

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

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## Supplementary Materials

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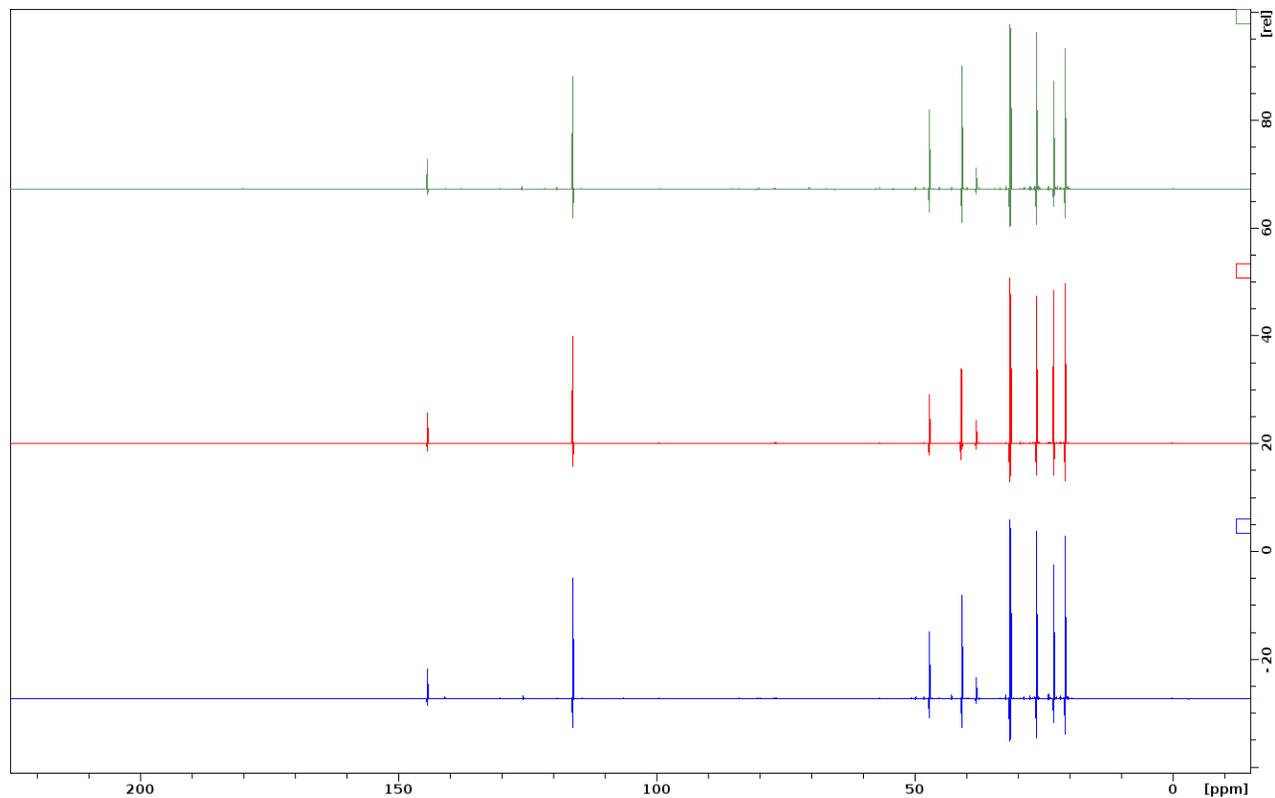
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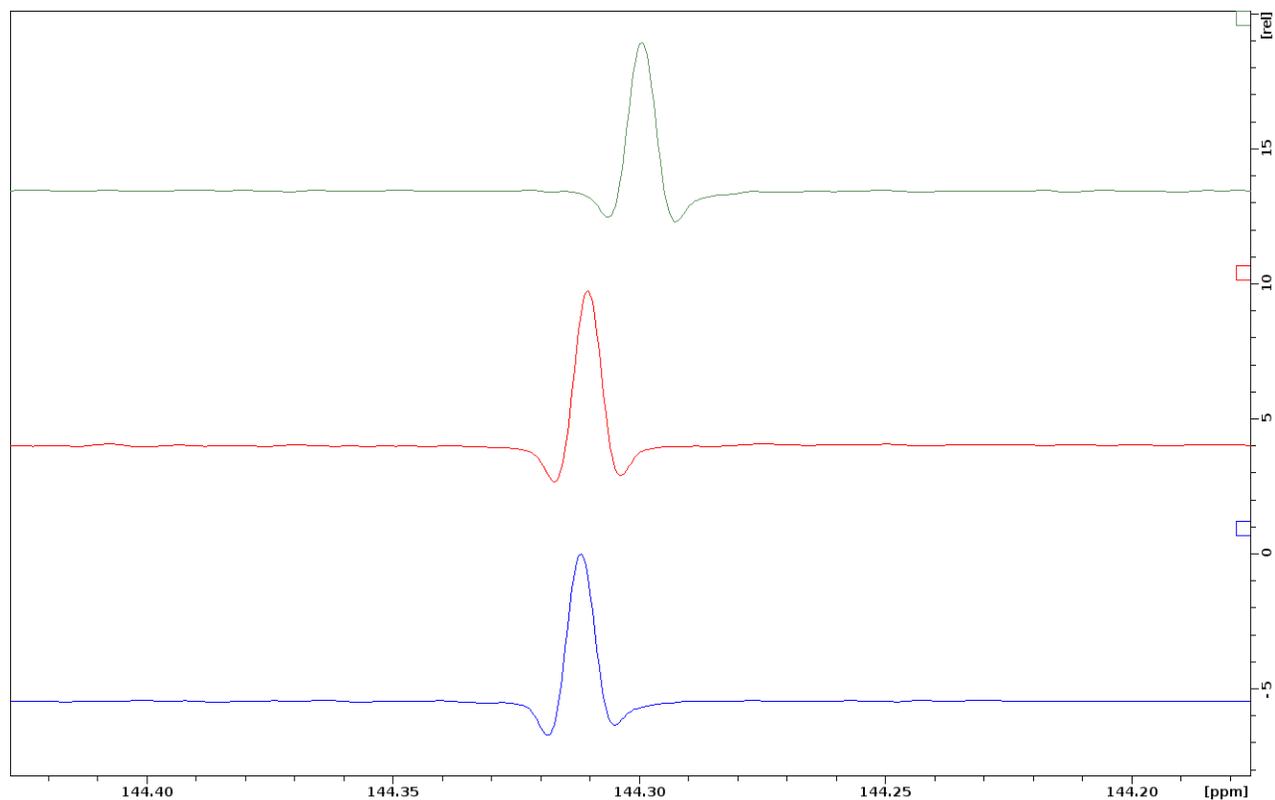
**Abstract:**  $\alpha$ -Pinene is an intriguing monoterpene as it has been reported to undergo the self-disproportionation of enantiomers (SDE) phenomenon via gas chromatography (GC), the only compound to decisively demonstrate this. Examples of the SDE involving the gaseous phase – sublimation aside – 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  $\alpha$ -pinene SDE via evaporation off silica gel and by foam fractionation – albeit the SDE magnitude for both was only very slight – to confirm that  $\alpha$ -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  $\alpha$ -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);  $\alpha$ -pinene; hydrocarbons; gas chromatography; silica gel; foam fractionation; evaporation; 2D chiral-based association packing; molecular associations; intermolecular interactions

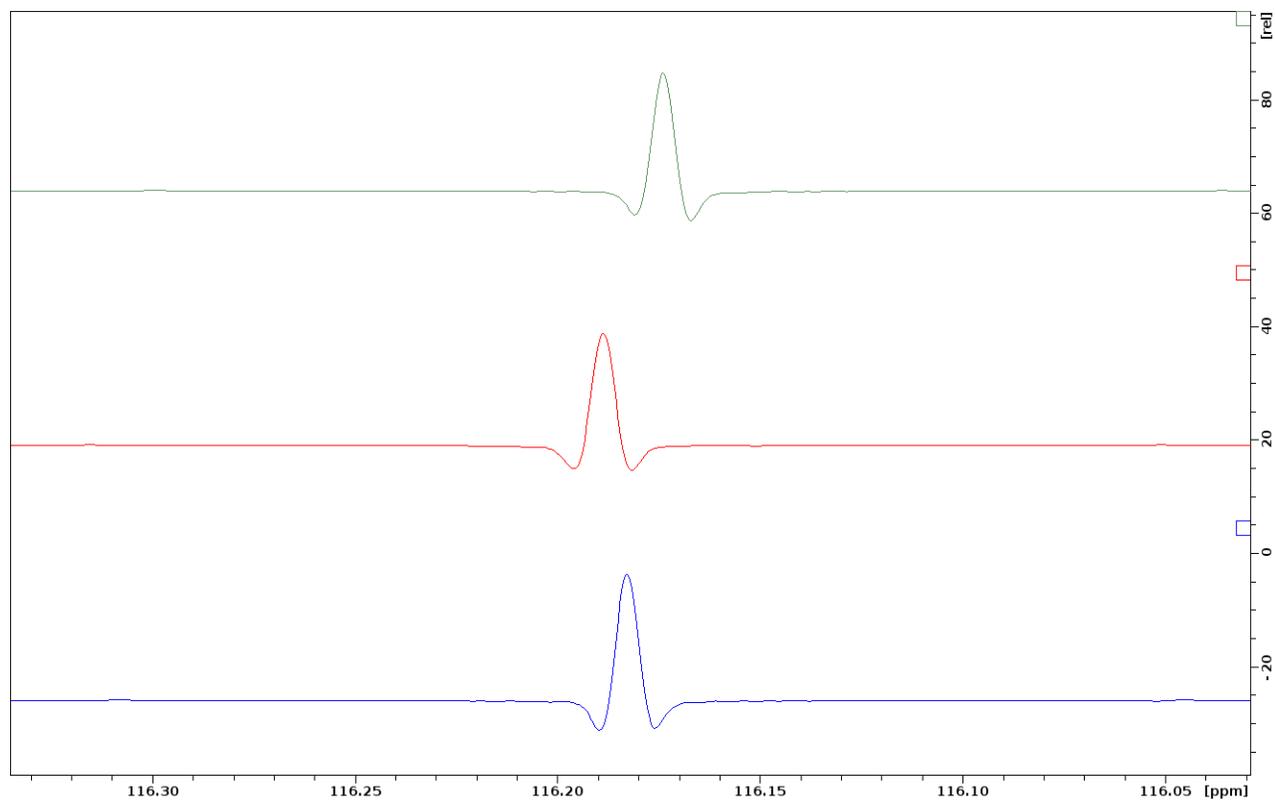
Contents: Low-temperature <sup>13</sup>C NMR spectra exhibiting the SIDA phenomenon.



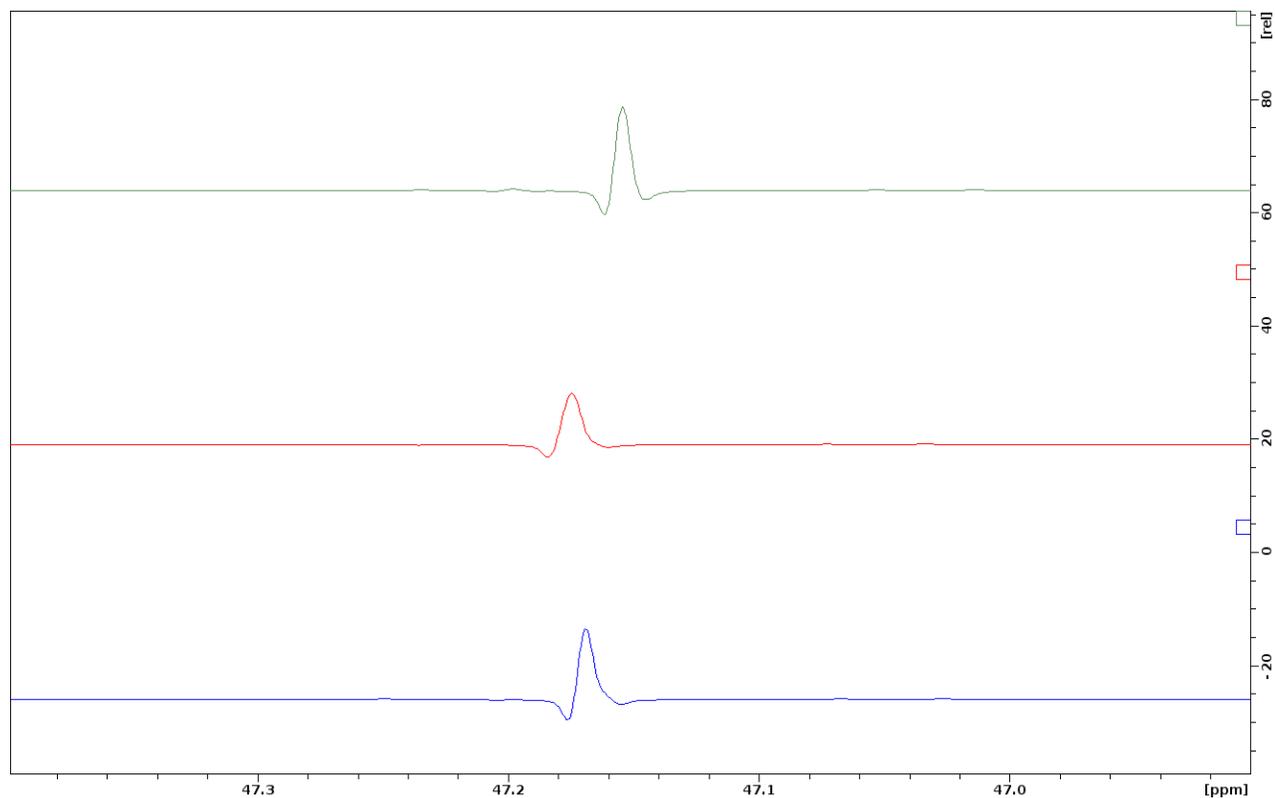
**Figure S1.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



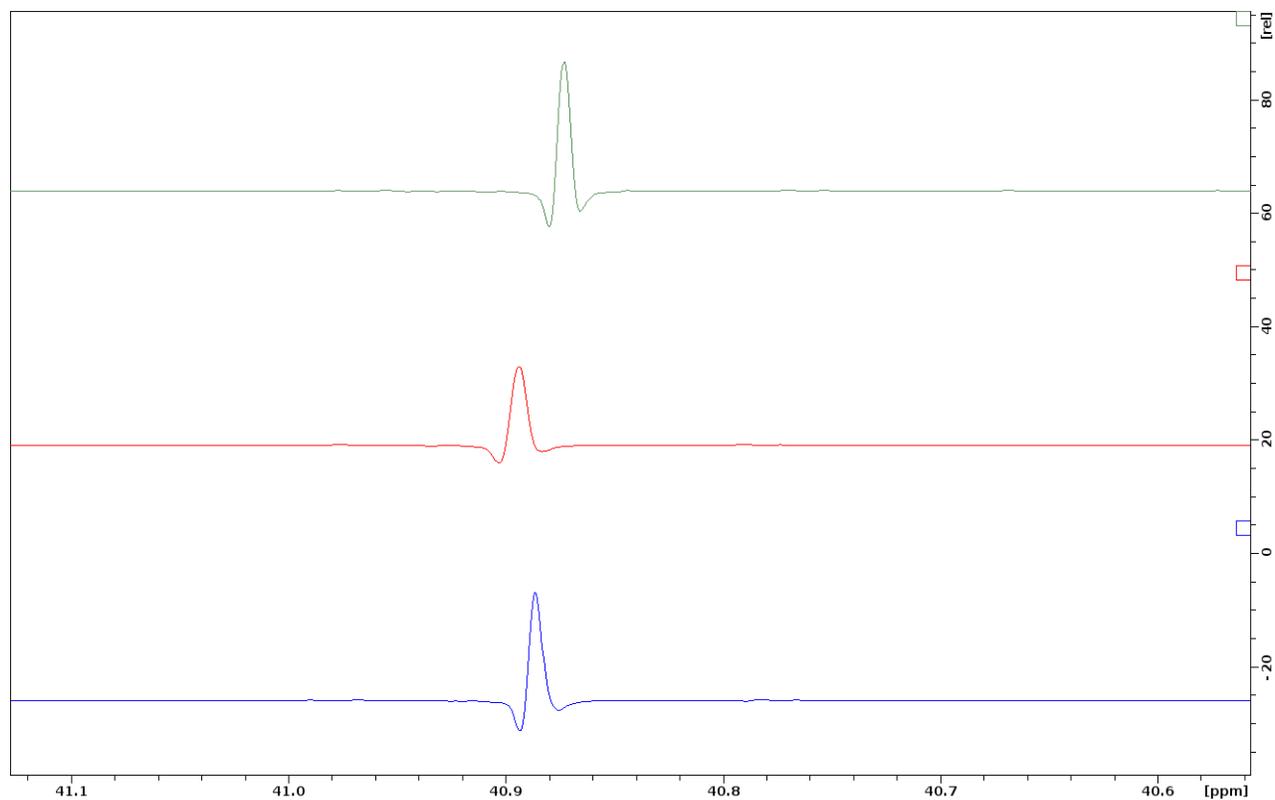
**Figure S2.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



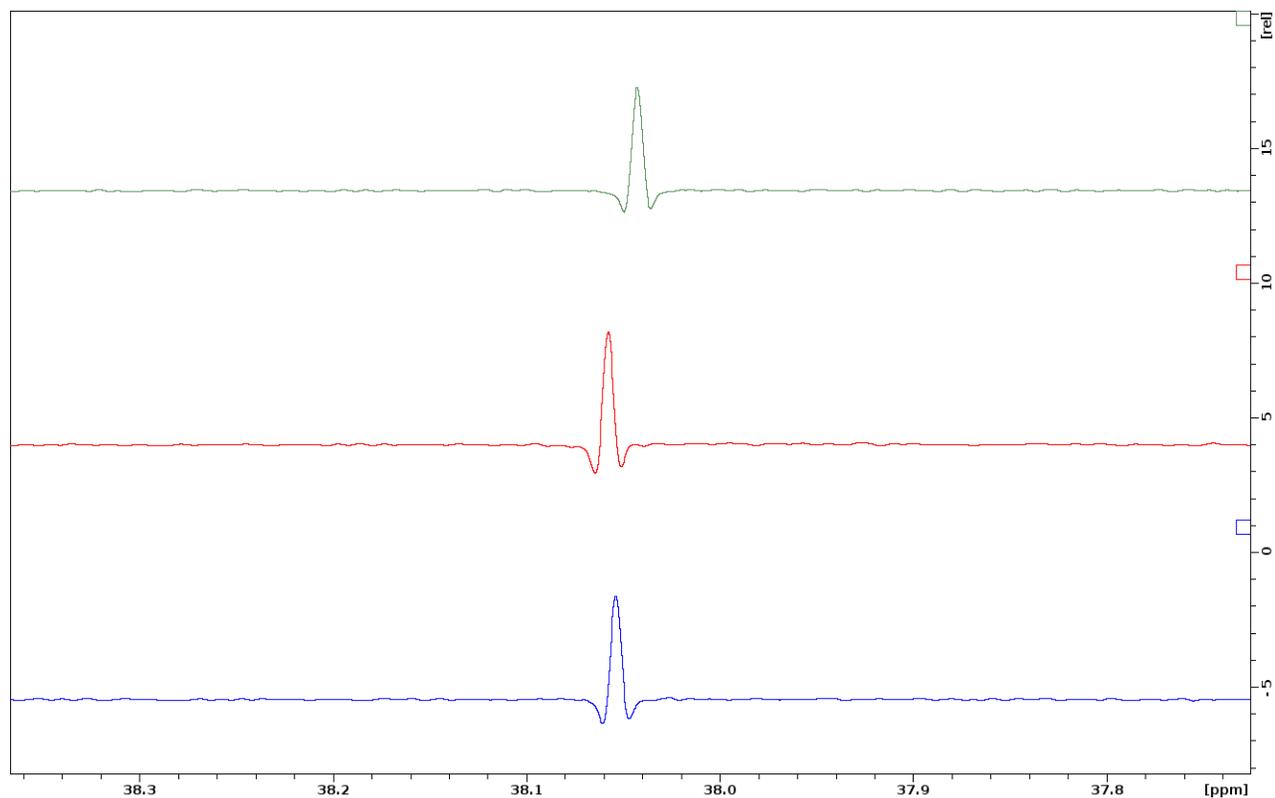
**Figure S3.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



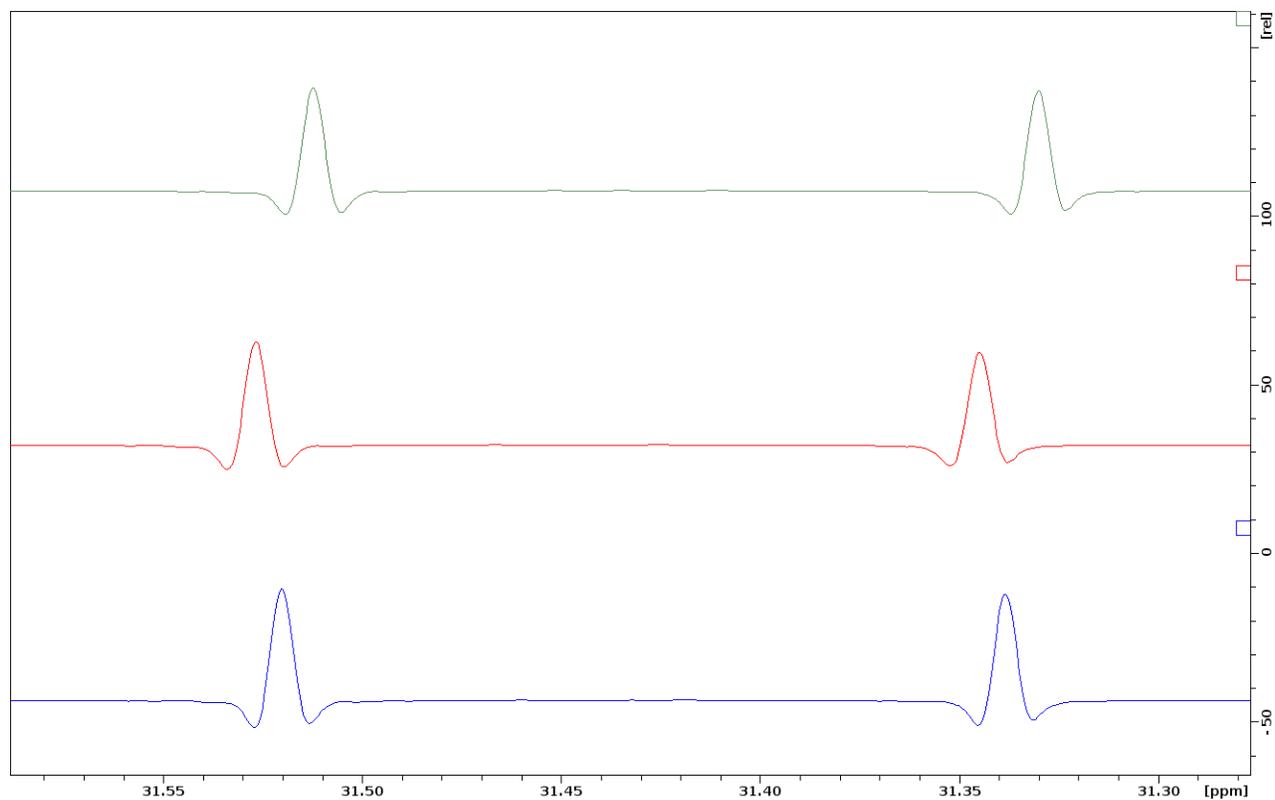
**Figure S4.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



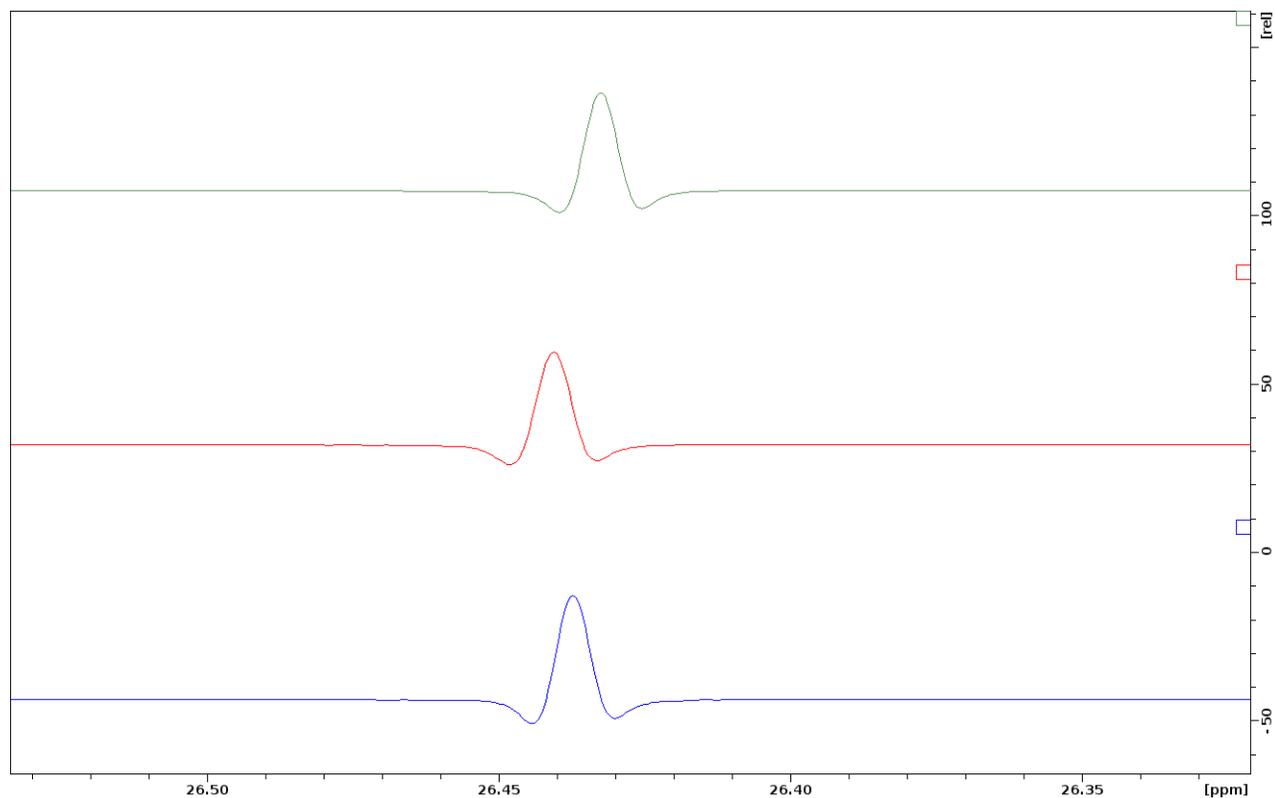
**Figure S5.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



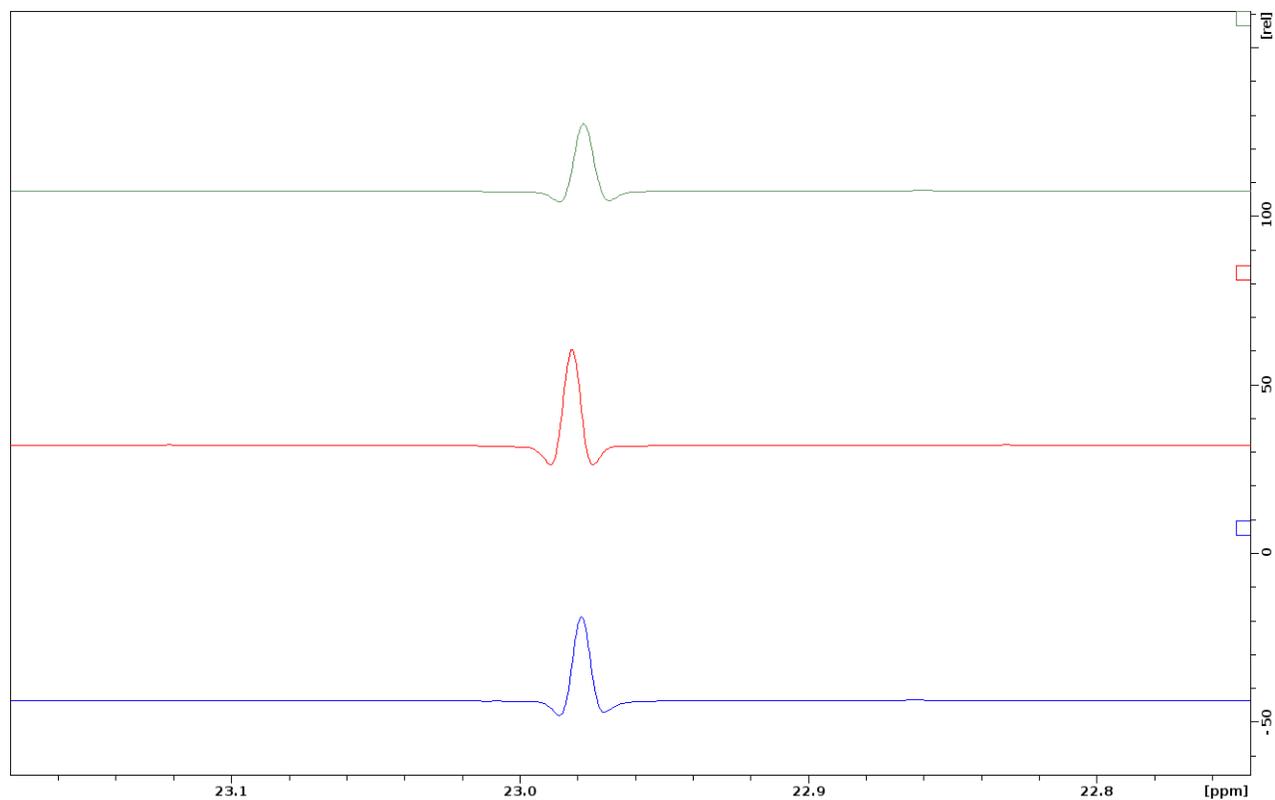
**Figure S6.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



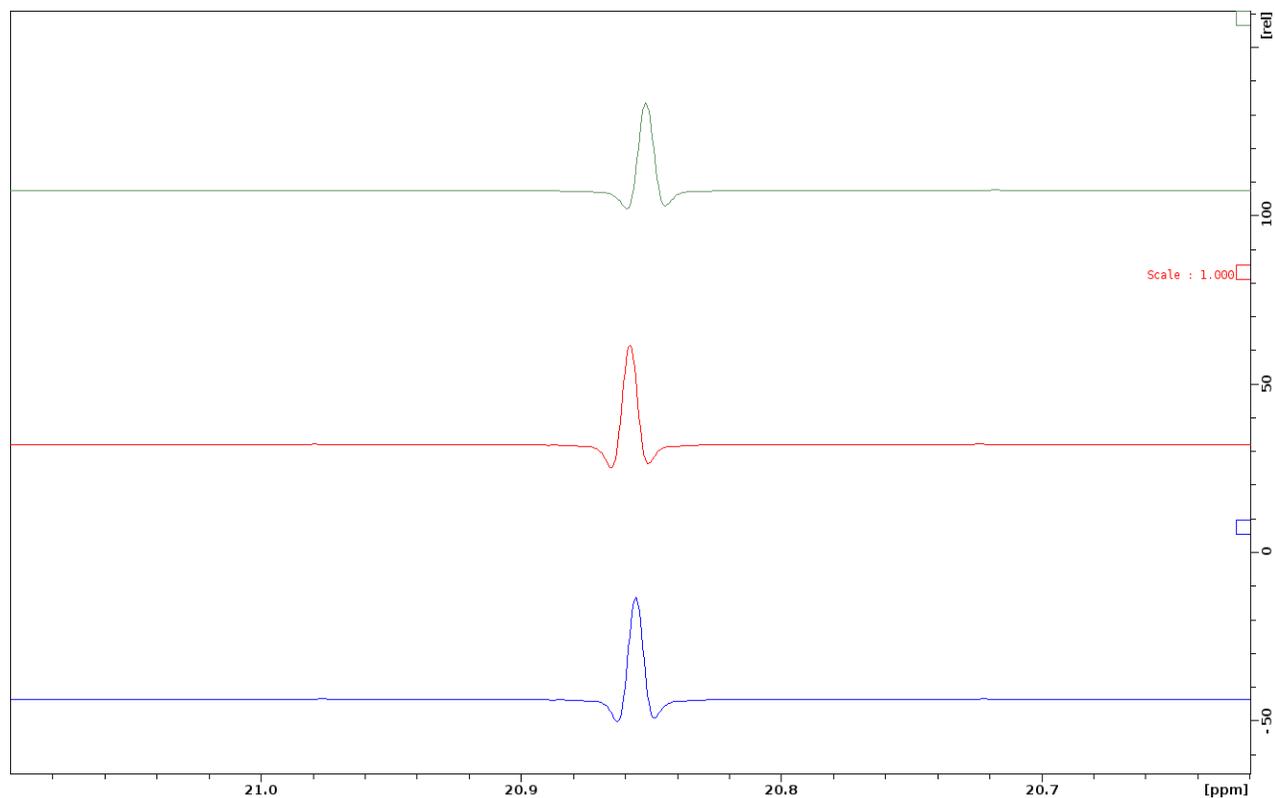
**Figure S7.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



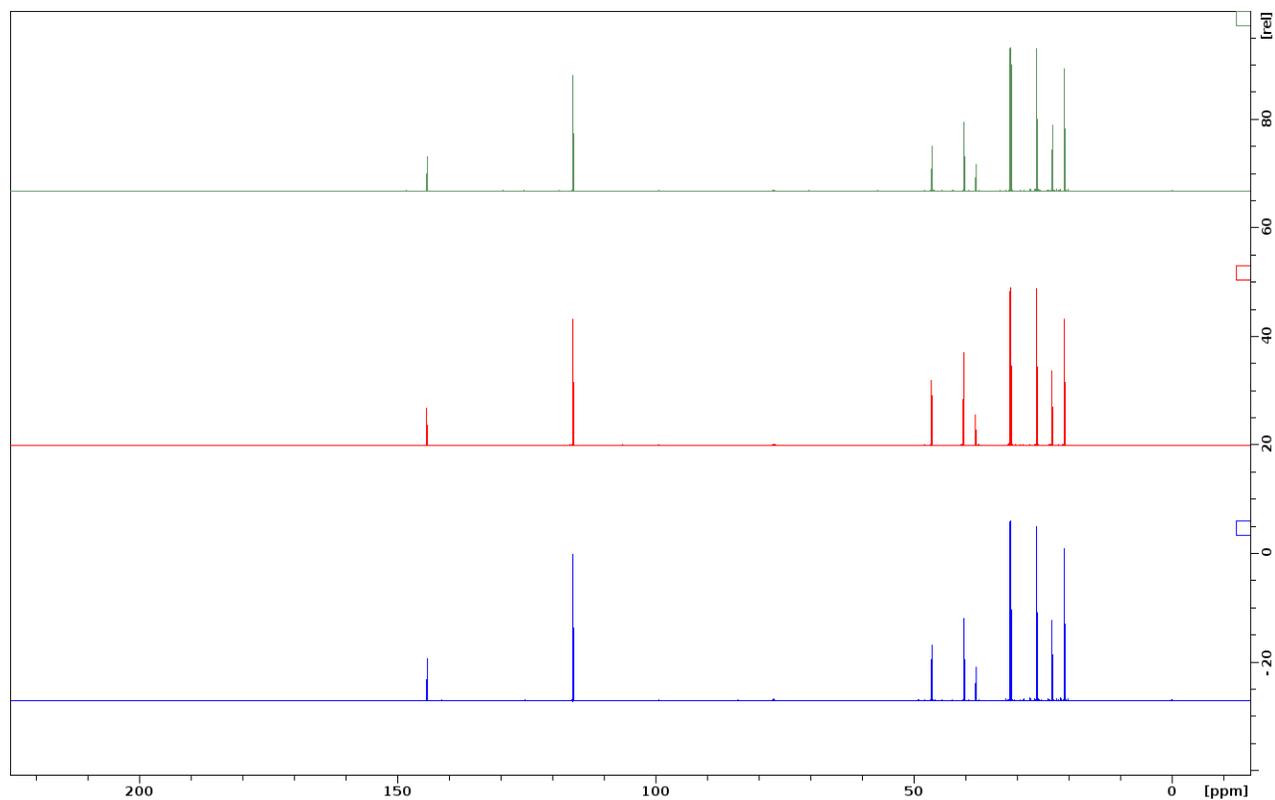
**Figure S8.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



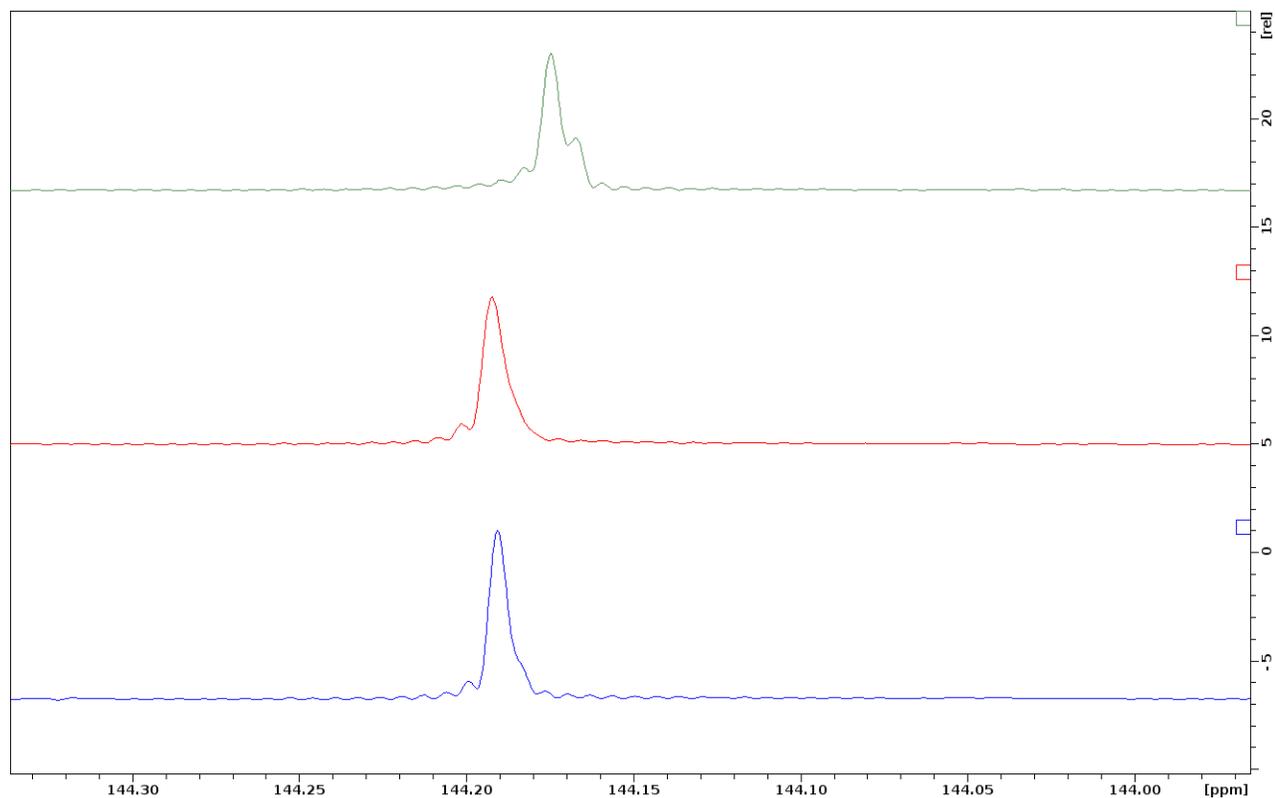
**Figure S9.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



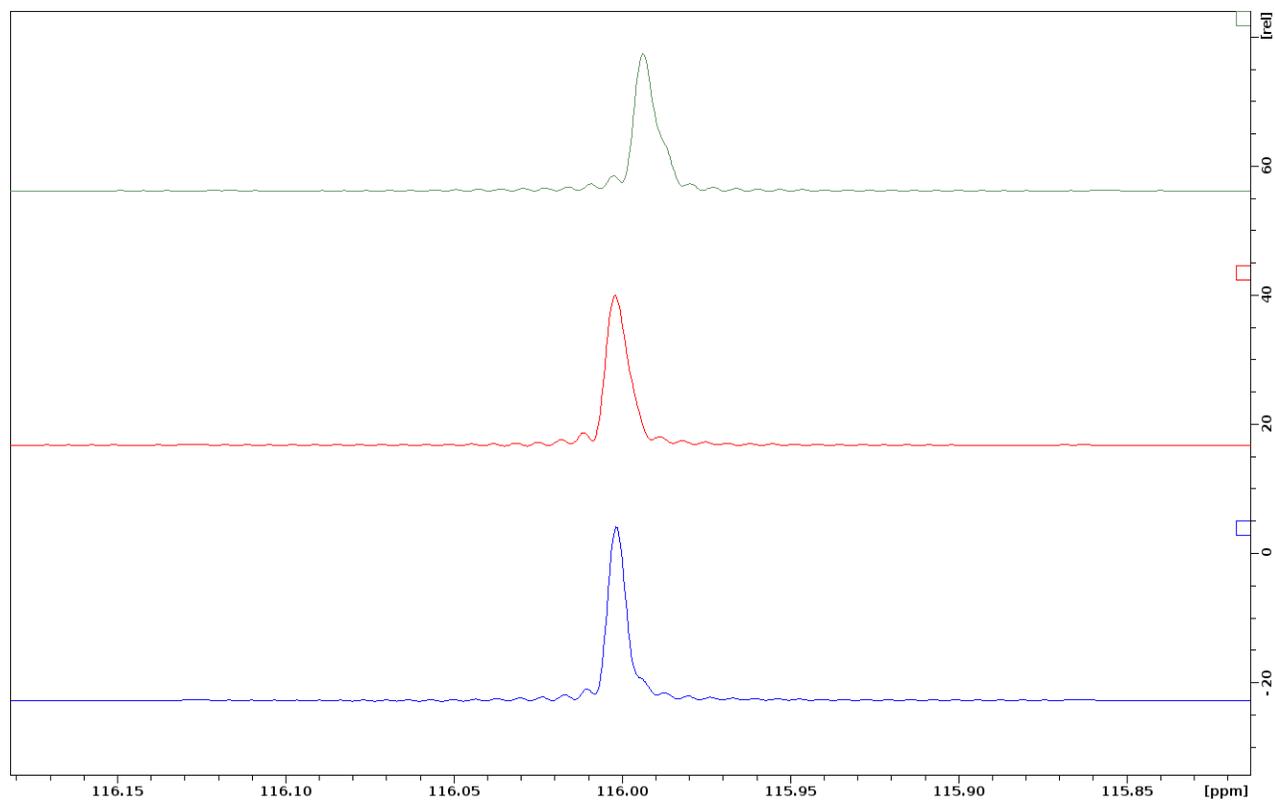
**Figure S10.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



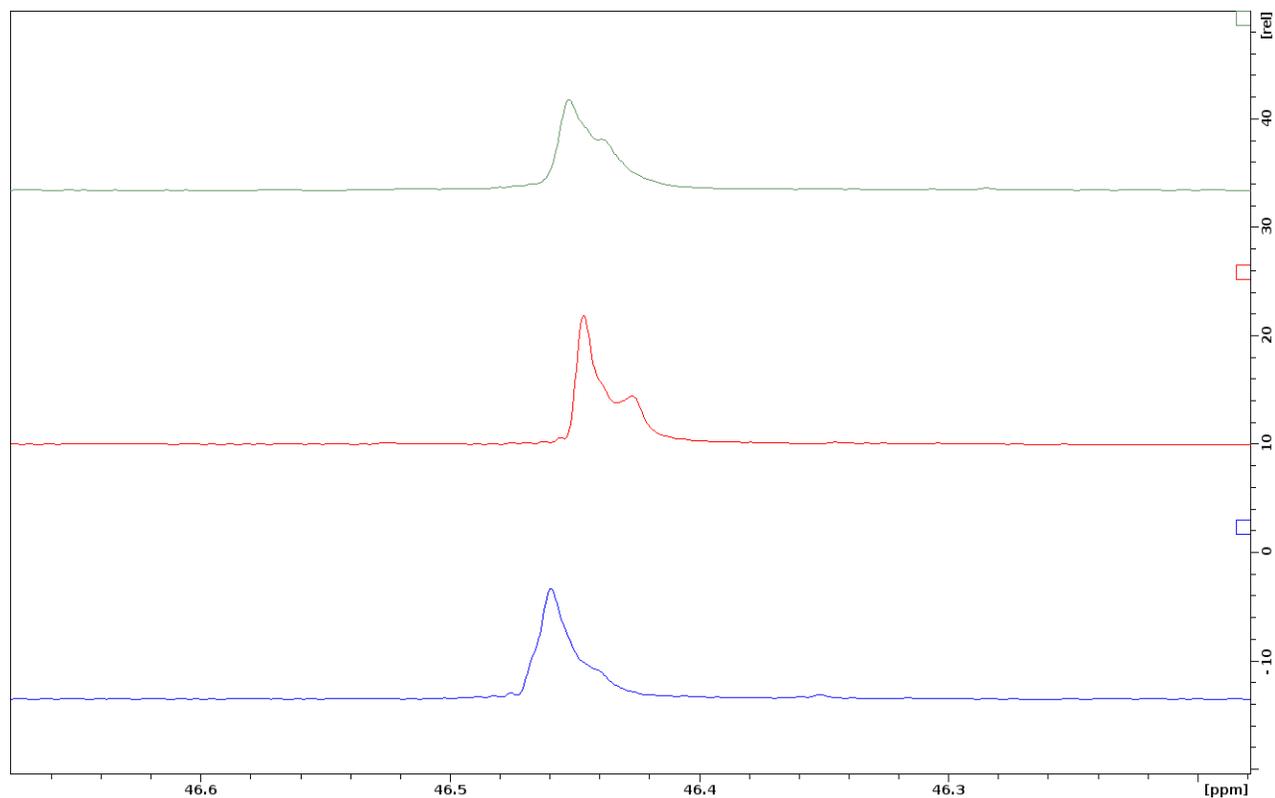
**Figure S11.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



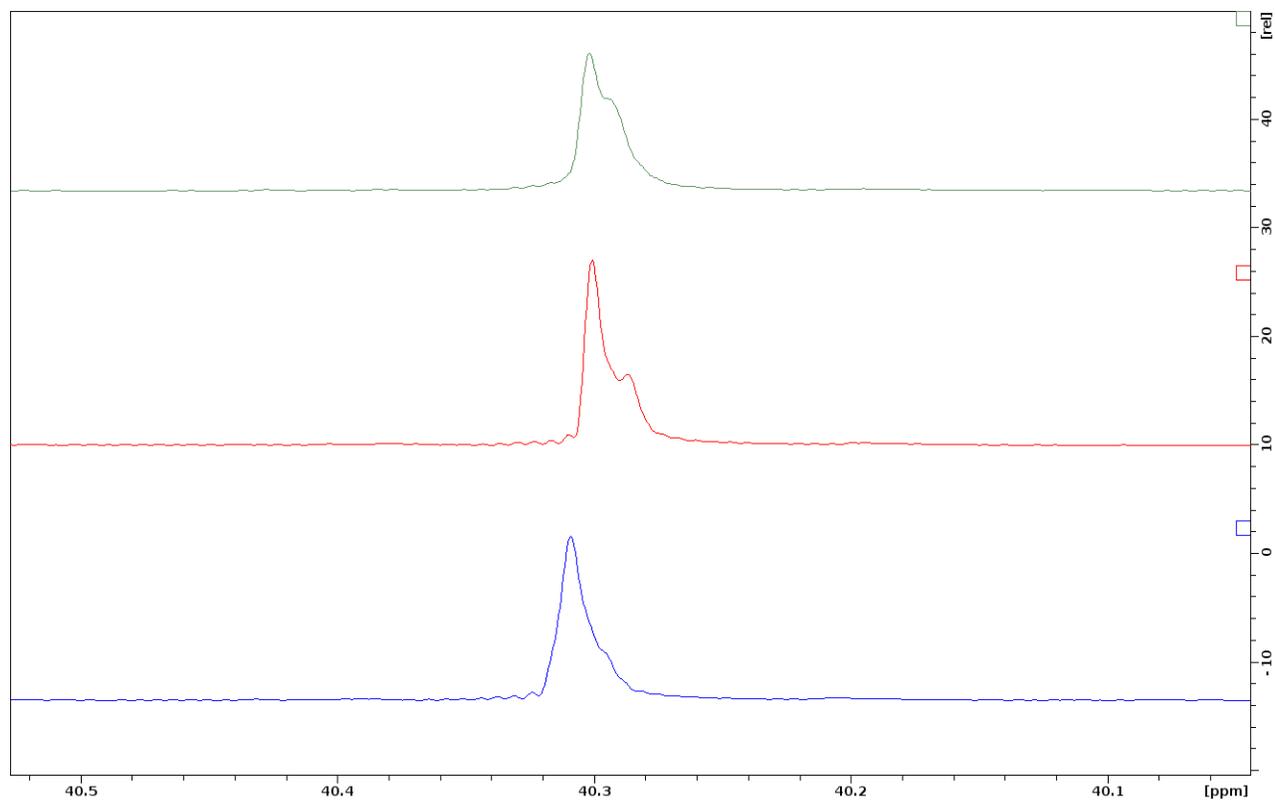
**Figure S12.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



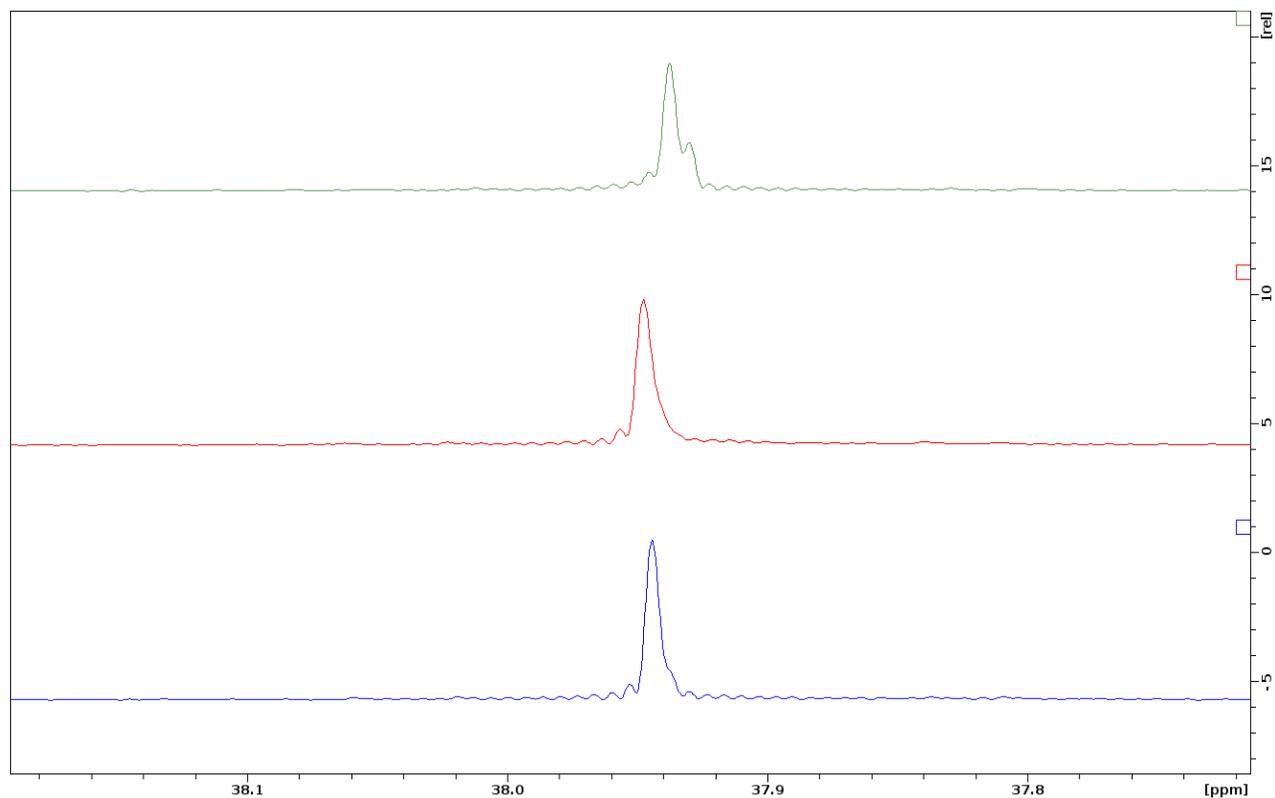
**Figure S13.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



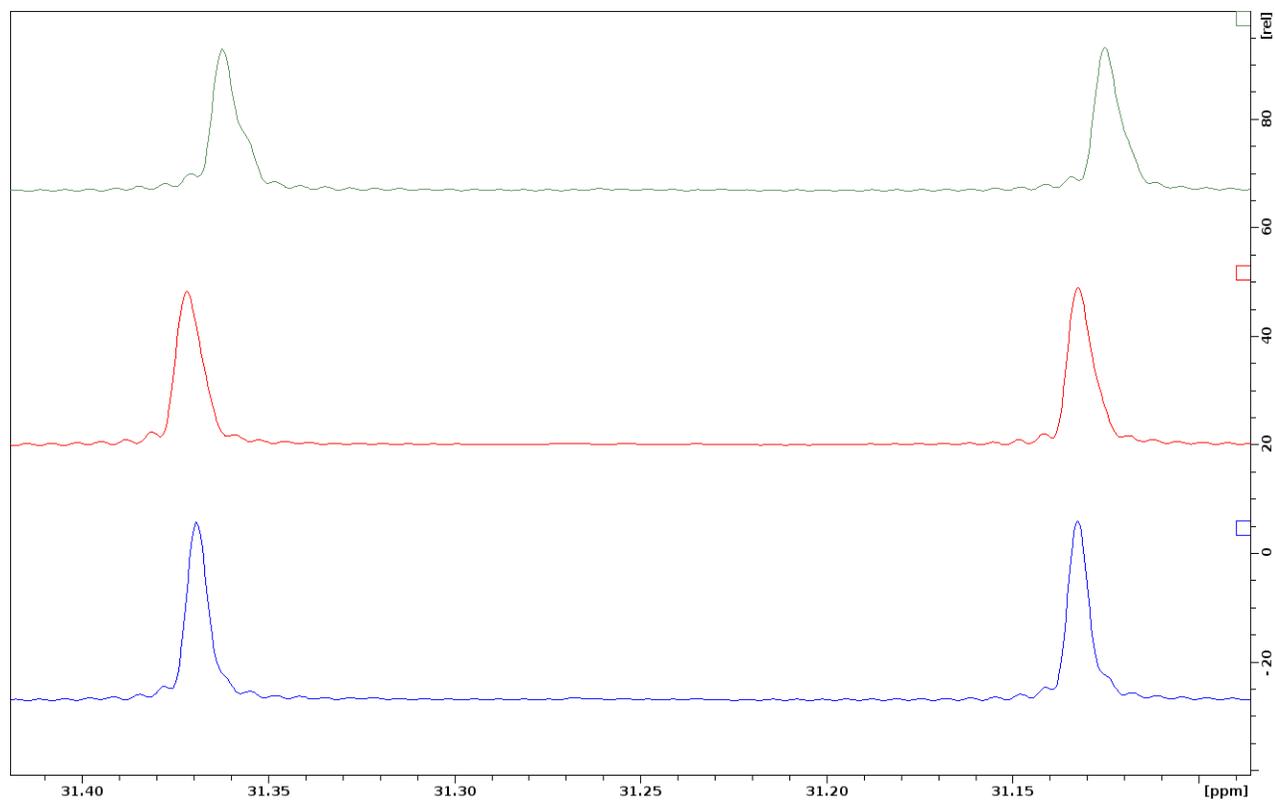
**Figure S14.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



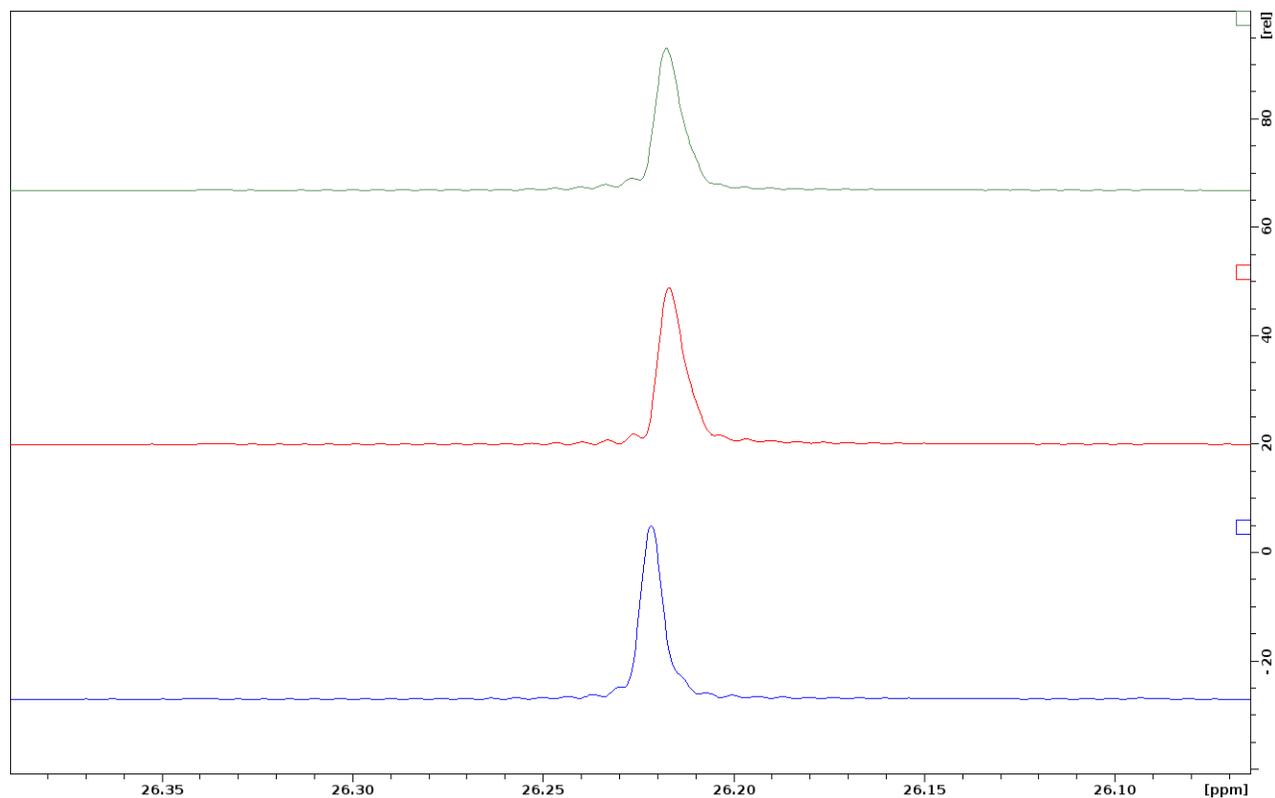
**Figure S15.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



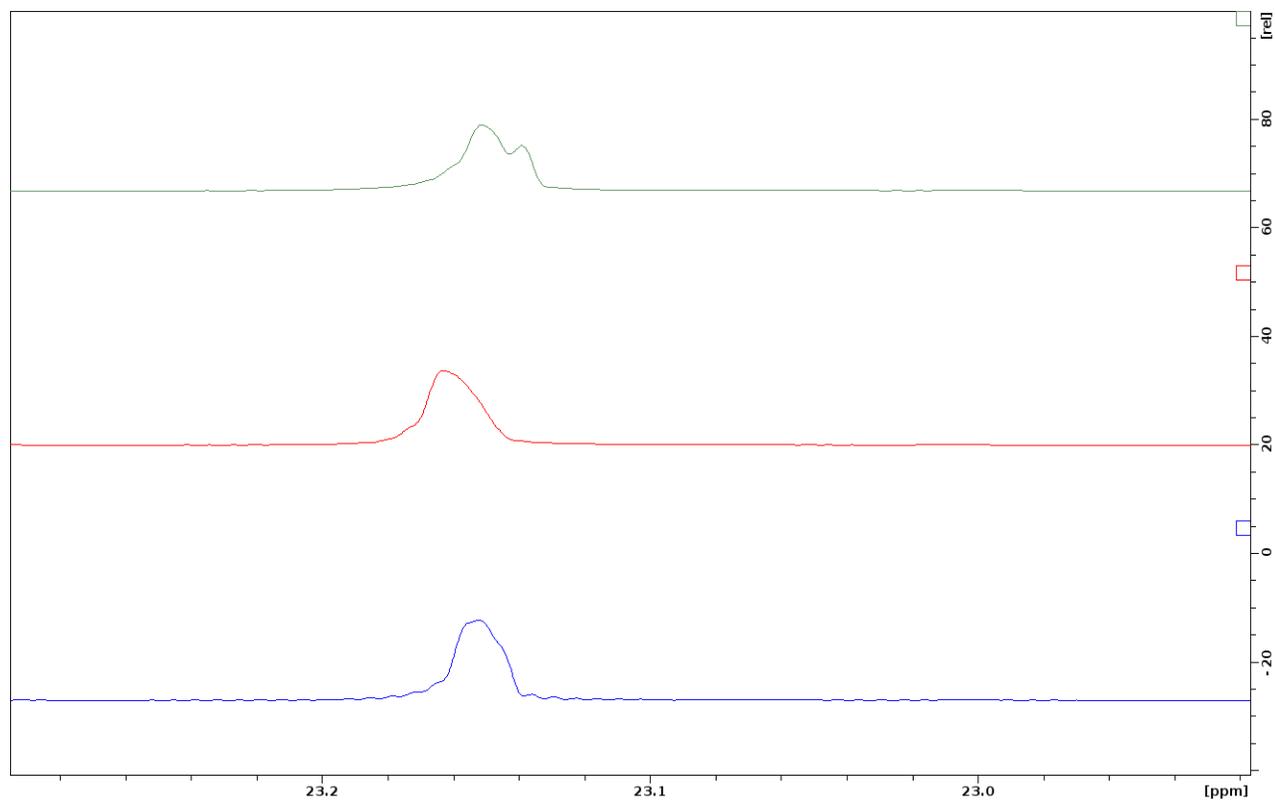
**Figure S16.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



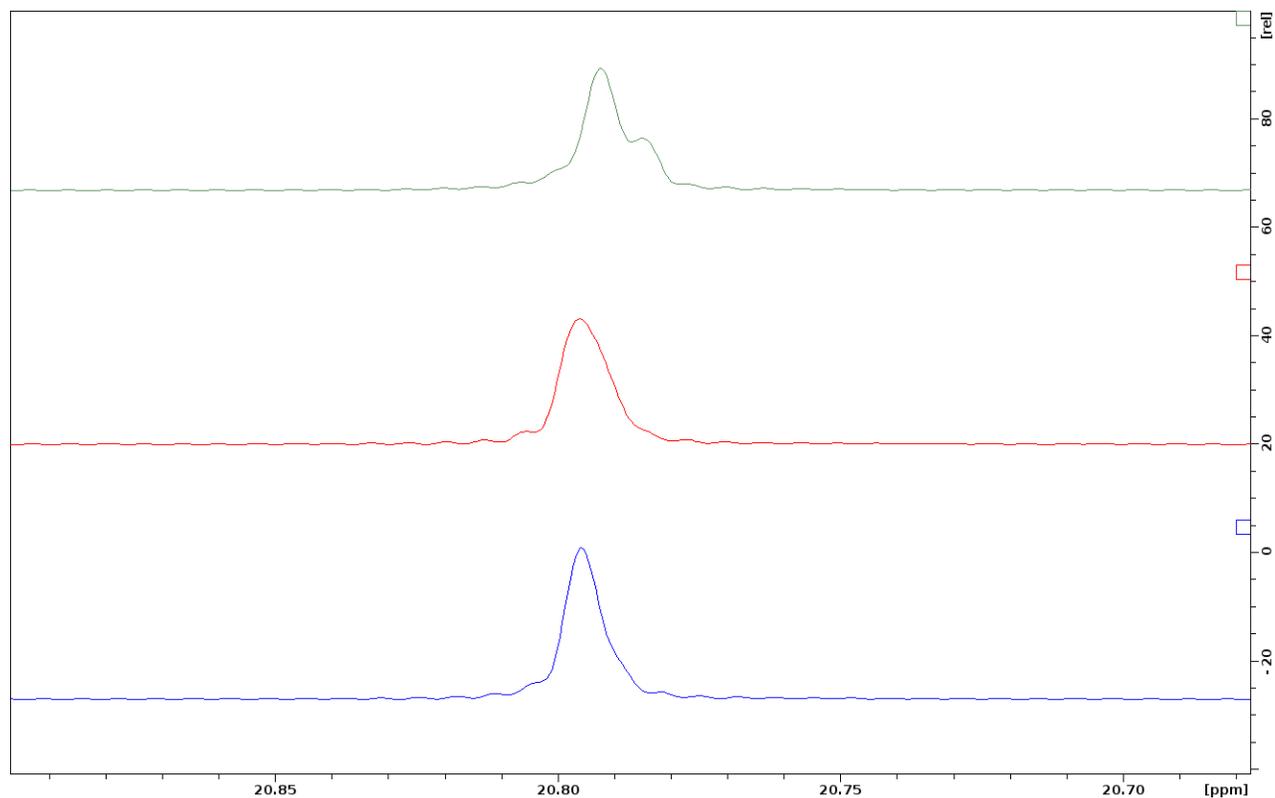
**Figure S17.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



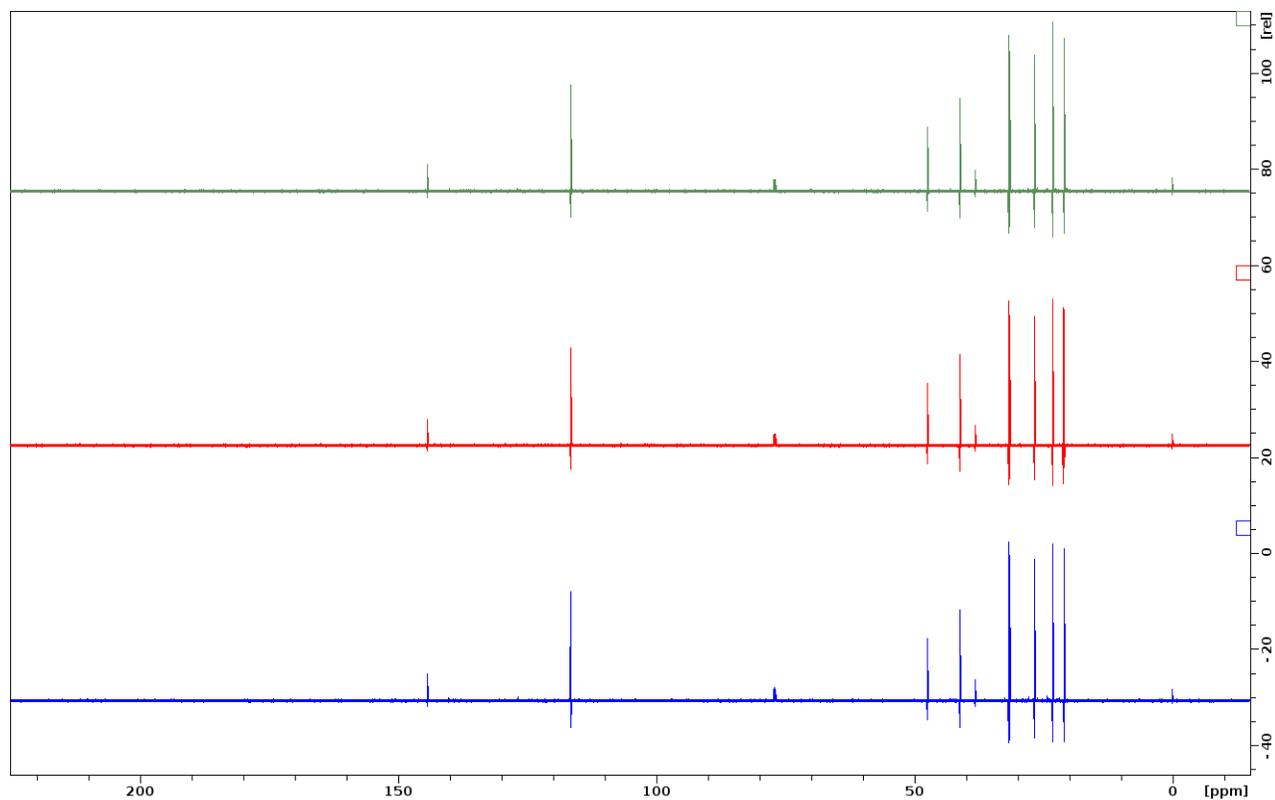
**Figure S18.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



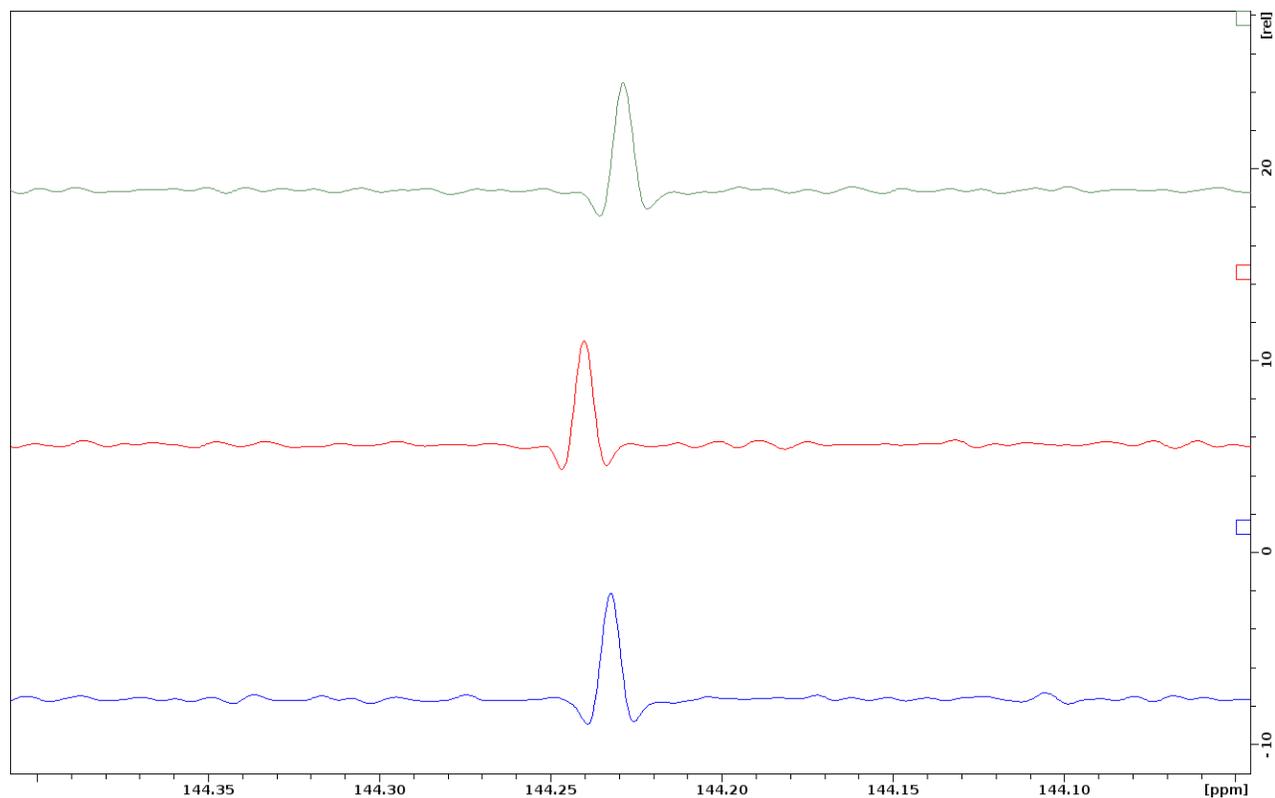
**Figure S19.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41$  °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



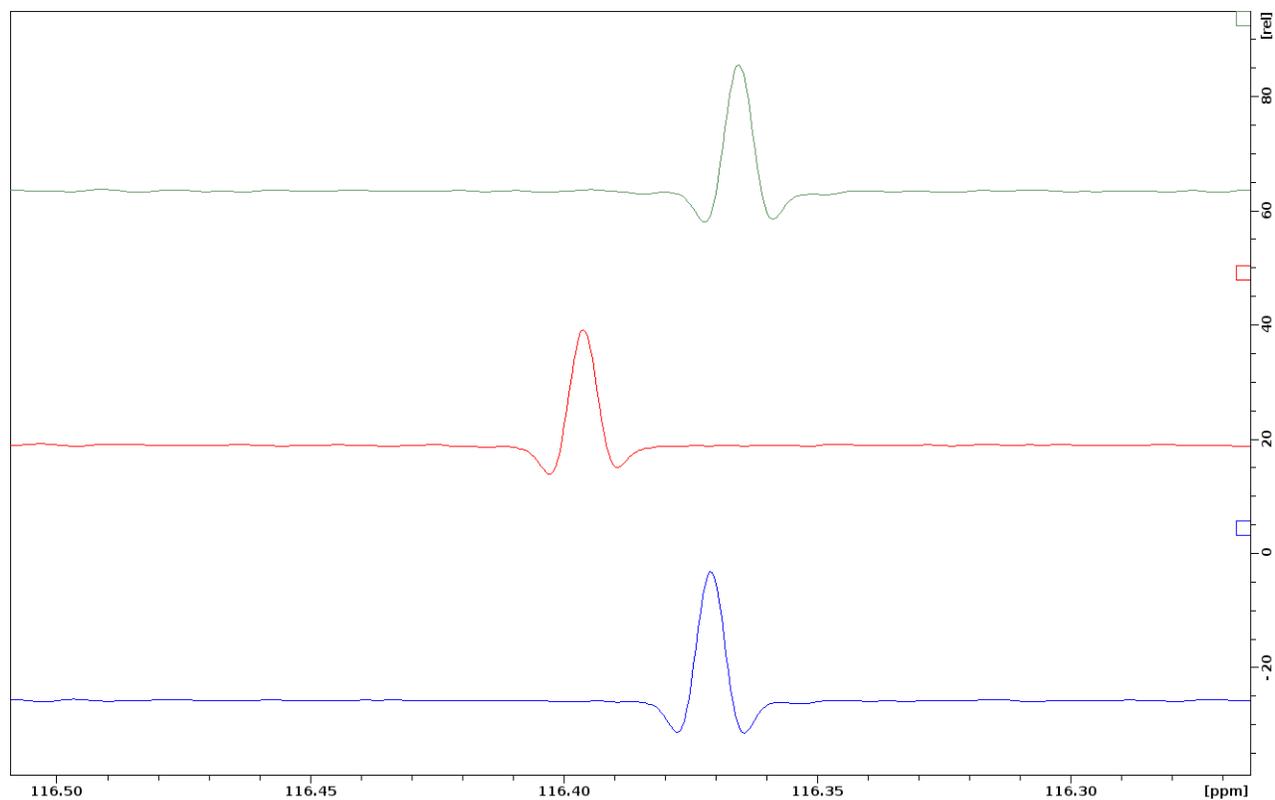
**Figure S20.** The  $^{13}\text{C}$  NMR spectra of  $\alpha$ -pinene in  $\text{CDCl}_3$  (68%) at  $-41$  °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



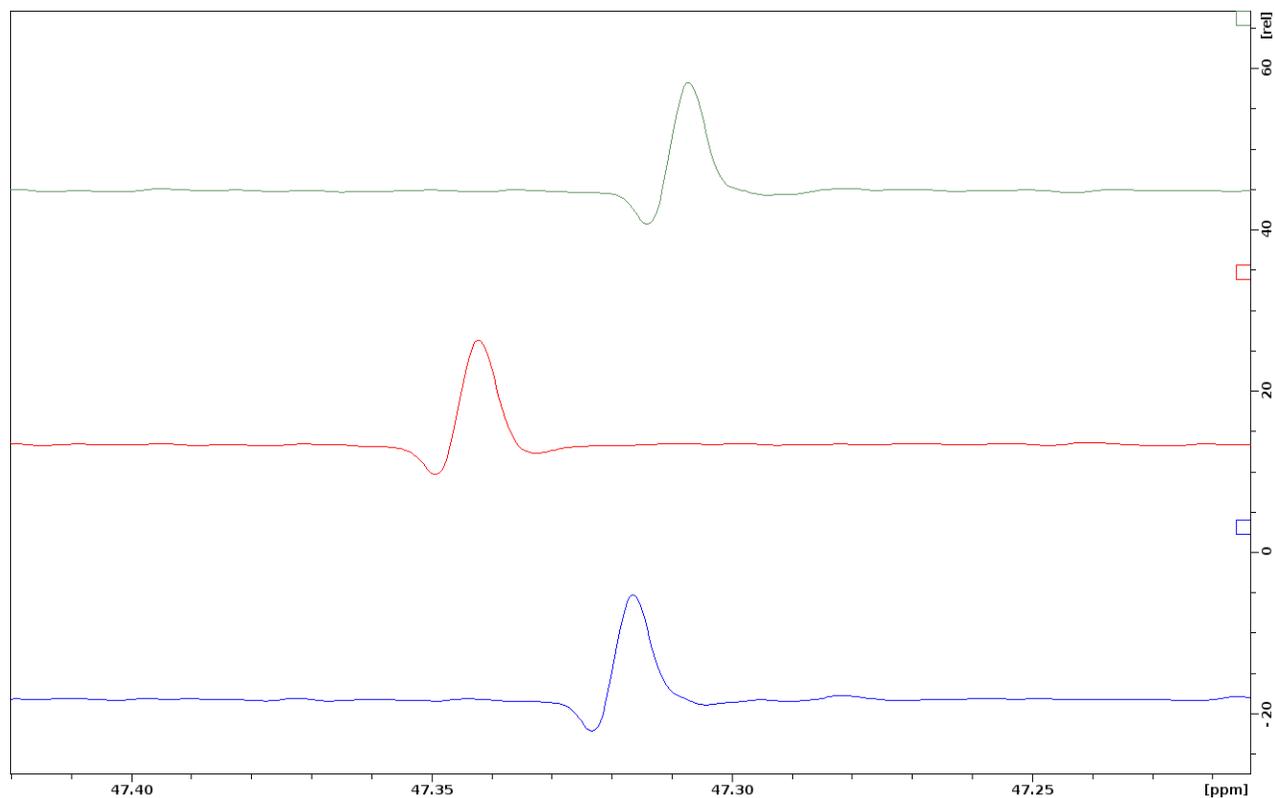
**Figure S21.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



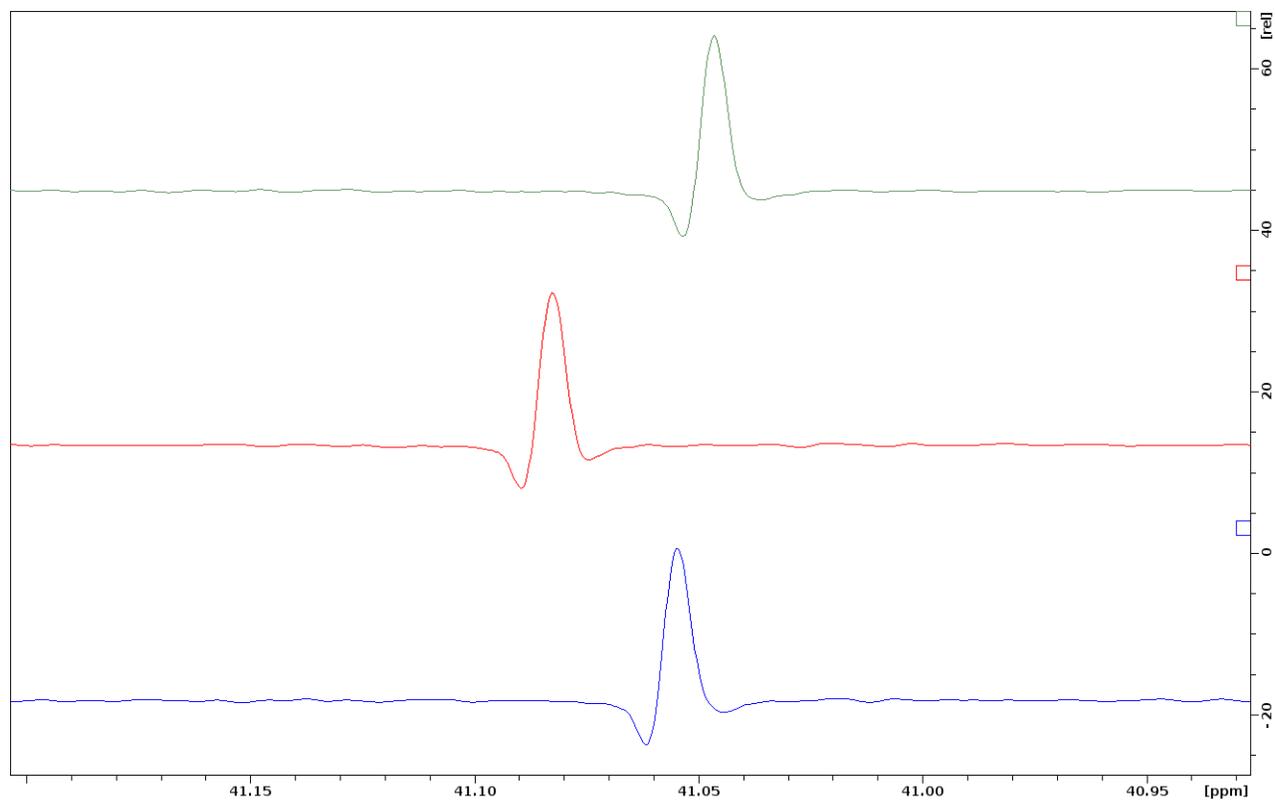
**Figure S22.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23 °C. From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



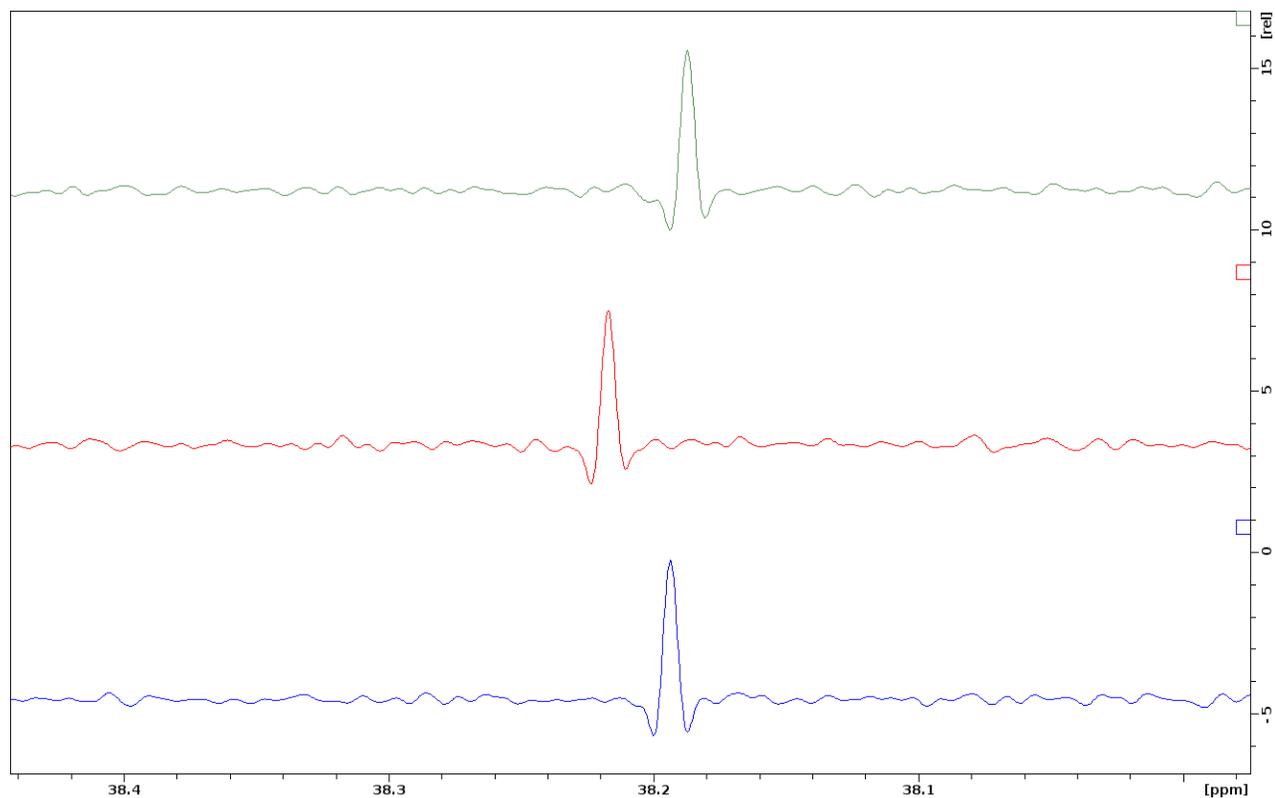
**Figure S23.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



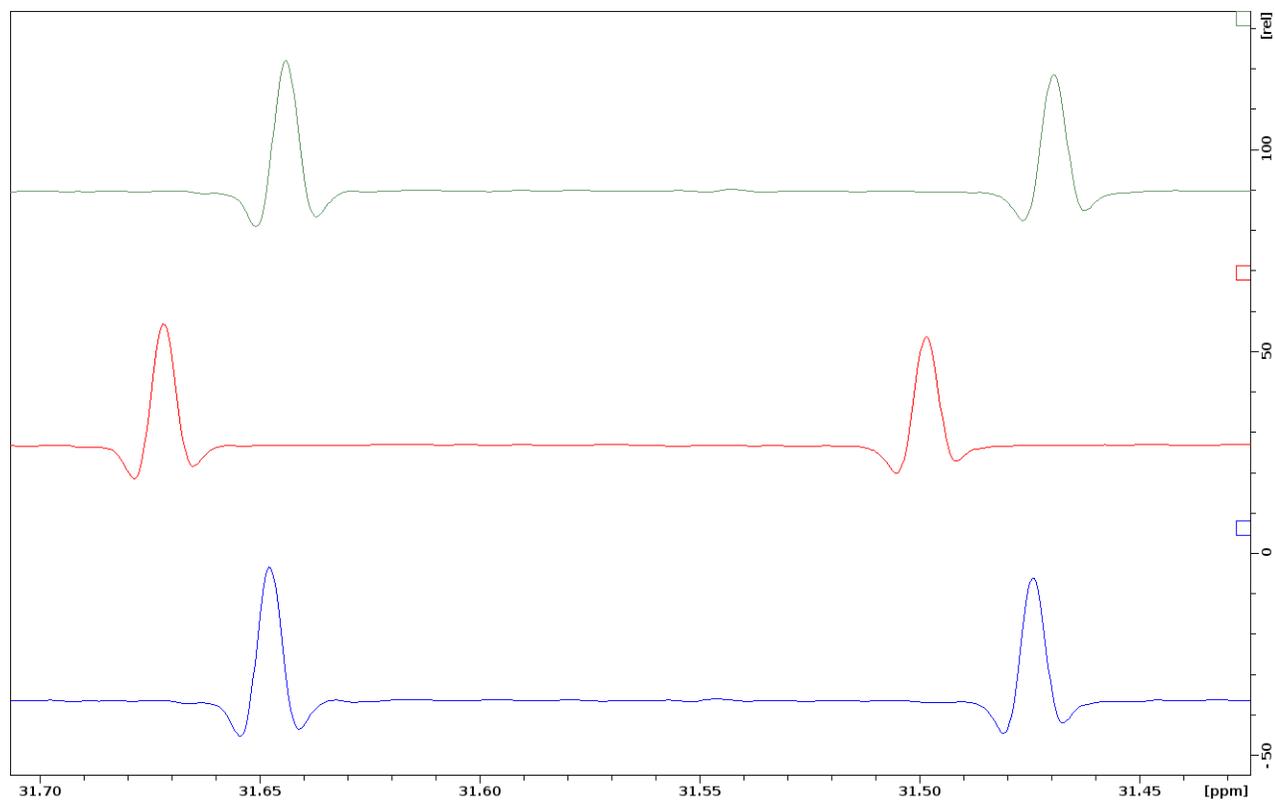
**Figure S24.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



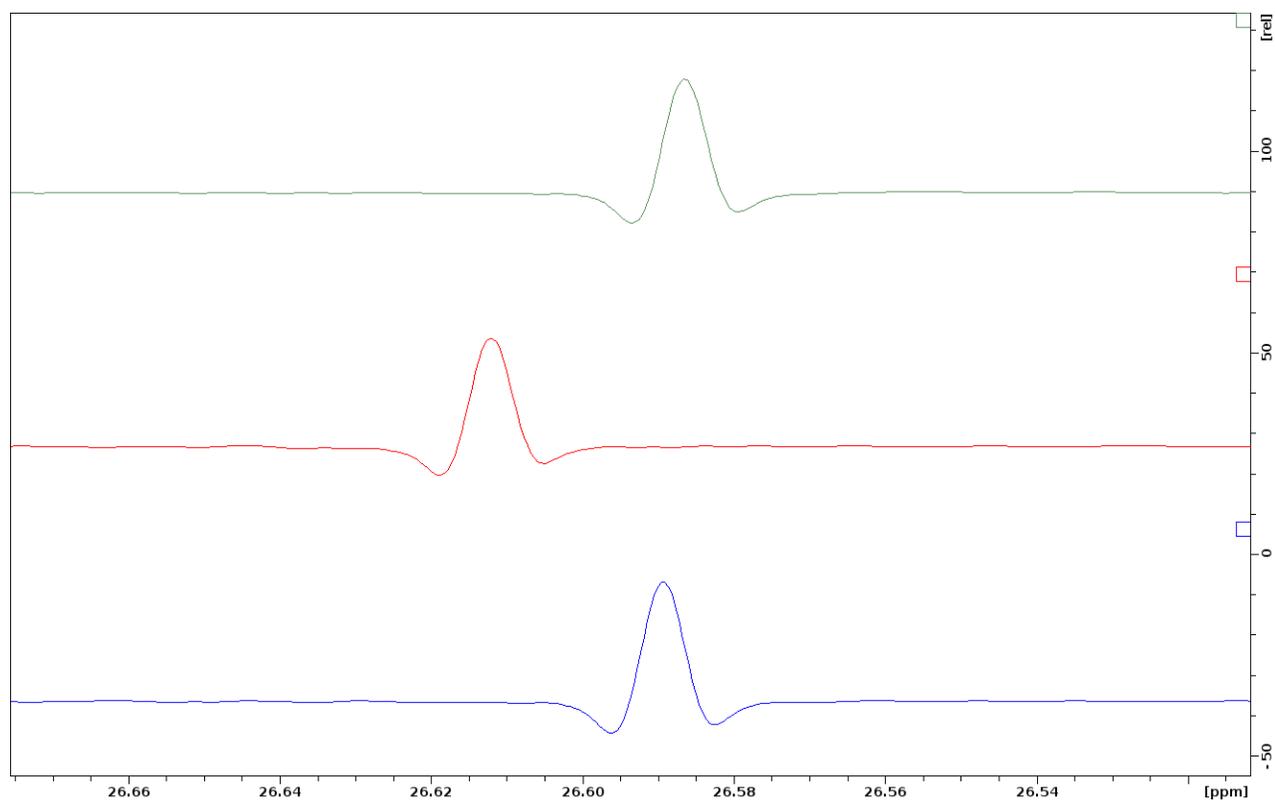
**Figure S25.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



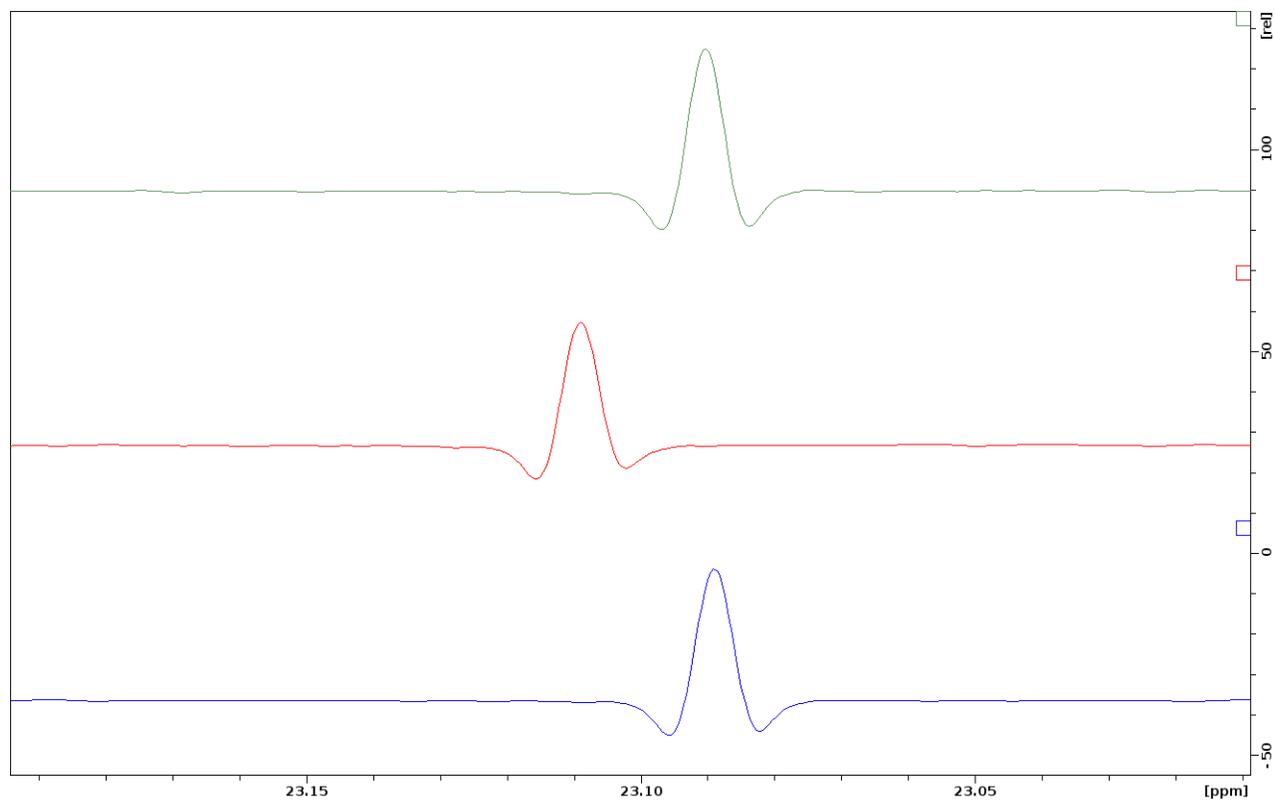
**Figure S26.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



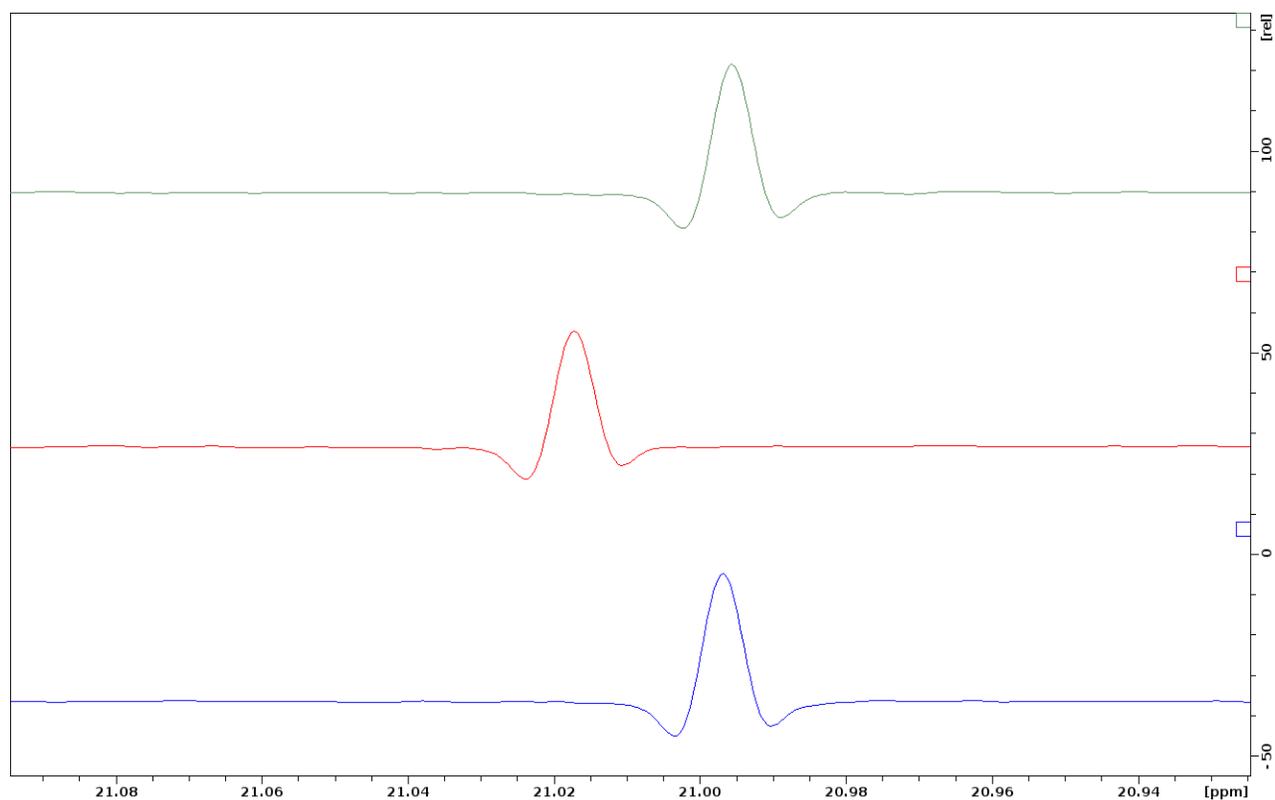
**Figure S27.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



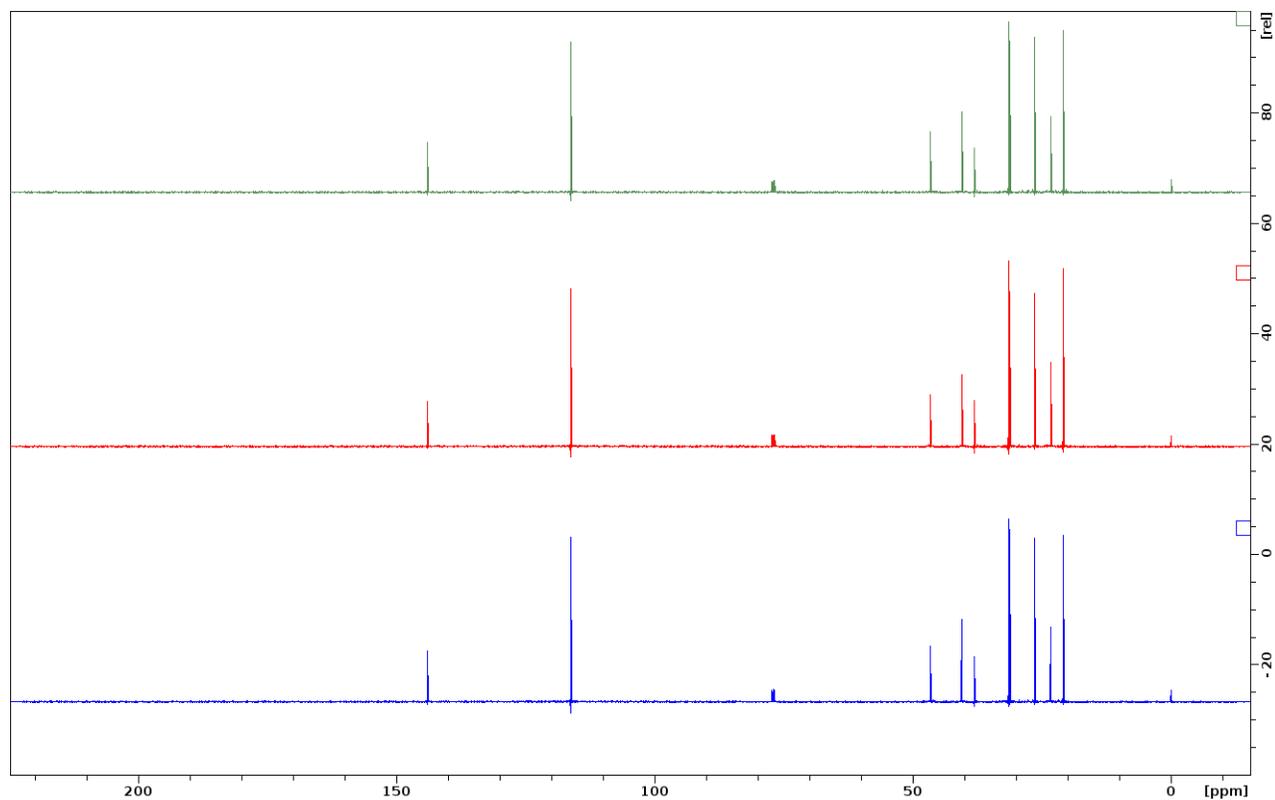
**Figure S28.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



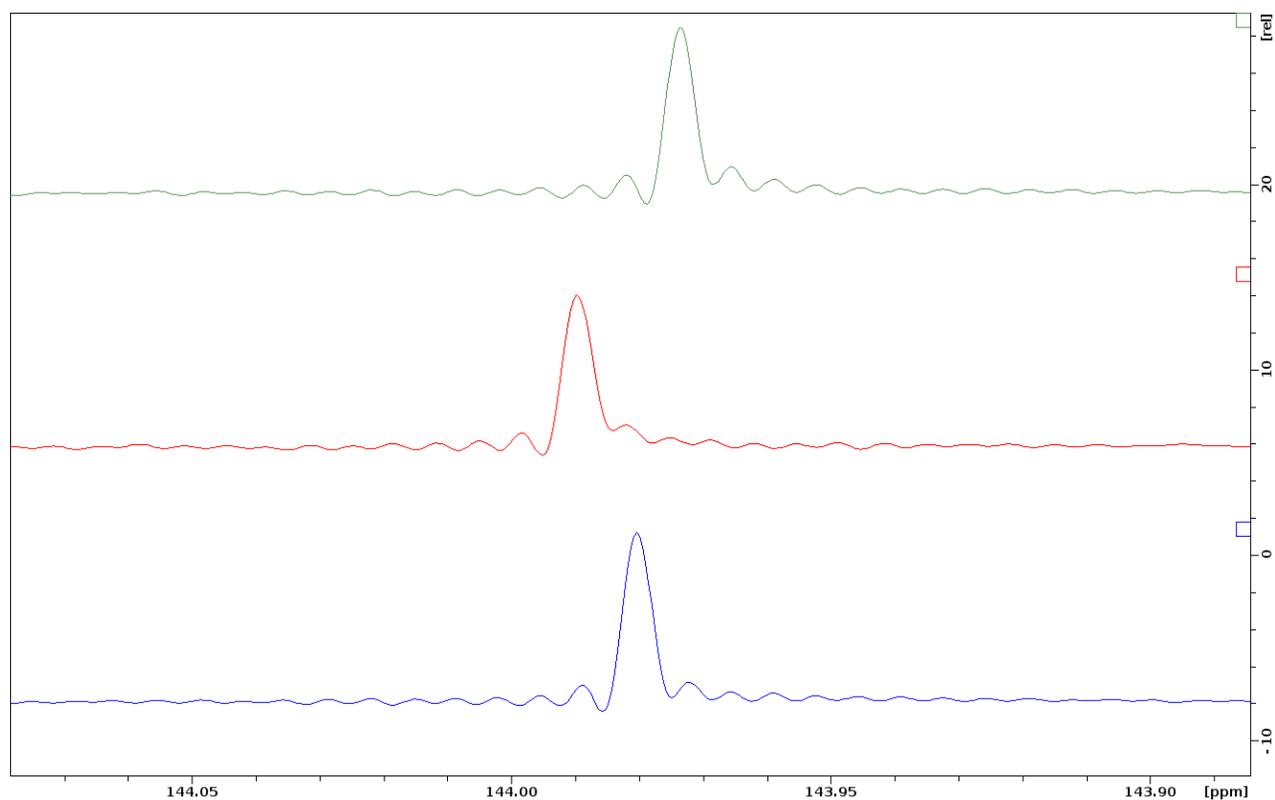
**Figure S29.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



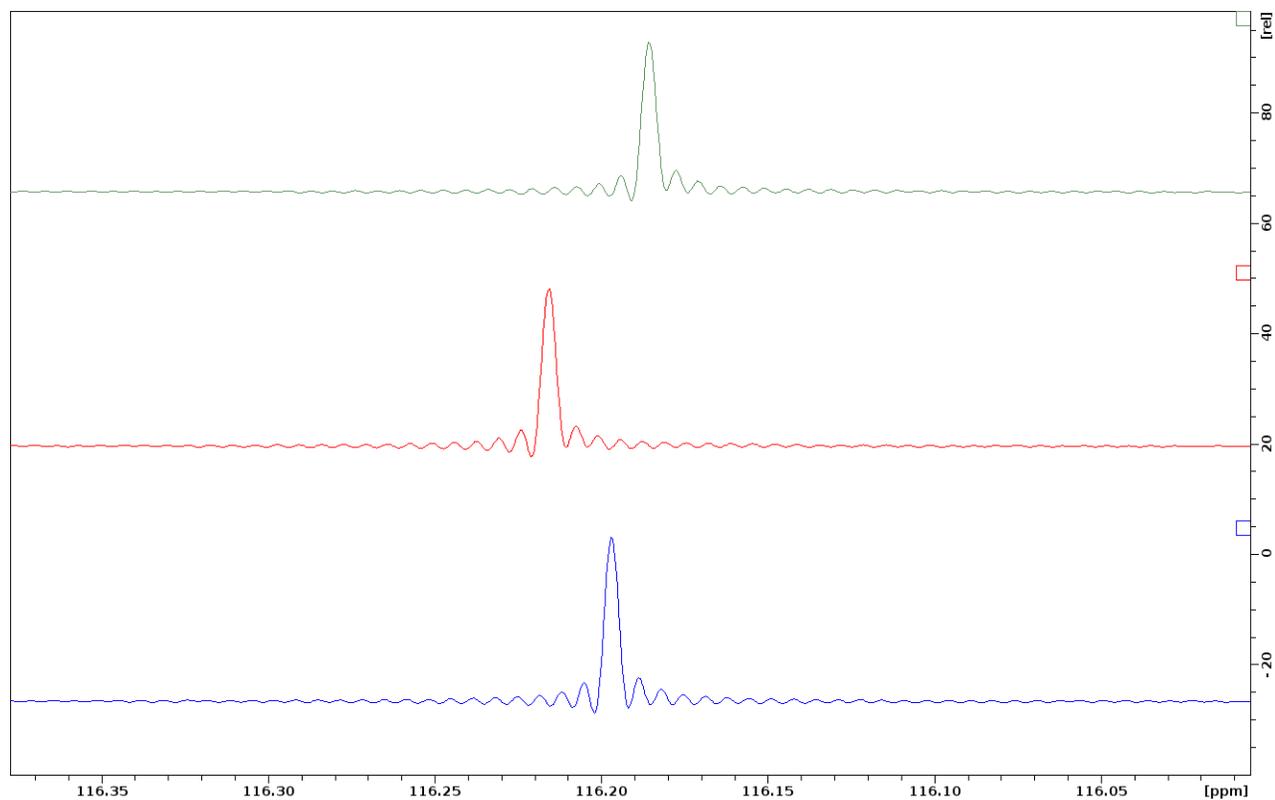
**Figure S30.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at 23  $^{\circ}\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



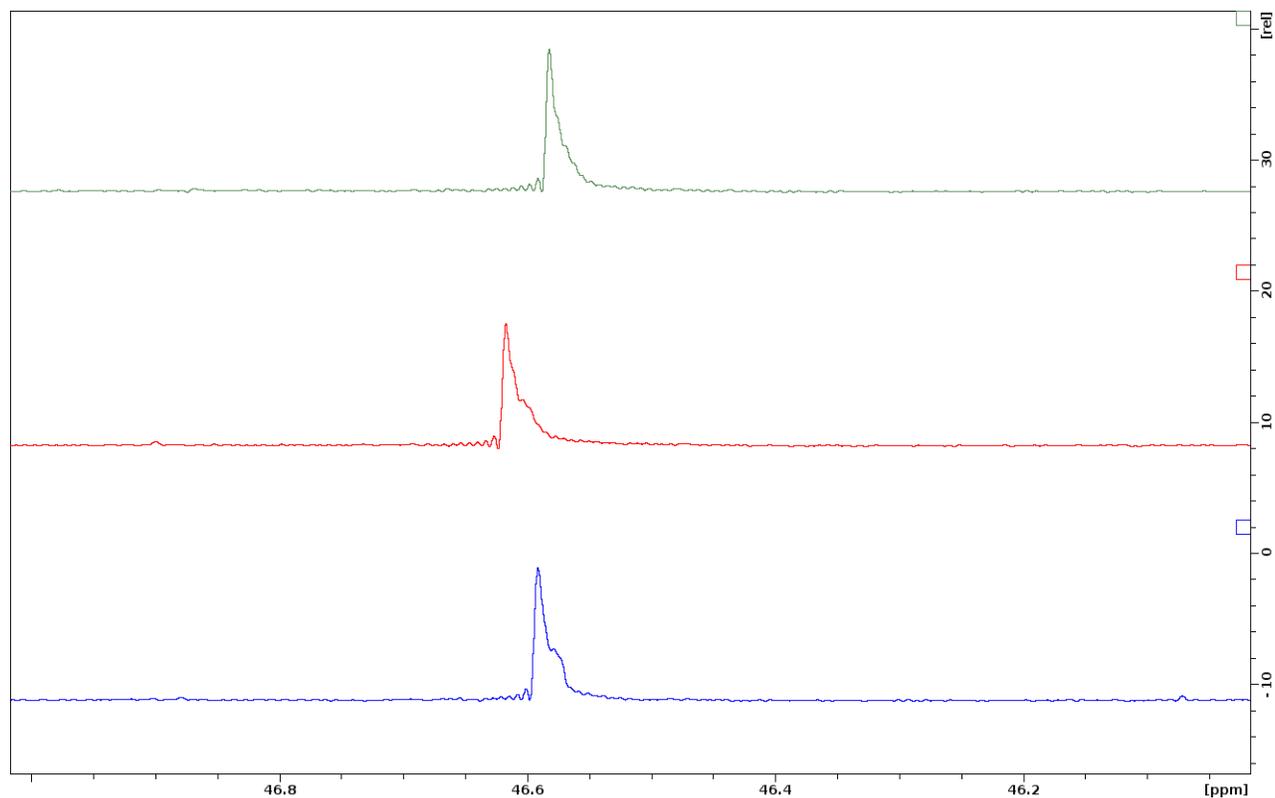
**Figure S31.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



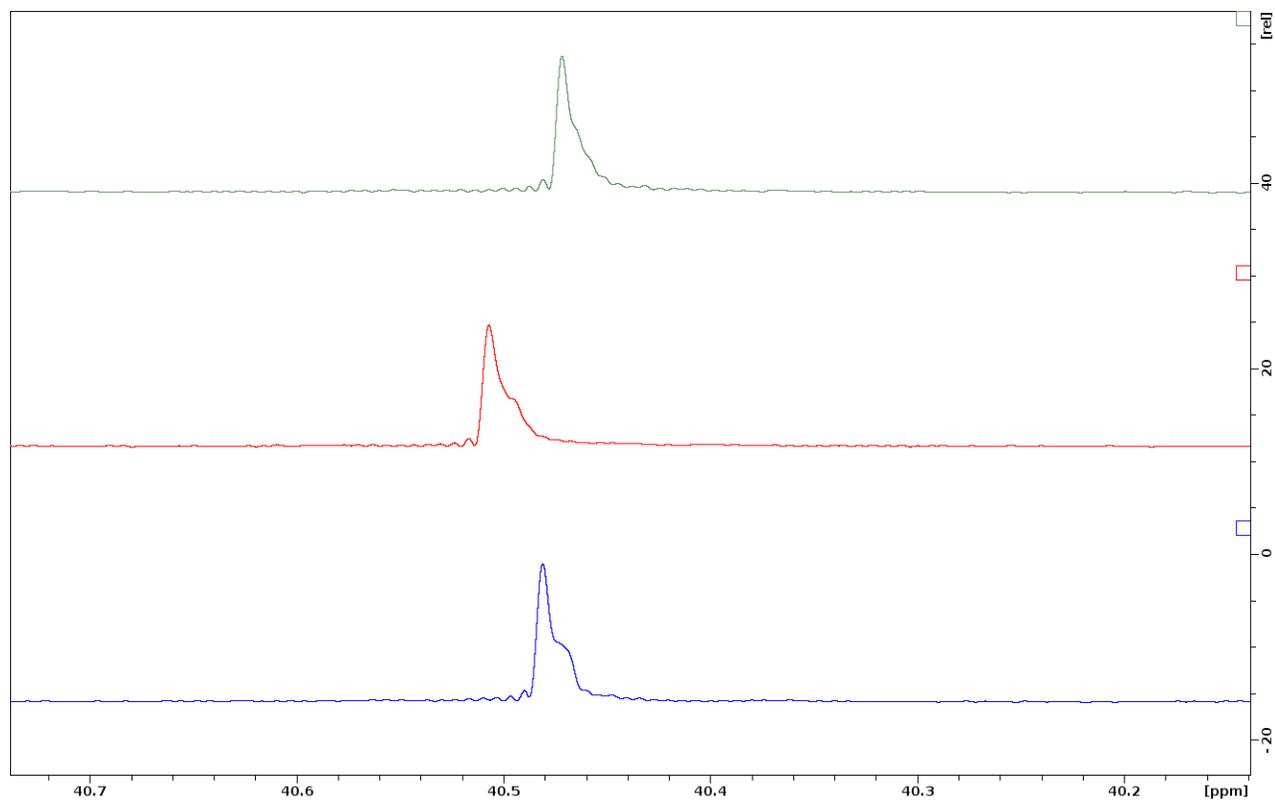
**Figure S32.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



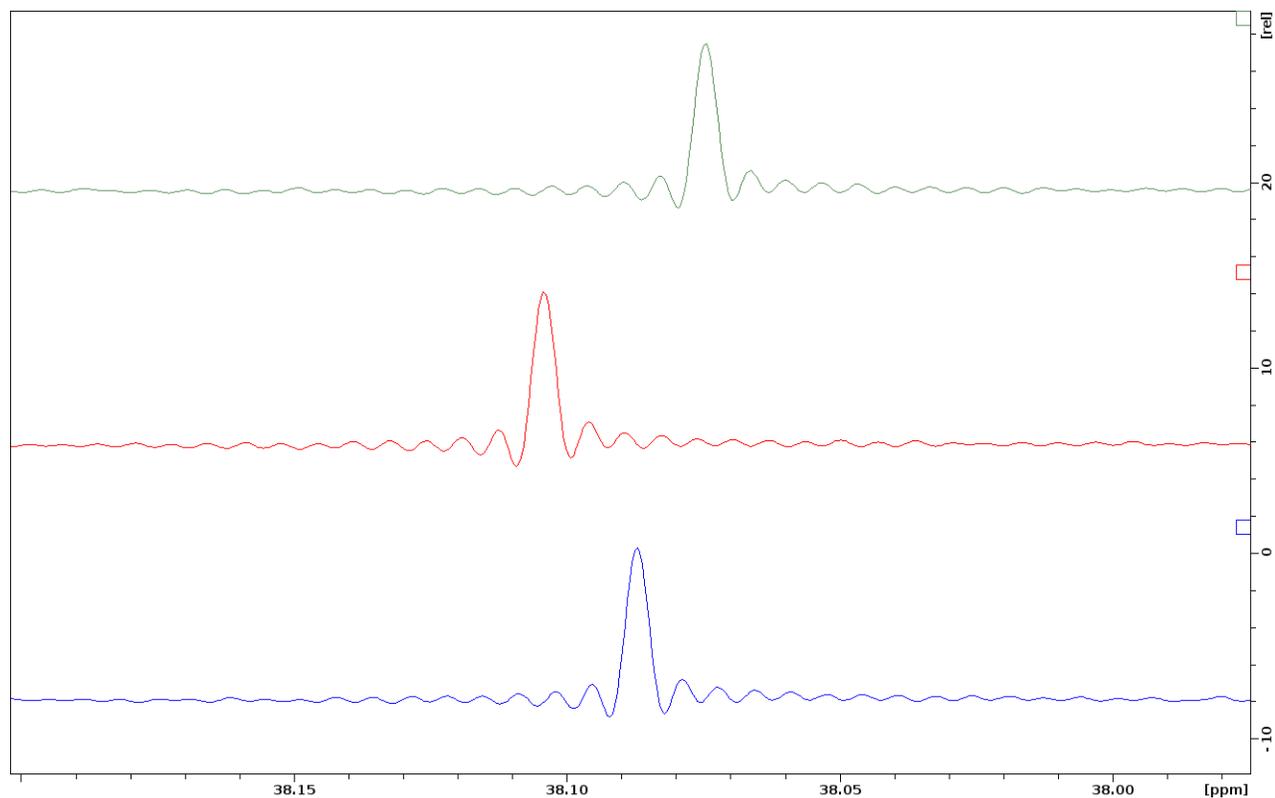
**Figure S33.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



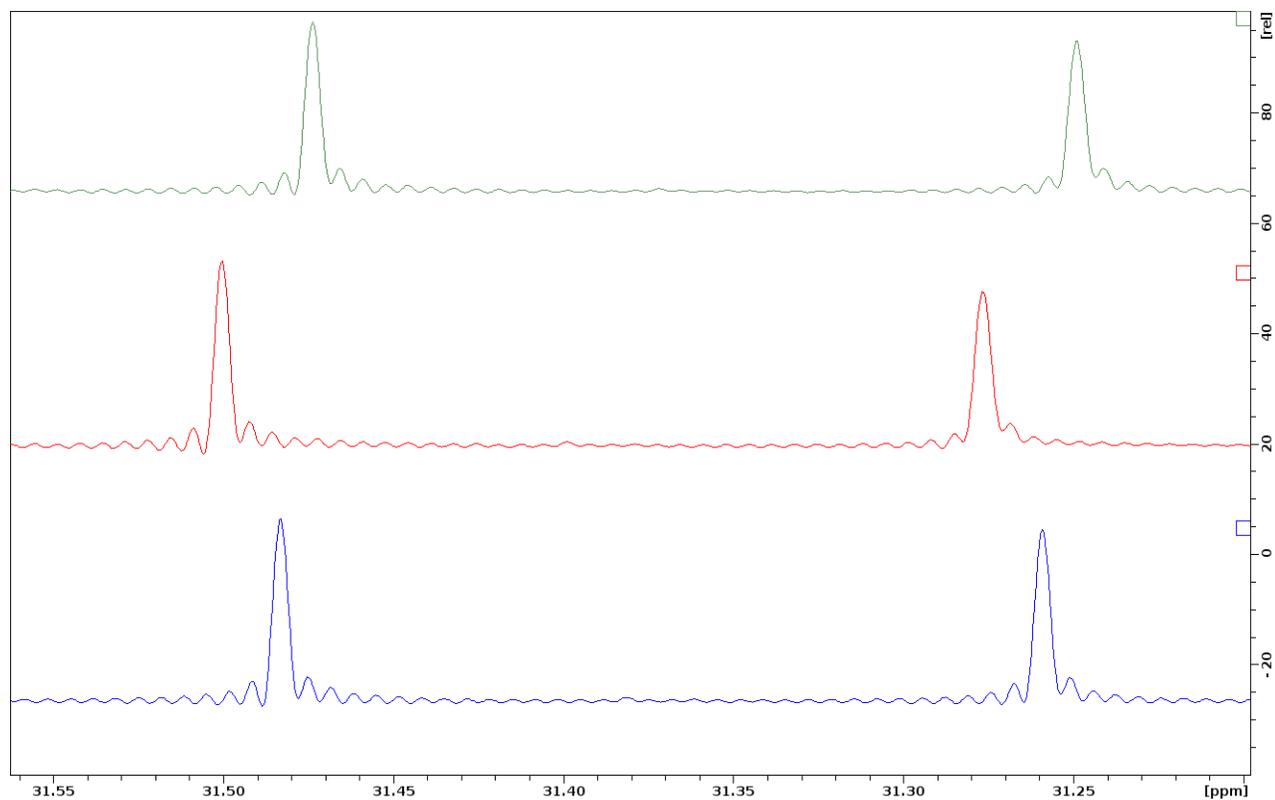
**Figure S34.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



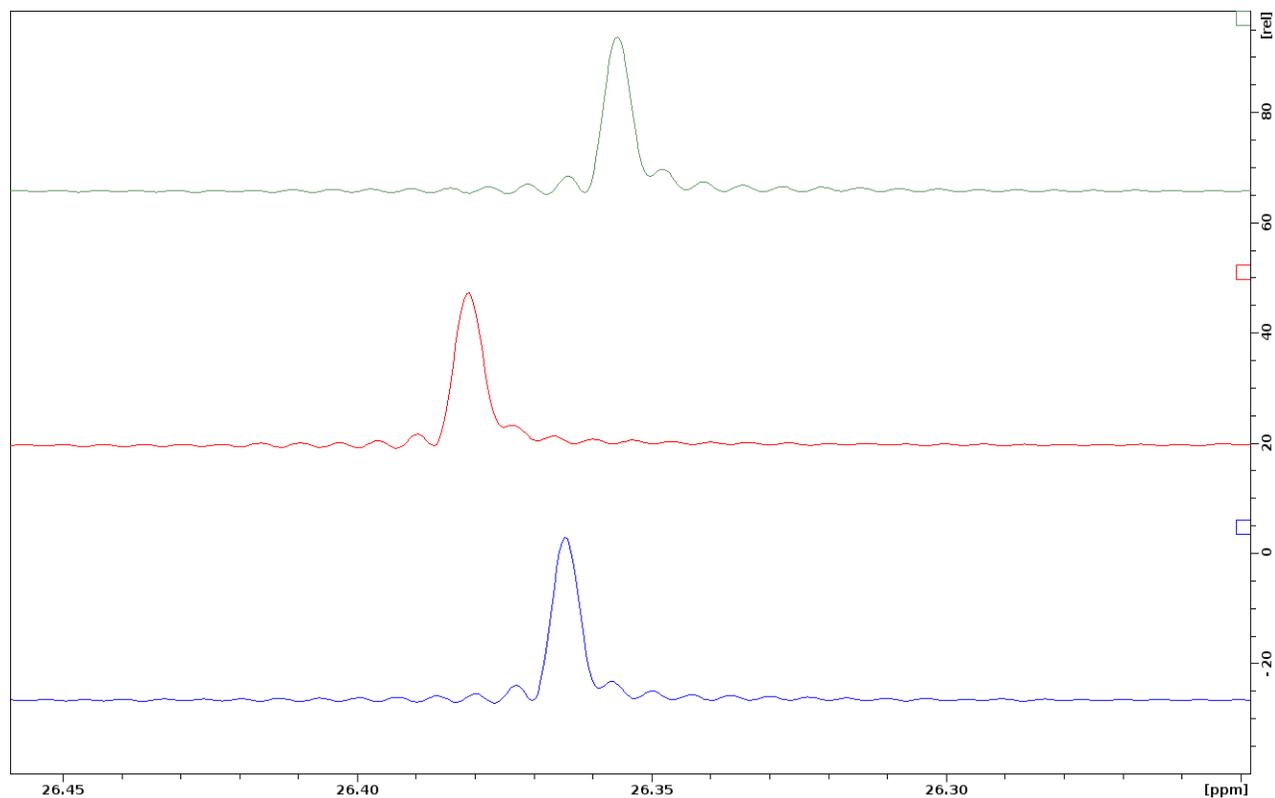
**Figure S35.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



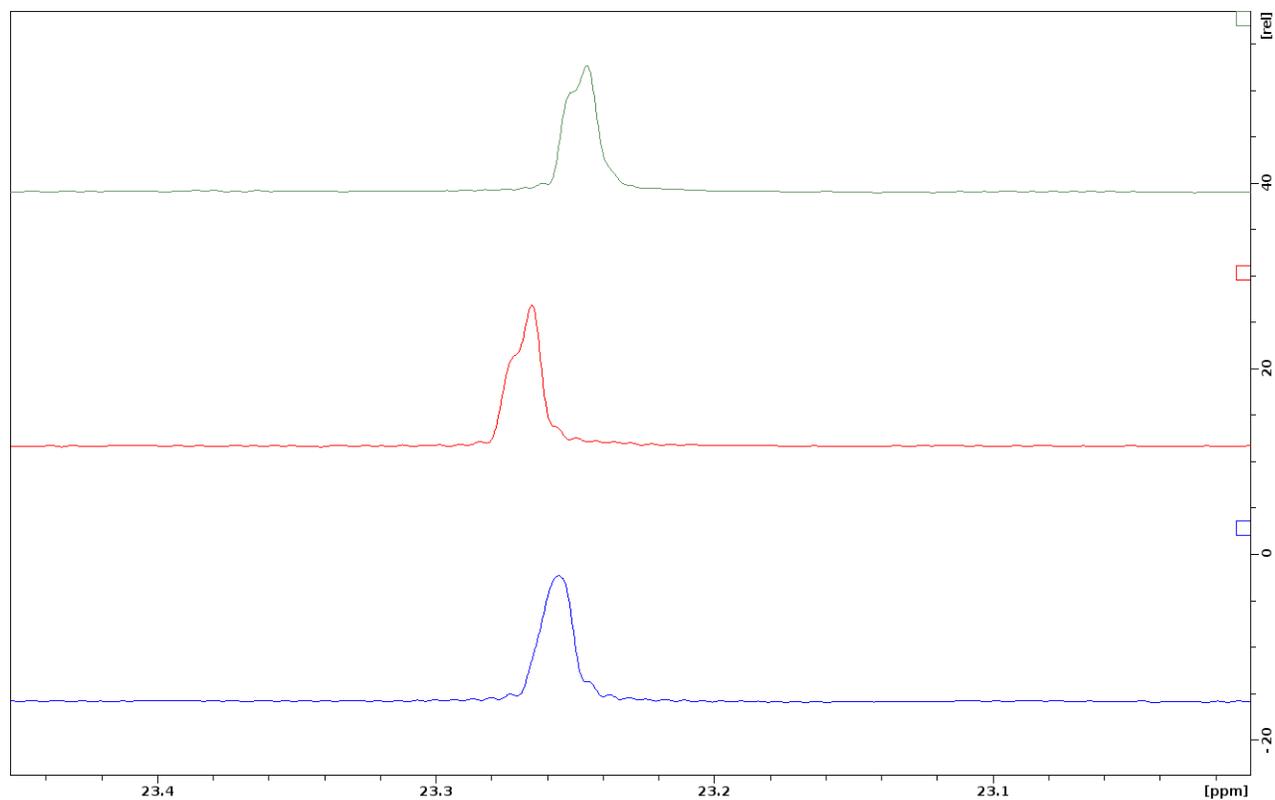
**Figure S36.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



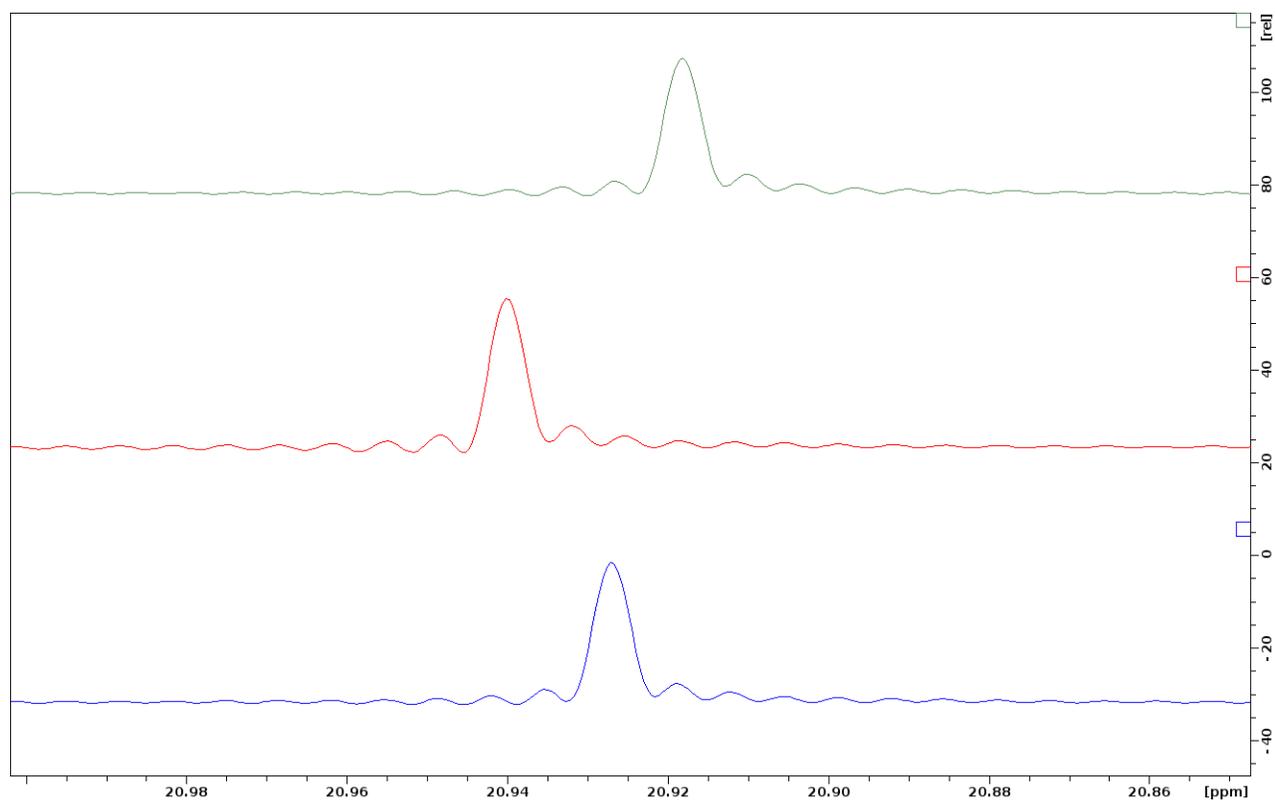
**Figure S37.** The  $^{13}\text{C}$  NMR spectra of neat  $\alpha$ -pinene at  $-41\text{ }^\circ\text{C}$ . From bottom to top, racemic  $\alpha$ -pinene (blue trace), (*S*)- $\alpha$ -pinene (red trace), and *S*-enriched scalemate (50% ee, green trace).



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



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



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