ACS Combinatorial Science

Letter

Cite This: ACS Comb. Sci. XXXX, XXX, XXX−XXX

pubs.acs.org/acscombsci

Selenium-Catalyzed Carbonylative Synthesis of 3,4-Dihydroquinazolin-2(1*H*)-one Derivatives with TFBen as the CO Source

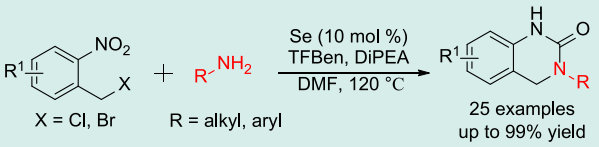
Rong Zhou,[†] Xinxin Qi,*[,†] and Xiao-Feng Wu*[,†,‡]

[†]Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, People's Republic of China

[‡]Leibniz-Institut für Katalyse e.V. an der, Institution Universität Rostock, Albert-Einstein-Straße 29a, Rostock 18059, Germany

Supporting Information

ABSTRACT: An efficient and general carbonylative procedure for the synthesis of 3,4-dihydroquinazolin-2(1*H*)-one from 1-(halomethyl)-2-nitrobenzenes and aryl/alkyl amines have been explored. In this approach, to avoid of using toxic CO gas, a solid and stable CO precursor, TFBen (benzene-1,3,5-triyl triformate), was utilized. With elemental selenium as the catalyst, a variety of aryl/alkyl amines has been tolerated well to afford the corresponding 3,4-dihydroquinazolin-2(1*H*)-one products in moderate to excellent yields under mild reaction condition.

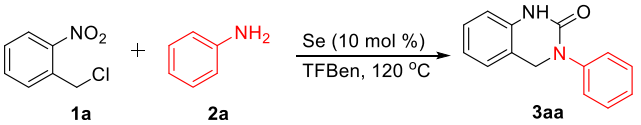


KEYWORDS: *carbonylative procedure, benzene-1,3,5-triyl triformate, elemental selenium, heterocycle synthesis*

Quinazolinones are a type of valuable structural scaffold in natural, pharmaceutical, and agrochemical products.[1] As a class of useful heterocycles, quinazolinones represent a wide range of biological activities, including anticancer, anticonvulsant, anti-inflammatory, antihypertensive, and diuretic properties.[2] As a consequence, numerous synthetic methods have been reported for the preparation of quinazolinones.[3,4] Typically, the strategies used in the synthesis of quinazolinones mainly rely on the condensation of anthranilic acid and its analogues with imidates or aldehydes.[3] Over recent years, transition-metal-catalyzed procedures have also emerged as effective alternatives.[4] Although some of the methods provide useful approaches for the construction of quinazolinones, some drawbacks, such as high temperature, multiple steps, long reaction times, and poor yields, are still exist. Thus, the development of an efficient and general strategy for the synthesis of quinazolinones is needed.

In recent decades, transition-metal-catalyzed carbonylation reactions have attracted intensive interest from the synthetic community for their wide application in the construction of carbonyl-containing compounds and have drawn attention for their applications in both academic and industrial fields.[5] In general, CO is used as one of the most important carbon source in carbonylation reactions. However, gaseous CO is toxic, flammable, and odorless and usually requires autoclave equipment. Unfortunately, these properties restrict its application in laboratory use. Thus, a variety of CO surrogates were explored in recent years, such as metal carbonyl complexes,[6] paraformaldehyde,[7] formic acid,[8] formates,[9] formamides,[10] alcohol,[11] CO_2,[12] and others.[13] On the other hand, transition metals, including palladium, ruthenium, rhodium, and iridium, have been commonly used in these carbonylative transformations. Nevertheless, in addition to the well-established noble metal systems, non-noble metal or metal-free conditions could possibly be more preferred in carbonylation reactions. Herein, we wish to report a selenium-catalyzed carbonylation reaction for the synthesis of 3,4-dihydroquinazolin-2(1*H*)-one derivatives with TFBen as the CO source.

Table 1. Screening of Reaction Conditions[a]



entry	base	solvent	time (h)	yield (%)[b]
1	Et_3N	DMF	24	54
2	Et_3N	DMSO	24	trace
3	Et_3N	1.4-dioxane	24	19
4	Et_3N	THF	24	40
5	Et_3N	toluene	24	4
6	Et_3N	DMF	28	71
7	DBU	DMF	28	trace
8	DiPEA	DMF	28	87
9	NaOH	DMF	28	55
10	K_2CO_3	DMF	28	trace
11	KOtBu	DMF	28	6

[a]Reaction conditions: 1-(chloromethyl)-2-nitrobenzene (1.0 mmol), aniline (1.5 mmol), Se (10 mol %), base (2.0 mmol), TFBen (1.5 mmol), and solvent (2 mL), 120 °C. [b]GC yield with dodecane as the internal standard.

Received: June 14, 2019
Revised: July 9, 2019
Published: July 18, 2019

DOI: 10.1021/acscombsci.9b00090
ACS Comb. Sci. XXXX, XXX, XXX−XXX

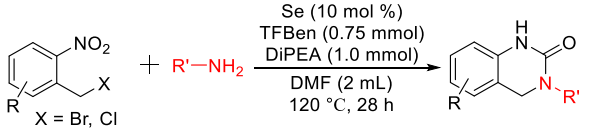
Initially, 1-(chloromethyl)-2-nitrobenzene and aniline were utilized as the model substrates, with selenium as the catalyst, Et_3N as the base, and TFBen as CO precursor in DMF at 120 °C for 24 h. To our delight, a 54% yield of the desired product was obtained (Table 1, entry 1). We next studied the effect of different solvents, including DMSO, 1,4-dioxane, THF, and toluene (Table 1, entries 2−5), DMF was found to be the optimal solvent. Because of the incomplete conversion of the substrates, subsequently, the reaction time was prolonged, and the yield of the target product increased to 71% (Table 1, entry 6). Moreover, various bases were investigated, such as DBU, DiPEA, NaOH, K_2CO_3, and KO^{t}Bu (Table 1, entries 7−11), it is noteworthy an 87% yield of the target product was produced with DiPEA as the base (Table 1, entry 8).

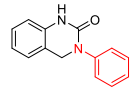
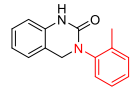
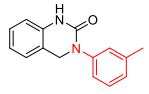
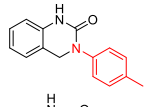
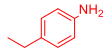
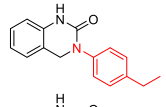
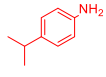
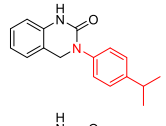
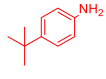
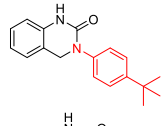
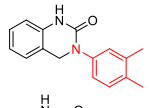
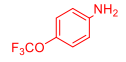
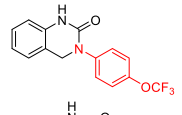
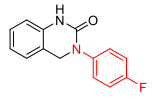
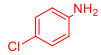
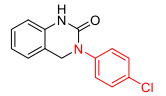
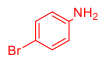
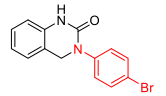
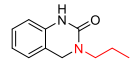
With the best reaction condition in hand, we next studied the substrate scope with a variety of amines (Table 2). Aryl amines with electron-donating group, such as methyl, ethyl, isopropyl, *tert*-butyl, and trifluoromethoxy group, all afforded the corresponding products in moderate to excellent yields (Table 2, entries 1−9). Notably, those substrates with *ortho*- and *para*-methyl groups resulted in higher yields than meta-substitution, probably due to the electronic effects. Aryl amines bearing halogen groups, including fluoro-, bromo-, and chloro-formed groups also afford the desired products in moderate to excellent yields (Table 2, entries 10−12). Moreover, the influence of alkyl amines has also been studied. Substrates bearing linear groups, such as propyl, butyl moieties, and heptyl groups worked well to produce the target products in moderate to good yields (Table 2, entries 13−15). Alkyl amine with *tert*-butyl group could also gave the desired product in good yield (Table 2, entry 16). Substrates containing cyclic groups including cyclopentyl, cyclohexyl, and 1-adamdantyl groups were investigated; the corresponding products were generated in moderate to good yields (Table 2, entries 17−19). Furthermore, 2-methoxyethan-1-amine could also afford the desired product in very good yield (Table 2, entry 20). We also tested 1-(bromomethyl)-2-nitrobenzenes with different aryl/alkyl amines; the reactions were tolerated well to afford the desired products in moderate to good yields (Table 2, entries 21−25).

On the basis of the above results, a proposed reaction mechanism is shown in Scheme 1. CO was initially generated from TFBen promoted by a base, and then reacted with selenium to afford carbonyl selenide (SeCO). At the same time, 1-(halomethyl)-2-nitrobenzenes **1** reacted with aryl/alkyl amines **2** to provide nitroanilines intermediate **I**, followed by a deoxygenation with SeCO to give nitrene intermediates **II**. Subsequently, isocyanate intermediate **III** was formed via the reaction of nitrene intermediates **II** with Se/CO, followed by an intramolecular nucleophilic addition to afford the final product **3**. The formation of CO_2 was also confirmed by bubbling the gas after the reaction into clear $Ca(OH)_2$ solution.

In conclusion, an efficient and convenient carbonylation reaction for the synthesis of 3,4-dihydroquinazolin-2(1*H*)-ones have been established. Through a selenium-catalyzed carbonylation reaction of 1-(halomethyl)-2-nitrobenzenes with aryl/alkyl amines using TFBen as the CO source. A variety of 3,4-dihydroquinazolin-2(1*H*)-one derivatives were generated in moderate to high yields under mild reaction conditions with good substrates toleration.

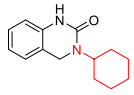
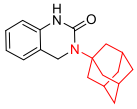
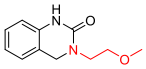
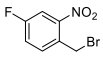
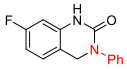
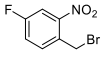
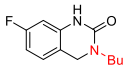
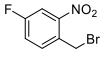
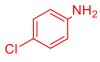
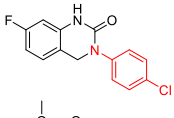
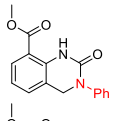
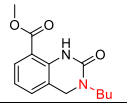
Table 2. Synthesis of 3,4-Dihydroquinazolin-2(1*H*)-ones[a]



Entry	Nitroarene	Amine	Product	Yield
1				86%
2				89%
3				77%
4				99%
5				81%
6				63%
7				72%
8				93%
9				53%
10				93%
11				95%
12				96%
13		$PrNH_2$		54%
14		$BuNH_2$		76%
15		1-Heptanamine		70%
16		$tBuNH_2$		76%
17				62%

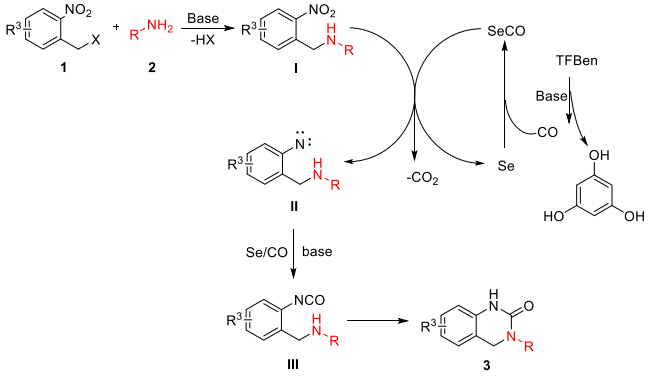
DOI: 10.1021/acscombsci.9b00090
ACS Comb. Sci. XXXX, XXX, XXX−XXX

Table 2. continued

Entry	Nitroarene	Amine	Product	Yield
18				75%
19				64%
20				83%
21				66%
22		$BuNH_2$		71%
23				40%
24				36%
25		$BuNH_2$		48%

[a]Reaction conditions: nitroarene (0.5 mmol), amines (0.75 mmol), Se (10 mol %), DiPEA (1.0 mmol), TFBen (0.75 mmol), DMF (2 mL), 120 °C, 28 h, isolated yield.

Scheme 1. Plausible Reaction Mechanism



EXPERIMENTAL PROCEDURES

Selenium (10 mol %), TFBen (0.75 mmol; 2.25 mmol of CO), and 1-(halomethyl)-2-nitrobenzenes (0.5 mmol) were added to a 15 mL tube equipped with a magnetic stirrer, which was then placed under vacuum and refilled with nitrogen three times. Aryl/alkyl amines (0.75 mmol), DMF (2 mL) and DiPEA (1.0 mmol) were added to the reaction tube; then, the tube was sealed, and the mixture was stirred at 120 °C for 28 h. After the reaction was completed, the mixture was filtered, extracted with ethyl acetate and concentrated under vacuum. The crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/2) to afford the desired product.

***Caution**: Because of the generation of CO gas from TFBen, special attention should be paid and proper protection should be given during the manipulation and workup process.*

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscombsci.9b00090.

General comments, general procedure, analytic data, and NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: xinxinqi@zstu.edu.cn.

*E-mail: xiao-feng.wu@catalysis.de.

ORCID

Xiao-Feng Wu: 0000-0001-6622-3328

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the financial supports from NSFC (21772177, 21602201).

REFERENCES

(1) (a) Dreyer, D. L.; Brenner, R. C. Alkaloids of Some Mexican Zanthoxylum Species. *Phytochemistry* **1980**, *19*, 935−939. (b) Alagarsamy, V.; Raja Solomon, V.; Dhanabal, K. Design and Synthesis of 2-Methylthio-3-substituted-5,6-dimethylthieno [2,3-d] pyrimidin-4(3H)-ones as analgesic, Anti-inflammatory and Antibacterial Agents. *Bioorg. Med. Chem.* **2007**, *15*, 235−241. (c) Rzasa, R. M.; Kaller, M. R.; Liu, G.; Magal, E.; Nguyen, T. T.; Osslund, T. D.; Powers, D.; Santora, V. J.; Viswanadhan, V. N.; Wang, H.-L.; Xiong, X.; Zhong, W.; Norman, M. H. Structure-activity Relationships of 3,4-Dihydro-1*H*-quinazolin-2-one Derivatives as Potential CDK5 Inhibitors. *Bioorg. Med. Chem.* **2007**, *15*, 6574−6595.

(2) (a) Ismail, M. A. H.; Barker, S.; Abou El Ella, D. A.; Abouzid, K. A. M.; Toubar, R. A.; Todd, M. H. Design and Synthesis of New Tetrazoly-and Carboxy-biphenylylmethyl-quinazolin-4-one derivatives as Angiotensin II AT1 Receptor Antagonists. *J. Med. Chem.* **2006**, *49*, 1526−1535. (b) Goto, S.; Tsuboi, H.; Kanoda, M.; Mukai, K.; Kagara, K. The Process Development of a Novel Aldose Reductase Inhibitor, FK366. Part 1. Improvement of Discovery Process and New Syntheses of 1-Substituted Quinazolinediones. *Org. Process Res. Dev.* **2003**, *7* (5), 700−706. (c) Park Choo, H.-Y.; Kim, M.; Lee, S. K.; Woong Kim, S.; Kwon Chung, I. Solid-phase Combinatorial Synthesis and Cytotoxicity of 3-Aryl-2,4-quinazolindiones. *Bioorg. Med. Chem.* **2002**, *10*, 517−523. (d) Buckley, G. M.; Davies, N.; Dyke, H. J.; Gilbert, P. J.; Hannah, D. R.; Haughan, A. F.; Hunt, C. A.; Pitt, W. R.; Profit, R. H.; Ray, N. C.; Richard, M. D.; Sharpe, A.; Taylor, A. J.; Whitworth, J. M.; Williams, S. C. Quinazolinethiones and Quinazolinediones, Novel Inhibitors of Inosine Monophosphate Dehydrogenase: Synthesis and Initial Structure-activity Relationships. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 751−754. (e) Chan, J. H.; Hong, J. S.; Kuyper, L. F.; Jones, M. L.; Baccanari, D. P.; Tansik, R. L.; Boytos, C. M.; Rudolph, S. K.; Brown, A. D. Selective Inhibitors of Candida Albicans Dihydrofolate Reductase: Activity and Selectivity of 5-(Arylthio)-2,4-diaminoquinazolines. *J. Heterocycl. Chem.* **1997**, *34*, 145−151. (f) Dempcy, R. Q.; Skibo, E. B. Rational Design of Quinazoline-based Irreversible Inhibitors of Human Erythrocyte Purine Nucleoside Phosphorylase. *Biochemistry* **1991**, *30*, 8480−8487. (g) Campbell, S. F.; Davey, M. Doxazosin, A Case History. *J. Drug Design Delivery* **1986**, *1*, 83−99. (h) Imagawa, J.; Sakai, K. Further Evaluation of the Selectivity of a Novel Antihypertensive Agent, SGB-1534, for Peripheral α1-Adrenoceptors in the Spinally Anestherized Dog. *Eur. J. Pharmacol.* **1986**, *131*, 257−264.

(3) (a) Ried, W.; Sinharay, A. Über 2-Aziridino-1-phenyl-cyclobutendion(3,4). *Chem. Ber.* **1963**, *96*, 3306−3311. (b) Henne-

DOI: 10.1021/acscombsci.9b00090
ACS Comb. Sci. XXXX, XXX, XXX−XXX

quin, L. F.; Boyle, F. T.; Wardleworth, J. M.; Marsham, P. R.; Kimbell, R.; Jackman, A. L. Quinazoline Antifolates Thymidylate Synthase Inhibitors: Lipophilic Analogues with Modification to the C2-Methyl Substituent. *J. Med. Chem.* **1996**, *39*, 695−704. (c) Connolly, D. J.; Guiry, P. J. A Facile and Versatile Route to 2-Substituted-4(3H)-quinazolinones and Quinazolines. *Synlett* **2001**, 1707−1710. (d) Connolly, D. J.; Cusack, D.; O'Sullivan, T. P.; Guiry, P. J. Synthesis of Quinazolinones and Quinazolines. *Tetrahedron* **2005**, *61*, 10153−10202.

(4) (a) Picos-Corrales, L. A.; Sarmiento-Sanchez, J. I. Microwave-assisted Synthesis of Benzoxazinediones under Solvent-free Conditions. *Chem. Heterocycl. Compd.* **2018**, *54*, 762−764. (b) Maiden, T. M. M.; Harrity, J. P. A. Recent Developments in Transition Metal Catalysis for Quinazolinone Synthesis. *Org. Biomol. Chem.* **2016**, *14*, 8014−8025. (c) Abdou, I. M.; Al-Neyadi, S. S. Synthesis and Antimicrobial Evaluation of Newly Synthesized N,S-bisphosphonate Derivatives. *Heterocycl. Commun.* **2015**, *21*, 115−132. (d) Rohokale, R. S.; Kshirsagar, U. A. Advanced Synthetic Strategies for Constructing Quinazolinone Scaffolds. *Synthesis* **2016**, *48*, 1253−1268. (e) He, L.; Li, H.; Chen, J.; Wu, X.-F. Recent Advances in 4(3H)-Quinazolinone Syntheses. *RSC Adv.* **2014**, *4*, 12065−12077.

(5) For selected recent reviews, see: (a) Brennführer, A.; Neumann, H.; Beller, M. Palladium-catalyzed Carbonylation Reactions of Aryl Halides and Related Compounds. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114−4133. (b) Peng, J.-B.; Qi, X.; Wu, X.-F. Visible Light-induced Carbonylation Reactions with Organic Dyes as the Photosensitizers. *ChemSusChem* **2016**, *9*, 2279−2283. (c) Liu, Q.; Zhang, H.; Lei, A. Copper-catalyzed Cross-coupling Reaction of Organoboron Compounds with Primary Alkyl Halides and Pseudohalides. *Angew. Chem., Int. Ed.* **2011**, *50*, 10788−10799. (d) Gabriele, B.; Mancuso, R.; Salerno, G. Oxidative Carbonylation as a Powerful Tool for the Direct Synthesis of Carbonylated Heterocycles. *Eur. J. Org. Chem.* **2012**, *2012*, 6825−6839. (e) Peng, J.-B.; Qi, X.; Wu, X.-F. Recent Achievements in Carbonylation Reactions: A Personal Account. *Synlett* **2017**, *28*, 175−194. (f) Wu, X.-F. Palladium-catalyzed Carbonylative Transformation of Aryl Chlorides and Aryl Tosylates. *RSC Adv.* **2016**, *6*, 83831−83837. (g) Peng, J.- B.; Wu, F.-P.; Wu, X.-F. First-row Transition-metal-catalyzed Carbonylative Transformations of Carbon Electrophiles. *Chem. Rev.* **2019**, *119*, 2090−2127.

(6) (a) Chen, J.; Natte, K.; Wu, X.-F. Palladium-catalyzed Carbonylative Cyclization of Arenes by C-H Bond Activation with DMF as the Carbonyl Source. *J. Organomet. Chem.* **2016**, *803*, 9−12. (b) Kim, D.-S.; Park, W.-J.; Lee, C.-H.; Jun, C.-H. Hydroesterification of Alkenes with Sodium Formate and Alcohols Promoted by Cooperative Catalysis of $Ru_3(CO)_{12}$ and 2-Pyridinemethanol. *J. Org. Chem.* **2014**, *79*, 12191−12196. (c) Wu, X.-F.; Oschatz, S.; Sharif, M.; Flader, A.; Krey, L.; Beller, M.; Langer, P. Palladium-catalyzed Carbonylative Synthesis of Phthalimides from 1,2-Dibromoarenes with Molybdenum Hexacarbonyl as Carbon Monoxide Source. *Adv. Synth. Catal.* **2013**, *355*, 3581−3585. (d) Wu, X.-F.; Sharif, M.; Shoaib, K.; Neumann, H.; Pews-Davtyan, A.; Langer, P.; Beller, M. A Convenient Palladium-catalyzed Carbonylative Synthesis of 2-Aminbenzoxazinones from 2-Bromoanilines and Isocyanates. *Chem. - Eur. J.* **2013**, *19*, 6230−6233. (e) Jafarpour, F.; Rashidi-Ranjbar, P.; Kashani, A. O. Easy-to-execute Carbonylative Arylation of Aryl Halides Using Molybdenum Hexacarbonyl: Efficient Synthesis of Unsymmetrical Diaryl Ketones. *Eur. J. Org. Chem.* **2011**, *2011*, 2128−2132. (f) Nordeman, P.; Odell, L. R.; Larhed, M. Synthesis of 4-Quinolonesvia a Carbonylative Sonogashira Cross-coupling using Molybdenum Hexacarbonyl as a CO Source. *J. Org. Chem.* **2012**, *77*, 11393−11398.

(7) (a) Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. CO-transfer Carbonylation Reactions. A Catalytic Pauson-Khand-type Reaction of Enynes with Aldehydes as a Source of Carbon Monoxide. *J. Am. Chem. Soc.* **2002**, *124*, 3806−3807. (b) Shibata, T.; Toshida, N.; Takagi, K. Catalytic Pauson-Khand-type Reaction using Aldehydes as a CO Source. *Org. Lett.* **2002**, *4*, 1619−1621. (c) Morimoto, T.; Yamasaki, K.; Hirano, A.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K.; Harada, Y.; Fukumoto, Y.; Chatani, N.; Nishioka, T. Rh(I)-catalyzed CO Gas-free Carbonylative Cyclization Reactions of Alkynes with 2-Bromophenylboronic Acids using Formaldehyde. *Org. Lett.* **2009**, *11*, 1777−1780. (d) Li, W.; Wu, X.-F. Palladium-catalyzed Carbonylative Synthesis of Benzoxazinones from N-(o-Bromoaryl)-amides using Paraformaldehyde as the Carbonyl Source. *J. Org. Chem.* **2014**, *79*, 10410−10416. (e) Natte, K.; Dumrath, A.; Neumann, H.; Beller, M. Palladium-catalyzed Carbonylations of Aryl Bromides using Paraformaldehyde: Synthesis of Aldehydes and Esters. *Angew. Chem., Int. Ed.* **2014**, *53*, 10090−10094.

(8) (a) Qi, X.; Jiang, L.-B.; Li, C.-L.; Li, R.; Wu, X.-F. Palladium-catalyzed One-pot Carbonylative Sonogashira Reaction Employing Formic Acid as the CO Source. *Chem. - Asian J.* **2015**, *10*, 1870−1873. (b) Qi, X.; Jiang, L.-B.; Li, H.-P.; Wu, X.-F. A Convenient Palladium-catalyzed Carbonylative Suzuki Coupling of Aryl Halides with Formic Acid as the Carbon Monoxide Source. *Chem. - Eur. J.* **2015**, *21*, 17650−17656. (c) Qi, X.; Li, H.-P.; Wu, X.-F. A Convenient Palladium-catalyzed Carbonylative Synthesis of Benzofuran-2(3H)-ones with Formic Acid as the CO Source. *Chem. - Asian J.* **2016**, *11*, 2453−2457. (d) Qi, X.; Li, C.-L.; Jiang, L.-B.; Zhang, W.-Q.; Wu, X.-F. Palladium-catalyzed Alkoxycarbonylation of Aryl Halides with Phenols Employing Formic Acid as the CO Source. *Catal. Sci. Technol.* **2016**, *6*, 3099−3107. (e) Jiang, L.-B.; Li, R.; Li, H.-P.; Qi, X.; Wu, X.-F. Palladium-catalyzed Carbonylative Synthesis of Aryl Formates under Mild Conditions. *ChemCatChem* **2016**, *8*, 1788−1791. (f) Qi, X.; Li, C.-L.; Wu, X.-F. A Convenient Palladium-catalyzed Reductive Carbonylation of Aryl Iodides with Dual Role of Formic Acid. *Chem. - Eur. J.* **2016**, *22*, 5835−5838. (g) Qi, X.; Li, R.; Wu, X.-F. Selective Palladium-catalyzed Carbonylative Synthesis of Aurones with Formic Acid as the CO Source. *RSC Adv.* **2016**, *6*, 62810−62813. (h) Jiang, L.-B.; Qi, X.; Wu, X.-F. Manganese-catalyzed Sonogashira Coupling of Aryl Iodides. *Tetrahedron Lett.* **2016**, *57*, 3368−3370. (i) Li, H.-P.; Ai, H.-J.; Qi, X.; Peng, J.-B.; Wu, X.-F. Palladium-catalyzed Carbonylative Synthesis of Benzofuran-2(3*H*)-ones from 2-Hydroxybenzyl Alcohols using Formic Acid as the CO Source. *Org. Biomol. Chem.* **2017**, *15*, 1343−1345. (j) Wu, F.-P.; Peng, J.-B.; Meng, L.-S.; Qi, X.; Wu, X.-F. Palladium-catalyzed Ligand-controlled Selective Synthesis of Aldehydes and Acids from Aryl Halides and Formic Acid. *ChemCatChem* **2017**, *9*, 3121−3124. (k) Wu, F.-P.; Peng, J.-B.; Qi, X.; Wu, X.-F. Palladium-catalyzed Carbonylative Sonogashira Coupling of Aryl Diazonium Salts with Formic Acid as the CO Source: the Effect of 1,3-Butadiene. *Catal. Sci. Technol.* **2017**, *7*, 4924−4928. (l) Peng, J.-B.; Wu, F.-P.; Li, C.-L.; Qi, X.; Wu, X.-F. A Convenient and Efficient Palladium-catalyzed Carbonylative Sonogashira Transformation with Formic Acid as the CO Source. *Eur. J. Org. Chem.* **2017**, *2017*, 1434−1437. (m) Wu, F.-P.; Peng, J.-B.; Qi, X.; Wu, X.-F. Palladium-catalyzed Carbonylative Transformation of Organic Halides with Formic Acid as the Coupling Partner and CO Source: Synthesis of Carboxylic Acids. *J. Org. Chem.* **2017**, *82*, 9710−9714. (n) Wu, F.-P.; Peng, J.-B.; Fu, L.-Y.; Qi, X.; Wu, X.-F. Direct Palladium-catalyzed Carbonylative Transformation of Allylic Alcohols and Related Derivatives. *Org. Lett.* **2017**, *19*, 5474−5477. (o) Qi, X.; Ai, H.-J.; Zhang, N.; Peng, J.-B.; Ying, J.; Wu, X.-F. Palladium-catalyzed Carbonylative Bis(indolyl)methanes Synthesis with TFBen as the CO Source. *J. Catal.* **2018**, *362*, 74−77. (p) Wu, F.-P.; Peng, J.-B.; Qi, X.; Wu, X.-F. Palladium-catalyzed Carbonylative Homocoupling of Aryl Iodides for the Synthesis of Symmetrical Diaryl Ketones with Formic Acid. *ChemCatChem* **2018**, *10*, 173−177.

(9) (a) Formenti, D.; Ferretti, F.; Ragaini, F. Synthesis of N-Heterocycles by Reductive Cyclization of Nitro Compounds using Formate Esters as Carbon Monoxide Surrogates. *ChemCatChem* **2018**, *10*, 148−152. (b) Konishi, H.; Nagase, H.; Manabe, K. Concise Synthesis of Cyclic Carbonyl Compounds from Haloarenes using Phenyl Formate as the Carbonyl Source. *Chem. Commun.* **2015**, *51*, 1854−1857. (c) Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Facile Palladium-catalyzed Hydrocarboxylation of Olefins without External CO Gas. *Org. Lett.* **2014**, *16*, 5960−5963. (d) Li, H.; Neumann, H.; Beller, M.; Wu, X.-F. Aryl Formate as Bifunctional Reagent: Applications in Palladium-catalyzed Carbonylative Coupling Reac-

DOI: 10.1021/acscombsci.9b00090
ACS Comb. Sci. XXXX, XXX, XXX−XXX

tions using in situ Generated CO. *Angew. Chem., Int. Ed.* **2014**, *53*, 3183−3186. (e) Ueda, T.; Konishi, H.; Manabe, K. Palladium-catalyzed Reductive Carbonylation of Aryl Halides with N-Formylsaccharin as a CO Source. *Angew. Chem., Int. Ed.* **2013**, *52*, 8611−8615. (f) Ueda, T.; Konishi, H.; Manabe, K.; et al. Remarkable Improvement Achieved by Imidazole Derivatives in Ruthenium-catalyzed Hydroesterification of Alkenes using Formates. *Org. Lett.* **2012**, *14*, 4722−4725. (g) Ueda, T.; Konishi, H.; Manabe, K. Trichlorophenyl Formate: Highly Reactive and Easily Accessible Crystalline CO Surrogate for Palladium-catalyzed Carbonylation of Aryl/alkenyl Halides and Triflates. *Org. Lett.* **2012**, *14*, 5370−5373. (h) Ueda, T.; Konishi, H.; Manabe, K. Palladium-catalyzed Carbonylation of Aryl, Alkenyl, and Allyl Halides with Phenyl Formate. *Org. Lett.* **2012**, *14*, 3100−3103. (i) Fujihara, T.; Hosoki, T.; Katafuchi, Y.; Iwai, T.; Terao, J.; Tsuji, Y. Palladium-catalyzed Esterification of Aryl Halides using Aryl Formates without the Use of External Carbon Monoxide. *Chem. Commun.* **2012**, *48*, 8012−8014. (j) Katafuchi, Y.; Fujihara, T.; Iwai, T.; Terao, J.; Tsuji, Y. Palladium-catalyzed Hydroesterification of Alkynes Employing Aryl Formates without the Use of External Carbon Monoxide. *Adv. Synth. Catal.* **2011**, *353*, 475−482. (k) Ko, S.; Lee, C.; Choi, M.-G.; Na, Y.; Chang, S. Chelation-accelerated Sequential Decarbonylation of Formate and Alkoxycarbonylation of Aryl Halides using a Combined Ru and Pd Catalyst. *J. Org. Chem.* **2003**, *68*, 1607−1610.

(10) (a) Chen, J.; Feng, J.-B.; Natte, K.; Wu, X.-F. Palladium-catalyzed Carbonylative Cyclization of Arenes by C-H Bond Activation with DMF as the Carbonyl Source. *Chem. - Eur. J.* **2015**, *21*, 16370−16373. (b) Wu, X.; Zhao, Y.; Ge, H. Direct Aerobic Carbonylation of $C(sp^2)$-H and $C(sp^3)$-H Bonds Through Ni/Cu Synergistic Catalysis with DMF as the Carbonyl Source. *J. Am. Chem. Soc.* **2015**, *137*, 4924−4927.

(11) (a) Verendel, J. J.; Nordlund, M.; Andersson, P. G. Selective Metal-catalyzed Transfer of H_2 and CO from Polyols to Alkenes. *ChemSusChem* **2013**, *6*, 426−429. (b) Christensen, S. H.; Olsen, E. P. K.; Rosenbaum, J.; Madsen, R. Hydroformylation of Olefins and Reductive Carbonylation of Aryl Halides with Syngas Formed *ex-situ* from Dehydrogenative Decarbonylation of Hexane-1,6-diol. *Org. Biomol. Chem.* **2015**, *13*, 938−945.

(12) (a) Laitar, D. S.; Müller, P.; Sadighi, J. P. Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO. *J. Am. Chem. Soc.* **2005**, *127*, 17196−17197. (b) Kleeberg, C.; Cheung, M. S.; Lin, Z.; Marder, T. B. Copper-mediated Reduction of CO_2 with PinB-$SiMe_2$Ph via CO_2 Insertion into a Copper-silicon Bond. *J. Am. Chem. Soc.* **2011**, *133*, 19060−19063.

(13) (a) Wang, Z.; Yin, Z.; Wu, X.-F. Copper-catalyzed Carbonylative Transformations of Indoles with Hexaketocyclohexane. *Chem. Commun.* **2018**, *54*, 4798−4801. (b) Zhao, H.; Du, H.; Yuan, X.; Wang, T.; Han, W. Iron-catalyzed Carbonylation of Aryl Halides with Arylborons using Stoichiometric Chloroform as the Carbon Monoxide Source. *Green Chem.* **2016**, *18*, 5782−5787. (c) Korsager, S.; Taaning, R. H.; Skrydstrup, T. Effective Palladium-catalyzed Hydroxycarbonylation of Aryl Halides with Substoichiometric Carbon Monoxide. *J. Am. Chem. Soc.* **2013**, *135*, 2891−2894. (d) Burhardt, M. N.; Taaning, R. H.; Skrydstrup, T. Pd-catalyzed Thiocarbonylation with Stoichiometric Carbon Monoxide: Scope and Applications. *Org. Lett.* **2013**, *15*, 948−951. (e) Cunico, R. F.; Maity, B. C. Direct Carbamoylation of Alkenyl Halides. *Org. Lett.* **2003**, *5*, 4947−4949. (f) Morimoto, T.; Kakiuchi, K. Evolution of Carbonylation Catalysis: No Need for Carbon Monoxide. *Angew. Chem., Int. Ed.* **2004**, *43*, 5580−5588. (g) Jiang, L.-B.; Qi, X.; Wu, X.-F. Benzene-1,3,5-triyl Triformate (TFBen): A Convenient, Efficient, and Non-reacting CO Source in Carbonylation Reactions. *Tetrahedron Lett.* **2016**, *57*, 3368−3370.

DOI: 10.1021/acscombsci.9b00090
ACS Comb. Sci. XXXX, XXX, XXX−XXX