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# Palladium-Catalyzed Asymmetric Addition of Diarylphosphines to α,β-Unsaturated Sulfonic Esters for the Synthesis of Chiral Phosphine Sulfonate Compounds

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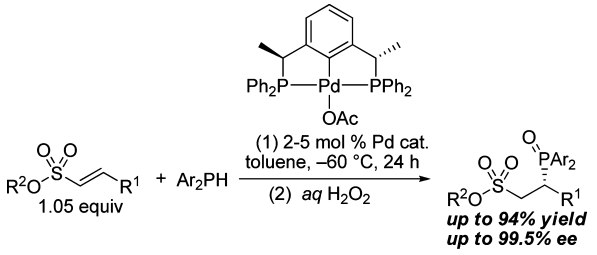
## ABSTRACT




**Highly stereoselective addition of diarylphosphines to α,β-unsaturated sulfonic esters catalyzed through a PCP pincer−Pd complex is developed to synthesize chiral phosphine sulfonic esters with excellent enantioselectivity (up to 99.5% ee). The transformation of the chiral adduct into a useful palladium phosphine sulfonate complex is also demonstrated.**

Phosphorus compounds are ligands that are widely used in organometallic chemistry and catalysis.[1] Introducing another heteroatom, such as nitrogen, sulfur, or oxygen atoms, into the ligand to form hybrid phosphorus ligands can significantly extend the application fields of these ligands.[2] Phosphine sulfonates, as a new family member of phosphorus bidentate ligands, has received considerable attention in the past 10 years and has proven to be effective in polymerization, hydroformylation, dehydrogenation, and C−H bond activation processes.[3,4] However, the synthesis and application of optically active phosphine sulfonate has been seldom explored.[5] The first optically active phosphine sulfonate ligand was recently prepared

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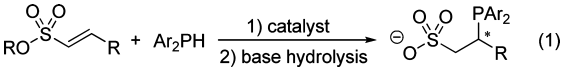
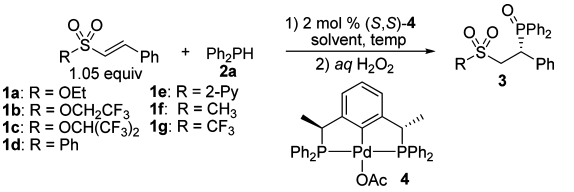
through chiral HPLC resolution of the racemates and applied in an asymmetric polymerization reaction by Nozaki et al.[5a] Therefore, the development of efficient methods to provide an array of optically active phosphine sulfonates is highly desirable. We wondered, as part of our ongoing interest in the synthesis of chiral phosphorus compounds,[6] if the asymmetric addition of phosphorus nucleophiles to α,β-unsaturated sulfonic esters could be a direct approach to provide chiral phosphine sulfonates (eq 1).[7,8] In this context, we report the first highly enantioselective synthesis of chiral phosphine sulfonate compounds through the Pd-catalyzed asymmetric addition of diarylphosphines to α,β-unsaturated sulfonic esters.




α,β-Unsaturated sulfonyl compounds are good acceptors of various carbon nucleophiles in asymmetric addition reactions.[9] Most examples are limited to alkenyl 2-pyridyl sulfones for the transition-metal catalyzed processes because of the unique reactivity of the compounds derived from the coordination of a nitrogen atom to metal catalysts.[9b,c] α,β-Unsaturated sulfonic esters must be used as electrophilic acceptors to realize our proposed reaction. The only example of asymmetric nucleophilic addition to α,β-unsaturated sulfonic esters was pioneered by Hayashi/Nishimura and co-workers very recently.[10] First, we examined the reactions of a series of α,β-unsaturated sulfonyl compounds with diphenylphosphine in the presence of a bisphosphino (Pincer) palladium

**Table 1.** Palladium-Catalyzed Addition of Diphenylphosphine to α,β-Unsaturated Sulfonyl Compounds **1**




| entry | sulfonyl compound | solvent | temp (°C) | time (h) | yield (%)[a] | ee (%)[b] |
|---|---|---|---|---|---|---|
| 1 | **1a** | toluene | rt | 24 | NR | – |
| 2 | **1b** | toluene | rt | 12 | 55 | 95 |
| 3 | **1c** | toluene | rt | 12 | 91 | 83 |
| 4 | **1d** | *t*-AmOH | rt | 12 | NR | – |
| 5 | **1e** | *t*-AmOH | rt | 36 | NR | – |
| 6 | **1f** | toluene | rt | 24 | NR | – |
| 7 | **1g** | toluene | rt | 4 | 85 | 43 |
| 8 | **1g** | *t*-AmOH | rt | 2 | 88 | 60 |
| 9 | **1c** | *t*-AmOH | rt | 12 | 87 | 56 |
| 10 | **1c** | THF | rt | 18 | 89 | 52 |
| 11 | **1c** | $CH_2Cl_2$ | rt | 18 | 90 | 45 |
| 12 | **1c** | toluene | −30 | 24 | 91 | 95 |
| 13 | **1c** | toluene | −60 | 8 | 89 | 97 |
| 14 | **1c** | toluene | −78 | 24 | 78 | 97 |

[a] Isolated yield. [b] Determined by HPLC with hexane/2-propanol.

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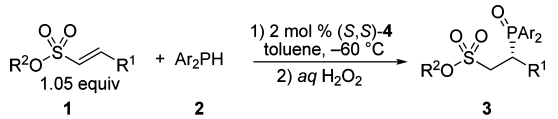
(12) Due to the oxygen sensitivity of phosphine, the 1,4-adducts were oxidized to the corresponding phosphine oxides for analysis.

**Table 2.** Palladium-Catalyzed Asymmetric Addition of Diarylphosphines to α,β-Unsaturated Sulfonic Esters




| entry | $R^1$ | $R^2$ | Ar | yield (%)[a] | ee (%)[b,c] |
|---|---|---|---|---|---|
| 1 | Ph | $CH(CF_3)_2$ | Ph | 88 | 97 |
| 2 | $p$-$MeOC_6H_4$ | $CH(CF_3)_2$ | Ph | 91 | 97 |
| 3 | $p$-($t$-Bu)$C_6H_4$ | $CH(CF_3)_2$ | Ph | 92 | 97 |
| 4 | $m$-$MeC_6H_4$ | $CH(CF_3)_2$ | Ph | 86 | 96 |
| 5 | $p$-$FC_6H_4$ | $CH(CF_3)_2$ | Ph | 88 | 94 |
| 6 | $p$-$BrC_6H_4$ | $CH(CF_3)_2$ | Ph | 87 | 95 |
| 7 | $m$-$BrC_6H_4$ | $CH(CF_3)_2$ | Ph | 90 | 93 |
| 8 | 2-naphthyl | $CH(CF_3)_2$ | Ph | 92 | 97 |
| 9[d] | 3-pyridinyl | $CH_2CF_3$ | Ph | 72 | 94 |
| 10[d] | 2-thienyl | $CH_2CF_3$ | Ph | 88 | 96 |
| 11[d,e] | cyclohexyl | $CH_2CF_3$ | Ph | 60 | 85 |
| 12[d] | $i$-butyl | $CH_2CF_3$ | Ph | 79 | 93 |
| 13[d] | Ph | $CH_2CF_3$ | Ph | 94 | 99.5 |
| 14[d,f] | Ph | 4-$NO_2C_6H_4$ | Ph | 85 | 95 |
| 15[d] | $p$-($t$-Bu)$C_6H_4$ | 4-$NO_2C_6H_4$ | Ph | 92 | 97 |
| 16[d] | $m$-$MeC_6H_4$ | 4-$NO_2C_6H_4$ | Ph | 88 | 94 |
| 17[d] | $p$-$FC_6H_4$ | 4-$NO_2C_6H_4$ | Ph | 92 | 91 |
| 18[d] | $p$-$BrC_6H_4$ | 4-$NO_2C_6H_4$ | Ph | 89 | 93 |
| 19 | Ph | $CH(CF_3)_2$ | $p$-$MeOC_6H_4$ | 92 | 96 |
| 20 | Ph | $CH(CF_3)_2$ | $p$-$ClC_6H_4$ | 90 | 96 |

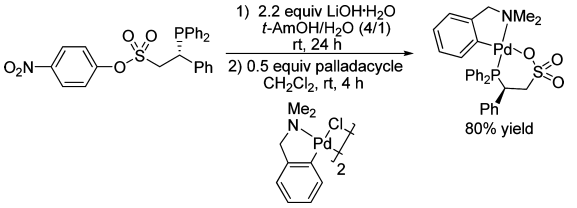
[a] Isolated yields. [b] Determined by HPLC with hexane/2-propanol. [c] The absolute configurations of products were determined to be *R* by X-ray crystal diffraction of the adduct in entry 1 (see Supporting Information for details). [d] 5 mol % cat. (*S*,*S*)-**4** was used. [e] The reaction was conducted at rt. [f] The adduct was isolated as the trivalent phosphine without oxidation.

catalyst.[6a,11,12] The ethyl sulfonic ester **1a** did not show any reactivity toward the phosphorus addition (Table 1, entry 1). Trifluoroethyl and hexafluoroisopropyl were introduced into the sulfonic esters instead of an ethyl group to increase the electrophilicity of the esters, and the reactions were examined. The reaction proceeded smoothly with moderate to high yields and good enantioselectivity (entries 2 and 3). A similar phenomenon was also observed for phenyl-, 2-pyridyl-, and methyl-substituted sulfonyl compounds (entries 4–6). The introduction of a trifluoromethyl group into the sulfonyl acceptors significantly increased the reactivity of the compounds to achieve the desired product with moderate enantioselectivity (88% yield, 60% ee; entry 8). The screening solvent indicated that toluene is better than dichloromethane, THF, and *tert*-amyl alcohol (entries 9–11). Finally, lowering the temperature to −60 °C increased the enantioselectivity of the adduct to 97% ee with an 89% yield (entry 13).

The scope of substrates was examined under optimized conditions, and the results are shown in Table 2. Various

(13) CCDC 944780, 944781 contain 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.

**Scheme 1.** Synthesis of a Chiral Palladium Phosphine Sulfonate Complex Based on the Obtained Adduct



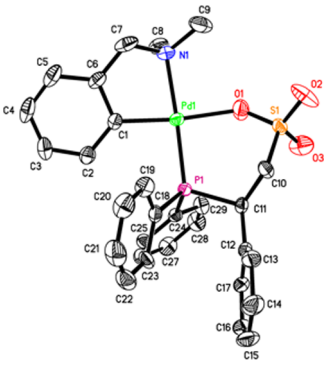
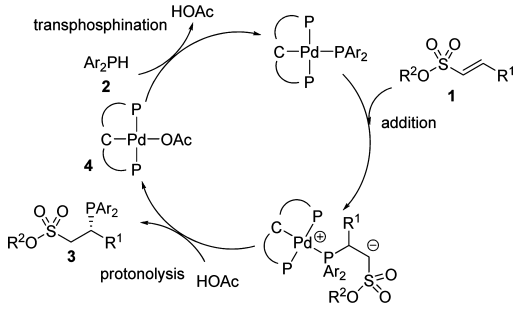



**Figure 1.** X-ray structure of the palladium phosphine sulfonate with the thermal ellipsoids drawn at the 50% probability level.

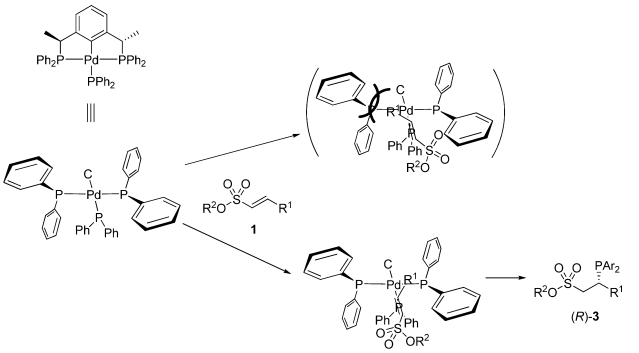
sulfonic esters **1** that contain electron-donating or -withdrawing groups on the aromatic ring, such as methoxy, halide, and alkyl moieties, can be coupled with diphenylphosphine, which uniformly form chiral phosphine oxides in high yields and with excellent stereoselectivity (86–97% yield, 93–97% ee; Table 2, entries 1–8). Notably, the heteroatom-containing substrates that have a strong coordination ability to transition metals, such as 2-thienyl and 3-pyridinyl moieties, were tolerated under the current catalytic system (72–88% yield, 94–96% ee; Table 2, entries 9 and 10). In addition to the aromatic ring, alkyl substituted groups at the β-position of the sulfonic esters, such as cyclohexyl and isobutyl moieties, could also be employed as acceptors for this phosphorus addition reaction (60–79% yield, 86–93% ee; entries 11 and 12). Moreover, various 4-nitrophenyl sulfonic esters are also suitable reaction partners besides polyfluoroalkyl sulfonic esters to extend the applicability of the current protocols (88–92% yield, 91–97% ee; entries 14–18). For the phosphorus nucleophilic component, substituted phosphines that bear electron-rich or -poor groups can be effectively added to **1c** to obtain excellent yields and enantioselectivity (90–92% yield, 96% ee; entries 19 and 20).

To illustrate the utility of the current method, the obtained phosphorus compound was converted into a chiral palladium phosphine sulfonate complex (Scheme 1). Thus, the optically active phosphine sulfonic ester (Table 2, entry 14) was hydrolyzed to obtain a sulfonic acid. The acid then reacted with a palladacycle salt and

**Scheme 2.** Proposed Catalytic Cycle for the Pd-Catalyzed Addition of Diarylphosphines to α,β-Unsaturated Sulfonic Esters




**Scheme 3.** Proposed Stereochemical Pathway (partial groups in (*S*,*S*)-**4** are omitted for clarity)




yielded a Pd complex of phosphine sulfonate (Scheme 1, Figure 1)[13] which may act as a possible catalyst in asymmetric reactions.[4,5]

The proposed catalytic cycle for the current process is illustrated in Scheme 2. First, transphosphination occurs between the diarylphosphine and the pincer−PdOAc, which affords a palladium phosphido intermediate.[6a] Then, the nucleophilic phosphorus addition to the β-position of the sulfonic ester **1** generates a palladium phosphine complex that bears a pendant anion.[7f] Finally, the reaction of this Pd intermediate with HOAc releases product **3** and regenerates active catalyst **4**. The tentative stereochemical pathway for the formation of (*R*)-product is shown in Scheme 3. The spatial orientations of the phenyl rings on the phosphorus atoms are different from one another because of the existence of two chiral methyl groups at the benzylic position of catalyst (*S*,*S*)-**4**. Therefore, a chiral environment is established around the palladium atom. The α,β-unsaturated sulfonic ester **1** reaches the palladium phosphido intermediate with its α-Re face preferentially to avoid the unfavorable steric interactions between the substituent at the β-position of sulfonic esters and the phenyl groups that protrude from the phosphorus atom of the Pd catalyst. This reaction affords the product with the (*R*)-configuration.

In summary, we have reported the pincer palladium-catalyzed enantioselective addition of diarylphosphines to α,β-unsaturated sulfonic esters for preparing chiral phosphorus sulfonyl compounds in high yields and excellent enantiomeric excess under mild conditions. The investigation of optically active phosphine sulfonyl compounds, such as bidentate ligands, toward transition metals, and the application of these compounds as a catalyst in asymmetric processes are currently under study.

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**Supporting Information Available.** Experimental procedures and characterization of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.