Supporting Information For:

Stress-Responsive Polymers Containing Cyclobutane Core Mechanophores: Reactivity and Mechanistic Insights

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Table of Contents

I. General Procedures

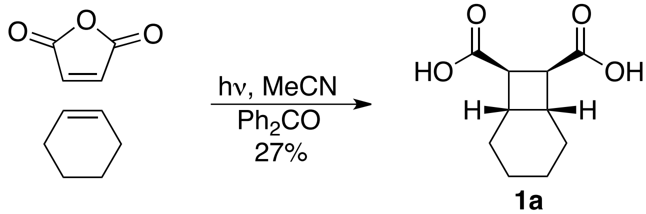
Dry solvents were obtained from Sigma-Aldrich and purified with a Pure Solv^{TM} solvent purification system before use. $CDCl_3$ and DMSO-d_6 were purchased from Cambridge Isotope Laboratories. All GPC experiments were performed using inhibitor free Chromasolv grade THF obtained from Sigma-Aldrich. Ethyl thioglycolate (97%) and 1,4-butanediol bis(thioglycolate) (95%) were purchased from TCI and used without further purification. Maleic anhydride was recrystallized from chloroform and cyclohexene was washed with acidic aqueous ferrous sulfate and distilled over calcium hydride before use. All other reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise noted.

All ^{1}H and ^{13}C spectra were collected in either $CDCl_3$ (δ = 7.26 (^{1}H) and 77.16(^{13}C)) or DMSO-d_6 (δ = 2.50 (^{1}H) and 39.52 (^{13}C)) and referenced to residual solvent peak on either a Varian 400 or 500 MHz spectrometer. All chemical shifts are given in ppm (δ) and coupling constants (J) in Hz as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), or broad (br). Column (flash) chromatography was performed using Silicycle F60 (230-400 mesh) silica gel.

Gel permeation chromatography (GPC) was performed on two in series columns (Agilent Technology PL gel 10^4 Å, 10^3 Å) with THF as the mobile phase at 0.5 mL min^{-1} with the flow rate set with a Varian Prostar Model 210 pump. Molecular weights were determined using an inline Wyatt Dawn EOS multi-angle light scattering (MALS) detector and a Wyatt Optilab DSP Interferometric Refractometer (RI). The dn/dc values were determined in-line, assuming 100% mass recovery based on known injection mass. All dn/dc values for *cis* and *trans* BCO polymers (**P1, P2, P12, PC**) were determined to be within 0.058 ± 0.004 for both sonicated and unsonicated samples, a value of 0.058 was used for these polymers, while **P3** (dn/dc = 0.058 ± 0.003) and **P4** (dn/dc = 0.048 ± 0.001) were determined independently.

Small Molecule Synthesis and Characterization

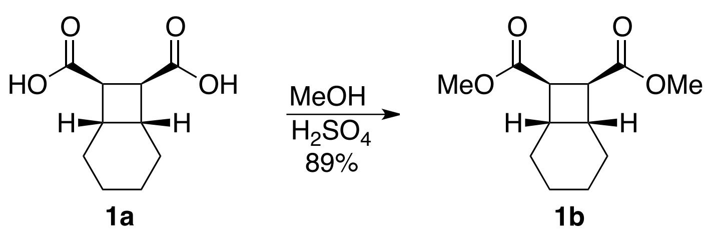
Compound 1a: *cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylic acid



Using procedure modified from those previously reported,[1-4] benzophenone (5.00 g, 27.4 mmol), maleic anhydride (20.0 g, 197 mmol), and cyclohexene (100 mL, 987 mmol) were dissolved in 300 mL acetonitrile in a 500 mL photochemical reactor fitted with a water-cooled quartz emersion well. The solution was sparged with argon for 30 minutes then irradiated with a 450 W medium pressure mercury arc lamp through a Pyrex filter for 5 hours under argon. During the course of the reaction, the internal temperature stabilized at 35 °C. Acetonitrile and cyclohexene were removed under reduced pressure and resulting residue was distilled under high vacuum, collecting all volatiles distilling between 110 and 200 °C (200-500 mTorr). The distillate was stirred with 100 mL 2 N aqueous NaOH for 1 hour then extracted with 50 mL diethyl ether. The aqueous layer was then neutralized carefully with concentrated HCl at which point a white precipitate formed with was filtered and washed with MeOH (20 mL) to yield **1a** as a white powder in 27% yield (10.6 g, 53.5 mmol). Due to poor solubility, the compound was further characterized as the methyl ester.

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 2.92 (br d, 2H, J = 4.88 Hz), 2.48 (br, 2H), 1.64 (br, 2H), 1.43 (br, 4H), 1.24 (br, 2H); ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 174.86, 43.82, 34.07, 26.86, 21.92

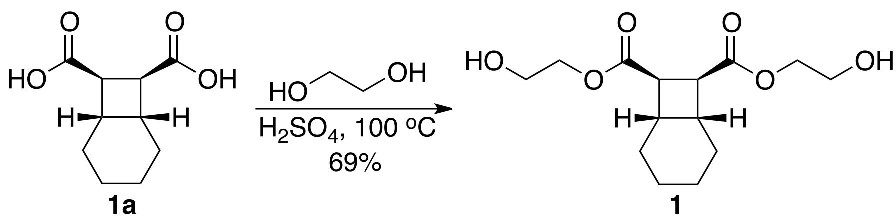
Compound 1b: Dimethyl *cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylate



Diacid **1a** (1.00 g, 5.05 mmol) was suspended in 20 mL dry MeOH in an oven dried 50 mL round bottom flask under argon. Concentrated H_2SO_4 (0.540 mL, 10.1 mmol) was carefully added and the solution was heated at reflux overnight, becoming homogenous after approximately 1 hour. The solution was cooled and carefully quenched with $NaHCO_3$ until effervescence ceased. Methanol was removed under reduced pressure and the residue was suspended in 100 mL water and extracted with EtOAc (3 x 50 mL), the combined organics were dried over $MgSO_4$ and solvent evaporated to give crude yellow oil which was purified by column chromatography (80:20 Hexanes:EtOAc) to give a clear oil in 88.5 % yield (1.01 g, 4.47 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 6H), 3.10 (d, 2H, J = 4.88), 2.74 (br, 2H), 1.76 (br, 2H), 1.47 (br, 4H), 1.33 (br, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.02, 51.28, 42.98, 33.07, 26.54, 21.67. HRMS-ESI (*m/z*): calcd for $C_{12}H_{18}O_4$ [MH+], 227.1278; found, 227.1279

Compound 1: Bis(2-hydroxyethyl)-*cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylate



Diacid **1a** (4.02 g, 20.3 mmol) was suspended in 31 mL dry ethylene glycol in an oven dried 100 mL round bottom flask under argon. Concentrated H_2SO_4 (2.15 mL, 40.6 mmol) was carefully added at which point the mixture became homogenous. The solution was heated at 100 °C overnight under a stream of argon. After cooling, the reaction was quenched by pouring into 100 mL sat. $NaHCO_3$ and extracted with EtOAc (4 x 100 mL). The combined organics were washed with 200 mL water and dried over Na_2SO_4, then evaporated under reduced pressure to give a light yellow oil which was subjected to column chromatography (gradient, DCM to 2% MeOH in DCM) to give **X** as a clear yellow oil in 69.4 % yield (4.03 g, 14.1 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26-4.32 (m, 2H), 4.12-4.18 (m, 2H), 3.80 (br, 4H), 3.19 (d, 2H, J = 5.08), 2.78 (br, 2H), 2.63 (br, 2H), 1.72-185 (m, 2H), 1.42-1.55 (m, 4H), 1.27-1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.68, 66.10, 60.37, 43.72, 33.53, 26.99, 21.99. HRMS-ESI (*m/z*): calcd for $C_{14}H_{22}O_6$ [M+Na]+, 309.1309; found, 309.1306

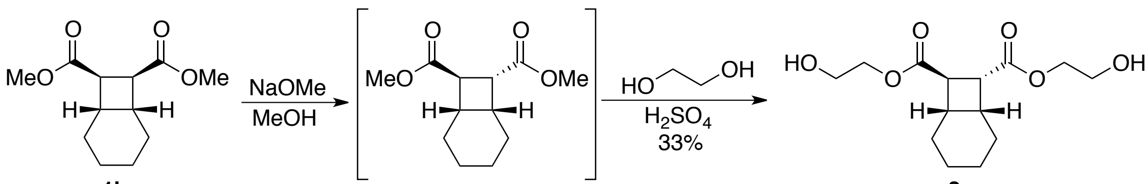
Compound 2a: Dimethyl *cis*-Bicyclo[4.2.0]octane-*trans*-7,8-dicarboxylate (racemic)

Under argon, methyl ester **1b** (1.50 g, 6.64 mmol) was dissolved in dry MeOH (5 mL) in a 25 mL oven dried round bottom flask with reflux condenser and stir bar. A 50 % (wt/wt) solution of sodium methoxide in methanol was added and the solution heated at reflux overnight. After cooling, the solution was poured into 100 mL of 1N HCl and extracted with DCM (3 x 50 mL), dried over $MgSO_4$, and evaporated to yield an 5:1 mixture of trans:cis diester. Purification by flash chromatography (SiO_2, 95:5

Hexanes:Ethyl Acetate) yielded pure trans isomer as a clear oil in 13.3 % yield (200 mg, 0.885 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.66 (s, 3H), 3.29 (m, 2H), 2.50 (m, 2H), 0.95-1.82 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.24, 172.28, 51.79, 51.57, 42.03, 40.67, 34.54, 33.17, 25.25, 24.42, 22.73, 21.70. HRMS-ESI (*m/z*): calcd for $C_{12}H_{18}O_4$ [M+Na]+, 249.1097; found, 249.1094

Compound 2: Bis(2-hydroxyethyl)-*cis*-Bicyclo[4.2.0]octane-*trans*-7,8-dicarboxylate (racemic)

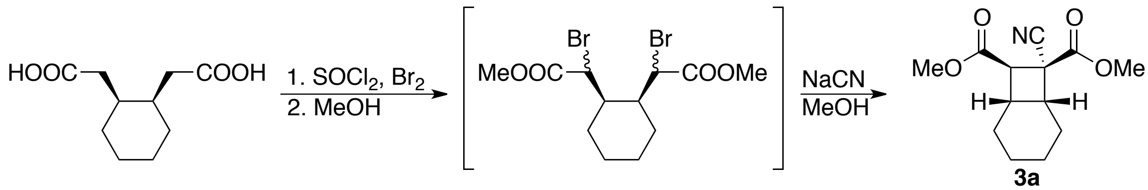


1b 2

Dimethyl ester **1b** (3.83 g, 17.0 mmol) was transferred to an oven dried 50 mL round bottom flask fitted with a reflux condenser under argon. Dry MeOH (12 mL) was added, followed by a solution of NaOMe in MeOH (25%, 7.6 mL). The solution was heated at reflux for 18 hours. After cooling, $NaHSO_4$ (6.3 g) was added carefully and solution evaporated under reduced pressure. The mixture was suspended in 30 mL dry ethylene glycol and concentrated H_2SO_4 (0.41 mL) was added dropwise. . The solution was heated at 100 ^{o}C overnight under a stream of argon. After cooling, the reaction was quenched by pouring into 100 mL sat. $NaHCO_3$ and extracted with EtOAc (4 x 100 mL). The combined organics were washed with water (2 x 150 mL) and dried over Na_2SO_4, then evaporated under reduced pressure to give a light yellow oil which was subjected to column chromatography (gradient, DCM to 2% MeOH in DCM) to give **2** as a clear yellow oil in 32.7 % yield (1.59 g, 5.56 mmol, 95:5 dr), two steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13-4.32 (m, 4H), 3.77-3.83 (m, 4H), 3.30-3.43 (m, 2H), 2.50-2.60 (m, 2H), 2.30 (br, 2H), 0.92-1.89 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.14, 172.20, 66.25, 66.11, 61.00, 42.52, 40.97, 34.20, 33.23, 25.23, 24.62, 22.74, 21.75. HRMS-ESI (*m/z*): calcd for $C_{14}H_{22}O_6$ [M+Na]+, 309.1309; found, 309.1299

Compound 3a: Dimethyl 7-cyano-*cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylate (racemic)



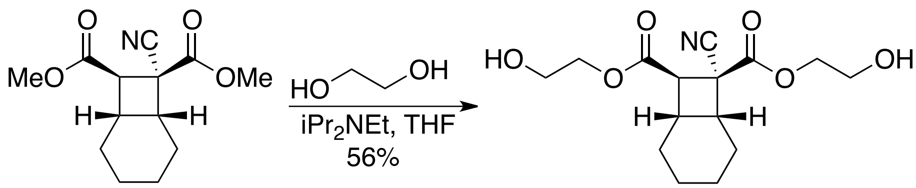
Cis-cyclohexanediacetic acid[5] (12.2 g, 60.8 mmol) was loaded into an oven dried 250 mL round bottomed flask with stir bar, addition funnel, and reflux condenser fitted with a N_2 bubbler. Thionyl chloride (30.0 mL, 413 mmol) was carefully added by addition funnel and the suspension was heated at reflux for 2 hours at which point the solid had completely dissolved. Bromine (6.92 mL, 134 mmol) was then added dropwise and the solution heated at 80 °C overnight then allowed to cool to 60 °C and excess thionyl chloride and bromine were removed under a stream of N_2. The brown oil was allowed to cool to room temperature and 30 mL of MeOH was carefully added followed by heating at reflux for 2 hr. After cooling, the mixture was poured into 1 L of cold water. The aqueous layer was decanted from the brown residue, which was dissolved in Et_2O and washed with aqueous sodium bisulfite (10%), potassium carbonate (10%), water, and brine. Drying over magnesium sulfate and evaporation under reduced pressure yielded a yellow oil, which was used for the next step without further purification (90.8 % crude yield, 21.2 g, 55.2 mmol).

HRMS-ESI (*m/z*): calcd for $C_{12}H_{18}Br_2O_4$ [MH+], 384.9645; found, 384.9647

The dibromide (21.0 g, 55.3 mmol) and finely ground potassium cyanide (10.8 g, 166 mmol) were loaded into a 250 mL round bottomed flask with stir bar and subsequently suspended in 20 mL of dry MeOH. The suspension was heated at reflux for 3 days under N_2. The resulting black oil was allowed to cool then diluted with 400 mL EtOAc and stirred over celite and filtered. The brown solution was then washed with water (3 x 150 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The dark brown oil was then subjected to column chromatography (SiO_2, 9:1 Hexane/EtOAc, $R_f \sim 0.15$) to give white crystals of X as a single diastereomer in 14.9 % yield (two steps, 2.07 g, 8.25 mmol).

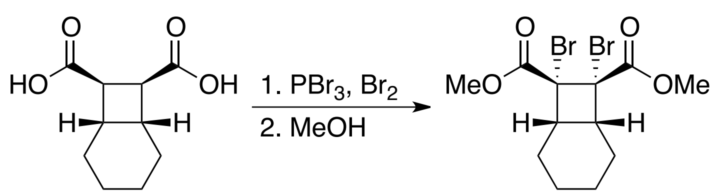
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.69 (s, 3H), 3.50 (d, 1H, J = 10.8), 3.19 (m, 1H), 2.65 (q, 1H, J = 8.59), 2.11 (m, 1H), 1.69 (m, 4H), 1.54 (m, 1H), 1.35 (m, 1H), 1.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.78, 167.95, 117.29, 53.77, 52.25, 46.63, 46.53, 37.63, 33.17, 26.09, 24.88, 22.15, 20.92. HRMS-ESI (*m/z*): calcd for $C_{13}H_{17}NO_4$ [MH+], 252.1230; found, 252.1232

Compound 3: Bis(2-hydroxyethyl)-7-cyano-*cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylate (racemic)



3a (1.38 g, 5.50 mmol) was dissolved in dry THF (5 mL) in a flame dried 25 mL under Argon. Ethylene glycol (10.2 mL, 165 mmol) and diisopropylethylamine (0.960 mL, 5.50 mmol) were subsequently added and the solution was stirred at room temperature for 72 hours. The solution was directly purified by column chromatography (SiO_2, gradient elution 1:1 to 4:1 EtOAc/Hexane) to yield **3** as a clear oil in 56 % yield (950 mg, 3.05 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (m, 4H), 3.85 (t, 2H, J = 4.48), 3.79 (t, 2H, J = 4.55), 3.59 (d, 1H, J = 11.0), 3.22 (m, 1H), 2.80 (br, 2H), 2.72 (q, 1H, J = 8.59), 2.13 (m, 1H), 1.66 (m, 5H), 1.37 (m, 1H), 1.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.87, 167.76, 117.33, 68.65, 66.92, 60.67, 60.43, 46.93, 46.75, 37.64, 33.21, 26.07, 24.88, 22.09, 20.88. HRMS-ESI (*m/z*): calcd for $C_{15}H_{21}NO_6$ [MH+], 312.1442; found, 312.1443

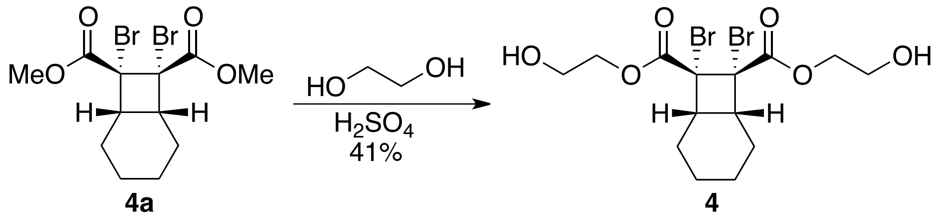


Compound 4a: Dimethyl *7,8-dibromo-cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylate

4a was synthesized as previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 6H), 3.04 (m, 2H), 1.93 (m, 2H), 1.79 (m, 4H), 1.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.98, 68.90. 53.54, 38.54, 25.50, 21.27. HRMS-ESI (*m/z*): calcd for $C_{12}H_{16}Br_2O_4$ [M+NH_4]+, 399.9754; found, 399.9746

Compound 4: Bis(2-hydroxyethyl)-*7,8-dibromo-cis*-Bicyclo[4.2.0]octane-*cis*-7,8-dicarboxylate



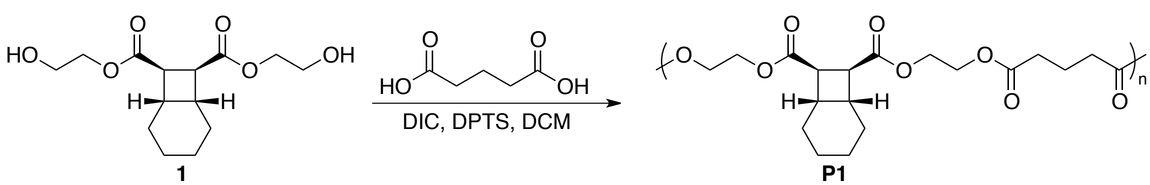
4a (1.04 g, 2.71 mmol) was suspended in ethylene glycol (10 mL) in a 25 mL round bottomed flask under argon. H_2SO_4 (0.2 mL) was added and the biphasic solution was heated at 100 °C for 24 hours (until 1 phase was formed) then 90 °C for 48 hours. The solution was then allowed to cool, was diluted with 125 mL EtOAc, and washed with 50 mL dilute $NaHCO_3$ and 50 mL brine, dried over magnesium sulfate and concentrated under reduced pressure. The light yellow oil was then subjected to column chromatography (SiO_2, gradient elution 1:1 to 4:1 EtOAc/Hexane) to yield **4** as a clear oil in 40.5 % yield (487 mg, 1.10 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (m, 2H), 4.24 (m, 2H), 3.83 (t, 4H, J = 4.52), 3.07 (m, 2H), 2.60 (br, 2H), 1.92 (m, 2H), 1.80 (m, 4H), 1.32 (m, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.96, 69.23, 68.37, 60.63, 38.70, 25.60, 21.27. HRMS-ESI (*m/z*): calcd for $C_{14}H_{20}Br_2O_6$ [M+NH$_4$]+, 459.9965; found, 459.9967

Polymer Synthesis

All polyesterifications were performed using a method modified from that of Moore and Stupp.[6]

Synthesis of P1 (*cis*-BCO)

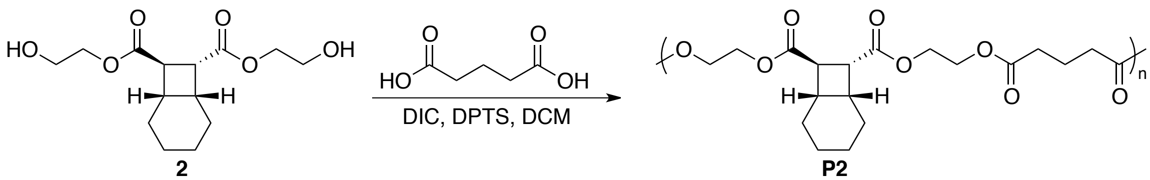


Diol **1** (3.77 g, 13.2 mmol), glutaric acid (1.74 g, 13.2 mmol), and DPTS (1.55 g, 5.28 mmol) were weighed into a 50 mL oven dried round bottom flask. The flask was purged with argon for 30 minutes, then 15 mL of dry DCM was added by syringe. The solution was heated to 37 °C and stirred until homogenous, then allowed to cool to room temperature. DIC (6.63 mL, 39.6 mmol) was added dropwise by syringe, and the polymerization was allowed to proceed for 48 hours. The viscous mixture was then precipitated three times from DCM into MeOH and dried under high vacuum to yield 3.47 g of white gummy polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21-4.30 (m, 8H), 3.13 (d, 2H), 2.73 (br, 2H), 2.41 (t, 4H, J = 7.32), 1.94 (quintet, 2H, J = 7.49), 1.70-1.82 (br, 2H), 1.42-1.54 (br, 4H), 1.26-1.40 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.03, 172.77, 62.29, 43.67, 34.00, 33.09, 27.31, 22.32, 19.99.

GPC-MALS: M_n = 179 kDa, PDI = 1.43

Synthesis of P2 (*trans*-BCO)

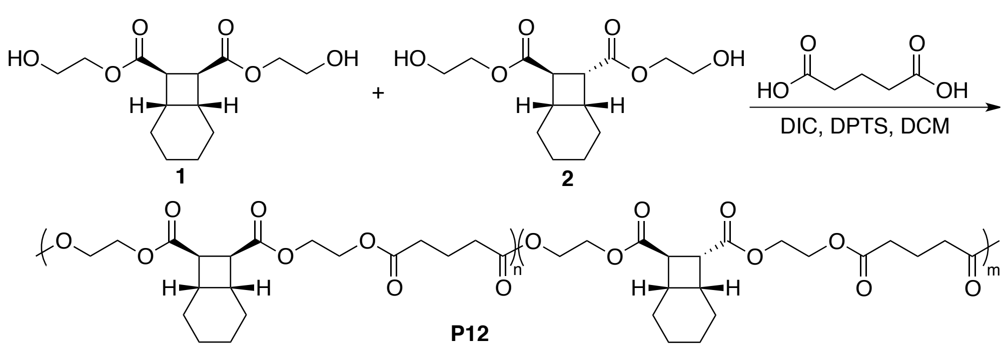


Diol **2** (1.12 g, 3.90 mmol), glutaric acid (0.515 g, 3.90 mmol), and DPTS (0.459 g, 1.56 mmol) were weighed into a 25 mL oven dried round bottom flask. The flask was purged with argon for 30 minutes, then 6 mL of dry DCM was added by syringe. The solution was heated to 37 °C and stirred until homogenous, then allowed to cool to room temperature. DIC (1.82 mL, 11.7 mmol) was added dropwise by syringe, and the polymerization was allowed to proceed for 48 hours. The viscous mixture was then precipitated three times from DCM into MeOH and dried under high vacuum to yield 692 mg of a tacky clear solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20-4.33 (m, 8H), 3.34 (m, 2H), 2.45-2.56 (m, 2H), 2.38 (t, 4H, J = 7.33), 1.94 (quintet, 2H, J = 7.36), 1.74-1.79 (br, 1H), 1.58-1.66 (br, 3H), 1.16-1.47 (m, 3H), 0.95-1.04 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.50, 172.66, 171.61, 62.30, 62.19, 41.82, 40.65, 34.81, 33.26, 33.10, 25.25, 24.48, 22.77, 21.75, 20.00.

GPC-MALS: M_n = 155 kDa, PDI = 1.34

Synthesis of P1,2 (*cis/trans*-BCO)

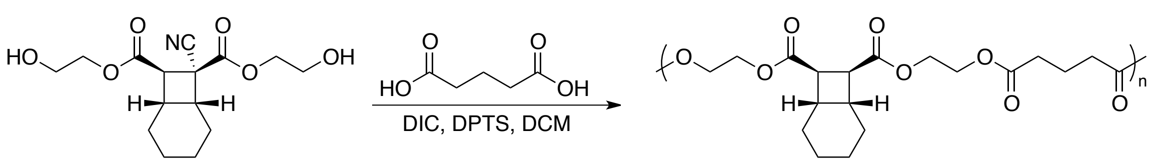


Diol **1** (576 mg, 2.01 mmol), diol **2** (578 mg, 2.03 mmol), glutaric acid (532 mg, 4.03 mmol), and DPTS (473 mg, 1.61 mmol) were added to a 25 mL oven dried round bottom flask. Dry DCM (6 mL) was added by syringe and the solution was heated to 37 °C and stirred until homogenous, then allowed to cool to room temperature. DIC (1.88 mL, 12.1 mmol) was added dropwise by syringe, and the polymerization was allowed to proceed for 48 hours. The viscous mixture was then precipitated three times from DCM into MeOH and dried under high vacuum to yield 1.015 g of white gummy polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16-4.34 (m, 8H), 3.32 (m, 1.06H), 3.10 (d, 0.94H), 2.70 (br, 0.94H), 2.45-2.56 (m, 1.06H), 2.38 (m, 4H), 1.91 (quintet, 2H, J = 7.34), 0.92-1.83 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.44, 172.94, 172.64, 171.55, 62.22, 62.13, 43.59, 41.73, 40.54, 34.72, 33.91, 33.17, 33.01, 27.23, 25.17, 24.42, 22.70, 22.24, 21.68, 19.91.

GPC-MALS: M_n = 161 kDa, PDI = 1.32

Synthesis of P3 (CN-*cis*-BCO)

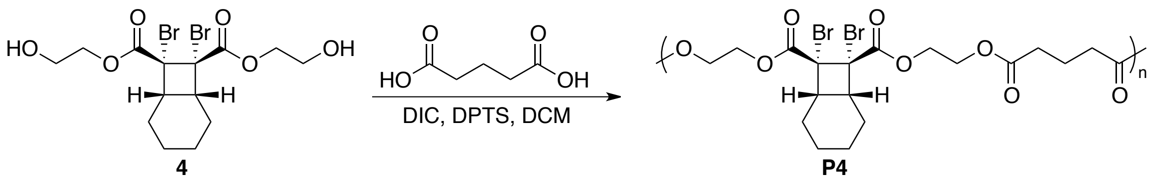


Diol **3** (906 mg, 2.91 mmol), glutaric acid (384 mg, 2.91 mmol), and DPTS (342 mg, 1.16 mmol) were added to a 25 mL oven dried round bottom flask. The flask was purged with argon for 30 minutes, then 4 mL of dry DCM was added by syringe. The solution was heated to 37 °C and stirred until homogenous, then allowed to cool to room temperature. DIC (1.35 mL, 8.73 mmol) was added dropwise by syringe, and the polymerization was allowed to proceed for 48 hours. The viscous mixture was then precipitated three times from DCM into MeOH and dried under high vacuum to yield 640 mg of solid white polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16-4.48 (m, 8H), 3.52 (d, 1H, J = 10.98), 3.16 (m, 1H), 2.65 (m, 1H), 2.39 (m, 4H), 2.11 (m, 1H),1.93 (quintet, 2H, J = 7.35), 1.47-1.80 (m, 6H), 1.36(m, 1H), 1.13(m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.66, 172.63, 170.00, 167.25, 116.87, 64.43, 62.74, 61.86, 61.54, 46.57, 46.42, 37.81, 33.22, 32.97, 26.07, 24.82, 22.11, 20.86, 19.89.

GPC-MALS: M_n = 133 kDa, PDI = 1.28

Synthesis of P4 (Br_2-*cis*-BCO)

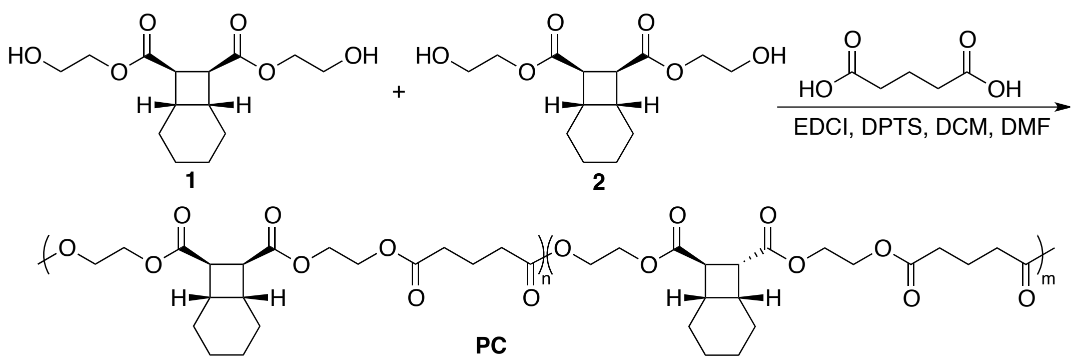


Diol **4** (417 mg, 0.940 mmol), glutaric acid (124 mg, 0.940 mmol), and DPTS (110 mg, 0.376 mmol) were added to a 10 mL oven dried round bottom flask. The flask was purged with argon for 30 minutes, and then 2 mL of dry DCM was added by syringe. The solution was heated to 37 ^{o}C and stirred until homogenous, then allowed to cool to room temperature. DIC (0.440 mL, 2.82 mmol) was added dropwise by syringe, and the polymerization was allowed to proceed for 48 hours. The viscous mixture was then precipitated three times from DCM into MeOH and dried under high vacuum to yield 276 mg of clear tacky polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22-4.44 (m, 8H), 3.00 (br, 2H), 2.41 (t, 4H, J = 7.30), 1.86-2.02 (m, 4H), 1.70-1.86 (br, 4H), 1.26-1.40 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.66, 169.30, 68.66, 64.04, 61.68, 38.66, 33.09, 25.58, 21.35, 19.98.

GPC-MALS: M_n = 51.0 kDa, PDI = 1.35

Synthesis of Control Polymer (PC)

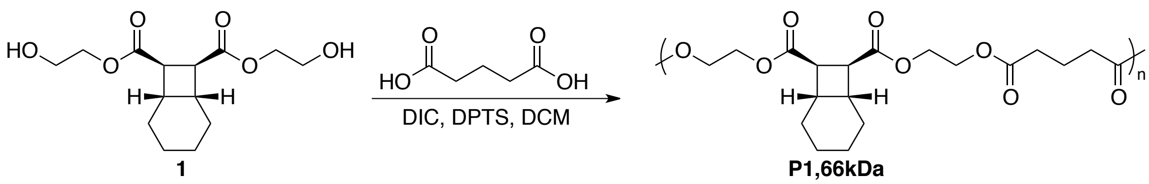


Diol **1** (285 mg, 1.00 mmol), Diol **2** (285 mg, 1.00 mmol), glutaric acid (250 mg, 1.89 mmol), and DMAP (97 mg, 0.80 mmol) were dissolved in 3 mL DCM and 3 mL DMF in a 25 mL round bottom flask and subsequently purged with argon. EDCI (1.14 g, 5.97 mmol) was added as a solid and the solution allowed to stir overnight. The solution was diluted with 150 mL DCM and washed with water (2 x 100 mL), and brine (100 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was dissolved in a minimal amount of DCM and passed through a plug of neutral alumina, eluting with DCM to yield 198 mg of clear viscous polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16-4.34 (m, 8H), 3.33 (m, 1.08H), 3.12 (d, 0.92H), 2.71 (br, 0.92H), 2.43-2.58 (m, 1.08H), 2.38 (m, 4H), 1.93 (quintet, 2H, J = 7.36), 0.93-1.83 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.50, 172.99, 172.70, 171.60, 62.28, 62.18, 43.67, 41.80, 40.63, 34.79, 33.91, 33.98, 33.24, 33.09, 27.29, 25.23, 24.47, 22.76, 22.30, 21.74, 19.99.

GPC-MALS: M_n = 13.3 kDa, PDI = 1.28

Synthesis of P1,66kDa (*cis*-BCO)



Diol **1** (1.24 g, 4.32 mmol), glutaric acid (0.570 g, 4.32 mmol), and DPTS (0.508 g, 1.73 mmol) were weighed into a 25 mL oven dried round bottom flask. The flask was purged with argon for 30 minutes, then 7 mL of dry DCM was added by syringe. The solution was heated to 38 ^{o}C and stirred until homogenous, then allowed to cool to room temperature. DIC (2.00 mL, 13.0 mmol) was added dropwise by syringe, and the polymerization was allowed to proceed for 48 hours. The viscous mixture was then concentrated to half volume and precipitated three times from DCM into MeOH and dried under high vacuum to yield 1.18 g of clear tacky polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19-4.33 (m, 8H), 3.13 (d, 2H, J = 3.12), 2.72 (br, 2H), 2.41 (t, 4H, J = 7.32), 1.95 (quintet, 2H, J = 7.30), 1.71-1.83 (br, 2H), 1.42-1.53 (br, 4H), 1.26-1.40 (br, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ 172.93, 172.68, 62.23, 43.63, 33.94, 33.04, 27.24, 22.25, 19.95.

GPC-MALS: M_n = 66.1 kDa, PDI = 1.52

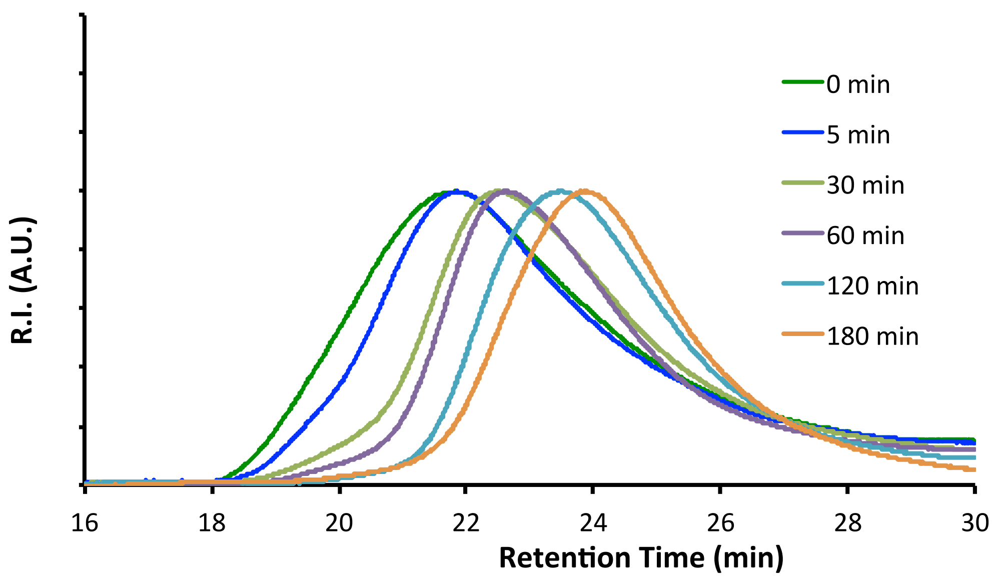
II. Activation of P1 (*cis*-BCO)

General Sonication Conditions and GPC-MALS Analysis

Ultrasound experiments were performed in dry acetonitrile on a Vibracell Model VCX500 (20 kHz frequency) with a 12.8 mm titanium probe. For polymer **4**, $CHCl_3$ was used due to insolubility in acetonitrile while all other conditions were identical. Solutions were irradiated at a concentration of 2 mg/mL in 16 mL of solvent unless otherwise noted. Prior to sonication, the solution was transferred to a 3-necked Suslick cell in an ice bath and sparged with nitrogen for 30 minutes prior to sonication. Irradiations were performed at 14.8 W/cm^2 with a pulse sequence of 1s on/1s off while maintaining a temperature of 6-9 ^{o}C under a nitrogen atmosphere. Power calibration was performed using the method of Berkowski et. al.[7]

Individual sonication experiments were performed for each time point. 32 mg of **P1** was dissolved in 16 mL MeCN, subjected to irradiation for the times indicated. The solution was filtered and evaporated under reduced pressure. 2 mg was dissolved in 1 mL of THF for GPC analysis, while the remainder was dissolved in 0.5 mL $CDCl_3$ for NMR analysis. Molecular weight was observed to degrade as a function of sonication time, indicated by an increase in retention time with prolonged irradiation. MWs are reported as number average molecular weight (M_n). **P1** sonication overlay below is representative of all polymers tested unless otherwise noted:

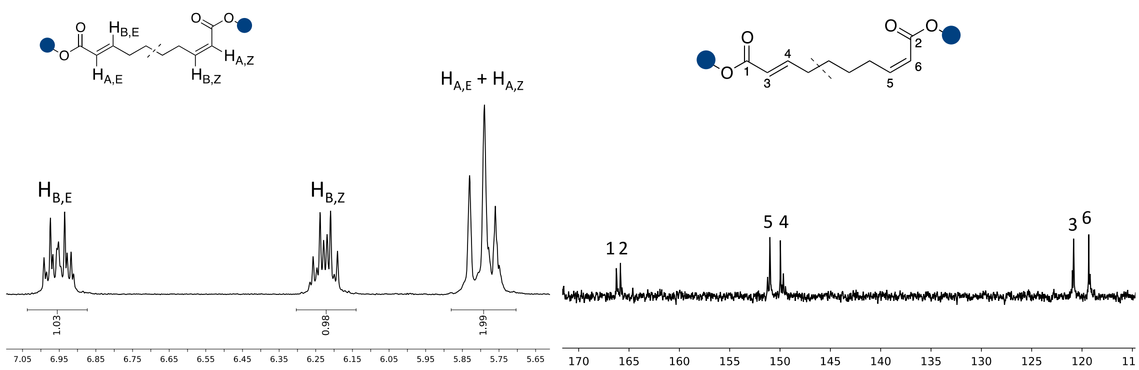
Figure S 1. GPC overlay of P1 molecular weight degradation at various sonication times.



^{1}H and ^{13}C Product Analysis

Assignment of mechanochemically generated products are shown below, peaks are consistent with expected shifts for substitution and stereochemical arrangement of analogous reported compounds.[8]

Figure S 2. ^{1}H and ^{13}C NMR assignments for unsaturated products of P1 activation.



Determination of % Ring Opening vs. Sonication Time

% Ring Opening was calculated via integration as shown below. Protons H and $H_{C,D}$ were chosen due to good resolution from neighboring peaks and because their resonances represent an equal number of protons (2) in both BCO and diene monomer units.

Figure S 3. Peak assignments and equation used in the calculation of % ring opening of *cis*-BCO as a function of sonication time.

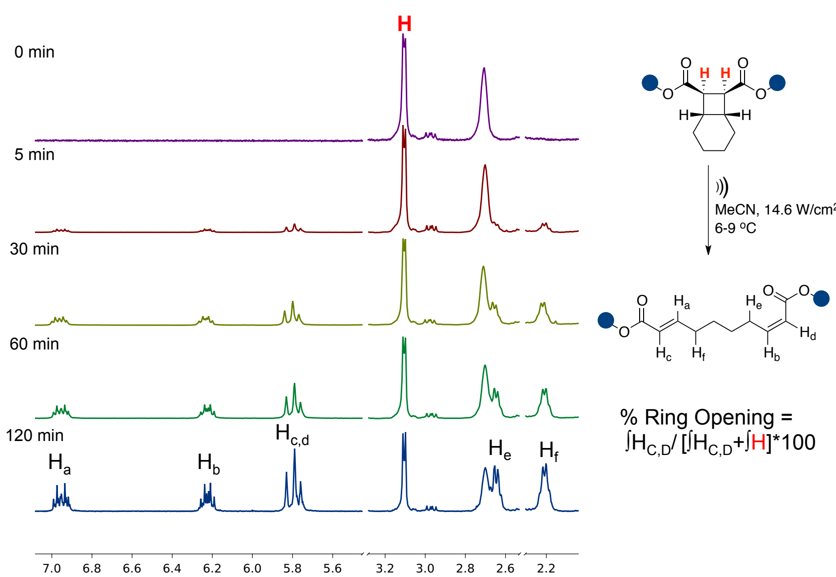
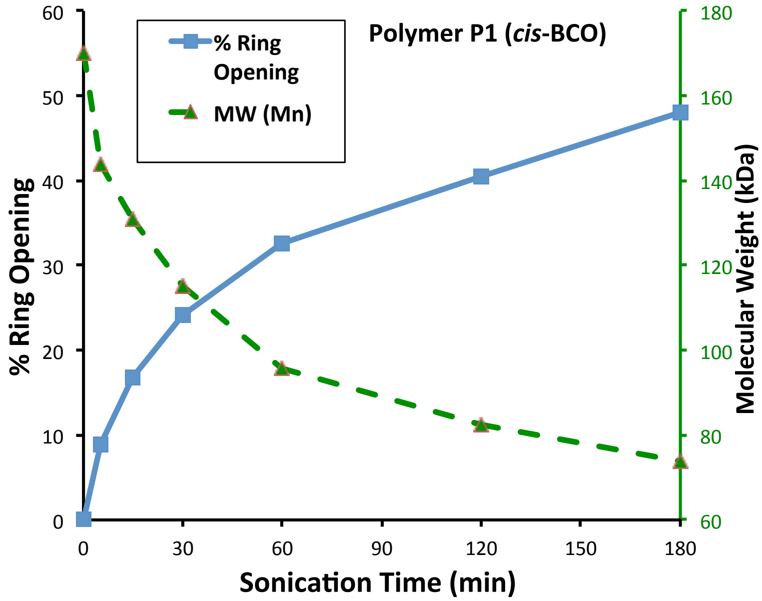


Figure S 4. Evolution of % Ring Opening and M_n as functions of sonication time.



Determination of Product Distribution by Deconvolution

Lorentzian peak fitting was performed using Mestrelab Mnova (Mestrelab Research S.L., Santiago de Compostela, Spain, www.mestrelab.com) peak fitting function. *β,E*-Protons were deconvoluted into two peak distributions, corresponding to major (*EZ*) and minor (*EE*) monomeric product dienes:

Figure S 5. Assignment of *E* and *Z* alkenes used in the determination of product ratios.

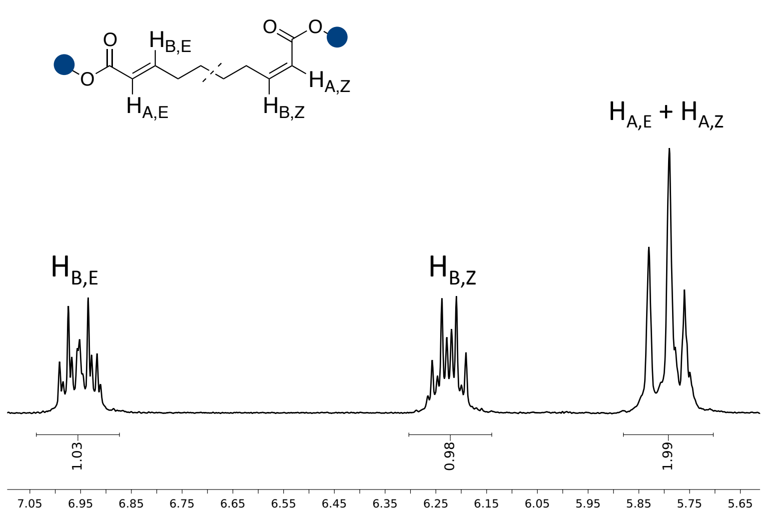
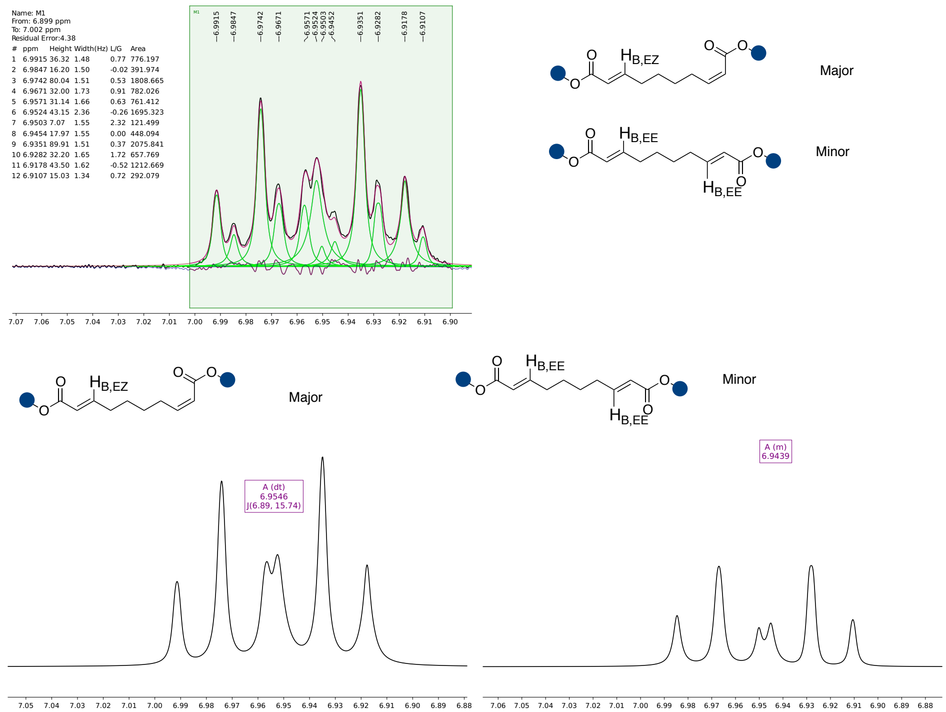


Figure S 6. Sample deconvolution of *E*-alkene peaks in the determination of major and minor isomer content.



Deconvolutions were performed for all time points. The chart and equations below detail determination of individual isomer ratios:

Sonication Time (min)	%E_{total}	%E_{major} (EZ)	%E_{minor} (EE)	%Z_{total}	%EZ	%EE	%ZZ
5	49.4	80.6	19.4	50.6	79.7	9.6	10.8
15	50.2	73.1	26.9	49.8	73.4	13.5	13.1
30	50.9	81.2	18.8	49.1	82.6	9.6	7.8
60	50.8	70.5	29.5	49.2	71.6	15.0	13.4
120	51.2	73.4	26.6	48.8	75.2	13.6	11.2
180	51.2	75.5	24.5	48.8	77.4	12.5	10.1

Table S 1. Summary of product ratios by deconvolution for P1

%E_{total} and %Z_{total} are the percent of total alkenes generated in the E and Z configurations respectively:

$$\%E_{total} = 100 \cdot \int H_{B,E} / [\int H_{B,E} + \int H_{B,Z}]$$

$$\%Z_{total} = 100 \cdot \int H_{B,Z} / [\int H_{B,E} + \int H_{B,Z}]$$

%E_{major} and %E_{minor} are the percent of E_{total} integration that is attributed to each isomer respectively:

$\%E_{major} = \%E_{total} \cdot \int H_{E,\ major} / [\int H_{E,\ major} + \int H_{E,\ minor}]$

$\%E_{minor} = \%E_{total} \cdot \int H_{E,\ minor} / [\int H_{E,\ major} + \int H_{E,\ minor}]$

Total isomer content in terms of % of monomeric diene generated are calculated as follows:

$\%EZ = [\%E_{major} \cdot \%E_{total} \cdot 2]/100$

$\%EE = [\%E_{minor} \cdot \%E_{total}]/100$

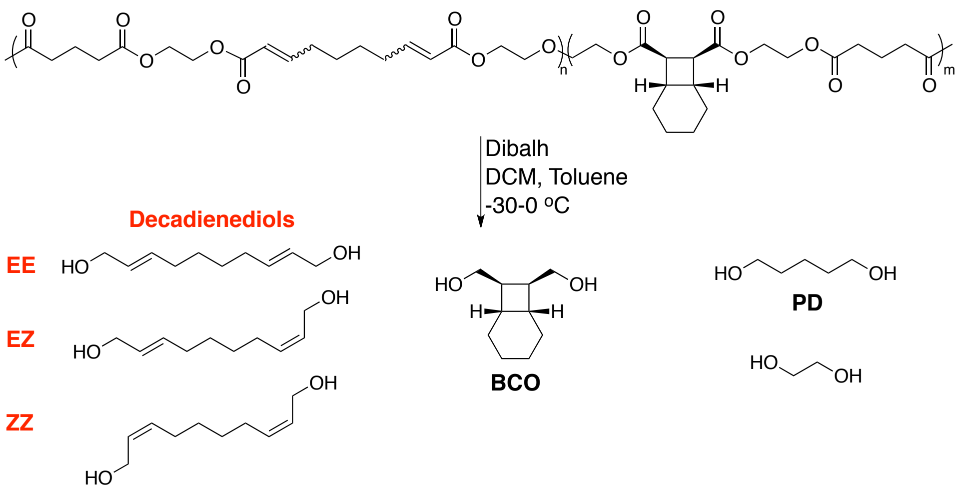
$\%ZZ = 100 - \%EZ - \%EE$

Note: Product ratios shown in table 5 (e.g. 77:13:10, 180 min) are based on the assumption that the E_{major} isomer is *EZ*. Without prior knowledge, another product ratio is possible if E_{major} is *EE* (e.g. 25:39:36). Given that $E_{total} \sim Z_{total}$ and unsatisfactory deconvolution of $H_{B,z}$ we were unable to distinguish between the two by ^{1}H NMR. This necessitated GC analysis. For CN and Br derivatives, asymmetry within the monomer unit and different E_{total}:Z_{total} content allowed for full characterization by ^{1}H NMR.

Determination of Product Distribution by GC

Reduction of Polyester **P1:**

P1 was sonicated using standard conditions to achieve a 52% ring opening by ^{1}H NMR. The polymer (31 mg, 0.649 mmol ester groups) was transferred to a 25 mL Schlenk flask with a stir bar and dried under high vacuum. Under argon, 3.5 mL dry DCM was added and the solution was cooled to -30 ^{o}C. A 1M solution of Dibalh in toluene (2.60 mL, 2.60 mmol) was added dropwise with the solution first turning to a gelled suspension and eventually a homogenous solution upon completion of addition. The solution was allowed to warm to 0 ^{o}C over 1.5 hr. The reaction was quenched by addition of 50 µL water, 100 µL 2 N NaOH, and 75 µL water in succession. $MgSO_4$was then added and the suspension stirred for 15 minutes. The mixture was then filtered and evaporated to yield 12 mg of a clear oil, which was then subjected to GC analysis.



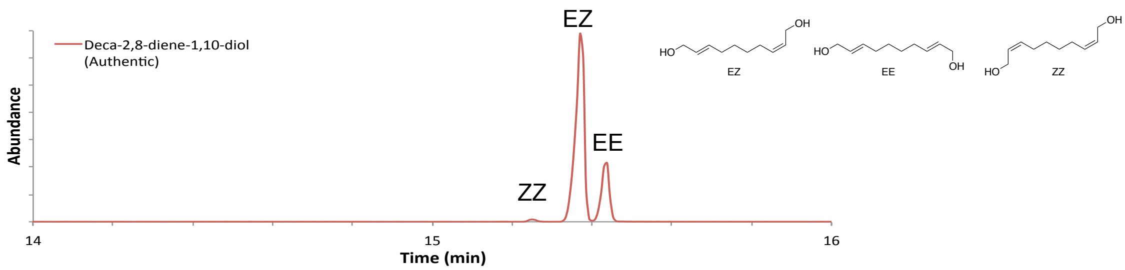
Scheme S 1. Reduction of P1 into constituent diols.

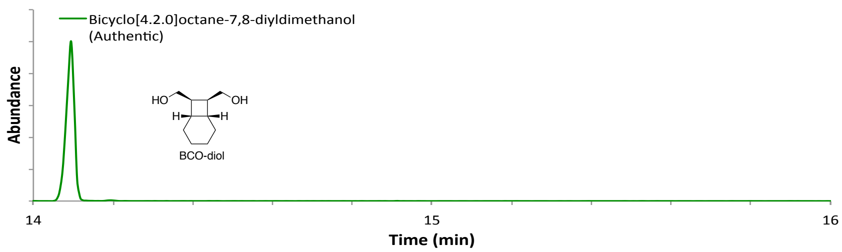
All GC analysis was performed using a Shimadzu QP2010 GC/MS with autosampler. All samples were derivatized before injection:

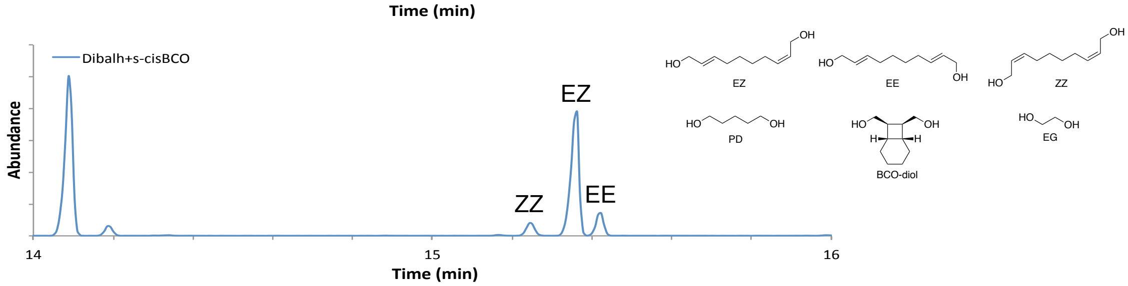
A 2 mg/mL sample in dry DCM was prepared in an oven dried 4 mL scintillation vial. BSTFA (5:1 mol% vs. hydroxyl content) was added via microsyringe and the vial was sealed and heated in a sand bath at 60 ^{o}C then immediately subjected to GC analysis.

Retention times were confirmed by comparing with authentic samples[8] as shown in red and green curves below. Blue curve shows result of analysis of **P1** sample after reduction and derivatization. Percent content of each isomer was determined by integration of the decadienediol peaks:

Figure S 7. GC chromatograms for authentic decadienediols (red), reduced cis-BCO (green), and P1 after sonication and reduction (blue).





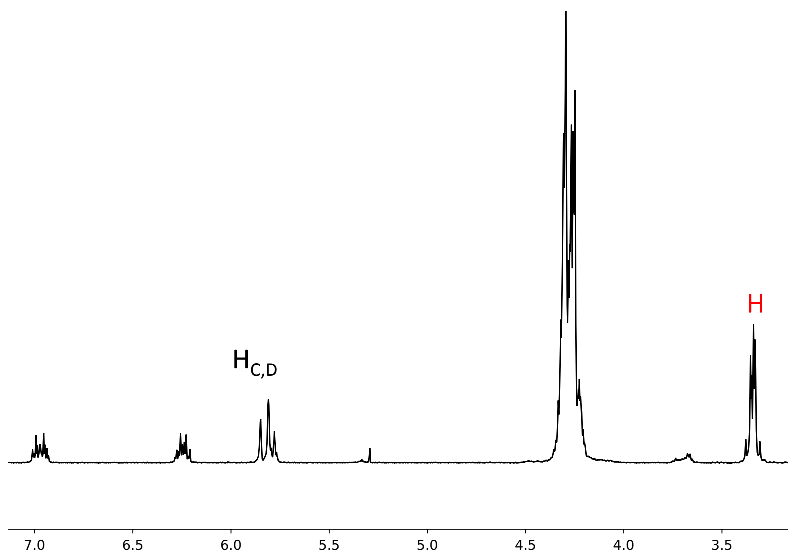


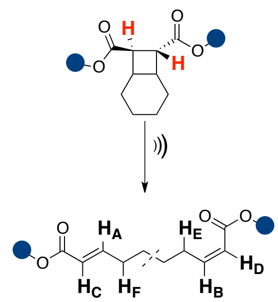
Integration Result:
EZ (77.5%), EE (13.6%), ZZ (8.9%)

III. Activation of P2 (*trans*-BCO)

Determination of % Ring Opening vs. Sonication Time

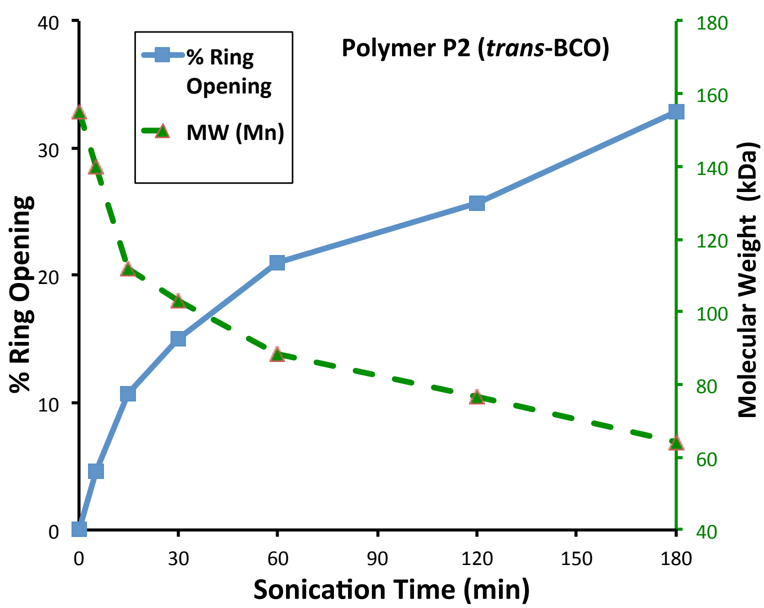
Figure S 8. Peak assignments and equation used in the calculation of % ring opening of *trans*-BCO as a function of sonication time.





% Ring Opening = $(\int H_{C,D}/[\int H_{C,D}+\int H])*100$

Figure S 9. Evolution of % Ring Opening and M_n as functions of sonication time.



Determination of Product Distribution by Deconvolution

Deconvolution was performed in a manner identical to that of **P1.**

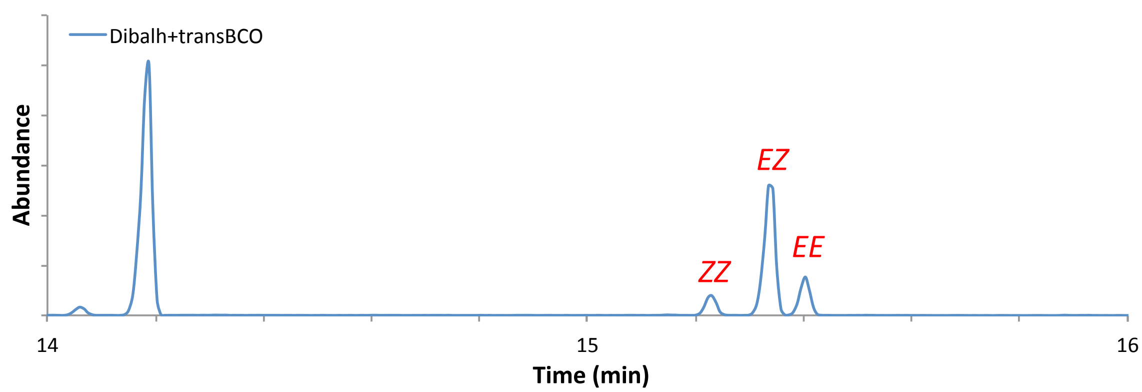
Sonication Time (min)	%E_{total}	%E_{major} (EZ)	%E_{minor} (EE)	%Z_{total}	%EZ	%EE	%ZZ
5	53.0	70.2	29.8	47.0	74.4	15.8	9.8
15	52.9	70.0	30.0	47.1	74.0	15.9	10.1
30	52.7	69.2	30.8	47.3	73.0	16.2	10.8
60	53.0	64.6	35.4	47.0	68.4	18.8	12.8
120	54.0	69.7	30.3	46.0	75.3	16.3	8.3
180	53.2	68.1	31.9	46.8	72.5	17.0	10.6

Table S 2. Summary of product ratios by deconvolution for P2.

Determination of Product Distribution by GC

The **P2** product distribution was determined in an identical fashion to **P1**.

Figure S 10. GC chromatogram of P2 after sonication and reduction.

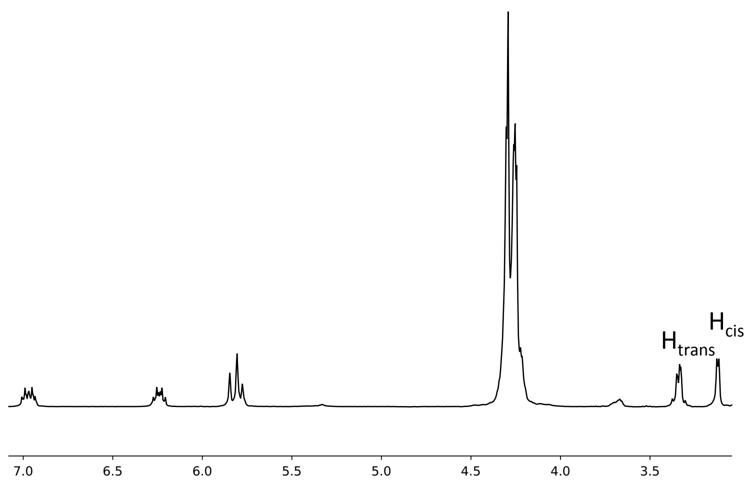


Integration Result:
EZ (70.7%), EE (18.8%), ZZ (10.5%)

IV. Activation of P1,2 (cis/*trans*-BCO)

Determination of % Ring Opening vs. Sonication Time

Figure S 11. Peak assignments used in the calculation of % ring opening of *cis and trans* isomers in P1,2 as a function of sonication time.



^{1}H NMR spectra for all time points were normalized based on peak integration to –OCH_2CH_2O- shifts from ethylene glycol subunits at 4.2-4.4 ppm.

% Ring Opening as a function of time (t) was calculated based on change in H_{trans} and H_{cis} integrals from initial values $H_{trans,0}$ and $H_{cis,0}$:

$\%RO_{trans}(t) = [(\int H_{trans,0} - \int H_{trans,t}) / \int H_{trans,0}] \cdot 100$

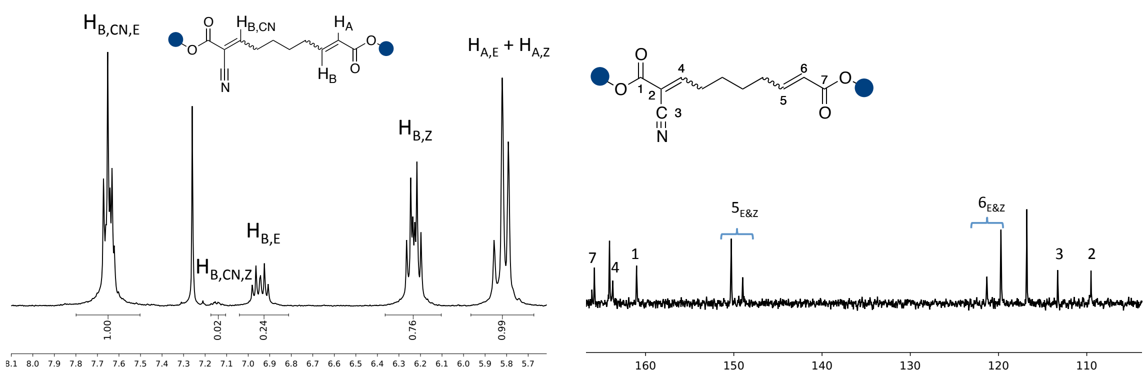
$\%RO_{cis}(t) = [(\int H_{cis,0} - \int H_{cis,t}) / \int H_{cis,0}] \cdot 100$

V. Activation of P3 (*cis*-CN-BCO)

^{1}H and ^{13}C Product Analysis

Assignment of mechanochemically generated products are shown below, peaks are consistent with expected shifts for substitution and stereochemical arrangement of analogous reported compounds.[9]

Figure S 12. ^{1}H and ^{13}C NMR assignments for unsaturated products of P3 activation.



Determination of % Ring Opening vs. Sonication Time

Figure S 13. Peak assignments and equation used in the calculation of % ring opening of *cis*-CN-BCO as a function of sonication time.

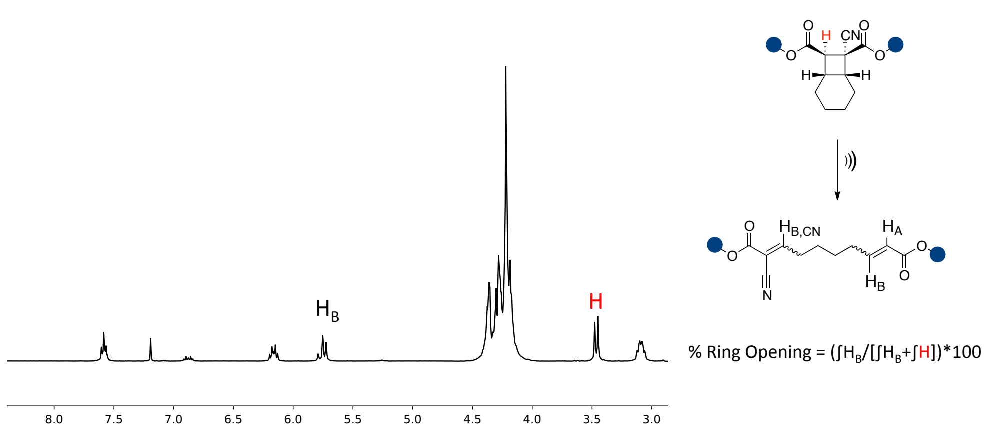
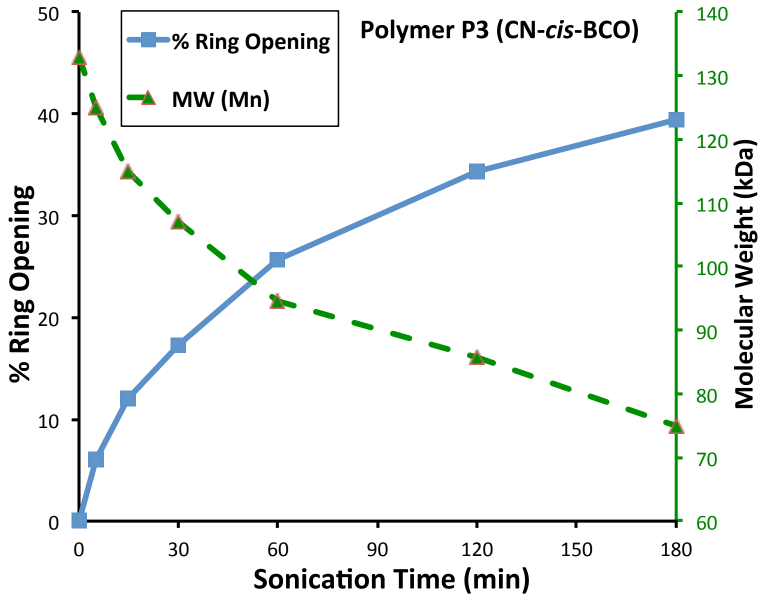


Figure S 14. Evolution of % Ring Opening and M_n as functions of sonication time.



Determination of Product Distribution by Deconvolution

Figure S 15. Assignment of *E* and *Z* alkenes used in the determination of product ratios.

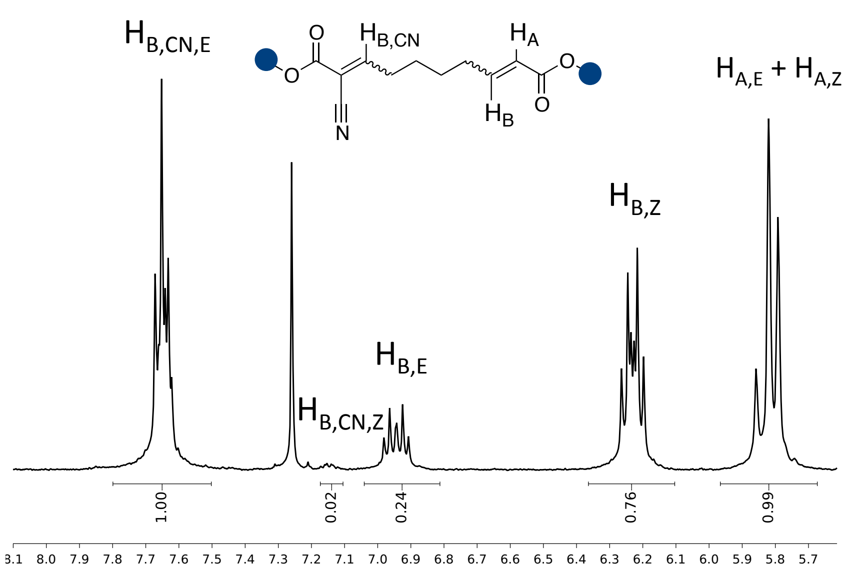
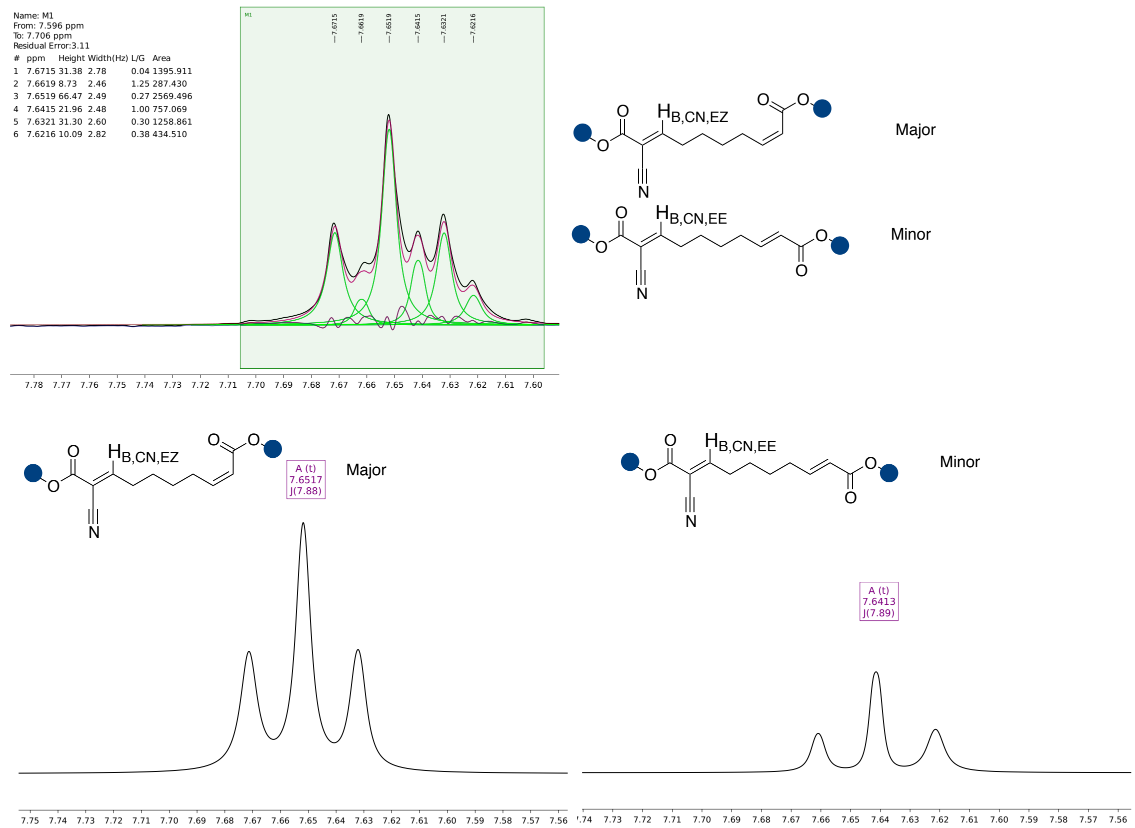


Figure S 16. Sample deconvolution of *E*-alkene peaks in the determination of major and minor isomer content.



Deconvolutions were performed for all time points. The chart and equations below detail determination of individual isomer ratios:

Sonication Time (min)	$\%E_{CN,total}$	$\%E_{CN,major}$ (EZ)	$\%E_{CN,minor}$ (EE)	$\%Z_{CN,total}$	$\%E_{unsub,total}$	$\%Z_{unsub,total}$	%EZ	%EE	%ZX
5	91.3	83.0	17.0	8.7	22.5	77.5	75.7	15.5	8.7
15	93.4	80.7	19.3	6.6	22.2	77.8	75.4	18.0	6.6
30	94.3	79.2	20.8	5.7	22.3	77.7	74.7	19.6	5.7
60	91.5	78.2	21.8	8.5	22.9	77.1	71.6	19.9	8.5
120	94.0	79.2	20.8	6.0	23.6	76.4	74.4	19.5	6.0
180	98.4	77.9	22.1	1.6	24.0	76.0	76.7	21.7	1.6

Table S 3. Summary of product ratios by deconvolution for P3.

$\%E_{CN,\mathrm{total}}$ and $\%Z_{CN,\mathrm{total}}$ are the percent of total cyano-alkenes generated in the *E* and *Z* configurations respectively:

$\%E_{CN,\mathrm{total}} = 100 \cdot \int H_{B,CN,E} / [\int H_{B,CN,E} + \int H_{B,CN,Z}]$

$\%Z_{CN,\mathrm{total}} = 100 \cdot \int H_{B,CN,Z} / [\int H_{B,CN,E} + \int H_{B,CN,Z}]$

$\%E_{\mathrm{major}}$ and $\%E_{\mathrm{minor}}$ are the percent of $E_{CN,\mathrm{total}}$ integration that is attributed to each isomer respectively:

$\%E_{CN,\mathrm{major}} = \%\ E_{CN,\mathrm{total}} \cdot \int H_{E,\ CN,\mathrm{major}} / [\int H_{E,\ CN,\mathrm{major}} + \int H_{E,\ CN,\mathrm{minor}}]$

$\%E_{CN,\mathrm{minor}} = \%\ E_{CN,\mathrm{total}} \cdot \int H_{E,\ CN,\mathrm{minor}} / [\int H_{E,\ CN,\mathrm{major}} + \int H_{E,\ CN,\mathrm{minor}}]$

$\%E_{\mathrm{unsub,total}}$ and $\%Z_{\mathrm{unsub,total}}$ are the percent of total unsubstituted unsaturated esters generated in the *E* and *Z* configurations respectively:

$\%E_{\mathrm{unsub,total}} = 100 \cdot \int H_{B,E} / [\int H_{B,E} + \int H_{B,Z}]$

$\%Z_{\mathrm{total}} = 100 \cdot \int H_{B,Z} / [\int H_{B,E} + \int H_{B,Z}]$

Total isomer content in terms of % of monomeric diene generated are calculated as follows:

$\%EZ = [\%E_{\mathrm{CN,major}} \cdot \%E_{\mathrm{CN,total}}]/100$

$\%EE = [\%E_{\mathrm{CN,minor}} \cdot \%\ E_{\mathrm{CN,total}}]/100$

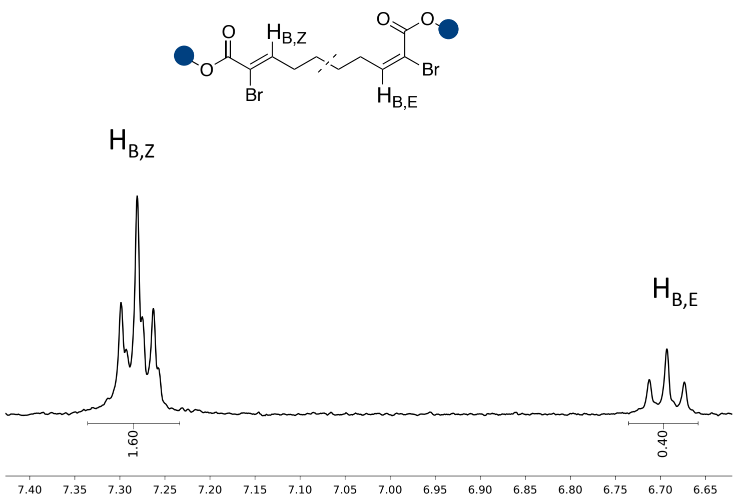
$\%\mathrm{ZX} = 100 - \%EZ - \%EE$

VI. Activation of P4 (*cis*-Br_2-BCO)

^{1}H Product Analysis

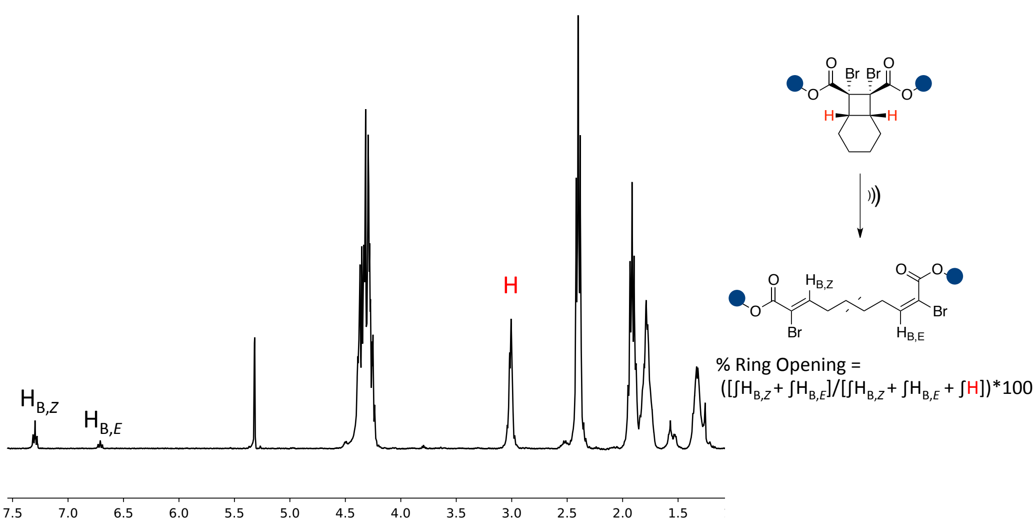
Assignment of mechanochemically generated products are shown below, peaks are consistent with expected shifts for substitution and stereochemical arrangement of analogous reported compounds.[10]

Figure S 17. ^{1}H assignments for unsaturated products of P1 activation.



Determination of % Ring Opening

Figure S 18. Figure S 19. Peak assignments and equation used in the calculation of % ring opening of *cis*-Br_2-BCO as a function of sonication time.



Determination of Product Distribution by Deconvolution

Figure S 20. Assignment of *E* and *Z* alkenes used in the determination of product ratios.

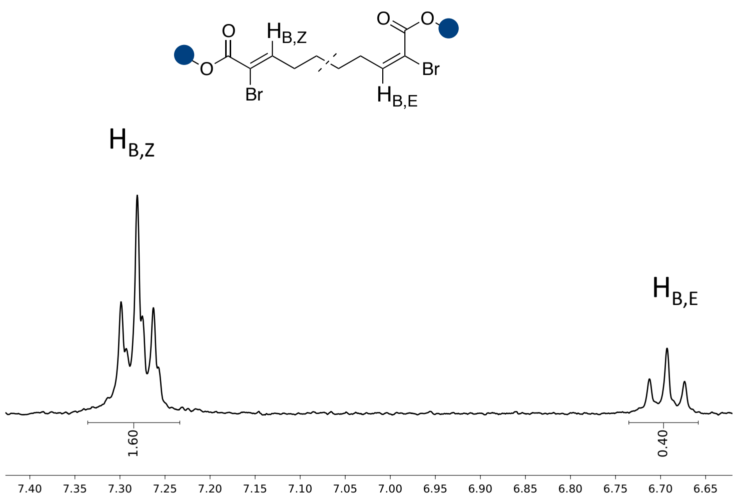
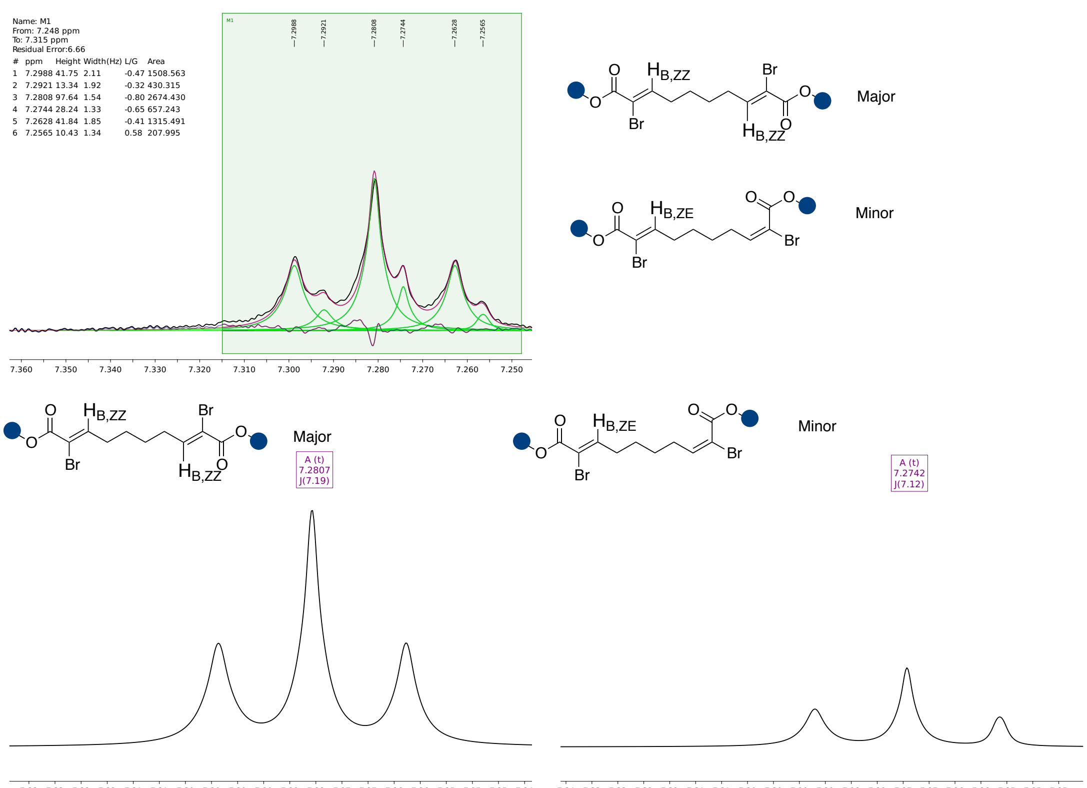


Figure S 21. Sample deconvolution of *Z*-alkene peaks in the determination of major and minor isomer content.



The table and equations below detail determination of individual isomer ratios:

Sonication Time (min)	%Z_{major} (*ZZ*)	%Z_{minor} (*ZE*)	%Z_{total}	%E_{total}	*ZZ*	*EZ*	*EE*
180	83.3	16.7	79.8	20.2	66.4	26.7	6.8

Table S 4. Summary of product ratios by deconvolution for P4.

%E_{total} and %Z_{total} are the percent of total alkenes generated in the *E* and *Z* configurations respectively:

$\%E_{total} = 100 \cdot \int H_{B,E} / [\int H_{B,E} + \int H_{B,Z}]$

$\%Z_{total} = 100 \cdot \int H_{B,Z} / [\int H_{B,E} + \int H_{B,Z}]$

%E_{major} and %E_{minor} are the percent of E_{total} integration that is attributed to each isomer respectively:

$\%Z_{major} = \%Z_{total} \cdot \int H_{Z,\ major} / [\int H_{Z,\ major} + \int H_{Z,\ minor}]$

$\%Z_{minor} = \%Z_{total} \cdot \int H_{Z,\ minor} / [\int H_{Z,\ major} + \int H_{Z,\ minor}]$

Total isomer content in terms of % of monomeric diene generated are calculated as follows:

$\%EZ = [\%Z_{minor} \cdot \%Z_{total} \cdot 2]/100$

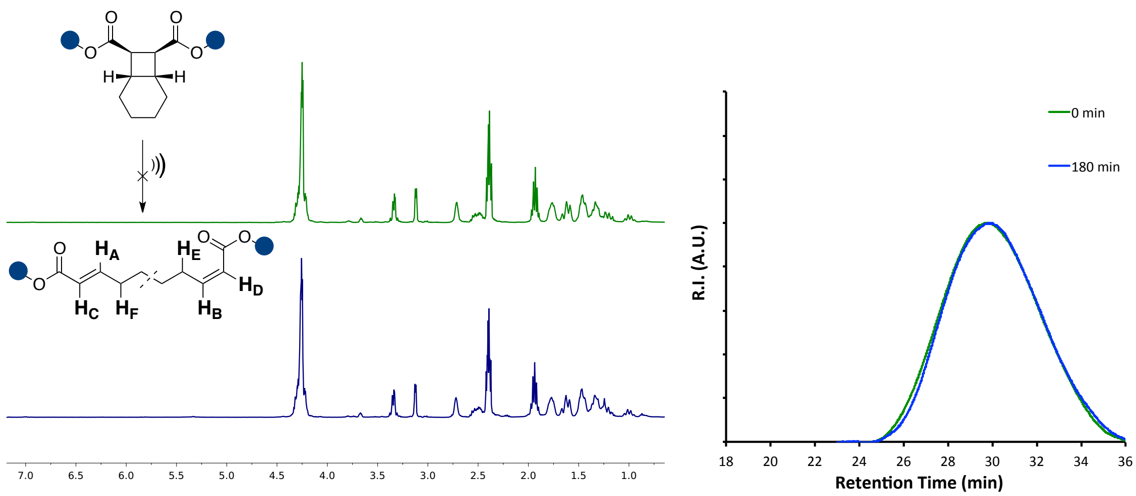
$\%ZZ = [\%Z_{major} \cdot \%Z_{total}]/100$

%EE = 100 - %*EZ* - %*ZZ*

VII. Sonication of PC (control-*cis*-BCO)

Polymer **PC** was sonicated using the standard procedure. Due to the low molecular weight (13.3 kDa) forces experienced by the polymer would be insufficient for ring opening, supporting the mechanical nature of the reaction. No ring opening was observed by ^{1}H NMR and the final MW was determined to be 12.6 kDa.

Figure S 22. ¹H NMR (left) and GPC trace (right) of 13.3 kDa control polymer PC before (green) and after (blue) 180 minutes of sonication.



VIII. Product distribution vs. MW evolution and activation of P1,66kDa

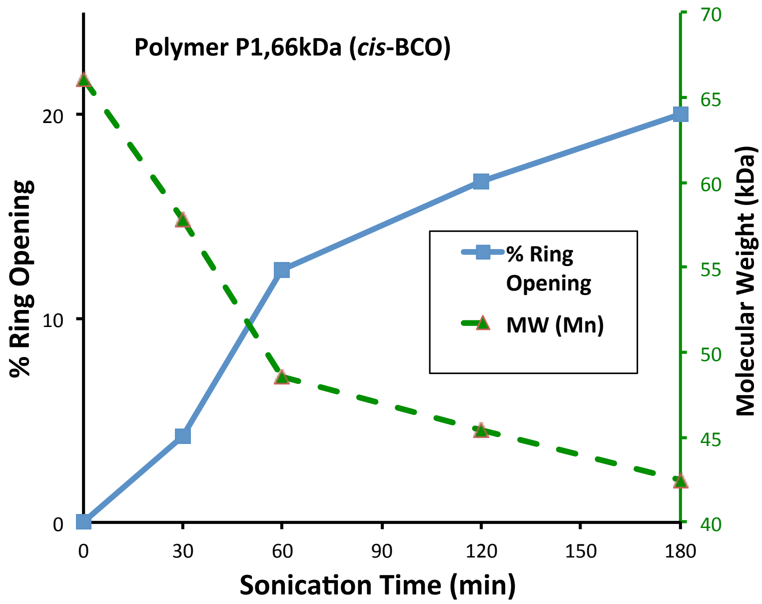
While the **P4** product distribution is dramatically different from all other examples, the M_n is also significantly lower. To show a lack of sensitivity of mechanochemical product distributions to initial MW a lower MW cis-BCO polymer (**P1,66kDa**) was tested:

Deconvolution of **P1,66kDa** was performed in a manner identical to that of **P1.**

Sonication Time (min)	%E_{total}	%E_{major} (EZ)	%E_{minor} (EE)	%Z_{total}	%EZ	%EE	%ZZ
30	56.0	69.0	31.0	44.0	77.2	17.4	5.4
60	57.2	71.5	28.5	42.8	81.8	16.3	1.9
120	56.7	68.5	31.5	43.3	77.7	17.8	4.4
180	55.7	68.8	31.2	44.3	76.6	17.4	6.0

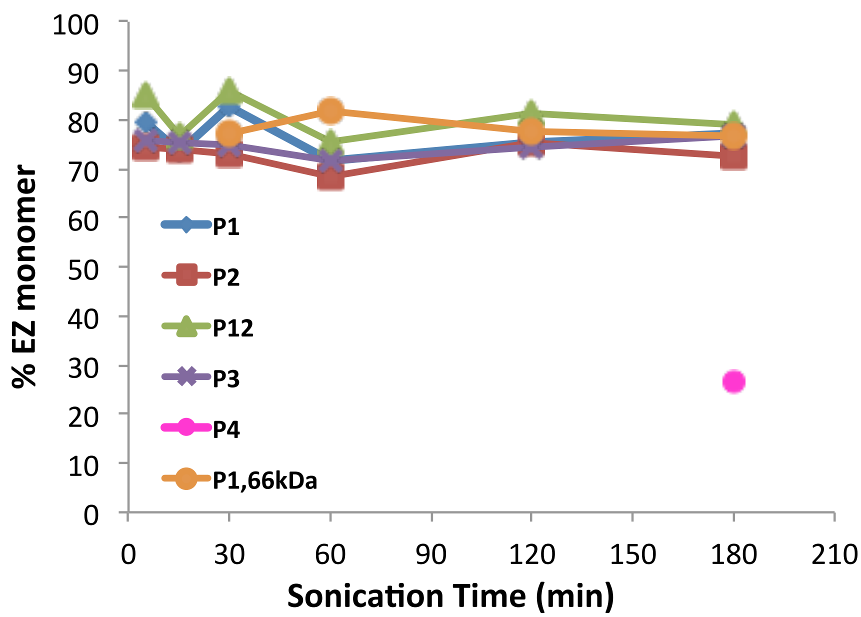
Table S 5. Summary of product ratios by deconvolution for P1,66kDa.

Figure S 23: Evolution of % Ring Opening and M_n as functions of sonication time.



While a slight increase in %*EE* is observed, this is at the cost of *ZZ* isomer content, which is not reflected in the product distribution of **P4**. If a decrease in *EZ* predominance in the product distribution is a product of low MW, one might anticipate that %*EZ* content would decrease throughout sonication:

Figure S 24. Evolution of %*EZ* content vs. sonication time for all polymers tested.



No such trend is observed, and **P4** *EZ* content (pink) is significantly lower than all other polymers tested at all time points. Trendlines for the above plot are summarized below:

	Slope	R^2
P1	-0.0086	0.021
P2	-0.0019	0.003
P12	-0.0175	0.076
P3	0.0055	0.047
P1,66kDa	-0.0159	0.205

Table S 6: Trendline slope and R^2 values for %*EZ* vs. sonication time shown in Figure S 24.

IX. Functionalization of P1 by Thiol-ene Addition

Small Molecule Conjugation:

P1 was sonicated for 3 hr. as a 4 mg/mL solution in MeCN to obtain 53 mg of 33% ring opened (0.092 mmol alkenes). Polymer was dissolved in 0.75 mL MeCN-d_3 and ethyl thioglycolate (16.4 mg, 0.137 mmol) was added. DBU (0.6 mg, 0.004 mmol) was added from a stock solution in 0.1 mL of MeCN-d_3 to initiate reaction and time-points were recorded.

Formation of Cross-linked Polymer Networks:

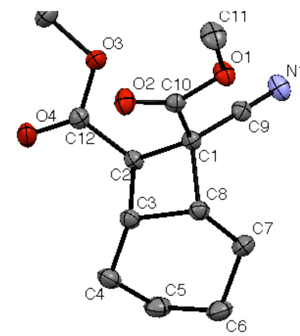
P1 was sonicated for 3 hr. as a 4 mg/mL solution in MeCN to obtain 55 mg of 36% ring opened (0.10 mmol alkenes). The polymer was dissolved in 0.5 mL MeCN in a 7 mL vial. 1,4-butanediol dithioglycolate (12 mg, 5.0 mmol) was added followed by DBU (0.80 mg) from a stock solution in 0.1 mL MeCN. The vial was vortexed for 1 second and allowed to stand for 1 minute at which time a gel was formed (left).

An identical experiment was run with unsonicated **P1** as a control. No gelation was observed and the solution remained free flowing upon inversion (right). No change was observed over the course of two weeks.

X. X-ray Crystallography

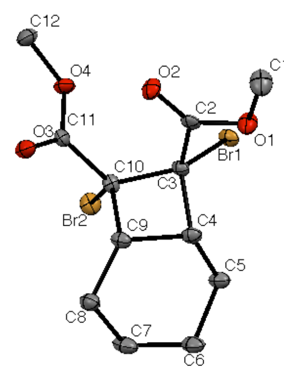
Compound 3: Colorless prisms crystallized from pentane/acetone at 3-6°C by employing liquid/liquid diffusion method. Crystal data: Prism, colorless, crystal size = 0.4157 x 0.3474 x 0.1977 mm^3, $C_{13}H_{17}NO_4$, FW 251.28, monoclinic, space group P 1 $2_1/c$ 1, a = 8.89070(11), b = 12.16463(14), c = 12.12008(14) Å, α = 90°, β = 93.0379(10)°, γ = 90°, V = 1308.97(3) Å^3, Z = 4, D_c = 1.275 mg/m^3, T = 100(1) K, μ = 0.785 mm^{-1}, 11312 measured reflections, 2689[R(int) = 0.0238] independent reflections, 2689 / 0 / 165 Data / restraints / parameters, $F(000)$ = 536, $R1$ = 0.0381, $wR2$ = 0.0950, $R1$ = 0.0362, $wR2$ = 0.0934[I>2sigma(I)], Max. residual density 0.358 e.Å^{-3}, Max. and min. transmission 1.894 and 0.821, and goodness-of-fit (F^2) = 1.048.

Figure S 25. Crystal structure of 3a (*cis*-CN-BCO dimethyl ester.



Compound 4: Colorless plates crystallized from pentane/acetone at room temperature by employing vapor diffusion method. Crystal data: plates, colorless, crystal size = 0.24 x 0.24 x 0.10 mm^3, $C_{12}H_{16}Br_2O_4$, FW 384.07, Monoclinic, space group P2(1)/c, a = 8.4288(2), b = 13.7579(4), c = 12.3099(3) Å, α = 90°, β = 106.9400(10)°, γ = 90°, V = 1365.55(6) Å^3, Z = 4, D_c = 1.868 mg/m^3, T = 100(2) K, μ = 7.588 mm^{-1}, 8416 measured reflections, 2391[R(int) = 0.0519] independent reflections, 2391 / 0 / 165 Data / restraints / parameters, $F(000)$ = 760, $R1$ = 0.0450, $wR2$ = 0.1017, $R1$ = 0.0409, $wR2$ = 0.0988 [I>2sigma(I)], Max. residual density 1.090 e.Å^{-3}, Max. and min. transmission 0.5175 and 0.2632, and goodness-of-fit (F^2) = 1.074.

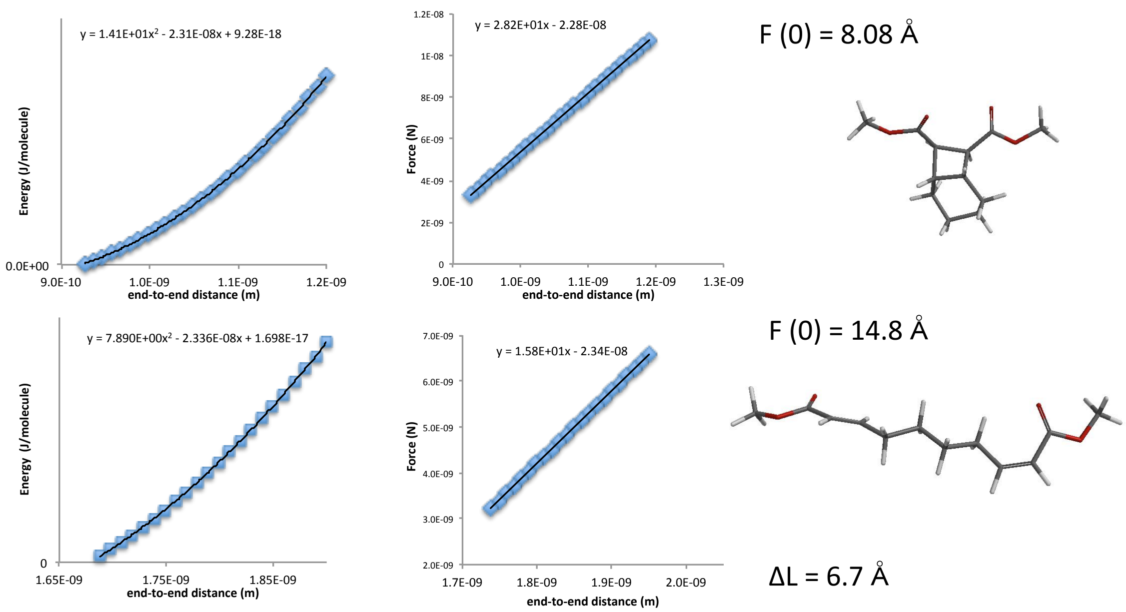
Figure S 26. Crystal structure of 4a (*cis*-Br_2-BCO dimethyl ester.



XI. Determination of Elongation

Modeling to determine change in monomer length was performed using Spartan ® software as previously described.[11] In short, Molecular Mechanics was performed for both closed (*cis*-BCO dimethyl ester) and opened (*EZ* dimethyl ester) to generate a CoGEF[12]-type constrained potential relating molecular energy to end-to-end distance (left plot). This was fitted to a second order polynomial, the derivative of which relates force to end-to-end distance (right). By solving the linear equation of force vs. distance for f = 0 N a contour length was obtained, the difference of which between the opened and closed form equals the net elongation upon ring opening.

Figure S 25. Energy vs. Elongation curves (left) and Force vs. Elongation curves (right) used in the determination of change in length of *cis*-BCO upon activation.



XII. Effect of Bromine Substitution on Heat of Reaction

ΔH_{rxn} for analogous cyclobutanes were calculated using Spartan ® software in the ground state using thermochemical recipe T1 starting from semi-empirical AM1 geometry:

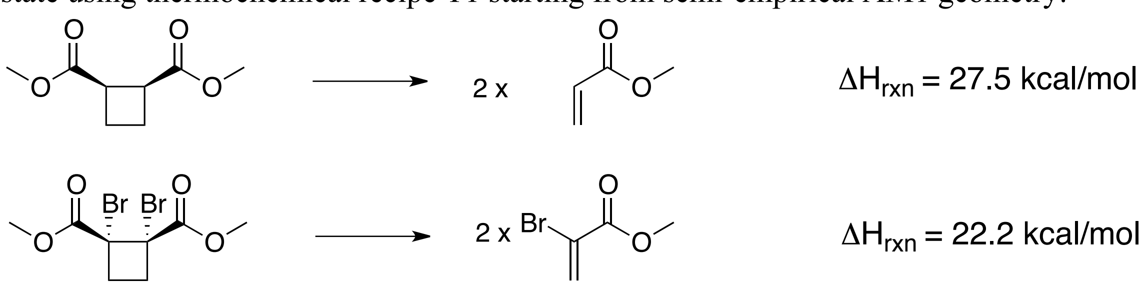
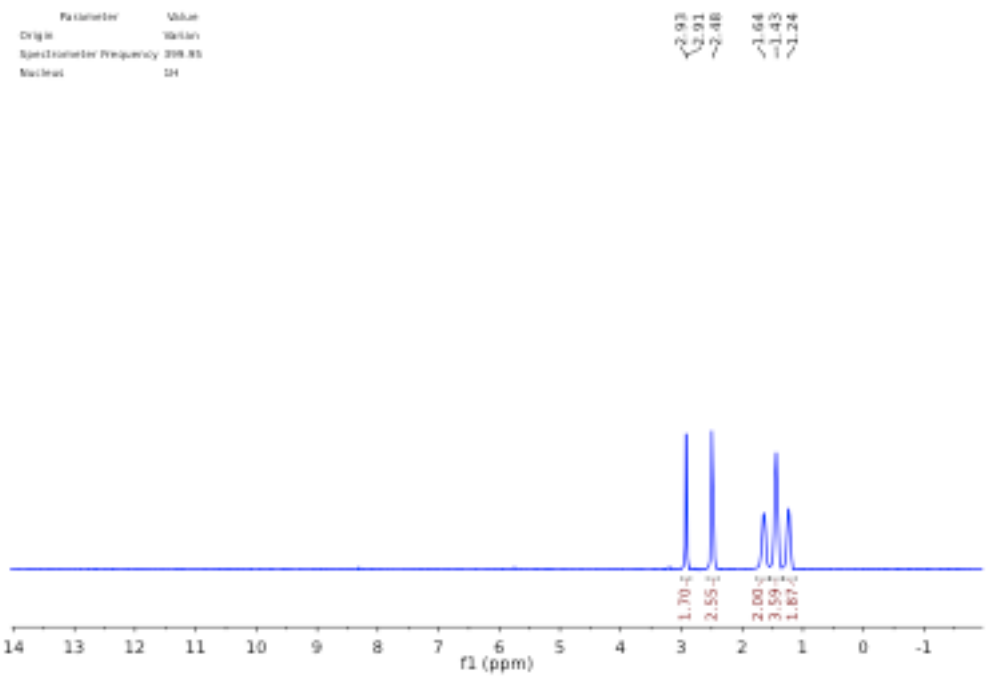
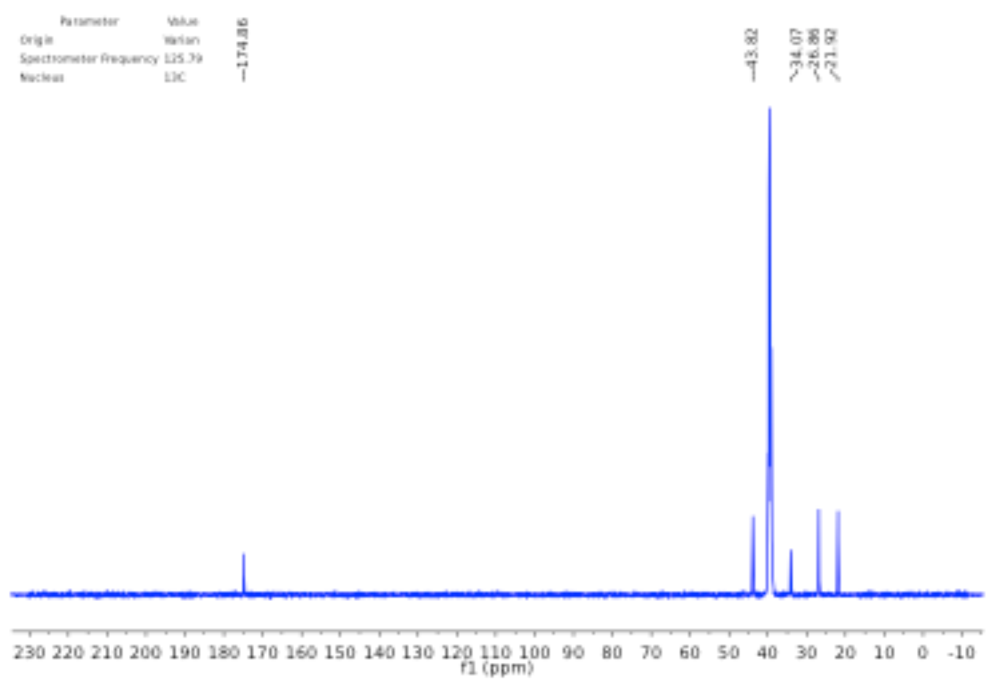


Figure S 26. Comparison of heat of reaction for fragmentation of substituted and unsubstituted cyclobutane.

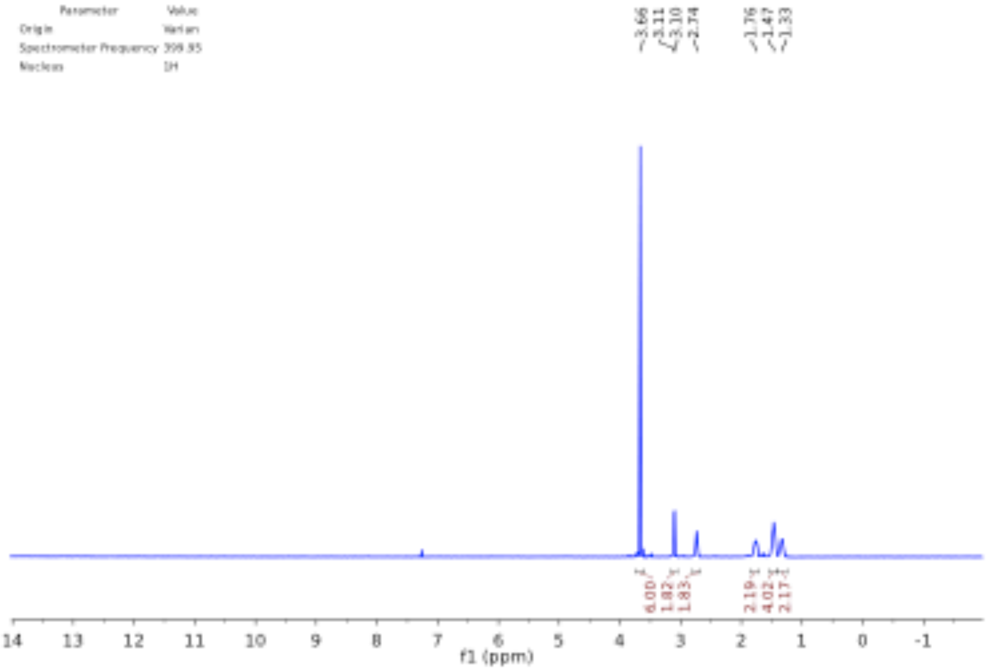
XIII. ^{1}H and ^{13}C Spectra

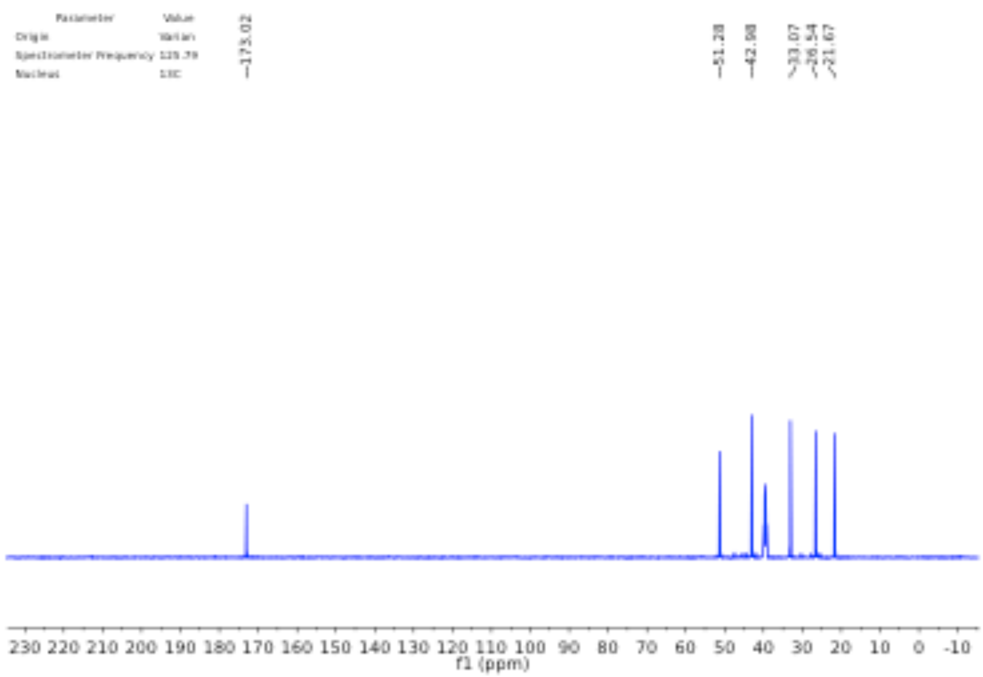
Compound 1a



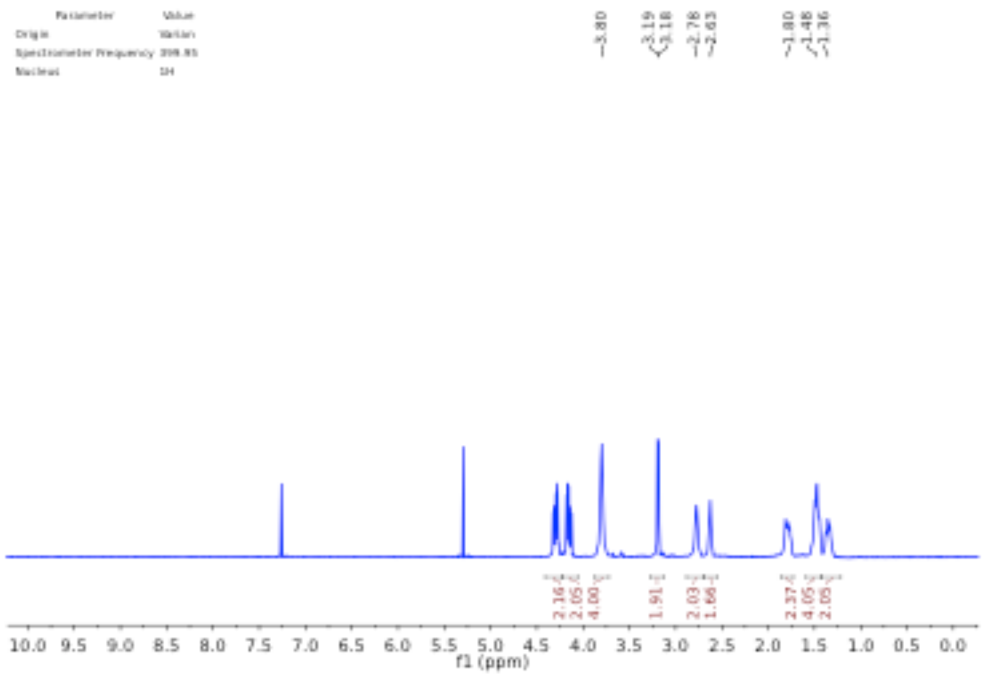


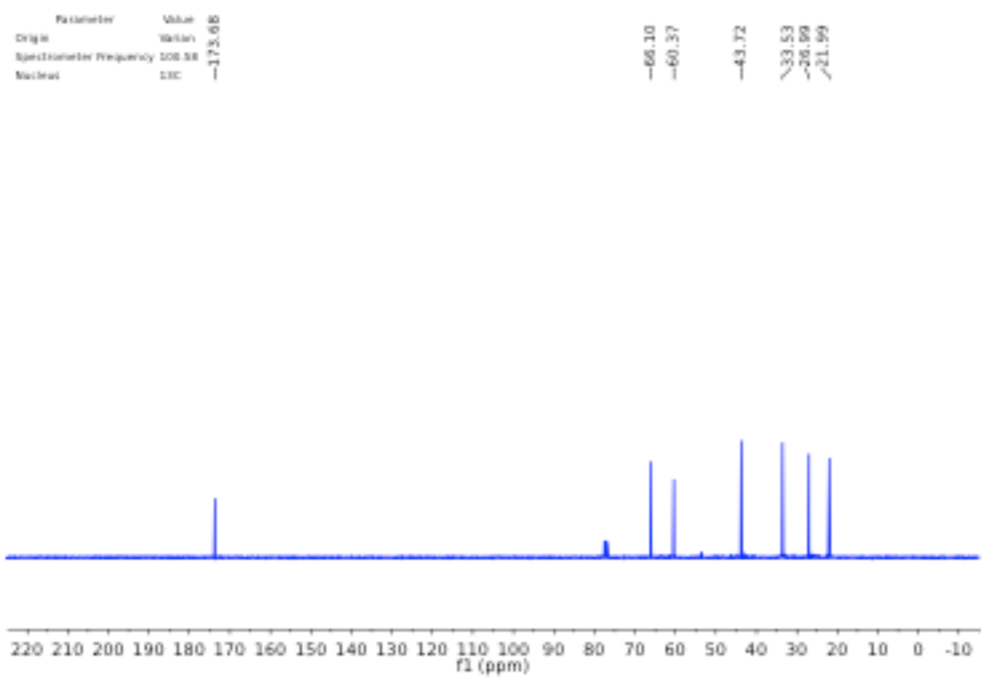
Compound 1b


Parameter Value
Origin Varian
Spectrometer Frequency
Nucleus 1H
3.66
3.11
3.10
2.74
1.76
1.47
1.33
6.00
1.82
1.83
2.19
4.02
2.17
f1 (ppm)

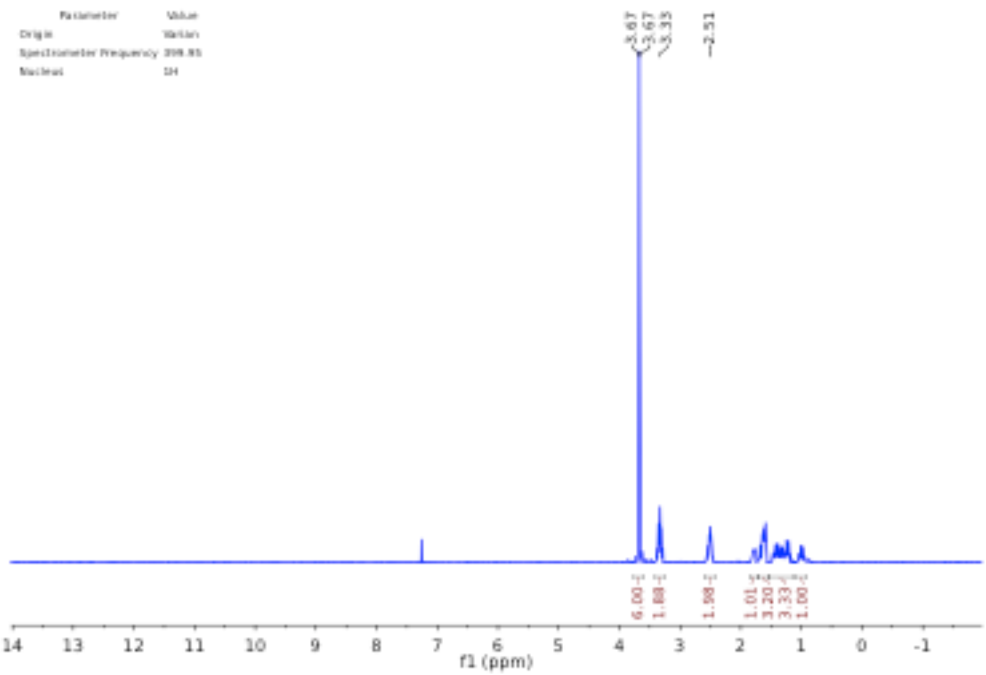

Parameter Value
Origin Varian
Spectrometer Frequency
Nucleus 13C
173.02
51.28
42.98
33.07
26.54
21.67
f1 (ppm)

Compound 1

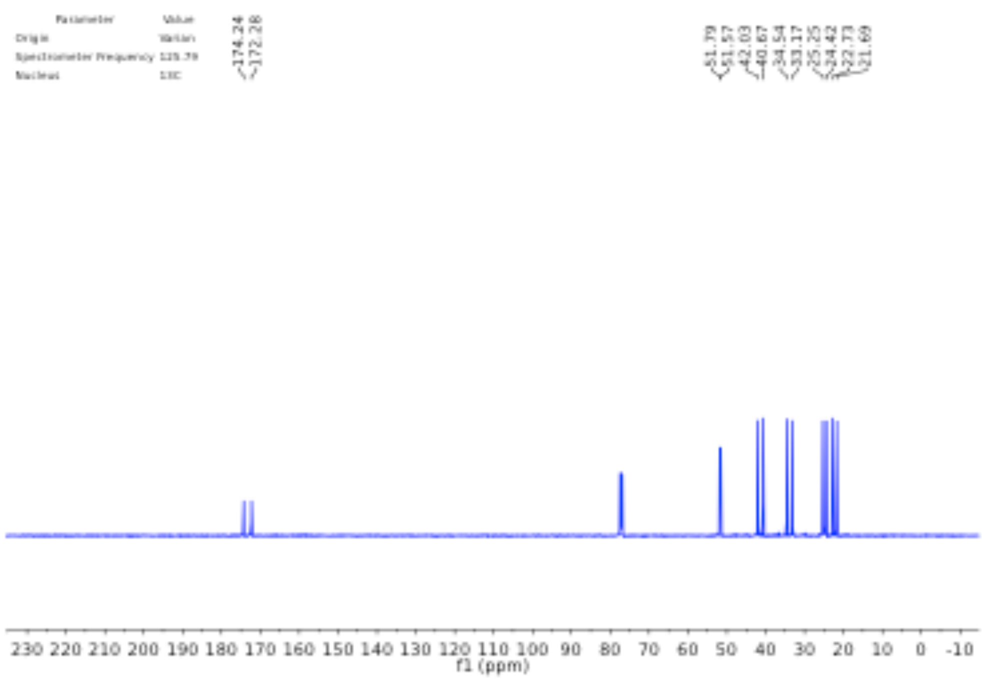




Compound 2a

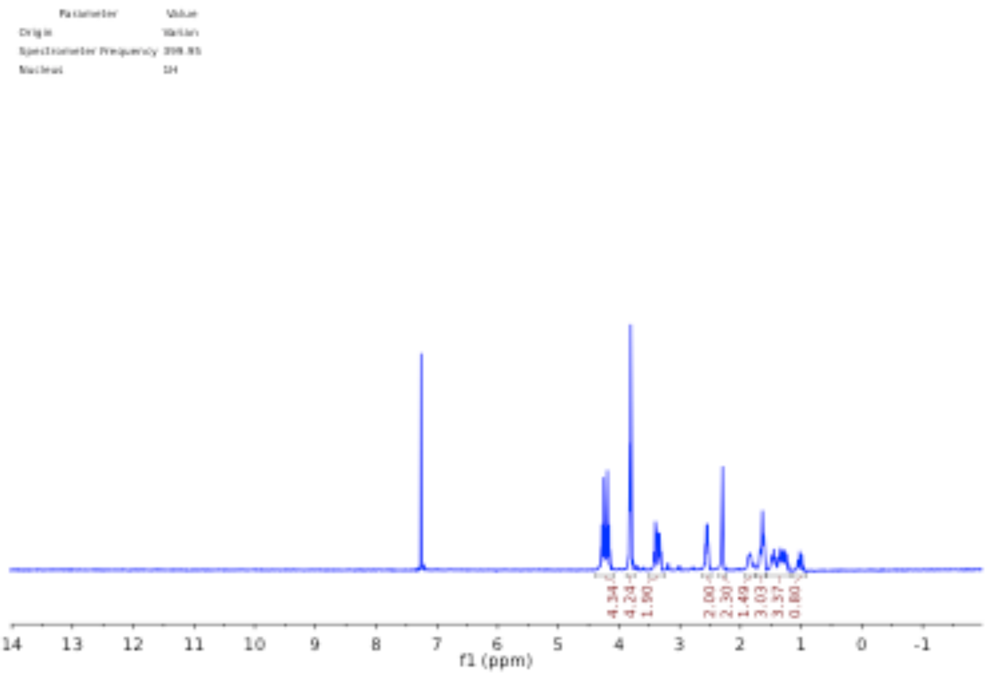


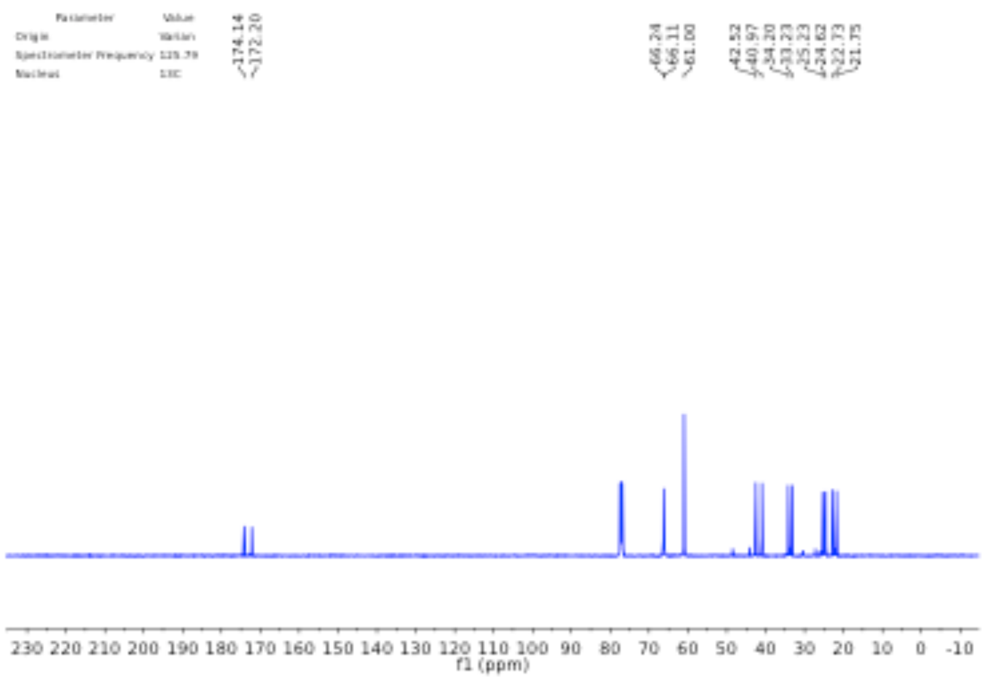
Parameter
Value
Origin
Varian
Spectrometer Frequency
399.95
Nucleus
1H
3.67
3.67
3.35
2.51
6.00
1.88
1.98
1.01
3.20
3.33
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



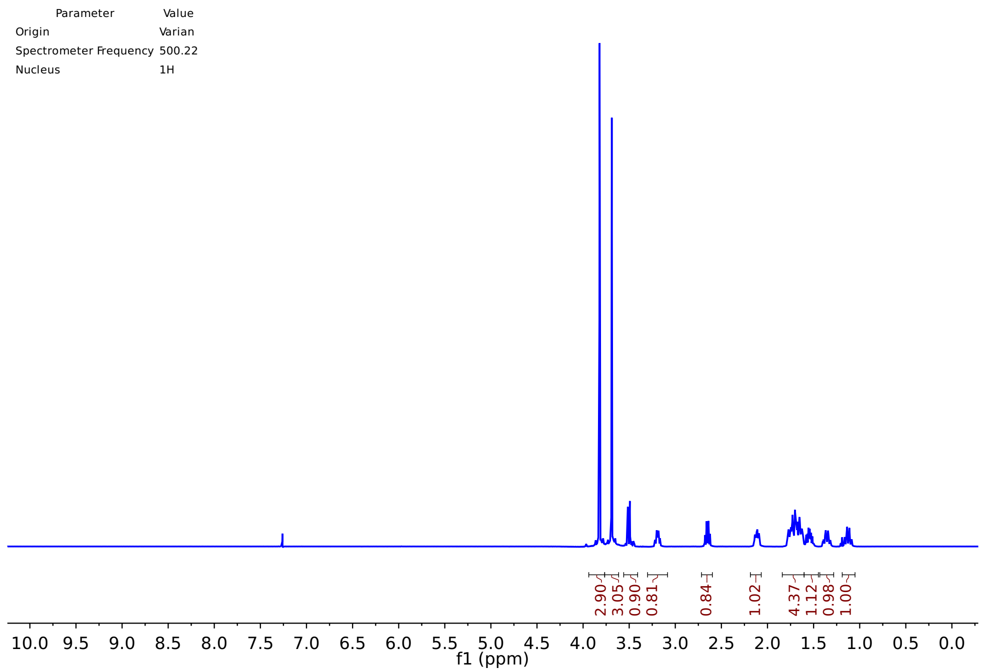
Parameter
Value
Origin
Varian
Spectrometer Frequency
125.79
Nucleus
13C
174.24
172.28
51.79
51.57
42.03
40.67
34.54
33.17
25.25
24.42
22.73
21.69
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

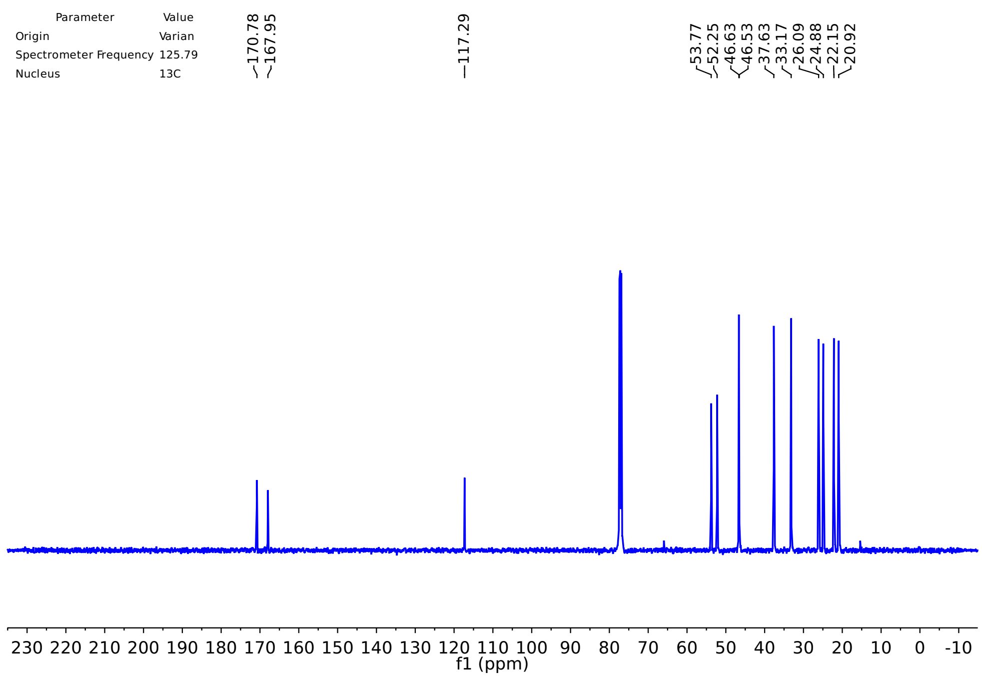
Compound 2


Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
4.34
4.24
1.90
2.00
2.30
1.49
3.03
3.37
0.80
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

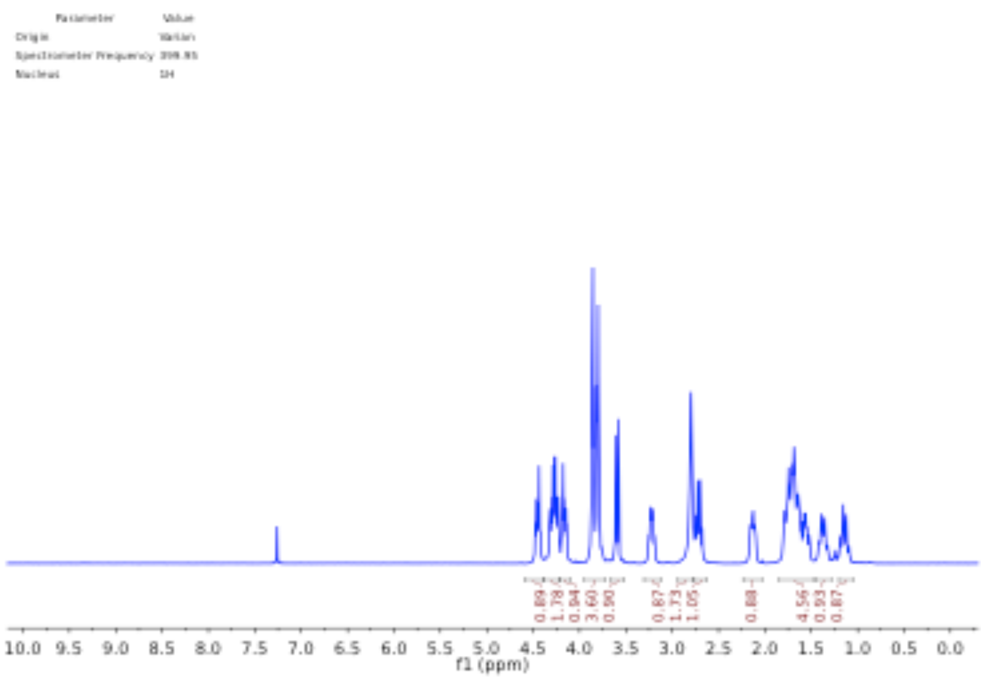

Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
174.14
172.20
66.24
66.11
61.00
42.52
40.97
34.20
33.23
25.23
24.62
22.73
21.75
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3a

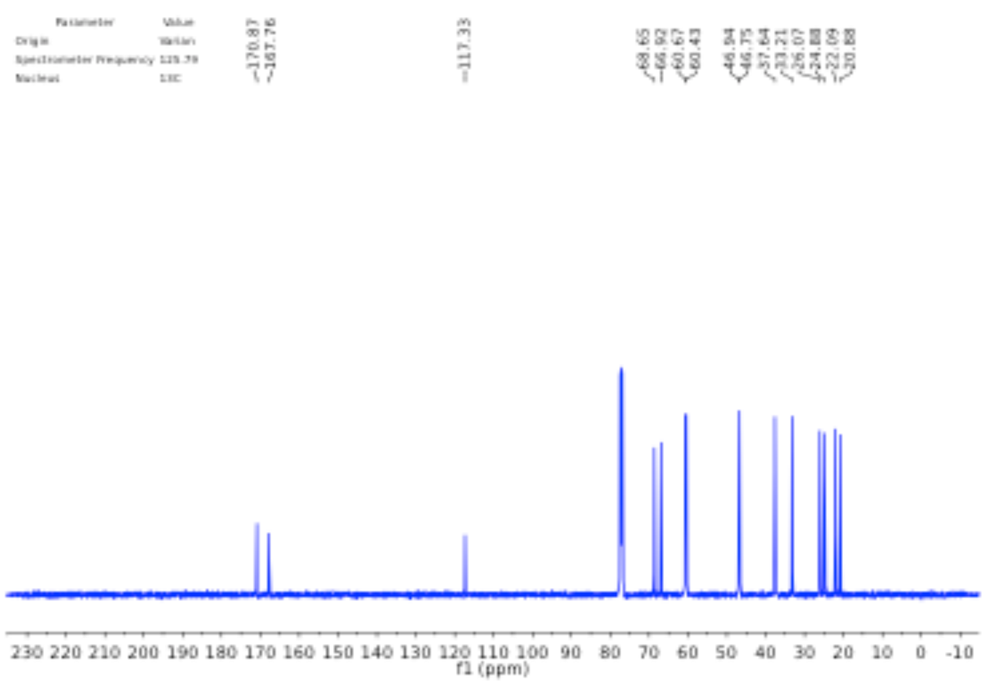

Parameter Value
Origin Varian
Spectrometer Frequency 500.22
Nucleus 1H
2.90
3.05
0.90
0.81
0.84
1.02
4.37
1.12
0.98
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
170.78
167.95
117.29
53.77
52.25
46.63
46.53
37.63
33.17
26.09
24.88
22.15
20.92
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3

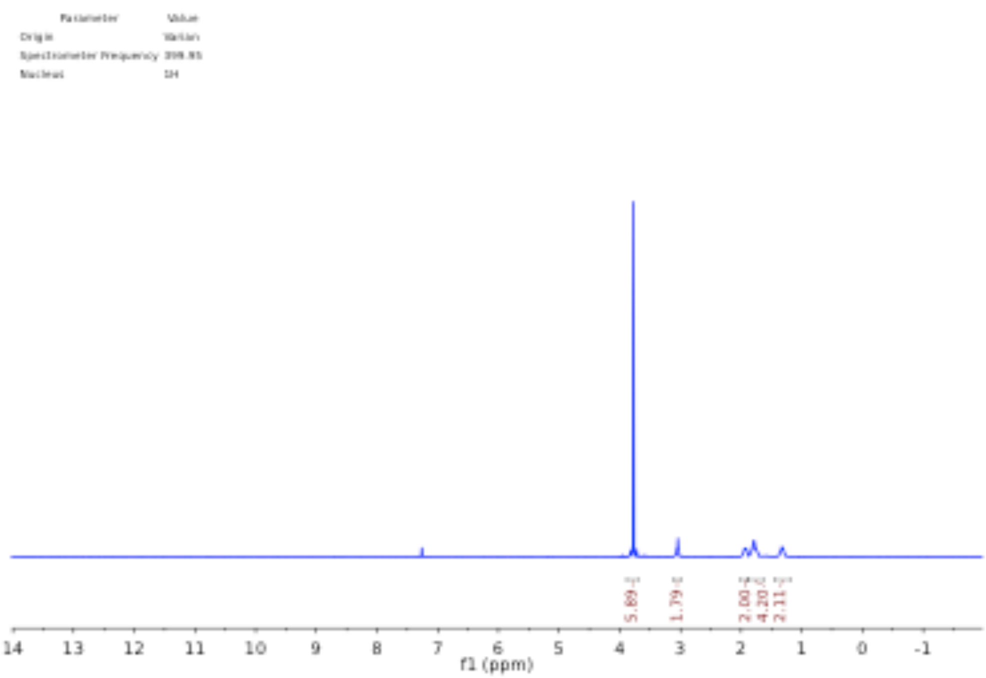


Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
0.89 1.78 0.94 3.60 0.90 0.87 1.73 1.05 0.88 4.56 0.93 0.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

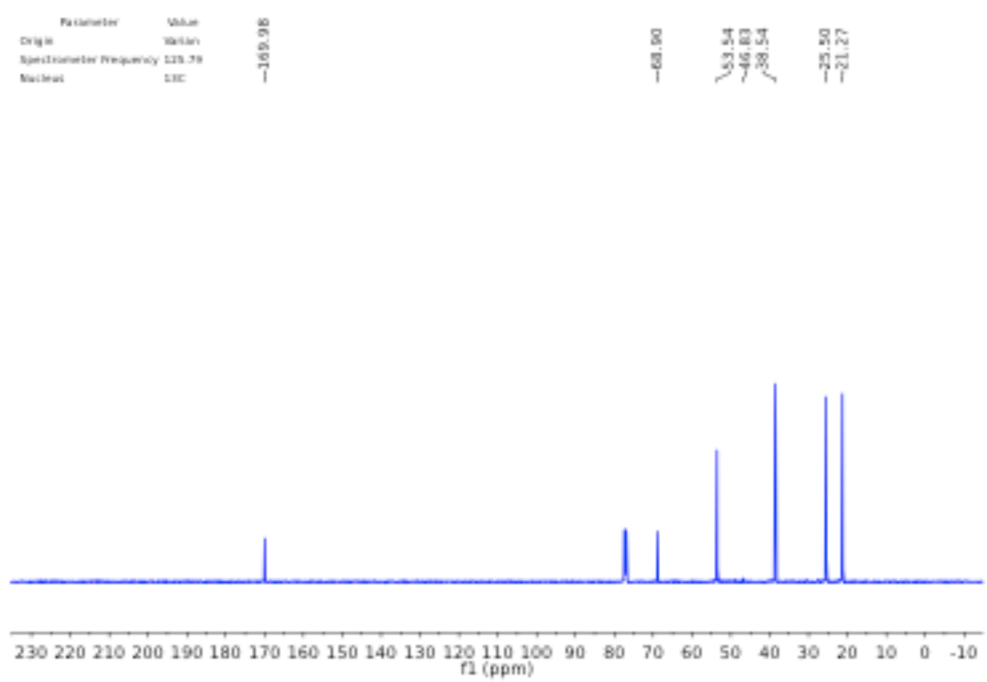


Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
170.87 167.76 117.33 68.65 66.92 60.67 60.43 46.94 46.75 37.64 33.21 26.07 24.88 22.09 20.88
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 4a

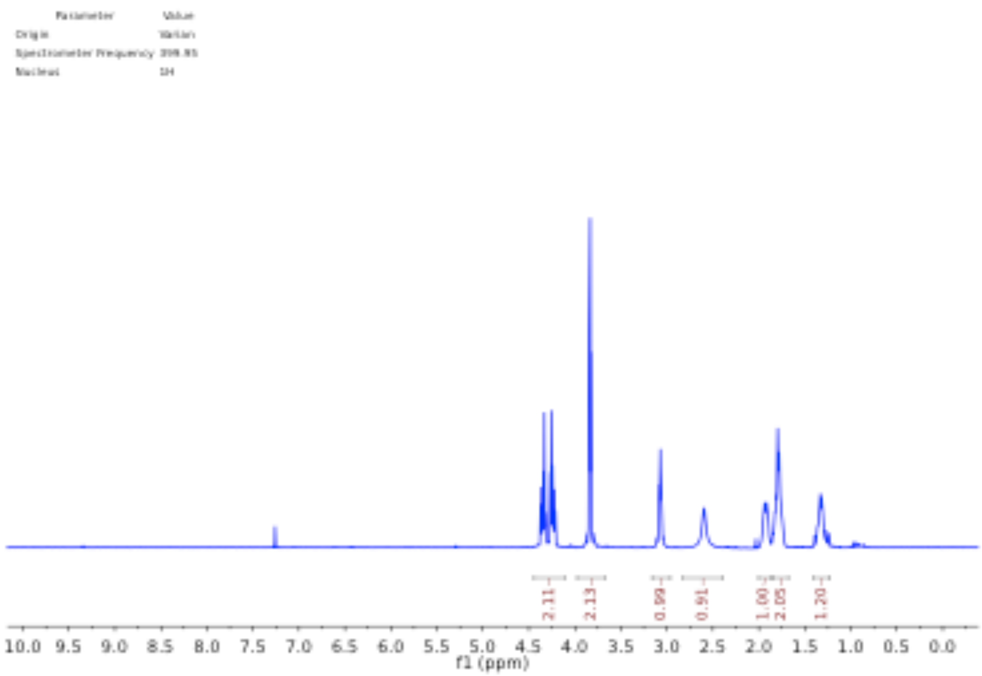


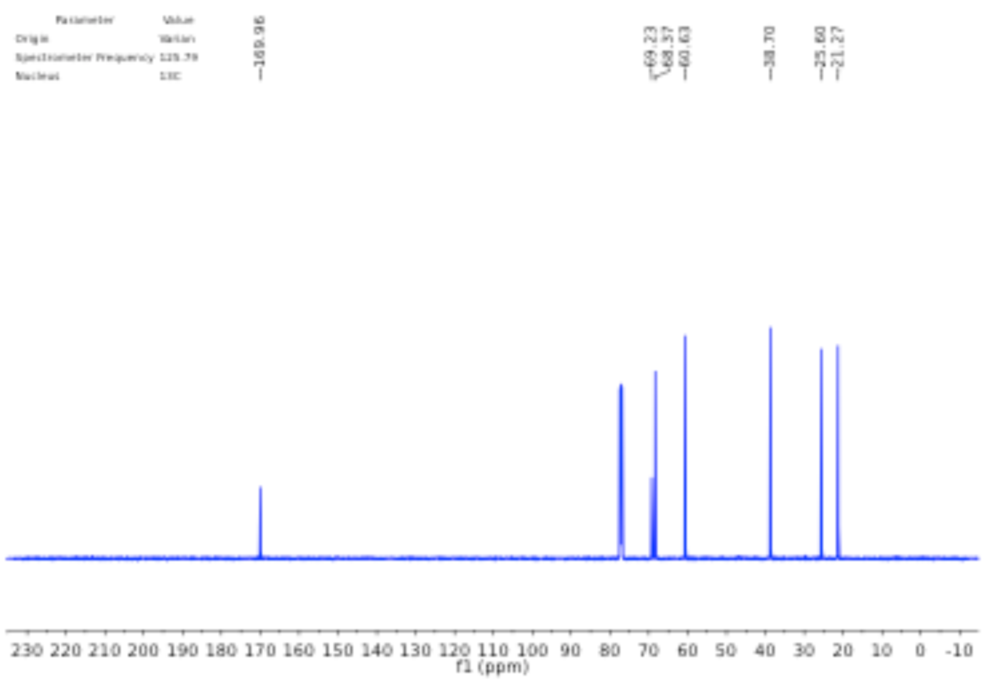
Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
5.89
1.79
2.00
4.20
2.11
f1 (ppm)



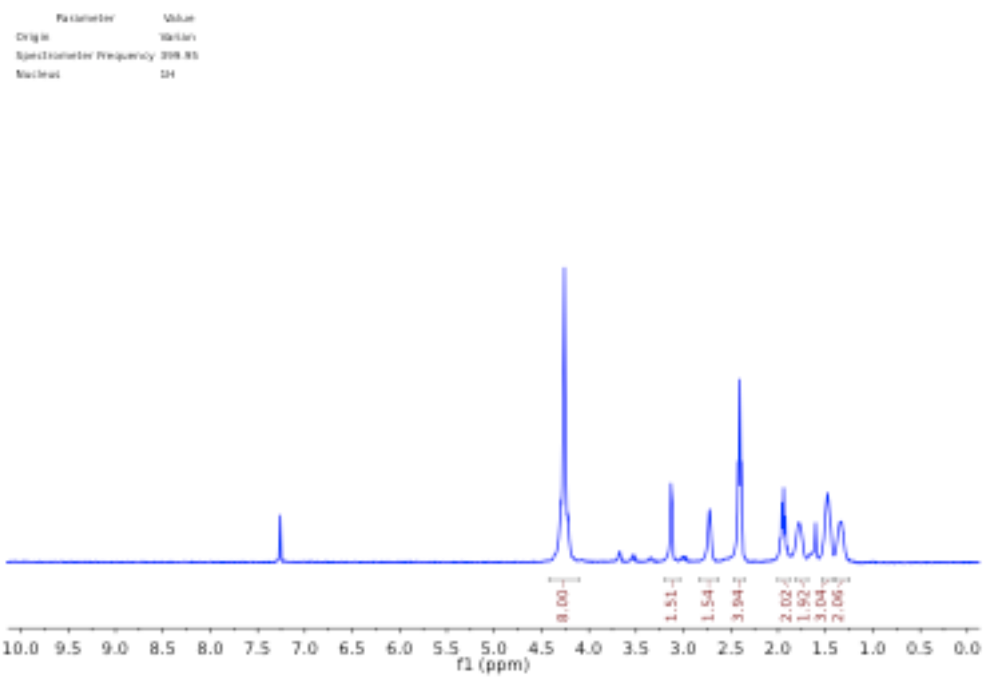
Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
169.98
68.90
53.54
46.83
38.54
25.50
21.27
f1 (ppm)

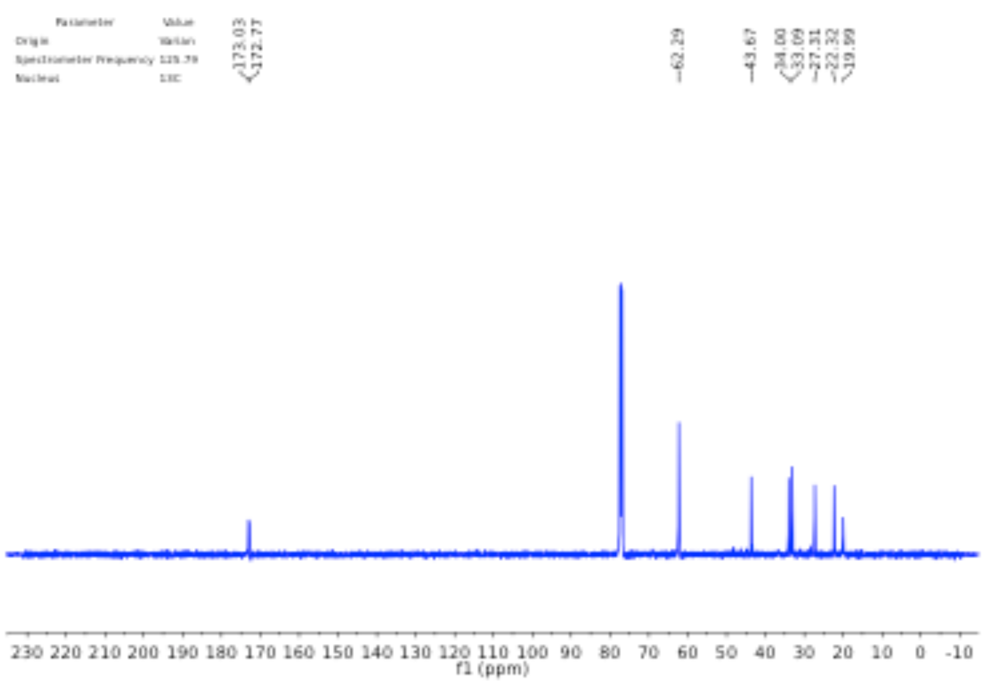
Compound 4


2.11
2.13
0.99
0.91
1.00
2.05
1.20
f1 (ppm)

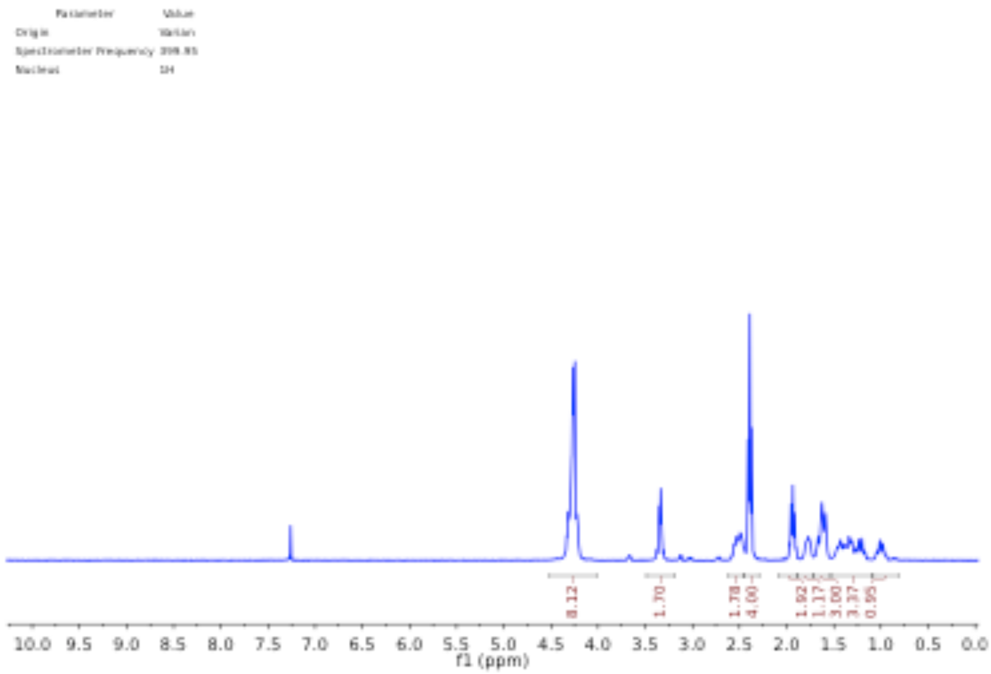

169.96
69.23
68.57
60.63
38.70
25.60
21.27
f1 (ppm)

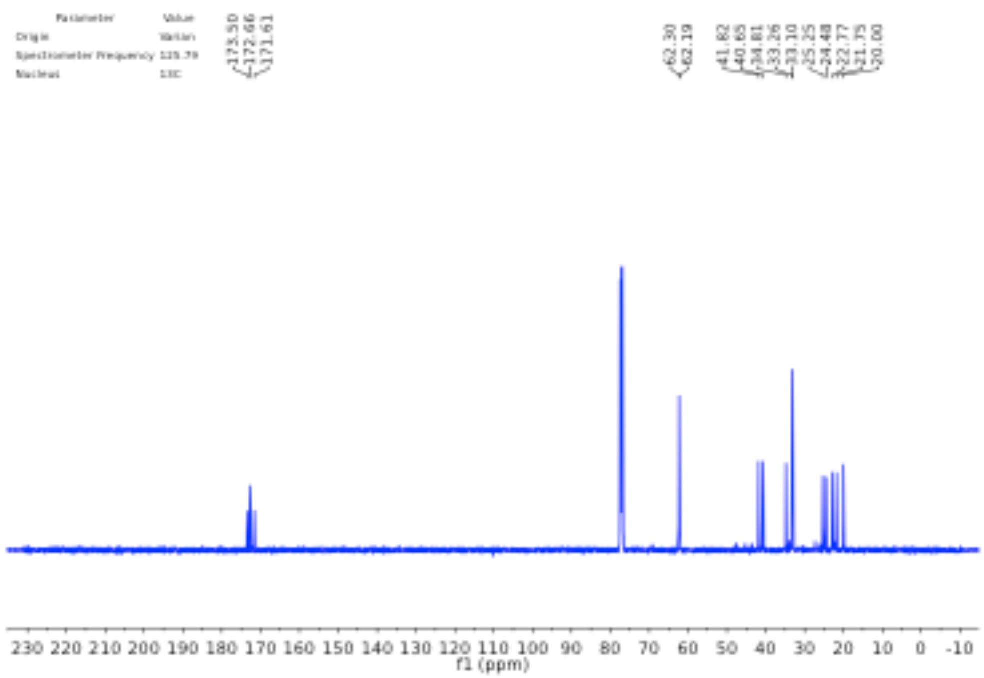
P1


8.00
1.51
1.54
3.94
2.02
1.92
3.04
2.06
f1 (ppm)

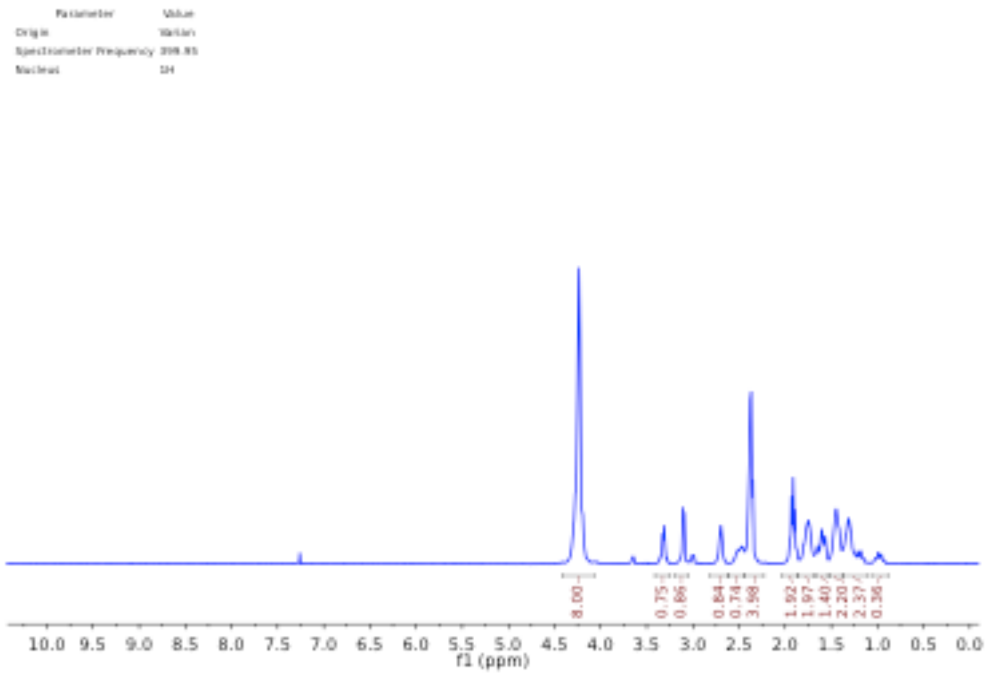

173.03
172.77
62.29
43.67
34.00
33.09
27.31
22.32
19.99
f1 (ppm)

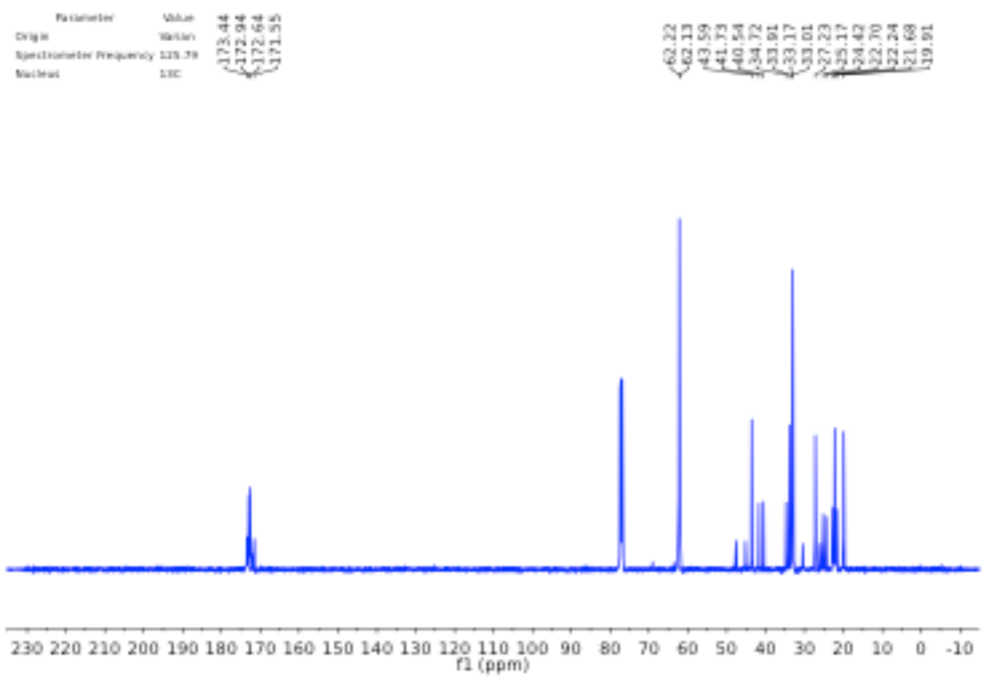
P2


Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
8.12
1.70
1.78
4.00
1.92
1.17
3.00
3.37
0.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

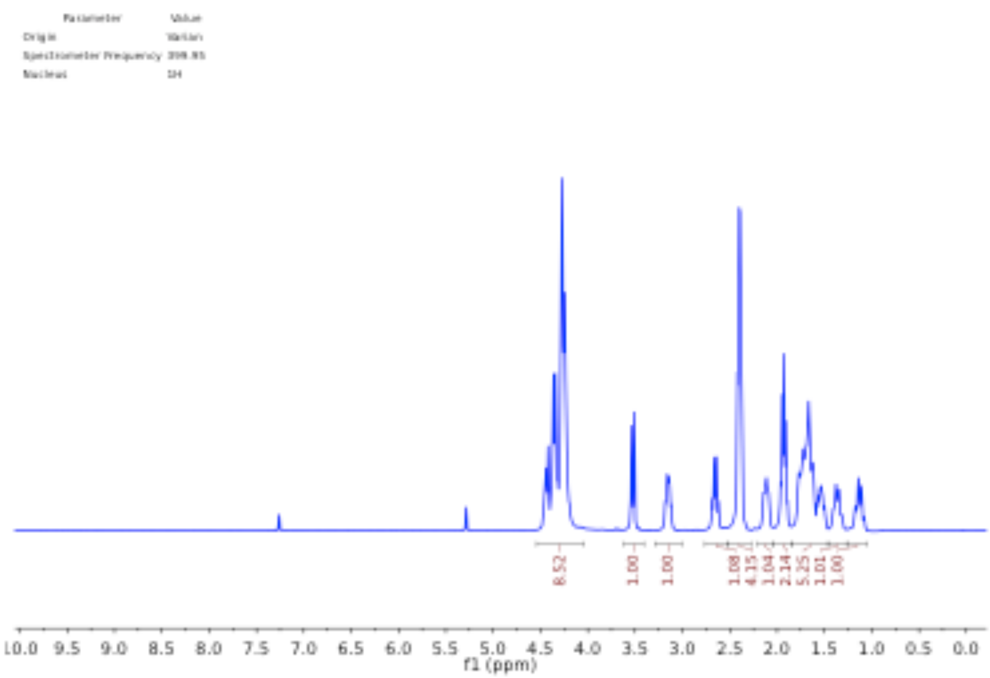

Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
173.50
172.66
171.61
62.30
62.19
41.82
40.65
34.81
33.26
33.10
25.25
24.48
22.77
21.75
20.00
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

P1,2

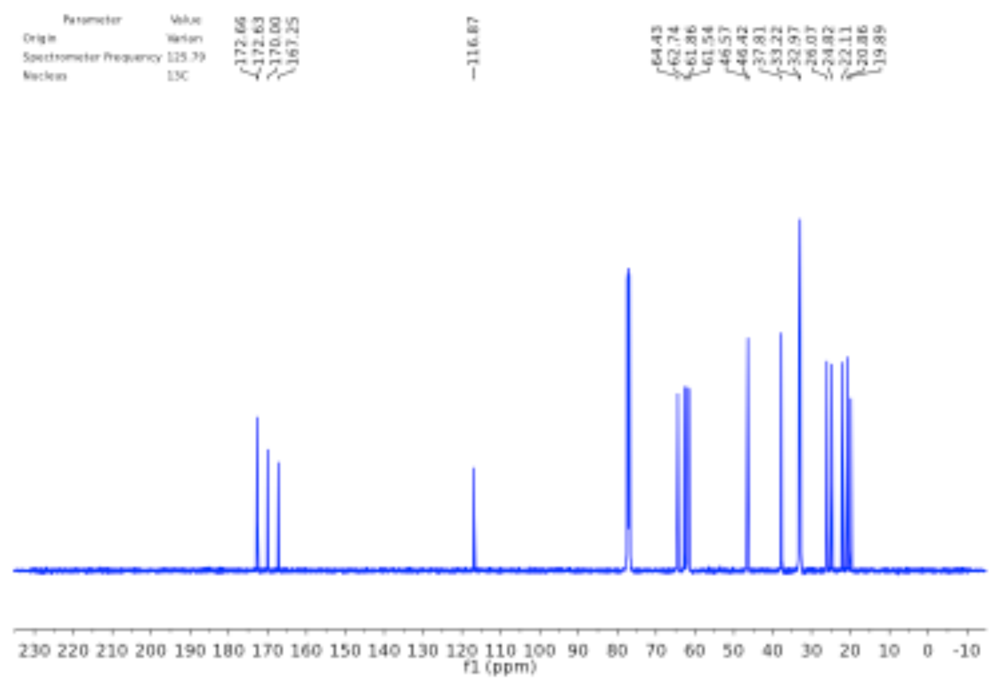




P3

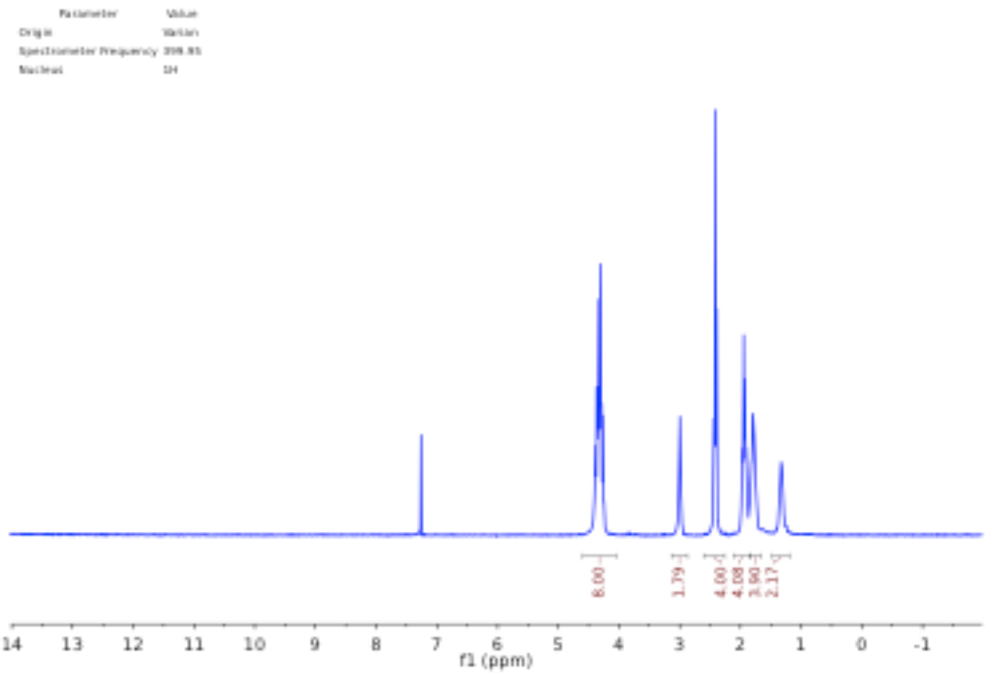


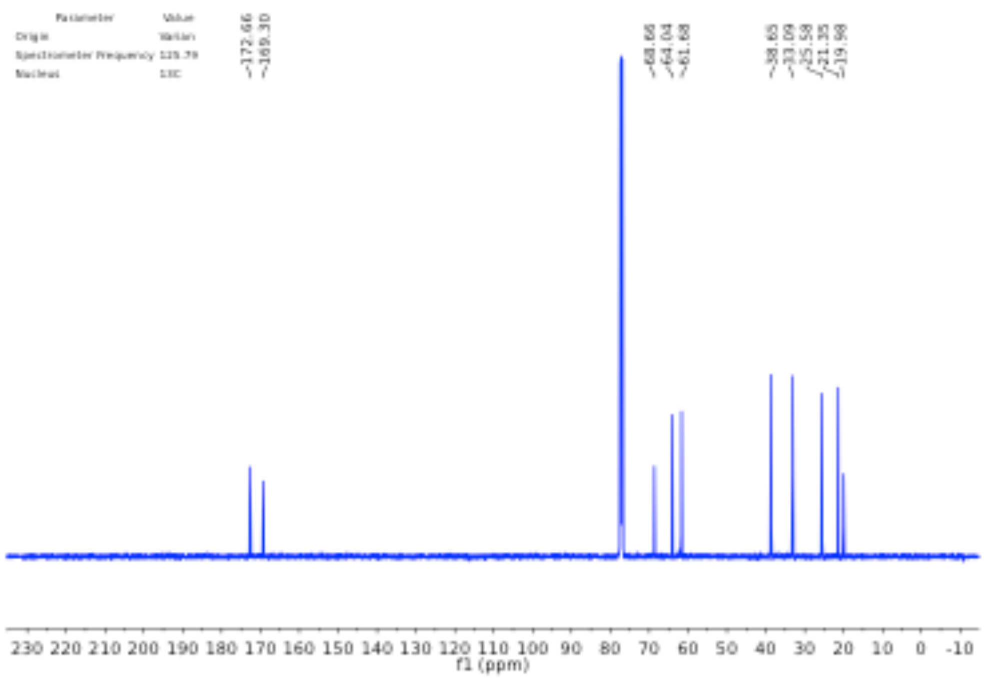
Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
8.52
1.00
1.00
1.08
4.15
1.04
2.14
5.25
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



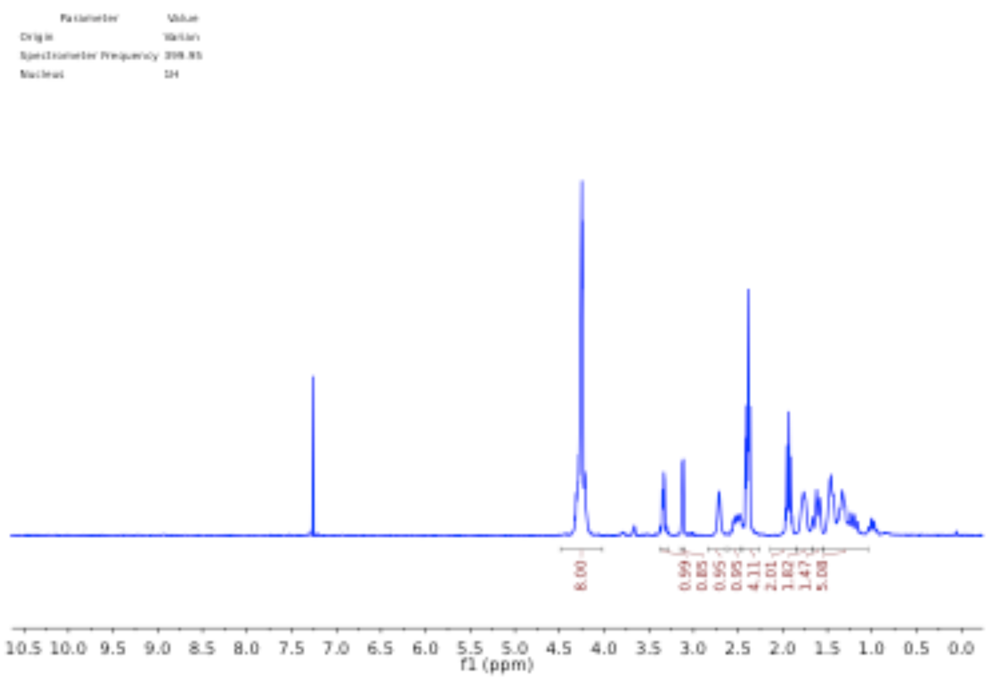
Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
172.66
172.63
170.00
167.25
116.87
64.43
62.74
61.86
61.54
46.57
46.42
37.81
33.22
32.97
26.07
24.82
22.11
20.86
19.89
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

P4

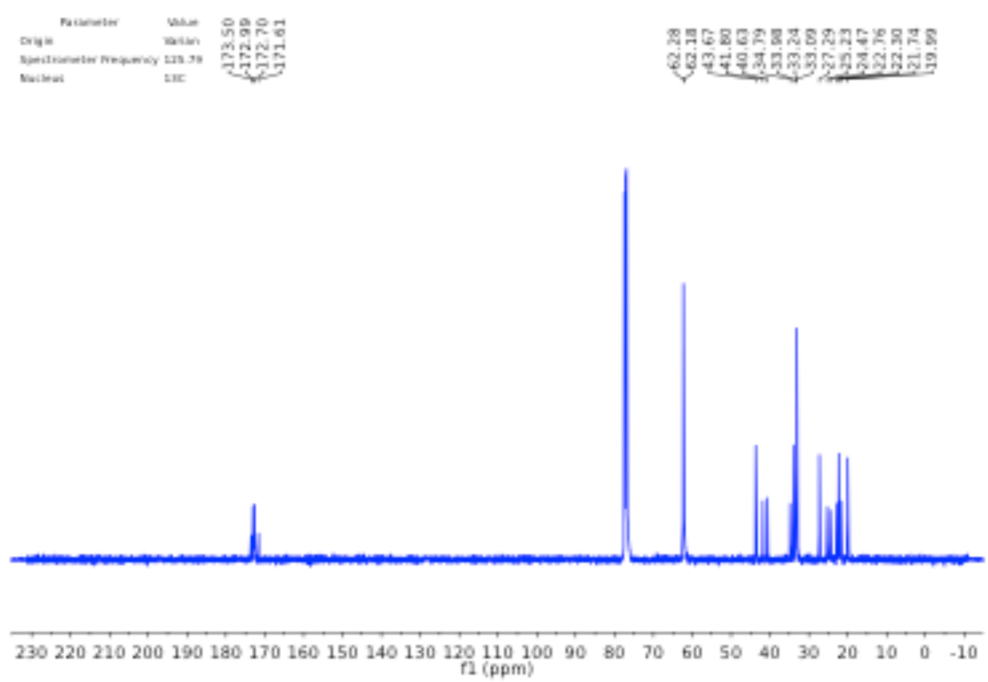

Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
8.00
1.79
4.00
4.08
3.90
2.17
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
172.66
169.30
68.66
64.04
61.68
38.65
33.09
25.58
21.35
19.98
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

PC

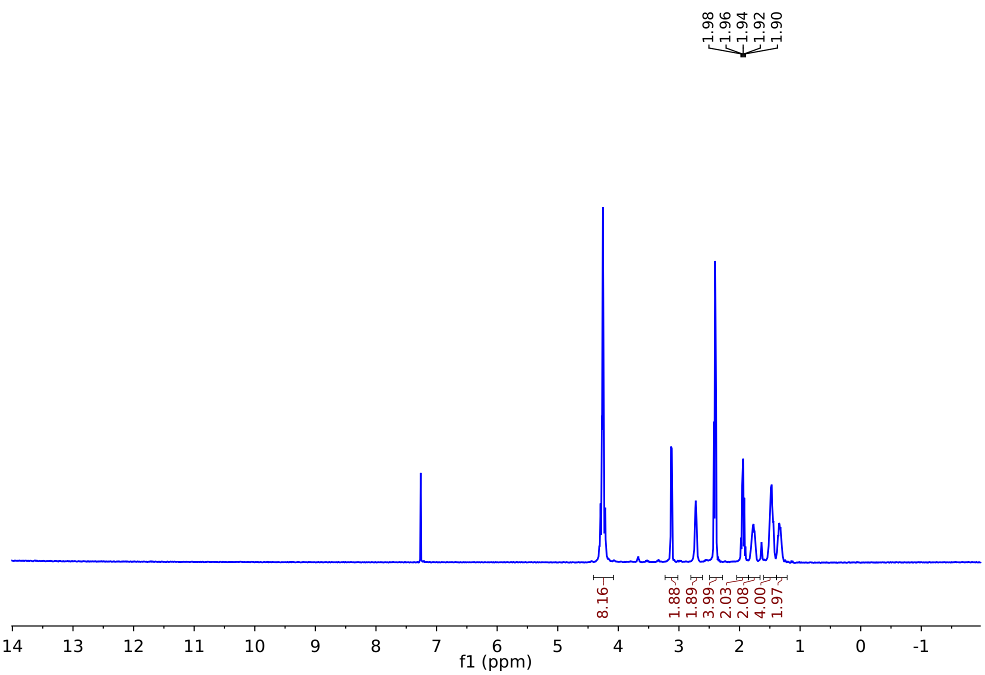


Parameter Value
Origin Varian
Spectrometer Frequency 399.95
Nucleus 1H
8.00
0.99
0.85
0.95
0.95
4.11
2.01
1.82
1.47
5.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

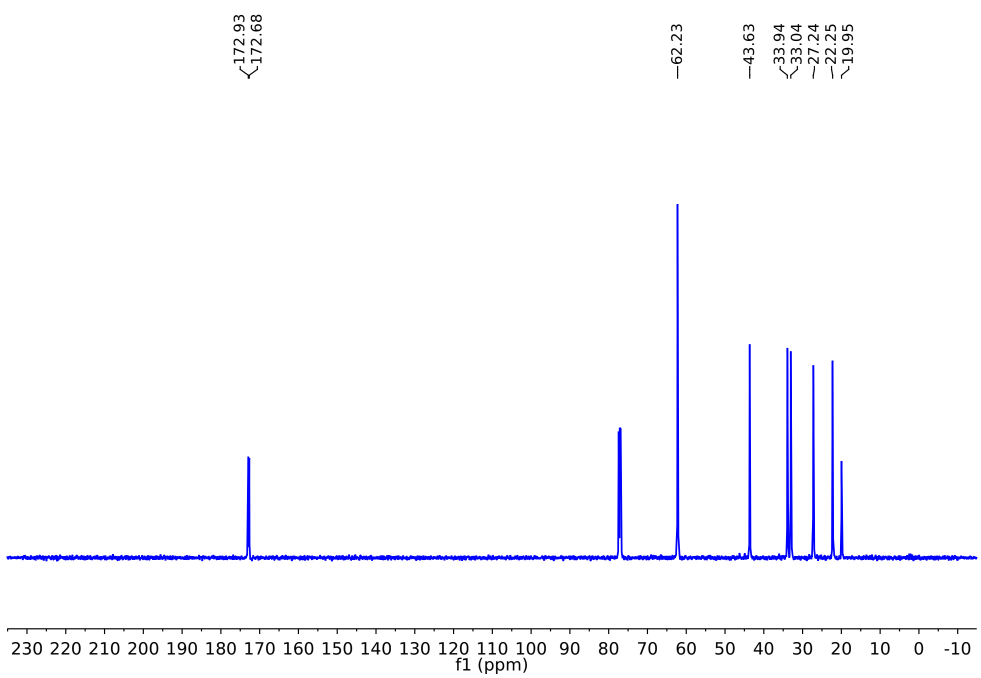


Parameter Value
Origin Varian
Spectrometer Frequency 125.79
Nucleus 13C
173.50
172.99
172.70
171.61
62.28
62.18
43.67
41.80
40.63
34.79
33.98
33.24
33.09
27.29
25.23
24.47
22.76
22.30
21.74
19.99
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

P1,66kDa



1.98
1.96
1.94
1.92
1.90
8.16
1.88
1.89
3.99
2.03
2.08
4.00
1.97
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



172.93
172.68
62.23
43.63
33.94
33.04
27.24
22.25
19.95
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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