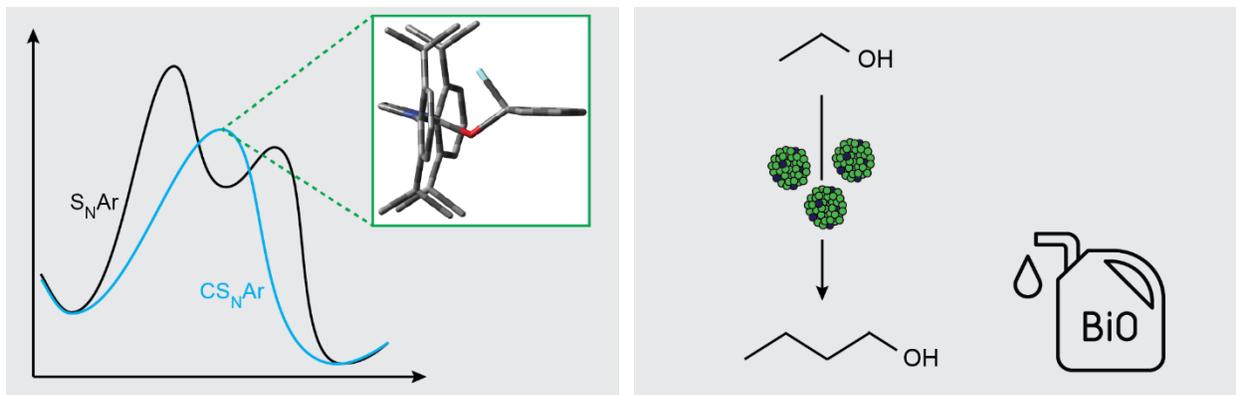


# Facilitating Access to PET Probes and Advanced Biofuels

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Nucleophilic aromatic substitution ( $S_NAr$ ) has long been the predominant method to introduce  $^{18}F$  into aromatic molecules in the synthesis of tracer molecules for  $^{18}F$  PET, a non-invasive medical imaging technique.  $S_NAr$  is limited in its scope to arenes bearing electron-withdrawing substituents as a direct consequence of the reaction mechanism; the negatively charged 'Meisenheimer' intermediate formed through nucleophilic attack ipso to the leaving group is only energetically accessible when the arene substrate bears electron-withdrawing substituents. The first part of this talk will showcase an alternative: concerted nucleophilic aromatic substitution ( $C_{S_N}Ar$ ), which is not restricted to electron-deficient arenes.  $C_{S_N}Ar$  is shown to be the preferred mechanism of nucleophilic displacement for aromatic deoxyfluorination with the reagent 'PhenoFluor', even with substrates for which an  $S_NAr$  pathway would be energetically accessible. Detailed mechanistic analysis permitted the adaptation of PhenoFluor-mediated deoxyfluorination, which requires both a fluoride-containing reagent and extraneous fluoride, for  $^{18}F$ -chemistry, where fluoride is, by necessity, the limiting reagent. The resulting radio-deoxyfluorination is operationally convenient, and tolerates a wide range of functional groups. Stabilization of a crucial reaction intermediate through  $\eta^6$ -coordination to ruthenium resulted in a substantial extension of the scope to yield a practical and general  $^{18}F$ -labeling method.

The second part of my talk will focus on the use of metal-organic frameworks (MOFs) in the development of catalysts for the synthesis of biofuels. While ethanol can be sustainably sourced in large quantities, its properties as a fuel additive are sub-optimal. 1-Butanol, on the other hand, can serve as a drop-in replacement for gasoline, but it is currently made from petrochemicals. We have shown that MOF-supported RuNi alloy nanoparticles can catalyze the Guerbet reaction of ethanol to form 1-butanol with turnover numbers over 725,000. Catalytically active RuNi nanoparticles are formed under the reaction conditions from commercially available ruthenium(II) precursors heterogenized in a nickel-based MOF. 1-Butanol is formed with 99.9% selectivity among liquid products at 21% ethanol conversion, despite 1-butanol being itself a competent substrate for the Guerbet reaction.