

Gold Catalysis | *Hot Paper*

Gold-Catalyzed Annulation of 1,8-Dialkynyl naphthalenes: Synthesis and Photoelectric Properties of Indenophenylene-Based Derivatives

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Abstract: A simple gold-catalyzed annulation of 1,8-dialkynyl naphthalenes utilizing a cationic gold catalyst was developed. Such a *peri*-position of two alkynyl substituents has not been studied in gold catalysis before. Dependent on the substrate, the reactions either follow a mechanism involving vinyl cation intermediates or involve a dual gold catalysis mechanism which in an initial *6-endo-dig*-cyclization gener-

ates gold(I) vinylidene intermediates that are able to insert into C–H bonds. Indenophenylene derivatives were obtained in moderate to high yields. In addition, the bidirectional gold-catalyzed annulation of tetraynes provided even larger conjugated π -systems. The optoelectronic properties of the products were also investigated.

Introduction

Over the last two decades, homogeneous gold catalysis^[1] has been utilized for the electrophilic activation of alkynes. Gold most commonly acts as a redox-neutral and carbophilic π -acid that activates carbon-carbon multiple bonds towards nucleophilic attack.^[2] Alkynes are still the dominating class of substrates, among them diyne systems^[3] are very important as starting materials for gold-catalyzed annulations to extended π -systems. Different from the majority of gold-catalyzed reactions, diyne substrates lead to high-energy intermediates, in the case of two internal alkynes to vinyl cations as intermediates,^[4] when at least one terminal alkyne is present, gold vinylidene intermediates^[5] are generated. Both types of intermediates are able to insert into non-activated aliphatic C(sp³)–H or aromatic C(sp²)–H bonds. This provides easy access to a diverse set of interesting organic scaffolds,^[3,4] including π -extended structures. Polycyclic aromatic hydrocarbons (PAHs), which might be the largest class of organic molecules, have been intensively investigated, due to their small HOMO–LUMO gaps these highly conjugated systems are promising for applications in the field of organic electronics.^[6] Therefore, the development of modular synthetic methods to access polycyclic π -extended conjugated systems is a promising research topic.

1,8-Dialkynyl naphthalene structures are flexible and have been extensively used as substrates in intramolecular^[7] and intermolecular^[8] annulations. Recently Wang's group reported an iodine-mediated electrophilic poly-cyclization in one step, which provides two different products, probably generated from vinyl cation intermediates or radical intermediates.^[7] Additionally, the synthesis of indeno[2,1-*a*]phenylene derivatives by an iodine-mediated electrophilic cyclization of 1,8-dialkynyl naphthalenes was published (Figure 1).^[7j,k] Tobe's group



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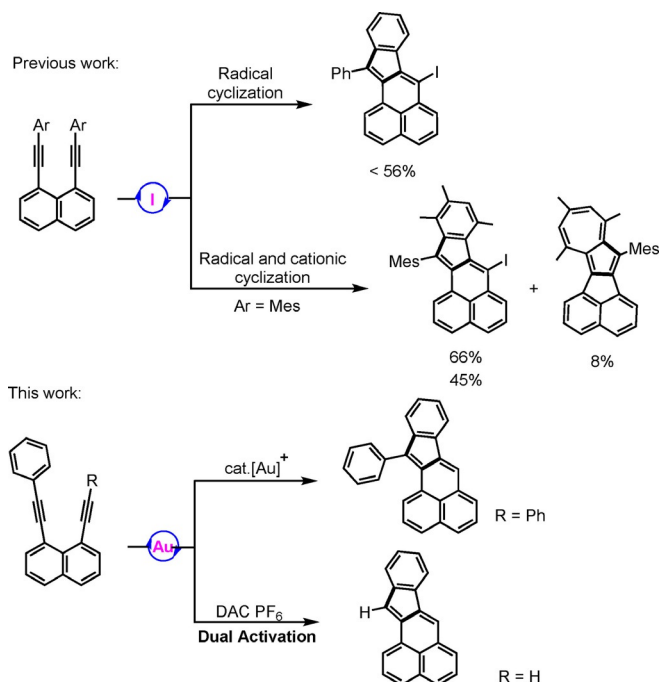


Figure 1. Known iodocyclization of 1,8-(bisalkynyl)naphthalene by a tandem radical/cationic pathway and the new gold-catalyzed annulation reaction.

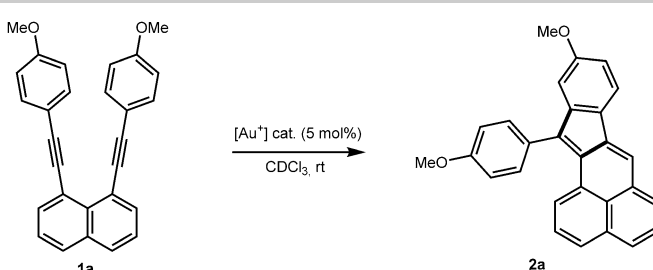
elegantly designed a synthesis of a variety of rigid carbocyclic platforms, which are stabilized by flanking aromatic groups.^[7o] Such fused five- or six-membered carbocyclic rings are key substructures of π -extended systems or organic functional materials.^[7j,k,9] Gold catalysts represent mild carbophilic π -Lewis acids,^[10] we here for the first time use 1,8-dialkynyl naphthalenes with the parallel *peri*-arrangement of the alkynes.

Results and Discussion

The 1,8-diyne **1a** was chosen as a model substrate (Table 1). 5 mol% of various gold catalysts with sterically demanding ligands were examined in CDCl₃. Even at room temperature the conversions were fast (2.5 h or less, Table 1, entries 1–5). With the IPr ligand the product **2a** was obtained in 94% yield (Table 1, entry 1).^[11] With the triphenylphosphine ligand no improvement in the yield was achieved, but the yield was slightly higher than in the case of the electron-poor phosphine ligand (CF₃CH₂O)₃P (94% versus 90%) (Table 1, entries 2 and 3). Despite a complete conversion of all starting material, the SPhos-ligated cationic gold catalyst gave a lower yield (88%, Table 1, entry 4). In C₆D₆, the reaction was completed within 15 min to afford **2a** in 96% yield (Table 1, entry 5). (IPr)AuCl gave poor results even after prolonged reaction times (4 h), (Table 1, entry 6), and (IPr*)AuCl/AgSbF₆ delivered **2a** in 90% yield (Table 1, entry 7). With a silver(I) catalyst only low yields of **2a** were obtained (Table 1, entry 8).

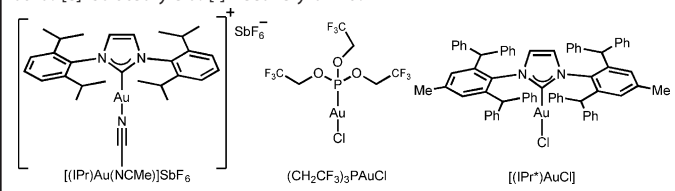
Then we explored the reaction scope under the optimized conditions from Table 1, entry 1. A series of diynes with phenyl groups with various substituents at the aromatic system were synthesized, all diynes provided the corresponding products (**2a–2k**, Table 2). Electron-donating substituents (Me and OMe)

Table 1. Optimization of the reaction conditions.^[a]



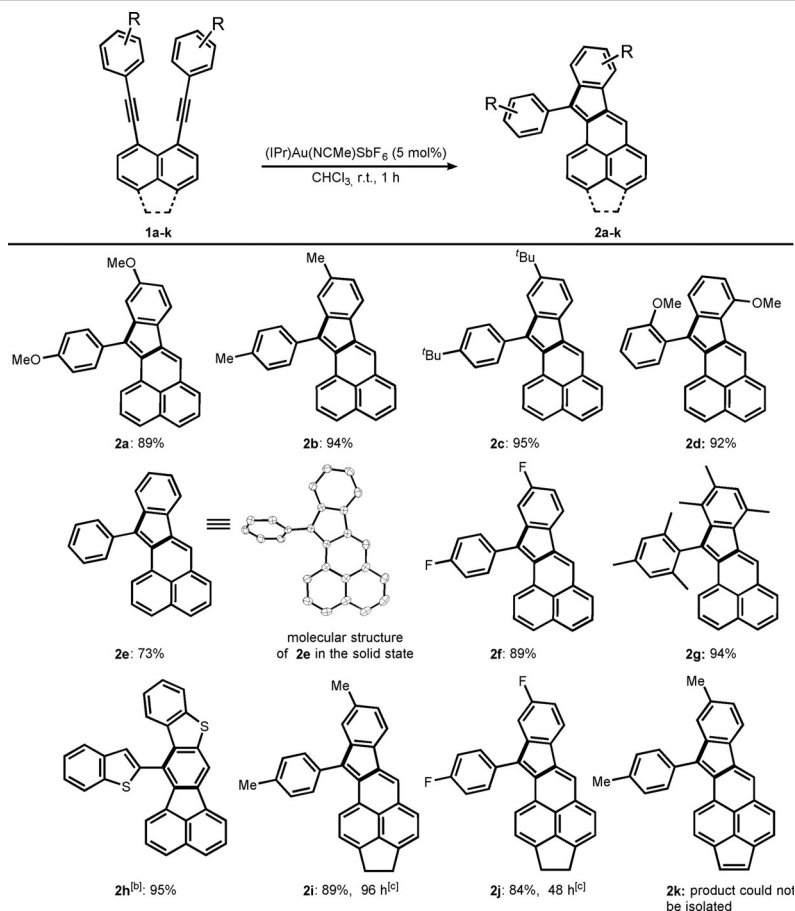
Entry ^[a]	Catalysts	Time	Yield [%] ^[d]
1	(IPr)Au(NCMe)SbF ₆	1 h	94
2	Ph ₃ PAuNTf ₂	1 h	94
3 ^[b]	(CF ₃ CH ₂ O) ₃ PAuCl/NTf ₂	2.5 h	90 ^[e]
4	(SPhos)AuCl/AgNTf ₂	1 h	88
5 ^[c]	(IPr)Au(NCMe)SbF ₆	15 min	96
6	(IPr)AuCl	4 h	10 (89) ^[f]
7	(IPr*)AuCl/AgSbF ₆	1 h	90 ^[e]
8	AgNTf ₂	5 h	48 (36) ^[f]

[a] Reactions were run on 0.01 mmol scale in CDCl₃, and were afterwards directly analyzed by ¹H NMR spectroscopy. [b] 60 °C. [c] In [D₆]benzene. [d] Yield was determined by ¹H NMR by using hexamethylbenzene as the internal standard. [e] Isolated yield. [f] Recovery of **1a**.



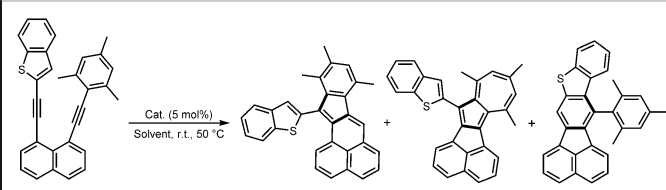
at *para*- and *ortho*-positions of the phenyl ring gave yields between 89–95% (**2a–2d**), while for arene **2e** the yield dropped significantly (73%). The structure of **2e** at the solid state was confirmed by the single-crystal X-ray structural analysis.^[12] Also substrates with fluorine substituents were smoothly converted to the corresponding phenalenes **2f** and **2j** in 89 and 84% yield, but for **2j** heating to 50 °C for 48 h was necessary. The mesitylene-substituted substrate **1g** was also converted to the corresponding phenalene **2g** in 94% yield via the carbocation rearrangement. Amazingly, product **2h** was directly obtained from the general procedure for the Sonogashira-coupling to form **1h**, no gold catalyst was needed, the palladium did the conversion; for none of the other substrates this was observed. This probably is induced by the significantly more electron-rich thiophene ring, which allows the palladium species present during the cross coupling to interact with the alkyne units more strongly—unlike in the other substrates, which are dependent on the gold catalyst. Acenaphthene substrates with different substituents (Me and F) at *para*-position on the phenyl groups were successfully converted to the corresponding phenalene **2i** and **2j** in 89 and 84% yield. The reaction of 5,6-diethynylacenaphthelene **1k** did not give the corresponding phenalene at all.

Then we tested the reactivity of the unsymmetrical diyne **1l** to investigate the effect of the mesitylethynyl and 2-benzo[*b*]-thiopheneethynyl substituents (Table 3). First different steric hindered ligands were examined. The reaction of **1l** under the

Table 2. Scope of the reaction.^[a]

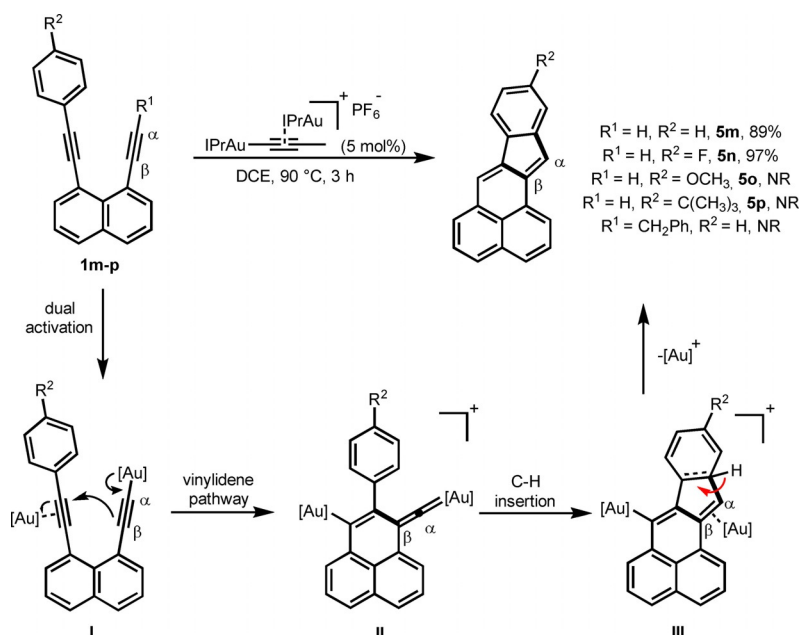
[a] Reaction conditions: **1a** (0.05 mmol), catalyst (5 mol%), solvent (CHCl₃, 1 mL), r.t. [b] Product **2h** was obtained directly from the palladium-catalyzed coupling, which should have provided **1h**. [c] 50 °C.

standard conditions (Table 3, entry 1) through 5 mol% of (IPr)Au(NCMe)SbF₆ in 1,2-dichloroethane (DCE), resulting in azuleno[1,2-*a*]acenaphthylene **3I** (36%) and phenalene **4I** (18%) as a major products due to a 5-*exo* pathway as well as a small amount of [*b*]fluorantheno[8,9-*d*]thiophene **2I** (36%) due to a 6-*endo* pathway (Scheme 1). The structures of **2I** and **4I** at the solid state were unambiguously confirmed by X-ray structural analysis (Figure 2).^[12] The more sterically hindered gold catalyst (IPr*)AuCl/AgNTf₂ dramatically diminished the formation of the phenalene **2I** and improved regioselectivity of products **3I** and **4I** (Table 3, entry 2). Switching the counter ion from NTf₂⁻ to SbF₆⁻ were able to efficiently produce the compound **4I** with less of **3I**, but the product **2I** was not observed at all (Table 3, entry 3). Changing the solvent to benzene and toluene improved regioselectivity towards **3I** (Table 3, entries 4 and 5). Interestingly, when the reaction was conducted with electron-poor ligands, P(OCH₂CF₃)₃ and P(C₆F₅)₃, azuleno[1,2-*a*]acenaphthylene **3I** was obtained as a major product (Table 3, entries 6 and 9). Further screening showed that in the present of the bulky phosphine ligand *t*BuXPhos the reaction proceeded faster and three isomers were obtained in 89% yield in a ratio of 1:2:2 (Table 3, entry 7). In contrast, neither (IPr)AuCl,

Table 3. Optimization of the reaction conditions for diene **1k**.^[a]


Entry ^[a]	Cat.	Time [h]	Solvent	Ratio ^[b] 2I/3I/4I	Yield [%] ^[c]
1	(IPr)Au(NCMe)SbF ₆	2.5	DCE	2:2:1	90
2	(IPr*)AuCl/AgNTf ₂	5	DCE	3.4:1:1	92
3	(IPr*)AuCl/AgSbF ₆	5	DCE	3.5:1:0	94
4	(IPr*)AuCl/AgSbF ₆	3	PhH	3:1:0	70
5	(IPr*)AuCl/AgSbF ₆	4	toluene	3:1:1	70
6	(CF ₃ CH ₂ O) ₃ PAuCl/AgSbF ₆	3	DCE	1:3:0.5	95
7	<i>t</i> BuXPhos)AuCl/AgSbF ₆	1.5	DCE	1:2:2	89
8	(IPr)AuCl/AgSbF ₆	3	DCE	1:2:2	88
9 ^[d]	[(C ₆ F ₅) ₃ PAuCl]SbF ₆	4	DCE	1:2.5:0.5	73
10	AgSbF ₆	5	DCE	ND	ND
11	(IPr)AuCl	5	DCE	ND	ND

[a] General reaction conditions: 0.05 mmol **1k**, 5 mol% of Au catalyst, 5 mol% of Ag catalyst, solvent (1 mL). [b] Ratio of **2I/3I/4I** were determined by ¹H NMR analysis of the crude product. [c] Yield of the mixture. [d] 10 mol% [(C₆F₅)₃PAuCl]SbF₆ was used at 50 °C.



Scheme 1. Synthesis of **5m** and **5n** by dual gold-catalyzed cascade transformations.

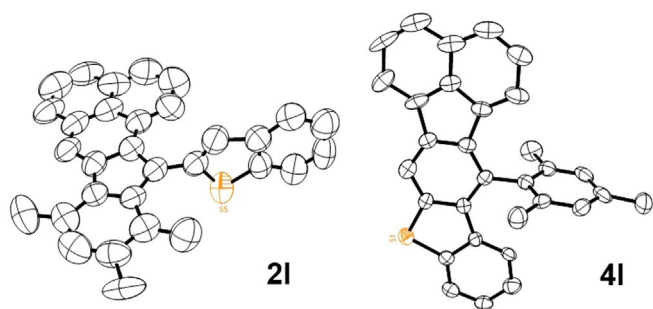


Figure 2. Solid-state molecular structures of compounds **2I** and **4I**.

nor $AgSbF_6$ alone promoted the desired reaction, showing that a cationic gold species is necessary for the annulation (Table 3, entries 10 and 11).

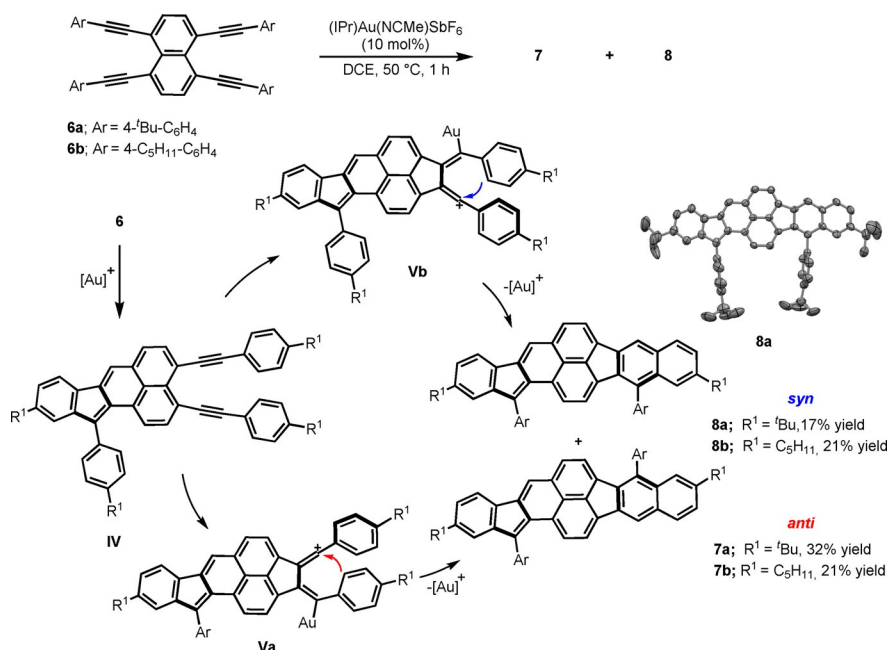
Recently, Zhang's group^[3a] and our group^[3b-f,4a] showed that gold vinylidenes, accessible from an internal and a terminal alkyne, are highly reactive intermediates and can efficiently insert into $C(sp^2)-H$ bonds or $C(sp^3)-H$ bonds. Thus, we next tested our naphthalene-linked diyne systems (**1m**, **1n**) with a dual activation gold catalysts (TDAC[PF_6]) in DCE at 90 °C. These were efficiently converted into the targets **5m** and **5n** in 89 and 97% yields, respectively (Scheme 1). On the other hand, for yet unknown reasons no conversions were observed for the electron-rich substituents ($R^2 = OMe$, tBu) **1o** and **1p** (Scheme 1).

Next, the bidirectional gold-catalyzed conversion of the 1,4,5,8-tetra-(phenylethynyl)naphthalenes **6a** and **6b** was explored (Scheme 2). First we tested the standard reaction conditions, when the solution of the tetrayne **6a** in DCE was treated with $(IPr)Au(NCM)SbF_6$ (10 mol%) at 50 °C, the two dark purple isomers **7a** and **8a** were isolated in 32% and 17% yield (Scheme 2). The lack of symmetry of the compound visible

from the 1H NMR spectra of these products indicated that neither of them are the expected symmetrical products. Interestingly, an unexpected mode of intramolecular cyclization was observed. The expected 6-endo-dig-cyclization proceeded in one side to construct a phenalene moiety, but the unexpected 5-exo-dig-cyclization in the other side occurred to form a fluoranthane moiety. Regioisomers **7** and **8** were potentially produced via vinyl cation intermediates **Va** and **Vb** (Scheme 2). The connectivity of **8a** was unambiguously confirmed by single-crystal X-ray diffraction analysis.^[12]

In the case of 1,4,5,8-tetrakis-(phenylethynyl)naphthalene **6a** and **6b**, additional mode of distortion to reduce steric repulsion is effect to obtain the unsymmetrical products. According to the X-ray structure of phenylethynyl naphthalene derivatives,^[8a] while the structure of diene **1** is involved the expanding mode of distortion in the naphthalene core, in the case of tetrayne **6**, both the twisting and expanding modes are observed together with bending of phenylethynyl units, in particular the carbons attached directly to the naphthalene core move away from each other compared to **1**.^[13]

We used density functional theory (DFT) calculations at the SMD/M06/def2-TZVP//SMD/B3LYP-D3//6-31G(d), SDD(Au) level of theory in DCE to understand the mechanistic details of the bidirectional gold-catalyzed reaction by considering **6c** as a model for **6b** (Figure 3). This combination of methods and basis sets has been recently confirmed by us to provide results having a better consistency with the experimental data.^[14] Accordingly, the reaction commences with coordination of the gold complex to one of the alkyne moieties^[15] of **6c** in an endergonic fashion with $\Delta G = 3.5 \text{ kcal mol}^{-1}$. The resultant intermediate **VI** is a branching point for two routes, A 6-endo-dig-cyclization via **TS^{VI}-a** and a 5-exo-dig-cyclization via **TS^{VI}-b**. The calculations indicate that **TS^{VI}-a** is lower in energy than **TS^{VI}-b**, implying that in agreement with the experimental finding, the



Scheme 2. Gold-catalyzed conversions of the substrates **6a** and **6b**.

cyclization prefers the 6-*endo*-cyclization mode. Once the first cyclization has occurred, intermediate **VII** is formed by another cyclization via transition structure **TS^{VII}**, furnishing intermediate **VIII**. Since **TS^{VII}** lies much lower in energy than **TS^{VI-a}** and intermediate **VIII** is highly stable with a relative free energy of -17.8 , the transformation **VI**→**VII**→**VIII** is not reversible and thus the regioselectivity of the cyclization is determined by the energy difference between **TS^{VI-a}** and **TS^{VI-b}**. Subsequently, the organic molecule **IX** is produced with $\Delta G = -66.1$ kcal mol⁻¹ followed by a series of chemical steps from intermediate **VII**, as shown in Figure 3.

The organic molecule **IX** has two different sites for coordination of the gold complex. If the gold complex coordinates to **IX** to give **X**, the ensuing intermediate then is a bifurcation point for two processes, 6-*endo-dig*-cyclization via **TS^{X-a}** and 5-*exo-dig*-cyclization via **TS^{X-b}**. In line with the experimental observations, the calculations support favorability of the 5-*exo-dig*-cyclization, as evidenced by the finding that **TS^{X-b}** is 3.9 kcal mol⁻¹ lower in energy than **TS^{X-a}**. The same is true if we assume that the cyclization occurs from the other π -complex that is, intermediate **XI**; similarly, for this case, transition structure of the 5-*exo-dig*-cyclization (**TS^{XI-b}**) lies 2.1 kcal mol⁻¹ below that of the 6-*endo-dig*-cyclization (**TS^{XI-a}**), a result which agrees with the regioselectivity observed experimentally. Finally, we want to note that due to the closeness of the relative free energies of **TS^{X-b}** and **TS^{XI-b}**, both the *syn*- and *anti*-products are predicted computationally to be produced with a nearly equal amount. This prediction is fully consistent with our experimental observations, the results of which are given in Scheme 2.

The optical properties of phenalenes **2a–2k** were examined by UV/Vis absorption spectroscopy in dichloromethane (Figure 4). In view of maximum absorption wavelengths of **2a**, **2f** and **2i**, they show strong absorption at long wavelength

(about 460 nm). Comparison with phenalenes structures, azulenoacenaphthylene **31** exhibits the distinct broad peak between 500–750 nm. The π -extension has a significant effect on the absorption of **7a** and **8a** ($\lambda = 510$ and 550 nm). The HOMO and LUMO levels of **2a**, **2f**, **7a**, and **8a** were estimated by cyclic voltammetry (Table 4). The HOMO energy level of **2a** containing an electron donor group (-5.33 eV) was higher than **2f** containing an electron acceptor (-5.47 eV). Based on the compounds **7a** and **8a**, π -extension with fluoranthene provided lower LUMO levels and smaller HOMO–LUMO energy gaps.

In conclusion, an efficient gold-catalyzed annulation protocol through vinyl cation or -vinylidene intermediates via a selective shift towards a 6-*endo-dig*-cyclization mode for the indeno[2,1-*a*]phenalenes synthesis was developed. In addition, the bidirectional gold-catalyzed annulation of tetraynes provided even larger conjugated π -systems, the interesting different mode of the first and the second cyclization, leading to unsymmetrical products, was explored by a computational study.

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Conflict of interest

The authors declare no conflict of interest.

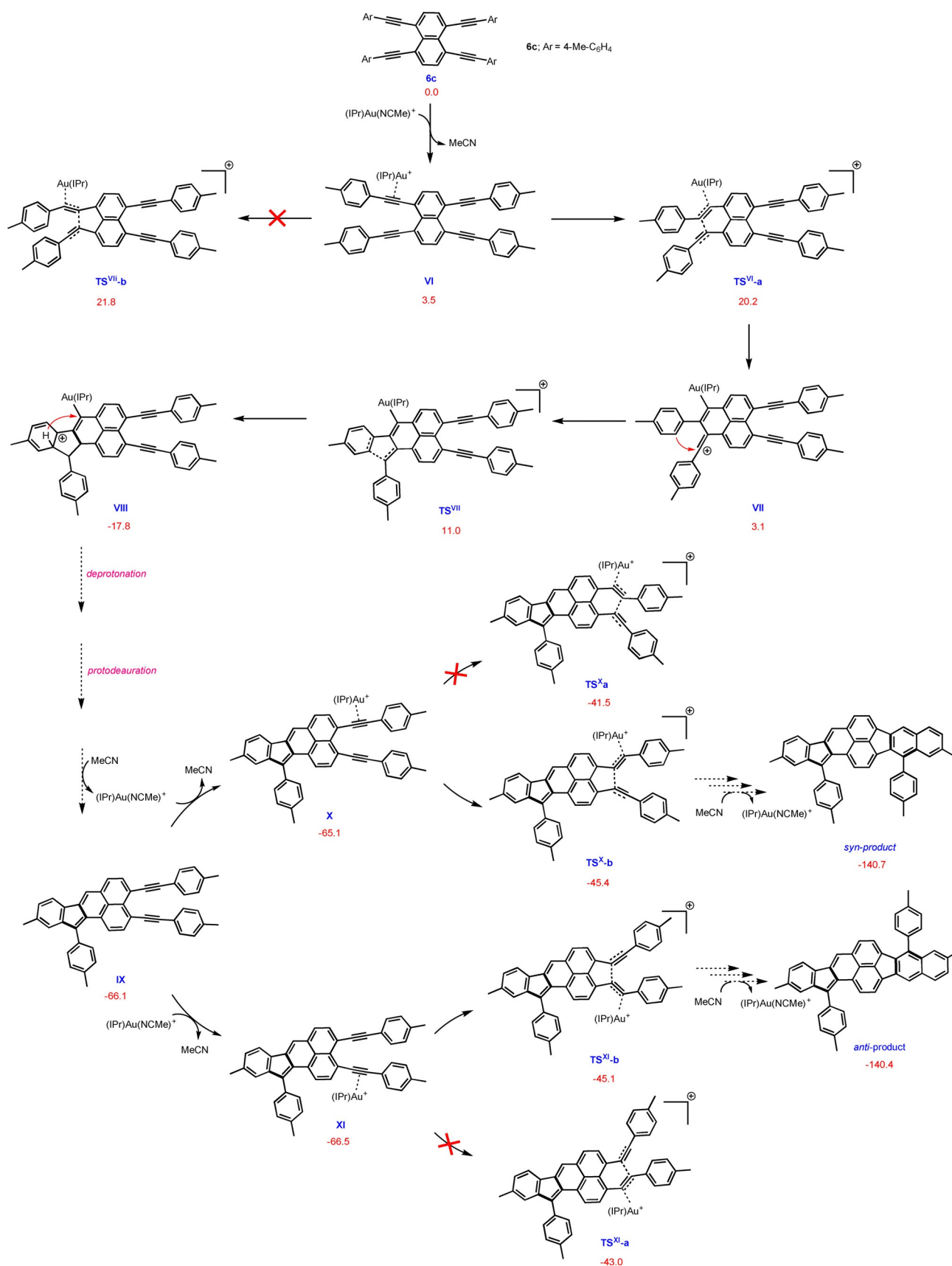
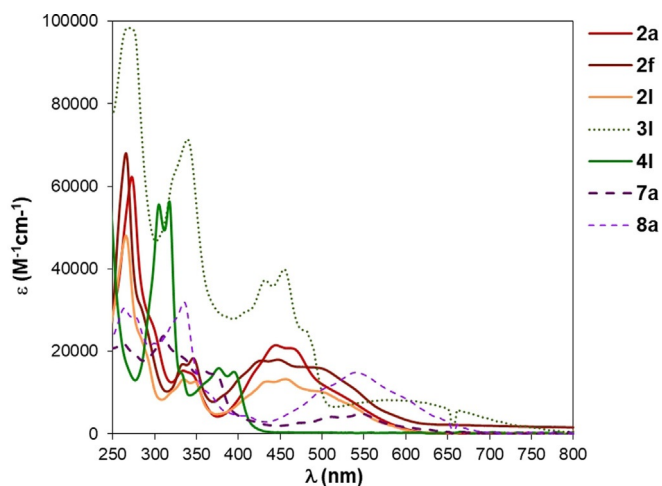


Figure 3. Calculated mechanism for cyclization of **6c** catalyzed by $[(\text{IPr})\text{Au}(\text{NCMe})]^+$. The relative free energies (in red) are given in kcal mol⁻¹.

Figure 4. UV absorption of **2a**, **2f**, **4l**, **7a**, and **8a**.Table 4. Cyclic voltammetry data and estimated HOMO and LUMO energies.^[a]

	E_{ox} [V]	E_{red} [V]	$E_{HOMO}^{[b]}$ [eV]	$E_{LUMO}^{[b]}$ [eV]	$E_{gap}^{[c]}$ [eV]
2a	0.53	-1.93	-5.33	-2.87	2.46
2f	0.67	-1.74	-5.47	-3.06	2.41
7a	0.41	-1.20	-5.21	-3.60	1.61
8a	0.54	-1.16	-5.34	-3.64	1.70

[a] Cyclic voltammetry in CH_2Cl_2 containing $0.1\text{ M }^nBu_4NPF_6$. [b] HOMO and LUMO energy levels in eV were approximated using the equation $HOMO = -(4.80 + E_{ox})$, $LUMO = -(4.80 + E_{red})$. [c] $E_{gap} = LUMO - HOMO$.

Keywords: alkynes · annulation · bidirectional synthesis · dual gold catalysis · extended π systems

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