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A Sulfur Ylides-Mediated Domino Benzannulation Strategy to Construct Biaryls, Alkenylated and Alkynylated Benzene Derivatives

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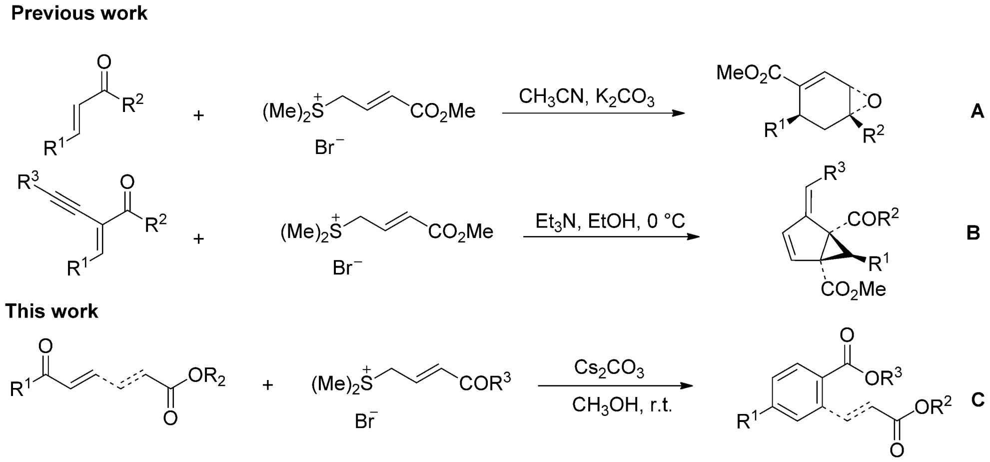
Abstract: An efficient domino benzannulation strategy with the participation of sulfur ylides for the construction of biaryl compounds is disclosed. It could also be extended to the synthesis of alkenylated and alkynylated benzene derivatives under mild conditions. This versatile strategy combined with traditional metal-catalyzed cross-coupling methods should offer a practical route to construct complex multiaryl compounds.

Keywords: benzannulation; biaryls; domino reactions; multiaryl compounds; sulfur ylides

Biaryl skeletons are the key blocks of many natural products, bioactive molecules and functional materials.[1] Consequently, efficient strategies to construct multiaryl compounds are of the utmost importance and have been intensively investigated. Current synthetic strategies for accessing such motifs mainly focus on transition metal-catalyzed cross-coupling reactions.[2] Recently, benzannulation reactions have attracted considerable attention.[3] Tang and Liu have reported two methods to construct multiply substituted benzenes without metal catalysts. Our group has reported on phosphine-mediated benzannulation reactions.[3a,b,e] So far, to the best of our knowledge, no multiaryl compounds have been directly constructed from sulfonium salts.

Sulfur ylides, which have been developed as valuable and versatile synthetic reagents in organic synthesis,[4] are widely applied, also in domino reactions. Corey and Chaykovsky,[5] Aggarwal,[6] Tang,[7] Xiao[8] and others[9] have developed a series of elegant domino reactions of sulfur ylides that include traditional cyclization reactions to build three-membered ring compounds (such as epoxides,[6a–d,f,g] aziridines,[6e,7g,9d] and cyclopropanes[6h,7b,e,9e]) and some annulation processes to form the 5- and 6-membered heterocyclic compounds.[7a–d,8,9a–c,h–k] In further investi-



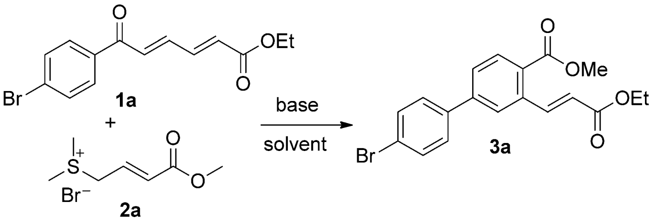
Scheme 1. Reactions of crotonate-derived sulfonium salts.

gations, Tang et al. reported a tandem Michael addition/ylide epoxidation of the crotonate-derived sulfonium salt with α,β-unsaturated ketones for the synthesis of functionalized cyclohexadiene epoxides in high efficiency (Scheme 1, **A**).[7e] Recently, Zhang and coworkers reported an appealing domino approach using thw crotonate-derived sulfonium salt with electron-deficient enynes to construct bicyclo-[3.1.0]hexenes (Scheme 1, **B**).[9g]

Based upon these studies, we were keen to develop an efficient, practical benzannulation strategy to construct multisubstituted biaryls with sulfur ylides for the first time (Scheme 1, **C**).

We initiated our investigation by subjecting enone-ester **1a**[10] to sulfonium salt **2a** in the presence of Cs_2CO_3 in CH_3CN at room temperature. To our delight, the biaryl compound **3a** was obtained in 77% yield (Table 1, entry 1). The configuration of the product **3a** was confirmed by combination of NMR, HR-MS and X-ray crystallographic analysis[11] (see the Supporting Information). Encouraged by this result, we next explored the influence of other bases on this reaction. As shown in Table 1, other bases, such as K_2CO_3, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), Et_3N gave no better results than Cs_2CO_3 (Table 1, entries 2–4). When *t*-BuOK was used, no product was obtained (Table 1, entry 5). These results indicate that Cs_2CO_3 shows the highest activity for the reaction. With the addition of 20 μL H_2O as additive,[7f] the yield could not be improved (Table 1, entry 6). On screening for solvents, we found that the reaction also worked in $CHCl_3$, CH_2Cl_2 THF albeit in somewhat low yields (entries 7–9). Reactions in polar solvents, such as DMF, DMSO gave moderate yields rapidly (entries 10 and 11). However, this reaction could not proceed in the non-polar solvent toluene (Table 1, entry 14). It is worthwhile to note that the reaction gave higher yields in the polar protic solvents (Table 1, entries 12 and 13). We also found that the product **3a** underwent a transesterification process with methanol and ethanol as solvent. On decreasing the amount of Cs_2CO_3, the yield of **3a** also decreased (Table 1, entries 15 and 16). Changing the ratio of **1a**/**2a** did not improve the yield (Table 1, entries 17 and 18). Finally, we established the optimal reaction conditions as follows: the ratio of **1a/2a** was 1:2, with 4.0 equivalents of Cs_2CO_3, in CH_3OH (3 mL) at room temperature for the synthesis of compounds **3.**

Table 1. Optimization of the domino benzannulation reaction with sulfur ylides.[a]



Entry	Base	Solvent	Time [h]	Yield [%][b]
1	Cs_2CO_3	CH_3CN	5	77
2	K_2CO_3	CH_3CN	5	67
3	DBU	CH_3CN	4.5	51
4	Et_3N	CH_3CN	4.5	62
5	*t*-BuOK	CH_3CN	5	NR
6[c]	Cs_2CO_3	CH_3CN	4	75
7	Cs_2CO_3	CH_2Cl_2	9	41
8	Cs_2CO_3	$CHCl_3$	6	45
9	Cs_2CO_3	THF	7	43
10[d]	Cs_2CO_3	DMF	2	58 (48)
11[d]	Cs_2CO_3	DMSO	2	57 (45)
12[j]	Cs_2CO_3	C_2H_5OH	6	70
13[e]	Cs_2CO_3	CH_3OH	6	86
14	Cs_2CO_3	toluene	12	NR
15[f]	Cs_2CO_3	CH_3OH	5	80
16[g]	Cs_2CO_3	CH_3OH	5	71
17[h]	Cs_2CO_3	CH_3OH	6	57
18[i]	Cs_2CO_3	CH_3OH	5	84

[a] Unless otherwise noted, the reactions were carried out on a 0.3 mmol scale, using 4.0 equivalents of base, in solvent (3 mL) at room temperature. The ratio of **1a**/**2a** was 1:2.

[b] Yields of isolated products.

[c] 20 μL of H_2O were added.

[d] In parentheses are the yields obtained when the reaction time was extended to 6 h.

[e] The transesterification product **3c**.

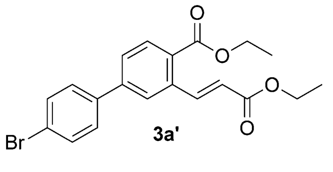
[f] 3 equivalents of Cs_2CO_3 were used.

[g] 2 equivalents of Cs_2CO_3 were used.

[h] The ratio of **1a**/**2a** was 1:1.

[i] The ratio of **1a**/**2a** was 1:3.

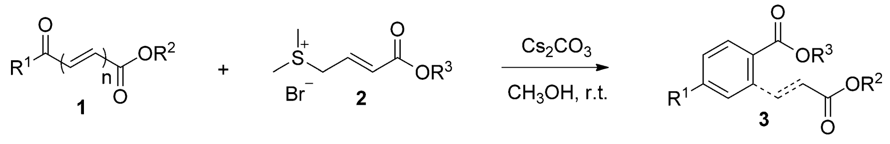
[j] The structure of transesterification product **3a′** is:



3a'

With the optimized reaction conditions in hand, we explored the substrate scope of the benzannulation reaction. As shown in Table 2, the desired products **3** were achieved in good to excellent yields, irrespective of the electronic properties and the position of the substituents on the benzene ring of **1** (Table 2, entries 1–10). Also, increasing the size of the ester group in the sulfonium salt **2** decreased the yield of **3** (Table 2, entries 2, 14 and 15). In addition, we chose acetonitrile (CH_3CN) as the solvent to avoid transesterification in some cases, which could also give moderate to good yields (Table 2, entries 11–15). To our delight, the alkyl- and furan-2-yl-substituted unsaturated enone-esters **1** could react smoothly to construct the monobenzene skeleton and heterocyclic aromatic ring system (Table 2, entries 16 and 17). Afterwards, the substrate scope was further expanded. Substituted

Table 2. Investigating the scope of the sulfur ylides participating in the domino benzannulation reaction.[a]



Entry	1	R^1	n	R^2	R^3	Time [h]	Product	Yield [%][b]
1	**1b**	C_6H_5	2	Me	Me	5	**3b**	82
2	**1c**	4-BrC_6H_4	2	Me	Me	5	**3c**	94
3	**1d**	4-ClC_6H_4	2	Me	Me	5	**3d**	86
4	**1e**	4-FC_6H_4	2	Me	Me	5	**3e**	83
5	**1f**	4-$CH_3C_6H_4$	2	Me	Me	5	**3f**	65
6	**1g**	4-$OCH_3C_6H_4$	2	Me	Me	5	**3g**	78
7	**1h**	4-$BnOC_6H_4$	2	Me	Me	5	**3h**	75
8	**1i**	3-BrC_6H_4	2	Me	Me	2	**3i**	73
9	**1j**	2-$CH_3C_6H_4$	2	Me	Me	4	**3j**	68
10	**1k**	2,4-ClC_6H_3	2	Me	Me	5	**3k**	60
11[c]	**1a**	4-BrC_6H_4	2	Et	Me	5	**3a**	80
12[c]	**1l**	4-ClC_6H_4	2	Et	Me	4.5	**3l**	53
13[c]	**1m**	4-$CH_3C_6H_4$	2	Et	Me	4.5	**3m**	58
14[c]	**1c**	4-BrC_6H_4	2	Me	Et	5	**3n**	89
15[c]	**1c**	4-BrC_6H_4	2	Me	*i*Pr	5	**3o**	76
16	**1p**	CH_3	2	Me	Me	3	**3p**	81
17	**1q**	furyl	2	Me	Me	5	**3q**	61
18	**1r**	4-BrC_6H_4	1	Me	Me	4	**3r**	84
19	**1s**	4-$CH_3C_6H_4$	1	Me	Me	4	**3s**	82
20[d]	**1c**	4-BrC_6H_4	2	Me	Me	6	**3c**	72

[a] *Reaction conditions:* **1** (1.0 equiv., 0.3 mmol), **2** (2.0 equiv.), Cs_2CO_3 (4.0 equiv.), CH_3OH (3 mL) at room temperature.
[b] Isolated yields.
[c] The solvent was CH_3CN.
[d] Multigram scale experiment.

(*E*)-methyl 4-oxo-4-arylbutenoates[12] **1r** and **1s** were also successfully employed in the reaction (Table 2, entries 18 and 19).

To test the practicality of the current methodology, a gram-scale reaction was carried out (Table 2, entry 20) whereby 5 mmol **1c** and 10 mmol **2a** in 70 mL methanol gave 1.35 g of the desired product (72% yield) in 6 h.

Encouraged by the successful synthesis of the biaryl products as described above, we envisioned that this strategy could also be used for the preparation of alkenylated benzene derivatives. Delightfully, various dienones **4a–4d**,[13] bearing phenyl(**4a**), electron-deficient aryl (**4b**, **4c**) and electron-rich aryl (**4d**) groups reacted with sulfonium salt **2a** to afford the corresponding products **5a–5d** in modest yields (Table 3).

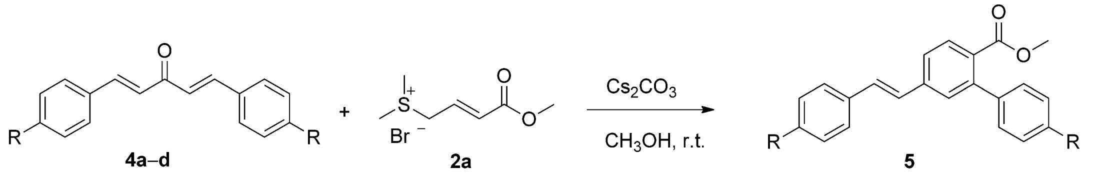
When the unsymmetrical dienone **4e** was used, a mixture of products **5e** and **5e′** was obtained in 42% yield(Figure 1). The ratio of the two isomers was 4.8:1 as determined by ^{1}H NMR analysis. Unfortunately, it was hard to determine which one was the main product.

Stimulated by the above investigations, we were pleased to find that this domino benzannulation strategy could also be used to construct alkynylated benzene derivatives. The reactions of enynones[14] **6a–6d** with sulfonium salt **2a** proceeded smoothly in a short time at room temperature, although with slight lower yields (Table 4). The low yields of products **7** are probably due to polymerization of enynones **6** under alkaline conditions. Although further optimization of the reaction conditions could not improve the yield of products **7** (see the Supporting information, Table S1), to the best of our knowledge, this is the first report on the construction of alkynylated benzene products in a transition metal-free manner.

To demonstrate the versatility of this domino reaction, the transformations of **3c**, **3i** and **5b** into the corresponding more complex multiaryl compounds **3c′**, **3i′**and **5b′** were realized by traditional cross-coupling methods (Figure 2). Therefore, we believe that the combination of sulfur ylides participating in a domino benzannulation strategy with the traditional metal-catalyzed cross-coupling methods should offer a platform to construct complex multiaryl compounds.

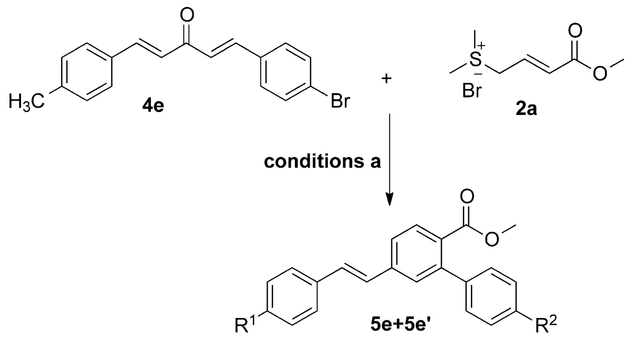
On the basis of our experimental results[3a,10a,9h] and previous related studies,[7f,9g,3c,d] several possible mechanisms are depicted in Scheme 2. The sulfonium salt **2** could be converted to allyic ylides **A** and **B** with the aid of Cs_2CO_3, then Michael addition of **B** to enone-

Table 3. The synthesis of the alkenylated benzene products **5**.[a]



Entry	Substrate	R	Time [h]	Product	Yield [%][b]
1	**4a**	H	5	**5a**	43
2	**4b**	Br	5	**5b**	65
3	**4c**	Cl	6	**5c**	54
4	**4d**	Me	6	**5d**	49

[a] *Reaction conditions:* **4** (1.0 equiv., 0.3 mmol), **2a** (3.0 equiv.), Cs$_2$CO$_3$ (4.0 equiv.), CH$_3$OH (3 mL) at room temperature.
[b] Isolated yields.



total yield 42%
5e: R^1 = CH$_3$, R^2 =Br
5e': R^1 = Br, R^2 = CH$_3$

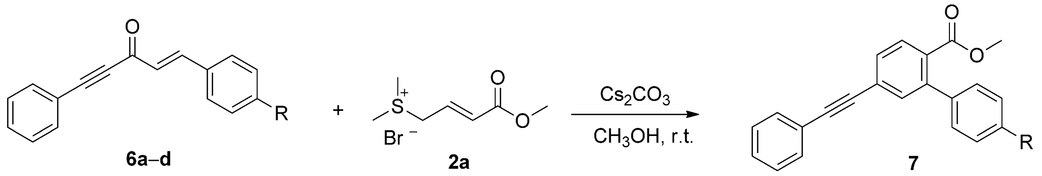
conditions a: **4e** (1.0 equiv., 0.3 mmol), **2a** (2.0 equiv,) Cs$_2$CO$_3$ (4 equiv.), CH$_3$OH (3 mL), r.t., 5 h

Figure 1. The reaction of the unsymmetrical dienone **4e** and sulfonium salt **2a.**

ester **1** would lead to enolate **C**, which could be further transferred to **E** by proton transfer and isomerization. Intramolecular nucleophilic addition of **E** could lead to **F**, which could subesquently undergo proton transfer and isomerization to furnish **G** (Path A). Elimination of dimethyl sulfide could afford cyclohexadiene **H** which finally would give product **3** *via* dehydration.

Intermediate **E** may also give **E1** through intramolecular epoxidation and elimination of Me$_2$S (Path **B**). Then product **3** is formed by base-mediated ring opening and dehydration. In order to get additional information on possible reaction intermediates **E1**, we have tried the reaction at low temperatures, unfortunately, no formation of intermediate **E1** could be observed (see the Supporting Information, Table S2). Intermediate **E** could also undergo nucleophilic addition and a sulfur-Wittig-type reaction followed by oxidative aromatization to deliver the corresponding product **3** (Path C). However, when the reaction was conducted under an N$_2$ atmosphere, no cyclohexadiene **F1** could be isolated, instead, product **3** was obtained in high yield (see the Supporting Information). In addition, no DMSO could be detected by MS even in the gram-scale reaction. Therefore, we consider that path A is the more reasonable pathway for the reaction.

Table 4. The synthesis of alkynylated benzene products **7**.[a]



Entry	Substrate	R	Time [min]	Product	Yield [%][b]
1	**6a**	H	10	**7a**	29
2	**6b**	Br	15	**7b**	34
3	**6c**	Cl	10	**7c**	36
4	**6d**	CH$_3$O	40	**7d**	25

[a] *Reaction conditions:* **6** (1.0 equiv., 0.3 mmol), **2a** (2.0 equiv.), Cs$_2$CO$_3$ (4.0 equiv.), CH$_3$OH (3 mL) at room temperature.
[b] Isolated yields.

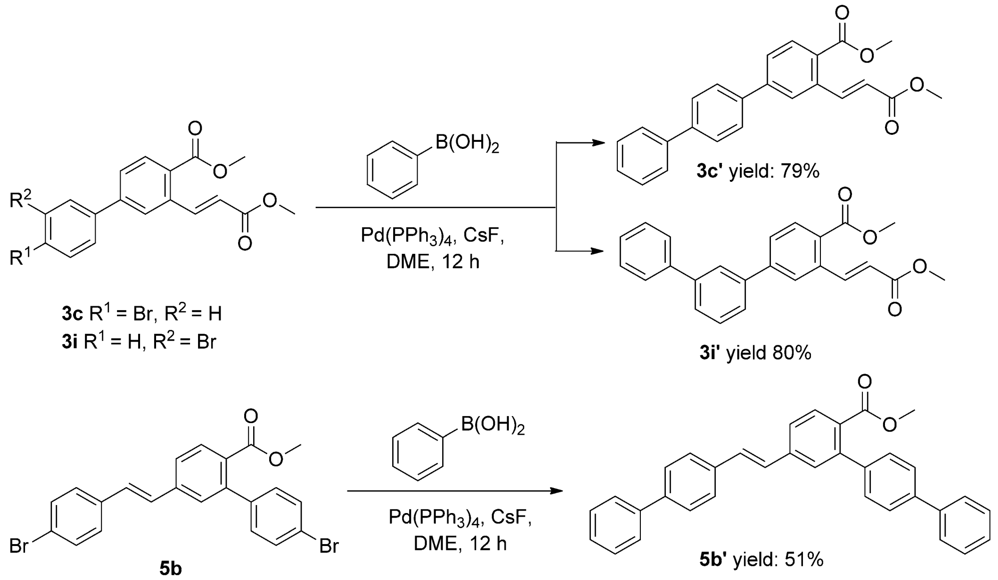
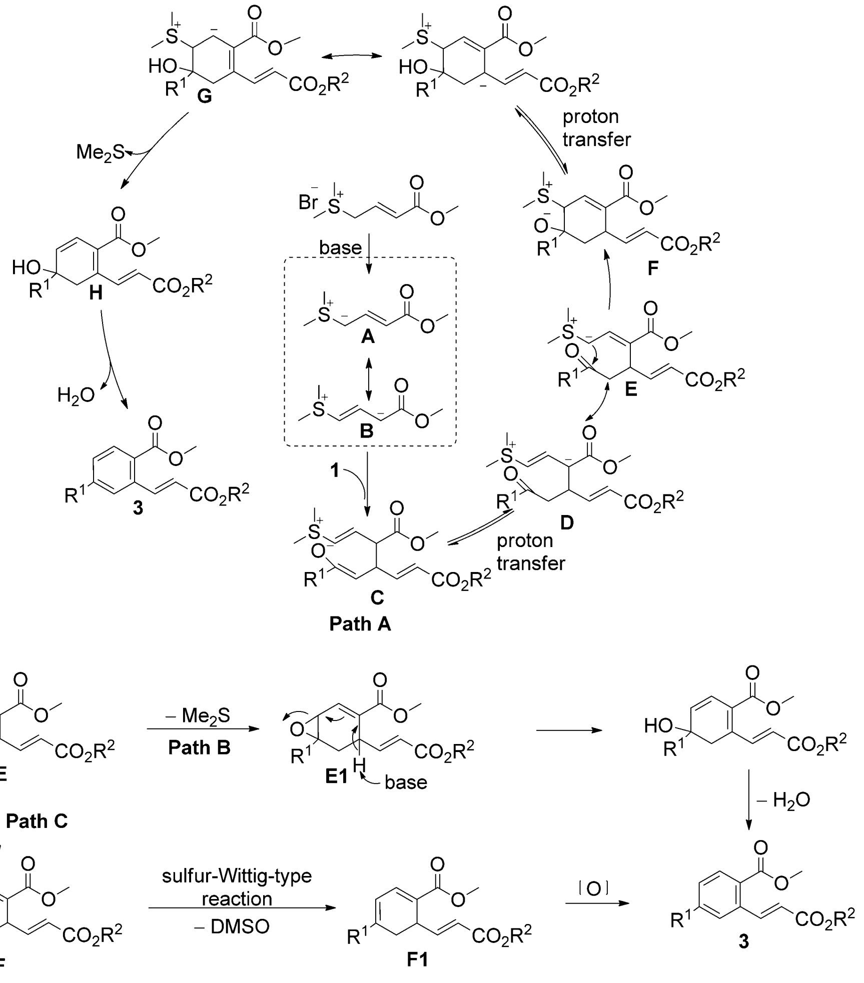


Figure 2. Synthetic transformations of products **3c**, **3i**, and **5b** (DME = dimethoxyethane).



Scheme 2. Plausible mechanism for the formation of compounds **3**.

In conclusion, we have developed a versatile, efficient domino benzannulation strategy with participation of sulfur ylides for the construction of biaryl compunds in moderate to high yields under mild conditions. Also, alkenylated and alkynylated benzene derivatives could also be constructed through this procedure. Thus, our domino benzannulation strategy combined with traditional metal-catalyzed cross-coupling methods should provide an efficient route to construct complex multiaryl compounds. Further efforts toward the application of this strategy in organic synthesis and investigations on the detailed mechanism are currently ongoing in our laboratory.

Experimental Section

General Procedure for the Synthesis of Biaryls 3

Cesium carbonate (390 mg, 1.20 mmol) was added to a stirred mixture of sulfonium salt **2** (0.6 mmol) and enone-ester **1** (0.3 mmol) in CH_3OH (3 mL) at room temperature. The resulting mixture was stirred at the same temperature until the reaction was completed (as monitored by TLC). All volatiles were removed under vacuum and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate = 40:1–30:1) to afford biaryls **3**.

General Procedure for the Synthesis of Alkenylated Benzene Products 5

To a stirred mixture of sulfonium salt **2a** (216 mg, 0.9 mmol) and dienone **4** (0.3 mmol) in CH_3OH (3 mL) cesium carbonate (390 mg, 1.20 mmol) was added in one portion at room temperature. The resulting mixture was stirred at the same temperature until the reaction was completed (as monitored by TLC). All volatiles were removed under vacuum and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate = 40:1–30:1) to afford alkenylated benzene products **5**.

General Procedure for the Synthesis of Alkynylated Benzene Products 7

Cesium carbonate (390 mg, 1.20 mmol) was added to a stirred mixture of sulfonium salt **2a** (144 mg, 0.6 mmol) and enynone **6** (0.3 mmol) in CH_3OH (3 mL). The resulting mixture was stirred at room temperature until the reaction was completed (as monitored by TLC). All volatiles were removed under vacuum and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate = 40:1–30:1) to afford alkynylated benzene products **7**.

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