**Enantioselective Synthesis of 3,4-Dihydrothiacarbazol-2(9H)-ones**

**Significance:** Reported is the enantioselective synthesis of 3,4-dihydrothiacarbazol-2(9H)-ones 3 by reaction of indoline-2-thiones 1 with N-alkenoylphthalimides 2 catalyzed by the chiral squaramide 4. Screening of organocatalysts with double hydrogen-bond donor ability led to squaramide 4 derived from L-tert-leucine as the best catalyst for this transformation affording high enantioselectivity. The reaction conditions were optimized in terms of solvent, temperature, and catalyst loadings. Lower temperatures (0 °C) culminated in lengthy reaction time and lower yield but equivalent ee, while higher temperatures (40 °C) provided equivalent reaction yields but loss of stereocontrol. The study of the reaction scope showed that the presence of different substituents on both 1 and 2 were tolerated, but in some cases loss of stereocontrol without following a pattern was observed.

**Comment:** The indole skeleton is an important class of heterocycles present in many natural products with broad biological activities, and can be synthesized by many well-described methodologies (see Review below). The thiopyran indole 3 was obtained by an activation process promoted by two hydrogen-bonding interactions of 2 with the squaramide organocatalyst, followed by a Michael addition step and a thiolysis reaction. The starting materials 1 and 2 are readily available. Although a mild process, the reported approach has long reaction times and the study of the reaction scope is narrow.