Supramolekulare Chemie und Katalyse

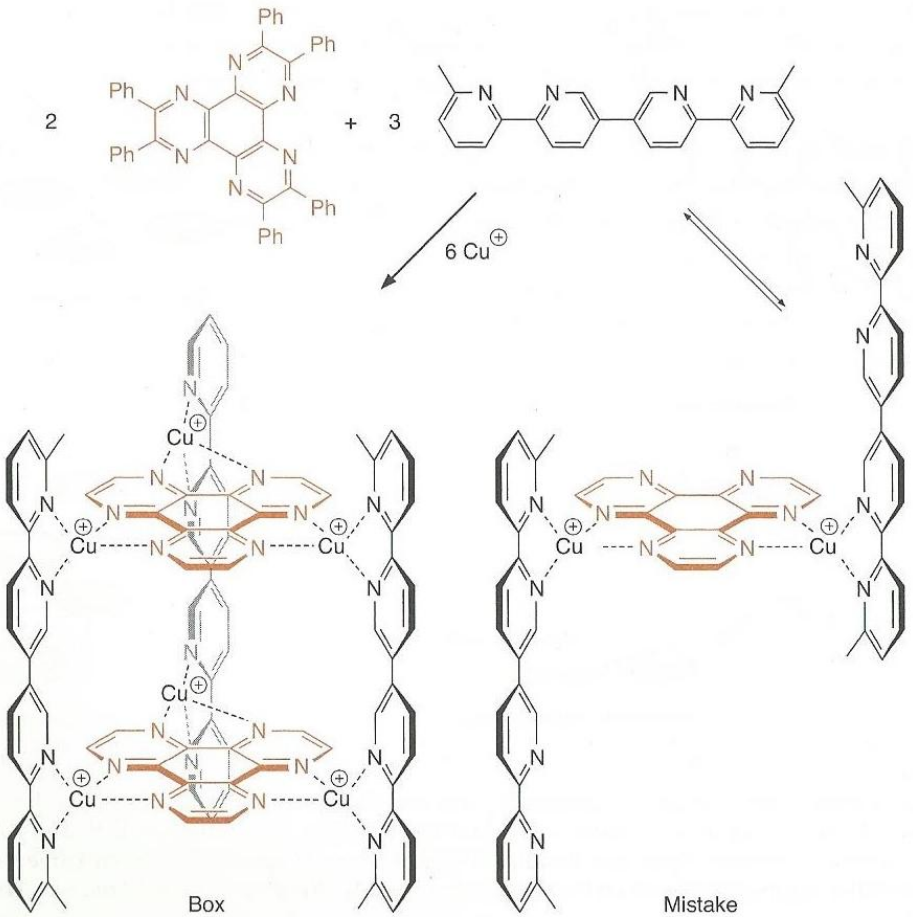
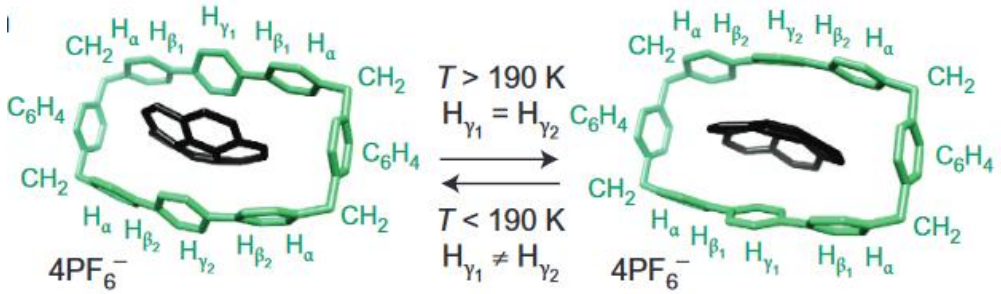
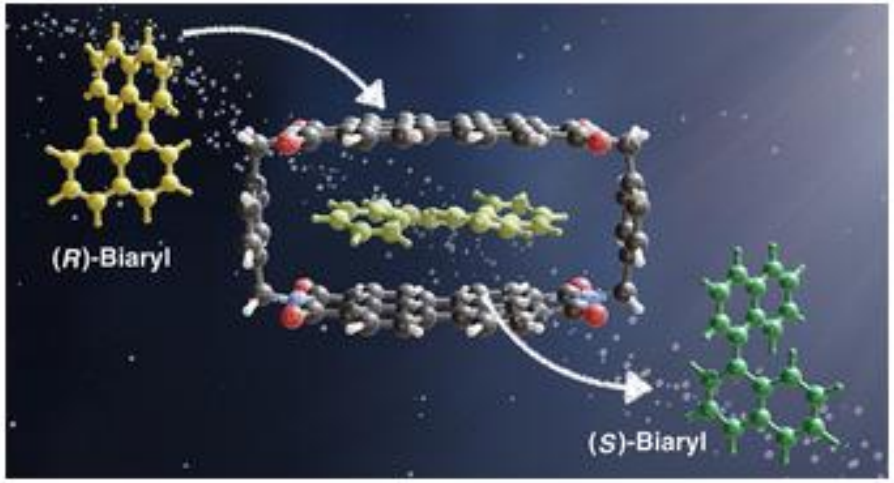


Figure 4.13
Supramolecular assembly of a complex "box" from 11 separate components by spontaneous self-assembly. Note that the phenyl groups of the precursor hexaphenylhexaazatriphenylene are omitted in the complex for clarity, and the back quaterpyridine is gray. The complex on the right is a "mistake" that is corrected by equilibration. Baxter, P., Lehn, J. M., Decian, A., and Fischer, J. "Multicomponent Self-Assembly—Spontaneous Formation of a Cylindrical Complex from 5 Ligands and 6 Metal-Ions." *Angew. Chem. Int. Ed. Eng.*, **32**, 69–72 (1993).

Einen molekulareren Käfig, der ein Substrat umschließt und dessen Isomerisierung katalysiert, kennen wir vom **Corannulen**.

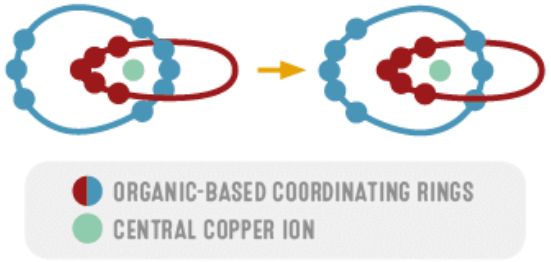


Ein ähnlicher **Cyclophan-Käfig** racemisiert den chiralen Liganden BINOL. Abgebildet ist das einfachere 1,1-Binaphthyl (JOC 2022, 5485)



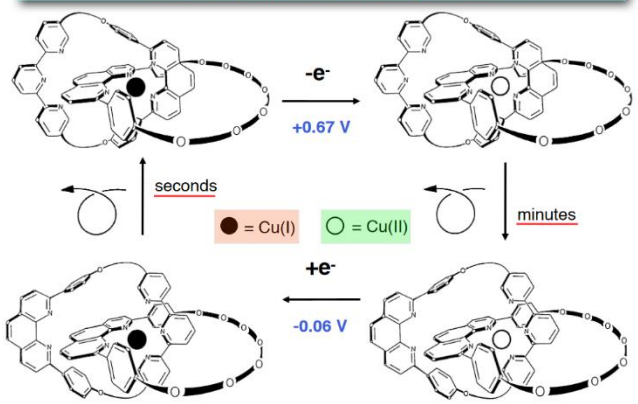
Nobel prize 2016: "for the design and synthesis of **molecular machines**“

Catenane

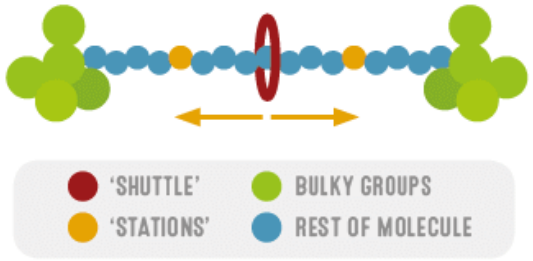


Jean-Pierre Sauvage created a pair of interlocking rings (called a catenane). One ring could rotate around the other when energy was added.

rotation of a ring within another ring (**no directionality**): use of the Cu(II)/Cu(I) couple (*Livoreil et al., 1994*)
Real rotary motors : ***B. Feringa**, 1999*



Rotaxane



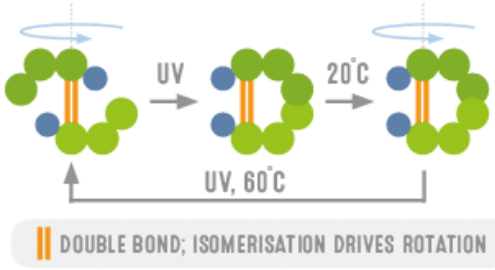
Fraser Stoddart made a ring-shaped molecule attached to an axle (a rotaxane) which could shuttle up and down. He also helped produce a rotaxane-based computer chip.

Rearrangement of chemical topology, Coulomb repulsion

Thermodynamically driven redox cycles without directionality of rotation.

Catenanes and rotaxanes belong to the lecture topic supramolecular chemistry

double bond isomerism



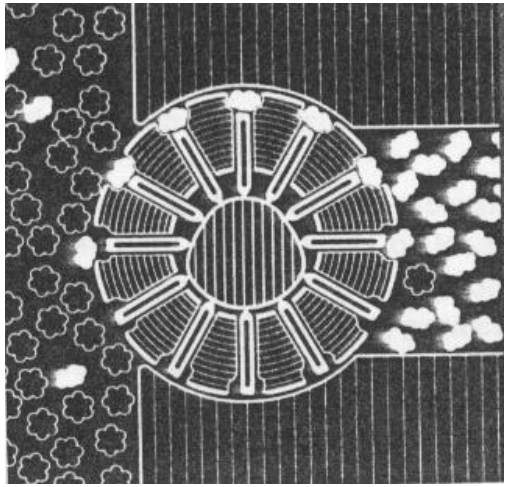
Ben Feringa produced the first molecular motor by constructing a molecule that responded to light and heat and spun in a particular direction.

Chiral rotation!
Kinetically trapped intermediates!

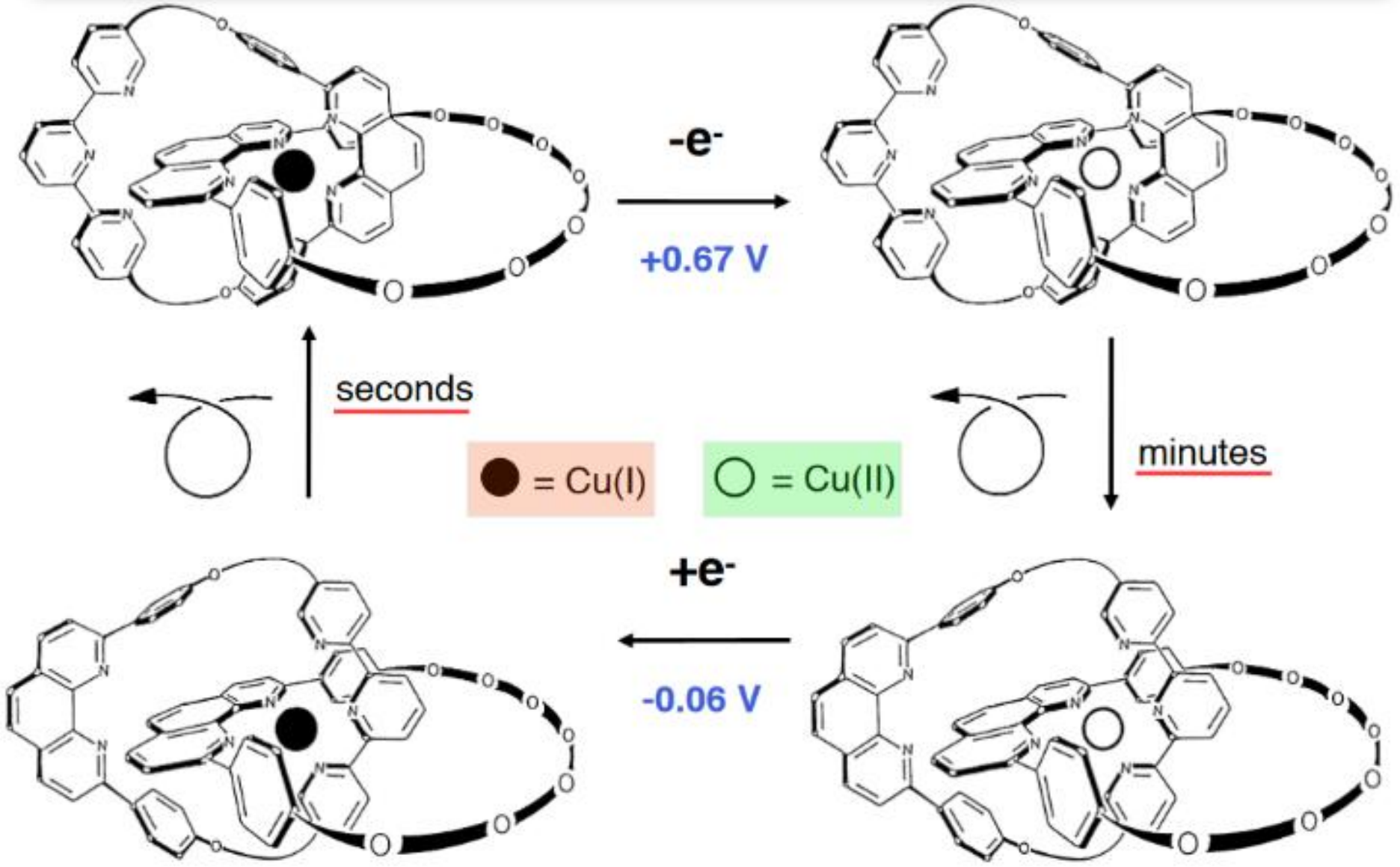
Light and heat-driven double bond isomerism of overcrowded alkenes are the only **molecular rotors** which exhibit directionality of rotation.

Ausblick:
Eine technische Utopie?

Nanopumpe zur Trennung von Molekülgemischen

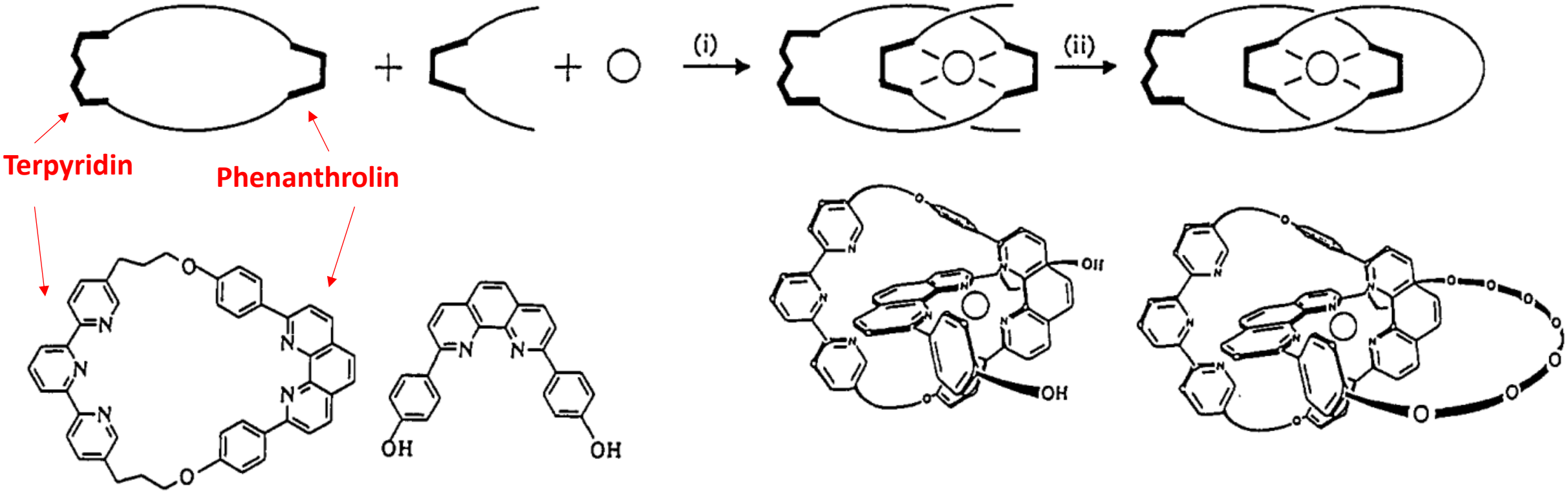


rotation of a ring within another ring (**no directionality**): use of the Cu(II)/Cu(I) couple (*Livoreil et al., 1994*) Real rotary motors : ***B. Feringa**, 1999*



Cu(I) ist tetraedrisch und Cu(II) planar. Cu(I) bindet bevorzugt an die beiden Phenanthroline. Cu(II) bindet das flexiblere Terpyridin.

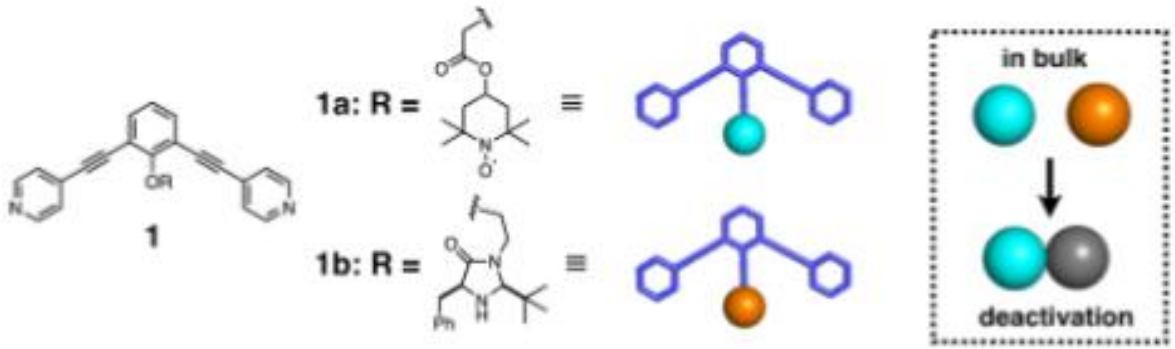
Catenenan aus VL-Woche 6 Molekulare Maschinen
An der Tafel: Synthese der Bausteine Terpyridin und Phenanthrolin
Allg Synthesestrategie Catenane: Zuerst über Metallkomplexierung einfädeln, dann zweiter Ringschluß



(i) Room temperature, CH_3CN (ii) 60 °C, DMF, Cs_2CO_3, $ICH_2(CH_2OCH_2)_5CH_2I$.
The circle represents Cu(I)

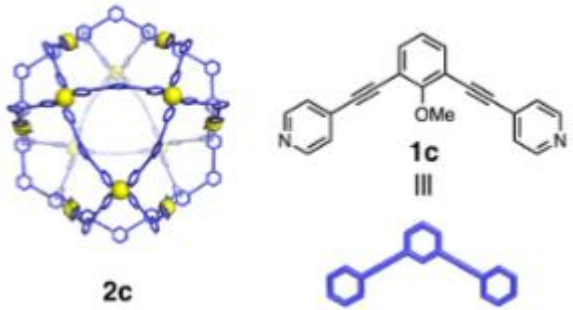
J. Am. Chem. Soc. 1994,116, 9399-9400

Synthesis in confined spaces: *Permeable self-assembled molecular containers for catalyst isolation enabling two-step cascade reactions by Makoto Fujita et al.*

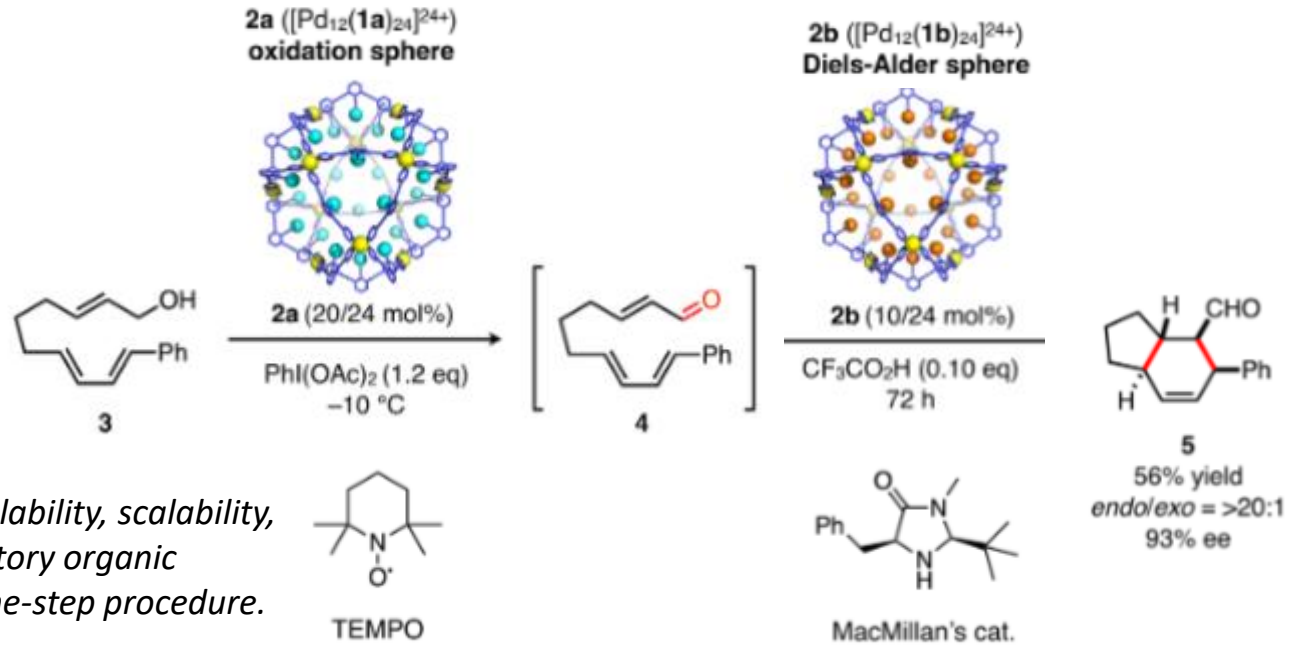


Der blaue und der rote Katalysator würden sich gegenseitig deaktivieren, wenn sie gemeinsam in Lösung vorliegen. Indem man jeden Kat in einen eigenen Käfig sperrt, kann das Substrat **3** in einer **Kaskadeneraktion** zu **5** umgesetzt werden. Vorteil: Der instabile Aldehyd **4** wird nicht isoliert sondern gleich weiter umgesetzt.

Selbstassemblierter durchlässiger **$[Pd_{12}(1c)_{24}]^{24+}$-Käfig** ohne katalytisch aktive Gruppen.



Synthese von **1b** an der Tafel und nächste Seite!
Wie würden Sie **1a** synthetisieren?

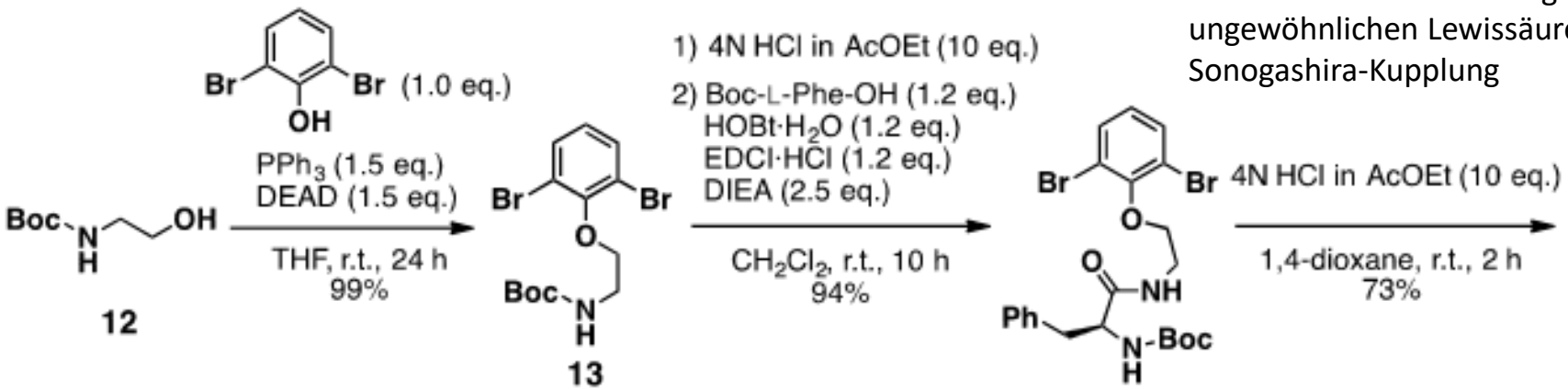


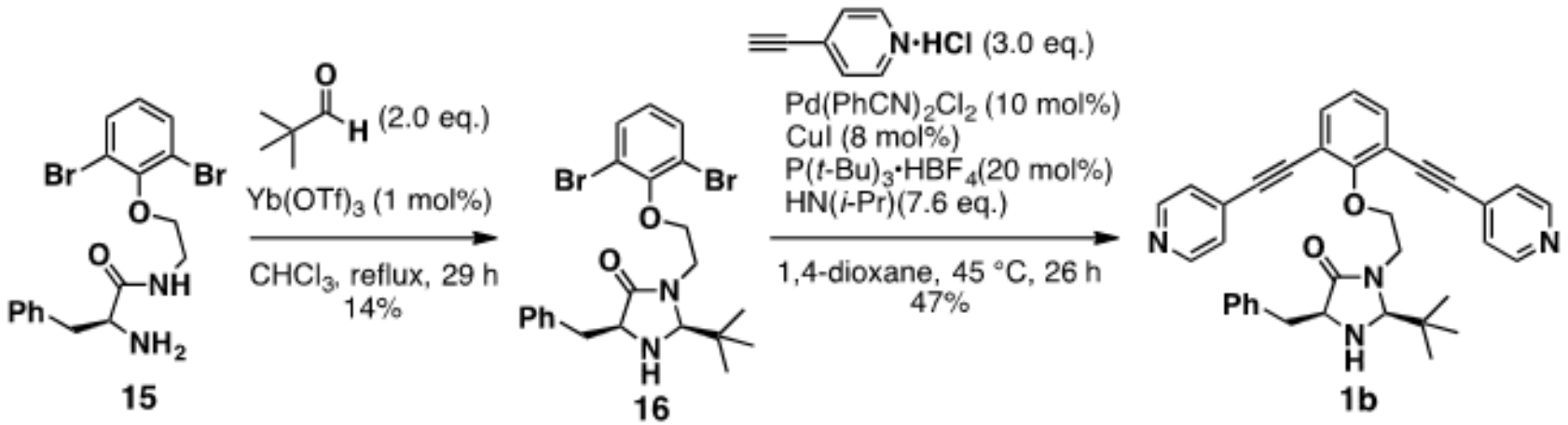
Originaltext: *$Pd_{12}L_{24}$ self-assembled complexes serve as catalyst carriers for enabling continuous chemical transformations. A stereo-selective **cascade reaction** (allylic oxidation followed by Diels–Alder cyclization) with two intrinsically incompatible catalysts was demonstrated. Our system is advantageous in terms of availability, scalability, and predictability. Ideally, future laboratory organic synthesis should be a simple one-pot/one-step procedure.*

Der Mechanismus der Organokatalyse mit Pyrrolidinen (z.B. Pro oder hier der MacMillan-Kat.) wird in OC-3 besprochen. Dabei bildet sich eine Iminium-Zwischenstufe, die das Enal zum Dienophil aktiviert.

DOI: 10.1021/jacs.7b02745
J.Am.Chem.Soc. 2017, 139, 6090−6093

• Synthesis and physical properties of ligand 1b





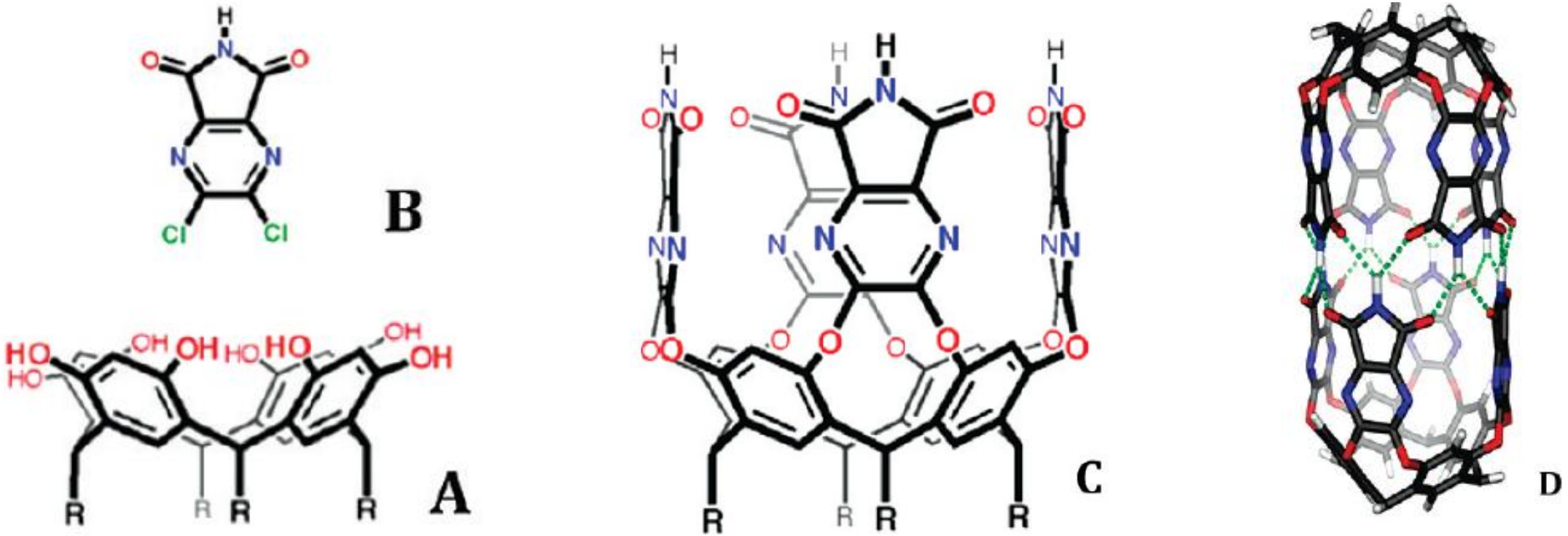
Eine Abfolge bekannter Reaktionen:
Mitsunobu (welcher der beiden Alkohole wird zum Ether-Sauerstoff?)
Racemisierungsfreie Amidkondensation mit EDCI/HOBt
Fragmentierung der urethanischen Schutzgruppe mit Säure
Diastereoselektive Bildung eines Aminals (Ring: Imidazolidinon) mit einer ungewöhnlichen Lewissäure als Kat.
Sonogashira-Kupplung

Molecular Behavior in Small Spaces

JULIUS REBEK, JR.*

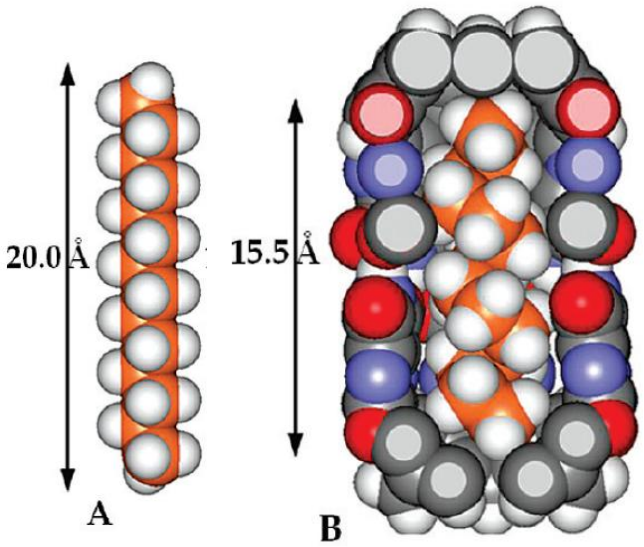
Das elektronenreiche Resorcinaren A reagiert in acht S_NAr Reaktionen zum Cavitand C, welcher über Wasserstoff-brücken zur Kapsel D dimerisiert

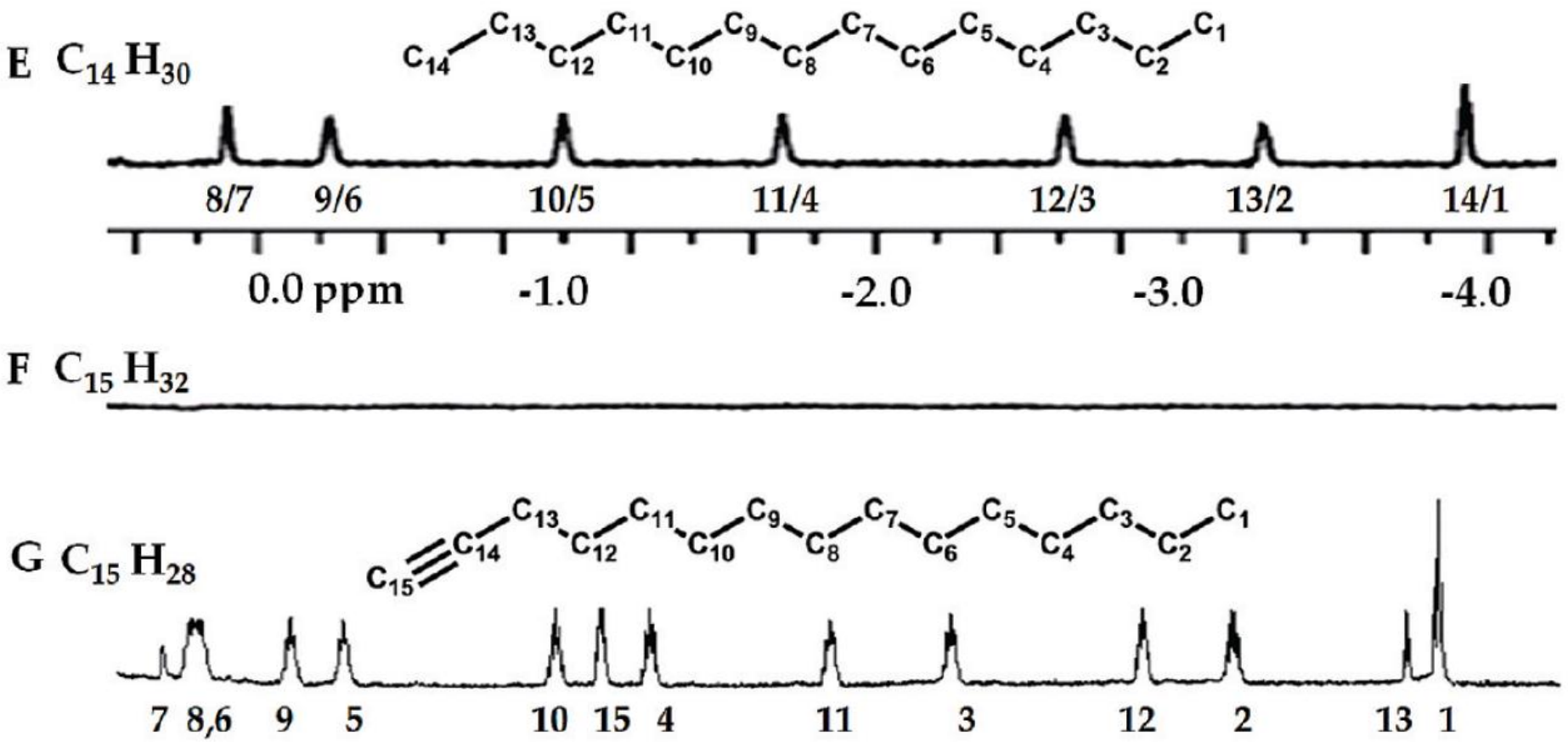
The study of physical organic chemistry in solution is a mature science, over a century old, but over the last 10 years or so, reversible encapsulation has changed the way researchers view molecular interactions. It is now clear that the behavior of molecules in dilute solution is really quite different from their behavior in capsules. Molecules isolated from bulk media in spaces barely large enough to accommodate them and a few neighbors show new phenomena: their activities resemble those of molecules inside biochemical structures—pockets of enzymes, interiors of chaperones, or the inner space of the ribosome—rather than conventional behavior in solution.



Originaltext: *The resorcinarene octol (A) and activated aromatic halides (B) combine to give the cavitand (C). The hydrogen-bonding sites on the upper rim allow dimerization in the presence of a suitable guest; (D) the cylindrical capsule is shown without peripheral groups, R, which are long chain alkyls.*

Das lineare Alkan $C_{14}H_{32}$ (A) wird von der Kapsel D (vorige Seite) in seiner helikalen Konformation gebunden (B) und durch den direkten Kontakt mit den Aromaten in den negativen ppm-Bereich abgeschirmt. Aufgrund der Symmetrie sieht man genau sieben Signale im ^{1}H-NMR (E). Das um nur eine Methylengruppe längere Alkan wird überhaupt nicht erkannt und das Spektrum ist leer im negativen ppm-Bereich (F). Das zu lange Alkin streckt die schlanke Alkin-Gruppe durch die Resorcin-Kappe und wird deshalb wieder erkannt (G).



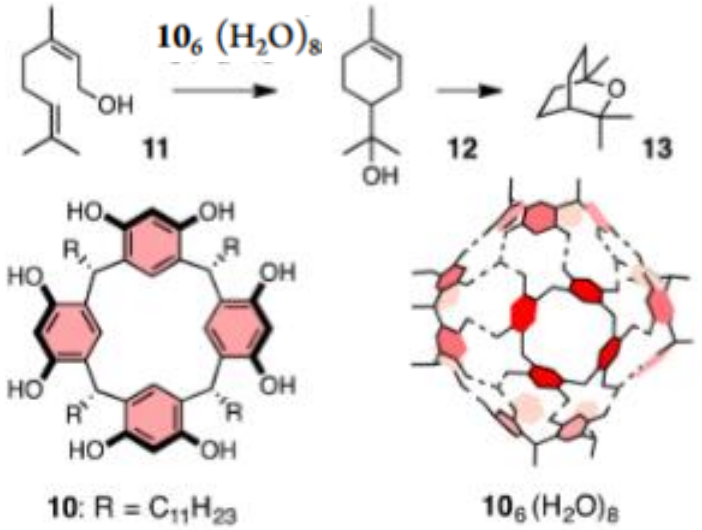


(A) A space-filling model of tetradecane in its fully extended conformation. (B) A crosssection of the capsule with tetradecane inside: the guest is coiled in a helical conformation that allows it to fit and make CH-π contacts with the inner lining of the capsule.

π-Kation-Wechselwirkung im Inneren molekularer Käfige

The capsule $\mathbf{10}_6(H_2O)_8$, formed by self-assembly of **resorcinarene 10**, is a cation−π catalyst. The high Brønsted acidity within this capsule catalyzes the formation of an allylic carbocation from nerol **11**. Stabilized by cation−π interactions within the capsule, this carbocation then cyclizes first into α-terpineol **12** and then into the bicyclic eucalyptol **13**.

J. Am. Chem. Soc. 2016, 138, 4270−4277



Das Trichloracetimidat ist ein Tautomer des Trichloracetamids. Protonenkatalyse setzt dieses sowie ein benzylisches Kation frei.

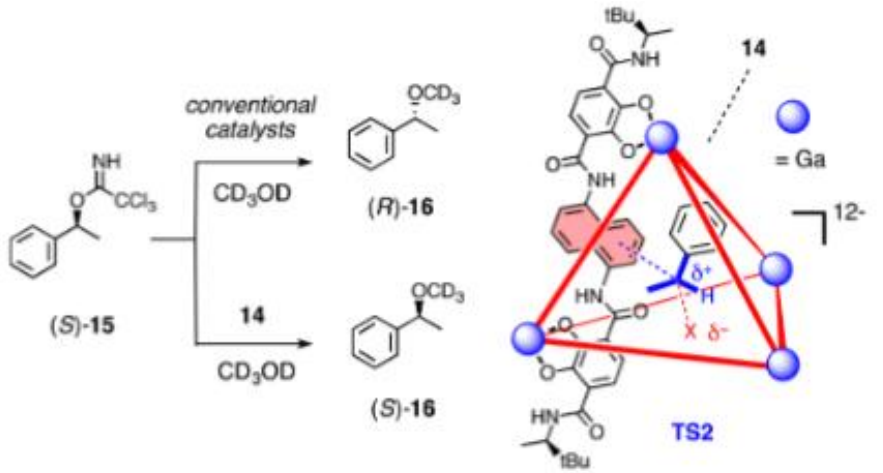


Figure 3. Retention of configuration during the nucleophilic substitution from (*S*)-**15** to (*S*)-**16** is thought to originate the stereoselective stabilization of reactive intermediate **TS2** by cation−π interactions within the supramolecular catalyst **14**.