

## SUPPORTING INFORMATION

### Reductive cleavage of organic peroxides by iron salts and thiols

(10 pages)

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**Figure S-1.** Visible monitoring of Fe/RSH promoted reduction (time lapse)

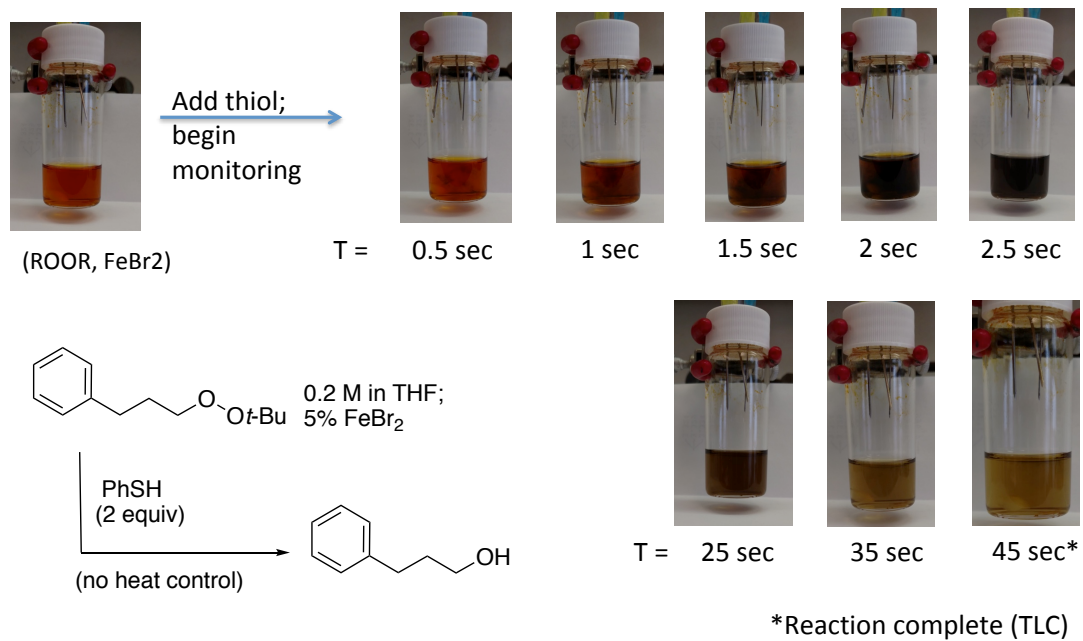
**Figure S-2.** <sup>1</sup>H NMR monitoring of the disproportionation of diacetone diperoxide (**6**) and the reductive decomposition of dialkyl peroxide (**3**).

**Figure S-3.** <sup>1</sup>H and <sup>13</sup>C NMR spectra related to synthesis of alkoxy radical probe **8**.

**Figure S-4.** <sup>1</sup>H NMR of reaction mixture from reaction of probe **8**.

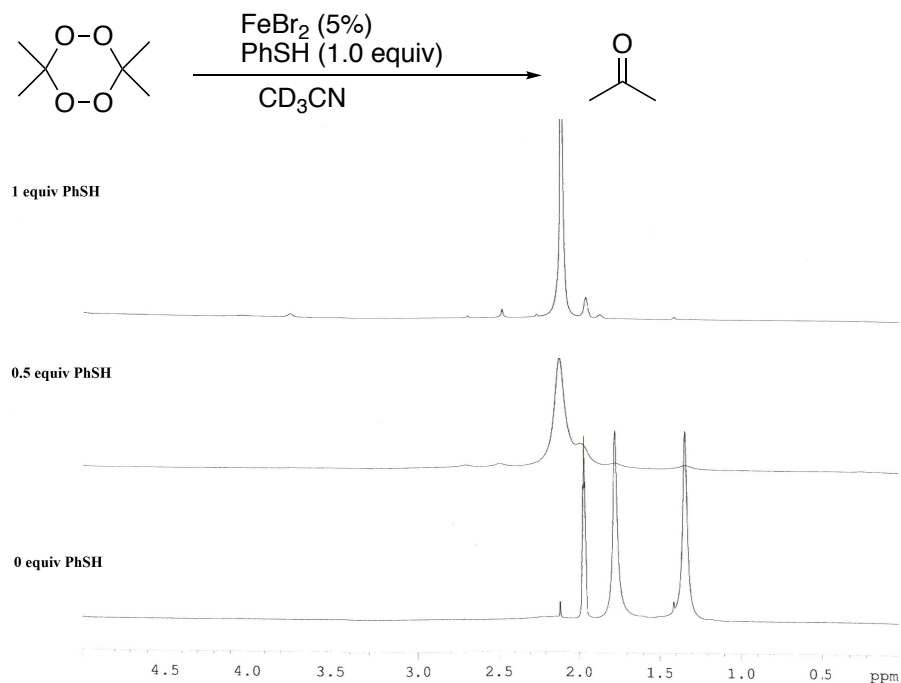
**Figure S-5.** <sup>1</sup>H NMR spectra of purified reaction mixtures from reduction of peroxides **1-4**.

**Figure S-1.** Visual monitoring of Fe/thiol promoted reduction

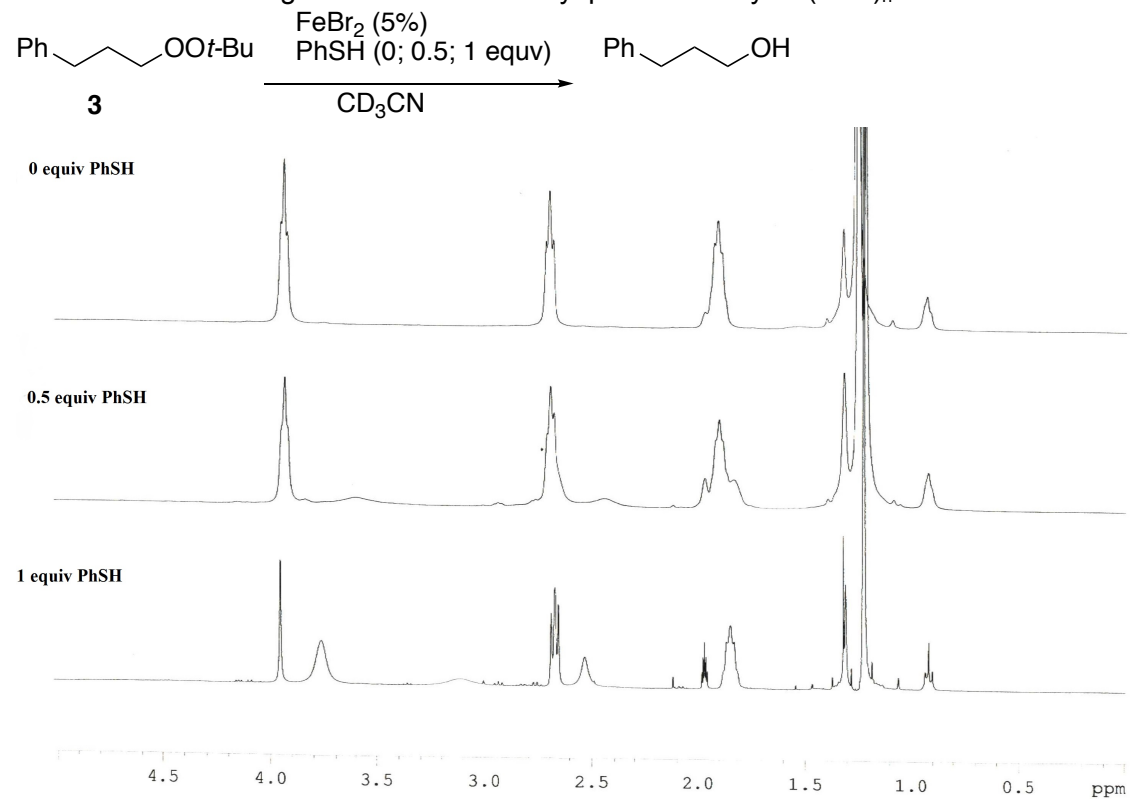


**Figure S-2**

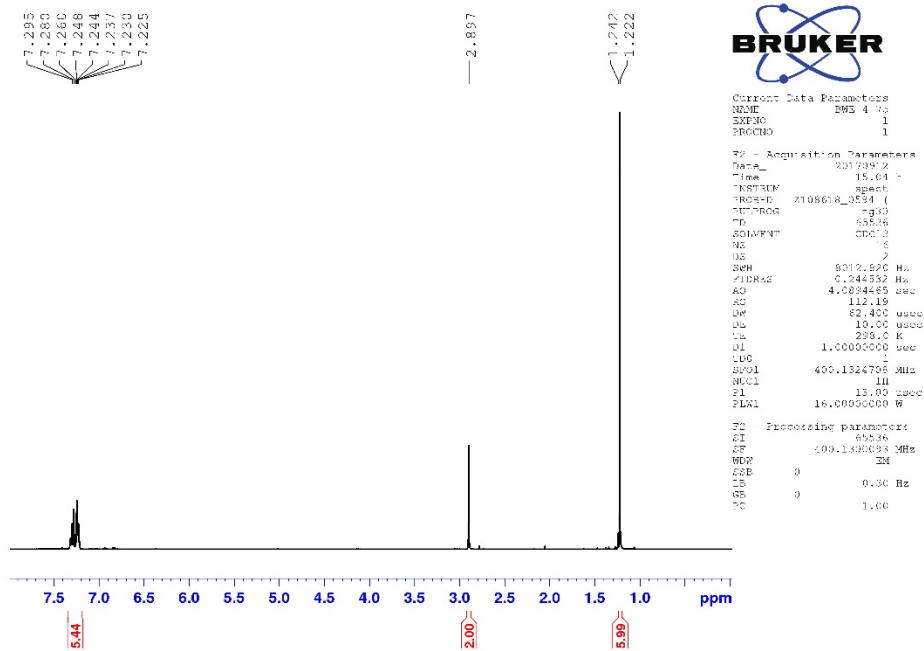
**a.**  $^1\text{H}$  NMR monitoring of the  $\text{FeBr}_2/\text{PhSH}$ -promoted decomposition of diacetone diperoxide (**6**)



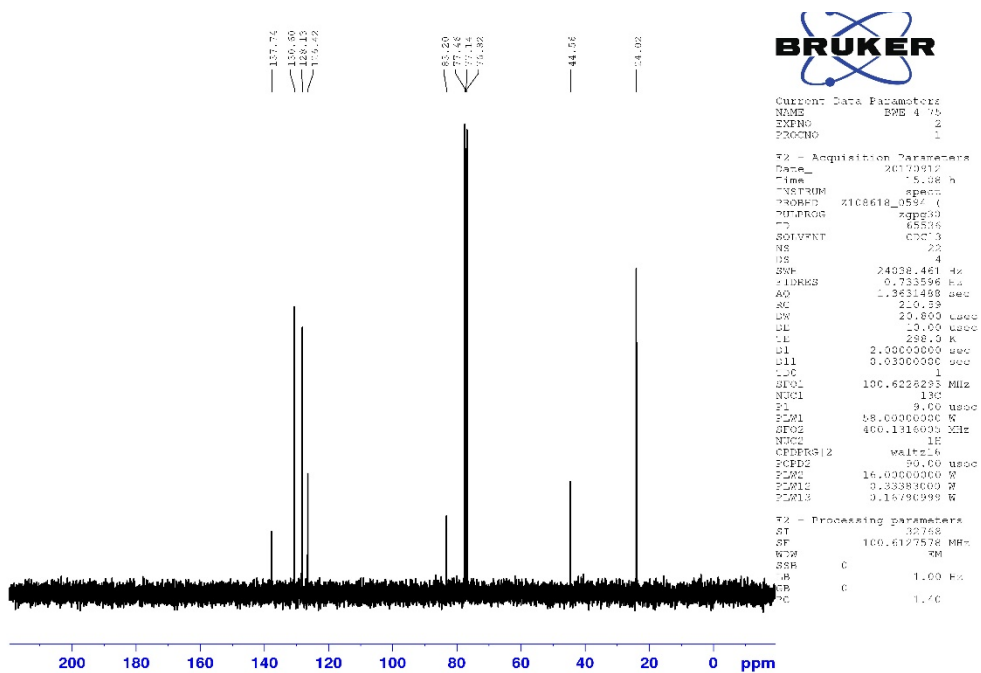
**b.**  $^1\text{H}$  NMR monitoring of reduction of dialkyl peroxide **3** by  $\text{Fe}(\text{SPh})_n/\text{stoichiometric PhSH}$ .



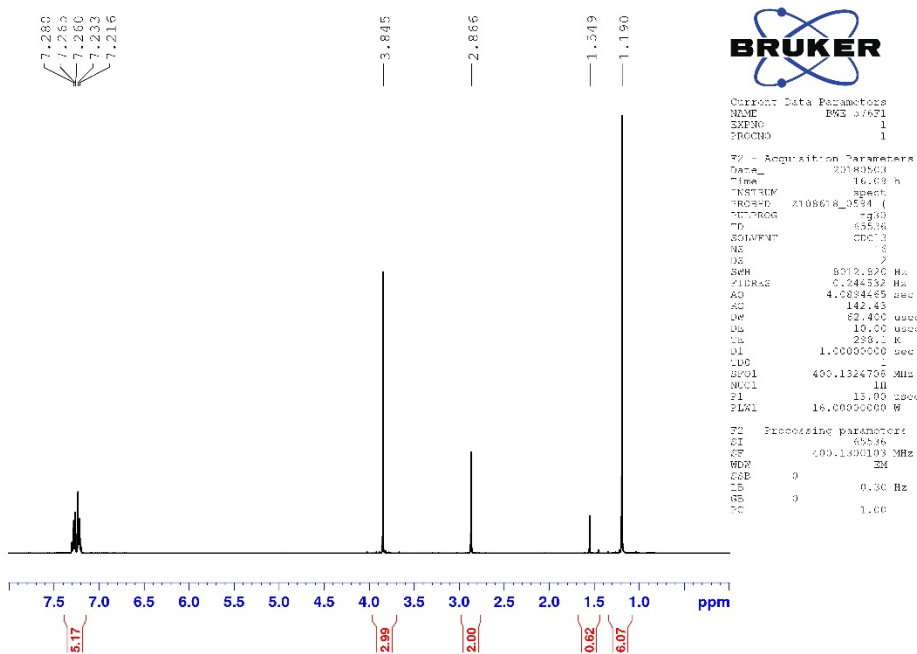
**Figure S-3.** NMR spectra related to synthesis of probe **8**  
**a.**  $^1\text{H}$  NMR of 1-phenyl-2-methyl-2-propyl hydroperoxide



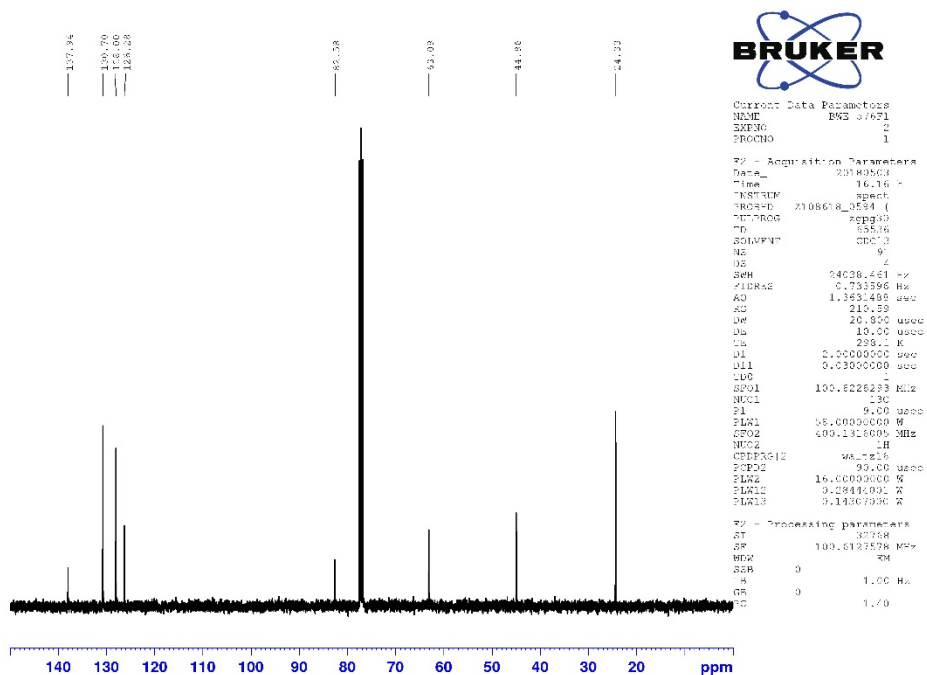
**b.**  $^{13}\text{C}$  NMR of 1-phenyl-2-methyl-2-propyl hydroperoxide



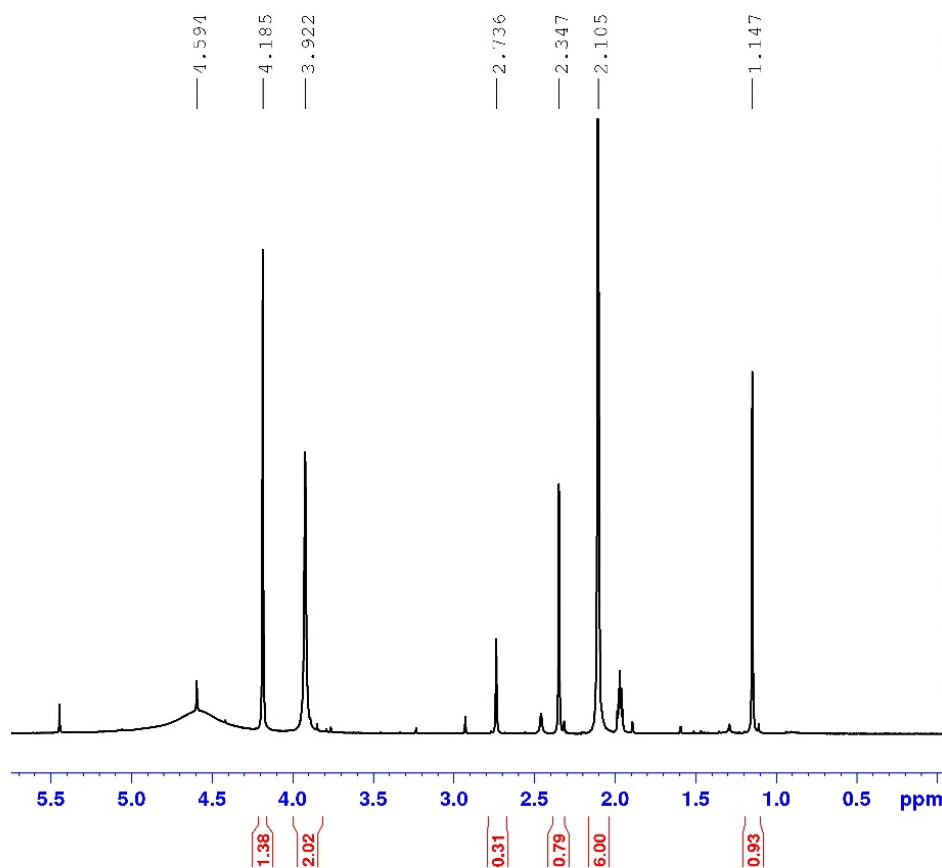
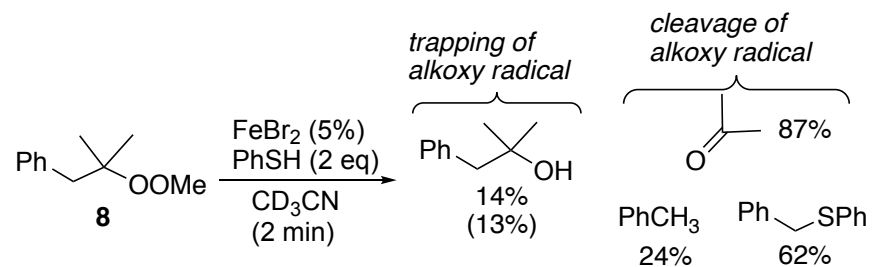
c.  $^1\text{H}$  NMR of Methyl 1-phenyl-2-methyl-2-propyl peroxide (**8**)



d.  $^{13}\text{C}$  NMR of Methyl 1-phenyl-2-methyl-2-propyl peroxide (**8**)



**Figure S-4.**  $^1\text{H}$  NMR analysis of reductive fragmentation of radical probe **8**. (Relative yields shown; isolated yield of 2-methyl-1-phenyl-2-propanol in parentheses).



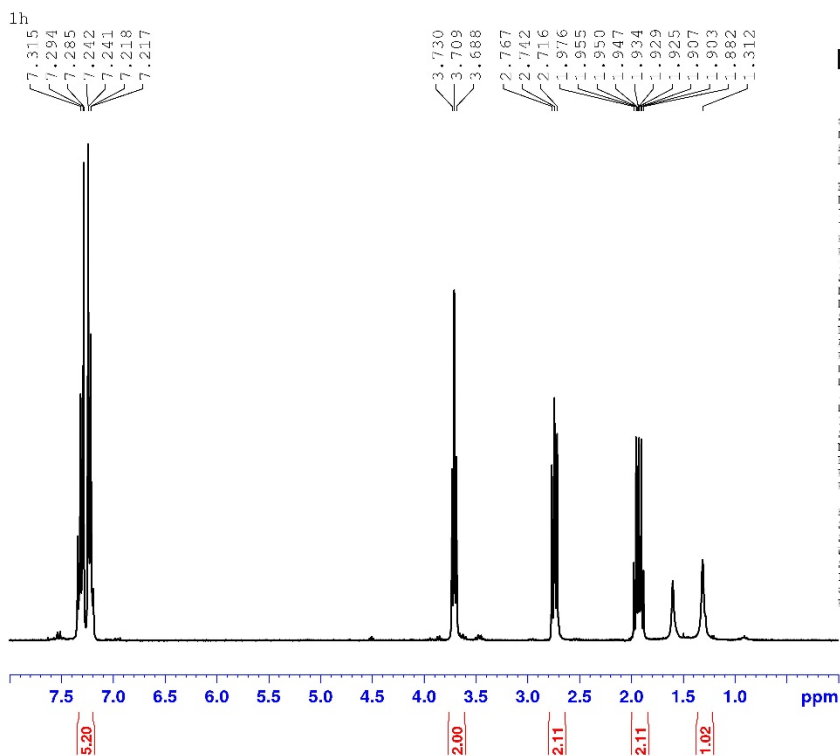
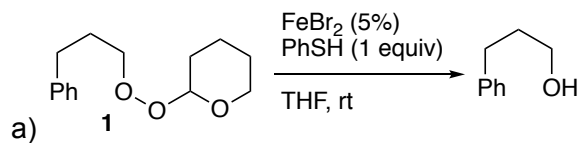
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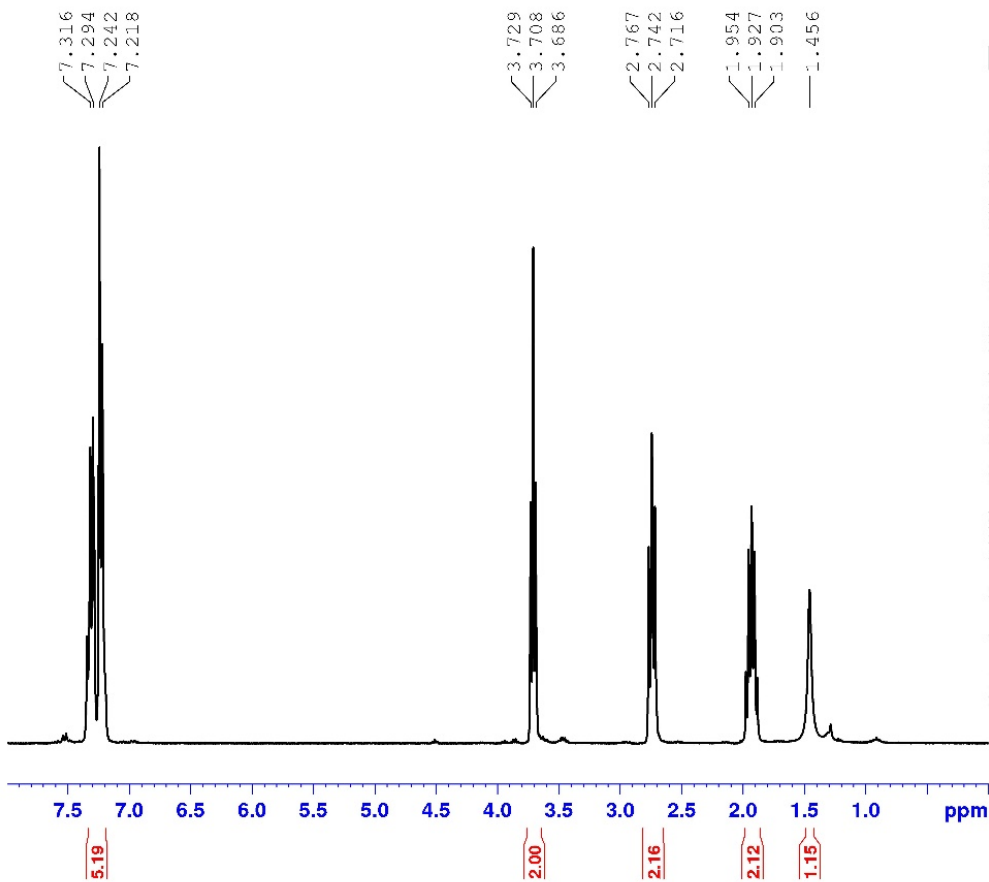
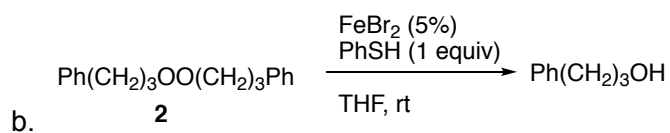
**Figure S-5.** <sup>1</sup>H NMR spectra of purified reaction mixtures from reduction (5% FeBr<sub>2</sub>, 1.0 equiv PhSH) of peroxides: a) **1**; b. **2**; c. **3**; d. **4**.



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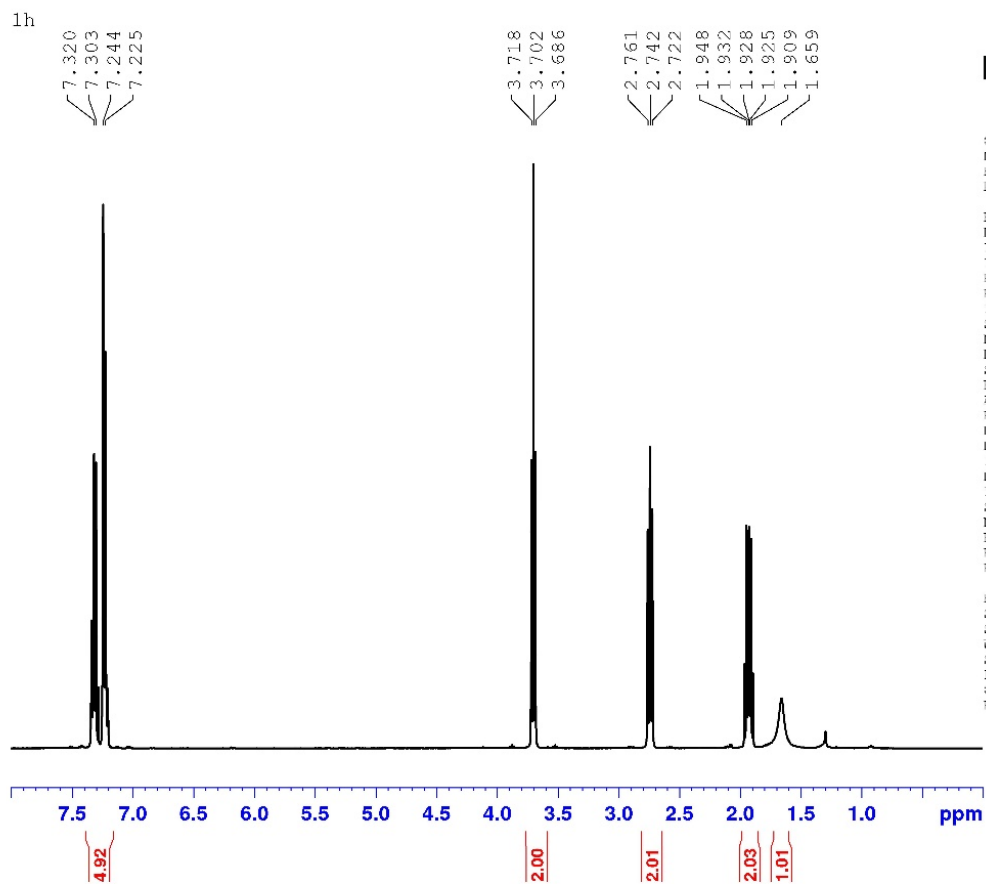
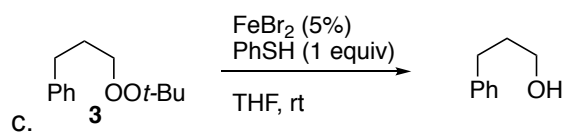


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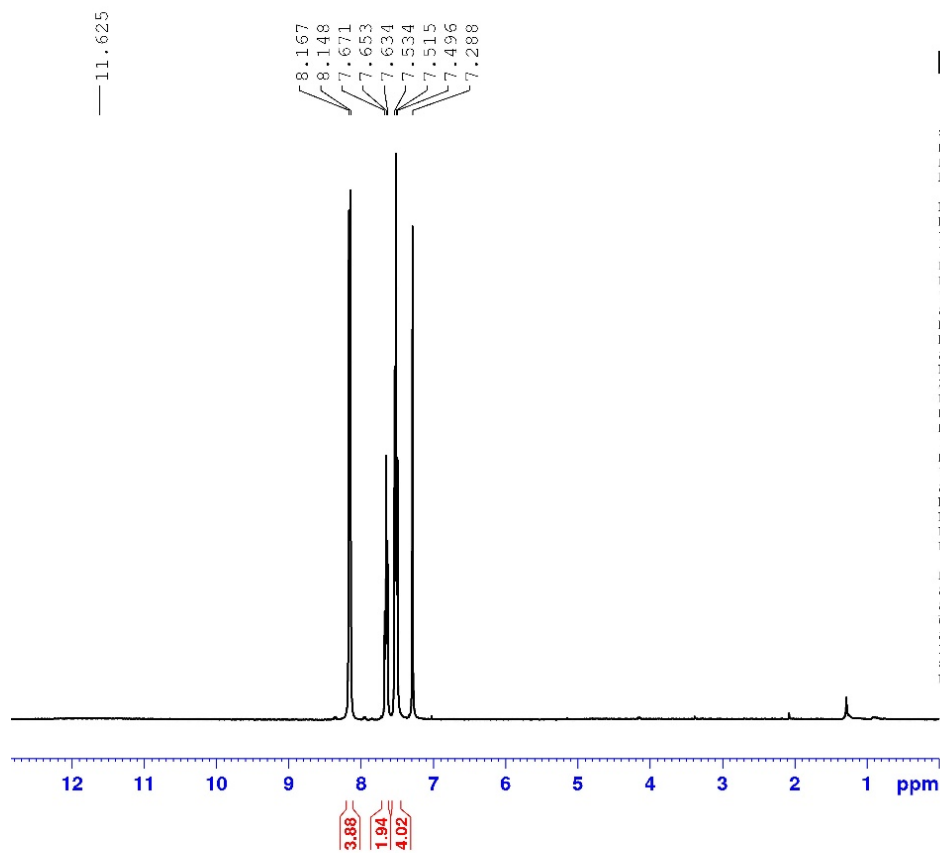
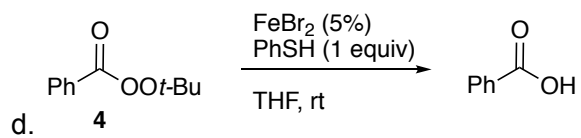




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