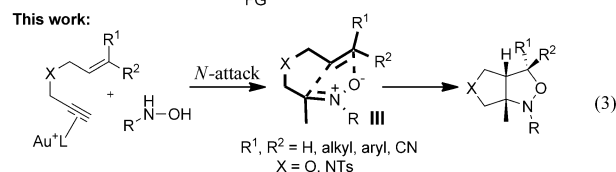
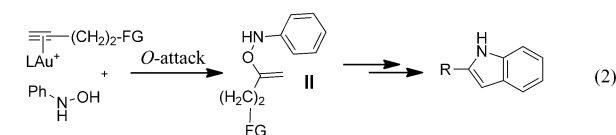
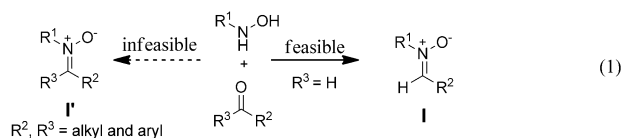


Alkene-Directed *N*-Attack Chemoselectivity in the Gold-Catalyzed [2+2+1]-Annulations of 1,6-Enynes with *N*-Hydroxyanilines

Deepak B. Huple, Bhanudas D. Mokal, and Rai-Shung Liu*

Abstract: Kinetically unstable nitrones are generated from gold-catalyzed reactions of 1,6-enynes with *N*-hydroxyanilines, and subsequently trapped by tethered alkenes to furnish [2+2+1]-annulations. Our experimental data reveal that such nitrones arise from atypical *N*-attack chemoselectivity that is triggered by tethered alkenes to facilitate the key protodeauration reaction.

Nitrones are versatile precursors to access *N,O*-containing molecules through their stereoselective [3+2]-cycloadditions with alkenes; these reactive species are commonly generated in situ from the intermolecular reactions of *N*-hydroxyamines and aldehydes [Eq. (1)].^[1–2] Unfortunately, nitrones (**I'**)



cannot be generated from the intermolecular reactions of ketones (R², R³ = alkyl or aryl)^[3–4] with *N*-hydroxyamines, rendering their [3+2]-cycloadditions infeasible. Gold-catalyzed intramolecular reactions of *N*-hydroxyamines with alkynes have been intensively studied.^[5] Zhang and co-workers reported gold-catalyzed intermolecular reactions of *N*-hydroxyamines with alkyl-substituted terminal alkynes (R = (CH₂)₂-FG) to afford indole products;^[6] the key step involves an *O*-attack of *N*-hydroxyanilines at gold π -alkynes [Eq. (2)]. Herein, we report gold-catalyzed [2+2+1]-annulations of *N*-hydroxyanilines with diverse 1,6-enynes to give

transient nitrones (**III**) that can be trapped efficiently by tethered alkenes to furnish cycloadditions [Eq. (3)]. The success of such cycloadditions is remarkable because such nitrones arise from a distinct *N*-attack of *N*-hydroxyamines at π -alkynes, as opposed to the *O*-attack mode reported by Zhang and co-workers [Eq. (2)].^[6] Our mechanistic analysis indicates that this chemoselective *N*-attack is triggered by tethered alkenes to facilitate the protodeauration, so to alter the typical *O*-attack chemoselectivity.

Table 1 shows the annulations of 1,6-enyne **1a** with *N*-hydroxyaniline **2a** using various gold catalysts (5 mol %) in

Table 1: Reactions over various gold catalysts.

Entry	Catalyst ^[b] (mol %)	Solvent	<i>t</i> [h]	Compound yields [%] ^[c]				
				1a	3a	4	5	
1	LAuCl/AgSbF ₆ (5)	DCM	7	–	78	12	5	
2	LAuCl/AgOTf (5)	DCM	7	–	76	14	6	
3	LAuCl/AgNTf ₂ (5)	DCM	5	–	80	–	trace	
4	PPh ₃ AuCl/AgNTf ₂ (5)	DCM	20	50	33	7	25	
5	L'AuCl/AgNTf ₂ (5)	DCM	20	55	15	4	20	
6	IPrAuCl/AgNTf ₂ (5)	DCM	20	10	70	8	7	
7	AgNTf ₂ (10)	DCM	30	90	–	5	12	
8	LAuCl/AgNTf ₂ (5)	DCE	5	–	71	10	4	
9	LAuCl/AgNTf ₂ (5)	toluene	4	–	78	5	trace	
10	LAuCl/AgNTf ₂ (5)	1,4-dioxane	6	–	70	10	trace	

[a] **1a** (0.19 M, 1 equiv), **2a** (1.1 equiv), [b] L = P(*t*Bu)₂(*o*-biphenyl), IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene. L' = tris(2,4-di-*tert*-butylphenyl)phosphite. [c] Product yields are given after purification from a silica column.

dichloromethane (25 °C). Notably, the competitive cycloisomerizations of 1,6-enynes were completely suppressed, whereas side-product **4** and 1,2-diphenyldiazene oxide **5** were present in minor proportions (< 20 %). Indole species **4** arose from gold-catalyzed reactions of *N*-hydroxyanilines with terminal alkynes [Eq. (2)]. Among the tested catalysts (entries 1–6), electron-rich and bulky LAuCl/AgX (L = P(*t*Bu)₂(*o*-biphenyl); X = SbF₆, OTf, NTf₂) and IPrAuCl/AgNTf₂ (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) were efficient enough to give the desired annulation product **3a** in high yields (70–80 %), with LAuCl/AgNTf₂ being the most productive (entry 3). In contrast, PPh₃AuCl/AgNTf₂ and highly acidic L'AuCl/AgNTf₂ (L' = tris(2,4-di-*tert*-butyl)phosphite) were much less reactive, leading to

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incomplete conversions of about 45–50% (entries 4,5). Electron-rich gold catalysts facilitate protodeauration, thus increasing the reaction efficiency. AgNTf₂ alone was an ineffective catalyst even at 10 mol% loading. The product yields of compound **3a** varied with solvents, with a yield of 71% in dichloroethane (DCE), 78% in toluene, and 70% in 1,4-dioxane (entries 8–10). In entries 1–10, only one diastereomeric form of **3a** was formed with the two methine protons *trans* to each other, according to the ¹H NOE effect. This stereochemistry is in accordance with starting *trans*-configured 1,6-enyne **1a**. The molecular framework of compound **3a** was confirmed by X-ray diffraction of its NTs-bridged analogue **3c** (Table 2, entry 2).^[7]

Table 2 assesses the scope of the annulation reactions with various acyclic *O*- and *N*-linked 1,6-enynes **1b–1e** bearing

Table 2: Scope of 1,6-enynes with *N*-hydroxyanilines.^[a]

Entry	Substrates	<i>t</i> (h)/°C	Yields (%) ^[b]
1		12/25	3b (72), 1b-H (13)
2		6/25	3c (74), 4c (17)
3		2.5/25	3d (92)
4		2.5/25	3e (88)
5		12/55	3f (79)
6		12/25	3g (61)
7		12/25	3h (50)
8		36/25	3i (57); 1i' (5)

[a] **1a** (0.19 M, 1 equiv), **2a** (1.1 equiv), L = P(*t*Bu)₂(*o*-biphenyl),

[b] Product yields are given after purification from a silica column. [c] **2a** (2.0 equiv) and [d] **2a** (3.0 equiv).

various mono- and 1,2-disubstituted alkenes, yielding bicyclic products **3b–3e** in 72–92% yields (entries 1–4), together with hydration product **1b-H** and indole species **4c** in a minor proportion (13–17%). X-ray diffraction of the **3c** cycloadduct confirmed the molecular structure with the nitrogen linked to the CMe carbon and the oxygen linked to the CPh carbon.^[7] We prepared C(3)-phenyl substituted 1,6-enynes **1f** and **1g** to test the stereocontrol of the reaction. Gratifyingly, their resulting products **3f** and **3g** were obtained with single diastereomers (*d.r.* > 30:1) in 79% and 61% yields, respectively. ¹H NOE of compound **3f** was performed to elucidate its stereochemistry. For 1,6-enynes **1h** and **1i** bearing

a trisubstituted alkene (entries 7,8), their corresponding reactions delivered the desired bicyclic compounds **3h** and **3i** in moderate yields (50–57%), whereas cycloisomerization product **1i'** was produced in 5% yield (entry 8). For compound **3h**, the *N*-phenyl protons have a ¹H NOE on the single methyl but no effect on the two *gem*-methyl groups. In Table 2, high product yields (> 70%) could be easily obtained if 1,6-enynes did not bear electron-rich trisubstituted alkenes.

We examined the scope of *N*-hydroxyamines to understand their effects on reaction chemistry (Table 3). In

Table 3: Scope of *N*-hydroxyamines.

Entry	<i>N</i> -hydroxyamines	<i>t</i> (h)	Yields [%] ^[c]
1	R = 4-Me-C ₆ H ₄ (2b) ^[d]	16	6b (61)
2	R = 4-F-C ₆ H ₄ (2c)	4	6c (81)
3	R = 4-Cl-C ₆ H ₄ (2d)	5	6d (80)
4	R = 4-Br-C ₆ H ₄ (2e)	4.5	6e (82)
5	R = 4-CO ₂ Et-C ₆ H ₄ (2f)	6	6f (70)
6	R = Isopropyl (2g) ^[d]	24	6g (39), 1a (30)

[a] **1a** (0.19 M, 1 equiv), **2a** (1.1 equiv). [b] L = P(*t*Bu)₂(*o*-biphenyl).

[c] Product yields are given after purification from a silica column. [d] **2b** and **2g** (2.2 equiv).

entries 1 and 6, less efficient amines **2b** and **2g** were used with two-fold proportions whereas other amines were used with 1.1 equivalents. The reaction duration and product yields reveal superior reactivity for less basic *N*-hydroxyanilines **2c–2f** to afford desired annulation products **6c–6f** in satisfactory yields (70–81%) at brief periods (4–6 h). In contrast, highly nucleophilic amines **2b** and **2g** gave desired products **6b** and **6g** in relatively low yields, 61% and 39%, over protracted periods (16–24 h). These data indicate that less basic *N*-hydroxyamines **2c–2f** enable satisfactory products yields (> 70%), presumably because of their highly efficient protodeauration reactions (see Scheme 1).

Alkene- and benzene-bridged 1,6-enynes **7** were also investigated, with a goal of constructing useful carbocyclic frameworks (Table 4). In entries 1,2, 1,6-enynes **7a** and **7b** bearing a *trans*-1,2-disubstituted alkene (R² = H, R³ = Ph, CN) gave expected products **8a** and **8b** in good yields (78–92%), whereas an electron-rich alkene, such as 1,6-enyne **7c** (R¹ = R² = Me), delivered compound **8c** in only 55% yield (entry 3). Alkoxy-derived 1,6-enynes **7d** and **7e** yielded **8d** and **8e, 8e'** (entries 4,5).^[7] The enhanced yields (78–85%) of resulting **8d** and **8e** relative to that of their unsubstituted analogue **8a** reflected the Ingold-Thorpe effect.^[8] X-ray diffraction of annulations were applicable to cycloalkene-bridged 1,6-enynes **7f** and **7g**, yielding the expected products **8f** and **8g** in 54% and 89% yields, respectively. The data from Tables 2 and 4 clearly indicate that 1,6-enynes **1h, 1i, 7c**, and **7f** bearing electron-rich alkenes are less efficient substrates; this reaction trend matches well with the well-known cycloadditions between nitrones and alkenes.^[1]

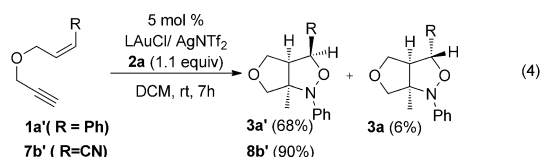
Table 4: Reactions with benzene- or alkene-bridged 1,6-enynes.

Entry	1,6-enynes ^[a]	t (h)	Yields ^[b]
1		12	8a (82)
2		8	8b (92)
3		36	8c (55)
4		10	8d (78)
5		10	8e (85), 8e' (10)
6		16	8f (54)
7		2.5	8g (89)

[a] **1a** (0.19 M, 1 equiv), **2a** (1.1 equiv), L = P(*t*Bu)₂(*o*-biphenyl).

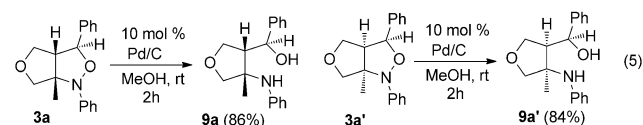
[b] Product yields are given after purification from a silica column. [c] **2a** (2.0 equiv) for entries 3–5 and **2a** (3.0 equiv) for entries 1 and 6–7.

To examine the reaction stereospecificity, *Z*-configured 1,6-enyne **1a'** was found to yield two diastereomeric products **3a'** and **3a** in 68 % and 6 % yields respectively [Eq. (4)].

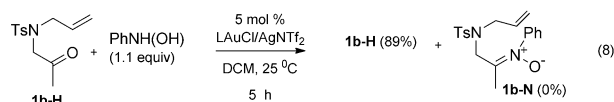
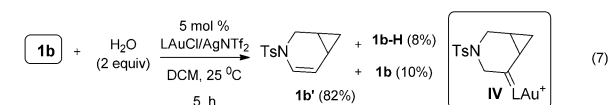
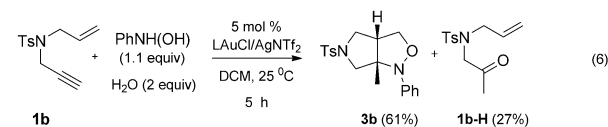


Particularly notable is the case of CN-derived 1,6-enyne **7b'**, giving cycloadduct **8b'** in excellent yield [90 %, Eq. (4)], of which the NMR data are distinct from those from its *E*-configured analogue **7b**. Accordingly, the annulations generated products **3a'** and **8b'** bearing the same configurations as those of initial 1,6-enynes **1a'** and **7b'**.

Equation (5) shows the application to the stereoselective synthesis of 1,3-aminoalcohols. Treatment of compound **3a** with Pd/C (10 mol %) in MeOH gave 1,3-aminoalcohol **9a** in 86 % yield. We performed this reductive N–O cleavage on its epimer **3a'** to deliver distinct 1,3-aminoalcohol **9a'** in 84 % yield.



Gold catalysts can implement the cycloisomerizations of 1,*n*-enynes (*n* = 5, 6) through gold carbene intermediates;^[11] these carbenes implement the cycloadditions of 1,*n*-enynes with carbonyl,^[9] nitrosoarenes,^[10a] or nitrones.^[10b] With CN-derived 1,6-enynes **7b** and **7b'** as efficient substrates, the intermediacy of gold carbenes can be excluded because no cycloisomerization occurs with the gold catalyst. Treatment of 1,6-enyne **1b** with *N*-hydroxyaniline (1.1 equiv) and external H₂O (2 equiv) in DCM (25 °C, 6 h) yielded annulation product **3b** and ketone **1b-H** in 61 % and 27 % yields respectively [Eq. (6)] whereas its anhydrous condition gave

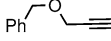
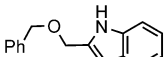
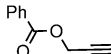
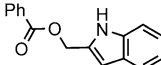
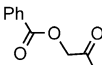
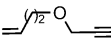
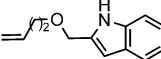
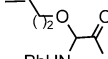
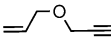
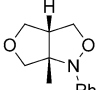


3b and **1b-H** in 72 % and 13 % yields respectively (Table 2, entry 1). Notably in Equation (7), the gold-catalyzed reaction of 1,6-enyne **1b** with H₂O (2 equiv) gave cycloisomerization product **1b'** in 82 % yield together with ketone **1b-H** in only 8 %; gold carbene IV generated in this cycloisomerization^[12] is inaccessible to the desired **3b**. A significant portion of ketone **1b-H** in Eq. 6 seems to arise from the hydration of unstable nitron intermediate IV. As we expected, this nitron could not be generated from the reaction of ketone **1b-H** and *N*-hydroxyaniline in dry DCM [Eq. (8)].

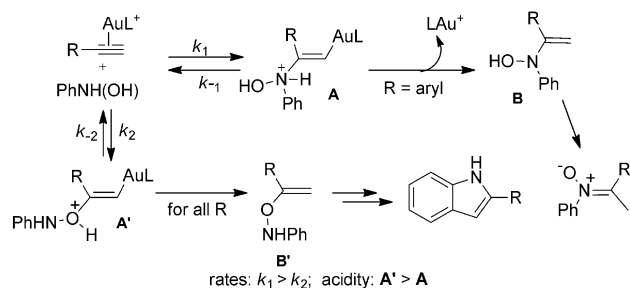
To acquire insight into the *N*- versus *O*-attack chemoselectivity, we examined gold-catalyzed reactions of various propargyl ethers with *N*-hydroxyaniline (Table 5). We observed the *O*-attack chemoselectivity occurring with benzyl propargyl ether **10a** and its benzoate derivative **10b**, yielding indole compounds **11a** and **11b** in 73 % and 53 % yields, respectively. Hydration compound **11b-H** was formed in 41 % yield in the latter. We tested the reaction on 1,7-enyne **10c** to yield indole **11c** and α -amino ketone **11c'** in comparable proportions (36–41 %); both compounds arose from the *O*-chemoselectivity.^[13] For model 1,6-enyne **1j**, the gold-catalyzed reaction yielded desired annulation product **3j** in 88 % yield. Among these propargyl ethers **10a–10c** and **1j**, only 1,6-enyne **1j** proceeded exclusively with *N*-chemoselectivity without formation of indole products. Finally, phenylacetylene **10e** delivered acetophenone **10e-H** exclusively, presumably from the hydrolysis of unstable nitron intermediates (entry 5).

The *N*- and *O*-attack chemoselectivity is distinct between aryl- and alkyl-substituted alkynes (Table 4). As shown in Scheme 1, the *N*-attack of *N*-hydroxyaniline on π -alkyne is expected to be more rapid than the corresponding *O*-attack

Table 5: Alkene-directed chemoselectivity.

Entry	1,6-ynes ^[a]	<i>t</i> (h)	Products (% Yield) ^[b]
1		6	 11a (73%)
2		6	 11b (53%)  11b-H (41%)
3		8	 11c (41%)  11c' (36%)
4		8	 3j (88%)
5		4	 10e-H (98%)

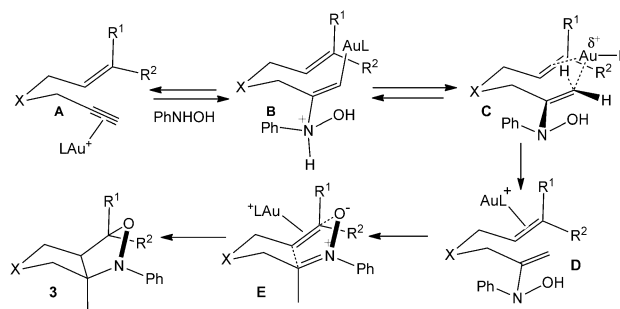
[a] **1a** (0.22 M in DCM), 5 mol% AuCl(P(*t*Bu)₂(*o*-biphenyl))/5 mol% AgNTf₂. For **2a**, 2.0 equiv for entries 1–5. [b] Product yields are given after purification from a silica column.



Scheme 1. N- versus O-attack chemoselectivity.

under neutral conditions because amines are better than alcohols as nucleophiles ($k_1 > k_2$),^[14] both paths are likely to be reversible. As the Brønsted acidity of intermediates **A** and **A'** differs with **A'** > **A**; we propose that the protodeauration process (**A'**→**B'**) can occur with all R substituents, whereas the *N*-attack process (**A**→**B**) is only applicable to aryl substituents (R = aryl) that have strong ammonium acidity to achieve protodeauration.^[15] Acidic *N*-hydroxyanilines (Table 3) are also favorable for this *N*-attack process (**A**→**B**) because of their increased ammonium acidity. In species **A** with R = Ar, this ammonium N–H proton is very close to the Au–C=C bond to facilitate its migration to form a stable benzylic cation. In the case of alkyl-substituted alkynes (R = alkyl), their corresponding states **A** are less acidic but their initial rates are fast; *O*- and *N*-attack selectivity are thus competitive.

Preference of acyclic 1,6-enynes **1** toward the *N*-attack chemoselectivity is particularly notable because other propargyl ethers **10a–10c** afford indole products through the *O*-attack selectivity. The alkene group of 1,6-enynes **1** completely alter the reaction chemoselectivity according to the following rationales (Scheme 2). An initial *N*-attack of *N*-hydroxyani-



Scheme 2. A postulated mechanism.

line at π -alkyne **A** is expected to yield alkenylgold species **B**. To achieve protodeauration, the alkenylgold moiety of species **B** undergoes protonation at the $=\text{CAu}$ carbon, forming species **C** according to a recent theoretical model.^[14a] We envisage that the loss of energy in the cleavage of the $\sigma\text{-Au-C}$ bond in species **C** is compensated by an attack of the olefin at Au to generate species **D**, ultimately giving nitrone species **E** after a facile tautomerization. For species **E**, the nitrone moiety has a high-lying HOMO whereas $\text{Au}^1\text{-}\pi$ -alkene has a low-lying LUMO, thus accelerating the dipolar [3+2]-cycloadditions with high stereospecificity.

Kinetically unstable trisubstituted nitrones are generated from the gold-catalyzed reactions of 1,6-enynes with *N*-hydroxyanilines. Such transient species are efficiently trapped with tethered alkenes to achieve stereospecific cycloadditions. Notably, these annulations involve an atypical *N*-attack of hydroxyamines at gold- π -alkynes. Our data reveal that most propargyl ethers show the *O*-attack selectivity, whereas allyl propargyl ether proceeds exclusively through the *N*-attack selectivity. This alkene-directed chemoselectivity is postulated to accelerate the protodeauration by an alkene coordination to gold. This new concept helps the design of new catalytic reactions.

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Keywords: annulations · chemoselectivity · gold catalyst · *N*-attack

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