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Gold-Catalyzed 1,2-Difunctionalizations of Aminoalkynes Using Only N- and O-Containing Oxidants

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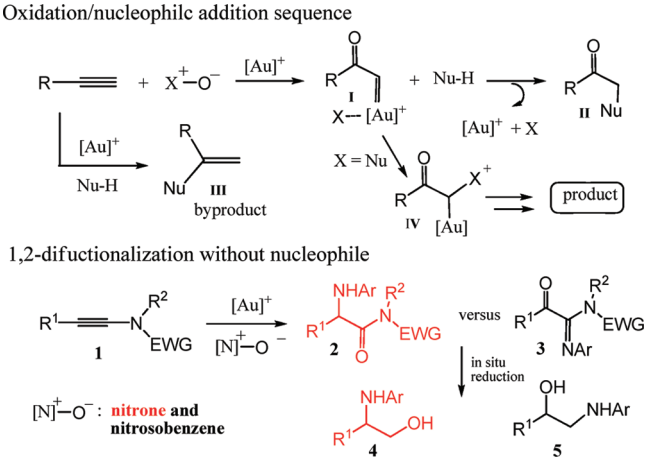
Supporting Information

ABSTRACT: We report two viable routes for the 1,2-difunctionalization of aminoalkynes using only oxidants. In the presence of a gold catalyst, nitrones enable the oxoamination of aminoalkynes **1** to form 2-aminoamides **2**. With a suitable gold catalyst, nitrosobenzenes implement an alkyne/nitroso metathesis of the same substrates to give 2-oxoiminylamides **3**. These two novel oxidations also provide 1,2-aminoalcohols with opposite regioselectivity via $NaBH_4$ reduction *in situ*.

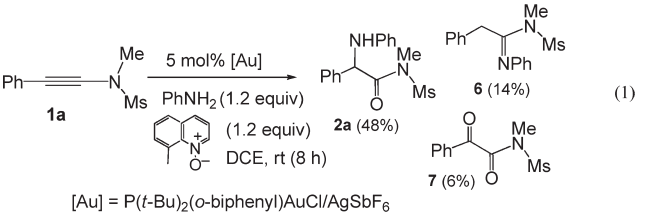
The generation of α-carbonyl carbenes via gold-catalyzed intermolecular oxidation of alkynes represents a significant advance in gold catalysis.[1−3] This oxidation is promising to generate new 1,2-difunctionalizations of alkynes, which are less common than alkene oxidations.[4] Scheme 1 shows one viable route to access α-functionalized carbonyl **II** via a sequence of oxidation/nucleophilic addition. The reported reactions focus mainly on those alkynes tethered with a nucleophile, including hydroxy and sulfinamide.[5] Intermolecular alkyne oxidation with external nucleophiles[6] is a formidable task because most nucleophiles also attack alkynes, catalyzed by gold species, although gold carbene is very reactive. Zhang recently reported the synthesis of 2,3-disubstituted oxazoles via a gold-catalyzed intermolecular alkyne oxidation with external nitriles that served as solvents.[7] We seek new oxidants X^+-O^-, the reduced form of which, i.e. X, upon in situ generation, could serve as a nucleophile to immediately trap gold carbene **I**, giving α-functionalized carbonyl intermediate **IV**. This new strategy inhibits the occurrence of byproduct **III** with no participation of an external nucleophile. Herein, we report two new 1,2-difunctionalizations of aminoalkynes using only N- and O-containing oxidants. As shown in Scheme 1, the use of nitrones[8] enables oxoamination of these alkynes, whereas nitrosobenzenes induce their oxoimination reactions.[9] These two oxidations introduce oxygen and nitrogen functionalities onto alkynes with different regioselectivities. Notably, the two new products **2** and **3** can further provide two distinct aminoalcohols **4** and **5** upon $NaBH_4$ reductions *in situ*.[10] Generation of four 1,2-difunctionalized compounds **2**−**5** from a single substrate highlights the value of this new catalysis.

Equation 1 shows our attempts to realize the oxoamination of aminoalkyne **1a** according to an oxidation/nucleophilic addition sequence. The corresponding intramolecular oxoamination was recently reported by Zhang and co-workers.[5c] Aminoalkynes are selected because of their high electrophilicity, activated by a gold complex, to generate α-carbonyl gold carbenoids.[6,11] The treatment

Scheme 1. 1,2-Difunctionalization of Aminoalkynes Using Oxidants Only



of aminoalkyne **1a** with P(*t*-Bu)$_2$(*o*-biphenyl)AuCl/$AgSbF_6$ (5 mol %), 8-methylquinoline *N*-oxide (1.2 equiv), and aniline (1.2 equiv) in dichloroethane (DCE, 25 °C, 8 h) produced 2-aminoamide **2a** (48% yield), 1-aminoimine **6** (14%), and 2-oxoamide **7** (6%) at 100% conversion.



(1)

1-Aminoimine **6** arose from the gold-catalyzed hydroamination of aminoalkyne **1a**;[12] to circumvent this side reaction, we employed *N*-benzylideneaniline oxide **8a** as the oxidant.[8] In this new approach (eq 2), we expect that nitrone **8a** enables the oxidation of aminoalkyne **1a** to generate gold carbenoid **A** that is trapped with newly generated imine to form gold enolate **B**, further giving 2-aminoamide **2a** through hydrolysis. Indeed, gold-catalyzed nitrone oxidation of aminoalkyne **1a** in wet DCE (25 °C, 10 h) delivered **2a** in 81% yield after workup. Addition of a THF solution of $NaBH_4$ (2.2 equiv) in an equal volume to this wet DCE solution containing **2a** gave

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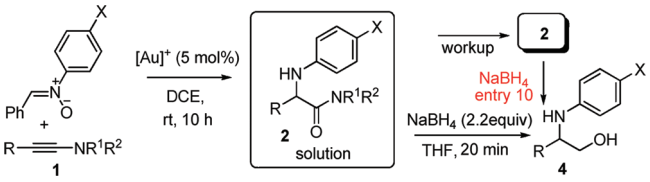
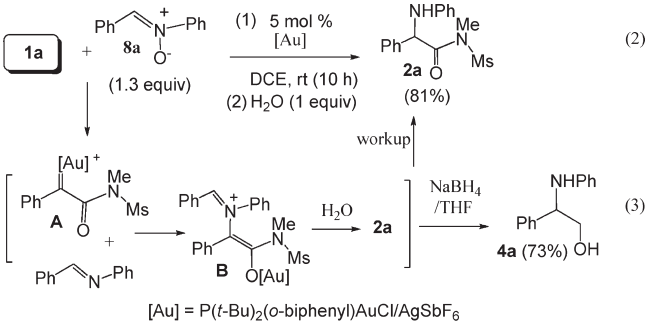
Table 1. Scope for Gold-Catalyzed Oxoaminations and Aminohydroxylations



entry	alkyne[a]	nitrone[b]	compounds[c]	
	NR^1R^2 = NMeMs			
1	R = Ph (**1a**)	X = F (**8b**)	**2b** (71%)	**4b** (67%)
2	R = Ph (**1a**)	X = Cl (**8c**)	**2c** (77%)	**4c** (74%)
3	R = Ph (**1a**)	X = Br (**8d**)	**2d** (78%)	**4d** (72%)
4	R = Ph (**1a**)	X = Me (**8e**)	**2e** (73%)	**4e** (69%)
5	R = Ph (**1a**)	X = OMe (**8f**)	**2f** (83%)	**4f** (76%)
6	R = 4-FC_6H_4 (**1b**)	X = H (**8a**)	**2g** (72%)	**4g** (65%)
7	R = 4-ClC_6H_4 (**1c**)	**8a**	**2h** (71%)	**4h** (62%)
8	R = 4-BrC_6H_4 (**1d**)	**8a**	**2i** (73%)	**4i** (69%)
9	R = 4-MeC_6H_4 (**1e**)	**8a**	**2j** (68%)	**4j** (63%)
10	R = 4-$MeOC_6H_4$ (**1f**)	**8a**	**2k** (66%)	**4k** (-, 98%[d])
11	R = 2-thienyl (**1g**)	**8a**	**2l** (74%)	**4l** (70%)
12	R = 3-thienyl (**1h**)	**8a**	**2m** (71%)	**4m** (65%)
	R = Ph			
13	NR^1R^2 = NPhMs (**1i**)	**8a**	**2n** (78%)	**4a** (69%)
14	NR^1R^2 = NBnMs (**1j**)	**8a**	**2o** (62%)	**4a** (55%)

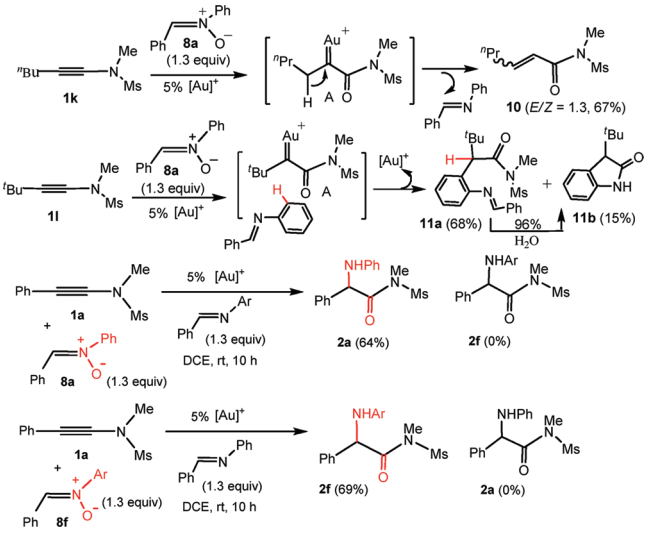
[a] [**1**] = 0.12 M, [Au] = P(*t*-butyl)$_2$(*o*-biphenyl)AuSbF$_6$. [b] [Nitrone] = 1.3 equiv. [c] Product yields are reported after purification from silica column. [d] This yield corresponds to $NaBH_4$ reduction of purified **2k**.

2-aminoalcohol **4a** in 73% yield (eq 3). Efforts to improve this alkyne oxoamination were unsuccessful using other gold catalysts: PPh_3AuSbF_6 (**2a**, 43%; **7**, 13%), P(*t*-Bu)$_2$(*o*-biphenyl)$AuNTf_2$ (**2a**, 26%; **7**, 38%), and $IPrAuSbF_6$ (**2a**, 41%; **7**, 10%; IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene).



We examined the scope of this new oxoamination on various aminoalkynes **1a**−**1j** and nitrones **8a**−**8f**; one-pot syntheses of 2-aminoalcohols are also depicted in Table 1. Entries 1−5 show the oxoaminations of aminoalkyne **1a** using varied nitrones **8b**−**8f** bearing fluoro, chloro, bromo, methyl, and methoxy groups at the aniline moiety, producing the desired 2-aminoamides **2b**−**2f** in 71−83% yields, with the methoxy-containing nitrone **8f** giving the best efficiency. Reduction of the above DCE solution *in situ* with a THF solution of $NaBH_4$ (2.2 equiv) delivered the expected 2-aminoalcohols **4b**−**4f** in 67−76% yields. The 1,2-difunctionalizations of alkynes are also

Scheme 2. Control Experiments Confirming Gold Carbenoids (Ar = 4-$MeOC_6H_4$)



compatible with varied *p*-phenyl substituents, as in substrates **1b**−**1f**, including fluoro, chloro, bromo, methyl, and methoxy; their corresponding oxoamination products **2g**−**2k** were obtained in 66−73% yields (entries 6−10). Similarly, aminoalcohols **4g**−**4j** were produced in 62−69% yields following the same reduction sequence. In entry 10, we were unable to obtain pure aminoalcohol **4k**; its production (98% yield) relied on the $NaBH_4$ reduction of 2-aminoamides **2k**. The scope of this catalysis is further expanded to alkyne substrates **1g** and **1h** bearing 2- and 3-thienyl that gave desired products **2l** and **2m** in 71−74% yields; the reduction *in situ* gave **4l** and **4m** in 65−70% yields (entries 11 and 12). For substrates **1i** and **1j** bearing alterable amino substituents, the same reaction sequence delivered aminoamides **2n** and **2o** in 62−78% yields, further giving 2-aminoalcohols **4a** in 55−69% yields.

Among various organic oxides, only pyridine-based oxides are confirmed to generate α-carbonyl carbenoid **A** from alkyne oxidations.[5,6] Scheme 2 shows crucial results to confirm the participation of α-carbonyl carbenoid **A** using nitrone. Treatment of 1-amino-2-(*n*-butyl)ethyne **1k** with nitrone **8a** and P(*t*-Bu)$_2$(*o*-biphenyl)$AuSbF_6$ (5 mol %) in DCE (25 °C, 8 h) gave enamide **10** (*E*/*Z* = 1.3) in 67% yield through a 1,2-hydride shift of gold carbenoid **A**. We also found evidence for an intermolecular arylation of gold carbenoid **A** via treatment of 1-amino-2-(*tert*-butyl)ethyne **1l** with nitrone **8a** under the same conditions, which produced α-arylamide **11a** and γ-lactam **11b** in 68% and 15% yields, respectively. Acid-catalyzed hydrolysis of **11a** gave **11b** in 96% yield. We performed crossover experiments to understand further the hypothetical α-carbonyl carbenoid **A**. As shown in Scheme 2, treatment of aminoalkyne **1a** with nitrone **8a** (1.3 equiv), *N*-benzylidene-4-methoxyaniline (1.3 equiv) and gold catalyst in DCE (25 °C, 10 h) produced only aminoamide **2a** in 64% yield, with the other analogue **2f** in a negligible amount. A subsequent experiment also revealed that nitrone **8f** is the source for both the amino and oxo groups of the resulting aminoamide **2f**.

The control experiments ambiguously verify the intermediacy of gold carbenoids, which are trapped instantly by imine in the inner sphere. To rationalize this behavior, we propose that the newly generated gold carbenoids form a strong dipole−dipole

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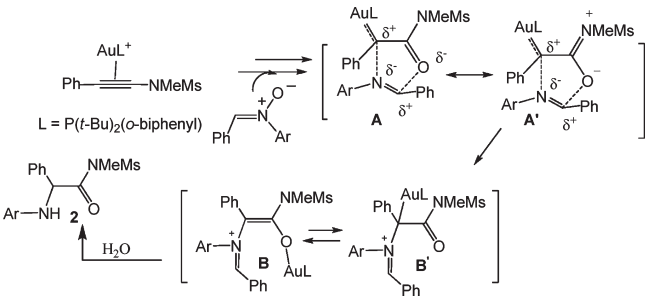
Scheme 3. Proposed Mechanism for Gold-Catalyzed Oxoamination Reactions

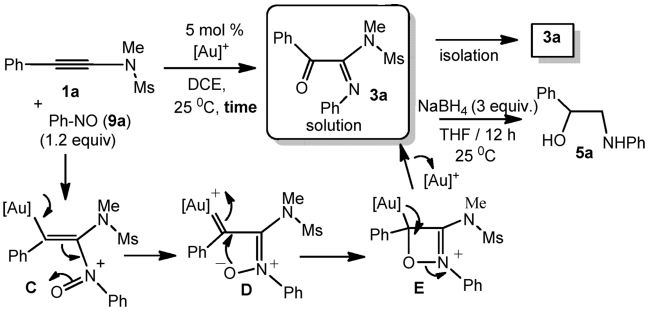


interaction with imine to prevent its diffusion to the outer sphere, as depicted in state **A** or its resonance form **A′**. This complex pair facilitates the addition of imine at gold carbenoid to give species **B′** or its enolate form **B**, ultimately generating observed product **2** through hydrolysis (Scheme 3).

Using the same aminoalkyne **1a** and gold catalysts, to our delight, we discover a distinct 1,2-difunctionalization using nitrosobenzene (**9a**) as the oxidant. As depicted in Table 2, various gold complexes implemented efficiently this unprecedented alkyne/nitroso metathesis, giving the oxoimination product **3a**. As shown in entries 1 and 2, P(*t*-Bu)$_2$(*o*-biphenyl)AuCl/AgX (X = SbF_6 and NTf_2) gave 2-oxoiminylamide **3a** in 86−88% yields. IPrAuCl/$AgSbF_6$ and IPrAuCl/$AgNTf_2$ showed pronounced activities to give the desired 2-oxoiminylamides **3a** in excellent yields (90−91%, entries 3 and 4); herein, we also performed the $NaBH_4$ reduction of their parent DCE solution (25 °C, 12 h), producing 2-aminoalcohols **5a** in 71−74% yields. In contrast, PPh_3AuCl/$AgSbF_6$ and $AuCl_3$ gave the desired **3a** in only 55−58% yields. In this novel metathesis reaction, we envisage that nitrosobenzene attacks the π-aminoalkyne **1a** via its nitrogen, giving intermediate **C**, further giving gold carbenium species **D**. Intramolecular cyclization of species **D** is expected to give 4*H*-oxazet-2-ium species **E** that will lose its gold fragment to facilitate the ring cleavage to give observed **3a**.

We examined the scope of this alkyne/nitroso metathesis on aminoalkynes **1a**−**1o** and nitroso benzene **9a**−**9d**; one-pot syntheses of 2-aminoalcohols **5a**−**5n** are also summarized in Table 3. All catalytic operations were done with 5 mol % IPrAuCl/$AgNTf_2$ in dry DCE at 25 °C. In entries 1−5, this new metathesis works satisfactorily with aminoalkynes **1b**−**1f** bearing *p*-phenyl substituents including fluoro, chloro, bromo, methyl, and methoxy; their oxoimination products **3b**−**3f** were obtained in 69−90% yields. $NaBH_4$ reduction of these 2-oxoiminylamides *in situ* delivered the desired 2-aminoalcohols **5b**−**5f** in 64−88% yields. The reactions were also extensible to aminoalkynes **1g**,**1h**, which delivered the desired 2-oxoiminylamides **3g**,**3h** and 2-aminoalcohols **5g**,**5h** in 80−85% and 75−77% yields, respectively (entries 6 and 7). Entries 8 and 9 show our reactions with new aminoalkynes **1l**,**1m** bearing aliphatic substituents (R^1 = cyclopropyl and *tert*-butyl), which gave good yields of both 2-oxoiminylamides **3i**,**3j** (89−93%) and aminoalcohols **5i**,**5j** (78−86%). The molecular structure of **3j** was confirmed by X-ray diffraction.[13] As shown in entry 10, we obtained moderate yields of 2-oxoiminylamide **3k** (48%) and aminoalcohol **5k** (41%), derived from starting **1n** bearing R^1 = isopropyl, because of unknown components that were inseparable. This metathesis reaction also works well for nitrosobenzenes **9b**−**9d**, giving the desired oxoimination products

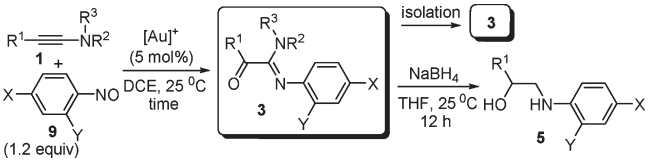
Table 2. Gold-Catalyzed Oxoimination Reactions



entry	[Au][a]	time (h)	compound 3a[b]	5a[b]
1	LAuCl/$AgSbF_6$	1.5	86%	—
2	LAuCl/$AgNTf_2$	1.0	88%	—
3	IPrAuCl/$AgSbF_6$	1.0	90%	71%
4	IPrAuCl/$AgNTf_2$	1.0	91%	74%
5	PPh_3AuCl/$AgSbF_6$	2.0	58%	—
6	$AuCl_3$	1.0	55%	—

[a] L = P(*t*-Bu)$_2$(*o*-biphenyl), IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene), [**1**] = 0.12 M. [b] Product yields are reported after purification from silica column.

Table 3. Gold-Catalyzed Oxoiminations and Aminohydroxylations



entry	alkyne[a]	nitrosobenzene	time(h)	compounds[b]	
	NR^2R^3 = NMeMs				
1	R^1 = 4-FC_6H_4 (**1b**)	X = Y = H (**9a**)	2	**3b** (87%)	**5b** (81%)
2	R^1 = 4-ClC_6H_4 (**1c**)	**9a**	1	**3c** (90%)	**5c** (88%)
3	R^1 = 4-BrC_6H_4 (**1d**)	**9a**	1	**3d** (84%)	**5d** (76%)
4	R^1 = 4-MeC_6H_4 (**1e**)	**9a**	2	**3e** (81%)	**5e** (73%)
5	R^1 = 4-$MeOC_6H_4$ (**1f**)	**9a**	2	**3f** (69%)	**5f** (64%)
6	R^1 = 2-thienyl (**1g**)	**9a**	1.5	**3g** (85%)	**5g** (77%)
7	R^1 = 3-thienyl (**1h**)	**9a**	2	**3h** (80%)	**5h** (75%)
8	R^1 = cyclopropyl (**1m**)	**9a**	2	**3i** (93%)	**5i** (86%)
9	R^1 = *t*-butyl (**1l**)	**9a**	2	**3j** (89%)	**5j** (78%)
10	R^1 = *i*-propyl (**1n**)	**9a**	12	**3k** (48%)[c]	**5k** (41%)
11	R^1 = Ph (**1a**)	X = Cl, Y = H (**9b**)	1	**3l** (82%)	**5l** (73%)
12	R^1 = Ph (**1a**)	X = Br, Y = H (**9c**)	1	**3m** (85%)	**5m** (75%)
13	R^1 = Ph (**1a**) R^1 = Ph	X = H, Y = Br (**9d**)	1	**3n** (91%)	**5n** (76%)
14	NR^2R^3 = NPhMs (**1i**)	**9a**	1	**3o** (85%)	**5a** (71%)
15	NR^2R^3 = NBnMs (**1j**)	**9a**	1	**3p** (87%)	**5a** (81%)
16	NR^2R^3 = oxazolidinone (**1o**)	**9a**	1	**3q** (83%)	**5a** (73%)

[a] [Au] = lPrAuCl/$AgNTf_2$, [**1**] = 0.12 M. [b] Product yields are reported after purification from silica column. [c] Unknown mixtures were formed and difficult to purify in entry 10.

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3l−**3n** in 82−91% yields and further generating 2-aminoalcohols **5l**−**5n** *in situ* in good yields (73−76%, entries 11−13). For aminoalkynes **1i**, **1j**, and **1o**[14] bearing different amino groups, the same reaction sequence afforded 2-oxoiminylamides **3o**−**3q** in 83−87% yields, further producing 2-aminoalcohol **5a** in 71−81% yields (entries 14−16).

Before this work, very few instances of gold-catalyzed oxidative 1,2-difunctionalizations of alkynes with external nucleophiles were reported.[47] Herein, we have developed two independent routes for gold-catalyzed 1,2-difunctionalizations of aminoalkynes[15] using only external oxidants. In the presence of $P(t\text{-Bu})_2(o\text{-biphenyl})AuSbF_6$, nitrones enable the oxoamination of aminoalkynes **1** to form 2-aminoamides **2** that are then subjected to $NaBH_4$ reduction *in situ* to deliver 2-aminoalcohols **4**. Control experiments confirm the occurrence of α-carbonyl carbenoids that are trapped instantly by the released imine in the inner sphere. We subsequently discovered that nitrosobenzene implements a novel gold-catalyzed alkyne/nitroso metathesis to give 2-oxoiminylamides **3**, and subsequent $NaBH_4$ reduction *in situ* delivered 2-aminoalcohols **5** with opposite regioselectivity. With two oxidants, selective production of diversified 1,2-difunctionalized products from a single substrate highlights the significance of these catalytic reactions.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization of new compounds, and X-ray crystallographic data of **3j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(10) Selected examples of metal-catalyzed synthesis of 2-aminoalcohols from alkenes and metal-catalyzed aminohydroxylation of unfunctionalized alkenes: (a) Sharpless, K. B.; Chong, A. O.; Oshima, J. *J. Org. Chem.* **1976**, *41*, 177. (b) Desai, L. V.; Sanford, M. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5737. (c) Liu, G.; Stahl, S. *J. Am. Chem. Soc.* **2006**, *128*, 7179. (d) Michaelis, D. J.; Shaffer, C. J.; Yoon, T. P. *J. Am. Chem. Soc.* **2007**, *129*, 1866. (e) Williamson, K. S.; Yoon, T. *J. Am. Chem. Soc.* **2010**, *132*, 4570. (f) Alexanian, E. J.; Lee, C.; Sorenson, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 7690.

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(12) Kramer, S.; Dooleweerdt, K.; Lindhardt, A. T.; Rottländer, M.; Skrydstrup, T. *Org. Lett.* **2009**, *11*, 4208.

(13) Crystallographic data of **3j** are provided in the SI.

(14) For alkynyloxazolidinone **1o**, its gold-catalyzed oxidation with nitrone **8a** gave dicarbonyl compound **12** exclusively (76%) via a secondary oxidation of gold carbenoid **A**.[4] Spectral data of **12** are provided in the SI.

(15) For 1-hexyne and phenylacetylene, we exclusively recovered these two alkynes for both nitrone and nitrosobenzene oxidations in dichloroethane at room temperature, whereas we obtained a messy mixture of products when the reactions were performed at 80 °C. These results indicate that the amino group activates the oxidation of alkynes with external oxidants.