Selective Palladium-Catalyzed Cocyclotrimerization of Arynes with Dimethyl Acetylenedicarboxylate: A Versatile Method for the Synthesis of Polycyclic Aromatic Hydrocarbons†

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Benzyne (**1a**) and the substituted derivatives 4,5-difluorobenzyne (**1b**) and 3-methoxybenzyne (**2**) undergo chemoselective palladium-catalyzed [2 + 2 + 2]-cocyclotrimerization with dimethyl acetylenedicarboxylate (DMAD) to afford the corresponding phenanthrenes and/or naphthalenes. The major products are phenanthrenes if $Pd(PPh_3)_4$ is used as the catalyst, naphthalenes if $Pd_2(dba)_3$ is used. When the method is applied to polycyclic arynes **3**−**6**, which are generated from the corresponding *o*-trimethylsilylaryl triflates, the same reactivity pattern is observed: the reaction can be selectively directed either toward the cocyclization of one molecule of aryne and two molecules of alkyne or to the reaction of two molecules of aryne with one molecule of alkyne, by appropriate choice of the palladium catalyst. The synthesis of polycyclic aromatic compounds **33**−**39** using this methodology is reported.

Introduction

Polycyclic aromatic hydrocarbons (PAHs)[1] are of interest for scientists in several areas of research, from environmental chemistry to supramolecular chemistry or materials science. The PAH targets of synthetic organic chemists, once simple compounds such as naphthalenes or phenanthrenes,[2] are now more challenging objectives including strained molecules such as helicenes[3] or fullerene fragments,[4] nanostructures with interesting optical or electrical properties, and extended graphite-like compounds.[5] This evolution as regards targets has been paralleled by evolution of the synthetic methods used, which have advanced from classical Friedel−Crafts chemistry to pericyclic reactions, photochemistry, flash vacuum pyrolysis, and cyclizations mediated by transition metals. Although "high-energy methods" can be very useful for the synthesis of some strained PAHs, there seems likely to be a shift toward the use of transition metal strategies that afford mild, high-yielding, selective reactions.

One of the most convergent methods for assembling benzene rings is the metal-catalyzed [2 + 2 + 2] cyclotrimerization of alkynes,[6] an extensively studied reaction that proceeds with a variety of transition metal systems and has been generalized to include the participation of various unsaturated compounds in addition to alkynes, such as alkenes and nitriles. Our group recently demonstrated that benzyne and substituted derivatives[7] can also be efficiently cyclotrimerized to the corresponding triphenylenes by palladium(0) catalysts,[8] and that the extension of this reaction to polycyclic arynes provides straightforward access to complex PAHs.[9] These results, and the known insertion chemistry of stoichiometric metal−benzyne complexes,[10] led us to consider the possibility of arynes participating in Pd-catalyzed cocyclizations with alkynes, which would dramatically expand the

† This paper is dedicated to Prof. José Luis Soto on the occasion of his 70th birthday.

(1) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: Weinheim, 1997.

(2) Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 509−562.

(3) (a) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649−660. (b) Laarhoven, W. H.; Prinsen, W. J. C. In *Top. Curr. Chem.* **1984**, *125*, 65−127. (c) Grimme, S.; Harren, J.; Sobanski, A.; Vögtle, F. *Eur. J. Org. Chem.* **1998**, *37*, 2659−2661.

(4) (a) Siegel, J. S.; Sieders, T. J. *Chem. Br.* **1995**, *31*, 313−316. (b) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (c) Scott, L. T. *Pure. Appl. Chem.* **1996**, *68*, 291−300. (d) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (d) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813.

(5) (a) Broene, R. D.; Diederich, F. *Tetrahedron Lett.* **1991**, *32*, 5227−5230. (b) Müller, M.; Kubel, C.; Müllen, K. *Chem. Eur. J.* **1998**, *4*, 2099−2109. (c) Weiss, K.; Beernink, G.; Dötz, F.; Birkner, A.; Müllen, K.; Wöll, C. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3748−3752.

(6) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−556. (b) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (c) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Hegedus, L. H., Volume Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 741−770. (d) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (e) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523−596.

(7) General reviews on aryne chemistry: (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967; (b) Hart, H. In *The Chemistry of Functional Groups, Suppl. C2: The Chemistry of Triple-Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1994; pp 1017−1134.

(8) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2659−2661.

(9) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555−1557.

(10) Reviews on transition metal complexes of arynes and cycloalkynes: (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. (b) Bennett, M. A. *Pure Appl. Chem.* **1989**, *61*, 1695−1700. (c) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296−1320. (d) Buchwald, S. L.; Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Hegedus, L. H., Volume Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 771−784. (e) Bennett, M. A.; Wenger, E. *Chem. Ber./Recueil* **1997**, *130*, 1029−1042.

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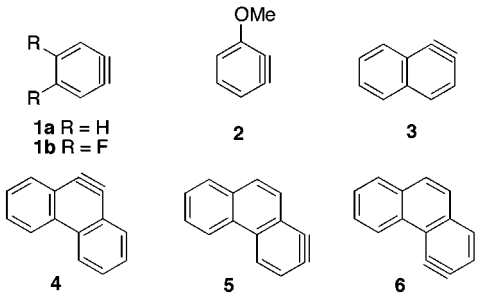
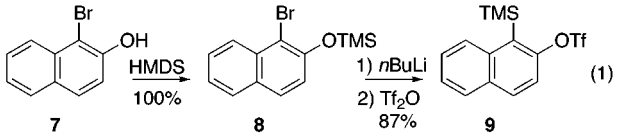
synthetic potential of our methodology. We now report in full the results of our studies in this field.[11,12]



Results and Discussion

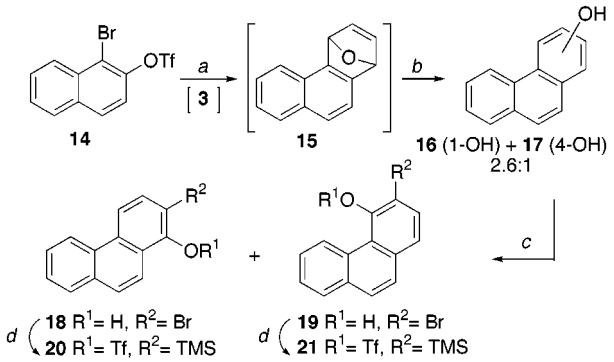
Preparation of the Aryne Precursors. As substrates for our experiments we selected the arynes **1**−**6**. 1,2-Didehydrobenzene (benzyne, **1a**) was selected as the simplest and more easily available aryne. To test the scope of the cyclization, 4,5-difluorobenzyne (**1b**) was chosen as an example of an aryne with strong electron-withdrawing groups, while 3-methoxybenzyne (**2**) would allow us to study the regioselectivity of the cycloaddition. Polycyclic arynes **3**−**6** would give a broader view of these aspects and of the possibility of constructing more complex PAHs.

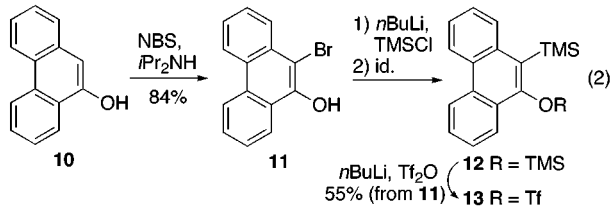
In our previous work we found that the method of choice for the generation of arynes was treatment of the corresponding *o*-trimethylsilylaryl triflates with CsF at room temperature. The synthesis of triflates **22** and **26** has already been reported,[8] and the precursors of the polycyclic arynes can easily be prepared by similar two- or three-step procedures from the corresponding *o*-bromohydroxyarenes. Thus 1-trimethylsilylnaphthyl 2-trifluoromethanesulfonate (**9**) was prepared from commercially available 1-bromo-2-naphthol (**7**) (eq 1). Treatment of **7** with hexamethyldisilazane (HMDS) at 70 °C gave a quantitative yield of trimethylsilyl ether **8**, which was transformed into triflate **9** in one pot by successive treatment with *n*-BuLi (1 equiv, −78 °C to room temperature) and Tf_2O.



The precursor of aryne **4**, 10-trimethylsilylphenanthryl 9-trifluoromethanesulfonate (**13**), was prepared from commercially available 9-phenanthrol (**10**) (eq 2). Selective *ortho*-bromination was achieved in good yield by reaction of **10** with *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of diisopropylamine.[13] Sequential treatment of the bromide **11** with *n*-BuLi and TMSCl (twice) in one pot afforded trimethylsilyl ether **12**, which was used in the next step without further purification because of its instability. Reaction of crude **12** with *n*-BuLi and quenching with Tf_2O afforded triflate **13** in 55% overall yield from **11**.

Scheme 1





Similar procedures were followed for the synthesis of triflates **20** and **21**, although the 4-phenanthrol corresponding to **21** was not commercially available. Preparation of this starting material also involved aryne chemistry as follows. 1,2-Naphthyne (**3**) was generated in the presence of furan by treatment of triflate **14** with *n*-BuLi. Acidic workup of the products of its Diels−Alder reaction afforded phenanthrols **16** and **17** in 2.6:1 ratio and 78% overall yield. Bromination of the crude mixture in the conditions described above yielded a mixture of *o*-bromophenanthrols which were easily separated by column chromatography, allowing the isolation of 2-bromo-1-phenanthrol (**18**) and 3-bromo-4-phenanthrol (**19**) in 48% and 19% yields, respectively. The corresponding trimethylsilylaryl triflates **20** and **21** were obtained in one-pot transformations from **18** and **19**, respectively, in good overall yields (Scheme 1).

Cocyclotrimerization of Simple Arynes with DMAD. The main objective of our work was to test the feasibility and efficiency of palladium-catalyzed cocyclotrimerization between benzyne and alkynes. A problem generally encountered with cocyclotrimerization reactions of alkynes is lack of chemoselectivity, which leads to complex mixtures of products and limits the synthetic utility of these reactions. Previous solutions to this problem have consisted in partial intramolecular cyclotrimerization of α,ω-diynes with a monoalkyne,[6a] or in reaction of a preformed metallacyclopentadiene with a third alkyne.[14] Purely intermolecular selective cotrimerizations are rare, and the known examples are usually based on the individual alkynes having very different reactivities for simple cyclotrimerization.[15]

Analysis of the literature on palladium-catalyzed cyclotrimerizations suggests that arynes and alkynes do

(11) For preliminary communications, see: (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827−5828. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Synlett* **2000**, 1061−1063.

(12) After our communication, other palladium-catalyzed cycloadditions of benzyne were reported: (a) Radhakrishnan, K. V.; Yoshikawa, E.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7533−7535. (b) Yoshikawa, E.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 173−175.

(13) Fujisaki, S.; Eguchi, H.; Omura, A.; Okamoto, A.; Nishida, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1576−1579.

(14) (a) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549. (b) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169−175.

(15) See, for example: Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1985**, *293*, 103.

Scheme 2

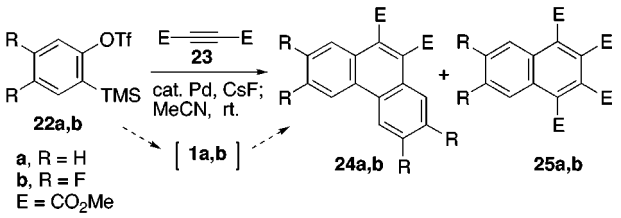


Table 1. Pd-Catalyzed Cocyclization of Benzyne (1a), 4,5-Difluorobenzyne (1b) and 3-Methoxybenzyne (2) with DMAD[a]

			product yields, %[c]		
entry	aryne	cond[b]	phenanthrene	naphthalene	triphenylene
1	**1a**	A	84 (**24a**)	7 (**25a**)	2
2	**1a**	B	10 (**24a**)	83 (**25a**)	–
3	**1b**	A	64 (**24b**)	8 (**25b**)	8[d]
4	**1b**	B	9 (**24b**)	54 (**25b**)	–
5	**2**	A	22 (**27**) 60 (**28**)	6 (**29**)	–
6	**2**	B	3 (**27**) 11 (**28**)	82 (**29**)	–

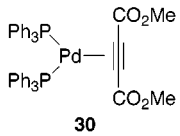
[a] See Schemes 2, 3. [b] Procedure A: DMAD (1.4 equiv), CsF (2 equiv), $Pd(PPh_3)_4$ (0.1 equiv); CH_3CN, rt. Procedure B: DMAD (5 equiv), CsF (2 equiv), $Pd_2(dba)_3$ (0.05 equiv); CH_3CN, rt. [c] Yield of isolated products. [d] 2,3,6,7,10,11-Hexafluorotriphenylene.

have very different reactivities: while we recently showed that arynes, which are strongly electrophilic, are efficiently cyclotrimerized by Pd(0) catalysts,[8] there are few examples of efficient cyclotrimerization of alkynes using these complexes.[16−19] We envisaged that this difference in reactivity, rather than being a disavantage, might provide the chemoselectivity required for a synthetically useful cocyclization reaction. With this in mind we started our study with the Pd(0)-catalyzed reactions of simple arynes with the electron-deficient alkyne dimethyl acetylenedicarboxylate (DMAD, **23**).

We found that in the presence of **23** and catalytic amounts of Pd(0), slow generation of benzyne by room-temperature treatment of **22a** with CsF[20] in acetonitrile afforded mixtures of phenanthrene **24a** and naphthalene **25a**, together with minor amounts of triphenylene (Scheme 2). When various reaction conditions were tried in order to direct the reaction toward the formation of either the phenanthrene or the naphthalene, the best yield of **24a** was obtained using 1.4 equiv of the alkyne and $Pd(PPh_3)_4$ as catalyst (Table 1, entry 1). Larger excess of the alkyne produced less phenanthrene and more naphthalene, but selective formation of **25a** was not achieved even with 10 equiv of alkyne. However, naphthalene **25a** was obtained in good yield and with very good selectivity when $Pd_2(dba)_3$ was used as the catalyst (entry 2).

The same chemoselectivity was observed when DMAD was reacted with the substituted arynes **1b** and **2** under similar reaction conditions. In the presence of excess DMAD and 0.1 equiv of $Pd(PPh_3)_4$, generation of 4,5-difluorobenzyne (**1b**) by treatment of triflate **22b** with CsF afforded a mixture of phenanthrene **24b** (64%), naphthalene **25b** (8%), and 2,3,6,7,10,11-hexafluorotriphenylene (8%) (entry 3), while the use of $Pd_2(dba)_3$ as catalyst resulted in the formation of naphthalene **25b** as major product (54%) and only a 9% yield of **24b** (entry 4). In the case of 3-methoxybenzyne (**2**), treatment of triflate **26** with CsF in the presence of DMAD and catalytic $Pd(PPh_3)_4$ afforded the isomeric phenanthrenes **27** and **28** in 22% and 60% yield respectively, together with naphthalene **29** in 6% yield (Scheme 3; Table 1, entry 5). Selective formation of naphthalene **29**, in 82% yield, was again achieved using $Pd_2(dba)_3$ as catalyst; in these conditions phenanthrenes **27** and **28** were isolated in 3% and 11% yield, respectively.

These results show that the intermolecular cocycloaddition of arynes with DMAD can be made highly chemoselective and can easily be switched between the formation of phenanthrenes and the formation of naphthalenes, by appropriate selection of the catalyst. This latter result can be attributed to the different nature of the ligands coordinated to palladium in each complex, which can lead to the formation of different reaction intermediates. In the experiments carried out using $Pd(PPh_3)_4$ (entries 1, 3, and 5) it was observed the initial formation and eventual disappearance of a compound that upon isolation was characterized as complex **30**[21] and is assumed to be one of the intermediates involved in the formation of the phenanthrenes. By contrast, the "lightly stabilized" complex $Pd_2(dba)_3$ (entries 2, 4, and 6) is expected to form complex **31**,[17,22] which upon reaction with a molecule of aryne would directly afford the naphthalenes.



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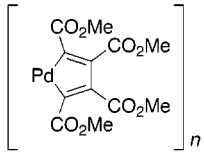


31

Cocyclotrimerization of Polycyclic Arynes with DMAD. Having proved the efficiency of the above method for selective cocyclization of simple arynes with DMAD, we decided to study its applicability to polycyclic arynes. Gratifyingly, we found the same reactivity pattern: $Pd_2(dba)_3$ selectively promotes the cocyclization of one molecule of aryne with two molecules of alkyne, while $Pd(PPh_3)_4$ catalyzes the cocyclization of two molecules of aryne with one molecule of alkyne. For example when 1,2-naphthyne (**3**) generated from triflate **9** was reacted with a 5-fold excess of DMAD in the presence of $Pd_2(dba)_3$ (0.05 equiv), the tetrasubstituted phenanthrene **32** was isolated as the only product in an excellent 94% yield (Scheme 4); when the catalyst was $Pd(PPh_3)_4$ (0.1 equiv) and a lower excess of alkyne was used (1.4 equiv), the

(16) (a) Maitlis, P. M. *Pure Appl. Chem.* **1973**, *33*, 489−512. (b) Yamamoto, Y.; Nagata, A.; Itoh, K. *Tetrahedron Lett.* **1999**, *40*, 5035−5038.

(17) Very electron-deficient alkynes (e.g., DMAD) undergo cycloaddition reactions when palladacyclopentadiene complexes are used as precursors of Pd(0) catalysts: (a) Brown, L. D.; Itoh, K.; Suzuki, H.; Hirai, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 8232−8238. (b) Stephan, C.; Munz, C.; Dieck, H. *J. Organomet. Chem.* **1993**, *452*, 223−227.

(18) Cyclization of alkynes by Pd(0) complexes and AcOH occurs via a different mechanism, involving Pd(II)−H complexes as active catalysts: (a) Negishi, E.; Harring, S. L.; Owczarczyk, Z.; Mohamud, M. M.; Ay, A. *Tetrahedron Lett.* **1992**, *33*, 3253−3256. (b) Brown, S.; Clarkson, S.; Grigg, R.; Sridharan, V. *Tetrahedron Lett.* **1993**, *34*, 157−160.

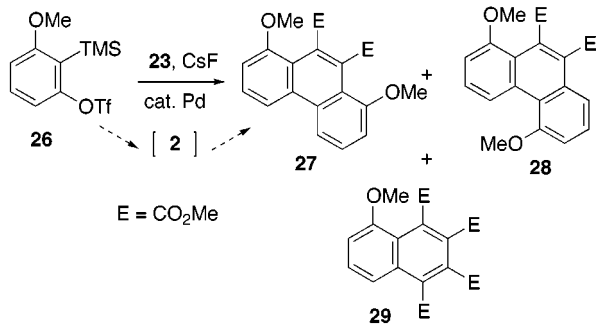
(19) Cyclotrimerizations promoted by Pd/C and Me_3SiCl in THF probably involve Pd(II) species (e.g., $PdCl_2$) as active catalysts: Jhigan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 1161−1165.

(20) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211−1214.

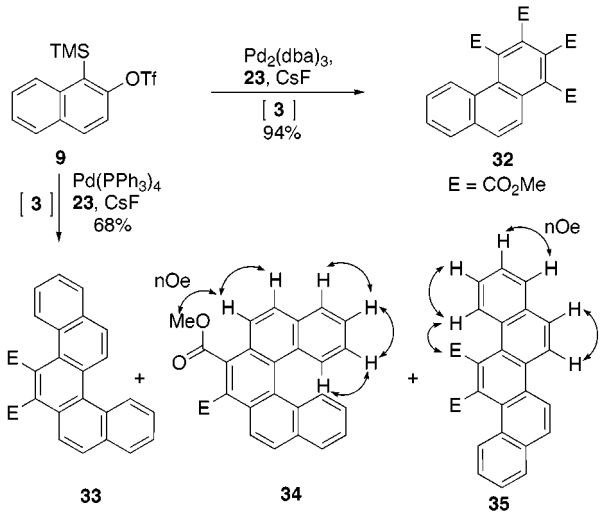
(21) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879−3891.

(22) (a) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1604−1606. (b) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169−175.

Scheme 3



Scheme 4



product was a mixture of the three possible regioisomers resulting from the cycloaddition of two molecules of naphthyne and one molecule of alkyne, **33**, **34**, and **35** (in 7.2:2.6:1 ratio as determined by ^{1}H NMR). As expected, the major product was the asymmetric isomer **33**. Identification of the symmetric isomers was based on their ^{1}H NMR spectra, particularly on diagnostic chemical shifts and on COSY and NOESY experiments (NOE correlations shown in Scheme 4). Despite the low regioselectivity of this reacion, which limits its synthetic utility, it nevertheless allows the construction of three interesting polycyclic systems, remarkably the pentahelicene **34**, a system for which few synthetic approaches are available.[23,3b]

The above results, and those obtained in analogous cycloaddition experiments with arynes **4**, **5**, and **6** (generated from the corresponding *o*-trimethylsilylaryl triflates **13**, **20**, and **21**, respectively) are summarized in Table 2. Particular attention is drawn to the synthesis of the highly strained dibenzo[*f*,*j*]picene **37** in good yield by Pd(PPh$_3$)$_4$-catalyzed cocyclotrimerization of phenanthryne **4** with DMAD (entry 3) and to the excellent yields obtained in the reactions catalyzed by Pd$_2$(dba)$_3$ (entries 2, 4, 5, and 6), which afforded the tetrasubstituted triphenylene **36**, chrysene **38**, and benzo[*c*]phenanthrene ([4]-helicene) **39**.

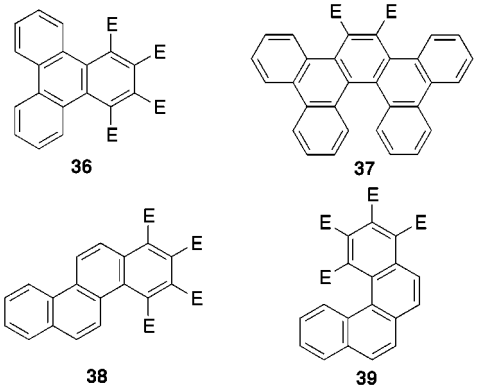
In conclusion, this work shows that arynes can undergo selective palladium-catalyzed cocyclotrimerization with DMAD, and that by appropriate choice of the catalyst

(23) Willmore, N. D.; Liu, L.; Katz, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1093−1095.

Table 2. Pd-Catalyzed Cocyclizations of Polycyclic Arynes 3−6 with DMAD

			product yields, %[b]		
entry	aryne	cond.[a]	[2 aryne + 1 DMAD]	[1 aryne + 2 DMAD]	aryne trimers
1	**3**	A	68 (**33** + **34** + **35**)[c]	−	21
2	**3**	B	−	94 (**32**)	−
3	**4**	A	62 (**37**)	−	13
4	**4**	B	−	91 (**36**)	−
5	**5**	B	−	96 (**38**)	−
6	**6**	B	−	74 (**39**)	−

[a] Procedure A: DMAD (1.4 equiv), CsF (2 equiv), Pd(PPh$_3$)$_4$ (0.1 equiv); CH$_3$CN, rt. Procedure B: DMAD (5 equiv), CsF (2 equiv), Pd$_2$(dba)$_3$ (0.05 equiv); CH$_3$CN, rt. [b] Yield of isolated products. [c] Ratio **33**/**34**/**35**, 7.2:2.6:1, as determined by ^{1}H NMR.



the reaction can be selectively directed either toward the cocyclization of one molecule of aryne with two molecules of alkyne or to the reaction of two molecules of aryne with one molecule of alkyne. The method can be applied to polycyclic arynes and provides convergent access to a variety of polycyclic aromatic compounds.

Experimental Section

General. All reactions were performed under argon. Solvents were dried by distillation from a drying agent: Et$_2$O and THF from Na/benzophenone; toluene from Na; CH$_3$CN from CaH$_2$. TMSCl and *i*-Pr$_2$NH were distilled from CaH$_2$ prior to use. Reported melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 250.13 and 62.83 MHz, respectively. LR and HR mass spectra were recorded using EI (70 eV) or FAB. TLC was performed on Merck silica gel 60 F_{254} or type E Merck aluminum oxide 60 F_{254}; chromatograms were visualized with UV light (254 and 360 nm), phosphomolybdic acid, and/or *p*-anisaldehyde. Column chromatography was performed on Merck silica gel 60 (ASTM 230−400 mesh) or Merck neutral alumina 90 (ASTM 70−230 mesh), deactivated with 6% water. 2-Trimethylsilylphenyl triflate[20] and Pd(PPh$_3$)$_4$[24] were prepared following published procedures. Commercial reagents were purchased from Aldrich Chemical Co. and were used without further purification, except 9-phenanthrol, which was chromatographed before used.

Preparation of the Precursors of the Arynes.[25]

1-Trimethylsilylnaphthyl 2-Trifluoromethanesulfonate (9). A solution of 1-bromo-2-naphthol (**7**, 2.23 g, 10 mmol) and HMDS (2.06 mL, 10 mmol) in THF (40 mL) was refluxed for 90 min. 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 reaction mixture showed

(24) Hegedus, L. S. In *Palladium in Organic Synthesis*, in *Organometallics in Synthesis: A Manual*; Schlosser, M., Ed.; John Wiley & Sons: New York, 1994.

(25) For the preparation of **22b** and **26**, see Supporting Information of ref 11.

the formation of silyl ether **8** in quantitative yield. The crude product was dissolved in THF (40 mL), the solution was cooled to −100 °C, and *n*-BuLi (4.46 mL, 2.41 M, 11 mmol) was added dropwise. Stirring was kept up for 20 min while the temperature reached −80 °C, whereupon Et_2O (40 mL) was added. The mixture was again cooled to −100 °C, Tf_2O (2.1 mL, 12.5 mmol) was added dropwise, and stirring was again kept up for 20 min while the temperature returned to −80 °C. Cold saturated aqueous $NaHCO_3$ (20 mL) was added, 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; 5:95 Et_2O/hexane) to afford **9** as a colorless oil (3.032 g, 87%): ^{1}H NMR ($CDCl_3$) δ 8.21 (d, J = 9.0 Hz, 1H), 7.93−7.87 (m, 2H), 7.61−7.51 (m, 2H), 7.40 (d, J = 9.1 Hz, 1H), 0.58 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.5, 137.5, 132.4, 132.3, 129.3, 129.0, 128.8, 126.7, 126.3, 119.1, 118.7 (q, J = 321 Hz), 2.2; MS, *m*/*z* (%): 348 (1.2).

10-Bromo-9-phenanthrol (11). A solution of NBS (819 mg, 4.6 mmol) in CH_2Cl_2 (45 mL) was added dropwise over 30 min to a solution of 9-phenanthrol (882 mg, 4.6 mmol) and *i*-Pr_2NH (64 μL, 0.46 mmol) in CH_2Cl_2. After addition was complete, the mixture was stirred at room temperature for 1 h, poured on H_2O (80 mL), and acidified to pH 1 by careful addition of concentrated H_2SO_4. The resulting mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue (SiO_2, 1:3 AcOEt/hexane) afforded **11** as a white solid (1.064 g, 84%): ^{1}H NMR ($CDCl_3$) δ 8.54 (t, J = 7.6 Hz, 2H), 8.29 (dd, J = 7.4, 1.7 Hz, 1H), 8.05 (dd, J = 8.1, 1.2 Hz, 1H), 7.67−7.44 (m, 4H), 6.22 (s, 1H); ^{13}C NMR (THF-d_8) δ 150.2, 132.9, 132.4, 129.5, 129.3, 129.0, 128.6, 128.1, 128.0, 126.5, 125.1, 124.6, 124.5, 105.1; MS, *m*/*z* (%): 274 (20), 272 (20); HRMS for $C_{14}H_9{}^{79}BrO$, calcd: 271.9837, found: 271.9841; HRMS for $C_{14}H_9{}^{81}BrO$, calcd: 273.9816, found: 273.9811.

10-Trimethylsilylphenanthryl 9-Trifluoromethanesulfonate (13). *n*-BuLi (480 μL, 2.35 M, 1.125 mmol) was added dropwise to a solution of **11** (205 mg, 0.75 mmol) in THF (10 mL) cooled to −78 °C. After stirring at −78 °C for 15 min, TMSCl (150 μL, 1.2 mmol) was added, the cooling bath was removed, and stirring was kept for 10 min at room temperature. The mixture was again cooled to −78 °C, *n*-BuLi (320 μL, 2.35 M, 0.75 mmol) was added dropwise, stirring was kept up at −78 °C for 15 min, and TMSCl (150 μL, 1.2 mmol) was added. Stirring at room temperature was kept up overnight, H_2O (15 mL) was added, and the resulting mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford crude **12**, which was taken to the next step without further purification. To a solution of this crude residue in Et_2O (10 mL) at 0 °C, *n*-BuLi (335 μL, 2.35 M, 0.79 mmol) was dropwise added. The mixture was stirred at room temperature for 4 h and cooled again to 0 °C, and then Tf_2O (880 μL, 1.5 mmol) was added. Stirring was kept for 40 min, and then saturated aqueous $NaHCO_3$ (15 mL) was added. The mixture was extracted with Et_2O, and 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; hexane) to afford **13** (138 mg, 55%): ^{1}H NMR ($CDCl_3$) δ 8.53−8.47 (m, 2H), 8.07 (m, 1H), 7.97 (m, 1H), 7.60−7.44 (m, 4H), 0.46 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 147.9, 134.6, 132.7, 130.5, 130.0, 129.7, 128.4, 127.3, 127.1, 126.6, 125.8, 123.3, 122.7, 122.2, 118.8 (q, J = 320 Hz), 2.2; MS, *m*/*z* (%): 398 (13); HRMS for $C_{18}H_{17}F_3O_3SSi$, calcd: 398.0620, found: 398.0626.

1-Bromonaphthyl 2-Trifluoromethanesulfonate (14). *i*-Pr_2NH (3 mL, 17.2 mmol) and Tf_2O (5.8 mL, 34.4 mmol) were added to a solution of 1-bromo-2-naphthol (**7**, 3.84 g, 17.2 mmol) in CH_2Cl_2 (30 mL) cooled to 0 °C, and the reaction mixture was stirred at room temperature for 2 h. Aqueous $NaHCO_3$ (5%, 20 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2. 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; 3:97 CH_2Cl_2/hexane) to afford **14** (5.49 g, 90%): ^{1}H NMR ($CDCl_3$) δ 8.33 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.7 Hz, 2H), 7.74−7.60 (m, 2H), 7.44 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 144.7, 132.5, 132.1, 129.5, 128.4, 127.9, 127.3, 127.0, 119.3, 118.8 (q, J = 320 Hz), 115.8; MS, *m*/*z* (%): 356 (19), 354 (18); HRMS for $C_{11}H_6{}^{79}BrF_3O_3S$, calcd: 353.9173, found: 353.9165; HRMS for $C_{11}H_6{}^{81}BrF_3O_3S$, calcd: 355.9153, found: 355.9159.

1-Phenanthrol (16) and 4-Phenanthrol (17). *n*-BuLi (7.4 mL, 2.29 M, 16.8 mmol) was dropwise added to a solution of **14** (5.44 g, 15.3 mmol) and furan (7.3 mL, 153 mmol) in THF (40 mL) cooled to −78 °C. The mixture was allowed slowly to reach room temperature and was stirred overnight. Then 10% aqueous HCl (20 mL) was added, and vigorous stirring was kept up for 5 h. The resulting mixture was extracted with Et_2O, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was chromatographed (SiO_2, 1:9 AcOEt/hexane) to afford a mixture of phenanthrols **16** and **17** (2.31 g, 78%, 2.6:1 ratio as determined by ^{1}H NMR) which was taken to the next step without further purification. A small portion of this mixture was subjected to a second column chromatography (SiO_2; 1:9 AcOEt/hexane) to obtain analytical samples of **16** and **17**. Data for **16**: ^{1}H NMR ($CDCl_3$) δ 8.66 (d, J = 8.5, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 9.1 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 9.1 Hz, 1H), 7.69−7.57 (m, 2H), 7.49 (t, J = 8.1 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 5.33 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 151.8, 132.1, 131.9, 130.0, 128.6, 126.7, 126.6 (2 CH), 126.2, 123.1, 121.8, 119.9, 115.5, 110.6; MS, *m*/*z* (%): 194 (95), 165 (100); HRMS for $C_{14}H_{10}O$, calcd: 194.0732, found: 194.0723. Data for **17**: ^{1}H NMR ($CDCl_3$) δ 9.51 (dd, J = 8.4, 1.4 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.61−7.42 (m, 4H), 7.35 (dd, J = 7.9, 1.3 Hz, 1H), 7.25 (t, J = 7.7 Hz, 1H), 6.77 (dd, J = 7.6, 1.3 Hz, 1H), 5.62 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 154.3, 134.9, 133.5, 130.2, 128.5, 128.2, 128.0, 127.0, 126.5, 126.3, 125.9, 121.6, 119.3, 113.2; MS, *m*/*z* (%): 194 (100); HRMS for $C_{14}H_{10}O$, calcd: 194.0732, found: 194.0728.

2-Bromo-1-phenanthrol (18) and 3-Bromo-4-phenanthrol (19). A solution of NBS (2.07 g, 11.6 mmol) in CH_2Cl_2 (70 mL) was added dropwise over 30 min to a solution of the previously obtained mixture of **16** and **17** (2.25 g, 11.6 mmol) and *i*-Pr_2NH (162 μL, 1.16 mmol) in CH_2Cl_2 (50 mL). After addition was complete, the mixture was stirred at room temperature for 1 h, poured on H_2O (150 mL), and acidified to pH 1 by careful addition of concentrated H_2SO_4. The resulting mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue (SiO_2, 5:95 AcOEt/hexane) afforded **18** (1.520 g, 48%) and **19** (600 mg, 19%) as white solids. Data for **18**: ^{1}H NMR ($CDCl_3$) δ 8.58 (m, 1H), 8.24 (d, J = 9.1, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.96−7.62 (m, 5H), 6.07 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 148.4, 131.9, 130.7, 129.5, 128.6, 128.5, 127.0, 126.9, 126.7, 122.8, 122.1, 120.2, 116.0, 105.9; MS, *m*/*z* (%): 274 (100), 272 (97). Data for **19**: ^{1}H NMR ($CDCl_3$) δ 9.56 (d, J = 8.3 Hz, 1H), 7.80 (dd, J = 7.6, 1.6 Hz, 1H), 7.68−7.49 (m, 5H), 7.28 (d, J = 8.5 Hz, 1H), 6.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 150.3, 134.1, 132.6, 129.8, 129.0, 128.60, 128.55, 128.3, 126.8, 126.53, 126.48, 121.8, 119.9, 108.8; MS, *m*/*z* (%): 274 (76), 272 (73).

2-Trimethylsilylphenanthryl 1-Trifluoromethanesulfonate (20). A solution of 1-bromo-2-phenanthrol (**18**) (221 mg, 0.81 mmol) and HMDS (165 μL, 0.81 mmol) in THF (5 mL) was refluxed for 90 min. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH_3 and unreacted HMDS. Following the procedure described above for the preparation of **9**, the crude product so obtained was treated with *n*-BuLi (385 μL, 2.41 M, 0.93 mmol) and Tf_2O (170 μL, 1.01 mmol). The residue obtained after workup was purified by column chromatography (SiO_2; hexane) to afford **20** (263 mg, 82%) as a white solid: mp 68 °C; ^{1}H NMR ($CDCl_3$) δ 8.55−8.50 (m, 2H), 7.88−7.51 (m, 6H), 0.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.0, 133.3, 132.4, 132.1, 131.9, 129.2, 128.7, 128.5, 127.7, 127.4, 125.2, 123.0,

122.5, 119.3, 118.8 (q, J = 321 Hz), 0.1; MS, *m/z* (%): 398 (23); HRMS for $C_{18}H_{17}F_3O_3SSi$, calcd: 398.0620, found: 398.0624.

3-Trimethylsilylphenanthryl 4-Trifluoromethanesulfonate (21). A solution of 3-bromo-4-phenanthrol (**19**, 650 mg, 2.38 mmol) and HMDS (490 μL, 2.83 mmol) in THF (10 mL) was refluxed for 90 min. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH_3 and unreacted HMDS. Following the procedure described above for the preparation of **9**, the crude product was treated with *n*-BuLi (1.09 mL, 2.41 M, 2.62 mmol) and Tf_2O (500 μL, 3.0 mmol). The residue obtained after workup was purified by column chromatography (SiO_2; hexane) to afford **21** as a white solid (747 mg, 79%): mp 49 °C; ^{1}H NMR ($CDCl_3$) δ 9.10 (m, 1H), 7.96−7.66 (m, 7H), 0.66 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.5, 135.5, 134.1, 133.1, 132.4, 129.0, 128.5, 128.1, 127.9, 127.6, 127.3, 126.5, 125.5, 123.9, 118.5 (q, J = 321 Hz), 0.5; MS, *m/z* (%): 398 (17); HRMS for $C_{18}H_{17}F_3O_3SSi$, calcd: 398.0620, found: 398.0620.

General Procedures for the Cocyclization of Arynes with DMAD. Procedure a. A solution of the aryne precursor (0.5 mmol approximately) in CH_3CN (5 mL) was added to a suspension of finely powdered anhydrous CsF (2 equiv), DMAD (**23**, 1.4 equiv), and $Pd(PPh_3)_4$ (0.1 equiv) in CH_3CN (5 mL). The mixture was stirred under argon at room temperature for 12 h. The solvent was evaporated, and the residue was subjected to column chromatography to isolate the products. **Procedure b.** As for Procedure a, but using a larger excess of **23** (5 equiv) and $Pd_2(dba)_3$·$CHCl_3$ (0.05 equiv) as catalyst.

Cocyclization of 1,2-Didehydrobenzene (benzyne, 1a). Synthesis of Dimethyl Phenanthrene-9,10-dicarboxylate (24a). Procedure a was followed, using **22a** (209 mg, 0.7 mmol), $Pd(PPh_3)_4$ (81 mg, 0.07 mmol), **23** (0.120 mL, 0.98 mmol), and CsF (213 mg, 1.4 mmol) in CH_3CN (16 mL). Column chromatography (Al_2O_3; 1:4 CH_2Cl_2/hexane, then 1:1:2 CH_2Cl_2/Et_2O/hexane) afforded triphenylene (1 mg, 2%), **24a** (86 mg, 84%) and **25a** (18 mg, 7%). **Synthesis of Tetramethyl Naphthalene-1,2,3,4-tetracarboxylate (25a).** Procedure b was followed, using **22a** (179 mg, 0.6 mmol), $Pd_2(dba)_3$·$CHCl_3$ (31 mg, 0.03 mmol), **23** (0.380 mL, 3 mmol), and CsF (182 mg, 1.2 mmol) in CH_3CN (12 mL). Column chromatography (Al_2O_3; 1:4 CH_2Cl_2/hexane, then 1:1:2 CH_2Cl_2/Et_2O/hexane) afforded **24a** (9 mg, 10%) and **25a** (180 mg, 83%). Data for **24a**: mp 130 °C; ^{1}H NMR ($CDCl_3$) δ 8.67 (d, J = 7.9 Hz, 2 H), 8.15 (dd, J = 8.1, 1.1 Hz, 2 H), 7.71−7.64 (m, 4 H), 4.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 168.3, 130.9, 129.8, 128.4, 127.6, 126.9, 126.8, 122.8, 52.8; MS, *m/z* (%): 294 (16); HRMS for $C_{18}H_{14}O_4$, calcd: 294.0892, found: 294.0905; Anal. for $C_{18}H_{14}O_4$, calcd: C, 73.46; H, 4.80; found: C, 73.90; H, 5.24. Data for **25a**:[26] mp 147 °C; ^{1}H NMR ($CDCl_3$) δ 8.07 (dd, J = 6.5, 3.3 Hz, 2H), 7.69 (dd, J = 6.5, 3.3 Hz, 2H), 4.02 (s, 6H), 3.92 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 167.1, 166.6, 133.8, 129.9, 129.7, 127.4, 126.1, 53.1; MS, *m/z* (%): 360 (25); HRMS for $C_{18}H_{16}O_8$, calcd: 360.0845, found: 360.0804.

Cocyclization of 4,5-Difluoro-1,2-didehydrobenzene (4,5-difluorobenzyne, 1b). Synthesis of Dimethyl 2,3,6,7-Tetrafluorophenanthrene-9,10-dicarboxylate (24b). Procedure a was followed, using **22b** (117 mg, 0.35 mmol), $Pd(PPh_3)_4$ (41 mg, 0.035 mmol), **23** (0.172 mL, 1.4 mmol) and CsF (106 mg, 0.7 mmol). Column chromatography (SiO_2; 1:3 to 1:1 CH_2Cl_2/hexane then 1:1:2 CH_2Cl_2/Et_2O/hexane) afforded 2,3,6,7,10,11-hexafluorotriphenylene (3 mg, 8%), phenanthrene **24b** (46 mg, 64%), and naphthalene **25b** (12 mg, 8%). **Synthesis of Tetramethyl 6,7-Difluoronaphthalene-1,2,3,4-tetracarboxylate (25b).** Procedure b was followed, using **22b** (100 mg, 0.3 mmol), $Pd_2(dba)_3$·$CHCl_3$ (16 mg, 0.015 mmol), **23** (0.184 mL, 1.5 mmol), and CsF (91 mg, 0.6 mmol) in CH_3CN (6 mL). Column chromatography (SiO_2; 1:1 CH_2Cl_2/hexane then 1:1:2 CH_2Cl_2/Et_2O/hexane) afforded **24b** (5 mg, 9%) and **25b** (64 mg,54%). Data for **24b**: mp 223 °C; ^{1}H NMR ($CDCl_3$) δ 8.12 (dd, J = 11.6, 7.5 Hz, 2H), 7.93 (dd, J = 11.7, 8.0 Hz, 2H), 3.97 (s, 6H); MS, *m/z* (%): 366 (35); HRMS for $C_{18}H_{10}O_4F_4$, calcd: 366.0515, found: 366.0512. Data for **25b**:[27] mp: 196 °C; ^{1}H NMR ($CDCl_3$) δ 7.87 (t, J = 9.6 Hz, 2H), 3.94 (s, 6H), 3.85 (s, 6H); MS *m/z* (%): 396 (19).

Cocyclization of 3-Methoxy-1,2-didehydrobenzene (3-methoxybenzyne, 2). Synthesis of Dimethyl 1,8-Dimethoxyphenanthrene-9,10-dicarboxylate (27) and Dimethyl 1,5-Dimethoxyphenanthrene-9,10-dicarboxylate (28). Procedure a was followed, using **26** (164 mg, 0.5 mmol), $Pd(PPh_3)_4$ (16 mg, 0.025 mmol), **23** (0.074 mL, 0.6 mmol), and CsF (152 mg, 1 mmol). Column chromatography (Al_2O_3; 1:3 CH_2Cl_2/hexane then 1:1:2 CH_2Cl_2/Et_2O/hexane) afforded 1,5,12- and 1,5,9-trimethoxytriphenylenes (3 mg, 6%), **27** (20 mg, 22%), **28** (53 mg, 60%), and **29** (12 mg, 6%). **Synthesis of Tetramethyl 5-Methoxynaphthalene-1,2,3,4-tetracarboxylate (29).** Procedure a was followed, using **26** (115 mg, 0.35 mmol), $Pd_2(dba)_3$·$CHCl_3$ (18 mg, 0.018 mmol), **23** (0.215 mL, 1.75 mmol), and CsF (106 mg, 0.7 mmol) in CH_3CN (7 mL). Column chromatography (SiO_2; 1:1:2 CH_2Cl_2/Et_2O/hexane) afforded **27** (2 mg, 3%), **28** (7 mg, 11%), and **29** (112 mg, 82%). Data for **27**: mp 252 °C; ^{1}H NMR ($CDCl_3$) δ 8.27 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 8.2 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 3.96 (s, 12H); ^{13}C NMR (DMSO-d_6) δ 155.2, 131.2, 129.2, 125.5, 117.8, 116.2, 109.1, 56.8, 52.2; MS, *m/z* (%): 354 (92); HRMS for $C_{20}H_{18}O_6$, calcd.: 354.1103, found: 354.1103. Data for **28**: mp 159 °C; ^{1}H NMR ($CDCl_3$, 0.05 M) δ 9.33 (dd, J = 8.8, 0.7 Hz, 1H), 7.65−7.51 (m, 3H), 7.18 (dd, J = 7.2, 1.8 Hz, 1H), 7.08 (dd, J = 7.5, 0.4 Hz, 1H), 4.06 (s, 3H), 4.01 (s, 3H), 3.95 (s, 3H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.0, 168.7, 158.4, 155.2, 132.3, 129.6, 129.1, 128.2, 127.7, 127.5, 121.3, 121.0, 118.8, 118.6, 109.8, 108.3, 56.7, 55.7, 52.7, 52.3; MS, *m/z* (%): 354 (100); HRMS for $C_{20}H_{18}O_6$, calcd: 354.1103, found: 354.1102; Anal. for $C_{20}H_{18}O_6$, calcd: C, 67.79; H, 5.12; found: C, 67.78; H, 5.39. Data for **29**: mp 134 °C; ^{1}H NMR ($CDCl_3$) δ 7.61−7.59 (m, 2H), 7.02 (dd, J = 6.1, 2.7 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.95 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.7, 167.4, 166.6, 166.5, 155.4, 133.2, 132.2, 131.4, 130.2, 127.9, 126.5, 122.0, 118.5, 108.8, 56.7, 53.1 (overlap), 52.6; MS, *m/z* (%): 390 (59); HRMS for $C_{19}H_{18}O_9$ calcd: 390.0951, found: 390.0993.

Cocyclization of 1,2-Didehydronaphthalene (1,2-naphthyne, 3). Synthesis of Tetramethyl Phenanthrene-1,2,3,4-tetracarboxylate (32). Procedure b was followed, using **9** (52 mg, 0.15 mmol), $Pd_2(dba)_3$·$CHCl_3$ (8 mg, 0.0075 mmol), **23** (92 μL, 0.75 mmol), and CsF (46 mg, 0.3 mmol) in CH_3CN (3 mL). Column chromatography (SiO_2; 3:7 CH_2Cl_2/hexane then 1:1:3 CH_2Cl_2/Et_2O/hexane) afforded **32** as white solid (58 mg, 94%): mp 162 °C; ^{1}H NMR ($CDCl_3$) δ 8.25 (d, J = 8.2 Hz, 1H), 7.90−7.85 (m, 2H), 7.77 (d, J = 9.1 Hz, 1H), 7.69−7.55 (m, 2H), 4.03 (s, 3H), 4.01 (s, 3H), 3.99 (s, 3H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.9, 167.6, 167.3, 166.2, 133.9, 133.3, 131.9, 131.2, 130.3, 129.5, 128.9, 128.6, 128.2, 127.2, 126.9, 125.7, 122.8, 53.24, 53.21, 53.18, 53.13; IR (film): 1729 cm^{-1}; UV (hexane), λ_{max}: 268, 222, 202 nm; MS, *m/z* (%): 410 (71); HRMS for $C_{22}H_{18}O_8$, calcd: 410.1002, found: 410.1016. **Synthesis of Dimethyl Benzo[*c*]chrysene-13,14-dicarboxylate (33), Dimethyl Dibenzo[*c,g*]phenanthrene-3,4-dicarboxylate (34), and Dimethyl Picene-13,14-dicarboxylate (35).** Procedure a was followed, using **9** (67 mg, 0.19 mmol), $Pd(PPh_3)_4$ (22 mg, 0.019 mmol), **23** (38 μL, 0.31 mmol), and CsF (59 mg, 0.38 mmol) in CH_3CN (4 mL). Column chromatography (SiO_2; 1:1:8 CH_2Cl_2/Et_2O/hexane) afforded a mixture of the naphthyne trimers (5 mg, 21%) and a mixture of cotrimers **33**, **34**, and **35** (26 mg, 68%, 7.2:2.6:1 ratio, as determined by ^{1}H NMR). Analytical samples were obtained by preparative TLC. Data for **33**: ^{1}H NMR ($CDCl_3$) δ 8.88 (d, J = 9.2 Hz, 2H), 8.30 (d, J = 8.2 Hz, 1H), 8.05−7.96 (m, 5H), 7.7−7.61 (m, 4H), 4.10 (s, 3H), 3.99 (s, 3H); MS, *m/z* (%): 394 (100); HRMS for $C_{26}H_{18}O_4$, calcd: 394.1205, found: 394.1202. Data for **34**: ^{1}H NMR ($CDCl_3$) δ 8.31 (d, J = 8.6 Hz, 2H, H-10 and H-11), 8.12 (d, J = 9.0 Hz, 2H, H-2 and H-5), 7.99 (d, J = 9.1 Hz, 2H, H-1 and H-6), 7.95 (d, J = 8.6 Hz, 2H, H-7 and H-14), 7.55 (t, J = 7.3 Hz, 2H, H-8 and H-13), 7.25 (d, J = 7.6 Hz, 2H, H-9 and H-11),

(26) Sakakibara, T.; Tanaka, Y.; Yamasaki, S. *Chem. Lett.* **1986**, 797−800.

(27) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, *14*, 1267−1277.

4.07 (s, 6H); MS, *m*/*z* (%): 394 (64), 363 (16), 347 (39), 276 (100); HRMS for $C_{26}H_{18}O_4$, calcd: 394.1205, found: 394.1200. Data for **35**: ^{1}H NMR ($CDCl_3$) δ 8.74 (d, J = 9.2 Hz, 2H, H-6 and H-7), 8.48 (m, 2H, H-1 and H-11), 8.09 (d, J = 9.3 Hz, 2H, H-5 and H-8), 8.02 (m, 2H, H-4 and H-9), 7.74−7.62 (m, 4H; H-2, H-3, H-10 and H-11), 4.03 (s, 6H); MS, *m*/*z* (%): 394 (100); HRMS for $C_{26}H_{18}O_4$, calcd: 394.1205, found: 394.1214.

Cocyclization of 9,10-Didehydrophenanthrene (9,10-phenanthryne, 4). Synthesis of Tetramethyl Triphenylene-1,2,3,4-tetracarboxylate (36). Procedure b was followed, using **13** (40 mg, 0.10 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mg, 0.005 mmol), **23** (67 μL, 0.5 mmol), and CsF (30 mg, 0.2 mmol) in CH_3CN (2 mL). The resulting suspension was filtered under vacuum. The solid obtained was washed with CH_3CN (2 × 1 mL) and dissolved in CH_2Cl_2/H_2O 7:1 (40 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure to afford **36**[28] (42 mg, 91%): mp 250 °C; ^{1}H NMR ($CDCl_3$) δ 8.56 (d, J = 8.2 Hz, 2H), 8.07 (d, J = 8.3 Hz, 2H), 7.70 (dt, J = 7.6 y 1.0 Hz, 2H), 7.55 (dt, J = 7.7 y 1.2 Hz, 2H), 3.95 (s, 6H), 3.90 (s, 6H); IR (film): 1728 cm^{-1}; UV ($CHCl_3$), λ_{max}: 280, 252 nm; MS, *m*/*z* (%): 460 (100); HRMS for $C_{26}H_{20}O_8$, calcd: 460.1158, found: 460.1169. **Synthesis of Dimethyl Dibenzo[*f*,*j*]picene-17,18-dicarboxylate (37).** Procedure a was followed, using **13** (61 mg, 0.15 mmol), $Pd(PPh_3)_4$ (18 mg, 0.015 mmol), **23** (26 μL, 0.22 mmol), and CsF (47 mg, 0.31 mmol) in CH_3CN (3 mL). The resulting suspension was filtered under vacuum. The solid obtained was washed with CH_3CN and dissolved in 7:1 CH_2Cl_2/H_2O (40 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure to afford a mixture of the aryne trimer[9] and **37** (27 mg, 1:6.9 ratio, as determined by ^{1}H NMR). Column chromatography of the mixture (SiO_2; 1:1 CH_2Cl_2/hexane then 4:1 CH_2Cl_2/hexane) afforded **37**[28] (23 mg, 62%) as a white solid: mp 331 °C; ^{1}H NMR ($CDCl_3$) δ 8.62 (d, J = 8.2 Hz, 2H), 8.49 (d, J = 7.8 Hz, 2H), 8.15 (d, J = 8.3 Hz, 2H), 8.14 (dd, J = 8.2 y 0.9 Hz, 2H), 7.72 (dt, J = 7.6 y 1.2 Hz, 2H), 7.60 (dt, J = 7.7 y 1.3 Hz, 2H), 7.52 (dt, J = 7.7 y 1.2 Hz, 2H), 7.18 (dt, J = 7.7 y 1.2 Hz, 2H), 3.97 (s, 6H); IR (film): 1729 cm^{-1}; UV ($CHCl_3$), λ_{max}: 366, 322, 290, 246 nm; MS, *m*/*z* (%): 494 (72); HRMS for $C_{34}H_{22}O_4$, calcd: 494.1518, found: 494.1517.

Cocyclization of 1,2-Didehydrophenanthrene (1,2-phenanthryne, 5). Synthesis of Tetramethyl Chrysene-1,2,3,4-tetracarboxylate (38). Procedure b was followed, using **20** (40 mg, 0.10 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mg, 0.005 mmol), **23** (67 μL, 0.5 mmol), and CsF (30 mg, 0.2 mmol) in CH_3CN (2 mL). Column chromatography (SiO_2; CH_2Cl_2/hexane 1:1 then CH_2Cl_2/Et_2O/hexane 3:3:4) afforded **38** as a white solid (44 mg, 96%): mp 183 °C; ^{1}H NMR ($CDCl_3$) δ 8.83 (d, J = 9.3 Hz, 1H), 8.70 (dd, J = 8.9 y 1.3 Hz, 1H), 8.18 (d, J = 9.3 Hz, 1H), 8.05 (d, J = 9.3 Hz, 1H), 7.98−7.90 (m, 2H), 7.72−7.67 (m, 2H), 4.08 (s, 3H), 3.99 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.0, 167.61, 167.56, 166.1, 134.2, 132.3, 132.1, 130.8, 130.0, 129.74, 129.68, 129.1, 128.3, 127.8, 127.6, 127.3, 127.0, 126.3, 125.4, 123.7, 123.4, 123.2, 53.5, 53.27, 53.25, 53.20; IR (film): 1734 cm^{-1}; UV ($CHCl_3$), λ_{max}: 294, 252 nm; MS, *m*/*z* (%): 460 (100); HRMS for $C_{26}H_{20}O_8$, calcd: 460.1158, found: 460.1158.

Cocyclization of 3,4-Didehydrophenanthrene (3,4-phenanthryne, 6). Synthesis of Tetramethyl Benzo[*c*]-phenanthrene-1,2,3,4-tetracarboxylate (39). Procedure b was followed, using **21** (40 mg, 0.10 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mg, 0.005 mmol), **23** (67 μL, 0.5 mmol), and CsF (30 mg, 0.2 mmol) in CH_3CN (2 mL). Column chromatography (SiO_2; CH_2Cl_2/hexane 1:1 then CH_2Cl_2/Et_2O/hexane 3:3:4) afforded **39** as a white solid (34 mg, 74%): mp 141 °C; ^{1}H NMR ($CDCl_3$) δ 8.31 (m, 1H), 8.03−7.93 (m, 4H), 7.81 (d, J = 8.5 Hz, 1H), 7.63−7.57 (m, 2H), 4.07 (s, 3H), 3.97 (s, 6H), 3.11 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.2, 167.7, 167.1, 165.9, 134.7, 132.4, 132.2, 132.1, 131.9, 130.8, 130.6, 130.1, 130.0, 128.9, 127.9, 127.0, 126.9, 126.72, 126.66, 125.5, 125.1, 123.6, 53.3, 53.2, 53.1, 52.4; IR (film): 1733 cm^{-1}; UV ($CHCl_3$), λ_{max}: 314, 270, 244 nm; MS, *m*/*z* (%): 460 (44); HRMS for $C_{26}H_{20}O_8$, calcd: 460.1158, found: 460.1151.

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Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **9**, **11**, **13**, **14**, **16**, **18**−**21**, **32**, **38**, and **39**, ^{1}H NMR spectra for compounds **33**−**37**, and COSY and NOESY spectra for compounds **34** and **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Satisfactory ^{13}C NMR spectra of **36** and **37** could not be obtained due to the poor solubility of these compounds in common solvents.