

Brønsted Acid Typed Cavitands in Catalytic Use

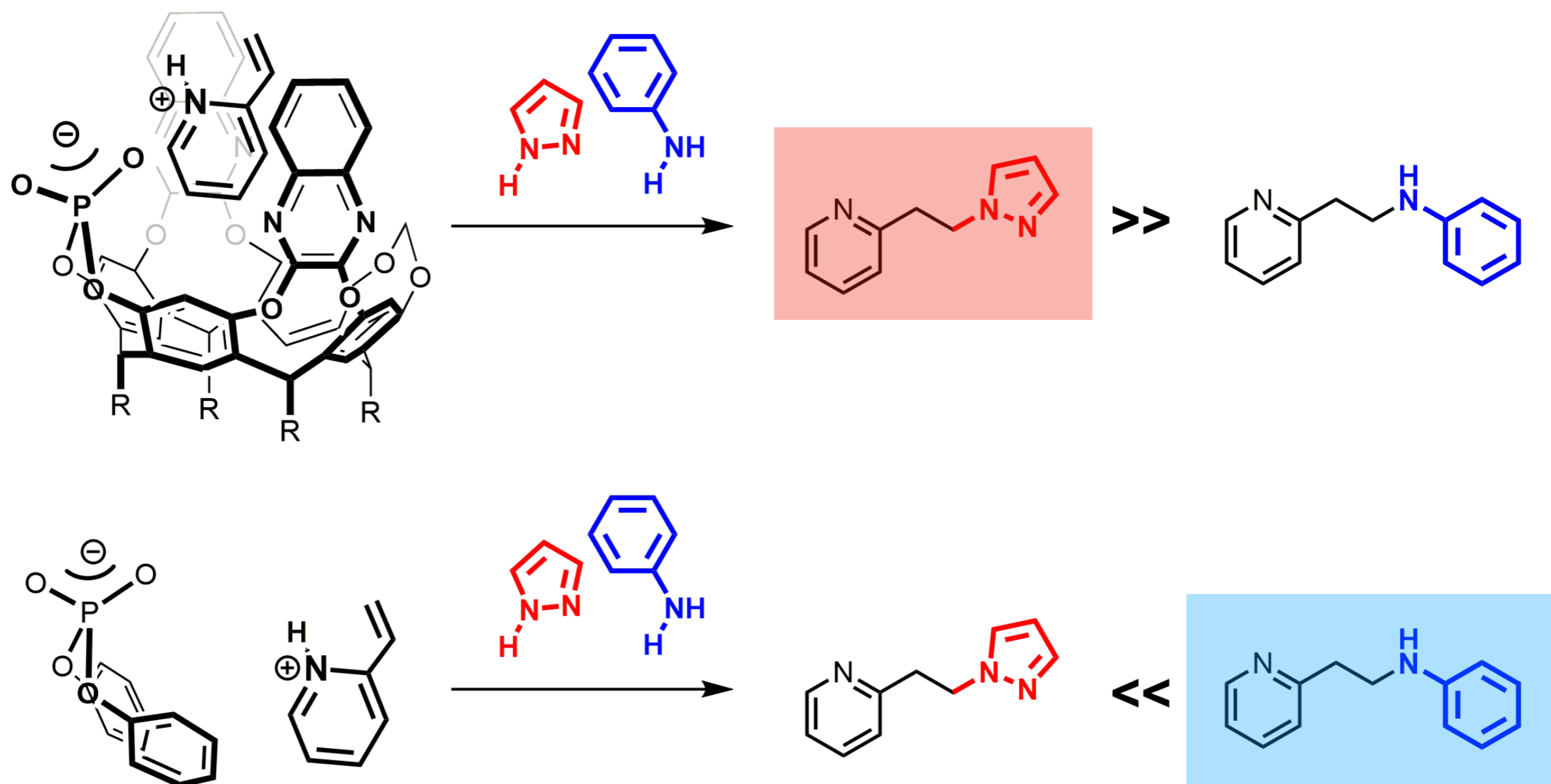
キャビタンド型ブレンステッド酸の開発と 触媒性能の評価

龍谷大学 理工学部 物質化学科

岩澤 研究室

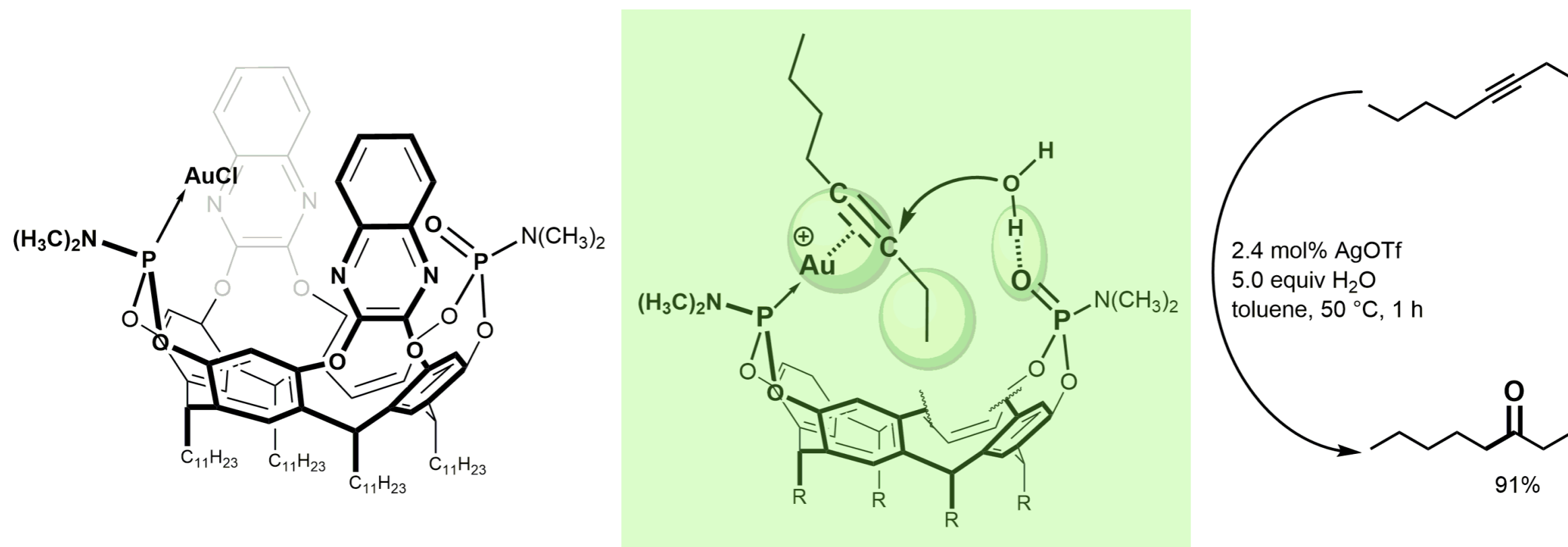
吉田 匠完

Brønsted Acid Typed CavitanDs in Catalytic Use



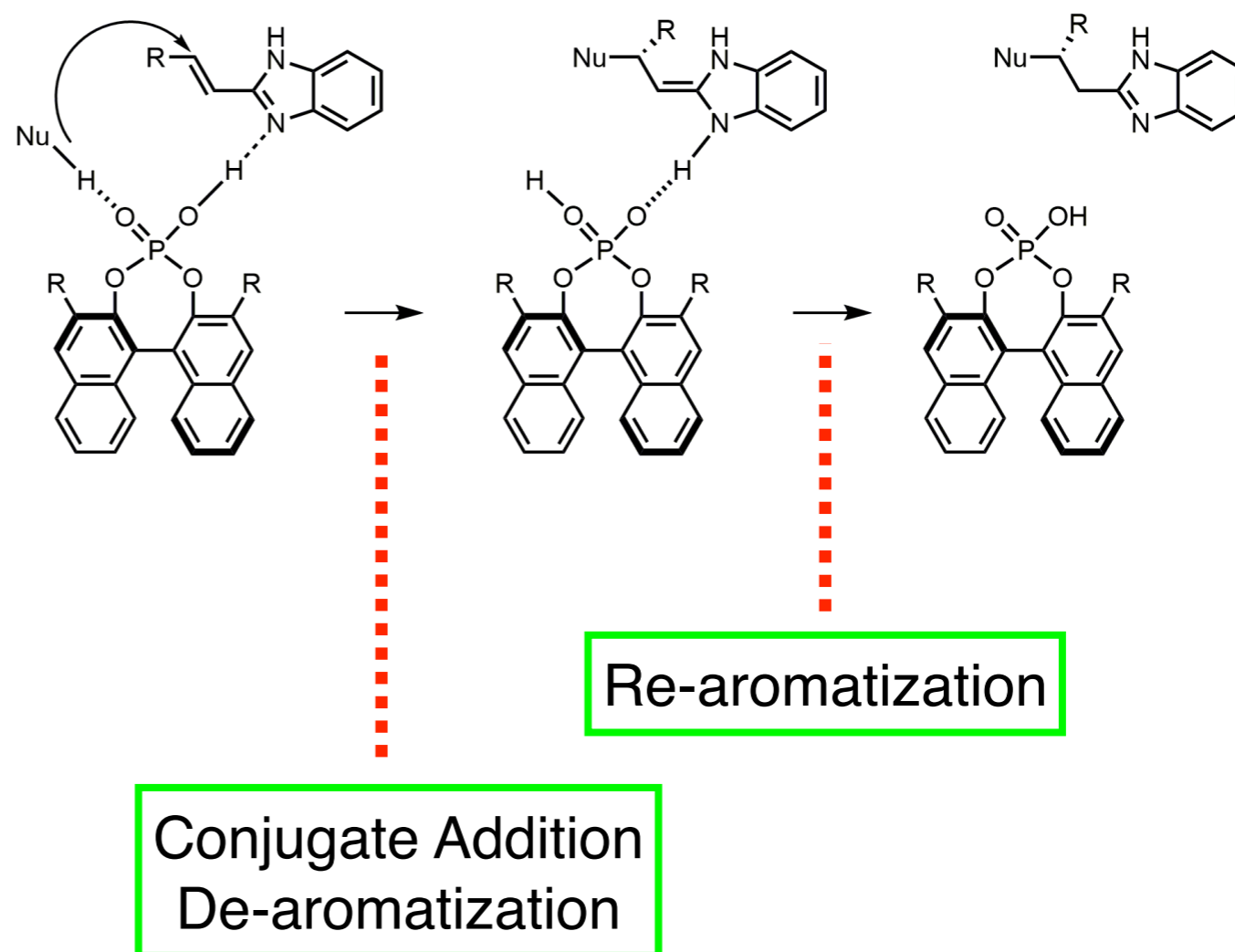
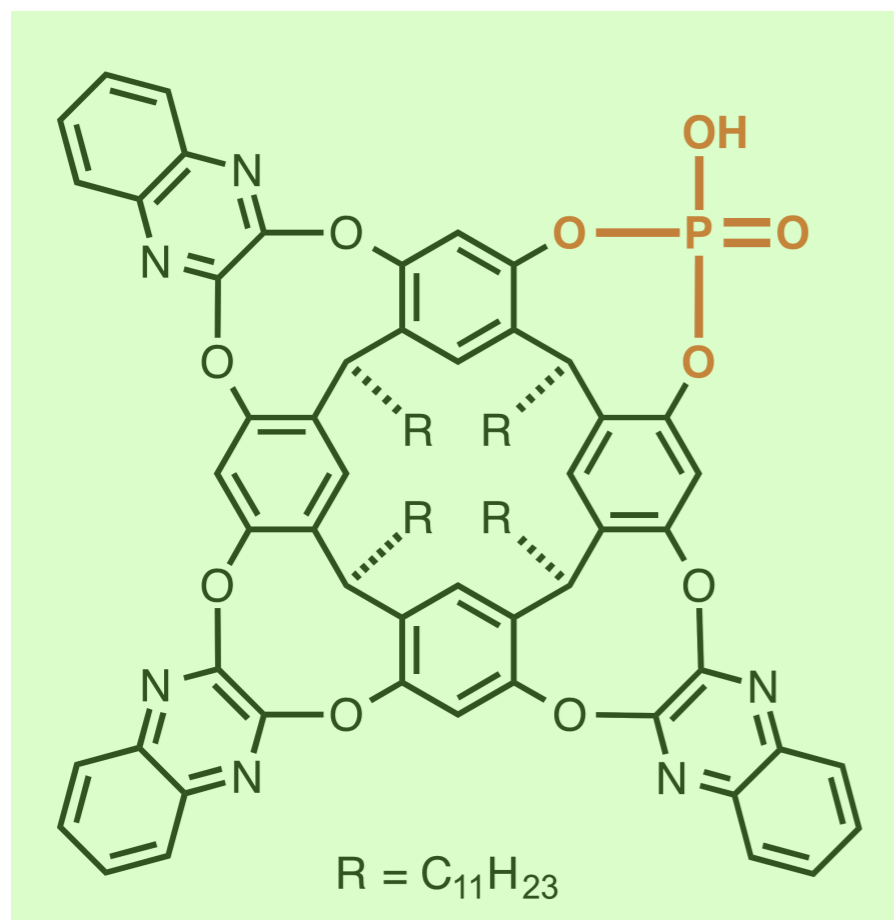
Y. Matsumoto, Y. Taguchi, N. Yoshida, S. Tokai, T. Maruyama, T. Iwasawa, *Supramol. Chem.* **2021**, *in press*.

Background: we have developed the phosphorous cavitands which enabled us to achieve catalytic selective transformations.



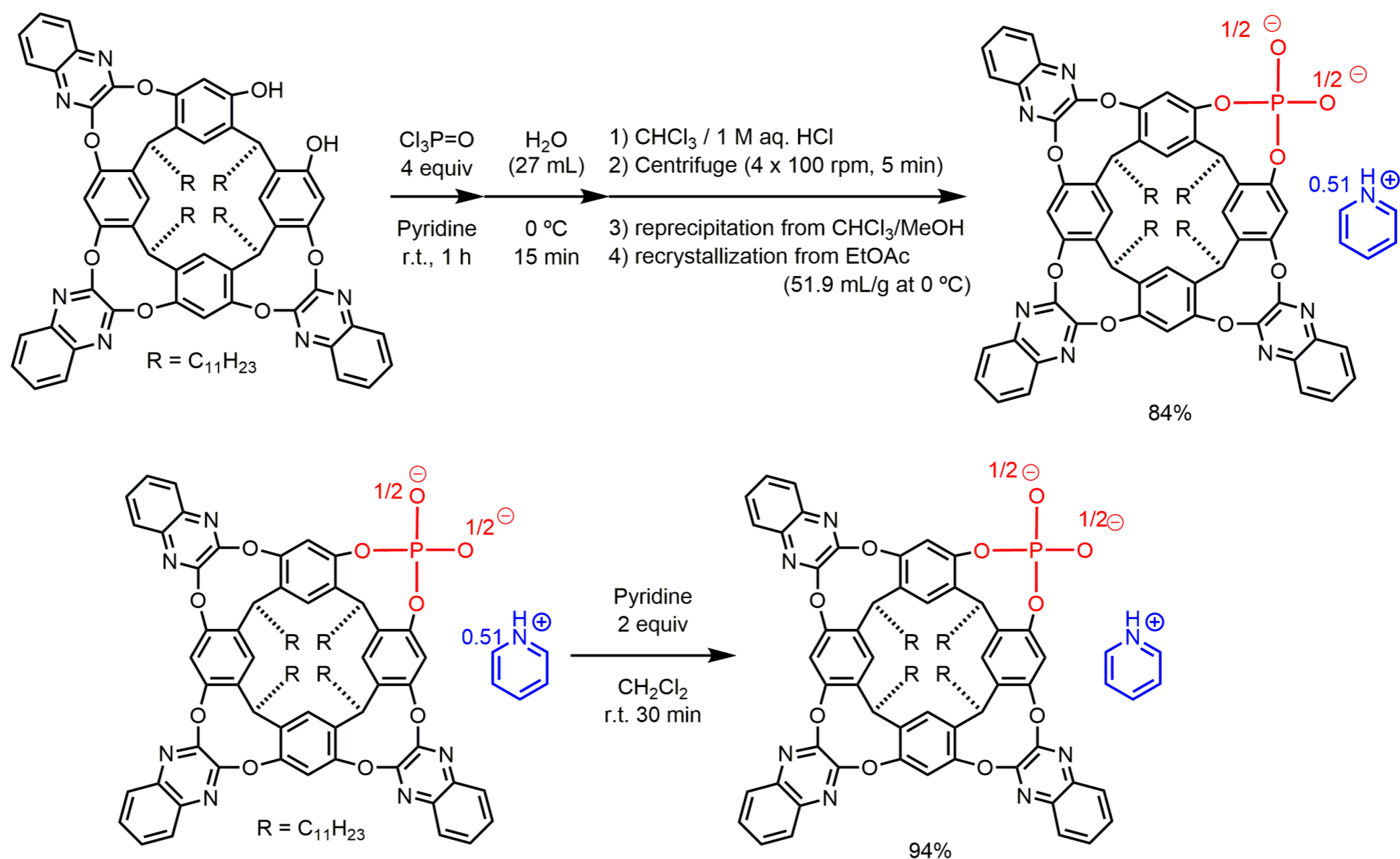
1. N. Endo, M. Inoue, T. Iwasawa, *Eur. J. Org. Chem.* **2018**, 1136-1140.
2. M. Inoue, K. Ugawa, T. Maruyama, T. Iwasawa, *Eur. J. Org. Chem.* **2018**, 5304-5311.

Approach to a catalytic cavitant as a phosphoric acid ester tethered to a *tri*-quinoxaline-spanned resorcin[4]arene.



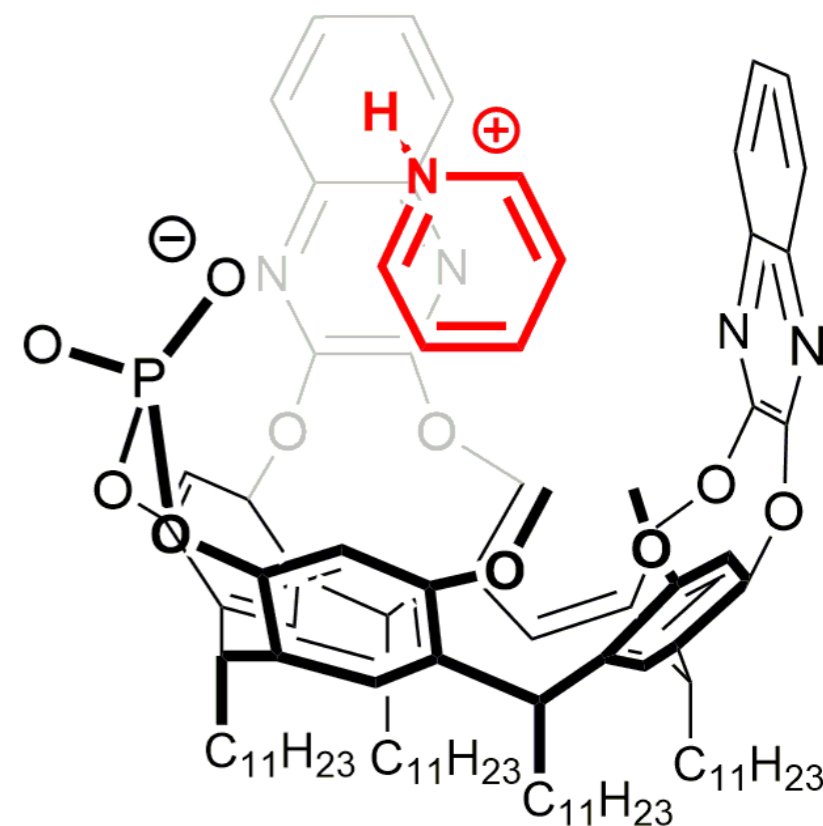
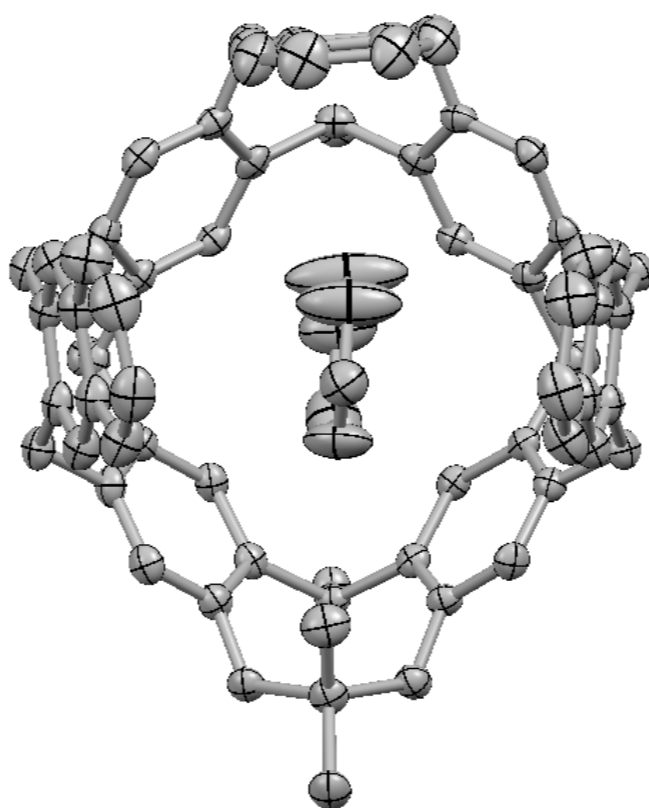
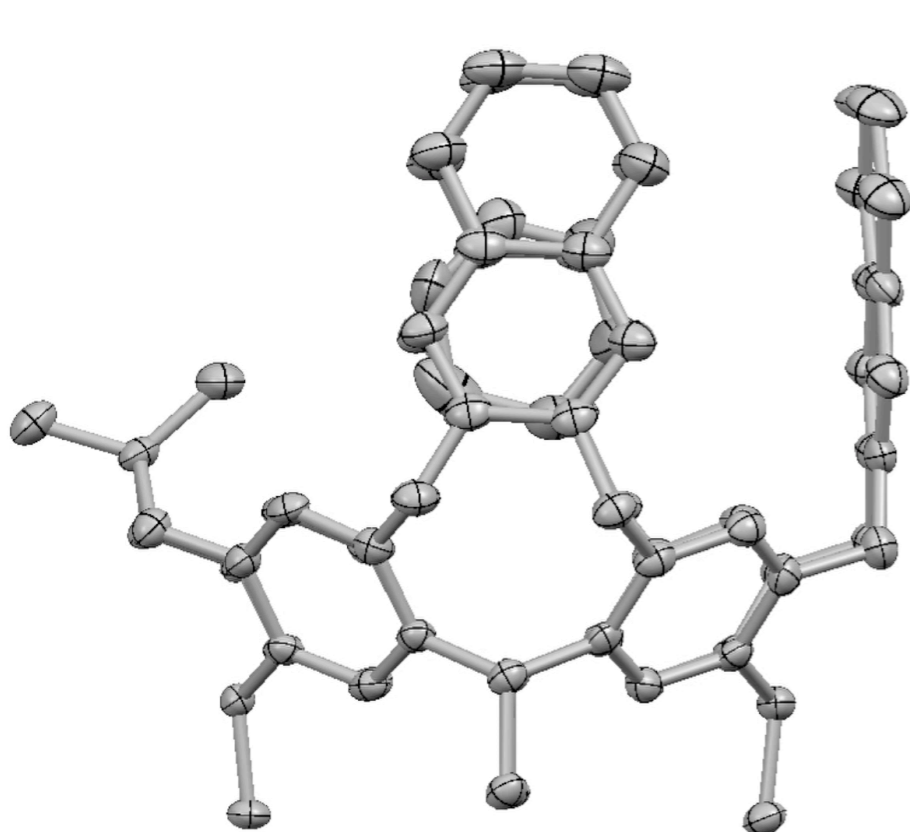
1. T. Akiyama, J. Itoh, K. Yokota, K. Fuchibe, *Angew. Chem. Int. Ed.* **2004**, *43*, 1566-1568.
2. M. Terada, Y. Wang, K. Kanomata, T. Korenaga, *Angew. Chem. Int. Ed.* **2016**, *55*, 927-931.

Synthesis of a *tri*-quinoxaline-spanned resorcin[4]arene-based phosphoric acid ester was performed.



pKa* ~1.39** for diethyl phosphate: L. D. Quin, *A Guide to Organophosphorus Chemistry*, Wiley, New York, 2000, chap. 5, pp. 133-165. (pKa* 5 ~ 6 for pyridinium salt**)

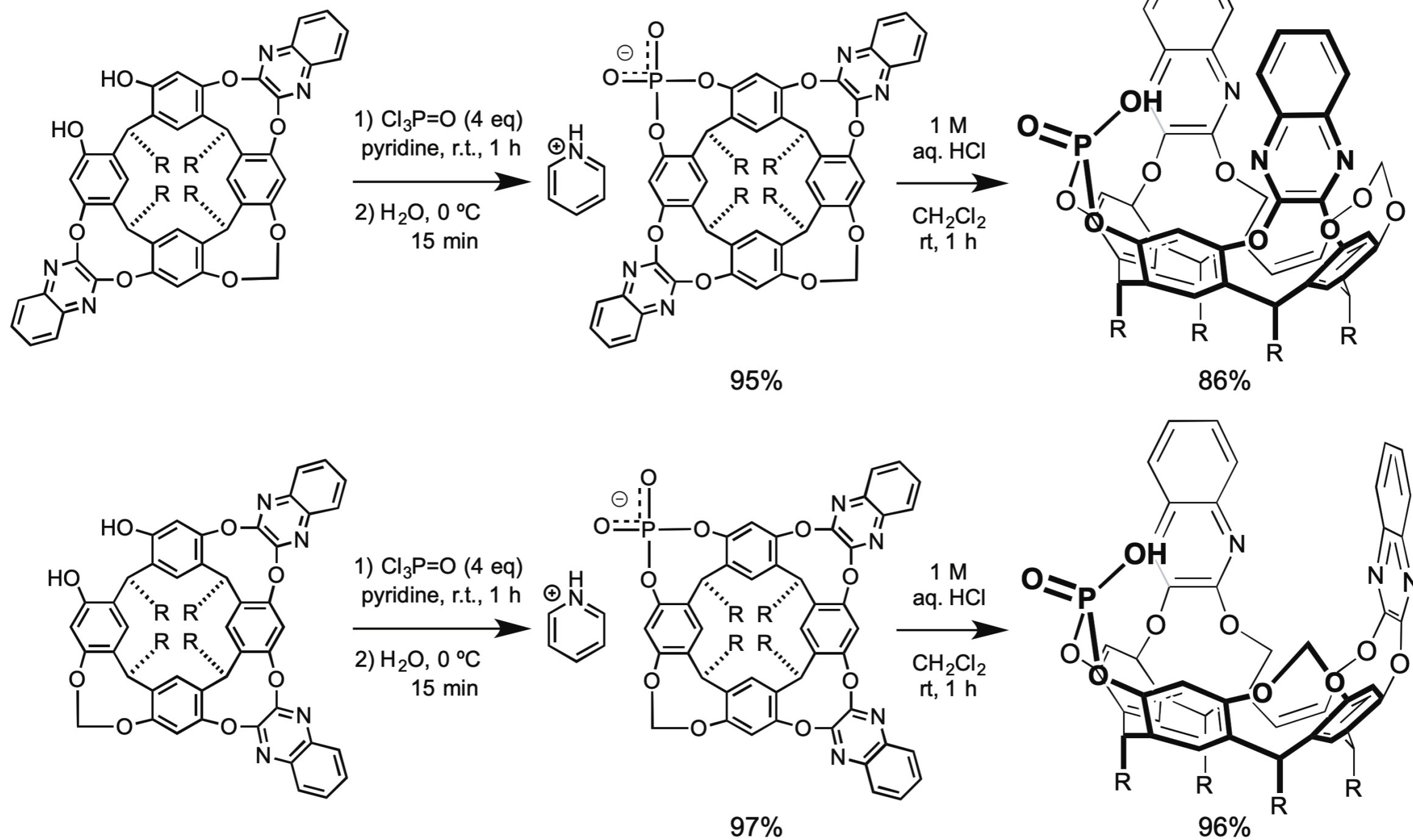
Crystallographic analysis revealed the inclusion of a pyridine moiety *via* the acid-base pair.



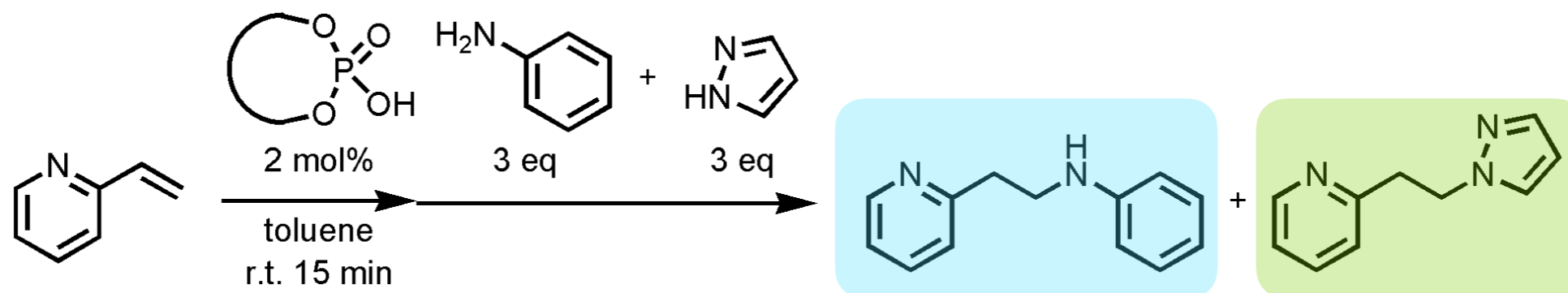
Selected bond lengths [Å]:
P1-O9 1.469, P1-O10 1.474.

CCDC-1875354: the data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Triclinic, space group *P*-1, colorless, $a = 13.6025(4)$ Å, $b = 18.7915(7)$ Å, $c = 19.1394(7)$ Å, $\alpha = 93.895(7)^\circ$, $\beta = 106.371(8)^\circ$, $\gamma = 105.465(7)^\circ$, $V = 4469.4(4)$ Å³, $Z = 2$, $T = 173$ K, $d_{\text{calcd.}} = 1.207$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.094$ mm⁻¹, $R_1 = 0.0914$, $wR_2 = 0.2331$, GOF = 1.012.

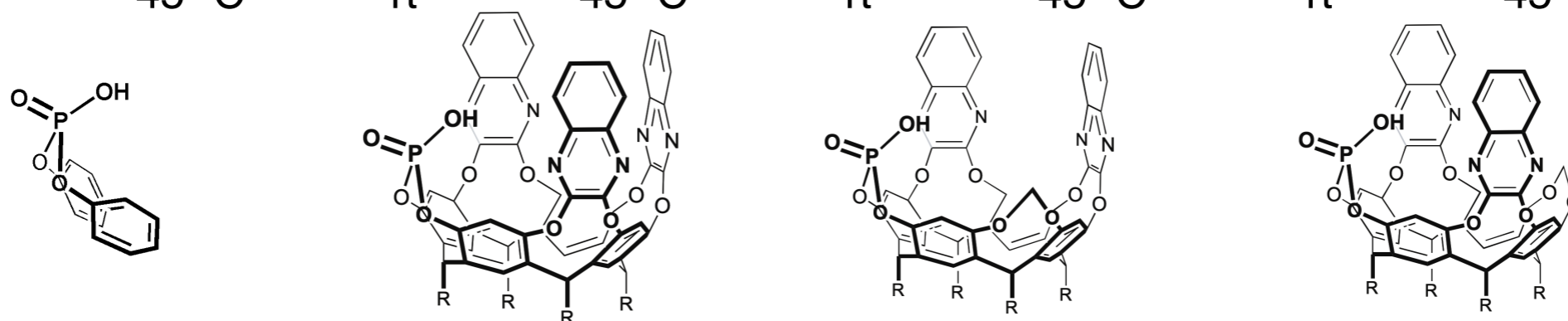
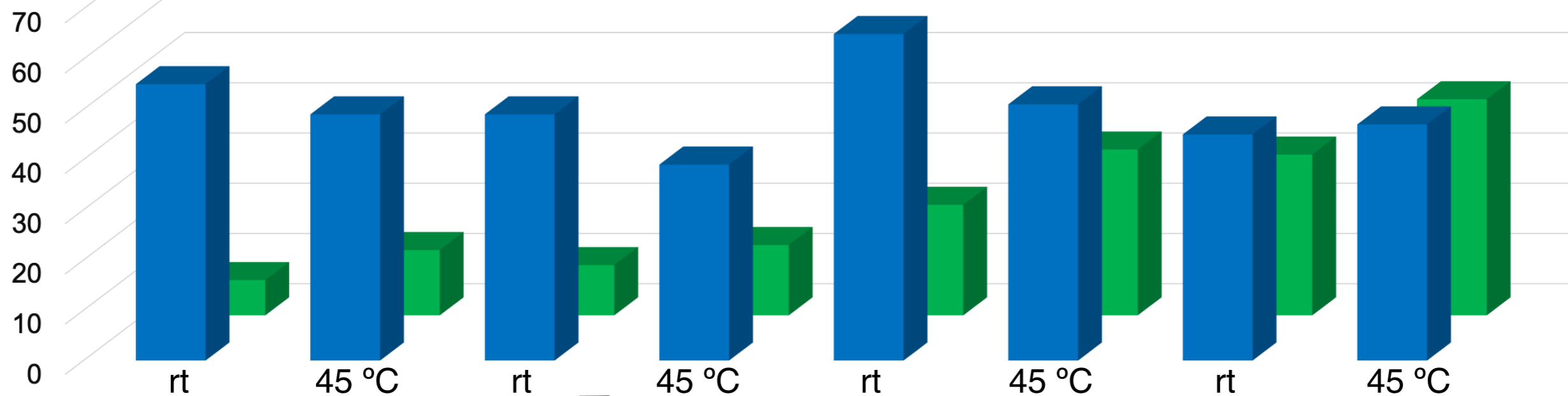
Two-walled cavitands in *trans*- and *cis*-versions were successfully prepared along with ^1H NMR analyses.



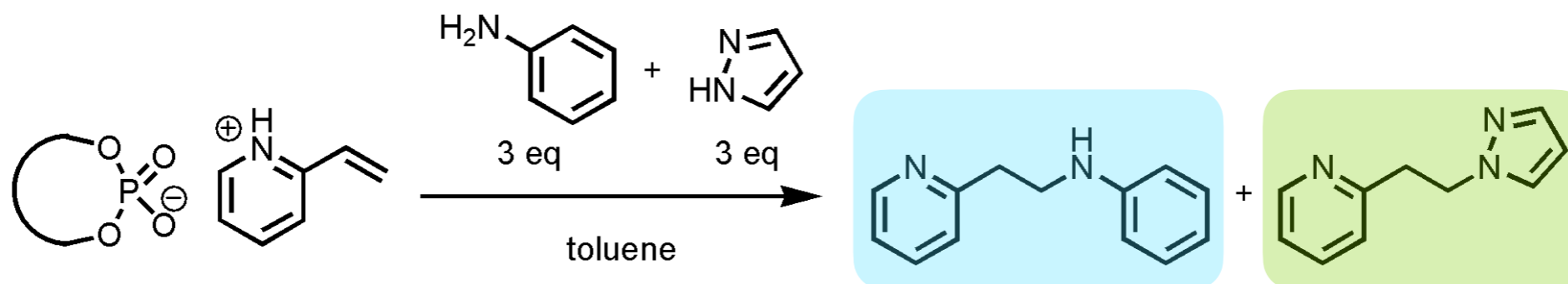
Cavitands catalyzed the conjugate addition reactions.



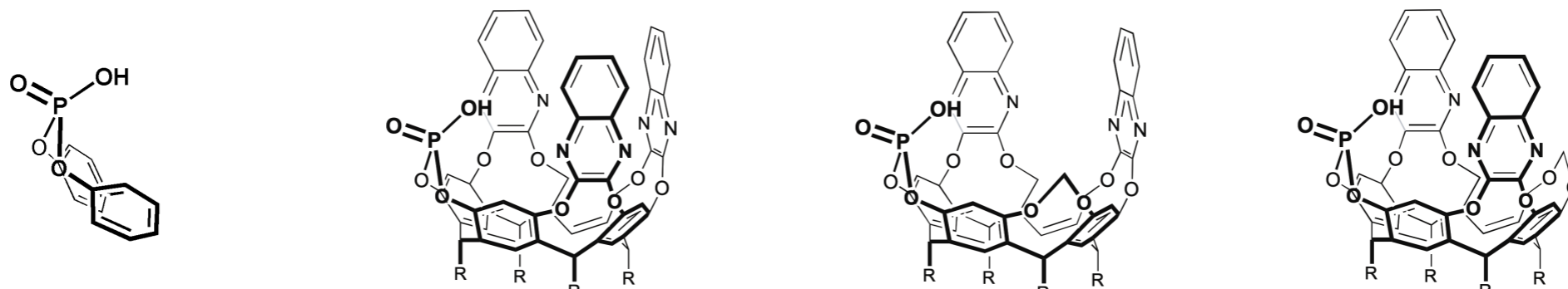
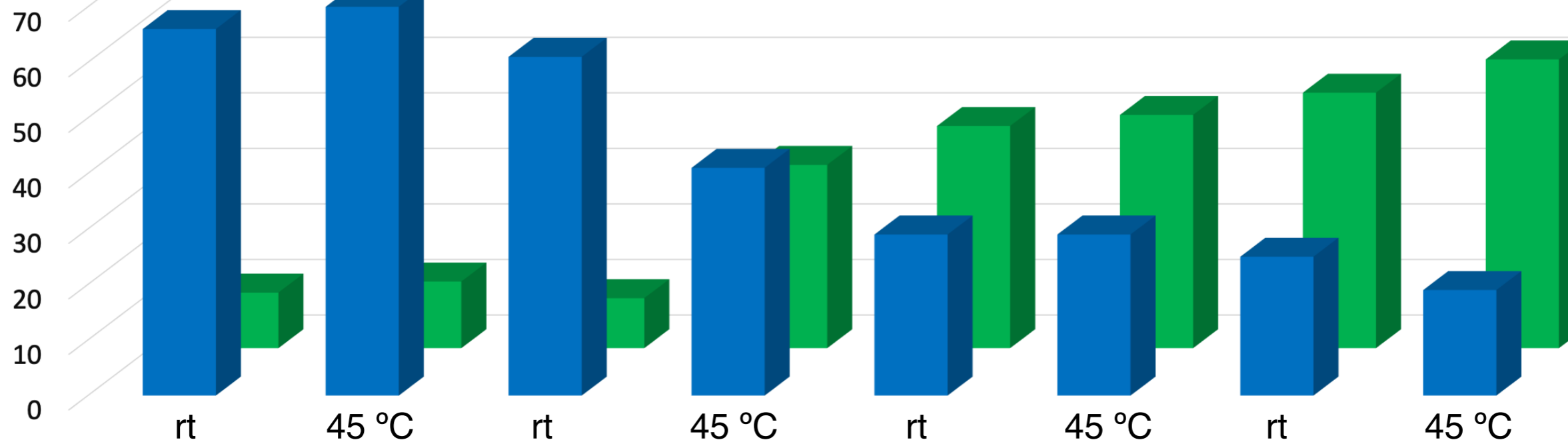
%Yield



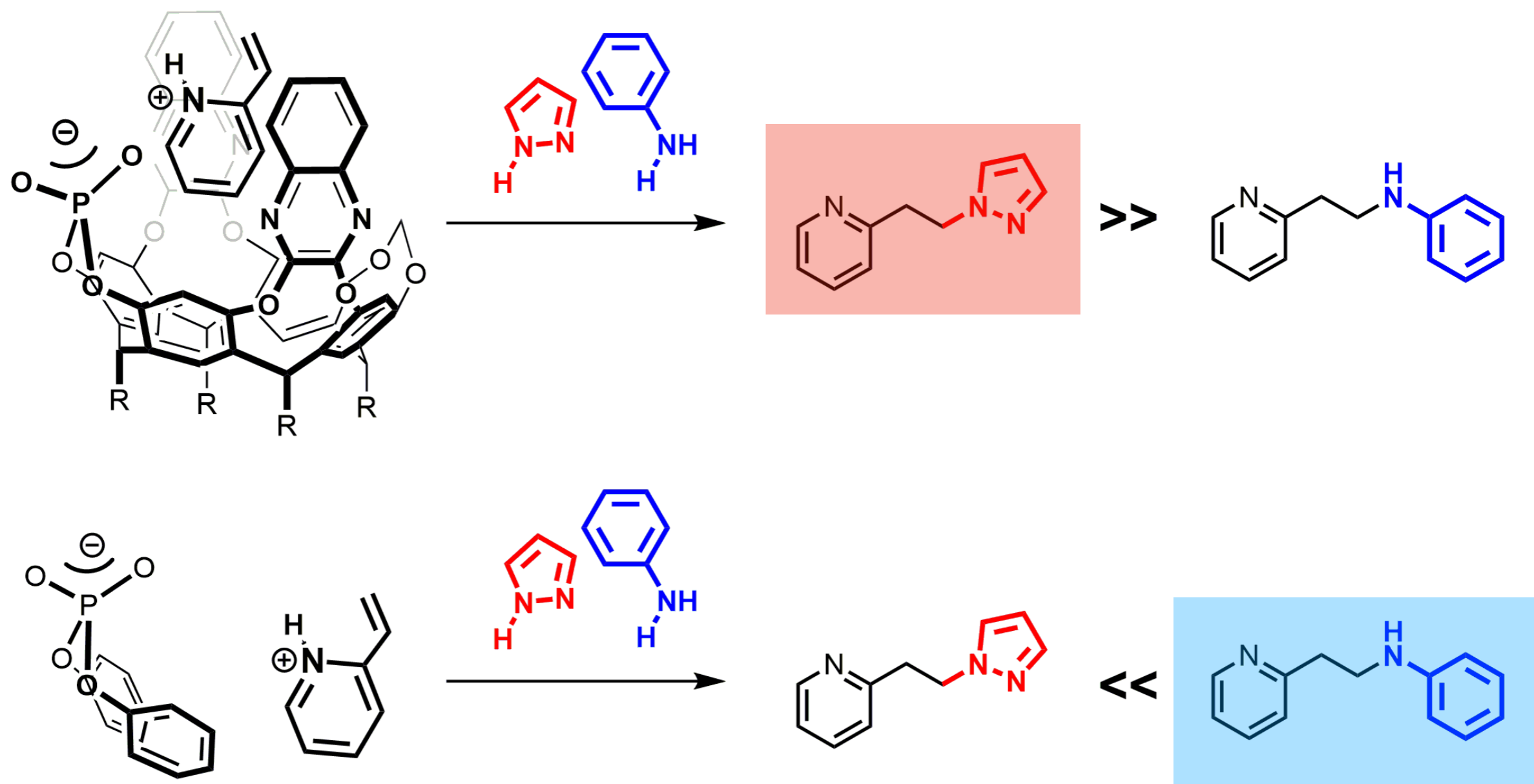
Host-guest complexes reversed the product distribution!



%Yield



Summary



Y. Matsumoto, Y. Taguchi, N. Yoshida, S. Tokai, T. Maruyama, T. Iwasawa, *Supramol. Chem.* **2021**, *in press*.