Supplementary Material for Chemical Communications

Supporting Information

Stereoselective *E*/*Z* Photoisomerization of Oxazolidinone Functionalized Enecarbamates: Direct and Triplet Sensitized Irradiation.

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1. Materials and Methods

Deuterated solvents obtained from Cambridge Isotope Labs were used as received. Products ratio and diastereoselectivities were determined by ^{1}H NMR (300MHz, Bruker). The *Z* and *E* enecarbamates were synthesized as previously described.[S1]

2. Compounds Characterization

***E*-(4*R*,3'*R*)-3-(2',3'-Diphenylbut-1'-enyl)-4-isopropyloxazolidin-2-one**

[(*E*,4*R*,3'*R*)-1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.76 (d, *J* = 7.03, 3H), 0.86 (d, *J* = 6.85, 3H), 1.33 (d, *J* = 7.20, 3H), 2.00-2.12 (m, 1H), 3.65 (ddd, *J* =8.10, 4.23, 3.66, 1H), 4.04 (dd, *J* =8.95, 4.33, 1H), 4.10 (t, *J* =8.68, 1H), 4.32 (q, *J* = 7.20, 1H), 5.89 (s, 1H), 6.96-7.01 (m, 2H), 7.10-7.22 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.6, 17.8, 18.4, 28.2, 39.2, 62.7, 63.1, 121.0, 126.3, 127.5, 127.6 (2C), 127.7 (2C), 128.2 (2C), 129.0 (2C), 138.9, 143.1, 146.1, 157.1; MS (FAB): M+H$^+$ calcd 336.1958, exptl 336.1972.

***E*-(4*R*,3'*S*)-3-(2',3'-Diphenylbut-1'-enyl)-4-isopropyloxazolidin-2-one**

[(*E*,4*R*,3'*S*)-1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.87 (d, *J* = 6.92, 6H), 1.39 (d, *J* = 7.20, 3H), 2.01-2.15 (m, 1H), 3.75 (ddd, *J* = 8.70, 4.78, 3.92, 1H), 4.08 (dd, *J* = 8.95, 4.88, 1H), 4.19 (t, *J* = 8.80, 1H), 4.28 (q, *J* = 7.20, 1H), 5.88 (s, 1H), 6.84-6.87 (m, 2H), 7.07-7.27 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.6, 17.3, 18.6, 29.5, 39.5, 63.2, 63.9, 121.9, 126.7, 127.9, 128.0 (4C), 128.7 (2C), 129.4 (2C), 138.4, 142.2, 144.9, 157.1; MS (FAB): M+H$^+$ calcd 336.1958, exptl 336.1961.

***E*-(4*S*,3'*S*)-3-(2',3'-Diphenylbut-1'-enyl)-4-isopropyloxazolidin-2-one**

[(*E*,4*S*,3'*S*)-1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.85 (d, 3H), 0.92 (d, 3H), 1.42 (d, 3H), 2.11-2.18 (m, 1H), 3.71-3.76 (ddd, 1H), 4.12 (dd, 1H), 4.19 (t, 1H), 4.41 (q, 1H), 5.97 (s, 1H), 7.06-7.11 (m, 2H), 7.20-7.34 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.1, 18.5, 19.0, 28.2, 39.9, 62.9, 63.2, 121.4, 126.7, 127.9, 128.1 (4C), 128.7 (2C), 129.5 (2C), 138.9, 143.3, 146.6, 157.1; MS (FAB) M+H$^+$ calcd 336.1958, exptl 336.1952.

***E*-(4*S*,3'*R*)-3-(2',3'-Diphenylbut-1'-enyl)-4-isopropyloxazolidin-2-one**

[(*E*,4*S*,3'*R*)-1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.96 (d, 6H), 1.42 (d, 3H), 2.12-2.22 (m, 1H), 3.81-3.87 (ddd, 1H), 4.16 (dd, 1H), 4.28 (t, 1 H), 4.37 (q, 1 H), 5.96 (s, 1H), 6.93-6.97 (m, 2H), 7.16-7.35 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.6, 17.3, 18.6, 29.5, 39.5, 63.2, 63.9, 121.9, 126.7, 127.9, 128.0 (4C), 128.7 (2C), 129.4 (2C), 138.4, 142.2, 144.9, 157.1; MS (FAB) M+H$^+$ calcd 336.1958, exptl 336.1950.

***Z*-(4*S*,3'*R*)-3-(2',3'-Diphenylbut-1'-enyl)-4-isopropyloxazolidin-2-one**

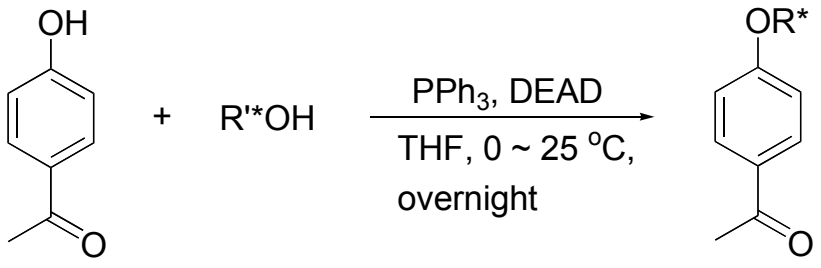
[(*Z*,4*S*,3'*R*)-1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.40 (d, *J* = 7.10, 3H), 0.75 (d, *J* = 6.88, 3H), 1.43 (d, *J* = 7.20, 3H), 1.74-1.85 (m, 1H), 2.85 (td, *J* = 5.70, 3.10, 1H), 3.89 (q, *J* = 7.20, 1H), 3.95 (d, *J* = 5.70, 2H), 6.70 (s, 1H), 6.82-6.86 (m, 2H), 7.18-7.28 (m, 8H); ^{13}C

NMR (75 MHz, CD_3CN) δ = 13.2, 16.8, 20.4, 27.2, 45.8, 59.2, 63.0, 120.0, 126.6, 127.7, 128.0, 128.3, 128.6, 128.8, 129.2, 133.4, 138.8, 144.8

***Z*-(4*S*,3'*S*)-3-(2',3'-Diphenylbut-1'-enyl)-4-isopropyloxazolidin-2-one [(*Z*,4*S*,3'*S*)-1]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.43 (d, J = 7.10, 3H), 0.72 (d, J = 6.87, 3H), 1.51 (d, J = 7.20, 3H), 1.78-1.89 (m, 1H), 2.87 (td, J = 5.80, 3.10, 1H), 3.75 (q, J = 7.20, 1H), 3.94 (d, J = 5.80, 2H), 6.46 (s, 1H), 6.96-6.99 (m, 2H), 7.18-7.36 (m, 8H); ^{13}C NMR (75 MHz, CD_3CN) δ = 13.3, 16.8, 20.3, 27.2, 46.3, 59.3, 63.0, 120.5, 126.8, 127.8, 128.0, 128.4, 128.6, 128.8, 129.5, 134.8, 139.6, 145.0

3. Synthesis of chiral sensitizers

General. Mitsunobu reaction [S2, S3] was applied for the synthesis of chiral sensitizers (**3b**~**3d**).



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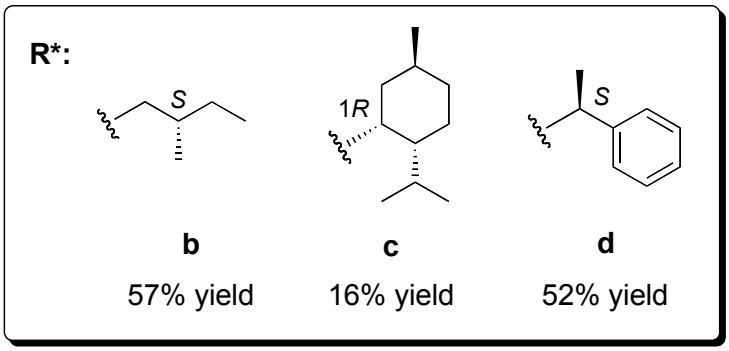


(*S*)-2-Methyl-1-butyl ether of 4'-hydroxyacetophenone (3b): 4'-Hydroxyacetophenone (6.9 g, 51 mmol), triphenylphosphine (13.4 g, 51 mmol) and (*S*)-2-methyl-1-butanol (3.0 g, 34 mmol) were stirred in 60 mL of dry THF under N_2 at 0 ^{o}C. Diethyl azodicarboxylate (DEAD, 8.9 g, 51 mmol) was added into the solution by drop wise for 20 min, followed by warming up to room temperature and stirred overnight. The reaction mixture was purified by silica gel chromatography (hexanes/ethyl acetate =

95/5).colorless liquid, 4.0 g (57% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.962 (t, J = 7.5 Hz ,3H), 1.03 (d, J = 6. Hz, 3H), 1.28 (m, 1H), 1.58 (m, 1H), 1.88 (m, 1H), 2.56 (s, 3H), 3.79 (dd, J = 6.5, 9.0 Hz, 1H), 3.88 (dd, J = 6.0, 9.0 Hz, 1H), 6.91 (d, J = 6.8 Hz, 2H), 7.91 (d, J = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 16.5, 26.0, 26.4, 34.5, 72.8, 114, 131, 163, 197 Hz.

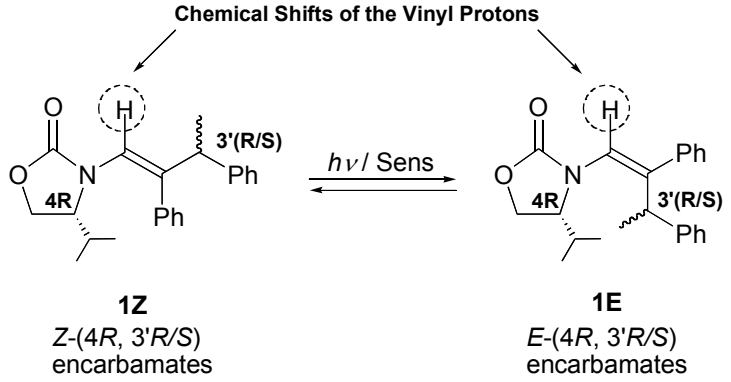
(1*R*,2*R*,5*S*)-Neomenthyl ether of 4'-hydroxyacetophenone (3c): (1*S*,2*R*,5*S*)-(+)-menthol and the same procedure as for **3b** was employed. Colorless liquid (16% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.745 (d, J = 5.0 Hz, 3H), 0.768 (d, J = 4.8, 3H), 0.854 (d, J = 6.6 Hz, 3H), 0.971 (m, 1H), 1.01 (m, 2H), 1.56 (m, 3H), 1.69 (m, 2H), 2.01 (m, 1H), 2.47 (s, 3H), 4.64 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.4, 22.6, 25.2, 26.6, 27.0, 29.7, 35.2, 38.0, 48.0, 74.1, 115, 130, 131, 163, 197 Hz.

(*S*)-1-Phenyl-1-ethyl ether of 4'-hydroxyacetophenone (3d): (*R*)-(+)-1-Phenylethanol and the same procedure as for **3b** was employed. White solid (52% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (d, J = 6.4 Hz, 3H), 2.5 (s, 3H), 5.39 (q, J = 6.4 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.25-7.35 (m, 5H), 7.83 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.9, 26.7, 76.6, 116, 126, 128, 129, 130.5, 130.9, 143, 162, 197.

4. Photoreactions

General. Direct irradiations of enecarbamates **1** in solution were performed in quartz NMR tubes by irradiating the solutions at 254 nm (monochromatic) in a Rayonet reactor. Triplet sensitizations were performed by irradiating solutions of **1** and the triplet sensitizers (**2**, **3**) at 300 nm (Gaussian distribution) under N_2 atmosphere in a Rayonet reactor.

5. Typical ^{1}H NMR Spectra of Photoisomerization of 1*Z* with the sensitizer 3c in CD_3OD: Temperature Effect



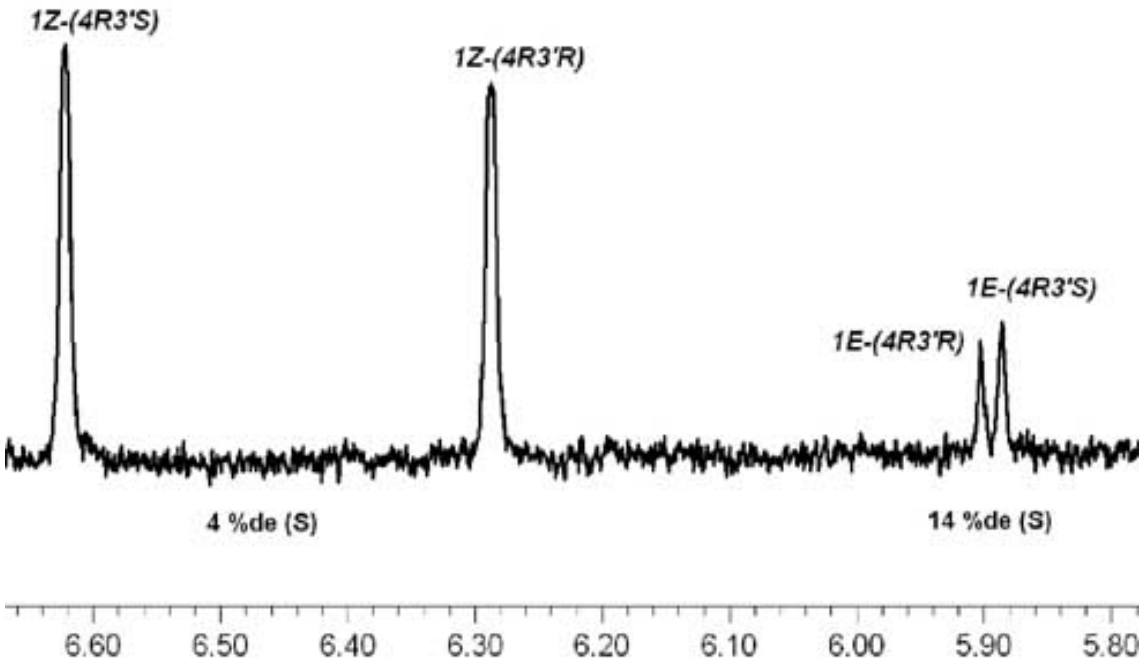


Chart S1. ^{1}H NMR Chemical Shift of the vinyl proton of **1*Z*** or **1*E*** after 5min Photoirradiation in CD_3OD at 20^{o}C.

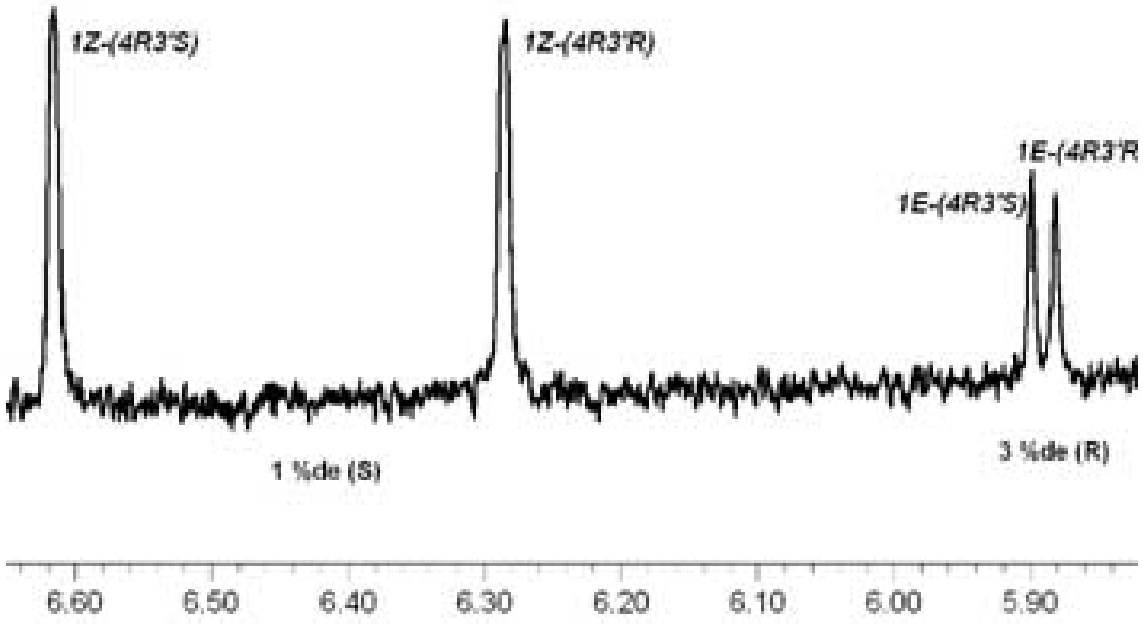


Chart S2. ^{1}H NMR Chemical Shift of the vinyl proton of **1*Z*** or **1*E*** after 5min Photoirradiation in CD_3OD at -40^{o}C.

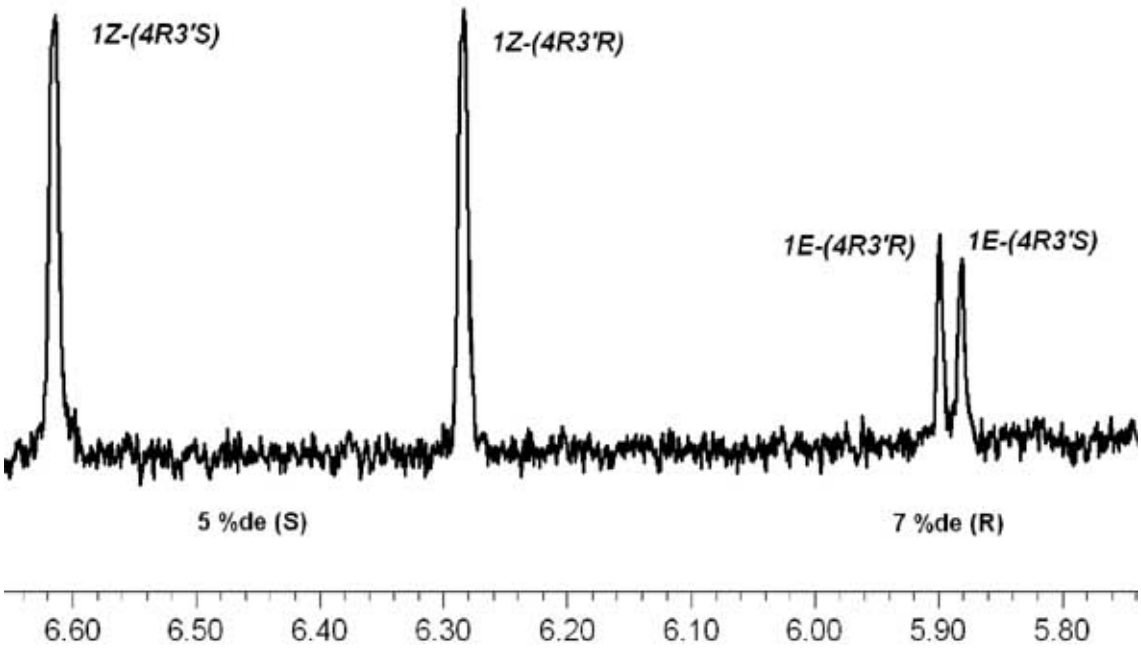


Chart S3. ^{1}H NMR Chemical Shift of the vinyl proton of **1*Z*** or **1*E*** after 5min Photoirradiation in CD_3OD at -65^{o}C.

6. Comparison of Directirracdiation of Z-enecarbamates at 254 and 300 nm

Table S1 Direct irradiation of **1*Z***: *Z* : *E* ratio dependence on excitation wavelength at photo-stationary state.[a]

Solvent	*Z* : *E*	
	Irdn. at 254 nm	Irdn. at ~300 nm
CD_3CN	62 : 38	76 : 24
CD_3OD	53 : 47	65 : 35
CD_2Cl_2	53 : 47	57 : 43
$CDCl_3$	54 : 46	61 : 39
C_6D_6	54 : 46	-

[a][**1*Z***] = 4.3 mM. Irradiations performed at 20^{o}C under N_2 atmosphere. de values and *Z*/*E* ratio determined by ^{1}H-NMR spectroscopy.

Table S2 Direct irradiation of **1*Z*** at 300 nm.[a]

Solvent	time/min	%de (**1E**)[b]	%de (**1Z**)[b]	*Z* : *E*
CD_3CN	1	4 (3'R)	4 (3'S)	88 : 12
	2	5 (3'R)	6 (3'S)	82 : 18
	5	2 (3'R)	6 (3'S)	76 : 24
	10	1 (3'R)	4 (3'S)	74 : 26
	15	2 (3'R)	5 (3'S)	76 : 24
CD_3OD	2	8 (3'S)	4 (3'S)	83 : 27
	5	10 (3'S)	10 (3'S)	74 : 26
	10	7 (3'S)	5 (3'S)	64 : 36
	15	6 (3'S)	10 (3'S)	64 : 36
CD_2Cl_2	2	6 (3'S)	2 (3'S)	71 : 29
	5	6 (3'S)	8 (3'S)	57 : 43
	10	7 (3'S)	8 (3'S)	58 : 42
	15	3 (3'S)	9 (3'S)	55 : 45
$CDCl_3$	2	7 (3'R)	12 (3'S)	81 : 19
	5	2 (3'R)	19 (3'S)	61 : 39

[a] [**1Z**] = 4.3 mM. Irradiations were performed at >300 nm at 20°C in Pyrex NMR tubes under N_2 atmosphere. A product's de and a *Z*/*E* ratio were determined by NMR analyses. [b] Stereochemistry for 3'-position of the predominated encarbamate was shown in a parenthesis.

7. References

S1 W. Adam, S. G. Bosio, N. J. Turro, and B. T. Wolff, *J. Org. Chem.*, 2004, **69**, 1704.

S2 O. Mitsunobu, *Synthesis*, 1981, 1.

S3 Y.-J. Shi, D. L. Hughes, and J. M. McNamara, *Tetrahedron Lett.*, 2003, **44**, 3609.