

Abstract

We have developed new synthetic methodologies for the preparation of novel camphor derived 1,2-, 1,3- and 1,4-diamine building blocks. From these diamine building blocks, novel bifunctional thiourea and squaramide organocatalysts with camphor as the exclusive chiral framework were prepared in a single step. We tested the efficiency of the prepared catalysts in asymmetric *Michael* additions of 1,3-dicarbonyl nucleophiles to *trans*- β -nitrostyrene derivatives. 3-((3,5-Bis(trifluoromethyl)benzyl)amino)-4-(((1*R*,2*S*,4*R*)-7,7-dimethyl-1-(pyrrolidin-1-ylmethyl)bicyclo[2.2.1]heptan-2-yl)amino)cyclobut-3-ene-1,2-dione turned out to be an exceptionally good organocatalyst for this type of reactions. Reactions proceed excellent in non-polar organic solvents as well as in water medium with a variety of 1,3-diketones and β -keto esters with differently substituted *trans*- β -nitrostyrenes. Most of the products were formed in full conversion and with excellent enantiomeric excesses ($\geq 96\%$). Particularly high enantioselectivities ($\geq 99\%$ ee) were observed in reactions with *ortho*-monosubstituted derivatives of *trans*- β -nitrostyrene. The reaction between acetylacetone and 2-Br-*trans*- β -nitrostyrene in toluene-*d*₈ at 302 K with 0.50 mol% catalyst loading proceeded with 100% conversion in 80 min with 99% enantiomeric excess. The catalyst is prepared in a short five step synthetic route from commercially available chemicals and it is insensitive to water and air. It is based on a 1,3-diamine camphor framework whose synthesis allows the preparation of a large number of its analogues. This chiral 1,3-diamine building block based on camphor represents a new privileged chiral scaffold, which is extremely important because most of the successful bifunctional organocatalysts are based on 1,2-diamine scaffolds.