The barrier for the cyclisation of 4,4-dimethyl-7-oxo-7-(tosyloxy)heptanoate (BCI) to form 5,5-dimethyl-1,3-dioxan-2-one is shown.

Table S5. Computed free Gibbs energies for the cyclisation of BCI to form 5,5-dimethyl-,1-3dioxane-2-one at the rωb97xD/6-31+g(d)/cpcm=acetonitrile/298K level of theory

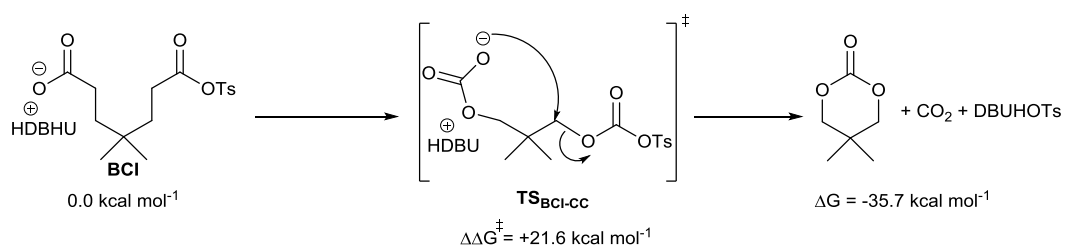| Structure	G (Hartree)	ΔG (kcal/mol)
BCI	-2005.496591	0.0 (reference)
TS	-2005.462199	+21.6
CC	-460.099307	-
CO_2	-188.536520	-
DBUHOTs	-1356.917683	-
CC + CO_2 + DBUHOTs	-2005.553510	- 24.6

Fig. S1. Computed free Gibbs energies for the cyclisation of BCI to form 5,5-dimethyl-1,3-dioxane-2-one at the rωb97xD/6-31+g(d)/cpcm=acetonitrile/298K level of theory