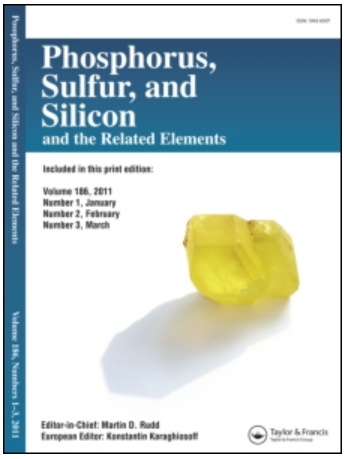

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Asymmetric Syntheses of α-Sulfinylphosphonates in the Thiolane Series

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Asymmetric Syntheses of α-Sulfinylphosphonates in the Thiolane Series

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Enantiopure α-sulfinyl phosphonates are useful chiral olefinating reagents for the generation of α,β-ethylenic sulfoxides, which in turn can be used as asymmetric dienophiles or Michael acceptors.[1] The first enantioselective synthesis of a 1-oxo 2-phosphonothiolane **2** had already been achieved *via* the [2,3]-sigmatropic rearrangement of the carbanion derived from di(-)-menthyl (allylsulfanyl)methanephosphonate.[2] We now describe more direct and general ways to prepare nonracemic sulfoxides of the same series by the methods involving asymmetric oxidations of racemic or achiral thiolanes.

When racemic 2-phosphonothiolanes **1** (R = ethyl, isopropyl, 2,2-dimethylpropane-1,3-diyl), prepared from 1-oxothiolane by a Pummerer-phosphorylation reaction,[3] were treated with one half equiv of (+)-(2*S*, 8a*R*)-8,8-dichloro-camphorsulfonyloxaziridine, a preferential oxidation of one of the enantiomers of thiolane **1**, together with a diastereoselective formation of the *trans*-sulfoxides **2**, was observed leading to enantioenriched **1** and **2** (ee $\sim$ 75% with R = iPr)

2-Phosphono-2,3-didehydrothiolanes **3** were further prepared from the racemic sulfoxides **2** under Pummerer conditions. Their enantioselective oxidation using the same oxaziridine led to the enantioenriched

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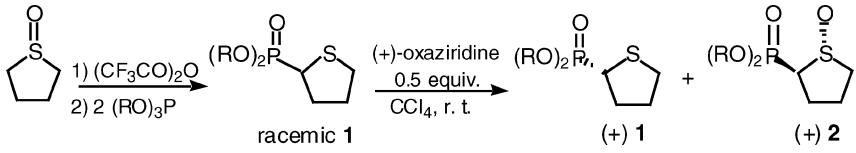
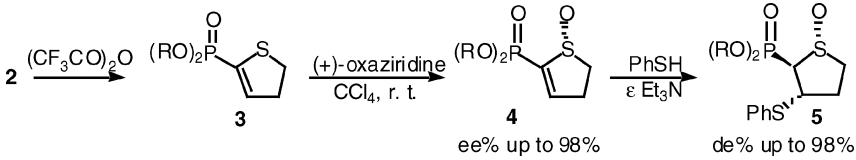


ethylenic sulfoxides **4** (ee up to 98% with R = 2,2-dimethylpropane-1,3 diyl). A highly diastereoselective 1,4-addition of benzenethiol to these sulfoxides resulted in the formation of 1-oxo-2-phosphono-3-phenylthio-thiolanes **5** with three stereogenic centers controlled simultaneously.



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