-bis-(4-(3-methyl-3-hydroxy-butynyl)phenyl)benzene (14): Bis(triphenylphosphine)palladium(II) dichloride (42 mg) and CuI (12 mg) were added successively to **11** (200 mg; 0.247 mmol) in freshly distilled DMF (10 mL) and triethylamine (5 mL) under argon. 2-Methyl-3-butyn-2-ol (0.10 mL; 1.03 mmol) was injected and the mixture was stirred for 24 h at 90 °C under argon. The reaction mixture was washed with water (20 mL) and extracted with chloroform (3×40 mL). The organic fractions were combined, dried over

$MgSO_4$, and reduced in vacuo. Column chromatography (SiO_2, diethyl ether) was used to separate the products. Unreacted starting material **11** (R_f=0.5), monosubstituted **13** (R_f=0.4), and disubstituted **14** (R_f=0.3) were collected. Recrystallization from acetone/water yielded colorless crystals. Yield: 0.075 g, 38% of **13** and 0.064 g, 30% of **14**.

Compound **13**: m.p. 253–255°C; ^{1}H NMR (400 MHz, $CDCl_3$, 21°C): δ= 8.77, 8.76 (s, 1H; H_{aryl}), 8.21, 8.20 (s, 2H; H_{aryl}), 7.05 (d, ^3J(H,H)=8.5 Hz, 2H; H_{aryl}), 6.99 (m, 6H; H_{aryl}), 6.78 (d, ^3J(H,H)=8.5 Hz, 2H; H_{aryl}), 6.70 (m, 6H; H_{aryl}), 1.74 (s, 1H; −OH), 1.57 (s, 6H; $-CH_3$), 1.15 ppm (s, 18H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21°C): δ=157.4, 157.3 (2C; C_{aryl}), 155.6, 155.5 (1C; C_{aryl}), 149.34 (1C), 149.27 (1C), 141.24 (1C), 141.20 (1C), 140.8 (1C), 138.9 (1C), 137.8 (1C), 134.50 (2C), 134.47 (1C), 133.4 (1C), 133.3 (1C) ($C_{quat/aryl}$), 132.0 (2C), 130.3 (2C), 130.1 (4C), 130.0 (2C), 129.7 (2C) (C_{aryl}), 129.60, 129.57 (1C; $C_{quat/aryl}$), 124.11, 124.08 (2C; C_{aryl}), 119.88, 119.79 (1C; $C_{quat/aryl}$), 93.4, 81.5 (1C; −C≡C−), 65.1 (1C), 33.8 (2C) ($C_{quat/alkyl}$), 31.0 (2C; $-CH_3$), 30.6 ppm (6C; $-CH_3$); ESI-MS (CH_3CN) *m/z* (%): calcd: 812.8; found: 812.6 (100) $[M+H]^+$; ESI-MS (CH_3CN): *m/z*: calcd for $C_{51}H_{48}BrN_4O_2$: 811.3011 $[M+H]^+$; found: 811.3002.

Compound **14**: m.p. 264–266°C; ^{1}H NMR (400 MHz, $CDCl_3$, 21°C): δ= 8.76 (s, 2H; H_{aryl}), 8.20 (s, 4H; H_{aryl}), 6.98 (m, 8H; H_{aryl}), 6.77 (d, ^3J(H,H)=8.0 Hz, 4H; H_{aryl}), 6.71 (d, ^3J(H,H)=8.5 Hz, 4H; H_{aryl}), 1.97 (s, 2H; −OH), 1.58 (s, 12H; $-CH_3$), 1.16 ppm (s, 18H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21°C): δ=157.4 (4C; C_{aryl}), 155.5 (2C; C_{aryl}), 149.2, 141.3, 141.1, 140.0, 134.5, 133.4, 133.3 (2C; $C_{quat/aryl}$), 130.4, 130.2, 130.0, 124.1 (4C; C_{aryl}), 119.7 (2C; $C_{quat/aryl}$), 93.2, 81.6 (2C; −C≡C−), 65.4, 33.8 (2C; $C_{quat/alkyl}$), 30.0 (4C; $-CH_3$), 30.6 ppm (6C; $-CH_3$); ESI-MS (CH_3CN) *m/z* (%): calcd: 816.1; found: 815.4 (100) $[M+H]^+$; ESI-MS (CH_3CN): *m/z*: calcd for $C_{56}H_{55}N_4O_2$: 815.4323; found: 815.4334 $[M+H]^+$.

1,2-di(2-thienyl)-3,4,5,6-tetra-(4-*tert*-butylphenyl)benzene (15): Di(2-thienyl)acetylene (69.5 mg, 0.37 mmol), tetra(4-*tert*-butyl)cyclopentadienone (200 mg, 0.33 mmol), and benzophenone (1 g) were combined and heated to reflux for 1 h. Purification by column chromatography (SiO_2, diethyl ether:hexane 1:9) and recrystallization from hexane yielded the product as a white powder. Yield: 190 mg, 75%; m.p. 270–271°C; ^{1}H NMR (400 MHz, $CDCl_3$, 21°C): δ=7.02 (dd, J(H,H)=1.0–5.0 Hz, 2H; $H_{thienyl}$), 6.92 (d, ^3J(H,H)=8.5 Hz, 4H; H11), 6.83 (d, ^3J(H,H)=8.0 Hz, 4H; H10), 6.81 (d, ^3J(H,H)=8.0 Hz, 4H; H8), 6.66 (d, ^3J(H,H)=8.5 Hz, 4H; H7), 6.63 (dd, J(H,H)=3.5–5.0 Hz, 2H; $H_{thienyl}$), 6.51 (dd, J(H,H)=1.0–3.5 Hz, 2H; $H_{thienyl}$), 1.16 (s, 18H; H16), 1.11 ppm (s, 18H; H_{alkyl}); ^{13}C NMR (100 MHz, $CDCl_3$, 21°C): δ=147.6 (2C; C14), 147.2 (2C; C13), 141.6 (2C; C3), 141.4, 141.4 (2C; $C_{quat/aryl}$), 137.1 (2C; C5), 137.0 (2C; C4), 133.4 (2C; $C_{quat/thienyl}$), 130.4 (4C; C7), 130.0 (4C; C8), 128.6, 125.1, 125.0 (2C; $C_{thienyl}$), 122.9 (4C; C11), 122.7 (4C; C10), 33.7 (2C; $C_{quat/alkyl}$), 33.6 (2C; C15), 30.8 (6C; C16), 30.7 ppm (6C; $-CH_3$); IR (KBr disk): $\tilde{\nu}$= 3031 ($CH_{aromatic}$), 2958, 2901, 2866 (CH_3), 1510, 1461, 1390, 1362, 1269, 1019, 827, 699 cm^{-1}; ESI-MS ($CHCl_3$): *m/z* (%): calcd: 793.4; found: 793.4 (100) $[M+Na]^+$; elemental analysis calcd (%) for $C_{54}H_{58}S_2$ (771.1): C 84.10, H 7.58; found: C 84.10, H 7.62.

1′,4′-bis-(4-*tert*-butylphenyl)-2′,3′-dipyrimidyl-7′-methoxy-6-oxospiro[cyclohexa-1,4-diene-3,9′-fluorene] (16): A solution of iron(III) chloride (2.252 g; 13.883 mmol) in nitromethane (6 mL) was added dropwise to a stirred solution of **10** (100 mg; 0.141 mmol) in freshly distilled dichloromethane (20 mL) under argon. An argon stream was bubbled through the mixture throughout the course of the reaction. After stirring for another 30 min, the reaction was quenched with methanol (6 mL). The resulting mixture was poured into water and extracted with dichloromethane. The organic washings were combined, dried over $MgSO_4$, and reduced. The extract was purified by column chromatography (SiO_2, diethyl ether) and recrystallized from dichloromethane to afford colorless crystals of **16**. Yield: 84 mg, 86%; m.p. >300°C; ^{1}H NMR (400 MHz, $CDCl_3$, 21°C): δ=8.78, 8.73 (s, 1H; H1, H13), 8.31, 8.29 (s, 2H; H2, H12), 7.40 (d, ^3J(H,H)=8.0 Hz, 2H; H_{aryl}), 7.17 (d, ^3J(H,H)=8.0 Hz, 2H; H_{aryl}), 7.09 (d, ^3J(H,H)=8.0 Hz, 2H; H_{aryl}), 6.91 (d, ^3J(H,H)=8.0 Hz, 2H; H_{aryl}), 6.62 (dd, J(H,H)=2.5–8.5 Hz, 1H; H8), 6.57 (d, ^4J(H,H)=2.5 Hz, 1H; H7), 6.51 (d, ^3J(H,H)=9.5 Hz, 2H; H_{aryl}), 6.32 (d, ^3J(H,H)=8.5 Hz, 1H; H9), 6.08 (d, ^3J(H,H)=10.0 Hz, 2H; H_{aryl}), 3.72 (s, 3H; $-CH_3$), 1.34 (s, 9H; $-CH_3$), 1.23 ppm (s, 9H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21°C): δ=184.9 (1C; C=O), 159.9 (1C; $C_{quat/aryl}$), 157.3, 157.2 (2C; C2, C12), 155.9, 155.8 (1C; C1, C13), 153.3, 151.1, 150.9 (1C; $C_{quat/aryl}$), 148.2 (2C; C_{aryl}), 144.6, 141.8, 140.5, 140.3, 135.8, 135.1, 133.7, 132.5, 132.2, 131.8 ($C_{quat/aryl}$), 129.4 (2C), 128.9 (2C), 128.8 (2C), 125.5 (2C), 124.7 (1C), 123.8 (2C), 114.7 (1C), 108.8 (1C) (C_{aryl}), 55.1 (1C; $-CH_3$), 34.2, 34.0 (1C; $C_{quat/alkyl}$), 30.8, 30.6 ppm (3C; $-CH_3$); IR (KBr disk): $\tilde{\nu}$=3040 ($CH_{aromatic}$), 2960, 2906, 2868 (CH_3), 1663 (C=O), 1604 (C=C), 1549 (C=N), 1399 (CH_3), 1244 cm^{-1} (O−CH_3); ESI-MS (toluene): *m/z* (%): calcd: 695.9; found: 695.3 (100) $[M+H]^+$; ESI-MS (toluene): *m/z*: calcd for $C_{47}H_{43}N_4O_2$: 695.3386; found: 695.3411 $[M+H]^+$.

10-acetoxy-1,4-bis-(4-*tert*-butylphenyl)-2,3-dipyrimidyl-7-methoxytriphenylene (17): Five drops of H_2SO_4 (20%) in acetic anhydride was added to a hot solution of **16** (50 mg; 0.072 mmol) in acetic anhydride (4 mL). The reaction was heated on a water bath for 1 h and then allowed to stand overnight. After this time, the reaction mixture was poured onto ice and then warmed to 80°C. The yellow solid was filtered off, washed with water, and purified by column chromatography (SiO_2, toluene:MeOH 9:1), to produce **17** as a pale yellow crystalline product. Yield: 38 mg, 72%; m.p. 282–284°C; ^{1}H NMR (400 MHz, $CDCl_3$, 21°C): δ= 8.85, 8.84 (s, 1H; H1 and H14), 8.09 (s, 5H; H2, H13 and H7), 7.74 (d, ^4J(H,H)=2.05 Hz, 1H; H8), 7.64 (d, ^3J(H,H)=8.88 Hz, 1H; H5), 7.54 (d, ^3J(H,H)=8.87 Hz, 1H; H10), 7.21 (d, ^3J(H,H)=8.19 Hz, 4H; H4 and H12), 6.94 (app. d, ^3J(H,H)=8.19 Hz, 2H; H3), 6.93 (app. d, ^3J(H,H)= 8.19 Hz, 2H; H11), 6.81 (dd, J(H,H)=2.7–9.6 Hz, 1H; H6), 6.68 (dd, J(H,H)=2.7–9.6 Hz, 1H; H9), 3.95 (s, 3H; $-OCH_3$), 2.37 (s, 3H; $-COOCH_3$), 1.27 ppm (s, 18H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 21°C): δ=169.4 (1C; C=O), 158.5 (1C; $C_{quat/aryl}$), 158.15, 158.10 (2C; C2 or C13), 155.80, 155.77 (1C; C1 or C14), 150.7, 150.6, 149.4, 138.3, 138.2, 138.0, 137.8 (1C; $C_{quat/aryl}$), 134.3 (br, 2C; $C_{quat/aryl}$), 133.1, 133.0, 132.6, 132.5, 131.9 (1C; $C_{quat/aryl}$), 131.46, 131.43 (2C; C3 or C11), 131.37 (1C; C10), 131.2 (1C; C5), 131.0, 128.2 (1C; $C_{quat/aryl}$), 125.84, 125.81 (2C; C4 or C12), 124.0 (1C; $C_{quat/aryl}$), 119.6 (1C; C6), 115.6 (1C; C7), 114.5 (1C; C9), 106.0 (1C; C8), 55.4 (1C; $-OCH_3$), 34.5 (2C; $C_{quat/alkyl}$), 31.2 (6C; $-CH_3$), 21.2 ppm (1C; $-COOCH_3$); IR (KBr disk): $\tilde{\nu}$=3030 ($CH_{aromatic}$), 2958, 2903, 2868 (CH_3), 1770 (−CO−O−), 1614 (C=C), 1550, 1509 (C=N), 1422 (CH_3), 1391 (−C−CH_3), 1367 (−O−CO−CH_3), 1238, 1187 cm^{-1} (O−CH_3); ESI-MS ($CHCl_3$): *m/z* (%): calcd: 737.9; found: 737.3 (100) $[M+H]^+$; ESI-MS ($CHCl_3$); calcd for $C_{49}H_{45}N_4O_3$: $[M+H]^+$ *m/z*: 737.3492; found: 737.3495.

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