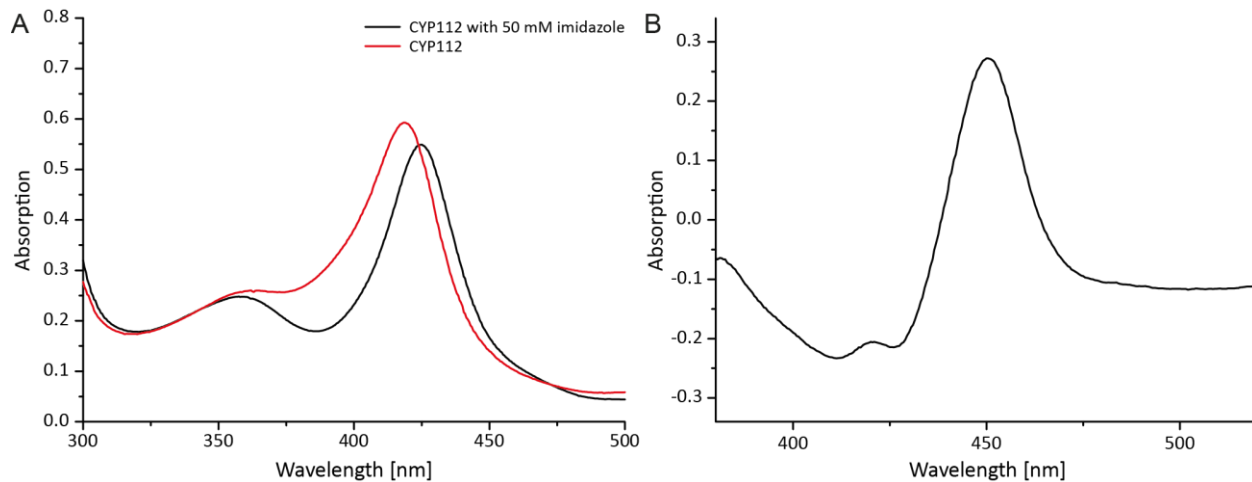


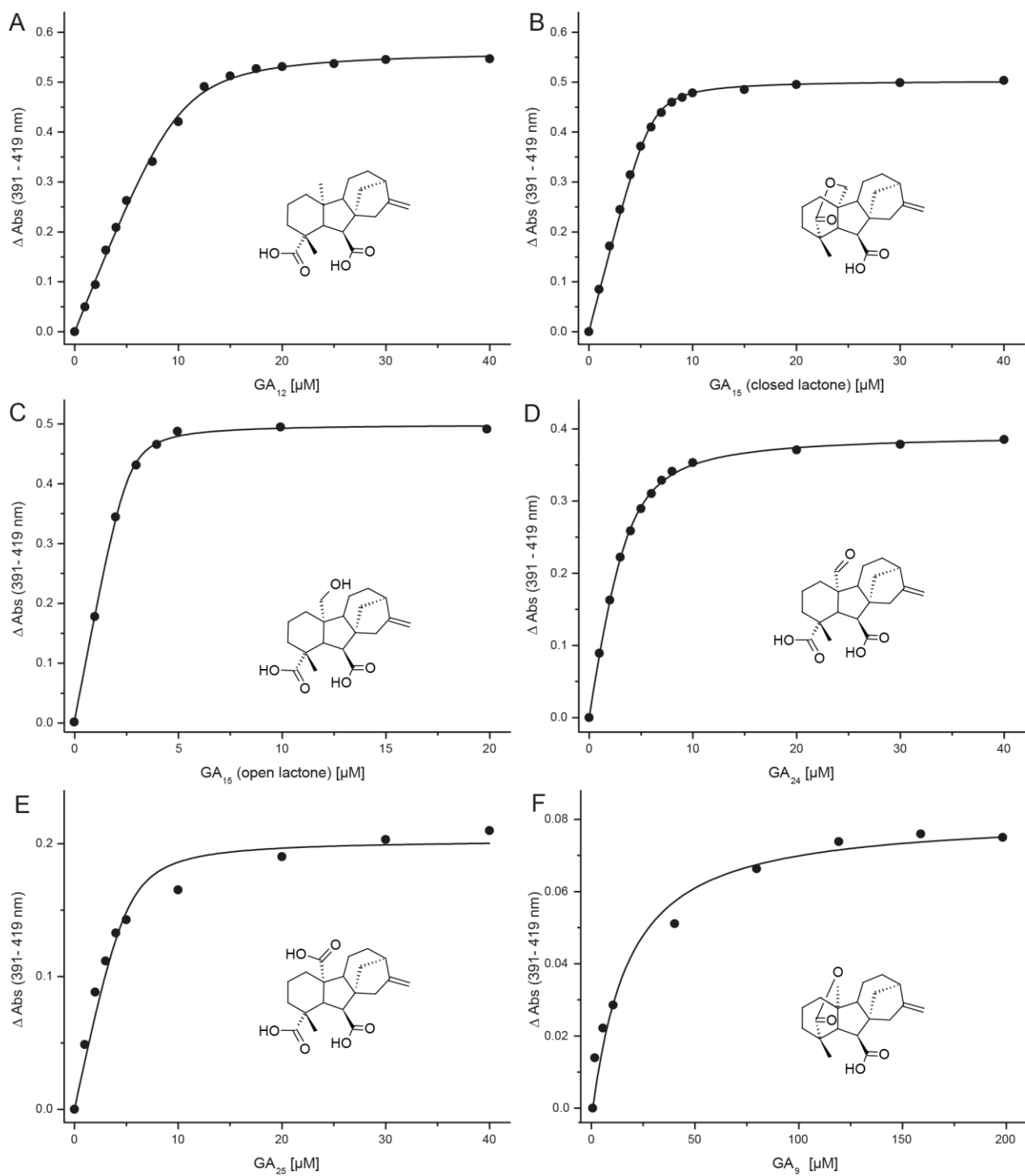
## Supplemental Figures

### Supplemental Figure S1



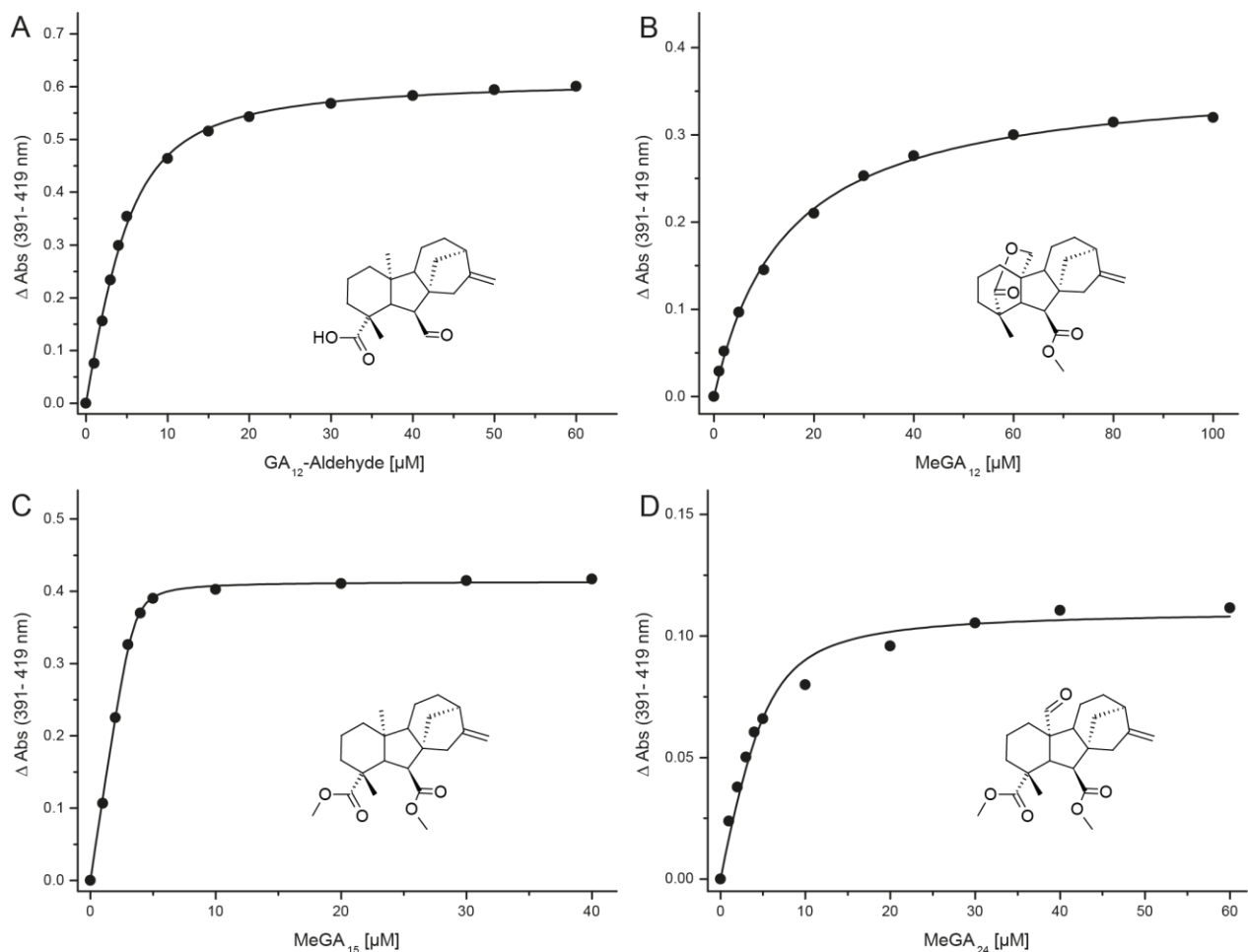
**Supplemental Figure S1:** Spectral properties of *EtCYP112*. (A) UV-Vis spectral changes of *EtCYP112* in its free or imidazole bound state. (B) Carbon monoxide difference spectrum of *EtCYP112*.

Supplemental Figure S2



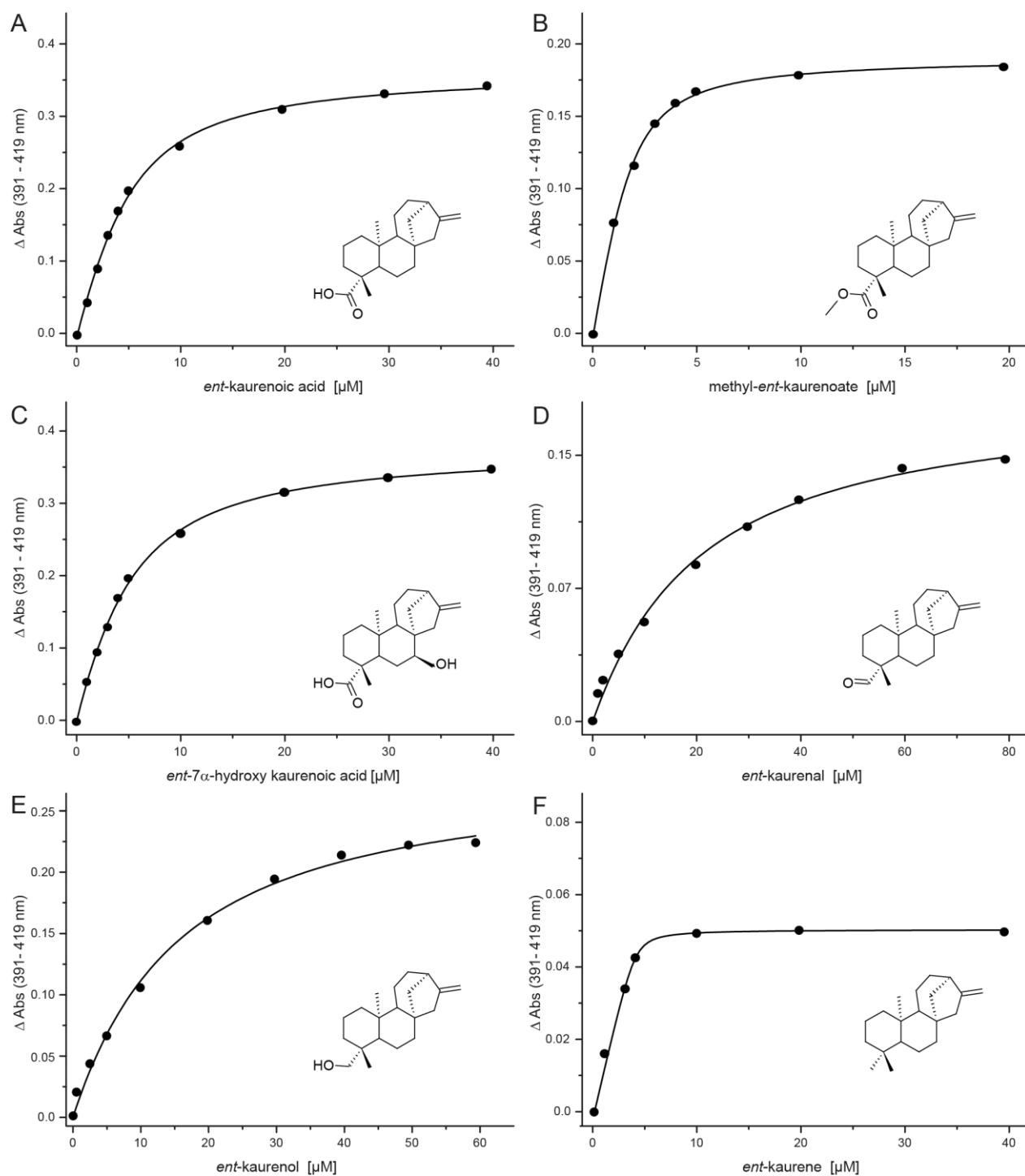
**Supplemental Figure S2:** Fitted binding curves of *EtCYP112* with substrates and products. Plot of the induced spectral shifts in *EtCYP112* and fit to a hyperbolic function for calculation of  $K_d$  upon binding (A)  $\text{GA}_{12}$ , (B)  $\text{GA}_{15}$  (closed lactone), (C)  $\text{GA}_{15}$  (open lactone), (D)  $\text{GA}_{24}$ , (E)  $\text{GA}_{25}$ , and (F)  $\text{GA}_9$ .  $K_d$  values averaged from three independent replicates of this experiment are reported in Table 1, with the exception of those for  $\text{GA}_{25}$  and  $\text{GA}_9$ , due to the relatively low quality of the fit.

Supplemental Figure S3



**Supplemental Figure S3:** Fitted binding curves of *EtCYP112* with methylated substrates, as well as immediate precursor  $GA_{12}$ -aldehyde. Plot of the induced spectral shifts in *EtCYP112* and fit to a hyperbolic function for calculation of  $K_d$  upon binding (A)  $GA_{12}$ -aldehyde, (B)  $MeGA_{12}$ , (C)  $MeGA_{15}$  (closed lactone), and (D)  $MeGA_{24}$ .  $K_d$  values averaged from three independent replicates of this experiment are reported in Table 1, with the exception of that for  $MeGA_{24}$ , due to the low quality of the fit.

Supplemental Figure S4



**Supplemental Figure S4:** Fitted binding curves of *EtCYP112* with kaurane precursors. Plot of the induced spectral shifts in *EtCYP112* and fit to a hyperbolic function for calculation of  $K_d$  upon binding (A) *ent*-karenoic acid, (B) methyl *ent*-karenoate, (C) *ent*-7 $\alpha$ -hydroxy karenoic acid, (D) *ent*-karenal, (E) *ent*-karenel, and (F) *ent*-karene.  $K_d$  values averaged from three independent replicates of this experiment are reported in Table 1, with the exception of that for *ent*-karenal, as there was no change in  $\alpha$ -band absorption.