## Supplementary materials

Spectra of the reaction mixtures demonstrating influence of radical traps on the yield of investigated reaction; spectra illustrating photochemical stability of *O*-thioacyl hydroxylamines.

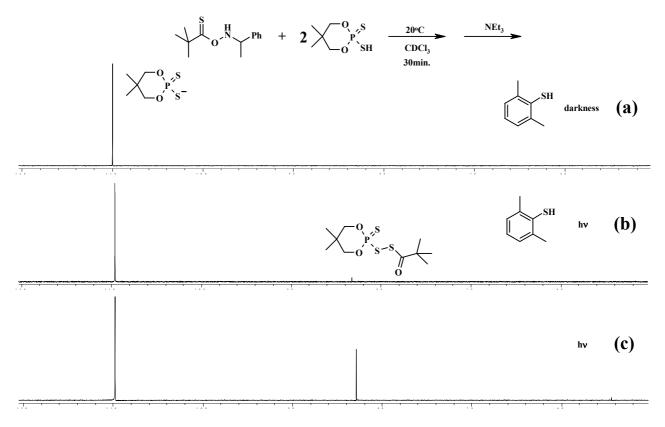
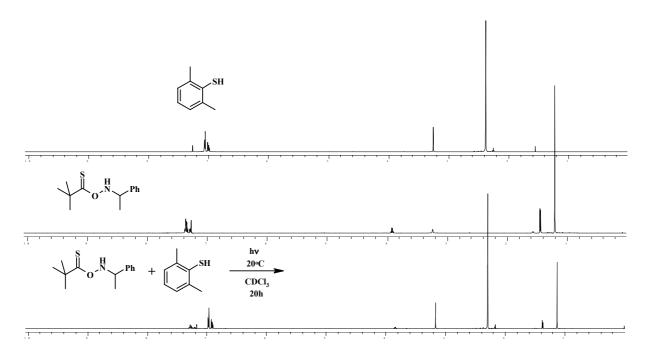


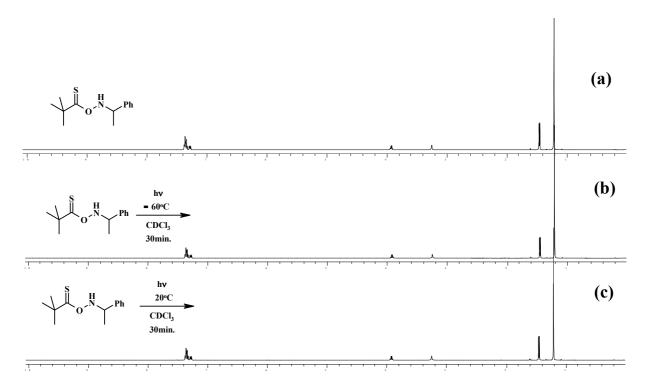
Figure S1. <sup>31</sup>P NMR spectra of reaction mixtures formed from *O*-thiopivaloyl

N-1-phenylethylhydroxylamine 7c and dithiophosphoric acid 1 in the presence of

1,6-dimethylthiophenole at different experimental conditions.



**Figure S2.** <sup>1</sup>H NMR spectrum of the reaction mixture formed after irradiation of *O*-thiopivaloyl *N*-1-phenylethylhydroxylamine **7c** in the presence of thiophenol **14**. Comparison with the starting materials.



**Figure S3.** <sup>1</sup>H NMR spectra of the reaction mixtures formed after irradiation of *O*-thiopivaloyl *N*-1-phenylethylhydroxylamine **7c**. Comparison with the starting material.