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Gold-Catalyzed Oxidative Cross-Coupling of Terminal Alkynes: Selective Synthesis of Unsymmetrical 1,3-Diynes

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Supporting Information

ABSTRACT: Gold-catalyzed oxidative cross-coupling of alkynes to unsymmetrical diynes has been achieved for the first time. A N,N-ligand (1,10-Phen) and $PhI(OAc)_2$ were identified as crucial factors to promote this transformation, giving the desired cross-coupled conjugated diynes in excellent heteroselectivity (>10:1), in good to excellent yields, and with large substrate tolerability.

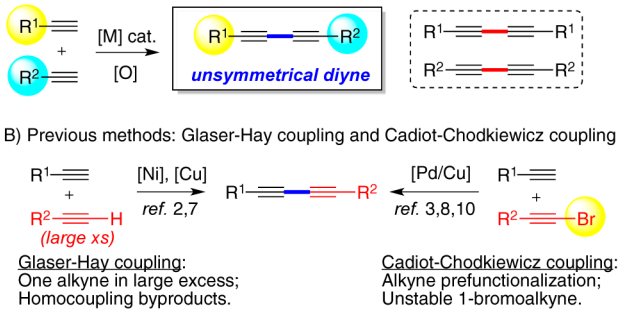
Conjugate diynes and polyynes are valuable building blocks in chemical, pharmaceutical, and material sciences.[1] Methods for the synthesis of conjugate diynes, especially unsymmetrical diynes, are thus of great importance. Typical ways of making conjugate diynes include Glaser−Hay coupling[2] and Cadiot−Chodkiewicz coupling.[3,4] However, Glaser−Hay coupling (catalyzed by Cu or Ni) suffers from undesired competing homocoupling and often requires a large excess of one alkyne, and Cadiot−Chodkiewicz coupling involves alkyne prefunctionalization, which significantly increases the overall cost of the reaction and is impractical due to the low stability of 1-bromoalkyne. Thus, simple heteroselective alkyne coupling remains very challenging yet desirable. Here we report a highly selective heterocoupling of terminal alkynes for the synthesis of 1,3-unsymmetric diynes[5] enabled by gold catalysis (Scheme 1),[6] which requires neither one coupling counterpart in large excess[7] nor alkyne prefunctionalization.[8]

In general, undesired alkyne homocoupling is the main problem associated with any direct C−H alkynylation.[9] To develop a direct alkyne cross-coupling, homocouplings of both alkynes must be suppressed to a minimum level. This has been a big challenge for Cu and Pd systems, possibly due to the disproportionation of $[LM(C{\equiv}CR)_2]^{n+}$ intermediates.[10] Thus, to achieve selective alkyne cross-coupling, rapid reductive elimination (to avoid $[LM(C{\equiv}CR)_2]^{n+}$ transmetalation/disproportionation) and selective formation of a specific metal acetylide are crucial. It is well known that Au(I)/Au(III) redox potential is high,[11] and recent studies suggested that strong oxidants such as PIDA and Selectfluor can facilely oxidize Au(I) to Au(III).[12] Recently, Toste et al. demonstrated that highly oxidative Au(III) complexes might undergo rapid reductive elimination.[13] This process could be further accelerated with proper choice of ancillary ligand (e.g., π-acceptor and favored *cis*-reductive elimination).[8,14] On the basis of these analyses, we postulated that, with fast reductive elimination, Au catalysis might open new avenues to achieve the challenging alkyne cross-coupling.

Another important feature for successful cross-coupling is the selective coordination of electronically biased alkynes, i.e., discrimination of alkynes through metal acetylide formation. As a superior π-acid, Au salt could form the σ-acetylide more facilely than Cu, even without the presence of a strong base.[15] We hypothesized that gold cations might provide this "discrimination effect" toward different alkynes, which was supported by our investigations on the gold acetylide formation between PPh_3AuOAc and different types of alkynes (Figure 1).

As revealed by reaction NMR studies (^1H and ^{19}F), under both stoichiometric (1 equiv of Au) and substoichiometric conditions (15% Au), $Ph_3PAuOAc$[16] reacted selectively with aliphatic alkyne **2** over aromatic alkyne **1** to form the corresponding gold acetylides (3:1 selectivity; see SI). Although the selectivity was modest, this result implied the intrinsically distinct response of aliphatic and aromatic alkynes toward Au catalysts, which might be used to "discriminate" alkynes for heterocoupling.

Scheme 1. Gold-Catalyzed Oxidative Alkyne Cross-Coupling



catalyst	1:2 ratio	ligand	yield	hetero/homo
15 mol % CuCl	1:1.3	15% TMEDA	45%	1.6:1
5 mol % $dppm(AuBr)_2$	1:5	none	0%	---
2.5 mol % $dppm(AuBr)_2$	**1:1.3**	**10 mol % Phen**	**83%**	**12:1**

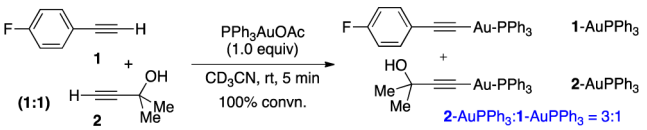


Figure 1. Substrate-dependent gold acetylide formation.

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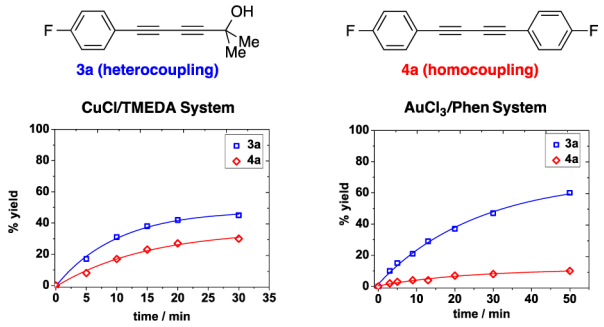


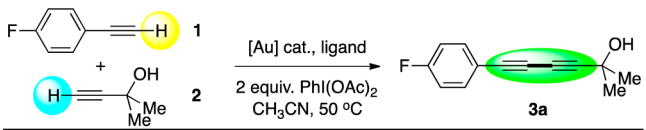
Figure 2. Kinetics comparison of Cu and Au systems. Conditions: (left) **1** (0.1 mmol), **2** (0.13 mmol), CuCl (15 mol%), TMEDA (15 mol%), acetone (0.3 M), 50 °C; (right) **1** (0.1 mmol), **2** (0.13 mmol), $AuCl_3$ (5 mol%), Phen (5 mol%), CH_3CN (0.3 M), 50 °C.

To further test our hypothesis, a series of kinetics experiments were conducted to compare the Cu and Au catalytic systems. As shown in Figure 2, with **1a** and **1b** as the substrates (1:1.3 ratio),[17] the standard CuCl/TMEDA conditions[18] gave very poor selectivity, close to the statistical distribution.

Interestingly, when $AuCl_3$ (5 mol%) was used as the catalyst and $PhI(OAc)_2$ as the oxidant, no alkyne coupling products were observed at either room temperature or 50 °C. Addition of Phen ligand (5 mol%)[19] dramatically improved the reactivity, giving the desired conjugated diynes in good yield. Good hetero-/homoselectivity (**3a** vs **4a**) was obtained, and the selectivity was further improved at higher temperature (50 °C, **3a**:**4a** = 60%:13%). At both room temperature and 50 °C, only a small amount of aliphatic alkyne homocoupling product **4a** was observed. With these exciting results, we initiated a conditions screening with the focus on both Au precatalysts and ligands to further improve the reaction performance. The results were summarized in Table 1 (see detailed conditions screening in SI).

Under the standard reaction conditions (50 °C in CH_3CN with $PhI(OAc)_2$ as the oxidant), various catalysts were tested. While Cu catalyst gave very poor cross-coupling selectivity (1.6:1, entry 4), Pd did not catalyze the reaction at all (entry 5),

Table 1. Optimization of Conditions[a]



entry	cat. (%)	Ligand (%)	time	convn (%)[b]	yield (%) 3a	yield (%) 4a	3a:4a
1	None	-	8 h	100	0	0	-
2	$AuCl_3$ (5)	-	2 h	60	trace	trace	-
3	$AuCl_3$ (5)	Phen (5)	2 h	88	60	13	4.6
4	CuCl (15)	TMEDA (15)	2 h	100	45	27	1.6
5	$(PPh_3)_2PdCl_2$ (3)	Phen (5)	2 h	60	0	0	-
6	Ph_3PAuCl (5)	Phen (5)	2 h	100	67	15	4.5
7	Ph_3PAuBr (5)	Phen (5)	1 h	100	77	11	7.0
8	$Ph_3PAuNTf_2$ (5)	Phen (5)	1 h	100	65	10	6.5
9	IPrAuCl (5)	Phen (5)	2 h	18	trace	trace	-
10	dppm$(AuCl)_2$ (2.5)	Phen (5)	1 h	100	67	13	5.2
11	dppm$(AuBr)_2$ (2.5)	Phen (5)	30 min.	100	72	9	8.0
12	dppm$(AuBr)_2$ (2.5)	py (5)	2 h	<10	trace	trace	-
13	dppm$(AuBr)_2$ (2.5)	bpy (5)	2 h	63	43	10	4.3
14	dppm$(AuBr)_2$ (2.5)	Phen (10)	30 min.	100	81	9	9.0
15[c]	**dppm$(AuBr)_2$ (2.5)**	**Phen (10)**	**15 min.**	**100**	**83**	**7**	**12**
16	dppm$(AuBr)_2$ (1)	Phen (4)	45 min.	100	80	9	8.2

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.13 equiv), catalyst (5 mol%), and ligand (5 mol%) in CH_3CN (0.3 mL), 50 °C, 2 h. [b]Determined by ^{19}F NMR using benzotrifluoride as internal standard. [c]Solvent: CH_3CN/1,4-dioxane (3:1). 5% $ArC(O)CH_2OAc$ was detected from alkyne **1** oxidized by $PhI(OAc)_2$ along with some unidentified decomposition products.

which ruled out the possibility that trace amounts of Cu or Pd in commercial Au salts catalyzed the reaction. Improved reactivity was observed with Au(I) precatalyst (entry 6). Furthermore, compared with chloride salt, the gold bromide gave better results for both reaction rate and selectivity (entries 6 and 7).[20] Application of a digold catalyst[21] further improved the reaction performance, giving the desired cross-coupling product in good yield (72%, entry 11). Pyridine as the ligand could not promote this reaction (entry 12), while bidentate ligand bipyridine (bpy) gave diyne **3a** in 43% yield (entry 13). This result suggested the importance of bidentate N,N-ligands for this transformation. Through screening of various ligands, Phen was identified as the optimal choice (entry 14). Finally, application of a slight excess of Phen (10%) and MeCN/dioxane (3:1) cosolvents gave the cross-coupling product in excellent selectivity (12:1, entry 15). Notably, increasing the **1**:**2** ratio to 1:3 gave the cross-coupling diyne **3a** as the dominant product with >95% isolated yield.

Surprisingly, based on our screening, $PhI(OAc)_2$ was the only effective oxidant to promote this transformation (see SI). Other oxidants, including the Selectfluor, which was previously used in alkyne homocoupling,[5] yielded only a trace amount of diyne.

As illustrated in Table 2, this new system indicated excellent substrate compatibility, giving the desired cross-coupling products in good to excellent isolated yields. First, for aromatic alkynes, both electron-rich and electron-deficient alkynes furnished the conjugated diynes in good yields (**3a**−**3j**). The halogen-substituted aromatic alkynes (**3c**, **3e**, **3g**) gave the desired products in excellent yields, highlighting the orthogonal reactivity of Au catalyst over Pd, Cu, and Ni catalysts, which undergo oxidative addition. Heteroaromatic alkynes, including pyridine (**3m**, **3n**), thiophene (**3l**), and indole (**3k**), also proceeded efficiently. Great functional group tolerability was also observed with aliphatic alkynes. Substrates containing unprotected alcohol (**3o**), carboxylic acid (**3p**), amide (**3q**), silyl (**3v**), ester (**3r** and **3t**), and 1,2,3-triazole (**3u** and **3w**) were all suitable for this reaction. In particular, some highly reactive functional groups, such as vinyl ether (**3s**), propargyl ester (**3r**), and conjugated alkyne ester (**3t**), could also tolerate the reaction conditions, given the desired diynes in good yields. Moreover, to further evaluate the synthetic practicability of this method, we attempted to modify alkyne-derived natural product-like molecules, such as estrone (**3za** and **3zb**), sugar (**3y**), and amino acid (**3x**) derivatives. Fortunately, satisfactory yields were obtained with all these substrates, which not only highlighted the excellent substrate compatibility but also implied the great potential of this new method for complex molecule synthesis/modification.

The resulting conjugated diynes are very useful synthons that can be easily converted into other useful compounds. Scheme 2A summarizes some known transformations of diynes to important heteroaromatic molecules.[22] A gram-scale synthesis was also performed to verify the practical synthesis using this method, as shown in Scheme 2B. In addition, considering the importance of polyynes in chemical and material research, we explored the feasibility of using this method to achieve polyyne synthesis. As shown in Scheme 2C, using the terminal alkyne synthesized from TIPS deprotection of **3v** gave the conjugated triyne **5** in excellent yield under standard conditions (85% in two steps). It is anticipated that a variety of polyynes could be readily prepared using this strategy, highlighting the broad synthetic application of the reported method.

Several examples involving Au-catalyzed C−C bond coupling under oxidative conditions have been reported in the literature.

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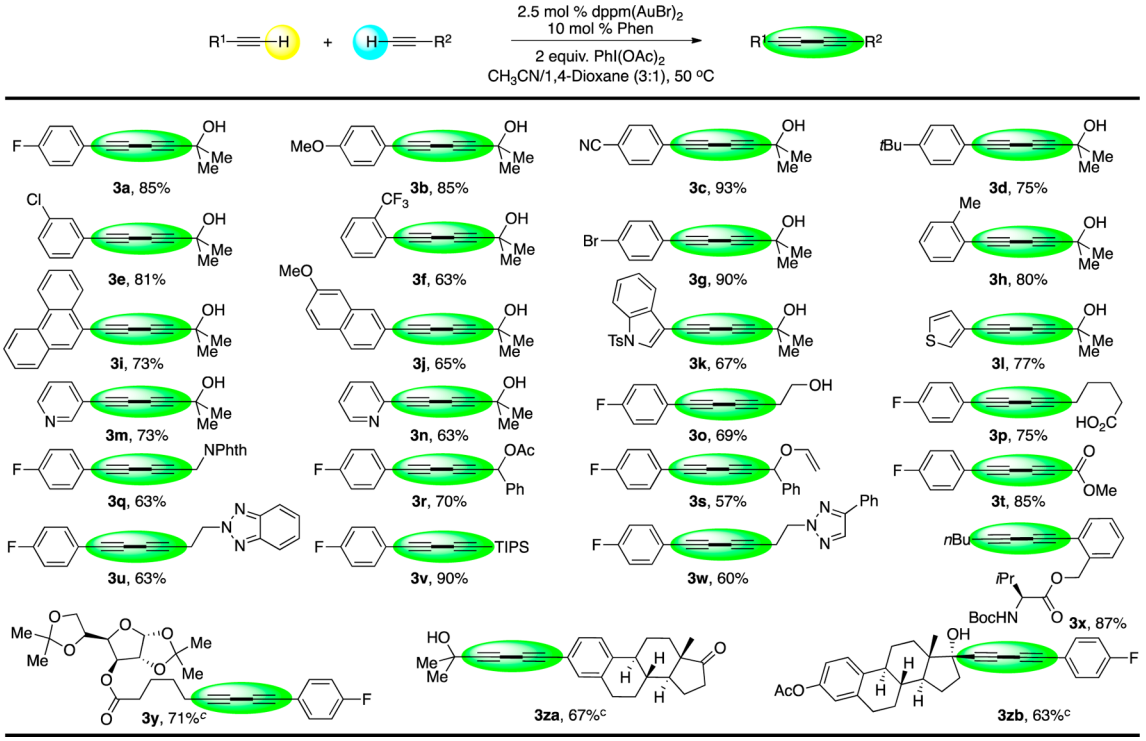
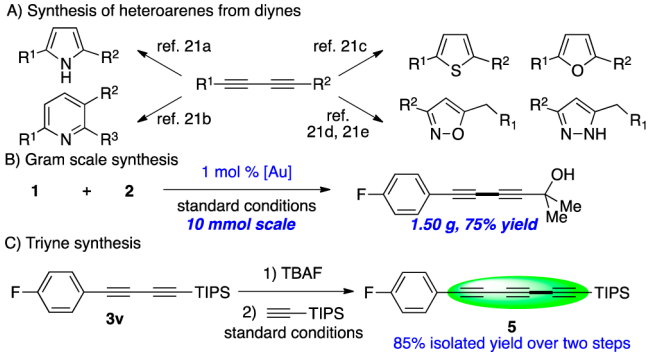
Table 2. Generality[a,b]

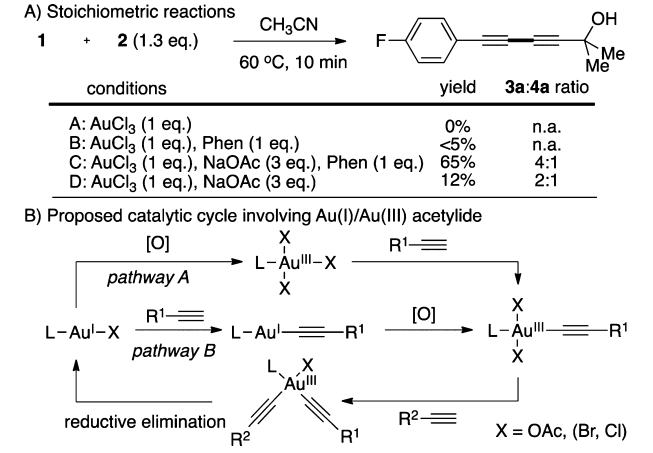


[a]General reaction conditions: R^1-alkyne (0.2 mmol, 1.3 equiv), 2.5 mol% dppm$(AuBr)_2$, 10 mol% Phen, and $PhI(OAc)_2$ (0.4 mmol, 2 equiv) in CH_3CN/1,4-dioxane (0.6 mL/0.2 mL), 50 °C. [b]Isolated yield. [c]**1** (0.26 mmol, 1.3 equiv); the yield was based on the R^1-alkyne.

Scheme 2. Synthetic Utility



Scheme 3. Mechanistic Implication



However, there has been much uncertainty regarding the exact mechanism, namely, whether Au(I)/Au(III) redox catalysis or sole Au(I) catalysis through π-activation is operative.[6a,e] To verify if this reaction indeed involves a Au(III) intermediate, we conducted a set of single-turnover experiments using stoichiometric $AuCl_3$ as the sole oxidant and gold source.[23]

As shown in Scheme 3A, when only stoichiometric $AuCl_3$ was reacted with alkynes **1** and **2** (without any additive and/or ligand), no diynes were detected. Interestingly, addition of Phen ligand gave only trace amounts of products (<5%). Further addition of acetate ion (NaOAc) significantly improved the reaction performance, with a 65% yield of **3a**, despite low heteroselectivity (4:1). These results suggest that (1) the reaction can undergo Au(III) reductive elimination; (2) the Phen ligand is vital to the reaction and presumably has a large influence on the rate of reductive elimination and (3) the acetate ion from $PhI(OAc)_2$ may play an important role as base to sequester free protons, consistent with the fact that $PhI(TFA)_2$ does not promote this transformation.[24] Based on these results, two different pathways are proposed in Scheme 3B.

With Au(I) as the precatalyst (the optimal condition), the key mechanistic concern is the timing of gold monoacetylide formation.[25] As shown in Scheme 3B, oxidation might occur either at the stage of Au(I) salt (prior to the formation of gold acetylide, path A) or at the stage of gold(I) acetylide (path B). The reaction with a stoichiometric amount of Au(III) shown in Scheme 3A gave lower selectivity (4:1) compared with the reaction using Au(I) precatalyst (12:1). This result provides strong evidence against pathway A. In addition, the selective formation of aliphatic gold(I) acetylide and fast reaction rates shown in Figure 1 provide strong support for the late oxidation. Thus, based on current information, we favor a mechanism the same as or similar to pathway B. Obviously, the ligand (Phen)

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plays a very important role in tuning the rate of reductive elimination of three distinct dialkynylgold(III) species.[26] In addition, improved performance from bis-gold catalysts offers some possibilities for alternative mechanisms. Overall, the exact mechanism and origin of selectivity await further study and will be reported in due course.

In summary, we report the first example of Au-catalyzed alkyne oxidative cross-coupling for the synthesis of unsymmetrical conjugated diynes. This method is straightforward, efficient, and highly selective. Compared with the literature methods, this new approach does not require a large excess of one coupling partner or prefunctionalization of alkyne. Broad substrate scope and excellent functional group tolerance are demonstrated. Preliminary investigations reveal that both the Phen ligand and the distinct nature of alkynes are crucial to the high selectivity. The selectivity picture with any two random alkynes can be complicated. In fact, brief screening of two different aromatic alkynes showed no selectivity (forming 1:2:1 coupling mixtures). However, the fact that highly selective coupling is achieved through the effective alkyne alkyne discrimination suggests the strong potential of using Au(I/III) redox catalysis to develop other selective C(sp)−C bond-forming reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) A 1:1.3 mixture of **1a**:**1b** was used for practical reasons. Kinetic studies with a 1:1 mixture were less accurate due to the experimental errors when trying to match the exact amount of all samples.

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(24) We observed a dramatic color change from yellow to orange-red when NaOAc was added to a solution of $AuCl_3$, presumably leading to the formation of species like $AuCl_n(OAc)_{3-n}$ or $NaAuCl_n(OAc)_{4-n}$.

(25) It is also possible that the formation of gold(III) bisacetylide is enabled by transmetalation of gold(I) acetylide and gold(III) monoacetylide; see ref 5.

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