Fluorine-containing molecules are widely used as important pharmaceuticals and agrochemicals. Among them fluorinated heterocycles are the compounds of special interest, possessing different types of biological activity.\[^{[1]}\]

We have reported the efficient method for the two-step synthesis of α-fluoronitroalkenes from aromatic aldehydes.\[^{[2]}\] In the present work a number of routes to previously inaccessible fluorinated heterocycles from fluoronitroalkenes was developed.

First, the reactivity of α-fluoronitroalkenes in [3+2]-cycloadditions as 2π-components was studied. While synthesis of different fluorinated heterocycles via [3+2]-cycloaddition was limited due to extreme instability of 1-fluoroalkynes,\[^{[3]}\] α-fluoronitroalkenes 1 were found to act as their suitable synthetic equivalents. Thus, a route to previously inaccessible 4-fluoro-1,2,3-NH-triazoles 2 by cycloaddition with sodium azide was developed. Sulfamic acid was found to be the optimal catalyst for this transformation. Oxidative [3+2]-annulation of α-fluoronitroalkenes with pyridinium ylides and imines mediated by copper (II) acetate provides a direct route to novel fluorinated indolizines 3 and pyrazolo[1,5-a]pyridines 4.

Next, the reactivity of nitroalkenes as 4π-components was explored. The one-pot reaction of α-fluoronitroalkenes, bromomalonic ester and different dipolarophiles in basic conditions resulted in formation of bicyclic 5,5-annulated nitroso acetals 5. The mechanism involving tandem [4+1]/[3+2]-cycloaddition was discussed. Nitroso acetals formed with complete regioselectivity and high diastereoselectivity, and both electron-rich and electron-deficient dipolarophiles were suitable substrates for cycloaddition.

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