

A Well-Defined Ni(II) α -Diimine Catalyst Supported on Sulfated Zirconia for Polymerization Catalysis

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Table of Contents

General Considerations	S2 – S3
Synthetic Methods and Characterization Data	S4 – S16
Polymerization Conditions and Characterization Data	S17 – S25

General Considerations and Instrumentation

All reactions and manipulations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. C_6D_6 was purchased from Cambridge Isotope Laboratories, dried over Na/benzophenone and freeze-pump-thawed three times before use. Solvents were purchased from Fisher Scientific, dried by passing through a double-column J. C. Meyer solvent system and degassed before use. Dioxane and diethyl ether were dried over Na/benzophenone and distilled under vacuum before use. Other chemicals were purchased from standard suppliers. Polymer grade ethylene 99.97% was purchased from Praxair, and was passed through a trap (Trigon Technologies) prior to polymerization to remove traces of H_2O/O_2 . Bis(2,6-diisopropylphenyl)butane-2,3-diimine (**a**)¹ and (bis(2,6-diisopropylphenyl)butane-2,3-diimine)NiBr₂ (**b**)² were reported previously.

Solution NMR spectra were recorded on Bruker Avance 300 MHz, and were referenced to C_6D_5H peak at 7.16 ppm. Solid-state NMR experiments were performed on a 600 MHz Bruker Avance. ¹H and ¹³C CPMAS NMR spectra were recorded in 4 mm zirconia rotors at 10 KHz magic angle spinning. The probe was cooled to ca. -20 °C using an airjet cooling system during sample spinning. N₂ adsorption/desorption analysis was performed on Micromeritics ASAP 2020 plus. FT-IR spectra were recorded as pressed pellets using a Bruker Alpha IR spectrometer in an argon-filled glovebox. Gas chromatography was carried out using Agilent 7820A GC system equipped with an Alumina/KCl column. Powder X-ray diffraction was performed on a Rigaku MiniFlex 600.

Elemental analysis was carried out in Microanalysis Laboratory at University of Illinois Urbana-Champaign. High-temperature GPC measurements were performed at Chevron Phillips Chemical Company, LP using a Viscotek High Temperature Triple Detection GPC system that

incorporates a differential refractive index, a viscometer, and a light scattering detector. 1,2,4-Trichlorobenzene (TCB) stabilized with 2,6-di(tert-butyl)-4-methylphenol was used as the mobile phase at a flow rate of 1 mL min⁻¹. Columns and detectors were maintained at 150°C. All polymers were injected at a concentration of 0.5 mg mL⁻¹. Polymer samples were analyzed by ¹H and ¹³C{¹H} NMR in tetrachloroethane-d₂ at 120 °C on a Bruker Avance spectrometer operating at 600 MHz.

Synthetic Methods and Characterizations

Synthesis of SZO₃₀₀: 70 g of zirconyl nitrate was dissolved in 420 ml of water and warmed to 65 °C. 280 ml of 2.2 M NH₄OH was added dropwise to the vigorously stirred solution over 1 h. After complete addition of NH₄OH, the pH of the white slurry was ~ 8.5. The slurry was heated to 95 °C for 24 h. The precipitate was filtered hot and collected. The white precipitate was dispersed in 700 ml of water and stirred for 30 minutes, filtered, and washed with 3 L of water. The white precipitate was dried at 120 °C for 24 h yielding 26.72 g Zr(OH)₄.

5 g of crushed Zr(OH)₄ was dispersed in 100 ml of 0.5 M sulfuric acid at room temperature. After 30 min, the solvent was poured off. The white solid was dispersed in 100 ml of water for 30 min, the H₂O decanted, and dried at 120 °C for 1 h. This material was calcined under air at 600 °C (5 °C/min) for 4 h and cooled to room temperature under air to yield **SZO**. **SZO** was dehydroxylated by heating to 300 °C (5 °C/min) under air for 3 h, and evacuated to 10⁻⁶ torr for 15 min to form **SZO₃₀₀**, which was stored in an argon-filled glovebox. Elemental analysis: 0.9% S. The surface area of **SZO** using this procedure is 98 m² g⁻¹, the N₂ adsorption/desorption isotherm is shown in Figure S1.

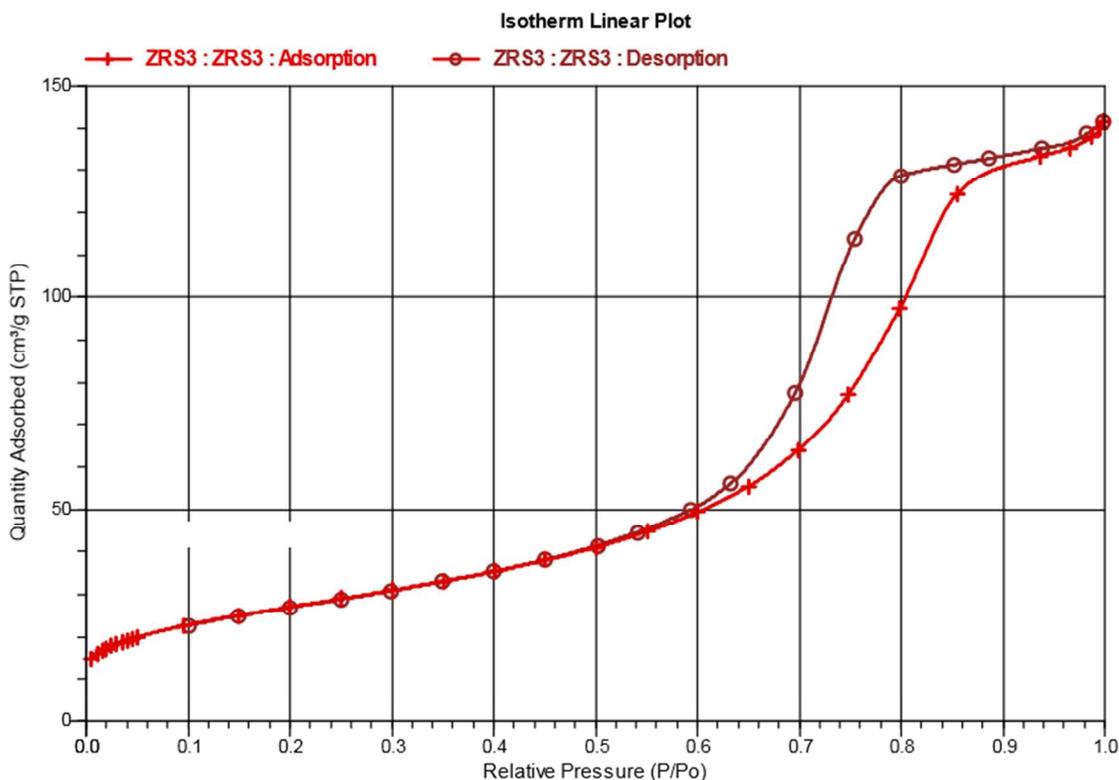
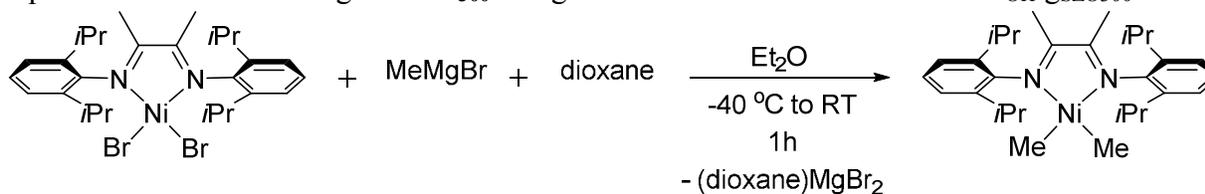
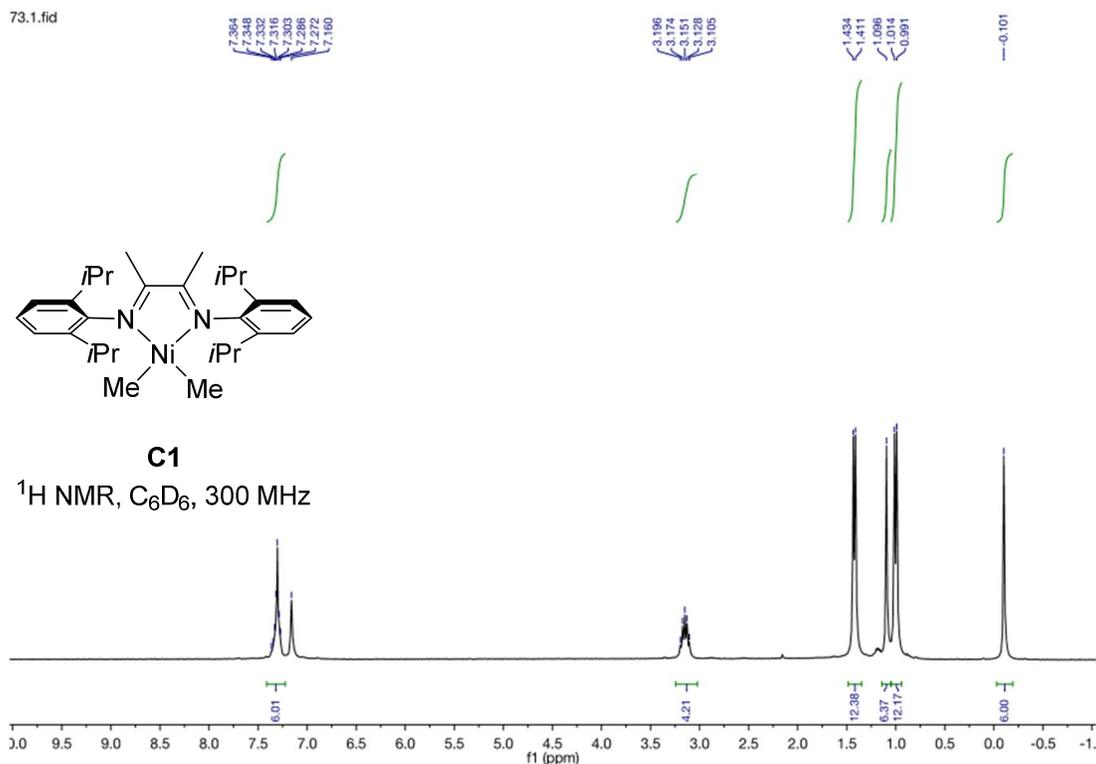


Figure S1. N₂ adsorption/desorption isotherm plot of SZO₃₀₀; BET surface area: 97.7663 m²/g; t-plot micropore volume: 0.000708 cm³/g.

The -OH loading of SZO₃₀₀ was determined by adding 0.5 ml C₆D₆ to 100 mg of sulfated zirconia and 10 mg of LiCH₂SiMe₃ in a J. Young NMR tube. After 1 hour @ RT, 15-20 mg of ferrocene was added to the mixture as an internal standard. ¹H NMR spectra were recorded and the SiMe₄ was quantified by integration relative to Cp₂Fe. These measurements were run in triplicate. The -OH loading of SZO₃₀₀ using this method is 0.133±0.007 mmol_{OH}/gSZO₃₀₀.



(bis(2,6-diisopropylphenyl)butane-2,3-diimine)Ni(Me)₂ (C1) was previously reported.² A slurry of (bis(2,6-diisopropylphenyl)butane-2,3-diimine)NiBr₂ (0.150 g, 0.24 mmol) in Et₂O (40 ml) was treated with MeMgBr (1.4 M, 0.4 ml, 0.56 mmol) at -40 °C. Dioxane (2 ml) was added by syringe at -40 °C after 5 min. The cold bath was removed, the mixture warmed to room temperature, and was stirred for 1 h at room temperature. The solution turns green and a precipitate forms. The solution was filtered and volatiles were removed under vacuum to leave a dark green solid as the product which was characterized by ¹H and ¹³C NMR spectroscopy (87 mg, 73%). ¹H NMR (C₆D₆, 300 MHz): 7.33-7.27 (m, 6H, ArH), 3.15 (sept, ³J_{H-H} = 6.9 Hz, 4H, CHMe₂), 1.42 (d, ³J_{H-H} = 6.9 Hz, 12H, CHMe₂), 1.10 (s, 6H, NiMe), 1.00 (d, ³J_{H-H} = 6.9 Hz, 12H, CHMe₂), -0.10 (s, 6H, backbone Me); ¹³C {¹H} NMR (C₆D₆, 75.4 MHz): 163.0, 147.4, 139.5, 126.7, 123.8, 28.9, 23.8, 21.3, -3.7.



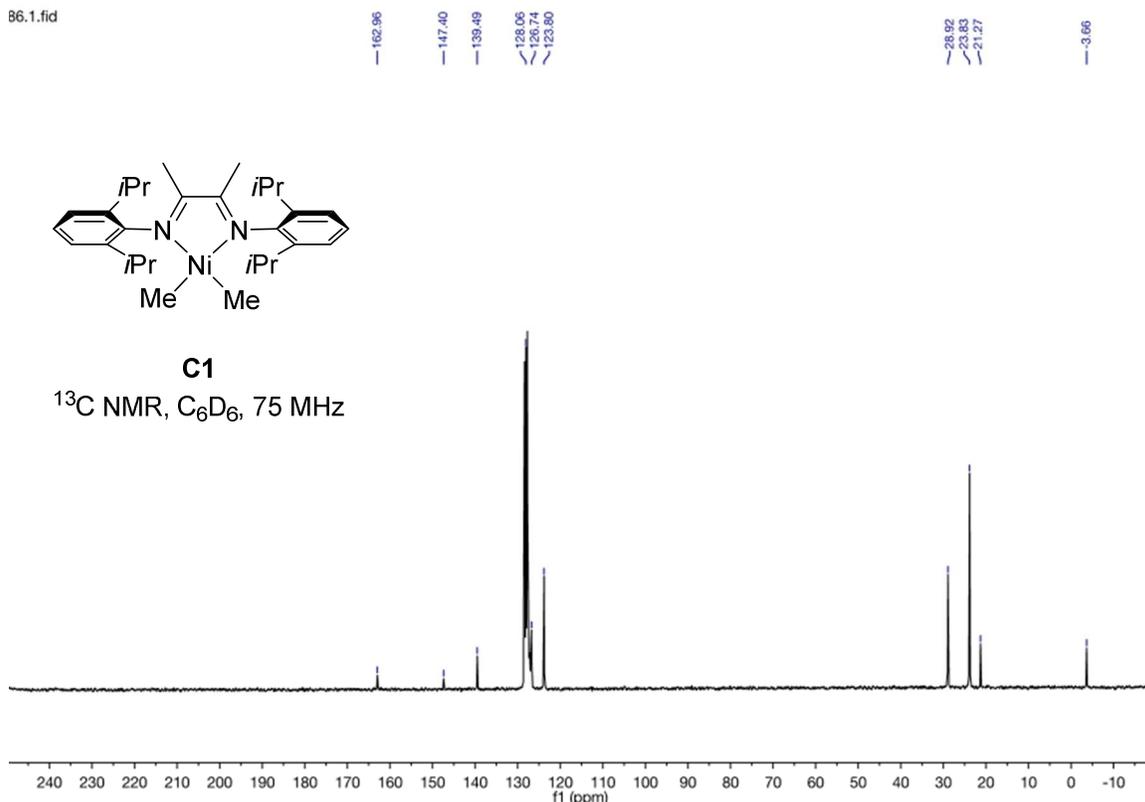
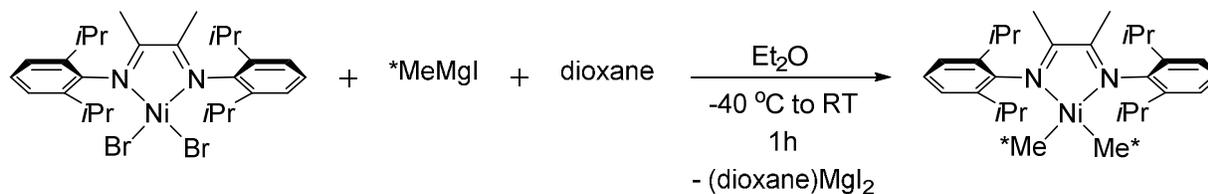


Figure S2. ^1H (300 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (75 MHz) NMR spectra of the nickel complex **C1**.



(bis(2,6-diisopropylphenyl)butane-2,3-diimine)Ni(*Me)₂ (C2)²: Diethyl ether (40 ml) was added to magnesium turnings (50 mg, 2.06 mmol), followed by the addition of *MeI (0.1 ml, 1.61 mmol). The mixture was gently refluxed for 2 h. The mixture was cooled to room temperature and cannula filtered into a slurry of (bis(2,6-diisopropylphenyl)butane-2,3-diimine)NiBr₂ (**b**) (200 mg, 0.32 mmol) in 10 ml of diethyl ether at -40 °C. After the addition of *MeMgI the mixture was treated as described for the synthesis of the **C1**. The product was extracted with pentane (2x20 ml) and crystallized from concentrated pentane solution at -20 °C overnight to yield 72 mg (45%). ^1H NMR (C_6D_6 , 300 MHz): 7.35-7.27 (m, 6H, ArH), 3.15 (sept,

$^3J_{H-H} = 6.9$ Hz, 4H, $CHMe_2$), 1.42 (d, $^3J_{H-H} = 6.9$ Hz, 12H, $CHMe_2$), 1.09 (d, $^1J_{C-H} = 128.4$ Hz, 6H, Ni-Me), 1.00 (d, $^3J_{H-H} = 6.9$ Hz, 12H, $CHMe_2$), -0.10 (s, 6H, backbone Me); ^{13}C $\{^1H\}$ NMR (C_6D_6 , 75.4 MHz): 163.0, 147.4, 139.5, 126.7, 123.8, 28.9, 23.8, 21.3, -3.6.

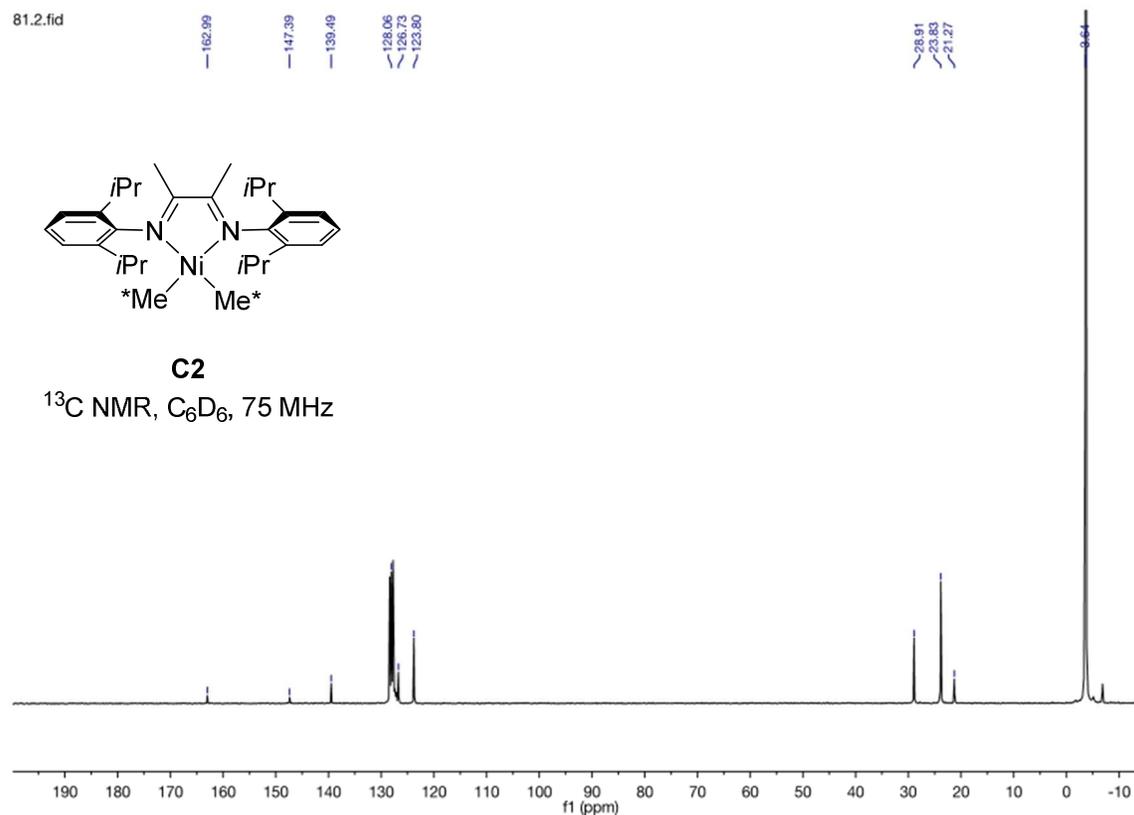
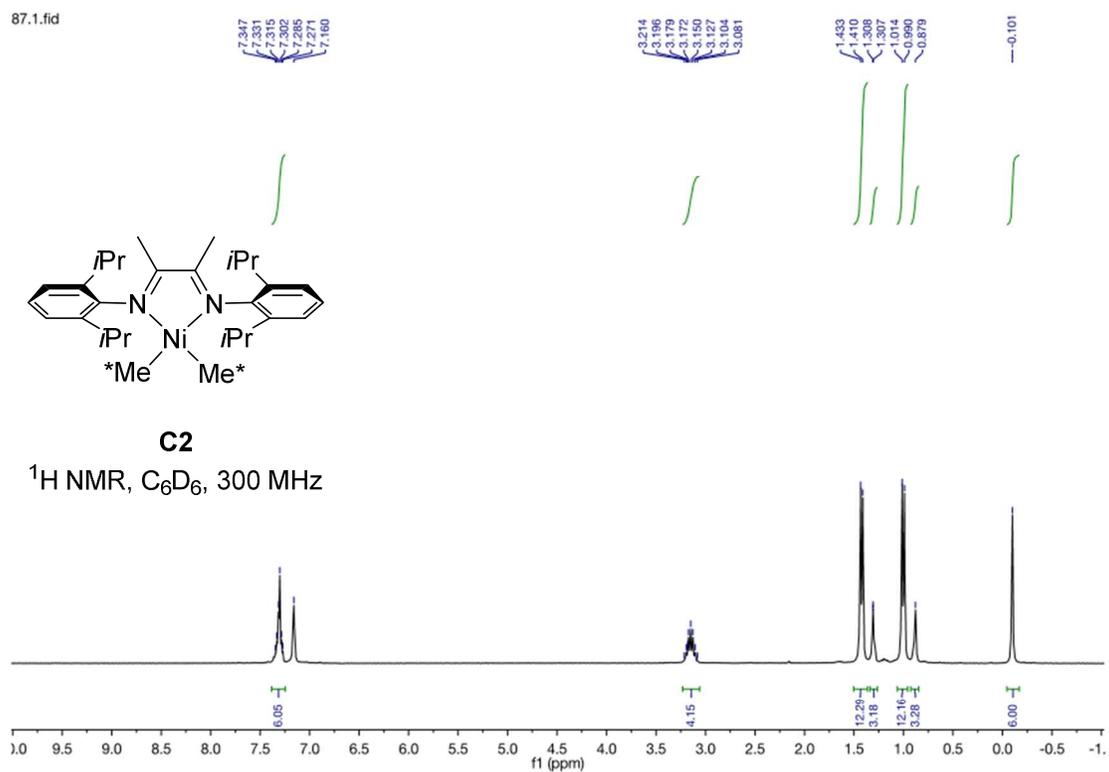
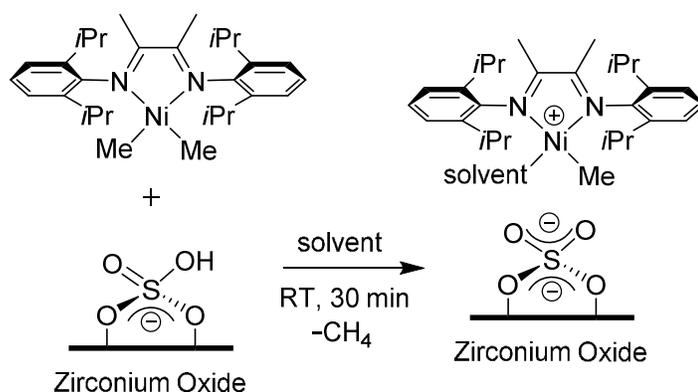


Figure S3. ^1H (300 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (75 MHz) NMR spectra of the nickel complex C2.



Grafting the (diimine)Ni(Me)₂ C1-C2 complexes on SZO₃₀₀: All grafting reactions were carried out in double-Schlenk flasks connected by a frit filter using high vacuum Schlenk lines.³ SZO₃₀₀ (100-500 mg) and (diimine)Ni(Me)₂ (1.1 eq based on the –OH loading of the surface) were transferred to the double-Schlenk flask inside an argon-filled glovebox, diethyl ether or acetonitrile (ca. 3-5 ml) was transferred under vacuum to the flask at 77 K. The heterogeneous mixture was warmed to room temperature and gently stirred for 30 min. The blue/green solution was filtered to the other side of the double Schlenk. The Ni-containing SZO₃₀₀ was washed by condensing solvent from the other arm of the double Schlenk at 77 K, warming to room temperature from 2 minutes, and filtering the solvent back to the other side of the flask. This was repeated three times; the final washing was clear and colorless. The volatiles were removed under vacuum (10⁻⁶ torr) at room temperature and the colored solid was stored in an argon-filled glovebox at -20 °C. The surface species are unstable when stored at room temperature decomposing to CH₄ and unidentified Ni-products.

Grafting Reactions in MeCN: Analysis of the volatiles from the reaction mixture by gas chromatography showed that 0.059 mmol CH₄/gSZO₃₀₀ were obtained in reactions run in MeCN. Elemental analysis For **C1** grafted on SZO₃₀₀ in acetonitrile ([**1**][SZO₃₀₀]) C: 2.14%; H: 0.15%; N: 0.27%; Ni: 0.50%. Solid-state NMR experiments are shown below in Figure S4. ¹H MAS NMR (10 kHz, -20 °C) δ: 8.07, 2.60, 0.50; ¹³C{¹H} CPMAS NMR (10 kHz, -20 °C) δ: 140, 126,

121, 28, 21, 1. ^{13}C CPMAS NMR (10 kHz, $-20\text{ }^\circ\text{C}$) of **C2** grafting contains Ni-Me* at -5.6 ppm , see Figure S5.

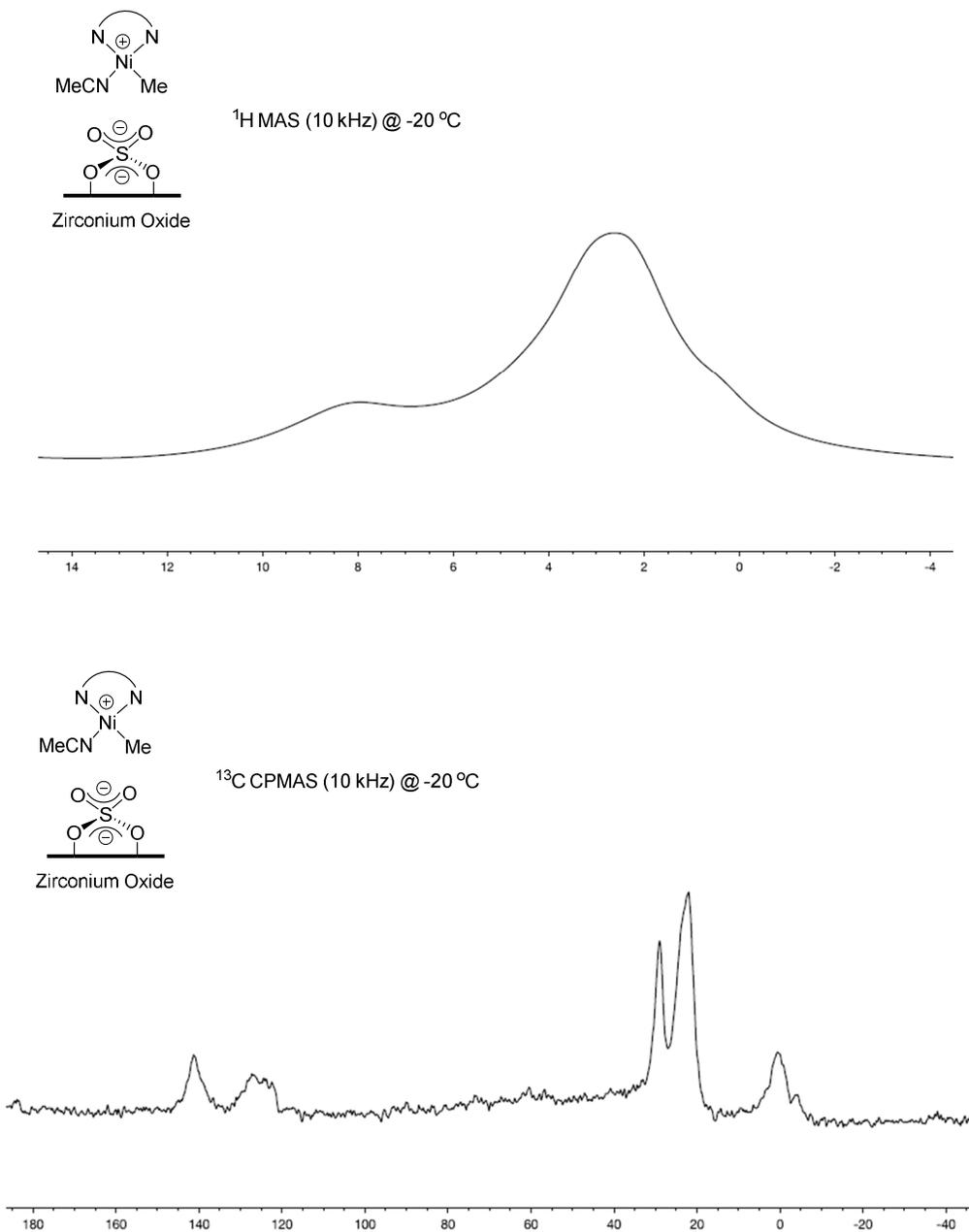


Figure S4. ^1H MAS (600 MHz) NMR and $^{13}\text{C}\{^1\text{H}\}$ CPMAS (150 MHz) spectra of grafted complex **C1** on SZO_{300} in MeCN (10 kHz @ $-20\text{ }^\circ\text{C}$): ^1H MAS, ns = 32; d1 = 3 s (top) and ^{13}C CPMAS, ns = 10240; CP = 2 ms; d1 = 3 s (bottom).

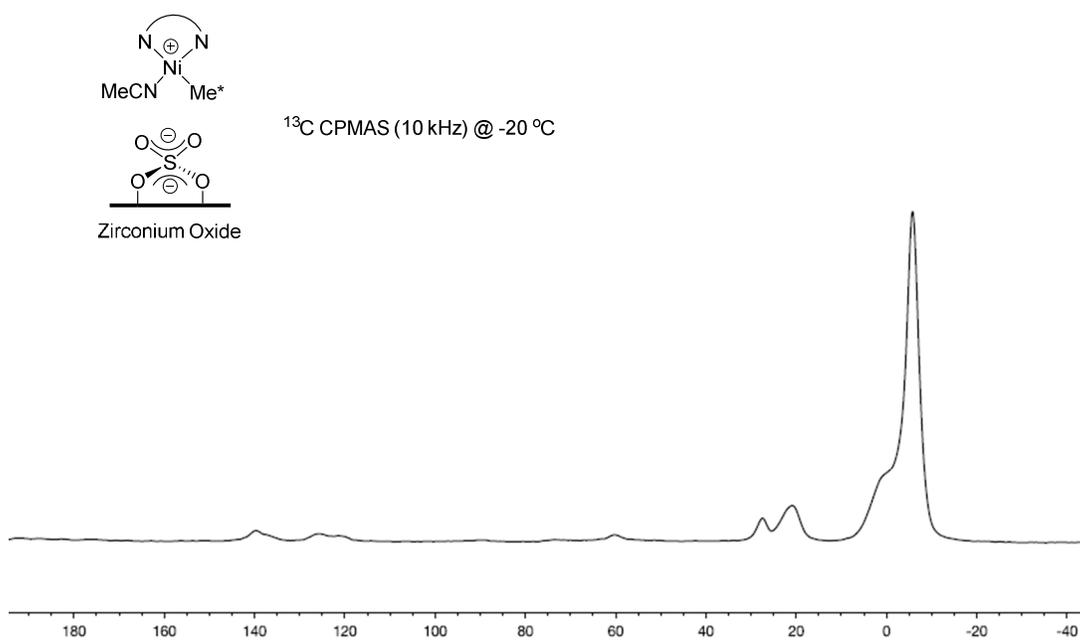
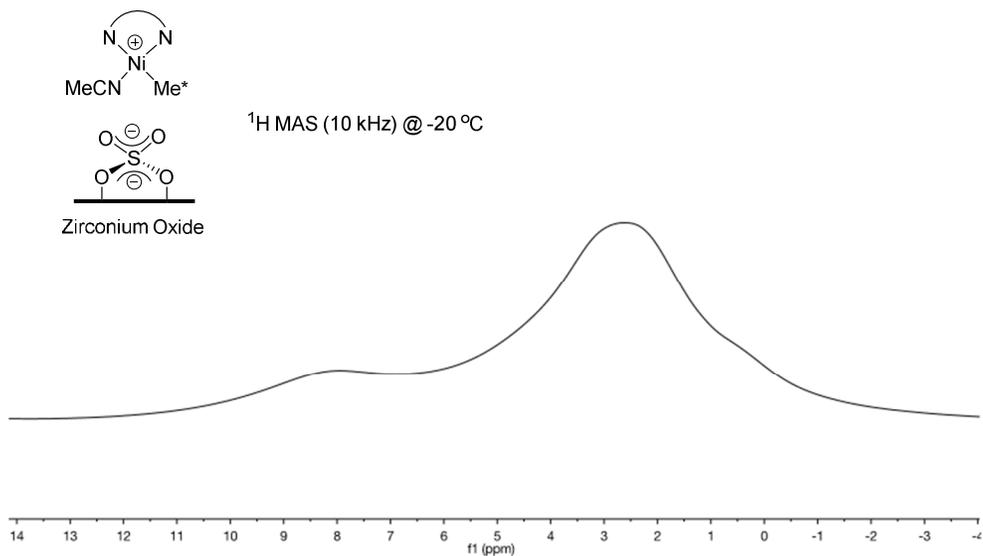


Figure S5. ^1H MAS (600 MHz) NMR and $^{13}\text{C}\{^1\text{H}\}$ CPMAS (150 MHz) spectra of grafted complex C2 on SZO₃₀₀ in MeCN (10 kHz @ -20 °C): ^1H MAS, ns = 32; d1 = 3 s (top) and ^{13}C CPMAS, ns = 10240; CP = 2 ms; d1 = 3 s (bottom).

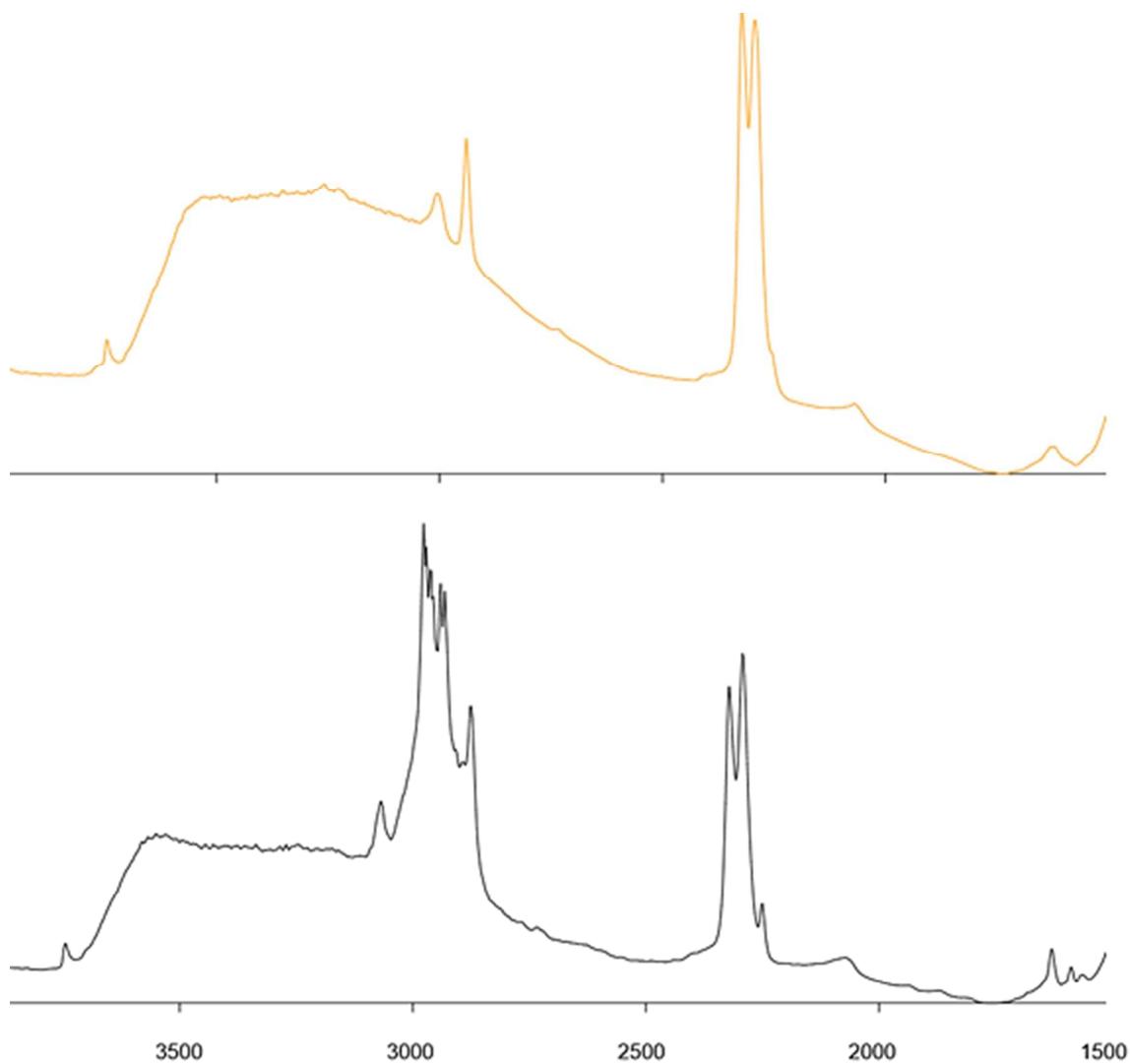


Figure S6. FT-IR spectra of SZO₃₀₀ support treated under the grafting conditions (top) and C1 grafted on SZO₃₀₀ (bottom).

Grafting Reactions in Et₂O: Analysis of the volatiles from the reaction mixture by gas chromatography showed that 0.066 mmol CH₄/gSZO₃₀₀ evolved in reactions run in Et₂O. Elemental analysis For **C1** grafted on **SZO₃₀₀** in diethyl ether ([2][SZO₃₀₀]/[2][MeSZO₃₀₀]) C: 2.48%; H: 0.21%; N: 0.16%; Ni: 0.40%. Solid-state NMR experiments are shown below in Figure S7. ¹H MAS NMR (10 kHz, -20 °C) δ: 7.45, 4.30, 1.50, 0.19; ¹³C{¹H} CPMAS NMR (10 kHz, -20 °C) δ: 165, 139.1, 127.4, 69.9, 39.9, 29.5, 23.1, 17.0, 16.0, 11.5. ¹³C{¹H} CPMAS NMR (10 kHz, -20 °C) of **C2** grafting contains Ni-Me* at 2.1 ppm and the Ze-Me⁻ signal at -32 ppm, Figure S8.

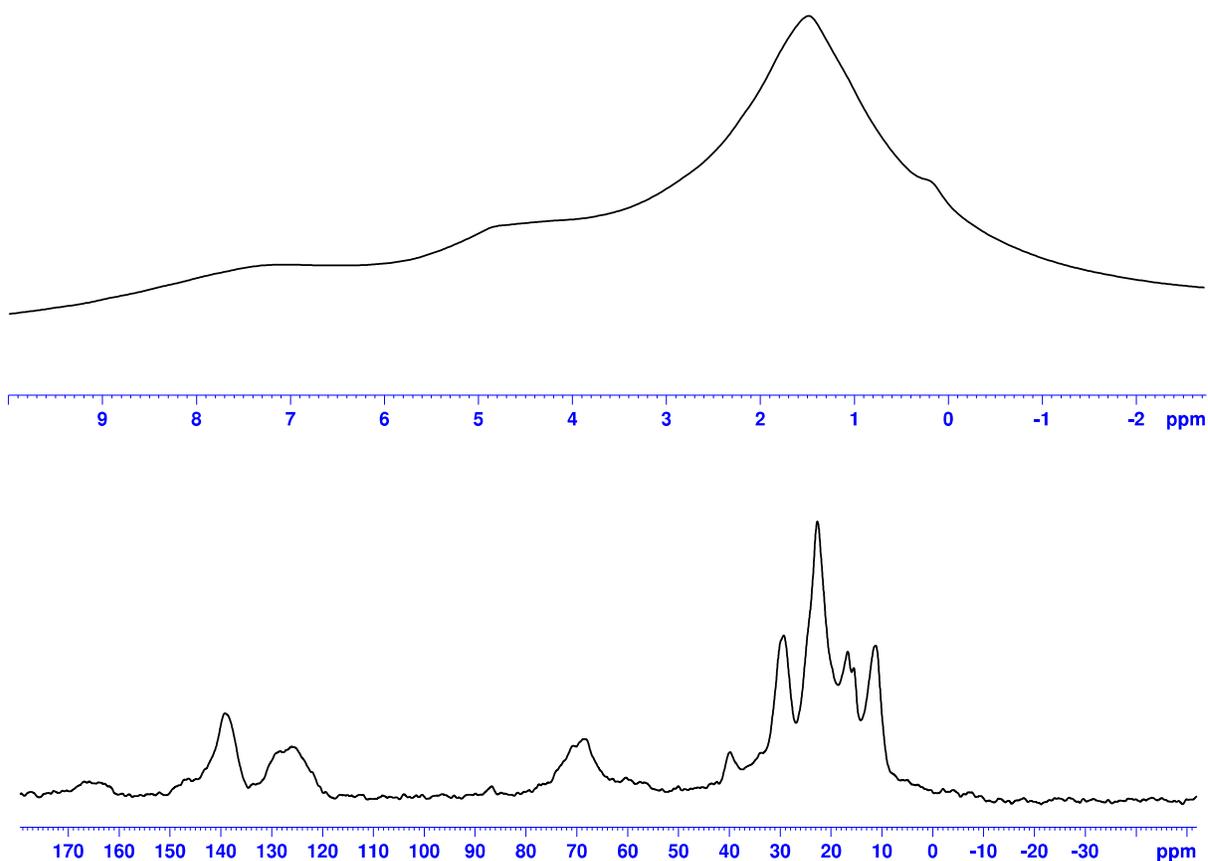


Figure S7. ¹H MAS (600 MHz) NMR and ¹³C{¹H} CPMAS (150 MHz) spectra of grafted complex **C1** on **SZO₃₀₀** in Et₂O (10 kHz @ -20 °C): ¹H MAS, ns = 32; d1 = 3 s (top) and ¹³C CPMAS, ns = 8192; CP = 2 ms; d1 = 2 s (bottom).

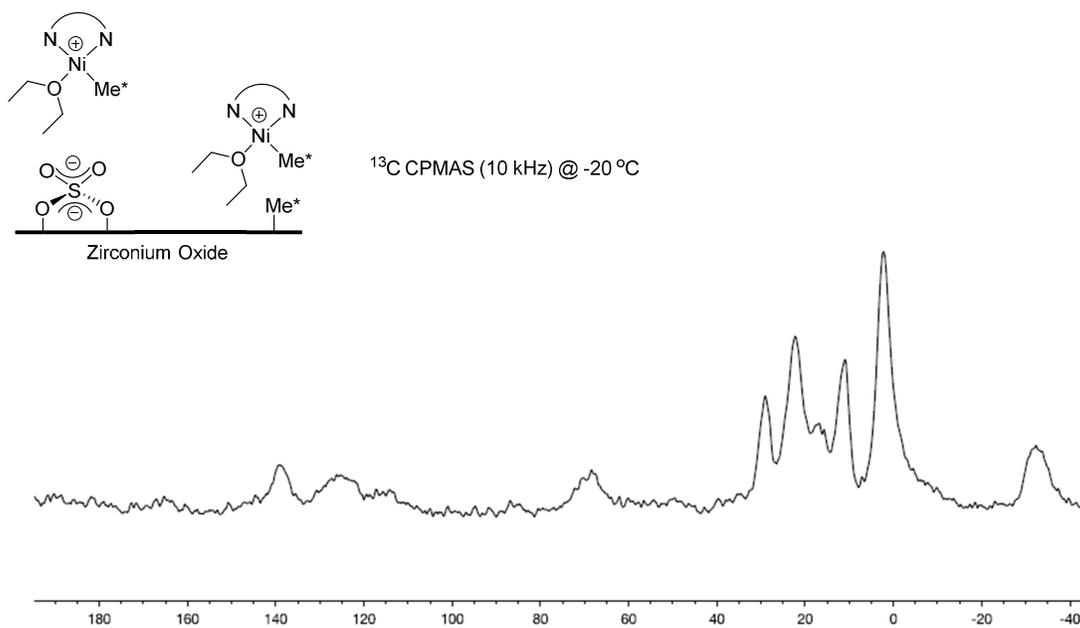
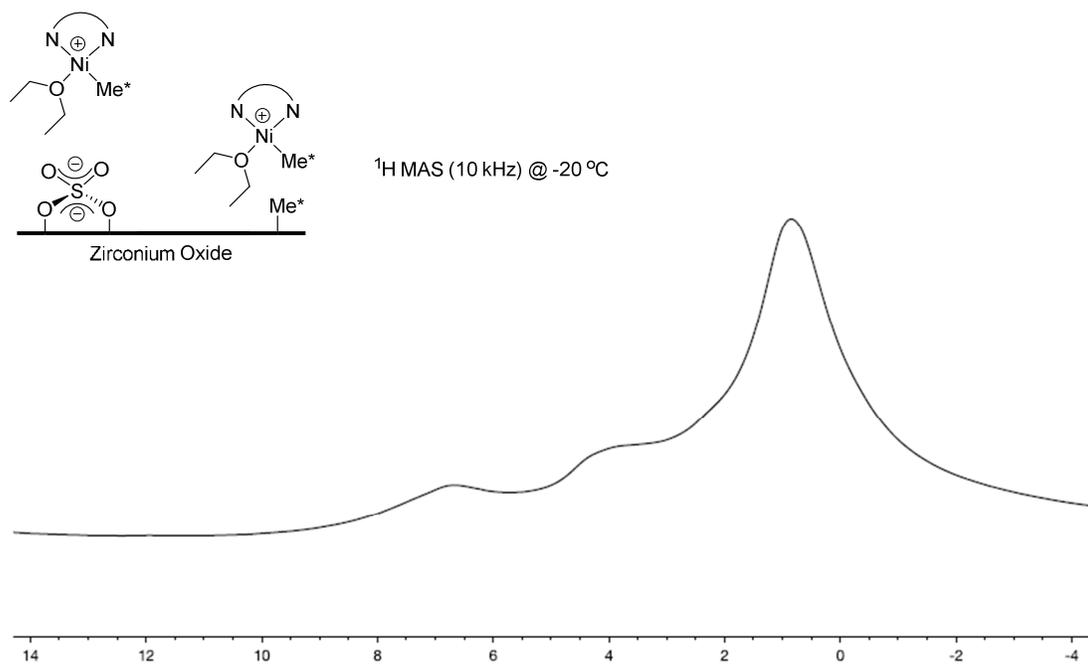


Figure S8. $^1\text{H MAS (600 MHz) NMR}$ and $^{13}\text{C}\{^1\text{H}\}$ CPMAS (150 MHz) spectra of grafted complex C2 on SZO₃₀₀ in Et₂O (10 kHz @ -20 °C): $^1\text{H MAS}$, ns = 32; d1 = 3 s (top) and $^{13}\text{C CPMAS}$, ns = 2048; CP = 2 ms; d1 = 2 s (bottom).

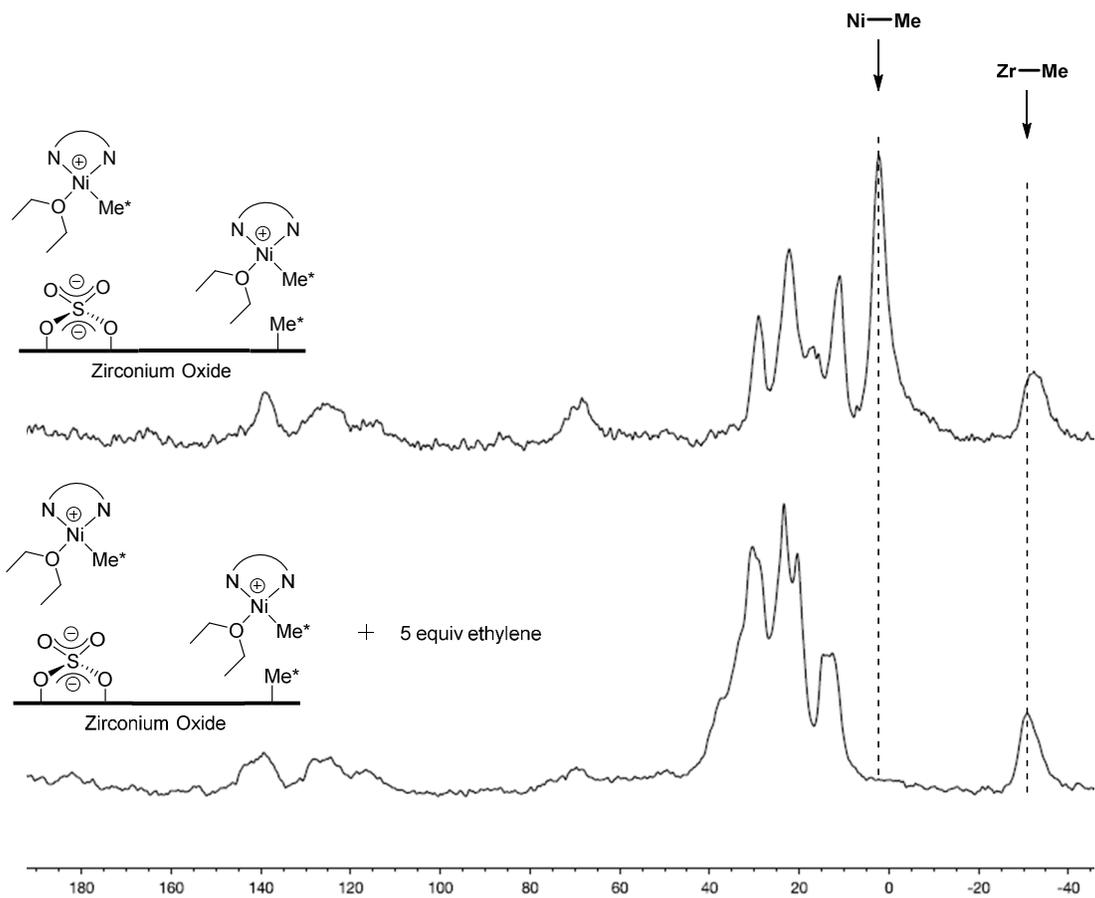


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ CPMAS (150 MHz) spectra of the C2 complex grafted on SZO₃₀₀ in Et₂O after 2 minutes exposure to excess ethylene (approx. 5 equiv/Ni), ns = 4094; CP = 2 ms; d1 = 2 s.

Polymerization Reactions

A Fisher Porter bottle was charged with **[1][SZO₃₀₀]** (40 mg , 3.4 μmol Ni) or **[2][SZO₃₀₀]/ [2][MeSZO₃₀₀]** (20 mg , 1.4 μmol Ni) and 20 ml of toluene. The bottle was pressurized with ethylene at the desired ethylene pressure (kept under pressure for approx. 30 seconds), placed in an oil bath preheated to a set temperature and stirred for 15 min at 800 rpm (see Table 1 in main text for pressure and temperature). After this time, the vessel was depressurized and methanol was added to stop polymerization and to precipitate polymer. The addition of methanol is only to aid the filtration step. If methanol is not added, identical polymer yields are obtained, though the filtration is slower without methanol. The polymer was isolated by filtration from toluene/methanol solution, dried under vacuum for 2 h at room temperature, and characterized by GPC, DSC and solution phase NMR spectroscopy. Catalytic copolymerizations in the presence of ethylene and methyl 10-undecenoate were performed with **[2][SZO₃₀₀]/ [2][MeSZO₃₀₀]** (150 mg, 11 μmol Ni). Methyl 10-undecenoate was added to the slurry of the catalyst under 10 psi pressure of the ethylene. Reactions were run at 40 and 60 °C under 45 psi pressure of ethylene for 3 h. The workup procedure is identical to ethylene polymerization.

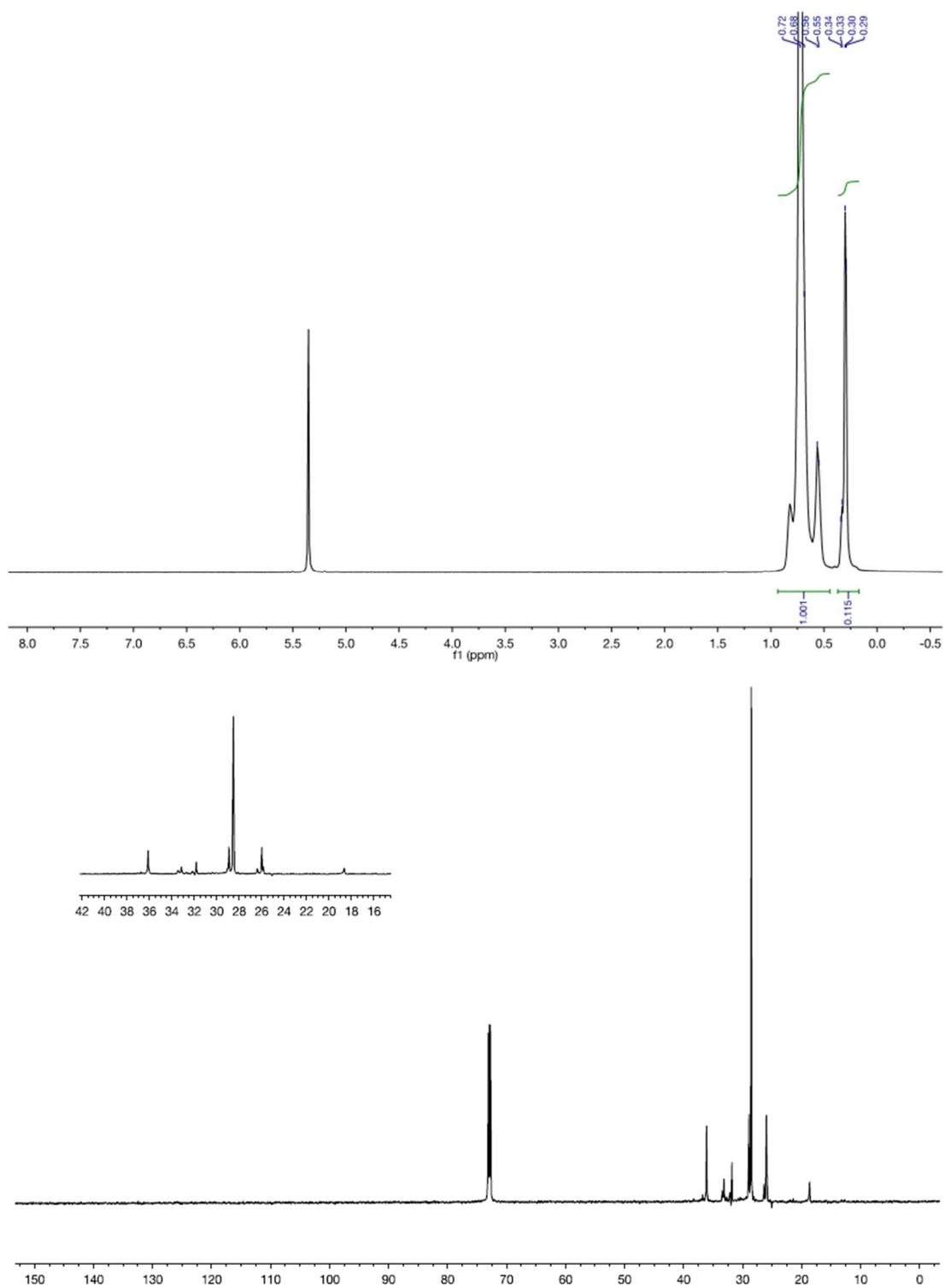


Figure S10. ^1H (600 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (150 MHz) NMR spectra ($n_s = 64$ and 10240 in $\text{C}_2\text{D}_2\text{Cl}_4$ @ 120 $^\circ\text{C}$) of polyethylene (entry 7, Table 1).

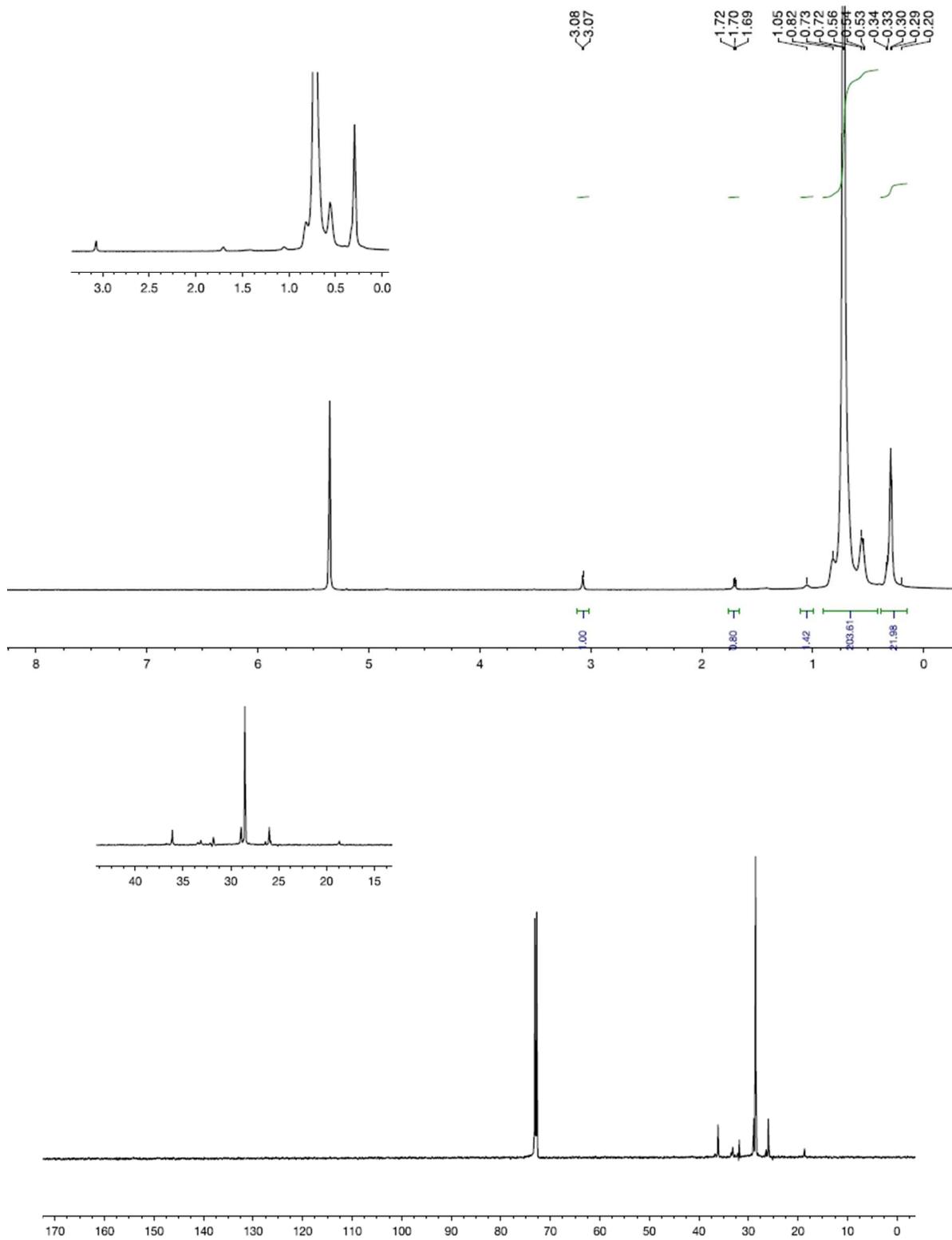


Figure S11. ^1H (600 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (150 MHz) NMR spectra (ns = 64 and 10240 in $\text{C}_2\text{D}_2\text{Cl}_4$ @ 120°C) of polar monomer-incorporated polyethylene obtained @ 40°C .

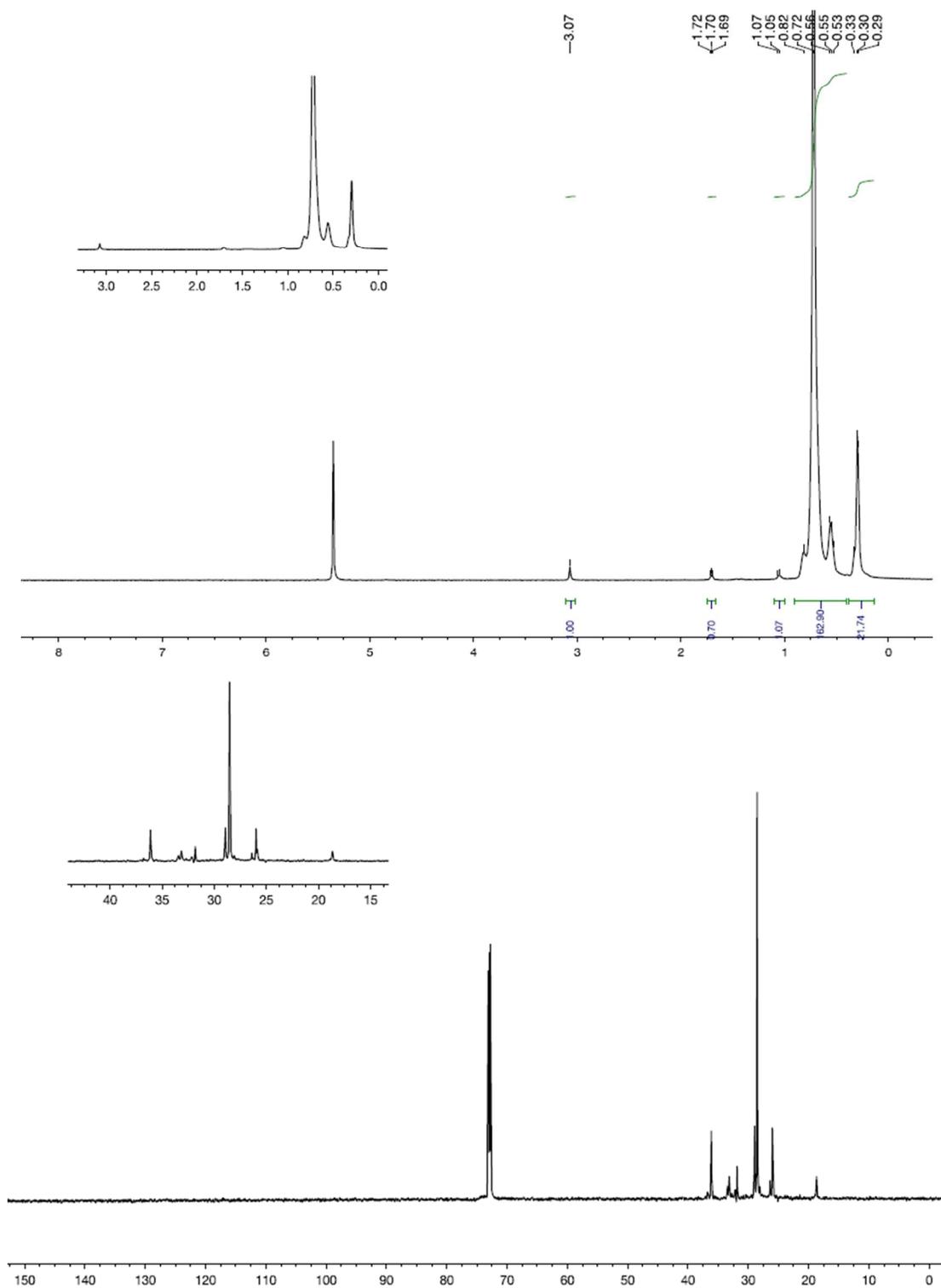


Figure S12. ^1H (600 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (150 MHz) NMR spectra ($n_s = 64$ and 10240 in $\text{C}_2\text{D}_2\text{Cl}_4$ @ 120°C) of polar monomer-incorporated polyethylene obtained @ 60°C .

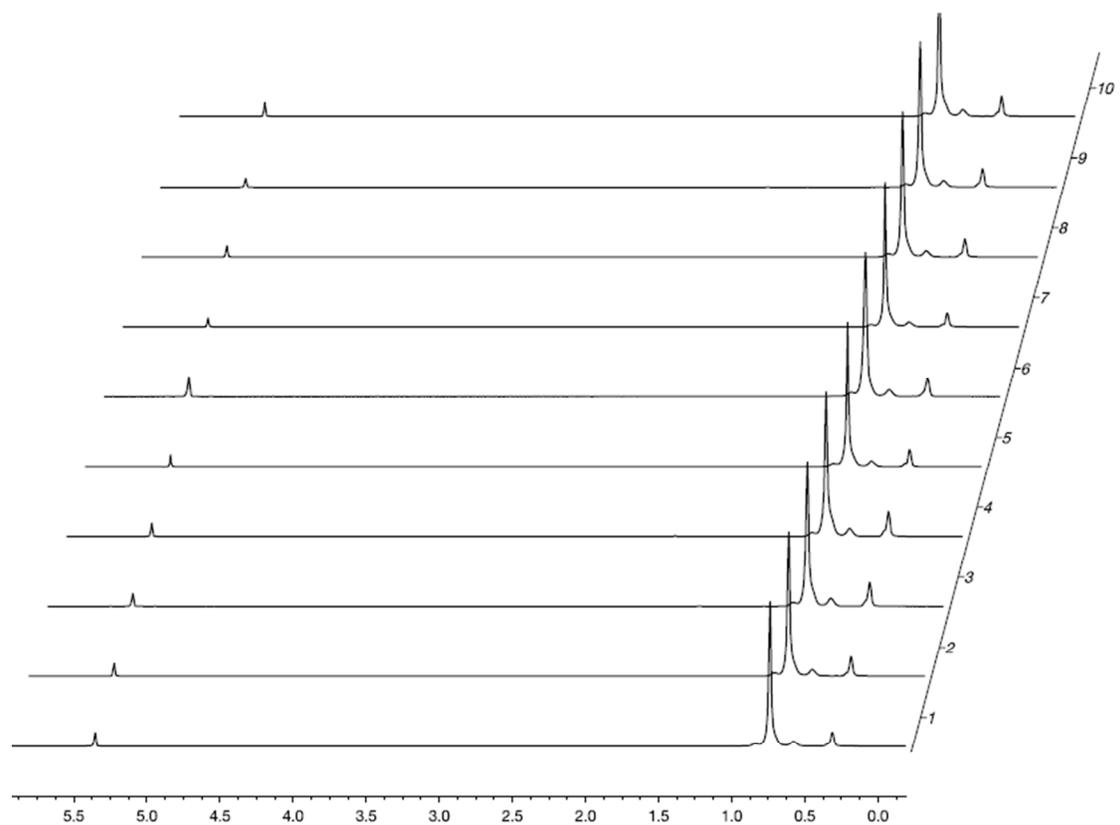


Figure S13. ¹H NMR (600 MHz) spectra (ns = 64 in C₂D₂Cl₄ @ 120 °C) polyethylene samples obtained at different conditions (entry 1-10, Table 1).

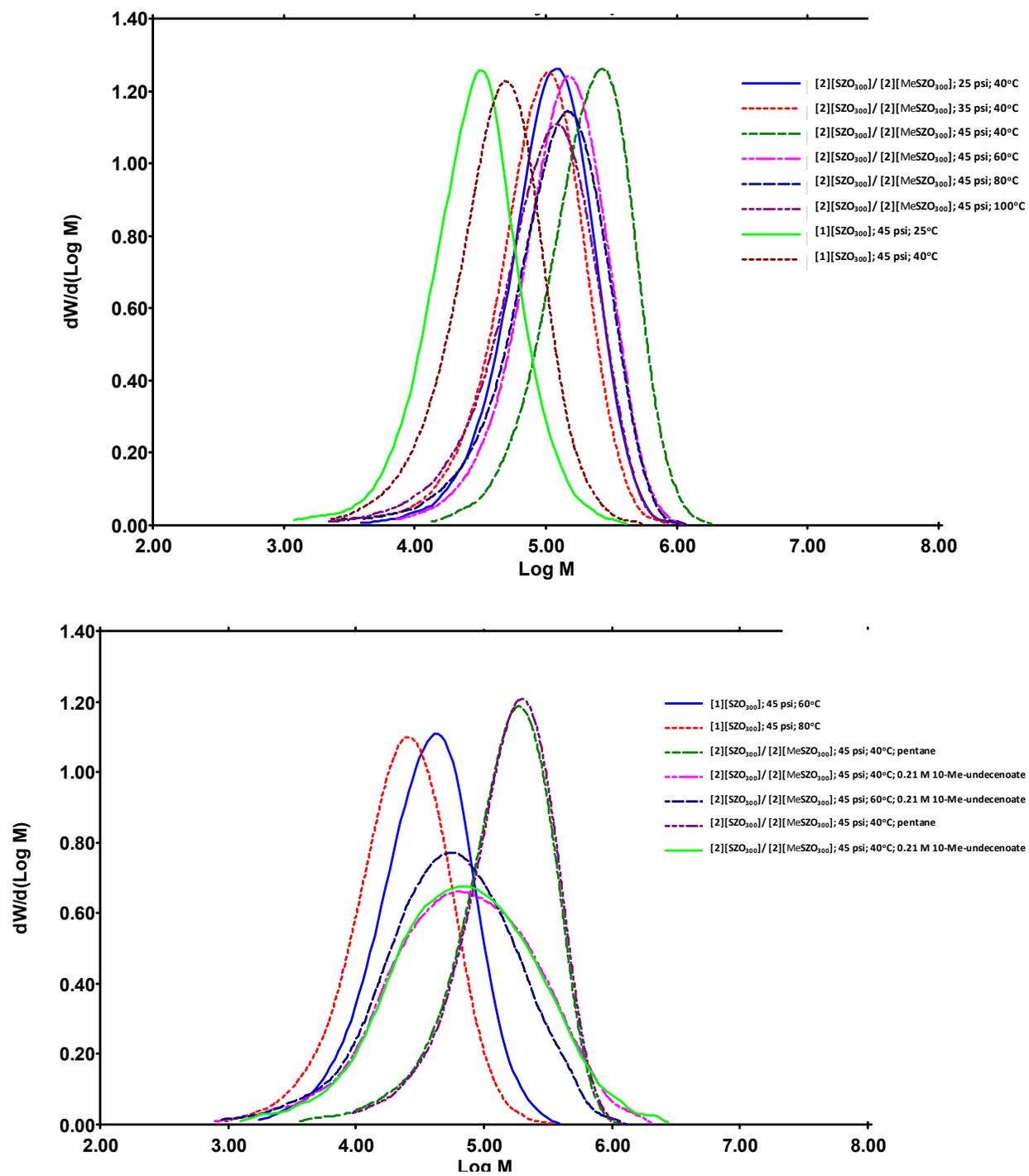


Figure S14. GPC traces of polymers and copolymers.

Table S1. GPC data for polymers

Sample ID	Mn/1000	Mw/1000	Mw/Mn
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 25 psi; 40°C	72.86	135.26	1.86
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 35 psi; 40°C	59.66	113.15	1.9
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 40°C	153.33	269.37	1.76
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 60°C	90.89	167.64	1.84
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 80°C	66.49	158.27	2.38
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 100°C	53.95	128.6	2.38
[1][SZO ₃₀₀]; 45 psi; 25°C	19.16	38.21	1.99
[1][SZO ₃₀₀]; 45 psi; 40°C	28.46	55.82	1.96
[1][SZO ₃₀₀]; 45 psi; 60°C	22.55	46.86	2.08
[1][SZO ₃₀₀]; 45 psi; 80°C	14.55	31.26	2.15
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 40°C (pentane)	84.47	189.84	2.25
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 40°C (0.21 M methyl 10-undecenoate)	25.37	142.24	5.61
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 60°C (0.21 M methyl 10-undecenoate)	23.59	97.88	4.15
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 40°C (pentane)	103.53	200.21	1.93
[2][SZO ₃₀₀]/[2][MeSZO ₃₀₀]; 45 psi; 40°C (0.21 M methyl 10-undecenoate)	29.67	153.33	5.17

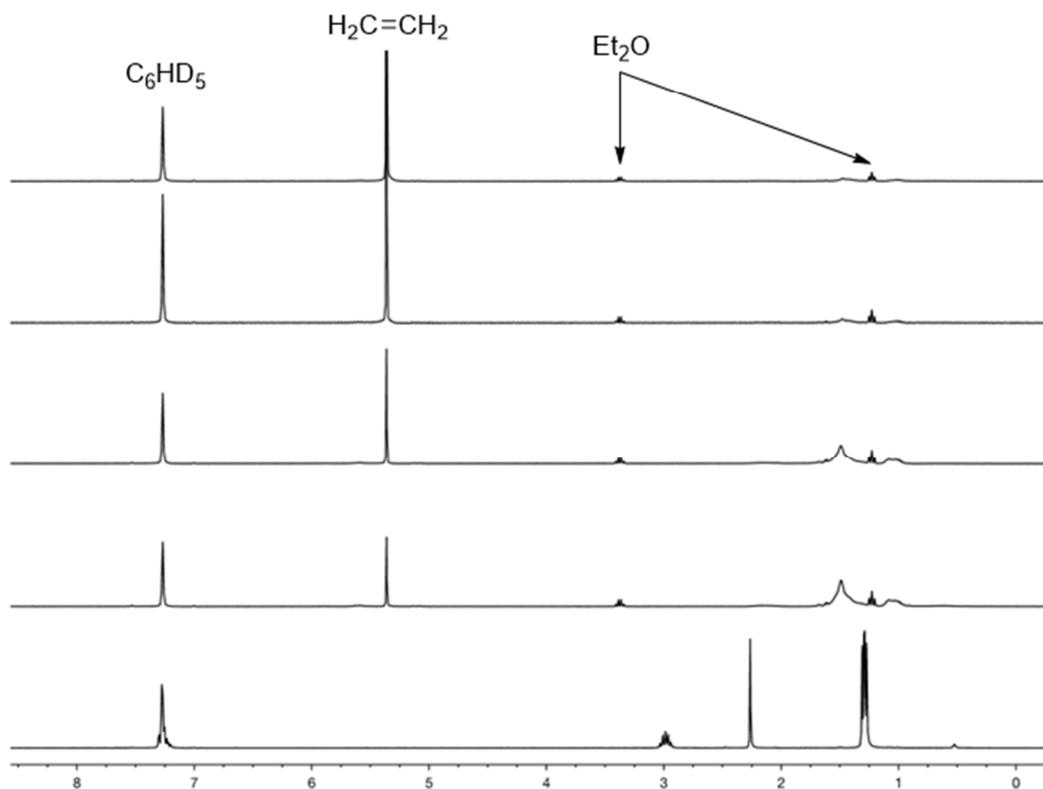


Figure S15. ^1H NMR (300 MHz) spectra of $[2][\text{SZO}_{300}]$ in the presence of ethylene after 10 min, 1 h, 10 h, and 20 h stacked on top of the ^1H NMR spectrum of the ligand.

Entry	mol Ni	Time (h)	T ($^{\circ}\text{C}$)	P (psi)	Yield (mg)	TOF ($\text{mol}_{\text{PE}}/\text{mol}_{\text{Ni}}*\text{h}$)	Activity ($\text{kg}_{\text{PE}}/\text{mol}_{\text{Ni}}*\text{h}$)
1/homogeneous	2.8E-6	0.25	40	45	490	25000	700
2/supported	1.4E-6	0.25	40	45	190	21000	586

Table S2. Comparison of the activity of the homogeneous catalyst $\text{C1}+[\text{H}(\text{OEt}_2)][\text{B}(\text{C}_6\text{F}_5)_4]$ to the supported catalyst (this work).

Entry	mol Ni	Time (h)	T ($^{\circ}\text{C}$)	P (psi)	Yield (mg)	TOF ($\text{mol}_{\text{PE}}/\text{mol}_{\text{Ni}}*\text{h}$)	Activity ($\text{kg}_{\text{PE}}/\text{mol}_{\text{Ni}}*\text{h}$)	$\text{g}_{\text{Ni}}/\text{g}_{\text{PE}}$ (ppm)
1/supported	1.4E-6	0.25	40	45	190	21000	586	430
2/supported	1.4E-6	1	40	45	257	6600	184	320
3/supported	1.4E-6	3	40	45	405	3400	96	200
4/supported	1.4E-6	6	40	45	503	2100	60	160

Table S3. Polymerization activity data for 15 minutes (short run) to 6 hours (long runs).

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1. Chang, Y. C.; Lee, Y. C.; Chang, M. F.; Hong, F. E. *J. Organomet. Chem.* **2016**, *808*, 23-33.
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3. Coperet, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougel, V.; Nagae, H.; Nunez-Zarur, F.; Zhizhko, P. A. *Chem. Rev.* **2016**, *116*, 323-421.