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Gold-Catalyzed Carbazolation Reactions of Alkynes

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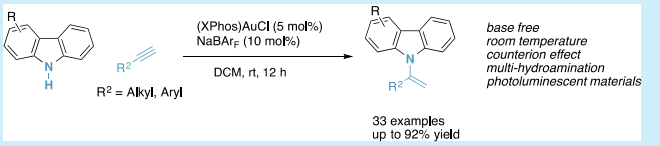
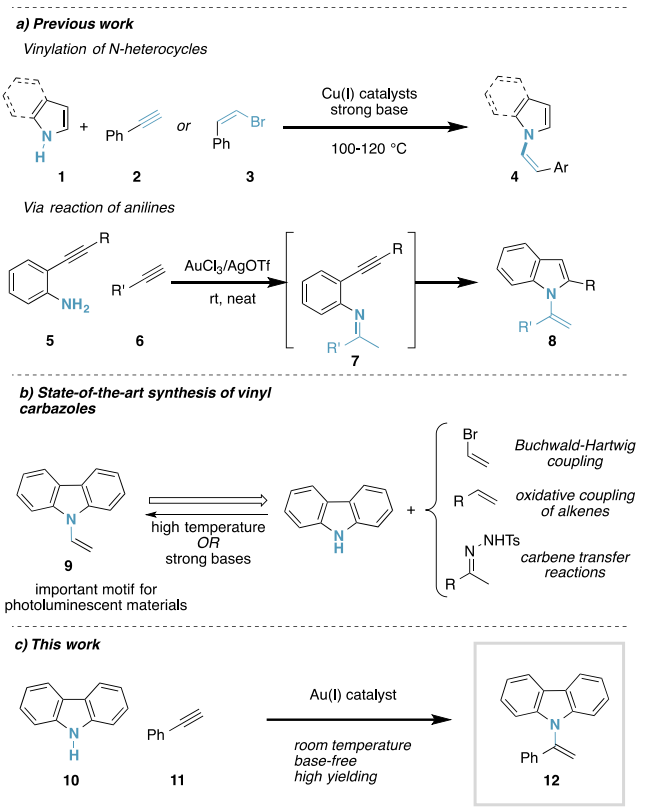
ABSTRACT: Herein, we report on a Au(I)-catalyzed reaction of alkynes with carbazoles that enables a one-step synthesis of vinyl carbazoles that are important molecules for applications as photoluminescent materials. This reaction proceeds under mild conditions at room temperature, without the need of external bases, and can be employed to a variety of aromatic and aliphatic alkynes in monohydroamination and poly-hydroamination reactions. We conclude with photophysical studies of the vinyl carbazole products, which feature distinct fluorescence properties.



The high prevalence of the C−N bond in natural products, agrochemicals, drugs, or materials renders the catalytic formation of new C−N bonds as one of the most important reactions in organic synthesis.[1,2] With the recent advances of metal-catalyzed cross-coupling reactions, methods for the coupling of aryl halides with nitrogen nucleophiles became one of the most important strategies for this purpose. However, mandatory prefunctionalization of at least one reaction partner hampers the overall process efficiency.[2] On the contrary, the hydroamination allows for direct C−N coupling reactions of amines with unsaturated bonds via activation of the π-system of the unsaturated reaction partner.[3,4] Hydroamination reactions have consequently developed as an important timely strategy to conduct atom-efficient C−N coupling reactions. The currently available synthetic repertoire covers the reaction of a diverse set of olefins and alkynes with nitrogen nucleophiles, such as amines, amides, or anilines.[3,4] On the contrary, hydroamination reactions of unprotected aromatic *N*-heterocycles are much less developed.[5−8] Different groups described the catalytic hydroamination of alkynes with indole or pyrrole heterocycles using catalysts based on Cu(I) yet requiring high reaction temperatures and strong base to achieve this reaction and giving the product of *endo-dig* addition (Scheme 1a).[5,6] Echavarren, Verma, and Larock reported on the intramolecular hydroamination of indole.[7] Li and co-workers reported on an intermolecular reaction of anilines with alkynes using a Au(III) catalyst at high temperatures to give the formal hydroamination product of indole and phenylacetylene. However, careful mechanistic experiments have shown that this reaction does not proceed via a hydroamination route (Scheme 1a).[8]

Based on our interest in the functionalization of *N*-heterocycles via carbene intermediates,[9] we hypothesized that the hydroamination of carbazole heterocycles with alkynes should provide an elegant entry into *N*-vinyl-substituted carbazoles (Scheme 1b). *N*-Vinyl carbazoles are important building blocks in the synthesis of carbazole-based electro-

Scheme 1. (a) Hydroamination Reactions of *N*-Heterocycles; (b) Synthesis of *N*-Vinyl Carbazoles; (c) Gold-Catalyzed Hydroamination of Alkynes with Carbazoles



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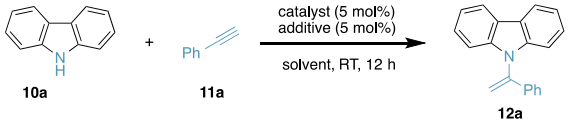
luminescent materials,[10] and currently available synthesis methods involve cross-coupling of vinyl bromides,[11] oxidative coupling of olefins,[12] addition reactions under strongly basic conditions,[13] or carbene transfer of tosylhydrazones (Scheme 1b).[14] The direct synthesis of vinyl carbazoles from readily available starting materials at ambient conditions thus remains a challenge in organic synthesis, and the development of a hydroamination reaction of alkynes with unprotected carbazole would open up an direct approach toward this important structural element (Scheme 1c).

We set out our studies toward the hydroamination reaction of *N*-heterocycles by studying the reaction of carbazole **10a** and phenylacetylene **11a** in DCM solvent. Different Cu, Ag, Rh, or Pd catalysts proved unreactive or inefficient as determined by ^{1}H NMR analysis of crude reaction mixtures (for details, see the Supporting Information).[15] A notable difference was observed when employing Au(I) catalysts.[16] While only trace amounts of the desired hydroamination product **12a** were observed using the bidentate dppf ligand, moderate reaction yields could be obtained even at room temperature when employing phosphite or the sterically demanding tri-*tert*-butyl phosphine ligand (Table 1, entries 1−5). The best yield of **12a** was obtained when using XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) as ligand (Table 1, entry 6). Further investigations concerned the effect of counterion, reaction stoichiometry, temperature, and solvent.[15] A remarkable effect of the counterion was observed (Table 1, entries 6−10), and no reaction was observed using BF_4 or PF_6 anion, indicating a strong influence of the counterion on the reactivity of the Au(I) complex. We thus examined the weakly coordinating BAr_F^- anion, which led to excellent yields of the desired hydroamination product (Table 1, entries 10−12). This observation is also in line with the results of the solvent screen, which revealed that polar, coordinating solvents have a detrimental effect on the product yield. In contrast to previous reports on Cu(I)-catalyzed high-temperature hydroamination reactions of pyrrole, we could observe the selective formation of the *exo*-addition product.[13]

With the optimized conditions in hand, we embarked on the applicability of this hydroamination reaction and studied different terminal alkynes **11** in the reaction with carbazole **10a**. Aromatic alkynes bearing electron-donating or halogen substituents in the *para*- or *meta*-position underwent the hydroamination reaction in high isolated yield even on a 3 mmol scale (see Scheme 2, **12a−h**, 2 mol % (XPhos)AuCl and 5 mol % $NaBAr_F$ on 3 mmol scale). When investigating *ortho*-substituted arylacetylene derivatives (Scheme 2, **12i−j**) or thiophene-substituted acetylene (Scheme 2, **12k**), a slightly reduced yield was observed. Only in the case of electron-withdrawing substituents, such as a CF_3-substituted phenylacetylenes **11l,m**, was a notable reduction in product yield of

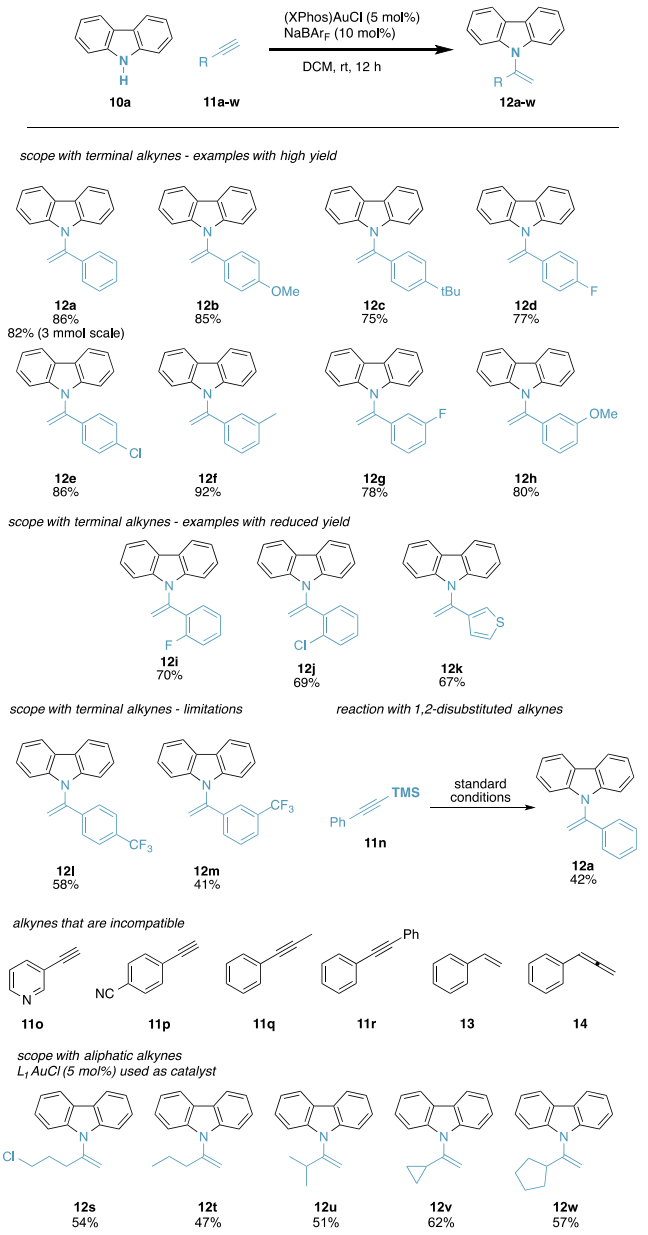
Table 1. Optimization of Reaction Conditions



no.[a]	catalyst	additive	solvent	% yield[b]
1	dppf(AuCl)$_2$	$AgSbF_6$	DCM	traces
2	(L_1)AuCl	$AgSbF_6$	DCM	42
3	(IMes)AuCl	$AgSbF_6$	DCM	no rxn
4	(tBu_3P)AuCl	$AgSbF_6$	DCM	32
5	(tBuXPhos)AuCl	$AgSbF_6$	DCM	32
6	(XPhos)AuCl	$AgSbF_6$	DCM	60
7	(XPhos)AuCl	$AgPF_6$	DCM	traces
8	(XPhos)AuCl	$AgBF_4$	DCM	traces
9	(XPhos)AuCl	$AgNTf_2$	DCM	38
10	(XPhos)AuCl	$NaBAr_F$	DCM	72
11[c]	(XPhos)AuCl	$NaBAr_F$	DCM	82
12[d]	(XPhos)AuCl	$NaBAr_F$	DCM	86

[a]Reaction conditions: 0.2 mmol (1.0 equiv) of **10a**, 0.2 mmol of **11a**, 5 mol % of catalyst, and 5 mol % of additive were dissolved in 2.0 mL of DCM, and the reaction mixture was stirred at rt until the completion of the reactions. [b]Isolated yield. [c]1.5 equiv of **11a** was used. [d]2 equiv of **11a** and 10 mol % of **$NaBAr_F$** (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were used. L_1 = tris(2,4-di-*tert*-butylphenyl)phosphite. IMes = 1,3-dimesitylimidazol-2-ylidene. tBuXPhos = 2-di(*tert*-butyl)phosphino-2′,4′,6′-triisopropylbiphenyl.

Scheme 2. Substrate Scope of Alkynes



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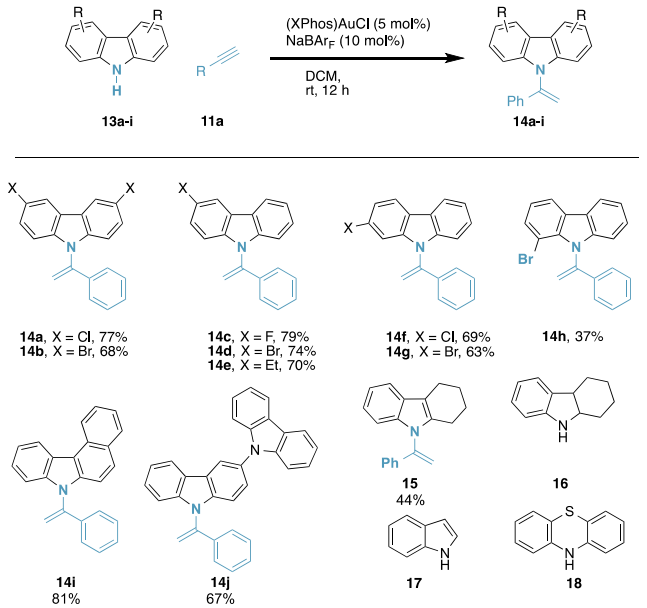
the hydroamination product **12l,m** observed, which can be rationalized by the higher reactivity of the hydroamination product and, consequently, a rapid hydrolysis by trace amounts of water in the reaction mixture. The limitations of the present methodology lie within the use of strong electron-withdrawing groups (e.g., CN) or the use of *N*-heterocycles (Scheme 2, **11o,p**). For both, no product of the hydroamination was observed, which might be explained by poisoning of the cationic Au(I) catalyst by the Lewis basic 3-pyridylacetylene or by hydrolysis of the reaction product in the case of the cyano-substituted phenylacetylene. Similarly, 1,2-disubstituted alkynes (**11q,r**), styrene (**13**), or phenylallene (**14**) did not react in this hydroamination reaction. An interesting observation was made with 1-trimethylsilyl-2-phenylacetylene **11n**: in this case, the hydroamination reaction proceeded in moderate yield with concomitant cleavage of the silyl group to give product **12a**.

Subsequently, we applied this hydroamination protocol under slightly modified conditions (L_1 instead of XPhos; for the optimization of conditions, see the Supporting Information) to aliphatic, terminal alkynes, which reacted in moderate yield to the desired vinyl-substituted carbazole (**12s−w**). Even cyclopropyl acetylene smoothly reacted in this hydroamination reaction without ring opening of the cyclopropane ring.

Further studies focused on the influence of the substitution pattern of the carbazole heterocycle (Scheme 3). While

Scheme 3. Substrate Scope of *N*-Heterocycles



substitution in the 2-, 3-, and 6-position of the carbazole framework had only little influence on the hydroamination reaction, a pronounced decrease in the reaction yield was observed for 1-bromocarbazole. In this case, the hydroamination product was isolated in only 37% yield, which can be attributed to steric hindrance of the bromo substituent. In this context, we also studied bis-carbazole **13j** and the benzannellated carbazole **13i**, both of which gave the desired hydroamination product **14j** and **14i** in high yield, respectively. In this context, we also studied the application of different unprotected *N*-heterocycles. While the hydroamination product **15** of [H_4]-carbazole could be isolated in moderate yield, only trace amounts of the corresponding hydroamination product were observed when employing [H_6]-carbazole (**16**), indole (**17**), or phenothiazine (**18**) as the reaction partner, which might be related to the ease of hydrolysis of the reaction product or poisoning of the electrophilic Au(I) catalyst as observed by ^{31}P NMR of the Au(I) catalyst in the presence of heterocycles **17** and **18**.[15]

Based on the importance of carbazole heterocycles in materials' applications, we next studied this protocol in multi-hydroamination reactions (Figure 1). For this purpose, we

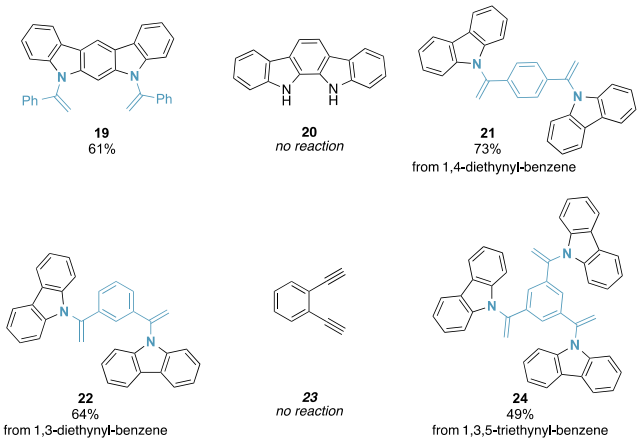


Figure 1. Multi-hydroamination reactions (reaction conditions: 5 mol % of (XPhos)AuCl, 10 mol % of NaBAr$_F$, carbazole (1.0 equiv for **19** and **20**, 2.0 equiv for **21−23**, 3.0 equiv for **24**) and acetylene derivative (for **19** and **20**: **11a**, 4.0 equiv; for **21−24**: 1.0 equiv) were dissolved in 2.0 mL of DCM and stirred for 12 h at room temperature).

studied 5,7-dihydroindolo[2,3-*b*]carbazole in the reaction with phenylacetylene under the previously optimized conditions, which gave the double hydroamination product **19** in moderate yields. The closely related isomer **20** did not react in the hydroamination reaction. The missing reactivity of **20** might be related to the strong coordinating properties of the two adjacent nitrogen atoms, which shuts down the catalytic activity of the Au(I) complex. Next, we employed all isomers of di(ethynyl)benzene to probe a double hydroamination reaction onto one alkyne reaction partner. The double hydroamination products **21** and **22** could indeed be obtained under the same reaction conditions in good isolated yields for 1,4-di(ethynyl)benzene and 1,3-di(ethynyl)benzene, respectively. On the contrary, no reaction was observed when studying 1,2-di(ethynyl)benzene (**23**). Finally, we probed the hydroamination reaction of 1,3,5-tri(ethynyl)benzene, which gave the product of triple hydroamination **24** in 49% yield.

From a mechanism perspective, we hypothesize that the present reaction proceeds via π-coordination of the alkyne to the cationic Au(I) complex **26** as can be observed by a distinct shift in ^{31}P NMR upon addition of alkyne **11a** to in situ formed **26**. A competitive complexation of the Au(I) complex **26** with carbazole **10a** is not likely to occur as no change of chemical shift in ^{31}P NMR was observed. The Au(I)−alkyne complex **27** then undergoes addition of the carbazole heterocycle leading to formation of a putative Au(I)−vinyl complex **29**.[17] Release of the reaction product by protodeauration refurnishes the catalytically active Au(I) complex **26** (Scheme 4). The distinct role of NaBAr$_F$ in this transformation still remains unclear, and detailed studies via DFT calculations will be necessary to fully understand the role of the counterion in this transformation.

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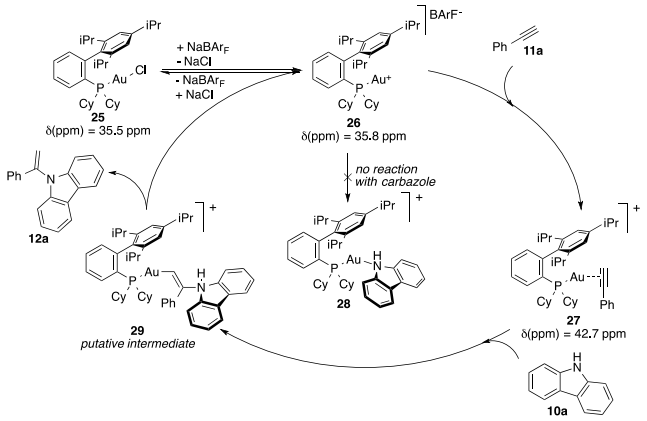
Scheme 4. Putative Mechanism for the Carbazolation Reaction of Alkynes



Given the relevance of carbazole as photoluminescent materials,[10] we performed initial studies on the photochemical properties of selected products of this hydroamination reaction. For this purpose, we measured UV−vis and fluorescence spectra of a selected series of vinyl carbazoles. Spectra were obtained from 25 μM solution in DCM solvent with absorbance peaks at 290 nm, disregarding of the substitution pattern. Fluorescence data of 25 μM solution (Figure 2) showed a significant influence of the substitution

	12a	21	22	24
$\lambda_{Abs,max}$ [nm]	292	288	292	290
$\lambda_{Em,max}$ [nm]	401	435	416	423

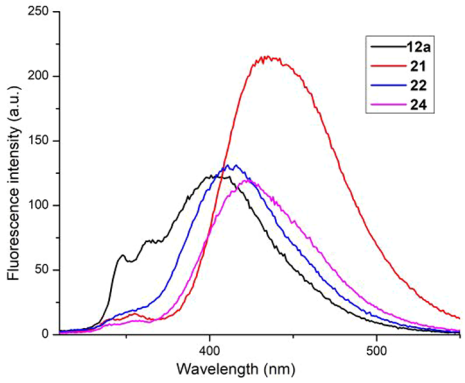


Figure 2. Photochemical properties of selected carbazole derivatives.

pattern, and a marked red shift of the fluorescence peak into the near-visible-light region could be observed for the hydroamination product **12a**. We subsequently studied the photochemical properties of polycarbazoles **21**, **22**, and **24**. Fluorescence data indicate a further red shift, depending on the substitution pattern of the central phenyl ring.

In summary, we herein report on the gold-catalyzed hydroamination reaction of terminal alkynes with carbazole heterocycles to furnish valuable vinyl carbazole derivatives in a highly regioselective fashion and yield (33 examples, up to 92% yield). This hydroamination features mild reaction conditions and can be performed at room temperatures without the need of basic additives for activation of one of the reaction partners. The vinyl carbazole derivatives were subsequently studied for the photoluminescent properties for potential further applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01719.

Experimental procedures, reaction optimization tables, NMR studies of gold complexes, characterization data, analytical data, NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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