

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.

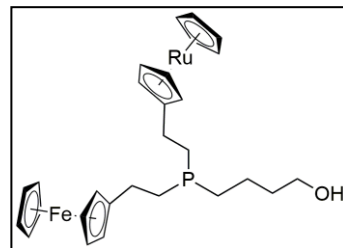
Thermal Analysis

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

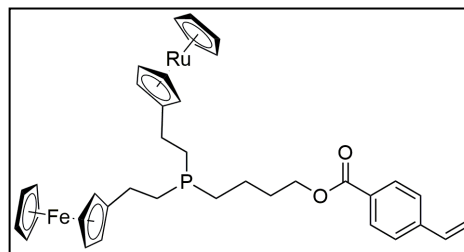
In a sealed tube, secondary phosphine **1** (1.00 g, 1.99 mmol), 3-buten-1-ol (500 µL, 5.81 mmol, 2.9 equiv.), and AIBN (21 mg, 0.13 mmol, 0.065 equiv.) were combined with THF (5 mL) before the mixture was heated with stirring for 24 h at 75 °C. After cooling to



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

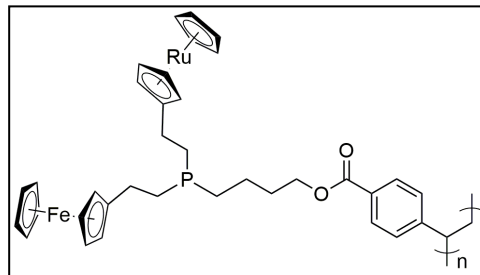
In a sealed tube and in the absence of external light/heat sources, 4-vinylbenzoic acid (0.30 g, 2.0 mmol, 1.15 equiv.), 4-(dimethylamino)pyridine (0.25 g, 2.0 mmol, 1.15 equiv.), and *N,N'*-dicyclohexylcarbodiimide (0.43 g,



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, $\text{ArCH}=\text{CH}_2$), 5.87 (d, 1H, $^3J_{\text{HH},\text{trans}} = 18$ Hz, $\text{ArCH}=\text{CH}_2$), 5.39 (d, 1H, $^3J_{\text{HH},\text{cis}} = 11$ Hz, $\text{ArCH}=\text{CH}_2$), 4.53 [s, 7H, $\beta\text{-C}_5\text{H}_4\text{R}$ (Rc) and C_5H_5 (Rc)], 4.46 [s, 2H, $\alpha\text{-C}_5\text{H}_4\text{R}$ (Rc)], 4.36 (t, 2H, $^3J_{\text{HH}} = 7$ Hz, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}$), 4.11 [s, 5H, C_5H_5 (Fc)], 4.08 [s, 4H, $\alpha\text{-C}_5\text{H}_4\text{R}$ (Fc) and $\beta\text{-C}_5\text{H}_4\text{R}$ (Fc)], 2.52–2.41 [m, 2H, $\text{FcCH}_2\text{CH}_2\text{P}$], 2.37–2.27 [m, 2H, $\text{RcCH}_2\text{CH}_2\text{P}$], 1.97–1.81 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}$), 1.69–1.55 [m, 6H, $\text{FcCH}_2\text{CH}_2\text{P}$, $\text{RcCH}_2\text{CH}_2\text{P}$, and $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}$], 1.54–1.45 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}$). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{37}\text{H}_{41}\text{O}_2\text{PFcRu}$: C, 62.98; H, 5.86. Found: C, 62.29; H, 5.78.

Preparation of Tertiary Phosphine Polymer 4

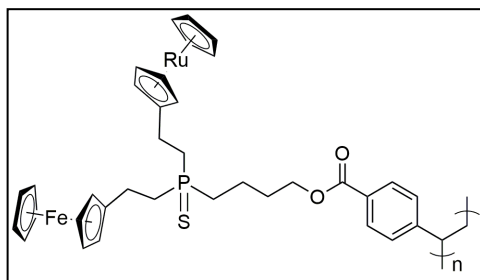
In a grease-free Schlenk flask, monomer **3** (0.40 g, 0.57 mmol) was dissolved in 2.00 mL of a THF stock solution containing AIBN (0.93 mg, 0.0057 mmol, 0.01 equiv.). The resulting solution was stirred at 75 °C for 16 h. After



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 twice more. The polymer **4** was dried *in vacuo* 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 (Fc) 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

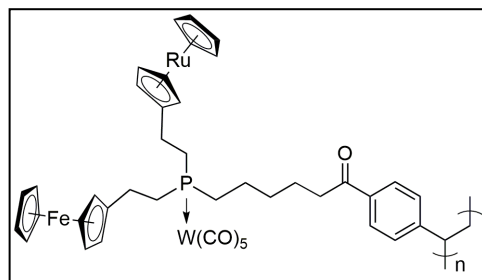


minimum amount of CHCl₃, and precipitated in Et₂O twice more. The tertiary phosphine sulfide polymer **4•S** was dried *in vacuo* in the presence of P₂O₅, at 60 °C for 16 h to yield a yellow powder. Yield = 0.14 g, 67%. ¹H NMR: δ 7.56 (s, br, 2H, aryl CH), 6.77–6.01 (m, br, 2H, aryl CH), 4.52 [s, 7H, 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 dropwise to the W(CO)₅•THF solution before the resulting solution was 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* 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>Đ</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

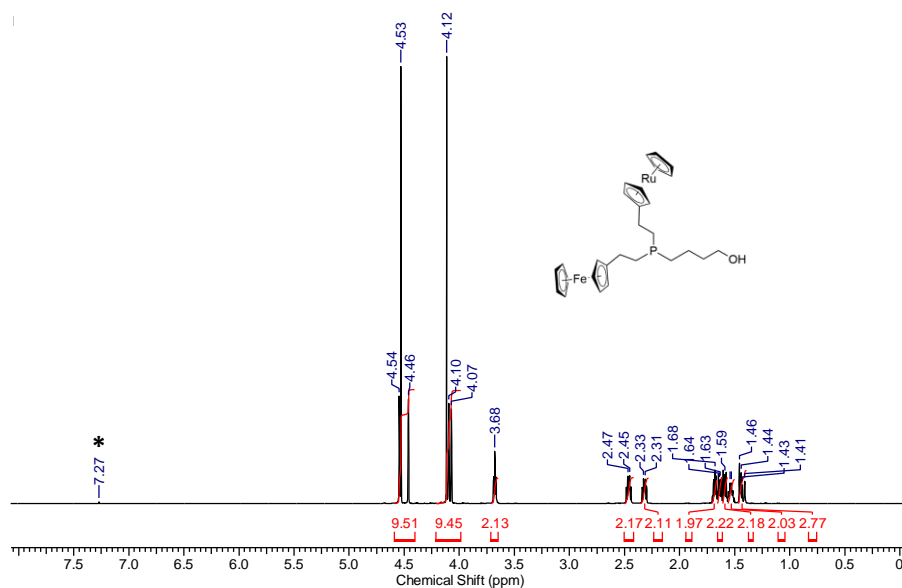


Figure S1. ^1H NMR spectrum of **2** in CDCl_3 . The asterisk denotes residual CHCl_3 signal.

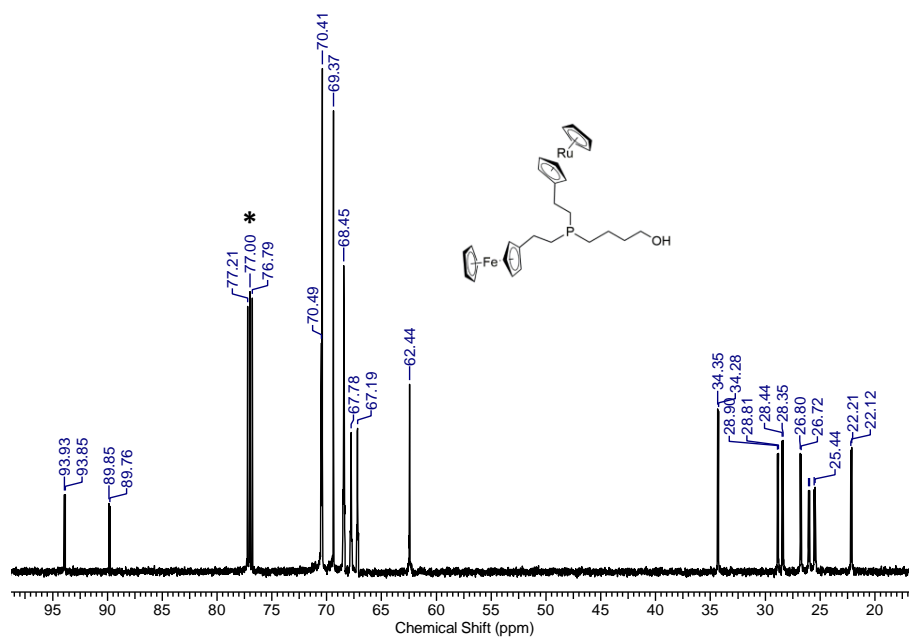


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 . The asterisk denotes the CDCl_3 signal.

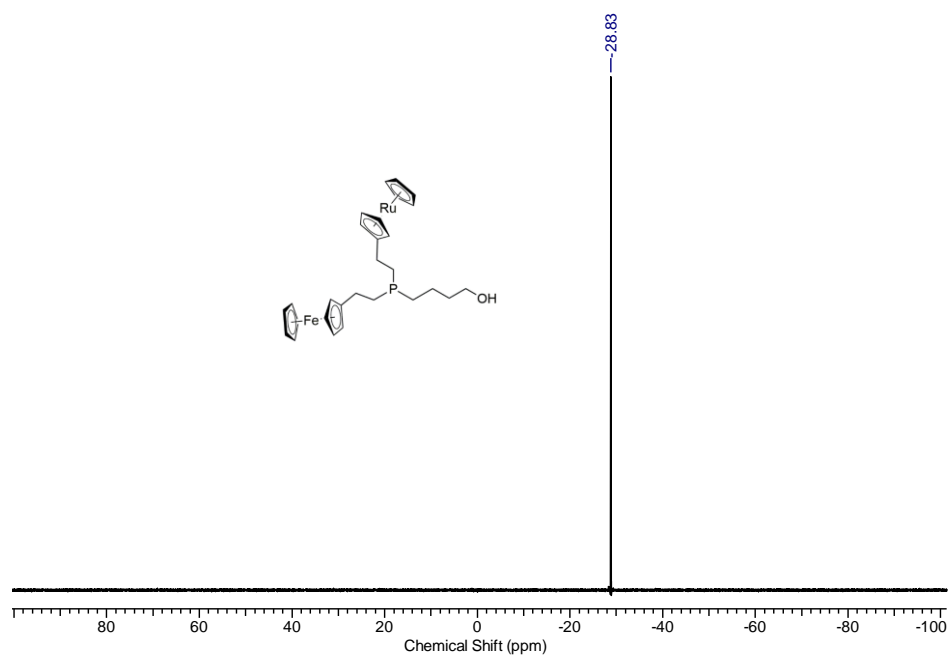


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 .

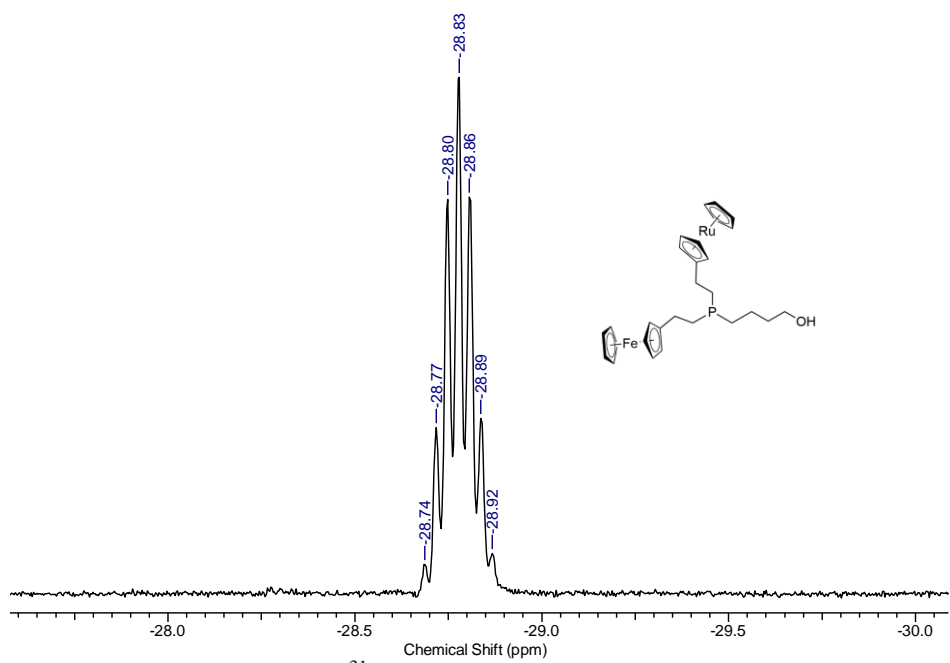


Figure S4. ^{31}P NMR spectrum of **2** in CDCl_3 .

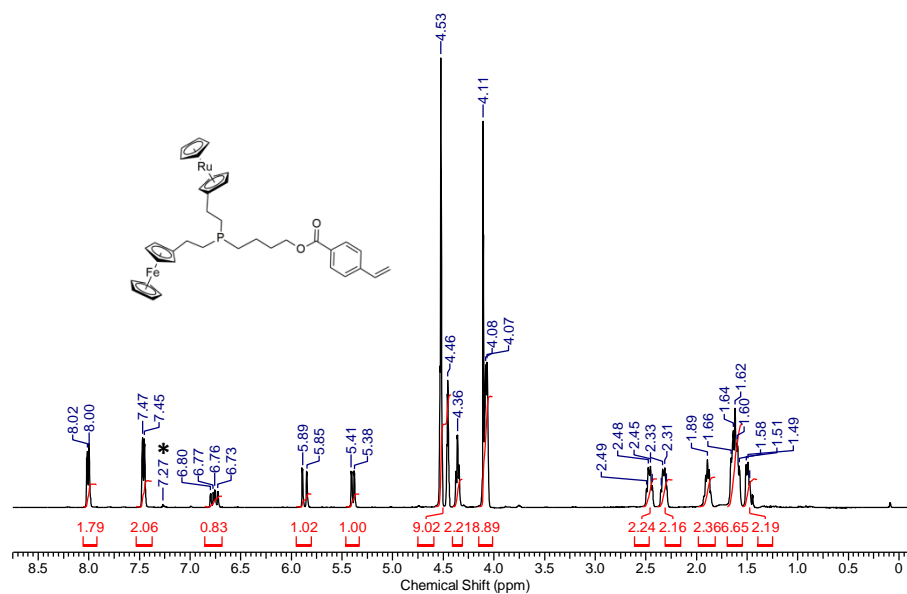


Figure S5. ¹H NMR spectrum of **3** in CDCl₃. The asterisk denotes residual CHCl₃ signal.

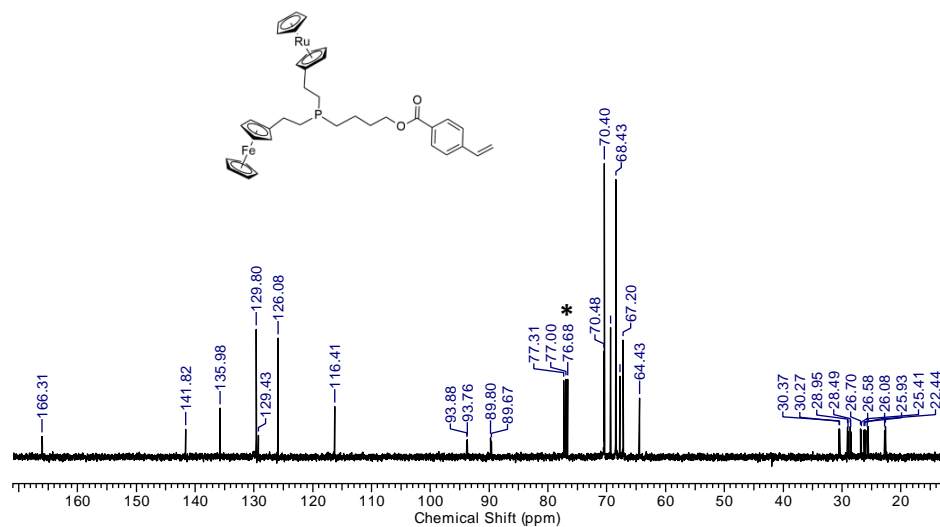


Figure S6. ¹³C{¹H} NMR spectrum of **3** in CDCl₃. The asterisk denotes the CDCl₃ signal.

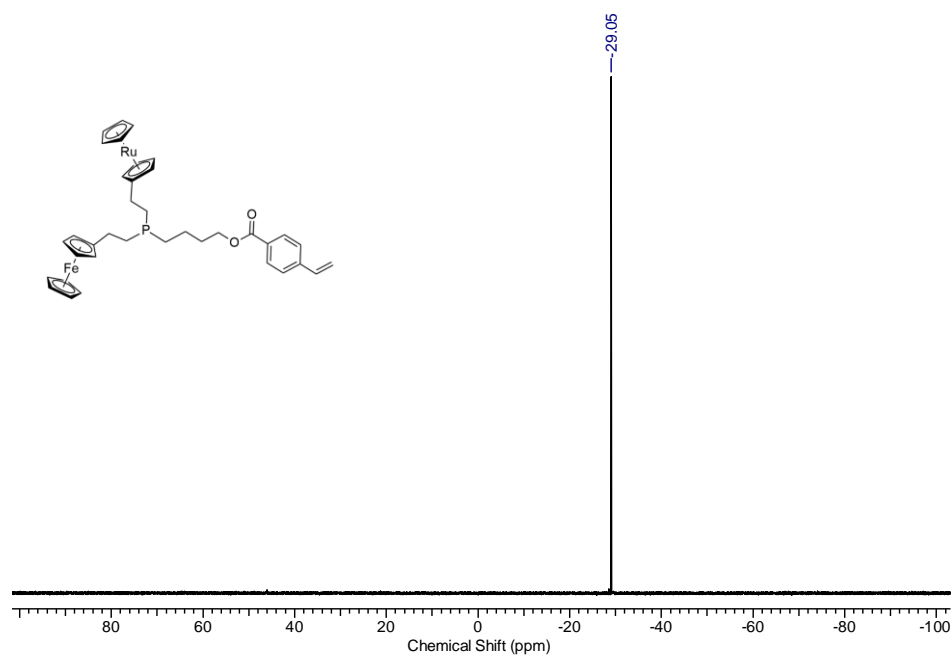


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

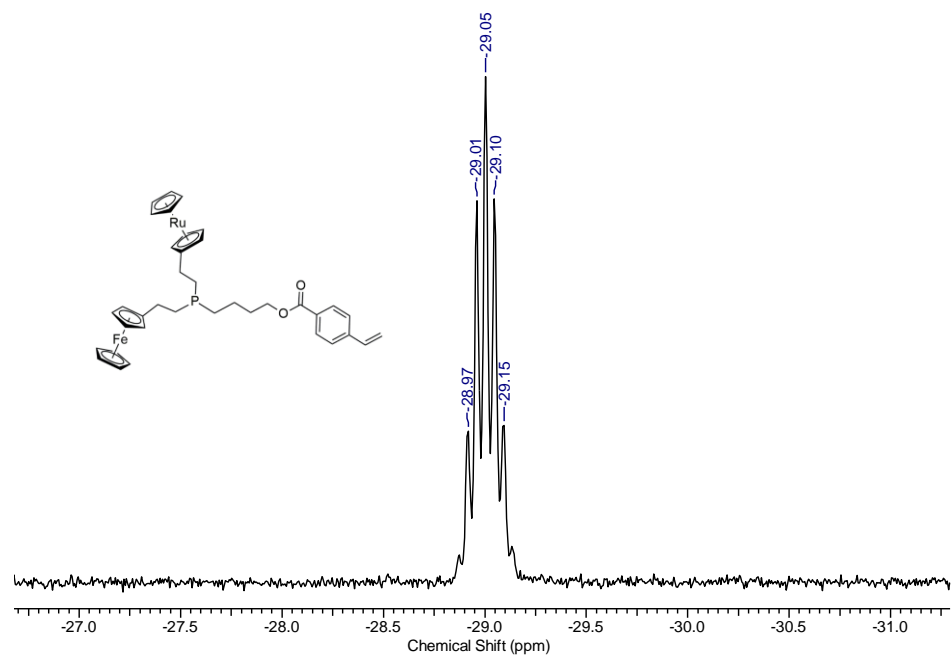


Figure S8. ^{31}P NMR spectrum of **3** in CDCl_3 .

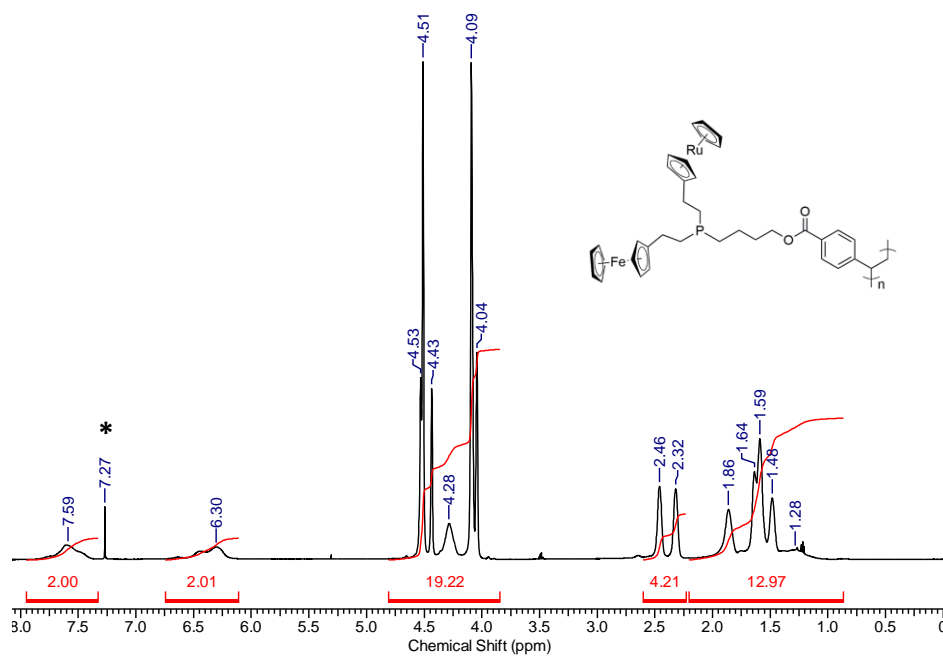


Figure S9. ¹H NMR spectrum of **4** in CDCl₃. The asterisk denotes residual CHCl₃ signal.

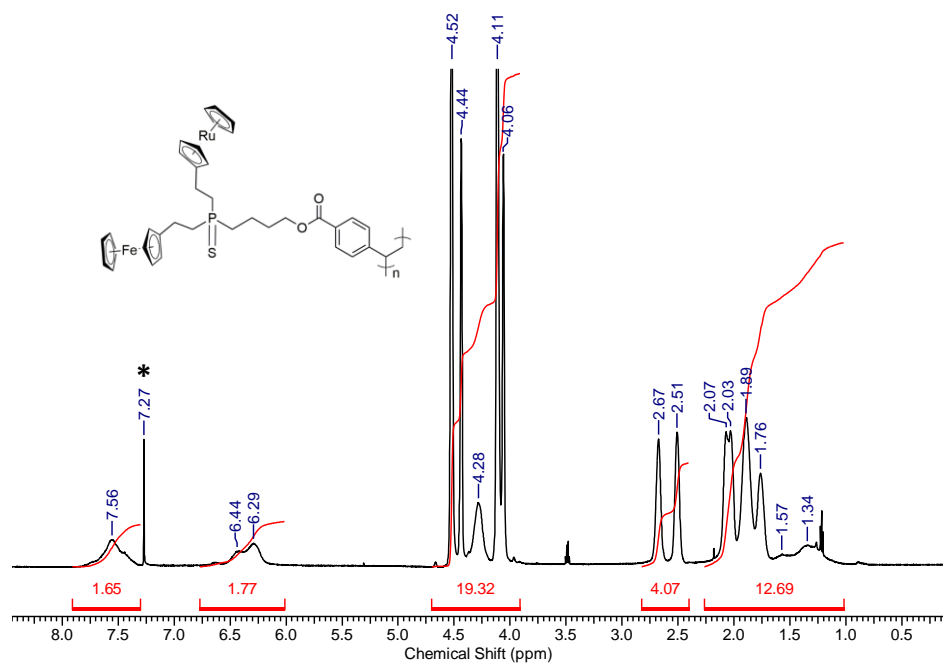
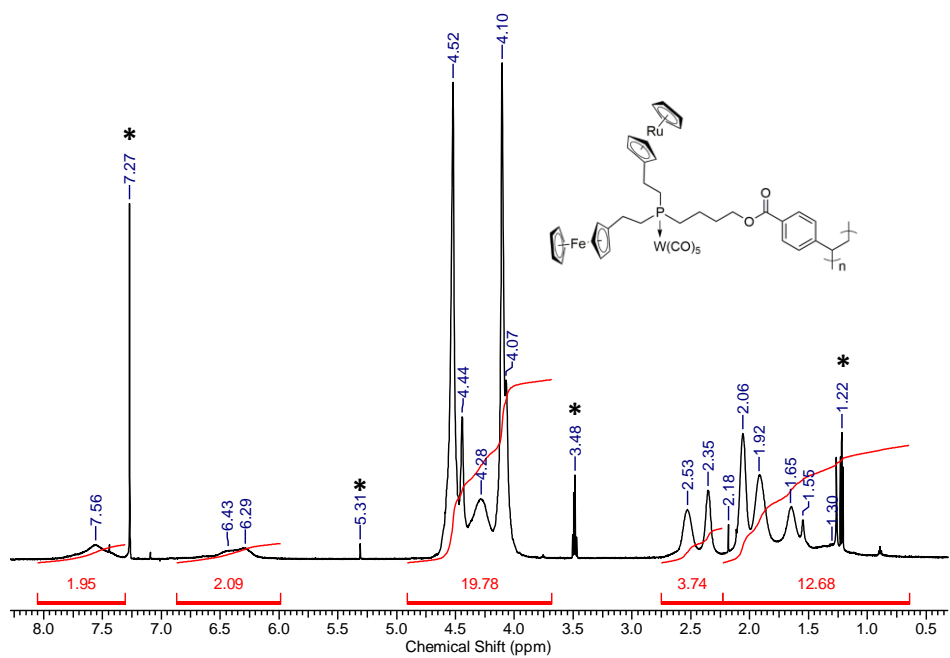
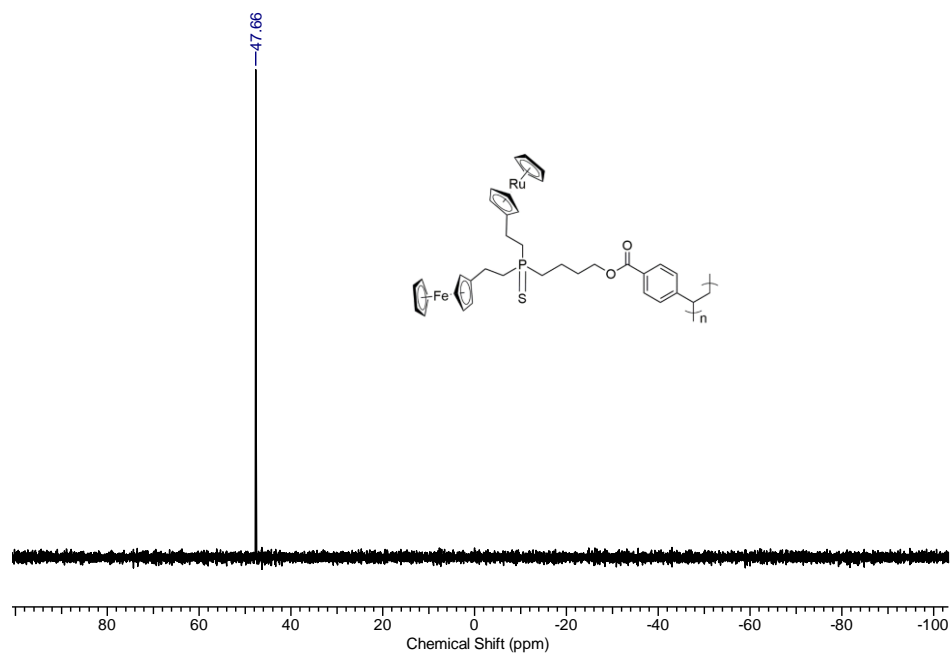


Figure S10. ¹H NMR spectrum of **4•S** in CDCl₃. The asterisk denotes residual CHCl₃ signal.



GPC DATA

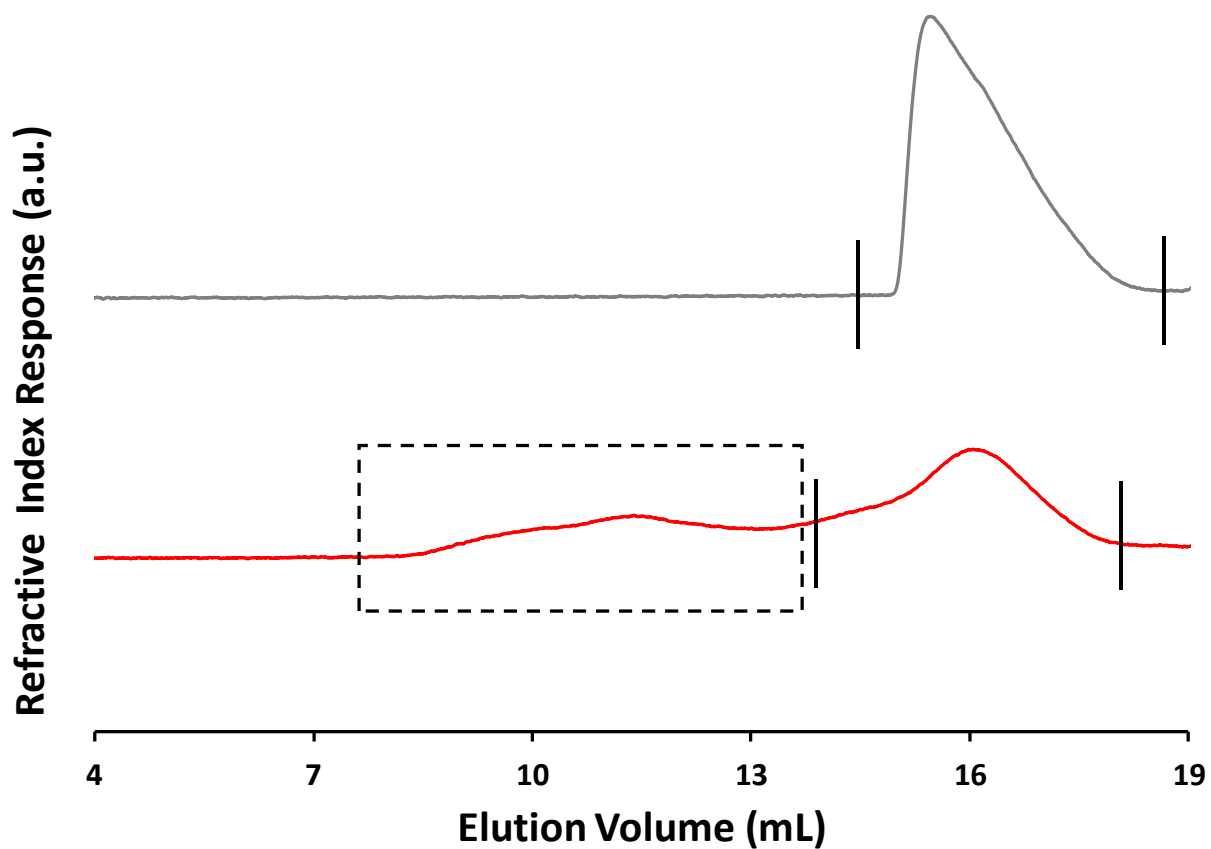


Figure S13. GPC traces collected for the soluble fractions of polymers **4•S** (grey) and **4•W(CO)₅** (red) in THF. The limits used to estimate the molecular weights relative to monodisperse polystyrene standards are shown as black bars and the signal attributed to aggregates of **4•W(CO)₅** in solution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

THERMAL ANALYSIS DATA

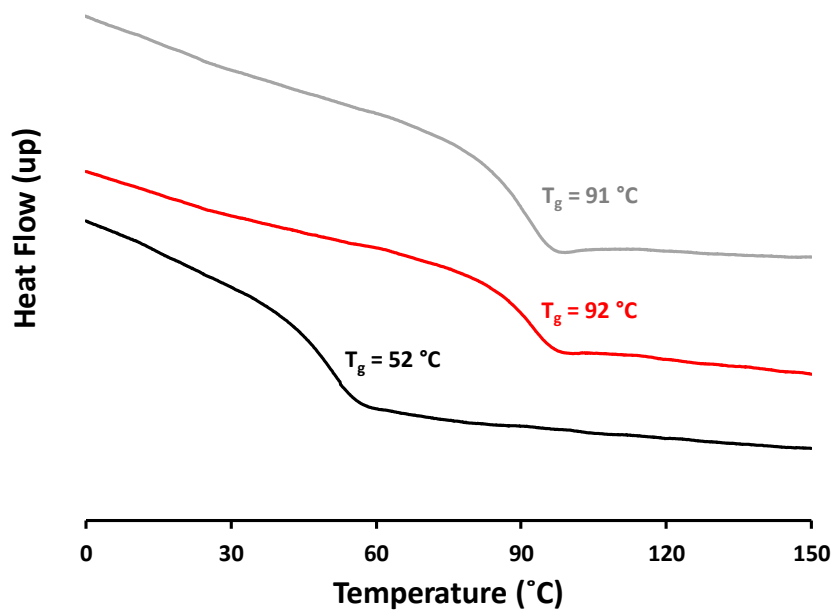


Figure S14. DSC thermograms of polymers **4** (black), **4•W(CO)₅** (red), and **4•S** (grey) recorded at heating/cooling rates of 10 °C min⁻¹.

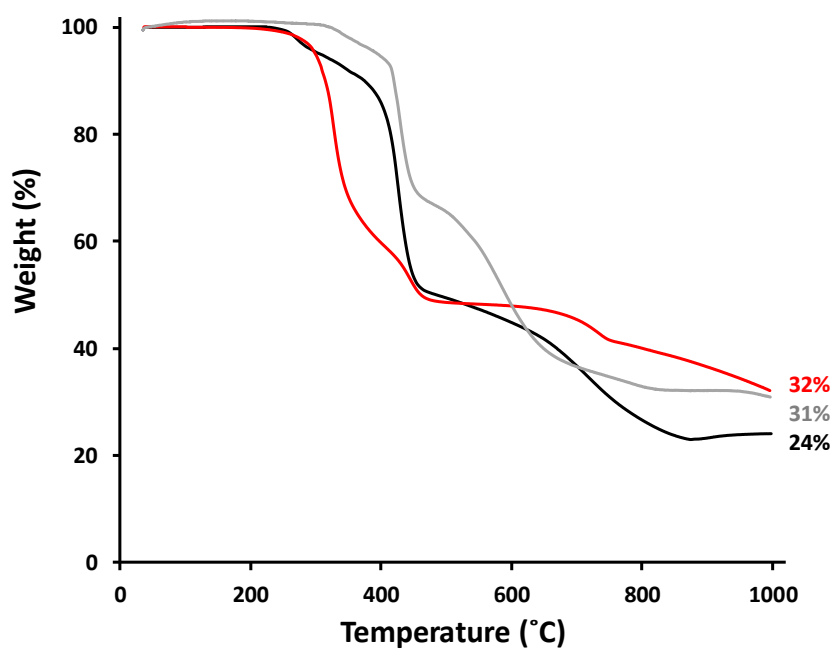


Figure S15. TGA traces obtained for polymers **4** (black), **4•W(CO)₅** (red), and **4•S** (grey) recorded at heating rates of 10 °C min⁻¹.

UV-VIS ABSORPTION SPECTRA

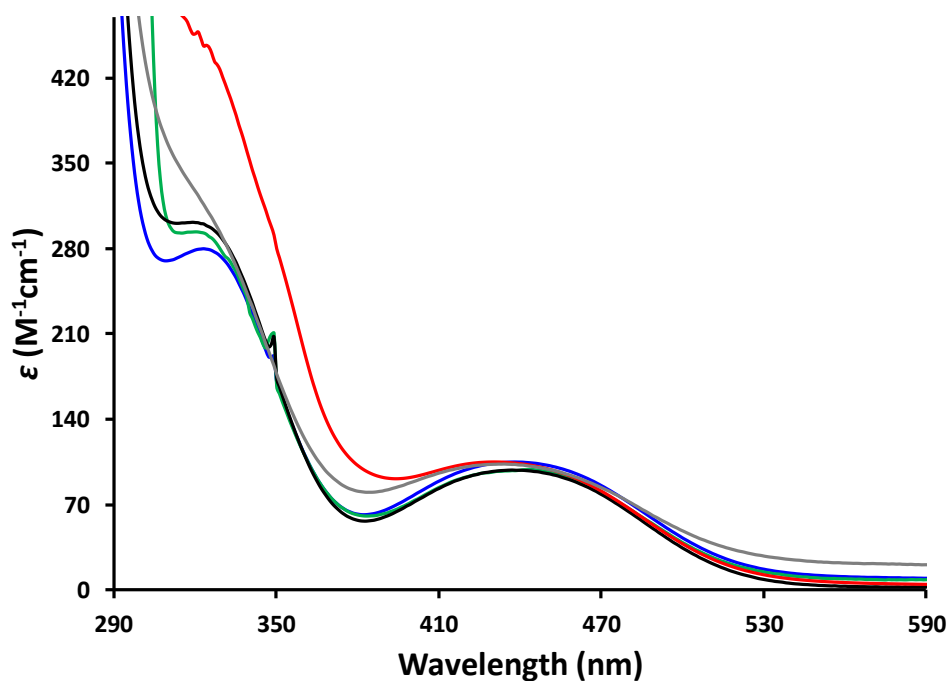


Figure S16. UV-Vis absorption spectra recorded for **2** (blue), **3** (green), **4** (black), **4•S** (grey), and **4•W(CO)₅** (red) in CH₂Cl₂.

CYCLIC VOLTAMMOGRAMS

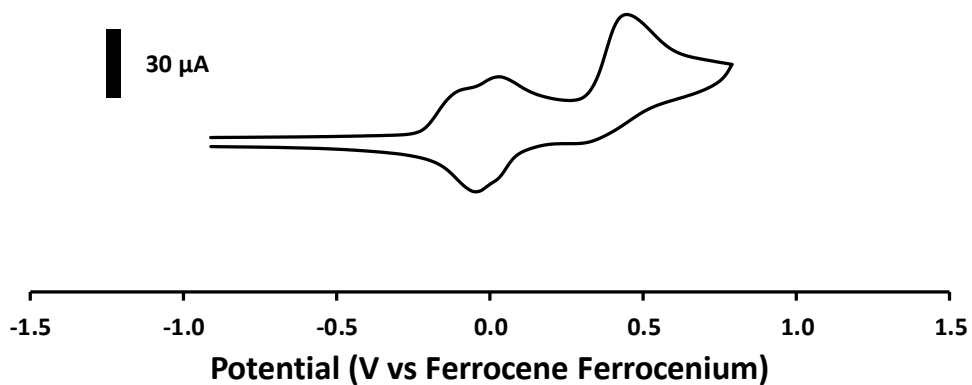


Figure S17. Cyclic voltammogram recorded at 250 $mV s^{-1}$ for a 1 mM THF solution of monomer **2** containing 0.1 M [*n*-Bu₄N][OTf] as supporting electrolyte.

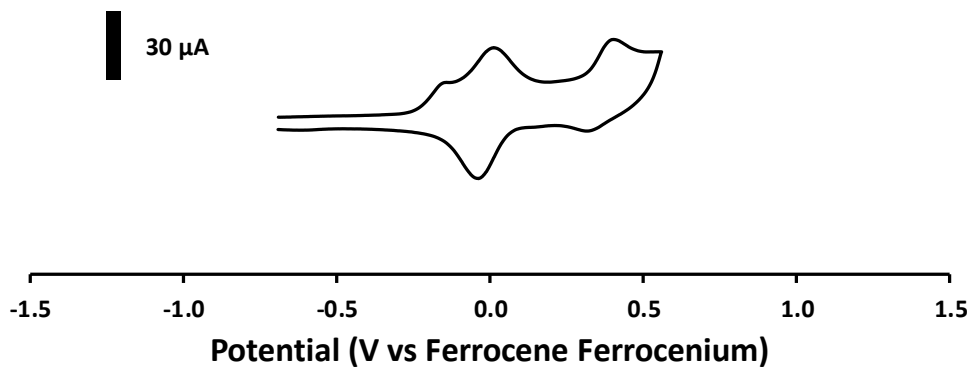


Figure S18. Cyclic voltammogram recorded at 250 mV s^{-1} for a 1 mM THF solution of monomer **3** containing 0.1 M $[n\text{-Bu}_4\text{N}][\text{OTf}]$ as supporting electrolyte.

REFERENCES

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