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

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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 (R^2, R^3 = 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 = $(CH_2)_2$-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.

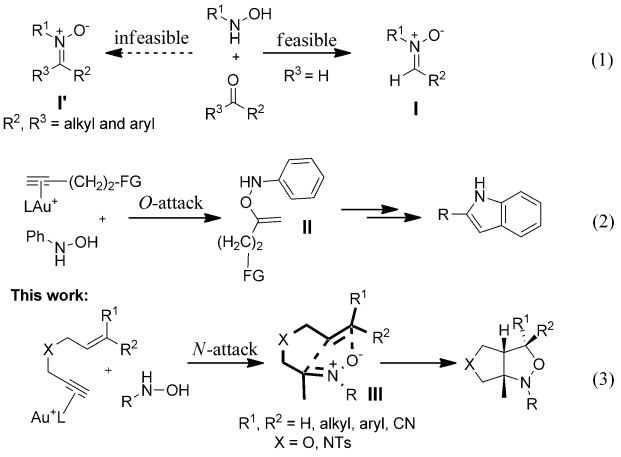
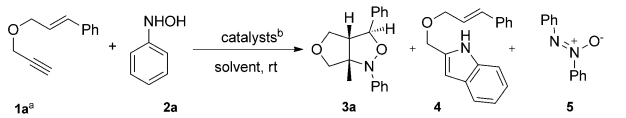


Table 1 shows the annulations of 1,6-enyne **1a** with *N*-hydroxyaniline **2a** using various gold catalysts (5 mol%) in dichloromethane (25 °C). Notably, the competitive cycloisomerizations of 1,6-enynes were completely suppressed, whereas side-product **4** and 1,2-diphenyldiazene oxide **5** were 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-(tBu)$_2$(o-biphenyl); X = SbF_6, OTf, NTf_2) and IPrAuCl/$AgNTf_2$ (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/$AgNTf_2$ being the most productive (entry 3). In contrast, PPh_3AuCl/$AgNTf_2$ and highly acidic L′AuCl/$AgNTf_2$ (L′ = tris(2,4-di-*tert*-butyl)phosphite) were much less reactive, leading to

Table 1: Reactions over various gold catalysts.



Entry	Catalyst[b] (mol%)	Solvent	t [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_3AuCl/$AgNTf_2$ (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(tBu)$_2$(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.

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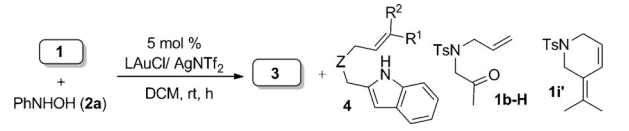
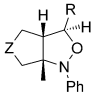
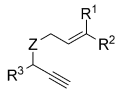
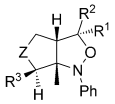
incomplete conversions of about 45–50% (entries 4,5). Electron-rich gold catalysts facilitate protodeauration, thus increasing the reaction efficiency. $AgNTf_2$ alone was an ineffective catalyst even at 10 mol% loading. The product yields of compound **3a** varied with solvents, with a yield of 71% 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 ^{1}H 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	t (h)/°C	Yields (%)[b]
			
1	Z = NTs, R = H (**1b**)[c]	12/25	**3b** (72), **1b-H** (13)
2	Z = NTs, R = Ph (**1c**)	6/25	**3c** (74), **4c** (17)
3	Z = O, R = 2-furyl (**1d**)	2.5/25	**3d** (92)
4	Z = O, R = 3-thienyl (**1e**)	2.5/25	**3e** (88)
			
5	Z = O, R^1 = H, R^2 = Ph R^3 = Ph (**1f**)	12/55	**3f** (79)
6	Z = O, R^1 = R^2 = Me R^3 = Ph (**1g**)[c]	12/25	**3g** (61)
7	Z = O, R^1 = R^2 = Me R^3 = H (**1h**)	12/25	**3h** (50)
8	Z = NTs, R^1 = R^2 = Me R^3 = H (**1i**)[d]	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 *C*Me carbon and the oxygen linked to the *C*Ph 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. ^{1}H 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 ^{1}H 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.

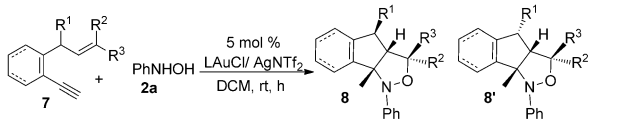
Entry	N-hydroxyamines	t (h)	Yields [%][c]
1	R = 4-Me-C_6H_4 (**2b**)[d]	16	**6b** (61)
2	R = 4-F-C_6H_4 (**2c**)	4	**6c** (81)
3	R = 4-Cl-C_6H_4 (**2d**)	5	**6d** (80)
4	R = 4-Br-C_6H_4 (**2e**)	4.5	**6e** (82)
5	R = 4-CO_2Et-C_6H_4 (**2f**)	6	**6f** (70)
6	R = Isopropyl (**2g**)[d]	24	**6g** (39), **1a** (30)

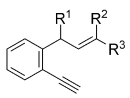
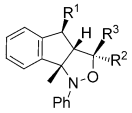
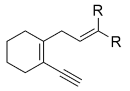
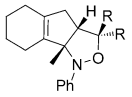
[a] **1a** (0.19 M, 1 equiv), **2a** (1.1 equiv). [b] L = P(*t*Bu)2(*o*-biphenyl). [c] Product yields are given after purification from a silica column. [d] **2b** and **2g** (2.2 equiv).

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 (R^2 = H, R^3 = Ph, CN) gave expected products **8a** and **8b** in good yields (78–92%), whereas an electron-rich alkene, such as 1,6-enyne **7c** (R^1 = R^2 = 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]

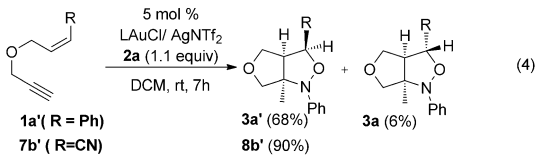
Table 4: Reactions with benzene- or alkene-bridged 1,6-enynes.



Entry	1,6-enynes[a]	t (h)	Yields[b]
			
1	R^1 = H, R^2 = H, R^3 = Ph (**7a**)[c]	12	**8a** (82)
2	R^1 = H, R^2 = H, R^3 = CN (**7b**)	8	**8b** (92)
3	R^1 = H, R^2 = R^3 = Me (**7c**)	36	**8c** (55)
4	R^1 = OTBS, R^2 = R^3 = Me (**7d**)	10	**8d** (78)
5	R^1 = OMe, R^2 = R^3 = Me (**7e**)	10	**8e** (85), **8e′** (10)
			
6	R = Me (**7f**)[c]	16	**8f** (54)
7	R = H (**7g**)	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.

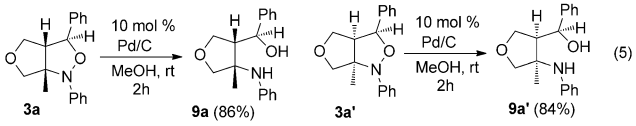
To examine the reaction stereospecificity, *Z*-configured 1,6-enyne **1a′** was found to yield two diastereomeric products **3a′** and **3a** in 68% and 6% yields respectively [Eq. (4)].



(4)

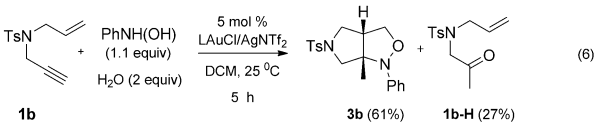
Particularly notable is the case of CN-derived 1,6-enyne **7b′**, giving cycloadduct **8b′** in excellent yield [90%, Eq. (4)], of which the NMR data are distinct from those from its *E*-configured analogue **7b**. Accordingly, the annulations generated products **3a′** and **8b′** bearing the same configurations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

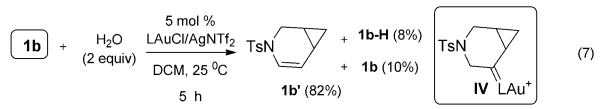


(5)

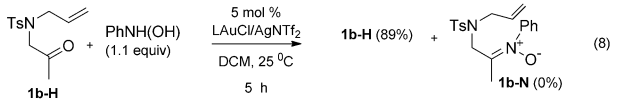
Gold catalysts can implement the cycloisomerizations of 1,*n*-enynes (n = 5, 6) through gold carbene intermediates;[11] these carbenes implement the cycloadditions of 1,n-enynes with carbonyl,[9] nitrosoarenes,[10a] or nitrones.[10b] With CN-derived 1,6-enynes **7b** and **7b′** as efficient substrates, 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 H_2O (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



(6)



(7)



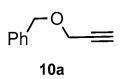
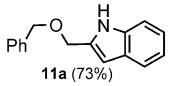
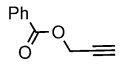
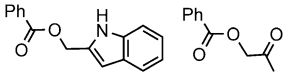
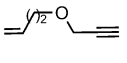
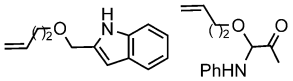
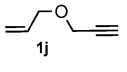
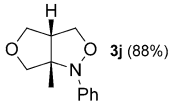
(8)

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 H_2O (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 nitrone intermediate IV. As we expected, this nitrone could not be generated from the reaction of ketone **1b-H** and *N*-hydroxyaniline in dry DCM [Eq. (8)].

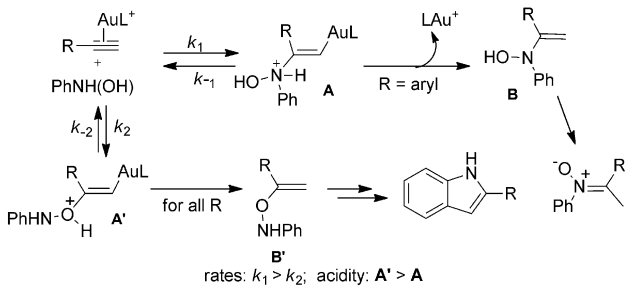
To acquire insight into the *N*- versus *O*-attack chemoselectivity, we examined gold-catalyzed reactions of various propargyl ethers with *N*-hydroxyaniline (Table 5). We observed the *O*-attack chemoselectivity occurring with benzyl propargyl ether **10a** and its benzoate derivative **10b**, yielding 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 nitrone 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-enynes[a]	*t* (h)	Products (% Yield)[b]
1	 **10a**	6	 **11a** (73%)
2	 **10b**	6	 **11b** (53%) **11b-H** (41%)
3	 **10c**	8	 **11c** (41%) **11c'** (36%)
4	 **1j**	8	 **3j** (88%)
5	 **10e**	4	 **10e-H** (98%)

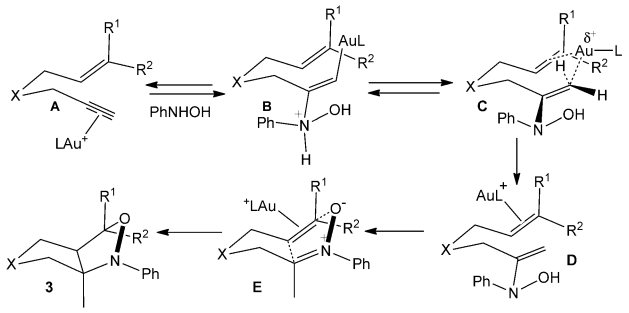
[a] **1a** (0.22 M in DCM), 5 mol% $AuCl(P(tBu)_2(o\text{-biphenyl}))$/5 mol% $AgNTf_2$. For **2a**, 2.0 equiv for entries 1–5. [b] Product yields are given after purification from a silica column.



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*-hydroxyaniline at π-alkyne **A** is expected to yield alkenylgold species **B.** To achieve protodeauration, the alkenylgold moiety of species **B** undergoes protonation at the =CAu carbon, forming species **C** according to a recent theoretical model.[14a] We envisage that the loss of energy in the cleavage of the σ-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 Au^I-π-alkene has a low-lying LUMO, thus accelerating the dipolar [3+2]-cycloadditions with high stereospecificity.



Scheme 2. A postulated mechanism.

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 hydoxyamines 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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