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SYNFACTS Highlights in Current Synthetic Organic Chemistry

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Key words

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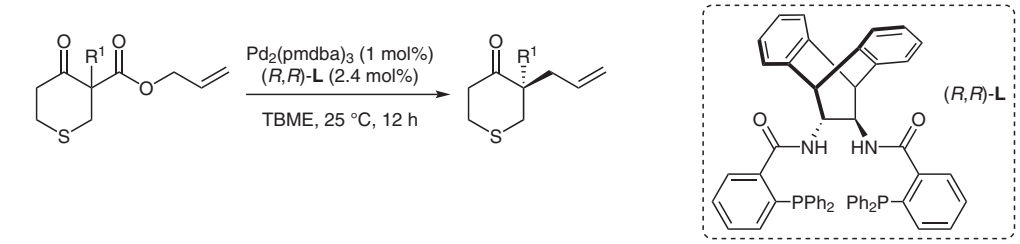
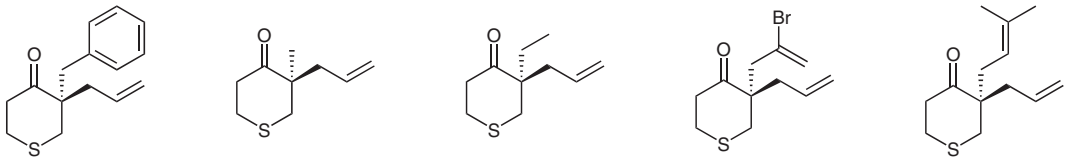
Enantioselective Pd-Catalyzed Decarboxylative Allylic Alkylation of Thiopyranones. Access to Acyclic, Stereogenic α-Quaternary Ketones

Org. Lett. **2017**, *19*, 5007–5009.

Palladium-Catalyzed Enantioselective Allylic Alkylation of Thiopyranones



Selected examples:



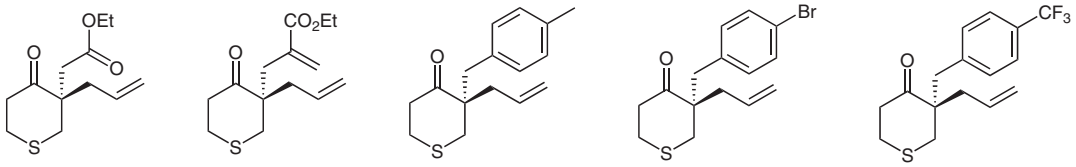
92% yield
94% ee

74% yield
93% ee

70% yield
82% ee

82% yield
50% ee

76% yield
78% ee



91% yield
69% ee

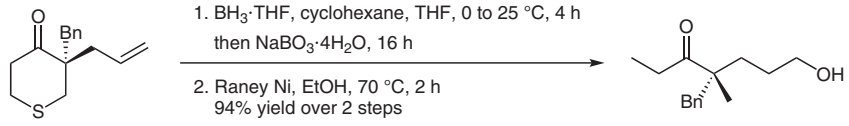
87% yield
66% ee

86% yield
90% ee

91% yield
91% ee

80% yield
93% ee

Transformation of the cyclic alkylated product to an acylic ketone:



Significance: The synthesis of chiral α-quaternary thiopyranones is interesting because these compounds can serve as useful building block for the pharmaceutical industry. A palladium-catalyzed decarboxylative asymmetric allylic alkylation of thiopyranones to give α-quaternary thiopyranones is reported. The chiral products were obtained in good yields and with excellent enantioselectivities.

Comment: Appropriate conditions were identified that tolerated Lewis basic thioethers, and did not produce any ring-opening β-elimination. The cyclic product can be transformed into a wide variety of products, for example, an acyclic ketone containing an all-carbon quaternary stereocenter was obtained in two steps. However, the substrate scope is limited to thiopyranones.

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