Supplementary Information

Vibrational Deactivation Of Singlet Oxygen : Does It Play A Role In Stereoselectivity During Photooxygenation?

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i) General

Spectrophotometric grade solvents were used as received from Aldrich. Methylene blue was used as received from Aldrich. Deuterated solvents and *L*-(d_8)-Valine were obtained from Cambridge Isotope Labs. Chloroform-*d*, methylene chloride-d_2 and methanol-d_4 were used as received.[Si,Sii] Dioxetanes were analyzed using ^{1}H NMR (500Mhz, Bruker). Diols **4** were analyzed using a Hewlett-Packard 1100 HPLC, equipped with a Chiralcel OD normal phase chiral column. The *Z* and *E* enecarbamates *Z*-**1-h$_8$** and *E*-**1-h$_8$** and Diols **4** were synthesized as previously described.[Sii] Synthesis of *L*-(d_8)-Valinol precursor to the ***Z*-1-d$_8$** enecarbamate followed published procedures.[Siii]

ii) Reaction Procedures

a) General procedure for photooxidation of the Z-1-h$_8$, Z-1-d$_8$ and E-1-h$_8$ enecarbamates by singlet oxygen:

The enecarbamate was dissolved in CD_2Cl_2 (kept over $NaHCO_3$) and 2 mg 5,10,15,20-Tetrakis-(Pentafluorophenyl)-Porphine (TFPP) added. The solution was irradiated at –23ºC (Ccl4/Dry Ice) and irradiated with a 300W lamp using <400 nm cutoff filter. The appearance of the $C_{1'}$-*H* peak in the dioxetane and the disappearance of the $C_{1'}$-*H* peak of the starting enecarbamate was monitored by low temperature ^{1}H-NMR until >90% conversion. The resulting dioxetane was maintained at –23ºC and characterized by ^{1}H-NMR.

Compound	^{1}H-NMR shift of Dioxetane C_1-*H* (δ, ppm)
Z(*S,S*)-1-h_8	6.63
Z(*S,S*)-1-d_8	6.20, 6.12
E(*R,S*)-1-h_8	6.28

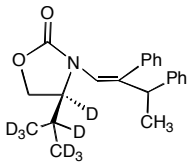
*iii) HPLC (Chiral Stationary Phase) analysis condition Diol **4**:*

HPLC : Hewlett-Packard Series 1100

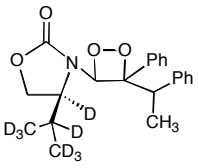
Column : Chiralcel OD, Normal Phase

Program : 90:10 Hexanes:2-Propanol, Flow 0.5ml/min

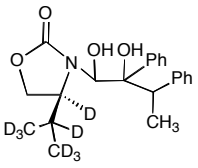
iv) Structure Matrix:



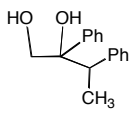
Z-1-d_8



Z-2-d_8



Z-3-d_8



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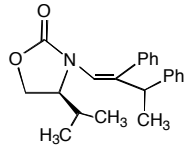
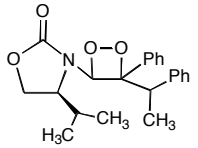


Z-1-h_8



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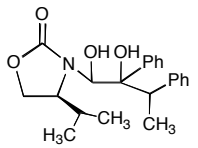
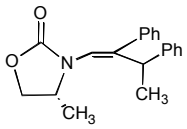
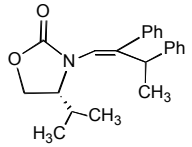


Z-3-h_8



E-1-h_4



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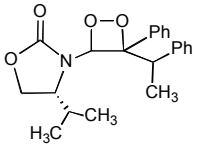
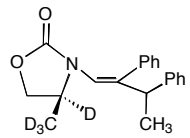
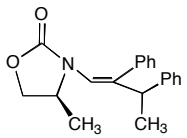


E-2-h_8



Z-1-d_4



Z-1-h_4

v) Summary results:

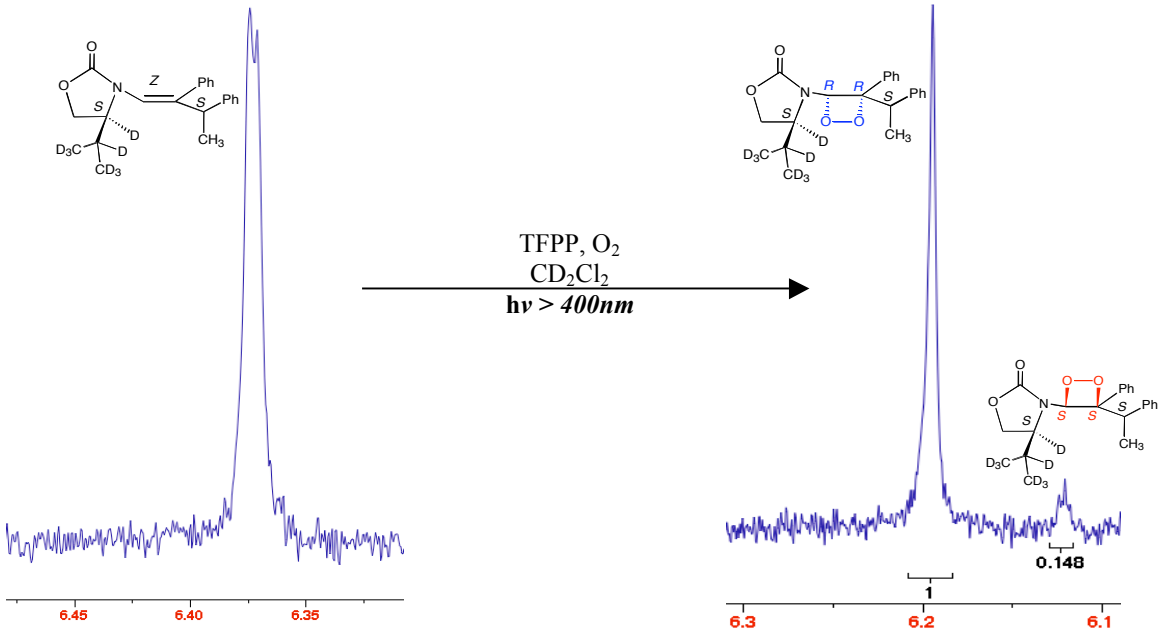


Figure 1: ^{1}H-NMR resulting from photooxygenation of enecarbamate ***Z(4S,3'S)*-1-d$_8$** to dioxetane ***Z*-2-d$_8$**. The reaction was carried out in CD_2Cl_2 at –23ºC using a 300W lamp and <400 nm cutoff filter. Two dioxetanes result from the reaction of the enecarbamate with $^{1}O_2$ with an 80% *de* favoring the (1'*R*,2'*R)* diastereomer over the (1'*S*,2'*S*) diastereomer.

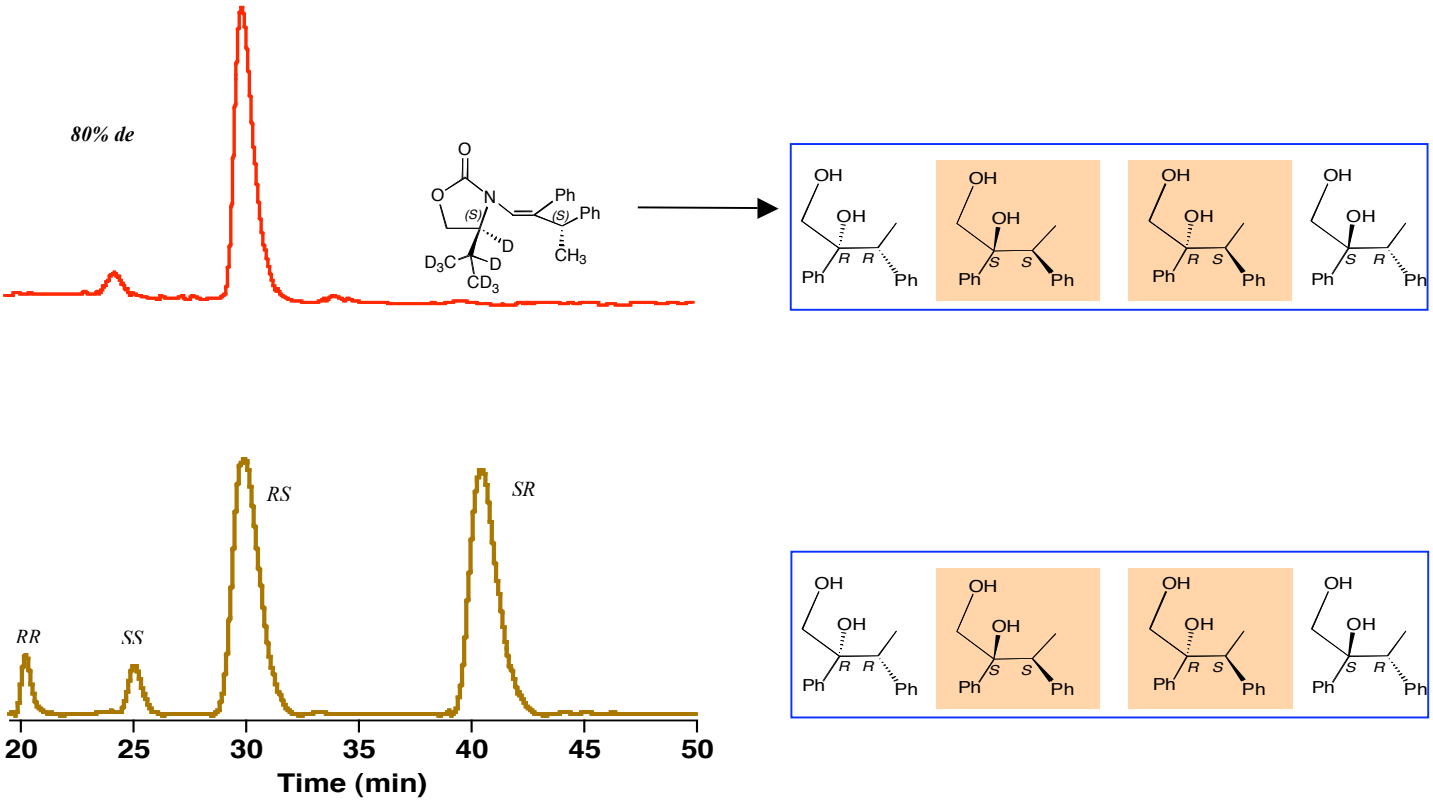


Figure 2: *Top:* HPLC trace of diols (4) resulting from the reduction of dioxetane *Z*-2-d_8 (obtained from photooxygenation of enecarbamate *Z(4S,3'S)*-1-d_8) to diol *Z*-3-d_8 and the subsequent reaction with $NaBH_4$/DBU. *Bottom:* HPLC trace of the four isomers of Diol 4.

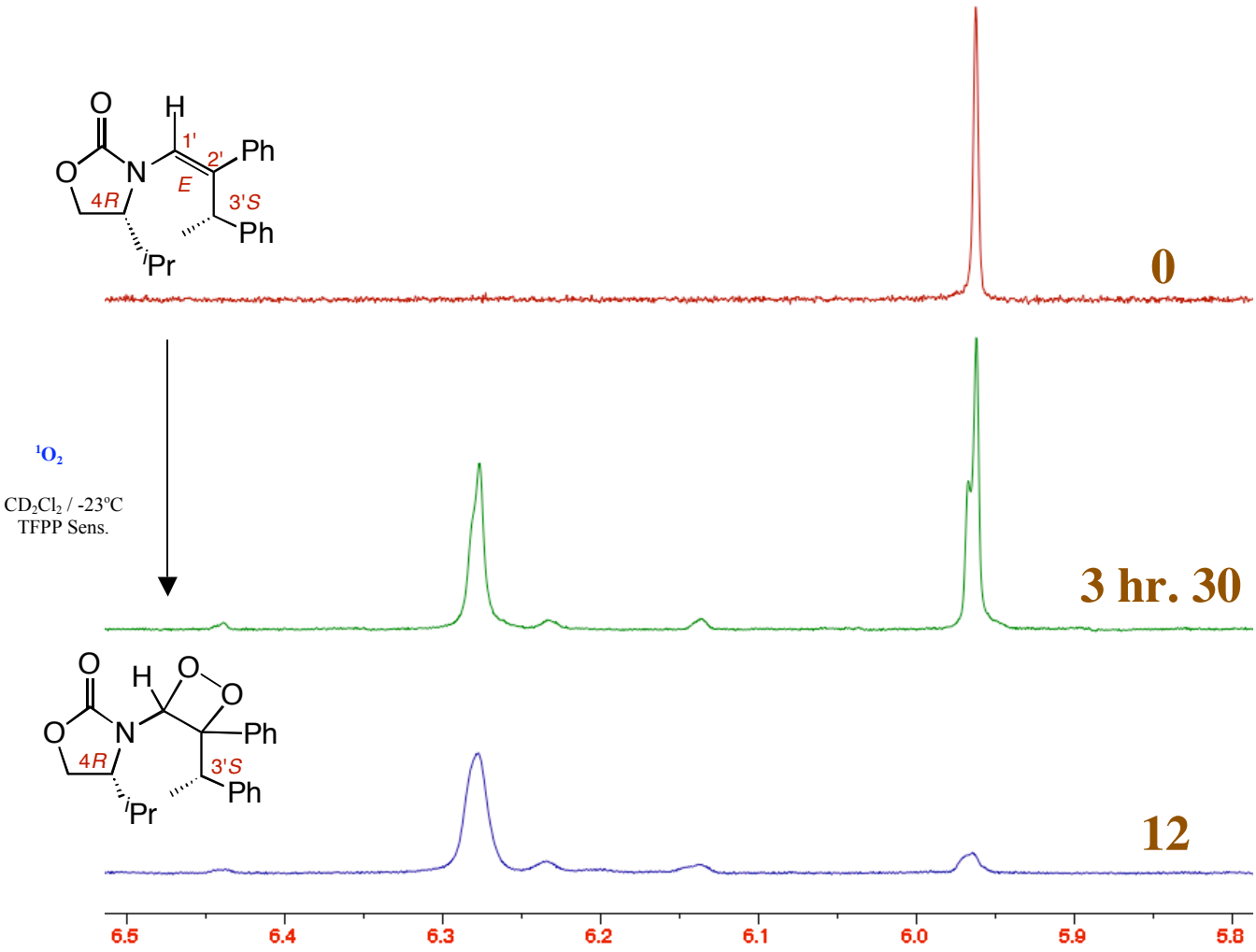


Figure 3: ^{1}H-NMR spectra monitoring the photooxygenation of enecarbamate ***E(4R,3'S)*-1-h$_8$** to dioxetane ***E*-2-h$_8$** by the disappearance of the enecarbamate peak and the appearance of the dioxetane peak. The reaction was carried out in CD_2Cl_2 at –23°C using a 300W lamp and <400 nm cutoff filter.

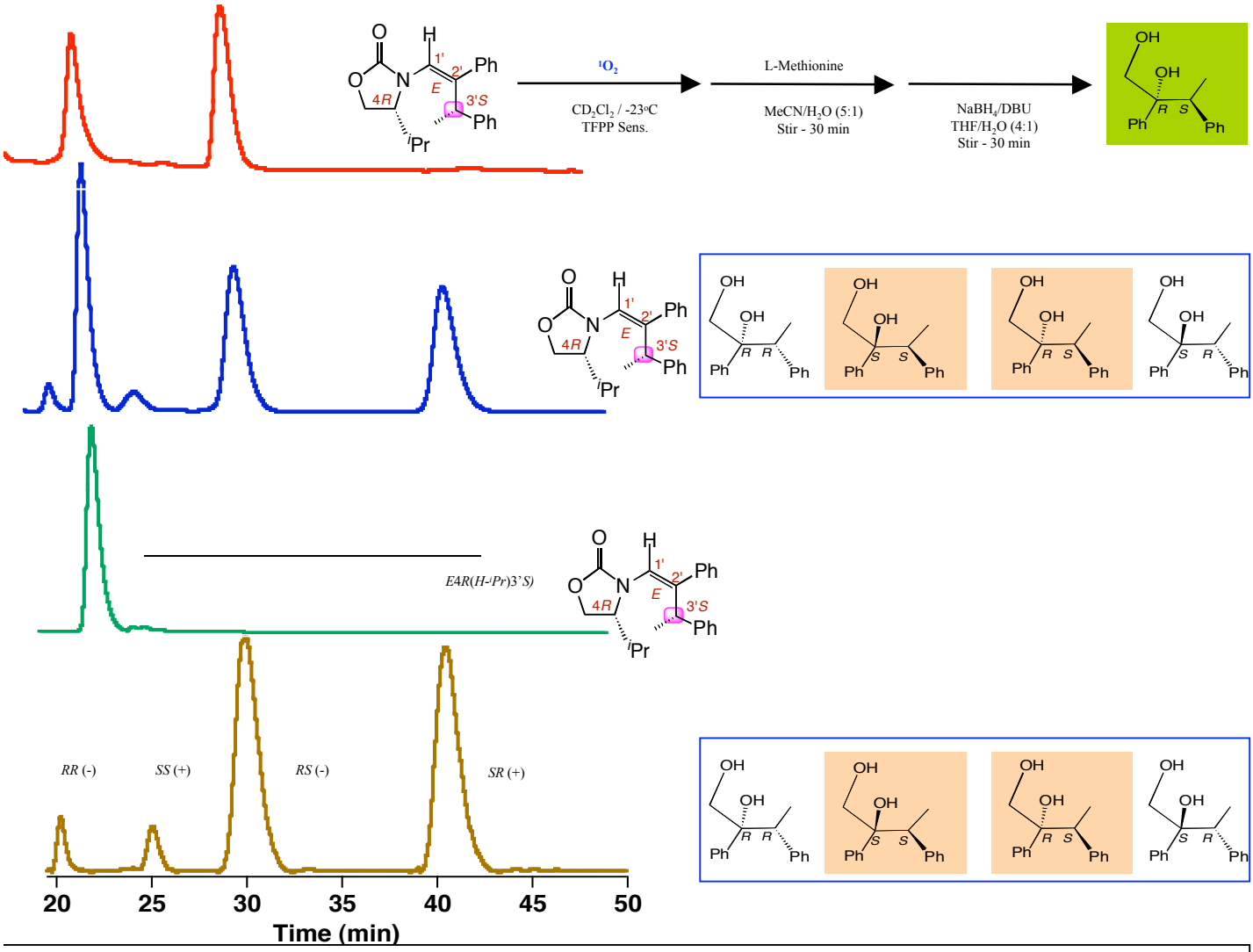


Figure 4: *Brown:* HPLC trace of the four isomers of Diol **4**. *Green:* HPLC trace of ***E(R,S)*-1-h$_8$**. *Blue:* HPLC trace for coinjection of ***E(R,S)*-1-h$_8$** and the four isomers of Diol **4**. *Red:* HPLC trace of diols (**4**) resulting from the reduction of dioxetane ***E*-2-h$_8$** (obtained from photooxyenation of enecarbamate ***E(R,S)*-1-h$_8$**) to diol ***E*-3-h$_8$** and the subsequent reaction with $NaBH_4$/DBU.

vi) Additional References:

Si Poon, T.; Turro, N. J.; Chapman, J.; Lakshminarasimhan, P.; Lei, X.; Adam, W.; Bosio, S. G. *Org. Lett.* **2003**, *5*, 2025-28.

Sii For the synthesis procedure and the product characterizations of *Z* and *E* enecarbamates (**1**), Dioxetanes (**2**) and Diols **4**: a) Adam, W.; Bosio, S. G.; Turro, N. J.; *J. Am. Chem. Soc*. **2002**, *124*, 8814-5. b) Poon, T.; Sivaguru, J.; Franz, R.; Jockusch, S.; Martinez, C.; Washington, I.; Adam, W.; Inoue, Y.; Turro, N. J.; *J. Am. Chem. Soc.;* **2004**; *126*; 10498-10499. c) Sivaguru, J.; Poon, T.; Franz, R.; Jockusch, S.; Adam, W.; Turro, N. J.; *J. Am. Chem. Soc.;* **2004**; *126*; 10816-10817. d) Adam, W.; Bosio, S. G.; Turro, N. J., Wolff, B. T.; *J. Org. Chem.* **2004**, *69*, 1704-5.

Siii Hsiao, Y., Hegedus, L. S.; *J. Org. Chem.* **1997**, *62*, 3586-91.