

Vinylcyclopropane Pyrrolidone Polymers

Free radical polymerization of vinylcyclopropanes(VCP) is well known. Some of the driving interest is the fact that such polymerizations result in volume expansion rather than contraction as in regular free radical polymerizations. This is of great importance in dental applications; however, VCP's are very useful monomers for a variety of other applications.

Can VCP be combined with the pyrrolidone functionality?

Synthesis of cyclopropanes is well documented in several reviews and a wide variety of structures are possible, for example:

Lebel, H., Marcoux, J. F., Molinaro, C., & Charette, A. B. (2003). Stereoselective cyclopropanation reactions. *Chemical Reviews*, 103(4), 977-1050.

Lautens, M., Klute, W., & Tam, W. (1996). Transition metal-mediated cycloaddition reactions. *Chemical reviews*, 96(1), 49-92.

Wong, H. N., Hon, M. Y., Tse, C. W., Yip, Y. C., Tanko, J., & Hudlicky, T. (1989). Use of cyclopropanes and their derivatives in organic synthesis. *Chemical Reviews*, 89(1), 165-198.

Pellissier, H. (2008). Recent developments in asymmetric cyclopropanation. *Tetrahedron*, 64(30-31), 7041-7095.

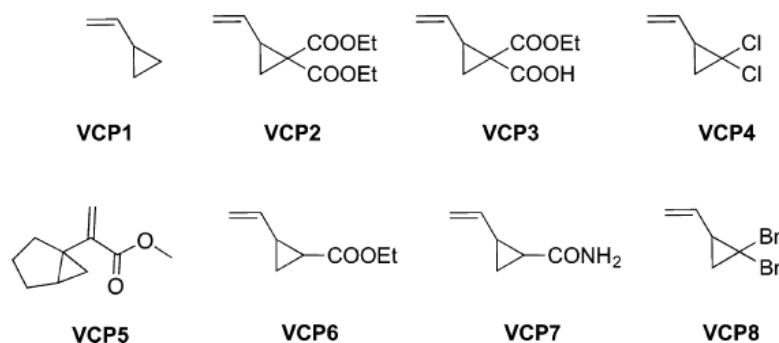
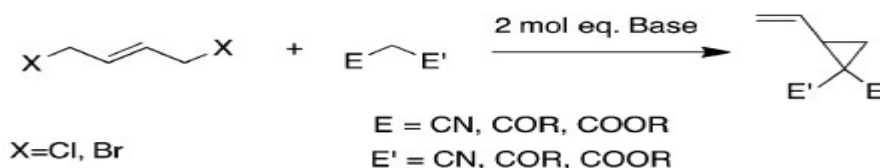


Figure 7. Structures of several vinyl cyclopropane reported in the literature.

Synthesis:



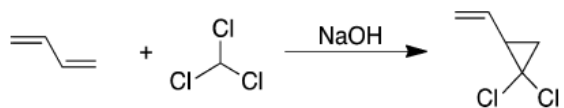


Figure 49. Synthesis of 1,1-dichloro-2-vinyl cyclopropane VCP4.

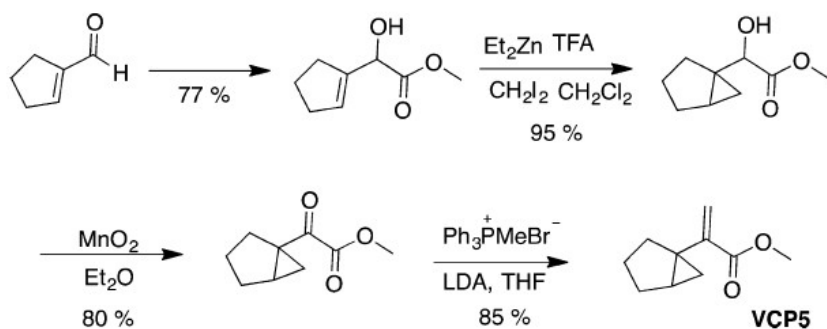


Figure 50. Preparation of methyl 2-(bicyclo[3.1.0]hex-1-yl)acrylate VCP5.

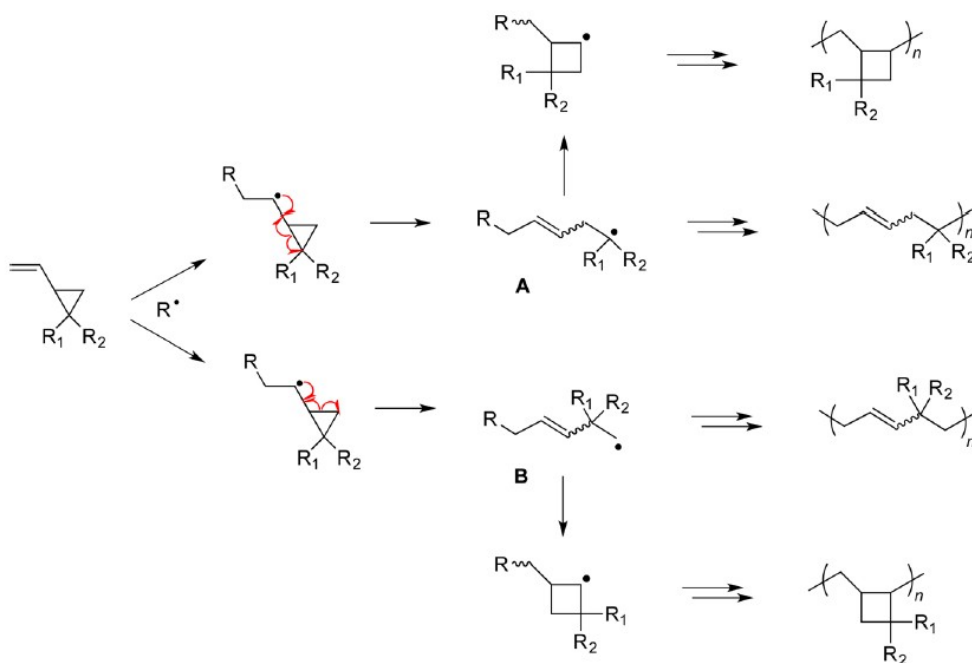


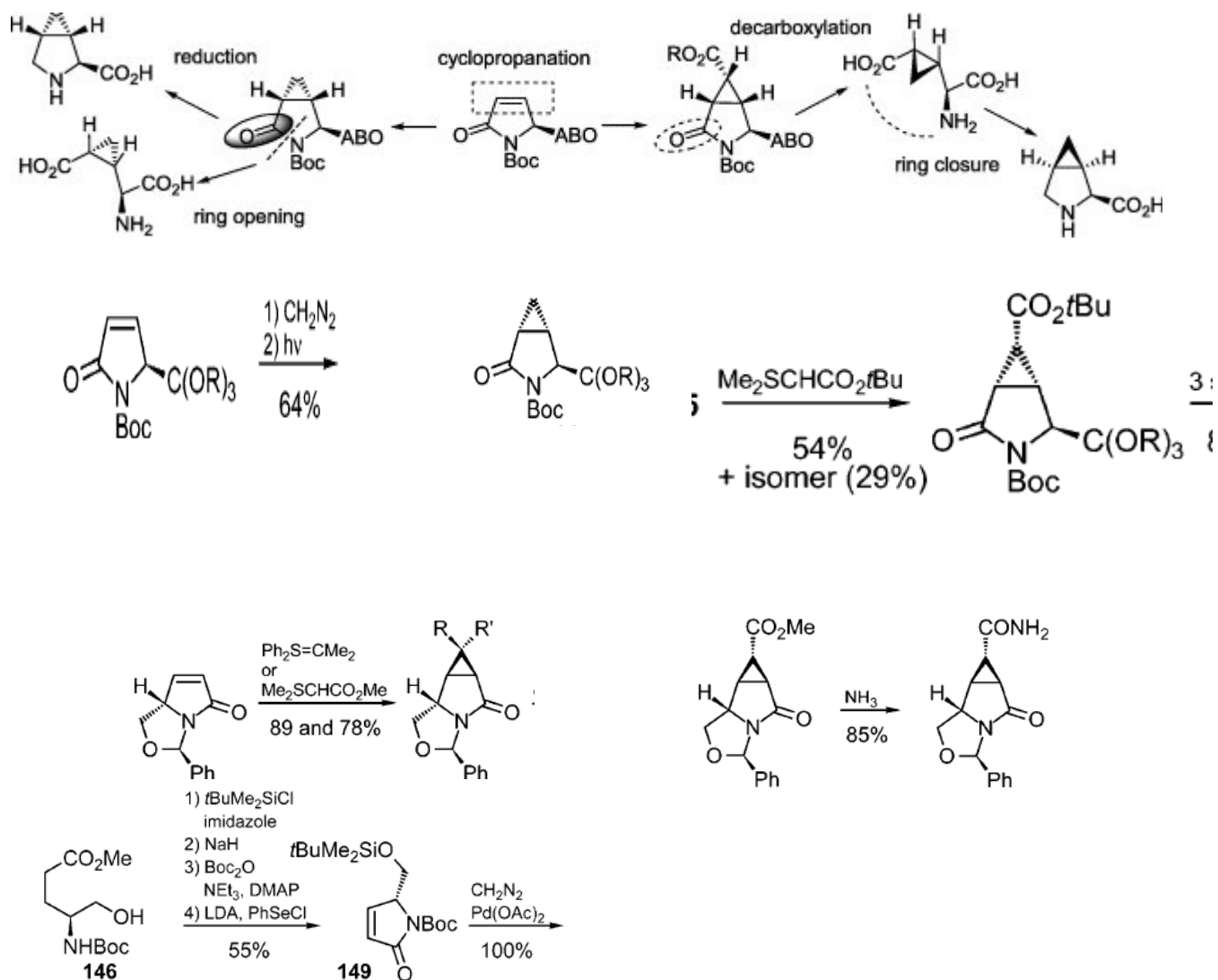
Figure 51. Different polymer repeat units that are formed during the rROP of 1,1-disubstituted-2-vinyl cyclopropane.

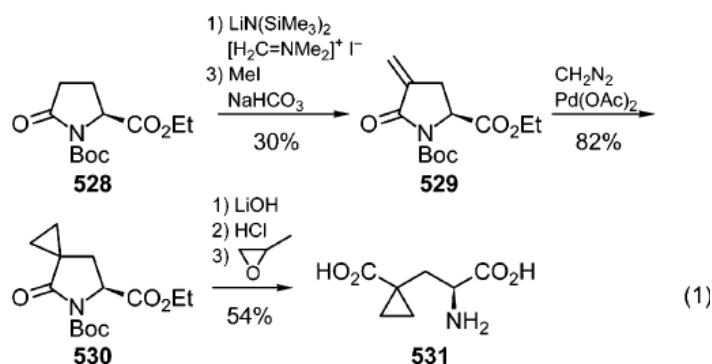
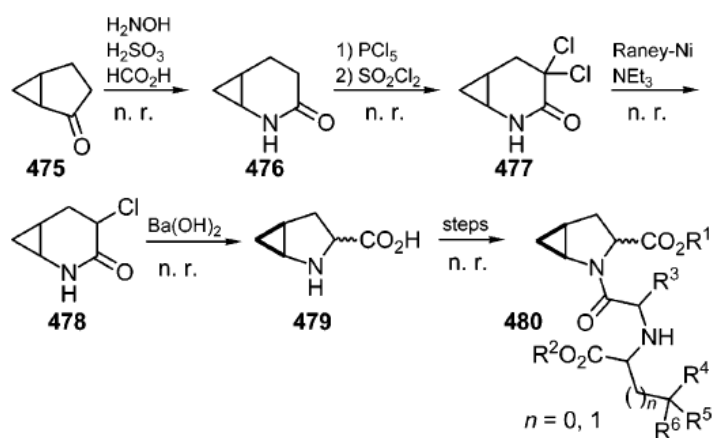
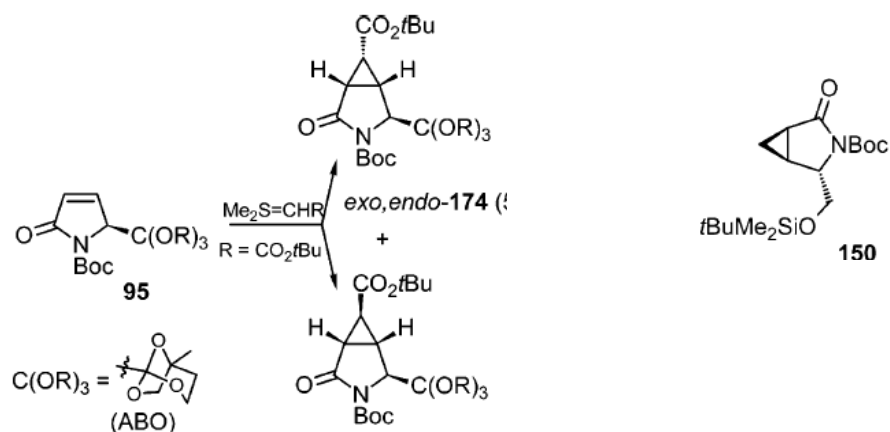
Tardy, A., Nicolas, J., Gimes, D., Lefay, C., & Guillaenuef, Y. (2017). Radical ring-opening polymerization: Scope, limitations, and application to (bio) degradable materials. *Chemical reviews*, 117(3), 1319-1406.

The above reference is very detailed and well worth reading! I presented a few charts above to highlight its value. Fig. 51 illustrates the possibility of having cyclobutanes in the polymer backbone; however, the 1,5 linear version predominates especially if the

intermediate radical can be stabilized by an adjacent group.

I now present several examples to highlight the chemistry involved, then my proposals for your consideration.

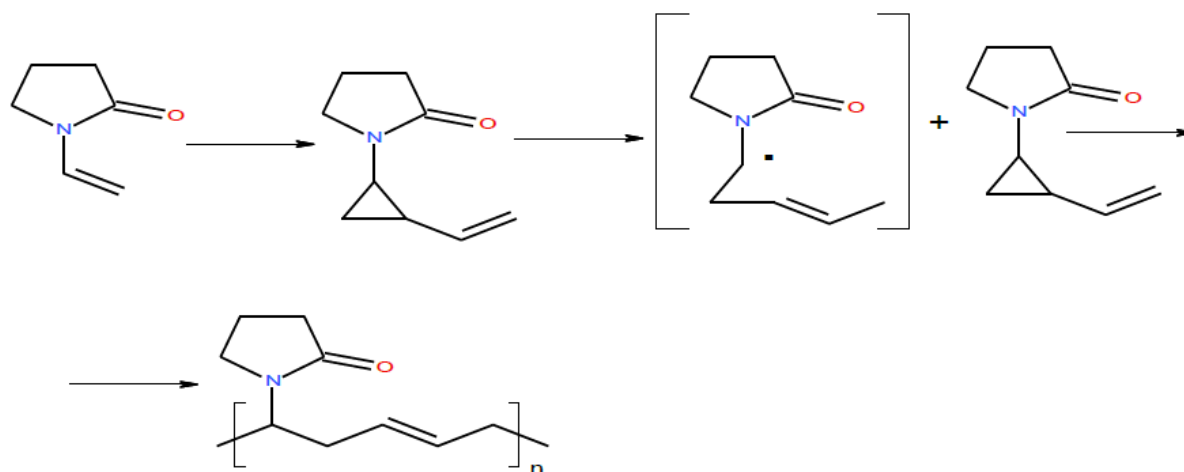




Brackmann, F., & de Meijere, A. (2007). Natural occurrence, syntheses, and applications of cyclopropyl-group-containing α -amino acids. 2, 3, 4- and 4, 5-methanoamino acids. *Chemical reviews*, 107(11), 4538-4583.

The above sequences led me to think of other potential VCP applications containing pyrrolidones.

For example:

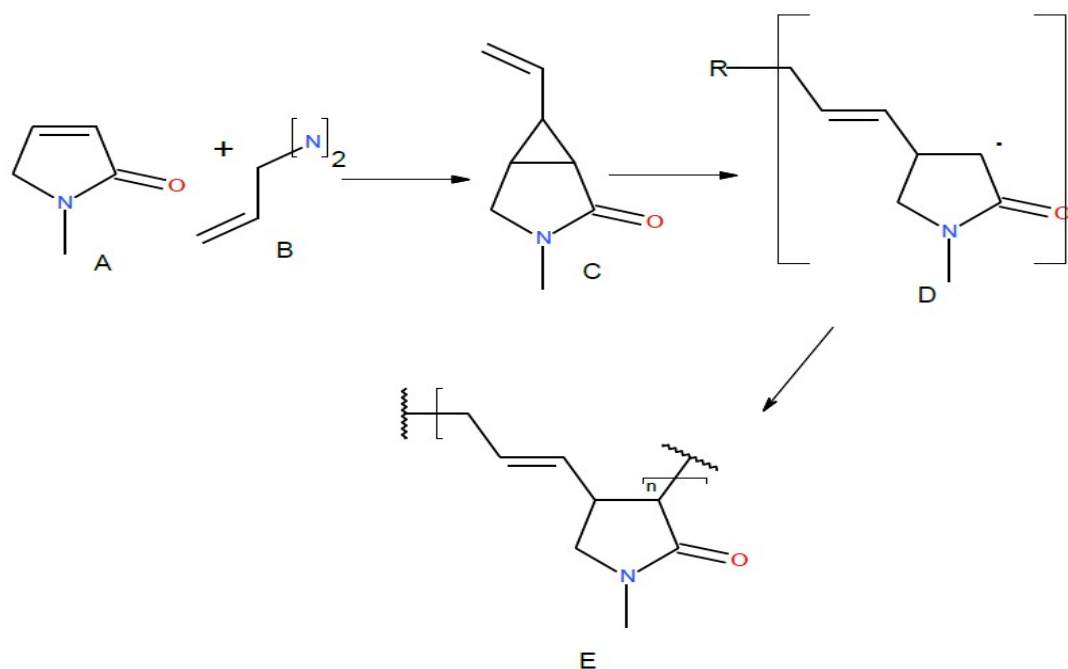


Scheme 1: N-Vinylpyrrolidone(VP) converted to a VCP could place the pyrrolidone group on the polymer backbone with a flexible 1-5 unsaturated alkene. Since this VCP like most of the other VCPs can be copolymerized by free radical mechanism with other monomers or with VP itself. PVP homopolymers form hard if not brittle films on dry down. Adding some percentage of this VCP would conceivably reduce this hardness making such copolymers of greater cosmetic value.

I also point out that VP itself readily polymerizes because the forming free radical intermediate is stabilized by the pyrrolidone nitrogen hence with the VCP version the 1-5 unsaturated polymer should be the only product instead of any cyclobutanes for the same reason.

Sanda, F., Takata, T., & Endo, T. (1993). Radical ring-opening polymerization of α -cyclopropylstyrenes. Polymerization behavior and mechanistic aspects of polymerization by the molecular orbital method.

Macromolecules, 26(21), 5748-5754.



Scheme 2: This proposal illustrates what I believe is doable chemistry. Instead of B other synthesis methods might also work. FR polymerization would produce E.

Pellissier, H. (2008). Recent developments in asymmetric cyclopropanation. *Tetrahedron*, 64(30-31), 7041-7095.

[https://scholar.google.com/scholar?](https://scholar.google.com/scholar?hl=en&as_sdt=0%2C48&q=Recent+developments+in+asymmetric+cyclopropanation&btnG=)

[hl=en&as_sdt=0%2C48&q=Recent+developments+in+asymmetric+cyclopropanation&btnG=](https://scholar.google.com/scholar?hl=en&as_sdt=0%2C48&q=Recent+developments+in+asymmetric+cyclopropanation&btnG=)

Lebel, H., Marcoux, J. F., Molinaro, C., & Charette, A. B. (2003). Stereoselective cyclopropanation reactions. *Chemical Reviews*, 103(4), 977-1050.

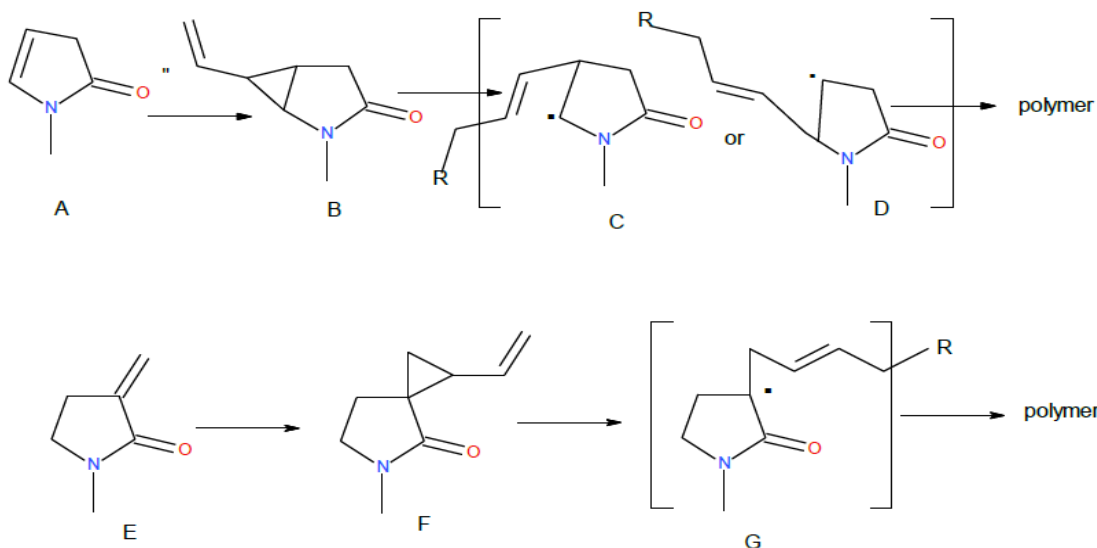
Post reaction of the polymeric backbone unsaturation is also possible.

Ntoukam, D. H. S., Mutlu, H., & Theato, P. (2020). Post-polymerization modification of Poly (vinylcyclopropanes): A potential route to periodic copolymers. *European Polymer Journal*, 122, 109319.

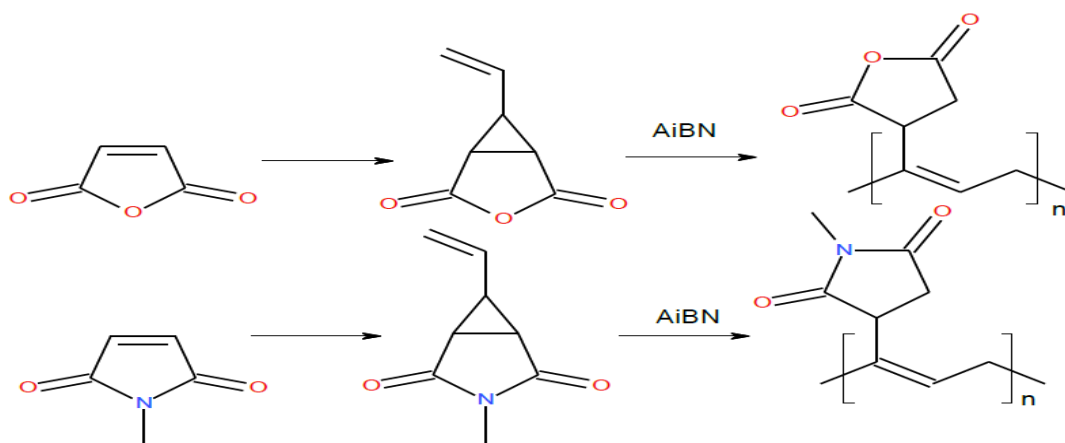
These FR polymerizations require standard FR catalysts such as AIBN etc. Having the FR intermediate radical next to nitrogen is probably the major pathway for this polymerization. Such stabilizing groups should prevent cyclobutanes from forming.

Sanda, F., Takata, T., & Endo, T. (1993). Radical ring-opening polymerization of α -cyclopropylstyrenes. Polymerization behavior and mechanistic aspects of polymerization by the molecular orbital method.

Macromolecules, 26(21), 5748-5754.

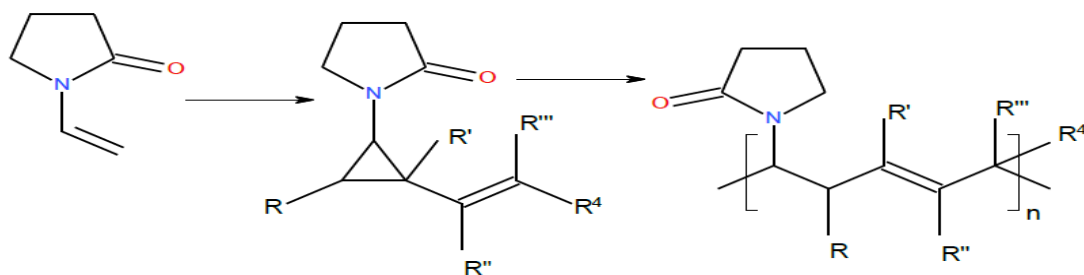


Scheme 3: Other pyrrolidone VCP possibilities.



Scheme 4: Why not employ maleic anhydride or the imide? Such polymers with the proper N-R groups might have applications in biochemistry. This again suggests to me the possibility for Gantrez Man/MVE resins(Ashland) employed as hair fixatives and false teeth adhesives such copolymerization with maleic anhydride and MVE might afford new possibilities by incorporation of flexible alkylene groups,

Review of Cyclopropane Synthesis:



Scheme 5: Possibilities for derivatives of just this VCP. To synthesize any or all of these derivatives will require extensive research beginning with the following methods.

To give you an idea of the extensive VCP synthesis literature I'm reviewing some of its literature, I thought it would be worth while to review those references that I found interesting. I selected examples to show but they are just the tip of the iceberg and please read the reference themselves!

Name reactions:

Simmons-Smith Cyclopropanation

Corey-Chaykovsky Cyclopropanation

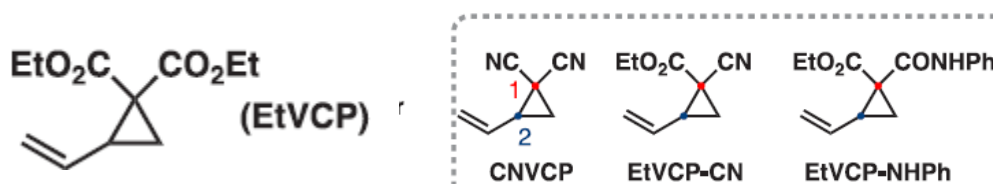
Kulinkovich Reaction

Vinylcyclopropane-Cyclopentene Rearrangement

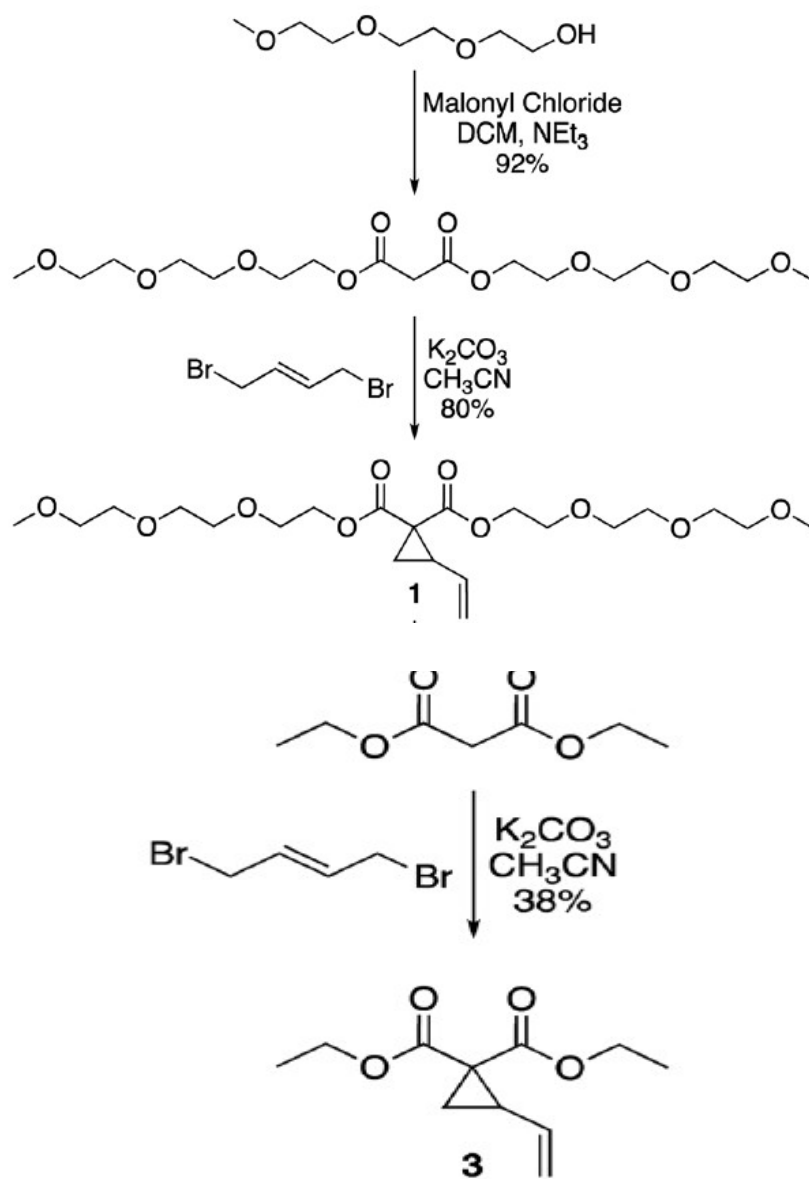
Buhner Method Ring Expansion

Regitz Diazo Transfer

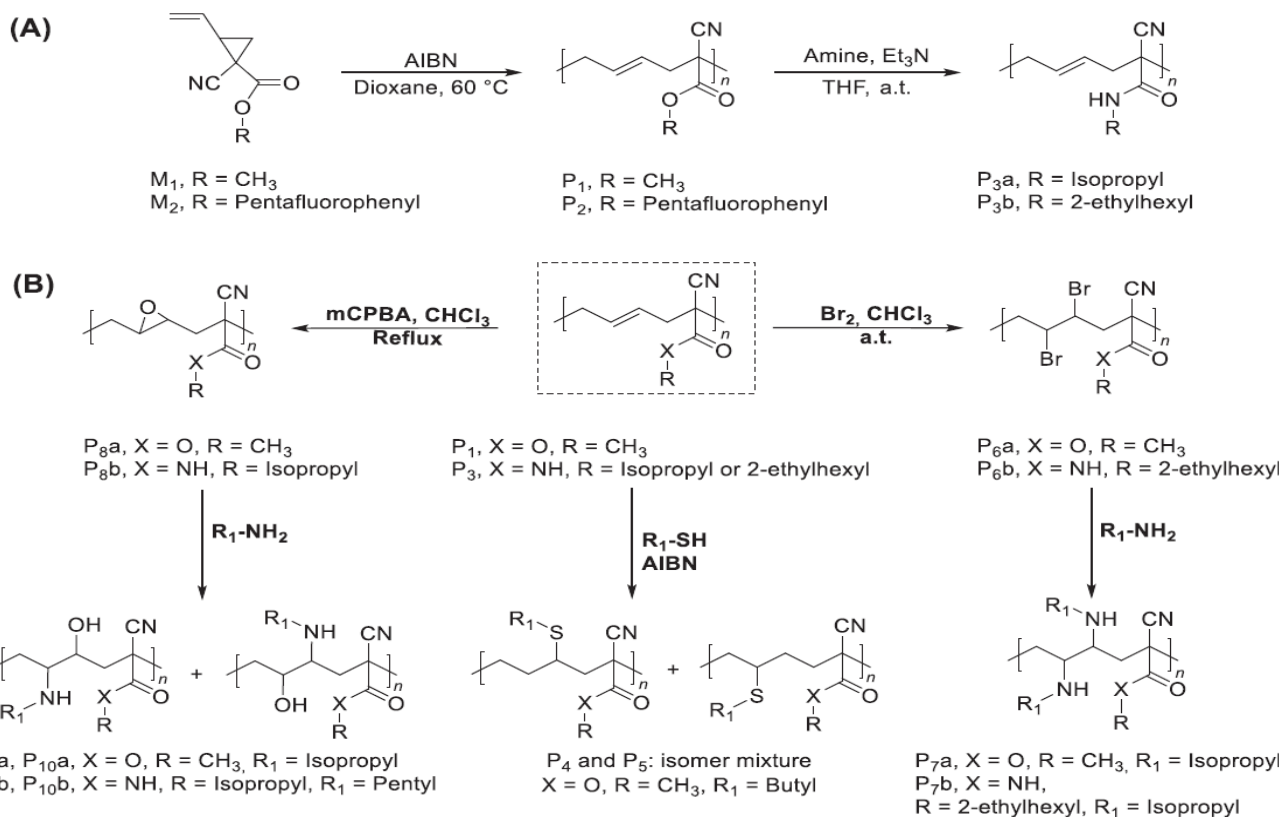
<https://www.organic-chemistry.org/namedreactions/>



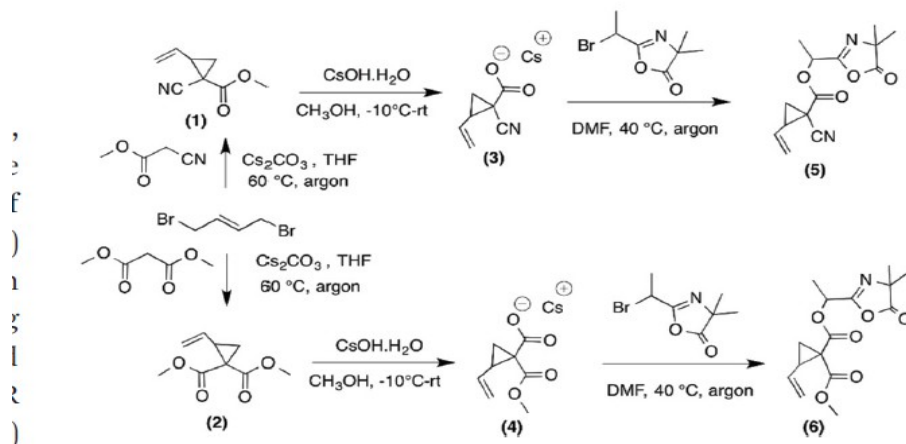
Chen, D. F., Bernsten, S., & Miyake, G. M. (2020). Organocatalyzed Photoredox Radical Ring-Opening Polymerization of Functionalized Vinylcyclopropanes. *Macromolecules*, 53(19), 8352-8359.



Stanojkovic, J., Oh, J., Khan, A., & Stuparu, M. C. (2020). Synthesis of thermoresponsive oligo (ethylene glycol) polymers through radical ring-opening polymerization of vinylicyclopropane monomers. *RSC Advances*, 10(4), 2359-2363.

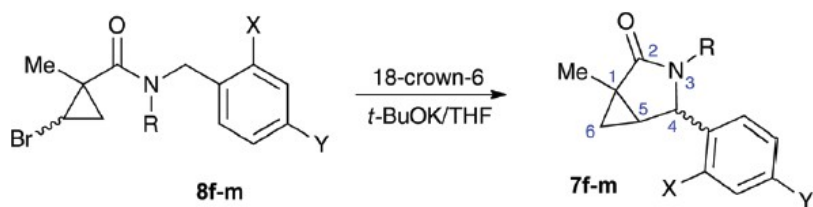


Ntoukam, D. H. S., Mutlu, H., & Theato, P. (2020). Post-polymerization modification of Poly (vinylcyclopropanes): A potential route to periodic copolymers. *European Polymer Journal*, 122, 109319.



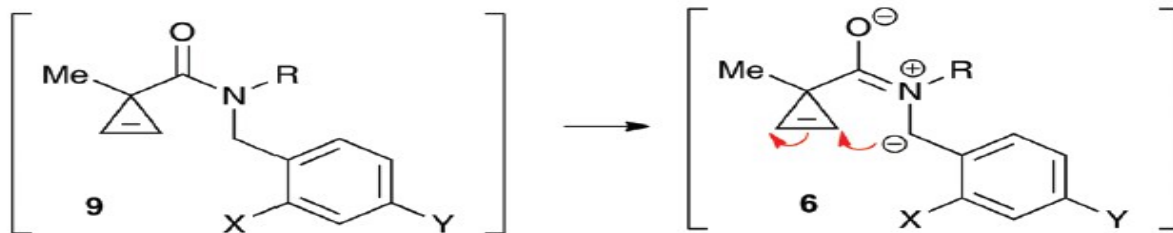
Scheme 1 Synthesis of azlactone-functionalized vinylcyclopropanes (5) and (6).

Montembault, V., Rollet, M., Aboudou, S., Mabrouk, K., Pascual, S., Fontaine, L., ... & Phan, T. T. (2020). Radical ring-opening polymerization of novel azlactone-functionalized vinyl cyclopropane. *Polymer Chemistry*.



8f, 7f: R = *n*-Bu, X = Y = H;
8g, 7g: R = *i*-Pr, X = Y = H;
8h, 7h: R = Cy, X = Y = H;
8i, 7i: R = *t*-Bu, X = Y = H;

8j, 7j: R = Me, X = H, Y = F;
8k, 7k: R = Me, X = Y = F;
8l, 7l: R = Me, X = Cl, Y = H;
8m, 7m: R = Me, X = F, Y = Br.



Maslivets, V., Barrett, C., Aksenov, N. A., Rubina, M., & Rubin, M. (2018). Intramolecular nucleophilic addition of carbanions generated from N-benzylamides to cyclopropenes. *Organic & biomolecular chemistry*, 16(2), 285-294.

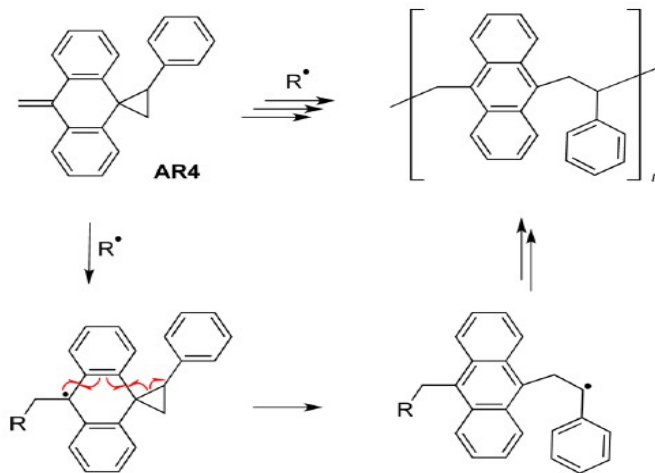
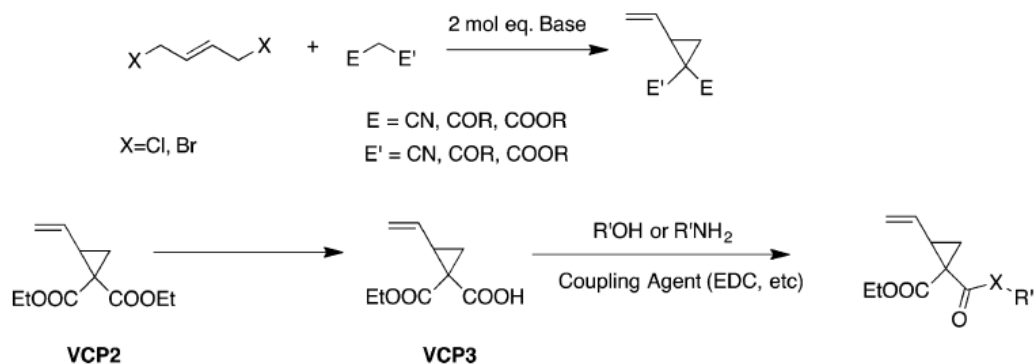
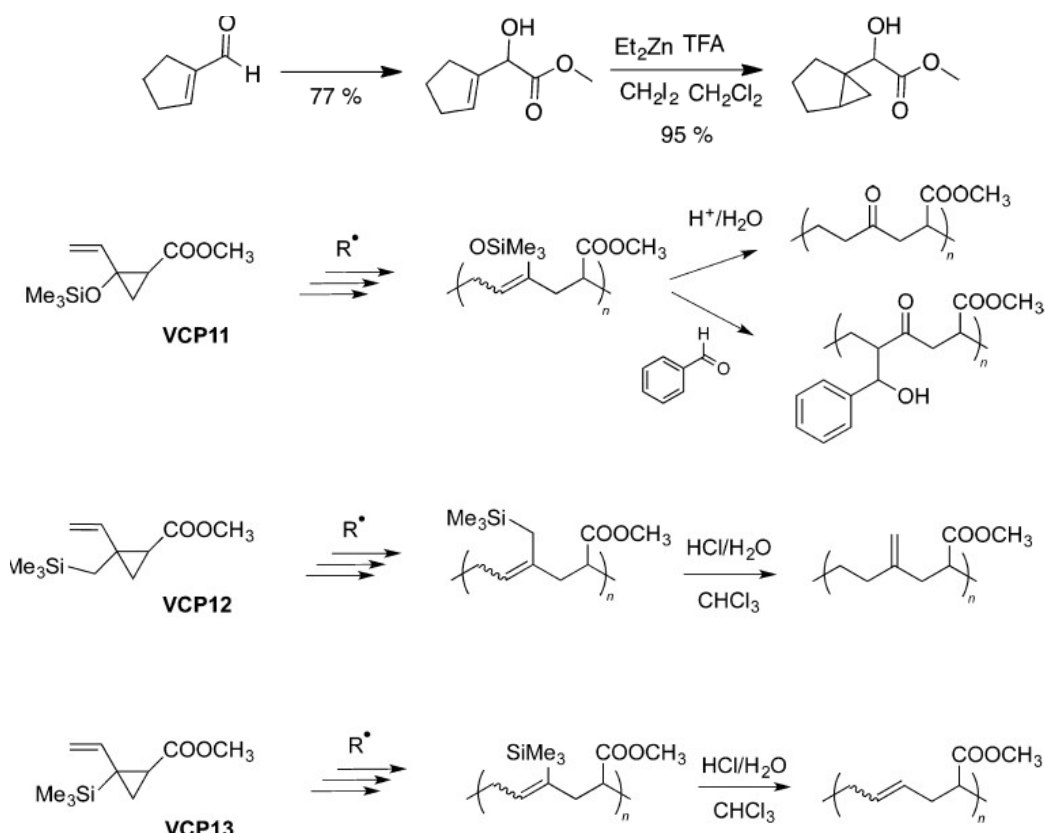
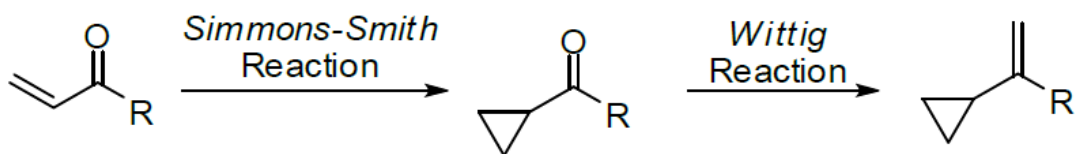


Figure 37. rROP mechanism of cyclopropane with a dihydroanthracene moiety (AR4).





Tardy, A., Nicolas, J., Gigmes, D., Lefay, C., & Guillaneuf, Y. (2017). Radical ring-opening polymerization: Scope, limitations, and application to (bio) degradable materials. *Chemical reviews*, 117(3), 1319-1406.



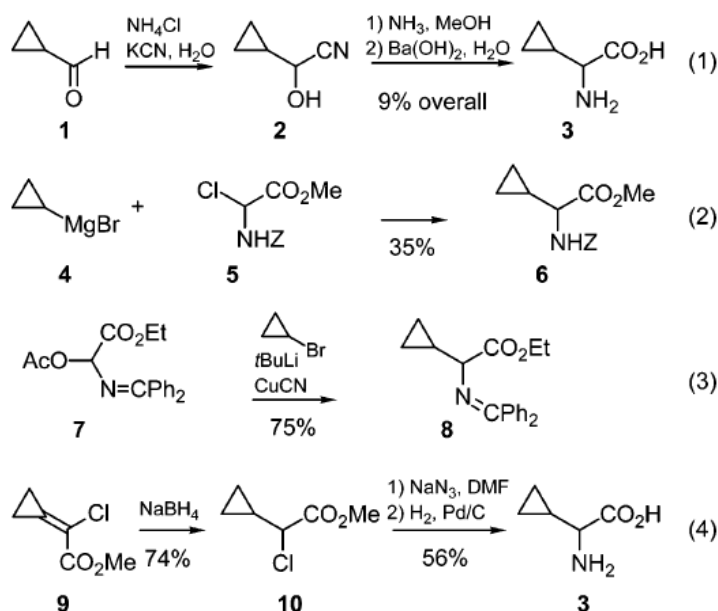
Scheme 4: Exemplary synthesis of VCPs by applying a multi-step reaction.

Contreras, P. P. (2017). *Design and Investigation of Vinylcyclopropanes (VCPs) as Fast Curing Resins* (Doctoral dissertation, Universität Bayreuth).



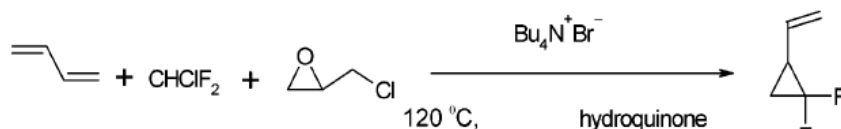
Appel, R., Hartmann, N., & Mayr, H. (2010). Scope and limitations of cyclopropanations with sulfur ylides. *Journal of the American Chemical Society*, 132(50), 17894-17900.

Scheme 1. Syntheses of Racemic Cyclopropylglycine¹²⁻¹⁶

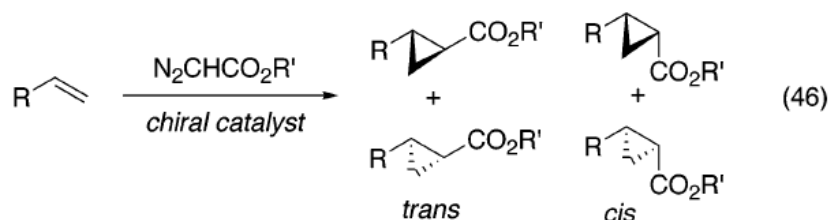
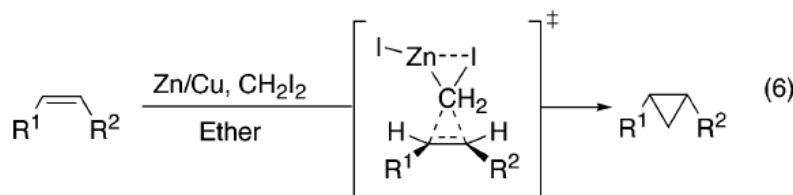
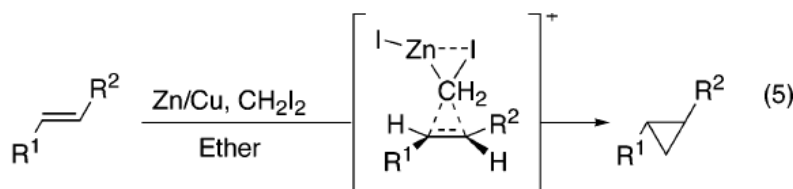


Brackmann, F., & de Meijere, A. (2007). Natural occurrence, syntheses, and applications of cyclopropyl-group-containing α -amino acids. 2, 3, 4- and 4, 5-methanoamino acids. *Chemical reviews*, 107(11), 4538-4583. This reference has numerous examples, too many to show!

Scheme 1. Synthesis of 1,1-Difluoro-2-vinylcyclopropane



Feast, W. J., Gimeno, M., & Kenwright, A. M. (2006). Synthesis and radical polymerization of 1, 1-difluoro-2-vinylcyclopropane: A reexamination and structural reassignment. *Macromolecules*, 39(12), 4076-4080.



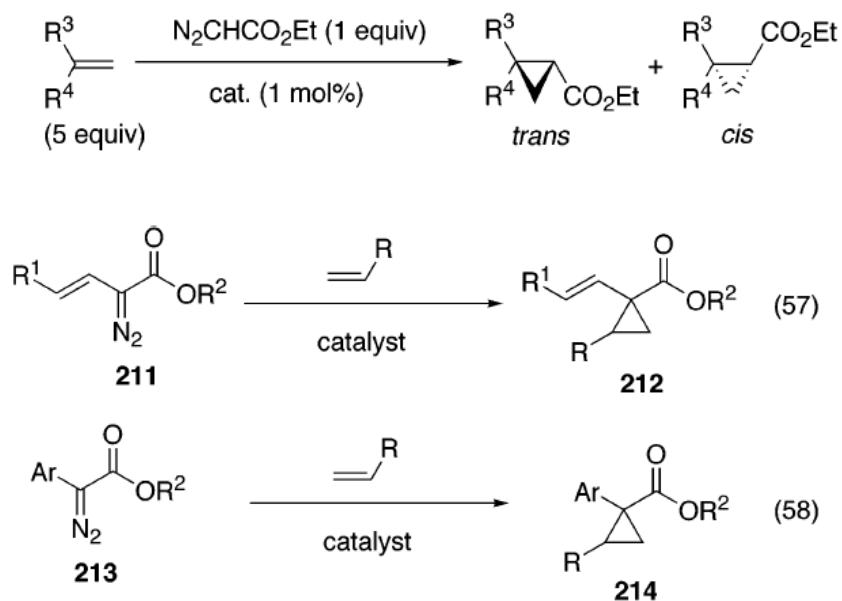


Table 31. Chiral Auxiliary in the Cyclopropanation of Rhodium-Catalyzed Vinyldiazoester Decomposition

R	dr	yield (%)
Ph	98:2	84
4-ClC ₆ H ₄	>98:2	92
4-MeOC ₆ H ₄	>98:2	75
EtO	96:4	71
AcO	95:5	42

The above are but a very small number of the numerous examples in this valuable 2003 review, Lebel, H., Marcoux, J. F., Molinaro, C., & Charette, A. B. (2003). Stereoselective cyclopropanation reactions. *Chemical Reviews*, 103(4), 977-1050.

Thank you for reading my proposals!

Dr. Robert B. Login rloginconsulting.com