



文献报告

Synthesis of Enaminones by Rhodium Catalyzed Denitrogenative Rearrangement of 1-(*N*-Sulfonyl-1,2,3-triazol-4-yl)alkanols

Reporter: Zhi-Shi Ye

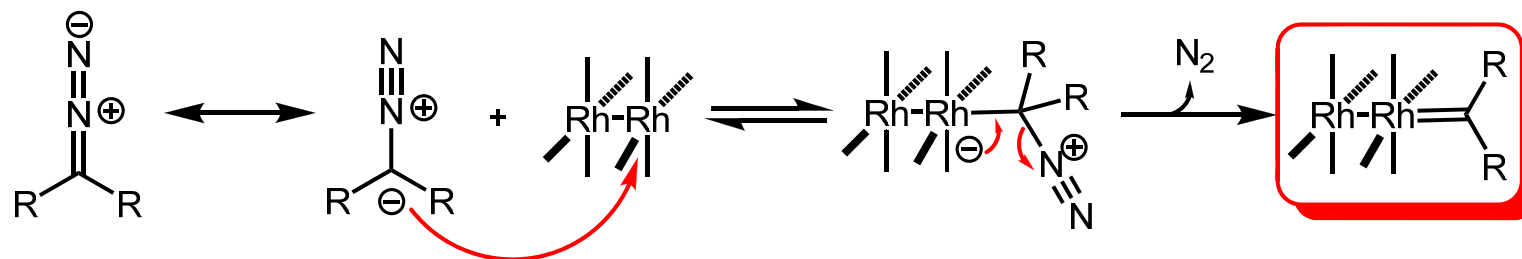
Checker: Duan Ying

Date: 2012-12-11

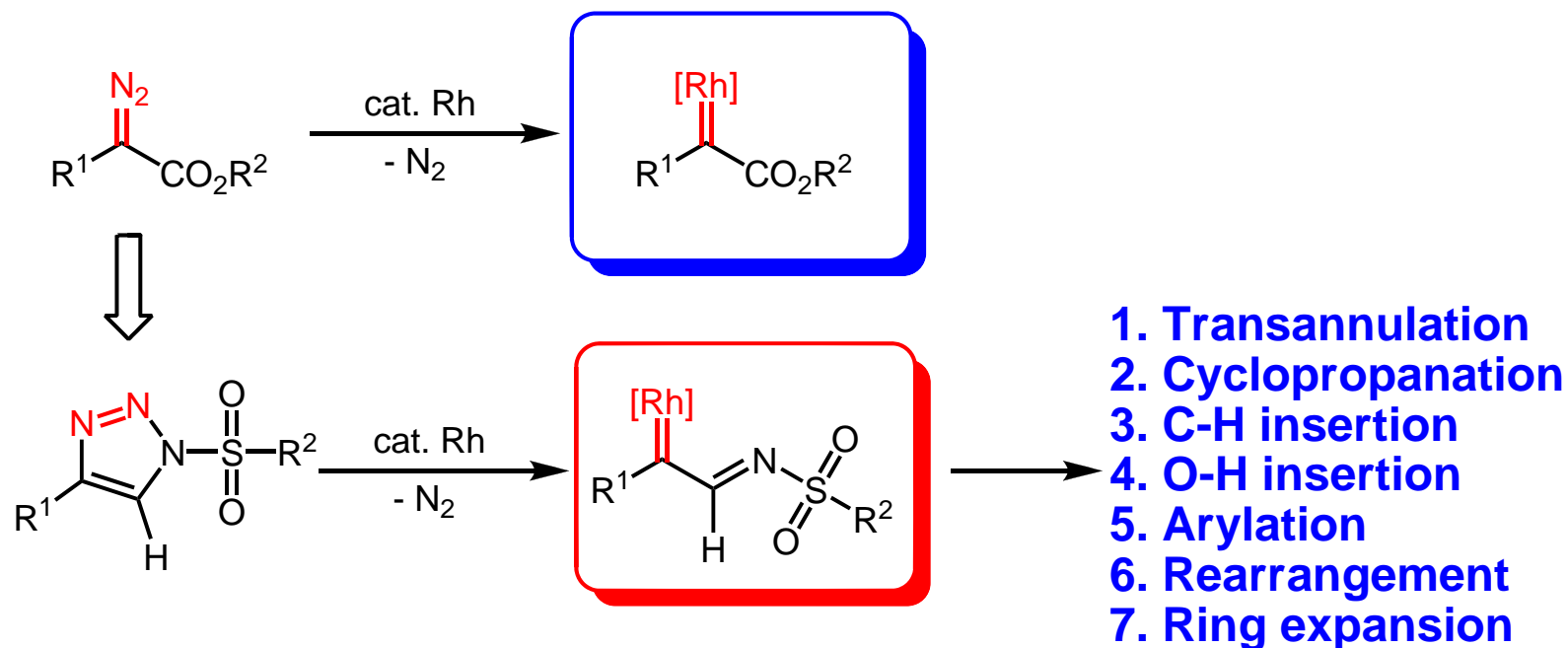
Murakami, M. *et al.*
J. Am. Chem. Soc. **2012**, *134*, 17440.

Carbenoid Formation from Diazo Compounds

Lewis acidic transition metal complexes, like Rh(II) complexes, are effective catalysts for diazo decomposition. Activity of transition metal complexes depends on coordinative unsaturation at metal center, which allows them to react as "electrophiles" for diazo compound:

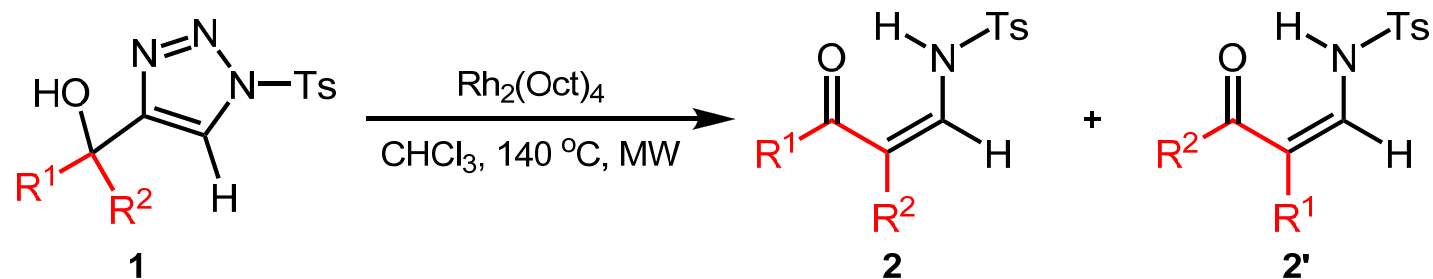


Utility of Rhodium(II) Azavinyl Carbenes



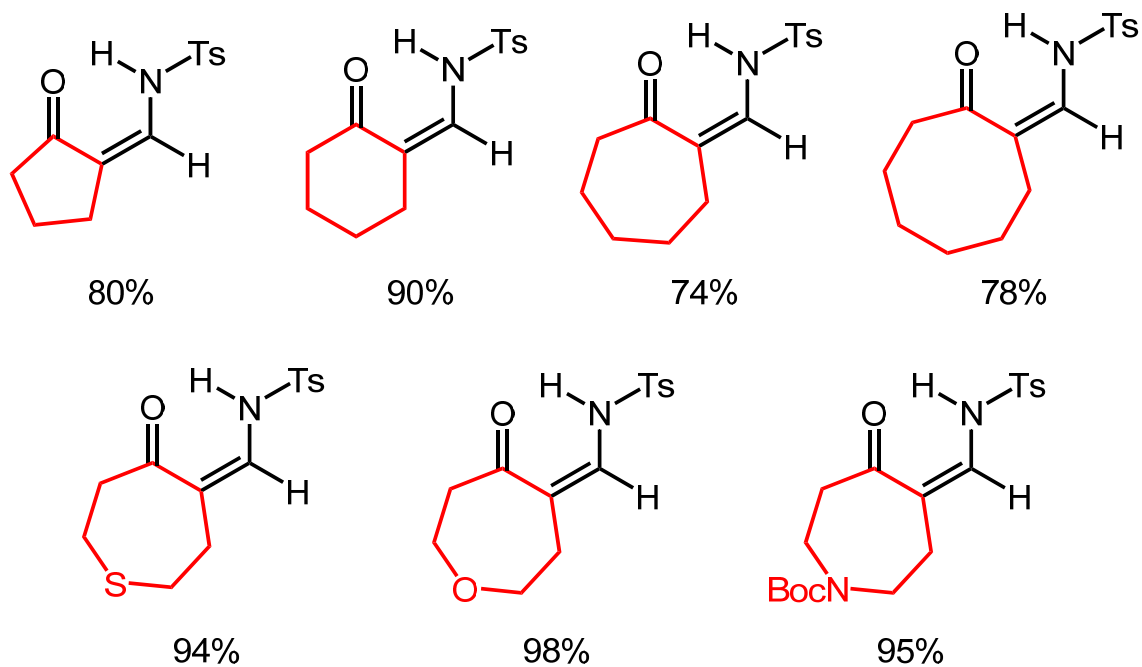
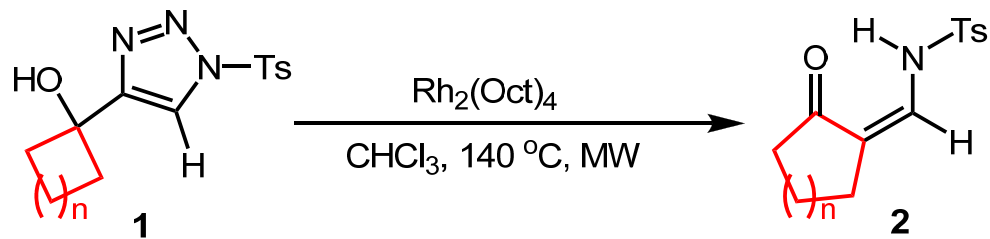
Research Groups: Fokin, Gevorgyan, Murakami *et al.*

Rearrangement and Ring Expansion

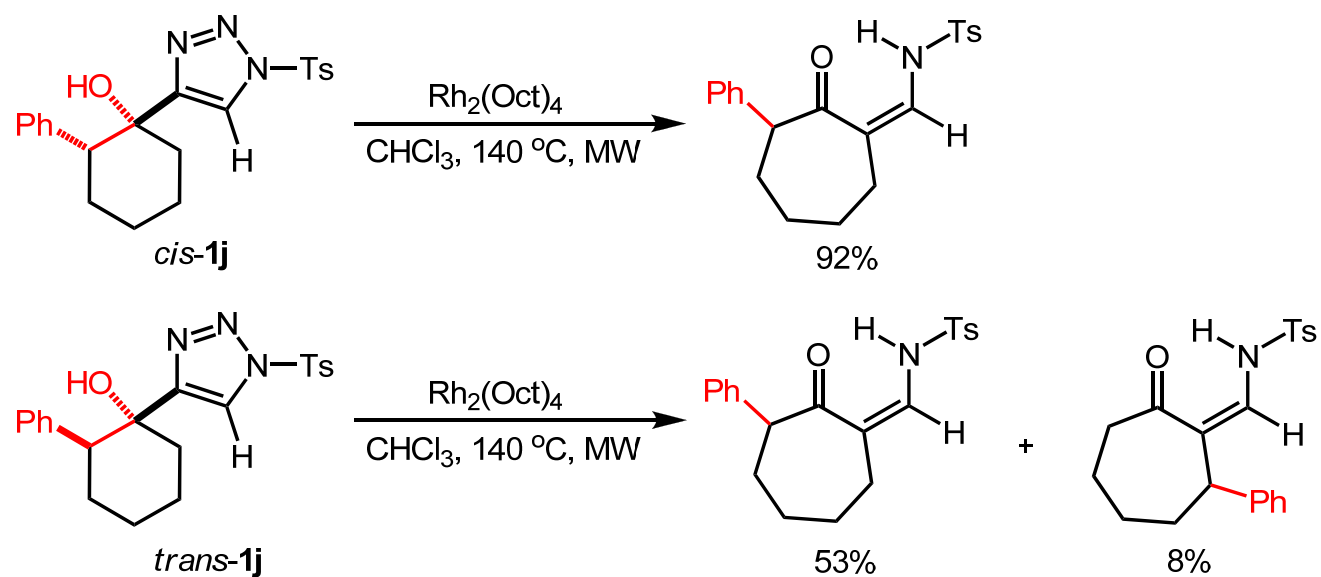


entry	R ¹	R ²	2 (yield %)	2' (yield %)
1	Me	H	94	0
2	<i>n</i> -Pr	H	91	0
3	<i>i</i> -Pr	H	87	0
4	Ph	H	58	25
5	Me	Ph	86	5
6	<i>i</i> -Pr	Me	47	19
7	Me	Me	90	-

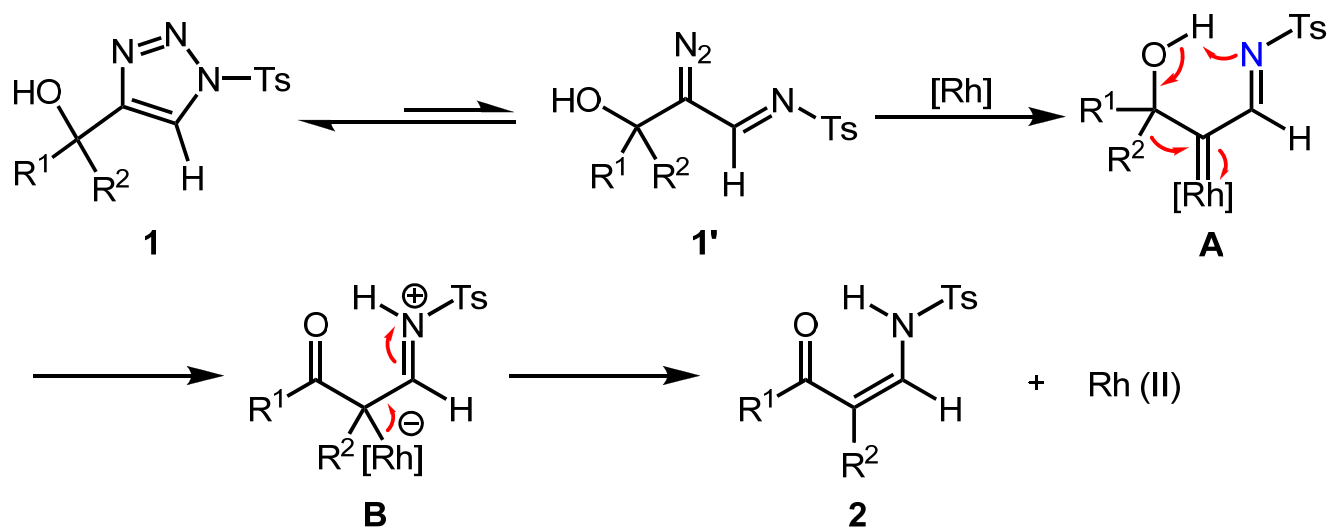
Rearrangement and Ring Expansion



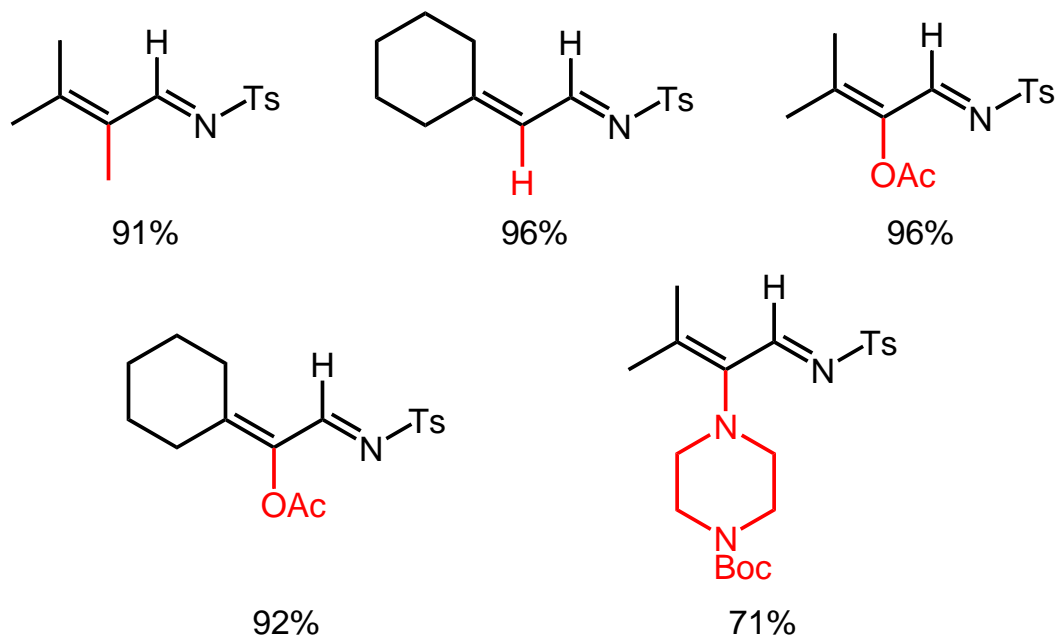
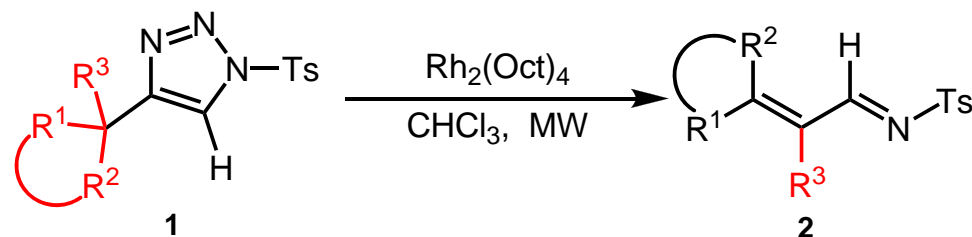
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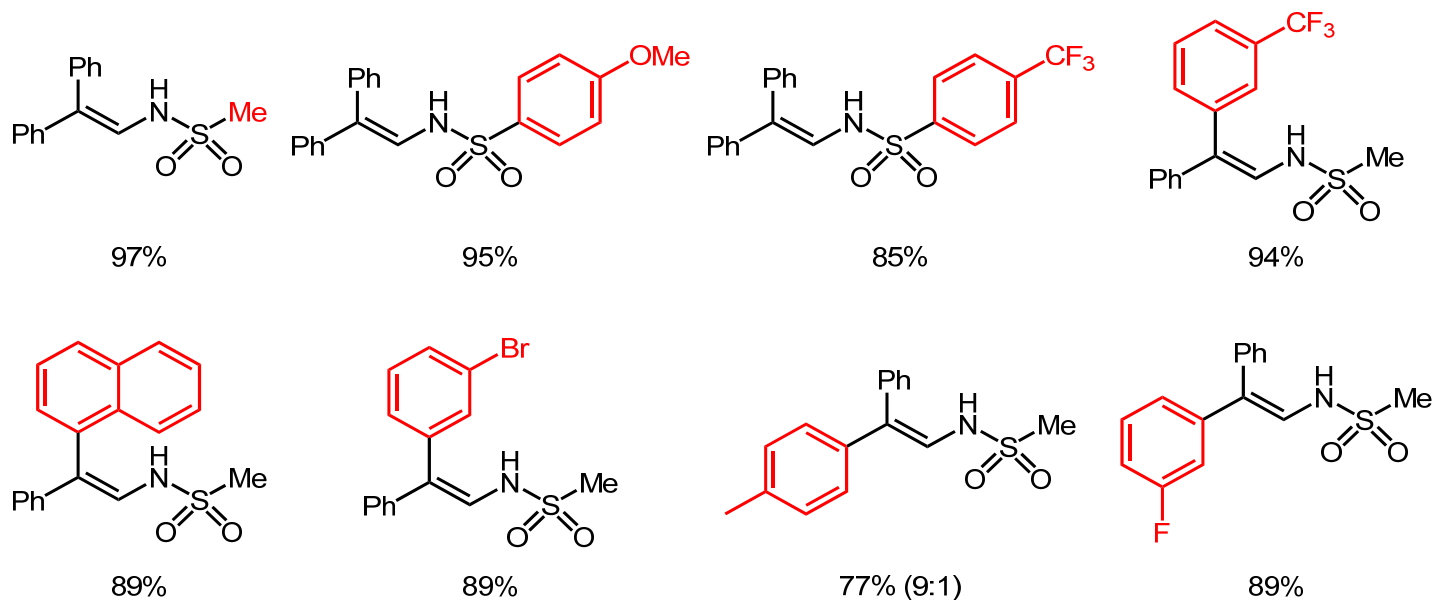
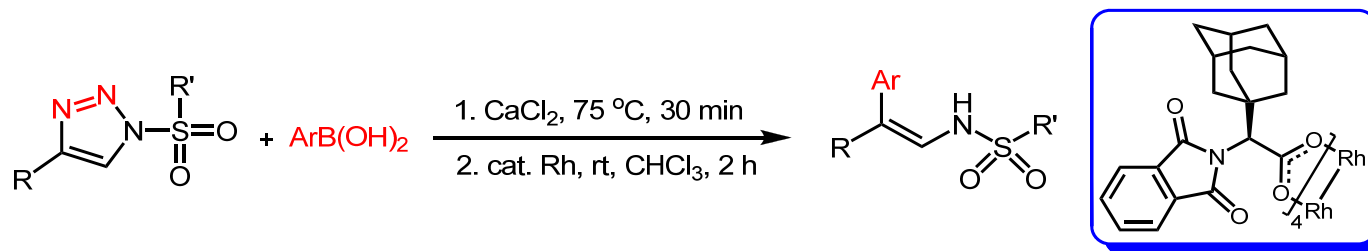
Plausible Mechanism



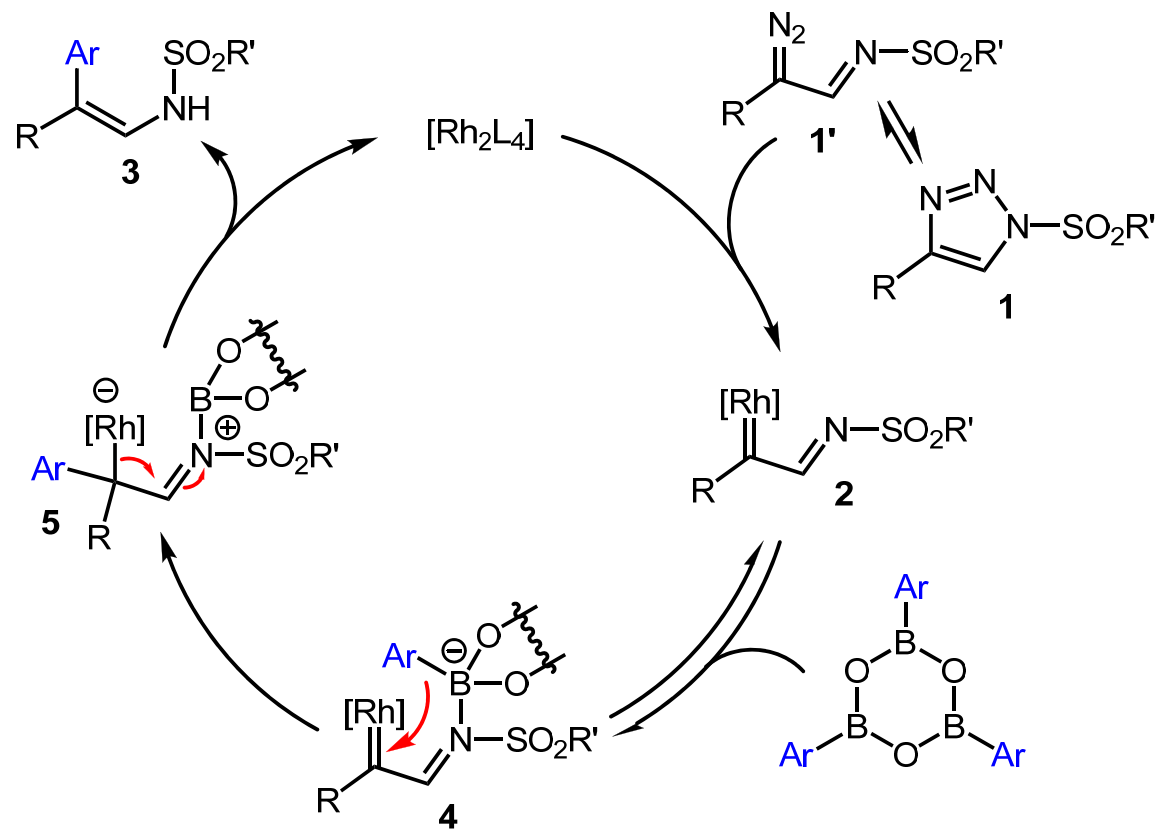
Rearrangement and Ring Expansion



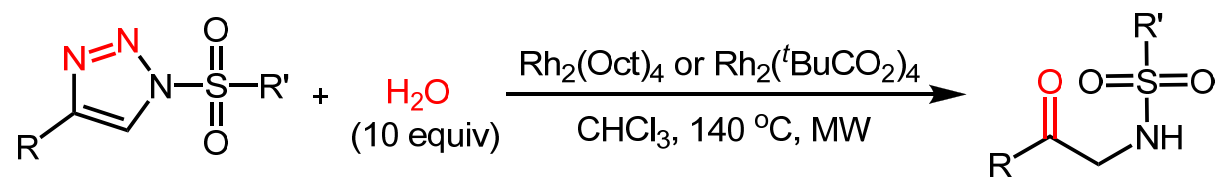
Arylation



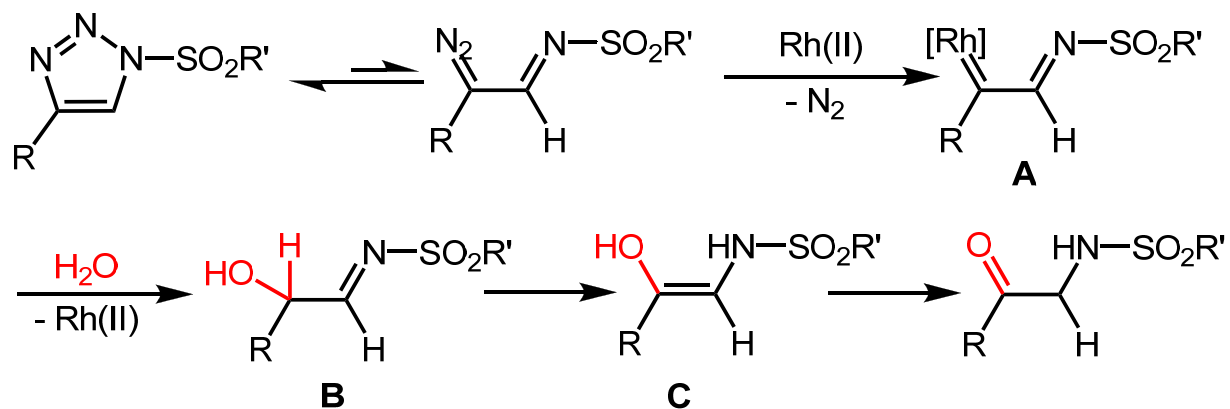
Plausible Mechanism



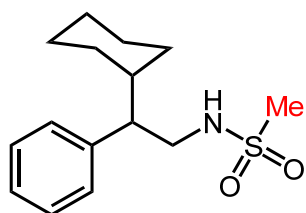
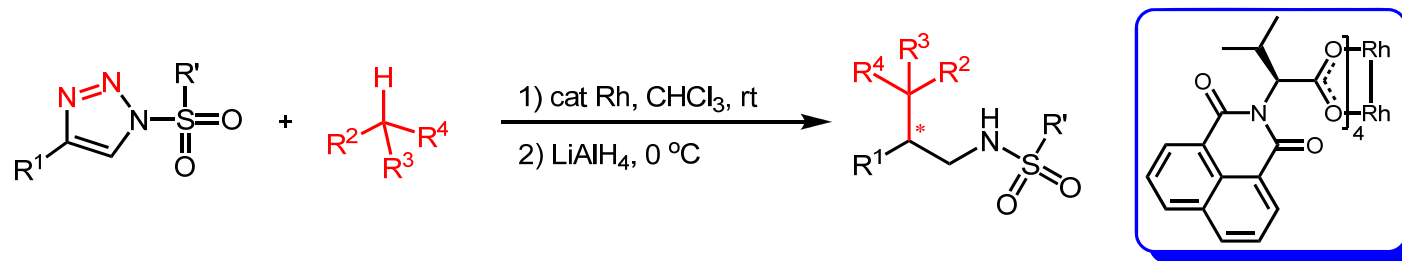
O-H Insertion



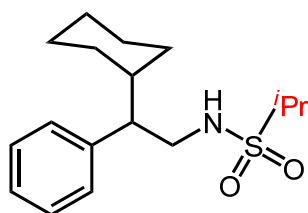
R = alkyl, aryl; R' = alkyl, aryl.



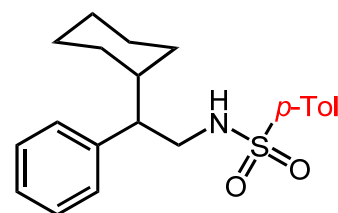
Asymmetric C-H Insertion



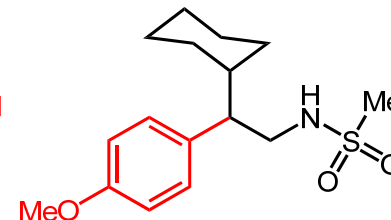
96% ee, 95% yield



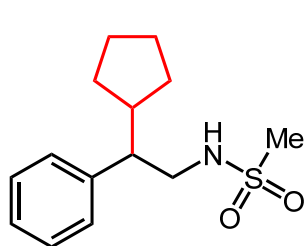
94% ee, 82% yield



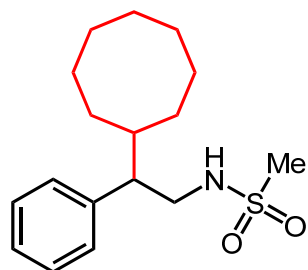
88% ee, 71% yield



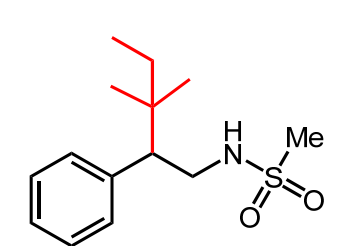
97% ee, 61% yield



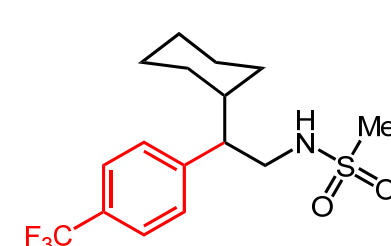
93% ee, 75% yield



93% ee, 82% yield

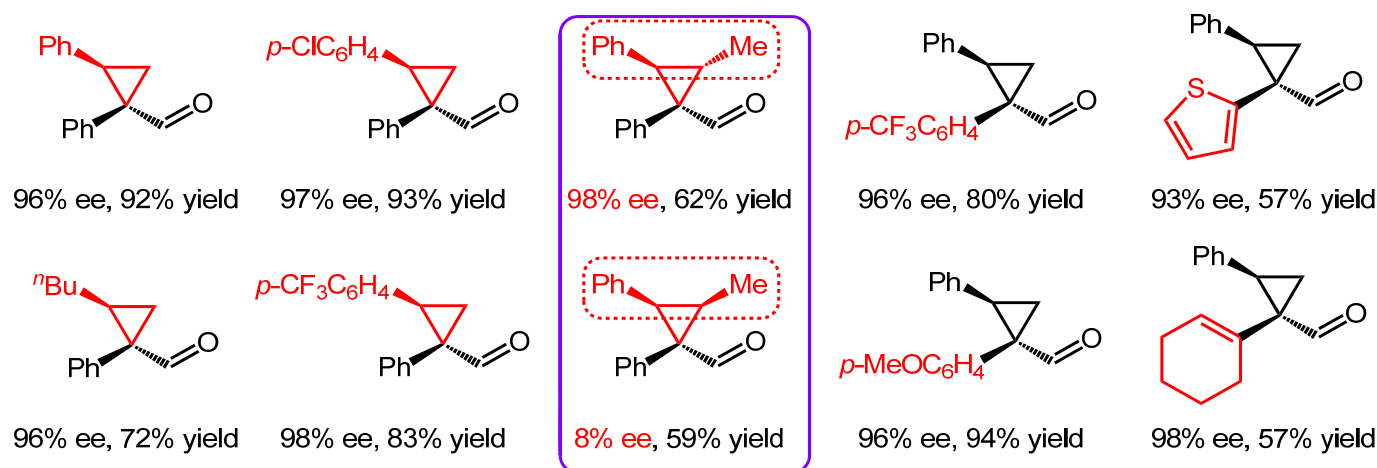
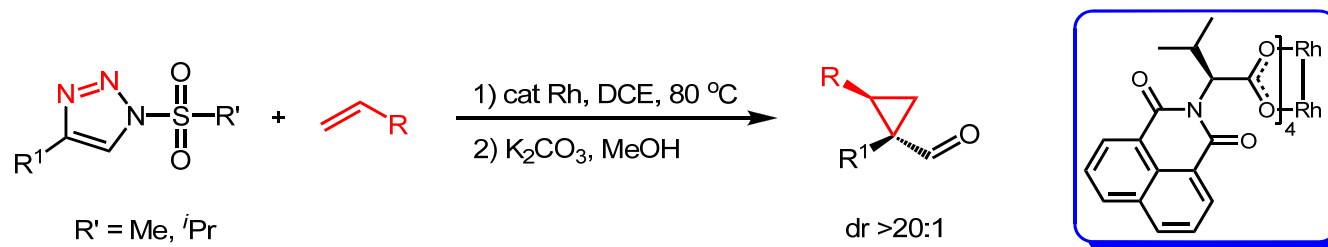


87% ee, 95% yield

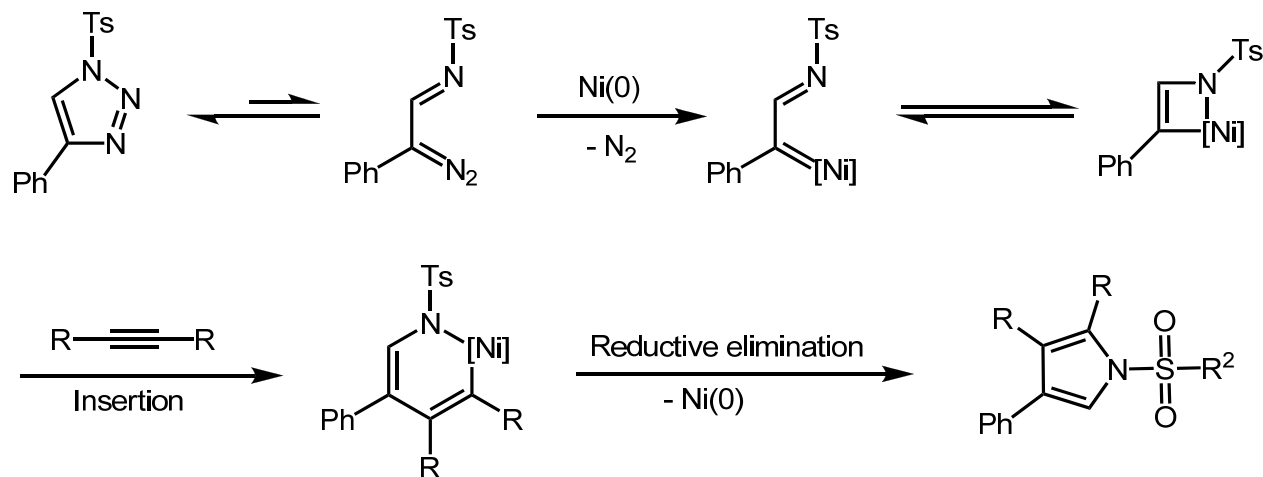
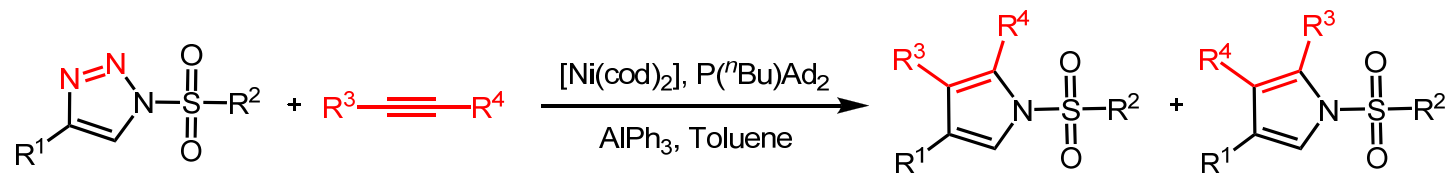


97% ee, 92% yield

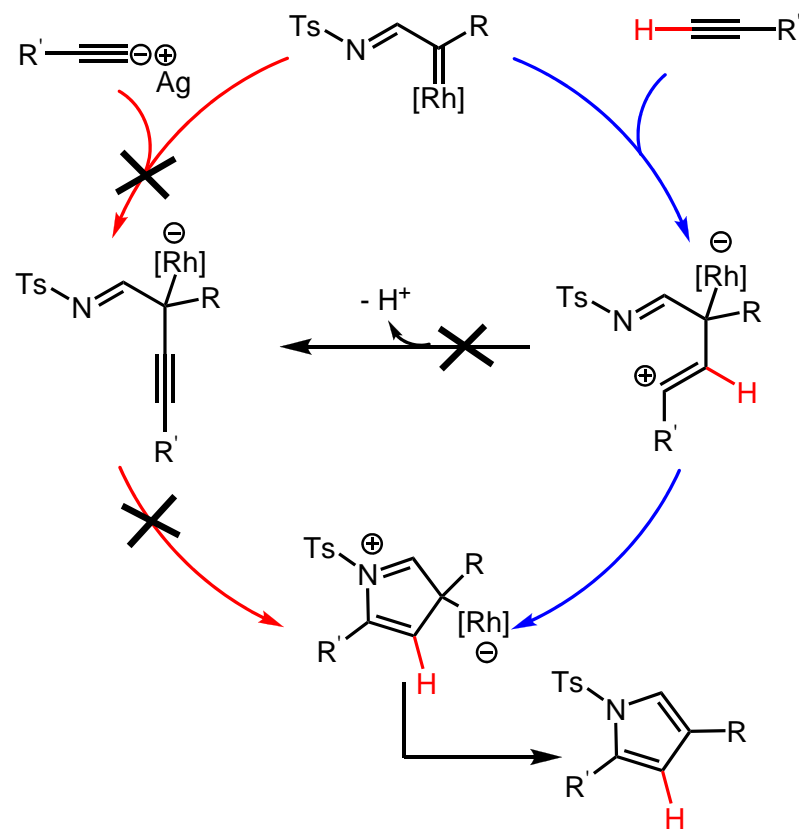
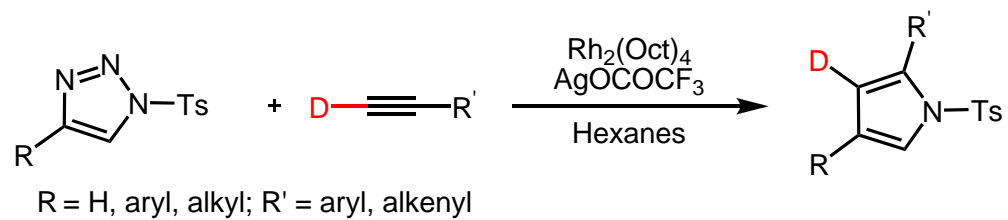
Asymmetric Cyclopropanation



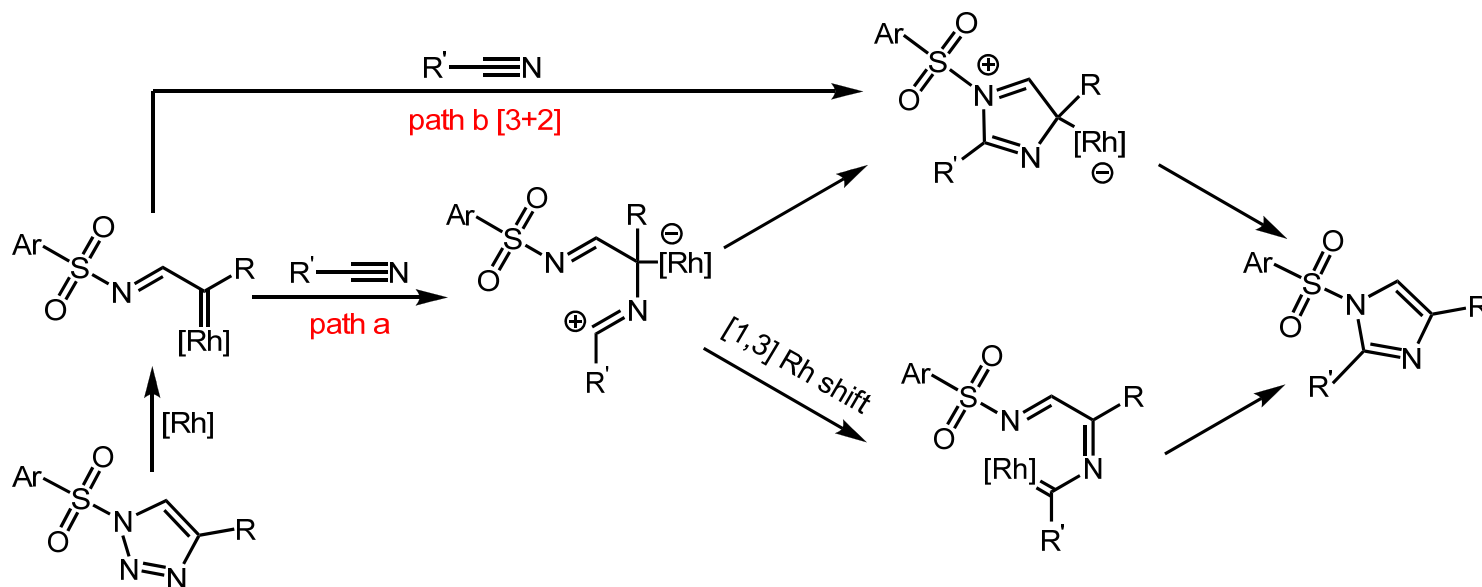
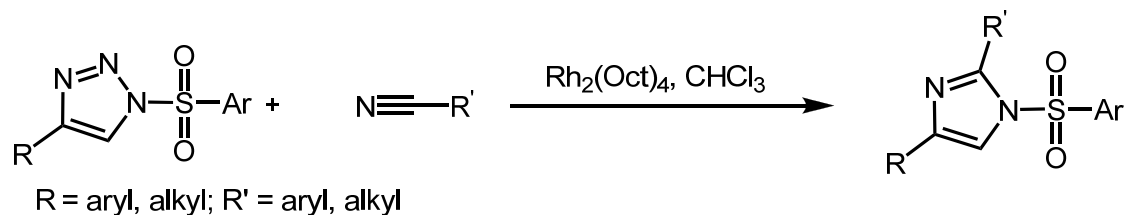
Transannulation



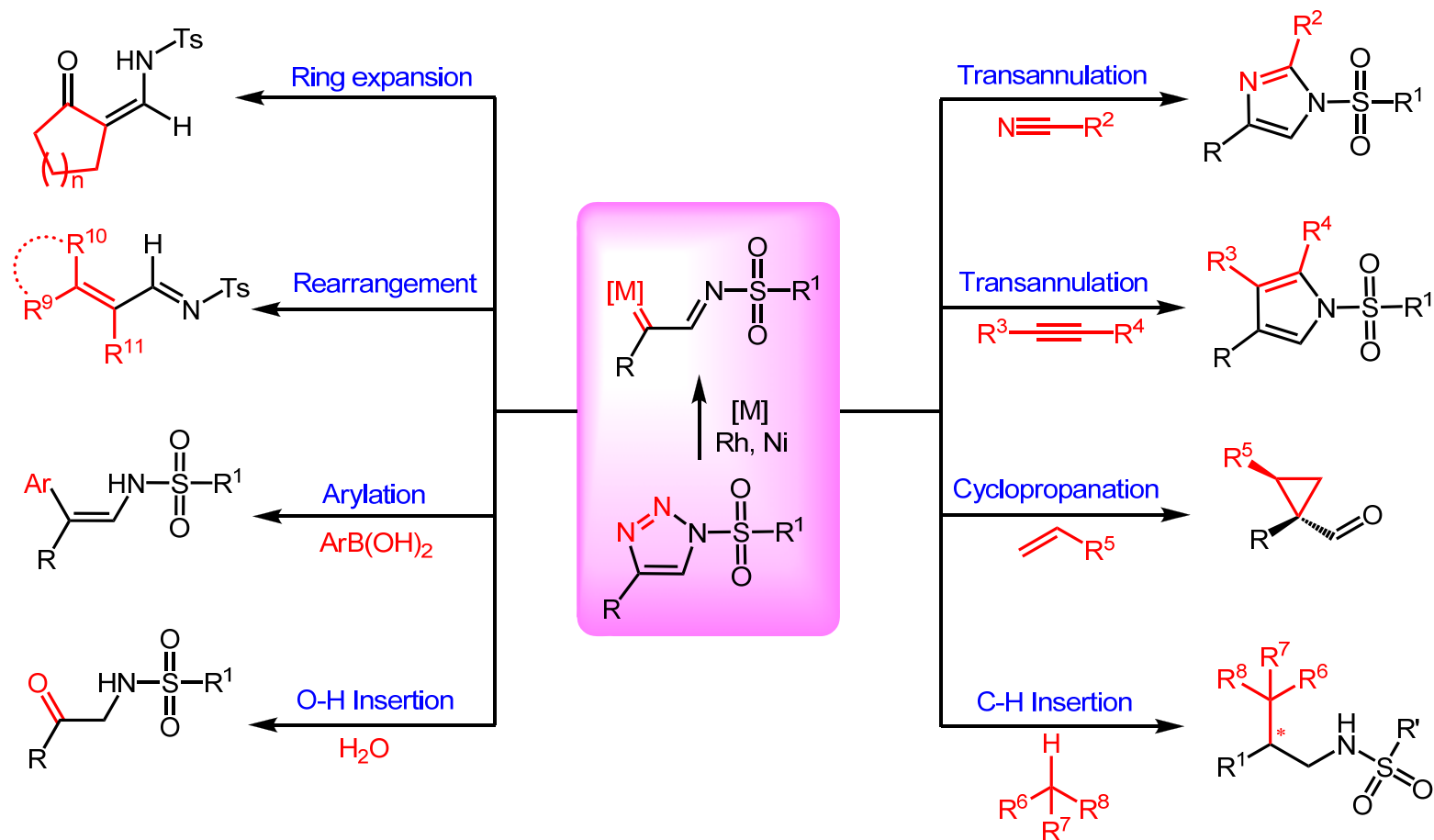
Transannulation



Transannulation

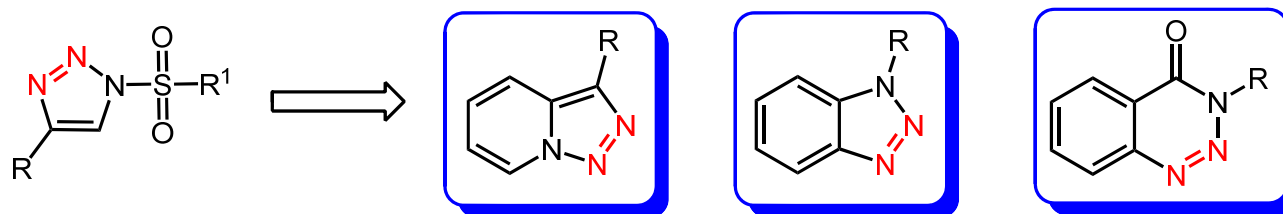


Summary



Summary

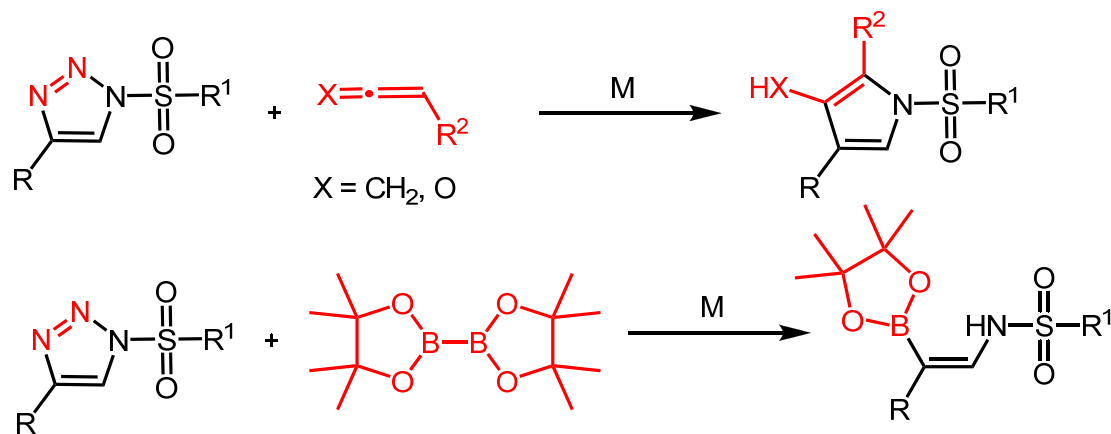
Substrates:



Catalyst:

Ru, Pd, Cu, Ni et al.

Reaction:



Enaminones are important synthetic intermediates for a wide variety of heterocycles contained in natural products and pharmaceutical compounds, and the development of new methods for their synthesis is highly desired. We report herein a rhodium(II)-catalyzed denitrogenative rearrangement reaction of 1-(*N*-sulfonyl-1,2,3-triazol-4-yl)alkanols, leading to the formation of enaminones. The starting 1-triazolylalcohols are readily prepared from propargylic alcohols and *N*-sulfonyl azides. Figure 1 depicts how the segments of a propargylic alcohol and *N*-sulfonyl azide construct the product structure through the whole process.

In summary, we have developed a significantly step-economical method for the synthesis of enaminones starting from propargylic alcohols and *N*-sulfonyl azides, where molecular nitrogen is the only waste product.

Thanks for your attention

