

## Supporting Information For:

### **Bicyclo[3.2.0]Heptane Mechanophores for the Non-Scissile and Photochemically Reversible Generation of Reactive Bis-Enones**

Zachary S. Kean,<sup>‡</sup> Ashley L. Black Ramirez,<sup>‡</sup> Yufan Yan, Stephen L. Craig\*

Department of Chemistry, Duke University, Durham, North Carolina 27708

\*To whom correspondence should be addressed. Phone: (919) 660-1538.

Fax: (919) 660-1605. Email: [stephen.craig@duke.edu](mailto:stephen.craig@duke.edu)

### Table of Contents

General Procedures	S3
Synthetic Schemes	S4
Synthesis of 1a	S4
Synthesis of 1b	S5
Synthesis of 2	S6
Synthesis of 3	S6
Synthesis of 5	S7
Synthesis of BCH-PMA <sub>2,151k</sub>	S8
Synthesis of BCH-PMA <sub>1,158k</sub>	S8
Synthesis of BCH-PMA <sub>2,182k</sub>	S9
Synthesis of BCH-PMA <sub>2,23k</sub>	S9
Synthesis of PMA <sub>LRP, 149k</sub>	S9
Synthesis of PMA <sub>FRP,157k</sub>	S10
Reaction of 5 with MAMA	S11
Reaction of 4 with MAMA	S11
Determination of $\epsilon$ (MAMA <sub>365nm</sub> )	S13
Sonication and GPC-UV Experiments	S14
General	S14
Table S1: Summary of GPC and Labeling Experiments	S14
Sonication and Labeling of BCH-PMA <sub>2,151k</sub>	S15

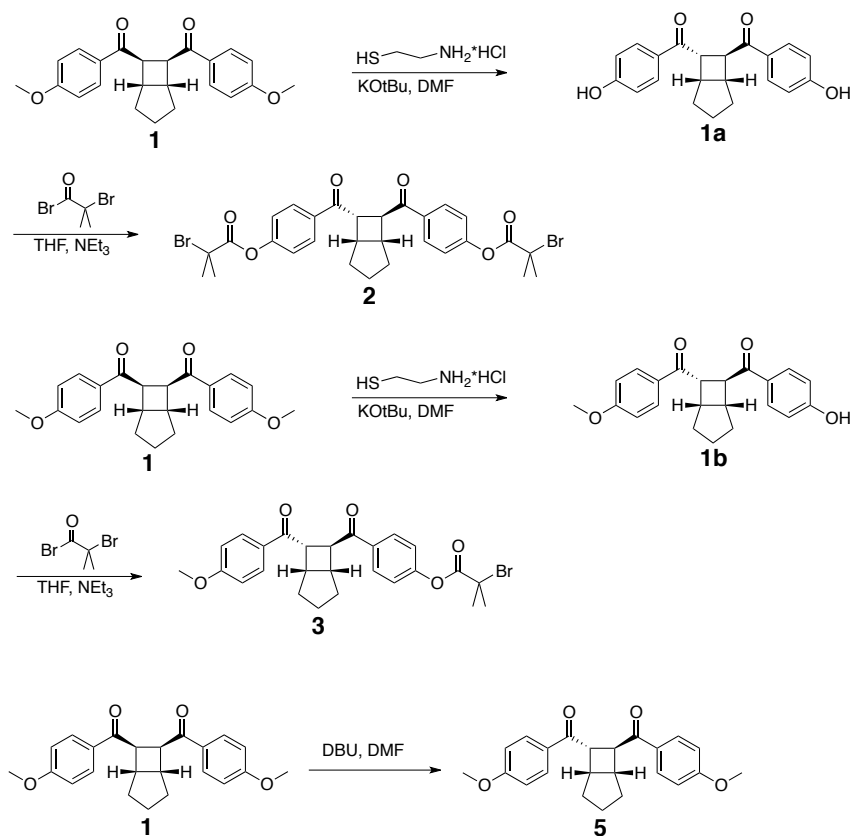
Representative Calculation of MAMA incorporation	S16
Sonication and Labeling of BCH-PMA <sub>1,158k</sub>	S17
Sonication and Labeling of BCH-PMA <sub>2,23k</sub>	S18
Sonication and Labeling of PMA <sub>LRP, 149k</sub>	S18
Sonication and Labeling of PMA <sub>FRP,157k</sub>	S18
Recyclization of BCH-PMA <sub>2,182k</sub>	S19
CoGEF Calculations	S20
Determination of Rupture Force	S20
Determination of Elongation	S21
<sup>1</sup> H and <sup>13</sup> C Spectra	S24-S38
References	S39

## General Procedures

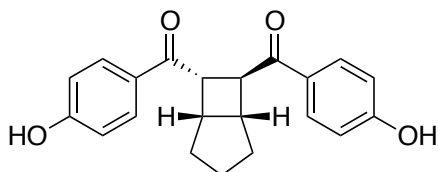
Dry tetrahydrofuran (THF) was obtained from Sigma-Aldrich and purified with a Pure Solv™ solvent purification system before use. 2-(dimethylamino)ethanethiol hydrochloride (95%),  $\alpha$ -bromoisobutyryl bromide (98%), triethylamine (99.5%, Sure/Seal™), potassium *tert*-butoxide (99.7%), ethylene bis(2-bromoisobutyrate) (97%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (98%), and all other solvents were purchased from Sigma-Aldrich and used without further purification unless otherwise specified. 2,2'-azobis(2-methylpropionitrile) (AIBN) (98%) was purchased from Sigma-Aldrich and recrystallized from MeOH before use. Methyl acrylate (99%) was passed through a column of basic alumina to remove inhibitor before use. Cu-wire (20 gauge) was purchased from McMaster-Carr and CDCl<sub>3</sub> and DMSO (d<sub>6</sub>) were purchased from Cambridge Isotope Laboratories. Me<sub>6</sub>TREN,<sup>1</sup> **1** and **4**,<sup>2</sup> and coumarin-2,2,6,6-tetramethylpiperidine-1-oxyl (CT)<sup>3</sup> were prepared as previously reported. All GPC experiments were performed using inhibitor free Chromasolv grade THF obtained from Sigma-Aldrich.

All <sup>1</sup>H and <sup>13</sup>C spectra were collected in either CDCl<sub>3</sub> ( $\delta = 7.26$ ) or DMSO (d<sub>6</sub>,  $\delta = 2.50$ ) and referenced to residual solvent peak on either a Varian 400 or 500 MHz spectrometer. Gel permeation chromatography (GPC) was performed on two in series columns (Agilent Technology PL gel 10<sup>4</sup> Å, 10<sup>3</sup> Å) with THF as the mobile phase at 0.5 mL min<sup>-1</sup>. Data for Beer's law plot to determine  $\epsilon$  (MAMA<sub>365nm</sub>) was collected on a Varian model Cary 50 Conc UV-Visible Spectrophotometer. The flow rate was set using a Varian Prostar Model 210 pump, and molecular weights were determined using an inline Wyatt Dawn EOS multi-angle light scattering (MALS) detector and a Wyatt Optilab DSP Interferometric Refractometer (RI), while absorption spectra were collected using an inline Varian Prostar Model 320 UV-Vis detector. The dn/dc of PMA polymers was set to 0.068 as previously reported.<sup>4</sup> Preparatory GPC was performed using 3 columns in series (Waters Ultrastyrigel 10<sup>6</sup> Å, 10<sup>5</sup> Å, 10<sup>4</sup> Å), with inhibitor free THF as the eluent. The flow rate was set to 6 mL min<sup>-1</sup> with a Varian Prostar Model 210 pump, and peak detection was determined using a Waters 2414 RI detector. GPC peak integrations and normalizations were performed using Origin™ Software and CoGEF calculations were performed using Spartan™ software.

## Scheme S1: Synthesis of small molecules



### Synthesis of 1a:



(+/-)-bicyclo[3.2.0]heptane-6,7-diylbis((4-hydroxyphenyl)methanone)

Compound **1** (364 mg, 0.865 mmol) was dissolved in 1.7 mL DMF in a flame-dried round bottom flask under argon. 2-(Dimethylamino)ethanethiol hydrochloride (292 mg, 2.08 mmol) was added as a solid and the resulting suspension was cooled to 0 °C in an ice bath. Potassium *tert*-butoxide (498 mg, 4.45 mmol) was added as a solid and the resulting red solution was stirred for 5 min at 0 °C, 15 min at room temperature, and then subjected to reflux at 153 °C for 3 h. The solution was allowed to cool, carefully acidified with 1 N HCl, and extracted with 2 x 100 mL EtOAc. The combined organics were washed with water, brine, and dried over  $\text{MgSO}_4$ . Upon evaporation under reduced pressure an orange residue was obtained which was then

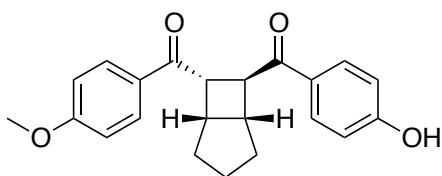
subjected to column chromatography (2:1 hexanes:EtOAc) to obtain 240 mg (0.714 mmol, 83 % yield) of **1a** as a white crystalline solid.

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.38 (s, 2H, OH), 7.83 (d,  $J$  = 8.0 Hz, 4H, ArH), 6.85 (d,  $J$  = 8.0 Hz, 4H, ArH), 4.37 (t,  $J$  = 9.2, 1H), 4.00 (t,  $J$  = 7.0, 1H), 3.18 (dd,  $J$  = 16.8, 8.0, 1 H), 2.91 (dd,  $J$  = 12.8, 6.4, 1H), 1.81 (m, 1H), 1.67 (m, 2H), 1.42 (m, 1H), 1.26 (m, 2H);

$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  197.79, 196.04, 162.21, 162.18, 130.80, 130.68, 127.39, 126.70, 115.49, 115.41, 42.30, 39.61, 31.58, 27.89, 25.22.

HRMS-DART ( $m/z$ ): calcd for  $\text{C}_{21}\text{H}_{20}\text{O}_4$  [ $\text{MH}^+$ ], 337.1434; found, 337.1436.

### Synthesis of **1b**:



7-(4-hydroxybenzoyl)bicyclo[3.2.0]heptan-6-yl(4-methoxyphenyl)methanone (mixture of diastereomers)

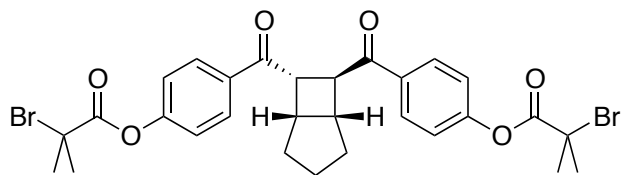
Compound **1** (434 mg, 1.20 mmol) was dissolved in 4 mL DMF in a flame-dried round bottom flask under argon. 2-(Dimethylamino)ethanethiol hydrochloride (142 mg, 1.20 mmol) was added as a solid and the resulting suspension was cooled to 0 °C in an ice bath. Potassium tert-butoxide (112 mg, 3.13 mmol) was added as a solid and the resulting red solution was stirred for 5 min at 0 °C, 15 min at room temperature, and then subjected to reflux at 153 °C for 3 h. The solution was allowed to cool, carefully acidified with 1 N HCl, and extracted with 2 x 100 mL EtOAc. The combined organics were washed with water, brine, and dried over  $\text{MgSO}_4$ . Upon exaporation under reduced pressure an orange residue was obtained which was then subjected to column chromatography (gradient elution: 4:1 to 2:1 hexanes:EtOAc) to obtain 80 mg (0.23 mmol, 19 % yield) of **1b** as a yellow oil (mixture of diastereomers) which was used without further purification.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (br s, 1H), 7.74-8.00 (m, 4H), 6.89-6.94 (m, 4H), 4.45-4.59(m, 1H), 4.19-4.27 (m, 1H), 3.84 (s, 3H), 3.13-3.17 (m, 1H), 2.99-3.03 (m, 1H), 1.74-1.86 (m, 3H), 1.36-1.51 (m, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.59, 199.77, 198.15, 197.28, 163.85, 163.76, 161.39, 161.29, 131.29, 131.14, 130.89, 130.75, 128.91, 128.55, 128.41, 128.05, 115.66, 115.63, 113.96, 113.89, 55.48, 42.79, 42.71, 42.65, 40.80, 40.60, 40.42, 32.15, 32.10, 28.28, 25.56;

HRMS-DART ( $m/z$ ): calcd for  $\text{C}_{23}\text{H}_{24}\text{O}_4$  [ $\text{MH}^+$ ], 365.1747; found, 365.1738.

### Synthesis of 2:



(+/-)-bicyclo[3.2.0]heptane-6,7-dicarboxylbis(4,1-phenylene) bis(2-bromo-2-methylpropanoate)

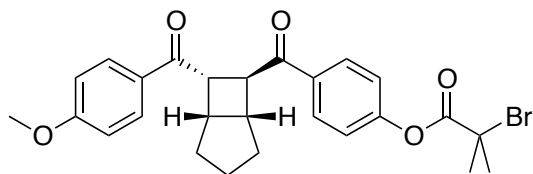
Compound **1a** (108 mg, 0.321 mmol) was dissolved in dry THF (5 mL) in a 10 mL round bottom flask under argon. Dry  $\text{NEt}_3$  (0.22 mL, 1.7 mmol) was added by syringe and the solution cooled to 0 °C.  $\alpha$ -Bromoisobutyryl bromide (0.12 mL, 0.96 mmol) was added dropwise by syringe. After 30 minutes, the solution was allowed to warm to room temperature and was stirred overnight under argon. The reaction mixture was taken up in 100 mL  $\text{Et}_2\text{O}$  and washed with 3 x 100 mL saturated aqueous  $\text{K}_2\text{CO}_3$ . The organic layer was dried over  $\text{MgSO}_4$  and solvent removed under reduced pressure to afford a yellow residue. The crude residue was subjected to column chromatography (9:1 hexanes:  $\text{EtOAc}$ ) to afford 140 mg (220  $\mu\text{mol}$ , 69 % yield) of **2** as a white crystalline solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8$  Hz, 2H), 7.99 (d,  $J = 8.0$  Hz, 2H), 7.24 (d,  $J = 3.2$  Hz, 2H), 7.22 (d,  $J = 3.2$  Hz, 2H), 4.54 (t,  $J = 8.8$  Hz, 1H), 4.24 (t,  $J = 6.8$ , 1H), 3.16-3.27 (m, 1H), 3.01-3.09 (m, 1H), 2.05 (s, 12H), 1.74-1.89 (m, 1H), 1.46-1.54 (m, 1H), 1.33-1.42 (m, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.84, 196.77, 169.73, 169.68, 154.46, 154.44, 133.98, 133.51, 130.39, 130.05, 121.53, 121.43, 55.16, 43.08, 43.04, 40.40, 40.33, 32.14, 30.56, 28.46, 25.57;

HRMS-DART ( $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{30}\text{Br}_2\text{O}_6$  [ $\text{MH}^+$ ], 633.0482; found, 633.0471.

### Synthesis of 3:



(4-methoxybenzoyl)bicyclo[3.2.0]heptane-6-carboxylphenyl 2-bromo-2-methylpropanoate (mixture of diastereomers)

Compound **1b** (76 mg, 0.22 mmol) was dissolved in dry THF (4 mL) and transferred to an oven-dried round bottom flask under argon. Triethylamine (60  $\mu\text{L}$ , 0.43 mmol) was added by syringe and the reaction mixture was cooled to 0°C.  $\alpha$ -Bromoisobutyryl bromide (40  $\mu\text{L}$ , 0.33 mmol) was added dropwise and the solution was allowed to warm to room temperature and stir for 1.5

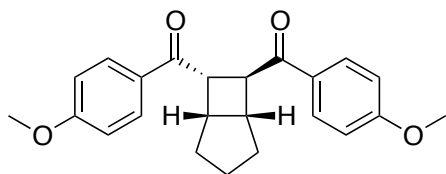
hours. The solvent was then evaporated under reduced pressure and subjected to column chromatography (silica gel, 9:1 hexanes: EtOAc) to yield 76 mg (0.15 mmol, 70% yield) of **3** as a white crystalline solid (mixture of diastereomers).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-8.06 (m, 4H), 7.20-7.24 (m, 2H), 6.91-6.93 (m, 2H), 4.42-4.54 (m, 1H), 4.17-4.24 (m, 1H), 3.83-3.84 (m, 3H), 3.16-3.20 (m, 1H), 3.00-3.09 (m, 1H), 2.04-2.05 (m, 6H), 1.73-1.87 (m, 3H), 1.35-1.53 (m, 3H);

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.22, 198.77, 197.04, 196.49, 169.78, 169.74, 163.62, 154.40, 134.15, 133.65, 130.95, 130.63, 130.44, 130.04, 129.23, 128.64, 121.51, 121.39, 113.95, 113.87, 55.53, 55.16, 43.14, 43.06, 42.74, 40.54, 40.37, 40.08, 32.24, 32.15, 30.58, 28.49, 28.45, 25.66, 25.62;

HRMS-DART (m/z): calcd for  $\text{C}_{26}\text{H}_{27}\text{BrO}_5$  [ $\text{MH}^+$ ], 499.1115; found, 499.1108.

### Synthesis of **5**:



(+/-)-bicyclo[3.2.0]heptane-6,7-diylbis((4-methoxyphenyl)methanone)

**1** (231 mg, 0.634 mmol) was dissolved in 2 mL of DMF under argon. DBU (0.190 mL, 1.27 mmol) was added by syringe and stirred overnight. The solution was diluted with 50 mL ethyl acetate and extracted 3x with 1 N HCl, 1x with sat. aq.  $\text{NaHCO}_3$ , and brine. The organic layer was dried over  $\text{MgSO}_4$ , filtered, and evaporated under reduced pressure to afford **5** as a yellow solid in quantitative yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 10$  Hz, 2H), 7.91 (d,  $J = 10.0$  Hz, 2H), 6.92 (d,  $J = 10$  Hz, 4H), 4.47 (t,  $J = 9$  Hz, 1H), 4.22 (t,  $J = 7$ , 1H), 3.85 and 3.84 (s, 3H), 3.16-3.22 (m, 1H), 3.01-3.10 (m, 1H), 1.71-1.89 (m, 3H), 1.37-1.54 (m, 3H);

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.70, 199.89, 198.27, 197.40, 163.97, 163.88, 161.51, 161.41, 131.41, 131.26, 131.01, 130.87, 128.67, 128.53, 128.17, 115.78, 115.74, 114.08, 114.01, 55.60, 42.91, 42.89, 42.83, 42.77, 40.92, 40.72, 40.54, 32.27, 32.22, 28.40, 25.68

HRMS-DART (m/z): calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_4$  [ $\text{MH}^+$ ], 351.1591; found, 351.1599.

### Synthesis of BCH-PMA<sub>2,151k</sub>

**2** (20 mg, 0.032 mmol), methyl acrylate (6.6 mL, 73 mmol), and DMSO (13.3 mL) were combined in a 25 mL pear-shaped Schlenk flask with side-arm and a stirbar wrapped with 2 cm Cu-wire (20 gauge). The solution was sparged via three freeze-pump-thaw cycles and placed in a thermostated water bath (25 °C) under argon. While stirring, Me<sub>6</sub>TREN (9.5 μL, 0.064 mmol) was added by syringe to initiate the polymerization. After approximately 2.5 hours, the reaction was terminated by exposure to air, diluted with DCM, and twice precipitated into ice cold MeOH. The tacky solid was collected and dried under vacuum overnight to yield 3.61 g of polymer.

SEC-MALLS:  $M_n = 151$  kDa, PDI = 1.11;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.15-3.90 (br, 3H), 2.05-2.30 (br, 1H), 1.25-1.90 (br, 2H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.79, 51.68, 41.18, 34.84.

### Synthesis of BCH-PMA<sub>1,158k</sub>

Mono-initiator **3** (3.0 mg, 0.0060 mmol), methyl acrylate (1.27 mL, 14.0 mmol), and DMSO (2.5 mL) were combined in a 10 mL pear-shaped Schlenk flask with side-arm and a stirbar wrapped with 2 cm Cu-wire (20 gauge). The solution was degassed via three freeze-pump-thaw cycles and placed in a thermostated water bath (25 °C) under argon. While stirring, Me<sub>6</sub>TREN (0.88 μL, 0.0060 mmol) was added by syringe to initiate the polymerization. After approximately 4 hours, the reaction was terminated by exposure to air, diluted with DCM, and twice precipitated into ice cold MeOH. The tacky solid was collected and dried under vacuum overnight to yield 681 mg of polymer.

SEC-MALLS:  $M_n = 158$  kDa, PDI = 1.12;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.15-3.90 (br, 3H), 2.05-2.30 (br, 1H), 1.25-1.90 (br, 2H);

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.77, 51.63, 41.16, 34.82.

### Synthesis of BCH-PMA<sub>2,182k</sub>

**2** (8.6 mg, 0.014 mmol), methyl acrylate (2.9 mL, 32 mmol), and DMSO (5.7 mL) were combined in a 25 mL pear-shaped Schlenk flask with side-arm and a stirbar wrapped with 2 cm Cu-wire (20 gauge). The solution was sparged via three freeze-pump-thaw cycles and placed in a thermostated water bath (25 °C) under argon. While stirring, Me<sub>6</sub>TREN (4.1 μL, 0.027 mmol) was added by syringe to initiate the polymerization. After approximately 2.5 hours, the reaction was terminated by exposure to air, diluted with DCM, and twice precipitated into ice cold



MeOH. The tacky solid was collected and dried under vacuum overnight to yield 1.53 g of polymer.

SEC-MALLS:  $M_n = 182$  kDa, PDI = 1.11;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.15-3.90 (br, 3H), 2.05-2.30 (br, 1H), 1.25-1.90 (br, 2H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.72, 51.60, 41.10, 34.76.

### Synthesis of BCH-PMA<sub>2,23k</sub>

**2** (20 mg, 0.032 mmol), methyl acrylate (1.0 mL, 11 mmol), and DMSO (2.0 mL) were combined in a 25 mL pear-shaped Schlenk flask with side-arm and a stirbar wrapped with 2 cm Cu-wire (20 gauge). The solution was sparged via three freeze-pump-thaw cycles and placed in a thermostated water bath (25 °C) under argon. While stirring, Me<sub>6</sub>TREN (9.6  $\mu\text{L}$ , 0.064 mmol) was added by syringe to initiate the polymerization. After approximately 45 minutes, the reaction was terminated by exposure to air, diluted with DCM, and twice precipitated into ice cold MeOH. The tacky solid was collected and dried under vacuum overnight to yield 230 mg of polymer.

SEC-MALLS:  $M_n = 23.4$  kDa, PDI = 1.08;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.15-3.90 (br, 3H), 2.05-2.30 (br, 1H), 1.25-1.90 (br, 2H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.73, 51.60, 41.09, 34.77.

### Synthesis of PMA<sub>LRP, 149k</sub>

Ethylene bis(2-bromoisobutyrate) (5.0 mg, 0.014 mmol), methyl acrylate (3 mL, 32 mmol), and DMSO (6 mL) were combined in a 25 mL pear-shaped Schlenk flask with side-arm and a stirbar wrapped with 2 cm Cu-wire (20 gauge). The solution was sparged via three freeze-pump-thaw cycles and placed in a thermostated water bath (25 °C) under argon. While stirring, Me<sub>6</sub>TREN (4.2  $\mu\text{L}$ , 0.028 mmol) was added by syringe to initiate the polymerization. After approximately 2.5 hours, the reaction was terminated by exposure to air, diluted with DCM, and twice precipitated into ice cold MeOH. The tacky solid was collected and dried under vacuum overnight to yield 1.34 g of polymer.

SEC-MALLS:  $M_n = 149$  kDa, PDI = 1.10;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.15-3.90 (br, 3H), 2.05-2.30 (br, 1H), 1.25-1.90 (br, 2H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.97, 51.83, 41.45, 35.00.

## Synthesis of PMA<sub>FRP,157k</sub>

A solution of AIBN (9.5 mg, 0.058 mmol), methyl acrylate (1.2 mL, 0.060 mmol), and benzene (5 mL) was added to a 25 mL Schlenk flask with side-arm and a stirbar. The solution was sparged via three freeze-pump-thaw cycles and placed in a thermostated oil bath (60 °C) under argon for 17 hours. The solution was diluted with DCM, and twice precipitated into ice cold MeOH. The tacky solid was collected and dried under vacuum overnight to yield 891 mg of polymer.

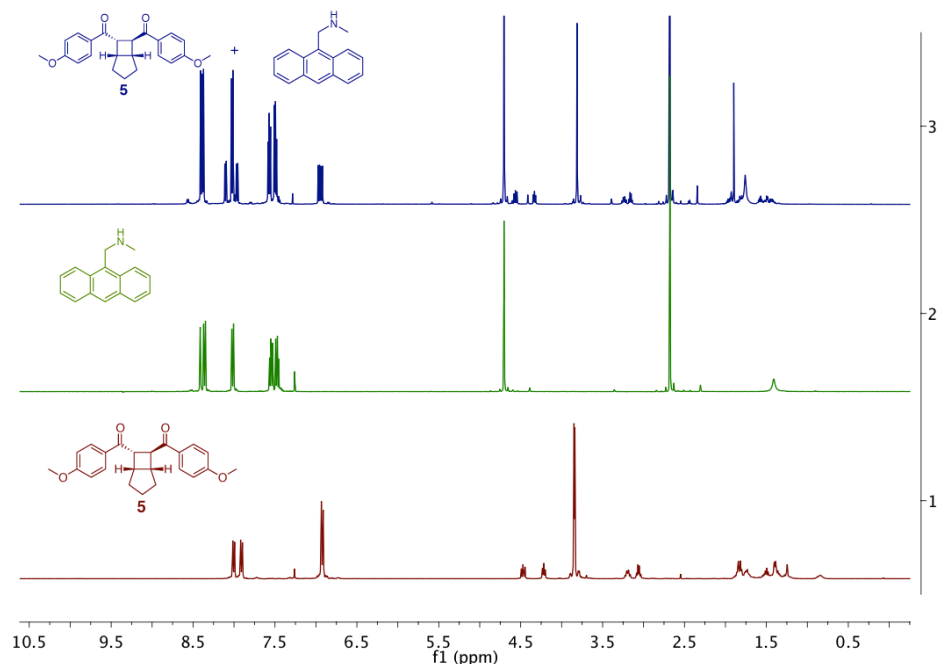
SEC-MALLS:  $M_n = 157$  kDa, PDI = 2.12;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.15-3.90 (br, 3H), 2.05-2.30 (br, 1H), 1.25-1.90 (br, 2H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.83, 51.68, 41.23, 34.89.

## Reaction of **5** with MAMA

**5** (36 mg, 0.10 mmol) was dissolved in 2 mL MeCN and MAMA (110 mg, 0.50 mmol) was added as a powder. The solution was stirred overnight in a 5 mL vial flushed with nitrogen. The solution was evaporated under reduced pressure and redissolved in  $\text{CDCl}_3$  for  $^1\text{H}$  analysis. Stacked spectra below show no change in the peak shifts of **5** (red) or MAMA (green) after reaction (blue).

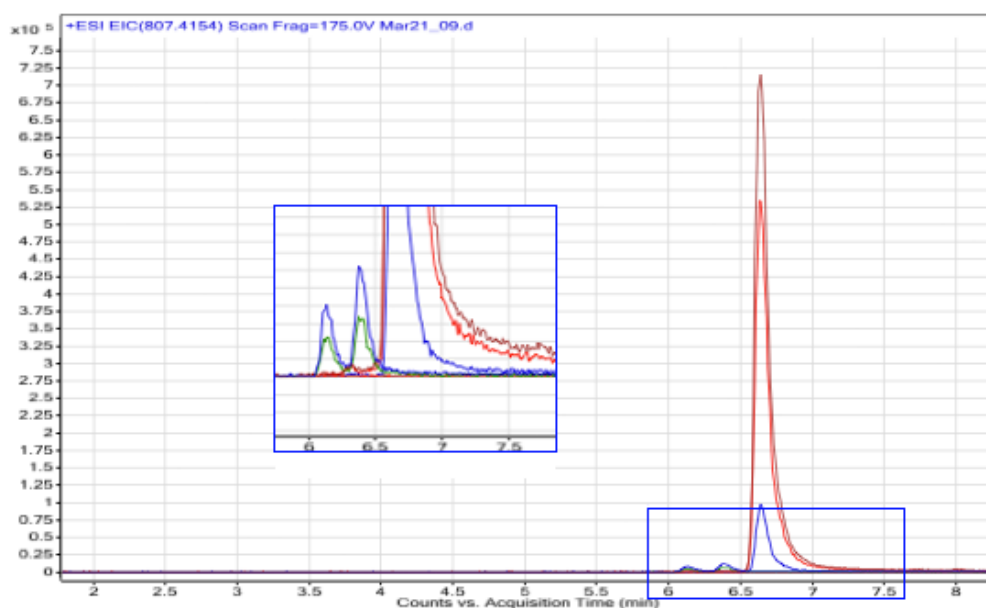


**Figure S1:**  $^1\text{H}$  NMR of **5** (red), MAMA (green), and **5** treated with MAMA (blue). No detectable changes in chemical shifts are seen to occur.

## Reaction of 4 with MAMA

Liquid chromatography-mass spectrometry was performed on an Agilent Technologies 6224 TOF LC/MS using an Ascentis 2 x 50 mm C<sub>18</sub> column with a particle size of 2.6  $\mu\text{m}$ . Gradient elution was performed for all runs from 70:30 (A:B) to 90:10 (A:B) over 10 minutes (A: 98% H<sub>2</sub>O/2% MeCN/0.3% HCOOH, B: 98% MeCN/2% H<sub>2</sub>O/0.3% HCOOH).

**4** (150 mg, 0.412 mmol) was dissolved in 2 mL MeCN and MAMA (455 mg, 2.06 mmol) was added as a powder. The solution was stirred in a 5 mL vial flushed with nitrogen. The resulting solution was subject to analysis by LC-MS at 0.5, 5, and 6 hours. Chromatogram shown below illustrates relative content of mono and di-MAMA adducts.



**Figure S2:** Chromatogram of MAMA addition to **4** at 0.5 (blue), 5 (red), and 6 (maroon) hours. Inset: minor peaks at 6-6.5 min correspond to diastereomeric di-adducts. Two peaks between 6.0 and 6.5 minutes correspond to species of identical mass, presumably the R,S and R,R/S,S diastereomeric products of the di-adduct.

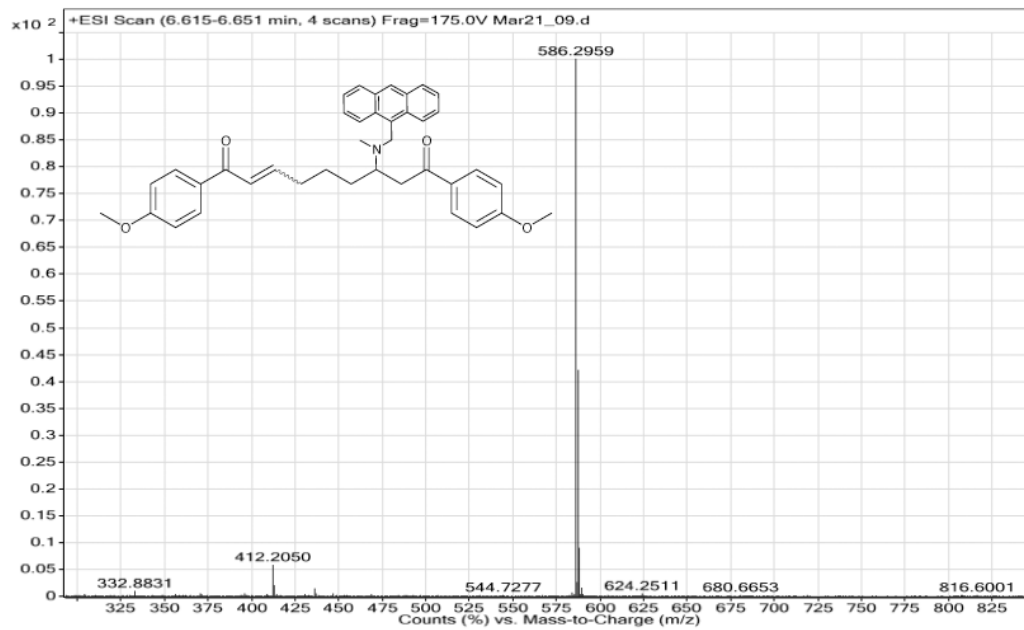


Figure S3: Mass spectra of mono-adduct.

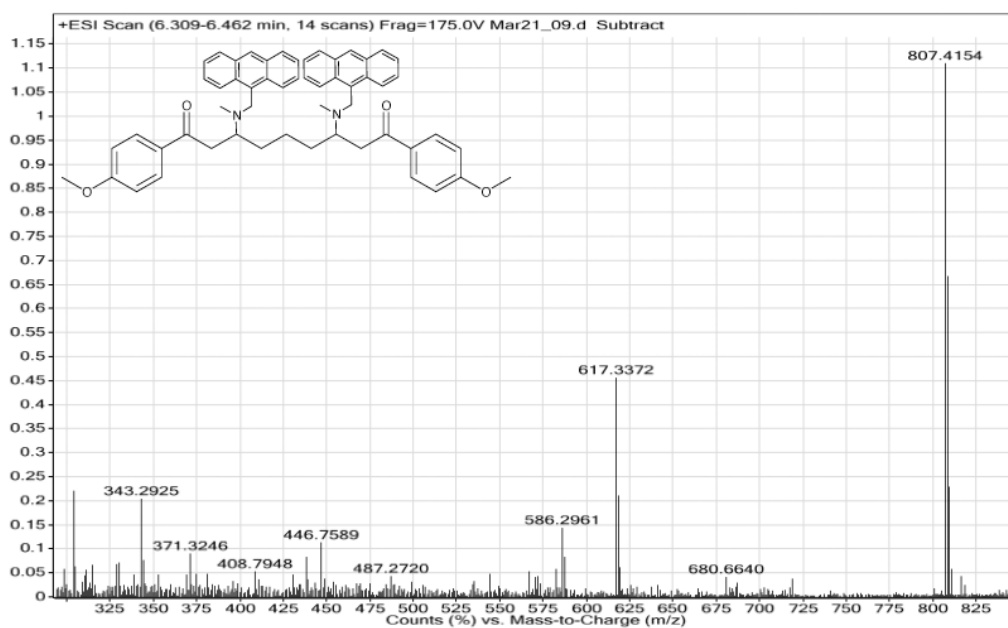
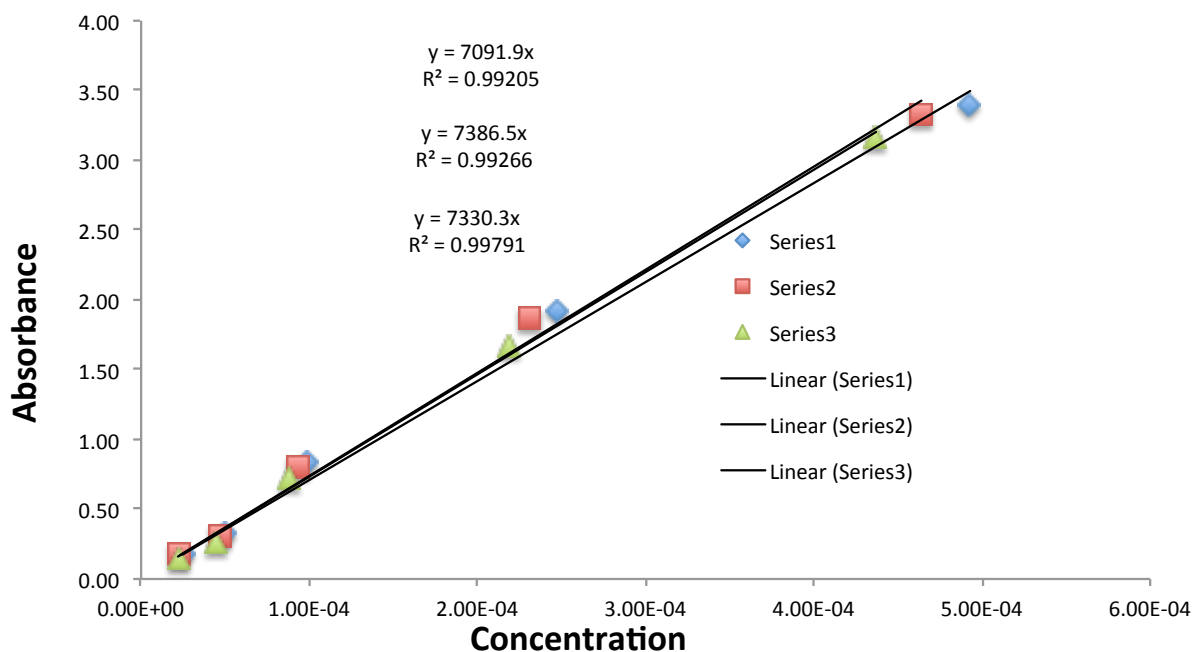


Figure S4: Mass spectra of di-adduct.

## Determination of $\epsilon$ (MAMA<sub>365nm</sub>)

Absorbances were determined at the concentrations shown below in THF.



**Figure S6:** Beer's law plot for MAMA at 365 nm.

SAMPLE A		SAMPLE B		SAMPLE C	
Conc (M)	Abs	Conc (M)	Abs	Conc (M)	Abs
4.37E-04	3.166	4.64E-04	3.328	4.93E-04	3.390
2.19E-04	1.664	2.31E-04	1.865	2.47E-04	1.910
8.74E-05	0.713	9.27E-05	0.805	9.85E-05	0.841
4.37E-05	0.265	4.64E-05	0.308	4.93E-05	0.334
2.19E-05	0.153	2.31E-05	0.180	2.47E-05	0.184
	$\epsilon$				
A	7092				
B	7387				
C	7330				
Average	7270				
Std. Dev.	156				

## Sonication and GPC-UV Experiments

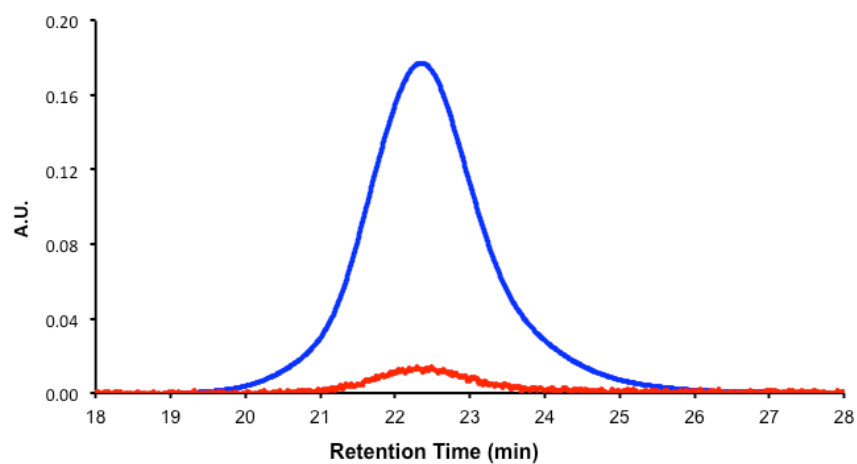
### General

A solution of 70 mg BCH-PMA<sub>2</sub> solution in 16 mL MeCN was transferred to a Suslick vessel. This was bubbled with nitrogen for 30 min. before sonication. The solution was sonicated under N<sub>2</sub> in an ice water bath (~6–9 °C) at 6.0 W cm<sup>-2</sup> with a pulse sequence of 1 s on 2 s off. Aliquots were periodically withdrawn at various time points. In labeling experiments, the aliquots were reacted with MAMA overnight before being analyzed by SEC-MALLS-UV-Vis. This was done by directly reacting the sonicated solution with MAMA (20 mg/mL) in a 7 mL scintillation vial equipped with a stirbar. Labeling was performed after sonication to minimize any potential side reactions involving MAMA and to ensure homogenous reaction conditions across all experiments. Before GPC analysis the solutions were filtered through a 0.2 μm pore size PTFE syringe filter, evaporated under reduced pressure, redissolved in THF to an identical volume, and directly injected onto the GPC. Baselines and peak integrations were generated using Origin™ software. All UV integrations were normalized with respect to each other by setting the integral of the corresponding RI peak to unity and scaling the UV integrations accordingly.

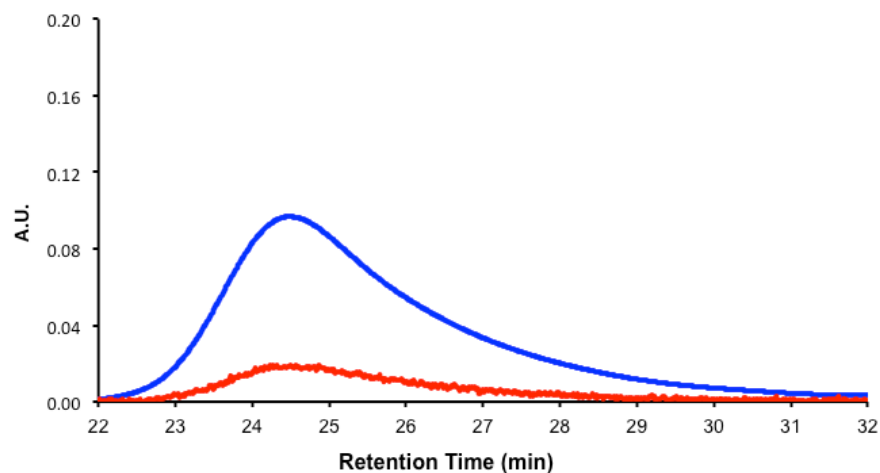
**Table S1:** Summary of Sonication and Labeling Experiments

		mass inj(mg)	RI <sub>raw</sub>	RI <sub>norm</sub>	N	UV <sub>raw</sub>	UV <sub>norm</sub>	UV <sub>net</sub>	M <sub>n</sub> (kDa)	mol <sub>polymer</sub>	mol <sub>MAMA</sub>	χ <sub>MAMA</sub>
BCH-PMA <sub>2,151k</sub>	Control 1	0.5712	0.3388	0.5931	1.751	0.0227	0.0398		151			
	Control 2	0.5833	0.3525	0.6044	1.715	0.0229	0.0393		147			
	Control 3	0.5892	0.3496	0.5933	1.697	0.0237	0.0403		150			
	Control Avg	0.5812	0.3470	0.5970	1.721	0.0231	0.0398		149	6.696E-09		
	15 min 1	0.5933	0.3529	0.5948	1.685	0.0481	0.0811	0.0413	84		2.842E-09	0.4244
	15 min 2	0.5959	0.3498	0.5870	1.678	0.0493	0.0827	0.0429	86		2.954E-09	0.4411
	15 min 3	0.5003	0.3011	0.6018	1.999	0.0383	0.0765	0.0367	89		2.521E-09	0.3764
	15 min Avg	0.5632	0.3346	0.5941	1.776	0.0452	0.0803	0.0405	86		2.786E-09	0.4161
	30 min	0.6398	0.3910	0.6111	1.563	0.0658	0.1029	0.0631	74		4.337E-09	0.6476
	60 min	0.3743	0.2360	0.6305	2.672	0.0413	0.1104	0.0706	56		4.859E-09	0.7256
120 min	0.4948	0.3268	0.6604	2.021	0.0586	0.1185	0.0787	49		5.410E-09	0.8079	
PMA <sub>CRP,149k</sub>	Control	0.6690	0.3980	0.5949	1.495	0.0492	0.0736		148	6.757E-09		
	Sonicated	0.4110	0.2510	0.6107	2.433	0.0364	0.0885	0.0149	54		1.022E-09	0.1513
BCH-PMA <sub>2,23k</sub>	Control	0.6370	0.3830	0.6013	1.570	0.1338	0.2100		23	4.348E-08		
	Sonicated	0.8630	0.5150	0.5968	1.159	0.2409	0.2791	0.0691	23		4.752E-09	0.1093
BCH-PMA <sub>1,158k</sub>	Control	0.5880	0.3550	0.6037	1.701	0.0127	0.0216		158	6.329E-09		
	Sonicated	0.7690	0.4750	0.6177	1.300	0.0230	0.0299	0.0083	62		5.715E-10	0.0903
PMA <sub>FRP,157k</sub>	Control	0.3570	0.2140	0.5994	2.801	0.0000	0.0000		157	6.369E-09		
	Sonicated	0.5510	0.3210	0.5826	1.815	0.0060	0.0110	0.0110	51		7.539E-10	0.1184
BCH-PMA <sub>2,182k, Recyclization</sub>	Control	0.5600	0.3370	0.6018	1.786	0.0159	0.0284		171			
	Sonicated	0.5430	0.3290	0.6059	1.842	0.0404	0.0744		55			
	Recyclized	0.2680	0.1630	0.6082	3.731	0.0063	0.0235		65			

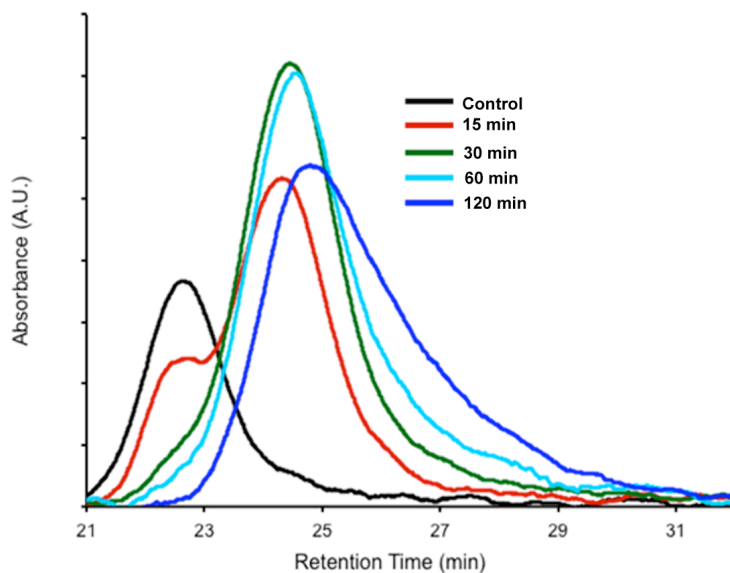
## Sonication and Labeling of BCH-PMA<sub>2,151k</sub>



**Figure S7:** RI (blue) and UV<sub>365nm</sub> (red) traces for BCH-PMA<sub>2,151k</sub> reacted with MAMA without sonication (control).



**Figure S8:** RI (blue) and UV<sub>365nm</sub> (red) traces for BCH-PMA<sub>2,151k</sub> reacted with MAMA after 120 min. sonication.



**Figure S9:** UV<sub>365nm</sub> traces for BCH-PMA<sub>2,151k</sub> at various sonication times. Shown as moving average (50 pt) for clarity.

The raw RI integrals were normalized to 1 mg by dividing by the injected mass:

$$\frac{\int RI_{Raw}}{Mass\ Injected(mg)} = \int RI_{Norm}$$

or

$$\frac{\int RI_{Norm}}{\int RI_{Raw}} = N$$

Where the normalization factor N is used to normalize the raw integral UV absorbance:

$$N * \int UV_{Raw} = \int UV_{Norm}$$

The normalized integral UV absorbance for the control was then subtracted from that of the sonicated sample to generate a net UV absorbance due to sonication:

$$\int UV_{Norm,sonicated} - \int UV_{Norm,control} = \int UV_{Norm,net}$$



The moles of MAMA incorporated due to sonication was determined using the following relation:

$$\frac{\int UV_{Norm,net} (A * \text{min}) * \text{flow rate} (mL * \text{min}^{-1})}{7270 (mol^{-1}Lcm^{-1}) * 1cm * \frac{1000mL}{L}} = mol_{MAMA}$$

Moles of initial polymer were determined based on  $MW_N$  for 1 mg of polymer:

$$\frac{0.001g}{MW_{N,Polymer}} = mol_{Polymer}$$

Finally, the  $\chi_{MAMA}$  value, defined as number of MAMA molecules per initial polymer chain was determined:

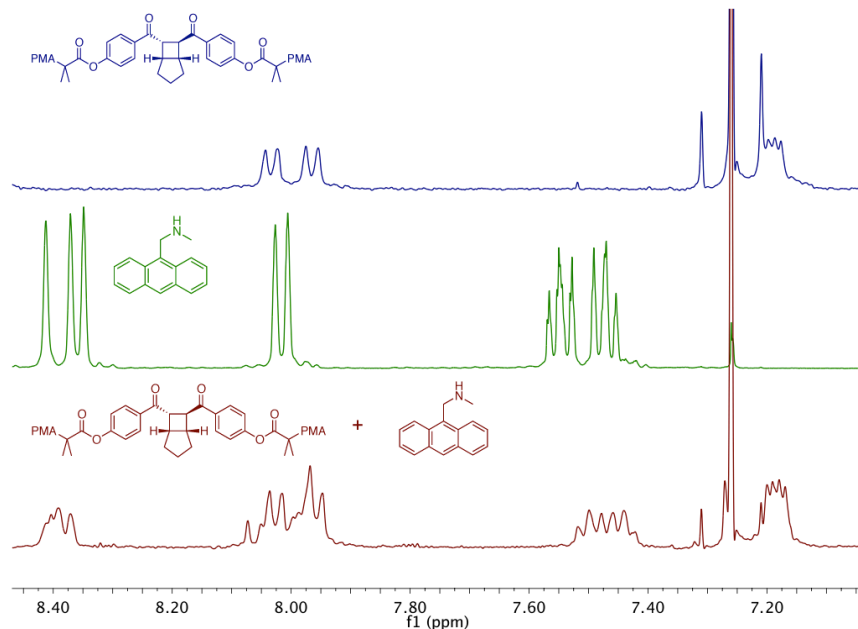
$$\frac{mol_{MAMA}}{mol_{Polymer}} = \chi_{MAMA}$$

### **Sonication and Labeling of BCH-PMA<sub>1,158k</sub>**

Experiment was performed as described in the general sonication and GPC-UV section. Data was analyzed in a fashion identical to that of BCH-PMA<sub>2,151k</sub> and results are summarized in Table S1.

### Sonication and Labeling of BCH-PMA<sub>2,23k</sub>

Experiment was performed as described in the general sonication and GPC-UV section. Data was analyzed in a fashion identical to that of BCH-PMA<sub>2,151k</sub> and results are summarized in Table S1. BCH-PMA<sub>2,23k</sub> (blue) was subjected to general sonication conditions and treated with MAMA (green). After typical GPC-UV analysis as described above, the polymer was purified by Preparatory GPC. The resulting <sup>1</sup>H NMR spectrum shown below (red), shows incorporated MAMA aromatic peaks due to chain-end functionalization, as well as unchanged BCH aromatic peaks.



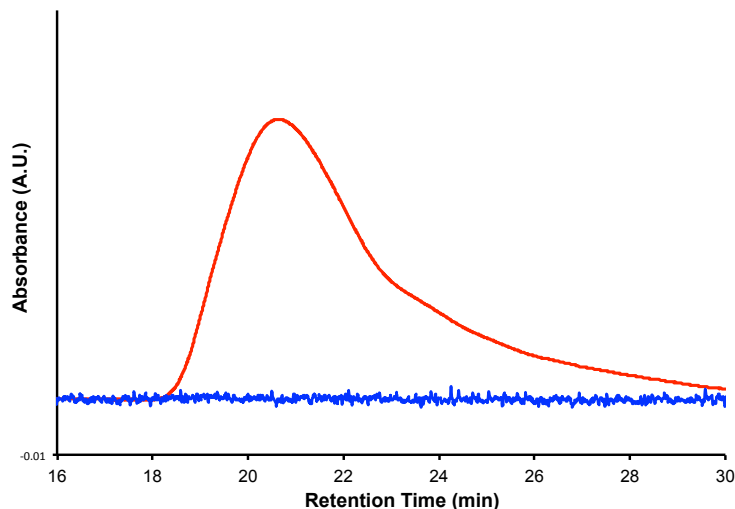
**Figure S10:** <sup>1</sup>H NMR of aromatic region showing no change (red) in peak patterns or shifts to the BCH aromatic protons (blue) after treatment with MAMA (green).

### Sonication and Labeling of PMA<sub>LRP, 149k</sub>

Experiment was performed as described in the general sonication and GPC-UV section. Data was analyzed in a fashion identical to that of BCH-PMA<sub>2,151k</sub> and results are summarized in Table S1.

### Sonication and Labeling of PMA<sub>FRP, 157k</sub>

Experiment was performed as described in the general sonication and GPC-UV section. Data was analyzed in a fashion identical to that of BCH-PMA<sub>2,151k</sub> and results are summarized in Table S1. Below is shown the UV and RI traces for PMA<sub>FRP, 157k</sub> (control).



**Figure S11:** RI (Red) and UV<sub>365nm</sub> (Blue) traces for PMA<sub>FRP,157k</sub> reacted with MAMA. No discernible UV absorbance is present due to lack of reactive end groups preventing MAMA addition.

### Recyclization of BCH-PMA<sub>2,182k</sub>

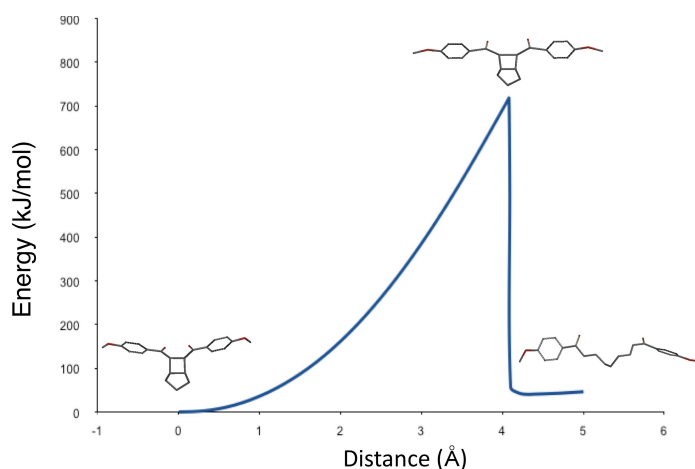
BCH-PMA<sub>2,182k</sub> was subjected to sonication and MAMA labeling as described above to generate UV and RI curves “Control” and “Sonicated.” A 50.3 mg (2.80  $\mu$ mol BCH) portion of sonicated BCH-PMA<sub>2,182k</sub> was reserved (without exposure to MAMA) and subjected to the following conditions:

Lithium tetrafluoroborate (61 mg, 0.65 mmol) and diisopropylethylamine (113  $\mu$ L, 0.65 mmol) were added to a 10 mL flame dried schlenk flask with sidearm under nitrogen. The sonicated BCH-PMA<sub>2,182k</sub> (50 mg) was added as a solution in 4 mL MeCN. The solution was subjected to three freeze-pump-thaw cycles, on the third cycle, while frozen, backfilling with nitrogen and adding Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (12 mg, 16  $\mu$ mol) as a solid while flushing with nitrogen. The flask was sealed with a rubber septum and subjected to three pump-backfill cycles while frozen. After thawing, the flask was placed 20 cm from a 300W sunlamp in a water bath and irradiated for 2 hr. The solution was concentrated to a minimal volume and precipitated into MeOH. This was repeated twice more before the polymer was dried in vacuo overnight. The polymer was then subjected to MAMA labeling and GPC-UV as described above to generate BCH-PMA<sub>2,182k</sub> (recyclized) (Table S1.).

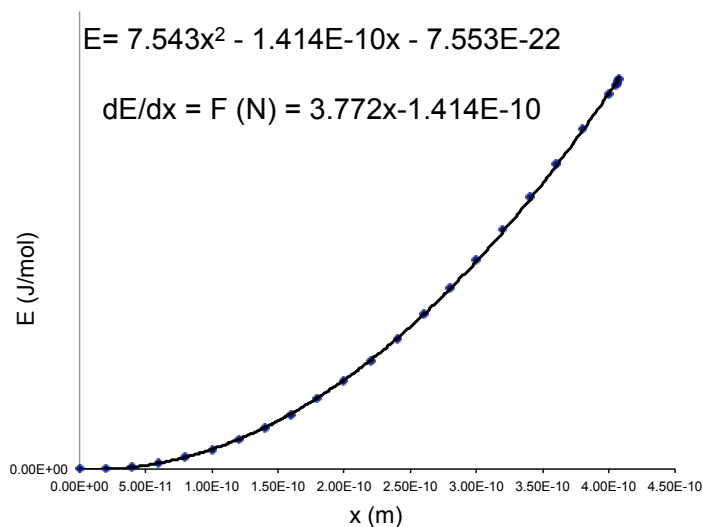
## CoGEF Calculations

### Methods

Procedure was performed similar to that described by Beyer.<sup>5</sup> All calculations were performed using DFT-B3LYP 6-31G\* level of theory. Structures were imported into Spartan 06 from .cdx files. After energy minimization, the structures were constrained at the terminal methyl carbons and the constraints were increased in increments of 0.2 Å, with increasingly smaller increments near rupture point as summarized in the table below. Relative energies were generated by setting that of the initial conformer to 0 kJ/mol. Failure was determined to be the precipitous drop in energy that occurred simultaneously with large elongations in cyclobutane C-C bond lengths (4.08 Å). The relationship between force and elongation was determined as the 1st derivative of a fit (2nd order polynomial) of the energy vs. distance curve (below).

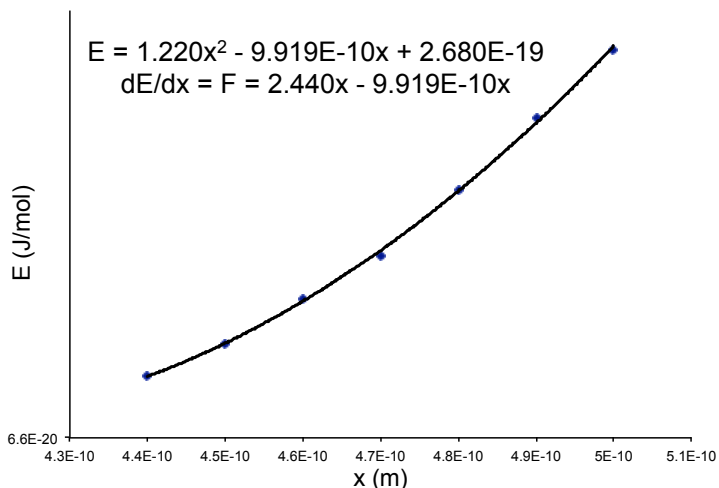


**Figure S12:** Energy vs. displacement curve

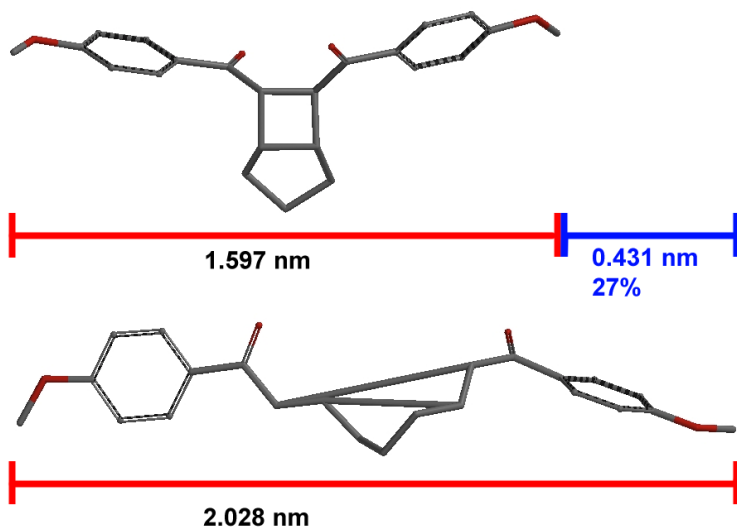


**Figure S13:** Polynomial fit and 1st derivative of energy vs. extension curve (pre-failure).

Percent extension was calculated by using the contour lengths for the model compound at 100 pN using the curve above for the initial length and the curve below (after failure) for the final contour length.



**Figure S14:** Polynomial fit and 1st derivative of energy vs. extension curve (post-failure).



**Figure S15:** Illustration of change in contour length due to ring opening.

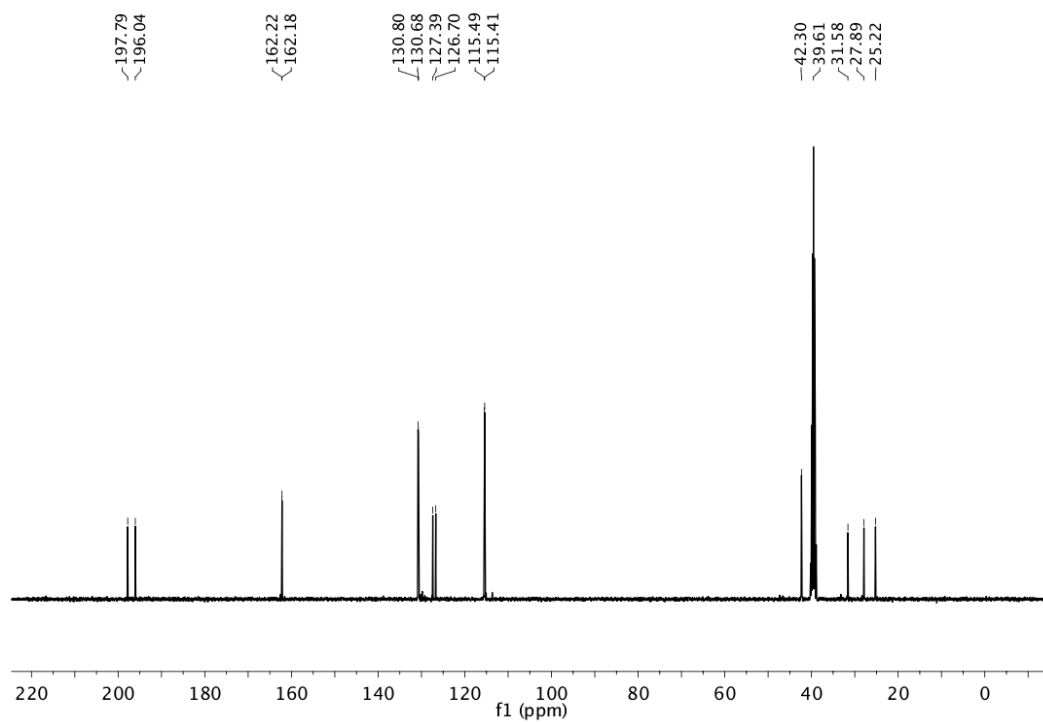
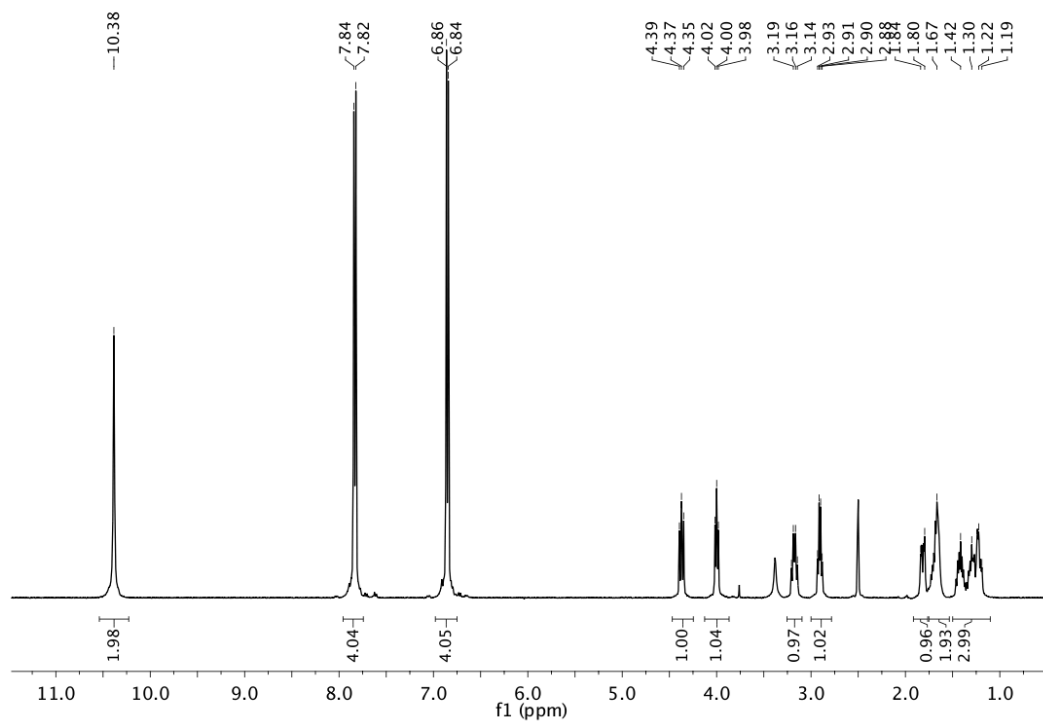
**Table S2:** Summary of CoGEF data points.

E(joules/molecule)	Distance(m)
0.00E+00	0.00E+00
1.68E-21	2.00E-11
7.53E-21	4.00E-11
1.91E-20	6.00E-11
3.66E-20	8.00E-11
6.00E-20	1.00E-10
8.94E-20	1.20E-10
1.25E-19	1.40E-10
1.66E-19	1.60E-10
2.14E-19	1.80E-10
2.69E-19	2.00E-10
3.30E-19	2.20E-10
3.98E-19	2.40E-10
4.73E-19	2.60E-10
5.53E-19	2.80E-10
6.40E-19	3.00E-10
7.33E-19	3.20E-10
8.31E-19	3.40E-10
9.33E-19	3.60E-10
1.04E-18	3.80E-10
1.15E-18	4.00E-10
1.18E-18	4.06E-10
1.18E-18	4.05E-10
1.19E-18	4.07E-10
1.19E-18	4.08E-10
8.76E-19	4.09E-10
9.51E-20	4.10E-10
7.19E-20	4.20E-10
6.70E-20	4.30E-10

6.78E-20	4.40E-10
6.86E-20	4.50E-10
6.99E-20	4.60E-10
7.11E-20	4.70E-10
7.30E-20	4.80E-10
7.50E-20	4.90E-10
7.69E-20	5.00E-10

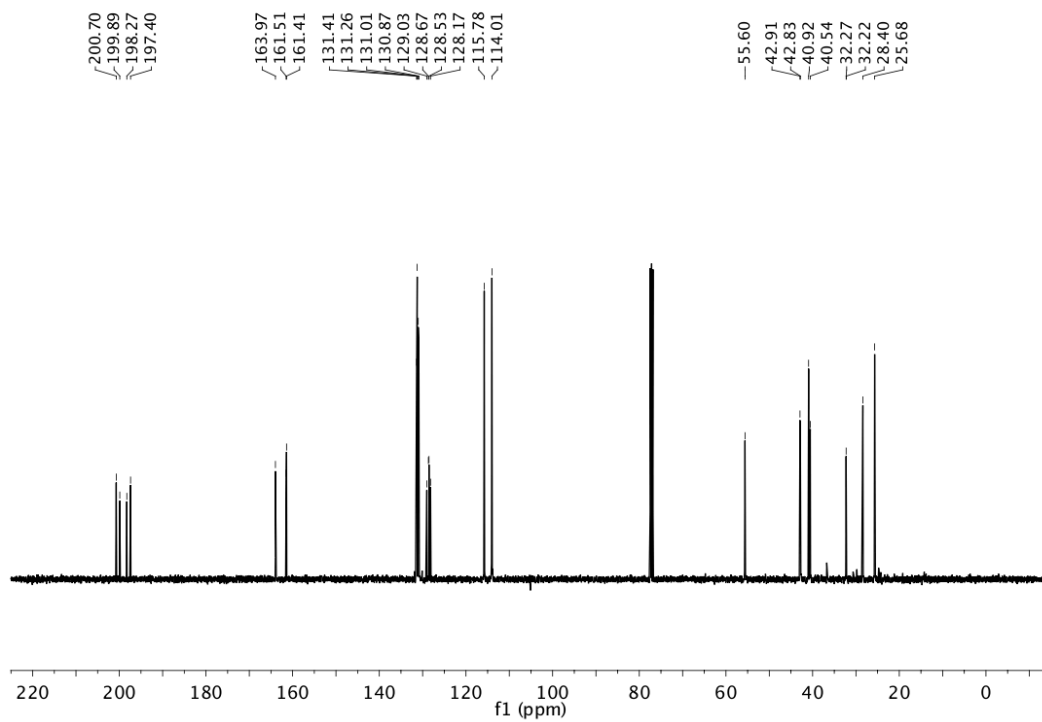
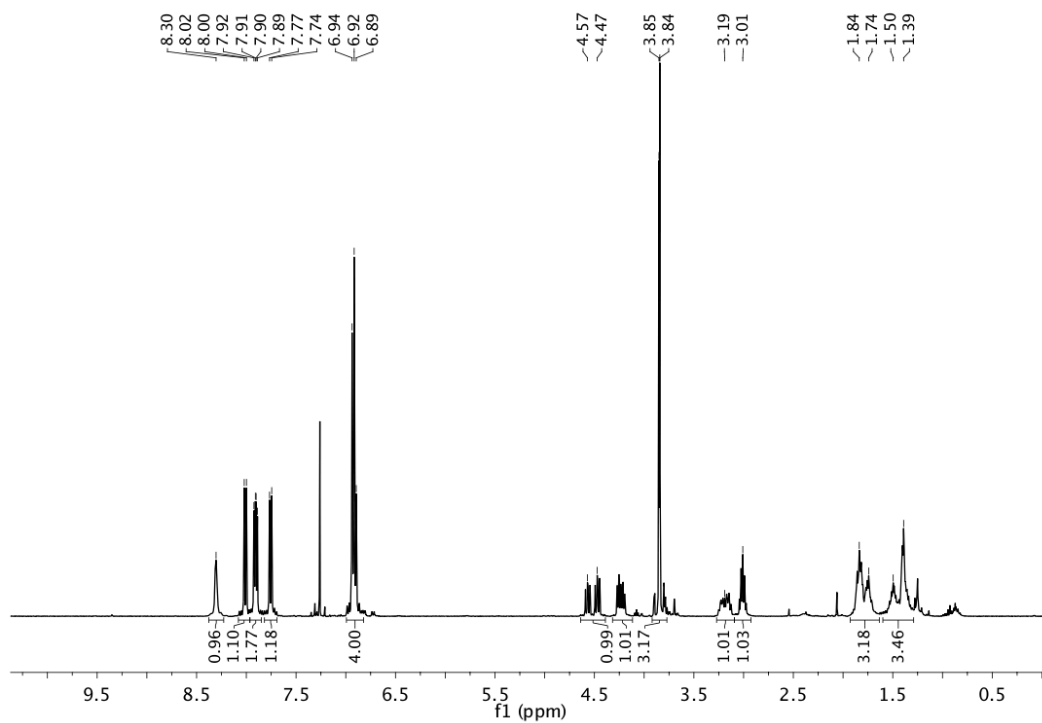
# $^1\text{H}$ and $^{13}\text{C}$ Spectra

1a

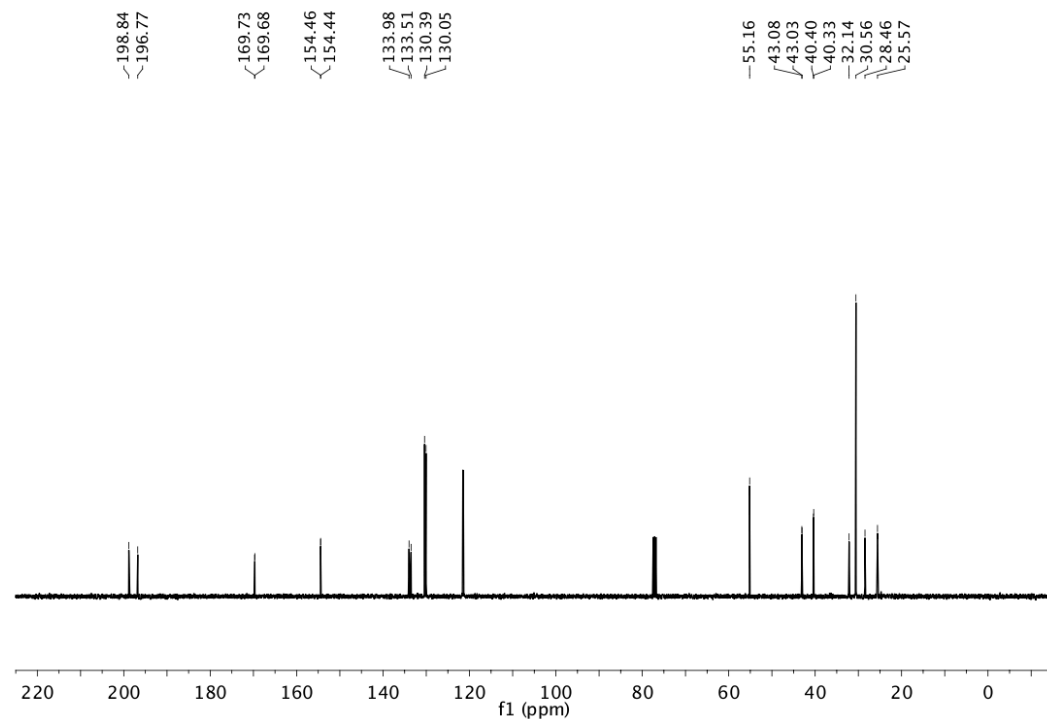
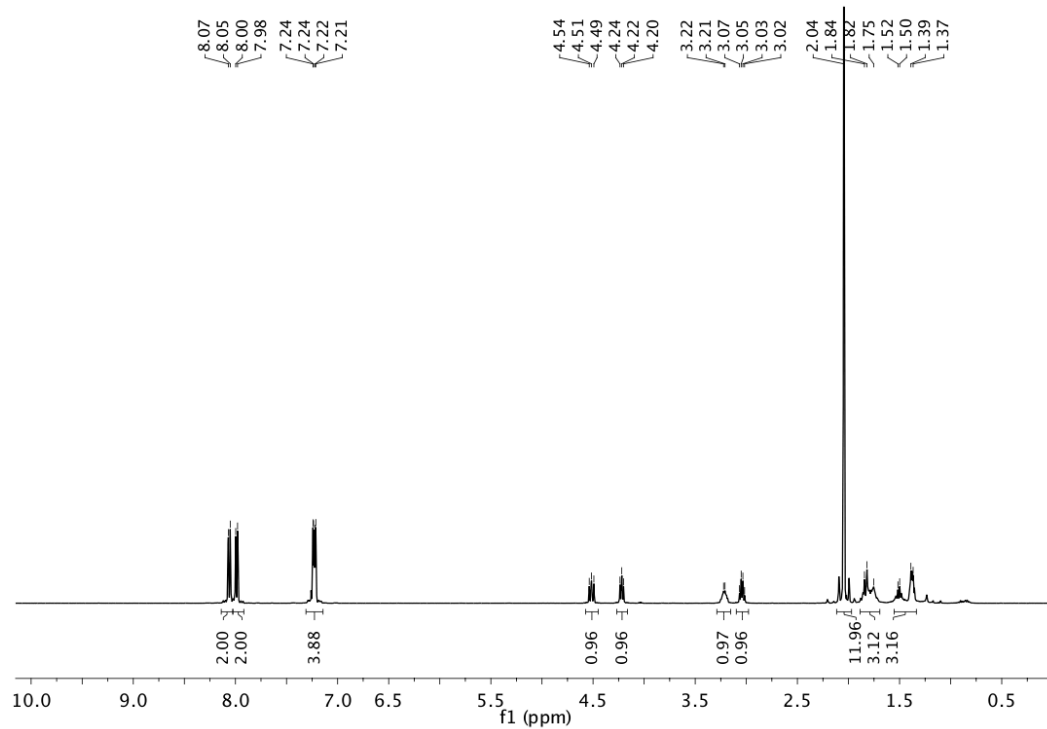




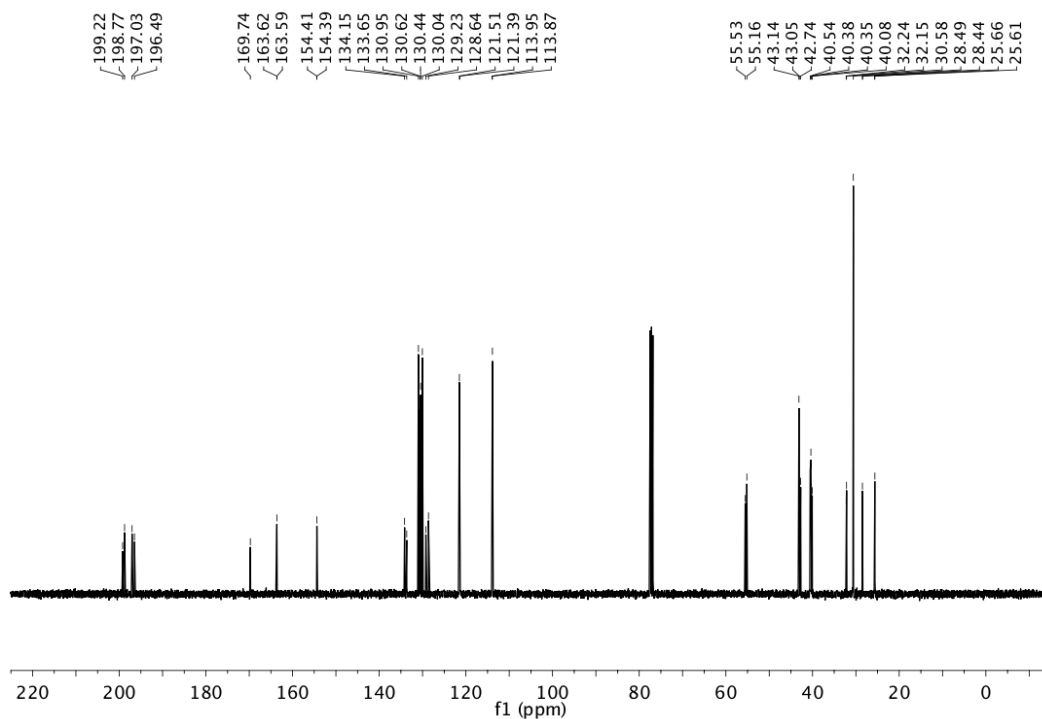
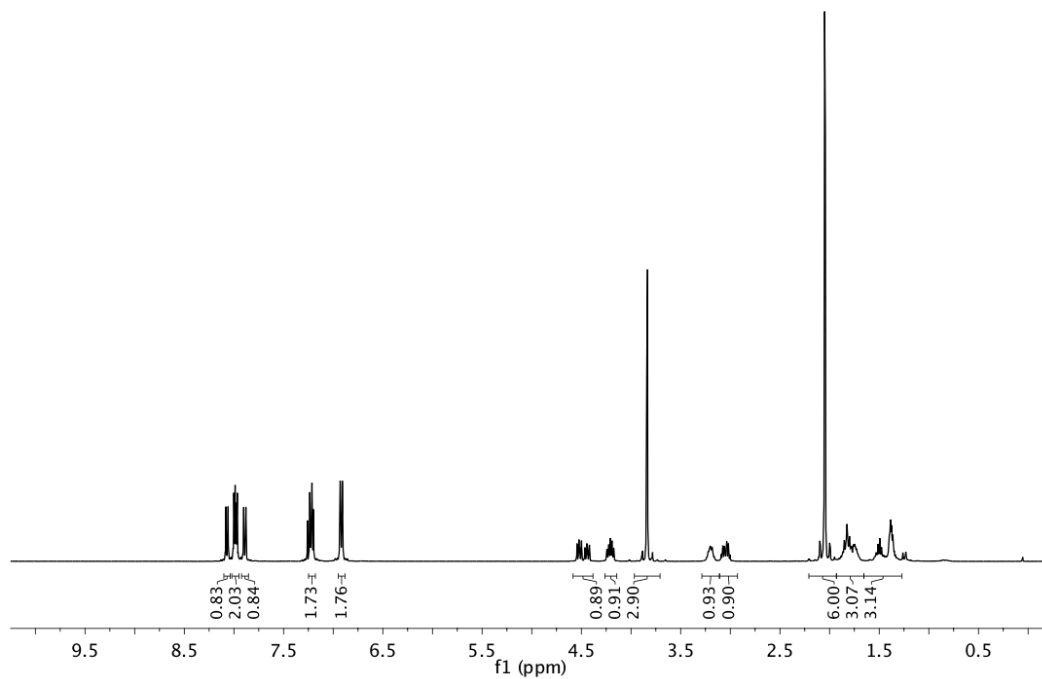
1b



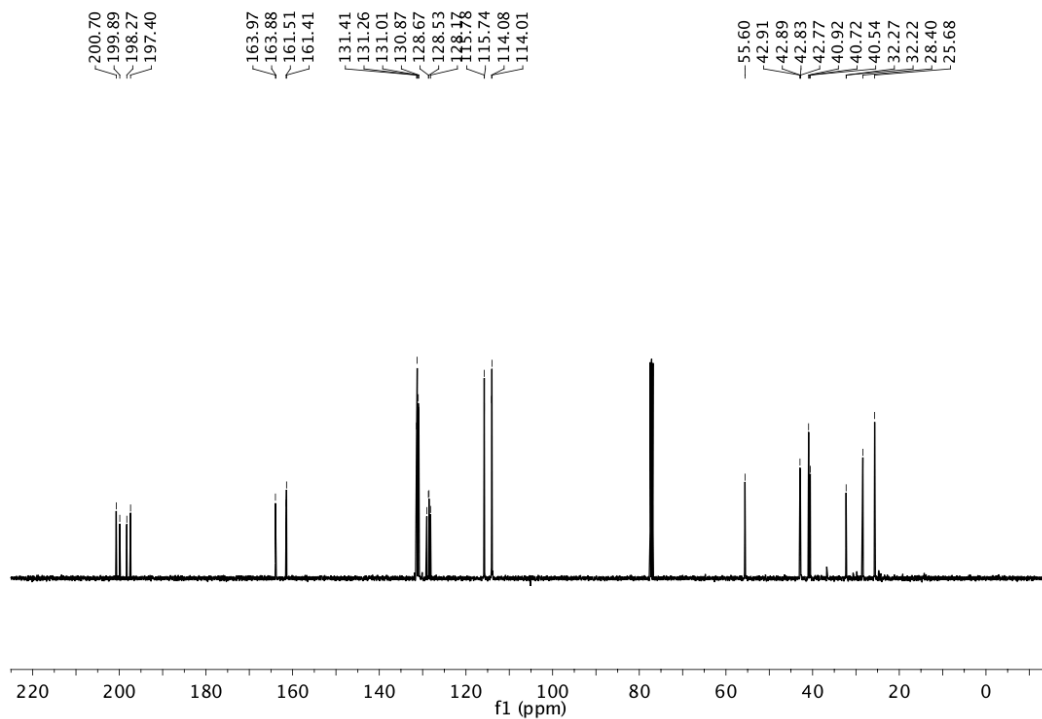
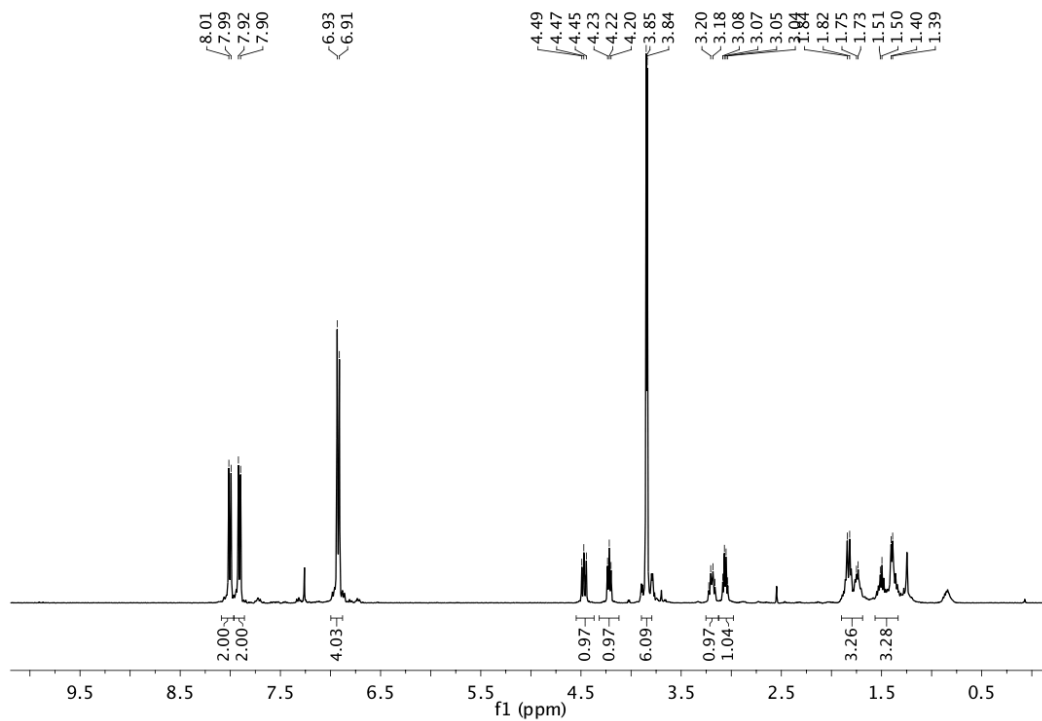
2



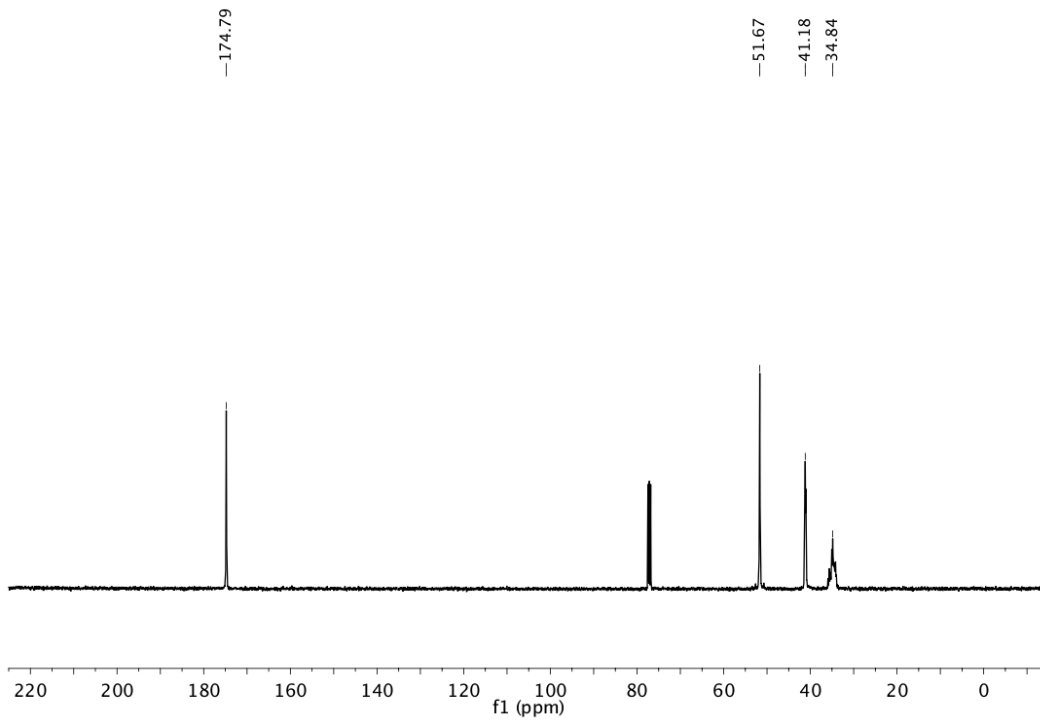
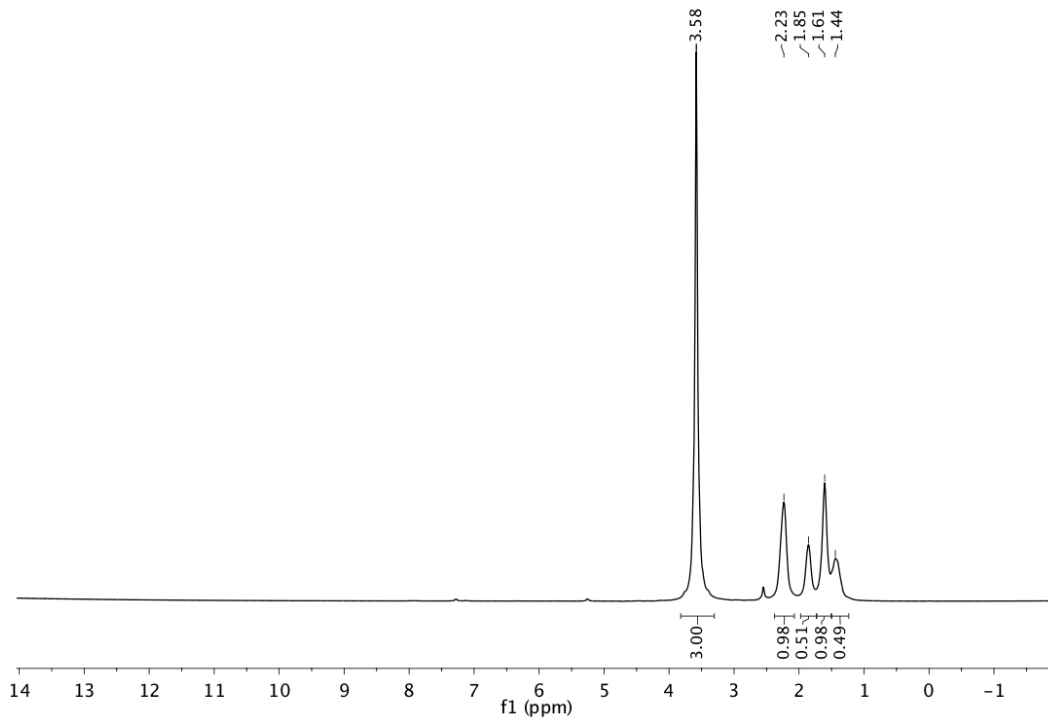
3



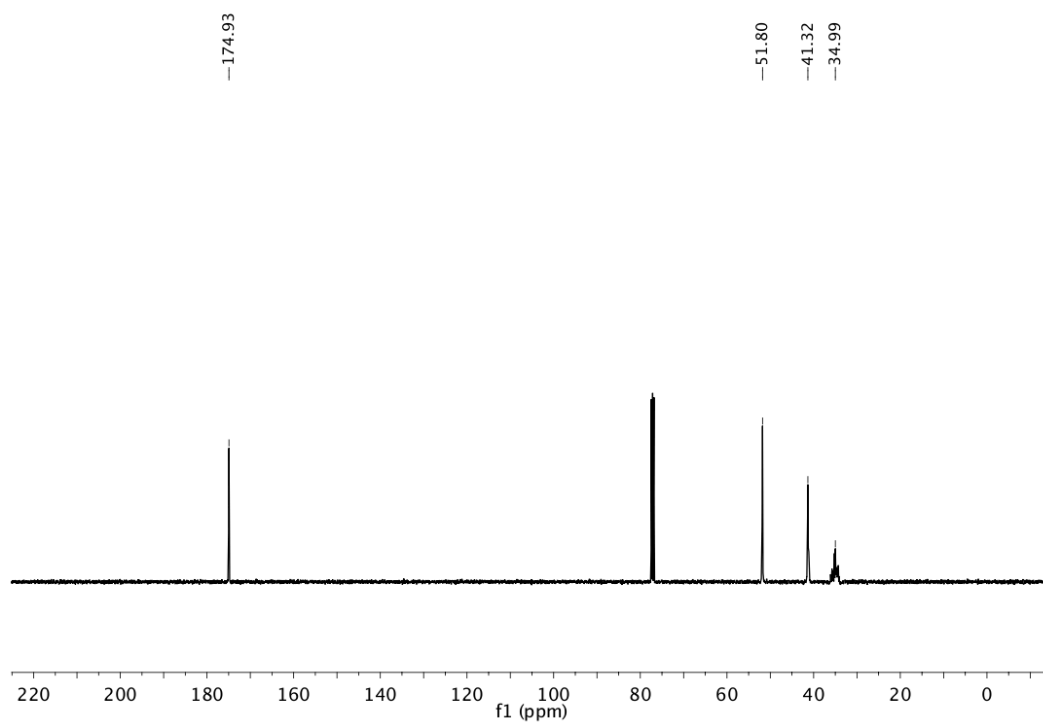
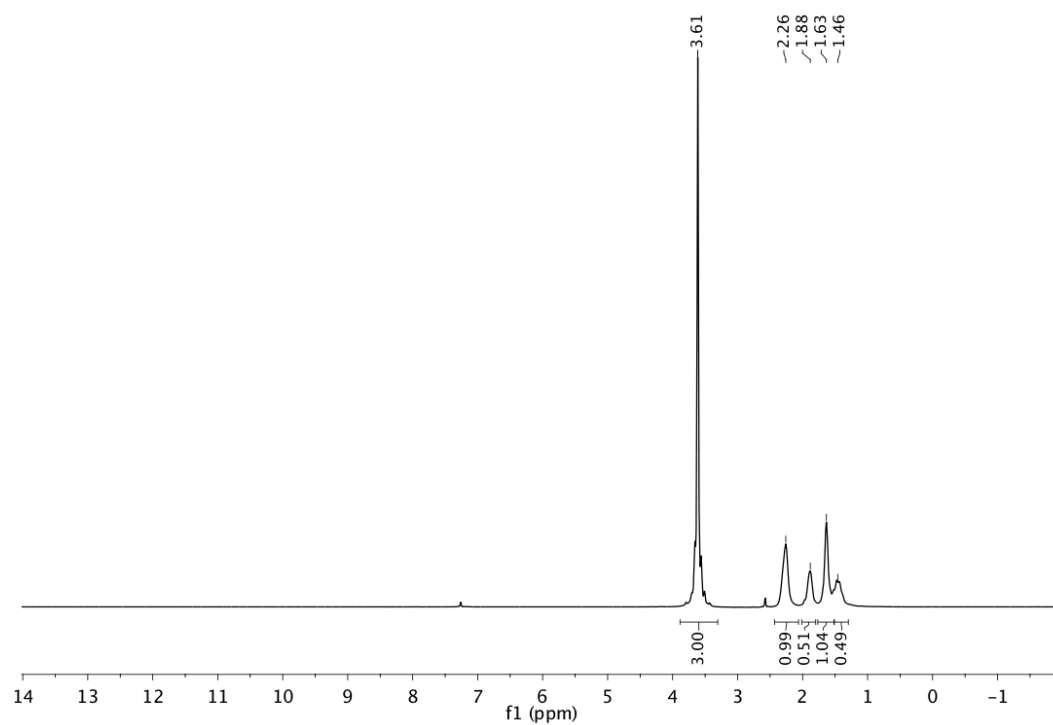
5



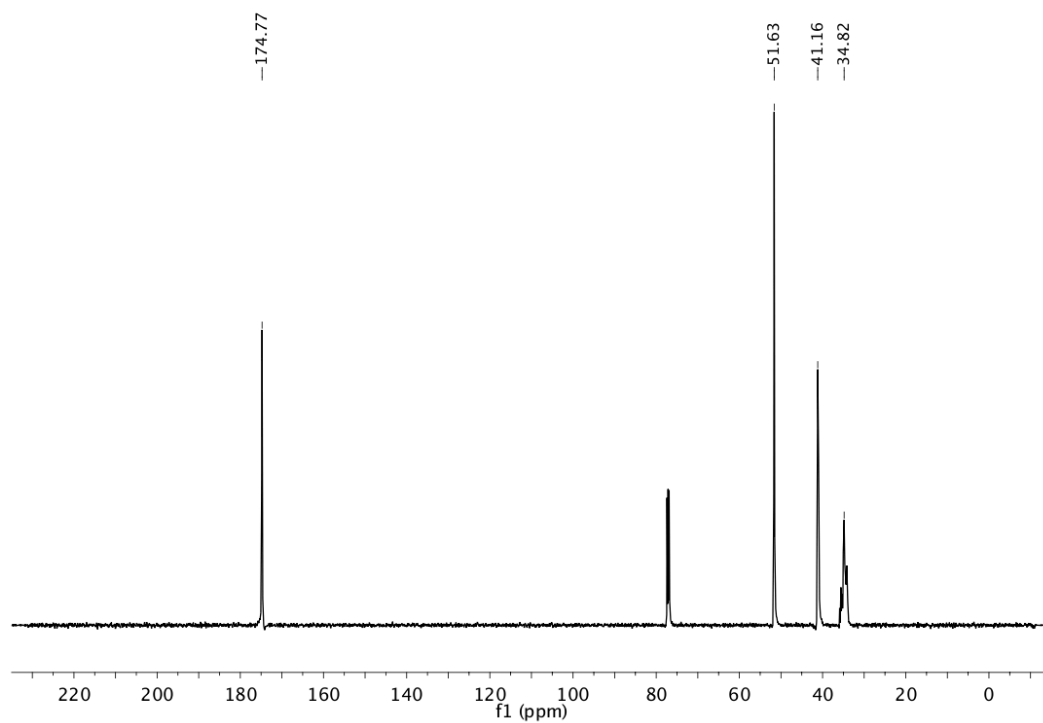
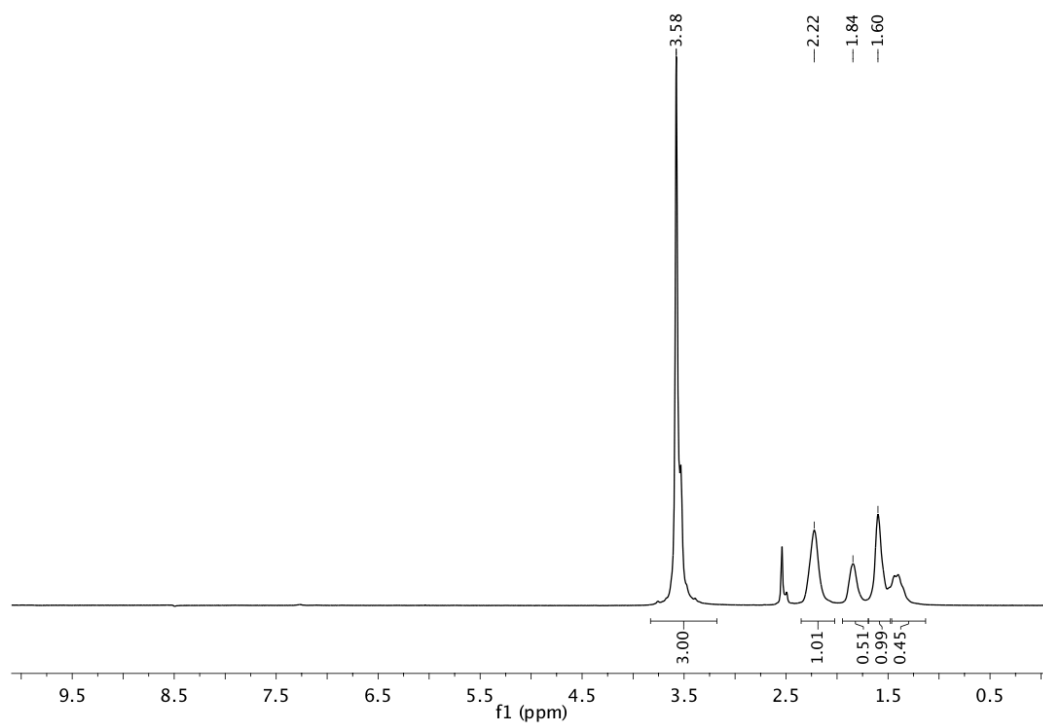
BCH-PMA<sub>2,151k</sub>



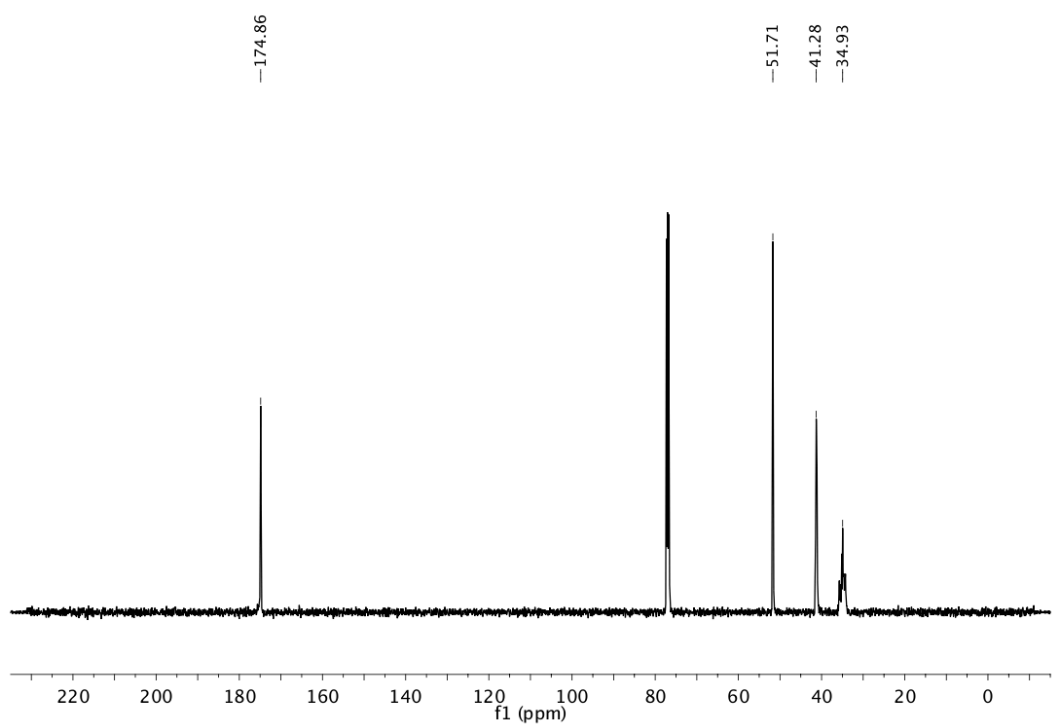
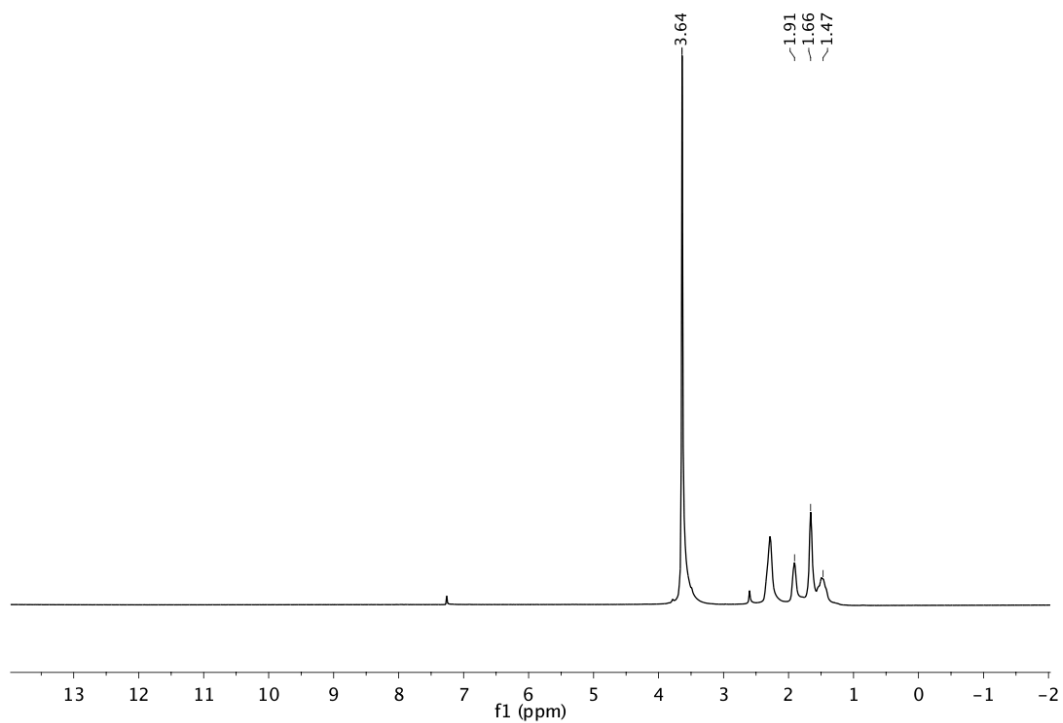
# BCH-PMA<sub>2,151k</sub> Sonicated



BCH-PMA<sub>1,158k</sub>

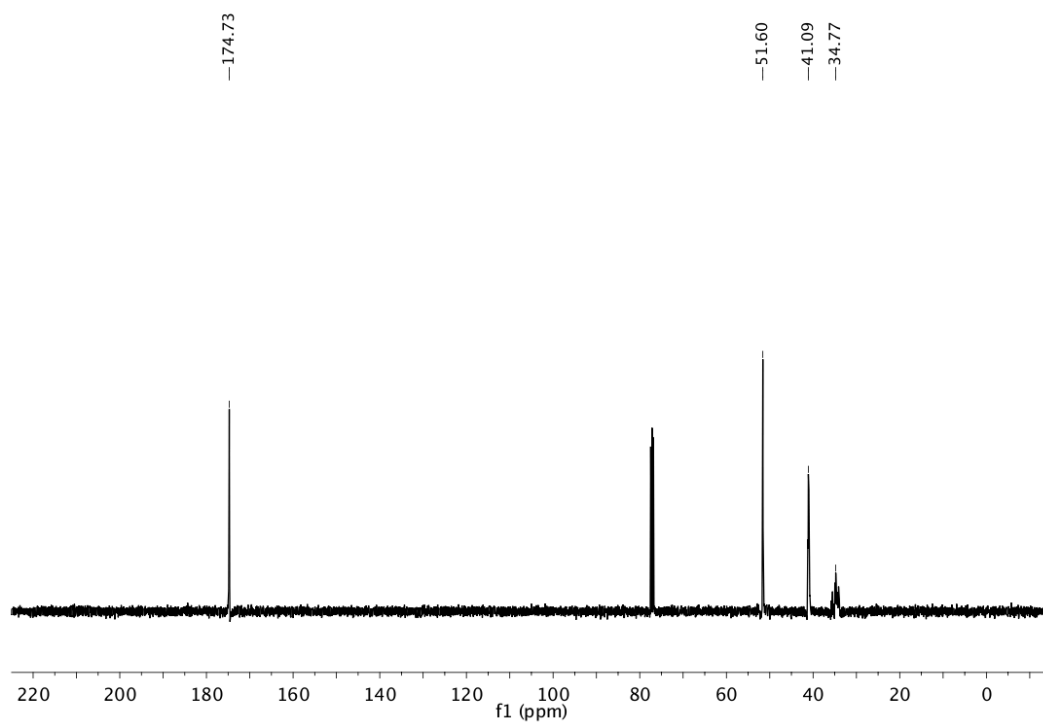
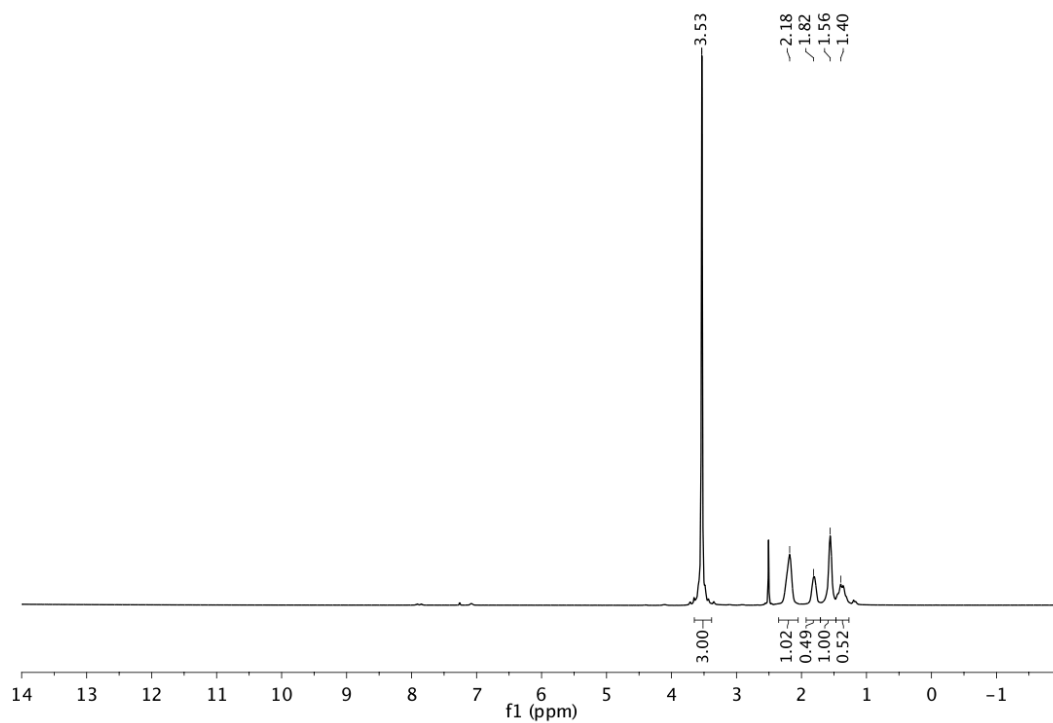


**BCH-PMA<sub>1,158k</sub> sonicated**

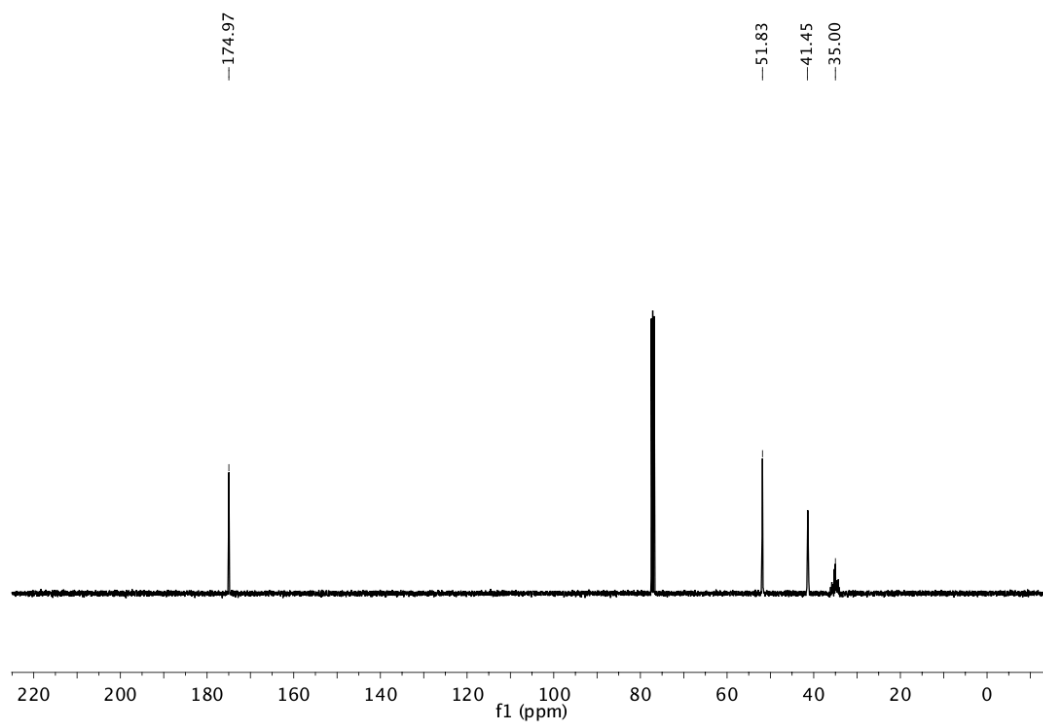
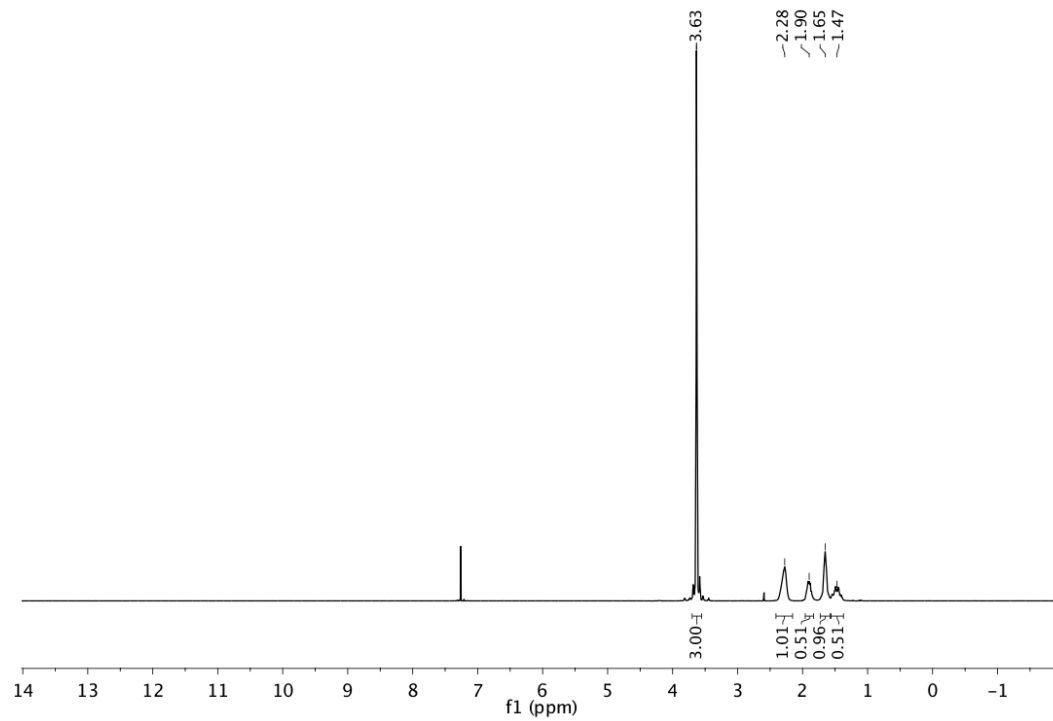




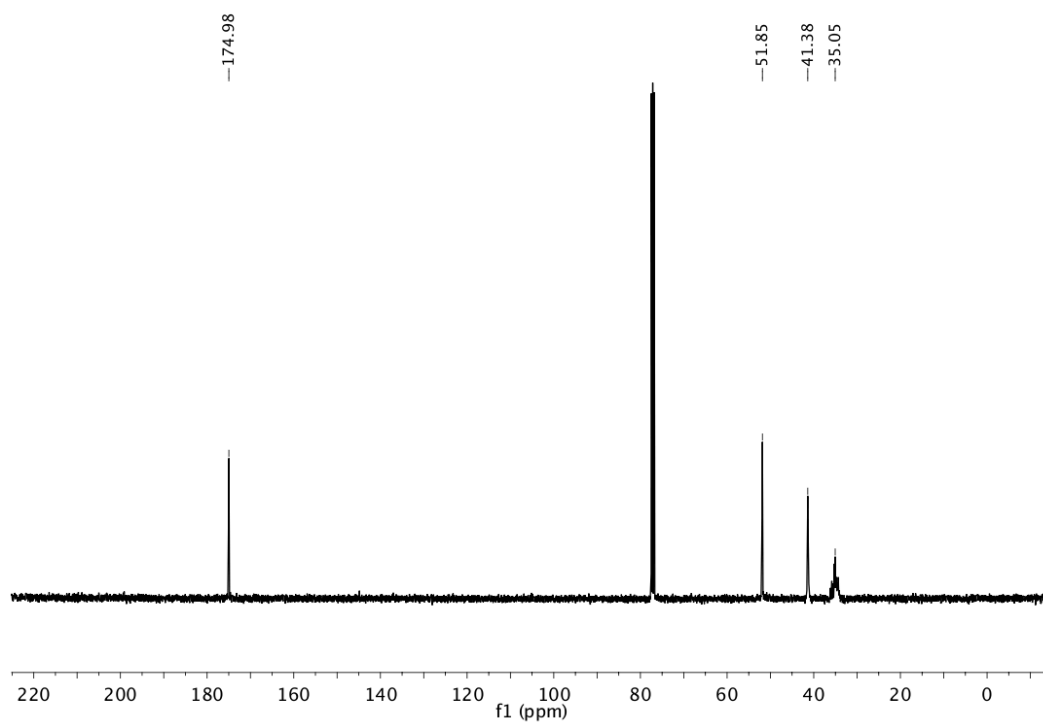
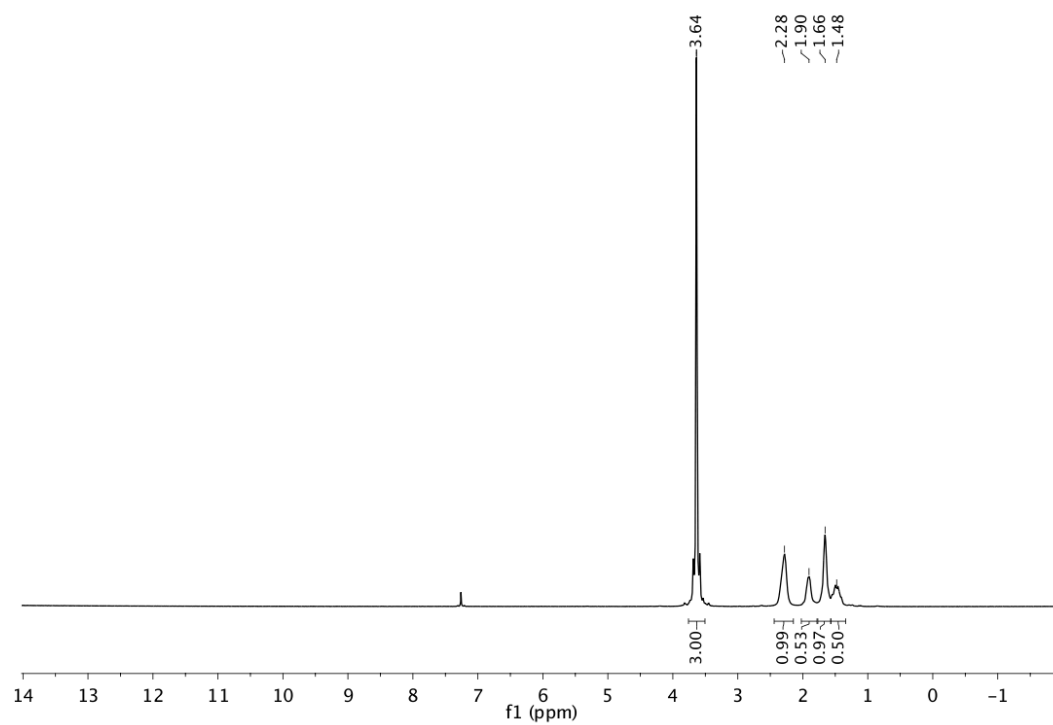
BCH-PMA<sub>2,23k</sub>



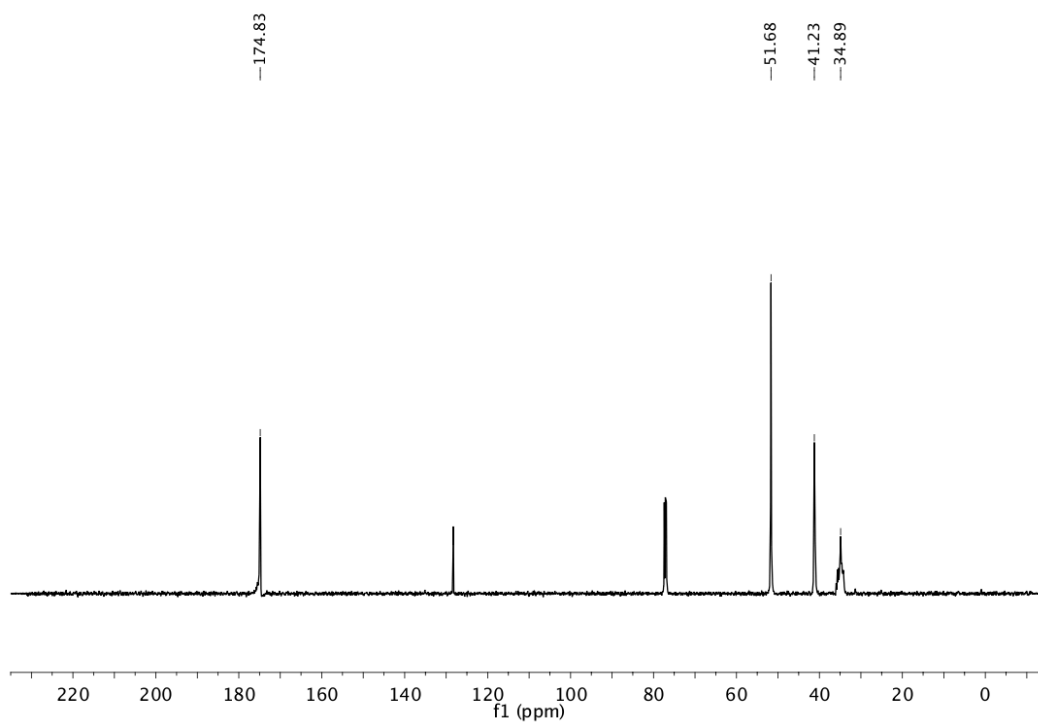
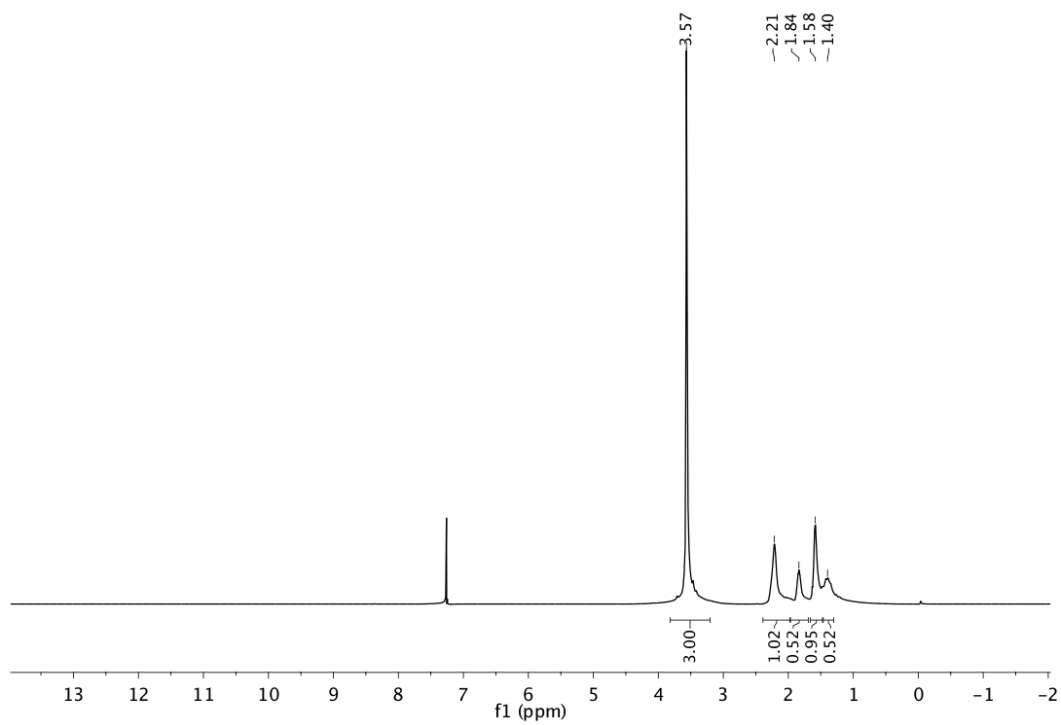
PMA<sub>CRP,149k</sub>



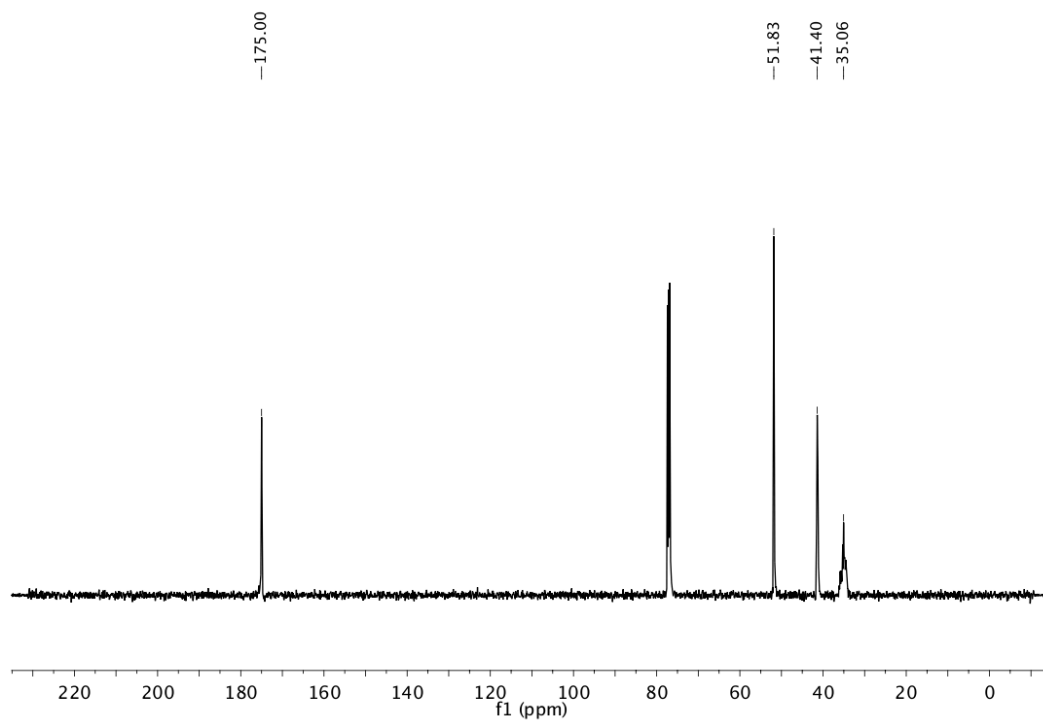
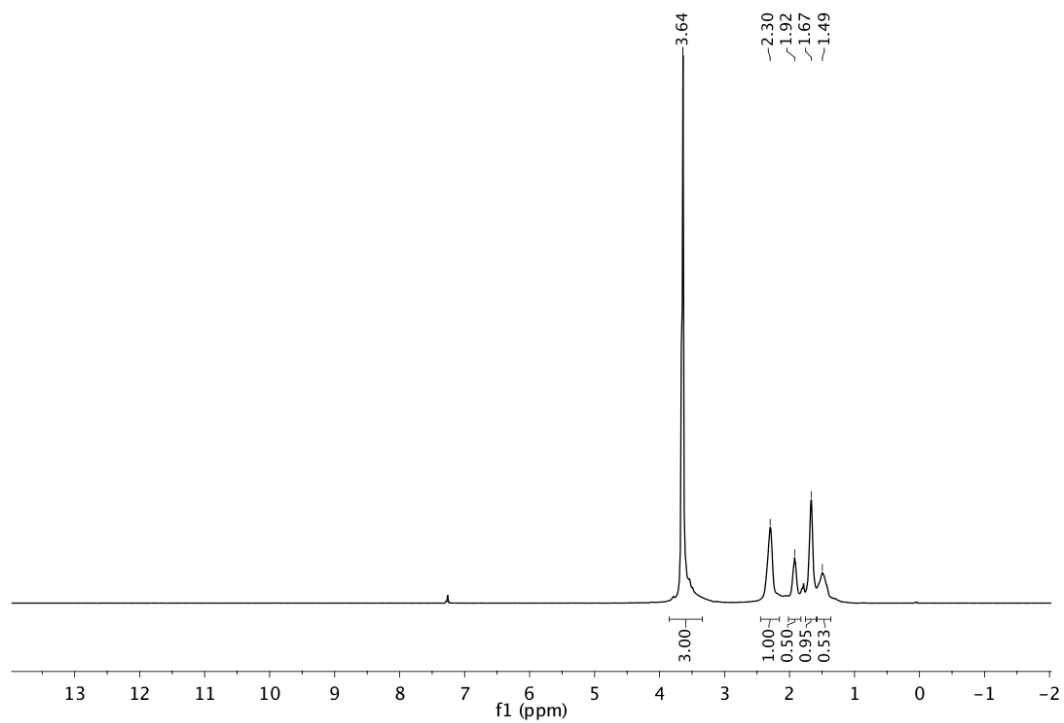
**PMA<sub>CRP,149k</sub> sonicated**



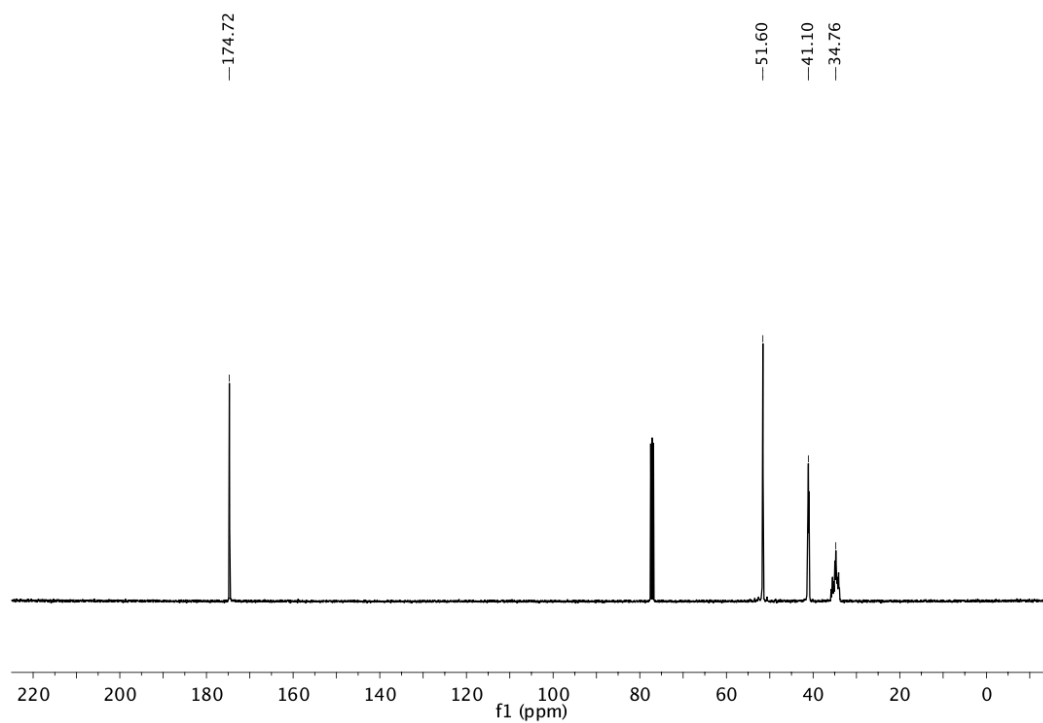
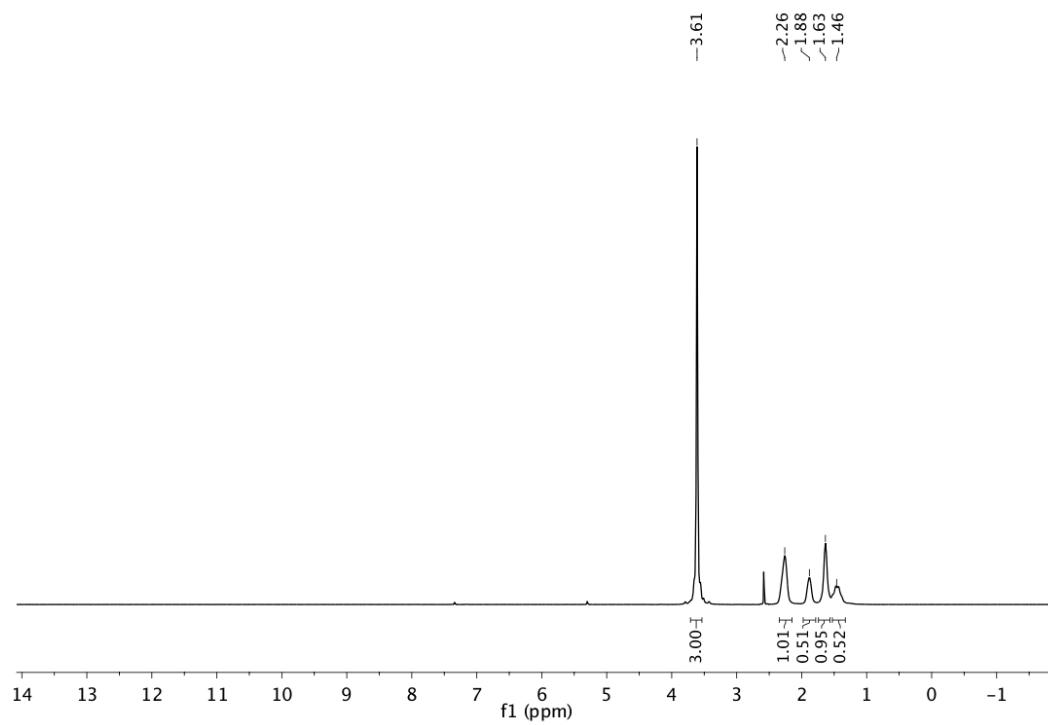
PMA<sub>LRP</sub>, 149k



# PMA<sub>LRP</sub>, 149k Sonicated



BCH-PMA<sub>2,182k</sub>



## Bibliography

- (1) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41-44.
- (2) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, *130*, 12886-12887.
- (3) Lenhardt, J. M.; Ong, M. T.; Choe, R.; Evenhuis, C. R.; Martinez, T. J.; Craig, S. L. *Science* **2010**, *329*, 1057-1060.
- (4) Podzimek, S. *Light Scattering, Size Exclusion Chromatography and Asymmetric Flow Field Flow Fractionation: Powerful Tools for the Characterization of Polymers, Proteins and Nanoparticles*; John Wiley & Sons, 2011.
- (5) Beyer, M. K. *J. Chem. Phys.* **2000**, *112*, 7307-7312.