Cluster Preface: Organosulfur and Organoselenium Compounds in Catalysis

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Sulfur and selenium are group 16 elements (chalco-
gen). While organosulfur and organoselenium compounds have been recognized as useful reagents in synthetic organic chemistry since the 1970s, the use of organosulfur/sele-
nium in catalysis has emerged in recent years. Catalysis plays a central role in modern synthetic chemistry. Thus, significant efforts have been devoted to the development of various catalytic protocols in the past decades. For catalyst structure design, oxygen, nitrogen and phosphorus are employed as the constitutional elements in many circumstanc-
es. For example, amines are frequently used as Lewis bases in organocatalysis and as ligands in transition-metal catalysis. Chalcogenides, including sulfides and selenides, are a separate class of Lewis base. The relatively soft Lewis basic nature of organosulfur and organoselenium compounds leads to interesting catalytic performance as compared with hard Lewis bases such as amines. As a result, research efforts to explore the chemistry of organosulfur and organoselenium compounds as organocatalysts and ligands for transition metals in various catalytic processes have received considerable attention from the scientific community.

Unlike oxygen, which is also a group 16 element, sulfur and selenium are multivalent in nature. As a result, they have fruitful chemistry in catalytic oxidation reactions. Other than applications as Lewis bases, using organochalco-
gen as soft Lewis acids through chalcogen bond interac-
tion has been studied in biological systems and in crystal engineering. This interaction has emerged as a new tool in catalytic organic reactions in the past few years.

Despite the usefulness of organosulfur/sele-
nium compounds as catalysts, the odor of sulfur and selenium re-
agents and inefficient classical preparation procedures are obstruc-
tions in this research field. As a result, the develop-
ment of more efficient and preferentially odorless method-
ologies to introduce C–S and C–Se bonds is highly relevant to boosting the progress of organochalcogen catalysis.

In this SYNLETT Cluster, we are delighted to feature 11 important contributions dedicated toward different themes and concepts related to organosulfur/sele-
nium catalysis. These endeavors include the development of new reactions and efficient methods for the preparation of chalcogen compounds, as well as a mechanistic study.

Lewis basic chalcogen-catalyzed electrophilic function-
alizations of olefinic substrates are very useful reactions which allow the rapid construction of structurally complex cyclic molecules in a single chemical operation. Halogen and chalcogen electrophilic reagents have been widely uti-
lized. The resulting cyclized products are valuable building blocks of biologically relevant molecules. In addition, the halogen/chalcogen functionalities can easily be manipu-
lated to give various derivatives. Some new catalytic protocols for electrophilic cyclizations are reported in this Cluster, in-
cluding catalyst-controlled regio- and stereoselective bro-
malactonization of stilbene-type carboxylic acids with chiral bifunctional sulfides (S. Shirakawa) and enantioselective halo-/selenocyclization of olefinic acids with C2-symmetric sulfur-based catalysts, which gave rise to
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