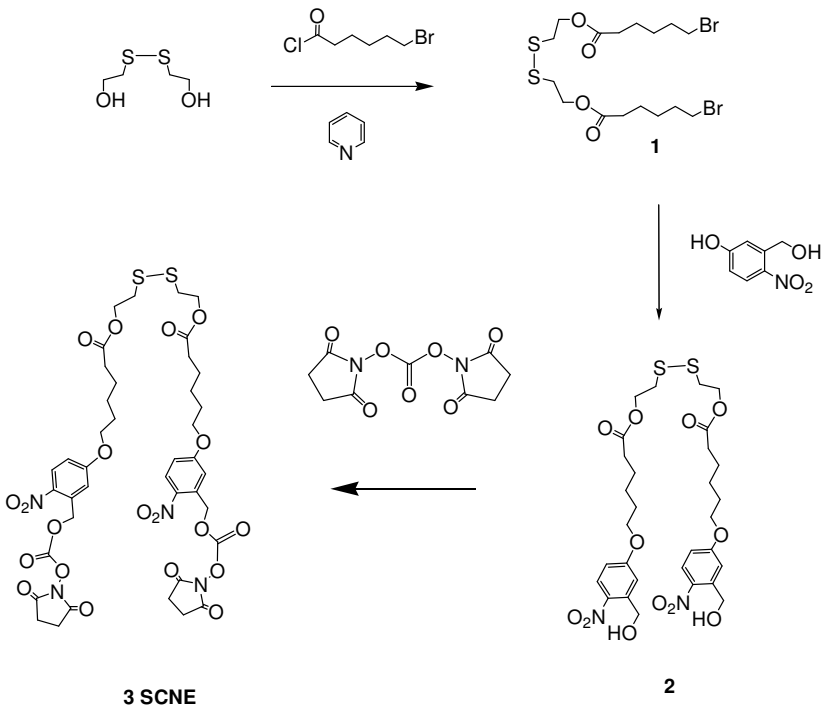
Supporting Information: Synthesis and Characterization of SCNE

The synthesis of the cross-linker SCNE was achieved in three steps by using 5-hydroxy 2-nitrobenzyl alcohol, 6-bromohexanoic chloride and 2-hydroxyethyl disulfide as the starting materials (Scheme 1). ^{1}H NMR spectra were recorded on a GE NMR-OMEGA (300 MHz) and ^{13}C NMR experiments was carried out by using a Bruker 500 MHz DMX. Elementary Analysis was performed by Atlantic Microlab Inc., Atlanta, GA. Mass spectroscopic characterization was carried out at the University of Chicago with a Finnigan 990 using atmospheric-pressure chemical ionization (APCI) in positive mode. The mass-to-charge ratio (m/z) is monoisotopic. The peaks at m/z 808, 657, 543 and 499 correspond to the major fragmentations due to ester bond cleavages followed by the loss of water. The formation of the final product of SCNE was confirmed by NMR, elemental analysis and mass spectroscopy. The overall reaction yield was ~24%.



Scheme 1. Synthesis route of SCNE.

*Synthesis of di 6-bromo-hexanoic acid (disulfide diethanol) ester (***1***).*

6-bromohexanoic chloride (6.4 g, 30 mmol) were dissolved in anhydrous DMF (30 mL). Under N_2 protection, 2-hydroxyethyl disulfide (1.54 g, 10 mmol) and pyridine (2.4 g, 30 mmol) in DMF (20 mL) were added dropwise. The reaction was kept at 40℃ under N_2 for 8 h, the resulting suspension was filtered, and the supernatant was collected. After removing the solvent, the residue was chromatographed on silica gel using ethyl acetate/n-hexane (1:2) to give **1** (4.7 g, yield 95%). Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): d4.35 (t, 4H, *J*=7.4 Hz), 3.40 (t, 4H, *J*=6.6 Hz), 2.91 (t, 4H, *J*=6.8 Hz), 2.31 (t, 4H, *J*=7.4 Hz), 1.90 (m, 4H), 1.78 (m, 4H), 1.51 (m, 4H).

*Synthesis of di 6 -(3-hydroxymethyl-4-nitro-phenoxy)-hexanoic acid disulfide diethanol ester (**2**).*

5-hydroxy 2-nitrobenzyl alcohol (0.5 g, 3 mmol) and K_2CO_3 (0.4 g, 3 mmol) were dissolved in DMF (25 mL) and heated to 65±5 ^oC under N_2 . **1** (0.5 g, 1 mmol) in DMF (5 mL) was added dropwise. The reaction was kept at 65±5 ℃ under N_2 for 14 h, the resulting suspension was filtered, and the supernatant was collected. After removing the solvent, the residue was dissolved in ethyl acetate and washed by 1% acetic acid (10 mL) and 1% $NaHCO_3$ (10 mL) consequently followed by washing with deionized water (15 mL) for three times and dried by Na_2SO_4. After rotary evaporation, the residue was then chromatographed on silica gel using ethyl acetate/n-hexane (1:1) to yield **2** (0.4 g, yield 60%). Yellow oil, ^1H NMR (300 MHz, $CDCl_3$): 8.18 (d, 2H, *J*=9.1 Hz), 7.20 (d, 2H, *J*=6.2 Hz), 6.90 (d, 2H, *J*=7.8 Hz), 5.00 (s, 4H), 4.35 (t, 4H, *J*=7.5 Hz), 4.09 (t, 4H, *J*=5.5 Hz), 2.94 (t, 4H, *J*=7.0 Hz), 2.38 (t,4H, *J*=7.0 Hz), 1.90 (m, 4H), 1.78 (m, 4H), 1.55 (m, 4H).

*Synthesis of di 6 - (3-succinimidyl carbonyloxymethyl-4-nitro-phenoxy)-hexanoic acid disulfide diethanol ester (**3, SCNE**)*

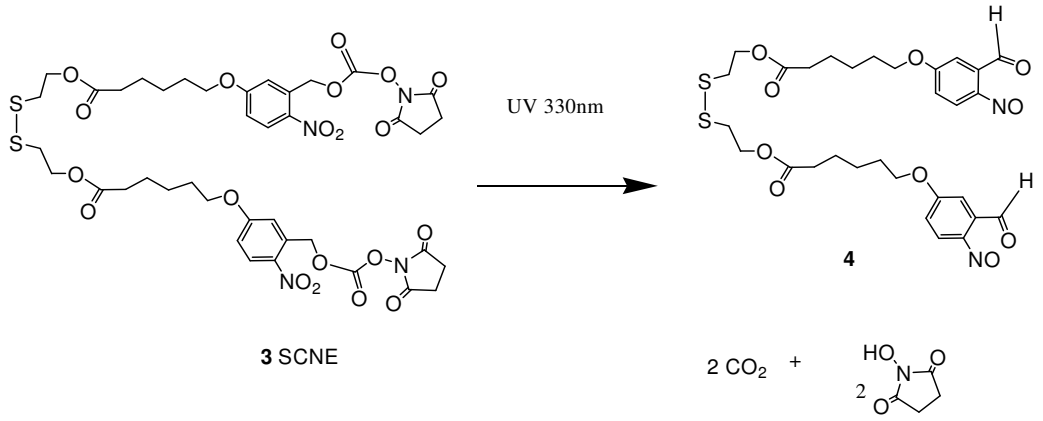
N, N'-disuccinimidyl carbonate (DSC) (1 g, 4 mmol) was dissolved in anhydrous acetonitrile (25 mL). Compound **2** (0.27 g, 0.4 mmol) and triethylamine (0.4 g, 4 mmol) in DMF (5 mL) were added drop-by-drop in an ice bath under N_2. This addition process continued for 1 h. The reaction was then kept at room temperature under N_2 for 16 h. The solvent was then removed under vacuum and the residue was dissolved in ethyl acetate and washed by 1% acetic acid (10 mL) and 1% $NaHCO_3$ (10 mL) consequently, followed

by washing with DI water (15 mL) for three times and drying with Na_2SO_4. After rotary evaporation, the residue was then chromatographed on a silica gel column using ethyl acetate/n-hexane (2:1) as the eluting solvent to give SCNE as yellow oil, which was further recrystalized in cold ethanol to yield a pale solid (0.15 g, 40%). ^{1}HNMR (300 MHz, $CDCl_3$): 8.21 (d, 2H, *J*=8.9 Hz), 7.10 (d, 2H, *J*=6.0 Hz), 6.90 (d, 2H, *J*=8.0 Hz), 5.80 (s, 4H), 4.35 (t, 4H, *J*=7.1 Hz), 4.12 (t, 4H, *J*=5.8 Hz), 2.94 (t, 4H, *J*=6.1 Hz), 2.88 (s, 8H), 2.35 (t, 4H, *J*=7.0 Hz), 1.90 (m, 4H), 1.75 (m, 4H), 1.53 (m, 4H). ^{13}CNMR (75 MHz, $CDCl_3$): δ173.25, 168.48, 168.48, 163.83, 157.26, 139.12, 133.44, 130.09, 114.42, 112.28, 69.10, 68.62, 62.00, 37.15, 33.88, 28.49, 29.37, 29.37, 29.36, 24.40. Theoretical elementary analysis: C 49.69% H 4.80% N 5.79% S 6.63%. Experimental analysis: C 49.49% H 4.94% N 6.09% S 6.46%. Mass Spectra: m/z 808, 764, 657, 649, 543 (100%), 499, 474.

Photolysis of SCNE

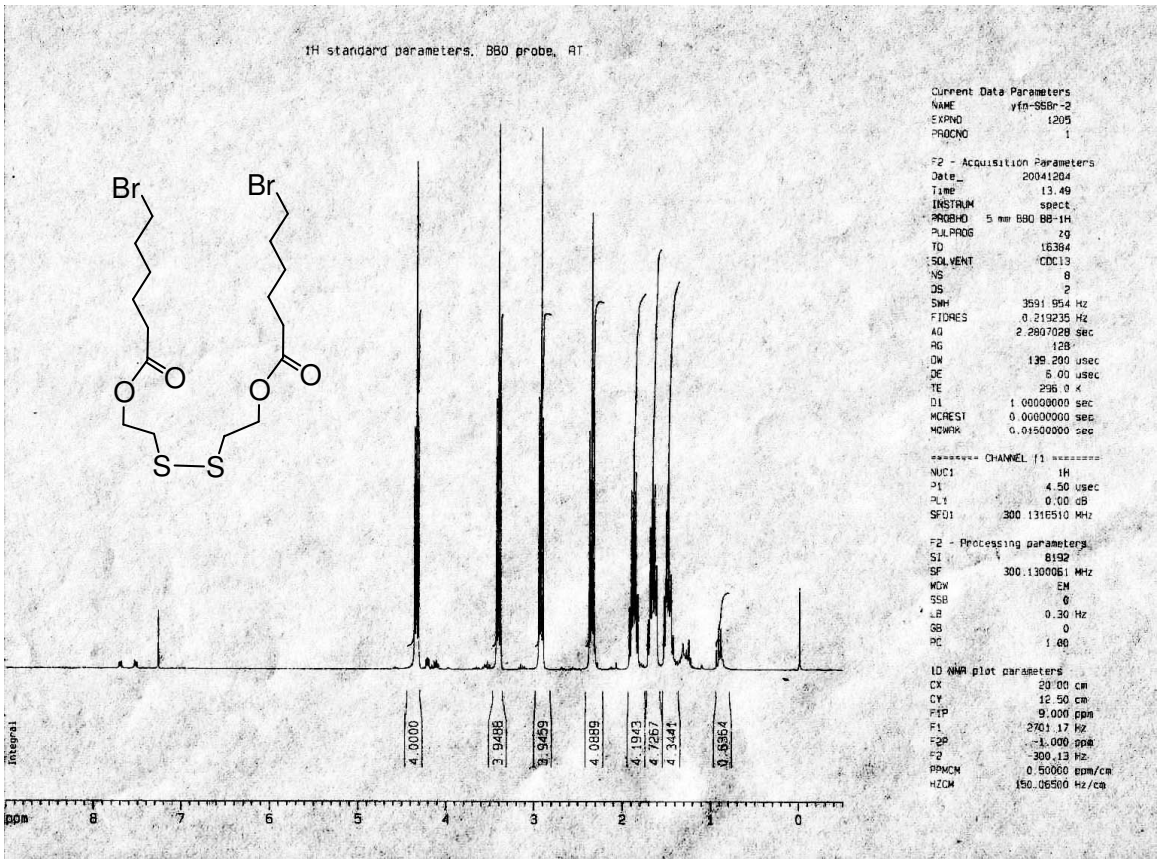
The photolytic reaction of SCNE was carried out by irradiating a 5.6×10^{-5} M of SCNE solution in CH_3CN for 2 h in a quartz cuvette. The irradiation was conducted by using a 125 W mercury lamp equipped with an interference filter (330 nm, Andover Corporation Optical Filter) to match the 330 nm mercury emission line. After separation and purification of the photolysis products, ^{1}H NMR spectra (300 MHz, $CDCl_3$) were collected. The chemical shifts of the products include δ 9.85 (s, 2H), δ 8.21 (d, 2H), 7.10 (d, 2H), 6.90 (d, 2H), 4.35 (t, 4H), 4.12 (t, 4H), 2.94 (t, 4H), 2.35 (t, 4H), 1.90 (m, 4H), 1.75 (m, 4H), and 1.53 (m, 4H), indicating the formation of nitrosobenzaldehyde and N-

hydroxysuccinimide. Based on TLC and NMR experimental results, we concluded the photolysis pathway as outlined in Scheme 2.

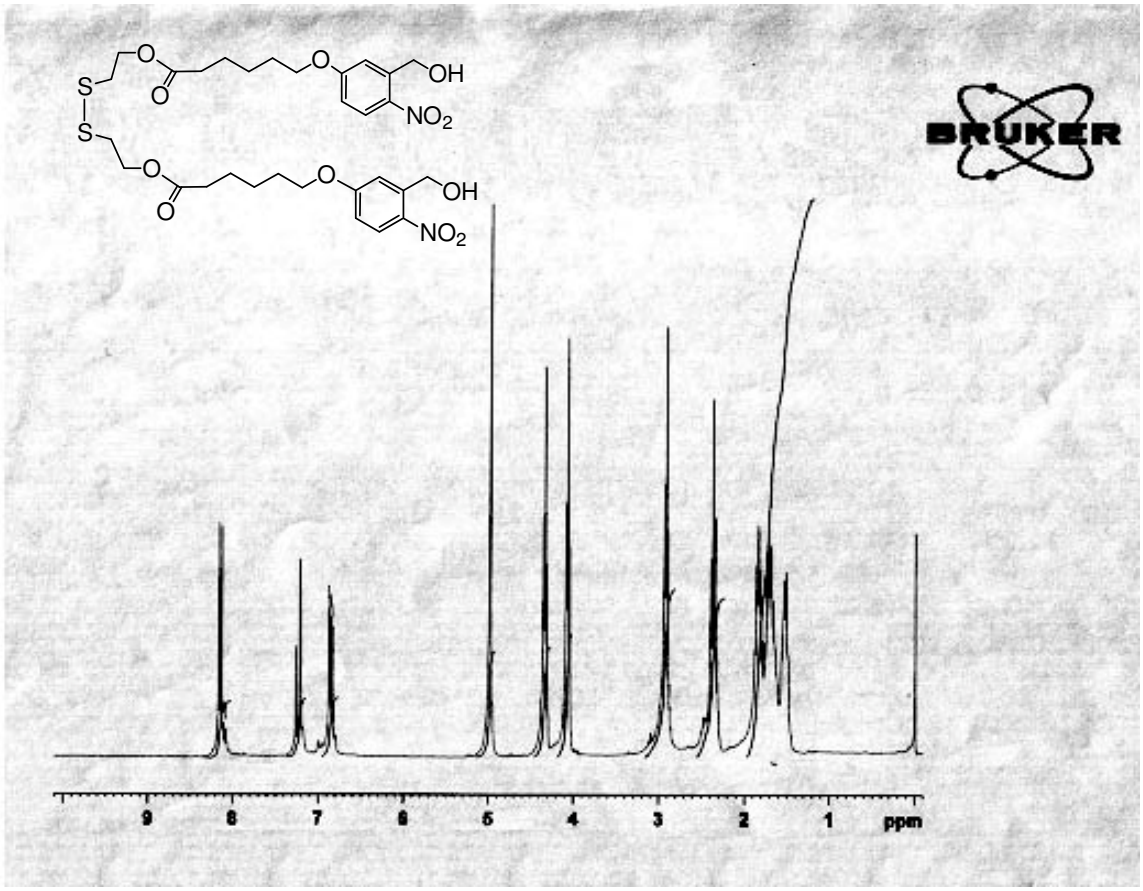


Scheme 2. Photolysis of SCNE under 330 nm irradiation.

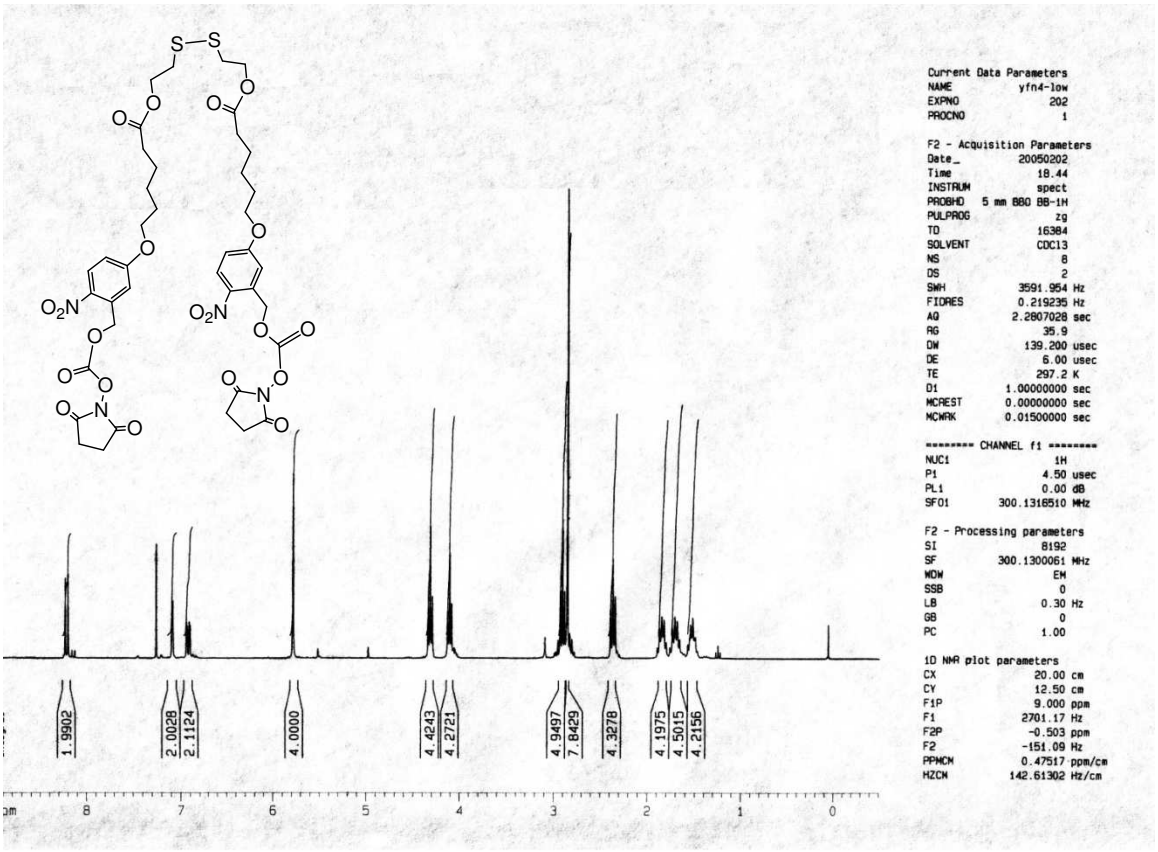
Appendix A. NMR spectra of SCNE and intermediate products



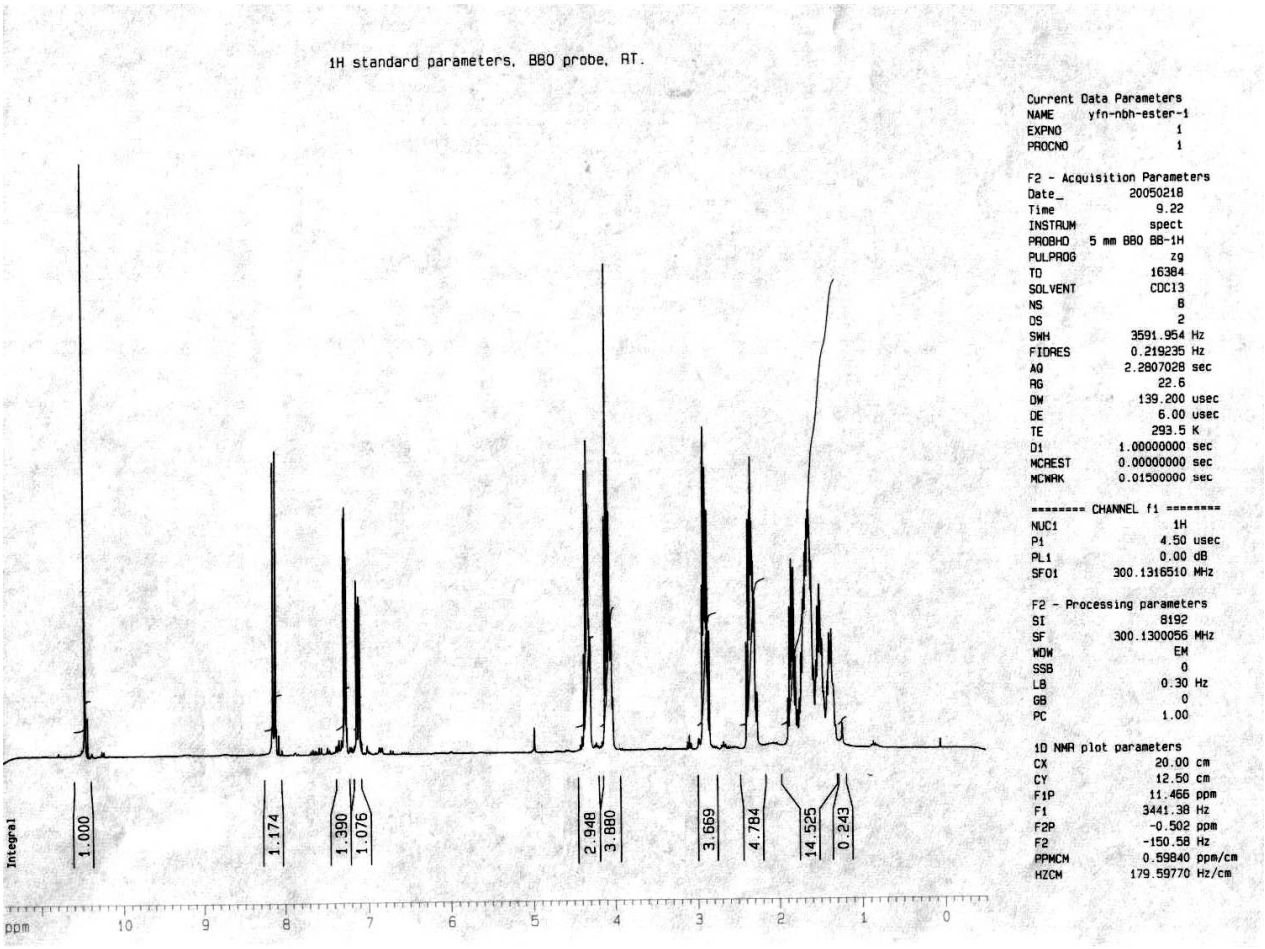
Appendix A-1 ^{1}HNMR of Compound 1



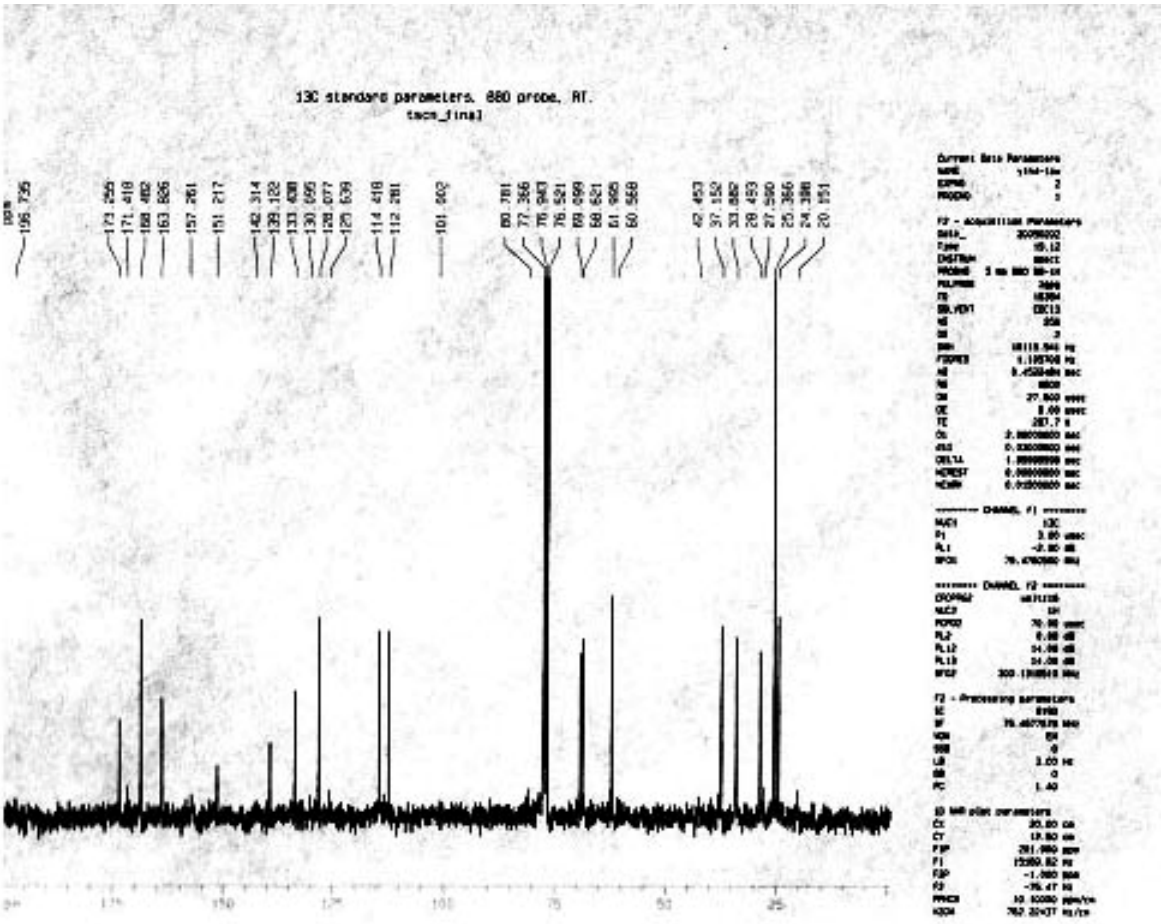
Appendix A-2 ^{1}HNMR of Compound 2



Appendix A-3 ^{1}HNMR of SCNE



Appendix A-4 ^{1}HNMR spectrum of photolysis product of SCNE



Appendix A-5 ^{13}C NMR of SCNE