



Figure 1 – figure supplement 1. Determination of the absolute configuration of discoidol. The HSQC for C2 of unlabelled discoidol (red) shows a broad crosspeak for coupling with H_α (1.47 ppm) and H_β (1.52 ppm). The enzymatic conversion of (*S*)-(1- ^{13}C ,1- ^2H)GPP ($H_S=^2\text{H}$) and IPP with FPP synthase (FPPS) and DdTPS8 results in labelled discoidol with a remaining crosspeak for H_β (purple), while labelled discoidol obtained from (*R*)-(1- ^{13}C ,1- ^2H)GPP ($H_R=^2\text{H}$) shows a remaining crosspeak for H_α (blue). The known absolute configuration at C2 of both enantioselectively deuterated isotopomers of discoidol together with the assignment of the relative orientations of H_α and H_β at C2 by NOESY allows to conclude on the absolute configuration of (4*S*,5*S*,7*S*)-discoidol.