

# Exploiting Cyanohydrin-Derived Carbanions for Stereochemical Control in Organic Synthesis

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## ABSTRACT

Cyanohydrins serve as acyl anion equivalents for carbon–carbon bond formation through carbonyl umpolung. This seminar explores complementary strategies that harness their reactivity to control alkene geometry and construct enantioenriched  $\alpha$ -tertiary ketones. The first part presents two approaches to *Z*-tetrasubstituted alkenes. Diastereomeric resolution exploits selective deprotonation and electrophilic trapping of the *E*-isomer, allowing recovery of the enriched *Z*-isomer. Dynamic thermodynamic resolution instead exploits allylic carbanion equilibration to favour the *Z*-isomer upon protonation, with application to the total synthesis of murralonginal. The second part describes transition-metal-free enantiospecific alkylation of cyanohydrins with enantioenriched secondary tosylates, affording  $\alpha$ -tertiary ketones after carbonyl unmasking. With alkenyl cyanohydrins, coupling alkylation with olefin dynamic kinetic resolution controls both alkene geometry and carbon stereochemistry. An enantiospecific synthesis of (*R*)-cyclamen aldehyde illustrates the method's synthetic utility. Overall, these studies establish cyanohydrin-derived nucleophiles as a platform for complementary control of geometric and configurational stereochemistry.

