Hexasubstituted guanidinium moieties have been used as ionic liquid tags for organocatalysts for the first time. Such conjugates were obtained in the (S)-proline and (S)-pyrrolidine-2-ylmethyl series by alkylation reactions of pentasubstituted guanidines. The resulting guanidinium-tagged organocatalysts were applied to asymmetric direct aldol reactions providing high stereoselectivities and yields and good recyclability, and thus performed better than (S)-proline itself.

Key words: Organocatalysis, Ionic Liquids, Guanidinium Salts, Proline, Asymmetric Synthesis, Aldol Reaction