Tightened restrictions call for cleaner transportation fuels to minimize environmental and societal problems caused by the presence of sulfur in transportation fuels. This emphasizes the need for new and better catalysts in the field of hydrodesulfurization (HDS), which aims at removing the refractory sulfur from different petroleum streams mostly found in the form of the alkyl-substituted dibenzothiophenes (β-DBTs). In this work we demonstrate how a setup dedicated to testing minute amounts (nanogram) of well-defined catalytic systems in μ-reactors can be used in the gas-phase HDS of the model compounds DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT) and the reaction pathways revealed by time-of-flight mass spectrometry. Specifically, we investigate HDS of DBT and 4,6-DMDBT on mass-selected Pt nanoparticles and show that only the direct desulfurization products are formed. The setup is a means to bridge the gap between structural characterization of model catalysts and their related activity in the HDS of DBT and 4,6-DMDBT.