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.

\[
\text{PhO}-\text{H} + 2 \text{PhS}-\text{O}\text{P}^\text{3S}_2\text{SH} \xrightarrow{\text{20°C}, \text{CDCl}_3, 30\text{min.}} \text{NEt}_3
\]

(a) \text{darkness}  

(b) \text{hν}  

(c) \text{hν}

Figure S1. \textsuperscript{31}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. $^1$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. $^1$H NMR spectra of the reaction mixtures formed after irradiation of $O$-thiopivaloyl $N$-1-phenylethylhydroxylamine 7c. Comparison with the starting material.