Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Pulsed-addition ring-opening metathesis polymerization with functional enyne reagents

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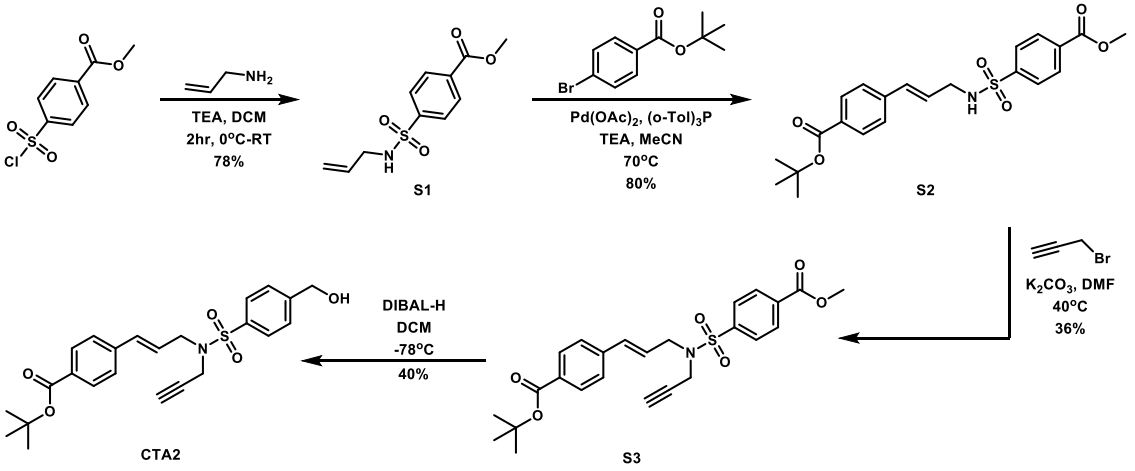
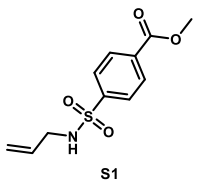
General procedures. All reactions were carried out under a nitrogen atmosphere with dry solvents using anhydrous conditions unless otherwise stated. Dry, degassed dichloromethane (CH_2Cl_2), *N*,*N*-dimethylformamide (DMF), and acetonitrile (MeCN) were obtained from a JC Meyer solvent purification system. $CDCl_3$ was stored under 4Å molecular sieves to remove water and acid. Unless otherwise stated, all other reagents were purchased at the highest commercial quality and used without further purification. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent and basic aqueous potassium permanganate ($KMnO_4$), and heat as developing agents. E. Merck silica gel (60, particle size 0.043–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker Avance 400 or 500 MHz instruments and calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra (MS) were recorded on LC/MS (Agilent Technologies 1260 Infinity II/6120 Quadrupole) or a time-of-flight mass spectrometer by ESI or matrix assisted laser desorption/ionization (MALDI) using a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix and AgTFA ionizing agent. Polymer samples were analyzed using a Tosoh EcoSEC HLC 8320GPC system with TSKgel SuperHZ-L columns eluting $CHCl_3$ containing 0.25% NEt_3 at a flow rate of 0.45 mL/min. All number-average molecular weights and dispersities were calculated from refractive index chromatograms using PStQuick Mp-M polystyrene standards. Melting points were measured on Bibby Scientific's MEL-TEMP Digital Melting Point Apparatus.

Experimental Procedures

Monomers **M1**[1], **M2**[1], **M3**[2], **M4**[2], and **CTA1**[3] were prepared according to literature procedures.

Scheme 1: Synthesis of CTA2.




S1

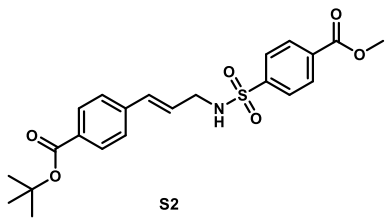
S1: To a stirred solution of allylic amine (741 mg, 13.0 mmol, 1.1 eq) and triethylamine (1.2 g, 11.8 mmol, 1.0 eq) in CH_2Cl_2 (60 ml) in an ice bath was added methyl-4-(chlorosulfonyl) benzoate (2.1 g, 11.8 mmol, 1.0 eq). Then the reaction was warmed to room temperature. After 2 hours, the reaction mixture was diluted with DCM (200 ml), washed with 1N HCl (200 ml), brine (200 ml), dried over Na_2SO_4 and concentrated in vacuo. The residual was purified by column chromatography (20% to 30% Et_2O in hexanes) to give the product as white solid (1.8 g, 78%).

m.p.: 88 – 90 °C

MS (m/z): cacld for $C_{11}H_{13}NO_4S$, $[M+H]^+$, 256.06; found, 256.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 5.66 (ddt, *J* = 11.4, 8.6, 5.8 Hz, 1H), 5.23 (s, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 3.93 (s, 3H), 3.60 (t, *J* = 5.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.63, 144.01, 133.80, 132.59, 130.31, 127.07, 117.95, 52.65, 45.74.



S2

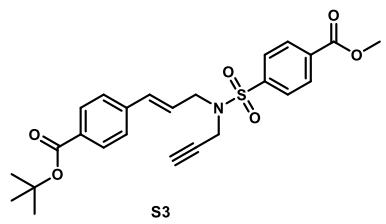
S2: *t*-Butyl-4-bromobenozate (1.31g, 5.09 mmol, 1.3 eq), **S1** (1.0 g, 3.92 mmol, 1.0 eq), palladium (II) acetate (66.9 mg, 0.30 mmol, 0.076 eq), tri(o-tolyl) phosphine (179 mg, 0.59 mmol, 0.15 eq) were dissolved in acetonitrile (MeCN, 10 ml) under N_2 gas. Triethylamine (1.1 ml, 7.84 mmol, 2.0 eq) was added via syringe and the mixture was placed in the oil bath that was preheated to 70 °C and stirred for 24 hrs. Then the reaction was quenched by H_2O (50 ml). The aqueous layer was extracted by dichloromethane (3×10 ml). The combined organics were washed with brine (50 ml), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 2:1) to give **S2** as a white solid (1.37 g, 80%).

m.p.: 127 – 130 °C

MS (m/z): cacld for $C_{18}H_{16}NO_5S^+$, $[M-C_4H_9O]^-$, 358.07; found, 358.3.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 10.2 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.11 (dt, *J* = 15.8, 6.3 Hz, 1H), 4.66 (t, *J* = 6.2 Hz, 1H), 3.96 (s, 3H), 3.83 (td, *J* = 6.2, 1.3 Hz, 2H), 1.58 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.50, 165.34, 144.05, 139.66, 133.93, 132.53, 131.41, 130.37, 129.75, 127.12, 126.11, 125.95, 81.07, 45.41, 28.14.



S3

S3: Compound **S2** (1.37 g, 3.17 mmol, 1.0 eq) and potassium carbonate (1.32 g, 9.52 mmol, 3.0 eq) was dissolved in DMF (16 ml) at room temperature, followed by addition of propargyl bromide (0.53 ml, 4.76 mmol, 1.5 eq). The mixture was placed in an oil bath that was preheated to 40 °C and stirred overnight, then was quenched by H_2O (200 ml). The aqueous layer was extracted by diethyl ether (3×50 ml). The combined organics were washed with brine (50 ml), dried over

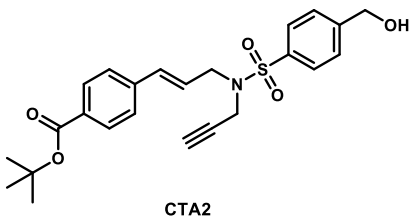
Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (33% EtOAc in hexane) to give **S3** as a white solid (541 mg, 36%).

m.p.: 83 – 85 °C

MS (m/z): cacld for $C_{25}H_{27}NNaO_6S^+$, $[M+Na]^+$, 492.15; found, 492.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.94 (dd, *J* = 14.1, 8.5 Hz, 4H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.17 (d, *J* = 2.4 Hz, 2H), 4.04 (dd, *J* = 6.7, 0.9 Hz, 2H), 3.97 (s, 3H), 2.03 (t, *J* = 2.4 Hz, 1H), 1.59 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.64, 165.34, 142.86, 139.73, 134.19, 133.95, 131.48, 130.11, 129.77, 127.74, 126.26, 124.88, 81.07, 75.95, 74.28, 52.63, 48.59, 36.12, 28.15.



CTA2

CTA2: **S3** was dissolved in DCM (9 mL), and the solution was cooled to -78 ℃. Then a DIBAL-H solution (1.1 M in cyclohexane, 1.8 mL, 1.99 mmol, 2.2 eq) was added dropwise. The reaction was warmed to room temperature slowly. After 1 hour, TLC showed completion of the reaction, and the reaction was quenched by Rochelle's salt (saturated aqueous sodium potassium tartrate solution) and stirred until homogeneous. The reaction mixture was diluted with DCM (30 mL), washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the crude mixture by column chromatography (20% to 35% EtOAc in hexanes) afforded the product as a colorless oil (157 mg, 40%).

MS (m/z): cacld for $C_{24}H_{27}NNaO_5S^+$, $[M+Na]^+$, 464.15; found, 464.7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.79 (s, 2H), 4.14 (d, *J* = 2.4 Hz, 2H), 4.01 (d, *J* = 6.7 Hz, 2H), 2.06 (t, *J* = 2.4 Hz, 1H), 1.59 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.43, 146.23, 139.90, 137.78, 133.88, 131.35, 129.75, 127.93, 126.82, 126.24, 125.29, 81.09, 76.39, 74.06, 64.19, 48.49, 36.11, 28.15.

General Procedure for PA-ROMP

CTA **1** or **2** (3.0 eq) was added to five 8ml vials equipped with a stir bar, placed under a nitrogen atmosphere, and dissolved in degassed $CDCl_3$ or DCM (200 μL). A solution of Grubbs 3rd generation catalyst (50 μL, 2.7 mg, 0.0037 mmol, 1.0 eq in $CDCl_3$ or DCM) is rapidly transferred to the stirred CTA solution and each vial using a microliter syringe. After 15 minutes, a degassed solution of monomer **M1-M4** (25 eq) in 300 μL $CDCl_3$ or DCM was added to each vial. CTA **1** or **2** (1.2 eq) was added to each reaction vial after 5 minutes to terminate the living polymer and regenerate new initiators. The reaction mixtures were stirred 30 minutes, then vial 1 was quenched with ethyl vinyl ether (EVE). Monomer solution **M1-M4** (25 eq) and CTA (1.2 eq) were added in order as previous steps until all vials were terminated. Polymer mixture was concentrated and precipitated twice into a 15-fold volume of MeOH or hexanes/diethyl ether (1/1). The precipitated polymer was then characterized using GPC, ^{1}H-NMR and MALDI-TOF-MS.

Calculation for determining catalyst death rate

Percentage catalyst living and catalyst death rate per cycle were calculated according to previous literature[4]. A theoretical data of 10 cycles of PA-ROMP is constructed in **Table S1**. The M_n for each pulse ($M_{n(pulse)}$) and the % catalyst living in each vial are calculated by the two equations shown below. An exponential trend is clearly observed, and the data are graphed in **Figure S2**. The equation determined from fit line is $y = 6715.8e^{0.0204x}$ ($R^2 = 0.8543$). Calculated values for each pulse are shown in **Table S2**. The total average catalyst death per cycle is calculated to 3.82%.

$M_{n(pulse)} = n*(M_n) - (n-1)(M_{n-1})$

% catalyst living = $M_1/M_{n(pulse)}$, where n = vial number.

Figure S1: PA-ROMP for **M1** up to 10 cycles with **CTA1**

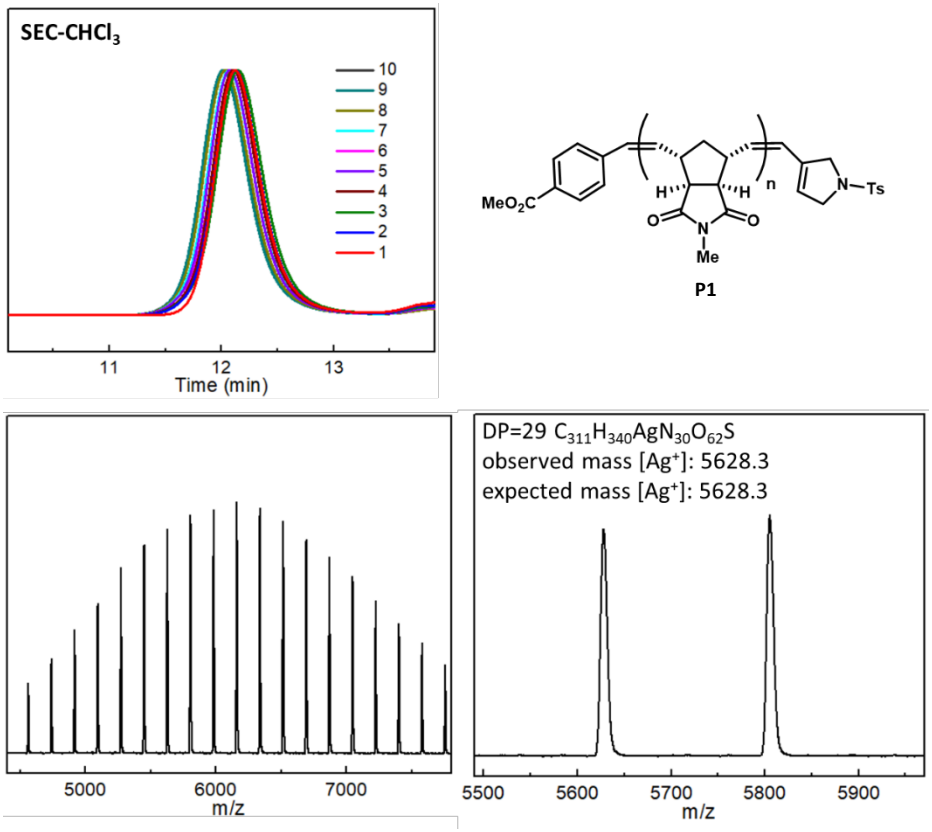


Table S1: Theoretical M_n trend over 10 cycles of PA-ROMP assuming initial molecular weight of 7025 Da

Cycle	M_n	% catalyst living	PDI
1	7025	100%	1.13
2	7079	98%	1.15
3	6852	110%	1.15
4	7324	80%	1.15
5	7591	81%	1.16
6	7289	122%	1.16
7	7681	70%	1.16
8	7900	74%	1.18
9	8362	58%	1.16
10	8202	104%	1.16

Figure S2: Exponential fit

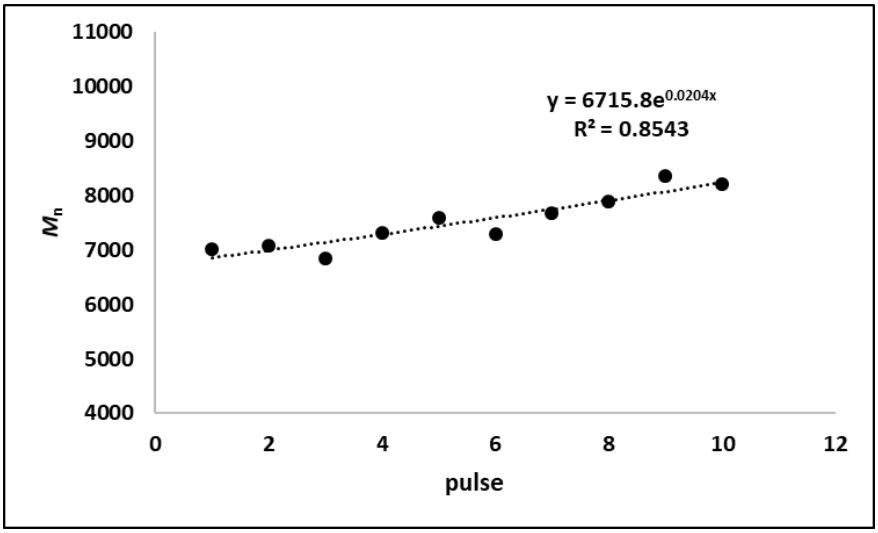
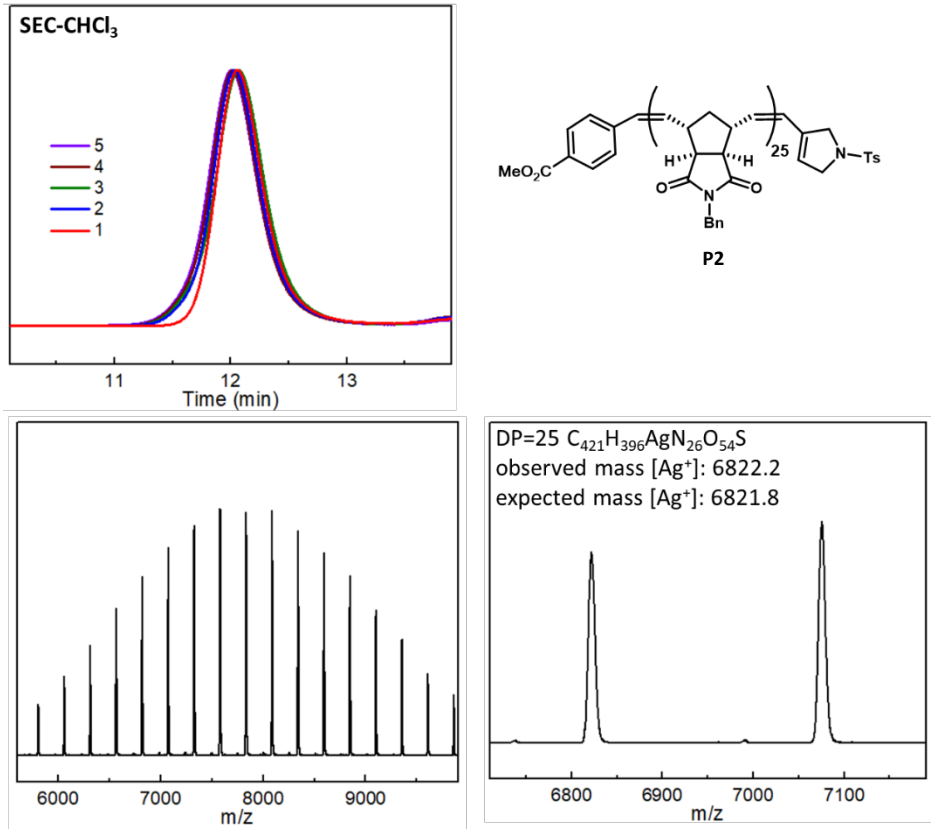


Table S2: Calculated Mn and catalyst death rate depend on exponential fit.

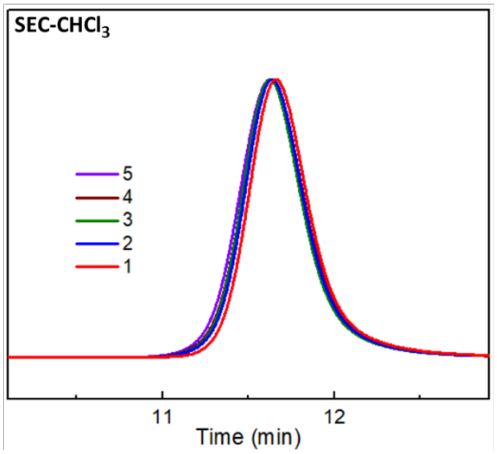
cycle	M_n (calc.)	M_n (pulse.calc)	% cat.death from initial	% cat.death from cycle
1	6854	6854	0%	N/A
2	6995	7137	3.96%	3.96%
3	7140	7428	7.72%	3.92%
4	7287	7728	11.31%	3.88%
5	7437	8038	14.72%	3.85%
6	7590	8357	17.98%	3.82%
7	7747	8685	21.08%	3.78%
8	7906	9024	24.04%	3.75%
9	8069	9373	26.87%	3.72%
10	8236	9732	29.57%	3.69%
				3.82% (Average)

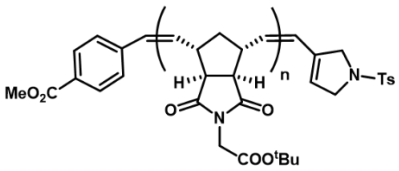
Figure S3: PA-ROMP for **M2** with **CTA1**



Cycle	Mn	% living catalyst	PDI
1	7683	100%	1.14
2	8214	88%	1.16
3	7881	106%	1.18
4	8521	74%	1.17
5	8590	87%	1.18

Figure S4: PA-ROMP for **M3** with **CTA1**

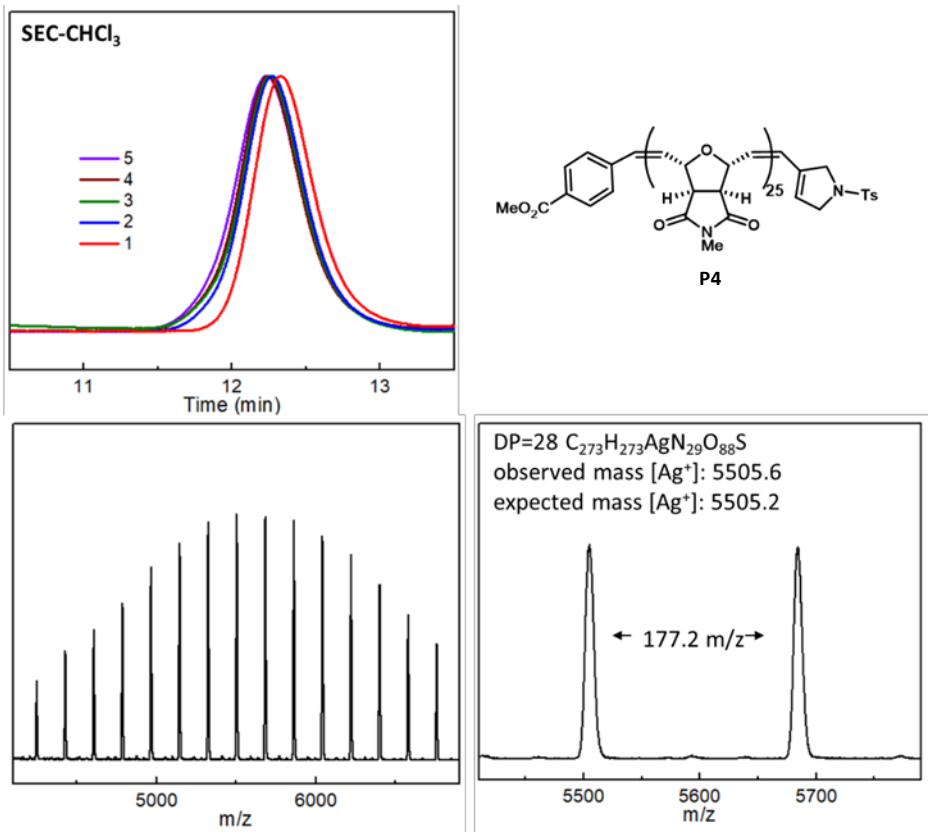




P3

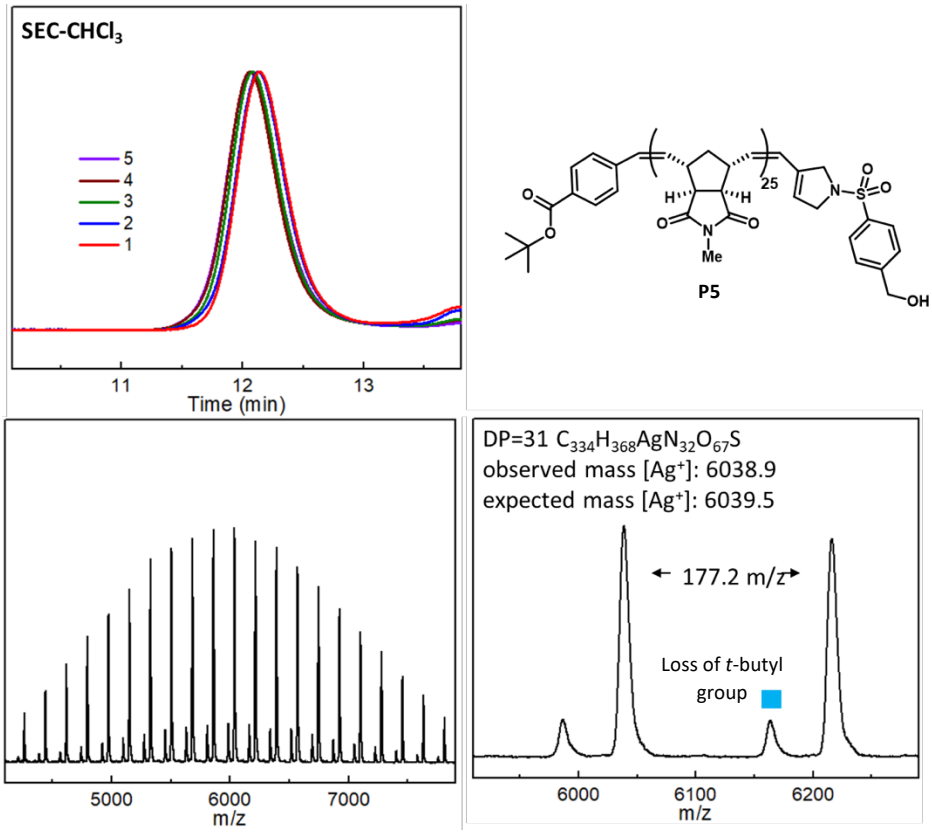
cycle	Mn	% living catalyst	PDI
1	14600	100%	1.13
2	15294	91%	1.13
3	15602	90%	1.13
4	15332	101%	1.14
5	15575	87%	1.14

Figure S5: PA-ROMP for **M4** with **CTA1**



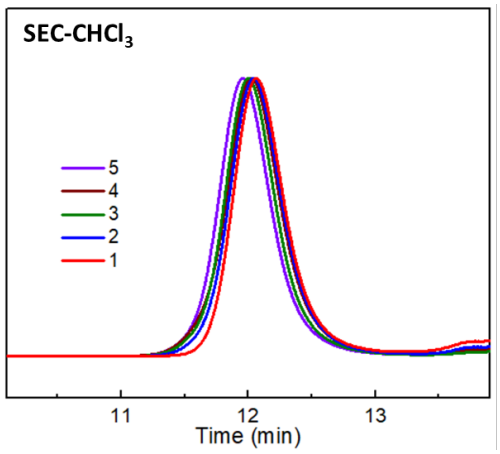
Cycle	Mn	% living catalyst	PDI
1	4987	100%	1.14
2	5667	79%	1.16
3	5932	77%	1.15
4	6062	77%	1.15
5	6188	75%	1.17

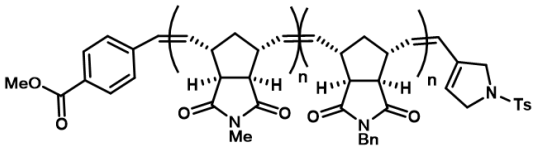
Figure S6: PA-ROMP for **M1** with **CTA2**



Cycle	Mn	% living catalyst	PDI
1	6984	100%	1.13
2	7070	98%	1.14
3	7488	84%	1.15
4	7773	81%	1.16
5	7614	100%	1.17

Figure S7: 5 cycles PA- ROMP for block polymers

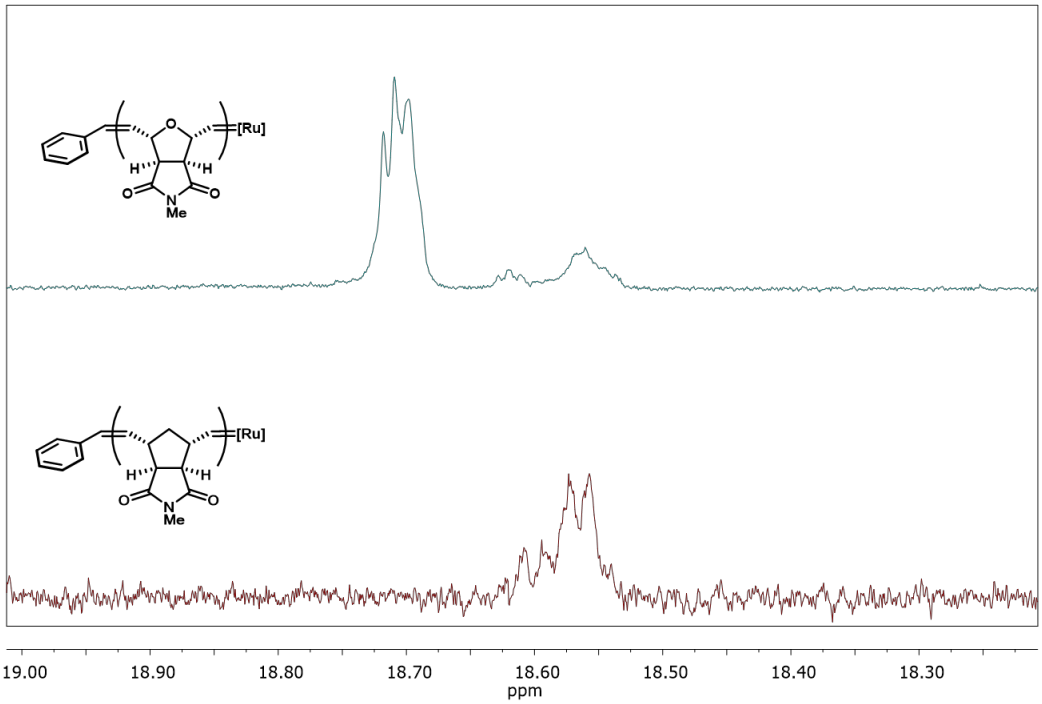




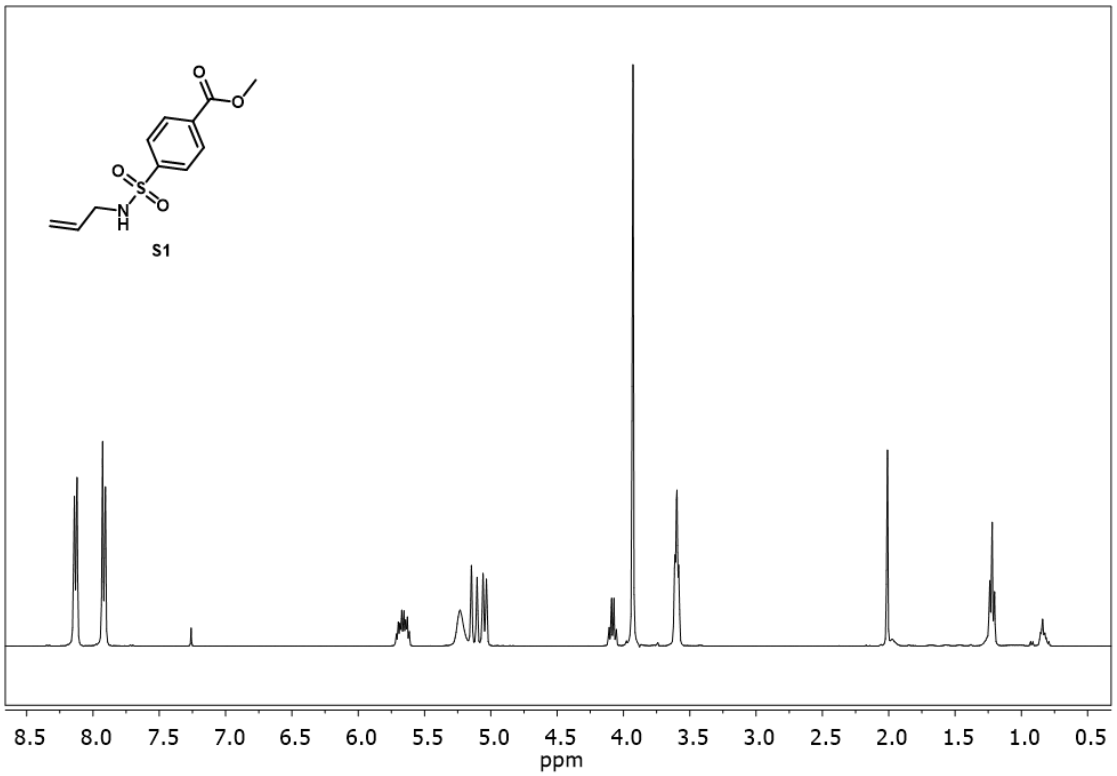
P1-*b*-P2

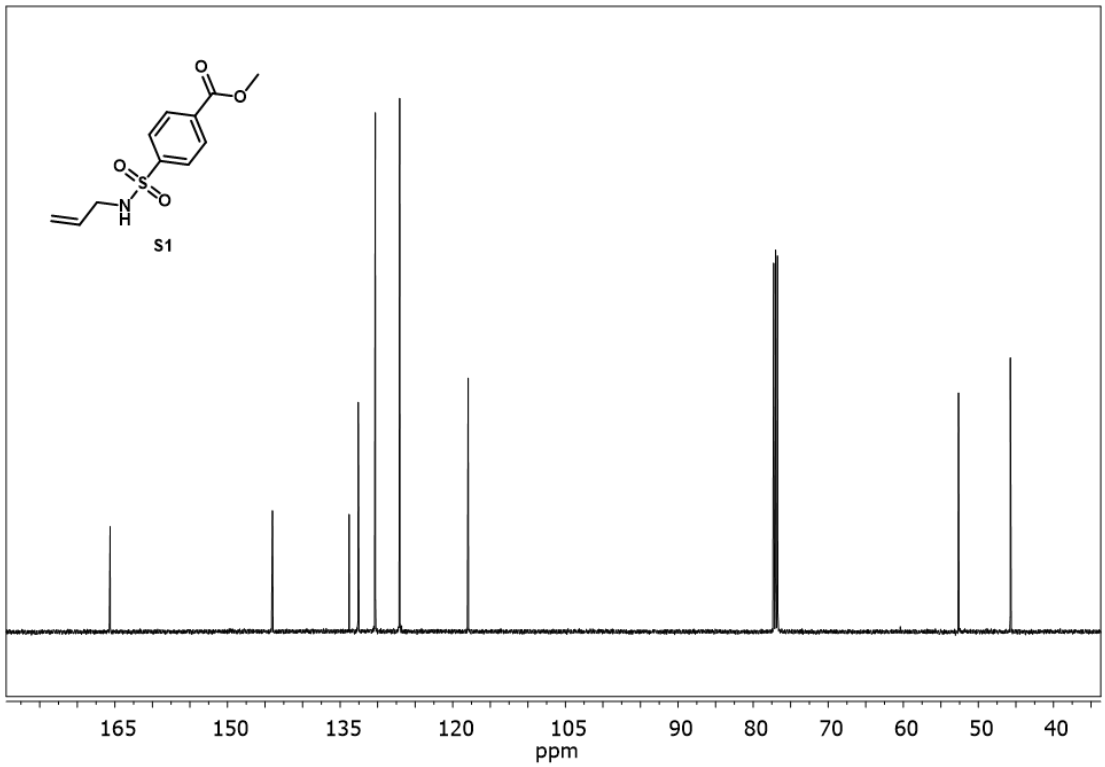
cycle	Mn	% living catalyst	PDI
1	7756	100%	1.13
2	8041	93%	1.15
3	8601	80%	1.16
4	8325	103%	1.17
5	9268	59%	1.16

Figure S8: ^{1}H-NMR of ruthenium alkylidene (oxanorbornene vs methyl norbornene)

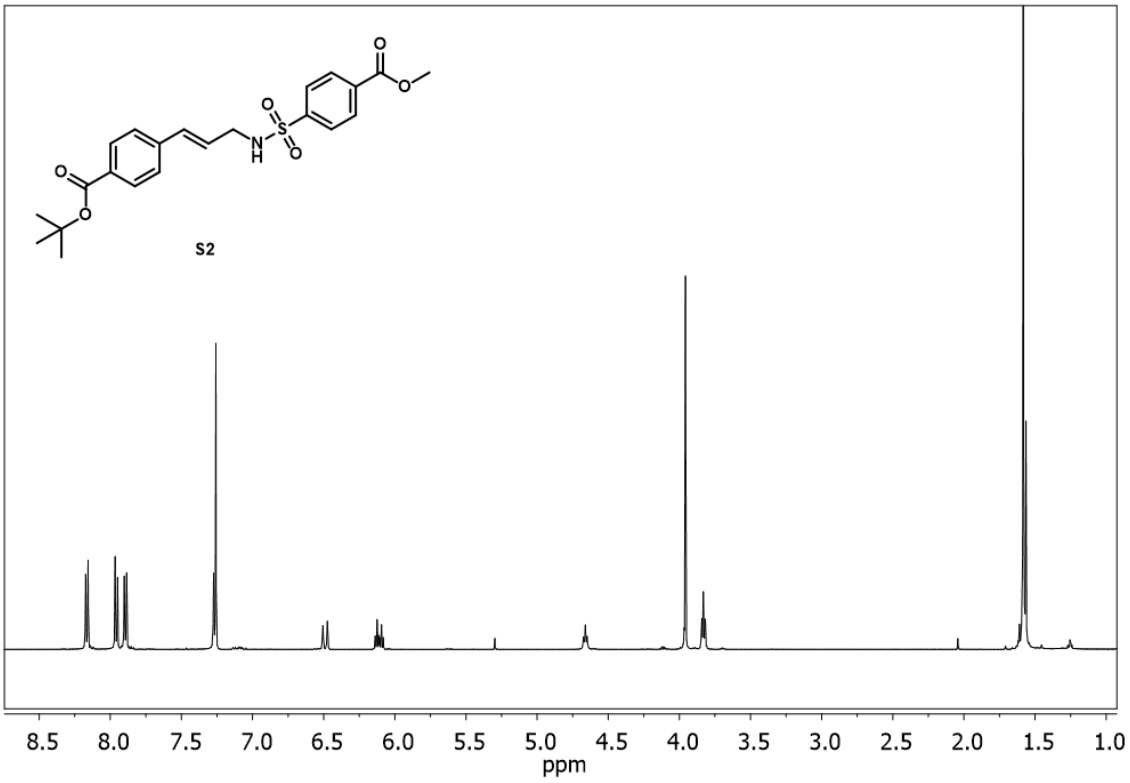


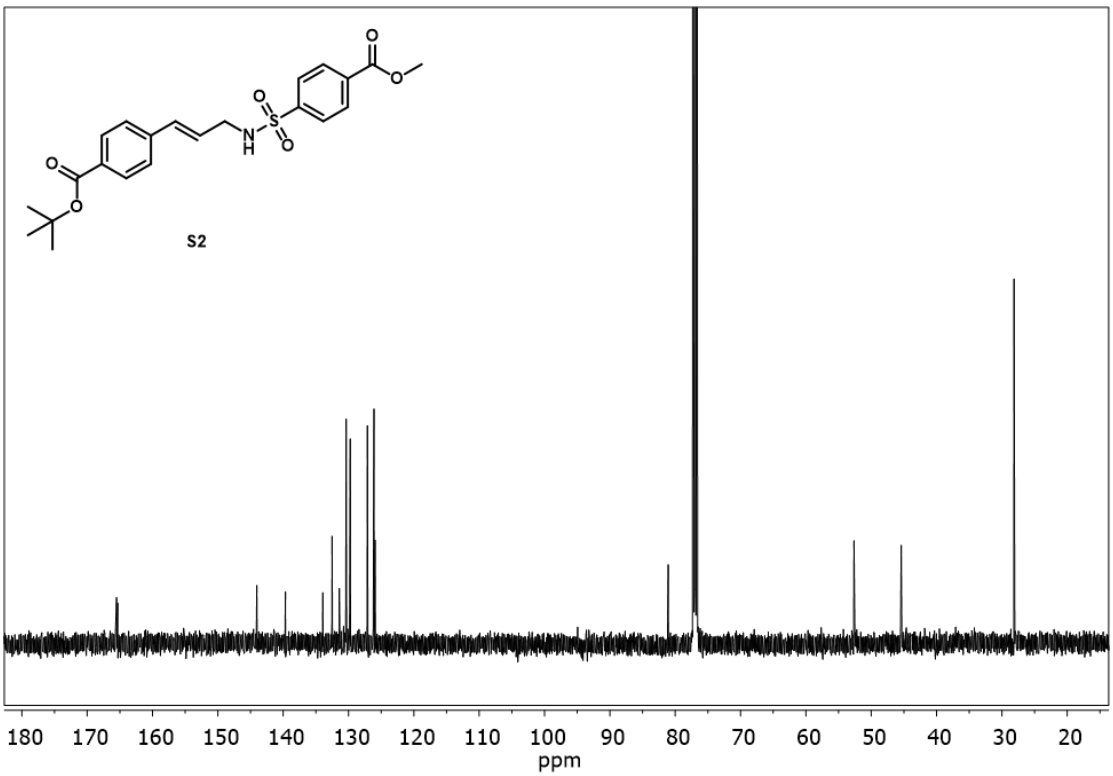
^{1}H NMR and ^{13}C NMR of **S1**



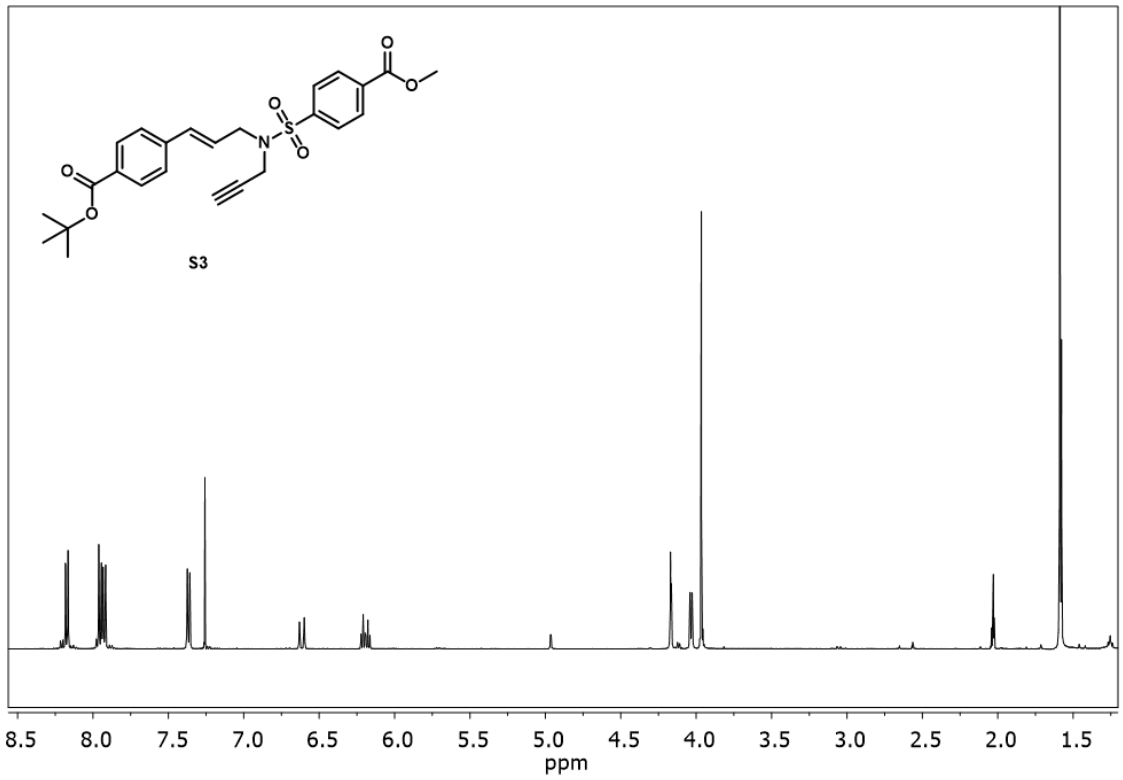


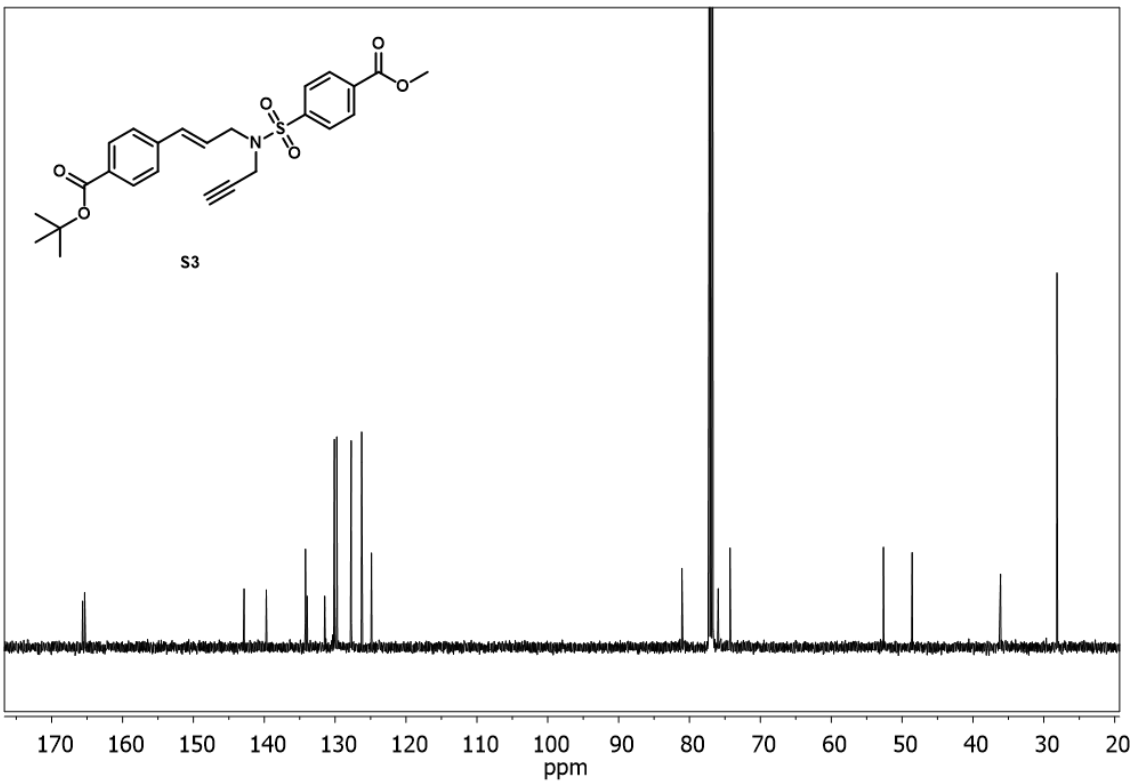
^{1}H NMR and ^{13}C NMR of **S2**



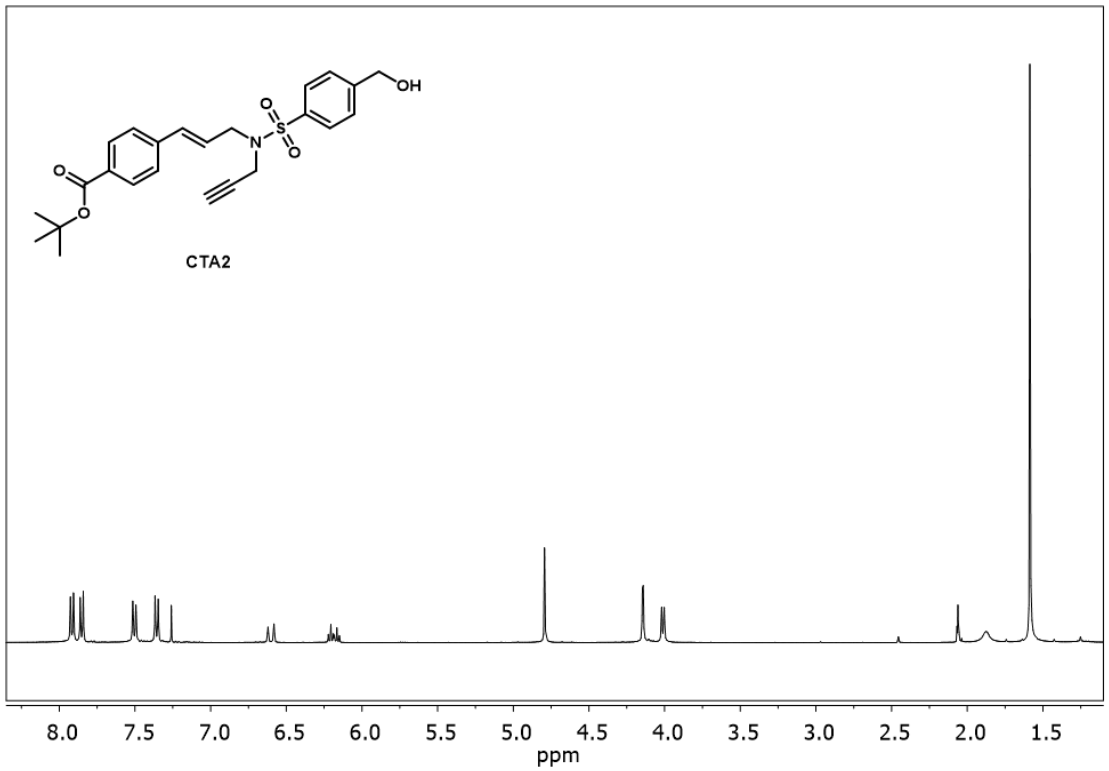


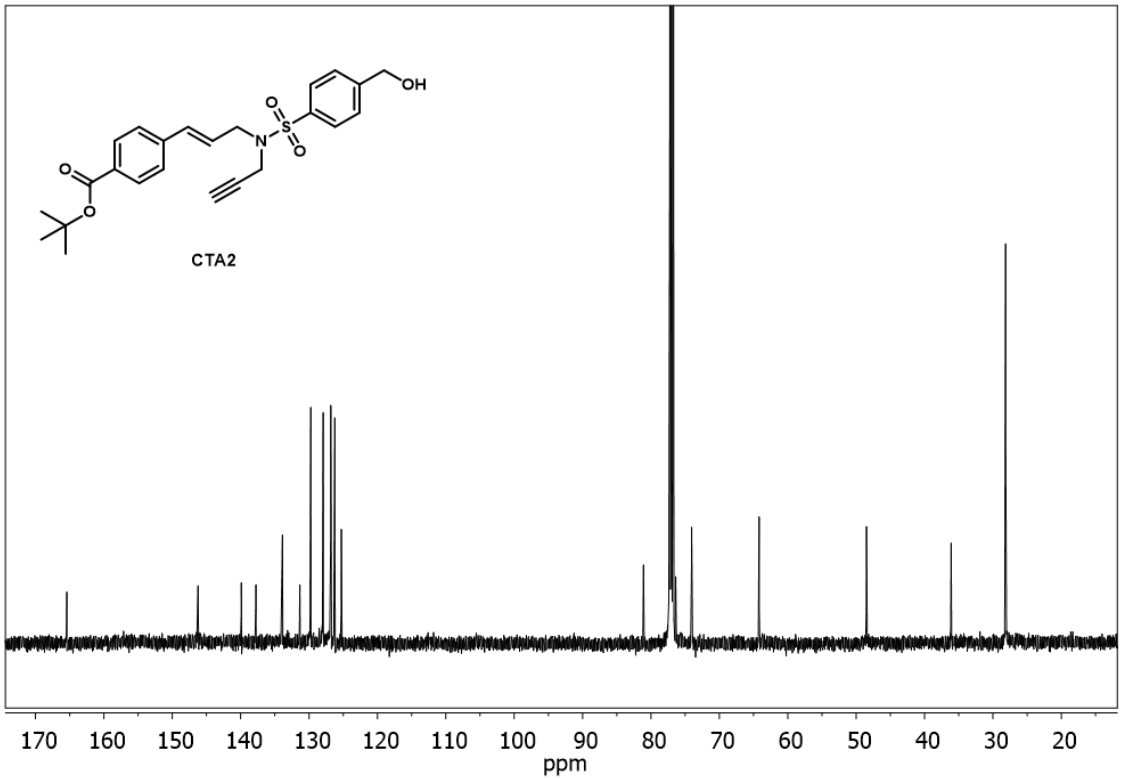
^{1}H NMR and ^{13}C NMR of **S3**



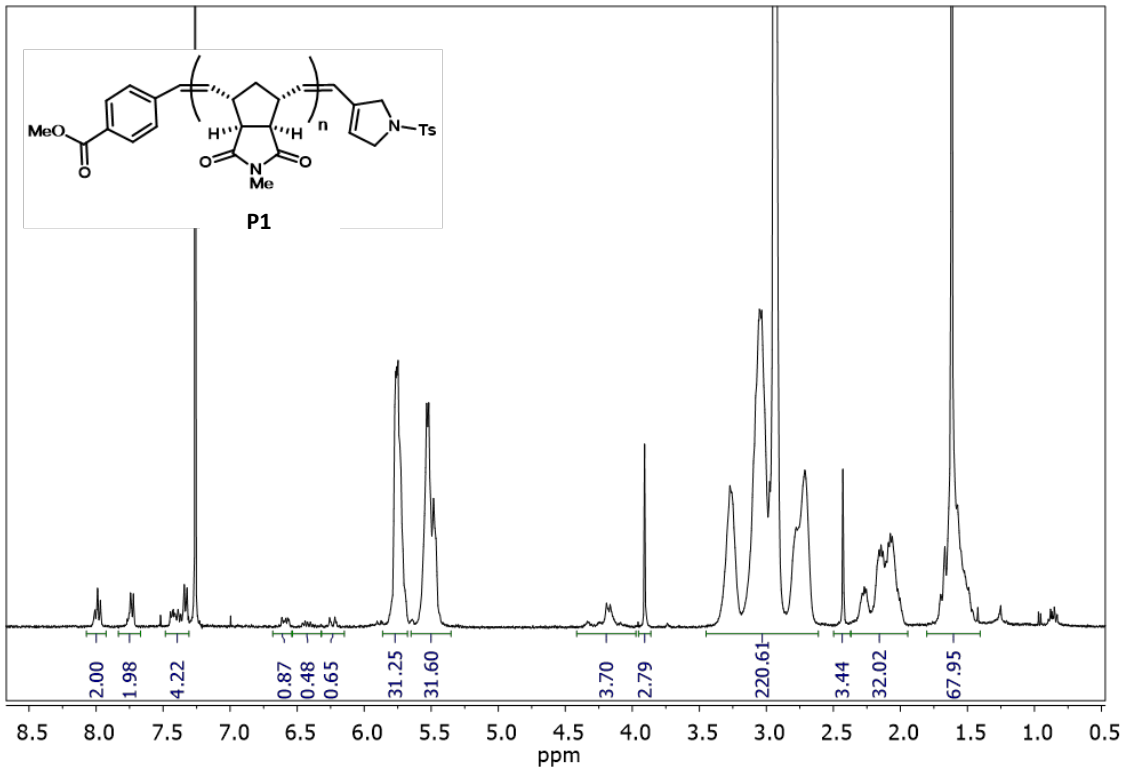


^{1}H NMR and ^{13}C NMR of **CTA2**

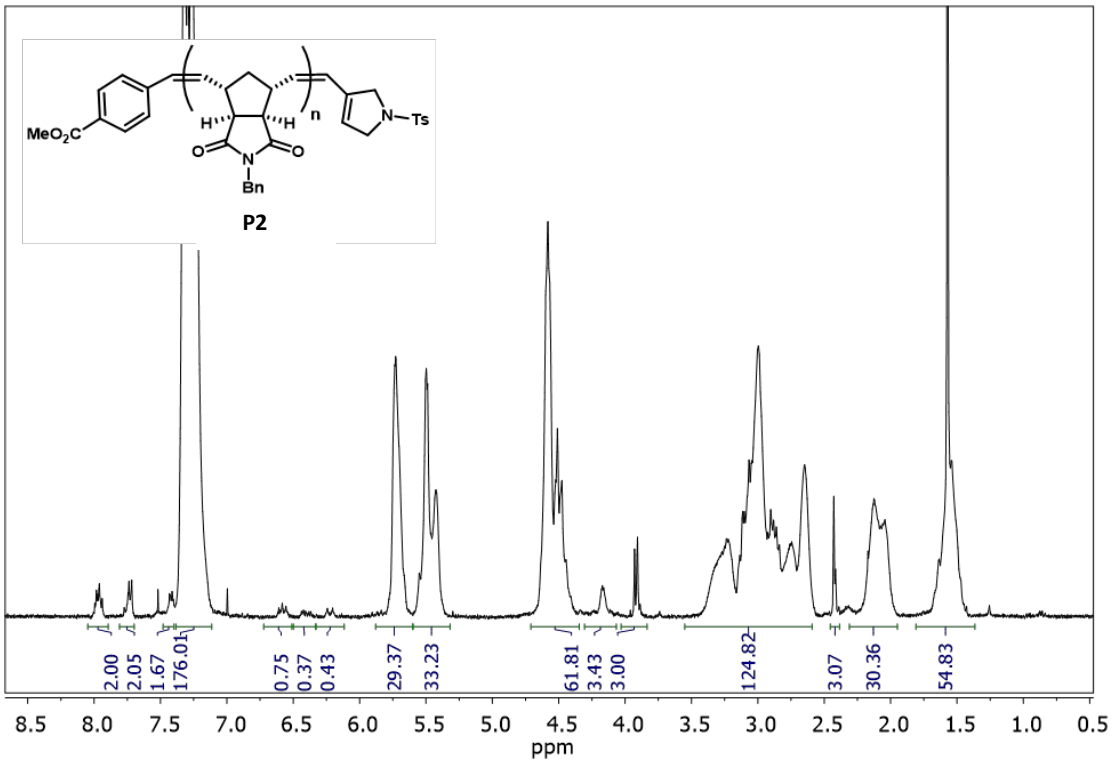




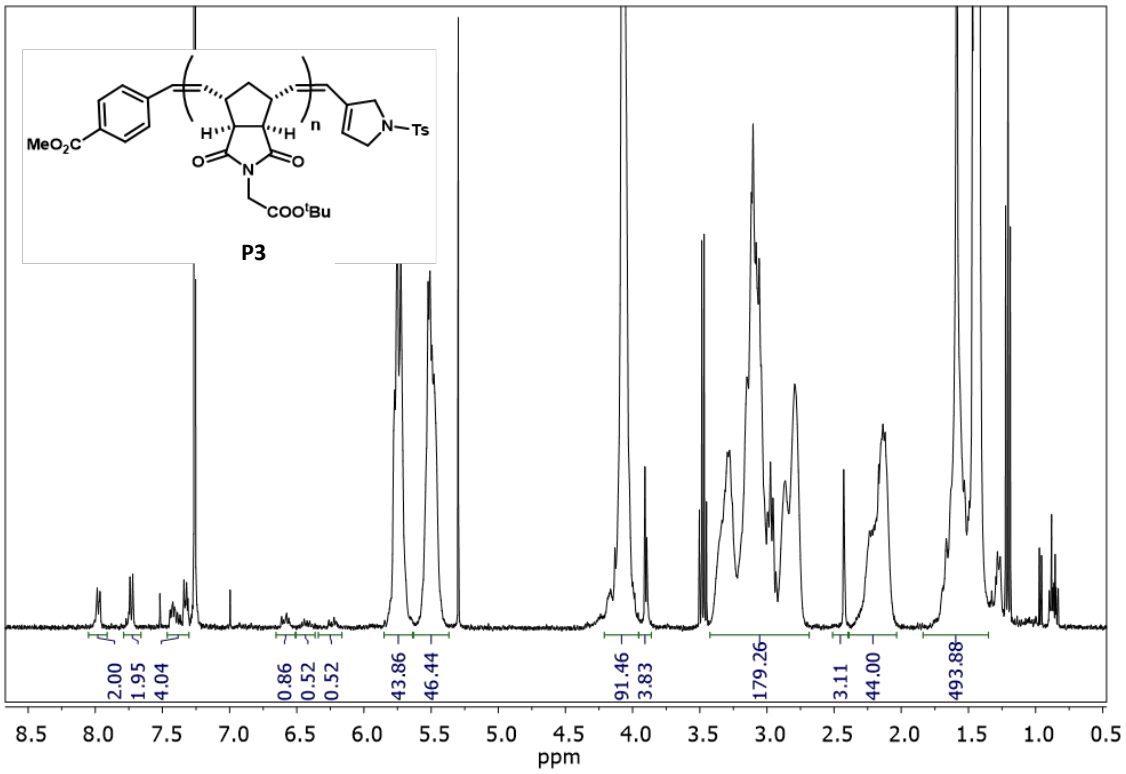
^{1}H NMR of **P1**



^{1}H NMR of **COOMe-P2-Ts**



^{1}H NMR of **P3**



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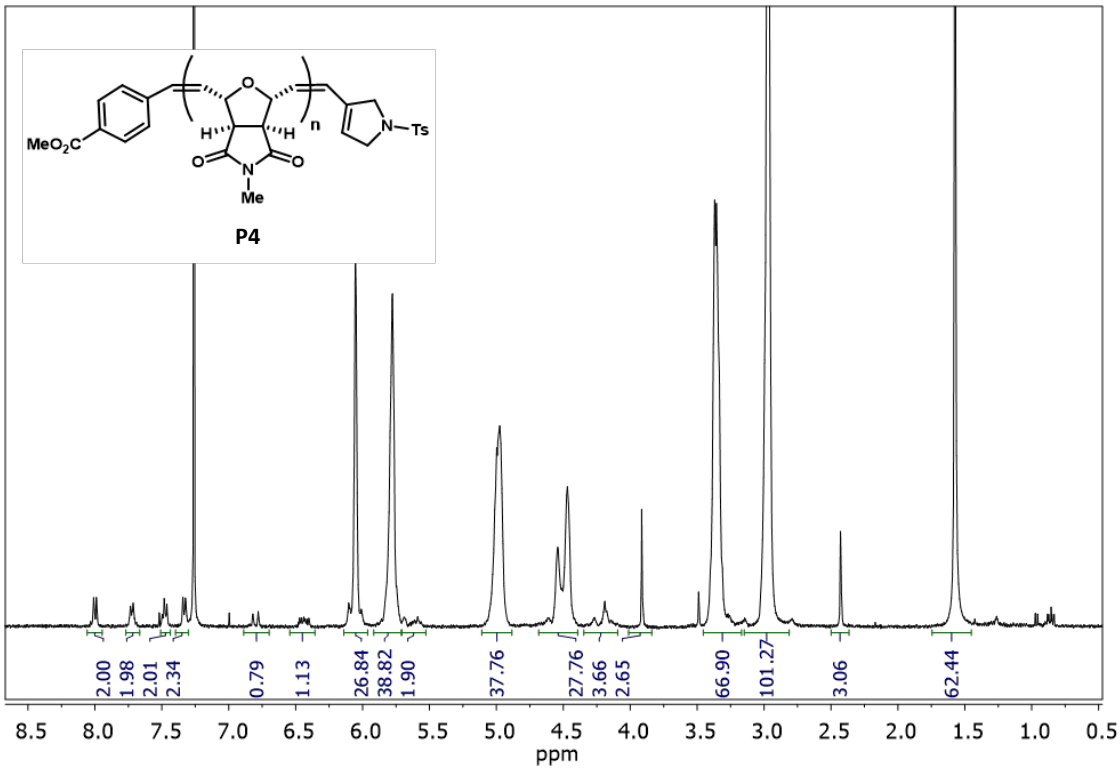
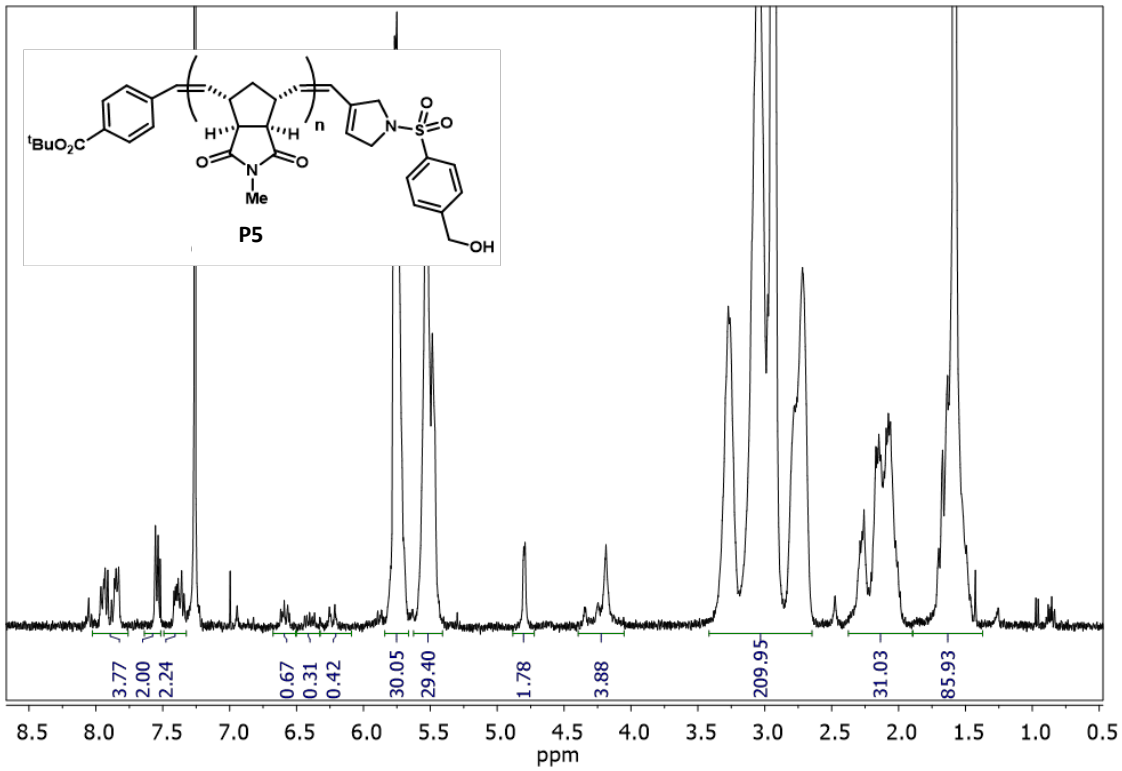
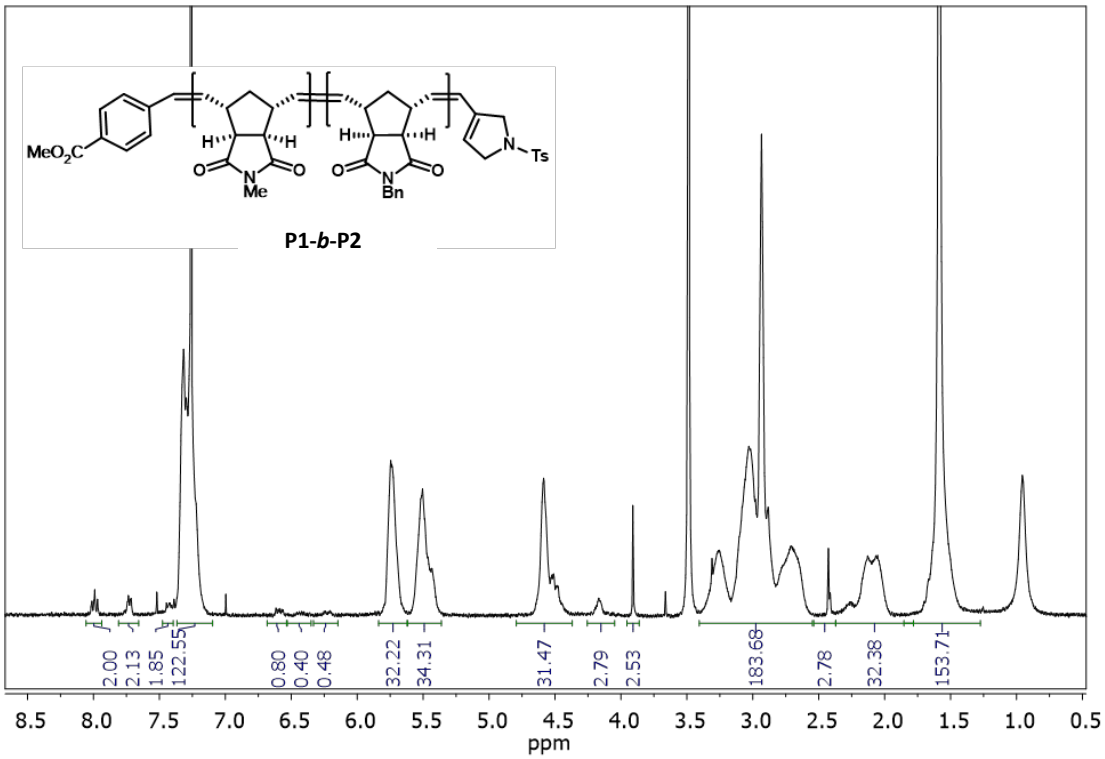


^{1}H NMR of **P5**



^{1}H NMR of **P1-*b*-P2**



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