Advanced Synthesis & Catalysis

Accepted Article

Title: Synthesis of Indenones via Palladium-Catalyzed Ligand-Free Carbonylation

Authors: Juan Song, Haisen Sun, Wei Sun, Yuxuan Fan, Cui Li, Haotian Wang, Kang Xiao, and Yan Qian

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201901309

Link to VoR: http://dx.doi.org/10.1002/adsc.201901309

10.1002/adsc.201901309

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Synthesis of Indenones via Palladium-Catalyzed Ligand-Free Carbonylation

Juan Song*, Haisen Sun, Wei Sun, Yuxuan Fan, Cui Li, Haotian Wang, Kang Xiao and Yan Qian

Key Laboratory for Organic Electronics and Information Display and Institute of Advanced Materials, Nanjing Univer-sity of Posts and Telecommunications, Nanjing 210023, Jiangsu, China
E-mail: iamjsong@njupt.edu.cn

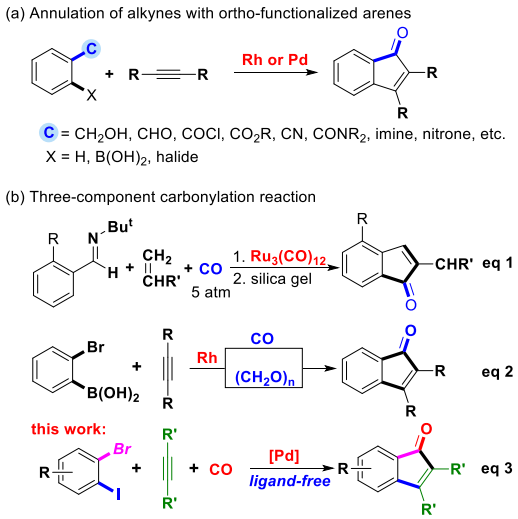
Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A palladium-catalyzed ligand-free carbonylation reaction has been developed for the synthesis of indenones. Under CO atmosphere, this cascade reaction proceeded smoothly to provide the desired indenones in moderate to excellent yields with good functional-group compatibility. The mechanistic investigations suggested the in situ formation of palladium nanoparticles and this transfor-mation was driven by a controlled reaction sequence of alkyne insertion followed by carbonylation and annulation to form the indenone framework.

Keywords: palladium-catalyzed; ligand-free; carbonylation; indenones.

Indenones, widely existing in natural products and synthetically bioactive molecules,[1] have attracted considerable synthetic interests and a number of methods have been developed including intramolecular cyclization,[2] two-component annulation[3-11] and a few examples of three-component annulation.[12] However, most of starting substrates of intramolecular cyclization were not readily commercially available and therefore suffered from multiple-step syntheses or narrow substrate scopes. Up to now, researches of efficient methods for preparation of indenones mainly have focused on two-component annulation, including transition-metal-mediated cyclization,[3], [5-9] radical cyclization,[11] Friedel-Crafts-type cyclization[4] and so on. Among them, the preferred strategies are Rh[9] or Pd[7] catalyzed annulation of alkynes with *ortho*-functionalized arenes(Scheme 1, **a**), which are usually time-requiring multiple functional transformation and thus less efficiency in a synthetic sequence. Therefore, it would be appealing if the introduction of carbonyl functional group of indenones through CO insertion rather than tedious pre-carbo-functionalized arenes. In the past decades, transition-metal-catalyzed carbonylation reactions have become a powerful tool for the direct construction of a wide variety of carbonyl-containing compounds. CO is employed as a less expensive, atom-economical and readily available C1 feedstock in a broad range of industrial chemical processes. In 1997, Murai's group[12d] reported a method for the preparation of indenones by $Ru_3(CO)_{12}$-catalyzed carbonylation reaction of aromatic imines and olefins (5 atm. of CO, Scheme 1, **b**, eq.1). Chatani's group[12c] reported a Rh-catalyzed three-component carbonylative cyclization of alkynes with 2-bromophenylboronic acid leading to indenones by CO insertion in 2007. And later, Morimoto's group[12b] reported a similar reaction by decarbonylation of formaldehyde and sequential carbonylation in 2009 (Scheme 1, **b**, eq. 2). Although palladium-catalyzed carbonylation reactions have been well studied and employed to manufacture a range of important industrial products, the π-acidic CO binding to palladium resulting in the difficulty of oxidative addition to aryl halides and also remarkably decrease the catalytic efficiency because of the formation of palladium black. To overcome the inherent limitation of these carbonylation reactions, most of the processes have utilized the ligands to keep the catalytic activity and lifetime of catalysts.[17] Thus, development of a ligand-free palladium-catalyzed carbonylation reaction under atmospheric pressure remains a challenge. Herein, we disclosed the first report on the construction of in denones by a ligand-free Pd-catalyzed multi-component cyclocarbonylation of *o*-bromoaryl iodides with alkynes



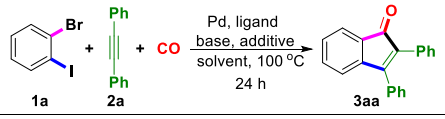
Scheme 1. Construction of Indenones

10.1002/adsc.201901309

under ambient pressure of CO (Scheme 1, c). In this cascade transformation, three new carbon–carbon single bonds were formed in one operation and thus a simple and efficient protocol for the construction of the indenone framework was established by readily available substrates.

In an initial attempt, commercially available *o*-bromophenyl iodide (**1a**) and diphenylacetylene (**2a**) were chosen for the exploration of this palladium-catalyzed cyclocarbonylation reaction under a balloon CO atmosphere. In the presence of $Pd(CH_3CN)_2Cl_2$/dppp (1,3-bis(diphenylphosphaneyl)propane) as the catalyst, KOAc as the base and PivOH as an additive in 1,4-dioxane at 100 °C for 24 h, to our delightfulness, it was found that 13% of the desired indenone (**3aa**) was observed. This preliminary result inspired us to further optimize this novel carbonylation reaction. Subsequently, the effects on the reaction with various factors, such as palladium catalyst precursors, ligands, bases and so on, were carefully examined. Unfortunately, no improved result was obtained.[13] Among the experimental results, it was noted that 12% of **3aa** was achieved in a reaction in the absence of ligand (Table 1, entry 1), together with the observation of quite a lot of palladium black. This result strongly suggested that ligands might be unnecessary in the reaction. Therefore, our efforts were devoted to seeking an appropriate condition, which can prevent the formation of palladium black, in other words, some additives were needed to stabilize the potential Pd(0). Accordingly, the yield of **3aa** was significantly improved to 80% when 1 equiv. of tetra-*n*-butyl ammonium bromide (TBAB) was introduced to the reaction system (Table 1, entry 3). Again, the bases and the solvents were screened another time but no improvement anymore (Table 1, entries 4-11). In the investigation of palladium sources (Table 1, entries 12-15),

Table 1. Screen of Reaction Conditions [a]



entry	[Pd]	base	additive	solvent	yield (%)
1	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	/	1,4-dioxane	12
2	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	PEG-400	1,4-dioxane	n.d.
3	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	TBAB	1,4-dioxane	80
4	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	TBAB	1,4-dioxane	57
5	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	TBAB	1,4-dioxane	n.d.
6	$Pd(CH_3CN)_2Cl_2$	K_3PO_4	TBAB	1,4-dioxane	65
7	$Pd(CH_3CN)_2Cl_2$	KOAc	TBAB	1,4-dioxane	6
8	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	TBAB	DMF	trace
9	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	TBAB	DMSO	n.d.
10	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	TBAB	toluene	62
11[b]	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	TBAB	CH_3CN	74
12	$Pd(OAc)_2$	Na_2CO_3	TBAB	1,4-dioxane	21
13	$PdCl_2(PPh_3)_2$	Na_2CO_3	TBAB	1,4-dioxane	n.d.
14	$PdCl_2$	Na_2CO_3	TBAB	1,4-dioxane	84
15	$Pd(dba)_2$	Na_2CO_3	TBAB	1,4-dioxane	74
16[c]	$PdCl_2$	Na_2CO_3	TBAB	1,4-dioxane	95
17[d]	$PdCl_2$	Na_2CO_3	TBAB	1,4-dioxane	99 (97[e])

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.25 mmol), Pd (10 mol%), base (0.75 mmol), additive (0.25 mmol) under CO (balloon) in solvent (2 mL) at 100 °C for 24 h. The yields were determined by GC with naphthalene as the internal standard. [b] 80 °C. [c] 1 mL of solvent. d 2 equiv. of Na_2CO_3. [e] isolated yield.

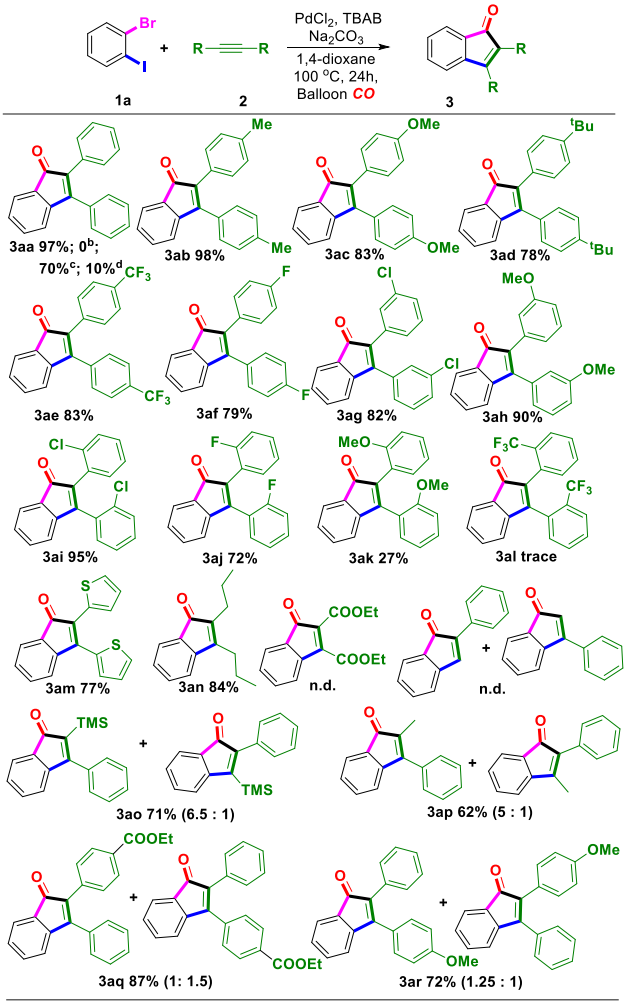
$PdCl_2$ exhibited a marginal higher yield (85%, Table 1, entry 14). Surprisingly, the yield of **3aa** was further improved to 95% when reducing the solvent from 2 mL to 1 mL (Table 1, entry 14 versus entry 16), and almost all diphenylacetylene (**2a**) was quantitatively converted into indenone **3aa** as decreasing the base of Na_2CO_3 loading from 3 equiv. to 2 equiv. (Table 1, entry 16 versus entry 17). Thus, a highly efficient Pd-catalyzed three-component carbonylation reaction was successfully established and the optimal reaction conditions were summarized as following: the reaction was carried out with *o*-bromophenyl iodide (**1a**, 2 equiv.), diphenylacetylene (**2a**, 1 equiv.), $PdCl_2$ (10 mol%), Na_2CO_3 (2 equiv.) and TBAB (1 equiv.) under a balloon CO atmosphere in 1,4-dioxane (1 mL) at 100 °C for 24 h. With this optimal procedure, up to 97% of indenone **3aa** was isolated.

The optimized reaction conditions were then applied to extend the generality of this newly established cascade Pd-catalyzed three-component transformation. A variety of alkynes were subjected to the reactions with *o*-bromophenyl iodide (**1a**) under CO atmosphere. The results were summarized in Table 2. The diarylacetylenes bearing either electron-donating groups, such as, Me (**3ab**), OMe (**3ac**, **3ah**), *t*-Bu (**3ad**) or electron-withdrawing groups, such as, CF_3 (**3ae**), F (**3af**), Cl (**3ag**) at *para*- or *meta*- position were well tolerated and proceeded smoothly to afford the corresponding products in good to excellent yields (78%-98%) (Scheme 2) and no obvious electron effect of the substituents were observed from these experimental results. However, the diarylacetylenes with groups at *ortho*-position, such as, OCH_3 (**3ak**), CF_3 (**3al**) afforded the corresponding indenones in low yields, which indicating a significant steric effect, and owing to the small steric profile of Cl and F, the *ortho*-chloro- and fluoro-substituted diphenylacetylene could be unexpectedly well tolerated and the corresponding indenone product **3ai** and **3aj** were obtained in good yield (95% or 72%). It was noteworthy that 1,2-di(2-thiophenyl)ethyne was an effective substrate for the transformation and produced the corresponding product **3am** in 77% yield. This result was extremely attractive because the thiophene contained motifs are widely used as the functionalized organic materials with their characteristic properties, while the syntheses of this type compounds have remained challenge in many transition-metal-catalyzed reactions where the catalysts can be usually deactivated by sulfur. Furthermore, a dialkylacetylene, 4-octyne, was also applied to the procedure, providing the annulation product **3an** in good yield (84%). However, in the case of diethyl but-2-ynedioate, no product obtained in the reaction. Some unsymmetrical internal alkynes were also tested in the reaction, except phenylethyne that no desired product obtained, all unsymmetrical alkynes gave the mixture of regio-isomers (**3ao, 3ap, 3aq, 3ar**). For trimethylsilyl phenylacetylene, a mixture **3ao** was isolated in 71% yield, and the ratio of two regio-isomers was 6.5:1, indicating the impact of steric hindrance on regioselectivities. The unsymmetrical alkyne bearing methyl and phenyl groups also gave a mixture of regio-isomers (**3ap**), the ratio of which was 5:1. Interestingly, if *o*-bromophenyl iodide (**1a**) was replaced by o-chlorophenyl iodide, the corresponding product of **3aa** was obtained in 70% yield. However, no

10.1002/adsc.201901309

3aa obtained for 1,2-dibromobenzene, and only 10% yield of **3aa** obtained for 1,2-diiodobenzene.

Table 2. Scope of alkyne substrates [a]

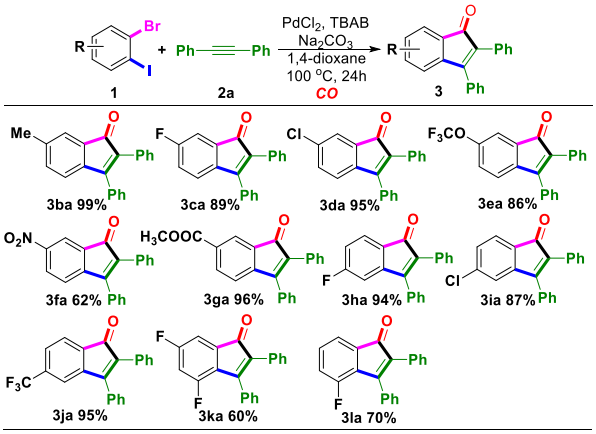


[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.25 mmol), $PdCl_2$ (0.025 mmol), Na_2CO_3 (0.5 mmol), TBAB (0.25 mmol), 1, 4-dioxane (1 mL) at 100 °C for 24h under CO (1atm balloon). Isolated yield. [b] *o*-bromophenyl iodide (**1a**) was replaced by 1,2-dibromobenzene. [c] *o*-bromophenyl iodide (**1a**) was replaced by *o*-chlorophenyl iodide. [d] *o*-bromophenyl iodide (**1a**) was replaced by 1,2-diiodobenzene.

Successively, the scope of various substituted *o*-bromophenyl iodides with diphenylacetylene (**2a**) were examined under the optimized conditions. As shown in Table 3, the catalytic system could tolerate a variety of functional substituents on *o*-bromophenyl iodide and gave the corresponding indenones in moderate to excellent yields (60%-99%). Except for the extremely electron-withdrawing NO_2 group (**3fa**), the electron nature of the substituents on the phenyl ring had no evidently effect on the reaction (**3ba**, **3ca**, **3da**, **3ea**, **3ga**, **3ha**, **3ia**, **3ja**), and the lower yields of **3ka** and **3la** could be attributed to their steric hindrance.

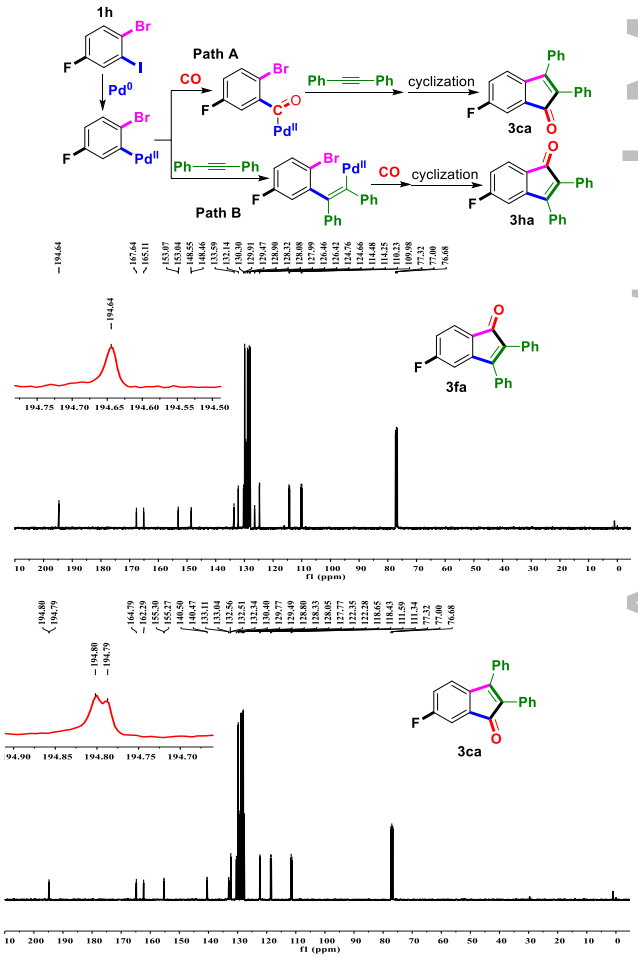
During our initial reaction conditions screening, it was found that the presence of the ligands did not favor to fulfill the three-component transformation. While without the ligands, the reaction could provide a comparable desired product together with the observation of Pd-black. Interestingly, introducing TBAB crucially changed the reaction. This result was reminiscent of literature reports that quaternary ammonium salts facilitated the formation

Table 3. Scope of o-bromophenyl iodide derivatives [a]



[a] Reaction Conditions: **1** (0.5 mmol), **2a** (0.25 mmol), $PdCl_2$ (0.025 mmol), Na_2CO_3 (0.5 mmol), TBAB (0.25 mmol), 1, 4-dioxane (1 mL) at 100 °C for 24 h under CO (balloon). Isolated yield.

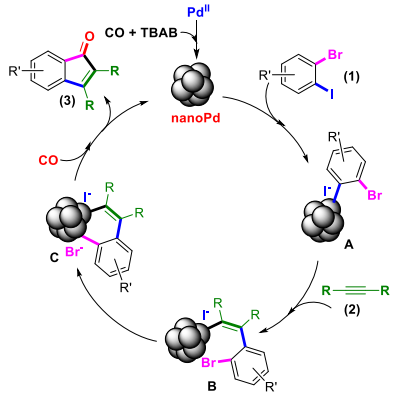
and stabilization of Pd nanoparticles.[14],[16] We speculated that the Pd^{II} precursor was *in situ* reduced into Pd^0 as nanoparticles. To verify the assumption, both mercury and ligand poisoning studies[15-16] were conducted. Either



Scheme 2. Mechanistic Investigations

addition of 10 equiv. of Hg or 40 mol% of PPh_3 to the reaction mixture,[13] no product was found under the standard condition, which suggested that TBAB stabilized palladium nanoparticles might the true catalyst. Furthermore, it was no doubted that oxidative addition of C-I bond to palladium nanoparticles to form arylpalladium intermediate was the first step in the catalytic cycle. However, which step occurred first between carbonylation or alkynes insertion (Scheme 2, path A and path B)? According the product structure presented in Table 3, path B sounded more reasonable. For example, using **1h** as the substrate, path A and path B would give different product **3ca** and **3ha** respectively, and only **3ha** obtained in the reaction. Both **3ca** and **3ha** were known compounds and easily identified with ^{13}C NMR spectrum (Scheme 2).

With the above evidence, a proposed reaction mechanism was then figured out in Scheme 3. In the presence of CO and TBAB, Pd^{II} precursor was reduced to Pd^0 nanoparticles firstly, followed by the oxidative addition of C-I bond to form the intermediate A. Subsequently, alkyne insertion generated the intermediate B, and on the surface of nano-Pd^0 cluster, C-Br converted to C-Pd bond by oxidative addition to form the intermediate C. Finally, the catalytic cycle completed by a sequence of CO insertion and reductive elimination to afford the desired indenone and regenerate the active catalyst.



Scheme 3. Proposed reaction mechanism

In summary, we have successfully developed an appealing approach for the construction of indenones via a ligand-free palladium-catalyzed three-component carbonylation reaction by using commercially available *o*-bromophenyl iodide derivatives and internal alkynes as substrates under a balloon CO atmosphere. This newly developed methodology is able to accommodate a variety of substrates and affords the anticipated products in moderate to excellent yields. This reaction may become a useful alternative approach for the synthesis of acridones derivatives. The desired indenones can be obtained in short reaction steps when such substrates are readily available. This cascade strategy provides the potential application in the field of medicinal chemistry and material science.

Experimental Section

General Procedure for the Synthesis of Indenones

To an oven dried Schlenk tube containing $PdCl_2$ (4.4 mg, 10 mol %), TBAB (80.6 mg, 0.25 mmol), Na_2CO_3 (53.0 mg, 0.5 mmol) and diphenylacetylene (44.6 mg, 0.25 mmol). A balloon filled with CO was connected to the Schlenk tube via the side tube and purged 3 times. Then *o*-bromoiodobenzene (141.0 mg, 0.5 mmol) was added to the tube. 1, 4-dioxane was then added to the tube via a syringe. The Schlenk tube was heated at 100 °C for 24h and then cooled to room temperature. After the balloon gas was released carefully, the reaction was quenched by water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with hexane/ethyl acetate.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21573111), Key Laboratory of Organic Synthesis of Jiangsu Province (KJS1747), the Funding from Nanjing University of Posts and Telecommunications (NY219058, NY217072, NY215016, NY215079).

References

[1] a) R. Nigam, K. R. Babu, T. Ghosh, B. Kumari, D. Akula, S. N. Rath, P. Das, R. Anindya, F. A. Khan, *Bioorg. Med. Chem.* **2018**, *26*, 4100-4112; b) T. A. Unzner, A. S. Grossmann, T. Magauer, *Angew. Chem. Int. Ed.* **2016**, *55*, 9763-9767; c) P.-C. Lv, M. S. A Elsayed, K. Agama, C. Marchand, Y. Pommier, M. Cushman, *J. Med. Chem.* **2016**, *59*, 4890-4899; d) J. T Mohr, M. R. Krout, B. M. Stoltz, *Nature* **2008**, *455*, 323-332; e) A. Morrell, M. Placzek, S. Parmley, B Grella, S. Antony, Y. Pommier, M. Cushman, *J. Med. Chem.* **2007**, *50*, 4388-4404; f) D. G. Nagle, Y. D. Zhou, P. U. Park, V. J. Paul, I. Rajbhandari, C. J. G. Duncan, D. S. Pasco, *J. Nat. Prod.* **2000**, *63*, 1431-1433.

[2] a) B. Zhou, H. Yang, H. Jin, Y. Liu, *J. Org. Chem.* **2019**; b) J. Guo, X. Peng, X. Wang, F. Xie, X. Zhang, G. Liang, Z. Sun, Y. Liu, M. Cheng, Y. Liu, *Org. Biomol. Chem.* **2018**, *16*, 9147-9151; c) J. Fang, M. Brewer, *Org. Lett.* **2018**, *20*, 7384-7387; d) S. Zhang, X.-T. Bai, D.-Y. Chen, P. Chen, Q.-Q. Zhang, Y.-B. Wang, *RSC Adv.* **2017**, *7*, 31142-31147; e) M. E. Domaradzki, Y. Long, Z. She, X. Liu, G. Zhang, Y. Chen, *J. Org. Chem.* **2015**, *80*, 11360-11368; f) C. Y. Wang, J. Y. Yang, X. C. Cheng, E. D. Li, Y. Z. Li, *Tetrahedron Lett.* **2012**, *53*, 4402-4404.

[3] a) W. Yu, W. Zhang, Z. Liu, Y. Zhang, *Chem. Commun.* **2016**, *52*, 6837-6840; b) M. Ueda, T. Ueno, Y. Suyama, I. Ryu, *Chem. Commun.* **2016**, *52*, 13237-13240; c) L. H. Kong, X. F. Yang, X. K. Zhou, S. J. Yu, X. W. Li, *Org. Chem. Front.* **2016**, *3*, 813-816;

[4] a) A. G. K. Reddy, G. Satyanarayana, *J. Org. Chem.* **2016**, *81*, 12212-12222; b) P. Zhao, Y. Liu, C. Xi, *Org. Lett.* **2015**, *17*, 4388-4391; c) X. Yan, S. Zou, P. Zhao, C. Xi, *Chem. Commun.* **2014**, *50*, 2775-2777;

[5] a) L. Ilies, Y. Arslanoglu, T. Matsubara, E. Nakamura, *Asian J. Org. Chem.* **2018**, *7*, 1327-1329; b) X. Yu, S.

Geng, G. Liu, W. Guo, J. Wang, *J. Organomet. Chem.* **2019**, *879*, 139-143;

[6] a) F. Liu, Z. Dong, J. Wang, G. Dong, *Angew. Chem. Int. Ed.* **2019**; b) B. Suchand, G. Satyanarayana, *J. Org. Chem.* **2017**, *82*, 372-381; c) T. Furusawa, T. Morimoto, N. Oka, H. Tanimoto, Y. Nishiyama, K. Kakiuchi, *Chem. Lett.* **2016**, *45*, 406-408; d) A. N. Butkevich, B. Ranieri, L. Meerpoel, I. Stansfield, P. Angibaud, A. Corbu, J. Cossy, *Org. Biomol. Chem.* **2014**, *12*, 728-731;

[7] a) K. Ramesh, G. Satyanarayana, *Eur. J. Org. Chem.* **2018**, *2018*, 4135-4146; b) W. Guo, S. Wu, T. Wang, Q. Xie, Y. Duan, S. Luo, J. Wang, X. Yu, *Org. Chem. Front.* **2018**, *5*, 1613-1621; c) J. Feng, G. P. Lu, M. F. Lv, C. Cai, *J. Org. Chem.* **2014**, *79*, 10561-10567; d) J. Zhang, F. Yang, Y. Wu, *Appl. Organomet. Chem.* **2011**, *25*, 675-679; e) H. Tsukamoto, Y. Kondo, *Org. Lett.* **2007**, *9*, 4227-4230; f) J. Vicente, J. A. Abad, B. Lopez-Pelaez, E. Martinez-Viviente, *Organometallics* **2002**, *21*, 58-67; g) A. A. Pletnev, Q. Tian, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 9276-9287; h) R. C. Larock, Q. Tian, A. A. Pletnev, *J. Am. Chem. Soc.* **1999**, *121*, 3238-3239; i) R. C. Larock, M. J. Doty, S. Cacchi, *J. Org. Chem.* **1993**, *58*, 4579-4583; j) W. Tao, L. J. Silverberg, A. L. Rheingold, R. F. Heck, *Organometallics* **1989**, *8*, 2550-2559;

[8] a) N. Lv, Z. Chen, Y. Liu, Z. Liu, Y. Zhang, *Org. Lett.* **2017**, *19*, 2588-2591; b) M. J. Rosenfeld, B. K. R. Shankar, H. Shechter, *J. Org. Chem.* **1988**, *53*, 2699-2705;

[9] a) X. Yu, Y. Duan, W. Guo, T. Wang, Q. Xie, S. Wu, C. Jiang, Z. Fan, J. Wang, G. Liu, *Organometallics* **2017**, *36*, 1027-1034; b) Y. Yokoyama, Y. Unoh, R. A. Bohmann, T. Satoh, K. Hirano, C. Bolm, M. Miura, *Chem. Lett.* **2015**, *44*, 1104-1106; c) Z. Qi, M. Wang, X. Li, *Org. Lett.* **2013**, *15*, 5440-5443; d) Y. Chen, F. Wang, W. Zhen, X. Li, *Adv. Synth. Catal.* **2013**, *355*, 353-359; e) S. Chen, J. Yu, Y. Jiang, F. Chen, J. Cheng, *Org. Lett.* **2013**, *15*, 4754-4757; f) B.-J. Li, H.-Y. Wang, Q.-L. Zhu, Z.-J. Shi, *Angew. Chem.* **2012**, *124*, 4014-4018; g) T. Miura, M. Murakami, *Org. Lett.* **2005**, *7*, 3339-3341; k) K. Kokubo, K. Matsumasa, M. Miura, M. Nomura, *J. Org. Chem.* **1996**, *61*, 6941-6946;

[10] a) P. Chuangsoongnern, C. Surinrach, J. Tummatorn, C. Thongsornkleeb, S. Ruchirawat, *Eur. J. Org. Chem.* **2017**, 5102-5109; b) T. Kawase, J.-i. Nishida, *Chem. Rec.* **2015**, *15*, 1045-1059; c) K. R. Babu, F. A. Khan, *Org. Biomol. Chem.* **2015**, *13*, 299-308; d) P. A. Wender, T. J. Paxton, T. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 14814-14815;

[11] a) K. Sun, X.-L. Chen, S.-J. Li, D.-H. Wei, X.-C. Liu, Y.-L. Zhang, Y. Liu, L.-L. Fan, L.-B. Qu, B. Yu, K. Li, Y.-Q. Sun, Y.-F. Zhao, *J. Org. Chem.* **2018**, *83*, 14419-14430; b) B. Banerji, L. Majumder, S. Adhikary, *Chemistryselect* **2018**, *3*, 1381-1384; c) Z. Yan, J. Xie, C. Zhu, *Adv. Synth. Catal.* **2017**, *359*, 4153-4157; d) J. Wen, W. Shi, F. Zhang, D. Liu, S. Tang, H. Wang, X.-M. Lin, A. Lei, *Org. Lett.* **2017**, *19*, 3131-3134; e) S. B. Nagode, A. K. Chaturvedi, N. Rastogi, *Asian J. Org. Chem.* **2017**, *6*, 453-457; f) C. Pan, B. Huang, W. Hu, X. Feng, J.-T. Yu, *J. Org. Chem.* **2016**, *81*, 2087-2093.

[12] a) Y. Kuninobu, T. Matsuki, K. Takai, *Org. Lett.* **2010**, *12*, 2948-2950; b) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, *Org. Lett.* **2009**, *11*, 1777-1780; c) Y. Harada, J. Nakanishi, H. Fujihara, M. Tobisu, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2007**, *129*, 5766-5771; d) T. Fukuyama, N. Chatani, F. Kakiuchi, S. Murai, *J. Org. Chem.* **1997**, *62*, 5647-5650.

[13] The details were summarized in support information.

[14] H. Bonnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joussen, B. Korall, *Angew. Chem. Int. Ed.* **1991**, *30*, 1312-1314;

[15] a) Q. Zhou, S. Wei, W. Han, *J. Org. Chem.* **2014**, *79*, 1454-1460. b) Y. Zhu, L. Chuanzhao, A. O. Biying, M. Sudarmadji, A. Chen, T. Dang Thanh, A. M. Seayad, *Dalton Trans.* **2011**, *40*, 9320-9325;

[16] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A-Chem.* **2003**, *198*, 317-341.

[17] a) X. F. Wu, H. Neumann, M. Beller, *Chem. Rev.* **2013**, *113*, 1-35; b) X. F. Wu, H. Neumann, M. Beller, *Chem. Soc. Rev.* **2011**, *40*, 4986-5009; c) R. Grigg, S. P. Mutton, *Tetrahedron* **2010**, *66*, 5515-5548; d) A. Brennfuhrer, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2009**, *48*, 4114-4133; e) C. F. J. Barnard, *Org. Process Res. Dev.* **2008**, *12*, 566-574; f) C. F. J. Barnard, *Organometallics* **2008**, *27*, 5402-5422.

10.1002/adsc.201901309

COMMUNICATION

Synthesis of Indenones via Palladium-Catalyzed Ligand-Free Carbonylation

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Juan Song*, Haisen Sun, Wei Sun, Yuxuan Fan, Cui Li, Haotian Wang, Kang Xiao and Yan Qian