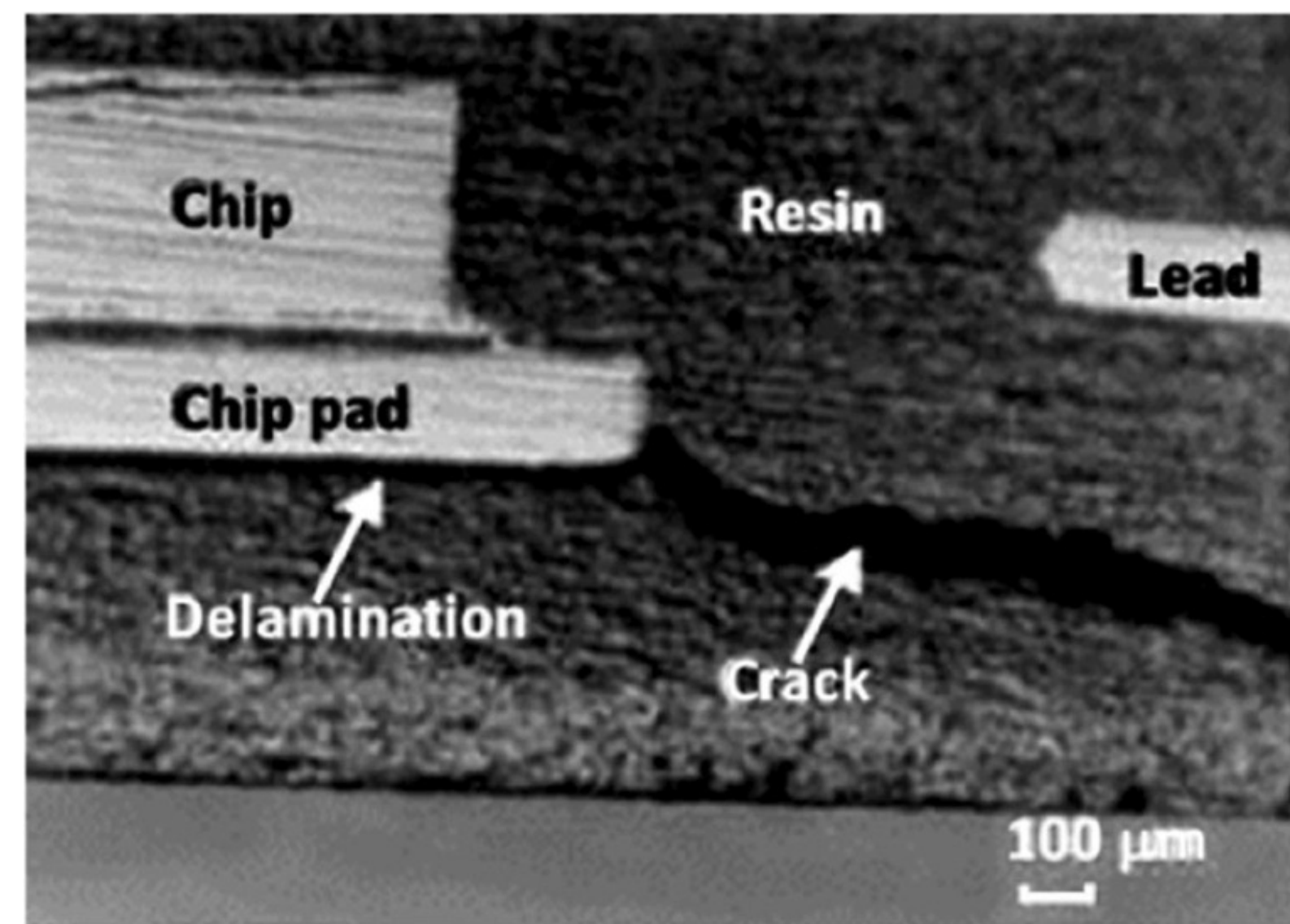




Resolving Thermal Expansion Mismatch in Epoxies

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Motivation



Material	Typical CTE Range (ppm/K)
Substrates	3-20
Unfilled epoxy	50-80
Filled epoxy (~45 vol%)	30-50

Macromolecules, 2018, 51, 8477-8485

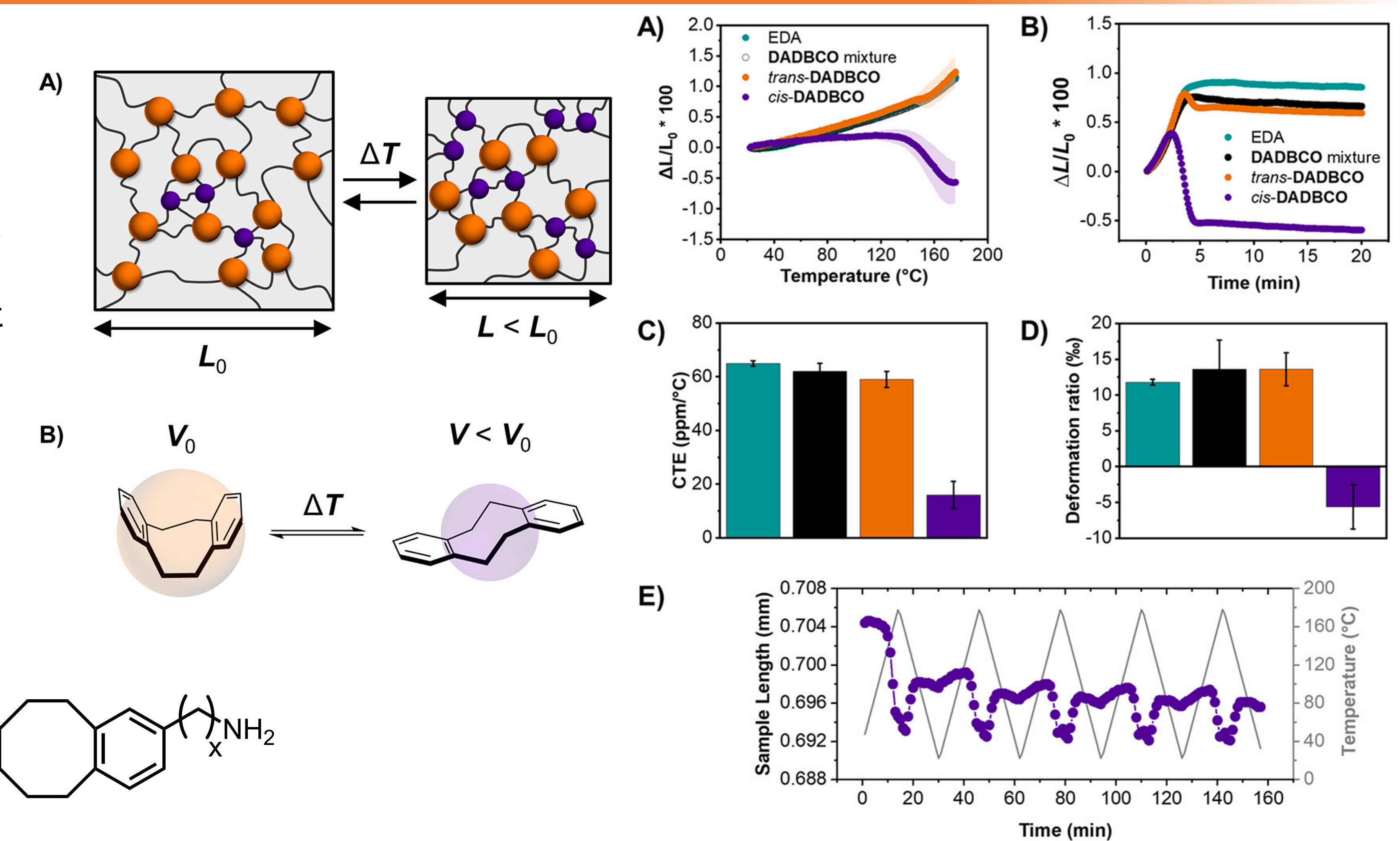
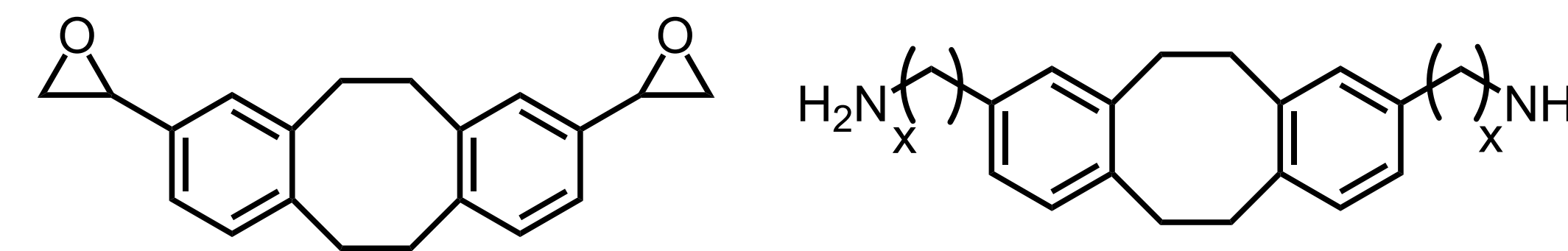
- CTE mismatch between encapsulants and underlying components often leads to cracking, delamination, or other issues.
- Attempts to mitigate this by using fillers such as mica or alumina create further issues like brittleness or stiffness.

Image from: NDT & E Int., 34, 49-56 (2001)

Approach

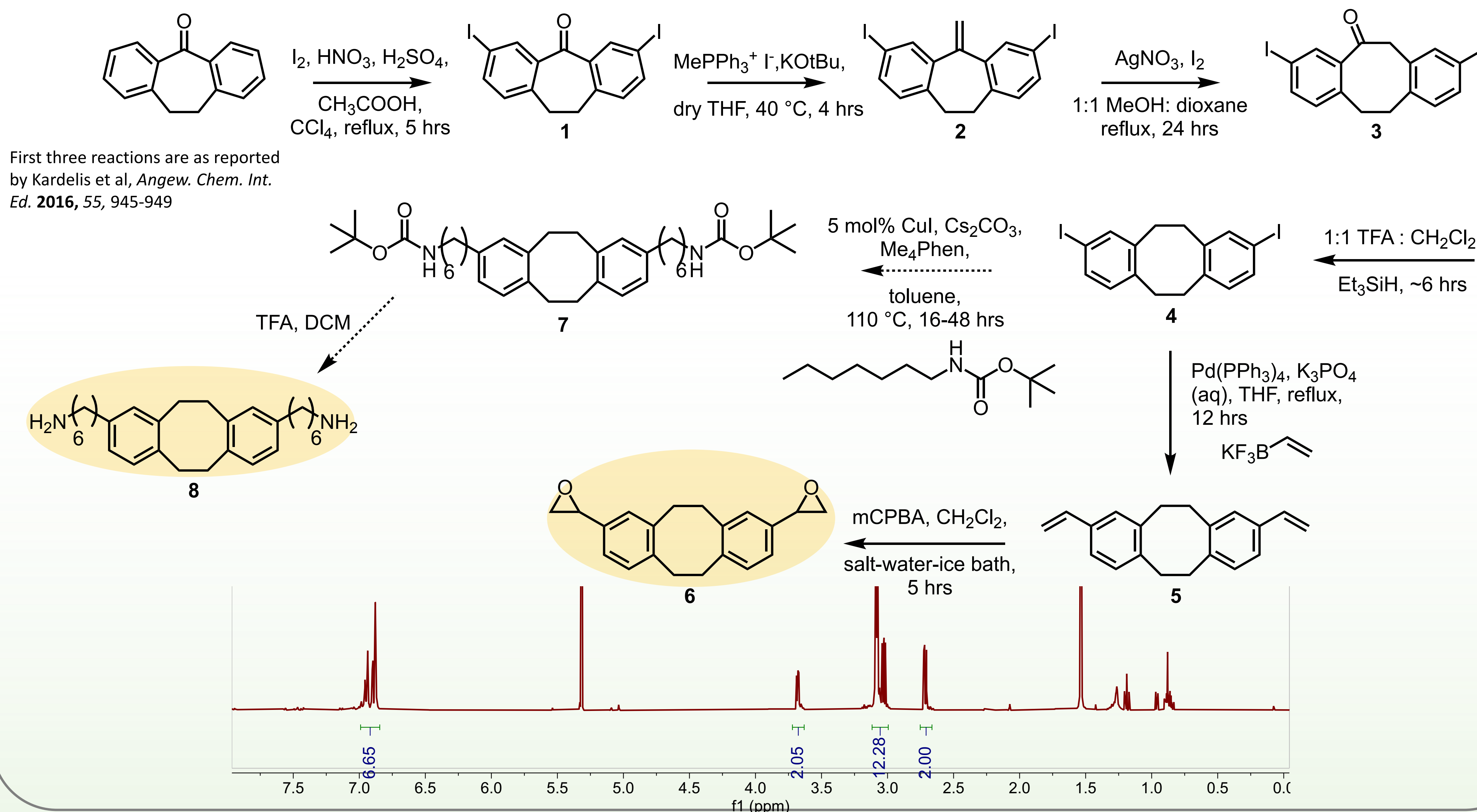
- Synthesize materials that exhibit a tunable CTE by incorporating a molecule with high negative CTE behavior into the backbone chemistry.
- The targeted molecule cyclic framework exhibits this NTE property. We plan to synthesize several novel derivatives to incorporate into encapsulant material.
- Previous methods give a mixture of the cis- and trans- substituted molecule. Our approach uses more steps but guarantees the cis- product.

Targeted molecules:



ACS Macro Lett. 2021, 10, 7, 940-944

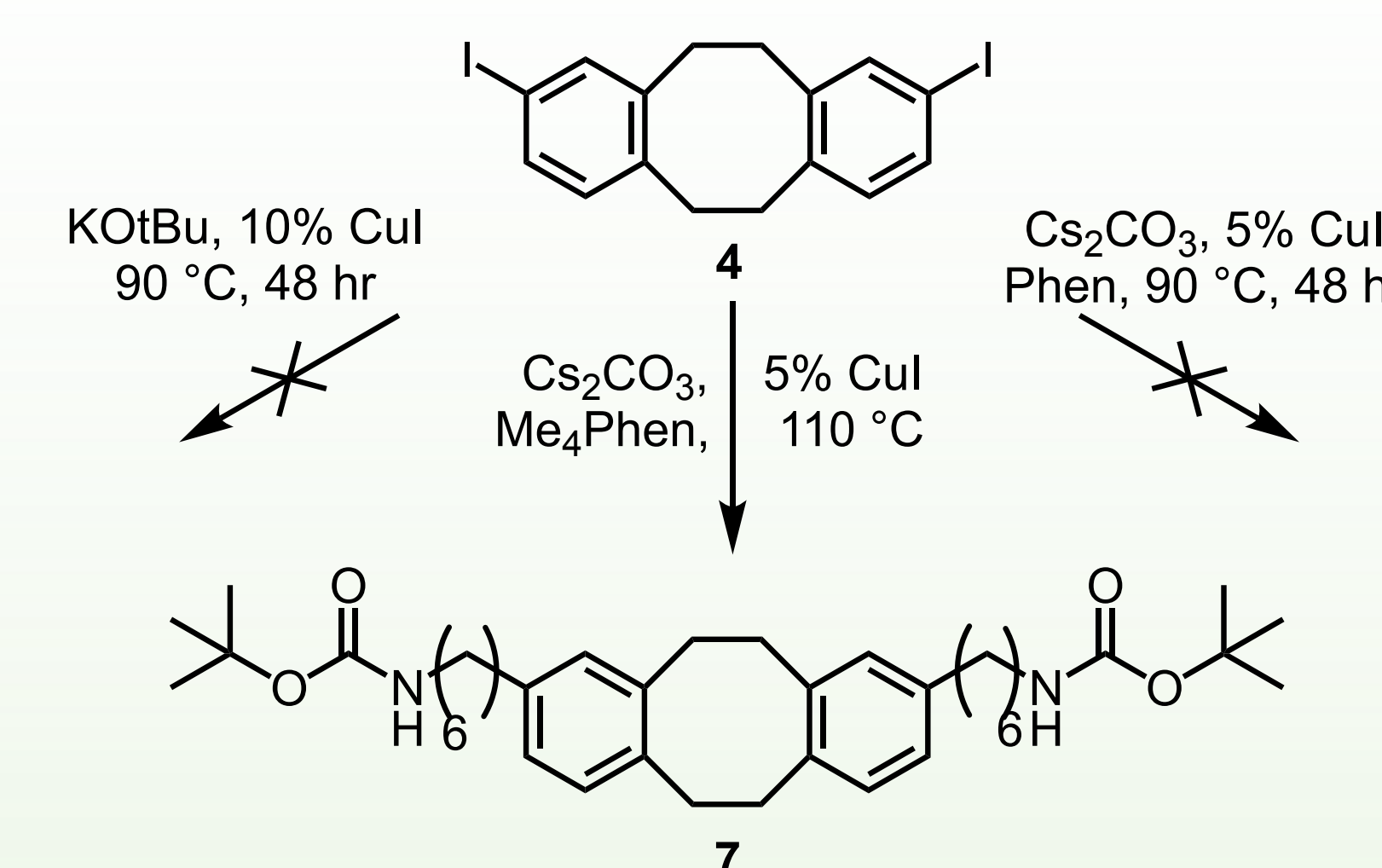
Current Status / Results



First three reactions are as reported by Kardelis et al, *Angew. Chem. Int. Ed.* 2016, 55, 945-949

Challenges

- While this route gives the cis only product, the overall yield is quite low and requires large amounts of starting material.
- Purification of diepoxy product can be difficult and lead to degradation of product.
- Ullmann couplings are selective towards N-arylation and require more optimized conditions to proceed to O-arylate in good conversion and yield.



Next Steps / Future Work

- Characterize the reaction kinetics of 6 with EDA by Fourier Transform-Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC).
- Further optimize Ullmann coupling conditions to get BOC-protected 7 in good yield.
- After deprotection of 7, polymerize with a commercial epoxy and gather kinetic and thermal characterization data and quantify NTE behavior.
- Work on synthesizing derivatives with -NCO and -OH functionalities to expand the scope of possible polymerizations.