

Highly Regio-, Diastereo-, and Enantioselective Gold(I)-Catalyzed Intermolecular Annulations with N-Allenamides at the Proximal C=C Bond

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Abstract: A highly enantioselective gold(I)-catalyzed intermolecular annulation of 2-(1-alkynyl)-2-alken-1-ones with N-allenamides is presented. The present work represents the first example of a gold-catalyzed annulation with the proximal C=C bond of an N-allenamide, and is distinctly different from the previously observed annulations at the distal C=C bond. Interestingly, both enantiomers of the products could be obtained in good yields with high regio-, diastereo-, and enantioselectivity by using either diastereomer of a binol-derived phosphoramidite as a chiral ligand.

Homogeneous gold catalysis has proven to be a useful and powerful synthetic tool in modern organic chemistry because of its remarkable capability to activate multiple C–C bonds.^[1] Among them, the gold-catalyzed cycloadditions/annulations of two or more unsaturated components, arguably the most direct and atom-economical route to various cyclic and polycyclic frameworks, has become an area of intense investigation in the past few years.^[2] However, the development of new types of gold-catalyzed intermolecular cycloadditions/annulations,^[3] in particular an asymmetric version, pose a considerable challenge.^[3f] In this context, N-allenamides, an easily available type of allenic scaffold, have been explored as versatile building blocks in a variety of transformations,^[4] including $[m+2]$ cycloadditions/annulations of N-allenamides with suitable synthons (Figure 1).^[5–9] Mascareñas, López, and co-workers documented a pioneering asymmetric gold-catalyzed intermolecular $[4+2]$ cycloaddition of N-allenamides with 1,3-dienes^[5b] and cascade cycloaddition with the alkene-tethered ketones.^[6] González and co-workers successfully developed an asymmetric $[2+2]$ cycloaddition of N-allenamides with alkenes, thus leading to optically active cyclobutanes.^[7e] An efficient asymmetric $[3+2]$ cycloaddition with nitrones was recently reported by Chen and co-workers.^[8b] Very recently, our group realized the enantioselective intermolecular $[2+2]$ or $[4+2]$ cycloaddition of N-allenamides

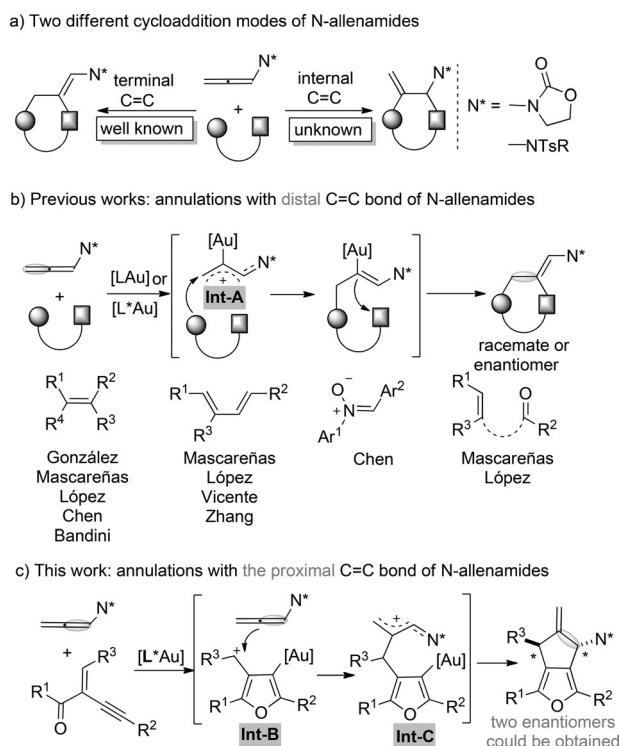


Figure 1. Gold-catalyzed annulations involving different C=C bond reactivities of N-allenamides. Ts = 4-toluenesulfonyl.

with 3-styrylindoles under the catalysis of chiral gold complexes, in which the cycloaddition mode highly depends on the N substituent of 3-styrylindoles.^[9b] However, despite these significant achievements, there still remain challenges (e.g., reaction manifold, substrate scope, as well as regio- and stereocontrol). Moreover, almost all previous studies on this topic have been focused on the distal C=C bond reactivity (**Int-A**) of N-allenamides (Figure 1b). In contrast, gold-catalyzed $[m+2]$ cycloadditions/annulations with the proximal C=C bond of N-allenamides remains unknown so far (Figure 1a). Herein, we demonstrate the first selective gold-catalyzed $[3+2]$ annulation of 2-(1-alkynyl)-2-alken-1-ones with the proximal C=C bond of an N-allenamide, and it provides facile access to enantioenriched 3,4-ring fused furans (Figure 1c). More interesting is that both enantiomers of the cycloadducts can be obtained in good yields with high regio-, diastereo-, and enantioselectivity (up to 99% *ee*) by using either diastereomer of a binol-derived phosphoramidite ligand.

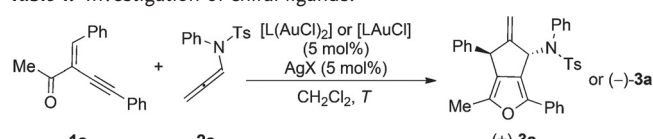
Meanwhile, 2-(1-alkynyl)-2-alken-1-ones, which could be easily prepared on large scale from readily available

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α -bromo- α,β -enones and simple terminal alkynes, have emerged as efficient and versatile precursors for gold-catalyzed cycloaddition/annulations.^[10] Gold all-carbon 1,3-dipole species (**Int-B**) is a commonly proposed key intermediate in these reactions (Figure 1c). Hence, we envisaged that if the formation of **Int-B** is more favored than the gold-allylic carbocation **Int-A** in the presence of gold(I) complexes, the subsequent [3+2] annulation may take place at the proximal C=C bond of an N-allenamide via the intermediate **Int-C**. Given the high reactivity of N-allenamides with gold,^[6,7b,c] we also anticipated a formidable challenge in controlling the regio-, diastereo-, and enantioselectivity of this novel reaction.

Initially, our investigation began with the ketone **1a** and N-allenamide **2a** under the catalysis of $\text{Ph}_3\text{PAuCl}/\text{AgSbF}_6$ (Table 1). Gratifyingly, the annulation with the proximal C=C bond of the N-allenamides indeed took place, thus delivering the desired racemic product ($\pm$)-**3a** in 55% yield. Encouraged by this result, we next focused on the asymmetric version of this novel annulation by the application of chiral gold complexes.^[11] Unfortunately, the privileged gold complex derived from the chiral bis(phosphine) ligand (*R*)-**L1**^[3a,10c] failed to induce good enantioselectivity (entry 1). Next, we turned to examine the family of binol-derived phosphoramidites.^[9b,12] Using the simplest phosphoramidite, (*S,S,S*)-**L2**, the reaction gave (+)-**3a** with 36% *ee* (entry 2). Then a series of phosphoramidites (**L3–L7**) with different substituents at the 3,3'-positions of the binol moiety

Table 1: Investigation of chiral ligands.^[a]



Reaction scheme for Table 1: Ketone **1a** (Me-C(=O)-CH=CH-Ph) reacts with N-allenamide **2a** (Ph-CH=N-Ts) in the presence of a chiral gold complex **L** (5 mol%) and AgX (5 mol%) in CH_2Cl_2 at temperature *T* to form product (+)-**3a** or (-)-**3a**.

Chemical structures of ligands **L** are shown below the reaction scheme:

- (*R*)-**L1**: Ar = 4-MeO-3,5-*i*Bu₂C₆H₂
- (*S,S,S*)-**L2**: G = H
- (*S,S,S*)-**L3**: G = SiMe₃
- (*S,S,S*)-**L4**: G = 2-naphthyl
- (*S,S,S*)-**L5**: G = 3,5-(CF₃)₂C₆H₃
- (*S,S,S*)-**L6**: G = 4-MeOC₆H₄
- (*S,S,S*)-**L7**: G = 9-anthracenyl
- (*R,R,R*)-**L7**: G = 9-anthracenyl

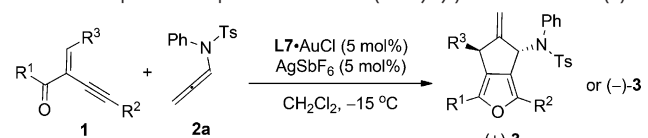
Entry	L	AgX	T [°C]	t [h]	ee [%] ^[b]
1	(<i>R</i>)- L1	AgSbF ₆	25	1	(+)- 3a , 14
2	(<i>S,S,S</i>)- L2	AgSbF ₆	25	0.5	(+)- 3a , 36
3	(<i>S,S,S</i>)- L3	AgSbF ₆	25	0.5	(+)- 3a , 4
4	(<i>S,S,S</i>)- L4	AgSbF ₆	25	0.5	(+)- 3a , 38
5	(<i>S,S,S</i>)- L5	AgSbF ₆	25	0.5	(+)- 3a , 6
6	(<i>S,S,S</i>)- L6	AgSbF ₆	25	0.5	(+)- 3a , 60
7	(<i>S,S,S</i>)- L7	AgSbF ₆	25	0.5	(+)- 3a , 90
8	(<i>R,R,R</i>)- L7	AgSbF ₆	25	1	(-)- 3a , 90
9	(<i>R,R,R</i>)- L7	AgOTf	25	1.5	(-)- 3a , 88
10	(<i>R,R,R</i>)- L7	AgNTf ₂	25	1	(-)- 3a , 89
11	(<i>R,R,R</i>)- L7	AgSbF ₆	0	2	(-)- 3a , 90
12	(<i>R,R,R</i>)- L7	AgSbF ₆	-10	12	(-)- 3a , 93
13	(<i>R,R,R</i>)- L7	AgSbF ₆	-15	24	(-)- 3a , 94
14	(<i>S,R,R</i>)- L7	AgSbF ₆	-15	12	(+)- 3a , 97

[a] Reaction conditions: chiral gold complexes (5 mol%), AgX (5 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol), CH_2Cl_2 (2.0 mL). Unless specified otherwise, conversions were determined by ¹H NMR analysis (> 99%, > 20:1 d.r.). [b] Determined by HPLC on a chiral stationary phase.

were examined (entries 3–8). We were pleased to find that (+)-**3a** could be obtained in 99% yield (NMR spectroscopy) with 90% *ee* by employing the (*S,R,R*)-**L7**, bearing 9-anthracenyl substituents, at ambient temperature (entry 7). More interestingly, the enantiomer of (+)-**3a**, that is, (-)-**3a** was also furnished with 90% *ee* using (*R,R,R*)-**L7**, the diastereomer of (*S,R,R*)-**L7** (entry 8). No further improvement in enantioselectivity was observed by a variation of the silver salts from AgSbF₆ to AgOTf and AgNTf₂ (entries 8–10). Finally, running the reaction at lower temperature (-15°C) led to a significant improvement in enantioselectivity, thus affording (+)-**3a** in 95% yield upon isolation with 97% *ee*, and the enantiomer (-)-**3a** in 90% yield upon isolation with 94% *ee* under the catalysis of a gold complex derived from a pair of diastereomers of **L7** (entries 13 and 14). The absolute configuration of the cycloadduct (+)-**3a** was unambiguously determined to be 4*S*,6*S* by X-ray crystal structure analysis.^[13]

With the optimal reaction conditions in hand, various 2-(1-alkynyl)-2-alken-1-ones (**1**) were explored to investigate the generality of this asymmetric annulation (Table 2). The substrate scope is quite general and all the annulations can be conducted with good to excellent enantioselectivity (up to 98% *ee*). Notably, all the reactions delivered the desired products (+)-**3a–n** in 71–95% yields with more than 90% *ee* by using (*S,R,R*)-**L7** as the chiral ligand, thus indicating that there is little effect of the substituent on the reaction (entries 1–15). Nevertheless, there is an obvious substituent effect on this transformation when the diastereomeric (*R,R,R*)-**L7** is employed as the chiral ligand. Furthermore, the introduction of a *para* substituent on the aryl group R³ resulted in a decrease of the enantioselectivity (entry 1 versus entries 7 and 8). In addition, changing the R² group from aryl

Table 2: Scope with respect to various 2-(1-alkynyl)-2-alken-1-ones (**1**).^[a]



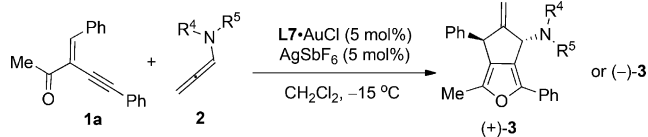
Reaction scheme for Table 2: 2-(1-alkynyl)-2-alken-1-one **1** (R¹-C(=O)-CH=CH-C≡C-R²) reacts with N-allenamide **2a** (Ph-CH=N-Ts) in the presence of L7·AuCl (5 mol%) and AgSbF₆ (5 mol%) in CH_2Cl_2 at -15°C to form product (+)-**3** or (-)-**3**.

Entry	R ¹ /R ² /R ³	Yield [%] ^[b] (ee [%]) ^[c]	
		Using (<i>S,R,R</i>)- L7	Using (<i>R,R,R</i>)- L7
1	Me/Ph/Ph (1a)	(+)- 3a , 95 (97)	(-)- 3a , 90 (94)
2	Me/4-MeOC ₆ H ₄ /Ph (1b)	(+)- 3b , 71 (98)	(-)- 3b , 64 (96)
3	Me/4-MeC ₆ H ₄ /Ph (1c)	(+)- 3c , 83 (96)	(-)- 3c , 76 (90)
4	Me/4-BrC ₆ H ₄ /Ph (1d)	(+)- 3d , 92 (98)	(-)- 3d , 80 (88)
5	Me/4-ClC ₆ H ₄ /Ph (1e)	(+)- 3e , 90 (98)	(-)- 3e , 81 (90)
6 ^[d]	Me/ <i>n</i> Pr/Ph (1f)	(+)- 3f , 72 (90)	(-)- 3f , 67 (82)
7	Me/Ph/4-MeOC ₆ H ₄ (1g)	(+)- 3g , 82 (98)	(-)- 3g , 74 (75)
8	Me/Ph/4-BrC ₆ H ₄ (1h)	(+)- 3h , 86 (98)	(-)- 3h , 83 (85)
9	Ph/Ph/Ph (1i)	(+)- 3i , 85 (96)	(-)- 3i , 80 (94)
10	Ph/4-MeOC ₆ H ₄ /Ph (1j)	(+)- 3j , 85 (96)	(-)- 3j , 82 (94)
11	Ph/1-Naphthyl/Ph (1k)	(+)- 3k , 72 (93)	(-)- 3k , 69 (88)
12	Ph/Ph/4-ClC ₆ H ₄ (1l)	(+)- 3l , 85 (96)	(-)- 3l , 80 (88)
13	4-MeOC ₆ H ₄ /Ph/Ph (1m)	(+)- 3m , 80 (97)	(-)- 3m , 77 (96)
14	4-BrC ₆ H ₄ /Ph/Ph (1n)	(+)- 3n , 89 (97)	(-)- 3n , 90 (95)

[a] All reactions were performed with **1** (0.20 mmol), **2a** (0.24 mmol), and [L7·AuCl]/AgSbF₆ (5 mol%) in CH_2Cl_2 at -15°C for 12–24 h.

[b] Yield of isolated products. d.r. > 20:1. [c] Determined by HPLC on a chiral stationary phase. [d] At 25°C.

Table 3: Scope with respect to various N-allenamides (**2**).^[a]



Entry	R ⁴ /R ⁵	Yield [%] ^[b] (<i>ee</i> [%]) ^[c] Using (S,R,R)-L7	Yield [%] ^[b] (<i>ee</i> [%]) ^[c] Using (R,R,R)-L7
1	Ph/Ns (2b)	(+)- 3o , 91 (99)	(-)- 3o , 84 (97)
2	Ph/Bs (2c)	(+)- 3p , 92 (98)	(-)- 3p , 87 (97)
3	Ph/Ms (2d)	(+)- 3q , 71 (98)	(-)- 3q , 63 (96)
4	4-BrC ₆ H ₄ /Ts (2e)	(+)- 3r , 80 (96)	(-)- 3r , 82 (92)
5	4-MeOC ₆ H ₄ /Ts (2f)	(+)- 3s , 83 (90)	(-)- 3s , 79 (90)
6	4-FC ₆ H ₄ CH ₂ /Ts (2g)	(+)- 3t , ^[d] 87 (98)	(-)- 3t , ^[d] 85 (94)

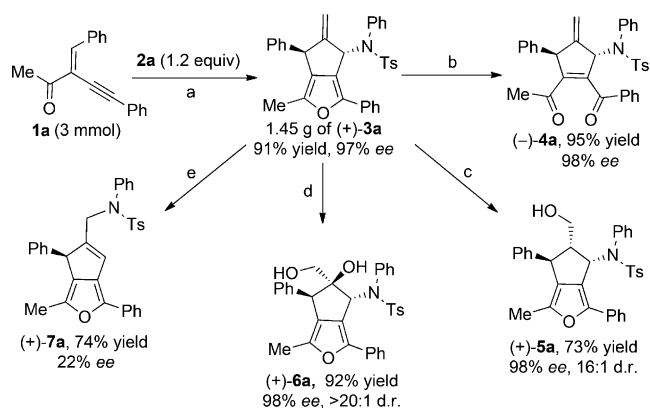
[a] All reactions were performed with **1a** (0.20 mmol), **2** (0.24 mmol), and [L7·AuCl]/AgSbF₆ (5 mol %) in CH₂Cl₂ at -15 °C for 12–24 h. [b] Yield of isolated product. d.r. > 20:1. [c] Determined by HPLC on a chiral stationary phase. [d] 7:1 d.r. [e] 1:2 d.r. Ns = 4-nitrobenzenesulfonyl, Bs = 4-bromobenzenesulfonyl, Ms = mesyl = methanesulfonyl.

to alkyl resulted in a reasonable enantioselectivity with the use of (R,R,R)-L7 (entry 1 versus 6).

The potential of the annulation with respect to N-allenamides (**2**) was further evaluated (Table 3). In general, both enantiomers of the products could be obtained with greater than 90 % *ee* under the optimal reaction conditions. Notably, by changing the substitution on the sulfonyl group R⁵, the reaction could proceed in good yields with excellent enantioselectivities (> 96 % *ee*; entries 1–3). Next, the reaction scope was evaluated by variation of R⁴ on the allenamides, and the desired products **3r,s** were produced in good yields with high *ee* values (entries 4 and 5). In addition, the reaction of **1a** and the N-allenamide **2g**, bearing a 4-fluorobenzyl group, furnished the desired products **3t** and (–)-**3t** in high yields with 98 and 94 % *ee*, respectively, albeit with a relatively low d.r. value for (–)-**3t** (entry 6).

To test the practicality of this new methodology, a gram-scale synthesis of (+)-**3a** was carried out. To our delight, the 3.0 mmol scale reaction produced 1.45 grams of (+)-**3a** in 91 % yield with 97 % *ee* by using the 2.5 mol % catalyst loading, thus indicating that this transformation is easy to scale-up to gram scale without loss of efficiency and selectivity (Scheme 1). To showcase potential synthetic utilities of this protocol, we performed several additional transformations on the representative (+)-**3a**. The oxidative furan ring-opening of (+)-**3a** was realized by treatment with *m*-CPBA in dichloromethane to give multifunctionalized cyclopentene (–)-**4a** in 95 % yield with the same *ee* value. The hydroboration of the double bond of (+)-**3a** and subsequent oxidation delivered the primary alcohol (+)-**5a**, having three continuous stereocenters, in 73 % yield, 98 % *ee*, and 16:1 d.r. Moreover, the diastereoselective dihydroxylation was also achieved with K₂OsO₄·2H₂O/NMO, thus furnishing the optically active (+)-**6a** as a single diastereomer in 92 % yield and 98 % *ee*. Finally, (+)-**7a** was obtained by palladium-catalyzed rearrangement of (+)-**3a** in 74 % yield, albeit with a low *ee* value.

In summary, we developed a highly regio-, diastereo-, and enantioselective gold(I)-catalyzed intermolecular annulation



Scheme 1. Gram-scale synthesis and synthetic applications of (+)-**3a**. Reaction conditions: a) (S,R,R)-L7·AuCl (2.5 mol %), AgSbF₆ (2.5 mol %), CH₂Cl₂, -15 °C to RT, 12 h; b) *m*-CPBA, K₂CO₃, CH₂Cl₂, RT, 3 h; c) 1. BH₃·THF, THF, RT, 3 h; 2. H₂O₂, NaOH, RT, 4 h; d) K₂OsO₄·H₂O, NMO, THF/H₂O 10:1, RT, 24 h; e) [Pd₂(dba)₃]·CHCl₃, dppe, PhCOONa, THF, 50 °C. THF = tetrahydrofuran.

of 2-(1-alkynyl)-2-alken-1-ones with the proximal C=C bond of N-allenamides. This unprecedented study is believed to proceed through a gold all-carbon 1,3-dipole species with the proximal C=C bond of an N-allenamide and, therefore, extends the types of processes amenable to enantioselective gold catalysis. Notably, with the pair of diastereomers of binol-derived phosphoramidite L7, both enantiomers of the enantioenriched 3,4-ring-fused furans were obtained in good yields with up to 99 % *ee* under mild reaction conditions. The salient features of the present method, including using readily available starting materials, good selectivities, high efficiency, practical utilization, and a variety of additional transformations, make it a straightforward approach to highly valuable building blocks in organic synthesis. Further studies including the development more novel cyclization modes involving N-allenamides are underway in our laboratory and will be reported in due course.

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