Electronic Supplementary Information

Tailoring molecular weight distribution *via* polymer degradability

*Yeonsu Kim and Cheoljae Kim**

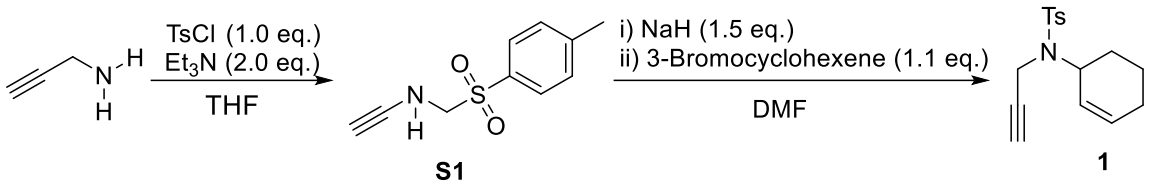
Department of Chemistry, Chungbuk National University, Cheongju 28644, Korea

E-mail: iamckim@chungbuk.ac.kr

1. General information

Grubbs 3rd generation catalyst **G3** was prepared following literature procedure.[1] Other reagents were obtained from commercial vendors and used as received unless otherwise noted. Tetrahydrofuran (THF) and dichloromethane (DCM) were obtained from a solvent purification system. All commercial reagents and solvents other than those mentioned above were used directly without further purification. Column chromatography was performed using silica gel (40-63 μm, 230-400 mesh) purchased from ZEOCHEM. Analytical thin layer chromatography (TLC) analysis was carried out on the precoated silica gel 60 F254 glass plates, staining with p-anisaldehyde (PAA), phosphomolybdic acid (PMA) and potassium permanganate ($KMnO_4$) as a developing agent. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 (400MHz) and AVANCE 500 (500 MHz) spectrometers. Chemical shifts for NMR were reported in parts per million (ppm) relative to residual protonated solvent for ^{1}H $CHCl_3$ = δ 7.26 and relative to carbon resonances of the solvent for ^{13}C $CDCl_3$ = δ 77.0. Peak multiplicities are annotated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constatns, J, were reported in Hertz unit (Hz). ^{13}C NMR was recorded by Bruker AVANCE 400 (100 MHz) and 500 (125 MHz) and was fully decoupled by broad band decoupling. Gel permeation chromatography (GPC) analysis with refractive index (RI) detection was used to determine number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (M_w/M_n). RI measurements were performed using a set of instruments consisting of a Waters 1515 isocratic pump, a 2414 differential refractive index detector, and a column heating module with Shodex KF-803, KF-804 and KF-805 columns connected in series. The column was eluted with tetrahydrofuran (preservative-free HPLC grade, Fisher) at 1.0 mL/min at 40 °C and calibrated against standard polystyrene (Shodex standard SM-105, *M*p 1,210-321,000).

2. Synthesis of monomer



2.1. Preparation of *N*-Propargyl-*p*-toluenesulfonamide from propargylamine[2]

The reaction was adapted from a literature procedure: To a solution of propargylamine (3.2 mL, 50.0 mmol, 1.0 eq.) and triethylamine (6.0 mL, 100.0 mmol, 2.0 eq.) in DCM (150 mL), *p*-toluenesulfonyl chloride (9.53 g, 50.0 mmol, 1.0 eq.) was added. The reaction mixture was stirred for 1 hour at room temperature and quenched with saturated sodium bicarbonate aqueous solution. The reaction solution was extracted with DCM, and the separated organic layer was dried with $MgSO_4$. The resulting solution was concentrated under reduced pressure. The desired product was obtained by silica gel column chromatography (ethyl acetate/hexane = 1/3).

2.1.1. Characterization of *N*-Propargyl-*p*-toluenesulfonamide (S1)

***N*-Propargyl-*p*-toluenesulfonamide (S1)** (9.468 g, 90%), white solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, *J*= 8.3Hz, 2H, ArH), 7.31 (d, *J*= 8.4Hz, 2H, ArH), 4.66 (s, 1H, NH), 3.83 (dd, *J*= 2.5Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.10 (t, *J*= 2.5Hz, 1H, CH)

The spectral data are in compete agreement with the literature value.[2]

2.2. Preparation of monomers 1 by Mitsunobu reaction[2]

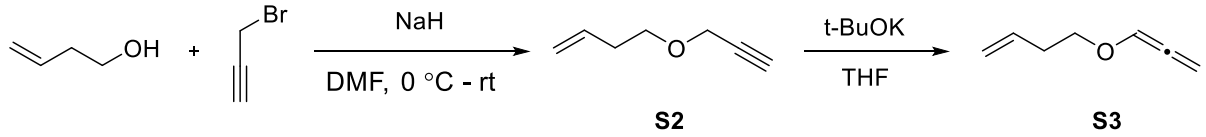
***N*-Propargyl-*p*-toluenesulfonamide** (4.35 g, 20.0 mmol, 1.0 eq.) was dissolved in THF to the nitrogen-purged flask. NaH (1.20 g, 30.0 mmol, 1.5eq., 60% dispersion in mineral oil) was added to the reaction mixture at 0 °C. The resulting mixture was stirred for 30 minutes at room temperature, and the added 3-bromocycloalkene (2.54 mL, 22.0 mmol, 1.1 eq.) to the mixture. Upon completion of the reaction, the solution was quenching with ammonium chloride solution. The solution was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo and the resulting crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/5).

2.2.1. Characterization of monomer 1

***N*-2-Cyclohexen-1-yl-4-methyl-N-2-propyn-1-ylbenzenesulfonamide (1)** (4.90 g, 84%), white solid; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.81 (d, *J*= 8.3Hz, 2H, ArH), 7.28 (d, *J*= 7.9Hz, 2H, ArH), 5.91-5.88 (m, 1H, CH), 5.31 (d, *J*= 10.1Hz, 1H, CH), 4.52-4.47 (m, 1H, CH), 4.13 (dd, *J*= 18.4Hz, 1H, CH), 3.92 (dd, *J*= 18.4Hz, 1H, CH), 2.42 (s, 3H, CH_3), 2.16(t, *J*= 2.4Hz, 1H, CH), 1.97-1.50 (m, 6H, CH_2).

The spectral data are in compete agreement with the literature value.[2]

2.3. Preparation of 4-(propa-1,2,dien-1-yloxy)but-1-ene (S3)



S2 **S3**

To a suspension of NaH (2.88 g, 72.0 mmol, 1.2 equiv., 60% dispersion in mineral oil) in DMF (200 ml) was added but-3-en-1-ol (5.2 ml, 60 mmol, 1.0 equiv.) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 5 min at room temperature. The solution of propargyl bromide (6.7 ml, 67 mmol, 1.1 equiv., 80% wt% in Toluene) was added to a reaction mixture at 0 °C. The resulting mixture was stirred at room temperature until TLC indicated complete conversion of starting material. The reaction was quenched with distilled water followed by extraction with diethyl ether. The organic layers were combined, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure.

2.3.1. Characterization of S2

S2 (4.60 g, 70%), Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$, δ): δ 5.83 (m, 1H), 5.11 (dq, J_1= 1.7, J_2= 17.2 Hz, 1H), 5.06 (dq, J_1= 1.3, J_2= 10.3 Hz, 1H), 4.16 (d, J= 2.4 Hz, 2H, CH_2), 3.59 (t, J= 6.7 Hz, 2H, CH_2), 2.42 (t, J= 2.4 Hz, 1H, CH), 2.37(m, 2H, CH_2).

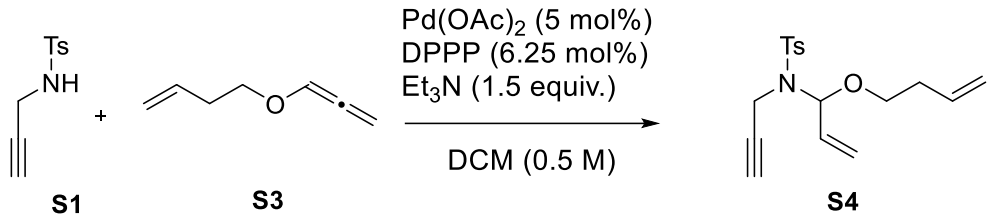
To a suspension of t-BuOK(3.36 g, 30.0 mmol, 1.0 equiv.) in THF(60 ml) was added **S2** slowly. Stir the suspension at room temperature for 1 hours. Filter the suspension through a pad of silica-celite and wash the suspension with Et_2O. Concentrate the combined solution in vacuo. A volatile yellow oil **S3** was obtained with used solvents.

2.3.2. Characterization of 4-(propa-1,2,dien-1-yloxy)but-1-ene (S3)

4-(propa-1,2,dien-1-yloxy)but-1-ene (S3) Volatile Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ): δ 6.73 (t, J= 5.9 Hz, 1H), 5.82 (m, 1H), 5.44 (d, J= 5.9 Hz, 1H), 5.09 (m, 2H), 3.61 (t, J= 6.7 Hz, 2H), 2.41(m, 2H).

The spectral data are in compete agreement with the literature value.[3]

2.4. Preparation of *N*-(1-(but-3-en-1-yloxy)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S4)



S1 **S3** **S4**

To a solution of $Pd(OAc)_2$ (112 mg, 0.500 mmol, 0.05 equiv.) and 1,3-bis(diphenylphosphino)propane **DPPP** (257 mg, 0.625 mmol, 0.0625 equiv.), trimethylamine (2.1 ml, 15 mmol, 1.5 equiv.) in DCM (20 ml), tosylamide S**1** (20.9 g, 10.0 mmol, 1.0 equiv.) was added. Then alkoxyallene **2** (2 equiv.) was added to the reaction mixture. The resulting mixture was stirred at room temperature until TLC indicated complete conversion of the starting material. Concentrate the combined solution in vacuo. The crude product was purified by column chromatography (ethyl acetate/hexane = 5/95) to obtain **S4.**

2.4.1. Characterization of *N*-(1-(but-3-en-1-yloxy)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S4)

***N*-(1-(but-3-en-1-yloxy)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S4)** (2.58g, 81%) White solid;

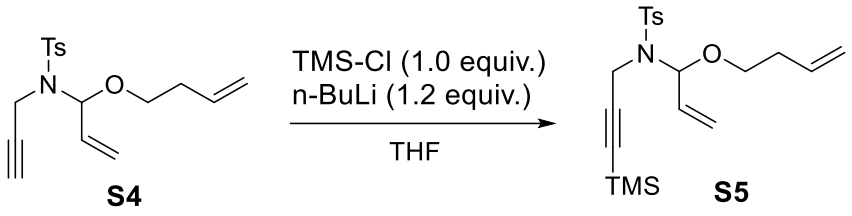
^{1}H NMR (500 MHz, $CDCl_3$, δ): δ 7.79 (d, *J*= 8.3 Hz, 2H), 7.28 (d, *J*= 8.0 Hz, 2H), 5.77 (m, 1H), 5.65 (m, 1H), 5.53 (m, 1H), 5.40 (dt, J_1= 1.5, J_2= 17.2 Hz, 1H), 5.22 (dt, J_1= 1.5, J_2= 10.5 Hz, 1H), 5.04 (m, 2H), 3.98 (d, *J*= 2.5 Hz, 2H), 3.62 (dt, J_1= 6.8, J_2= 9.5 Hz, 1H), 3.42 (dt, J_1= 6.7, J_2= 9.5 Hz, 1H), 2.42 (s, 3H), 2.31 (m, 2H), 2.04 (t, *J*= 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): δ 143.6, 137.7, 134.9, 133.6, 129.4, 127.5, 118.9, 116.5, 86.5, 79.5, 71.7, 67.2, 33.6, 31.1.

IR (cm^{-1}): 3290.6, 3074.8, 2980.0, 2927.0, 2874.4, 2122.8, 1641.9, 1597.7, 1495.0, 1426.9, 1404.7, 1336.3, 1225.8, 1214.7, 1158.8, 1114.7, 1091.2, 1074.9, 1018.1, 991.3, 936.4, 918.6, 876.5, 811.6, 706.0, 670.9, 564.4, 542.0.

HRMS (ESI) m/z: $C_{17}H_{21}NNaO_3S$ $[M+Na]^+$ *calcd*: 342.1134, *found*: 342.1134.

2.5. Preparation of *N*-(1-(but-3-en-1-yloxy)allyl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzene-sulfonamide (S5)



The n-butyllithium solution (3.5 ml, 8.8 mmol, 1.1 equiv., 2.5 M in hexane) was added dropwise to a stirred solution of dienyne **S4** (2.55 g, 8.00 mmol, 1.0 equiv.) dissolved in dry THF (16 ml) under N_2 atmosphere at -78 °C. Stirring was maintained at this temperature for 30 minutes before trimethylsilyl chloride (1.0 ml, 8.2 mmol, 1.2 equiv.) was added dropwise. Stirring was maintained for an additional 30 minutes at -78 °C before water was slowly added. The aqueous layer was extracted with ethyl acetate and dried over $MgSO_4$. After concentrating the solvent under reduced pressure. After purification by flash chromatography on silica gel (ethyl acetate/hexane = 10/90), desired product **S5** was obtained.

2.5.1. Characterization of *N*-(1-(but-3-en-1-yloxy)allyl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzene-sulfonamide (S5)

***N*-(1-(but-3-en-1-yloxy)allyl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzene-sulfonamide (S5)** (3.13g, 99%) Clear oil;

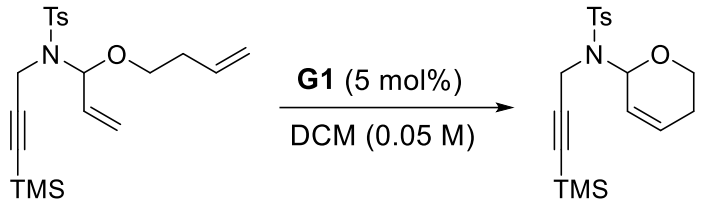
^{1}H NMR (500 MHz, $CDCl_3$, δ): δ 7.81 (d, *J*= 8.3 Hz, 2H), 7.27 (d, *J*= 8.7 Hz, 2H), 5.74 (m, 2H), 5.52 (m, 1H), 5.39 (dt, J_1= 1.5, J_2= 17.2 Hz, 1H), 5.19 (dt, J_1= 1.5, J_2= 10.6 Hz, 1H), 5.03 (m, 2H), 4.03 (d, *J*= 4.6 Hz, 2H), 3.59 (dt, J_1= 6.7, J_2= 9.4 Hz, 1H), 3.38 (dt, J_1= 6.7, J_2= 9.4 Hz, 1H), 2.41 (s, 3H), 2.30 (m, 2H), 0.03 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): δ 143.8, 138.4, 135.3, 134.3, 129.8, 128.0, 118.9, 116.9, 101.7, 88.8, 87.1, 67.6, 34.0, 32.3, 21.9, 0.00

IR (cm^{-1}): 3077.6, 3027.8, 2959.2, 2926.2, 2900.7, 2875.0, 2179.5, 1642.2, 1598.3, 1406.2, 1349.2, 1249.7, 1161.8, 1092.3, 1076.3, 1050.5, 1009.4, 880.4, 841.9, 811.7, 760.1, 705.6, 671.4, 638.3, 610.3, 544.1, 504.0.

HRMS (ESI) m/z: $C_{20}H_{29}NNaO_3SSi$ $[M+Na]^+$ *calcd*: 414.1530, *found*: 414.1530.

2.6. Preparation of *N*-(5,6-dihydro-2*H*-pyran-2-yl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzene-sulfonamide (S6)



S5 **S6**

A solution of dienyne **S5** (3.14 g, 8.00 mmol, 1.0 equiv.) in DCM (160 ml) was added with Grubbs catalyst 1st Generation **G1** (332 mg, 0.40 mmol, 0.05 equiv.) and stirred overnight. After monitoring the reaction by TLC, the reaction was terminated by adding ethyl vinyl ether. The crude mixture was purified by column chromatography (ethyl acetate/hexane = 10/90) to obtain desired enyne **S6**.

2.6.1. Characterization of *N*-(5,6-dihydro-2*H*-pyran-2-yl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzene-sulfonamide (S6)

***N*-(5,6-dihydro-2*H*-pyran-2-yl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzene-sulfonamide (S6)** (2.30g, 79%) Pale broen liquid;

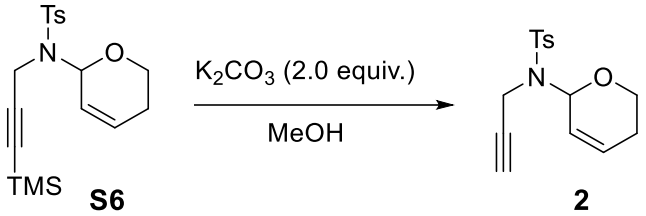
^{1}H NMR (500 MHz, $CDCl_3$, δ): δ 7.85 (d, *J*= 8.4 Hz, 2H), 7.26 (d, *J*= 8.0 Hz, 2H), 6.14 (m, 1H), 5.89 (quint, *J*= 2.4 Hz, 1H), 5.64 (dq, J_1= 2.1, J_2= 10.2 Hz, 1H), 4.04 (q, *J*= 18.7 Hz, 2H), 3.91 (dt, J_1= 4.9, J_2= 11.5 Hz, 1H), 3.73 (m, 1H), 2.40 (s, 3H), 2.20 (m, 1H), 1.99 (m, 1H) 0.03 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): δ 143.6, 137.9, 131.8, 129.6, 128.4, 126.1, 101.8, 89.0, 81.6, 62.4, 34.3, 24.7, 21.9, 0.00

IR (cm^{-1}): 3141.9, 3065.2, 2957.3, 1596.1, 1480.5, 1371.4, 1277.3, 1249.7, 1172.9, 1131.0, 1092.6, 1063.2, 1017.9, 838.4, 812.9, 759.6, 627.1, 553.8, 490.2.

HRMS (ESI) m/z: $C_{18}H_{25}NNaO_3SSi$ $[M+Na]^+$ *calcd*: 386.1217, *found*: 386.1217.

2.7. Preparation of *N*-(5,6-dihydro-2*H*-pyran-2-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2)



Potassium carbonate (1.75 g, 12.6 mmol, 2.0 equiv.) was added to the solution of the TMS-protected enyne **S6** (2.30 g, 6.33 mmol, 1.0 equiv.) in methanol (42.2 ml) and the heterogeneous mixture was vigorously stirred at room temperature for 8 hours. Total completion was monitored by TLC and then extracted with water and ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was purified on silica gel (ethyl acetate/hexane = 15/85) to give the desired enyne monomer **2** (1.80 g, 6.17 mmol, 98%) as a white solid.

2.7.1. Characterization of *N*-(5,6-dihydro-2*H*-pyran-2-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2)

***N*-(5,6-dihydro-2*H*-pyran-2-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2)** (1,80g, 98%) White solid;

^{1}H NMR (500 MHz, $CDCl_3$, δ): δ 7.84 (d, *J*= 8.4 Hz, 2H), 7.27 (d, *J*= 8.4 Hz, 2H), 6.15 (m, 1H), 5.90 (m, 1H), 5.69 (m, 1H), 3.85 (m, 4H), 2.41 (s, 3H), 2.24 (m, 1H), 2.12 (t, *J*= 2.5 Hz, 1H), 1.94 (m, 1H).

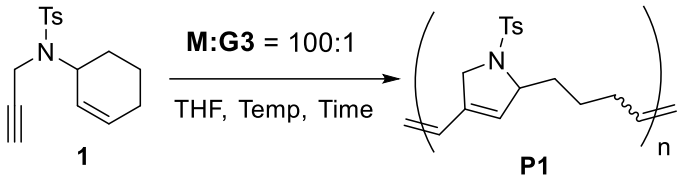
^{13}C NMR (125 MHz, $CDCl_3$, δ): δ 143.5, 137.0, 131.5, 129.3, 128.1, 126.0, 81.8, 79.9, 71.8, 62.6, 32.8, 24.3. 21.6.

IR (cm^{-1}): 3280.4, 3043.0, 2969.0, 2925.6, 2866.4, 1597.8, 1336.9, 1158.7, 1096.5, 1076.9, 1047.9, 869.2, 810.7, 662.6, 590.7, 548.7.

HRMS (ESI) m/z: $C_{15}H_{18}NO_3S$ $[M+H]^+$ *calcd*: 292.1002, *found*: 292.1002.

3. Polymerization

Table S1. Optimization process of Enyne metathesis polymerization of **1** monomer.



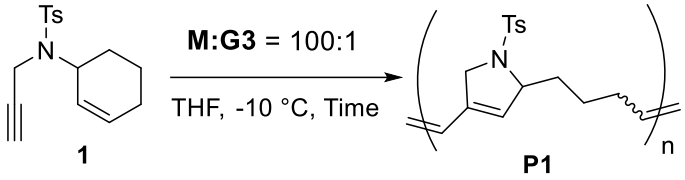
Entry	Solvent	initiator	DP (M/I)	[M]	Time (h)	Temp. (°C)	Conversion (%) [a]
1	THF	**G3**	100	0.1	1	-10	>98
2	THF	**G3**	100	0.2	1	-10	>98
3	THF	**G3**	100	0.4	1	-10	>98
4	THF	**G3**	100	0.2	10 min	-10	>98
5	THF	**G3**	100	0.2	0.5	-10	>98
6	THF	**G3**	100	0.2	2	-10	>98
7	THF	**G3**	100	0.2	2.5	-10	>98
8	THF	**G3**	100	0.2	0.5	-30	>98
9	THF	**G1**	100	0.2	0.5	-10	6.2
10	THF	**G2**	100	0.2	0.5	-10	0
11	THF	**HG2**	100	0.2	0.5	-10	>98

[a)] Conversions were determined by crude ^{1}H NMR

General procedure for polymerization[2]

A THF solution of monomer (0.125 mmol) is added to a solution of Grubbs 3rd generation catalyst (**G3**) at -10 °C. After the indicated time, the polymerization is stopped by addition of excess ethyl vinyl ether (EVE). The reaction mixture is stirred for 5 minutes, and the reaction mixture is concentrated under vacuum. The small portion of the crude sample was analyzed by ^{1}H NMR. The polymer was precipitated upon addition of methanol, and the polymer was isolated by centrifugation and decantation. The obtained polymer was dried under high vacuum. For the GPC analysis, the isolated polymer was diluted with THF (20 mg/mL), filtered, and then injected to GPC instrument.

Table S2. Enyne metathesis polymerization of **1** monomer using syringe pump.



Entry	[M]	Time (injection)	Time (additional)	Conversion (%) [a]	M_n (kDa) [b]	$Đ$ [b]
1	0.2	30 min	20 min	81.4	25.0	1.27
2	0.2	10 min	10 min	>98	21.6	1.29
3	0.2	5 min	5 min	>98	24.4	1.22

[a)] Conversions were determined by crude ^{1}H NMR. [b)] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

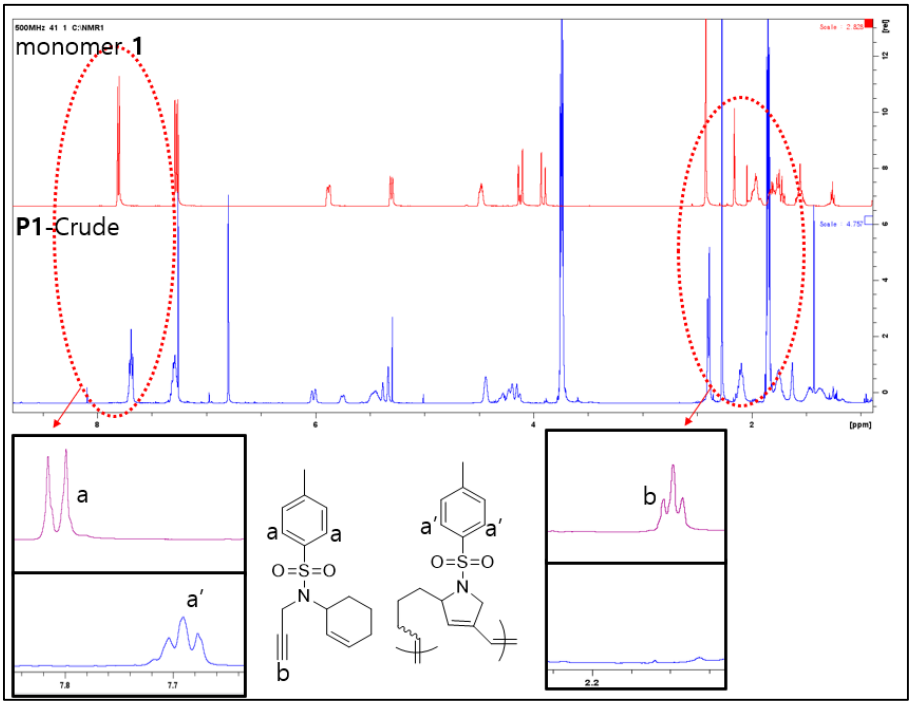
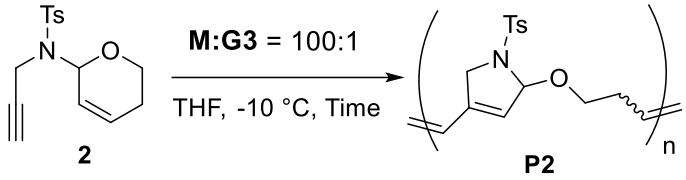


Figure S1. ^{1}H NMR spectra of **P1**

Table S3. Enyne metathesis polymerization of **2** monomer using syringe pump.



Entry	[M]	Time (injection)	Time (additional)	Conversion (%) [a]	M_n (kDa) [b]	$Đ$ [b]
1	0.2	30 min	20 min	78.8	12.5	1.66
2	0.2	10 min	10 min	>98	20.8	1.17
3	0.2	5 min	5 min	>98	22.8	1.11

[a] Conversions were determined by crude ^{1}H NMR. [b] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

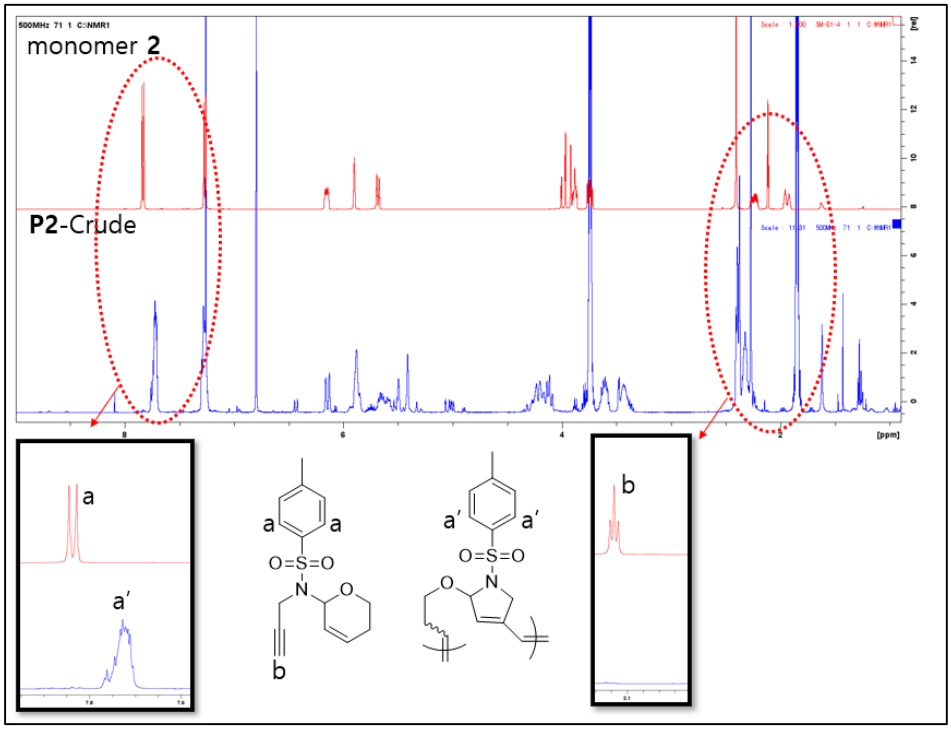


Figure S2. ^{1}H NMR spectra of **P2**

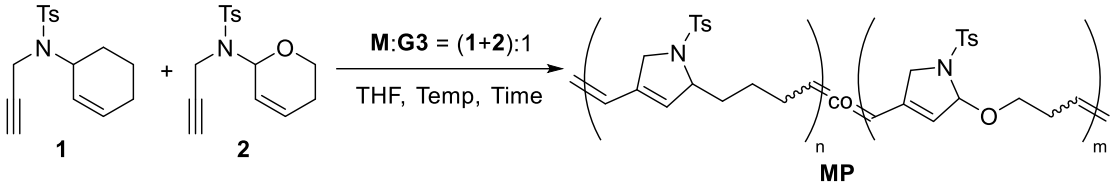
General procedure for copolymerization involves single-syringe pump addition.

Grubbs 3rd generation catalyst **G3** is added to an 4 mL vial equipped with a stir bar, placed under a nitrogen atmosphere, and is dissolved in THF at -10 ℃. In a separate syringe, a solution of monomer **1** and **2** together in THF was prepared. Monomer was added dropwise and stirred. After dropwise, the mixture was stirred for an additional time. After the indicated time, the polymerization is stopped by addition of excess ethyl vinyl ether (EVE) with triethylamine(TEA). The reaction mixture is stirred for 5 minutes, and the reaction mixture is concentrated under vacuum. The small portion of the crude sample was analyzed by ^{1}H NMR. The polymer was precipitated upon addition of methanol + triethylamine, and the polymer was isolated by centrifugation and decantation. The obtained polymer was dried under high vacuum. For the GPC analysis, the isolated polymer was diluted with THF (20 mg/mL), filtered, and then injected to GPC instrument.

P1; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.70-7.68 (m, 2H, ArH), 7.30-7.29 (m, 2H, ArH), 6.03-6.00 (d, 0.6H, CH), 5.76-5.74 (d, 0.4H, CH), 5.47-5.42 (br, 1H, CH), 5.38-5.33 (d, 1H, CH), 4.44 (br, 1H, CH), 4.30-4.12 (m, 2H, CH_2), 2.40-2.39 (m, 3H, CH_3), 2.11-2.09 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 1.51-1.29 (m, 2H, CH_2).

P2; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.80-7.65 (m, 2H, ArH), 7.31-7.23 (m, 2H, ArH), 6.15-5.82 (m, 2H, CH), 5.70-5.54 (m, 1H, CH), 5.52-5.36 (d, 1H, CH), 4.33-4.05 (m, 2H, CH_2), 3.69-3.34 (m, 2H, CH_2), 2.46-2.36 (m, 3H, CH_3), 2.36-2.15 (m, 2H, CH_2);

Table S4. Enyne metathesis Copolymerization of **1** and **2** monomer using syringe pump.



Entry	[M]	DP (M/G3)	Temp. (℃)	Time (injection)	Time (additional)	Conversion (%) [a]	M_n (kDa) [b]	$Đ$ [b]
1	0.2	100	-10	10 min	10 min	>98	24.2	1.47
2	0.2	100	-10	5 min	5 min	>98	25.1	1.33
3	0.2	100	0	5 min	5 min	69.1	39.8	1.66
4	0.2	100	rt	5 min	5 min	77.9	31.7	1.63
5	0.2	200	-10	5 min	5 min	53.1	-	-
6	0.2	300	-10	5 min	5 min	50.0	-	-
7	0.2	500	-10	10 min	10 min	17.3	-	-

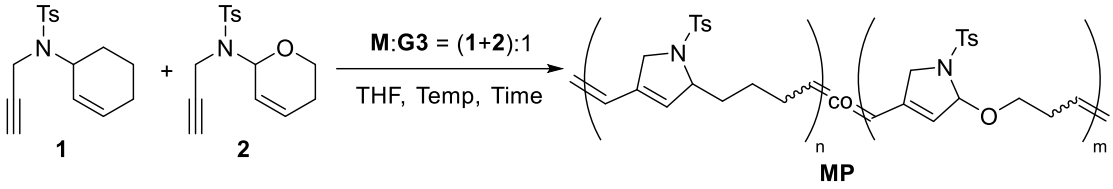
[a] Conversions were determined by crude ^{1}H NMR. [b] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

General procedure for copolymerization involves dual-syringe pumps addition.

Grubbs 3rd generation catalyst **G3** is added to an 4 mL vial equipped with a stir bar, placed under a nitrogen atmosphere, and is dissolved in THF at -10 ℃. In a separate syringe, a solution of monomer **1** in THF was prepared. And in another syringe, a solution of monomer **2** in THF was prepared. Monomers were added dropwise into the catalyst solution by two syringe pump and stirred. After dropwise, the mixture was stirred for an additional time. After the indicated time, the polymerization is stopped by addition of excess ethyl vinyl ether (EVE) with triethylamine(TEA). The reaction mixture is stirred for 5 minutes, and the reaction mixture is concentrated under vacuum. The small portion of the crude sample was analyzed by ^{1}H NMR. The polymer was precipitated upon addition of methanol, and the polymer was isolated by centrifugation and decantation. The obtained polymer was dried under high vacuum. For the GPC analysis, the isolated polymer was diluted with THF (20 mg/mL), filtered, and then injected to GPC instrument.

4. Control molecular weight

Table S5. Enyne metathesis Copolymerization of **1** and **2** monomer using two syringe pumps.



Entry	1:2	DP (M/G3)	Temp. (℃)	Time (injection)	Time (additional)	Conversion (%) [a]	M_n (kDa) [b]	$Đ$ [b]
1	6:1	100	-10	10 min	5 min	>98	24.6	1.27
2	10:1	100	-10	10 min	5 min	>98	28.1	1.32
3	20:1	100	-10	10 min	5 min	>98	31.2	1.26
4	40:1	100	-10	10 min	5 min	>98	33.8	1.31

[a] Conversions were determined by crude ^{1}H NMR. [b] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

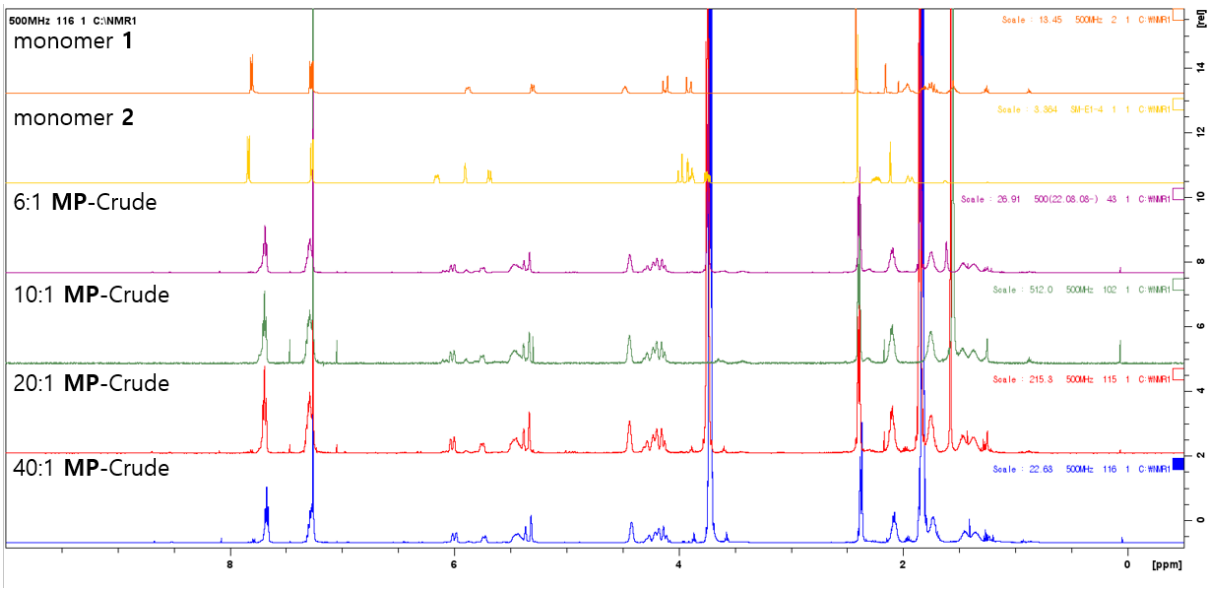
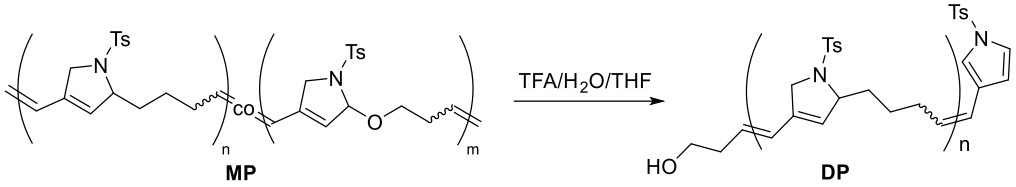


Figure S3. ^{1}H NMR spectra of **MP**(Table S5).

Table S6. Degradation of Copolymer **MP**(Table S5).



Entry	1:2	Time (min)	M_n (kDa) [a]	$Đ$ [a]
1	6:1	30	3.7	1.27
2	10:1	30	4.6	1.34
3	20:1	30	7.0	1.39
4	40:1	30	11.3	1.62

[a] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

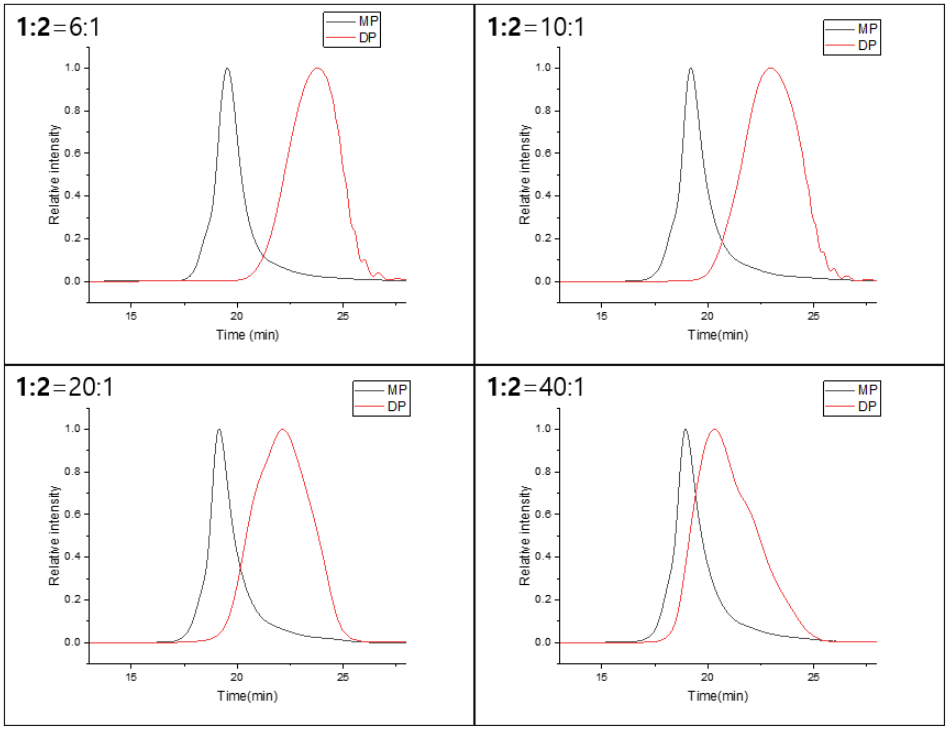
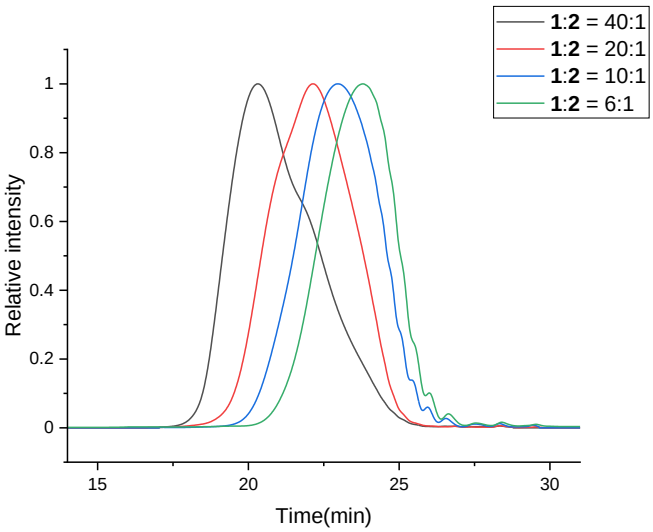
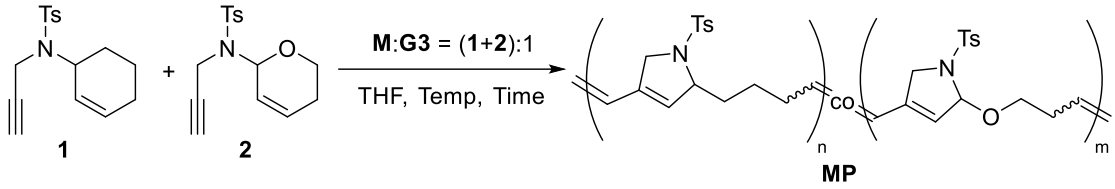


Figure S4. Polymer degradation of **MP**; (a)-(d) GPC data for degradation **MP** under acidic conditions at room temperature (black line: mother polymer **MP**, red line: daughter polymer **DP**)



Figuer S5. GPC data for **DP**

Table S7. Comparison of copolymerization of **1** and **2** using two syringe pumps with same flow rate in the same volume of monomer solutions (different concentrations) vs. different flow rate in the different volume of monomer solutions (same concentrations).

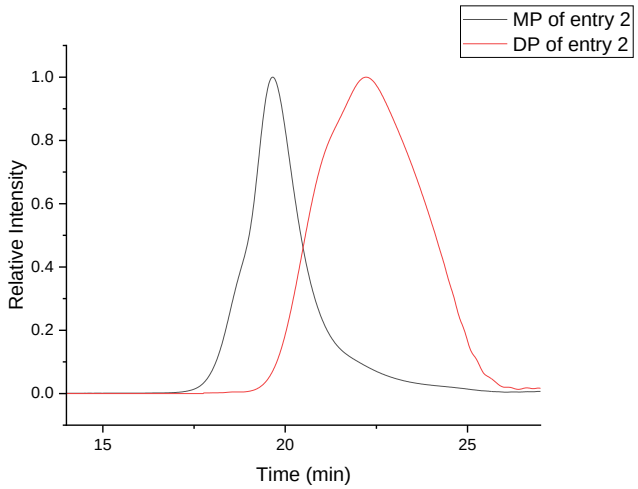


Entry[c]	1:2	[M]	MP M_n (kDa)/$Đ$[d]	DP M_n (kDa)/$Đ$ [d]	DP M_n^{theo} (kDa)[e]
1[a]	6:1	0.2	24.6/1.27	3.7/1.27	2.03
2[b]		0.2	23.7/1.32	6.3/1.41	

[a] Same injection flow rate, [b] Different injection flow rate with the same monomer concentration. [c] Reactions were conducted in 0.2 M THF solution with **G3** catalyst at -10℃. Monomers were fully converted to produce long-chain (co)**MP**s, which were subsequently degraded using TFA to produce **DP** chains. [d] *M*n and *Đ* were determined using GPC in THF and polystyrene standards (RI detection). [e] Calculated average molecular weight.

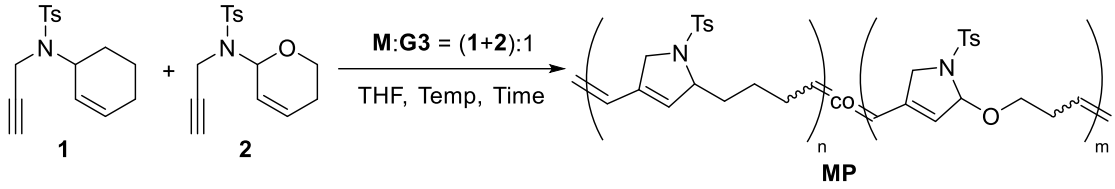
Table S8. Detailed experimental conditions of Table S7

Entry	Flow rate of 1 (mL/min)	Flow rate of 2 (mL/min)	Diluted volume of 1	Diluted volume of 2
1	0.02	0.02	0.2 mL	0.2 mL
2	0.03	0.005	0.3 mL	0.05 mL



Figuer S6. GPC data for Table S7, Entry 2

Table S9. Copolymerization of **1** and **2** using two syringe pumps with various concentrations.



Entry[a]	1:2	[M]	MP M_n (kDa)/$Đ$[b]	DP M_n (kDa)/$Đ$[b]	DP M_n^{theo} (kDa)[c]
1	6:1	0.05	13.6/1.81	3.8/1.22	2.03
2		0.2	24.6/1.27	3.7/1.27	
3		0.4	21.2/1.26	3.7/1.28	

[a)] Reactions were conducted in THF solution with **G3** catalyst at -10°C, Monomers were fully converted to produce long-chain (co)**MP**s, which were subsequently degraded using TFA to produce **DP** chains. [b)] Mn and Đ were determined using GPC in THF and polystyrene standards (RI detection). [c)] Calculated average molecular weight.

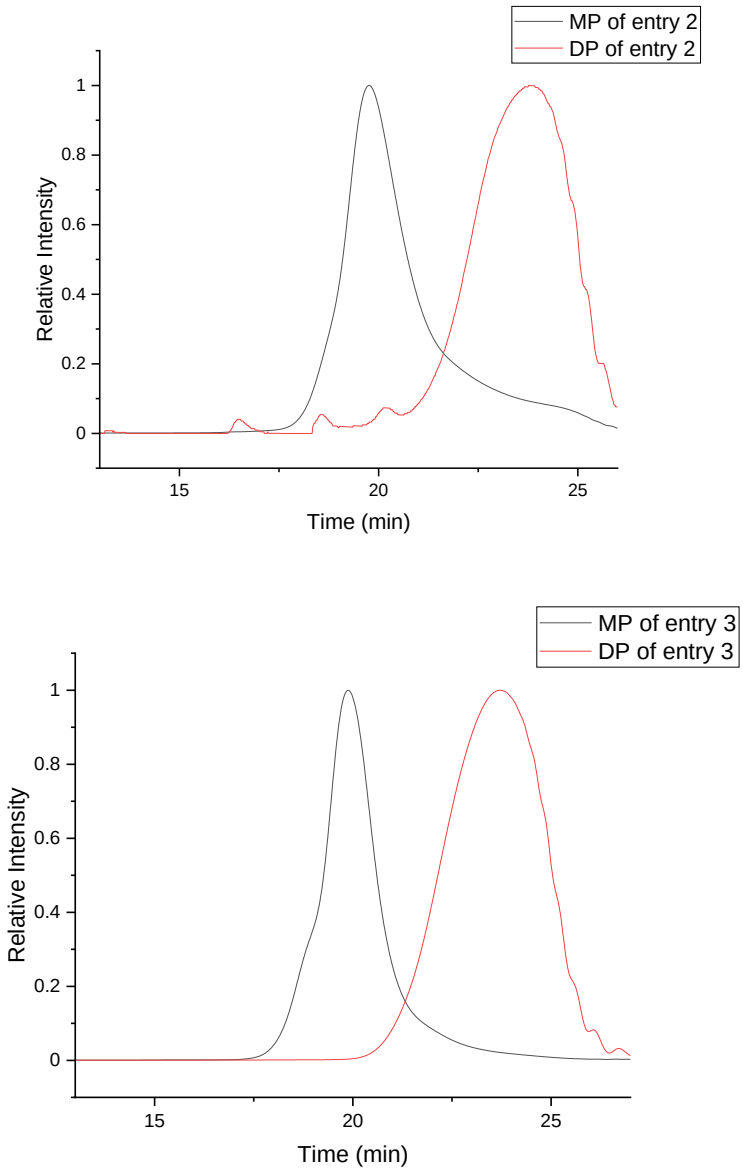


Figure S7. Polymer degradation of **MP** of Table S9; (black line: mother polymer **MP**, red line: daughter polymer **DP**)

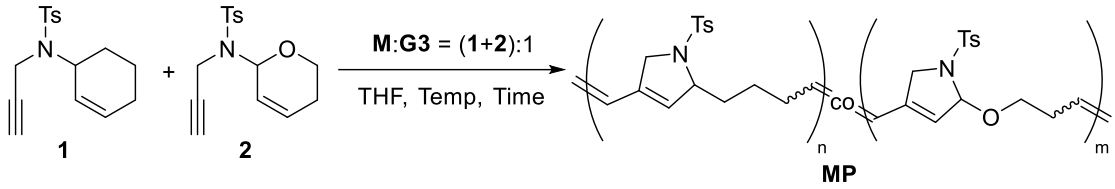
Table S10. Copolymerization of monomers **1** and **2** in the ratio of 100:1.

Entry[a]	1:2	[M]	MP M_n (kDa)/$Đ$[b]	DP M_n (kDa)/$Đ$[b]	DP M_n^{theo} (kDa)[c]
1	100:1	0.2	26.6/1.48	11.1/1.80	28.4

[a)] Reactions were conducted in THF solution with **G3** catalyst at -10°C, Monomers were fully converted to produce long-chain (co)**MP**s, which were subsequently degraded using TFA to produce **DP** chains. [b)] Mn and Đ were determined using GPC in THF and polystyrene standards (RI detection). [c)] Calculated average molecular weight.

5. Control molecular weight distribution(Gradient copolymerization)

Table S11. Enyne metathesis Copolymerization of **1** and **2** monomer using two syringe pump.



Entry	1:2	DP (M/I)	Temp. (°C)	Time (injection)	Time (additional)	Conversion (%) [a]	M_n (kDa) [b]	$Đ$ [b]
1	20:1	100	-10	10 min	5 min	>98	27.0	1.30
2	20:1	100	-10	10 min	5 min	>98	23.0	1.30

a) Conversions were determined by crude ^{1}H NMR. [b] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

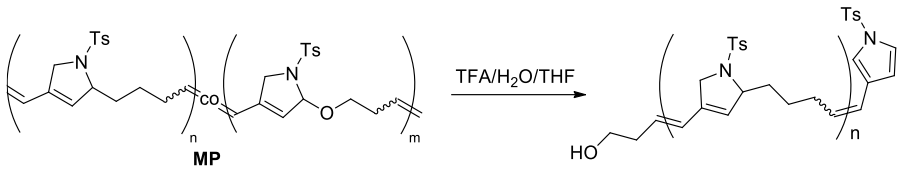
Table S12. Flow rate of monomer injection for Gradient Copolymerization for Entry 1

Step Number	Flow rate of **1** (mL/min)	Flow rate of **2** (mL/min)	Volume per step (mL)	Injection time (sec)
1	0.019	0.0666-0.04	0.045	49.5
2		0.04-0.02	0.045	90
3		0.02-0.01333	0.045	162
4		0.01333-0.01	0.065	331.5

Table S13. Flow rate of monomer injection for Gradient Copolymerization for Entry 2

Step Number	Flow rate of **1** (mL/min)	Flow rate of **2** (mL/min)	Volume per step (mL)	Injection time (sec)
1	0.02	0.0666-0.04	0.08	88
2		0.04-0.02	0.035	70
3		0.02-0.01333	0.035	126
4		0.01333-0.01	0.025	127.5
5		0.01-0.008	0.025	165

Table S14. Degradation of Gradient Copolymer **MP**.



Entry	Time (min)	MP (kDa) [a]	Mn (kDa) [a]	*Đ*
1	30	15.3	7.6	1.56
2	30	8.7	7.0	1.55

[a)] M_n's and *Đ*'s were determined by GPC (THF) using polystyrene standards (RI detection).

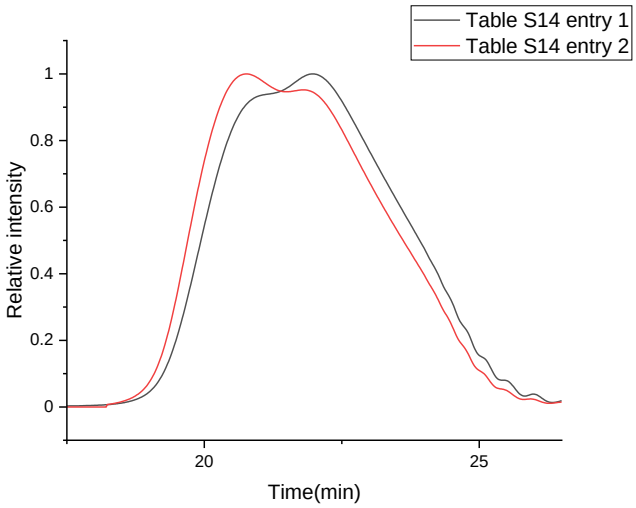


Figure S8. GPC data for Entries 1,2

6. Control Polydispersity

PDI Control by Polymerization Method – A, B, C

Method A: Normal Enyne metathesis homopolymerizaiton using **G3** catalyst as following the General procedure for polymerization in page S11.

Method B: Enyne metathesis Copolymerization using two syringe pump and degradation under acidic condition as following the general procedure for copolymerization involves dual-syringe pumps addition in page S15.

Method C: Enyne metathesis Copolymerization using syringe pump and degradation under acidic condition as following the general procedure for copolymerization involves single-syringe pump addition in page S14.

Table S15. Polymerization table for Control Polydispersity.

Entry	Method	1:2	DP (M/I)	Temp. (°C)	Time (injection)	Time (additional)	Conversion (%) [a]	M_n (kDa) [b]	$Đ$ [b]
1	A	-	10	-10	-	30 min	>98	5.1	1.19
2	B	10:1	100	-10	10 min	5 min	>98	4.6	1.34
3	C	10:1	100	-10	10 min	5 min	>98	4.7	1.37
4	A	-	20	-10	-	30 min	>98	7.6	1.19
5	B	20:1	100	-10	10 min	5 min	>98	7.0	1.39
6	C	20:1	100	-10	10 min	5 min	>98	7.0	1.51
7	A	-	40	-10	-	30 min	>98	11.4	1.18
8	B	40:1	100	-10	10 min	5 min	>98	11.3	1.62
9	C	40:1	100	-10	10 min	5 min	>98	11.1	1.68

a) Conversions were determined by crude ^{1}H NMR. [b)] M_n's and $Đ$'s were determined by GPC (THF) using polystyrene standards (RI detection).

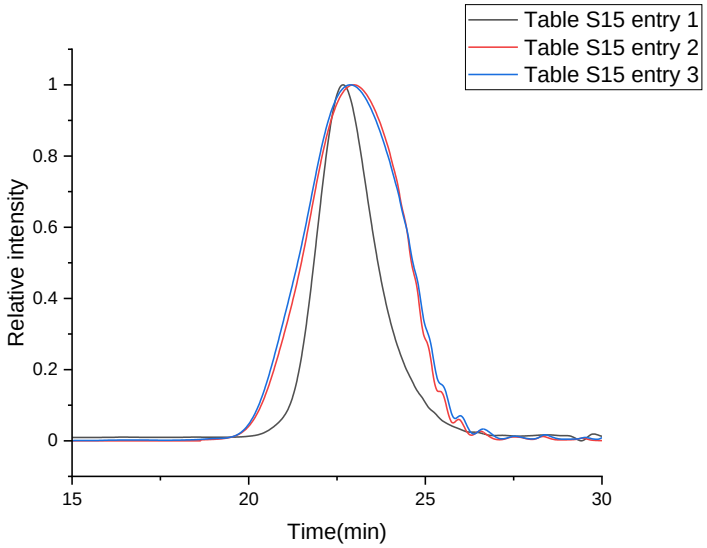


Figure S9. GPC data for Entries 1-3 in Table S15.

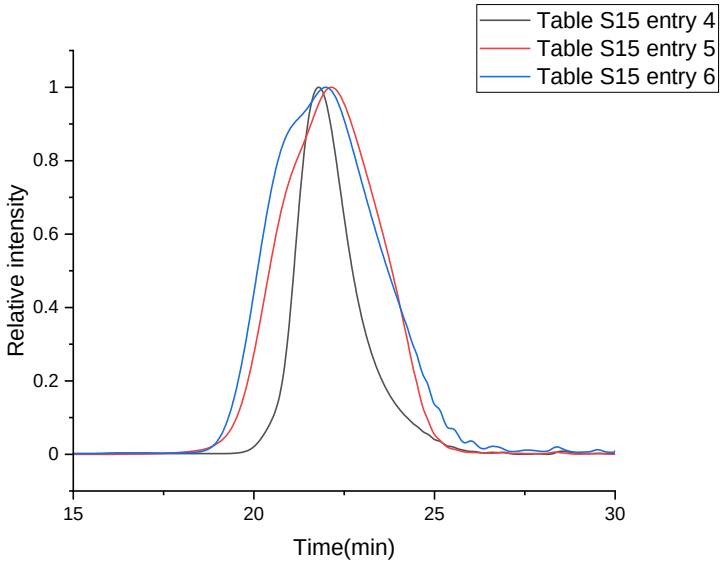


Figure S10. GPC data for Entries 4-6 in Table S15.

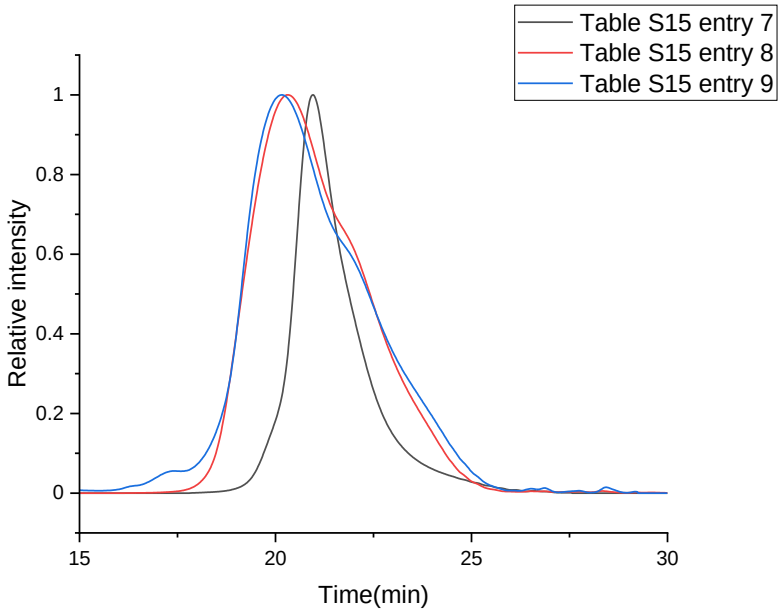
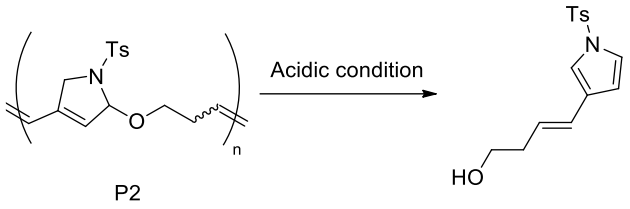


Figure S11. GPC data for Entries 7-9 in Table S15.

7. Degradability



Acidic condition: **P2** was dissolved in THF/H_2O (20/1) containing trifluoroacetic acid (TFA) (0.1M). Each aliquot was quenched with 0.1 mL triethylamine, concentrated under vacuum, and analyzed by GPC.

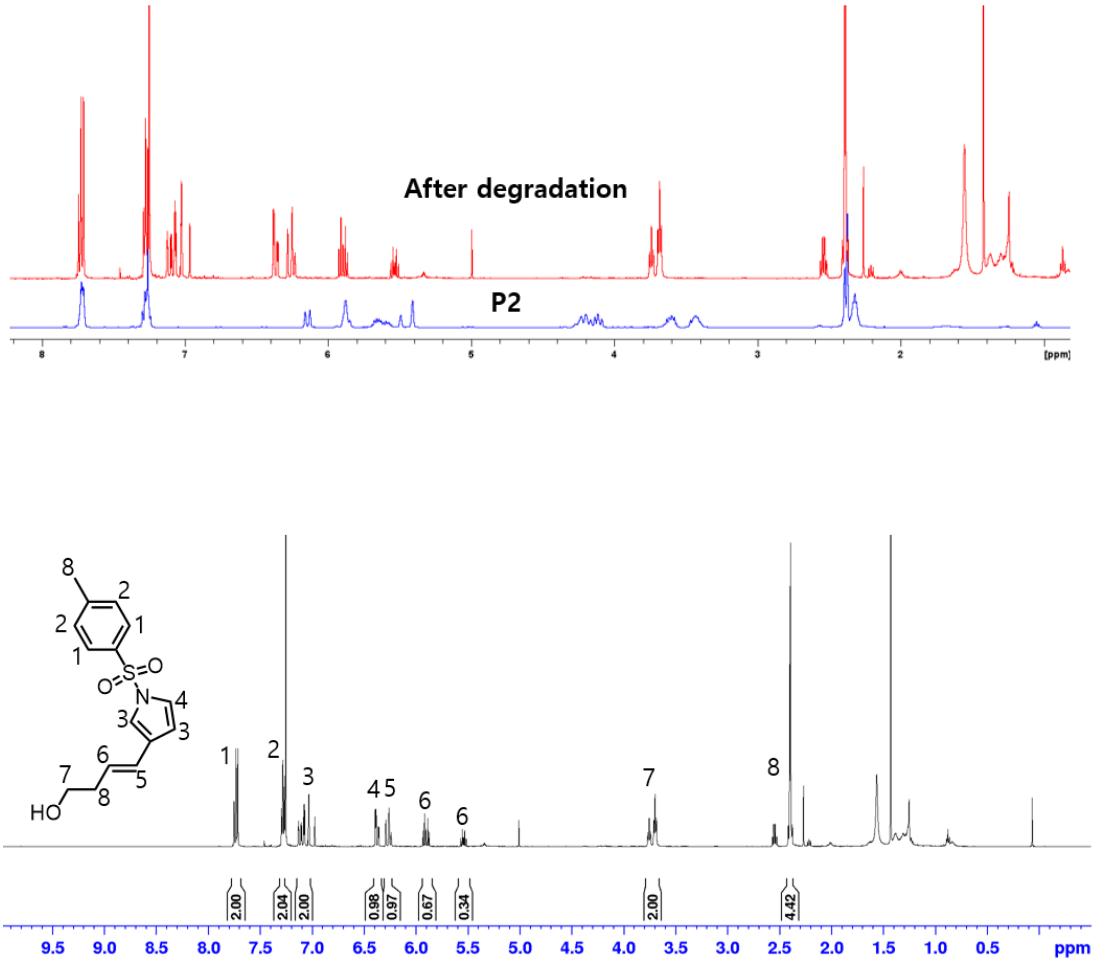
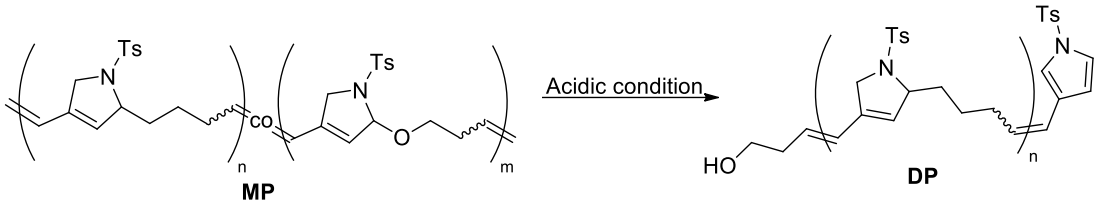


Figure S12. NMR data for degradation of **P2**



Acidic condition: **MP** was dissolved in THF/H_2O (20/1) containing trifluoroacetic acid (TFA) (0.1M). Each aliquot was quenched with 0.1 mL triethylamine, concentrated under vacuum, and analyzed by GPC.

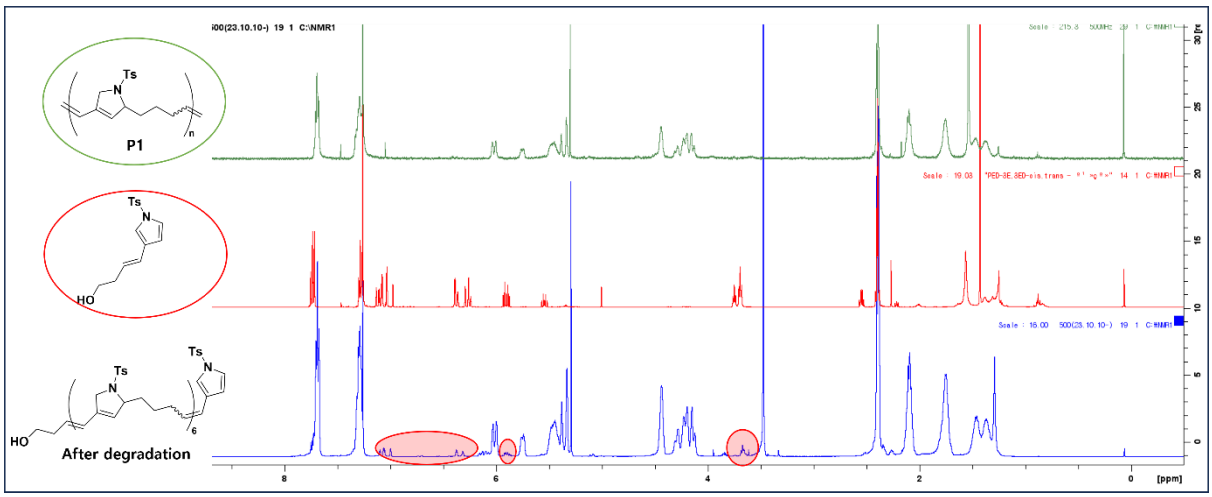
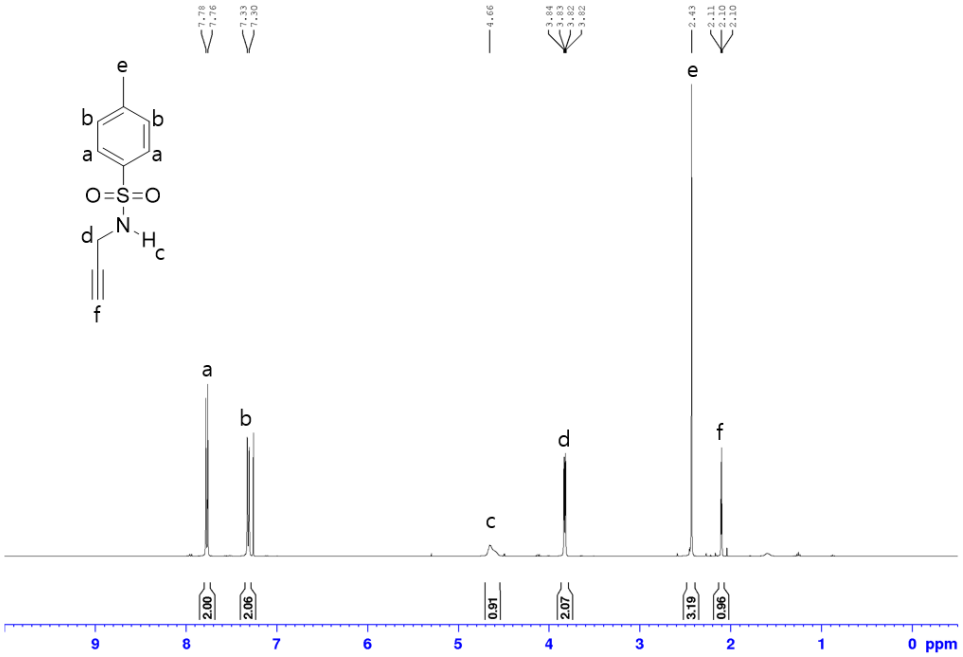
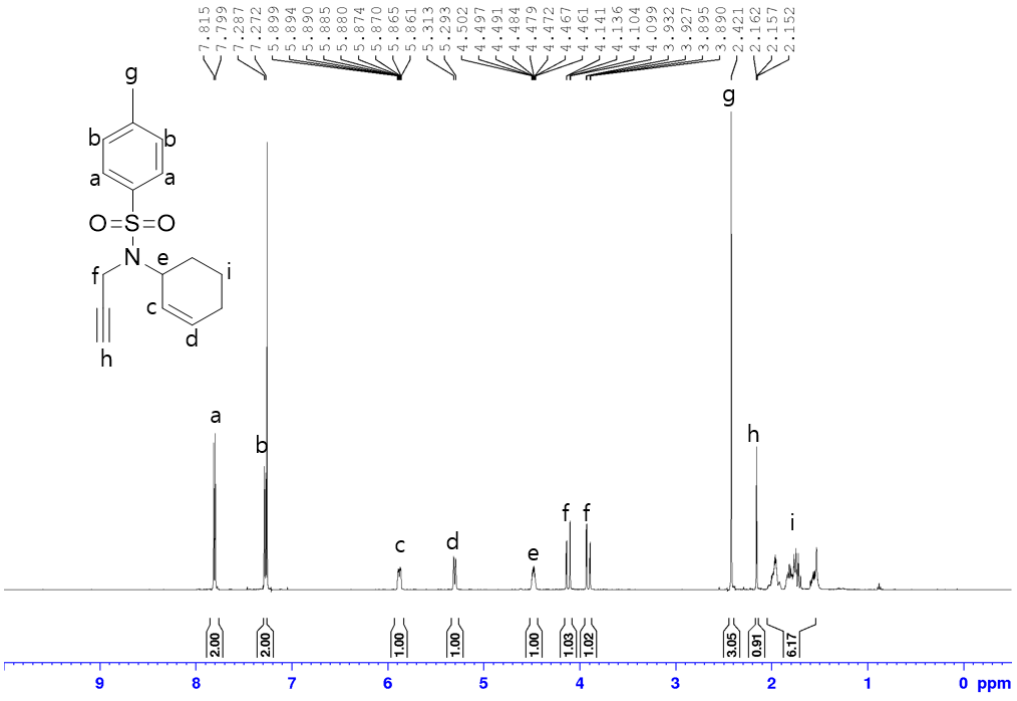


Figure S13. ^{1}H NMR spectra of homopolymer **P1** (green line), degraded product of degradable polymer **P2** (red line), and the obtained **DP** (blue line).

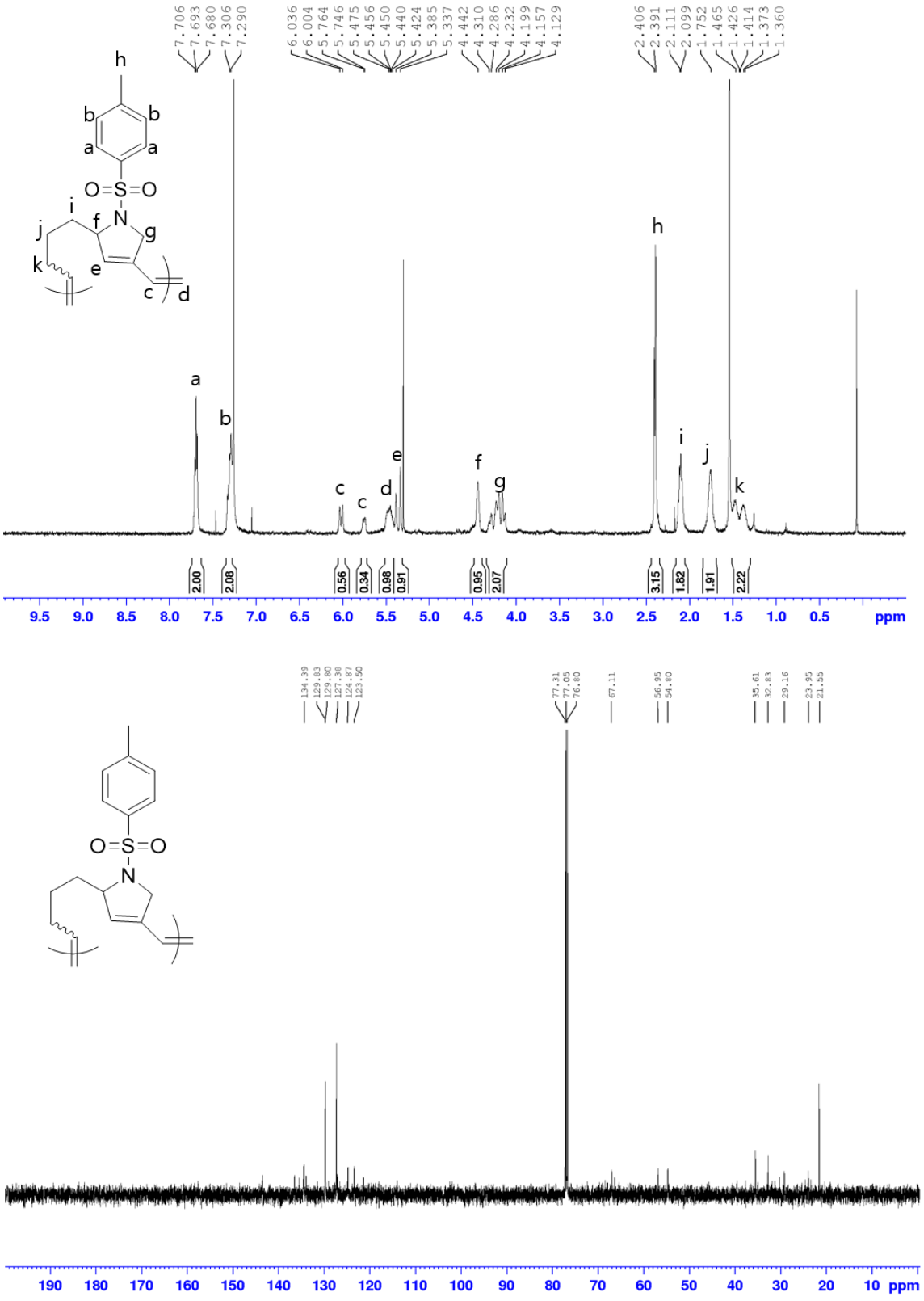
8. ^{1}H NMR and ^{13}C NMR spectra



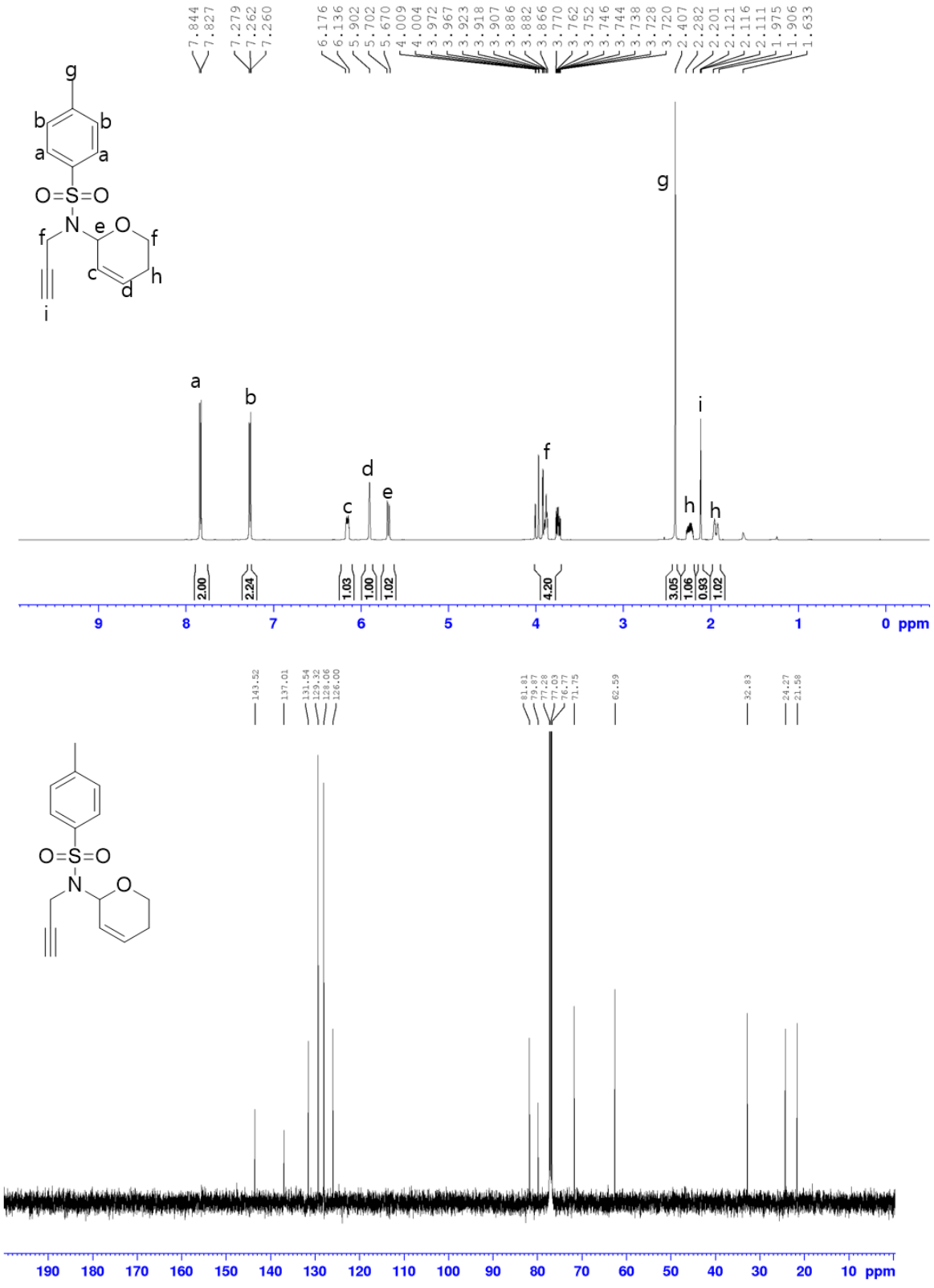
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of **N-Propargyl-p-toluenesulfonamide**



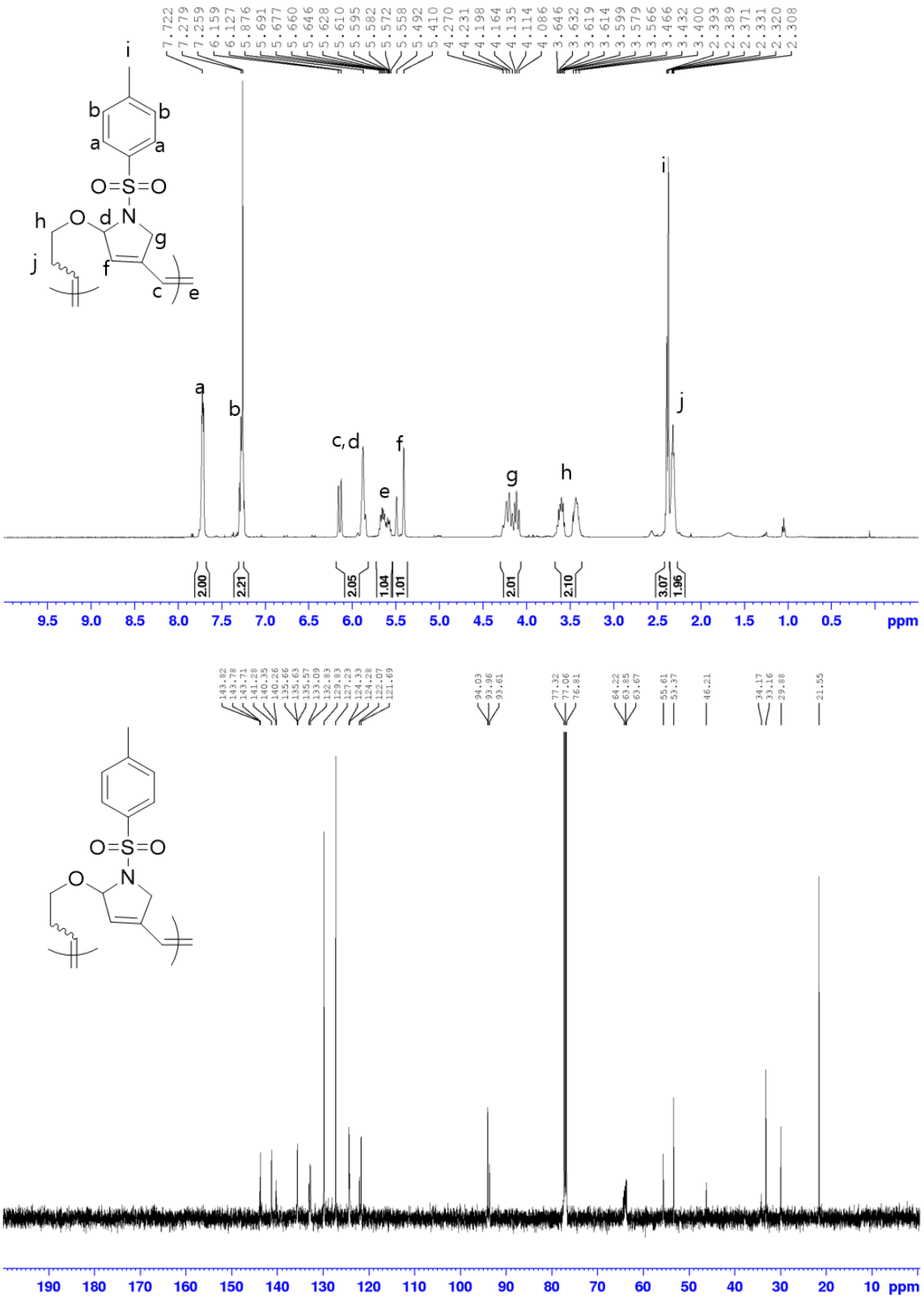
^{1}H NMR ($CDCl_3$, 500 MHz) spectra of compound **1**



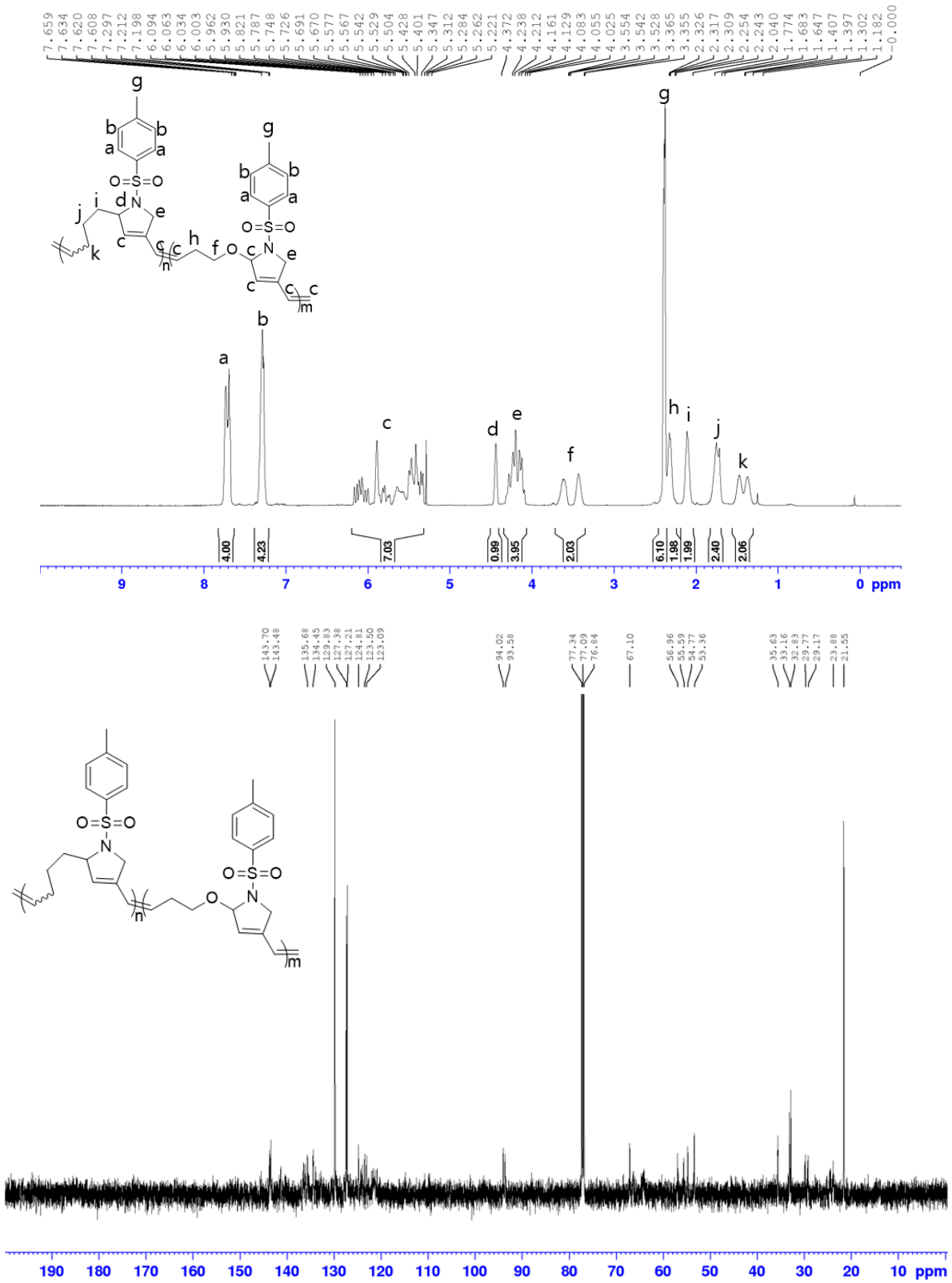
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of polymer P**1**



^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2**



^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of polymer P**2**



^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of polymer **MP**

9. References

1. I. Njoroge, M. W. Matson and G. K. Jennings, *J. Phys. Chem. C*, 2017, **121**, 20323-20334.

2. H. Park and T.-L. Choi, *J. Am. Chem. Soc.*, 2012, **134**, 7270-7273.

3. S.-H. Kim-Lee, I. Alonso, P. Mauleón, R. G. Arrayás and J. C. Carretero, *ACS Catal.*, 2018, **8**, 8993-9005.