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# Pd-Catalyzed Cross-Coupling of Organostibines with Styrenes to Give Unsymmetric (*E*)-Stilbenes and (1*E*,3*E*)-1,4-Diarylbuta-1,3-dienes and Fluorescence Properties of the Products

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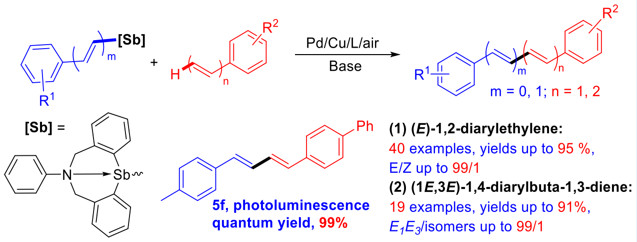
**ABSTRACT:** A general and effective palladium-catalyzed cross-coupling of organostibines with styrenes to give (*E*)-olefins was disclosed. By the use of an organostibine reagent, this method can produce unsymmetric (*E*)-1,2-diarylethylenes and (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes in good yields with high *E*/*Z* selectivity and good functional group tolerance. Resveratrol and DMU-212 were synthesized in high yield. The protocol can be extended to the synthesis of (1*E*,3*E*,5*E*)-1,6-diphenylhexa-1,3,5-triene in 40% yield. Products **5e**, **5f**, and **7a** showed good photoluminescence quantum yields ranging from 72 to 99%.



Unsymmetric (*E*)-stilbenes and related conjugated π-electron compounds are widely used in materials, medicine and health, cosmetics, and other important fields.[1−6] As shown in Figure 1, resveratrol (**A**), an example of an (*E*)-1,2-diarylethylene, can be used as a dietary supplement and has been observed to have chemoprophylaxis and cytoinhibitory effects on a variety of human tumor cell lines.[2] DMU-212 (**B**), which is also an (*E*)-1,2-diarylethylene, has been demonstrated to possess cytotoxic activity in ovarian, breast, and colorectal cancer cell lines.[3] In addition, unsymmetric conjugated polyolefins, such as (1*E*,3*E*)-1,4-diarylbuta-1,3-diene and (1*E*,3*E*,5*E*)-1,6-diarylhexa-1,3,5-triene, which exhibit good fluorescence properties, are of great value in the fields of optical functional materials, liquid crystals, and luminescent materials.[4] For example, conjugated dienes **C** and **D** with electron-withdrawing cyanide and nitro groups have good fluorescent probe properties,[5] while the conjugated trienes **E** and **F** can be used as fluorescent probes of lipid membranes for cancer research.[6]

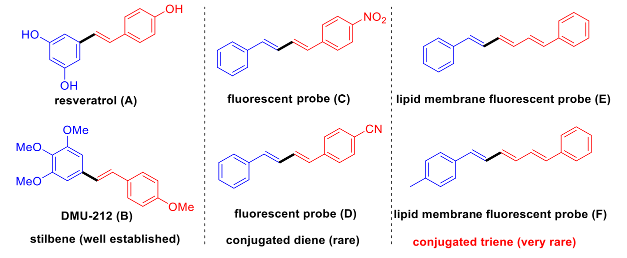


**Figure 1.** Representative (*E*)-stilbene-like olefins.

Because of their wide application in many fields, the synthesis of unsymmetric (*E*)-stilbene-like olefins has attracted much attention in organic synthesis. A variety of powerful methods have been disclosed.[7] Among them, the transition-metal-catalyzed Heck coupling reaction is one of the most powerful tools for the formation of (*E*)-olefins,[8] especially for the synthesis of (*E*)-1,2-diarylethylenes. Excellent examples based on catalysis by Pd,[7a,9] Ni,[10] and Cu[1b] with aryl halides or arylboronic acids have been developed, as shown in Scheme 1a. Compared with the well-established methodologies for unsymmetric (*E*)-1,2-diarylethylenes, the synthesis of unsymmetric (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes (Scheme 1b) is quite rare. Recently three examples demonstrated the synthesis of the above molecules. Kamigata et al.[11] disclosed the first example of Ru($PPh_3$)$Cl_3$-catalyzed Heck coupling of alkenesulfonyl chlorides with styrenes, which gave higher yields of (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes at 150 °C. Xu et al.[12] also successfully realized the Heck reaction between olefins and β-bromostyrene using a μ-OMs palladium dimer complex as the catalyst with the yield of 82%. Miura et al.[13] also disclosed a palladium-catalyzed coupling reaction of cinnamic acid with 1-bromostyrene. Besides common Heck coupling products, their protocol realized the synthesis of (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes and (1*E*,3*E*,5*E*)-1,6-diarylhexa-1,3,5-trienes (Scheme 1c).

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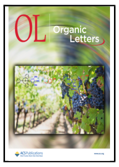

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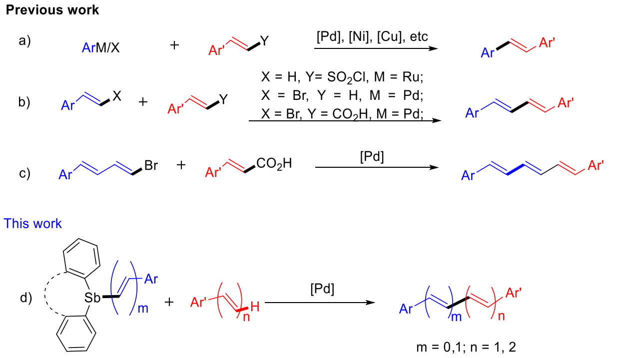
## Scheme 1. Strategy for Unsymmetric (*E*)-Stilbene-like Olefins

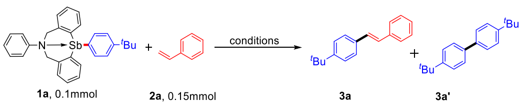


We are interested in organoantimony chemistry[14] and olefins.[15] Organoantimony reagents have been used for the Heck coupling by several groups for years. In 2020, Yasuike et al. disclosed a Pd-catalyzed oxidative Heck-type arylation of vinyl ketones, alkenes, and acrylates with *Sb*-aryltetrahydrodibenz[*c*,*f*][1,5]azastibocines, which is an important step forward in organoantimony chemistry.[14b] However, this protocol failed to efficiently produce (*E*)-1,2-diphenylethylene (52% yield). Very recently, by simple modification of the *N*-substitution group from *tert*-butyl to phenyl on the tetrahydrodibenz[*c*,*f*][1,5]azastibocines, we established an efficient protocol toward biaryls via Pd-catalyzed oxidative cross-coupling of arylated organostibines with arylboronic acids.[14c]

In the present work, we used 6-phenyl-12-aryl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocines as coupling reagents to react with styrenes, which can yield unsymmetric (*E*)-stilbene-like olefins with high efficiency and regioselectivity. This method can produce not only unsymmetric (*E*)-1,2-diarylethylenes in good yields but also unsymmetric (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes (Scheme 1d). Furthermore, this procedure can also be extended to produce (1*E*,3*E*,5*E*)-1,6-diphenylhexa-1,3,5-triene in satisfactory yield with good regioselectivity. This is the first example of an oxidative Mizoroki–Heck reaction using organostibine reagents to react with olefins for the synthesis of unsymmetric (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes.

As shown in Table 1, we initially conducted the screening for the Heck coupling with 6,12-diphenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (**1a**) and styrene (**2a**). We found that the ligand did not affect the reaction (see Table S2) and that the addition of $Cu(OAc)_2$ as an oxidant greatly improved the reaction efficiency (entries 1–3). Adding 100 $\mu$L of water increased the yield of **3a** to 85% (entry 6), which may be due to coordination of the water molecule to antimony, lowering the reaction activation energy (see Figure S4).[16] Then the solvent and the amount of oxidant were screened (entries 7–12). DMF was found to be the best solvent, and 1.5 equiv of $Cu(OAc)_2$ was enough to oxidize the reaction. $Pd(OAc)_2$ was the best catalyst under an air atmosphere, giving **3a** in 95% GC yield (entry 11), while the use of a nitrogen atmosphere lowered the yield of **3a** to 68%, indicating that the oxygen may also work as an oxidant to some extent (entries 13–15). All entries gave only a trace amount of **3a′** derived from homocoupling of **1a**, indicating the advantage of organoantimony reagents.

## Table 1. Screening of the Reaction Conditions[a]

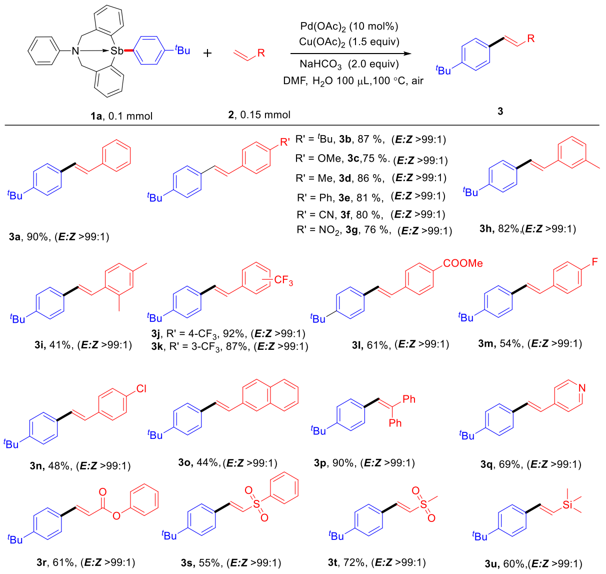


| entry | oxidant | $H_2O$ ($\mu$L) | solvent (2.0 mL) | catalyst (10 mol %) | yield of 3a (%) | yield of 3a' (%) |
|---|---|---|---|---|---|---|
| 1 | $Cu(OAc)_2$ (1.1 eq) | 20 | 1,4-dioxane | $Pd(OAc)_2$ | 56 | trace |
| 2 | BQ (1.1 eq) | 20 | 1,4-dioxane | $Pd(OAc)_2$ | 16 | 2 |
| 3 | $K_2S_2O_8$ (1.1 eq) | 20 | 1,4-dioxane | $Pd(OAc)_2$ | 18 | 6 |
| 4 | $Cu(OAc)_2$ (1.1 eq) | 60 | 1,4-dioxane | $Pd(OAc)_2$ | 80 | trace |
| 5 | $Cu(OAc)_2$ (1.1 eq) | 80 | 1,4-dioxane | $Pd(OAc)_2$ | 82 | trace |
| 6 | $Cu(OAc)_2$ (1.1 eq) | 100 | 1,4-dioxane | $Pd(OAc)_2$ | 85 | trace |
| 7 | $Cu(OAc)_2$ (1.1 eq) | 100 | DMSO | $Pd(OAc)_2$ | 80 | trace |
| 8 | $Cu(OAc)_2$ (1.1 eq) | 100 | DMF | $Pd(OAc)_2$ | 87 | trace |
| 9 | $Cu(OAc)_2$ (1.1 eq) | 100 | THF | $Pd(OAc)_2$ | 58 | 2 |
| 10 | $Cu(OAc)_2$ (2.0 eq) | 100 | DMF | $Pd(OAc)_2$ | 91 | trace |
| 11 | $Cu(OAc)_2$ (1.5 eq) | 100 | DMF | $Pd(OAc)_2$ | 95 | trace |
| 12 | $Cu(OAc)_2$ (1.0 eq) | 100 | DMF | $Pd(OAc)_2$ | 90 | trace |
| 13 | $Cu(OAc)_2$ (1.5 eq) | 100 | DMF | $PdCl_2$ | 93 | trace |
| 14 | $Cu(OAc)_2$ (1.5 eq) | 100 | DMF | $Pd(OTf)_2$ | 78 | trace |
| 15 | $Cu(OAc)_2$ (1.5 eq) | 100 | DMF | $Pd(OAc)_2$ | 68[b]; 23[c]; 8[d] | trace |

[a] **1a** (0.1 mmol), **2a** (0.15 mmol), Pd catalyst (0.01 mmol), and the base (0.2 mmol) in the solvent (2.0 mL) with the oxidant (1.0–2.0 equiv) and $H_2O$ (60–100 $\mu$L) at 100 °C in air for 2 h in a sealed tube. GC yields are shown. [b] Under $N_2$. [c] Without $Cu(OAc)_2$. [d] Under $N_2$ and without $Cu(OAc)_2$.

Table 2 shows the isolated yields of (*E*)-olefins **3a–u** obtained by the Pd-catalyzed Heck coupling of substituted styrenes **2** with **1a**. Good functional group tolerance was observed, as a variety of groups, such as $^t$Bu, Me, $NO_2$, $CF_3$, CN, F, Cl, pyridine, sulfone, and ester, are well-tolerated in this protocol. The expected stilbene derivatives **3a–h**, **3j**, **3k**, and **3p** were obtained by reaction with substituted styrenes in good yields (>75%) with excellent regioselectivity (*E*:*Z* > 99:1). The reaction is also compatible with halogenated olefins (X = F, Cl) but poor for bromostyrene and iodostyrene, which may due to side reactions of the active C–Br/C–I bonds of the halides. Meanwhile, because of the steric hindrance effect, the

## Table 2. Substrate Scope of Olefins for Unsymmetric (*E*)-1,2-Diarylethylenes[a]

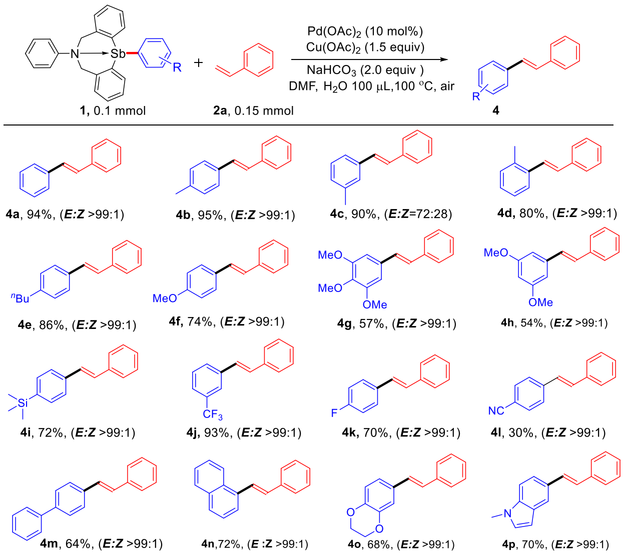


[a] **1a** (0.1 mmol), **2** (0.15 mmol), $Pd(OAc)_2$ (10 mol %), $NaHCO_3$ (0.2 mmol), and $Cu(OAc)_2$ (0.2 mmol) in 2.0 mL of DMF at 100 °C for 8 h. Isolated yields of **3** are shown. *E*:*Z* ratios are given in parentheses and were determined by $^1$H NMR analysis of the crude mixtures.

yields of **3i** and **3o** were lower (41% and 44%, respectively), but the regioselectivity still remained the same as for **3a–i**. For other olefins apart from styrenes, the corresponding products **3q–u** were also obtained in moderate to good yields with *E*:*Z* > 99:1.

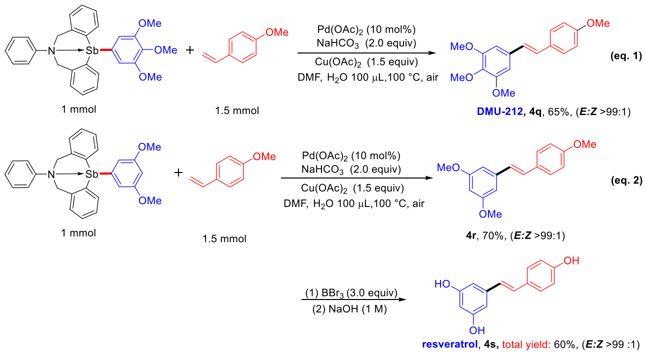
Then a series of *Sb*-aryl organostibines with the tetrahydrodibenz[*c*,*f*][1,5]azastibocine framework were synthesized and subjected to reaction with styrene in this reaction system (**4a–p**; Table 3). Alkyl and aryl substituents were tolerated in the system with good yields and regioselectivity. Various organostibines can achieve satisfactory yields, such as 4-methyl (**4b**, 95%), 4-*n*-butyl (**4e**, 86%), 4-methoxy (**4f**, 74%), 3-$CF_3$ (**4j**, 93%), and 4-Ph (**4m**, 64%). A cyano group afforded a modest 30% yield of **4l** in the catalytic reaction system, while some strong electron-withdrawing functional groups cannot be tolerated, such as ester, nitro, bromine, and other functional groups. We compared the yields of the methyl-substituted products (**4b–d**) and found that the yield decreased in the order **4b** > **4c** > **4d**, indicating steric hindrance of the reaction, with the *meta* position giving relative lower regioselectivity. Heteroatom-containing groups could also survive in this transformation, generating the corresponding products **4o** and **4p** in good yields with >99% *E*/*Z* selectivity.

### Table 3. Substrate Scope of *Sb*-Aryl Organostibines for Unsymmetric (*E*)-1,2-Diarylethylenes[a]



[a] **1** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol %), $NaHCO_3$ (0.2 mmol), and $Cu(OAc)_2$ (0.2 mmol) in 2.0 mL of DMF at 100 °C for 8 h. Isolated yields of **4** are shown. *E*:*Z* ratios are given in parentheses and were determined by $^1H$ NMR analysis of the crude mixtures.

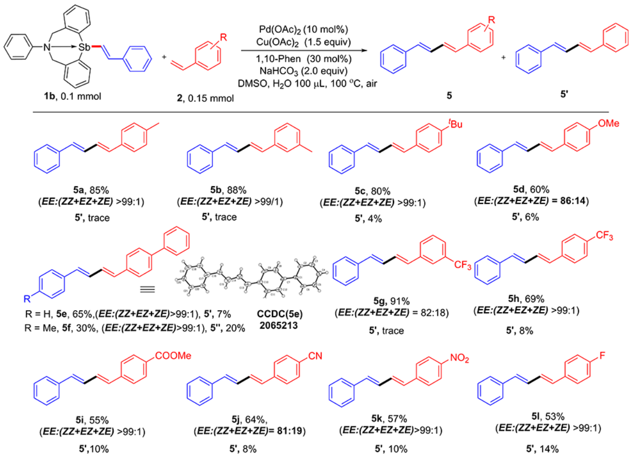
It has been reported that polyphenols and methyl ether derivatives have possible anticancer activity,[17] among which resveratrol and DMU-212 are two compounds that have been studied extensively.[2b,18] By means of the developed method, DMU-212 and resveratrol were prepared via a single-step or two-step procedure, respectively, in yields of 65% (**4q**) and 60% (**4s**) (eqs 1 and 2).



It was found that the reaction of **1b** with aromatic olefins provided conjugated dienes in low yields with poor selectivity, which inspired us to focus on the synthesis of 1,4-diaryl-1,3-butadienes. After investigating the reaction conditions, we found that ligands were needed to inhibit the generation of homocoupling products. Screening of a series of ligands showed that 1,10-phenanthroline (1,10-Phen) was the best ligand to improve the reaction effect (see Table S8).

Table 4 shows the results of the catalytic reaction of **1b** with various aromatic olefins. It shows a wide substrate scope toward to both electron-donating groups and electron-withdrawing groups in good yields (**5a-l**). The reaction exhibits different dependences on the electronic effect and spatial effect with respect to electron-donating groups and electron-withdrawing groups. When an electron-withdrawing group ($CF_3$) was attached at the *para* and *meta* position of the aromatic olefin, the yield was increased from 69% (**5h**) to 91% (**5g**). When an electron-donating methyl group was attached at the same position, almost the same yields were observed (85% for **5a** and 88% for **5b**).

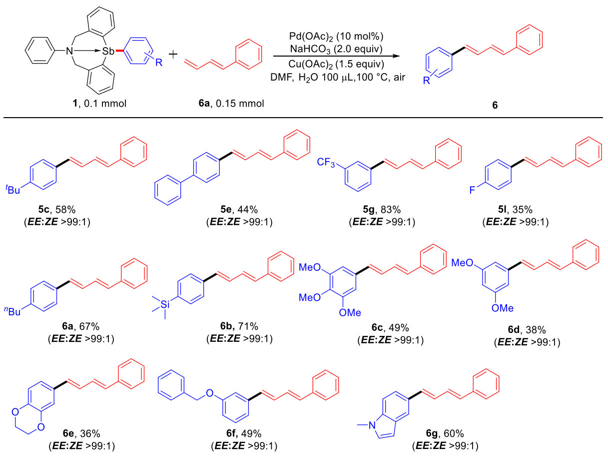
### Table 4. Substrate Scope of Stilbenes for Unsymmetric (1*E*,3*E*)-1,4-Diarylbuta-1,3-dienes[a]



[a] **1b** (0.1 mmol), **2** (0.15 mmol), $Pd(OAc)_2$ (10 mol %), $NaHCO_3$ (0.2 mmol), $Cu(OAc)_2$ (0.15 mmol), and 30 mol % 1,10-Phen in 2.0 mL of DMSO at 100 °C for 8 h. Isolated yields of the main products **5** and GC yields of **5′** and **5″** are shown. The ratios of *EE* isomers are given in parentheses and were estimated from the areas in GC and GC–MS of the crude mixtures.

Table 5 shows the use of 1-phenyl-1,3-butadiene as the substrate to synthesize conjugated dienes through the oxidative Heck coupling method. The reaction is compatible with a variety of substituted organostibine compounds, and all of the products were unsymmetric (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes

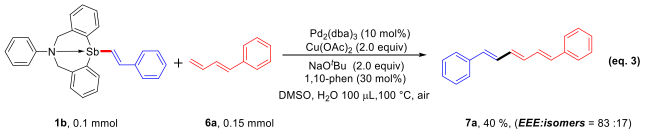
**Table 5. Substrate Scope of *Sb*-Aryl Organostibines for (1*E*,3*E*)-1,4-Diarylbuta-1,3-dienes**[a]



[a] **1** (0.1 mmol), **6a** (0.15 mmol), $Pd(OAc)_2$ (10 mol %), DMF (2.0 mL), $NaHCO_3$ (0.2 mmol), 1,10-Phen (30 mol %) and $Cu(OAc)_2$ (0.2 mmol) at 100 °C in air for 8 h. Isolated yields of the main products **5** and **6** are shown. The ratios of *EE* isomers are given in parentheses and were estimated from the areas in GC and GC−MS of the crude mixtures.

(**5c**, **5e**, **5l**, **5g**, **6a−g**) and were obtained in good yields with excellent regioselectivity (*EE*:*ZE* > 99:1).

Furthermore, we synthesized hexatriene **7a** in 40% yield under the standard conditions by regulation of the palladium catalyst and base, as shown in eq 3. Further research on conjugated polyenes such as conjugated trienes and tetraenes is underway in our laboratory.



(eq. 3)

Conjugated polyolefins have been demonstrated to have the potential in biochemistry because of their excellent fluorescence ability. We thus investigated the photophysical properties of selected examples of the obtained 1,3-dienes and 1,3,5-trienes (Figure 2). The UV−vis absorption and fluorescence emission spectra and the photoluminescence quantum yields (PLQYs) in toluene were acquired. The UV−vis absorption and fluorescence emission bands of 1,3,5-triene **7a** are bathochromically shifted compared with those of the dienes (**5e**, **5f**, **6e−g**) as a result of the enhanced conjugation. Besides, these compounds showed good PLQYs ranging from 72% to 99%, except for **6c** and **6g**. These primary results indicate that these polyolefins may have potential for use in the area of biochemistry.

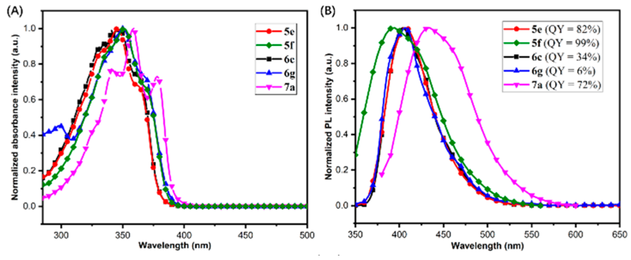
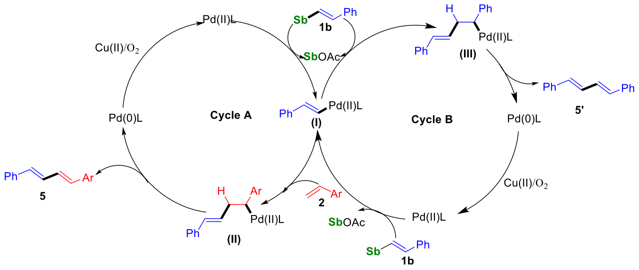


**Figure 2.** (A) UV−vis absorption and (B) fluorescence emission spectra of selected examples of 1,3-dienes and 1,3,5-trienes.

We began to investigate the yield of **3a** and **3a′** in the Heck reaction over time, and the simulated curve is shown in Figure S3. The yield of the oxidative Heck coupling product **3a** increased smoothly to 95% within 2 h, and the byproduct **3a′** reached a maximum yield of 2% at only 20 min. On the basis of the previously reported literature[14b,19] and the control experiments, a possible catalytic cycle for the reaction of organostibine compounds with olefins is proposed as shown in Scheme 2. First, organostibine compound **1b** reacts with Pd(II) to produce organic palladium intermediate **I**, which can react with olefin **2** to give intermediate **II** as a fast path as cycle **A**. Then *β*-H elimination from intermediate **II** occurs, giving the desired product **5** and a Pd(0) species. Finally, the Pd(0) species can be oxidized to the active Pd(II) intermediate in the presence of Cu(II)/$O_2$ to finish the catalytic cycle. However, there could be another route for homocoupling of **1b**, shown as cycle **B**, in which intermediate **I** could react with **1b** to generate intermediate **III** as a slow path. **III** would then undergo reductive elimination to give Pd(0) and the side product **5′** (Table 4).

**Scheme 2. Proposed Mechanism**



In summary, we have developed a new methodology for the formation of conjugated dienes via oxidative cross-coupling of organostibine compounds with olefins. The breaking of the Sb−C bond provides a good opportunity for the formation of unsymmetric stilbenes and conjugated dienes. The reaction system has good tolerance to olefin functional groups, including methoxy, fluorine, trifluoromethyl, ester, nitro, naphthalene ring, trimethylsilane, and ether groups. For organostibine compounds, electron-donating functional groups have achieved good yields. This reaction system provides potential value for the utilization of organostibine compounds and also provides a strategy for the generation of unsymmetric stilbenes and conjugated dienes.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01532.

Detailed experimental procedures, characterization data, and copies of the $^{1}H$, $^{19}F$, and $^{13}C$ NMR spectra of the obtained products (PDF)

FAIR data, including the primary NMR FID files, for compounds **3a−u**, **4a−s**, **5a−l**, **6a−g**, and **7a** (ZIP)

### Accession Codes

CCDC 2065213 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, U.K.; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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