

Reactions and Direct Generation of Carbon-centered Radicals

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During our study on a chiral amidophosphane–copper catalyzed reaction of dialkylzinc with imines, we accidentally found a radical addition reaction of the solvent, THF to the *N*-sulfonyl imine. Dimethylzinc reacted with air oxygen to form methyl radical, which initiated the radical reaction. In this reaction, a carbon-centered radical was directly generated from THF by the cleavage of a carbon–hydrogen bond, while carbon-centered radicals are often generated by homolytic cleavage of carbon–heteroatom bonds, such as C–I, C–S, or C–Se. Using this dimethylzinc initiator, α -alkoxyalkyl radicals were generated from the corresponding ethers and the radicals were made to react with C=N, C=O, and C=C bonds as well as amine functionalities. We also succeeded in the direct generation of alkyl radicals from plain cycloalkanes as well as the tin-free generation of primary alkyl radicals from the corresponding iodides. Recently, we have also reported an asymmetric radical addition of a hydroxymethyl equivalent to chiral *N*-sulfinyl imines.