DOI: 10.1002/chem.201301203

Gold-Catalyzed Cyclization of 1-(Indol-3-yl)-3-alkyn-1-ols: Facile Synthesis of Diversified Carbazoles

Zhen Zhang,[a] Xiangying Tang,*[a] Qin Xu,*[b] and Min Shi*[a, b]

Abstract: Efficient cyclization of 1-(indol-3-yl)-3-alkyn-1-ols in the presence of a cationic gold(I) complex, leading to annulated or specific substituted carbazoles, was observed. Depending on the reaction conditions and substitution pattern, divergent reaction pathways were discovered, furnishing diversified carbazole structures. Cycloalkyl-annulated [*b*]carbazoles are obtained through 1,2-alkyl migration of the metal-carbene intermediates; cycloalkyl-annulated [*a*]carbazoles are formed through a Wagner–Meerwein-type 1,2-alkyl shift; carbazole ethers are constructed through ring-opening of the cyclopropyl group by nucleophilic attack of water or an alcohol.

Keywords: carbazoles · catalysis · cyclization · gold · indoles

Introduction

The carbazole nucleus serves as a vital unit in naturally occurring alkaloids,[1] optoelectronic materials,[2] and polymers[3] due to its biological and unique material properties. A large array of bioactive carbazole-containing natural products contain specific substitutions or annulated rings, including tubingensin A,[4] xiamycin A,[5] and clausenamine A[6] (Figure 1). Although a lot of synthetic methodologies to construct carbozales have been reported,[7] an efficient and mild preparative route to specific substituted carbozales is still highly desirable.[8] Gold-catalyzed cyclization reactions are a powerful tool for the synthesis of indole-containing structures, including carbazoles.[9] For example, gold-catalyzed deacylative cycloisomerization of 3-acylindole/ynes (reported by Liu et al.) and intramolecular hydroarylation of 1-(indol-2-yl)-2,3-allenols or 1-(indol-2-yl)-3-alkyn-1-ols (reported by the groups of Ma, Alcaide) are efficient synthetic routes to carbazoles.[10] Another protocol to access aryl-annulated [*a*]carbazoles through gold-catalyzed intramolecular hydroamination/cycloisomerization of aniline-substituted diethynylarenes was explored by Ohno et al.[11] Herein, we wish to report a novel gold-catalyzed cyclization of 1-(indol-3-yl)-3-alkyn-1-ols to form annulated or specific substituted carbazoles. Significant molecular diversity can be obtained in one step starting from easily accessible 1-(indol-3-yl)-3-alkyn-1-ols.[12]

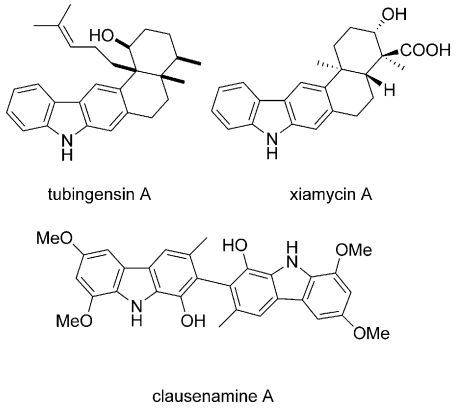

Figure 1. Bioactive natural products containing a carbazole.

Results and Discussion

We first investigated the reaction of 1-(indol-3-yl)-3-alkyn-1-ol **1a** in the presence of various catalysts and the results are summarized in Table 1. The treatment of **1a** with $AgNTf_2$ led to a complex product mixture (Table 1, entry 1). [AuCl(PPh_3)]/$AgSbF_6$, [Au(CH_3CN)(JackiePhos)][SbF_6], and $PtCl_2$ were not catalytically active in this reaction (Table 1, entries 2–4). When [Au(Me_4tBuXPhos)][SbF_6] was used as the catalyst, carbazole **2a** was obtained in 21% yield (Table 1, entry 5). Next, gold(I) complexes bearing bulky phosphanes (**A** and **B**) were tested in this reaction and we found that gold complexes with sterically bulky ligands, which have been explored by Echavarren et al., were much more effective for the transformation of **1a** into carbazole **2a**, probably

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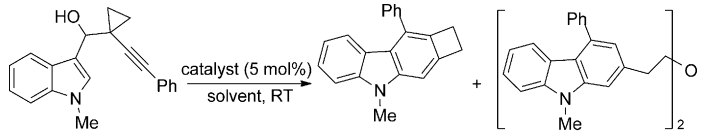
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301203.

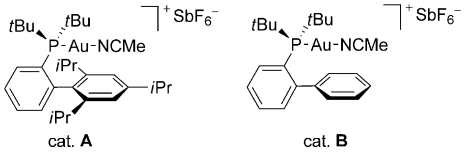
Table 1. Discovery of a gold-catalyzed cyclization of 1-(indol-3-yl)-2-cyclopropyl-3-alkyn-1-ol **1a**.[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Time	Yield [%][b]	
				2a	**3a**
1	$AgNTf_2$	CH_2Cl_2	5 min	complex	–
2	$[AuCl(PPh_3)]/AgSbF_6$	CH_2Cl_2	30 min	complex	–
3	$[Au(CH_3CN)(JackiePhos)][SbF_6]$	CH_2Cl_2	5 min	complex	–
4	$PtCl_2$	CH_2Cl_2	1 h	N.R.	–
5	$[Au(Me_4tBuXPhos)][SbF_6]$	CH_2Cl_2	1 h	21	–
6	**A**	CH_2Cl_2	30 min	75	–
7	**B**	CH_2Cl_2	4 h	10	–
8	**A**	$ClCH_2CH_2Cl$	30 min	54	–
9	**A**	C_6H_6	30 min	32	36
10[c]	**A**	toluene	30 min	10	68

[a] All reactions were performed on a 0.10 mmol scale. Tf = trifluoromethylsulfonyl, JackiePhos = 2-{bis[3,5-bis(trifluoromethyl)phenyl]phosphine}-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl, N.R. = no reaction, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl. [b] Yields are of the isolated products. [c] Compound **1a** was added to the solution of catalyst **A** in toluene at room temperature.

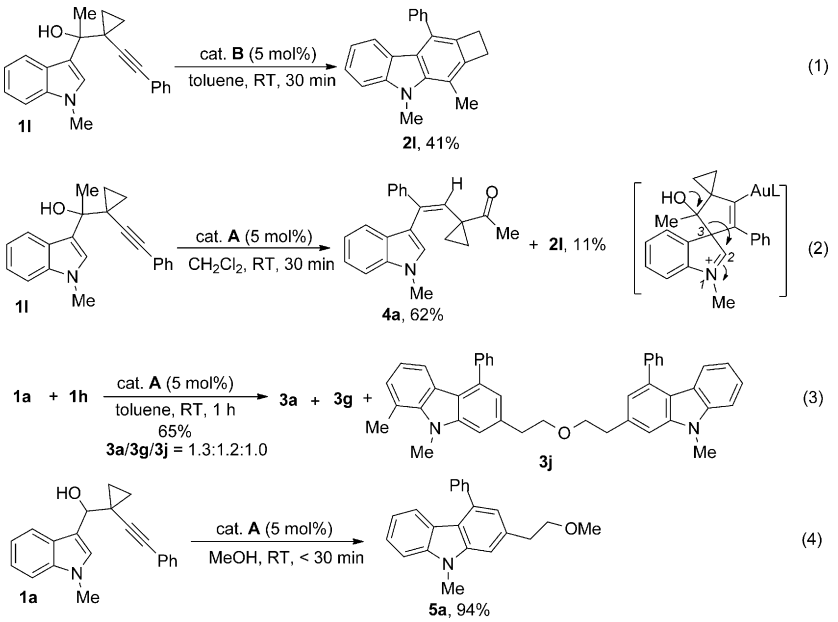


because the electron-donating dialkylbiarylphosphane ligands increased the selective activation with the substrate by modulating the high electrophilicity of gold(I).[13] Further investigations showed that other solvents, such as 1,2-dichloroethane, benzene, and toluene, gave no improvement in results compared with CH_2Cl_2, and the use of catalyst **A** (5 mol%) in dichloromethane at room temperature equated to the most efficient conditions for the formation of **2a** (Table 1, entries 6–10). Interestingly, adding **1a** to the solution of catalyst **A** in toluene afforded biscarbazole **3a** in 68% yield, along with **2a** as the minor product in 10% yield (Table 1, entry 10; for details, see Table S1 in the Supporting Information). The structure of **2a** has been unequivocally confirmed by X-ray diffraction.[14]

Next, we sought to expand the scope of this gold(I)-catalyzed cyclization and the results are shown in Table 2. For substrates **1b** and **1c** bearing electron-donating groups (methyl or methoxy group) on their benzene rings, the corresponding products **2b** and **2c** were obtained in 60 and 34% yields, respectively (Table 2, entries 1 and 2). The poor yield of **2c** was presumably due to electronic effects and many unidentified byproducts were observed in the reaction. For substrate **1d** bearing a bromine atom at the 4-position, a complex product mixture was formed (Table 2, entry 3). For 5-, 6-, or 7-substituted substrates **1e**–**1h**, the reactions proceeded smoothly to give the desired products **2e**–**2h** in 46–87% yields (Table 2, entries 4–7). However, substrate **1i** containing an azaindole ring was not suitable for this cyclization and no reaction took place (Table 2, entry 8). When R^1 was an alkyl group, the reaction also proceeded smoothly to give the corresponding carbazole **2j** in 64% yield (Table 2, entry 9). In the case of substrate **1k**, catalyst **B** produced better results than **A**, affording **2k** in 43% yield (Table 2, entry 10).

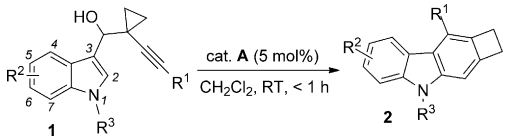
We then performed the reaction in toluene to synthesize biscarbazoles **3** and the results are summarized in Table 3. When R^1 was an aromatic ring bearing electron-donating or alkyl groups, products **3b**, **3c**, and **3d** were obtained in 35–63% yields along with small amounts of products **2**. For substrates **1e**, **1g**, **1h**, and **1k** bearing a substituent at the 5-, 6-, or 7-position, the reactions proceeded smoothly to give the corresponding products **3e**–**3h** in 63–76% yields. The structure of **3g** has also been confirmed by X-ray crystal diffraction.[14]

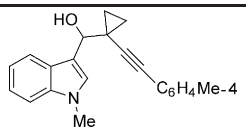
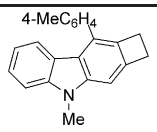
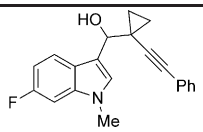
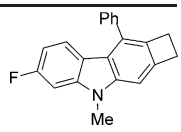
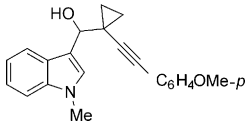
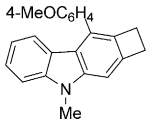
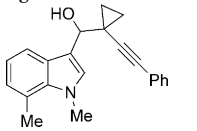
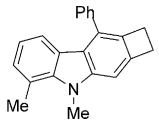
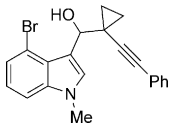
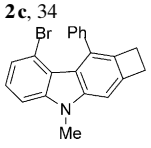
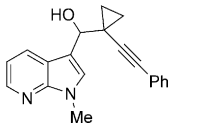
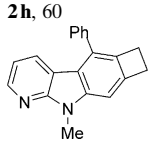
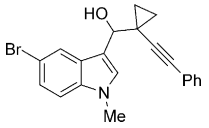
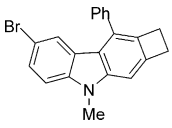
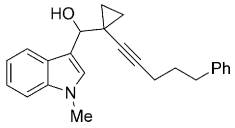
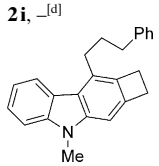
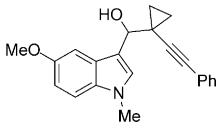
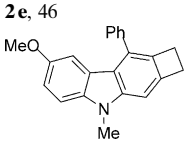
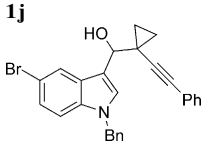
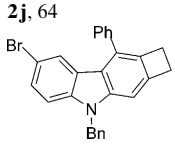
To determine more precisely the influence of substitution, we prepared tertiary alcohol **1l** and treated it with the gold catalyst. We found that carbazole **2l** could be obtained in 41% yield in the presence of **B** in toluene [Scheme 1,



Scheme 1. Control experiments.

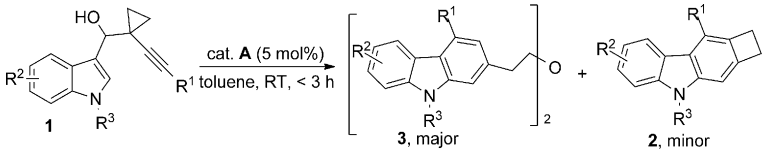
Table 2. Gold(I)-catalyzed cyclization of 1-(indol-3-yl)-2-cyclopropyl-3-alkyn-1-ols **1** to form carbazoles **2**.[a]

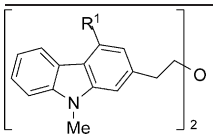


Entry	1	2, Yield [%][b]	Entry	1	2, Yield [%][b]
1			6		
	1b	**2b**, 60		**1g**	**2g**, 87
2			7		
	1c	**2c**, 34		**1h**	**2h**, 60
3			8		
	1d	**2d**, –[c]		**1i**	**2i**, –[d]
4			9		
	1e	**2e**, 46		**1j**	**2j**, 64
5			10		
	1f	**2f**, 61		**1k**	**2k**, 33 (43)[e]

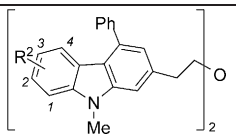
[a] Catalyst **A** (5 mol%), CH_2Cl_2 as solvent, room temperature, <1 h. Bn = benzyl. [b] Yields are of the isolated products. [c] Complex mixture. [d] No reaction. [e] Catalyst **B** (5 mol%) was used.

Table 3. Gold(I)-catalyzed cyclization of 1-(indol-3-yl)-2-cyclopropyl-3-alkyn-1-ols **1** to form biscarbazoles **3**.[a]

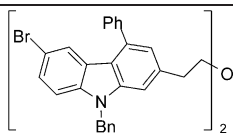




R^1 = 4-MeC_6H_4, **3b**, 63% (**2b**, 34%)
R^1 = 4-$MeOC_6H_4$, **3c**, 35% (**2c**, 15%)[b]
R^1 = $PhCH_2CH_2CH_2$, **3d**, 35% (**2j**, 33%)



R^2 = 3-Br, **3e**, 66% (**2e**, 26%)
R^2 = 2-F, **3f**, 76% (**2g**, 11%)
R^2 = 1-Me, **3g**, 67% (**2h**, 18%)

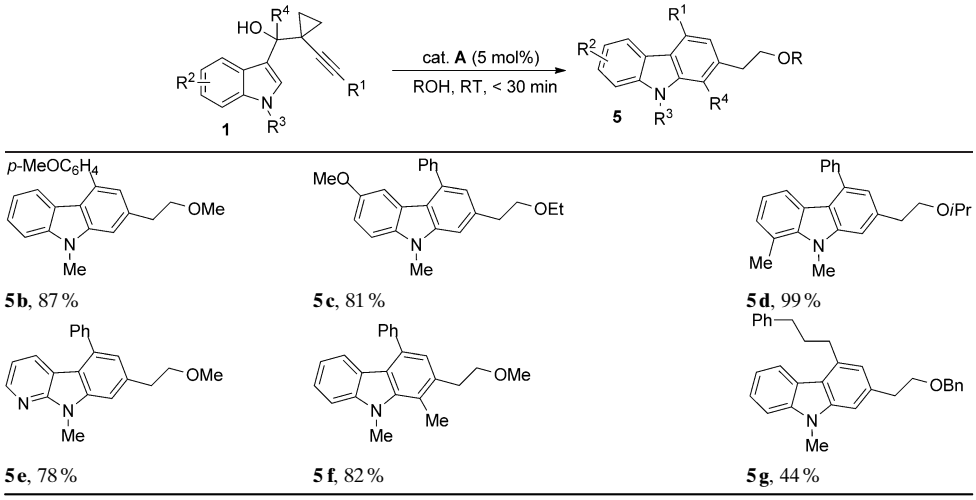


3h, 63% (**2k**, 7%)[b]

[a] Compound **1** was added to a solution of catalyst **A** (5 mol%) in toluene and stirred at room temperature (<3 h). Yields are of the isolated products. [b] Catalyst **B** was used instead of **A**.

Eq. (1)]. However, treatment of **1l** with **A** (5 mol%) in dichloromethane afforded the corresponding ketone **4a** in 62% yield, which was formed through heterolytic fragmentation rather than 1,2-migration [Scheme 1, Eq. (2)].[15] These results indicate that the initial C–C bond formation takes place at C3 of the indole ring rather than at C2. To verify the formation of biscarbazoles **3**, a crossover experiment was performed with a 1:1 mixture of **1a** and **1h** under the standard conditions, giving the corresponding products **3a** and **3g** and the crossover product **3j** in an overall 65% yield [1.3:1.2:1.0; Scheme 1, Eq. (3)]. This result clearly implies the formation of **3** in an intermolecular manner and the in situ generated H_2O may be the nucleophile. Thus, we attempted to use alcohol as the nucleophile instead of H_2O. Upon treating **1a** with **A** (5 mol%) in methanol, the corresponding ring-opened product **5a** was isolated in 94% yield [Scheme 1, Eq. (4)].[16] Other alcohols, such as ethanol, isopropyl alcohol, and benzyl alcohol, and various substituents on sub-

Table 4. Gold(I)-catalyzed cyclization of 1-(indol-3-yl)-2-cyclopropyl-3-alkyn-1-ols **1** to form carbazoles **5**.[a]



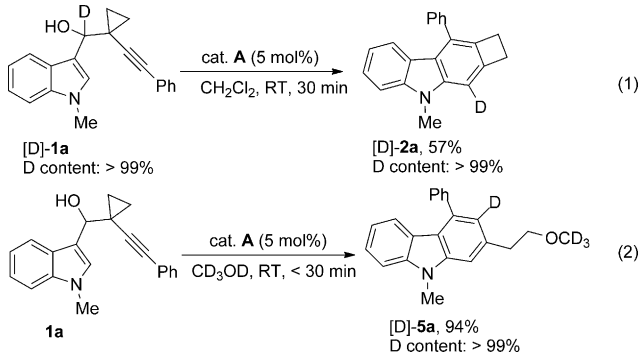
[a] Catalyst **A** (5 mol%), ROH as solvent, room temperature, <30 min. Yields are of the isolated products.

strates **1** afforded the corresponding carbazole products **5** in 44–99% yields (Table 4).[14]

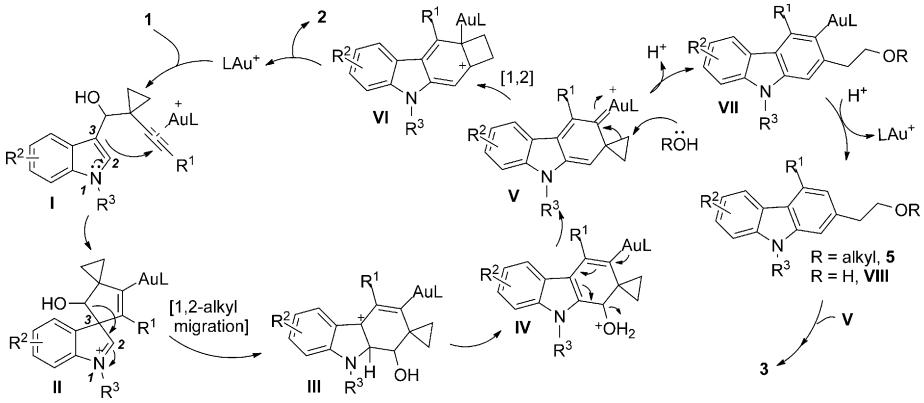
To verify the reaction pathway, an isotopic labeling experiment was performed by treating [D]-**1a** with gold(I) catalyst **A** (5 mol%) and the desired product [D]-**2a** was obtained in 57% yield [Scheme 2, Eq. (1)]. Upon treating **1a** with the gold catalyst in [D_4]methanol, the desired product [D]-**5a** was isolated in 94% yield, supporting the hypothesis that the hydrogen is transferred from methanol to the final product by protodeauration of the intermediate [Scheme 2, Eq. (2)].

A plausible mechanism for the cyclization of 1-(indol-3-yl)-2-cyclopropyl-3-alkyn-1-ols is shown in Scheme 3.[17] Spirocyclic intermediate **II** is formed via intermediate **I**, derived from the nucleophilic attack of the indolyl C3 onto the gold(I)-activated alkyne.[18] Subsequent 1,2-alkyl migration gives intermediate **III** and protonation of the hydroxyl group affords intermediate **IV**, followed by elimination of H_2O to generate cyclovinylic gold carbene intermediate **V**.[19] A 1,2-migaration to the adjacent carbenoid center leads to ring-expanded intermediate **VI**, and then elimination of LAu^+ forms carbazole **2** in a subsequent step.[20] When the reaction is performed in an alcohol or toluene, the cyclopropyl group in intermediate **V** undergoes nucleophilic ring-opening by the alcohol or H_2O to deliver intermediate **VII**. Subsequent protodeauration of intermediate **VII** gives ether **5** (R = alkyl) or intermediate **VIII** (R = H), which leads to biscarbazole **3** by further nucleophilic attack on intermediate **V**.

To examine the necessity of the cyclopropyl substitution, we prepared various 2,2-disubstituted 1-(indol-3-yl)-3-alkyn-1-ols, **1m**–**1s**, that do not contain a cyclopropyl moiety.[21] Screening of the reaction conditions revealed that [Au(CH_3CN)(JackiePhos)][SbF_6] was the best catalyst and dichloromethane the best solvent (see Table S2 in the Supporting Information). To our surprise, the results are different from the cyclization of 1-(indol-3-yl)-2-cyclopropyl-3-alkyn-1-ols **1**, with the formation of a mixture of carbazoles **6** and **7**, as shown in Table 5. Substrates **1m** and **1n** (R^4 = Me) afforded carbazoles **6a** and **6b** in moderate yields as the major products along with minor amounts of carbazoles **7a** and **7b** (Table 5, entries 1 and 2). The structure of **6b** has been unequivocally confirmed by X-ray diffraction.[14] With regard to the other cycloalkyl substituents, cyclobutyl, cyclopentyl, and cyclohexyl groups were all suitable for this reaction, with the formation of cycloalkyl-annulated [*a*]carbazoles in moderate to good yields and good regioselectivity (Table 5, entries 3–6).

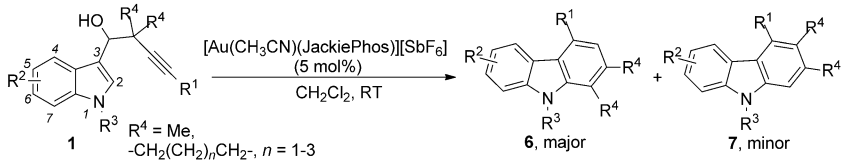


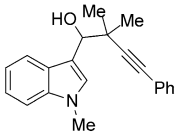
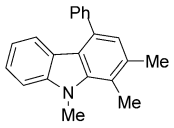
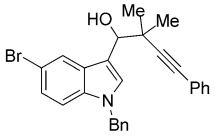
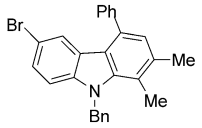
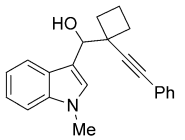
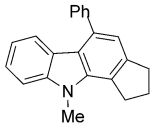
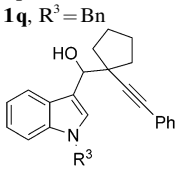
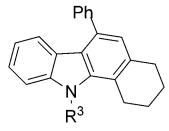
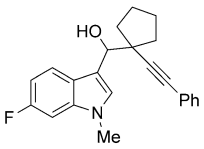
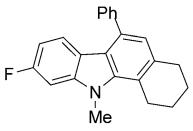
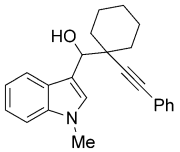
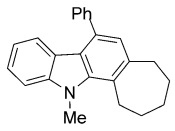
Scheme 2. Isotopic labeling experiments.



Scheme 3. A plausible reaction mechanism for the formation of carbazoles **2**, **3**, and **5**.

Table 5. Gold(I)-catalyzed cyclization of 2,2-disubstited 1-(indol-3-yl)-3-alkyn-1-ols **1**.[a,b]

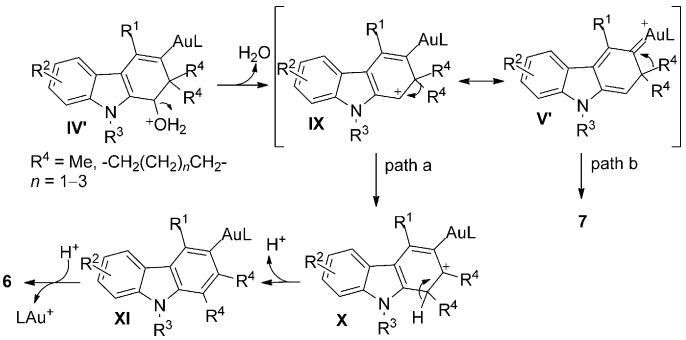


Entry	**1**	**6**, time, yield [%] (**6**/**7**)[a]	Entry	**1**	**6**, time, yield [%] (**6**/**7**)[a]
1			4		
	1m	**6a**, 6 h, 62 (87:13)		**1p**, R^3 = Me **1q**, R^3 = Bn	**6d**, R^3 = Me, 1 h, 81 (89:11) **6e**, R^3 = Bn, 1 h, 83 (80:20)
2			5		
	1n	**6b**, 3 h, 84 (94:6)		**1r**	**6f**, 40 min, 91 (75:25)
3			6		
	1o	**6c**, 10 min, 68 (82:18)		**1s**	**6g**, 1 h, 90 (80:20)

[a] Yields are of a mixture of two inseparable products, **6** and **7**. The ratio was determined by NMR spectroscopy.

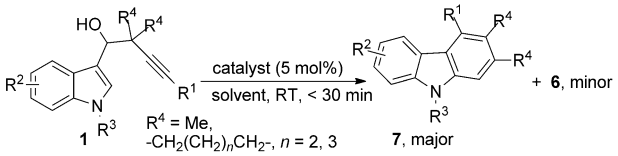
Substrates bearing a 5- or 6-substituent could be also incorporated well into the reaction (Table 5, entries 2 and 5).

Notably, when the reaction was performed in an alcohol in the presence of **A** or **B**, carbazoles **7** were formed predominantly (Table 6). Carbazoles **7** are formed through a 1,2-alkyl shift of cyclovinylic gold carbene intermediate **V′** in a similar manner to that for carbazoles **2** (Scheme 4, path b). Carbazoles **6** are probably formed through a Wagner–Meerwein-type 1,2-alkyl shift of the carbocationic intermediate **IX** (Scheme 4, path a).[22] We believe that the actual intermediate species is a resonance hybrid of **IX** and **V′**.[22e] An alcohol seems to stabilize or facilitate the formation of gold carbene **V′**, leading to the predominant formation of carbazoles **7**. Although no evidence of the Wagner–Meerwein rearrangement for cyclopropyl-substituted substrates has been found, we speculate that the unique ring-expansion aptitude is probably due to stereoelectronic effects: the carbon–carbon sigma bond in the cyclopropane ring cannot interact with the unoccupied orbital of carbocation **IX**, and thus the gold carbene **V** preferentially undergoes 1,2-migaration.



Scheme 4. A plausible reaction mechanism for the formation of carbazoles **6** and **7**.

Table 6. Gold(I)-catalyzed cyclization of 2,2-disubstited 1-(indol-3-yl)-3-alkyn-1-ols **1** in an alcohol.



Entry	**1**	Catalyst	Solvent	**7**+**6**, yield [%] (**7**/**6**)[a]
1	**1m**	**B**	EtOH	**7a**+**6a**, 47 (90:10)
2	**1q**	**A**	MeOH	**7e**+**6e**, 52 (80:20)
3	**1r**	**A**	MeOH	**7f**+**6f**, 70 (87:13)
4	**1o**	**A**	MeOH	**7g**+**6g**, 61 (87:13)

[a] Yields are of a mixture of two inseparable products, **7** and **6**. The ratio was determined by NMR spectroscopy.

Conclusion

We have developed a diversified gold-catalyzed intramolecular cyclization of 1-(indol-3-yl)-3-alkyn-1-ols, leading to an-

nulated or substituted carbazoles in moderate to good yields. Depending on the reaction conditions and the substitution pattern, 1) cycloalkyl-annulated [*b*]carbazoles are obtained through 1,2-alkyl migration to the adjacent carbenoid center; 2) cycloalkyl-annulated [*a*]carbazoles are formed through a Wagner–Meerwein-type 1,2-alkyl shift; or 3) carbazole ethers are obtained through ring-opening of the cyclopropyl group by nucleophilic attack of water or an alcohol. The cyclization approach presented is well suited to the divergent synthesis of various substituted and annulated carbazole libraries.

Experimental Section

General procedure for the preparation of compounds 2, 5, 6, and 7: The gold catalyst (5 mol%) was added to a stirred solution of **1** in dichloromethane or an alcohol (0.1 M) under ambient pressure at room temperature and the reaction mixture was stirred until the reaction was complete (monitored by TLC). The solvent was then evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1 v/v) to give the desired product.

Compound 2a: Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta=$ 3.19–3.22 (2H, m), 3.23–3.24 (2H, m), 3.77 (3H, s), 6.92–6.96 (1H, m), 7.08 (1H, s), 7.31–7.36 (2H, m), 7.40–7.44 (1H, m), 7.50 (2H, d, $J=$ 7.2 Hz), 7.58 (1H, d, $J=8.0$ Hz), 7.63 ppm (2H, d, $J=7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta=27.87$, 27.93, 29.2, 102.4, 108.0, 118.0, 118.7, 121.9, 122.7, 124.5, 127.4, 128.4, 129.2, 131.4, 134.6, 137.6, 140.3, 141.8, 143.1 ppm; HRMS (EI): *m*/*z* calcd for $C_{21}H_{17}N^+$: 283.1361 [M^+]; found: 283.1357.

Compound 5a: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta=3.12$ (2H, t, $J=7.2$ Hz), 2.39 (3H, s), 3.74 (2H, t, $J=7.2$ Hz), 3.85 (3H, s), 6.93–6.98 (2H, m), 7.25–7.26 (1H, m), 7.34–7.40 (2H, m), 7.44–7.53 (4H, m), 7.62–7.64 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta=29.1$, 36.8, 58.7, 74.0, 107.6, 108.1, 118.4, 118.6, 121.7, 122.0, 122.3, 125.1, 127.4, 128.3, 129.2, 136.6, 137.5, 141.3, 141.7 ppm; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{21}NO^+$: 315.1623 [M^+]; found: 315.1632.

Compound 6a: White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta=2.49$ (3H, s), 2.77 (3H, s), 4.11 (3H, s), 6.89–6.91(1H, m), 6.92 (1H, s), 7.28–7.37 (3H, m), 7.42–7.51 (3H, m), 7.55–7.57 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta=15.4$, 20.8, 33.5, 108.5, 117.8, 118.5, 119.6, 121.9, 122.6, 123.8, 125.0, 127.2, 128.3, 129.3, 134.6, 134.8, 141.0, 141.5, 142.6 ppm; HRMS (EI): *m*/*z* calcd for $C_{21}H_{19}N^+$: 285.1517 [M^+]; found: 285.1519.

Compound 7a: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta=2.13$ (3H, s), 2.53 (3H, s), 3.80 (3H, s), 6.64–6.66 (1H, m), 6.81–6.85 (1H, m), 7.23 (1H, s), 7.29–7.30 (2H, m), 7.34–7.37 (2H, m), 7.47–7.55 ppm (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta=16.1$, 21.8, 28.9, 107.9, 108.5, 118.2, 119.5, 121.6, 122.9, 124.6, 125.2, 127.1, 128.7, 129.4, 135.0, 136.2, 139.2, 141.0, 141.1 ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{20}N^+$: 286.1596 [M+H$^+$], found: 286.159.2.

General procedure for the preparation of compounds 3: Compound **1** was added to a stirred solution of **A** (5 mol%) in toluene (1.0 equiv), and the mixture was stirred at room temperature until the starting material disappeared (monitored by TLC). The solvent was then removed under reduced pressure and the crude product was purified by silica gel flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1–5:1 v/v) to afford the desired product **3**.

Compound 3a: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta=3.14$ (4H, t, $J=7.2$ Hz), 3.72 (6H, s), 3.85 (4H, t, $J=7.2$ Hz), 6.93–6.97 (2H, m), 6.98 (2H, d, $J=1.2$ Hz), 7.22 (2H, d, $J=0.8$ Hz), 7.29 (2H, d, $J=$ 8.4 Hz), 7.34–7.38 (2H, m), 7.45–7.52 (8H, m), 7.60–7.62 ppm (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta=28.9$, 36.9, 72.3, 107.7, 108.2, 118.4, 118.5, 121.8, 122.0, 122.3, 125.1, 127.4, 128.3, 129.2, 136.7, 137.4, 141.2, 141.3, 141.6 ppm; HRMS (ESI): *m*/*z* calcd for $C_{42}H_{37}N_2O^+$: 585.2906 [M^+], found: 585.2910.

X-ray crystal structures: CCDC-898159 (**2a**), CCDC-908377 (**3g**), CCDC-925337 (**5f**), CCDC-925326 (**6b**), and CCDC-926456 (**7e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology (08dj1400100–2), the National Basic Research Program of China ((973)-2009CB825300), the Fundamental Research Funds for the Central Universities and the National Natural Science Foundation of China (21102166, 21072206, 20472096, 20872162, 20672127, 21121062, and 20732008) for financial support.

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Received: March 29, 2013
Published online: July 10, 2013

