Abstract

This thesis deals with single-electron transfer (SET) radical processes mediated by ferrocenium hexafluorophosphate and TEMPO and their application in the total synthesis of natural products. Asymmetric aminooxygenation methodology for the synthesis of *anti*-β-amino-α-hydroxy acid derivatives has been developed by utilizing a highly diastereoselective aza-Michael addition of chiral lithium amides to various α,β-unsaturated esters or amides/SET oxidation/radical α-oxygenation. The potential of this methodology was demonstrated in short total syntheses of the *anti*-β-amino-α-hydroxy acid fragments of the macrocyclic (depsi)peptides perthamide C and largamide H, and (–)-cytoxazone, which is a selective modulator of T_H2 cytokine secretion.

The SET-catalyzed asymmetric tandem lithium amide conjugate addition/5-*exo* radical cyclization/oxygenation reactions were applied in the synthesis of highly substituted pyrrolidines, azabicyclo[n.3.0]alkanes and spiropyrrolidines.

An enantioselective total synthesis of the pyrrolidine alkaloid (–)-α-kainic acid was accomplished by employing the SET-catalyzed 5-*exo* radical cyclization/oxygenation.