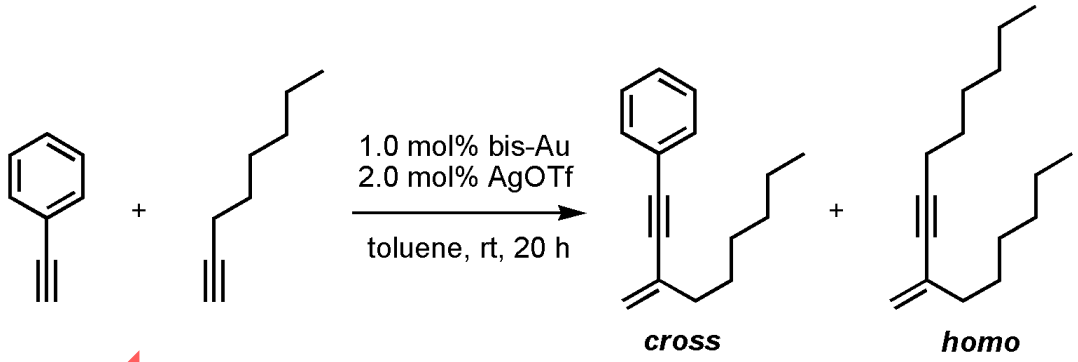
Evaluation of the Reactivity of Metallocatalytic Cavities in the Dimerization of Terminal Alkynes

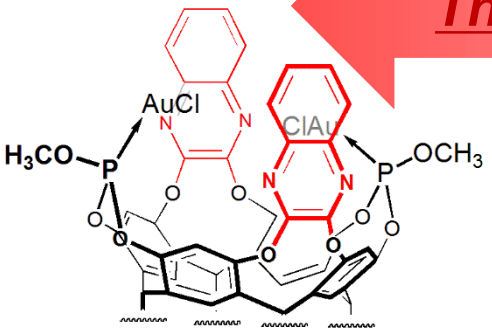
龍谷大学 RYUKOKU UNIVERSITY

Naoki Endo, Mao Kanaura, & Tetsuo Iwasawa*

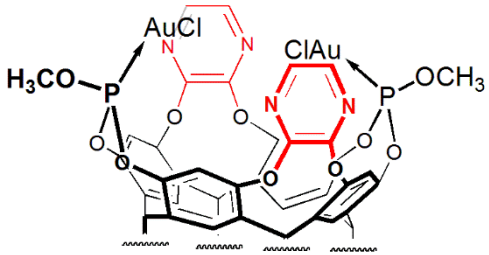
Ryukoku Univ.



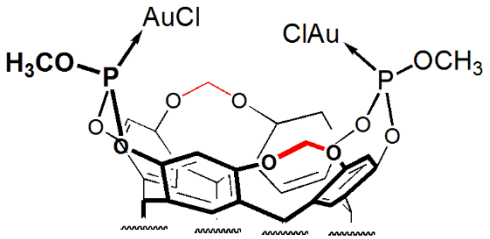
The walls promote the catalysis!



cross 58%
homo 19%



cross 6%
homo 1%



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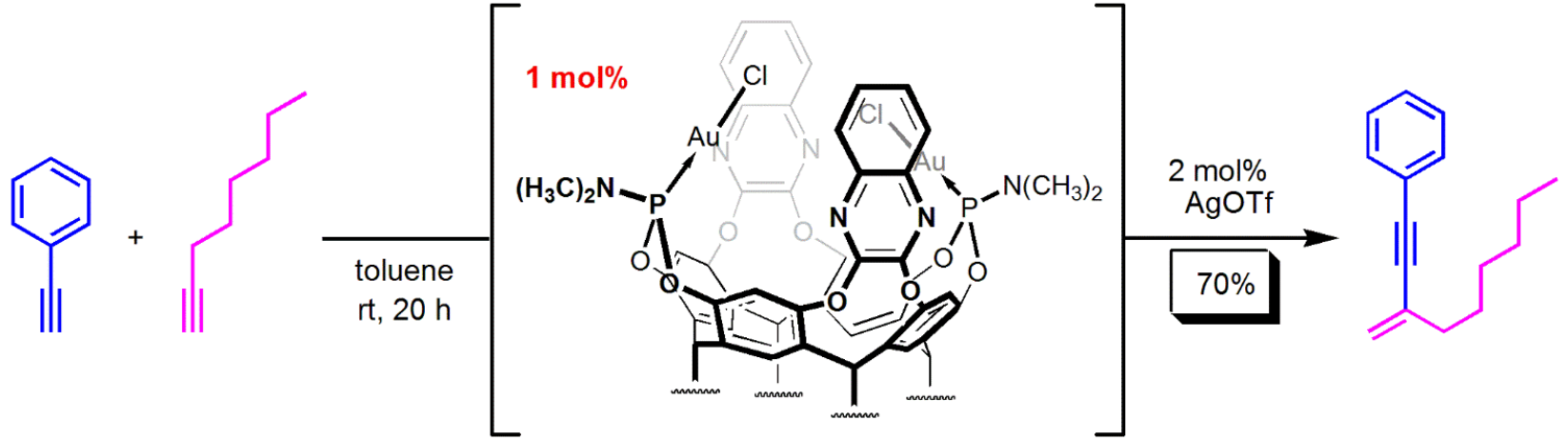
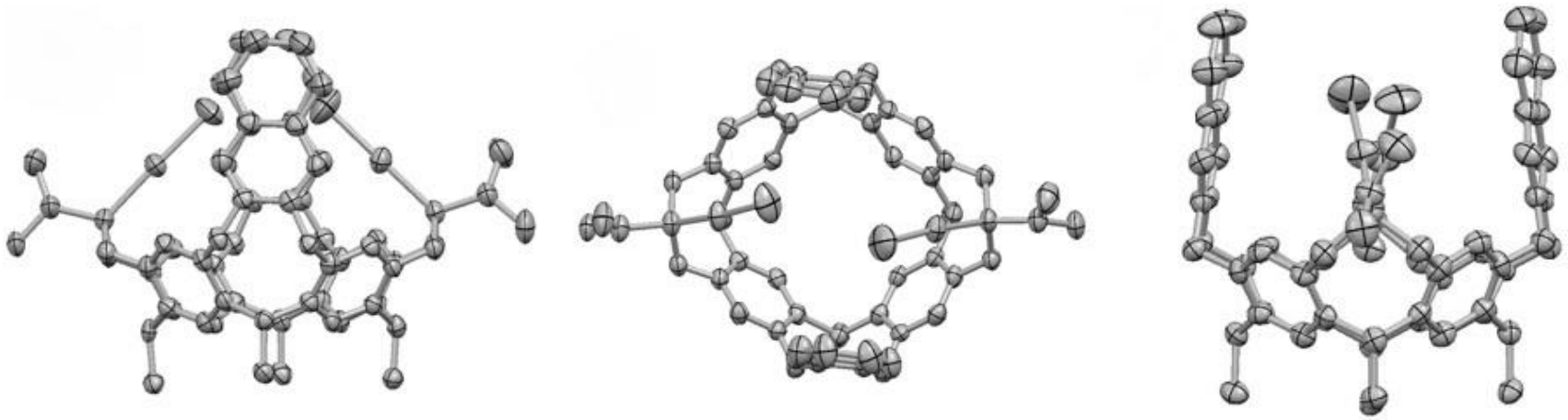
Kanaura, M.; Endo, N.; Schramm, M. P.; Iwasawa, T. *Eur. J. Org. Chem.* **2016**, 4970-4975.

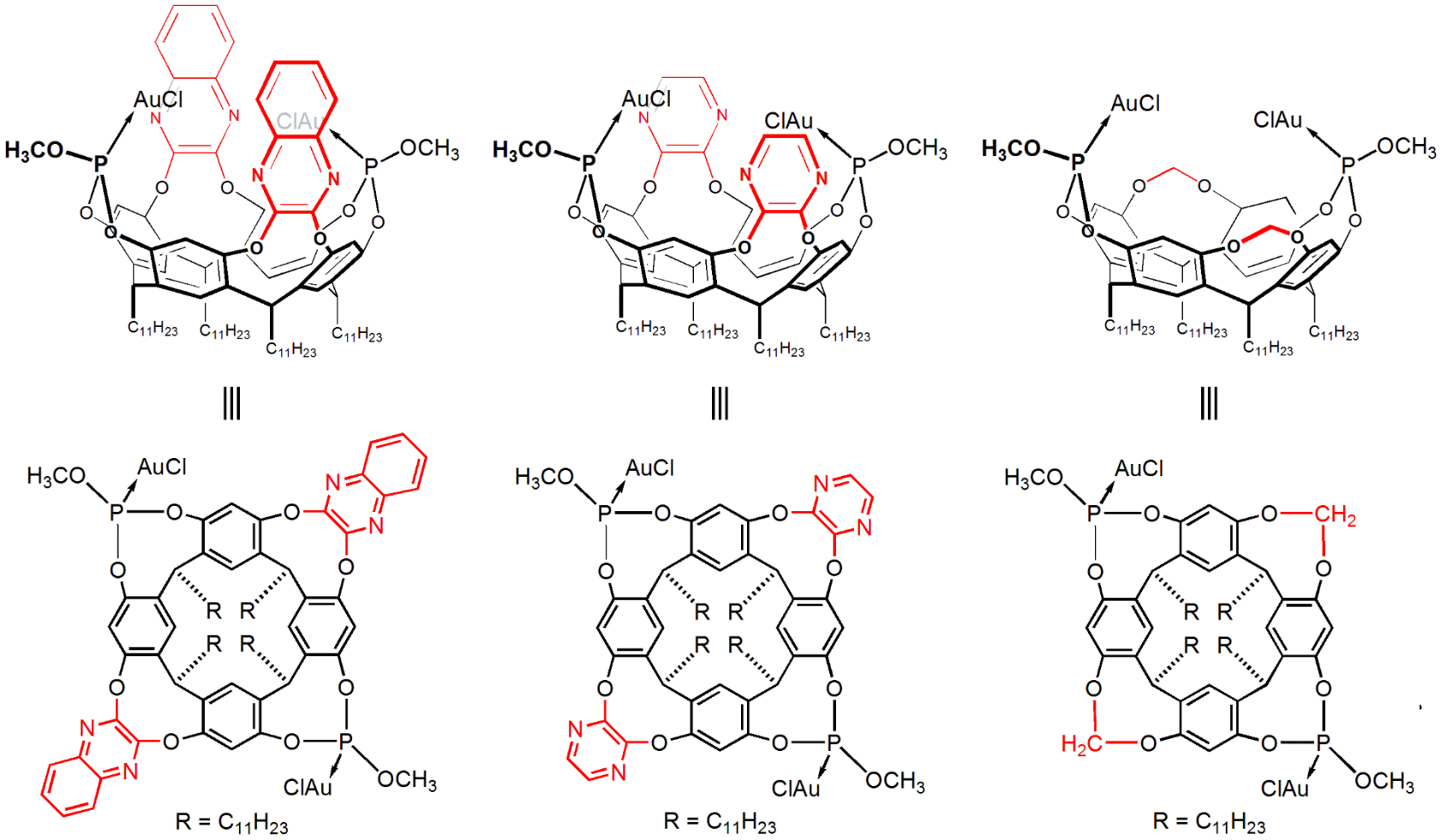
Background



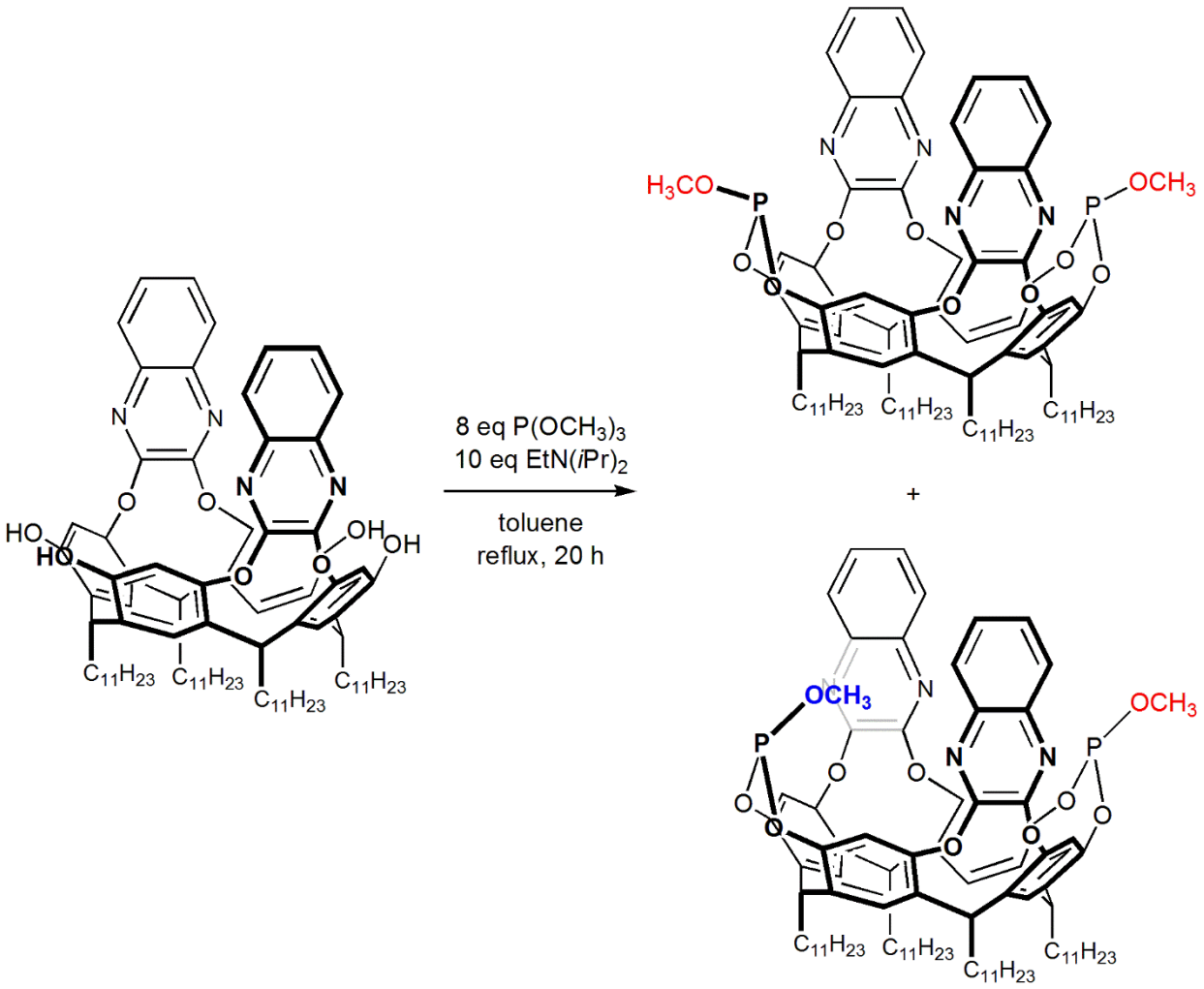


Endo, N.; Kanaura, M.; Schramm, M. P.; Iwasawa, T. *Eur. J. Org. Chem*. **2016**, 2514-2521.

Approach



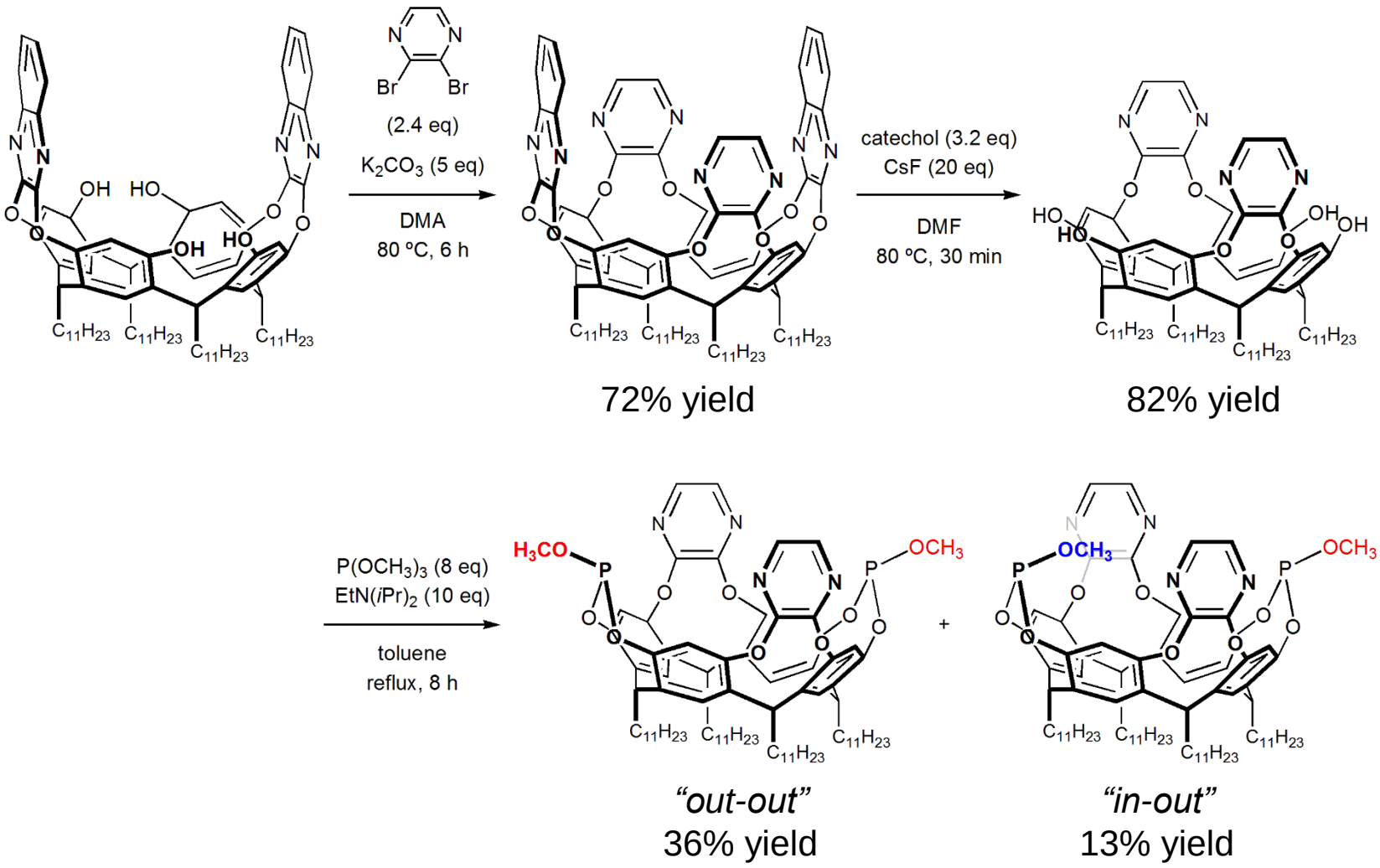
Synthesis of the diquinoxaline-walled cavitand



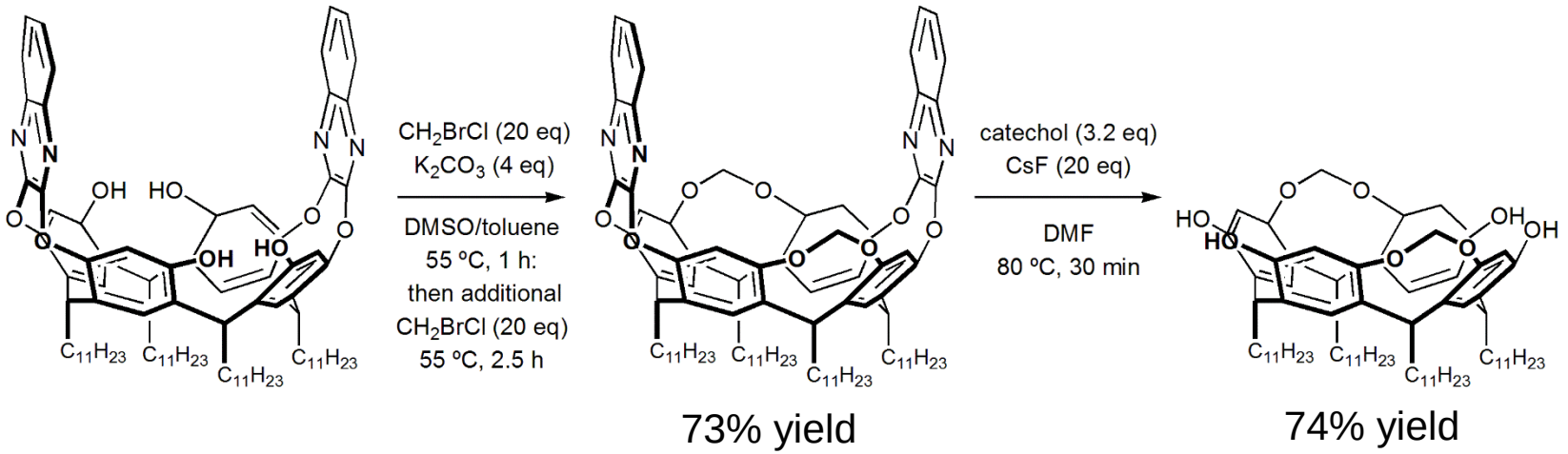
"out-out"
36% yield

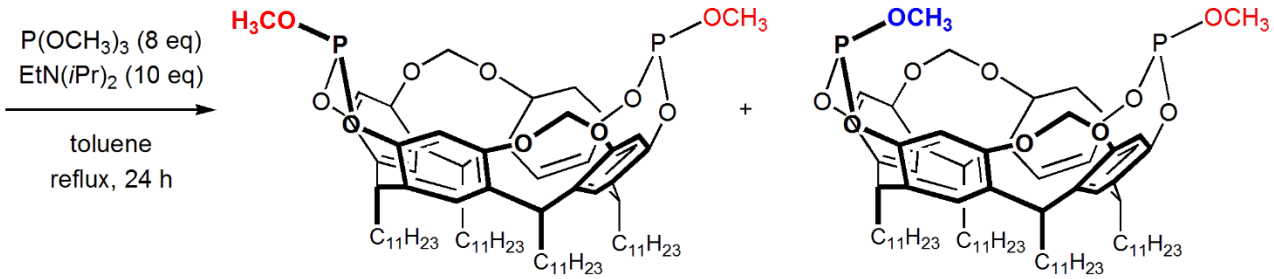
"in-out"
24% yield

Synthesis of the pyrazine-walled model

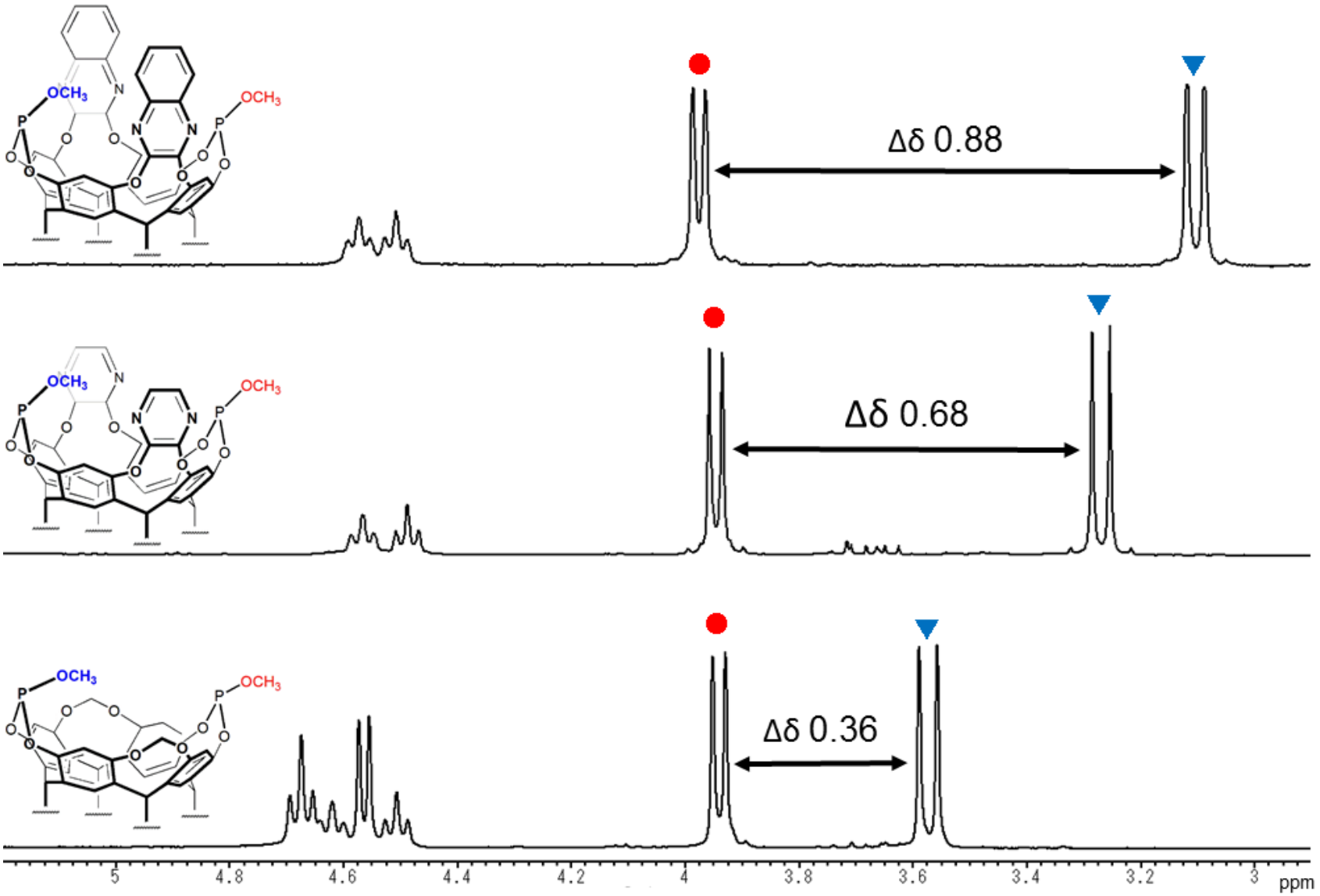


Synthesis of the non-walled model

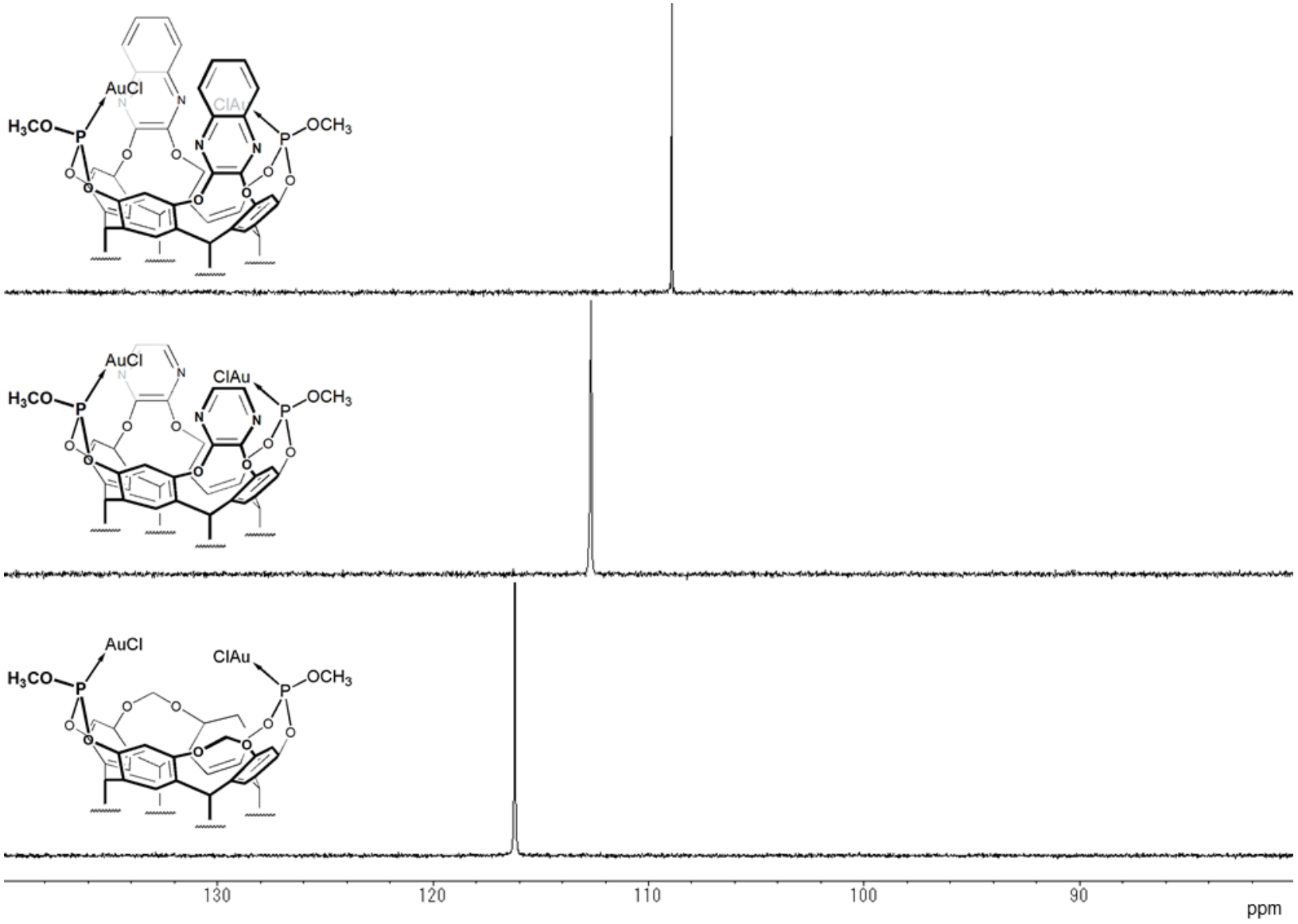




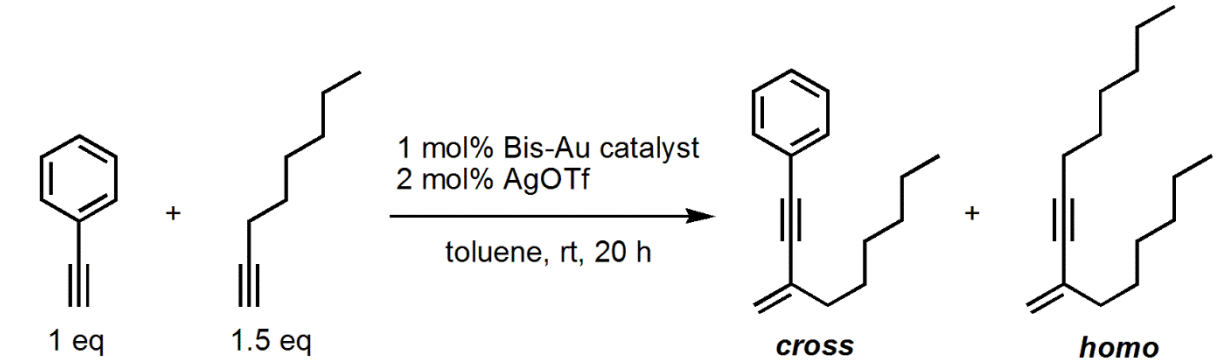
Differences in chemical shifts between these 3 compounds

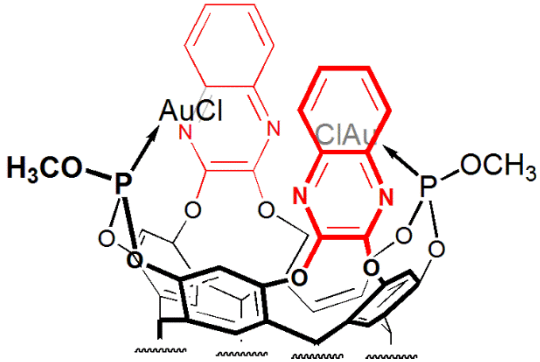


Complexation of $AuCl \cdot S(CH_3)_2$ with bis-phosphines

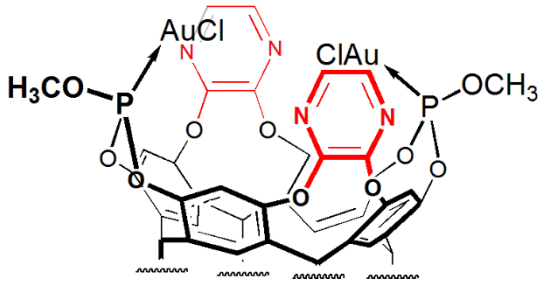


Comparison with the models in the *cross*-dimerization between 1-octyne and ethynylbenzene





cross 58%
homo 19%



cross 6%
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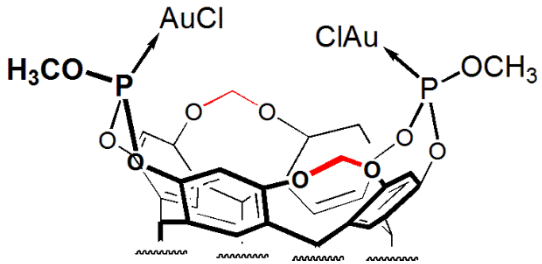

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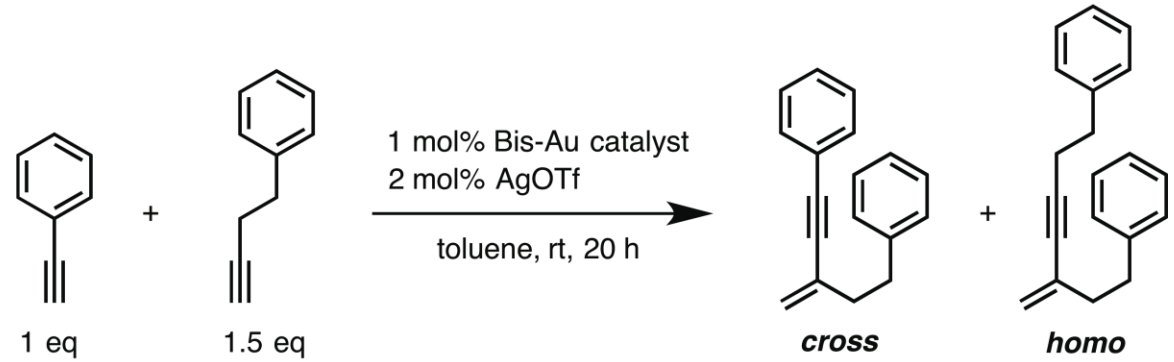
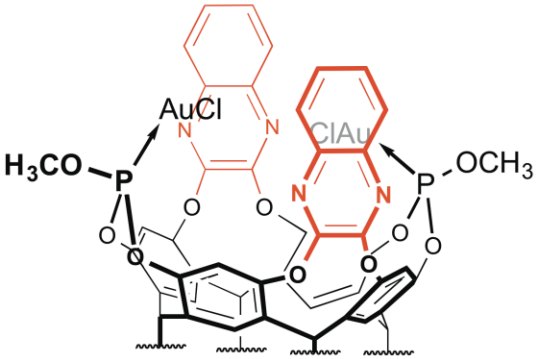
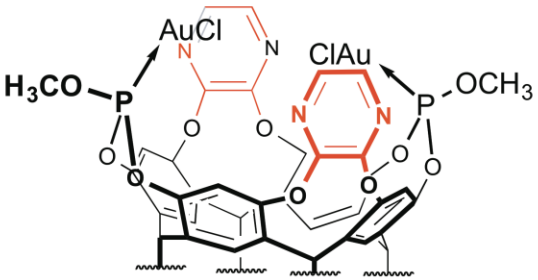
Comparison between ethynylbenzene and 4-phenyl-1-butyne

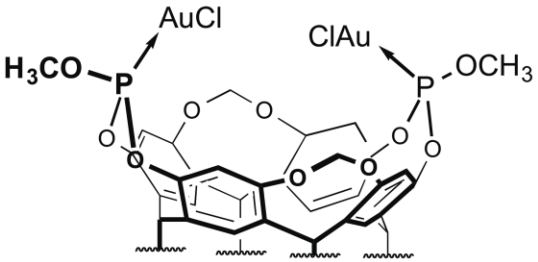




cross 57%
homo 18%



cross 9%
homo 3%



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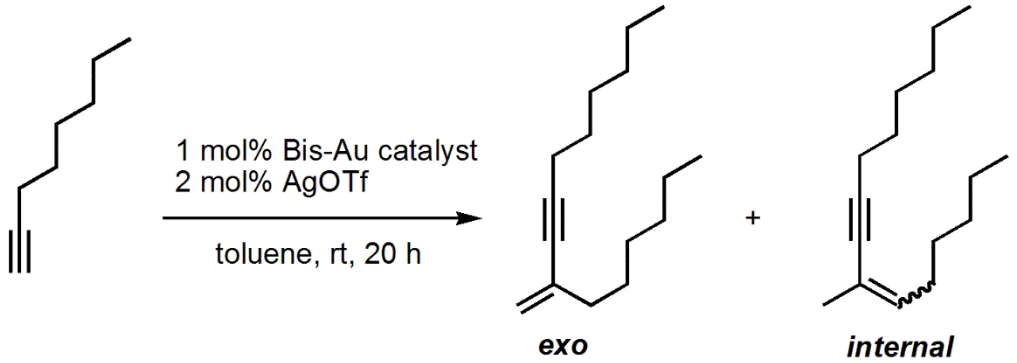
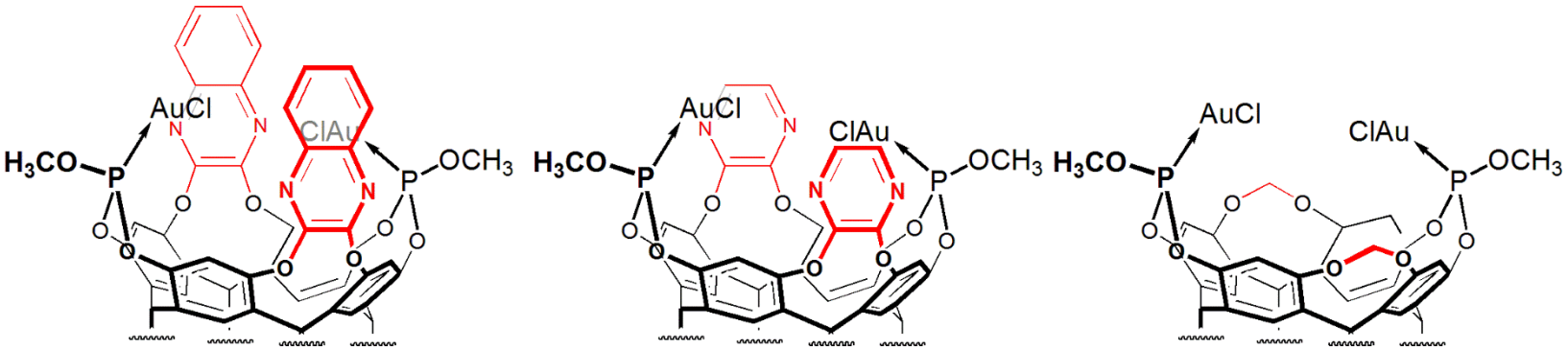
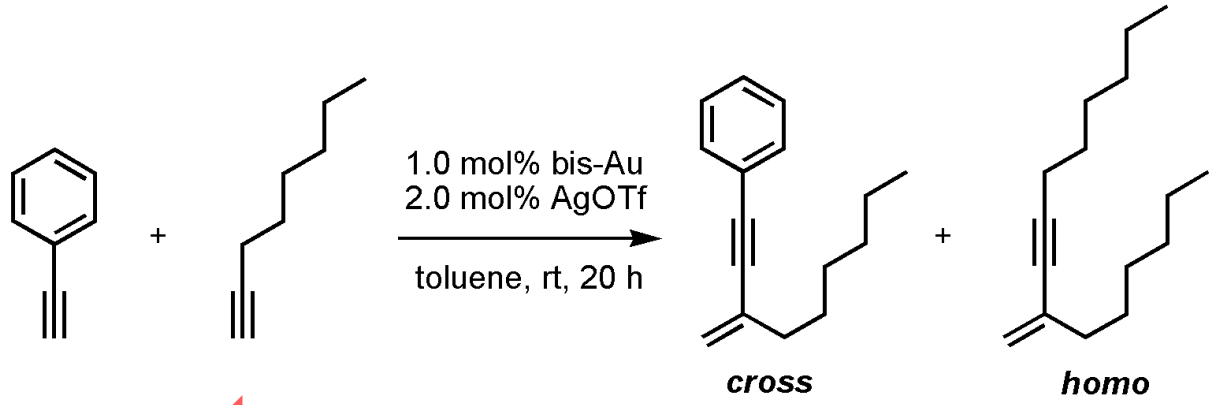
Comparison in the *homo*-dimerization of 1-octyne





63%	18%	trace
exolint. = ~100/0	***exolint.*** = ~97/3	***exolint.*** = 99/1

Summary



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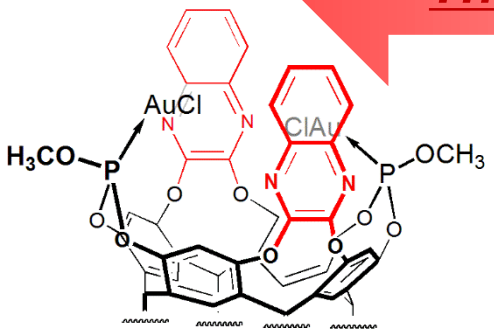
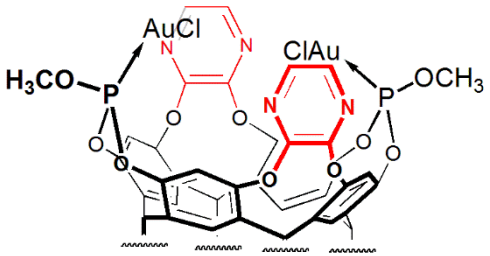


cross 58%
homo 19%



cross 6%
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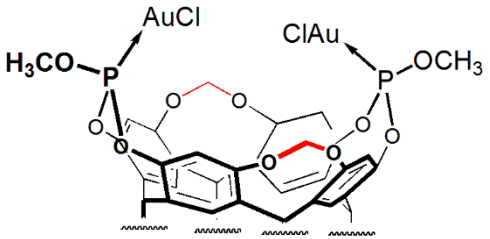

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