Supporting Information for:

Linear, High Molecular Weight Polyethylene from a Discrete, Mononuclear Phosphinoarenesulfonate Complex of Nickel(II)

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I. General considerations

All reactions were performed under an inert atmosphere, using Schlenk and glovebox techniques. CH_2Cl_2, CD_2Cl_2 (D, 99.9 %) and $CDCl_3$ (D, 99.8 %) (Cambridge Isotope Laboratories) were distilled from CaH_2. Toluene, THF and hexane (Aldrich) were purified using a two-column solid-state purification system (Glass Contour SPS, SG Water USA). Benzenesulfonic acid (90 %, Aldrich) was dehydrated by azeotropic distillation, then stored under N_2. Dichlorophenylphosphine (97%, Aldrich), 2′-bromo-2,6-dimethoxybiphenyl (97%, Aldrich), *n*-butyllithium (2.5 M solution in hexanes, Aldrich), and bis(1,5-cyclooctadiene)nickel(0) (98+ %, Strem Chemicals) were used as received. $[NiBr(C_3H_5)_2]_2$ [1] and *trans*-$[(PPh_3)_2Ni(Cl)Ph]$ [2] were prepared according to literature procedures. The ligand **1a** was provided by Japan Polychem Corp. Elemental analyses were performed by the Analytical Laboratory of the UCSB Marine Science Institute.

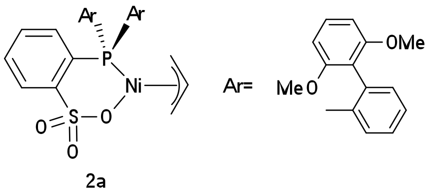
^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Varian VNMRS 600 spectrometer (600 MHz ^1H frequency), or on a Bruker Avance 500 spectrometer (500 MHz ^1H frequency). Chemical shifts were referenced to the residual signals of the deuterated solvents (CD_2Cl_2: ^1H: δ 5.32 ppm, ^{13}C: δ 54.00 ppm. $CDCl_3$: ^1H: δ 7.24 ppm, ^{13}C: δ 77.23 ppm). ^{31}P NMR spectra were referenced to an external standard (85 % H_3PO_4). Multiplicities are indicated as follows (or combinations thereof): s: singlet, d: doublet, t: triplet, m: multiplet, b: broad, v: virtual.

Electrospray ionization mass spectra were recorded on a Micromass QTOF2 instrument. Fresh solutions of the Ni(II) compounds (ca. 1 mg/mL) were prepared inside a N_2-filled glovebox with

CaH_2-dried acetonitrile. The solutions were sealed in air-tight scintillation vials and removed from the glovebox. Prior to each measurement, an aliquot of dry acetonitrile was injected into the mass spectrometer, then the vial was opened to air and the sample was rapidly injected into the instrument using the same microsyringe, to minimize air exposure. Traces of Na^+ present in the solvent or column were sufficient to generate observable molecular ions ($M + Na^+$) without external addition of a cationizing agent. Fragmentation was observed, and only representative *m/z* values are listed. The isotopic patterns for each *m/z* value match the calculated patterns closely.

II. Synthesis and characterization of compounds

Synthesis of $[2(2',6'-(OMe)_2-C_6H_3)C_6H_4]_2P(2-SO_3-C_6H_4)Ni(CH_2CHCH_2)$, 2a

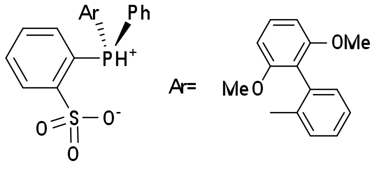


2a

A suspension of **1a** (250 mg, 0.41 mmol) and Na_2CO_3 (100 mg, 0.94 mmol) in 30 mL CH_2Cl_2 was stirred for 6.5 h at room temperature. $[Ni(Br)(C_3H_5)]_2$ (80 mg, 0.22 mmol) in 5 mL CH_2Cl_2 was then added dropwise and the reaction mixture stirred overnight. After filtration through Celite, the volatiles were removed in vacuo to afford an orange residue that was taken up in toluene (20 mL). The solution was filtered and concentrated to ca. 4 mL. The precipitate that formed upon addition of 10 mL hexanes was isolated by filtration and washed twice with hexanes. Overnight drying under vacuum afforded 71 mg (25 %) **2b** as a yellow-orange powder.

^{1}H NMR ($CDCl_3$, 500 MHz, 299 K): δ 7.75 (vt, 1H, J = 6.3 Hz), 7.55 (t, 1H, 8.4 Hz), 7.50 (bs, 2H), 7.44 (t, 2H, 7.4 Hz), 7.32 (t, 2H, 7.6 Hz), 7.18-7.71 (m, 6H), 6.57 (d, 2H, 8.3 Hz), 6.21 (bs, 2H), 4.90 (bs, 1H, $CH_2C\mathit{H}CH_2$), 3.75 (s, 6H, $OC\mathit{H}_3$), 3.21 (bs, 6H, $OC\mathit{H}_3$) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz, 299 K): δ 158.1 (s), 147.7 (d, J = 15.7 Hz), 141.3 (d, J = 12 Hz), 136.4 (d, J = 9.1 Hz), 135.5 (bs), 135.11 (s), 134.1 (d, 8.4), 130.45 (s), 130.1 (s), 129.9 (s), 128.9 (d, 5.3), 128.7 (s), 127.7 (d, J = 7.0 Hz), 127.3 (s), 127.0 (s), 126.7 (d, J = 18.3), 125.8 (s), 118.5 (bs), 114.9 (s), 104.3 (s), 103.3 (bs), 56.0 (s), 54.9 (s) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2, 243 MHz, 299 K): δ 3.57 ppm. ESI-MS (CH_3CN, positive ion scan, *m/z*): 671.08 ($M - C_3H_5^-$), 735.12 ($M + Na^+$), 1383.20 ($2M - C_3H_5^-$). Anal. Calcd for $C_{37}H_{35}NiO_7PS$: C, 62.29; H, 4.95. Found: C, 62.2; H, 4.99.

Synthesis of [2(2′,6′-(OMe)$_2$-C$_6$H$_3$)C$_6$H$_4$]P(H)(Ph)(2-SO$_3$-C$_6$H$_4$), 1b



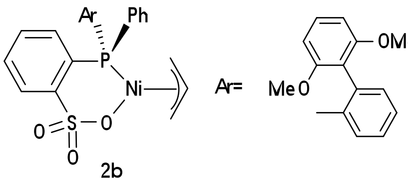
1b

A Schlenk flask was charged with benzenesulfonic acid (1.70 g, 10.7 mmol) and evacuated. Under dynamic vacuum, the solid was heated with a heat gun until it melted. The reduced pressure was maintained for 20 min, then the solid was dissolved in 80 mL THF. The flask was cooled with an ice bath and the temperature was allowed to equilibrate (ca. 10 min). ^{n}BuLi (8.6 mL, 21.5 mmol) was added dropwise and the mixture was stirred for 1 h at 0 °C. The resulting orange suspension was cooled to -78 °C and cannula-transferred over about 5 min to a second flask charged with a THF solution (80 mL) of $PhPCl_2$ (1.46 mL, 10.7 mmol), also at -78 °C. The resulting colorless solution was stirred at -78 °C for 30 min, then allowed to warm gradually to room temperature with stirring for 1.5 h. During this time, a third Schlenk flask was charged with 2´-bromo-2,6-dimethoxybiphenyl (3.14 g, 10.7 mmol) and THF (150 mL), and stirred for 10 min at room temperature. This reaction flask was cooled to -78 °C and ^{n}BuLi (4.3 mL, 10.7 mmol) was added dropwise. The resulting white slurry was vigorously stirred for 1 h while the temperature was kept at -78 °C. The contents of the second flask were then transferred at -78 °C to the third flask. The resulting mixture was allowed to warm gradually to room temperature and stirred overnight to yield a yellow solution. After removal of the volatiles under reduced pressure, CH_2Cl_2 and deionized water (200 mL each) were added to the flask and stirred for 5 min. Concentrated HCl (15 mL) was added dropwise with a pipette, then the mixture was transferred to a separatory funnel. The organic layer was recovered, dried over $MgSO_4$ and evaporated to dryness. The yellow residue was washed with THF (20 mL) and diethyl ether (3 x 20 mL), then dried under reduced pressure to yield 0.93 g (18 %) of **1b** as a white powder.

^{1}H NMR (CD_2Cl_2, 600 MHz, 300 K): δ 8.18 (dd, 1H, J = 7.1, 5.0 Hz), 7.79-7.44 (m, 2H), 7.64 (vt, 1H, J = 7.1 Hz), 7.51 (vt, 1H, J = 7.7 Hz), 7.48-7.46 (m, 4H), 7.41-7.33 (m, 4H), 7.29 (t, 1H, J = 8.4 Hz, C_6H_2H), 6.51 (d, 1H, J = 8.4, C_6H_2H), 6.47 (d, 1H, J = 8.4, C_6H_2H), 3.63 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 150 MHz, 299 K): δ 157.7 (s, C_{Ar}OMe), 157.4 (s, C_{Ar}OMe), 153.4 (d, Cq, J_{PC} = 9.7 Hz), 141.8 (d, Cq, J_{PC} = 9.9 Hz), 135.5 (d, J_{PC} = 10.5 Hz), 135.1 (d, J_{PC} = 3.0 Hz), 134.9 (d, J_{PC} = 11.3 Hz), 134.6 (d, J_{PC} = 2.8 Hz), 134.2 (d, J_{PC} =10.3 Hz), 134.1 (d, J_{PC} =3.0 Hz), 132.0 (d, J_{PC} =11.3 Hz), 130.0 (d, J_{PC} =12.4 Hz), 129.8 (d, J_{PC} =13.5 Hz), 128.9 (d, J_{PC} = 9.4 Hz), 128.4 (d, J_{PC} = 12.6 Hz), 120.6 (d, J_{PC} = 91.6 Hz, P-C_q), 120.0 (d, J_{PC} = 91.8 Hz, P- C_q), 114.5 (d, J_{PC} = 5.8 Hz), 113.5 (d, J_{PC} = 96.9 Hz, P- C_q), 104.4 (d, J_{PC} = 9.5 Hz), 56.0 (s, OCH_3), 56.0 (s, OCH_3) ppm. ^{31}P{^{1}H} NMR (CH_2Cl_2, 299 K): δ 1.18 ppm. ^{31}P NMR (CH_2Cl_2, 299 K): δ 1.04 (d, $^{1}J_{PH}$ = 458 Hz) ppm. ESI-MS (CH_3CN, positive ion scan, *m/z*):

479.11 (M + H$^+$), 501.09 (M + Na$^+$), 979.20 (2M + Na$^+$). Anal. Calcd for $C_{26}H_{23}O_5PS$: C, 65.26; H, 4.84. Found: C, 64.6; H, 4.83.

Synthesis of [2(2′,6′-$(OMe)_2$-C_6H_3)C_6H_4]P(Ph)(2-SO_3-C_6H_4)]Ni(CH_2CHCH_2), 2b



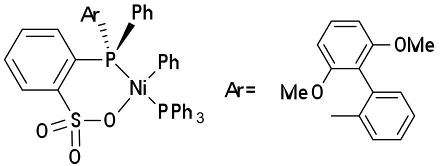
2b

A suspension of **1b** (200 mg, 0.417 mmol) and Na_2CO_3 (105 mg, 1.00 mmol) in 10 mL CH_2Cl_2 was stirred vigorously for 6 h at room temperature. A 5 mL aliquot of $[NiBr(C_3H_5)_2]_2$ (82 mg, 0.23 mmol) in CH_2Cl_2 was added dropwise to the milky solution and allowed to stirred overnight (ca. 17 h). The resulting brown-orange solution was filtered through Celite and the volatiles removed in vacuum. The residue was dissolved in the minimum amount of CH_2Cl_2 and the desired compound precipitated by the slow addition of hexanes (15 mL). The orange powder was filtered, washed with hexanes (3 x 10 mL) and dried under reduced pressure to afford 172 mg (74 %) of **2b**.

^{1}H NMR (CD_2Cl_2, 600 MHz, 299 K): δ 8.15 (bs, 1H), 7.57 (vt, 2H, J = 7.4 Hz), 7.50-7.45 (m, 3H), 7.40 (m, 4H), 7.34 (m, 2H), 7.11 (t, 2H, J = 9.0 Hz), 6.80 (bs, 1H), 6.60 (bs, 1H), 5.43 (bs, 0.3H, C_3H_5), 4.5 (bs, 0.7H, C_3H_5), 3.94 4.5 (bs, 0.7H, C_3H_5), 3.81 (bs, 3H, OCH_3), 3.30, 2.60 (bs, 0.7H, C_3H_5), 2.47 (bs, 0.7H, C_3H_5), 2.15 (bs, 0.6H, C_3H_5), 1.13 4.5 (bs, 0.7H, C_3H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz, 299 K): 158.4 (bs), 157.9 (s), 148.5 (d, 14.9 Hz), 142.4 (bs), 136.1 (bs), 134.8 (d, 9.3 Hz), 133.8 (s), 133.5 (d, 11.0), 131.5 (d, 17.5), 131.4 (d, 2), 131.3 (s), 131.0 (s), 130.8 (d, 2 Hz), 130.2 (d, 2Hz), 128.8 (d, 9.9 Hz), 127.8 (d, 6.7), 127.1 (bs), 104.95 (bs), 104.38 (s), 56.3 (s OCH_3), 54.5 (bs, OCH_3) ppm. ^{31}P{^{1}H} (CD_2Cl_2, 243 MHz, 299 K): 2.07 ppm.

ESI-MS (CH_3CN, positive ion scan, *m/z*): 535.26 ($M – C_3H_5^-$), 599.32 ($M + Na^+$), 1111.58 ($2M - C_3H_5^-$), 1175.64 ($2M + Na^+$), 1689.90 ($3M – C_3H_5^-$), 1754.96 ($3M + Na^+$). **2b** was isolated with 0.1 equiv. CH_2Cl_2 (^1H NMR). Anal. Calcd for $C_{29.1}H_{27.2}Cl_{0.2}NiO_5PS$: C, 59.67; H, 4.68. Found: C, 59.3; H, 4.27.

Synthesis of [2(2′,6′-(OMe)$_2$-C_6H_3)C_6H_4]P(Ph)(2-SO_3-C_6H_4)]Ni(Ph)PPh_3, 3b



3b

A suspension of **1b** (200 mg, 0.417 mmol) and Na_2CO_3 (130 mg, 1.23 mmol) in 15 mL toluene was stirred for 6 h at room temperature. The resulting mixture was cooled to -35 °C and solid *trans*-[$(PPh_3)_2Ni(Cl)Ph$] (290 mg, 0.417 mmol) was then added in small portions. Toluene was added until the volume of the solution reached 20 mL, and the reaction mixture was stirred for 17 h at room temperature. The resulting yellow-orange mixture was filtered over Celite and the volatiles were removed under vacuum. Toluene (3 mL) was first added to the orange residue to afford a slurry, then hexanes (5 mL) were added and the mixture was stirred for 5 mins. The precipitate was recovered by filtration, washed with hexanes (3 x 10 mL) and dried for 20 h under dynamic vacuum. 228 mg (62 %) of **3b** was obtained as a bright yellow powder.

^1H NMR (CD_2Cl_2, 600 MHz, 299 K): 7.70 (t, 2H, *J* = 9.5 Hz), 7.63-7.58 (m, 3H), 7.42 (t, 5H, *J* = 7.5Hz), 7.31 (t, 10H, *J* = 6 Hz), 7.27-7.18 (m, 6H), 7.11 (q, 2H, *J* = 8.5 Hz), 6.95 (t, 1H, *J* = 8.0 Hz), 6.77 (d, 1H, *J* = 7.5 Hz), 6.59 (d, 1H, *J* = 8.5 Hz), 6.54 (t, 1H, *J* = 9 Hz), 6.46 (t, 1H, *J* = 7.5 Hz), 6.22-6.16 (m, 2 H), 6.07 (t, 1H, *J* = 8.0 Hz), 3.81 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3) ppm. ^1H NMR ($CDCl_3$, 600 MHz, 299 K): 7.73 (m, 2H), 7.32-7.24 (m, 14H), 7.20 (d, 1H, *J* = 7.4

Hz), 7.14 (vq, 1H, *J* = 7.6 Hz), 7.08 (t, 1H, *J* = 7.3 Hz), 6.89 (t, 1H, *J* = 7.5 Hz), 6.79 (d, 1H, *J* = 8.0 Hz), 6.57 (d, 1H, *J* = 8.4 Hz), 6.47 (t, 1H, *J* = 8.9 Hz), 6.42 (t, 1H, *J* = 7.2 Hz), 6.2) (vt, 1H, *J* = 7.4 Hz), 6.10 (d, 2H, *J* = 8.0 Hz), 6.05 (vt, 1H, *J* = 7.3 Hz), 3.85 (s, 3H), 3.22 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): 157.6 (s), 156.9 (s), 146.9 (d, *J* = 13.5 Hz), 140.0 (s), 139.9 (s), 139.0 (s), 138.7 (s), 138.4 (d, *J* = 3.8 Hz), 138.1 (d, *J* = 3.5 Hz), 135.5 (d, *J* = 5.9 Hz), 134.6 (s), 134.7 (s), 134.7 (s), 134.1 (s), 133.8 (d, *J* = 8.8 Hz), 132.5 (s), 132.1 (s), 130.3 (s), 130.11 (s), 130.0 (bs), 129.79 (d, *J* = 3.5 Hz), 129.07 (d, *J* = 3.3 Hz), 128.7 (bs), 128.17 (d, 9.3 Hz), 127.9 (d, 10.1 Hz), 126.6 (s), 126.5 (s), 125.7 (d, *J* = 8.1 Hz), 124.7 (s), 121.8 (s), 118.5 (d, 3.6 Hz), 105.3 (s), 103.3 (s), 56.9 (s), 54.7 (s) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 243 MHz, 299 K): 10.00 (d, J_{PP} = 280 Hz), -2.70 (d, J_{PP} = 280 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 200 MHz, 300 K): 9.41 (d, J_{PP} = 280 Hz), -2.94 (d, J_{PP} = 280 Hz) ppm. ESI-MS (CH$_3$CN, positive ion scan, *m/z*): 535.03 (M – PPh$_3$ – Ph$^-$), 635.06 (M – PPh$_3$ + Na$^+$), 797.13 (M – Ph$^-$), 897.16 (M + Na$^+$), 1149.11 (2M – PPh$_3$ – Ph$^-$), 1249.13 (2M – 2PPh$_3$ + Na$^+$), 1411.19 (2M – PPh$_3$ – Ph$^-$). Spectroscopically pure **3b** did not afford satisfactory elemental analyses. The error is tentatively attributed to contamination of **3b** with a small amount of a paramagnetic decomposition product (e.g., a Ni(I) complex). ^{1}H and ^{31}P NMR spectra are shown below in proof. In addition, the error could be caused by the formation of some of the PPh$_3$-free complex [[PO]NiPh]$_2$ (formed by dissociation of PPh$_3$ from **3b,** followed by extraction of the free PPh$_3$ by washing).[3]

NMR-scale experiment with 3b

3b (6.7 mg, 8.4 µmol) was dissolved in toluene-*d*$_8$ (0.8 mL) and transferred to an air-free J. Young NMR tube. The sample was inserted into the probe of an NMR instrument (^{1}H 500 MHz). ^{1}H and ^{31}P NMR spectra were recorded in the following order: (a) at 27 °C, (b) at 45 °C, (c) at

60 °C, (e) at 90 °C, and finally again (f) at 27 °C. Sufficient time (> 10 min) was allowed for thermal equilibration between measurements. The ^{1}H and ^{31}P NMR resonances associated with **3b** gradually disappeared as the temperature increased, while no signals in the ^{31}P NMR spectrum were observed for free PPh_3 (δ -6.6 ppm). At 90 °C, only very weak resonances were observed for **3b**. Consistent with the presence of paramagnetic species, broadening of the signals of C_7D_7H was also observed. This process is fully reversible, and cooling the sample to 27 °C afforded ^{1}H and ^{31}P NMR spectra identical to those of an authentic sample of **3b**.

III. Polymerization procedures

Ethylene polymerization experiments were performed in a 300 mL Parr autoclave equipped with a magnetically-coupled stirrer and a water cooling loop, using a glass insert with a diameter 4 mm smaller than the interior of the reactor. The glass inserts were made in the glassblowing shop of the Chemistry Department at UC Santa Barbara (dimensions: h = 94 mm, OD = 60 mm, ID = 54 mm). Reaction temperatures were controlled using an internal water coolant and either an external water bath or a heating mantle. The temperatures of the reaction mixtures were monitored by an internal thermocouple and found to be constant within the target temperature ranges throughout the experiments (± 3 °C max.). Ethylene (99.999 %) was purchased from Praxair and used as received.

Polymer characterization. Turnover frequencies were calculated from the mass of polyethylene recovered. Polymer melting points were obtained by differential scanning calorimetry (TA Instruments, model DSC Q2000) using a heating rate of 10 °C/min for 3 cycles over the temperature range 0 - 200 °C. The reported T_m values were taken from the second heating cycle.

GPC analyses were performed using a high-temperature chromatograph from Polymer Laboratories, Pl-GPC 200. Polymers were characterized relative to polystyrene standards at 135 °C in 1,2,4-trichlorobenzene (99+ %, Aldrich).

Standard procedure for ethylene polymerization

In a N_2-filled glovebox, a glass insert was charged with the nickel precatalyst (10 or 20 μmol), as well as $Ni(COD)_2$ or $B(C_6F_5)_3$ (where specified), and toluene (80 mL). A small amount of toluene was added to the reactor to improve the thermal contact with the glass insert. The glass liner was placed in the autoclave, which was sealed and removed from the glovebox. The mixture was stirred for 5 min at the polymerization temperature, then the reactor was pressurized with 400 psi ethylene, fed continuously during the polymerization time. Temperatures were held constant throughout each experiment (± 3°C). After the desired reaction time, the ethylene pressure was released and the reaction mixture cooled to room temperature. The polymer was precipitated with methanol, isolated by filtration and washed with acidified methanol (5 % HCl), methanol and copious amounts of acetone. The polymer was air-dried for a minimum of 2 days.

Polymerization with 3b after pretreatment at 90 °C

To investigate whether the Ni(II) complex is irreversibly transformed thermally into a different, highly active catalyst producing low molecular weight polymer, for instance, by redistribution of the substituents on phosphorus, the following experiment was performed. A solution of **3b** (10 mg, 12.5 μmol) in 80 mL toluene was charged to a 300 mL Parr reactor, and warmed from 22 to 90 °C over about 10 min. The temperature was kept constant (± 3°C) for a further 20 min, as monitored by an internal thermometer. The mixture was then allowed to cool to room temperature in a cold water bath, requiring 7 min to bring the temperature inside the reactor down to 22 °C. After an additional 13 min at room temperature, the reactor was pressurized with ethylene on demand (400 psi) and polymerization was performed for 1 h at 25 °C. The reactor was then vented and the polymer recovered as described above. 0.4 g polyethylene was isolated (TOF = 1, 200 h^{-1}; M_n = 157,000 $g.mol^{-1}$; PDI = 2.13; T_m = 134.4 °C). The low activity is consistent with extensive decomposition of **3b**, presumably to Ni^0, prior to polymerization. The lower M_n observed in this experiment (compared to entry 4 in Table 1) likely results from reaction of the active catalyst with one of its decomposition product(s), e.g., the free [PO] ligand. Nevertheless this experiment shows that, upon thermal treatment, **3b** does not form a new, highly active catalytic species, but rather simply decomposes into inactive compounds.

IV. Representative GPC traces for polyethylene

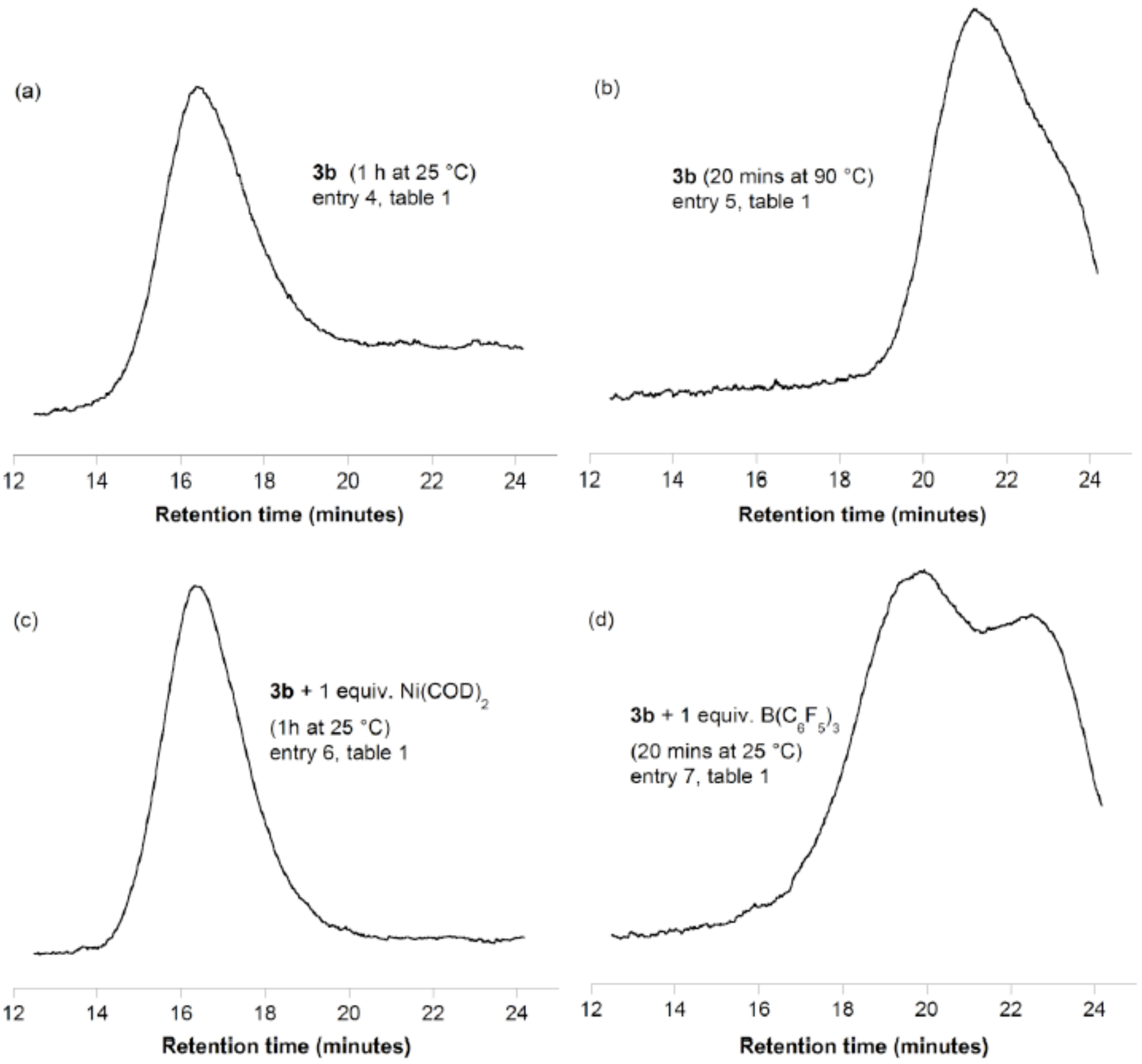


Figure S1. GPC traces for PE obtained from **3b** in toluene with $P(C_2H_4)$ = 400 psi, and variable polymerization conditions. The traces correspond to the following entries in Table 1: (a) entry 4; (b) entry 5; (c) entry 6; and (d) entry 7.

V. X-ray Crystallography

X-ray data collection, structure solution and refinement. Single crystals of the complexes **2a** and **2b** were grown from saturated benzene solutions. The crystals were isolated by decantation and covered with a layer of hydrocarbon oil. Suitable crystals were selected, mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[4] program was used to determine the unit cell parameters and data collection (15 s/frame, 0.3 °/frame, for a sphere of diffraction data). Data were measured with Mo K_{α} radiation ($\lambda = 0.71073$ Å), and collected at 150 K using an Oxford N_2 gas cryostream system. The raw frame data were processed using the SAINT[5] program. The empirical absorption correction was applied based on psi-scan. The structures were solved by direct methods and refined using the least-squares method on F^2 using the SHELXTL[6] program. All non-hydrogen atoms were refined anisotropically. Details of the data collection and refinement are given in Table S1. For crystallographic information files (CIF), see CCDC reference numbers 806742 and 806747.

Table S1. Crystallographic data

	2a	**2b**
formula	$C_{49}H_{47}NiO_7PS$	$C_{35}H_{33}NiO_5PS$
molecular weight [g.mol^{-1}]	869.61	655.35
crystal system	triclinic	monoclinic
space group	P-1	P2(1)/c
a [Å]	11.165(7)	12.848(4)
b [Å]	11.531(7)	11.461(4)
c [Å]	17.445(11)	22.104(7)
α [°]	72.330 (9)	90
β [°]	90.065 (10)	106.795(5)
γ [°]	83.002 (10)	90
V [Å^3]	2122(2)	3116.1(17)
Z	2	4
calculated density [Mg.m^{-3}]	1.361	1.397
absorption coefficient [mm^{-1}]	0.597	0.783
F(000)	912	1368
crystal size [mm^3]	0.35 x 0.25 x 0.1	0.3 x 0.2 x 0.15
θ range [°]	1.84 to 24.71	1.66 to 26.83
limiting indices	$-13 \leq h \leq 13$	$-16 \leq h \leq 16$
	$-13 \leq k \leq 13$	$-14 \leq k \leq 14$
	$-20 \leq l \leq 20$	$-27 \leq l \leq 27$
reflections collected	15376	24608
independent reflections	7172 [R(int) = 0.0414]	6423 [R(int) = 0.0827]
data/restraints/parameters	7172 / 5 / 539	6423 / 0 / 394
GOF	2.054	1.191
Final R indices [I>2sigma(I)] [a]	R1 = 0.0767, *w*R2 = 0.1855	R1 = 0.0455, *w*R2 = 0.1254
R indices (all data) [a]	R1 = 0.1002, *w*R2 = 0.1936	R1 = 0.0565, *w*R2 = 0.1313
largest diff. peak/hole	3.430/ -1.032	1.266/-0.731

[a] $R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$; $wR2 = \{\Sigma[w(F^2_0 - F^2_c)^2] / \Sigma[w(F^2_0)^2]\}^{1/2}$.

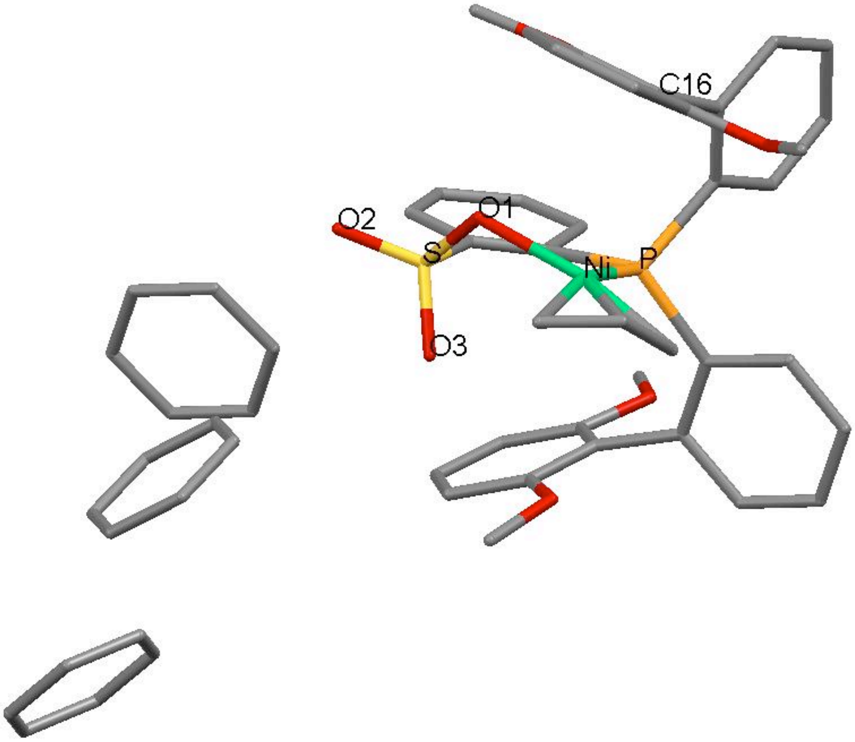


Figure S2. Molecular structure of **2a**, showing the three benzene molecules (per molecule of **2a**) that cocrystallized in the lattice. Hydrogen atoms have been omitted for clarity.

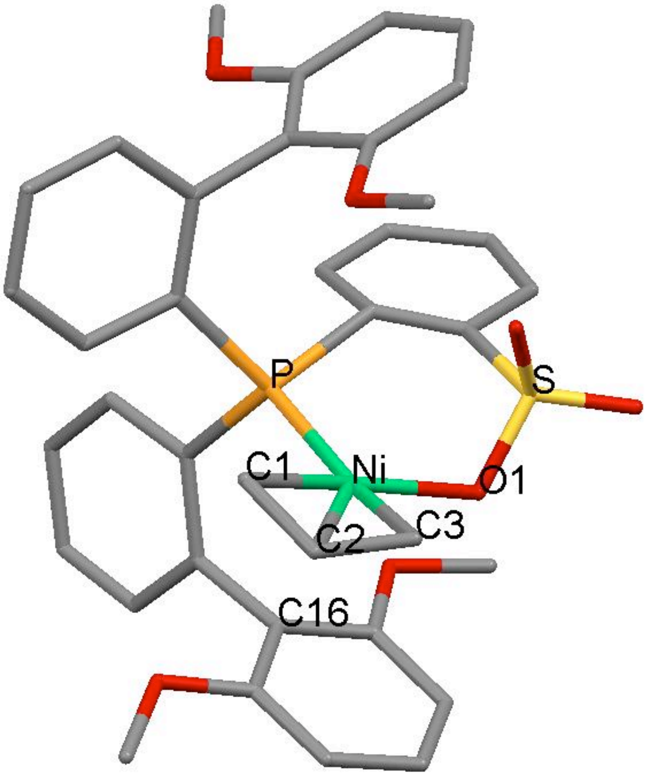


Figure S3. Molecular structure of **2a**. All hydrogen atoms and co-crystallized benzene molecules have been omitted for clarity. Selected bond lengths [Å], distances [Å] and angles [°]: Ni–P = 2.206(2); Ni–O(1) = 1.935(4); Ni–C(1) = 1.941(6); Ni–C(2) = 2.009(6); Ni–C(3) = 2.072(6), C(1)–C(2) = 1.367(9); C(2)–C(3) = 1.319(9); Ni–C(16) = 3.107(5); C(1)–C(2)–C(3) = 125.3(7); C(1)–Ni–C(3) = 72.9(2) ; C(1)–Ni–P = 96.47(18); O(1)–Ni–P = 96.67(11); O(1)–Ni–C(3) = 92.93(19); C(1)–C(3)–O(1)–P = 7.1(2).

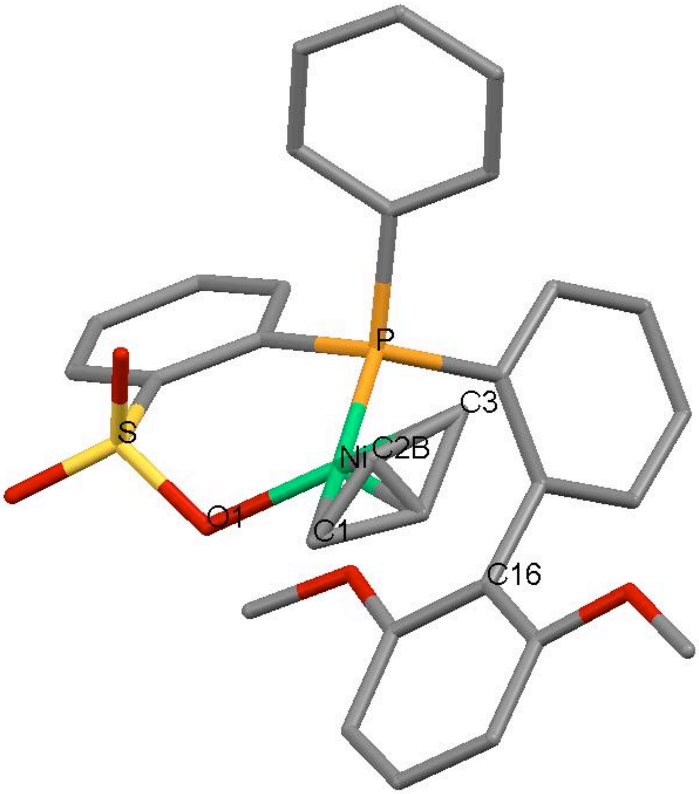


Figure S4. Molecular structure of **2b**. All hydrogen atoms and co-crystallized benzene molecules have been omitted for clarity. The central carbon of the -CH_2-CH=CH_2 group is disordered (2 positions). Selected bond lengths [Å], distances [Å] and angles [°]: Ni–P = 2.1768(8); Ni–O(1) = 1.9237(17); Ni–C(1) = 2.063(3); Ni–C(2A) = 1.992(4); Ni–C(2B) = 1.956(9); Ni–C(3) =1.990(3), C(1)–C(2A) = 1.348(5); C(1)–C(2B) = 1.223(11); C(2A)–C(3) = 1.391(5); C(2B)–C(3) = 1.410(11); Ni–C(16) = 3.151(2); C(1)–C(2A)–C(3) = 126.3(4); C(1)–C(2B)–C(3) = 136.2(9); C(1)–Ni–C(3) = 74.15(13); C(3)–Ni–P = 94.06(9); O(1)–Ni–P = 96.56(6); O(1)–Ni–C(1) = 94.33(11) ; C(1)–C(3)–P–O(1) = 4.4(1).

VI. NMR spectra for ligand 1b and complex 3b

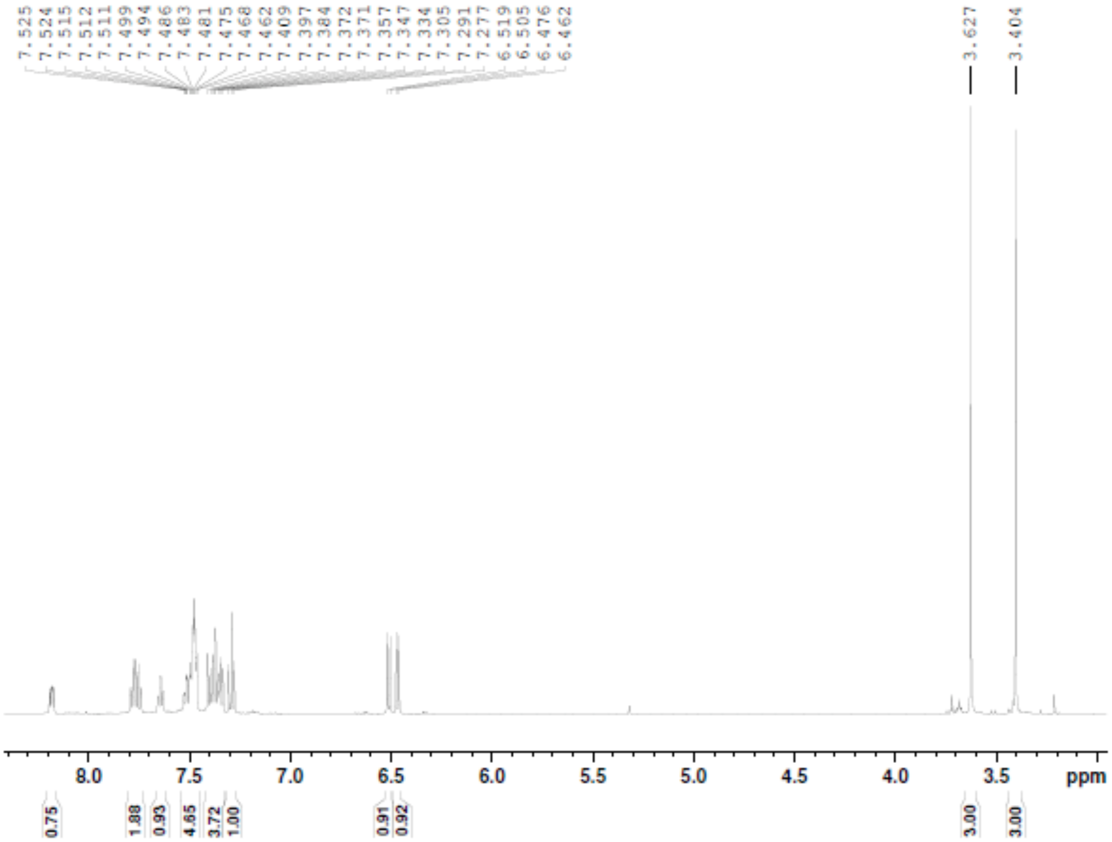


Figure S5. ^{1}H NMR spectrum of **1b** in CD_2Cl_2 at 300 K

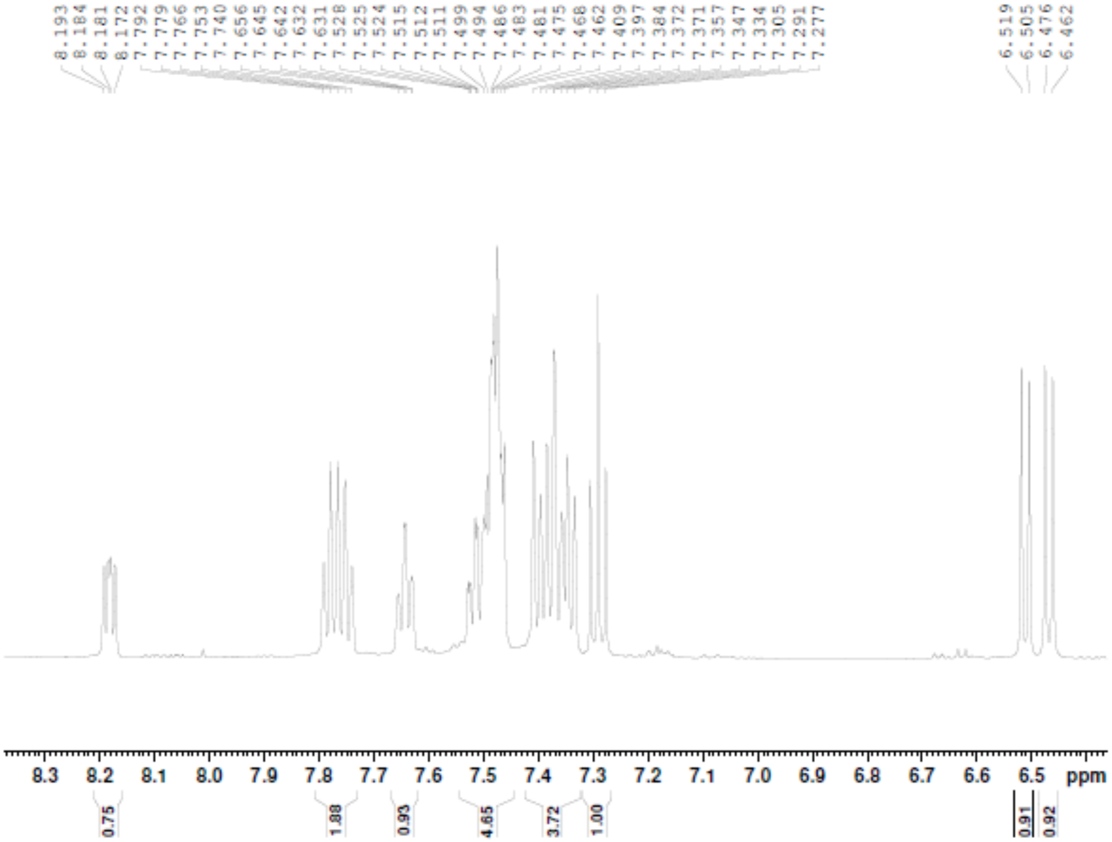


Figure S6. ^{1}H NMR spectrum of **1b** in CD_2Cl_2 at 300 K

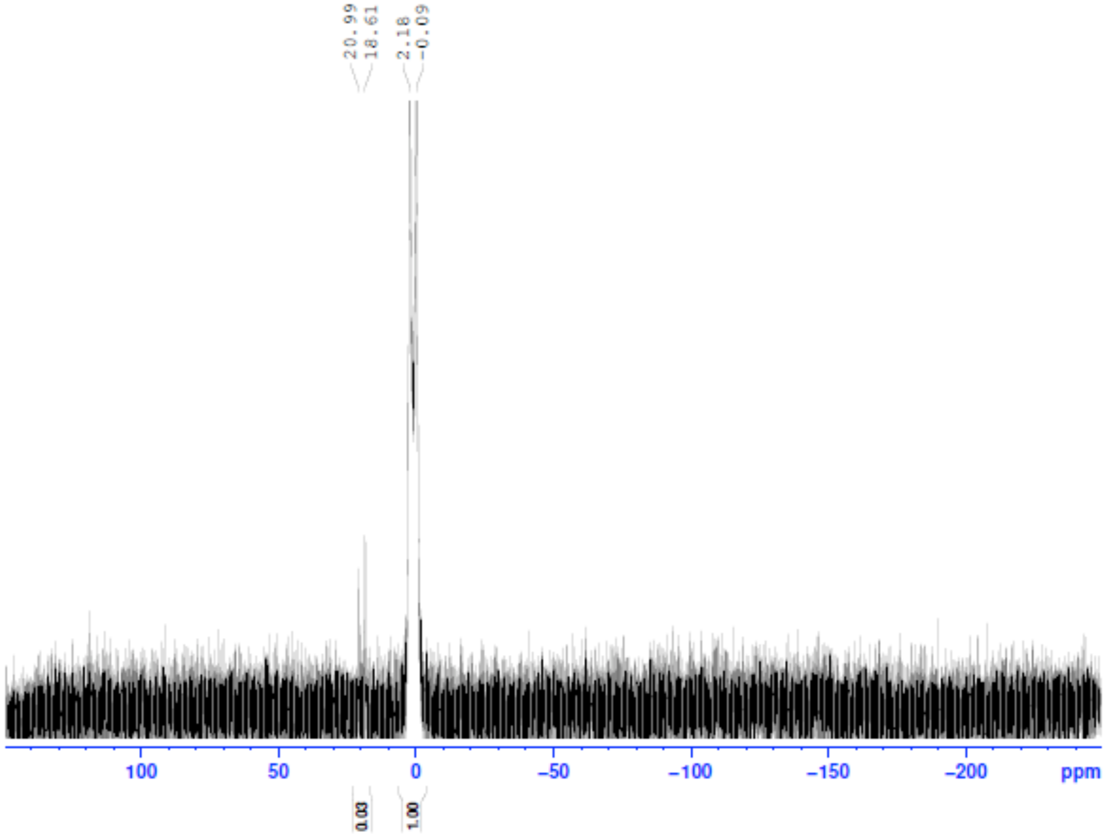


Figure S7. ^{31}P NMR spectrum of **1b** in CD_2Cl_2 at 300 K

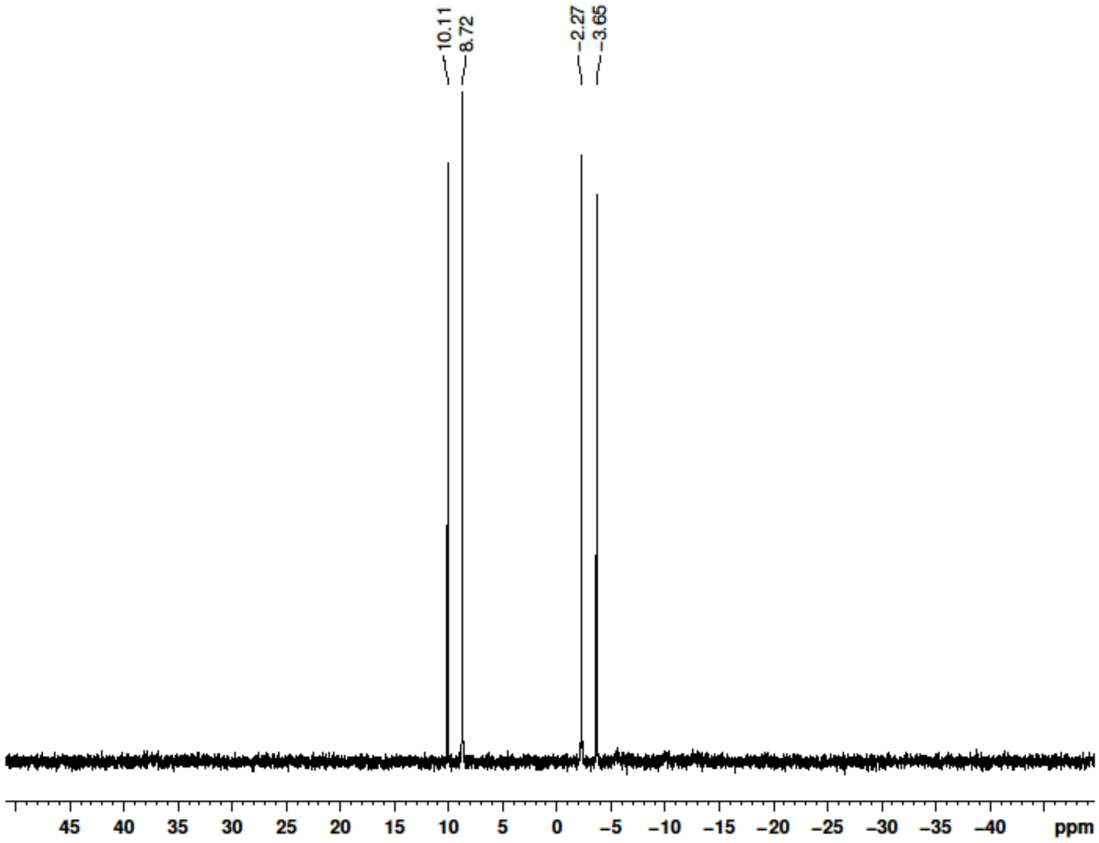


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$ at 300 K.

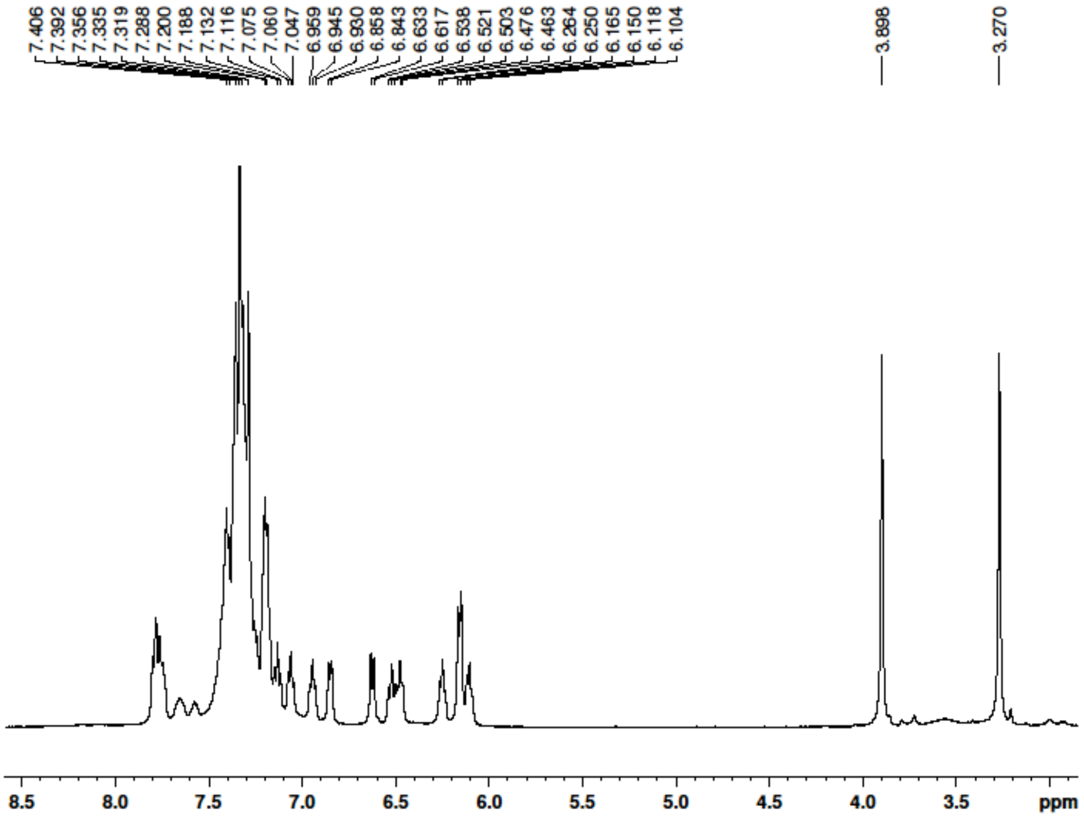


Figure S9. ^{1}H NMR spectrum of **3b** in $CDCl_3$ at 300 K.

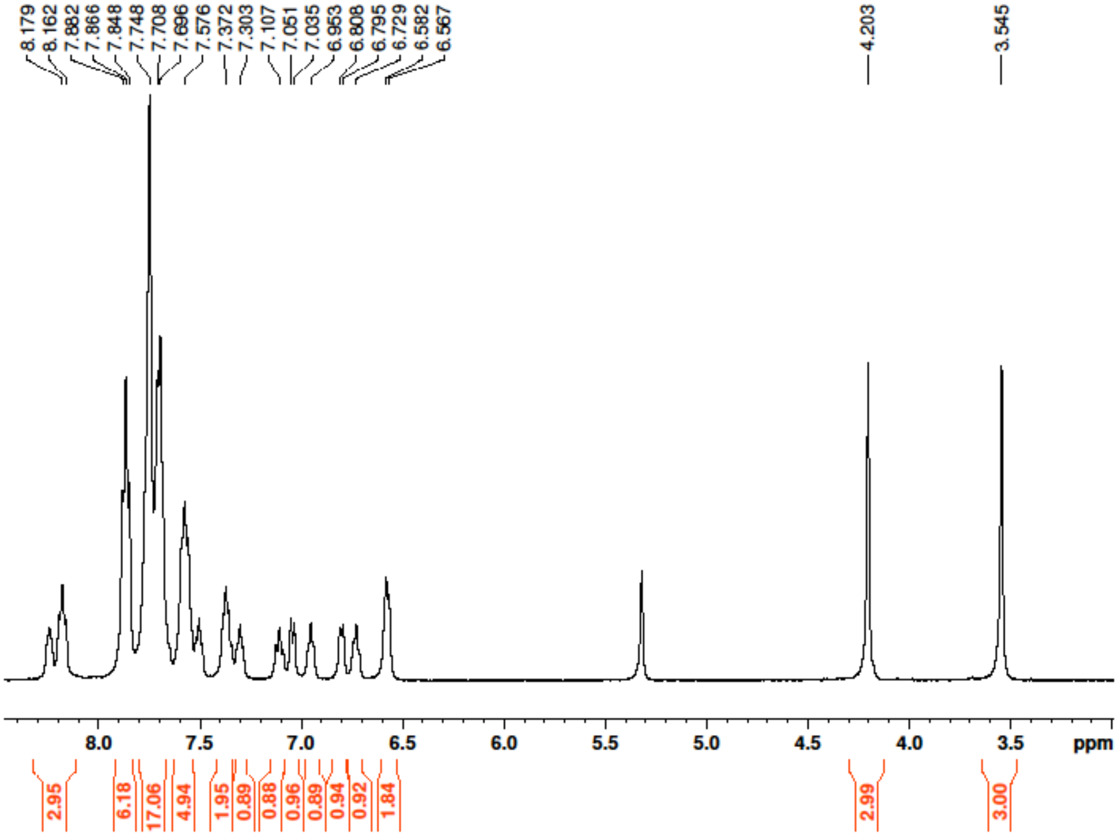


Figure S10. ^{1}H NMR spectrum of **3b** in CD_2Cl_2 at 300 K.

VII. Additional references

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