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Flexible and Practical Synthesis of Anthracenes through Gold-Catalyzed Cyclization of *o*-Alkynyldiarylmethanes

Chao Shu, Cheng-Bin Chen, Wei-Xi Chen, and Long-Wu Ye*

Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, P. R. China

longwuye@xmu.edu.cn

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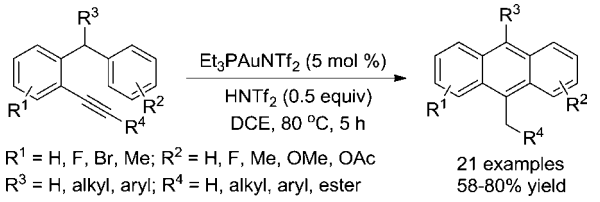
ABSTRACT



A concise gold-catalyzed method for the preparation of anthracenes from *o*-alkynyldiarylmethanes has been developed. Under mild reaction conditions, versatile anthracene derivatives were formed in moderate to good yields. The high flexibility, broad substrate scope, and mild nature of this reaction render it a viable alternative for the synthesis of anthracenes.

Among the polycyclic aromatic hydrocarbons (PAH), functionalized anthracene derivatives have been extensively investigated because of their wide and practical applications,[1] including as potential therapeutics,[2] optical devices,[3] and polymeric materials.[4] Most importantly, they possess interesting photophysical and photochemical properties.[5] It is surprising, however, that only a few preparative methods have been reported.[6] The synthesis of anthracenes has been mainly realized by a Lewis acid-induced Bradsher-type reaction from diarylmethanes (Scheme 1),[7] but it often suffers from limited substrate scope, harsh reaction conditions (normally in a solution of 34% HBr−HOAc),[7b] competitive reactions, and low yields. Therefore, novel approaches, especially those with high flexibility, efficiency, and good modularity, are highly demanded for its construction.

Recent rapid development in homogeneous gold catalysis[8] offers an alternative approach for generating methyl ketone compounds via hydration of terminal alkynes.[9] With this in mind, we envisioned that the preparation of anthracene compounds **2** might be achieved through the gold-catalyzed

(1) For reviews, see: (a) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43. (b) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145. (c) Desvergne, J.-P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. *Pure Appl. Chem.* **1992**, *64*, 1231.

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(6) For recent examples, see: (a) Yu, X.; Lu, X. *Adv. Synth. Catal.* **2011**, *353*, 569. (b) Kuninobu, Y.; Tatsuzaki, T.; Matsuki, T.; Takai, K. *J. Org. Chem.* **2011**, *76*, 7005. (c) Lin, C.-H.; Lin, K.-H.; Pal, B.; Tsou, L.-D. *Chem. Commun.* **2009**, 803. (d) Zou, Y.; Young, D. D.; Cruz-Montanez, A.; Deiters, A. *Org. Lett.* **2008**, *10*, 4661. (e) Xie, C.; Zhang, Y. *Org. Lett.* **2007**, *9*, 781. (f) Li, G.; Zhou, S.; Su, G.; Liu, Y.; Wang, P. G. *J. Org. Chem.* **2007**, *72*, 9830. (g) Asao, N.; Sato, K. *Org. Lett.* **2006**, *8*, 5361. (h) Takahashi, T.; Li, S.; Huang, W. Y.; Kong, F. Z.; Nakajima, K.; Shen, B. J.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967.

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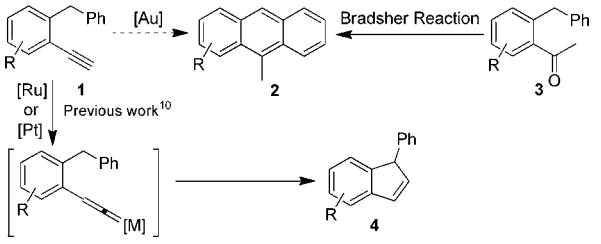
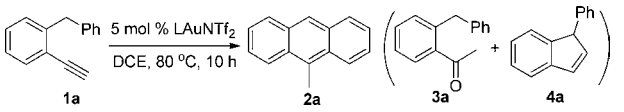
cyclization reaction of *o*-alkynyldiarylmethanes **1** (Scheme 1). In particular, it provides an atom-economic alternative to the Bradsher-type reaction. In this paper, we describe herein the realization of such an Au-catalyzed cyclization of *o*-alkynyldiarylmethanes, allowing the flexible and practical synthesis of versatile anthracene derivatives in moderate to good yields. Importantly, an appropriate choice of gold catalysts could suppress the formation of 1-substituted-1*H*-indenes **4**, which were obtained from the related Ru- or Pt-catalyzed cyclization reactions.[10]

Scheme 1. Design: Formation of Anthracenes **2** through Gold-Catalyzed Cyclization of *o*-Alkynyldiarylmethanes **1**



We set out to screen different conditions for this reaction by using *o*-alkynyldiphenylmethane **1a** as the model substrate. To our delight, the expected anthracene **2a** was indeed formed in 51% ^{1}H NMR yield in the presence of 5 mol % of $Ph_3PAuNTf_2$ (Table 1, entry 1). Here, we observed formation of two main byproducts. One was methyl ketone **3a** formed by gold-catalyzed hydration reaction. Another one was 1*H*-indene compound **4a**, the main product produced in the Ru-catalyzed cyclization reactions.[10a] Among the different gold catalysts screened (entries 1−8), $Et_3PAuNTf_2$ was found to be the best one and 65% yield could be achieved (entry 8). Notably, by employing $BrettPhosAuNTf_2$ as the gold catalyst, the occurrence of **4a** could become dominant (entry 4). The addition of 4 Å MS did not improve the reaction (entry 9). Then, the effect of acid was investigated (entries 10−15).

Table 1. Optimization of Reaction Conditions[a]



			yield[b] (%)		
entry	gold catalyst	acid	**2a**	**3a**	**4a**
1	$Ph_3PAuNTf_2$		51	17	6
2	Cy-JohnPhosAuNTf$_2$		34	20	4
3[c]	XPhosAuNTf$_2$		13	26	11
4	BrettPhosAuNTf$_2$		5	14	32
5[d]	IPrAuNTf$_2$		15	10	15
6	$(C_6F_5)_3PAuNTf_2$		53	12	<1
7	$(4\text{-}CF_3C_6H_4)_3PAuNTf_2$		40	24	<1
8	$Et_3PAuNTf_2$		65	10	<1
9[e]	$Et_3PAuNTf_2$	4 Å MS	10	<1	<1
10	$Et_3PAuNTf_2$	1.0 equiv of MsOH	69	5	<1
11[f]	$Et_3PAuNTf_2$	1.0 equiv of HNTf$_2$	77	<1	<1
12	$Et_3PAuNTf_2$	1.0 equiv of CF_3CO_2H	74	8	<1
13[f]	$Et_3PAuNTf_2$	0.5 equiv of HNTf$_2$	78[g]	<1	<1
14	$Et_3PAuNTf_2$	0.2 equiv of HNTf$_2$	72	5	<1
15[f]	$Et_3PAuNTf_2$	1.5 equiv of HNTf$_2$	76	<1	<1
16	$AgNTf_2$	0.5 equiv of HNTf$_2$	45	10	3
17	$PtCl_2$	0.5 equiv of HNTf$_2$	2	3	74

[a] Reaction conditions: [**1a**] = 0.05 M. DCE: 1,2-dichloroethane. [b] Estimated by ^{1}H NMR using diethyl phthalate as internal reference. [c] 15% of **1a** remained unreacted. [d] 25% of **1a** remained unreacted. [e] 60% of **1a** remained unreacted. [f] Time = 5 h. [g] Yield of isolated **2a** was 72%.

Gratifyingly, the addition of strong acid could substantially reduce the formation of **3a**, and the reaction yield could be further improved to 78% in the presence of 0.5 equiv of HNTf$_2$ (entry 13). It should be mentioned that without the use of gold catalyst, no desired product **2a** was observed under the acidic reaction conditions, and $AgNTf_2$ could also catalyze this reaction but with low yield (entry 16). Contrary to the gold catalysts, $PtCl_2$ promoted selective formation of **4a**, similar to Chatani's previously published results (entry 17).[10b]

Under the optimal reaction conditions, various *o*-alkynyldiarylmethane derivatives **1** were tested to examine the generality of the current reaction. As shown in Table 2, moderate to good yields were realized for all cases. The functionalities of F, Br, Me, OMe, and even the acid-sensitive OAc group on the aromatic ring could be well tolerated during the cyclization reaction, affording the corresponding 9-methylanthracenes **2b**−**m** in 58−71% yields. Notably, the formation of tetracene derivative **2k** could be achieved in a respectable 68% yield by the treatment of substrate **1k** (entry 10). Moreover, substrates **1l** and **1m** could also undergo smooth cyclization to furnish the corresponding **2l** and **2m** in 71 and 63% yields respectively (entries 11 and 12). Importantly, no 1-substituted 1*H*-indene **4** formation was observed in all cases.

We next considered the possibility of extending the reaction to internal alkyne substrates. To our delight, the reaction could also proceed well under the above optimized

(8) For selected reviews for gold catalysis, see: (a) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448. (b) Corma, A.; Leyva-Pèrez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1994. (c) Corma, A.; Leyva-Pèrez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657. (d) Hirner, J. J.; Shi, Y.; Blum, S. A. *Acc. Chem. Res.* **2011**, *44*, 603. (e) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208. (f) Sohel, S. M. A.; Liu, R.-S. *Chem. Soc. Rev.* **2009**, *38*, 2269. (g) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395. (h) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351. (i) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326. (j) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266. (k) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239. (l) Bongers, N.; Krause, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 2178. (m) Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev.* **2008**, *37*, 1766.

(9) For selected examples, see: (a) Velegraki, G.; Stratakis, M. *J. Org. Chem.* **2013**, *78*, 8880. (b) Ghosh, N.; Nayak, S.; Sahoo, A. K. *J. Org. Chem.* **2011**, *76*, 500. (c) Menz, H.; Binder, J. T.; Crone, B.; Duschek, A.; Haug, T. T.; Kirsch, S. F.; Klahn, P.; Liébert, C. *Tetrahedron* **2009**, *65*, 1880. (d) Jung, H. H.; Floreancig, P. E. *J. Org. Chem.* **2007**, *72*, 7359. (e) Wessig, P.; Teubner, J. *Synlett* **2006**, 1543. (f) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563. (g) Fukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729. (h) Fukuda, Y.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2013.

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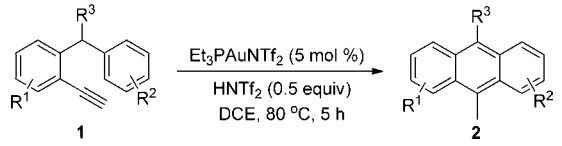
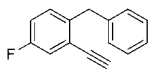
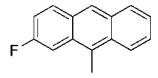
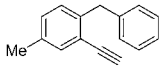
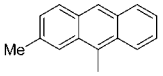
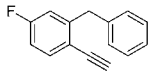
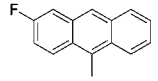
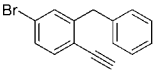
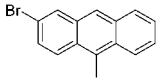
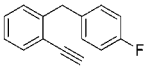
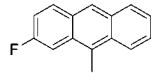
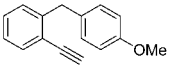
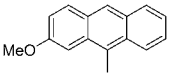
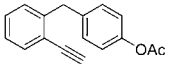
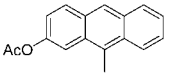
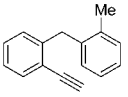
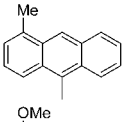
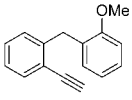
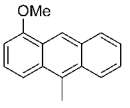
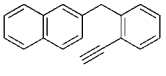
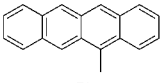
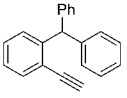
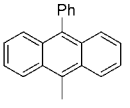
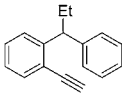
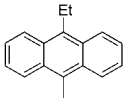
Table 2. Reaction Scope with Terminal Alkyne Substrates **1**[a]

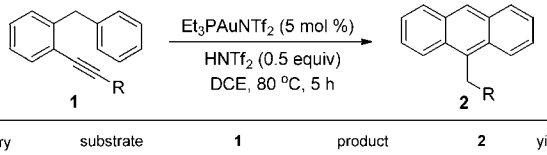


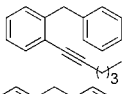
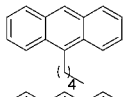
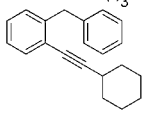
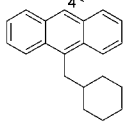
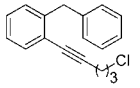
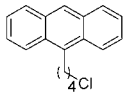
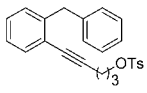
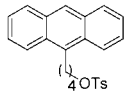
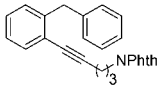
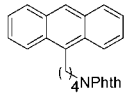
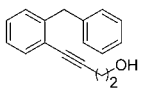
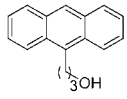
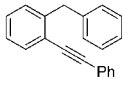
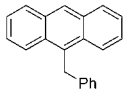
entry	substrate	1	product	2	yield
1		**1b**		**2b**	62%
2		**1c**		**2c**	60%
3		**1d**		**2d**	63%
4		**1e**		**2e**	68%
5		**1f**		**2b**	60%
6		**1g**		**2g**	67%
7[b]		**1h**		**2h**	63%
8		**1i**		**2i**	62%
9		**1j**		**2j**	58%
10		**1k**		**2k**	68%
11		**1l**		**2l**	71%
12		**1m**		**2m**	63%

[a] Reactions run in vials; [**1**] = 0.05 M; isolated yields are reported. [b] 1.0 equiv of CF_3CO_2H was used instead.

reaction conditions, furnishing versatile anthracenes **2n**–**u** in moderate to good yields. As summarized in Table 3, a range of internal alkyne substrates were allowed. In addition, the reaction was generally tolerant of various functional groups, including a remote Cl (entry 3), OTs group (entry 4), *N*-phthaloyl (entry 5), and even the unprotected OH (entry 6). Interestingly, employment of **1t**,**u** bearing phenyl and ester substituents also resulted in the formation of the corresponding **2t**,**u** in fairly good yields (entries 7 and 8). Finally, it should be pointed out that no 7-*endo-dig* cyclization

Table 3. Reaction Scope with Internal Alkyne Substrates **1**[a]



entry	substrate	1	product	2	yield
1		**1n**		**2n**	65%
2		**1o**		**2o**	66%
3		**1p**		**2p**	63%
4		**1q**		**2q**	65%
5		**1r**		**2r**	70%
6		**1s**		**2s**	80%
7		**1t**		**2t**	71%
8		**1u**		**2u**	72%

[a] Reactions run in vials; [**1**] = 0.05 M; isolated yields are reported.

product was formed in all cases, highlighting the high regioselectivity of this methodology.

These anthracenes are potentially useful in organic synthesis and will constitute valuable precursors for the construction of important anthracene derivatives, as depicted in Scheme 2. For anthracene **2a**, besides the known transformations,[11] it could also undergo smooth radical bromination and DDQ oxidation to yield the corresponding 9-bromomethylanthracene **5** and 9-formylanthracene **6** in 80% and 87% yield, respectively. In case of anthracene **2e**, it could be subjected to Suzuki cross-coupling with boronic acids to generate more conjugated systems **7** and **8** in good yields.

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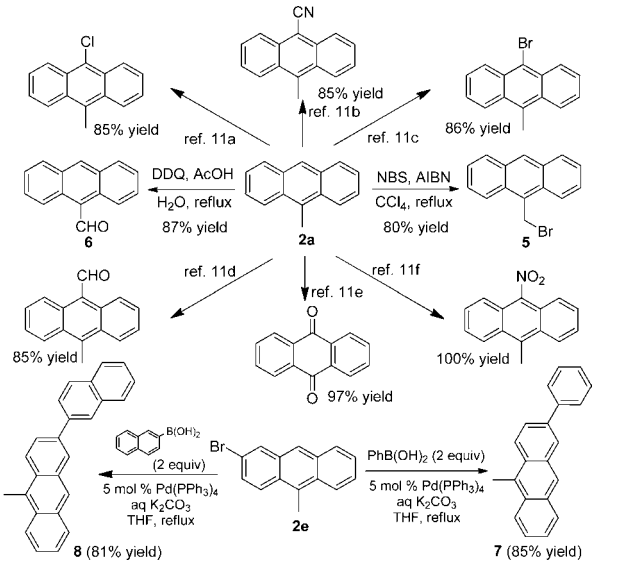
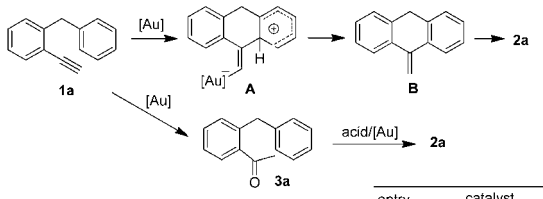
(12) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232.

Scheme 2. Synthetic Applications



Scheme 3. Proposed Reaction Mechanism



entry	catalyst	yield
1	5 mol % $Et_3PAuNTf_2$	<5%
2	$HNTf_2$ (0.5 equiv)	72%
3	5 mol %$Et_3PAuNTf_2$/ $HNTf_2$ (0.5 equiv)	70%

The mechanism for the formation of anthracene **2a** from *o*-alkynyldiphenylmethane **1a** was proposed as shown in Scheme 3.[12] The vinyl gold intermediate **A** might be initially formed by a gold-catalyzed 6-*exo*-*dig* cyclization.[13−15] Then, protodeauration yielded the intermediate **B**, which could be further isomerized into the final **2a** mediated by gold and/or proton acid.[16] Importantly, this speculation was further confirmed by the fact that ^{1}H NMR monitoring of the cyclization reaction under the optimal reaction conditions clearly detected the formation of intermediate **B** but only a trace of the *o*-acyldiphenylmethane **3a**. However, part of **2a** might come from an alternative pathway involving a gold-catalyzed hydration, followed by an acid-catalyzed cyclodehydration, as it was found that **3a** could be transformed into **2a** in 72% yield after 10 h (16% of **3a** remained unreacted) in the presence of only acid. This result may also explain that the role of acid here serves to accelerate the minor pathway that converts **3a** to **2a**.

In conclusion, we have developed a novel gold-catalyzed hydroarylation reaction, leading to the concise synthesis of versatile anthracene derivatives in moderate to good yields. Compared to a typical Bradsher-type reaction, this strategy provides much improved synthetic flexibility and offers an atom-economic and viable alternative for the preparation of anthracenes. Other notable features of this method include widespread availability of the substrates, compatibility with a broad range of functional groups, a simple procedure, mild reaction conditions, and in particular, no need to exclude moisture or air ("open flask"). Further investigations into the synthetic applications of the current reaction are in progress in our laboratory.

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Supporting Information Available. Experimental procedures; compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

(13) For reviews of the gold-catalyzed hydroarylation of alkynes, see: (a) de Mendoza, P.; Echavarren, A. M. *Pure Appl. Chem.* **2010**, *82*, 801. (b) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (c) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333. (d) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (e) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896. (f) Dyker, G., Ed. *Handbook of C−H Transformations*; Wiley-VCH: Weinheim, 2005.

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(15) For selected examples on the metal-catalyzed 6-*exo*-*dig* hydroarylation, see: (a) Kwon, Y.; Cho, H.; Kim, S. *Org. Lett.* **2013**, *15*, 920. (b) Hashmi, A. S. K. *Pure Appl. Chem.* **2010**, *82*, 1517. (c) Ferrer, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1105.

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The authors declare no competing financial interest.