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# Phosphine-Catalyzed Domino Benzannulation: An Efficient Method to Construct Biaryl Skeletons

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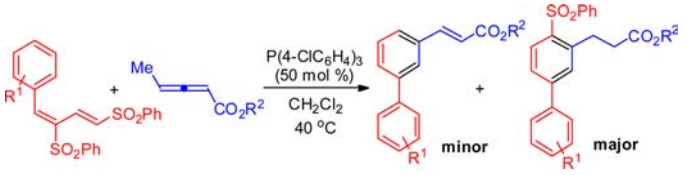
## ABSTRACT




**The first phosphine-catalyzed domino benzannulation reaction to prepare a variety of functionalized biaryls from allenoates and dienic sulfones is developed.**

Biaryls are important structural motifs in natural products and biologically active compounds that have received extensive attention.[1] Over the past decades, transition-metal-catalyzed cross-coupling strategies including Negishi, Suzuki, Hiyama, and Stille reactions have become fundamental methods to prepare biaryl compounds.[2,3] Because the concept of organocatalysis occurred to many at a similar time, Shi, Hayashi, Lei, and Itami independently prepared biaryls through organocatalyzed direct C−H activation.[4] Although these advances have been made in the construction of biaryls, such strategies rely on aryl−aryl bond formation, and difficulties associated with control of chemo-/regioselectivity and harsh reaction conditions have often impeded their application.

Recently, phosphine-mediated domino reactions involving allenoates or allylic carbonates have become a versatile platform to synthesize carbon- and heterocycles.[5] Only a few stoichiometric phosphine-mediated domino benzannulation reactions have been reported to date. For example, we developed a $PPh_3$-mediated domino

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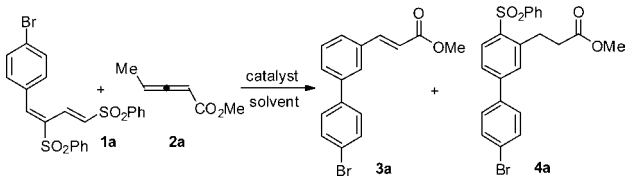
benzannulation strategy to construct multiaryl compounds from allylic carbonates.[6a] Recently, the Tang group reported a benzannulation method based upon allylic phosphorus ylides.[6b] However, resource-efficient, sustainable catalytic processes have not yet been realized.[7] In 2009, we discovered the first example that the $\gamma$-$CH_3$ of allenoate undergoes cyclization to form chroman derivates.[8] Very recently, we realized the first example of phosphine-promoted [4 + 2] cyclizations using $\gamma$-substituted allenoates.[9] Intrigued by these studies and the versatile reactivity of conjugated dienes in constructing bicyclic and highly functionalized cyclopentene skeletons,[10−12] we decided to investigate the reaction between $\gamma$-$CH_3$-substituted allenoates[13] and conjugated dienes. Herein, we report the first phosphine-catalyzed domino reaction to synthesize functionalized biaryls.

We first prepared a family of 1,3-bis(sulfonyl)butadiene substrates *via* a four-step reaction sequence.[14] Treatment of dienic sulfone **1a** with allenoate **2a** in the presence of $PPh_3$ at 40 °C gave **3a** and **4a** in 15% and 25% yield, respectively (Table 1, entry 1). Screening of phosphine catalysts revealed that alkyl phosphines and LBBA were ineffective (Table 1, entries 2−4, 8). To our delight, use of $(4\text{-}ClC_6H_3)_3P$ gave the products in good yield and moderate selectivity (Table 1, entry 5). Alternative catalysts such as $(4\text{-}CH_3OC_6H_4)_3P$ and $(4\text{-}CF_3C_6H_4)_3P$ resulted in lower yields (Table 1, entries 6 and 7). Solvents such as $CHCl_3$, toluene, and benzene gave the desired products in lower yield, and they were not detected using THF (Table 1, entries 9−11, 15). Meanwhile, $CH_3CN$, DCE, and DMF did not improve the yield compared with that using DCM (Table 1, entries 12−14). We found that temperature affected both the yield and selectivity of this reaction. Lowering the reaction temperature to 20 °C led to a lower yield (Table 1, entry 16). When the reaction was performed at 60 °C, the ratio of the yields of products was inversed (Table 1, entry 17). Reducing catalyst loading to 10% had a detrimental effect on product yield (Table 1, entry 18).

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




| | | | yield (%)[b] | |
|---|---|---|---|---|
| entry | catalyst | solvent | **3a** | **4a** |
| 1 | $Ph_3P$ | DCM | 15 | 25 |
| 2 | $Bu_3P$ | DCM | 0 | 0 |
| 3 | $Ph_2EtP$ | DCM | 4 | trace |
| 4 | LBBA[c] | DCM | 11 | 9 |
| 5 | $(4\text{-}ClC_6H_4)_3P$ | DCM | 26 | 60 |
| 6 | $(4\text{-}CH_3OC_6H_4)_3P$ | DCM | 17 | 19 |
| 7 | $(4\text{-}CF_3C_6H_4)_3P$ | DCM | 15 | 25 |
| 8 | DPPB[d] | DCM | 9 | 6 |
| 9 | $(4\text{-}ClC_6H_4)_3P$ | $CHCl_3$ | 4 | 9 |
| 10 | $(4\text{-}ClC_6H_4)_3P$ | toluene | 4 | 7 |
| 11 | $(4\text{-}ClC_6H_4)_3P$ | THF | 0 | 0 |
| 12 | $(4\text{-}ClC_6H_4)_3P$ | $CH_3CN$ | 21 | 13 |
| 13 | $(4\text{-}ClC_6H_4)_3P$ | $ClCH_2CH_2Cl$ | 18 | 25 |
| 14 | $(4\text{-}ClC_6H_4)_3P$ | DMF | 17 | 18 |
| 15 | $(4\text{-}ClC_6H_4)_3P$ | benzene | 8 | 10 |
| 16[e] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 12 | 15 |
| 17[f] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 41 | 25 |
| 18[g] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 17 | 17 |
| 19[h] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 23 | 52 |
| 20[i] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 26 | 63 |
| 21[j] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 23 | 29 |
| 22[k] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 32 | 36 |
| 23[l] | $(4\text{-}ClC_6H_4)_3P$ | DCM | 19 | 36 |

[a] Reaction conditions: 1.0 equiv (0.3 mmol) of **1a**, 3.0 equiv of **2a**, 50 mol % catalyst in 5.0 mL of solvent at 40 °C under Ar. [b] Isolated yields. [c] LBBA: (2′-hydroxy-biphenyl-2-yl)-diphenylphosphane. [d] DPPB: 1,4-bis(diphenylphosphino)butane. [e] 20 °C. [f] 60 °C. [g] 10 mol %. [h] 30 mol %. [i] 100 mol %. [j] 24 h. [k] 48 h. [l] 7.5 d.

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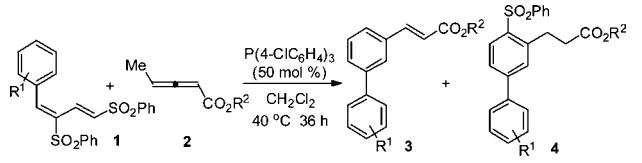
A catalyst loading of 30% gave a slightly lower yield (Table 1, entry 19). However, stoichiometric phosphine gave a similar result with a 50% catalyst loading (Table 1, entry 20). An investigation of different reaction times suggested that 36 h was optimal (Table 1, entries 21–23).

We then performed subsequent studies to probe the generality of this domino process. Under the optimized conditions, this process readily accommodates substitution at the 4-position of the aryl unit with electron-withdrawing and -donating groups (Table 2, entries 1–3). With regard to the substitution on the allenoates, it is noteworthy that increased steric hindrance does not result in a large decrease in efficiency (Table 2, entries 5–7). Dienic sulfones **1h**–**l** with a *meta*-substituent are compatible with the reaction conditions (Table 2, entries 8–12). However, compounds with *para*-$CH_3$ and *ortho*-substituents gave the corresponding intermediates in moderate yields (Table 2, entries 4, 13). This shows that electronic properties strongly affect the outcome of this reaction. In addition, we found that the reaction can be performed on 10 mmol scale with a similar yield (**3e**: 610 mg, 18% yield; **4e**: 2.661 g, 56% yield) and selectivity.

During the reaction, TLC analysis clearly showed that **3a** and an intermediate formed first and then the intermediate slowly transformed to product **4a**. We were able to separate the desired products **3a** and **4a**. When we subjected **1d** and **2a** to this reaction system, the main product was **5d** (containing **4d** as an inseparable byproduct) along with **3d**. When the reaction of **5d** and **2a** was carried out under the optimized reaction conditions, **5d** can transform into **3d** and **4d** (mixed with **5d**, which cannot be cleanly separated). It was deduced from the above that **5d** was an important intermediate in the reaction. Therefore, we used **5d′** to determine the exact structure of this intermediate. The structure and stereochemistry of **5d′** were determined by NMR spectroscopy (see the Supporting Information (SI)). $^1$H and $^{13}$C NMR spectral data obtained for **5d′** are summarized in Table 3. Further confirmation of the structure of **5d′** was derived from its HRMS analysis.

Interestingly, biaryls **3a** and **4a** could be transformed to the same compound **6** under the same reduction conditions (Scheme 1). When **1a** and **2a** were subjected to a one-pot two-step reaction, after the standard reaction condition,

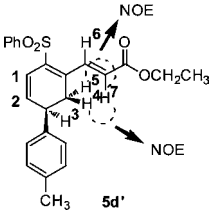
**Table 2.** Scope of Biaryl Formation[a]




| entry | $R^1$ | $R^2$ | yield (%)[b] | 4:3[c] |
|---|---|---|---|---|
| 1 | 4-Br | Me | 86 | 70:30 (**4a:3a**) |
| 2 | 4-$NO_2$ | Me | 36 | >99:1 (**4b:3b**) |
| 3 | 4-$OCH_3$ | Me | 28 | <1:99 (**4c:3c**) |
| 4[d] | 4-$CH_3$ | Me | 54 | 61:39 (**5d:3d**) |
| 5 | 4-Br | Et | 83 | 71:29 (**4e:3e**) |
| 6[e] | 4-Br | *t*-Bu | 87 | 78:22 (**4f:3f**) |
| 7 | 4-Br | Bn | 50 | 52:48 (**4g:3g**) |
| 8 | 3-Br | Me | 83 | 76:24 (**4h:3h**) |
| 9 | 3-Cl | Me | 89 | 73:27 (**4i:3i**) |
| 10 | 3-F | Me | 89 | 78:22 (**4j:3j**) |
| 11[e] | 3-F | Et | 73 | 78:22 (**4k:3k**) |
| 12 | 3-$NO_2$ | Me | 42 | 71:29 (**4l:3l**) |
| 13 | 2-Br | Me | 57 | 28:72 (**5m:3m**) |
| 14[e] | H | Me | 68 | 62:38 (**4n:3n**) |
| 15 | 2,4-Cl | Me | 54 | <1:99 (**4o:3o**) |
| 16[f] | R | Me | 65 | 80:20 (**4p:3p**) |

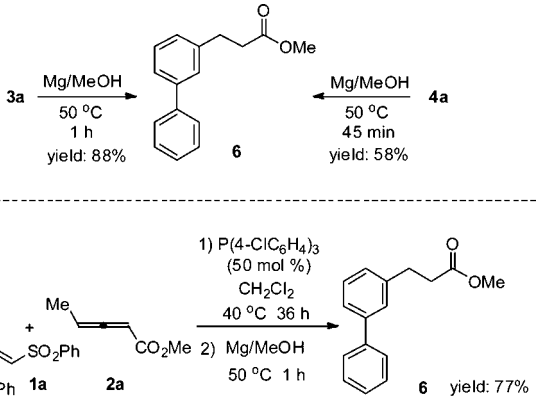
[a] Reaction conditions: 1.0 equiv (0.3 mmol) of **1a**, 3.0 equiv of **2a**, 50 mol % $(4\text{-}ClC_6H_4)_3P$ in 5.0 mL of $CH_2Cl_2$ at 40 °C under Ar. [b] Isolated yields. [c] The ratio of **4:3** (or **5:3**) was determined from the isolated yields. [d] A small amount of **4d** was present in product **5d** as an inseparable constituent. [e] A small amount of intermediate **5** was present in product **4** as an inseparable constituent. [f] R = thien-2-yl = $R^1C_6H_4$.

**Table 3.** $^1$H and $^{13}$C NMR Spectral Data for **5d′**

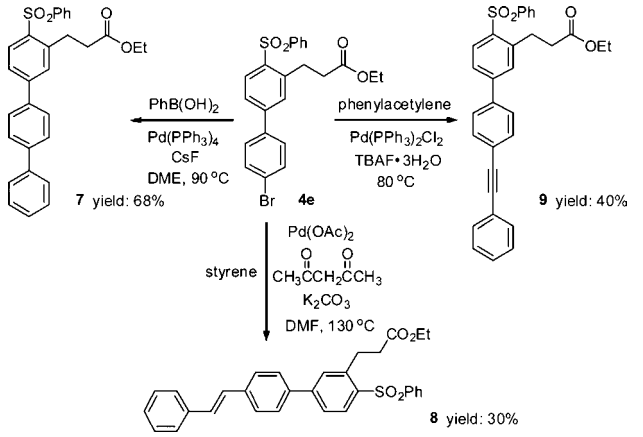



| position | $^1$H NMR (400 MHz) | $^{13}$C NMR (101 MHz) |
|---|---|---|
| 4 | 2.67 (dd, *J* = 16.8, 11.3 Hz, 1H) | 33.77 |
| 5 | 2.85 (dd, *J* = 17.0, 8.7 Hz, 1H) | 33.77 |
| 3 | 3.64–3.54 (m, 1H) | 38.55 |
| 7 | 6.04 (d, *J* = 15.8 Hz, 1H) | 123.97 |
| 2 | 6.23 (dd, *J* = 9.8, 3.9 Hz, 1H) | 135.96 |
| 1 | 6.74 (d, *J* = 9.7 Hz, 1H) | 122.63 |
| 6 | 8.66 (d, *J* = 15.8 Hz, 1H) | 138.48 |

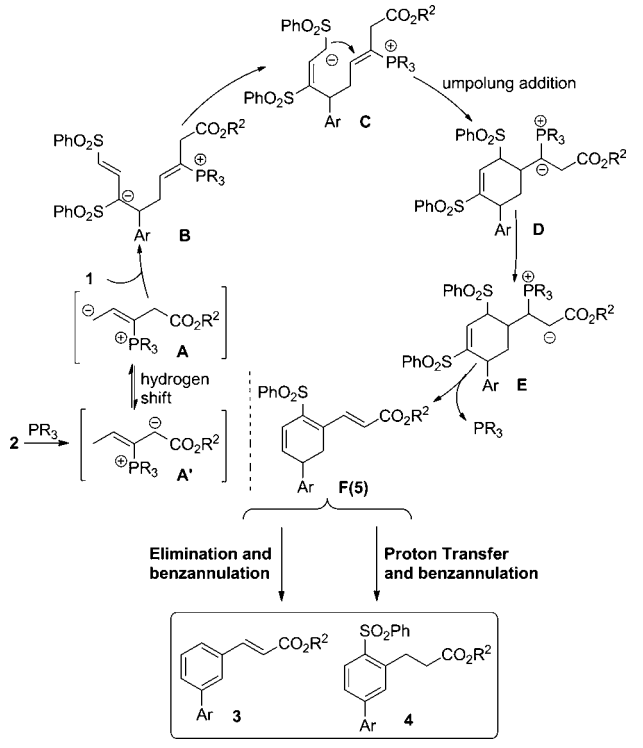
**Scheme 1.** Reduction of Biaryl Products and the One-Pot Reaction



**Scheme 2.** Synthetic Transformation of **4e**




**Scheme 3.** Plausible Mechanism for Biaryl Formation




the resulting reaction mixture was reduced by the Mg/MeOH system at 50 °C for another 1 h. Excitingly, product **6** was isolated in 77% yield (Scheme 1).

The products obtained through this domino reaction are useful building blocks in organic synthesis. To illustrate the synthetic utility of this method, **4e** was converted into the corresponding Suzuki, Heck, and Sonogashira products in moderate yields through traditional cross-coupling reactions (Scheme 2).

Based on the above experimental results and previous reports,[8,9] we propose the following mechanism for the developed reaction (Scheme 3). The reaction is triggered by nucleophilic addition of phosphine to electron-deficient allenoate to produce zwitterionic intermediate **A′**, followed by proton transfer[15] to give intermediate **A**. Then, **A** is added to dienic sulfones **1** to produce intermediate **B**. After another proton transfer, intermediate **B** is transformed to intermediate **C**. The subsequent intramolecular umpolung addition of intermediate **C** results in the formation of intermediate **D**, which proceeds *via* proton transfer and elimination of the catalyst and steps of proton transfer to give the key intermediate **F** (for more information, see the SI). Then, mediated by intermediate **A** or **A′**, the key intermediate **F** undergoes elimination and benzannulation to produce product **3**. Or **F** undergoes proton transfer and benzannulation to give the corresponding biaryl **4** (for more information, see the SI).

In conclusion, we have developed an efficient phosphine-catalyzed domino reaction between dienic sulfones and allenoates, which provides access to biaryls under mild reaction conditions. The key intermediate **5d′** was characterized, and its intermediacy in the conversion of **1** to biaryls **3** and **4** was demonstrated. The biaryl products were readily derivatized to a range of useful synthetic building blocks. Furthermore, we used $\gamma$-$CH_3$ allenoates in phosphine-catalyzed benzannulation for the first time. Further studies for the application of this strategy in organic synthesis will be investigated.

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**Supporting Information Available.** Detailed experimental procedures, spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(15) For mechanistic studies of the phosphine-catalyzed cycloaddition reaction, see: (a) Tran, Y. S.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 12632–12633. (b) Xia, Y.; Liang, Y.; Chen, Y.; Wang, M.; Jiao, L.; Huang, F.; Liu, S.; Li, Y.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007**, *129*, 3470–3471. (c) Liang, Y.; Liu, S.; Xia, Y.; Li, Y.; Yu, Z.-X. *Chem.—Eur. J.* **2008**, *14*, 4361–4373.

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