Alkoxyamines are widely used reagents that are particularly essential in polymer chemistry. Much work has been invested in the development of the nitroxide-mediated polymerization (NMP) for which the structure of the alkoxyamine plays an essential role in controlling the radical processes. The synthesis of alkoxyamines through a radical deformylation of aldehydes using aminoxyl radicals was published by Schöning and co-workers in 2008.\[1\] We further improved the method and extended the methodology to the synthesis of polyketide fragments.\[2\] Here, the use of various alkoxyamines and studies on the verification of the proposed reaction mechanism using a radical clock reaction are presented. In addition, the resulting products can be further utilized for radical C-C bond formations via carboaminoxylation.

Scheme 1: Radical deformylation of aldehydes using aminoxyl radicals and subsequent C-C bond formation via carboaminoxylation.
