

Asymmetric organocatalysis in liquid or supercritical carbon dioxide media

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The asymmetric organocatalysis is a powerful tool for enantioselective synthesis of organic compounds. In the presence of small chiral molecules, commonly amines, prochiral compounds generate chiral products in high yields and with excellent enantioselectivities. However, to the best of our knowledge, no asymmetric aminocatalytic reactions in carbon dioxide medium, which is extensively used as a green solvent in various chemical reactions, have been so far communicated. Moreover, a possibility of performing these reactions in liquefied CO₂ was under question because of the by-production of carbamic acid salts from primary or secondary amines and CO₂, which deactivate the catalyst. An undesirable interference of carbon dioxide with the hydrogen bond network generated by organocatalyst and reagents in the transition state might also take place.

We discovered that α -nitroolefins enantioselectively react with CH carbon acids in the presence of bifunctional organocatalysts bearing the tertiary amino group and the thiourea fragment in liquid carbon dioxide medium to afford corresponding Michael adducts in high yields and enantioselectivities. Bifunctional tertiary amine-squaramides efficiently catalyzed asymmetric additions of hetero-nucleophiles (diphenylphosphite or *o*-*N*-tosylaminophenyl α,β -unsaturated ketones) to α -nitroolefins to afford β -nitrophosphonates or densely functionalized chiral tetrahydroquinolines *via* Michael or double-Michael cascade reactions in supercritical carbon dioxide medium. Corresponding Michael adducts were generated in these reactions in moderate to high yields with very high diastereo- (*dr* up to 99:1) and enantioselectivity (up to 98% *ee*).