**Protocol S3: Vibrational Circular Dichroic Analysis of Enantiomers 1 and 1b**

The absolute configurations of **1** and **1b** were assigned using vibrational circular dichroism (VCD).

*Experimental:*

VCD spectra were acquired using a BioTools Dual-PEM ChiralIRTM FT-VCD spectrometer operating at 4 cm-1 resolution, with modulators calibrated at 1400 cm-1 and retardations set at PEM1 = 0.250 , PEM2 = 0.260 . A total of 18720 scans were accumulated for each VCD measurement. Spectra were acquired using an International Crystal Laboratories sealed transmission cell with BaF2 windows and 100 micron pathlength. Samples were dissolved in CDCl3 at 0.2-M concentration. The baseline artifact inherent in experimental VCD spectra was removed by the half-difference correction method: VCDcorr’d (**1**) = [(VCD**1** – VCD**1b**)/2]; VCDcorr’d (**1b**) = [(VCD**1b** – VCD**1**)/2].

*Computational Analysis:*

The VCD analysis was performed using a model with (5S,7R) absolute configuration. The conformational set was identified using a molecular mechanics conformational search. Spectra were calculated for each conformation using the B3LYP/DGDZVP computational method. VCD and IR spectra were synthesized using Gibbs free energies and Boltzmann statistics. The calculated line spectra were fitted with Lorentzian band shapes using an 8 cm-1 resolution factor (hwhh) and a uniform scaling factor of 0.975. The level of confidence in the VCD assignments was estimated using CompareVOATM (BioTools, Inc.; Jupiter, Fla. USA), an algorithm that uses overlap integrals to quantify the agreement between calculated and observed VCD spectra.

*Data Analysis:*

The VCD and IR spectra observed for **1** and **1b** are compared with calculated spectra in Figures 1 and 2, respectively. In the top panel of Figure 1, the calculated VCD spectrum is the mirror image of the VCD spectrum of **1**, while in the top panel of Figure 2, the calculated spectrum is coincident with the VCD spectrum of **1b**. These data are consistent with **1** being the mirror image stereo isomer of the model and **1b** being the same stereo isomer as the model, leading to the assignment of **1**as the (5R,7S) enantiomer and **1b** as the (5S,7R) enantiomer. The confidence limit for these assignments was estimated to be >99%.

The calculated IR spectrum is in good qualitative agreement with experimental, indicating adequate coverage of conformational space. [Note: Misalignment of the CF3 symmetric (obs’d 1275 cm-1; calc’d 1235 cm-1) and antisymmetric (obs’d 1155 cm-1; calc’d 1120 cm-1) stretching modes is due to limitations/errors in the computation method used for this analysis. The signs of CF3 bands in the VCD spectra, however, are consistent with overall VCD comparisons (CF3 bands oppositely signed for **1** versus model comparison, same signs for **1b** versus model comparison.]



Figure S-1: VCD spectra of **1** and the (5S,7R) model (top); IR spectra of **1** and the 5S,7R) model (bottom).



Figure S-2: VCD spectra of **1b** and the (5S,7R) model (top); IR spectra of **1b** and the 5S,7R) model (bottom).