Ionic interactions enable stereoselective access to mechanically planar chiral rotaxanes

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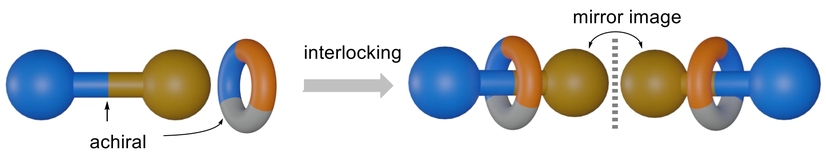
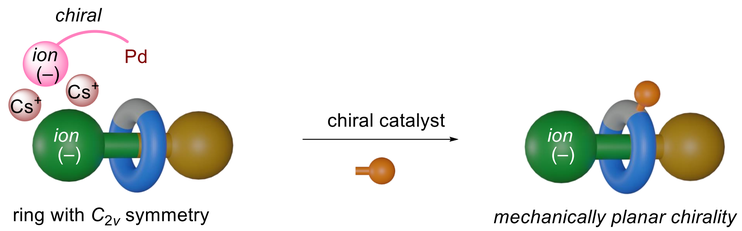
1. Introduction

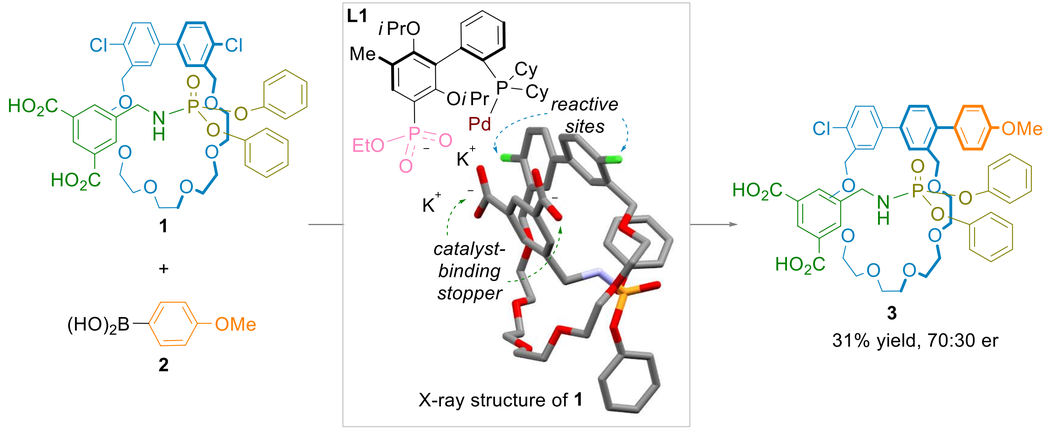
A. Mechanically planar chiral (MPC) rotaxanes



B. *This work*: MPC rotaxanes through catalytic desymmetrization enabled by distal ionic interactions [1]

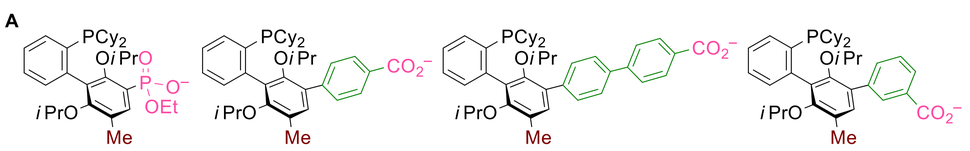


2.Proof of concept for catalytic desymmetrization to access MPC rotaxane



3. Catalyst evolution in Pd-catalyzed desymmetrization to chiral rotaxane

A

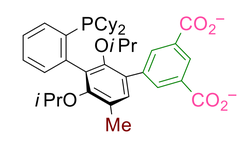


L1 31%, 70:30 er

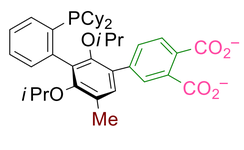
L2 33%, 77.5:22.5 er

L3 23%, 61:39 er

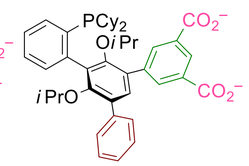
L4 30%, 82.5:17.5 er



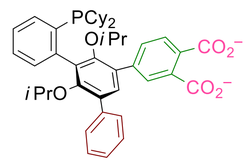
L5 30%, 82:18 er



L6 27%, 86.5:13.5 er

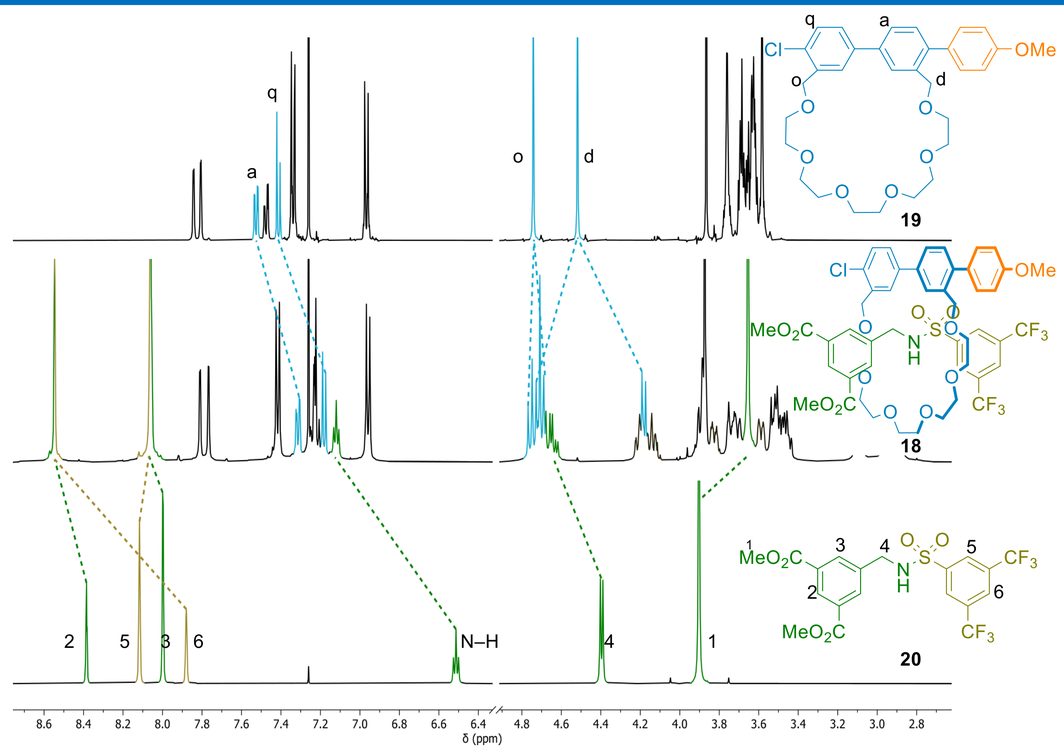


L7 34%, 92.5:7.5 er

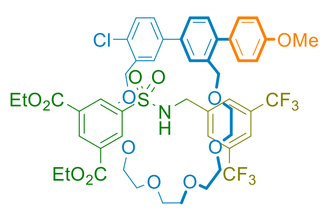


L8 34%, 94:6 er

5. Comparison of ^{1}H NMR spectra of rotaxane 18 and its subcomponents

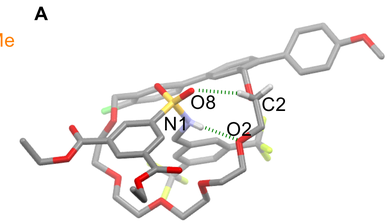


6. X-ray crystal structures of rotaxanes

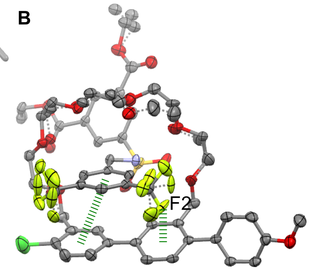


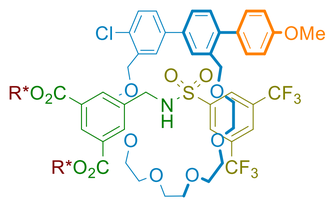
rac-**21**

A



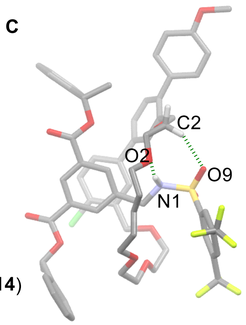
B



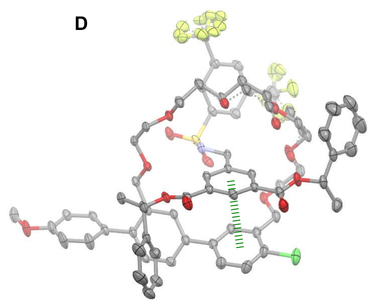


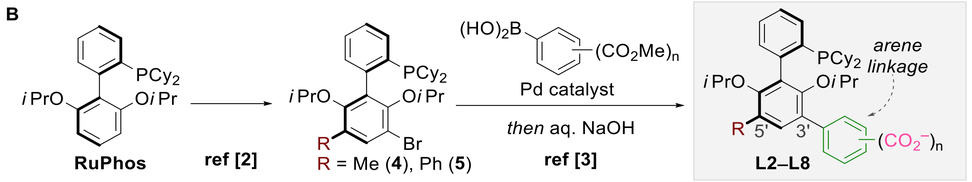
(*S*, *S*, R_{mp})-**22** (derived from (R_{mp})-**14**)

C

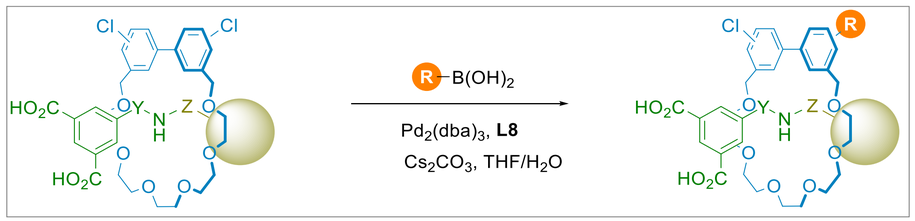


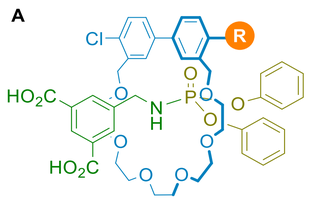
D



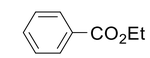


4. Scope of MPC rotaxanes



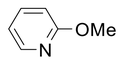


R = OMe
3: (31%) 24%, 93.5:6.5 er;
6 (des-Cl): 12%, 95.5:4.5 er;
7 (bis-coupling): 13%;
1 (unconsumed substrate): (40%)

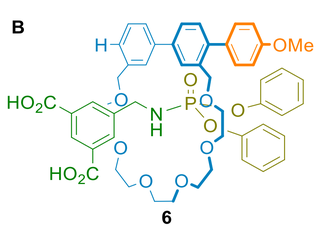


8: (25%) 25%, 94.5:5.5 er

9: (26%) 18%, 91.5:8.5 er

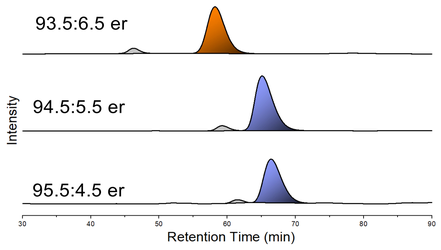


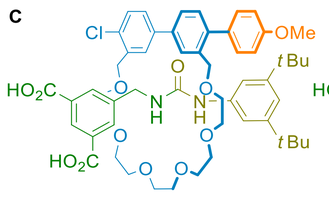
10: (15%) 12%, 92:8 er



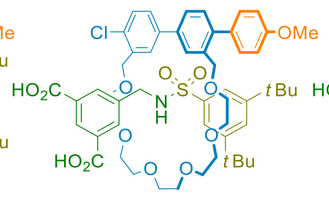
6

3 → Pd catalyst HCO_2Na → 6 (*identical stereochemistry*) 6 (side-product)

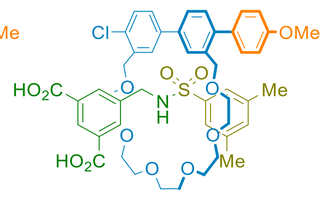




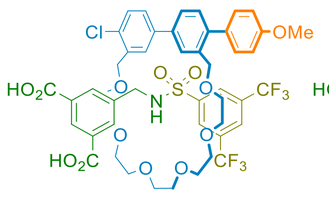
11: 38%, 86:14 er



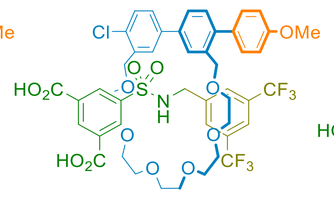
12: 28%, 96:4 er



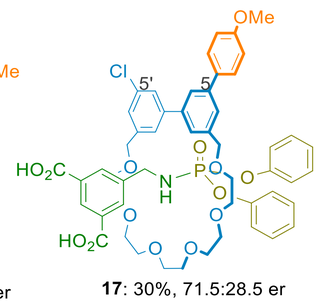
13: N.A.



(R_{mp})-**14**
26%, 96.5:3.5 er

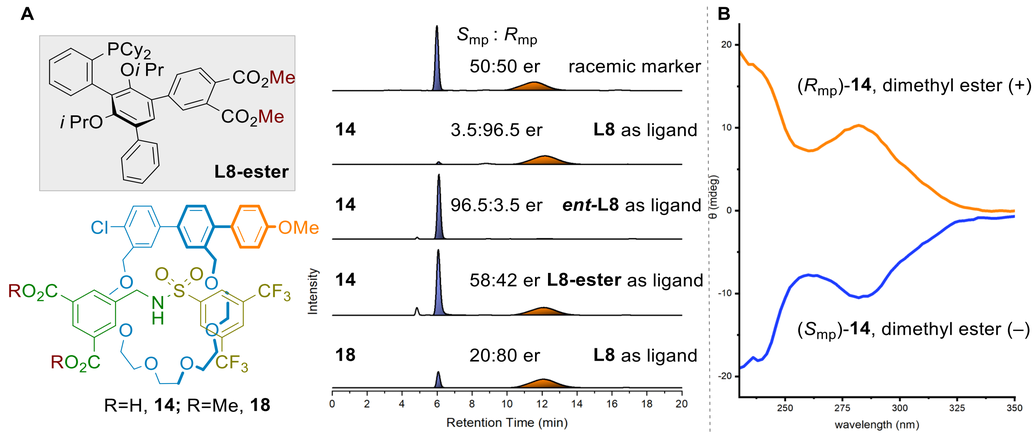


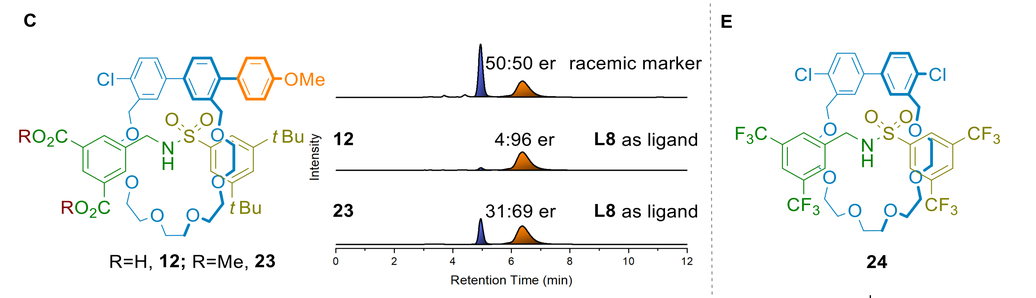
15: 24%, 94.5:5.5 er
16 (des-Cl): 11%, 95.5:4.5 er

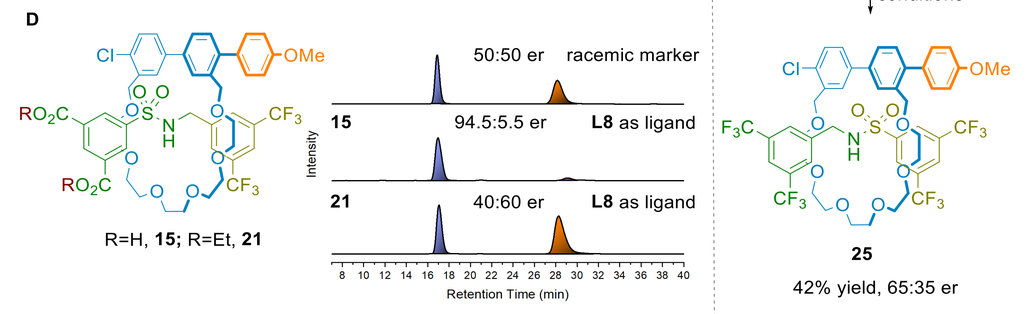


17: 30%, 71.5:28.5 er

7. The roles of ionic catalyst and ionic stoppers in desymmetrization







8. Acknowledgements and References

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References:

[1] Li, M., Chia, X. L., Tian, C., and Zhu, Y. (2022). Chem *8*, 2843–2855.
[2] Lou, Y., Wei, J., Li, M., and Zhu, Y. (2022). J. Am. Chem. Soc. *144*, 123–129.
[3] Li, M., Chia, X. L., and Zhu, Y. (2022). Chem. Commun. *58, 4719–4722*.