DOI: 10.1002/adsc.201801359
Advanced Synthesis & Catalysis

Palladium-Catalyzed Propargylic [n+2] Cycloaddition: An Efficient Strategy for Construction of Benzo-Fused Medium-Sized Heterocycles

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Manuscript received: October 8, 2018; Revised manuscript received: November 5, 2018;
Version of record online: December 14, 2018

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.201801359

The synthesis of medium-sized ring systems have attracted significant attention in recent years because of the broad abundance of these scaffolds in biologically significant molecules, e.g. taxol and polycyclic ethers.[1] Over the past decades, various strategies have been developed to form medium-sized rings including: macrocyclization, ring expansion, and ring-closing metathesis.[2] However, the efficient construction of these appealing frameworks remains a formidable synthetic challenge as it is often hampered by unfavorable transannular interactions and adverse entropic and/or enthalpic effects. To address this challenge, an alternative and more flexible strategy is the use of transition metal-catalyzed cycloadditions from readily available building blocks.[3] In this regard, much progress has been recently achieved, which maily focuses on the formation of seven- or eight-membered rings.[4] In constrast, there are limited catalytic examples for efficient access to medium-sized heterocycles larger than eight-membered rings, mostly to only one certain sized ring structure.[5–6] The development of a general and efficient strategy of the transition metal-catalyzed cycloaddition to construct a broad range of medium-sized heterocycles, especially those consisting of 8–11-membered rings, is highly desirable.

Recent studies have disclosed that propargylic compounds can serve as bis-electrophilic C_2 or C_3-synthons to undergo cycloaddition with bis-nucleophiles in the presence of transition-metal-catalysts, thus rapidly generating complexity in a single operation.[7] However, this methodology is usually used in the synthesis of five- and six-membered rings with scattered examples of seven- and eight-membered rings.[8] For the construction of larger medium-sized heterocycles, no catalytic intermolecular propargylic cycloaddition has yet been realized to the best of our knowledge. The challenge associated with medium-sized ring cycloaddition reactions is due to the longer-linked bis-nucleophile that has competing cyclization *versus* intermolecular coupling. It has been recently disclosed that the η^3-π-propargylpalladium complex can undergo sequential double addition with two seperate nucleophiles in an intermolecular sense.[9] Given this background, we wondered whether a palladium-catalyzed propargylic cycloaddition procedure could be extended to bis-nucleophiles with a linker longer than four atoms, and thus serve as a powerful and efficient method for the construction of medium-sized heterocycles. Herein we show the synthetic versatility of the palladium-catalyzed [n+2] cycloaddition of propargylic esters as C_2-synthons with readily available linker-tethered-bisphenols in the construction of medium-sized frameworks. This methodology provides a general, straightforward, and regioselective protocol for the creation of various functionalized eight to eleven-membered benzo-fused heterocycles in a simple manner (Figure 1).

In searching for suitable reaction partners for this palladium-catalyzed [n+2] cycloaddition, we were particularly interested in bisphenols as the cycloaddition would led to biologically and synthetically relevant polycyclic ethers. In particular, Sinou et al. have reported benzene-1,2-diol (catechol) can undergo palladium-catalyzed propargylic cycloaddition with propargylic carbonates, leading to six-membered rings.[10]

We started our studies to explore the possibility of the palladium-catalyzed [7+2] cycloaddition between 2,2′-sulfinylbis(4-(*tert*-butyl)phenol) **1a** and 1-phenyl-

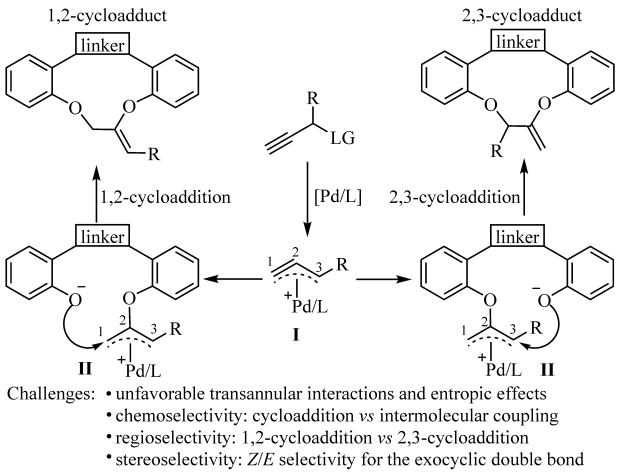
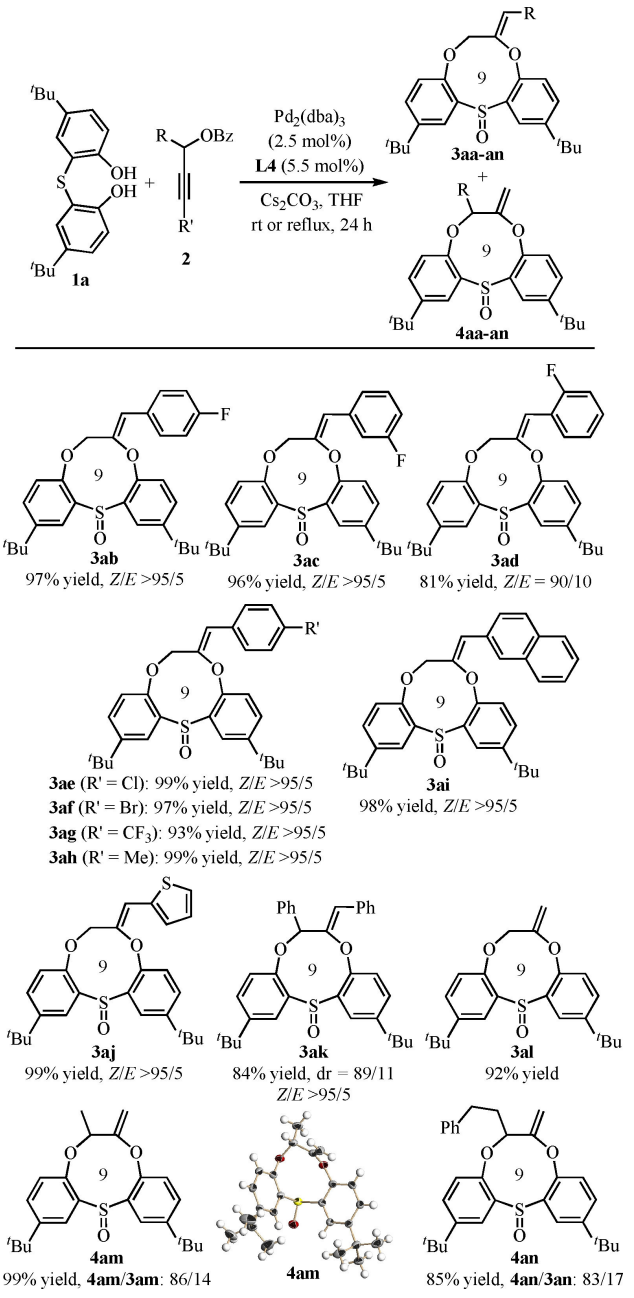


Figure 1. General strategy for the construction of benzo-fused medium-sized heterocycles via Pd-catalyzed propargylic [n+2] cycloaddition.

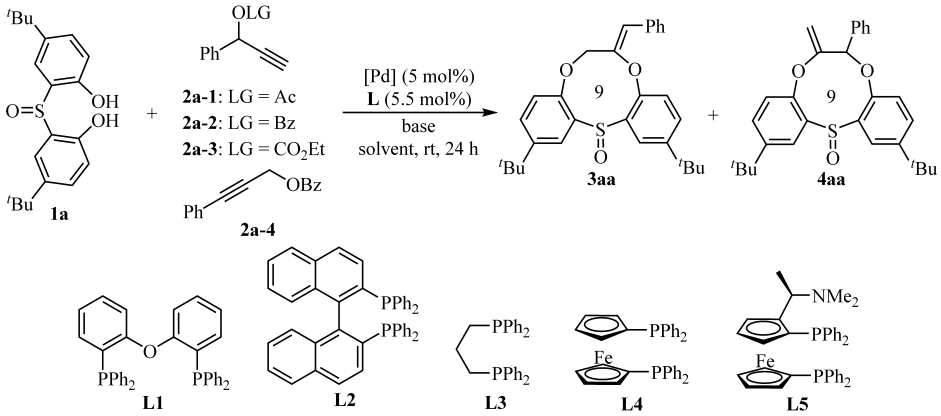
prop-2-yn-1-yl esters **2a**, which is expected to generate the nine-membered cyclic ethers (Table 1). Initial attempt using $Pd(OAc)_2$ in combination with bisphosphine ligand DPEPhos (**L1**) was disappointing, in which no cycloadduct was detected (entry 1). After careful screening of different palladium precursors (entries 1–4), we were excited to find that the use of $Pd_2(dba)_3 \cdot CHCl_3$ led to the predominate formation of nine-membered compound in 72% yield, albeit as a 95/5 mixture of 1,2-cycloadduct **3aa** and 2,3-cycloadduct **4aa** with a *Z*/*E*-selectivity of 91/9 for **3aa** (entry 4). Different leaving groups in propargylic position show some influence on the reactivity, in which the benzoyl group lead to higher product yields (entry 5). Unexpectedly, internal propargylic benzoate **2a–4** showed low reactivity under the same condition (entry 7). Ligand structure exhibited a dramatic effect on the reactivity (entries 8–11). With BINAP (**L2**) and DPPP (**L3**) as ligands, very low conversion was observed (entries 8 and 9). Ferrocenyl diphosphine ligands DPPF (**L4**) and BPPFA (**L5**) were identified as optimal ligands, and both displayed excellent performance (entries 10 and 11). At this point, different Pd-precursors were examined again, and the choice of $Pd_2(dba)_3$ led to nearly perfect results, in which the nine-membered 1,2-cycloadduct **3aa** was obtained as the only product in 98% yield with *Z*-selectivity >95/5 (entry 13). The addition of Cs_2CO_3 as the base additive was crucial since none of cycloadduct **3aa** was obtained in its absence or when an organic bases such as $^{i}Pr_2NEt$ was used (entries 14 and 15). The weak basicity of the organic base that is unable to effectively deprotonate bisphenols should be responsible for no reactivity with $^{i}Pr_2NEt$. Other inorganic bases such as $^{t}BuOK$ led to dramatically decreased yield (entry 16). Subsequent solvent screening did not improve the reaction outcome (entries 17 and 18). Due to low solubility of bisphenol **1a** in CH_2Cl_2, very low conversion was observed.

With the optimal reaction conditions in hand, we set out to explore the generality of this catalytic system. The substrate evaluation of various propargylic benzoates is shown in Scheme 1. Various aromatic propargylic benzoates are well tolerated and delivered the nine-membered 1,2-cycloadducts **3** as the only product in good to excellent yields. The substitution patterns on the phenyl rings show some



Scheme 1. Propargylic benzoate evaluation in the palladium-catalyzed [7+2] cycloaddition.

Table 1. Optimization of the propargylic [7+2] cycloaddition.[a]



Entry	2a	[Pd]	L	Base	Solvent	Yield (%)[b]	3aa/4aa[c]	Z/E (3aa)[c]
1	**2a-1**	$Pd(OAc)_2$	**L1**	Cs_2CO_3	THF	–	–	–
2	**2a-1**	$Pd(PPh_3)_4$	**L1**	Cs_2CO_3	THF	–	–	–
3	**2a-1**	$Pd_2(dba)_3$	**L1**	Cs_2CO_3	THF	39	94/6	90/10
4	**2a-1**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	Cs_2CO_3	THF	72	95/5	91/9
5	**2a-2**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	Cs_2CO_3	THF	99	95/5	92/8
6	**2a-3**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	Cs_2CO_3	THF	97	94/6	91/9
7	**2a-4**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	Cs_2CO_3	THF	–	–	–
8	**2a-2**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L2**	Cs_2CO_3	THF	–	–	–
9	**2a-2**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L3**	Cs_2CO_3	THF	–	–	–
10	**2a-2**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4**	Cs_2CO_3	THF	99	>95/5	95/5
11	**2a-2**	$Pd_2(dba)_3{\cdot}CHCl_3$	**L5**	Cs_2CO_3	THF	99	95/5	>95/5
12	**2a-2**	$Pd(OAc)_2$	**L4**	Cs_2CO_3	THF	14	94/6	95/5
13	**2a-2**	$Pd_2(dba)_3$	**L4**	Cs_2CO_3	THF	98	>95/5	>95/5
14	**2a-2**	$Pd_2(dba)_3$	**L4**	–	THF	–	–	–
15	**2a-2**	$Pd_2(dba)_3$	**L4**	$^iPr_2NEt$	THF	–	–	–
16	**2a-2**	$Pd_2(dba)_3$	**L4**	^{t}BuOK	THF	38	>95/5	94/6
17	**2a-2**	$Pd_2(dba)_3$	**L4**	Cs_2CO_3	CH_2Cl_2	–	–	–
18	**2a-2**	$Pd_2(dba)_3$	**L4**	Cs_2CO_3	PhMe	57	93/7	>95/5

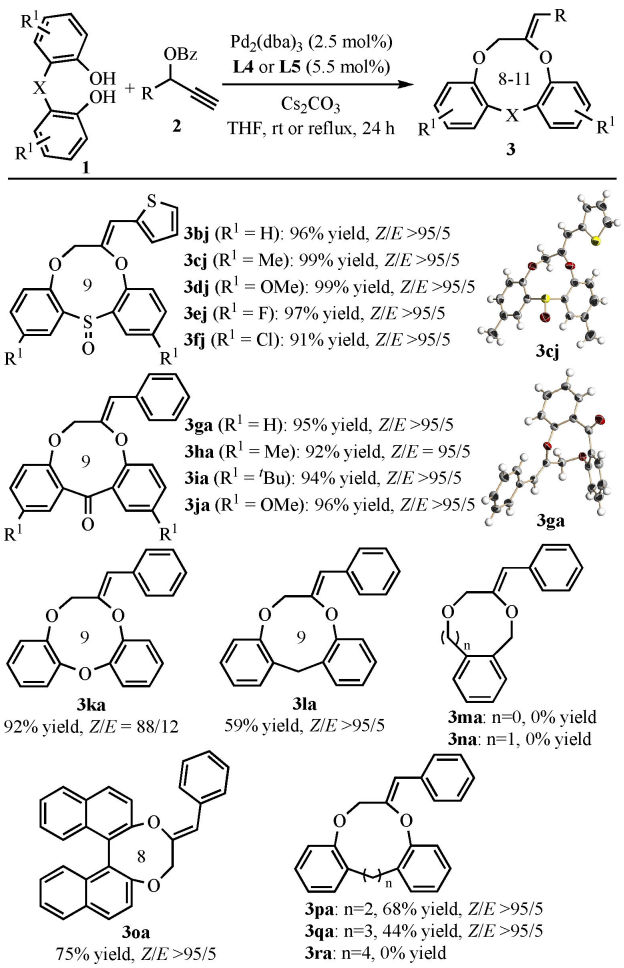
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [Pd] (0.01 mmol, 5 mol%), **L** (0.011 mmol, 5.5 mol%), base (0.24 mmol), solvent (6 mL), rt, 24 h.
[b] Yield of isolated products.
[c] Determined by ^{1}H NMR.

effect in this cycloaddition. Thus, the substrates with *para*- or *meta*-fluoro groups give similarly excellent results, while *ortho*-fluoro substituted substrate results in observably decreased yield (81%) and decreased olefin selectivity (Z/E=90/10). The reaction tolerates both electron-donating and electron-withdrawing groups at the *para*-position of the phenyl ring, and gives the corresponding nine-membered heterocycles **3ae**–**3ah** in excellent yields with Z/E-selectivity >95/5. 2-Naphthyl-substituted substrate works well for the reaction, gives the cycloadduct **3ai** in 98% yield and Z/E-selectivity >95/5. Heterocyclic substrate **2j** is also a suitable substrate, providing the cycloadduct **3aj** in 99% yield and Z/E-selectivity >95/5. The substrate, prop-2-yn-1-yl benzoate (**2l**), without a substitution at the propargylic position leads to the cycloadduct **3al** in 92% yield. We also examined the substrate, 1,3-diphenylprop-2-yn-1-yl benzoate (**2k**), with the substitution at both the propargylic and the acetylenic positions, which proceeds smoothly and gives the cycloadduct **3ak** in high yield and Z-selectivity but with moderate diastereoselectivity.

Interestingly, aliphatic propargylic benzoates leads to nine-membered 2,3-cycloadducts **4** as the major products. The use of but-3-yn-2-yl benzoate **2m** leads to a 86/14 mixture of **4am** and **3am**, while use of 5-phenylpent-1-yn-3-yl benzoate **2n** generates a 83/17 mixture of **4an** and **3an**. The different regioselectivity observed for aromatic and aliphatic substrates is presumably due to the formation of conjugated transition state with lower energy for aromatic substrates when the cyclization occurs at the less substituted position. As for aliphatic substrates, the cyclization occurs at the more substituted end since

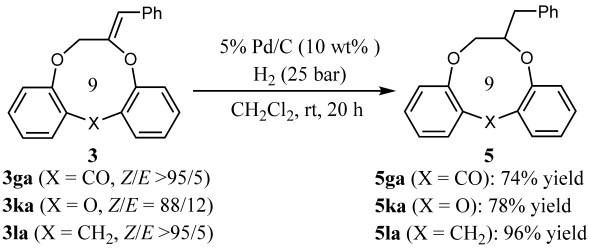
the alkyl group could stabilize the positive intermediate more effectively (Scheme 1). The structure of 2,3-cycloadducts was unambiguously assigned by single-crystal X-ray diffraction analysis of **4am**.[11]

To further demonstrate the utility of this remarkable reaction, we examined a wide range of bisphenols (Scheme 2). As expected, the reaction worked well with various substituted 2,2′-sulfinylbisphenols **1b–f**, and smoothly gave the nine-membered cyclic ethers **3bj–fj** as the only products in high yields with *Z*-selectivity (>95/5), regardless of the electronic property of the substituent at the *para*-position of the phenyl ring. Replacing the sulfinyl linker with carbonyl linker has little impact on the reaction yields and selectivity delivering the corresponding nine-membered 1,2-cycloadducts **3ga–ja** as the only products. The structures of these two series of products were unambiguously assigned by single-crystal X-ray diffraction analysis of **3cj** and **3ga**.[11] The reaction also tolerates an ether- and methylene-linkage although the yield and *Z*-selectivity were somewhat affected. Thus, the use of 2,2′-oxydiphenol **1k** as the bis-nucleophile leads to the nine-membered 1,2-cycloadduct **3ka** in 92% yield with a moderate *Z*/*E*-selectivity of 88/12. In contrast, the reaction with 2,2′-methylenediphenol **1l** gives the nine-membered 1,2-cycloadduct **3la** in 59% yield as a single olefin product (>95/5, *Z*/*E*). Moreover, the reaction could also be extended to the preparation of other medium-sized compounds including eight-, ten- and eleven-membered rings. However, for the substrates containing aliphatic alcohols such as 2-hydroxybenzyl alcohol or 1,2-benzenedimethanol, no desired product was observed. With BINOL **1o** as the substrate, the reaction gave the eight-membered 1,2-cycloadduct **3oa** in 75% yield and with *Z*/*E*-selectivity >95/5. When the reaction of 2,2′-(ethane-1,2-diyl)diphenol **1p** was carried out, a ten-membered 1,2-cycloadduct **3pa** was obtained in 68% yield and with *Z*/*E*-selectivity >95/5. 2,2′-(Propane-1,3-diyl)diphenol **1q** also works under reaction conditions, delivering the corresponding eleven-membered 1,2-cycloadduct **3qa** in 44% yield and with *Z*/*E*-selectivity >95/5. These results clearly demonstrates the generality and efficiency of the present methodology in the construction of medium-sized heterocycles. However, an attempt to synthesize 12-membered heterocycle **3ra** by use of 2,2′-(butane-1,4-diyl)diphenol **1r** was failed, in which a complex mixture was obtained.



Scheme 2. Substrate evaluation of bisphenols in the [7+2] cycloaddition.

The hydrogenation of the exocyclic C=C bond of nine-membered 1,2-cycloadducts **3** could be readily performed with 10 wt% of 5% Pd/C in CH_2Cl_2 at room temperature for 20 h (Scheme 3). Thus, the hydrogenation of a *Z*/*E* mixture of **3ka** gave the 9-crown-3 ether derivative **5ka** in 78% yield.



Scheme 3. Hydrogenation of cycloadducts **3**.

In summary, we have demonstrated a powerful procedure for the construction of benzo-fused medium-sized heterocyclic ethers through a palladium-catalyzed formal [n+2] cycloaddition of various linker-tethered-bisphenols with propargylic esters as C_2-synthons. This methodology represents one of few transition-metal-catalyzed intermolecular cycloadditions for the general synthesis of medium-sized heterocycles from eight to eleven-membered rings.

The reaction features a broad substrate scope, high yields and excellent regio- and *Z*-selectivities. Further exploration of new catalytic strategies for rapid access to various medium-sized rings is currently ongoing in our laboratory.

Experimental Section

General Procedure for Palladium-catalyzed Propargylic [n+2] Cycloaddition

Method **A**: A solution of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol) and **L4** (6.1 mg, 0.011 mmol) in 1 mL of anhydrous tetrahydrofuran placed in an oven-dried Schlenk flask was stirred at room temperature under a nitrogen atmosphere for 1 h. Then a solution of bisphenols **1** (0.2 mmol), propargylic esters **2** (0.24 mmol), and Cs_2CO_3 (78.2 mg, 0.24 mmol) in 5 mL of anhydrous tetrahydrofuran was added. The mixture was stirred at room temperature for 24 h. The reaction mixture was then concentrated under vacuum, and the residue was purified by silica gel chromatography to afford benzo-fused medium-sized heterocycles **3** or **4**.

Method **B**: A solution of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol) and **L5** (6.9 mg, 0.011 mmol) in 1 mL of anhydrous tetrahydrofuran placed in an oven-dried Schlenk flask was stirred at room temperature under a nitrogen atmosphere for 1 h. Then a solution of bisphenols **1** (0.2 mmol), propargylic esters **2** (0.24 mmol), and Cs_2CO_3 (78.2 mg, 0.24 mmol) in 5 mL of anhydrous tetrahydrofuran was added. The mixture was stirred under reflux for 24 h. The reaction mixture was then concentrated under vacuum and the residue was purified by silica gel chromatography to afford benzo-fused medium-sized heterocycles **3** or **4**.

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (21572226 and 21772196), and the Dalian Institute of Chemical Physics (DICP ZZBS201707). We also thank Dr. Daniel Kim for his linguistic assistance during the preparation of this manuscript.

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[11] CCDC 1855171 (**4am**), CCDC 1855168 (**3cj**) and CCDC 1855170 (**3ga**) 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.

