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# Twisted Polycyclic Arenes by Intramolecular Scholl Reactions of C3-Symmetric Precursors

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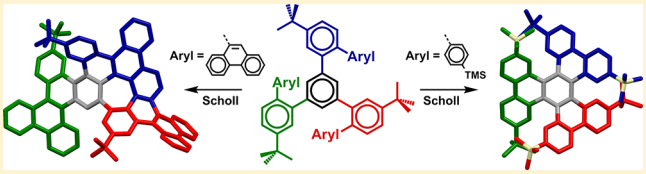
Supporting Information

**ABSTRACT:** With the aim of opening an efficient access to large and sterically crowded polycyclic arenes as well as improving insight into the geometrical preferences of the Scholl reaction, a versatile synthesis strategy has been developed to form a family of flexible yet strongly crowded substrates for multiple dehydrocyclizations. Their intramolecular Scholl reactions lead with high selectivity either to considerably twisted species where the initial C3 symmetry is maintained, or to strongly rearranged products where the formation of multiple [6]helicene fragments is avoided by the formation of unusual hexa[7]circulene moieties under loss of the C3 symmetry.




## INTRODUCTION

The field of extended polycyclic aromatic hydrocarbons (PAHs)[1] is currently benefitting from the raising interest in graphenes[2] and carbon nanoribbons,[3] and their predicted utility in organic electronics.[4] Top-down synthesis techniques quickly and efficiently lead to giant graphene molecules,[5] whereas longer and more laborious bottom-up synthetic strategies, pioneered by Müllen's group 15 years ago,[6] have the advantage of reproducibly forming monodisperse and physically homogeneous nanographenes.[7] Not all PAHs can be considered as nanographenes since not all of them may conceptually be cut out of a flat graphene sheet because of their twisted geometries. The distortion of such twisted arenes may result from cycle tensions by inclusion of nonhexagonal rings,[8] sometimes leading to fragments of fullerenes and nanotubes,[9] or from helicenic parts,[10] which might only be obtained in graphite by the introduction of screw disclinations.

Intramolecular Scholl reactions[11] (i.e., dehydrocyclization by acidic oxidants like $FeCl_3$ or $DDQ/MeSO_3H$) have been established as a powerful tool to form well-designed flat nanographenes,[12] but this well-known yet poorly understood reaction may show surprising performances and selectivities (Scheme 1a).[13] We have recently reported that the Scholl reaction is sometimes astonishingly insensitive to steric hindrance and can favor the formation of congested [5]-helicenes such as **5** instead of their flat isomers such as **4** (Scheme 1b).[14] We and Hilt's group[15] have also observed that even methoxy groups on protected compounds such as **6** may be expelled to maintain this regioselectivity and give only twisted [5]helicenes such as **7** (Scheme 1c).

## RESULTS AND DISCUSSION

An easy and quick synthesis of highly distorted propeller-shaped hexa-*tert*-butyl-hexabenzotriphenylene (*t*-$Bu_6$-HBTP) **11**, from the flexible precursor **10** obtained by trisubstitution of tribromobenzene **8** with three biphenylic blades (Scheme 2a), has already been described as a proof of the efficiency of the Scholl reaction to form multiple helicenic compounds.[14] We have now developed a systematic and versatile strategy to synthesize a family of such flexible C3-symmetrical substrates for subsequent Scholl treatment. This new method involves more steps than in the case of **10**, but it gives access to several compounds **17a−d** from a single common trifunctionalized precursor **15** by only changing the nature of the arylboronic acid **16** added in the last step (Scheme 2b).

The formation of the common precursor **15** relies on a trisubstitution of *sym*-tribromobenzene **8**, by a very efficient (95% yield) Suzuki cross-coupling reaction in classical conditions. This time **8** is not reacted with a complete blade (boronic ester **9**) but with the shorter methoxy substituted arylboronic acid **12**, which was synthesized in two steps following existing procedures.[16] The three methoxy groups of the resulting compound **13** are then deprotected by action of $BBr_3$, leading quantitatively to the triphenolic intermediate **14**, whose phenol functions are then transformed into triflate groups in excellent yield to give the common precursor **15**. Because of the important steric hindrance of the reacting sites on this substrate, optimized catalytic conditions had to be established for the last trisubstitution step by Suzuki cross-coupling reaction. A very satisfying catalytic system, developed by Buchwald's group,[17] is based on $Pd(OAc)_2$, SPhos as ligand and $K_3PO_4$ as base in a mixture of THF and water. Four commercially available arylboronic acids **16a−d** were thus used to give trisubstituted flexible Scholl substrates **17a−d** in excellent yields (between 92 and 98%).

The triple Suzuki reaction between 9-phenanthracenylboronic acid **16a** and tris-triflate **15** affords the flexible but

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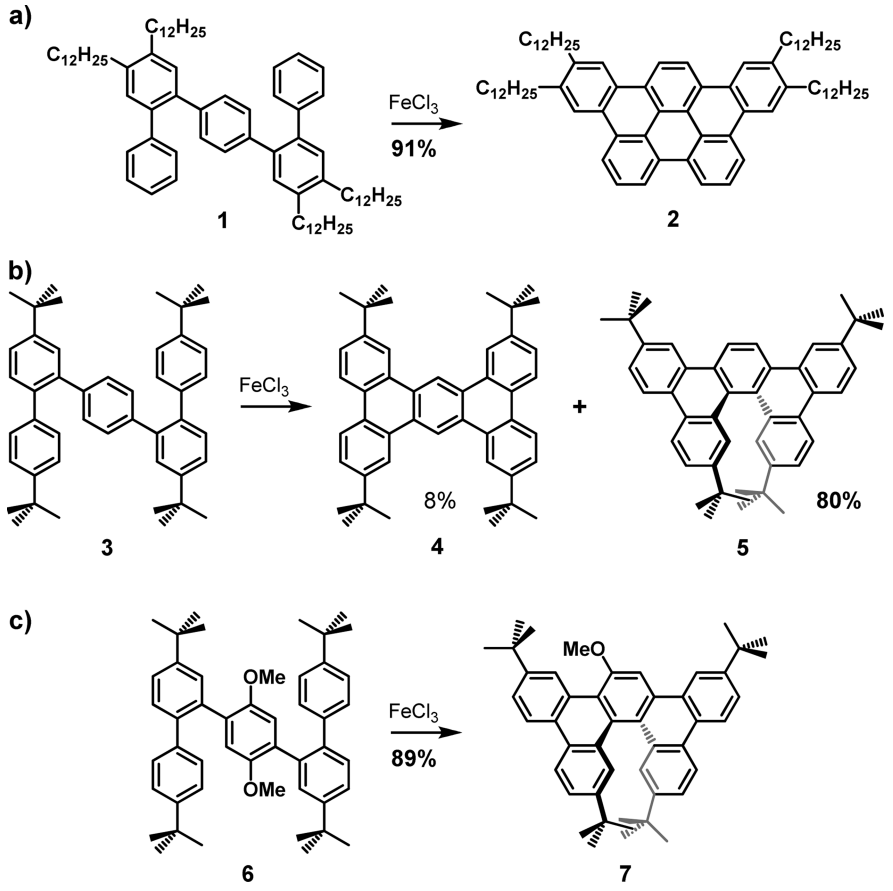
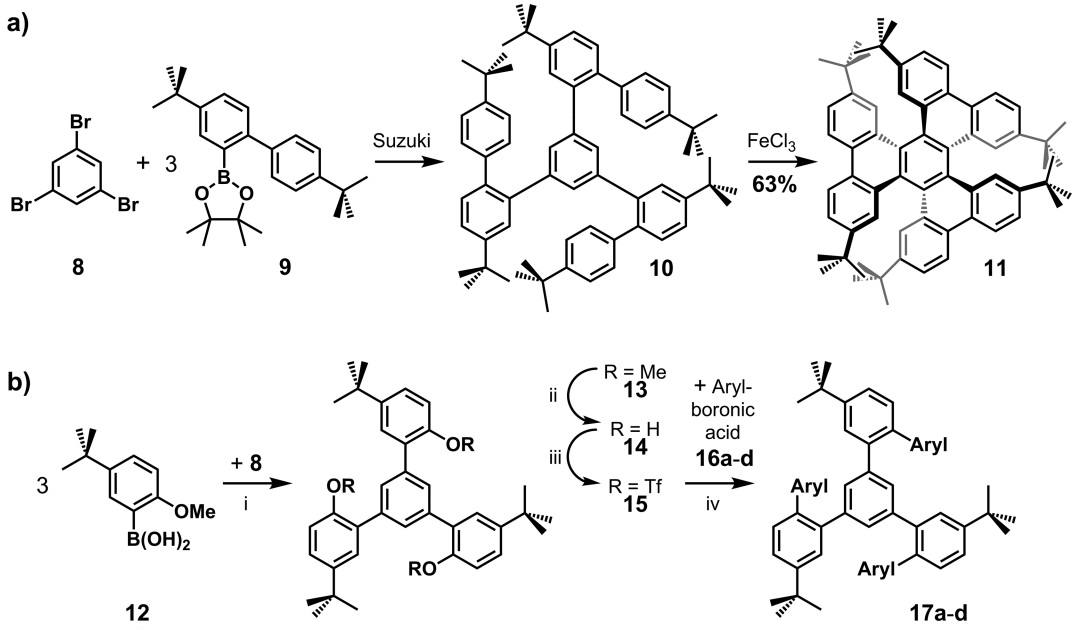
**Scheme 1. Examples of the Regioselectivity of Scholl Reaction on *o,p,o*-Pentaphenylene Substrates**




**Scheme 2. Formation of Trisubstituted Substrates for Intramolecular Scholl Reactions[a]**




[a](i) $Na_2CO_3$, $Pd(PPh_3)_4$ in PhMe/$H_2O$/EtOH, 90 °C, 48 h, 95%. (ii) $BBr_3$ in $CH_2Cl_2$, rt, 16 h, 99%. (iii) $Tf_2O$, pyridine in $CH_2Cl_2$, rt, 16 h, 96%. (iv) $Pd(OAc)_2$, SPhos, $K_3PO_4$ in THF/$H_2O$, 67 °C, 48 h, respectively 95, 92, 96, and 98%.

sterically very congested compound **17a** (Scheme 3). This molecule, if represented in 2D, shows several overlaps of carbons and has two stable conformers at room temperature, as indicated by a variable temperature $^1$H NMR study with coalescence reached around 125 °C in DMSO-$d_6$.[18] The Scholl reaction on this substrate was predicted to form 3 new C−C bonds, between the central benzene ring and position 10 of each phenanthrene part, and give a symmetrical triple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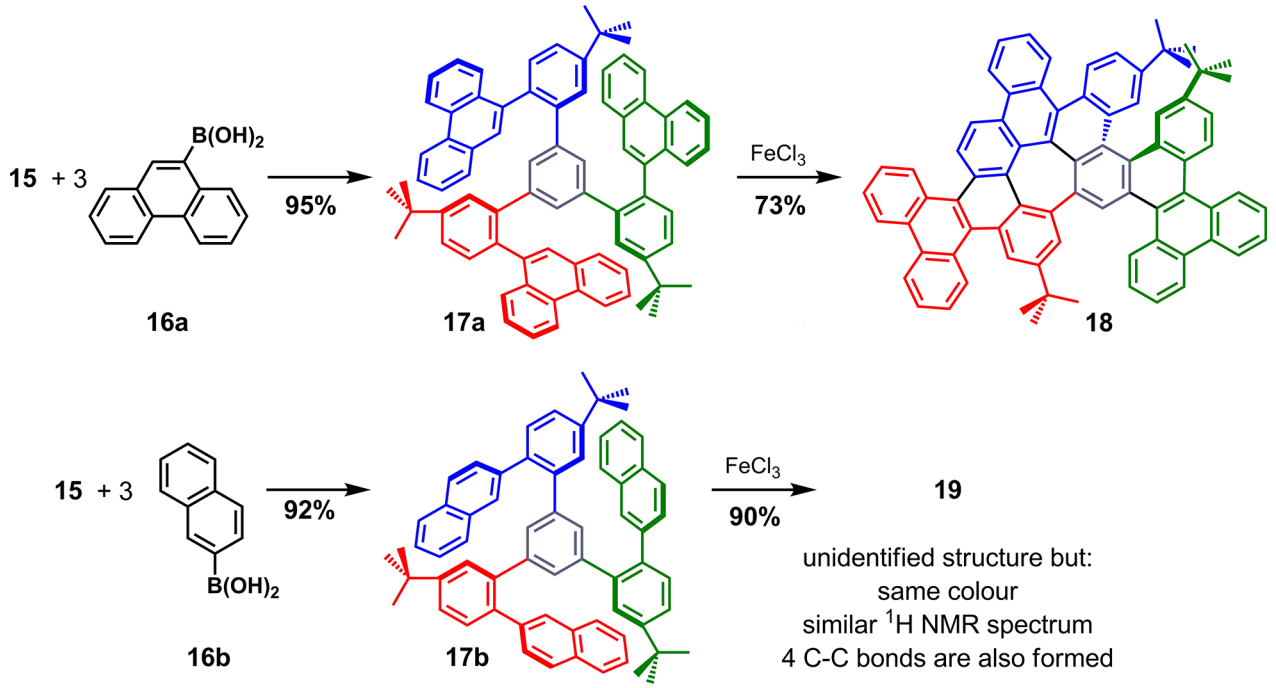
**Scheme 3. Scholl Reactions on Precursors 17a and 17b Leading to Rearranged Compounds 18 and 19**




[6]helicene. Nevertheless, we were surprised to reproducibly obtain, after purification, an asymmetrical major product **18** whose formula, unambiguously confirmed by mass spectrometry, indicates that 8 hydrogen atoms had been removed, implying the creation of four instead of three C−C bonds. Fortunately, we were able to crystallize this compound by slow diffusion of diisopropyl ether in $CCl_4$, and the analysis by X-ray diffraction on monocrystal revealed the very unexpected structure of oligoarene **18** (Figure 1). The latter is highly

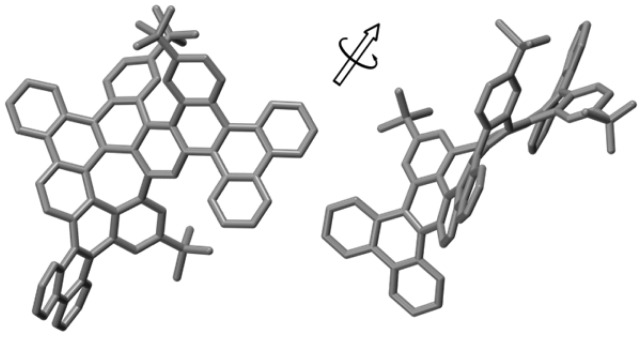


**Figure 1.** Two different views of the crystal structure of the strongly distorted [5]helicene- and hexa[7]circulene-based compound **18**.

distorted because of two different structural ingredients: (a) one [5]helicene, whereas [6]helicenes were expected; and (b) one 7-membered ring that is part of a hexa[7]circulene fragment. This final structure can be explained by two successive rearrangements during the Scholl process. One blade (blue on Scheme 3) cyclized correctly on the central benzene ring, then a second one (green on Scheme 3) migrated to an adjacent yet hindered carbon and also cyclized on the central benzene ring to form a [5]helicene, then the phenanthrene part of the third blade (red on Scheme 3) migrated to an adjacent carbon on the benzene part of the blade to allow its previous position to cyclize onto another phenanthrene (blue) to form the 7-membered ring, and a fourth cyclization finally occurs between two phenanthrene parts (red and blue). This reproducible and very efficient, yet absolutely unpredicted, outcome tells us that a highly twisted [5]helicenic fragment (between blue and green blades) bearing 2 *tert*-butyl groups on hindered positions is apparently very favored by the Scholl reaction since not only does it benefit from regioselectivity (Scheme 1b) but also rearrangements might have occurred to prevent its formation. The 7-membered ring formation by Scholl reaction is also noteworthy since known examples of such heptagonal structures are exceedingly rare, either with only $sp^2$-hybridized carbons[19] or even including one tetrahedral apex.[20]

When 2-naphthylboronic acid **16b** is used to form another flexible substrate **17b**, two adjacent carbons are free on the 2-naphthyl group. Therefore each blade can theoretically cyclize on the central benzene ring in two different ways. Nevertheless a unique compound **19** is isolated (90% yield) after Scholl treatment. This product has the same greenish color as compound **18** and a very similar $^1$H NMR spectrum with several identical peaks, and the mass spectrum also indicates that 4 C−C bonds were formed. For these reasons, we tend to think that the structure of **19** is comparable to the one of **18**, but unfortunately, we were not able to crystallize **19** and thus cannot give any clear evidence of its structure. Intramolecular rearrangements when trying to form [7]helicenes by Scholl reaction have already been reported,[21] and our results confirm that this reaction may not be suitable to make helicenes with more than five benzene rings in the helix.

Given the surprising rearrangements observed during the Scholl reaction of **17a** and probably **17b**, we wondered whether such reactions also occurred, but with no visible consequences, when cyclizing the fully symmetrical propeller-shaped *t*-$Bu_6$-HBTP **11**. In order to dissymmetrize its flexible precursor **10** without changing the global shape of the molecule, we coupled 4-(trimethylsilyl)phenylboronic acid **16c** on tris-triflate compound **15** to obtain the flexible substrate **17c**, which differs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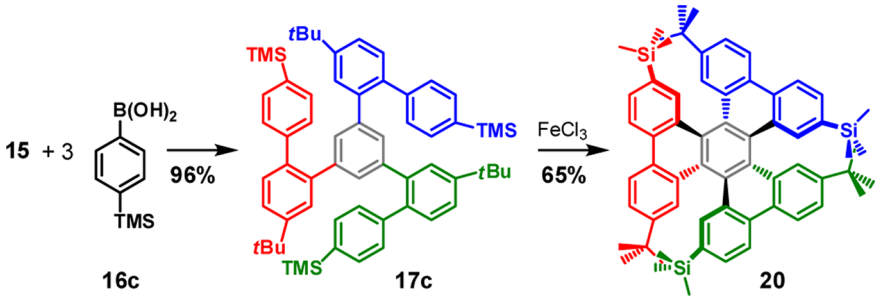
**Scheme 4. Scholl Reaction on Compound 17c Leading to TMS-Substituted Hexabenzotriphenylene 20**




from **10** only by the replacement of three carbons by three silicon atoms. The Scholl reaction of this TMS-substituted compound **17c** leads as expected, and with a comparable yield, to another propeller-shaped HBTP **20**, still bearing six tetrahedral substituents (Scheme 4).

This new oligoarene has been crystallized as a racemic mixture and analyzed by X-ray diffraction. The propeller shape of the molecule has thus been confirmed (Figure 2), but the

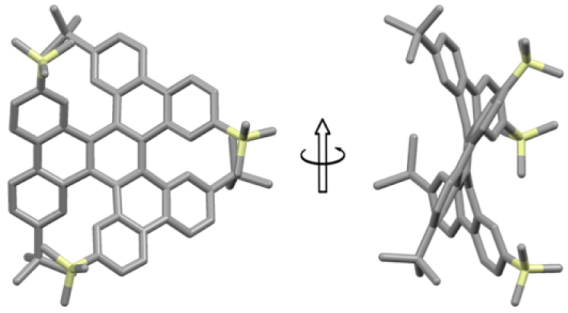


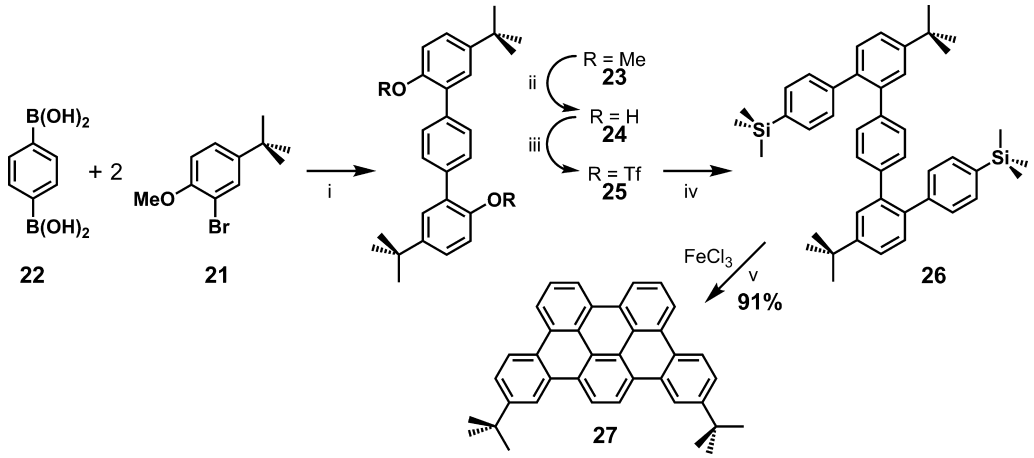
**Figure 2.** Two different views of the crystal structure of triply helicenic TMS-bearing hexabenzotriphenylene **20**.

TMS and *t*-Bu groups are indistinguishable in the crystal structure because of orientational disorder of the molecules in the unit cell (quaternary C from *t*-Bu and quaternary Si from TMS show 50/50 occupancy).[18] Nevertheless, the extreme simplicity of the $^1$H NMR spectrum of **20** (only 6 aromatic and 2 aliphatic signals) can only stand for a highly symmetrical molecule, i.e., a C3 symmetrical product, showing that no rearrangement occurred during the Scholl reaction.

The compatibility with TMS groups of this Scholl reaction is also noteworthy; we did not find a single other example in the literature. To further investigate this compatibility, and to check if TMS-substituted substrates obey the same reactivity rules as their *tert*-butylated counterparts, we synthesized pentaphenylene **26** (Scheme 5) following a similar strategy as for trisubstituted substrates **17**. But contrary to pentaphenylene **3**, which mainly leads to [5]helicene **5** by Scholl reaction (Scheme 1b), the silylated version **26**, under the same conditions, very quickly loses its two TMS groups and fully cyclizes to give the flat oligoarene **27**, whose structure was perfectly determined by NMR, mass spectrometry and even X-ray crystallography (Figure 3). So the compatibility of TMS groups with the Scholl reaction cannot be generalized since they may also be expelled to favor some bond formations.

Scholl cyclizations of 1,3,5-tris(2-biphenyl)ylbenzene species have already been studied by Müllen's group[22] but were only successful in the case of unsubstituted flexible precursors, or with iodides on nonhindering positions. When these deactivating iodides are located on hindering positions, the reaction remains incomplete. The triple Suzuki cross-coupling reaction of tris-triflate **15** with simple phenylboronic acid **16d** gives the flexible precursor **17d**, with only three *tert*-butyl substituents located on hindered positions. Submitted to Scholl reacting conditions, this molecule fully cyclizes, by forming six C−C bonds, in a good yield (72%) to give 1,7,13-tri-*tert*-butylhexabenzocoronene **28** (Scheme 6). This hexabenzocor-

**Scheme 5. Synthesis and Reactivity in Scholl Conditions of TMS-Bearing Pentaphenylene 26**[a]




[a](i) $Na_2CO_3$, $Pd(PPh_3)_4$ in $PhMe/H_2O/EtOH$, 90 °C, 48 h, 90%. (ii) $BBr_3$ in $CH_2Cl_2$, rt, 16 h, 99%. (iii) $Tf_2O$, pyridine in $CH_2Cl_2$, rt, 16 h, 95%. (iv) $Pd(OAc)_2$, SPhos, $K_3PO_4$ in $THF/H_2O$, 67 °C, 48 h, 90%. (v) $FeCl_3$ in $MeNO_2$/ $CH_2Cl_2$, rt, 1.5 h, 91%.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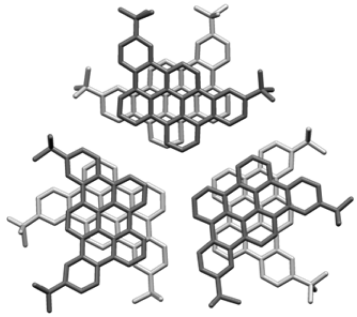


**Figure 3.** Crystal structure of flat oligoarene **27**.

onene, triply substituted by very bulky groups in bay regions, has been unambiguously characterized by mass spectrometry, $^{1}H$ and $^{13}C$ NMR, but unfortunately, we were not able to crystallize it to determine its structure. This undoubtedly distorted oligoarene[23] shows unusually high solubilities in many organic solvents compared to other flat hexabenzocoronenes.

When attempting to crystallize hexabenzocoronene **28**, we could obtain a few monocrystals from a crystallization tube containing an impure fraction of **28** (about 10% impurities). Disappointingly, X-ray analysis revealed that these crystals were only composed of unexpected rearranged products **30** and **31**, cocrystallizing together (in a 3:2 ratio). In this case, again, one blade migrates onto an adjacent carbon of the central benzene ring to form the usual [5]helicene, but in addition the *t*-Bu group, on the fully cyclized third blade, is removed and replaced by a chlorine (**31**) or two opposite hydroxyl groups (**30**). Such a loss of a *t*-Bu group on the symmetrical main product **28**, giving compound **29**, and the presence of **30** and **31** has also been observed by mass spectrometry (Scheme 7).

## CONCLUSION

We developed a versatile synthesis technique for the formation of a family of flexible yet strongly crowded $C_3$-symmetrical polyaromatic chains as substrates for graphitization by intramolecular Scholl reaction and found that the formation of [6]helicenes appears precluded with this approach because of surprising rearrangements leading to hexa[7]circulene species. Nevertheless, under the same conditions, strongly congested [5]helicenes, with bulky groups on hindered positions, seem to be highly favored even when a labile TMS group replaces one of the two *t*-Bu substituents. Finally, a distorted and soluble bay-substituted hexabenzocoronene can efficiently be synthesized by Scholl reaction on a tris(biphenyl)ylbenzene precursor bearing three activating *t*-Bu groups on congesting positions.

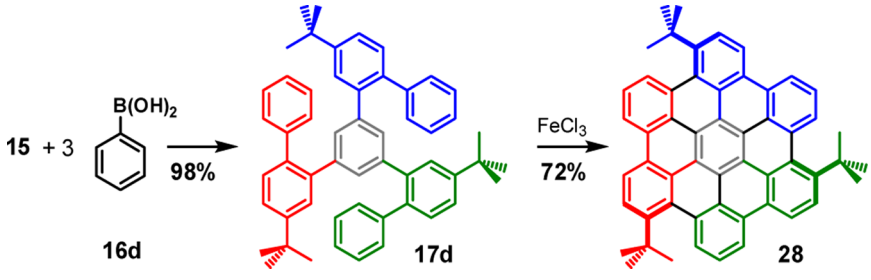
## EXPERIMENTAL SECTION

**1,4-Bis(4,4′-di-*tert*-butylbiphenyl-2-yl)-2,5-dimethoxybenzene (6).** Commercially available 1,4-dibromo-2,5-dimethoxybenzene (296 mg, 1.0 mmol), 2-(4,4′-di-*tert*-butylbiphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **9**[14] (823 mg, 2.1 mmol) and $Na_2CO_3$ (1.06 g, 10 mmol) were dissolved in toluene (24 mL), water (8 mL) and ethanol (4 mL). The solution was degassed, $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) was added under an Ar stream, and the mixture was degassed again. The solution was heated at 90 °C overnight. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (20%) as the eluent to give the title compound **6** (Scheme 8; white solid, 547 mg, 82%): mp 172−173 °C; $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.41 (dd, 2H, $J$ = 2.2, 8.2 Hz), 7.34 (d, 2H, $J$ = 7.2 Hz), 7.33 (d, 2H, $J$ = 2.4 Hz), 7.30 (d, 4H, $J$ = 8.4 Hz), 7.07 (d, 4H, $J$ = 8.4 Hz), 6.55 (s, 2H), 3.07 (s, 6H), 1.34 (s, 18H), 1.27 (s, 18H); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.2, 150.0, 149.3, 139.0, 138.6, 136.8, 130.6, 129.2, 128.6, 127.9, 124.7, 124.3, 115.2, 55.5, 34.5, 34.3, 31.1; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{48}H_{58}O_2$ 666.44368, found 666.44045.

**2,7,10,15-Tetra-*tert*-butyl-17-methoxydibenzo[f,j]picene (7).** Compound **6** (100 mg, 0.15 mmol) was dissolved in 30 mL of unstabilized dichloromethane and degassed with an Ar stream for 15 min. A solution of $FeCl_3$ (145 mg, 0.89 mmol) in 5 mL of nitromethane was added dropwise while continuously degassing with an Ar stream. After 30 min the reaction was stopped by adding 100 mL of methanol. The organic phase was then washed twice with water and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (8%) as the eluent to give the title compound **7** (Scheme 8; yellow solid, 84 mg, 89%): mp 314−315 °C; $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) $\delta$ 9.56 (d, 1H, $J$ = 2.0 Hz), 8.60 (d, 1H, $J$ = 8.8 Hz), 8.58 (s, 1H), 8.57 (d, 1H, $J$ = 9.2 Hz), 8.44 (d, 1H, $J$ = 8.4 Hz), 8.41 (d, 1H, $J$ = 8.8 Hz), 8.09 (s, 1H), 8.03 (d, 1H, $J$ = 2.4 Hz), 8.00 (d, 1H, $J$ = 2.0 Hz), 7.79 (dd, 1H, $J$ = 2.0, 8.8 Hz), 7.75 (dd, 1H, $J$ = 2.2, 8.8 Hz), 7.52 (dd, 1H, $J$ = 1.6, 8.8 Hz), 7.47 (dd, 1H, $J$ = 2.2, 8.6 Hz), 4.31 (s, 3H), 1.54 (s, 9H), 1.50 (s, 9H), 1.02 (s, 18H); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) $\delta$ 157.0, 149.6, 149.1, 147.3,147.2,131.9, 130.7, 130.6,130.2,128.7, 128.4, 128.3, 128.1, 127.7, 127.4, 126.9, 126.3, 125.2, 124.9, 124.8, 124.5, 123.7, 122.9, 122.8, 122.2, 122.0, 119.2, 102.4, 56.3, 35.0, 34.9, 34.2, 31.3,31.2, 30.6; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{47}H_{52}O$ 632.40181, found 632.40384.

**1,3,5-Tris(5-*tert*-butyl-2-methoxyphenyl)benzene (13).** 1,3,5-Tribromobenzene **8** (1.0 g, 3.2 mmol), 5-*tert*-butyl-2-methoxyphenylboronic acid **12** (2.4 g, 11.5 mmol) and $Na_2CO_3$ (3.4 g, 32 mmol) were dissolved in toluene (30 mL), water (10 mL) and ethanol (5 mL). The solution was degassed, $Pd(PPh_3)_4$ (369 mg, 0.32 mmol) was added under an Ar stream, and the mixture was degassed again and then heated at 90 °C for 48 h. The organic layer was decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (20%) as the eluent to give the title compound **13** (white solid, 1.67 g, 95%): mp 119−120 °C; $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) $\delta$

**Scheme 6. Scholl Reaction on Precursor 17d Leads to Distorted Hexabenzocoronene 28**





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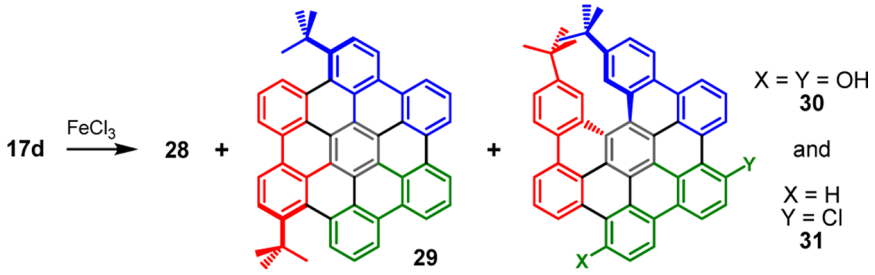
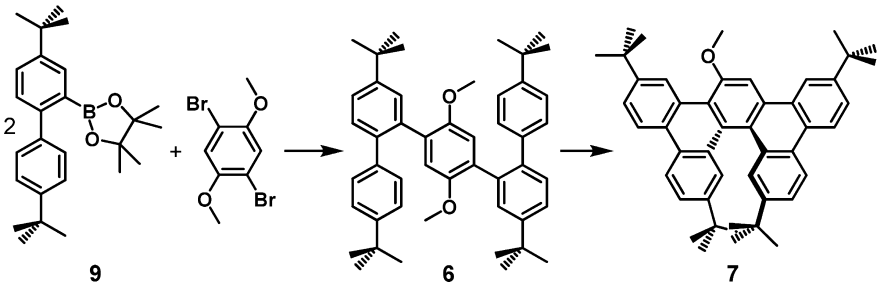
**Scheme 7. Scholl Reaction on 17d Also Gives Traces of Rearranged Compounds**




**Scheme 8. Synthesis Scheme of Compounds 6 and 7**




7.55 (s, 3H), 7.39 (d, 3H, $J$ = 2.8 Hz), 7.33 (dd, 3H, $J$ = 2.8, 8.8 Hz), 6.93 (d, 3H, $J$ = 8.4 Hz), 3.79 (s, 9H), 1.30 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 154.4, 143.5, 138.5, 130.0, 129.4, 128.3, 125.3, 110.6, 55.5, 34.1, 31.3; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{39}H_{48}O_3$ 564.36034, found 564.35856.

**1,3,5-Tris(5-*tert*-butyl-2-hydroxyphenyl)benzene (14).** Compound **13** (1.72 g, 3.05 mmol) was dissolved in 50 mL of dry $CH_2Cl_2$ under Ar and brought to −20 °C. $BBr_3$ (1 M in $CH_2Cl_2$, 12.2 mmol, 12.2 mL) was added dropwise with vigorous stirring, and the reaction mixture was stirred overnight and finally warmed to room temperature. The reaction mixture was then poured on crushed ice, the organic layer was decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and dried over anhydrous $Na_2SO_4$. The solvent was removed under a vacuum, yielding **14** without further purification (1.57 g, 99%) as a white solid: mp 247−248 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.63 (s, 3H), 7.34 (d, 3H, $J$ = 2.4 Hz), 7.28 (dd, 3H, $J$ = 2.6, 8.2 Hz), 6.88 (d, 3H, $J$ = 8.8 Hz), 5.24 (s, 3H), 1.29 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.3, 143.9, 139.4, 128.9, 127.5, 126.9, 126.3, 115.5, 34.1, 31.3; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{36}H_{42}O_3$ 522.31339, found 522.31410.

**1,3,5-Tris(5-*tert*-butyl-2-trifluoromethylsulfonyloxyphenyl)-benzene (15).** To compound **14** (1.50 g, 2.87 mmol) dissolved in 100 mL of anhydrous $CH_2Cl_2$ were added 5 mL of pyridine, and the solution was cooled to 0 °C. Trifluoromethanesulfonic anhydride (1.9 mL, 11 mmol) was added dropwise, and the mixture was warmed to room temperature and stirred overnight. The solvent was removed under a vacuum. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (15%) as the eluent to give the title compound **15** (white solid, 2.53 g, 96%): mp 173−174 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.65(s, 3H), 7.64 (d, 3H, $J$ = 2.8 Hz), 7.48 (dd, 3H, $J$ = 2.6, 9.0 Hz), 7.31 (d, 3H, $J$ = 8.8 Hz), 1.36 (s, 27 Hz); $^{19}$F NMR (400 MHz, $CD_2Cl_2$) $\delta$ −74.21; $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 152.3, 144.7, 136.9, 133.8, 130.1, 129.4, 126.7, 121.4, 34.8, 30.9; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{39}H_{39}O_9F_9S_3$ 918.16125, found 918.16261.

**1,3,5-Tris(5-*tert*-butyl-2-phenanthren-9-ylphenyl)benzene (17a).** Compound **15** (400 mg, 0.435 mmol) and phenanthrene-9-boronic acid **16a** (386 mg, 1.74 mmol) and $K_3PO_4$ (1.11 g, 5.22 mmol) were dissolved in a mixture of THF (10 mL) and water (2 mL). The solution was degassed, $Pd(OAc)_2$ (14.6 mg, 0.065 mmol) and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl SPhos (32 mg, 0.078 mmol) were added under an Ar stream, and the mixture was degassed again. The solution was heated at 70 °C for 72 h. The organic layer was then decanted, and the aqueous layer extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (12%) as the eluent to give the title compound **17a** (white solid, 414 mg, 95%): mp 214−215 °C; $^1$H NMR (400 MHz, DMSO,150 °C) $\delta$ 8.67−8.63 (m, 6H), 7.58−7.43 (m, 9H), 7.42 (d, 3H, $J$ = 8.0 Hz), 7.31 (d, 3H, $J$ = 8.0 Hz), 7.25−7.21 (m, 6H), 7.01 (d, 3H, $J$ = 8.4 Hz), 6.96 (s, 3H), 6.68 (s, 3H), 6.49 (s, 3H), 1.05 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.5,150.4, 140.8, 140.3, 138.1, 137.9, 135.4, 131.9, 131.4, 130.2, 129.5, 128.7, 128.6, 128.2, 127.1, 126.6, 126.4, 126.1, 126.0, 123.4, 122.8, 122.5, 34.2, 34.1, 31.0, 30.9; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{78}H_{66}$ 1002.51645, found 1002.52118.

**Hexa[7]circulene- and [5]Helicene-Based Rearranged Compound (18).** Compound **17a** (300 mg, 0.3 mmol) was dissolved in 50 mL of unstabilized dichloromethane and degassed with an Ar stream for 15 min. Then a solution of $FeCl_3$ (970 mg, 6.0 mmol) in 10 mL of nitromethane was added dropwise while continuously degassing with an Ar stream. After 1 h the reaction was stopped by adding 100 mL of ethanol. The organic phase was then washed twice with water and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (4%) as the eluent to give the title compound **18** (greenish yellow solid, 218 mg, 73%): mp > 400 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 9.10−9.07 (m, 1H), 8.95−8.91 (m, 1H), 8.76−8.72 (m, 1H), 8.67−8.63 (m, 2H), 8.54 (d, 1H, $J$ = 8.4 Hz), 8.52 (d, 1H, $J$ = 8.4 Hz), 8.43 (d, 1H, $J$ = 8.0 Hz), 8.15 (dd, 2H, $J$ = 2.2, 7.8 Hz), 7.87 (d, 1H, $J$ = 8.0 Hz), 7.75 (d, 1H, $J$ = 8.0 Hz), 7.72−7.68 (m, 5H), 7.59 (dd, 1H, $J$ = 2.0, 8.4 Hz), 7.50 (t, 1H, $J$ = 8.4 Hz), 7.45−7.42 (m, 2H), 7.31 (t, 1H, $J$ = 7.6 Hz), 7.17 (t, 1H, $J$ = 7.2 Hz), 7.14−7.7.05 (m, 4H), 6.98 (d, 1H, $J$ = 7.6 Hz), 6.71 (t, 1H, $J$ = 7.0 Hz), 6.44 (d, 1H, $J$ = 7.6 Hz), 6.43 (d, 1H, $J$ = 7.6 Hz), 1.18 (s, 9H), 1.02 (s, 9H), 0.63 (s, 9H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 148.1, 147.7, 147.4, 142.3, 138.2, 136.8, 136.2, 136.1, 134.9, 134.8, 133.5, 133.0, 132.4, 131.6, 131.4, 131.3, 131.1, 130.7, 130.6, 129.8, 129.7, 129.6, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.4, 127.3, 127.2, 126.8, 126.7, 126.6, 126.0, 125.8, 125.6, 125.5, 125.2, 125.1, 124.9, 124.7, 124.5, 124.4, 124.3, 123.9, 123.6, 123.5, 122.5, 122.2, 121.3, 121.1, 35.9, 34.7, 34.4, 32.3, 30.9, 30.5; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{78}H_{58}$ 994.45385, found 994.45604.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**1,3,5-Tris(5-*tert*-butyl-2-naphthalen-2-ylphenyl)benzene (17b).** Compound **15** (600 mg, 0.65 mmol), naphthalene-2-boronic acid **16b** (448 mg, 2.6 mmol) and $K_3PO_4$ (1.67 g, 7.82 mmol) were dissolved in a mixture of THF (10 mL) and water (2 mL). The solution was degassed, $Pd(OAc)_2$ (22 mg, 0.1 mmol) and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl SPhos (48 mg, 0.12 mmol) were added under an Ar stream, and the mixture was degassed again. The solution was heated at 70 °C for 48 h. The organic layer was then decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (10%) as the eluent to give the title compound **17b** (white solid, 511 mg, 92%): mp 186−187 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.81−7.77 (m, 6H), 7.76 (s, 3H), 7.64 (d, 3H, $J$ = 8.8 Hz), 7.47−7.40 (m, 6H), 7.31 (d, 3H, $J$ = 8.0 Hz), 7.29 (d, 3H, $J$ = 8.4 Hz), 6.89 (s, 3H), 6.84 (dd, 3H, $J$ = 2.0, 8.8 Hz), 6.69 (s, 3H),1.01 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.6, 141.6, 139.8, 139.3, 137.3, 133.6, 132.0, 130.6, 129.8, 128.9, 128.1, 128.0, 127.8, 126.6, 126.1, 125.9, 124.4, 34.1, 30.8; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{66}H_{60}$ 852.46950, found 852.47021.

**Unidentified Rearranged Compound (19).** Compound **17b** (200 mg, 0.24 mmol) was dissolved in 50 mL of unstabilized dichloromethane and degassed with an Ar stream for 15 min. Then a solution of $FeCl_3$ (760 mg, 4.7 mmol) in 10 mL of nitromethane was added dropwise while continuously degassing with an Ar stream. After 1.5 h the reaction was stopped by adding 100 mL of ethanol. The organic phase was then washed twice with water and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (4%) as the eluent to give the title compound **19** (greenish yellow solid, 178 mg, 90%): mp > 400 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 9.17 (s, 1H), 9.13 (d, 1H, $J$ = 8.4 Hz), 9.03(d, 1H, $J$ = 8.4 Hz), 8.78 (d, 1H, $J$ = 9.2 Hz), 8.66 (d, 1H, $J$ = 8.0 Hz), 8.59 (d, 1H, $J$ = 8.8 Hz), 8.49 (d, 1H, $J$ = 8.4 Hz), 8.45 (d, 1H, $J$ = 8.4 Hz), 8.30 (d, 1H, $J$ = 8.4 Hz), 8.17 (d, 1H, $J$ = 8.4 Hz), 8.14 (d, 1H, $J$ = 8.8 Hz), 7.87 (d, 1H, $J$ = 8.4 Hz), 7.83 (d, 1H, $J$ = 7.6 Hz), 7.68−7.57 (m, 6H), 7.43−7.40 (m, 2H), 7.23 (t, 1H, $J$ = 7.4 Hz), 7.17 (t, 1H, $J$ = 7.2 Hz), 6.80 (t, 1H, $J$ = 7.6 Hz), 6.62 (t, 1H, $J$ = 8.2 Hz), 1.04 (s, 9H), 0.79 (s, 9H), 0.76 (s, 9H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 149.3, 149.0, 148.8, 132.9, 132.8, 132.7, 132.0, 132.6, 131.0, 130.8, 130.7, 130.4, 129.4, 128.8, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.2, 126.9, 126.8, 126.2, 125.9, 125.8, 125.6, 125.5, 125.3, 125.2, 125.0, 124.6, 124.5, 124.4, 124.2, 124.0, 123.7, 122.9, 122.4, 121.4, 121.0, 120.8, 120.0, 118.3, 39.3, 34.1, 34.0, 32.6, 30.5, 30.4; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{66}H_{52}$ 844.40690, found 844.40311.

**1,3,5-Tris(5-*tert*-butyl-2-(4-trimethylsilylphenyl)phenyl)-benzene (17c).** Compound **15** (400 mg, 0.44 mmol), 4-(trimethylsilyl)phenylboronic acid **16c** (338 mg, 1.7 mmol) and $K_3PO_4$ (1.1 g, 5.2 mmol) were dissolved in a mixture of THF (10 mL) and water (2 mL). The solution was degassed, $Pd(OAc)_2$ (14.7 mg, 0.065 mmol) and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl SPhos (32 mg, 0.078 mmol) were added under an Ar stream, and the mixture was degassed again. The solution was heated at 70 °C for 48 h. The organic layer was then decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (12%) as the eluent to give the title compound **17c** (white solid, 384 mg, 96%): mp 254−255 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.53 (d, 6H, $J$ = 7.6 Hz), 7.39 (dd, 3H, $J$ = 2.0, 8.4 Hz), 7.28 (d, 3H, $J$ = 8.4 Hz), 7.14 (d, 3H, $J$ = 1.6 Hz), 6.98 (d, 6H, $J$ = 7.6 Hz), 6.82 (s, 3H), 1.28 (s, 27H), 0.20 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.5, 142.5, 141.5, 139.9, 138.1, 137.4, 132.9, 130.4, 129.6, 128.0, 124.8, 34.5, 31.1, −1.2; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{63}H_{78}Si_3$ 918.54113, found 918.54367.

**3,11,19-Tri-*tert*-butyl-6,14,22-tris(trimethylsilyl)hexabenzo-triphenylene (20).** Compound **17c** (200 mg, 0.22 mmol) was dissolved in 50 mL of unstabilized dichloromethane and degassed with an Ar stream for 15 min. Then a solution of $FeCl_3$ (700 mg, 4.3 mmol) in 10 mL of nitromethane was added dropwise while continuously degassing with an Ar stream. After 1.5 h the reaction was stopped by adding 100 mL of ethanol. The organic phase was then washed twice with water and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (2%) as the eluent to give the title compound **20** (yellow solid, 129 mg, 65%): mp > 300 °C (decomposes at 300 °C); $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 8.55 (d, 3H, $J$ = 8.4 Hz), 8.53 (d, 3H, $J$ = 8.4 Hz), 8.29 (s, 3H), 8.14 (d, 3H, $J$ = 2.0 Hz), 7.65 (dd, 3H, $J$ = 1.8, 8.4 Hz), 7.60 (dd, 3H, $J$ = 1.8, 8.4 Hz), 1.05 (s, 27H), −0.02 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 148.1, 136.6, 136.5, 131.7, 130.9, 130.6, 130.2, 128.5, 128.4, 127.6, 124.5, 122.9, 122.2, 34.5, 30.8, −1.7; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{63}H_{72}Si_3$ 912.49418, found 912.49536.

**1,3,5-Tris(4-*tert*-butylbiphenyl-2-yl)benzene (17d).** Compound **15** (430 mg, 0.47 mmol), phenylboronic acid **16d** (230 mg, 1.9 mmol) and $K_3PO_4$ (1.2 g, 5.7 mmol) were dissolved in a mixture of THF (10 mL) and water (2 mL). The solution was degassed, $Pd(OAc)_2$ (15.8 mg, 0.070 mmol) and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl SPhos (35 mg, 0.084 mmol) were added under an Ar stream, and the mixture was degassed again. The solution was heated at 70 °C for 48 h. The organic layer was then decanted, and the aqueous layer was extracted 2 times with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (10%) as the eluent to give the title compound **17d** (white solid, 322 mg, 98%): mp 263−264 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.36 (dd, 3H, $J$ = 2.0, 8.0 Hz), 7.31−7.21 (m, 12H), 7.00 (d, 6H, $J$ = 7.2 Hz), 6.91 (d, 3H, $J$ = 2.0 Hz), 6.77 (s, 3H), 1.28 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.4, 141.6, 141.5, 139.9, 137.7, 130.2, 130.1, 129.7, 127.8, 127.7, 126.5, 124.4, 34.5, 31.2; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{54}H_{54}$ 702.42255, found 702.42535.

**1,7,13-Tri-*tert*-butyl-hexa-peri-hexabenzocoronene (28).** Compound **17d** (150 mg, 0.21 mmol) was dissolved in 50 mL of unstabilized dichloromethane and degassed with an Ar stream for 15 min. Then a solution of $FeCl_3$ (690 mg, 4.3 mmol) in 10 mL of nitromethane was added dropwise while continuously degassing with an Ar stream. After 1 h the reaction was stopped by adding 100 mL of ethanol. The organic phase was then washed twice with water and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (5%) as the eluent to give the title compound **28** (yellow solid, 106 mg, 72%): mp > 400 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 8.94 (d, 3H, $J$ = 8.8 Hz), 8.92 (d, 3H, $J$ = 8.8 Hz), 8.46 (d, 3H, $J$ = 7.6 Hz), 8.39 (d, 3H, $J$ = 8.8 Hz), 7.92 (t, 3H, $J$ = 7.6 Hz), 1.61 (s, 27H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 147.2, 131.7, 130.5, 130.3, 129.5, 128.3, 123.8, 121.6, 120.7, 120.3, 120.0, 38.5, 34.4; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{54}H_{42}$ 690.32865, found 690.32689.

*Traces of **29**, **30** and **31**.* MS (FD-TOF) $m/z$ [M]+ Calcd for $C_{50}H_{34}$ (**29**) 634.3, found 634.2; [M]+ Calcd for $C_{50}H_{36}O_2$ (**30**) 668.3, found 668.2; [M]+ Calcd for $C_{50}H_{35}Cl$ (**31**) 670.2, found 670.2.

**1,4-Bis(5-*tert*-butyl-2-methoxyphenyl)benzene (23).** 1,4-Phenylenediboronic acid **22** (1.0 g, 6.0 mmol), 5-*tert*-butyl-2-methoxyphenylbromide **21** (3.2 g, 13.1 mmol) and $Na_2CO_3$ (6.30 g, 59.5 mmol) were dissolved in toluene (48 mL), water (16 mL) and ethanol (8 mL). The solution was degassed, $Pd(PPh_3)_4$ (690 mg, 0.60 mmol) was added under an Ar stream, and the mixture was degassed again. The solution was heated at 90 °C for 48 h. The organic layer was then decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (20%) as the eluent to give the title compound **23** (white solid, 2.15 g, 90%): mp 165−166 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.50 (s, 4H), 7.35 (d, 2H, $J$ = 2.8 Hz), 7.32 (dd, 2H, $J$ = 2.6, 8.6 Hz), 6.93 (d, 2H, $J$ = 8.4 Hz), 3.79 (s, 6H), 1.31 (s, 18H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 154.4, 143.5, 137.7, 129.8,


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129.1, 128.0, 125.3, 110.7, 55.5, 34.0, 31.3; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{28}H_{34}O_2$ 402.25588, found 402.25699.

**1,4-Bis(5-*tert*-butyl-2-hydroxyphenyl)benzene (24).** Compound **23** (1.86 g, 4.6 mmol) was dissolved in 50 mL of dry $CH_2Cl_2$ under Ar and brought to −20 °C. $BBr_3$ (1 M in $CH_2Cl_2$, 11.6 mmol, 11.6 mL) was added dropwise with vigorous stirring, the reaction mixture was stirred overnight and finally warmed to room temperature. The reaction mixture was then poured onto crushed ice, the organic layer was then decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and dried over anhydrous $Na_2SO_4$. The solvent was removed under a vacuum, yielding **24** (1.71 g, 99%) as a white solid: mp 161−162 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.59 (s, 4H), 7.29 (d, 2H, $J$ = 2.8 Hz), 7.27 (dd, 2H, $J$ = 2.6, 7.8 Hz), 6.87 (d, 2H, $J$ = 8.4 Hz), 5.10 (s, 2H), 1.31 (s, 18H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.3, 143.8, 137.2, 129.8, 127.3, 127.1, 126.1, 115.4, 34.1, 31.3; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{26}H_{30}O_2$ 374.22458, found 374.22408.

**1,4-Bis(5-*tert*-butyl-2-trifluoromethylsulfonyloxyphenyl)-benzene (25).** To compound **24** (1.50 g, 4.0 mmol) in 100 mL of anhydrous $CH_2Cl_2$ were added 3.5 mL of pyridine, and the solution was cooled to 0 °C. Trifluoromethanesulfonic anhydride (1.7 mL, 10 mmol) was added dropwise, and the mixture was warmed to room temperature and stirred overnight. The solvent was removed under a vacuum. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (15%) as the eluent to give the title compound **25** (white solid, 2.43 g, 95%): mp 180−181 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.56 (s, 4H), 7.50 (d, 2H, $J$ = 2.4 Hz), 7.47 (dd, 2H, $J$ = 2.0, 8.8 Hz), 7.32 (d, 2H, $J$ = 8.4 Hz), 1.35 (s, 18H); $^{19}$F NMR (400 MHz, $CD_2Cl_2$) $\delta$ −74.24; $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 152.1, 144.6, 136.2, 134.0, 129.5, 129.2, 126.4, 121.6, 34.8, 31.0; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{28}H_{28}F_6O_6S_2$ 638.12315, found 638.12510.

**1,4-Bis(5-*tert*-butyl-2-(4-trimethylsilylphenyl)phenyl)-benzene (26).** Compound **25** (600 mg, 0.94 mmol), 4-(trimethylsilyl)phenylboronic acid **16c** (460 mg, 2.4 mmol) and $K_3PO_4$ (1.6 g, 7.5 mmol) were dissolved in a mixture of THF (10 mL) and water (2 mL). The solution was degassed, $Pd(OAc)_2$ (21 mg, 0.09 mmol) and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl SPhos (46 mg, 0.11 mmol) were added under an Ar stream, and the mixture was degassed again. The solution was heated at 70 °C for 48 h. The organic layer was then decanted, and the aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (10%) as the eluent to give the title compound **26** (white solid, 540 mg, 90%): mp 305−306 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 7.58 (d, 1H, $J$ = 2.4 Hz), 7.41 (d, 1H, $J$ = 2.0 Hz), 7.39 (d, 2H, $J$ = 1.6 Hz), 7.38 (d, 4H, $J$ = 7.6 Hz), 7.32 (d, 2H, $J$ = 8.4 Hz), 7.10 (d, 4H, $J$ = 8.0 Hz), 6.99 (s, 4H), 1.35 (s, 18H), 0.22 (s, 18H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.6, 141.9, 140.2, 139.9, 138.2, 137.6, 132.8, 130.3, 129.5, 129.2, 127.6, 124.6, 34.5, 31.1, −1.4; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{44}H_{54}Si_2$ 638.37640, found 638.37464.

**2,13-Di-*tert*-butyltribenzo[fg,ij,rst]pentaphene (27).** Compound **26** (200 mg, 0.31 mmol) was dissolved in 50 mL of unstabilized dichloromethane and degassed with an Ar stream for 15 min. Then a solution of $FeCl_3$ (610 mg, 3.8 mmol) in 5 mL of nitromethane was added dropwise while continuously degassing with an Ar stream. After 1 h the reaction was stopped by adding 100 mL of methanol. The organic phase was then washed twice with water and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel by using petroleum ether/$CH_2Cl_2$ (4%) as the eluent to give the title compound **27** (yellow solid, 139 mg, 91%): mp 276−277 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 9.06 (s, 2H), 8.87 (d, 2H, $J$ = 7.6 Hz), 8.84 (d, 2H, $J$ = 1.6 Hz), 8.78 (d, 2H, $J$ = 8.0 Hz), 8.68 (d, 2H, $J$ = 8.8 Hz), 8.95 (t, 2H, $J$ = 8.0 Hz), 7.82 (dd, 2H, $J$ = 1.6, 8.8 Hz), 1.60 (s, 18H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 150.4, 129.9, 129.7, 129.5, 127.6, 127.5, 126.4, 125.6, 124.1, 123.4, 121.3, 121.2, 120.7, 119.6, 35.2, 31.3; HRMS (FD-TOF) $m/z$ [M]+ Calcd for $C_{38}H_{32}$ 488.25040, found 488.25075.

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic characterization for **18**, **20**, **27**, and **30+31** (CIF). $^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR (if applicable) spectra for new isolated compounds: **6**, **7**, **13**−**15**, **17a**−**d** to **20**, **23**−**28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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