



Figure S2. (Supplementary Material) - Experimental ¹H-NMR chemical shifts of *4-(cyclohex-2-enyl)-1-phenyl-1H-tetrazol-5(4H)-one* (**4b**), recorded in CD₃OD.



Figure S3. (Supplementary Material) - Experimental ¹H-NMR chemical shifts of *4-(3-methylcyclohex-2-enyl)-1-phenyl-1H-tetrazol-5(4H)-one* (**4c**), recorded in CD₃OD.



Figure S1. (Supplementary Material) - Experimental ¹H-NMR chemical shifts of two conformers (distended configuration and a π - π stacking interation) of 4-methyl-4-(4-methylpent-3-enyl)-1-phenyl-3,4-dihydropyrimidin-2(1H)-one (**10a**). Recorded in CD₂OD



Figure S5. (Supplementary Material) - Experimental ¹H-NMR chemical shifts of *1-phenyl-3a,4,5,6-tetrahydro-1H-benzoimidazol-2(3H)-one* (**10b**), recorded in CD₃OD.



Figure S6. (Supplementary Material) - Experimental ¹H-NMR chemical shifts of *3-(1-methylcyclohex-2-enyl)-benzoimidazol-2(1H)-one* (**11**), recorded in CD₃OD.





Figure S7. (Supplementary Material) - Extinction coefficients (ε), as function of wavelength, for tetrazolones 4a-c (blue line) and corresponding photoproducts, pyrimidinones 10a, 10b and benzimidazolone 11 (red line), in methanol.



Figure S8. (**Supplementary Material**) - GC analysis of the photoproduct 4-methyl-4-(4methylpent-3-enyl)-1-phenyl-3,4-dihydropyrimidin-2(1H)-one (10a). The peak shoulder probably results from the presence of two conformers one with a distended configuration of the nerol residue, and other with the nerol residue in a orientation parallel to the tetrazole moiety.



Figure S9. (Supplementary Material) - Variation of the amount of reagents and photoproducts during irradiation of tetrazolones **4a-c** (λ =254nm) in methanol (1x10⁻⁴ M). The amount of reagent before irradiation was assumed to be 100%. The yields of different photoproducts were monitored by gaseous chromatography. Note that the ordinate scale is logarithmic.



Figure S10. (Supplementary Material) - Variation of the amount of reagents and photoproducts during irradiation of tetrazolones **4a-c** (λ =254nm) in acetonitrile (1x10⁻⁴ M). The amount of reagent before irradiation was assumed to be 100%. The yields of different photoproducts were monitored by gaseous chromatography. Note that the ordinate scale is logarithmic.

Compound	$\lambda_{\sf max}$ (nm)	ε/10 ⁴ (L.mol ⁻¹ .cm ⁻¹)
4a	249	1.167
4b	249	1.195
4c	249	1.463
10a	241	1.553
10b	238	1.810
11	231; 283	0.739; 0.709

 Table 1. Extinction coefficients values for tetrazolones 4a-c and photoproducts 10a,b

and **11**, calculated at λ_{max} .