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Palladium-Catalyzed [2 + 2 + 2] Cycloadditions of 3,4-Didehydrophenanthrene and 1,2-Didehydrotriphenylene

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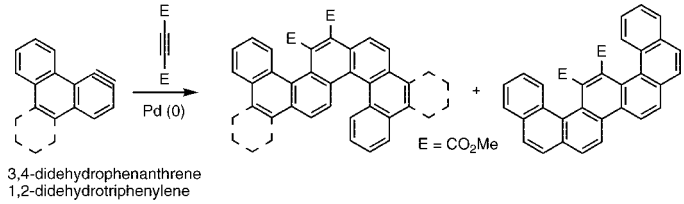


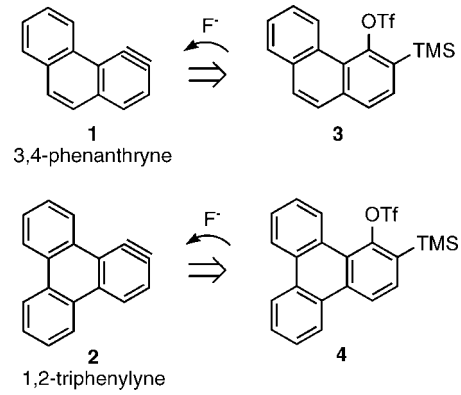
Palladium-catalyzed [2 + 2 + 2] cycloaddition reactions of 3,4-didehydrophenanthrene (3,4-phenanthryne) and 1,2-didehydrotriphenylene (1,2-triphenylyne) afford sterically congested polycyclic aromatic hydrocarbons with novel structures.

Introduction

In recent years, interest in fullerenes, nanographenes, and carbon nanotubes has led to a remarkable revival in the development of methods for the preparation of large and/or sterically congested polycyclic aromatic hydrocarbons (PAHs).[1] Aryne-based reactions[2] have been extensively used for this purpose;[3] in particular, our group has applied the palladium-catalyzed cyclotrimerization of arynes to the synthesis of a number of strained or large PAHs.[4−6]

Recently, we reported the generation and palladium-catalyzed [2 + 2 + 2] cycloaddition reactions of 2,3-didehydrotriphenylene (2,3-triphenylyne) to afford planar extended triphenylenes.[7] In this paper, we describe cyclotrimerization reactions of 3,4-didehydrophenanthrene (3,4-phenanthryne, **1**, Scheme 1) and 1,2-didehydrotriphenylene (1,2-triphenylyne, **2**) to yield nonplanar extended polyarenes,[8] increasing the scope of this synthetic methodology. Based on our experience in this field,

SCHEME 1. Arynes 1 and 2 and Aryne Precursors 3 and 4



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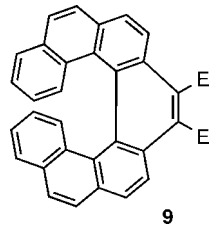

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FIGURE 1. [2 + 2 + 2] cocycloaddition product not detected from route b described in Scheme 2.

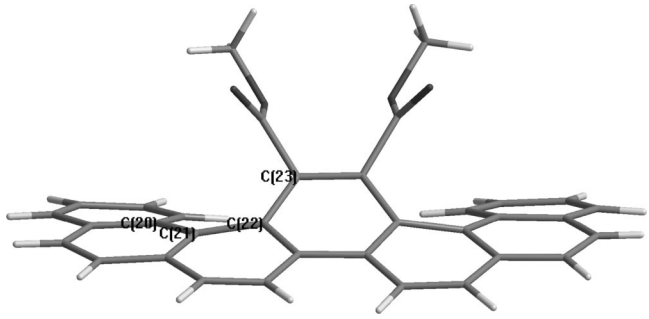


FIGURE 2. X-ray structure of saddle-shaped compound **7**.

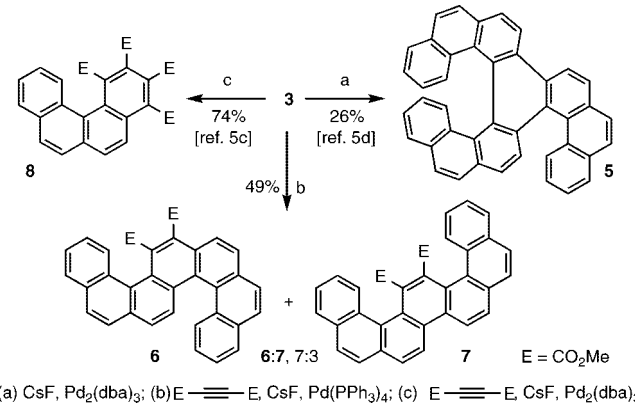
we chose *o*-(trimethylsilyl)aryl triflates **3** and **4** as 3,4-phenanthryne (**1**) and 1,2-triphenylyne (**2**) precursors, respectively. Fluoride-induced decomposition of these triflates would generate arynes **1** and **2** under mild and neutral conditions.

Results and Discussion

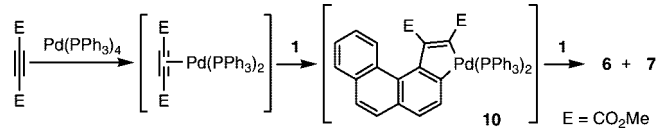
Palladium-catalyzed [2 + 2 + 2] cycloaddition reactions of aryne **1** have previously been studied to some extent by our group.[5c,d] In particular, generation of 3,4-phenanthryne (**1**) by treatment of triflate **3** with CsF in the presence of 5 mol % of $Pd_2(dba)_3$ afforded the double helicene **5** in 26% yield (Scheme 2).[5d] On the other hand, generation of **1** in the presence of an excess of dimethyl acetylenedicarboxylate (DMAD) afforded compound **8**, resulting from the reaction of one aryne and two alkyne moieties, in 74% yield.[5c]

As expected on the basis of the previously observed chemoselectivity of the palladium-catalyzed cycloadditions of arynes and alkynes,[4b] here we confirmed that the use of $Pd(PPh_3)_4$ results in the preferential reaction of two molecules of aryne and one molecule of alkyne. In particular, treatment of triflate **3** with CsF in the presence of DMAD and 10 mol % of $Pd(PPh_3)_4$ led to the isolation of a mixture of polyarenes **6** and **7** in 49% yield (ratio **6**:**7** = 7:3), while heptahelicene **9** (Figure 1) was not isolated. Assuming a [2 + 2 + 2] cycloaddition mechanism,[9] selective formation of **6** and **7** (as opposed to **9**) can be explained on the basis of the preferential formation of metallacycle **10** as an intermediate (Scheme 3). Reaction of DMAD with $Pd(PPh_3)_4$ led to the initial formation of the corresponding palladium(0) alkyne complex. Coordination of aryne **1** to palladium followed by oxidative coupling would afford metallacycle **10**, avoiding the unfavorable steric interaction between the phenanthrene moiety and the triphenylphosphine coordinated to the metal center. Reaction of this metallacycle with phenanthryne **1** can exclusively afford polycyclic arenes **6** and **7**.

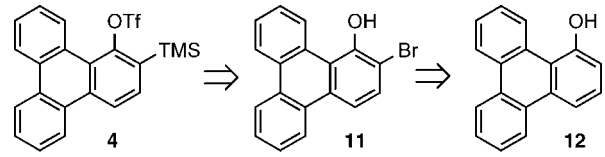
SCHEME 2. [2 + 2 + 2] Cycloaddition Reactions of Phenanthryne 1



SCHEME 3. Proposed Metallacyclic Intermediate 10



SCHEME 4. Retrosynthetic Analysis of Triflate 4



Disubstituted dibenzopicene **7** has an interesting nonplanar structure, as determined by single-crystal X-ray diffraction studies (Figure 2). In the crystalline state, compound **7** adopts a saddle-shaped conformation, a molecular structure with few reported precedents in the field of polycyclic aromatic hydrocarbons.[10] The streric demand present in the two fjord regions of the molecule causes this distorted conformation, with a C(20)−C(21)−C(22)−C(23) dihedral angle of 31.9°.

We next planned to apply these cyclotrimerization reactions to a polycyclic aryne of increased size and structural complexity: 1,2-didehydrotriphenylene (**2**, Scheme 1). Triflate **4**, the precursor of aryne **2**, should be readily accessible from triphenylenol (**12**, Scheme 4) by selective *ortho*-bromination followed by a simple one-pot transformation previously developed by us for the transformation of *o*-bromophenols into *o*-(trimethylsilyl)aryl triflates.[11]

We first considered the synthesis of triphenylenol (**12**) by palladium-catalyzed [2 + 2 + 2] cocycloaddition of one molecule of 3-methoxybenzyne (**16**) and two molecules of benzyne (**17**, Scheme 5). There are seven possible products from the homo- and heterocyclotrimerization of these arynes: triphenylene, 1-methoxytriphenylene (**15**), 1,5-, 1,8-, and 1,12-dimethoxytriphenylenes, and 1,5,9- and 1,5,12-trimethoxytriphenylenes.[12] The composition of the mixture would depend on the ratio of reagents, the rate of formation of the different aryne−palladium complexes, and the rate of transformation of these into the different products. Although a priori the selective synthesis of one of the cotrimers seems to be a difficult task, we tried to obtain 1-methoxytriphenylene (**15**) by this methodol-

(8) Arynes **1** and **2** have been proposed as intermediates in the flash vacuum pyrolysis of the corresponding dicarboxylic anhydrides. See: Brown, R. F. C. *Eur. J. Org. Chem.* **1999**, 3211.

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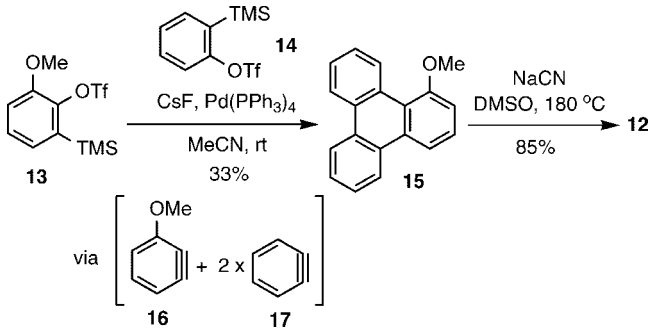
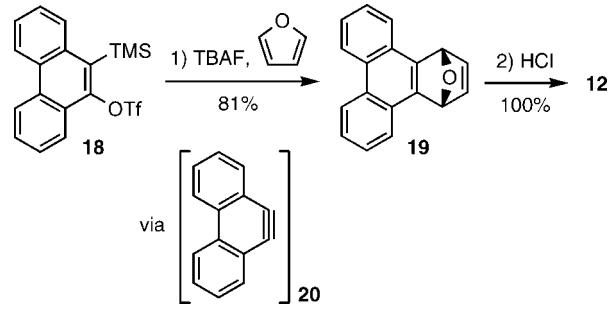
(12) See the Supporting Information for details.

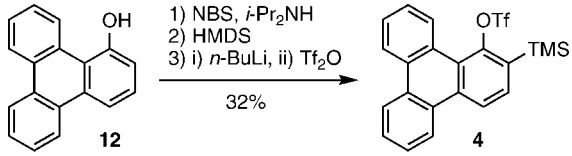
SCHEME 5. Cocyclotrimerization of Aryne 16 with Benzyne (17)



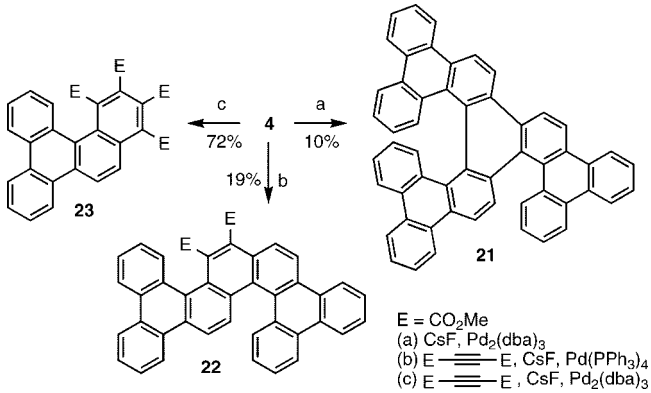
SCHEME 6. Synthesis of 1-Triphenylenol (12) by Diels−Alder Cycloaddition of 9,10-Phenanthryne (20) with Furan



SCHEME 7. Synthesis of Triflate 4



SCHEME 8. [2 + 2 + 2] Cycloaddition Reactions of Triphenylyne 2



ogy. After some experimentation, we found that treatment of a 1:4 molar ratio of aryne precursors **13** and **14** with CsF in the presence of 10 mol % of $Pd(PPh_3)_4$ allowed us to isolate compound **15** in a remarkable 33% yield.[13] Treatment of this compound with NaCN in DMSO at 180 °C led to the isolation of 1-triphenylenol (**12**) in 85% yield.

Alternatively, 1-triphenylenol (**12**) was prepared in higher yield by means of Diels−Alder cycloaddition of 9,10-phenanthryne (**20**) with furan (Scheme 6).[14] Reaction of triflate **18**, the precursor of phenanthryne **20**,[5b] with tetrabutylammonium fluoride (TBAF) in the presence of an excess of furan in THF afforded compound **19** in 81% yield. Acidic treatment of this compound gave a quantitative yield of 1-triphenylenol (**12**). *ortho*-Bromination of compound **12** with *N*-bromosuccinimide (NBS), catalyzed by *i*-Pr_2NH in DCM, led to the isolation of compound **11**. One-pot treatment with hexamethyldisilazane (HMDS) in refluxing THF, followed by successive addition of *n*-BuLi and Tf_2O at −100 °C, afforded triflate **4** in 32% overall yield from **12** (Scheme 7).

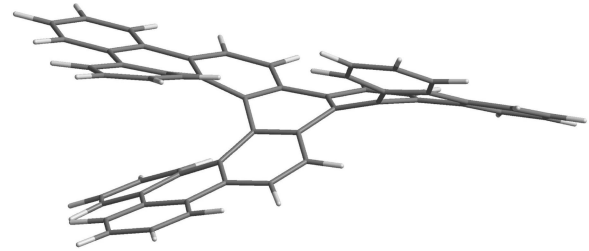


FIGURE 3. Optimized geometry (MM2) for the proposed conformation of double helicene **21**.

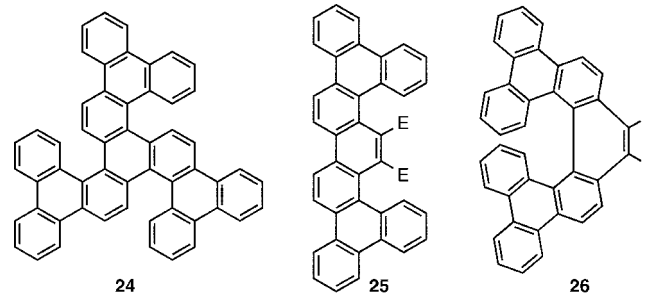


FIGURE 4. [2 + 2 + 2] cycloaddition products not detected from the reactions described in Scheme 8.

Next, we applied the palladium-catalyzed cyclotrimerization procedures to 1,2-triphenylyne (**2**). Generation of this intermediate by treatment of triflate **4** with CsF in the presence of 5 mol% of $Pd_2(dba)_3$ in MeCN at 40 °C resulted in the formation of the sterically congested trimer **21** in 10% yield (route a, Scheme 8).[15] The structure of nonplanar polycyclic arene **21** contains a double helicene with a heptahelicene and a pentahelicene with two rings in common. Comparison of its characteristic ^1H NMR spectrum with that of double helicene **5**,[5d] suggested that **21** was isolated in the conformation in which both helicenes rotate in opposite senses (Figure 3).[12] The other possible cyclotrimerization product **24** (Figure 4) was not detected from the reaction mixture.

Treatment of triflate **4** with CsF in the presence of DMAD and 10 mol % of $Pd(PPh_3)_4$ led to the isolation of polyarene **22** in 19% yield (route b, Scheme 8). Remarkably, neither of the two other cocyclotrimerization products resulting from the reaction of two arynes and one alkyne were obtained (**25** and **26**, Figure 4). By contrast, when 5 mol % of $Pd_2(dba)_3$ and an excess of DMAD were used, polycyclic arene **23**, resulting from the reaction of one aryne and two alkynes, was isolated as the major product in a good yield (72%, route c, Scheme 8).[16] Therefore, triphenylyne **2** exhibits in its reactions with DMAD

(13) Triphenylene was also obtained in 57% yield.

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the chemoselectivity pattern previously described for benzyne and other polycyclic arynes.[6]

In conclusion, new sterically congested polycyclic aromatic hydrocarbons have been prepared by successive aryne cycloaddition reactions. Remarkably, the polycyclic arynes studied here have been only reported sporadically, and their reaction products have provided some insights into the palladium-catalyzed cyclotrimerization of arynes.

Experimental Section

1-Methoxytriphenylene (15).[17] Finely powdered anhydrous CsF (1.90 g, 12.5 mmol) was added to a solution of triflate **13** (410 mg, 1.25 mmol), triflate **14** (1.49 g, 5.00 mmol), and $Pd(PPh_3)_4$ (720 mg, 0.62 mmol) in CH_3CN (21 mL), and the mixture was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; 1:9 CH_2Cl_2/hexane), affording triphenylene[4a] (246 mg, 57%) and 1-methoxytriphenylene (**15**, 106 mg, 33%) as white solids. Data for **15**: mp 165−167 °C (lit.[17] mp 172 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.65 (m, 1H), 8.68−8.61 (m, 3H), 8.33 (d, J = 7.9 Hz, 1H), 7.66−7.57 (m, 5H), 7.22 (dd, J = 7.9, 0.9 Hz, 1H), 4.14 (s, 3H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 158.8 (C), 132.3 (C), 130.2 (C), 130.1 (C), 129.7 (C), 129.5 (C), 129.1 (CH), 127.3 (CH), 127.0 (2CH), 126.6 (CH), 126.5 (CH), 123.9 (CH), 123.1 (CH), 122.6 (CH), 120.3 (C), 115.9 (CH), 109.8 (CH), 55.8 (CH_3); MS (EI) *m*/*z* 258 (100).

1-Triphenylenol (12) via 15. NaCN (321 mg, 6.55 mmol) was added to a solution of **15** (249 mg, 0.97 mmol) in dry DMSO (3.4 mL), and the mixture was stirred at 180 °C for 8 h. Then, the mixture was cooled to room temperature, H_2O (10 mL) was added, and the mixture was acidified to pH 1 by careful addition of 20% aqueous HCl solution (CAUTION: HCN evolution). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:2 EtOAc/hexane), affording 1-triphenylenol (**12**, 201 mg, 85%) as a white solid: mp 178−180 °C (lit.[18] mp 180−182 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.62 (m, 1H), 8.69−8.59 (m, 3H), 8.21 (d, J = 8.2 Hz, 1H), 7.66−7.60 (m, 4H), 7.49 (dd, J = 8.0 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 5.62 (s, OH); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 154.4 (C), 132.8 (C), 130.3 (C), 130.1 (C), 129.7 (C), 129.5 (C), 128.9 (CH), 127.4 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 124.0 (CH), 123.2 (CH), 122.8 (CH), 118.9 (C), 116.2 (CH), 114.7 (CH); MS (EI) *m*/*z* 244 (100).

1,4-Dihydro-1,4-epoxytriphenylene (19).[14] NBu_4F (4.6 mL, 1 M in THF, 4.6 mmol) was added dropwise to a solution of triflate **18** (1.5 g, 3.77 mmol) and furan (2.7 mL, 37.2 mmol) in THF (50 mL) at 0 °C. The mixture was stirred under argon at room temperature for 2 h. Then, H_2O (30 mL) and Et_2O (30 mL) were added, the phases were separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:2 CH_2Cl_2/hexane), affording 1,4-dihydro-1,4-epoxytriphenylene (**19**, 745 mg, 81%) as a yellow solid: mp 179−180 °C (lit.[14c] mp 180−181 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.89−8.53 (m, 2H), 7.96−7.89 (m, 2H), 7.67−7.56 (m, 4H), 7.26 (s, 2H), 6.38 (s, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 146.8 (2C), 143.9 (2CH), 128.7 (2C), 127.1 (2C), 126.7 (2CH), 125.9 (2CH), 123.4 (2CH), 123.1 (2CH), 82.0 (2CH); MS (EI) *m*/*z* 244 (100).

1-Triphenylenol (12) via 19. Concentrated aqueous HCl solution (36%, 0.4 mL) was added to a solution of **19** (22 mg, 0.090 mmol) in THF (2 mL), and the mixture was stirred at 85 °C for 4 h. Then, this mixture was cooled to room temperature, H_2O (2 mL) and Et_2O (2 mL) were added, the phases were separated, and the aqueous layer was extracted with Et_2O (2 × 4 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:2 EtOAc/hexane), affording 1-triphenylenol (**12**, 22 mg, 100%) as a white solid.[18]

2-Bromo-1-triphenylenol (11). A solution of NBS (130 mg, 0.73 mmol) in CH_2Cl_2 (7.3 mL) was added to a solution of 1-triphenylenol (**12**, 160 mg, 0.66 mmol) and *i*-Pr_2NH (10 μL, 0.070 mmol) in CH_2Cl_2 (8.3 mL) at −78 °C. The resulting mixture was stirred for 8 h while the temperature reached 20 °C. Then, H_2O (15 mL) was added, and the mixture was acidified to pH 1 by careful addition of concentrated aqueous H_2SO_4 solution. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:4 Et_2O/hexane), affording 2-bromo-1-triphenylenol (**11**, 135 mg, 63%) as a white solid: mp 143−145 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.64 (m, 1H), 8.54 (d, J = 7.8 Hz, 1H), 8.68−8.62 (m, 2H), 8.11 (d, J = 9.0 Hz, 1H), 7.70−7.57 (m, 5H), 6.63 (s, OH); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 150.2 (C), 132.0 (C), 130.2 (C), 129.3 (CH), 129.1 (CH), 129.0 (2C), 128.9 (C), 127.6 (CH), 127.0 (2CH), 126.9 (CH), 123.6 (CH), 123.2 (CH), 122.7 (CH), 119.5 (C), 116.5 (CH), 110.3 (C); MS (EI), *m*/*z* (%): 324 (59), 322 (59); HRMS (EI) for $C_{18}H_{11}O^{79}Br$ calcd 321.9993, found 321.9991; HRMS (EI) for $C_{18}H_{11}O^{81}Br$ calcd 323.9973, found 323.9966; UV/vis ($CHCl_3$) λ_{max} (ϵ) 294 (18060), 284 (21450), 267 (79900), 260 (sh, 64800 mol^{-1} dm^3 cm^{-1}) nm.

2-(Trimethylsilyl)triphenylenyl 1-Trifluoromethanesulfonate (4). A solution of 2-bromo-1-triphenylenol (**11**, 140 mg, 0.43 mmol) and HMDS (100 μL, 0.47 mmol) in THF (1.5 mL) was refluxed for 1 h. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH_3 and unreacted HMDS. ^{1}H NMR of the crude residue showed quantitative formation of the corresponding silyl ether. This crude product was dissolved in THF (3.0 mL), and the solution was cooled to −100 °C (external temperature). *n*-BuLi (190 μL, 2.42 M, 0.47 mmol) was added dropwise, and the reaction mixture was stirred for 30 min while the temperature reached −80 °C. The mixture was again cooled to −100 °C, Tf_2O (90 μL, 0.52 mmol) was added dropwise, and stirring was continued for 30 min while the temperature returned to −80 °C. Then, saturated aqueous $NaHCO_3$ (2 mL) was added at low temperature, the phases were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 6:4 CH_2Cl_2/hexane), affording **4** (100 mg, 52%) as a white solid: mp 168−170 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.77 (d, J = 8.2 Hz, 1H), 8.60−8.52 (m, 4H), 7.76−7.56 (m, 5H), 0.55 (s, 9 H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 149.9 (C), 134.4 (C), 134.0 (C), 133.1 (CH), 130.6 (C), 130.4 (C), 128.8 (CH), 128.3 (C), 128.2 (CH), 128.0 (CH), 127.7 (CH), 126.8 (C), 126.6 (CH), 124.2 (C), 123.6 (CH), 123.4 (CH), 123.3 (CH), 122.2 (CH), 118.3 (q, J = 321 Hz, CF_3), 0.4 ($3CH_3$, TMS); MS (EI) *m*/*z* 448 (75); HRMS (EI) for $C_{22}H_{19}O_3F_3SiS$, calcd 448.0776, found 448.0776; UV/vis ($CHCl_3$) λ_{max} (ϵ) 284 (12400), 267 (18000), 260 (15260 mol^{-1} dm^3 cm^{-1}) nm.

Dimethyl Naphtho[2,1-*c*]pentahelicene-15,16-dicarboxylate (6) and Dimethyl Dibenzo[*a*,*o*]picene-13,14-dicarboxylate (7). Finely powdered anhydrous CsF (61 mg, 0.40 mmol) was added to a solution of triflate **3** (80 mg, 0.20 mmol), dimethyl acetylene-

(15) $Pd_2(dba)_3$ usually affords higher yields than $Pd(PPh_3)_4$ in homocyclotrimerization reactions of sterically demanding arynes, probably due to the presence of bulky and strongly coordinated phosphine ligands in the latter catalyst.

(16) The "lightly stabilized" complex $Pd_2(dba)_3$ reacts with two molecules of DMAD leading to the corresponding metallacycle, which upon reaction with aryne **2** would afford compound **23**. See ref 4b.

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dicarboxylate (DMAD, 47 μL, 0.38 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) in CH_3CN (4 mL), and the mixture was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; 1:1:2 CH_2Cl_2/Et_2O/hexane), affording a mixture of **6** and **7** (24 mg, 49%, 7:3 **6**/**7**). Data for **6**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.60 (dd, J = 8.2, 2.5 Hz, 1H), 8.19 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.06−7.92 (m, 7H), 7.82 (d, J = 8.5 Hz, 1H), 7.67−7.48 (m, 4H), 7.17 (dt, J = 7.7, 1.3 Hz, 1H), 4.08 (s, 3H), 3.17 (s, 3H); MS (EI) m/z 494 (33); HRMS (EI) for $C_{34}H_{22}O_4$ calcd 494.1518, found 494.1533. Data for **7**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.02 (d, J = 8.2 Hz, 2H), 8.84 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 8.7 Hz, 2H), 8.01−7.89 (m, 6H), 7.79 (t, J = 8.2, 1.3 Hz, 2H), 7.67 (t, J = 7.5, 1.1 Hz, 2H), 3.06 (s, 6H); MS (EI) m/z 494 (42); HRMS (EI) for $C_{34}H_{22}O_4$ calcd 494.1518, found 494.1519.

Dibenzo[*f*,*r*]triphenyleno[1,2-*l*]heptahelicene (21). Finely powdered anhydrous CsF (31 mg, 0.21 mmol) was added to a solution of triflate **4** (31 mg, 0.069 mmol) and $Pd_2(dba)_3\cdot CHCl_3$ (3.6 mg, 3.5 μmol) in 4:1 CH_3CN/CH_2Cl_2 (2.4 mL), and the mixture was stirred at 40 °C for 14 h. The resulting suspension was filtered, and the solid residue was purified by column chromatography (SiO_2; 1:1 CH_2Cl_2/hexane), affording **21**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.97 (s, 2H), 8.92 (d, J = 8.6 Hz, 1H), 8.88 (d, J = 9.0 Hz, 1H), 8.82−8.76 (m, 4H), 8.72 (d, J = 7.9 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 7.9 Hz, 1H), 8.32 (d, J = 9.4 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.83−7.79 (m, 2H), 7.77−7.64 (m, 4H), 7.63 (ddd, 8.0, 7.1, 1.3 Hz, 1H), 7.58 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 7.52 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 6.99 (ddd, J = 7.9, 6.8, 1.2 Hz, 1H), 6.80 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 6.61 (dd, J = 8.4, 1.2 Hz, 1H), 6.34 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 5.99 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H); MS (FAB) m/z 678 (100); HRMS (FAB) for $C_{54}H_{30}$ calcd 678.2348, found 678.2351.

Dimethyl Benzo[*l*]phenanthro[9,10-*c*]pentahelicene-7,8-dicarboxylate (22). Finely powdered anhydrous CsF (66 mg, 0.44 mmol) was added to a solution of triflate **4** (80 mg, 0.20 mmol), DMAD (28 μL, 0.23 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.014 mmol) in 4:1 CH_3CN/CH_2Cl_2 (2.9 mL), and the mixture was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; 5:1:4 CH_2Cl_2/Et_2O/hexane), affording **22** (8.1 mg, 19%) as a yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81−8.66 (m, 5H), 8.63 (d, J = 8.2 Hz, 1H), 8.55 (d, J = 8.7 Hz, 1H), 8.48 (d, J = 7.9 Hz, 1H), 8.29 (s, 2H), 8.16−8.09 (m, 2H), 7.85−7.59 (m, 6H), 7.55 (dd, J = 8.1, 7.2 Hz, 1H), 7.13 (dd, J = 7.7, 7.3 Hz, 1H), 4.07 (s, 3H), 3.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4 (C), 168.5 (C), 134.5 (C), 133.2 (C), 131.6 (C), 131.5 (C), 131.0 (C), 130.8 (C), 130.4 (2C), 130.2 (C), 130.0 (C), 129.9 (CH), 129.5 (CH), 129.3 (C), 129.2 (C), 129.0 (CH), 128.9 (C), 128.3 (2C), 128.0 (CH), 127.7 (CH), 127.5 (2CH), 127.4 (C), 127.3 (CH), 127.1 (C), 127.0 (CH), 126.7 (CH), 125.8 (CH), 125.4 (C). 124.7 (CH), 124.1 (CH), 123.7 (CH), 123.6 (CH), 123.3 (4CH), 122.9 (CH), 120.2 (CH), 53.1 (CH_3), 52.2 (CH_3); MS (CI) m/z 594 (81); HRMS (CI) for $C_{42}H_{26}O_4$ calcd 594.1831, found 594.1852.

Tetramethyl Benzo[*g*]chrysene-11,12,13,14-tetracarboxylate (23). Finely powdered anhydrous CsF (78 mg, 0.51 mmol) was added to a solution of triflate **4** (75 mg, 0.17 mmol), DMAD (0.15 mL, 1.19 mmol), and $Pd_2(dba)_3\cdot CHCl_3$ (18 mg, 0.018 mmol) in 4:1 CH_3CN/CH_2Cl_2 (3.3 mL), and the mixture was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; 1:1:2 CH_2Cl_2/Et_2O/hexane), affording **23** (62 mg, 72%) as a yellow solid: mp 187−190 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.66−8.59 (m, 3H), 8.54 (d, J = 7.4 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.73−7.69 (m, 2H), 7.63 (dd, J = 7.4 Hz, 1H), 7.52 (dd, J = 7.5 Hz, 1H), 4.09 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 168.1 (C), 167.5 (C), 167.0 (C), 165.9 (C), 134.4 (C), 132.6 (C), 131.7 (C), 130.8 (C), 130.6 (C), 130.3 (C), 129.9 (C), 129.3 (C), 128.5 (C), 128.4 (C), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.6 (C), 127.3 (CH), 126.6 (CH), 125.3 (C), 124.3 (CH), 124.2 (CH), 124.0 (CH), 123.2 (2CH), 53.3 (CH_3), 53.2 (CH_3), 53.1 (CH_3), 52.3 (CH_3); MS (EI) m/z 510 (23); HRMS (EI) for $C_{30}H_{22}O_8$ calcd 510.1315, found 510.1310; UV/vis ($CHCl_3$) λ_{max} (ϵ) 342 (8650), 311 (36300), 269 (35800), 262 (37000 mol^{-1} dm^3 cm^{-1}) nm.

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Supporting Information Available: Experimental, spectroscopic, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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