**Electronic Supplementary Information**

Role of Vibrational Deactivation in the Stereoselective Photooxygenation of
Oxazolidinone-functionalized Enecarbamates

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## 1) General

*Trans*-4-octene was obtained from Alfa Aesar and 1-methyl-1-cyclohexene from Aldrich. Both compounds were distilled before use. Hexamethyldisilane (HMDS) and 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TFPP) were used as received from Aldrich. 1,4-Dimethylnapthalene endoperoxide was synthesized following established procedures.[S1] Deuterated solvents were obtained from Cambridge Isotope Laboratories and kept over dry $NaHCO_3$. The *Z* and *E* enecarbamates were synthesized as previously described.[S2] ^{1}H-NMR spectra were obtained using 400MHz Bruker NMR instrument.

## 2) Reaction Procedures

### a) Exemplar procedure for competitive kinetics to determine $k_{cq}$:

Stock solution of HMDS [0.35ml to 25ml with $CDCl_3$], TFPP [5.26mg to 10ml with $CDCl_3$], *trans*-4-octene [ ***Stock 1***: 0.15ml to 5ml with $CDCl_3$; ***Stock 2***: 0.2ml Stock 1 diluted to 5ml with $CDCl_3$] and enecarbamate [147.2mg to 25 ml with $CDCl_3$] were made up. Using the stock solutions, 0.45 ml of the enecarbamate, 0.1ml *trans*-4-octene and 0.05ml TFPP were added to NMR tube. Oxygen was bubbled into samples and they were irradiated under ambient conditions using a 300W halogen lamp and a <400 nm cutoff filter. Low conversions (<20%) were maintained. After irradiation, 0.1ml of HMDS stock solution was added and the sample characterized using ^{1}H-NMR. Chemical quenching rates were calculated based on the disappearance of enecarbamate and *trans*-4-octene peaks and therefore the HMDS was used as a standard to calculate the amount of enecarbamate remaining after irradiation.
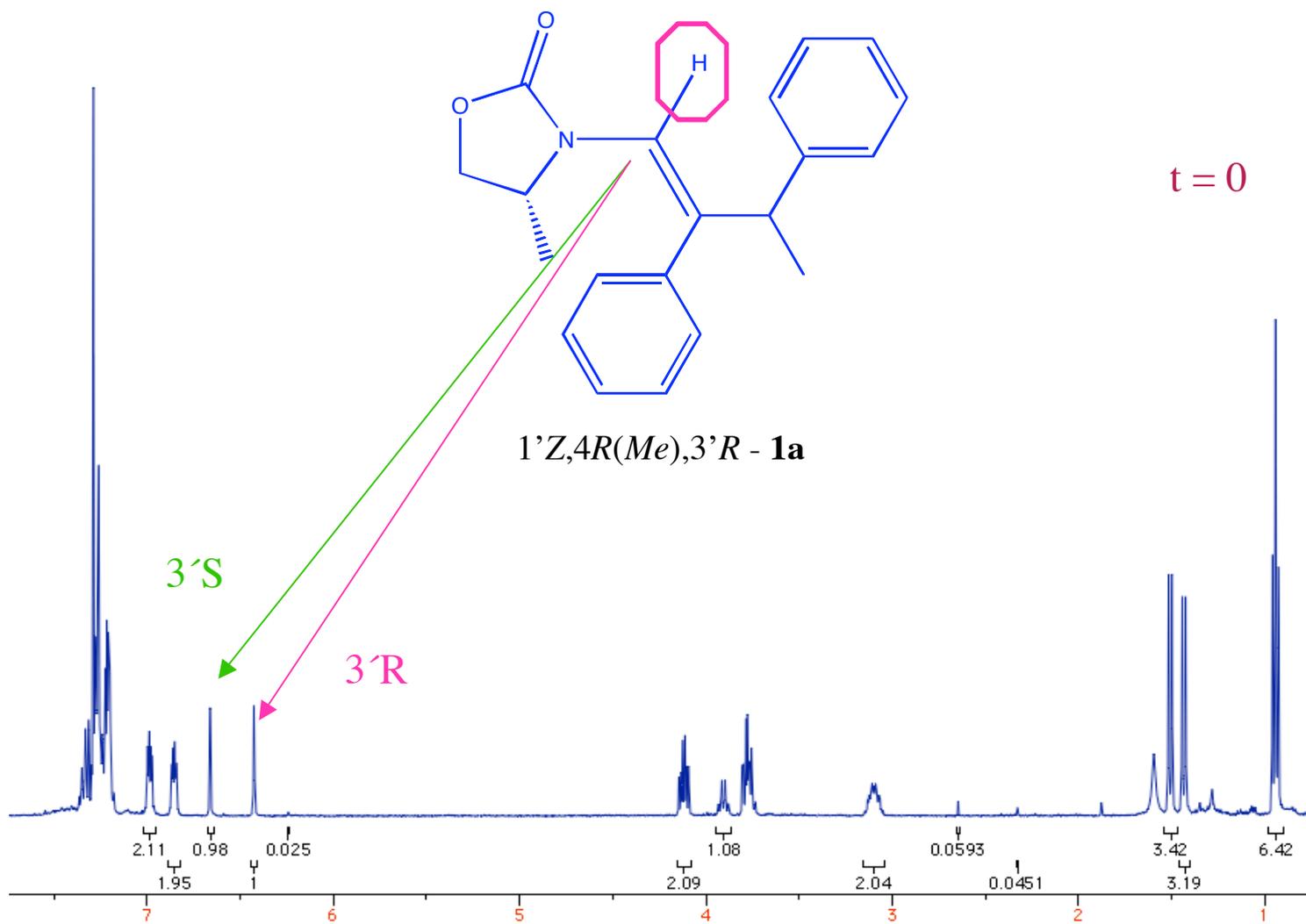
In later experiments **1a** was used as a standard in addition to *trans*-4-octene.

***b) General procedure for $^1O_2$ chemiluminescence quenching experiment to determine $k_q$:***

All compounds were purified, dried and pumped for several days under vacuum at ambient temperature. Stock solutions of enecarbamate quenchers, 1-methyl-1-cyclohexene (0.05M), *trans*-4-octene (0.4M) and 1,4-dimethylnaphthalene endoperoxide (10mM) were prepared. In a quartz cuvette (1×1×4 cm) with 200μl of 1,4-dimethylnaphthalene endoperoxide solution in 2700μl $CDCl_3$, aliquots of quencher (enecarbamate or standard) were added. After the addition of each aliquot chemiluminescence spectra were recorded from 1200 to 1340nm at 22°C using a modified Fluorolog 2 spectrofluorimeter (Horiba Jobin-Yvon) in conjunction with a NIR sensitive photomultiplier detector (H9170-45, Hamamatsu) (Figure S3). Stern-Volmer constants ($K_{SV}$) were determined from the slope of the plot of the $^1O_2$ phosphorescence intensity vs quencher concentration (Figure S4). To convert $K_{SV}$ into the total quenching rate constant ($k_q$) using Eqn S1, the singlet oxygen lifetime in the absence of quencher ($\tau_0$) is required. Because $\tau_0$ under our experimental condition is expected to be shorter than the published value in high purity $CDCl_3$, we determined $\tau_0$ using *trans*-4-octene as standard ($k_q$ = 1.8 x $10^4$ $M^{-1}s^{-1}$).[S3]

$$K_{SV} = k_q \tau_0 \qquad \text{(S1)}$$

## 3) ^{1}H-NMR spectra for Competitive Kinetics:



1'Z,4R(Me),3'R - **1a**

3´S

3´R

t = 0

2.11  0.98  0.025  1.08  0.0593  3.42  6.42
1.95  1  2.09  2.04  0.0451  3.19

7  6  5  4  3  2  1
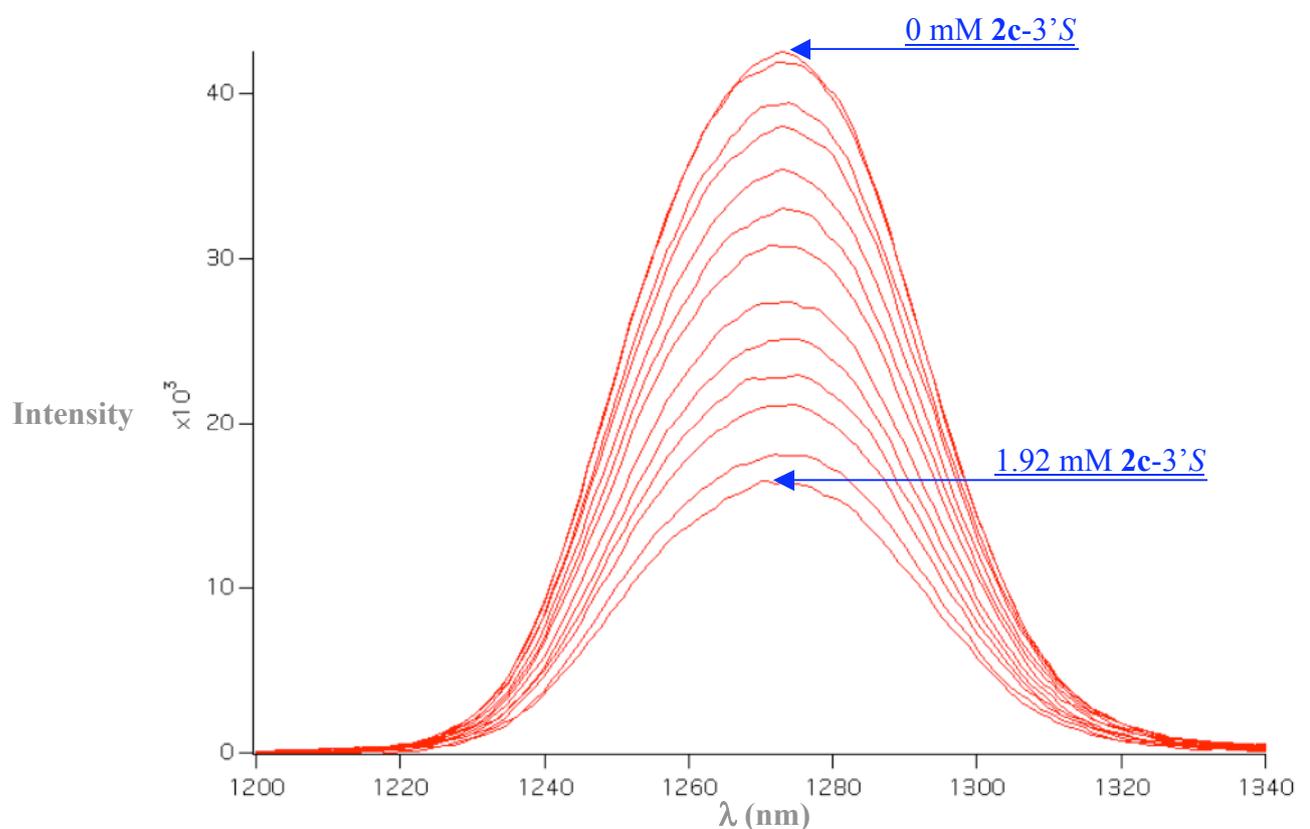
**Figure S1:** ^{1}H NMR spectrum of the enecarbamate standard **1a** before irradiation. The disappearance of the enecarbamate was monitored mainly with the vinylic hydrogen peaks.
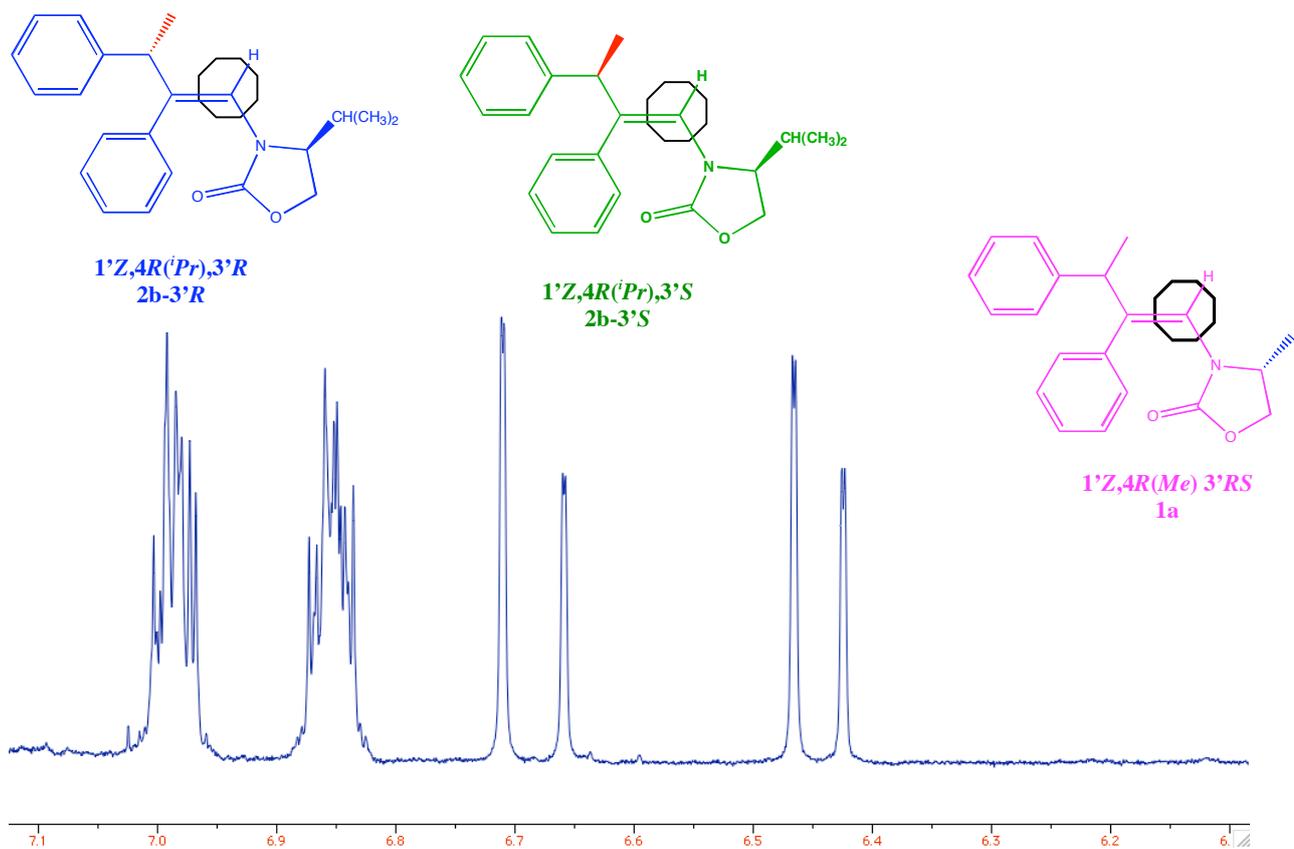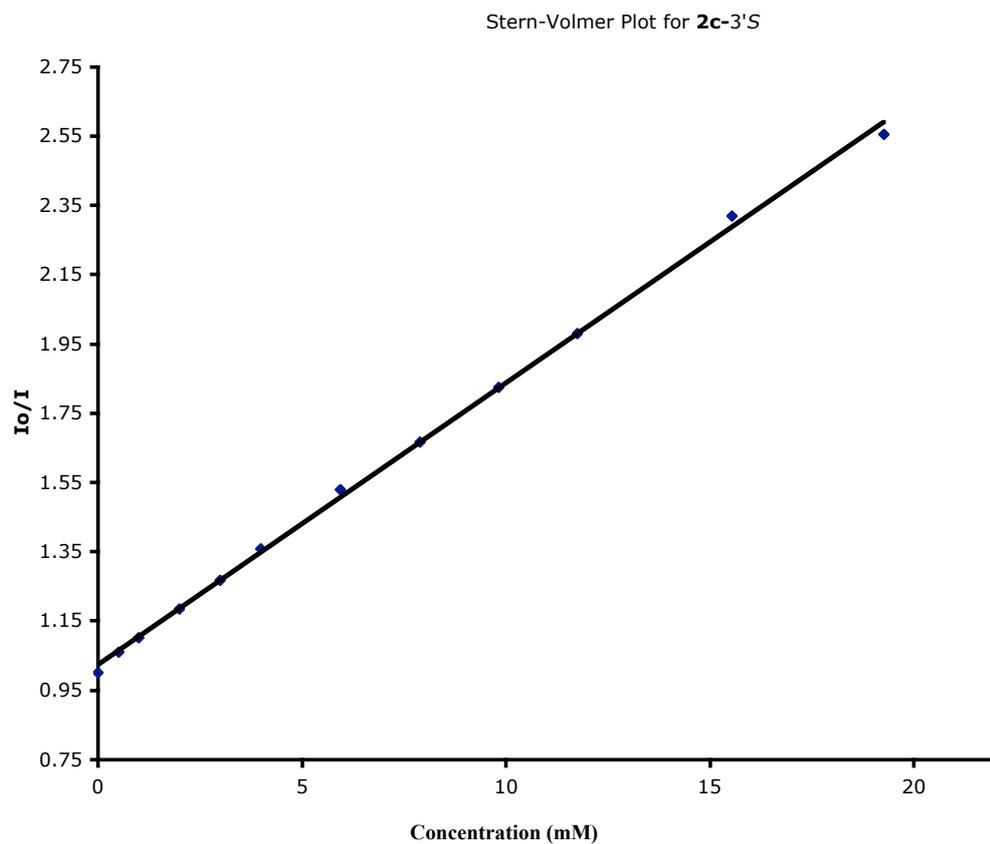
**Figure S2:** $^1$H NMR spectra of enecarbamates **1a** (standard) and **2b** before irradiation.

## 4) Stern-Volmer Quenching to determine the Total Quenching Rate Constants ($k_q$):



**Figure S3:** Chemiluminescence (phosphorescence) spectra of singlet oxygen generated by decomposition of 1,4-dimethylnaphthalene endoperoxide (22 °C) in the presence of varying concentrations of **2c**-3'*S*.

**Figure S4:** Stern-Volmer plot for **2c**-3'*S* using data obtained in Figure S3.

## 5) Enantioselectivities as a function of C-4 alkyl group (15°C, CDCl₃):[S4-7]

$$s = \frac{k_{cq}^{3'R}}{k_{cq}^{3'S}} = \frac{\ln[1 - C(1 + ee_{MDB})]}{\ln[1 - C(1 - ee_{MDB})]} \qquad \textbf{(S2)}$$

**Table S1**

| Entry | Substrate [a] | Configuration | | $s^a$ | $s^b$ |
|:---:|:---|:---:|:---:|:---:|:---:|
| | | C-4 | C-3' | 15°C | 20°C |
| 1. | Z(*Me*)-**1a** | R | R/S | 1.2 [R] | 1.3 [R] |
| 2. | Z(*Me*)-**1b** | S | R/S | 0.7 [S] | |
| 3. | E(*Me*)-**1c** | R | R/S | 9.1 [R] | |
| 4. | E(*Me*)-**1d** | S | R/S | 0.1 [S] | 0.5 [S] |
| 5. | Z(*iPr*)-**2a** | R | R/S | 2.2 [R] | 1.2 [R] |
| 6. | Z(*iPr*)-**2b** | S | R/S | 0.7 [S] | 0.8 [S] |
| 7. | E(*iPr*)-**2c** | R | R/S | 5.0 [R] | 1.8 [R] |
| 8. | E(*iPr*)-**2d** | S | R/S | 0.3 [S] | 0.6 [S] |
| 9. | Z(*tBu*)-**6b** | S | R/S | 0.7 [R] | |
| 10. | E(*tBu*)-**6d** | S | R/S | 0.3 [S] | |

The $s^a$ calculated using $ee_{mdb}$ and C, $s^b$ calculated using $k_{cq}$ values in Table S2.

The stereoselectivity (*s*) factor[S8] is a ratio of the relative reactive rate constants (chemical quenching) between two epimers that only differ in the *R/S* configuration at the C-3' center (Eqn S2). In previous work (Table S1)[S5,S 9] the *s*-factor (*s*ᵃ) was determined as only a ratio via the enantioselectivity in the MDB product (*ee*_MDB) and *C*, the conversion (Eqn S2). While *ee* may change with conversion, the *s*-factor is conversion independent and is a way of comparing different compounds where the *ee* has been determined over different conversion. However, the *s*-factors can also be computed (Eqn S2) from $k_{cq}$ values shown in Table S2 (*s*ᵇ) and compared to the *s*-factors in Table S1. The difference

in the $s^a$ and $s^b$ values can be attributed to the two sets of experiments being conducted at different temperatures (Table S3) and different concentrations.
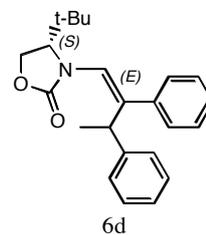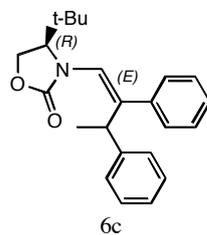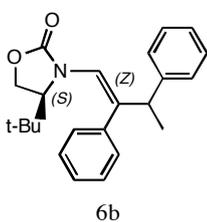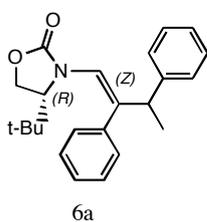
**Table S2**

| Entry | Substrate [a] | Configuration | | Chemical Quenching[$M^{-1}s^{-1}$] ($k_{cq}$ x $10^{-3}$) |
|:---:|:---|:---:|:---:|:---:|
| | | $C$-4 | $C$-3' | |
| 1. | $Z(Me)$-**1a** | $R$ | $R$ | 2.4 |
| 2. | $Z(Me)$-**1a** | $R$ | $S$ | 1.8 |
| 3. | $E(Me)$-**1d** | $S$ | $R$ | 0.9 |
| 4. | $E(Me)$-**1d** | $S$ | $S$ | 1.9 |
| 5. | $Z(^iPr)$-**2a** | $R$ | $R$ | 1.6 |
| 6. | $Z(^iPr)$-**2a** | $R$ | $S$ | 1.3 |
| 7. | $Z(^iPr)$-**2b** | $S$ | $R$ | 1.3 |
| 8. | $Z(^iPr)$-**2b** | $S$ | $S$ | 1.6 |
| 9. | $E(^iPr)$-**2c** | $R$ | $R$ | 1.6 |
| 10. | $E(^iPr)$-**2c** | $R$ | $S$ | 0.9 |
| 11. | $E(^iPr)$-**2d** | $S$ | $R$ | 1.0 |
| 12. | $E(^iPr)$-**2d** | $S$ | $S$ | 1.7 |

**Table S3 –** Determination of *s*-factor for **2c** upon photoxygenation in in CDCl$_3$

| Entry | Temp [a] | % ee$_{MDB}$ | %C | *s*[a] |
|-------|----------|--------------|-----|--------|
|       | °C       |              |     |        |
| 1.    | *Z*(*Me*)-**1a** | 8 [S]  | 5  | 1.2  |
| 2.    | *Z*(*Me*)-**1b** | 63 [R] | 17 | 5.0  |
| 3.    | *E*(*Me*)-**1c** | 78 [R] | 37 | 13.0 |
| 4.    | *E*(*Me*)-**1d** | 88 [R] | 43 | 31.0 |

# 6) Structure Matrix:

**1a**     **1b**     **1c**     **1d**

**2a**     **2b**     **2c**     **2d**

**3**     **4**     **5**

**6a**     **6b**     **6c**     **6d**
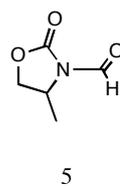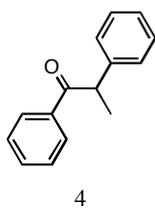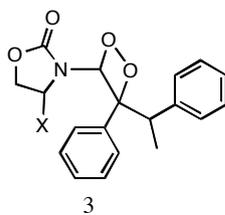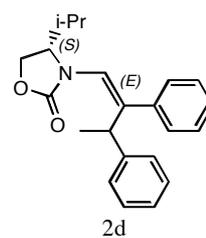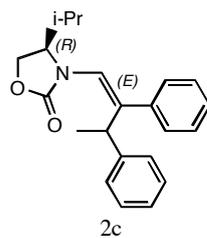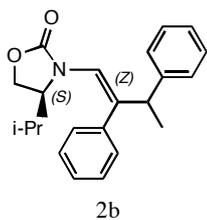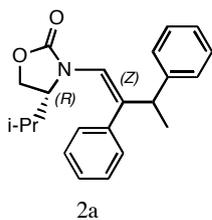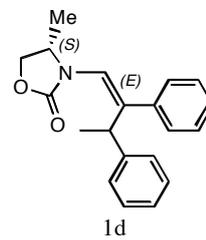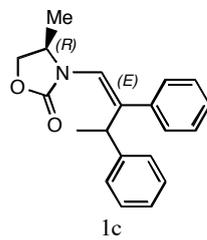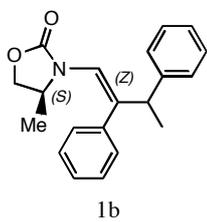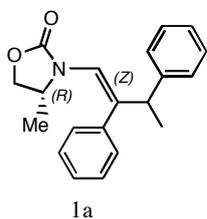
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