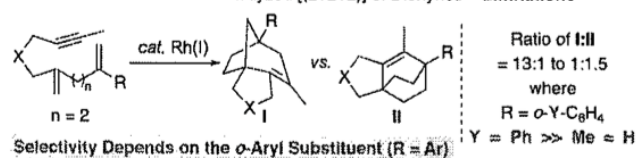


**Intramolecular Rhodium-Catalyzed [(3+2+2)] Carbocyclization Reactions with Dienyldenecyclopropanes:
A Concise and Stereoselective Total Synthesis of the Sesquiterpene (+)-Zizaene:** Yu Zhu, Jie Zheng, and P. Andrew Evans*
Cite this: J. Am. Chem. Soc. 2023, 145, 7, 3833–3838

Previous higher-order metal catalyzed carbocyclization

B. Intramolecular Rhodium-Catalyzed [(2+2+2)] of Dienes – *Limitations*



Selectivity Depends on the *o*-Aryl Substituent (R = Ar)

C. Semi-Intermolecular Rhodium-Catalyzed [(3+2+2)] of ACPs – *Bicyclic Product*

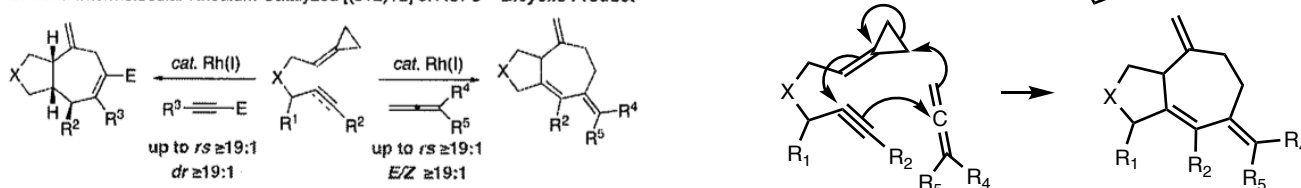
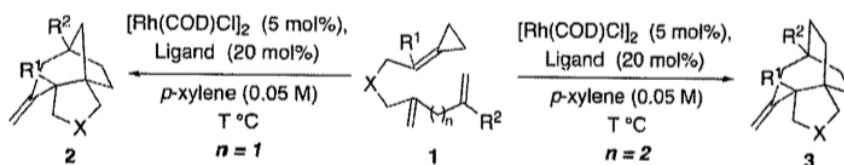


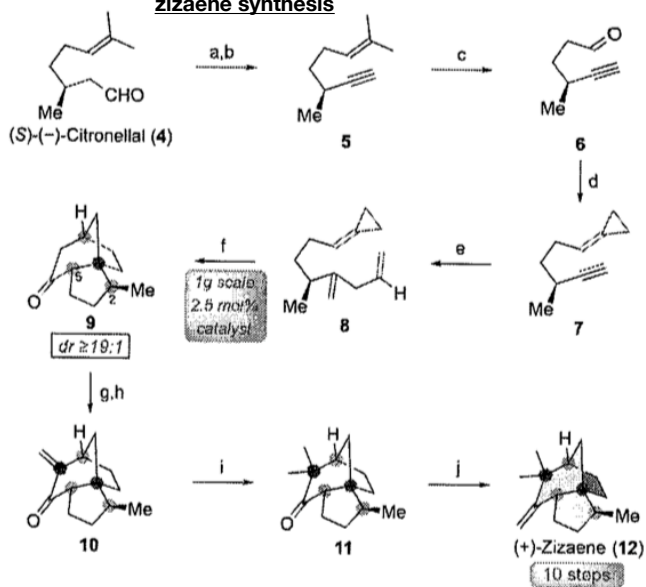
Table 2. Scope of the Rhodium-Catalyzed [(3+2+2)] Carbocyclization of ACPs Tethered to 1,4- and 1,5-Dienes^{a,b}

X=O, NHTs, CE₂

18 examples
< 95%



zizaene synthesis



^aReagents: (a) Br₂, P(OPh)₃, NEt₃, DCM, -78 °C to rt, 90%. (b) ^tBuOK, 18-crown-6, hexane, 60 °C, 74%. (c) O₃, DCM, -78 °C then DMS, 67%. (d) Cyclopropyltriphenylphosphonium bromide, NaH, TDA-1, THE, 65 °C, 78%. (e) Indium, allyl iodide, THE, 70 °C, 84%. (f) [Rh(COD)Cl]₂ (2.5 mol %), PPh₃ (10 mol %), dioxane, 125 °C, then *cat.* OsO₄, NaIO₄, 2,6-lutidine, dioxane/water (3:1), rt, 51%. (g) LiHMDS, [(CH₃)₂NCH₂]⁺I⁻, THE, -40 °C to rt. (h) *m*-CPBA, DCM, 0 °C to rt, 77% over two steps. (i) Li/NH₃, H₂O, THE, -78 °C, then MeI, 66%. (j) TMSCH₂Li, THE, -78 °C, then aq. NH₄Cl, conc. H₂SO₄, rt, 54%.

optimized

C5 epimerization prevented

