Natural indole alkaloids featuring bridged or fused cores often possess diverse biological and pharmacological activities. As a result, organic chemists have accomplished lots of effective strategies for the target-oriented synthesis of individual natural products appertaining to these families. However, the rapid and streamlined construction of these natural products and their mimics with highly architectural complexity and diversity, from easily available feedstocks is still in hot demand, as it should allow fast access to large libraries of molecular architectures, serving as potential candidates for biological activity screenings in drug discovery.

We have already demonstrated various approaches for the construction of bridged and fused indole alkaloid-like heterocycles via a modular assembly of skeletally diverse precursors through Ugi four-component reaction (Ugi-4CR) with subsequent intramolecular transition metal-catalyzed cyclizations. Specifically, the ortho-phenol, indole and propiolamide moiety could be easily introduced into multifunctional precursors 1 through the well-developed Ugi-4CR (Scheme). We will comment on these gold-catalyzed intramolecular dearomatization of the phenol moiety/spirocarbocyclization processes, leading to complex spirocyclic frameworks. [1].

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\text{R}^1\text{C}═\text{N}═\text{C}(\text{Imes})\text{AuCl/AgOTf (10 mol%) CHCl}_3 \text{ 70}^\circ\text{C, 2 h} \rightarrow \text{R}^1\text{N}═\text{C}═\text{N}═\text{R}^3
\]