

Supplementary Information

A Heterogeneous Multinuclear Nickel Catalyst Supported by a Crosslinked Alpha Diimine Ligand Network

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General Considerations

All polymerizations were prepared under dry nitrogen using a Vigor Sci-Lab glovebox. Polymerizations were run outside of the glovebox in a Fisher-Porter pressure reaction vessel and supplied with monomer grade ethylene dried through a column of activated 4 Å molecular sieves. Metalation of the ligand was carried out under dry nitrogen using an MBraun Unilab glovebox. All NMR data was collected using 5 mm O.D. tubes. Ligand precursor (**7**) ^1H NMR spectra were recorded using a Varian Inova 500 (MHz) spectrometer and were referenced versus residual non-deuterated solvent shifts (CHCl_3 $\delta = 7.26$ ppm) (^1H) and ligand precursor (**7**) ^{13}C NMR spectra were recorded using a Varian Inova 500 (MHz) and referenced to the solvent shift (CDCl_3 $\delta = 77.16$ ppm) (^{13}C). High temperature ^1H NMR spectra of polymers were recorded using a Varian Inova 400 (MHz) spectrometer at 125 °C and were referenced to residual non-deuterated solvent shifts ($\text{C}_2\text{H}_2\text{Cl}_4$ $\delta = 6.03$ ppm) (^1H). High-temperature ^{13}C NMR spectra of polymers were recorded using a Varian Inova 750 (MHz) spectrometer at 125 °C and were referenced to solvent shifts ($\text{C}_2\text{H}_2\text{Cl}_4$ $\delta = 74.40$ ppm) (^{13}C). NMR spectra were processed via ACD/NMR Processor Academic Edition software. The NMR overlay of all polyolefin spectra were processed using OpenVnmrJ software. Molecular weights (M_n and M_w) and molecular weight distributions ($\mathcal{D} = M_w/M_n$) were determined by high temperature gel permeation chromatography (HT-GPC). Analyses were performed using a Tosoh EcoSEC HLC-8321 GPC RI Detector. Columns consisted of one TSKgel Hhr (30) HT2 Guard Column (7.5 mm ID x 7.5 cm, 30 μm), two TSKgel GMHhr-H (20) HT2 columns (7.8 mm ID x 30 cm, 20 μm), and one TSKgel Hhr HT-RC reference column (7.8 mm ID x 30 cm, 13 μm). HPLC grade 1,2,4-trichlorobenzene (0.1 wt.% BHT added as stabilizer) was used as the eluent at a flow rate of 1 mL/min at 140 °C. Data was measured relative to polystyrene standards ($\mathcal{D} < 1.1$) a Mark-Houwink correction for the polyethylene (0.725, 0.000406).^{S1} Attenuated-total-reflectance Fourier Transform Infrared (ATR FT-IR) spectra were recorded on a Perkin Elmer Frontier spectrometer equipped with an attenuated-total-reflection (ATR) system. Polymer melting temperatures (T_m s) and degree of crystallinity (χ_c) were measured by differential scanning calorimetry using a DSC-TA Discovery DSC 250. Analyses were performed in hermetic aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from -90 to 180 °C. Polymer T_m and degree of crystallinity was measured using TA TRIOS Software using peak integration (enthalpy) value and referenced versus the theoretical melting enthalpy value for polyethylene (293 J/g).^{S2} Polymer glass transition (T_g s) were measured via DSC as well, analyzed with the TA Trios software using the inflection point analysis value.

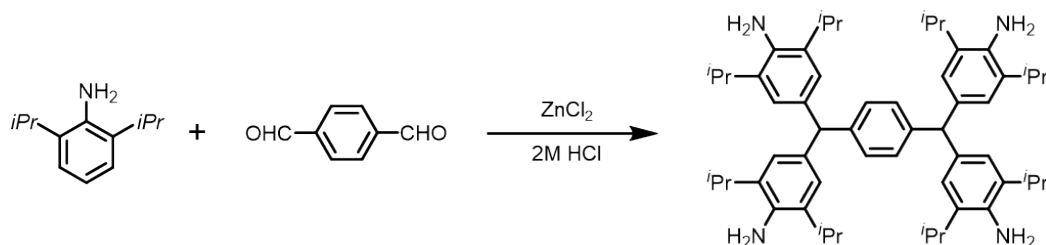
Electrospray ionization mass spectrometry (ESI-MS) was carried out on a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) mass spectrometer equipped with an ESI source. A stock solution of the sample was prepared in methanol at 10 mg/mL. The solution was then diluted in methanol to 0.1 $\mu\text{g/mL}$ before being introduced to the ESI source via direct infusion at a flow rate of 20 $\mu\text{L/min}$. For ESI-MS measurements, the instrument was operated in positive ion mode with a capillary voltage of 2.8 kV, an extraction cone voltage of 2.6 V, sampling cone voltage of 40.0 V, desolvation gas flow rate of 400.0 L/h (N_2), trap cell collision energy (CE) of 4.0 eV, transfer cell CE of 4.0 eV, trap gas flow of 1.5 mL/min (argon), source temperature of 100 °C, and desolvation temperature of 350 °C. SEM imaging was carried out on a JEOL JSM-7401F Field Emission Scanning Electron Microscope and on a Tescan Lyra3 XMU Focused Ion Beam Scanning Electron Microscope. Samples were adhered to an aluminum billet using carbon tape and sputter coated with gold (JEOL) or platinum (Tescan). Powder X-ray diffraction (PXRD)

was conducted on a Rigaku SmartLab 3kW X-Ray Diffractometer. Data was measured from $2\theta = 5^\circ$ to 120° with 0.01° increments. The samples were loaded into a glass-well sample holder, ensuring the surface of the powder is level. Data was processed through the Rigaku PDLX: Integrated X-Ray Diffraction Software. ICP-OES was performed using an Agilent Technologies 710 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Agilent Technologies Expert II software was used for analysis. Nickel was analyzed at a wavelength of 231.604 nm. Catalyst samples were prepared for ICP-OES by digestion in trace metal grade nitric acid for 24 hours and subsequently diluted in nanopure H_2O . Polymer samples were prepared for ICP-OES by first decomposing the polyethylene. Decomposition was achieved by combustion. The residue was then digested in trace metal grade nitric acid for 96 hours. The acid was subsequently diluted using nanopure H_2O . Standards were prepared using a stock solution of 10 ppm nickel in H_2O with 2% (v/v) nitric acid. Standard calibration curves demonstrated a linear fit $R^2 \geq 0.995$.

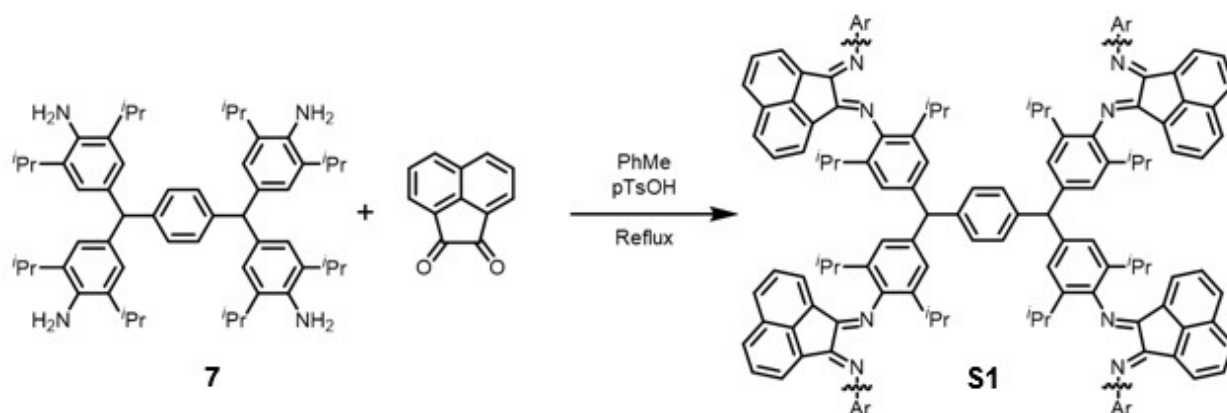
Materials

Ethylene (Polymer Grade 99.9%) was purchased from Matheson Gas. Nickel(II) bromide dimethoxyethane adduct ($\geq 97\%$) was purchased from Strem Chemicals Incorporated. Diisobutylaluminum chloride (97%), diethylaluminum chloride solution (25 wt. % in toluene), MMAO-12, (7 wt. % aluminum in toluene), and terephthaldehyde (99%) were purchased from Millipore Sigma and used as received. Toluene ($\geq 99.5\%$) and tetrahydrofuran (inhibitor free, $\geq 99.5\%$) were purchased from Millipore Sigma and purified by passing through a Vigor Tech solvent purification system. PMAO-IP (13 wt. % in toluene) was purchased from Nouryon Functional Chemicals LLC and used as received. The p-toluenesulfonic acid monohydrate (99%) and acenaphthenequinone (95%) were purchased from Acros Organics. 2,6-diisopropylaniline ($\geq 90\%$) was purchased from Alfa Aesar. Zinc chloride ($\geq 98\%$) was purchased from Fluka Chemika. Hydrochloric acid (Certified ACS Plus) and TraceMetal™ grade nitric acid were purchased from Fisher Chemical. Nickel standard (10 ppm) in 2% v/v nitric acid was purchased from Inorganic Ventures. Unless otherwise noted, all of the reagents were used as received.

Synthetic Procedures

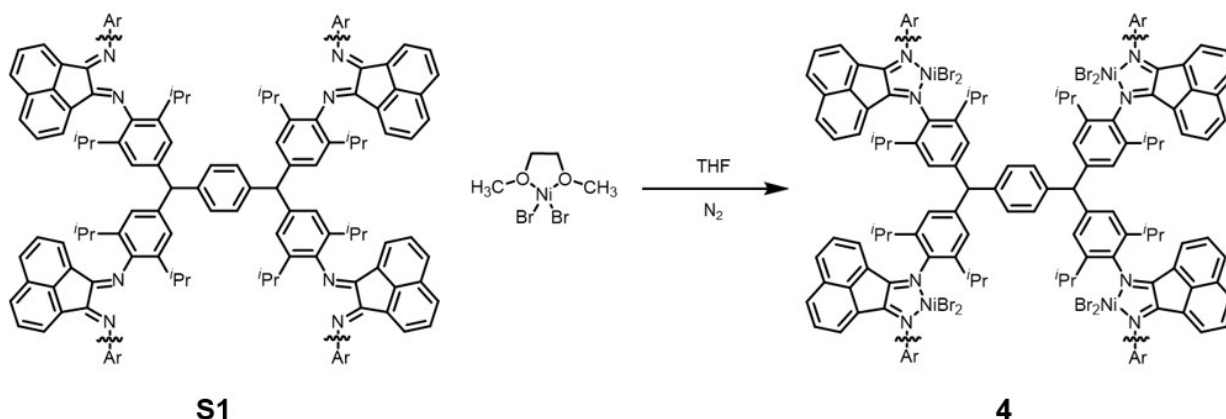


Synthesis of Tetra-aniline (7); (4,4',4'',4''''-(1,4-phenylenebis(methanetriyl))tetrakis(2,6-diisopropylaniline)): In a 1 L round-bottom flask, 2,6-diisopropylaniline (14.20 g, 80 mmol) was added to 2M HCl (400 mL) to yield a white precipitate. To the slurry was added terephthalaldehyde (2.68 g, 20 mmol) followed by solid ZnCl₂ (8.16 g, 60 mmol). The mixture was then heated to reflux for 20 hours, during which time the reaction turned blue in color. The reaction was cooled to room temperature and 6M NaOH was added dropwise, carefully to avoid excessive exothermic reaction, until pH = 10. The precipitate that formed was filtered, collected, and recrystallized in hot methanol/dichloromethane. The isolated solids from MeOH/CH₂Cl₂ recrystallization were subsequently dissolved in CH₂Cl₂ (200 mL), filtered, and the CH₂Cl₂ soluble fraction was evaporated to dryness to afford the violet tetra-aniline (**7**) (7.30 g, 45% yield). **¹H NMR (500 MHz, CDCl₃):** δ 6.99 (s, 1H), δ 6.80 (s, 1H), δ 5.27 (s, 1H), δ 3.50 (s, 1H), δ 2.93–2.84 (m, *J* = 6.7 Hz, 1H), δ 1.17–1.15 (d, *J* = 6.7 Hz, 6H). **¹³C NMR (500 MHz):** δ 143.23, 137.71, 135.00, 132.26, 128.92, 123.97, 56.26, 28.03, 22.63. **HRMS (ESI-MS):** Exact mass [M] calculated for C₅₆H₇₈N₄, 806.6208. [M+H]⁺ detected at 807.6240. **FT-IR (ATR):** Primary amine (N–H) stretching (3486, 3382 cm⁻¹), Primary amine (N–H) deformation (1621 cm⁻¹).

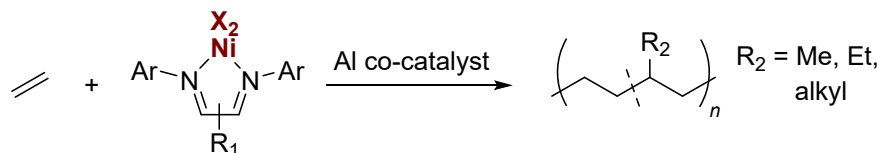


Synthesis of Crosslinked Ligand (S1): Tetra-aniline (**7**) (1.00 mmol, 0.807 g), acenaphthenequinone (2.00 mmol, 0.365 g), and *p*-toluenesulfonic acid (0.125 mmol, 0.025 g) were added to a 500 mL round-bottom flask. To the flask was added 100 mL of PhMe. The mixture was stirred vigorously and refluxed for 48 hours with a Dean-Stark adapter. The insoluble dark red solids that formed became suspended in the PhMe and lined the flask walls during the course of the reaction. The flask was removed from heat and the mixture was filtered via vacuum filtration. The solids were rinsed three times with CH₂Cl₂ (20 mL). The solids were transferred to a mortar and pestle and ground from flakey small particles (c.a. 1–2 mm), vacuum filtered, and transferred back to the mortar and pestle for further grinding in order to acquire a

fine powder (c.a. <0.5 mm particles). This final powder was vacuum filtered and rinsed with three washes of CH₂Cl₂ (20 mL). The crosslinked ligand (**S1**) was collected as dark red powder and transferred to a vial to be dried in a vacuum oven overnight at 60 °C (0.455 g, 46% yield). **FT-IR (ATR)**: Imine (N=C) stretching (1627 cm⁻¹) observed. No Primary amine (N–H) stretching observed (1650–1590 cm⁻¹). No α-diketone (C=O) stretching observed (1730–1710 cm⁻¹).



Metalation and Synthesis of Crosslinked Catalyst (4): In an MBraun Unilab glovebox under anhydrous nitrogen, nickel(II) bromide (dimethoxyethane adduct) (0.20 mmol, 0.617 g) was added to a 20 mL vial and dissolved in 15 mL of anhydrous THF, during which a violet solution immediately formed. The solution was stirred for 24 hours for complete solvation. To this vial, the crosslinked ligand (0.10 mmol, 0.055 g) was added and stirred for an additional 48 hours. Over the duration of the experiment, the intensity of the violet color decreased as it transitioned to a faint red solution. Once complete, stirring was stopped and the catalyst was allowed to settle to the bottom of the vial. The supernatant solution was removed carefully using a pipette. The remaining catalyst was washed once with THF (3 mL), followed by three washes with pentane (3 mL). The crosslinked catalyst (**4**) was obtained as a dark red powder (0.059 g, 77% yield).



General Slurry-Phase Polymerization of Ethylene: A Fisher-Porter reaction vessel (6 oz) and stir bar were dried overnight in an oven at 150 °C. The the reaction vessel and stir bar, a Swagelok® head assembly, a small rubber septa, and a 1 mL syringe with a 22G needle were transferred into a positive pressure N₂ atmosphere Vigor Sci-Lab glovebox. Nickel pre-catalyst was massed in a 1-dram vial. The aluminum co-catalyst was acquired via syringe and massed in a separate 1-dram vial. Anhydrous PhMe (100 mL) was measured in a graduated cylinder. From this, 2 mL was distributed to dilute the co-catalyst and 2 mL was used to suspend the catalyst. The remaining PhMe was transferred to the Fisher-Porter vessel, followed by the co-catalyst solution. The catalyst suspension was then transferred to the vessel. The head assembly was fixed to the vessel to complete the reactor, and the injection port was closed and capped with the rubber septa before transferring the reactor out of the glovebox. The reactor was placed on a stir plate at 300 rpm with a water bath at room temperature for temperature regulation. Monomer grade ethylene was introduced via continuous flow through a quick-connect adapter for the duration of the reaction. At the end of the experiment, the ethylene supply was closed and the reactor was vented. Once near atmospheric pressure, 5 mL of 5% (v/v) HCl in MeOH was injected and stirred for an additional 5 minutes. The reactor was then disassembled and the polymer was precipitated in 250 mL of MeOH, isolated via vacuum filtration, and dried in a vacuum oven at 60 °C overnight in preparation for characterization.

Gas-Phase Polymerization of Ethylene: A Fisher-Porter reaction vessel (6 oz) and stir bar were dried overnight in an oven at 150 °C. The reaction vessel and stir bar, Swagelok® head assembly, a small rubber septa, and a 1 mL syringe with a 22G needle were transferred into a positive pressure N₂ atmosphere Vigor Sci-Lab glovebox. The catalyst was massed in a 1-dram vial and suspended in anhydrous PhMe (2 mL). The suspension was transferred to the reaction vessel. The catalyst was allowed to settle to the bottom of the reactor. The co-catalyst was then added and allowed to contact the heterogeneous catalyst for 5 minutes. The supernatant solution was then removed from the reactor via pipette, extracting the PhMe and co-catalyst, which left behind a thin powder coating of now activated catalyst particles on the bottom of the vessel. The head assembly was fixed to the vessel to complete the reactor, and the injection port was closed before transferring the reactor out of the glovebox. Dried, monomer grade ethylene was introduced slowly at 3 atm. The immediate consumption of ethylene and an exotherm were qualitatively observed. The ethylene supply maintained at 3 atm of pressure and the exotherm was observed for approximately 40 min of the 1 hour reaction time. Polyethylene formation was visually observed over the course of the reaction. After 1 hour, the ethylene supply was closed and the reactor was vented. Once at atmospheric pressure, 5 mL of 5% (v/v) HCl in MeOH was injected and stirred for an additional 5 minutes. The reactor was then disassembled and the polymer was removed from the vessel using a plastic spatula with little to no observable polyethylene residue left lining the vessel walls.

Table S1.

Entry [#]	Activator	t_{rxn} (min)	C_2H_4 (atm)	T_{rxn} (°C)	Yield (g)	M_n (kg/mol) ^a	\bar{D} (M_w/M_n) ^a	N_b ^b	T_m (°C) ^c	ΔH_f (kJ/g) ^c	χ (%) ^d
1	1/iBu ₂ AlCl	60	3	25	5.17	163	2.27	85	N.D.	N.D.	<1
2	1/iBu ₂ AlCl	60	3	80	5.58	67.2	2.56	104	N.D.	N.D.	<1
3	PMAO	60	3	25	0.48	301	4.92	10	127	121	41
4	MMAO-12	60	3	25	0.53	283	5.37	17	126	116	40
5	Et ₂ AlCl	60	3	25	7.95	258	4.42	25	120	100	34
6	iBu ₂ AlCl	60	3	25	13.80	217	3.52	43	118	58	20
7	iBu ₂ AlCl	60	1	25	3.10	262	3.19	45	114	55	16
8	iBu ₂ AlCl	60	5	25	14.12	266	3.75	32	120	83	28
9	iBu ₂ AlCl	60	3	0	0.71	409	3.88	7	128	146	50
10	iBu ₂ AlCl	60	3	50	6.42	82.8	3.80	74	112	14	5
11	iBu ₂ AlCl	60	3	80	3.41	67.7	3.33	97	N.D.	N.D.	<1
12 ^e	iBu ₂ AlCl	60	3	80	5.73	65.6	3.40	85	N.D.	N.D.	<1
13	iBu ₂ AlCl	60	5	0	1.03	409	4.05	4	130	129	44
14	PMAO	60	5	0	0.33	321	4.33	4	130	132	45
15 ^f	iBu ₂ AlCl	60	3	25	3.75	78.9	5.02	65	112	27	9
16	iBu ₂ AlCl	30	3	25	9.05	149	3.88	44	113	52	18
17	iBu ₂ AlCl	10	3	25	1.91	134	4.02	37	114	65	22

Polymerizations were conducted in PhMe (100 mL) with 10 μmol of catalyst **4** (catalyst **1** used for entries 1 and 2) activated with aluminum co-catalyst (1 mmol, 100 equiv). ^aDetermined by gel-permeation chromatography using 1,2,4-trichlorobenzene at 140 °C relative to polystyrene standards.¹ ^bAlkyl branches (CH_3) per 1,000 carbons (N_b) determined from ¹H NMR using 1,1,2,2-tetrachloroethane as solvent at 125 °C. ^cDetermined by differential scanning calorimetry from the second heat cycle with a heating rate of 10 °C/min. ^dCalculated using the enthalpy of fusion for crystalline PE ($\Delta H_f = 293 \text{ J/g}$).^{S2} ^eReplication of high temperature polymerization with catalyst **4**. ^fGas-phase polymerization.

GPC of Polymers

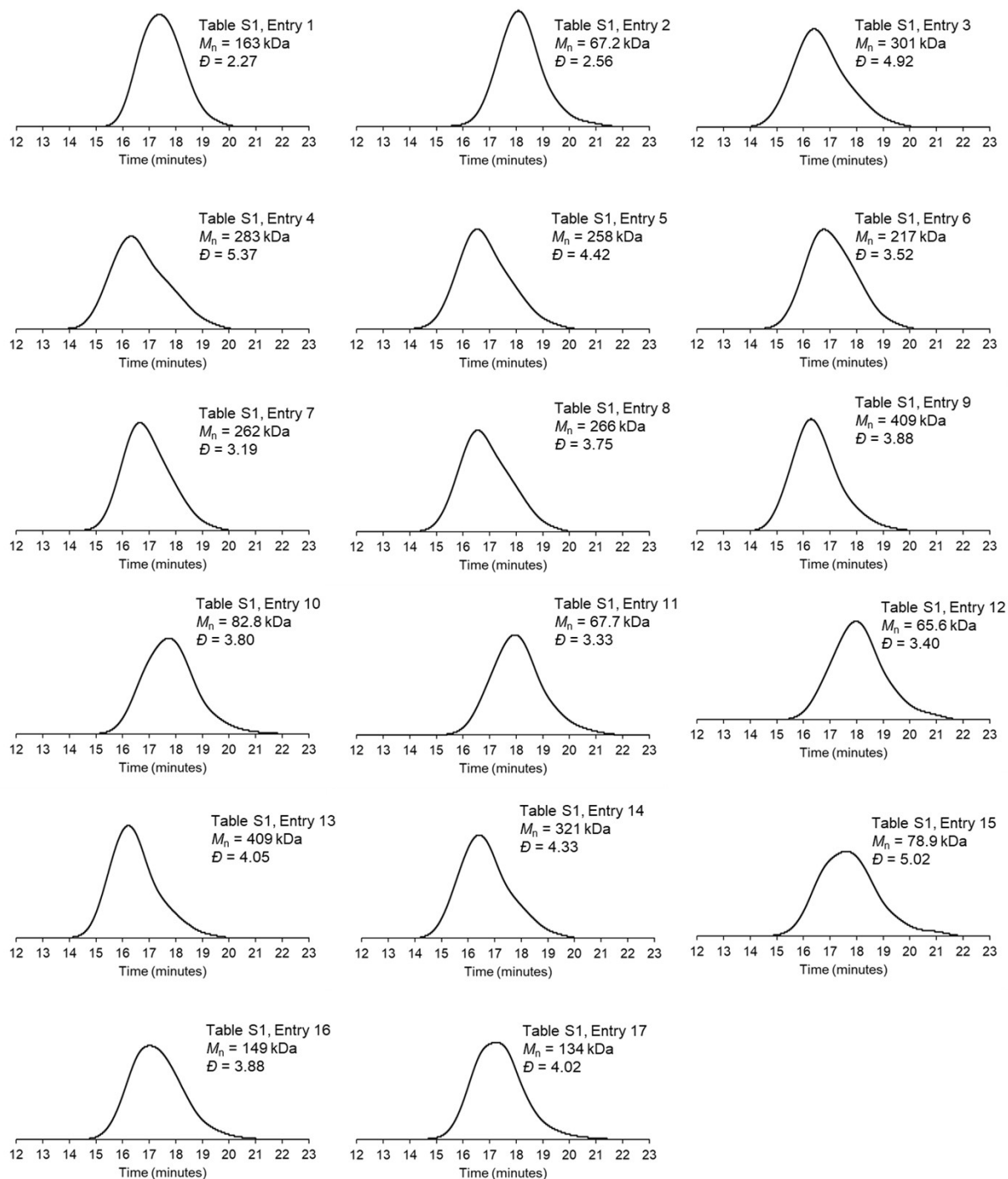


Figure S1. High temperature gel permeation chromatography (HT-GPC) of polyolefin samples in Table S1. GPC calculations based on integrated peaks between the retention times of 12–23 minutes for all samples.

DSC of Polymers

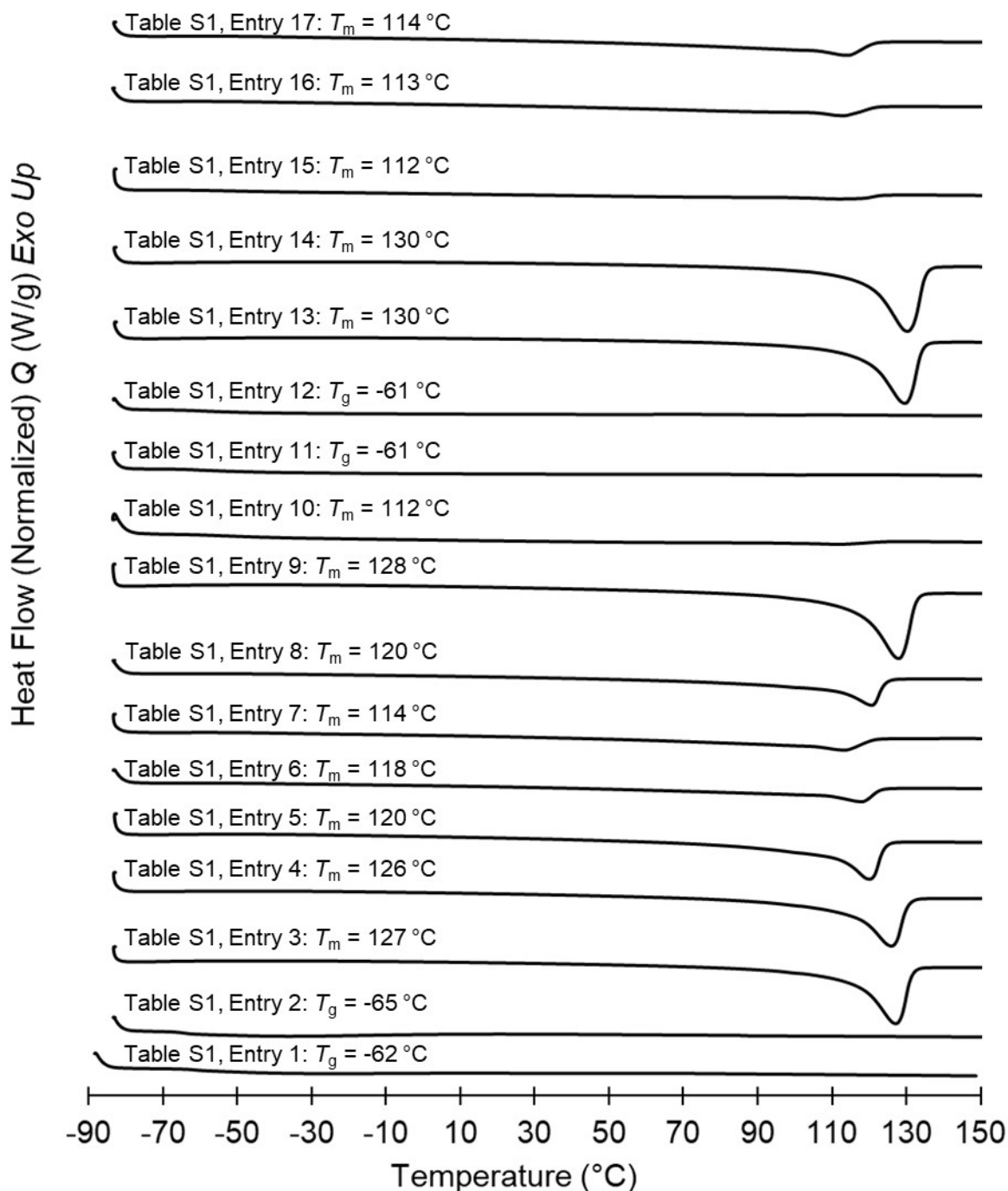


Figure S2. Differential Scanning Calorimetry (DSC) of second heating cycles from -90 °C to 150 °C of polyolefin samples in Table S1. Melting temperatures were calculated according to peak values reported by peak integration (enthalpy) analysis. Crystallinity values were calculated by comparing enthalpy values to pure crystalline polyethylene values reported by Wunderlich and Czornyj.^{S2}

NMR Analysis

NMR of Tetra-aniline (7)

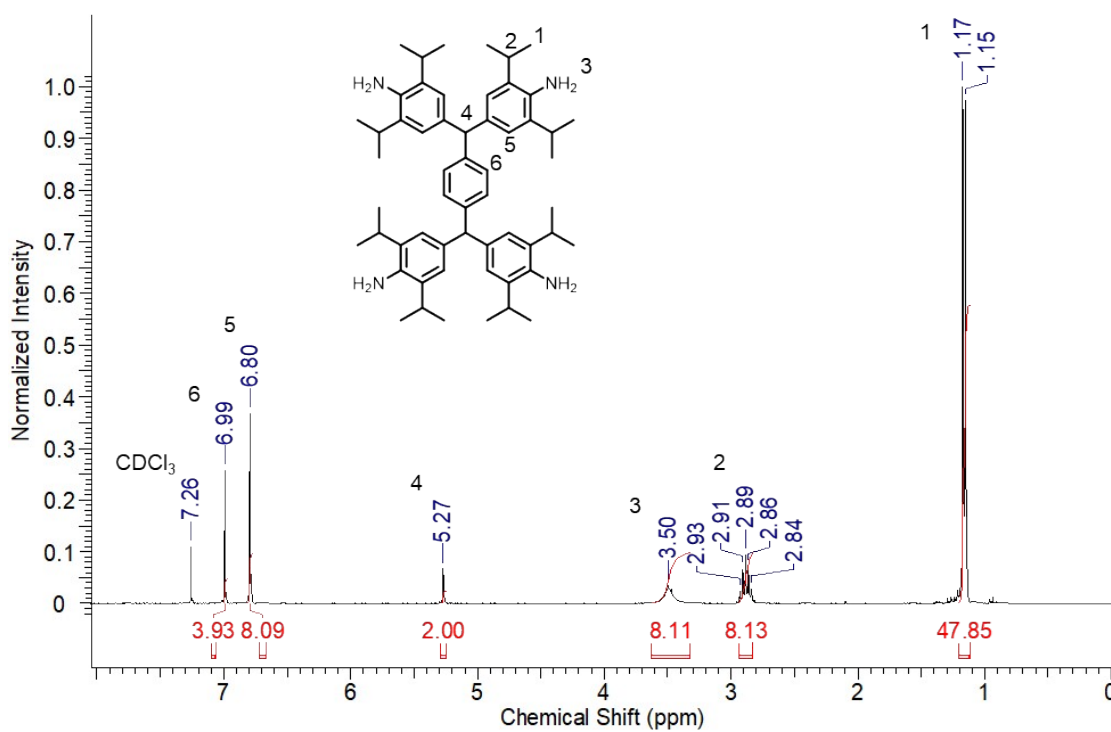


Figure S3. ^1H NMR (CDCl_3) of tetra-aniline (7).

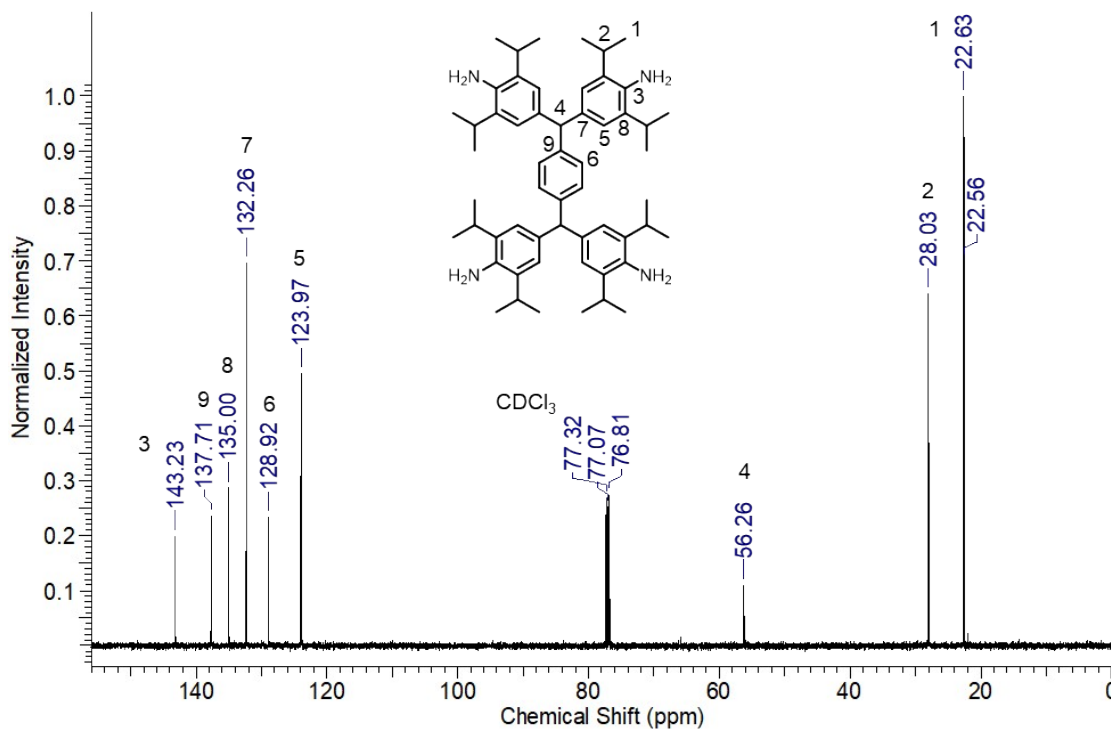


Figure S4. ^{13}C NMR (CDCl_3) of tetra-aniline (7).

NMR of Polymers

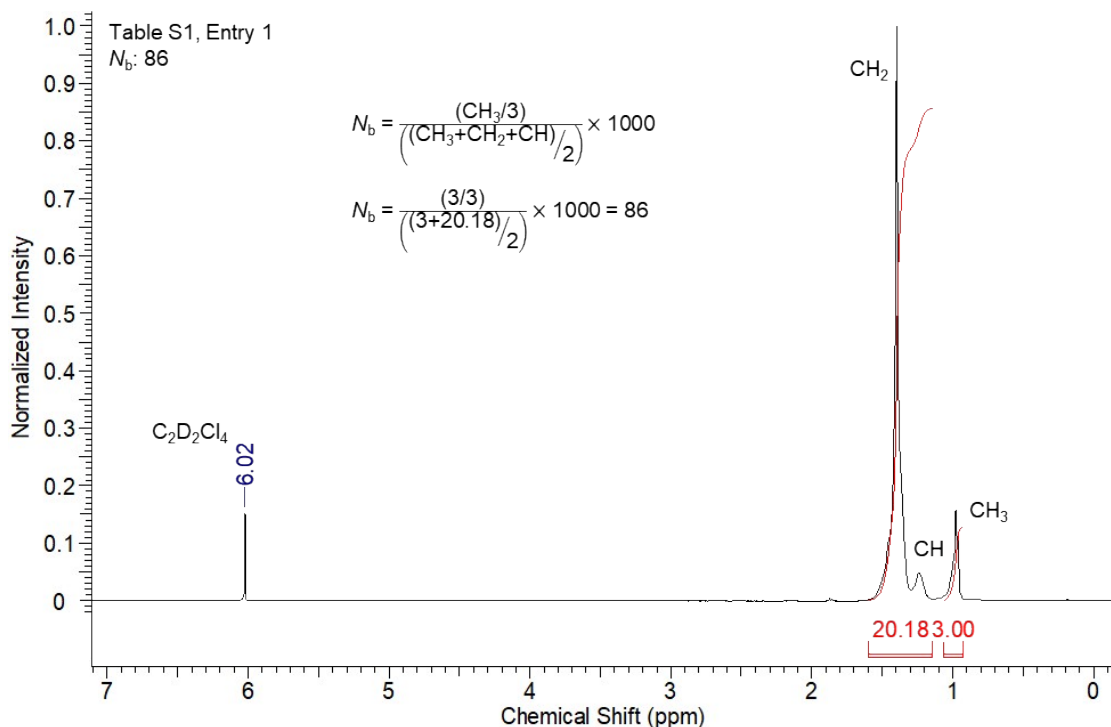


Figure S5. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 1. Polymerization ran with catalyst **1** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 25 $^\circ C$. Branching number (N_b) calculation shown. Values for N_b calculated based on the work of Brookhart and coworkers.^{S3}

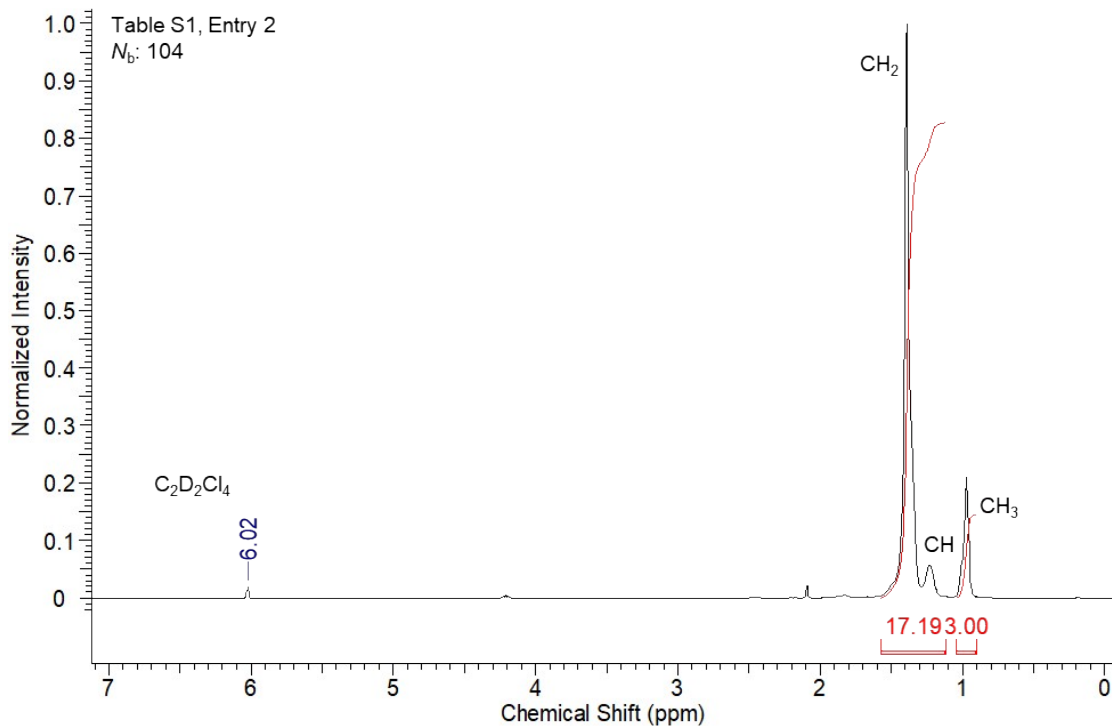


Figure S6. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 2. Polymerization ran with catalyst **1** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 80 $^{\circ}C$.

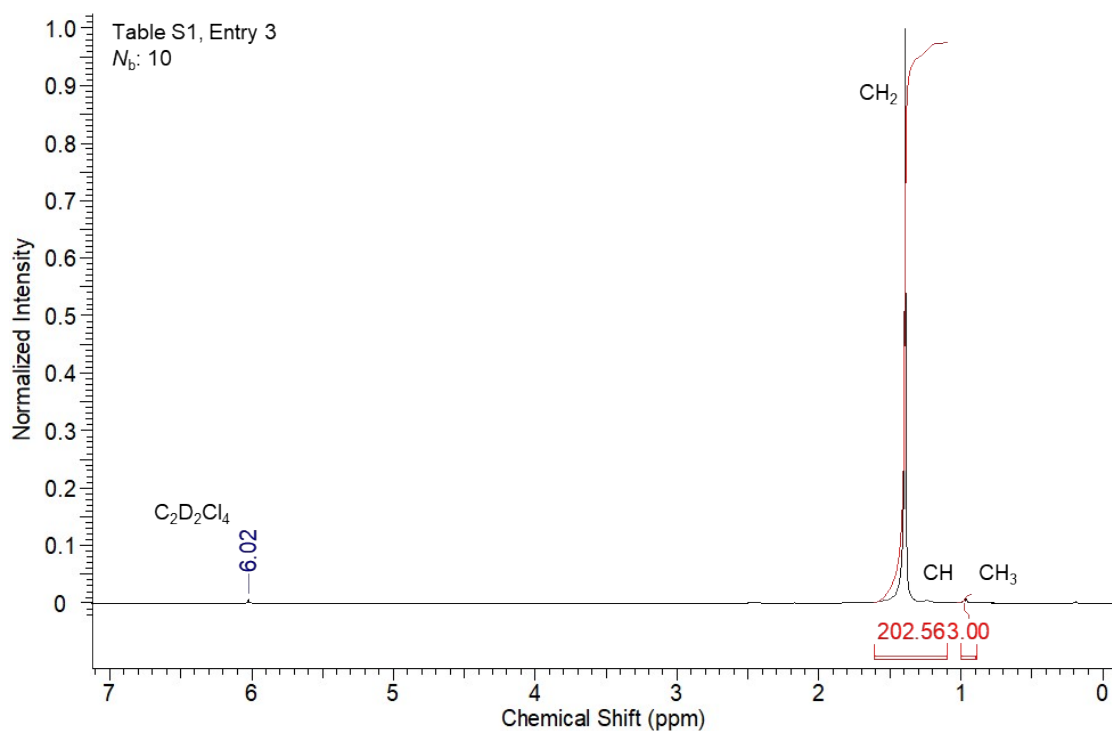


Figure S7. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 3. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using PMAO (100 equiv. Al to catalyst) and ethylene (3 atm) at 25 $^{\circ}C$.

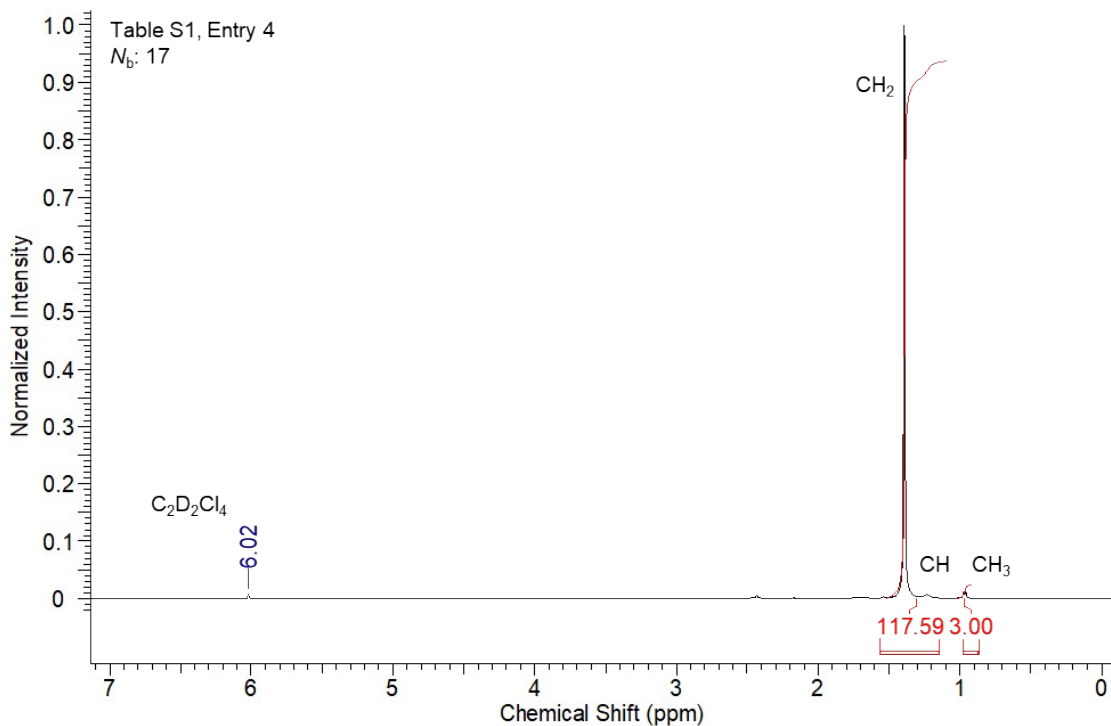


Figure S8. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 4. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using MMAO-12 (100 equiv. Al to catalyst) and ethylene (3 atm) at 25 $^\circ$ C.

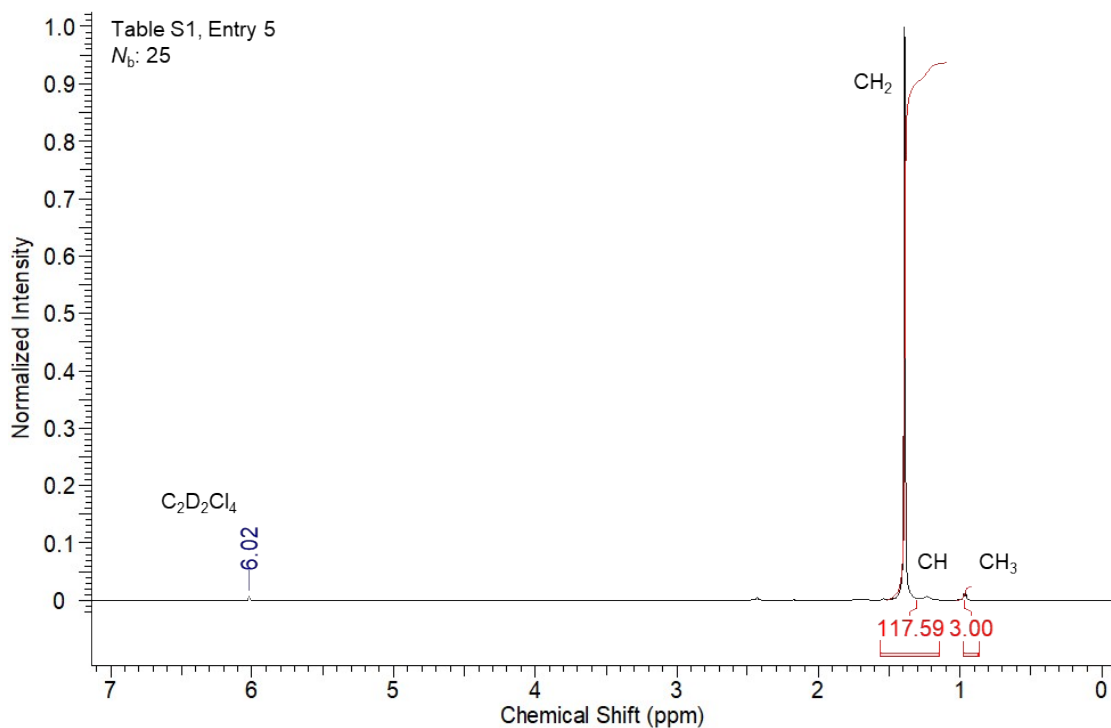


Figure S9. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 5. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using Et_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 25 $^\circ$ C.

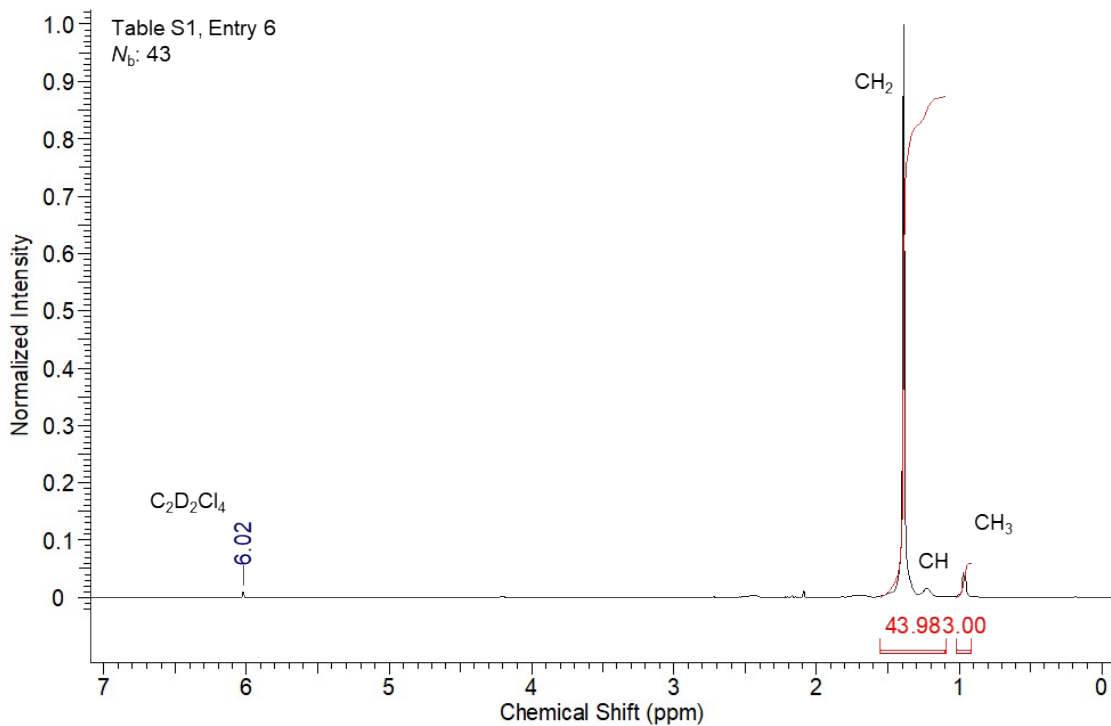


Figure S10. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 6. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 25 °C.

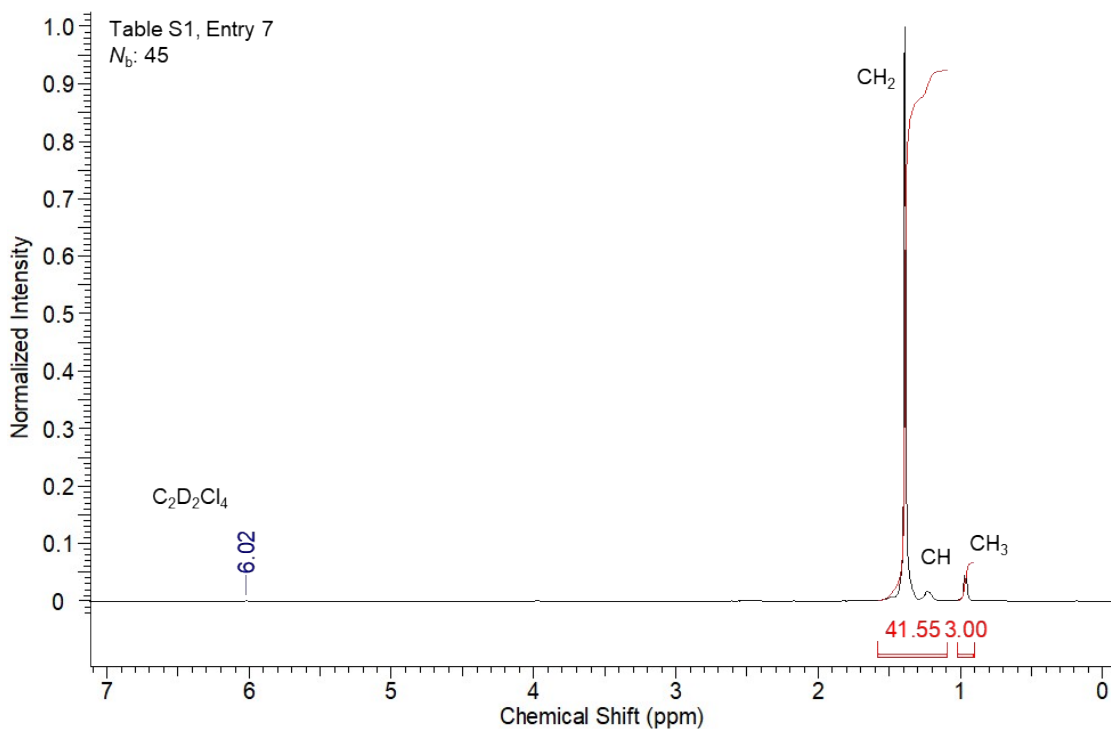


Figure S11. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 7. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (1 atm) at 25 °C.

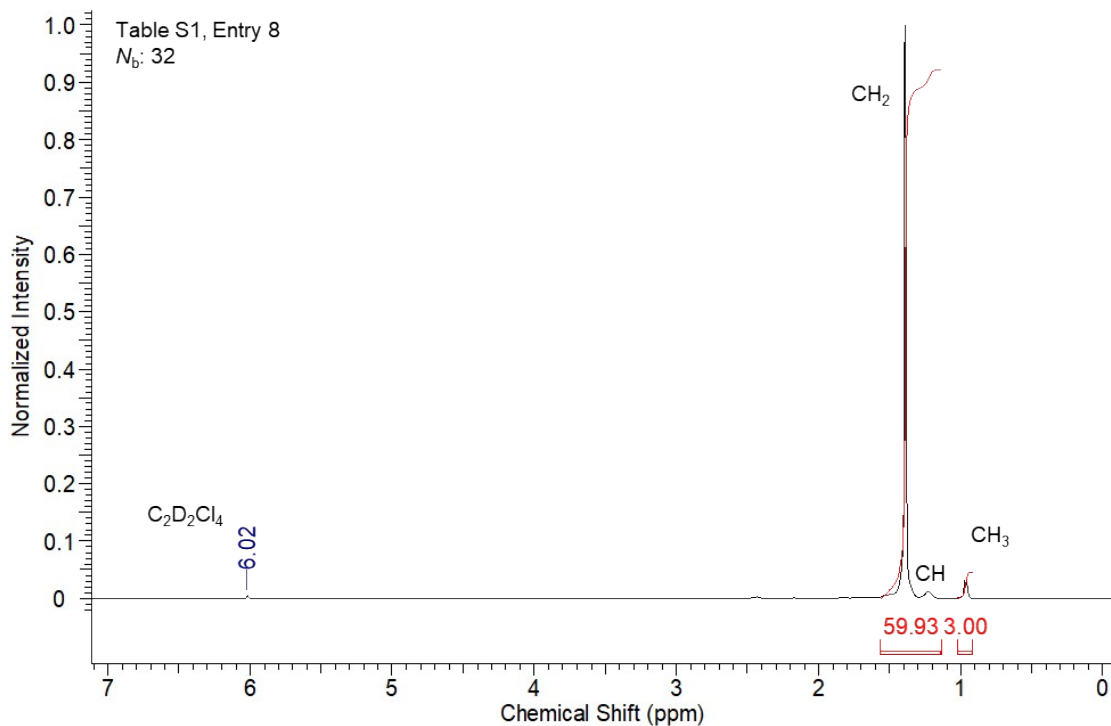


Figure S12. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 8. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (5 atm) at 25 °C.

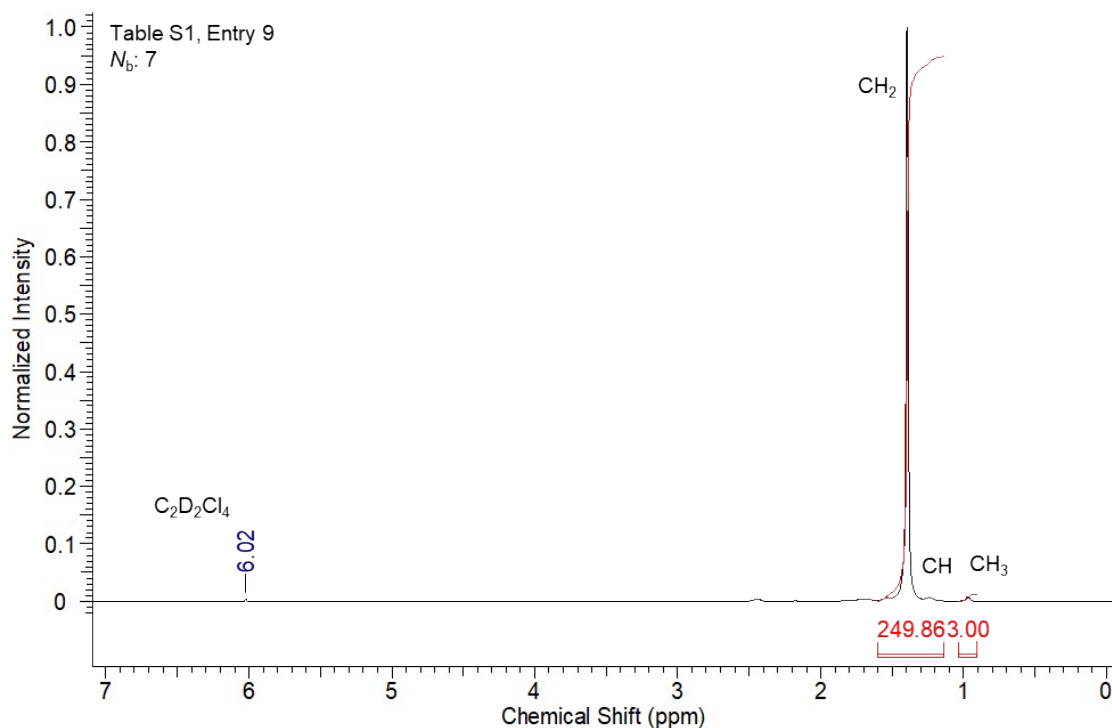


Figure S13. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 9. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 0 °C.

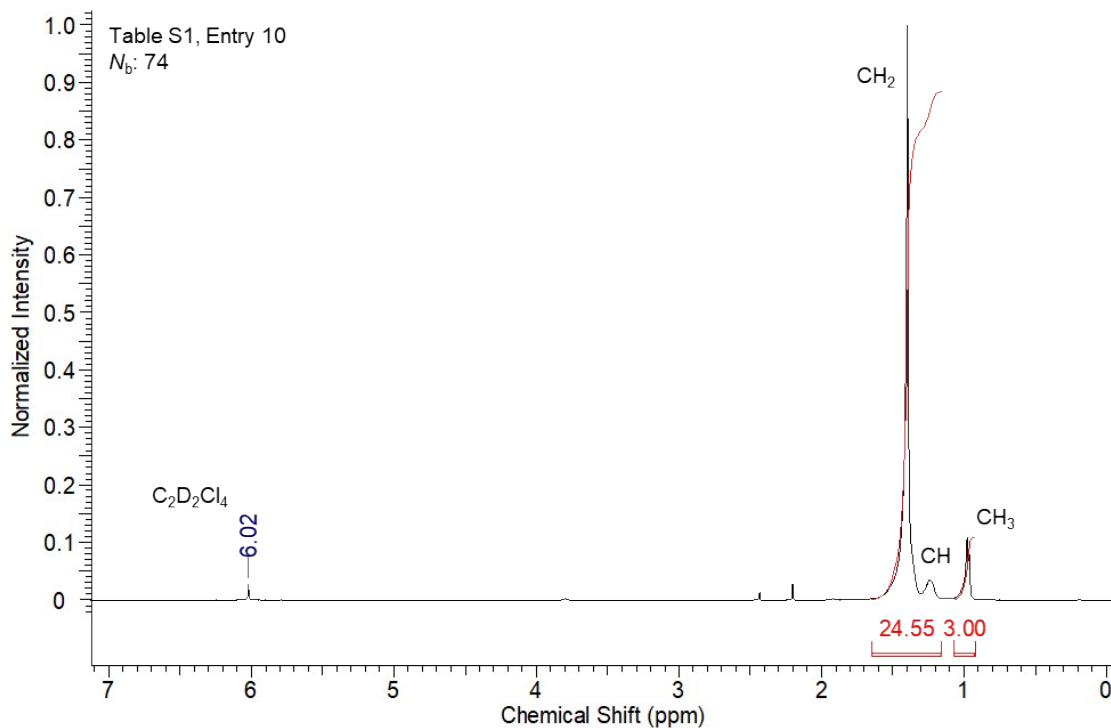


Figure S14. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 10. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 50 °C.

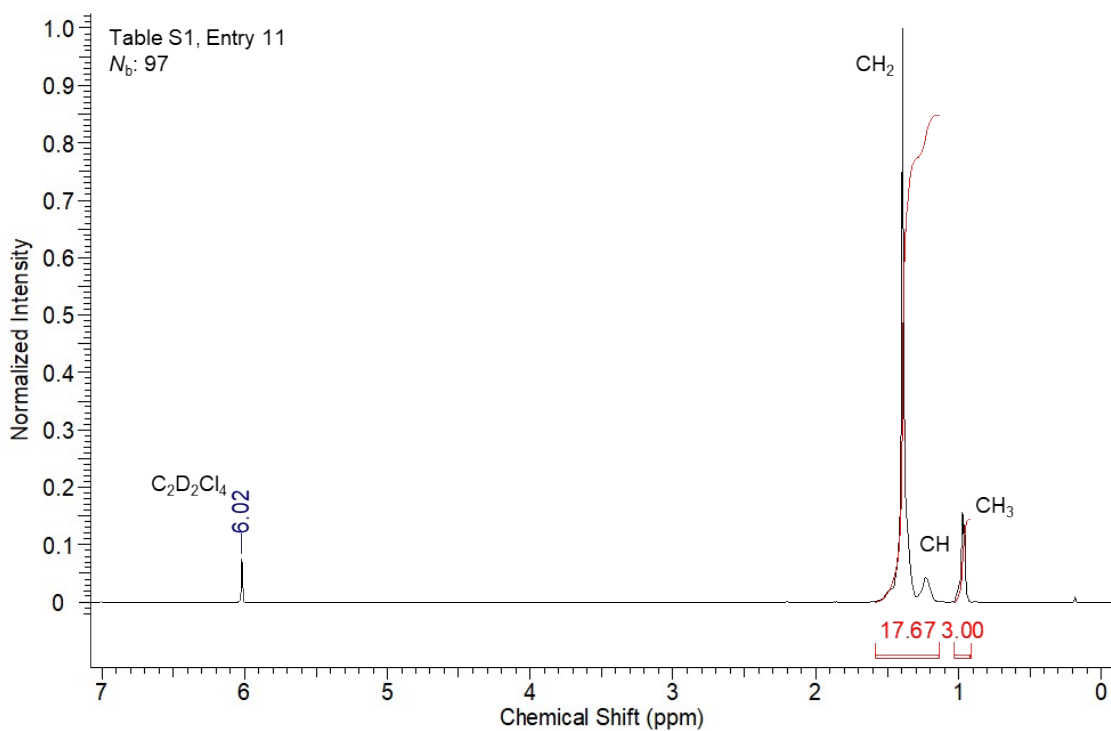


Figure S15. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 11. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 80 °C.

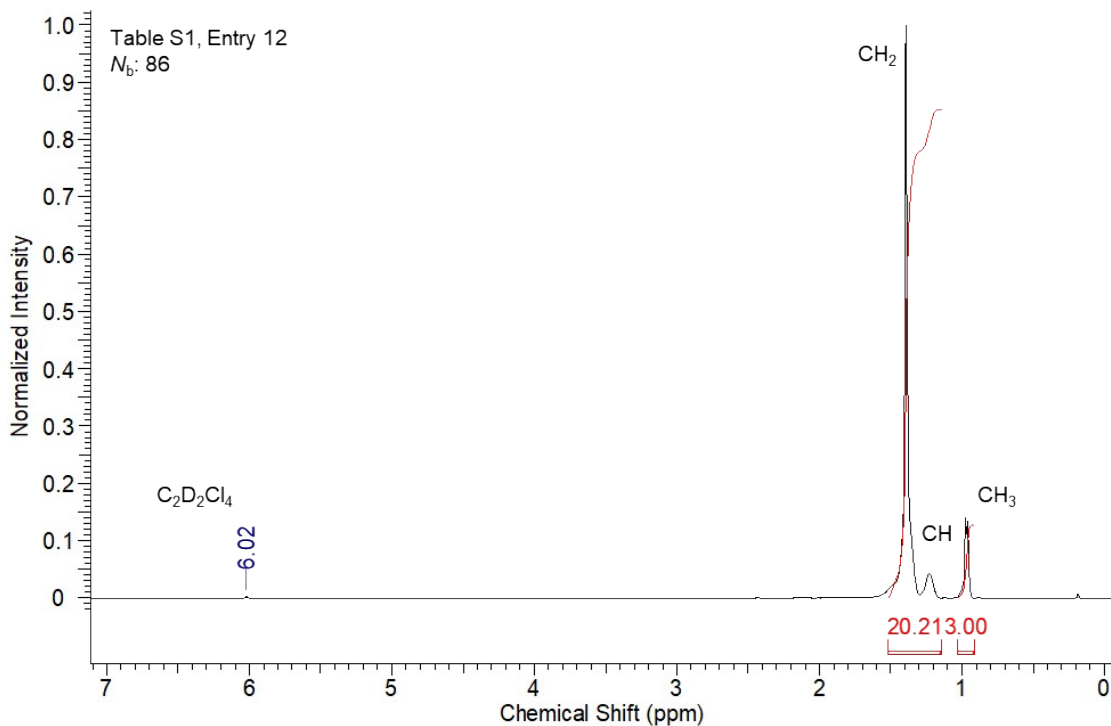


Figure S16. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 12. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 80 °C.

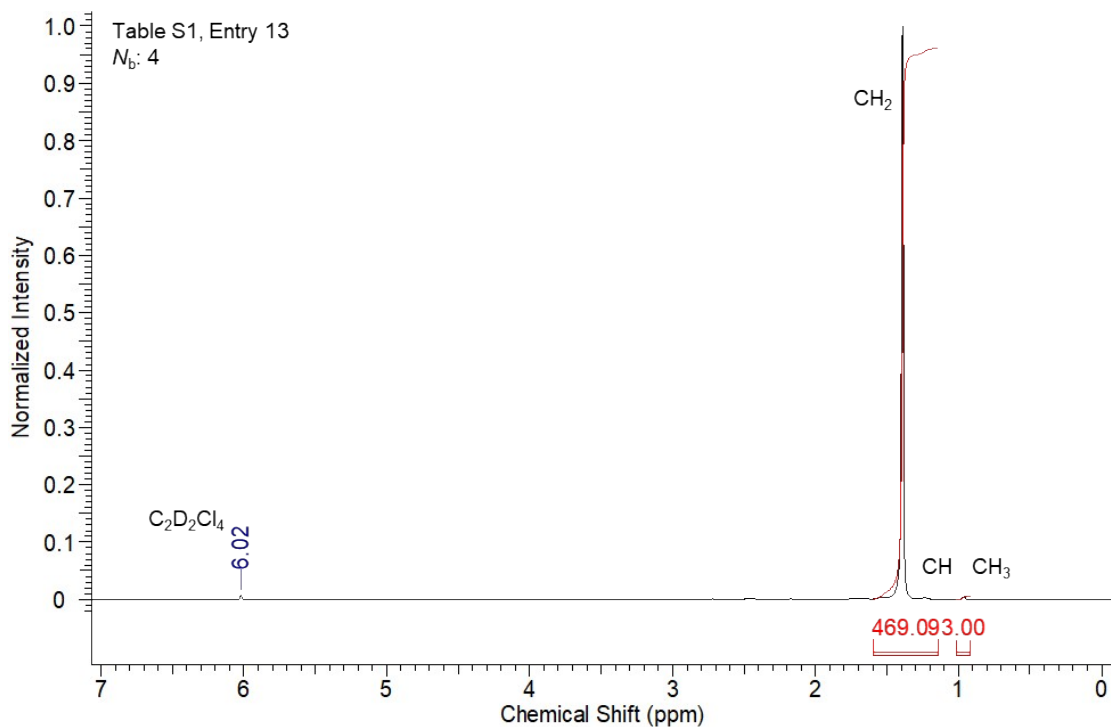


Figure S17. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 13. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (5 atm) at 0 °C.

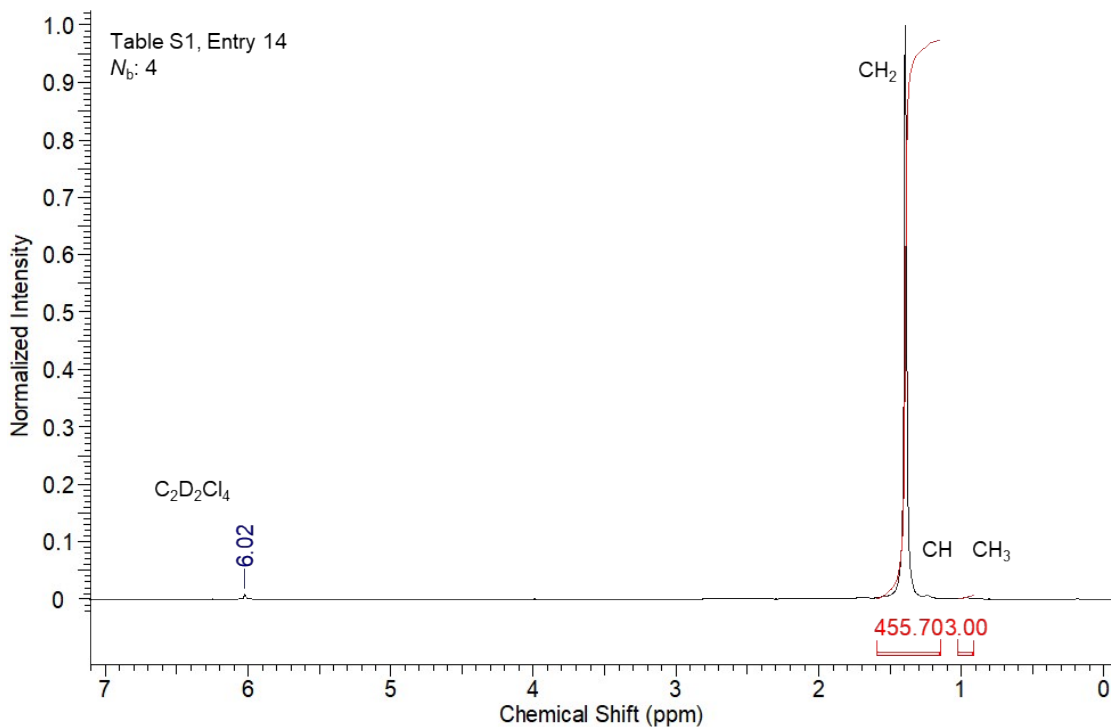


Figure S18. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 14. Polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using PMAO (100 equiv. Al to catalyst) and ethylene (3 atm) at 0 °C.

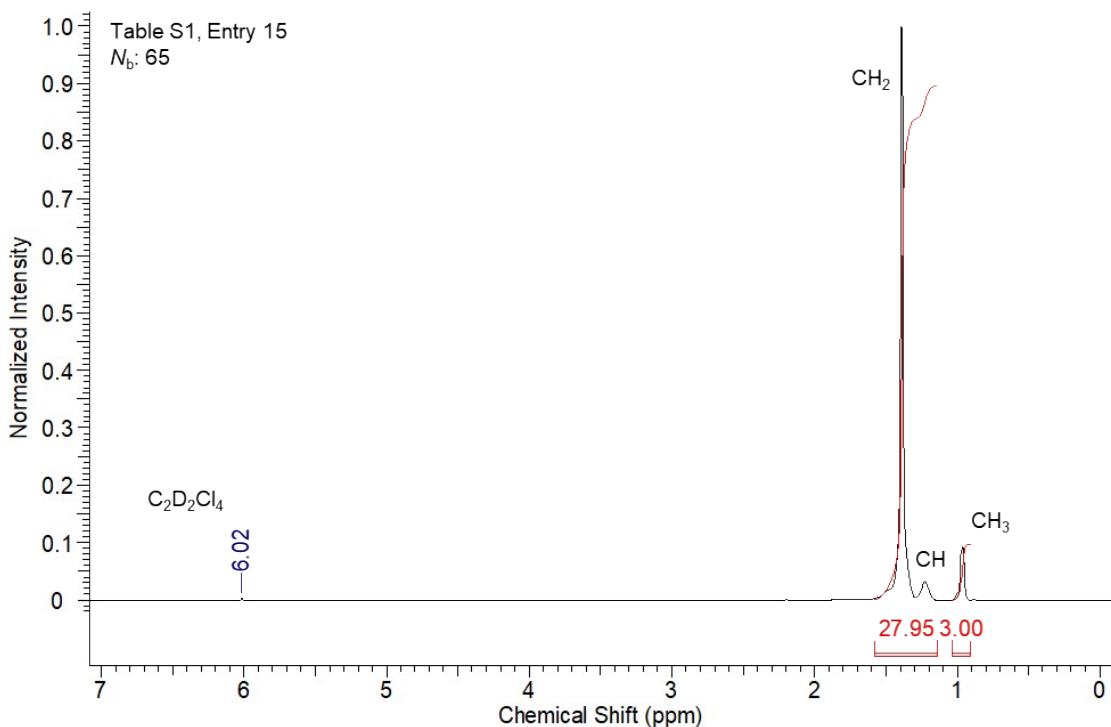


Figure S19. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 15. Gas-phase polymerization ran with catalyst **4** (10 μ mol) for 60 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 25 °C.

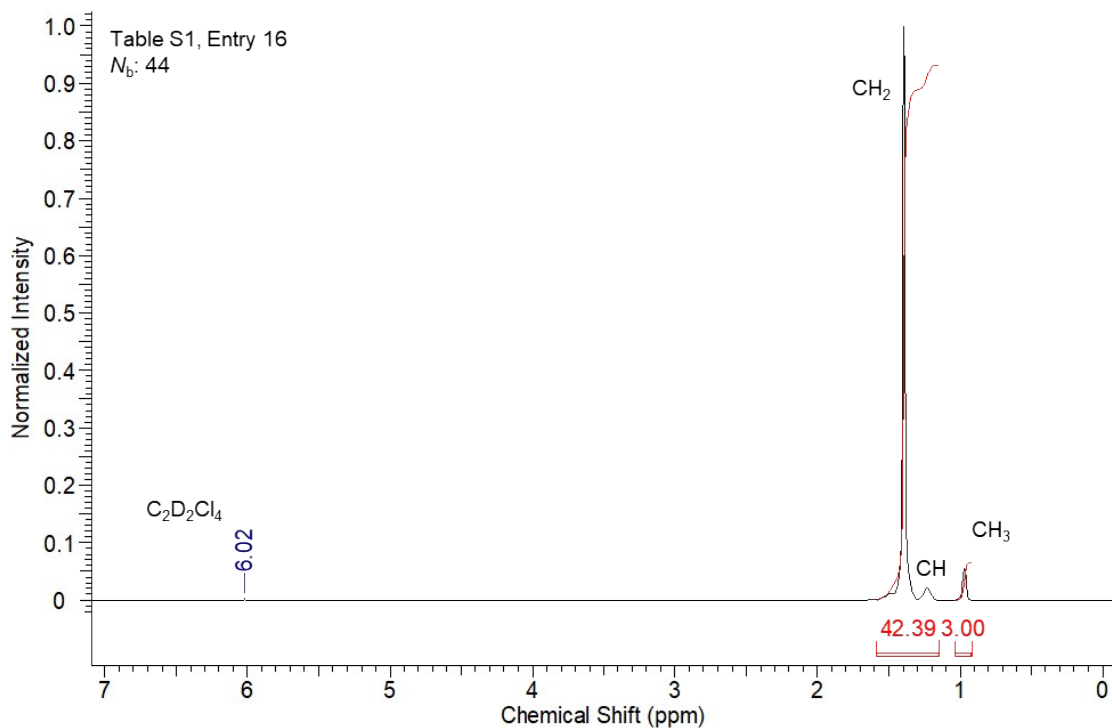


Figure S20. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 16. Polymerization ran with catalyst **4** (10 μ mol) for 30 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 25 °C.

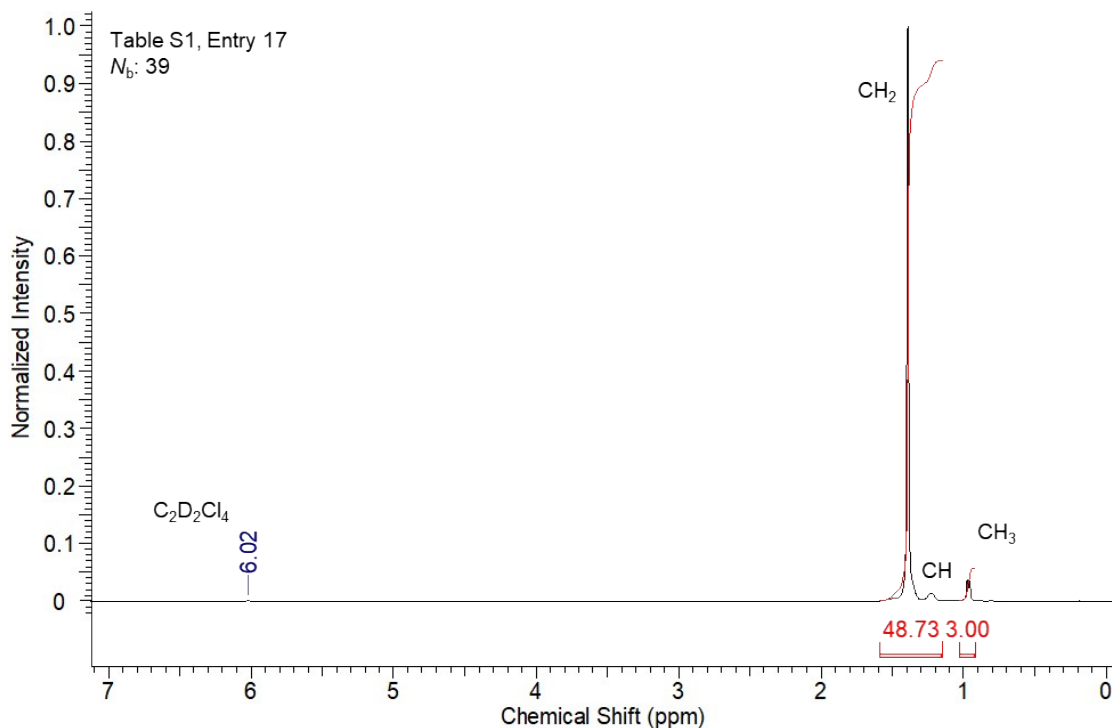


Figure S21. 1H NMR ($C_2D_2Cl_4$) of Table S1, Entry 17. Polymerization ran with catalyst **4** (10 μ mol) for 10 minutes using iBu_2AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 80 °C.

^1H NMR Overlay of Polymers

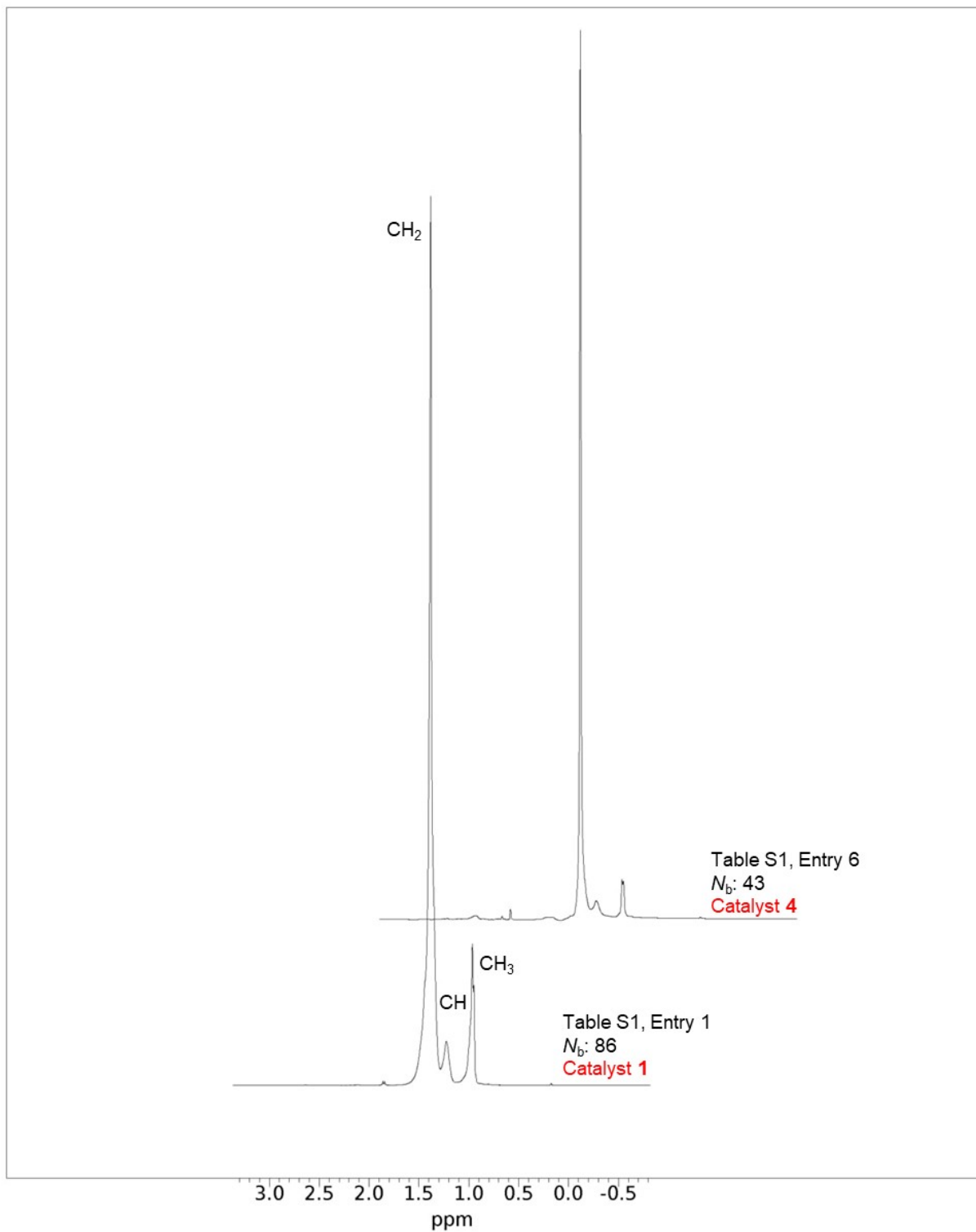


Figure S22. ^1H NMR overlay of polymers from catalyst **1** and **4** polymerized under identical conditions of 10 μmol catalyst, 25 $^\circ\text{C}$, 3 atm ethylene, $i\text{Bu}_2\text{AlCl}$ (100 equiv) and 60 minutes of reaction time. Spectra are normalized.

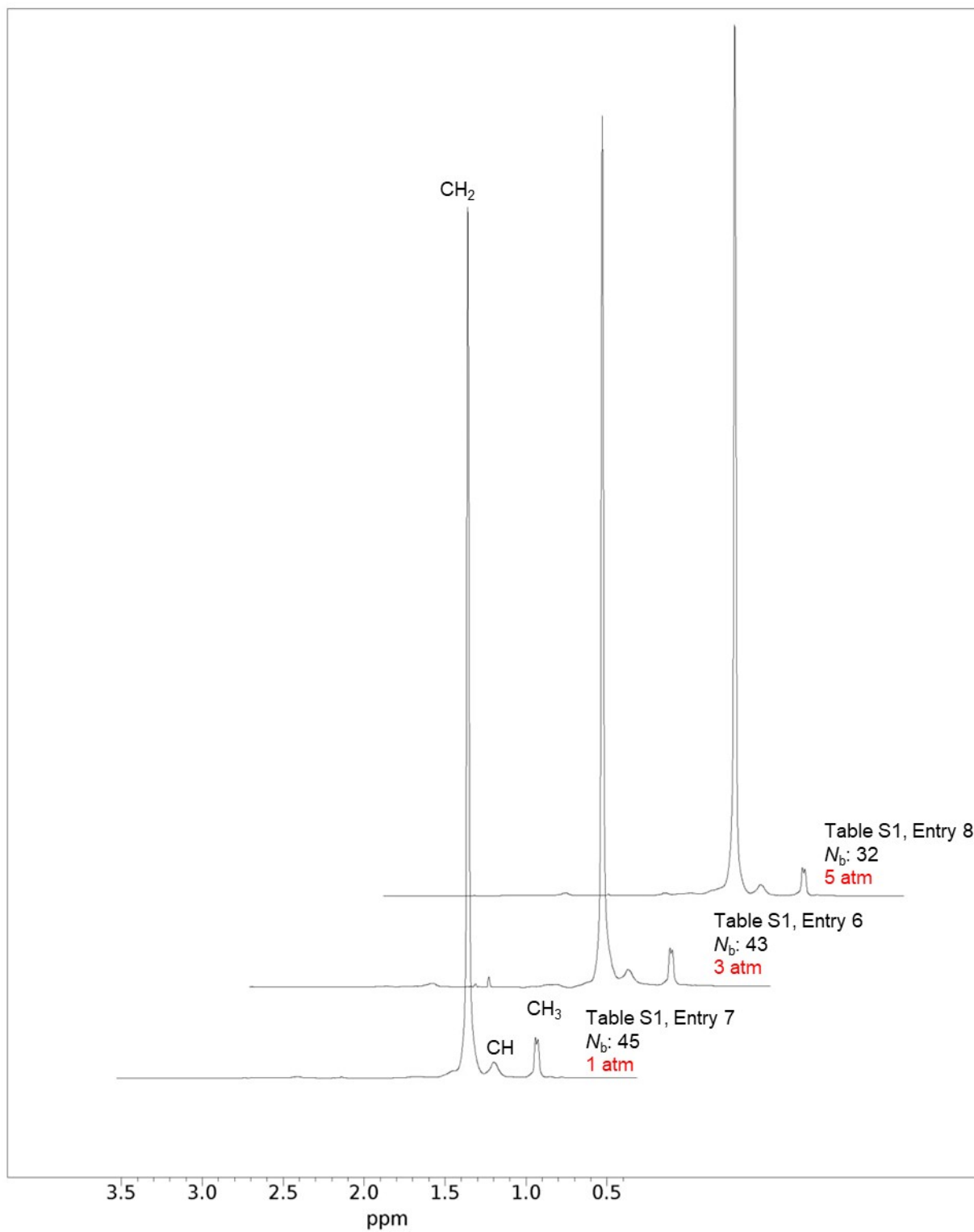


Figure S23. ¹H NMR overlay of polymers from catalyst **4** at various pressures. Spectra are normalized.

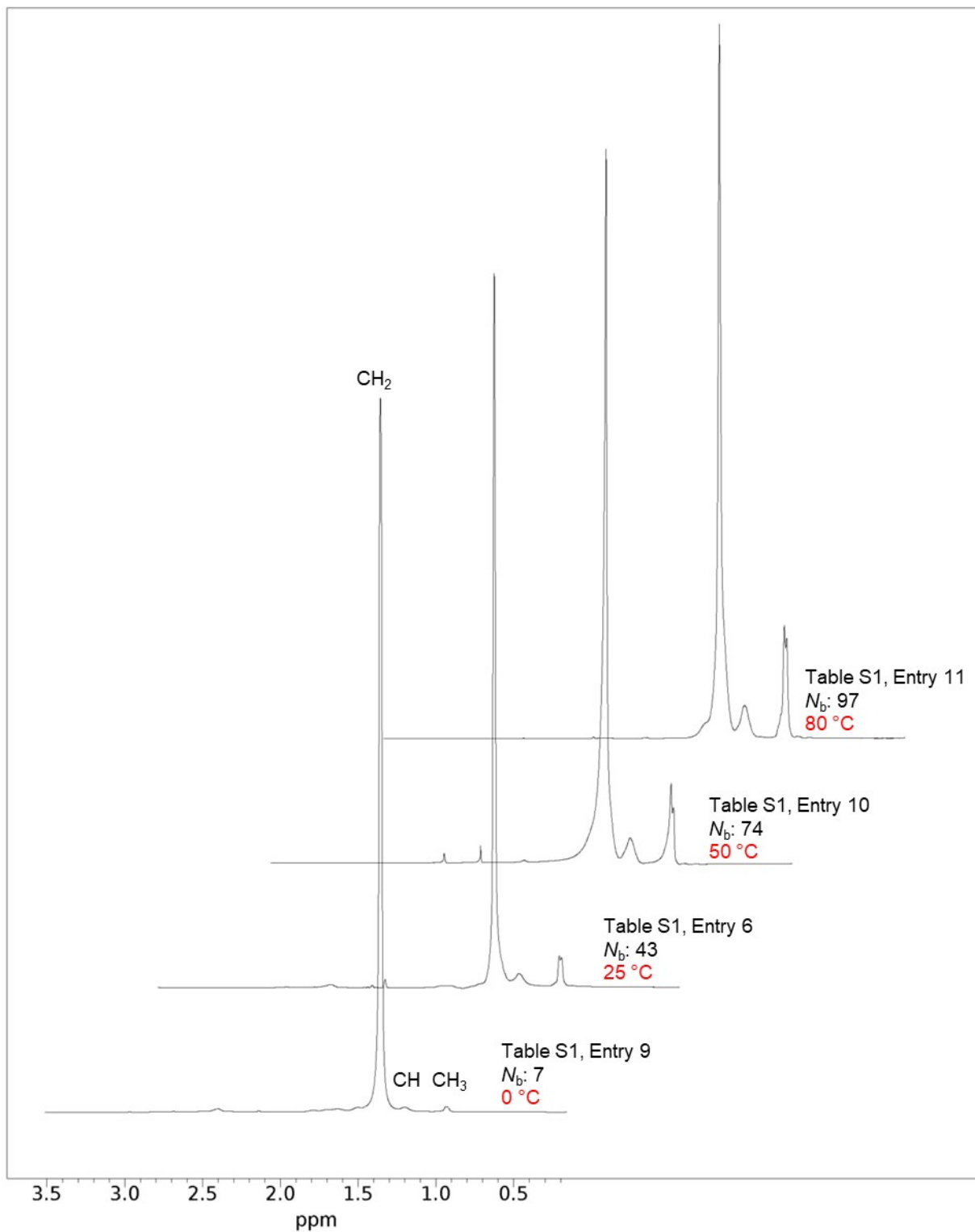


Figure S24. ¹H NMR overlay of polymers from catalyst **4** at various temperatures. Spectra are normalized.

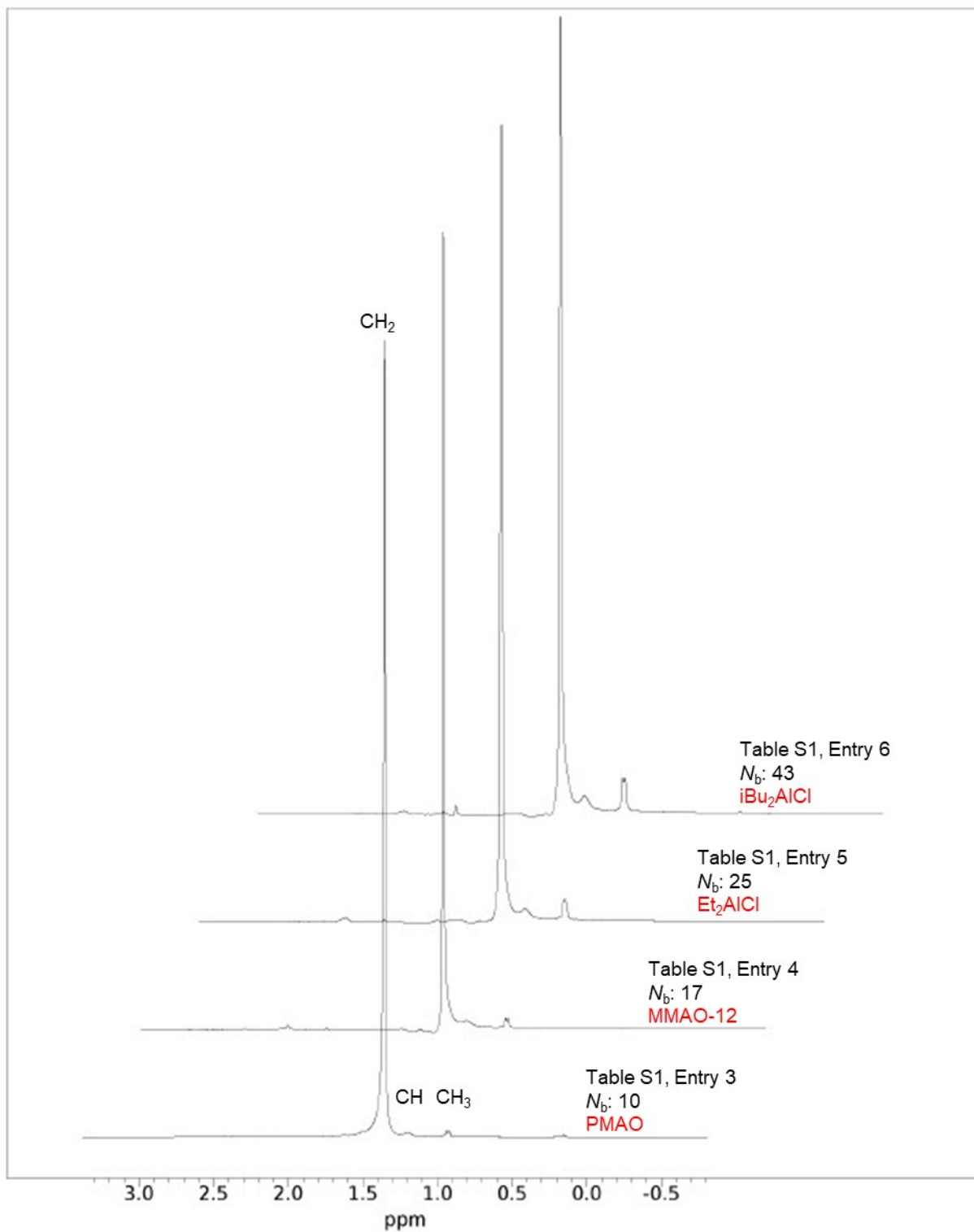


Figure S25. ¹H NMR overlay of polymers from catalyst **4** activated by various co-catalysts. Spectra are normalized.

¹³C NMR of Polymers

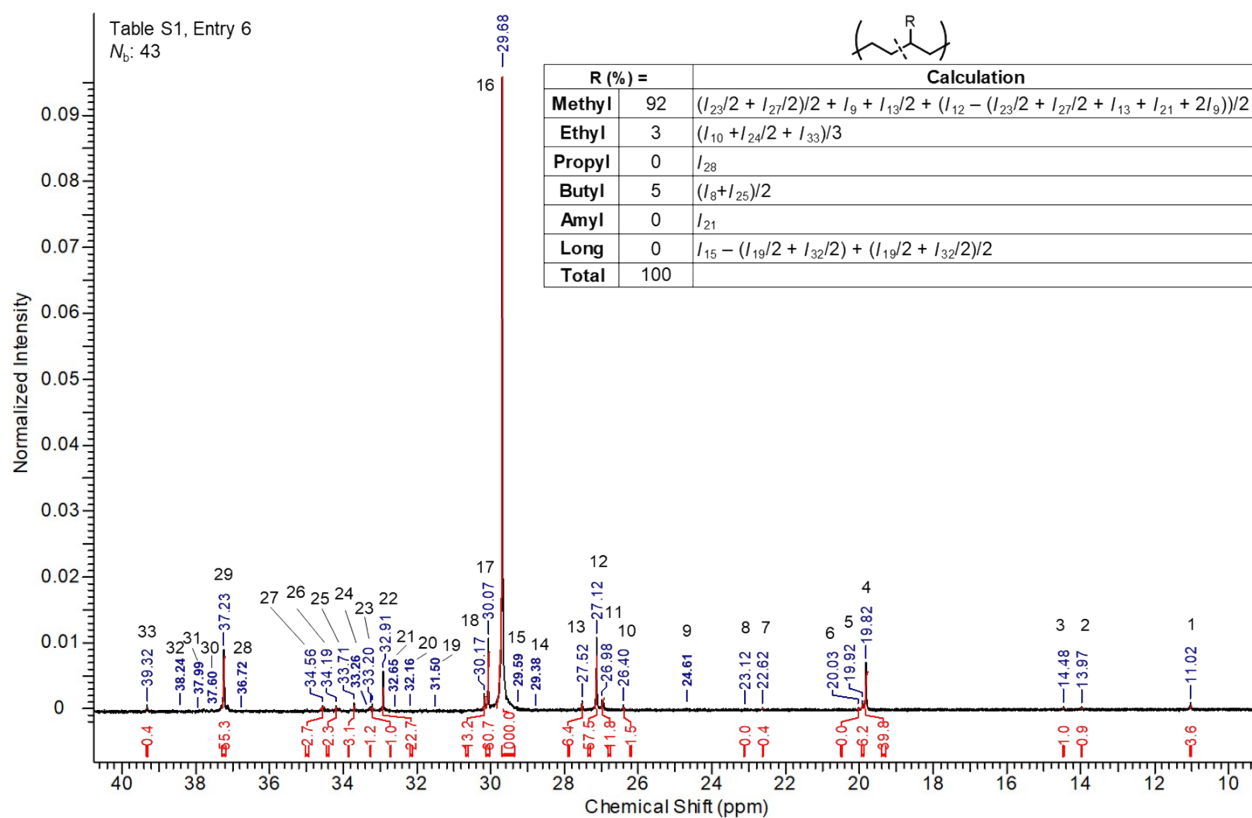


Figure S26. ¹³C NMR (C₂D₂Cl₄) of Table S1, Entry 6. Polymerization ran with catalyst **4** (10 μmol) for 60 minutes using iBu₂AlCl (100 equiv. to catalyst) and ethylene (3 atm) at 25 °C. Chemical shifts of branching identities assigned and calculated according to Nunes and coworkers.^{S4}

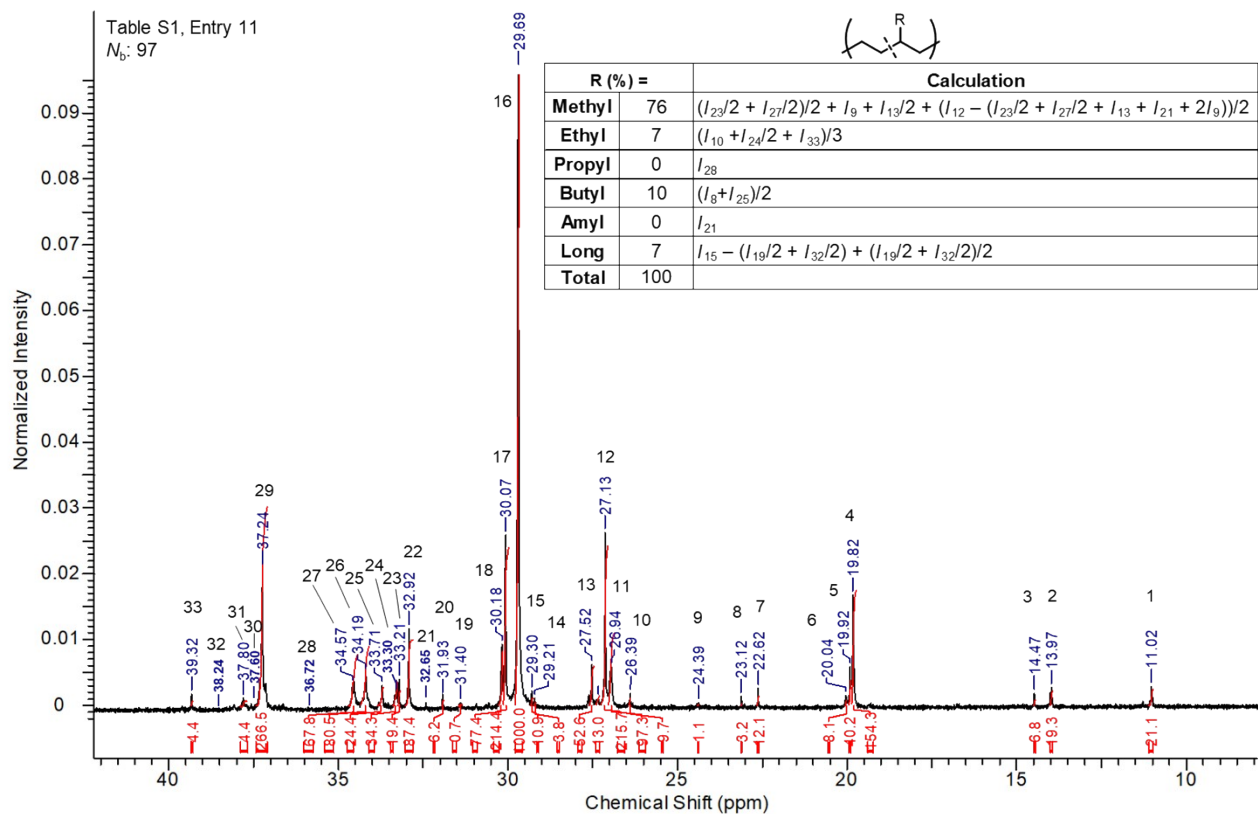


Figure S27. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$) of Table S1 Entry 11. Polymerization ran with catalyst **4** (10 μmol) for 60 minutes using $i\text{Bu}_2\text{AlCl}$ (100 equiv. to catalyst) and ethylene (3 atm) at 80 $^\circ\text{C}$. Chemical shifts of branching identities assigned and calculated according to Nunes and coworkers.^{S4}

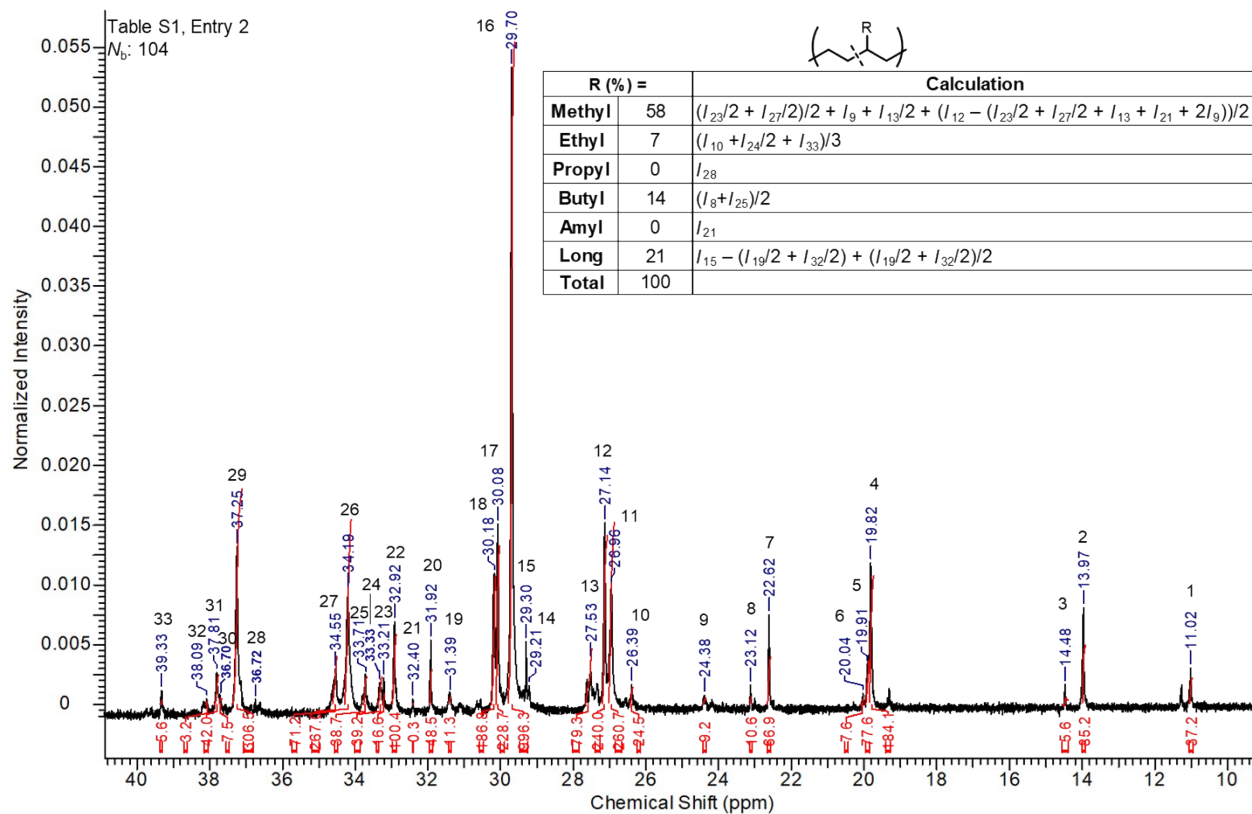


Figure S28. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$) of Table S1 Entry 2. Polymerization ran with homogeneous catalyst **1** (10 μmol) for 60 minutes using $i\text{Bu}_2\text{AlCl}$ (100 equiv. to catalyst) and ethylene (3 atm) at 80 $^\circ\text{C}$. Chemical shifts of branching identities assigned and calculated according to Nunes and coworkers.^{S4}

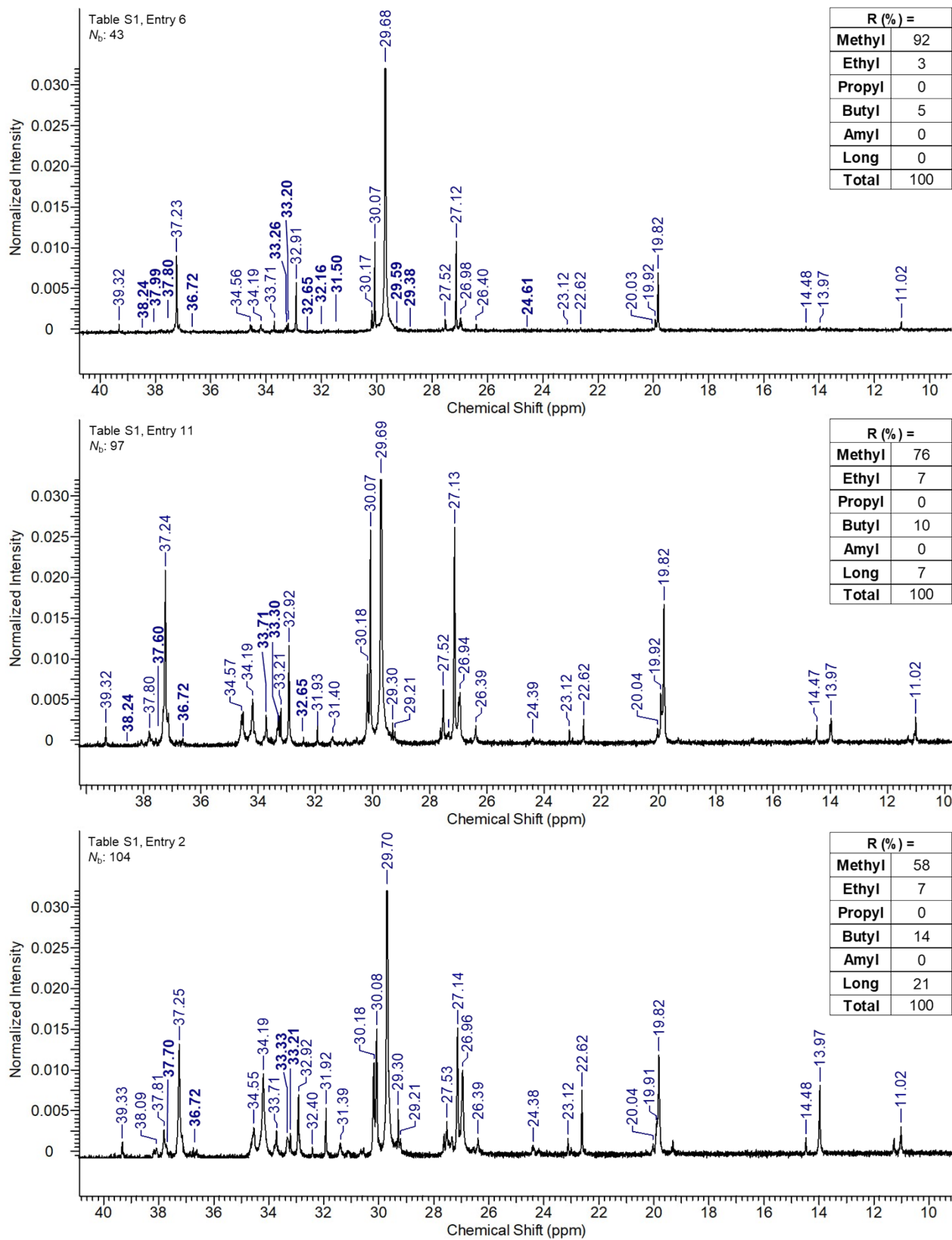


Figure S29. Comparative ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$) of Table S1 Entries 6, 11, and 2, respectively.

ESI-MS Analysis

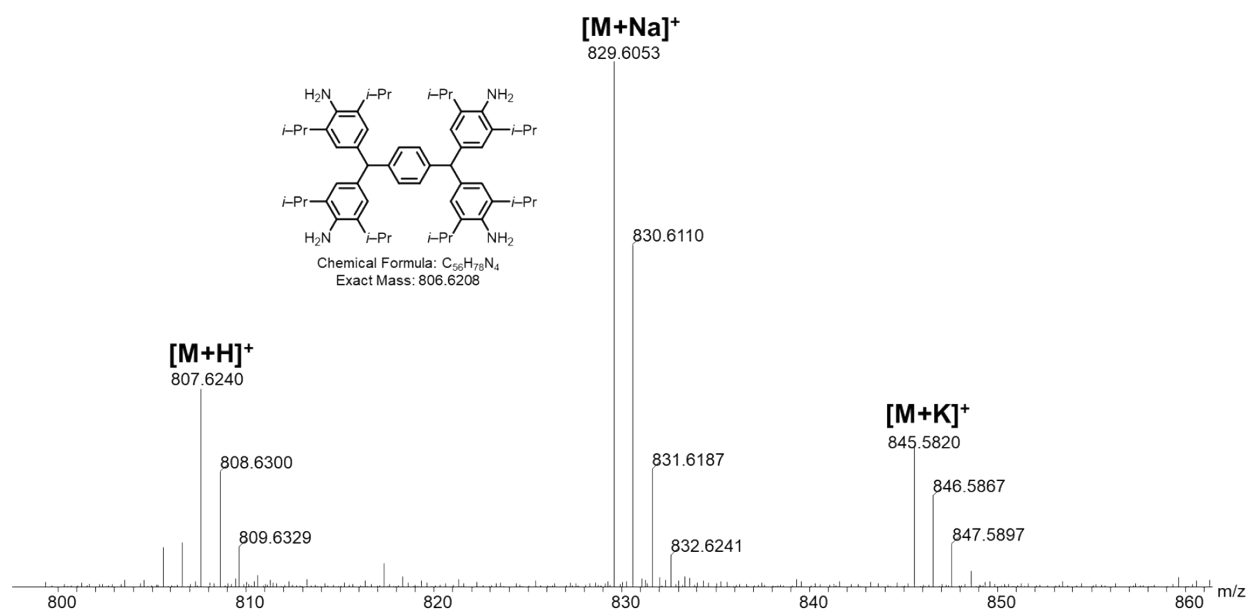


Figure S30. ESI-MS spectra of tetra-aniline (**7**). Sodium and potassium ions are introduced from glassware.

FT-IR Analysis

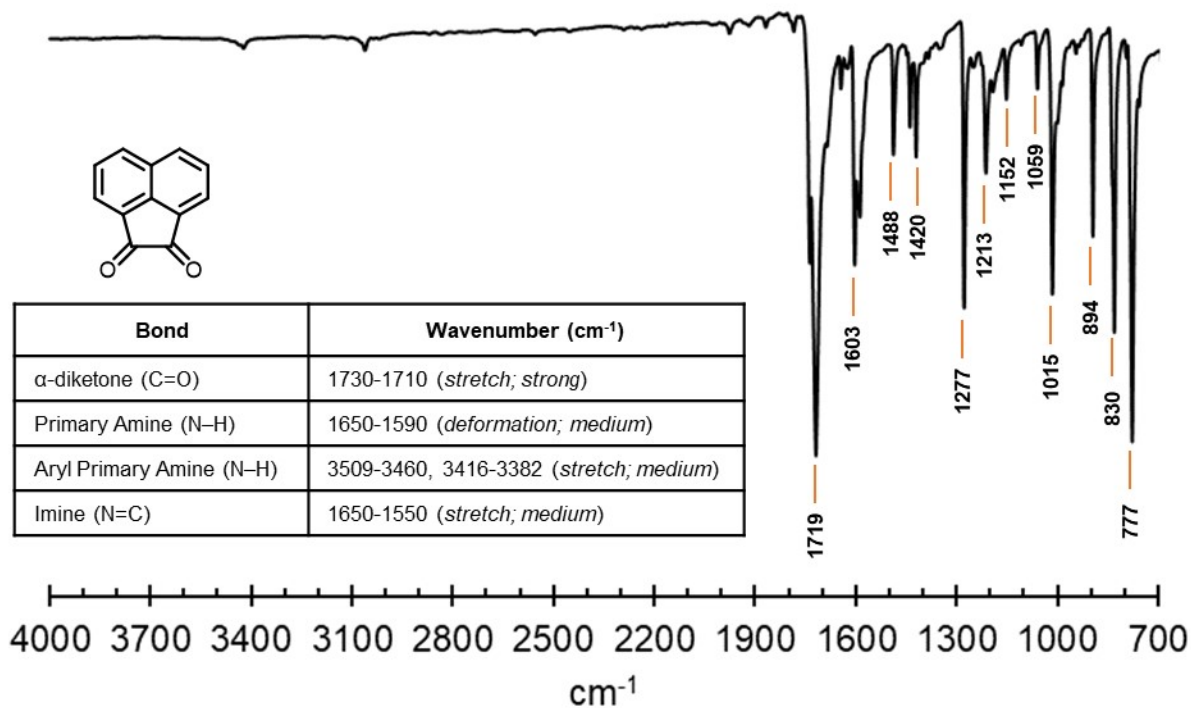


Figure S31. ATR FT-IR of acenaphthenequinone (**8**). Wavenumber references from Bellamy.^{S5}

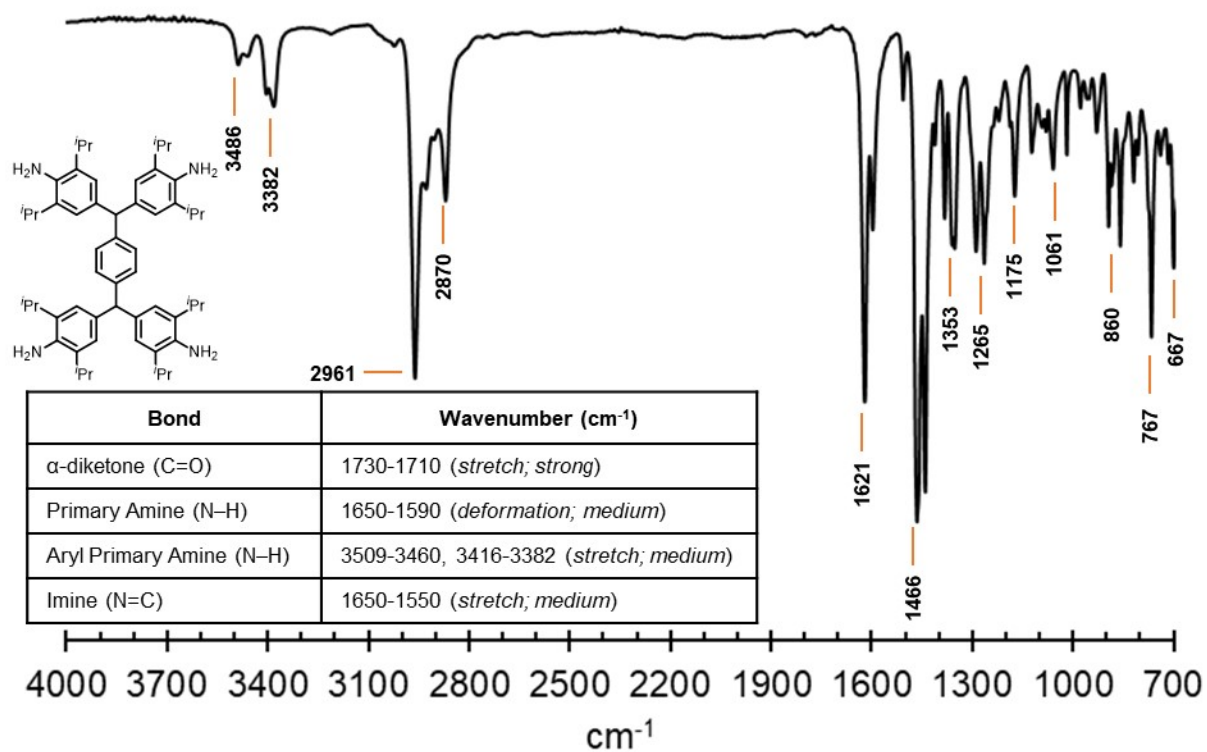


Figure 32. ATR FT-IR of tetra-aniline (**7**). Wavenumber references from Bellamy.^{S5}

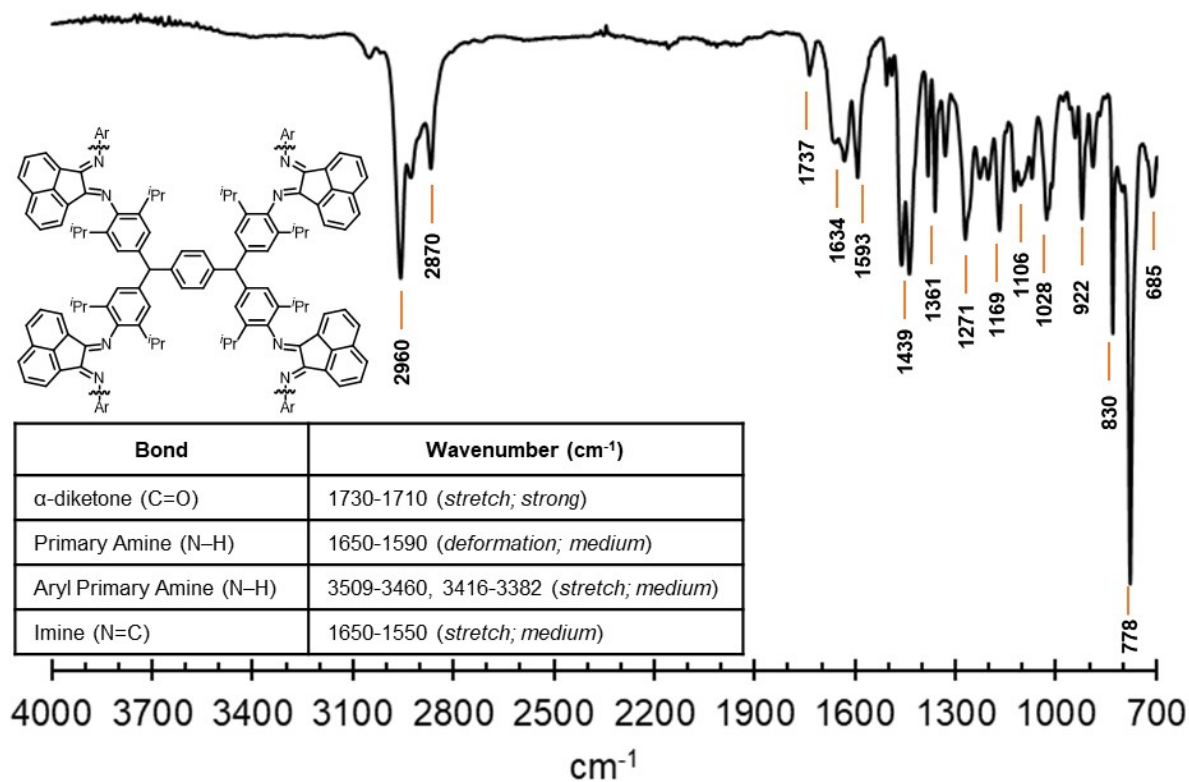


Figure S33. ATR FT-IR of crosslinked ligand (**S1**). Wavenumber references from Bellamy.^{S5}

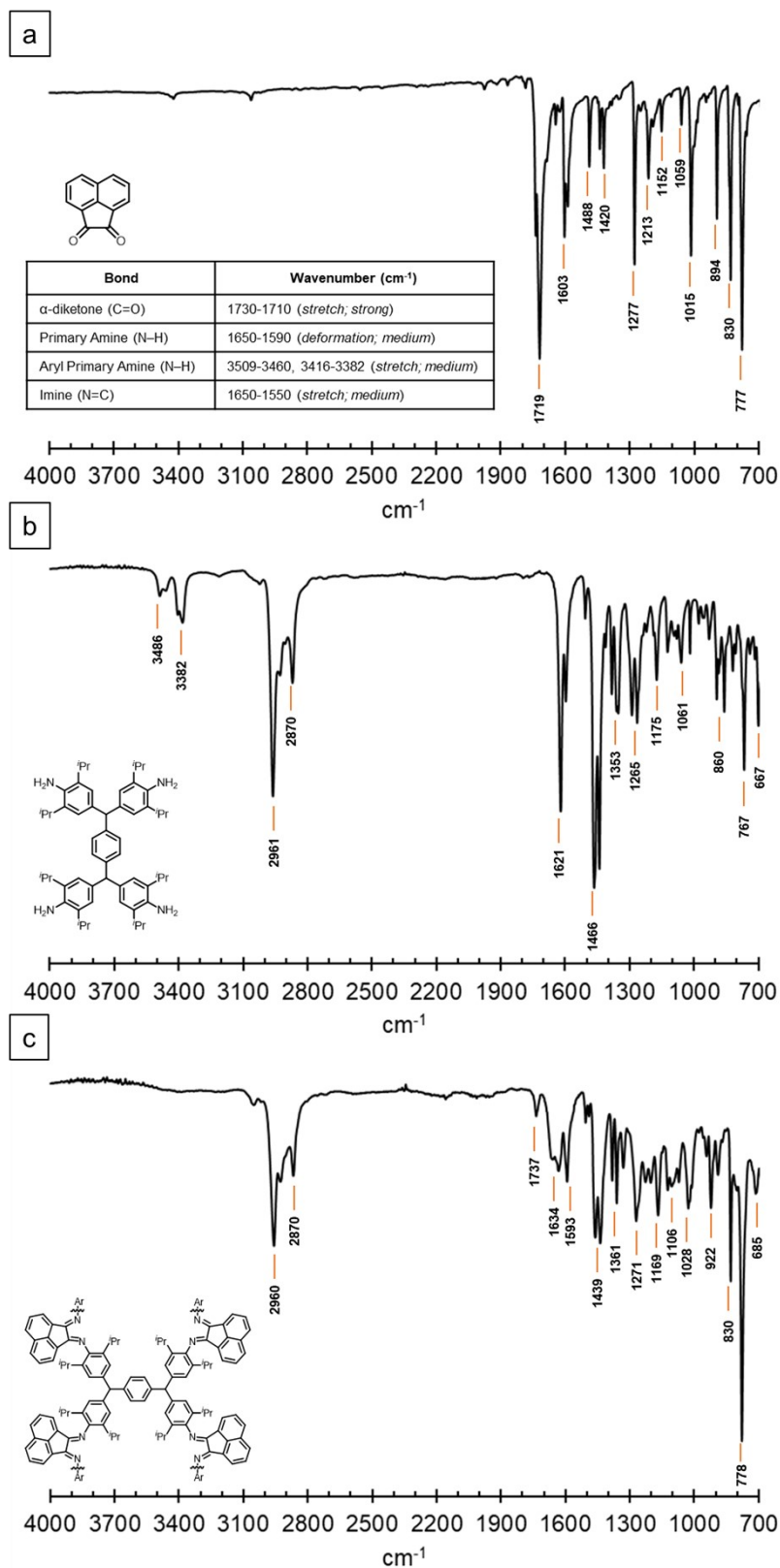


Figure S34. Stacked ATR FT-IR traces. a) Acenaphthenequinone (**8**). b) Tetra-aniline (**7**). c) Ligand (**S1**). Wavenumber references from Bellamy.^{S5}

ICP-OES Analysis

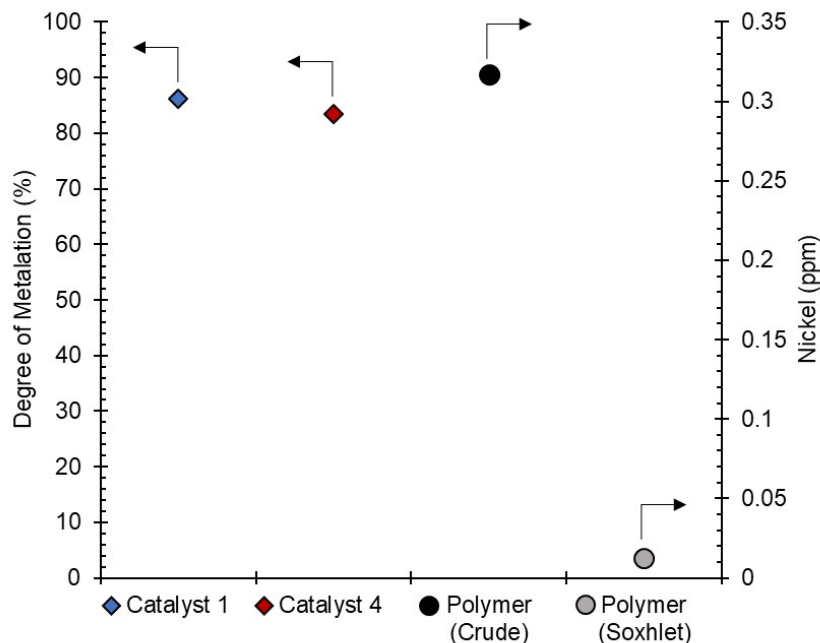


Figure S35. ICP-OES data showing the degree of metalation with respect to calculated diimine functionality (left axis) and the demonstration of removal of nickel from the polymer of Table S1, Entry 15 via Soxhlet extraction in PhMe (right axis).

Table S2.

ICP-OES Analysis				
Sample	ppm (calc)	ppm (obs)	Metalation (%)	Removal (%)
Catalyst 1	8.9786	7.7227	86.0	-
Catalyst 4	9.4736	7.9086	83.5	-
Polymer (Crude)	1.0698	0.31682	-	-
Polymer (Soxhlet)	1.0698	0.01238	-	96.1

ICP-OES data. Metalation determined relative to the calculated diimine functionality. A Ni standard solution was acquired (10 ppm) and standards of 0, 2.5, 5, 7.5, and 10 ppm were prepared via serial dilution in volumetric flasks (10 mL). Catalyst samples were massed in a 2 dram vial and digested for 24 hours in trace metal grade nitric acid (0.5 mL). After 24 hours, the red/brown catalyst had digested into a yellow solution. This solution was diluted with ultra-pure H₂O in a volumetric flask (10 mL). Polymer samples were degraded by combustion in a borosilicate test-tube over an open flame to improve digestion efficiency. The samples were then digested in trace metal grade nitric acid (1 mL) for 96 hours after which a pale yellow solution was extracted and diluted with ultra-pure pure H₂O in a volumetric flask (25 mL). Prior to data acquisition, the Ni standards were analyzed to create a standard curve by analysis at a wavelength of 234.601 nm and required to achieve a linear fit of R² >0.995.

ICP-OES Data

Ni 231.604 Calibration (ppm)		7/20/2022, 1:30:31 PM		Correlation Coefficient: 0.999933		
Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		21.4211	0.000000	-0.035856	-	-
Standard 1		2310.22	2.50000	2.55568	0.055675	2.2
Standard 2		4439.01	5.00000	4.96604	-0.033957	-0.7
Standard 3		6716.09	7.50000	7.54431	0.044313	0.6
Standard 4		8858.26	10.0000	9.96982	-0.030176	-0.3

Curve Type: Linear

$$\text{Equation: } y = 883.2 x + 53.1$$

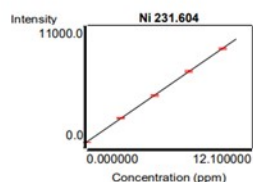


Figure S36. Calibration curve used for the ICP-OES analysis of the nickel catalysts.

Sample 1 (Samp)

7/20/2022, 1:32:03 PM

Tube 6

Weight: 1

Volume: 1

Dilution: 1

Label	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)
Ni 231.604	7.90860	ppm	0.032060	0.4	7037.82

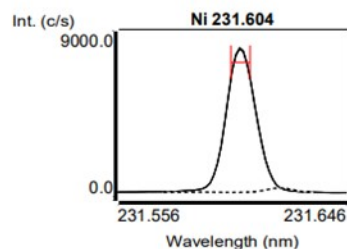


Figure S37. ICP-OES raw data of Catalyst 4

Sample 2 (Samp)

7/20/2022, 1:33:36 PM

Tube 7

Weight: 1

Volume: 1

Dilution: 1

Label	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)
Ni 231.604	7.72271	ppm	0.029972	0.4	6873.65

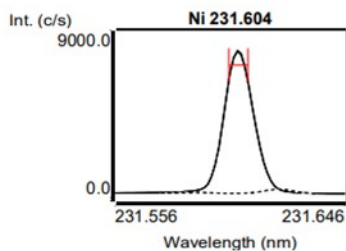


Figure S38. ICP-OES raw data of Catalyst 1.

Ni 231.604 Calibration (ppm)		8/25/2022, 11:41:14 AM		Correlation Coefficient: 0.999783		
Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		9.05659	0.000000	-0.063412	-	-
Standard 1		2482.80	2.50000	2.55574	0.055741	2.2
Standard 2		4780.91	5.00000	4.98894	-0.011061	-0.2
Standard 3		7255.09	7.50000	7.60855	0.108547	1.4
Standard 4		9428.94	10.0000	9.91018	-0.089816	-0.9

Curve Type: Linear

Equation: $y = 944.5 x + 68.9$

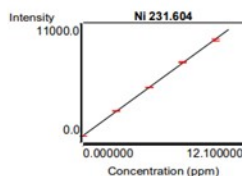


Figure S39. Calibration curve used for the ICP-OES analysis of polymer samples.

Sample 1 (Samp)

8/25/2022, 11:42:42 AM

Tube 6

Weight: 1

Volume: 1

Dilution: 1

Label	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)
Ni 231.604	0.316821	ppm	0.016023	5.1	368.180

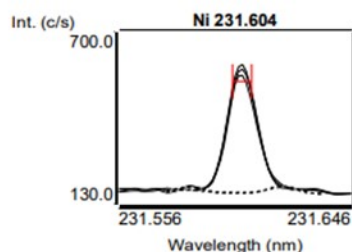


Figure S40. ICP-OES raw data of polymer (Table S1, Entry 15) before Soxhlet extraction (crude).

Sample 2 (Samp)

8/25/2022, 11:44:09 AM

Tube 7

Weight: 1

Volume: 1

Dilution: 1

Label	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)
Ni 231.604	0.012382	ppm	0.009291	75.0	80.6433

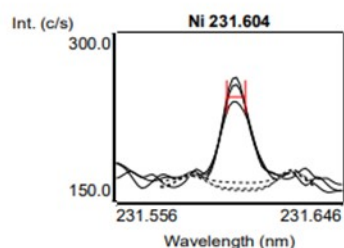


Figure S41. ICP-OES raw data of polymer (Table S1, Entry 15) after Soxhlet extraction.

SEM Images

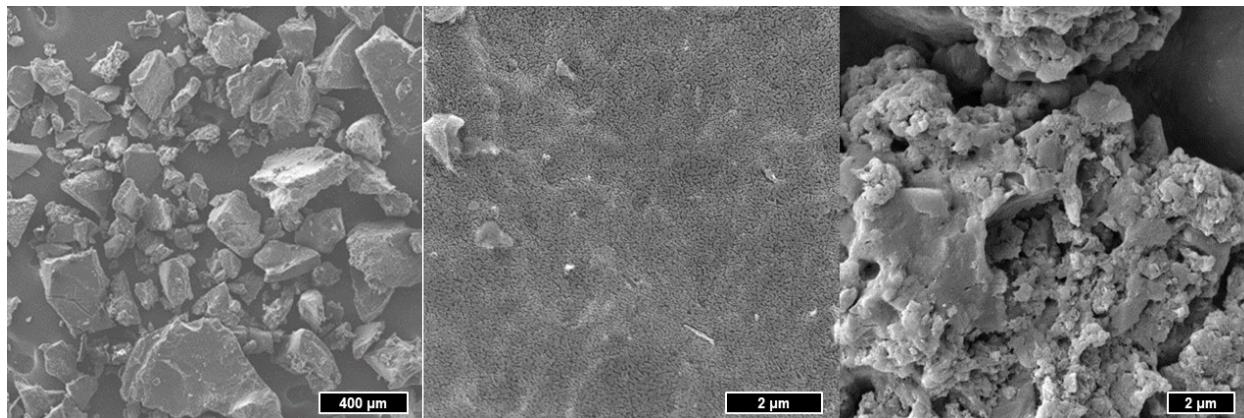


Figure S42. Additional SEM images of ligand **S1**.

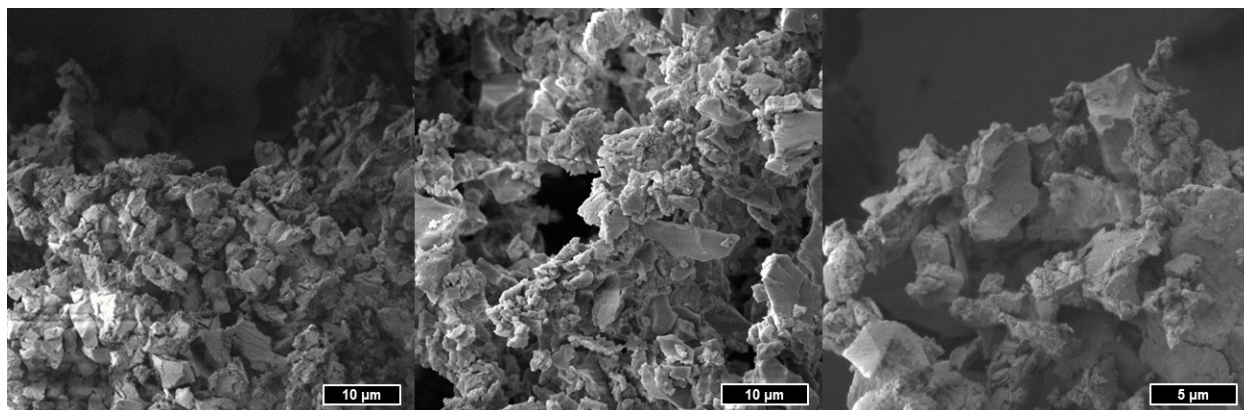


Figure S43. Additional SEM images of catalyst **4**.

References

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