



Significance:

Li and coworkers achieved the first asymmetry total synthesis of Bufogargarizins A and B in 28 and 30 steps. The challenging [7-5-6-5] ring system could be constructed effectively via a Ru-catalyzed [5 + 2] cycloaddition reaction, and the [5-7-6-5] tetracyclic skeleton of Bufogargarizin B was assembled from the [7-5-6-5] skeleton.

Comment:

- Intramolecular Ru-catalyzed [5 + 2] cycloaddition reaction as the key step to construct the [7-5-6-5] core skeleton efficiently, enabling the diverse syntheses of other natural bufogargarizins, bufadienolides, and analogues that also have similar structural features.