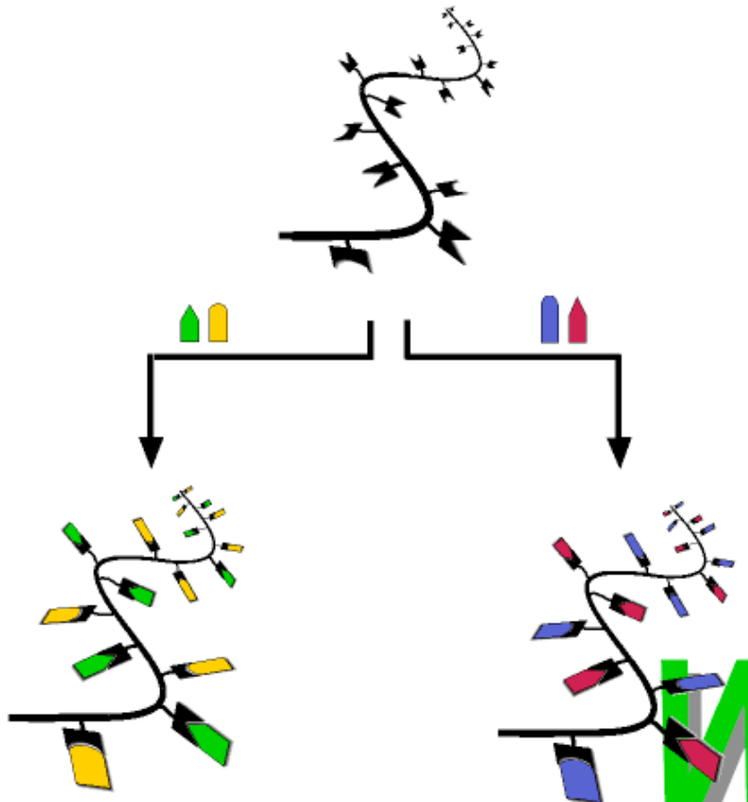
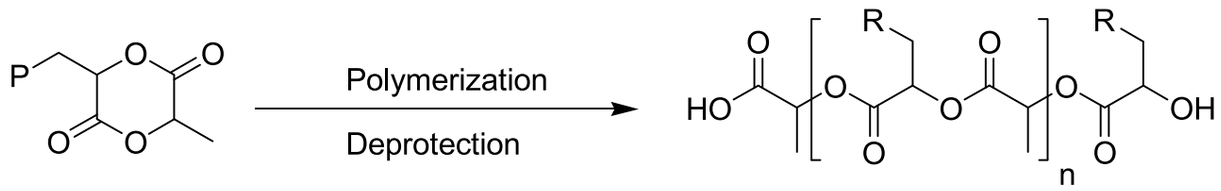
Polymer Methodology

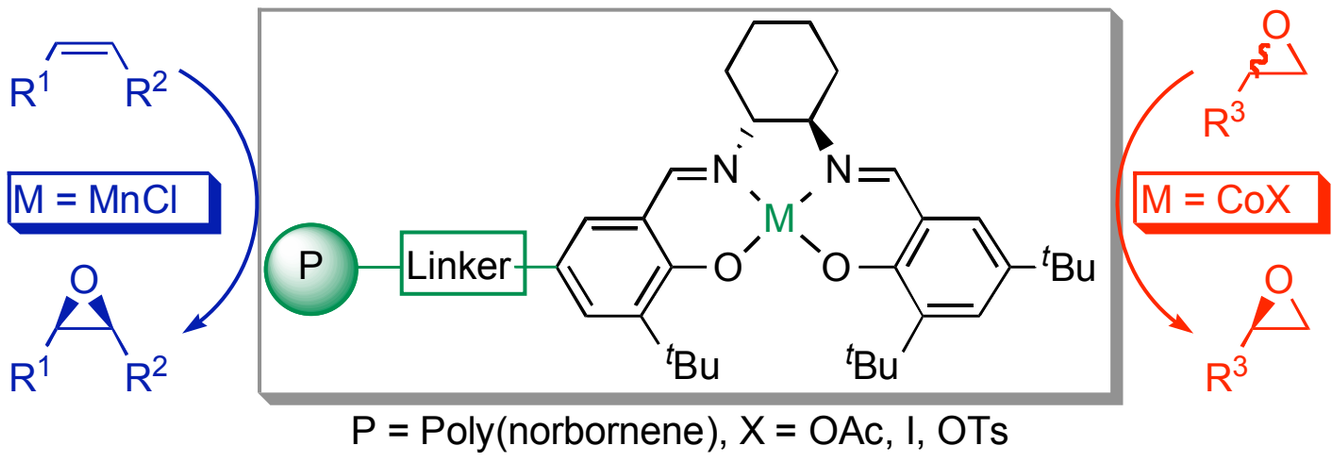


Biomaterials



Weck Group

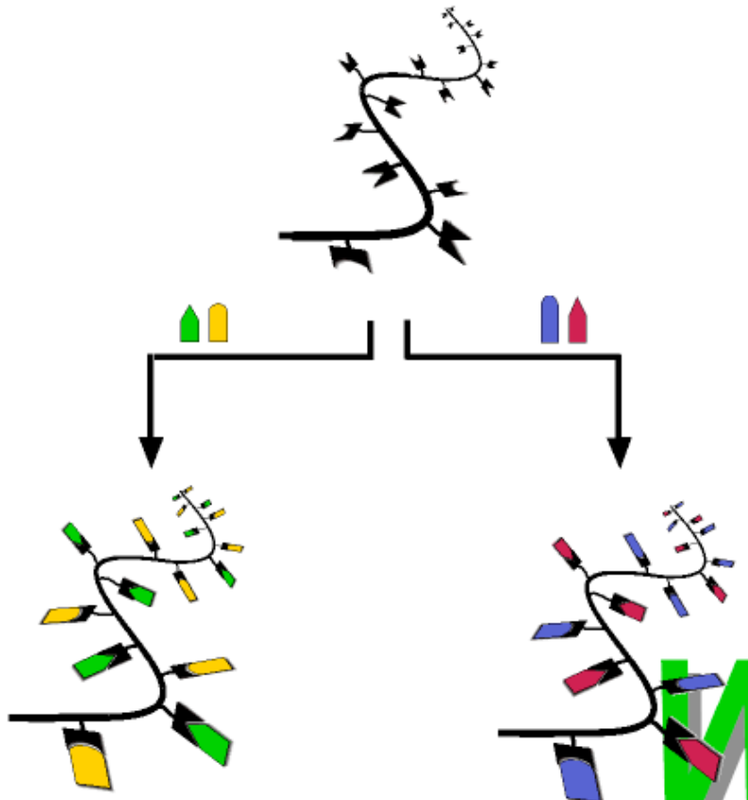
Catalysis



P = Poly(norbornene), X = OAc, I, OTs

Materials Science

Polymer Methodology



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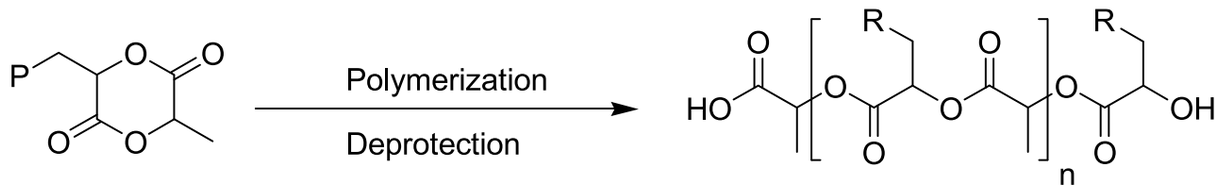

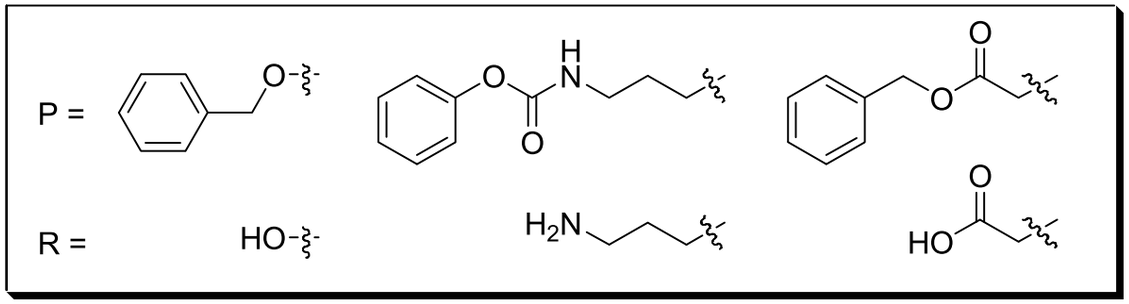

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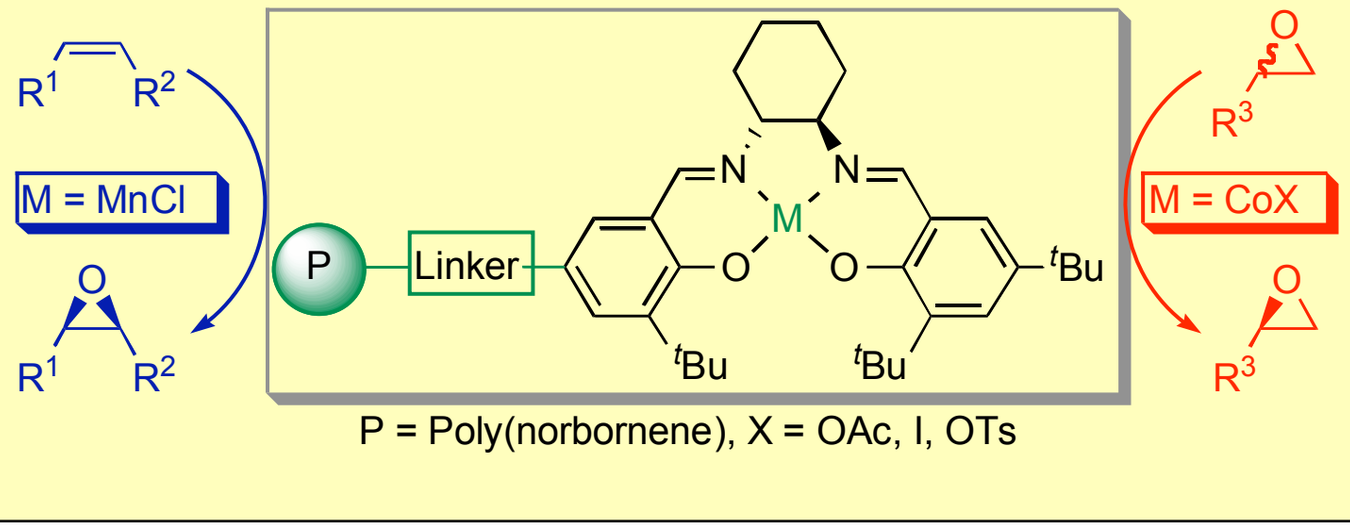

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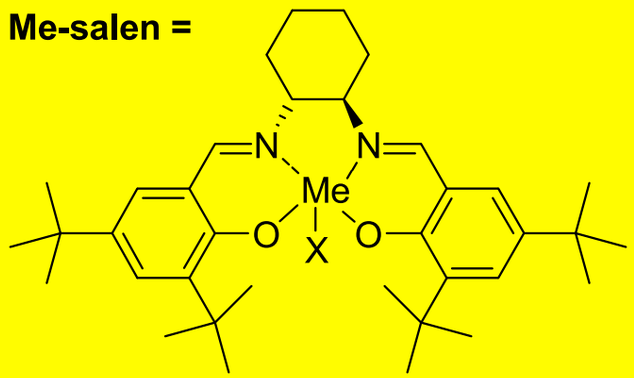
Materials Science

Our 'Work Horse': Salen Complexes in Catalysis

Me-salen =



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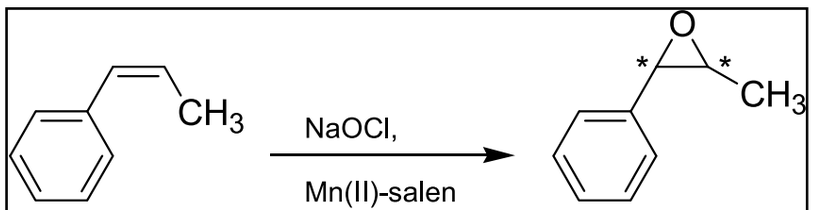

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Asymmetric ring opening (ARO)

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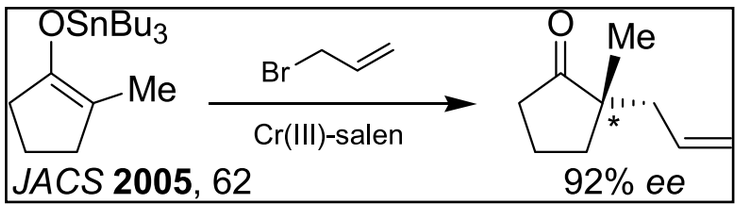

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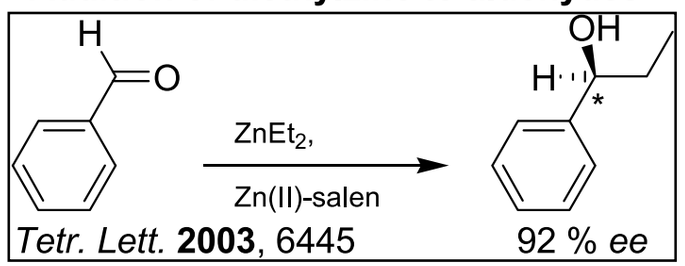
Addition of diethylzinc to aldehydes



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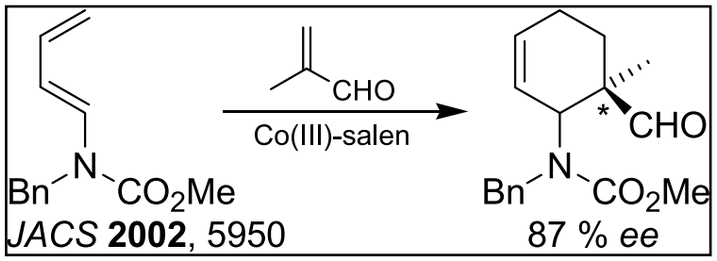

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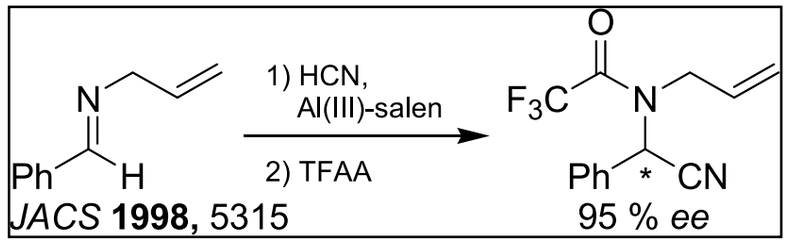
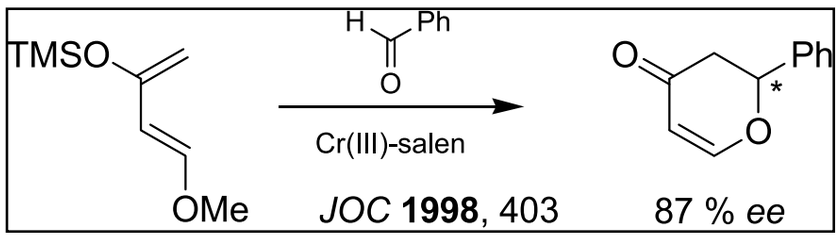


JACS **1998,** 5315 — 95 % *ee*

Hetero Diels-Alder reactions



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Other reactions, e.g.

- Conjugated addition of weakly acidic nucleophiles
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- Oxidations of sulfides
- ...

Chem. Soc. Rev. **1999**, 85
Topics Organomet. Chem. **2004**, 123

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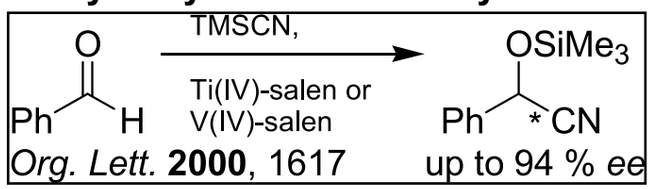

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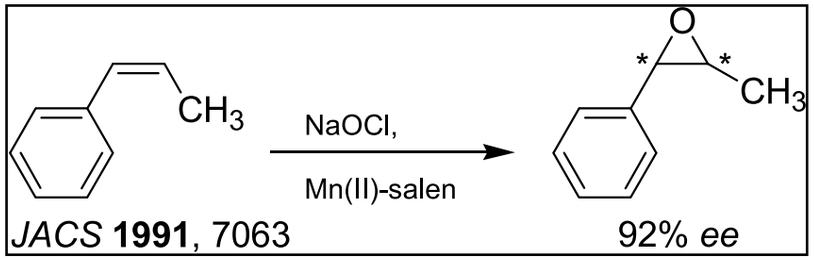

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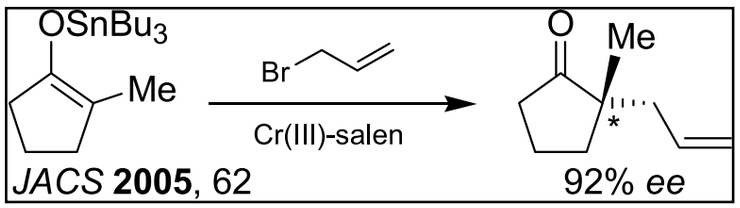

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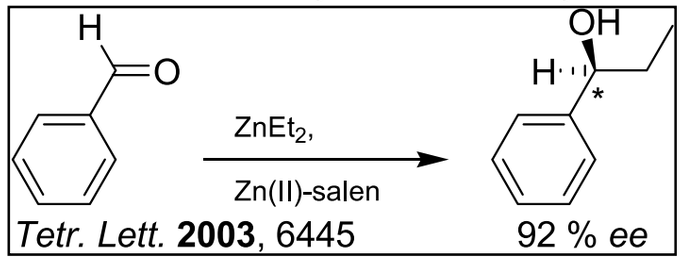

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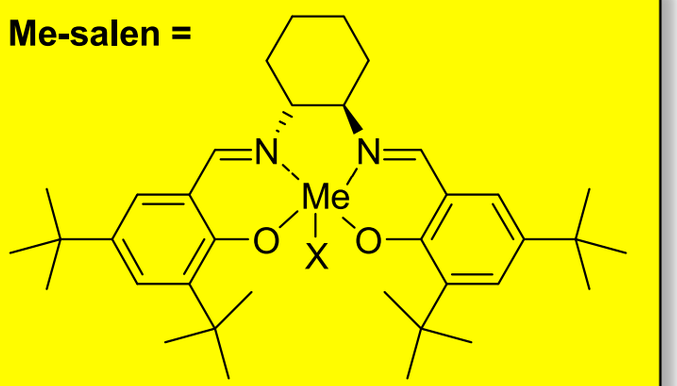

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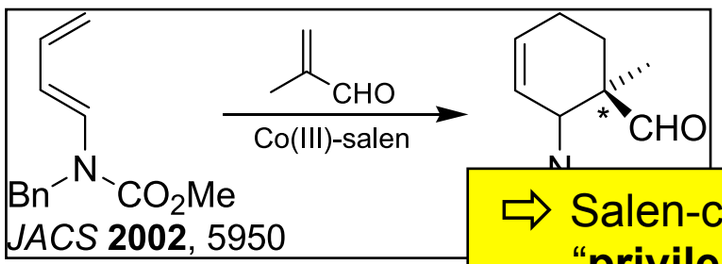

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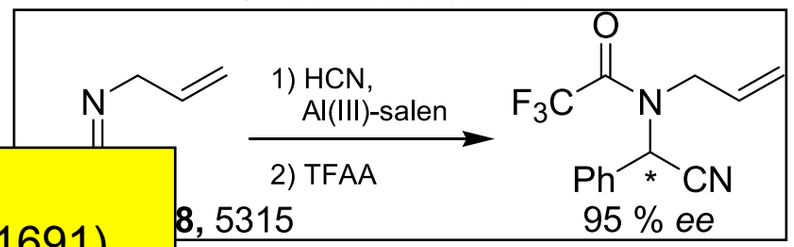

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⇨ Salen-complexes (like BINOL, BINAP, PyBox, …) are "**privileged catalysts**" (Jacobsen *et al.*, *Science* **2003**, 1691)

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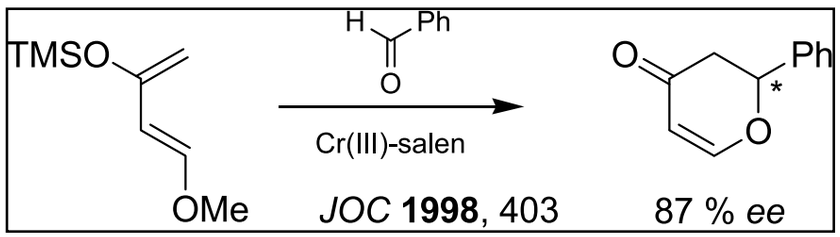

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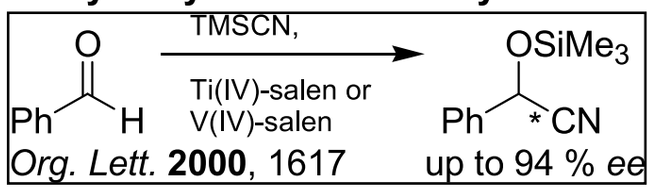

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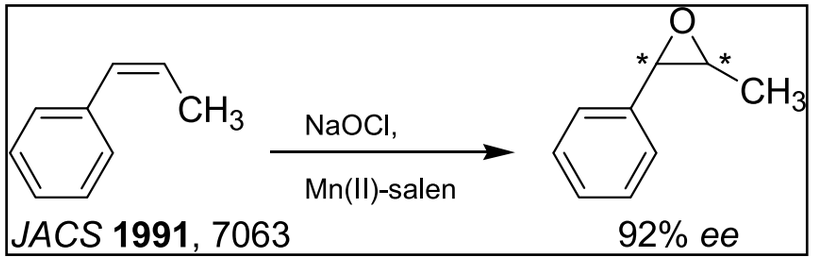

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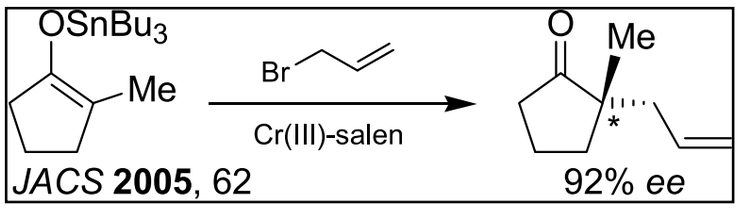

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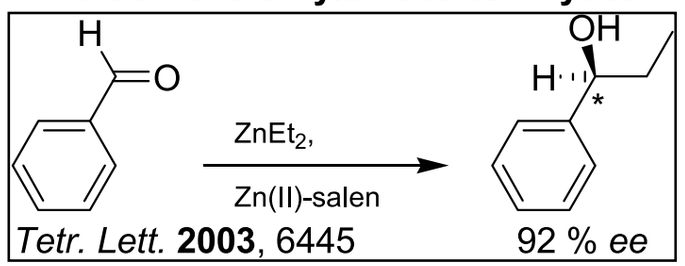

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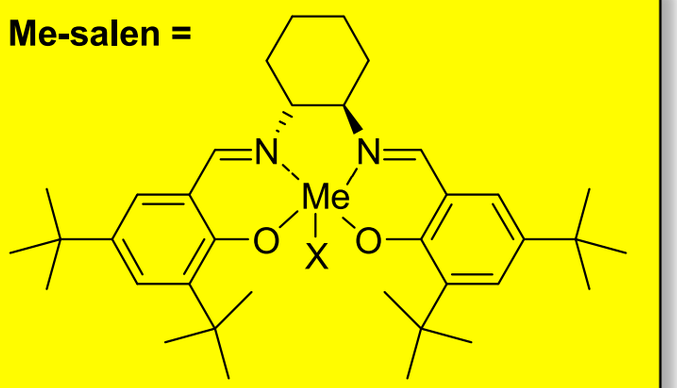

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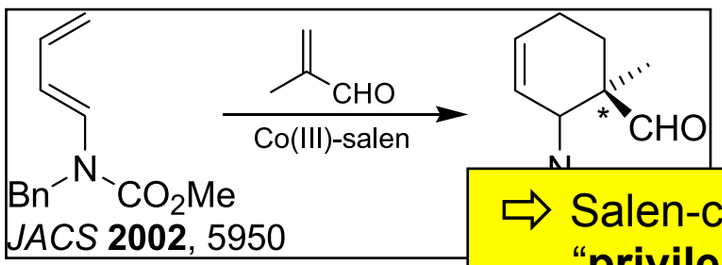

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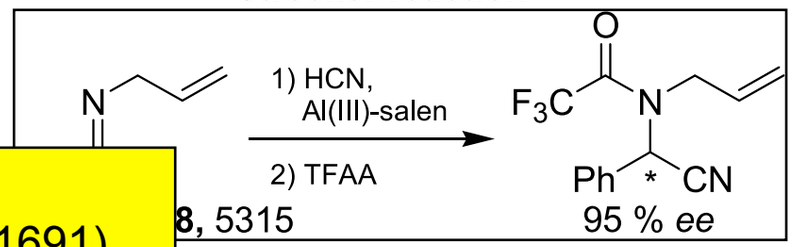

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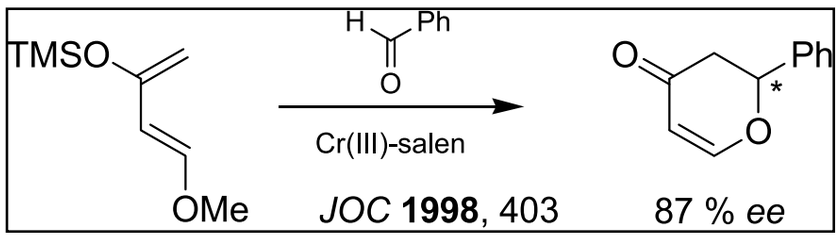

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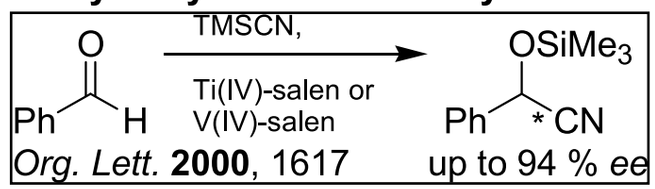

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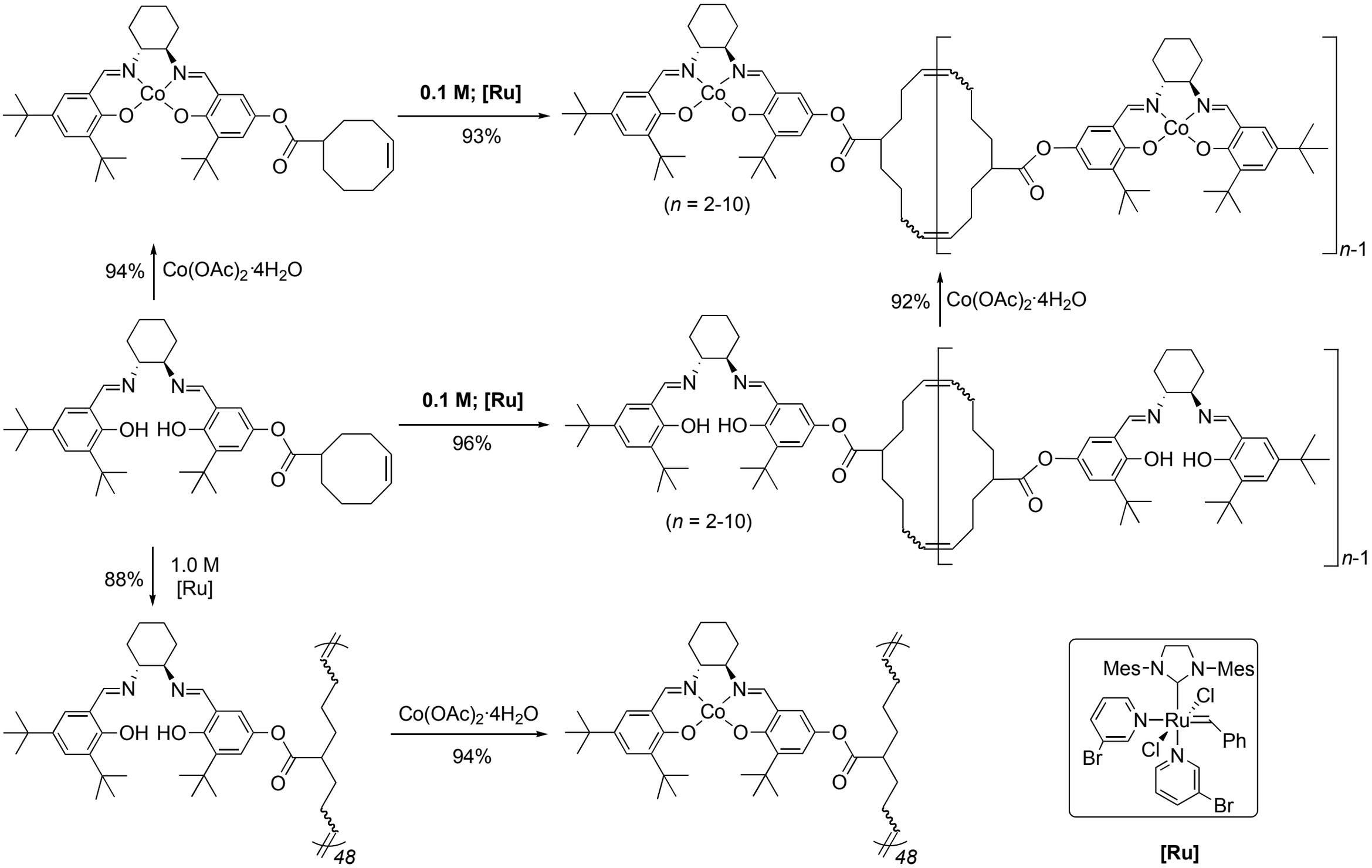
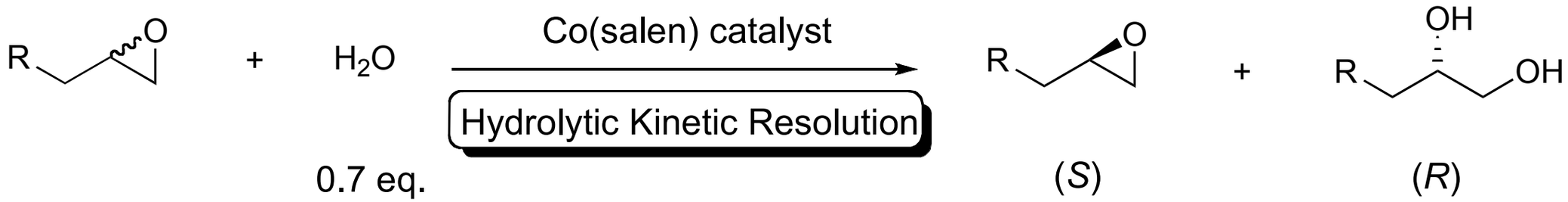
Cyclic Versus Linear



Zheng, Jones, and Weck *J. Am. Chem. Soc.* **2007**, 1105-1112

Catalytic Activity of Cyclic Co-Salen Catalysts

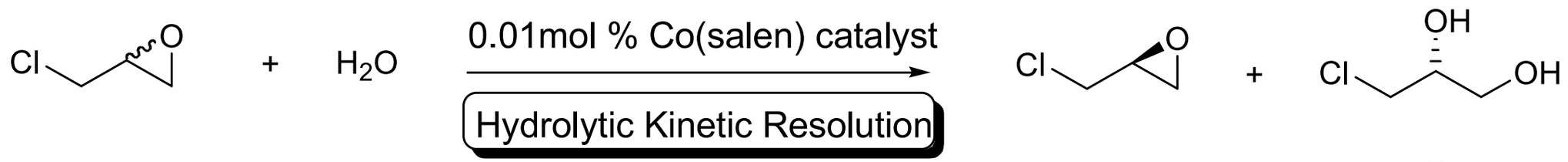


Entry	R	Loading (mol%)	Time (h)	*ee* (%)	Yields (%)
1	*n*-Bu	0.01	2	>99	44
2	CH_2Cl	0.01	2.5	>99	43
3	$CH_2OAllyl$	0.01	6	>99	48
4	CH_2OPh	0.01	6	>99	46
5	Ph	0.1	18	>99	48
7	*t*-Bu	0.25	48	98	42

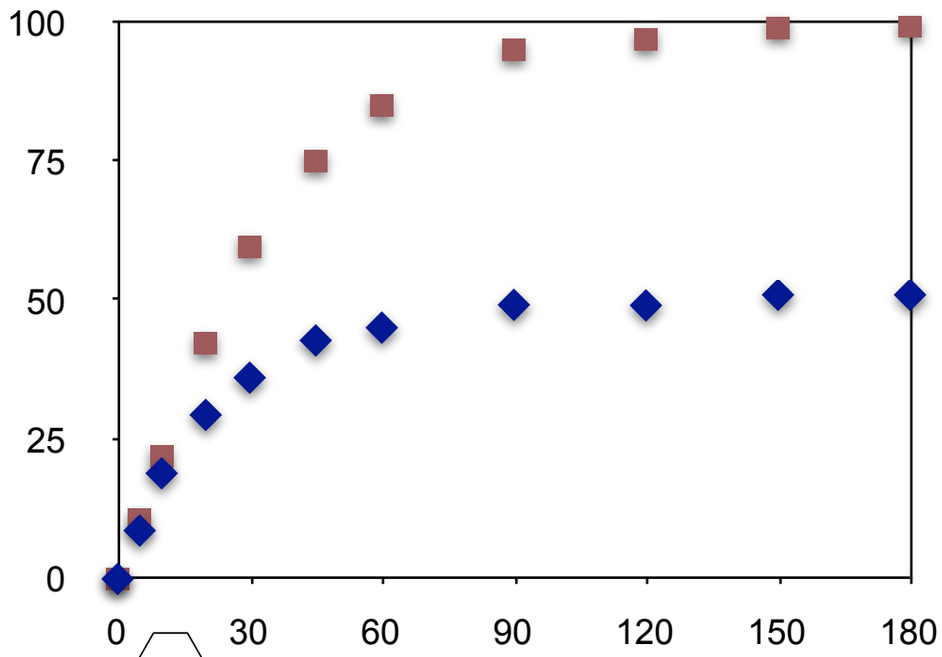
⇨ Most active unsymmetric Co-salen HKR catalyst to date

Zheng, Jones, and Weck *J. Am. Chem. Soc.* **2007**, 1105-1112

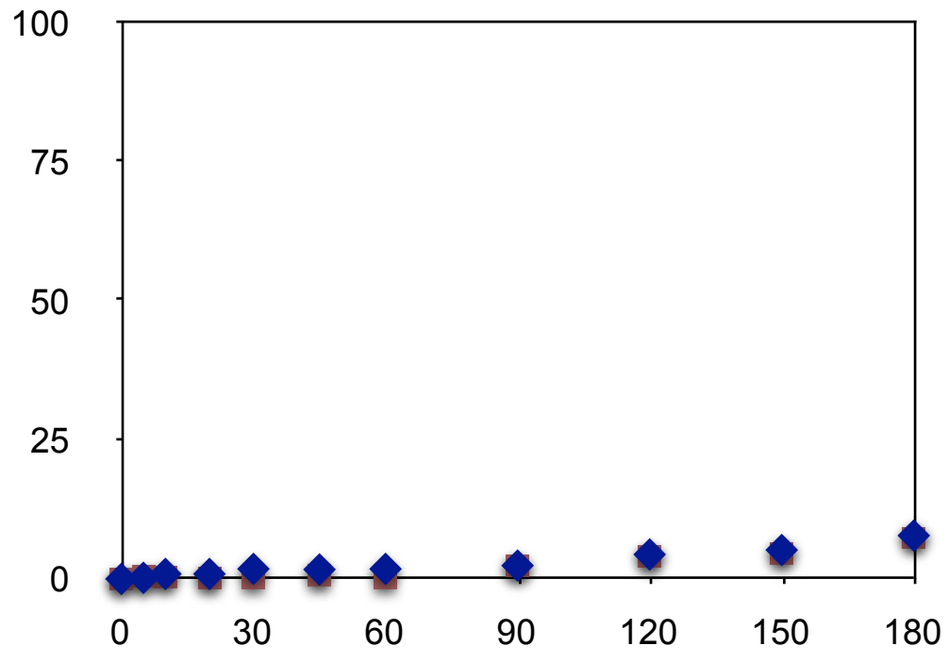
Comparison Between Cyclic Oligomers and the Monomer



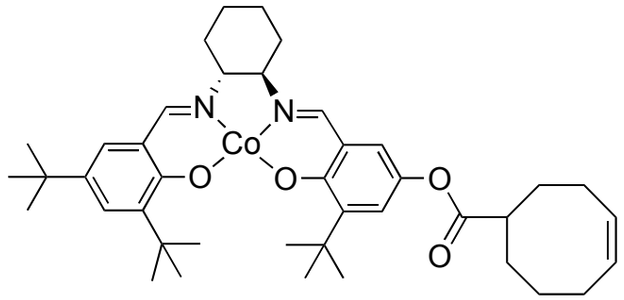
(*rac*)-epichlorohydrin 0.6 eq.



(*S*)



(*R*)



- Non-oligomeric species not as active ⇨ polymer effect
- Linear polymeric catalyst only half as active as cyclic one

Zheng, Jones, and Weck *J. Am. Chem. Soc.* **2007**, 1105-1112

Supported Salen Summary

- Highly active and selective supported salen catalysts have been synthesized using a variety of polymeric supports
- Strong dependance of catalyst site density along the support on the catalyst activity
- Poly(styrene)-based catalysts can be recycled
- Investigated the first 'ROMP' that yields 100% cyclic oligomers
- Cyclic oligomer catalysts significant more active and selective that their homogeneous and polymeric analogues
- Cyclic oligomer catalysts are the most active and selective unsymmetrically substituted Co-salen catalysts to date
- The polymeric enhancement has been also demonstrated using Al-salen catalysts suggesting a general principle for bimetallic pathways
- Developed basic structure property relationships between support (polymer) and the catalytic moiety (linker length, copolymers)