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Synthesis of Phenanthrene-Based Polycycles by Gold(I)-Catalyzed Cyclization of Biphenyl-Embedded Trienynes

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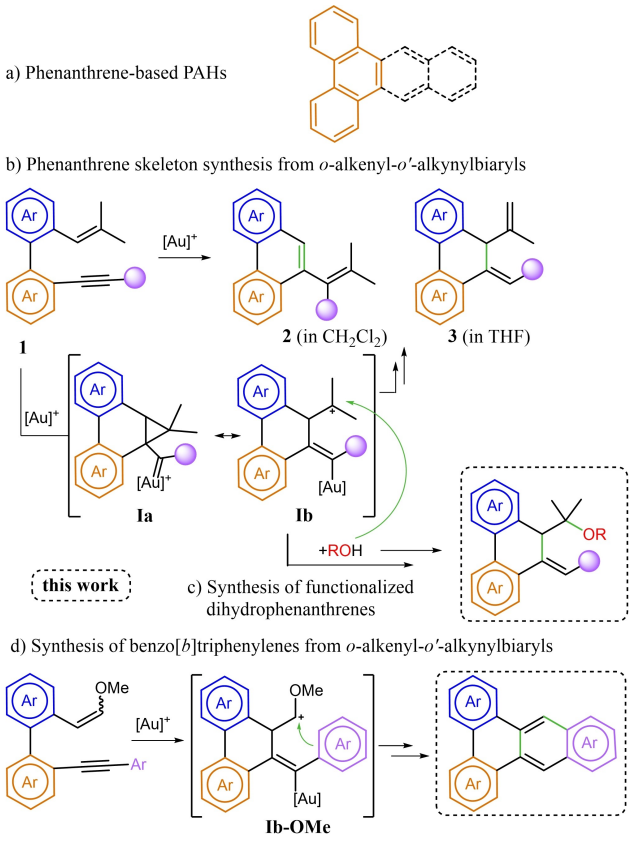
Abstract: Gold(I)-catalyzed cyclization of *o*-alkenyl-*o'*-alkynylbiaryls in the presence of external or internal nucleophiles provides a straightforward access to phenanthrene-based polycycles, which are of considerable interest in materials science. Thus, their reactions with alcohols yield functionalized dihydrophenanthrenes, in a process that can also be carried out intramolecularly, to provide phenanthrene-derived heteropolycyclic compounds. Moreover, benzo[*b*]triphenylenes can be synthesized from *o*-methoxyvinyl-*o'*-alkynylbiaryls, in a reaction in which an (hetero)aryl substituent at the triple bond acts as an internal nucleophile.

Keywords: Polycycles; Gold; Cyclization; Benzo[*b*]triphenylenes; Dihydrophenanthrenes

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have gained considerable attention due to their outstanding electrochemical and photophysical properties and widespread applications in optical, organic and electronic materials.[1] In particular, phenanthrene-based PAHs (Scheme 1a), such as benzo[*b*]triphenylenes,[2] exhibit excellent photochemical properties, good stability under irradiation and have been described as useful



Scheme 1. Phenanthrene-based compounds via gold(I)-catalyzed reactions of 1,3,5-trien-7-ynes.

singlet oxygen photosensitizers and components of semiconductor devices.[3] A plethora of synthetic approaches to these PAHs have been reported, including aryne cyclotrimerizations, oxidative cyclizations, cycloadditions, cross-coupling reactions and C–H activation.[4] However, most of these strategies usually result in low yields, limited substrate scope and/or require harsh reaction conditions. As such, the development of mild and effective routes to phenanthrene-based PAHs remains challenging and of great interest.

Gold(I)-catalyzed electrophilic π-activation of alkynes has become one of the most powerful tools for the straightforward construction of complex cyclic molecules from readily available starting materials under mild conditions.[5] Endowed with unsaturated C–C bonds, enynes are privileged building blocks and have been extensively used in direct and selective tandem cyclizations across C=C and C≡C bonds in a one-step operation.[6] The outcome of these reactions is mainly determined by the reaction conditions, the catalyst, and the substitution pattern of the enyne. In addition, the high tolerance of gold(I) complexes to functionality has allowed the synthesis of densely decorated carbo- and heterocycles via intra- or intermolecular cyclizations with nucleophiles.[7] In this scenario, and as part of our studies on gold(I)-catalyzed cycloisomerizations of conjugated polyenynes,[8,9] we have recently reported a solvent-controlled, gold-catalyzed selective synthesis of phenanthrenes **2** and dihydrophenanthrenes **3** from readily available *o*-alkenyl-*o'*-alkynylbiaryls **1**, a particular type of 1,7-enynes (Scheme 1b).[10] These reactions are proposed to proceed by way of a 6-*exo* nucleophilic addition of the olefin to the activated alkyne to generate a cyclopropyl gold carbene-like species **Ia**, which can also be considered to be a carbocationic intermediate **Ib**.[6b,11] As such, we envisioned that intermediate **I** could be inter- or intramolecularly trapped by suitable nucleophiles to access more elaborate polycyclic compounds.

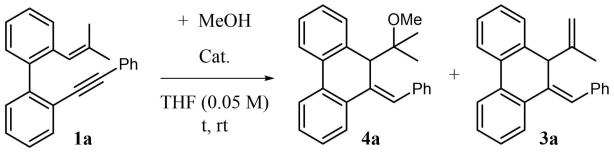
Herein we report that gold(I)-catalyzed reactions of *o*-alkenyl-*o'*-alkynylbiaryls in the presence of nucleophiles selectively produce phenanthrene-based compounds. Thus, the reaction of these substrates in the presence of alcohols gives dihydrophenanthrenes with enhanced complexity (Scheme 1c).[12] Moreover, given the appropriate design of the substitution pattern at the alkene and the alkyne of the starting trienynes, benzo[*b*]triphenylenes can be selectively synthesized in a single cascade process involving a Friedel-Crafts-type cyclization and subsequent aromatization with methanol elimination (Scheme 1d).

Results and Discussion

At the outset, and based on our previous report (Scheme 1b),[10] we explored the viability of the intended catalytic nucleophilic cyclization of the model substrate **1a** with an alcohol. Thus, we found that the use of PPh_3AuNTf_2 or JohnPhosAu(MeCN)SbF_6 (5 mol%) as catalyst in the presence of MeOH (50 equiv.) in THF at room temperature triggers selective formation of the desired alkoxy-functionalized dihydrophenanthrene **4a** (Table 1, entries 2–3 *vs* 1), although minor amounts of **3a** are formed. Of these catalysts, JohnPhosAu(MeCN)SbF_6 displayed better selectivity and was chosen to optimize the reaction conditions. A slightly improved selectivity was observed when lowering the catalyst loading to just 1 mol% (entry 4). No impact on the yield was detected upon reducing the reaction time to 8 h (entry 5) or scaling the reaction to 1 mmol (entry 6). Reactions in neat MeOH selectively afforded dihydrophenanthrene **4a**, although incomplete conversions were achieved after 24 h even at 50 °C (entries 7–8). However, phenanthrene **2a** (Scheme 1b) was formed as major product when dichloromethane was used as solvent instead of THF. Moreover, a decrease in the excess of MeOH in the reaction mixture resulted in lower selectivity for **4a** (entries 9–10). In addition, an inert atmosphere and dry solvents seem to be crucial for reproducing the selectivity.[13]

The scope of the selective gold(I)-catalyzed alkoxycyclization to produce functionalized dihydrophenanthrenes **4** was then examined employing a series of biphenyl-embedded trienynes **1** and alcohols, under the

Table 1. Optimization of reaction conditions.[a]

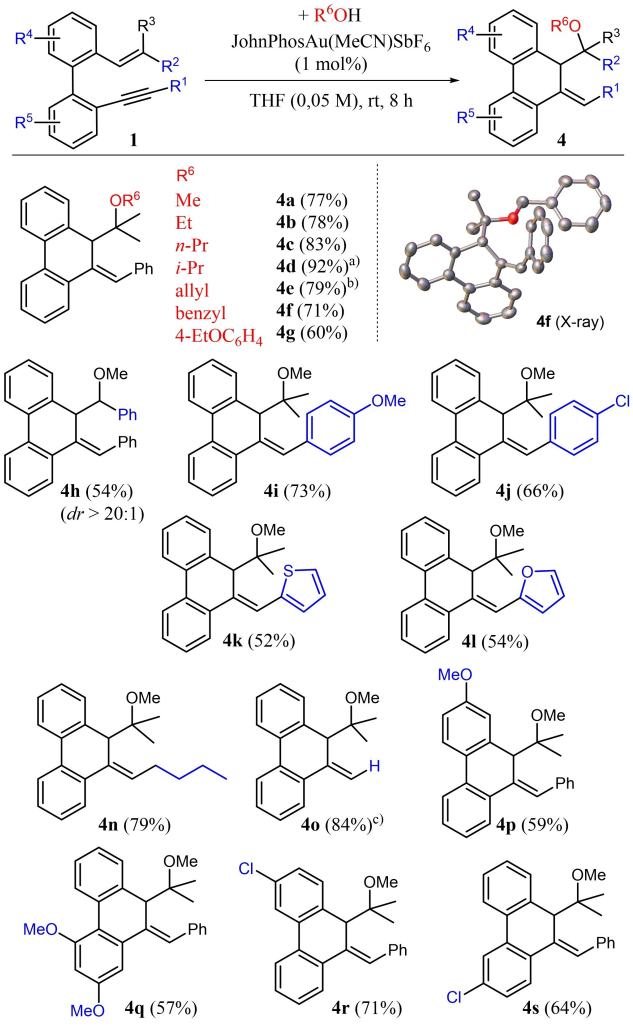


1a 4a 3a

Entry	Cat.[b]	mol%	MeOH (equiv.)	t (h)	**4a**/**3a**[c]
1	A	5	–	72	0/1
2[d]	A	5	50	24	74/26
3	B	5	50	24	89/11
4	B	1	50	24	93/7
5	B	1	50	8	93(77)/7
6[e]	B	1	50	8	94(79)/6
7[f]	B	1	solvent	24	>95/<5
8[d,f]	B	1	solvent	24	>95/<5
9	B	1	20	8	79/21
10	B	1	5	8	44/56

[a] Reactions conducted using 0.2 mmol of **1a** under argon.
[b] Cat.: A = PPh_3AuNTf_2; B = JohnPhosAu(MeCN)SbF_6.
[c] Ratio estimated by ^{1}H NMR spectroscopy (300 MHz); isolated yield in brackets.
[d] Reaction conducted at 50 °C.
[e] Reaction conducted with 1 mmol of **1a**.
[f] Incomplete conversions: 64% (entry 7), 83% (entry 8).

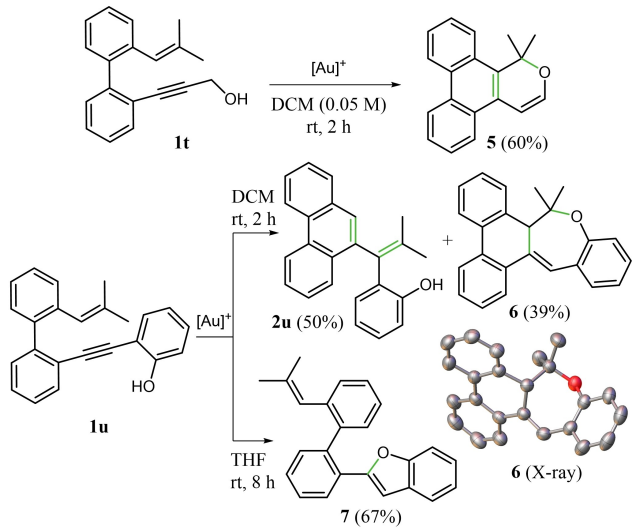
optimal catalytic conditions established for the preparation of **4a** (Table 1, entry 5). The results are summarized in Scheme 2. Thus, substrate **1a** successfully reacts with different primary alcohols, including allylic and benzylic alcohols, and isopropanol to afford good to excellent yields of the corresponding functionalized dihydrophenanthrenes **4a–f**. The reactions with allylic alcohol and isopropanol were sluggish and required higher temperatures or longer reaction times to go to completion. A single-crystal X-ray diffraction analysis of **4f** confirmed the structural assignment and alkene *E*-configuration for dihydrophenanthrenes **4**,[14] which was initially determined on the basis of NMR studies. Less nucleophilic *para*-ethoxyphenol could also be used, although a lower yield of **4g** was observed. However, reactions with other O-nucleophiles, such as phenol or acetic acid, occurred with low conversions to adducts **4**, with dihydrophenanthrene **3a** being the major product in both cases. Moreover, no significant evolution was observed when *p*-nitroaniline or 1,3-dimethoxybenzene were used as nucleophiles.



Scheme 2. Synthesis of alkoxy-functionalized dihydrophenanthrenes **4**. Isolated yields for reactions performed using 0.4 mmol of **1** and 50 equiv. of alcohol are given in brackets. [a] Reaction time: 24 h. [b] Reaction conducted at 50 °C. [c] Performed in MeOH (0.05 M).

Next, representative trienynes **1** modified at the olefin, the alkyne or the biphenyl core were evaluated in the presence of methanol as nucleophile. In this regard, we found that **1h**, which is *Z*-phenyl monosubstituted at the β carbon of the styrene moiety, gives cycloadduct **4h** as a single diastereoisomer,[15] although the relative configuration of the two stereogenic centers generated could not be determined. Moreover, the method developed tolerates a broad range of substituents at the alkyne of the starting material, including electron-donating and electron-withdrawing arenes, heteroarenes,[16] aliphatic groups and hydrogen, thereby leading to the corresponding tricyclic derivatives **4i–l**, **n–o**, which were isolated in good yields. The reaction of substrate **1o**, which possesses a terminal acetylene, was incomplete under the standard conditions, whereas the use of neat MeOH as solvent led to full conversion and a good yield in this case. Furthermore, the biphenyl unit could also be decorated with methoxy or chloro substituents, thus allowing the selective synthesis of highly functionalized dihydrophenanthrenes **4p–s**.

To extend the utility of the reported procedure we prepared trienynes **1t**, **u**, which bear a hydroxyl group attached to the alkyne moiety, as potential precursors for complex polycyclic scaffolds via a related intramolecular alkoxycyclization (Scheme 3). The reaction of substrate **1t**, under the optimized conditions determined for the intermolecular reaction, gave a



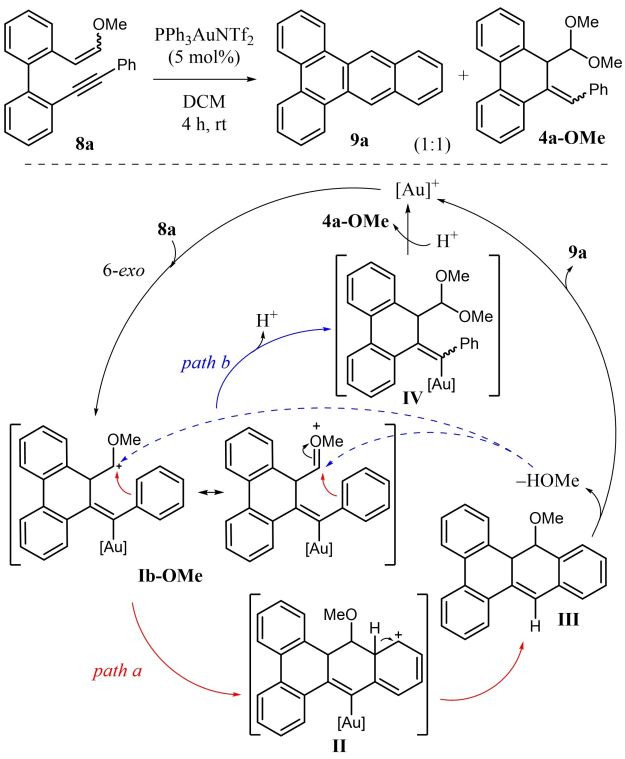
Scheme 3. Synthesis of polyheterocyclic compounds by gold(I)-catalyzed intramolecular alkoxycyclizations. $[Au]^+$ = JohnPhosAu(MeCN)SbF_6 (1 mol%).

complex mixture of compounds. However, a simple change of solvent to dichloromethane allowed the selective production of phenanthrene-fused pyran **5** in good yield as a result of the planned intramolecular alkoxycyclization followed by a spontaneous oxidation. Similarly, pentacyclic compound **6** could be isolated in a synthetically useful yield from **1u**, thus implying a more challenging benzo[*b*]oxepine formation. The cycloisomerization product **2u** was also obtained in this case, whereas conducting the reaction in THF led to the selective generation of benzofuran **7** as a result of direct attack of the alcohol at the activated triple bond. The structure of pentacyclic compound **6** was confirmed by X-ray diffraction analysis.[14]

Having demonstrated the feasibility of inter- and intramolecularly trapping carbocationic intermediates **I** with O-nucleophiles, we turned our attention to the synthesis of phenanthrene-based PAHs. Inspired by Echavarren's hydroacene synthesis,[17] we considered that biphenyls **8** bearing an enol ether moiety and (hetero)aromatic alkynes should be appropriate substrates to provide benzo[*b*]triphenylenes under gold catalysis (Scheme 1d).

An initial experiment with model substrate **8a** in dichoromethane and PPh_3AuNTf_2 as catalyst gave an equimolecular mixture of the desired fully aromatic phenanthrene-based PAH **9a** accompanied by ketal **4a-OMe** (Scheme 4). The formation of both compounds could be explained by an initial coordination of the acetylene to the gold complex, followed by an intramolecular 6-*exo*-*dig* nucleophilic addition of the alkene to give the key cationic intermediate **Ib-OMe** (Scheme 4). This species could evolve by two different pathways. Thus, an intramolecular attack of the phenyl originally bonded to the enyne acetylene would furnish pentacyclic intermediate **II** (*path a*). Subsequent rearomatization and protodemetalation would regenerate the catalyst and lead to methoxydihydrobenzo[*b*]triphenylene **III** which, after loss of methanol, would afford the observed benzo[*b*]triphenylene **9a**. On the other hand, intermediate **Ib-OMe** could be trapped by the MeOH generated in pathway *a* to give vinylgold species **IV** (*path b*).[18] A final protodemetalation would account for formation of the dihydrophenanthrene ketal **4a-OMe** and would release the gold catalyst to participate in a new catalytic cycle.

Next, we analysed all the reaction parameters involved in the cyclization of **8a** to determine the optimum reaction conditions for selectively obtaining the desired benzo[*b*]triphenylene **9a** (Table 2).[13] We tested various cationic gold catalysts first. No ketal **4a-OMe** was detected in the reaction with JohnPhosAu(MeCN)SbF_6 after 4 hours, although **9a** was isolated in a moderate 47% yield due to the formation of other unidentified compounds (entry 2).

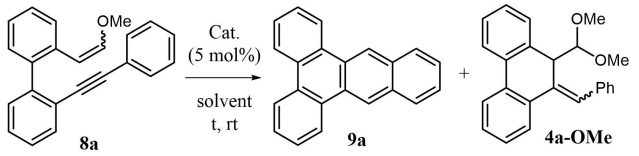


Scheme 4. Gold(I)-catalyzed cycloisomerization of **8a**: Initial experiment and mechanistic proposal.

Nevertheless, both phosphite- and *N*-heterocyclic carbene-derived gold catalysts cleanly and exclusively gave benzo[*b*]triphenylene **9a** in good yields (entries 3–4). The best yield was achieved with IPrAuCl/$AgNTf_2$ and, therefore, this was selected as catalyst for subsequent studies. Similarly to substrate **1t**, and in contrast to the reactions of enyne **1a** in the presence or absence of alcohols, the use of THF as solvent for the cyclization of **8a** afforded a complex mixture of products (entry 5). On the other hand, reducing the catalyst loading or the reaction time resulted in a lower proportion and/or yield of **9a** (entries 6–7). Finally, by modifying the reaction dilution, we found that reducing the concentration to 0.025 M resulted in the formation of an equimolecular mixture of **9a** and **4a-OMe** (entry 8), whereas increasing the concentration had no significant impact on either the selectivity or the isolated yield (entry 9). As a result of the optimization,[19] we found that **8a** exclusively produced benzo[*b*]triphenylene **9a** in high yield after 4 hours when performing the reaction in dichloromethane (0.1 M) at room temperature and using 5 mol% of the combination IPrAuCl/$AgNTf_2$ as catalytic system (entry 9). Interestingly, a similar behaviour was detected at 1 mmol scale (entry 10).

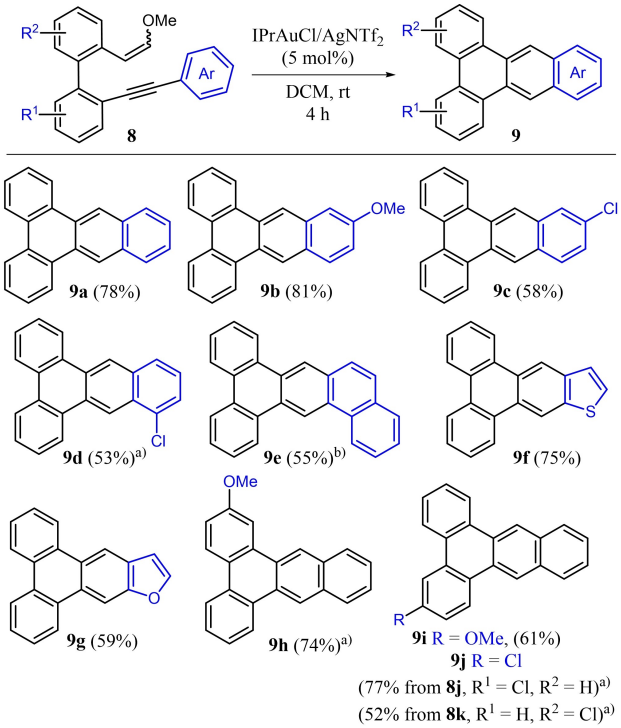
The scope of this new gold-catalyzed cascade process was then examined (Scheme 5). Benzo[*b*]triphenylenes **9b–e** were obtained in good

Table 2. Optimization of reaction conditions for the cyclization of **8a** to benzo[*b*]triphenylene **9a**.[a]

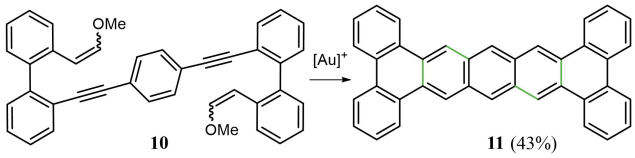


Entry	Cat.[b]	Solvent (M)	t (h)	**9a**/**4a-OMe**[c]
1	A	CH_2Cl_2 (0.05)	4	1(20)/1
2[d]	B	CH_2Cl_2 (0.05)	4	1(47)/0
3	C	CH_2Cl_2 (0.05)	4	1(72)/0
4	D	CH_2Cl_2 (0.05)	4	1(75)/0
5	D	THF (0.05)	4	–[e]
6[f]	D	CH_2Cl_2 (0.05)	4	4(64)/1
7	D	CH_2Cl_2 (0.05)	2	1(70)[d]/0
8	D	CH_2Cl_2 (0.025)	4	1/1
9	D	CH_2Cl_2 (0.1)	4	1(78)/0
10[g]	D	CH_2Cl_2 (0.1)	4	1(83)/0

[a] Reactions conducted using 0.2 mmol of **8a** under argon.
[b] Cat.: A = PPh_3AuNTf_2; B = JohnPhosAu(MeCN)SbF_6; C = [(2,4-(*t*Bu)$_2$C$_6$H$_4$)O$_3$P]AuCl/$AgNTf_2$; D = IPrAuCl/$AgNTf_2$. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.
[c] Ratio estimated by ^{1}H NMR spectroscopy (300 MHz); isolated yield in brackets.
[d] Significant amounts of other unidentified products were observed.
[e] A complex mixture of compounds is formed.
[f] Reaction conducted with 2.5 mol% of catalyst.
[g] Reaction conducted with 1 mmol of **8a**.



Scheme 5. Synthesis of benzo[*b*]triphenylenes **9**. Isolated yields for reactions performed using 0.4 mmol of **8** are given in brackets. [a] Reaction conducted for 12 h at 50 °C. [b] Reaction conducted for 12 h at 80 °C.



Scheme 6. Synthesis of tetrabenzopentacene **11**. Reaction performed using 0.18 mmol of **10** in DCM at 80 °C for 24 h. $[Au]^+$ = IPrAuCl/$AgNTf_2$ (10 mol%).

yields from trienynes **8b–e**, respectively, which possess both electron-rich and electron-deficient arenes at the triple bond. Not surprisingly, lower yields were observed, and harsher reaction conditions were typically required, for substrates **8c–e**, which bear less nucleophilic and/or more hindered arenes. The catalytic method also tolerates heterocycles as nucleophilic partners, as demonstrated with the formation of triphenylen[2,3-*b*]-thiophene **9f** and triphenylen[2,3-*b*]-furan **9g**. In addition, substitution at the biphenyl core of **8** allowed the synthesis of methoxy- or chloro-substituted benzo[*b*]triphenylenes **9h–j** in good yields. Compound **9j** can be prepared from both isomeric substrates **8j** and **8k**, although a better yield was achieved with the former.

Finally, to further prove the strength of the developed methodology as regards access to complex extended phenanthrene-based PAHs, we prepared bis-(biphenyl embedded trienyne) **10** from the corresponding terminal enyne and 1,4-diiodobenzene.[13] Although reaction under the optimized conditions was found to be sluggish, increasing the temperature to 80 °C and the catalyst loading to 10 mol% resulted in the double gold-catalyzed cyclization, which was complete after 24 h (Scheme 6). Under these conditions, tetrabenzopentacene **11**[20] was selectively produced and could be isolated in a remarkable 43% yield.

Conclusion

In summary, we have described a straightforward, gold(I)-catalyzed method for synthesizing different phenanthrene-based polycycles from readily available biphenyl-embedded trienynes. Thus, catalytic alkoxycyclizations of these unsaturated systems in the presence of various alcohols allowed the selective synthesis of functionalized dihydrophenanthrenes in high yields and with broad scope. In addition, the formation of polyheterocyclic adducts from the appropriate O-decorated enynes, via an analogous intramolecular reaction, has also been demonstrated. The catalytic methodology developed is also useful for the

synthesis of phenanthrene-derived PAHs such as benzo[*b*]triphenylenes by a rational design of the enyne, which should bear an enol ether moiety and (hetero)aromatic alkynes. The scope of this selective process is broad, including substitution at all the external arenes of the synthesized PAH. Moreover, tetrabenzopentacene, a more complex phenanthrene-based PAH, has also been synthesized by a double cyclization of a suitable polyene. This methodology could emerge as a useful strategy for preparing other non-linear PAHs for use in organic electronic devices given the appropriate choice of starting materials.

Experimental Section

General procedure for the gold(I)-catalyzed synthesis of alkoxy-functionalized dihydrophenanthrenes 4: The appropriate alcohol (50 equiv., 20 mmol) was added to a solution of the corresponding 2-alkenyl-2′-alkynyl-1,1′-biphenyl **1** (1 equiv., 0.4 mmol) in THF (8 mL), in a round-bottomed flask, and the mixture was stirred for 5 min. JohnPhosAu(MeCN)SbF_6 (1 mol%, 3 mg) was subsequently added and the reaction mixture was stirred for 8 h at room temperature. The resulting mixture was then filtered through a short plug of Celite, eluting with a mixture of hexane and EtOAc (40:1), and the solvents subsequently removed under reduced pressure. The crude mixture obtained was purified by flash chromatography on silica gel using mixtures of hexane and EtOAc as eluents to give the corresponding dihydrophenanthrenes **4** in the yields depicted in Scheme 2.

General procedure for the gold(I)-catalyzed synthesis of benzo[*b*]triphenylenes 9: A solution of the appropriate 2-(2-methoxyvinyl)-2′-(phenylethynyl)-1,1′-biphenyl **8** (1 equiv., 0.4 mmol) in dichloromethane (3 mL) was added to a solution of IPrAuCl (5 mol%, 12 mg) and $AgNTf_2$ (5 mol%, 8 mg) in anhydrous dichloromethane (1 mL), pre-stirred at room temperature for 5 min. The resulting mixture was stirred at room temperature, unless otherwise stated, in a Schlenk flask under argon for 4 h, and then filtered through a short plug of Celite using a 40:1 mixture of hexane and EtOAc as eluent. The crude product obtained upon removing the solvents under reduced pressure was purified by flash chromatography on silica gel using mixtures of hexane and EtOAc as eluents to give the corresponding benzo[*b*]triphenylenes **9** in the yields shown in Scheme 5.

Acknowledgements

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[15] In this particular case, the corresponding phenanthrene **2h** was also formed as byproduct.

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