Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Sequestration of Ruthenium Residues via Efficient Fluorous-enyne Termination

Xuelin Sui, Chenxiao Wang and Will R. Gutekunst*

School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive NW, Atlanta, Georgia 30332, United States.

* Corresponding author: E-mail: willgute@gatech.edu (Dr. Will R. Gutekunst)

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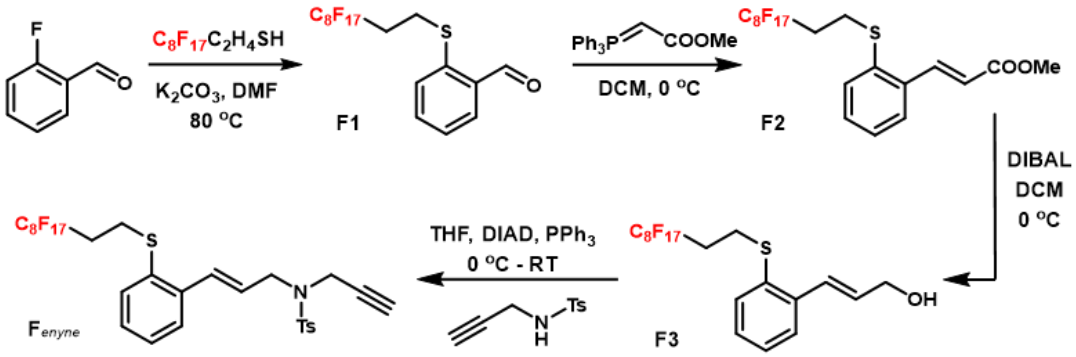
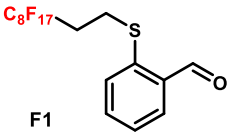
General Procedures. All reactions were carried out under a nitrogen atmosphere with dry solvents using anhydrous conditions unless otherwise stated. Dry, degassed dichloromethane (CH_2Cl_2), *N*,*N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were obtained from a JC Meyer solvent purification system. Deionized (DI) water with a resistivity of 18.2 MΩ.cm was used for all experiments. $CDCl_3$ 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. SiliCyclic 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). 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 at 40 ^{o}C. 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. Ruthenium content was determined by inductively coupled plasma mass spectrometry (IPC-MS, NexION 300Q, Perkin Elmer, USA). Anhydride endo-Tricyclo-[4.2.2.02,5]deca-3,9-diene,[1] N-tosyl-propargylamine,[2] M2,[3] M3,[3] M4,[4] and M6[5] were prepared according to literature procedures.

Experimental Procedures

Scheme S1: Route for the synthesis of fluorous enyne (**F***enyne*)





2-Fluorobenzaldehyde (2.0 g, 16.1 mmol, 1.0 eq) was dissolved in DMF (10 ml) at room temperature, followed by addition of K_2CO_3 powder (2.67 g, 19.3 mmol, 1.2 eq). The mixture was bubbled with nitrogen gas for 5 minutes, and *1H,1H,2H,2H*-perfluorodecanethiol (8.2 g, 16.9 mmol, 1.05 eq) in DMF (5 ml) was added via syringe. The reaction was placed in an oil bath that was preheated to 70 °C and stirred for 48 hours, then was quenched by H_2O (20 ml). The aqueous layer was extracted by diethyl ether (3×30 ml). The combined organics were washed with brine (30 ml), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (7% EtOAc in hexane) to give **F1** as a light-yellow solid (7.71 g, 82%).

LC-MS (m/z): $[M+2H_2O-F]^+$ calcd. for $C_{17}H_{13}F_{16}O_3S$, 601.0, found, 601.1

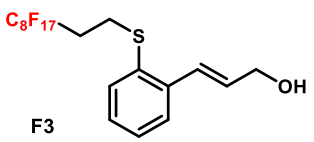
Melting point: 52 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.33 (s, 1H), 7.88 (dd, J = 7.6, 1.6 Hz, 1H), 7.59 (ddd, J = 8.0, 7.3, 1.6 Hz, 1H), 7.48 – 7.32 (m, 2H), 3.26 – 3.12 (m, 2H), 2.54 – 2.40 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 191.32, 139.52, 134.25, 134.11, 133.22, 127.44, 126.04, 121.60 – 120.18 (m), 119.52 (t, J = 32.1 Hz), 117.87 (dt, J = 93.9, 32.6 Hz), 116.95 – 114.51 (m), 114.26 – 111.97 (m),

111.61 – 109.46 (m), 109.13 – 107.61 (m), 106.20 (d, J = 39.8 Hz), 30.85 (t, J = 22.1 Hz), 23.58 (d, J = 4.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.72 (d, J = 9.5 Hz), -114.13 (d, J = 4.1 Hz), -121.63, -121.87 (d, J = 19.5 Hz), -122.67, -123.22, -126.06 (ddd, J = 18.1, 9.2, 3.6 Hz).



F3

To a solution of **F1** (5.84 g, 10 mmol) in dry CH_2Cl_2 (50 ml) was added $Ph_3P{=}CHCO_2Me$ (3.68 g, 11 mmol, 1.1 equiv) at -10 °C. After stirring for 1 hour at 0 °C, the solution was placed at rt overnight. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (10% EtOAc in hexane) to give **F2** (a mixture of *trans* isomers and *cis* isomers, *trans/cis* = 99:1), which was used without further purification. Then, to a solution of **F2** in dry DCM (50 ml) at –30 °C was added dropwise DIBAL-H (20 ml of a 1.1 M solution in tol, 22 mmol, 2.2 equiv). The reaction was stirred further at 0 °C for 5 hours. Then the reaction was quenched by careful addition of a saturated solution of Rochelle salt (20 ml), and the mixture was allowed to warm to rt. The aqueous layer was extracted by DCM (3×30 ml). The combined organics were washed with brine (30 ml), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (20% EtOAc in hexane) to give **F3** as a light yellow liquid (4.1 g, 67% over 2 steps).

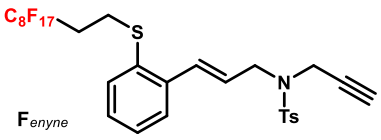
LC-MS (m/z): $[M+2H_2O-F]^+$ calcd. for $C_{19}H_{17}F_{16}O_3S$, 629.1, found, 629.1

Melting point: 40 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.49 (m, 1H), 7.46 – 7.35 (m, 1H), 7.31 – 7.23 (m, 1H), 7.14 (dt, J = 15.8, 1.7 Hz, 1H), 6.32 (dt, J = 15.8, 5.6 Hz, 1H), 4.37 (dd, J = 5.6, 1.7 Hz, 2H), 3.20 – 2.77 (m, 2H), 2.35 (tt, J = 17.6, 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.54, 132.42, 131.40, 131.24, 128.19, 128.17, 127.72, 126.82, 121.40 (t, J = 33.0 Hz), 120.60 – 119.45 (m), 118.93 – 117.05 (m), 116.51 – 114.43 (m), 114.37 – 112.18 (m), 112.10 – 109.30 (m), 108.02 (dd, J = 69.1, 38.9 Hz), 105.67 (d, J = 38.6 Hz), 63.54, 31.46 (t, J = 22.0 Hz), 25.03 (t, J = 4.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.73, -112.45 – -117.08 (m), -121.70, -121.89, -122.69, -123.27, -126.07 (td, J = 13.2, 12.1, 5.5 Hz).



To a stirred and cooled (0 °C) solution of **F3** (613 mg, 1.0 mmol, 1 equiv), N-tosyl-propargylamine (209 mg, 1.0 mmol, 1 equiv) and PPh3 (420 mg, 1.6 mmol, 1.6 equiv) in anhydrous THF (8 ml) was added dropwise DIAD (0.3 ml, 1.5 mmol, 1.5 equiv). The reaction was placed in a water bath and stirred for 24 hours at room temperature. Then the reaction was concentrated in vacuo. Chromatography gave the target enyne **F_{enyne}** (0.7 g, 87%) as a light yellow oil.

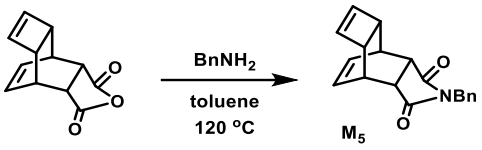
LC-MS (m/z): $[M+2H_2O-F]^+$ calcd. for $C_{29}H_{26}F_{16}NO_4S_2$, 820.1, found, 820.1

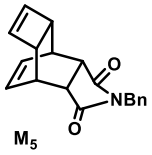
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.45 – 7.38 (m, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.15 (d, J = 15.7 Hz, 1H), 6.08 (dt, J = 15.7, 6.9 Hz, 1H), 4.17 (d, J = 2.5 Hz, 2H), 4.05 (dd, J = 6.9, 1.3 Hz, 2H), 3.10 – 2.94 (m, 2H), 2.46 (s, 3H), 2.34 (dp, J = 17.5, 8.1 Hz, 2H), 2.07 (t, J = 2.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.51, 137.90, 135.72, 132.28, 132.14, 131.50, 129.35, 128.42, 127.74, 127.62, 126.77, 125.61, 120.22 (d, J = 32.6 Hz), 119.38 (t, J = 31.5 Hz), 118.06 (t, J = 33.1 Hz), 117.34 (t, J = 31.7 Hz), 116.44 – 114.63 (m), 113.44 – 111.89 (m), 111.50 – 109.43 (m), 108.34 (t, J = 32.4 Hz), 76.18, 73.78, 48.50, 35.82, 31.27 (t, J = 22.0 Hz), 25.04 (d, J = 4.3 Hz), 21.26.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.73, -109.85 – -116.63 (m), -121.70, -121.89 (d, J = 19.6 Hz), -122.68, -123.23, -126.07 (td, J = 13.1, 11.9, 4.1 Hz).

Scheme S2: Route for the synthesis of **M5**





Anhydride endo-Tricyclo-[4.2.2.02.5]deca-3,9-diene (1.00 g, 4.94 mmol) and benzylamine (0.28 ml, 4.94 mmol) was purged with argon gas. Then 20 mL of anhydrous toluene was added, and the flask was fitted with a Dean-Stark trap and a condenser. The reaction mixture was refluxed at 120 °C for 16 h. After completion of reflux, the solvent was removed on a rotary evaporator. The residue was purified by column chromatography (25% EtOAc in hexane) to give **M5** as a white solid (1.11 g, 77%).

LC-MS (m/z): $[M+H]^+$ calcd. for $C_{19}H_{18}NO_2$, 292.1, found, 292.2.

Melting point: 150-151 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.20 (m, 5H), 5.87 (s, 2H), 5.79 (dd, J = 4.7, 3.2 Hz, 2H), 4.57 (s, 2H), 3.16 (ddt, J = 3.5, 2.4, 1.3 Hz, 2H), 2.83 – 2.79 (m, 2H), 2.79 (t, J = 1.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 178.24, 137.76, 135.66, 128.31, 128.24, 128.08, 127.50, 43.95, 43.18, 41.99, 36.49.

General Polymerization Procedure

Grubbs 3 catalyst with desired amount was added to an 8 mL vial (Chemglass, CG-4909-03), placed under a nitrogen atmosphere, at room temperature. Then the desired amount of DCM or THF was

added to make a stock solution (0.015 M). In another 8 mL vial equipped with a stir bar, a solution of **M1-M6** (30-500 eq) in degassed DCM or THF was prepared. Appropriate volume of Grubbs 3 solution is rapidly added to the vial containing monomers using a microliter syringe. After the desired time, the polymerization was stopped by addition of ethyl vinyl ether (**EVE**, 0.2 ml) or **F_{enyne}** (1.5eq for **M1-M4** and **M6**, 5 eq for **M5**). The reaction mixture was further stirred for 10 minutes (**M1-M4**) or 4 hours (**M5**) before it was precipitated using 15-fold volume of methanol or purified via Fluorous Solid-phase Extraction (**F-SPE**). Polymer parts were dried under vacuum for analysis using GPC and NMR.

Polymerization Data

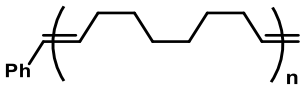
Table S1. Polymerization of M1-M5.

Entry[a]	Monomer	[M] (mol/L)	Solvent	DP	Terminator	Method[b]	Recovery (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	**M1**	1	DCM	30	EVE	MeOH	85	8.5	2.03
2	**M1**	1	DCM	30	F_{enyne}	MeOH	84	9.2	1.98
3	**M1**	1	DCM	30	F_{enyne}	CF_3-OH	82	9.3	1.97
4	**M1**	1	DCM	30	F_{enyne}	F-SPE	47	8.1	1.96
5	**M2**	0.2	DCM	30	EVE	MeOH	91	8.9	1.11
6	**M2**	0.2	DCM	30	F_{enyne}	MeOH	91	9.2	1.11
7	**M2**	0.2	DCM	30	F_{enyne}	F-SPE	91	9.3	1.10
8	**M2**	0.2	DCM	60	F_{enyne}	MeOH	92	17.6	1.09
9	**M2**	0.2	DCM	60	F_{enyne}	F-SPE	92	17.6	1.09
10	**M2**	0.2	DCM	100	F_{enyne}	F-SPE	92	29.9	1.09
11	**M2**	0.2	DCM	500	F_{enyne}	F-SPE	92	116	1.11
12	**M3**	0.2	DCM	30	EVE	MeOH	90	8.3	1.12
13	**M3**	0.2	DCM	30	F_{enyne}	MeOH	91	8.8	1.11
14	**M3**	0.2	DCM	30	F_{enyne}	F-SPE	91	8.8	1.11
15	**M4**	0.2	DCM	30	EVE	MeOH	82	7.2	1.19
16	**M4**	0.2	DCM	30	F_{enyne}	MeOH	81	7.9	1.18
17	**M4**	0.2	DCM	30	F_{enyne}	F-SPE	85	7.9	1.18
18	**M5**	0.2	DCM	30	EVE	MeOH	92	7.4	1.12
19[d]	**M5**	0.2	DCM	30	F_{enyne}	MeOH	92	8.0	1.13
20[d]	**M5**	0.2	DCM	30	F_{enyne}	F-SPE	93	8.1	1.13
21	**M6**	0.2	THF	30	EVE	MeOH	84	9.4	1.39
22	**M6**	0.2	THF	30	F_{enyne}	MeOH	84	10	1.32
23	**M6**	0.2	THF	30	F_{enyne}	F-SPE	88	10	1.31
24	**M2**	0.2	THF	30	F_{enyne}	MeOH	90	9.6	1.12
25	**M2**	0.2	THF	30	F_{enyne}	F-SPE	92	9.6	1.12
26	**M2**	0.2	EtOAc	30	F_{enyne}	MeOH	88	6.6	1.38

27	**M2**	0.2	Tol	30	F_{enyne}	MeOH	89	3.8	1.82

[a]Polymerization Condition: 3 μmol **G3** catalyst, termination using 0.2 ml **EVE** or 1.5 eq $\mathbf{F_{enyne}}$. [b]MeOH or CF3-OH: precipitation using 6 ml of MeOH or CF_3CH_2OH, F-SPE: Flourous Solid Phase Extraction. [c]Determined by $CHCl_3$ size-exclusion chromatography (SEC) calibrated using polystyrene standards. [d]Termination using 5 eq $\mathbf{F_{enyne}}$.

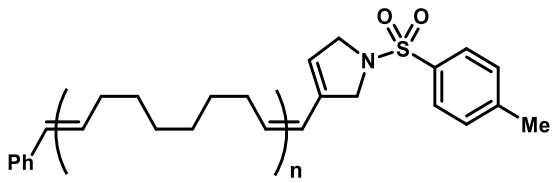
Characterization Data of Polymers (P1 – P6, $P1_F$ – $P6_F$)



P1: Prepared according to Polymerization General Procedure using **M1** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 1.7 Hz, 1H), 7.35 (d, J = 1.3 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.30 (d, J = 1.8 Hz, 1H), 7.26 – 7.10 (m, 1H), 6.55 – 6.34 (m, 1H), 6.24 (dt, J = 15.8, 6.8 Hz, 1H), 5.83 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.64 – 5.19 (m, 63H), 5.14 – 4.83 (m, 2H), 2.13 – 1.86 (m, 126H), 1.41 – 1.12 (m, 256H).

SEC ($CHCl_3$, RI): M_n = 8.5 kg/mol, $Đ$ = 2.03.



$P1_F$: Prepared according to Polymerization General Procedure using **M1** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.69 (m, 2H), 7.46 – 7.29 (m, 5H), 7.26 – 7.17 (m, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.9, 6.9 Hz, 1H), 5.61 – 5.23 (m, 67H), 4.44 – 3.97 (m, 4H), 2.52 – 2.37 (m, 3H), 2.28 – 1.84 (m, 134H), 1.53 – 1.04 (m, 268H).

SEC ($CHCl_3$, RI): M_n = 9.2 kg/mol, $Đ$ = 1.98.

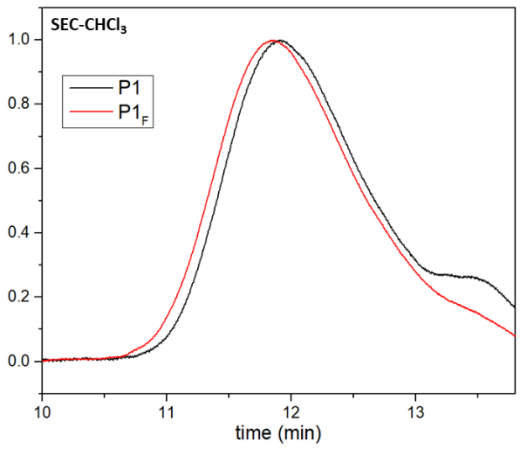
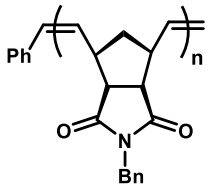


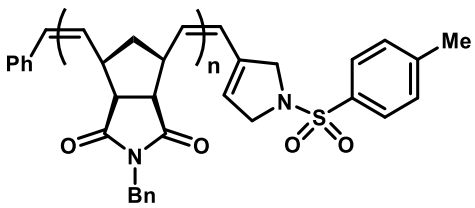
Figure S1. SEC traces for **P1** and **P1$_F$**.



P2: Prepared according to Polymerization General Procedure using **M2** and dihydrofuran with targeted degrees of polymerization of 30.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 6.94 (m, 153H), 6.66 – 6.42 (m, 1H), 6.00 – 5.87 (m, 1H), 5.91 – 5.65 (m, 30H), 5.61 – 5.34 (m, 30H), 5.18 (dd, J = 34.7, 13.7 Hz, 2H), 4.86 – 4.25 (m, 60H), 3.38 – 2.59 (m, 121H), 2.33 – 1.93 (m, 30H), 1.75 – 1.45 (m, 30H).

SEC ($CHCl_3$, RI): M_n = 8.9 kg/mol, $Đ$ = 1.11.



P2$_F$: Prepared according to Polymerization General Procedure using **M2** and dihydrofuran with targeted degrees of polymerization of 30, 60, 100, and 500.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 8.2, 3.0 Hz, 2H), 7.50 – 7.02 (m, 160H), 6.73 – 6.49 (m, 1H), 6.39 – 6.16 (m, 1H), 5.97 – 5.64 (m, 32H), 5.60 – 5.42 (m, 32H), 4.71 – 4.43 (m, 64H), 4.37 – 3.93 (m, 4H), 3.53 – 2.56 (m, 127H), 2.44 (d, J = 5.1 Hz, 3H), 2.24 – 2.01 (m, 32H), 1.75 – 1.43 (m, 32H).

SEC (DP30, $CHCl_3$, RI): M_n = 9.2 kg/mol, $Đ$ = 1.11.

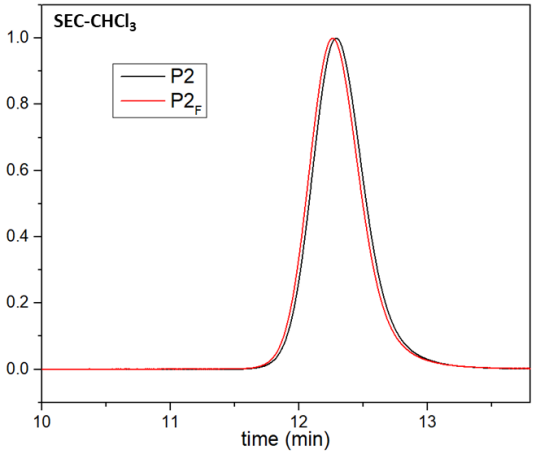
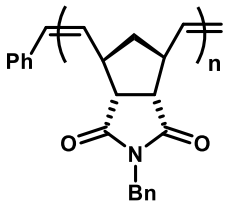


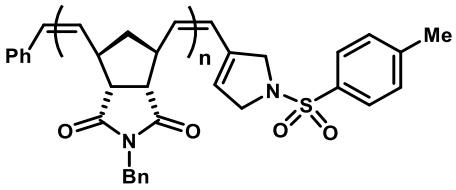
Figure S2. SEC trace for **P2** and **P2$_F$**.



P3: Prepared according to Polymerization General Procedure using **M3** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.08 (m, 152H), 6.78 – 6.23 (m, 1H), 5.94 (dt, J = 17.5, 8.4 Hz, 1H), 5.80 – 5.12 (m, 61H), 5.29 – 4.92 (m, 2H), 4.91 – 4.17 (m, 62H), 3.57 – 2.54 (m, 124H), 2.25 – 1.45 (m, 31H), 1.40 – 0.75 (m, 32H).

SEC ($CHCl_3$, RI): M_n = 8.3 kg/mol, $Đ$ = 1.12.



$P3_F$: Prepared according to Polymerization General Procedure using **M3** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (q, J = 6.8, 5.7 Hz, 2H), 7.65 – 6.98 (m, 178H), 6.72 – 6.21 (m, 1H), 6.14 – 5.84 (m, 1H), 5.89 – 5.14 (m, 70H), 5.07 – 4.07 (m, 70H), 4.45 – 4.06 (m, 4H), 3.39 – 2.67 (m, 141H), 2.59 – 2.30 (m, 3H), 2.08 – 1.43 (m, 32H), 1.54 – 0.83 (m, 33H).

SEC ($CHCl_3$, RI): M_n = 8.8 kg/mol, $Đ$ = 1.11.

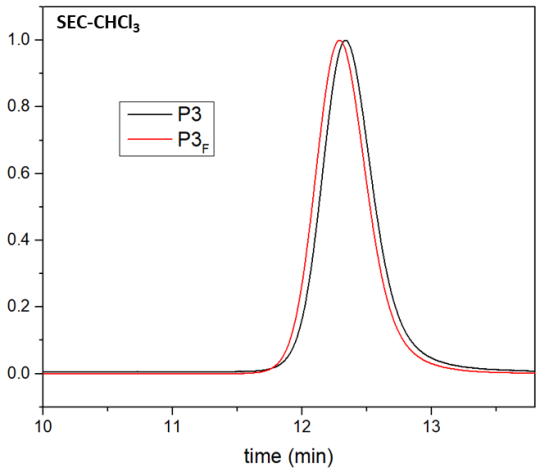
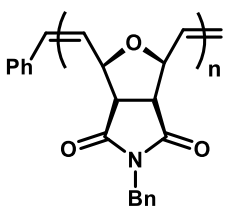


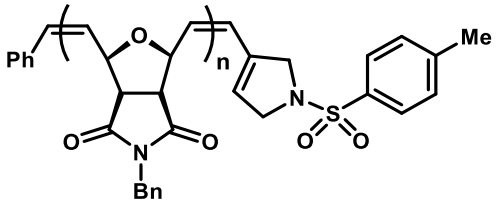
Figure S3. SEC trace for **P3** and **$P3_F$**.



P4: Prepared according to Polymerization General Procedure using **M4** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 – 7.08 (m, 140 H), 6.91 – 6.65 (m, 1H), 6.47 – 6.24 (m, 1H), 6.19 – 5.92 (m, 27H), 5.89 – 5.51 (m, 28H), 5.49 – 5.19 (m, 2H), 5.11 – 4.85 (m, 27H), 4.72 – 4.49 (m, 56H), 4.52 – 4.32 (m, 28H), 3.59 – 2.91 (m, 54H).

SEC ($CHCl_3$, RI): M_n = 7.2 kg/mol, $Đ$ = 1.19.



P4$_F$: Prepared according to Polymerization General Procedure using **M4** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.64 (m, 2H), 7.57 – 7.14 (m, 144H), 6.96 – 6.69 (m, 1H), 6.53 – 6.26 (m, 1H), 6.16 – 5.90 (m, 27H), 5.82 – 5.59 (m, 28H), 5.13 – 4.83 (m, 28H), 4.77 – 4.49 (m, 57H), 4.49 – 4.27 (m, 28H), 4.29 – 4.03 (m, 4H), 3.44 – 2.92 (m, 58H), 2.51 – 2.26 (m, 3H).

SEC ($CHCl_3$, RI): M_n = 7.9 kg/mol, $Đ$ = 1.18.

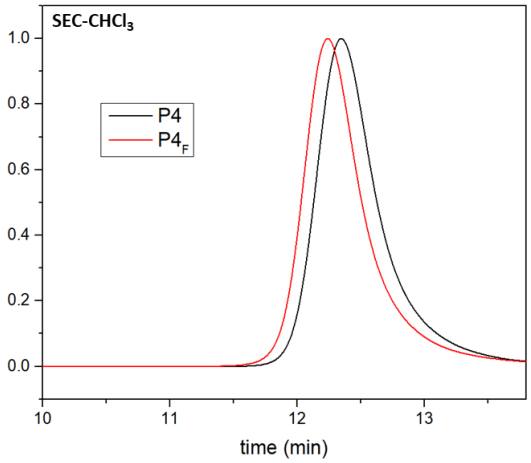
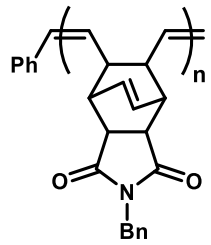


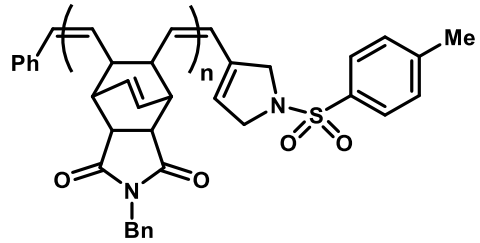
Figure S4. SEC trace for **P4** and **P4$_F$**.



P5: Prepared according to Polymerization General Procedure using **M5** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.07 (m, 162H), 6.59 – 6.43 (m, 1H), 6.44 – 5.98 (m, 64H), 5.49 (dt, J = 18.0, 9.4 Hz, 1H), 5.38 – 5.21 (m, 1H), 5.25 – 4.89 (m, 63H), 4.69 – 4.11 (m, 63H), 3.42 – 2.40 (m, 190H).

SEC ($CHCl_3$, RI): M_n = 7.4 kg/mol, $Đ$ = 1.12.



P5$_F$: Prepared according to Polymerization General Procedure using **M5** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 – 7.68 (m, 2H), 7.42 – 6.95 (m, 165H), 6.61 – 5.96 (m, 64H), 5.95 – 5.78 (m, 2H), 5.40 – 4.64 (m, 64H), 4.77 – 4.21 (m, 64H), 4.32 – 4.00 (m, 4H), 3.41 – 2.54 (m, 192H), 2.48 – 2.23 (m, 3H).

SEC ($CHCl_3$, RI): M_n = 8.0 kg/mol, $Đ$ = 1.11.

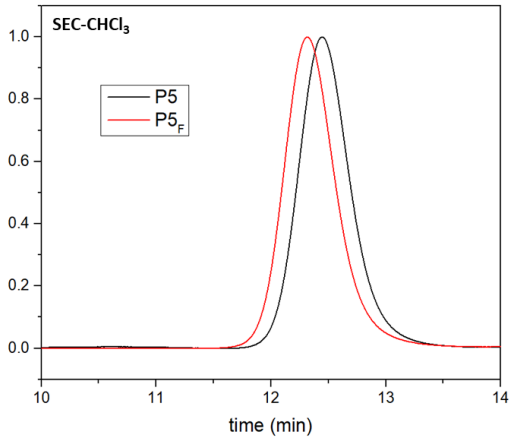
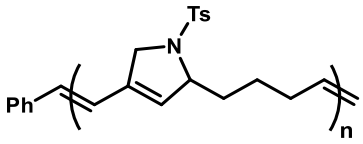


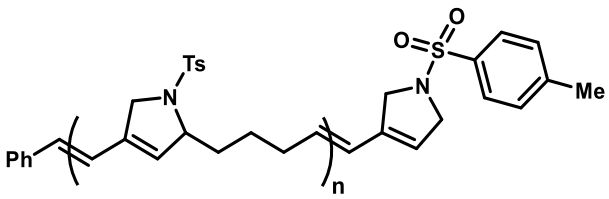
Figure S5. SEC trace for **P5** and **P5$_F$**.



P6: Prepared according to Polymerization General Procedure using **M6** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 – 7.61 (m, 63H), 7.36 – 7.29 (m, 63H), 6.66 (m, 1H), 6.35 (dd, J = 16.3, 7.3 Hz, 1H), 6.04 (dd, J = 15.8, 3.9 Hz, 18H), 5.84 – 5.70 (m, 14H), 5.65 – 5.28 (m, 61H), 5.11 – 4.90 (m, 2H), 4.46 (s, 31H), 4.22 (m, 63H), 2.42 (d, J = 7.9 Hz, 98H), 2.13 (q, J = 7.9 Hz, 61H), 1.88 – 1.69 (m, 61H), 1.54 – 1.35 (m, 61H).

SEC ($CHCl_3$, RI): M_n = 9.4 kg/mol, $Đ$ = 1.39.



P6$_F$: Prepared according to Polymerization General Procedure using **M6** and dihydrofuran with a targeted degree of polymerization of 30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 – 7.65 (m, 64H), 7.42 – 7.29 (m, 64H), 6.79 – 6.52 (m, 1H), 6.41 – 6.18 (m, 1H), 6.12 – 5.98 (m, 20H), 5.84 – 5.63 (m, 12H), 5.57 – 5.23 (m, 61H), 4.46 (s, 31H), 4.35 – 4.03 (m, 62H), 2.46 – 2.34 (m, 97H), 2.24 – 2.03 (m, 61H), 1.89 – 1.72 (m, 63H), 1.56 – 1.31 (m, 62H).

SEC ($CHCl_3$, RI): M_n = 10 kg/mol, $Đ$ = 1.31.

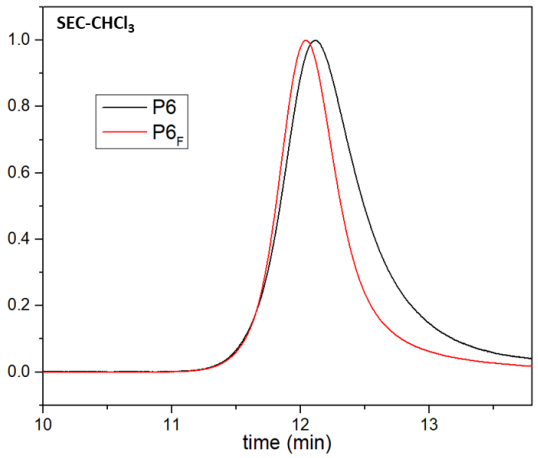


Figure S6. SEC trace for **P6** and **P6$_F$**.

Analysis of ^{1}H NMR signal assignment for polymer P2 and $P2_F$.

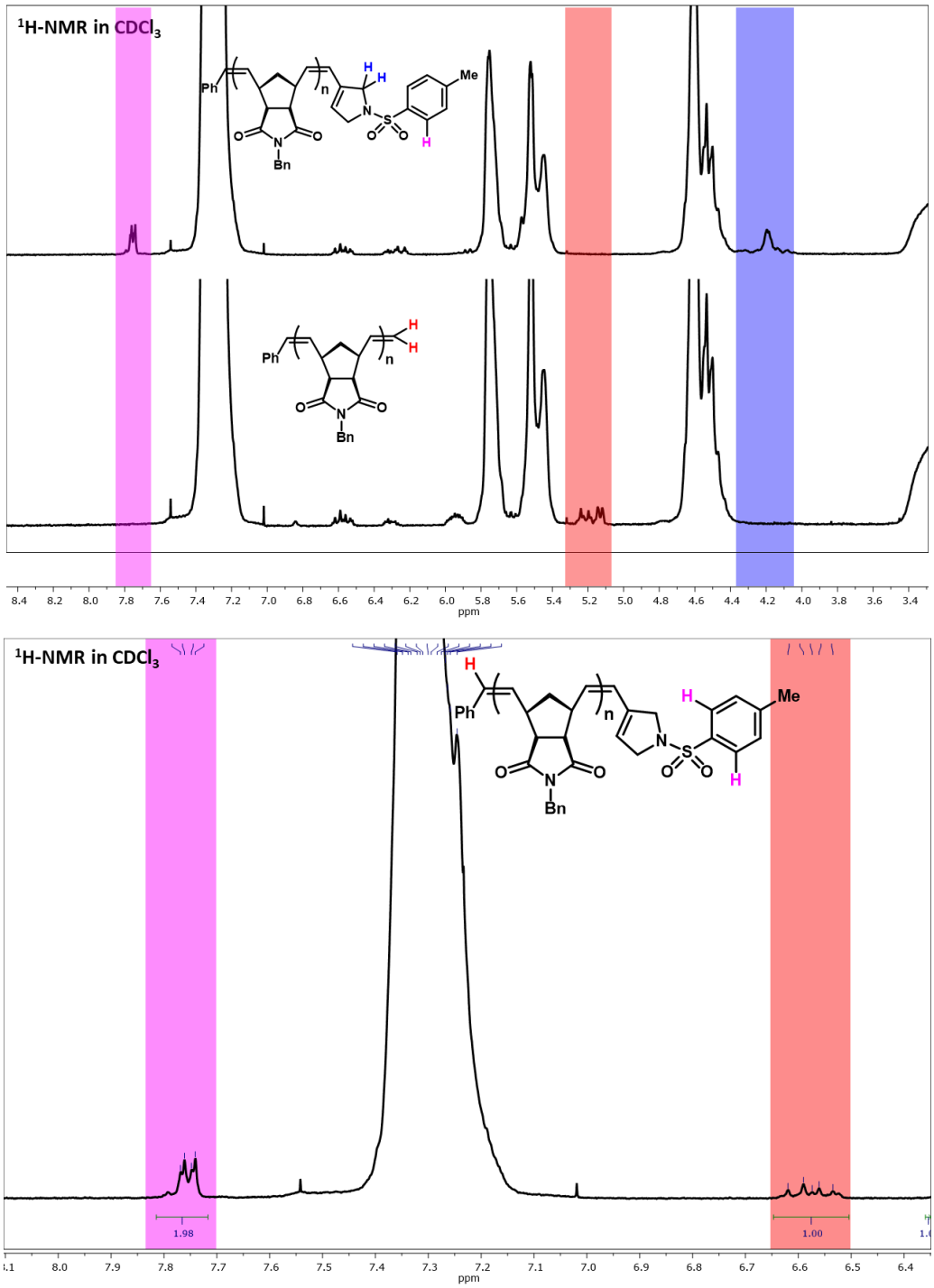
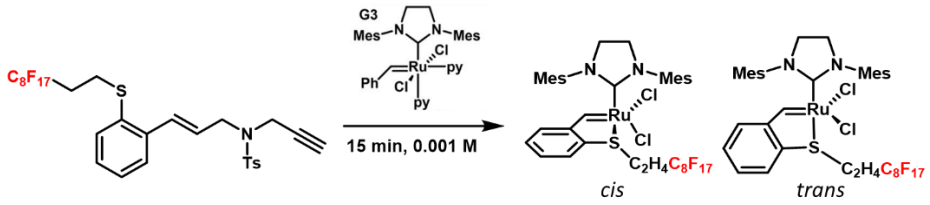


Figure S7. ^{1}H NMR for polymers: a.**P2**, b. $\mathbf{P2_F}$. ^{1}H NMRs shows no terminal alkene could be observed in $\mathbf{P2_F}$, exhibiting high efficiency of $\mathbf{F}_{enyne}$ termination and quantitative conversion of Ru chain-end into **Ru-S**.

Model metathesis reaction of F_{enyne} with Grubbs initiators



Grubbs 3 catalyst with desired amount was added to an 8 mL vial (Chemglass, CG-4909-03), placed under a nitrogen atmosphere, at room temperature. Then the desired amount of $CDCl_3$ was added to make a stock solution (0.001 M). In another 8 mL vial equipped with a stir bar, a solution of **F_{enyne}** (1.5eq) in degassed $CDCl_3$ was prepared. Appropriate volume of Grubbs 3 solution is rapidly added to the vial containing monomers using a microliter syringe. The reaction mixture was stirred at RT and aliquots (0.1 mL each) were taken after desired time periods. Each aliquot analyzed by ^{1}H NMR.

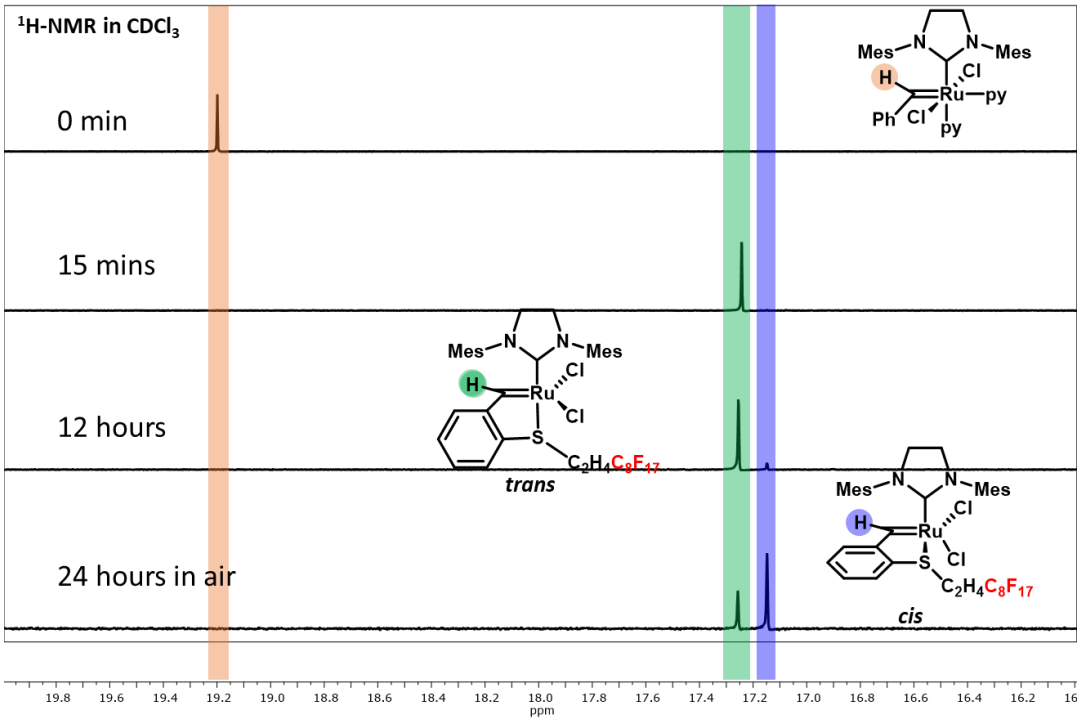
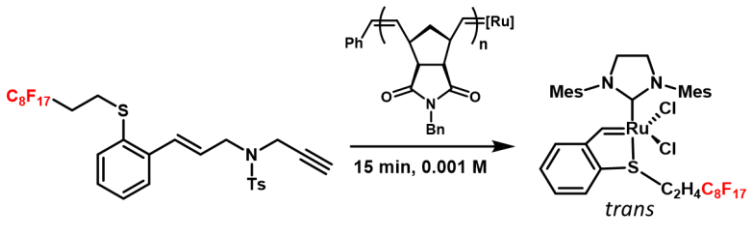


Figure S8. ^{1}H NMR for analysis of model reaction of **G3** with **F_{enyne}**.

Grubbs 3 catalyst with desired amount was added to an 8 mL vial (Chemglass, CG-4909-03), placed under a nitrogen atmosphere, at room temperature. Then the desired amount of $CDCl_3$ was added to make a stock solution (0.015 M). In another 8 mL vial equipped with a stir bar, a solution of monomers

(10 eq) in degassed $CDCl_3$ was prepared. At the same time, a stock solution of $\mathbf{F}_{enyne}$ (0.01M) in degassed $CDCl_3$ was prepared. Appropriate volume of Grubbs 3 solution is rapidly added to the vial containing monomers using a microliter syringe. After 10 mins, a desired volume of a stock solution of $\mathbf{F}_{enyne}$ (1.5eq) was added into the polymerization mixture. The mixture was stirred at RT and aliquots (0.1 mL each) were taken after desired time periods. Each aliquot analyzed by ^{1}H NMR.



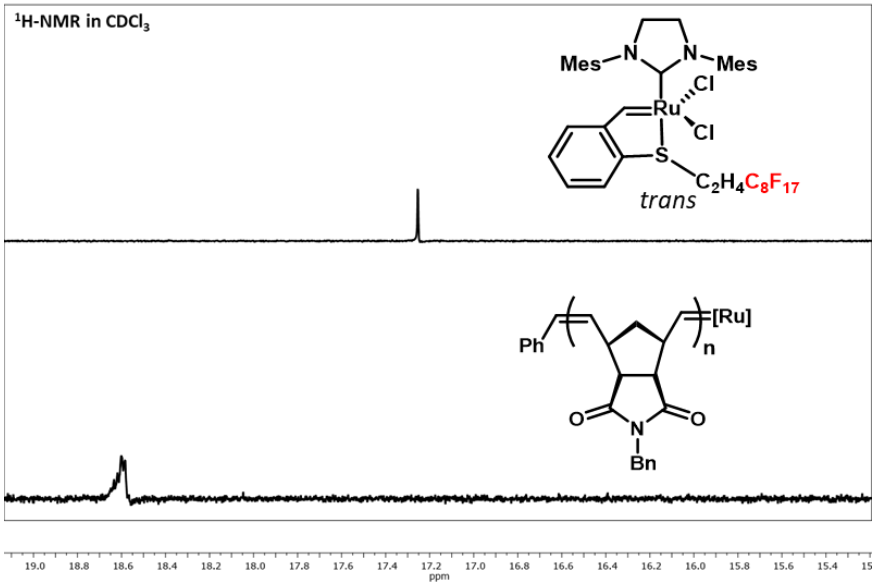
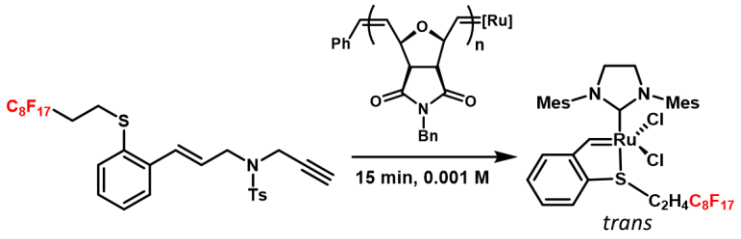


Figure S9. ^{1}H NMR analysis for the chain-end termination in polymerization of **M2**.



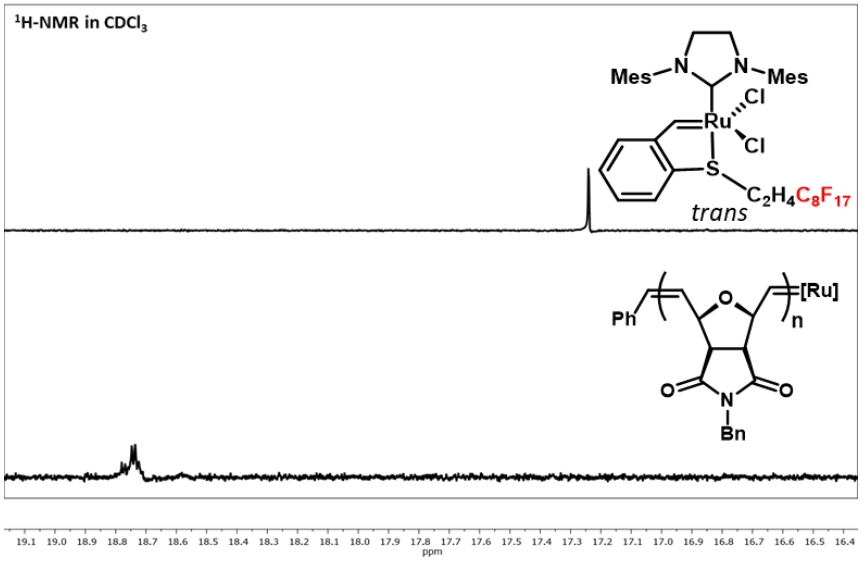
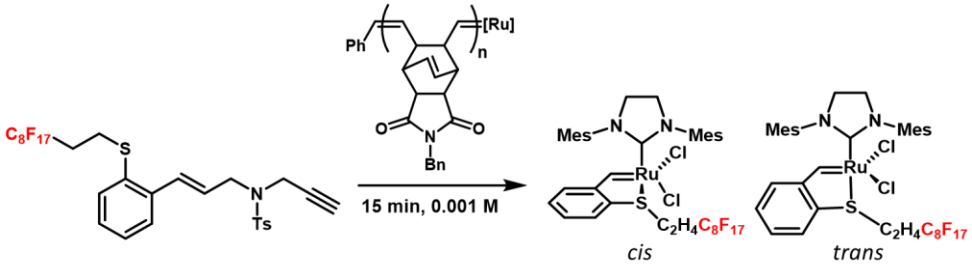


Figure S10. ^{1}H NMR analysis for the chain-end termination in polymerization of **M4**.



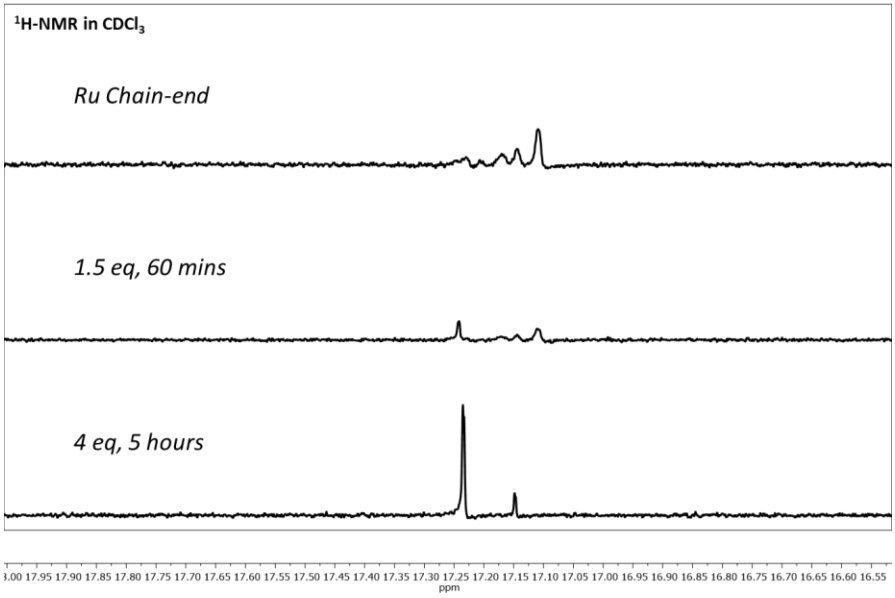


Figure S11. ^{1}H NMR analysis for the chain-end termination in polymerization of **M5**.

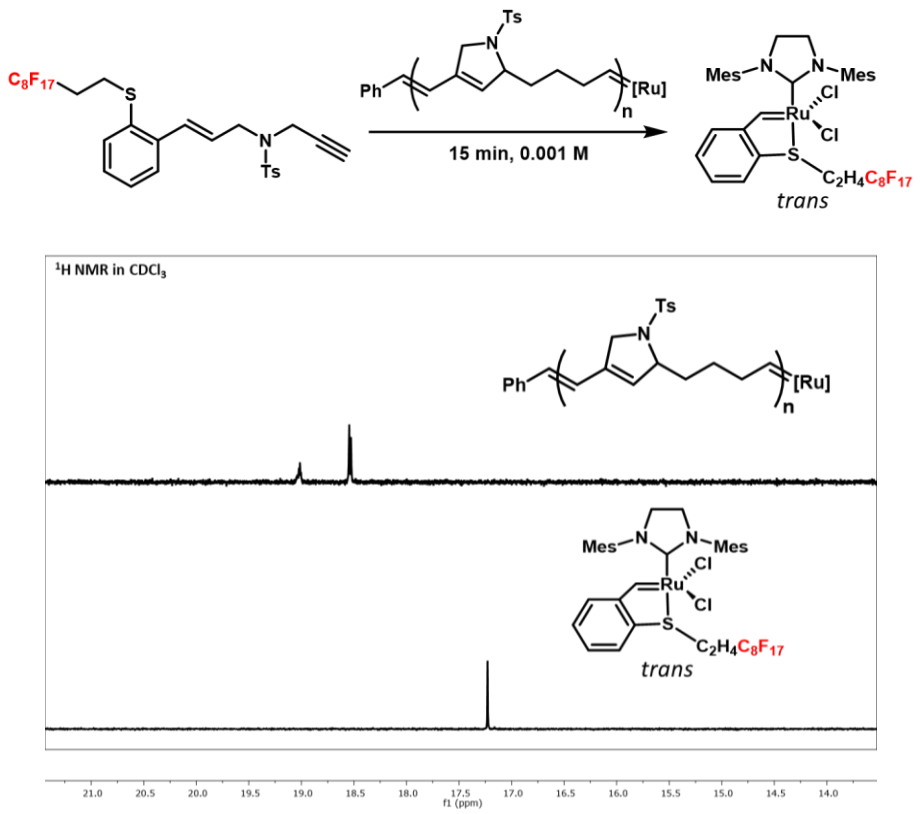


Figure S12. ^{1}H NMR analysis for the chain-end termination in polymerization of **M6**.

Ruthenium removal protocols and analysis of ruthenium content of polymer samples

MeOH wash: After termination via addition of desired amount of EVE or $\mathbf{F}_{enyne}$, 15-fold volume of methanol was added into the mixture, followed by stirring for 5 minutes. After centrifugation at 4300 rpm for 20 minutes, the solvent was decanted, and polymers were collected. Obtained polymer parts were dried under vacuum for analysis using GPC, NMR, and ICP-MS.

Fluorous Solid-phase Extraction (**F-SPE**): Following termination via addition of desired amount of $\mathbf{F}_{enyne}$, the solvent of mixture was evaporated. Then, the desired amount of DCM was added, and the mixture was loaded onto the pre-activated fluorous cartridge, followed by elution using DCM/DMSO (v/v=3/7). Obtained polymer parts were dried under vacuum for analysis using GPC, NMR, and ICP-MS.

Digestion method for ICP-MS: Samples ranging in mass from 10 to 15 mg were digested in Parr instrument A280AC vessels placed in a heat oven (Fisherbrand™ 180L Gravity Oven) with 4 mL of 65% HNO_3 (Suprapur™, MilliporeSigma™) and 0.15 mL of 70% $HClO_4$ (99.999% trace metals basis, Sigma-Aldrich). Samples were pre-digested before heat by aging the sample mixed with acids for 16 h at room temperature. Then, the oven system was set at 130 °C for 8 hours. Final digests were diluted with deionized water to 10 ml stock solution in volumetric flasks and measured within 24 h.

ICP-MS: Calibration curve was obtained by measuring a series of standard solutions with concentrations ranging from 0.001 mg/L to 0.200 mg/L (prepared by diluting a standard solution containing 10 mg/L of ruthenium in a matrix of 10% HCl and 1% HNO_3, PerkinElmer TruQms). The measurement was obtained as a count of ions with mass-to-charge ratio of 102. The apparatus was purged with 1% HNO_3 for 90 s after each sample and the signal from each sample was allowed to stabilize for 30 s before each measurement. Three measurements were obtained for each sample and averaged. The limit of quantification calculated from obtained results for blank solutions was 0.03 ppm.

Table S2. Ruthenium residue content of polymers (P1 – P6, $P1_F$ – $P6_F$).

Entry[a]	Monomer	[M] (mol/L)	Solvent	DP	Teminator	Method[b]	Ru level[c] (ppm)	Ru Removal (%)
1	**M1**	1	DCM	30	EVE	MeOH	634±8	98.40
2	**M1**	1	DCM	30	F_{enyne}	MeOH	182±3	99.54
3	**M1**	1	DCM	30	F_{enyne}	CF_3-OH	132±7	99.67
4	**M1**	1	DCM	30	F_{enyne}	F-SPE	14±3	99.96
5	**M2**	0.2	DCM	30	EVE	MeOH	506±9	97.70
6	**M2**	0.2	DCM	30	F_{enyne}	MeOH	179±4	99.19
7	**M2**	0.2	DCM	30	F_{enyne}	F-SPE	70±4	99.68
8	**M2**	0.2	DCM	60	F_{enyne}	MeOH	98±3	99.12
9	**M2**	0.2	DCM	60	F_{enyne}	F-SPE	36±4	99.67
10	**M2**	0.2	DCM	100	F_{enyne}	F-SPE	16±4	99.76
11	**M2**	0.2	DCM	500	F_{enyne}	F-SPE	4±1	99.89
12	**M3**	0.2	DCM	30	EVE	MeOH	508±14	97.69
13	**M3**	0.2	DCM	30	F_{enyne}	MeOH	180±5	99.18
14	**M3**	0.2	DCM	30	F_{enyne}	F-SPE	75±3	99.66
15	**M4**	0.2	DCM	30	EVE	MeOH	802±14	96.33

16	**M4**	0.2	DCM	30	F_{enyne}	MeOH	687±24	96.85
17	**M4**	0.2	DCM	30	F_{enyne}	F-SPE	544±16	97.51
18	**M5**	0.2	DCM	30	EVE	MeOH	686±8	96.42
19[d]	**M5**	0.2	DCM	30	F_{enyne}	MeOH	254±5	98.67
20[d]	**M5**	0.2	DCM	30	F_{enyne}	F-SPE	59±4	99.69
21	**M6**	0.2	THF	30	EVE	MeOH	633±19	96.72
22	**M6**	0.2	THF	30	F_{enyne}	MeOH	385±8	98.01
23	**M6**	0.2	THF	30	F_{enyne}	F-SPE	167±5	99.13
24	**M2**	0.2	THF	30	F_{enyne}	MeOH	179±7	99.19
25	**M2**	0.2	THF	30	F_{enyne}	F-SPE	72±2	99.67
26	**M2**	0.2	EtOAc	30	F_{enyne}	MeOH	21783±211	1.03
27	**M2**	0.2	Tol	30	F_{enyne}	MeOH	21685±198	1.47

[a]Polymerization Condition: 3 μmol **G3** catalyst, termination using 0.2 ml **EVE** or 1.5 eq $\mathbf{F_{enyne}}$. [b]MeOH or CF3-OH: precipitation using 6 ml of MeOH or CF_3CH_2OH, F-SPE: Flourous Solid Phase Extraction. [c]Determined by ICP-MS, and results were obtained from 3 runs. [d]Termination using 5 eq $\mathbf{F_{enyne}}$.

Table S3. Ruthenium residue content of polymers ($P4_F$).

Entry[a]	Monomer	[M] (mol/L)	DP	Method[b]	Elution solvent[b]	Ru level[c] (ppm)
1	**M4**	0.2	30	MeOH	DCM/DMSO (v/v=3/7)	532±21
2	**M4**	0.2	30	MeOH	THF/DMSO (v/v=1/5)	574±27
3	**M4**	0.2	30	F-SPE	DCM/MeOH (v/v=1/1)	593±22

[a]Polymerization Condition: 3 μmol **G3** catalyst in DCM, termination using 1.5 eq $\mathbf{F_{enyne}}$. [b] MeOH: precipitation once using 6 mL methanol, F-SPE: Flourous Solid Phase Extraction, Elution solvent: hydrophobic solvent used for polymers purification. [c]Determined by ICP-MS, and results were obtained from 3 runs.

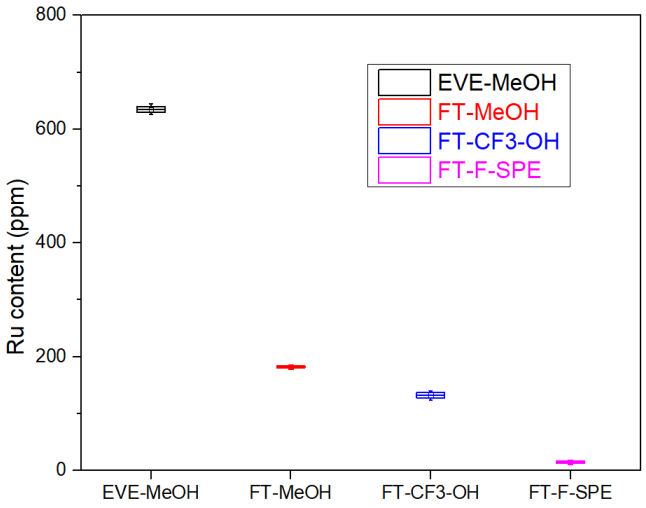


Figure S13. Residual Ruthenium content in **P1 and P1$_F$** purified by different methods.

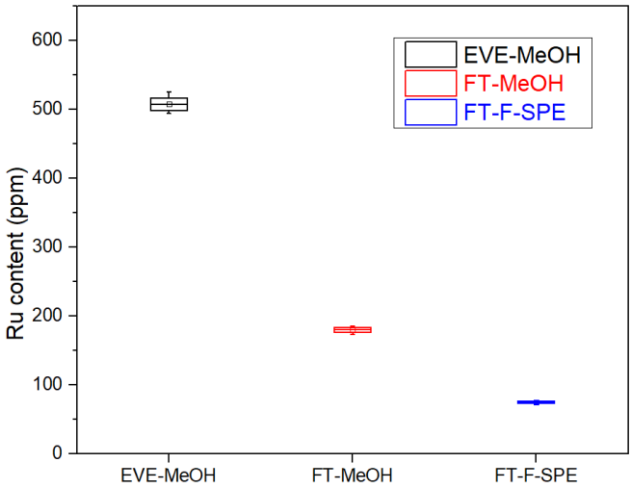


Figure S14. Residual Ruthenium content in **P3** and **P3$_F$** purified by different methods.

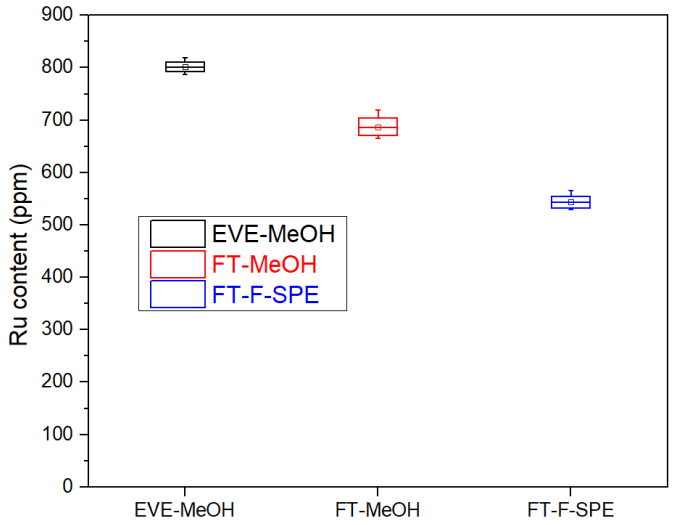


Figure S15. Residual Ruthenium content in **P4** and **P4$_F$** purified by different methods.

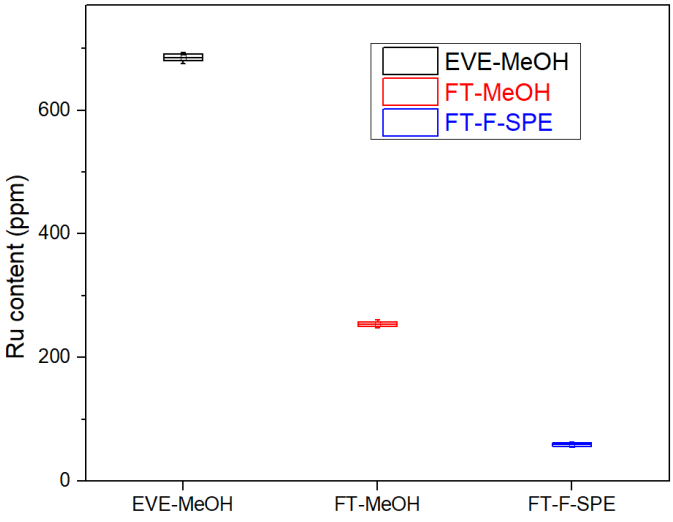


Figure S16. Residual Ruthenium content in **P5** and **P5$_F$** purified by different methods.

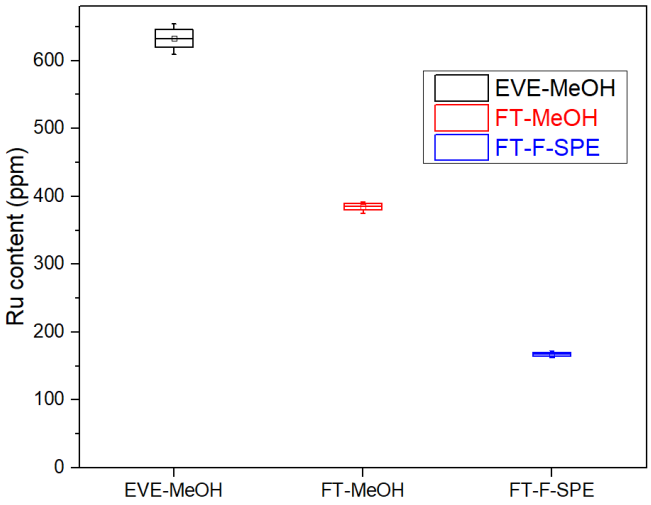


Figure S17. Residual Ruthenium content in **P6** and **P6$_F$** purified by different methods.

Table S4. Ruthenium residue content of polymers without purification.

Entry[a]	Monomer	[M] (mol/L)	DP	Ru level[b] (ppm)
1	**M1**	1	30	49741±531
2	**M2**	0.2	30	22009±241
3	**M2**	0.2	60	11077±135
4	**M2**	0.2	100	6664±100
5	**M2**	0.2	500	4005±74
6	**M3**	0.2	30	22046±211
7	**M4**	0.2	30	21842±198
8	**M5**	0.2	30	19168±173
9	**M6**	0.2	30	19296±187

[a]Polymerization Condition: 3 μmol **G3** catalyst in DCM or THF, termination using EVE. [b]Determined by ICP-MS, and results were obtained from 3 runs.

TGA of polymer samples ($P2_F$)

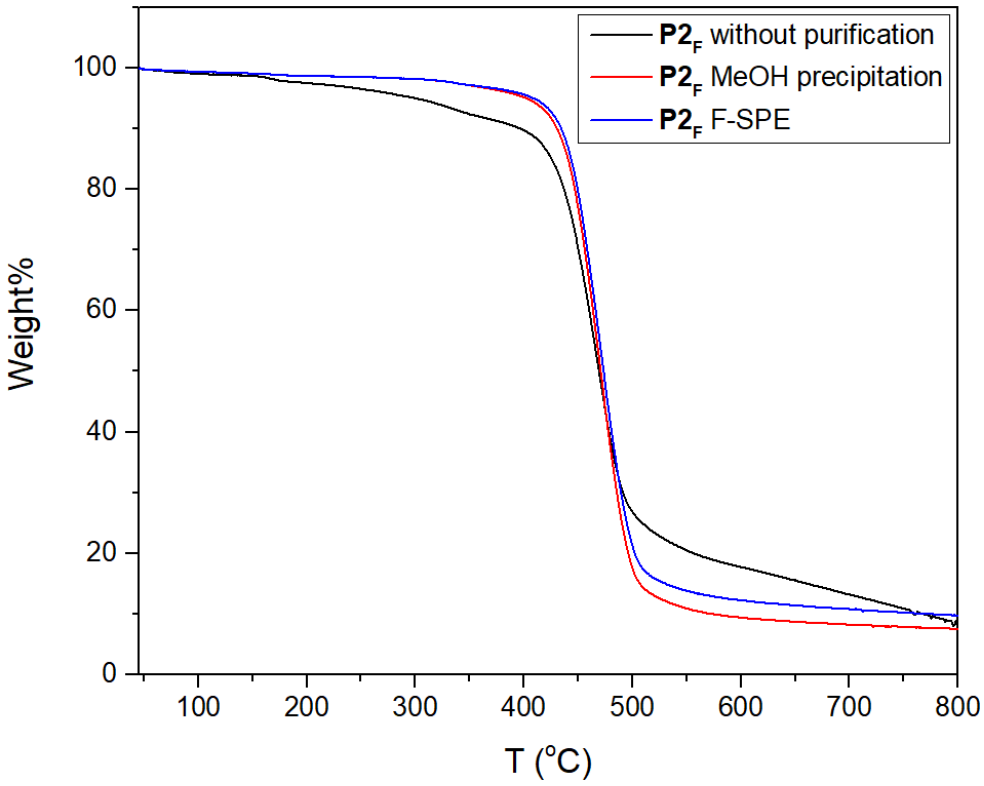


Figure S18. TGA curves of **$P2_F$** in N_2. For **$P2_F$** without purification, 92% loss at 300 °C, for **$P2_F$** with methanol precipitation, 92% at 403 °C, and for **$P2_F$** with F-SPE, 88% loss at 410 °C in the N_2.

Stability Test of Ru-S and Ru Fischer Carbene

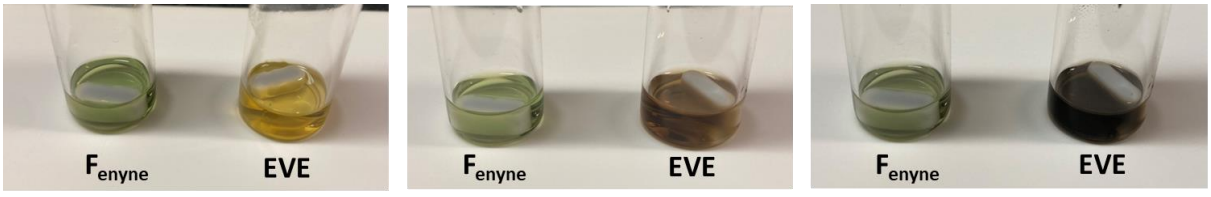
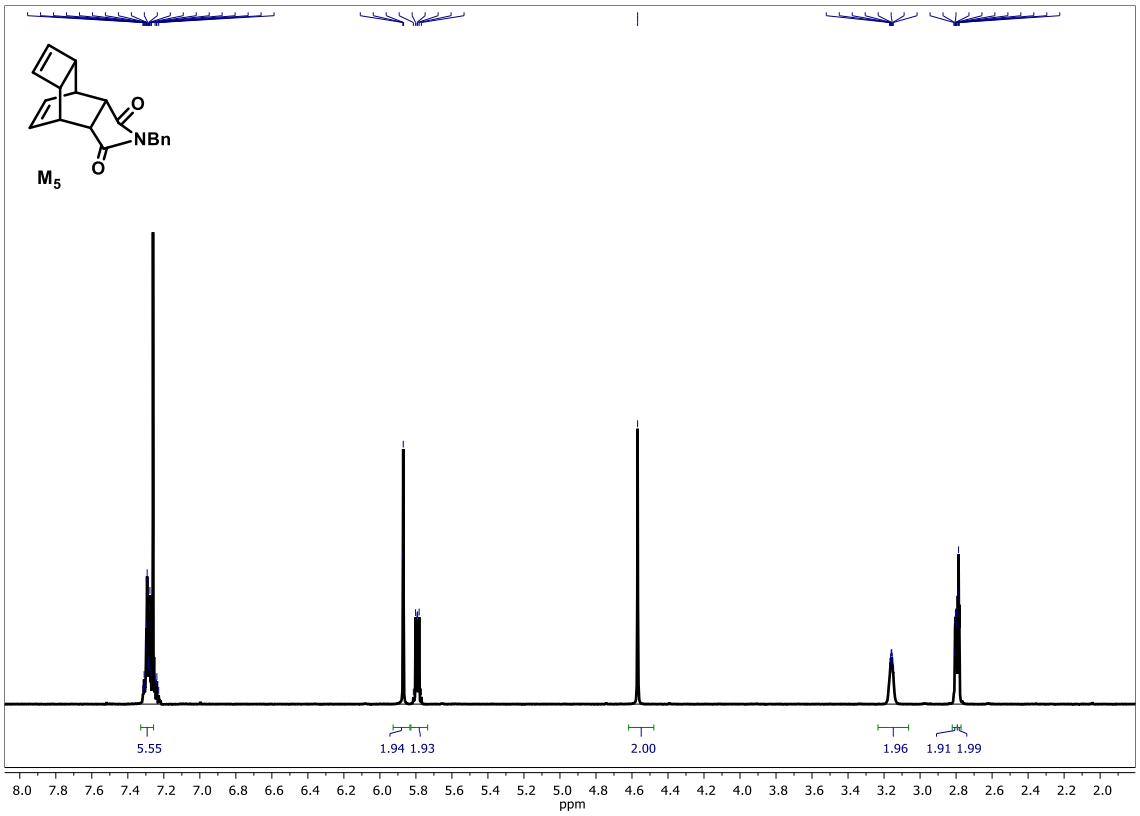
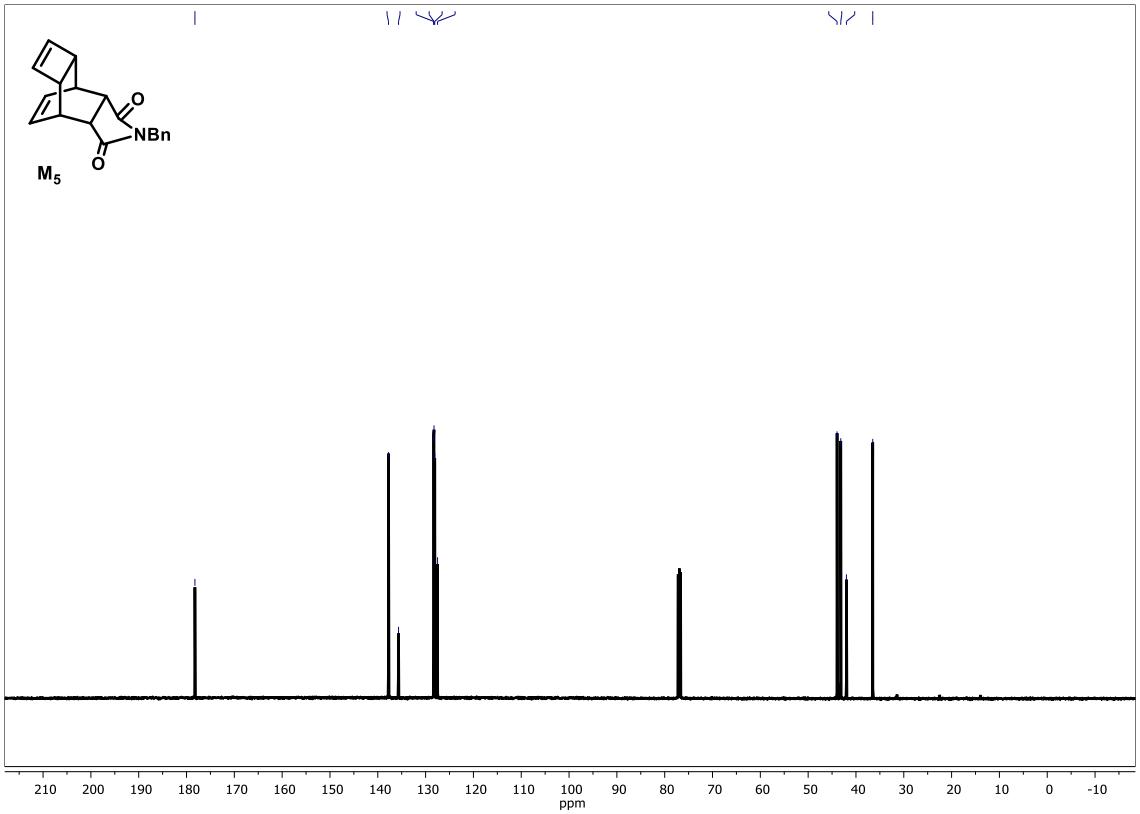
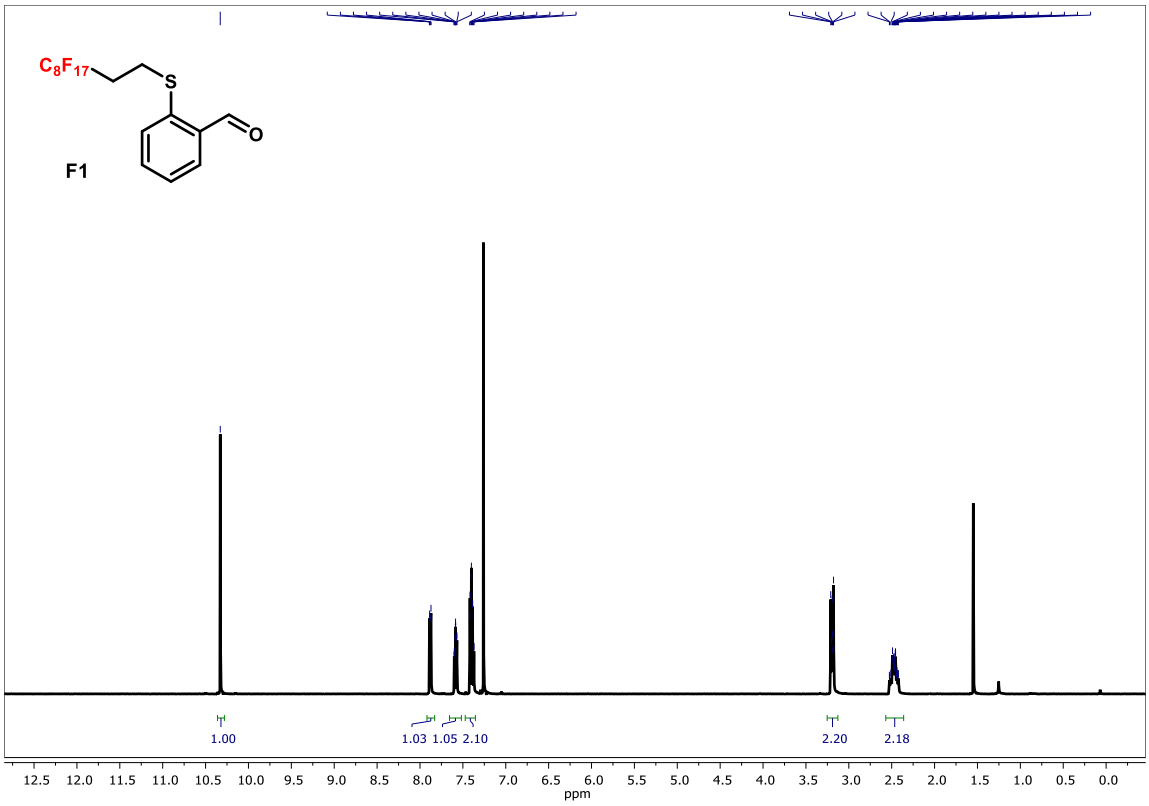


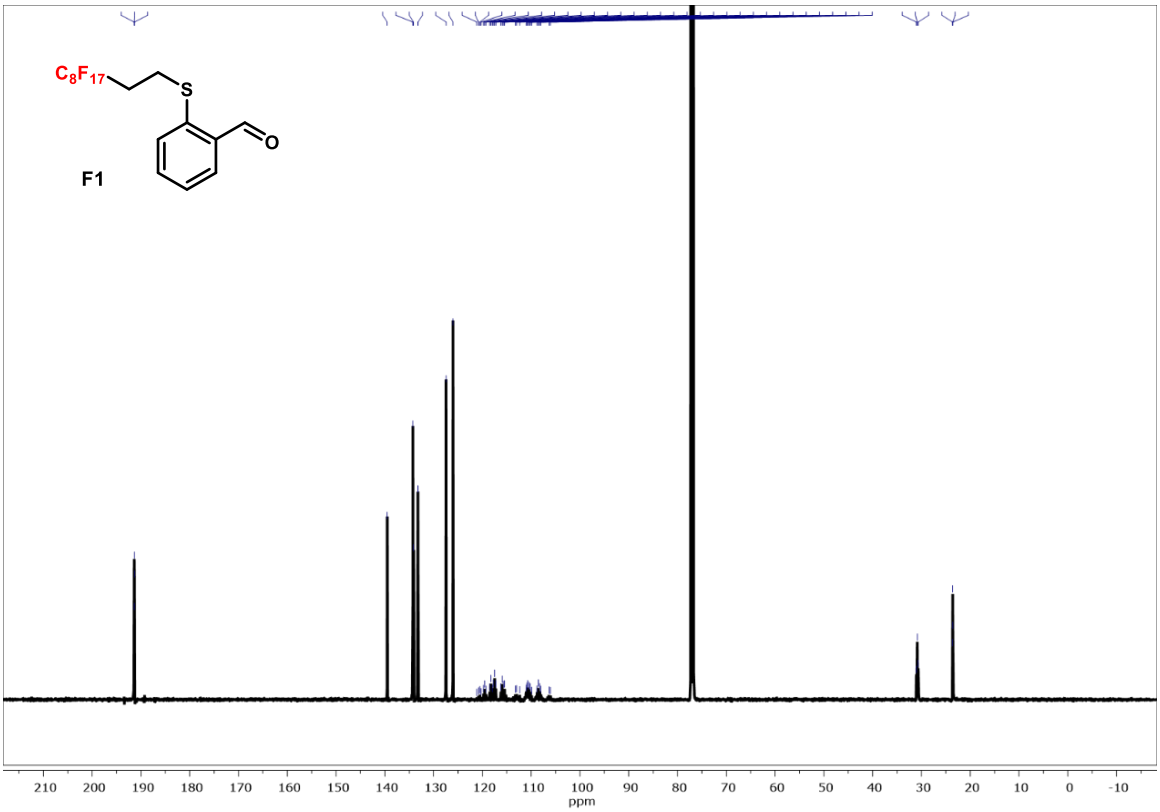
Figure S19. Stability test of formed Ru complexes after termination using EVE or F_{enyne}. **Ru-S** could be stable in the air after 24 hours, and Ru Fischer carbene decomposed fast in the air.

^{1}H and ^{13}C NMR Spectra






C8F17
S
O
F1
1.00
1.03 1.05 2.10
2.20
2.18
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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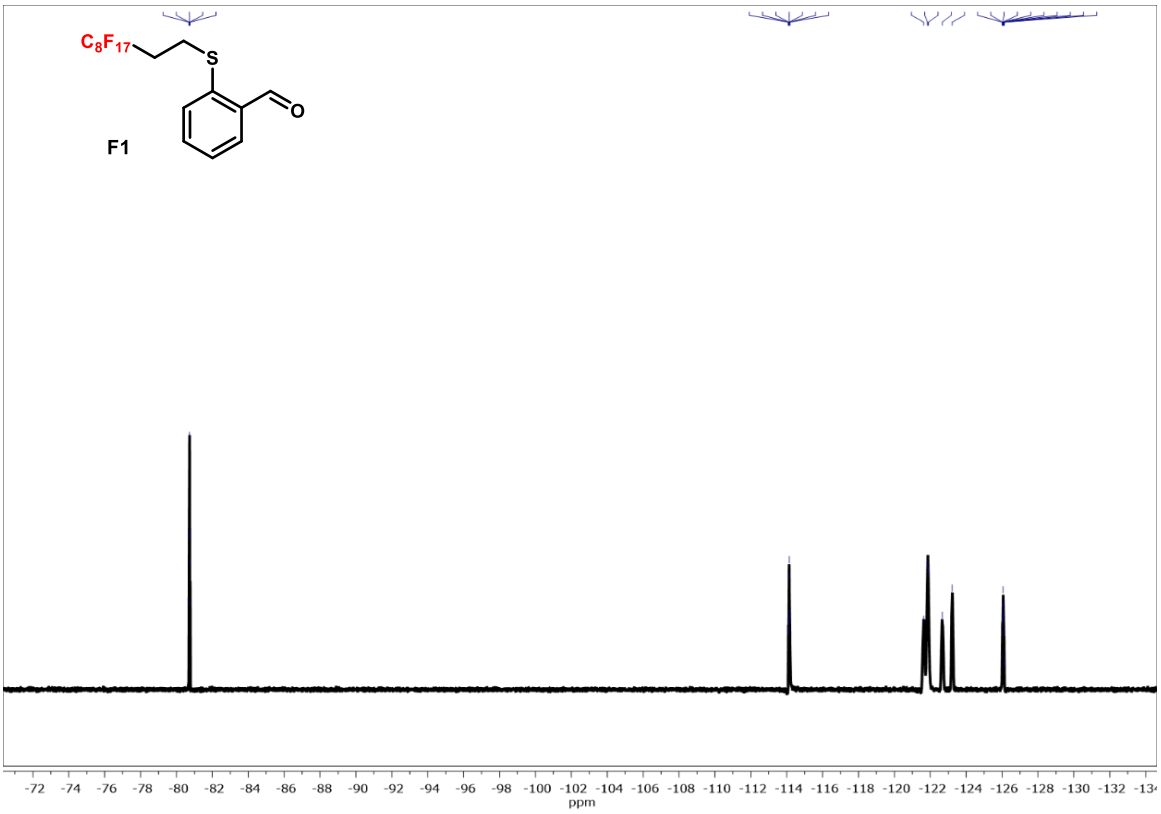
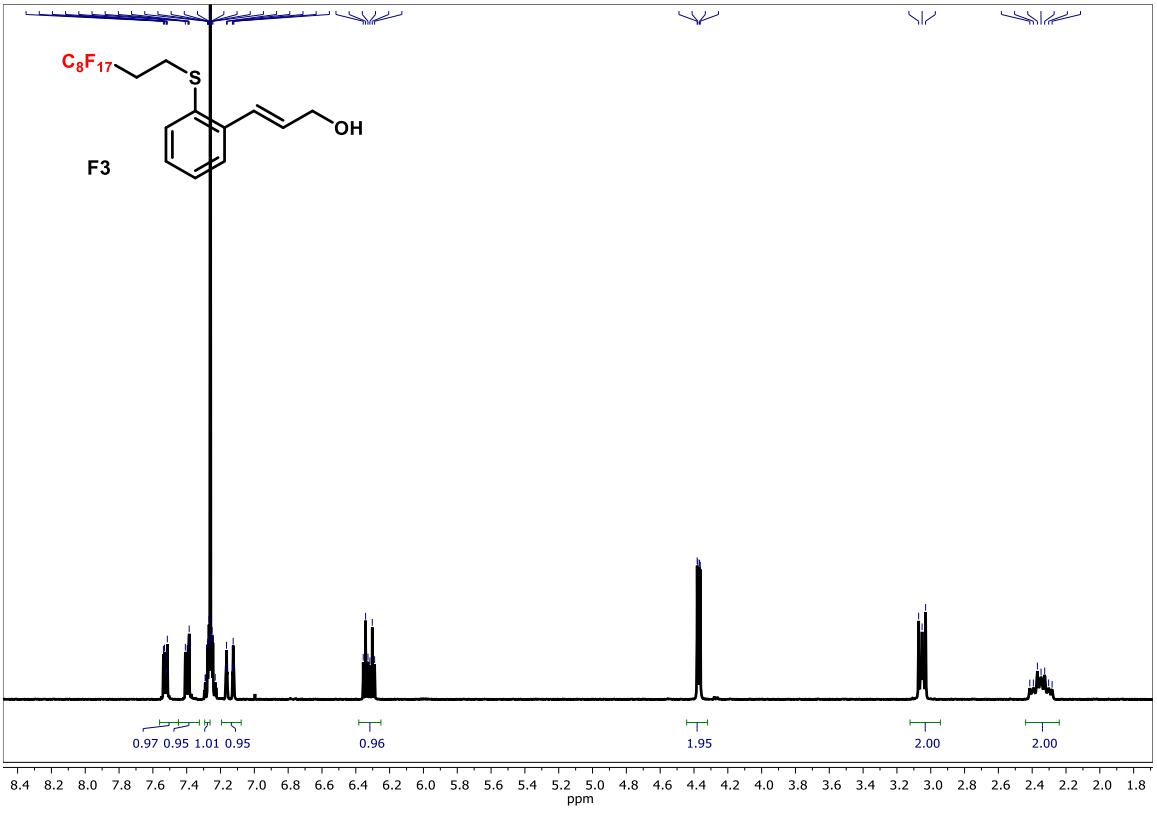
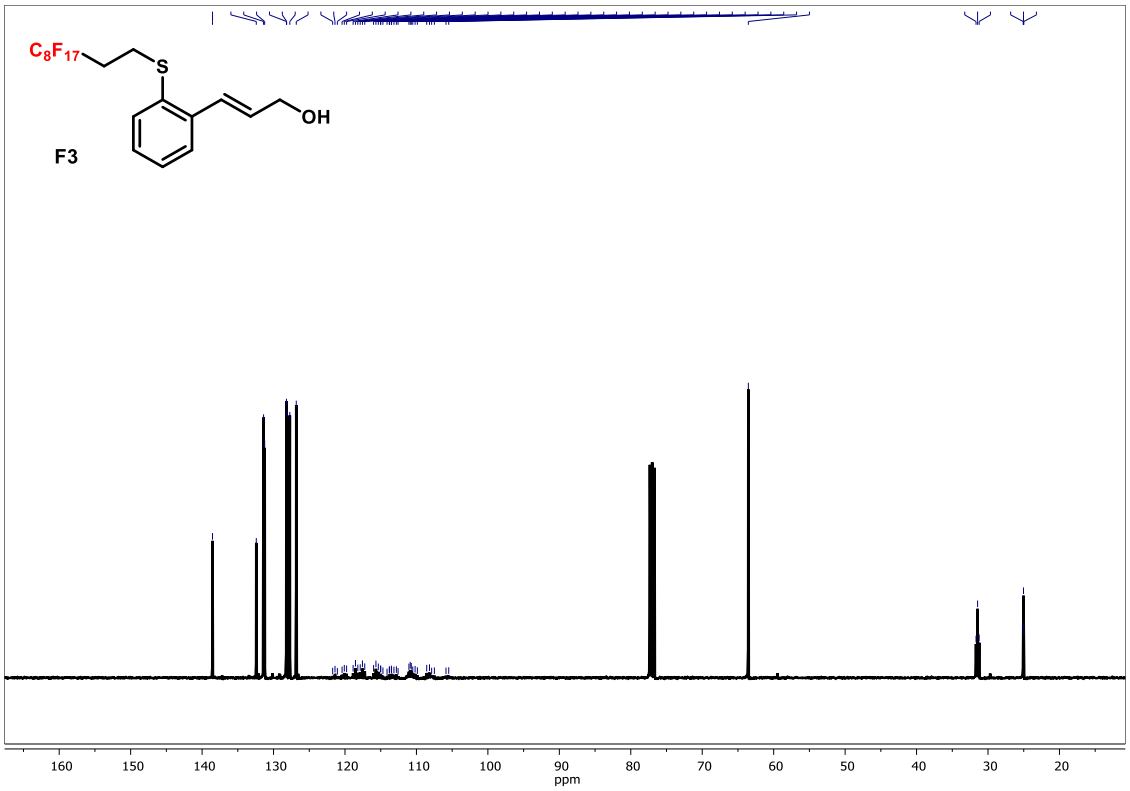
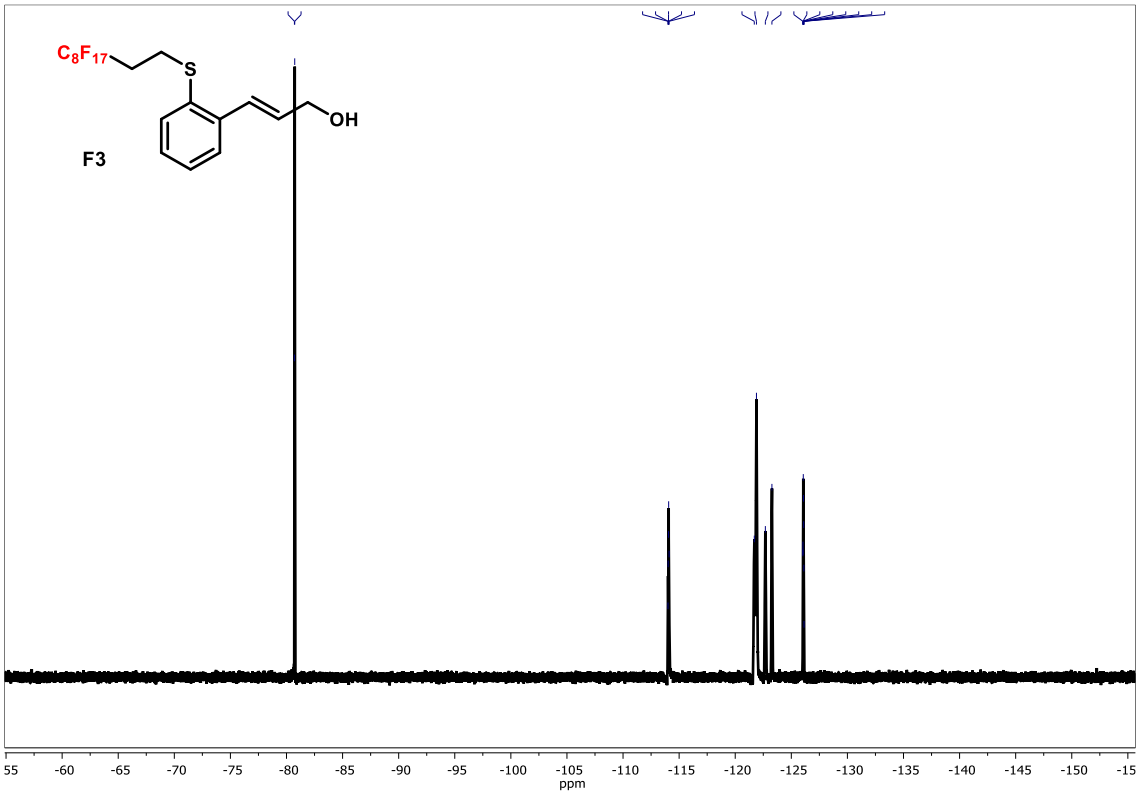
S
O
F1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


C8F17
S
O
F1
-72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132
ppm


C8F17
S
OH
F3
0.97 0.95 1.01 0.95
0.96
1.95
2.00
2.00
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
ppm


C8F17
S
OH
F3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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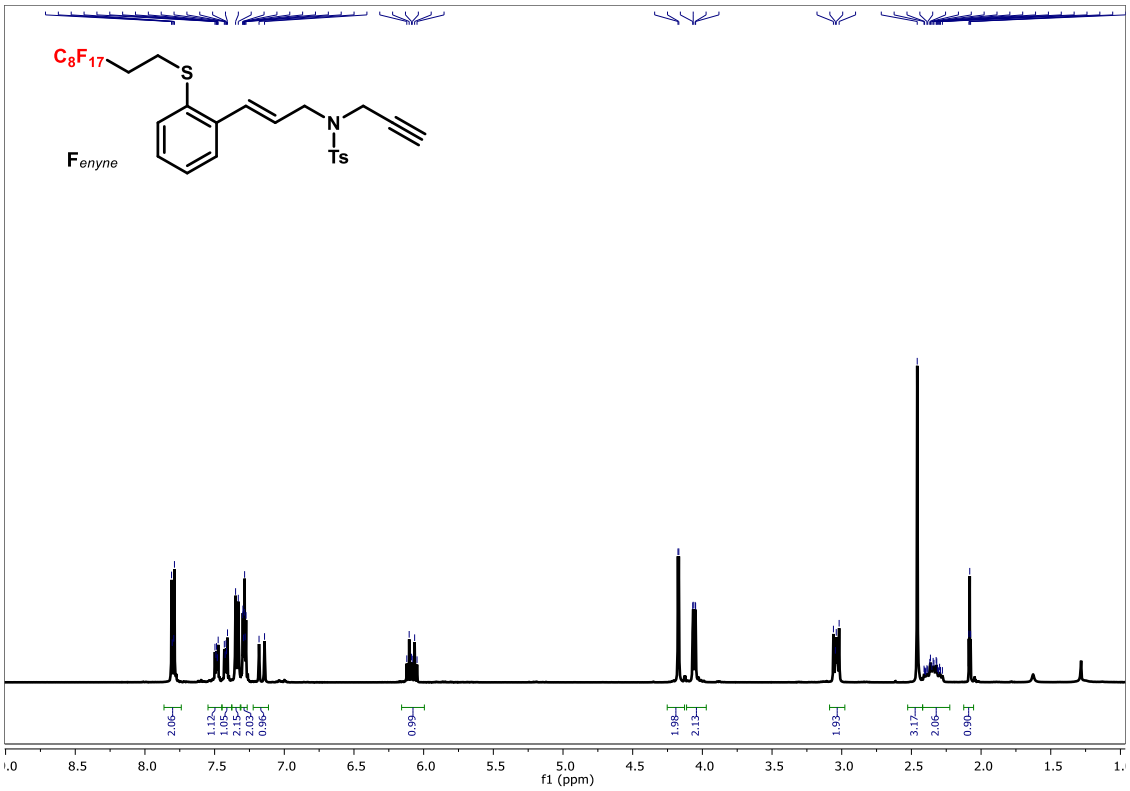
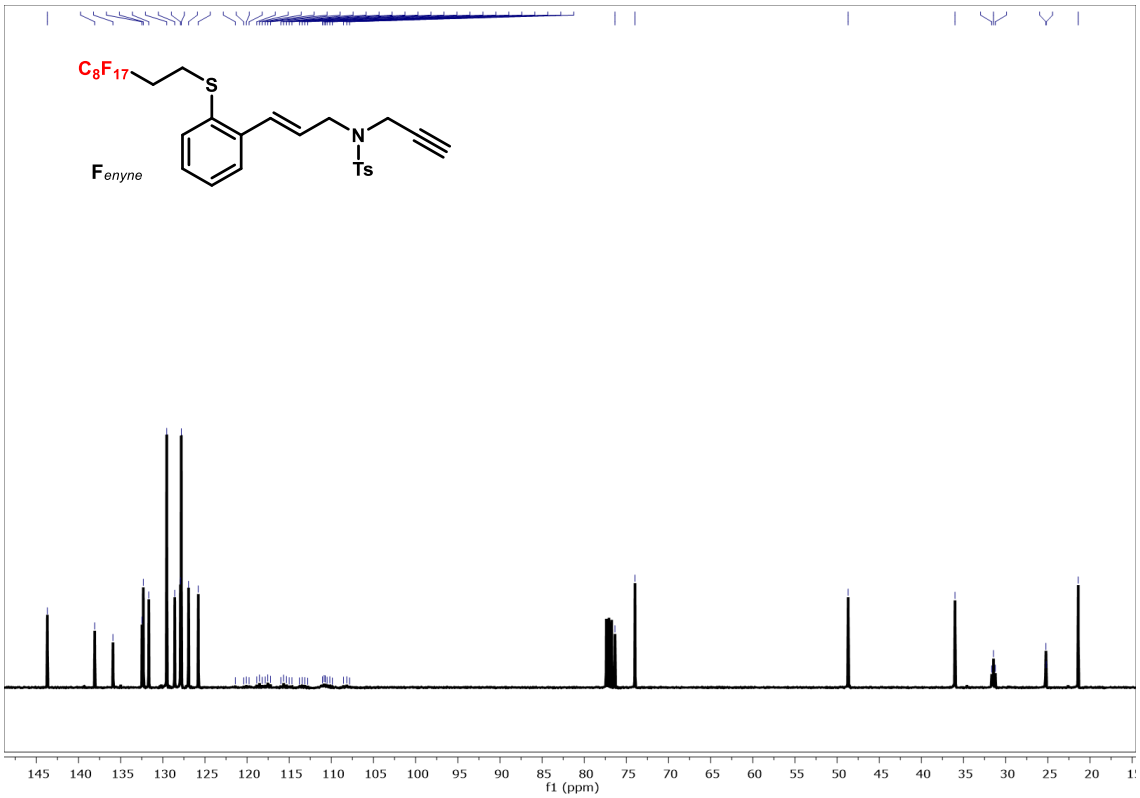
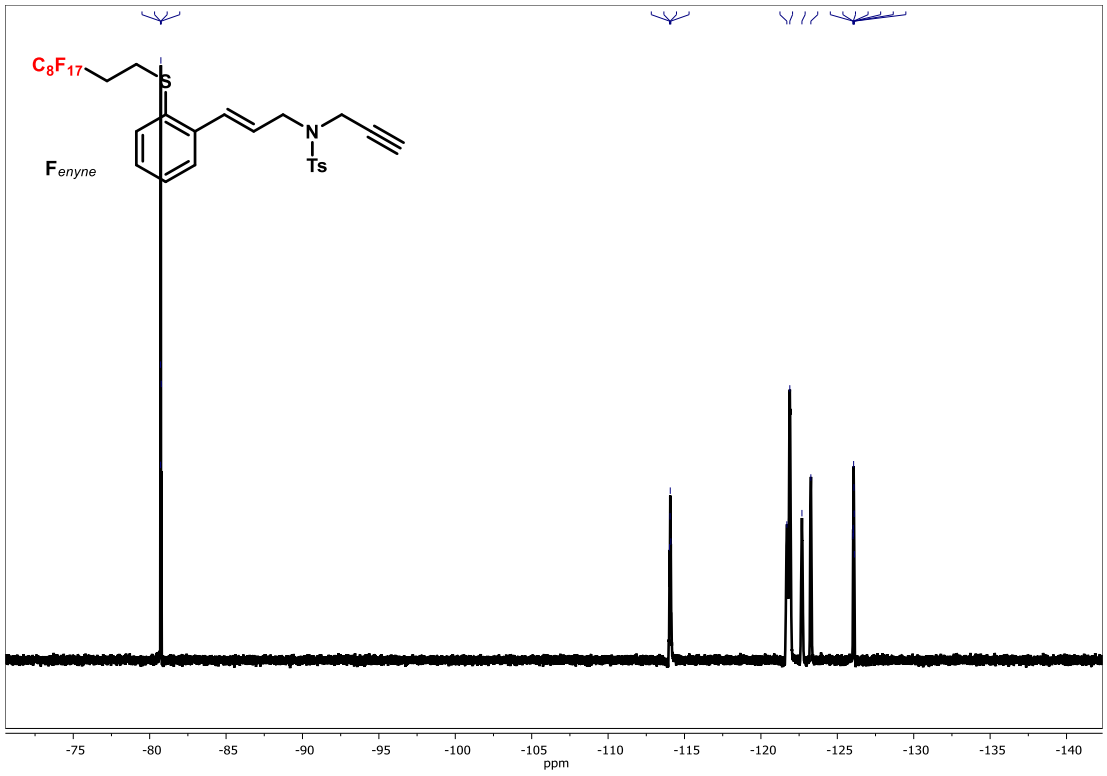
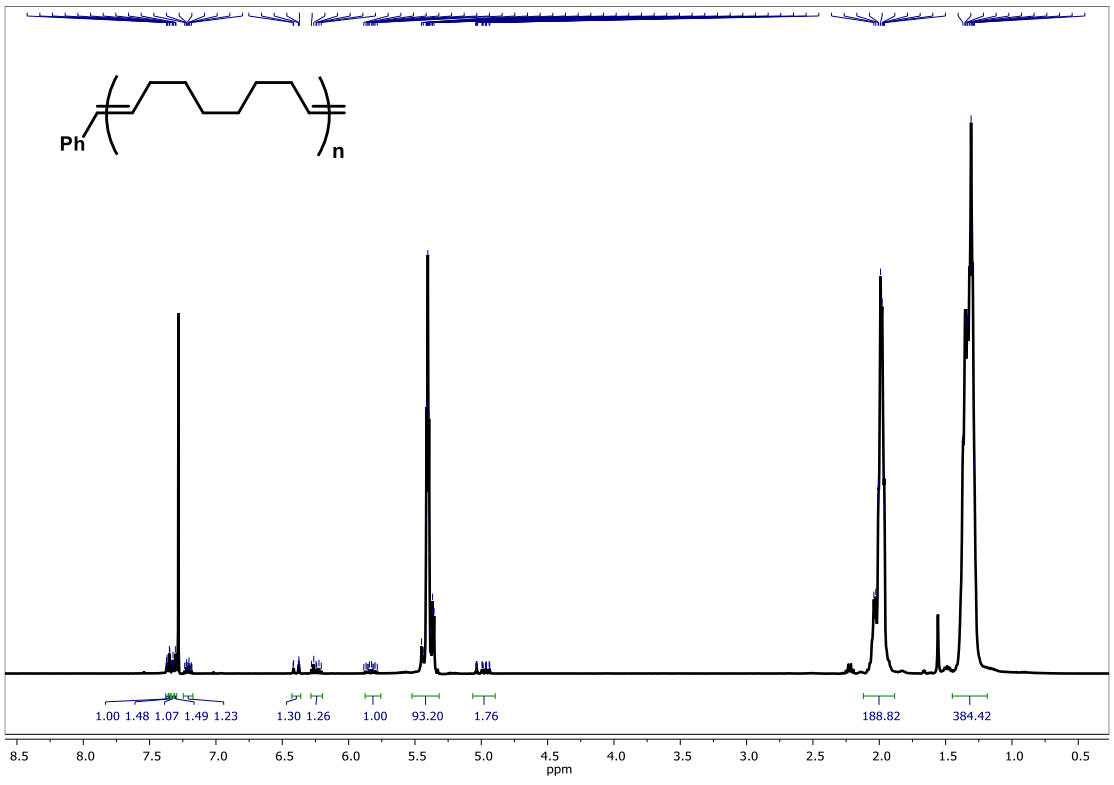
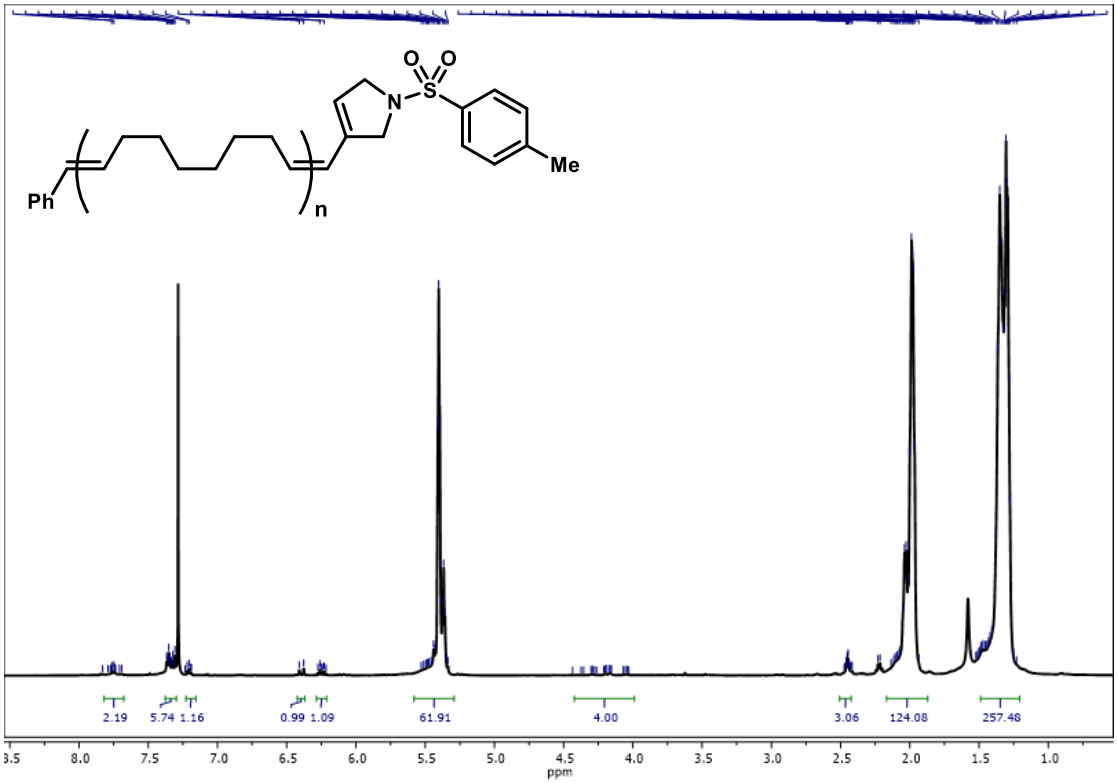
S
OH
F3
55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-15
ppm


C8F17
S
N
Ts
Fenyne
2.06
1.12
1.05
2.15
2.03
0.96
0.99
1.98
2.13
1.93
3.17
2.06
0.90
f1 (ppm)


C8F17
S
N
Ts
Fenyne
f1 (ppm)


C8F17
S
N
Ts
Fenyne
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
ppm


Ph
n
1.00 1.48 1.07 1.49 1.23
1.30 1.26
1.00
93.20
1.76
188.82
384.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


O
O
S
N
Me
Ph
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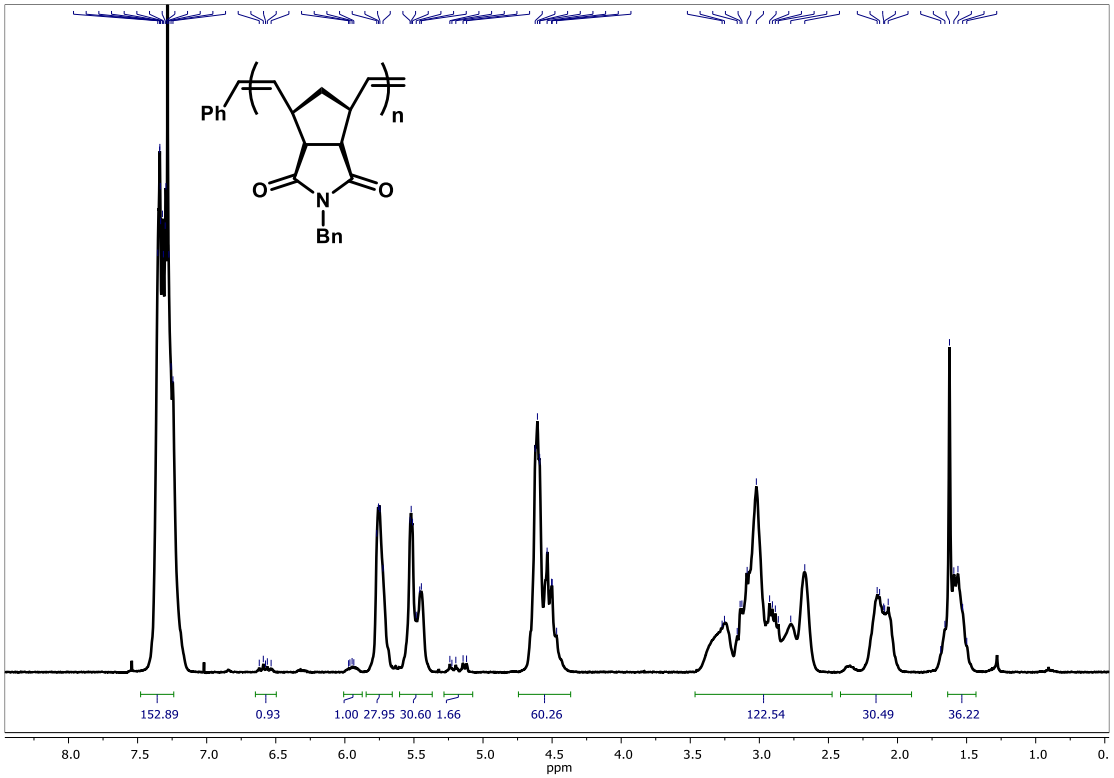
61.91
4.00
3.06
124.08
257.48
ppm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O
O
N
Bn
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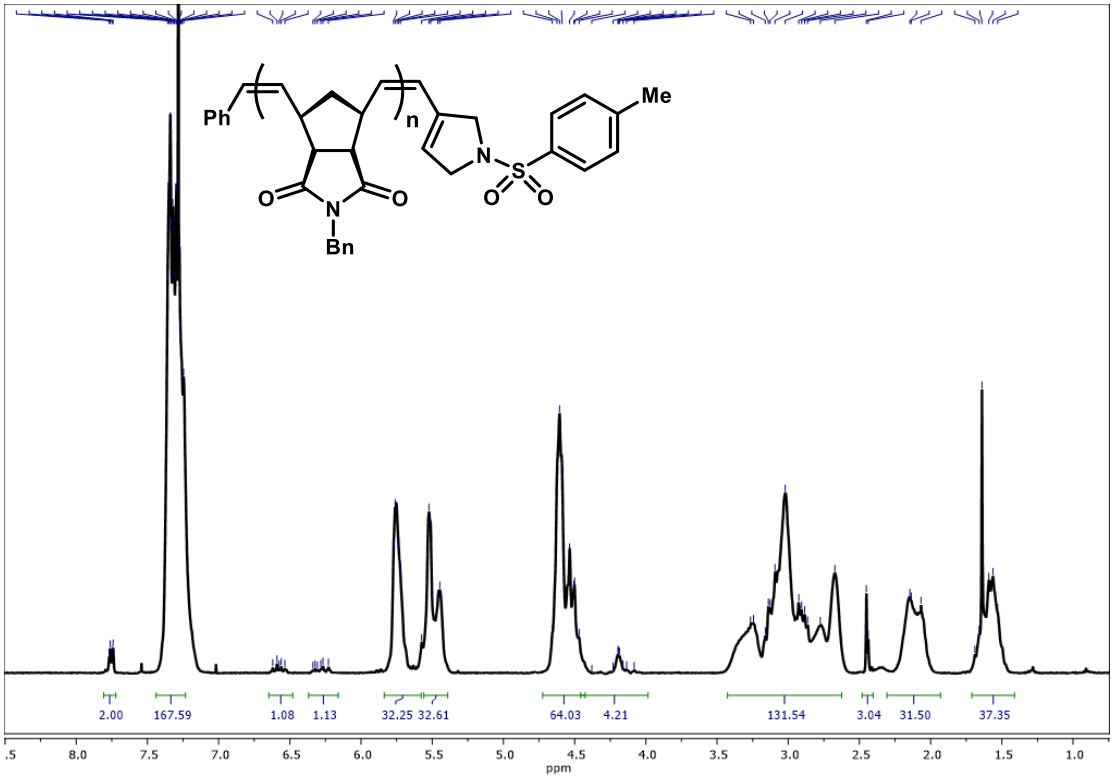
60.26
122.54
30.49
36.22
ppm


Ph
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Me
N
S
O
O
O
N
O
Bn
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1.13
32.25
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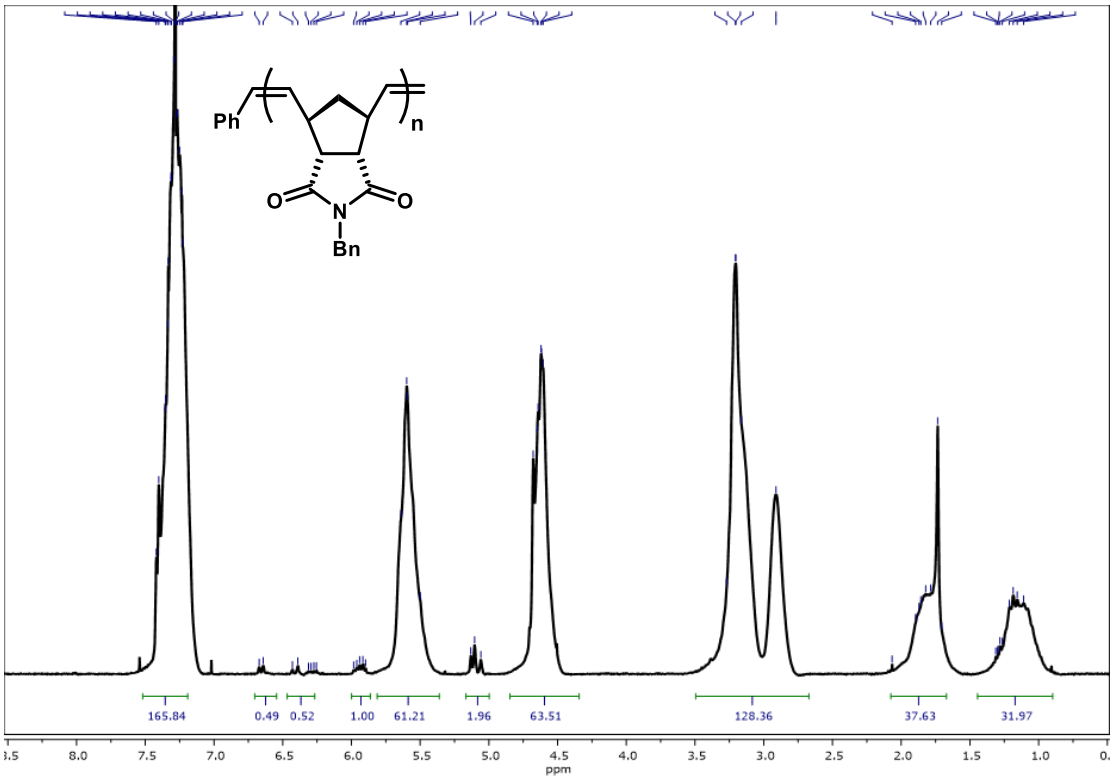
131.54
3.04
31.50
37.35
ppm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N
O
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63.51
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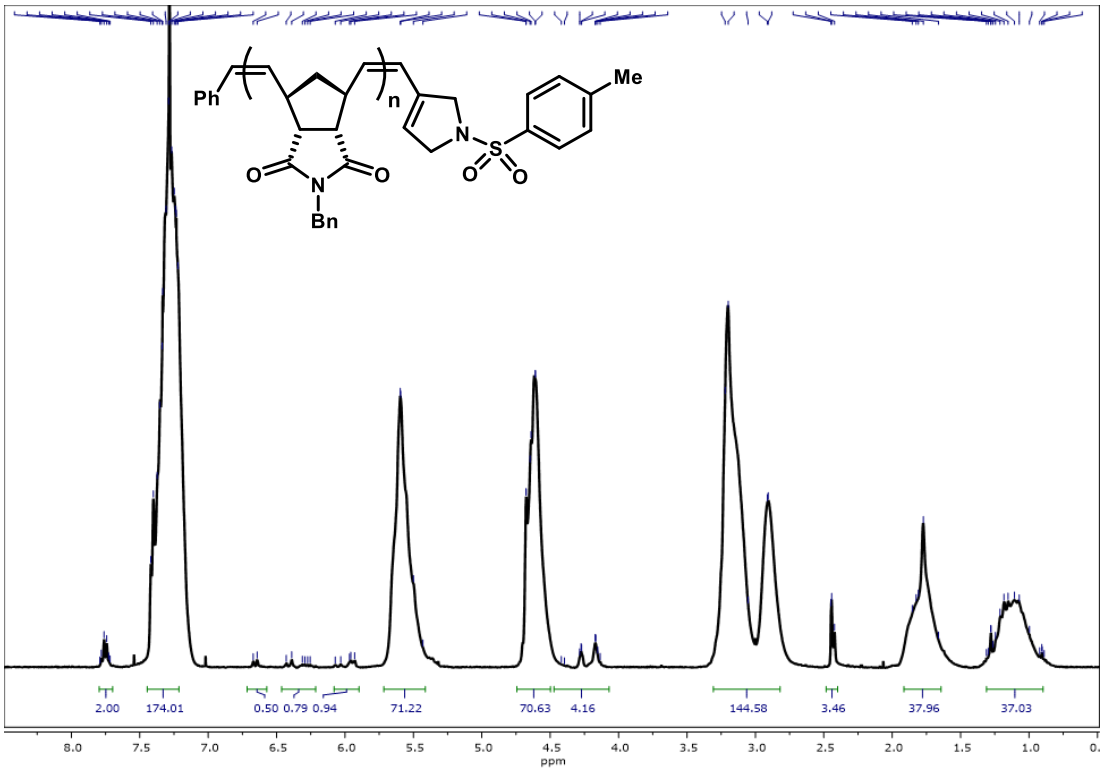
37.63
31.97
ppm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Me
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S
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O
O
O
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71.22
70.63
4.16
144.58
3.46
37.96
37.03
8.0
7.5
7.0
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6.0
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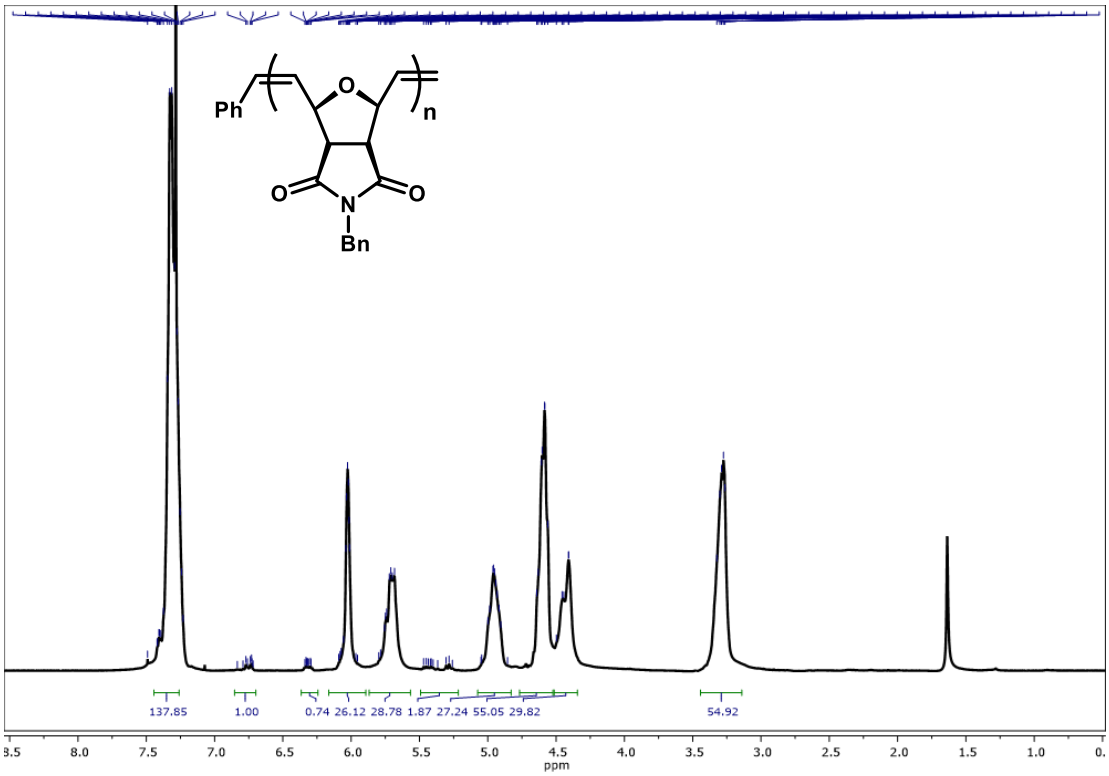
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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O
O
N
Bn
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54.92
8.5
8.0
7.5
7.0
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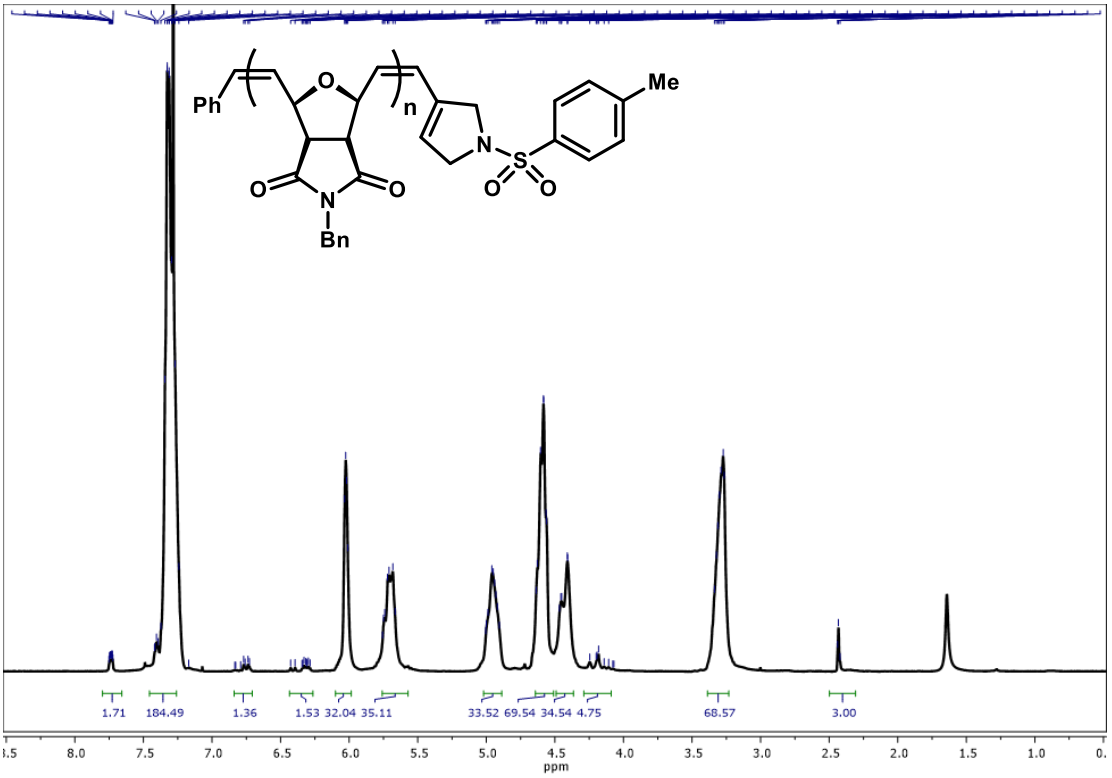
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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n
Me
N
S
O
O
O
N
O
Bn
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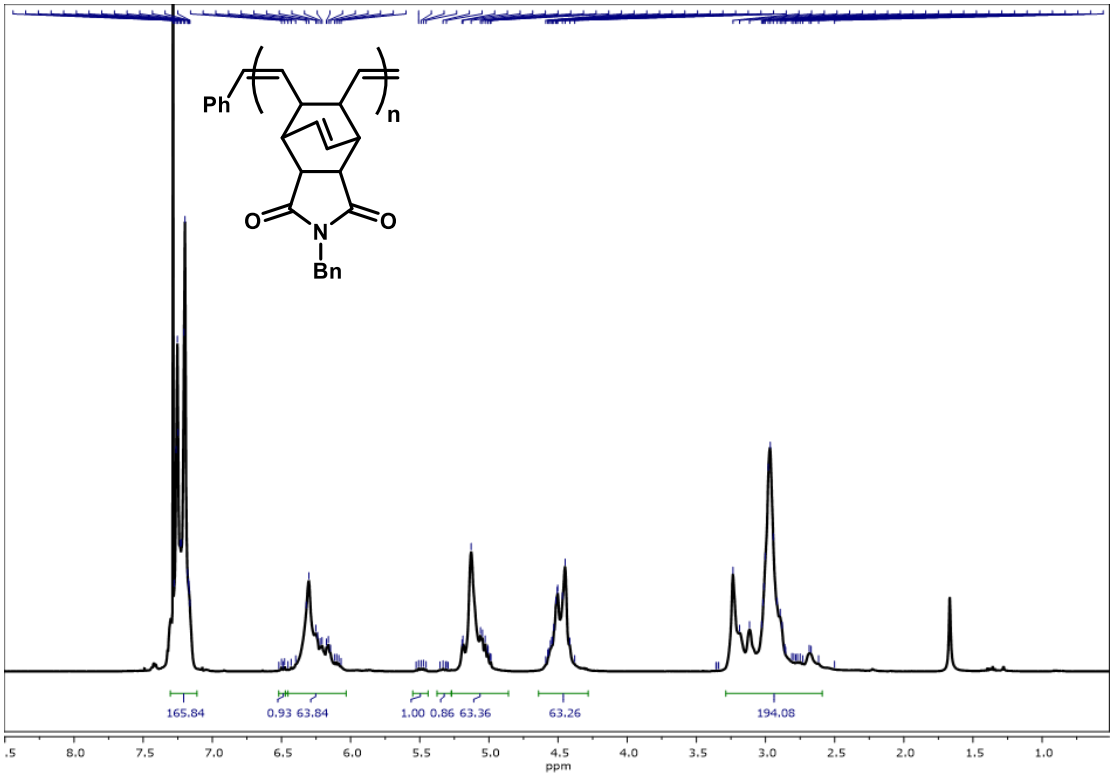
1.36
1.53
32.04
35.11
33.52
69.54
34.54
4.75
68.57
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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O
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Bn
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8.0
7.5
7.0
6.5
6.0
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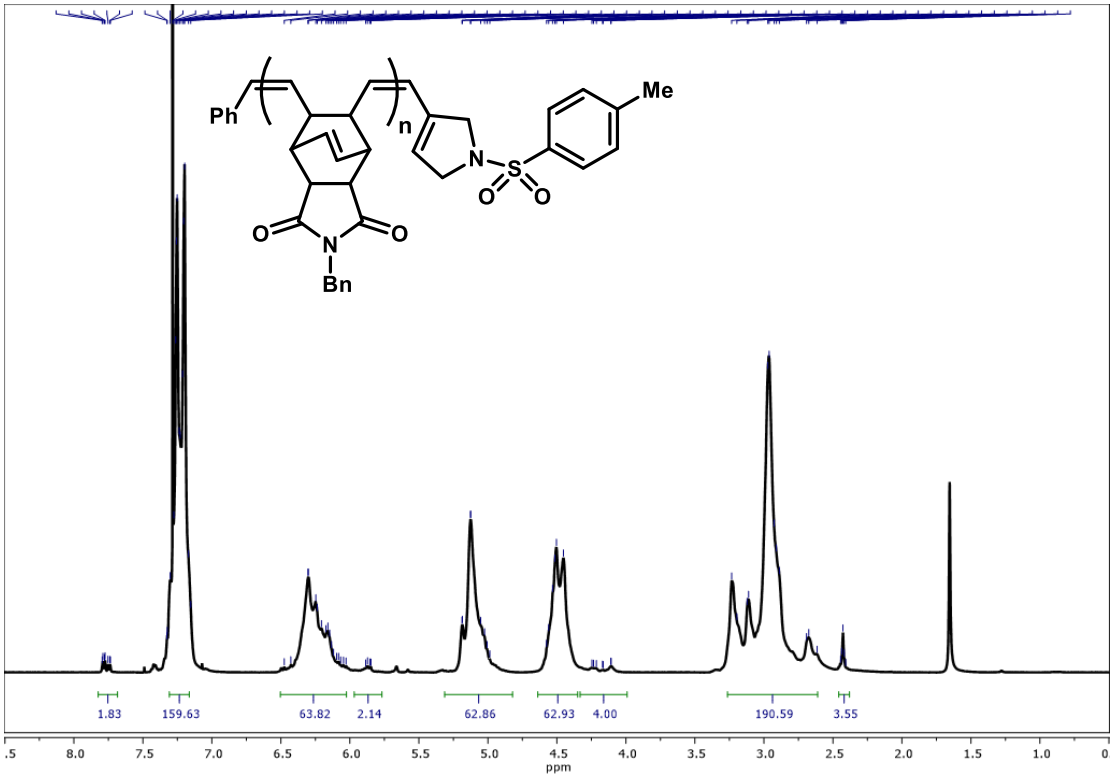
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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Me
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S
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Bn
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62.93
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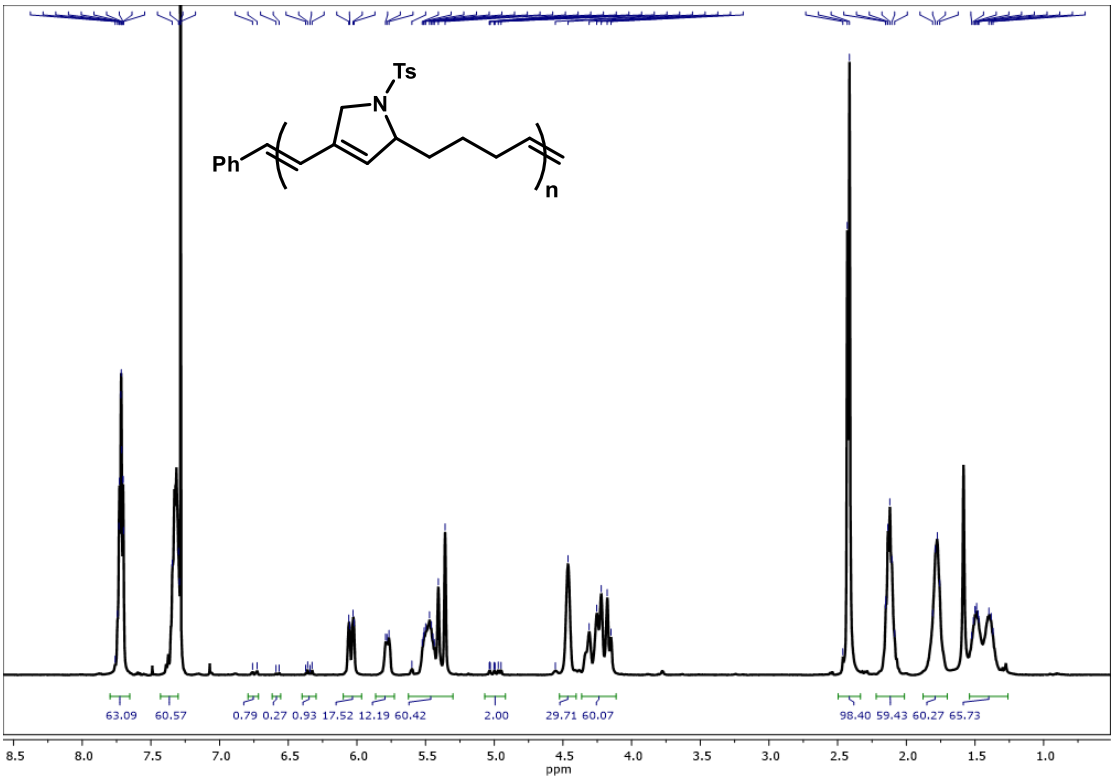
190.59
3.55
ppm


Ts
N
Ph
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2.00
29.71
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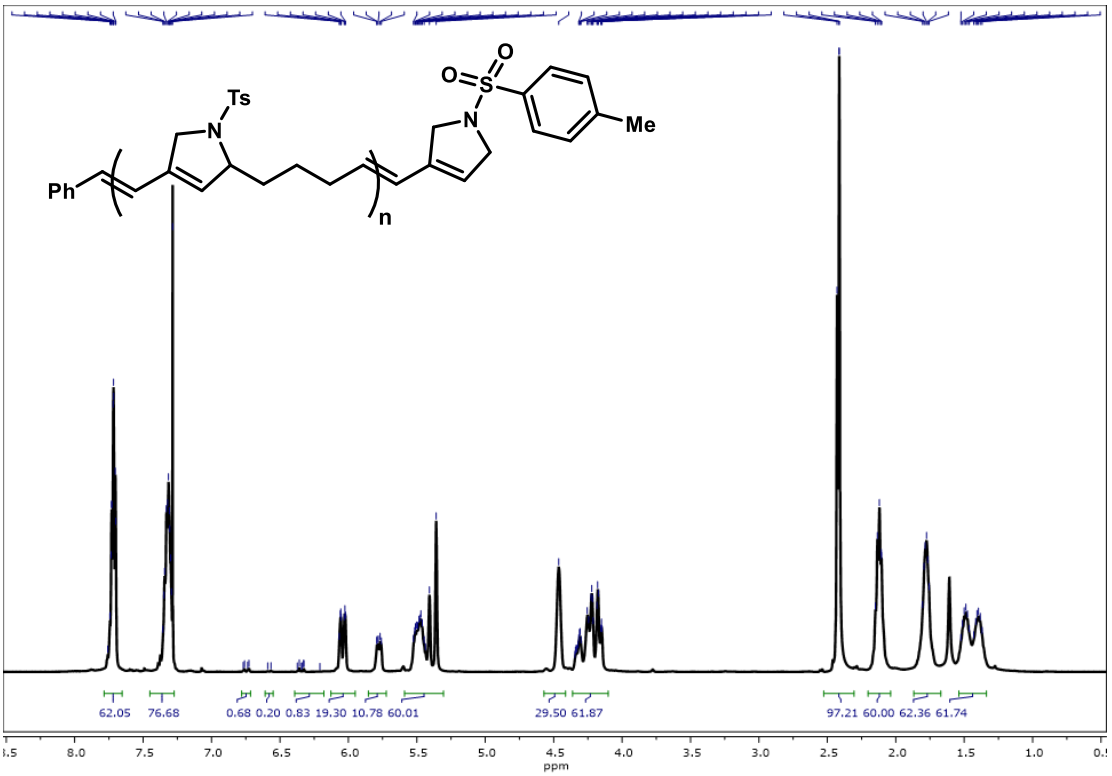
60.27
65.73
ppm



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