Master's Thesis

Redox-Switchable Cross Metathesis and Acyclic Diene Metathesis Polymerization

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2019

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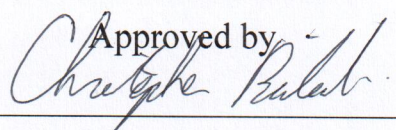
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Redox-Switchable Cross Metathesis and Acyclic Diene Metathesis Polymerization

A thesis/dissertation
submitted to the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
Master of Science

Yeonkyeong Ryu

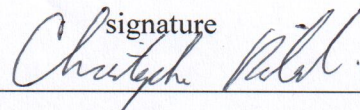01/07/2019 of submission

Approved by
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Advisor
Christopher W. Bielawski

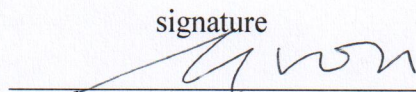# Redox-Switchable Cross Metathesis and Acyclic Diene Metathesis Polymerization

Yeonkyeong Ryu

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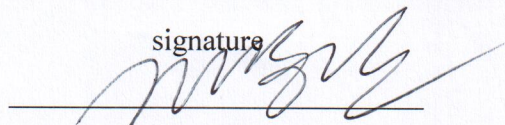
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Abstract

Acyclic diene metathesis (ADMET) polymerization grant the opportunity to synthesize precisely defined polymers. One of the limitations of this method is the lack of control on the molecular weight of the final products. We reasoned that the use of redox switchable catalysis can be used to achieve enhanced levels of control. Herein, a Ru(II)-based redox-switchable catalyst, containing a quinone-annulated N-heterocyclic carbine is used in order to modulate the reactivity of ADMET polymerization by using redox agents ($CoCp_2$ and DDQ). The oxidation state of the ligand switched by reducing and oxidizing agents allow us to control directly the kinetic of the reaction. Whereas the neutral form of the complex catalyzes the reaction (in the same rate as commercially-available catalyst), the reduced complex inhibits the reaction by a decrease in the rate constant by around one order of magnitude, compared to the neutral form. Furthermore, the molecular weight of polymers by ADMET polymerization with this redox-switchable catalysis was related to the same chemistry as mentioned before. In this thesis we investigate the cross metathesis (CM) reaction because it shares the fundamental mechanism with ADMET polymerization and we will show that it is possible to modulate the molecular weights of the final products.

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1. Introduction

Olefin metathesis is a useful and widely-implemented transformation for the synthesis of small molecules and polymeric materials.[1] Acyclic diene metathesis (ADMET) polymerization is a variation of olefin metathesis that affords unsaturated polymers in a step-growth manner through cross metathesis (CM), a process wherein terminal olefins are coupled concomitantly with the formation of ethylene.[2] ADMET has been used to prepare a broad range of polymers, including those that feature pendant groups in precisely defined positions along their corresponding backbones.[3,4] As with other step-growth techniques, the average molecular weights of the polymers produced using ADMET are dependent on extent of the corresponding polymerization reaction. As such, the synthesis of polymers with pre-determined molecular weights generally involves adding chain transfer agents or quenching the polymerization reactions at pre-determined conversions.[5,6]

We reasoned that the use of a catalyst that can be rapidly deactivated and subsequently re-started, may a means to control ADMET polymerizations as well as the molecular weights of the polymers produced. Such a goal is a part of the blossoming field of switchable catalysis, which seeks to modulate the intrinsic activities and selectivities displayed by catalysts through the introduction of thermal, chemical, photochemical, redox or mechanical stimuli.[7] Redox chemistry is a particularly attractive stimulus due to the broad range of chemical oxidants and reductants that are currently available.[8]

To the best of our knowledge, the first example of a redox-controlled transformation was demonstrated by Wrighton.[9] As shown in Scheme 1, the Rh I_{red} was found to promote hydrogenation or isomerization reactions; however, oxidation of the 1,1-bis(diphenylphosphino)cobaltocene ligand afforded a hydrosilylation catalyst (I_{ox}). Gibson and Long subsequently demonstrated that the ring-opening polymerization (ROP) of rac-lactide may be modulated by changing the oxidation state of the ferrocenyl units in II.[10] Control over ROPs using various Al, Fe, and Ti catalysts supported by ferrocenyl containing ligands were reported by Diaconescu, Byers, and Chen.[11],[12],[13] Redox-controlled olefin polymerizations have also been explored by Long.[14]
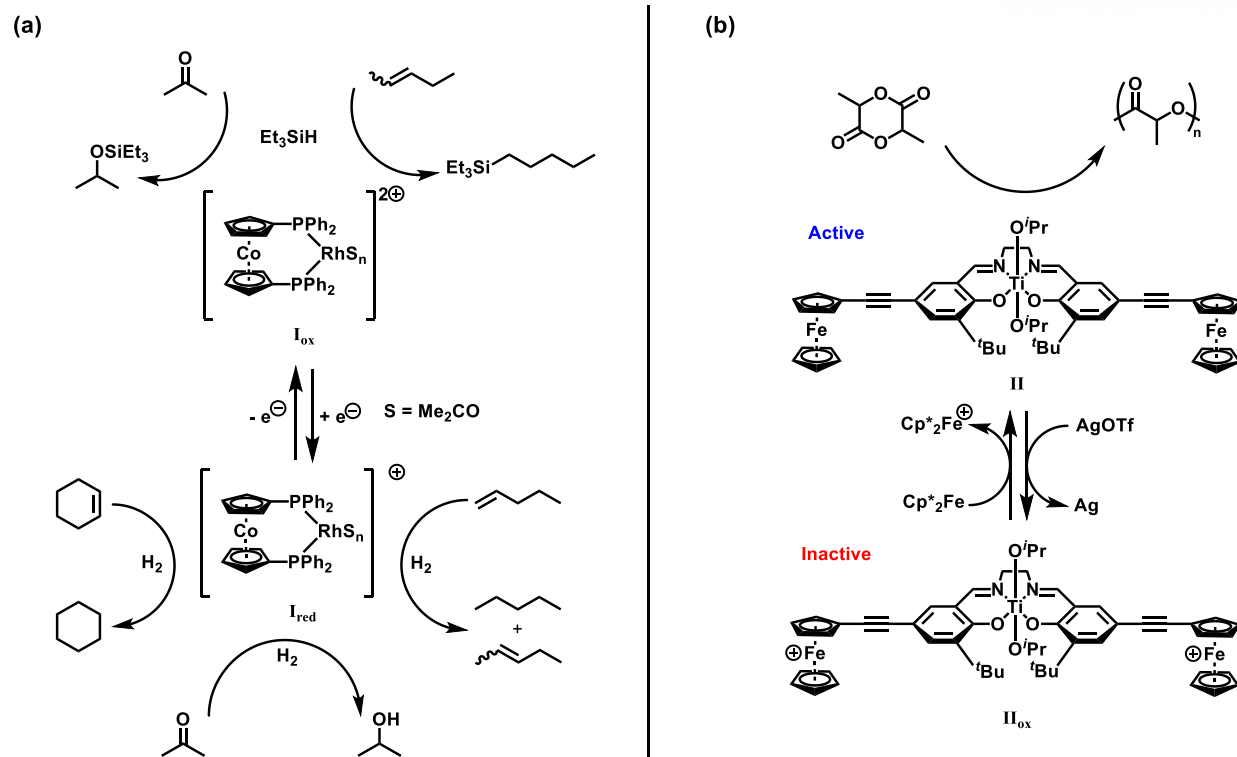
Scheme 1. Examples of a redox-switchable catalysts for controlling (a) hydrogations and isomerizations or hydrosilylation as well as (b) ring-opening polymerizations.

Our efforts have been focused on the development of redox-switchable catalysts based on Ru and their deployment in controlling olefin metathesis reactions.[15] We demonstrated that catalysts outfitted with a naphthoquinones undergo reduction upon exposure to a reductant (e.g., cobaltocene; CoCp2); subsequent exposure of the reduced catalyst to an oxidant (e.g., 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; DDQ) restored the neutral catalyst (e.g., see Scheme 2). The activity of the catalyst was found to be dependent on the oxidation state of the quinone group. For example, the rate constants measured for various ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions were significantly reduced upon reduction of the catalyst.[16,17] Moreover, some catalysts exhibited monomer selectivities that depended on the oxidation state of the redox active ligand, a feature that permitted control over copolymerization reactions.
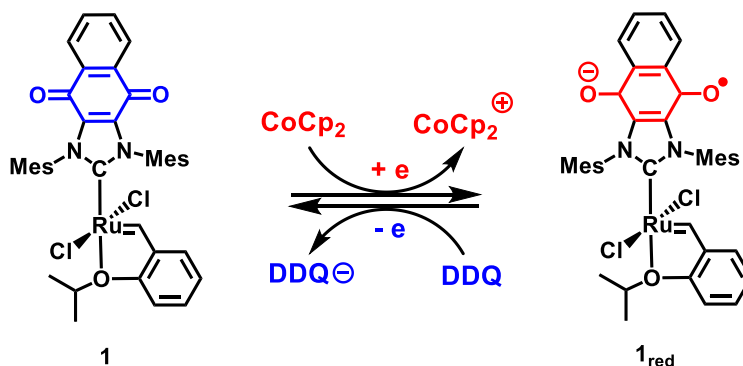
Scheme 2. Reversible reduction of **1**.

Building on our previously reported results, we describe herein a series of redox-controlled ADMET polymerizations. Since such polymerizations are predicated on cross metathesis (CM) chemistry, a summary of efforts to control such reactions are also described as the results obtained therefrom were envisioned to guide the polymerization chemistry. Finally, we will show that the molecular weights of the polymers produced using ADMET can be modulated using redox-switchable catalysts.

2. Experimental

2.1. General Considerations

All procedures were performed in a nitrogen-filled glove box or using standard air-free techniques unless otherwise noted. Solvents were dried and degassed using a Vacuum Atmospheres Company solvent purification system and stored over 4 Å molecular sieves in a nitrogen-filled glove box. Unless otherwise specified, monomers and substrates were purchased from commercial sources and distilled from CaH_2 under reduced pressure into a Straus flask equipped with a Teflon valve, degassed by three freeze-pump-thaw cycles, and stored in a nitrogen-filled glove box. Catalyst 1 was synthesized according to previously reported procedures.[16] NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts (δ) are given in ppm and are referenced to tetramethylsilane (TMS) using the residual solvent (^{1}H: $CDCl_3$, 7.26 ppm). Gel permeation chromatography (GPC) was performed on a Viscotek GPCmax system. Two fluorinated polystyrene columns (I-OLIGO-3078) were used in series and maintained at 35 °C. THF was used as the mobile phase at a flow rate of 0.8 mL/min. Molecular weight data are reported as their polystyrene equivalents.
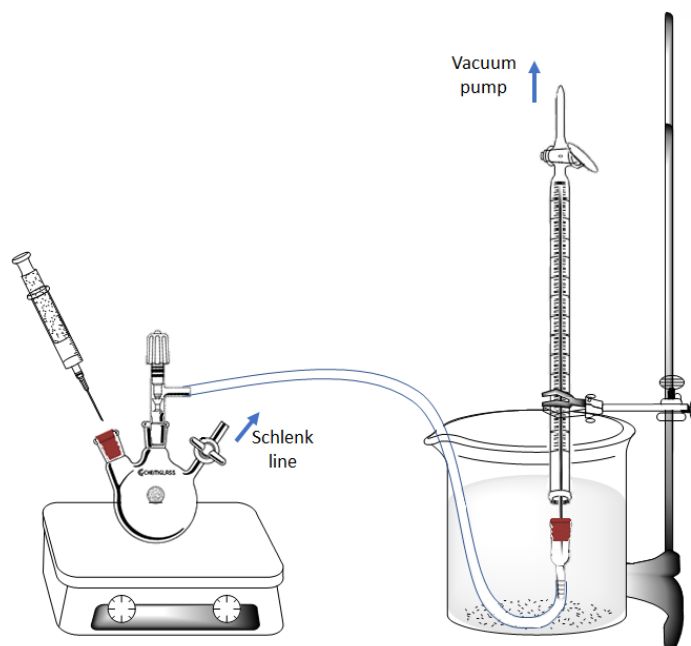
Figure 1. Illustration of the apparatus used for kinetic measurements.

2.2. Kinetics Measurements

Reaction kinetics were monitored by measuring the quantity of gaseous byproducts (e.g., ethylene) that were produced over time using a modified setup reported in the literature (see Figure 1).[18] A flame-dried 50 mL 2-neck Schlenk flask equipped with a 14/20 ground-glass joint was connected via Tygon tubing using a Schlenk adapter. The end of the tubing was connected to the 24/40 ground-glass joint glass apparatus which was capped with a rubber septum and one side of a 60 cm cannula (18 gauge) was connected. The other side of the cannula was placed in a water-filled burette that was partially submerged in a pool of water. The ideal gas equation in conjunction with the change in volume over time were used to calculate the quantity of gas produced and thus the extent of the reaction.

2.3. General Procedures

2.3.1. Monitored Cross Metatheses (CM)

A flame-dried 50 mL 2-neck Schlenk flask equipped with 14/20 ground-glass joint equipped with a magnetic stir bar was cooled to room temperature under vacuum. Afterward, the flask was purged

with nitrogen, charged with **1** (5.0 µmol) and finally connected to the apparatus described above. For the case of monitoring the reaction kinetic with $\mathbf{1_{red}}$, 0.08 mL of 100 mM solution of $CoCp_2$ (7.5 µmol, 1.5 eq. rel. to **1**) in 1,2-dichlorobenzene was added at this step and waited for 5 min to let $CoCp_2$ reduce **1**. Reducing the pressure inside of the 50 mL burette through the application of a vacuum to the top of the system caused the water level to rise. Before the water reached the tip of the cannula, the vacuum was closed. Next, the valve that connects the reaction flask to the burette was opened. After waiting for 5 min for the system to equilibrate, 2.25 mmol of the substrate was injected into the reaction flask (time = 0). For the control of the oxidation state of **1** during the reaction, 0.05 mL of 100 mM solution of $CoCp_2$ (7.5 µmol, 1.5 eq. rel. to **1**) in 1,2-dichlorobenzene and 0.15 mL of 50 mM solution of DDQ (11.25 µmol, 1.5 eq. rel. to $CoCp_2$) in 1,2-dichlorobenzene were added. After 10 min, the reactions were quenched by adding 1.0 mL of chloroform solution containing 10 mM ethyl vinyl ether and 4.3 mM 2,6-di-tert-butyl-4-methylphenol (BHT). The extent of reaction was calculated from the amount of ethylene that evolved over the course of the reaction as determined by the change in volume. The crude products were analyzed by ^{1}H NMR spectroscopy.

2.3.2. Monitored ADMET Polymerizations

A procedure similar as that described in *Section 2.3.1* was used with the following quantities of reagents: 0.4 mL of 7.50 mM solution of **1** (3 µmol) dissolved in 1,2-dichlorobenzene and 1.35 mmol of monomer were used. For the polymerizations with $\mathbf{1_{red}}$, 0.03 mL of 100 mM solution of $CoCp_2$ (1.0 eq. rel. to **1**) was added. For the control of the oxidation state of 1 during the reaction, 0.03 mL of 100 mM solution of $CoCp_2$ (3 µmol, 1.0 eq. rel. to **1**) and 0.09 mL of 50 mM solution of DDQ (4.5 µmol, 1.5 eq. rel. to $CoCp_2$) were added. 0.5 mL of a chloroform solution containing 10 mM ethyl vinyl ether and 4.3 mM BHT to quench the reaction.

2.3.3. Variation of the Reductant to Catalyst Ratio

A procedure similar as that described in *Section 2.3.1* with a modification: various quantities of $CoCp_2$ (see Figure 4) were injected at t = 30 s as a form of 100 mM solution in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl).

2.3.4. Bulk Polymerizations

Three oven-dried 25 mL Schlenk tubes were equipped with a magnetic stir bar each and then taken into a nitrogen filled glove box. Each tube was charged with the solid catalyst **1** (24.11 µmol) followed by $CoCp_2$ in 1,2-dichlorobenzene added from 0.0 eq., 0.5 eq. and 1.0 eq. rel. to **1**. After 5

min, 1,9-decadiene (2 mL, 10.85 mmol) was added to the reaction vessels. The tubes were then sealed, removed from the glove box, and connected to a high vacuum manifold. Applying a static vacuum caused the formation of bubbles. Once the bubbling ceased, a full vacuum (c.a. 0.1 mmHg) was applied to the reaction vessels for 5 days. Excess ethyl vinyl ether was added to quench the reaction followed by removal of residual solvent under high vacuum. The crude products were collected and analyzed using GPC.

3. Results and Discussion

3.1. CM of 1-Decene

Figure 2. The cross metathesis of 1-decene (top) and the corresponding plot of conversion vs time (bottom). Conditions: 65 °C, 2_0 = 2.25 mmol, 1_0 = 5.0 µmol. The labels "$CoCp_2$" and "DDQ" indicate when said reagent was added (see text). The label "1_{red}" refers to an experiment where the catalyst was subjected to $CoCp_2$ prior to introduction to **2**.

Initial efforts were directed toward the self-cross metathesis of 1-decene (**2**). Although CM and ADMET polymerizations are often conducted under vacuum ($< 10^{-2}$ Torr) to drive product formation,[19,20] we adapted a system reported in the literature to monitor the evolution of ethylene and thus the reaction conversion over time.[18] Adding 1-decene (**2**) to catalyst **1** ($[2]_0/[1]_0 = 450$) at 65 °C initiated a reaction that proceeded with a pseudo-first order rate constant (k) of 8.5×10^{-3} s^{-1}. In a separate experiment, adding a concentrated solution of CoCp$_2$ in 1,2-dichlorobenzene ($[CoCp_2]_0 = 11.6$ mM; 1.0 equiv. rel. to **1**) to the reaction vessel prior to the addition of **2** resulted in a slower reaction ($k_{red} = 4.3 \times 10^{-4}$ s^{-1}). In accord with previous results,[16] we surmise that **1** underwent reduction in situ in the latter experiment. For comparison, the rate constant for analogous reaction performed with the commercially-available catalyst HG2 was measured to be (k) of 9.7×10^{-3} s^{-1}.

To determine if the aforementioned condensation can be temporally controlled, redox agents were added to the reaction mixture at various points in time. As summarized in Figure **2**, the CM of **2**, as initiated with **1** ($[2]_0/[1]_0 = 450$), was measured to proceed with an initial rate constant (k) of 7.5×10^{-3} s^{-1} at 65 °C. After a 19% conversion of **2** to **3** was reached (30 s), CoCp$_2$ (1 equiv. rel. to **1**) was introduced to the reaction mixture. The addition resulted in a lower measured rate constant, $k_{red} = 4.3 \times 10^{-4}$ s^{-1} ($k/k_{red} = 17$). At a later point in time (120 s), a slight excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.5 equiv. rel. to **1**) was added which resulted in a significant restoration of the initial catalytic activity, $k_{red-ox} = 2.5 \times 10^{-3}$ s^{-1} ($k_{red-ox}/k_{red} = 5.8$).
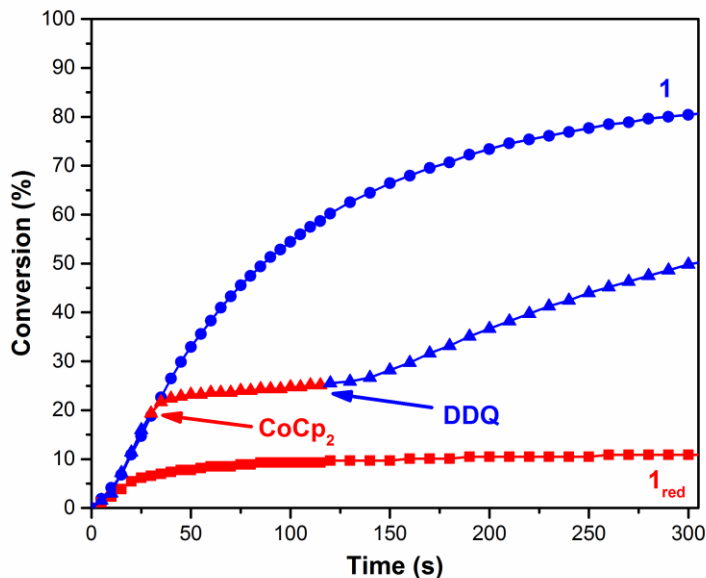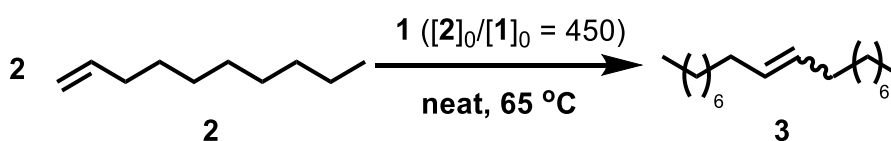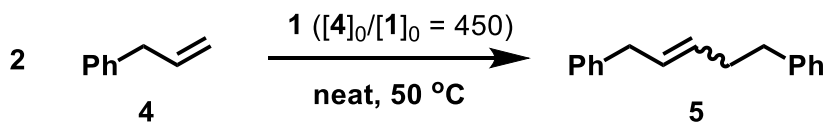
3.2. CM of Allylbenzene
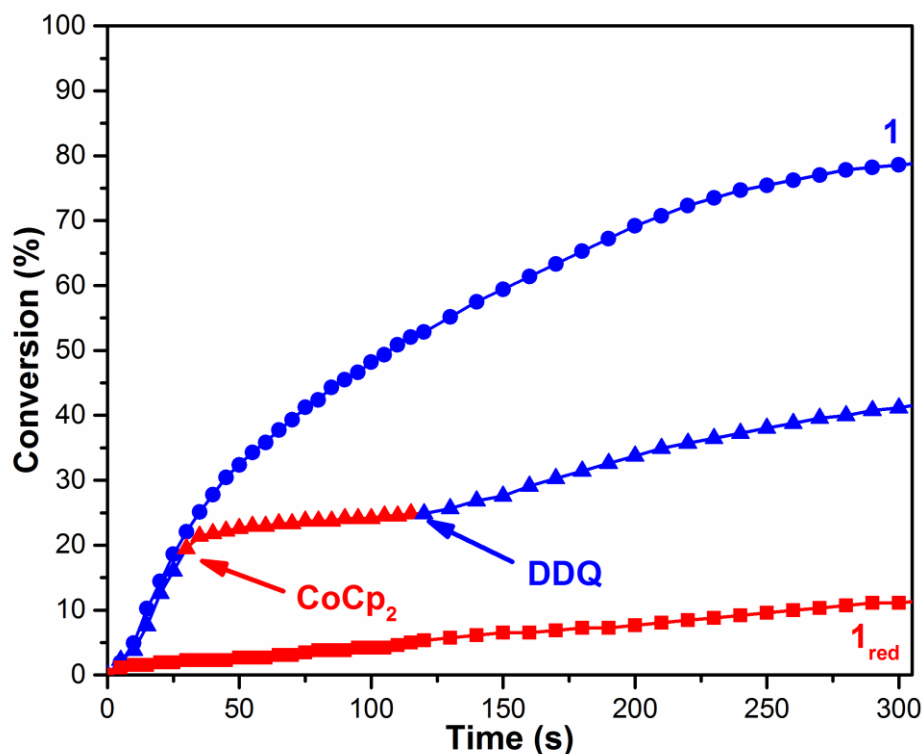
Figure 3. The cross metathesis of allylbenzene (top) and the corresponding plot of conversion vs time (bottom). Conditions: 50 °C, 4_0 = 2.25 mmol, **1** = 5.0 µmol. The labels "CoCp2" and "DDQ" indicate when said reagent was added (see text). The label "**1**red" refers to an experiment where the catalyst was subjected to CoCp2 prior to introduction to **4**.

Next, efforts shifted toward exploring the scope of substrates that are amenable to control using a redox-switchable catalyst. Attention was directed toward the CM of an aromatic monomer, allylbenzene (**4**), in part because relatively rigid monomers can be expected to afford stiffer polymers that are less prone to intramolecular cyclization and thus can be of higher molecular weight.[21] The addition of **1** to neat **4** at 50 °C ($[4]_0/[1]_0$ = 450) resulted in the condensation of (ethylene) gas whose evolution was measured to proceed with a rate constant (k) of 7.9×10^{-3} s^{-1}. For comparison, the reduced catalyst, which was generated in situ with CoCp2 using the procedure described above, resulted in a significantly slower reaction ($k_{red} = 3.5 \times 10^{-4}$ s^{-1}). As summarized in Figure 3, the CM of **4** was also temporally controlled. The initial rate of the reaction ($k = 7.5 \times 10^-$

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^{3} s^{-1}) was significantly reduced upon reduction of the catalyst (k_{red} = 4.9 × 10^{-4} s^{-1}; k/k_{red} = 15); subsequent addition of DDQ enhanced the rate of the reaction (k_{red-ox} = 1.4 × 10^{-3} s^{-1}; k_{red-ox}/k_{red} = 2.9).

3.3. ADMET of 1,9-Decadiene
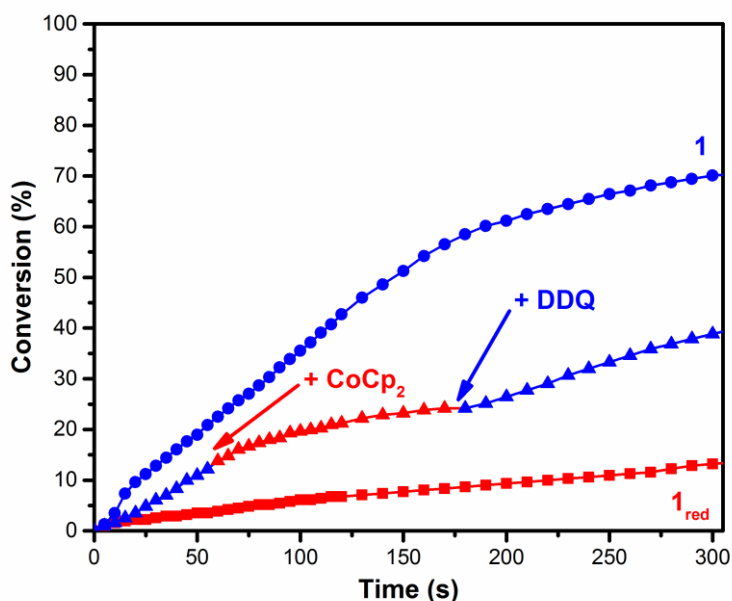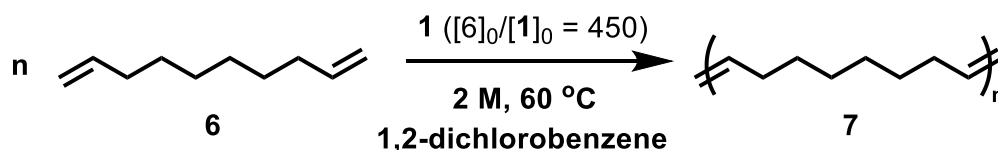
Figure 4. The ADMET polymerization of 1,9-decadiene (top) and the corresponding plot of conversion vs time (bottom). Conditions: [**6**]$_0$ = 2.09 M, [**1**]$_0$ = 7.50 mM, 1,2-dichlorobenzene, 60 °C. The labels "CoCp$_2$" and "DDQ" indicate when said reagent was added (see text). The label "**1$_{red}$**" refers to an experiment where the catalyst was subjected to CoCp$_2$ prior to introduction to **7**.

After demonstrating that the redox-active catalyst may be used to control CM reactions, efforts were directed toward the ADMET polymerization of ditopic analogues. As summarized in Figure 4, a suitable monomer, 1,9-decadiene (**6**), was added to the reaction vessel which contained a

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solution of **1** in 1,2-dichlorobenzene ($[6]_0/[1]_0 = 450$, 60 °C, $[4]_0 = 2$ M). The corresponding polymerization reaction proceeded with a rate constant (k) of 3.7×10^{-3} s^{-1}. For comparison, an analogous reaction conducted with **1$_{red}$**, which was prepared by reducing the catalyst in situ prior to introduction to the monomer, was measured to proceed a slower rate ($k_{red} = 5.6 \times 10^{-4}$ s^{-1}). To determine if the polymerization reaction can be modulated over time, redox agents were added to the reaction mixture at pre-determined intervals and the corresponding changes were monitored. For example, the ADMET of **4**, as initiated with **1** ($[4]_0/[1]_0 = 450$, 60 °C) was measured to proceed with an initial rate constant (k) of 2.4×10^{-3} s^{-1}. After 14% of **4** was converted to polymer, a slight excess of CoCp$_2$ (1.5 equiv. rel. to **1**) was introduced to the reaction mixture. The addition resulted in a lower measured reaction constant, $k_{red} = 9.7 \times 10^{-4}$ s^{-1} ($k/k_{red} = 2.5$). At a later point in time, a slight excess of DDQ (1.5 equiv. rel. to added CoCp$_2$) was introduced, which resulted in a restoration of the initial catalytic activity, $k_{red-ox} = 2.0 \times 10^{-3}$ s^{-1} ($k_{red-ox}/k_{red} = 2.1$).

3.4. Variation of the Reductant to Catalyst Ratio

Figure 5. Plots of conversion of **2** to **3** vs time using various quantities of CoCp$_2$. Conditions: $[2]_0 = 5.28$ M, **1** = 5.0 μmol, 65 °C. The labels refer to the molar equivalents of CoCp$_2$ (rel. to **1**)

at 30 s. The label "**1**" refers to a control experiment wherein CoCp$_2$ was not added to the reaction mixture.

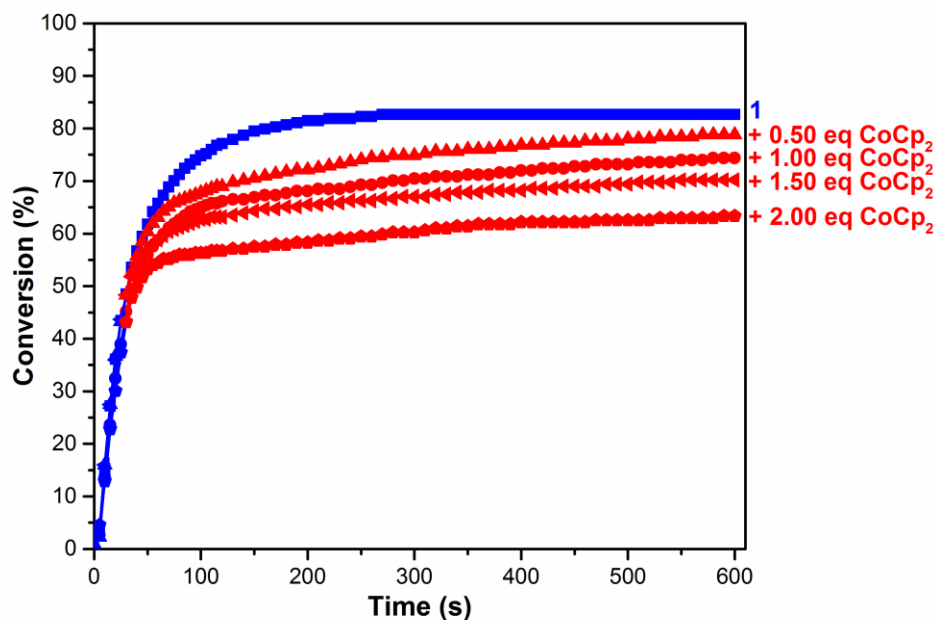To determine if the condensation chemistry described above can be further tuned using the redox-switchable catalyst, a series of reactions were conducted wherein the ratio of reductant to catalyst was varied. The ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, was employed as the reaction medium to minimize volume changes in due solvent evaporation and thus increase the accuracy of the measurements. As shown in Figure 4 and Table S1, increasing the quantity of added CoCp$_2$ pronounced attenuation in catalytic activity and final conversion.

3.5. Molecular Weight Control

Finally, efforts were directed toward controlling the molecular weights of the polymers afforded via ADMET using the redox-switchable catalyst. Three experiments were conducted in parallel at 75 °C: one experiment utilized the neutral form of the catalyst (**1**) and the others used its reduced derivative (**1**$_{red}$; generated in situ from **1** and 0.5 eq. or 1.0 eq. of CoCp$_2$). The initial monomer concentration ([**6**]$_0$ = 1.85 M; [**6**]$_0$/[**1**]$_0$ = 450) was kept constant for both experiments. After 5 days, the reactions were independently quenched and the corresponding polymers were formed. In accord with the kinetics measurements described above, the polymer synthesized with **1** was measured to be exhibited a higher molecular weight (6 kDa) than those prepared with **1**$_{red}$, that with 0.5 eq. CoCp$_2$ showed 1.3 kDa and those prepared with 1.0 eq. CoCp$_2$ showed 0.8 kDa in GPC (See Figure S15).

4. Discussion

Collectively, the results indicate that the reduced form of catalyst **1** exhibited a lower catalytic activity in CM and ADMET polymerizations than the neutral form. These observations are in accord with those described for RCM and ROMP reactions using similar catalysts. In these latter cases, computational studies revealed that the reduced form of the ligand stabilizes ruthenacyclobutane intermediates and effectively raises the activation barrier for the rate-determining retro-[2+2] cycloaddition step.[16] Such effects maybe operative in other olefin metathesis reactions catalyzed by **1**, including CM transformations and ADMET polymerizations, and thus provide a rationalization for the redox-state dependent activities described herein.

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5. Conclusion

A series of CM and ADMET polymerizations were temporally controlled using a redox-switchable Ru-based catalyst. The relatively high activities displayed by the catalyst in its neutral form were effectively attenuated upon reduction and activity was restored upon subsequent oxidation. Likewise, the reduced form of the catalyst afforded a polymer that was lower in molecular weight than an analogous reaction performed using the neutral form of the catalyst. Control over catalytic activity was also tuned by varying the ratio of added reductant to catalyst. In a broader context, these results represent the first example of controlling a step-growth polymerization using a redox-switchable catalyst and demonstrate the potential of using redox-switchable catalysts to control a broad range of olefin metathesis reactions.

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Supplementary Information
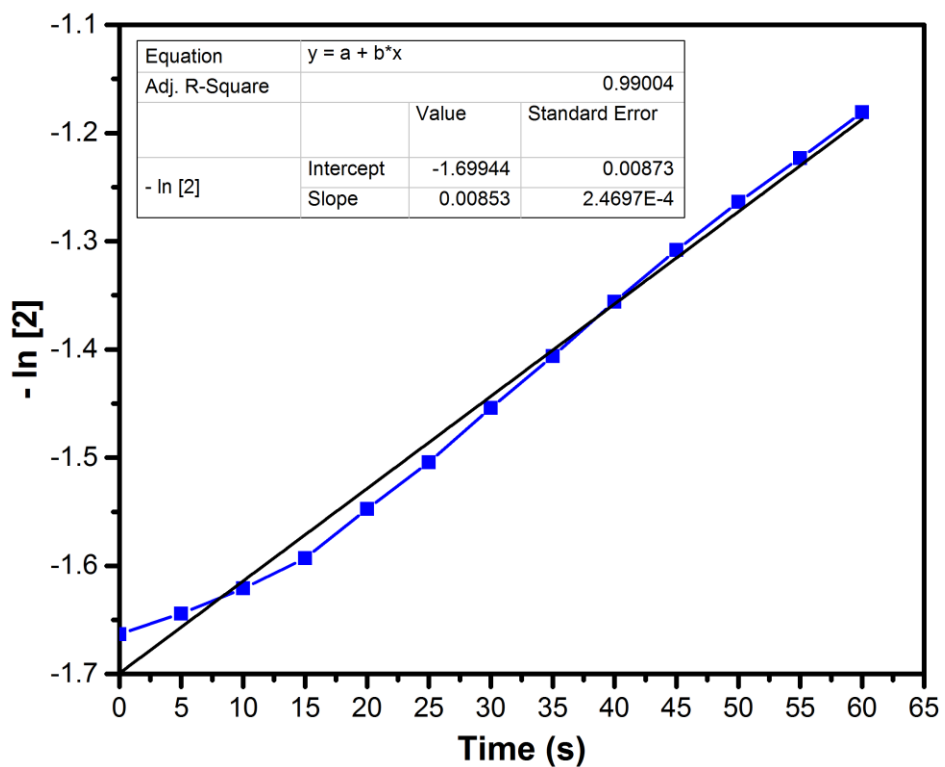
Figure S 1. Plot of -ln [**2**] versus time using **1** as the initiator. Conditions: $[2]_0 = 5.28$ M, $[2]_0/[1]_0 = 450$, 65 °C, neat.

Equation	$y = a + b*x$		
Adj. R-Square			0.88289
		Value	Standard Error
- ln [2]	Intercept	-1.35075	0.00528
	Slope	0.00143	1.49258E-4
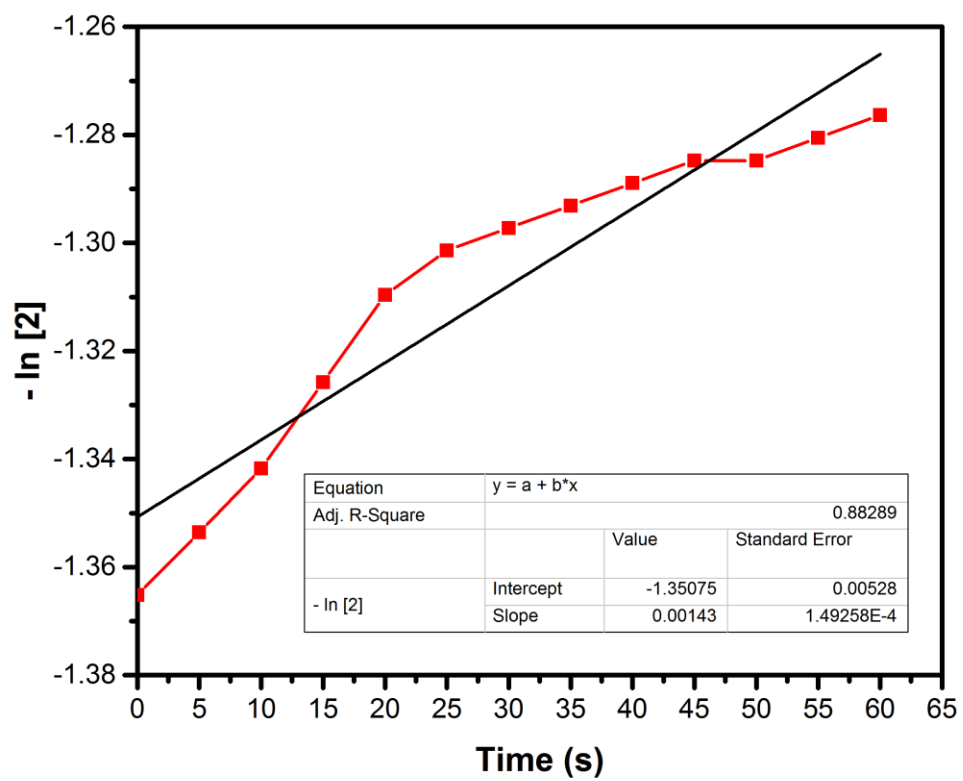
Figure S 2. Plot of -ln [**2**] versus time using in situ generated **1**$_{red}$ as the initiator. Conditions: [**2**]$_0$ = 4.45 M, [**2**]$_0$/[**1**]$_0$ = 450, 65 °C, 1,2-dichlorobenzene.

Equation	y = a + b*x	
Adj. R-Square		0.97085
	Value	Standard Error
Intercept	-0.73183	0.00156
- ln [2] Slope	4.31951E-4	1.93058E-5

Equation	y = a + b*x	
Adj. R-Square		0.99916
	Value	Standard Error
Intercept	-1.01478	0.0045
- ln [2] Slope	0.00249	2.40249E-5

Equation	y = a + b*x	
Adj. R-Square		0.95621
	Value	Standard Error
Intercept	-0.99397	0.01177
- ln [2] Slope	0.0075	6.52899E-4

Figure S 3. Plot of -ln [**2**] versus time using **1** as the initiator followed by the reduction and re-oxidation of the catalyst using $CoCp_2$ (1.5 equiv. rel. to **1**) and DDQ (1.5 equiv. rel. to added $CoCp_2$), respectively (indicated).

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Equation	y = a + b*x		
Adj. R-Square			0.98975
		Value	Standard Error
- ln [4]	Intercept	-2.02693	0.00823
	Slope	0.00793	2.32899E-4

Figure S 4. Plot of -ln [**4**] versus time using **1** as the initiator. Conditions: $[\mathbf{4}]_0 = 7.55$ M, $[\mathbf{4}]_0/[\mathbf{1}]_0 = 450$, 50 °C, neat.
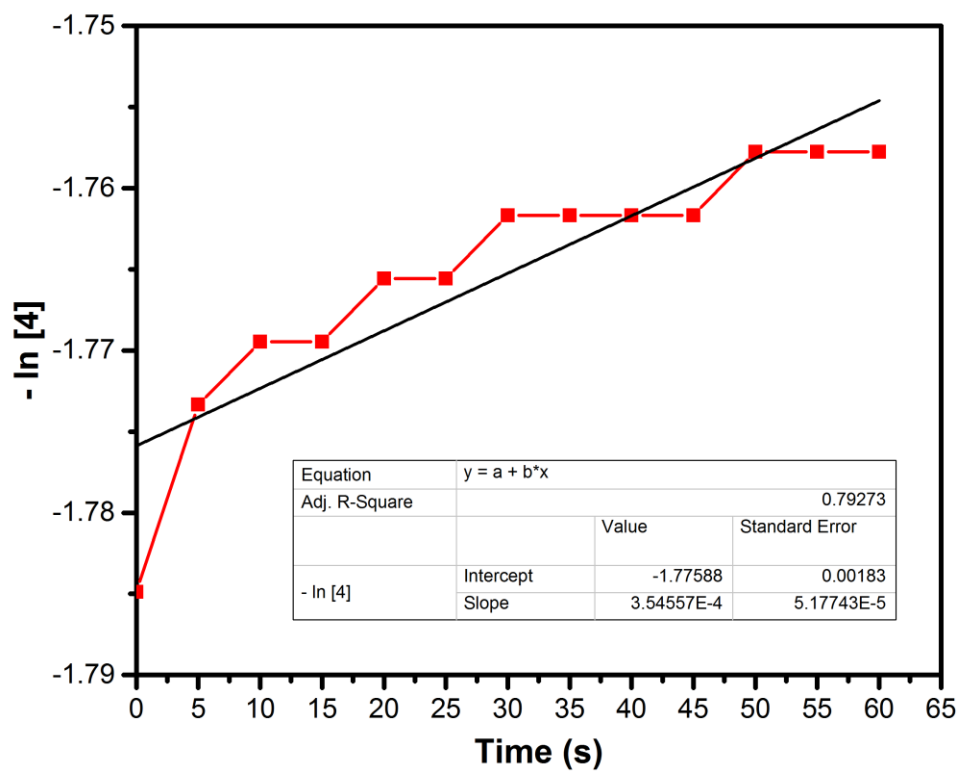
Figure S 5. Plot of -ln [**4**] versus time using in situ generated **1**$_{red}$ as the initiator. Conditions: [**4**]$_0$ = 5.96 M, [**4**]$_0$/[**1**]$_0$ = 450, 50 °C.
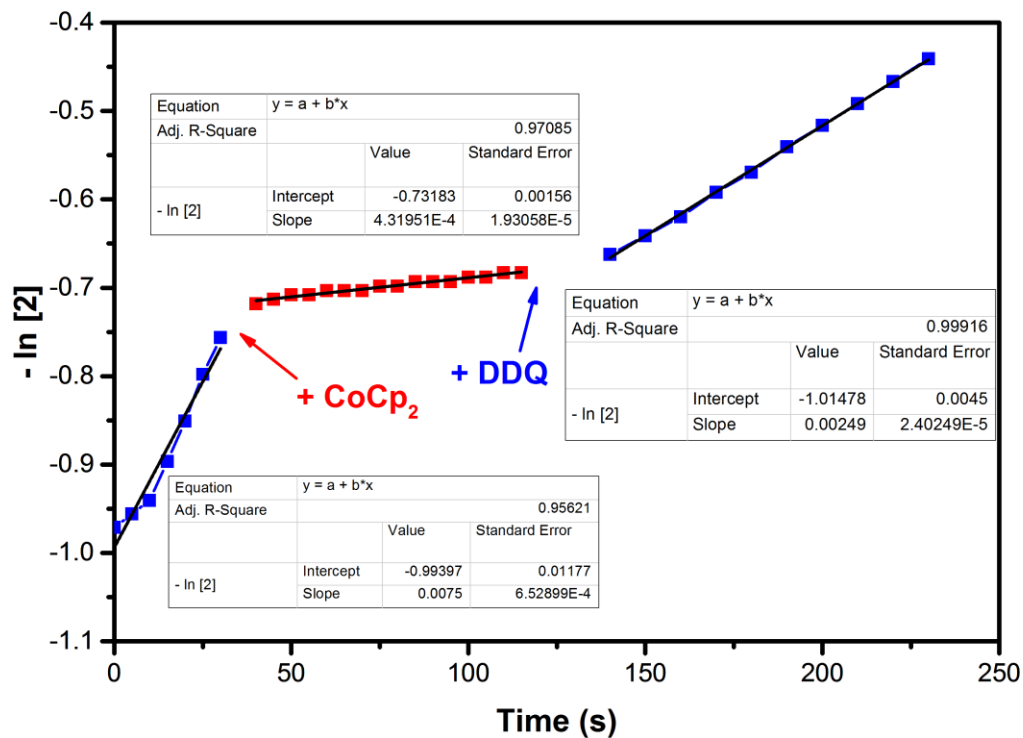
Figure S 6. Plot of -ln [**4**] versus time using 1 as the initiator followed by the reduction and re-oxidation of the catalyst using CoCp$_2$ (1.5 equiv. rel. to **1**) and DDQ (1.5 equiv. rel. to added CoCp$_2$), respectively (indicated).
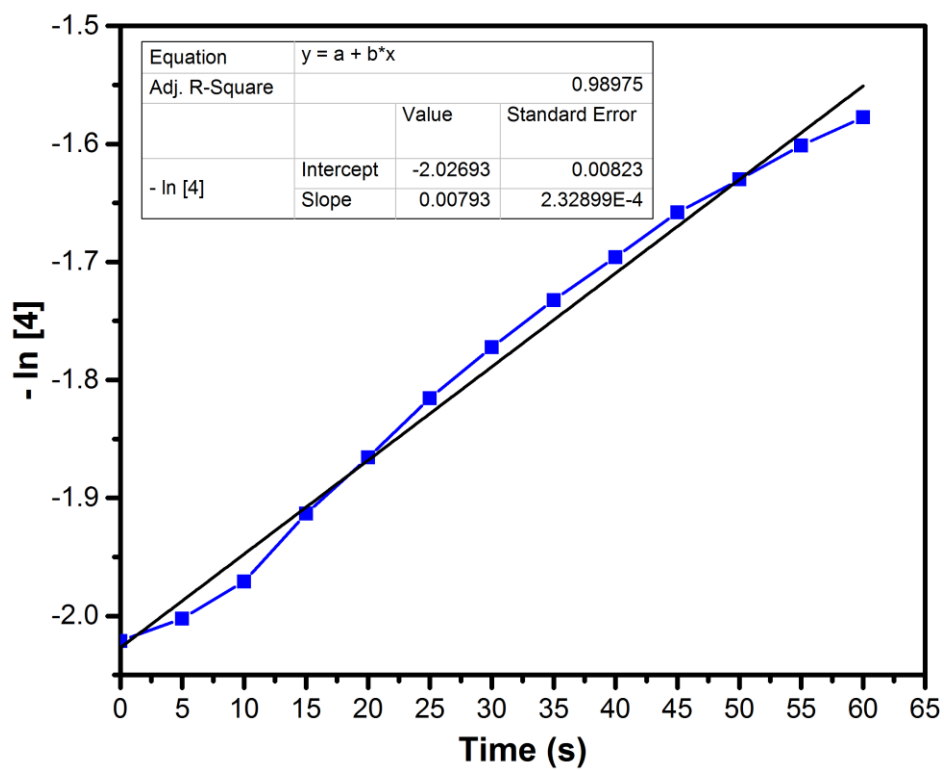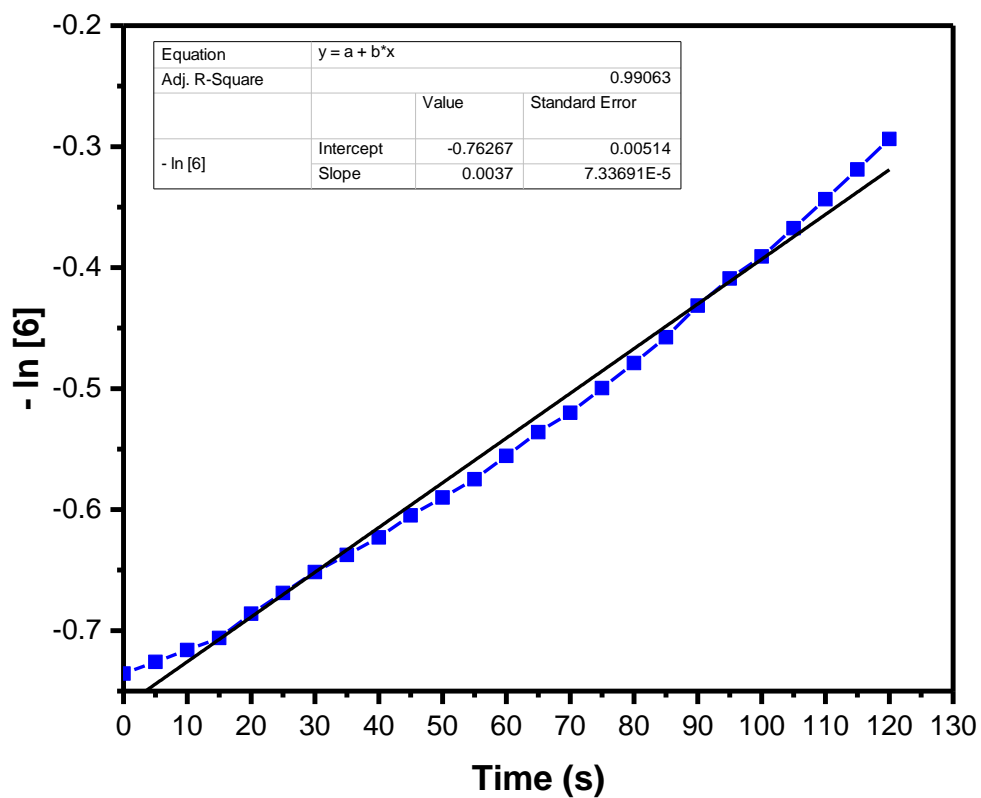
Figure S 7. Plot of -ln [**6**] versus time using **1** as the initiator. Conditions: [**6**]$_0$ = 2.09 M, [**6**]$_0$/[**1**]$_0$ = 450, 60 °C, 1,2-dichlorobenzene.
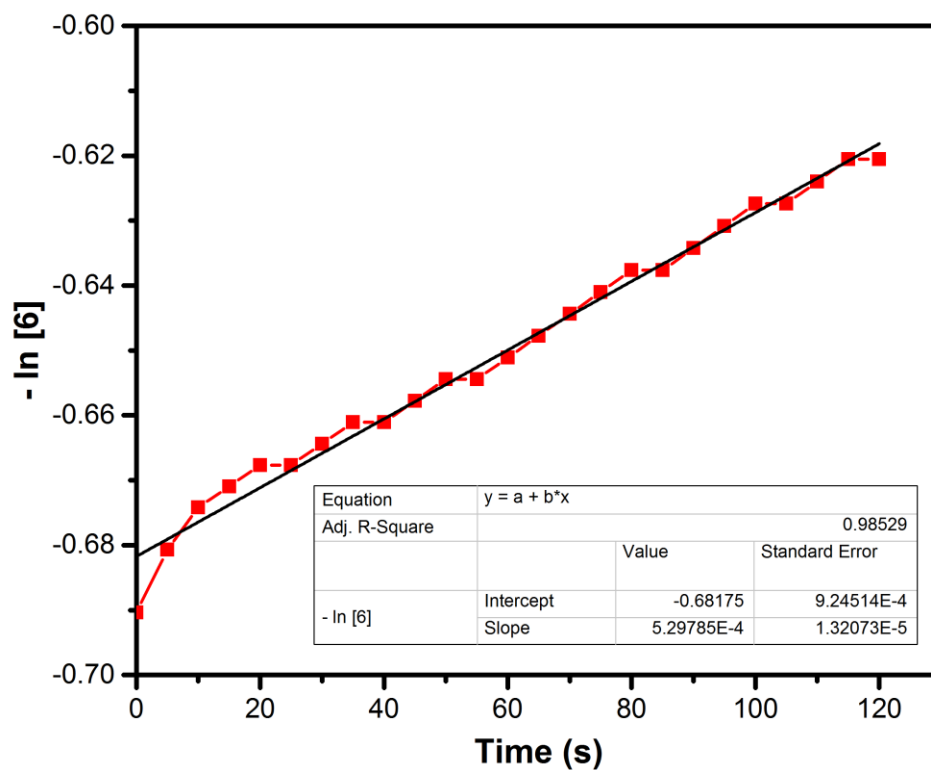
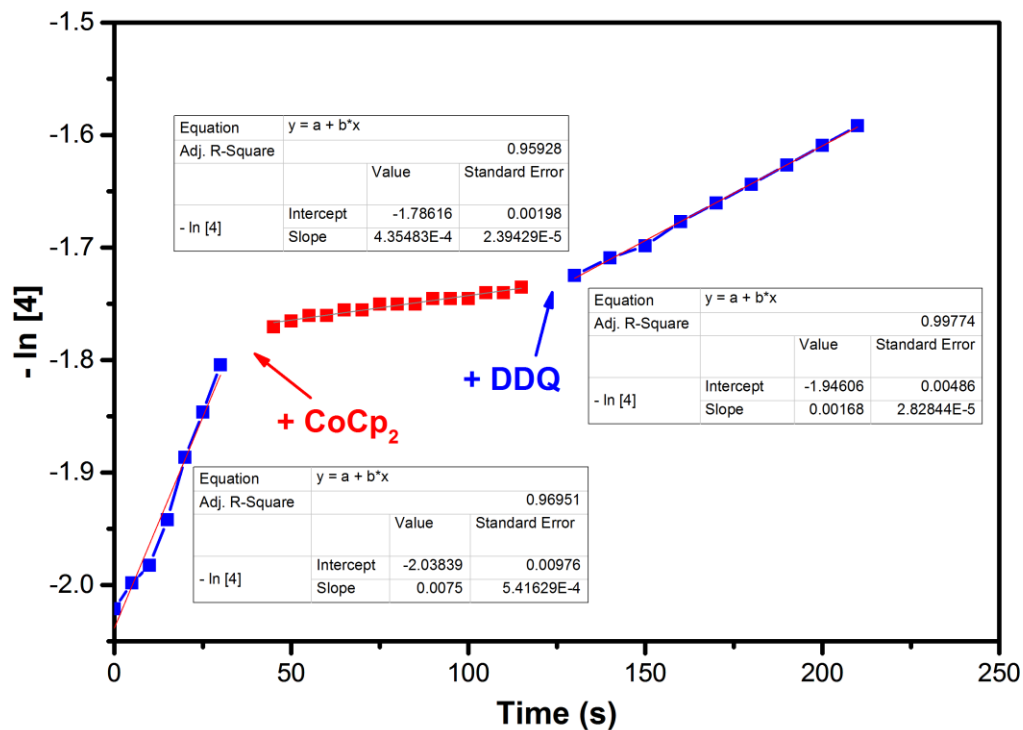| Equation	y = a + b*x		
Adj. R-Square			0.98529
		Value	Standard Error
- ln [6]	Intercept	-0.68175	9.24514E-4
	Slope	5.29785E-4	1.32073E-5

Figure S 8. Plot of -ln [**6**] versus time using in situ generated **1**$_{red}$ as the initiator. Conditions: [**6**]$_0$ = 1.99 M, [**6**]$_0$/[**1**]$_0$ = 450, 60 °C, 1,2-dichlorobenzene.

Equation	y = a + b*x		
Adj. R-Square			0.98032
		Value	Standard Error
- ln [6]	Intercept	-0.61389	0.00636
	Slope	9.72605E-4	5.20115E-5

+ CoCp$_2$

+ DDQ

Equation	y = a + b*x		
Adj. R-Square			0.99841
		Value	Standard Error
- ln [6]	Intercept	-0.82524	0.00796
	Slope	0.00198	3.52793E-5

Equation	y = a + b*x		
Adj. R-Square			0.98859
		Value	Standard Error
- ln [6]	Intercept	-0.7415	0.00236
	Slope	0.00235	7.97973E-5

Figure S 9. Plot of -ln [**6**] versus time using **1** as the initiator followed by the reduction and re-oxidation of the catalyst using CoCp$_2$ (1.0 equiv. rel. to **1**) and DDQ (1.5 equiv. rel. to added CoCp$_2$), respectively (indicated).
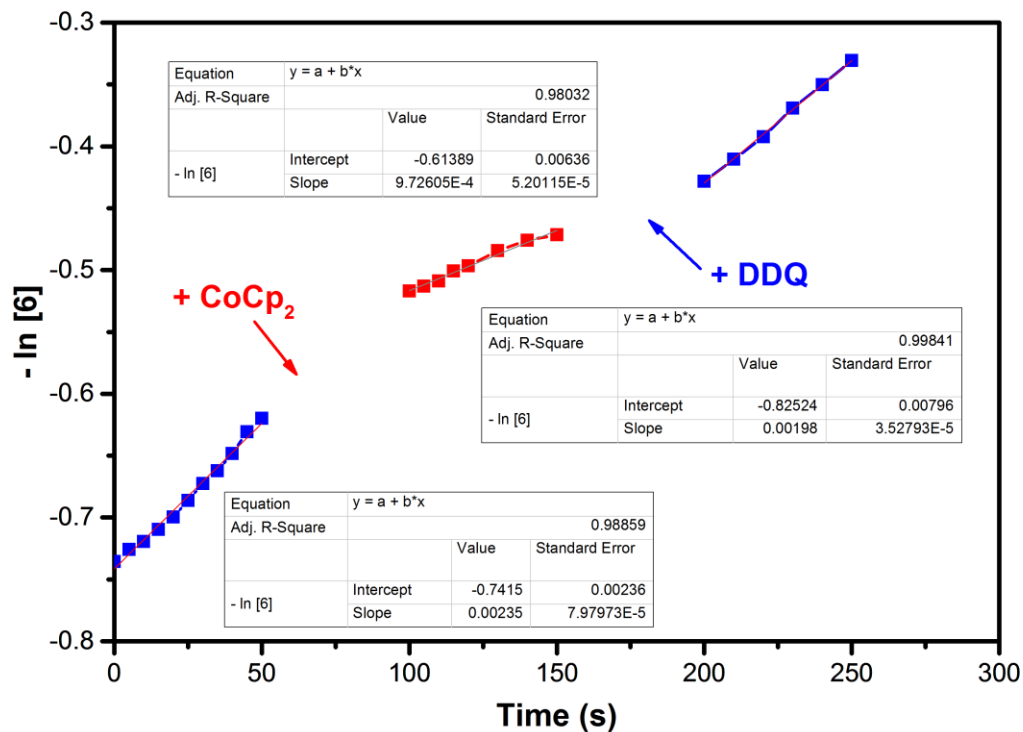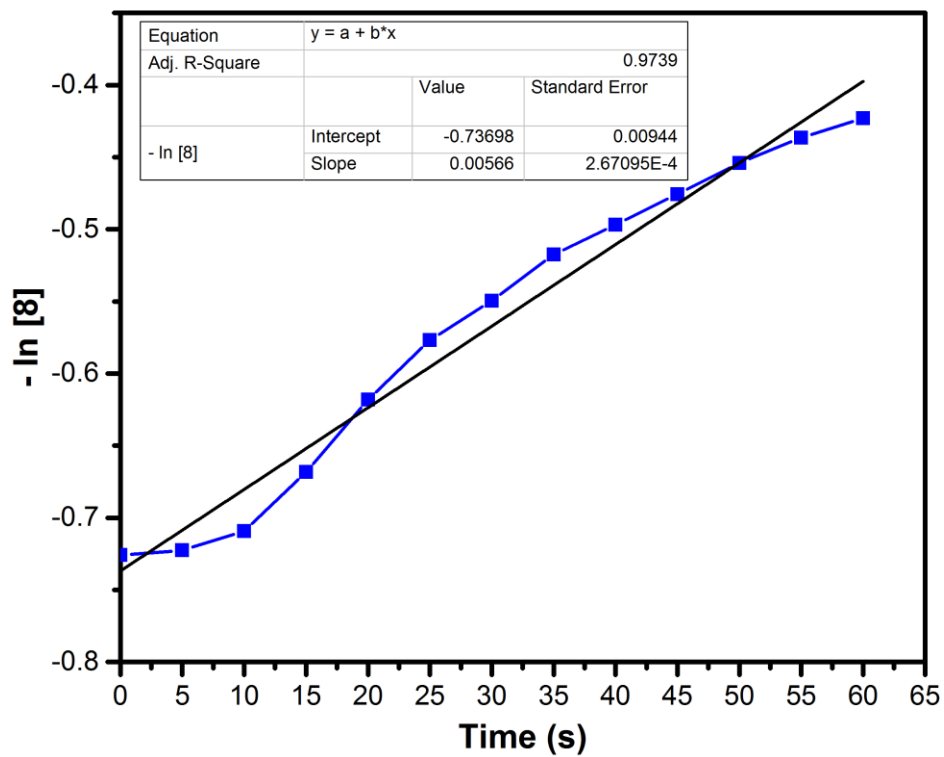
Equation	y = a + b*x		
Adj. R-Square			0.9739
		Value	Standard Error
- ln [8]	Intercept	-0.73698	0.00944
	Slope	0.00566	2.67095E-4

Figure S 10. Plot of -ln [**8**] versus time using **1** as the initiator. Conditions: [**8**]$_0$ = 2.07 M, [**8**]$_0$/[**1**]$_0$ = 450, 60 °C, 1,2-dichlorobenzene.
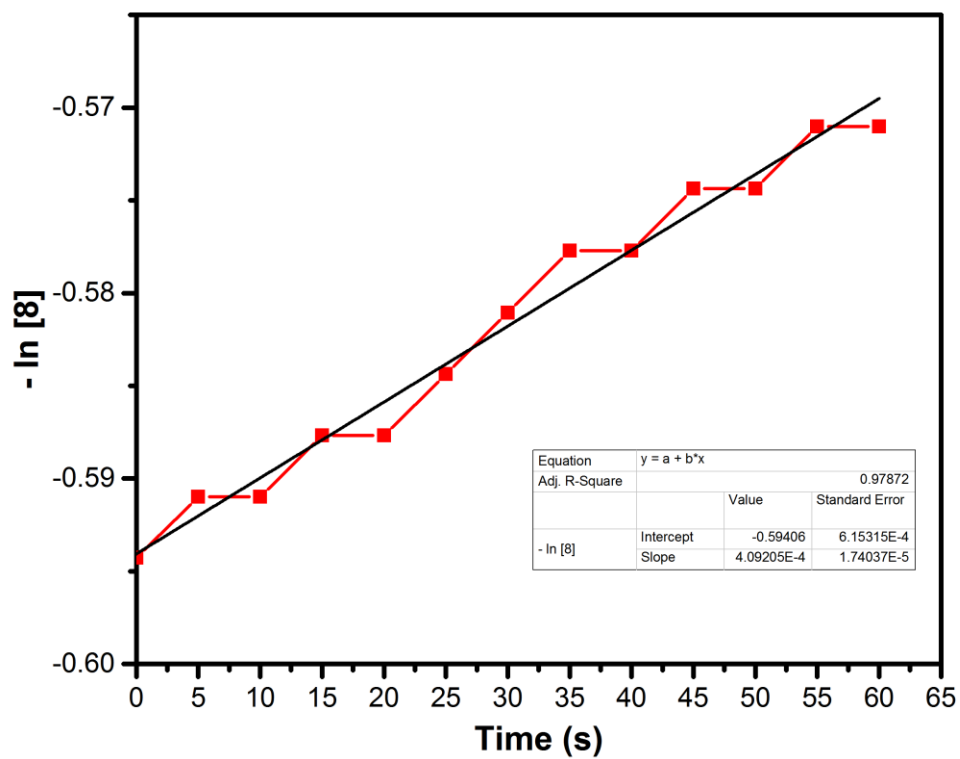
Equation	y = a + b*x		
Adj. R-Square			0.97872
		Value	Standard Error
- ln [8]	Intercept	-0.59406	6.15315E-4
	Slope	4.09205E-4	1.74037E-5

Figure S 11. Plot of -ln [**6**] versus time using in situ generated **1$_{red}$** as the initiator. Conditions: [**6**]$_0$ = 1.81 M, [**6**]$_0$/[**1**]$_0$ = 450, 60 °C, 1,2-dichlorobenzene.
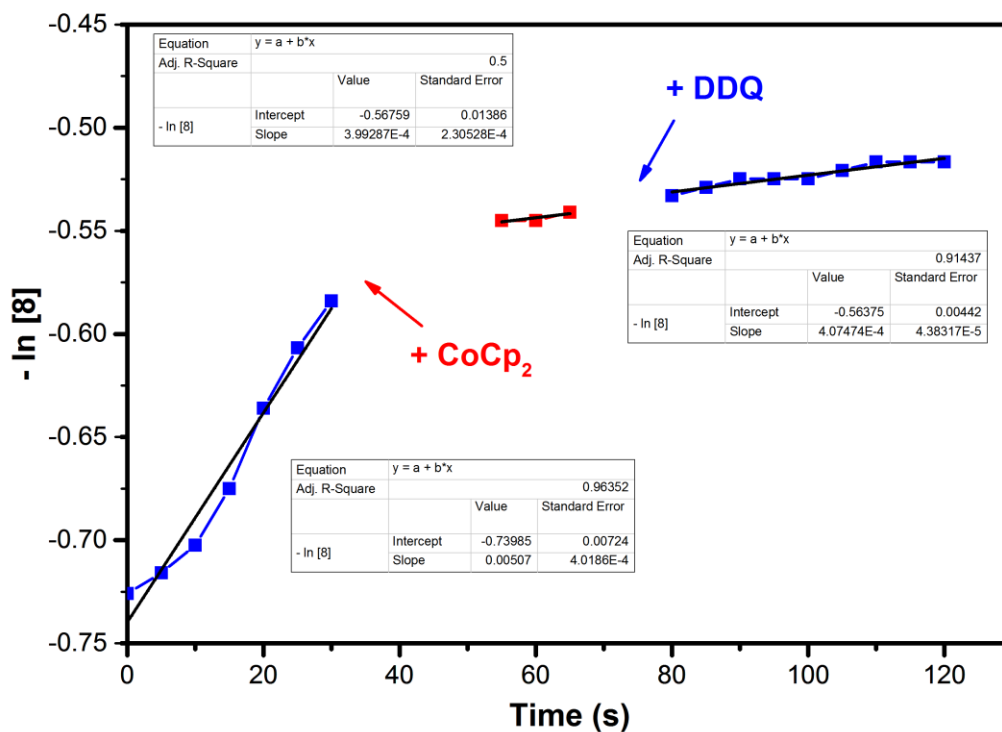
Figure S 12. Plot of -ln [**8**] versus time using **1** as the initiator followed by the reduction and re-oxidation of the catalyst using CoCp$_2$ (1.0 equiv. rel. to **1**) and DDQ (1.5 equiv. rel. to added CoCp$_2$), respectively (indicated).
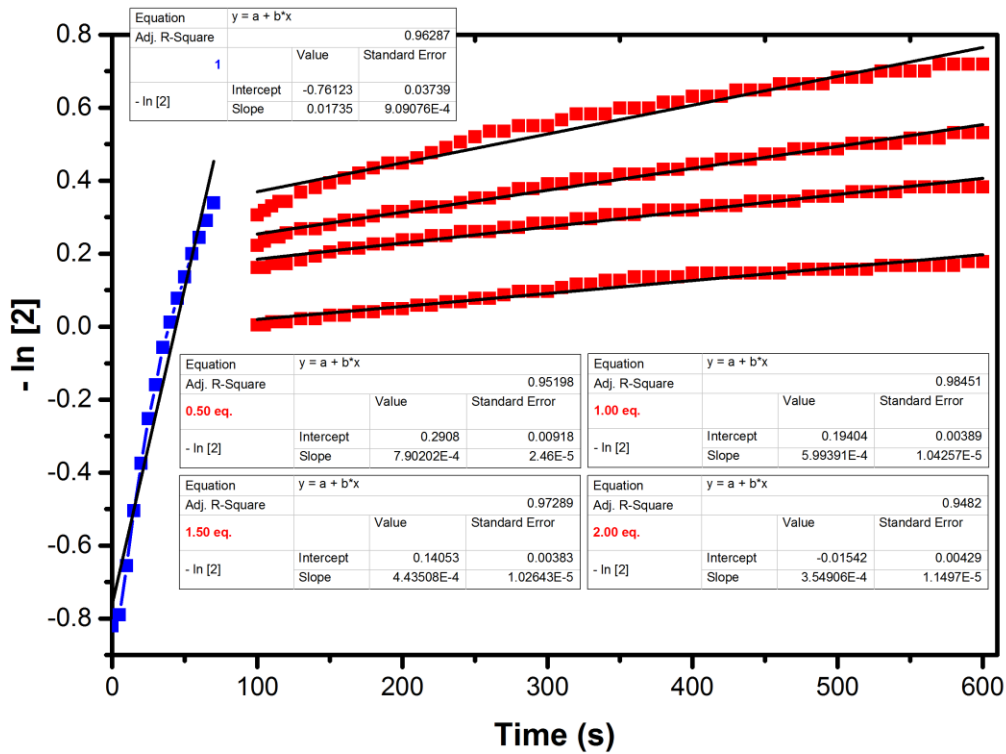
Figure S 13. Plot of -ln [**2**] versus time using **1** as the initiator (blue line) and using different equivalent of CoCp$_2$ (red lines).
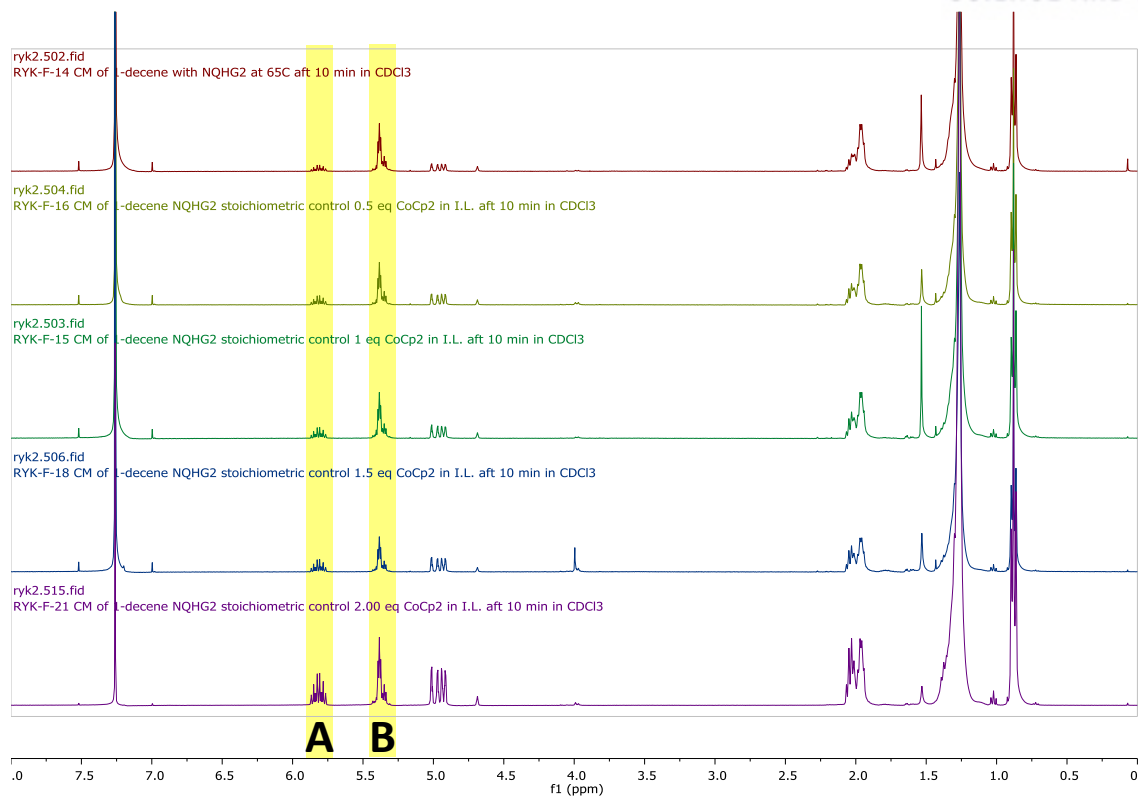
Figure S 14. Representative ^{1}H NMR spectra recorded for the CM of **2** using **1** in conjunction with various quantities of added CoCp$_2$. The signals labeled as "A" were assigned to the proton on terminal olefin in **2**. The signals labels as "B" were assigned to two protons on internal olefin in **3**. The integrated values were used to determine conversions (see Table S1).

Table S 1. ^{1}H NMR integration values as obtained from the spectra shown in Figure S14 and generated using a data analysis option implemented in the Mestrelab Mnova software package (v.10.0.2).

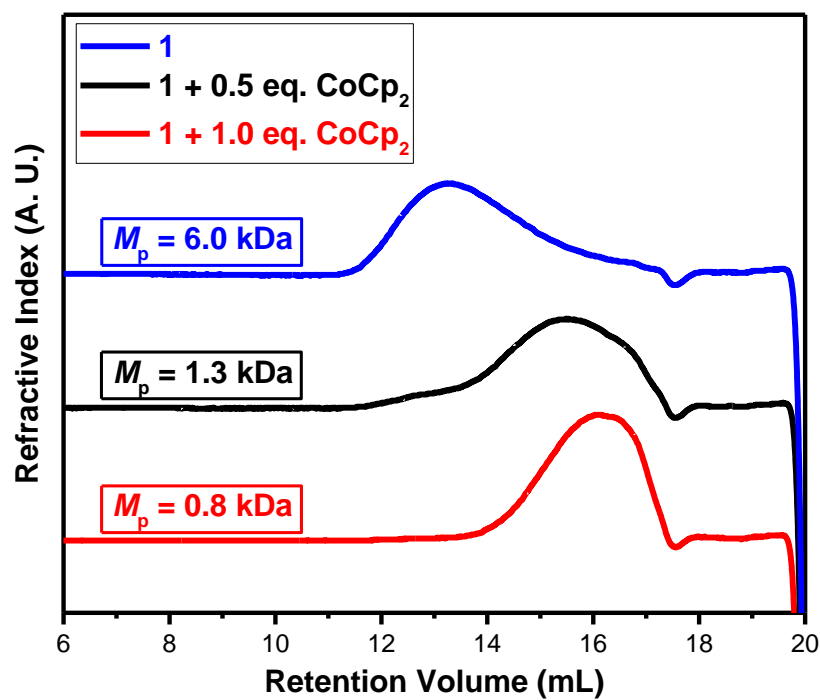| Equivalents of added $CoCp_2$ relative to **1**	Integrated value of **A** (I_A)	Integrated value of **B** (I_B)	Conversion $I_B/(I_A+I_B) \times 100\%$	Conversion as determined by gas evolution (%)
0.00	1.00	6.58	87	82
0.50	1.00	4.07	80	79
1.00	1.00	3.77	79	74
1.50	1.00	2.58	72	70
2.00	1.00	1.80	64	63

Figure S 15. Gel permeation chromatograms of a polymer obtained from 1,9-decadiene as catalyzed with **1** (blue line), **1** + 0.5 eq. CoCp$_2$ (black line) or **1** + 1.0 eq. CoCp$_2$ (red line).