Gold and Brønsted Acid Catalyzed Spirocyclization of 2- and 3-Indolyl-Tethered 1,4-Enyne Acetates to Spiro[4,*n*]alkyl[*b*]indoles

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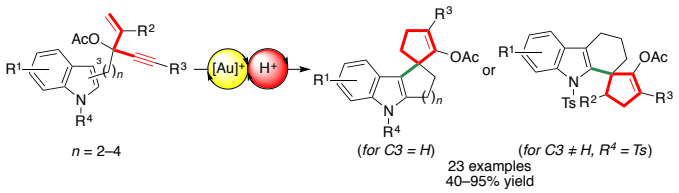
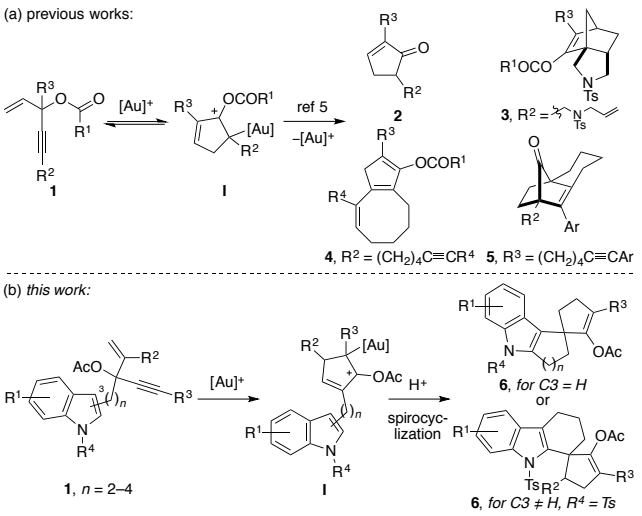
Supporting Information Placeholder



ABSTRACT: A synthetic method to prepare spiro[4,*n*]alkyl[*b*]indoles (*n* = 4–6) efficiently that relies on the gold(I)- and Brønsted acid-mediated spirocyclization of 2- and 3-indolyl-tethered 1,4-enyne acetates at room temperature and open to air is described.

One of the most versatile synthetic tools to emerge in recent years for the rapid assembly of molecular complexity from readily accessible substrates in a single operation is homogeneous gold catalysis.[1–10] In carbocyclic synthesis, for example, it has provided a convenient method for the efficient preparation of cyclopentenones **2** by mediating the tandem [2,3]-sigmatropic rearrangement/metallo-Nazarov cyclization of 1,4-enyne esters (Scheme 1a).[5c,e] Often referred to as the Rautenstrauch rearrangement, subsequent studies by us showed that a suitably placed alkene tether in the posited cyclopentenyl gold species **I** resulted in it undergoing a Diels-Alder reaction to give isoindoles **3**.[5d,12] On the other hand, substrates containing a pendant alkyne motif in place of the alkene group were found to lead to a gold(I)-catalyzed 8-*endo*-*dig* cyclization pathway being realized to afford bicyclo[6.3.0]undeca-2,4,9-trienyl esters **4**.[5a] By placing the alkyne tether at the ester carbon center of the substrate and with an *in situ* generated Brønsted acid as a co-catalyst, a formal [3 + 2] cycloaddition/deacetylation to deliver bridged cyclic ketones **5** was also accomplished.[5b] As part of this ongoing program, we were drawn to the potential spirocyclization chemistry of 2- and 3-indolyl tethered 1,4-enyne acetates **1** mediated by a gold(I) complex and Brønsted acid catalytic system, which has so far remained unexplored (Scheme 1b).[7–11] It was anticipated that such substrates would likewise be prone to a gold(I)-catalyzed Rautenstrauch rearrangement. In the presence of a Brønsted acid, the ensuing 1,3-cyclopentenylgold species **I** might then be expected to undergo spirocyclization to give a wide variety

Scheme 1. Au(I)-Catalyzed Reactivities of 1,4-Enyne Esters

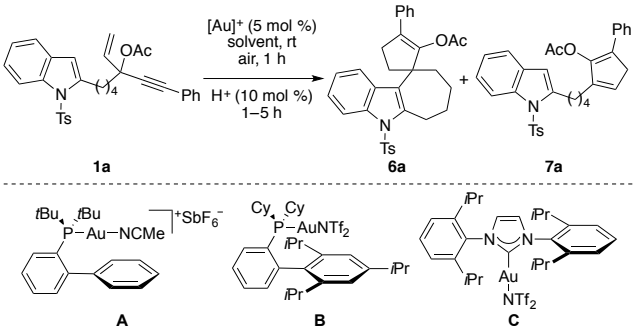


of indole derivatives containing a fused spiro[4,4]non-, spiro[4,5]dec-, or spiro[4,6]undecane ring system. Herein, we disclose the details of this Au(I)-catalyzed method for the efficient and selective synthesis of two members of the *N*-heterocyclic compound family of pharmacological potential in good to excellent yields from 2- and 3-indolyl-tethered 1,4-enyne acetates.[13] Achieved at room temperature under mild conditions that did not require the exclusion of air or moisture,

the reactions represent the first example of 1,3-cyclopentadienes formed *in situ* in this manner using gold catalysis to participate in a spirocyclization pathway.

Our studies began by examining the gold(I)- and Brønsted acid-catalyzed cycloisomerization of 2-indolyl tethered 1,4-enyne acetate **1a** to establish the optimum reaction conditions (Table 1). This initially revealed treating the substrate to 5 mol % of $Ph_3PAuNTf_2$ in 1,2-dichloroethane under ambient conditions for 1 h followed by $NHTf_2$ (10 mol %) in the same solvent and continuing the experiment for a further hour gave **6a** in 37% yield (entry 1). The structure of the *N*-spirocycle was ascertained by NMR measurements and X-ray crystallography. Comparable product yields of 43 and 39% were obtained on increasing the reaction time from 1 to 2.5 h or the Brønsted acid catalyst loading from 10 to 60 mol % for 5 h (entries 2 and 3). In these reactions, the Rautenstrauch adduct **7a** was additionally afforded in 6 and 7% yield. Likewise, repeating the reaction with the gold(I) phosphine complexes **A** or **B**, or NHC–gold(I) (NHC = *N*-heterocyclic carbene) complex **C** in place of $Ph_3PAuNTf_2$ as the catalyst afforded **6a** and **7a** in yields of 31–35 and 4–5% (entries 4–6). Our studies subsequently found the desired *N*-spirocyclic product **6a** was produced in 56% yield when the Brønsted acid was introduced to the NHC–gold(I) complex **C**-mediated reaction conditions without prior dilution (entry 7). Switching the reaction solvent from 1,2-dichloroethane to dichloromethane, acetonitrile or toluene were observed to give product yields of 50–79% (entries 8–10). Under these latter reaction conditions with dichloromethane as the solvent, replacing $NHTf_2$ with either TfOH or *p*TSA was found to give the best result, delivering **6a** in 86% yield in both instances (entries 11 and 12). A slightly lower product yield of 78% was obtained when the substrate was simultaneously subjected to both the NHC–gold(I) complex **C** and *p*TSA (entry 13). However, lower product yields of 36 and 32% were observed with the less Brønsted acidic catalysts TFA and acetic acid (entries 14 and 15).

Table 1. Optimization of the Reaction Conditions[a]



entry	[Au]$^+$	H$^+$	solvent	Yield[b]	
				6a	**7a**
1	$Ph_3PAuNTf_2$	$NHTf_2$[c]	$(CH_2Cl)_2$	37	-
2	$Ph_3PAuNTf_2$	$NHTf_2$	$(CH_2Cl)_2$	43	6
3	$Ph_3PAuNTf_2$	$NHTf_2$[d,e]	$(CH_2Cl)_2$	39	7
4	**A**	$NHTf_2$	$(CH_2Cl)_2$	35	5
5	**B**	$NHTf_2$	$(CH_2Cl)_2$	31	3
6	**C**	$NHTf_2$	$(CH_2Cl)_2$	31	4
7	**C**	$NHTf_2$[f]	$(CH_2Cl)_2$	56	-
8	**C**	$NHTf_2$[f]	CH_2Cl_2	79	-
9	**C**	$NHTf_2$[f]	MeCN	60	-
10	**C**	$NHTf_2$[f]	toluene	50	-
11	**C**	TfOH[f]	CH_2Cl_2	86	-
12	**C**	*p*TSA[f]	CH_2Cl_2	86[g]	-
13[h]	**C**	*p*TSA	CH_2Cl_2	78	-
14	**C**	TFA[f]	CH_2Cl_2	36	-
15	**C**	acetic acid[f]	CH_2Cl_2	32	-

[a]All reactions were performed with 0.1 mmol of **1a** and 5 mol % of gold(I) complex in 1 mL of non-distilled solvent at room temperature and open to air. The Brønsted acid (10 mol %) in 1 mL of non-distilled solvent was added to the reaction mixture after 1 h and stirred for a further 2.5 h. [b]Product yield estimated by ^{1}H NMR analysis with 2-(bromomethyl)naphthalene as the internal standard. [c]Total reaction time = 2 h. [d]Total reaction time = 6 h. [e]Reaction performed with 60 mol % of $NHTf_2$. [f]Brønsted acid added without solvent dilution. [g]Isolated product yield. [h]Gold(I) complex and Brønsted acid added at the beginning of the reaction.

To define the generality of the present procedure, the reaction of a variety of 2-indolyl tethered 1,4-enyne acetates were first evaluated, and the results are summarized in Figure 1. For every substrate examined, all three Brønsted acids $NHTf_2$, TfOH and *p*TSA were undertaken to determine which gave the highest product yield. Overall, these reactions demonstrated the NHC–gold(I) complex **C**/Brønsted acid-catalyzed conditions to be broad, providing access to a series of indolyl-fused spirocyclic derivatives in 32−90% yield from the corresponding substrates **1b**–**n**. The rearrangement of substrates containing other aryl motifs (**1b**–**d**) or a 2-thienyl group (**1e**) at the alkynyl carbon center were found to be tolerated, giving the corresponding *N*-heterocycles **6b**–**e** in 52–88% yield. Similarly, the presence of a *n*butyl (**1f**) or cyclohexyl (**1g**) substituent at this position of the substrate was found to have little influence on the course of the reaction. In these reactions, the corresponding spirocyclic adducts **6f** and **6g** were furnished in respective yields of 74 and 87%. The spirocyclization of starting materials containing a pendant indolyl motif with an electron-withdrawing (**1h**–**k**) or methoxy (**1l**) group were found to furnish the corresponding *N*-heterocyclic products **6h**–**l** in 48–89% yield. The cycloisomerization of substrates where the *N*-tosyl protecting group was replaced by an *N*-alkyl motif, as in **1n** and **1m**, were also found to proceed well and gave **6n** and **6m** in respective yields of 70 and 86%. The analogous experiments with starting materials with an ethyl (**1o**) or *n*propyl (**1p**) in place of the *n*butyl carbon tether were likewise found to give the corresponding indolyl-fused spiro[4,4]non- and spiro[4,5]decane ring systems **6o** and **6p** in 90 and 91% yield.

We next turned our attention to evaluate the scope of the NHC–gold(I) complex **C**/Brønsted acid-mediated protocol to a variety of 3-indolyl tethered 1,4-enyne acetates (Figure 2). Under the optimized conditions with $NHTf_2$ found as the preferred Brønsted acid, this revealed substrates containing a phenyl (**1q**), electron-withdrawing (**1r**,**s**,**v**) or -donating (**1t**,**u**) aryl group at the alkynyl carbon center were well tolerated. In these experiments, the corresponding spirocyclic products **6q**–**v** in 51–91% yield with the structure of **6r** confirmed by X-ray

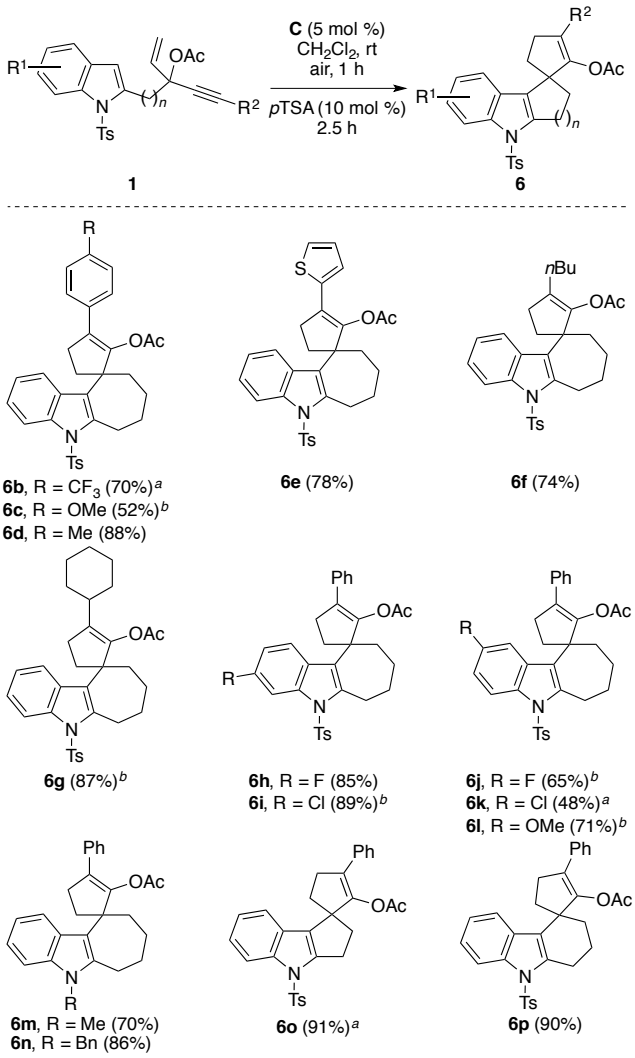


Figure 1. NHC–Au(I) complex **C** and Brønsted acid-catalyzed spirocyclization of **1b**–**p**. All reactions were performed at the 0.1 mmol scale with 5 mol % of NHC–Au(I) complex **C** in CH_2Cl_2 (1 mL) at room temperature and open to air for 1 h followed by the addition of 10 mol % of *p*TSA and continuing the experiment for 2.5 h. Values in parenthesis denote isolated product yields. [a]Reaction performed with $NHTf_2$ instead of *p*TSA. [b]Reaction performed with TfOH instead of *p*TSA.

single crystal analysis. The spirocyclization of a substrate with a pendant phenyl-substituted alkene motif (**1w**) was also observed to furnish the ketone adduct **8w** as a single diastereomer in 78% yield, presumably due the propensity of its acetate precursor to undergo hydrolysis under the Brønsted acidic conditions.

A tentative mechanism for the present Au(I)/Brønsted acid-catalyzed spirocyclization method is outlined in Scheme 2a. With **1a** as a representative example, this could involve the activation of the acetylene bond in the substrate by the metal complex to give the gold-coordinated species **IIa**. As a consequence, this may trigger [2,3]-sigmatropic rearrangement of the acetate motif to provide the putative vinyl gold species **IVa** *via* the 1,3-dioxin-1-ium adduct **IIIa**, as shown in Scheme 2a, path a. Its subsequent metallo-Nazarov cyclization and deauration of the ensuing cyclopentenium species **Ia** put forward in Scheme 1 would provide the 1,3-cyclopentadiene

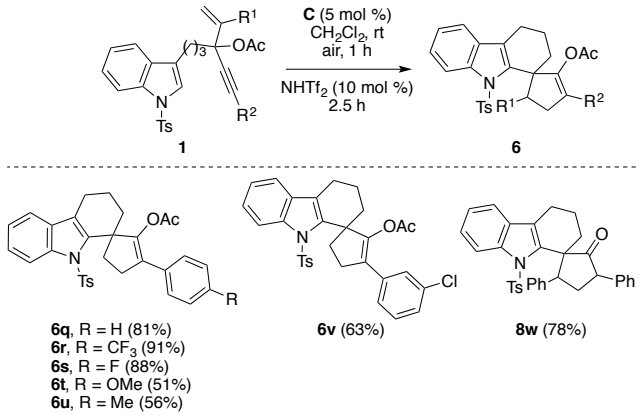
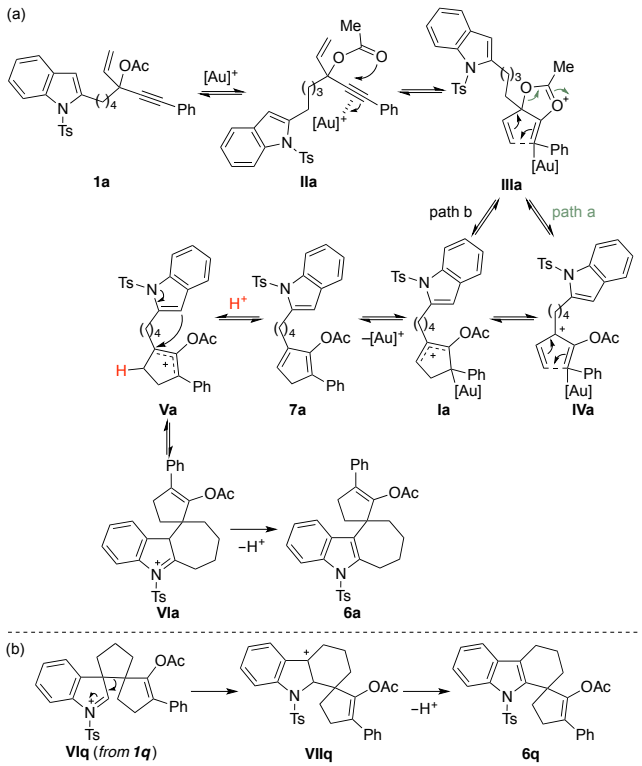


Figure 2. NHC–Au(I) complex **C** and Brønsted acid-catalyzed spirocyclization of **1q**–**w**. All reactions were performed at the 0.1 mmol scale with 5 mol % of NHC–Au(I) complex **C** in CH_2Cl_2 (1 mL) at room temperature and open to air for 1 h followed by the addition of 10 mol % of $NHTf_2$ and continuing the experiment for 2.5 h. Values in parenthesis denote isolated product yields.

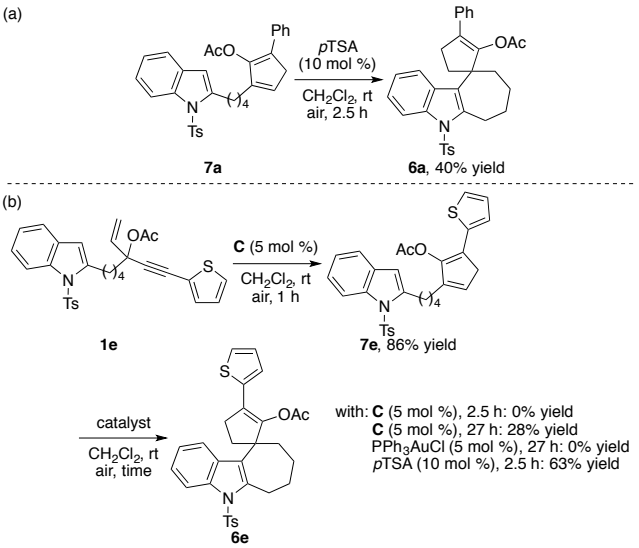
adduct **7a**.[6] Alternatively, the carbocycle could have been directly assembled from the metallo-Nazarov cyclization of **IIIa** as it occurs followed by deauration of **Ia** (Scheme 2a, path b).[5e] In the presence of the Brønsted acid, succeeding protonation of the carbocyclic motif might afford the 1,3-cyclopentenylium species **Va**, which is then thought to be poised for spirocyclization.[5c] This could proceed through nucleophilic attack by the tethered indolyl group at the C3 position onto the allylic carbocation motif in **IVa** and rearomatization of the resulting spirocyclic species **VIa** to reveal the product **6a**. For reactions involving 3-indolyl tethered 1,4-

Scheme 2. Proposed Mechanism for the Au(I)/Brønsted Acid-Catalyzed 2- and 3-Indolyl-Tethered 1,4-Enyne Acetate Spirocyclization Represented by 1a and 1q



enyne acetates with **1q** as a representative example, re-aromatization might proceed through a 1,2-shift followed by deprotonation in the corresponding dispirocyclic species **VIq** to deliver **6q** *via* the cationic species **VIIq** (Scheme 2b). While fortuitous, the detection of **7a** under the various Au(I)-mediated reaction conditions detailed in Table 1 supports its surmised involvement. This was further corroborated by treating the 1,3-cyclopentadiene compound with 10 mol % of *p*TSA under the reaction conditions described in Scheme 3a and obtaining the spirocyclic product **6a** in 40% yield.[14] The role of the Brønsted acid in facilitating the spirocyclization step was shown by performing the following control reactions (Scheme 3b). In a first set of experiments, treating **1e** to the NHC–gold(I) complex **C** in dichloromethane at room temperature for 1 h was found to give **7e** in 86% yield. Re-subjecting the Rautenstrauch adduct to the Au(I)-mediated reaction conditions for 2.5 h led to the detection of the substrate along with a mixture of unknown decomposition products based on ^{1}H NMR analysis. Formation of **6e** in 28% yield was only observed on extending the reaction time from 2.5 to 27 h, presumably due to the formation of a sufficient amount of $NHTf_2$ as a result of protonation of the counteranion.[5b] This was further supported by performing the control experiment for a third time with Ph_3PAuCl in place of NHC–gold(I) complex as the catalyst, which gave no reaction after 27 h based on ^{1}H NMR measurements. In contrast, the analogous control experiment with **7e** mediated by 10 mol % of *p*TSA for 2.5 h was found to lead to the formation of **6e** in 63% yield.[14]

Scheme 3. Control Experiments with 1e, 7a and 7e



In summary, we have shown an efficient gold(I)/Brønsted acid-catalyzed spirocyclization process to assemble spiro[4,*n*]alkyl[*b*]indoles from 2- and 3-indolyl-tethered 1,4-enyne acetates under mild conditions at room temperature. The cycloisomerization was shown to be robust as it did not require the exclusion of air or moisture and demonstrated a facile and convenient tactic to install an all-carbon spirocyclic motif onto the indole ring system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data and ^{1}H and ^{13}C NMR spectra for all compounds, and ORTEP drawings of **6a** and **6r** (PDF)

Accession Codes

CCDC 1974954 (**6a**) and CCDC 1974955 (**6r**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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(14) 1,3-Cyclopentadienes **7a** and **7e** were found to partially decompose at room temperature after their purification and characterization by ^{1}H NMR analysis. This was necessary as TLC analysis of the two 1,3-cyclopentadienes and their corresponding spirocyclic products have the same R_f values.