The History of Homogeneous Gold Catalysis and its Applications in Total Synthesis

---

Dylan Hsu

Literature Presentation

March 20, 2026

SORENSEN LAB



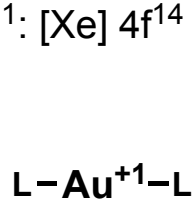
Chemistry of Homogeneous Gold Catalysis

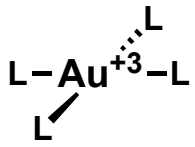
8	9	10	11	12
26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38
44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.414
76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.085	79 **Au** Gold 196.967	80 **Hg** Mercury 200.592
108 **Hs** Hassium [269]	109 **Mt** Meitnerium [278]	110 **Ds** Darmstadtium [281]	111 **Rg** Roentgenium [280]	112 **Cn** Copernicium [285]

Common Oxidation States

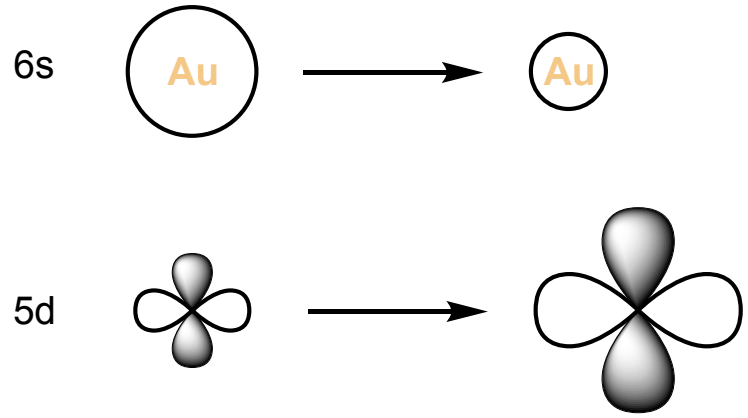
Au^{+1}: [Xe] $4f^{14}$ $5d^{10}$

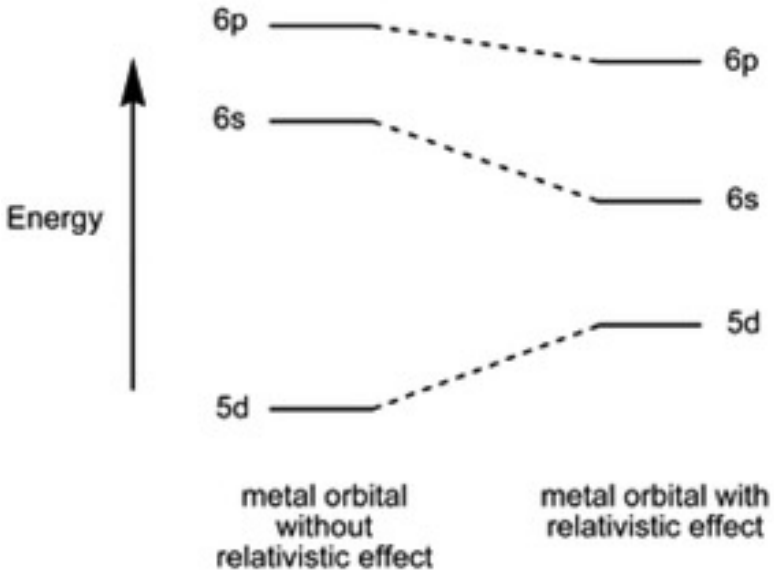
Au^{+3}: [Xe] $4f^{14}$ $5d^{8}$





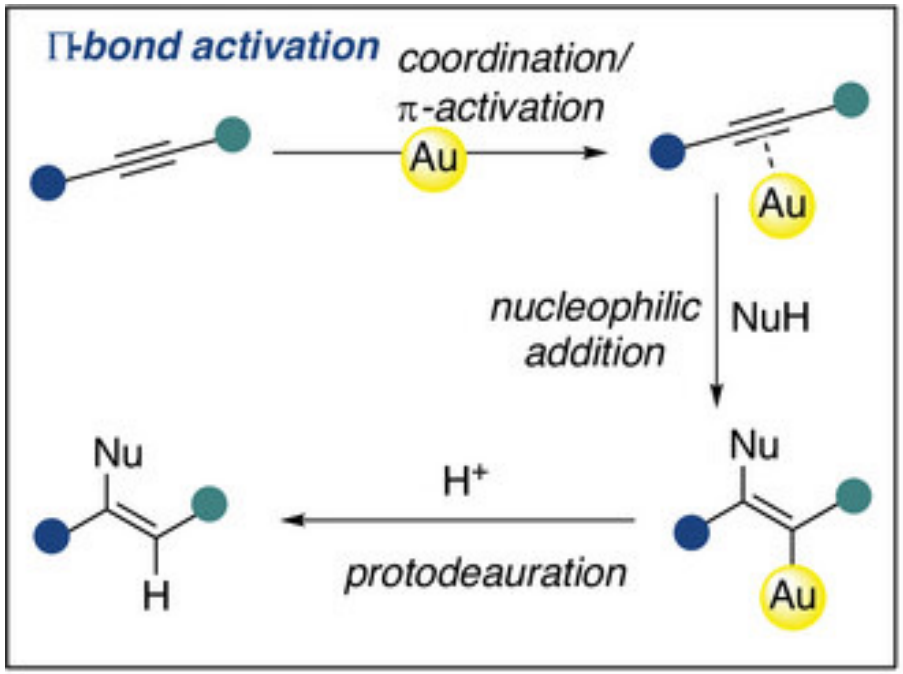
Relativistic Effect

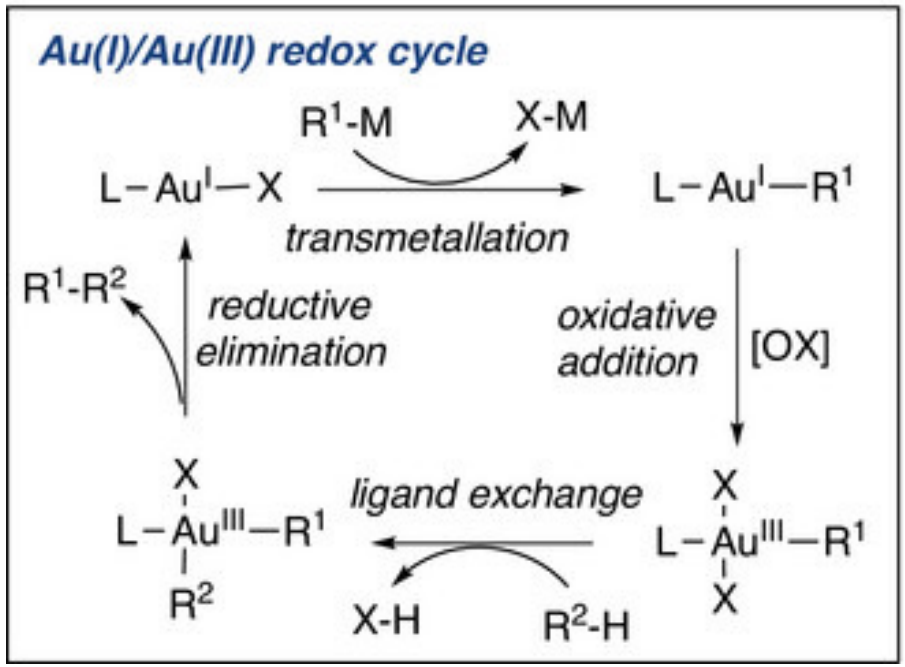




Nature **2007**, 446, 395.

Chemistry of Homogeneous Gold Catalysis





Chem Asian J. **2025**, 20, e202500040.

Origins of Homogeneous Gold Catalysis

Why gold is the noblest of all the metals

B. Hammer*† & J. K. Nørskov*

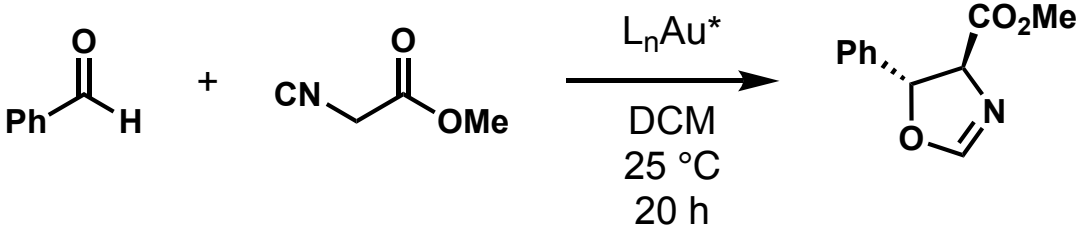
* Centre for Atomic-scale Materials Physics, Physics Department, Technical University of Denmark, DK-2800 Lyngby, Denmark
† Joint Research Center for Atom Technology (JRCAT), 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

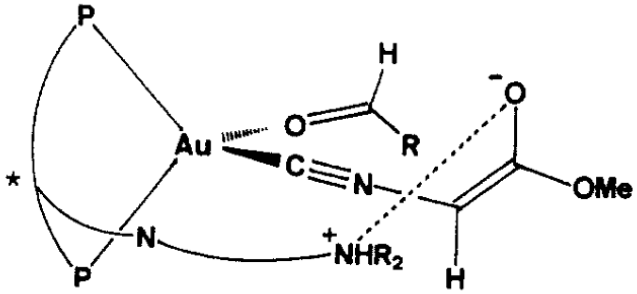
THE unique role that gold plays in society is to a large extent related to the fact that it is the most noble of all metals: it is the least reactive metal towards atoms or molecules at the interface with a gas or a liquid. The inertness of gold does not reflect a general inability to form chemical bonds, however—gold forms very stable alloys with many other metals. To understand the nobleness of gold, we have studied a simple surface reaction, the dissociation of H_2 on the surface of gold and of three other metals (copper, nickel and platinum) that lie close to it in the periodic table. We present self-consistent density-functional calculations of the activation barriers and chemisorption energies which clearly illustrate that nobleness is related to two factors: the degree of filling of the antibonding states on adsorption, and the degree of orbital overlap with the adsorbate. These two factors, which determine both the strength of the adsorbate–metal interaction and the energy barrier for dissociation, operate together to the maximal detriment of adsorbate binding and subsequent reactivity on gold.

Nature **1995**, 376, 238.

Origins of Homogeneous Gold Catalysis

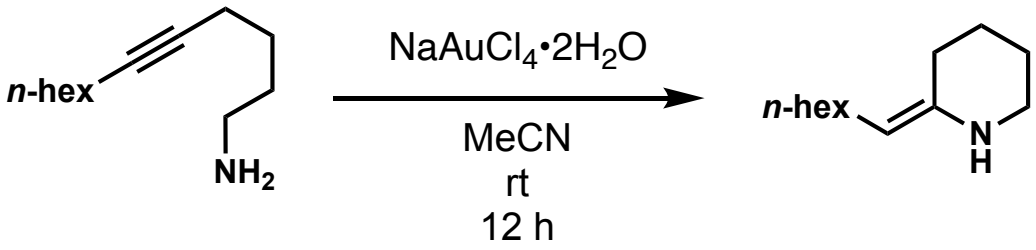
Ito and Hayashi (1986)

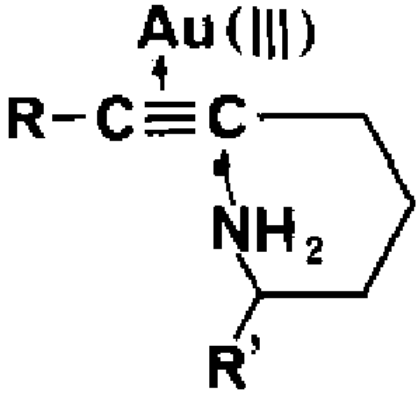




J. Am. Chem. Soc. **1986**, 108, 6405.

Utimoto (1987)

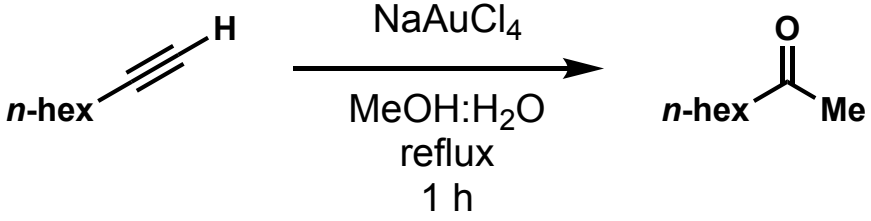




Heterocycles **1987**, 25, 297.

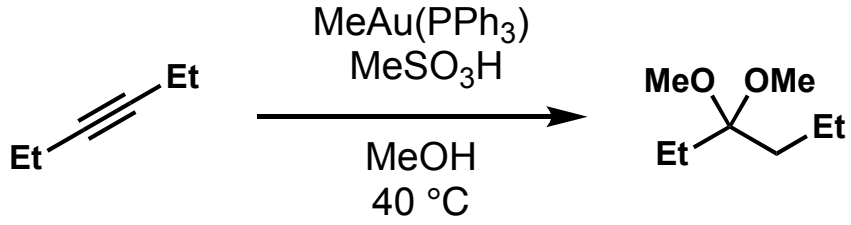
Additions of Water and Alcohol to Alkynes

Utimoto (1991)



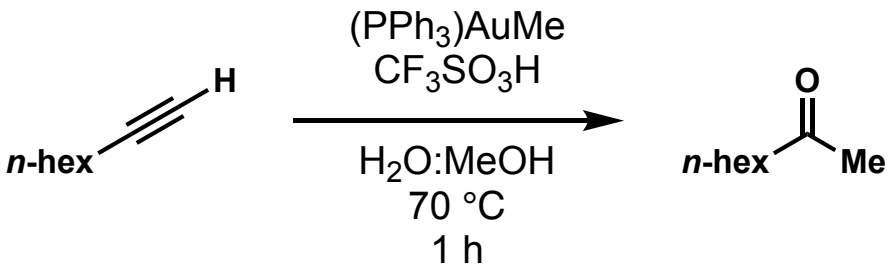
J. Org. Chem. **1991**, 56, 3729.

Teles (1998)



Angew. Chem. Int. Ed. **1998**, 37, 1415.

Tanaka (2002)



Angew. Chem. Int. Ed. **2002**, 41, 4563.

Cycloisomerizations to Form Furans and Arenes

Hashmi (2000)

A New Gold-Catalyzed C–C Bond Formation**

A. Stephen K. Hashmi,* Lothar Schwarz,
Ji-Hyun Choi, and Tanja M. Frost

While a manifold on the stoichiometric organometallic chemistry of gold is known, only a few catalytical applications have been reported.[1] As far as the *homogeneous* catalysis of organic reactions is concerned, there exist only two reactions that have reached any importance. The first forms C–X bonds (X = heteroatom) by the addition of O- or N-nucleophiles to alkenes or alkynes, as developed by Utimoto et al.[2] and Teles et al.[3] The second application forms C–C bonds by the

[*] Priv.-Doz. A. S. K. Hashmi, Dipl.-Chem. L. Schwarz, J.-H. Choi, T. M. Frost
Institut für Organische Chemie
Johann Wolfgang Goethe-Universität
Marie-Curie-Strasse 11, 60439 Frankfurt a. M. (Germany)
Fax: (+49) 69-79829464
E-mail: hashmi@chemie.uni-frankfurt.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (Ha 1932/5-1, Ha 1932/6-1) and the Fonds der Chemischen Industrie. Gold salts were donated by Degussa-Hüls AG. A.S.K.H. is indebted to Prof. M. Göbel for laboratory space.

Angew. Chem. Int. Ed. **2000**, 39, 2285.

Hashmi (2000)

Highly Selective Gold-Catalyzed Arene Synthesis

A. Stephen K. Hashmi,* Tanja M. Frost, and J. W. Bats

Institut für Organische Chemie
Johann Wolfgang Goethe-Universität, Marie-Curie-Strasse 11
60439 Frankfurt am Main, Germany

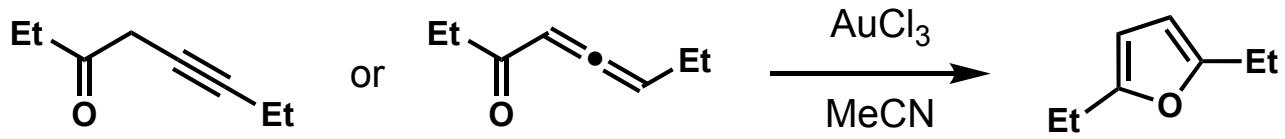
Received September 3, 2000

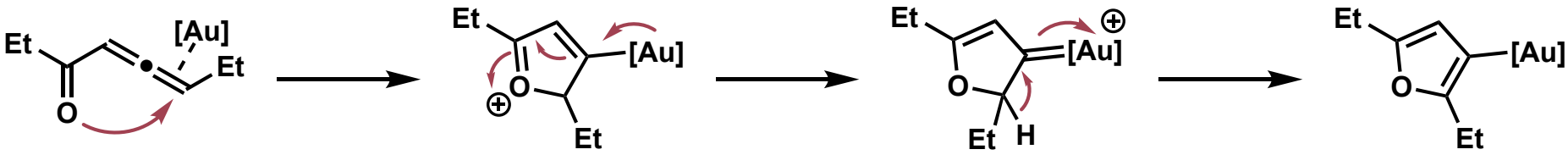
The classic route to aromatic compounds with specific substitution patterns is the aromatic substitution which introduces or exchanges substituents at an already existing arene.[1] A different mechanism but the same synthetic principle is applied in the different transition-metal-catalyzed (cross-) coupling reactions[2] or ortho-metalation and subsequent functionalization reactions.[3] Other approaches assemble the arene, e.g. use cycloaddition reactions such as the Diels–Alder reaction followed by a subsequent oxidation of the unsaturated six-membered ring to an arene.[4] Some major achievements in this field of cycloadditions or cycloisomerizations of the past years stem from transition metal catalysis.[5] For arene synthesis Vollhardt's [2+2+2] cycloaddition[6] and variations thereof[7] as well as the Dötz reaction[8] are among the most prominent.

J. Am. Chem. Soc. **2000**, 122, 11553.

Cycloisomerizations to Form Furans

Hashmi (2000)

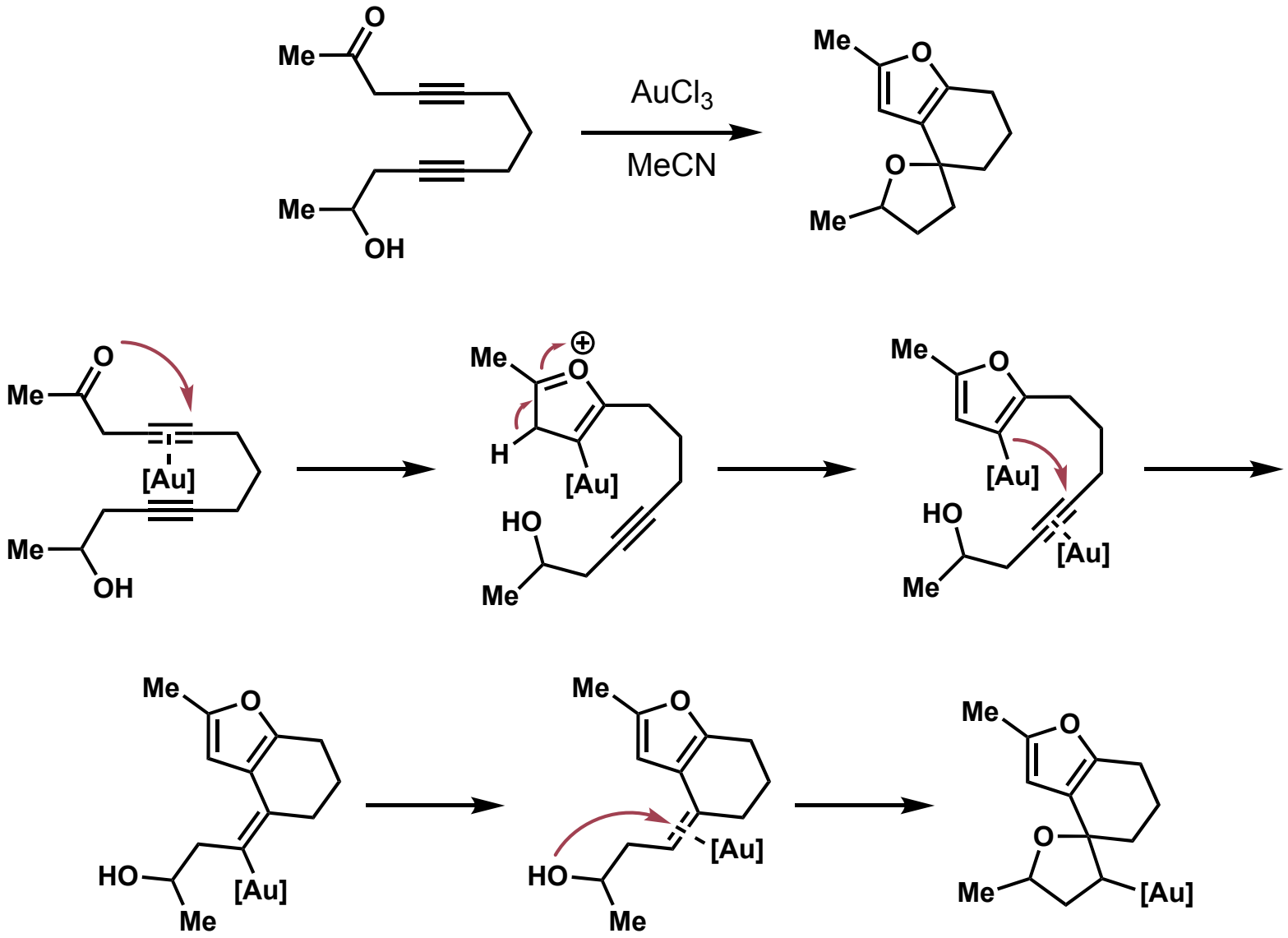




Angew. Chem. Int. Ed. **2000**, 39, 2285.

Cycloisomerizations to Form Furans

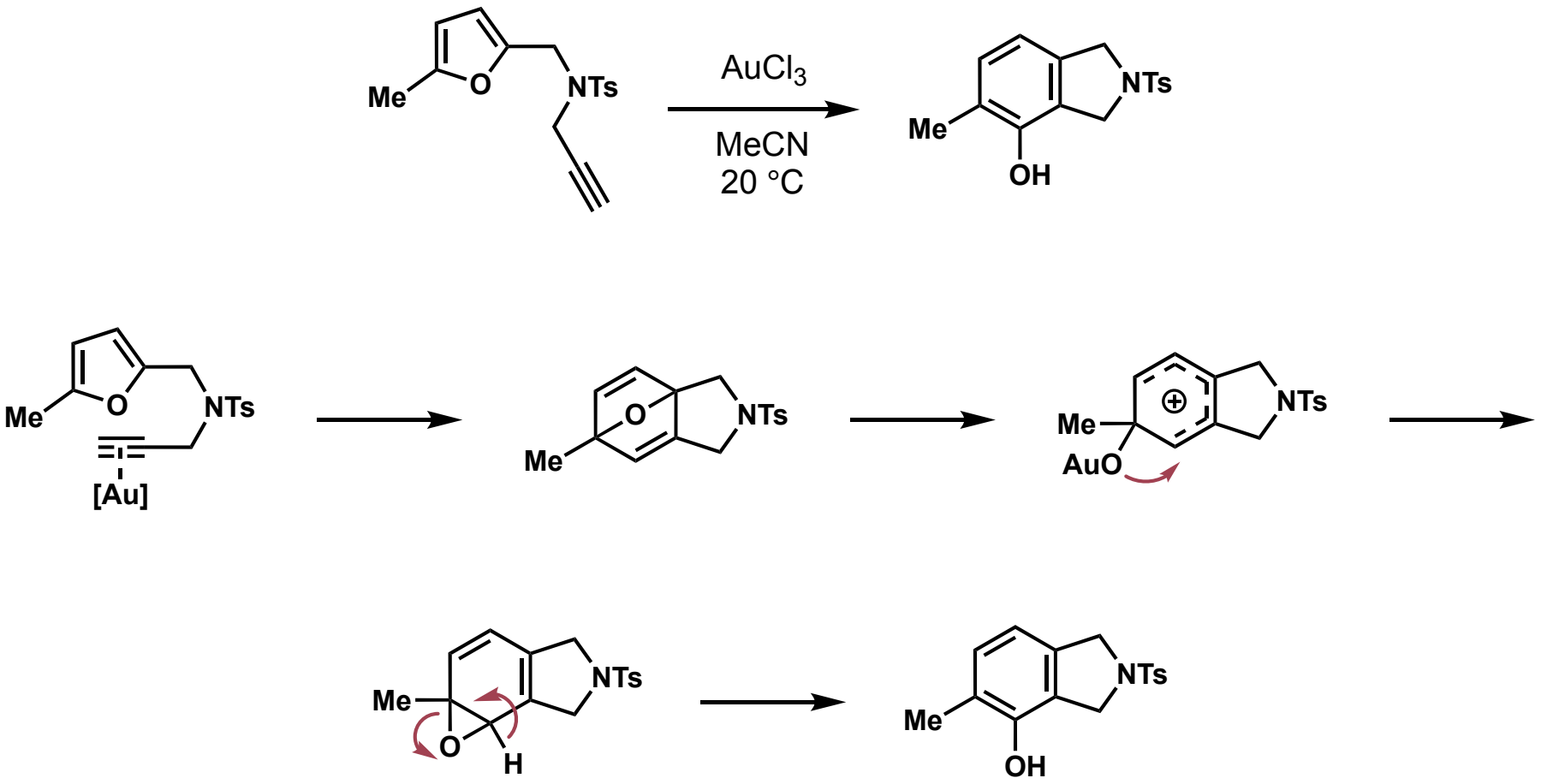
Hashmi (2000)



Angew. Chem. Int. Ed. **2000**, 39, 2285.

Cycloisomerizations to Form Arenes

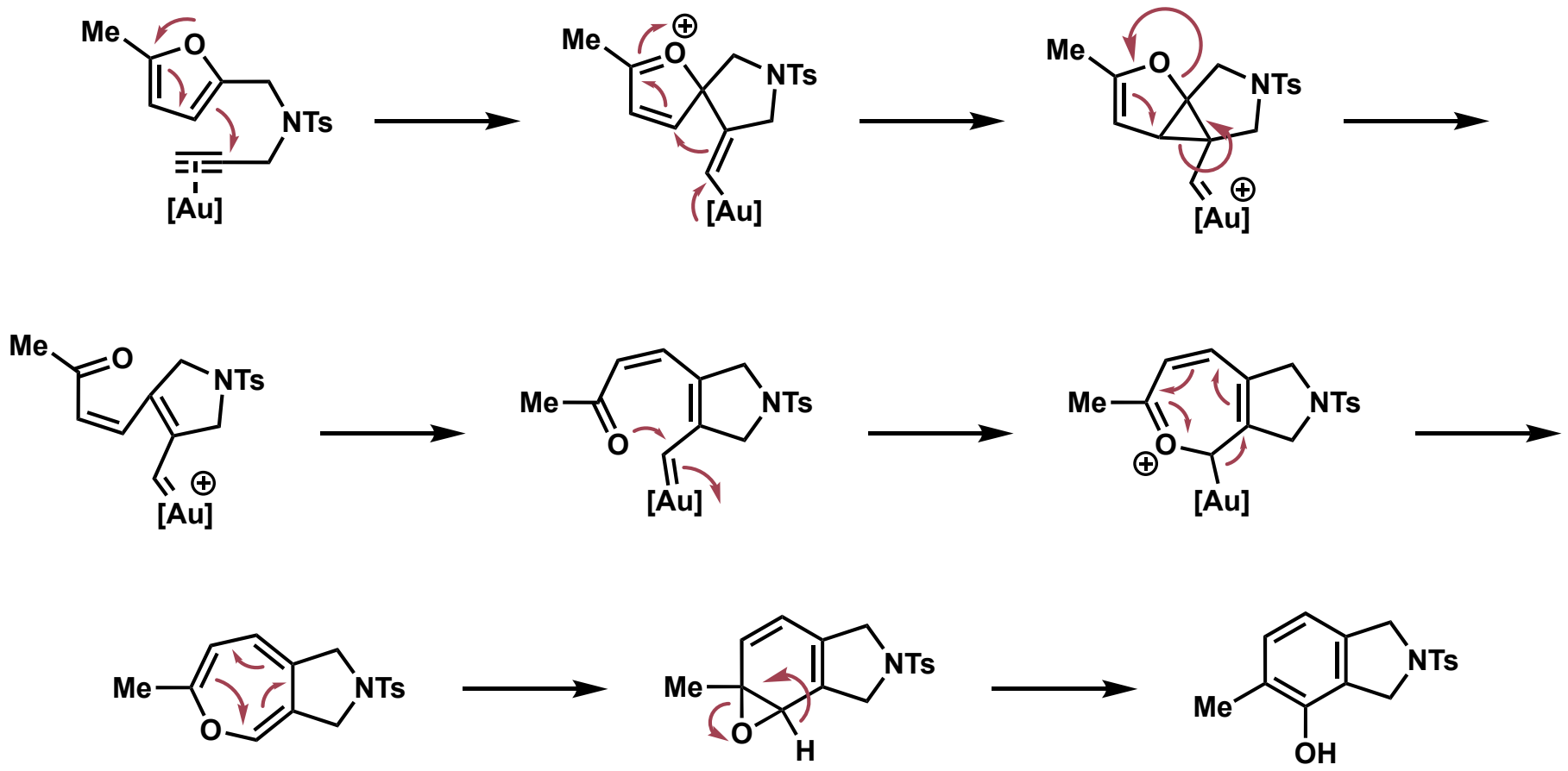
Hashmi (2000)



J. Am. Chem. Soc. **2000**, 122, 11553.

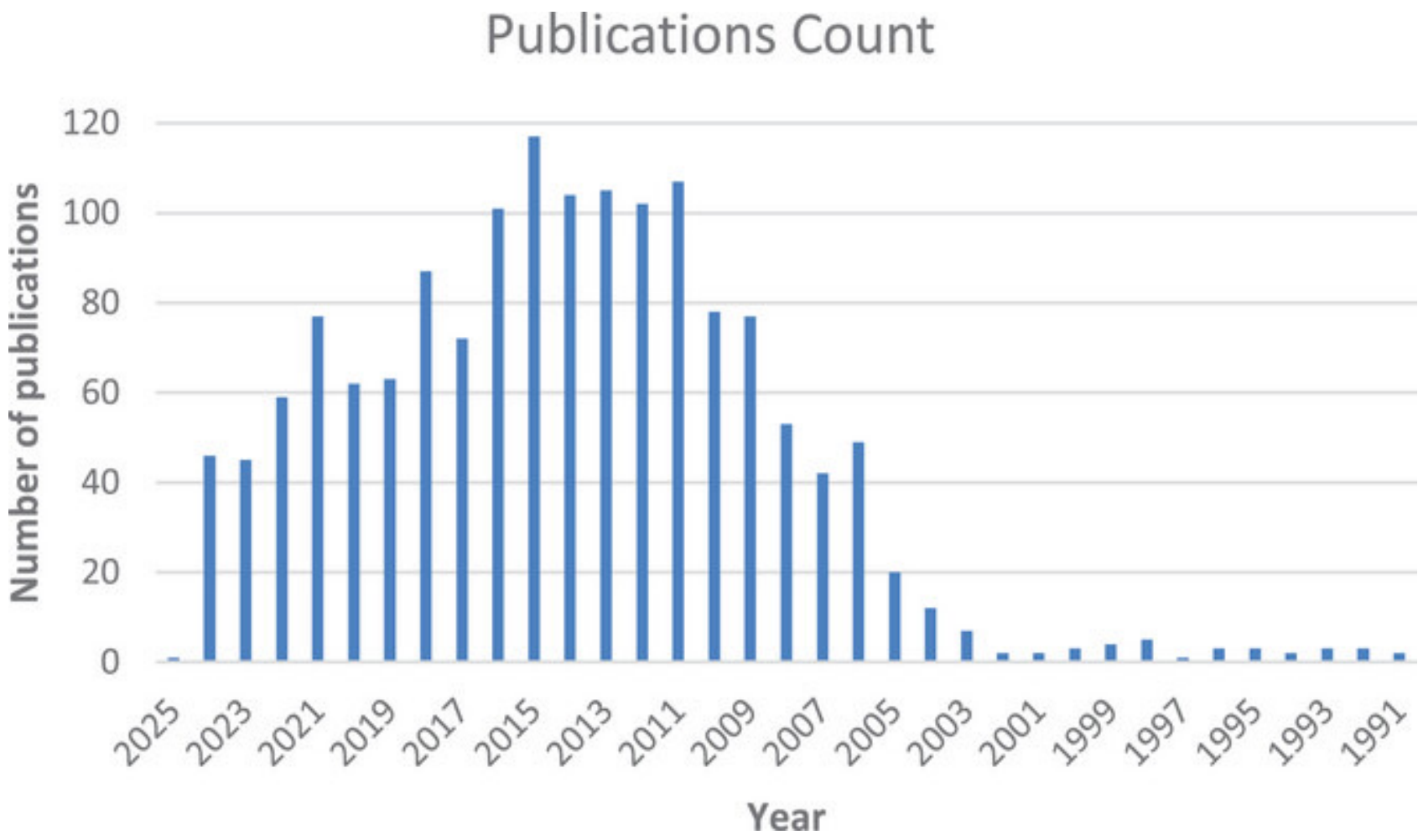
Cycloisomerizations to Form Arenes

Hashmi (2000)



Angew. Chem. Int. Ed. **2005**, 44, 2798.
Adv. Synth. Catal. **2006**, 348, 709.

The “Gold Rush”



Chem Asian J. **2025**, 20, e202500040.

Total Synthesis Using Gold Catalysis Reviews

Hashmi, A. S. K.; Rudolph, M. Gold catalysis in total synthesis. *Chem. Soc. Rev.* **2008**, 37, 1766–1775.

Rudolph, M.; Hashmi, A. S. K. Gold catalysis in total synthesis—an update. *Chem. Soc. Rev.* **2012**, 41, 2448–2462.

Pflästerer, D.; Hashmi, A. S. K. Gold catalysis in total synthesis – recent achievements. *Chem. Soc. Rev.* **2016**, 45, 1331–1367.

Zhang, Y.; Luo, T.; Yang, Z. Strategic innovation in the total synthesis of complex natural products using gold catalysis. *Nat. Prod. Rep.* **2014**, 31, 489–503.

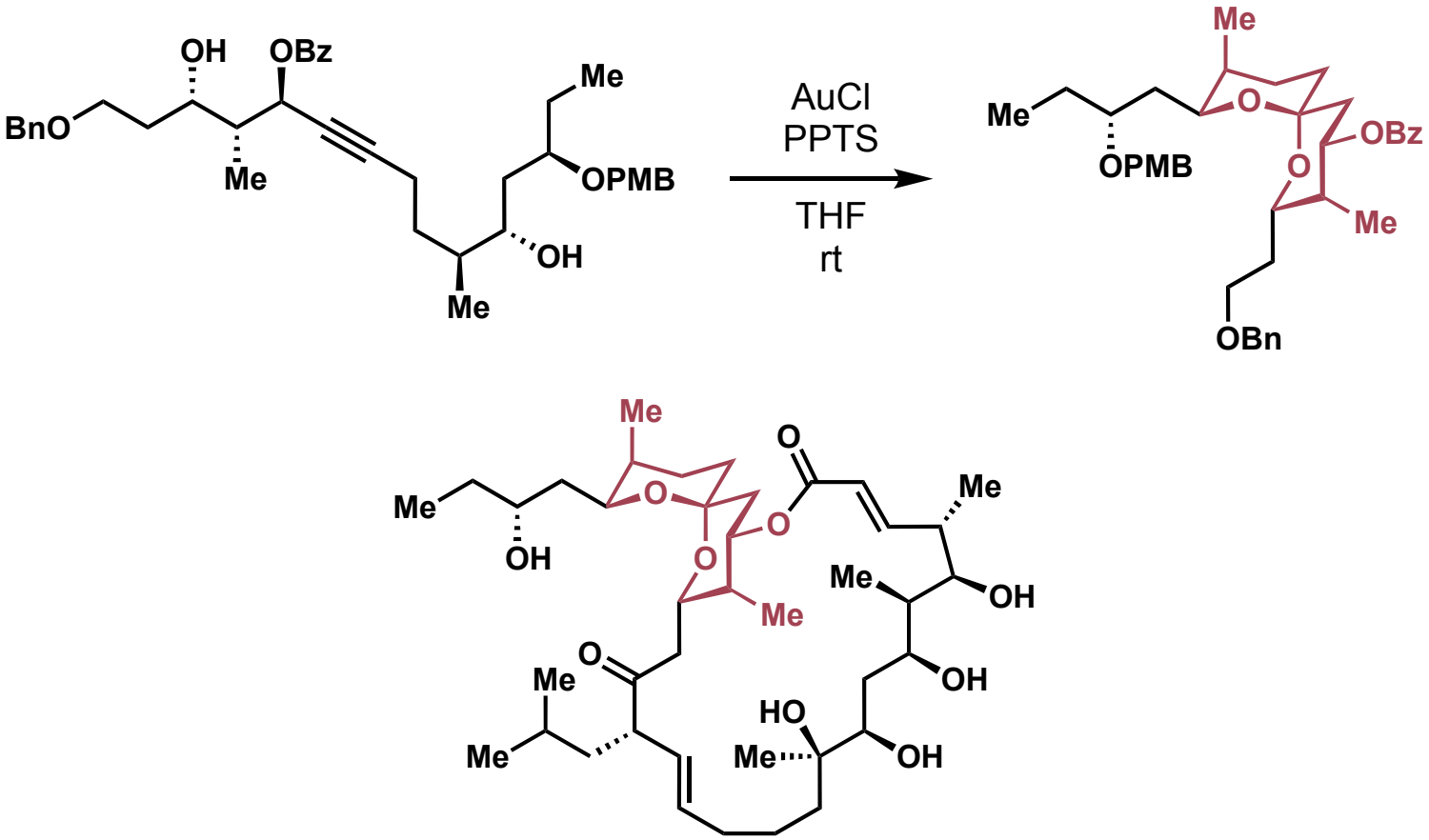
Sugimoto, K.; Matsuya, Y. Recent applications of gold-catalyzed cascade reactions in total synthesis of natural product. *Tetrahedron Lett*. **2017**, 58, 4420–4426.

Quach, R.; Furkert, D. P.; Brimble, M. A. Gold catalysis: synthesis of spiro, bridged, and fused ketal natural products. *Org. Biomol. Chem*. **2017**, 15, 3098–3104.

De, S.; Dan, A. K.; Sahu, R.; Parida, S.; Das, D. Total Synthesis of Natural Products using Gold Catalysis. *Chem Asian J.* **2022**, 17, e202200896.

(–)-Ushikulide A

Trost (2009)

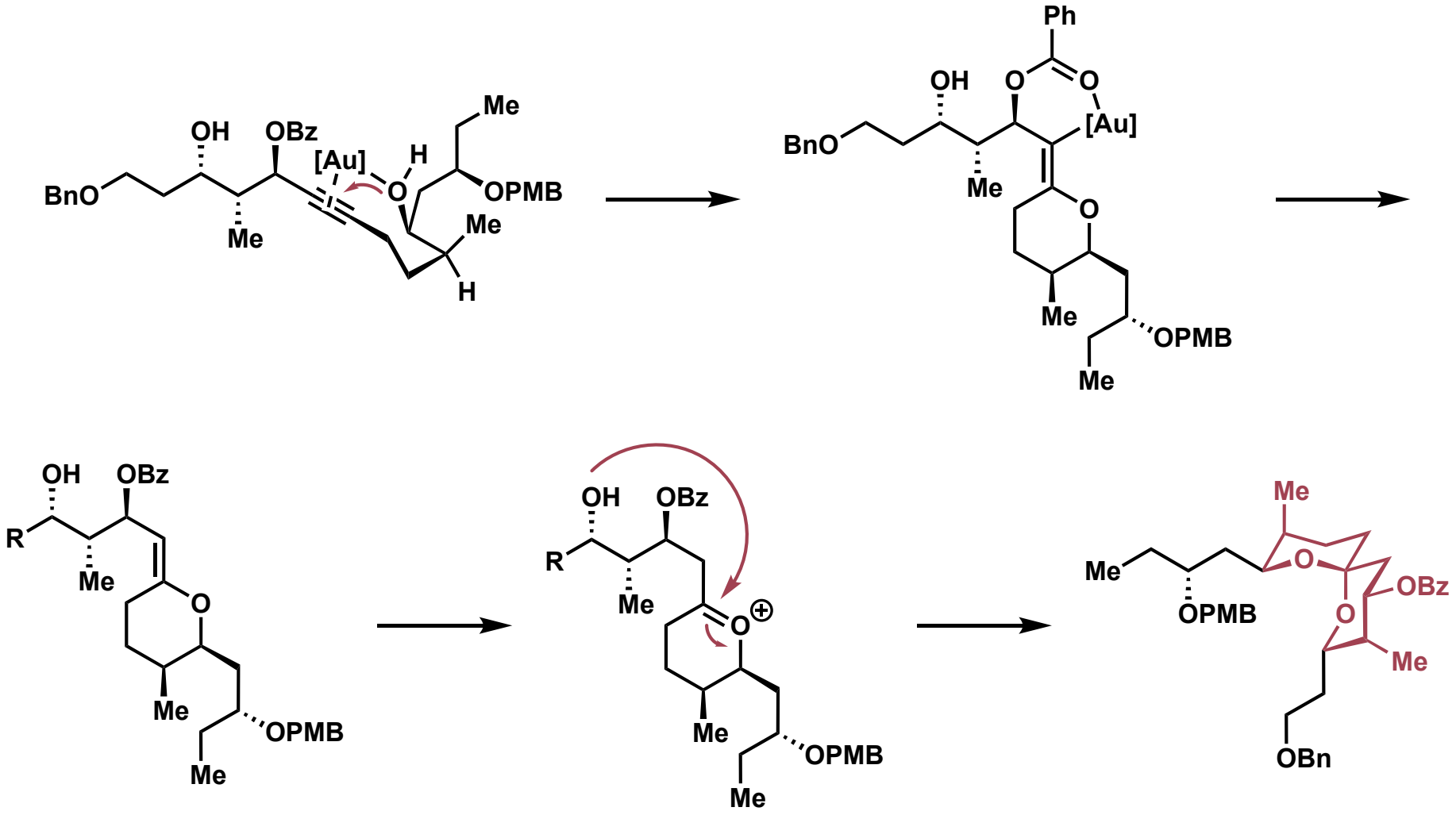


(–)-Ushikulide A

J. Am. Chem. Soc. **2009**, 131, 15061.

(–)-Ushikulide A

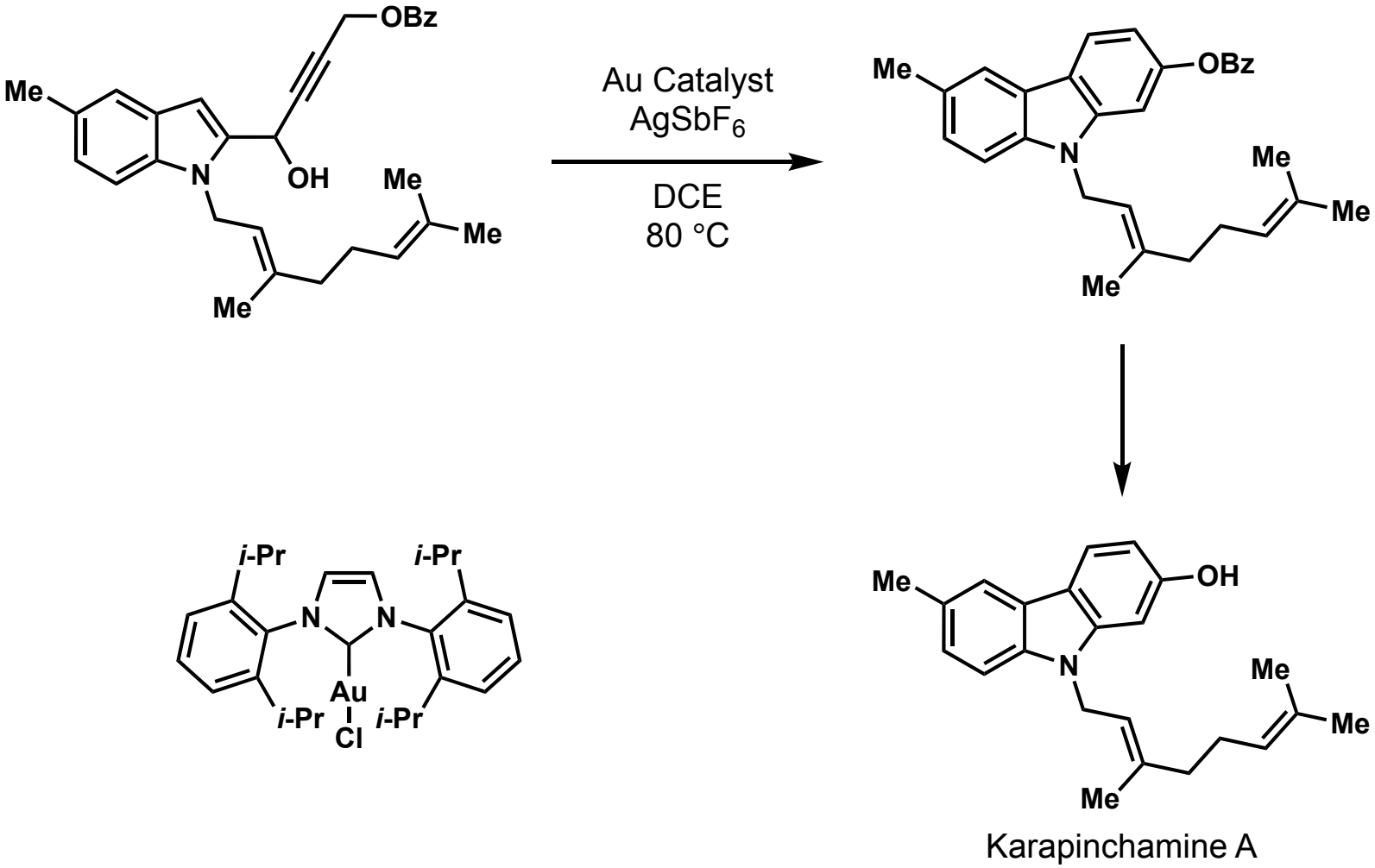
Trost (2009)



J. Am. Chem. Soc. **2009**, 131, 15061.

Karapinchamine A

Ma (2014)

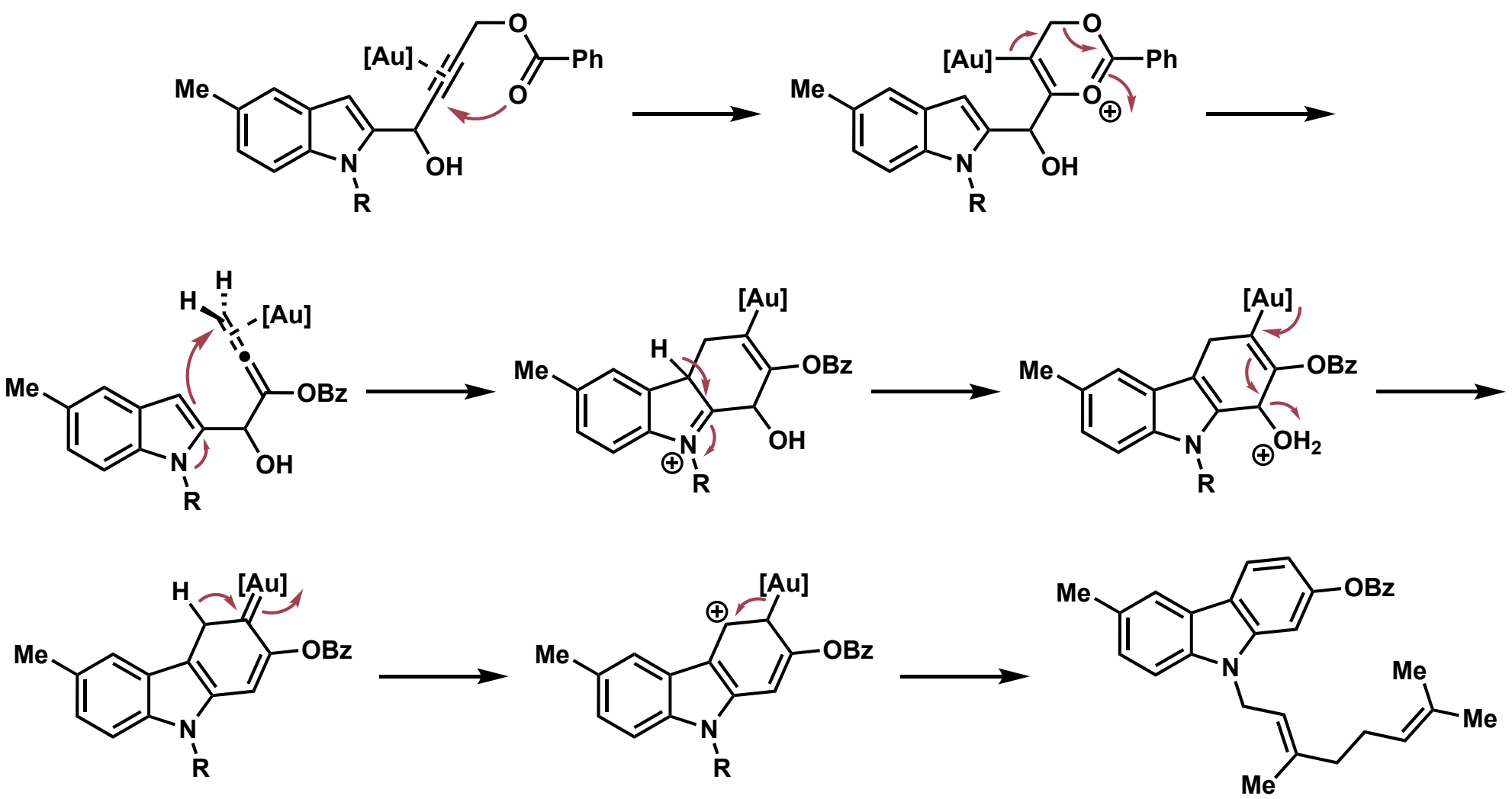


Karapinchamine A

Chem. Eur. J. **2014**, 20, 14589.

Karapinchamine A

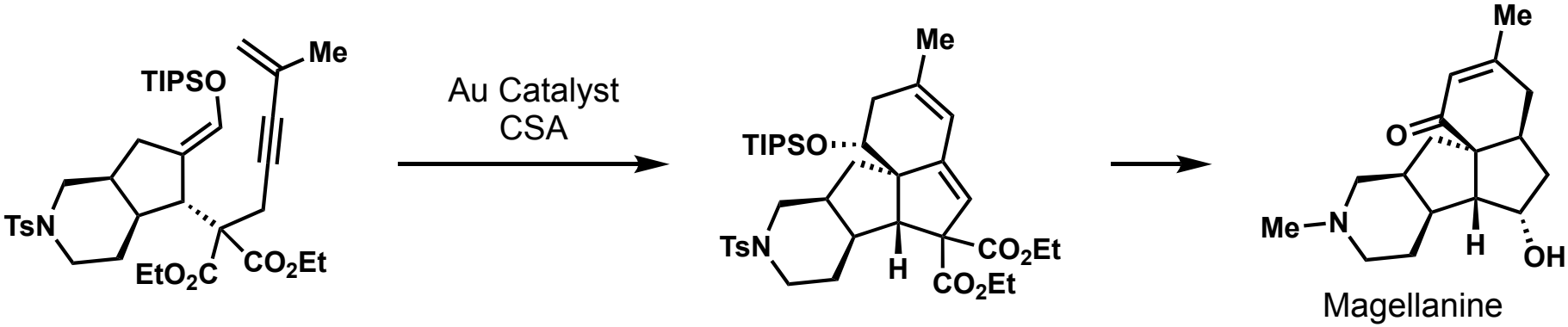
Ma (2014)

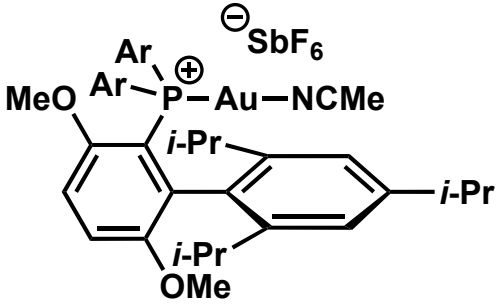


Chem. Eur. J. **2014**, 20, 14589.

(+/–)-Magellanine

Barriault (2017)



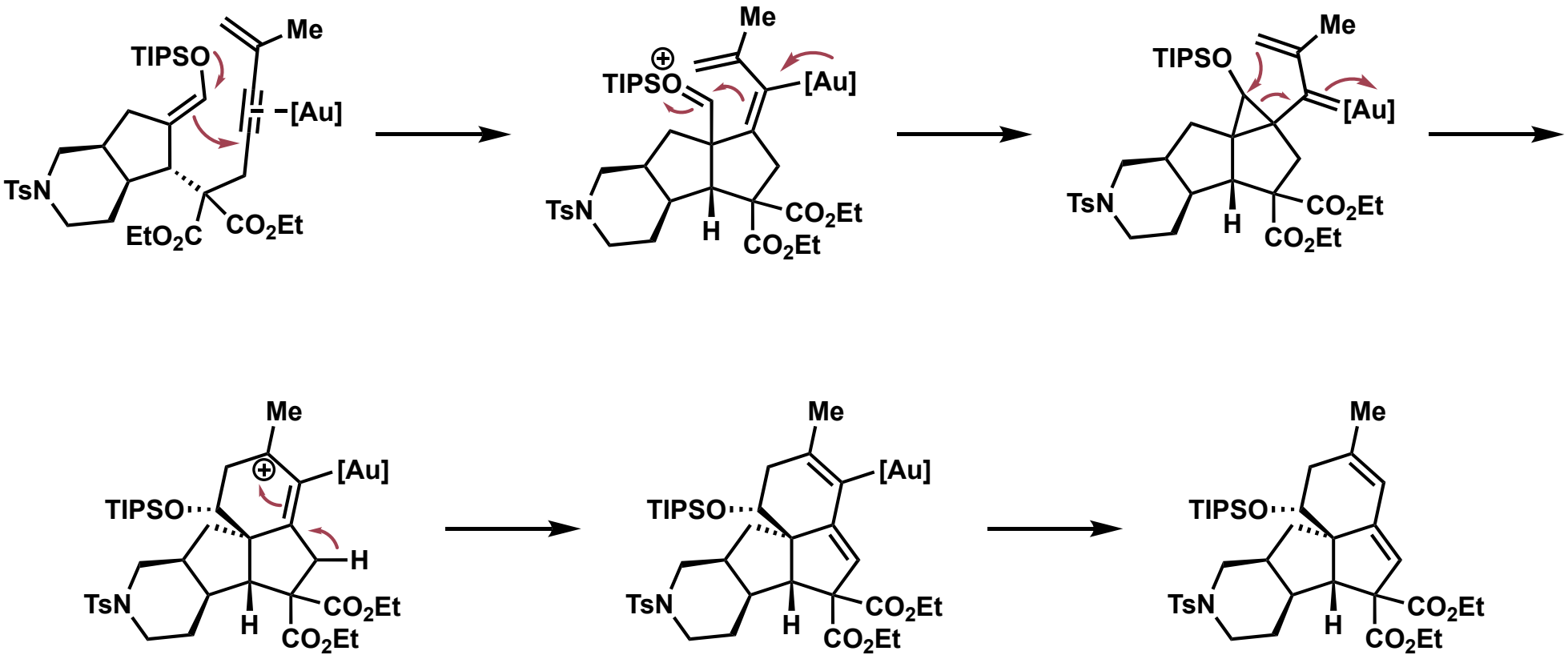


Ar = 3,5-$CF_3C_6H_3$

Angew. Chem. Int. Ed. **2017**, 56, 6280.

(+/–)-Magellanine

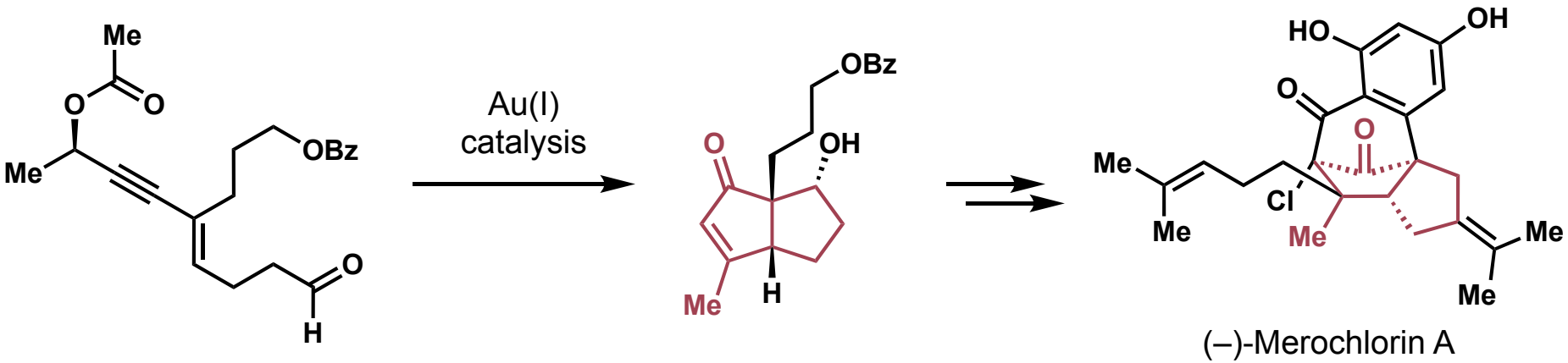
Barriault (2017)



Angew. Chem. Int. Ed. **2017**, 56, 6280.

(–)-Merochlorin A

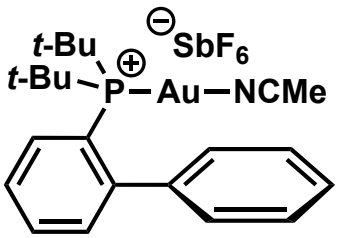
Carreira (2019)

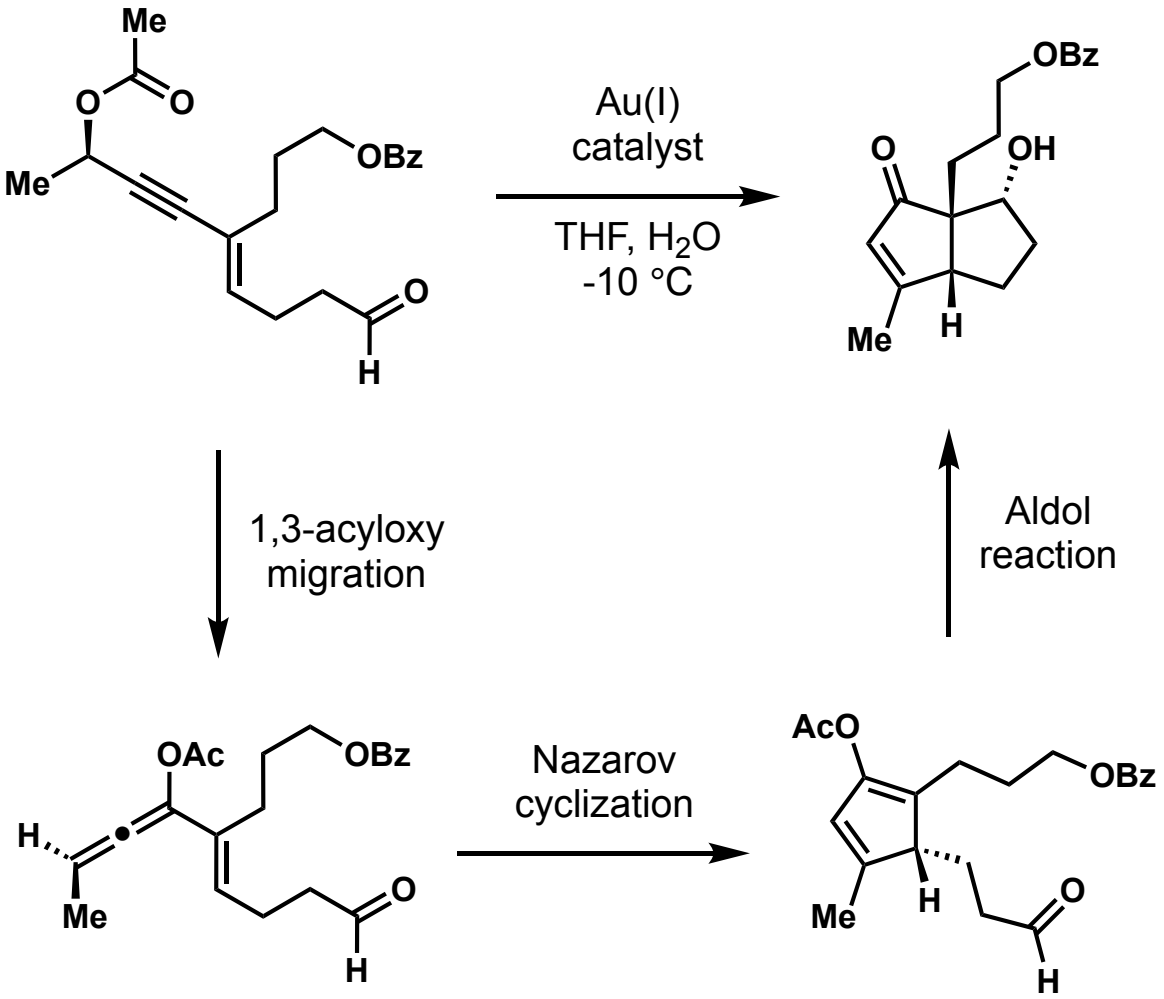


Angew. Chem. **2019**, 131, 2512.

(–)-Merochlorin A

Carreira (2019)

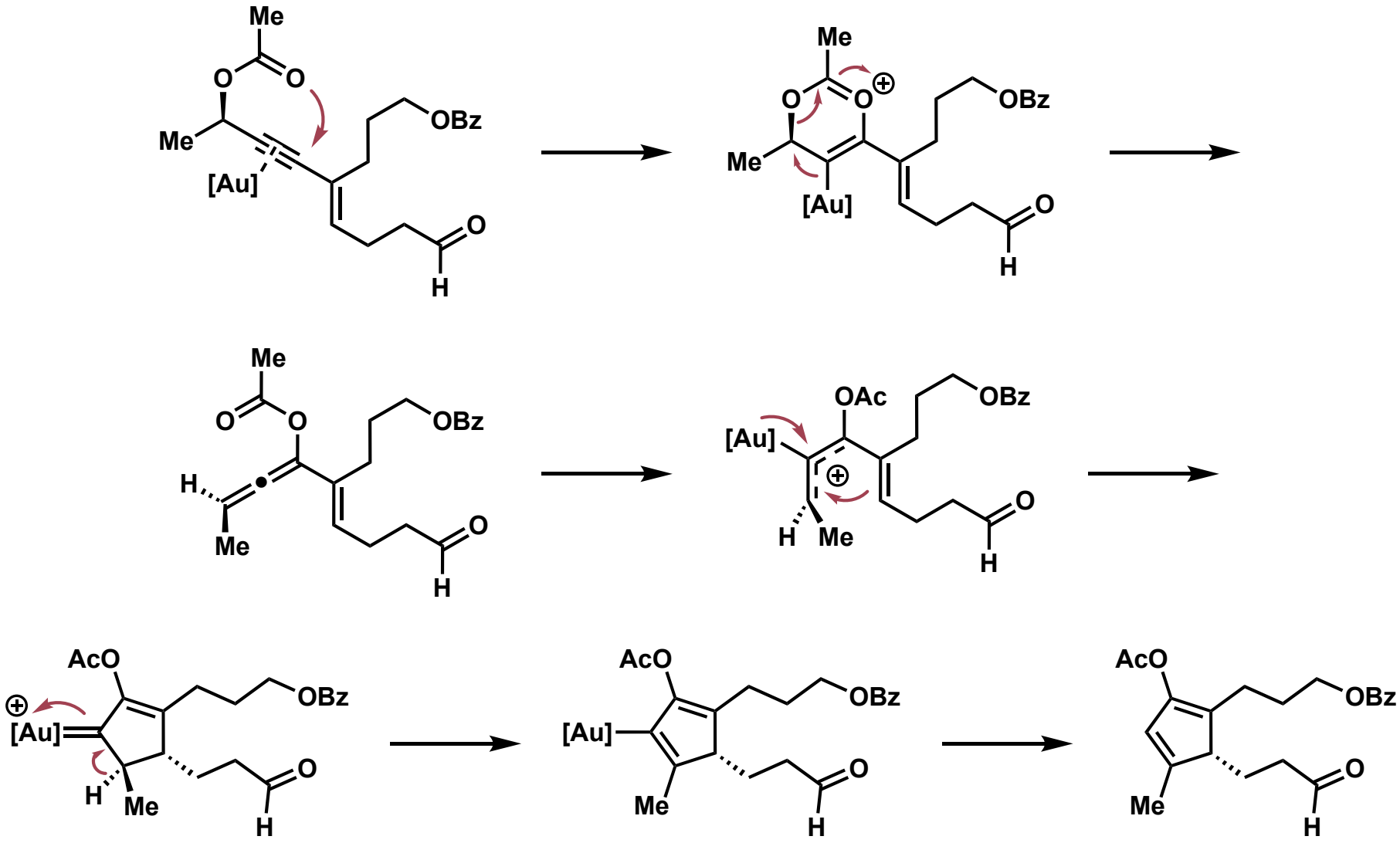




Angew. Chem. **2019**, 131, 2512.

(–)-Merochlorin A

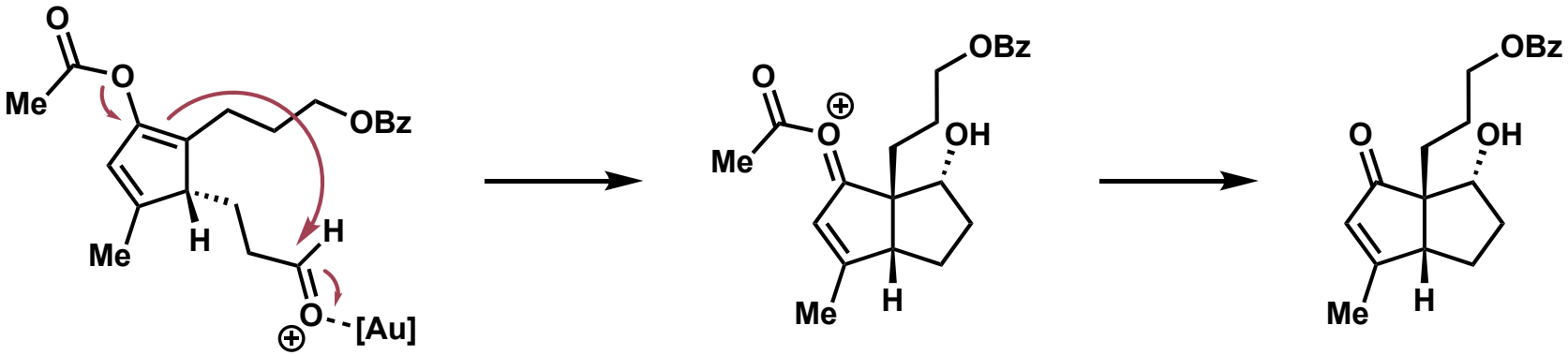
Carreira (2019)



J. Am. Chem. Soc. **2006**, 128, 1442.
J. Am. Chem. Soc. **2009**, 131, 2993.

(–)-Merochlorin A

Carreira (2019)



Angew. Chem. **2019**, 131, 2512.

Total Synthesis Using Gold Catalysis Reviews

Hashmi, A. S. K.; Rudolph, M. Gold catalysis in total synthesis. *Chem. Soc. Rev.* **2008**, 37, 1766–1775.

Rudolph, M.; Hashmi, A. S. K. Gold catalysis in total synthesis—an update. *Chem. Soc. Rev.* **2012**, 41, 2448–2462.

Pflästerer, D.; Hashmi, A. S. K. Gold catalysis in total synthesis – recent achievements. *Chem. Soc. Rev.* **2016**, 45, 1331–1367.

Zhang, Y.; Luo, T.; Yang, Z. Strategic innovation in the total synthesis of complex natural products using gold catalysis. *Nat. Prod. Rep.* **2014**, 31, 489–503.

Sugimoto, K.; Matsuya, Y. Recent applications of gold-catalyzed cascade reactions in total synthesis of natural product. *Tetrahedron Lett*. **2017**, 58, 4420–4426.

Quach, R.; Furkert, D. P.; Brimble, M. A. Gold catalysis: synthesis of spiro, bridged, and fused ketal natural products. *Org. Biomol. Chem*. **2017**, 15, 3098–3104.

De, S.; Dan, A. K.; Sahu, R.; Parida, S.; Das, D. Total Synthesis of Natural Products using Gold Catalysis. *Chem Asian J.* **2022**, 17, e202200896.