A New Photoclick Reaction Strategy: Photo-induced Catalysis of the Thiol-Michael Addition via a Caged Primary Amine

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SUPPORTING INFORMATION

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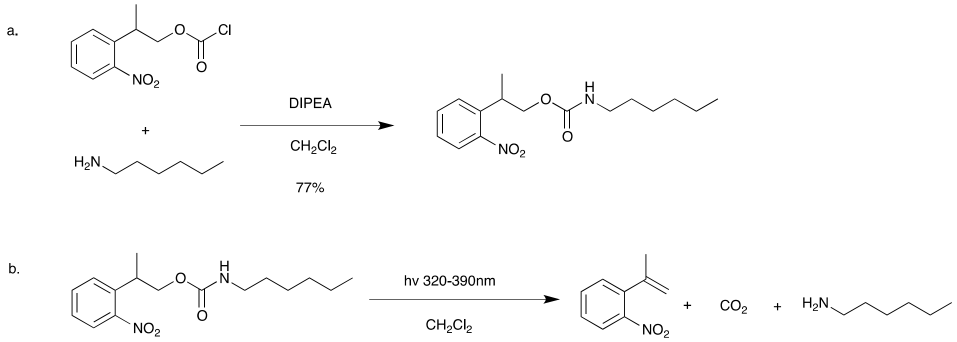
General Information:

Unless otherwise noted, all reactions were run under air. All chemical reagents were obtained commercially without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-III 400 spectrometers. Mass spectral and analytical data were obtained *via* the PE SCIEX/ABI API QSTAR Pulsar Hybrid LC/MS/MS, Applied Biosystems operated in the central analytical laboratory, University of Colorado at Boulder. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer.

Experimental:

1. General Procedure

1.1 Synthesis (a) and Photolysis (b) of NPPOC-Hexylamine

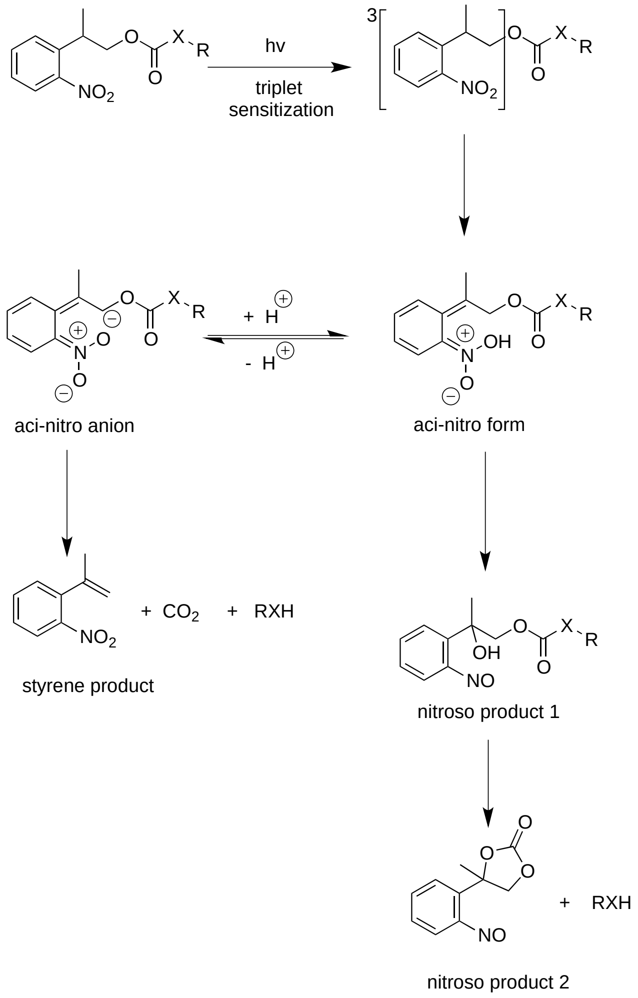


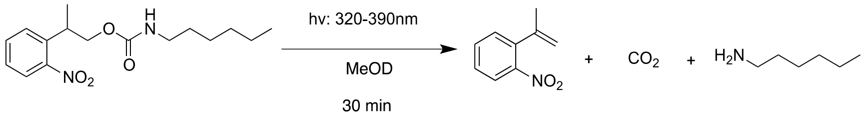
a. 2-(2-Nitrophenyl)propyl chloroformate (2mmol, 587mg) in 10ml CH_2Cl_2 was added dropwise to a stirred solution of hexylamine (2mmol, µl)and DIPEA (4mmol, µl)in 20 ml CH_2Cl_2 at 0°C. The reaction was stirred at room temperature for 8 hours. The mixture was washed with Brine (30ml x 3) and dried with anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using Hexane: EtOAc (1:1) to give a pure product (445mg, 76%) as light yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.70 (m, 1H), 7.57 (ddd, J = 8.6, 7.4, 1.4 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.36 (ddd, J = 8.5, 7.4, 1.5 Hz, 1H), 4.67 (br, J = 6.5 Hz, 1H), 4.37 – 4.18 (m, 1H), 4.16 – 4.05 (m, 1H), 3.80 – 3.62 (m, 2H), 3.18 – 3.03 (m, 2H), 1.53 – 1.15 (m, 14H), 0.93 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 156.09 , 150.77 , 137.45 , 132.52 , 128.25 , 127.25 , 123.95 , 68.57 , 67.21 , 44.35 , 41.60 , 40.98 , 33.25, 31.42 , 29.82 , 28.79 , 26.32 , 26.03 , 22.51 , 17.78 , 17.32 , 13.98 . Mass: $C_{16}N_{24}N_2O_4[M+Na]^+$ 331.1626, Found: 331.1634.

b. NPPOC-Hexylamine (0.1mmol, 29.3mg) was dissolved in MeOH (10ml) and then stirred under 320-390 nm irradiation (20mW/cm^2) for 3 hours. After irradiation, a 100 µl aliquot was diluted to 10ml (0.05mM) in MeOH and upon which a UV/Vis spectrum was obtained (scanning 1nm/s from 200 to 600nm).

Scheme S1: Principal cleavage pathways and products of NPPOC-protected (X=O, NH) amine or alcohol. [1,2]


hv
triplet sensitization
3
X
R
O
NO2
+ H+
- H+
aci-nitro anion
aci-nitro form
OH
+ CO2
+ RXH
styrene product
NO
nitroso product 1
+ RXH
nitroso product 2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MeOD
30 min
H
N
NO2
+
CO2
+
H2N

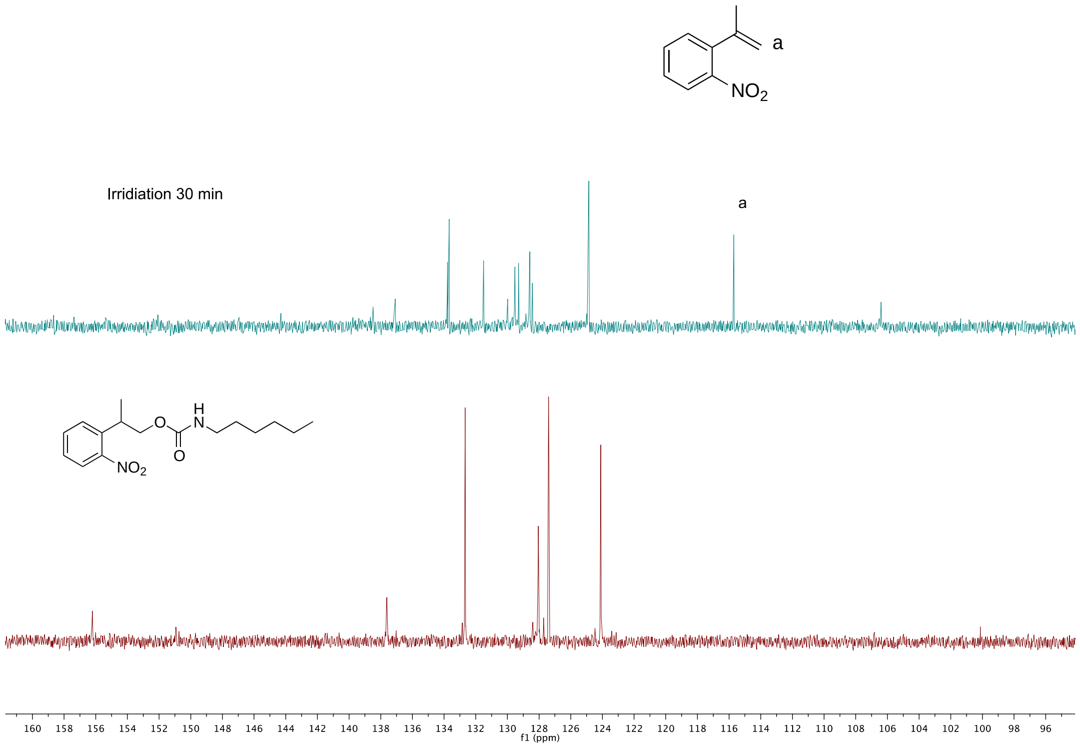
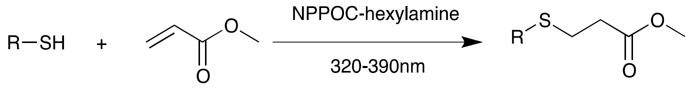


Fig S1. ^{13}C-NMR of Photolysis of NPPOC-hexylamine.

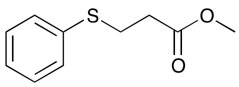
1.2 Model photo triggered NPPOC-Hexylamine catalyzed thiol-acrylate addition

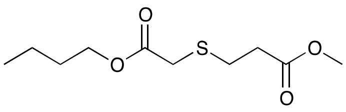
To a 10 ml glass vial was added thiol (2mmol) and catalyst (0.1mmol) and to this was added methyl acrylate (2mmol, 0. 182 ml). The mixture was vortexed until fully mixed. The mixture was then stirred under 320-390nm irradiation (20mW/cm^2).



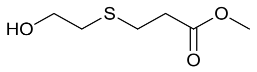
1.

Methyl 3-(phenylthio)propanoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 3.68(s, 1H), 3.17 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H) ^{13}C NMR δ (101 MHz, $CDCl_3$) 172.29, 135.33, 130.27, 129.16, 127.67, 127.29, 126.73, 51.94, 34.38, 29.22.

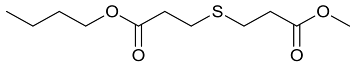




Methyl 3-((2-butoxy-2-oxoethyl)thio)propanoate: ^{1}H NMR (400 MHz, Chloroform-d) 4.13 (t, *J* = 6.7 Hz, 2H), 3.69 (s, 3H), 3.23 (s, 2H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.59 (t, J = 7.7 Hz, 2H), 1.68 -1.57 (m, 2H), 1.46-1.30 (m, 2H), 0.93 (t, *J* = 7.4 Hz，3H). ^{13}C NMR (101 MHz, Chloroform-d) 172.21, 170.49 , 65.46 , 51.96 , 34.28 , 33.87 , 30.72 , 27.70 , 19.21 , 13.81 .



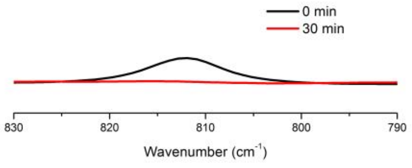
Methyl 3-((2-hydroxyethyl)thio)propanoate: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.77 – 3.72 (m, 2H), 3.70 (s, *J* = 3H), 2.81 (t, *J* = 7.1 Hz, 2H), 2.77 – 2.71 (t, J=7.1 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) 172.46 , 60.69 , 52.01 , 35.58 , 34.80 , 26.78 .



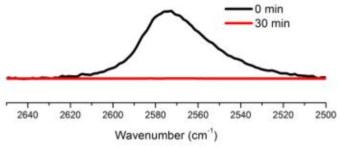
Butyl 3-((3-methoxy-3-oxopropyl)thio)propanoate: ^{1}H NMR (400 MHz, Chloroform-d) δ 4.09 (t, J = 6.7 Hz, 2H), 3.69 (s, 3H), 2.80 (tdd, J = 7.6, 1.8, 0.6 Hz, 4H), 2.66 – 2.52 (m, 4H), 1.65 – 1.55 (m, 2H), 1.37 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 172.01, 64.77, 51.95, 34.96, 34.73, 30.77, 27.23, 27.15, 19.95, 13.82

2. Kinetics study

Real-Time Fourier Transform Infrared (FT-IR) Spectroscopy**:** Reaction kinetics were monitored by FT-IR spectroscopy at a series scan rate of one scan per 2 seconds. These studies were performed on a Nicolet 750 Magna FT-IR spectrometer with a KBr beam splitter and an MCT/A detector under dry air. Samples were sandwiched between to NaCl windows and placed into a horizontal transmission apparatus. The sample thicknesses were approximately 200 microns. The conversion of thiol and vinyl functional groups was assessed by monitoring the disappearance of peak areas centered around 2567 and v812 cm^{-1}, respectively.



(a)



(b)

Figure S2: FT-IR spectra indicating the conversion of vinyl (a) and thiol (b) functional groups for the reaction between Butyl thiolglycolate and methyl acrylate. The disappearance of the two peak areas occur in a one-to-one manner, indicating a one-to-one stoichiometry.

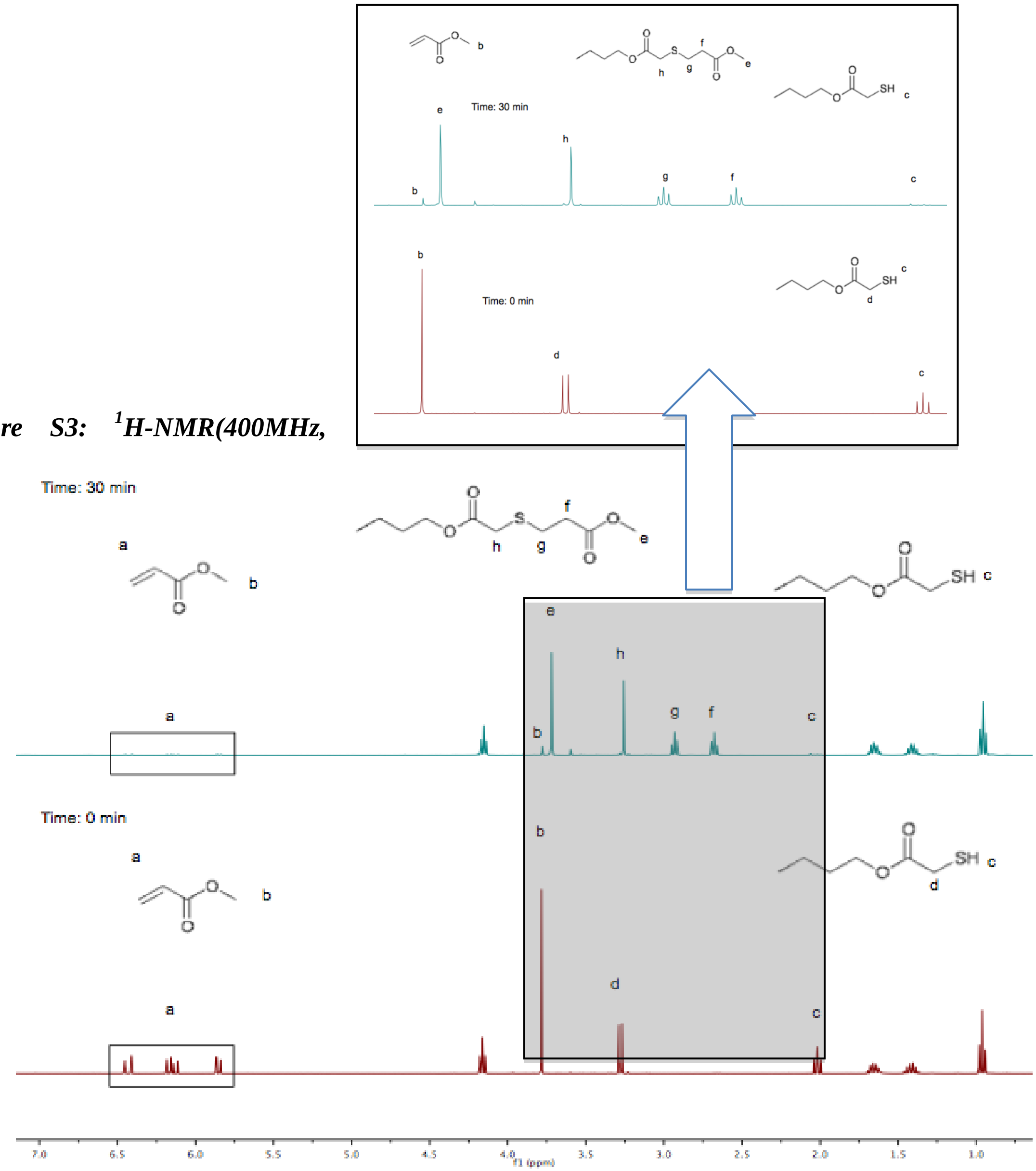


Figure S3: ^{1}H-NMR(400MHz, CDCl$_3$) spectra indicating the conversion of vinyl and thiol groups for the reaction between butyl thiogylcolate and methyl acrylate.

3. Mechanical Study

***Dynamic mechanical analysis (DMA)*:** The mechanical properties (E′ and E″) of fully formed polymer networks was performed with a DMAQ800 dynamic mechanical analyzer.[3] A rectangular sample geometry was used with dimensions of 11.32mm×1.89mm×1.04mm and 14.96mm×4.48mm×0.96mm for the PETMA/bisphenol A ethoxy diacrylate and PETMP/bisphenol A ethoxy diacrylate specimens, respectively.

Experiments were performed over a temperature range of –40 to 80°C with a scanning rate of 2°C/min. Finally, the T_g was determined as the maximum of the tan δ curve (where tan δ = E″/E′).

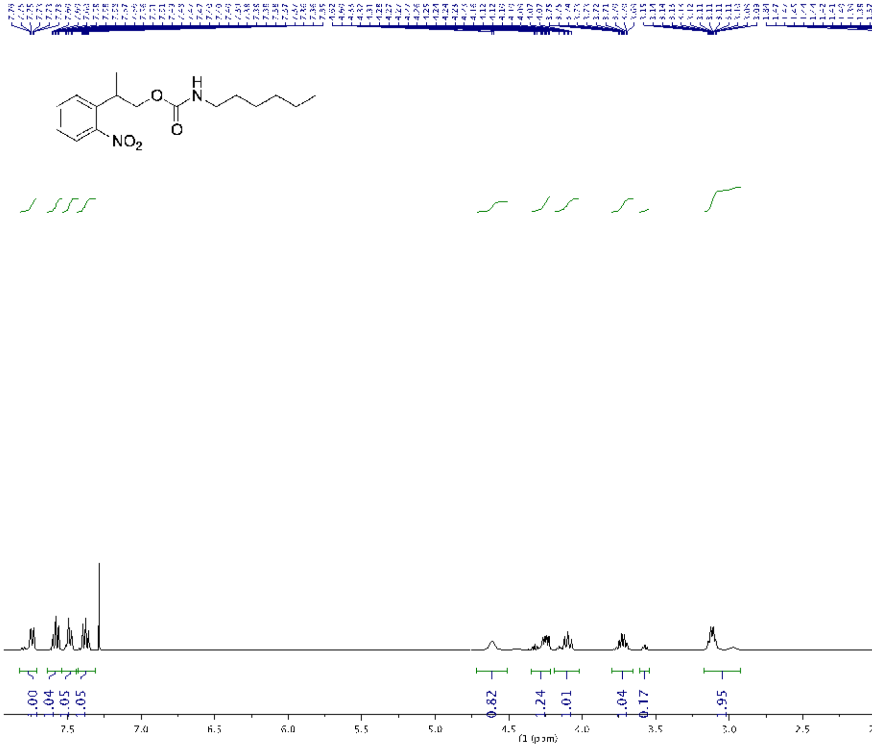
Reference:

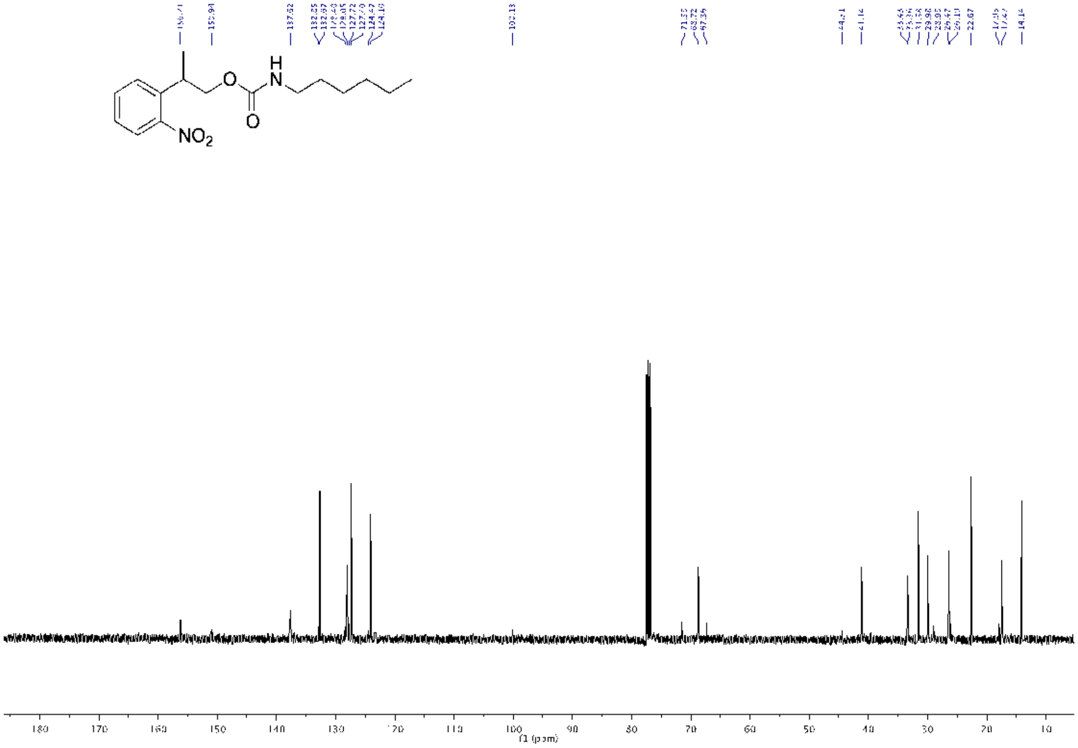
(1) D. Woll, J. Smirnova, M. Galetskaya, T. Prykota, J. Buhler, K. P. Stengele, W. Pfleiderer and U. E. Steiner, *Chem-Eur J*, 2008, **14**, 6490-6497

(2) A. Hasan, K. P. Stengele, H. Giegrich, P. Cornwell, K. R. Isham, R. A. Sachleben, W. Pfleiderer and R. S. Foote, *Tetrahedron*, 1997, **53**, 4247-4264.

(3) S. Ye, N. B. Cramer, B. E. Stevens, R. L. Sani, C. N. Bowman, *Macromolecules* **2011**, 44, 4988.

NMR Spectra

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127.72
124.47
100.13
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68.72
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29.98
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H
N
O
NO2
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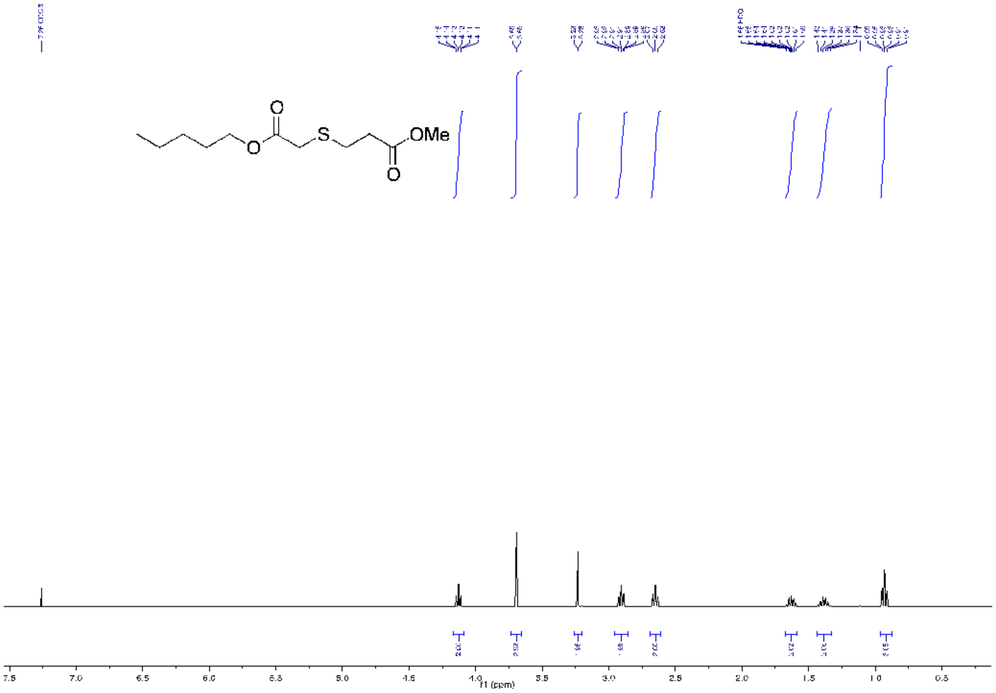
f1 (ppm)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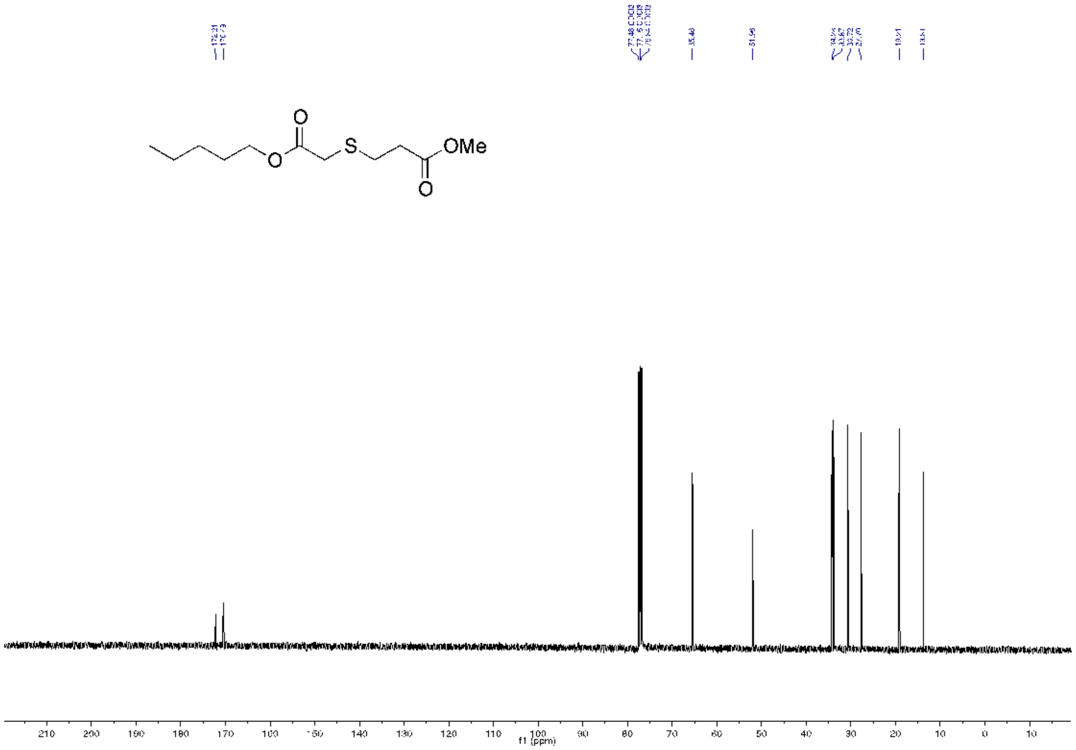
f1 (ppm)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77.48 CDCl3
77.16 CDCl3
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65.43
51.96
34.24
33.67
30.72
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19.21
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200
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180
170
160
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140
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120
110
100
90
80
70
60
50
40
30
20
10
0
10
f1 (ppm)


7.26 CDCl3
3.76
3.75
3.74
3.72
3.70
2.83
2.83
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2.79
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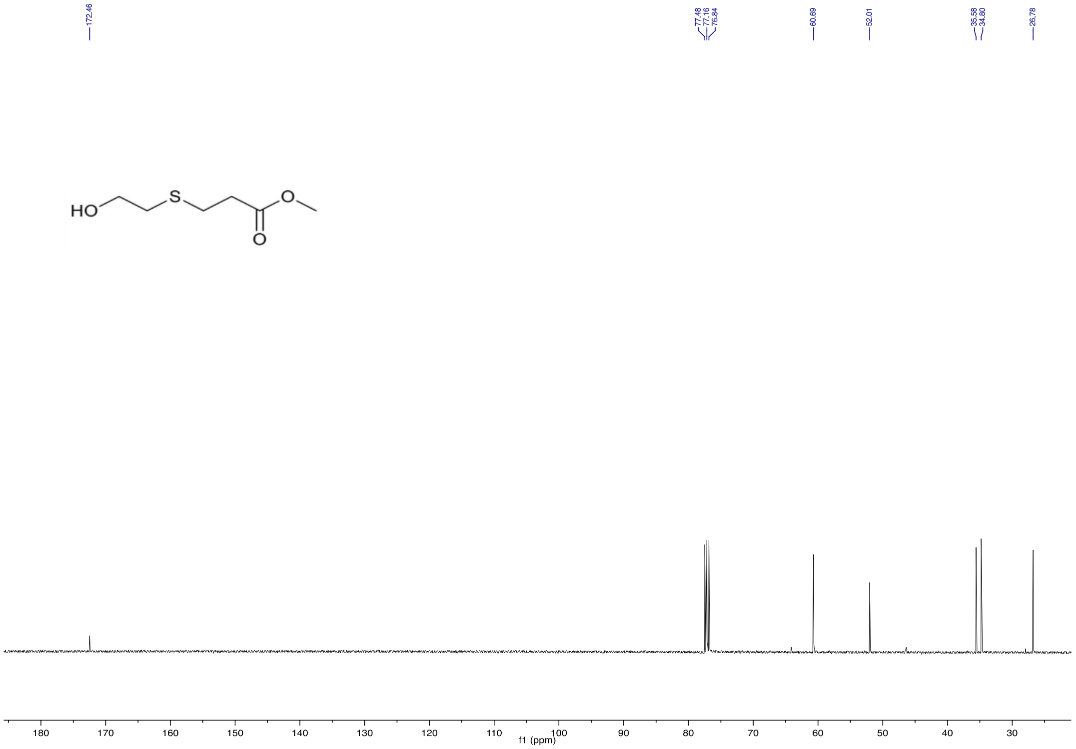
f1 (ppm)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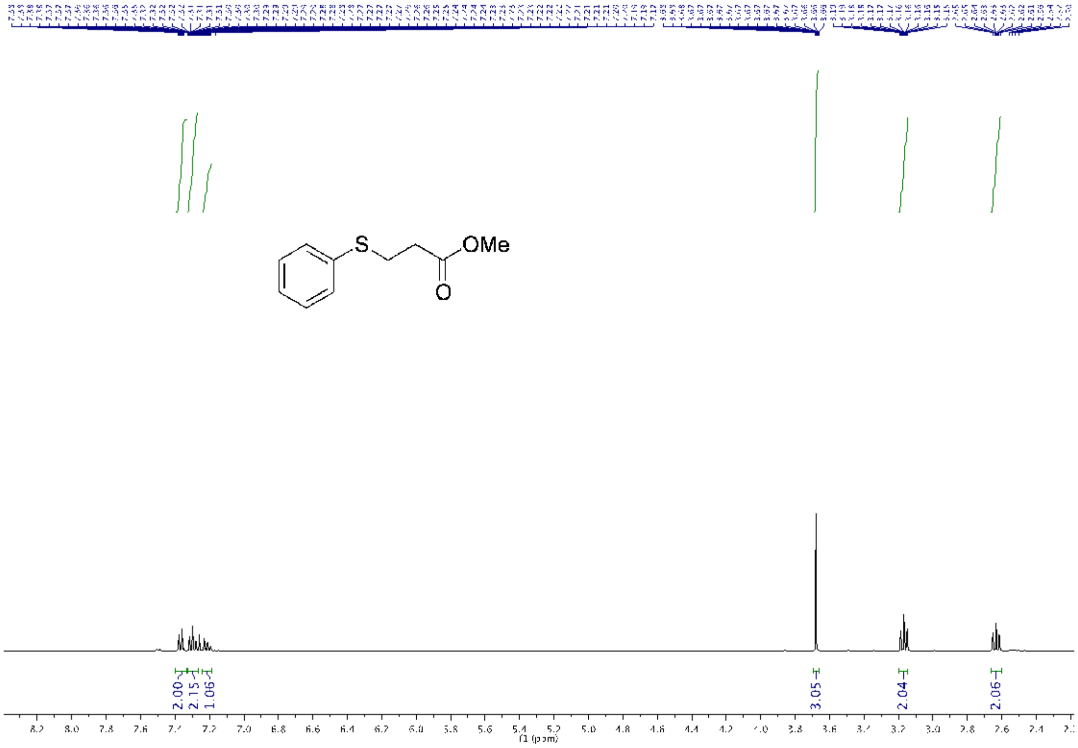
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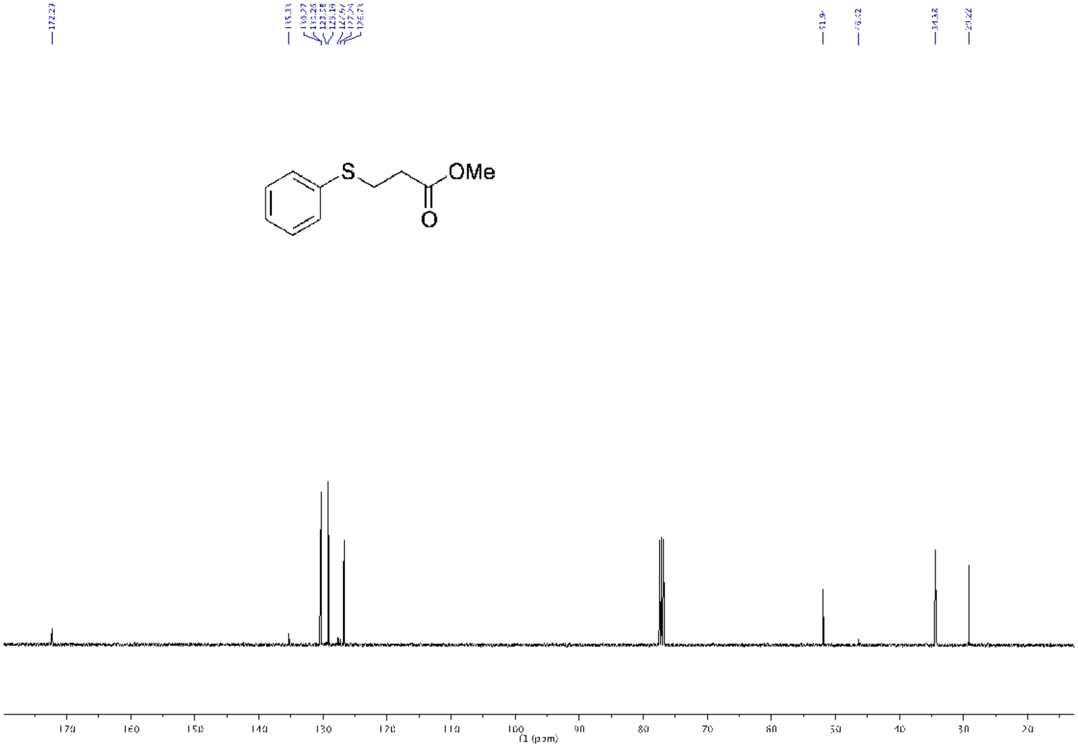
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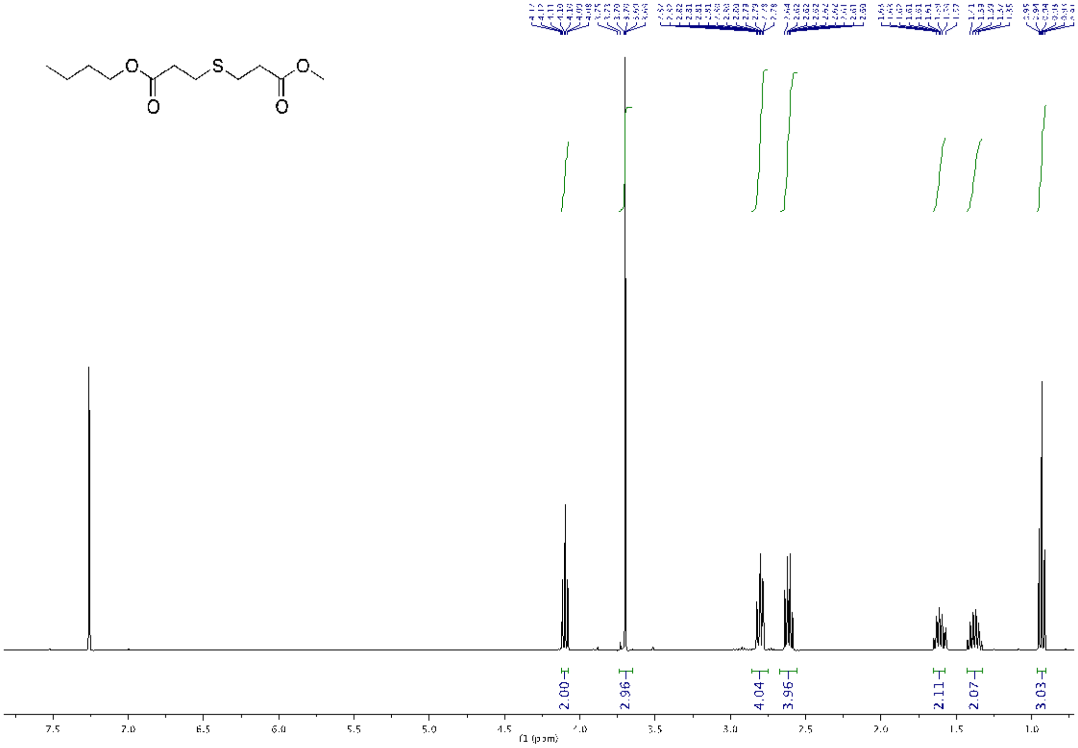
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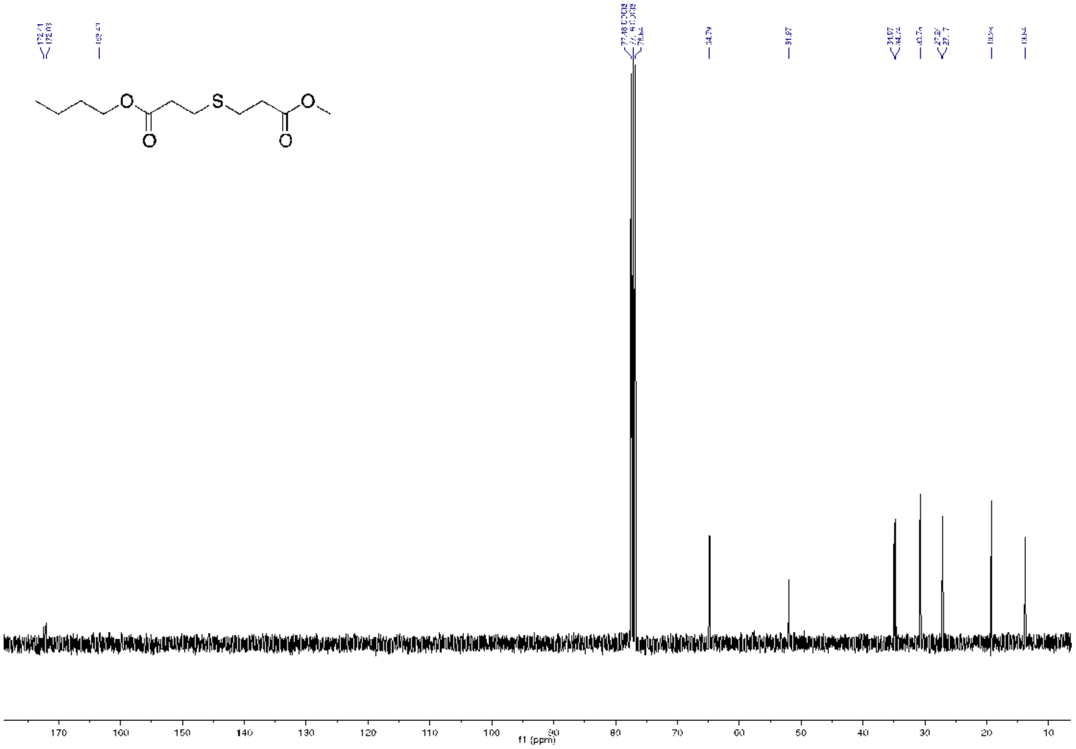
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f1 (ppm)