

Substituent effects of phenyl ring in different positions from α - carbon of TEMPO-type nitroxide

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Table of Contents

1. Cyclic voltammetry	S2
2. Molecular calculation	S3
3. NMR spectra	S5
4. HPLC chromatograms	S10

1. Cyclic voltammetry

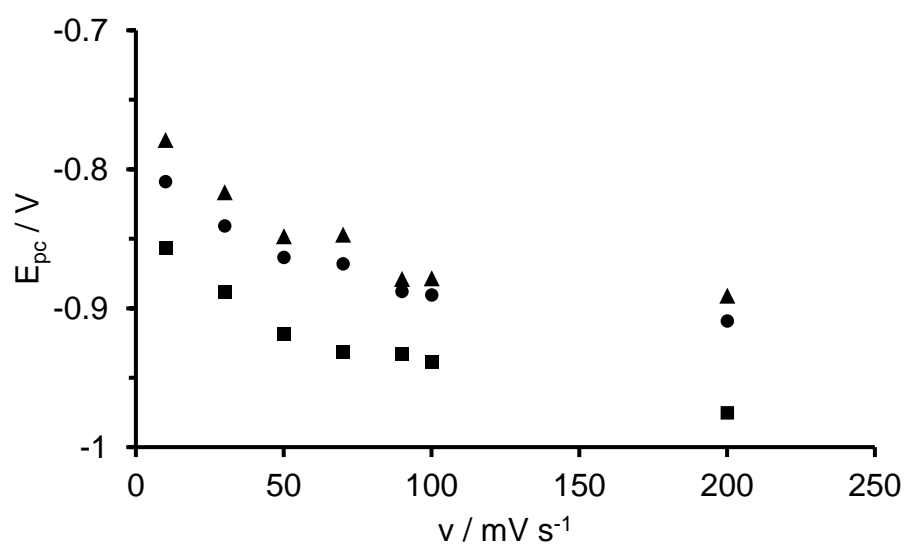


Figure S1. E_{pc} of nitroxide and hydroxylamine redox couple toward the scan rate. Square symbol: **1**; circle: **2**; triangle: **3**. The experimental conditions are described in Materials and Methods.

2. Molecular calculation

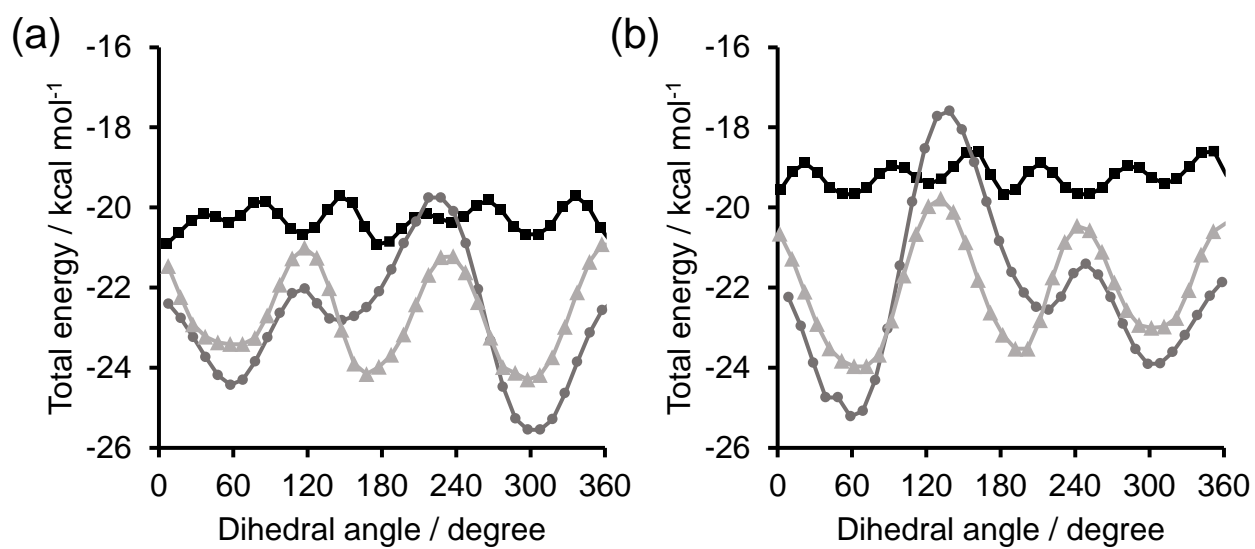


Figure S2. Energy diagram for the rotation of substituted group. (a) twisted boat conformation; (b) chair conformation. Black line and square symbol: **1**; dark gray line and circle symbol: **2**; light gray line and triangle symbol: **3**.

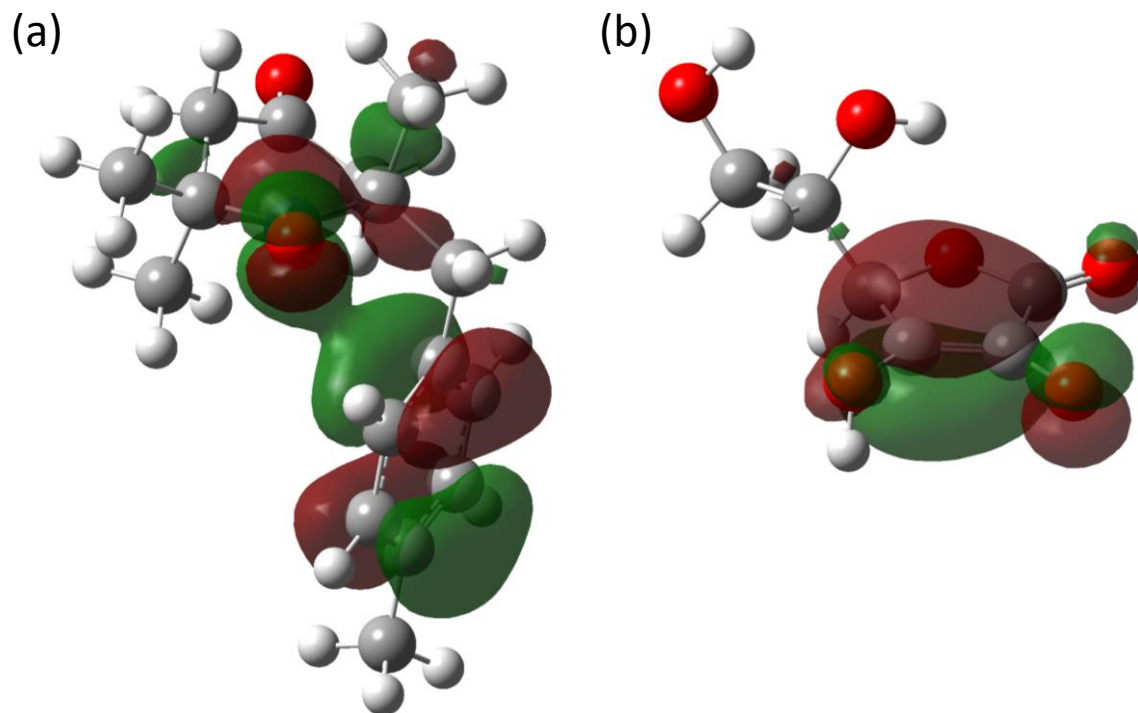


Figure S3. Molecular orbital contours. (a) SOMO of **2**; (b) HOMO of ascorbate anion.

3. NMR spectra

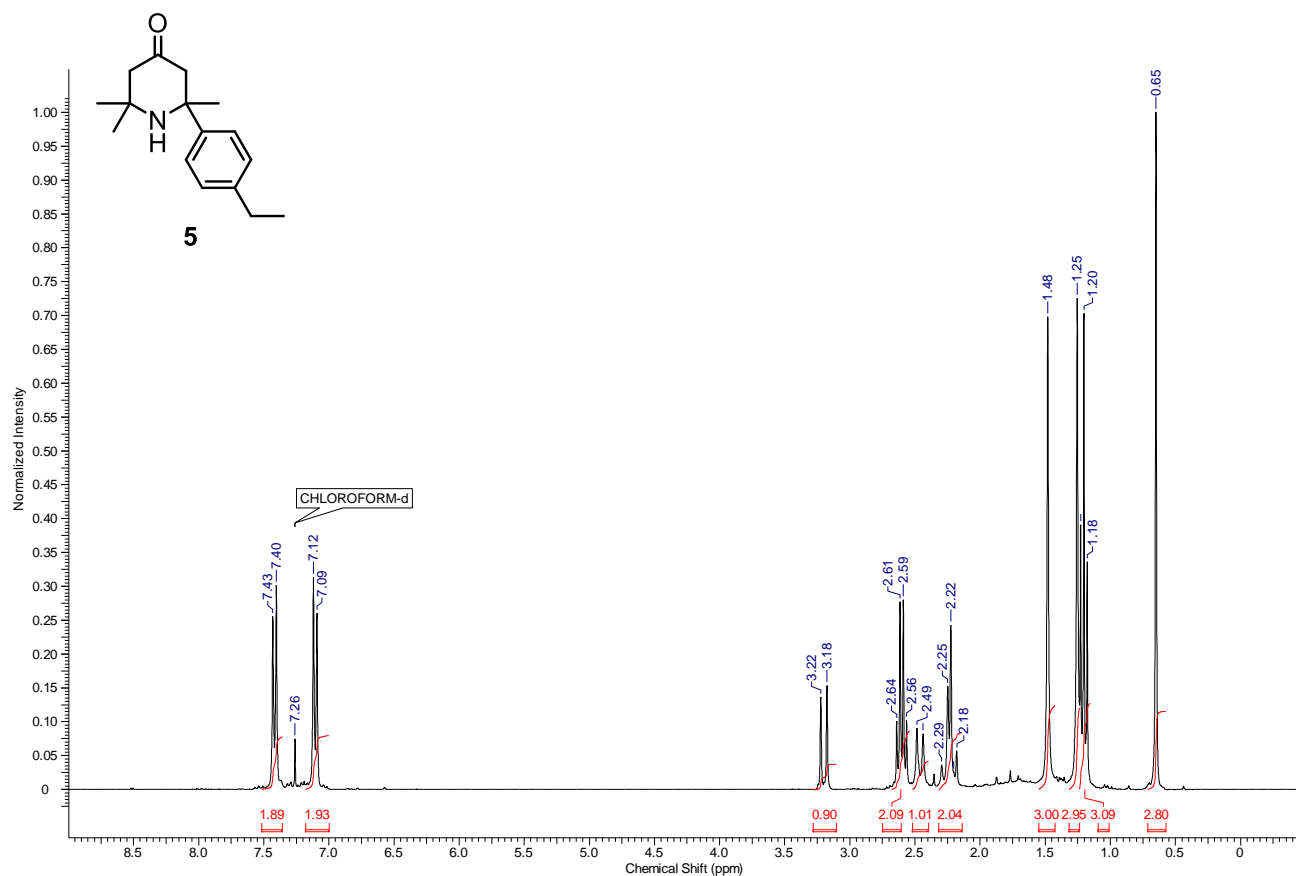


Figure S4. ¹H-NMR spectrum of 5.

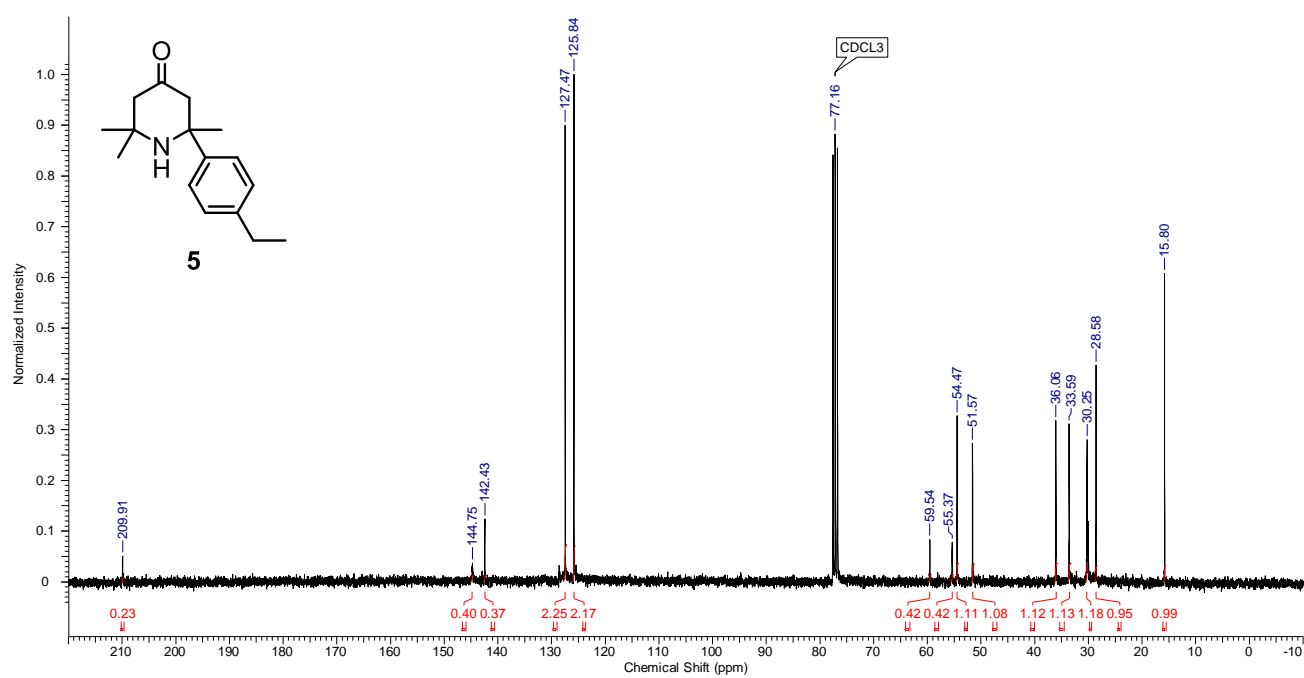


Figure S5. ¹³C-NMR spectrum of 5.

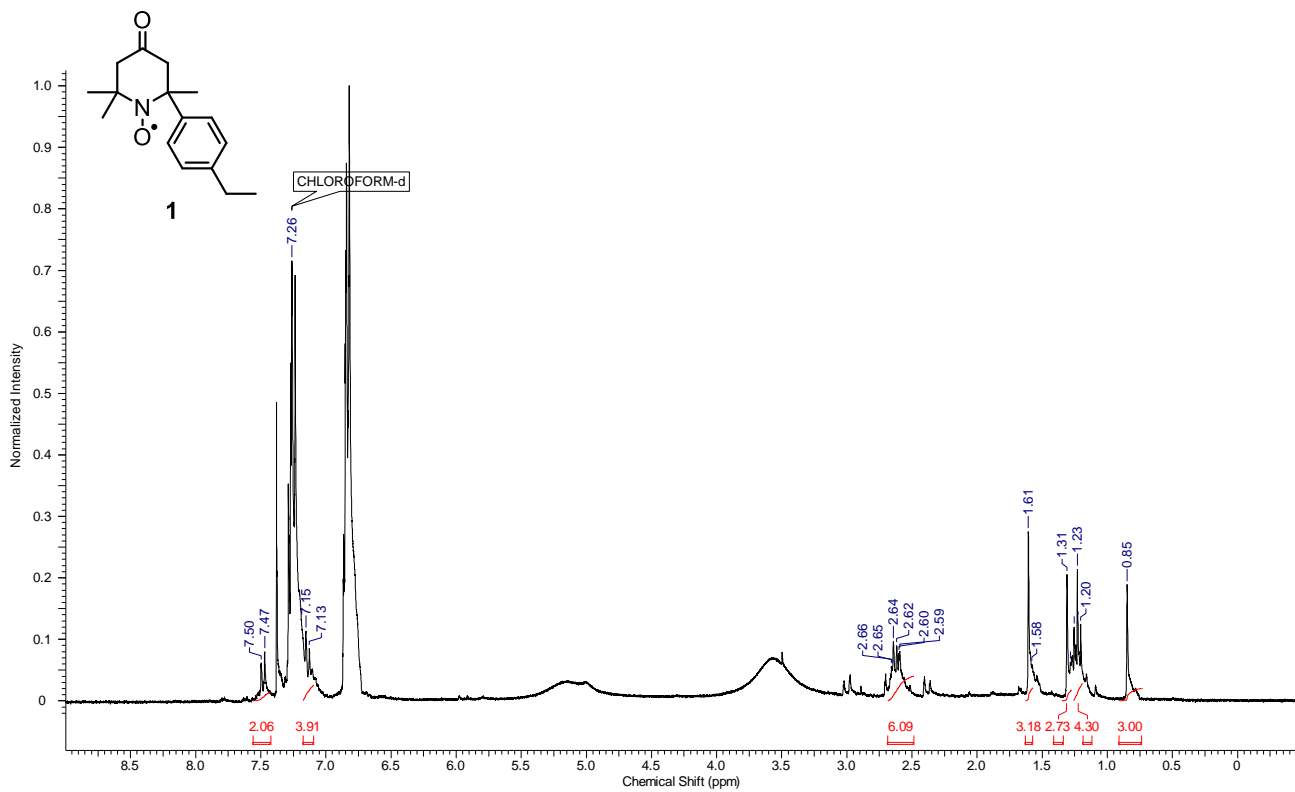


Figure S6. $^1\text{H-NMR}$ spectrum of **1** added with phenylhydrazine.

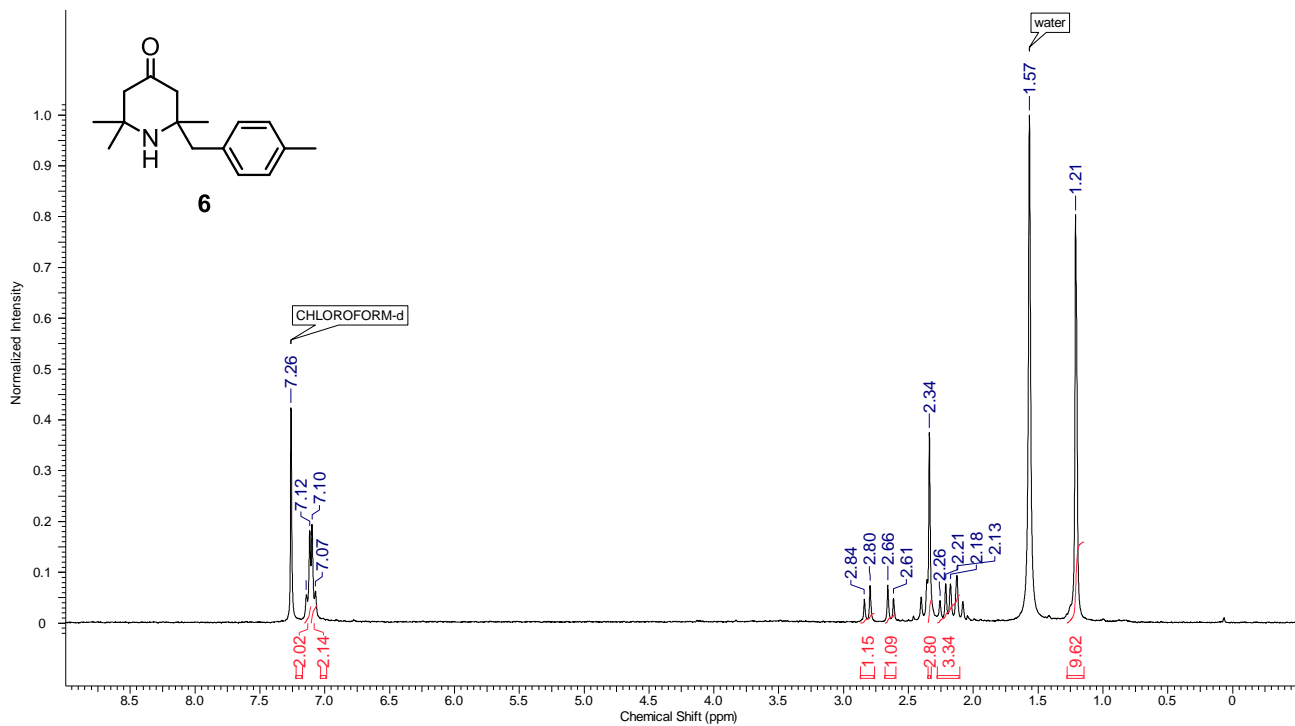


Figure S7. $^1\text{H-NMR}$ spectrum of **6**.

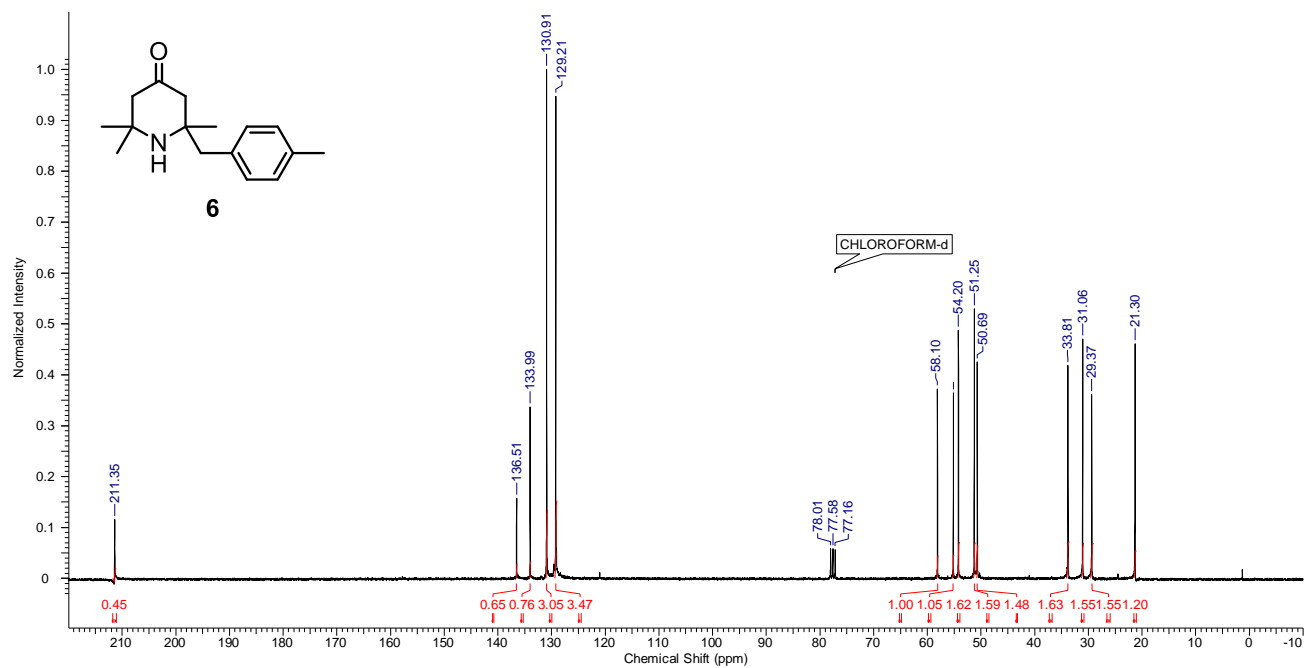


Figure S8. ^{13}C -NMR spectrum of **6**.

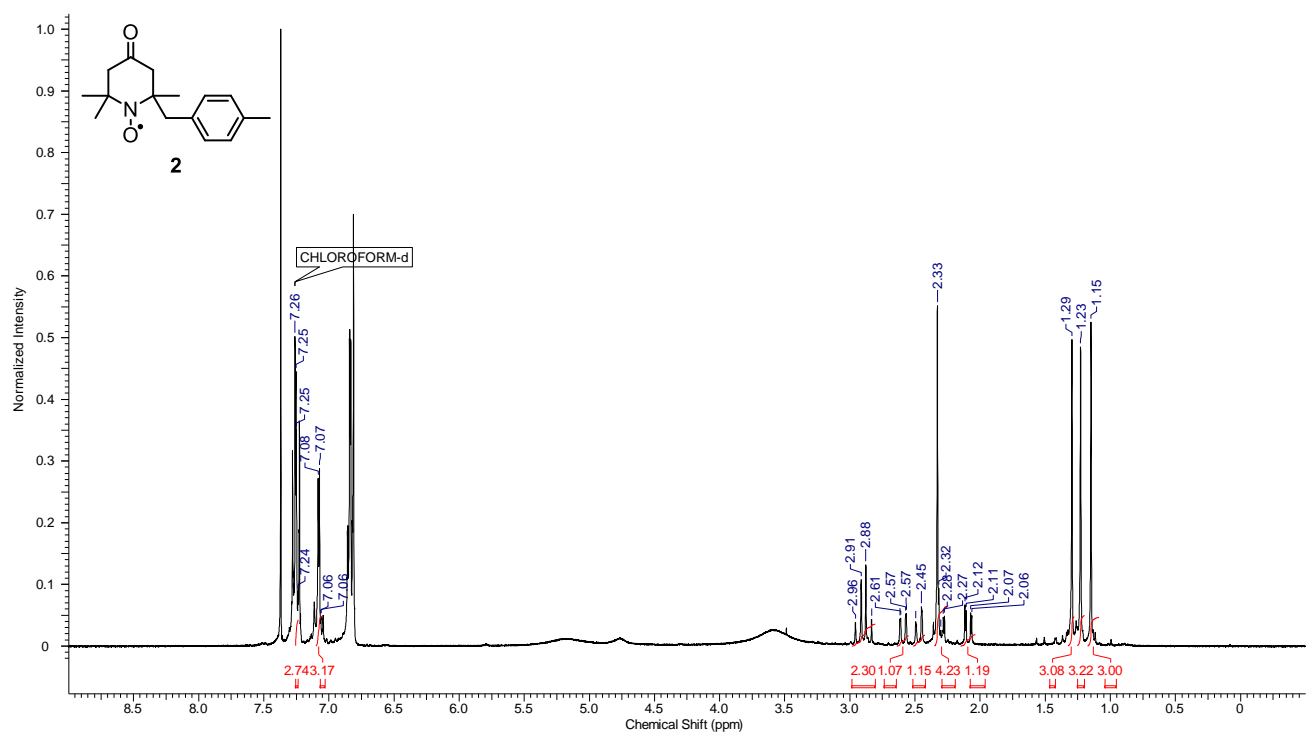


Figure S9. ^1H -NMR spectrum of **2** added with phenylhydrazine.

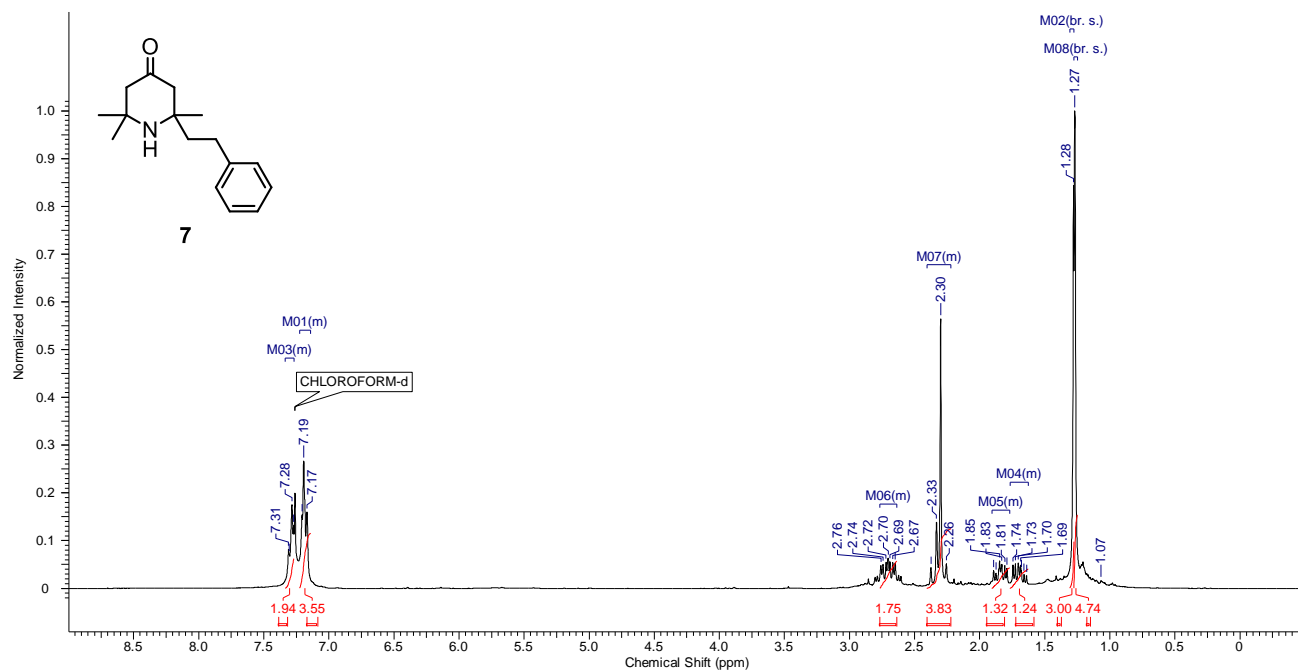


Figure S10. ¹H-NMR spectrum of 7.

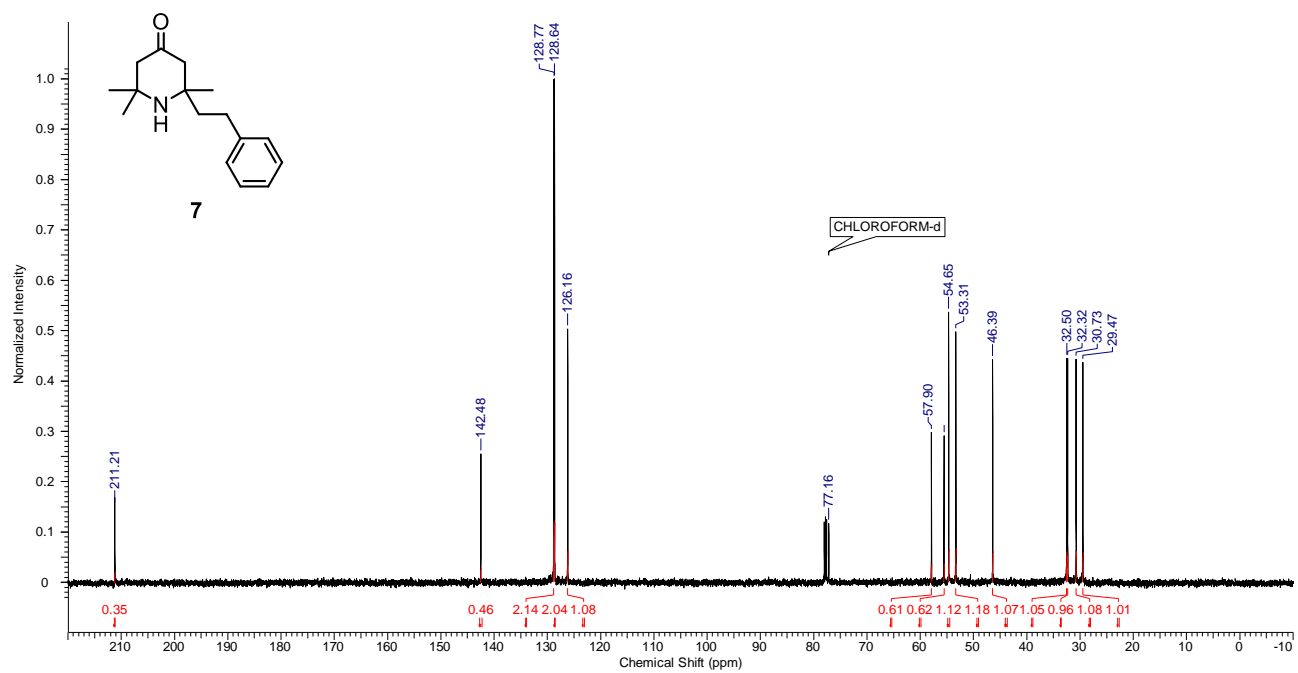


Figure S11. ¹³C-NMR spectrum of 7.

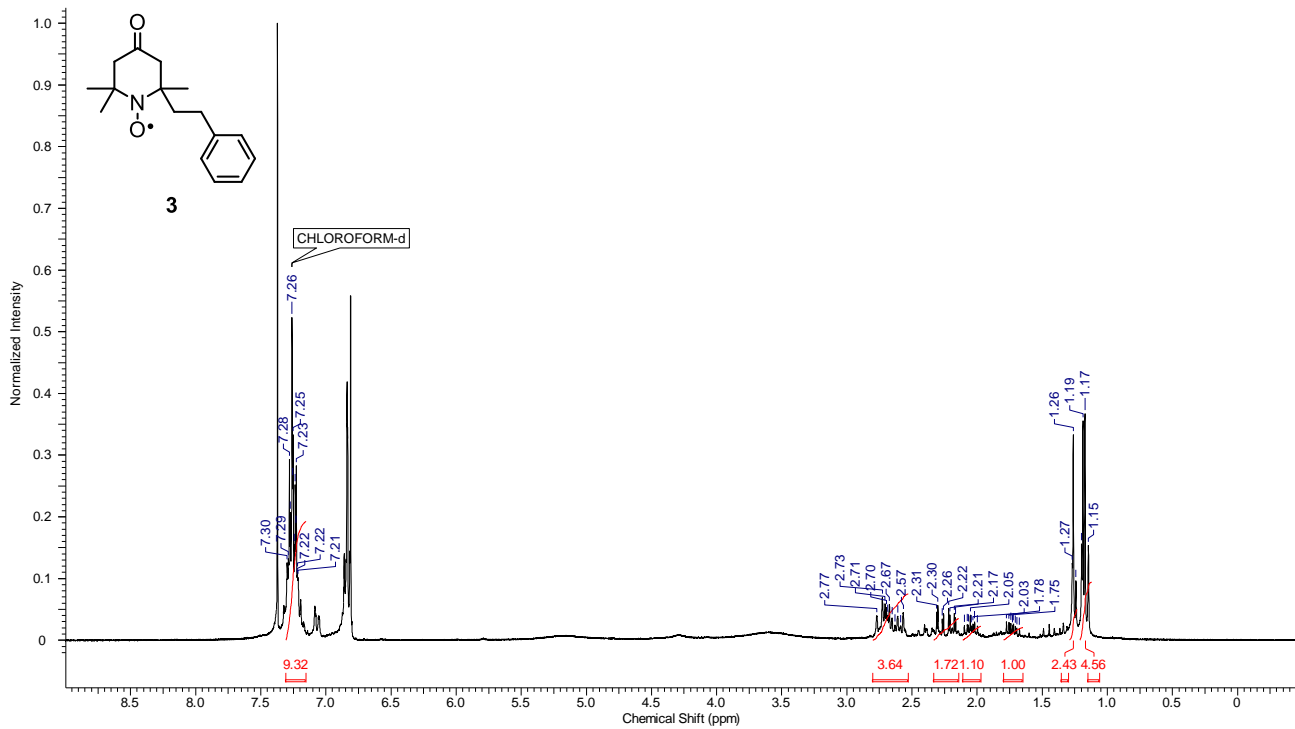


Figure S12. ¹H-NMR spectrum of **3** added with phenylhydrazine.

4. HPLC chromatograms

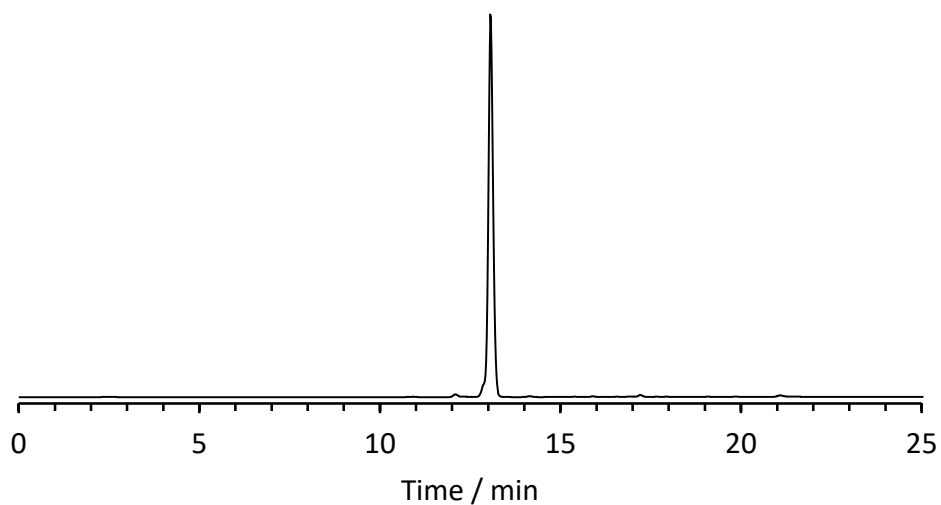


Figure S13. HPLC chromatogram of **1**. Measured conditions were as follows. Mobile phase: A: H₂O, B: MeCN; 50% B (t = 0-5 min), 100% B (t = 15 to 25 min); column: COSMOSIL 5C₁₈-AR-II, 4.6 mm I.D. x 250 mm; flow rate: 1 mL/min; detection: UV 254 nm.

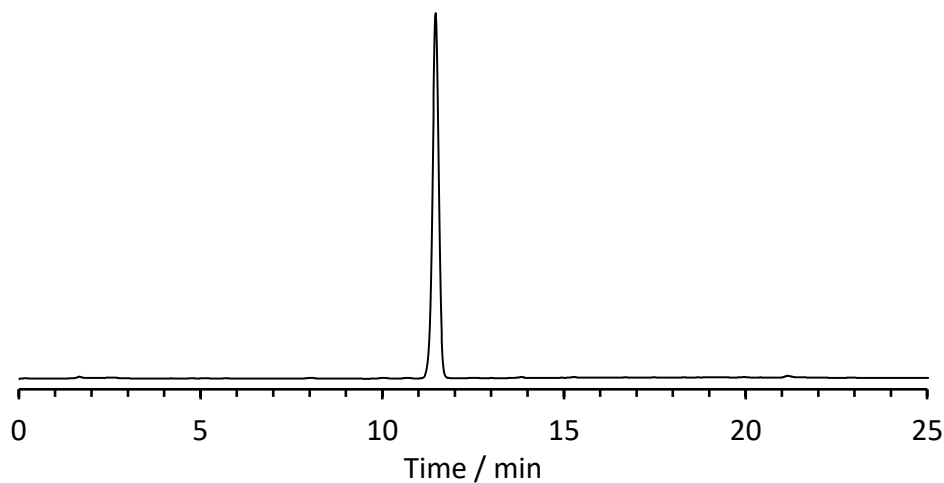


Figure S14. HPLC chromatogram of **2**. Measured conditions were as follows. Mobile phase: A: H₂O, B: MeCN; 50% B (t = 0-5 min), 100% B (t = 15 to 25 min); column: COSMOSIL 5C₁₈-AR-II, 4.6 mm I.D. x 250 mm; flow rate: 1 mL/min; detection: UV 254 nm.

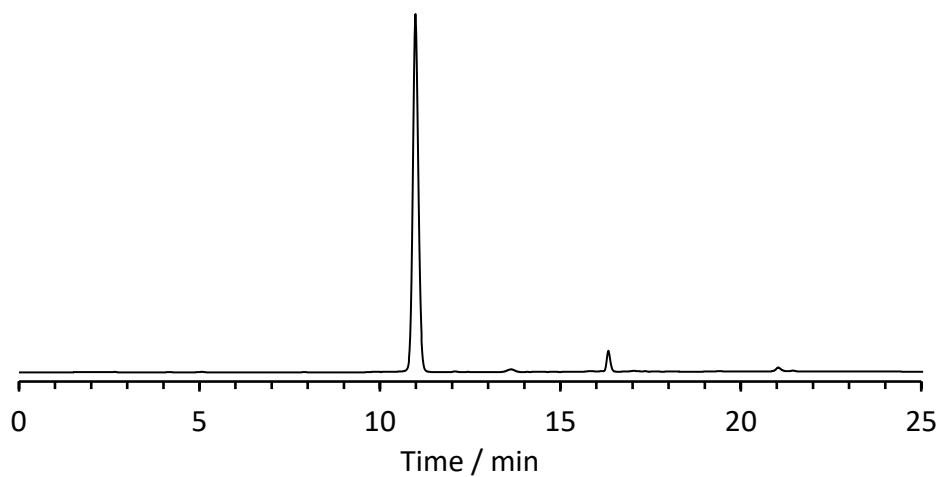


Figure S15. HPLC chromatogram of **3**. Measured conditions were as follows. Mobile phase: A: H₂O, B: MeCN; 50% B (t = 0-5 min), 100% B (t = 15 to 25 min); column: COSMOSIL 5C₁₈-AR-II, 4.6 mm I.D. x 250 mm; flow rate: 1 mL/min; detection: UV 254 nm.