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Palladium-Catalyzed Multicomponent Reaction of Alkynes, Carboxylic Acids, and Isocyanides: A Direct Approach to Captodative Olefins

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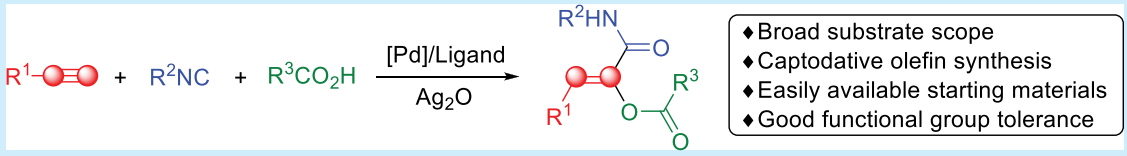
Supporting Information



ABSTRACT: A palladium-catalyzed multicomponent reaction of alkynes, carboxylic acids, and isocyanides has been developed with the assistance of silver salt under mild conditions. Highly functionalized captodative olefins are synthesized efficiently by this method, which can find many applications as versatile synthons in organic synthesis.

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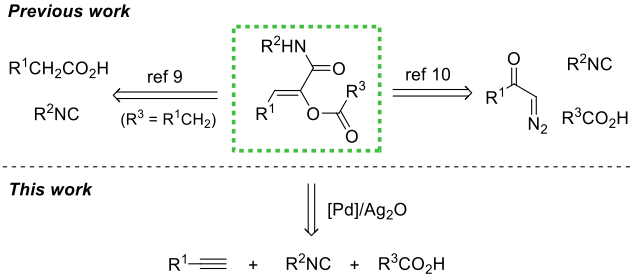
Isocyanides have been proven to be versatile building blocks in organic synthesis in the past several decades due to their reactivities toward electrophiles, nucleophiles, and radicals.[1] Therefore, isocyanide-based multicomponent reactions (MCRs) are unparalleled in terms of effectiveness and economy for the preparation of complicated molecules in a single synthetic step,[2] where the Passerini 3CR reaction and Ugi 4CR reaction are two representative examples. In recent years, palladium-catalyzed reactions involving isocyanides have been extensively studied.[3] However, reactions of unactivated terminal alkynes with isocyanides are less studied,[4] probably due to their competitively facile homocoupling reactions. Among them, much attention has been centered on C(sp)−H insertion of isocyanide under the catalysis of uncommon rare earth or actinide complexes, leading to 2-yn-1-ones or 1-aza-1,3-enynes.[5] Very recently, *N*-acyl propiolamides were synthesized by a palladium-catalyzed three-component reaction of alkynes, isocyanides, and sodium carboxylates through direct isocyanide insertion of alkyne-complexed Pd species.[4a] Thus, the development of facile methods to diverse product skeletons from alkynes and isocyanide as well as their related mechanistic study is of great value.

Captodative olefins, with both an electron-withdrawing and an electron-donating substituent at the same α-carbon,[6] have demonstrated broad utility in cyclization reactions and heterocycle synthesis,[7] thus rendering convenient access to them of great value and highly desirable. 2-Acyloxyacrylamides represent a class of typical captodative olefins and useful synthons in organic synthesis. However, only a few methods have been introduced for their preparation.[8] These reactions mainly focused on the condensation of two molecules of the same arylacetic acids and one of isocyanide with limited product diversity under high concentrations[9a] or microwave heating[9b,c] (Scheme 1). An elegant example has been disclosed by Basso and co-workers using a three-component tandem reaction of isocyanides, acids, and preactivated diazonium compounds upon irradiation to achieve the highly functionalized captodative olefins (Scheme 1).[10] In continuation of our previous efforts on isocyanide chemistry,[3h,j,11] herein we report a novel palladium-catalyzed three-component reaction for straightforward access to diversified captodative olefins under mild reaction conditions (Scheme 1). To the best of our knowledge, the given approach represents the first example for 2-acyloxyacrylamide synthesis from commercially available alkynes, isocyanides, and carboxylic acids. Notably, the significance of silver oxide should be highlighted, which provides an alternative reaction pathway and affords distinct products.[4a,5]

Scheme 1. Synthesis of captodative olefins



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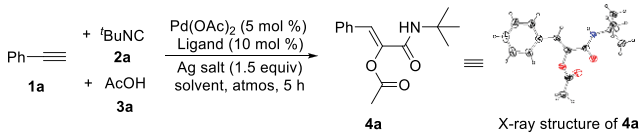
Our preliminary investigation was started by examining the reaction of phenylacetylene and *tert*-butyl isocyanide with acetic acid in the presence of $Pd(OAc)_2$ and Ag_2O in dichloromethane. Intriguingly, different from the previously reported propiolamide product,[4a] the unexpected (*Z*)-3-aryl-2-acyloxyacrylamides **4a** was obtained in 64% yield (entry 1, Table 1), and the structure was further determined by X-ray crystallographic analysis.[12] Ag_2O was the best choice among various silver salts (entries 1−3). Screening of solvents such as DCE, THF, CH_3CN, and toluene indicated PhCl to be the most suitable one, affording the product **4a** in 77% yield (entries 4−8). The yield decreased when the temperature was increased (entries 9 and 10) or the reaction was conducted in air or oxygen atmosphere (entries 11 and 12). Ligands were found to have a profound effect on this reaction (entries 13−18) and the alkene **4a** could be isolated in 83% yield in the presence of P(*o*-tol)$_3$, while the bidentate ligand (dppp) inhibited the reaction significantly. Further investigation on the ratio of starting materials suggested 2.0 equiv of ^{t}BuNC and 3.0 equiv of HOAc were necessary for this reaction (entries 19 and 20). Trace amounts or no product was formed in the absence of palladium catalyst and/or silver salt (entries 21−23), which indicated both the palladium catalyst and silver salt were crucial to this reaction. When alkyne **1a** was added together with other reagents from the beginning, the yield decreased greatly owing to the undesired formation of 1,3-diyne (entry 24).

With the optimized conditions in hand, various alkynes were examined for captodative olefin synthesis as summarized in Scheme 2. A wide variety of substitution patterns and functional groups were tolerated. Aryl acetylenes containing different substitutions, such as alkyl (**4b**, **4j**), alkoxy (**4c**, **4l**), halides (**4d**, **4e**, **4g**, **4k**), acyl (**4f**), nitro (**4h**), and amide (**4i**), were compatible with the reaction conditions, regardless of their different electronic properties and steric effect. Alternatively, olefin **4a** could also be obtained in 87% yield when phenylpropiolic acid was used instead of phenylacetylene, which might undergo decarboxylative process. The reaction is not only limited to simple benzene-substituted alkynes. For example, thienyl alkyne could be transformed into the desired product smoothly (**4m**), and enyne substrate could afford the corresponding dienyl product (**4n**) in moderate yield. To our

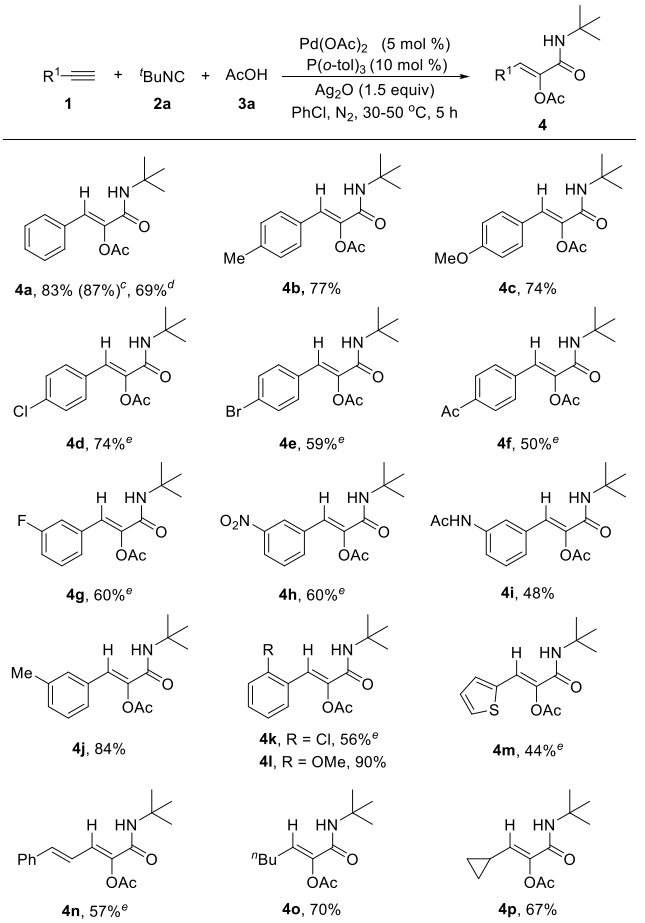
Table 1. Optimization of Reaction Conditions[a]



entry	Ag salt	ligand	solvent	temp (°C)	yield[b] (%)
1	Ag_2O		DCM	30	64
2	Ag_2CO_3		DCM	30	57
3	AgOAc		DCM	30	15
4	Ag_2O		DCE	30	30
5	Ag_2O		THF	30	63
6	Ag_2O		CH_3CN	30	60
7	Ag_2O		toluene	30	34
8	Ag_2O		PhCl	30	77
9	Ag_2O		PhCl	50	62
10	Ag_2O		PhCl	70	39
11	Ag_2O		PhCl	30	65[c]
12	Ag_2O		PhCl	30	58[d]
13	Ag_2O	PPh_3	PhCl	30	68
14	**Ag_2O**	**P(*o*-tol)$_3$**	**PhCl**	**30**	**83**
15	Ag_2O	PCy_3	PhCl	30	59
16	Ag_2O	X-Phos	PhCl	30	72
17	Ag_2O	P(^{t}Bu)$_3$	PhCl	30	71
18	Ag_2O	dppp	PhCl	30	24
19	Ag_2O	P(*o*-tol)$_3$	PhCl	30	51[e]
20	Ag_2O	P(*o*-tol)$_3$	PhCl	30	56[f]
21	Ag_2O	P(*o*-tol)$_3$	PhCl	30	trace[g]
22		P(*o*-tol)$_3$	PhCl	30	trace
23		P(*o*-tol)$_3$	PhCl	30	0[g]
24	Ag_2O	P(*o*-tol)$_3$	PhCl	30	36[h]

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), **3a** (0.9 mmol), $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), Ag salt (1.5 equiv), and solvent (1.5 mL) under N_2. The alkyne **1a** was added over 3 h by syringe pump. dppp = 1,3-bis(diphenylphosphino)propane, X-Phos = 2-dicyclohexylph-osphino-2′,4′,6′-triisopropyl-1,1′-biphenyl, PCy_3 = tricyclohexylphosphine, P(*o*-tol)$_3$ = tri(*o*-tolyl)phosphine. [b]Isolated yields. [c]Under air. [d]Under O_2. [e]1.5 equiv of ^{t}BuNC was used. [f]2.0 equiv of HOAc was used. [g]Without $Pd(OAc)_2$ catalyst. [h]Without using syringe pump.

Scheme 2. Substrate Scope of Alkynes[a,b]



[a]Reaction conditions: alkynes **1** (0.3 mmol), isocyanide **2a** (0.6 mmol), acetic acid **3a** (0.9 mmol), $Pd(OAc)_2$ (5 mol %), P(*o*-tol)$_3$ (10 mol %), Ag_2O (1.5 equiv), and PhCl (1.5 mL) under N_2 at 30−50 °C for 5 h. Alkyne **1** was added by syringe pump. [b]Yields shown are of the isolated products. [c]Phenylpropiolic acid was used instead of phenylacetylene **1a**. [d]The reaction was conducted on 1.0 mmol scale over 14.5 h. [e]At 50 °C.

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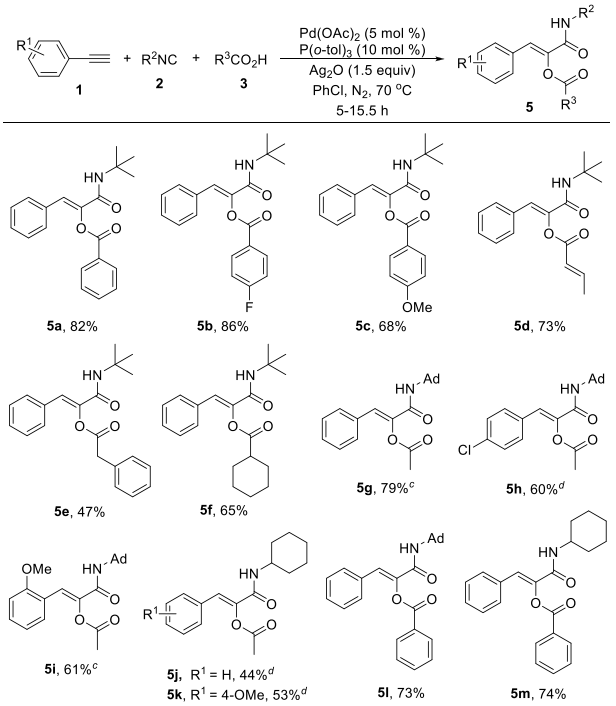
delight, success of this conversion could be further extended to alkyl acetylenes, providing products (**4o** and **4p**) in good yields. Notably, the product **4a** could be obtained in good yield when the reaction was scaled up to 1.0 mmol.

To further explore the scope and generality of this method, we next applied various acids and isocyanides for this tandem reaction under the optimized conditions (Scheme 3). It was found that relatively higher temperature was more favorable for other carboxylic acids (**5a**–**f**). To further demonstrate the general applicability of isocyanides in this reaction, commercially available 1-adamantyl and cyclohexyl isocyanide were examined, respectively. The corresponding products could be afforded in moderate to good yields (**5g**–**m**). However, when α-acidic isocyanides, for example, isocyanoacetates, were employed, no corresponding products could be observed. The reason might be due to the easy formation of highly reactive α-metalated isocyanides or isocyanide–metal complexes over desired metal acetylide,[13] thus rendering messy reactions.

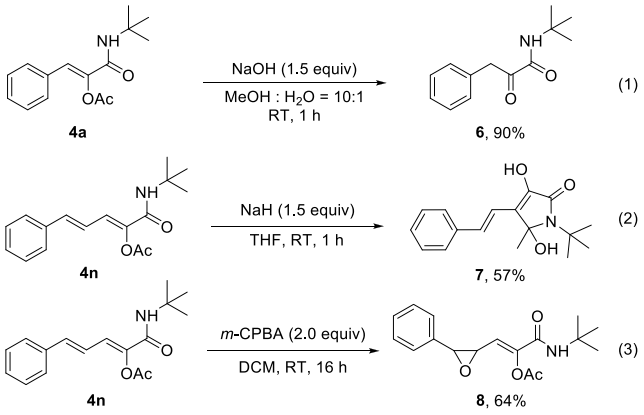
Scheme 3. Substrate Scope of Alkynes, Isocyanides, and Carboxylic acids[a,b]



[a]Reaction conditions: alkynes **1** (0.3 mmol), isocyanides **2** (0.6 mmol), acids **3** (0.9 mmol), $Pd(OAc)_2$ (5 mol %), Ag_2O (1.5 equiv), and PhCl (1.5 mL) under N_2 for 5–15.5 h by syringe pump, 70 °C. [b]Yields shown are of the isolated products. [c]At 30 °C. [d]At 50 °C.

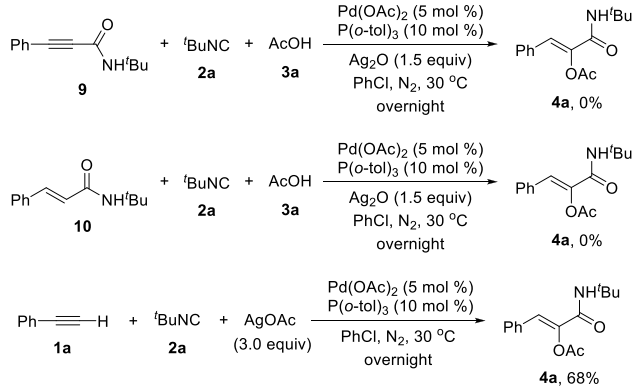
To illustrate the synthetic utility of the given method, we tried to verify the application of this tandem reaction (Scheme 4). α-Ketoamides **6** was smoothly obtained in 90% yield from produced **4a** through hydrolysis (eq 1), which could be used as inhibitor of enzyme activity.[14] Interestingly, a base-promoted rearrangement–cyclization reaction occurred from diene **4n**, leading to dihydropyrrolone derivative **7** in 57% yield instead of the formation of ketoamide (eq 2).[9b,c,10c] Furthermore, substrate **4n** could also undergo the selective epoxidation reaction and afforded epoxide **8** in good yield (eq 3), which could be applied as the key intermediate for the analogue synthesis of nature product Jatropham.[15]

Scheme 4. Synthetic Applications of the Captodative Olefins



To gain insight into the possible intermediates and pathway of this multicomponent reaction, control experiments were carried out as shown in Scheme 5. Both propiolamide **9** and acrylamide **10**, instead of phenylacetylene **1a**, were treated with isocyanide and acetic acid under the standard conditions, respectively (Scheme 5). However, no product **4a** could be observed for either substrate, which suggested that neither compound **9** nor **10** was the key intermediate in this reaction. Furthermore, based on the fact that product **4a** was isolated in 68% yield in the presence of AgOAc in lieu of Ag_2O and HOAc, we speculated that AgOAc might be the effective species in the reaction.

Scheme 5. Preliminary Mechanistic Studies



A plausible mechanism was proposed for this reaction as depicted in Scheme 6. Silver acetylide **A**[16] was formed from Ag_2O, alkyne **1**, and carboxylic acid **3**, along with the formation of silver carboxylate. Attack of the carboxylic anion on the silver acetylide center occurred to obtain complex **B**,[17] followed by the transmetalation process with Pd(II). An isocyanide insertion reaction happened to the generated vinyl palladium complexes **C**, leading to the imidoyl palladium(II) intermediate **D**. The final 2-acyloxyacrylamide product **4** or **5** was afforded after treatment with water and successive reductive elimination process. The generated Pd(0) was reoxidized to Pd(II) in the presence of silver salt to complete the entire catalytic cycle.[18]

In summary, a palladium-catalyzed tandem reaction was disclosed with the assistance of silver oxide for the synthesis of

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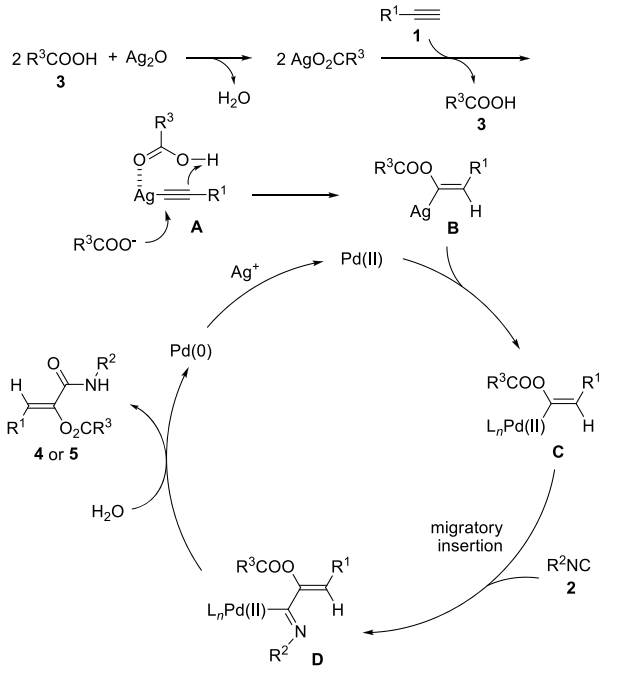
Scheme 6. Plausible Mechanism



functionalized captodative olefins from commercially available terminal alkynes, carboxylic acids, and isocyanides. This approach features broad substrate scope, good functional group tolerance, and promising application prospect on complicated molecule synthesis. Further application of this method is now under investigation in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00137.

Experimental procedures and characterization data for all compounds (PDF)

Accession Codes

CCDC 1836502 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For recent reviews on isocyanides, see: (a) Song, B.; Xu, B. *Chem. Soc. Rev.* **2017**, *46*, 1103. (b) Giustiniano, M.; Basso, A.; Mercalli, V.; Massarotti, A.; Novellino, E.; Tron, G. C.; Zhu, J. *Chem. Soc. Rev.* **2017**, *46*, 1295. (c) Boyarskiy, V. P.; Bokach, N. A.; Luzyanin, K. V.; Kukushkin, V. Y. *Chem. Rev.* **2015**, *115*, 2698. (d) Wang, H.; Xu, B. *Youji Huaxue* **2015**, *35*, 588. (e) Qiu, G.; Ding, Q.; Wu, J. *Chem. Soc. Rev.* **2013**, *42*, 5257. (f) Wilson, R. M.; Stockdill, J. L.; Wu, X.; Li, X.; Vadola, P. A.; Park, P. K.; Wang, P.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 2834. (g) Nenajdenko, V. *Isocyanide Chemistry: Applications in Synthesis and Material Science*; Wiley-VCH: Weinheim, 2012.

(2) For selected reviews, see: (a) Dömling, A. *Chem. Rev.* **2006**, *106*, 17. (b) Bienaymé, H.; Hulme, C.; Oddon, G.; Schmitt, P. *Chem. - Eur. J.* **2000**, *6*, 3321. (c) Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168.

(3) For selected reviews, see: (a) Lang, S. *Chem. Soc. Rev.* **2013**, *42*, 4867. (b) Vlaar, T.; Ruijter, E.; Maes, B. U. W.; Orru, R. V. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7084. For recent examples, see: (c) Kong, W.; Chen, X.; Wang, M.; Dai, H.; Yu, J. *Org. Lett.* **2018**, *20*, 284. (d) Chen, S.; Wei, W.; Wang, J.; Xia, Y.; Shen, Y.; Wu, X.; Jing, H.; Liang, Y. *Adv. Synth. Catal.* **2017**, *359*, 3538. (e) Kong, W.; Liu, Y.; Xu, H.; Chen, Y.; Dai, H.; Yu, J. *J. Am. Chem. Soc.* **2016**, *138*, 2146. (f) Pan, Y.; Wu, Y.; Chen, Z.; Hao, W.; Li, G.; Tu, S.; Jiang, B. *J. Org. Chem.* **2015**, *80*, 5764. (g) Jiang, X.; Tang, T.; Wang, J.; Chen, Z.; Zhu, Y.; Ji, S. *J. Org. Chem.* **2014**, *79*, 5082. (h) Fang, T.; Tan, Q.; Ding, Z.; Liu, B.; Xu, B. *Org. Lett.* **2014**, *16*, 2342. (i) Liu, Y.; Xu, H.; Kong, W.; Shang, M.; Dai, H.; Yu, J. *Nature* **2014**, *515*, 389. (j) Xu, S.; Huang, X.; Hong, X.; Xu, B. *Org. Lett.* **2012**, *14*, 4614.

(4) For selected examples, see: (a) He, Y.; Wang, Y.; Liang, X.; Huang, B.; Wang, H.; Pan, Y. *Org. Lett.* **2018**, *20*, 7117. (b) Xue, Y.; Zhu, Y.; Gao, L.; He, X.; Liu, N.; Zhang, W.; Yin, J.; Ding, Y.; Zhou, H.; Wu, Z. *J. Am. Chem. Soc.* **2014**, *136*, 4706. (c) Tang, T.; Fei, X.; Ge, Z.; Chen, Z.; Zhu, Y.; Ji, S. *J. Org. Chem.* **2013**, *78*, 3170. (d) Tsukada, N.; Wada, M.; Takahashi, N.; Inoue, Y. *J. Organomet. Chem.* **2009**, *694*, 1333.

(5) For selected examples, see: (a) Zhang, W.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 9700. (b) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K.; Takaki, K. *J. Org. Chem.* **2005**, *70*, 10679. (c) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K.; Takaki, K. *Chem. Commun.* **2005**, 634. (d) Barnea, E.; Andrea, T.; Kapon, M.; Berthet, J.; Ephritikhine, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 10860.

(6) Viehe, H. G.; Janousek, Z.; Merényi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

(7) For selected examples, see: (a) Lasri, J.; Mukhopadhyay, S.; Charmier, M. A. J. *J. Heterocycl. Chem.* **2008**, *45*, 1385. (b) Sanabria, R.; Herrera, R.; Aguilar, R.; González-Romero, C.; Jiménez-Vázquez, H. A.; Delgado, F.; Söderberg, B. C. G.; Tamariz, J. *Helv. Chim. Acta* **2008**, *91*, 1807. (c) Herrera, R.; Mendoza, J. A.; Morales, M. A.; Méndez, F.; Jiménez-Vázquez, H. A.; Delgado, F.; Tamariz, J. *Eur. J. Org. Chem.* **2007**, *2007*, 2352. (d) del Carmen Cruz, M.; Tamariz, J. *Tetrahedron Lett.* **2004**, *45*, 2377. (e) Herrera, R.; Nagarajan, A.; Morales, M. A.; Méndez, F.; Jiménez-Vázquez, H. A.; Zepeda, L. G.; Tamariz, J. *J. Org. Chem.* **2001**, *66*, 1252.

(8) For selected examples, see: (a) Zhang, L.; Deng, X.; Du, F.; Li, Z. *Macromolecules* **2013**, *46*, 9554. (b) Kovács, J.; Pintér, I.; Kajtár-Peredy, M.; Somsák, L. *Tetrahedron* **1997**, *53*, 15041.

DOI: 10.1021/acs.orglett.9b00137
Org. Lett. XXXX, XXX, XXX−XXX

(9) (a) Polisar, J. G.; Norton, J. R. *Tetrahedron* **2012**, *68*, 10236. (b) Basso, A.; Banfi, L.; Riva, R. *Molecules* **2011**, *16*, 8775. (c) Basso, A.; Banfi, L.; Galatini, A.; Guanti, G.; Rastrelli, F.; Riva, R. *Org. Lett.* **2009**, *11*, 4068.
(10) (a) Garbarino, S.; Protti, S.; Basso, A. *Synthesis* **2015**, *47*, 2385. (b) Garbarino, S.; Banfi, L.; Riva, R.; Basso, A. *J. Org. Chem.* **2014**, *79*, 3615. (c) Basso, A.; Banfi, L.; Garbarino, S.; Riva, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 2096.
(11) (a) Hong, X.; Tan, Q.; Liu, B.; Xu, B. *Angew. Chem., Int. Ed.* **2017**, *56*, 3961. (b) Mao, H.; Gao, M.; Liu, B.; Xu, B. *Org. Chem. Front.* **2016**, *3*, 516. (c) Huang, X.; Xu, S.; Tan, Q.; Gao, M.; Li, M.; Xu, B. *Chem. Commun.* **2014**, *50*, 1465. (d) Hong, X.; Wang, H.; Qian, G.; Tan, Q.; Xu, B. *J. Org. Chem.* **2014**, *79*, 3228. (e) Wang, H.; Yu, Y.; Hong, X.; Xu, B. *Chem. Commun.* **2014**, *50*, 13485. (f) Qian, G.; Hong, X.; Liu, B.; Mao, H.; Xu, B. *Org. Lett.* **2014**, *16*, 5294.
(12) For crystallographic data of compound **4a**, see the Supporting Information.
(13) For selected review on isocyanoacetates, see: (a) Gulevich, A. V.; Zhdanko, A. G.; Orru, R. V. A.; Nenajdenko, V. G. *Chem. Rev.* **2010**, *110*, 5235. For selected examples, see: (b) Lygin, A. V.; Larionov, O. V.; Korotkov, V. S.; de Meijere, A. *Chem. - Eur. J.* **2009**, *15*, 227. (c) Liu, J.; Fang, Z.; Zhang, Q.; Liu, Q.; Bi, X. *Angew. Chem., Int. Ed.* **2013**, *52*, 6953. (d) Gao, M.; He, C.; Chen, H.; Bai, R.; Cheng, B.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 6958.
(14) Steuer, C.; Gege, C.; Fischl, W.; Heinonen, K. H.; Bartenschlager, R.; Klein, C. D. *Bioorg. Med. Chem.* **2011**, *19*, 4067.
(15) Dittami, J. P.; Bordner, J.; Decosta, D. L.; Kiplinger, J.; Reiche, P.; Ware, R. *Tetrahedron Lett.* **1995**, *36*, 4201.
(16) For review on silver acetylide, see: Halbes-Letinois, U.; Weibel, J.; Pale, P. *Chem. Soc. Rev.* **2007**, *36*, 759.
(17) Zalesskiy, S. S.; Khrustalev, V. N.; Kostukovich, A. Y.; Ananikov, V. P. *Organometallics* **2015**, *34*, 5214.
(18) For recent reviews on the roles of silver salts in palladium-catalyzed reactions, see: (a) Mudarra, Á. L.; Martínez de Salinas, S.; Pérez-Temprano, M. H. *Org. Biomol. Chem.* **2019**, *17*, 1655. (b) Bay, K. L.; Yang, Y.; Houk, K. N. *J. Organomet. Chem.* **2018**, *864*, 19.

DOI: 10.1021/acs.orglett.9b00137
Org. Lett. XXXX, XXX, XXX−XXX