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# Ag/Brønsted Acid Co-Catalyzed Spiroketalization of β-Alkynyl Ketones toward Spiro[chromane-2,1′-isochromene] Derivatives

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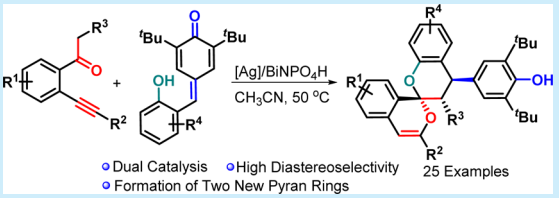
Supporting Information

**ABSTRACT:** A new Ag/Brønsted acid co-catalyzed spiroketalization of β-alkynyl ketones with *para*-quinone methides (*p*-QMs) has been established, enabling multiple C−C and C−O bond-forming events to access densely functionalized spiro[chromane-2,1′-isochromene] derivatives with generally excellent diastereoselectivity and good yields. A reasonable mechanism for forming these 6,6-dibenzannulated spiroketals involving 6-*endo*-*dig* *oxo*-cyclization and 1,6-addition-cyclization cascades is proposed.




Spiroketal appears as a privileged structural motif that exists in a broad array of both natural products and synthetic bioactive molecules. Compounds incorporating a spiroketal core structure have been found to exhibit a wide spectrum of biological activities.[1] Among the family of spiroketals, the 6,6-benzannulated spiroketals behave as a key pharmacophore in many bioactive natural products, such as cynandione B,[2] chaetoquadrin B,[3] and virgatolide B[4] (Figure 1). In particular,

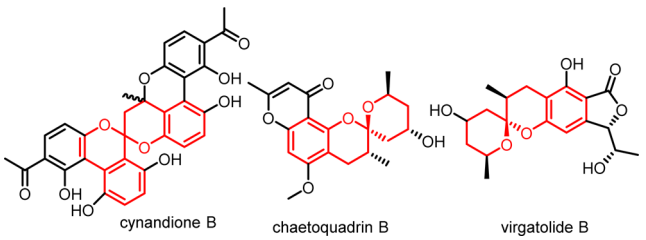
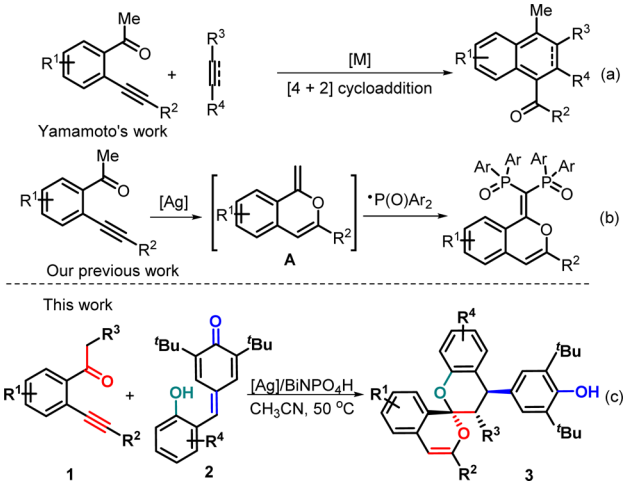



**Figure 1.** 6,6-Benzannulated spiroketal-containing natural products.

cynandione B displays significant in vitro cytotoxic activity against both T-24 cell lines and PLC/PRF/5 cell lines[5] and anti-inflammatory activity.[6] Consequently, much effort has been made toward identifying general methods for the synthesis of these 6,6-benzannulated spiroketals. Generally, strategies for 6,6-benzannulated spiroketal syntheses include acid-promoted cyclization of protected diol with ketone precursors[7] or dehydration-cyclization of dihydroxy ketones,[8] intramolecular Michael reaction,[9] Ti-mediated spirocyclization,[10] and oxidative cyclization,[11] hetero Diels−Alder reaction,[12] reductive cyclization reaction,[13] and $Me_3SiI$-promoted spiroketalization of salicylic aldehydes.[14] In spite of all these significant achievements, Ag/Brønsted acid co-catalysis toward 6,6-benzannulated spiroketals via bicyclization cascade of β-alkynyl ketones, to the best of our knowledge, is virtually unexplored so far.

Catalytic cyclization of β-alkynyl ketones offers a flexible and reliable method for the synthesis of biologically interesting cyclic structures in a convergent manner.[15,16] Specifically, the group of Yamamoto pioneered the seminal work on metal-catalyzed [4 + 2] cycloaddition between β- alkynyl ketones and alkenes or alkynes (Scheme 1a).[15a,b] Very recently, we have

**Scheme 1. Profile Application of Cycloadditions**




reported silver-mediated *oxo*-cyclization and C($sp^3$)−H biphosphinylation of β-alkynyl ketones toward functionalized isochromenes, in which the in situ generation of methyleneisochromenes **A** is a key step to capture diarylphosphine oxide radicals (Scheme 1b).[17] In view of these successful transformations and our recent findings on dual synergistic catalysis,[18] we envisaged that under Ag-catalyzed conditions, β-alkynyl ketones could be transformed into methyleneisochromenes **A** with a nucleophilic site, enabling their 1,6-addition

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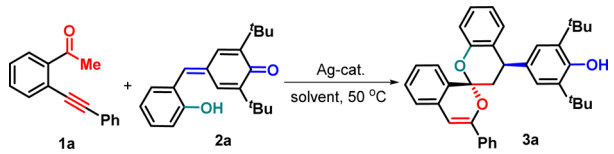
reactions with *para*-quinone methides (*p*-QMs)[19] catalyzed by Brønsted acid through [4 + 2] cycloaddition toward spiro-[chromane-2,1′-isochromene] derivatives. As expected, the combination of silver trifluoroacetate (AgTFA) and 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate ($BiNPO_4H$) as a dual catalyst system makes these transformations work well, accessing the desired 6,6-dibenzannulated spiroketals (Scheme 1c). Interestingly, the diastereoselectivity of 6,6-dibenzannulated spiroketals could be controlled well by using a Ag/Brønsted acid co-catalytic system, together with realization of $C(sp^3)$−H functionalization adjacent to the carbonyl group on the *β*-alkynyl ketone unit. Herein, we report these interesting observations in which new and selective 6-*endo*-*dig* *oxo*-cyclization and 1,6-addition-cyclization cascades were first achieved.

Initially, *β*-alkynyl ketone **1a** was selected as a model substrate and subjected to the reaction with *p*-QM **2a** in acetonitrile ($CH_3CN$) using silver trifluoroacetate (AgTFA, 10 mol %) as a catalyst at 50 °C under air conditions (Table 1,

**Table 1. Optimization of Reaction Conditions**[a]



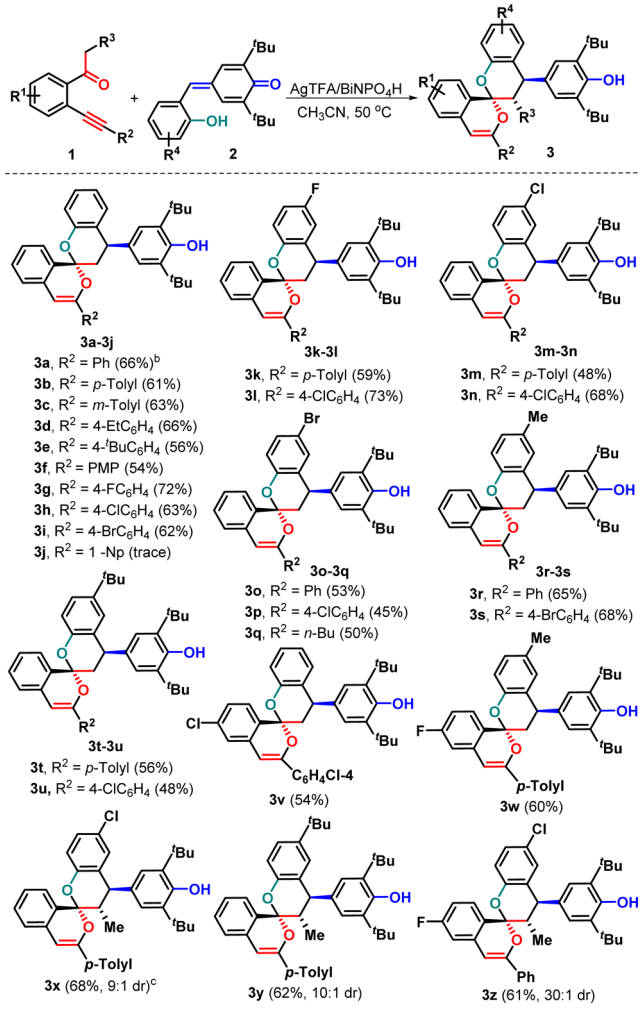

| entry | co-catalyst (mol %) | solvent | yield (%)[b] |
|---|---|---|---|
| 1 | AgTFA (10) | $CH_3CN$ | trace |
| 2 | AgTFA (10)/$BiNPO_4H$ (20) | $CH_3CN$ | 66[c] |
| 3 | AgOAc (10)/$BiNPO_4H$ (20) | $CH_3CN$ | NR[d] |
| 4 | AgOTf (10)/$BiNPO_4H$ (20) | $CH_3CN$ | 35. |
| 5 | $AgNO_3$ (10)/$BiNPO_4H$ (20) | $CH_3CN$ | NR |
| 6 | AgTFA (10)/PivOH (20) | $CH_3CN$ | trace |
| 7 | AgTFA (10)/*p*-TsOH (20) | $CH_3CN$ | 20 |
| 8 | AgTFA (10)/TFA (20) | $CH_3CN$ | 46 |
| 9 | AgTFA (10)/$BiNPO_4H$ (10) | $CH_3CN$ | 30 |
| 10 | AgTFA (5)/$BiNPO_4H$ (20) | $CH_3CN$ | 43 |
| 11 | AgTFA (10)/$BiNPO_4H$ (20) | toluene | 55 |
| 12 | AgTFA (10)/$BiNPO_4H$ (20) | 1,4-dioxane | trace |
| 13 | AgTFA (10)/$BiNPO_4H$ (20) | THF | trace |
| 14 | AgTFA (10)/$BiNPO_4H$ (20) | $CH_3CN$ | 53[e] |
| 15 | AgTFA (10)/$BiNPO_4H$ (20) | $CH_3CN$ | 60[f] |

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Ag-catalyst (*x* mol %), Brønsted acid catalyst (*y* mol %), solvent (3.0 mL), under air conditions. [b]Isolated yield based on substrate **2a**. [c]$BiNPO_4H$ (1,1′-binaphthyl-2,2′-diyl hydrogen phosphate). [d]No reaction (NR). [e]The reaction was carried out at room temperature. [f]The reaction was carried out at 60 °C.

entry 1). This reaction gave a trace amount of product **3a** which failed to be isolated, and substrate **2a** was recovered. To our delight, when $BiNPO_4H$ (20 mol %) as a Brønsted acid co-catalyst was added into the above reaction system, the desired 6,6-benzannulated spiroketal **3a** was generated in 66% yield (entry 2), indicating that Brønsted acid catalyst may play a key role in accelerating the intermolecular 1,6-addition reaction.[19] The following screening of several other silver salts such as AgOAc, AgOTf and $AgNO_3$ showed that these silver catalysts did not show any improvements in the yield of product **3a** (entries 3−5). Exchanging $BiNPO_4H$ for pivalic acid (PivOH) as a Brønsted acid catalyst completely suppressed the reaction process (entry 6). Employment of both *p*-toluenesulfonic acid (*p*-TsOH) and trifluoroacetate acid (TFA) had no positive effect on the yield of **3a** as compared with $BiNPO_4H$ (entry 2 vs entries 7−8). Lowering the $BiNPO_4H$ or AgTFA loading is not beneficial for this transformation (entries 9−10). We next investigated the solvent effect by employing different solvents including toluene, 1,4-dioxane, and tetrahydrofuran (THF), but <55% yield was observed (entries 11−13). Movever, the reaction could proceed at either room temparetue or 60 °C, but provided the slightly lower conversion into **3a** as compared with the reaction temperature being 50 °C (entry 2 vs entries 14−15).

With these acceptable reaction conditions in hand, we then systematically investigated the generality of this Ag/$BiNPO_4H$ co-catalyzed spiroketalization cascades for accessing spiro-[chromane-2,1′-isochromene] derivatives **3** by examining *β*-alkynyl ketone and *p*-QM components (Scheme 2). At first, *β*-alkynyl ketones with diverse functionalities were evaluated in combination with *p*-QM **2a**. Various substituents with electronically poor and rich nature at different positions of arylalkynyl ($R^2$) moiety were proven not to hamper this Ag/$BiNPO_4H$ co-catalysis, affording the corresponding 6,6-benzannulated spiroketals **3b**−**3i** with excellent diastereoselec-

**Scheme 2. Substrate Scope for Synthesis of 3**[a,b,c]




[a]Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), AgTFA (10 mol %), $BiNPO_4H$ (20 mol %), $CH_3CN$ (3.0 mL), air conditions. [b]Isolated yield based on substrate **2**. [c]dr Value based on the analysis of $^1H$ NMR.



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tivity (single diastereoisomer) and yields ranging from 54% to 72% (see SI). Functional groups like methyl (**1b** and **1c**), ethyl (**1d**), *tert*-butyl (**1e**), methoxy (*p*-methoxyphenyl = PMP, **1f**), fluoride (**1g**), chloride (**1h**), and bromide (**1i**) were compatible with the catalytic conditions. Among them, a slight increase in the yield was obtained (**3g**, 72%) as the *p*-fluorophenyl counterpart (**1g**) was served as a reaction partner, whereas the methoxy group resulted in a decreased yield (**3f**). *β*-Alkynyl ketone **1j** having a 1-naphthyl (1-Np) group on the alkynyl moiety was not an appropriate candidate, as only a trace amount of product **3j** was detected under the standard conditions (Scheme 2). Next, *p*-QMs **2** carrying fluoro, chloro, bromo, methyl, and *t*-butyl groups at 4-position of the phenol ring were successfully engaged in the current Ag/$BiNPO_4H$ co-catalyzed spiroketalization, enabling 6-*endo*-*dig* *oxo*-cyclization/[4 + 2] cycloaddition toward the sole diastereoisomeric 6,6-dibenzannulated spiroketals **3k**−**3u** in 48%−73% yields. Notably, substrate **1k** with an *n*-butyl (*n*-Bu) group on the alkynyl moiety was proven to be a suitable reaction partner, accessing the corresponding product **3q** as a sole diastereoisomer in 50% yield. Moreover, representative chloro (**1l**) and fluoro (**1m**) substituents at 4-position of the internal arene ring of substrates **1** would be accommodated, confirming the success of transformations, as the corresponding 6,6-dibenzannulated spiroketals **3v** and **3w** were afforded with 54% and 60% yields, respectively. In view of these results, we considered changing the substituents ($R^3$) located at *α*-position of carbonyl group of substrates **1** to explore the feasibility of this Ag/$BiNPO_4H$ co-catalysis. Replacing the methyl group with an ethyl functionality at *α*-position of carbonyl group, *β*-alkynyl ketones **1n** and **1o** were tolerated well under the standard catalytic conditions, furnishing the corresponding inseparably diastereoisomeric spiroketals **3x**−**3z** with 61%−68% yields and 9:1 to 30:1 dr (Scheme 2). It is noteworthy that the current protocol represents a new and practical pathway for assembly of richly decorated 6,6-dibenzannulated spiroketals **3** with generally excellent diastereoselectvity through Ag/$BiNPO_4H$ co-catalyzed bicyclization involving C($sp^3$)−H functionalization of *β*-alkynyl ketones. The structures of these spiroketals **3** were characterized by their NMR spectroscopy and HRMS. In the case of **3i**, its structure was unequivocally confirmed by carrying out single crystal X-ray diffraction (Figure 2).

To expand potential application of this method, a gram-scale reaction of **1b** (6 mmol) with **2a** (4 mmol) was conducted under the standard conditions, offering **3b** in 57% yield (Scheme 3).

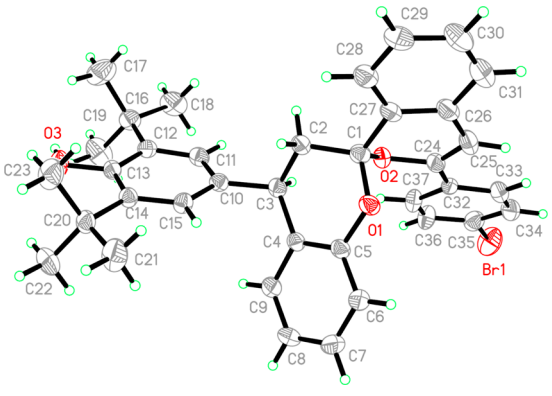
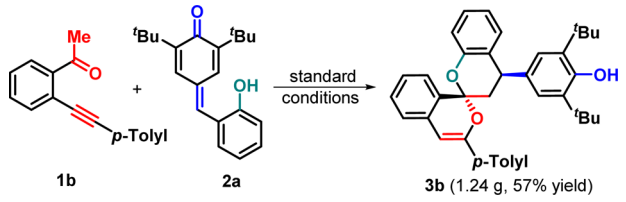


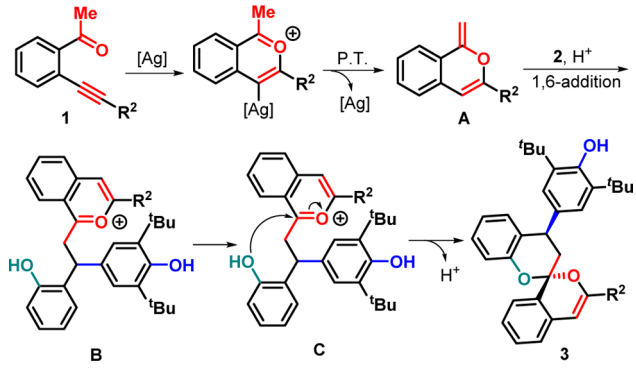

**Figure 2.** ORTEP drawing of **3i**.

**Scheme 3. Gram-Scale Experiment**




Combining the above observations and the literature precedents of silver-catalyzed *oxo*-cyclization,[16,20] a reasonable mechanism for forming products **3** was proposed as shown in Scheme 4. First, Ag-catalyzed 6-*endo*-*dig* *oxo*-cyclzation of *β*-

**Scheme 4. Plausible Reaction Pathway**




alkynyl ketones **1** generates isobenzopyrylium intermediate,[16] followed by proton transfer (PT) to afford isochromene **A**. Next, $BiNPO_4H$-catalyzed 1,6-addition between **A** and **2** yields intermediate **B**,[19] which undergoes intramolecular *oxo*-nucleophilic addition and subsequent deprotonation to offer products **3**.

In conclusion, starting from *β*-alkynyl ketones and *p*-QMs, we have established Ag/$BiNPO_4H$ co-catalyzed 6-*endo*-*dig* *oxo*-cyclization/[4 + 2] cycloaddition cascades for highly diaseteroselective synthesis of structurally diverse spiro[chromane-2,1′-isochromene] derivatives with generally good yields. The present dual catalytic system provides an efficient and practical pathway for constructing 6,6-dibenzannulated spiroketals, in which *β*-alkynyl ketones with a methyl group adjacent to a carbonyl group were converted into the sole diastereoisomeric spiro compounds containing an isochromene unit via C($sp^3$)−H functionalization. Further assessment of the bioactivity of these spiroketal compounds is in progress in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01705.

Experimental procedures and spectroscopic data for all new compounds **3a**−**3z** (PDF)
X-ray crystal data (CIF) for **3i** (CIF)

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## Notes

The authors declare no competing financial interest.

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