Computational details. All calculations were performed using the Gaussian09 suite of codes (revision D.01).[1] Geometries were fully optimised without any symmetry or geometry constraints using functional ωB97XD.[2] Calculations were carried out using a temperature of 398.15 K and solvent effects in 1,4-dioxane were considered using a conductor-like polarisable continuum model (CPCM).[3] The nature of all the stationary points as minima was verified by calculations of the vibrational frequency spectrum. Free energies were calculated within the harmonic approximation for vibrational frequencies. Only the most stable conformational isomers are reported for all intermediates.

Thermodynamics of the Baeyer-Villiger oxidation with H_2O_2 of 4-alkyl-cyclohexanone

The increasing intrinsic reactivity of 4-R-CyO against CyO for BVO was evaluated using Density Functional Theory by calculating the thermodynamics of the reaction with H_2O_2 for each substrate. Geometry optimisation were performed at the ωB97XD level and 398.15 K, using a mixed valence triple ζ basis set 6-311++g(2d,p) for all atoms, and a conductor-like polarisable continuum model of 1,4-dioxane. The results of these calculations are summarised in Table S1.
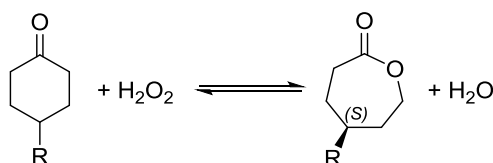

Table S1. DFT computed Free Gibbs energies of the oxidation of 4-R-cyclohexanone into 4-R-caprolactone[a]

	Structure	**G** **(Hartree)**	**ΔΔG** **(kcal mol^{-1})**
Starting Materials	Hydrogen peroxide	−151.560207	-
	CyO	−309.781068	-
	H_2O	−76.439011	
	4-Me-CyO	−349.071807	-
	4-Et-CyO	−388.359145	-
	4-iPr-CyO	−427.647051	
	4-tBu-CyO	−466.93444	
Capr formation	H_2O_2 + CyO	−461.341275	0.0 (reference)
	Capr	−385.006241	-
	Capr + H_2O	−461.445252	−65.2
(S)-4-Me-Capr formation	H_2O_2 + 4-Me-CyO	−500.632014	0.0 (reference)
	(S)-4-Me-Capr	−424.296656	-
	(S)-4-Me-Capr + H_2O	−500.735667	−65.0
(S)-4-Et-Capr formation	H_2O_2 + 4-Et-CyO	−539.919352	0.0 (reference)
	(S)-4-Et-Capr	−463.583974	-
	(S)-4-Et-Capr + H_2O	−540.022985	−65.0
(S)-4-iPr-Capr formation	H_2O_2 + 4-iPr-CyO	−579.207258	0.0 (reference)
	(S)-4-iPr-Capr	−502.870265	-
	(S)-4-iPr-Capr + H_2O	−579.309276	−64.0
(S)-4-tBu-Capr formation	H_2O_2 + 4-tBu-CyO	−618.494647	0.0 (reference)
	(S)-4-tBu-Capr	−542.158735	-
	(S)-4-tBu-Capr + H_2O	−618.597746	−64.7

[a] Protocol: ωB97XD/6-311++g(2d,p)/ 398.15K/cpcm=1,4-dioxane; calculations were performed on the S enantiomers, with the alkyl substituent in equatorial position.

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