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Synthesis of Benzannulated [6,6]-Spiroketals by a One-Pot Carbonylative Sonogashira Coupling/Double Annulation Reaction

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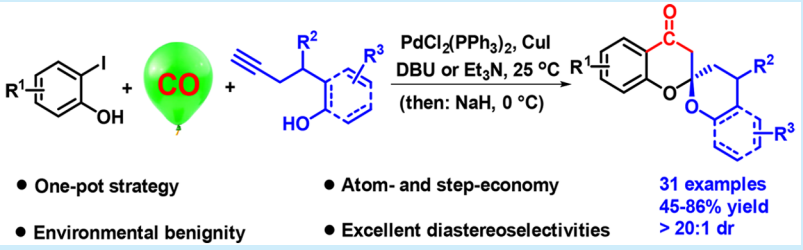
Supporting Information



ABSTRACT: A one-pot Pd-catalyzed carbonylative Sonogashira coupling in tandem with double annulation reaction to synthesize benzannulated [6,6]-spiroketals from *o*-iodophenols and terminal alkynols or alkynyl phenols was achieved. The protocol provides straightforward and facile access to benzannulated [6,6]-spiroketals in moderate to good yields and excellent diastereoselectivities under balloon pressure of CO at room temperature.

Spiroketals are prevalent motifs in a diverse range of biologically active natural products and pharmaceuticals.[1] Among the family of spiroketals, the benzannulated [6,6]-spiroketal is a key skeleton that exists in many bioactive natural products and chiral ligands (Figure 1).[2] Key examples include

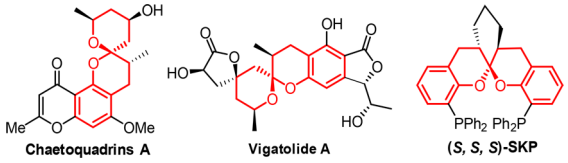


Figure 1. Representative bioactive natural products and ligand containing benzannulated [6, 6]-spiroketal cores.

the chaetoquadrin[3] and virgatolide families,[4] which have demonstrated compelling bioactivities; (*S*,*S*,*S*)-SKP is a type of privileged chiral ligands with excellent performance in catalytic enantioselective transformations.[5] In view of the critical roles of benzannulated [6,6]-spiroketal moiety, a range of novel spirocyclization methodologies have been developed in recent years. The preparation involves acid-catalyzed cyclization of a dihydroxyketone precursor (or equivalent),[6] intramolecular hetero-Michael addition,[7] [4+2] cycloaddition,[8] chromone epoxide spirocyclization,[9] allylic rearrangement,[10] oxidative radical cyclization,[11] and iridium-catalyzed spiroketalization of allylic carbonates.[12]

Despite these advances, the development of more atom- and step-economic methods starting from easily available substrates under mild conditions is still highly desirable for the synthesis of benzannulated [6,6]-spiroketals. Our group has a long-standing interest in this field and has developed a series of efficient methods for the syntheses of benzannulated [5,6]-spiroketals.[13] In accordance with our interest in developing synthetic tools for the synthesis of natural products containing benzannulated [6,6]-spiroketal motifs, we wish to develop a new and efficient method for the stereocontrolled synthesis of this skeleton.

Employing CO as a cheap and abundant C1 source, the carbonylation reaction represents an atom-economical and environmentally benign strategy for the preparation of various carbonyl-containing compounds and their derivatives.[14] Since first reported by Tanaka in 1981,[15a] palladium-catalyzed carbonylative Sonogashira reaction of aryl halides has become an interesting alternative strategy for the synthesis of alkynones, and notable improvements have been achieved by Xia[15d] Yang,[15h] Beller,[15j] etc. (Scheme 1A). Specifically, several groups, including Ortar,[16d] Yang,[16f] and Capretta[16e] have developed novel approaches to chromones via the Pd-catalyzed carbonylation/cyclization reaction between *o*-iodophenols and terminal alkynes (Scheme 1B).[16] Inspired by these elegant works, we envisaged that a one-pot Pd-catalyzed carbonylative Sonogashira coupling/double annulation[16i,j] process would result in the straightforward formation of monobenzannulated [6,6]-spiroketal **5** or bisbenzannulated [6,6]-spiroketal **6** via the chromone intermediate **4** (Scheme 1C). Herein, we report a highly efficient route for the rapid synthesis of benzannulated [6,6]-spiroketals starting from *o*-iodophenols, CO, and alkynols or alkynyl phenols under mild conditions.

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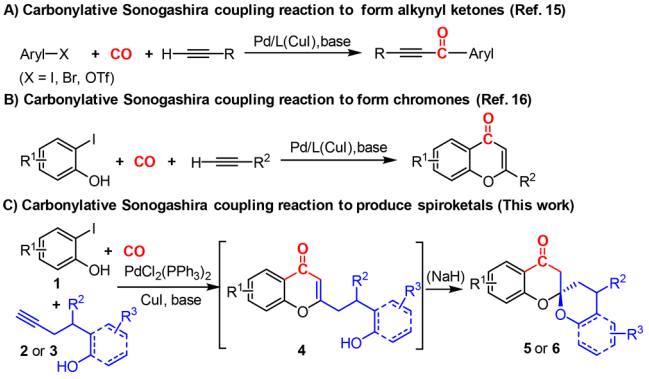
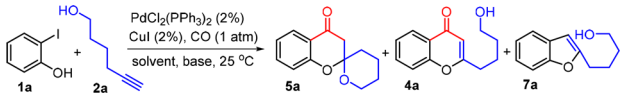
Scheme 1. Palladium-Catalyzed Carbonylative Sonogashira Coupling Reaction of Aryl halides



We initiated our studies by using 2-iodophenol **1a** and alkynol **2a** as the model substrates to explore the reaction conditions (Table 1). Initially, a series of bases were screened in the presense of 2 mol % of $PdCl_2(PPh_3)_2$ and 2 mol % of CuI in DMF with a CO balloon at 25 °C (entries 1−3). Although no spiroketal **5a** was observed, chromone **4a** could be obtained in 92% yield (entry 1), revealing that DBU is the ideal base for the carbonylation reaction. We next screened several common solvents. To our delight, the desired spiroketal **5a** could be generated in 15−30% yields jointly with plenty of chromone **4a** remaining when toluene, Et_3N (also as the base), or THF was used as the solvent (entries 7−9). Notably, though benzofuran **7a** was obtained in some cases, no ester byproduct was detected. We speculated that the insufficient strength of the base might result in a large amount of the chromone remaining. However, subsequent experimental results showed that stronger bases such as LiOH, NaOH, or MeONa could damage the activity of the palladium catalyst and the palladium precipitate was formed very rapidly under the drastic reaction conditions (for details, see Supporting Information). These results indicated that different bases should be added in two steps. Thanks to this awareness, chromone **4a** could be fully transformed into **5a** when 10 mol % of NaH was added to the reaction system after complete consumption of alkynol **2a**, with an 81% isolated yield (88% NMR yield) (entry 10). The reaction was also carried out in the absence of CuI (entry 11). The longer reaction time and extremely low yield confirmed that CuI was essential for this reaction as a cocatalyst. Moreover, **5a** could also be generated in 55% and 10% yields, respectively, when $Mo(CO)_6$ and phenyl formate were applied as the CO sources. To further evaluate the catalyst effect on reaction outcome, several other palladium catalysts were screened, and $PdCl_2(PPh_3)_2$ proved to be the ideal catalyst (entries 12 and 13).

Table 1. Optimization of Reaction Conditions[a]

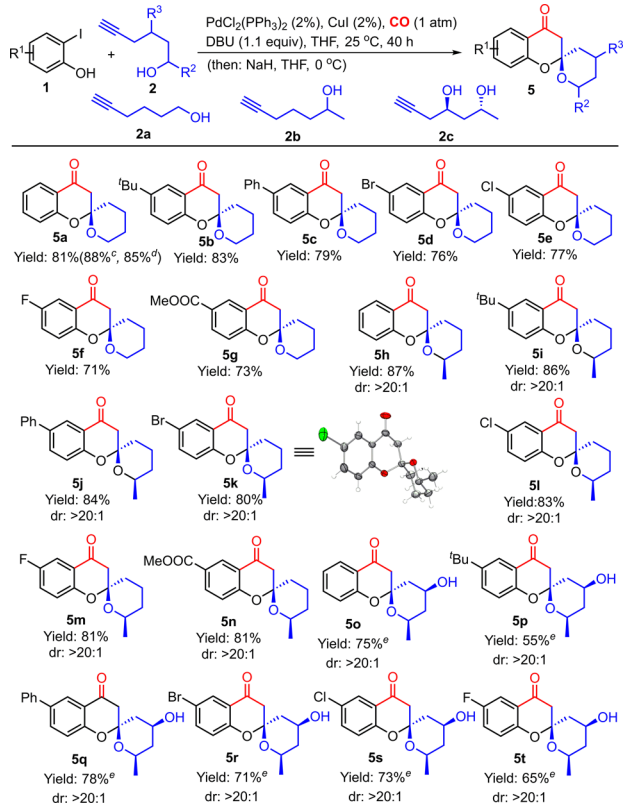


entry	solvent	base	time (h)	yield (%)[b] 5a: 4a: 7a
1	DMF	DBU	20	0:92:0
2	DMF	Et_3N	30	0:79:0
3	DMF	Cs_2CO_3	24	0:73:0
4	CH_2Cl_2	DBU	10	0:0:83
5	CH_3CN	DBU	24	0:16:63
6	1,4-dioxane	DBU	24	0:10:61
7	Et_3N	Et_3N	40	25:48:13
8	Toluene	DBU	48	15:44:25
9	THF	DBU	40	30:58:5
10[c]	**THF**	**DBU**	**40**	**81:7:4**
11[d]	THF	DBU	60	4:38:0
12[c,e]	THF	DBU	40	55:6:17
13[c,f]	THF	DBU	40	35:6:8

[a]All reactions were carried out by using **1a** (1.1 mmol), **2a** (1.0 mmol), $PdCl_2(PPh_3)_2$ (0.02 mmol), CuI (0.02 mmol), and solvent (5 mL) under CO (1 atm) at 25 °C, except as noted. [b]Isolated yield. [c]NaH (10 mol %) was added after complete consumption of alkynol **2a**. [d]The reaction was performed without CuI. [e]$PdCl_2$(dppf) (0.02 mmol) was used instead of $PdCl_2(PPh_3)_2$. [f]$PdCl_2$ (0.02 mmol) and BINAP (0.02 mmol) were used instead of $PdCl_2(PPh_3)_2$.

With the optimal conditions in hand (Table 1, entry 10), we next examined the reaction with a broad range of substrates to determine the scope of substrates, and the results are summarized in Scheme 2. First, various *o*-iodophenols were reacted with alkynol **2a**. From the results, it is evident that all of the reactions tolerated a variety of functional groups and provided the corresponding spiroketals in good to excellent yields. As discussed in Tanak's[15a] and Mori's[15c] research, electron-withdrawing substituents on the *o*-iodophenols resulted in the slightly lower yields of the products (**5f**, **5g**).

Scheme 2. Substrate Scope for the Syntheses of Monobenzannulated Spiroketals[a,b]



[a]Reaction conditions: **1** (1.1 mmol), **2** (1.0 mmol), $PdCl_2(PPh_3)_2$ (0.02 mmol), and CuI (0.02 mmol) in THF (5 mL) under CO (1 atm) at 25 °C for 40 h and then NaH (0.1 mmol) at 0 °C for 1 h, except as noted. [b]Isolated yield, except as noted. [c]NMR yield. [d]The reaction was performed on a 10 mmol scale. [e]The reaction was performed without NaH.

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Additionally, secondary alcohol **2b** was also used as a substrate for this reaction, affording the corresponding spiroketals (**5h**–**5n**) in higher yield and excellent diastereoselectivities (dr >20:1). The relative stereochemistry of **5k** was characterized via X-ray crystallography analysis.[17] Surprisingly, when chiral diol **2c** was utilized as substrate, the reactions proceeded smoothly in the absence of NaH, giving the corresponding spirokrtals **5o**–**5t** in good yields and excellent diastereoselectivities (dr >20:1). Because **5o**–**5t** were obtained as oils, the steric configurations were assigned on the basis of the analysis of the CD spectrum of **5s**. The electronic circular dichroisms (ECDs) of two possible candidate isomers (*S*-**5s**, *R*-**5s**) were calculated for the purpose of comparison (for details, see the Supporting Information). From the comparison of CEs at 212.5, 250, and 316 nm (Figure 2), the experimental spectrum

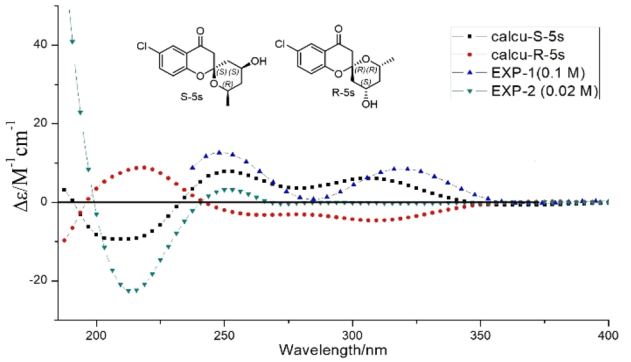


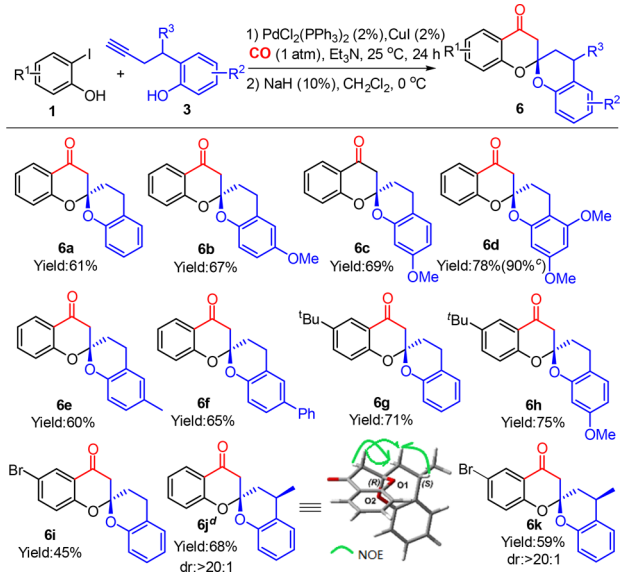
Figure 2. Comparison of calculated CD spectra of *S*-**5s** and *R*-**5s** and experimental CD spectrum of **5s** (EXP-1 and EXP-2).

could match well with the calculated ECD curve of *S*-**5s**. Therefore, the spiroketal moiety of **5s** prepared by our method herein is more likely to have the *S*-configuration.

To demonstrate the utility of this methodology, the model reaction was conducted on a gram-scale (10 mmol). To our delight, the desired product **5a** was obtained in a slightly higher yield of 85% (Scheme 2).

Unfortunately, the one-pot reaction of alkynyl phenol **3a** with **1a** failed to give bisbenzannulated [6,6]-spiroketal **6a** under the optimal conditions. After a series of careful conditional optimizations (see Supporting Information for full details), Et_3N (also as the base) and CH_2Cl_2 were respectively selected as the optimal solvents for this one-pot reaction. Then various *o*-iodophenols were reacted with a diverse array of alkynyl phenols, and the results are summarized in Scheme 3. Overall, most of substitution pattern on the aromatic rings of *o*-iodophenols and alkynyl phenols proceeded well in the reaction. In comparison with the results of the monobenzannulated spiroketals, the corresponding bisbenzannulated spiroketals were produced in relatively lower yields. It should be pointed out that the carbonylative Sonogashira coupling and intramolecular hetero-Michael addition were performed efficiently in each case, as monitored by thin-layer chromatography (TLC) and NMR (e.g., the NMR yield of **6d** is 90%, see Figure S7). The relatively low isolated yields of products could be attributed to their low stabilities on silica gel. In general, electron-donating groups contributed to higher yields. In order to examine the diastereoselectivity of the reaction, the alkynyl phenol with a methyl group at the homopropargyl position was adopted. Fortunately, the corresponding spiroketals **6j** and **6k** were

Scheme 3. Substrate Scope for the Syntheses of Bisbenzannulated Spiroketals[a,b]



[a]All reactions were carried out by using **1** (1.1 mmol), **3** (1.0 mmol), $PdCl_2(PPh_3)_2$ (0.02 mmol), CuI (0.02 mmol), and Et_3N (5 mL) under CO (1 atm) at 25 °C for 24 h, then NaH (0.1 mmol) and CH_2Cl_2 (5 mL) at 0 C for 30 min. [b]Isolated yield, except as noted. [c]NMR yield. [d]The stick model is the most stable conformer on the basis of the computational works.

generated in good yields and excellent diastereoselectivities. The relative configuration of **6j** was assigned on the basis of the analysis of the NOE spectrum, which could match well with the computational results of the most stable conformer of **6j** (see Supporting Information for full details).

To further explore the possible reasons for the excellent stereoselectivities in our reactions, the relative Gibbs free energies of possible stereomers and conformers of **5h** and **6j** were computed using the Gaussian 09 suite of program, in view of the conformation of dihydropyran ring, anomeric effect, and direction of methyl group (see Supporting Information for full details). The computational results indicate that the configurations obtained from our experiments are significantly more thermally stable, and the equilibriums tend to them according to Boltzmann distribution. These results could well explain the excellent stereoselectivities.

In summary, a novel Pd-catalyzed carbonylative Sonogashira coupling in tandem with double annulation reaction to synthesize benzannulated [6,6]-spiroketals was achieved. Notably, this process was conducted under very mild conditions (under balloon pressure of CO at room temperature). This approach enables access to a wide range of benzannulated [6,6]-spiroketals in moderate to good yields, together with good functional group tolerance and excellent stereoselectivities. With the advantages of environmental benignity and atom and step economy, this protocol would serve as an efficient and convergent way to synthesize benzannulated [6,6]-spiroketals.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03586.

Detailed experimental procedures, analytical data, X-ray crystal structure, DFT calculations, computational details, stereomer and conformer structures, Gibbs free energies and structural data, spectral data for all products, and optimization of reaction for synthesis of **5a** and **6a** (PDF)

Accession Codes

CCDC 1876072 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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(17) CCDC 1876072 (**5k**) contains 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.

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