Supporting Information for

Ketoprofen as Photoinitiator for Anionic Polymerization

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Contents:

Photographic images of photopolymerization process via Method B (solvent-free condition):

Following the photopolymerization procedure described in Method B:

(1) Left vial (marked as A157) contains a mixture of sodium salt of **1** (10 mg) and MA (3.5 mL);

(2) Right vial (marked as B157) contains a mixture of sodium salt of **4** (10 mg) and MA (3.5 mL)

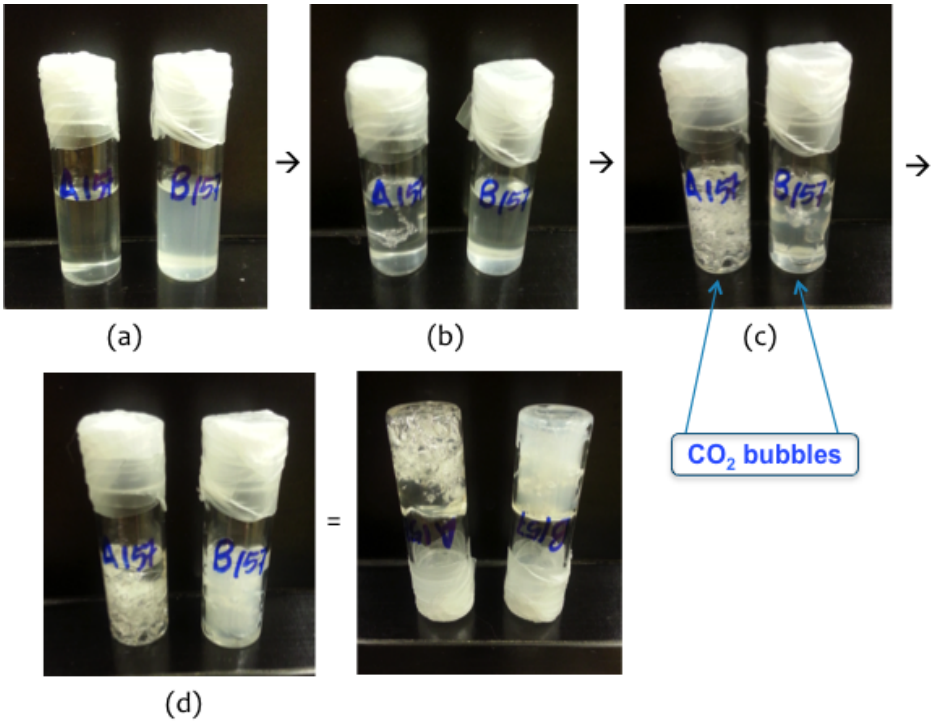
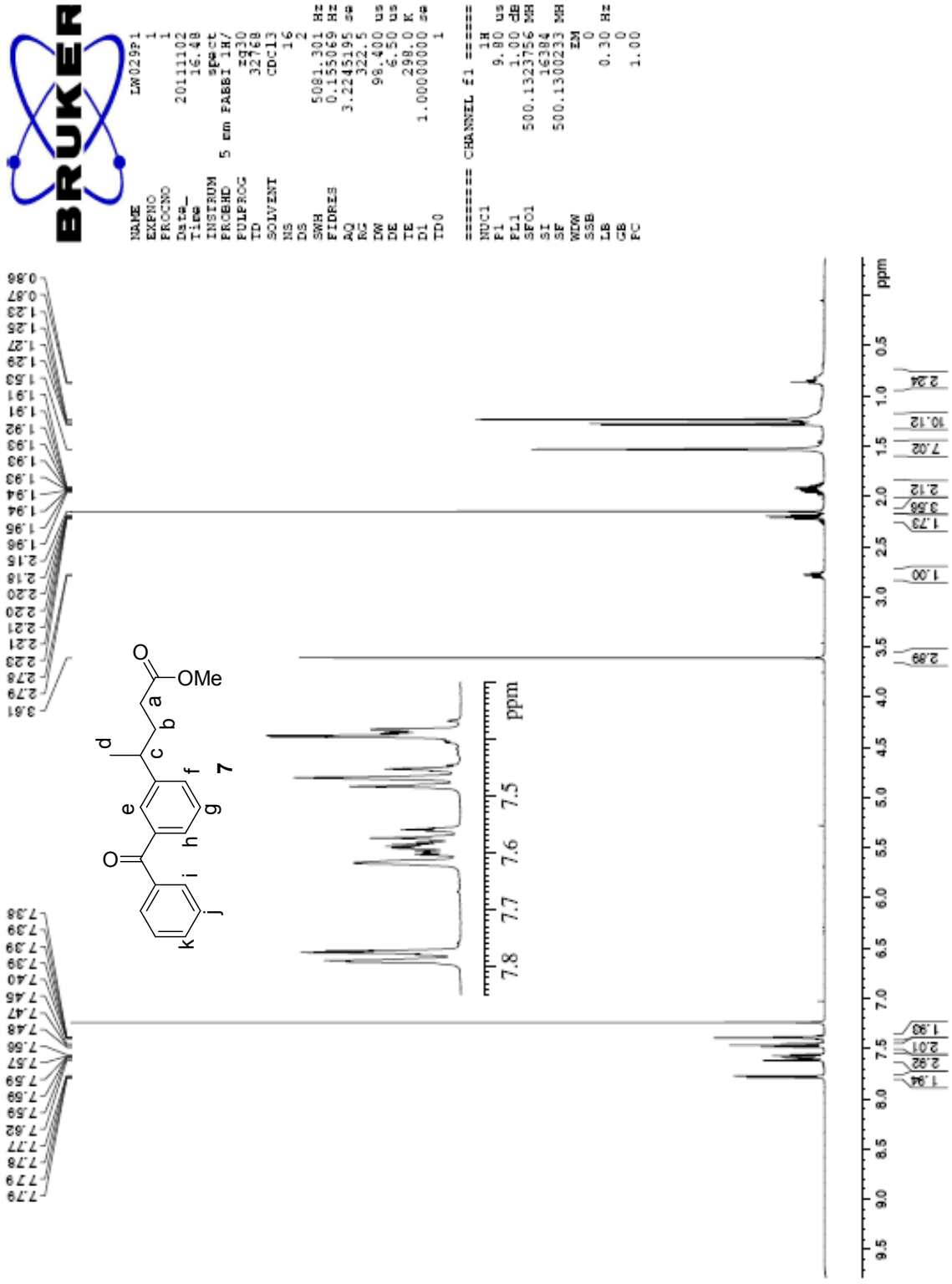
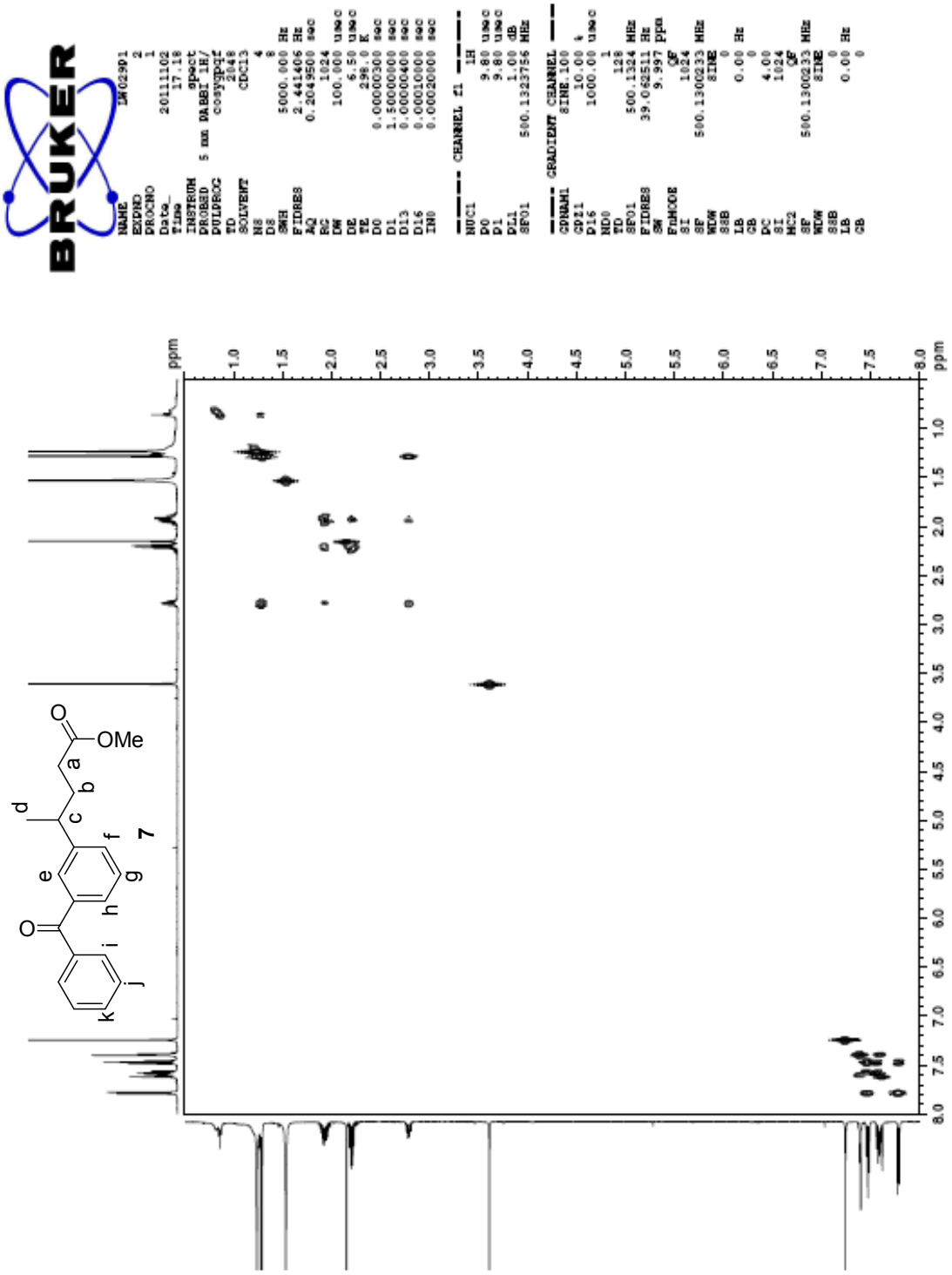


Fig. S1 Photographic images showing formation of polymerization process *via* Method B. (a) before photolysis of sodium carboxylate salts of **1** (left vial) and **4** (right vial) in 3.5 mL of MA; after photolysis (350 nm, N_2-purged) of a mixture for (b) 3 min, (c) 5 min, and (d) 10 min. A significant amount of entrapped gas bubbles (CO_2) was formed accompanying with the formation of PMA, transitioning to a viscous gel into a rubbery solid. Polymers were characterized by GPC analysis (in THF, polystyrene standards): M_n = 16,910 and M_w/M_n = 1.05 for **1**; whereas M_n = 7919 and M_w/M_n = 1.13 for **4**.

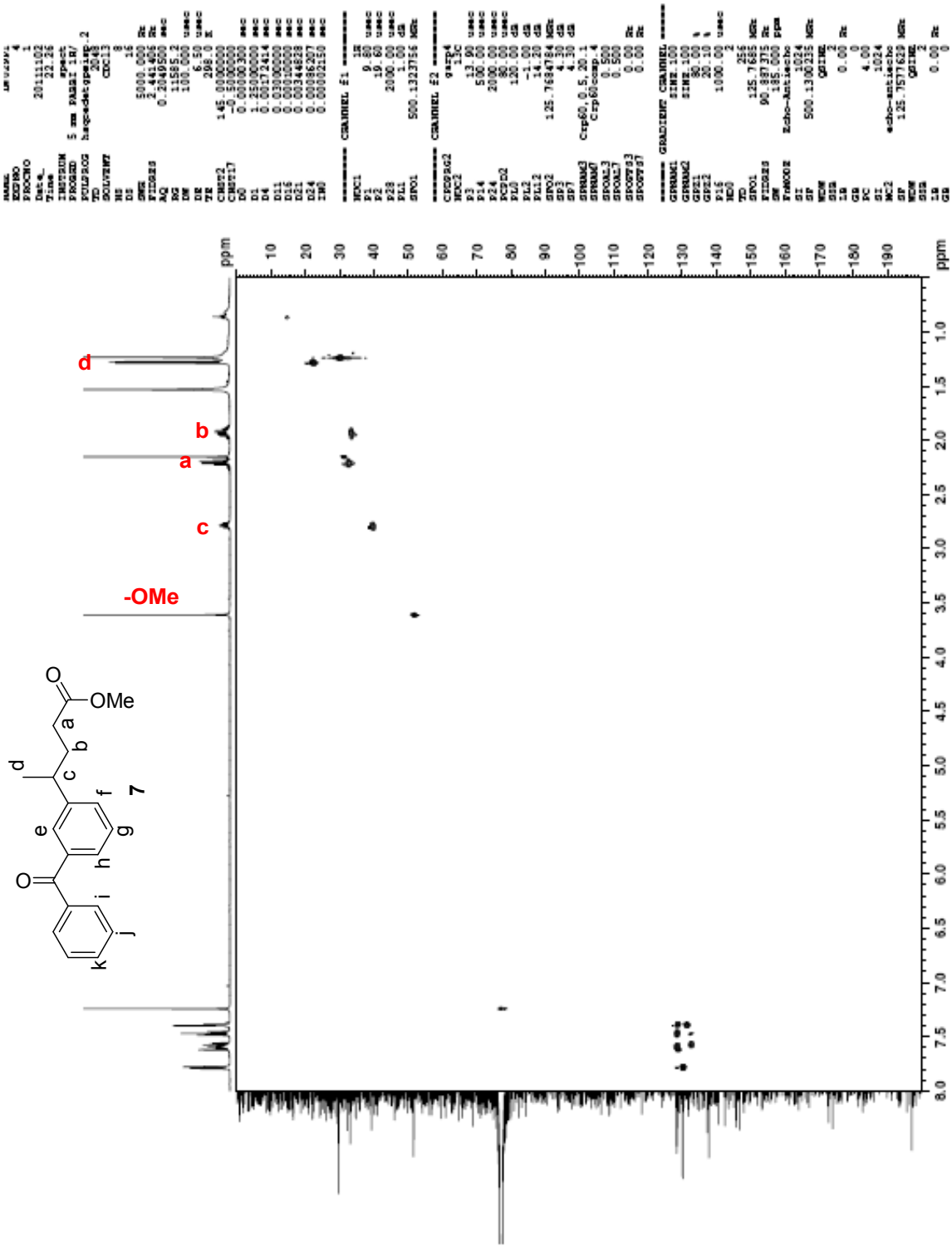
^{1}H-NMR spectra (500 MHz, $CDCl_3$) of 7:



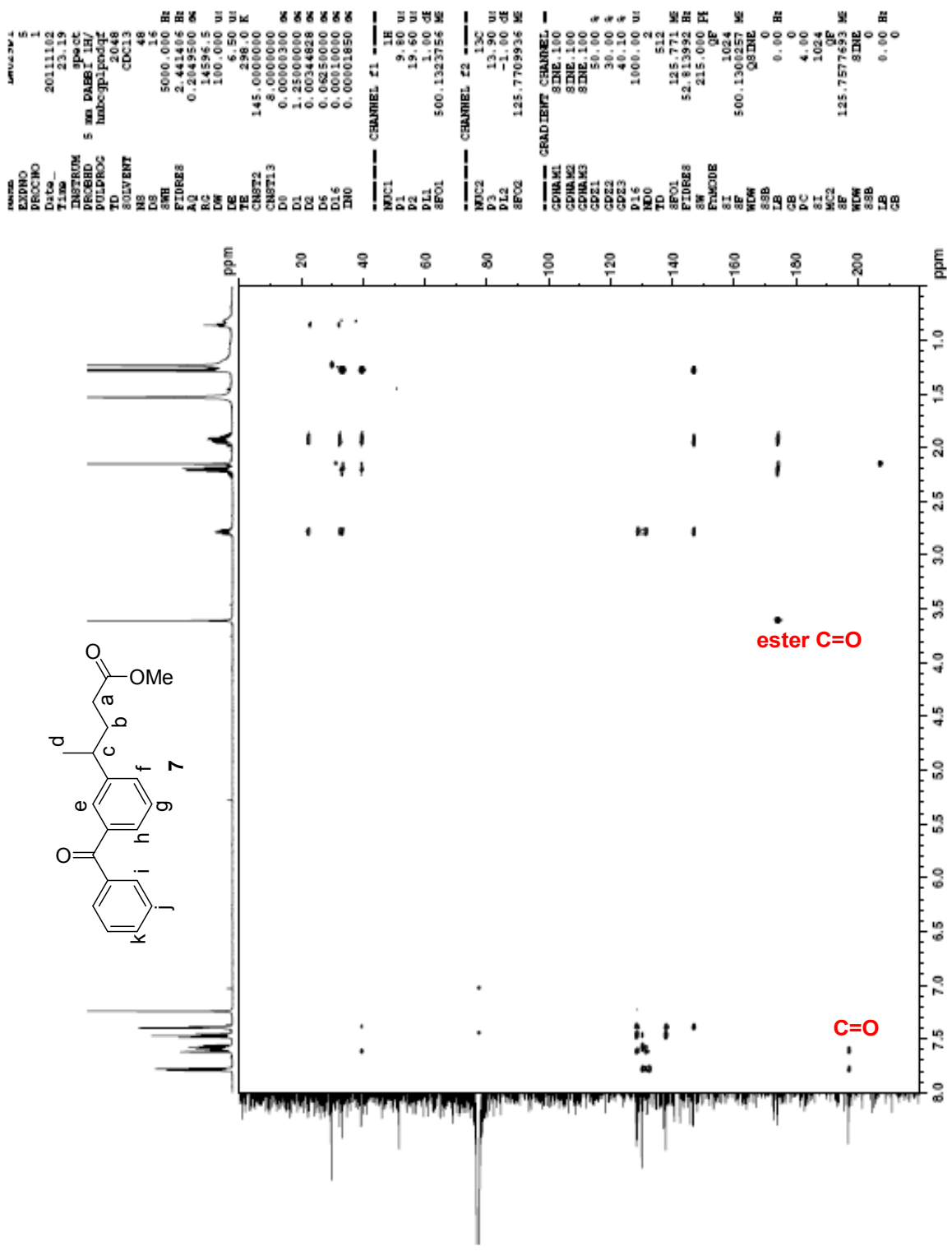
gCOSY spectrum of 7 in $CDCl_3$:



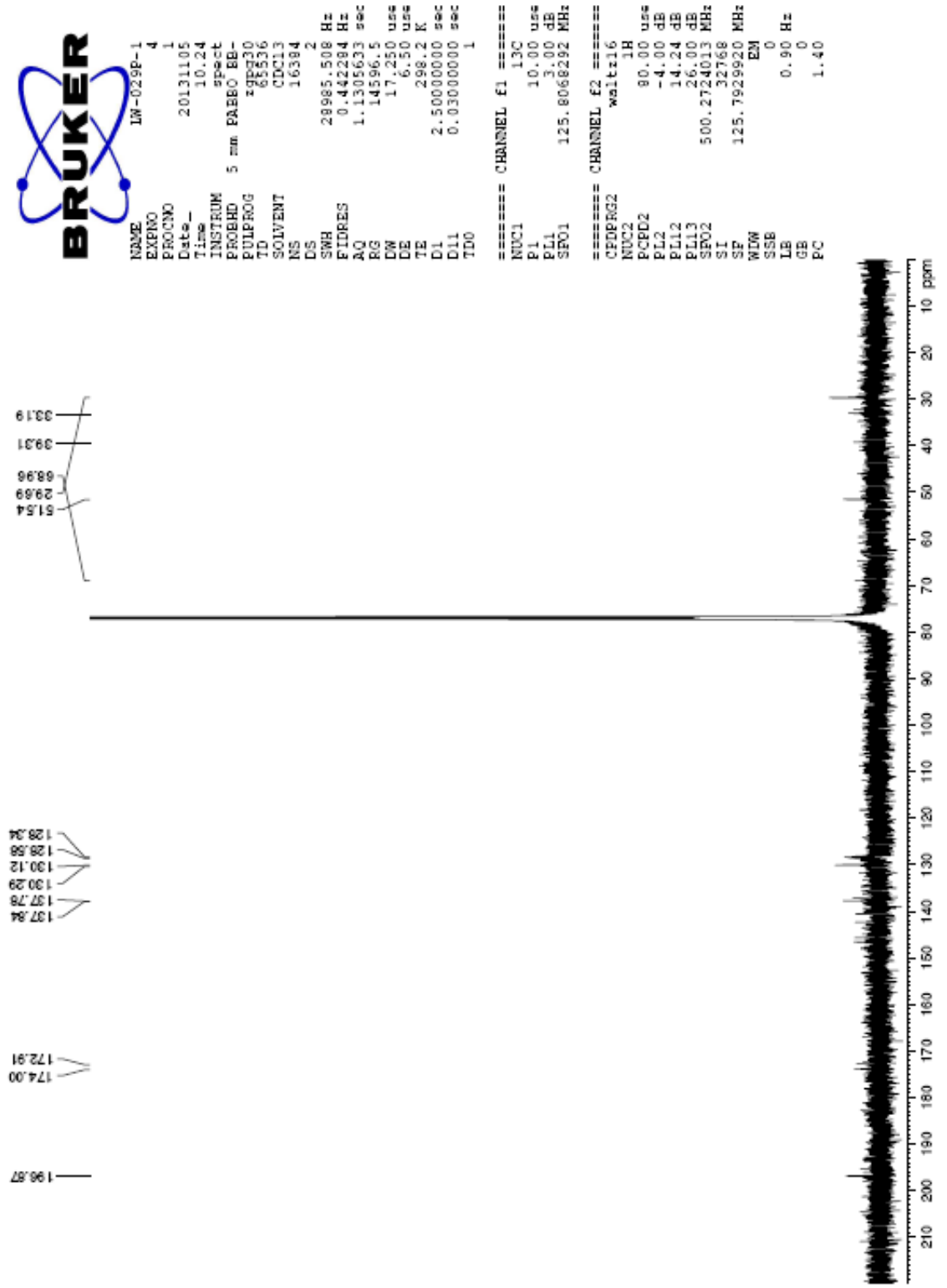
gHSQC spectrum of 7 in $CDCl_3$:



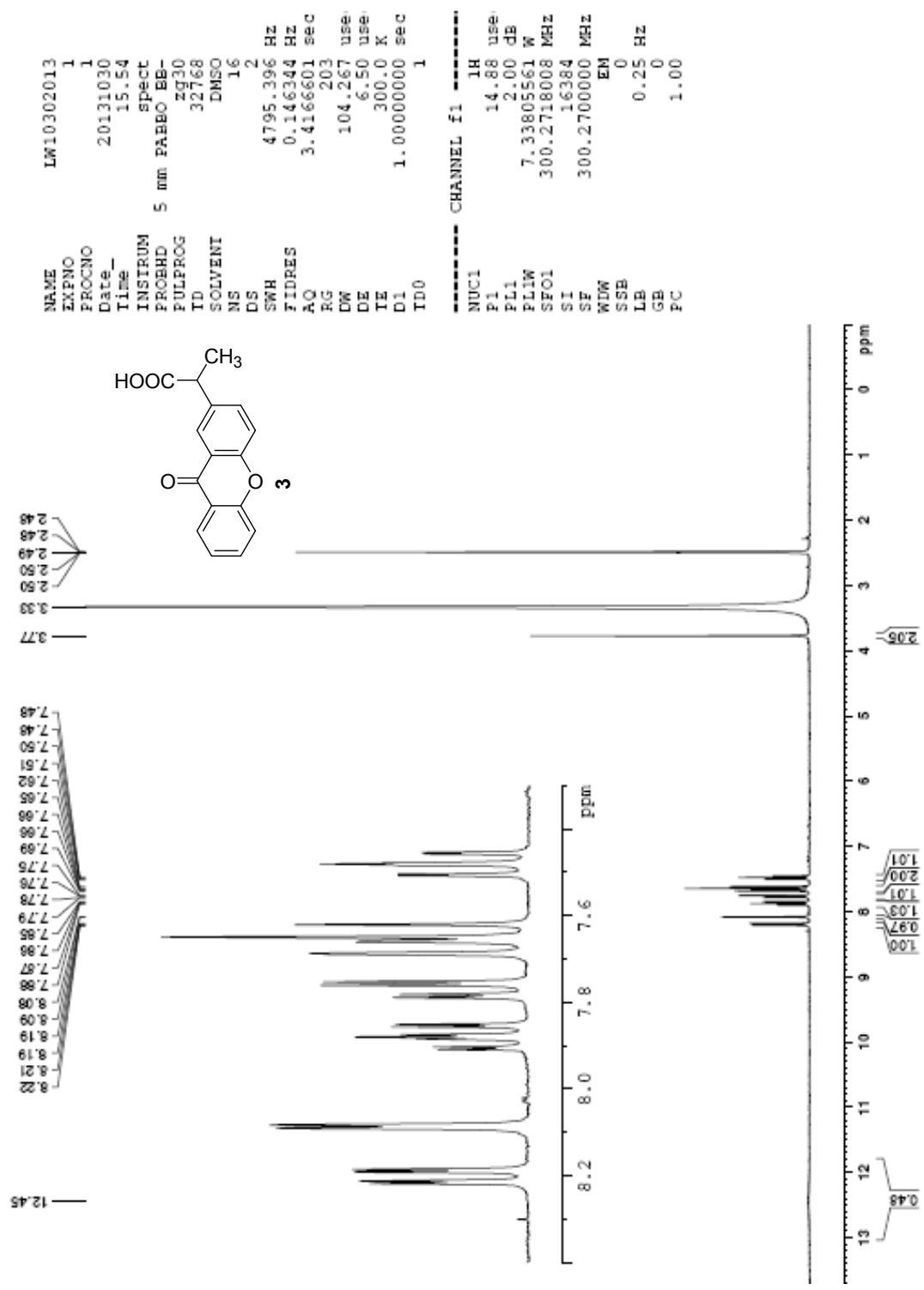
gHSQC spectrum of 7 in $CDCl_3$:



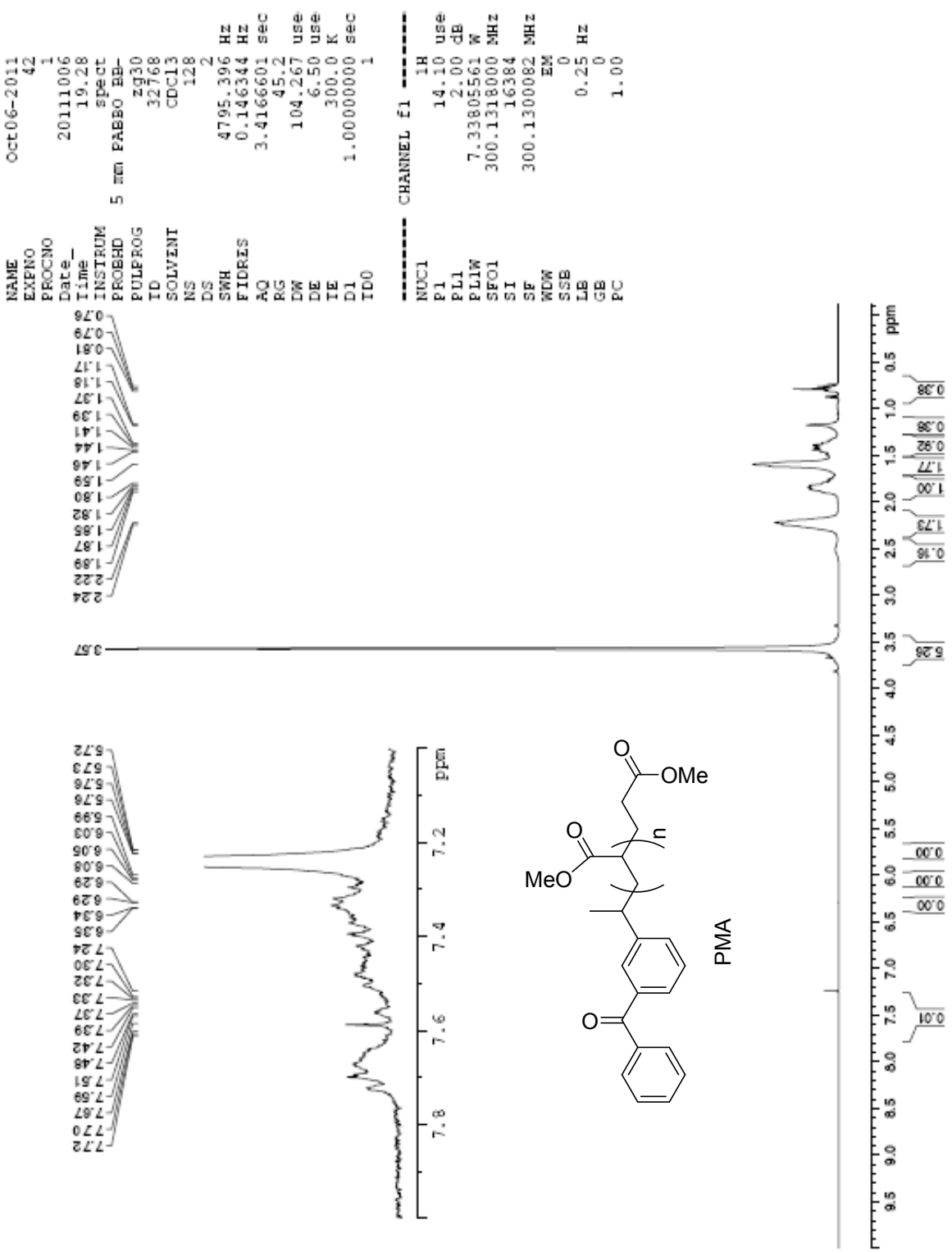
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 7:



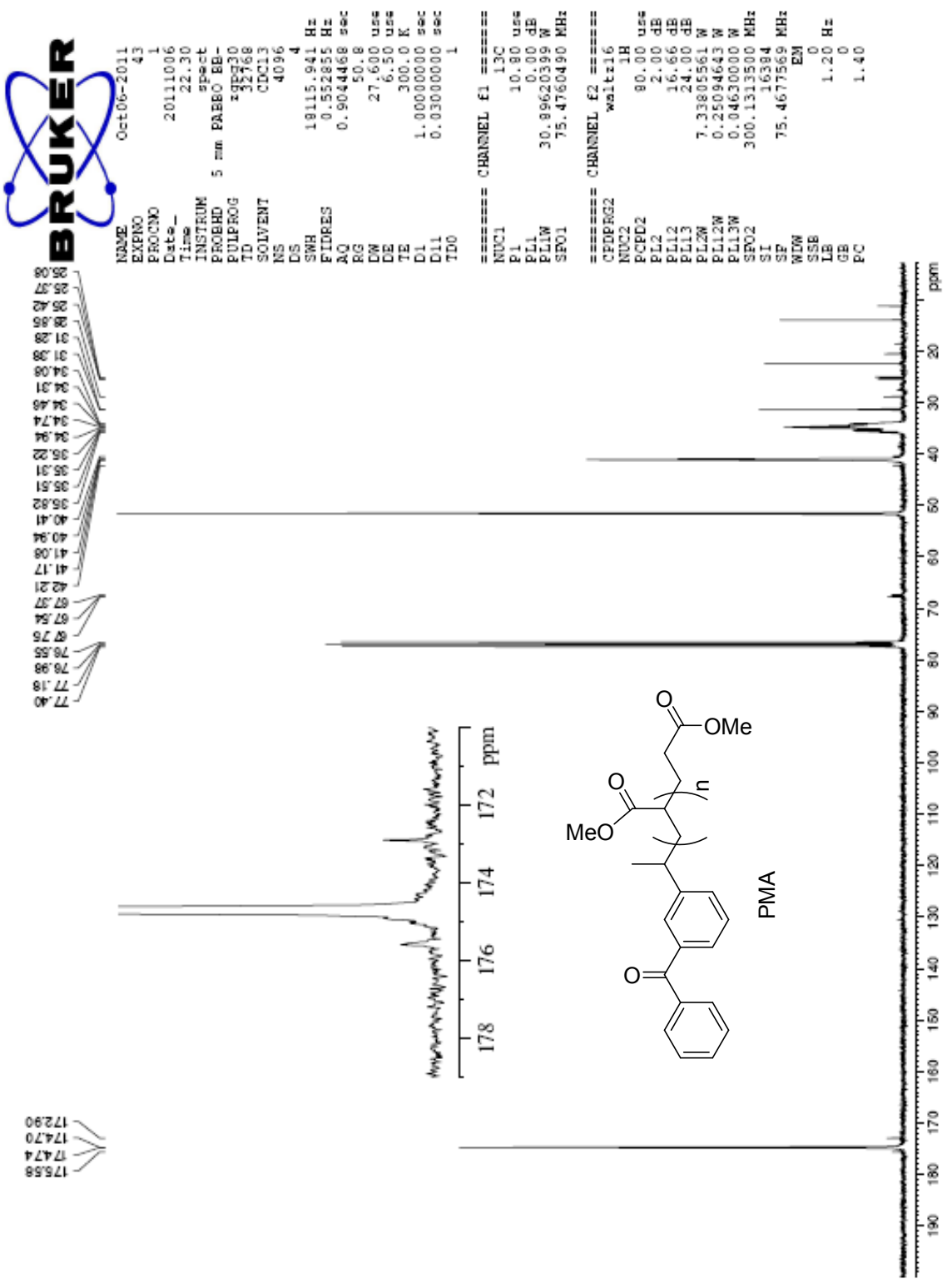
[1]H-NMR (300 MHz, DMSO-d6) spectrum of 3 before photolysis:



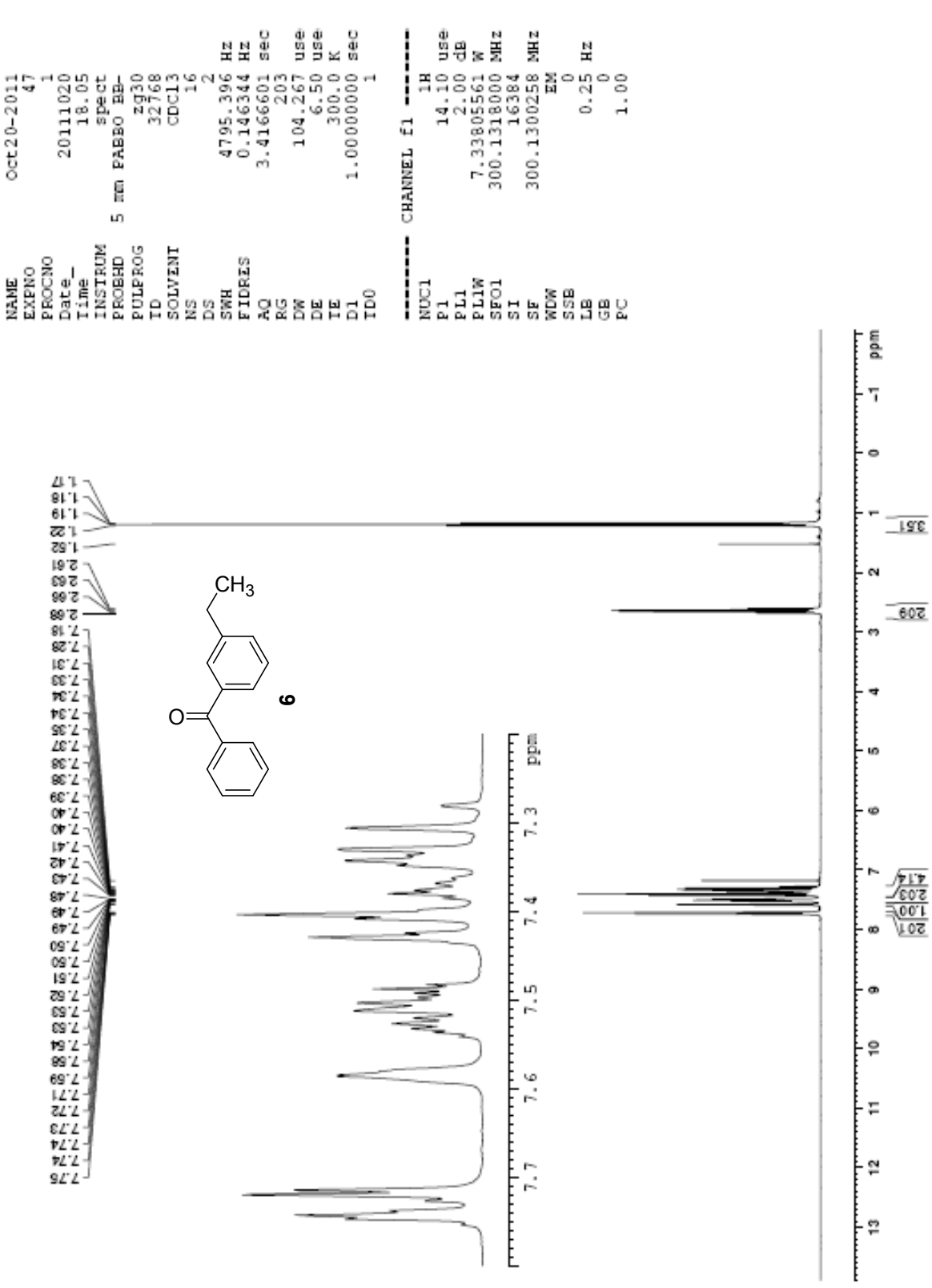
Representative ^{1}H-NMR spectra of PMA:



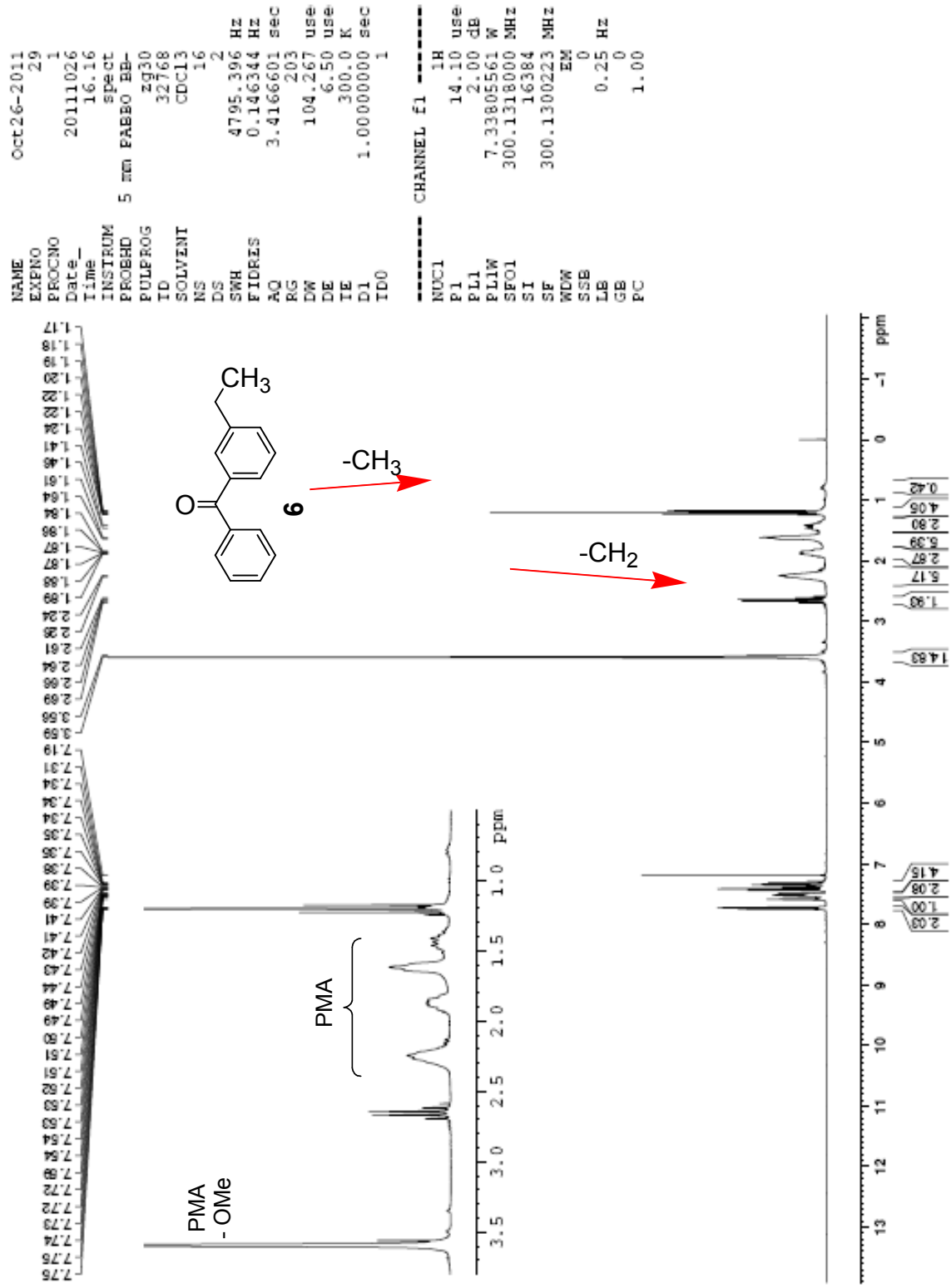
Representative ^{13}C-NMR spectra of PMA:



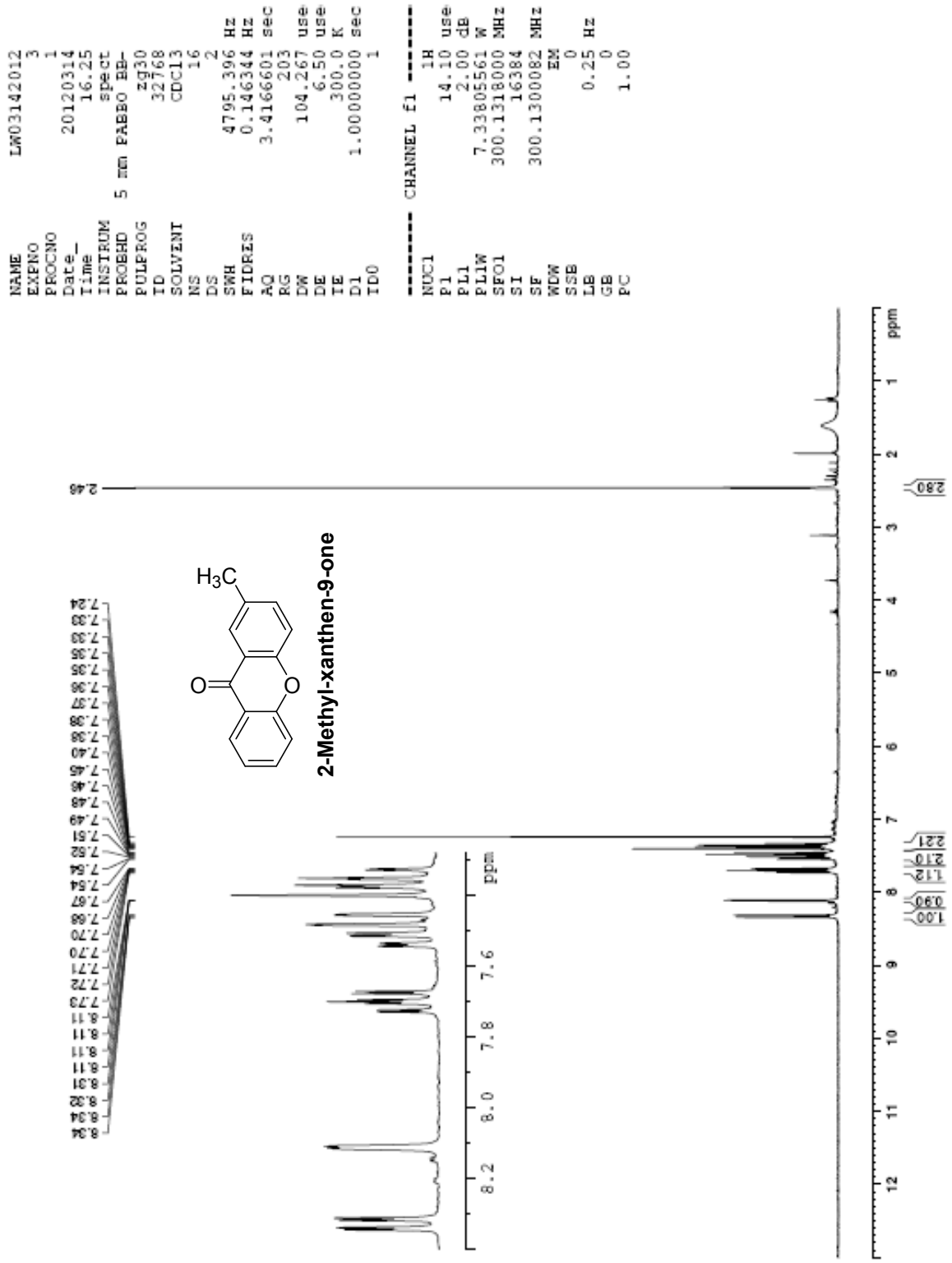
[1]H-NMR spectra of compound 6:



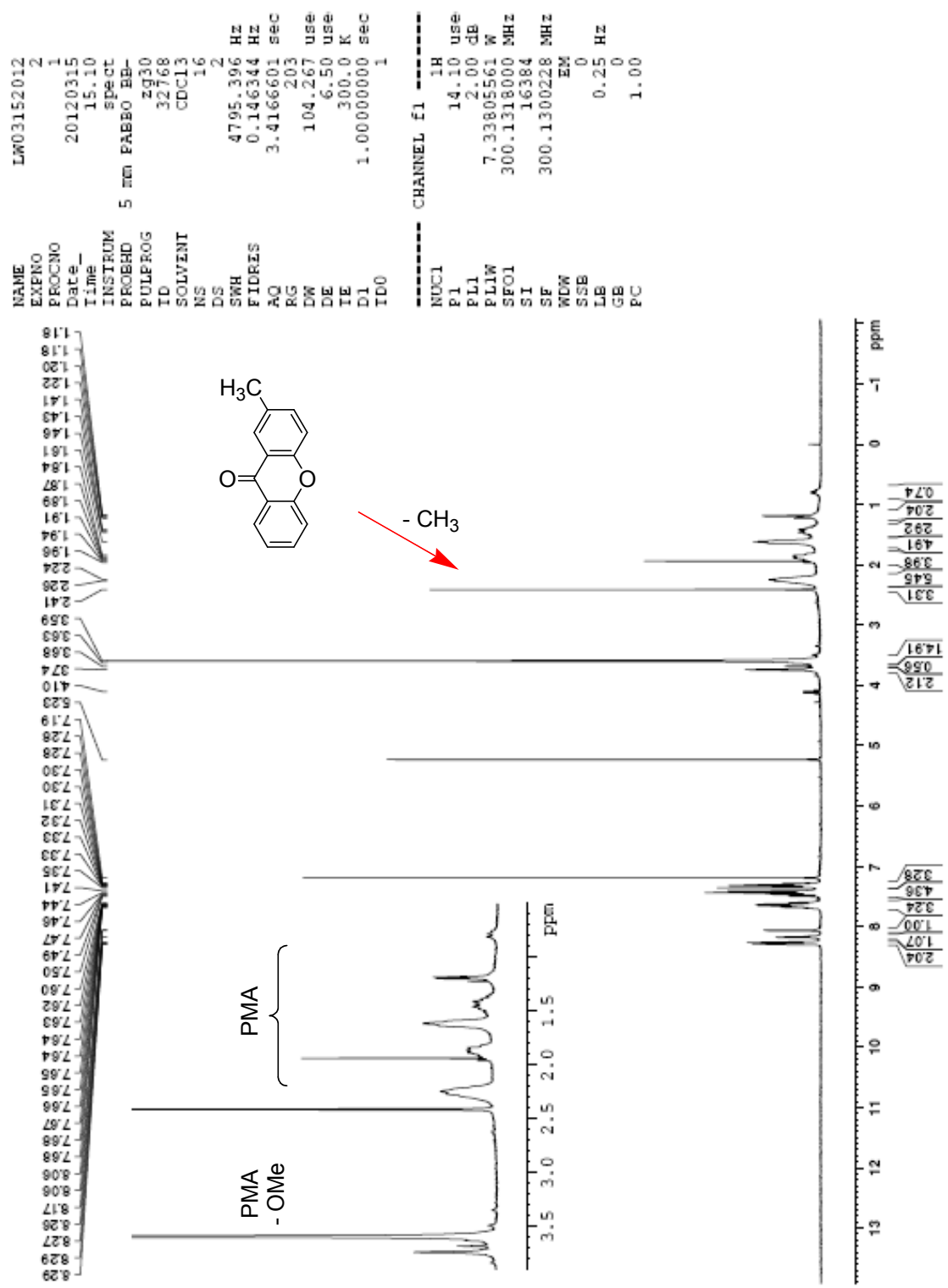
^{1}H-NMR after photolysis of KP and MA (0.25% v/v NaOH/CH_3CN, 5 min):



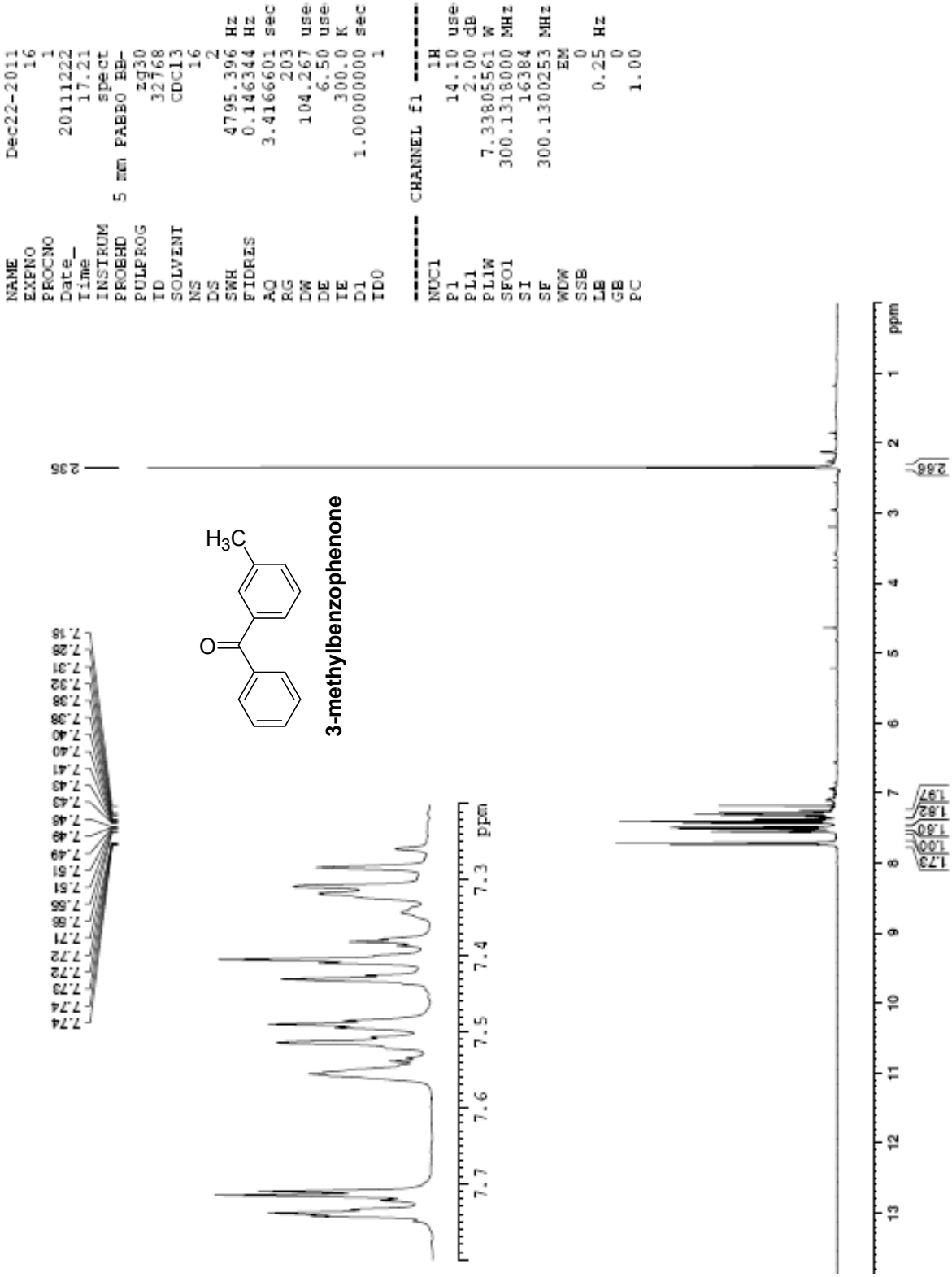
[1]H-NMR after photolysis of 3 without addition of MA (0.25% v/v NaOH/CH_3CN, 5 min):



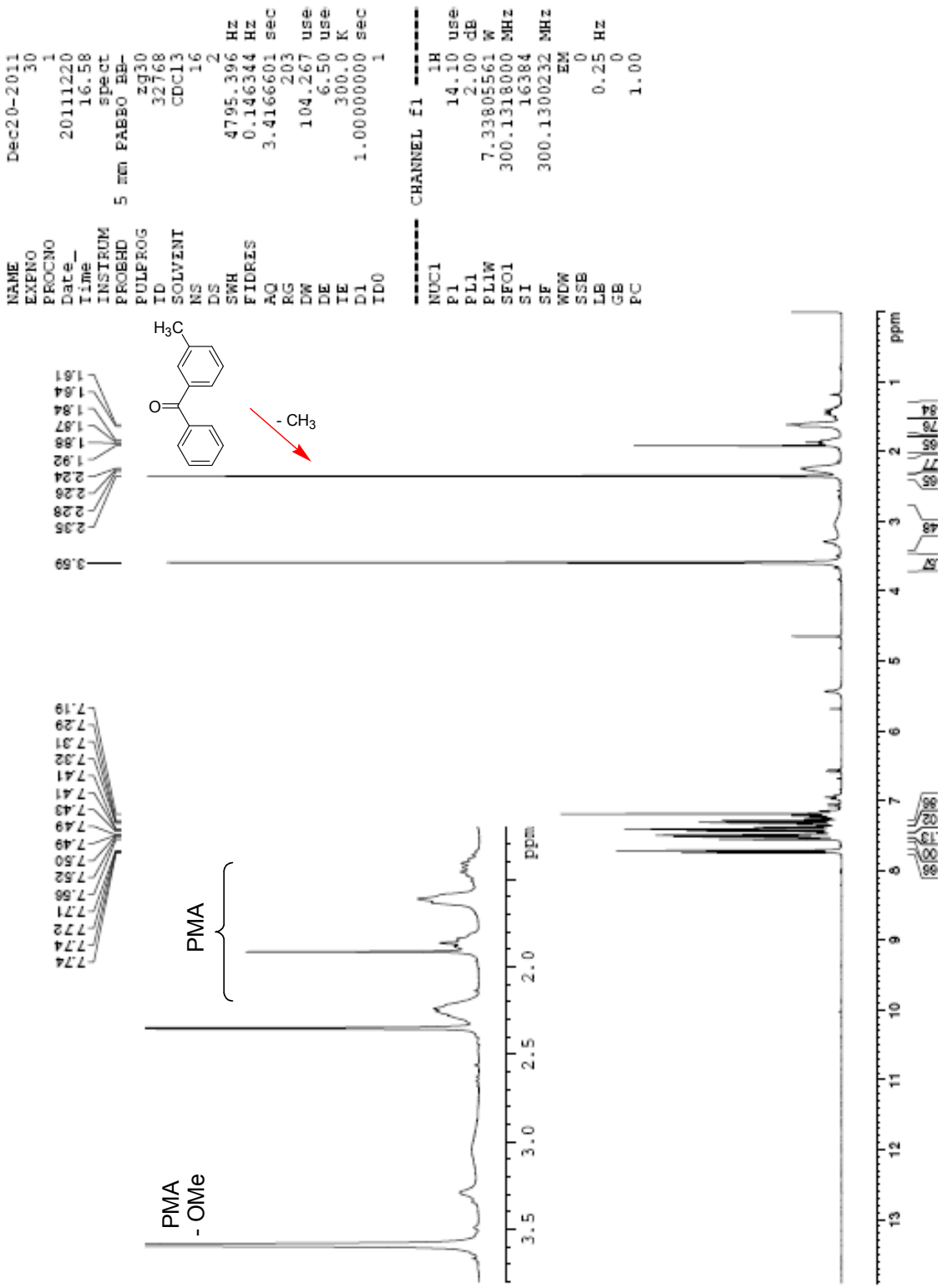
^{1}H-NMR after photolysis of 3 and MA (0.25% v/v NaOH/CH_3CN, 5 min):



[1]H-NMR after photolysis of 4 without addition of MA (0.25% v/v NaOH/CH_3CN, 5 min):



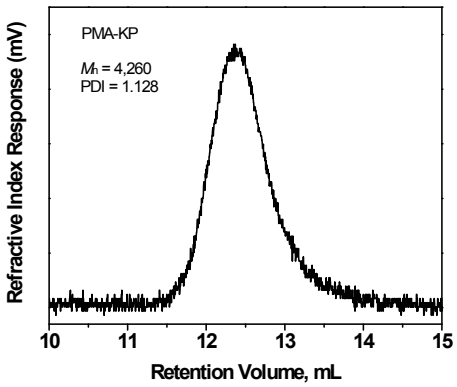
[1]H-NMR after photolysis of 4 and MA (0.25% v/v NaOH/CH_3CN, 5 min):



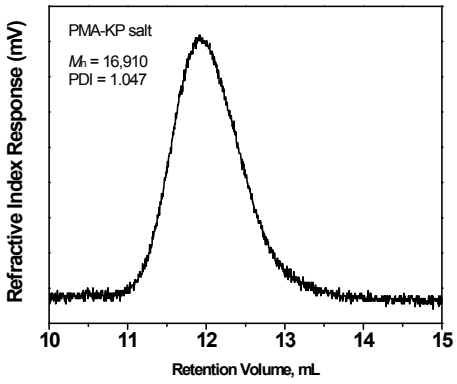
Gel Permeation Chromatography (GPC) Analyses: GPC measurements were performed using a Viscotek model 302 liquid chromatography system equipped with refractive index (RI), low-angle light scattering (LALS, θ = 7°), right-angle light scattering (RALS, θ = 90°), and UV detectors. THF was used as the eluent at a flow rate of 1 mL/min, and the column temperature was set at 35 °C. All polymer solutions were filtered through membrane filters with a nominal pore size of 0.45 μm before injection into the GPC column. The data were collected and analyzed on a Dell Dimension 2300 computer with appropriate GPC software from Viscotek. Two ViscoGEL HR high-resolution columns (styrene-divinylbenzene columns) in series were used: G3000 HR 60 k and GMHHR-MMixed Bed 4 M columns. The molecule weight distribution for the PMA polymer was determined from GPC data using an algorithm from Viscotek, which relies on LALS detection from a 670 nm diode laser source.

Representative gel permeation chromatograms (refractive index detector response) of PMA by different initiators *via* indicated method:

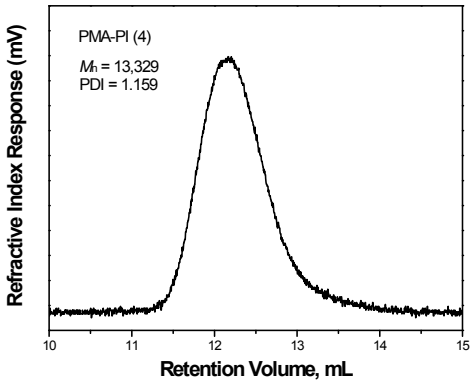
(a) KP as initiator *via* Method A



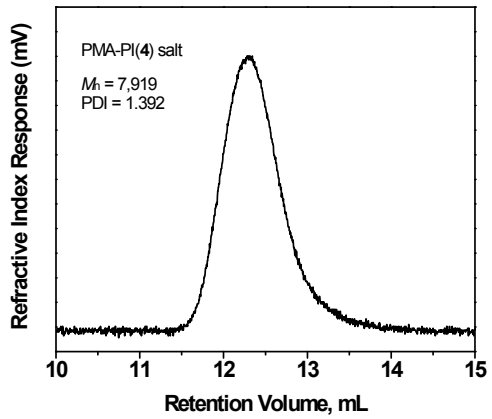
(b) KP carboxylate salt as photoinitiator *via* Method B



(c) PI **4** as initiator *via* Method A

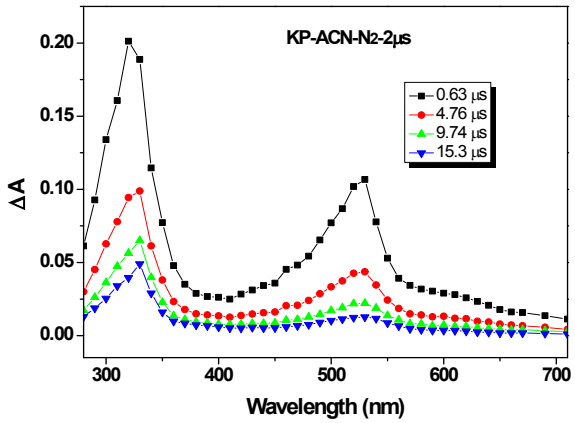


(d) PI **4** carboxylate salt as initiator *via* Method B

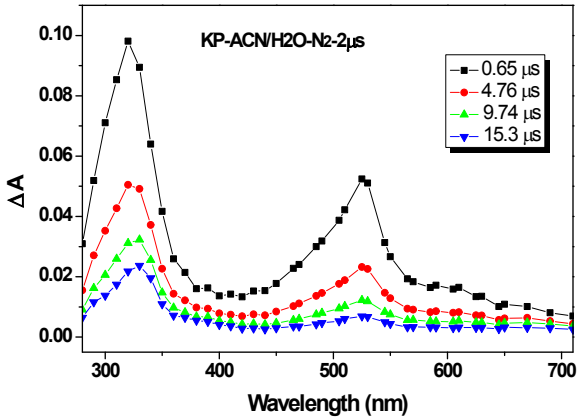


Transient absorption spectra observed for KP in various solvents:

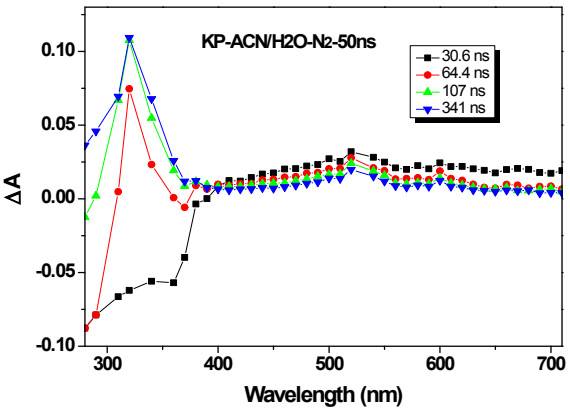
(a) CH_3CN under N_2-purged



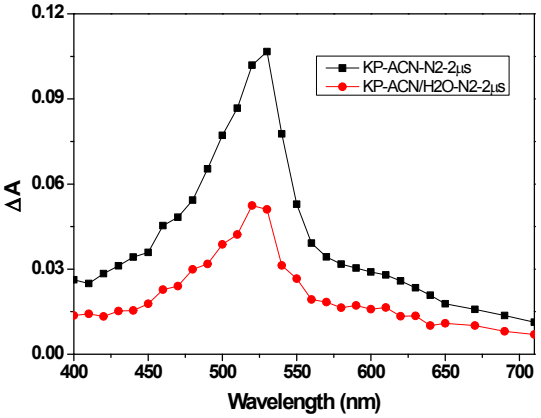
(b) 0.25 %$NaOH_{(aq)}$/ CH_3CN, N_2-purged



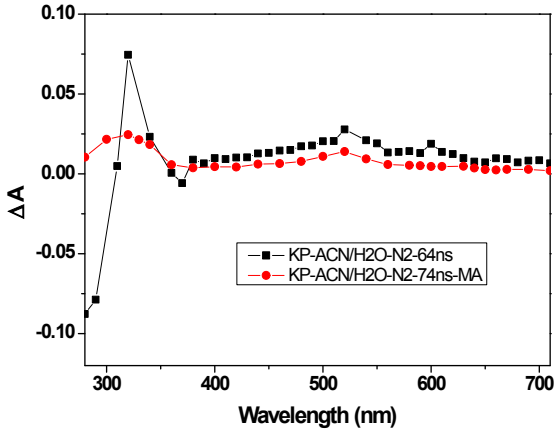
(c) 0.25%$NaOH_{(aq)}$/ CH_3CN, N_2-purged



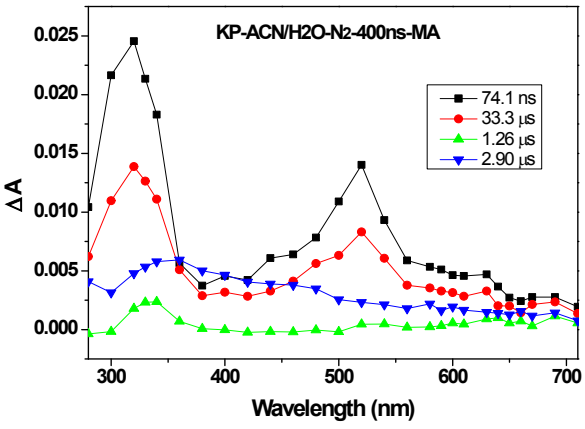
(d) CH_3CN vs. 0.25%$NaOH_{(aq)}$/ CH_3CN



(f) without vs. with MA



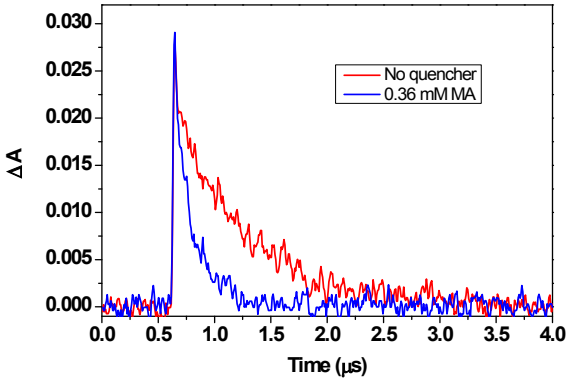
(g) addition of MA to $NaOH_{(aq)}$/CH_3CN



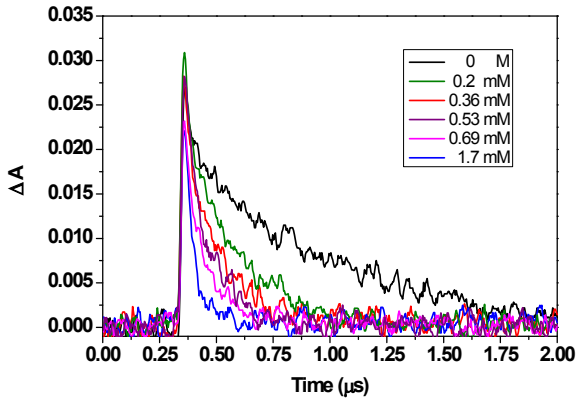
Quenching Experiments:

A. Decay of the signal at 600 nm, without quencher and after adding methyl acrylate (MA) to Ketoprofen in 0.25% v/v $NaOH_{(aq)}/CH_3CN$. Without the quencher, the lifetime of KP carbon anion in 0.25% v/v $NaOH_{(aq)}/CH_3CN$ is 622 ns; $k_q = 1.20 \times 10^{10}$ $lmol^{-1}s^{-1}$

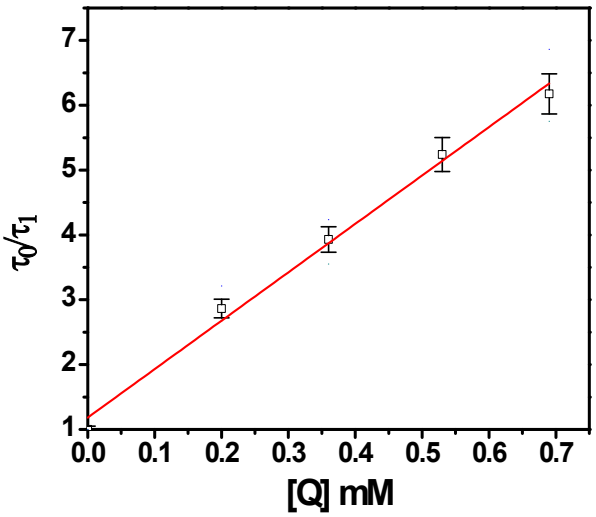
(a) after delay time of 400 ns



(b) after delay time of 200 ns

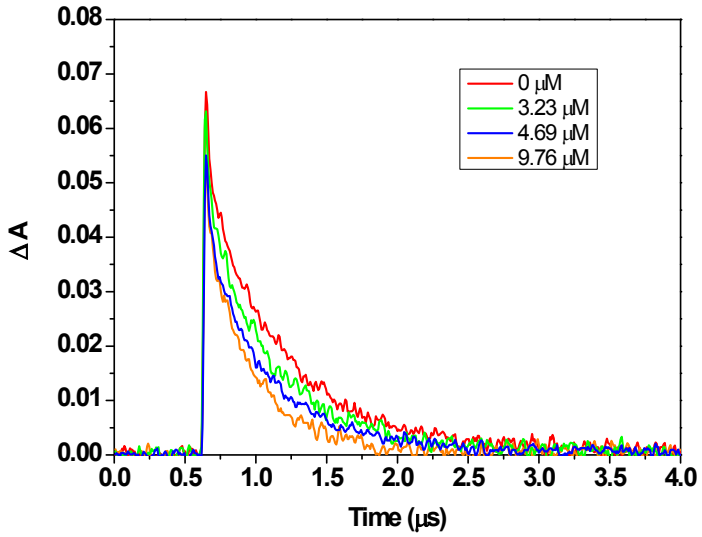


(b) Stern-Volmer plot: quenching rate constant of each decay as a function of quencher (methyl acrylate) concentration [Q]:



B. Decay of the signal at 600 nm, without quencher and after adding methyl methacrylate (MMA) to Ketoprofen in 0.25% v/v $NaOH_{(aq)}/CH_3CN$. Without the quencher, the lifetime of KP carbon anion in 0.25% v/v NaOH(aq)/ACN is 579 ns; $k_q = 1.24\times10^{11}$ $lmol^{-1}s^{-1}$

(a) after delay time of 400 ns



(b) Stern-Volmer plot: quenching rate constant of each decay as a function of quencher methyl methacrylate (MMA) concentration [Q].