

Abstract

The incorporation of the trifluoromethyl and perfluoroalkyl motifs into organic compounds has been a hot topic in synthetic organofluorine chemistry. There is a plethora of methods for the introduction of the CF_3 moiety at carbon, oxygen and sulfur centers. In sharp contrast, methods for synthesizing N-trifluoromethyl and N-perfluoroalkyl compounds are very limited and new approaches are highly sought-after. The scarcity of these compounds prompted us to develop reagents capable of transferring the perfluoroalkyl unit to nitrogen atom. To fulfil this purpose, we have regarded azidoperfluoroalkanes as ideal reagents, therefore, this thesis is concerned with the synthesis and applications of these azides.

The first part describes the preparation of azidoperfluoroalkanes. Upon activation by cesium fluoride, TMSCF_3 transfers the trifluoromethyl group to an electrophilic azide to produce the desired azidotrifluoromethane. Longer carbon chain azidoperfluoroalkanes were prepared in a similar way, starting from the corresponding organosilane. A different synthetic strategy was applied for the preparation of azidopentafluoroethane where the perfluoroalkyl anion was generated from pentafluoroethane with $^t\text{BuLi}$, followed by the addition of tosyl azide. The isolation of these fluorinated azides was accomplished by distillation with a suitable solvent.

The second part showcases the synthetic potential of azidoperfluoroalkanes through various transformations. The azides exhibited good reactivity in the copper(I)-catalyzed azide-alkyne cycloaddition and in the organocatalytic azide-ketone cycloaddition to furnish diverse 1,2,3-triazoles bearing the N-perfluoroalkyl group. At last, protonation of azidotrifluoromethane in superacid is demonstrated. The protonated azide was characterized by low-temperature NMR spectroscopy and the experimental results were validated by computational studies.