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Catalytic dehydration of modified carbohydrates as a new approach to efficient biomass utilization in organic synthesis

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Integration of renewable bio-resources for sustainable applications is one of the key challenges of modern chemical science and technology. The most perspective approach to the synthetic utilization of plant biomass involves the catalytic conversion of carbohydrates to low-molecular-weight building blocks, which are defined as bio-based platform chemicals. 5-(Hydroxymethyl) furfural (HMF) is one of the key platform chemical that can be used for a wide range of applications. Low stability and difficult isolation process limits utilization of HMF as a reagent in organic synthesis (Figure 1, a). This presentation will introduce an efficient approach to the preparation of stable HMF analogues by direct conversion of modified carbohydrates (figure 1, b). A highly efficient biomass conversion process based on introduction of a silyl protecting group to glucose allowed to significantly increase the selectivity of furan formation and facilitated its isolation from the reaction mixture. New aspects of synthesis and utilization of HMF and derivatives for biofuels, materials and pharmaceuticals production were also described. We have shown that the aldehyde group in HMF can be easily modified into an alkyne fragment using the Ohira-Bestmann reaction. A number of polyunsaturated products from alkynyl furans were prepared using rhodium catalysis. The first example of the Diels-Alder reaction of un-substituted 2, 5-bis (hydroxy methyl) furan with maleimide was carried out under green conditions with high diastereo selectivity. The implementation of described synthetic approaches opens new opportunities for the synthesis of demanded functional derivatives from bio-based furans.

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