

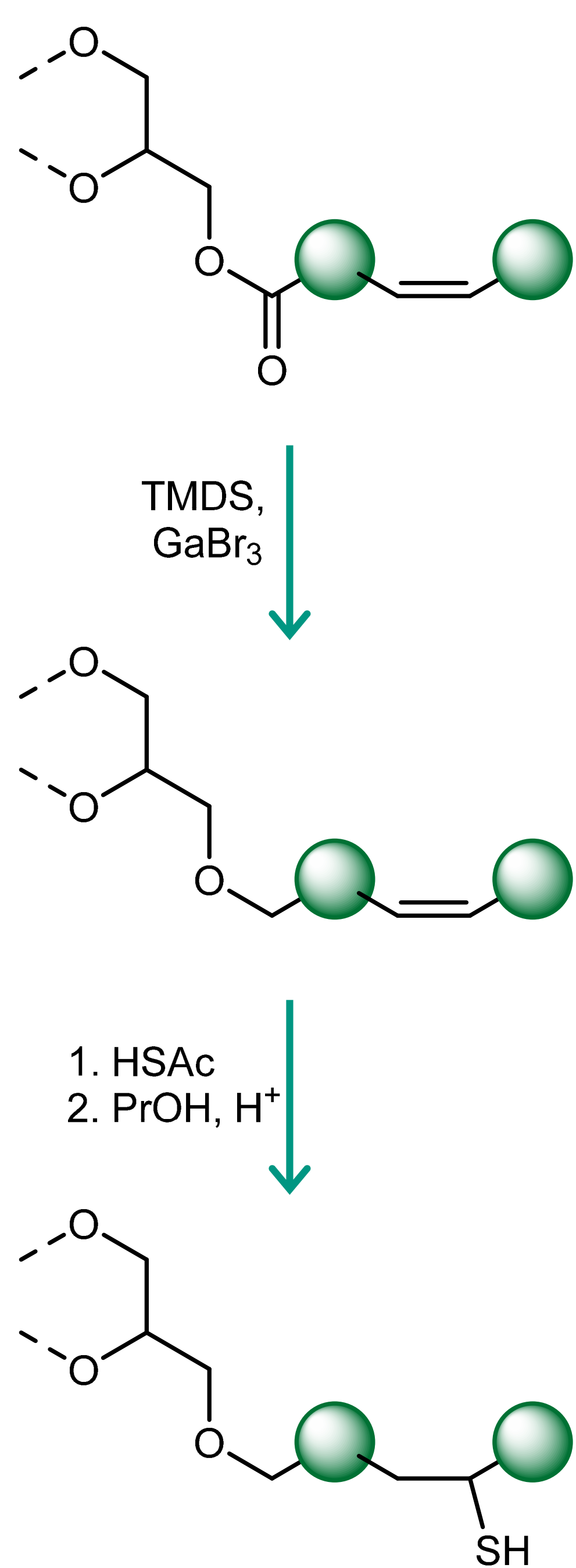
Synthesis of Novel Vegetable Oil-based Polythiol Crosslinking Agents

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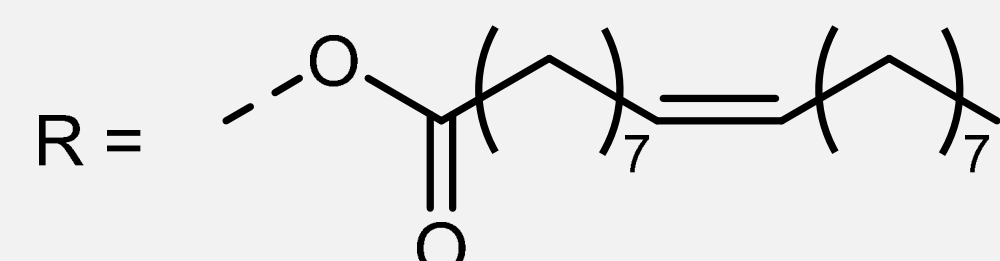
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Synthetic Strategy

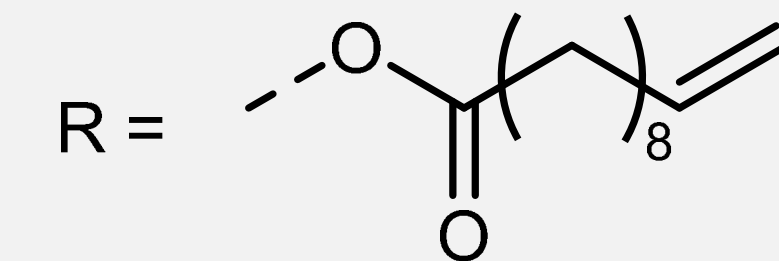
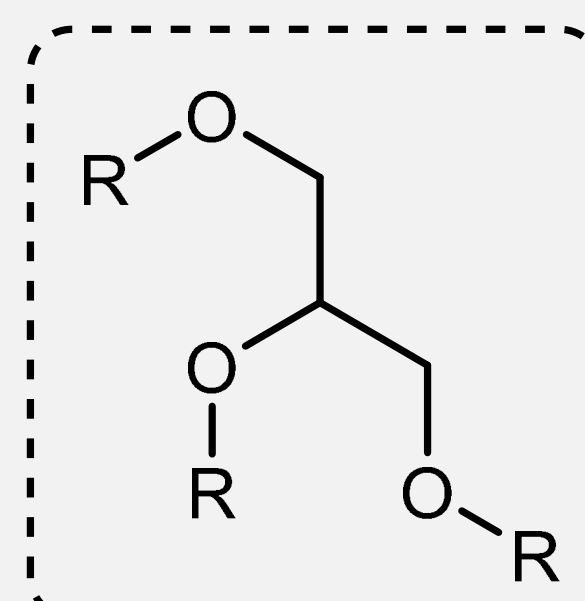


Renewable Triglyceride Substrates



High Oleic Sunflower Oil (HOSO)

- Cheap, commercially available
- >85 % oleic acid

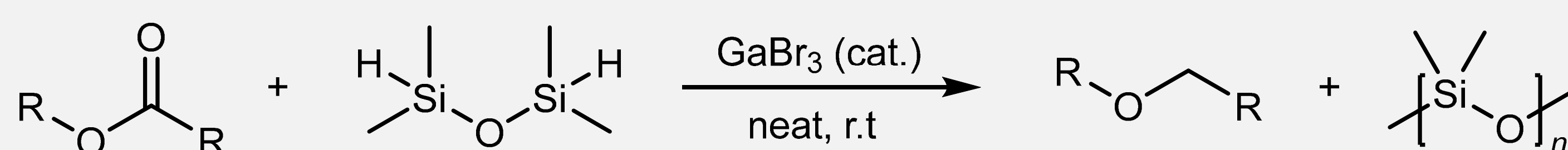


Glyceryl triundecenoate (GTU)

- Undecenoic acid from Castor oil
- Scalable 1-step synthesis

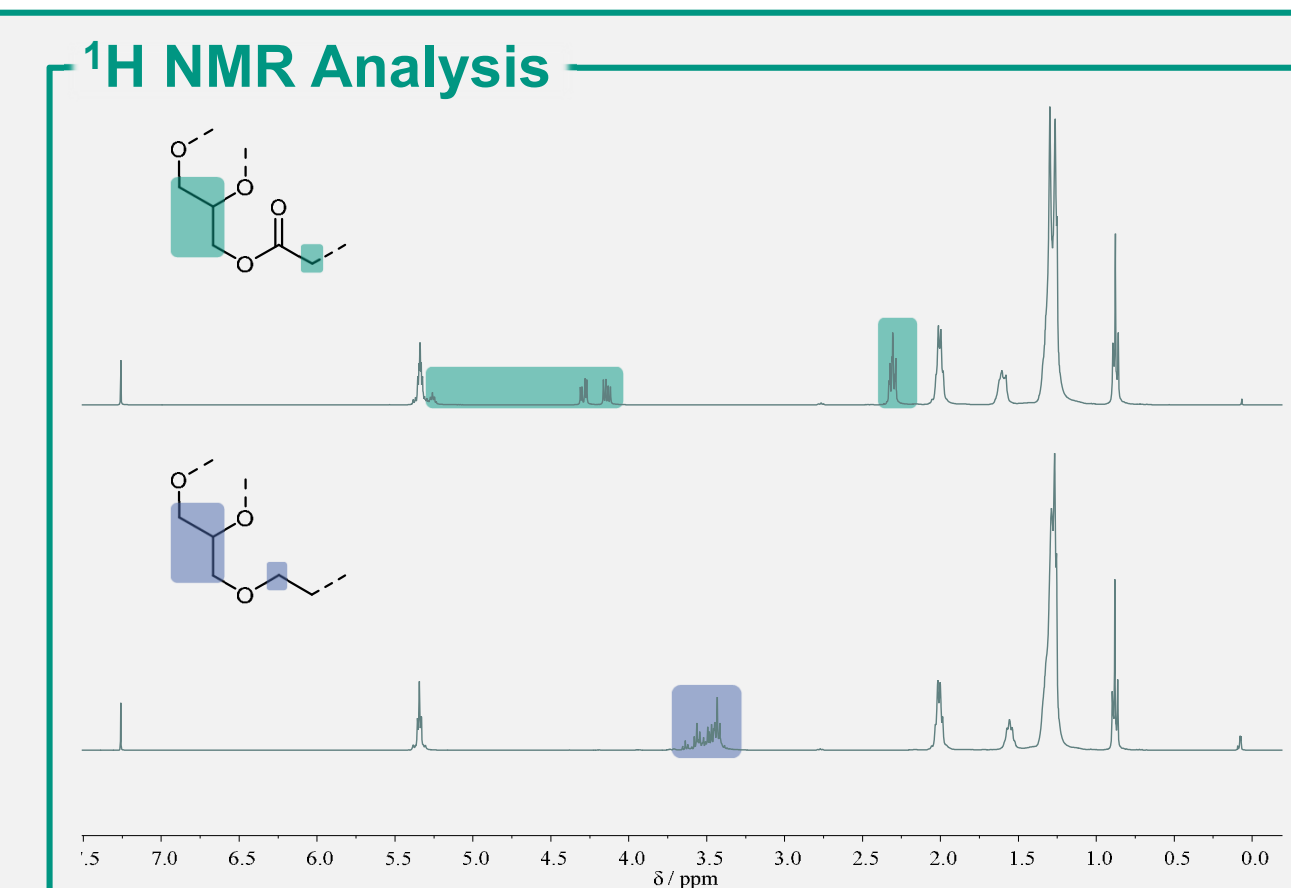


Ester Deoxygenation

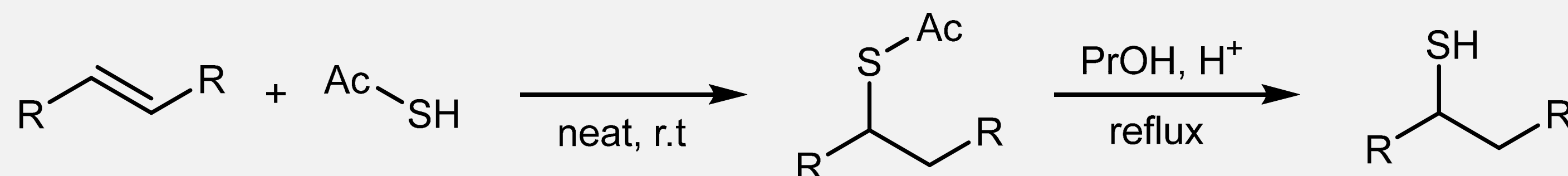


Gallium bromide-catalyzed ester reduction

- Tetramethyldisiloxane (TMDS) as reducing agent → cheap industrial waste product
- Polysiloxane byproduct separated via alkaline hydrolysis
- Mild conditions, benign materials, scalable up to 50 g triglyceride, up to 75 % yield

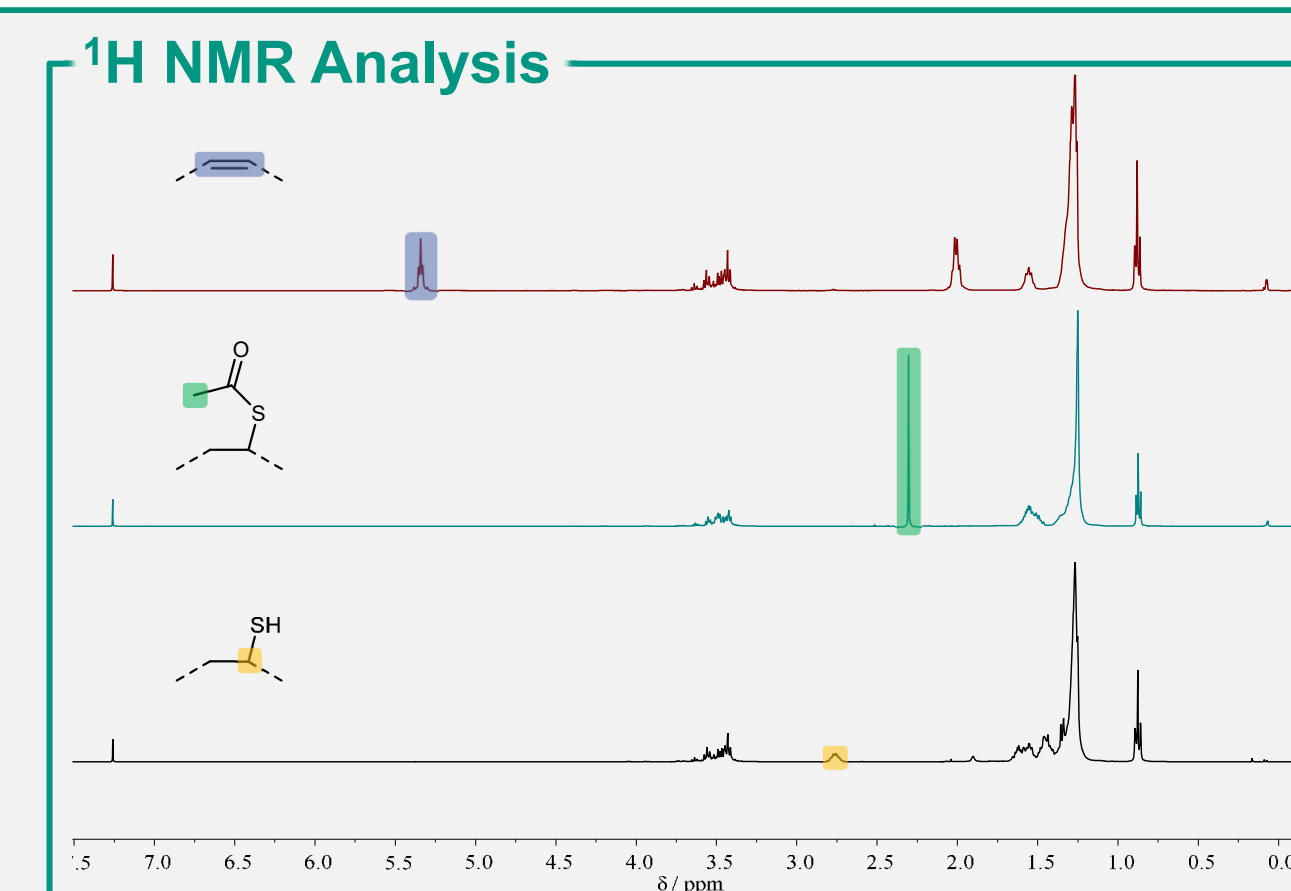


Thiols from Olefins



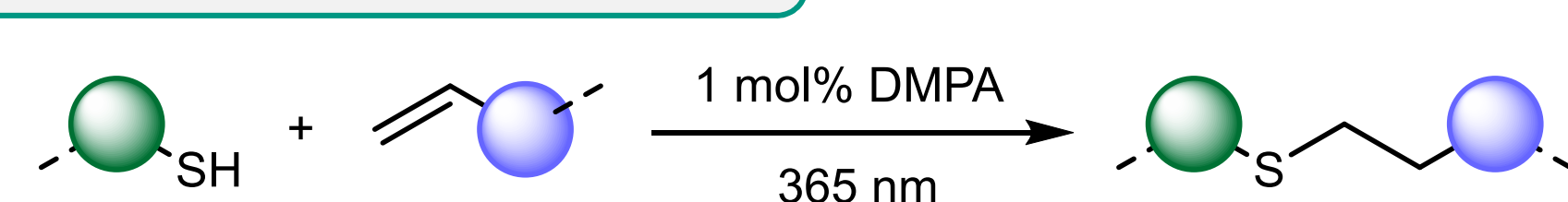
Thiol synthesis via acetylthiolation and transesterification

- Quantitative acetylthiolation under ambient conditions without radical initiator
- Excess HSAc can be recovered and reused
- Acid-catalyzed transesterification of thioester with *n*-propanol
- Total thiol yield up to 95% across both steps



Thermoset Materials

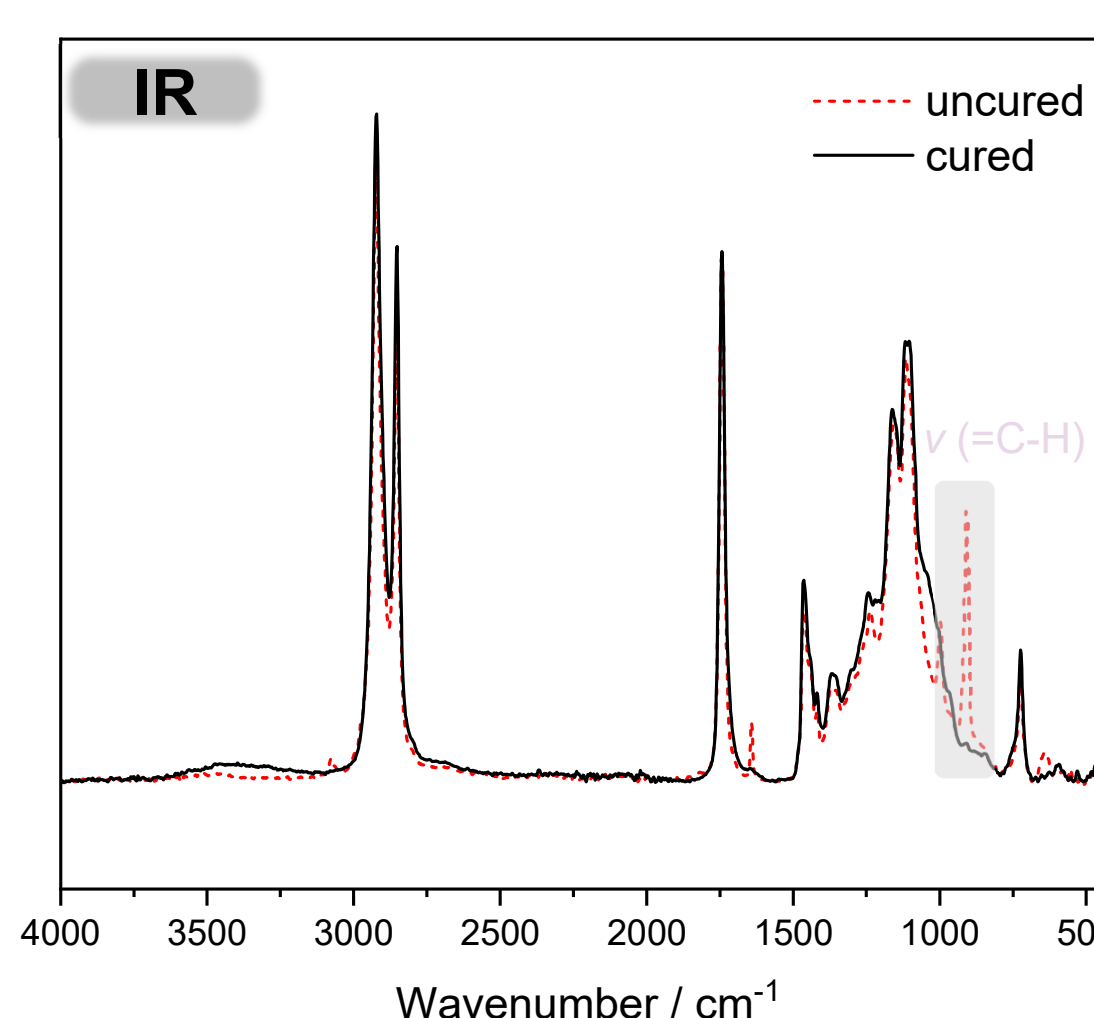
Thiol-Ene Thermosets



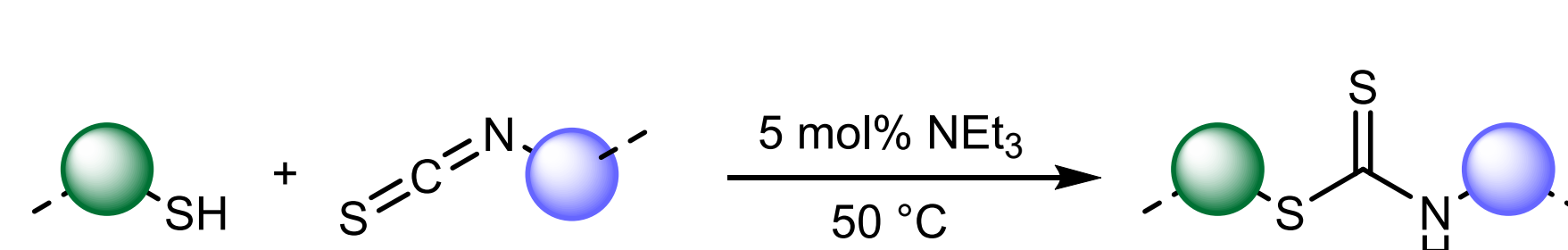
| Polythiol | Polyene | Gel ct. (THF) |
|-----------|---------------|---------------|
| HOSO | 1,7-Octadiene | 61 % |
| HOSO | GTU | 98 % |
| GTU | 1,7-Octadiene | > 99 % |
| GTU | GTU | > 99 % |



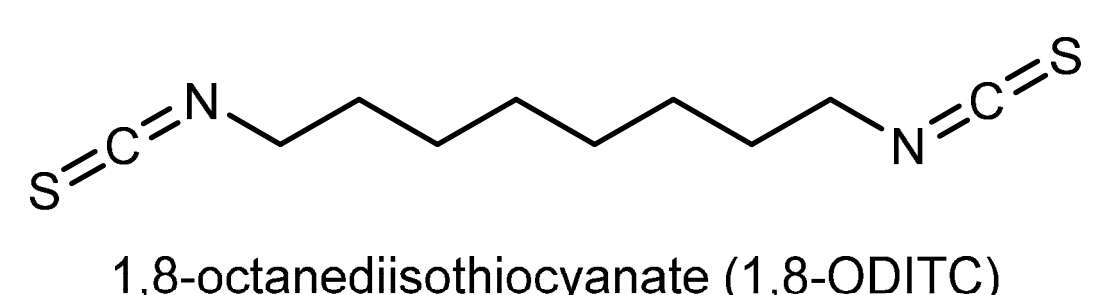
- Curing under UV irradiation overnight
- 1,7-Octadiene as comonomer
 - Gel content <99% for GTU-based polythiol
 - Low gelation for HOSO-based polythiol
- GTU as trifunctional comonomer
 - High gel content also for HOSO-based polythiol
- Transparent, flexible materials
- -45 °C < *T_g* < -11 °C



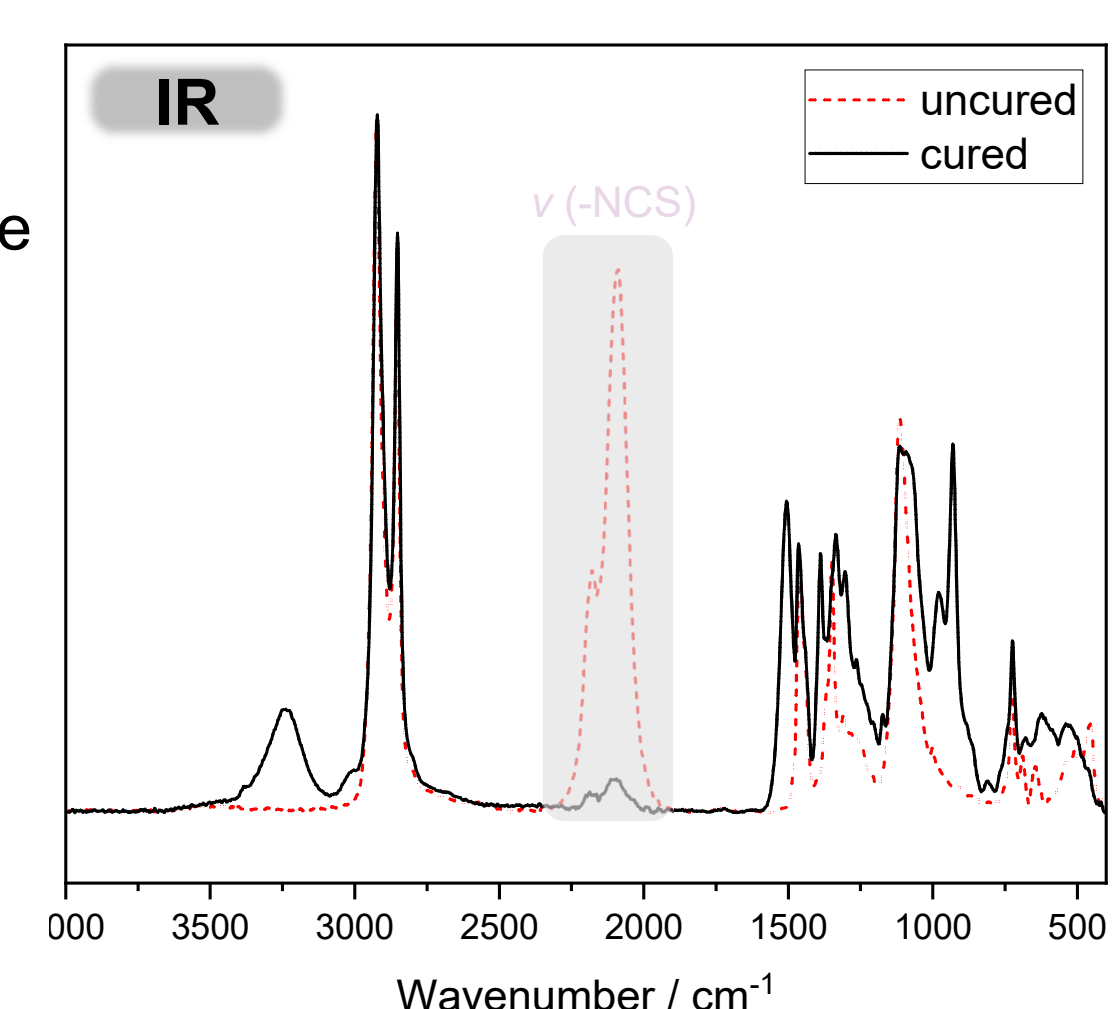
Polydithiocarbamate Thermosets



| Polythiol | Electrophile | Gel ct. (THF) |
|-----------|--------------|---------------|
| HOSO | 1,8-ODITC | 89 % |
| GTU | 1,8-ODITC | < 99 % |

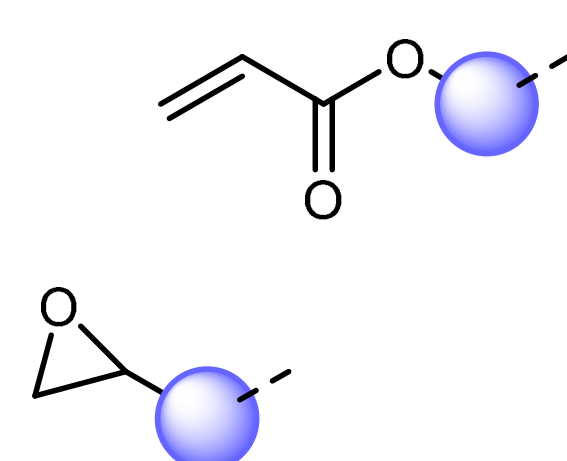


- 1,8-octanediisothiocyanate as comonomer
 - Accessible from amine in sustainable 2-step synthesis
- Base-catalyzed curing at 50 °C overnight
 - Triethylamine as model catalyst
- High gel contents for both polythiols
- Transparent, flexible materials
- 30 °C < *T_g* < -8 °C



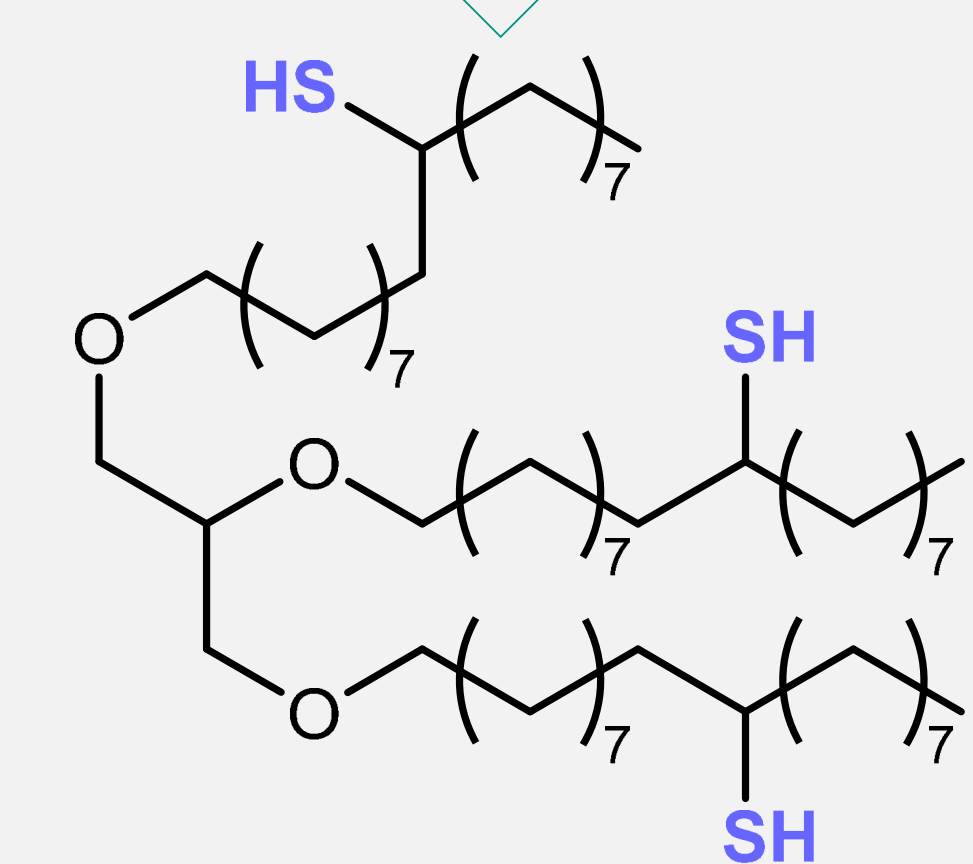
Outlook

- Optimization of polymerization conditions
- Thermoset characterization: mechanical properties
- Monomer Scoping
- Other functional groups as co-monomers



Acknowledgements

- Karlsruhe House of Young Scientists (KHYS)
- Graduate Funding of the German States
- Mathilde Bourcier
- Dr. Jonas Wenzel (KIT Breher Group)
- Meier Group



2 novel bio-based polythiols

