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Total synthesis of natural products via type II [5+2] cycloaddition

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Developing efficient reactions for achieving bridged ring systems is a long-standing challenge but very significant in organic chemistry, considering that such motif is widely found in natural products (such as Taxol®) with significant biological activities. So far there are no general reactions available for the single-step synthesis of bridged seven-membered-ring systems efficiently. Recently, we have developed the first type II intramolecular [5+2] cycloaddition reaction, which allows the efficient and diastereoselective construction of various highly functionalized and synthetically challenging bridged seven-membered ring systems. The highly strained tricyclic cores of ingenol and eurifoloid A2 were synthesized efficiently and diastereoselectively using this methodology. The first asymmetric total synthesis of cyclocitrinol and cerorubenic acid have been accomplished via the type II intramolecular [5+2] cycloaddition.