Supporting Information

URUSHIOL DETECTION USING A PROFLUORESCENT NITROXIDE

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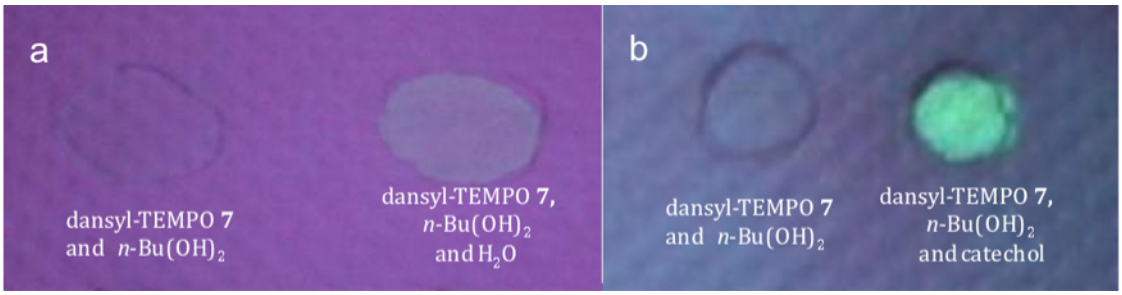
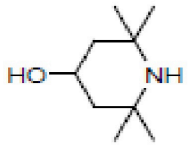
General Experimental Methods

Tetrahydrofuran (THF), toluene and dichloromethane (CH_2Cl_2) were purified from a PureSolv solvent system. Water was deionized. All other reagents were used as received. 4-Oxo-2,2,6,6-tetramethyl-1-piperidine was purchased from Tokyo Chemical Industry Company. This starting material was reduced with sodium borohydride to form 2,2,6,6-tetramethylpiperidin-4-ol following the procedure of Rozantsev *et al*,[1] and then oxidized to form TEMPOL following Rozanstev's procedure.[1] Mesylation following the procedure of Misharin[2] formed TEMPOL-mesylate. *p*-Anisaldehyde (PAA) TLC stain was made from a mixture of ethanol (37.5 mL), concentrated sulfuric acid (2.08 mL), glacial acidic acid (0.427 mL) and *p*-anisaldehyde (2.5 mL). NMR spectra were collected at ambient temperature in $CDCl_3$. FTIR were recorded in deuterochloroform. Fluorescence measurements were performed using a Perkin-Elmer LS50-B luminescence spectrometer controlled by FL WinLab™ (version 2.0) software using standard 10 x 10 mm quartz cuvets. Acetone was used as the solvent in all experiments unless otherwise stated.

Spot Tests of dansyl-TEMPO 7 and *B-n*-butylboronic acid on a paper towel: with water, and with catechol



a) A drop of an acetone solution containing both dansyl-TEMPO **7** (3 μmol) and *B-n*-butylboronic acid (1.5 μmol) on a paper towel as a control (left), and the same solution spotted over a drop of water (right); and b) spot of the same acetone solution of dansyl-TEMPO **7** (3 mmol) and n-butylboronic acid (1.5 μmol) as a control (left), and co-spotted with a 3 μmol solution of catechol (right), as seen under illumination by a long-wave 365 nm UV TLC lamp. Spots were circled with a pencil for clarity.



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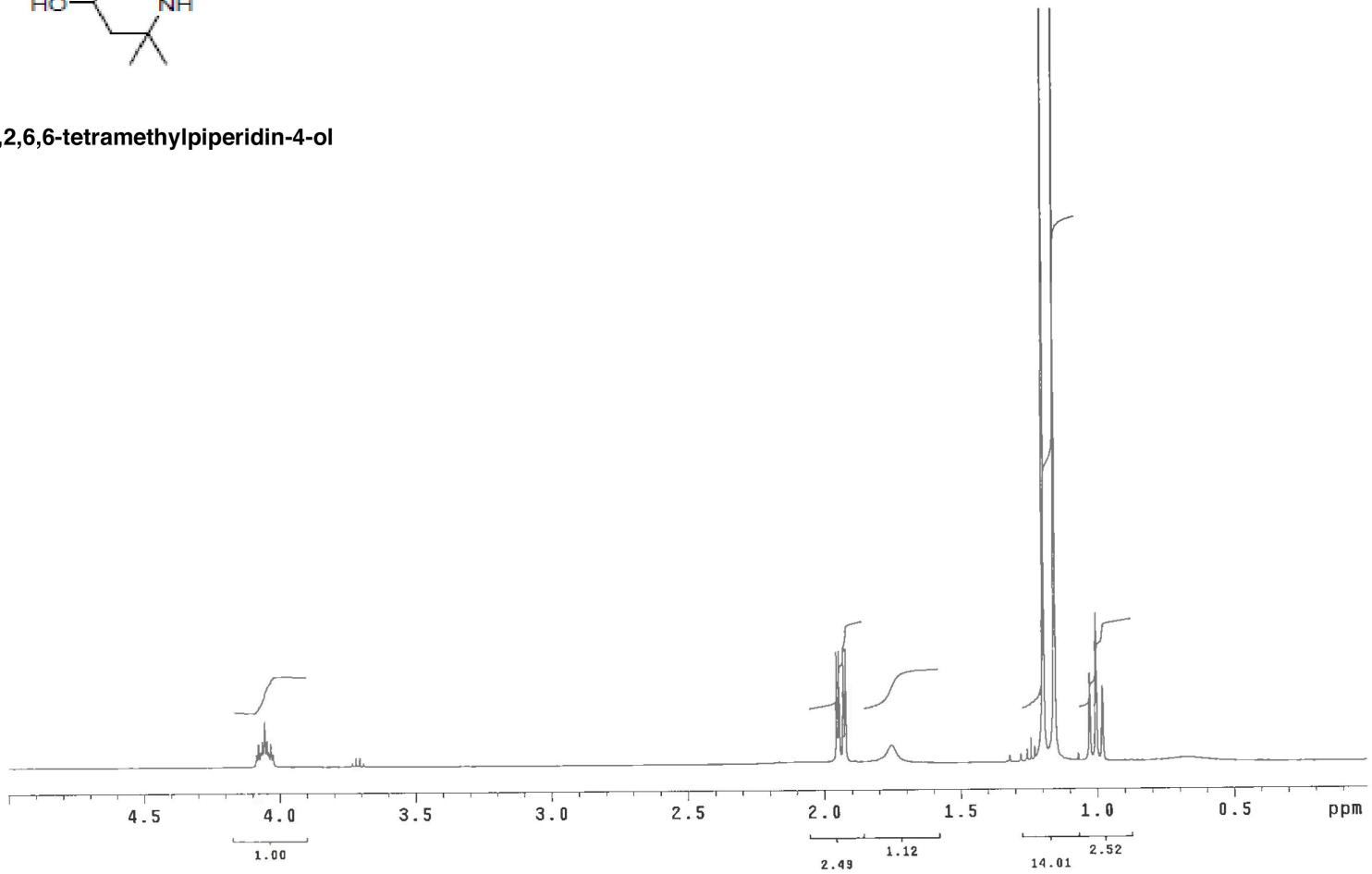
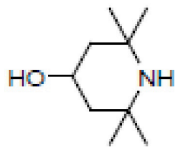
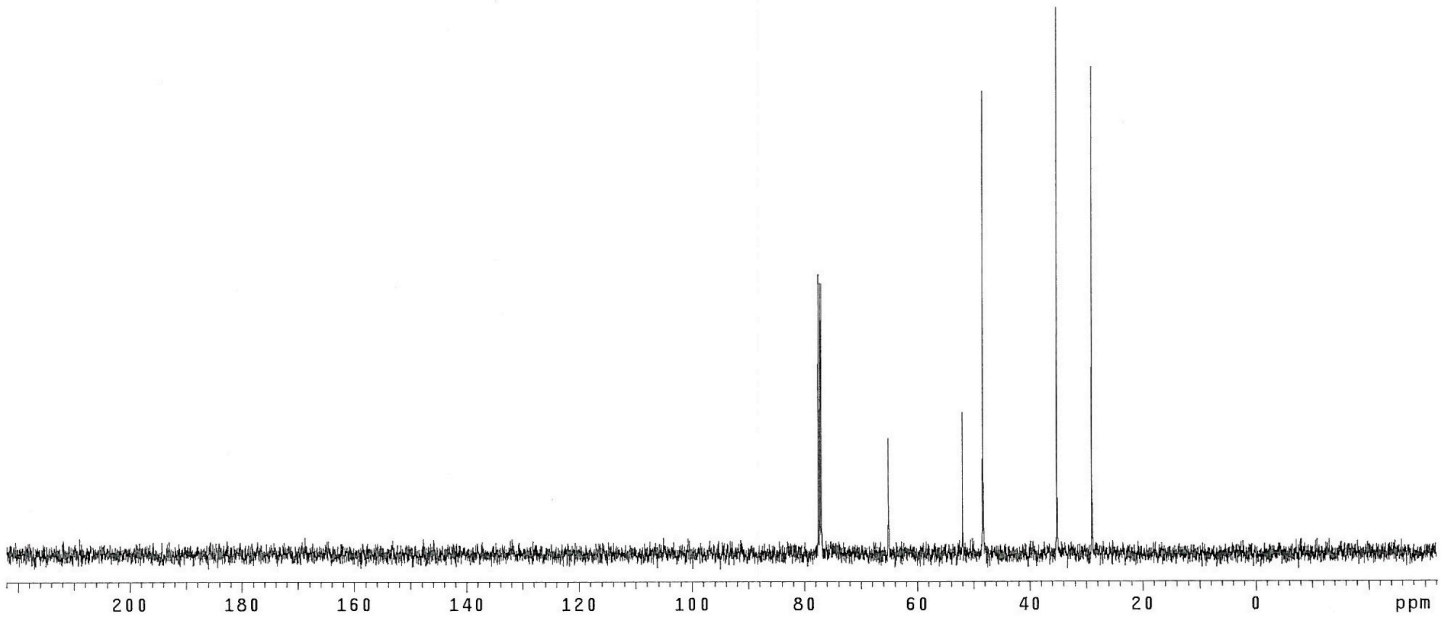
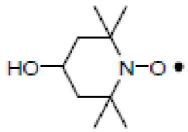




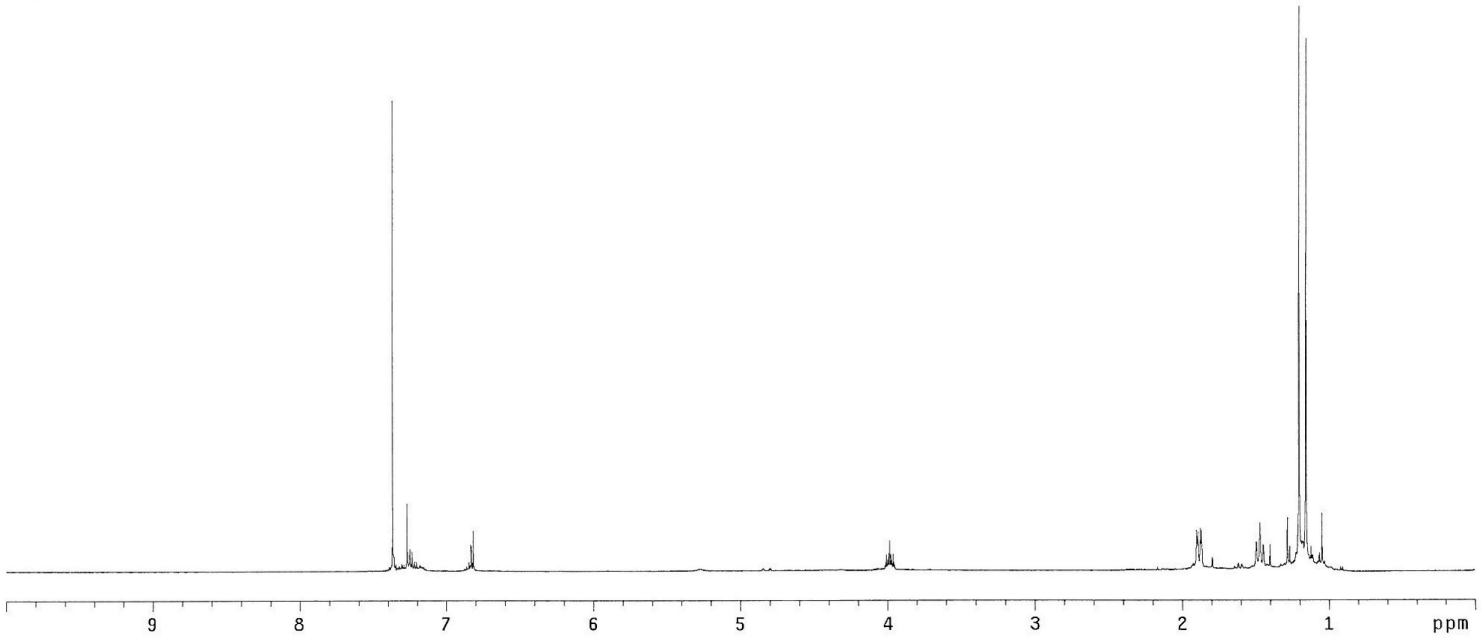
2,2,6,6-tetramethylpiperidin-4-ol

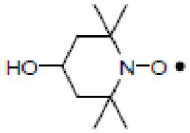




+ $PhNHNH_2$

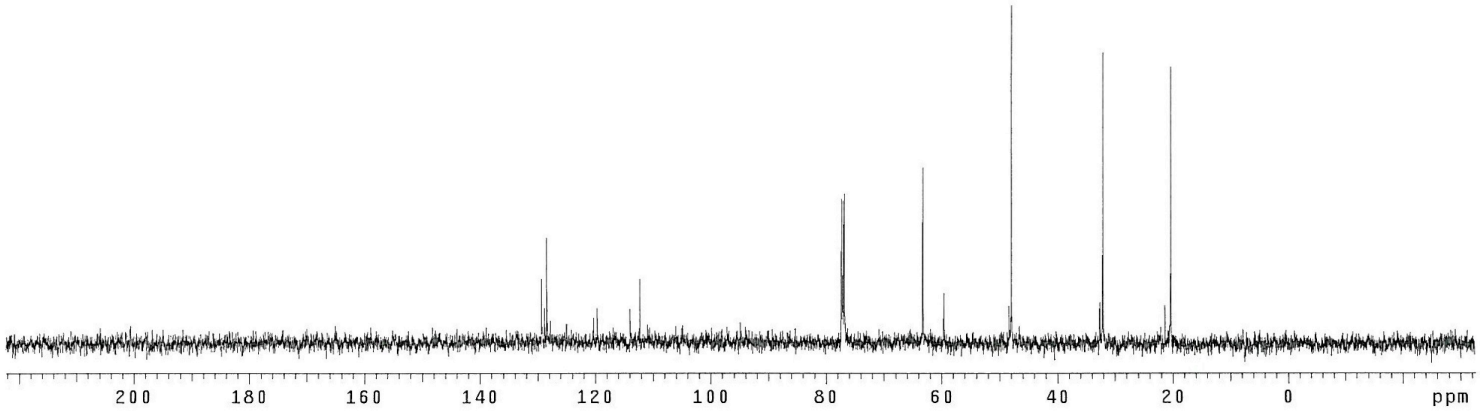
4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-1-oxyl free radical (TEMPOL) + $PhNHNH_2$

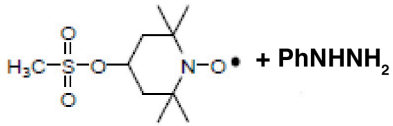




+ $PhNHNH_2$

4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-1-oxyl free radical (TEMPOL) + $PhNHNH_2$





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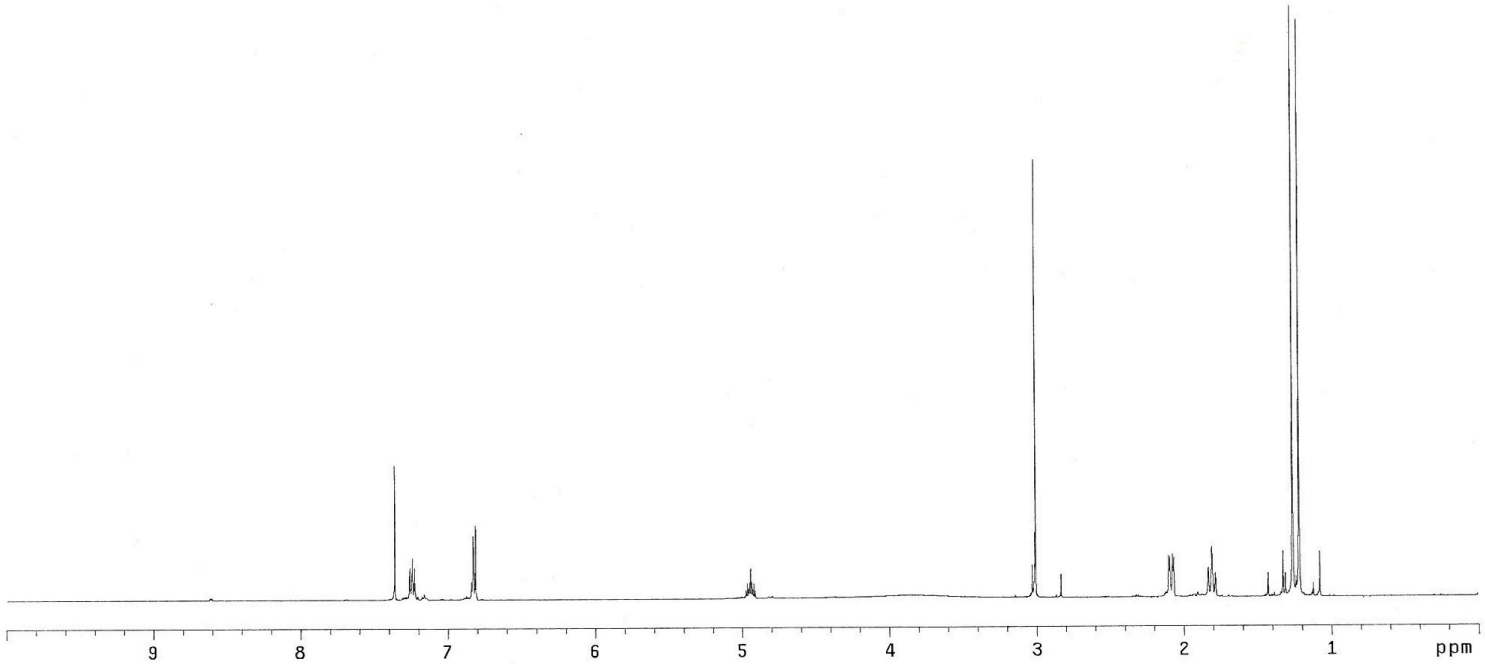

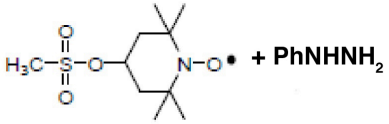

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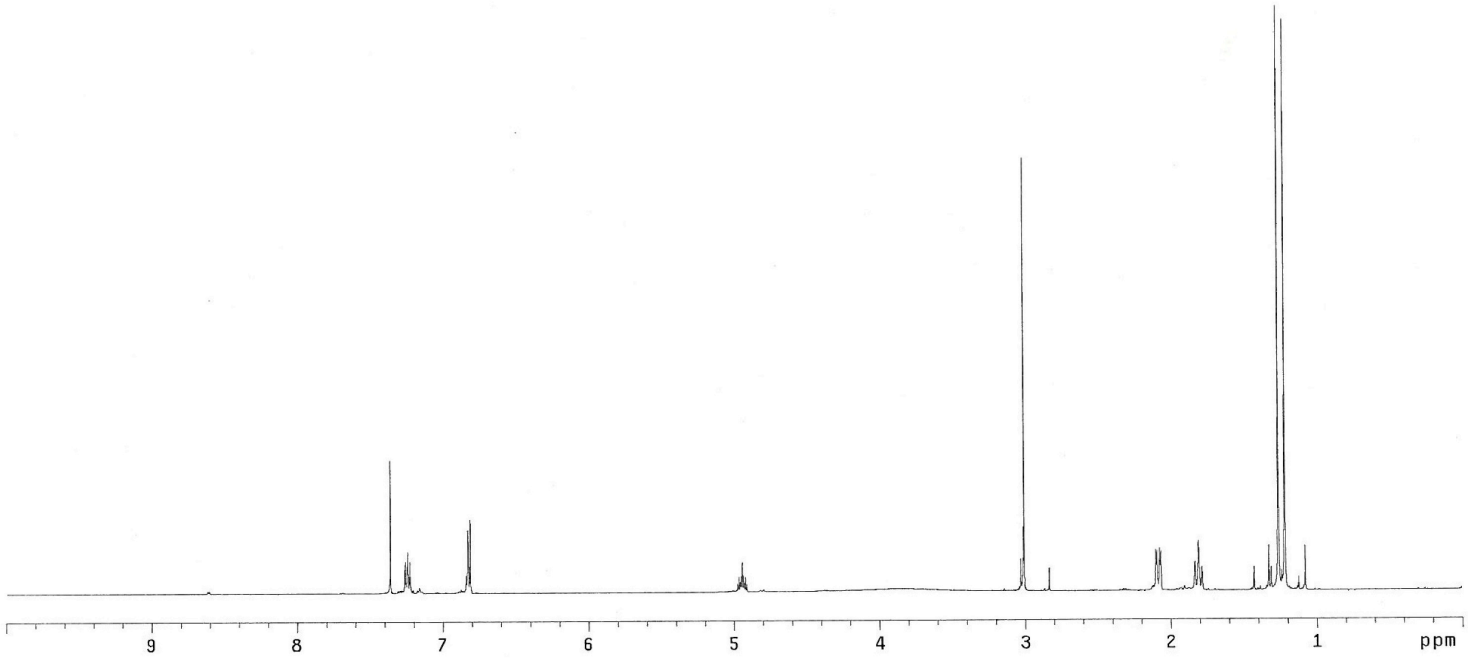

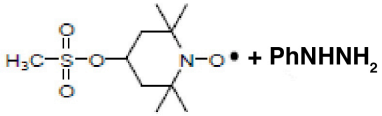

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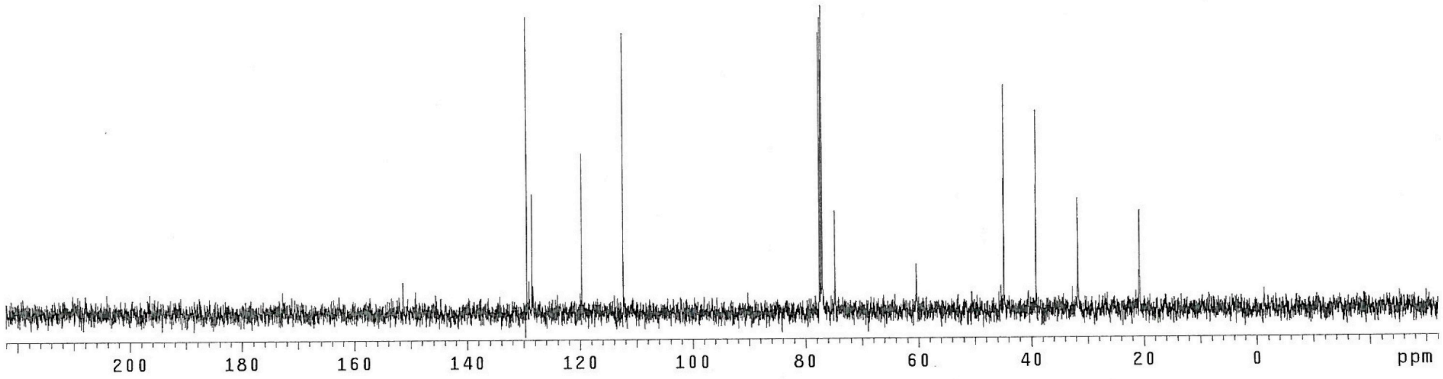
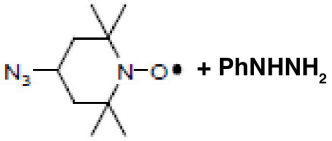
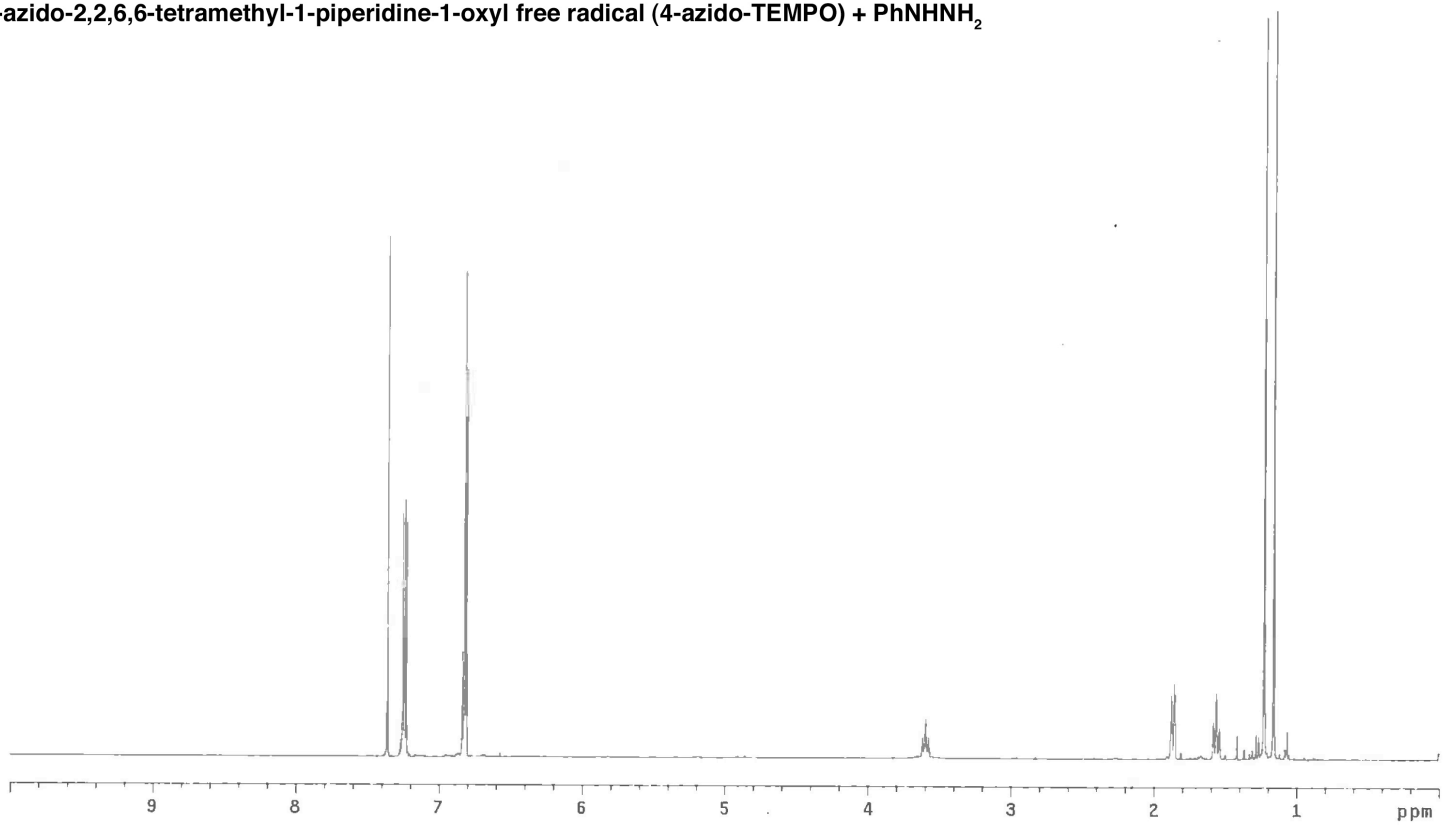
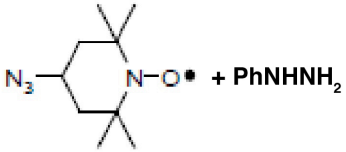




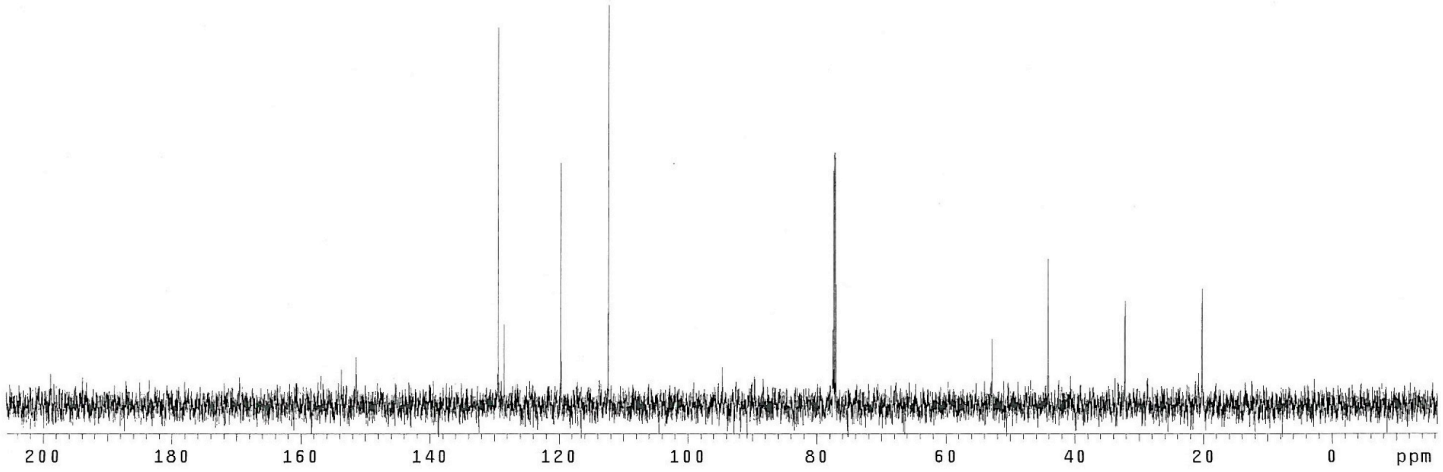
+ PhNHNH$_2$

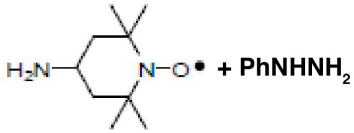
4-azido-2,2,6,6-tetramethyl-1-piperidine-1-oxyl free radical (4-azido-TEMPO) + PhNHNH$_2$





4-azido-2,2,6,6-tetramethyl-1-piperidine-1-oxyl free radical (4-azido-TEMPO) + $PhNHNH_2$





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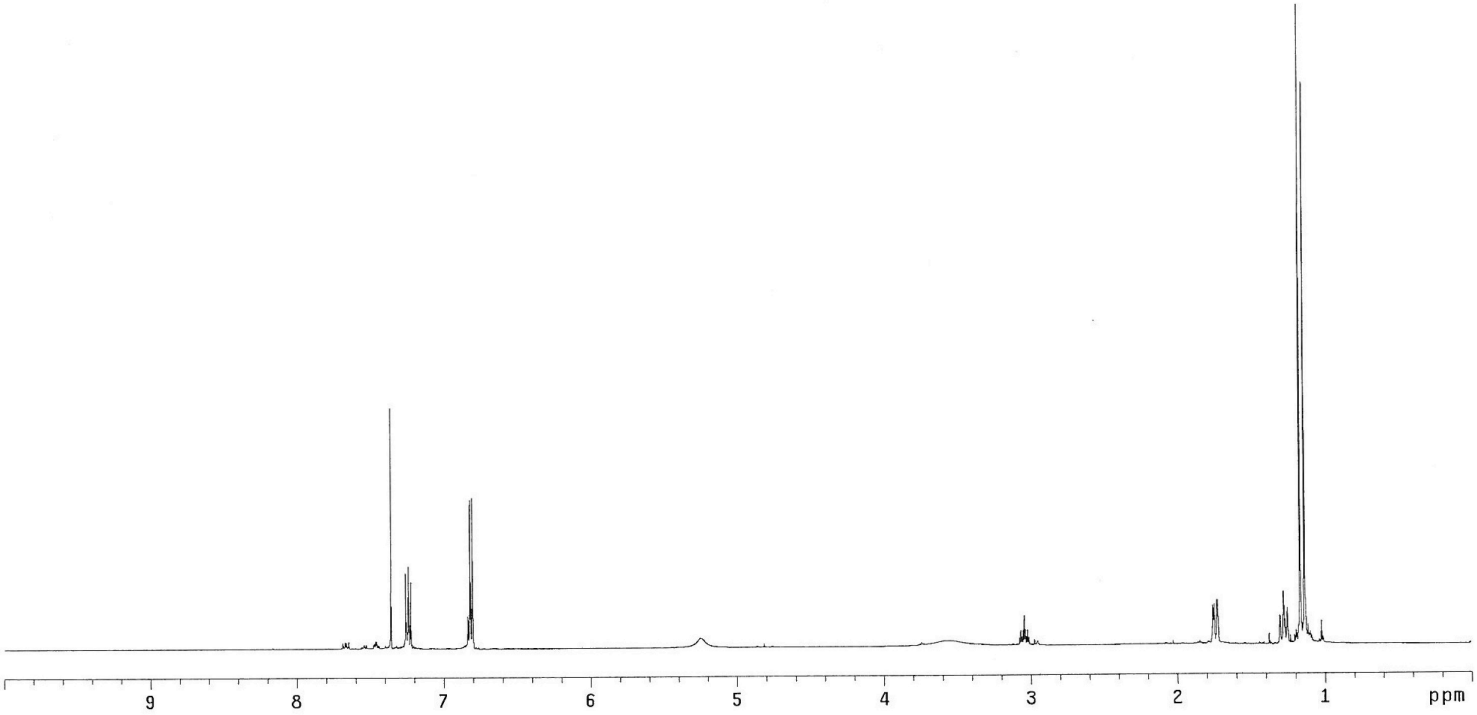
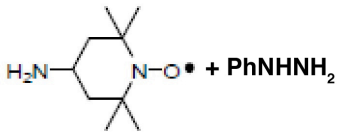
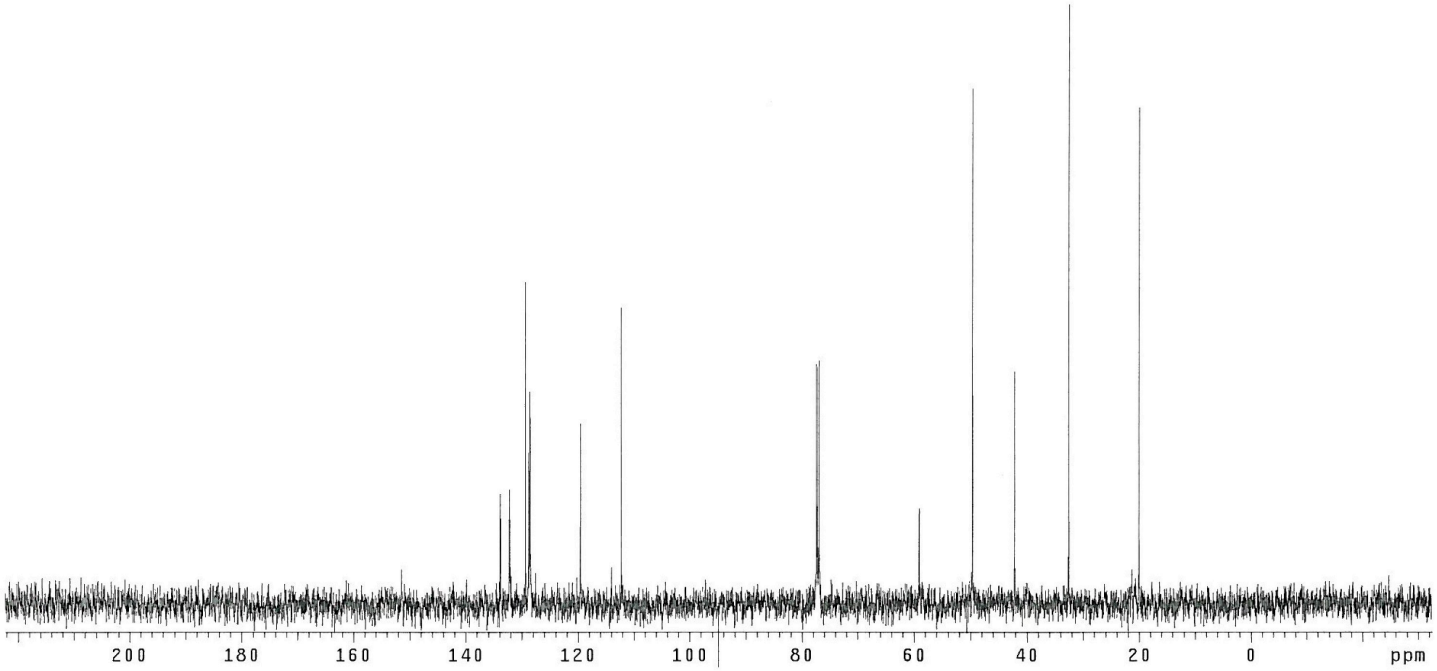
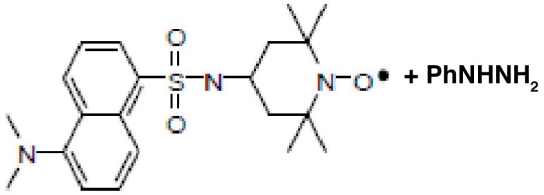


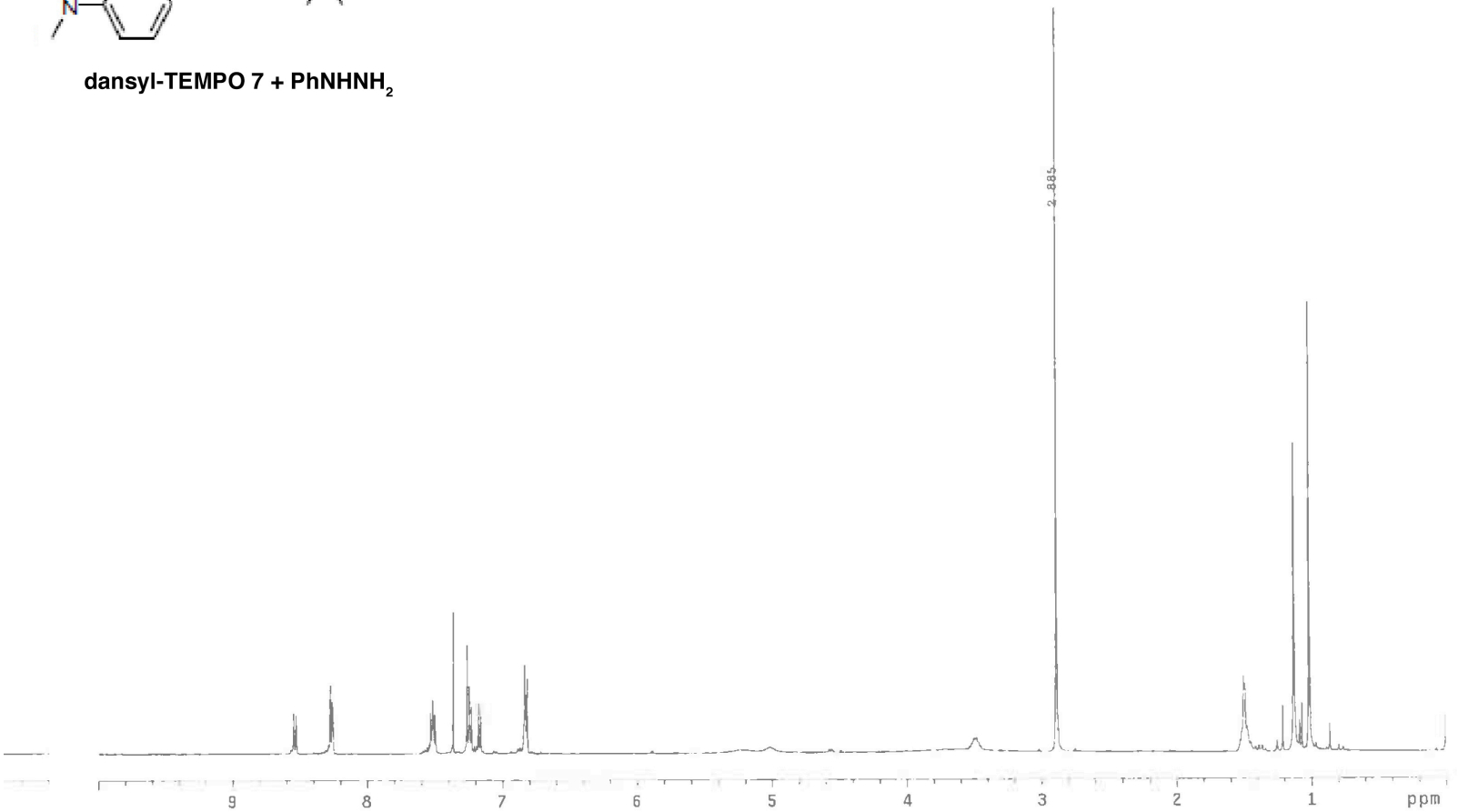


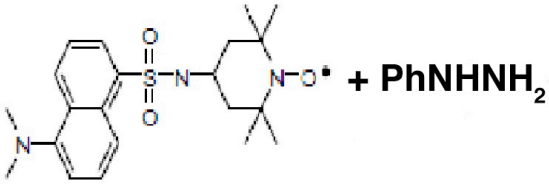
4-amino-2,2,6,6-tetramethyl-1-piperidine-1-oxyl free radical (4-amino-TEMPO) + $PhNHNH_2$





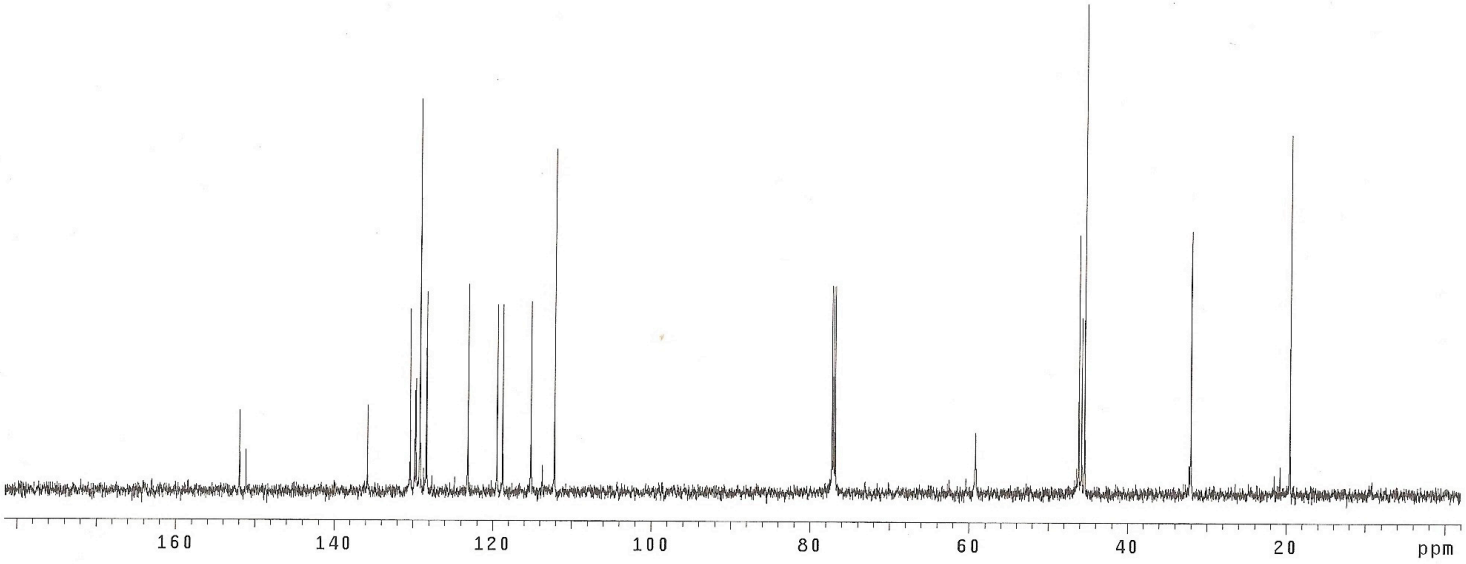
dansyl-TEMPO 7 + $PhNHNH_2$

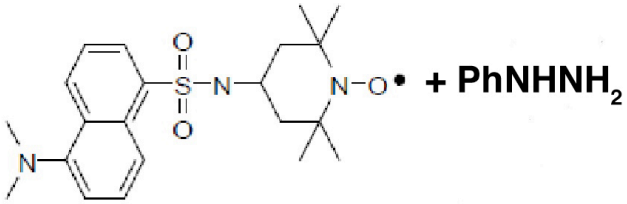




+ PhNHNH$_2$

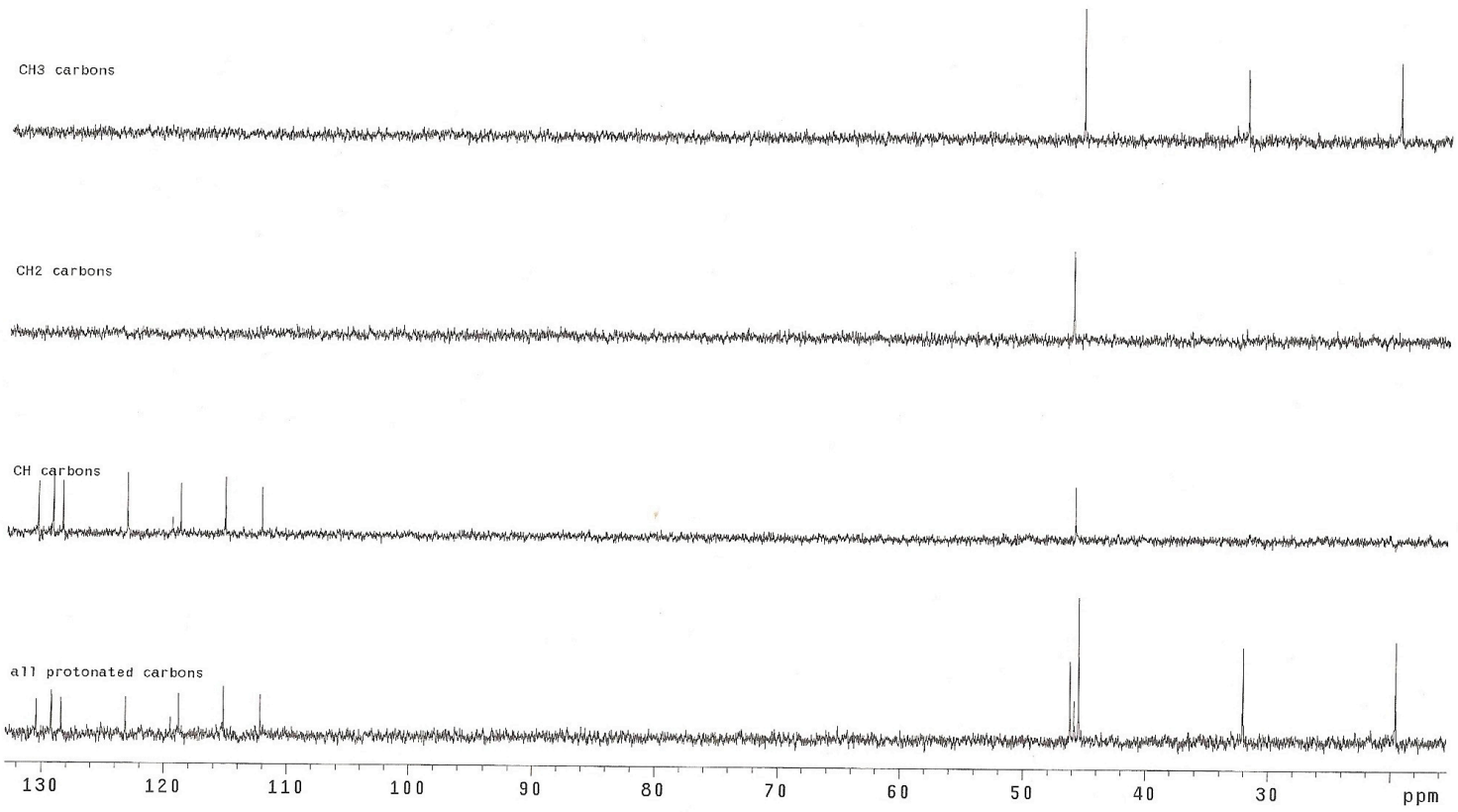
dansyl-TEMPO 7 + PhNHNH$_2$

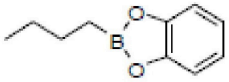




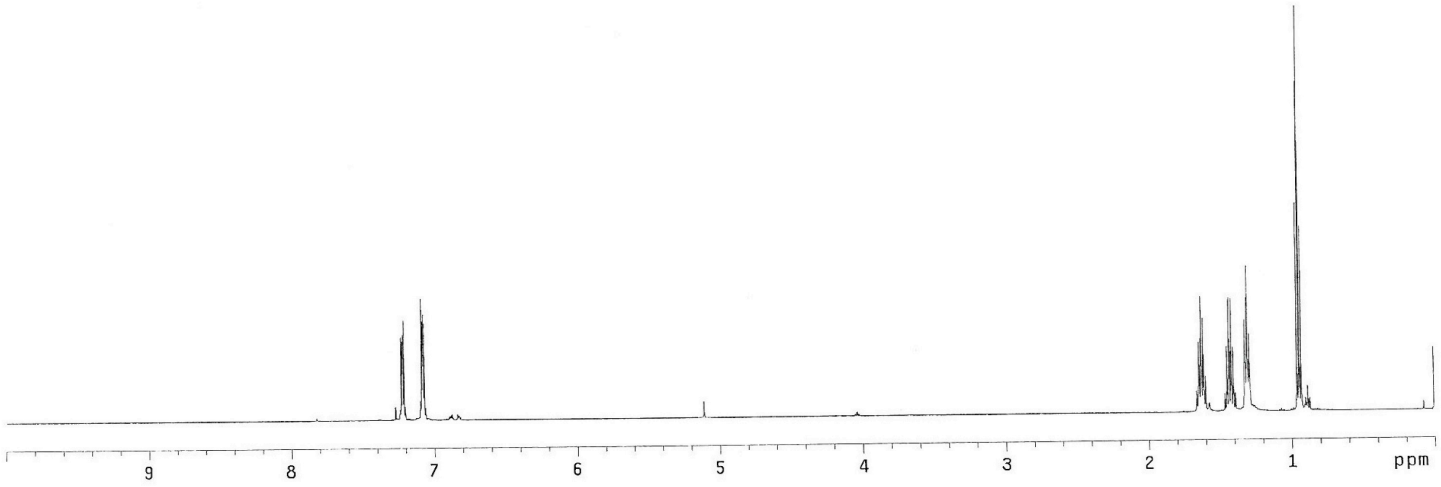
DEPT

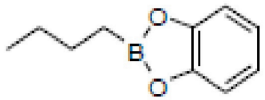
dansyl-TEMPO 7 + $PhNHNH_2$





***B-n*-butylcatecholboronate ester 1**





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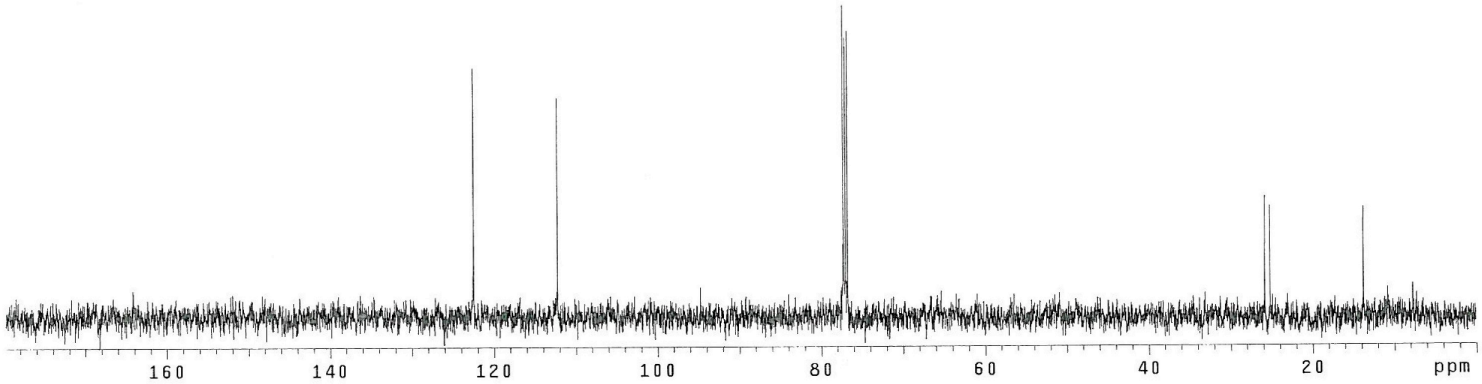
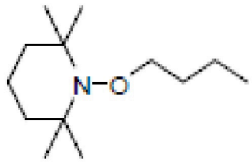
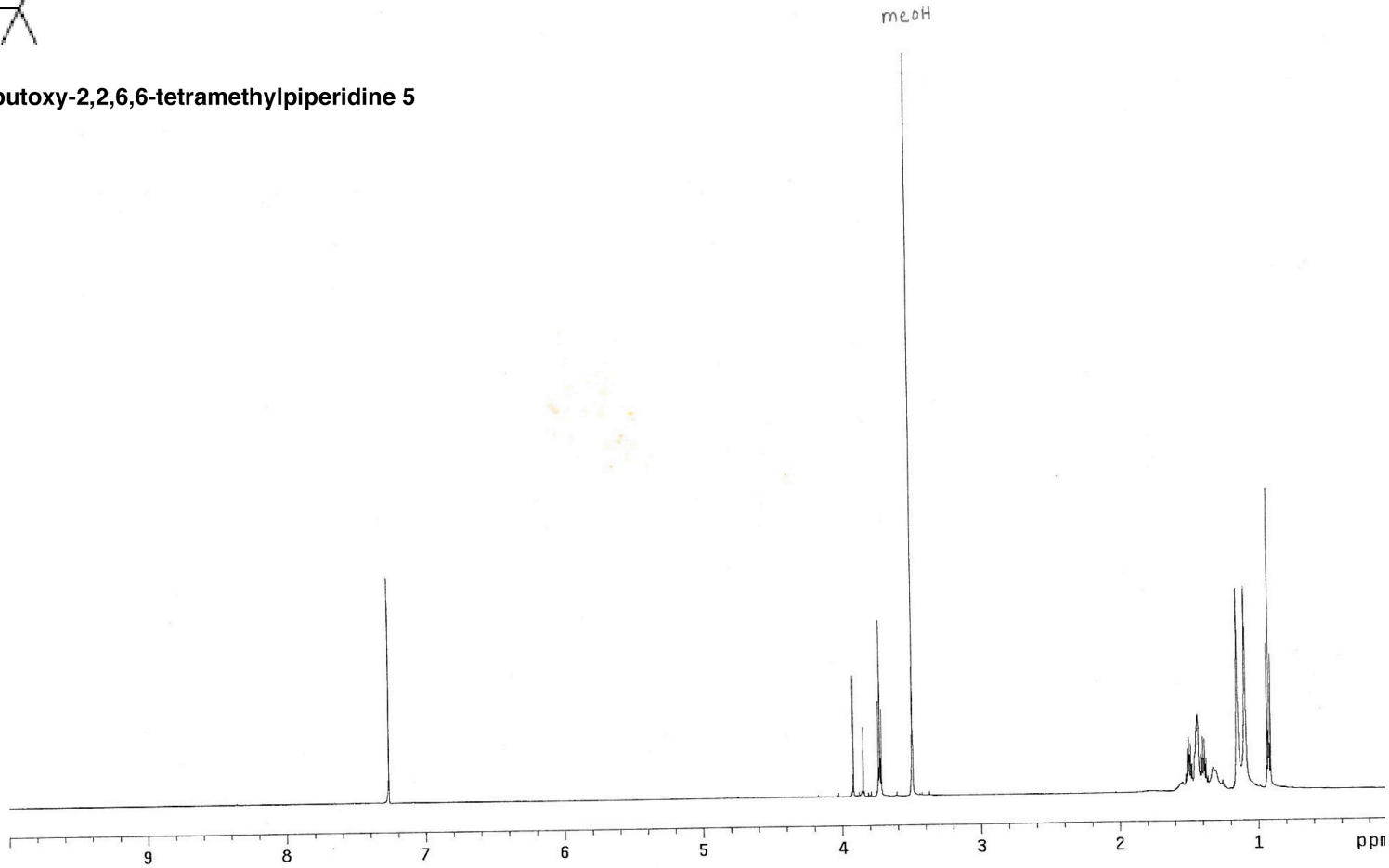
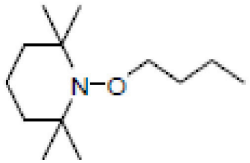




1-*n*-butoxy-2,2,6,6-tetramethylpiperidine 5





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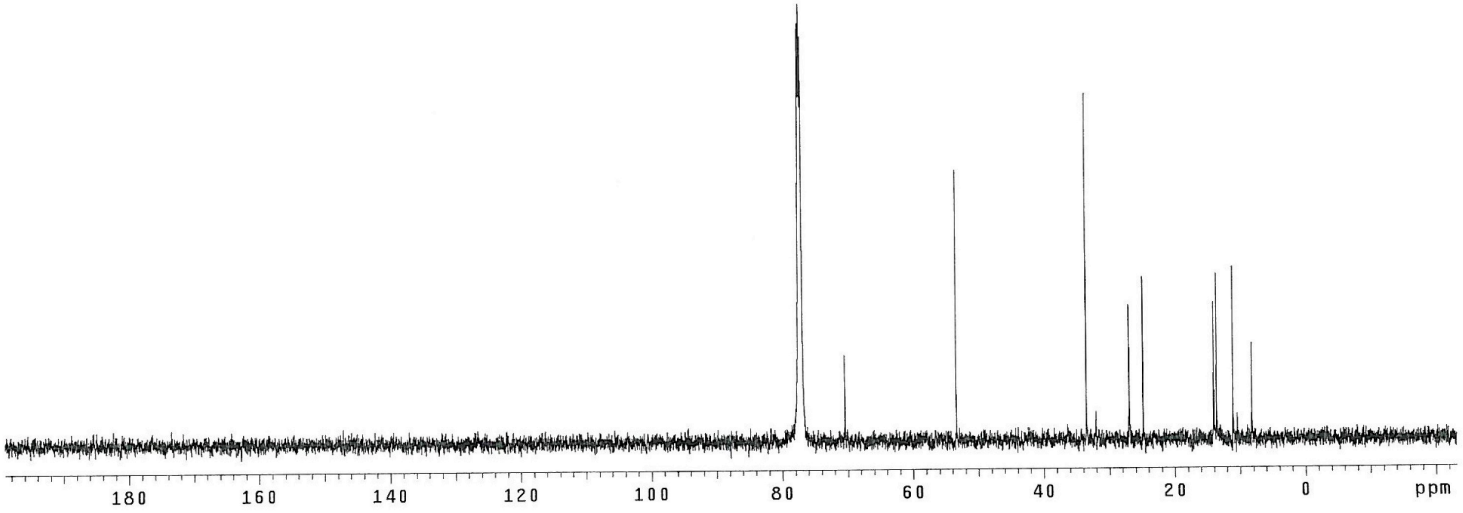
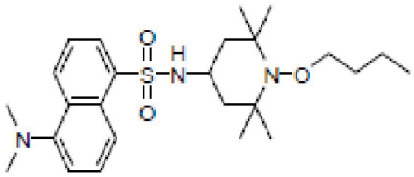
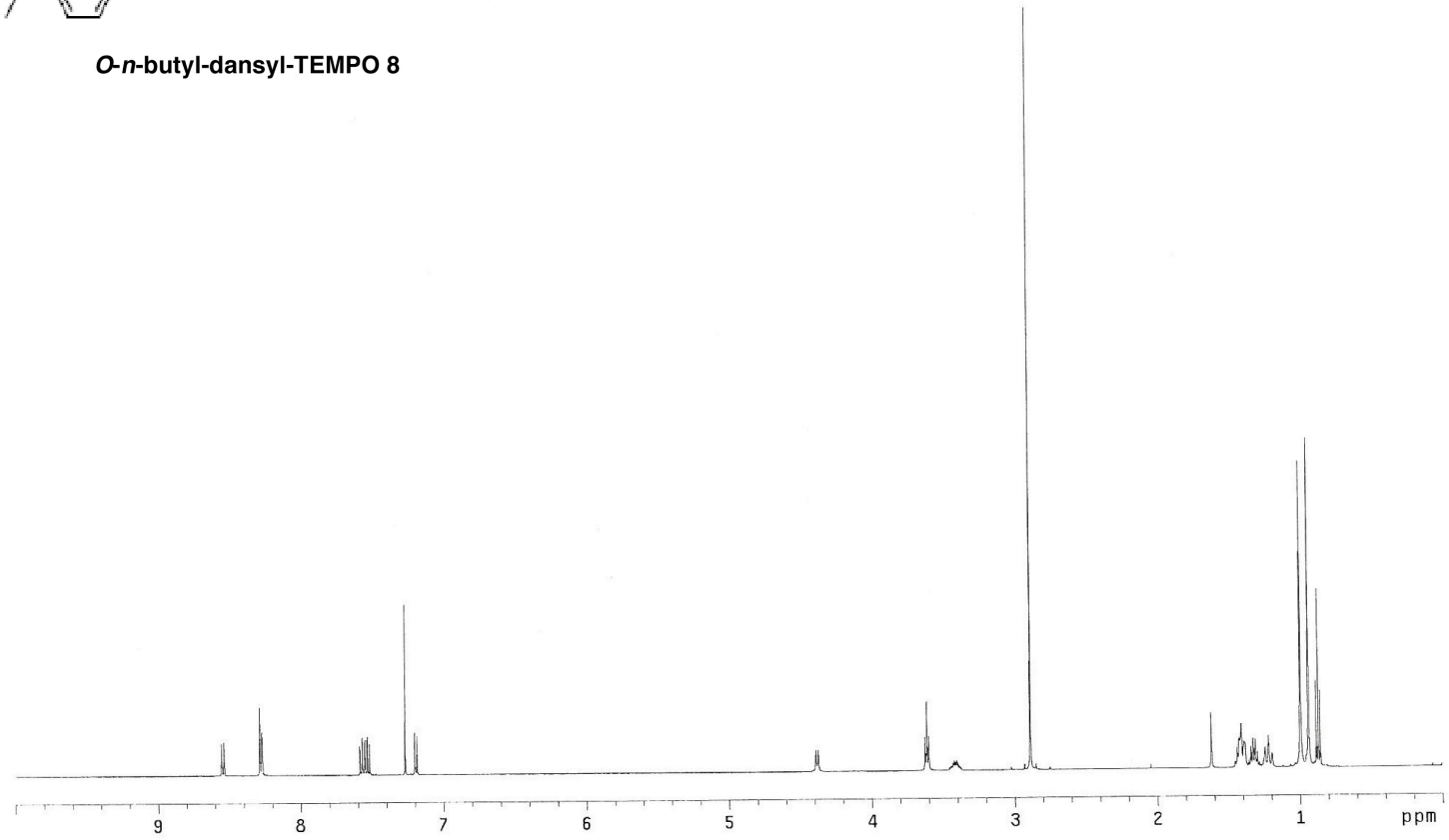
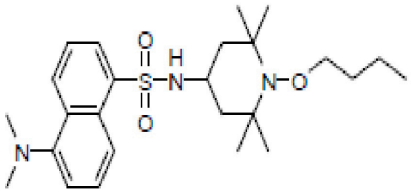


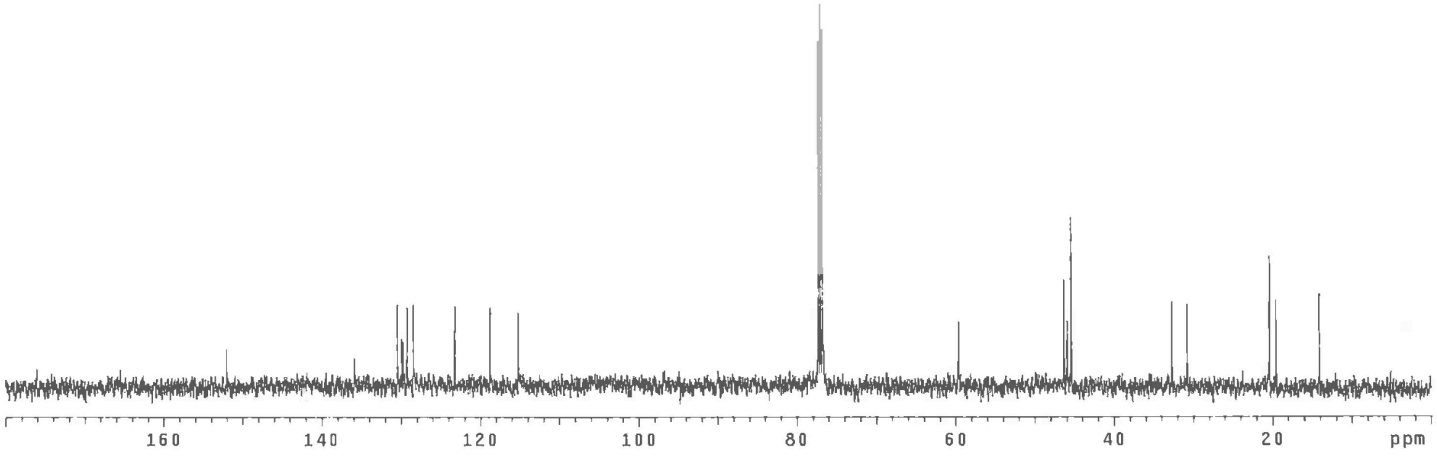


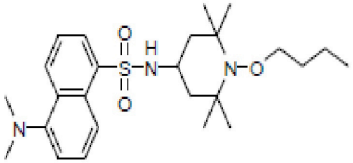
***O-n*-butyl-dansyl-TEMPO 8**





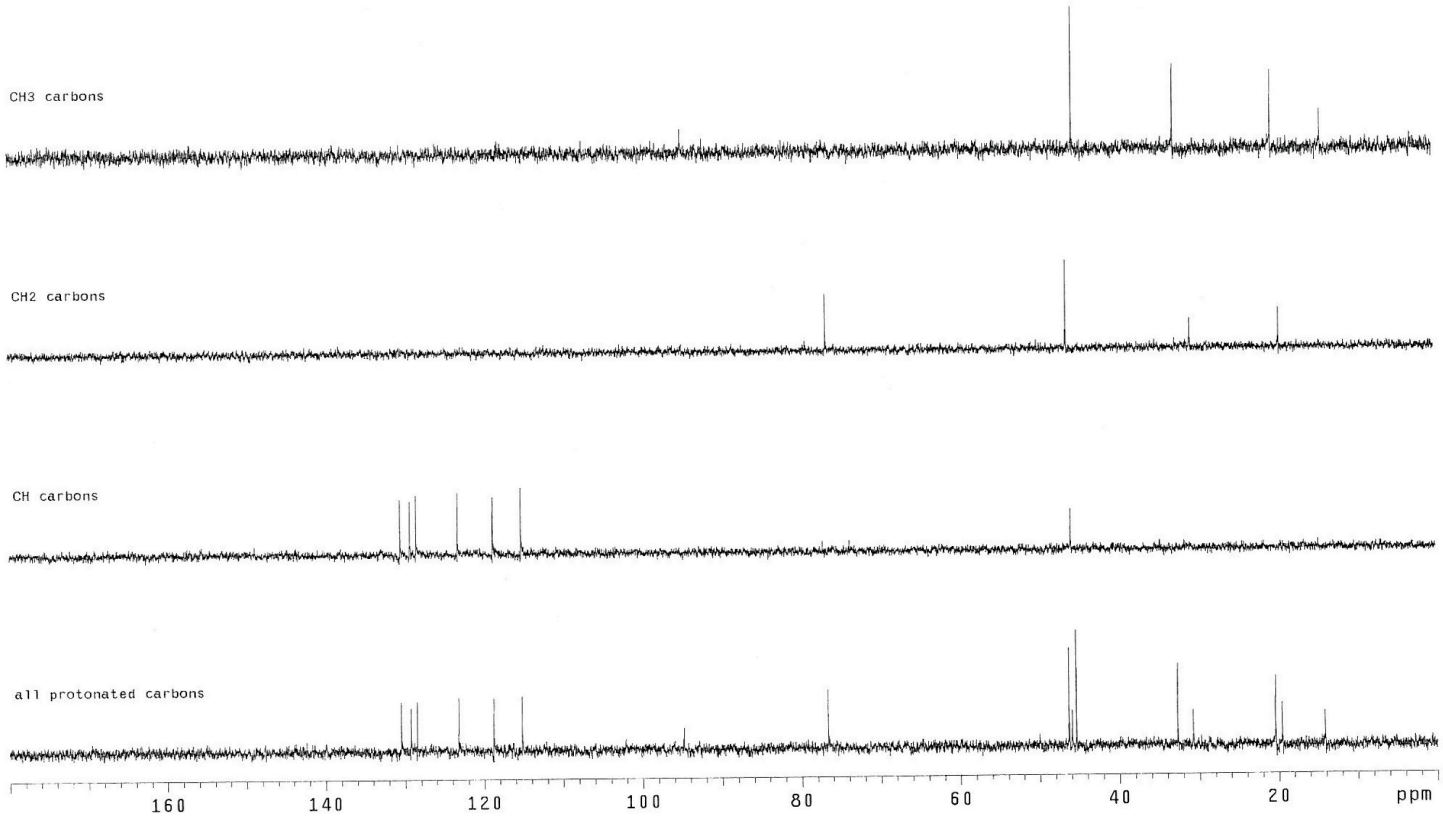
***O-n*-butyl-dansyl-TEMPO 8**





***O-n*-butyl-dansyl-TEMPO 8**

DEPT



References to Supporting Information:

1. Rozantsev, E. G. *Free Nitroxyl Radicals*; Plenum Press: New York, 1970, pp 213-214.
2. Bushmakina, N. G.; Misharin, A. Y. *Synthesis* **1986**, 966-966.