

Catalyst-Dependent Routes to Alternating Ring-Opening Metathesis Copolymers of Substituted Oxanorbornenes and Cyclooctene

Supporting Information

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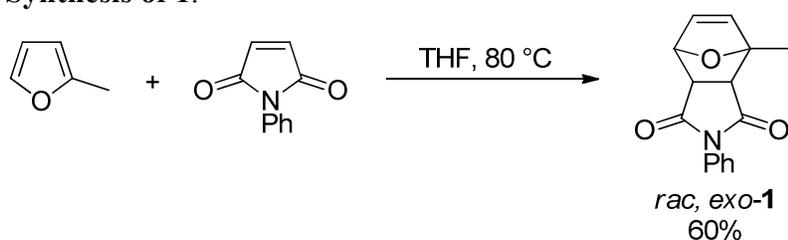
## General Information

NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  on Varian Mercury 300 MHz or INOVA 500 MHz spectrometers in the High-Resolution Nuclear Magnetic Resonance Facility at the California Institute of Technology (Caltech) operating VnmrJ software, unless otherwise noted.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced relative to the residual solvent peak ( $\text{CDCl}_3$   $\delta=7.27$  for  $^1\text{H}$  and  $\delta=77.23$  for  $^{13}\text{C}$ ;  $\text{CD}_2\text{Cl}_2$   $\delta=5.32$  for  $^1\text{H}$  and  $\delta=54.00$  for  $^{13}\text{C}$ ). Spectral analysis was performed on MestReNova software. High-resolution mass spectra were provided by the Caltech's Mass Spectrometry Facility. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) on two MZ-Gel 10  $\mu\text{m}$  columns composed of styrene-divinylbenzene copolymer (Analysentechnik) and connected in series, with a miniDAWN TREOS multiangle laser light scattering (MALLS) detector, ViscoStar viscometer and Optilab rEX differential refractometer (all three from Wyatt Technologies). No calibration standards were used, as light scattering is considered an accurate measurement of molecular weight. Each sample was weighed and the  $\text{dn}/\text{dc}$  was calculated assuming 100% mass elution from the column. GPC data analysis was performed with ASTRA software.

## Materials

$\text{CH}_2\text{Cl}_2$  was purified by passage through a solvent purification system.<sup>1</sup>  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$  were obtained from Cambridge Isotopes.  $\text{CD}_2\text{Cl}_2$  was purified by vacuum transfer from  $\text{P}_2\text{O}_5$ . Catalysts **A**, **B**, **C**, and **D** were gifts from Materia, Inc. All other solvents and chemicals were obtained from Sigma-Aldrich Corporation and used as received.

## Synthesis of 1.



A 500 ml roundbottom flask equipped with a magnetic stirbar was charged with N-phenylmaleimide (34.6 g, 0.2 mol, 1 equiv), 2-methylfuran (35 ml, 0.4 mol, 2 equiv) and THF (200 ml). The mixture was heated to 80 °C and refluxed for 6 hours. The yellow solution was then cooled to room temperature. A white microcrystalline solid precipitates upon standing. After further cooling to -20 °C in a freezer overnight, the solid was filtered and washed with a small amount of cold THF to give **1** (30.9 g, 0.12 mol, 60%). HRMS (EI+): calculated = 255.0895, found = 255.0894. NMR characterization matches that already reported in the literature.<sup>2</sup>

## Initial Experiments.

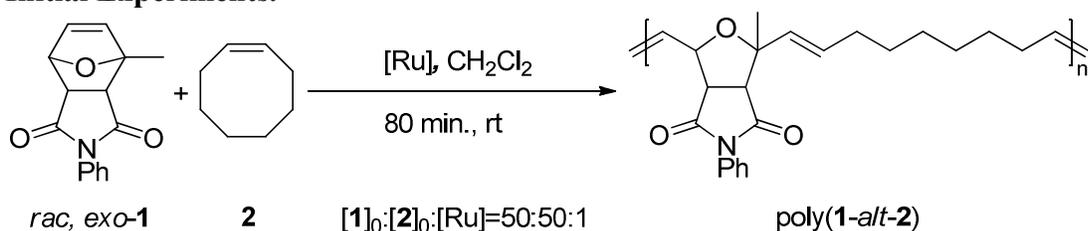




Table 1. Reactivity Ratio Monomer Feeds

1 (mmol)	1 (g)	2 (mmol)	2 (ul)	Molar feed ratio 1/2	Catalysts			
					A	B	C	D
3	0.77	7	912	0.43				X
4	1.02	6	782	0.67		X	X	X
5	1.28	5	651	1.00	X	X	X	X
6	1.53	4	521	1.50	X	X	X	X
7	1.79	3	391	2.33	X	X	X	X
8	2.04	2	261	4.00	X	X	X	
9	2.30	1	130	9.00	X			

The symbols for the Kelen-Tüdös and Kuo-Chen models are defined below.

$M_1$ =mole fraction of **1** in the monomer feed.

$M_2$ =mole fraction of **2** in the monomer feed.

$m_1$ =mole fraction of **1** in the polymer

$m_2$ =mole fraction of **2** in the polymer

$$F=(m_2/m_1)(M_1/M_2)^2$$

$$G=(M_1/M_2)(1-(m_2/m_1))$$

$\alpha=\alpha=(F_{\min}F_{\max})^{1/2}$ , where  $F_{\min}$  and  $F_{\max}$  are the lowest and highest values for a set of experimental points, respectively.

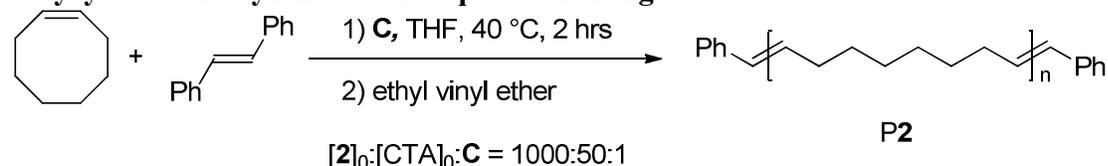
$$\eta=\eta=G/(\alpha+F)$$

$$\zeta=\zeta=F(\alpha+F)$$

The Fineman-Ross (FR) linear method is the simplest way to determine  $r_1$  and  $r_2$ . The FR method plots  $G$  against  $F$ , where  $r_1$  is the slope and  $r_2$  is the intercept. The Kelen-Tüdös linear method adds the correction factor  $\alpha$  to utilize the characteristics of the experiment and lessen the effect of the extreme points. The KT linear method plots  $\zeta$  against  $\eta$ , and gives  $-r_2/\alpha$  as the intercept and  $r_1+r_2/\alpha$  as the slope.

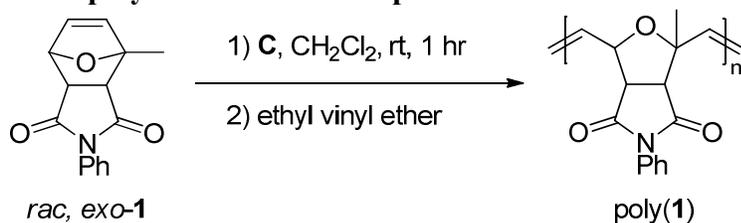
The Kuo-Chen exponential method plots  $(M_1M_2)/(m_1m_2)$  against  $M_1$ . The exact exponential is subjective, but is commonly second-order for  $M_1$ . This is the case for our experiments. The reactivity ratios  $r_1$  and  $r_2$  are calculated from the extrapolation of the equation to  $M_1=1$  and  $M_1=0$ , respectively.

### Polycyclooctene Synthesis for Sequence Editing



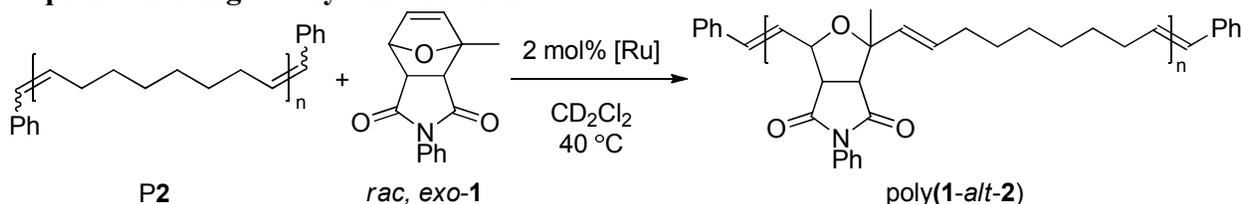
In a nitrogen-filled glovebox, *cis*-cyclooctene (2.6 ml, 20 mmol, 1000 equiv.), *trans*-stilbene (180 mg, 1 mmol, 50 equiv.) and catalyst **C** (17 mg, 0.02 mmol, 1 equiv.) were dissolved in THF (10 ml) in a scintillation vial. The vial was sealed, removed from the glovebox and heated at 40 °C in an oil bath for 2 hours. Once the reaction was complete, the vial was cooled and the reaction was quenched with ethyl vinyl ether (~1 ml). The polymer (1.19 g) was recovered by precipitation into MeOH.  $M_n=3632$  Da,  $M_w=5770$  Da, PDI=1.588.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra correspond with reported data.<sup>3</sup>

### Homopolymerization of compound 1.



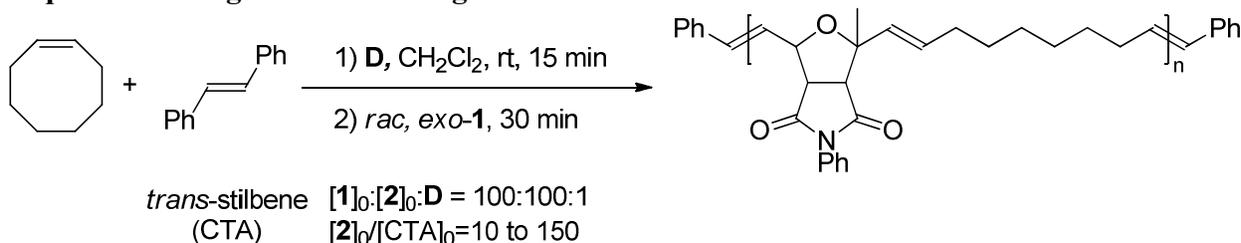
In a nitrogen-filled glovebox, **1** (290 mg, 1.1 mmol) was dissolved in methylene chloride (3 ml) in a scintillation vial with a stirbar. Catalyst **C** (10 mg, 0.012 mmol,  $[1]/[C]=92$ ) was added to the monomer solution. The scintillation vial was sealed, removed from the glovebox and allowed to stir at room temperature for 1 hour. The polymerization was quenched with ethyl vinyl ether (0.5 ml). The polymer solution was precipitated into diethyl ether (30 ml) and centrifuged to collect the solid. The supernatant was decanted. The polymer was washed with diethyl ether (30 ml), collected by centrifugation and dried *in vacuo*. Poly(**1**) was recovered as a white solid (48 mg, 17 % isolated yield). The NMR spectra for poly(**1**) are given below.

### Sequence Editing Catalyst Evaluation



In a nitrogen-filled glove-box, **P2** (140 mg, 1.3 mmol) and **1** (330 mg, 1.3 mmol) were dissolved in  $\text{CD}_2\text{Cl}_2$  (6.3 ml) in a scintillation vial. This monomer stock solution was aliquotted into 4 septum screw cap NMR tubes, with 1 ml of the stock solution in each tube. A stock solution of each catalyst was prepared (~0.4 ml, 0.02M) with  $\text{CD}_2\text{Cl}_2$  in septum screw cap vials. All solutions were removed from the glovebox. For each NMR rate experiment, the catalyst solution (0.2 ml) was injected into the monomer stock solution in the NMR tube. The course of the reaction was monitored, with 5 s intervals between each 8-transient experiment.

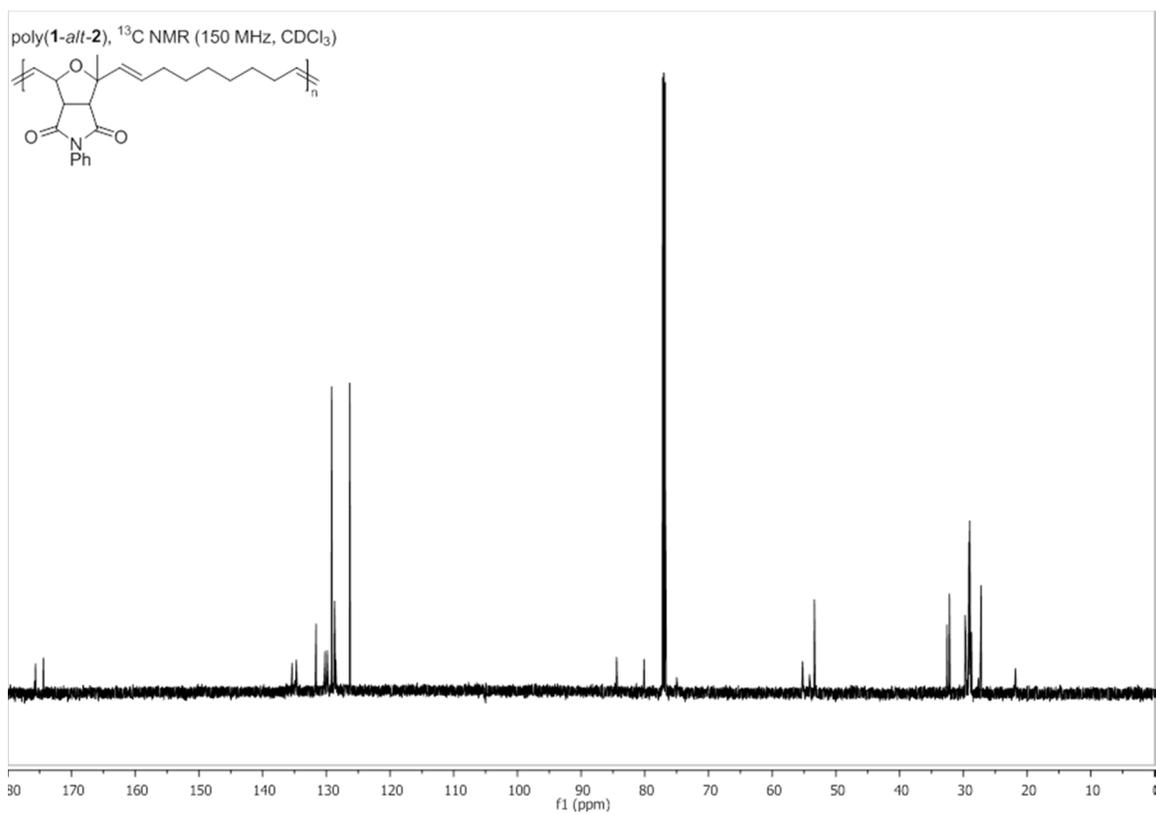
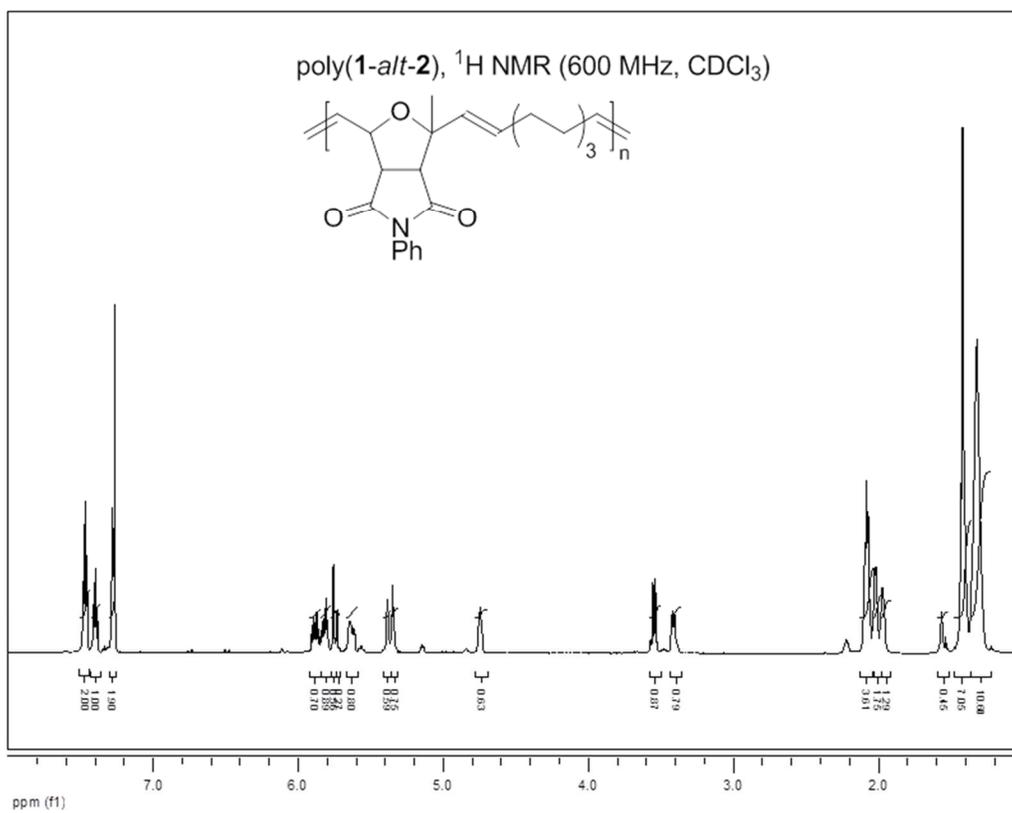
### Sequence Editing Molecular Weight Control

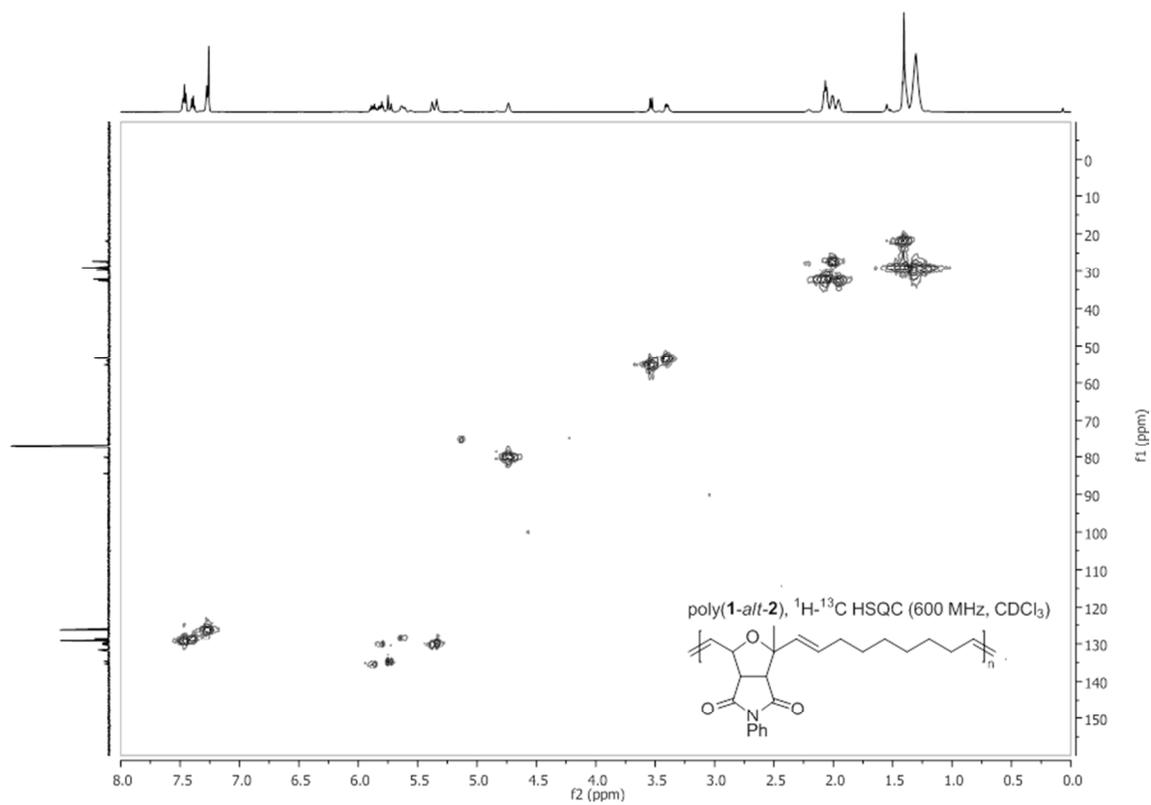
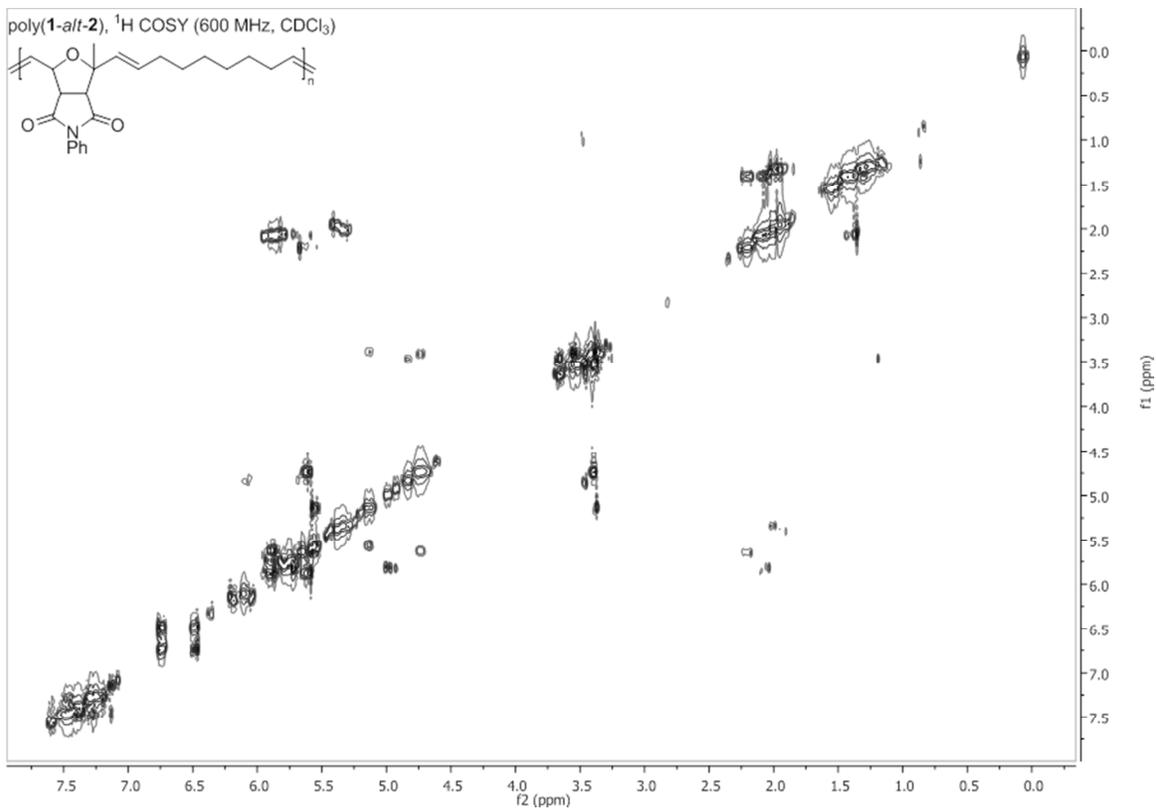


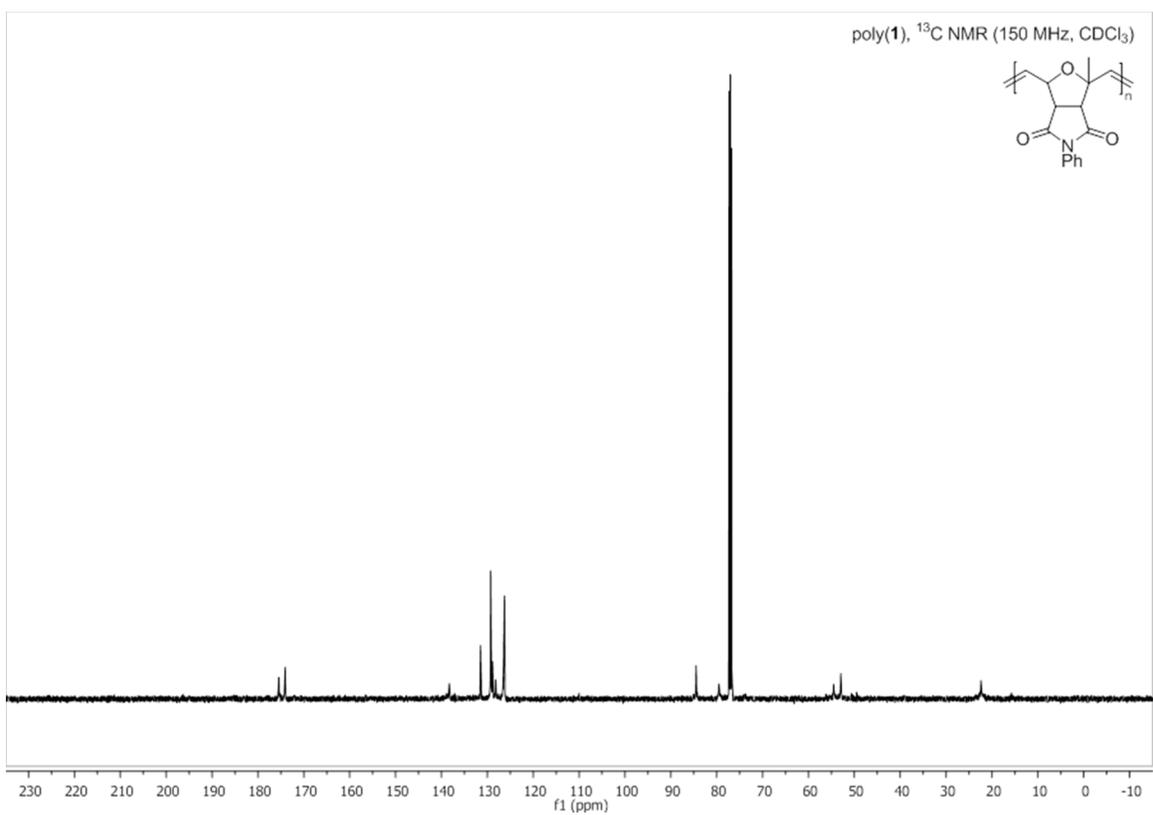
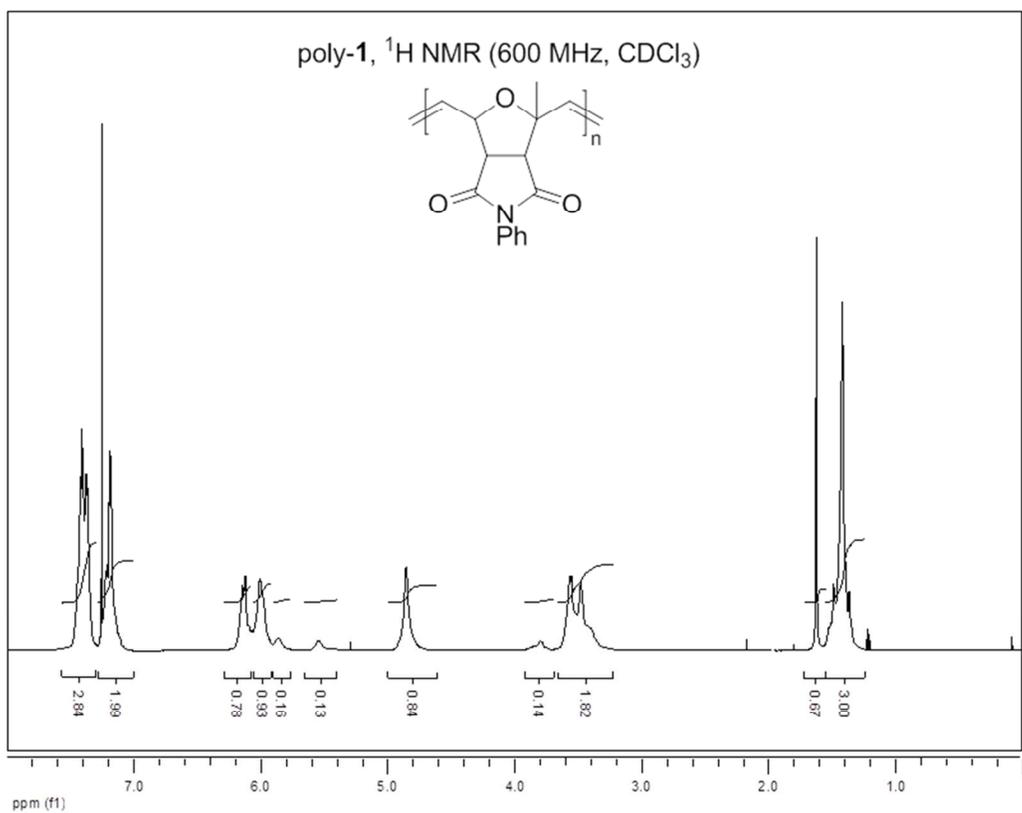
In a nitrogen-filled glovebox, four stock solutions were prepared. A stock solution of **2** (130  $\mu\text{l}$ , 1 mmol) was made in  $\text{CH}_2\text{Cl}_2$  (2 ml). Aliquots (200  $\mu\text{l}$ ) were placed in 6 vials, each equipped with a stirbar. A chain-transfer agent (CTA) stock solution of *trans-stilbene* (18 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 ml) was made. The appropriate amount of CTA stock solution was added to each vial to have the correct **2**/CTA ratio. A catalyst stock solution of **D** (9.3 mg, 0.01 mmol) was prepared in  $\text{CH}_2\text{Cl}_2$  (1 ml). To each **2**+CTA solution, 100  $\mu\text{l}$  of catalyst stock solution was added to initiate polymerization. The polymerization and chain transfer of **2** was allowed to proceed for 30 minutes. While this step proceeded, the sequence editing stock solution was prepared

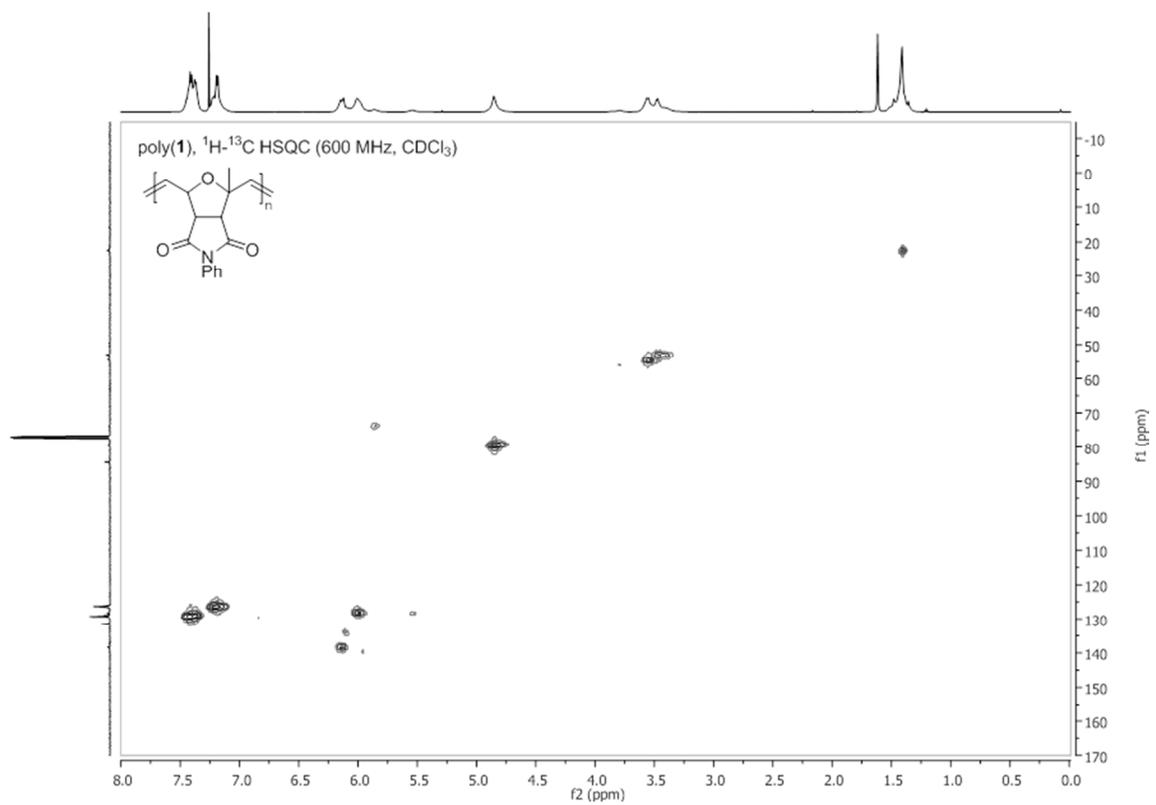
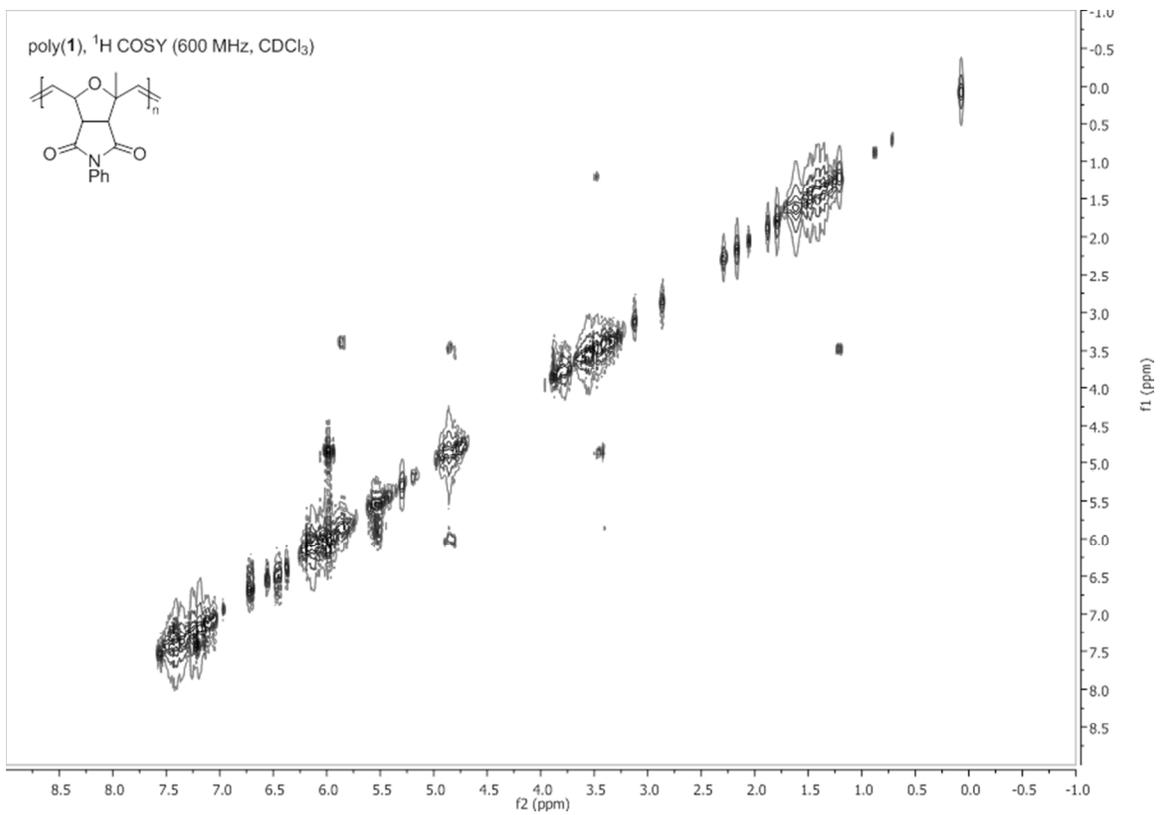
from **1** (255 mg, 1 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (2 ml). After the polymerization of **2** was complete, 200  $\mu$ l of the sequence editing stock solution was added to the reaction mixture in each vial. All of the vials were sealed and removed from the glovebox. After stirring for 15 minutes to complete the sequence editing step, the reactions were quenched with ethyl vinyl ether (200  $\mu$ l). The volatiles were removed *in vacuo* to yield crude polymer, which was analyzed by GPC to obtain the molecular weight data.

$[\mathbf{2}]_0/[\text{CTA}]_0$	mmol CTA	mg CTA	$\mu$ l CTA solution
10	0.0100	1.80	100
20	0.0050	0.90	50
30	0.0033	0.60	33
50	0.0020	0.36	20
75	0.0013	0.24	13
150	0.0007	0.12	7









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- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
- (2) Goussé, C.; Gandini, A.; Hodge, P. *Macromolecules* **1998**, *31*, 314-321.
- (3) Alonso-Villanueva, J.; Cuevas, J. M.; Laza, J. M.; Vilas, J. L.; León, L. M. *J. App. Poly. Sci.* **2010**, *115*, 2440-2447.