JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Polysubstituted 2-Aminopyrrole Synthesis via Gold-Catalyzed Intermolecular Nitrene Transfer from Vinyl Azide to Ynamide: Reaction Scope and Mechanistic Insights

Yufeng Wu,[†] Lei Zhu,[‡] Yinghua Yu,[‡] Xuesong Luo,[§] and Xueliang Huang*[,‡]

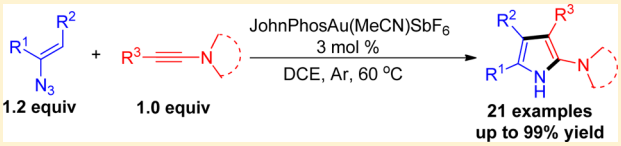
[†]College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian 350108, P. R. China

[‡]Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

[§]School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur Autonomous Region, 832000, P. R. China

Supporting Information

ABSTRACT: A gold-catalyzed intermolecular reaction of vinyl azides and ynamides is described. This process presents an efficient and mild approach to multisubstituted 2-aminopyrroles in good-to-excellent yields. Control experiments were carried out to distinguish the reactivity between vinyl azides and the corresponding 2*H*-azirines. A plausible reaction mechanism was also proposed according to previous reports and our preliminary mechanistic studies.

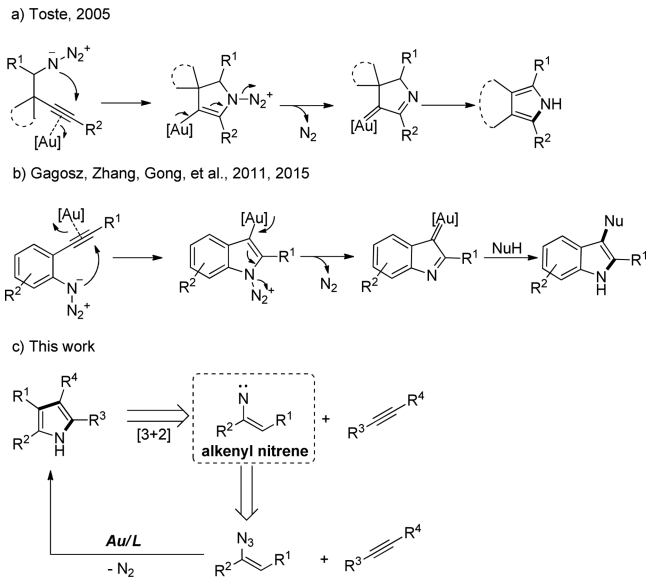


INTRODUCTION

In the past decades, homogeneous gold catalysis has been recognized as a convenient tool for assembling complex functionalized structures from readily available, simple building blocks through electrophilic activation of π systems.[1] α-Oxo gold carbene generated by alkyne oxidation is a reactive intermediate. It can further react with various nucleophiles, leading to useful molecules.[2] Compared with α-oxo gold carbenes, the studies on generation of azavinyl gold carbenes are still far from fully explored.[3] Recently, the research groups of Zhang and Davies reported elegant works on the gold-catalyzed intermolecular reaction of iminopyridium ylides with ynamides, affording α,β-unsaturated amidines and substituted oxazole, respectively.[4] Alkynes and organic azides[5] are fundamental feedstocks, which are inexpensive and easily accessible. In 2005, Toste and co-workers realized the first gold-catalyzed intramolecular nitrene transfer by the reaction of alkyne with tethered azide moiety, giving multiply substituted pyrroles in an atom economic manner (Scheme 1a).[6] This strategy was further explored by the research groups of Zhang,[7] Gagosz,[8] and others[9] (Scheme 1b). Intriguingly, the seemingly simple concept of gold-catalyzed intermolecular reactions of alkynes with organic azides leading to useful *N*-heterocycles by nitrene transfer is still in its infancy.[10−12]

Pyrroles are important heterocycles that are embedded in a broad range of natural products and pharmaceutical agents.[13] Not surprisingly, recently people have witnessed the development of myriad methods for their synthesis.[14] From a synthetic standpoint, the ability to assemble these heterocycles from simple precursors in an atom- and step-economic manner would be highly rewarding. Retrosynthetic cleavage of the C2−N and C3−C4 bonds of the pyrrole core furnishes two fragments, an alkynyl unit and a three-atom unit. Vinyl azide,

Scheme 1. Gold-Catalyzed Reactions of Organic Azides with Alkynes

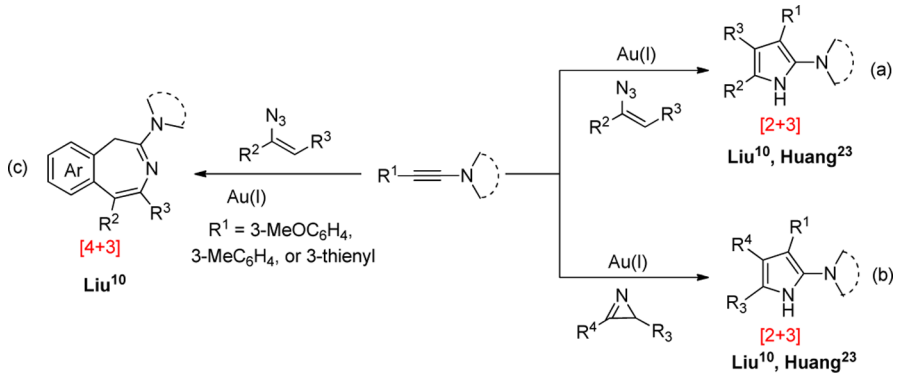


which has been proved to be a versatile reagent employed in a variety of aza-heterocycle synthesis,[15] could be considered as an alkenyl nitrene precursor. Thus, it may fulfill the mission for the simple concept on pyrrole synthesis by formal [2 + 3] cycloaddition of alkyne and vinyl azide. With this consideration in mind, and inspired by the seminal work of Toste and co-workers (Scheme 1a), we sought to develop a straightforward

Received: September 3, 2015
Published: October 27, 2015

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

Scheme 2. Gold-Catalyzed Divergent Formal Cycloadditions of Ynamides with Vinyl Azides or 2*H*-Azirines

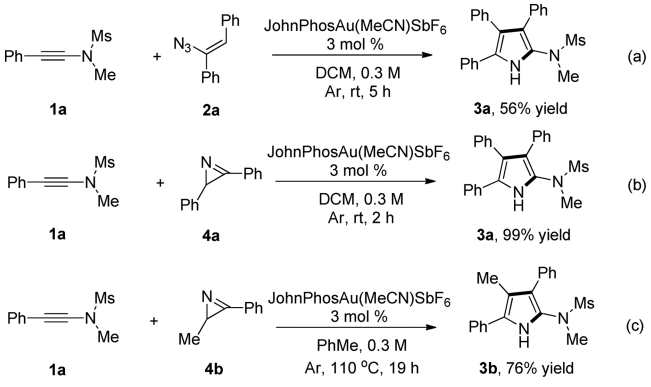


approach for multiply substituted pyrrole synthesis[16,17] by gold-catalyzed intermolecular reaction of alkyne and vinyl azide (Scheme 1c). Recently, Liu and co-workers reported a conceptually similar process for gold-catalyzed formal cycloadditions of ynamides with vinyl azides or 2*H*-azirines,[10] yielding substituted pyrroles (Scheme 2a,b) and 1*H*-benzo[b]azepine derivertives (Scheme 2c), respectively (mostly R^3 = H). The divergent reaction modes and regioselectivity of the corresponding products indicated that the pathway involving gold carbene intermediate was less likely.

RESULTS AND DISCUSSION

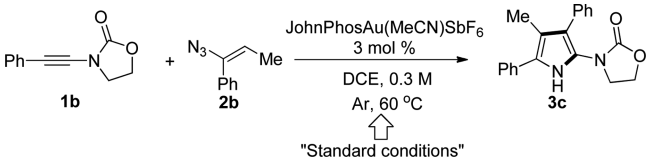
As shown in Scheme 3a, in the presence of the Echavarren's catalyst [JohnPhosAu(MeCN)SbF_6],[18] the reaction of vinyl azide **2a** with ynamide[19,20] **1a** indeed took place under remarkably mild conditions, giving multisubstituted 2-aminopyrrole **3a** in moderate yield. Noticing that vinyl azide **2a** could slowly convert to 2*H*-azirine **4a** at room temperature, a control experiment using 2*H*-azirine **4a** as nitrene precursor was carried out consequently.[21,22] This led to our recent unexpected discovery of gold-catalyzed pyrrole synthesis by formal cycloaddition of 2*H*-azirines and ynamides (Scheme 3b).[23] However, when 2*H*-azirine **4b** was tested, higher temperature and extended reaction time were required for the reaction to reach full conversion (Scheme 3c). Combining these intriguing observations with our initial hypothesis, we decided to explore further the gold-catalyzed intermolecular nitrene transfer reaction of vinyl azides with ynamides.

Scheme 3. Gold-Catalyzed Nitrene Transfers Using Vinyl Azide or 2*H*-Azirine as Nitrene Precursors



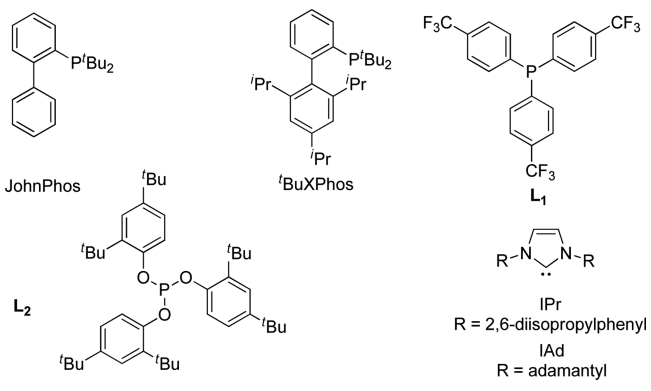
Optimization of the Reaction Conditions. Pleasingly, by employing a cationic gold complex (JohnPhosAu(MeCN)-SbF_6) as catalyst, the reaction of ynamide **1a** with vinyl azide **2b** proceeded smoothly under relatively mild conditions (60 °C, in DCE), affording pyrrole **3b** in high yield (Table 1, entry 2). Replacing ynamide **1a** by **1b**, which contains an oxazolidonyl ring, led to nearly quantitative formation of pyrrole **3c**. It is

Table 1. Effect of Reaction Parameters on the Gold-Catalyzed Reaction of 1b and 2b[a]



entry	variation from the standard conditions	time (h)	yield (%)[b]
1	no change	2.5	98
2	ynamide **1a** was tested instead of **1b**	2.5	80
3	JohnPhosAuNTf$_2$ was used as catalyst	2.5	74
4	$Ph_3PAuNTf_2$ was used as catalyst	10.5	37
5	L_1AuNTf_2 was used as catalyst	9.5	10
6	L_2AuNTf_2 was used as catalyst	15	42
7	IPrAuNTf$_2$ was used as catalyst	16	25
8	^{t}BuXPhosAu(MeCN)SbF_6 was used as catalyst	2.5	98
9	IPrAu(PhCN)SbF_6 was used as catalyst	16	55
10	IAdAu(PhCN)SbF_6 was used as catalyst	2.5	96
11	the reaction was run in PhMe	2.5	93
12	the reaction was run in MeCN	2.5	81
13	the reaction was run in $CHCl_3$	2.5	95
14	the reaction was run in THF	24	17
15	the reaction was run in 1,4-dioxane	2.5	98

[a]All the reactions were carried out in 0.3 mmol scale. The ratio of **1b** to **2b** was 1:1.2. [b]Pyrrole **3b** was obtained.

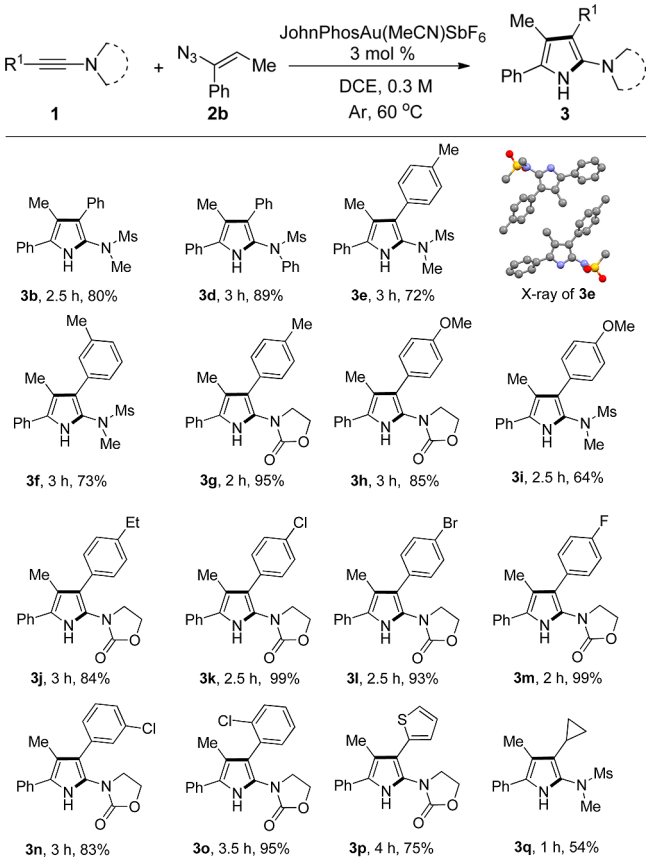


DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

worthwhile to mention that we did not observe any formation of 2*H*-azirine **4b** in the reaction mixture (vide infra). Upon switching the counteranion to bis(trifluoromethanesulfonyl)-imide (NTf_2^-) in the catalyst, a slightly lower conversion of ynamide **1b** was observed (Table 1, entry 3). A brief screening of the gold catalyst revealed that the catalysts bearing bulky electron-rich phosphine ligands gave the best results, and the reactions were complete in relatively short time while high efficiency was maintained (Table 1, entries 3–6 and 8). The catalyst IAdAu(PhCN)SbF_6 could catalyze the reaction well (Table 1, entry 10). Surprisingly, the reaction catalyzed by IPrAu(PhCN)SbF_6 was significantly slow (Table 1, entry 9). To our delight, the current gold-catalyzed nitrene transfer was compatible with a varietyof solvents, except tetrahydrofuran (Table 1, entries 11–15).

Scope of Ynamides. With the optimal reaction conditions established, the scope of the ynamides was investigated. As shown in Table 2, changing the protecting groups of the amide

Table 2. Reaction Scope of Ynamides 1 with Vinyl Azide 2b[a]

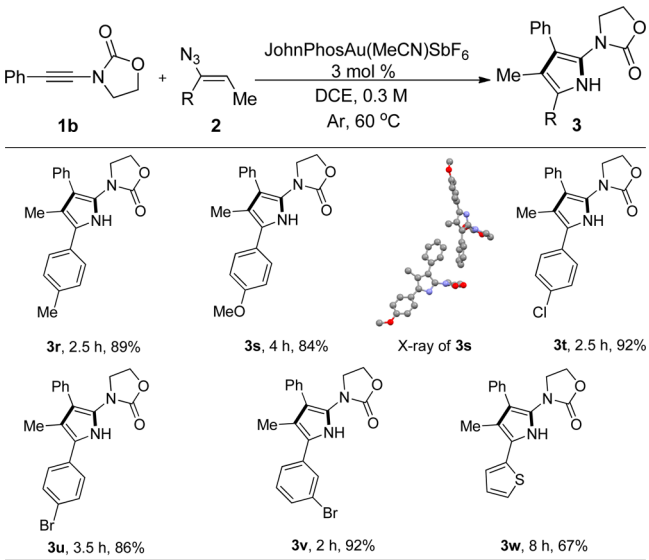


[a]All the reactions were carried out in 0.3 mmol scale. The ratio of **1** to **2b** was 1:1.2.

moiety had no significant influence on the reaction efficiency (cf. **3b** and **3d**). In general, a series of ynamides bearing both electron-donating (methyl, ethyl, and methoxy, cf., **3e**, **3g**–**3j**) and electron-withdrawing (chloro, bromo, and fluoro, cf., **3k**–**3m**) groups on the phenyl ring were compatible with the reaction conditions, providing the desired products in satisfactory yields. The ynamides containing methyl or chloro group at the meta position of the phenyl ring reacted well with **2b**, affording the corresponding 2-aminopyrroles (cf. **3f** and **3n**) in high yields. Ynamide possessing an ortho substituent was tolerated as well, and pyrrole **3o** was isolated in high yield. In addition, the ynamide derived from thiophenyl acetylene was also suitable for this reaction (cf., **3p**). Interestingly, the reaction of cyclopropyl ynamide took place well, and pyrrole **3q** was obtained in 54% yield.

Scope of Vinyl Azides. Subsequently, an array of vinyl azides **2** was surveyed under the standard conditions to react with ynamide **1b**. As shown in Table 3, vinyl azides bearing

Table 3. Reaction Scope of Vinyl Azides 2 with Ynamides 1b[a]



[a]All the reactions were carried out in 0.3 mmol scale. The ratio of **1b** to **2** was 1:1.2.

electron-donating groups (methyl, methoxy) at the para position of the phenyl ring reacted well with ynamide **1b**, giving the corresponding pyrroles in high yields (Table 3, **3r** and **3s**). Similarly, substrates **2t**, **2u**, and **2v**, bearing electron-withdrawing groups, exhibited good reactivity, affording the desired pyrroles **3t**–**3v** in good-to-excellent yields. Again, vinyl azide **2w** containing a thiophenyl group could react with ynamide **1b**, furnishing pyrrole **3w** in high yield, albeit slightly longer reaction time was required. Furthermore, the structure and regioselectivity were confirmed by single-crystal X-ray analysis of pyrroles **3e** and **3s**.[24]

Elucidation of the Mechanism. It is well-known that vinyl azide could transform to 2*H*-azirine upon heating.[21b] To verify whether 2*H*-azirine **4b** is a real intermediate for the nitrene transfer, we monitored the reaction of ynamide **1b** with a slight excess (1.2 equiv) of vinyl azide **2b** by ^{1}H NMR spectroscopy. As depicted in Figure 1, the reaction is selective and highly efficient. Again, we did not observe any formation of 2*H*-azirine **4b**, and the excess amount of **2b** remained intact. Additionally, we performed a controlling experiment by using 2*H*-azirine **4b** as reaction partner instead of **2b**. Surprisingly, the reaction of **4b** with ynamide **1b** was significantly slow. Even after extended reaction time, low conversion of both starting materials was observed (Scheme 4).

It should be noted that, slightly prior to our completion of this work, Liu and co-workers reported a related gold-catalyzed formal cycloaddition of ynamides with vinyl azides or 2*H*-azirines.[10] Nevertheless, under their standard conditions, 2*H*-

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407–11416

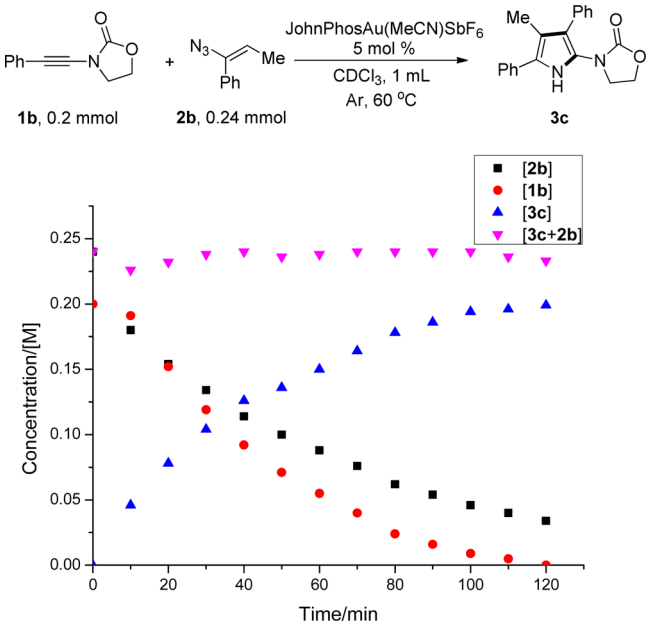
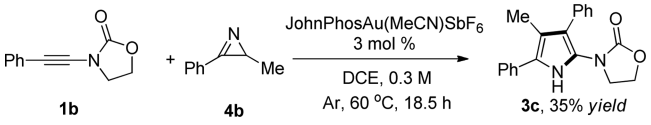


Figure 1. ^{1}H NMR monitoring of the reaction of ynamide **1b** with vinyl azide **2b**.

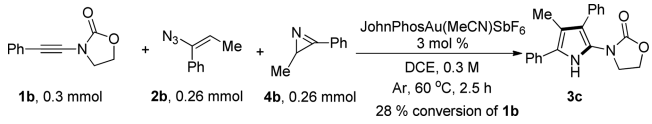
Scheme 4. Gold-Catalyzed Reaction of Ynamide 1b with 2*H*-Azirine 4b



azirine was proposed as the reactive intermediate for the nitrene transfer based on their observation. However, when the vinyl azide derived from styrene was tested under our standard conditions, very low conversion of the ynamide was observed.[25] Interestingly, with ynamide possessing an electron donating group (MeO−) at the meta position of the phenyl ring, a switched reaction mode was observed by Liu and co-workers (from [2 + 3] to [4 + 3]).[10] The regioselectivity of the product further indicated the involvement of 2*H*-azirine as a reactive intermediate. Thus, the ynamide **1r** was prepared and subjected to our optimal conditions; as depicted, the reaction of **1r** with vinyl azide **2b** gave pyrrole **3rb** ([2 + 3]) and 1*H*-benzo[b]azepine **5rb** ([4 + 3]) in 23% and 36% yields, respectively (Scheme 5). On the basis of all the observation from Liu[10] and ourselves (Figure 1), we speculate that a process involving the slow generation of 2*H*-azirine, which was further consumed spontaneously, was possible.[26]

For comparison of the reactivity of vinyl azide **2** and 2*H*-azirine **4**, several factors need to be considered. For example, according to Mayr's nucleophilicity scale, azide anion (N/S_N 20.50/0.59) exhibits better nucleophilicity than DBU (1,8-diazabicycloundec-7-ene, which also possesses a C═N double bond inside the ring system, N/S_N 15.29/0.70).[27] However, vinyl azide is a neutral molecule; the nucleophilicity of the azide moiety may be further undermined by the adjacent double bonds. Moreover, the three-member ring of 2*H*-azirine may increase the reactivity of C═N, thus making it more nucleophilic than the corresponding vinyl azide **2**. On the other hand, 2*H*-azirine **4b** bears an aliphatic group (the inductive effect of the methyl group is electron-donating) on the three-member ring; thus, the nitrogen atom is more electron-releasing than the one in **4a** (the resonance effect of the phenyl group may reduce the nucleophilicity of the nitrogen atom). Furthermore, considering that **4a** is more sterically hindered than **4b**, one can easily assume that 2*H*-azirine **4b** could coordinate better to the bulky cationic gold catalyst [JohnPhosAu(MeCN)SbF_6] than **4a**. In other words, for the reaction of ynamide **1** with 2*H*-azirine **4b** under standard conditions, the large excess of **4b** compared to gold catalyst, may lead to partial poisoning of the gold catalyst.[26] To test this speculation, a control experiment was carried out. As expected, under otherwise identical conditions, addition of 1.2 equiv of 2*H*-azirine **4b** to the reaction of **1b** and **2b** led to a low conversion of ynamide **1b** (Scheme 6). These considerations well-explained the distinct behaviors of vinyl azides and the corresponding 2*H*-azirines as shown in Schemes 3 and 4.

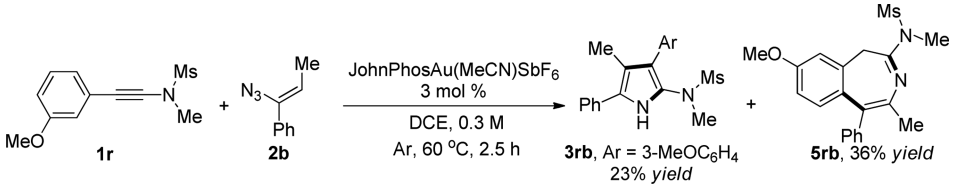
Scheme 6. Reaction of Ynamide 1b of with Vinyl Azide 2b in the Presence of 4b



To identify the mechanism of this formal cycloaddition of ynamides with vinyl azides, ynamide **1z** bearing an *n*-Bu group was prepared and subjected to the reaction with vinyl azide **2b**. Pyrrole **3z** was isolated in 28% yield, but we could not verify the formation of aza-triene **6a** from the complicated reaction mixture (Scheme 7a). Interestingly, upon altering the amide moiety (Scheme 7b, from carbamate-substituted ynamide to sulfonyl-substituted ynamide), from the reaction mixture of ynamide **1aa** with **2b**, we could observe the formation of aza-triene **6b** by ^{1}H NMR spectroscopy analysis, which may be generated from the potential gold carbene intermediate.[28,29]

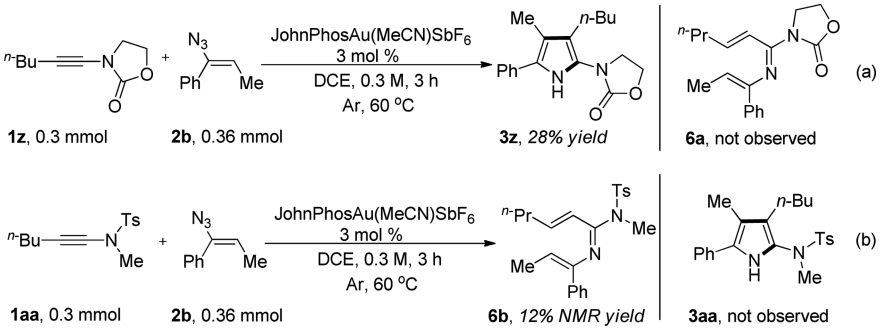
To further probe the involvements of gold carbene intermediate, we envisioned that the introduction of a benzyl group on the terminal position of the triple bond may facilitate 1,2-H insertion of the suspecting gold carbene intermediate. Much to our delight, under the standard conditions, from the reaction of ynamide **1ab** with vinyl azide **2b**, we could observe the formation of pyrrole **3ab** and dihydropyridine **7**, which were isolated in 7% and 8% yields, respectively (Scheme 8a).

Scheme 5. Gold-Catalyzed Reaction of Ynamide 1r with Vinyl Azide 2b

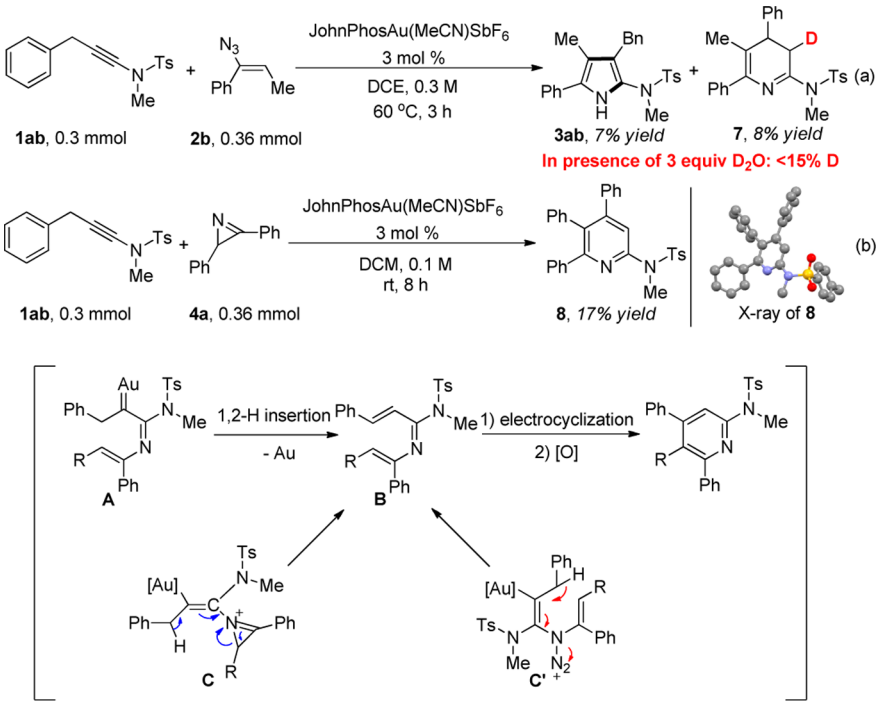


DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

Scheme 7. Reaction of Ynamide 1z or 1aa with Vinyl Azide 2b



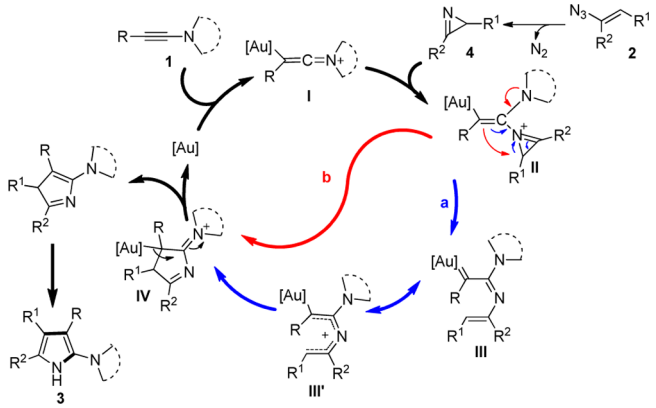
Scheme 8. Reaction of Ynamide 1ab with Vinyl Azide 2b or 2*H*-Azirine 4a



Similarly, under our previous conditions,[23] polysubstituted 2-aminopyrridine **8** was isolated in 17% yield by the reaction of ynamide **1ab** with 2*H*-azirine **4a**. The structure of **8** was confirmed by X-ray crystallographic analysis (Scheme 8b). From a mechanistic viewpoint, the generation of **7** or **8** may be attributed to 1,2-H insertion of the gold carbene intermediate **A** giving aza-triene **B**. A sequence of electrocyclization, isomerization, or oxidation[30] will lead to the formation of dihydropyridine or 2-aminopyrridine. To further clarify the existence of carbene intermediate **A**, we performed a deuterium-labeling experiment.[26,31] As depicted, in the presence of 3 equiv of D_2O, less than 15% deuterium incorporation was observed in dihydropyridine **7**. The small deuterium incorporation in **7** cannot fully exclude the existence of carbene intermediate and indicates that a nonmetal carbene pathway for the generation of **B** from **C**/**C**′ is also possible.

Combining all the results obtained by Liu[10] and us, a plausible reaction mechanistic rationale for current nitrene transfer is depicted in Scheme 9. The reaction of keteniminium intermediate **I** with 2*H*-azirine **4**, which may be generated in situ in a very small amount from vinyl azide **2**, gives zwitterions intermediate **II**. Subsequent ring opening may produce gold

Scheme 9. Plausible Catalytic Cycles for the Pyrrole Synthesis



carbene **III**.[32] **III** may equilibrate to a more stabilized intermediate **III**′.[4b] An intramolecular cyclization of **III**′ leads to the formation of species **IV**, which contains an aza-heterocycle backbone (pathway a, blue). Alternatively, a direct ring closure of **II** would also give **IV** (pathway b, red).[33]

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

Sequential elimination of the gold catalyst and isomerization would eventually afford substituted 2-aminopyrrole **3**.

CONCLUSION

In summary, a gold-catalyzed polysubstituted pyrrole synthesis by formal cycloaddition of ynamides with vinyl azides is described. Although the precise mechanism is still not clear at this stage, the current method for polysubstituted pyrrole synthesis complements the studies of Liu[10] and us.[23] Mechanistic experiments suggest that 2*H*-azirine may be slowly generated in situ and consumed spontaneously. Moreover, 2*H*-azirine bearing an alkyl group on the three-membered ring (e.g., **4b**), especially when it is in large excess compared to the catalyst, could partially poison the gold catalyst. Further studies on gold-catalyzed aza-heterocycle synthesis via intermolecular reactions of organic azides with alkynes are ongoing, and the results will be reported in due course.

EXPERIMENTAL SECTION

General Information. Unless otherwise indicated, all glassware was dried by a heat gun before use and all reactions were performed under an atmosphere of argon. All ynamides were synthesized according to known procedures reported in the literature.[23,34,35] All solvents were distilled from appropriate drying agents prior to use. Reaction progress was monitored by thin layer chromatography (TLC). Visualization was achieved by ultraviolet light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (200−300 mesh). Pressed KBr disks for infrared spectra were recorded using a FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. Melting points were recorded using a melting point thermometer. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_3CN, or DMSO-d_6. Chemical shifts were given in parts per million (ppm, δ), referenced to the peak of tetramethylsilane, defined at δ = 0.00 (^1H NMR); the solvent peak of $CDCl_3$, defined at δ = 77.0 (^{13}C NMR); the peak of CD_3CN, defined at δ = 1.94 (^1H NMR) or δ = 1.32 (^{13}C NMR); or the peak of DMSO-d_6, defined at δ = 2.50 (^1H NMR) or δ = 40.0 (^{13}C NMR). Coupling constants are quoted in Hz (J). ^1H NMR spectroscopy splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), septet (se), and octet (o). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). High-resolution mass spectra were obtained using a high-resolution ESI-TOF mass spectrometer.

*3-(Thiophen-2-ylethynyl)oxazolidin-2-one (**1o**).*[34d] Compound **1o** was obtained as a yellow solid (0.164 g) in 36% yield: R_f = 0.4 (petroleum ether:ethyl acetate = 3:1); mp 101−103 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30−7.27 (m, 1H), 7.243−7.236 (m, 1H), 6.99−6.97 (m, 1H), 4.49 (t, J = 8.0 Hz, 2H), 4.00 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 133.2, 128.0, 127.0, 121.9, 82.3, 64.6, 63.1, 46.9; IR (KBr) ν 3102, 2260, 1756, 1475, 1445, 1397, 1208, 1145; HRMS-(ESI) (m/z) $[M + H]^+$ calcd for $C_9H_8NO_2S$ 194.0276, found 194.0269.

*1-Methyl-4-((5-phenylpent-3-yn-2-yl)sulfonyl)benzene (**1ab**).*[34b,35] Compound **1ab** was obtained as a colorless oil or white solid (2.25 g) in 73% yield: R_f = 0.4 (petroleum ether:ethyl acetate = 10:1); ^1H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.34−7.30 (m, 2H), 7.26−7.22 (m, 3H), 3.69 (s, 2H), 3.02 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.9, 136.9, 132.3, 130.0, 128.4, 127.7, 127.5, 126.5, 76.8, 66.5, 23.6, 21.1; IR (KBr) ν 3068, 3030, 2928, 2255, 2055, 1689, 1599, 1492, 1362, 1173; HRMS-(ESI) (m/z) $[M + H]^+$ calcd for $C_{17}H_{18}NO_2S$ 300.1058, found 300.1057.

Procedure for Preparation of Vinyl Azide.[36a] *Step 1.* A slurry of sodium azide (3.58 g, 22 mmol) in acetonitrile (50 mL) was placed in a 100 mL three-neck round-bottom flask, which was fitted with two 50 mL pressure-equalizing dropping funnels. This flask was cooled by an ice bath, and iodine monochloride (2.75 g, 42.4 mmol) was added dropwise via one of the dropping funnels over a period of 15 min. The solution was stirred for an additional 10 min, and (1*E*)-1-propenylbenzene (2.0 g, 16.9 mmol) was added via the other dropping funnel over a period of 15 min. The resulting reaction mixture was stirred for 12 h at ambient temperature and then poured into water (50 mL) and extracted diethyl ether (50 mL × 3). The combined organic extracts were washed with 5% aqueous solution of sodium thiosulfate (100 mL) and water (100 mL) successively. The combined organic layer was dried over magnesium sulfate anhydrous. Then the solvent was removed under vacuum at ambient temperature to yield the crude product as a pale-yellow oil (4.5 g) which is in sufficient purity to be used for next step.

Note that for the preparation of **2s** and **2w**, 1 equiv of iodine monochloride was employed and the starting temperature was −10 °C.

Step 2. A solution of alkyl azide (obtained from step 1, 15.7 mmol) in dry diethyl ether (100 mL) was cooled by an ice bath, and to this solution was added ^{t}BuOK (2.3 g, 20.4 mmol). After stirring for 4 h at 0 °C, the reaction mixture was washed with water (100 mL × 2). The organic layer was dried over anhydrous $MgSO_4$. Then the solvent was removed under vacuum. The resulting residue was purified by column chromatography on silica gel (petroleum ether), giving **2** as a pale-yellow oil.

*(E)-(1-Azidoprop-1-en-1-yl)benzene (**2b**).*[36a] Compound **2b** was obtained as a yellow oil (1.86 g) in 78% yield: R_f = 0.85 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44−7.31 (m, 5H), 5.48 (q, J = 7.2 Hz, 1H), 1.72 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 133.2, 128.8, 128.6, 128.4, 112.1, 13.8.

*(E)-1-(1-Azidoprop-1-en-1-yl)-4-methylbenzene (**2r**).* Compound **2r** was obtained as a yellow oil (0.6 g) in 44% yield: R_f = 0.7 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.21−7.19 (m, 4H), 5.44 (q, J = 7.2 Hz, 1H), 2.37 (s, 3H), 1.70 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.3, 130.2, 129.1, 128.6, 111.7, 21.3, 13.8.

*(E)-1-(1-Azidoprop-1-en-1-yl)-4-methoxybenzene (**2s**).* Compound **2s** was obtained as a yellow oil (0.98 g) in 89% yield: R_f = 0.7 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.28 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 5.45 (q, J = 7.2 Hz, 1H), 3.86 (s, 3H), 1.73 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 137.0, 130.1, 125.6, 113.8, 111.5, 55.3, 13.8.

*(E)-1-(1-Azidoprop-1-en-1-yl)-4-chlorobenzene (**2t**).* Compound **2t** was obtained as a yellow oil (0.55 g) in 47% yield: R_f = 0.8 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.52 (q, J = 7.2 Hz, 1H), 1.74 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 134.5, 131.7, 130.2, 128.7, 112.6, 13.8.

*(E)-1-(1-Azidoprop-1-en-1-yl)-4-bromobenzene (**2u**).* Compound **2u** was obtained as a yellow oil (0.6 g) in 72% yield: R_f = 0.8 (petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.50 (q, J = 7.2 Hz, 1H), 1.72 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 132.2, 131.6, 130.4, 122.7, 112.6, 13.8.

*(E)-1-(1-Azidoprop-1-en-1-yl)-3-bromobenzene (**2v**).* Compound **2v** was obtained as a yellow oil (0.5 g) in 82% yield: R_f = 0.83 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53−7.51 (m, 2H), 7.33−7.27 (m, 2H), 5.54 (q, J = 7.2 Hz, 1H), 1.76 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 135.4, 131.8, 131.6, 129.9, 127.4, 122.4, 112.9, 13.8.

*(E)-2-(1-Azidoprop-1-en-1-yl)thiophene (**2w**).* Compound **2w** was obtained as a yellow oil (0.6 g) in 43% yield: R_f = 0.78 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J_1 = 5.2 Hz, J_2 = 0.8 Hz, 1H), 7.20−7.19 (m, 1H), 7.10−7.08 (m, 1H), 5.57 (q, J = 7.2 Hz, 1H), 1.96 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 131.7, 127.3, 127.0, 126.3, 112.3, 14.1.

Transformation of Vinyl Azide to 1,2,3-Triazole.[37] CuTC (28.6 mg, 0.15 mmol) was added to a solution of **2** (0.5 mmol) and phenylacetylene (0.11 mL, 1.0 mmol) in toluene (2 mL). The reaction mixture was then stirred for 2.0 h at 25 °C until the disappearance of **2**, as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3 × 15 mL). The organic layer was

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

washed with brine (3 × 40 mL), dried over $MgSO_4$, and concentrated. Purification of the crude product with flash column chromatography gave triazole.

*(E)-4-Phenyl-1-(1-(p-tolyl)prop-1-en-1-yl)-1H-1,2,3-triazole (**2rc**).* Compound **2rc** was obtained as a white solid (106.2 mg) in 95% yield: R_f = 0.4 (petroleum ether:ethyl acetate = 12:1); mp 81−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H, Ar), 7.44 (s, 1H, Ar), 7.28−7.24 (m, 2H, Ar), 7.19−7.07 (m, 5H, Ar), 6.41 (q, J = 7.2 Hz, 1H, CH), 2.29 (s, 3H, CH_3), 1.78 (d, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 139.1, 136.0, 130.34, 130.26, 129.4, 129.2, 128.6, 127.9, 125.5, 120.3, 119.2, 21.2, 13.8; IR (KBr) ν 3127, 2918, 1417, 1038, 821, 769, 697, 502; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{18}H_{18}N_3$ 276.1501, found 276.1490.

*(E)-1-(1-(4-Methoxyphenyl)prop-1-en-1-yl)-4-phenyl-1H-1,2,3-triazole (**2sc**).* Compound **2sc** was obtained as a white solid (120 mg) in 95% yield: R_f = 0.57 (petroleum ether:ethyl acetate = 5:1); mp 84−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.67 (m, 2H, Ar), 7.47 (s, 1H, Ar), 7.28−7.24 (m, 2H, Ar), 7.20−7.16 (m, 1H, Ar), 7.11 (d, J = 8.8 Hz, 2H, Ar), 6.84 (d, J = 8.8 Hz, 2H, Ar), 6.37 (q, J = 7.2 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 1.77 (d, J = 7.2 Hz, 3H, CH_3C); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 147.0, 135.7, 130.6, 130.3, 128.6, 128.0, 125.5, 125.4, 119.9, 119.3, 114.1, 55.2, 13.8; IR (KBr) ν 3125, 2921, 1609, 1512, 1248, 1178, 1028, 834, 762, 692; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{18}H_{18}N_3O$ 292.1450, found 292.1444.

*(E)-1-(1-(4-Chlorophenyl)prop-1-en-1-yl)-4-phenyl-1H-1,2,3-triazole (**2tc**).* Compound **2tc** was obtained as a white solid (193.4 mg) in 82% yield: R_f = 0.45 (petroleum ether:ethyl acetate = 8:1); mp 74−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.2 Hz, 2H, Ar), 7.62 (s, 1H, Ar), 7.43−7.37 (m, 4H, Ar), 7.33−7.29 (m, 1H, Ar), 7.24 (d, J = 8.4 Hz, 2H, Ar), 6.53 (q, J = 7.2 Hz, 1H, CH), 1.89 (d, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 135.1, 135.0, 131.6, 130.6, 130.1, 129.0, 128.7, 128.1, 125.5, 121.5, 119.1, 13.8; IR (KBr) ν 3122, 1494, 1415, 1091, 1036, 1013, 879, 826, 766, 694, 525, 500; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{17}H_{15}ClN_3$ 296.0955, found 296.0947.

*(E)-1-(1-(4-Bromophenyl)prop-1-en-1-yl)-4-phenyl-1H-1,2,3-triazole (**2uc**).* Compound **2uc** was obtained as a white solid (114.3 mg) in 84% yield: R_f = 0.3 (petroleum ether:ethyl acetate = 10:1); mp 87−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.49 (s, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.29−7.25 (m, 2H), 7.21−7.16 (m, 1H), 7.06 (d, J = 8.8 Hz, 2H), 6.41 (q, J = 7.2 Hz, 1H), 1.77(d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 135.0, 132.0, 131.9, 130.9, 130.1, 128.7, 128.1, 125.5, 123.3, 121.5, 119.1, 13.8; IR (KBr) ν 3122, 1489, 1412, 1073, 841, 821, 764, 692, 520, 492; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{17}H_{15}BrN_3$ 340.0449, found 340.0443.

*(E)-1-(1-(3-Bromophenyl)prop-1-en-1-yl)-4-phenyl-1H-1,2,3-triazole (**2vc**).* Compound **2vc** was obtained as a white solid (122.5 mg) in 90% yield: R_f = 0.3 (petroleum ether:ethyl acetate = 10:1); mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.81 (m, 2H), 7.62 (s, 1H), 7.58−7.56 (m, 1H), 7.484−7.480 (m, 1H), 7.42−7.38 (m, 2H), 7.35−7.31 (m, 2H), 7.25−7.23 (m, 1H), 6.55 (q, J = 7.2 Hz, 1H), 1.91 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 135.2, 134.7, 132.2, 132.1, 130.3, 130.1, 128.7, 128.1, 127.9, 125.6, 122.7, 122.1, 119.1, 13.8; IR (KBr) ν 3135, 1457, 1417, 1076, 1033, 816, 786, 764, 749, 692; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{17}H_{15}BrN_3$ 340.0449, found 340.0442.

*(E)-4-Phenyl-1-(1-(thiophen-2-yl)prop-1-en-1-yl)-1H-1,2,3-triazole (**2wc**).* Compound **2wc** was obtained as a white solid (82.3 mg) in 99% yield: R_f = 0.3 (petroleum ether:ethyl acetate = 10:1); mp 115−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.73 (m, 2H, Ar), 7.66 (s, 1H, Ar), 7.37−7.36 (m, 1H, Ar), 7.33−7.29 (m, 2H, Ar), 7.24−7.21 (m, 1H, Ar), 7.01−6.96 (m, 2H, Ar), 6.40 (q, J = 7.6 Hz, 1H, CH), 1.94 (d, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 134.7, 130.4, 130.3, 129.1, 128.7, 128.1, 127.7, 127.1, 125.6, 123.5, 119.7, 14.2; IR (KBr) ν 3147, 3093, 1412, 1230, 1073, 1036, 771, 729, 697; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{15}H_{14}N_3S$ 268.0908, found 268.0903.

Procedure for the Construction of Pyrrole 3c. A dry Schlenk tube was charged with ynamide **1b** (56.2 mg, 0.3 mmol), vinyl azide **2b** (57.3 mg, 0.36 mmol, 1.2 equiv), and gold catalyst [JohnPhosAu(MeCN)SbF_6] (7.0 mg, 3 mol %). The tube was evacuated and backfilled with argon, and this procedure was repeated three times. To this mixture was added dry 1,2-dichloroethane (1 mL). The reaction was complete after stirring at 60 °C for 2.5 h, and the resulting mixture was purified by column chromatography on silica gel, providing **3c** as a white solid (98% yield).

*3-(4-Methyl-3,5-diphenyl-1H-pyrrol-2-yl)oxazolidin-2-one (**3c**).* [**1b**] = 0.3 M. Compound **3c** was obtained as a white solid (93.5 mg) in 98% yield: R_f = 0.28 (petroleum ether:ethyl acetate = 3:1); mp 162−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.93 (s, 1H), 7.23−7.18 (m, 4H), 7.34−7.22 (m, 5H), 7.11 (s, 1H), 4.34 (t, J = 8.0 Hz, 2H), 3.60 (t, J = 8.0 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 134.4, 132.8, 129.8, 128.3, 126.5, 126.21, 126.18, 125.8, 121.1, 119.4, 119.2, 114.1, 62.9, 47.1, 11.2; IR (KBr) ν 3287, 1729, 1592, 1502, 1223, 1145, 1026, 776, 759, 699; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{19}N_2O_2$ 319.1447, found 319.1439.

*N-(4-Methyl-3,5-diphenyl-1H-pyrrol-2-yl)-N-phenylmethanesulfonamide (**3d**).* [**1c**] = 0.3 M. Compound **3d** was obtained as a pale yellow solid (107.6 mg) in 89% yield: R_f = 0.37 (petroleum ether:ethyl acetate = 5:1); mp 168−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.57 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.43−7.30 (m, 5H), 7.25−7.18 (m, 4H), 7.15−7.13 (m, 2H), 2.76 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 134.1, 132.7, 129.9, 129.2, 128.7, 128.23, 128.18, 126.93, 126.90, 126.7, 126.0, 124.2, 123.7, 122.5, 115.0, 40.3, 11.2; IR (KBr) ν 3347, 3297, 1587, 1492, 1347, 1148, 963, 779, 697, 545; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{24}H_{23}N_2O_2S$ 403.1480, found 403.1472.

*N-Methyl-N-(4-methyl-5-phenyl-3-(p-tolyl)-1H-pyrrol-2-yl)-methanesulfonamide (**3e**).* [**1d**] = 0.3 M. Compound **3e** was obtained as a white solid (76.0 mg) in 72% yield: R_f = 0.40 (petroleum ether:ethyl acetate = 4:1); mp 194−195 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.35 (s, 1H), 7.46−7.39 (m, 4H), 7.29−7.23 (m, 5H), 3.26 (s, 3H), 2.60 (s, 3H), 2.40 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 132.8, 131.4, 129.7, 129.2, 128.7, 127.0, 126.8, 126.6, 124.1, 122.1, 114.8, 39.5, 38.0, 21.2, 11.2; IR (KBr) ν 3372, 1507, 1332, 1140, 976, 874, 821, 764, 697, 517; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{23}N_2O_2S$ 355.1480, found 355.1472.

*N-Methyl-N-(4-methyl-5-phenyl-3-(m-tolyl)-1H-pyrrol-2-yl)-methanesulfonamide (**3f**).* [**1e**] = 0.3 M. Compound **3f** was obtained as a white solid (77.3 mg) in 73% yield: R_f = 0.41 (petroleum ether:ethyl acetate = 4:1); mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.37 (s, 1H), 7.46−7.40 (m, 4H), 7.33−7.28 (m, 2H), 7.16−7.13 (m, 3H), 3.26 (s, 3H), 2.59 (s, 3H), 2.40 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 134.4, 132.7, 130.5, 128.7, 128.4, 127.7, 127.0, 126.9, 126.8, 126.6, 124.1, 122.3, 114.7, 39.6, 38.0, 21.5, 11.2; IR (KBr) ν 3362, 1332, 1140, 971, 884, 796, 766, 697, 512; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{23}N_2O_2S$ 355.1480, found 355.1472.

*3-(4-Methyl-5-phenyl-3-(p-tolyl)-1H-pyrrol-2-yl)oxazolidin-2-one (**3g**).* [**1f**] = 0.3 M. Compound **3g** was obtained as a white solid (94.3 mg) in 95% yield: R_f = 0.46 (petroleum ether:ethyl acetate = 3:1); mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.79 (s, 1H), 7.27−7.15 (m, 9H), 4.34 (t, J = 7.6 Hz, 2H), 3.59 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 136.3, 133.0, 131.4, 130.0, 129.0, 128.4, 126.5, 125.9, 125.3, 121.8, 117.6, 114.3, 62.9, 46.6, 21.2, 11.1; IR (KBr) ν 3267, 1746, 1719, 1592, 1512, 1235, 1145, 826, 762; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{21}H_{21}N_2O_2$ 333.1603, found 333.1596.

*3-(3-(4-Methoxyphenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3h**).* [**1g**] = 0.3 M. Compound **3h** was obtained as a pale yellow solid (88.7 mg) in 85% yield: R_f = 0.22 (petroleum ether:ethyl acetate = 3:1); mp 150−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.83 (s, 1H), 7.32−7.23 (m, 6H), 7.12 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 4.33 (t, J = 8.0 Hz, 2H), 3.86 (s, 3H), 3.60 (t, J = 8.0 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 158.2, 133.0, 131.0, 128.8, 128.7, 128.3, 127.5, 127.2, 126.7, 126.4, 125.8, 125.6, 121.3, 118.2, 114.5, 114.3, 113.7, 62.9, 55.2, 46.9, 11.1; IR (KBr) ν 3275, 1744, 1512, 1243, 1038, 839, 764; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{21}H_{21}N_2O_3$ 349.1552, found 349.1544.

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

*N-(3-(4-Methoxyphenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-N-methylmethanesulfonamide (**3i**).* [**1h**] = 0.3 M. Compound **3i** was obtained as a pale yellow (64 mg) in 64% yield: R_f = 0.4 (petroleum ether:ethyl acetate = 3:1); mp 149−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.37 (s, 1H), 7.46−7.39 (m, 4H), 7.29−7.25 (m, 3H), 6.97 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.26 (s, 3H), 2.61 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 132.8, 130.9, 128.7, 126.9, 126.8, 126.7, 126.5, 124.1, 121.8, 114.8, 113.9, 55.2, 39.5, 38.0, 11.1; IR (KBr) ν 3369, 3319, 1507, 1342, 1248, 1150, 978, 836, 766, 697, 520; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{23}N_2O_3S$ 371.1429, found 371.1422.

*3-(3-(4-Ethylphenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3j**).* [**1i**] = 0.3 M. Compound **3j** was obtained as a pale yellow solid (87.6 mg) in 84% yield: R_f = 0.28 (petroleum ether:ethyl acetate = 3:1); mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.78 (s, 1H), 7.34−7.26 (m, 8H), 7.18 (s, 1H), 4.36 (t, J = 8.0 Hz, 2H), 3.62 (t, J = 8.0 Hz, 2H), 2.74 (q, J = 8.0 Hz, 2H), 2.11 (s, 3H), 1.33 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.6, 133.0, 131.6, 130.1, 128.5 127.7, 126.5, 125.9, 125.2, 122.0, 117.4, 114.4, 62.9, 46.6, 28.5, 15.4, 11.1; IR (KBr) ν 3280, 1739, 1594, 1509, 1230, 1145, 1078, 839, 762, 697; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{22}H_{23}N_2O_2$ 347.1760, found 347.1750.

*3-(3-(4-Chlorophenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3k**).* [**1j**] = 0.1 M. Compound **3k** was obtained as a white solid (112 mg) in 99% yield: R_f = 0.3 (petroleum ether:ethyl acetate = 3:1); mp 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.93 (s, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.25−7.11 (m, 5H), 4.37 (t, J = 7.2 Hz, 2H), 3.62 (t, J = 7.2 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 132.9, 132.7, 132.6, 131.1, 128.6, 128.4, 126.5, 126.2, 126.1, 121.4, 117.7, 114.0, 63.0, 47.1, 11.1; IR (KBr) ν 3374, 1736, 1494, 1233, 1143, 1033, 834, 769, 699; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}ClN_2O_2$ 353.1057, found 353.1050.

*N-(4,5-Diphenyl-3-(4-propylphenyl)-1H-pyrrol-2-yl)-N-methylmethanesulfonamide (**3l**).* [**1l**] = 0.1 M. Compound **3l** was obtained as a white solid (110.5 mg) in 93% yield: R_f = 0.28 (petroleum ether:ethyl acetate = 3:1); mp 196−197 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.57 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.15−7.17 (m, 6H), 713−7.11 (m, 1H), 4.30 (t, J = 7.6 Hz, 2H), 3.52 (t, J = 7.6 Hz, 2H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 133.4, 132.6, 131.5, 131.3, 128.3, 126.6, 126.5, 126.0, 120.9, 120.6, 118.5, 113.9, 63.0, 47.3, 11.1; IR (KBr) ν 3367, 3284, 1736, 1602, 1497, 1233, 1143, 1073, 1033, 764, 697; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}BrN_2O_2$ 397.0552, found 397.0544.

*3-(3-(4-Fluorophenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3m**).* [**1l**] = 0.1 M. Compound **3m** was obtained as a pale yellow solid (120.7 mg) in 99% yield: R_f = 0.29 (petroleum ether:ethyl acetate = 3:1); mp 177−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.93 (s, 1H), 7.38−7.34 (m, 2H), 7.20−7.10 (m, 7H), 4.37 (t, J = 8.0 Hz, 2H), 3.62 (t, J = 8.0 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J_{C-F} = 243.5 Hz), 158.7, 132.7, 131.2 (d, J_{C-F} = 7.7 Hz), 130.2, 128.2, 126.5, 125.9, 120.8, 118.9, 115.3 (d, J_{C-F} = 21.1 Hz), 114.0, 63.0, 47.3, 11.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −115.7; IR (KBr) ν 3312, 3277, 1746, 1604, 1509, 1235, 1148, 849, 759, 699; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}FN_2O_2$ 337.1352, found 337.1347.

*3-(3-(3-Chlorophenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3n**).* [**1m**] = 0.3 M. Compound **3n** was obtained as a white solid (88.1 mg) in 83% yield: R_f = 0.24 (petroleum ether:ethyl acetate = 3:1); mp 147−148 °C; ^{1}H NMR (400 MHz, DMSO) δ 11.46 (s, 1H), 7.51−7.45 (m, 5H), 7.34−7.28 (m, 4H), 4.38 (t, J = 7.6 Hz, 2H), 3.76 (t, J = 7.6 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 136.5, 133.0, 132.7, 130.2, 128.6, 128.3, 127.4, 126.6, 126.20, 126.16, 126.0, 122.3, 119.1, 112.9, 62.5, 47.8, 11.4; IR (KBr) ν 3245, 1721, 1594, 1492, 1215, 1143, 1081, 1028, 766, 694; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}ClN_2O_2$ 353.1057, found 353.1049.

*(S)-3-(3-(2-Chlorophenyl)-4-methyl-5-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3o**).* [**1n**] = 0.3 M. Compound **3o** was obtained as a white solid (100.3 mg) in 95% yield: R_f = 0.23 (petroleum ether:ethyl acetate = 3:1); mp 75−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.88 (s, 1H), 7.48−7.20 (m, 9H), 4.34−4.27 (m, 2H), 3.58−3.44 (m, 2H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 135.6, 133.7, 133.4, 133.0, 129.3, 128.9, 128.5, 126.4, 126.2, 125.8, 124.0, 115.1, 112.1, 62.7, 45.5, 10.8; IR (KBr) ν 3270, 1744, 1602, 1492, 1228, 1148, 1083, 1031, 759, 697; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}ClN_2O_2$ 353.1057, found 353.1049.

*3-(4-Methyl-5-phenyl-3-(thiophen-2-yl)-1H-pyrrol-2-yl)-oxazolidin-2-one (**3p**).* [**1o**] = 0.3 M. Compound **3p** was obtained as a gray solid (73.4 mg) in 75% yield: R_f = 0.25 (petroleum ether:ethyl acetate = 5:2); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.69 (s, 1H), 7.39−7.36 (m, 5H), 7.25 (s, 1H), 7.12−7.10 (m, 1H), 7.03−7.02 (m, 1H), 4.42 (t, J = 8.0 Hz, 2H), 3.76 (d, J = 8.0 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 156.8, 135.5, 132.5, 128.6, 127.3, 126.9, 126.5, 126.3, 124.3, 124.2, 122.1, 113.5, 112.8, 62.6, 47.4, 11.8; IR (KBr) ν 3262, 1744, 1602, 1512, 1477, 1228, 1140, 1033, 762, 697; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{18}H_{17}N_2O_2S$ 325.1011, found 325.1004.

*N-(3-Cyclopropyl-4-methyl-5-phenyl-1H-pyrrol-2-yl)-N-methylmethanesulfonamide (**3q**).* [**1p**] = 0.3 M. Compound **3q** was obtained as a white solid (49.4 mg) in 54% yield: R_f = 0.38 (petroleum ether:ethyl acetate = 2:1); mp 153−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.27 (s, 1H), 7.35−7.23 (m, 5H), 3.30 (s, 3H), 3.01 (s, 3H), 2.20 (s, 3H), 1.55−1.52 (m, 1H), 0.86−0.84 (m, 2H), 0.63−0.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 128.5, 126.8, 126.5, 126.3, 124.7, 119.8, 119.7, 128.3, 116.2, 38.51, 38.46, 10.7, 6.0, 5.2; IR (KBr) ν 3369, 1604, 1589, 1335, 1143, 1016, 956, 859, 766, 702, 517; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{16}H_{21}N_2O_2S$ 305.1324, found 305.1317.

*3-(4-Methyl-3-phenyl-5-(p-tolyl)-1H-pyrrol-2-yl)oxazolidin-2-one (**3r**).* [**1b**] = 0.3 M. Compound **3r** was obtained as a white solid (88.7 mg) in 89% yield: R_f = 0.31 (petroleum ether:ethyl acetate = 3:1); mp 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.43−7.29 (m, 7H), 7.21−7.19 (m, 2H), 4.34 (t, J = 8.0 Hz, 2H), 3.57 (s, 2H), 2.38 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 135.6, 134.6, 130.1, 130.0, 129.1, 128.2, 126.5, 125.9, 121.2, 118.4, 113.7, 62.9, 46.9, 21.0, 11.1; IR (KBr) ν 3225, 2921, 1741, 1504, 1230, 1148, 1083, 821, 702; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{21}H_{21}N_2O_2$ 333.1603, found 333.1594.

*N-(3-(2-Chlorophenyl)-4,5-diphenyl-1H-pyrrol-2-yl)-N-methylmethanesulfonamide (**3s**).* [**1r**] = 0.1 M. Compound **3s** was obtained as a white solid (88.1 mg) in 84% yield: R_f = 0.21 (petroleum ether:ethyl acetate = 3:1); mp 204−205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.36−7.32 (m, 4H), 7.25−7.22 (m, 1H), 7.07 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 4.26 (t, J = 8.0 Hz, 2H), 3.64 (s, 3H), 3.52 (t, J = 8.0 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.9, 134.6, 129.9, 128.3, 128.0, 126.5, 125.72, 125.68, 120.9, 118.2, 113.9, 113.2, 62.9, 55.2, 46.9, 11.1; IR (KBr) ν 3282, 2928, 1736, 1604, 1509, 1253, 1145, 1033, 831; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{21}H_{21}N_2O_3$ 349.1552, found 349.1544.

*N-(4,5-Diphenyl-3-(thiophen-2-yl)-1H-pyrrol-2-yl)-N-methylmethanesulfonamide (**3t**).* [**1s**] = 0.3 M. Compound **3t** was obtained as a white solid (109 mg) in 89% yield: R_f = 0.41 (petroleum ether:ethyl acetate = 5:1); mp 187−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.37−7.27 (m, 5H), 7.25−7.19 (m, 4H), 4.27 (t, J = 8.0 Hz, 2H), 3.49 (t, J = 8.0 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 134.0, 131.5, 131.2, 129.6, 128.44, 128.40, 127.5, 126.7, 125.1, 121.2, 119.8, 114.5, 63.1, 47.1, 11.2; IR (KBr) ν 3272, 1732, 1604, 1497, 1233, 1150, 1088, 826, 762, 704; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}ClN_2O_2$ 353.1057, found 353.1050.

*3-(5-(3-Bromophenyl)-4-methyl-3-phenyl-1H-pyrrol-2-yl)-oxazolidin-2-one (**3u**).* [**1t**] = 0.3 M. Compound **3u** was obtained as a white solid (102.2 mg) in 86% yield: R_f = 0.28 (petroleum ether:ethyl acetate = 3:1); mp 168−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.09 (s, 1H), 7.37−7.33 (m, 2H), 7.29−7.23 (m, 3H), 7.14 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.26 (t, J = 8.0 Hz, 2H), 3.53 (t, J = 8.0 Hz, 2H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 133.9, 131.6, 131.3, 129.5, 128.4, 127.8, 126.7, 125.2, 121.0, 120.2, 119.5, 114.5, 63.1, 47.2, 11.3; IR (KBr) ν 3262, 1736, 1497, 1238,

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

1148, 1086, 1071, 826, 759, 724; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{18}BrN_2O_2$ 397.0552, found 397.0547.

*N-(3-Cyclopropyl-4, 5-diphenyl-1H-pyrrol-2-yl)-N-methylmethanesulfonamide (**3v**).* [**1u**] = 0.1 M. Compound **3v** was obtained as a white solid (106 mg) in 97% yield: R_f = 0.43 (petroleum ether:ethyl acetate = 5:1); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.90 (s, 1H), 7.34−7.23 (m, 6H), 7.17−7.14 (m, 1H), 6.97 (s, 2H), 4.27 (d, J = 8.0 Hz, 2H), 3.52 (t, J = 8.0 Hz, 2H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 134.9, 134.1, 130.00, 129.94, 129.0, 128.7, 128.3, 126.7, 124.7, 124.1, 122.5, 122.0, 119.0, 115.2, 63.0, 46.9, 11.2; IR (KBr) ν 3262, 1741, 1587, 1497, 1228, 1145, 1083, 705; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{20}H_{17}BrN_2O_2$ 397.0552, found 397.0544.

*3-(4-Methyl-3-phenyl-5-(thiophen-2-yl)-1H-pyrrol-2-yl)-oxazolidin-2-one (**3w**).* Compound **3w** was obtained as a pale yellow solid (79 mg) in 62% yield: R_f = 0.27 (petroleum ether:ethyl acetate = 3:1); mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.45−7.37 (m, 5H), 7.12−6.93 (m, 3H), 4.36 (t, J = 8.0 Hz, 2H), 3.62 (t, J = 8.0 Hz, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 134.9, 134.2, 129.9, 128.2, 127.0, 126.6, 122.6, 122.0, 121.2, 120.5, 118.4, 114.8, 62.9, 46.9, 10.8; IR (KBr) ν 3277, 1736, 1609, 1502, 1230, 1145, 1083, 1031, 774, 709; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{18}H_{17}N_2O_2S$ 325.1011, found 325.1004.

*3-(3-Butyl-4-methyl-5-phenyl-1H-pyrrol-2-yl)oxazolidin-2-one (**3z**).* Compound **3z** was obtained as a white solid (26 mg) in 28% yield: R_f = 0.4 (petroleum ether:ethyl acetate = 10:1); mp 124−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.21−7.17 (m, 2H), 7.07−7.05 (m, 3H), 4.44 (t, J = 8.0 Hz, 2H), 3.90 (t, J = 8.0 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.93 (s, 3H), 1.45−1.28 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 133.2, 128.2, 126.4, 126.1, 125.6, 120.4, 118.8, 114.4, 62.7, 48.1, 33.0, 23.9, 22.9, 14.0, 10.4; IR (KBr) ν 3217, 2955, 2928, 2856, 1726, 1599, 1475, 1238, 1033, 764, 697; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{18}H_{23}N_2O_2$ 299.1760, found 299.1759.

*N-(3-Benzyl-4-methyl-5-phenyl-1H-pyrrol-2-yl)-N,4-dimethylbenzenesulfonamide (**3ab**).* Compound **3ab** was obtained as a pale yellow solid (14 mg) in 7% yield: R_f = 0.25 (petroleum ether:ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.32−7.31 (m, 3H), 7.18−7.17 (m, 3H), 7.14−7.10 (m, 2H), 7.06−7.03 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 3.23 (s, 2H), 3.04 (s, 3H), 2.36 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 140.4, 135.3, 133.0, 129.9, 129.6, 128.7, 128.1, 128.0, 127.6, 126.6, 126.3, 125.6, 125.1, 118.3, 115.5, 39.2, 29.3, 21.6, 10.7; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{26}H_{27}N_2O_2S$ 431.1793, found 431.1792.

*N,4-Dimethyl-N-(5-methyl-4,6-diphenyl-3,4-dihydropyridin-2-yl)-benzenesulfonamide (**7**).* Compound **7** was obtained as a white solid (16 mg) in 8% yield: R_f = 0.5 (petroleum ether:ethyl acetate = 10:1); ^{1}H NMR (400 MHz, CD_3CN) δ 7.50 (d, J = 8.0 Hz, 2H), 7.41−7.35 (m, 4H), 7.31−7.25 (m, 4H), 7.22 (d, J = 8.0 Hz, 2H), 7.08−7.06 (m, 2H), 3.50 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 3.27 (dd, J_1 = 16.8 Hz, J_2 = 2.4 Hz, 1H), 3.12 (s, 3H), 2.68 (dd, J_1 = 16.8 Hz, J_2 = 8.8 Hz, 1H), 2.36 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 154.6, 145.4, 141.70, 141.66, 140.2, 136.6, 130.8, 130.0, 129.7, 128.7, 128.5, 128.1, 127.9, 127.8, 120.8, 118.3, 44.0, 35.3, 34.9, 21.5, 18.5; HRMS-(ESI) (m/z) [M + H]$^+$ calcd for $C_{26}H_{27}N_2O_2S$ 431.1793, found 431.1792.

*N,4-Dimethyl-N-(4,5,6-triphenylpyridin-2-yl)benzenesulfonamide (**8**).* Compound **8** was obtained as a white solid (25 mg) in 17% yield: R_f = 0.49 (petroleum ether:ethyl acetate = 10:1), mp 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61−7.59 (m, 3H), 7.20−7.18 (m, 3H), 7.14−7.11 (m, 3H), 7.06−6.96 (m, 9H), 6.76 (d, J = 6.8 Hz, 2H), 3.34 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 152.2, 151.7, 143.7, 140.1, 139.1, 137.4, 135.2, 131.44, 131.38, 130.0, 129.5, 129.4, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 126.7, 118.8, 35.6, 21.5; IR (KBr) ν 1542, 1543, 1380, 1165, 1088, 924, 702, 699, 587, 552; HRMS-(EI) (m/z) [M + H]$^+$ calcd for $C_{31}H_{27}N_2O_2S$ 491.1793, found 491.1791.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02057.

Mechanistic experiments; ^{1}H and ^{13}C NMR spectra for all described compounds; and crystal structures of compounds **3e**, **8**, **3s**, **2uc**, and **2vc** (PDF)

Crystal data of compounds **2uc**, **2vc**, **3e**, **3s**, and **8** in CIF format (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

*Fax: 86-591-63173587. E-mail: huangxl@fjirsm.ac.cn.

Author Contributions

Y.W., L.Z., and Y.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (Grant No. 21402197, 21502190) and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences for financial support. We thank Prof. Lutz Ackermann from the Georg-August-University Göttingen for his insightful suggestion on the mechanistic studies during his visit of our institute in April.

■ REFERENCES

(1) For selected reviews of gold catalysis, see the following: (a) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (b) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (c) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351. (d) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326. (e) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208. (f) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232. (g) Friend, C. M.; Hashmi, A. S. K. *Acc. Chem. Res.* **2014**, *47*, 729. (h) Fensterbank, L.; Malacria, M. *Acc. Chem. Res.* **2014**, *47*, 953. (i) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028. For pioneering works on a gold activating a triple bond, see the following: (j) Teles, J. H.; Brode, S.; Chabanas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1415. (k) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11553.

(2) For selected reviews on α-oxo gold carbenes in catalysis, see the following: (a) Xiao, J.; Li, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 7226. (b) Zhang, L. *Acc. Chem. Res.* **2014**, *47*, 877. (c) Yeom, H.-S.; Shin, S. *Acc. Chem. Res.* **2014**, *47*, 966. (d) Qian, D.; Zhang, J. *Chem. Soc. Rev.* **2015**, *44*, 677.

(3) (a) ref 2c.. (b) Davies, P. W.; Garzon, M. *Asian J. Org. Chem.* **2015**, *4*, 694.

(4) (a) Li, C.; Zhang, L. *Org. Lett.* **2011**, *13*, 1738. (b) Davies, P. W.; Cremonesi, A.; Dumitrescu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8931. (c) Chatzopoulou, E.; Davies, P. W. *Chem. Commun.* **2013**, *49*, 8617. (d) Garzon, M.; Davies, P. W. *Org. Lett.* **2014**, *16*, 4850.

(5) (a) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297. (b) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188. (c) Lang, S.; Murphy, J. A. *Chem. Soc. Rev.* **2006**, *35*, 146.

(6) Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 11260.

(7) (a) Lu, B.; Luo, Y.; Liu, L.; Ye, L.; Wang, Y.; Zhang, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8358. (b) Yan, Z.-Y.; Xiao, Y.; Zhang, L. *Angew. Chem., Int. Ed.* **2012**, *51*, 8624. (c) Xiao, Y.; Zhang, L. *Org. Lett.* **2012**, *14*, 4662.

(8) (a) Wetzel, A.; Gagosz, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 7354. (b) Gronnier, C.; Boissonnat, G.; Gagosz, F. *Org. Lett.* **2013**, *15*, 4234.

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416

(9) (a) Zhu, S.; Wu, L.; Huang, X. *J. Org. Chem.* **2013**, *78*, 9120. (b) Li, N.; Wang, T.-Y.; Gong, L.-Z.; Zhang, L. *Chem. - Eur. J.* **2015**, *21*, 3585. (c) Tokimizu, Y.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2014**, *16*, 3138. (d) Shen, C.-H.; Pan, Y.; Yu, Y.-F.; Wang, Z.-S.; He, W.; Li, T.; Ye, L.-W. *J. Organomet. Chem.* **2015**, *795*, 63.

(10) During the preparation of this manuscript, Liu and co-workers reported a similar pyrrole synthesis via gold-catalyzed intermolecular reaction of ynamides with vinyl azides or 2*H*-azirines: Pawar, S. K.; Sahani, R. L.; Liu, R.-S. *Chem. - Eur. J.* **2015**, *21*, 10843.

(11) Recently, Ye and co-workers reported a gold-catalyzed reaction of ynamides with benzyl azides: Shu, C.; Wang, Y.-H.; Zhou, B.; Li, X.-L.; Ping, Y.-F.; Lu, X.; Ye, L.-W. *J. Am. Chem. Soc.* **2015**, *137*, 9567.

(12) For gold-catalyzed reaction of alkynes and $TMSN_3$, see the following: (a) Qin, C.; Feng, P.; Ou, Y.; Shen, T.; Wang, T.; Jiao, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 7850. (b) Gaydou, M.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 13468.

(13) (a) Sundberg, R. J. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, UK, 1996; Vol. 2, p 119. (b) Shortt, M. F.; Thomas, E. J. *Science of Synthesis*; Joule, J. A., Ed.; Georg Thieme, Stuttgart, 2000; Vol. *10*. (c) Walsh, C. T.; Garneau-Tsodikova, S.; Howard-Jones, A. R. *Nat. Prod. Rep.* **2006**, *23*, 517. (d) Bellina, F.; Rossi, R. *Tetrahedron* **2006**, *62*, 7213. (e) Biava, M.; Porretta, G. C.; Manetti, F. *Mini-Rev. Med. Chem.* **2007**, *7*, 65. (f) Katritzky, A. R. *Comprehensive Heterocyclic Chemistry III*, 1st ed.; Elsevier: Amsterdam, 2008. (g) Fan, H.; Peng, J.; Hamann, M. T.; Hu, J.-F. *Chem. Rev.* **2008**, *108*, 264.

(14) For selected reviews, see the following: (a) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127. (b) Estévez, V.; Villacampa, M.; Menéndez, J. C. *Chem. Soc. Rev.* **2010**, *39*, 4402. (c) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084. (d) Yoshikai, N.; Wei, Y. *Asian J. Org. Chem.* **2013**, *2*, 466. (e) Estévez, V.; Villacampa, M.; Menéndez, J. C. *Chem. Soc. Rev.* **2014**, *43*, 4633.

(15) For selected review on vinyl azides, see the following: (a) Làbbé, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 775. (b) Reference 4a.. (c) Chiba, S. *Synlett* **2012**, *2012*, 21. (d) Hu, B.; DiMagno, S. G. *Org. Biomol. Chem.* **2015**, *13*, 3844. For selected examples on pyrrole synthesis from vinyl azides, see the following: (e) Chiba, S.; Wang, Y.-F.; Lapointe, G.; Narasaka, K. *Org. Lett.* **2008**, *10*, 313. (f) Wang, Y.-F.; Toh, K. K.; Chiba, S.; Narasaka, K. *Org. Lett.* **2008**, *10*, 5019. (g) Chen, F.; Shen, T.; Cui, Y.; Jiao, N. *Org. Lett.* **2012**, *14*, 4926.

(16) Gold-catalyzed tetrasubstituted pyrrole synthesis: (a) Binder, J. T.; Kirsch, S. F. *Org. Lett.* **2006**, *8*, 2151. (b) Istrate, F. M.; Gagosz, F. *Org. Lett.* **2007**, *9*, 3181. (c) Davies, P. W.; Martin, N. *Org. Lett.* **2009**, *11*, 2293. (d) Saito, A.; Konishi, T.; Hanzawa, Y. *Org. Lett.* **2010**, *12*, 372. (e) Ngwerume, S.; Lewis, W.; Camp, J. E. *J. Org. Chem.* **2013**, *78*, 920.

(17) Zhou, A.-H.; He, Q.; Shu, C.; Yu, Y.-F.; Liu, S.; Zhao, T.; Zhang, W.; Lu, X.; Ye, L.-W. *Chem. Sci.* **2015**, *6*, 1265.

(18) (a) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6146. (b) Pérez-Galán, P.; Delpont, N.; Herrero-Gómez, E.; Maseras, F.; Echavarren, A. M. *Chem. - Eur. J.* **2010**, *16*, 5324. (c) López-Carrillo, V.; Echavarren, A. M. *J. Am. Chem. Soc.* **2010**, *132*, 9292.

(19) (a) Zificsak, C. A.; Mulder, J. A.; Hsung, R. P.; Rameshkumar, C.; Wei, L.-L. *Tetrahedron* **2001**, *57*, 7575. (b) DeKorver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, *110*, 5064. (c) Evano, G.; Coste, A.; Jouvin, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2840. (d) Wang, X.-N.; Fang, S.-Z.; He, L.; Yeom, H.-S.; Kedrowski, B. L.; Hsung, R. P. *Acc. Chem. Res.* **2014**, *47*, 560.

(20) For selected recent examples on gold catalysis, see the following: (a) Karad, S. N.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2014**, *53*, 9072. (b) Li, L.; Shu, C.; Zhou, B.; Yu, Y.-F.; Xiao, X.-Y.; Ye, L.-W. *Chem. Sci.* **2014**, *5*, 4057.

(21) For reviews on 2*H*-azirines, see the following: (a) Nair, V.; Kim, K. H. *Heterocycles* **1977**, *7*, 353. (b) Palacios, F.; de Retana, A. M. O.; de Marigorta, E. M.; de los Santos, J. M. *Eur. J. Org. Chem.* **2001**, *2001*, 2401. (c) Huang, C.-Y.; Doyle, A. G. *Chem. Rev.* **2014**, *114*, 8153.

(22) For a gold-catalyzed intramolecular reaction of alkynes with 2*H*-azirines, see the following: Prechter, A.; Henrion, G.; Faudot dit Bel, P.; Gagosz, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 4959.

(23) Zhu, L.; Yu, Y.; Mao, Z.; Huang, X. *Org. Lett.* **2015**, *17*, 30.

(24) CCDC 1414855 (**3e**), CCDC 1414857 (**3s**), CCDC 1414859 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(25) The reaction of ynamide **1a** with monosubstituted vinyl azide under standard conditions (Table 1, entry 1), after 2.5 h, yielded the corresponding pyrrole in 8% yield.

(26) We thank the reviewers' insightful suggestion on the mechanistic studies.

(27) For the details of reactivity scale of different nucleophiles, please check the home page of Prof. Mayr's group via www.cup.lmu.de/oc/mayr/DBintro.html.

(28) (a) Lu, B.; Li, C.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 14070. (b) Ref 4a..

(29) See the Supporting Information for details.

(30) Allais, C.; Grassot, J.-M.; Rodriguez, J.; Constantieux, T. *Chem. Rev.* **2014**, *114*, 10829.

(31) Pan, F.; Shu, C.; Ping, Y.-F.; Pan, Y.-F.; Ruan, P.-P.; Fei, Q.-R.; Ye, L.-W. *J. Org. Chem.* **2015**, *80*, 10009.

(32) Wang, Y.; Muratore, M. E.; Echavarren, A. E. *Chem. - Eur. J.* **2015**, *21*, 7332.

(33) For furan synthesis via gold-catalyzed formal [3 + 2] cycloaddition of sulfonium ylides with alkynes, see the following: (a) Kramer, S.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 4681. (b) Huang, X.; Peng, B.; Luparia, M.; Gomes, L. F. R.; Veiros, L. F.; Maulide, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 8886.

(34) (a) Wei, L.-L.; Mulder, J. A.; Xiong, H.; Zificsak, C. A.; Douglas, C. J.; Hsung, R. P. *Tetrahedron* **2001**, *57*, 459. (b) Hamada, T.; Ye, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 833. (c) Karad, S. N.; Bhunia, S.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2012**, *51*, 8722. (d) Mukherjee, A.; Dateer, R. B.; Chaudhuri, R.; Bhunia, S.; Karad, S. N.; Liu, R.-S. *J. Am. Chem. Soc.* **2011**, *133*, 15372.

(35) Mulvaney, J. E.; Folk, T. L.; Newton, D. J. *J. Org. Chem.* **1967**, *32*, 1674.

(36) (a) Zhang, X.; Sarkar, S. K.; Weragoda, G. K.; Rajam, S.; Ault, B. S.; Gudmundsdottir, A. D. *J. Org. Chem.* **2014**, *79*, 653. (b) Zhang, L.; Dolbier, W. R., Jr.; Sheeller, B.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 6362.

(37) Liu, Z.; Liu, J.; Zhang, L.; Liao, P.; Song, J.; Bi, X. *Angew. Chem., Int. Ed.* **2014**, *53*, 5305.

DOI: 10.1021/acs.joc.5b02057
J. Org. Chem. 2015, 80, 11407−11416