

Supporting Information for

Ketoprofen as Photoinitiator for Anionic Polymerization

Yu-Hsuan Wang and Peter Wan

Department of Chemistry, Box 3065, University of Victoria,

British Columbia, Canada, V8W 3V6

Fax: +1 (250) 721-7147; Tel: +1(250) 721-8976; E-mail: pwan@uvic.ca

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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)

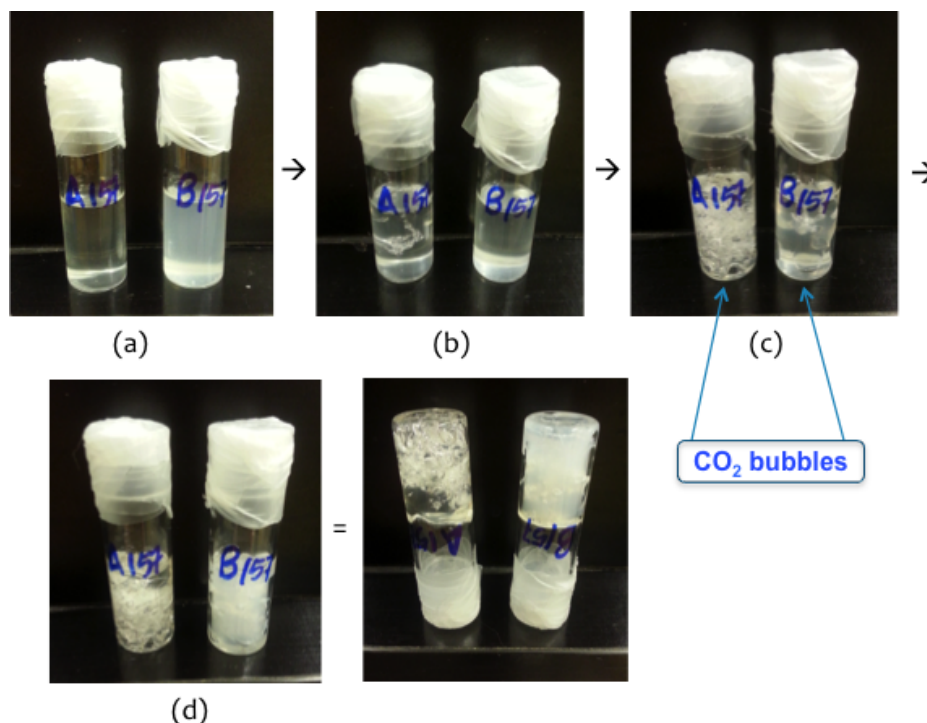


Fig. S1 Photographic images showing formation of polymerization process *via* Method B. (a) before photolysis of sodium carboxylate salts of **1** (left vial) and **4** (right vial) in 3.5 mL of MA; after photolysis (350 nm, N₂-purged) of a mixture for (b) 3 min, (c) 5 min, and (d) 10 min. A significant amount of entrapped gas bubbles (CO₂) 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**.

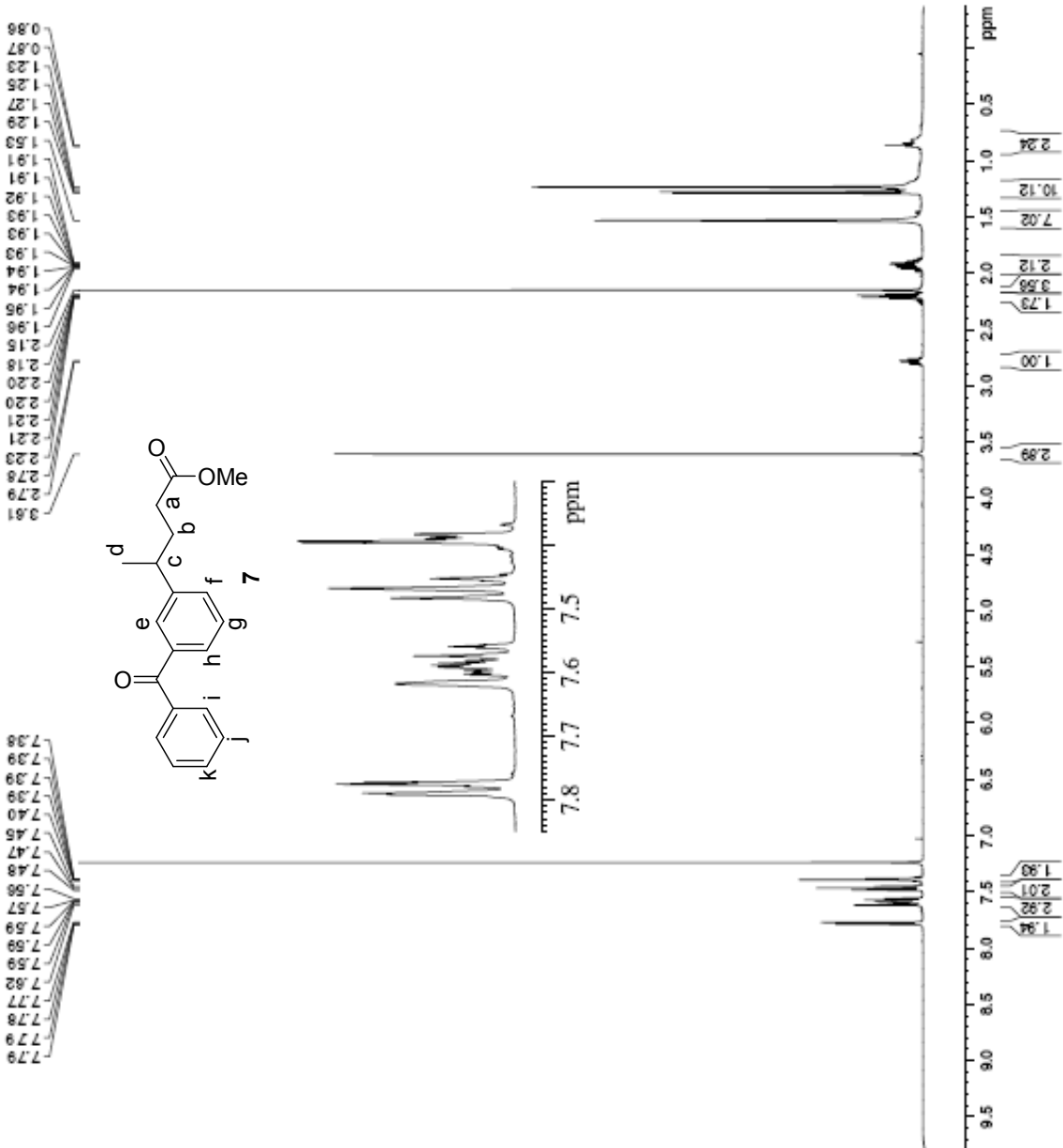
¹H-NMR spectra (500 MHz, CDCl₃) of 7:



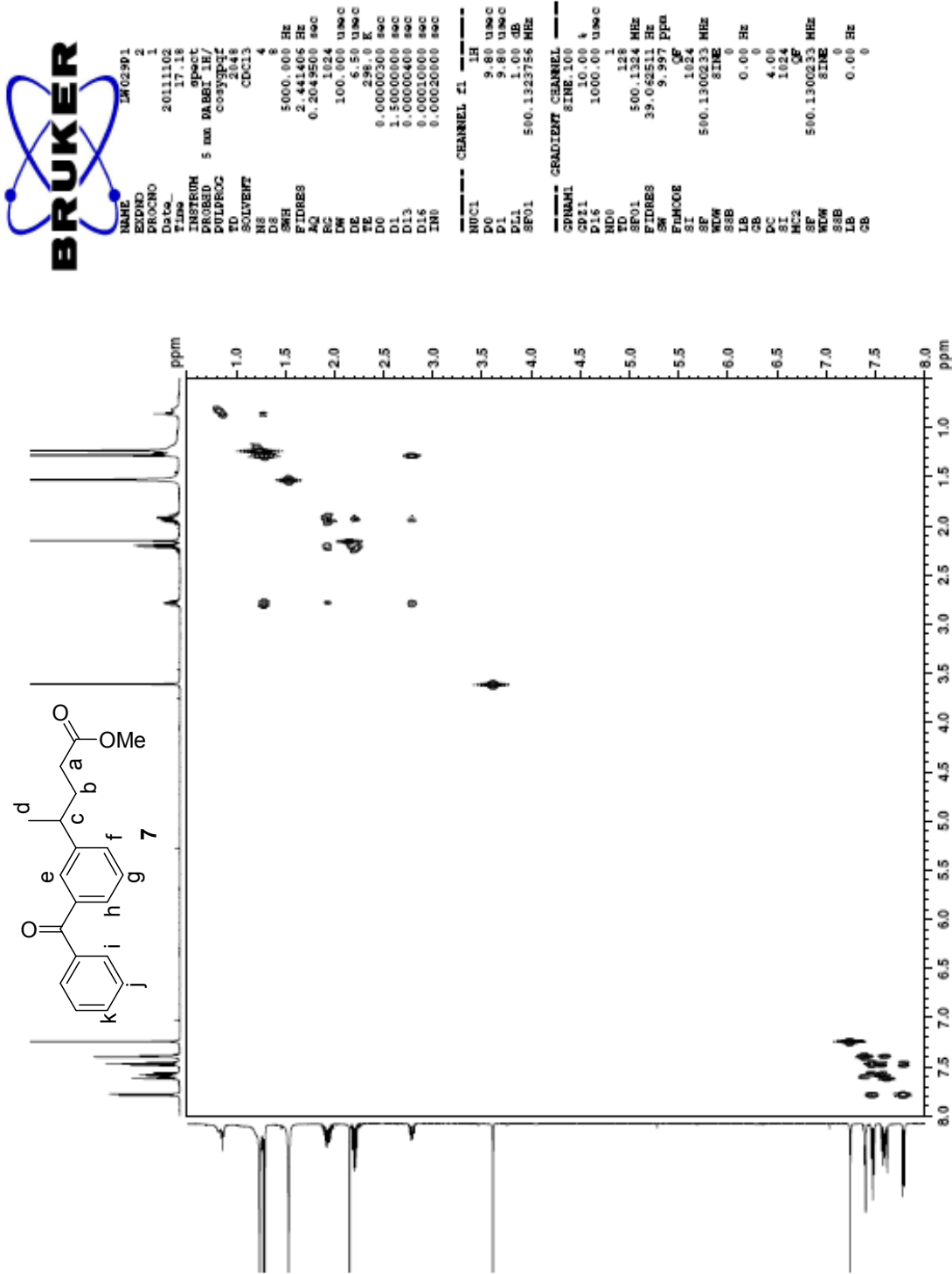
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PROCNO        1
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PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           5081.301 Hz
FIDRES        0.155069 Hz
AQ            3.224519 s
RG            322.5
DQ            98.400 us
DE            6.50 us
TE            298.0 K
D1            1.00000000 s
TD0           1

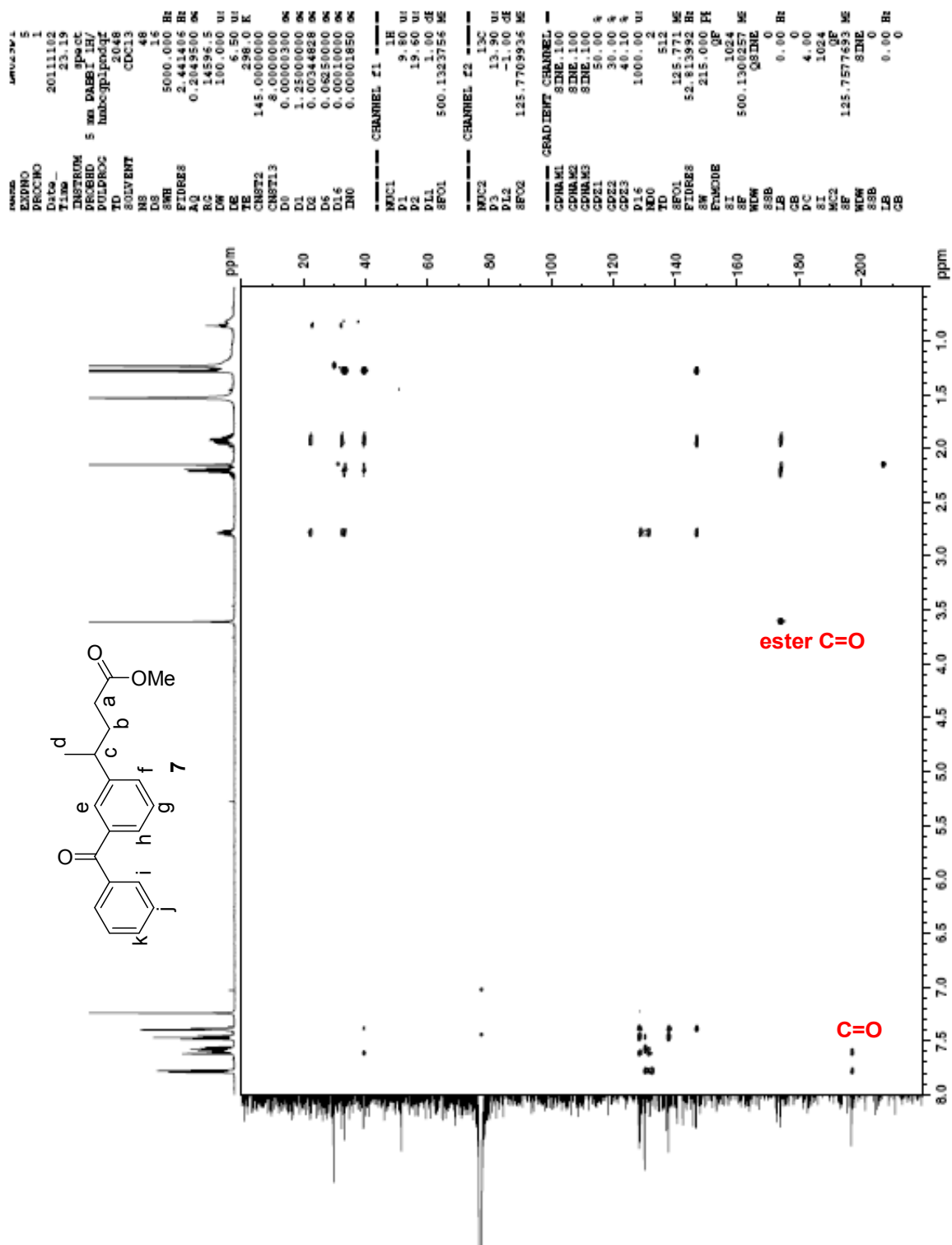
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WDW           EM
SSB           0
LB           0.30 Hz
GB           0
PC           1.00
    
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gCOSY spectrum of 7 in CDCl₃:



gHSQC spectrum of 7 in CDCl₃:



¹³C-NMR (125 MHz, CDCl₃) spectrum of 7:



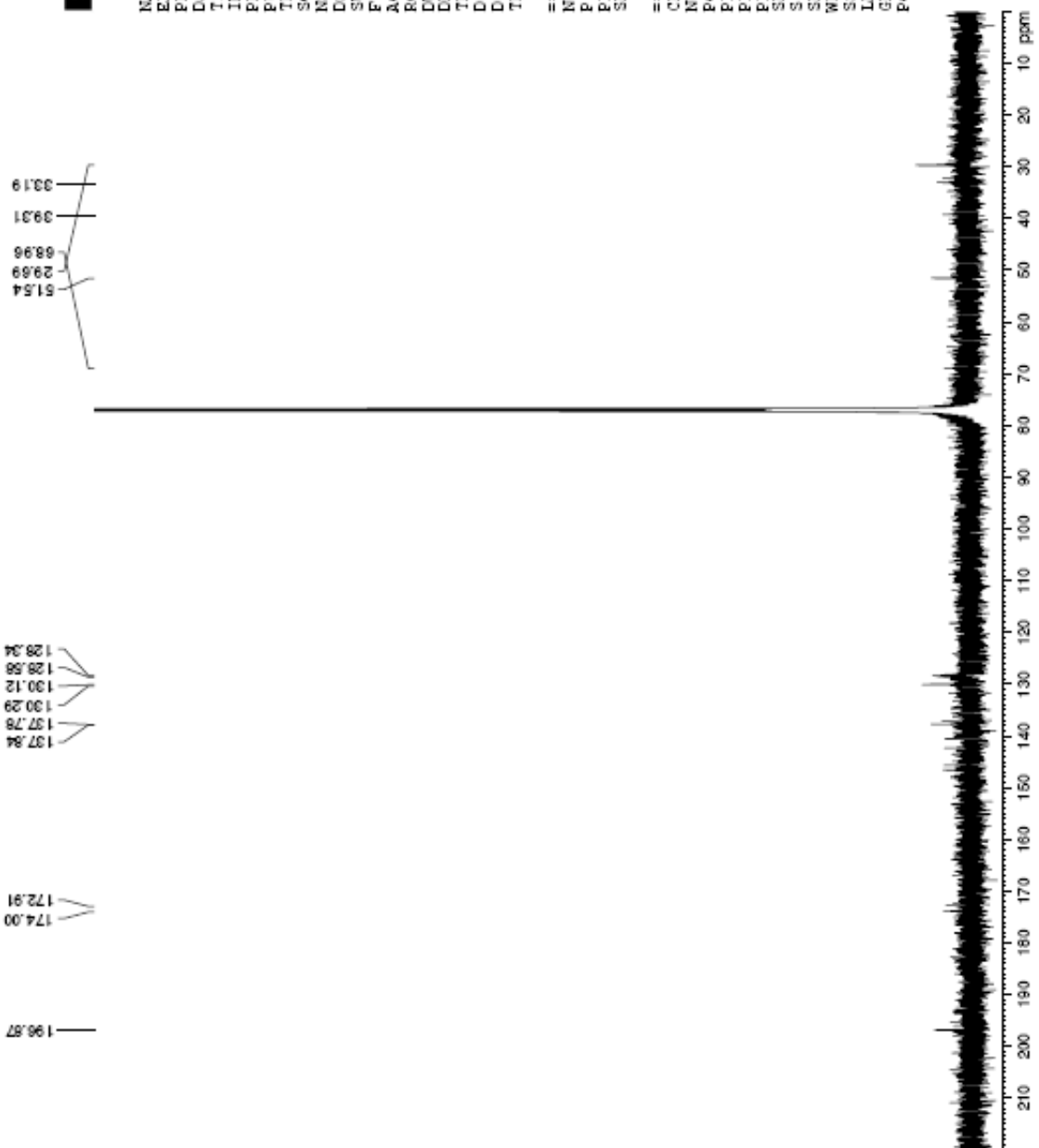
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PROCNO 1
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TD 65536
SOLVENT CDCl3
NS 16384
DS 2
SWH 29965.508 Hz
FIDRES 0.44284 Hz
AQ 1.1305633 sec
RG 14596.5
CW 17.250 use
DE 6.50 use
TE 298.2 K
D1 2.50000000 sec
D11 0.03000000 sec
TD0 1
  
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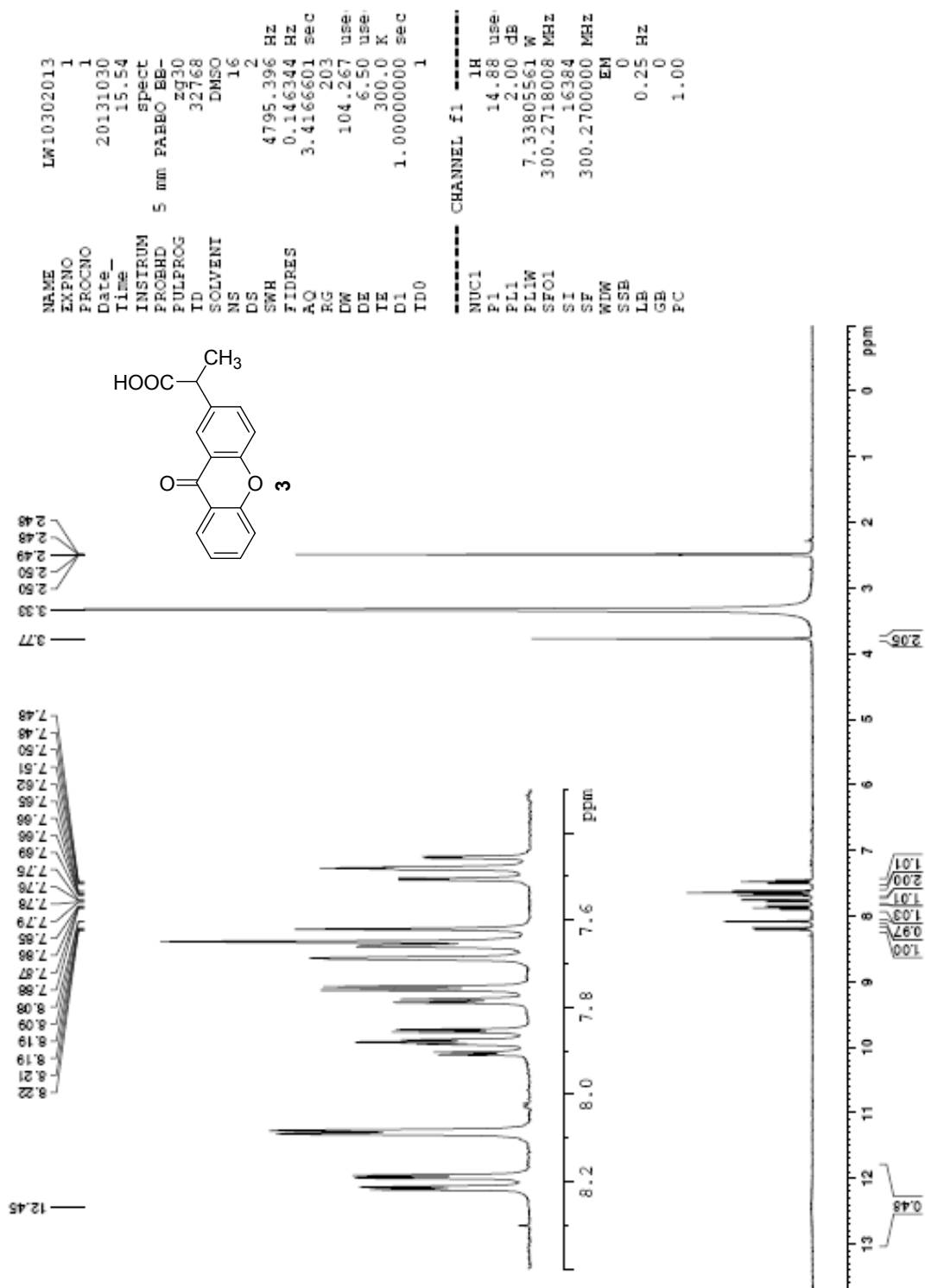
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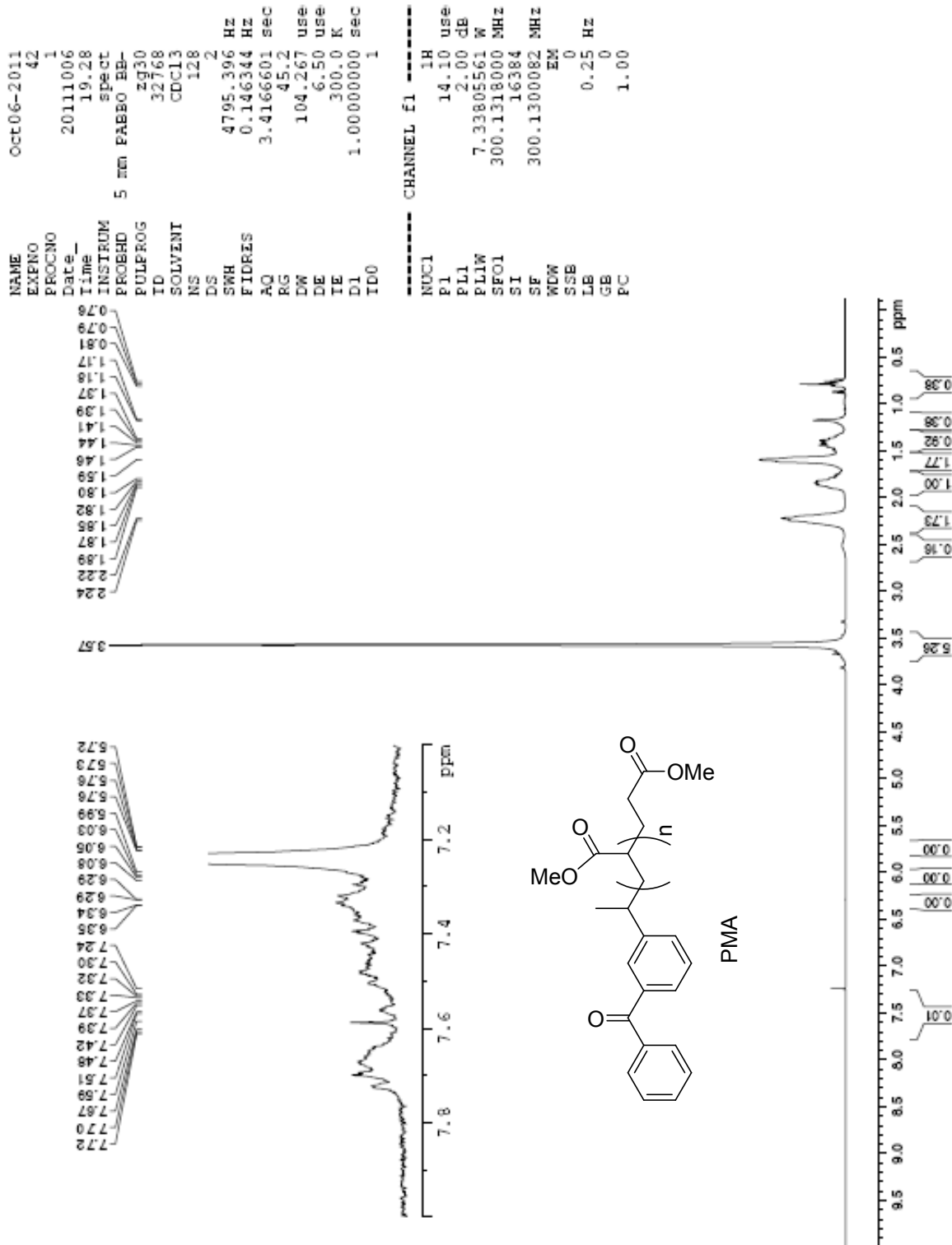
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GB 0
PC 1.40
  
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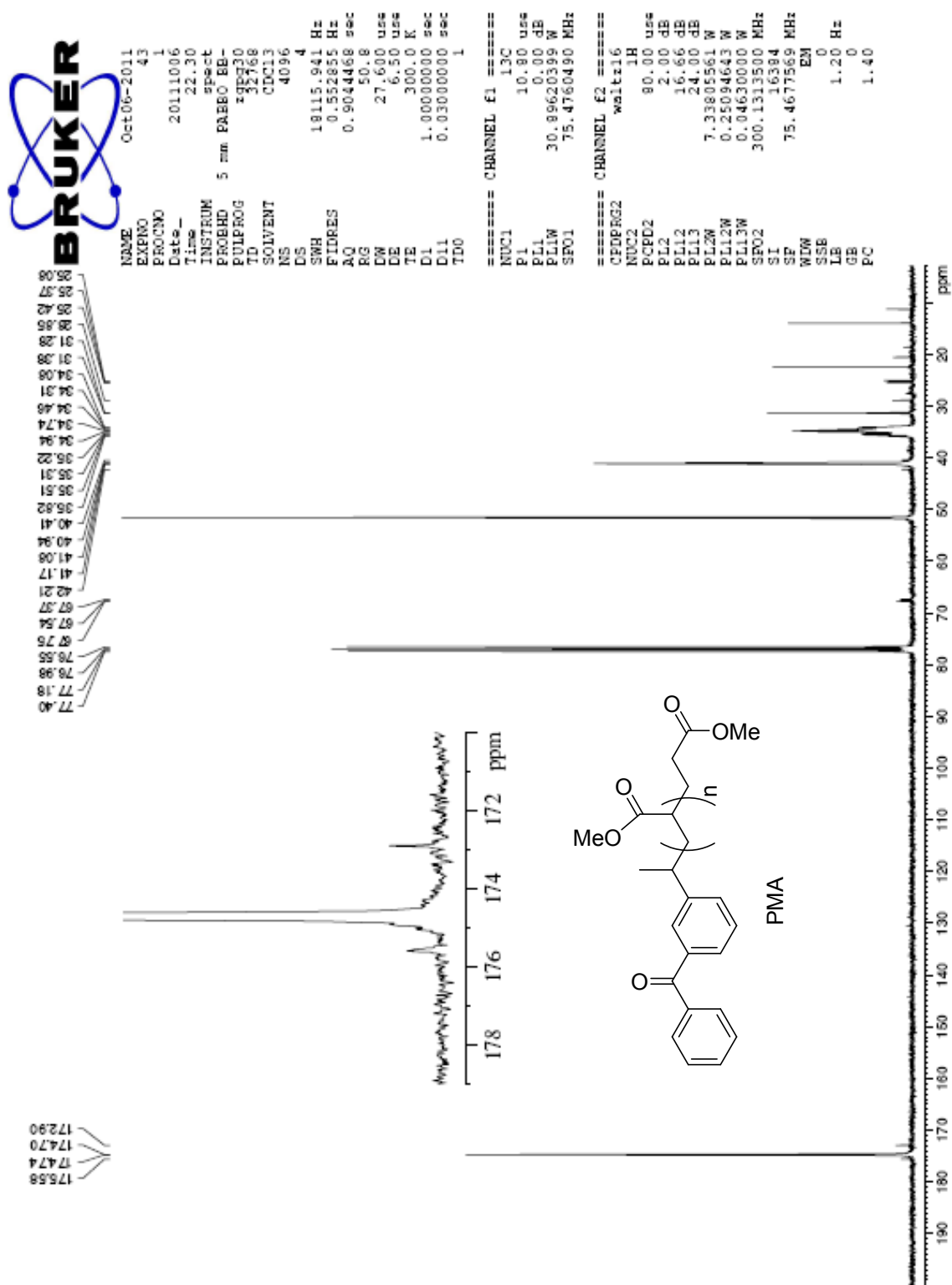
¹H-NMR (300 MHz, DMSO-d₆) spectrum of 3 before photolysis:



Representative ¹H-NMR spectra of PMA:



Representative ¹³C-NMR spectra of PMA:

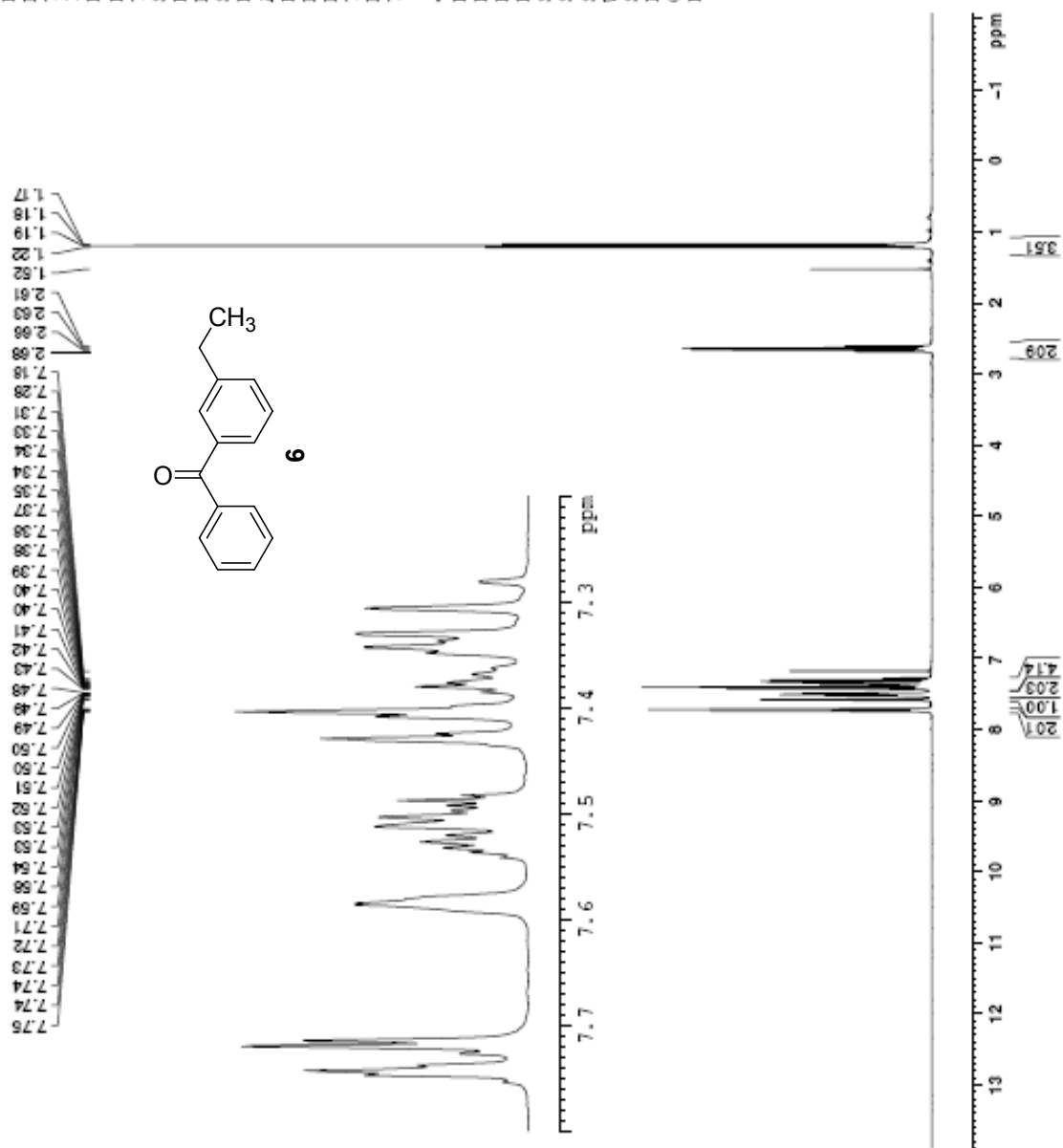


¹H-NMR spectra of compound 6:

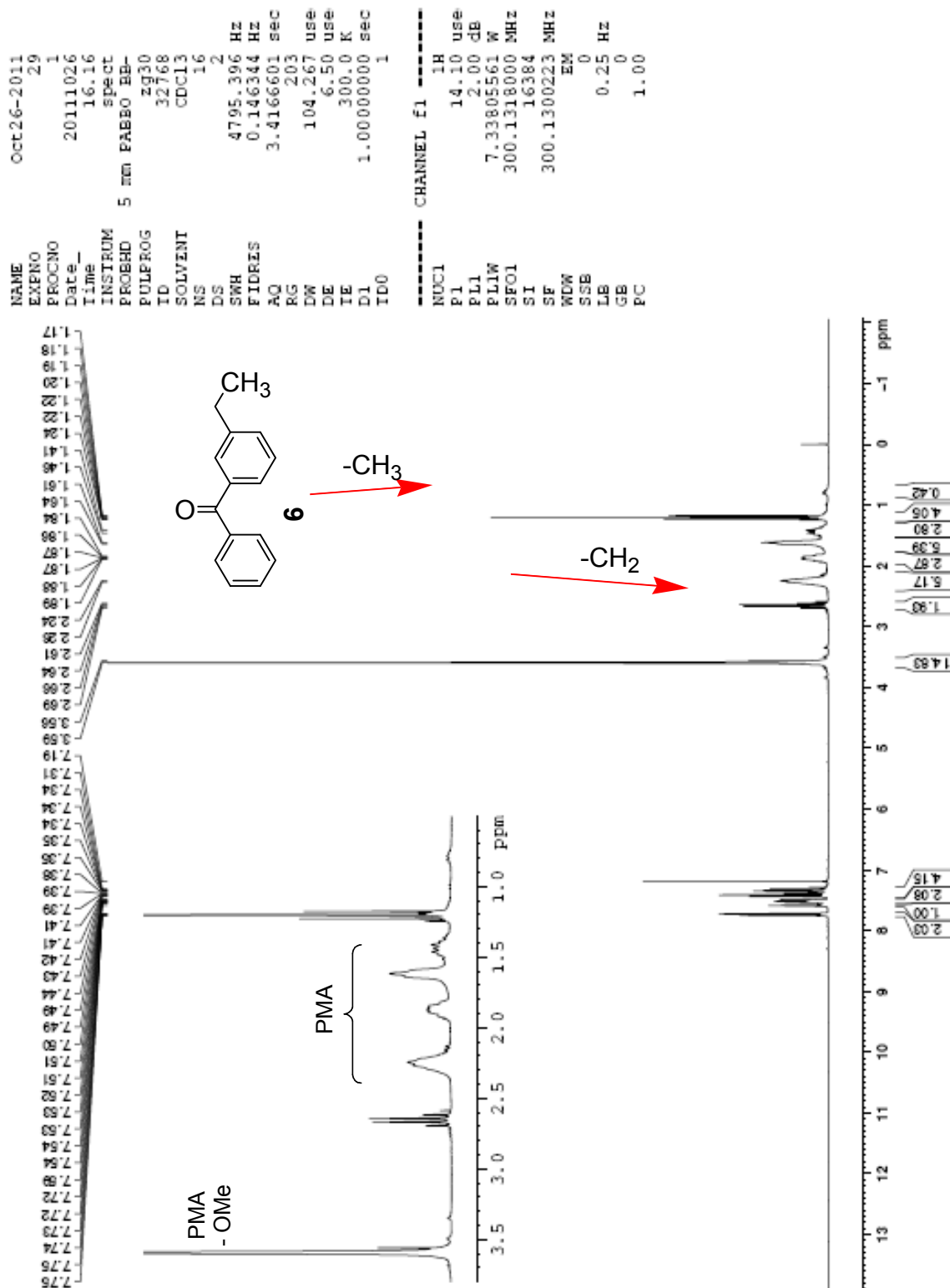
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PULPROG       zg30
ID            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           4795.396 Hz
FIDRIZ        0.146344 Hz
AQ            3.4166601 sec
RG            203
DW            104.267 use
DE            6.50 use
TE            300.0 K
D1            1.0000000 sec
TD0           1

----- CHANNEL f1 -----
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P1            14.10 use
PL1           2.00 dB
PL1W          7.33805561 W
SF01          300.1318000 MHz
SI            16384
SF            300.1300258 MHz
WDW           EM
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LB            0.25 Hz
GB            0
PC            1.00
  
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¹H-NMR after photolysis of KP and MA (0.25% v/v NaOH/CH₃CN, 5 min):

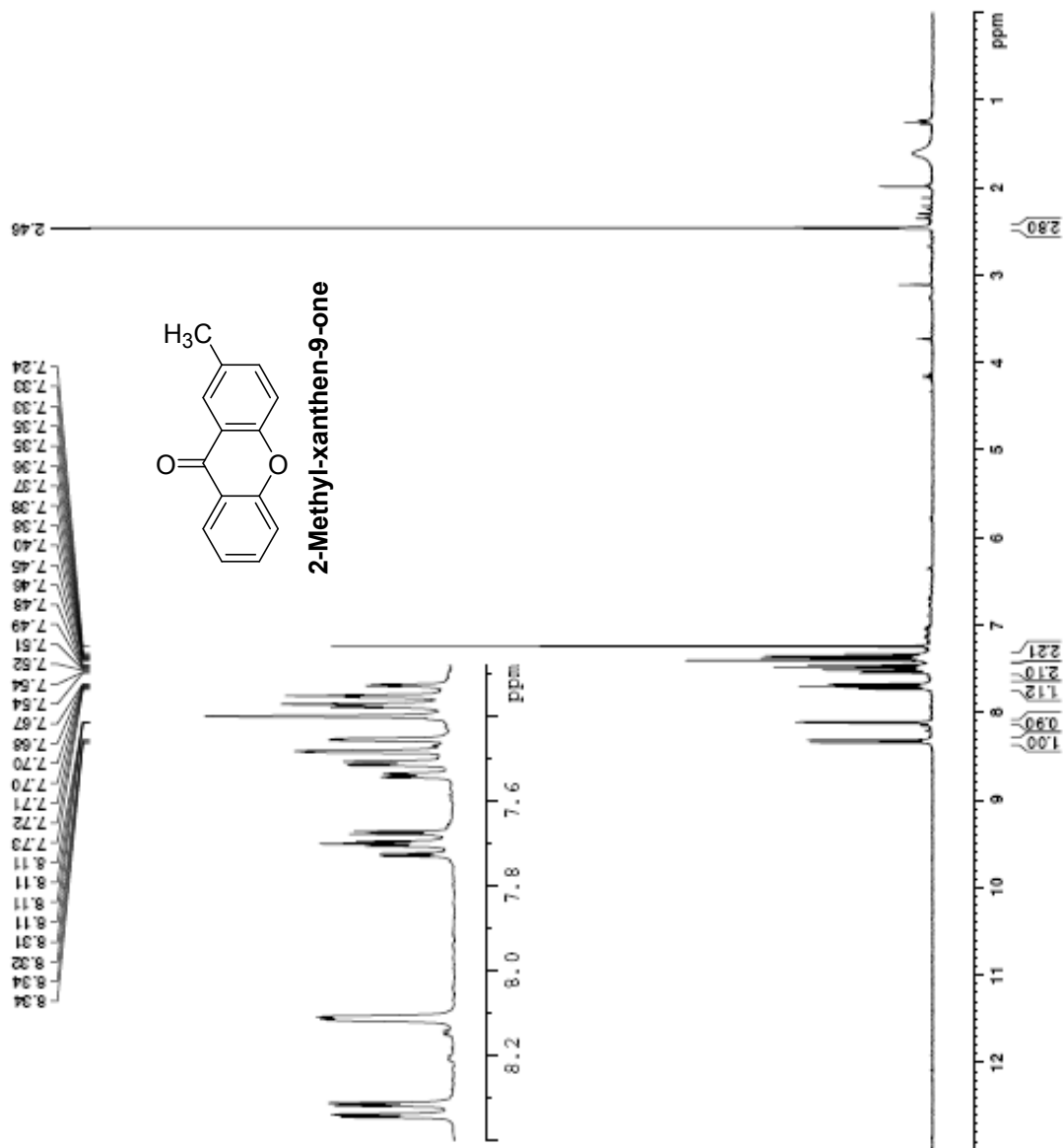


¹H-NMR after photolysis of 3 without addition of MA (0.25% v/v NaOH/CH₃CN, 5 min):

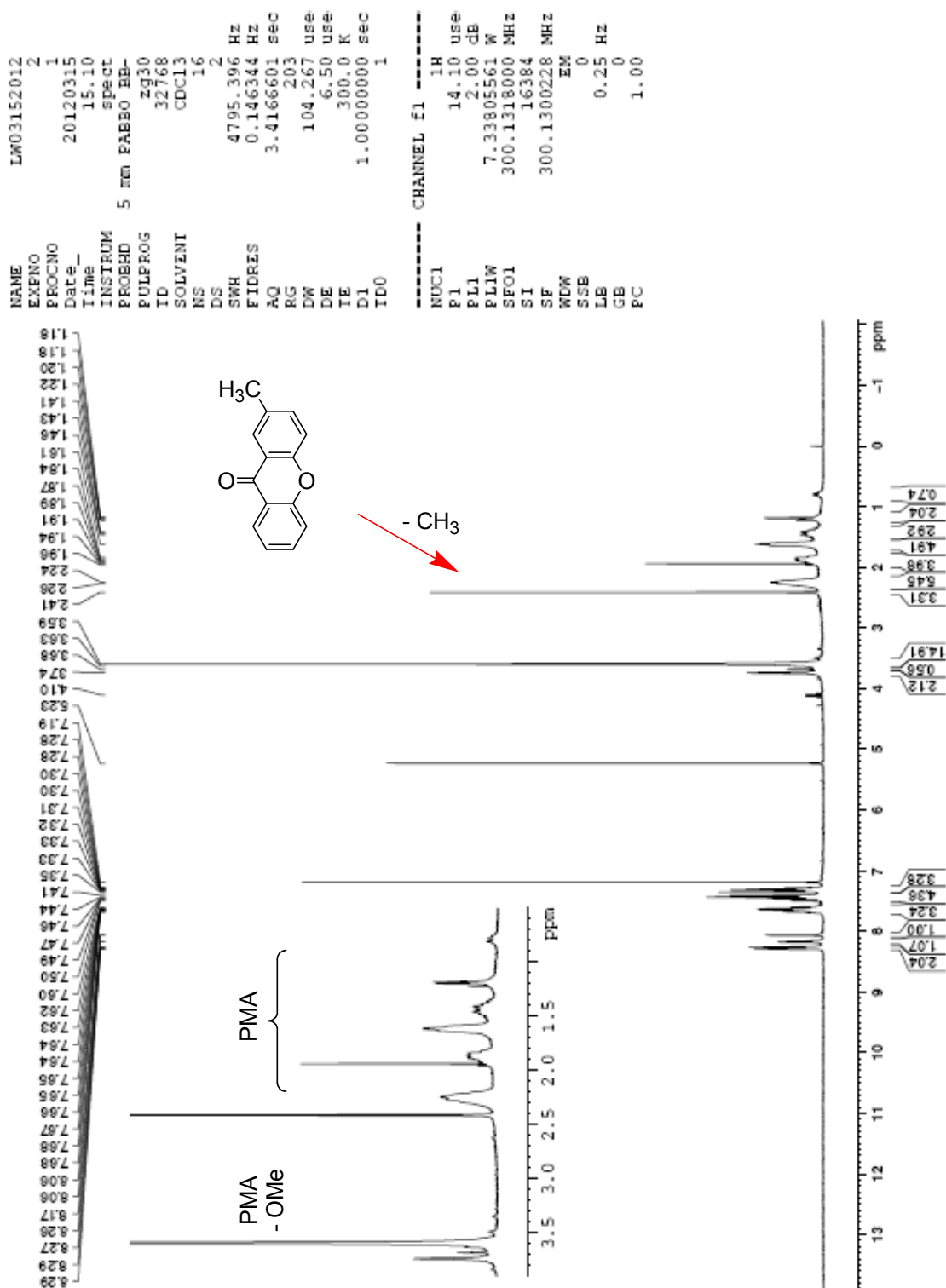
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TD            32768
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FIDRES        0.146344 Hz
AQ            3.4166601 sec
RG            203
DW            104.267 use
DE            6.50 use
TE            300.0 K
D1            1.00000000 sec
ID0           1

----- CHANNEL f1 -----
NUC1          1H
P1            14.10 use
PL1           2.00 dB
PL1W          7.33805561 W
SFO1          300.1318000 MHz
SI            16384
SF            300.1300082 MHz
WDW           EM
SSB           0
LB            0.25 Hz
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PC            1.00
  
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¹H-NMR after photolysis of 3 and MA (0.25% v/v NaOH/CH₃CN, 5 min):

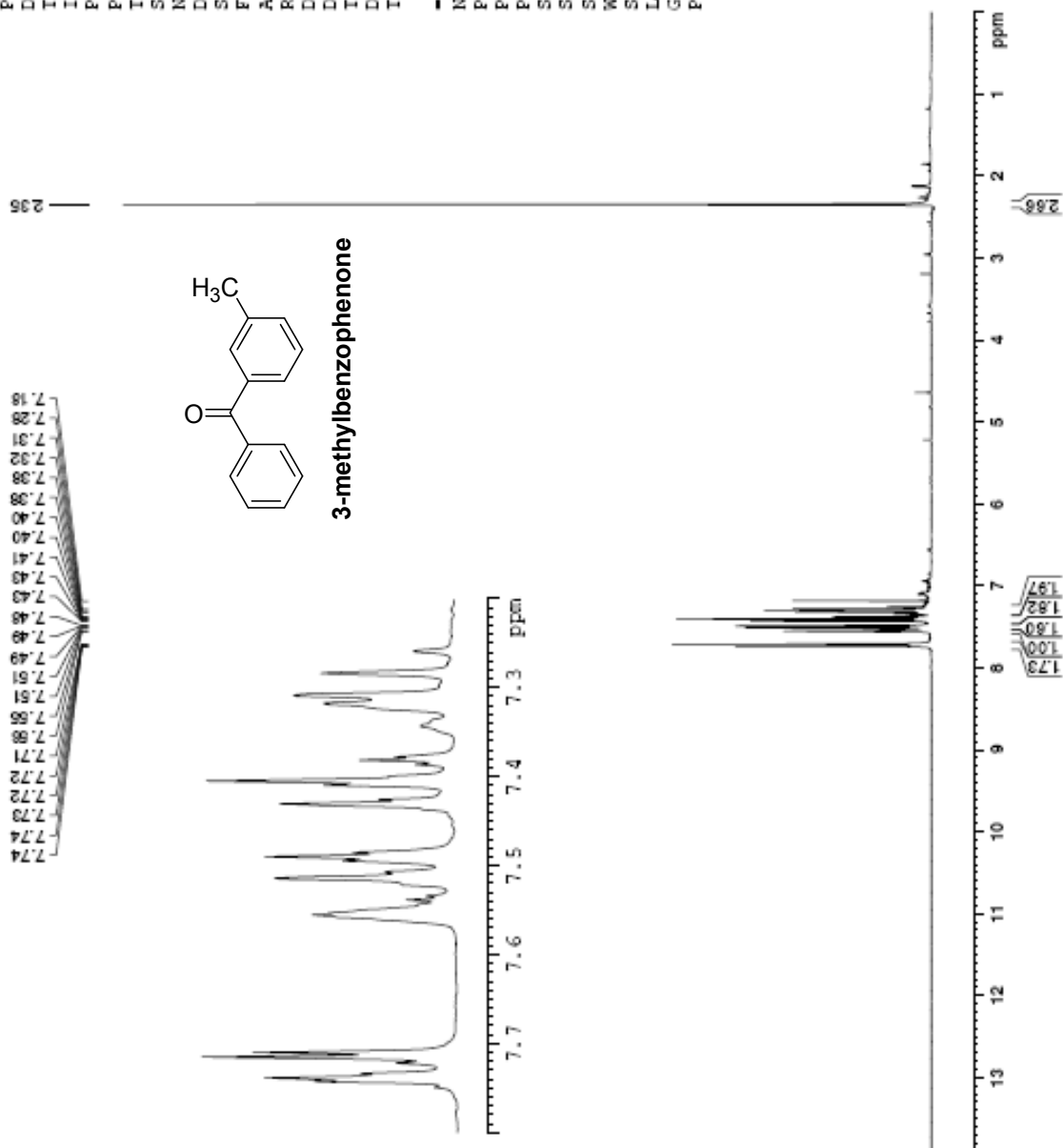


¹H-NMR after photolysis of 4 without addition of MA (0.25% v/v NaOH/CH₃CN, 5 min):

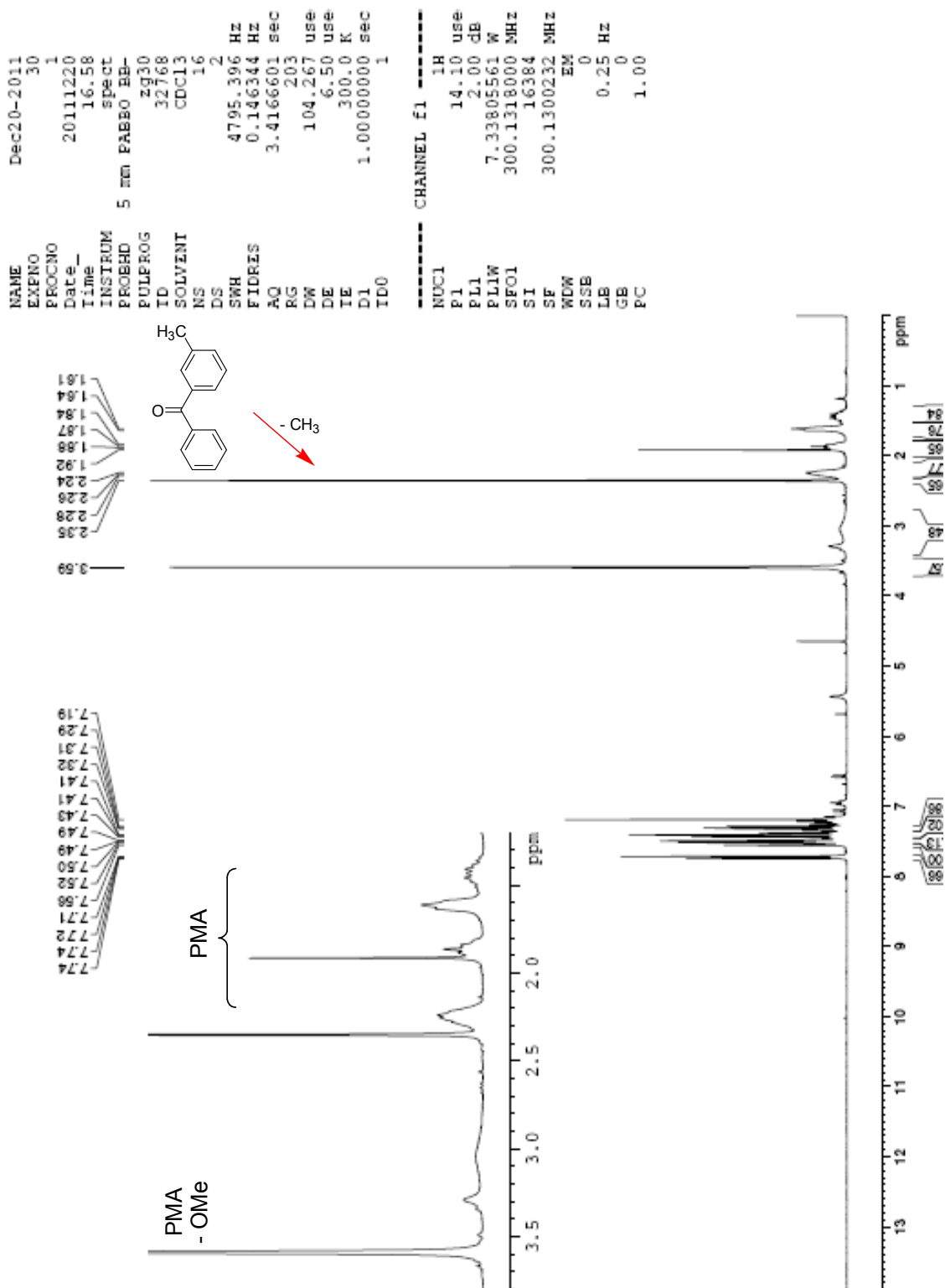
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PROCNO        1
Date_         20111222
Time_        17.21
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PULPROG       zg30
ID            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           4795.396 Hz
FIDRES        0.146344 Hz
AQ            3.4166601 sec
RG            203
DW            104.267 use
DE            6.50 use
TE            300.0 K
D1            1.00000000 sec
ID0           1

----- CHANNEL f1 -----
NUC1          1H
P1            14.10 use
PL1           2.00 dB
PL1W          7.33805561 W
SFO1          300.1318000 MHz
SI            16384
SF            300.1300253 MHz
WDW           EM
SSB           0
LB            0.25 Hz
GB            0
PC            1.00
  
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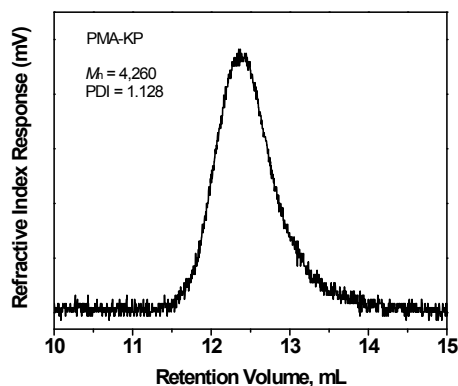
¹H-NMR after photolysis of 4 and MA (0.25% v/v NaOH/CH₃CN, 5 min):



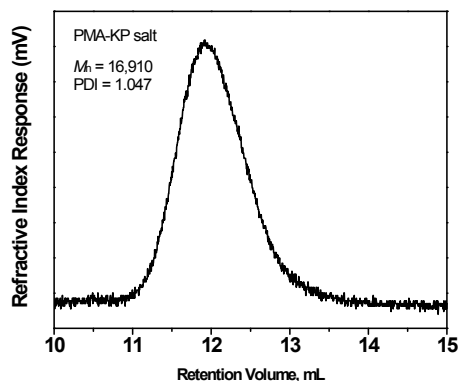
Gel Permeation Chromatography (GPC) Analyses: GPC measurements were performed using a Viscotek model 302 liquid chromatography system equipped with refractive index (RI), low-angle light scattering (LALS, $\theta = 7^\circ$), right-angle light scattering (RALS, $\theta = 90^\circ$), and UV detectors. 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:

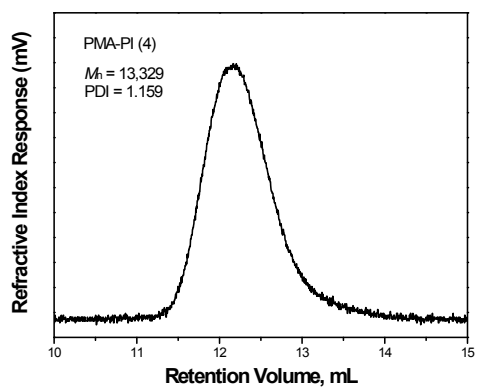
(a) KP as initiator *via* Method A



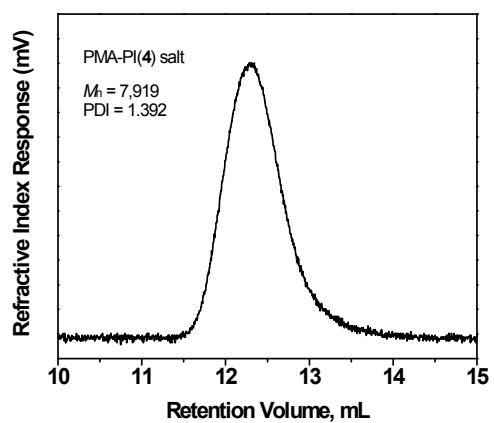
(b) KP carboxylate salt as photoinitiator *via* Method B



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

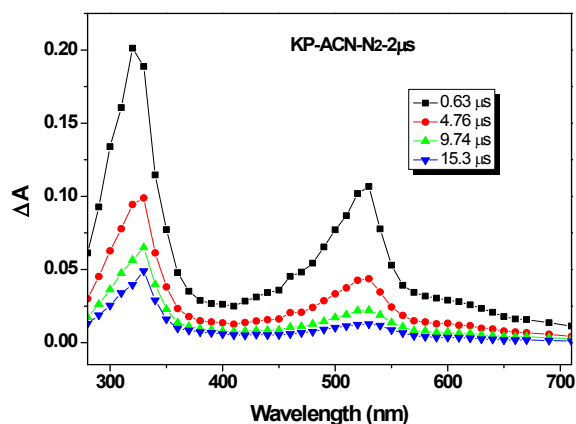


(d) PI 4 carboxylate salt as initiator *via* Method B

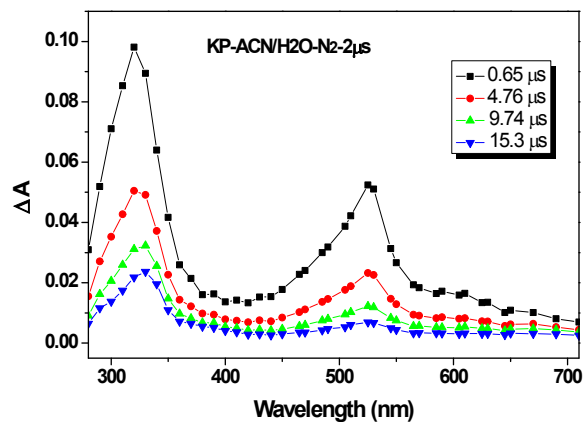


Transient absorption spectra observed for KP in various solvents:

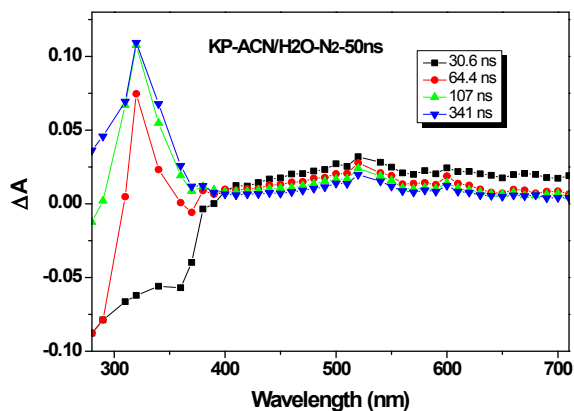
(a) CH₃CN under N₂-purged



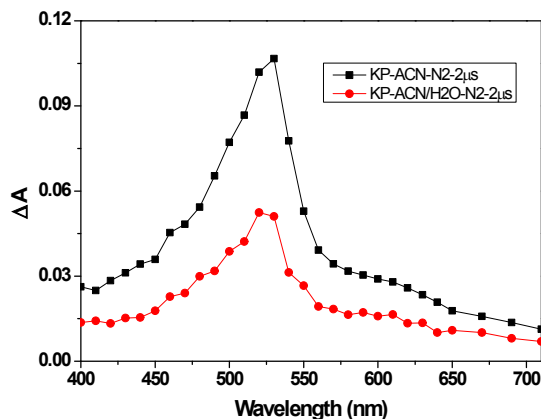
(b) 0.25 %NaOH_(aq)/ CH₃CN, N₂-purged



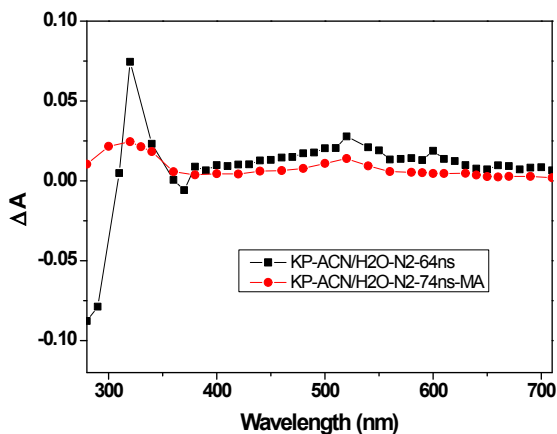
(c) 0.25%NaOH_(aq)/ CH₃CN, N₂-purged



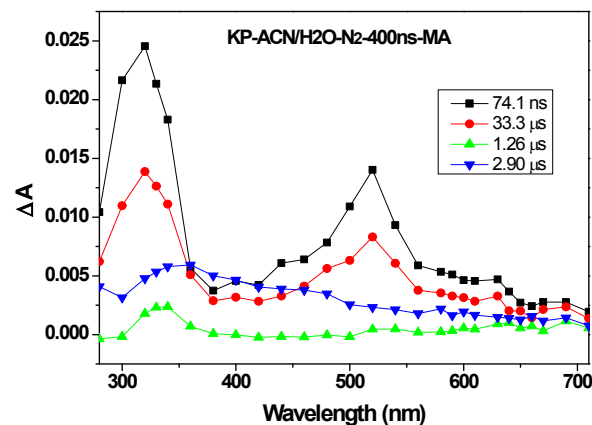
(d) CH₃CN vs. 0.25%NaOH_(aq)/ CH₃CN



(f) without vs. with MA



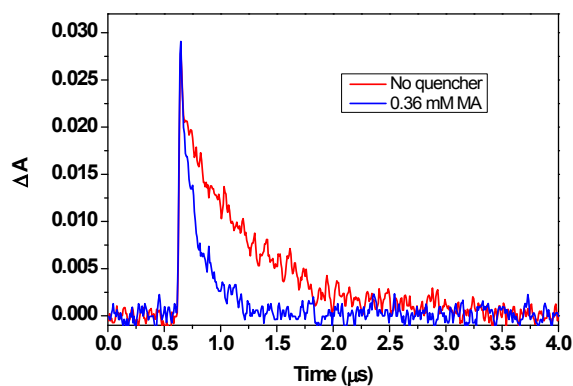
(g) addition of MA to NaOH_(aq)/CH₃CN



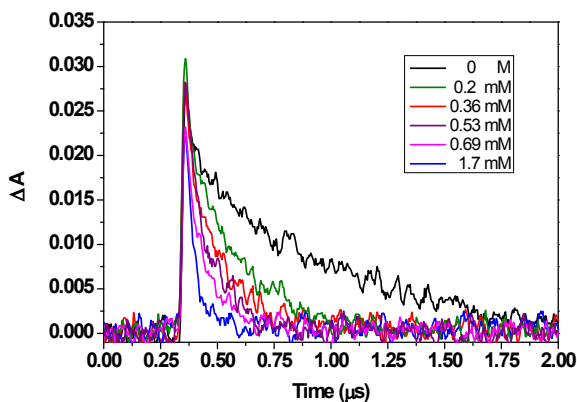
Quenching Experiments:

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)/CH₃CN. Without the quencher, the lifetime of KP carbon anion in 0.25% v/v NaOH_(aq)/CH₃CN is 622 ns; $k_q = 1.20 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$

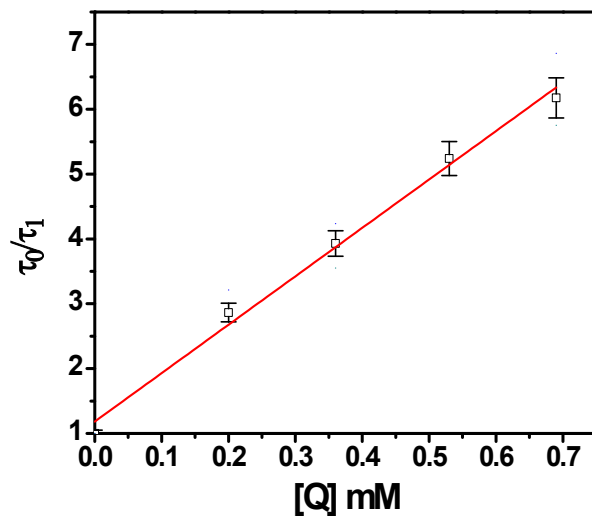
(a) after delay time of 400 ns



(b) after delay time of 200 ns

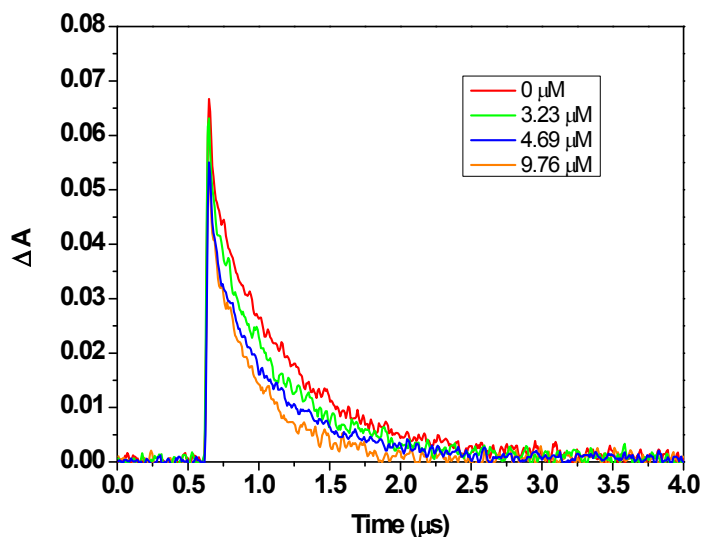


(b) Stern-Volmer plot: quenching rate constant of each decay as a function of quencher (methyl acrylate) concentration [Q]:



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)/CH₃CN. Without the quencher, the lifetime of KP carbon anion in 0.25% v/v NaOH(aq)/ACN is 579 ns; $k_q = 1.24 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$

(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].

