

Supplementary Information

Light-active azaphenalene alkoxyamines: Fast and efficient mediators of a photo-induced persistent radical effect

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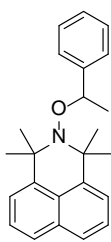
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Experimental Section

1. **General.** All air-sensitive reactions were carried out under ultra-high purity argon. Diethyl ether and xylene were dried by storage over sodium wire. Synthesis of precursor azaphenalene nitroxide 1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene-2-yloxy was achieved in 3 steps from 1,8-naphthalic anhydride using the established literature procedure.¹ All other reagents were purchased from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded with a Varian 400 MHz spectrometer and referenced to the relevant solvent peak. HRMS were recorded on an Agilent accurate mass QTOF LC-MS. Melting points were measured with a Gallenkamp Variable Temperature Apparatus by the capillary method and are uncorrected. Fluorescence Spectrofluorimetry was undertaken on a Agilent Cary Eclipse Fluorescence Spectrophotometer. Offline photolysis experiments were carried out by irradiation in Rayonet Photoreactor with 300 nm lamps (4 × 8W) with EPR spectra recorded on a MiniScope MS400 Spectrometer at room temperature. Online photolysis and thermolysis experiments were carried out in a Bruker ESP 300 ESR spectrometer at 9.5 GHz (X-band) employing 100 kHz field modulation and a microwave power of 10 mW, equipped with a variable temperature unit Bruker ER 4111 VT. The magnetic field strength and microwave frequency were measured with a Bruker ER 035 M NMR gaussmeter and a Hewlett–Packard 5350B frequency counter, respectively. The UV irradiations were performed with a tunable Hg–Xe lamp (Hamamatsu, L8252, 150 W) set at 1% overall power.

2. Synthesis of 2-phenylethoxy-1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene.



The nitroxide 1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene-2-yloxy (50.0 mg, 0.21 mmol, 1.0 eq.) and 1-bromoethylbenzene (57 μ L, 0.42 mmol, 2.0 eq.) were dissolved in MeCN (2 mL). Copper (13.3 mg, 0.21 mmol, 1.0 eq.) was added and the solution was degased by bubbling with argon for 15 min. Then *N,N,N',N',N''*-pentamethyldiethylenetriamine (52.0 μ L, 0.25 mmol, 1.2 eq.) was added. The orange solution turned over green to blue. After the reaction was stirred for 16 h the solution was filtered with Et₂O through

Celite®. The crude product was purified by chromatography (*n*-Hexane:Ethyl acetate 95:5, v:v) and the product was yielded in 62 % (43.8 mg, 0.13 mmol) as a light yellow solid.

$R_f = 0.45$ (*n*-Hexane:EtOAc 95:5, v:v).

mp = 75-76 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3 , 300 K, ppm): $\delta = 7.72\text{--}7.68$ (m, 2H, Naph-CH), 7.53–7.45 (m, 2H, Naph-CH), 7.44–7.34 (m, 6H, Naph-CH, Ph-CH_{ortho}, Ph-CH_{meta}), 7.34–7.27 (m, 1H, Ph-CH_{para}), 5.02 (q, $^3J_{\text{HH}} = 6.7$ Hz, 1H, OCHCH₃), 1.93 (s, 3H, CH₃) 1.65–1.64 (m, 6H, CH₃, OCHCH₃), 1.49 (s, 3H, CH₃), 1.27 (s, 3H, CH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): (Isomer 1) $\delta = 145.1$ (Naph-C_f), 142.7 (Ph-C_{ipso}), 133.2 (Naph-C_d), 128.2 (Naph-CH_b), 127.2 (Naph-CH_c), 126.9 (Naph-CH_a), 126.1 (Ph-C_{para}), 125.61 (Ph-C_{meta}), 124.9 (Naph-C_e), 121.5 (Ph-C_{ortho}), 84.1 (CHCH₃), 63.6 (C_q), 32.0 (CHCH₃), 26.9 (CH₃), 23.3 (CH₃); (Isomer 2) $\delta = 145.1$ (Naph-C_f), 142.6 (Ph-C_{ipso}), 133.2 (Naph-C_d), 128.2 (Naph-CH_b), 127.2 (Naph-CH_c), 126.9 (Naph-CH_a), 126.0 (Ph-C_{para}), 125.59 (Ph-C_{meta}), 124.9 (Naph-C_e), 121.3 (Ph-C_{ortho}), 84.1 (CHCH₃), 63.4 (C_q), 31.7 (CHCH₃), 26.9 (CH₃), 23.3 (CH₃).

HRMS (ESI): calc. for $[\text{C}_{24}\text{H}_{28}\text{NO}]^+$: $m/z = 346.2165$; found: $m/z = 346.2166$.

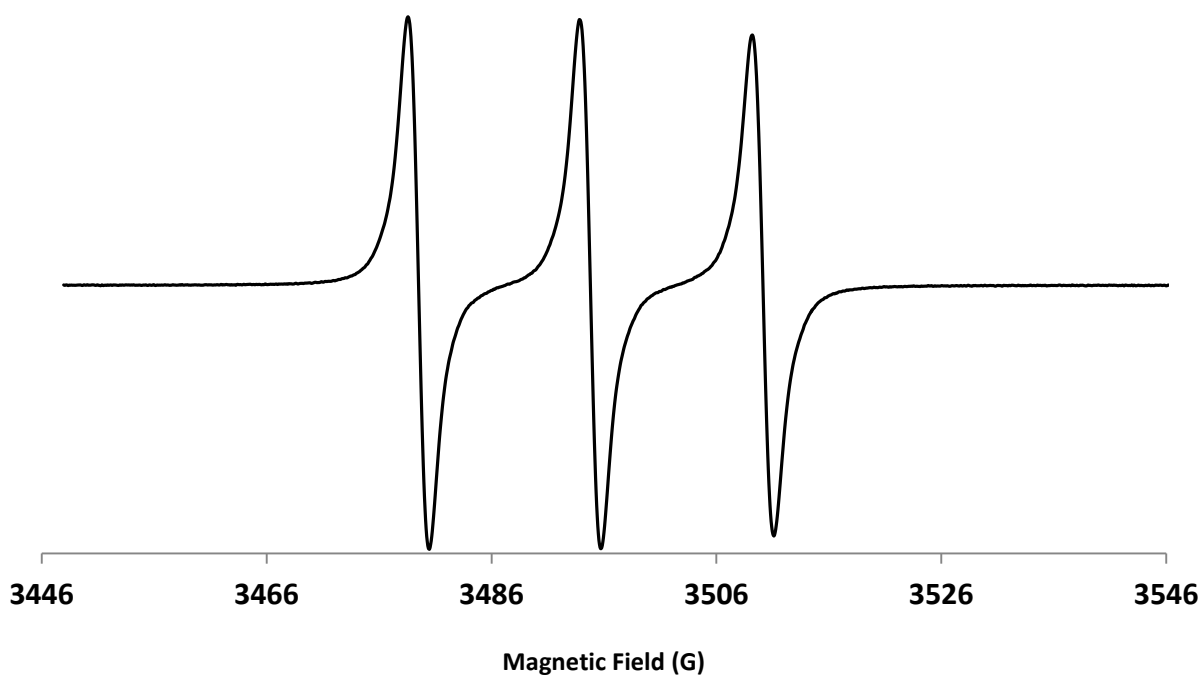


Figure S1. EPR Spectrum of TMAO

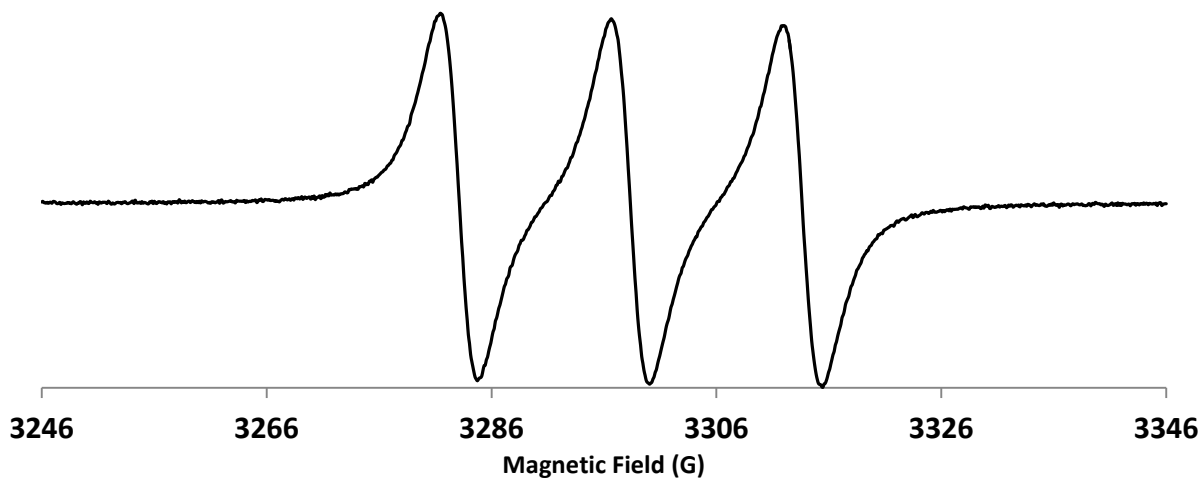


Figure S2. EPR Spectrum present of radical present after thermolysis of TMAO-Alkoxyamine at 92.5 °C for 1020 minutes. (4 mM solution in tBuBenz)

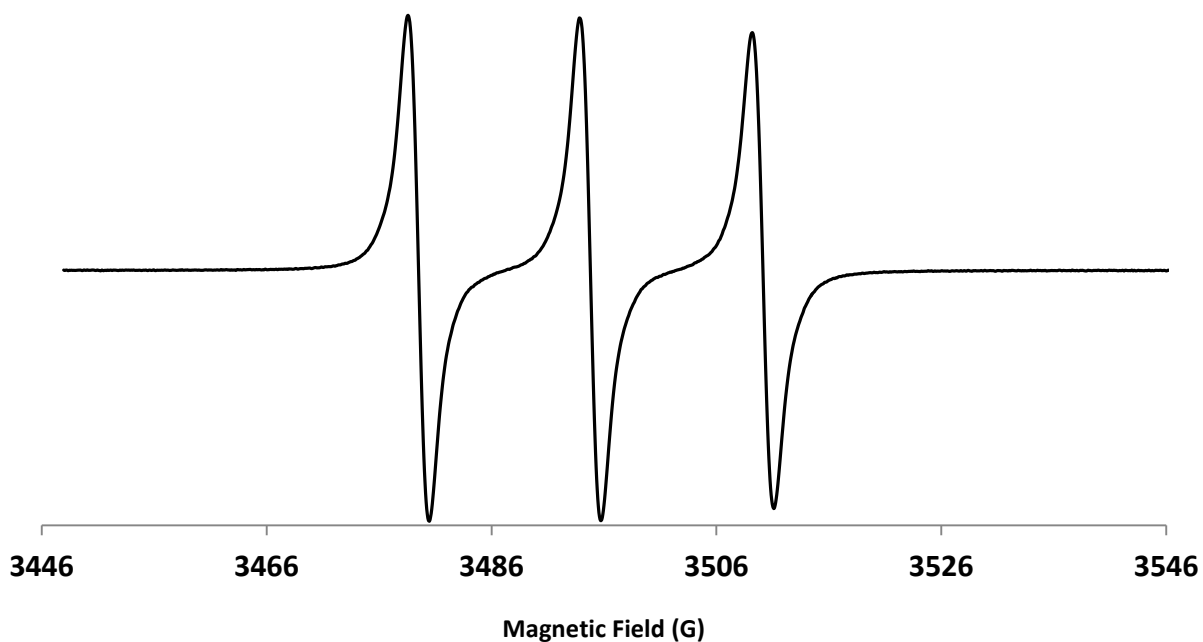


Figure S3. EPR Spectrum present of radical present after photolysis of TMAO-Alkoxyamine under UV irradiation for 120 seconds.

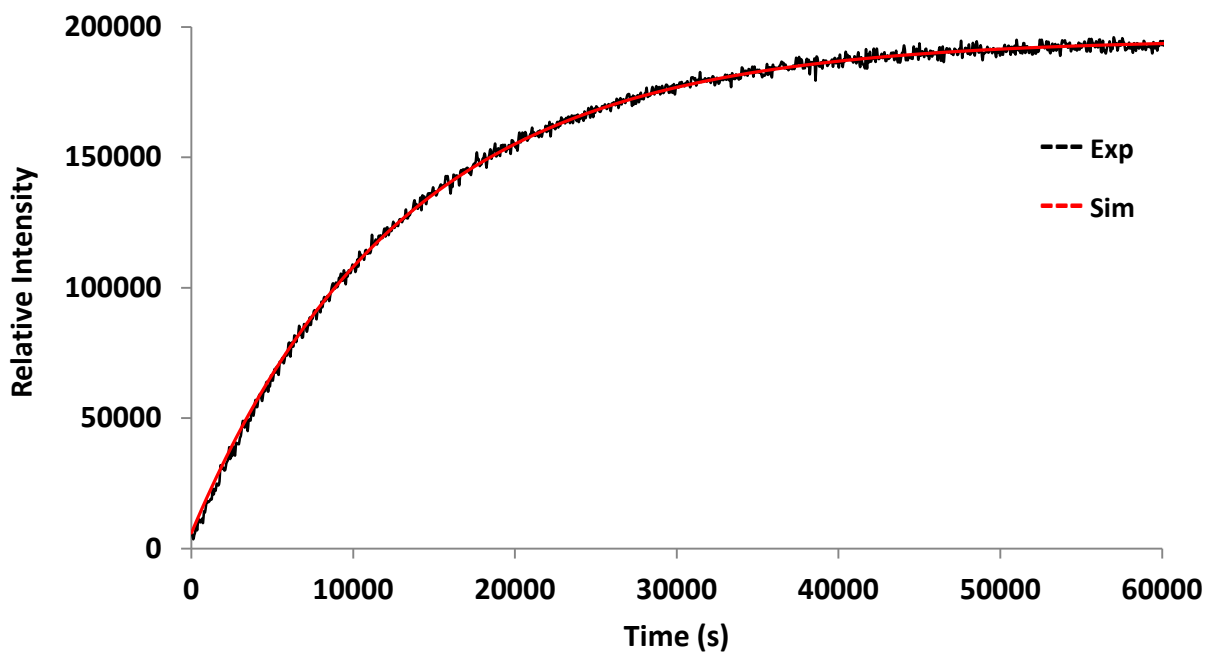


Figure S4. Comparison between experimental and calculated rate of decomposition of TMAO-Alkoxyamine at 92.5 °C. From this a $k_d = 7.733 \times 10^{-5} \text{ s}^{-1}$ was found giving a BDE of $129.6 \text{ kJ}\cdot\text{mol}^{-1}$.

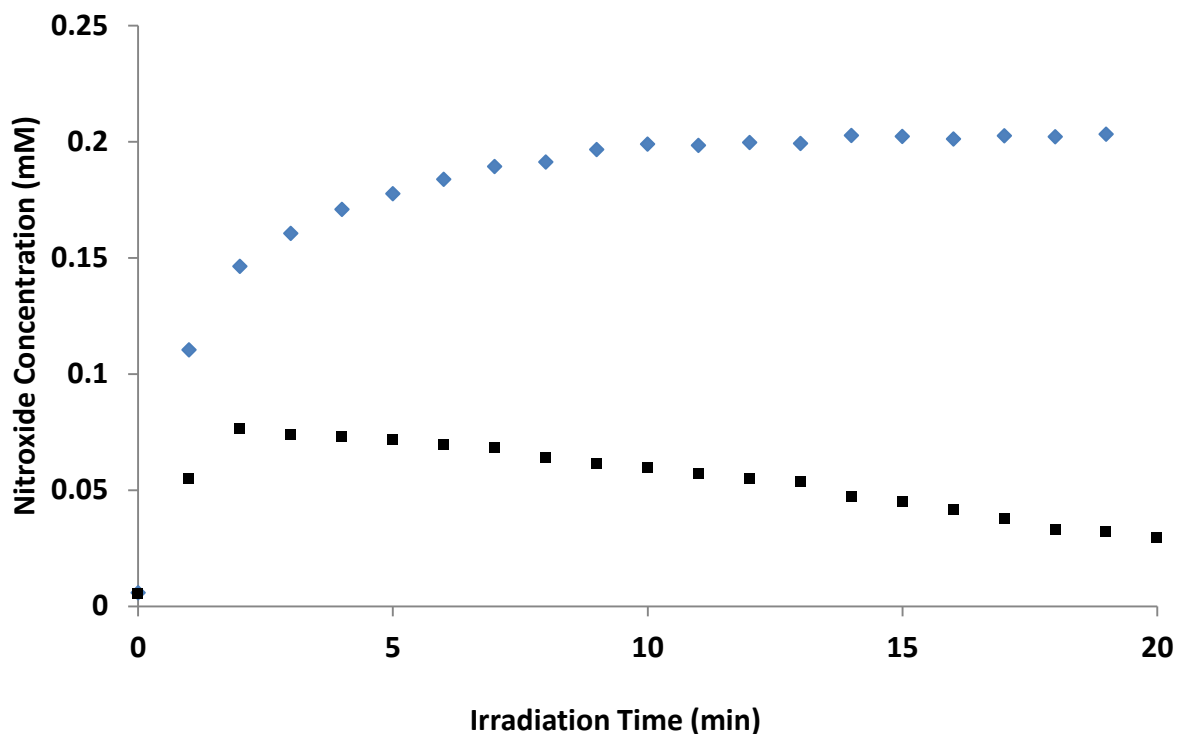


Figure S5. Comparison of nitroxide generation (concentrations calculated by double integration of EPR spectra) between irradiation of azaphenalene-alkoxyamine under normal atmosphere (blue) and in a deoxygenated environment (black).

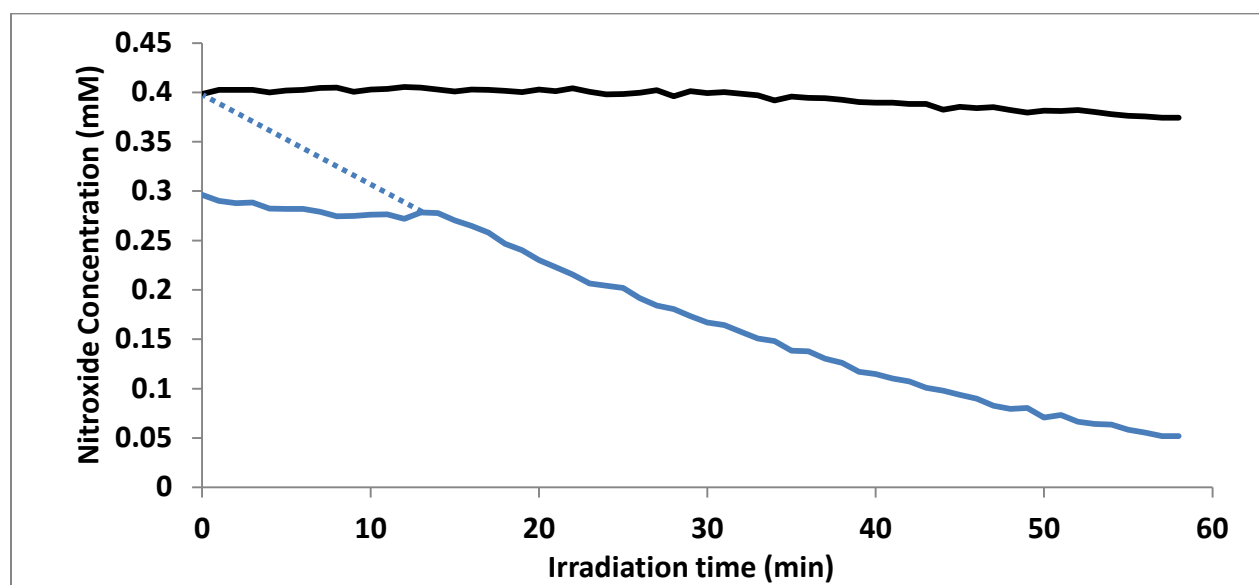


Figure S6. Comparison of nitroxide generation (concentrations calculated by double integration of EPR spectra) between irradiation of azaphenalene-nitroxide under normal atmosphere

(black) and in a deoxygenated environment (solid blue). Dotted line represents the true nitroxide concentration as under equivalent deoxygenated conditions at 0.4 mM starting concentration the signal saturated the detector.

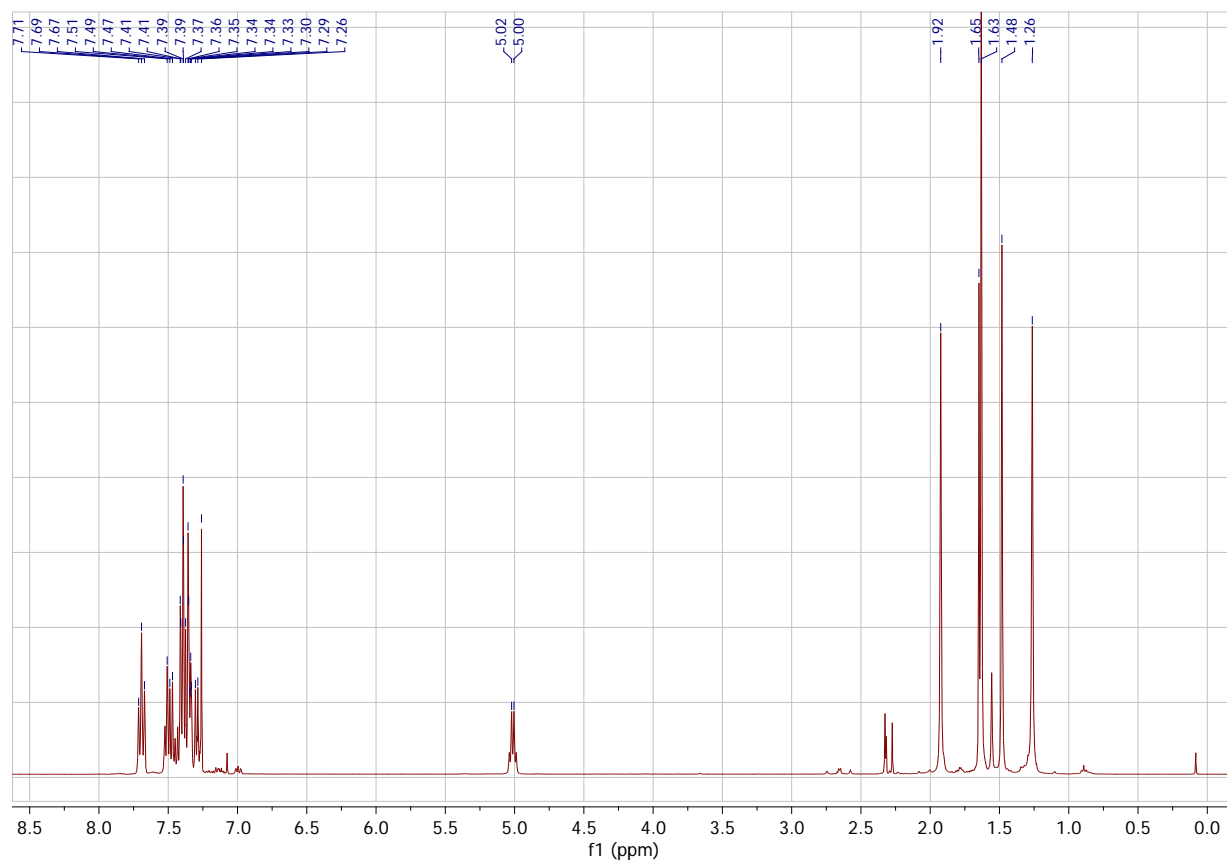


Figure S7. ¹H NMR Spectrum of azaphenalene-alkoxyamine.

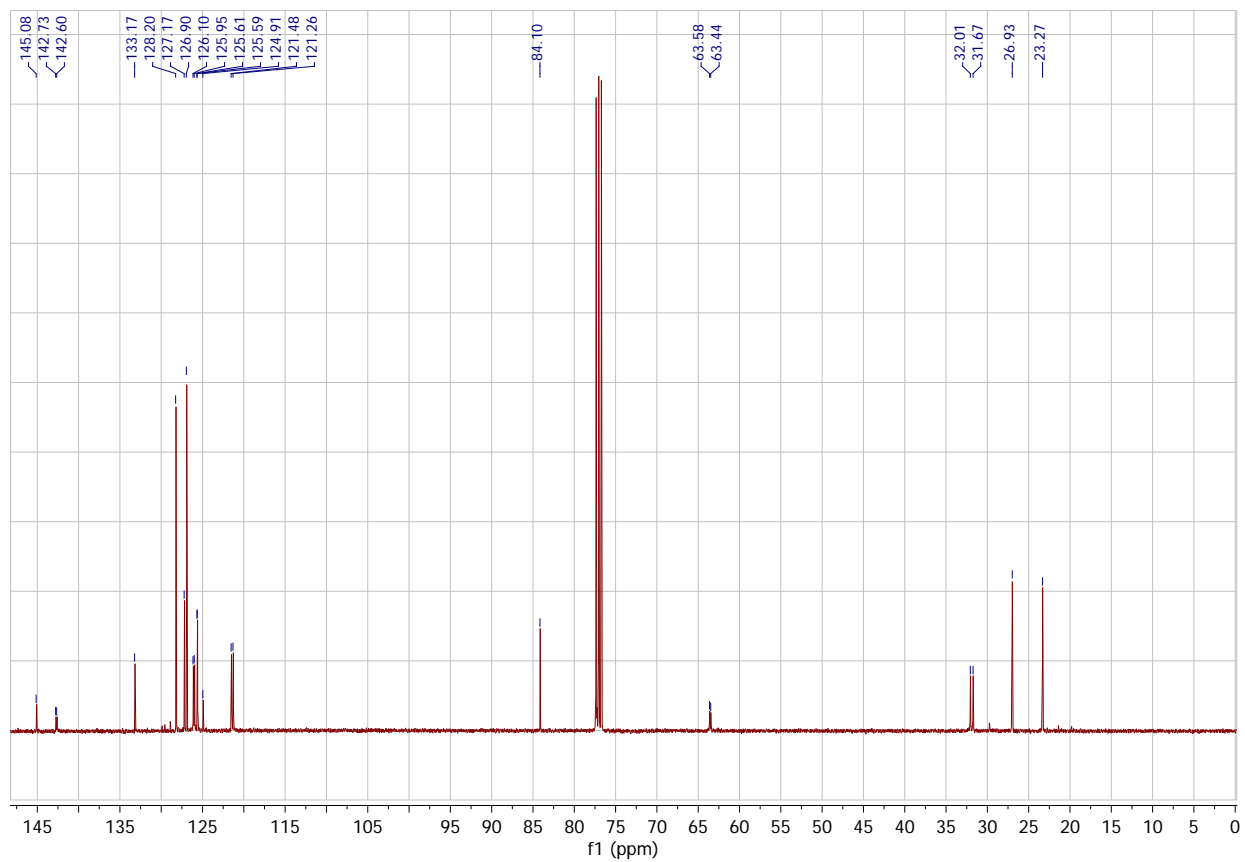


Figure S8. ^{13}C NMR Spectrum of azaphenalene-alkoxyamine.

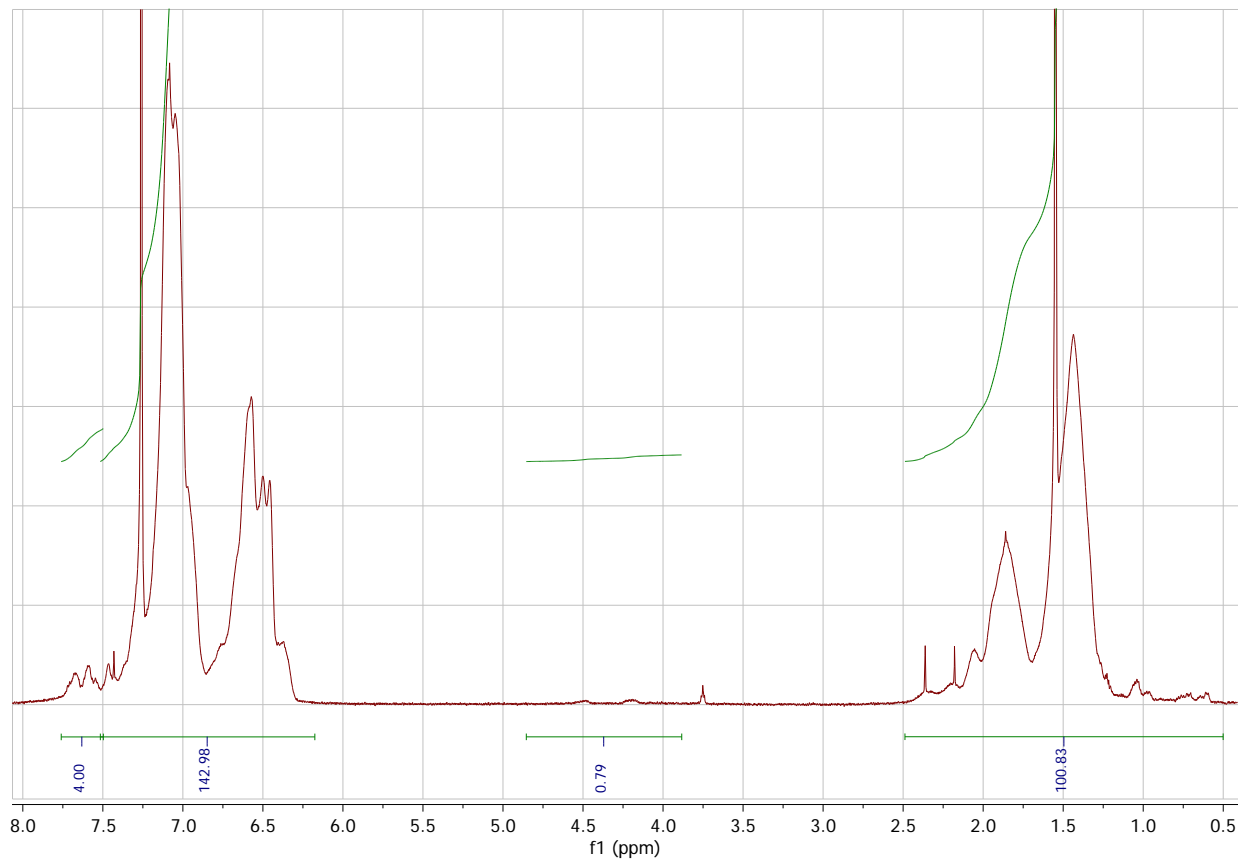


Figure S9. ^1H NMR spectrum of precipitated polymer from the reaction of a well stirred, degassed solution of the azaphenylene-alkoxyamine in styrene (ratio of 1:250) after 10 hours irradiation. Estimation of M_n based on protons related to the 1,3,5,8 protons from the naphthalene moiety visible between 7.5 and 7.8 ppm give $M_{n, \text{NMR}} = 3,150$.

Reference

- (1) Fairfull-Smith, K.E.; Bottle, S.E. *Eur. J. Org. Chem.* **2008**, 32, 5391-5400.