Supplemental Information

Table of Contents

General information

Materials

Celite, ethyl vinyl ether, Grubbs 2nd generation catalyst, chlorotriisopropylsilane, imidazole, triethyl amine, 1,3,5-trimethoxybenzene, 3-bromocyclohexene, CuI, phenylacetylene, 2-ethylfuran, 2-pentylfuran, NaH and hexylamine were purchased from Sigma-Aldrich and used without further purification. DIBAL-H in hexane, *N*-nromosuccinimide, cyclohexene, cyclopentene, cyclopentanecarboxaldehyde, cyclohexylacetylene, cyclopentylacetylene, cyclopropylacetylene, isopropylacetylene, 2-methylfuran, phenyllithium, *N*-methylmaleimide and *endo*-5-norbornene-2,3-dicarboxylic anhydride were purchased from Acros Organics and used without further purification. *Exo*-5-Norbornenecarboxylic acid and 3-bromopyridine were purchased from TCI. (Cyclopropylmethyl)triphenylphosphonium bromide was purchased from Alfa Aesar. Solvents of analytical grade were purchased from Honeywell, Acros Organics, Sigma Aldrich, Fischer Scientific and were used without further purification. Solvents of technical grade were purified by distillation. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were purchased from Cambridge Isotope Laboratories Inc. Grubbs 3rd generation catalyst was prepared from Grubbs 2nd generation catalyst which was dissolved in a large excess of 3-bromopyridine, precipitated in n-pentane and then dried under high vacuum.

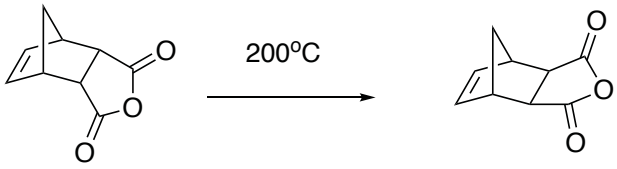
Instrumentation

ESI-MS analysis for synthesized compounds was carried out on a Bruker 4.7T BioAPEX II. GC-MS analysis for synthesized compounds was carried out on a Thermo Scientific Trace GC Ultra DSQ II system with Zebron capillary GC column (ZB-5MS 0.25 μm, 30m×0.25mm). MALDI-ToF MS analysis of the polymers was carried out on a Bruker ultrafleXtreme^{TM} using 2-(*2E*)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix and silver trifluoroacetate or sodium

trifluoroacetate as the added salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) with an Agilent Technologies 1260 Infinity II GPC system (pump, autosample, RI detector) and two MZ-Gel SDplus Linear columns (5 μm, 300×8.0mm), a MZ-Gel SDplus Linear precolumn (5 μm, 50×8.0mm) at a flow rate of 1mL/min for samples measured in $CHCl_3$. Calibrations were carried out using PSS-polymer polystyrene standards. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (^{1}H NMR 300 MHz, ^{13}C-NMR 75 MHz) or Bruker Avance III 400 MHz NMR spectrometer (^{1}H NMR 400 MHz, ^{13}C-NMR 101 MHz). Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was carried out on a Perkin Elmer Optima 7000DV ICP-OES instrument equipped with a CCD array detector, argon as the optical torch gas and nitrogen as the optical purge gas. The instrument was calibrated with solutions of $RuCl_3$ in hydrochloric acid solution (1.000g/L Ru). Results were processed with the WinLab32 software.

Synthesis of Monomers

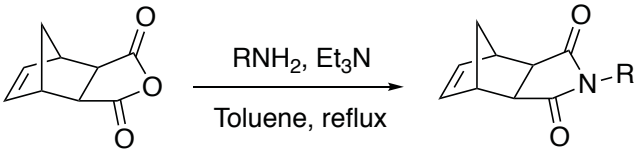
Synthesis of *exo*-*N*-methyl norbornene imide (MNI), *exo*-*N*-hexyl norbornene imide (HNI) and *exo*-*N*-phenyl norbornene imide (PNI)



Endo-5-Norbornene-2,3-dicarboxylic anhydride 50 g was isomerized by heating for 5 hours at 200°C in a 250ml round-bottom flask which was equipped with a condenser. The reaction mixture was cooled to 120°C, toluene (50ml) was added, cooled to room temperature and the precipitated pale yellow crystals were collected and dried. The purity of the collected crystals was evaluated by recording ^{1}H NMR spectra of their $CDCl_3$ solutions. Then, 20ml acetone was added to the collected crystals and the mixture heated to reflux until all crystals were dissolved. After cooling to room temperature the precipitated crystals were collected. The purity of the collected crystals was evaluated by recording ^{1}H NMR spectra of their $CDCl_3$ solutions. The procedure was repeated until the purity of *exo*-5-norbornene-2,3-dicarboxylic anhydride was more than 95%. Yield: 25%

***exo*-*N*-methyl norbornene imide**: white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.32-6.35 (m, 2H), 3.38-3.52 (m, 2H), 3.00 (d, J = 1.5 Hz, 2H), 1.65-1.70 (m, 1H), 1.43-1.47 (m, 1H).

***endo*-N-methyl norbornene imide**: white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.31-6.32 (m, 2H), 3.55-3.59 (m, 2H), 3.49-3.53 (m, 2H), 1.77-1.81 (m, 1H), 1.55-1.59 (m, 1H).



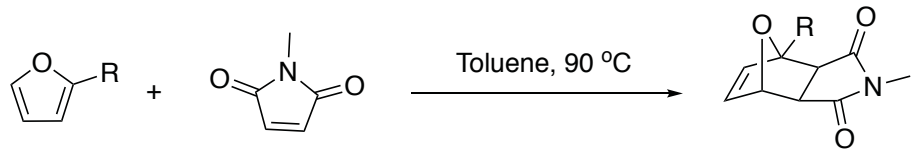
Toluene (20mL), triethyl amine (6 mL) and *alkylamine* (6.1mmol) was added at room temperature to the solution of *exo*-5-norbornene-2,3-dicarboxylic anhydride (1g, 6.1mmol) in a 100ml round-bottom flask which was equipped with a condenser. The resulting reaction mixture was kept stirring for 1 h at room temperature then heated at 120 °C for 2h. After completion of the reaction (TLC monitoring), the solvent was removed under vacuum. The crude residue was purified by silica column chromatography (15-25% ethyl acetate in hexane) to afford the product.

MNI, white solid. Yield: 90%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.26 (t, *J* = 1.9 Hz, 2H), 3.24-3.27 (m, 2H), 2.95 (s, 3H), 2.68 (d, *J* = 1.4 Hz, 2H), 1.48-1.52 (m, 1H), 1.16-1.20 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.18, 137.74, 47.95, 45.13, 42.92, 24.63. GC-MS:177.

HNI, colorless liquid. Yield: 82%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.27 (t, *J* = 1.9 Hz, 2H), 3.41--3.46 (m, 2H), 3.24-3.28 (m, 2H), 2.65 (d, *J* = 1.3 Hz, 2H), 1.46-1.55 (m, 3H), 1.19-1.31 (m, 7H), 0.83-0.88 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-d) δ 178.09, 137.82, 47.79, 45.16, 42.70, 38.75, 31.31, 27.72, 26.61, 22.46, 13.98. GC-MS: 247.

PNI, white solid. Yield: 93%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43-7.48 (m, 2H), 7.35-7.40 (m, 1H), 7.23-7.27 (m, 2H), 6.34 (t, *J* = 1.9 Hz, 2H), 3.34-3.44 (m, 2H), 2.85 (d, *J* = 1.4 Hz, 2H), 1.59-1.63 (m, 1H), 1.47-1.50 (m, 1H).

Synthesis of *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-4-methyl-5-ene-2,3-dicarboximide(MOMNI), *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-4-ethyl-5-ene-2,3-dicarboximide(EOMNI)[1,2,3]

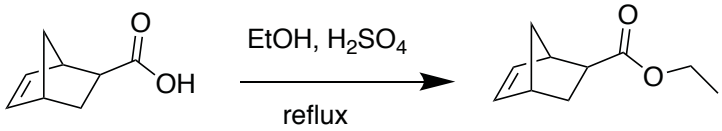


Furan (2.5eq) was added at room temperature to the solution of *N*- methylmaleimide (1.0eq) in toluene in a round-bottom flask which was equipped with a condenser. The resulting reaction mixture was stirred at 90 °C overnight. After completion of the reaction (TLC monitoring), the solvent was removed under vacuum. The crude residue was purified by silica column chromatography (50% ethyl acetate in hexane) to afford the product as a white solid.

MOMNI, Yield: 92%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.47 (dd, *J* = 5.6, 1.6 Hz, 1H), 6.28 (d, *J* = 5.6 Hz, 1H), 5.14 (d, *J* = 1.8 Hz, 1H), 2.91-2.94 (m, 4H), 2.68 (d, *J* = 6.5 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 176.29, 175.07, 140.55, 136.96, 88.14, 80.62, 50.73, 49.52, 24.92, 15.70. GC-MS:193.

EOMNI, Yield: 89%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.50 (dd, *J* = 6.1, 1.3 Hz, 1H), 6.38 (d, *J* = 5.7 Hz, 1H), 5.19 (d, *J* = 1.7 Hz, 1H), 2.91-2.94 (m, 4H), 2.76 (d, *J* = 6.5 Hz, 1H), 2.06 (m, 2H), 1.12 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 176.42, 175.06, 138.67, 137.13, 92.52, 80.56, 50.72, 48.86, 24.96, 22.76, 9.56. GC-MS:207.

Synthesis of *exo*-ethyl-5-norbornene carboxylate (ENC)

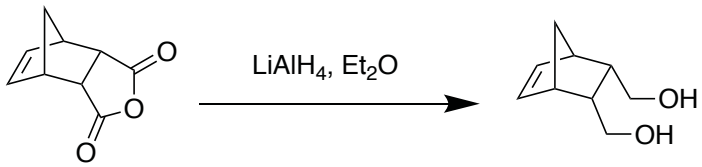


Concentrated H_2SO_4 (36mg, 0.36mmol, 5%eq.) was added to a solution of *exo*-5-norbornenecarboxylic acid (1g, 7.2mmol, 1.0eq.) in EtOH (10ml) and the mixture was

stirred at reflux temperature for 24 h. The reaction mixture was concentrated under vacuum and the residue was dissolved in ethyl acetate. The organic layer was washed with water, saturated $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. Filtration and concentration under vacuum gave *exo*-ethyl-5-norbornene carboxylate. The crude residue was purified by silica column chromatography (20% ethyl acetate in hexane) to afford the product as a colorless liquid. 1.15g

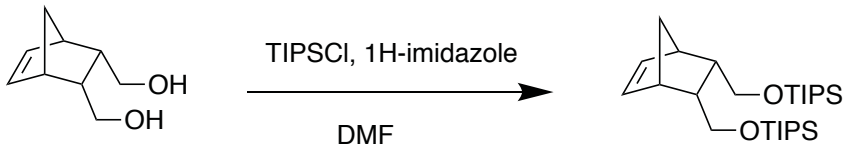
Yield: 95%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.10-6.15 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.19-2.23 (m, 1H), 1.90-1.95 (m, 1H), 1.33-1.39 (m, 2H), 1.24-1.29 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 176.28, 138.05, 135.79, 60.36, 46.63, 46.34, 43.18, 41.64, 30.32, 14.30. GC-MS:166.

Synthesis of *endo*-5-norbornene-2,3-bis(triisopropyl)silylmethanol (NBSM)



$LiAlH_4$ (2.7g. 70.4mmol, 2.1eq.) was added to the cooled (ice bath) solution of *endo*-5-norbornene-2,3-dicarboxylic anhydride (5.5g, 33.5mmol, 1.0eq.) in diethylether (67mL, 250ml round-bottom flask). The resulting reaction mixture was kept stirring overnight at room temperature. After completion of the reaction (TLC monitoring), NaOH solution (10ml 15%) and H_2O (30ml) were added slowly while cooling the mixture with an ice bath. The formed solid was removed by filtration, the solvent of the remaining solution was removed under reduced pressure to afford 5g crude product as a colorless viscous liquid which was used in the next step without further purification.

Yield: 97%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.04 (t, *J* = 1.9 Hz, 2H), 3.64-3.69 (m, 2H), 3.37-3.44 (m, 2H), 3.13 (s, 2H), 2.79-2.83 (m, 2H), 2.50-2.60 (m, 2H), 1.37-1.45 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.82, 63.67, 49.94, 46.60, 45.20
ESI-MS (m/z): 177 (M^++Na).

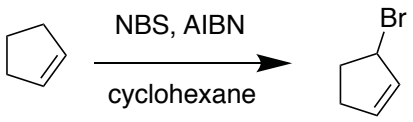


Endo-5-norbornene-2,3-dimethanol (2.9 g, 19 mmol, 1.0 equiv) and triiso-propylchlorosilane (11 g, 57 mmol, 3.0 equiv) were added in sequence to a stirred solution of imidazole (5.2 g, 76 mmol, 4.0 equiv) in *N*, *N*-dimethylformamide (30 mL) at room temperature. The homogenous mixture gradually became biphasic, and the biphasic mixture was vigorously stirred for 20 h at room temperature. The product mixture was poured into a separating funnel that had been charged with 50% ether–hexanes and aqueous sulfuric acid solution (1 N). The layers that formed were separated and the organic layer was washed sequentially with aqueous sodium hydroxide solution (1 N) and saturated aqueous sodium chloride solution. The washed organic layer was dried over sodium sulfate, and the solids removed by filtration. The filtrate was concentrated under reduced pressure to afford the crude product. The crude residue was purified by silica column chromatography (20% ethyl acetate in hexane) to afford the product as a white solid. 7.1g.

Yield: 80%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.12 (t, *J* = 1.7 Hz, 2H), 3.56-3.60 (m, 2H), 3.28-3.32 (m, 2H), 2.93-2.94 (m, 2H), 2.33-2.41 (m, 2H), 1.43-1.46 (m, 1H), 1.30-1.32 (m, 1H), 1.04-1.05 (m, 42H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.50, 62.59, 48.20, 44.72, 43.76, 17.22, 11.15. ESI-MS (m/z): 467 (M^{+}+H).

Synthesis of Chain Transfer Agents (CTAs)

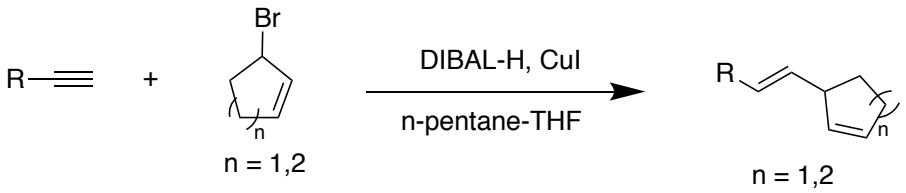
General Synthesis of Chain Transfer Agents (CTAs)



A mixture of cyclopentene (11g,161mmol, 1.0eq), NBS (30g, 168mmol, 1.1eq), and AIBN (0.8g, 4.83mmol, 3%eq) in cyclohexane (60ml) was heated at 90^{o}C for 1 h. The

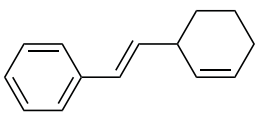
reaction mixture was cooled to 0°C and filtered through a pad of Celite. The filtrate was concentrated by evaporating the solvent. The residue was purified by distillation under reduced pressure (35-40^{o}C/30mbar) to give a colorless liquid. 7.6g.

Yield: 32%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.00-6.07 (m, 2H), 5.15-5.19 (m, 1H), 2.56-2.71 (m, 1H), 2.31-2.41 (m, 3H).



The alkyne (1.0eq) was dissolved in dry pentane, then DIBAL-H (1.5eq, 1M in hexane) was added slowly at 0^{o}C. After addition, the solution was stirred for 30min at room temperature and 4h at 50^{o}C. After cooling to room temperature, the pentane and hexane were moved under reduced pressure. Then, the mixture was dissolved in dry THF followed by addition of 3-bromocycloolefin (1.5eq) and CuI (1.5eq) in water bath. The mixture was kept stirring overnight at room temperature. The mixture was added slowly to an aqueous solution of H_2SO_4 (10%) cooled with an ice bath. The mixture was filtered through a pad of Celite. The aqueous layer was extracted with pentane three times. The combined organic phases were washed with aqueous saturated $NaHCO_3$ solution and dried with anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude product was purified by silica column chromatography (100% pentane) very slowly.

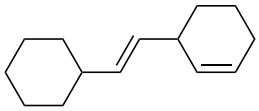
(*E*)-(2-(cyclohex-2-en-1-yl)vinyl)benzene (CTA1)



Colorless liquid. Yield: 53%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.37 (m, 2H), 7.27-7.31 (m, 2H), 7.17-7.21 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.4

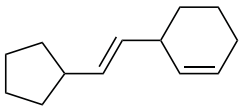
Hz, 1H), 5.78-5.83 (m, 1H), 5.62-5.66 (m, 1H), 2.65-2.97 (m, 1H), 2.00-2.05 (m, 2H), 1.85-1.92 (m, 1H), 1.71-1.79 (m, 1H), 1.48-1.64 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.81, 134.71, 129.49, 129.03, 128.46, 128.08, 126.88, 126.03, 38.67, 29.27, 25.09, 20.54. GC-MS: 184.

(*E*)-3-(2-cyclohexylvinyl)cyclohex-1-ene (CTA2)



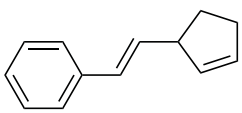
Colorless liquid. Yield: 83%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.68-5.72 (m, 1H), 5.52-5.57 (m, 1H), 5.28-5.39 (m, 2H), 2.66-2.73 (m, 1H), 1.86-1.99 (m, 3H), 1.61-1.81 (m, 6H), 1.47-1.57 (m, 2H), 1.03-1.41 (m, 6H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 135.73, 131.61, 130.68, 127.17, 40.65, 38.30, 34.14, 33.27, 29.56, 26.15, 22.36, 14.08. GC-MS:190.

(*E*)-3-(2-cyclopentylvinyl)cyclohex-1-ene (CTA3)



Colorless liquid. Yield: 80%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.68-5.73 (m, 1H), 5.53-5.57 (m, 1H), 5.30-5.42 (m, 2H), 2.67-2.74 (m, 1H), 2.3-2.43 (m, 1H), 1.94-2.00 (m, 2H), 1.48-1.81 (m, 10H), 1.21-1.42 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.34, 132.24, 130.63, 127.19, 43.31, 38.23, 34.14, 33.28, 29.52, 25.14, 22.36, 20.64, 14.08. GC-MS:176.

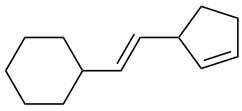
(*E*)-(2-(cyclopent-2-en-1-yl)vinyl)benzene (CTA4)



Colorless liquid. Yield: 55%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.36 (m, 2H), 7.27-7.30 (m, 2H), 7.17-7.21 (m, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.16 (dd, *J* = 15.8, 8.0

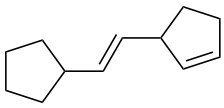
Hz, 1H), 5.83-5.86 (m, 1H), 5.67-5.70 (m, 1H), 3.44-3.51 (m, 1H), 2.30-2.49 (m, 2H), 2.15-2.23 (m, 1H), 1.62-1.71 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.73, 134.42, 133.59, 131.77, 128.46, 128.32, 126.87, 126.03, 48.84, 32.19, 30.78. GC-MS:170.

(*E*)-(2-(cyclopent-2-en-1-yl)vinyl)cyclohexane (CTA5)



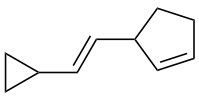
Colorless liquid. Yield: 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.73-5.76 (m, 1H), 5.57-5.60 (m, 1H), 5.26-5.40 (qd, *J* = 15.8, 6.9 Hz, 2H), 3.20-3.26 (m, 1H), 2.22-2.41 (m, 2H), 2.04-2.12 (m, 1H), 1.84-1.93 (m, 1H), 1.61-1.73 (m, 5H), 1.47-1.55 (m, 1H), 0.99-1.31 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.07, 134.62, 131.35, 130.78, 48.55, 40.51, 33.22, 32.13, 30.96, 26.26, 26.14. GC-MS:176.

(*E*)-3-(2-cyclopentylvinyl)cyclopent-1-ene (CTA6)



Colorless liquid. Yield: 70%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.75 (dq, *J* = 5.6, 2.3 Hz, 1H), 5.60 (dq, *J* = 5.7, 2.1 Hz, 1H), 5.25 -5.48 (m, 2H), 3.21-3.27 (m, 1H), 2.22-2.42 (m, 3H), 2.04-2.13 (m, 1H), 1.71-1.79 (m, 2H), 1.49-1.68 (m, 5H), 1.21-1.30 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.58, 133.69, 132.00, 130.80, 48.46, 43.18, 33.25, 32.13, 30.94, 25.13. GC-MS:162.

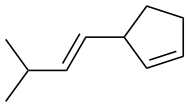
(*E*)-3-(2-cyclopropylvinyl)cyclopent-1-ene (CTA7)



Colorless liquid. Yield: 78%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.75 (dd, *J* = 5.6, 2.3 Hz, 1H), 5.59 (dd, *J* = 5.6, 2.2 Hz, 1H), 5.45 (dd, *J* = 15.2, 7.9 Hz, 1H), 4.97 (ddd,

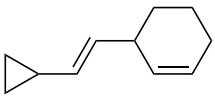
J = 15.2, 8.6, 1.0 Hz, 1H), 3.20-3.28 (m, 1H), 2.22-2.41 (m, 2H), 2.04-2.12 (m, 1H), 1.48-1.57 (m, 1H), 1.26-1.38 (m, 1H), 0.62-0.70 (m, 2H), 0.28-0.34 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.33, 132.51, 131.88, 130.95, 48.38, 32.10, 30.94, 13.47, 6.50, 6.48. GC-MS:134.

(*E*)-3-(3-methylbut-1-en-1-yl)cyclopent-1-ene (CTA8)



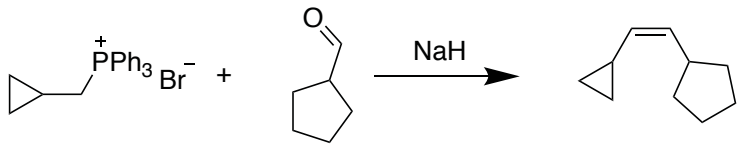
Colorless liquid. Yield: 69%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.75 (dq, *J* = 5.6, 2.3 Hz, 1H), 5.60 (dq, *J* = 5.6, 2.1 Hz, 1H), 5.26-5.42 (m, 2H), 3.20-3.27 (m, 1H), 2.17-2.43 (m, 2H), 2.04-2.13 (m, 1H), 1.47-1.56 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.22, 134.58, 130.88, 130.80, 48.43, 32.13, 30.93, 30.83, 22.65, 22.63. GC-MS:136.

(*E*)-3-(2-cyclopropylvinyl)cyclohex-1-ene (CTA9)



Colorless liquid. Yield: 74%. ^{1}H NMR (400 MHz, Chloroform-d) δ 5.68-5.73 (m, 1H), 5.45-5.56 (m, 2H), 4.96 (ddd, *J* = 15.3, 8.6, 1.2 Hz, 1H), 2.67-2.74 (m, 1H), 1.94-1.99 (m, 2H), 1.64-1.81 (m, 2H), 1.48-1.57 (m, 1H), 1.30-1.42 (m, 2H), 0.64-0.68 (m, 2H), 0.30-0.34 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 133.14, 132.10, 130.36, 127.32, 38.17, 29.53, 25.08, 20.61, 13.60, 6.50. GC-MS:148.

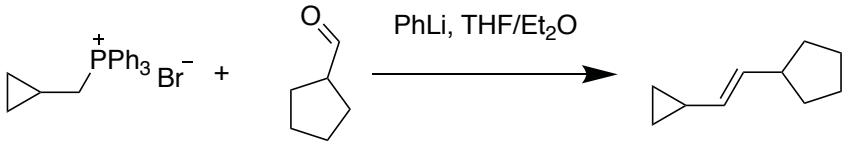
(*Z*)-(2-cyclopropylvinyl)cyclopentane (CTA10)



(Cyclopropylmethyl)triphenylphosphonium bromide (2.0 g, 5.0 mmol, 2.0 equiv) and NaH (0.20 g, 5.0 mmol, 2.0 equiv, 60% in oil) were added to a Schlenk flask, which was protected with Ar gas and cooled to 0 ^{o}C. Then, THF (10 mL) was added to the flask. The reaction was stirred at 0°C for 30 min. Cyclopentanecarboxaldehyde (0.25 g, 2.5 mmol, 1.0 equiv) dissolved in THF (10 mL) was added to the system. The reaction mixture was allowed to stir at room temperature for 24 hours. Solids were removed from the mixture by filtration and most of the solvent was evaporated under reduced pressure. Then, EtOAc (50 mL) and water (50 mL) were added to the mixture. The aqueous phase was extracted with EtOAc (30 mL x 2). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (100% pentane) to afford **CTA10** as a colorless liquid (0.25g, Yield: 73.4%, *Z:E*=80:20).

^{1}H NMR (400 MHz, Chloroform-d) δ 5.49 (dd, *J* = 15.2, 7.7 Hz, 0.25H), 5.24 (t, *J* = 9.9 Hz, 1H), 4.94 (ddd, *J* = 15.3, 8.6, 1.0 Hz, 0.25H), 4.57- 4.71 (m, 1H), 2.80-2.90 (m, 1H), 2.31-2.41 (m, 0.25H), 1.81-1.89 (m, 2H), 1.51- 1.75 (m, 7H), 1.20 -1.36 (m, 3H), 0.62-0.73 (m, 2.5H), 0.25-0.36 (m, 2.5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.76, 132.97, 132.50, 131.83, 43.31, 38.68, 33.91, 33.32, 25.37, 25.1, 13.52, 9.77, 6.89, 6.44. GC-MS:136.

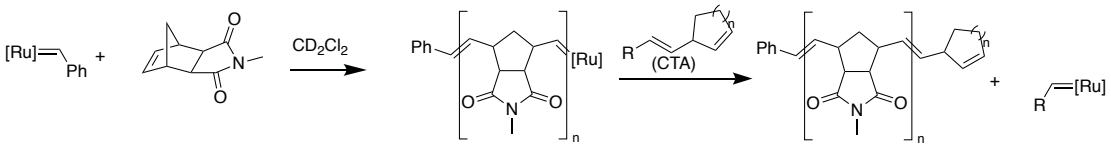
(*E*)-(2-cyclopropylvinyl)cyclopentane (CTA11)



(Cyclopropylmethyl)triphenylphosphonium bromide (2.0 g, 5.0 mmol, 1.0 equiv) was suspended in dry tetrahydrofuran (8 ml) and dry diethylether (5 ml) and stirred with phenyl-lithium (5 mmole of etheral solution) for 20 min. The solution was cooled to -70 °C and cyclopentanecarboxaldehyde (0.49 g, 5 mmol, 1.0 equiv) (dissolved in 4 ml of ether) was added. The mixture was stirred vigorously. As soon as the decoloration was complete (10 min at -70 °C to -40 °C), a further 5 mmole of phenyllithium solution is added and the mixture kept at -30 °C for 10 min. This solution is treated with hydrogen chloride in methanol (6 mmole) and with potassium *t*-butoxide (7.5 mmole) (as 1:1 mixture with *t*-butyl alcohol). The mixture is stirred at room temperature for 2 h, centrifuged, and the clear supernatant liquor is decanted, washed with water until neutral, and dried. After evaporation of the solvent, the residue was purified by column chromatography (100% pentane) to afford **CTA11** as a colorless liquid (0.43g, Yield: 63.2%, *Z*:*E*=15:85).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.49 (dd, *J* = 15.2, 7.7 Hz, 1H), 5.24 (t, *J* = 9.9 Hz, 0.18H), 4.94 (ddd, *J* = 15.2, 8.6, 0.9 Hz, 1H), 4.64-4.69 (m, 0.18H), 2.80-2.91 (m, 0.17H), 2.31-2.41 (m, 1H), 1.47-1.89 (m, 8.5H), 1.18-1.37 (m, 3.6H), 0.59-0.73 (m, 2.5H), 0.29-0.36 (m, 2.5H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.77, 132.97, 132.50, 131.83, 43.30, 38.67, 33.91, 33.32, 25.37, 25.11,13.52, 9.77, 6.89, 6.44. GC-MS:136

Kinetic NMR Reactions



Grubbs 3rd generation catalyst (**G3**, 4.45mg) and 1,3,5-trimethoxybenzene (3mg) were dissolved in degassed CD_2Cl_2 (0.45ml) in an argon filled glove box. Then **MNI** (30mg) was added. After 5min the ^{1}H NMR spectrum was recorded. Then, **CTA X** (10eq) dissolved in degassed CD_2Cl_2 (0.3ml) was added. After 8min the ^{1}H NMR spectrum was recorded. ^{1}H-NMR spectra were recorded at various intervals over time (see below). The peak of the internal standard (1,3,5-trimethoxybenzene) with a chemical shift of 6.06ppm was used as an integration reference (set to 100 for **CTA1-4** and 1000 for **CTA5-11**).

Table S1 ^{1}H NMR spectroscopic data for reaction with CTA1

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (19.06ppm, s)	Yield %	Conversion%
1	0	7.12	0	0	0
2	8	4.87	0.14	2.0	29.5
3	15	4.74	0.25	3.5	34.4
4	30	4.02	0.58	8.1	43.6
5	60	3.95	0.73	10.3	47.4
6	120	3.40	1.10	15.4	56.2
7	180	2.63	1.42	19.9	59.8
8	240	2.52	1.65	23.2	64.2
9	300	1.96	1.74	24.4	73.1
10	360	1.84	2.08	29.2	74.5
11	480	1.82	2.37	33.3	77.7
12	600	1.53	2.57	36.1	81.8
13	720	1.36	2.72	38.2	83.9

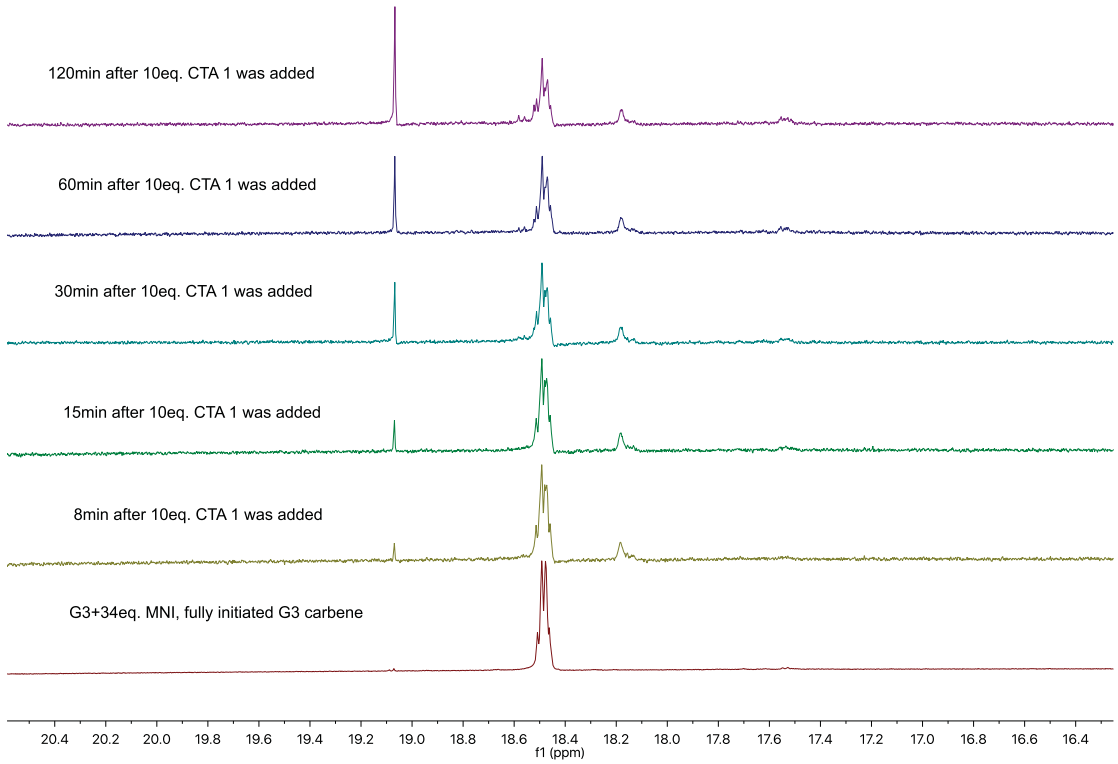


Figure S1 ^{1}H NMR spectroscopic data for reaction with CTA1

Table S2 ^{1}H NMR spectroscopic data for reaction with CTA2

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.97ppm, d)	Yield %	Conversion%
1	0	1.53	0	0	0
2	8	1.43	0.04	2.6	10.1
3	15	1.32	0.07	4.6	13.0
4	30	1.24	0.07	4.6	17.2
5	60	1.13	0.11	7.2	17.9
6	120	0.92	0.17	11.1	24.4
7	180	0.79	0.20	13.1	37.9
8	240	0.73	0.25	16.3	47.8
9	300	0.59	0.21	13.7	52.2
10	360	0.40	0.18	11.8	60.5
11	480	0.28	0.14	9.2	73.6
12	600	0.19	0.09	5.9	81.9
13	720	0	0	0	89.0

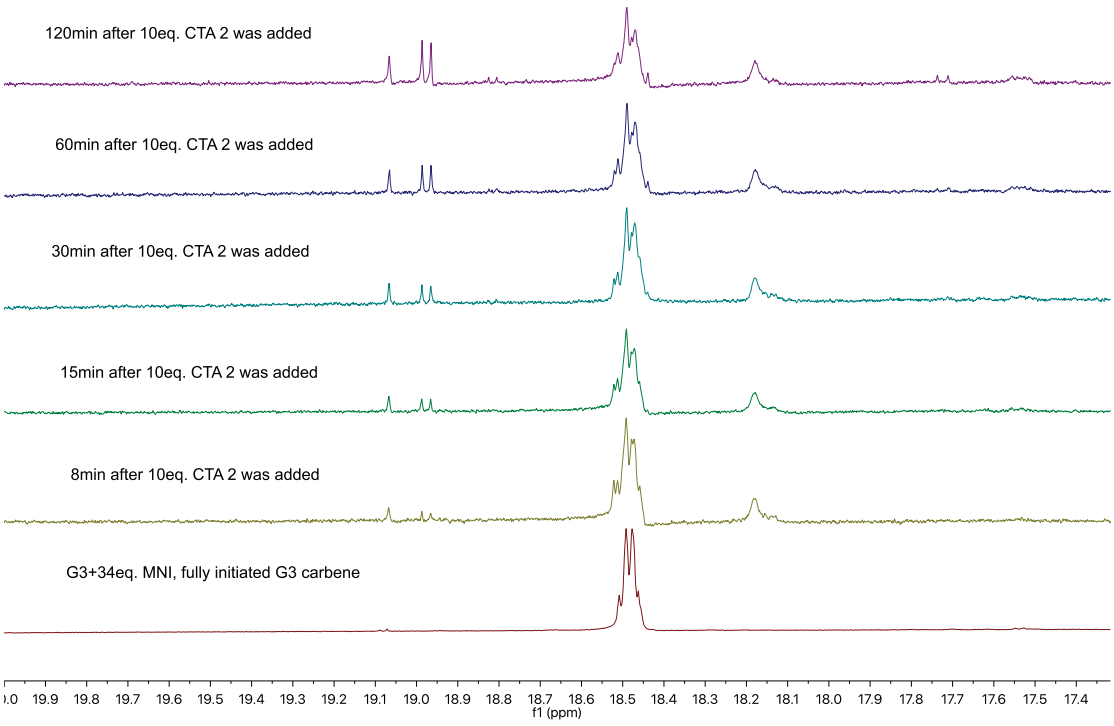


Figure S2 ^{1}H NMR spectroscopic data for reaction with CTA2

Table S3 ^{1}H NMR spectroscopic data for reaction with CTA3

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.58ppm, d)	Yield %	Conversion%
1	0	10.92	0	0	0
2	8	10.27	1.24	11.4	13.9
3	15	10.09	1.79	16.4	17.0
4	30	9.26	1.95	17.9	27.4
5	60	7.78	2.28	20.9	35.5
6	120	6.53	2.32	21.2	43.9
7	180	5.35	2.45	22.4	53.4
8	240	4.14	2.73	25.0	64.8
9	300	2.51	2.86	26.2	76.6
10	360	2.20	2.80	25.6	80.4
11	480	2.03	2.28	20.9	82.5
12	600	0.93	1.43	13.1	91.5
13	720	0.67	0.92	8.4	94.3

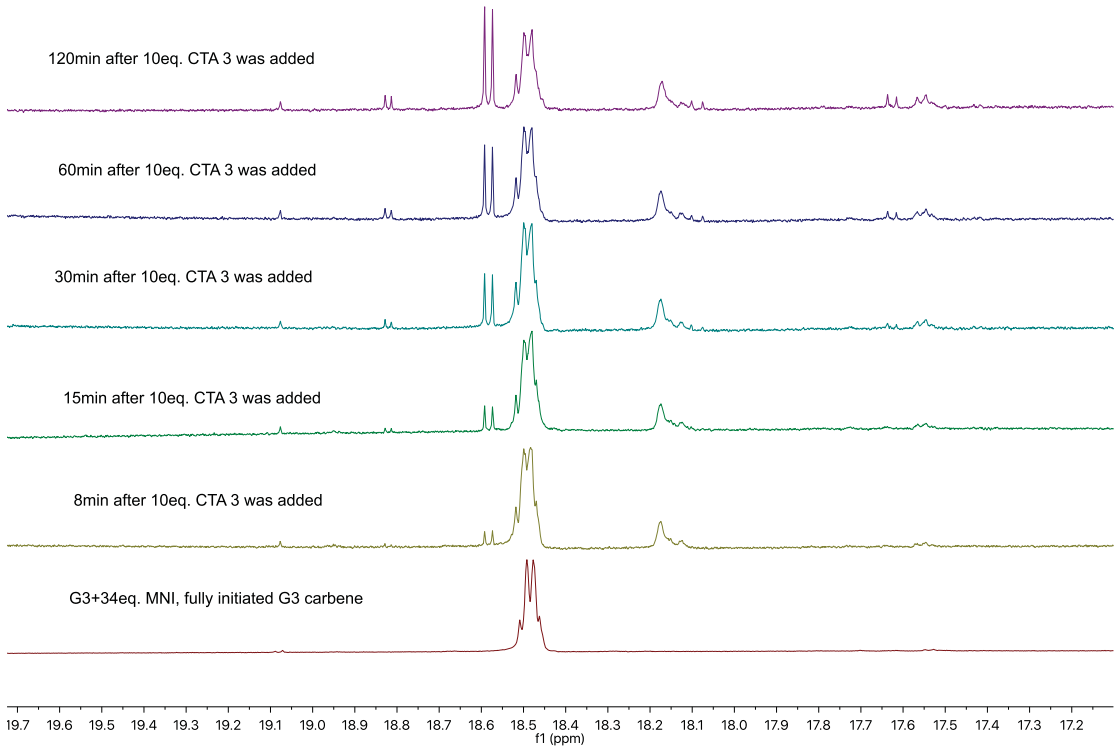


Figure S3 ^{1}H NMR spectroscopic data for reaction with CTA3

Table S4 ^{1}H NMR spectroscopic data for reaction with CTA4

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (19.06ppm, s)	Yield %	Conversion%
1	0	23.93	0	0	0
2	8	0	17.35	72.5	100
3	15	0	15.97	66.7	100
4	30	0	15.33	64.1	100
5	60	0	14.26	59.6	100
6	120	0	12.31	51.4	100
7	180	0	11.39	47.6	100
8	240	0	10.69	44.7	100
9	300	0	10.02	41.9	100
10	360	0	9.37	39.2	100
11	480	0	7.20	30.1	100
12	600	0	5.79	24.2	100
13	720	0	4.04	16.9	100

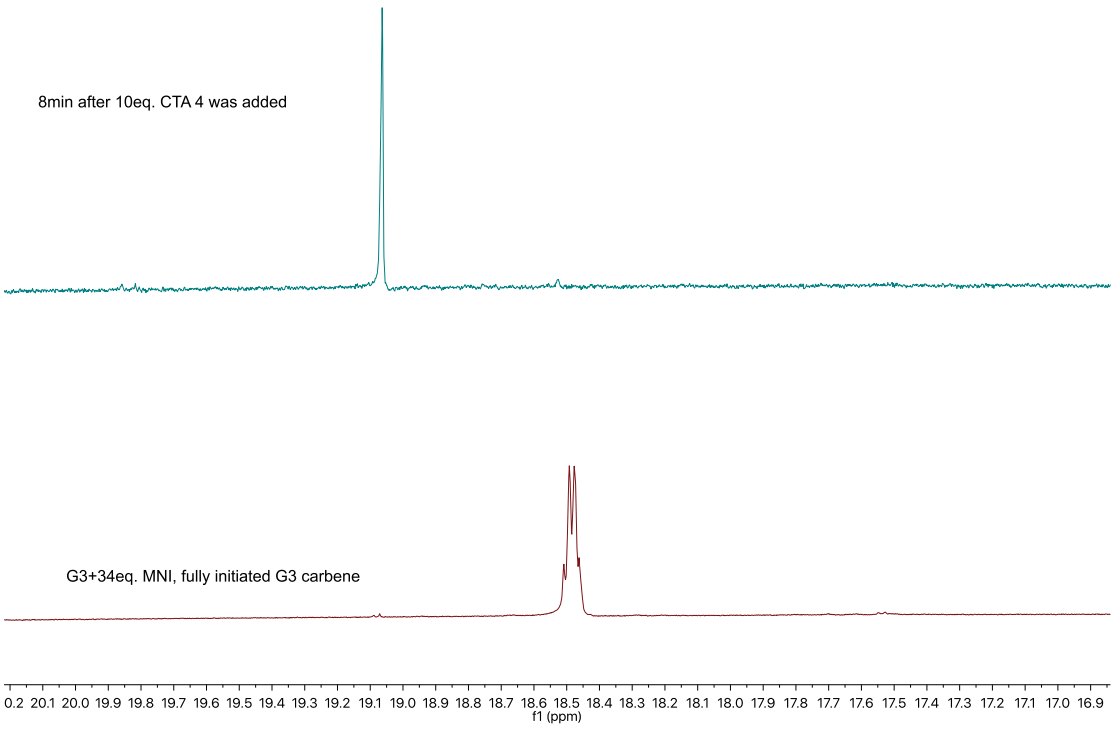


Figure S4 ^{1}H NMR spectroscopic data for reaction with CTA4

Table S5 ^{1}H NMR spectroscopic data for reaction with CTA5

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.97ppm, d)	Yield %	Conversion%
1	0	84.89	0	0	0
2	8	0	67.21	79.2	100
3	15	0	64.73	76.3	100
4	30	0	51.84	61.1	100
5	60	0	41.16	48.5	100
6	120	0	23.21	27.3	100
7	180	0	16.53	19.5	100
8	240	0	10.26	12.1	100
9	300	0	3.09	3.6	100
10	360	0	0	0	100
11	480	0	0	0	100
12	600	0	0	0	100
13	720	0	0	0	100

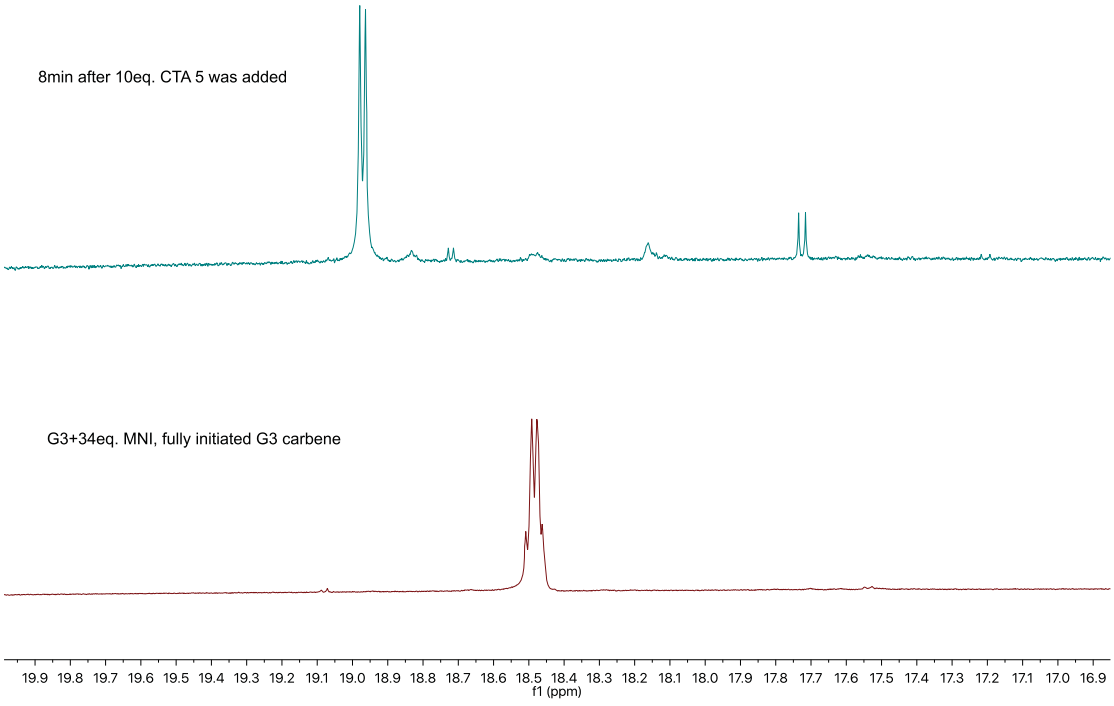


Figure S5 ^{1}H NMR spectroscopic data for reaction with CTA5

Table S6 ^{1}H NMR spectroscopic data for reaction with CTA6

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.58ppm, d)	Yield %	Conversion%
1	0	40.47	0	0	0
2	8	0	37.50	92.7	100
3	15	0	30.62	75.7	100
4	30	0	27.45	67.8	100
5	60	0	25.01	61.8	100
6	120	0	15.29	37.8	100
7	180	0	8.29	20.5	100
8	240	0	4.70	11.6	100
9	300	0	2.60	6.4	100
10	360	0	1.51	3.7	100
11	480	0	0	0	100
12	600	0	0	0	100
13	720	0	0	0	100

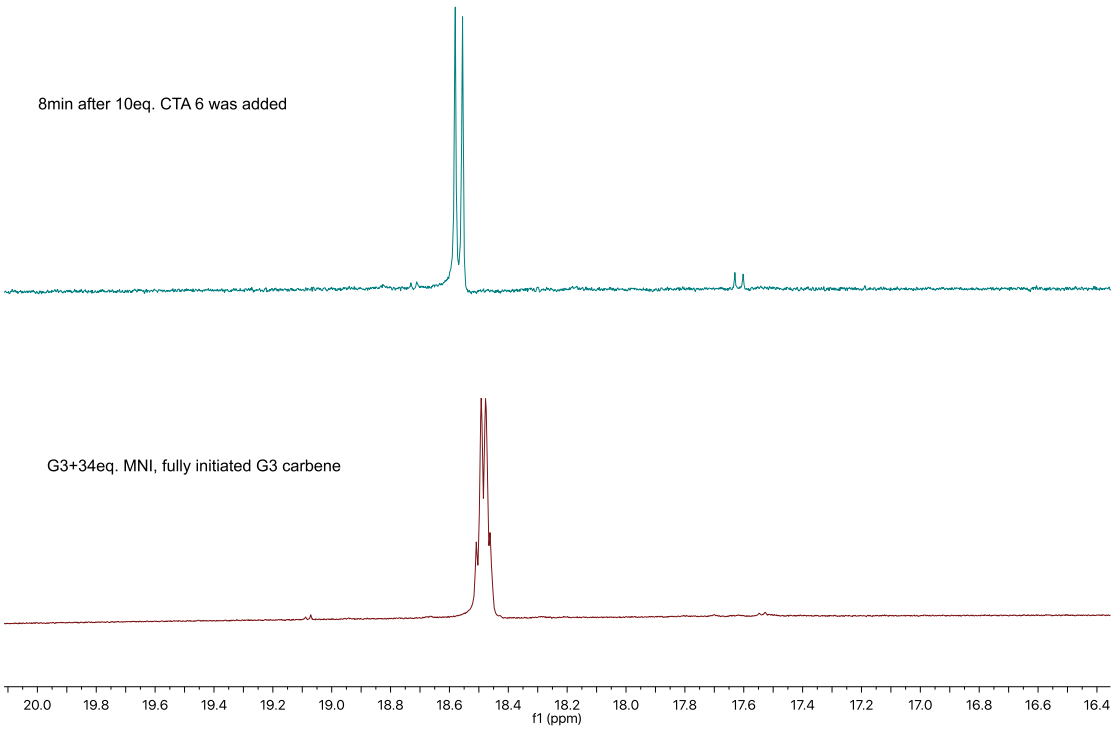


Figure S6 ^{1}H NMR spectroscopic data for reaction with CTA6

Table S7 ^{1}H NMR spectroscopic data for reaction with CTA7

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (17.20ppm, d)	Yield %	Conversion%
1	0	22.37	0	0	0
2	8	0	22.35	100	100
3	15	0	22.25	99.5	100
4	30	0	22.13	98.9	100
5	60	0	22.05	98.6	100
6	120	0	21.75	97.2	100
7	180	0	20.61	92.1	100
8	240	0	19.99	89.4	100
9	300	0	19.87	88.8	100
10	360	0	19.13	85.5	100
11	480	0	18.27	81.7	100
12	600	0	17.94	80.2	100
13	720	0	16.87	75.4	100

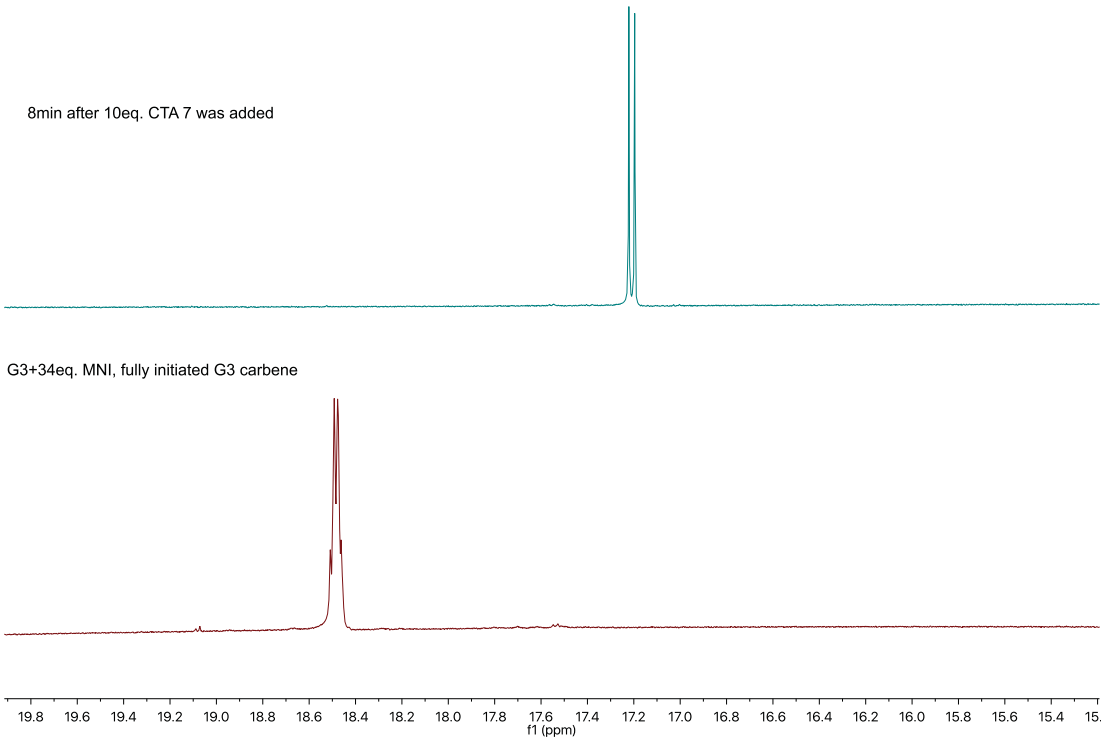


Figure S7 ^{1}H NMR spectroscopic data for reaction with CTA7

Table S8 ^{1}H NMR spectroscopic data for reaction with CTA8

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.66ppm, d)	Yield %	Conversion%
1	0	29.18	0	0	0
2	8	1.73	23.27	79.7	100
3	15	1.18	18.53	63.5	100
4	30	0	16.53	56.6	100
5	60	0	14.28	48.9	100
6	120	0	8.37	28.7	100
7	180	0	4.56	15.6	100
8	240	0	2.03	7.0	100
9	300	0	0	0	100
10	360	0	0	0	100
11	480	0	0	0	100
12	600	0	0	0	100
13	720	0	0	0	100

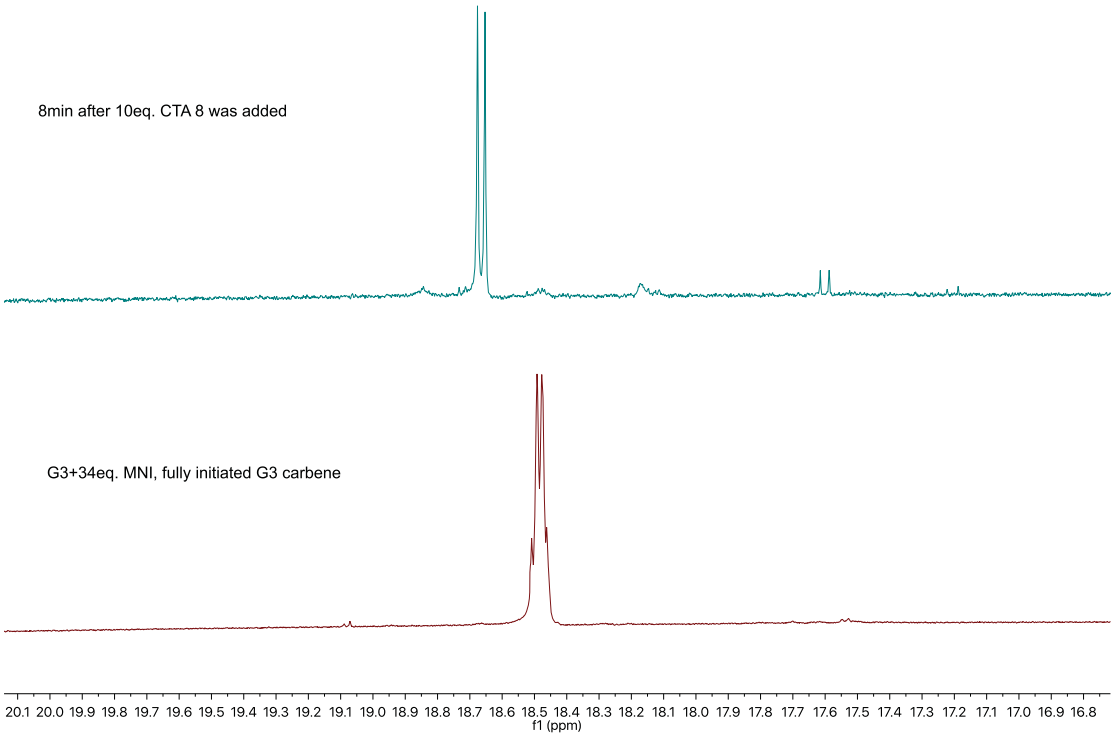


Figure S8 ^{1}H NMR spectroscopic data for reaction with CTA8

Table S9 Stability of propagating G3 (MNI) carbene without any CTA

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Yield / Conversion%
1	0	88.81	100
2	8	82.81	93.2
3	15	79.43	89.4
4	30	77.41	87.2
5	60	73.15	82.4
6	120	66.63	75.0
7	180	65.64	73.9
8	240	61.84	69.6
9	300	58.71	66.1
10	360	56.03	63.1
11	480	52.68	59.3
12	600	48.57	54.7
13	720	43.47	48.9

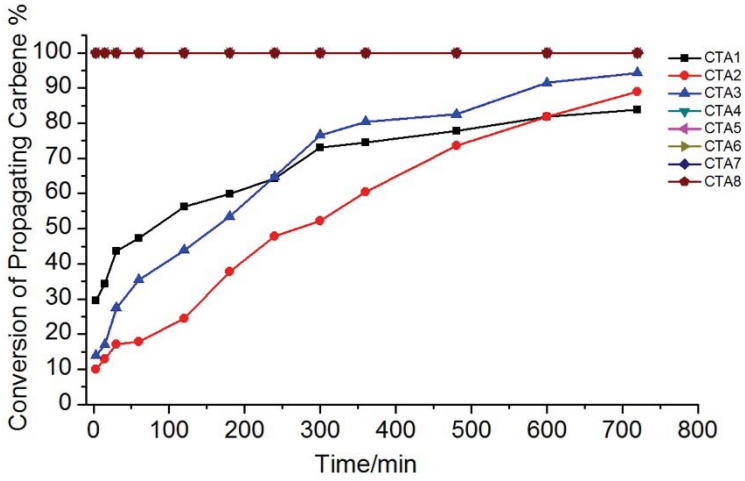


Figure S9 Conversion of reactions of propagating G3(MNI) with different CTAs (CTA4-8 were overlapped)

Table S10 ^{1}H NMR spectroscopic data for reaction with CTA9

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (17.20ppm, d)	Yield %	Conversion%
1	0	151.92	0	0	0
2	8	79.12	8.05	5.36	47.92
3	16	65.69	11.17	7.35	56.76
4	24	56.37	17.57	11.56	62.89
5	32	47.03	20.40	13.43	68.78
6	40	46.43	29.83	19.64	69.44
7	60	34.14	40.43	26.61	77.53
8	120	14.29	47.84	31.49	90.59
9	180	0	48.14	31.69	100

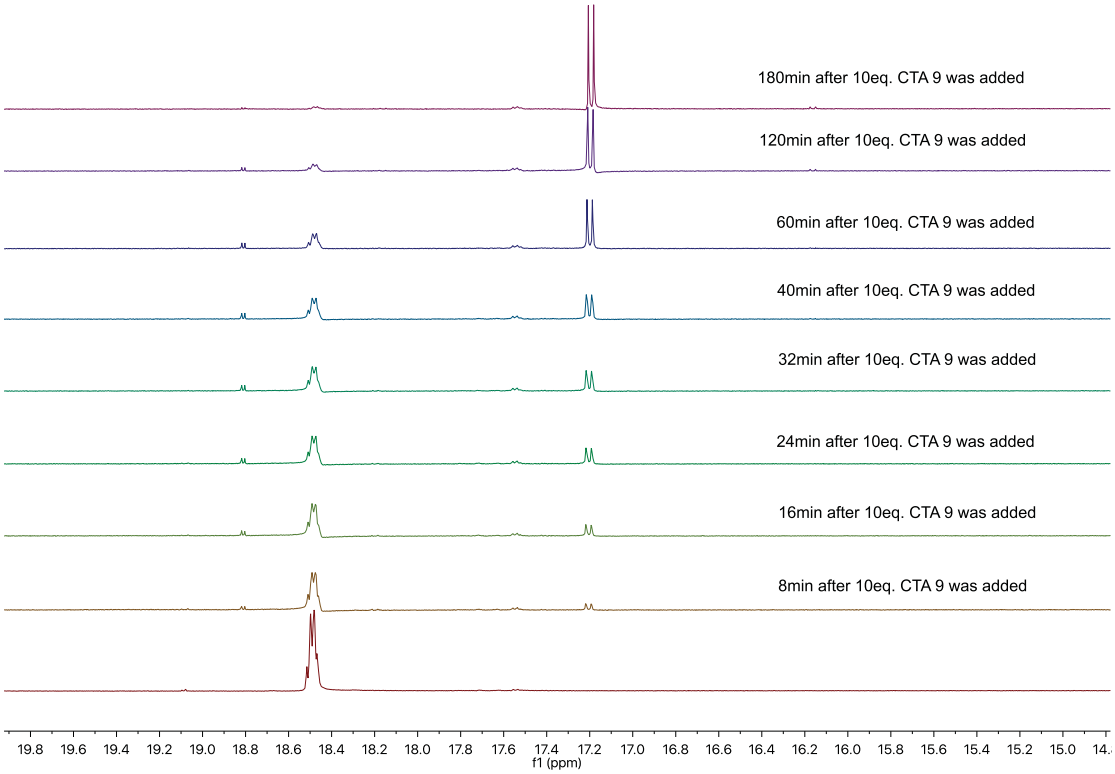


Figure S10 ^{1}H NMR spectroscopic data for reaction with CTA9

Table S11 ^{1}H NMR spectroscopic data for reaction with CTA10

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (17.20ppm, d)	Yield %	Conversion%
1	0	62.59	0	0	0
2	8	27.10	32.14	51.35	56.70
3	16	12.60	47.76	76.31	79.87
4	24	6.69	53.76	85.89	89.31
5	32	3.78	58.64	93.69	93.96
6	40	0	59.55	95.14	100

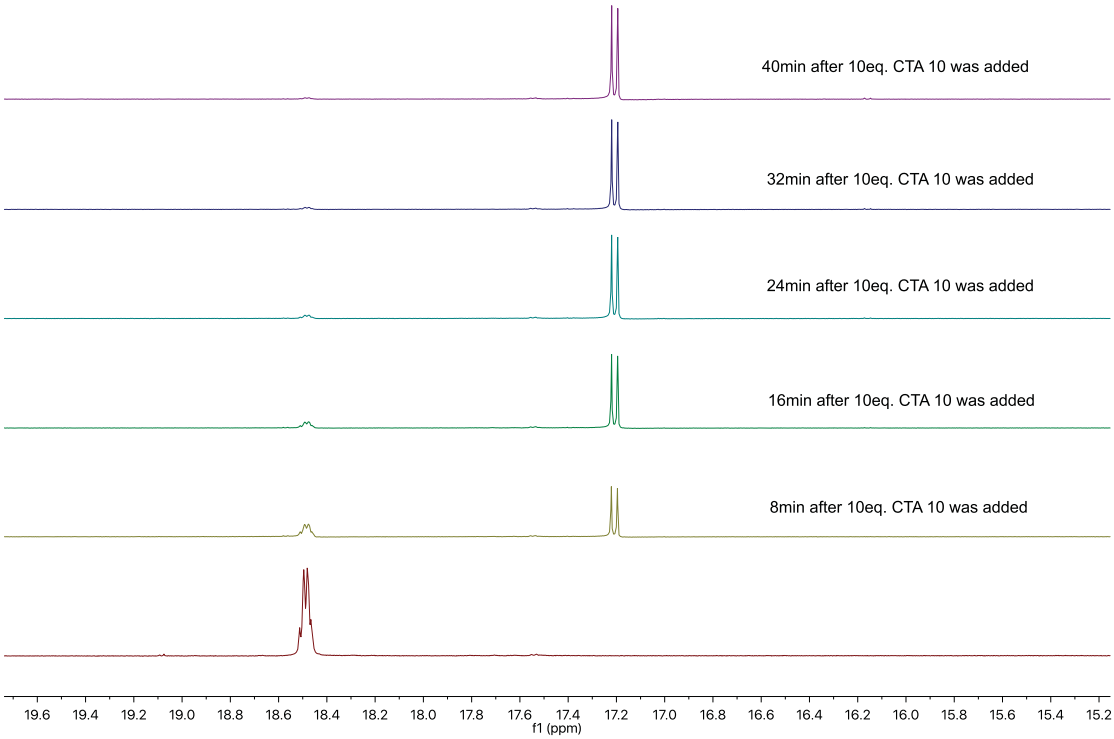


Figure S11 ^{1}H NMR spectroscopic data for reaction with CTA10

Table S12 ^{1}H NMR spectroscopic data for reaction with CTA11

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (17.20ppm, d)	Yield %	Conversion%
1	0	131.91	0	0	0
2	8	93.64	36.67	27.80	29.01
3	16	68.50	53.83	40.81	48.07
4	24	47.92	67.70	51.32	63.67
5	32	37.61	82.64	62.65	71.49
6	60	18.90	101.71	77.10	85.67

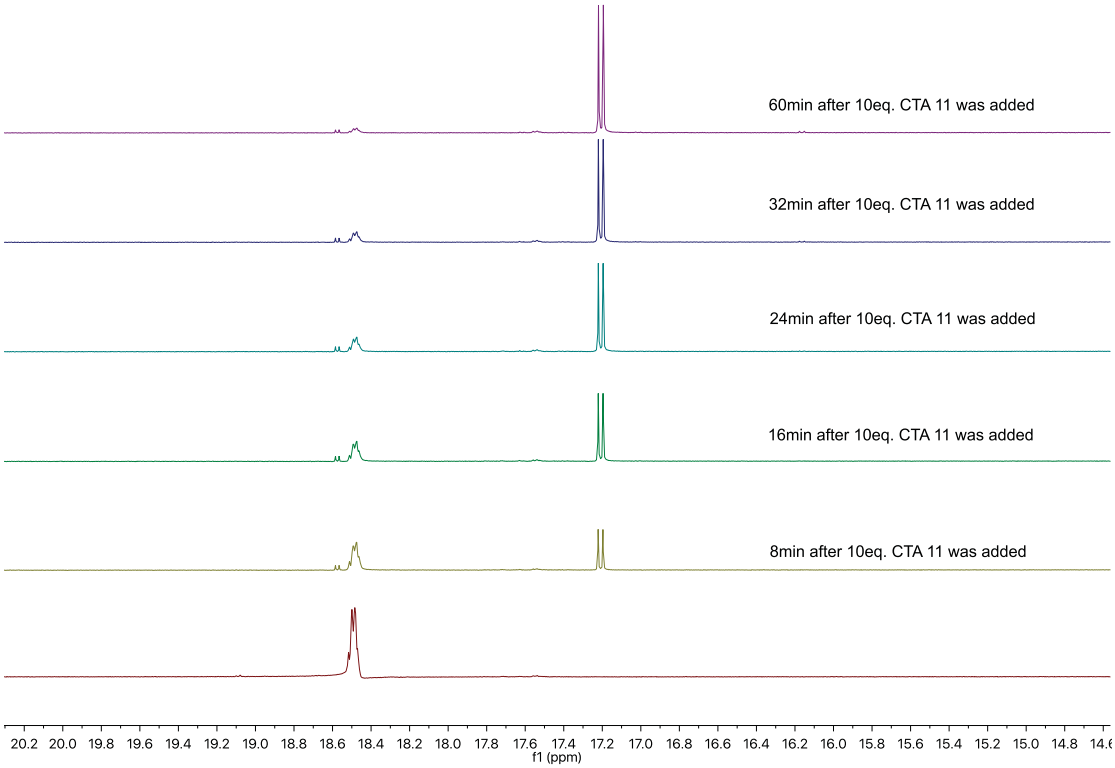
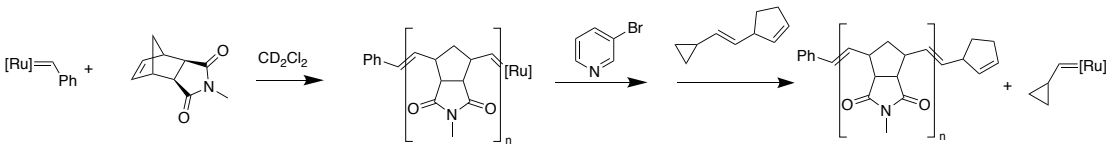


Figure S12 ^{1}H NMR spectroscopic data for reaction with CTA11

Determination of Reaction Rate Constants



8.84mg (0.01mmol, 1.0eq.) Grubbs third generation of catalyst (**G3**) and 3mg 1,3,5-trimethoxybenzene were dissolved in 1.0ml degassed CD_2Cl_2 under Ar. 50mg MNI was dissolved in 1ml degassed CD_2Cl_2 under Ar. The solution of MNI was added into the solution of **G3**. After 10min 16mg (0.1mmol, 10eq.) 3-bromopyridine which was dissolved in 0.5ml degassed CD_2Cl_2 was added to the solution. Then 1.6mg CTA7 (0.012mmol, 1.2 eq.) was dissolved in 2.5ml degassed CD_2Cl_2. Take 0.3ml **G3** solution to record ^{1}H NMR. Then 0.3ml CTA solution was added into the NMR tube under Ar. Follow this NMR reaction by time. Set the internal standard peak which shift was at 6.06ppm, integration as 1000. Then check the propagating carbene and catalyst carbene integration.

Table S13 ^{1}H NMR Kinetic reactions of CTA7 with 3-bromopyridine

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.66ppm, d)	Yield %	Conversion%
1	0	52.23	0	0	0
2	5	21.86	18.09	34.64	58.15
3	7	20.23	22.20	42.50	61.27
4	9	18.64	26.33	50.41	64.31
5	11	13.94	28.56	54.68	73.31
6	13	10.94	29.18	55.87	79.05
7	15	9.29	30.96	59.28	82.21

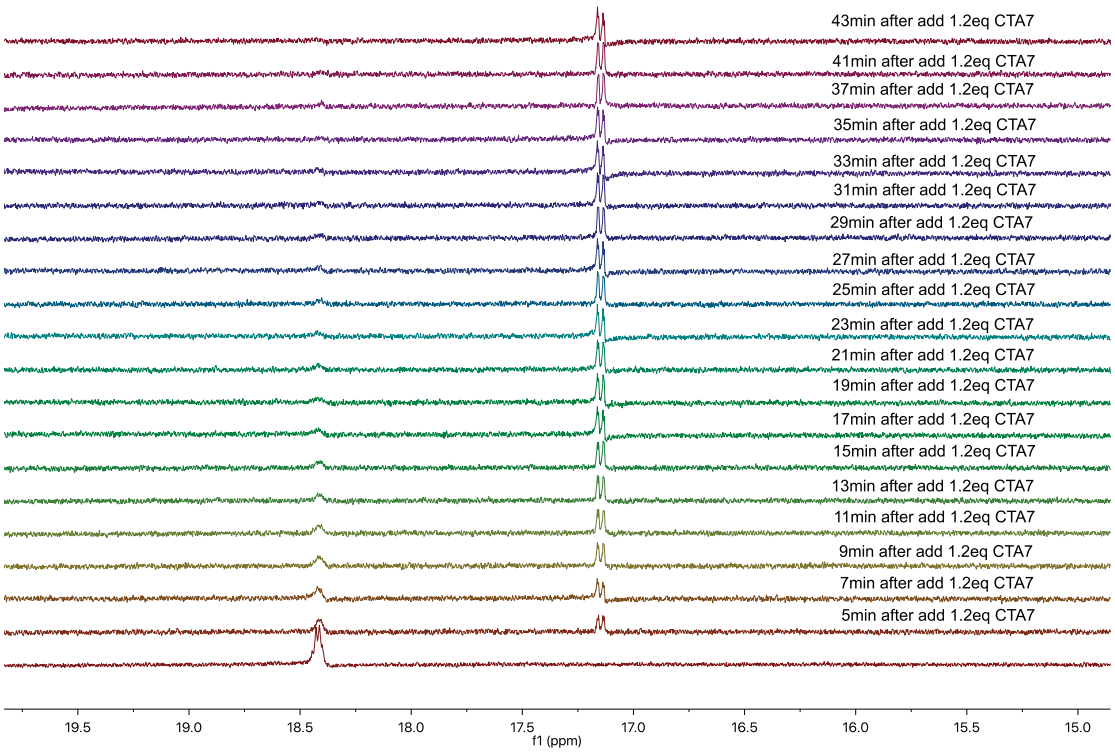
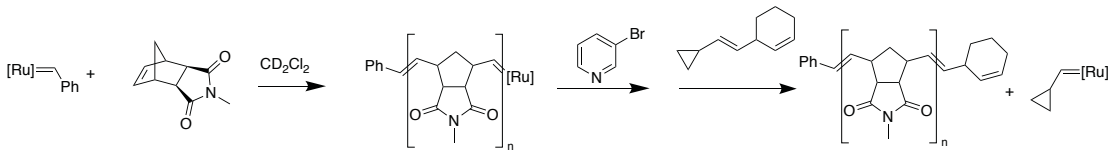


Figure S13 ^{1}H NMR Kinetic reactions of CTA7 with 3-bromopyridine



8.84mg (0.01mmol, 1.0eq.) Grubbs third generation of catalyst (**G3**) and 3mg 1,3,5-trimethoxybenzene were dissolved in 1.0ml degassed CD_2Cl_2 under Ar. 50mg MNI was dissolved in 1ml degassed CD_2Cl_2 under Ar. The solution of MNI was added into the solution of **G3**. After 10min 16mg (0.1mmol, 10eq.) 3-bromopyridine which was dissolved in 0.5ml degassed CD_2Cl_2 was added to the solution. Then 30mg CTA9 (0.2mmol, 20 eq.) was dissolved in 2.5ml degassed CD_2Cl_2. Take 0.3ml **G3** solution to record ^{1}H NMR. Then 0.3ml CTA solution was added into the NMR tube under Ar. Follow this NMR reaction by time. Set the internal standard peak which shift was at 6.06ppm, integration as 1000. Then check the propagating carbene and catalyst carbene integration.

Table S14 ^{1}H NMR Kinetic reactions of CTA9 with 3-bromopyridin

Entry	Time/min	Propagating Carbene (18.46-18.51ppm, m)	Catalyst Carbene (18.66ppm, d)	Yield %	Conversion%
1	0	68.76	0	0	0
2	9	44.16	0	0	35.78
3	31	35.96	0	0	47.70
4	60	34.46	9.39	13.66	49.88
5	120	24.45	9.70	14.11	64.44
6	180	14.33	10.42	15.15	79.16
7	240	9.35	10.52	15.30	86.40

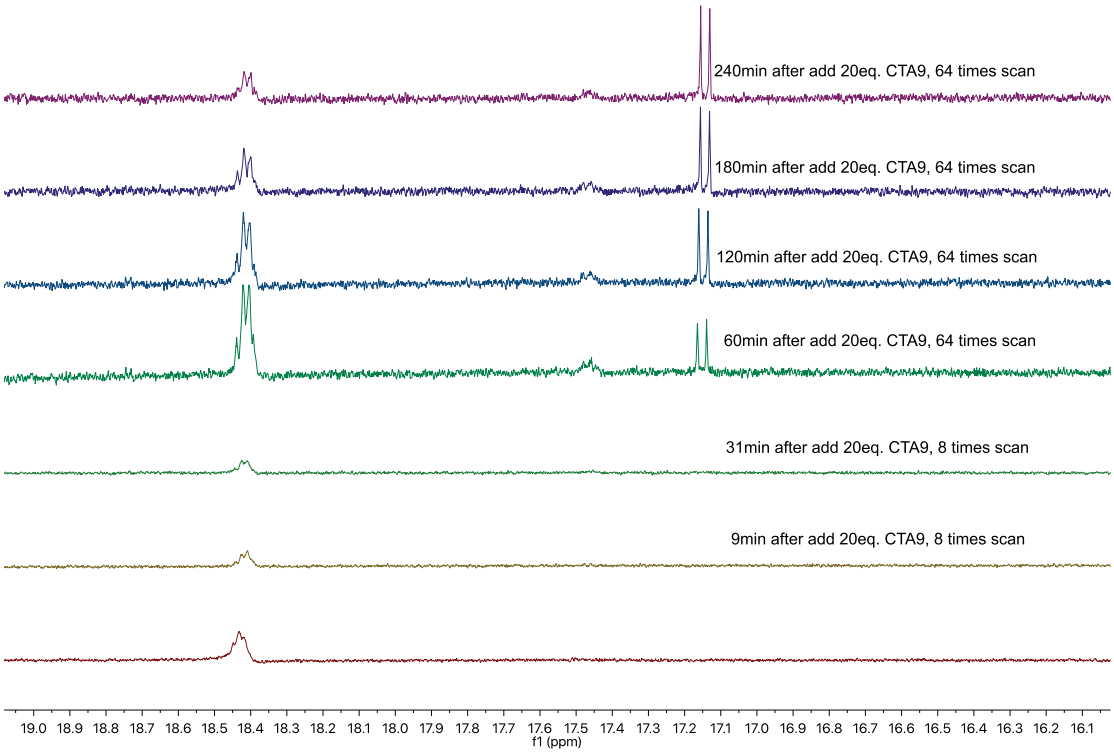


Figure S14 ^{1}H NMR Kinetic reactions of CTA9 with 3-bromopyridine

$$A = \frac{1}{[CTA]_0 - [Ru]_0} \ln \frac{[Ru]_0([CTA]_0 - x)}{([Ru]_0 - x)[CTA]_0}$$

The above equation was used for the rate constant determination of a reaction that follows a second-order rate law as adapted from Atkins and others[4]. $[Ru]_0$ corresponds to the initial concentration of propagating carbene, $[CTA]_0$ refers to the initial concentration of CTA, x represents the decrease in the concentration of propagating carbene at a given time and A is equal to t-k, whereby t stands for time and k is the

second-order rate constant.

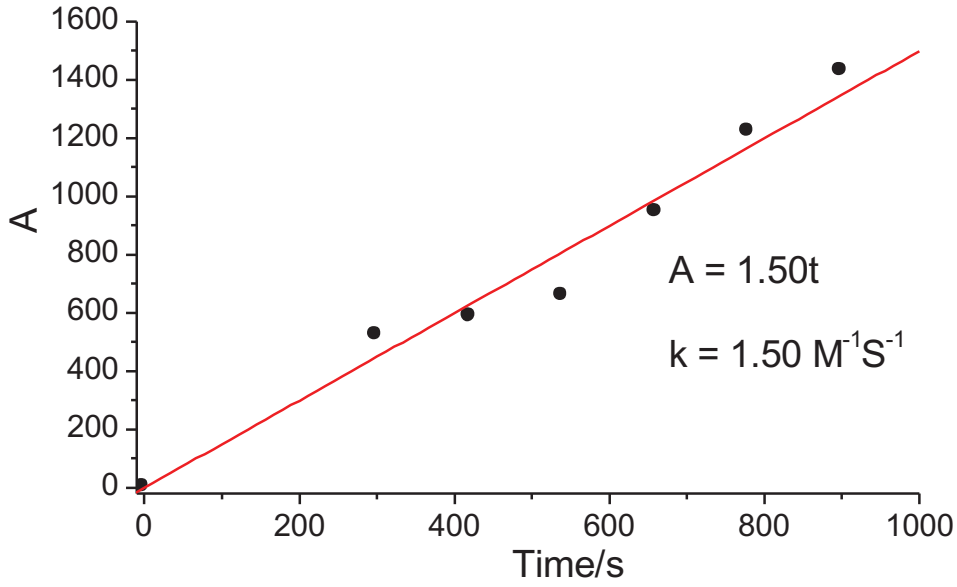


Figure S15 reaction rate constants of CTA7 with 10eq. 3-bromopyridine

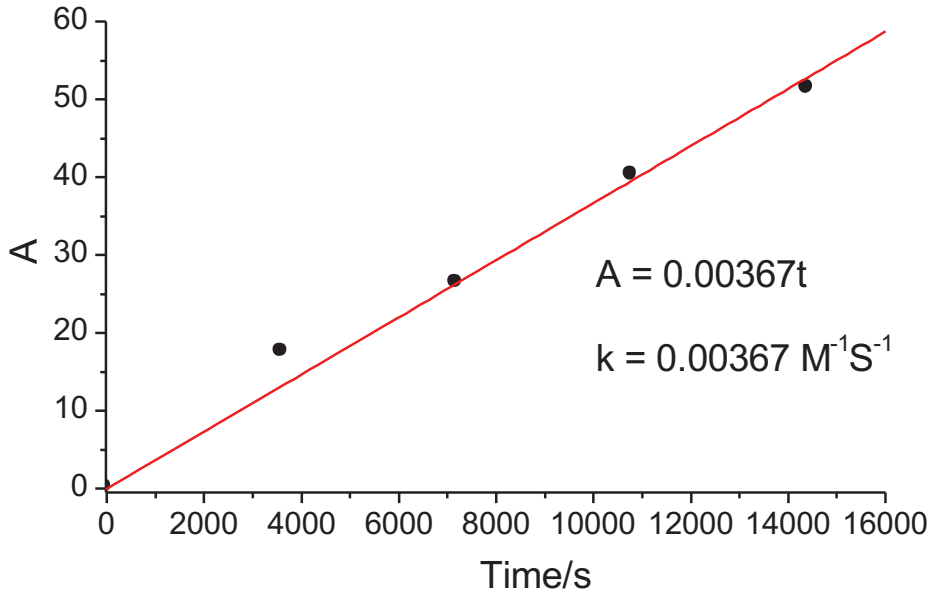


Figure S16 reaction rate constants of CTA9 with 10eq. 3-bromopyridine

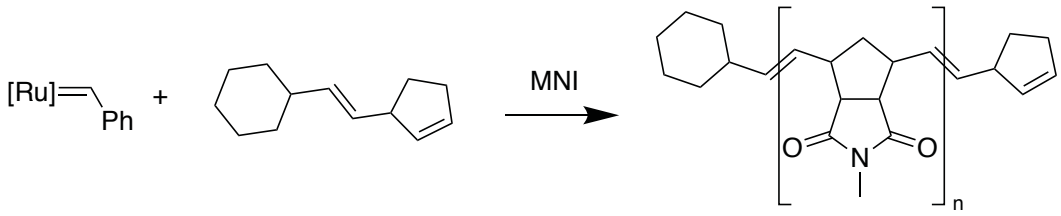
Kinetic GPC Reactions

G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA7** (7mg, 0.05mmol, 10eq.) which was dissolved in degassed DCM (0.5ml). **MNI** (266mg, 1.5mmol, 300eq) or **PNI** (360mg, 1.5mmol, 300eq) dissolved in degassed DCM (20ml) was added slowly to this solution by syringe pump (5ml/h). 0.2ml of the reaction solution was taken out and check the chloroform GPC every 30min.

Table S15 GPC Kinetic reactions of CTA7 with MNI and PNI

Time	MNI		PNI	
	Mn	**Đ**	**Mn**	**Đ**
0.5h	5700	1.25	7200	1.39
1h	1100	1.28	1800	1.36
1.5h	1800	1.33	2300	1.36
2h	2500	1.35	3500	1.35

Polymerisations



G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA5** which was dissolved in degassed DCM (0.5ml). **MNI** (266mg, 1.5mmol, 300eq) dissolved in degassed DCM was added slowly to this solution by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give the polymer.

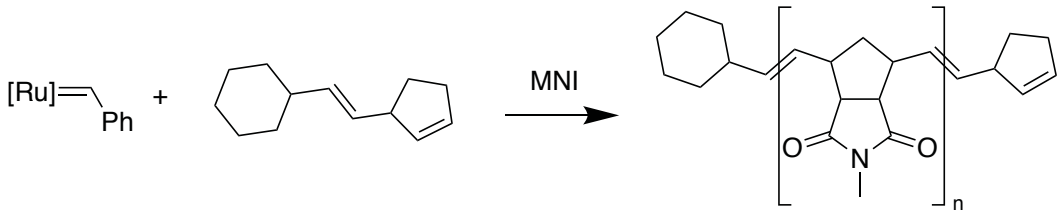
Table S16 Reaction Condition Optimization

Entry	Eq. CTA	Eq. MNI	Conc. of MNI	Mn Ther.	Mn Exp.	Đ	Speed	Yield%	Addition style
1	10	300	1.00mmol/ml	5310	23000	1.31	1.0ml/h	93	Dropwise
2	10	300	0.50mmol/ml	5310	16000	1.24	1.0ml/h	86	Dropwise
3	10	300	0.50mmol/ml	5310	18000	1.50	0.5ml/h	83	Dropwise
4	10	300	0.25mmol/ml	5310	14000	1.20	1.0ml/h	97	Dropwise
5	10	300	0.25mmol/ml	5310	15000	1.20	1.0ml/h	90	Continuous
6	10	300	0.10mmol/ml	5310	8500	1.17	2.0ml/h	95	Dropwise
7	10	300	0.10mmol/ml	5310	8500	1.15	3.0ml/h	93	Dropwise
8	10	300	0.10mmol/ml	5310	8200	1.18	5.0ml/h	93	Dropwise
9	10	300	0.10mmol/ml	5310	8300	1.17	10.0ml/h	94	Dropwise
10	10	300	0.10mmol/ml	5310	8100	1.24	20.0ml/h	94	Dropwise
11	10	300	0.075mmol/ml	5310	7900	1.20	10.0ml/h	99	Dropwise
12	10	300	0.075mmol/ml	5310	7100	1.18	5.0ml/h	98	Dropwise
13	10	300	0.05mmol/ml	5310	7800	1.17	20.0ml/h	95	Dropwise
14	20	300	0.05mmol/ml	2655	4000	1.23	20.0ml/h	99	Dropwise
15	10	300	0.05mmol/ml	5310	7500	1.20	10.0ml/h	92	Dropwise
16	10	300	0.05mmol/ml	5310	8000	1.25	5.0ml/h	95	Dropwise

Polymer 1 (Table S16, Entry 12)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.67-5.79 (m), 5.44-5.56 (m), 2.66 -3.31(m), 1.91-2.32 (m), 1.44-1.72 (m).^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.34, 133.44, 132.67, 132.03, 131.86, 52.98, 52.63, 51.84, 51.11, 50.99, 46.18, 46.05, 45.80, 45.67, 45.61, 42.94, 42.76, 42.47, 42.14, 41.98, 41.46, 41.22, 40.86, 32.94, 32.07, 30.63, 29.67, 26.16, 26.01, 24.88, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{223}H_{251}N_{21}O_{42}Ag^{+}$ [M+Ag^{+}]: 4001.72; Found: 4001.71

Different Catalyst

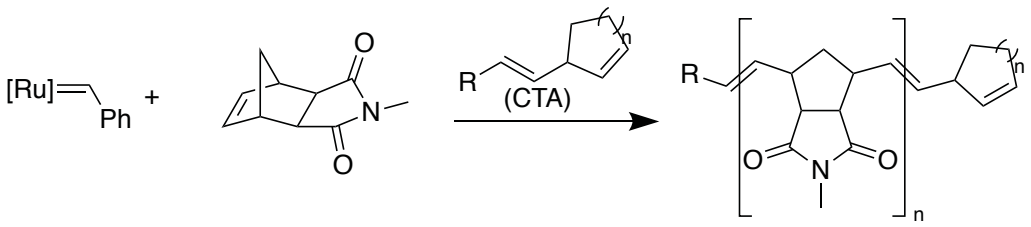


G2 (4.25mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA5** (9mg, 0.05mmol, 10eq) which was dissolved in degassed DCM (0.5ml). To this solution **MNI** (266mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml) was added at a speed of 5ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give the polymer (Yield: 98%, Mn_{GPC} ($CHCl_3$) = 7900 g mol^{-1}, Đ = 1.22).

Polymer 2

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.69-5.76 (m), 5.44-5.55 (m), 3.20-3.29 (m), 2.84-3.10 (m), 2.67-2.79 (m), 1.96-2.27 (m), 1.47-1.68 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.37, 133.43, 132.67, 132.02, 131.88, 131.70, 131.44, 52.97, 52.62, 51.83, 51.10, 50.98, 46.21, 46.06, 45.98, 45.81, 45.68, 45.62, 42.97, 42.77, 42.49, 42.16, 42.01, 41.45, 40.86, 32.94, 32.87, 32.09, 30.63, 26.16, 26.00, 24.88, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{203}H_{229}N_{19}O_{38}Ag^+$ [M+Ag^+]: 3647.56; Found: 3647.63

Different CTAs



G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA X** (0.05mmol, 10eq) which was dissolved in degassed DCM (0.5ml). To this solution **MNI** (266mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml) was added at a speed of 5ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give the polymer.

Table S17 Catalytic Living ROMP of Different CTAs

Entry	CTA	Eq. CTA	Eq. MNI	Conc. of MNI mmol/ml	Mn Ther.	Mn Exp.	Đ	Speed ml/h	Yield%
1	**CTA1**	10	300	0.075	5310	41000	1.29	5.0	99
2	**CTA2**	10	300	0.075	5310	38000	1.35	5.0	99
3	**CTA3**	10	300	0.075	5310	34000	1.25	5.0	99
4	**CTA4**	10	300	0.075	5310	9900	1.18	5.0	99
5	**CTA5**	10	300	0.075	5310	7100	1.18	5.0	98
6	**CTA6**	10	300	0.075	5310	7800	1.16	5.0	99
7	**CTA7**	10	300	0.075	5310	8900	1.17	5.0	99
8	**CTA8**	10	300	0.075	5310	9000	1.17	5.0	99

Polymer 3 (Table S17, Entry 1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23-7.35 (m), 6.12-6.36 (m), 5.62-5.83 (m), 5.43-5.55 (m), 2.65-3.27 (m), 1.97-2.25 (m), 1.45-1.68 (m), 1.18-1.29 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.33, 134.67, 133.81, 133.44, 132.91, 132.66, 132.02,

131.86, 131.70, 128.43, 126.85, 126.00, 52.97, 52.62, 51.82, 51.09, 50.98, 46.16, 46.04, 45.96, 45.79, 45.66, 45.60, 42.94, 42.47, 41.98, 41.44, 41.21, 40.85, 34.08, 29.65, 24.86, 24.82, 24.75, 22.30, 14.04. MALDI-ToF MS can not be detected due to the too high molecular weight.

Polymer 4 (Table S17, Entry 2)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.66-5.77 (m), 5.43-5.54 (m), 2.65-3.27 (m), 1.98-2.24 (m), 1.45-1.67 (m), 1.19-1.29 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.33, 133.82, 133.42, 132.65, 132.02, 131.86, 131.68, 52.96, 52.61, 51.82, 51.32, 51.09, 50.98, 46.16, 45.96, 45.78, 45.60, 42.93, 42.47, 41.98, 41.44, 41.20, 40.85, 34.08, 25.80, 24.86, 24.82, 24.78, 24.75, 22.30, 14.04. MALDI-ToF MS can not be detected due to the too high molecular weight.

Polymer 5 (Table S17, Entry 3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.66-5.78 (m), 5.43-5.52 (m), 2.65-3.27 (m), 2.01-2.26 (m), 1.43-1.68 (m), 1.19-1.29 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.33, 133.43, 132.66, 132.03, 131.86, 52.97, 52.62, 52.21, 51.83, 51.33, 51.09, 50.99, 45.96, 45.79, 45.60, 42.94, 42.46, 41.97, 41.45, 41.21, 40.85, 34.09, 29.66, 25.80, 24.86, 24.82, 24.75, 22.30, 14.04. MALDI-ToF MS can not be detected due to the too high molecular weight.

Polymer 6 (Table S17, Entry 4)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20-7.37 (m), 6.47-6.57 (m), 6.24-6.31 (m), 5.66-5.84 (m), 5.41-5.61 (m), 2.67-3.31 (m), 1.89-2.36 (m), 1.37-1.75 (m), 1.12-1.32 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.31, 133.45, 132.67, 132.03, 131.86, 131.68, 130.86, 128.53, 127.48, 126.28, 52.99, 52.64, 51.84, 51.10, 51.00, 48.22, 46.23, 45.96, 45.79, 45.65, 45.59, 43.11, 42.92, 42.75, 42.45, 41.95, 41.45, 41.22, 40.85, 34.10, 30.63, 29.66, 25.81, 24.82, 24.75, 22.31, 14.05. MALDI-ToF MS calcd. For $C_{203}H_{223}N_{19}O_{38}Ag^{+}$ [M+Ag^{+}]: 3647.52; Found: 3647.59

Polymer 7 (Table S17, Entry 6)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.66-5.78 (m), 5.43-5.56 (m), 2.60-3.28 (m), 1.99-2.29 (m), 1.41-1.71 (m), 1.14-1.32 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.31, 136.39, 133.43, 132.66, 132.03, 131.86, 131.68, 131.47, 52.97, 52.63, 51.83, 51.33, 50.99, 48.23, 46.16, 45.96, 45.79, 45.59, 42.92, 42.45, 41.94, 41.45, 41.21, 40.85, 34.09, 33.02, 32.06, 30.63, 25.11, 24.81, 24.75, 22.30, 14.04. MALDI-ToF MS calcd. For $C_{242}H_{271}N_{23}O_{46}Ag^{+}$ [M+Ag^{+}]: 4341.86; Found: 4341.81

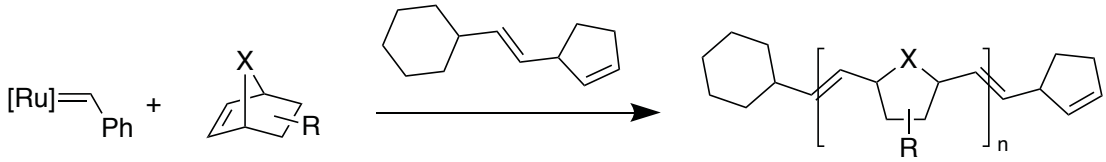
Polymer 8 (Table S17, Entry 7)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.66-5.76 (m), 5.40-5.61 (m), 2.59-3.27 (m), 1.98-2.26 (m), 1.46-1.64 (m), 1.20-1.27 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.32, 135.51, 133.43, 132.66, 132.03, 131.85, 131.68, 128.52, 128.06, 52.97, 52.62, 51.09, 50.99, 45.96, 45.78, 45.59, 42.93, 42.45, 41.95, 41.44, 41.21, 40.85, 34.08, 30.62, 25.80, 24.81, 24.75, 22.30, 14.04, 6.62. MALDI-ToF MS calcd. For $C_{210}H_{234}N_{20}O_{40}Ag^{+}$ [M+Ag^{+}]: 3782.59; Found: 3782.57

Polymer 9 (Table S17, Entry 8)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.65-5.80 (m), 5.42-5.56 (m), 2.58-3.26 (m), 1.94-2.31 (m), 1.44-1.66 (m).^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.32, 133.42, 132.65, 132.01, 131.85, 131.47, 128.52, 52.95, 52.60, 51.81, 51.31, 51.08, 50.98, 48.20, 46.15, 45.95, 45.77, 45.64, 45.58, 42.93, 42.46, 42.11, 41.96, 41.44, 41.20, 40.84, 34.07, 32.07, 30.62, 25.80, 24.81, 24.74, 22.29, 14.04. MALDI-ToF MS calcd. For $C_{220}H_{247}N_{21}O_{42}Ag^{+}$ [M+Ag^{+}]: 3961.68; Found: 3961.58

Different Monomers



G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 5** (9mg, 0.05mmol, 10eq) which was dissolved in degassed DCM (0.5ml). To this solution monomer (1.5mmol, 300eq) which was dissolved in degassed DCM (0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give the polymer.

Table S18 Catalytic Living ROMP of Different Monomers

Entry	Monomer	Eq. CTA	Eq. Monomer	Conc. of Monomer mmol/ml	Mn Ther.	Mn Exp.	Đ	Speed ml/h	Yield%
1	**MNI**	10	300	0.075	5310	7100	1.18	5.0	98
2	**HNI**	10	300	0.075	7410	9600	1.50	5.0	89
3[a]	**PNI**	10	300	0.3	7170	9000	1.24	1.2	95
4	**NBSM**	10	100	0.075	4670	4900	1.44	5.0	93
5	**ENC**	10	300	0.075	4980	6700	1.64	5.0	90
6	**MOMNI**	10	300	0.075	5790	4700	1.47	One pot	82
7	**EOMNI**	10	300	0.075	6217	5700	1.32	One pot	85

[a] **G3** (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 7** (7mg, 0.05mmol, 10eq) which was dissolved in degassed DCM (1.0ml). To this solution **PNI** (360mg, 1.5mmol, 300eq) which was dissolved in 5ml degassed DCM was added at a speed of 1.2ml/h by syringe pump (the top of the thin needle should be below the reaction solution surface). After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give the polymer.

Polymer 10 (Table S18, Entry 2)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.69-5.75 (m), 5.43-5.55 (m), 2.63-3.43 (m), 1.96-2.26 (m), 1.38-1.70 (m), 1.22-1.25 (m), 0.82-0.85 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.25, 133.57, 133.40, 132.66, 131.80, 52.95, 52.57, 51.76, 50.96, 50.73, 48.23, 46.24, 45.84, 42.22, 41.95, 41.32, 40.87, 38.88, 38.70, 38.53, 31.34, 31.26, 27.60, 26.52, 26.41, 22.48, 13.98. MALDI-ToF MS calcd. For $C_{163}H_{230}N_{10}O_{20}Ag^{+}$ [M+Ag^{+}]: 2754.63; Found: 2754.73

Polymer 11 (Table S18, Entry 3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21-7.47 (m), 5.51-5.79 (m), 2.87-3.49 (m), 2.16-2.37 (m), 1.62-1.71 (m). MALDI-ToF MS calcd. For $C_{295}H_{261}N_{19}O_{38}Ag^{+}$ [M+Ag^{+}]: 4783.81; Found: 4783.16

Polymer 12 (Table S18, Entry 4)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.26-5.74 (m), 3.74-4.07 (m), 2.93-3.06 (m), 2.62-2.74 (m), 2.04-2.44 (m), 1.82-1.96 (m), 1.43-1.61 (m), 0.72-1.32 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.33, 131.79, 130.69, 99.99, 63.43, 61.88, 48.73, 48.21, 45.56, 44.60, 44.15, 40.75, 38.95, 33.32, 32.09, 29.70, 26.31, 18.16, 12.07. MALDI-ToF MS calcd. For $C_{121}H_{236}O_{8}Si_{8}Ag^{+}$ [M+Ag^{+}]: 2148.53; Found: 2148.55

Polymer 13 (Table S18, Entry 5)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.15-5.39 (m), 4.06-4.17 (m), 2.93-3.12 (m), 2.43-2.51 (m), 1.82-2.14 (m), 1.48-1.70 (m) 0.95-1.23 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.84, 175.53, 134.58, 133.57, 132.58, 131.91, 131.60, 131.04, 81.44, 60.25, 50.54, 50.22, 49.54, 47.64, 42.95, 42.52, 41.78, 37.12, 36.35, 29.66, 14.31. MALDI-ToF MS calcd. For $C_{153}H_{216}O_{28}Ag^{+}$ [M+Ag^{+}]: 2608.45; Found: 2608.19

Polymer 14 (Table S18, Entry 6)

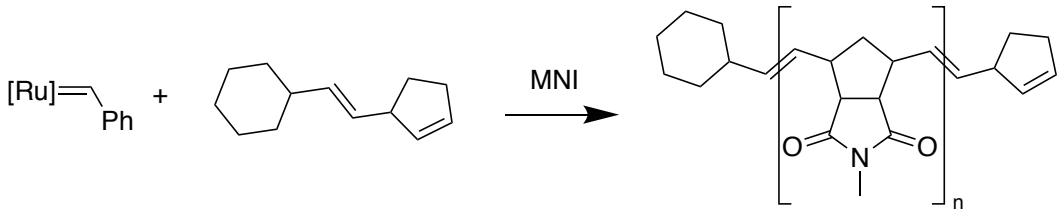
^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.82-6.06 (m), 4.61-4.65 (m), 3.25-3.49 (m), 2.86-2.94 (m), 1.08-1.36 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 176.43, 138.11,

127.99, 83.95, 79.12, 54.68, 52.94, 25.00, 22.31. MALDI-ToF MS calcd. For $C_{103}H_{119}N_9O_{27}Ag^+$ [M+Ag^+]: 2020.73; Found: 2020.73

Polymer 15 (Table S18, Entry 7)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.86-6.03 (m), 4.48-4.54 (m), 3.20-3.52 (m), 2.84-2.95 (m), 1.39-1.63 (m), 0.71-0.85 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 176.32, 175.05, 138.55, 137.02, 136.40, 128.81, 92.40, 86.47, 80.43, 78.61, 55.62, 53.02, 50.60, 48.75, 27.30, 24.89, 22.64, 9.44, 7.75. MALDI-ToF MS calcd. For $C_{178}H_{215}N_{15}O_{45}Ag^+$ [M+Ag^+]: 3389.40; Found: 3389.49

Different Mn



G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 5** which was dissolved in degassed DCM (0.5ml). To this solution, **MNI** (708mg, 4.0mmol, 800eq) which was dissolved in degassed DCM (0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give the polymer.

Table S19 Catalytic Living ROMP of Different Molecular Weight

Entry	Eq. CTA	Eq. MNI	Conc. of MNI mmol/ml	Mn Ther.	Mn Exp.	Đ	Speed ml/h	Yield%
1	10	800	0.075	14160	19000	1.14	5.0	96
2	20	800	0.075	7080	11000	1.15	5.0	99
3	40	800	0.075	3540	5400	1.22	5.0	99
4	60	800	0.075	2360	3800	1.33	5.0	97
5	100	800	0.075	1416	2300	1.32	5.0	90

Polymer 16 (Table S19, Entry 1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.67-5.81 (m), 5.44-5.54 (m), 2.67-3.28 (m), 1.47-1.70 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.35, 133.45, 132.66, 132.04, 131.84, 52.98, 52.63, 51.82, 51.10, 50.98, 46.23, 45.99, 45.85, 45.65, 42.94, 42.46, 41.97, 41.46, 41.22, 40.85, 30.64, 24.85, 24.78. MALDI-ToF MS calcd. For $C_{463}H_{515}N_{45}O_{90}Ag^{+}$ [M+Ag^{+}]: 8251.62; Found: 8251.21

Polymer 17 (Table S19, Entry 2)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.63-5.70 (m), 5.40-5.51 (m), 2.63-3.22 (m), 1.91-2.23 (m), 1.42-1.63 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.33, 137.60, 133.38, 132.86, 132.62, 131.98, 131.84, 53.53, 52.91, 52.56, 51.79, 51.06, 50.95, 46.13, 45.94, 45.74, 45.56, 42.92, 42.46, 41.95, 41.41, 40.83, 34.04, 30.59, 25.96, 24.79, 24.73, 22.26, 14.03. MALDI-ToF MS calcd. For $C_{263}H_{295}N_{25}O_{50}Ag^{+}$ [M+Ag^{+}]: 4710.04; Found: 4710.11

Polymer 18 (Table S18, Entry 3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.70-5.74 (m), 5.43-5.52 (m), 2.64-3.26 (m), 1.90-2.32 (m), 1.42-1.69 (m), 1.02-1.26 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.32, 137.72, 133.41, 132.65, 131.84, 127.82, 52.96, 52.61, 51.09, 50.98, 47.93,

46.04, 45.59, 45.11, 42.89, 41.44, 40.85, 32.94, 30.62, 25.99, 24.81, 24.60. MALDI-ToF MS calcd. For $C_{103}H_{119}N_9O_{18}Ag^+$ [M+Ag^+]: 1876.77; Found: 1876.75

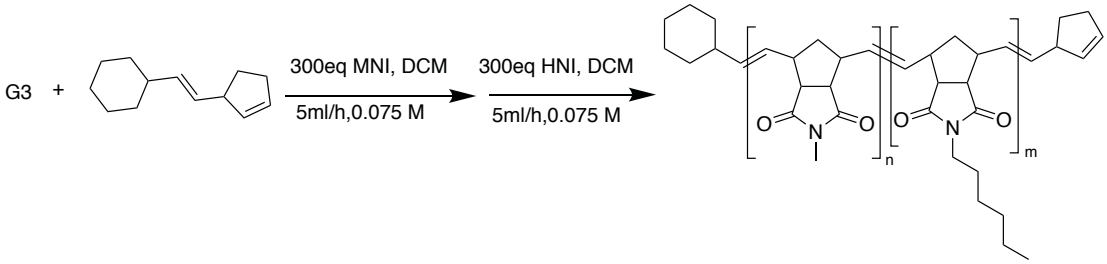
Polymer 19 (Table S19, Entry 4)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.67-5.78 (m), 5.42-5.60 (m), 2.69-3.31 (m), 1.85-2.36 (m), 1.47-1.71 (m), 1.03-1.32 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.34, 137.69, 135.29, 133.45, 132.66, 132.04, 131.84, 53.47, 52.98, 52.62, 51.82, 51.10, 51.00, 48.25, 46.23, 45.97, 45.81, 45.60, 42.91, 42.45, 41.90, 41.45, 41.21, 40.85, 40.47, 34.11, 32.87, 32.11, 30.63, 26.02, 24.84, 24.77, 22.34, 14.08. MALDI-ToF MS calcd. For $C_{143}H_{163}N_{13}O_{16}Ag^+$ [M+Ag^+]: 2585.09; Found: 2585.10

Polymer 20 (Table S19, Entry 5)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.67-5.75 (m), 5.42-5.59 (m), 5.18-5.32 (m), 2.59-3.28 (m), 1.95-2.27 (m), 1.02-1.69 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.43, 178.29, 138.07, 137.64, 135.25, 133.70, 133.41, 132.66, 131.83, 131.46, 128.99, 128.67, 127.83, 52.96, 52.61, 51.82, 51.10, 48.22, 46.03, 45.78, 45.57, 42.43, 41.44, 40.84, 40.43, 34.08, 32.94, 32.06, 30.62, 25.99, 24.80, 22.29, 14.04. MALDI-ToF MS calcd. For $C_{93}H_{108}N_8O_{16}Ag^+$ [M+Ag^+]: 1699.69; Found: 1699.74

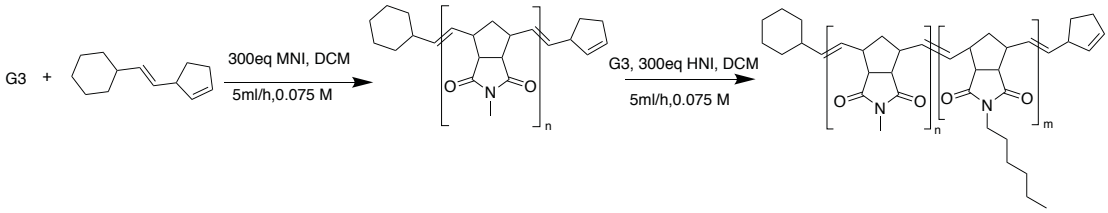
Block copolymerisation



Polymer 21

G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 5** which was dissolved in degassed DCM (0.5ml). To this solution **MNI** (266 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml, 0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, **HNI** (371 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml, 0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give 625mg of **polymer 21**. Yield: 98%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.67-5.83 (m), 5.44-5.62 (m), 3.20-3.45 (m), 2.86-3.10 (m), 2.64-2.78 (m), 1.91-2.32 (m), 1.50-1.71 (m), 1.15-1.35 (m), 0.79-0.88 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.36, 133.46, 132.67, 131.85, 52.98, 52.61, 51.84, 51.09, 50.99, 50.85, 46.23, 45.85, 45.62, 42.95, 42.48, 42.01, 41.45, 40.86, 38.74, 38.56, 31.35, 31.28, 27.62, 26.53, 26.42, 24.83, 24.76, 22.49, 22.46, 13.99. MALDI-ToF MS can not be detected due to the too high molecular weight. $M_{n\ GPC}$ ($CHCl_3$) = 17900 g mol^{-1}, Đ = 1.46.

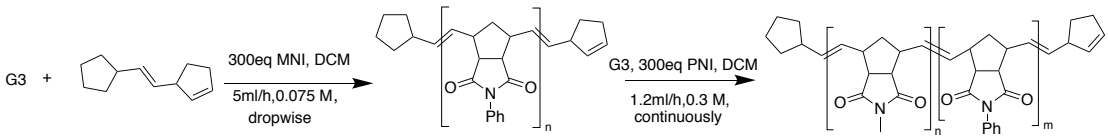


Polymer 22

G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 5** which was dissolved in degassed DCM (0.5ml) was added under Ar. To this solution **MNI** (266 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml, 0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, the solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give **polymer 1**.

G3 (4.45mg, 0.005mmol,1.0eq) and **polymer 1** (all from last step) were dissolved in degassed DCM (2ml) under Ar. To this solution, **HNI** (371 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml, 0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give 599mg of **polymer 22**. Yield: 94%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.65-5.80 (m), 5.45-5.55 (m), 3.38-3.47 (m), 3.22-3.29 (m), 2.91-3.07 (m), 2.65-2.80 (m), 1.98-2.36 (m), 1.49-1.72 (m), 1.20-1.32 (m), 0.80 – 0.90 (m).^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.34, 178.17, 133.48, 132.67, 132.15, 132.03, 131.83, 131.60, 53.01, 52.60, 51.84, 51.11, 51.00, 50.82, 45.91, 45.62, 42.90, 42.47, 41.97, 41.63, 41.47, 41.32, 40.86, 38.93, 38.76, 38.57, 31.36, 31.29, 27.63, 26.55, 26.43, 24.83, 24.76, 22.50, 22.47. MALDI-ToF MS can not be detected due to the too high molecular weight. $M_{n\ GPC}$ ($CHCl_3$) = 22500 g mol^{-1}, Đ = 1.36.



Block copolymerization with CTA-end capping of the first polymer block (polymer 23)

G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 6** (8.5mg, 0.05mmol, 10.0eq.) which was dissolved in degassed DCM (0.5ml) was added under Ar. To this solution **MNI** (266 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml, 0.075mmol/ml) was added at a speed of 5ml/h by syringe pump. After complete addition, **CTA6** (8.5mg, 0.05mmol, 10.0eq.) which was dissolved in 1ml degassed DCM was added to end-cap all the end-groups of the polymer chains and the solution stirred for another 1 hour. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give **polymer 7**.

G3 (4.45mg, 0.005mmol,1.0eq) and **polymer 7** (all from last step) were dissolved in degassed DCM (2ml) under Ar. To this solution, **PNI** (360 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (5ml, 0.3mmol/ml) was added at a speed of 1.2ml/h by syringe pump (the top of the thin needle should be below the reaction solution surface). After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The solvent was removed under reduced pressure until around 5ml of liquid remained. The concentrated solution obtained was precipitated into cold methanol (50ml) to give 567mg of **polymer 23**. Yield: 90%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20-7.46 (m), 5.71-5.85 (m), 5.46-5.60 (m), 2.71-3.51 (m), 2.00-2.30 (m), 2.91-3.07 (m), 2.65-2.80 (m), 1.98-2.36 (m), 1.49-1.72 (m), 1.20-1.32 (m), 0.80 – 0.90 (m). MALDI-ToF MS cannot be detected due to the too high molecular weight. $M_{n\ GPC}$ ($CHCl_3$) = 21000 g mol^{-1}, Đ = 1.26.

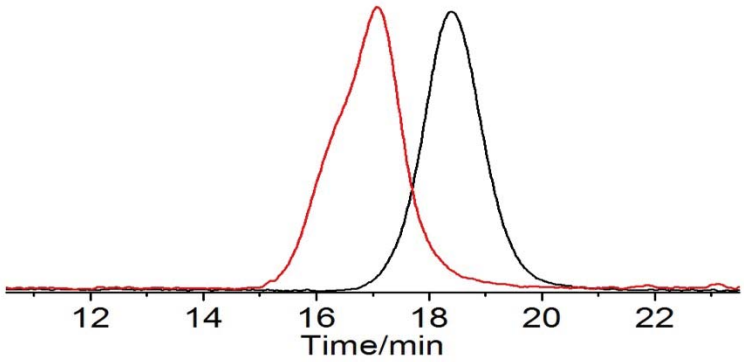


Figure S17 GPC trace for fully end-capped polymers re-initiated block copolymers. Polymer 7 (black, Mn $_{GPC}$ ($CHCl_3$) = 8000, Đ = 1.20), block copolymer polymer 23 (red, Mn $_{GPC}$ ($CHCl_3$) = 21000, Đ = 1.26).

Catalyst reinitiation

G3 (4.45mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA7** (7mg, 0.05mmol, 10eq.) which was dissolved in degassed DCM (0.5ml). **PNI** (360mg, 1.5mmol, 300eq) dissolved in degassed DCM (20ml) was added slowly to this solution by syringe pump (5ml/h). After complete addition, the solvent was removed under reduced pressure until around 10ml of liquid remained. 5ml the concentrated solution obtained was precipitated into cold methanol (50ml) and the GPC trace measured (black, Mn: 4700). The other 5ml of the concentrated solution obtained was precipitated into cold degassed pentane (50ml) under Ar. Then the pentane was removed under reduced pressure under Ar, following 4ml degassed DCM was added. Then **MNI** (50mg in 1ml degassed DCM) solution was added. After 1h the solution was precipitated into cold pentane (50ml) and measure the GPC (red, Mn: 8800).

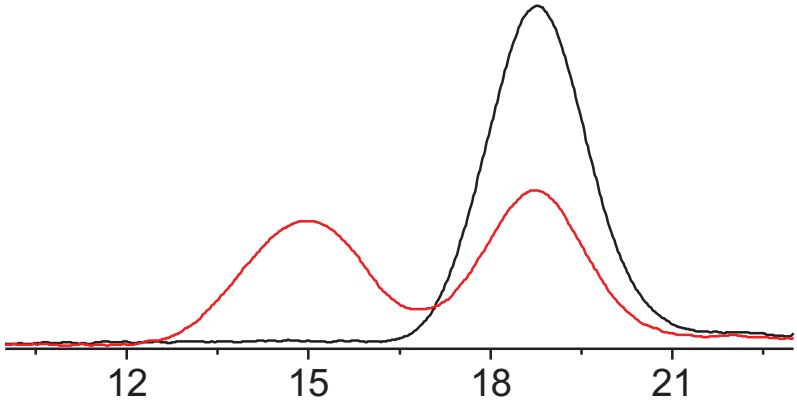


Figure S18 GPC trace for re-initiating catalyst

Ruthenium Content Experiment

Classic living ROMP: **G3** (4.45mg, 0.005mmol, 1.0eq) was dissolved in degassed DCM (2.5ml), then **MNI** (34mg, 0.19mmol, 38eq) was added under Ar. The solution was kept stirring for 30min, then vinyl ether (0.5ml) was added to terminate the reaction. 0.5ml of the solution was taken out to measure the ruthenium content (in 5ml 5% HNO_3 solution). The remaining solution was precipitated into cold methanol twice after which the ruthenium content of the dried polymer was determined again (3.5mg polymer in 5ml 5% HNO_3 solution).

Catalytic Living ROMP: **G3** (4.45mg, 0.005mmol, 1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by the addition of **CTA5** which was dissolved in degassed DCM (0.5ml). To this solution **MNI** (266mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (20ml) was added slowly by syringe pump at a speed of 5ml/h. After complete addition, vinyl ether (0.5ml) was added to quench the reaction. 0.5ml of the solution was taken out to measure the

ruthenium content (in 5ml 5% HNO_3 solution). The remaining solvent was removed under reduced pressure until around 2ml of liquid remained. Then the solution was precipitated twice into cold methanol (20ml) and the ruthenium content measure of the dried polymer sample (3.5mg polymer in 5ml 5% HNO_3 solution).

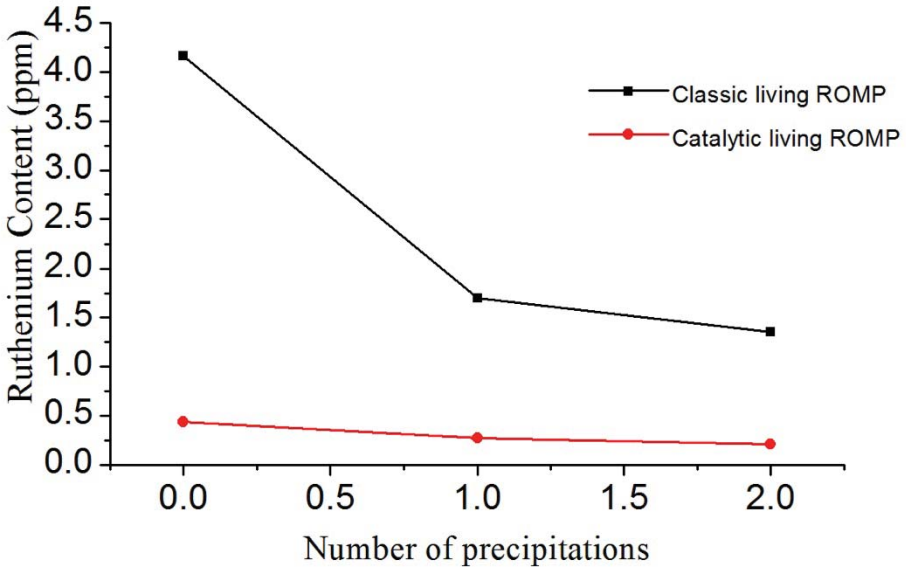


Figure S19 Residual ruthenium content by ICP-OES.

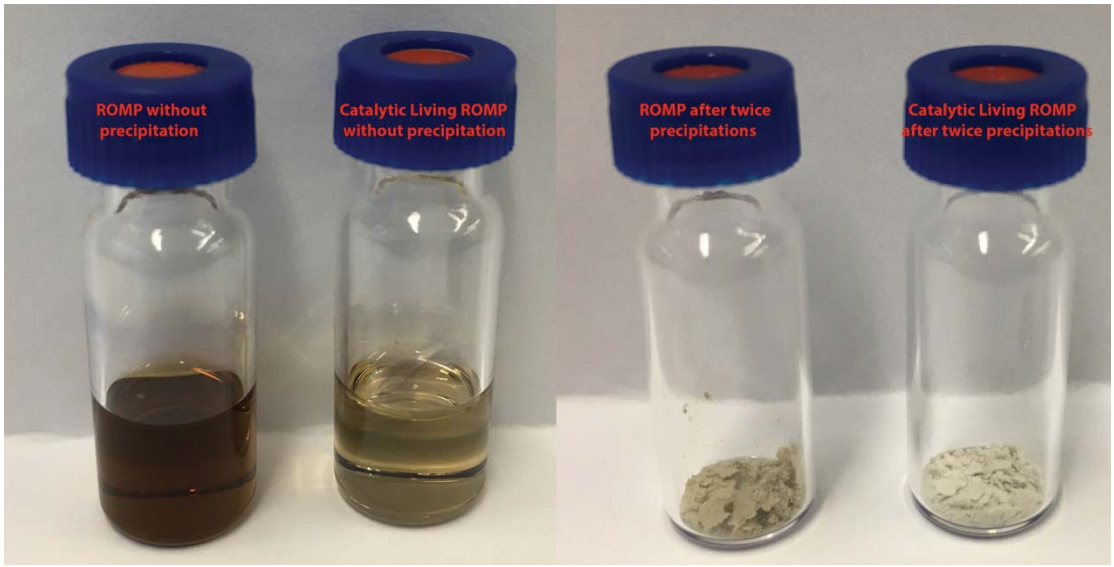


Figure S20 Similar Molecular Weight Polymers Synthesized by Classic living ROMP (left, 4.45mg G3 for 33mg MNI, Mn = 6900 g mol^{-1} Đ = 1.15) and Catalytic Living ROMP (right, 4.45mg G3 for 266mg MNI, Mn = 7200 g mol^{-1} Đ = 1.20)

Copies of NMR Spectra

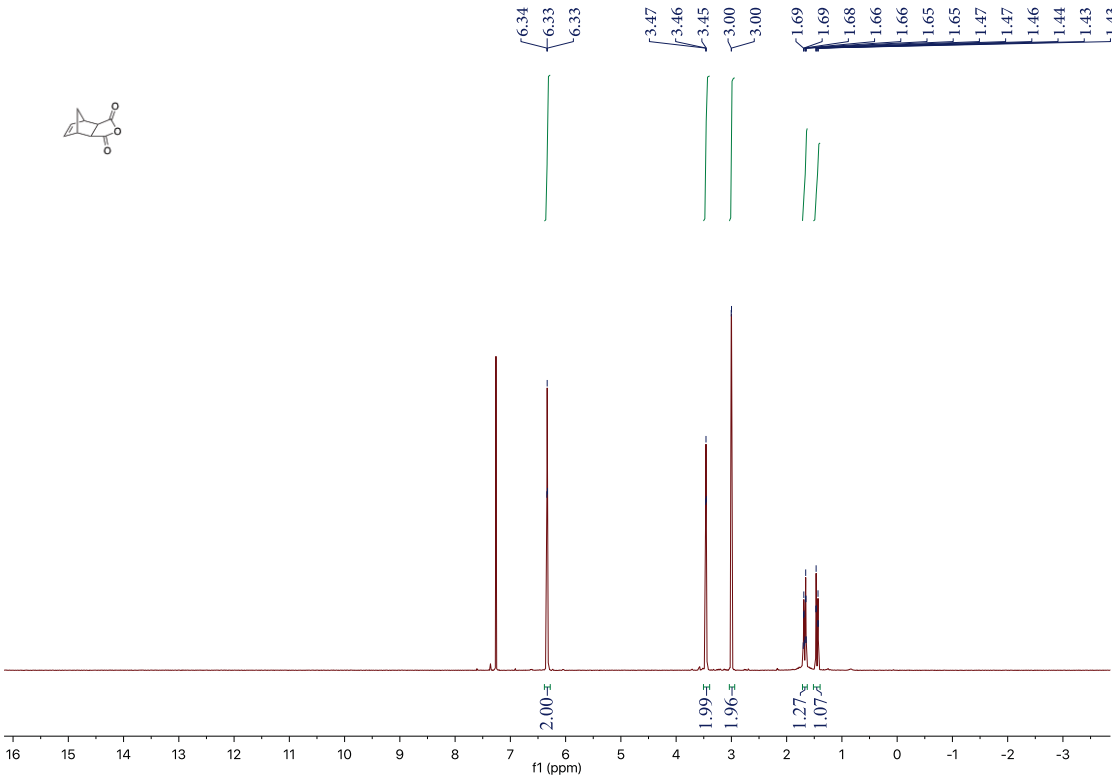


Figure S21 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of ***exo*-5-Norbornene-2,3-dicarboxylic anhydride**

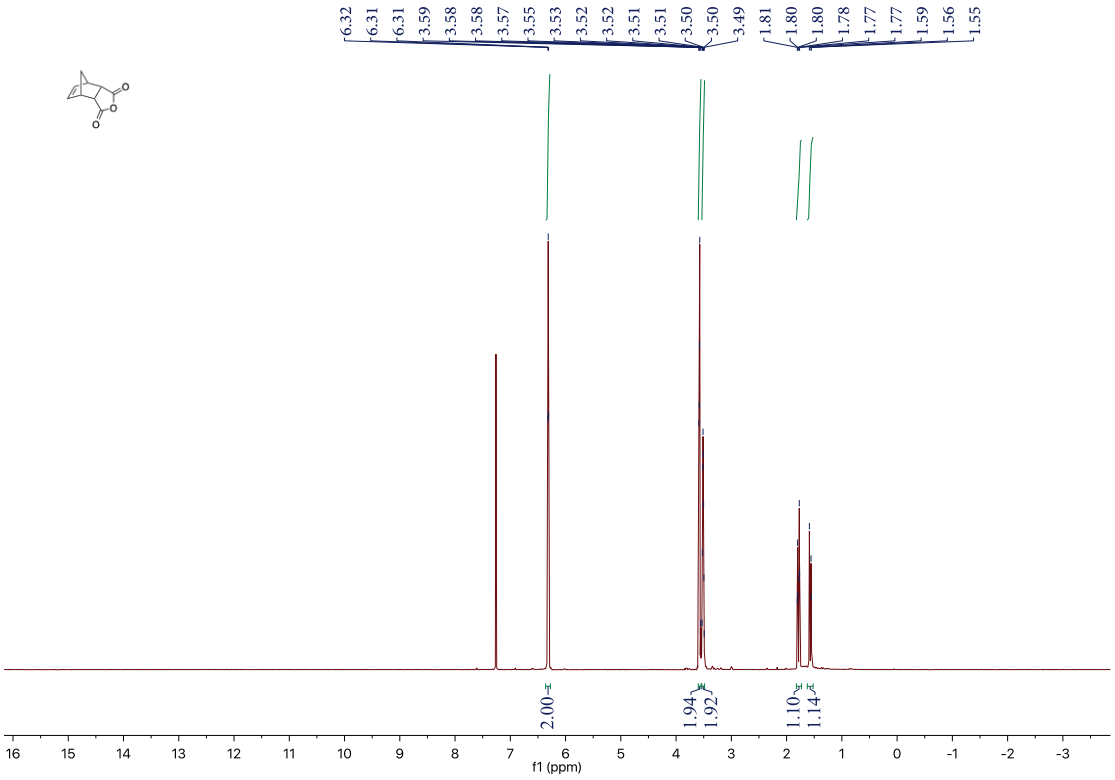


Figure S22 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of ***endo*-5-Norbornene-2,3-dicarboxylic anhydride**

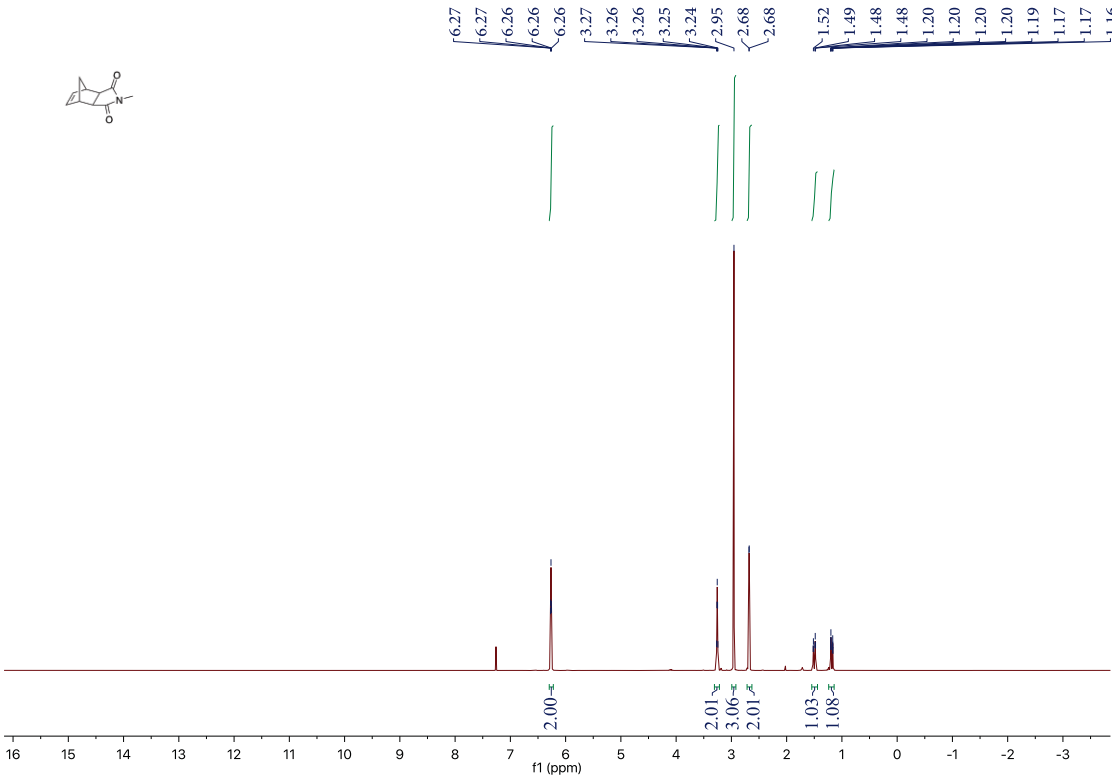


Figure S23 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **MNI**

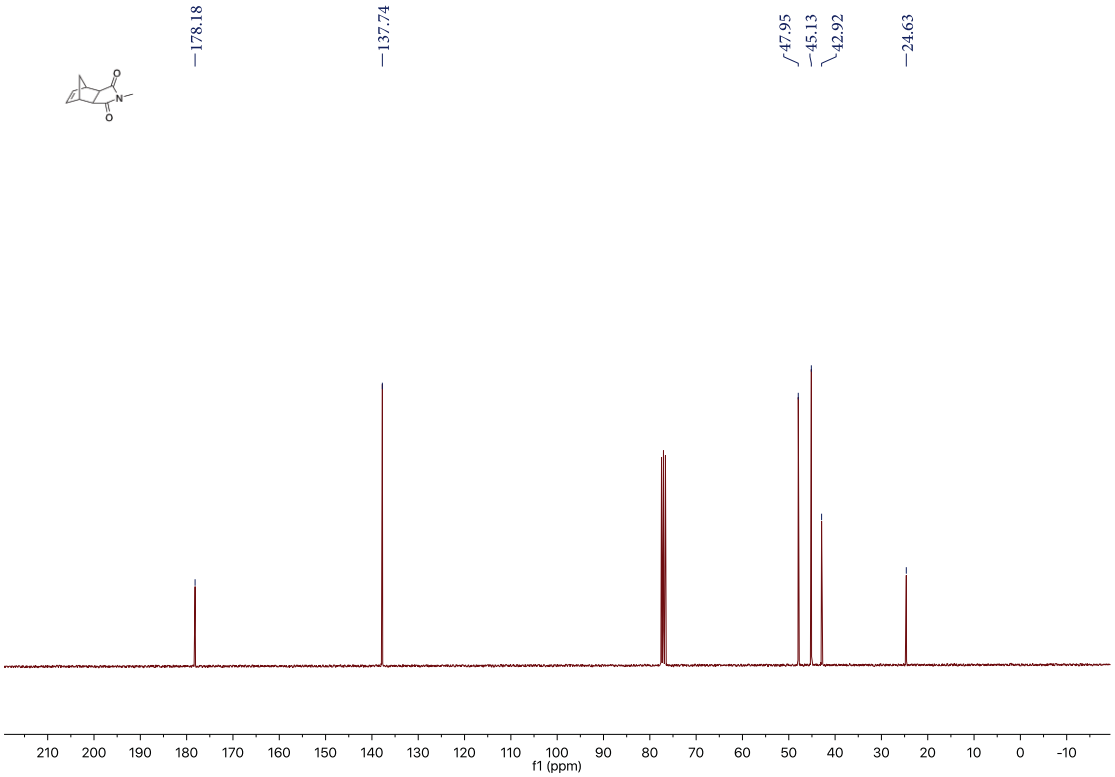


Figure S24 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **MNI**

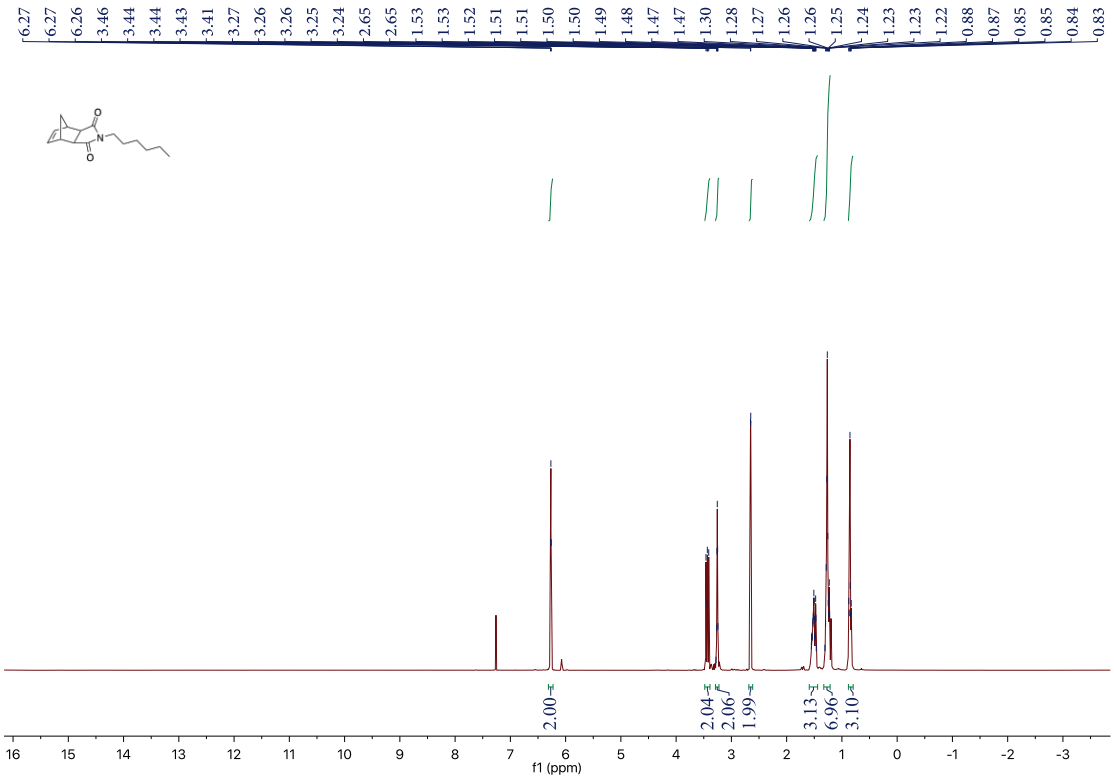


Figure S25 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **HNI**

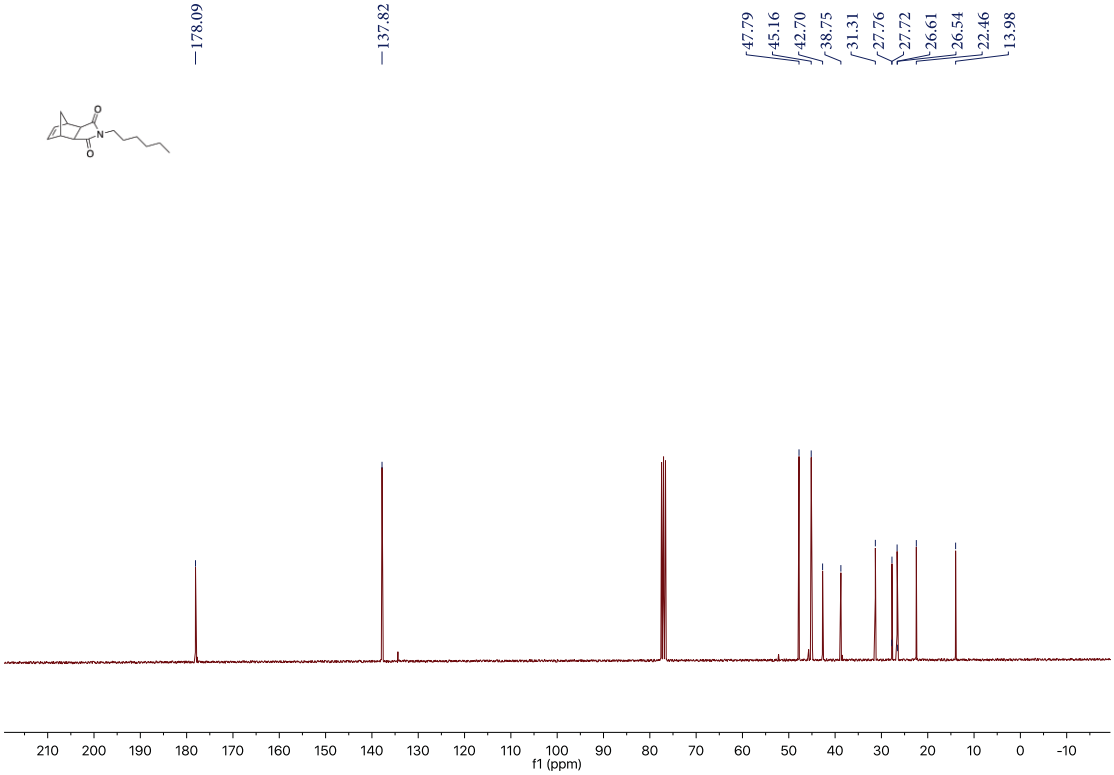


Figure S26 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **HNI**

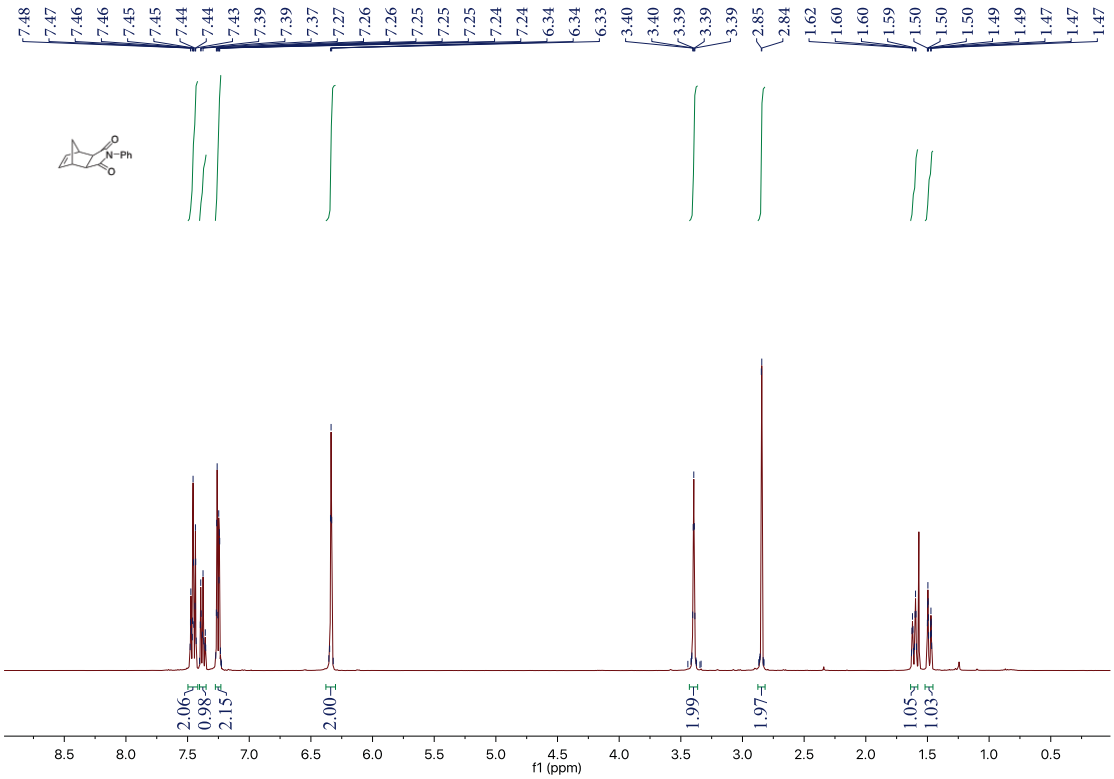


Figure S27 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **PNI**

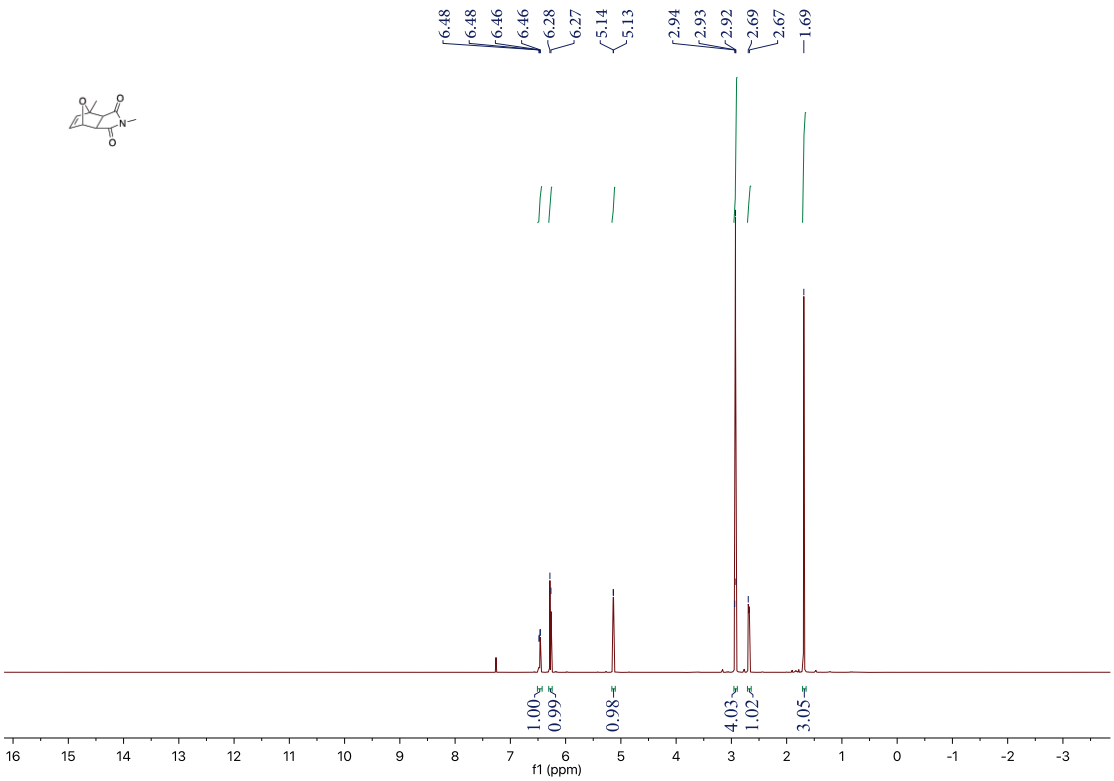


Figure S28 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **MOMNI**

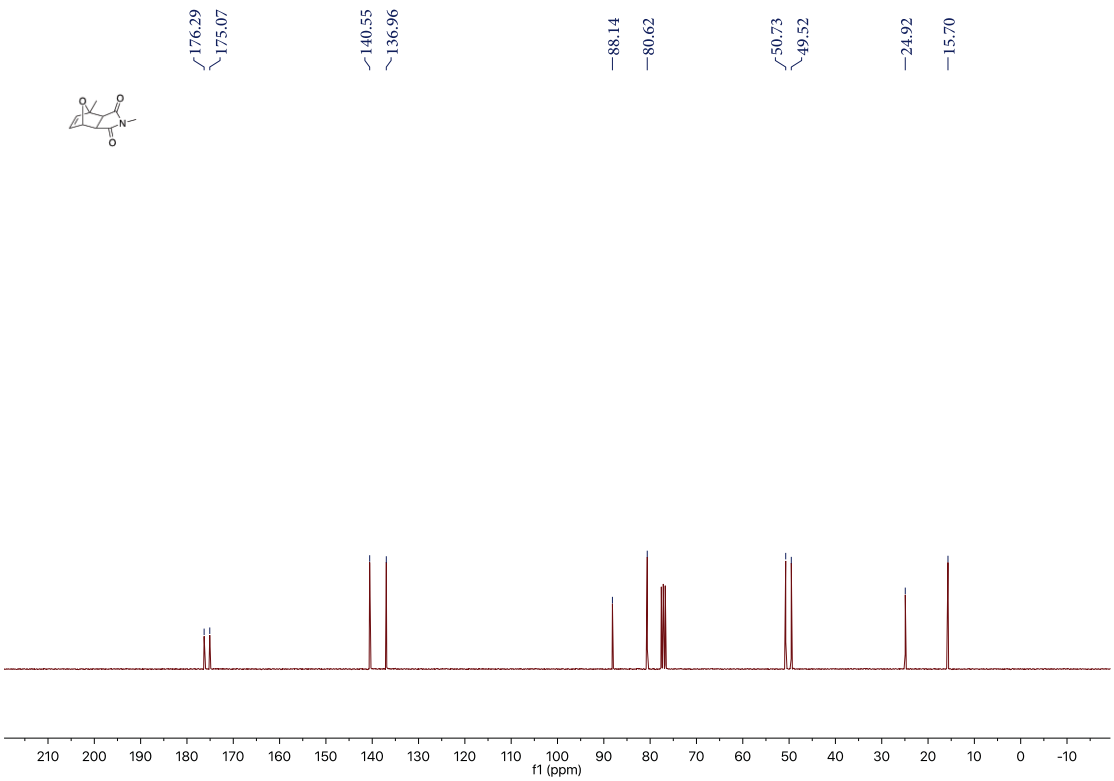


Figure S29 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **MOMNI**

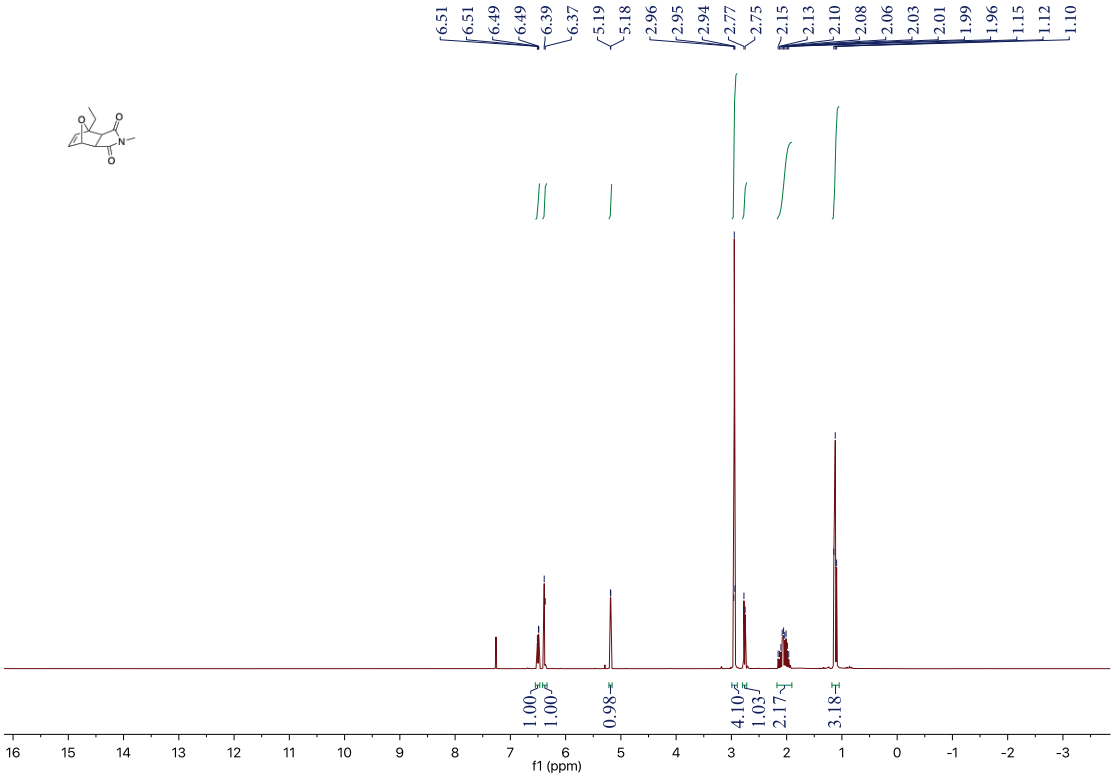


Figure S30 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **EOMNI**

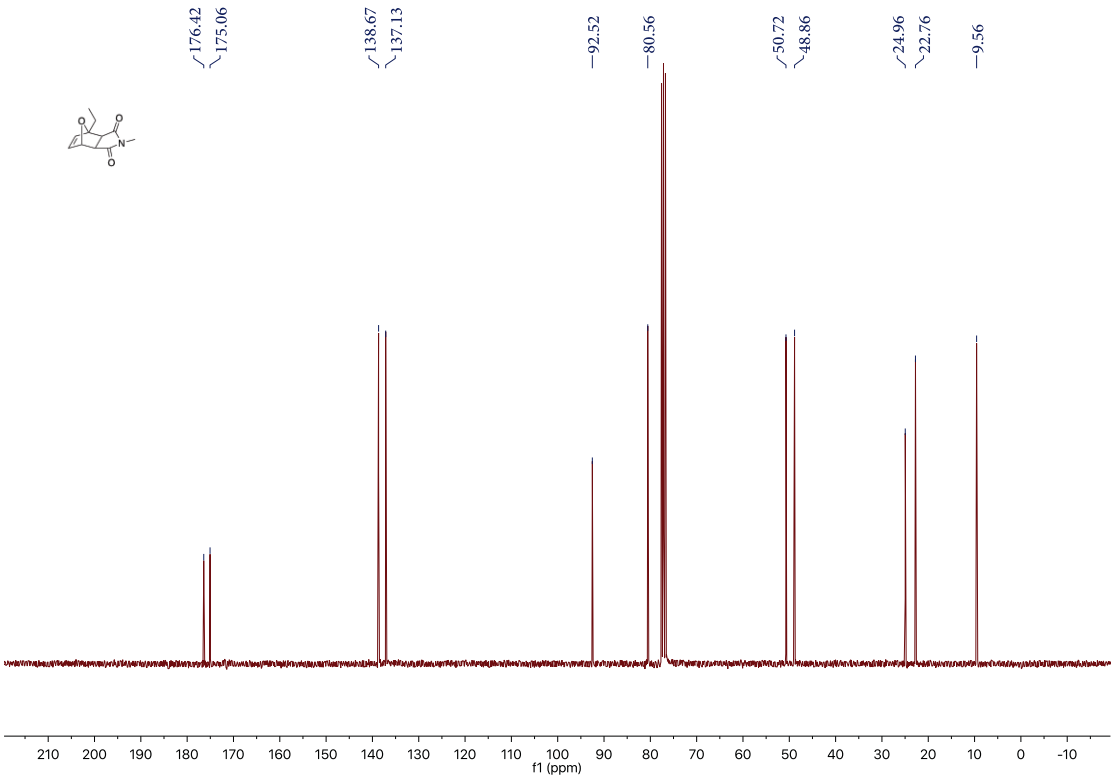


Figure S31 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **EOMNI**

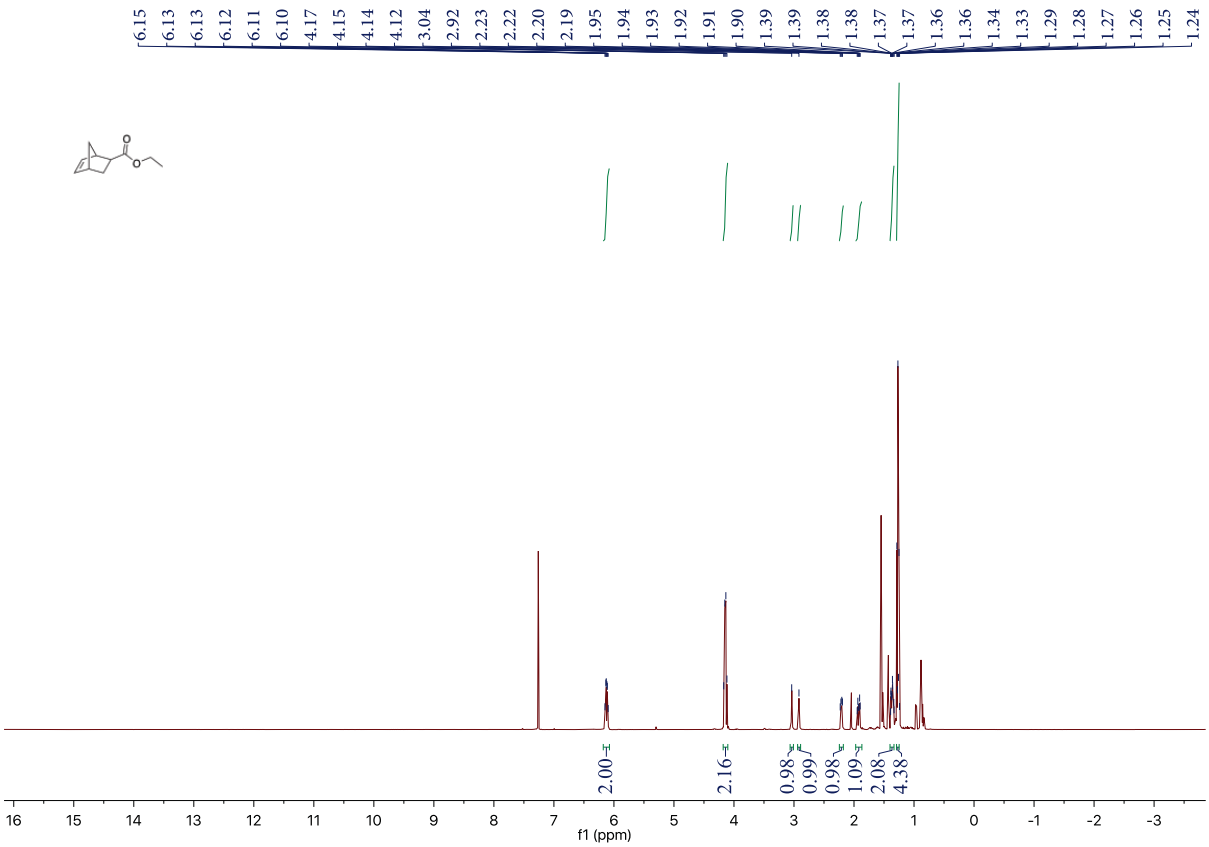


Figure S32 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **ENC**

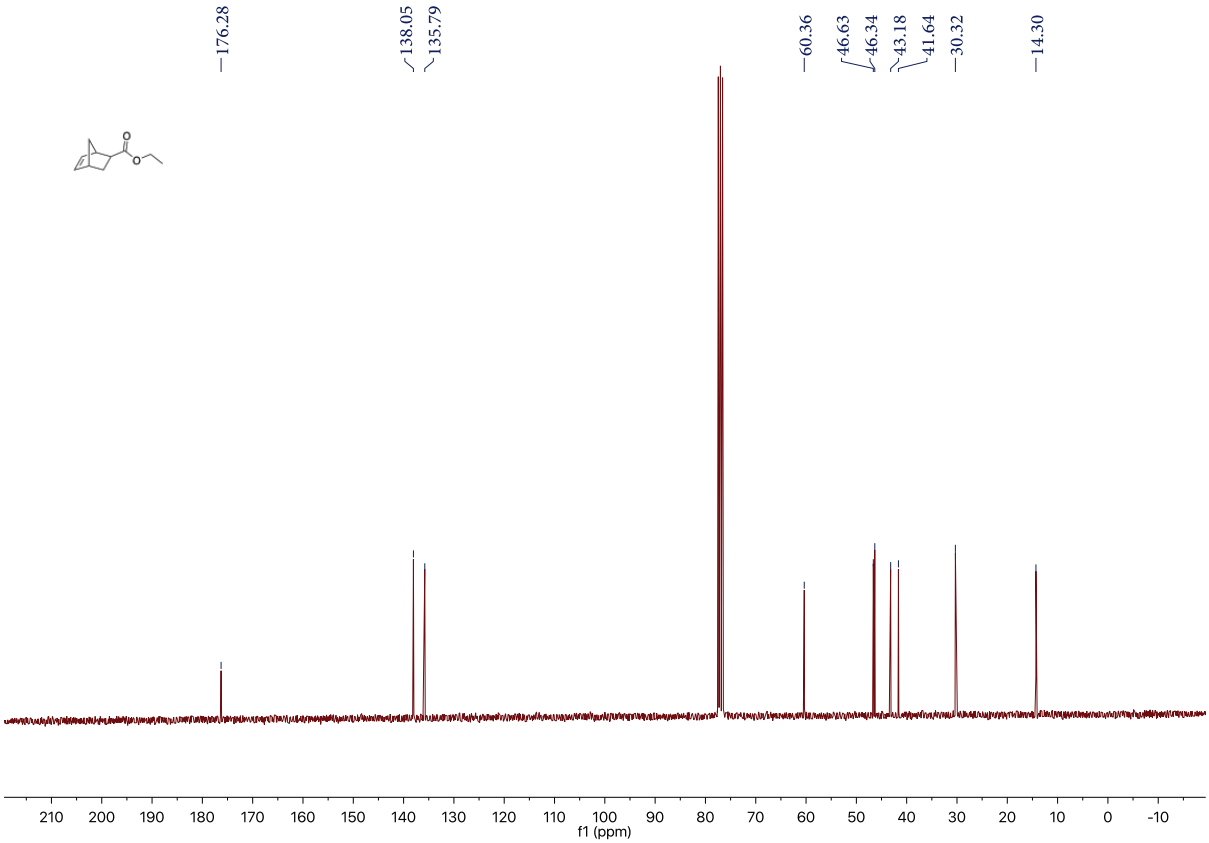


Figure S33 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **ENC**

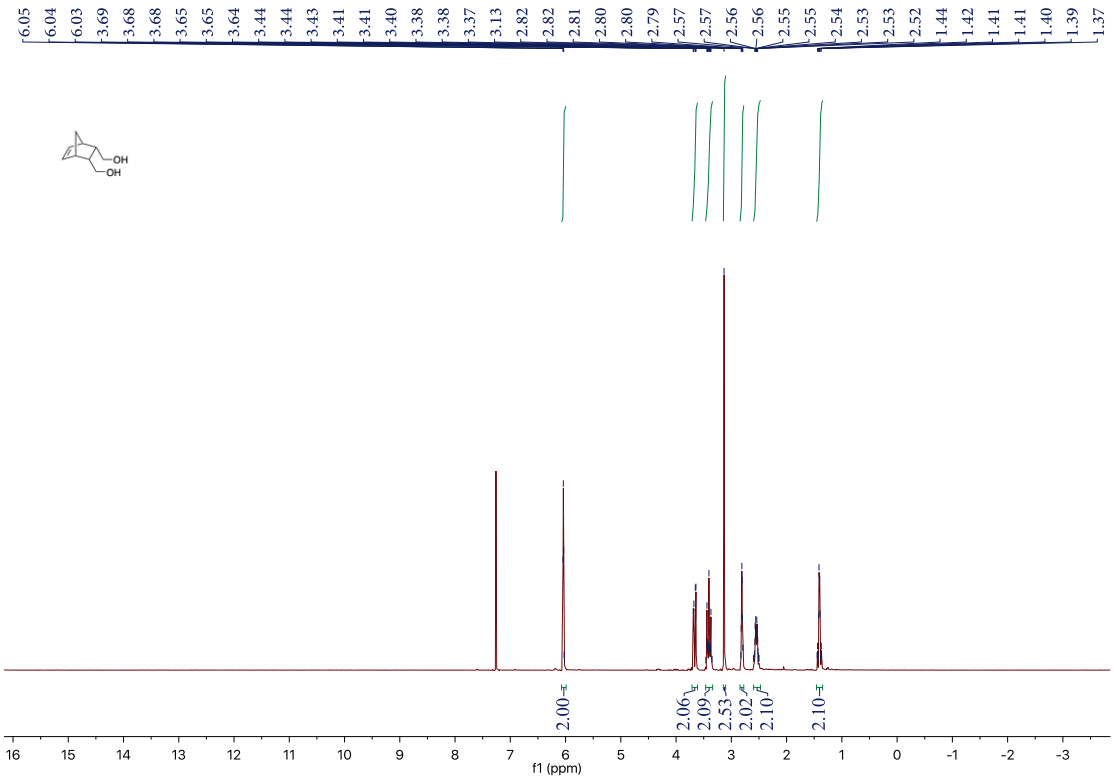


Figure S34 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of ***Endo*-5-norbornene-2,3-bismethanol**

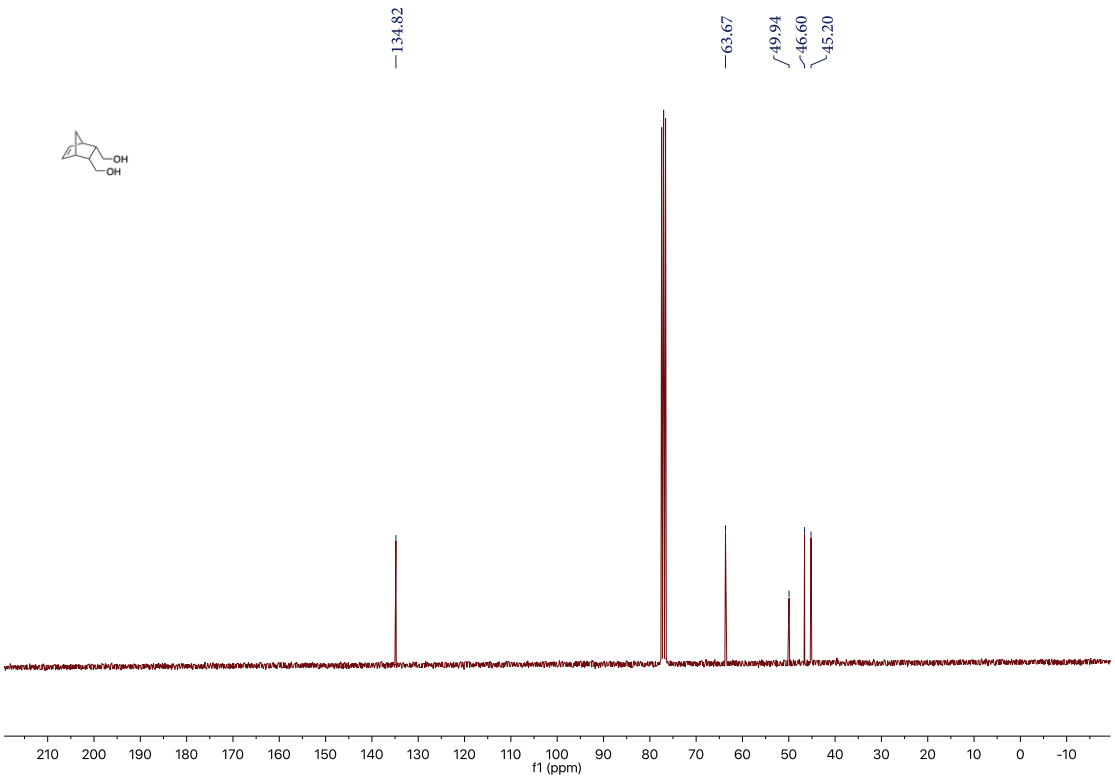


Figure S35 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of ***Endo*-5-norbornene-2,3-bismethanol**

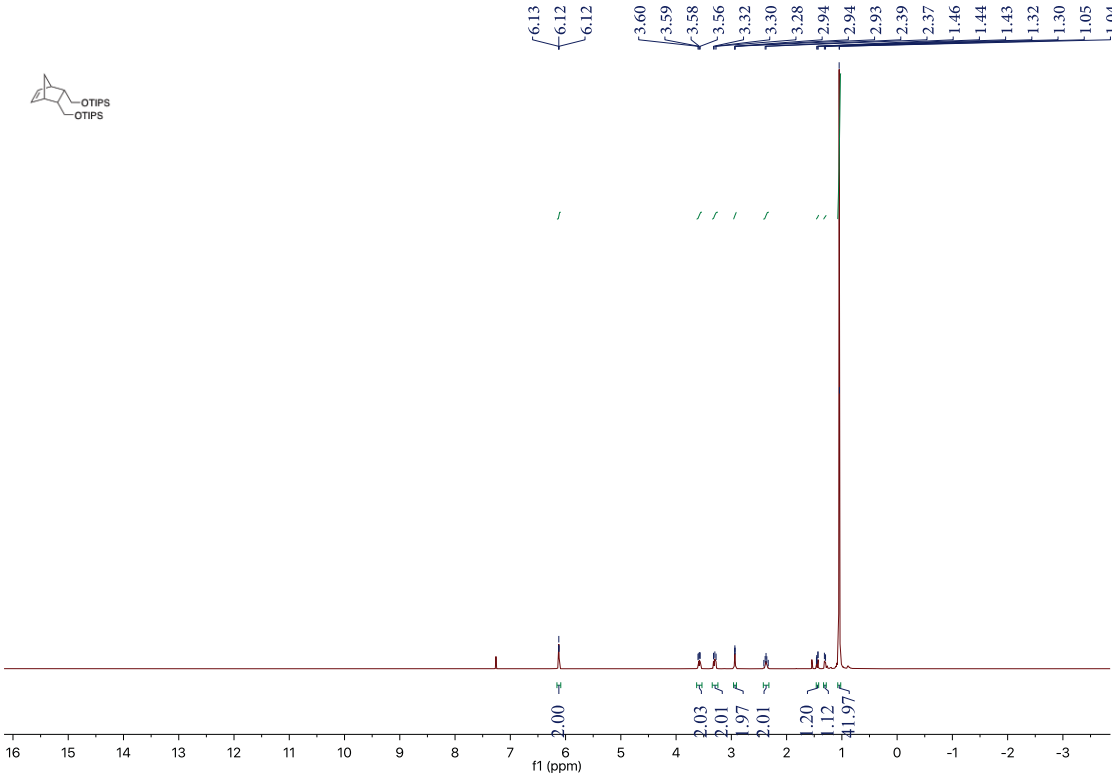


Figure S36 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **NBSM**

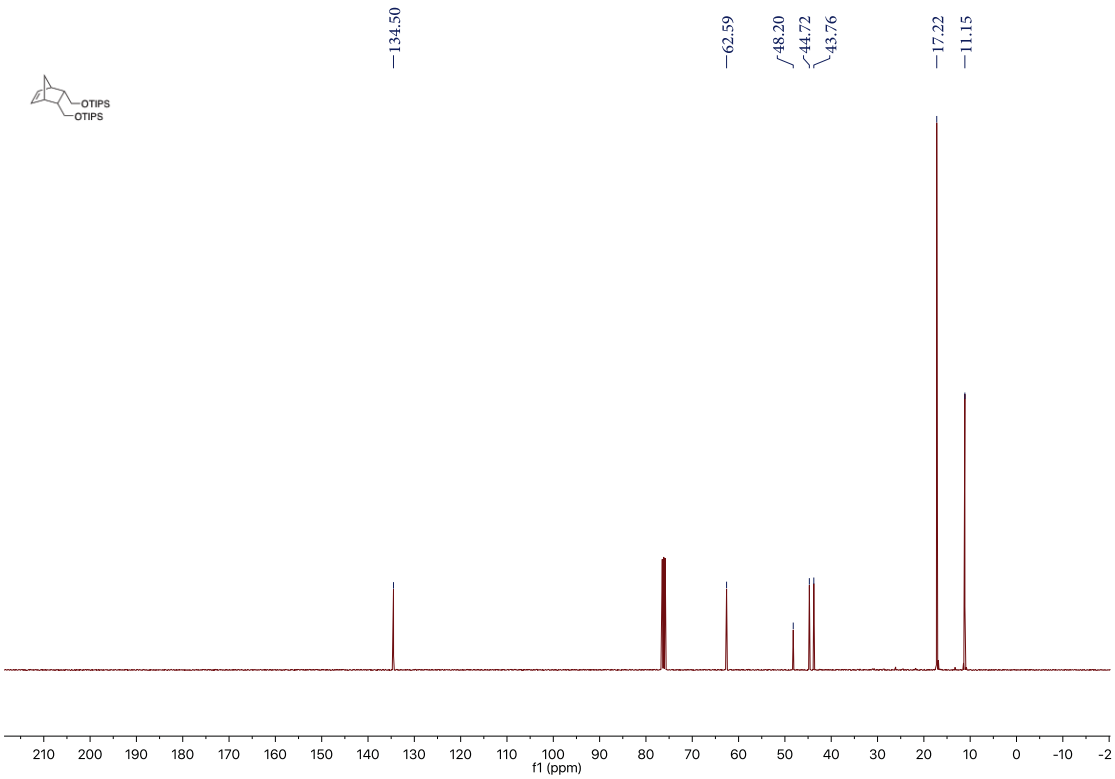


Figure S37 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **NBSM**

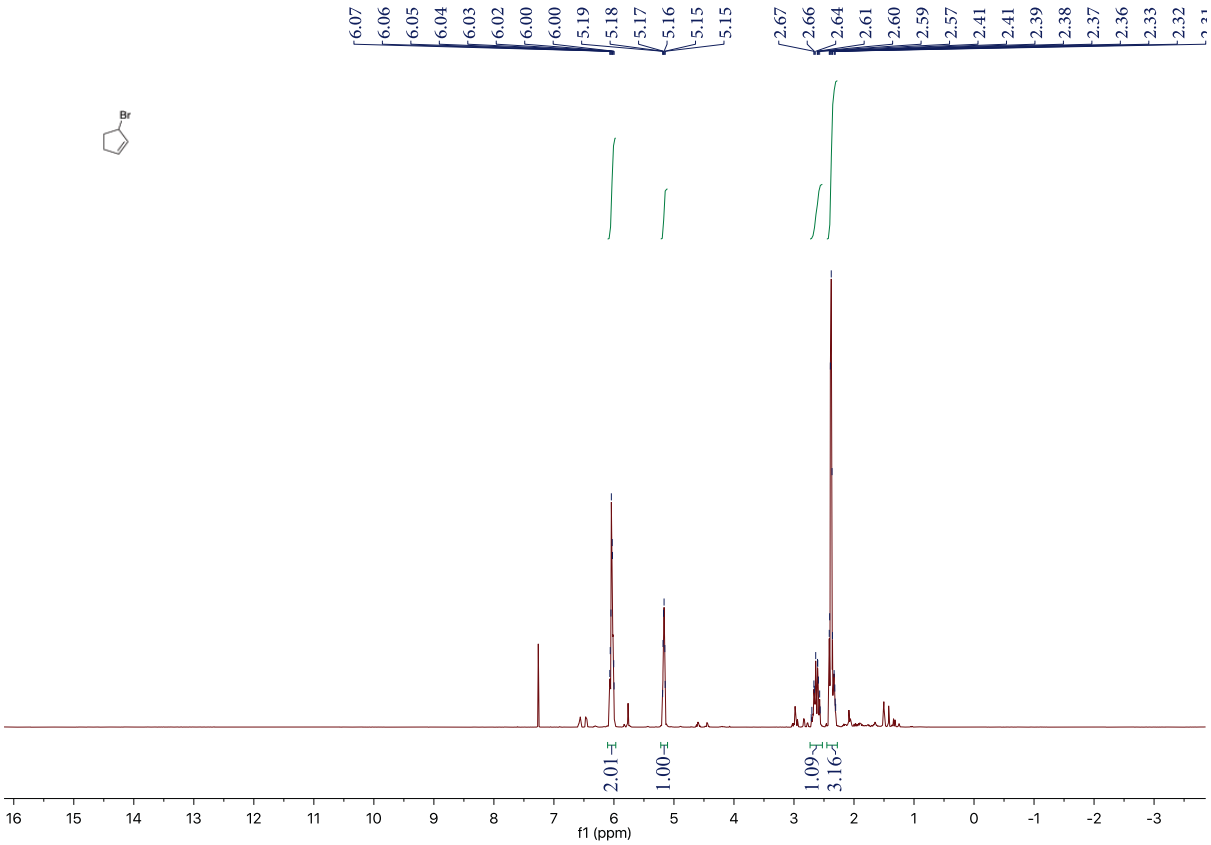


Figure S38 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **3-bromocyclopentene**

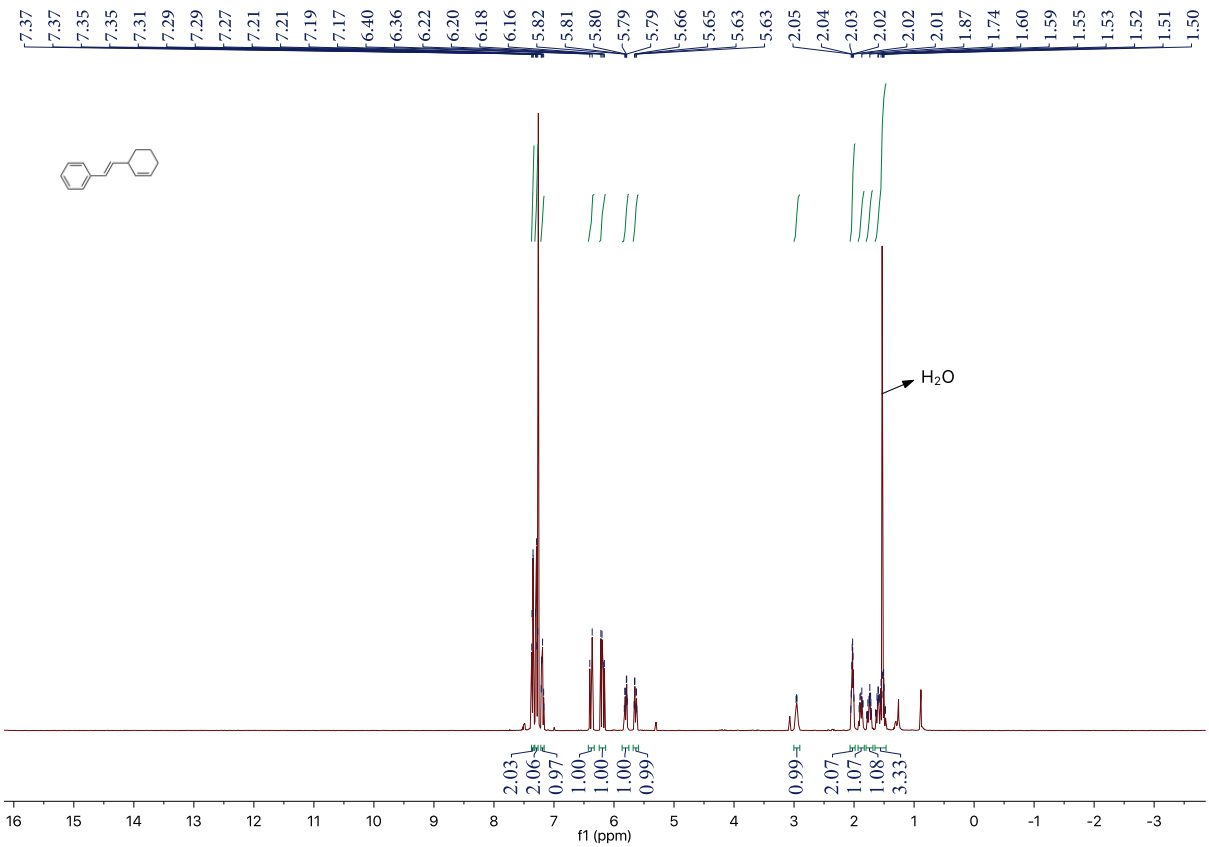


Figure S39 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA1**

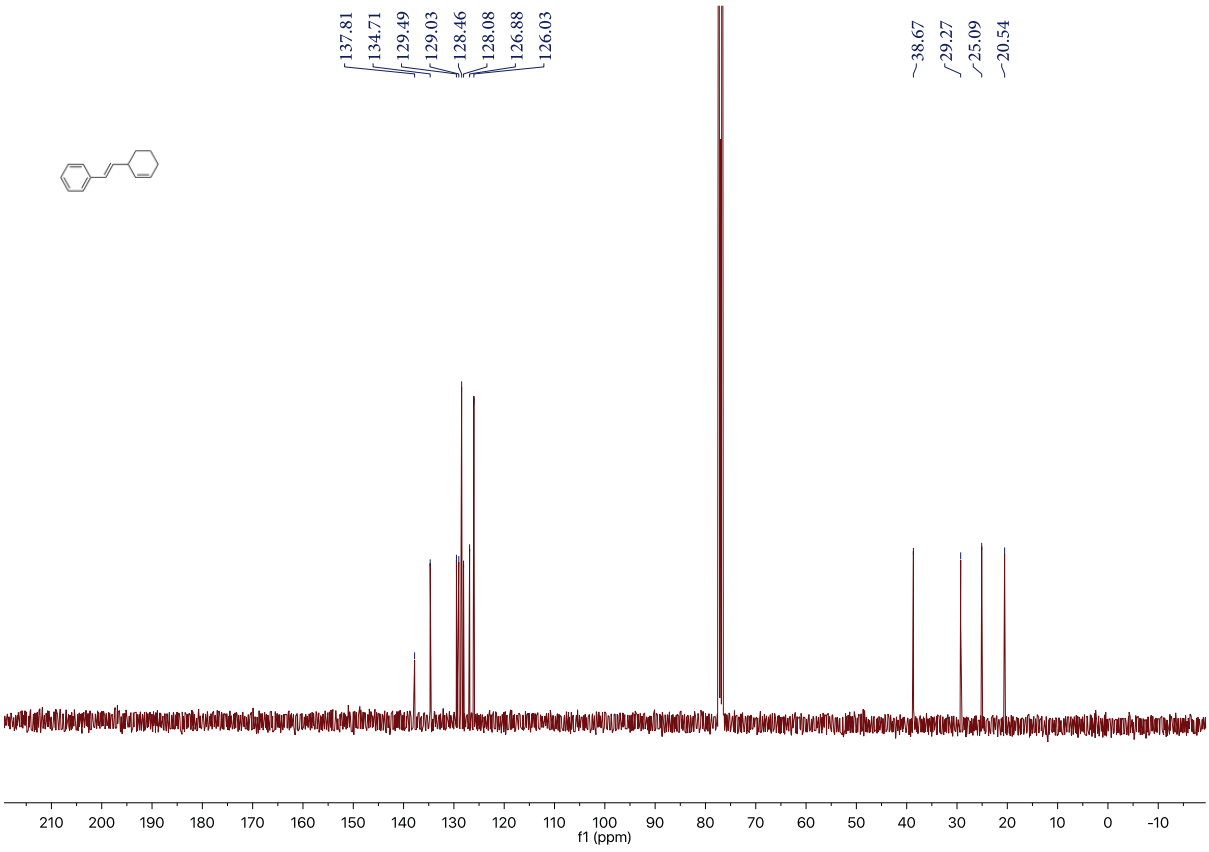


Figure 40 ^{13}C-NMR spectrum (101MHz, $CDCl_3$) of **CTA1**

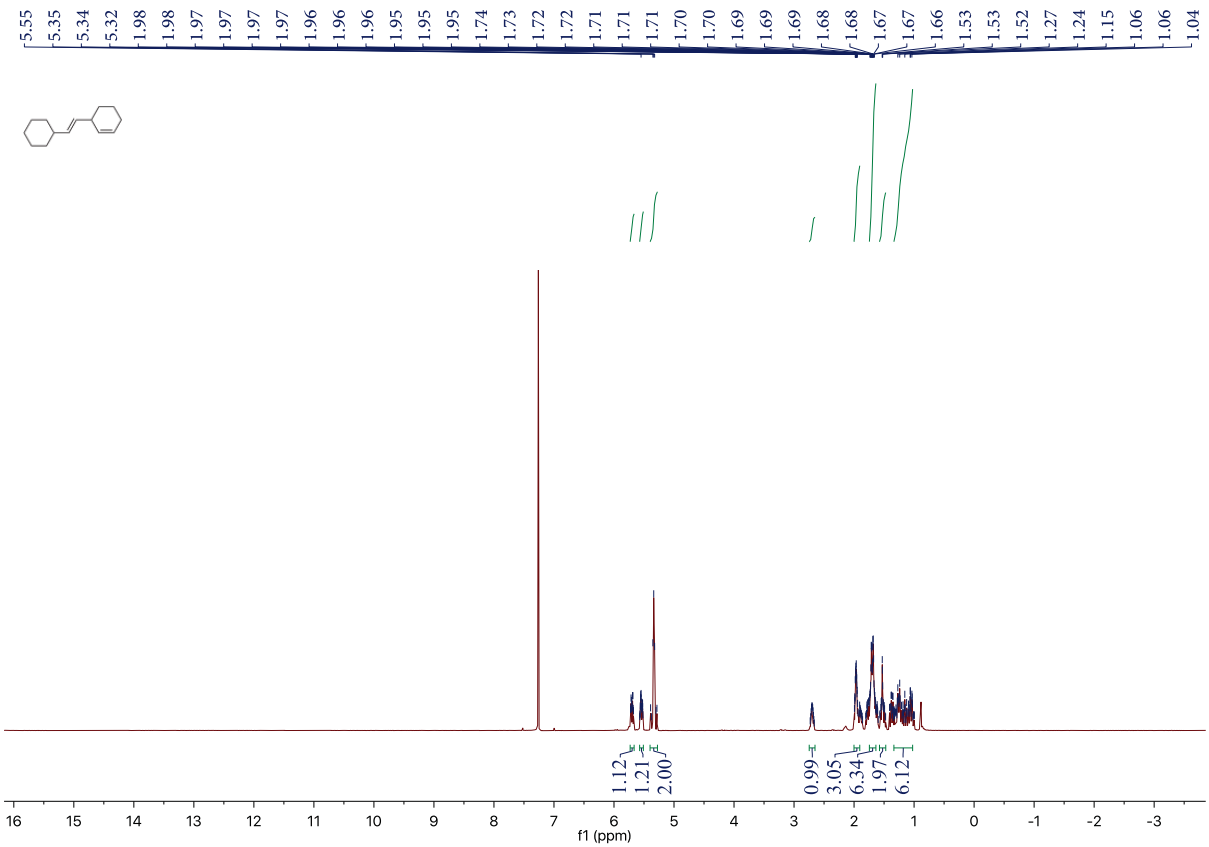


Figure S41 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **CTA2**

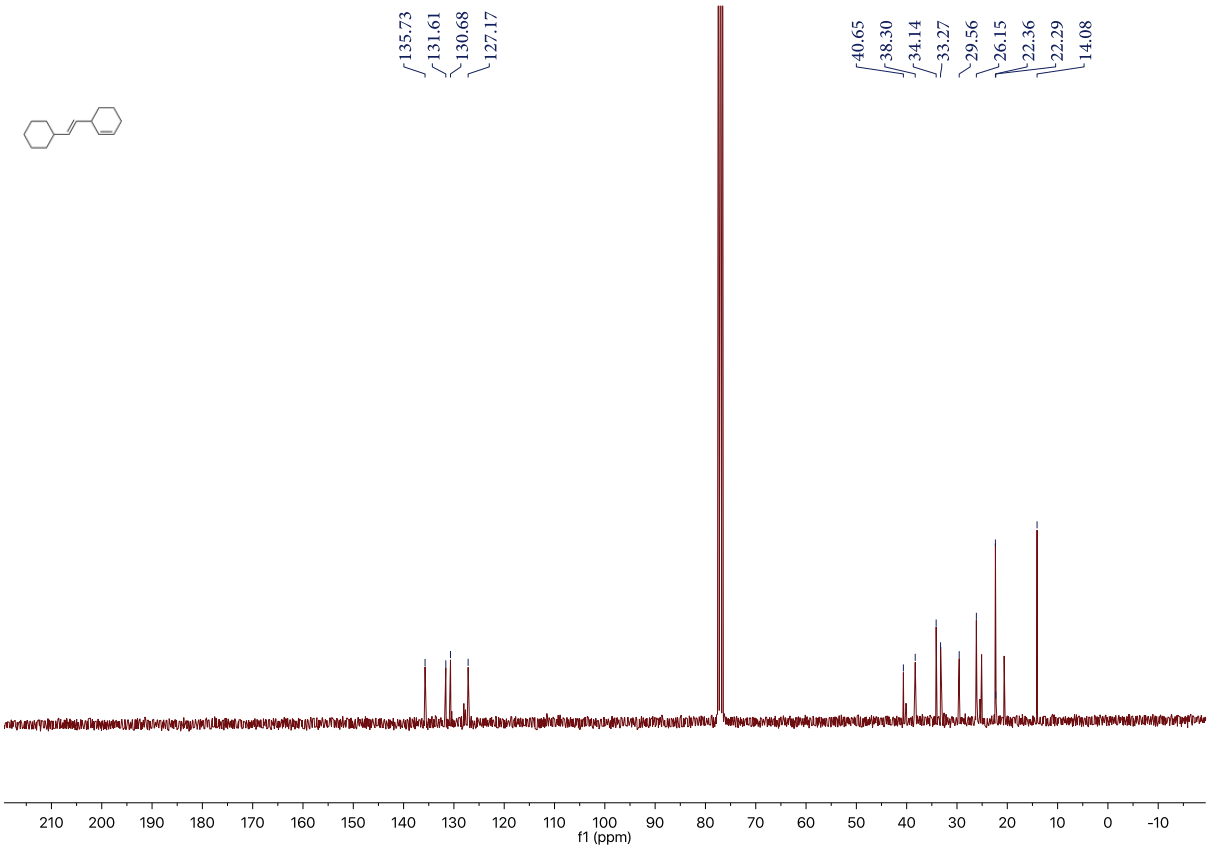


Figure S42 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **CTA2**

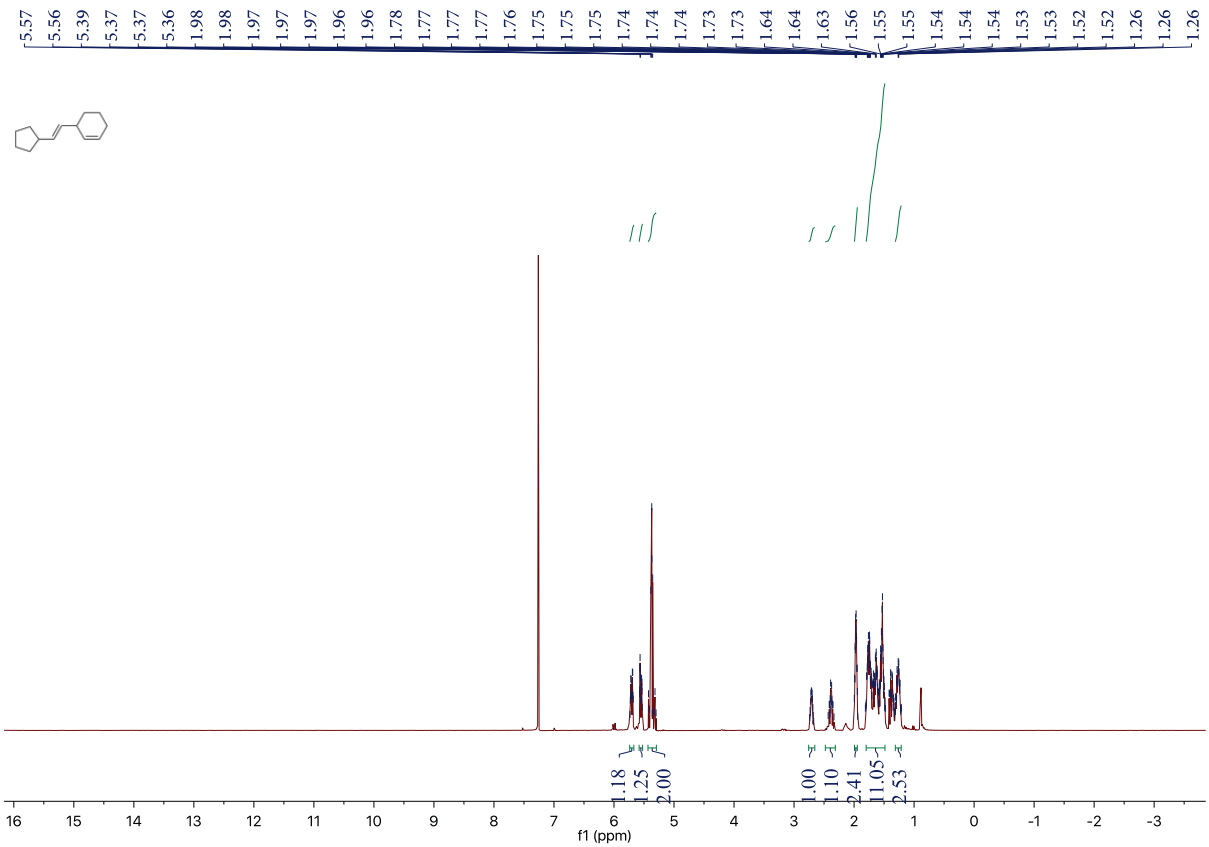


Figure S43 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **CTA3**

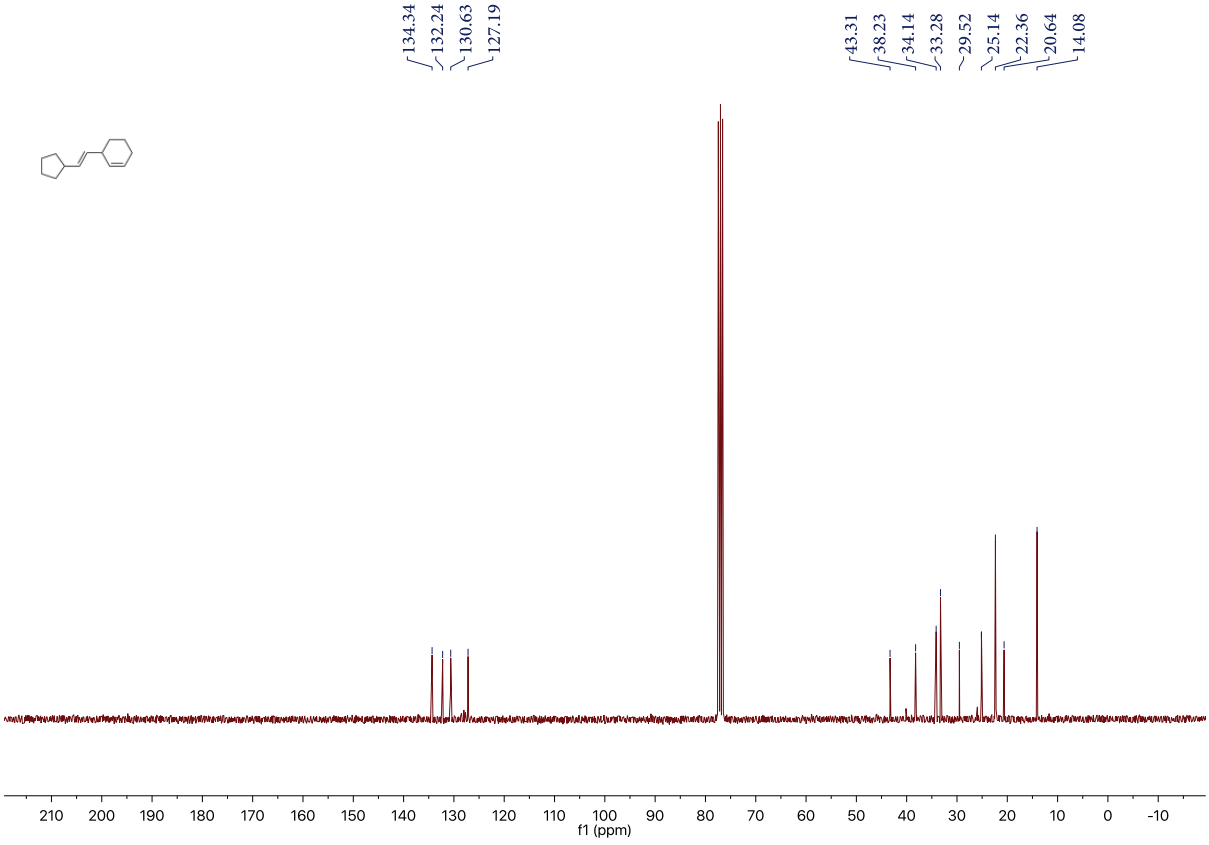


Figure S44 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **CTA3**

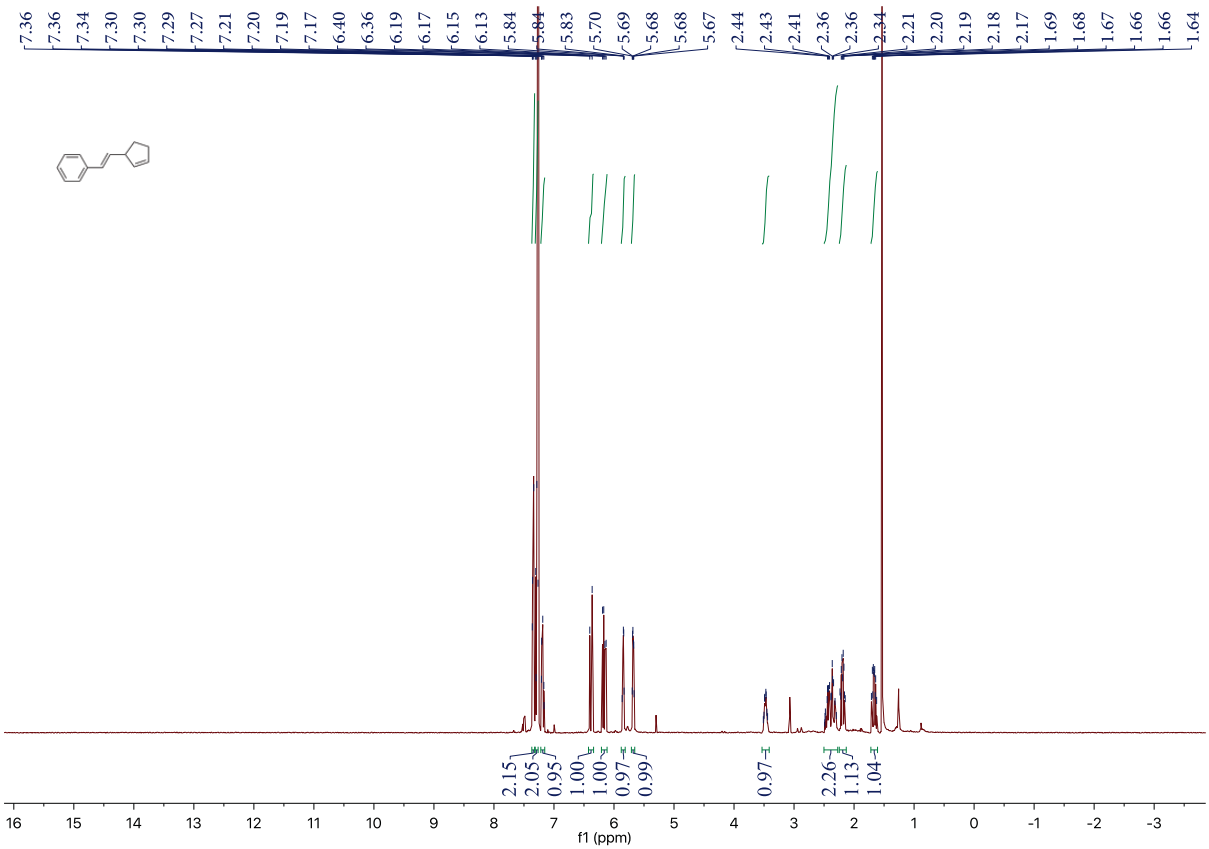


Figure S45 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA4**

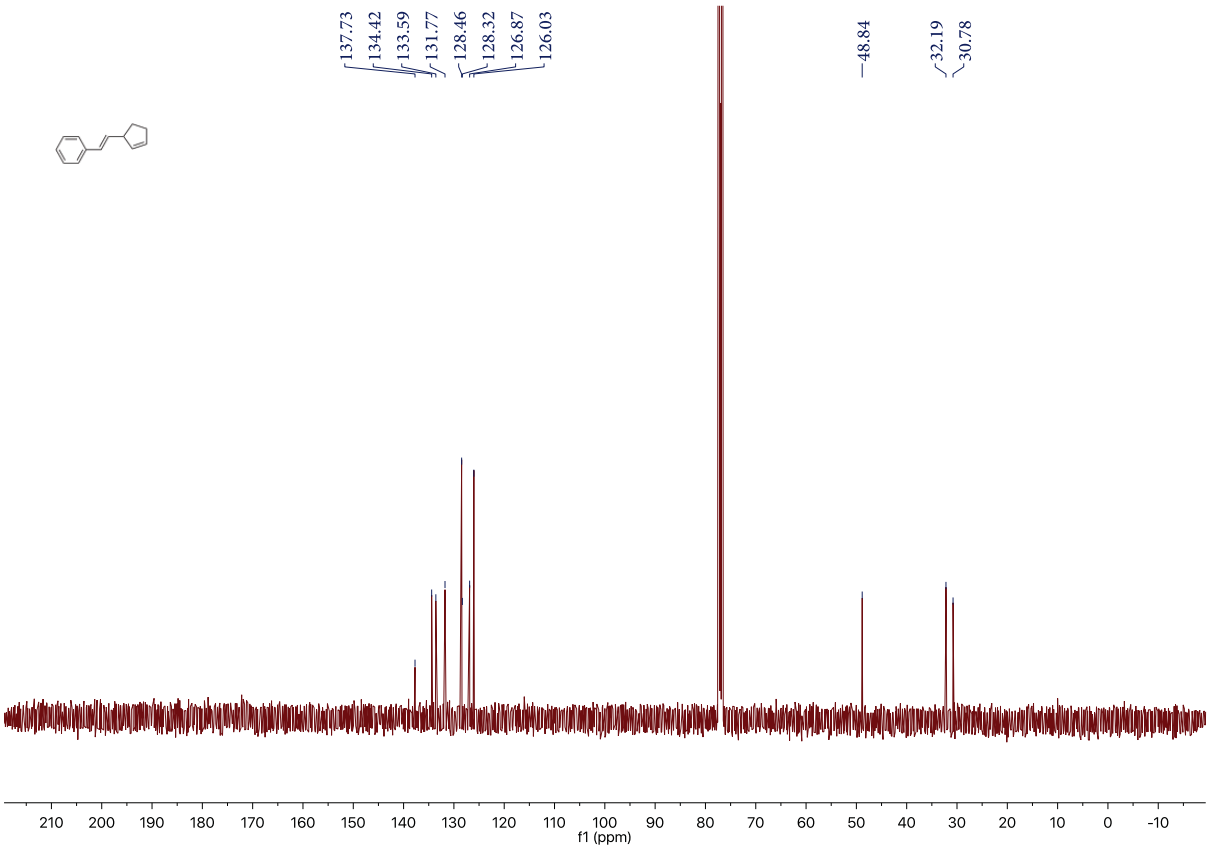


Figure S46 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA4**

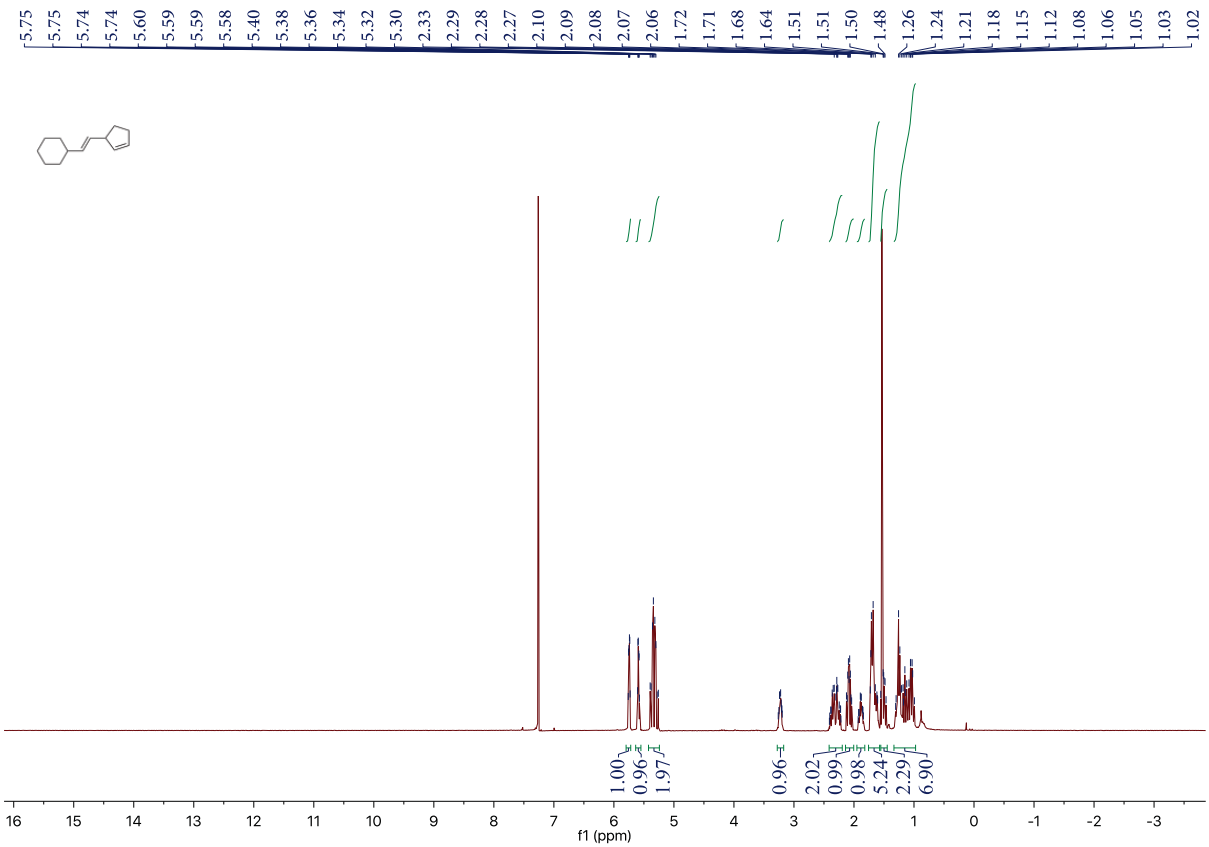


Figure S47 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA5**

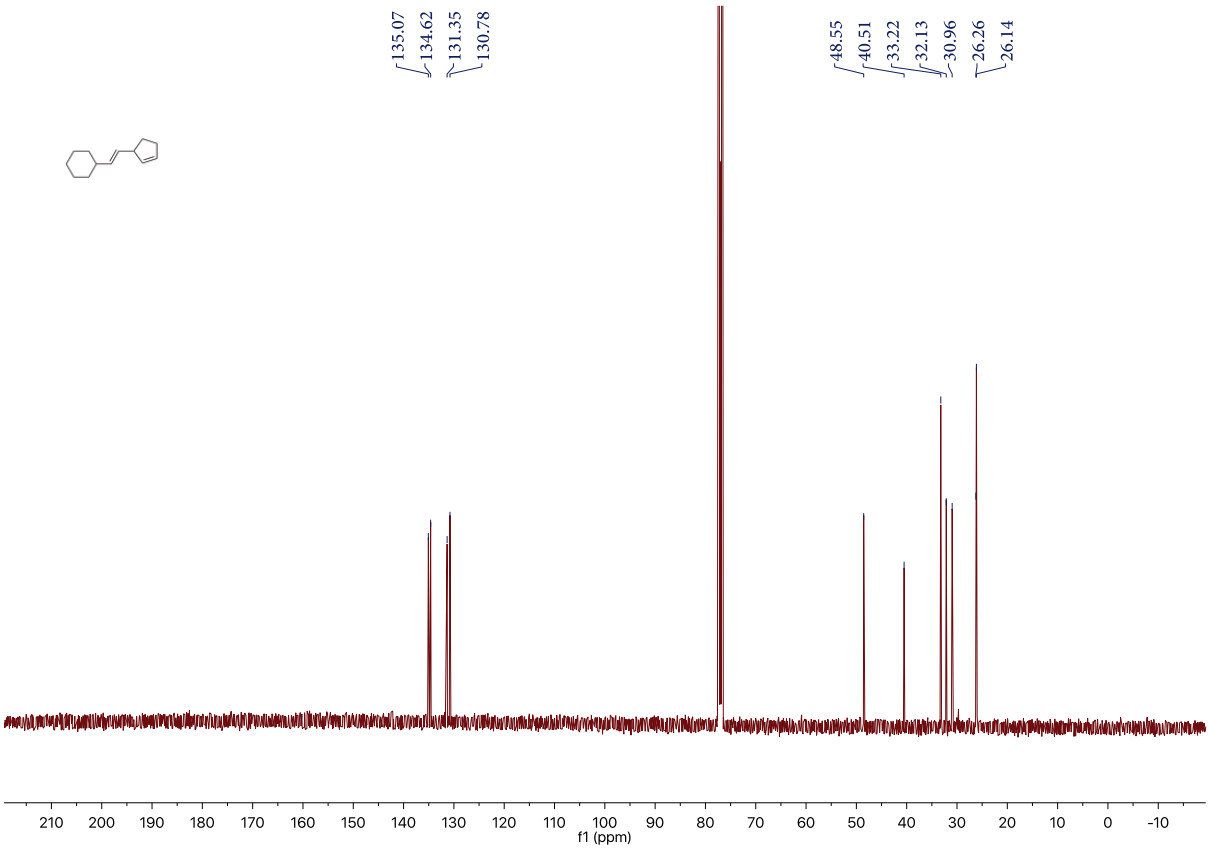


Figure S48 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA5**

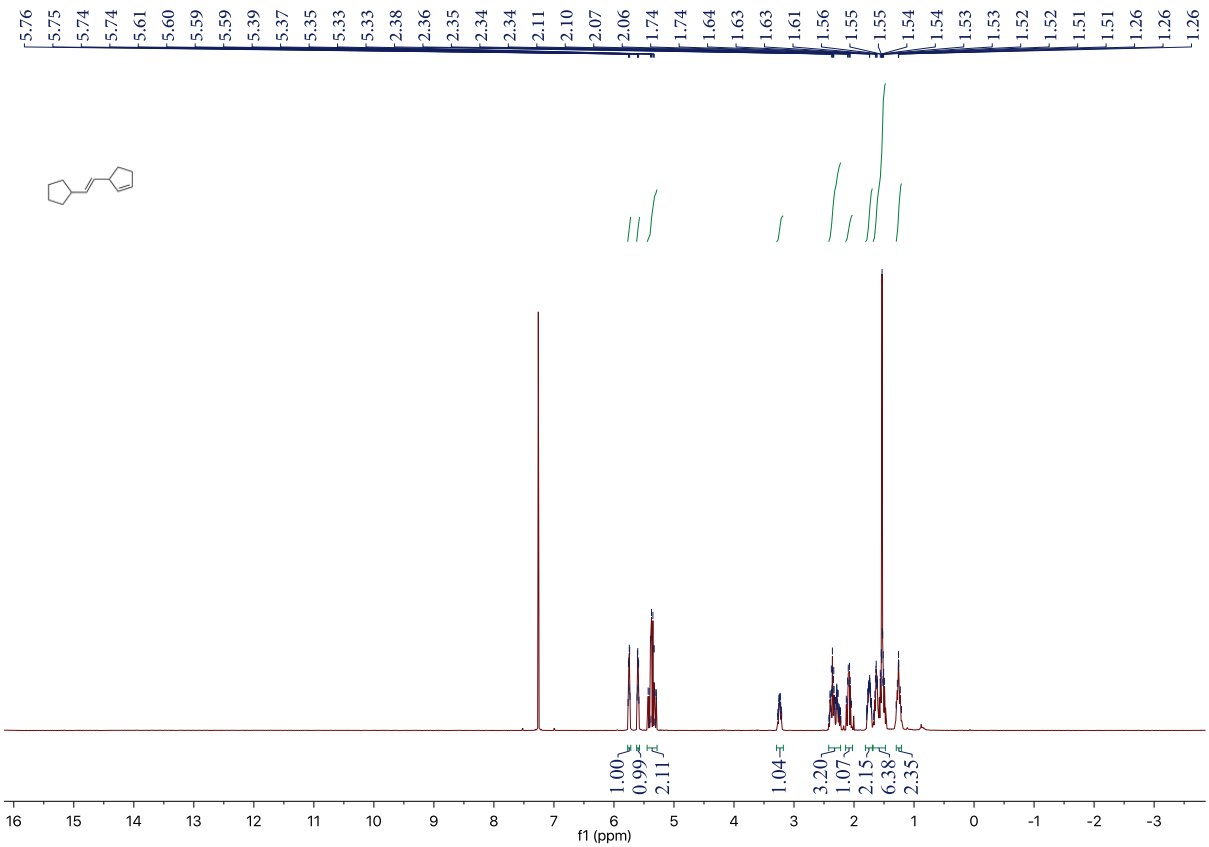


Figure S49 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA6**

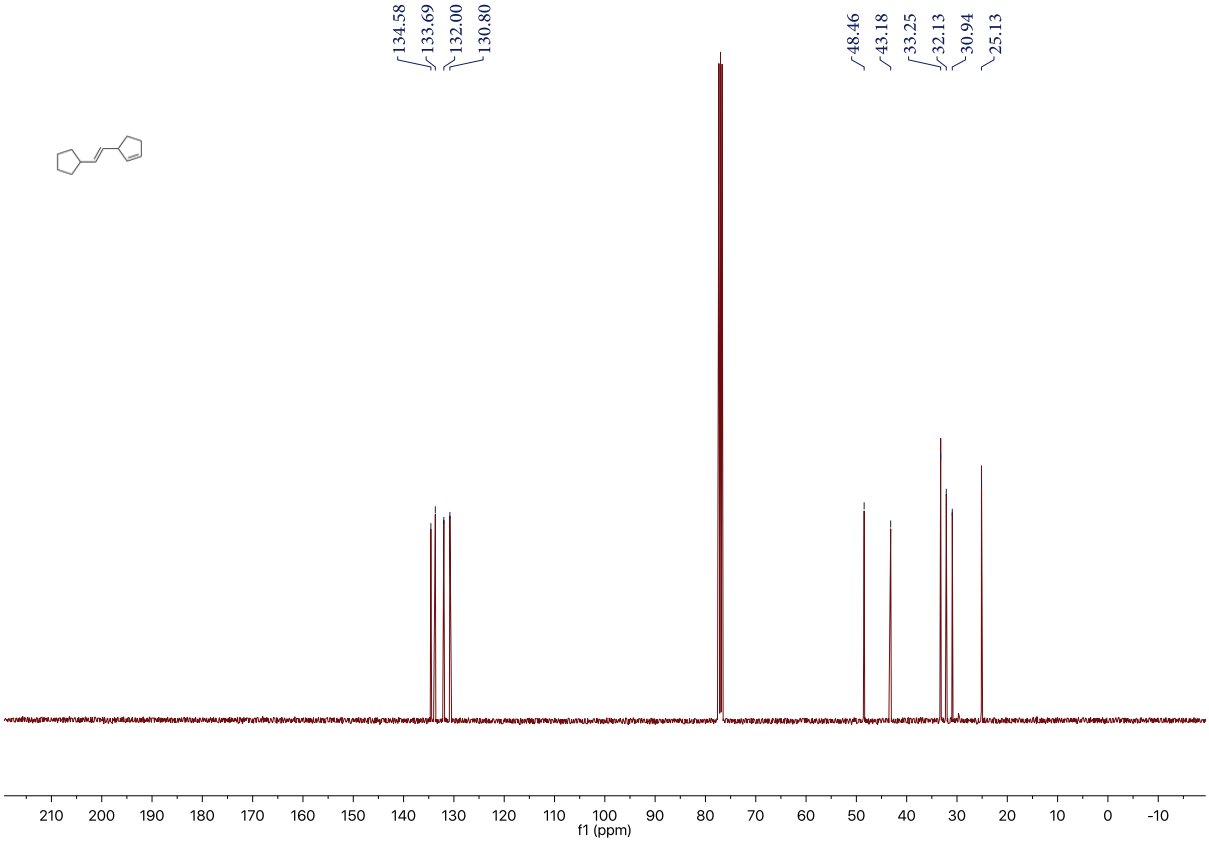


Figure S50 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA6**

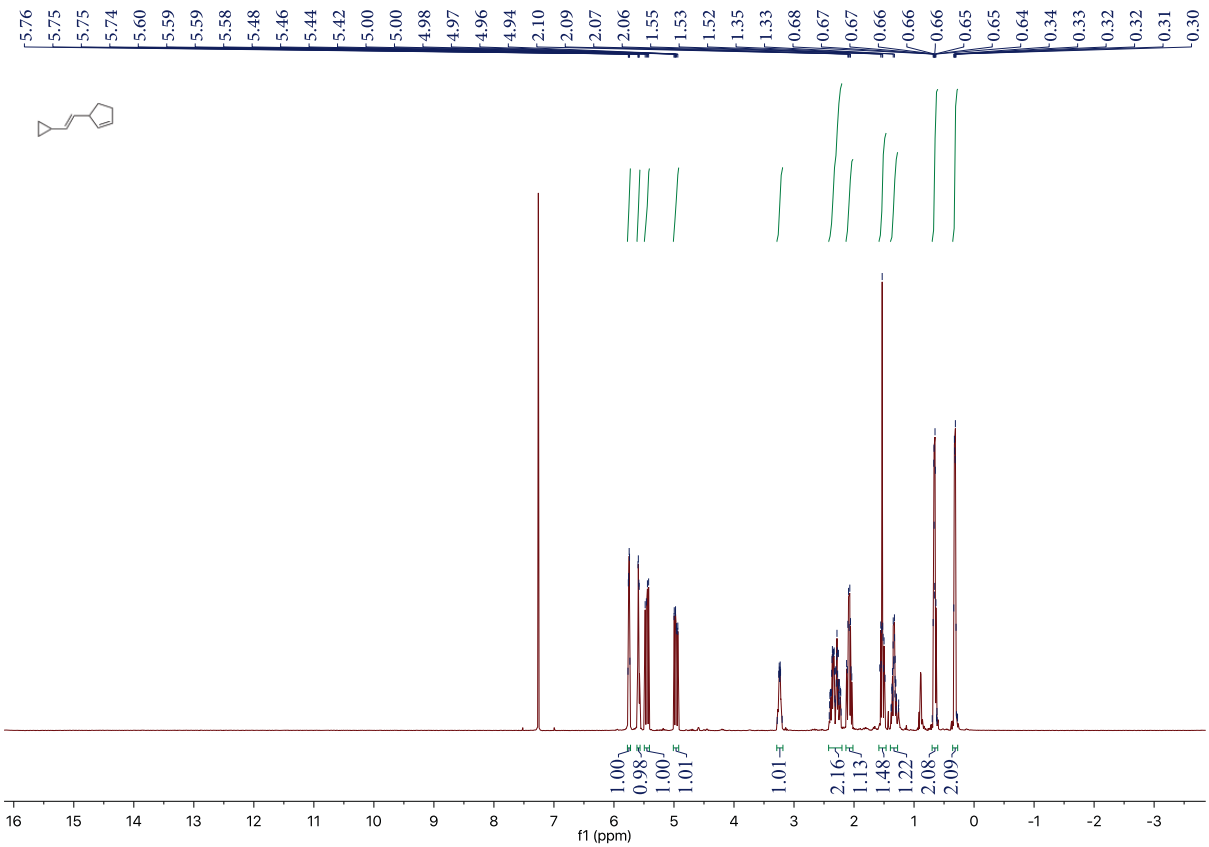


Figure S51 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA7**

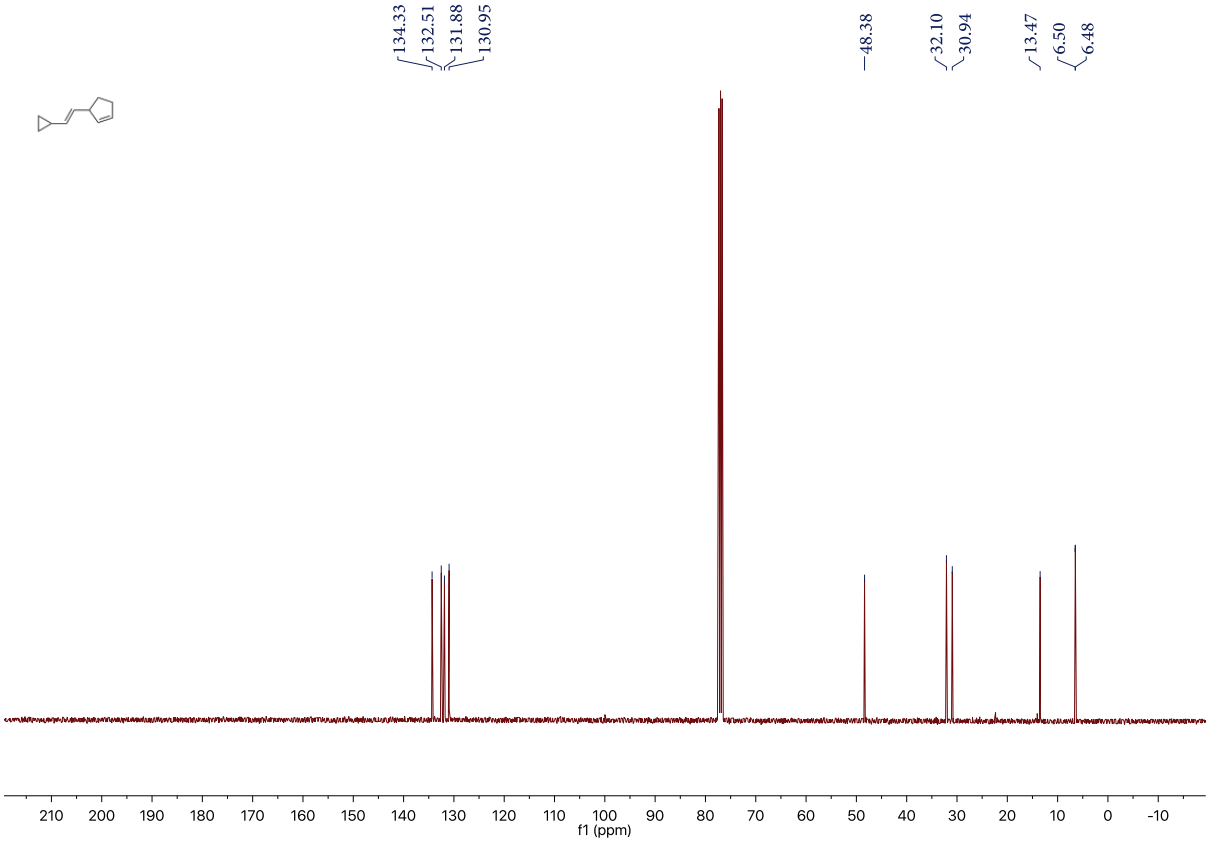


Figure S52 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA7**

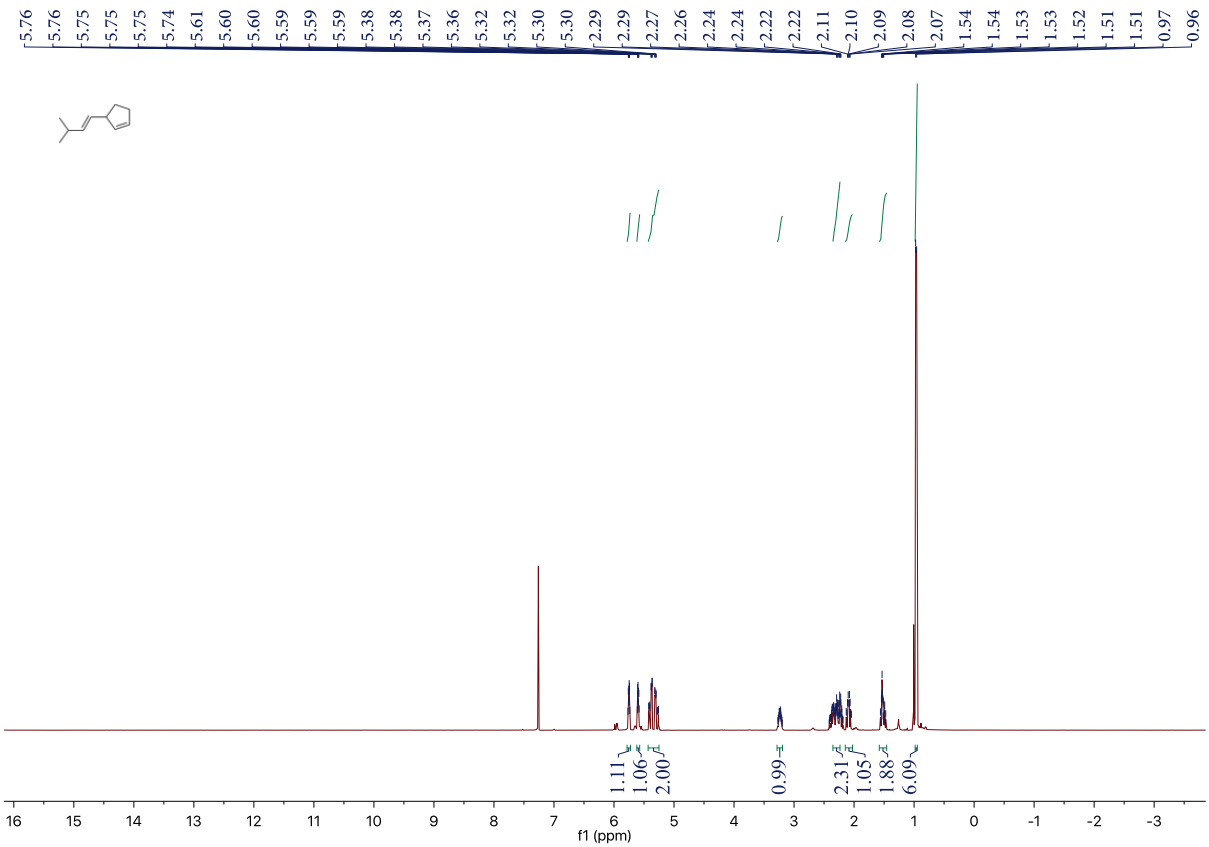


Figure S53 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA8**

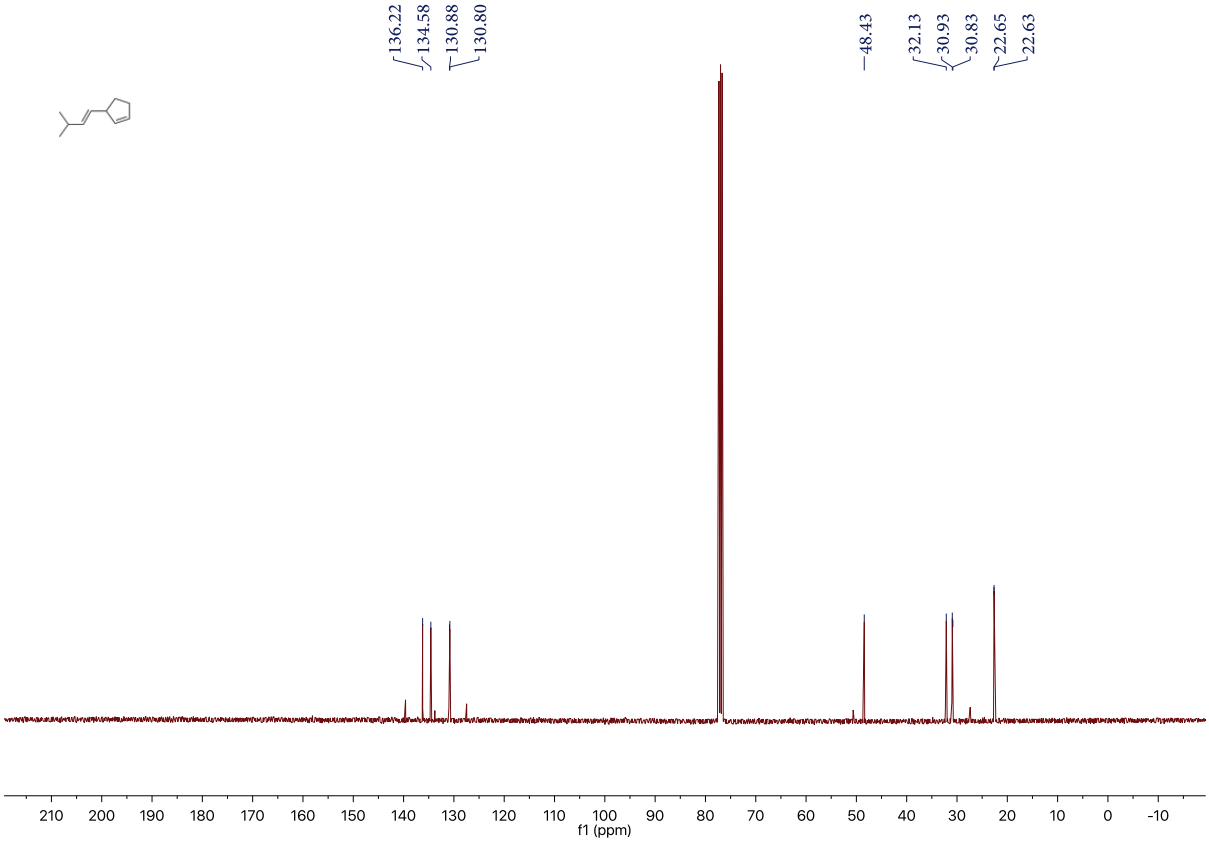


Figure S54 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA8**

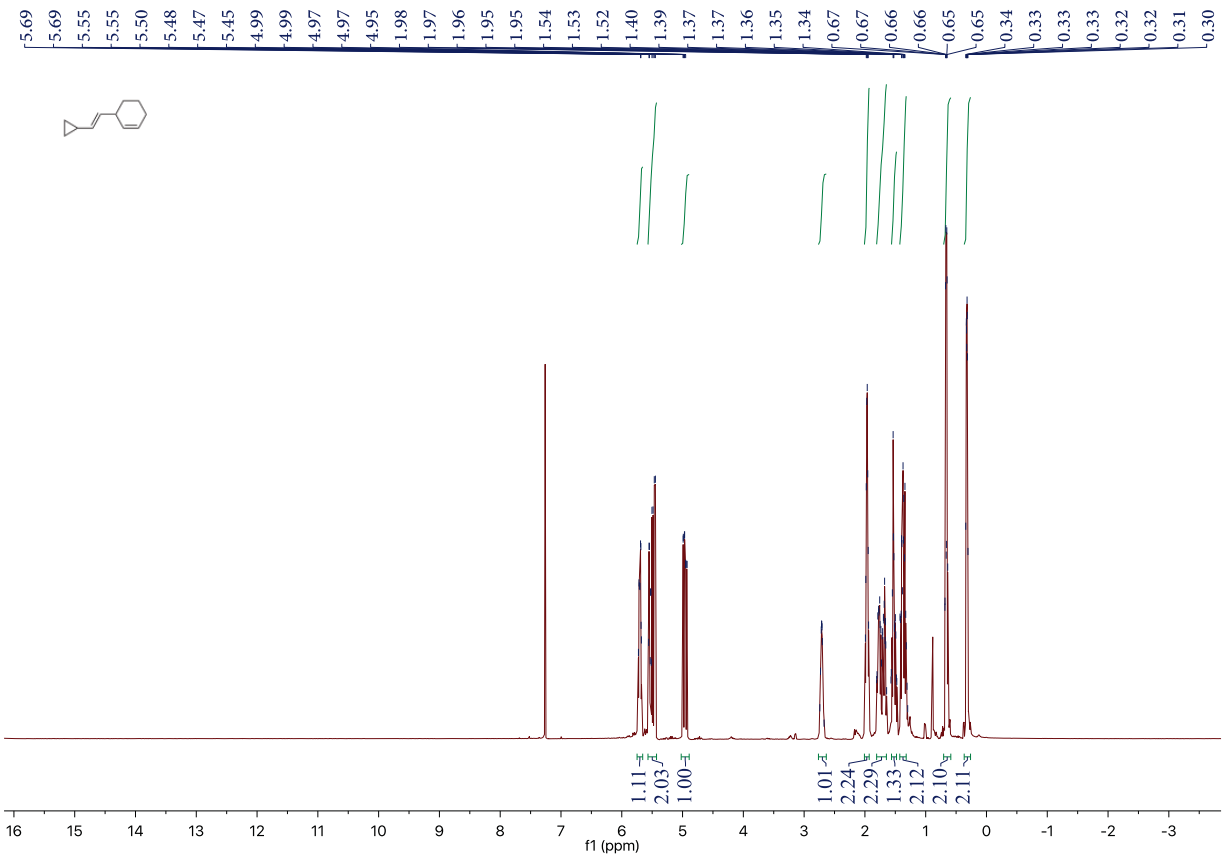


Figure S55 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA9**

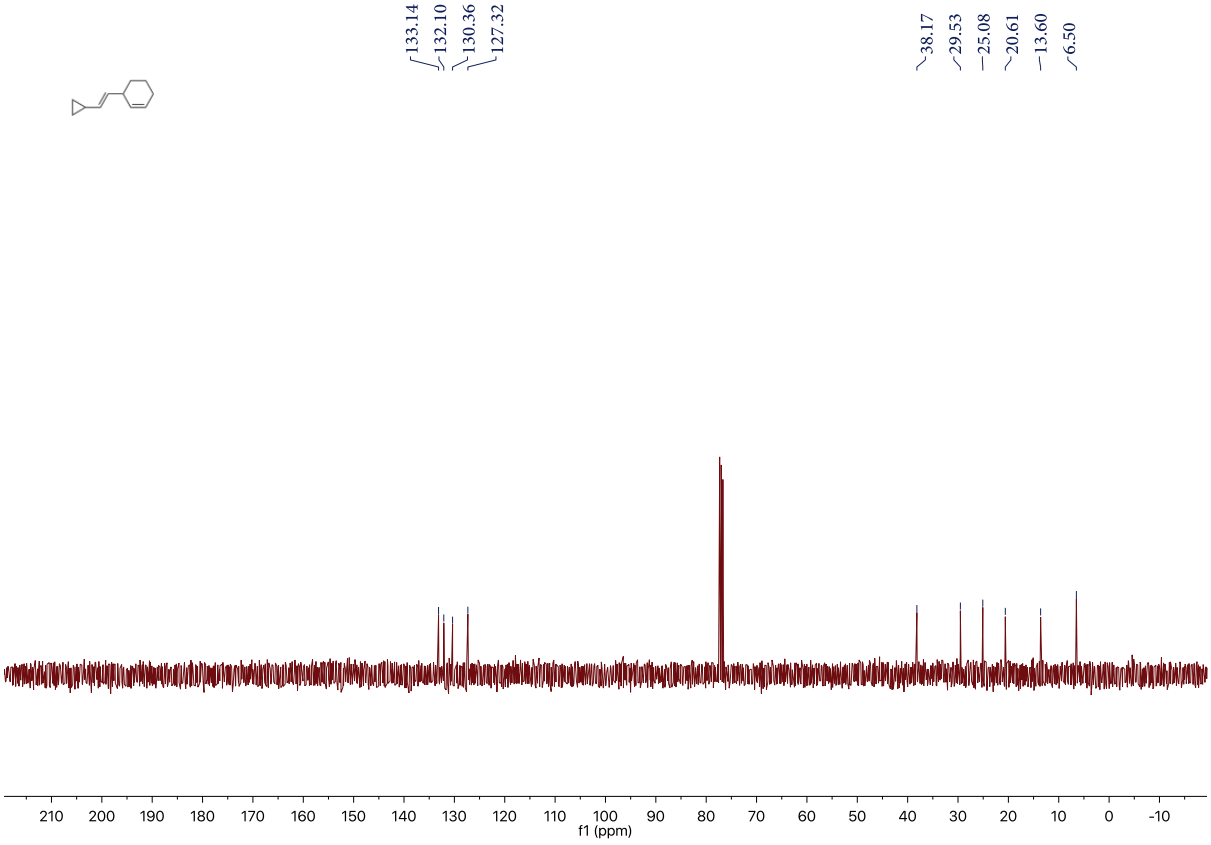


Figure S56 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA9**

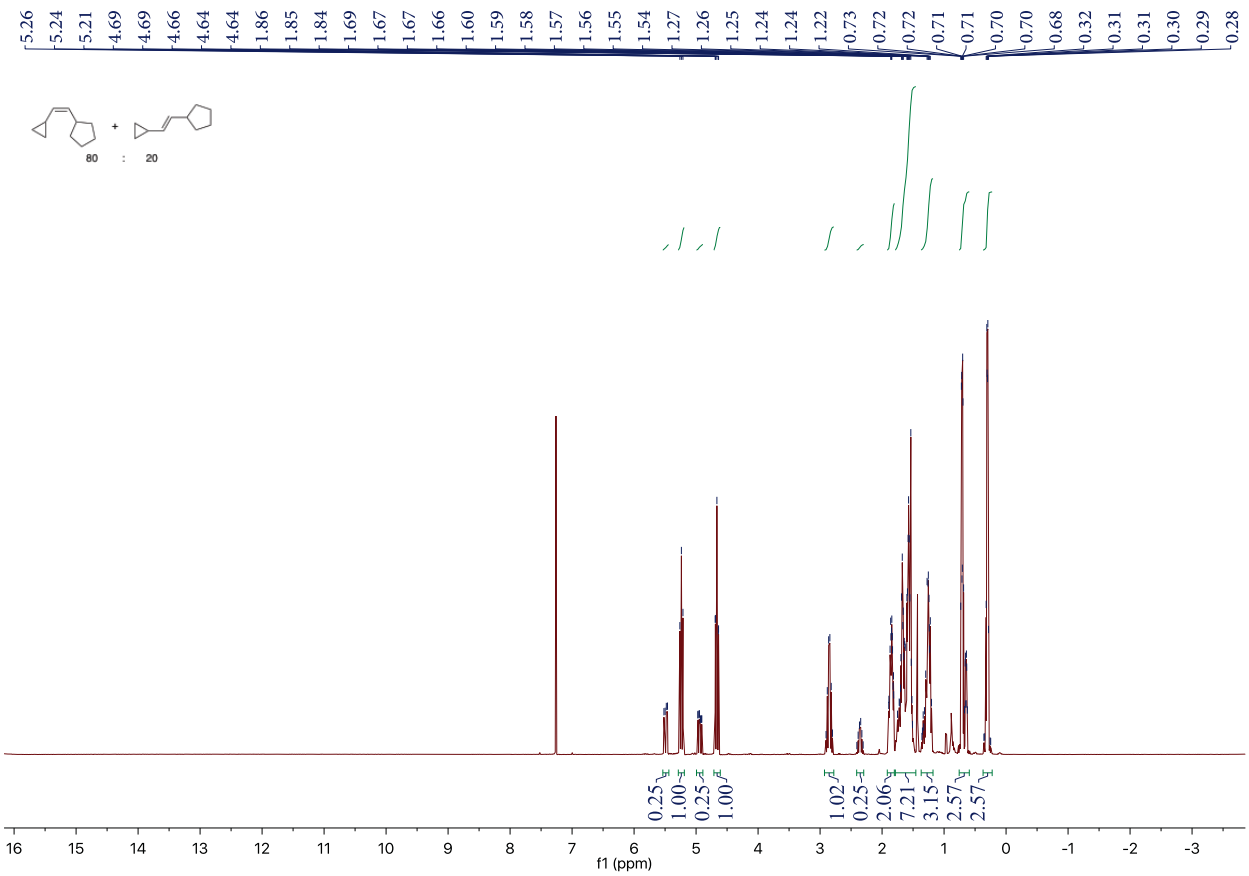


Figure S57 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA10**

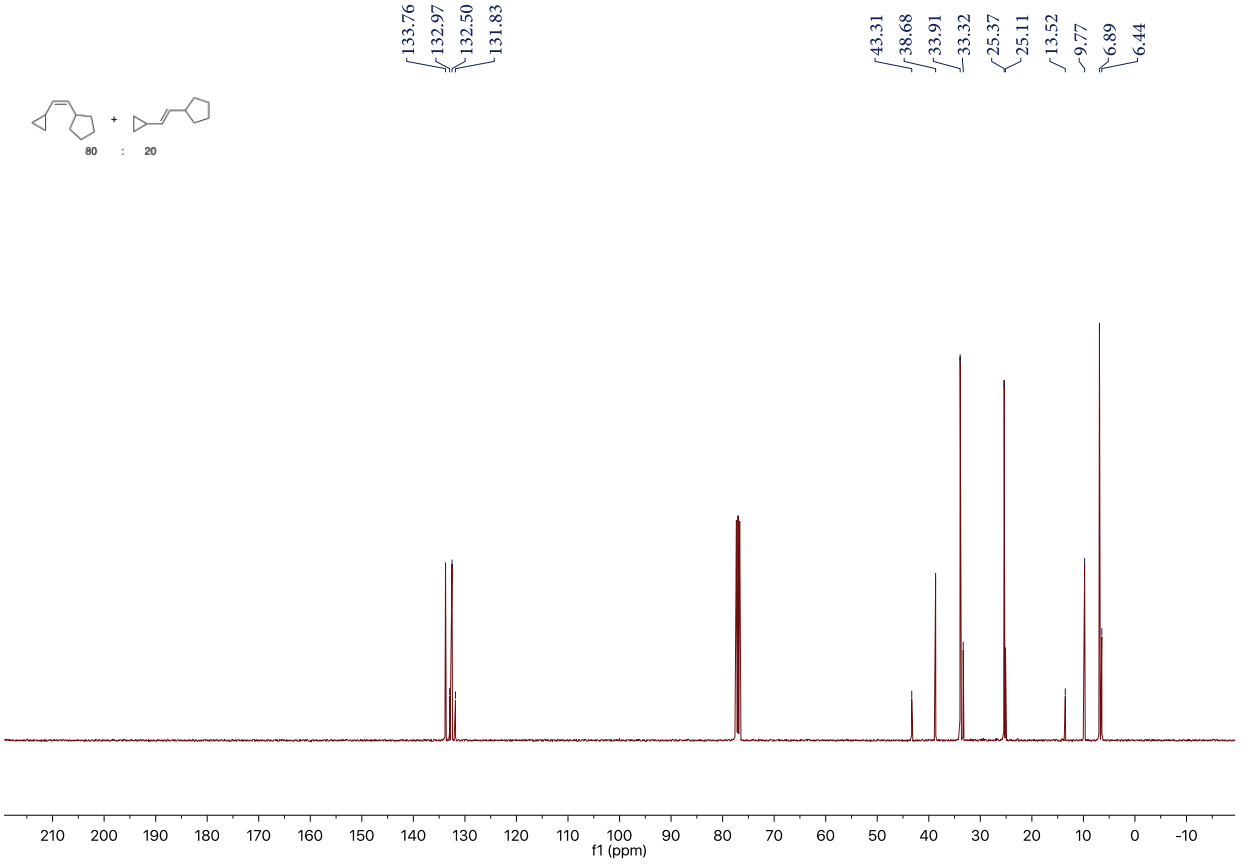


Figure S58 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA10**

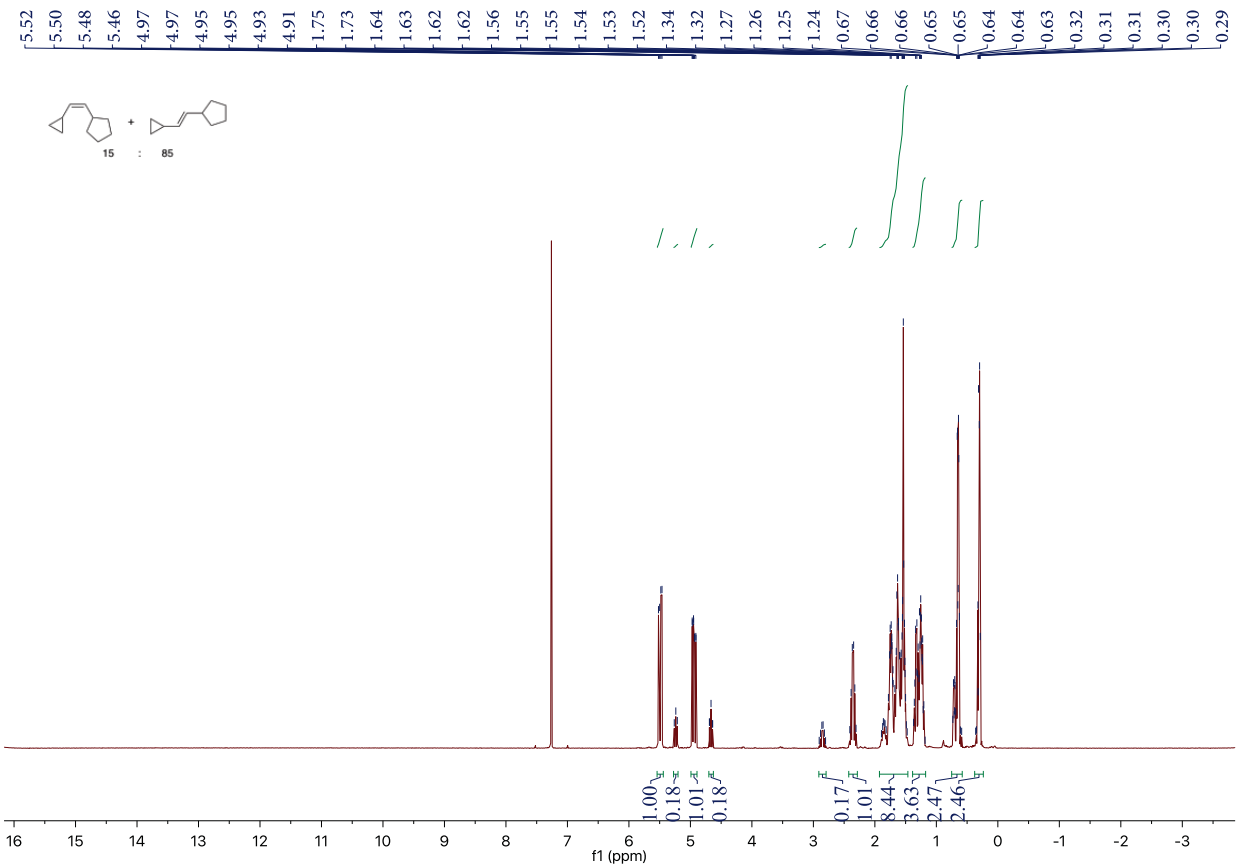


Figure S59 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA11**

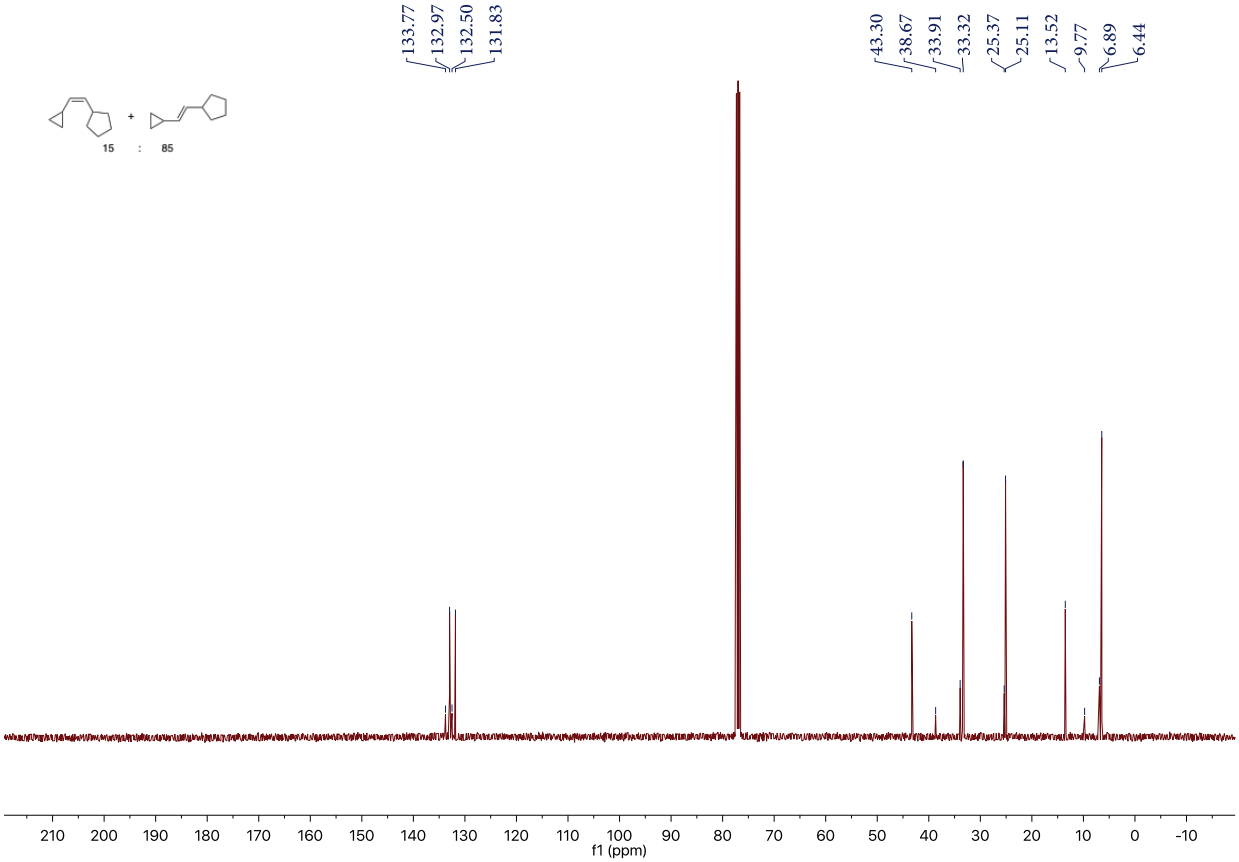


Figure S60 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA11**

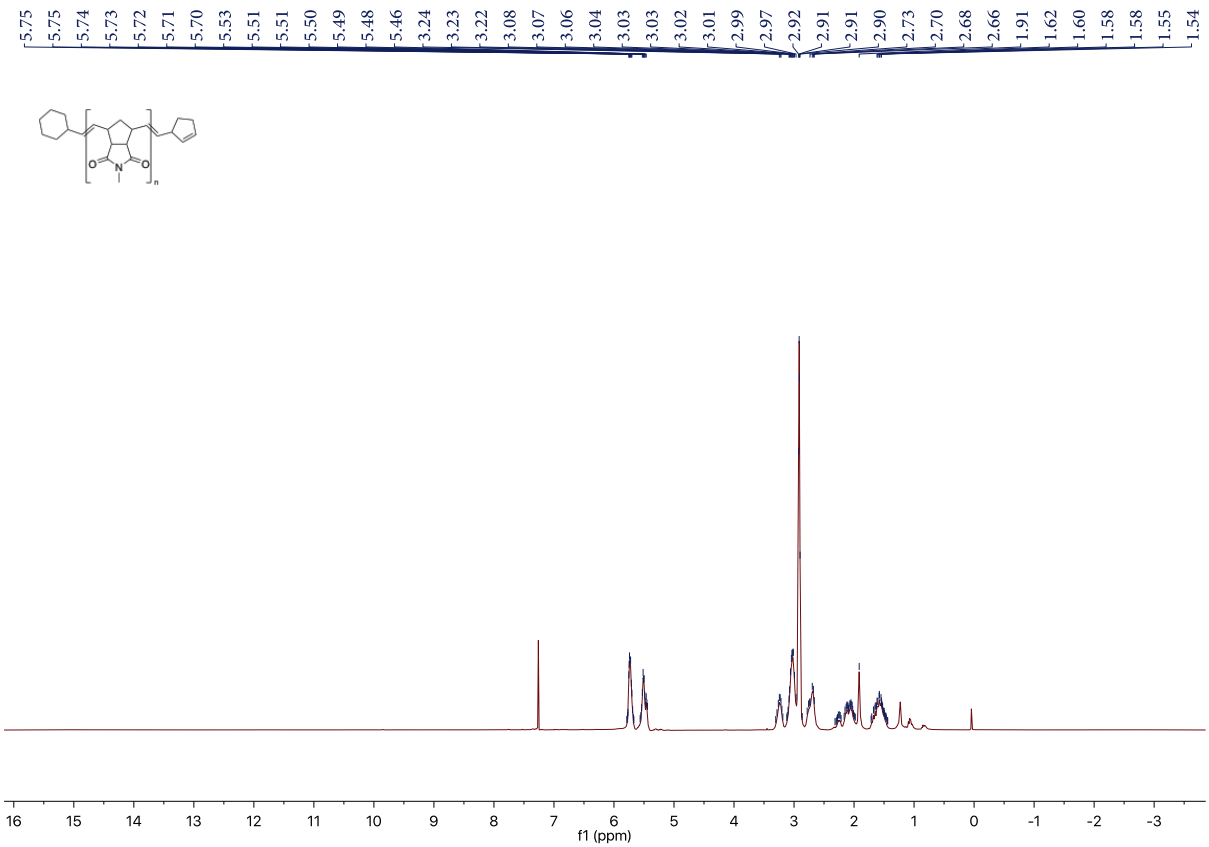


Figure S61 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 1**

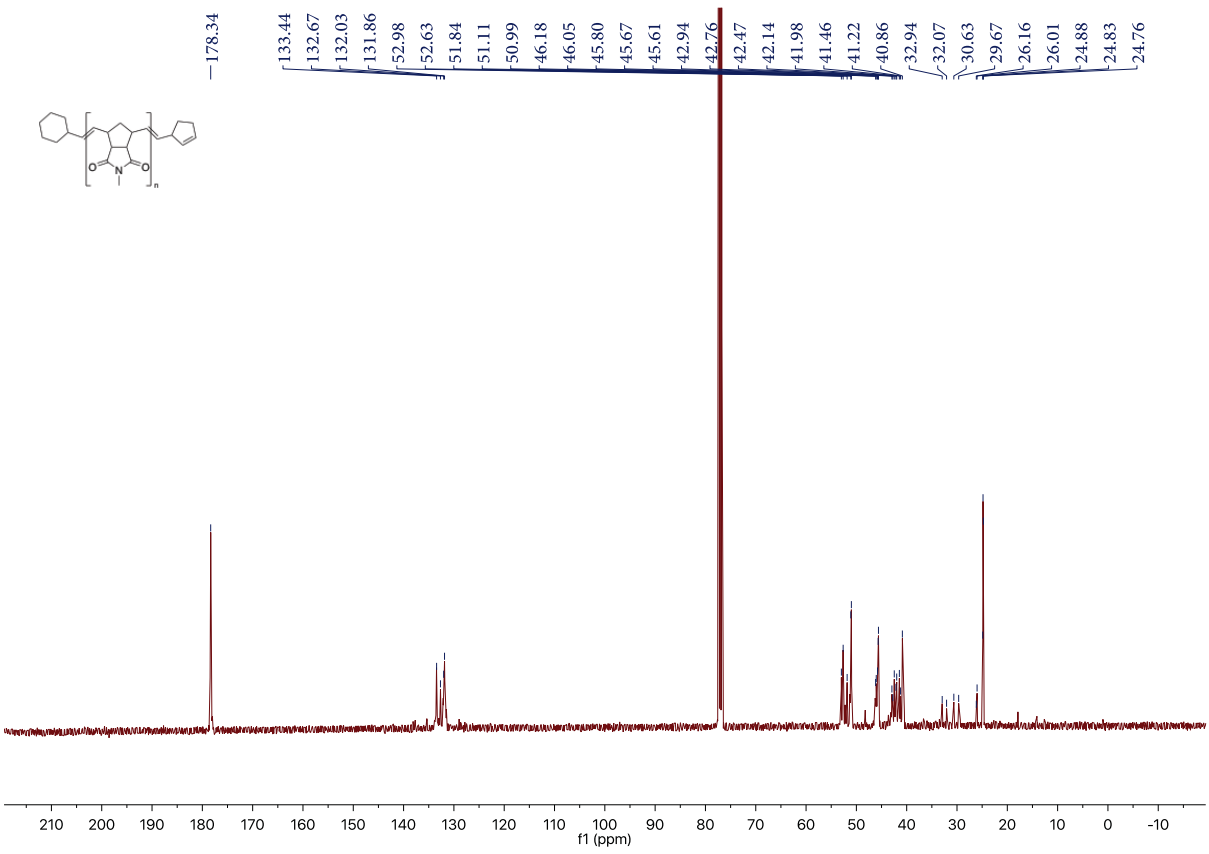


Figure S62 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 1**

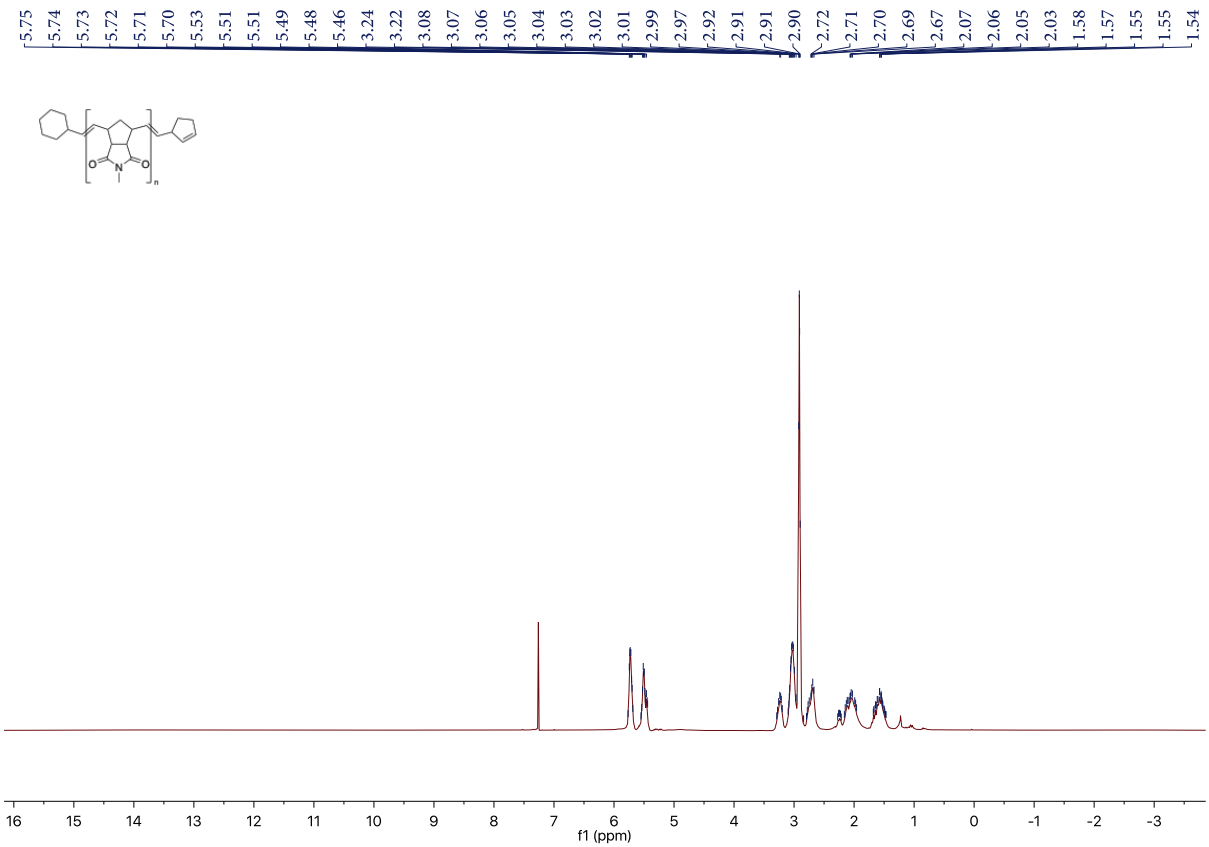


Figure S63 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 2**

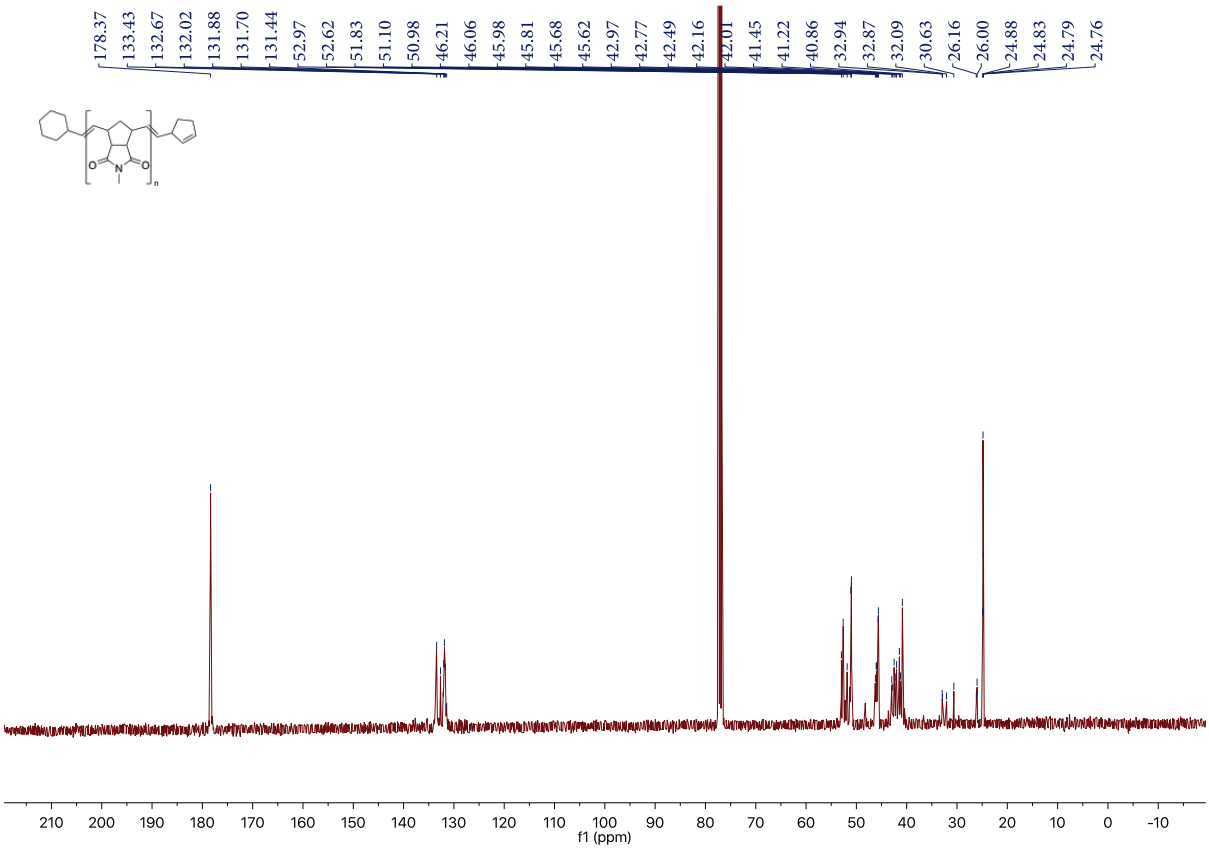


Figure S64 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 2**

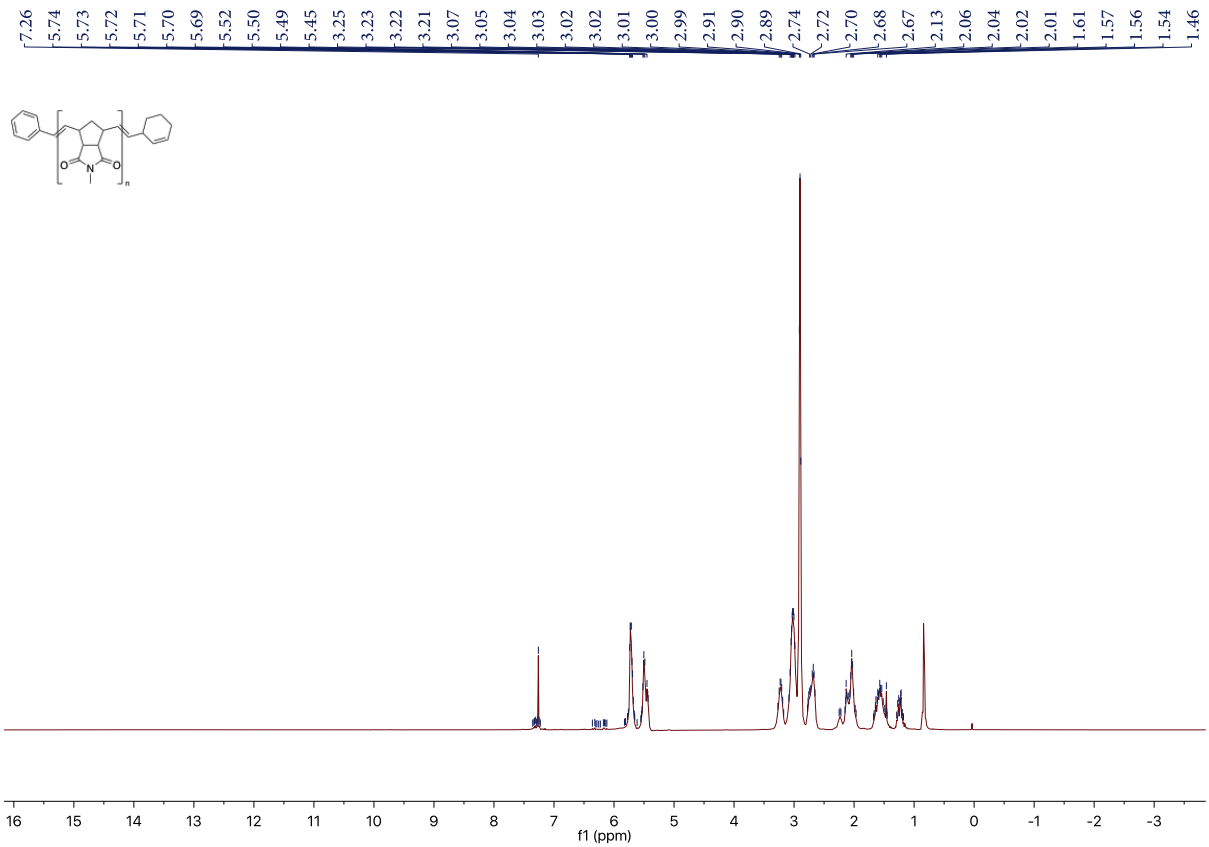


Figure S65 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 3**

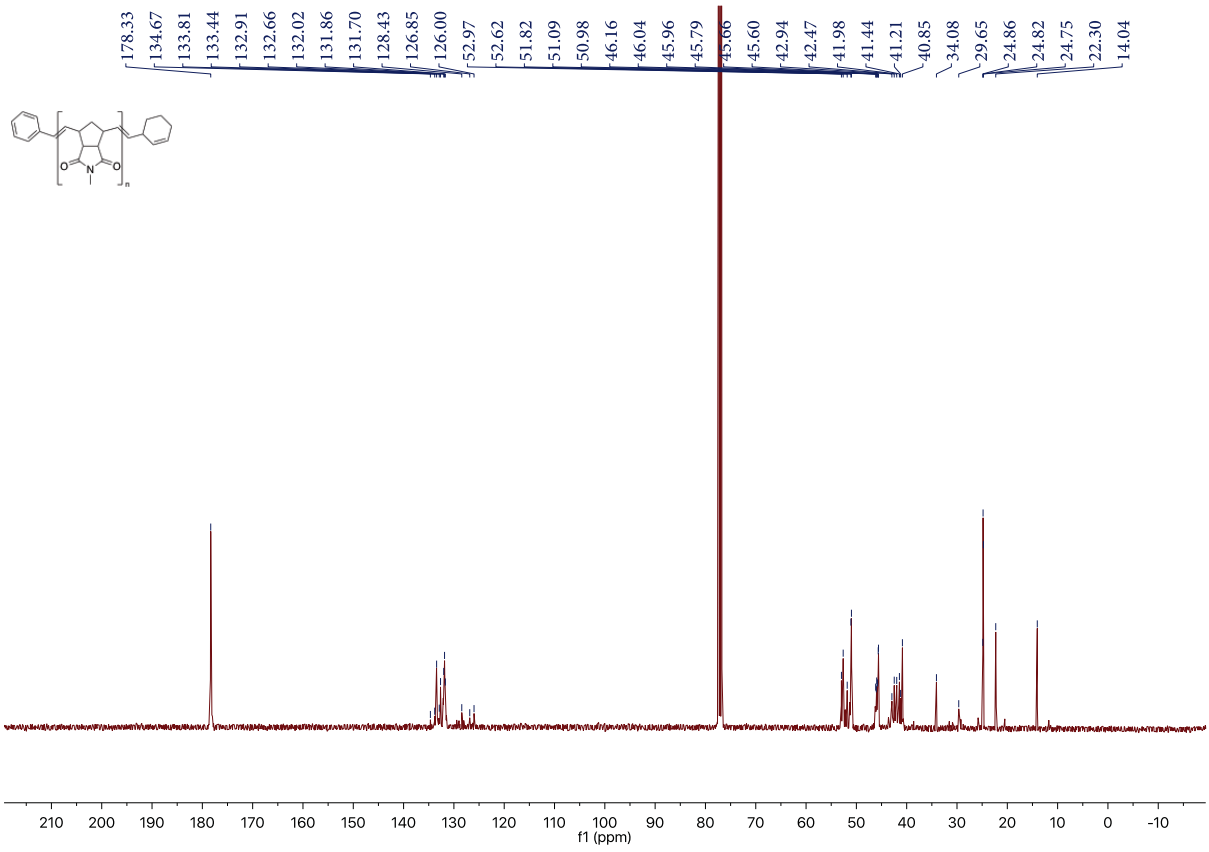


Figure S66 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 3**

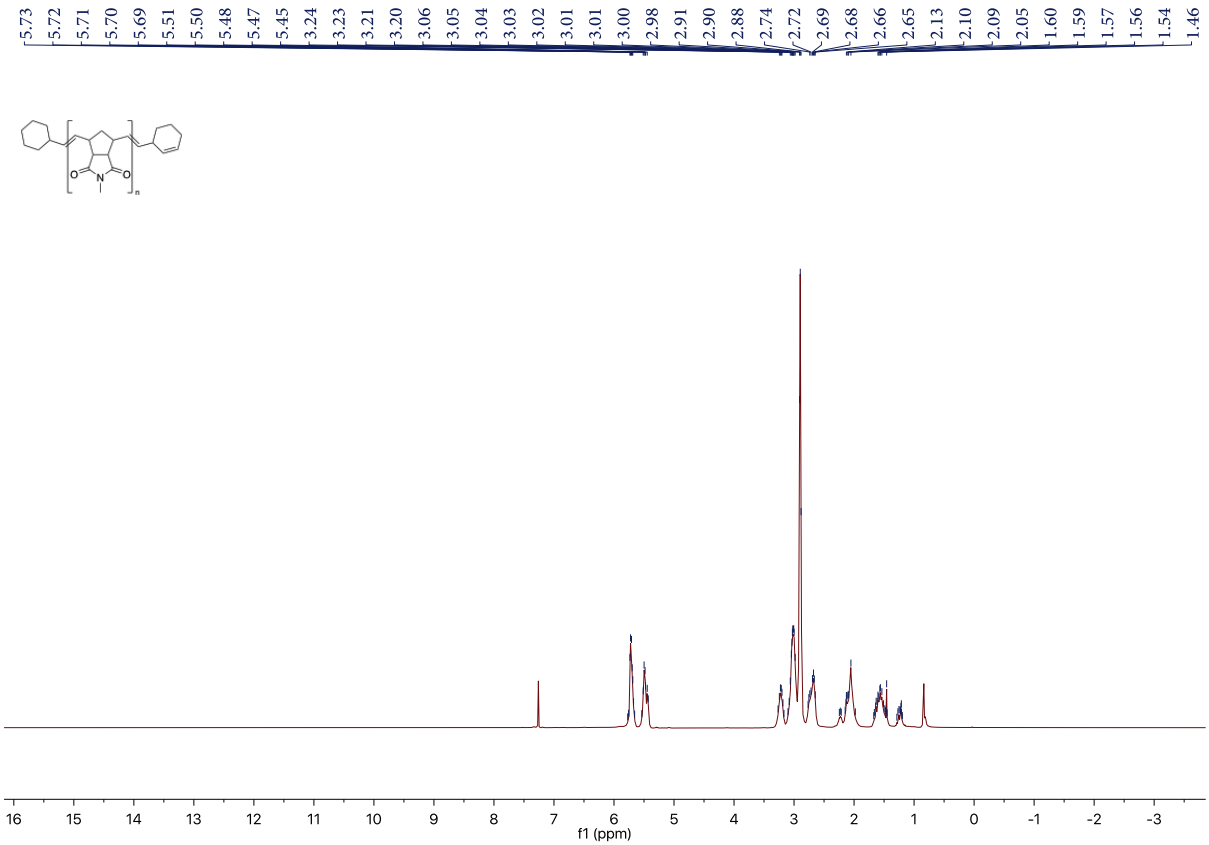


Figure S67 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 4**

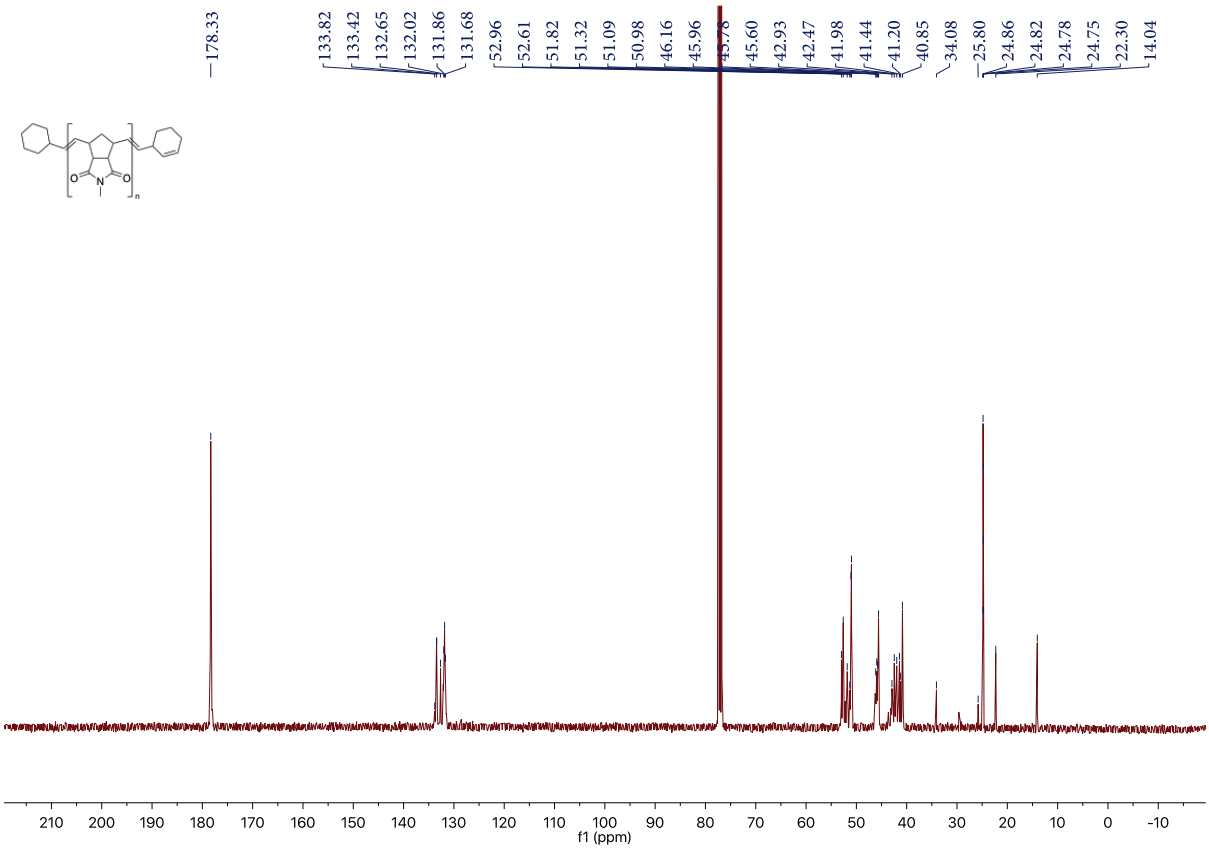


Figure S68 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 4**

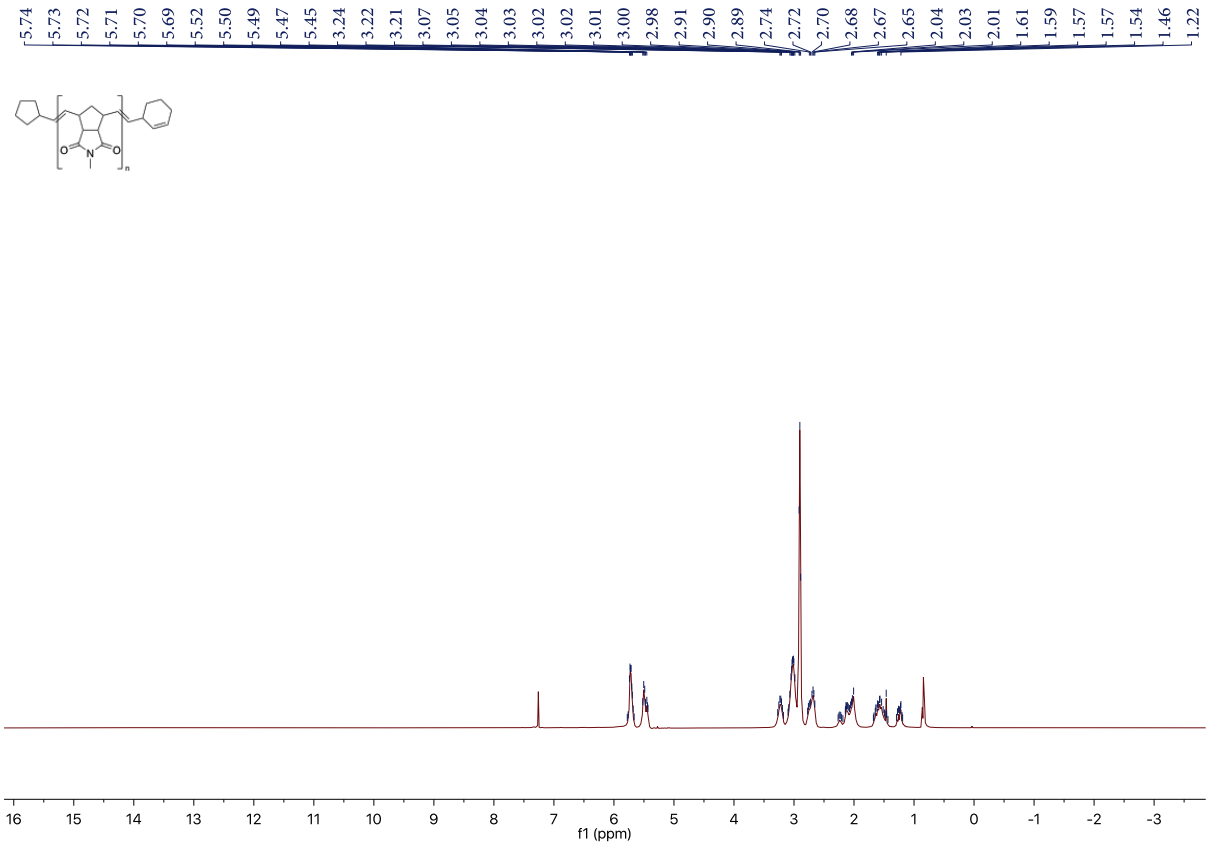


Figure S69 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 5**

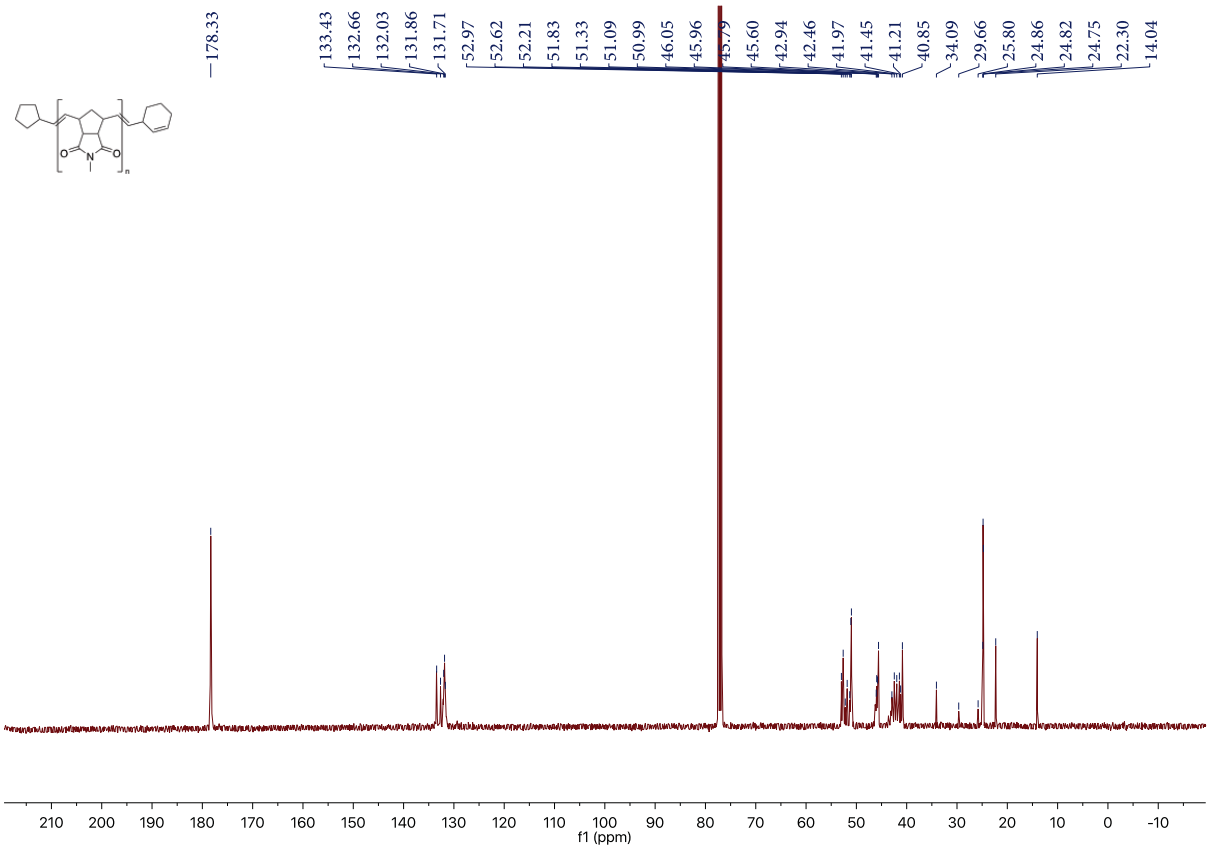


Figure S70 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 5**

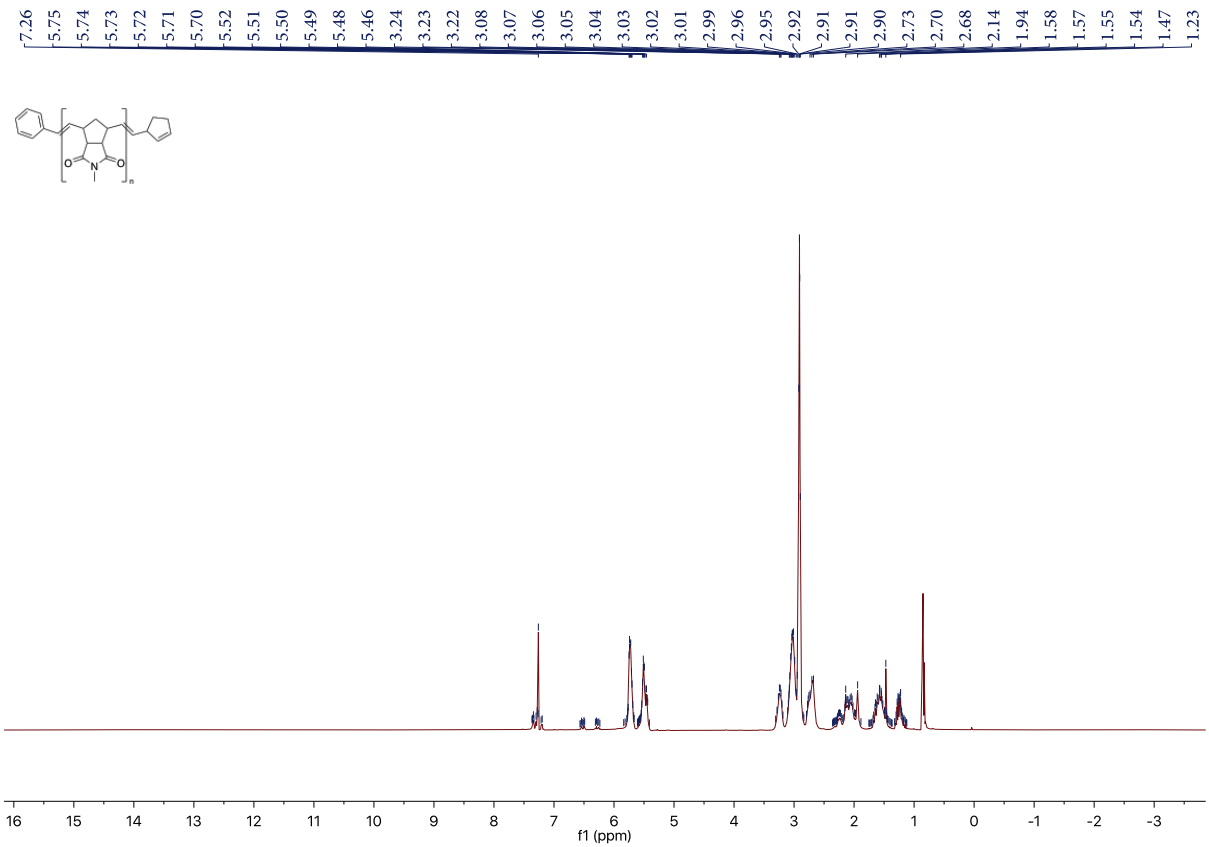


Figure S71 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 6**

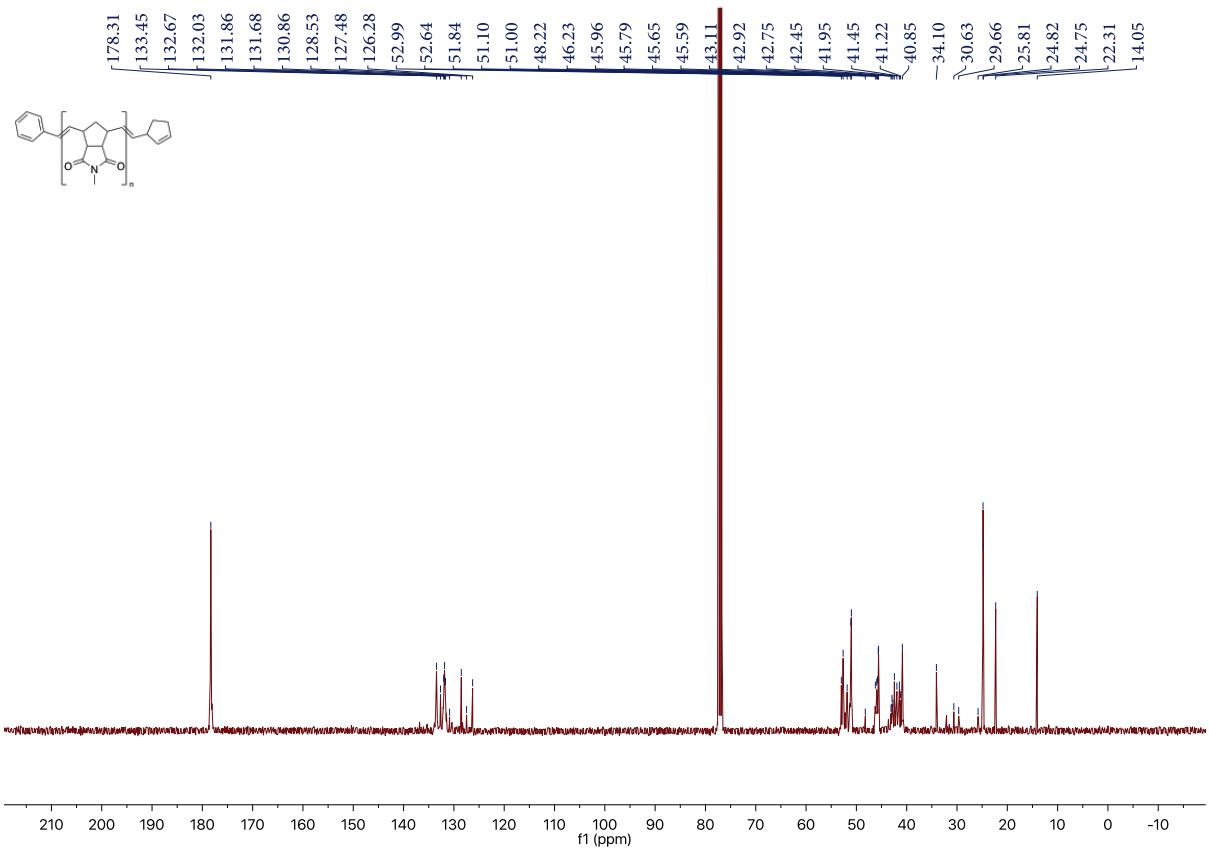


Figure S72 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 6**

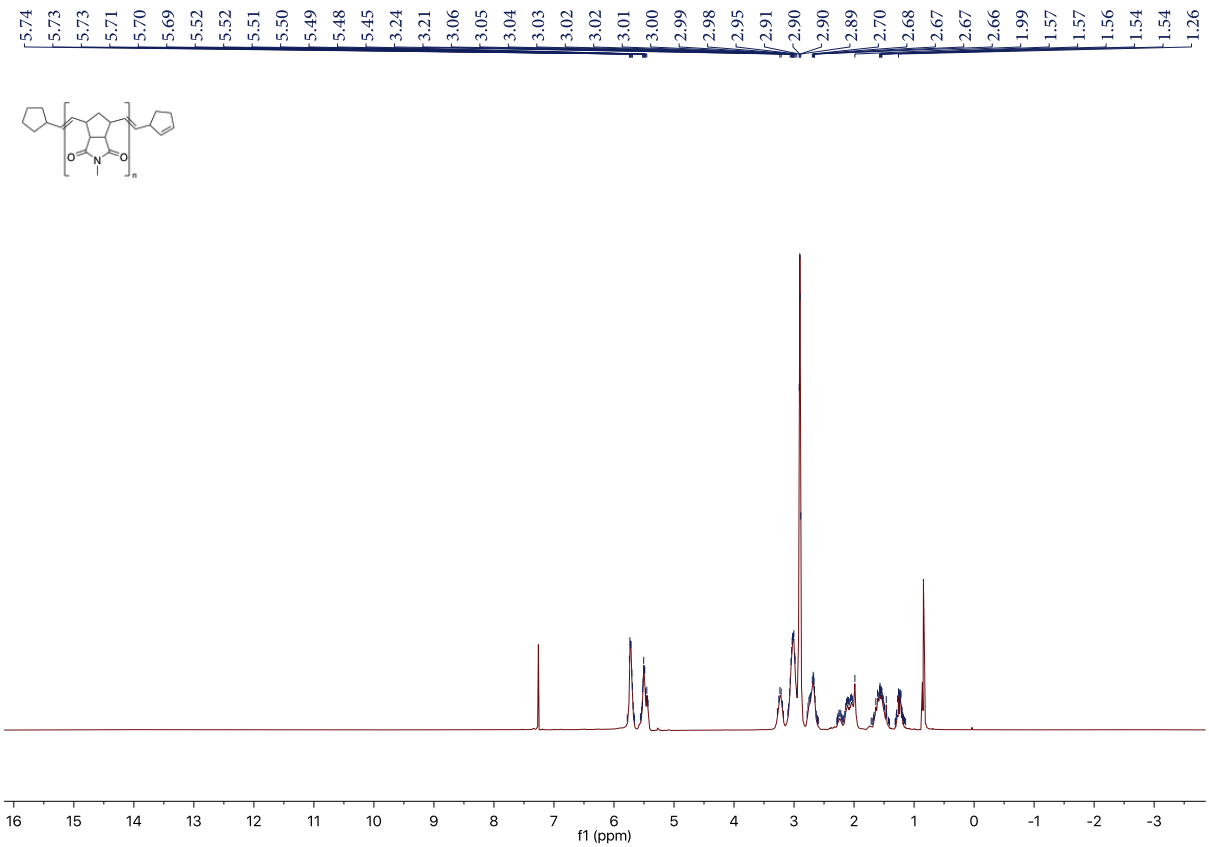


Figure S73 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 7**

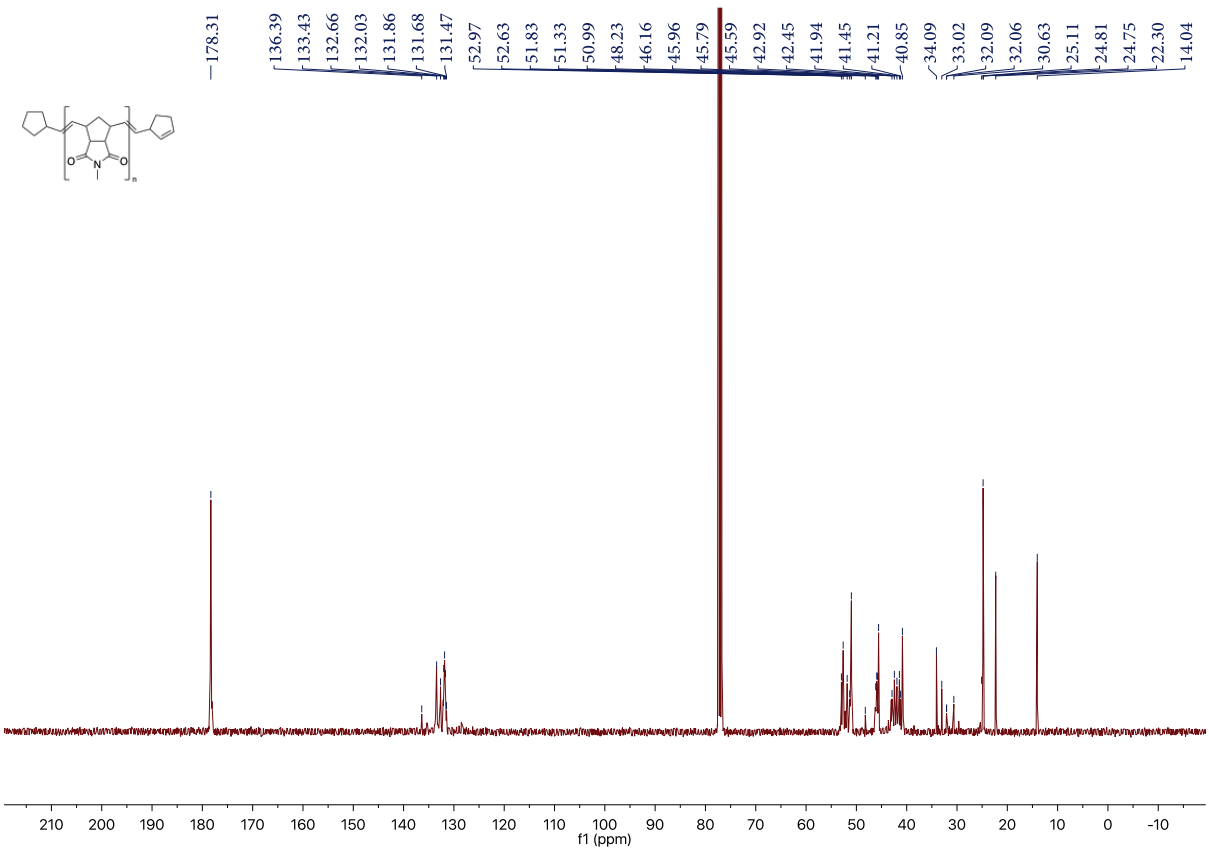


Figure S74 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 7**

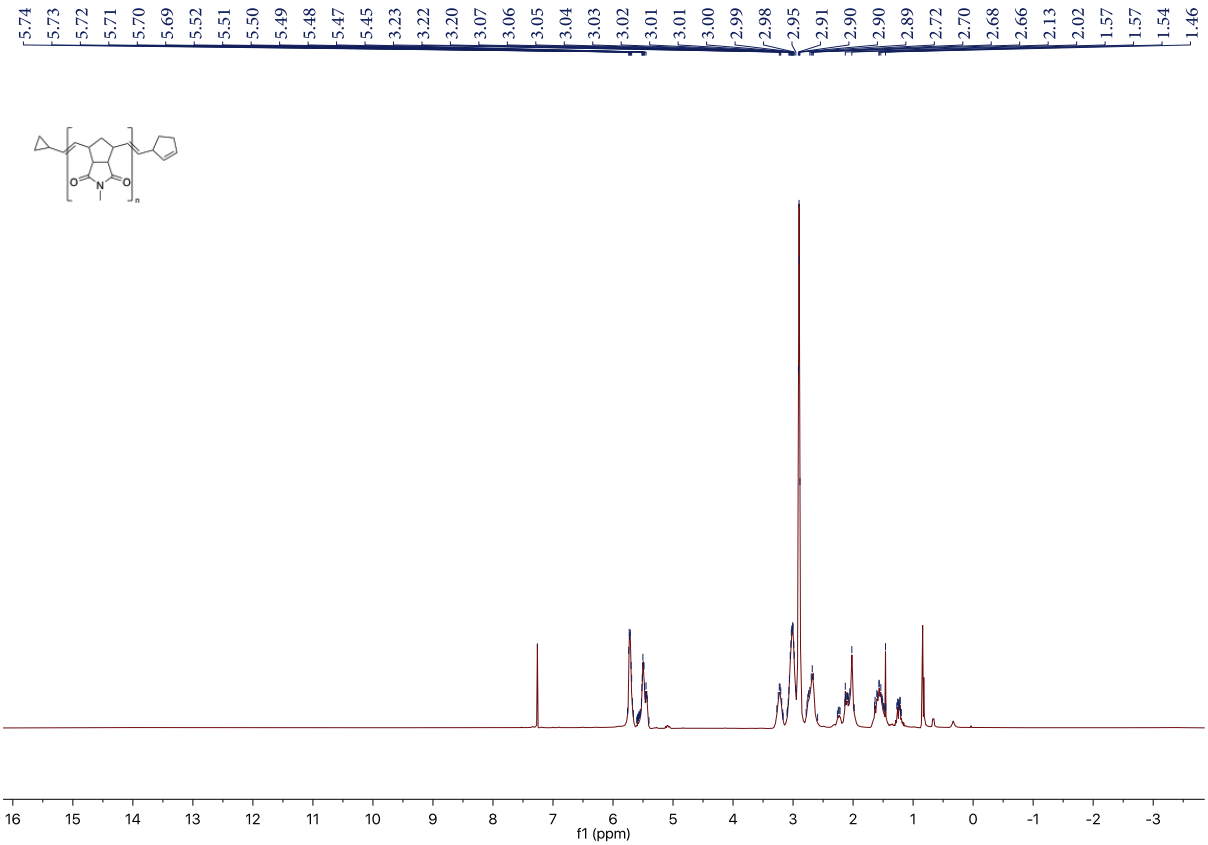


Figure S75 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 8**

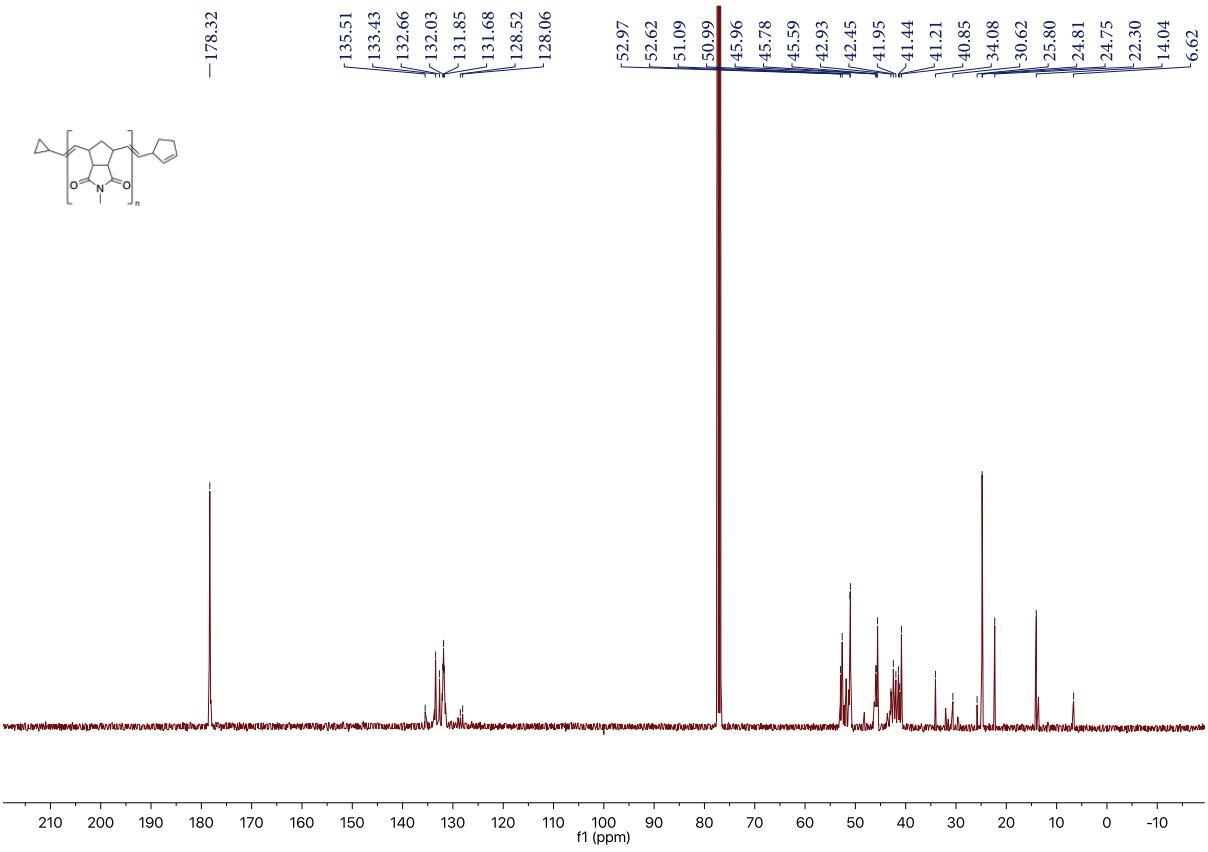


Figure S76 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 8**

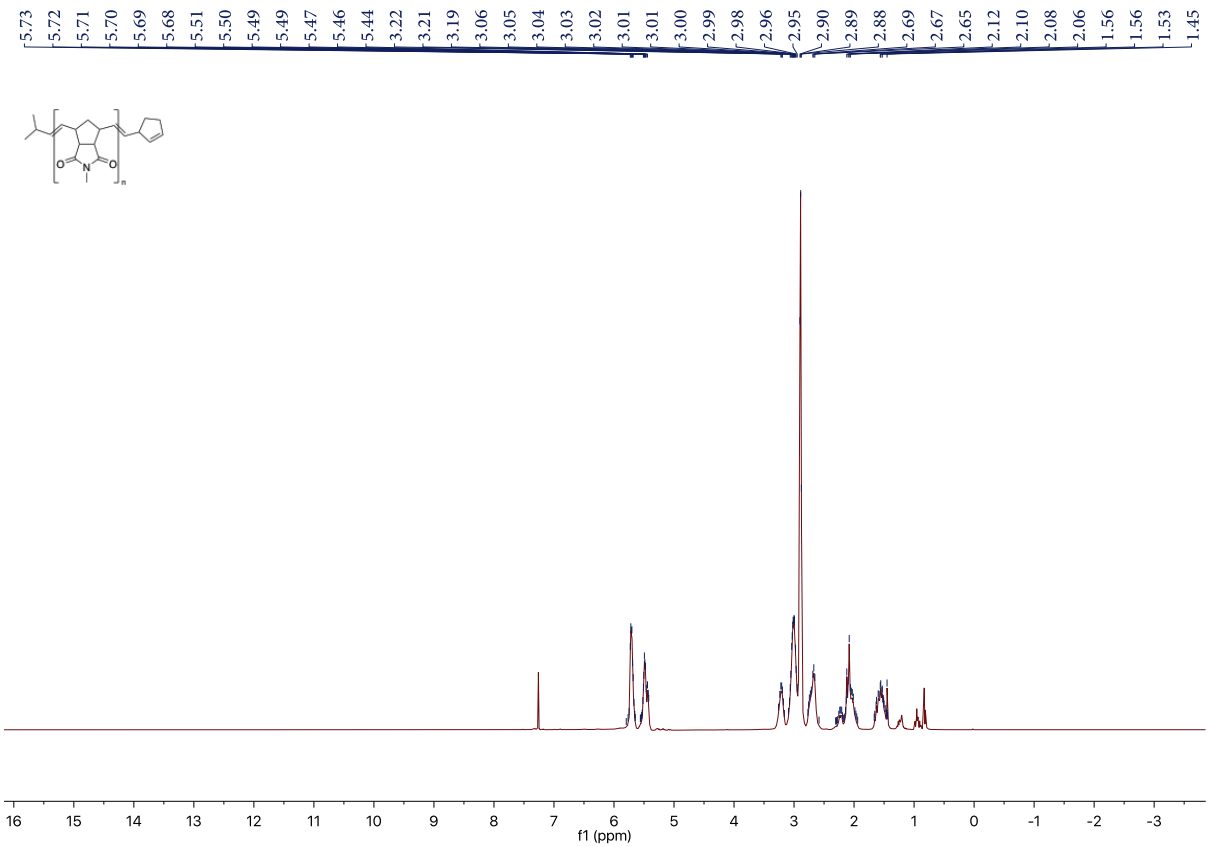


Figure S77 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 9**

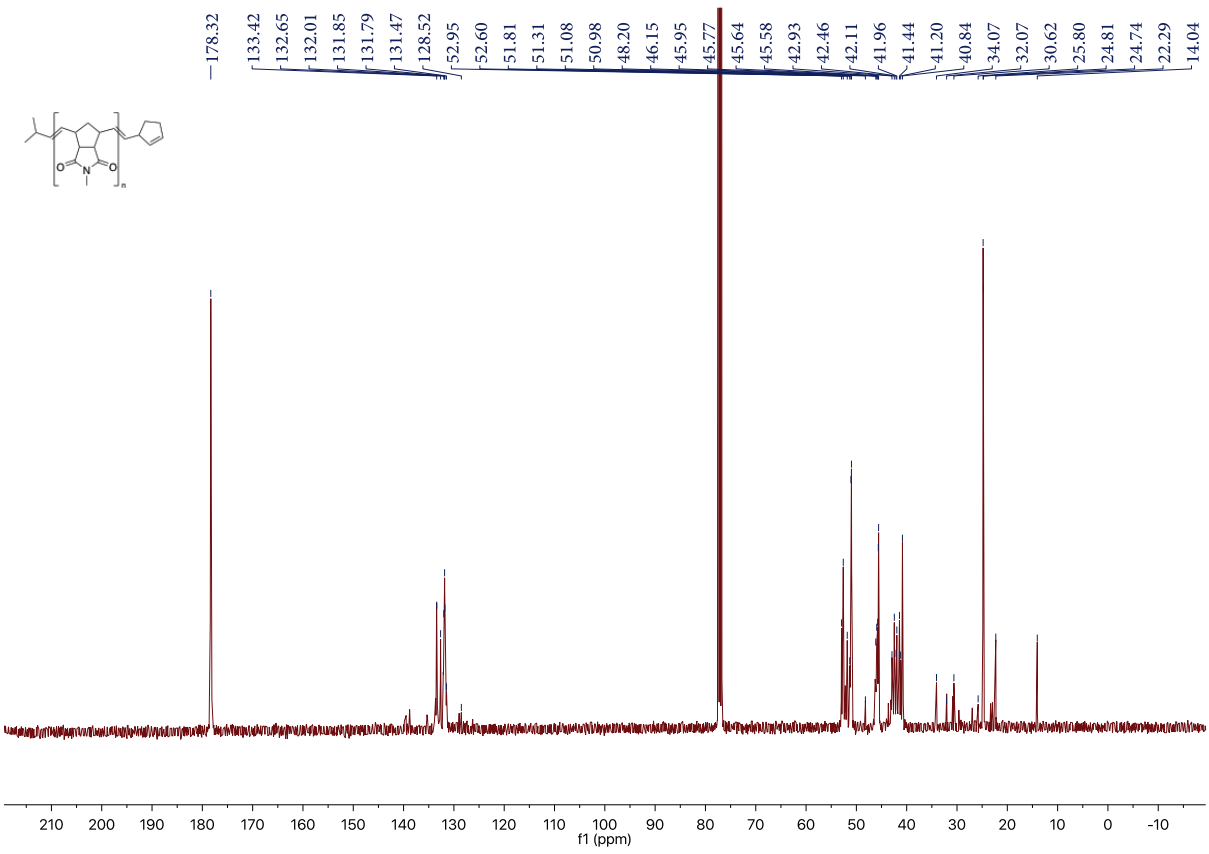


Figure S78 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 9**

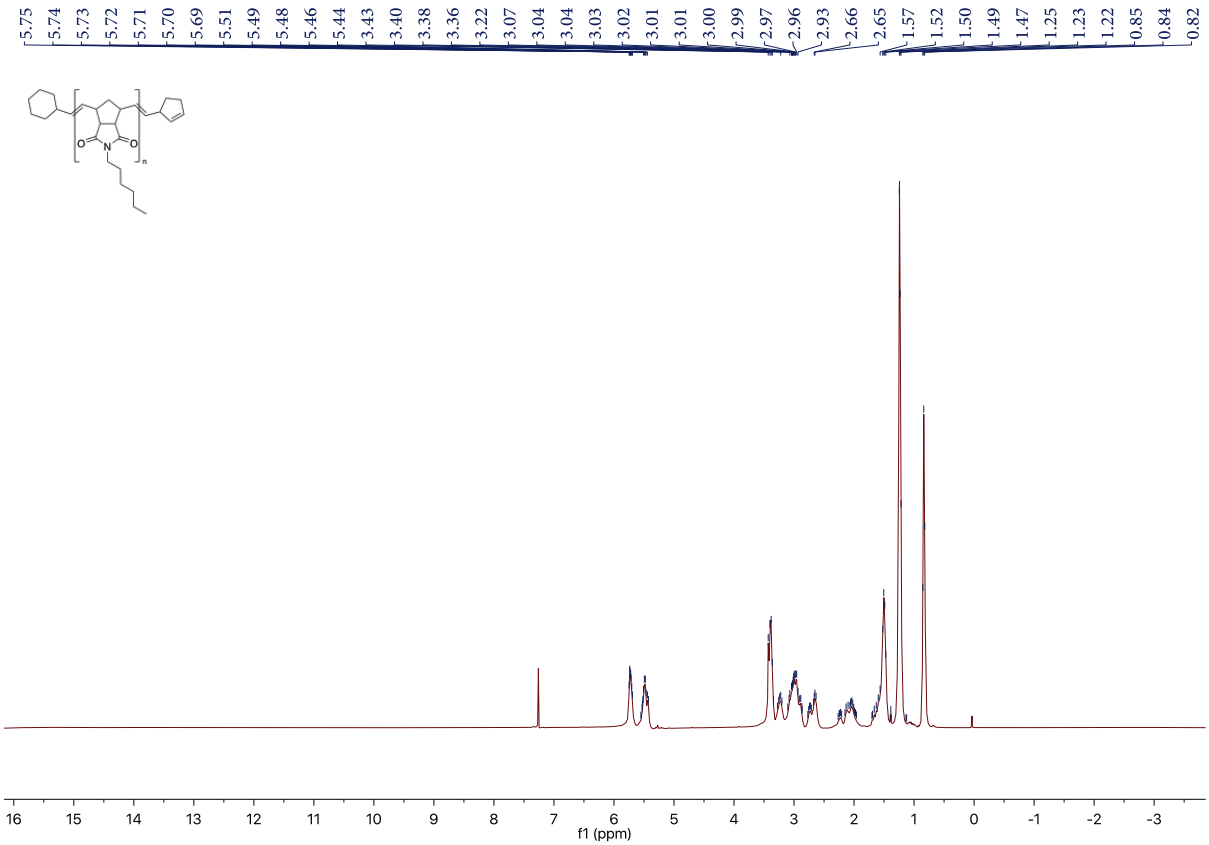


Figure S79 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 10**

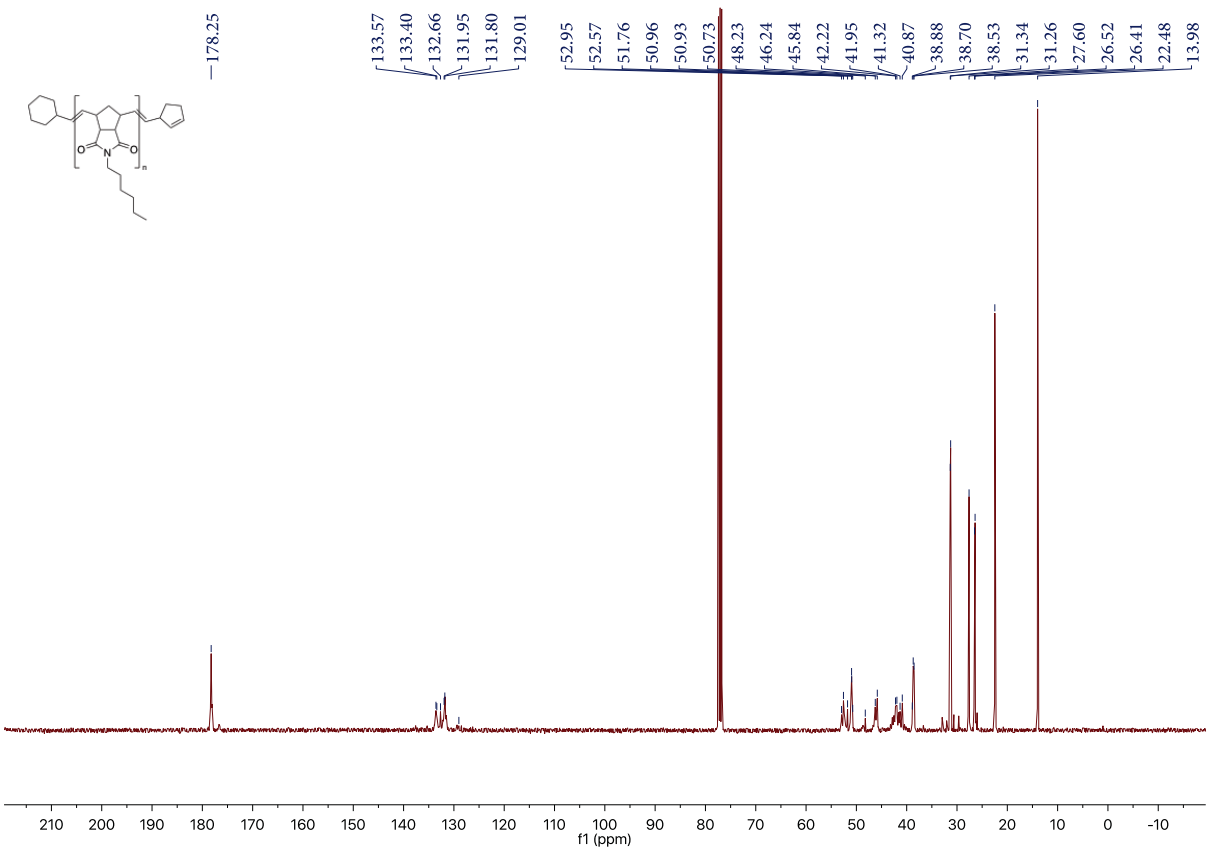


Figure S80 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 10**

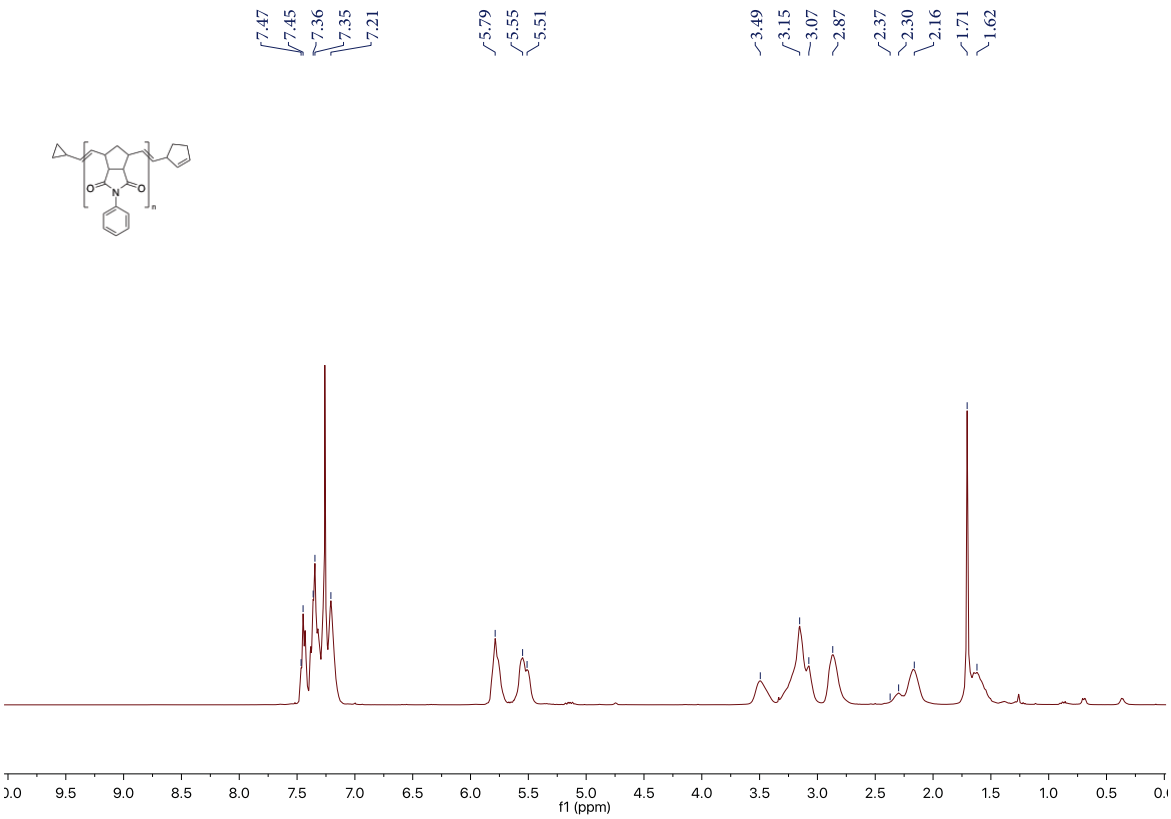


Figure S81 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 11**

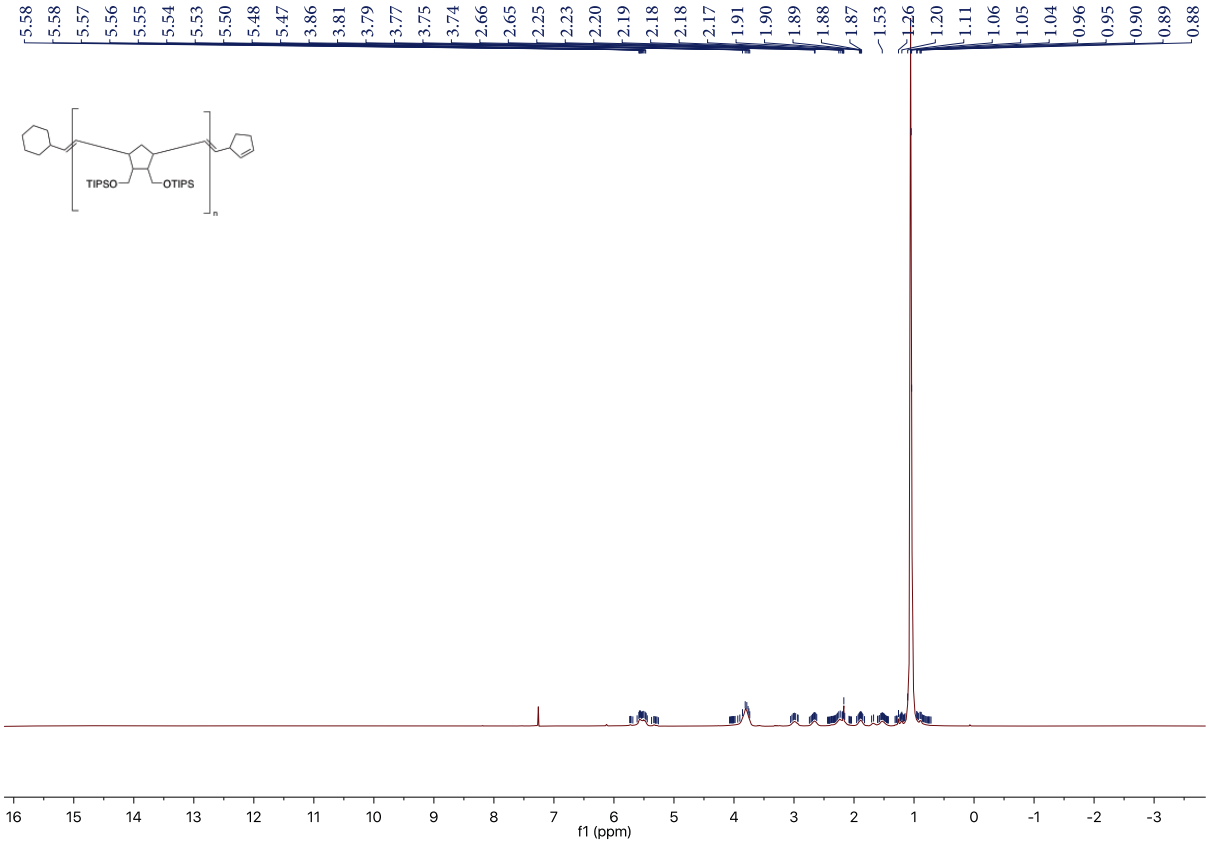


Figure S82 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 12**

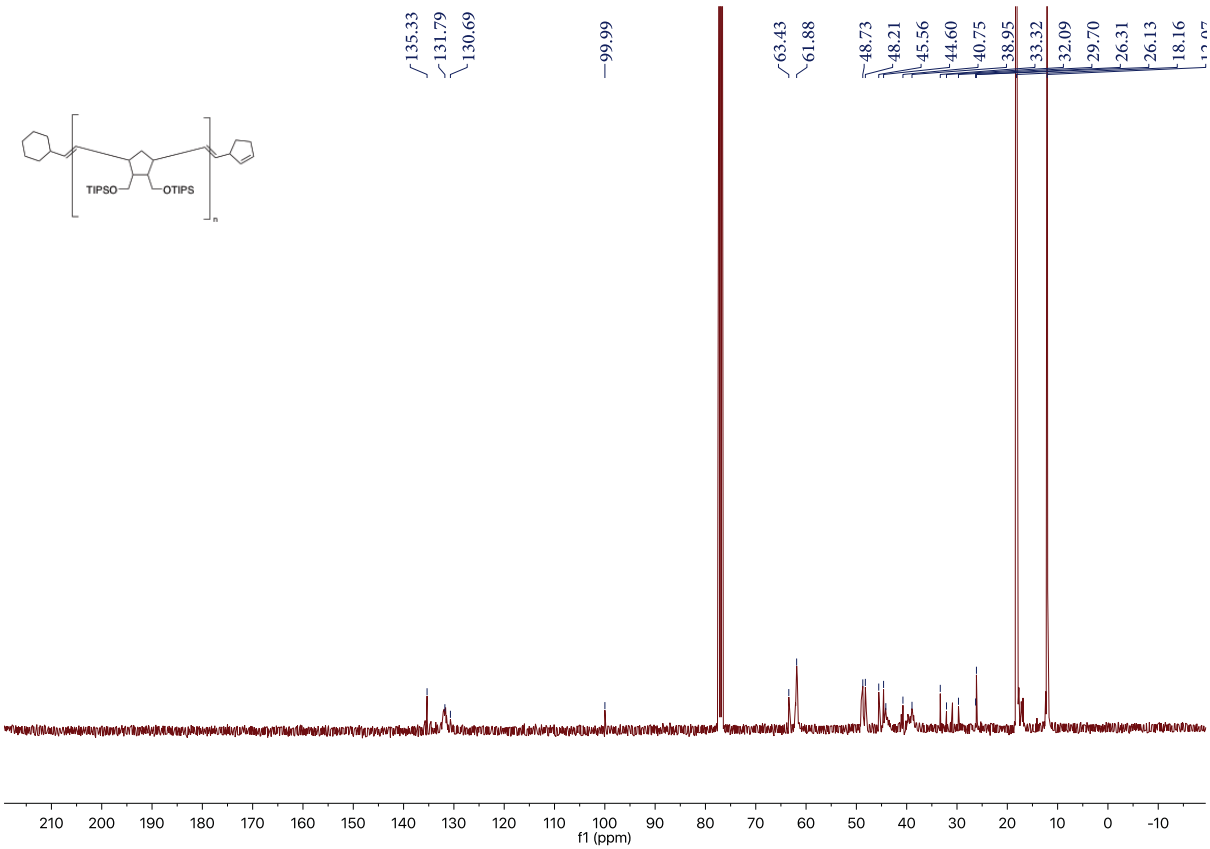


Figure S83 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 12**

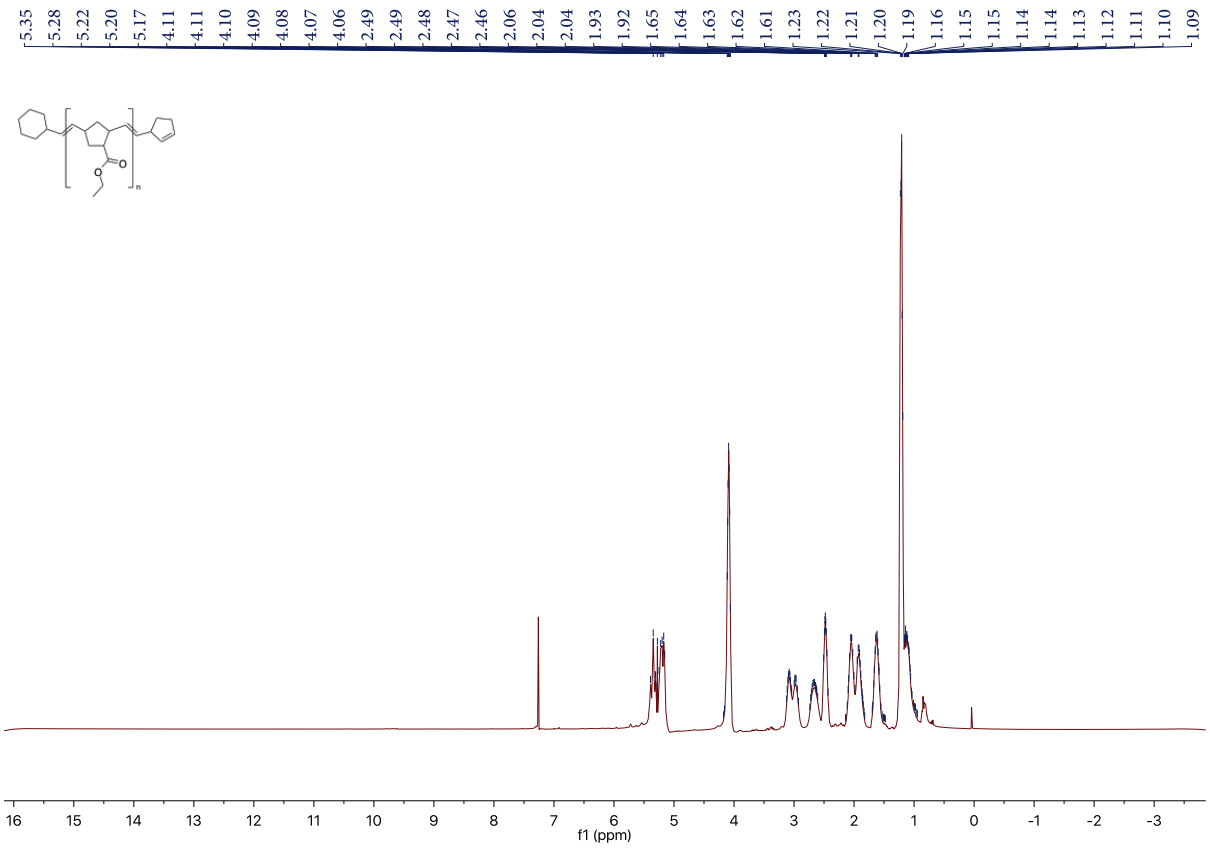


Figure S84 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 13**

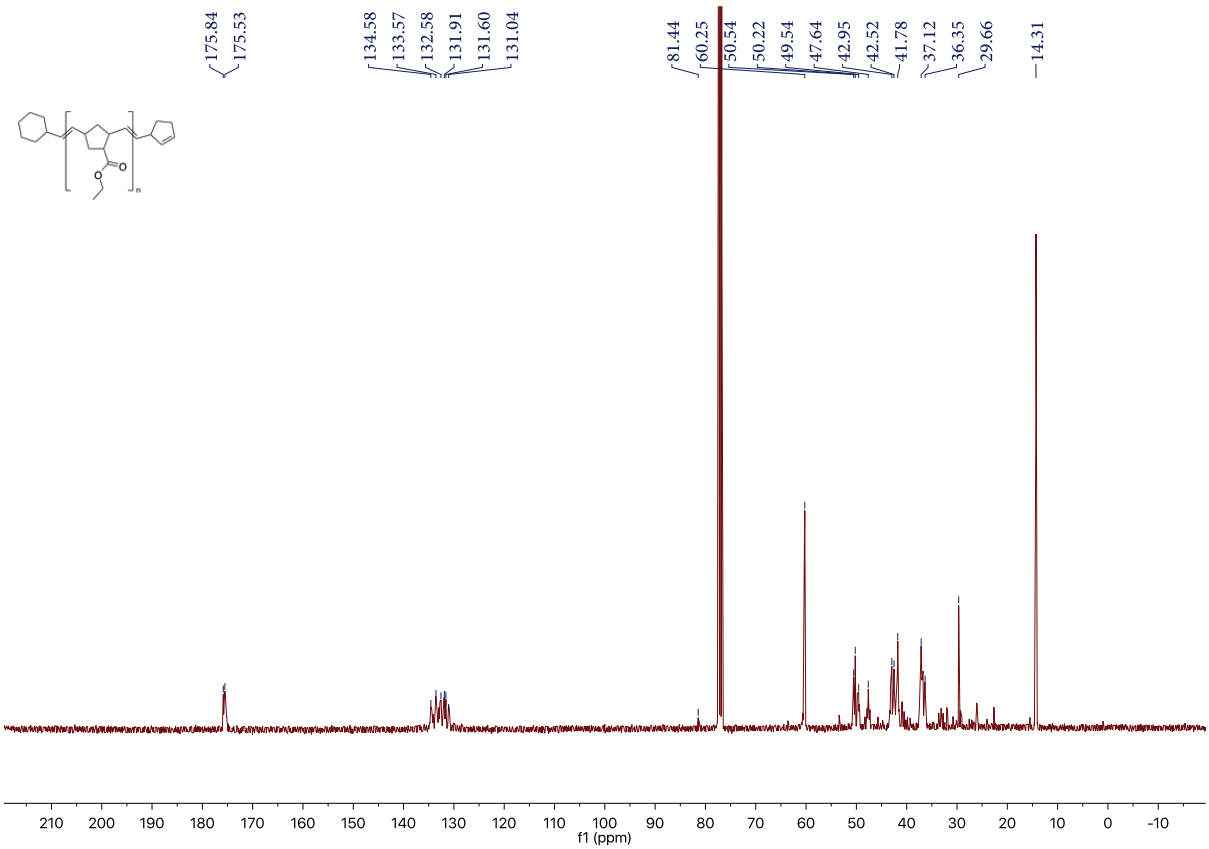


Figure S85 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 13**

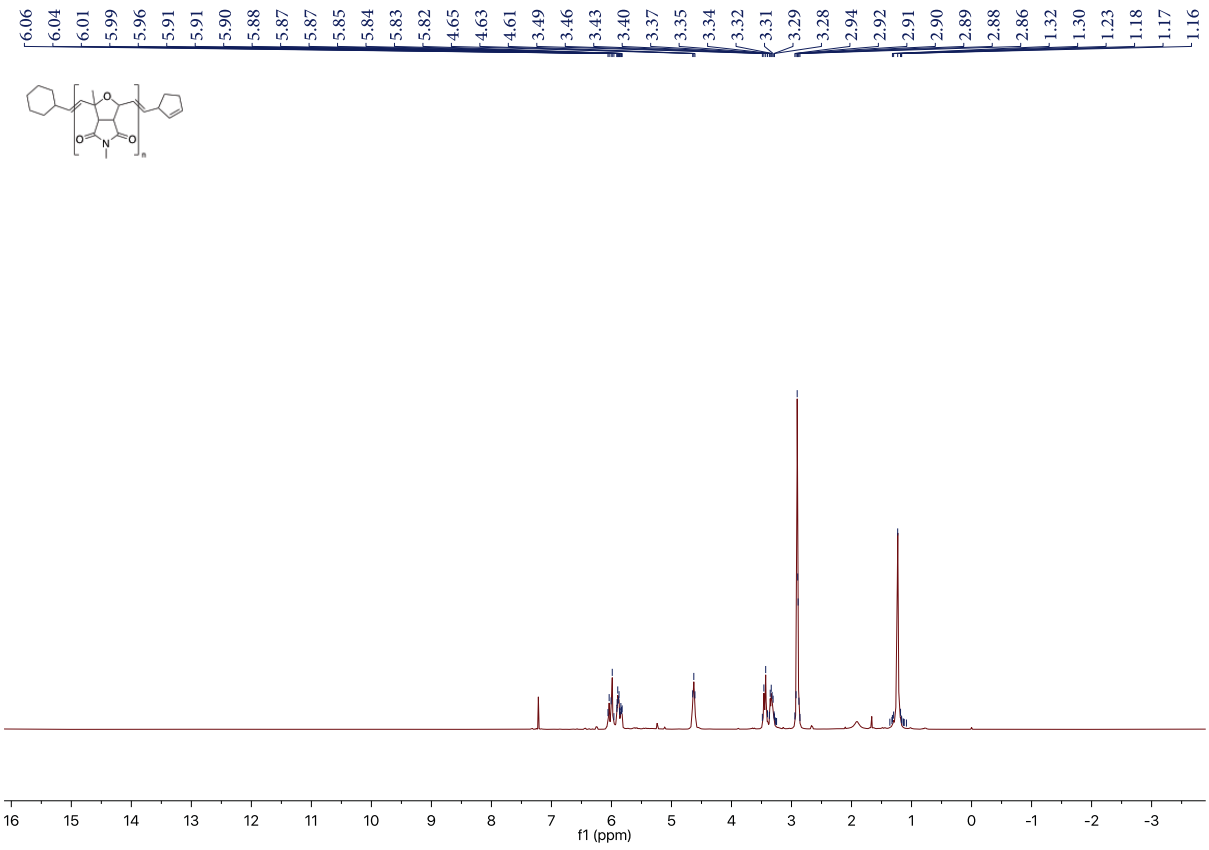


Figure S86 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **Polymer 14**

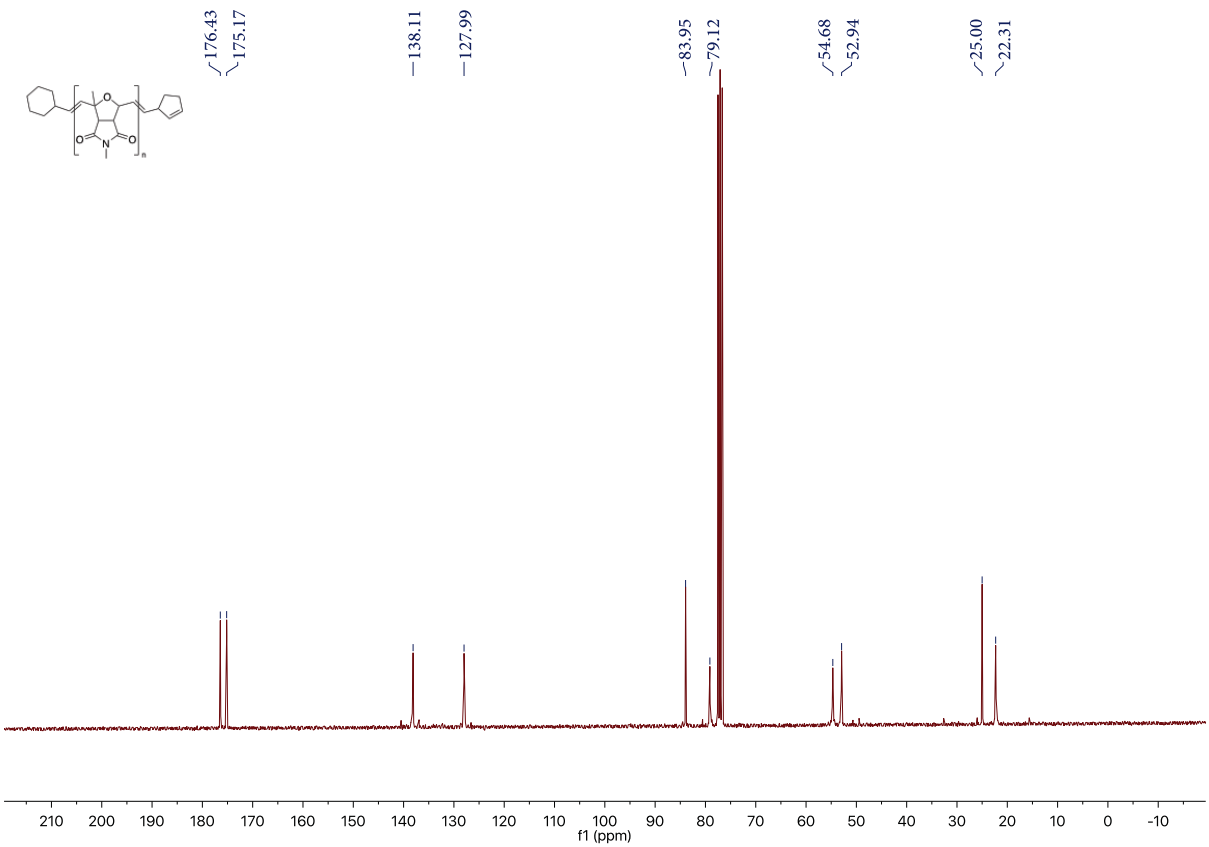


Figure S87 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **Polymer 14**

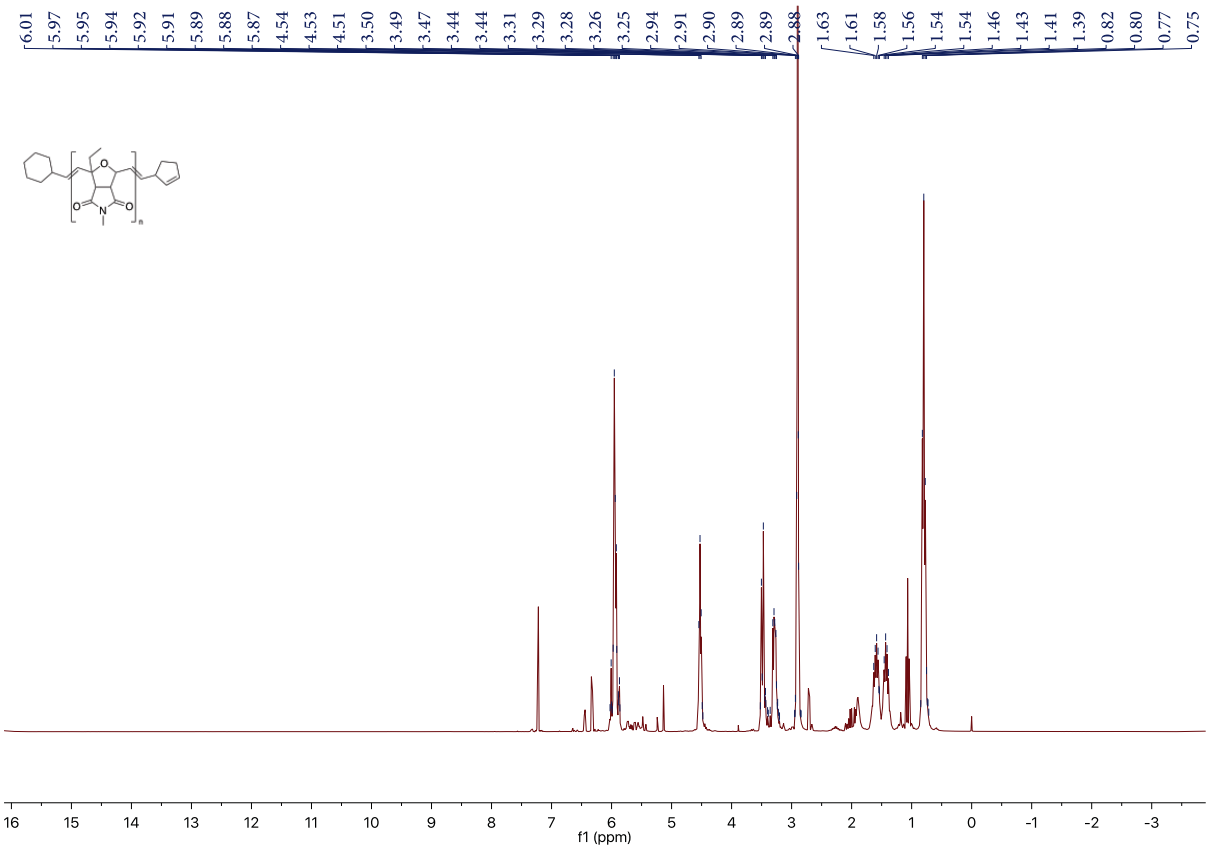


Figure S88 ^{1}H-NMR spectrum (300MHz, $CDCl_3$) of **Polymer 15**

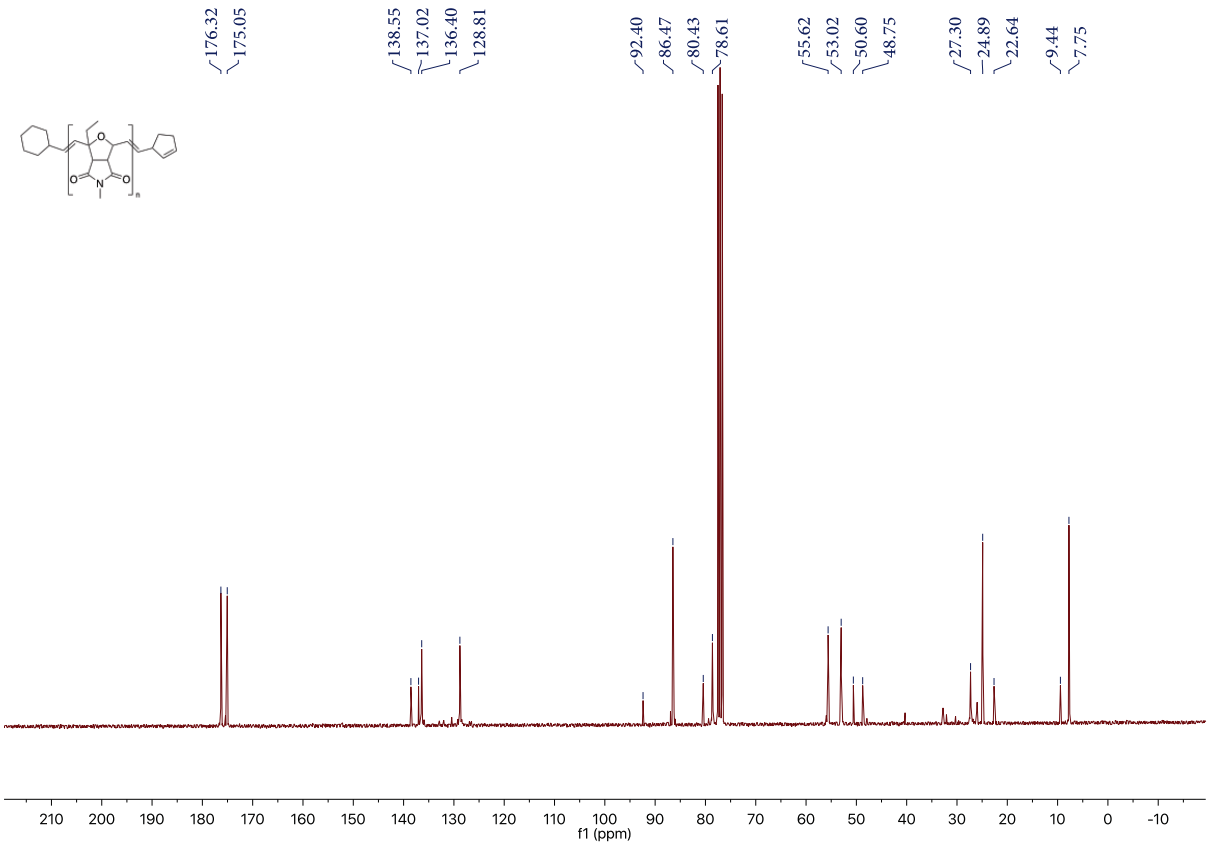


Figure S89 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **Polymer 15**

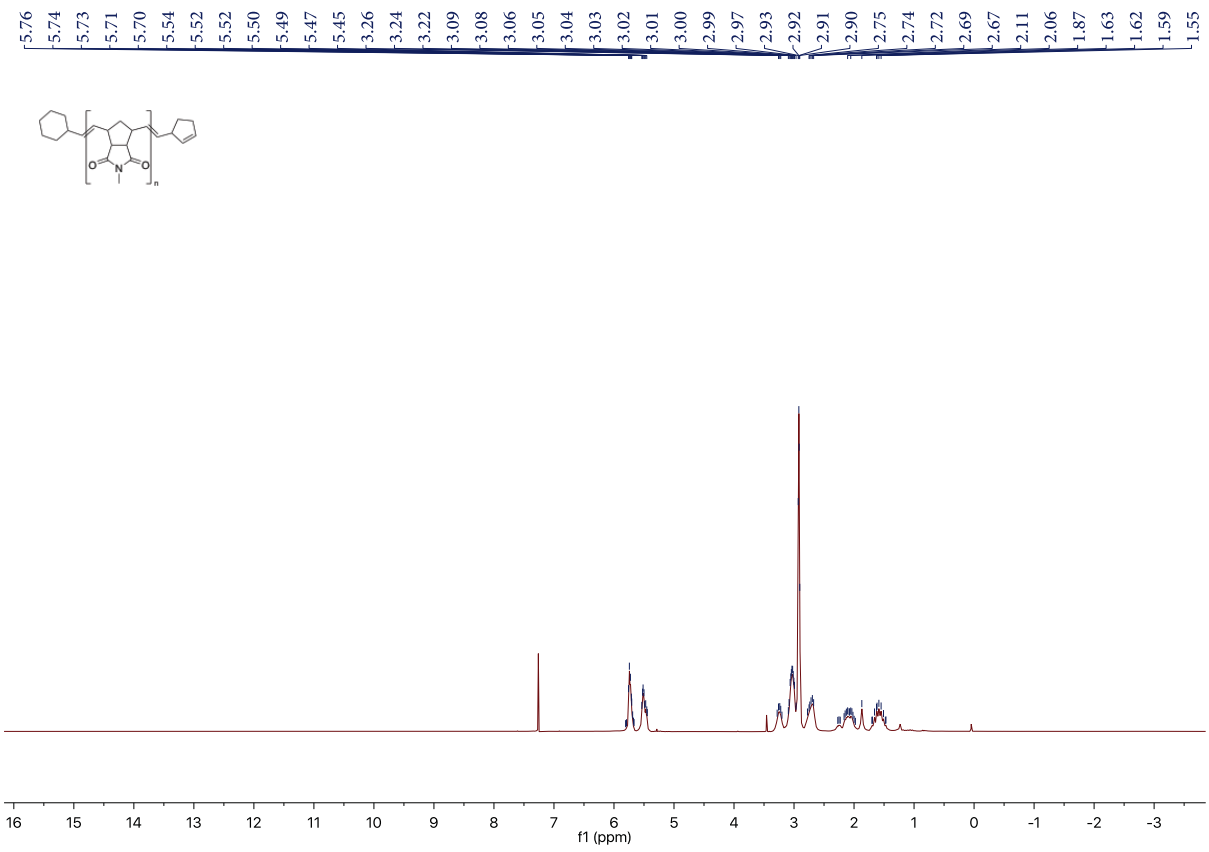


Figure S90 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **Polymer 16**

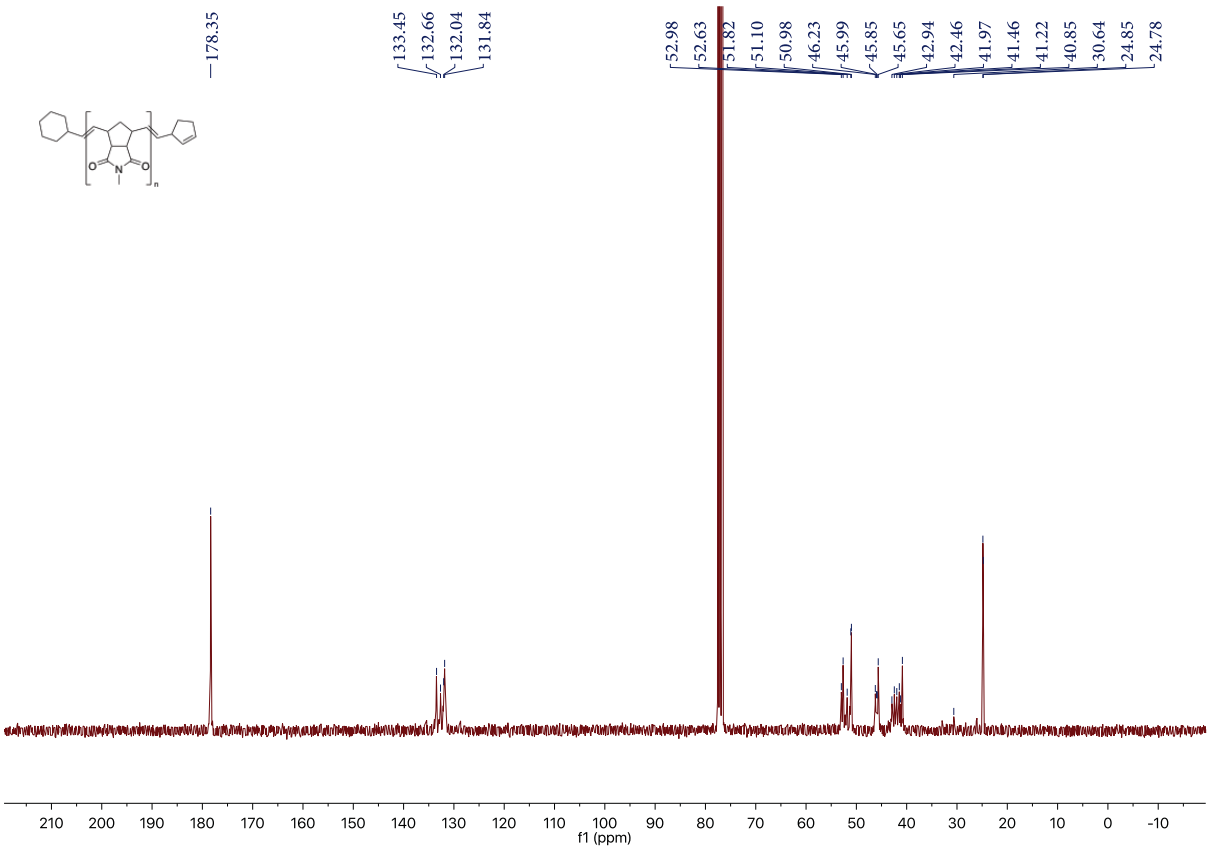


Figure S91 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **Polymer 16**

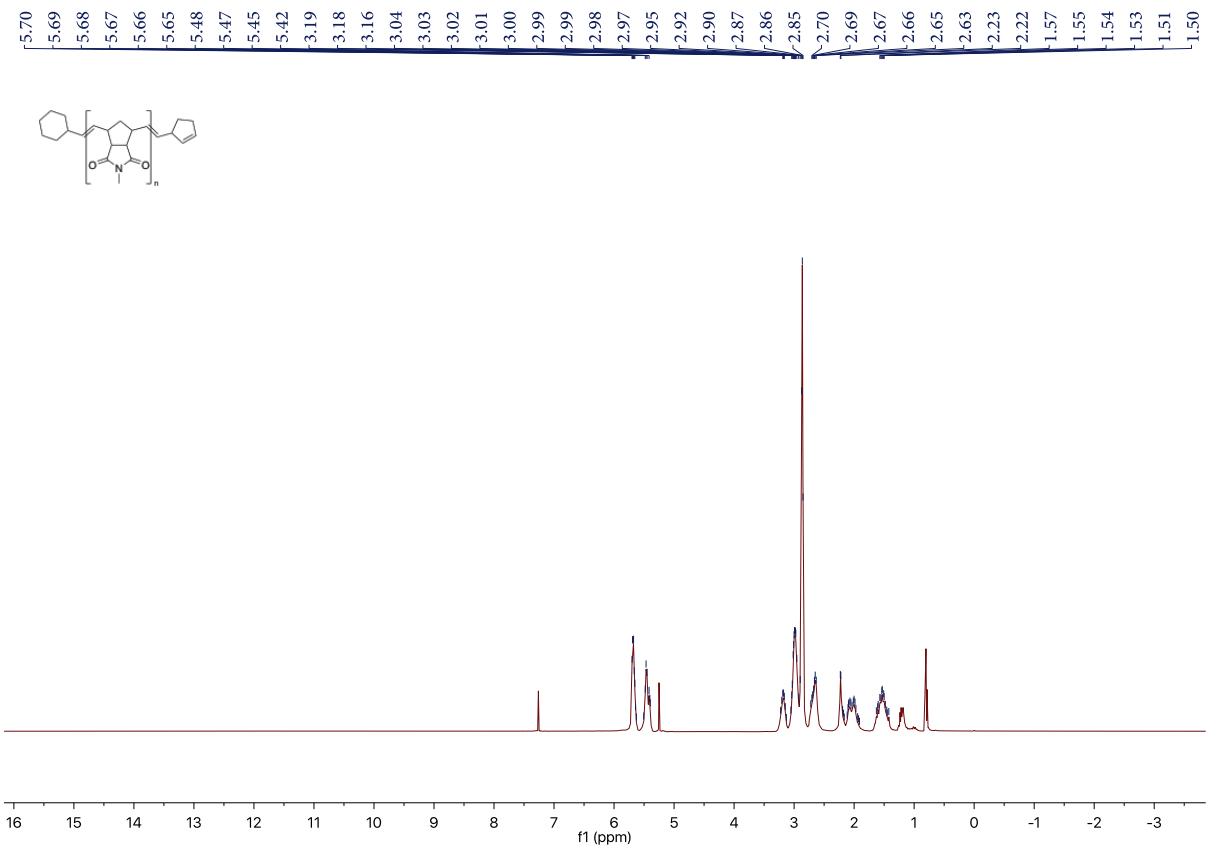


Figure S92 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 17**

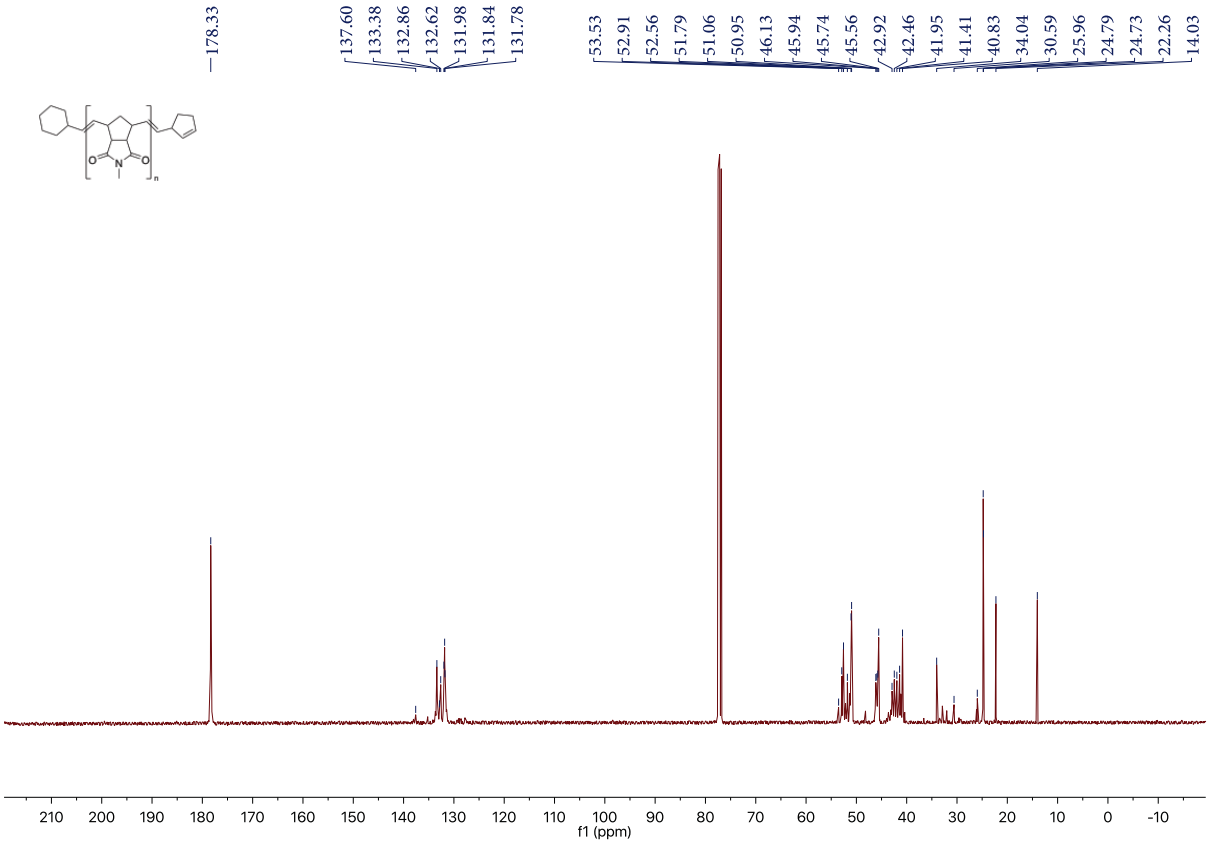


Figure S93 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 17**

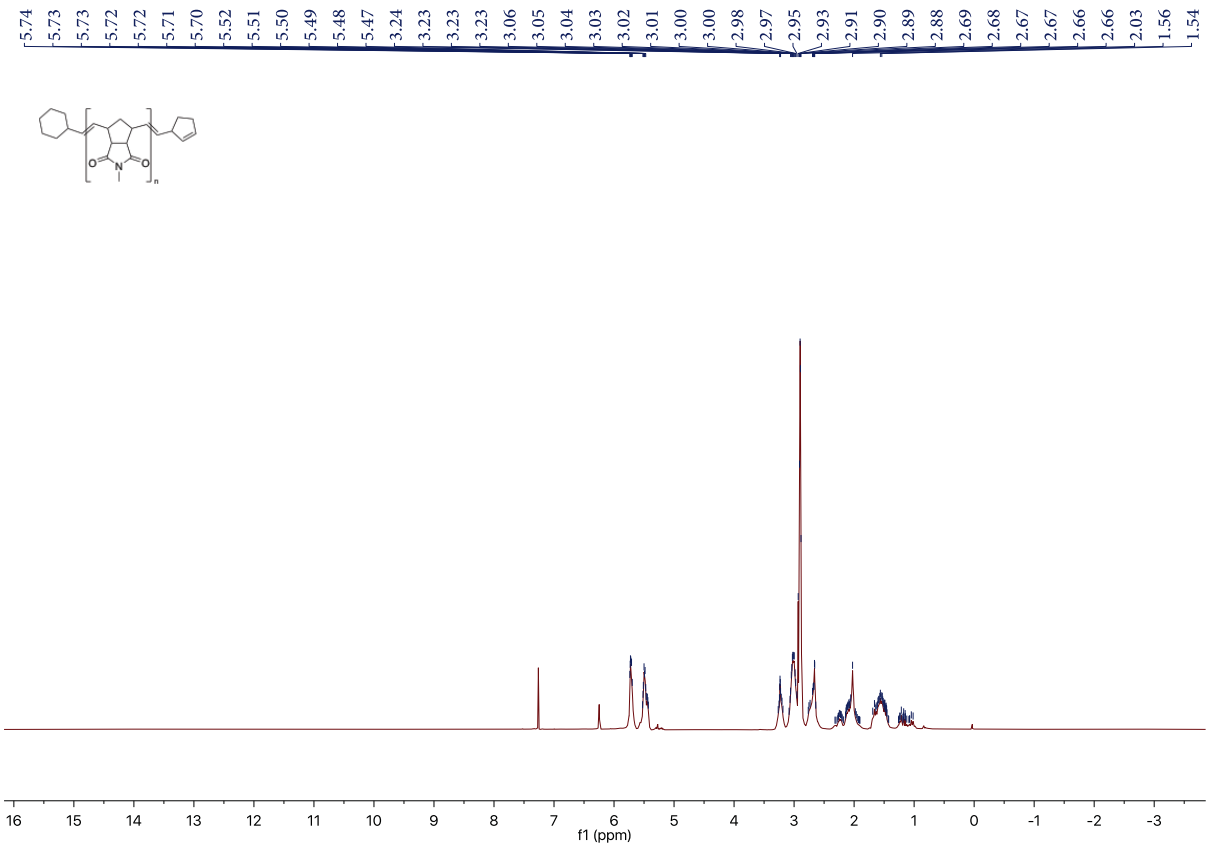


Figure S94 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 18**

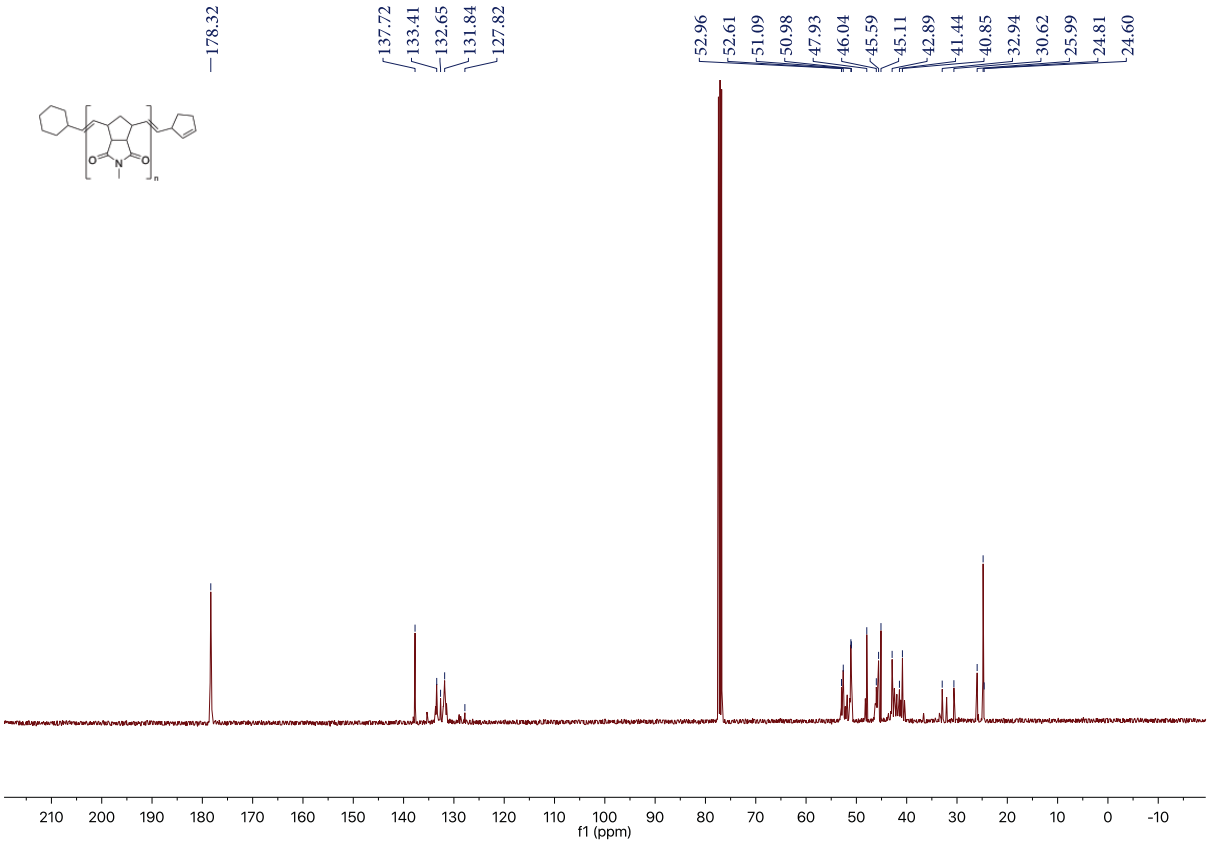


Figure S95 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 18**

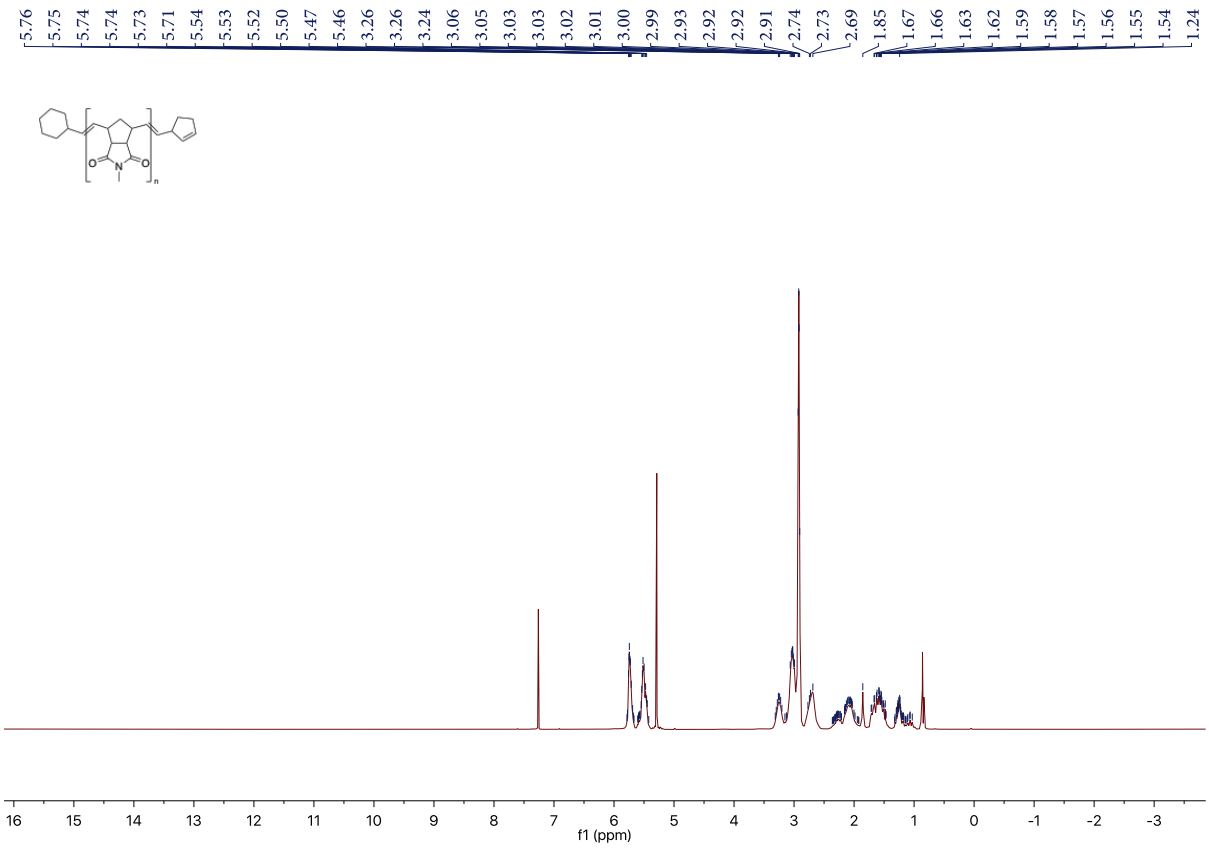


Figure S96 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 19**

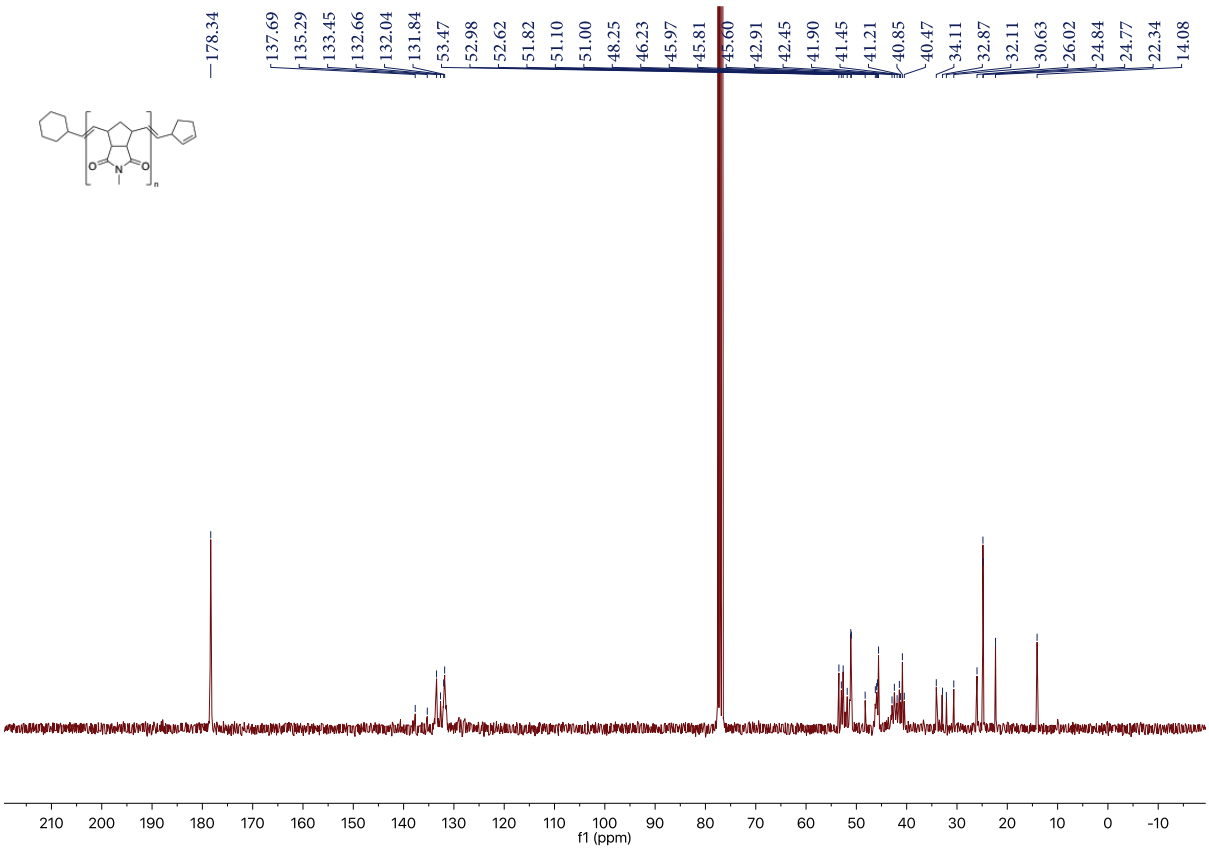


Figure S97 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 19**

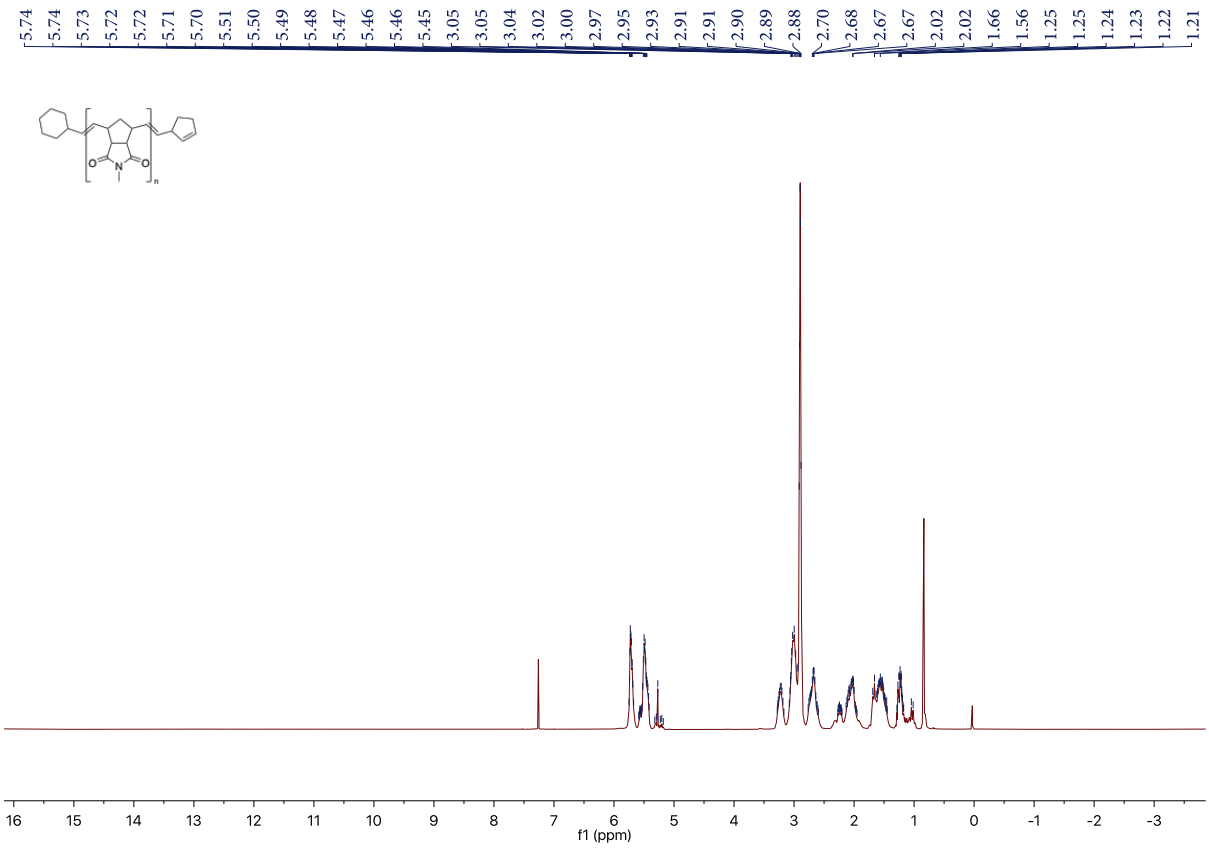


Figure S98 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 20**

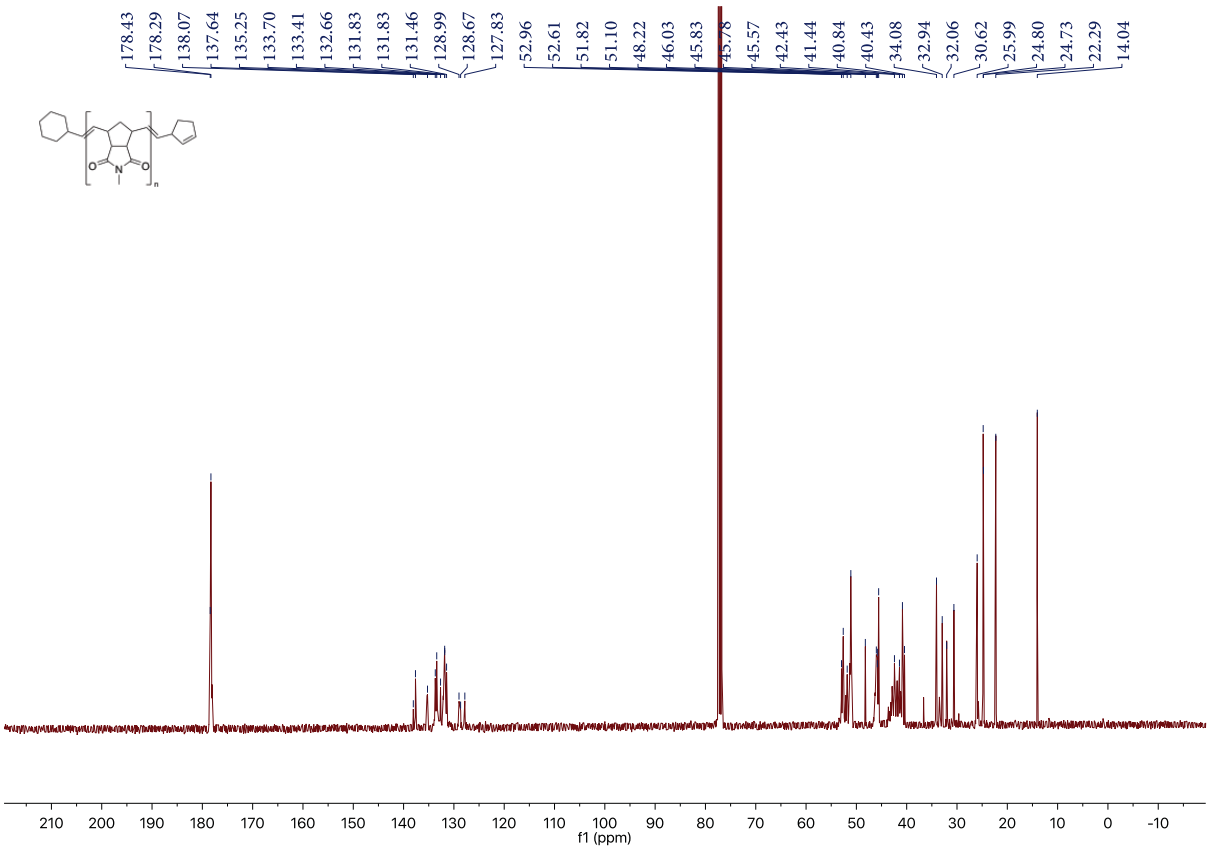


Figure S99 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 20**

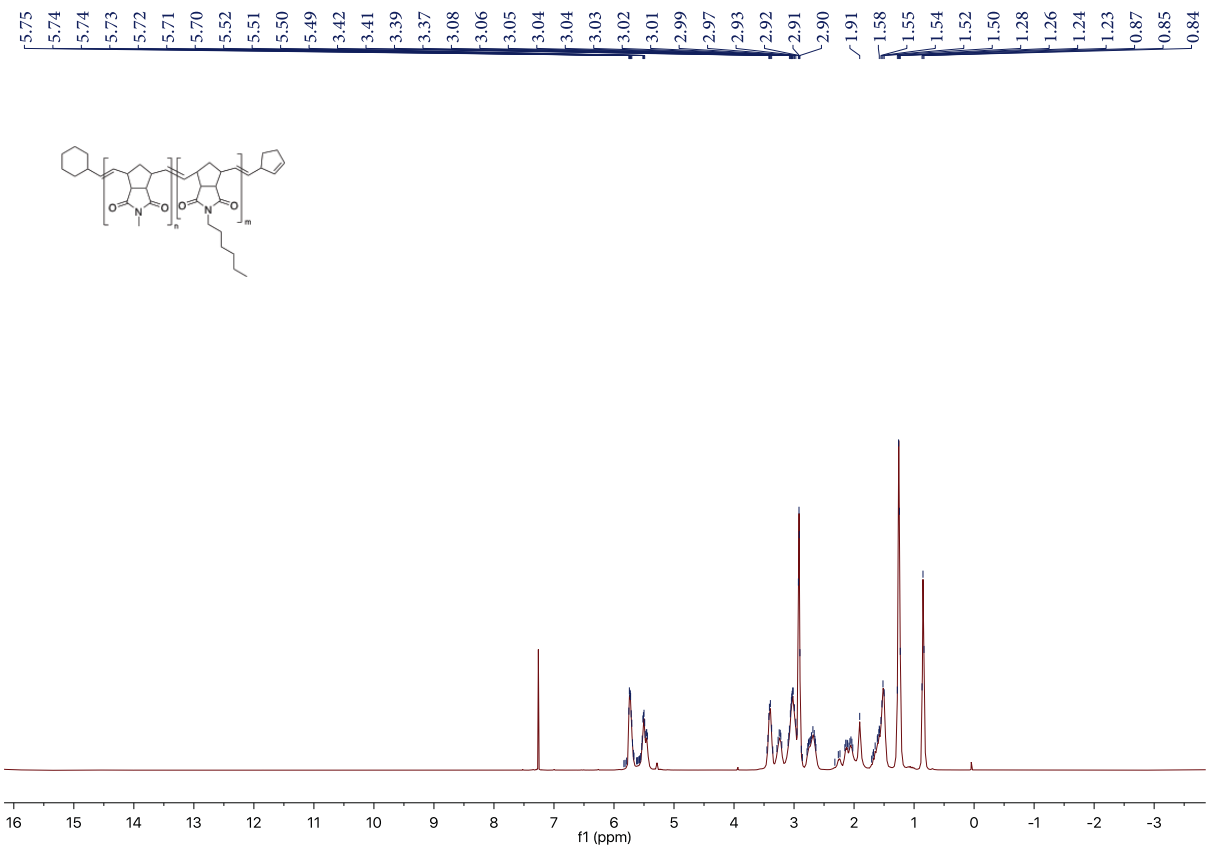


Figure S100 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 21**

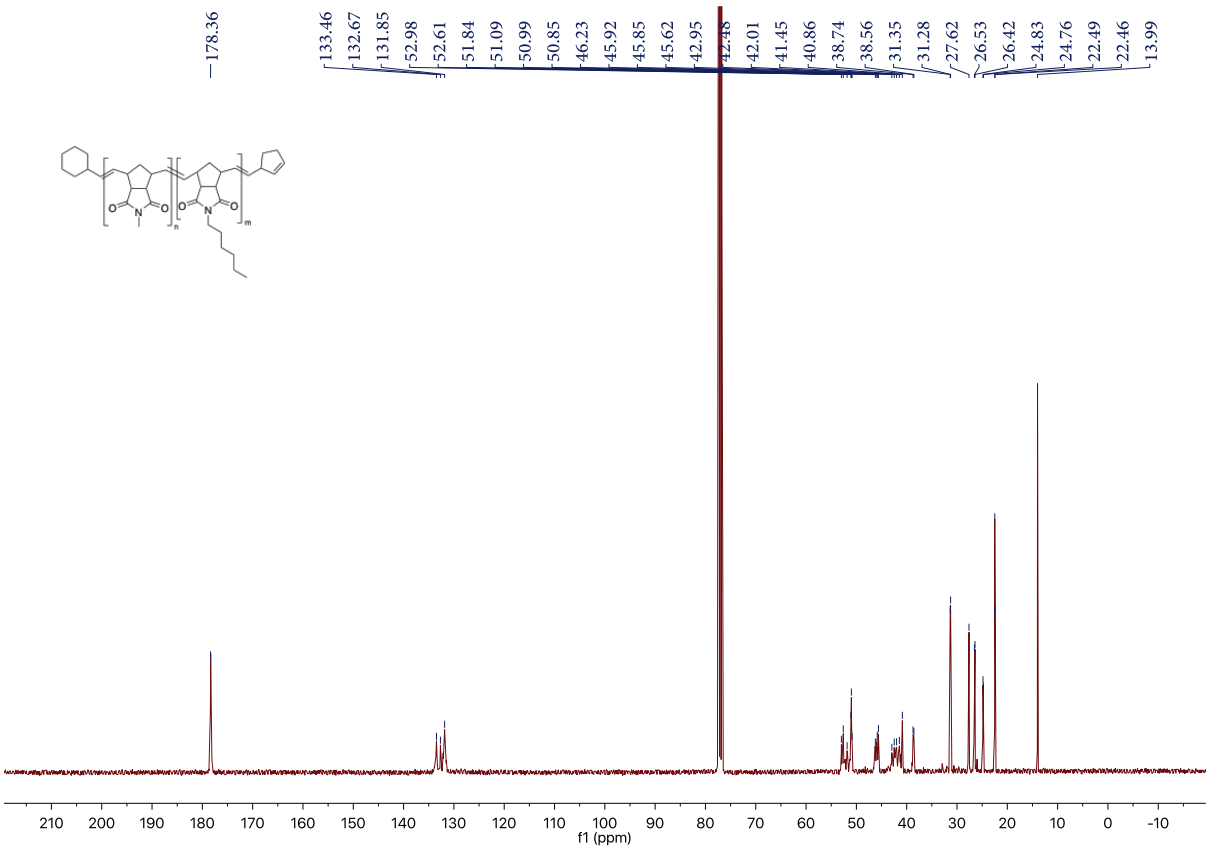


Figure S101 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 21**

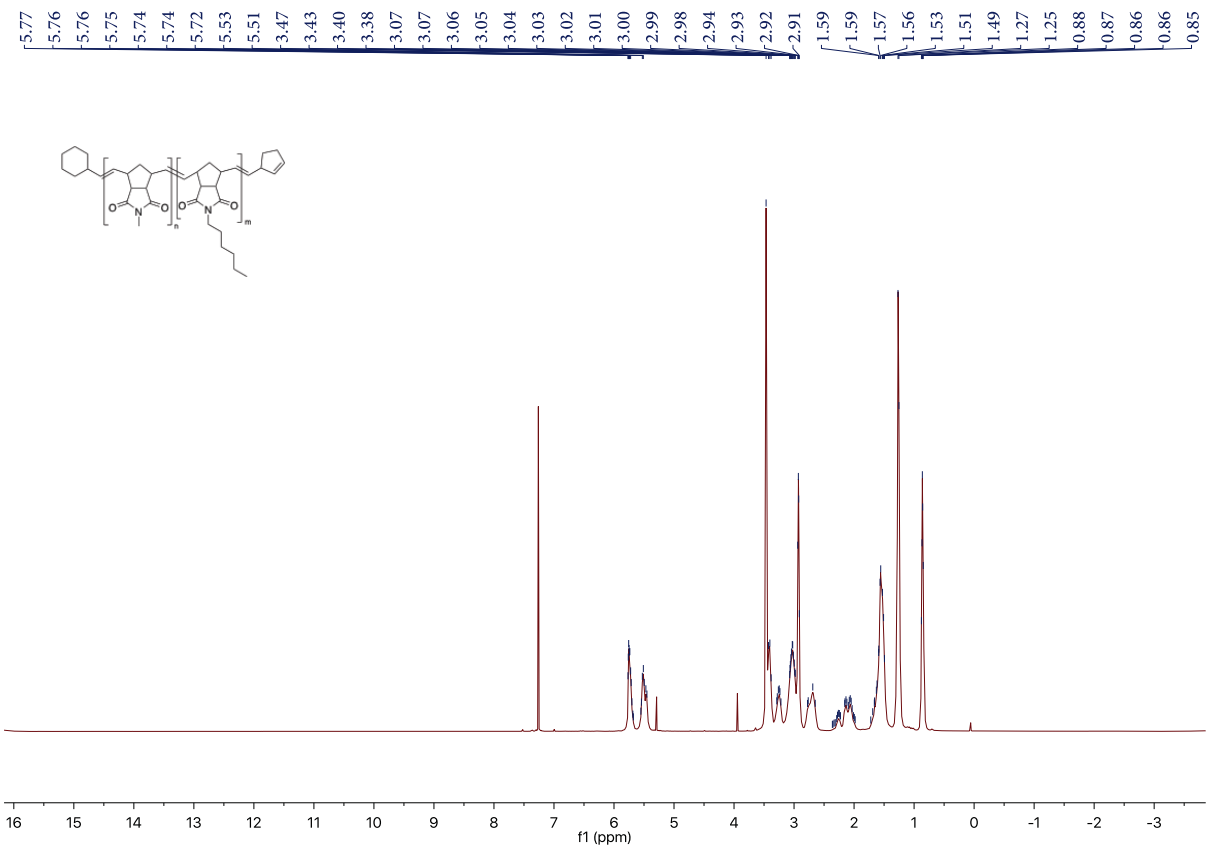


Figure S102 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 22**

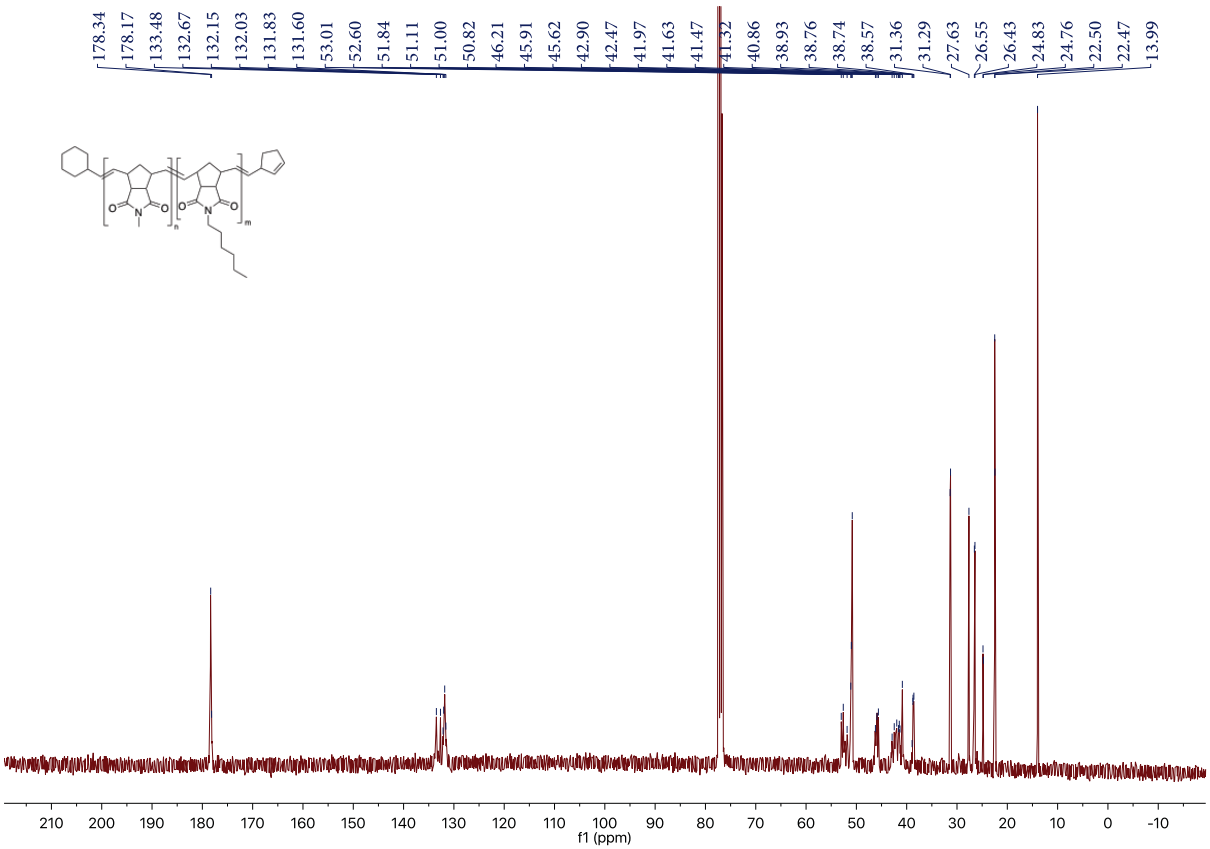


Figure S103 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 22**

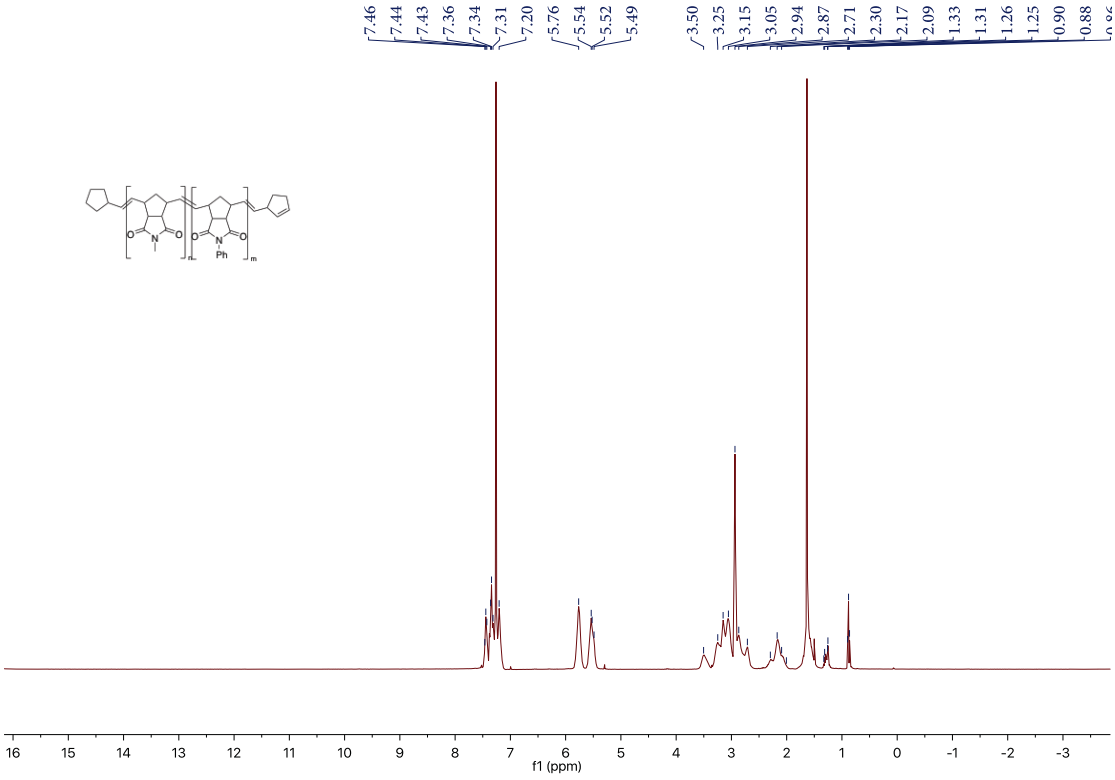


Figure S104 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 23**

Copies of MALDI-ToF Mass Spectra

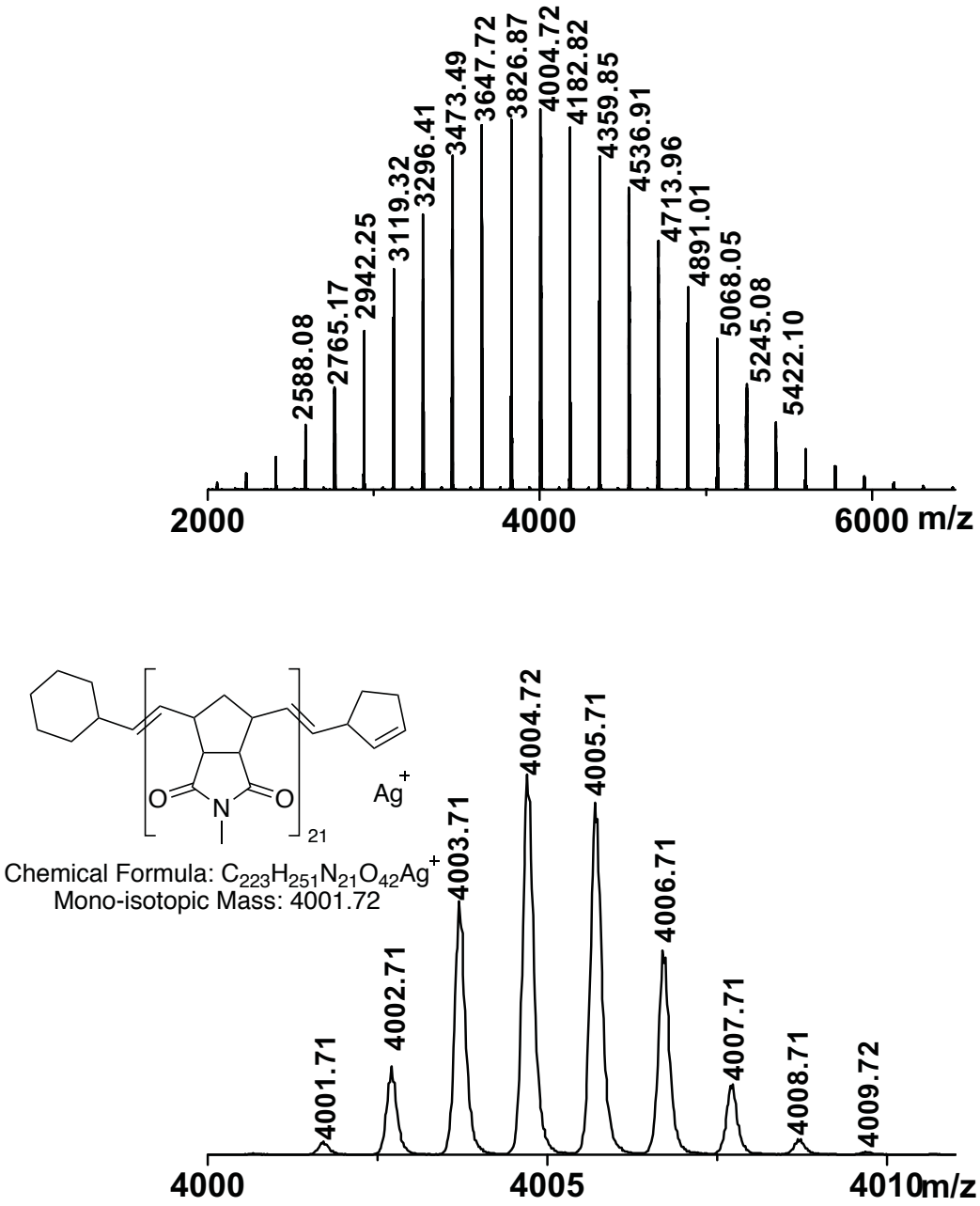


Figure S105 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 1**

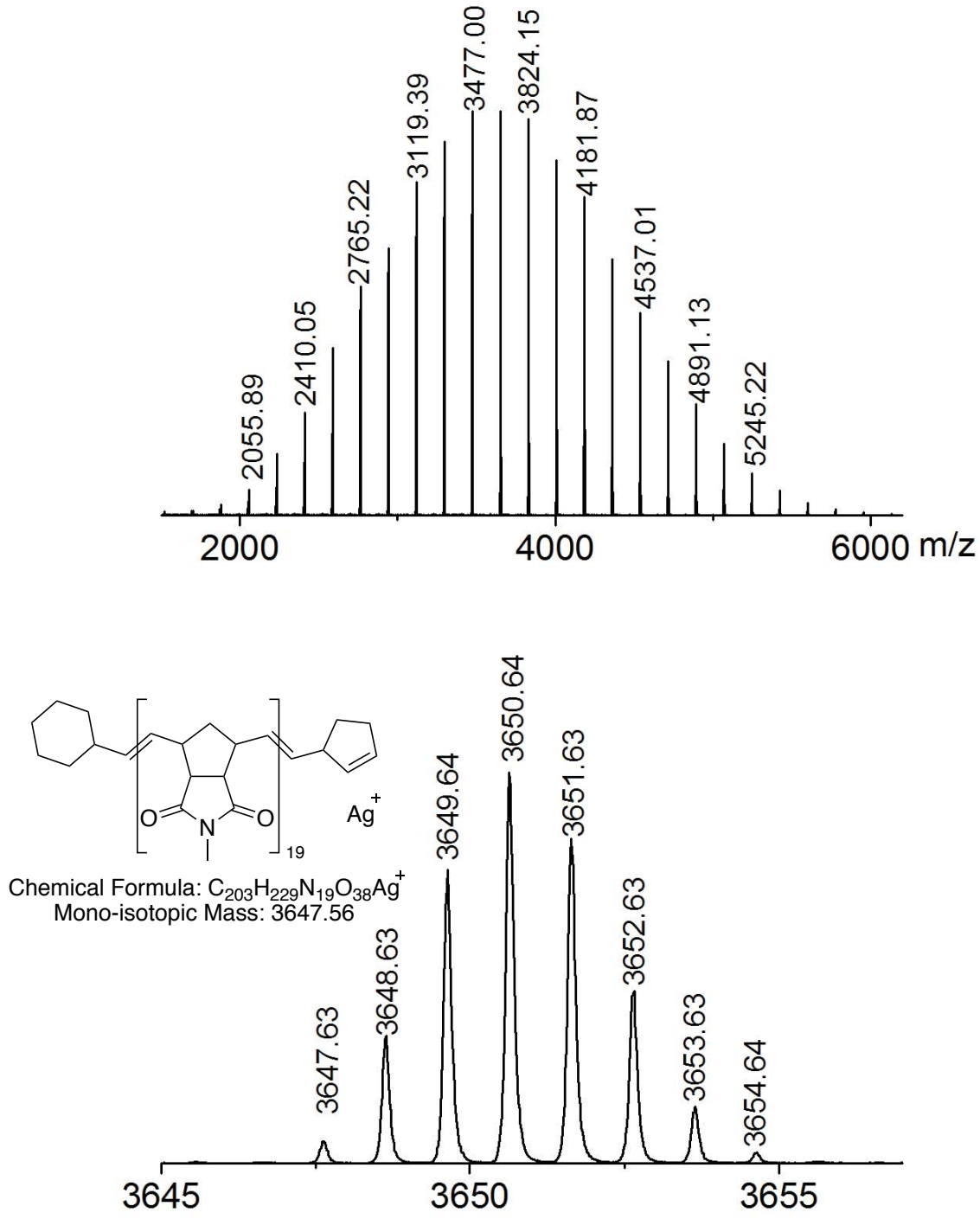


Figure S106 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 2**

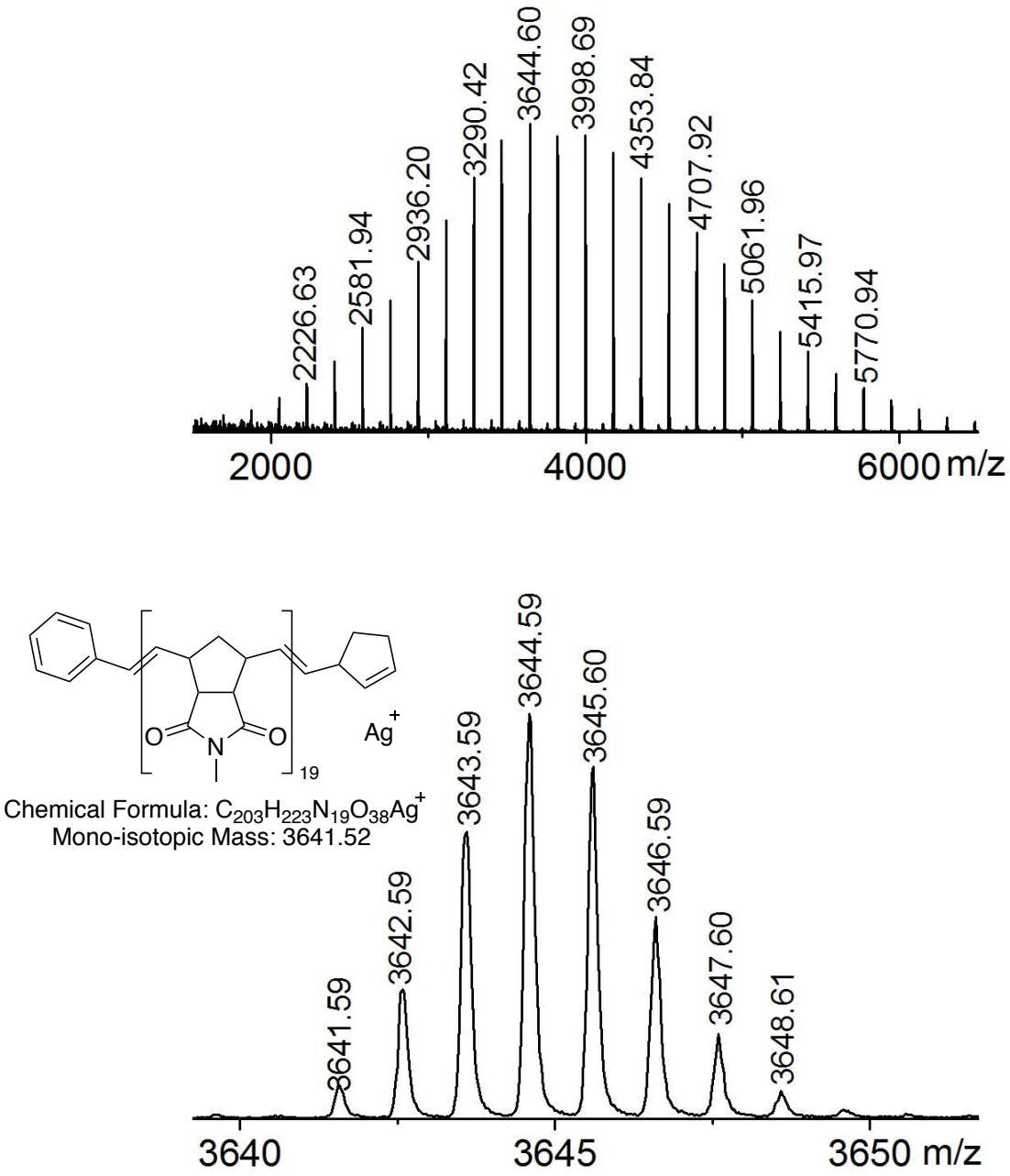


Figure S107 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 6**

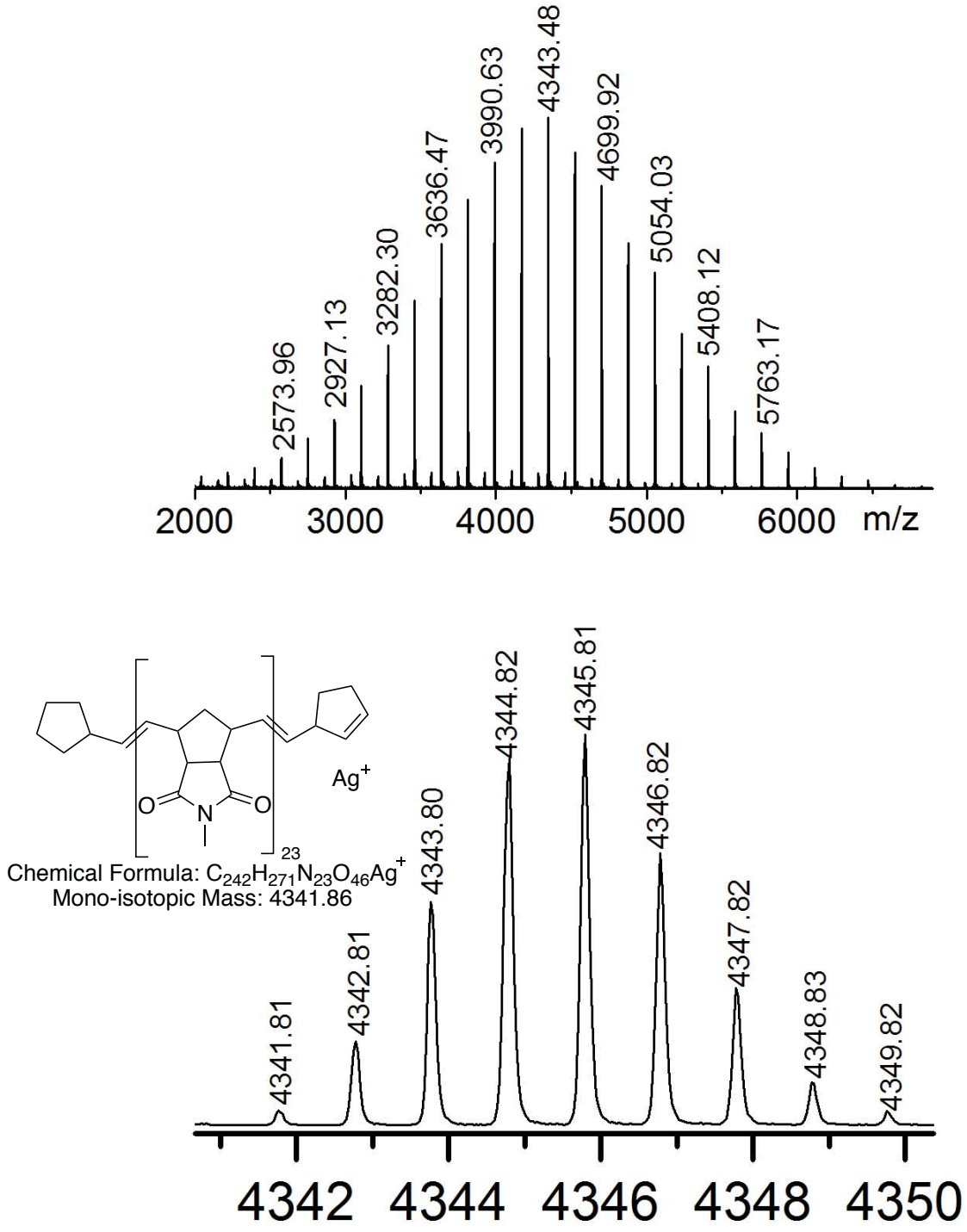


Figure S108 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 7**

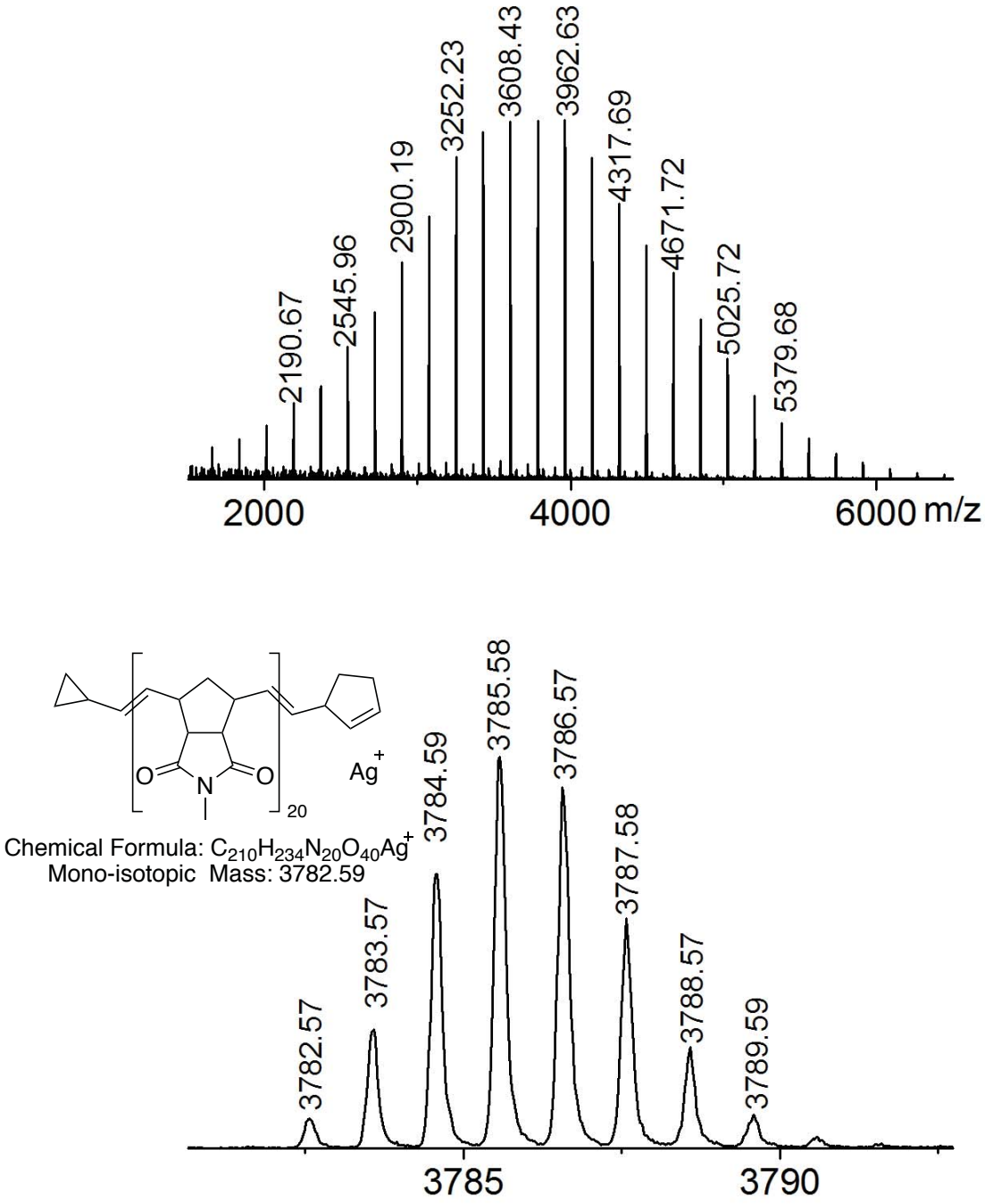


Figure S109 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 8**

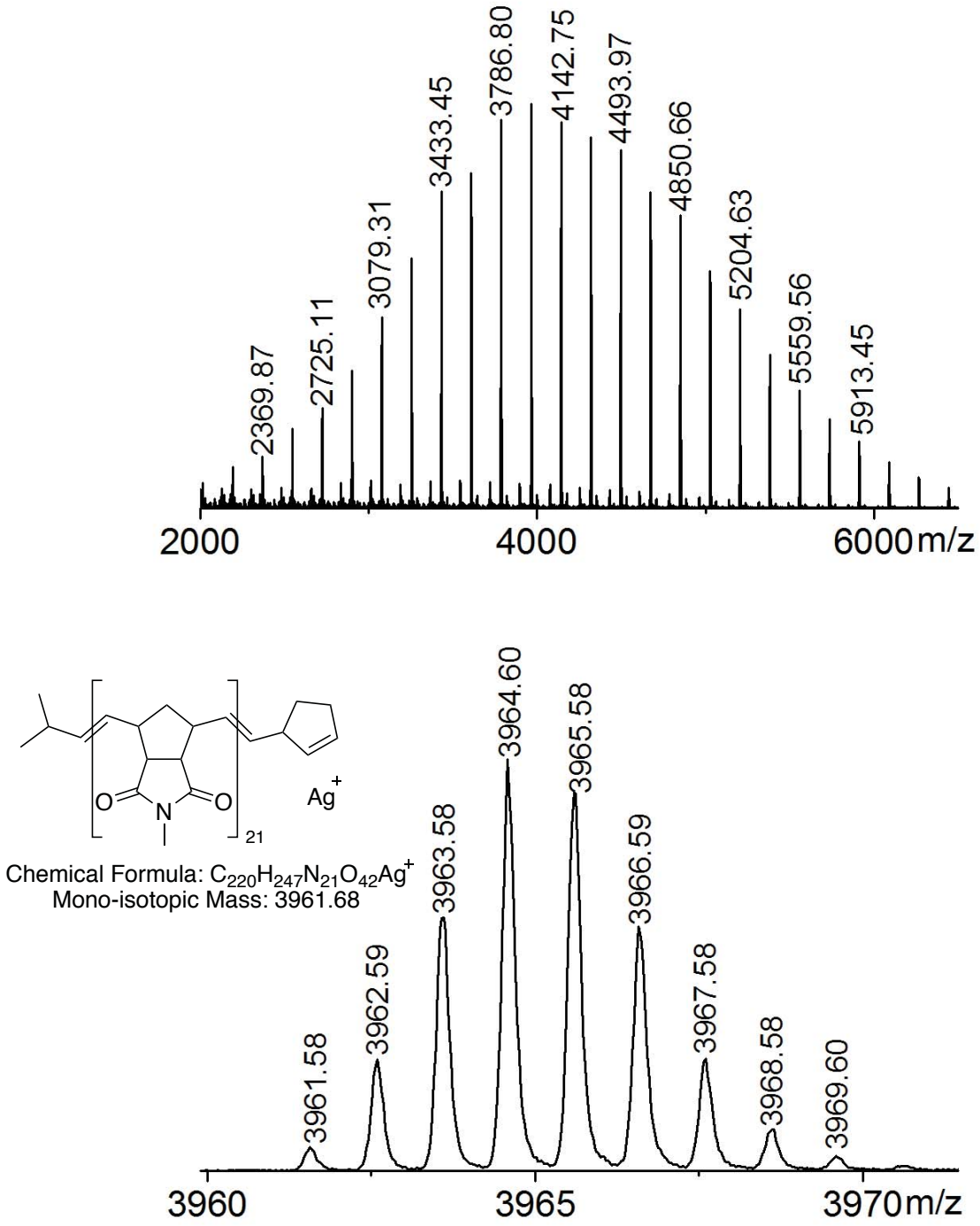


Figure S110 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 9**

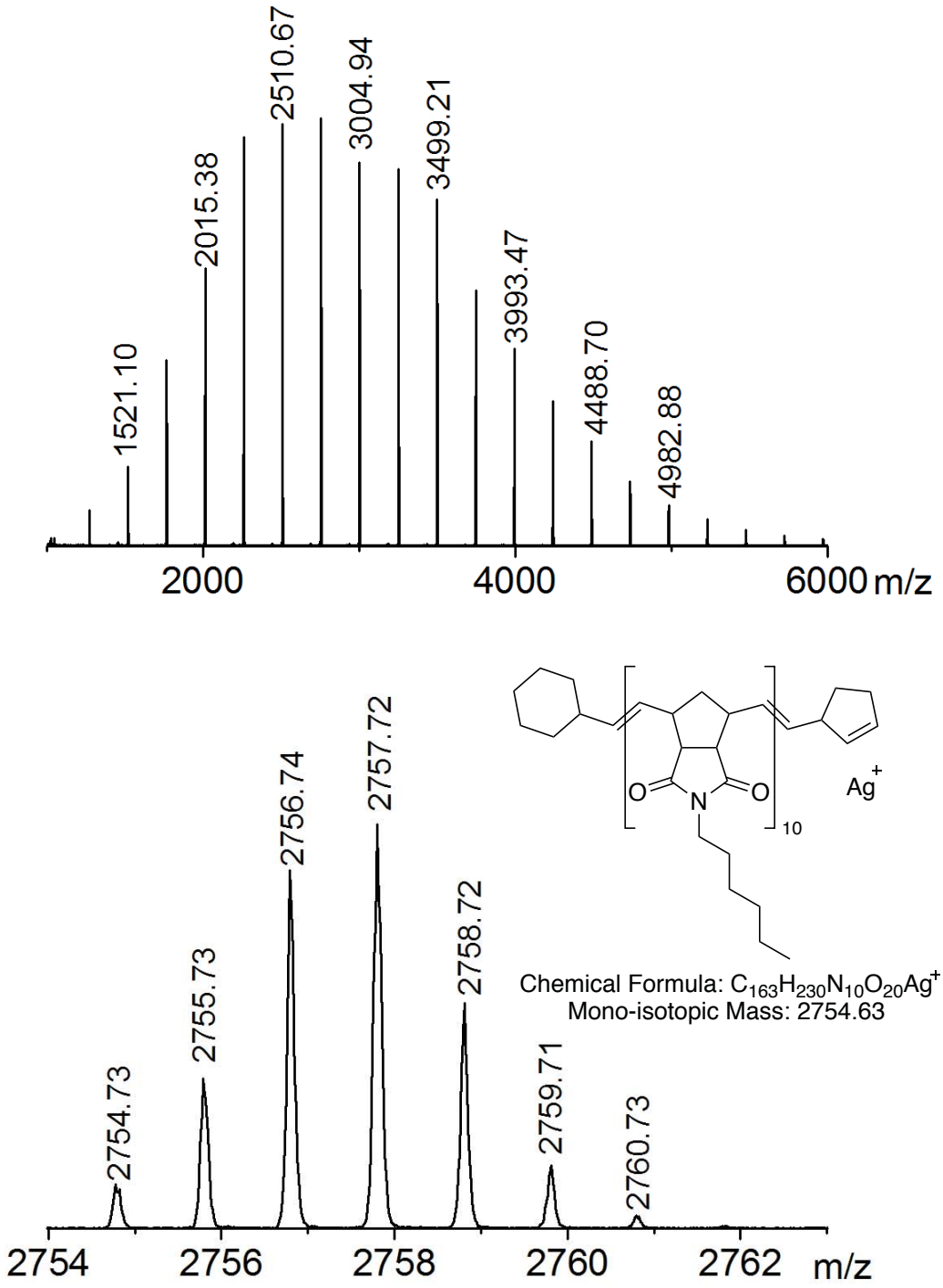


Figure S111 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 10**

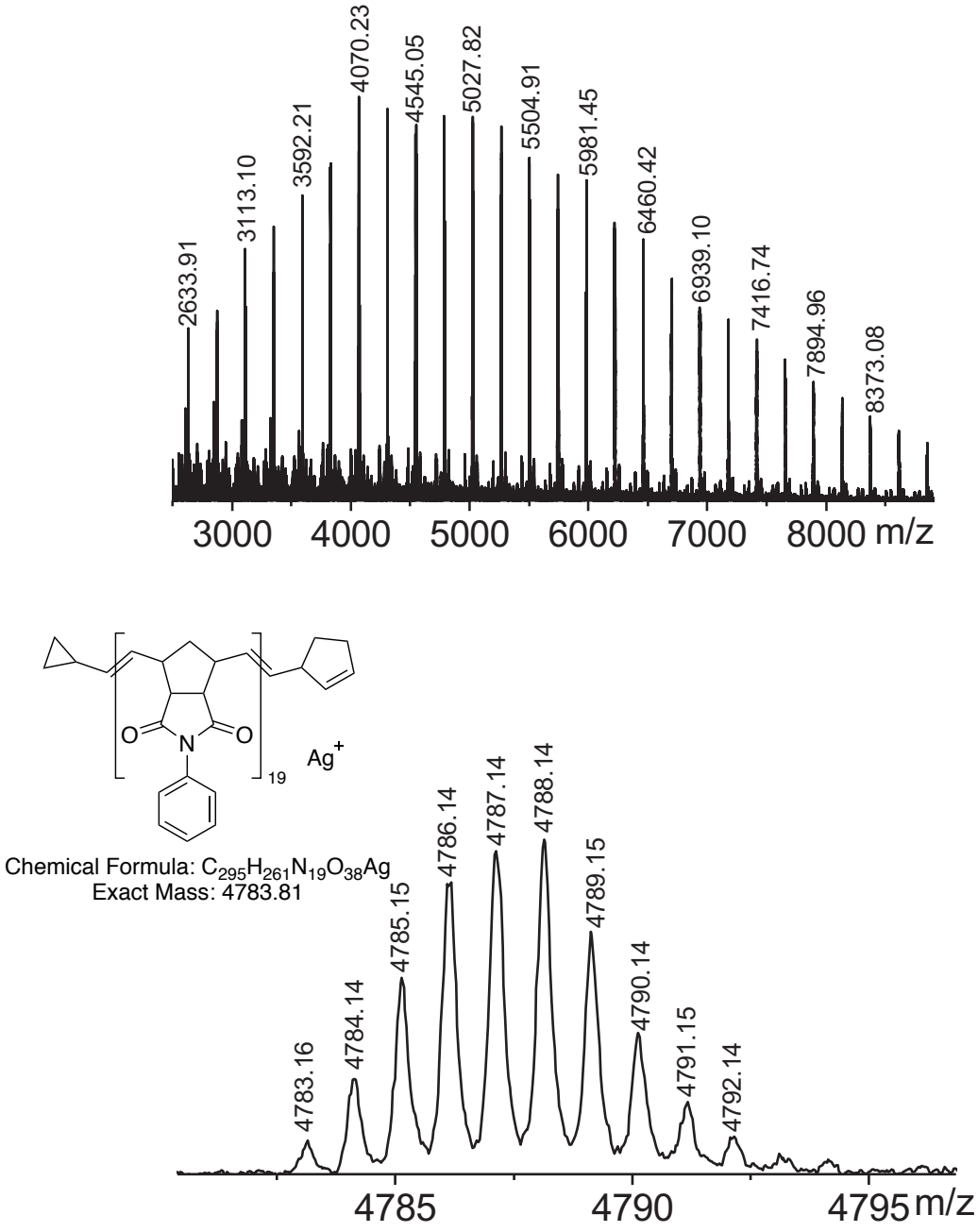


Figure S112 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 11**

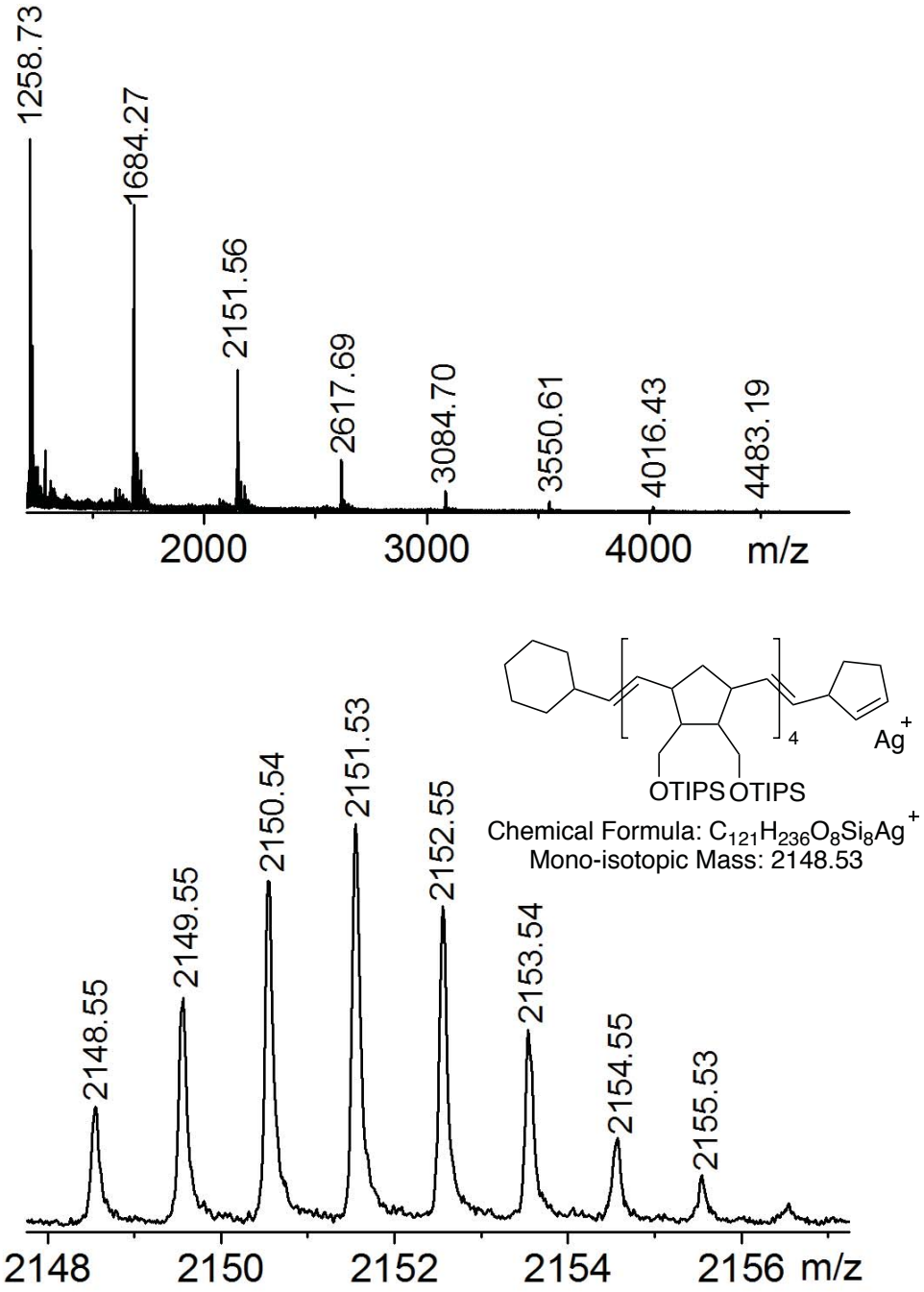


Figure S113 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 12**

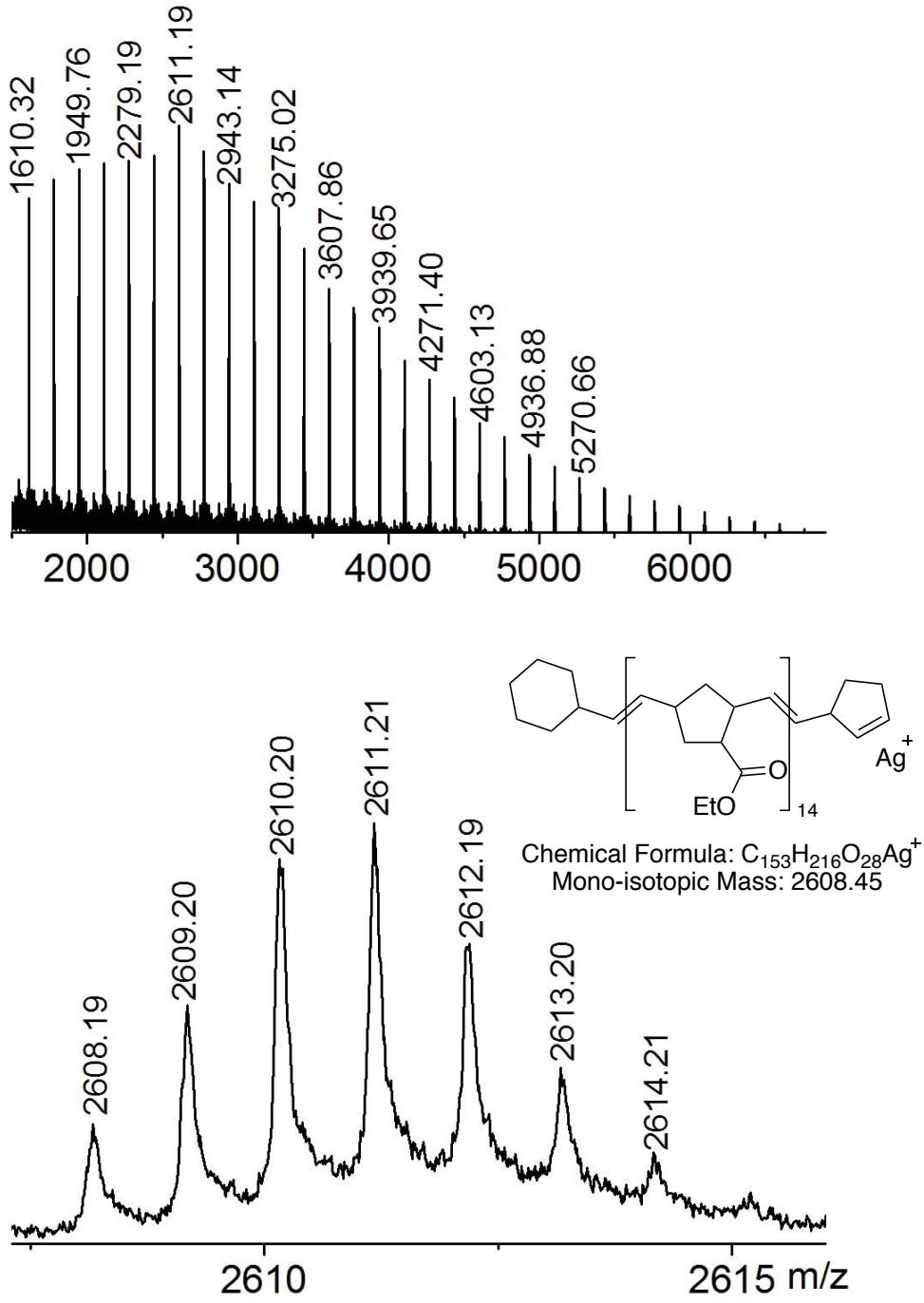


Figure S114 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 13**

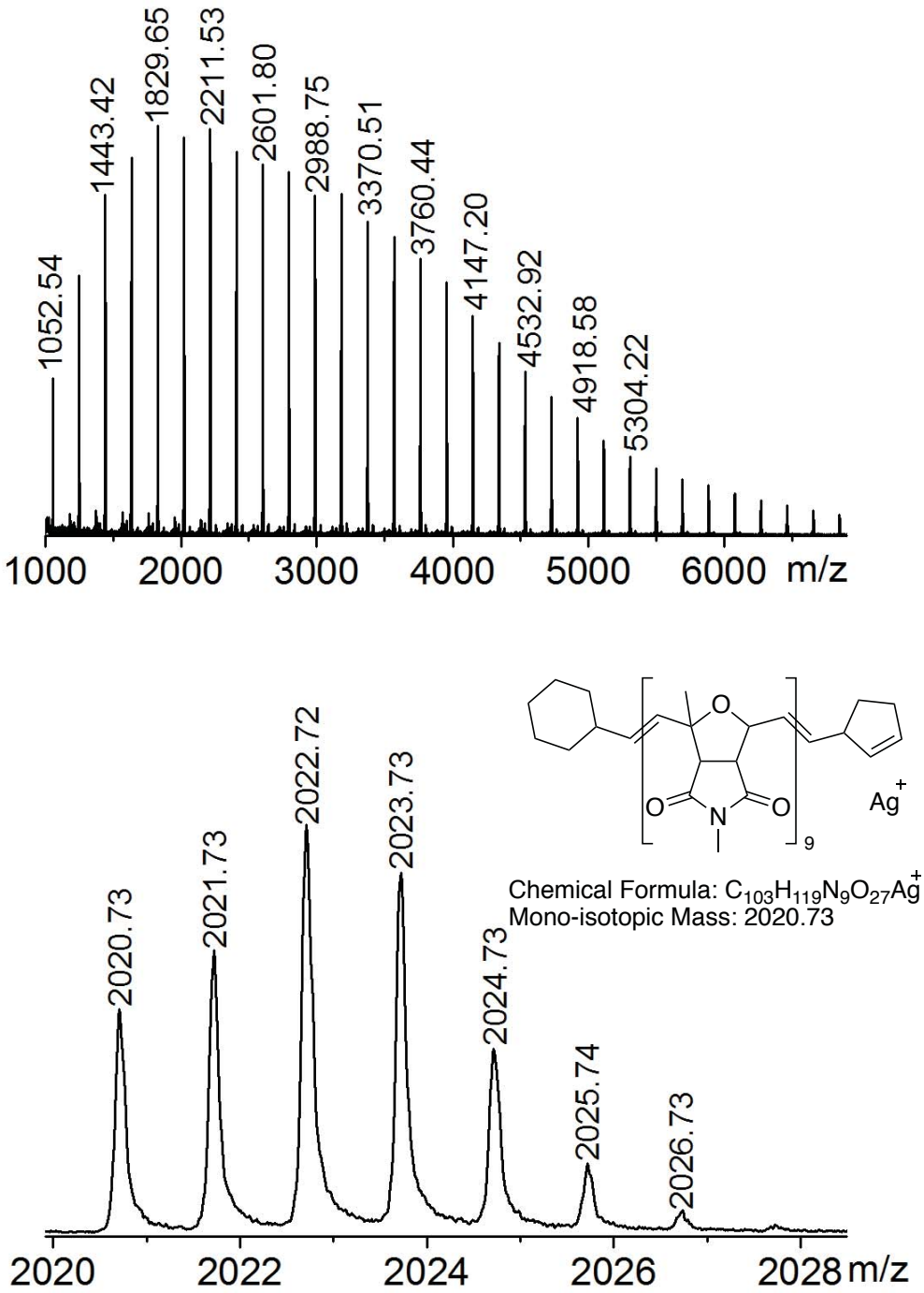


Figure S115 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 14**

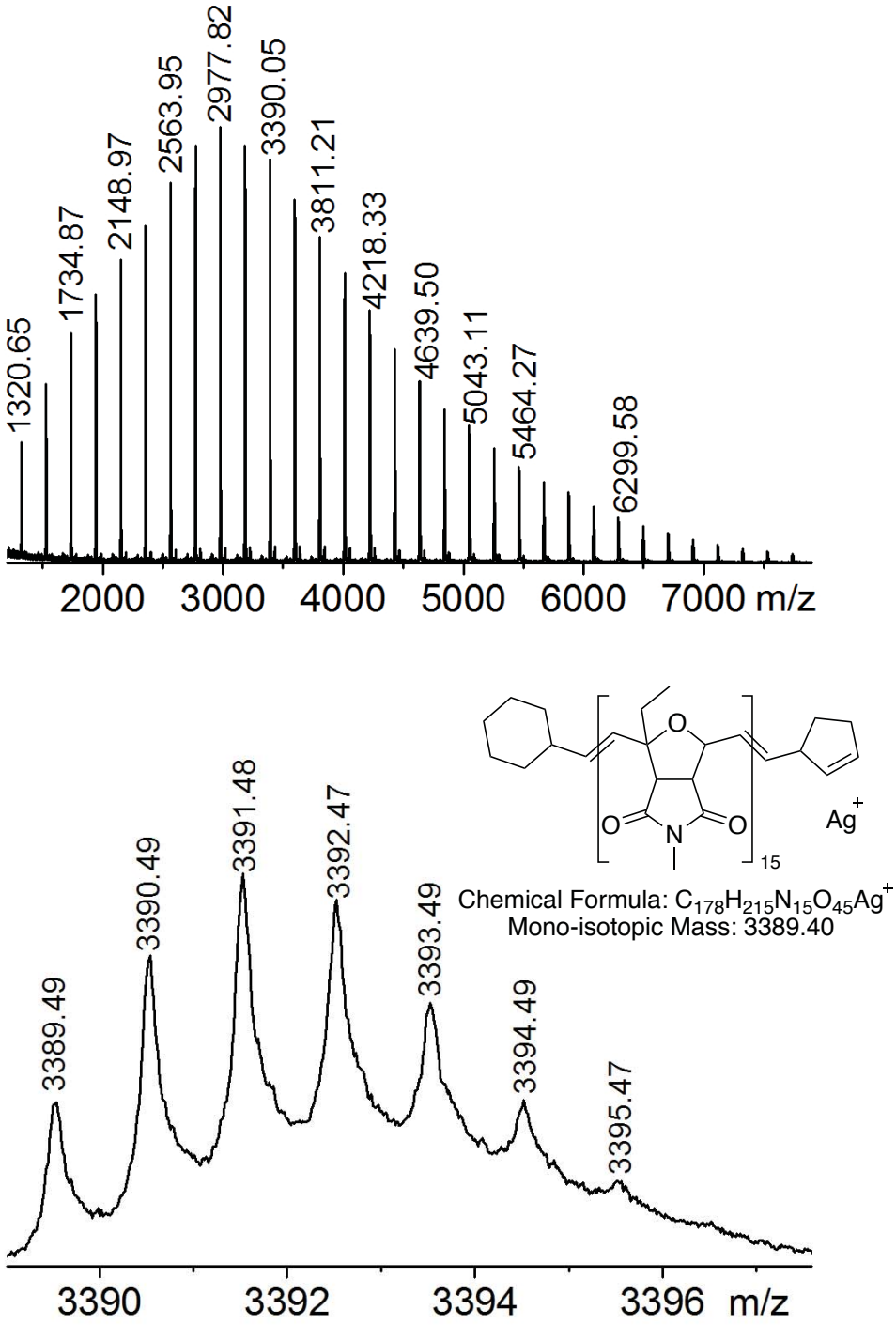


Figure S116 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 15**

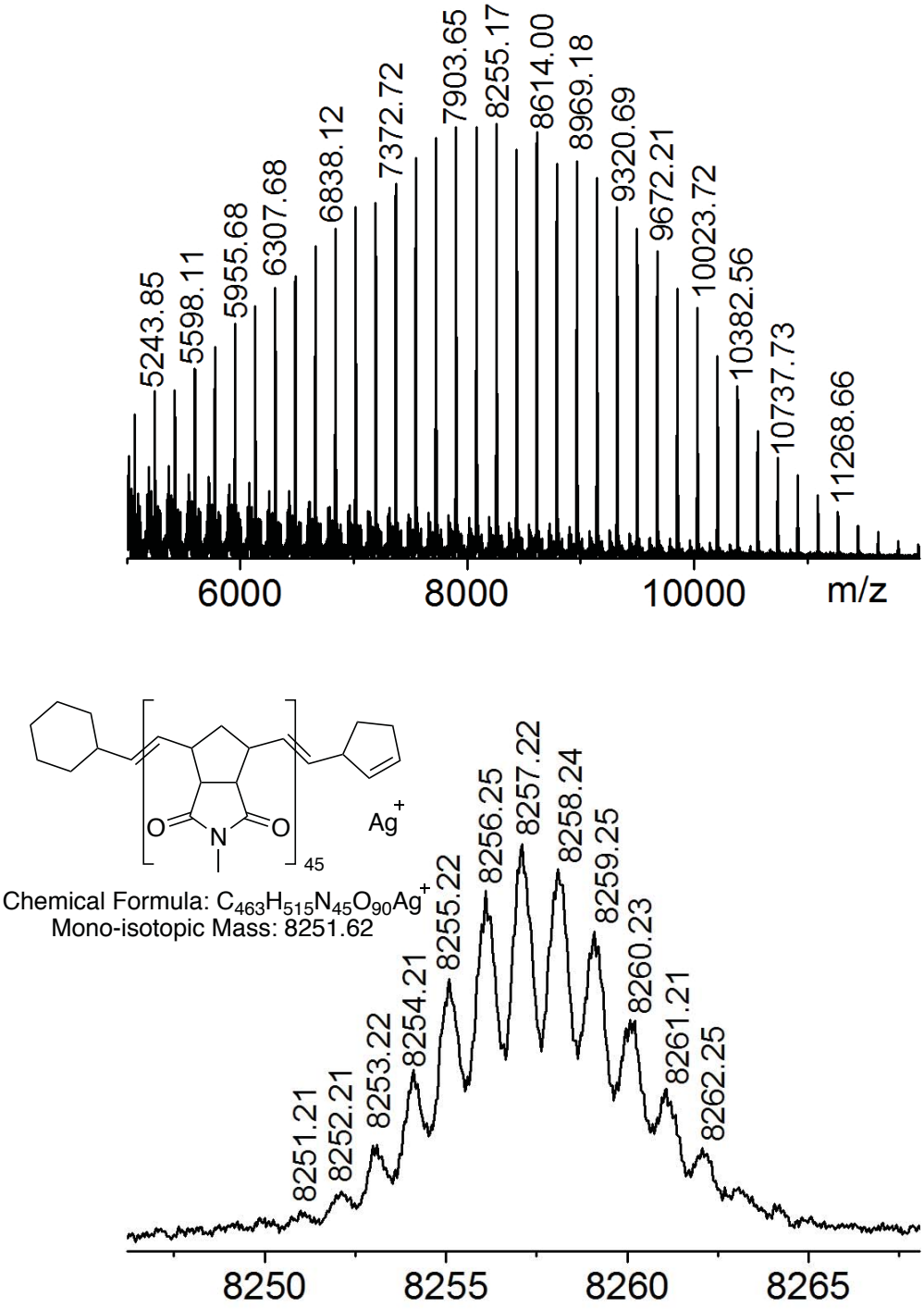


Figure S117 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 16**

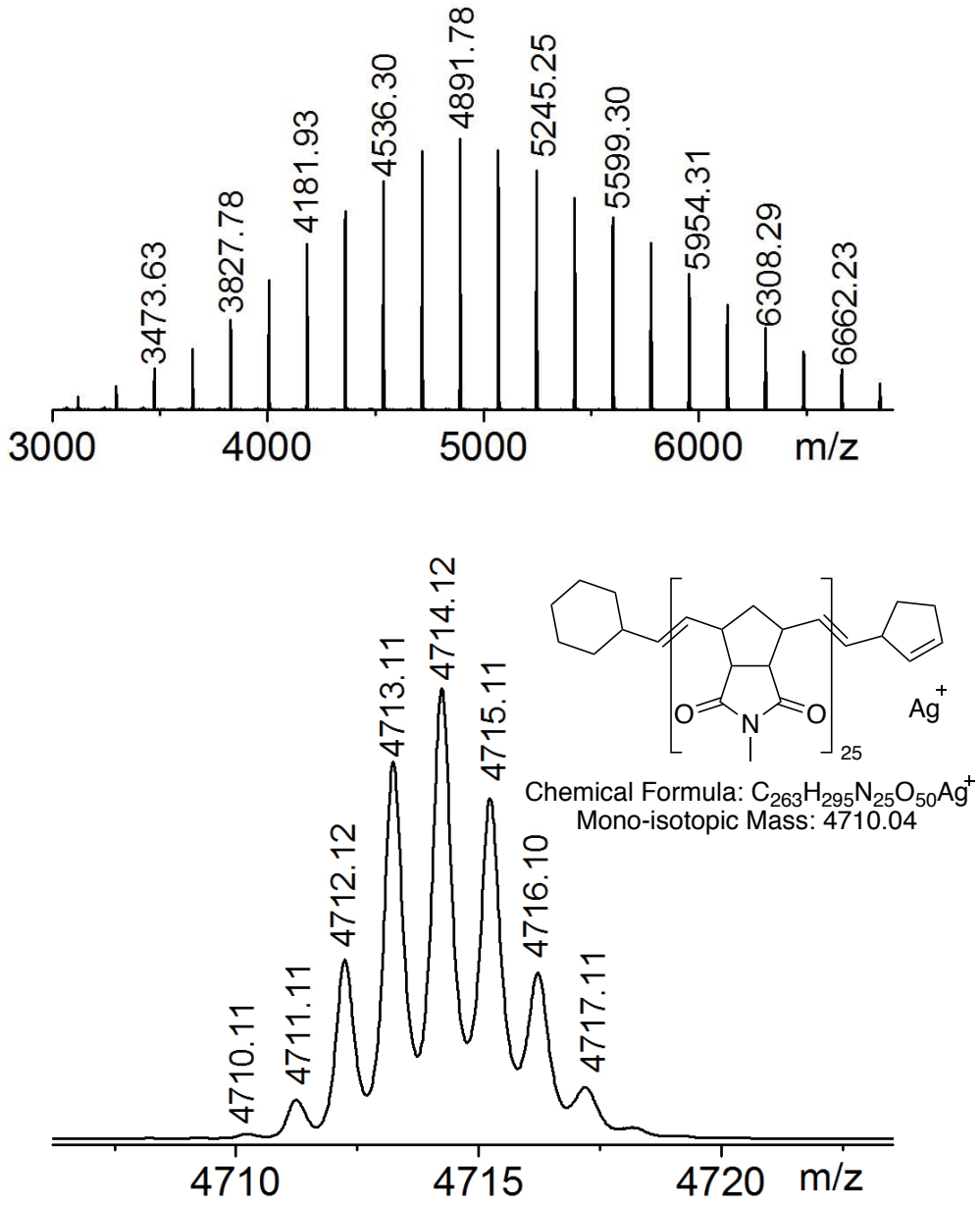


Figure S118 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 17**

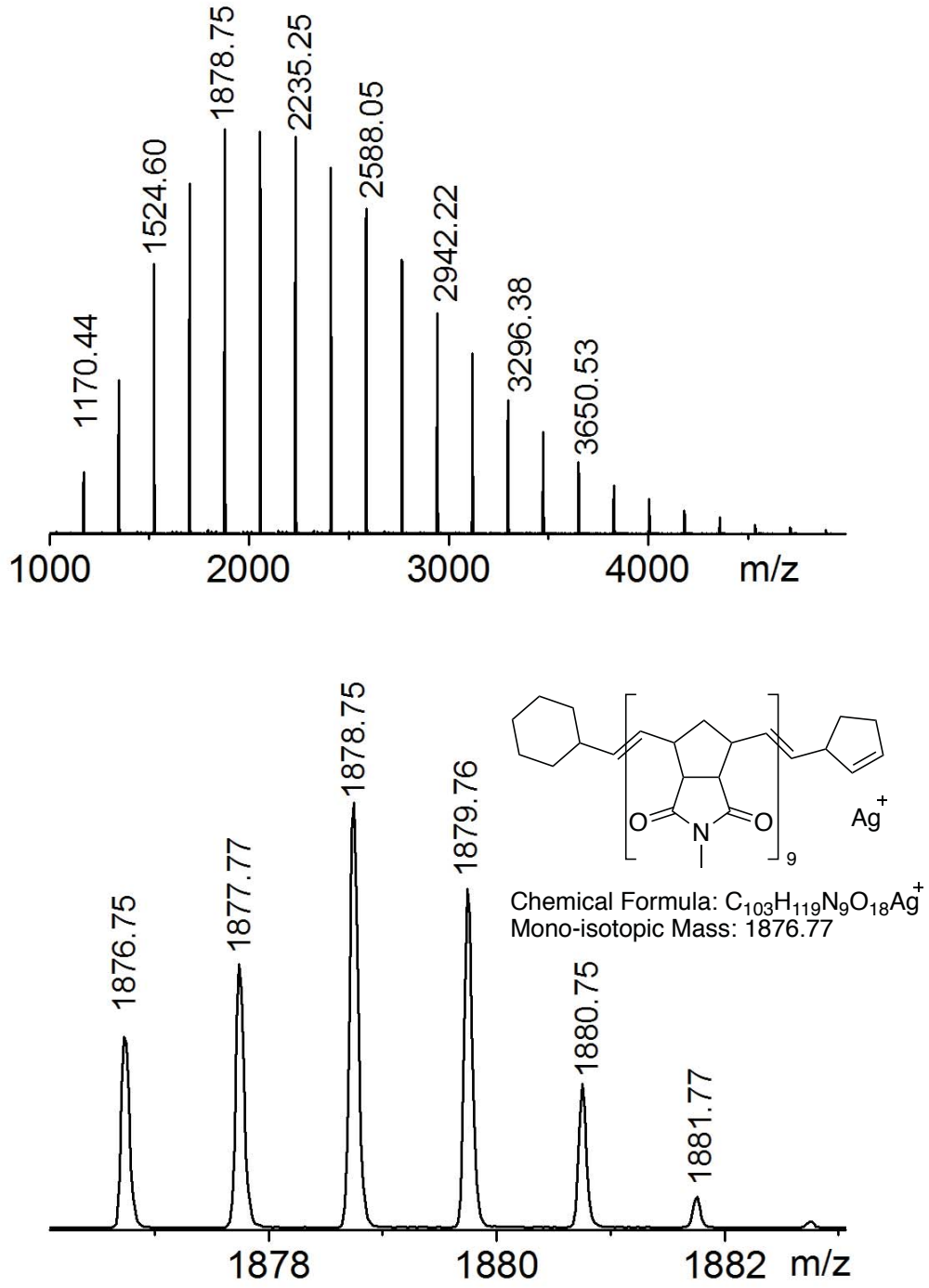


Figure S119 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 18**

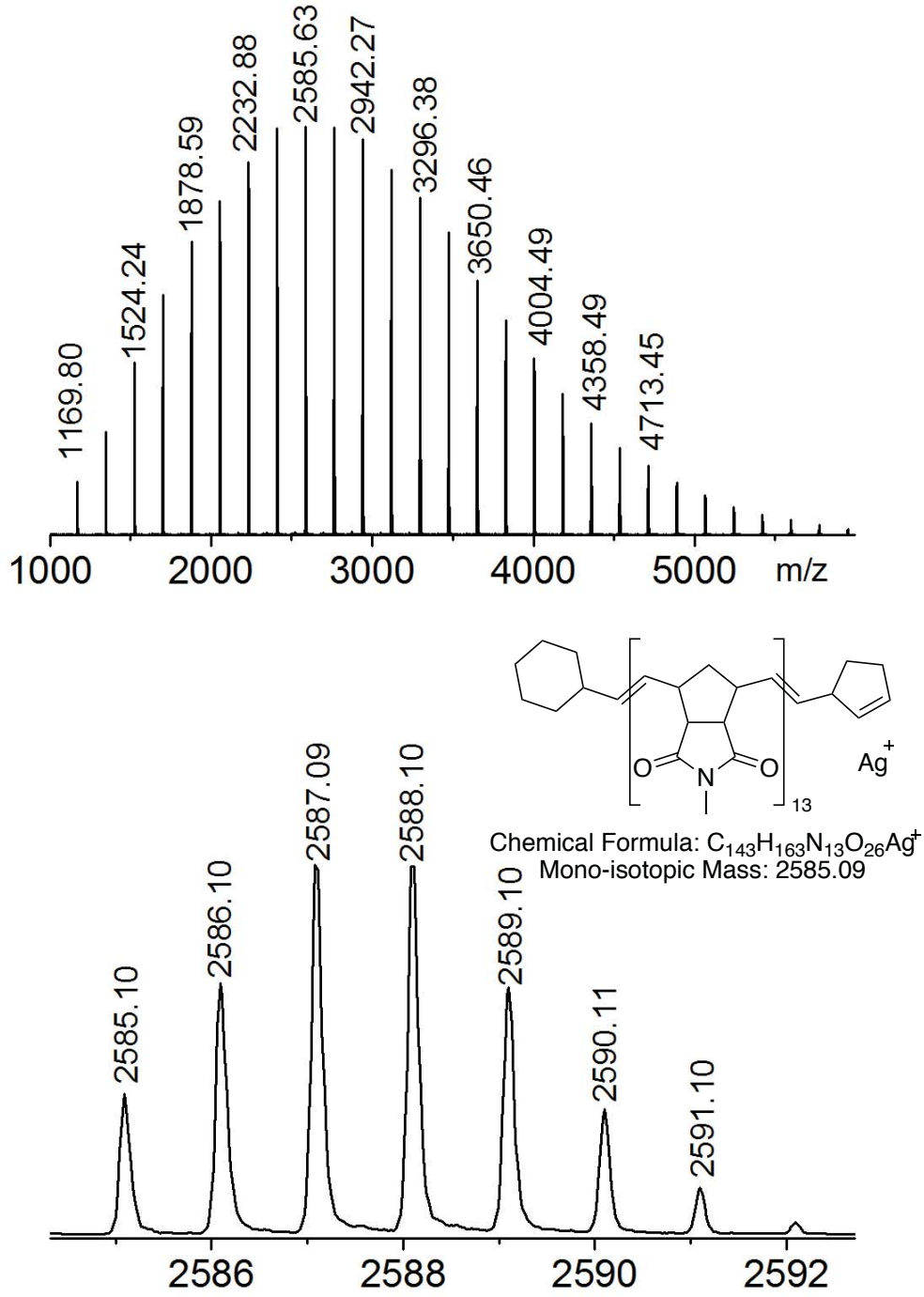


Figure S120 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 19**

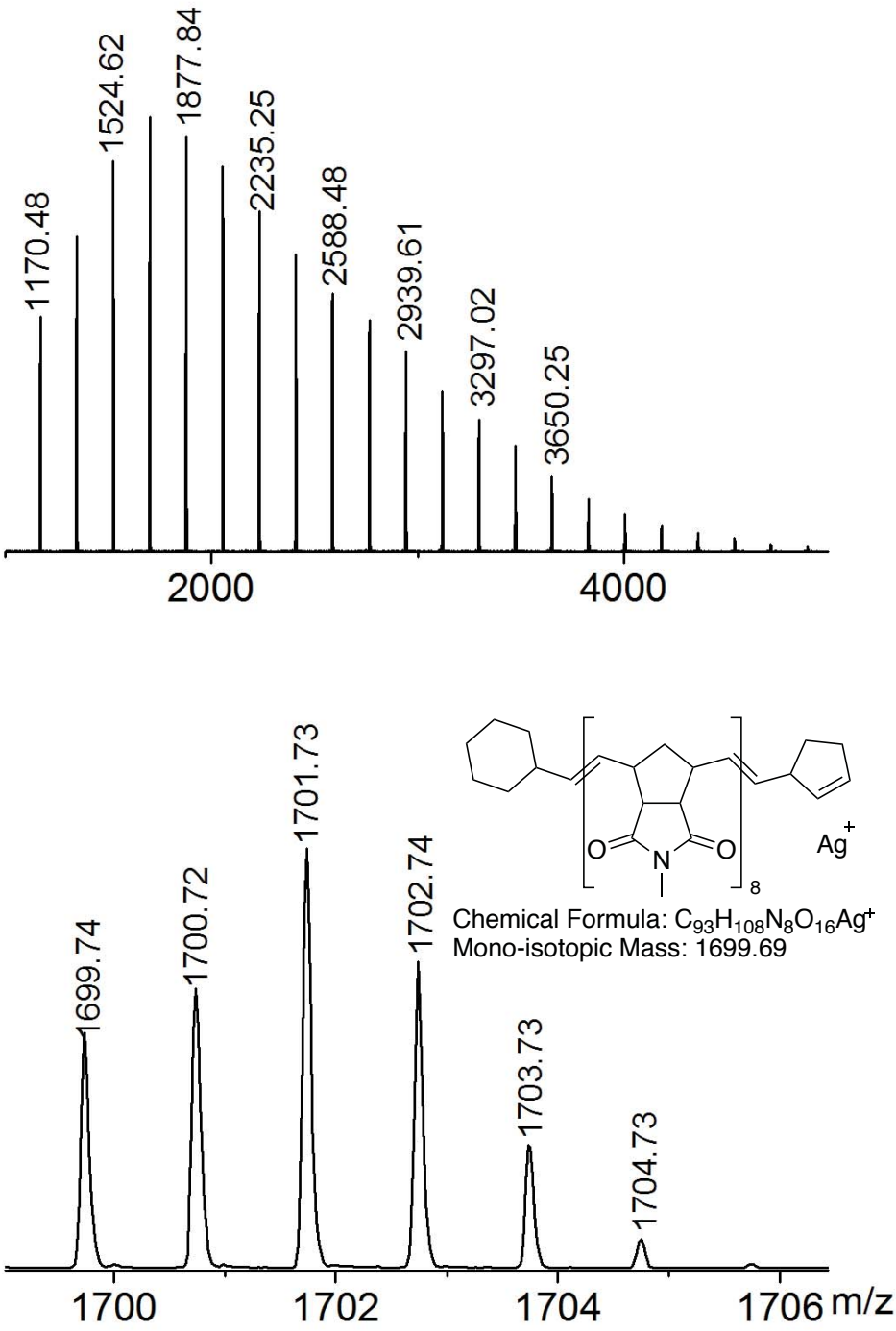


Figure S121 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 20**

Copies of GPC Elugrams

All shown elugrams were recorded in chloroform.

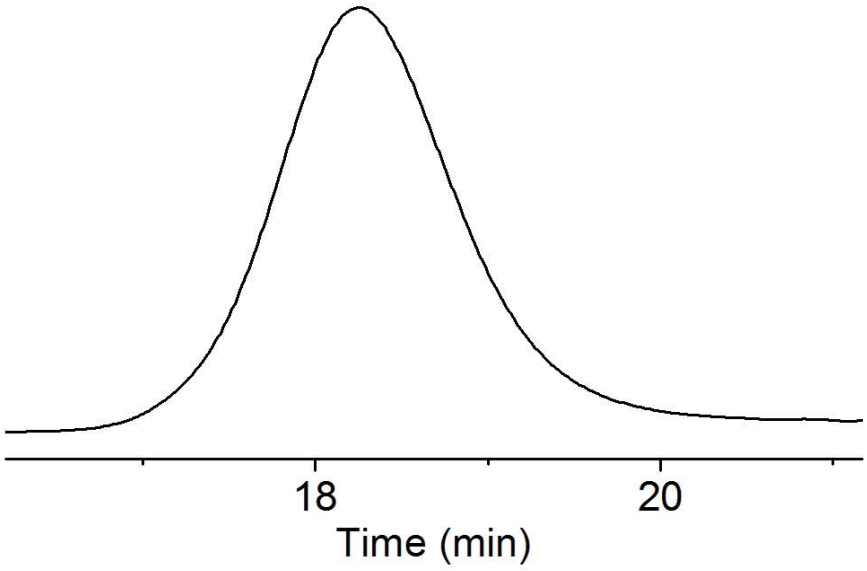


Figure S122 GPC trace of Polymer 1

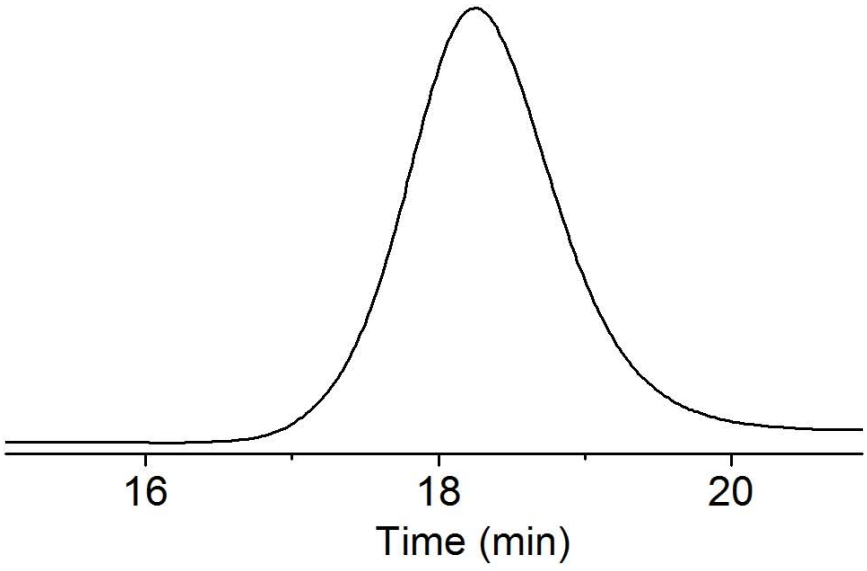


Figure S123 GPC trace of Polymer 2

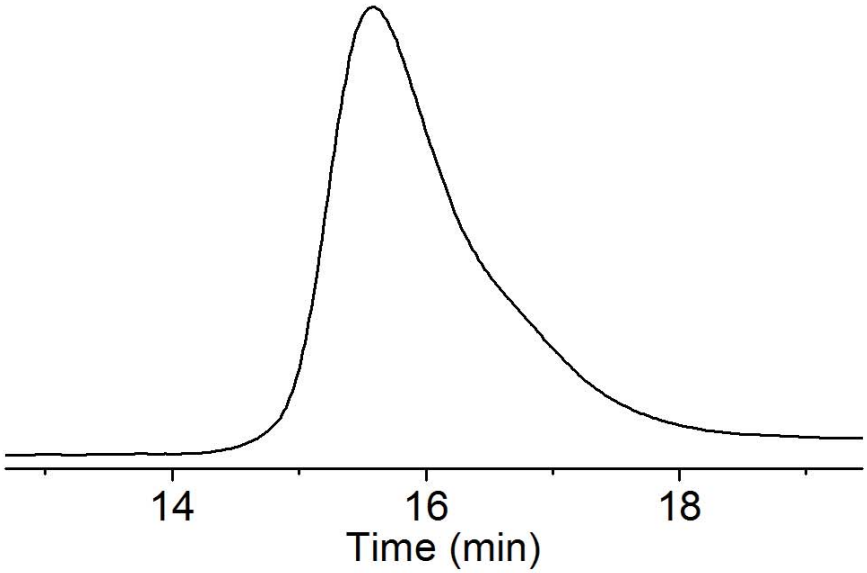


Figure S124 GPC trace of Polymer 3

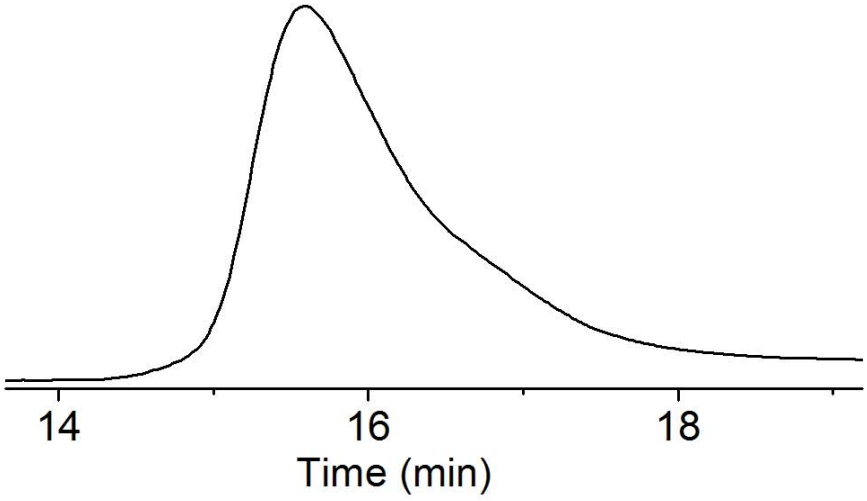


Figure S125 GPC trace of Polymer 4

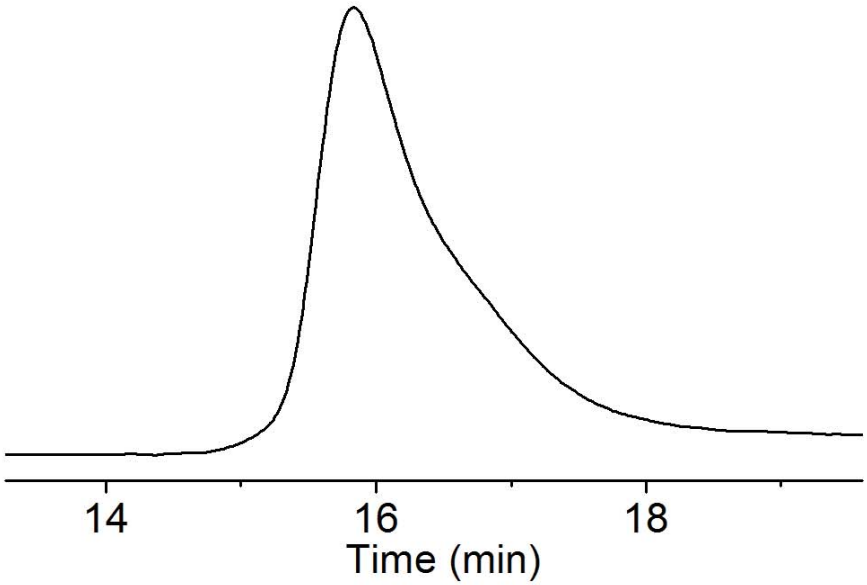


Figure S126 GPC trace of Polymer 5

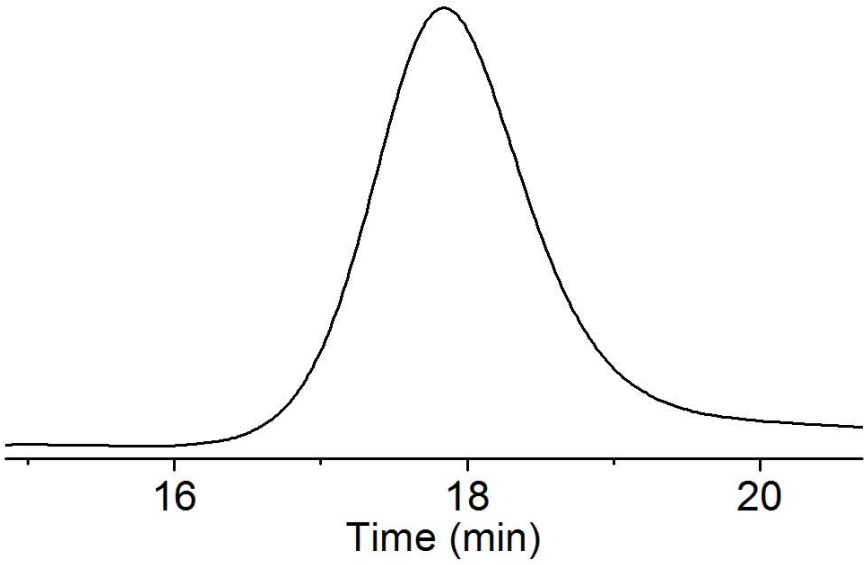


Figure S127 GPC trace of Polymer 6

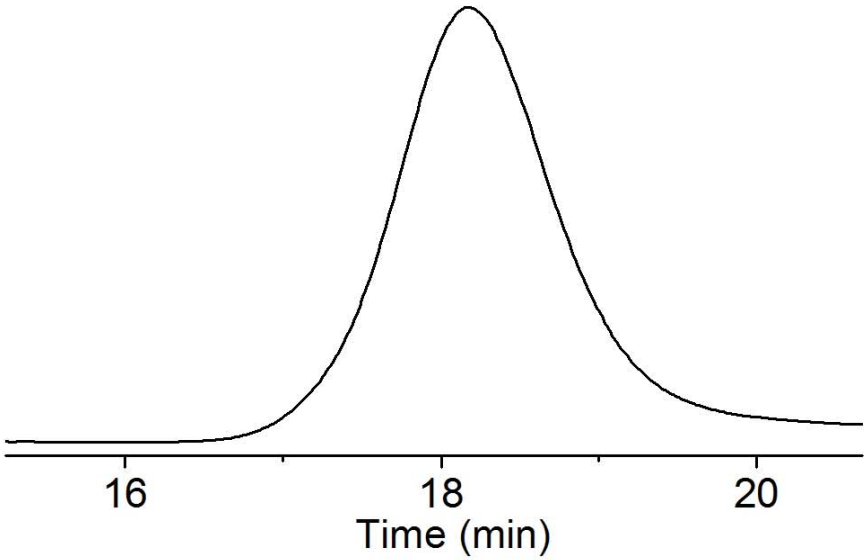


Figure S128 GPC trace of Polymer 7

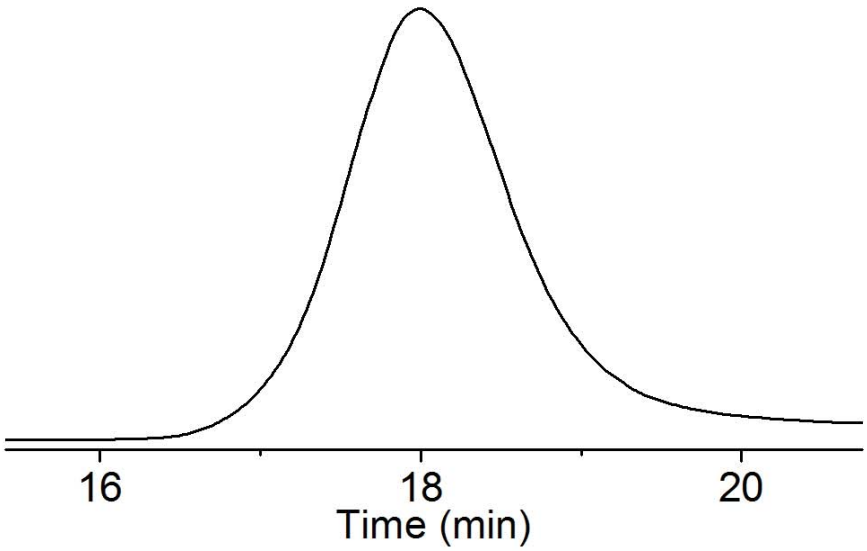


Figure S129 GPC trace of Polymer 8

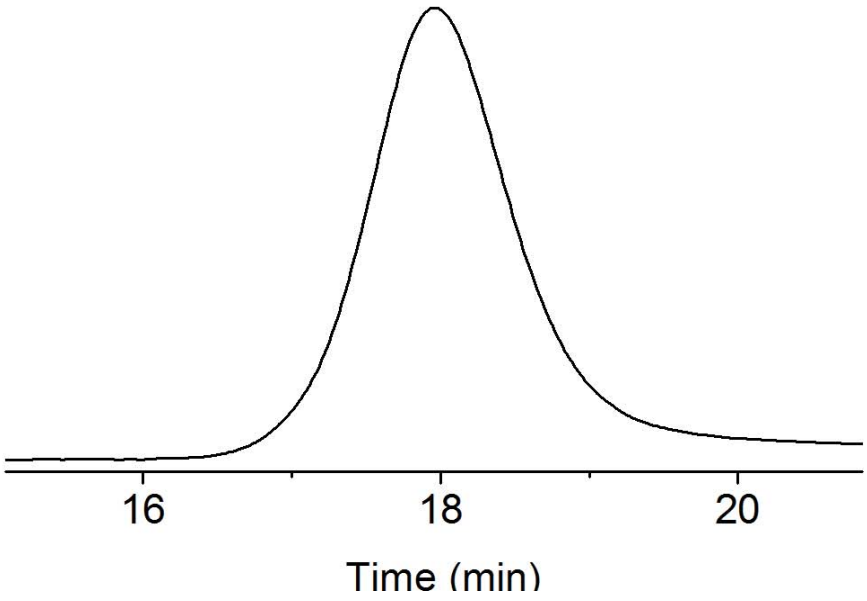


Figure S130 GPC trace of Polymer 9

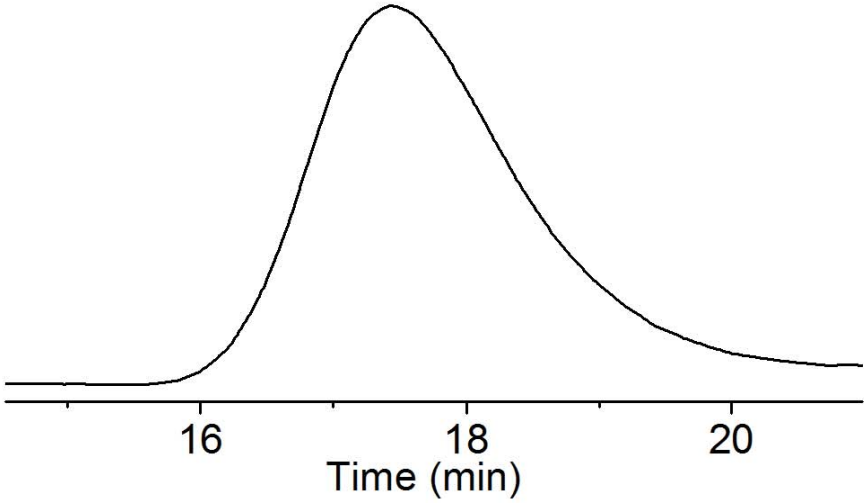


Figure S131 GPC trace of Polymer 10

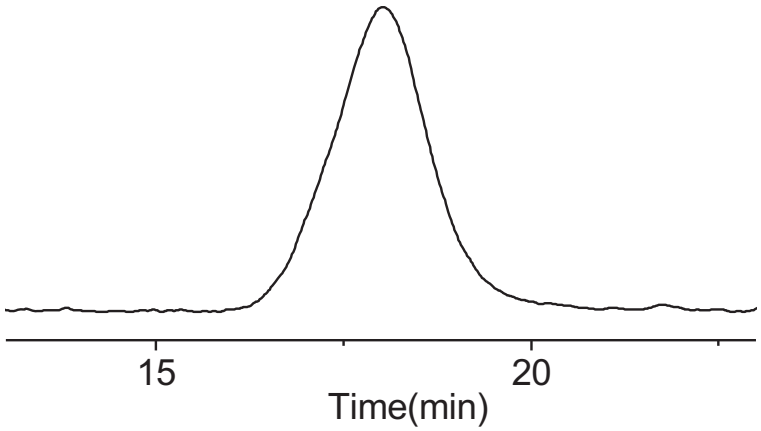


Figure S132 GPC trace of Polymer 11

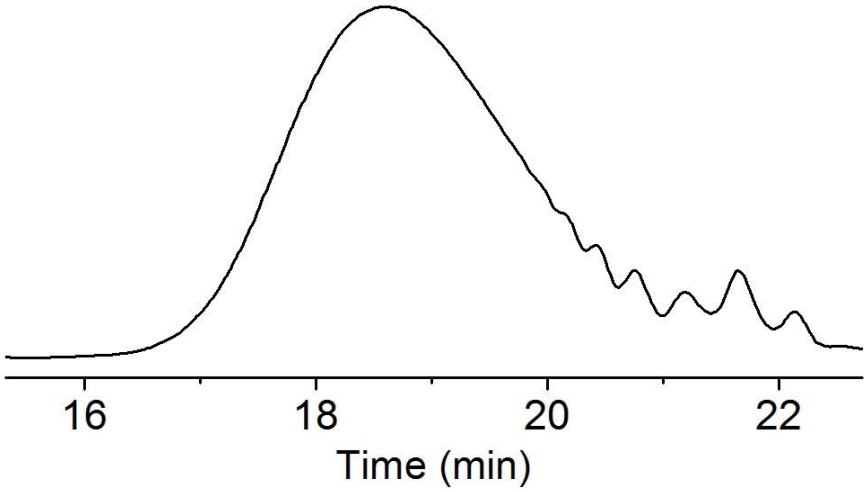


Figure S133 GPC trace of Polymer 12

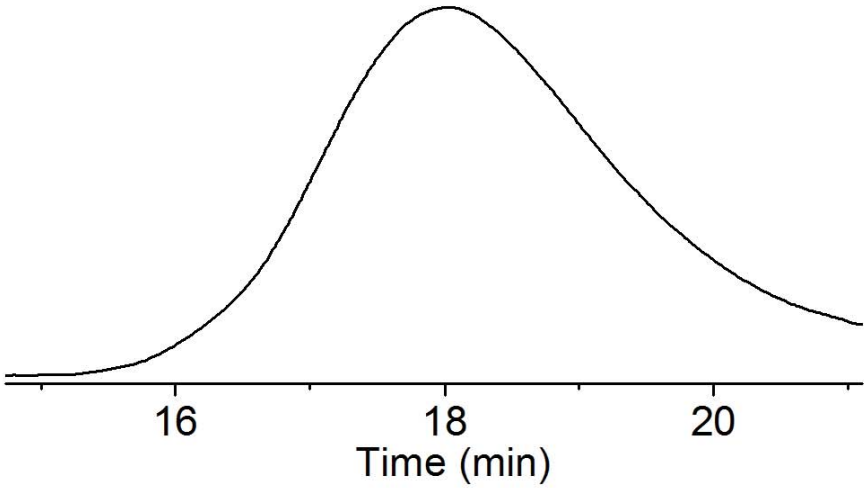


Figure S134 GPC trace of Polymer 13

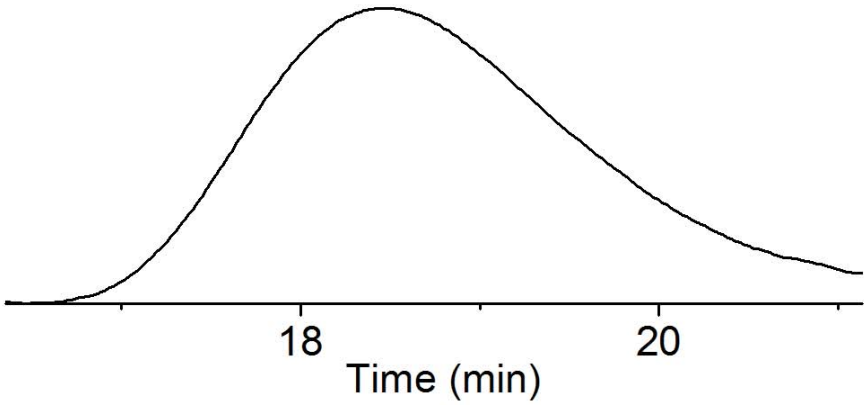


Figure S135 GPC trace of Polymer 14

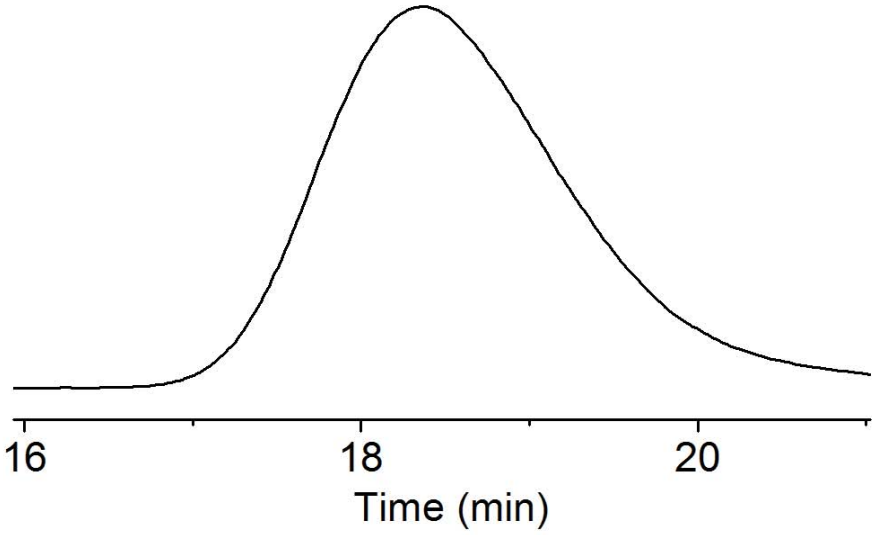


Figure S136 GPC trace of Polymer 15

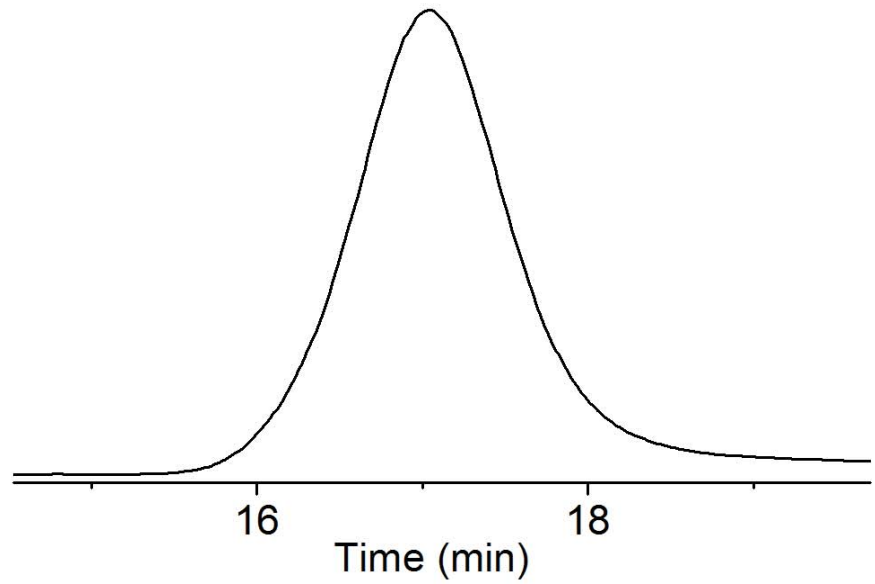


Figure S137 GPC trace of Polymer 16

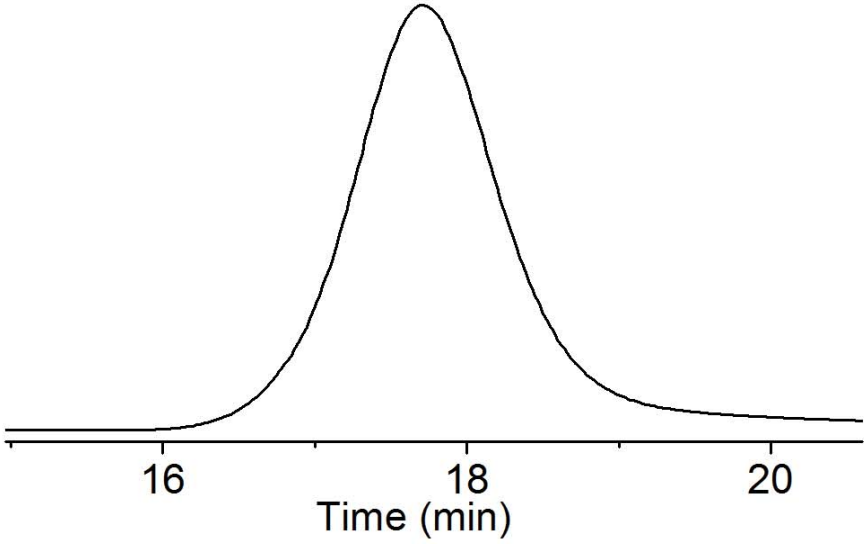


Figure S138 GPC trace of Polymer 17

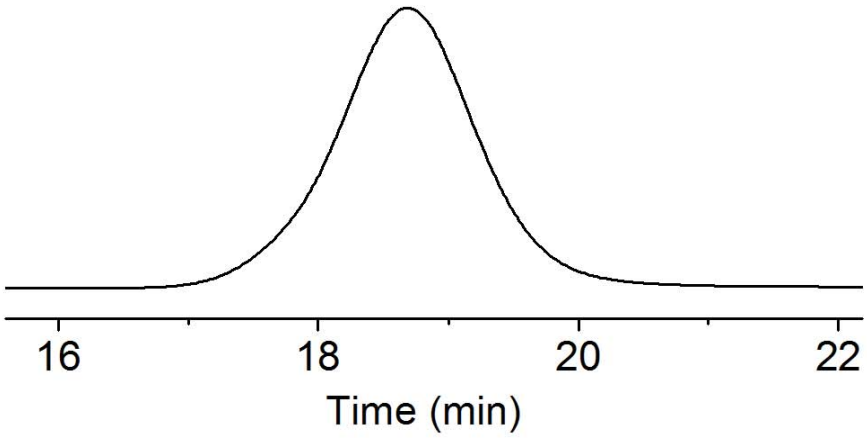


Figure S139 GPC trace of Polymer 18

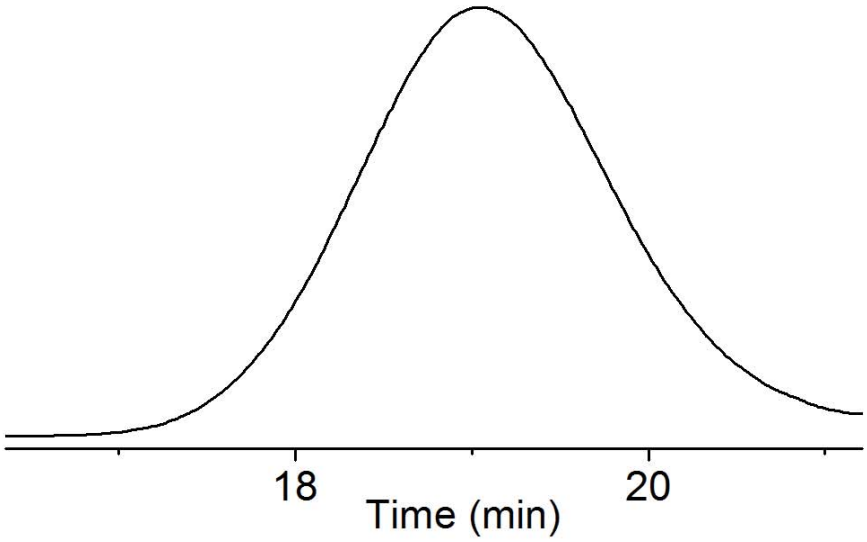


Figure S140 GPC trace of Polymer 19

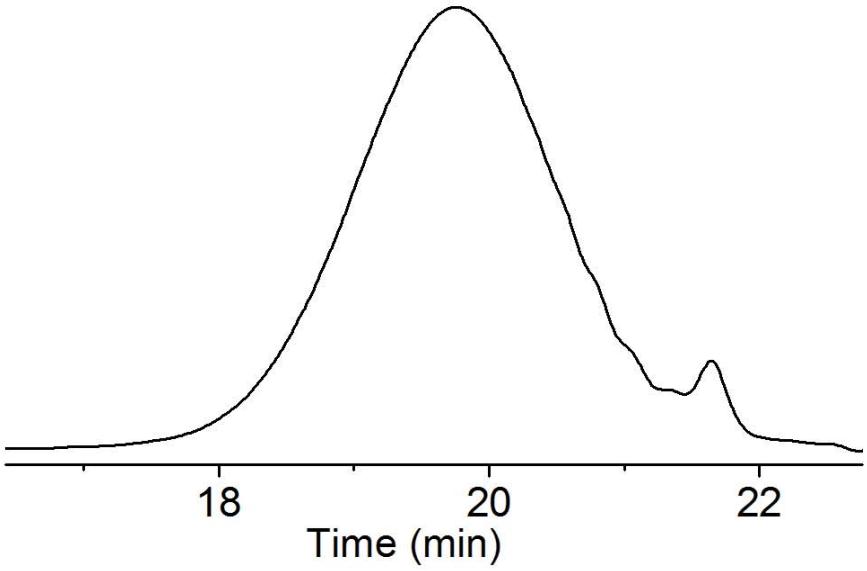


Figure S141 GPC trace of Polymer 20

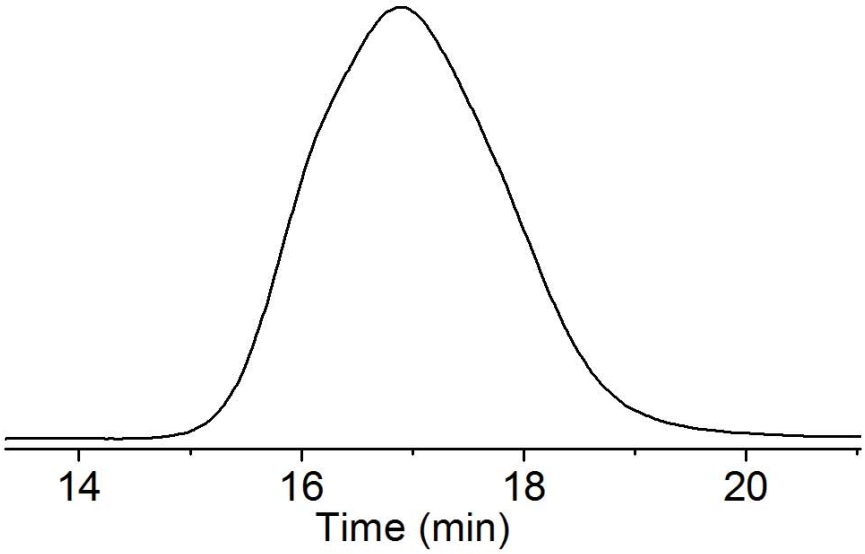


Figure S142 GPC trace of Polymer 21

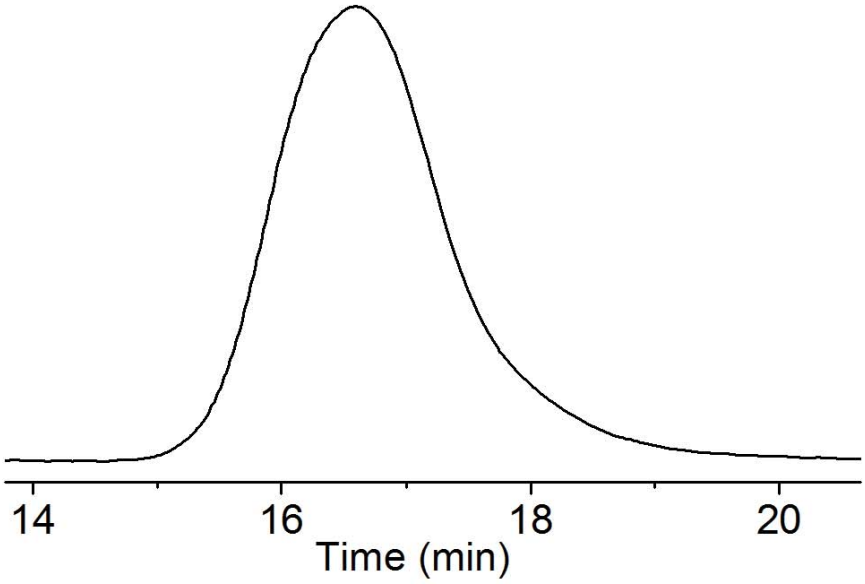


Figure S143 GPC trace of Polymer 22

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