# TOWARD THE REBIRTH OF THE AROMATIC COPE REARRANGEMENT

**Pierre Locquet [1], Emmanuel Riguet [2] and Aurelien Blanc [1]**

*[1] Laboratoire de Synthèse et Réactivité et Catalyse, Institut de Chimie de Strasbourg, UMR 7177, 4 rue Blaise Pascal, Strasbourg, France*

*[2] Méthodologie en Synthèse Organique, Institut de Chimie de Reims, UMR 7312, Campus Moulin de la Housse, Reims, France*

The Cope rearrangement, discovered in 1940 by Arthur C. Cope[1], is a powerful and well-studied pericyclic reaction involving a sigmatropic shift in a 1,5-hexadiene moiety. Yet, its aromatic version involving one of the alkenes within an aromatic ring has found to be very limited due to the impossibility to overcome thermodynamic and kinetic energetic barriers. Even if less than fifty papers[2] were consecrated to this reaction it has been theoretically studied and was performed using designed substrate under thermic condition[3].

Another way to achieve the rearrangement is the use of catalytic system in order to lower the energetic barrier and avoid high temperature. In this context, gold catalysis, especially $Au^I$, seems to be a perfect candidate due to its incredible π-acidity making it a strong carbophilic acid and has already shown activity in Cope rearrangement[4]. We thus demonstrated that, on an engineered substrate known to rearrange in thermic (> 110°C)[5], $Au^I$ catalyst drastically decreased the activation barrier of the aromatic cope reaction. After optimization, we develop an efficient method using 5 mol% of $(4-CF_3Ph)_3PAuOTf$ in HFIP to perform the aromatic Cope rearrangement on various substrates in milder reaction conditions than the thermic one (64 - 96 %, 29 examples).
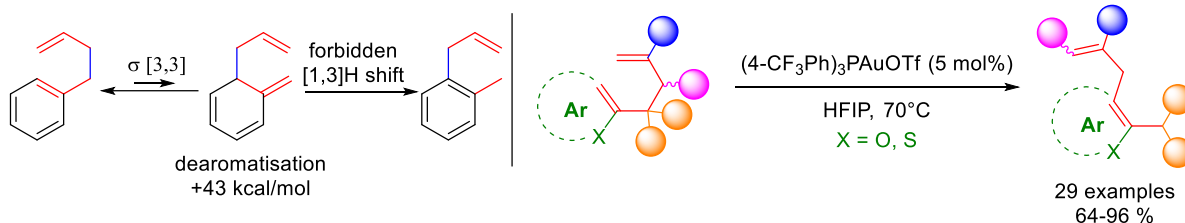


## References:

1) A.C. Cope, E.M. Hardy, *J. Am. Chem. Soc.,* 1940, 62, 2, 441
2) B.M. Tomiczek, A.J. Grenning, *Org. Biomol. Chem.*, 2021, 19, 2385
3) J. Barluenga, F. Azner, I. Gutiérrez, J.A. Martin, *Org. Lett.,* 2002, 4, 16, 2719
4) R.J. Felix, D. Weber, O. Gutierrez, D.J. Tantillo, M.R. Gagné, *Nat. Chem.*, 2012, 4, 405
5) M. Bos, E. Riguet, *Chem. Commun.*, 2017, 53, 4997