Dimethyl carbonate (DMC) has been used by our group for the methylation and carboxymethylation of a large array of nucleophiles. DMC is a green and practical alternative to reagents such as methyl iodide and dimethyl sulfate, for methylation, and chloromethyl formate and phosgene, for carboxymethylation.

DMC possesses many green features, but to understand fully DMC as a green alternative it is important to understand the selectivity that DMC displays. This feature, we wish to convey in this presentation. Although DMC is an ambident electrophile, great selectivity towards methylation and/or carboxymethylation is observed and is readily achievable. In fact, the selectivity of methylation is due to DMC’s ambidenticity, this will be discussed.

In order to explore, exploit and test the limits of the selectivity of DMC, we chose to investigate more complex molecules such as ambident nucleophiles. In this regard, we chose hydrazines, firstly looking at phenylhydrazine. From the reaction of phenylhydrazine and refluxing DMC with a base present, the following reaction pathway was proposed:

We found that many of these compounds in this scheme could be selectively produced by using DMC and phenylhydrazine and by changing reaction conditions. Investigations of this pathway will be presented as well as the effects that both electron withdrawing and donating groups have on the reaction pathway and reaction selectivity toward either carboxymethylation and/or methylation.