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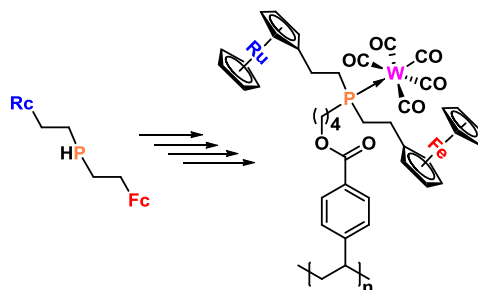
A Phosphine-Based Heterotrimetallic (M = Fe, Ru, W) Homopolymer

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Supporting Information Placeholder

ABSTRACT: An organometallic homopolymer containing three different metals per repeating unit was synthesized from an air- and moisture-stable secondary phosphine bearing ethylferrocene and ethylruthenocene groups. Hydrophosphination yielded a tertiary phosphine bearing an alcohol, which was then used to introduce a polymerizable styrene group via DCC coupling. Free-radical polymerization, followed by post-polymerization coordination to photogenerated $W(CO)_5$ units yielded the title polymer, which showed thermal, spectroscopic, and electrochemical properties associated with each of the transition metals involved.

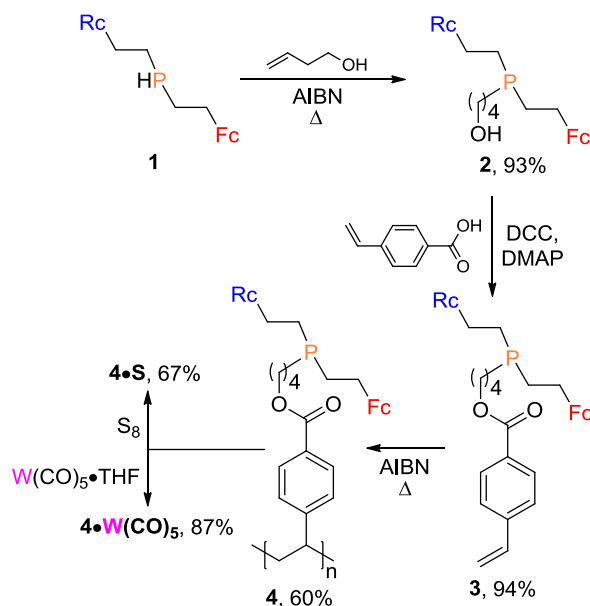


Metallopolymers have long received interest due to the combination of traits they possess, including the thermal/solution processability traditionally associated with polymers and the functionality (*e.g.*, redox activity, magnetism, catalysis) associated with transition metals.¹⁻⁴ The complexity of metallopolymer structures has increased as the field has evolved, and metallopolymers bearing multiple transition metals per repeating unit are now being targeted. Several strategies for the production of heterobimetallic polymers exist, including: post-polymerization functionalization,⁵⁻⁷ polymerization of heterobimetallic monomers,^{6,8-10} and copolymerization of monomers containing different metals.¹¹⁻¹⁴

While advances in synthetic protocols have been widespread, heterotrimetallic polymers that take advantage of the properties of three different metals remain scarce.¹⁵⁻¹⁶ In this brief communication, we report the synthesis, characterization, and electrochemistry of a metallopolymer bearing three different transition metals per repeating unit. In doing so, we have also expanded the subclass of phosphorus-based metallopolymers.¹⁷⁻²²

The synthetic strategy employed in this study is outlined in Scheme 1. The radical-catalyzed hydrophosphination of 3-buten-1-ol starting from secondary phosphine **1**,²³ which bears ethylruthenocene and ethylferrocene substituents, resulted in the formation of tertiary phosphine **2** in 93% yield. DCC coupling (DCC = *N,N'*-dicyclohexylcarbodiimide) in the presence of dimethylaminopyridine (DMAP) yielded monomer **3** in 94% yield. These molecular species were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy, FT-IR and UV-Vis absorption spectroscopy, mass spectrometry and elemental analysis (Table S1, Figures S1–S8). The free-radical polymerization of phosphines and related sulfides/oxides dates back to the 1960s.²⁴ In this case, free-radical polymerization of monomer **3** resulted in the formation of heterobimetallic polymer **4** (60%), with a polystyrene backbone. The pendant phosphine

moieties in polymer **4** were coordinated to $W(CO)_5$ units, which were generated via photolysis of $W(CO)_6$ in THF, to yield heterotrimetallic polymer **4•W(CO)₅** in 87% yield. The polymers described are soluble in CH_2Cl_2 and $CHCl_3$ and sparingly soluble in THF. They were characterized by ¹H and ³¹P NMR spectroscopy, FT-IR and UV-Vis absorption spectroscopy, and gel permeation chromatography (GPC) (Tables S1 and S2, Figures 1 and S9–S12).



Scheme 1. Synthesis of heterometallic polymers **4**, **4•S**, and **4•W(CO)₅**. Rc = ruthenocene, Fc = ferrocene.

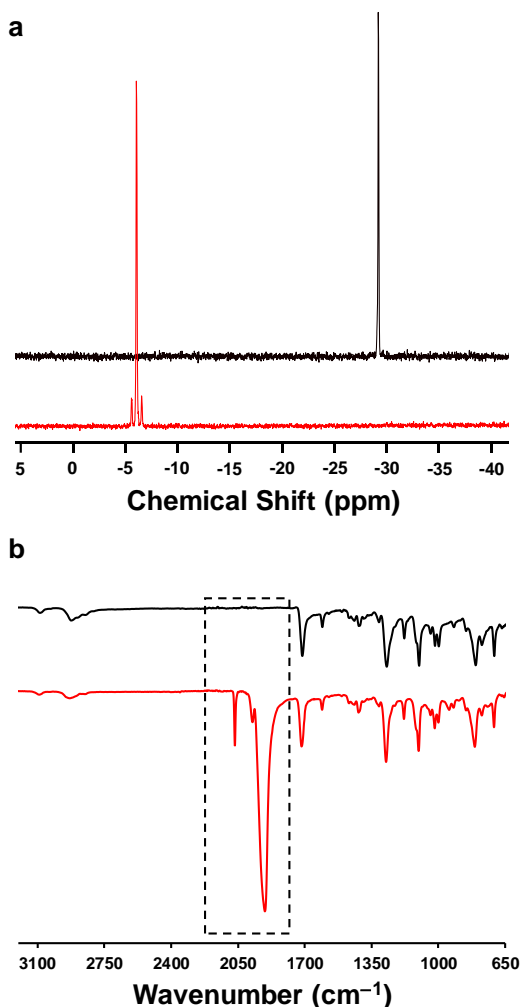


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (a) and FT-IR spectra (b) for polymers **4** (black lines) and **4**·**W(CO)₅** (red lines). The dashed box highlights the region of the IR spectra associated with carbonyl stretching frequencies.

The free-radical polymerization of monomer **3** was accompanied by the disappearance of the ^1H NMR signals associated with the mono-substituted alkene [6.76 ppm (d of d), 5.87 ppm (d), and 5.39 ppm (d)] group and the appearance of broad signals (1–2 ppm) associated with the saturated polystyrene backbone of polymer **4**. Upon coordination of each of the phosphine groups present in polymer **4** to **W(CO)₅**, the singlet observed in the ^{31}P NMR spectrum of polymer **4** (δ : -29.2 ppm) disappeared. Polymer **4**·**W(CO)₅** gave rise to a new ^{31}P NMR signal (δ : -6.1 ppm) upfield of that of the free phosphine polymer. The shifted signal was accompanied by satellites associated with ^{31}P - ^{183}W coupling ($^1J_{\text{PW}} = 233$ Hz), confirming that each pendant phosphine group had been coordinated to tungsten (Figure 1a). FT-IR spectroscopy was also used to monitor the post-polymerization coordination chemistry. As demonstrated in Figure 1b, three different CO stretches [$\nu(\text{CO})$: 1909, 1974, and 2066 cm^{-1}] were observed in the spectrum of **4**·**W(CO)₅**, which was otherwise very similar to that of polymer **4**. These data are consistent with those of closely related molecular species,²⁵ and support our previous conclusion that the pendant phosphine groups have been quantitatively converted to the corresponding $\text{R}_3\text{P} \rightarrow \text{W}(\text{CO})_5$ complexes.

GPC analysis of polymers **4** and **4**·**W(CO)₅** proved challenging. The polymers are poorly soluble in common GPC solvents, including H_2O and DMF, and had limited solubility in THF. Furthermore, the direct analysis of polymer **4** was not possible due to significant polymer-column interactions, requiring conversion to **4**·**S** through oxidation with elemental sulfur. The GPC data collected for the soluble portions **4**·**S** and **4**·**W(CO)₅** in THF represent minimum estimates of their molecular weights, and confirm their high polymer character (Table S2, Figure S13, **4**·**S**: $M_n = 9,700$ g mol^{-1} , $D = 1.46$; **4**·**W(CO)₅**: $M_n = 11,600$ g mol^{-1} , $D = 2.41$). It must be noted that the GPC trace collected for **4**·**W(CO)₅** also contained evidence of aggregate formation, potentially caused by intermolecular reactions involving the relatively polar carbonyl groups. Prolonged stirring in warm THF, even in dilute solution, did not result in the removal of the aggregate species in solution.

The differential scanning calorimetry (DSC) data collected for **4** and **4**·**W(CO)₅** were consistent with the hypothesis that the **W(CO)₅** groups enhance intermolecular interactions. This behavior is manifested as an increase in glass transition temperature (T_g) from 52 $^\circ\text{C}$ for **4** to 92 $^\circ\text{C}$ for **4**·**W(CO)₅** (Figure S14). Thermal gravimetric analysis (TGA) also revealed marked differences for polymers **4** and **4**·**W(CO)₅**. The onset of decomposition was *ca.* 220 $^\circ\text{C}$ for both polymers, and significantly, the char yields at 1000 $^\circ\text{C}$ of 24.0% (**4**) and 32.1% [**4**·**W(CO)₅**] were consistent with the metal content for the respective polymers (22.2% and 32.0%) (Figure S15).

The UV-Vis absorption spectra for each of the molecular and polymeric species described contain features associated with formally forbidden $d \rightarrow d$ transitions arising from ferrocene (*ca.* 440 nm) and ruthenocene (*ca.* 320 nm) that were consistent with those observed for related phosphines and metal complexes (Figure S16).^{23,25}

The electrochemical properties of compounds **1–3** and polymers **4** and **4**·**W(CO)₅** were explored using cyclic voltammetry (Table S1, Figures 2, S17–S18). The supporting electrolyte chosen for these studies was $[n\text{-Bu}_4\text{N}][\text{OTf}]$, as the triflate anion enhances the solubility of the electrogenerated polycations implicated in these studies. The voltammogram recorded for **4** is comprised of several distinct features, including: an irreversible wave at -150 mV (relative to the ferrocene/ferrocenium redox couple) associated with the oxidation of ferrocene in species adsorbed to the working electrode surface,^{23,26–27} a ferrocene oxidation wave with reversible character at -15 mV, and an irreversible oxidation associated with ruthenocene at 400 mV. The current response of the wave centered at -150 mV was less than that expected for a one-electron process, ruling out the possibility that it results from phosphine oxidation. Furthermore, the adsorption behavior observed has been previously explored in detail for closely related phosphines.^{21,23–24} The electrochemical properties of ruthenocene are far more complex than those of ferrocene, due to the extremely Lewis acidic character of ruthenocenium that often leads to the formation of acid/base adducts and/or disproportionation and dimerization reactions.^{23,28–29} This behavior is responsible for the irreversible character of the ruthenocene oxidation wave, and also effects the shape and symmetry of the ferrocene wave mentioned above. Upon coordination to tungsten, the electrochemical properties of **4**·**W(CO)₅** changed dramatically, revealing independent electrochemical features associated with each of the transition metals present. Firstly, as has been observed for related

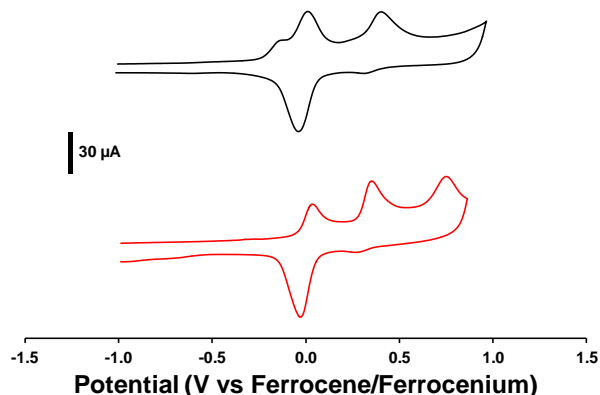


Figure 2. Cyclic voltammograms recorded at 250 mV s^{-1} for 1 mM THF solutions of polymers **4** (black line) and **4•W(CO)₅** (red line) containing 0.1 M $[n\text{-Bu}_4\text{N}][\text{OTf}]$ as supporting electrolyte.

molecular species,²⁵ the irreversible wave associated with phosphine adsorption at the working electrode disappeared. The ferrocene oxidation (0 mV) became less symmetric and was shifted slightly to more positive potentials. The irreversible oxidation of the ruthenocene moieties, observed at a potential of 350 mV, was once again observed for **4•W(CO)₅** and was essentially unchanged. Finally, an irreversible wave corresponding to the oxidation of tungsten was observed at a potential of 750 mV. This behavior was consistent with that observed for related halopentacarbonyltungsten complexes.^{30–31}

In this work, we have described the synthesis and characterization of polymers bearing two and three different metals per repeating unit. The polymers display thermal, spectroscopic, and electrochemical properties associated with each transition metal. We feel that the synthetic strategy described has the potential to open up a new area of metallopolymer chemistry, and our future work in this area will focus on expanding the scope of the chemistry of phosphine-based heterotrimetallic polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, NMR and UV-Vis absorption spectra, DSC, TGA, and GPC data, and CVs (PDF).

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Notes

The authors declare no competing financial interest.

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Supporting Information

A Phosphine-Based Heterotrimetallic (M = Fe, Ru, W) Homopolymer

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EXPERIMENTAL DETAILS

General Considerations

Reactions and manipulations were carried out under a N₂ atmosphere using standard glove box or Schlenk techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories and Fischer Scientific, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. Reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received, aside from W(CO)₆, which was sublimed at 50 °C under vacuum and stored under N₂. Secondary phosphine **1** was synthesized according to a reported protocol.¹ UV irradiation experiments were conducted using a custom built UV light source equipped with four high intensity light emitting diodes (LEDs) with irradiation peak centered at 350 nm. ¹H, ¹³C{¹H};, and ³¹P NMR spectra were recorded on a 600 MHz (¹H: 599.5 MHz; ¹³C{¹H}: 150.8 MHz; ³¹P: 242.6 MHz) Varian INOVA instrument. ¹H NMR spectra were referenced to residual CHCl₃ (7.27 ppm) and ¹³C{¹H} NMR spectra were referenced to CDCl₃ (77.0 ppm). Mass spectrometry data were recorded in positive-ion mode and using a high resolution Finnigan MAT 8400 or Micromass LCT electrospray ionization time-of-flight mass spectrometer. UV-vis absorption spectra were recorded using a Cary 300 Scan instrument. FT-IR spectra were recorded using a PerkinElmer Spectrum Two FTIR spectrometer with an attenuated total reflectance (ATR) attachment and a single reflection diamond.

Purity of New Compounds

The purity of compounds **2** and **3** were established using ¹H, ¹³C, and ³¹P NMR spectroscopy along with elemental analysis. In the case of compound **3**, the elemental analysis results for carbon were outside the range viewed as establishing analytical purity. However, these data are provided to illustrate the best values obtained to date and are supplemented by very clean ¹H, ¹³C, and ³¹P NMR spectra. Polymers **4**, **4•S** and **4•W(CO)₅** do not thermally decompose to volatile materials (see Figure S15). Furthermore, residual solvent peaks could not be removed due to the polymeric nature of these compounds. We are confident that the ¹H and ³¹P NMR spectra of these polymers demonstrate that the impurities present are limited to common organic solvents employed during their isolation.

Cyclic Voltammetry

Cyclic voltammograms were collected using a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum wire counter electrode, and silver wire *pseudo*-reference electrode. In a glovebox, 1 mM solutions of the analytes in dry and degassed THF were prepared and stirred overnight, before they were combined with supporting electrolyte (0.1 M [*n*-Bu₄N][OTf]) and run at a scan rate of 250 mV s⁻¹. Cyclic voltammograms were referenced relative to a decamethylferrocene internal standard (1 mM, -385 mV relative to ferrocene/ferrocenium under identical conditions) and corrected for internal cell resistance using the BASi Epsilon software.

Gel Permeation Chromatography

Solutions of polymers were prepared by combining **4•S** and **4•W(CO)₅** with chromatography-grade THF (5 mg mL⁻¹), stirring for 24 h, and filtering (Nylon membrane, 0.2 μm) before the gel permeation chromatography (GPC) experiments were conducted. The resulting solutions were analyzed using a Viscotek GPCmax VE 2001 GPC instrument equipped with an Agilent PolyPore guard column (PL1113-1500) and two sequential Agilent PolyPore GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles (MW range: 200–2,000,000 g mol⁻¹; PL1113-6500) regulated at a temperature of 30 °C. Signal responses were measured using a Viscotek VE 3580 RI detector, and molecular weights were determined by comparison of the maximum RI response with a calibration curve (10 points, 1,500–786,000 g mol⁻¹) established using monodisperse polystyrene standards purchased from Viscotek.

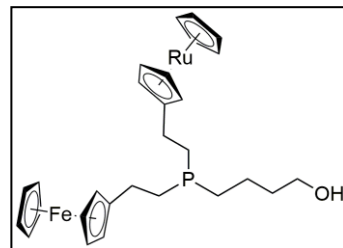
Thermal Analysis

Thermal degradation studies were performed using a TA Instruments Q50 TGA instrument under an atmosphere of N₂. Samples were placed in a platinum pan and heated at a rate of 10 °C min⁻¹ from 20 °C to 1000 °C under a flow of N₂ (60 mL min⁻¹). Glass transition temperatures were determined under an atmosphere of N₂ using differential scanning calorimetry (DSC) on a TA Instruments DSC Q20. The polymer samples were placed in an aluminum Tzero pan and heated from room temperature to the maximum temperature [200 °C for **4** and 180 °C for **4•W(CO)₅**] at

10 °C min⁻¹ under a flow of N₂ (50 mL min⁻¹) and cooled to -70 °C at 10 °C min⁻¹, before they underwent two more heat/cool cycles. The T_gs were determined from the second heat/cool cycle.

Preparation of Tertiary Phosphine 2

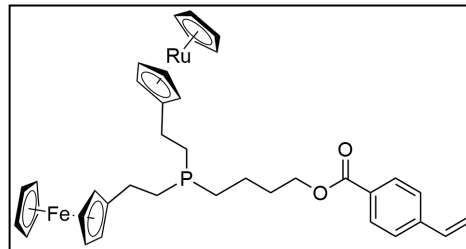
In a sealed tube, secondary phosphine **1** (1.00 g, 1.99 mmol), 3-buten-1-ol (500 μL, 5.81 mmol, 2.9 equiv.), and AIBN (21 mg, 0.13 mmol, 0.065 equiv.) were combined with THF (5 mL) before the mixture was heated with stirring for 24 h at 75 °C. After cooling to



room temperature, the resulting orange solution was concentrated *in vacuo*, dissolved in a minimum amount of CH₂Cl₂ and transferred to a silica/hexanes column (1'' × 6''). Using N₂ pressure and a 5:1 hexanes:Et₂O solvent mixture as eluent, tertiary phosphine **2** (R_f = 0.22) was isolated from the column. The solution containing **2** was concentrated *in vacuo* to yield an orange solid that was dried overnight *in vacuo* at 80 °C in the presence of P₂O₅. Yield = 1.06 g, 93%. M.p. 64–66 °C. ¹H NMR: δ 4.54 [s, 2H, β-C₅H₄R (Rc)], 4.53 [s, 5H, C₅H₅ (Rc)], 4.46 [s, 2H, α-C₅H₄R (Rc)], 4.12 [s, 5H, C₅H₅ (Fc)], 4.10 [s, 2H, β-C₅H₄R (Fc)], 4.07 [s, 2H, α-C₅H₄R (Fc)], 3.68 (t, 2H, ³J_{HH} = 7 Hz, PCH₂CH₂CH₂CH₂OH), 2.49–2.43 [m, 2H, FcCH₂CH₂P], 2.35–2.29 [m, 2H, RcCH₂CH₂P], 1.71–1.66 (m, 2H, PCH₂CH₂CH₂CH₂OH), 1.66–1.61 [m, 2H, FcCH₂CH₂P], 1.61–1.57 [m, 2H, RcCH₂CH₂P], 1.57–1.50 (m, 2H, PCH₂CH₂CH₂CH₂OH), 1.39–1.47 (m, 2H, PCH₂CH₂CH₂CH₂OH). ¹³C{¹H} NMR: δ 93.9 (d, J_{CP} = 13 Hz), 89.8 (d, J_{CP} = 13 Hz), 70.5, 70.4, 69.4, 68.5, 67.8, 67.2, 62.4, 34.3 (d, J_{CP} = 10 Hz), 28.9 (d, J_{CP} = 13 Hz), 28.4 (d, J_{CP} = 13 Hz), 26.8 (d, J_{CP} = 13 Hz), 26.0 (d, J_{CP} = 16 Hz), 25.5 (d, J_{CP} = 15 Hz), 22.2 (d, J_{CP} = 13 Hz). ³¹P{¹H} NMR: δ -28.8 (s). FT-IR: 3306 (br), 3082 (w), 2926 (w), 2878 (w), 2862 (w), 1638 (w), 1408 (w), 1315 (w), 1227 (w), 1099 (m), 1036 (m), 1022 (m), 998 (m), 922 (w), 806 (s), 666(w) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 323 nm (ε = 300 M⁻¹ cm⁻¹) and 438 nm (ε = 100 M⁻¹ cm⁻¹). Mass Spec. (ESI, +ve mode): exact mass calculated for [C₂₈H₃₆⁵⁶FeOP¹⁰²Ru]⁺: 577.0896; exact mass found: 577.0904; difference: +1.2 ppm. Anal. Calcd. (%) for C₂₈H₃₅OPFeRu: C, 58.44; H, 6.13. Found: C, 58.48; H, 6.14.

Preparation of Tertiary Phosphine Monomer 3

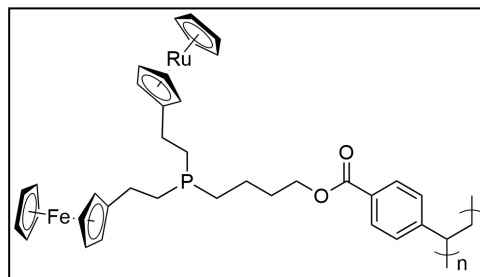
In a sealed tube and in the absence of external light/heat sources, 4-vinylbenzoic acid (0.30 g, 2.0 mmol, 1.15 equiv.), 4-(dimethylamino)pyridine (0.25 g, 2.0 mmol, 1.15 equiv.), and *N,N'*-dicyclohexylcarbodiimide (0.43 g,



2.1 mmol, 1.2 equiv.) were combined in dry CH_2Cl_2 (6 mL) and the resulting mixture was stirred for 15 min before tertiary phosphine **2** (1.00 g, 1.74 mmol) was added and the mixture stirred for an additional 90 min at room temperature. The resulting mixture was gravity filtered and the orange filtrate was concentrated *in vacuo*, before the resulting residue was dissolved in a minimum amount of CH_2Cl_2 and transferred to a silica/hexanes column (1'' \times 6''). Using N_2 pressure and a 4:1 hexanes: Et_2O solvent mixture as eluent, tertiary phosphine monomer **3** ($R_f = 0.29$) was isolated from the column. The solution containing **3** was concentrated *in vacuo* to yield an orange oil. Yield = 1.15 g, 94%. ^1H NMR: δ 8.01 (d, 2H, $^3J_{\text{HH}} = 8$ Hz, aryl CH), 7.46 (d, 2H, $^3J_{\text{HH}} = 8$ Hz, aryl CH), 6.76 (dd, 1H, $^3J_{\text{HH},\text{cis}} = 11$ Hz, $^3J_{\text{HH},\text{trans}} = 18$ Hz, ArCH=CH₂), 5.87 (d, 1H, $^3J_{\text{HH},\text{trans}} = 18$ Hz, ArCH=CH₂), 5.39 (d, 1H, $^3J_{\text{HH},\text{cis}} = 11$ Hz, ArCH=CH₂), 4.53 [s, 7H, β -C₅H₄R (Rc) and C₅H₅ (Rc)], 4.46 [s, 2H, α -C₅H₄R (Rc)], 4.36 (t, 2H, $^3J_{\text{HH}} = 7$ Hz, PCH₂CH₂CH₂CH₂OOC), 4.11 [s, 5H, C₅H₅ (Fc)], 4.08 [s, 4H, α -C₅H₄R (Fc) and β -C₅H₄R (Fc)], 2.52–2.41 [m, 2H, FcCH₂CH₂P], 2.37–2.27 [m, 2H, RcCH₂CH₂P], 1.97–1.81 (m, 2H, PCH₂CH₂CH₂CH₂OOC), 1.69–1.55 [m, 6H, FcCH₂CH₂P, RcCH₂CH₂P, and PCH₂CH₂CH₂CH₂OOC], 1.54–1.45 (m, 2H, PCH₂CH₂CH₂CH₂OOC). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 166.3, 141.8, 136.0, 129.8, 129.4, 126.1, 116.4, 93.8 (d, $J_{\text{CP}} = 12$ Hz), 89.7 (d, $J_{\text{CP}} = 12$ Hz), 70.5, 70.4, 69.4, 68.4, 67.8, 67.2, 64.4, 30.3 (d, $J_{\text{CP}} = 12$ Hz), 28.9 (d, $J_{\text{CP}} = 13$ Hz), 28.4 (d, $J_{\text{CP}} = 13$ Hz), 26.6 (d, $J_{\text{CP}} = 12$ Hz), 26.0 (d, $J_{\text{CP}} = 15$ Hz), 25.5 (d, $J_{\text{CP}} = 15$ Hz), 22.5 (d, $J_{\text{CP}} = 14$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ -29.0 (s). FT-IR: 3306 (br), 3088 (w), 2953 (m), 2922 (s), 2853 (m), 1710 (m), 1607 (w), 1461 (m), 1378 (w), 1270 (m), 1178 (w), 1101(m), 1016 (w), 995 (w), 914 (w), 804 (m), 781 (w), 711 (w) cm^{-1} . UV-vis (CH_2Cl_2): λ_{max} 322 nm ($\epsilon = 300 \text{ M}^{-1} \text{ cm}^{-1}$) and 440 nm ($\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$). Mass Spec. (EI, +ve mode): exact mass calculated for $[\text{C}_{37}\text{H}_{41}^{56}\text{FeO}_2\text{P}^{96}\text{Ru}]^+$: 700.1271; exact mass found: 700.1244; difference: -3.8 ppm. Anal. Calcd. (%) for $\text{C}_{37}\text{H}_{41}\text{O}_2\text{PFerRu}$: C, 62.98; H, 5.86. Found: C, 62.29; H, 5.78.

Preparation of Tertiary Phosphine Polymer 4

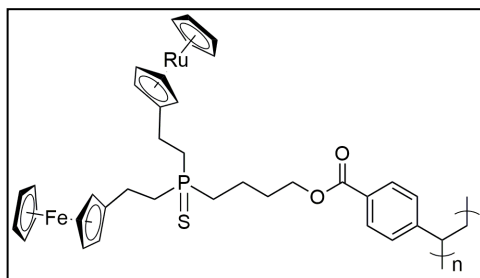
In a grease-free Schlenk flask, monomer **3** (0.40 g, 0.57 mmol) was dissolved in 2.00 mL of a THF stock solution containing AIBN (0.93 mg, 0.0057 mmol, 0.01 equiv.). The resulting solution was stirred at 75 °C for 16 h. After



cooling to room temperature, the polymerization mixture was poured into Et₂O and the solids were separated by centrifugation before they were collected, dissolved in a minimum amount of CHCl₃, and precipitated in Et₂O for twice more. The polymer **4** was dried *in vacuo*, and in the presence of P₂O₅, at 60 °C for 16 h to yield an orange powder. Yield = 0.24 g, 60%. ¹H NMR: δ 7.59 (s, br, 2H, aryl CH), 6.74–6.14 (m, br, 2H, aryl CH), 4.53 [s, 2H, β-C₅H₄R (Rc)], 4.51 [s, 5H, C₅H₅ (Rc)], 4.43 [s, 2H, α-C₅H₄R (Rc)], 4.28 (s, 2H, PCH₂CH₂CH₂CH₂OOC), 4.09 [s, 7H, β-C₅H₄R (c and C₅H₅ (Fc)], 4.04 [s, 2H, α-C₅H₄R (Fc)], 2.46 [s, 2H, FcCH₂CH₂P], 2.32 [s, 2H, RcCH₂CH₂P], 1.89 (s, 2H, CH₂CH₂CH₂CH₂OOC), 1.73–1.53 [m, 6H, FcCH₂CH₂P, RcCH₂CH₂P, PCH₂CH₂CH₂CH₂OOC], 1.48 (s, 2H, PCH₂CH₂CH₂CH₂OOC), 1.80–0.85 (m, br, 3H, ArCHCH₂, ArCHCH₂). ³¹P{¹H} NMR: δ -29.2 (s). FT-IR: 3086 (w), 2925 (w), 2850 (w), 1713 (s), 1608 (w), 1417 (w), 1312 (w), 1270 (s), 1178 (m), 1100 (s), 1040 (w), 1017 (m), 997 (m), 916 (w), 855 (w), 804 (s), 772 (m), 706 (s) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 322 nm (ε = 300 M⁻¹ cm⁻¹) and 437 nm (ε = 100 M⁻¹ cm⁻¹).

Preparation of Tertiary Phosphine Sulfide Polymer 4•S

In air, tertiary phosphine polymer **4** (0.02 g, 0.03 mmol) and S₈ (0.02 g, 0.08 mmol, 2.7 equiv.) were combined in 2.00 mL of a CHCl₃ and stirred for 30 min at room temperature. The resulting mixture was gravity filtered and poured into Et₂O and the solids were separated by centrifugation before they were collected, dissolved in a

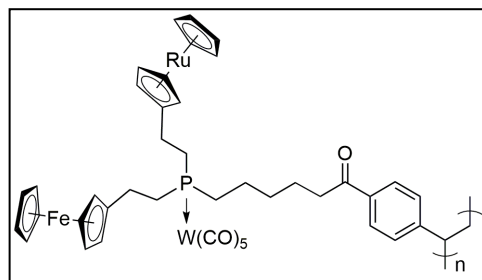


minimum amount of CHCl₃, and precipitated in Et₂O twice more. The tertiary phosphine sulfide polymer **4•S** was dried *in vacuo*, and in the presence of P₂O₅, at 60 °C for 16 h to yield a yellow powder. Yield = 0.14 g, 67%. ¹H NMR: δ 7.56 (s, br, 2H, aryl CH), 6.77–6.01 (m, br, 2H, aryl CH), 4.52 [s, 7H, β-C₅H₄R (Rc) and C₅H₅ (Rc)], 4.44 [s, 2H, α-C₅H₄R (Rc)], 4.28 (s, 2H, PCH₂CH₂CH₂CH₂OOC), 4.11 [s, 7H, β-C₅H₄R (Fc) and C₅H₅ (Fc)], 4.06 [s, 2H, α-C₅H₄R (Fc)],

2.67 [s, 2H, FcCH₂CH₂P], 2.51 [s, 2H, RcCH₂CH₂P], 2.18–1.97 (m, 4H, PCH₂CH₂CH₂CH₂OOC, PCH₂CH₂CH₂CH₂OOC), 1.98–1.67 [m, 6H, FcCH₂CH₂P, RcCH₂CH₂P, PCH₂CH₂CH₂CH₂OOC], 1.57 (s, br, 1H, ArCHCH₂), 1.34 (s, br, 2H, ArCHCH₂). ³¹P{¹H} NMR: δ 47.7 (s). FT-IR: 3088 (w), 2922 (w), 1710 (s), 1608 (w), 1438 (w), 1410 (w), 1271 (s), 1179 (m), 1101 (s), 1017 (m), 998 (m), 804 (s), 707 (m) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 321 nm (ε = 300 M⁻¹ cm⁻¹) and 434 nm (ε = 100 M⁻¹ cm⁻¹). GPC (THF, conventional calibration vs. PS standards): M_n = 9,700 g mol⁻¹, M_w = 14,200 g mol⁻¹, Đ = 1.46.

Preparation of Heterotrimetallic Polymer **4**•W(CO)₅

In a glovebox, a quartz tube was charged with W(CO)₆ (0.15 g, 0.43 mmol, 6 equiv.) and THF (4 mL) capped with a rubber septum, and transferred to a fumehood before it was exposed to UV light for 45 min to produce a golden yellow solution. In a second flask, tertiary



phosphine polymer **4** (0.05 g, 0.07 mmol) was dissolved in THF (4 mL) and added to the W(CO)₅•THF solution in a dropwise manner before the resulting solution stirred for 60 min, concentrated, and poured into dry Et₂O, and the solids were separated by centrifugation. The orange powder was collected, dissolved in a minimum amount of THF, and precipitated in Et₂O once more before the coordinated-tertiary phosphine polymer **4**•W(CO)₅ was dried *in vacuo*, and in the presence of P₂O₅, at 60 °C for 16 h to yield a yellow powder. Yield = 0.05 g, 66%. ¹H NMR: δ 7.56 (s, br, 2H, aryl CH), 6.81–6.00 (m, br, 2H, aryl CH), 4.52 [s, 7H, β-C₅H₄R (Rc) and C₅H₅ (Rc)], 4.44 [s, 2H, α-C₅H₄R (Rc)], 4.28 (s, 2H, PCH₂CH₂CH₂CH₂OOC), 4.10 [s, 7H, β-C₅H₄R (Fc) and C₅H₅ (Fc)], 4.07 [s, 2H, α-C₅H₄R (Fc)], 2.53 [s, 2H, FcCH₂CH₂P], 2.35 [s, 2H, RcCH₂CH₂P], 2.24–1.58 [m, 10H, PCH₂CH₂CH₂CH₂OOC, PCH₂CH₂CH₂CH₂OOC, FcCH₂CH₂P, RcCH₂CH₂P, PCH₂CH₂CH₂CH₂OOC], 1.55 (s, br, 1H, ArCHCH₂), 1.30 (s, br, 2H, ArCHCH₂). ³¹P{¹H} NMR: δ -6.1 [s (86%); d, ¹J_{PW} = 233 Hz (14%)]. FT-IR: 3088 (w), 2932 (w), 2848 (w), 2066 (m), 1974 (w), 1909 (s), 1717 (m), 1609 (w), 1418 (w), 1273 (m), 1180 (w), 1103 (m), 1018 (w), 809 (m), 708 (w), 600 (w) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 325 nm (ε = 450 M⁻¹ cm⁻¹) and 430 nm (ε = 100 M⁻¹ cm⁻¹). GPC (THF, conventional calibration vs. PS standards): M_n = 11,600 g mol⁻¹, M_w = 28,000 g mol⁻¹, Đ = 2.41.

TABLES OF SUMMARIZED DATA

Table S1. Selected characterization data for compounds **2–4** and **4•W(CO)₅**.

Compound	³¹ P NMR (δ)	ε, 322 nm (M ⁻¹ cm ⁻¹)	ε, 440 nm (M ⁻¹ cm ⁻¹)	<i>E</i> _{1/2, Fc} (mV)	<i>E</i> _{pa, Rc} ^b (mV)	<i>E</i> _{pa, W} ^b (mV)
2	-28.8	300	100	-15 (-120) ^a	440	-
3	-29.0	300	100	-15 (-150) ^a	390	-
4	-29.2	300	100	-15 (-150) ^a	400	-
4•W(CO)₅	-6.1	450	100	0	350	750

^aAnodic potential of ferrocene oxidation prewave (electrode adsorption) is reported in brackets.

^bIrreversible process; anodic peak potential reported.

Table S2. Selected characterization data for polymers **4**, **4•S**, and **4•W(CO)₅**.

Compound	<i>M</i> _n (g mol ⁻¹)	<i>M</i> _w (g mol ⁻¹)	<i>D</i>	<i>T</i> _g (°C)	Char Yield (%)	Polymer Metal Content (Mass %)
4	9,300 ^a	13,600 ^a	1.46 ^a	52	24.0	22.2
4•S	9,700	14,200	1.46	91	30.9	21.3
4•W(CO)₅	11,600	28,000	2.41	92	32.1	32.0

^aCalculated from the GPC data recorded for the corresponding sulfurized polymer **4•S**.

NMR SPECTRA

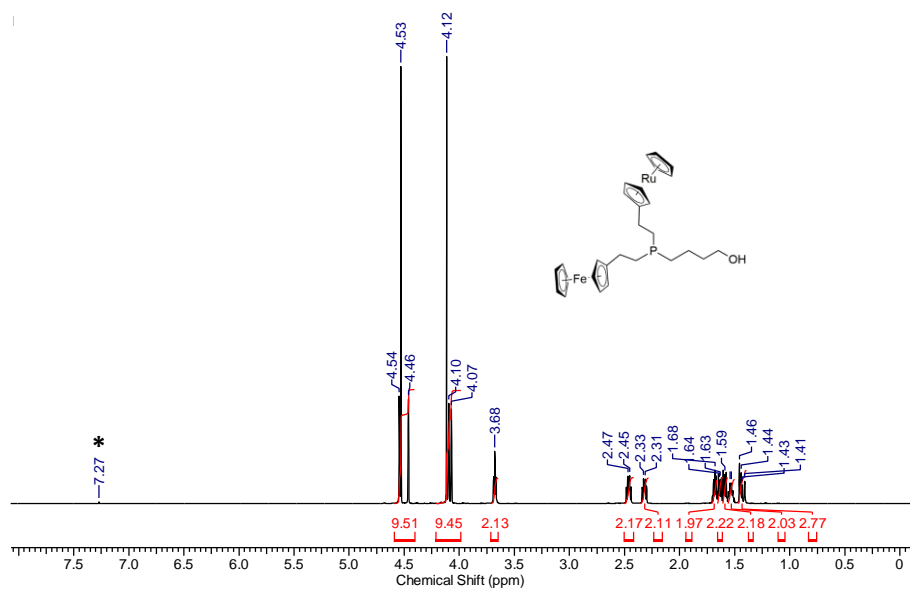


Figure S1. ^1H NMR spectrum of **2** in CDCl_3 . The asterisk denotes residual CHCl_3 signal.

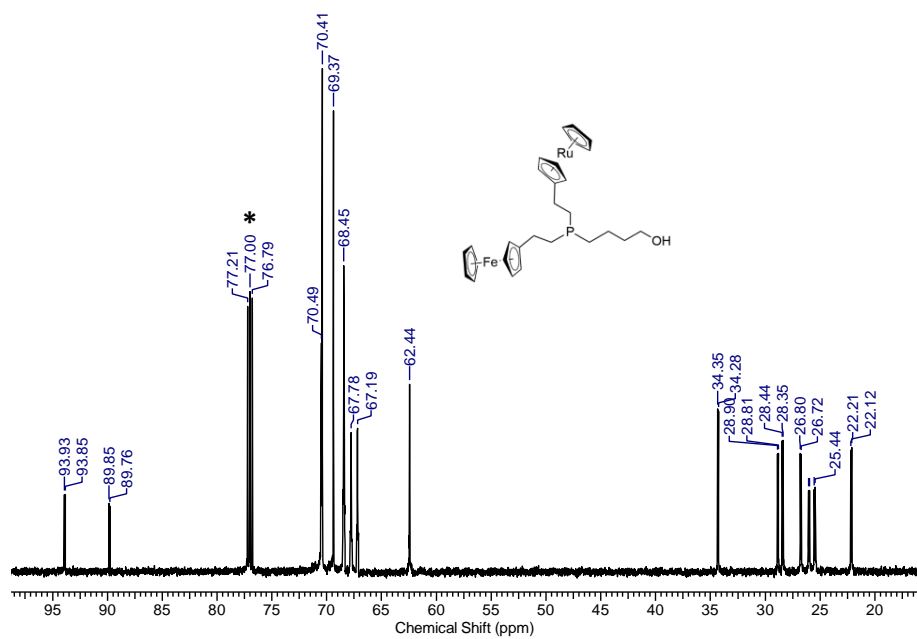


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 . The asterisk denotes the CDCl_3 signal.

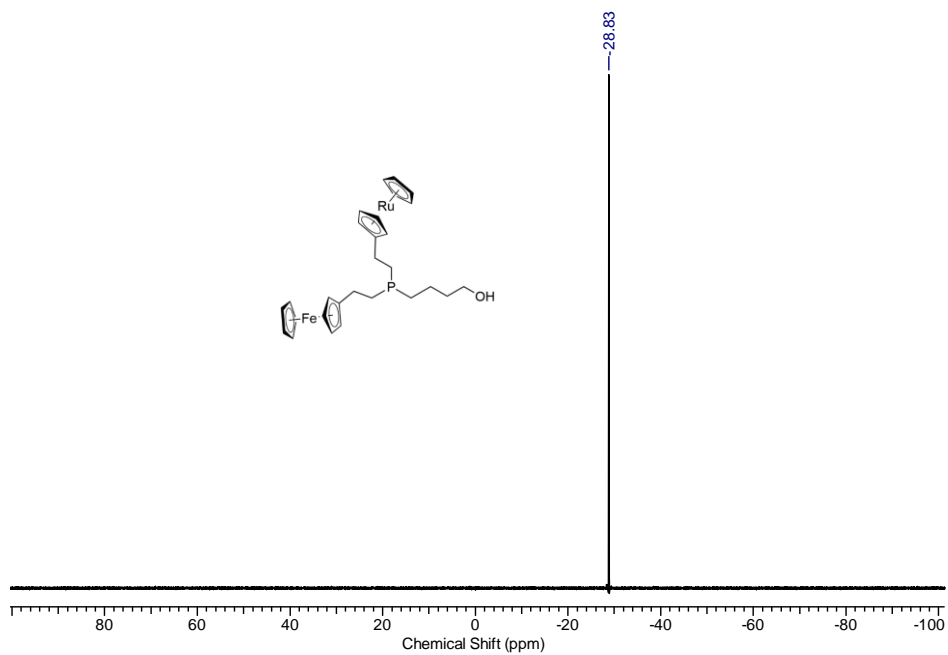


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 .

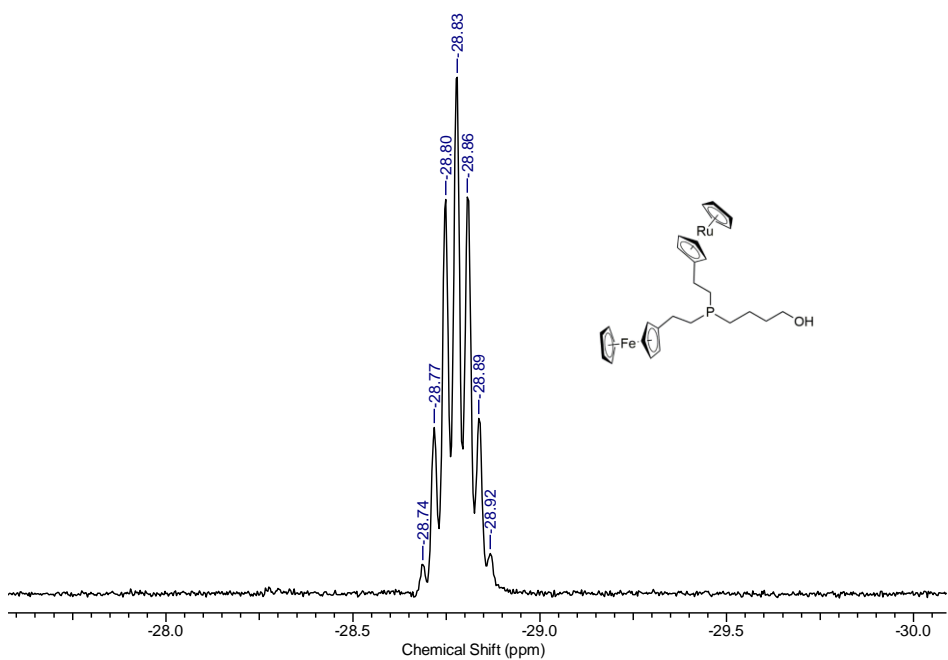


Figure S4. ^{31}P NMR spectrum of **2** in CDCl_3 .

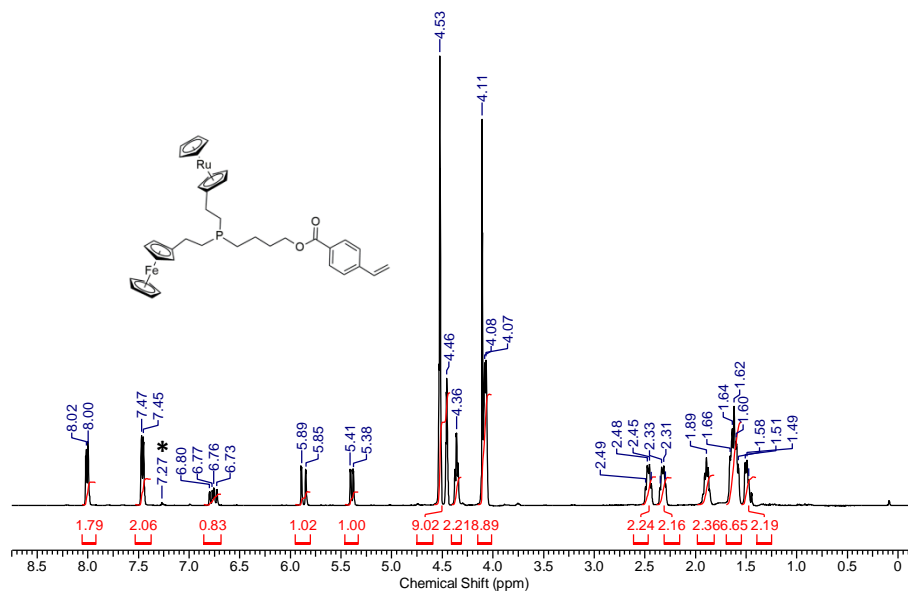


Figure S5. ^1H NMR spectrum of **3** in CDCl_3 . The asterisk denotes residual CHCl_3 signal.

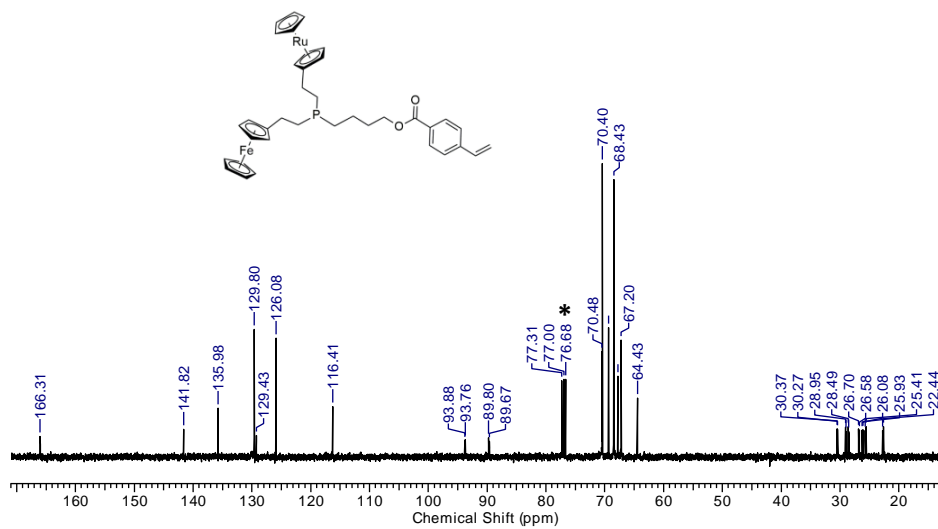


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 . The asterisk denotes the CDCl_3 signal.

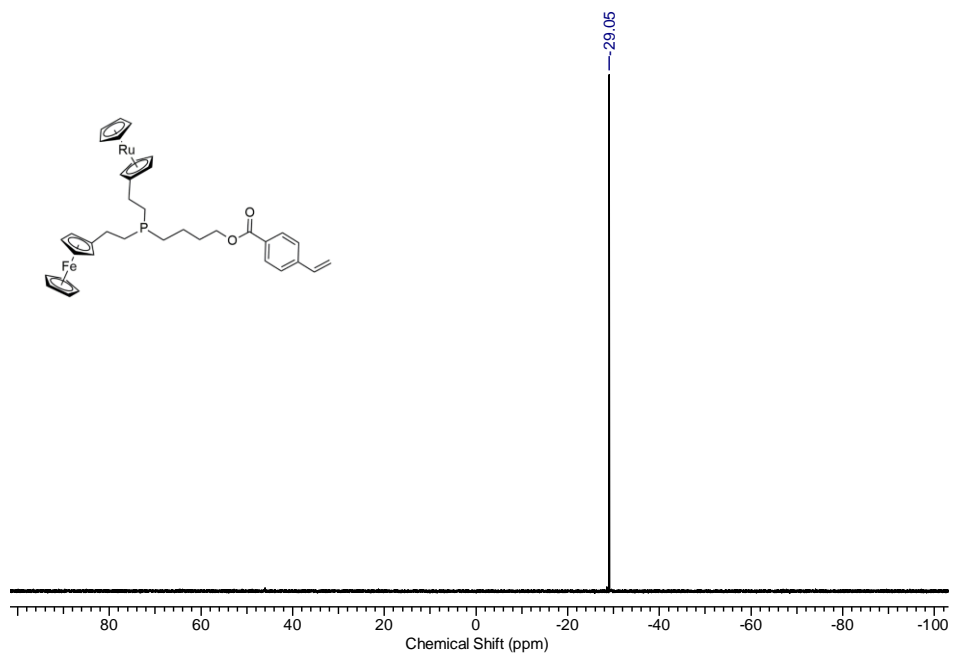


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

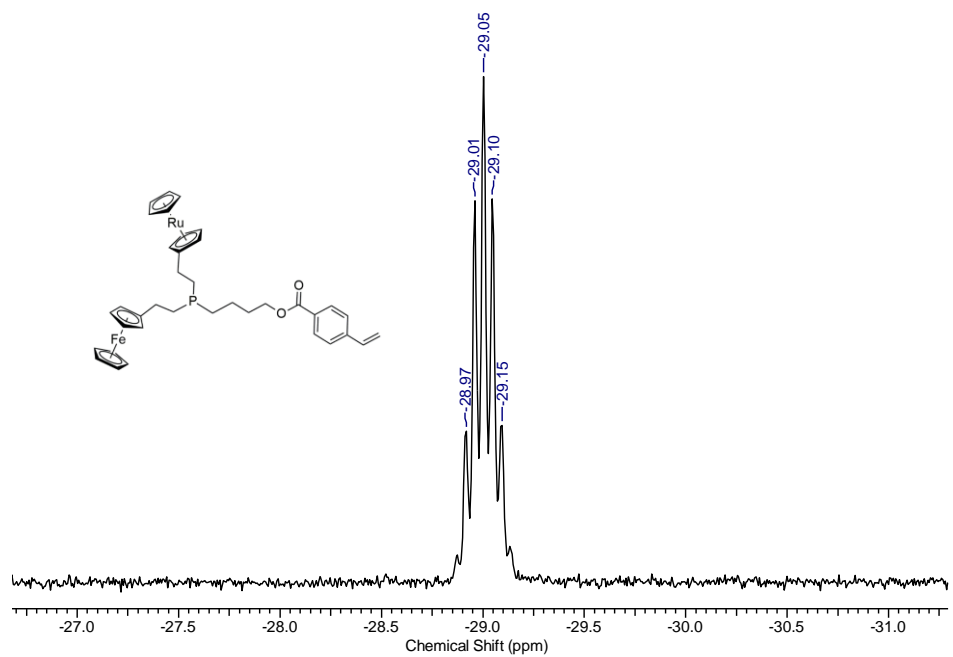


Figure S8. ^{31}P NMR spectrum of **3** in CDCl_3 .

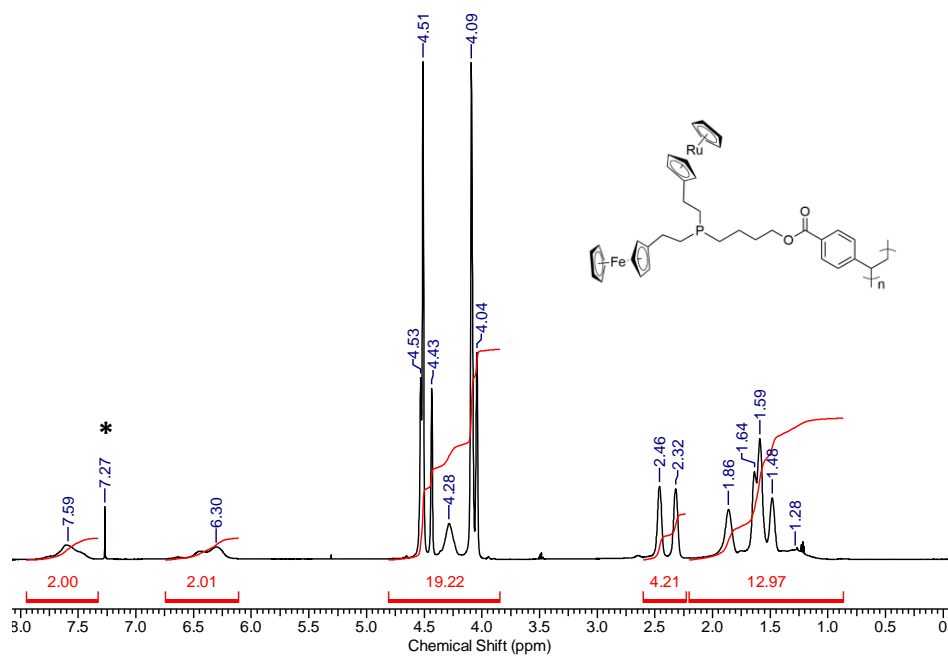


Figure S9. ¹H NMR spectrum of **4** in CDCl₃. The asterisk denotes residual CHCl₃ signal.

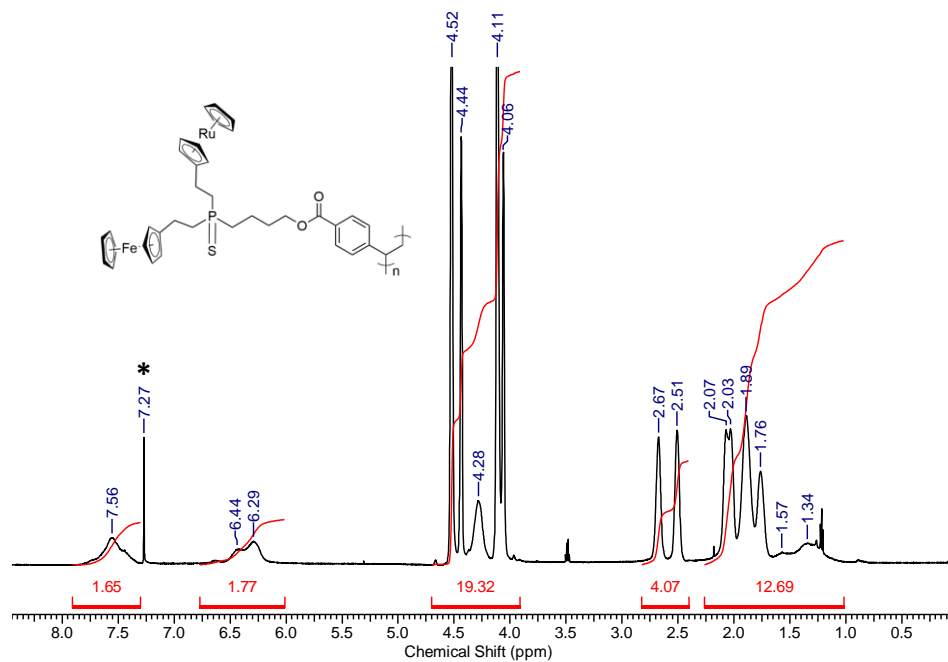


Figure S10. ¹H NMR spectrum of **4•S** in CDCl₃. The asterisk denotes residual CHCl₃ signal.

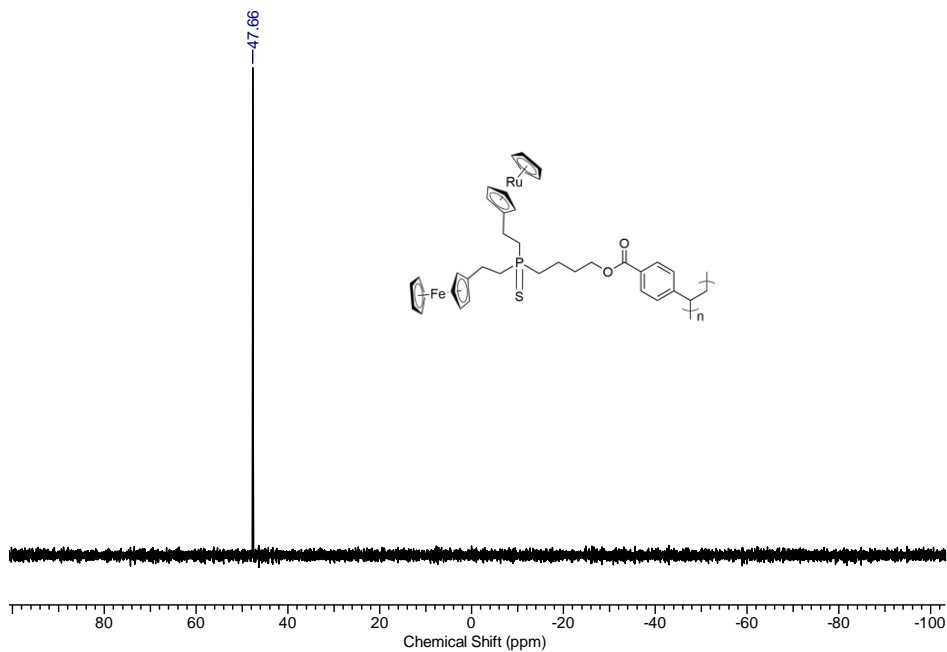


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4•S** in CDCl_3 .

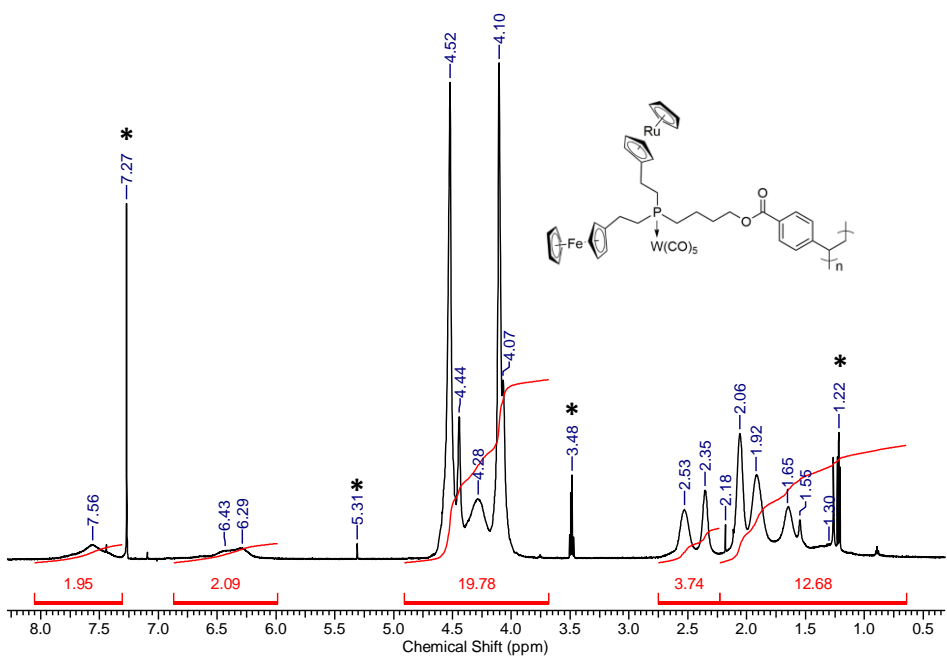


Figure S12. ^1H NMR spectrum of **4•W(CO)₅** in CDCl_3 . The asterisks denote residual CHCl_3 , Et_2O , and CH_2Cl_2 signals.

GPC DATA

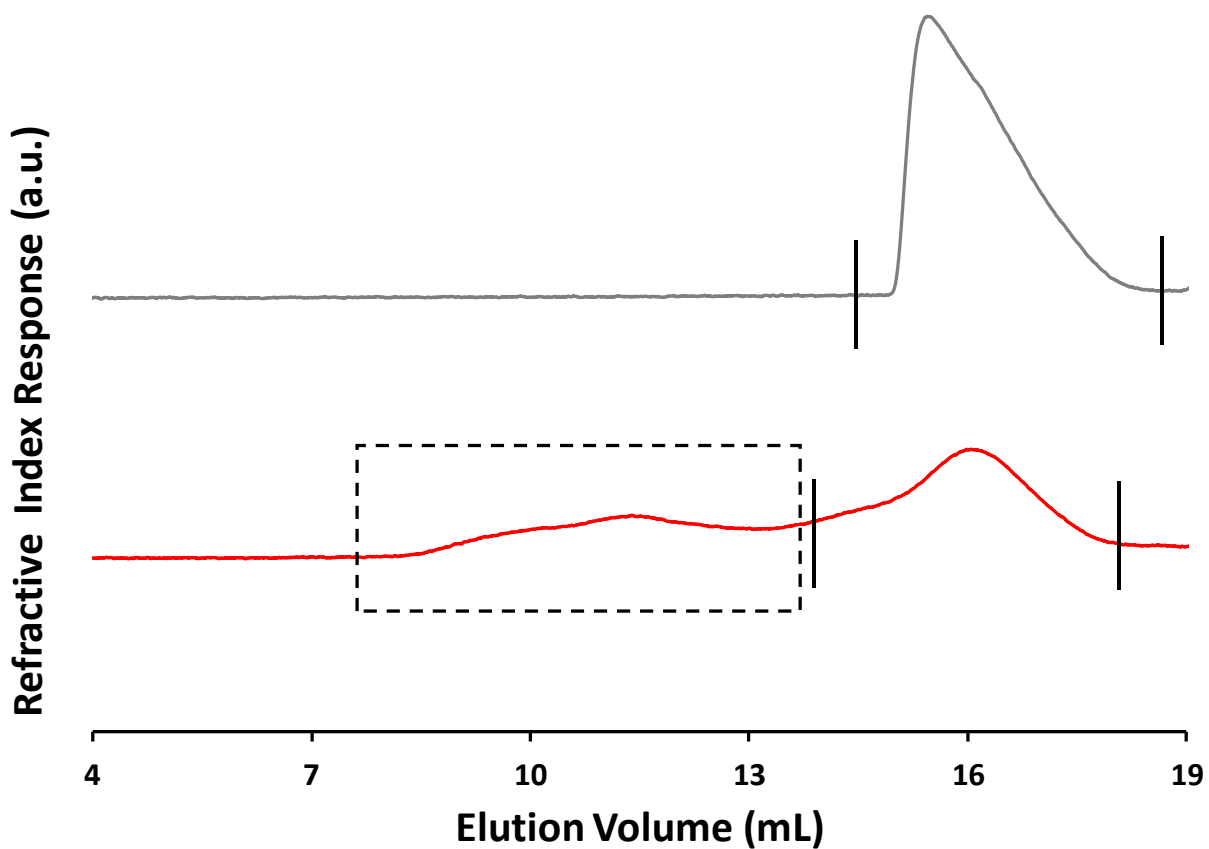


Figure S13. GPC traces collected for polymers **4•S** (grey) and **4•W(CO)₅** (red) in THF. The limits used to estimate the molecular weights relative to monodisperse polystyrene standards are shown as black bars and the signal attributed to aggregates of **4•W(CO)₅** in solution is shown in the dashed box.

THERMAL ANALYSIS DATA

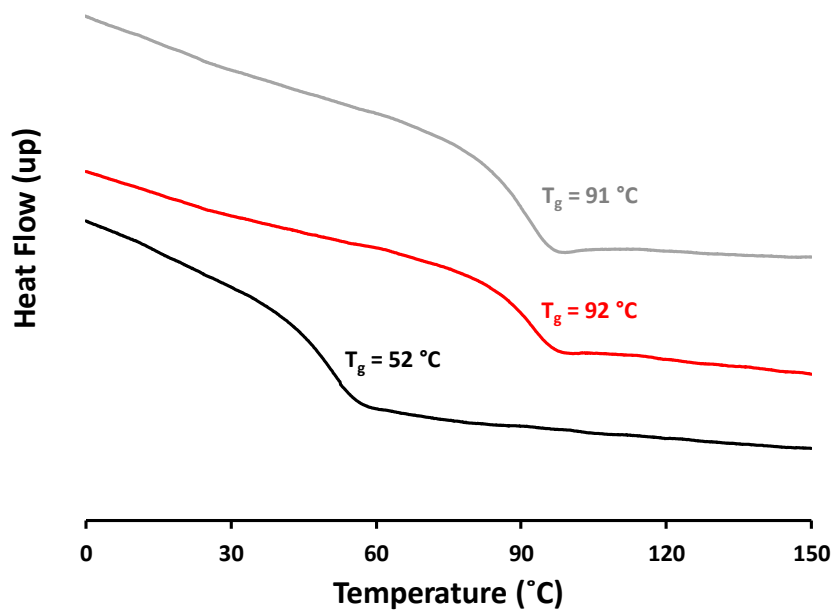


Figure S14. DSC thermograms of polymers **4** (black), **4•W(CO)₅** (red), and **4•S** (grey) recorded at heating/cooling rates of 10 °C min⁻¹.

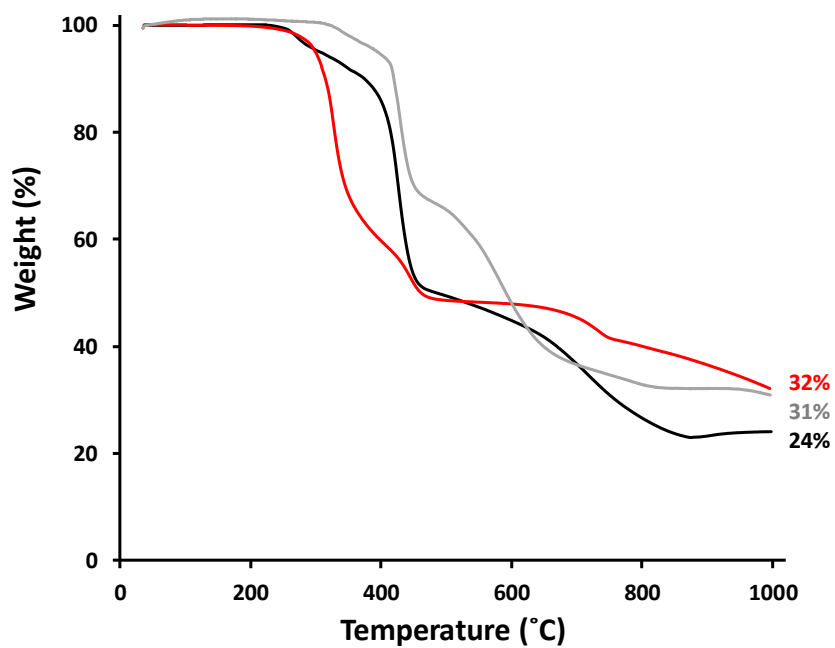


Figure S15. TGA traces obtained for polymers **4** (black), **4•W(CO)₅** (red), and **4•S** (grey) recorded at heating rates of 10 °C min⁻¹.

UV-VIS ABSORPTION SPECTRA

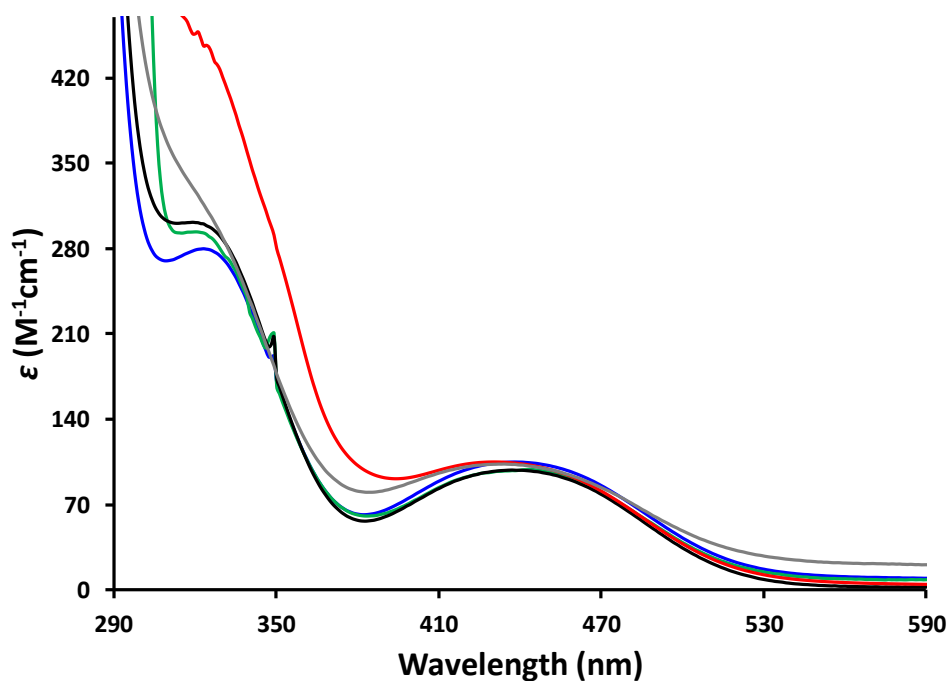


Figure S16. UV-Vis absorption spectra recorded for **2** (blue), **3** (green), **4** (black), **4•S** (grey), and **4•W(CO)₅** (red) in CH₂Cl₂.

CYCLIC VOLTAMMOGRAMS

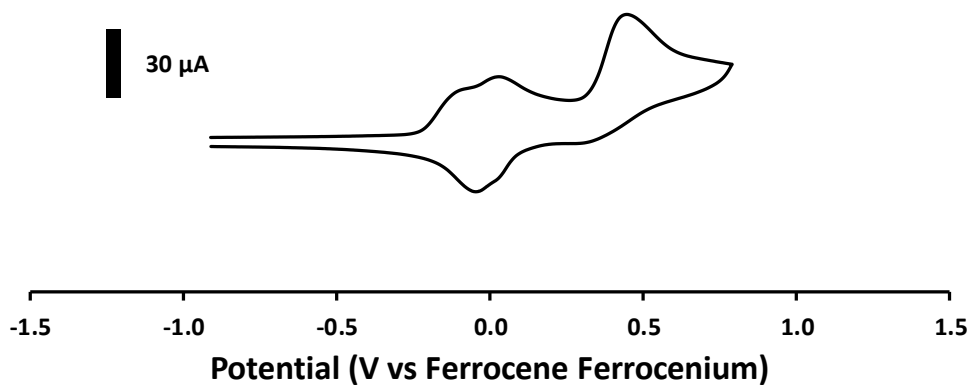


Figure S17. Cyclic voltammogram recorded at 250 $mV s^{-1}$ for a 1 mM THF solution of monomer **2** containing 0.1 M [*n*-Bu₄N][OTf] as supporting electrolyte.

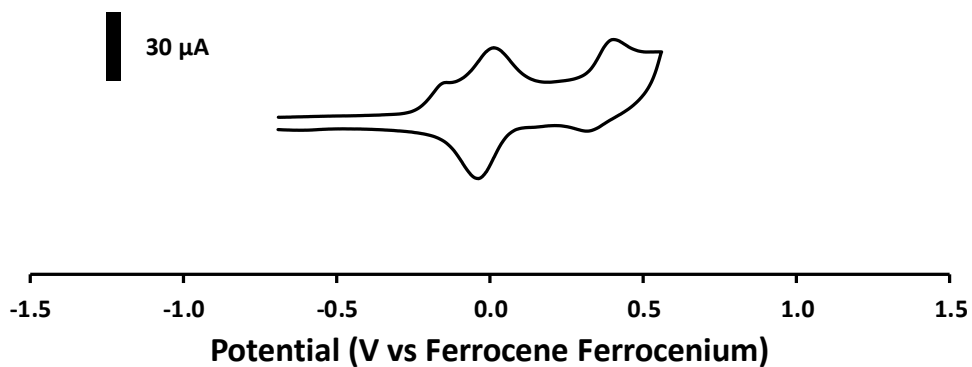


Figure S18. Cyclic voltammogram recorded at 250 mV s^{-1} for a 1 mM THF solution of monomer **3** containing 0.1 M $[n\text{-Bu}_4\text{N}][\text{OTf}]$ as supporting electrolyte.

REFERENCES

- (1) Rabiee Kenaree, A.; Cuthbert, T. J.; Barbon, S. M.; Boyle, P. D.; Gillies, E. R.; Ragogna, P. J.; Gilroy, J. B. *Organometallics* **2015**, *34*, 4272–4280.