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Synthesis of allylic sulfonic acids via regioselective Pd-catalyzed allylic substitutions of Na₂SO₃

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ABSTRACT

Palladium-catalyzed allylic sulfonations of the linear allylic carbonates with sodium sulfite (Na₂SO₃) were accomplished under mild conditions. This method gave allylic sulfonic acids in good to excellent yields with high level of the regioselectivities.

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1. Introduction

Sulfonic acid is one of the most important acids in the area of biochemistry and has remarkably effect on physiological processes.¹ 6-Ginger sulfonic acid isolated from *Zingiberis Rhizoma* displays antiulcer activity (Figure 1).² Taurine, 2-aminoethanesulfonic acid, is an essential acid in human body, which is vital for cardiovascular function, and development and function of skeletal muscle.³ A number of sulfonic acids such as Prempro®, Sulfotanshinone,⁴ Metamizole,⁵ Cefsulodin,⁶ and Sulbenicillin⁷ have been popular in the drug market (Figure 1).

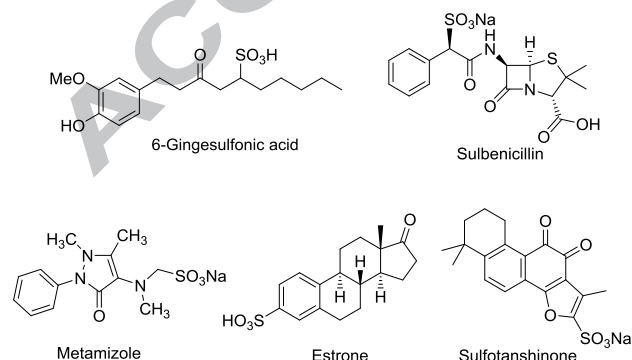


Figure 1. Several representative sulfonic acid-containing drugs

An economic, green, and direct method for the synthesis of sulfonic acids is by a sulfonation of sulfur trioxide (SO₃), such as the production of *p*-toluenesulfonic acid.¹ The conventional way to synthesize sulfonic acids is oxidation of thiols; for example, in 1992, Corey firstly developed (*R*)-1-phenylethanesulfonic acid derived from an enantiopure thiols in multistep reactions.⁸ Recently, Adamo reported organocatalytic asymmetric Michael reactions of chalcones with a bisulfite anion (-OSO₂H) for the formation of sulfonic acids.⁹ Several groups have studied on the transformation of sulfonic acids¹⁰. More recently, our group reported either iridium or palladium (Pd)-catalyzed allylic substitutions of sodium sulfite (Na₂SO₃), which produced sulfonic acids with high enantioselectivities.¹¹ To the best of our knowledge, Pd-catalyzed allylic sulfonations of the linear allylic carbonates with a sulfite anion has not yet been reported. Advances in transition metals promoted allylation reactions¹² inspired us to explore this strategy. Herein, we report Pd-catalyzed allylic substitutions of mono-substituted allylic carbonates with Na₂SO₃, which gives allylic sulfonic acids.

At the beginning, we carried out a sulfonation reaction between (*E*)-cinnamyl methyl carbonate **1a** and sulfite salt **2** in the presence of Pd(PPh₃)₄ at room temperature (Table 1). No desired products were observed when this reaction was carried out in either DCM or THF (Table 1, entries 1-2). Interestingly, the formation of the allylic sulfonic acids (**3a** and **4a**) was observed when both Na₂SO₃ **2a** and acetone were used (Table 1, entry 3). The nature of solvents has a great impact on the reaction outcomes. Therefore, other solvents such as MeOH, EtOH, and mixture solvents were examined. Both MeOH and EtOH were effective solvent (entries 4 and 5). Significantly, the mixed

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