

The Self-Disproportionation of Enantiomers (SDE) of α -Pinene via Evaporation Off Silica Gel and Foam Fractionation – Validation of the Plausibility of SDE via Gas Chromatography (GC) for α -Pinene

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Supplementary Materials

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Abstract: α -Pinene is an intriguing monoterpene as it has been reported to undergo the self-disproportionation of enantiomers (SDE) phenomenon via gas chromatography (GC), the only compound to decisively demonstrate this. Examples of the SDE involving the gaseous phase – sublimation aside – are extremely rare. Attempts to replicate the GC results were unsuccessful, though the authors argued convincingly for the difficulty of observing the phenomenon. However, we could effect for α -pinene SDE via evaporation off silica gel and by foam fractionation – albeit the SDE magnitude for both was only very slight – to confirm that α -pinene can undergo the SDE for processes involving a gaseous phase and thus validate the plausibility of the GC report. The indications are that the molecular associations responsible for the various SDE observations of α -pinene occur not in the gaseous phase or the bulk phase, but rather in two dimensional (2D) adsorbed monolayers and are not based on conventional functional group-based intermolecular interactions and instead are, most likely, as a result of homo- and heterochiral packing differences in the 2D monolayers – a well-known 2D chiral-based association packing effect. These are also the first reports of the occurrence of the SDE using an adsorptive bubble separation process (foam fractionation) and involving a gaseous phase other than sublimation, GC, and distillation.

Keywords: self-disproportionation of enantiomers (SDE); α -pinene; hydrocarbons; gas chromatography; silica gel; foam fractionation; evaporation; 2D chiral-based association packing; molecular associations; intermolecular interactions

Contents: Low-temperature ¹³C NMR spectra exhibiting the SIDA phenomenon.

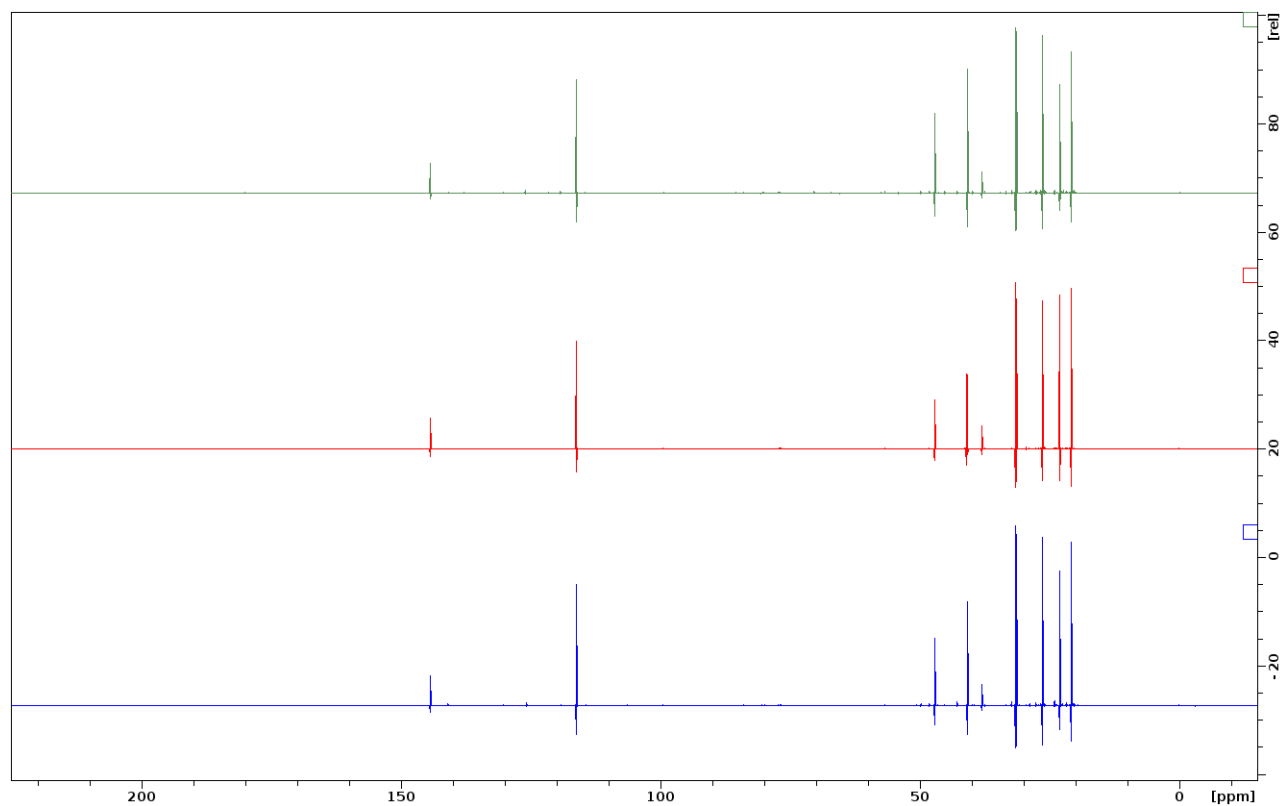


Figure S1. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 $^\circ\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

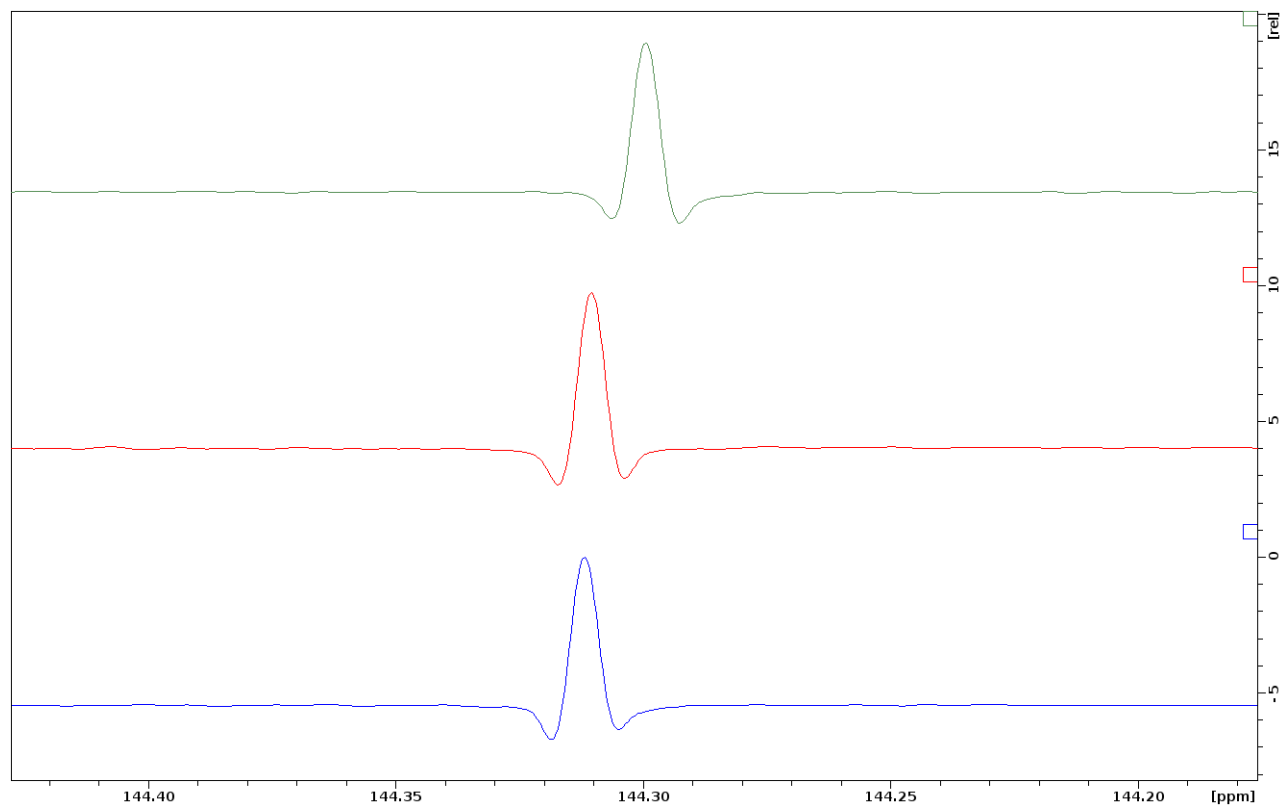


Figure S2. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 $^\circ\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

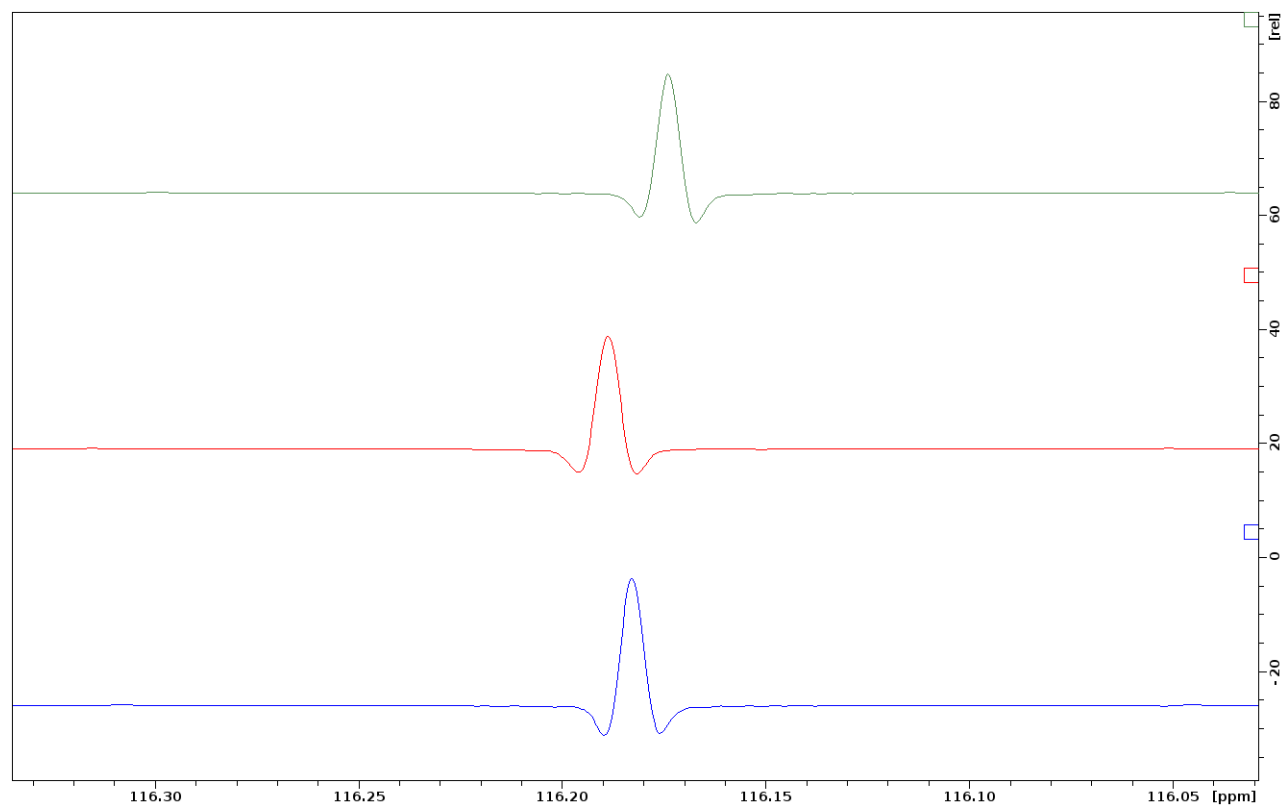


Figure S3. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 °C. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

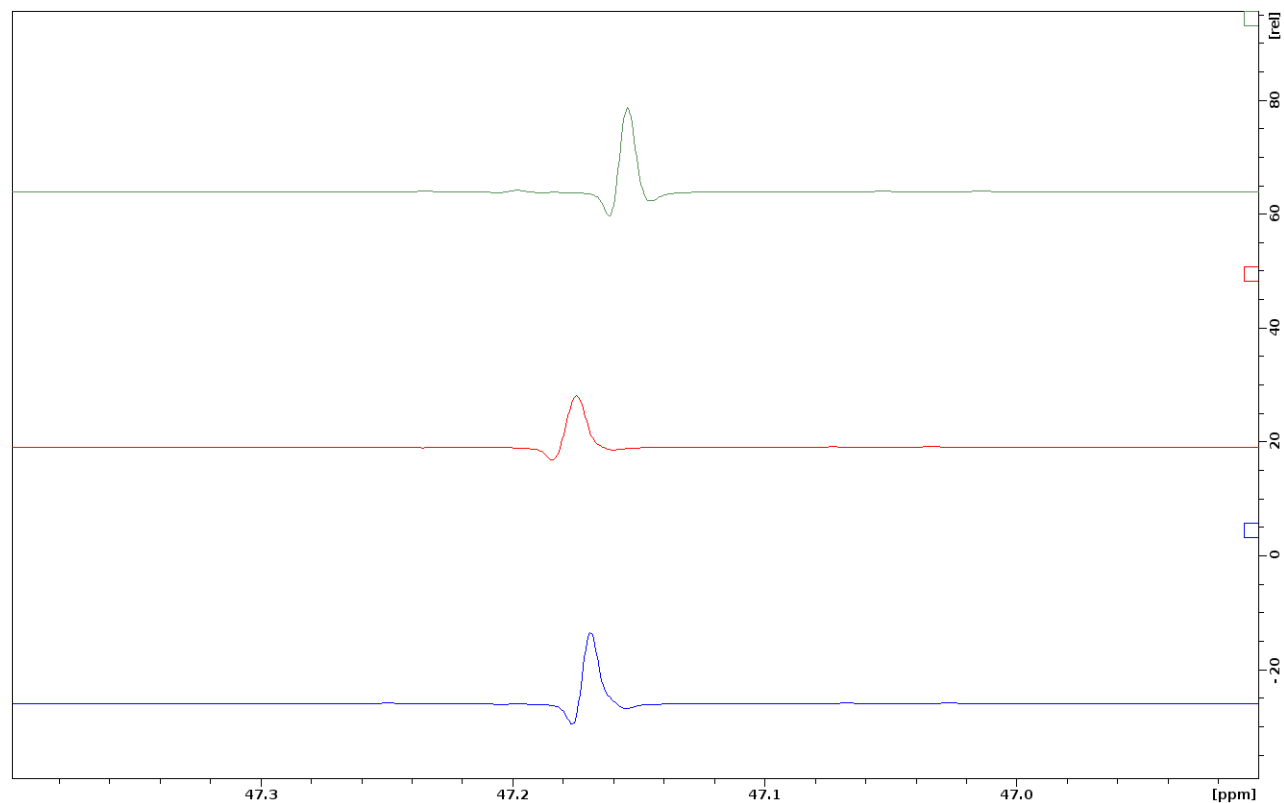


Figure S4. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 °C. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

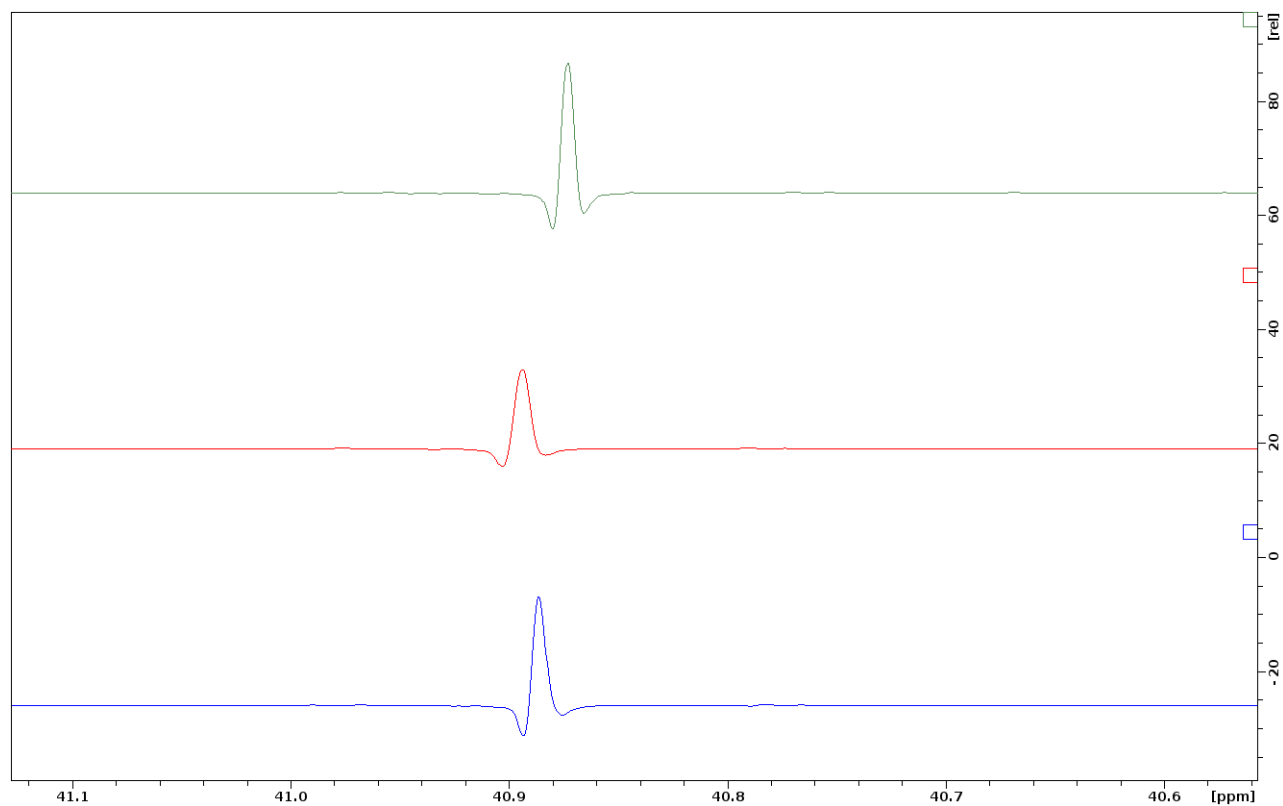


Figure S5. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 $^\circ\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

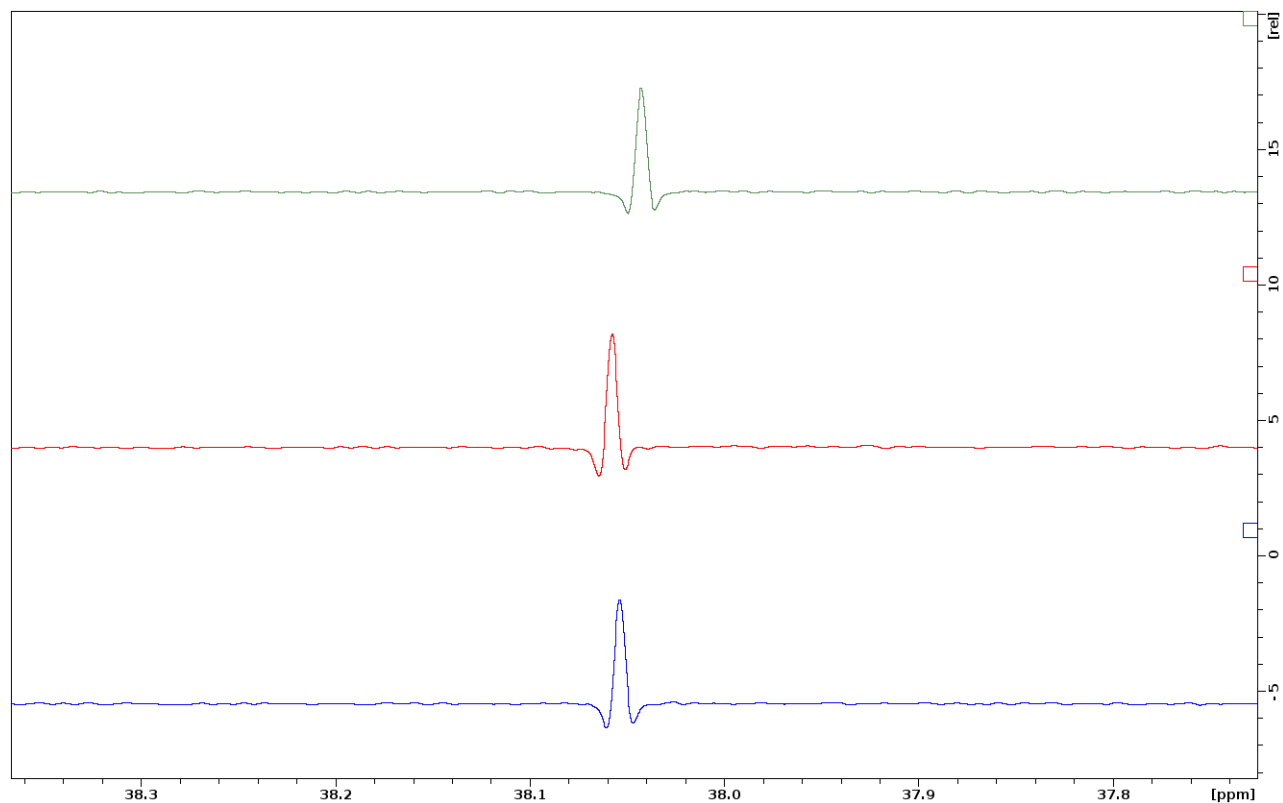


Figure S6. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 $^\circ\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

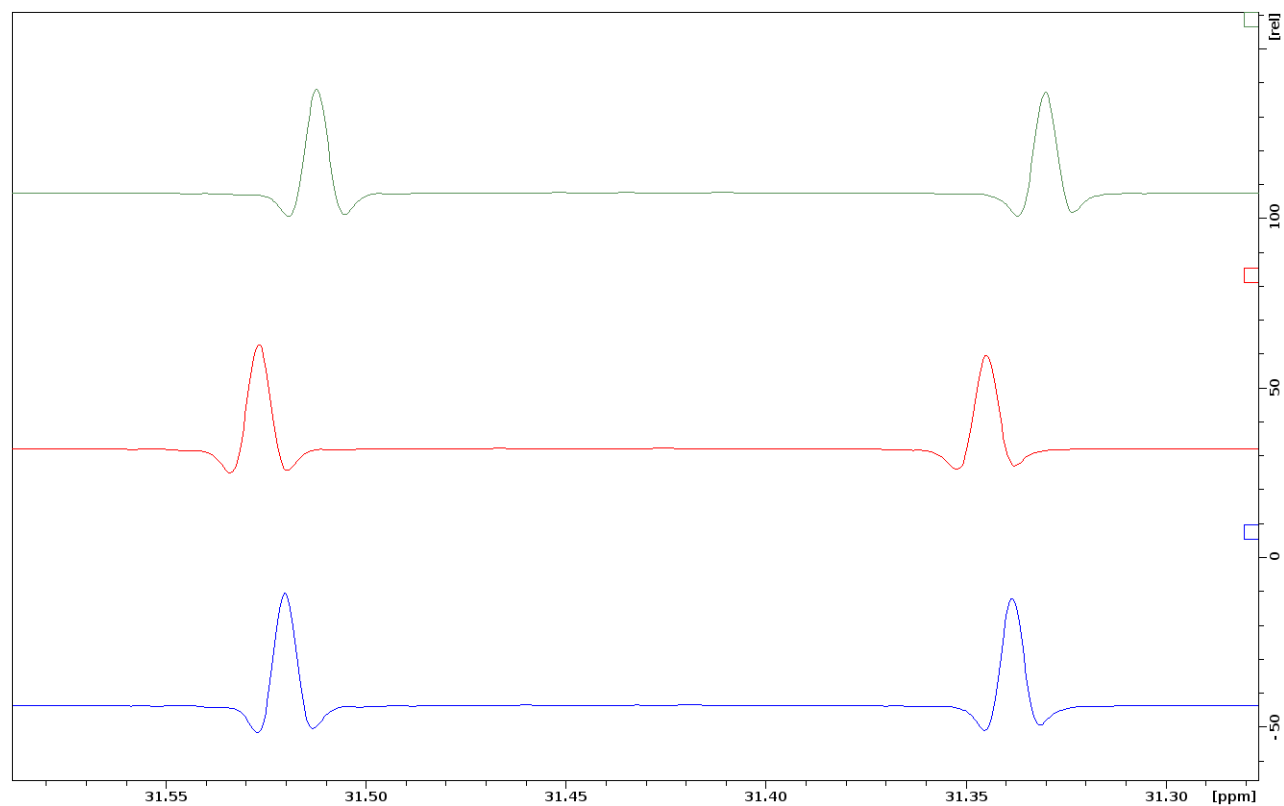


Figure S7. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 °C. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

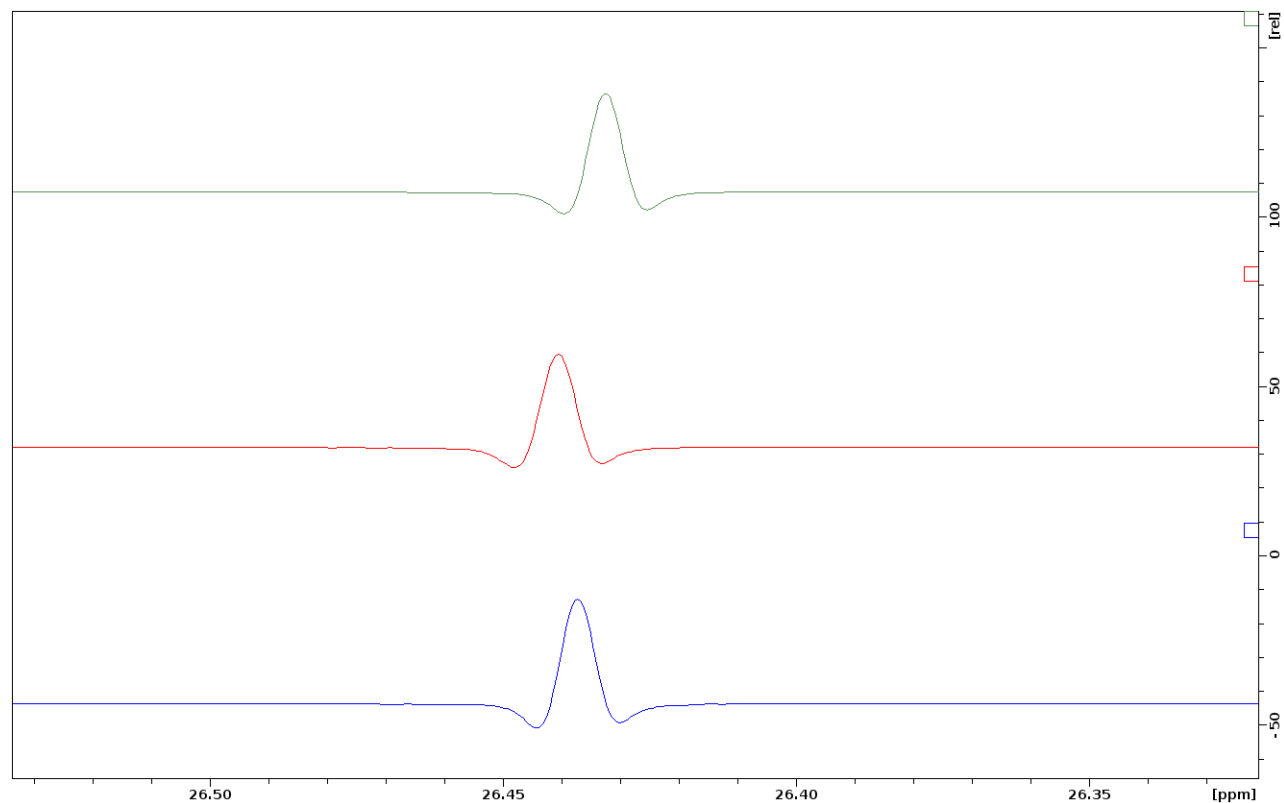


Figure S8. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 °C. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

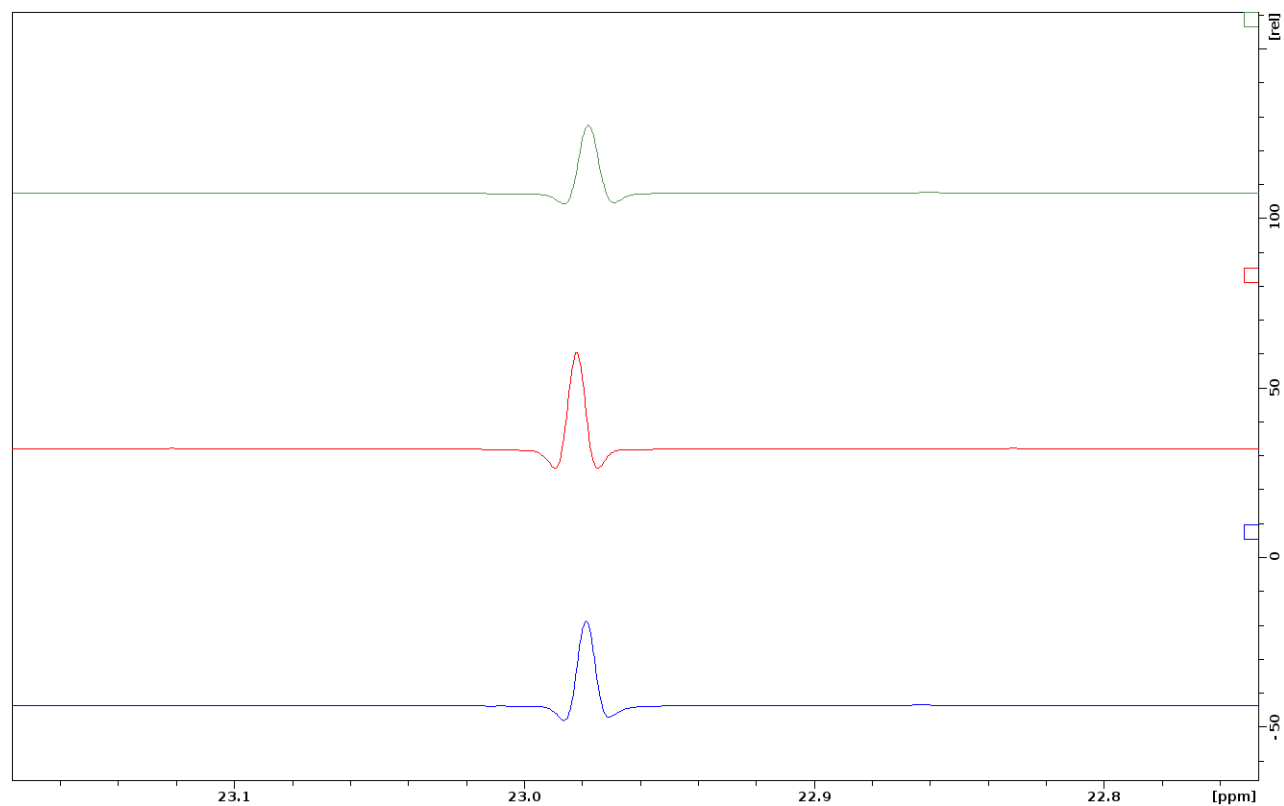


Figure S9. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 °C. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

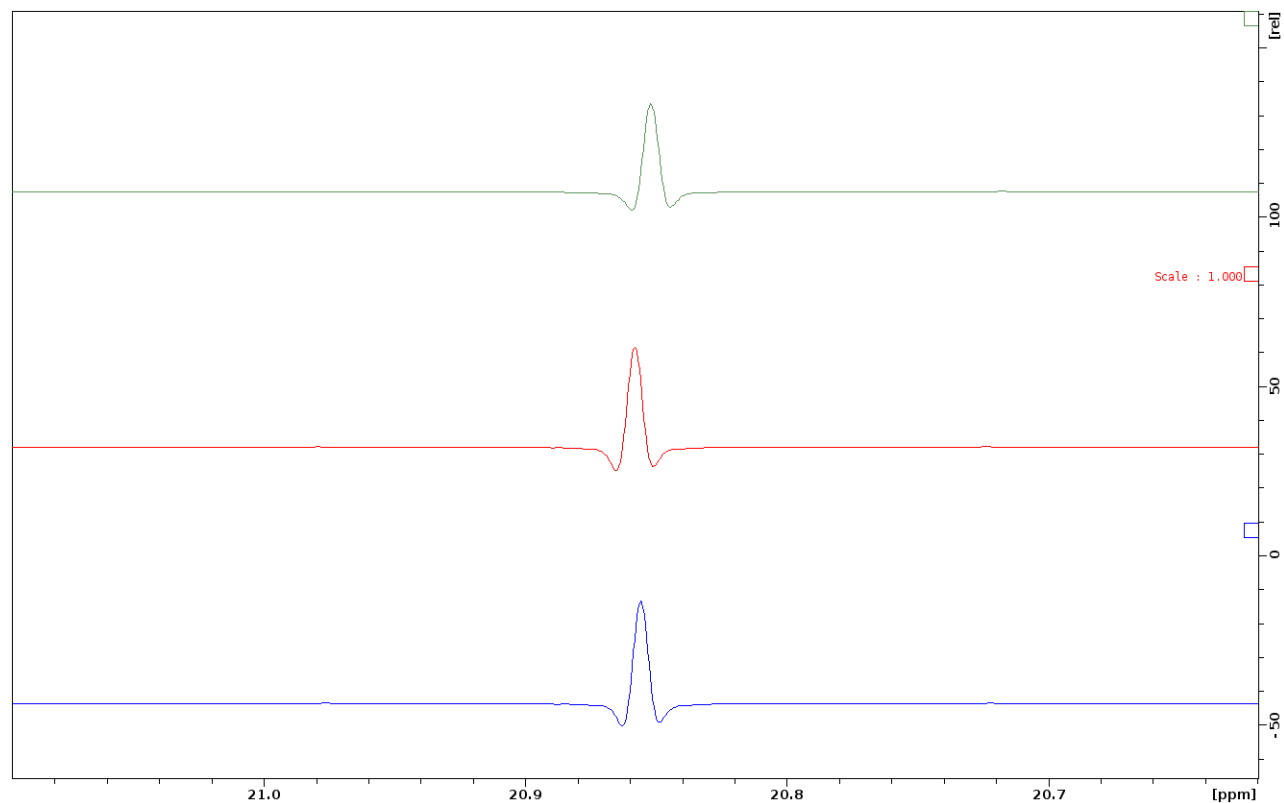


Figure S10. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at 23 °C. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

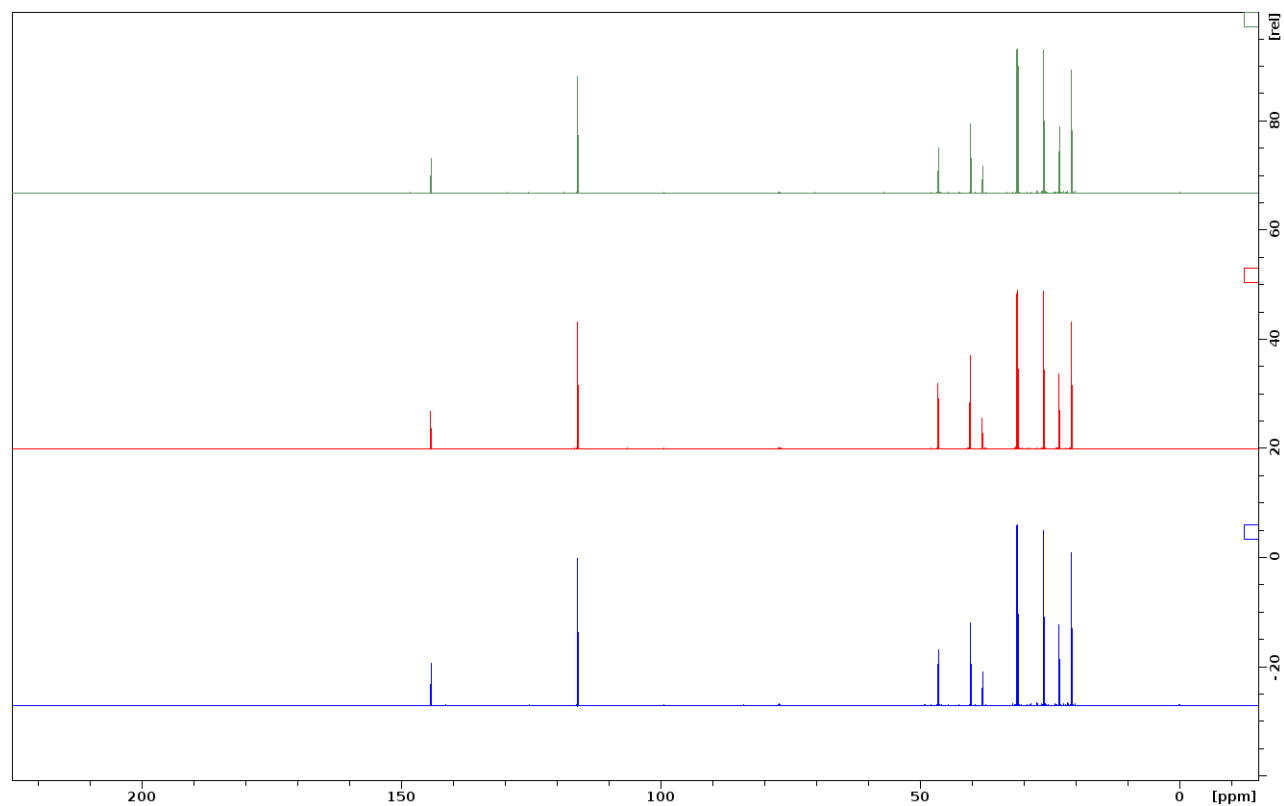


Figure S11. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (S)- α -pinene (red trace), and S -enriched scalemate (50% ee, green trace).

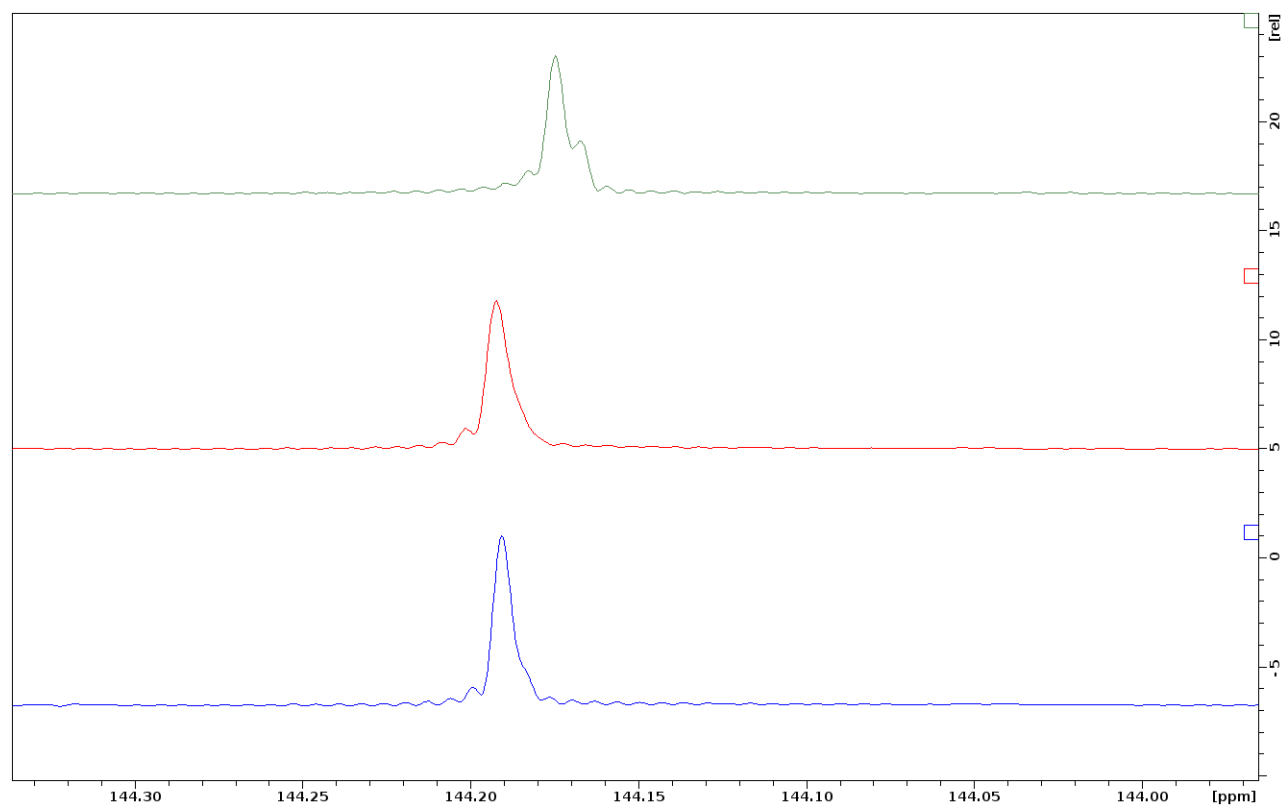


Figure S12. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (S)- α -pinene (red trace), and S -enriched scalemate (50% ee, green trace).

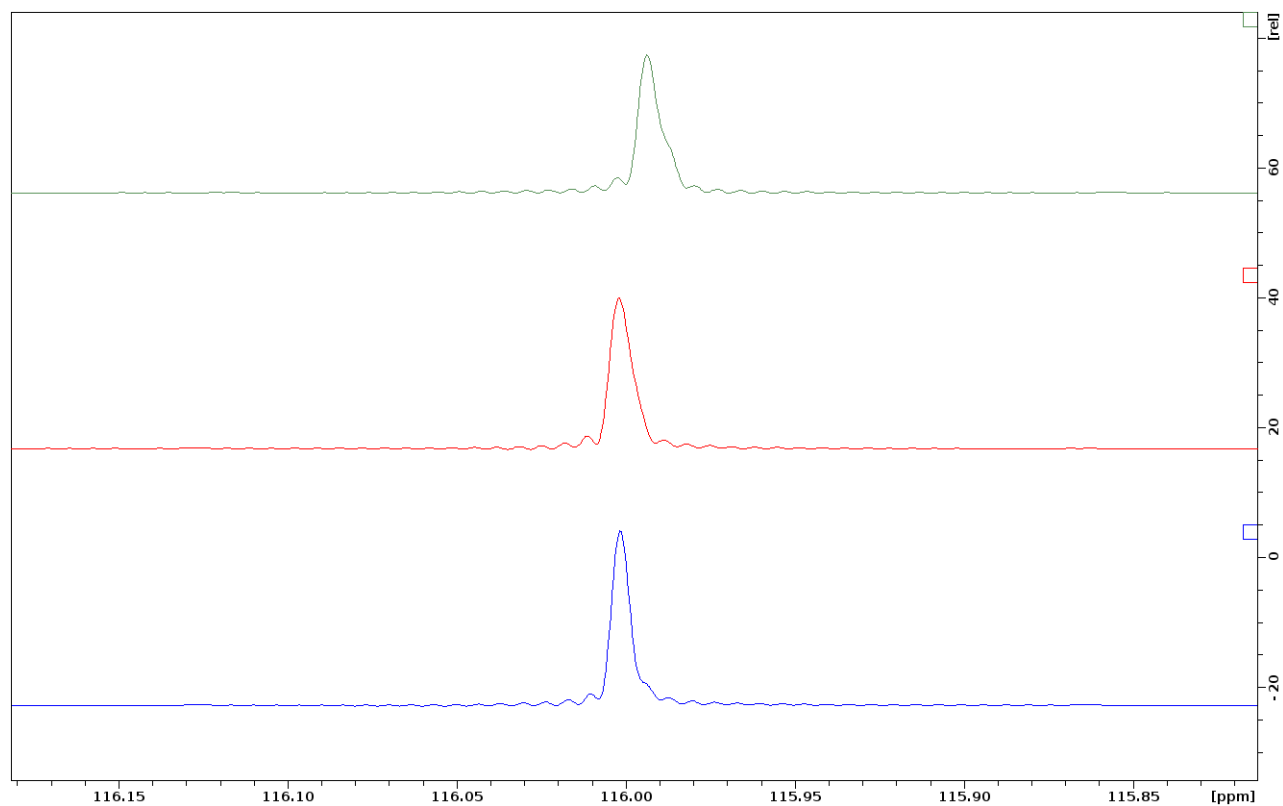


Figure S13. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

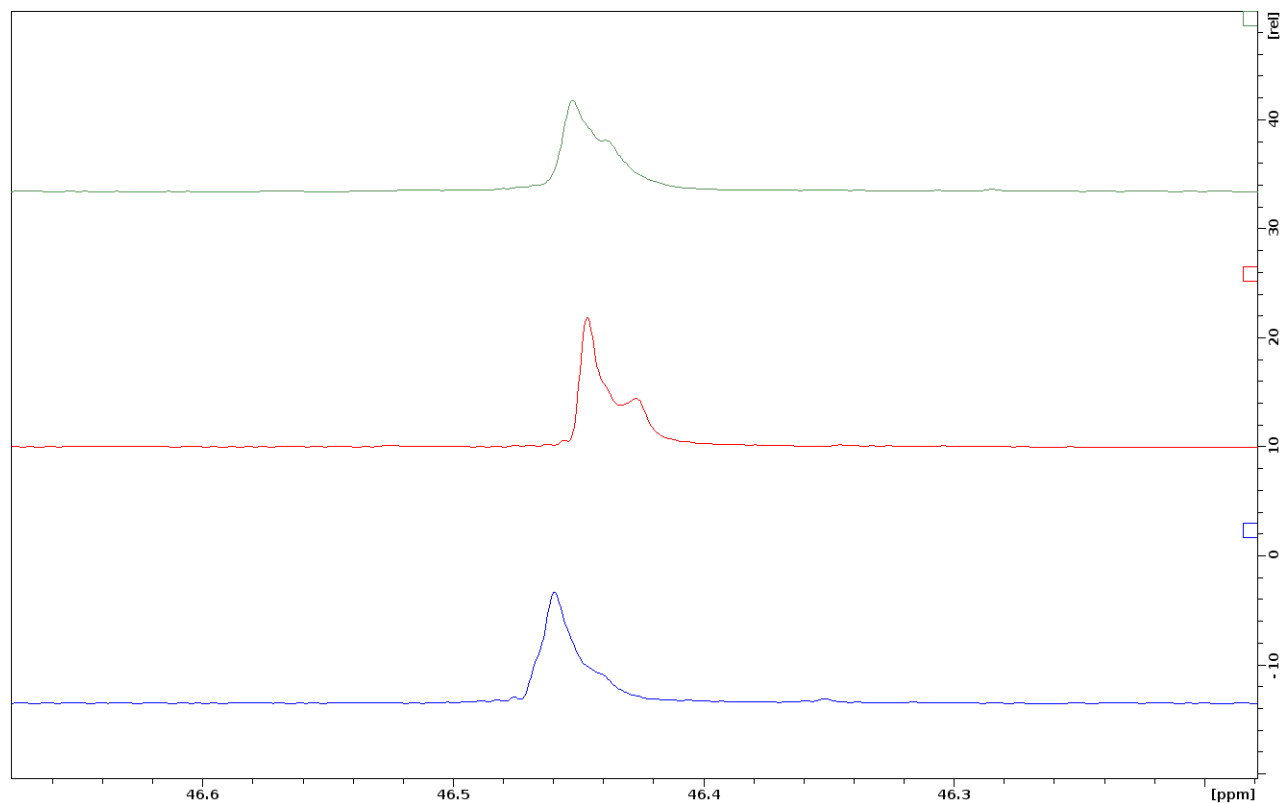


Figure S14. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

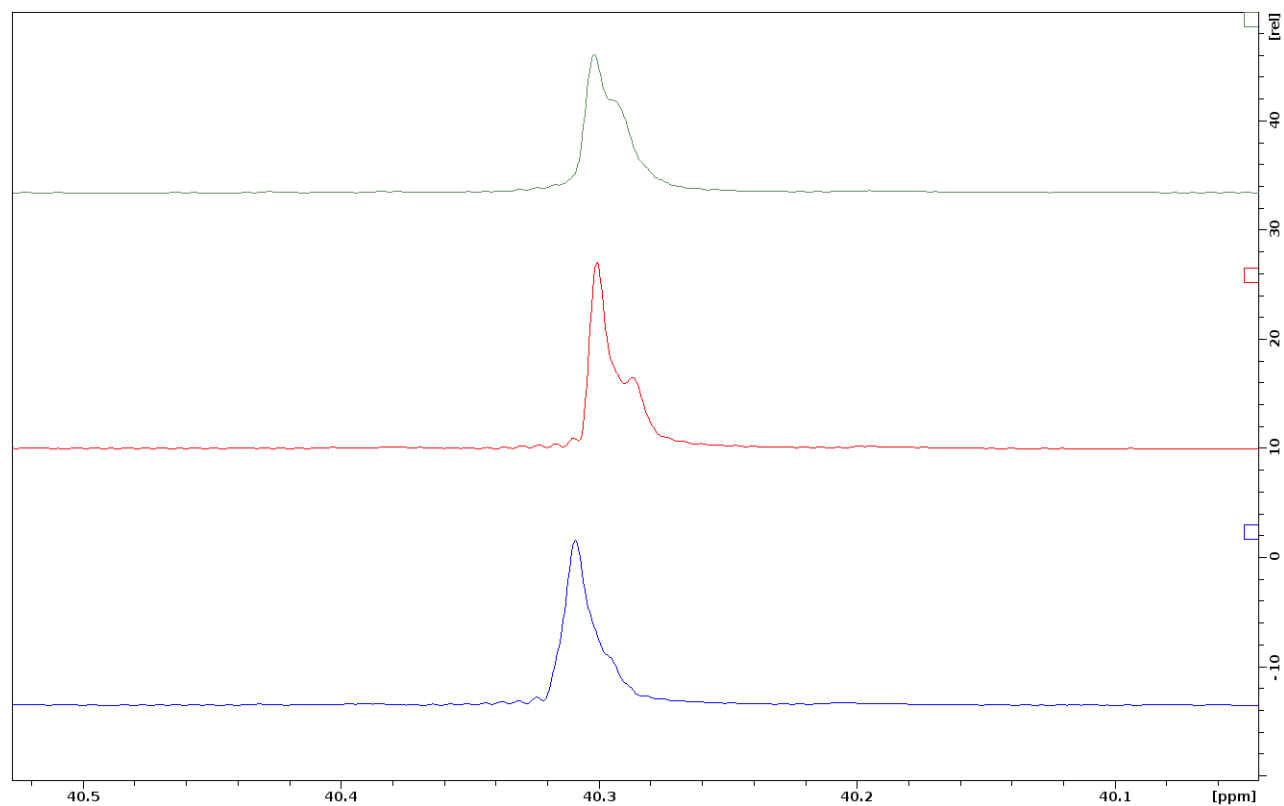


Figure S15. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (S) - α -pinene (red trace), and S -enriched scalemate (50% ee, green trace).

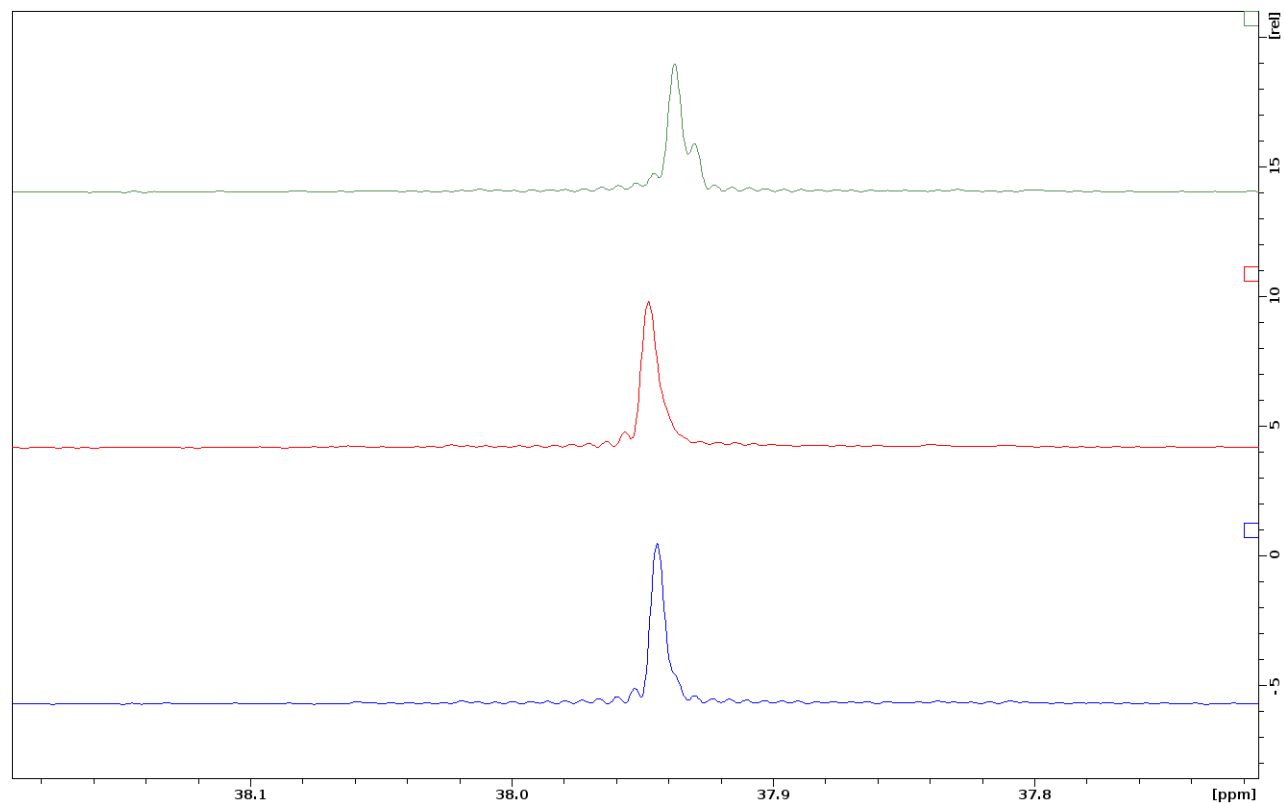


Figure S16. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (S) - α -pinene (red trace), and S -enriched scalemate (50% ee, green trace).

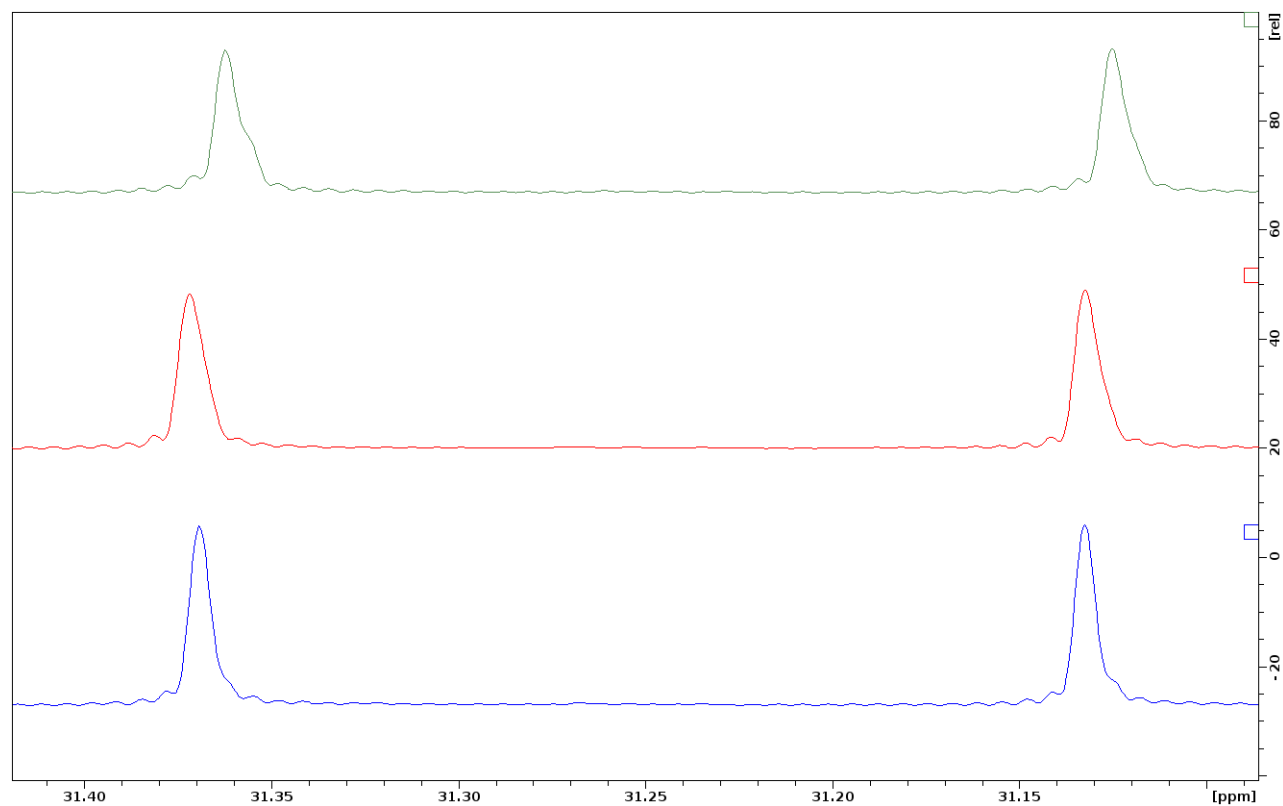


Figure S17. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

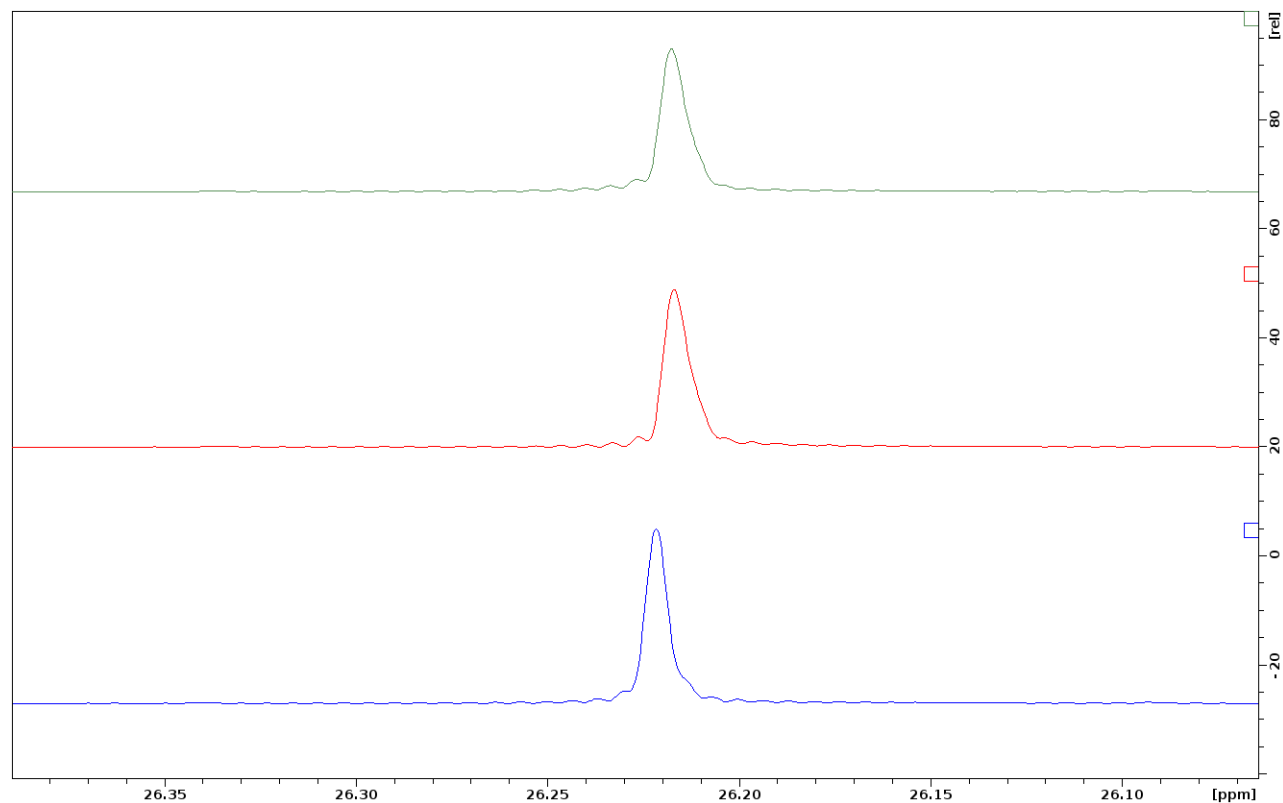


Figure S18. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at -41°C . From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

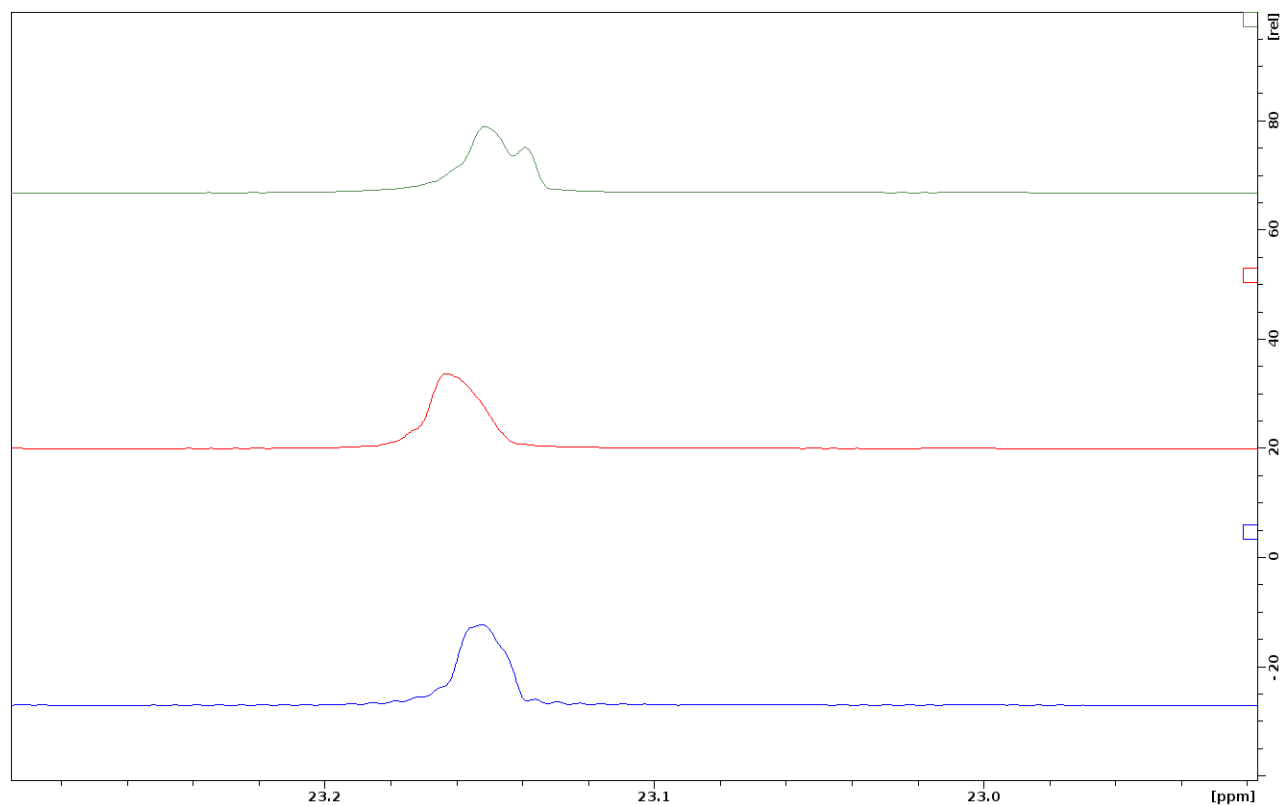


Figure S19. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at $-41\text{ }^\circ\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

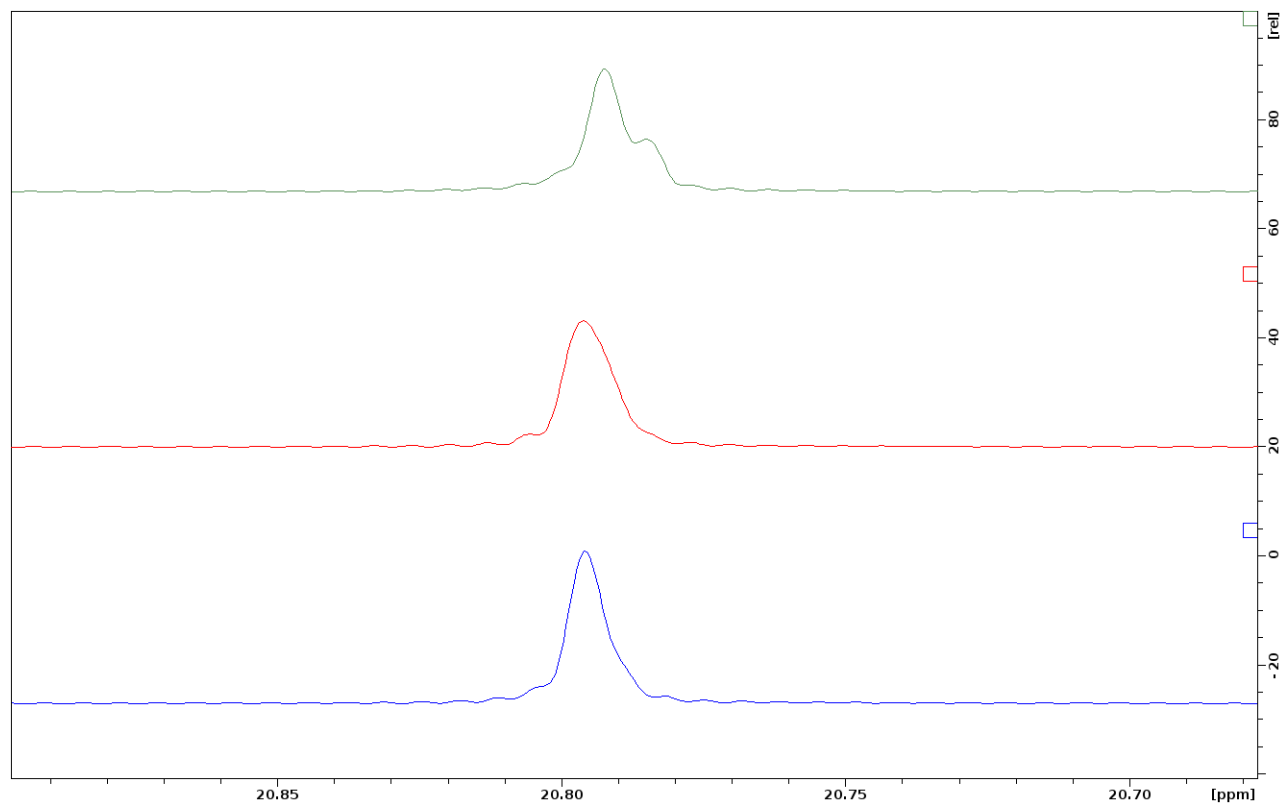


Figure S20. The ^{13}C NMR spectra of α -pinene in CDCl_3 (68%) at $-41\text{ }^\circ\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

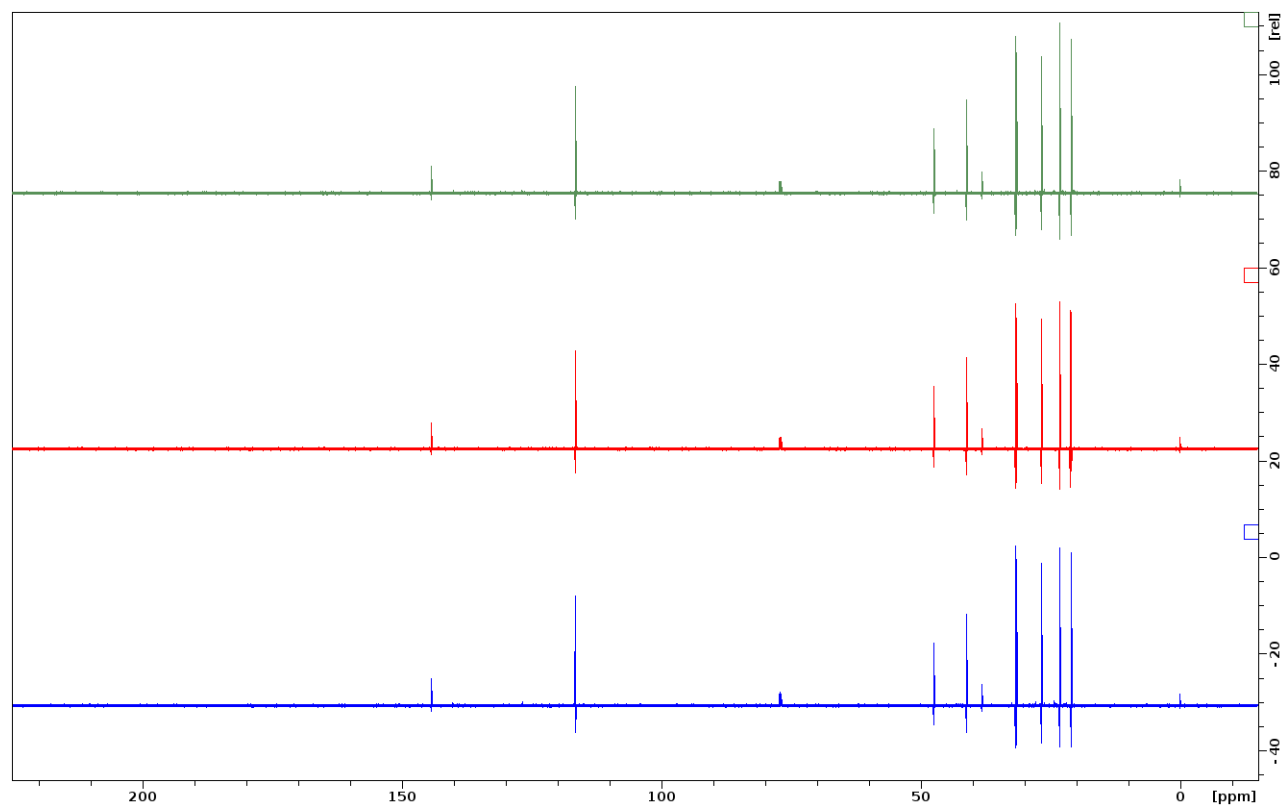


Figure S21. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

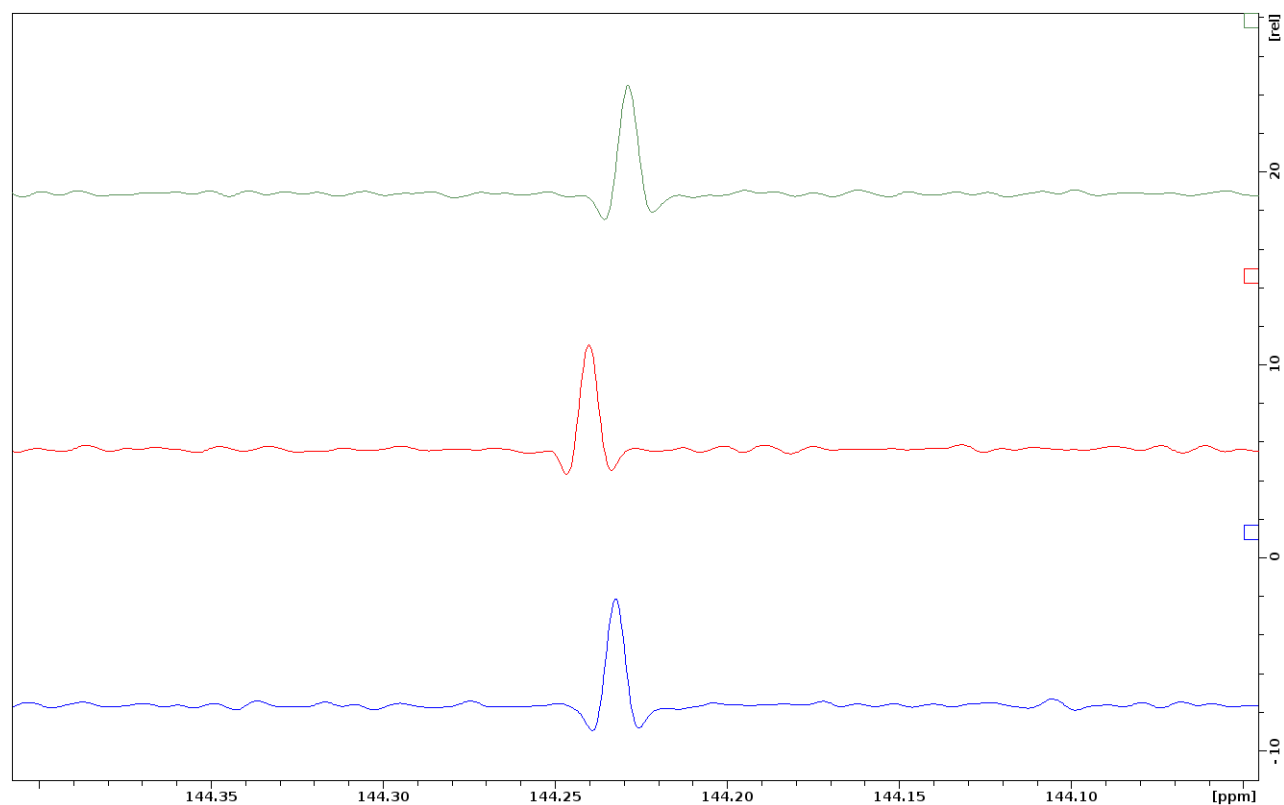


Figure S22. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

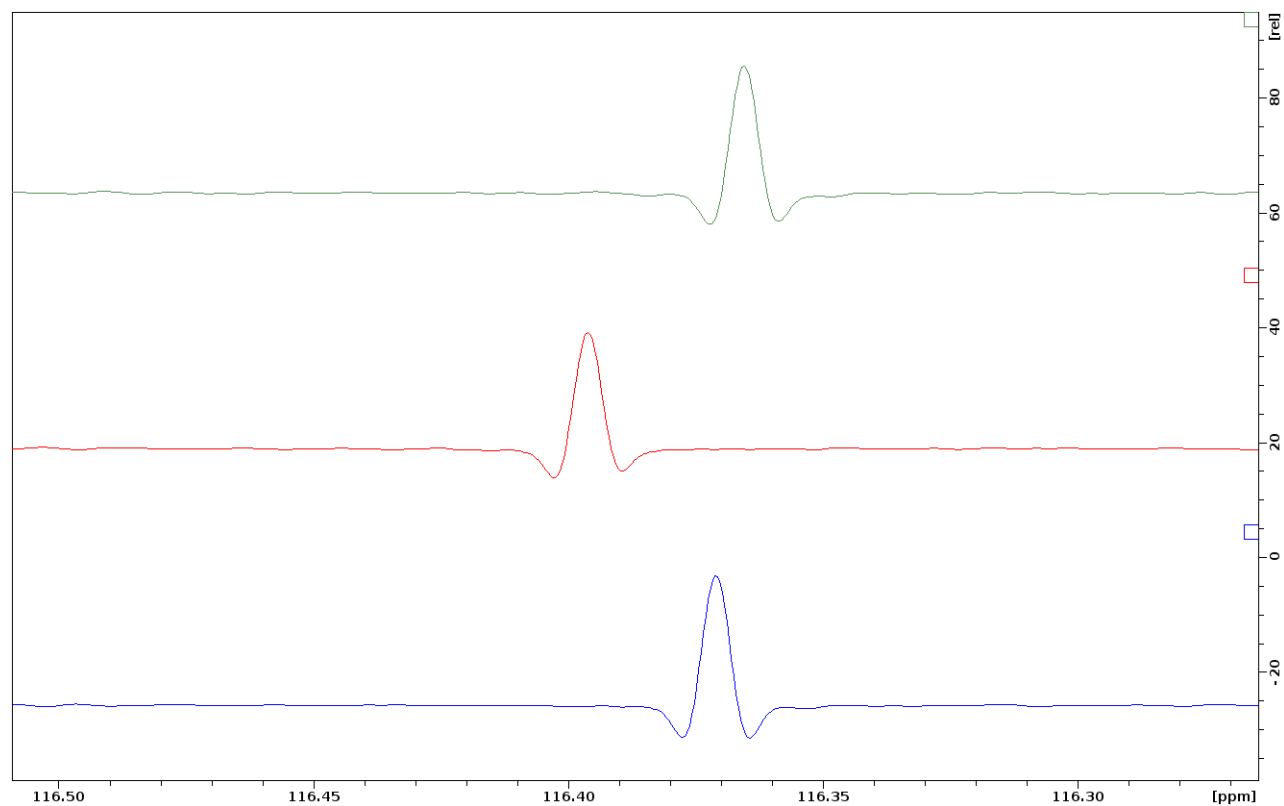


Figure S23. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

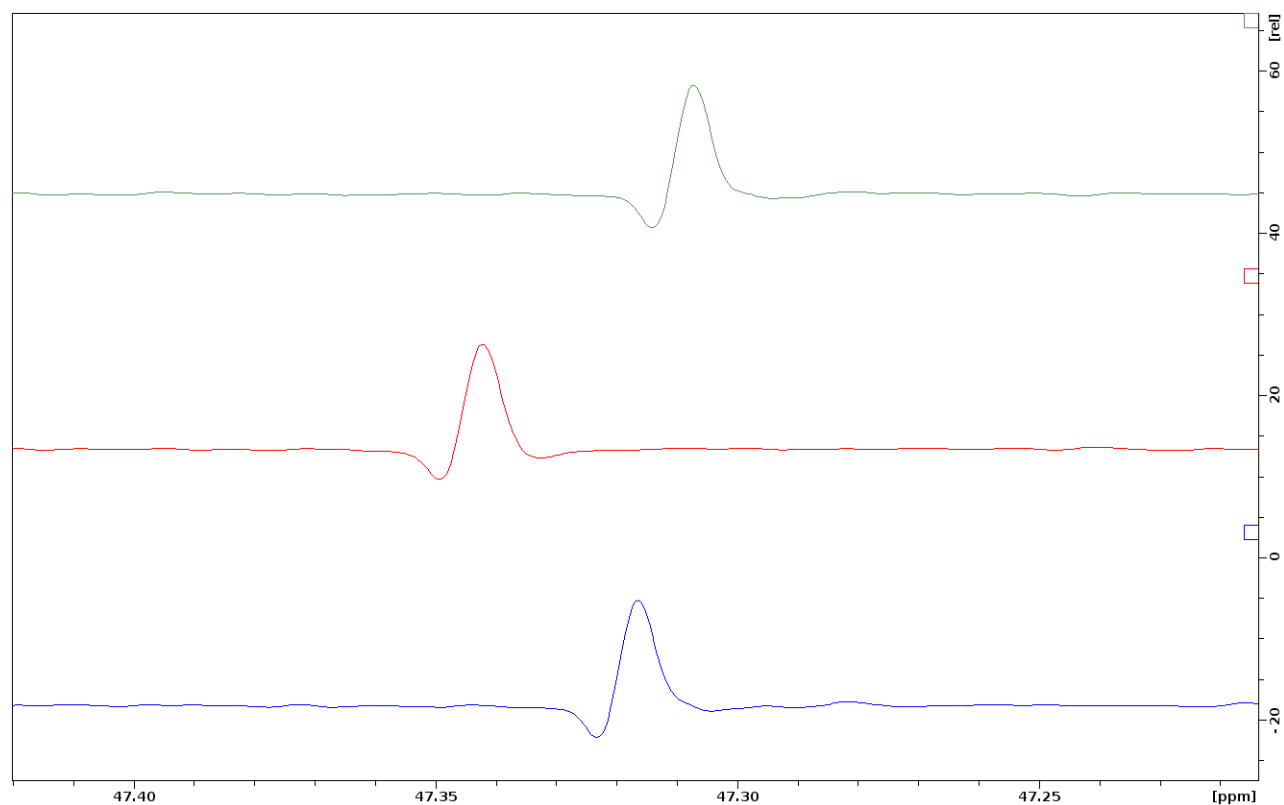


Figure S24. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

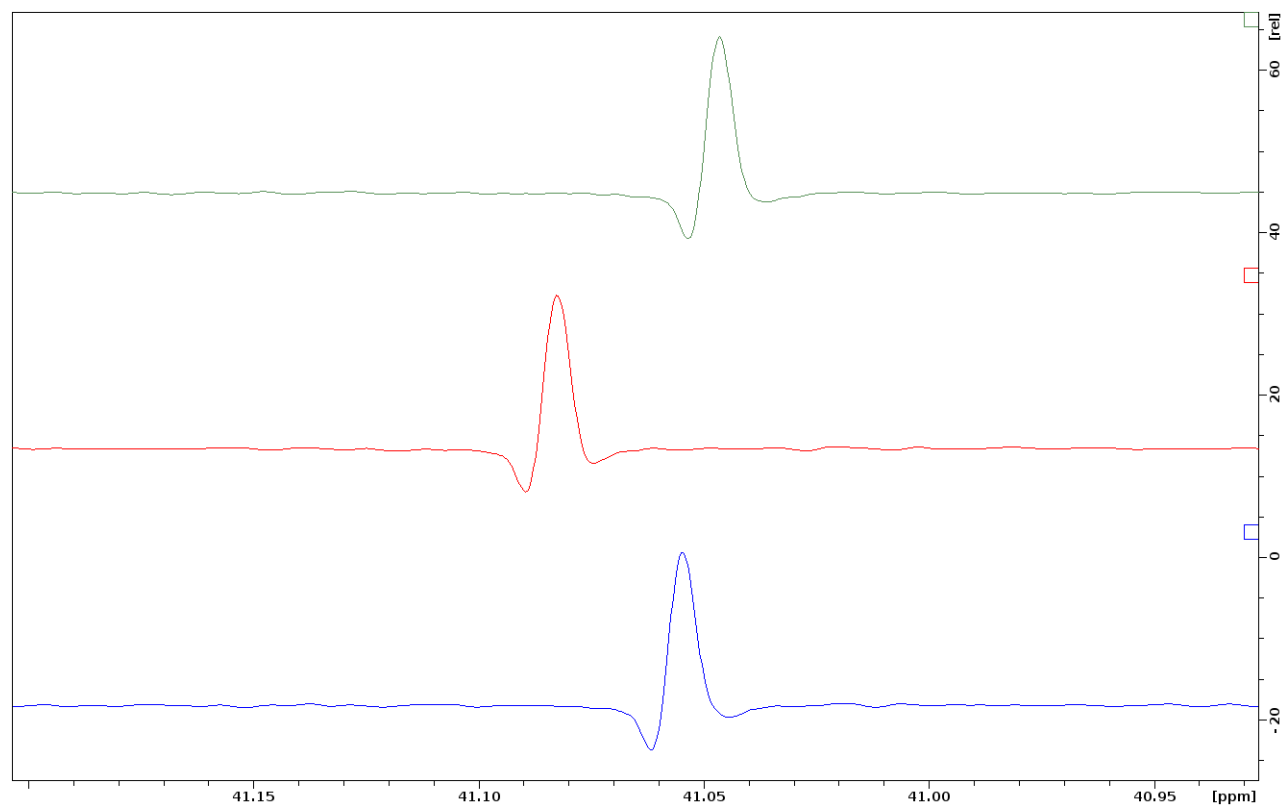


Figure S25. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (S)- α -pinene (red trace), and S -enriched scalemate (50% ee, green trace).

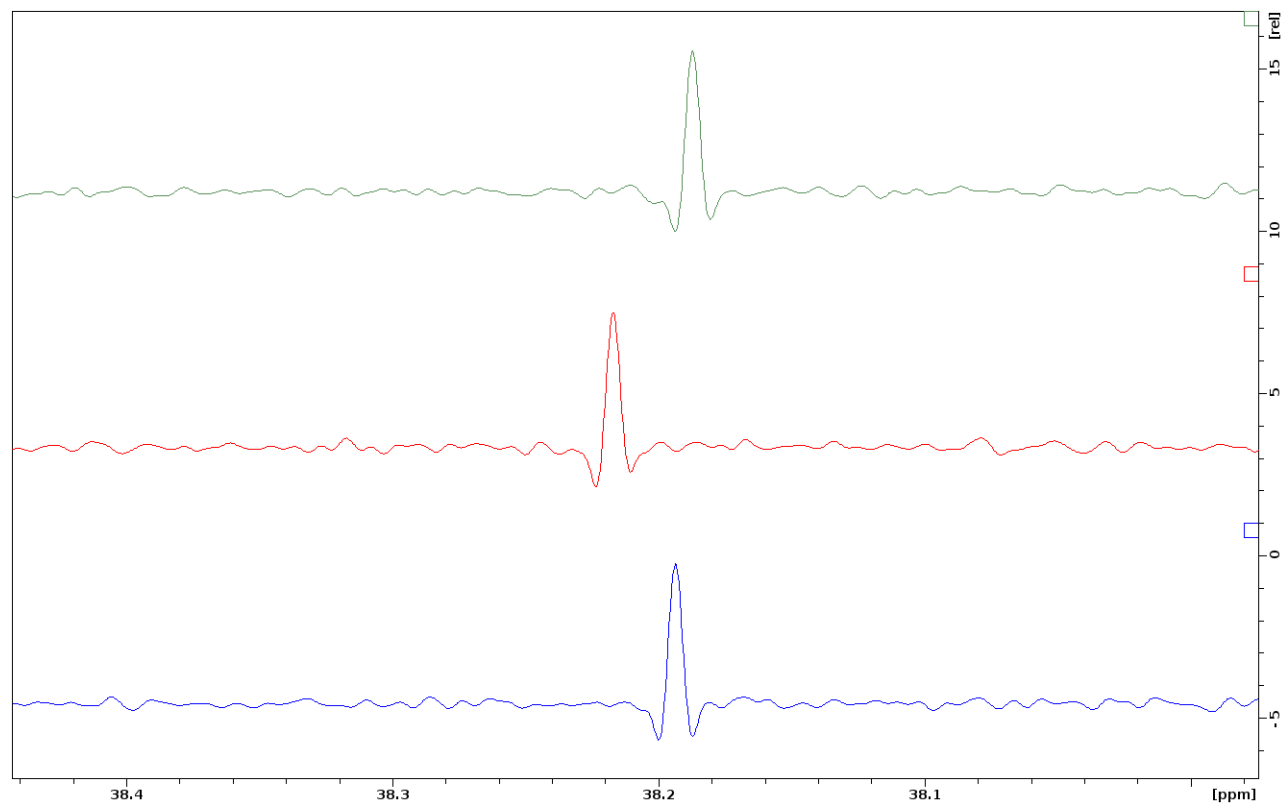


Figure S26. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (S)- α -pinene (red trace), and S -enriched scalemate (50% ee, green trace).

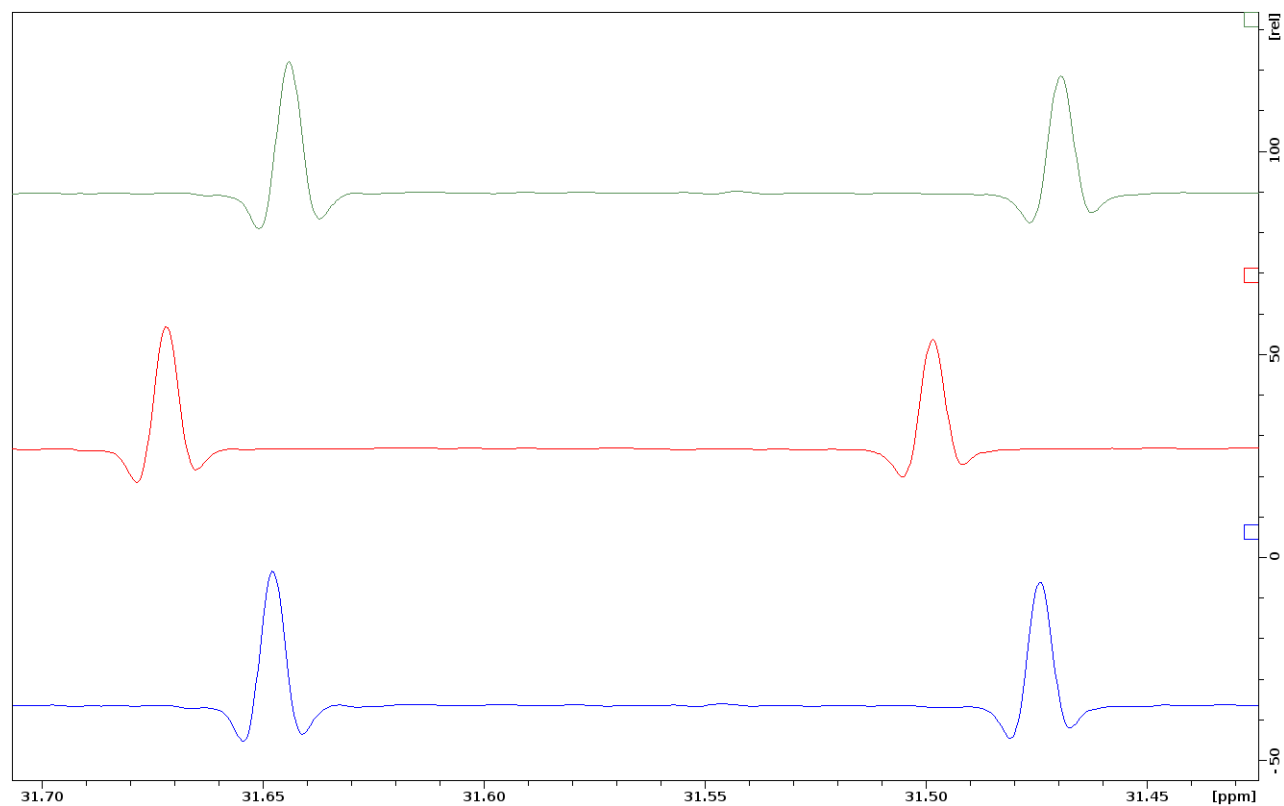


Figure S27. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

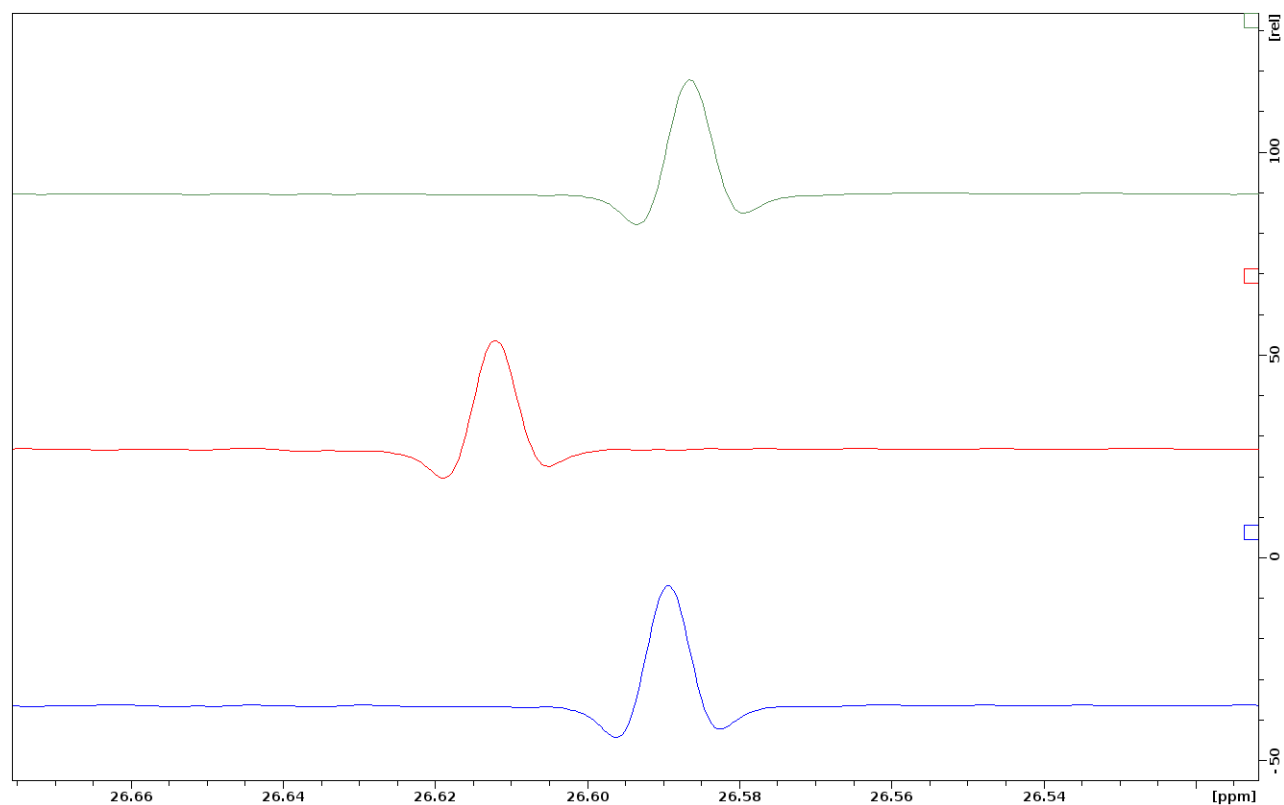


Figure S28. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

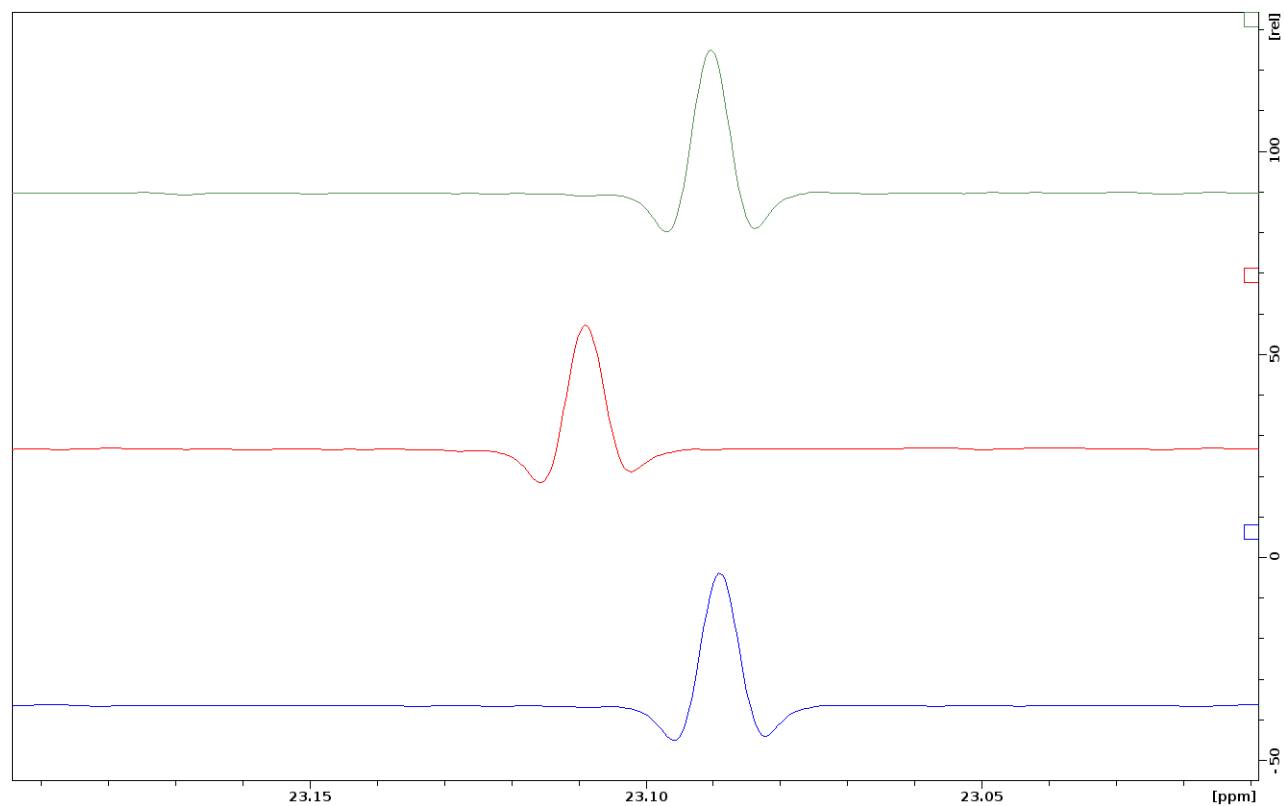


Figure S29. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

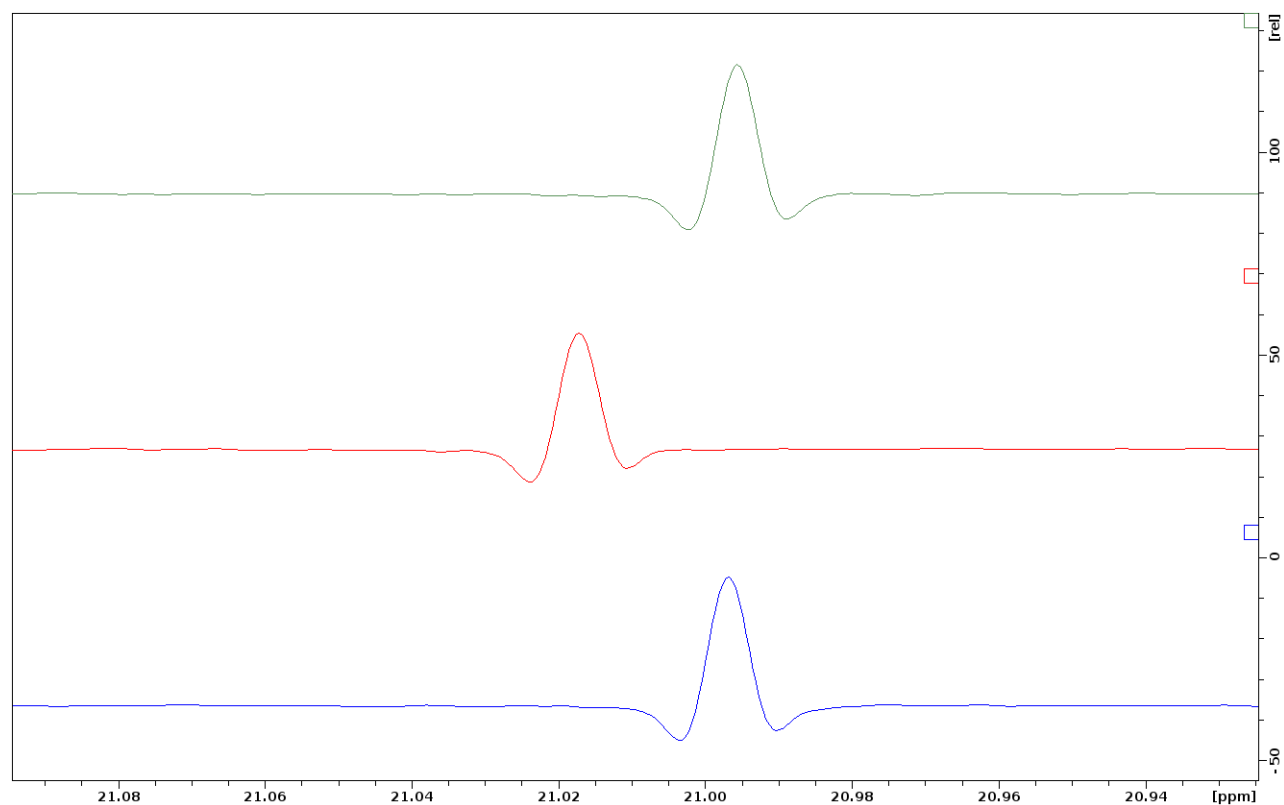


Figure S30. The ^{13}C NMR spectra of neat α -pinene at 23 $^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

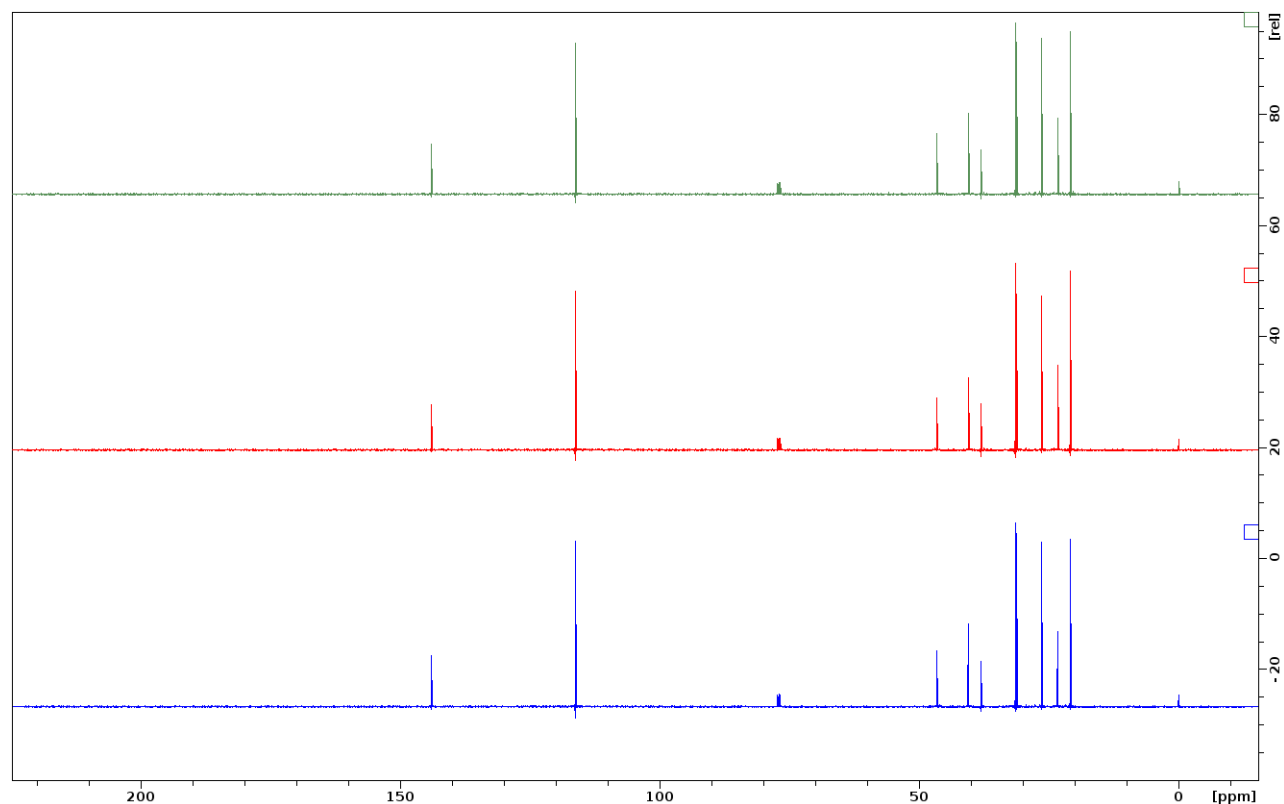


Figure S31. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

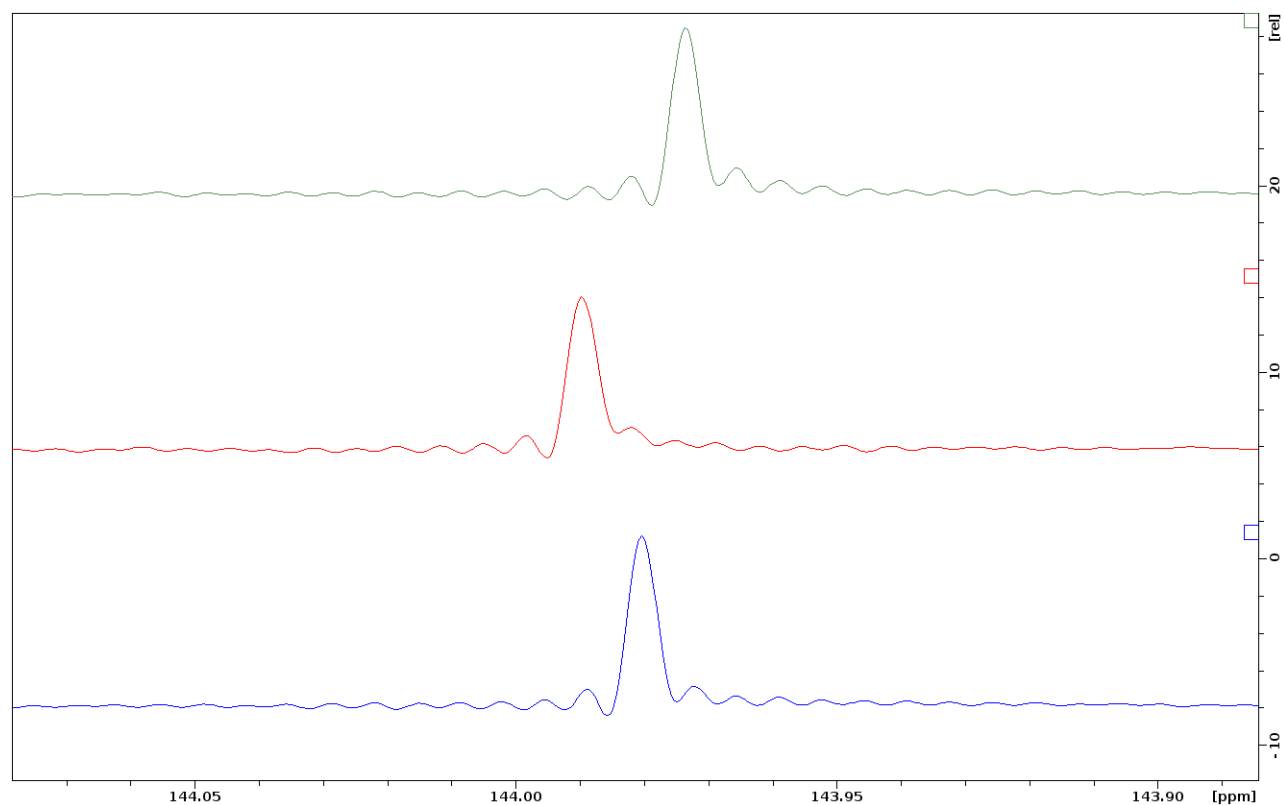


Figure S32. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

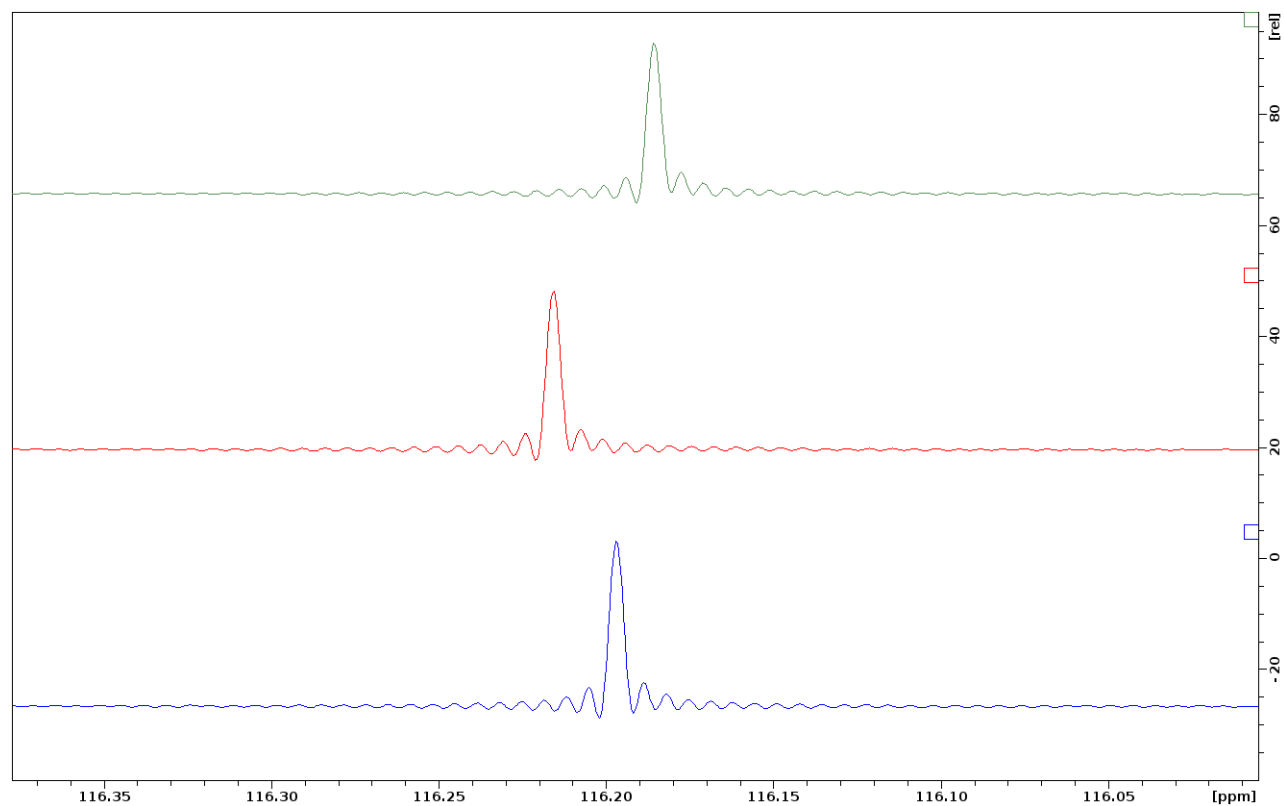


Figure S33. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

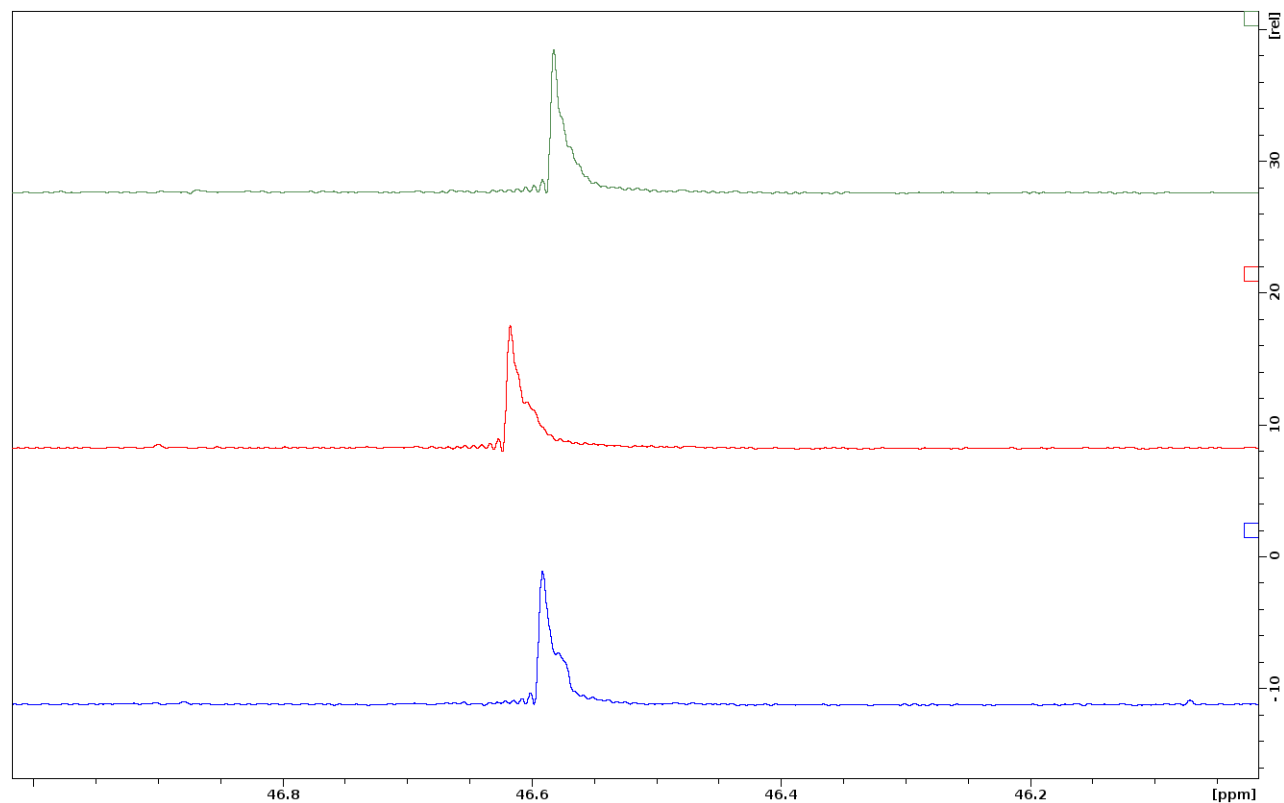


Figure S34. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

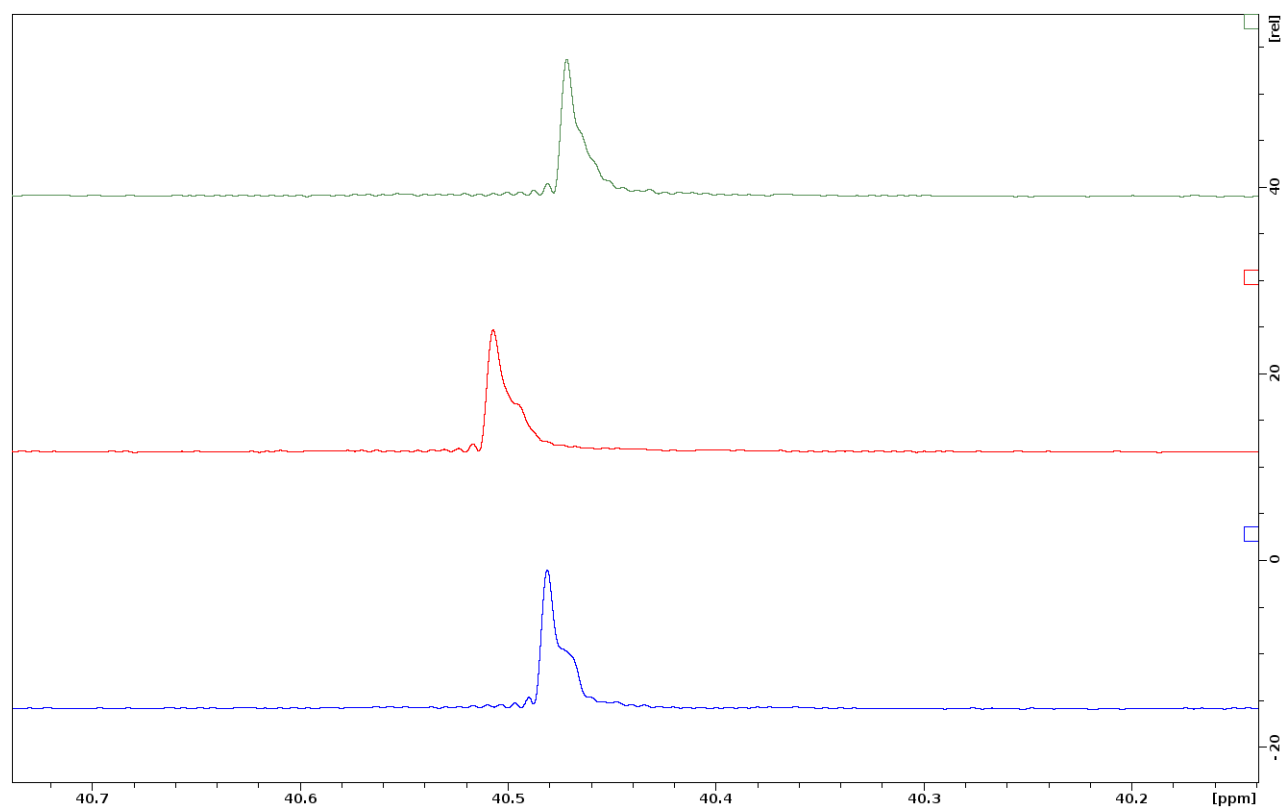


Figure S35. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

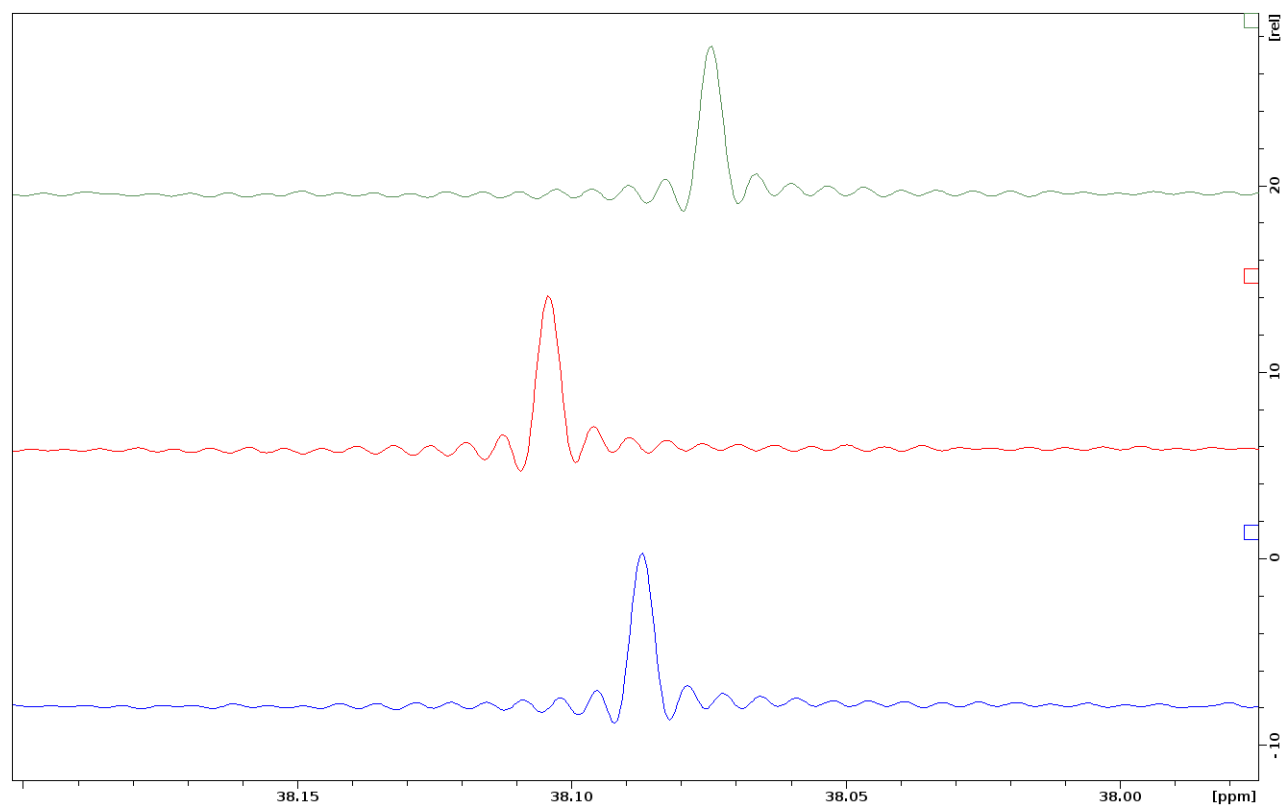


Figure S36. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

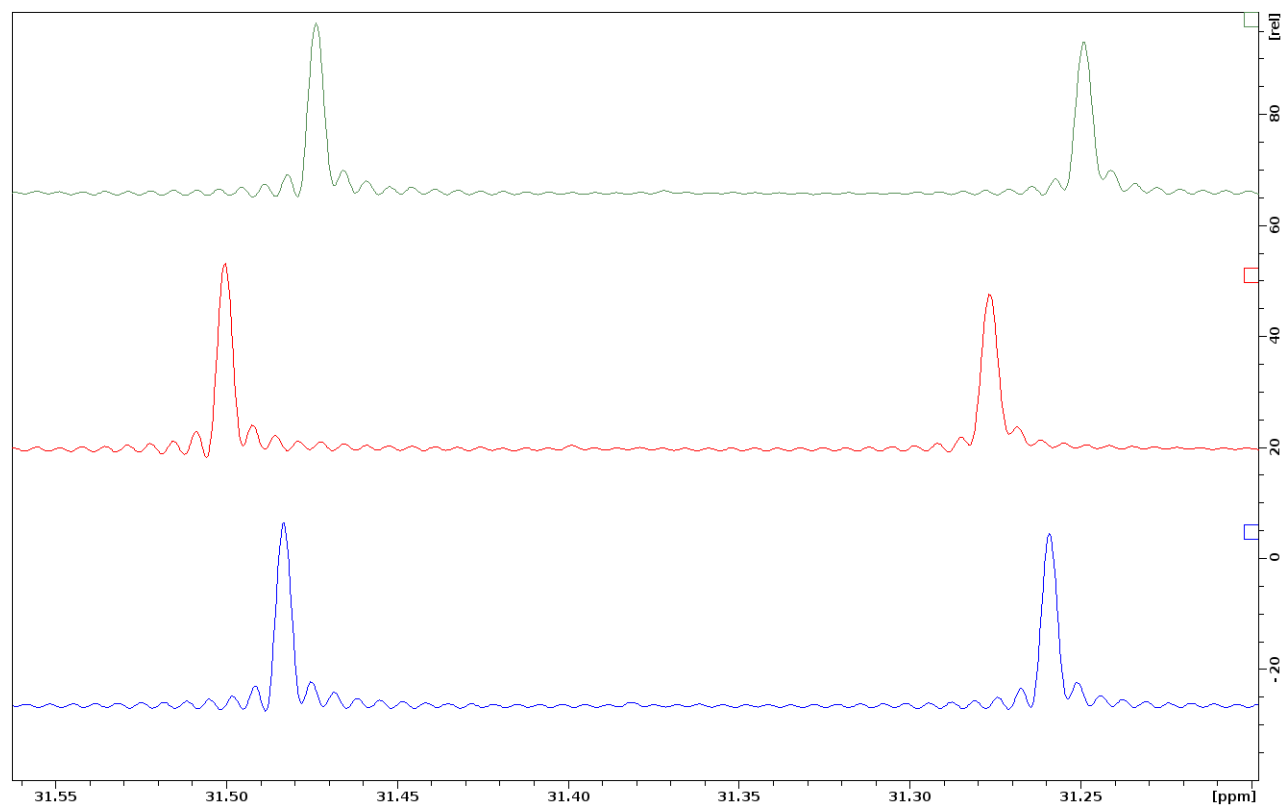


Figure S37. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

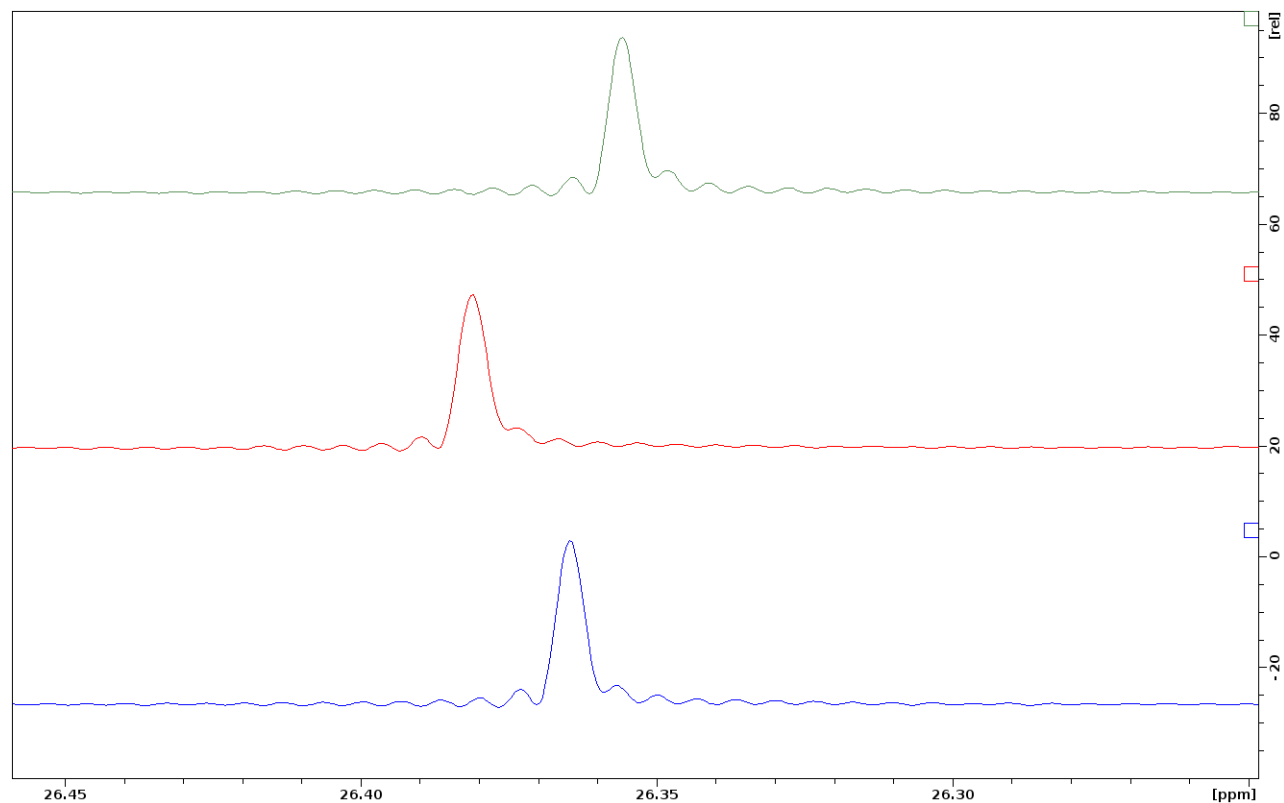


Figure S38. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

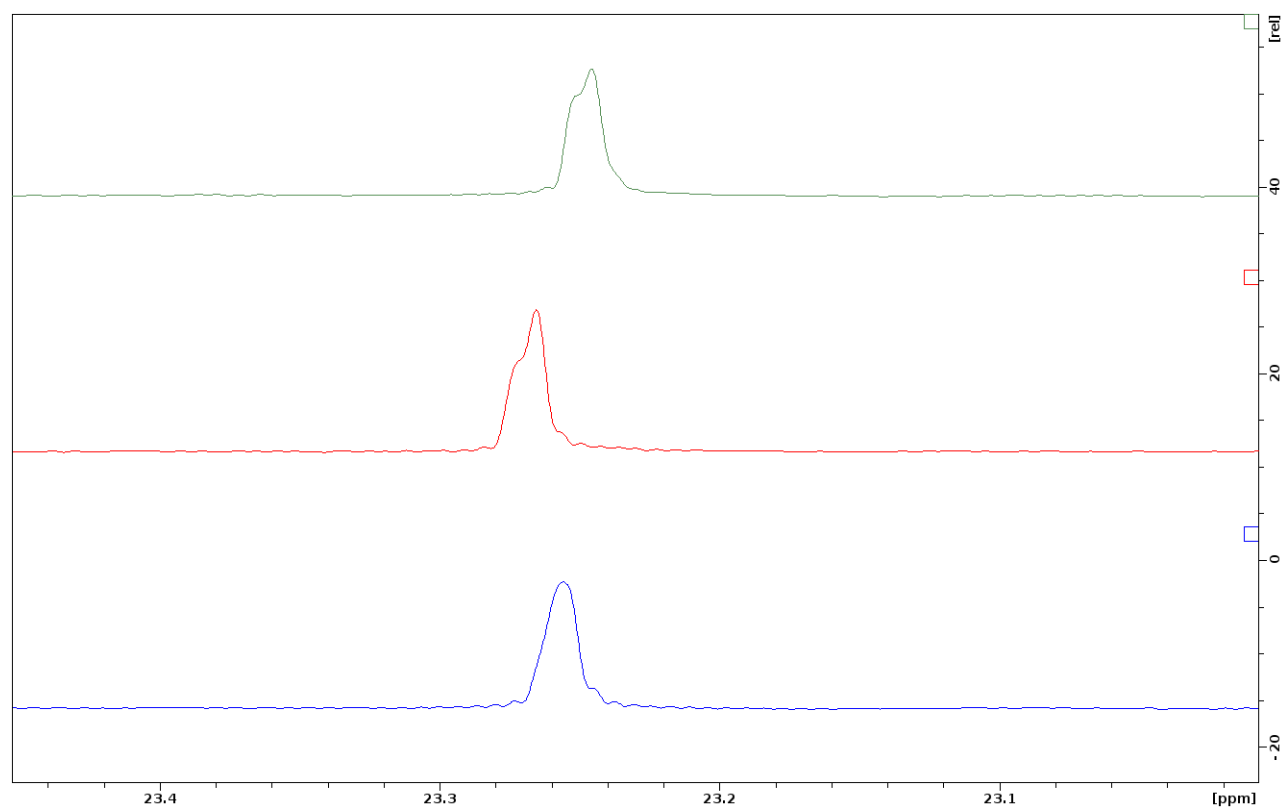


Figure S39. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).

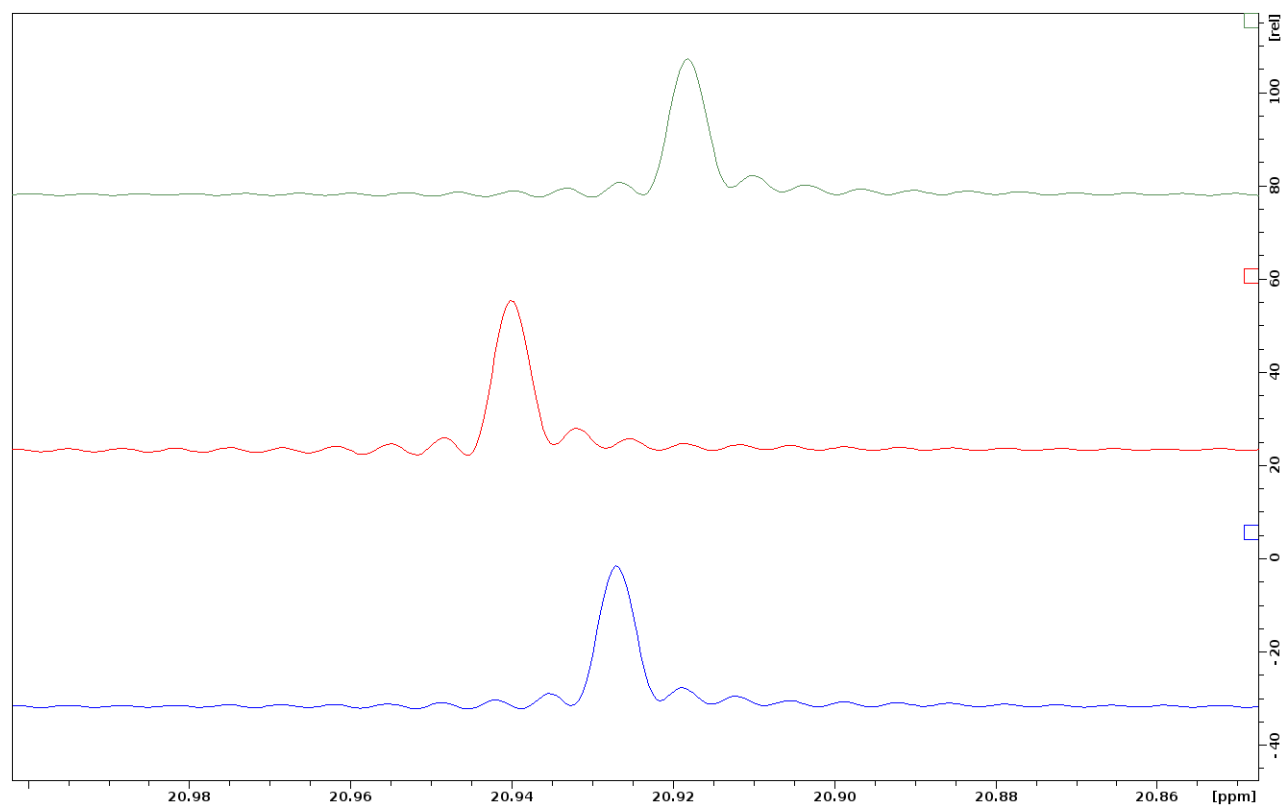


Figure S40. The ^{13}C NMR spectra of neat α -pinene at $-41\text{ }^{\circ}\text{C}$. From bottom to top, racemic α -pinene (blue trace), (*S*)- α -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).