PRF# 59173-ND1
Development of Selective C-C Bond Forming Reactions of Petroleum-Relevant Organosulfur Compounds.
Oleg Larionov, The University of Texas at San Antonio

Sulfur-containing compounds possess a rich and diverse reactivity that can be harnessed for development of new carbon-carbon bond-forming reactions. In particular, a combination of sulfur-containing reagents and transition metal catalysts offers numerous opportunities for cross-coupling reaction design. With this knowledge, in the first year of the project, we focused on the initial study of the sulfur-containing reagents and their preparation methods, as well as their behavior in the cross-coupling reactions with palladium and nickel complexes as catalysts. Given the necessity to use toxic sulfur dioxide gas for the syntheses of many organosulfur compounds, we investigated alternative reagents that can serve as sulfur dioxide precursors and equivalents. We also focused on the initial identification of ligands that can promote the carbon-carbon bond-forming reactions with organosulfur reagents and typical organic electrophiles. Biphosphines were identified as ligands of choice, and further reaction parameters that include temperature and solvent were then systematically evaluated. Another parameter whose role was found to be critical was base. It was found that addition of inorganic bases was necessary to mediate the reactions, presumably, due to the inhibitory and deleterious effects of sulfur dioxide that is produced as a by-product. Moisture was found to have a deleterious effect, and rigorous drying of the basic reagent was necessary to effect the cross-couplings. With the information gained in the first year of the project, we will now focus on further identification of new cross-coupling reactions based on organosulfur reagents. We will also investigate performance of sulfur-containing heterocycles as catalysts and co-catalysts. Overall, the first year off support by the ACS PRF has allowed us to produce an extensive amount of preliminary data that will now be developed into broader scope research programs at the interface of organosulfur chemistry and catalysis. The project has also had a positive effect on the careers of the students involved in the work. Thus, the undergraduate student who worked on the project graduated and was accepted in a PhD program with a fellowship.