Supporting Information

N-Bridged Strategy Enables Hemilabile Phosphine-Carbonyl Palladium and Nickel Catalysts to Mediate Ethylene Polymerization and Copolymerization with Polar Vinyl Monomers

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**General Procedures and Materials:** All syntheses involving air and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on a Bruker AV400 (\(^1\)H: 400 MHz, \(^{13}\)C: 100 MHz, \(^{31}\)P: 162 MHz, \(^{19}\)F: 376 MHz) or a Bruker AV500 (\(^1\)H: 500 MHz, \(^{13}\)C: 125 MHz, \(^{31}\)P: 202 MHz, \(^{19}\)F: 470 MHz). The molecular weights (\(M_n\)) and molecular weight distributions (\(M_w/M_n\)) of polymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 \(\mu\)m Mixed-B LS type columns at 150 °C. Melting points (\(T_m\)) of polyethylenes and polymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 20 °C/min (temperature range: 40-250 °C).

**Materials:** (COD)PdMeCl\(^1\) and [Ni(allyl)Cl]\(^2\) were prepared according to the literature procedures. The following polar monomers were commercially available and used after distillation under vacuum: methyl acrylate (MA), butyl vinyl ether (BVE), acrylic acid (AA). All other reagents were commercially available and used as received.

**X-Ray diffraction:** Data collections were performed at −100 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)) or Cu Kα radiation (\(\lambda = 1.54178 \text{ Å}\)). The determination of crystal class and unit cell parameters was carried out by the SMART program package.\(^3\) The raw frame data were processed using SAINT and SADABS to yield the reflection data file.\(^4\) All structures were solved by direct methods and refined by full-matrix least-squares procedures on \(F^2\) using SHELXTL or Olex2.\(^5\) Refinement was performed on \(F^2\) anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.
Preparation of ligands and catalysts

Chlorobis(2,6-dimethoxyphenyl)phosphine: 2-bromoanisole 27 g (0.144 mol) was dissolved in 150 mL ether under nitrogen, 60 mL n-BuLi (2.5 M in hexane, 0.144 mmol) was dropped at -78 °C. After 2 h, 12.1 g (0.07 mol) Et₂NPCI₂ prepared was added to the solution and stirred overnight at room temperature. Subsequently, 69 mL HCl/Et₂O (2 M, 0.07 mol) was added at room temperature and stirred overnight. The resulting was filtered over celite and the solvent was removed under vacuum to yield a white solid chlorobis(2,6-dimethoxyphenyl)phosphine (15 g, 76%). ³¹P NMR (202 Hz, CDCl₃): 69.34.

L1: To a solution of diisopropylamine (0.36 g, 14 mmol) in THF (10 mL) was added dropwise at -78 °C with n-BuLi (2.3 mL, 1.6 M, 3.7 mmol) under nitrogen. After the mixture was stirred for 0.5 h, a solution of acetophenone (0.43 g, 3.6 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 2 h at -78 °C and then transferred into a schlenk flask containing chlorobis(2,6-dimethoxyphenyl)phosphine (1 g, 3.5 mmol) in THF (10 mL). After the mixture was stirred for 12 h at room temperature, the solvent was removed in vacuo. The residue was treated with chloroform, and the resulting suspension was filtered in order to remove LiCl. The filtrate was then evaporated to dryness, and the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:10). The ligand was isolated by recrystallization (chloroform/petroleum ether) as a white solid L1 (0.8 g, 63%). ¹H NMR (500 MHz, CDCl₃): δ 8.12-8.08 (m, 2H), 7.56-7.51 (m, 1H), 7.46-7.41 (m, 2H), 7.37-7.31 (m, 2H), 7.24-7.19 (m, 2H), 6.97-6.91 (t, 2H), 6.88-6.83 (dd, J = 4.31 Hz, 2H), 3.80 (s, 2H, CH₂), 3.72 (s, 6H, OMe). ¹³C NMR (125 MHz, CDCl₃): δ 185.65 (d, J = 17.38 Hz), 161.66 (dd, J = 47.15Hz, J = 51.37Hz), 160.40 (s), 135.63 (s), 134.78 (s), 133.22 (s), 131.91 (s), 129.27 (s), 129.00 (s), 128.75 (s), 127.43 (s), 125.61 (s), 133.44 (s), 122.37 (d, J = 8.31Hz), 117.46 (s), 116.54 (s), 112.06 (d, J = 5.41Hz), 56.00 (s, OMe), 35.95 (d, J= 2.62Hz, -CH₂-). ³¹P NMR (202 MHz, CDCl₃): δ -29.76.
L2: N-methylbenzamide (2.02 g, 15 mmol) was dissolved in THF (30 mL) at -10 °C under nitrogen. A solution of 9.4 ml n-BuLi (1.6 M) in hexane was added dropwise. The white suspension was stirred at this temperature for 1.5 h and subsequently allowed to room temperature. Chlorobis (2,6-dimethoxyphenyl)phosphine (2.13 g, 7.59 mmol) in THF (20 mL) was added and the clear solution was stirred for 12 h at ambient temperature. The mixture was evaporated to dryness and subsequently suspended in CHCl₃ (40 mL). After that, the suspension was filtered through Celite. The ligand was isolated by recrystallization (THF) as a white solid L2 (1.9 g, 70.4%).

1H NMR (500 MHz, CDCl₃): δ 7.53-7.50 (m, 2H), 7.43-7.37 (m, 3H), 7.35-7.31 (m, 2H), 7.18-7.09 (m, 2H), 6.92-6.88 (m, 2H), 3.74 (s, 6H, OMe), 2.78 (s, 3H, N-Me).

13C NMR (125 MHz, CDCl₃): δ 177.91 (d, J = 28.87 Hz), 160.88 (d, J = 15.83 Hz), 137.34 (d, J = 3.21), 131.67 (d, J = 2.90), 131.06 (s), 128.05 (s), 127.69 (d, J = 7.36), 122.76 (d, J = 12.34), 110.27 (s), 55.63 (s, OMe), 33.73 (s, N-Me).

31P NMR (202 MHz, CDCl₃): δ 43.36.

Chlorobis(2-(trifluoromethyl)phenyl)phosphine: 11 mL n-BuLi (2.4 M in hexane, 26 mmol) was added dropwise to a solution of 5.9 g 2-bromobenzo trifluoride (26 mmol) in Et₂O (100 mL) at -78 °C under nitrogen. The reaction mixture was allowed to warm to room temperature. The solution was cooled to -78 °C and a solution of 2.3 g Cl₂PNEt₂ (13 mmol) in Et₂O (15 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 h, meanwhile a white precipitate formed. The reaction mixture was cooled to 0 °C and 13 mL HCl (2 M, 26 mmol) was added. The reaction mixture was allowed to warm to room temperature and the resulting slurry was stirred for 2 days. The precipitate was filtered off over celite and washed with Et₂O. The solvent was removed under vacuum to yield white solid (3.6 g, 78%).

31P NMR (202 MHz, CDCl₃): δ 72.60.
**L3**: N-methylbenzamide (0.5 g, 3.75 mmol) was dissolved in THF (20 mL) at -10 °C under nitrogen. A solution of 2.4 mL n-BuLi (1.6 M, 3.84 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. Chlorobis(2-(trifluoromethyl)phenyl)-phosphine (1.34 g, 3.79 mmol) in THF (20 mL) was added and the clear solution was stirred for 12 h at ambient temperature. The mixture was evaporated to dryness and subsequently suspended in CHCl₃ (40 mL). After that, the suspension was filtered through Celite. The ligand was isolated by recrystallization (THF/petroleum ether) as a white solid **L3** (1.45 g, 85.3%). **¹H NMR** (500 MHz, CDCl₃): δ 7.79-7.75 (m, 2H), 7.66-7.52 (m, 4H), 7.49-7.23 (m, 7H), 2.82 (s, 3H, N-Me). **¹³C NMR** (125 MHz, CDCl₃): δ 177.22 (d, J = 37.38 Hz), 136.27 (d, J = 3.55 Hz), 134.34 (d, J = 35.36 Hz), 133.45 (d, J = 28.49 Hz), 131.93 (s), 130.38 (s), 130.13 (s), 128.03 (s), 127.43 (d, J = 8.35 Hz), 125.10 (d, J = 1.94 Hz), 33.85 (s, NMe). **³¹P NMR** (202 MHz, CDCl₃): δ 46.26.

(2’,6’-dimethoxybiphenyl-2-yl)phenylphosphine chloride: 1.46 g (5 mmol) 2-Bromo-2’,6’-dimethoxybiphenyl was dissolved in 30 mL THF, 2.3 mL n-BuLi (2.4 M in hexane, 11 mmol) was added dropwise at -10 °C under nitrogen. After stirred for 3 h at room temperature, the reaction suspension was slowly transferred into the solution of PPhCl₂ (0.89 g, 5 mmol) in 15 mL THF, and the reaction mixture was stirred for 7 h. The resulting precipitate was filtered off celite and the solvent was removed under vacuum to yield a white solid (1.5 g, 69%)¹⁰. **³¹P NMR** (202 MHz, CDCl₃): δ 46.26 (80% purity without further purification).
L4: N-methylbenzamide (0.25 g, 1.85 mmol) was dissolved in THF (20 mL) at -10 °C under nitrogen. A solution of 1.2 mL n-BuLi (1.6 M, 1.92 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. (2',6'-dimethoxybiphenyl-2-yl)-phenylphosphine chloride (1.06 g, 1.85 mmol, 80% purity) in THF (20 mL) was added and the clear solution was stirred for 12 h at ambient temperature. The mixture was evaporated to dryness and subsequently suspended in CHCl₃ (40 mL). After that, the suspension was filtered through Celite. The ligand was isolated by recrystallization (THF/hexane) as a white solid L4 (0.8 g, 95%). 

1H NMR (500 MHz, CDCl₃): δ 7.49-7.44 (m, 1H), 7.41-7.34 (m, 3H), 7.32-7.17 (m, 8H), 7.16-7.09 (m, 2H), 7.01-6.97 (m, 2H), 6.64 (d, J = 9.96 Hz, 1H), 6.33 (d, J = 10.53 Hz, 1H), 3.67 (s, 3H, OMe), 3.46 (s, 3H, OMe), 2.87 (s, 3H, N-Me). 

13C NMR (125 MHz, CDCl₃): δ 177.03 (d, J = 34.35 Hz), 158.37 (s), 157.26 (s), 141.33 (d, J = 32.67 Hz), 136.63 (s), 136.55 (d, J = 15.61 Hz), 135.89 (d, J = 17.36 Hz), 132.51 (d, J = 2.88 Hz), 131.73 (d, J = 6.02 Hz), 131.04 (d, J = 20.43 Hz), 130.08 (s), 129.55 (d, J = 12.83 Hz), 128.60 (s), 128.49 (d, J = 6.81 Hz), 127.87 (d, J = 6.81 Hz), 127.40 (s), 117.92 (d, J = 6.14 Hz), 104.06 (d, J = 16.12 Hz), 55.82 (s, OMe), 32.71 (s, N-Me). 

31P NMR (202 MHz, CDCl₃): δ 51.96.

L5: 1.9 g 2-bromo-2’,6’-difluorobiphenyl (7.06 mmol) was dissolved in 20 mL THF, 4.2 mL n-BuLi (2.4 M in hexane, 8.47 mmol) was added dropwise at -78 °C under nitrogen. After stirring for 2 h at -78 °C, the reaction suspension was slowly transferred into the solution of PPhCl₂ (1.26 g, 7.06 mmol) in 15 mL THF, and the reaction mixture (A) was further stirred for 12 h at -30 °C. N-methylbenzamide (0.87 g, 6.5 mmol) was dissolved in THF (20 mL) at -10 °C. A solution of 4.9 mL n-BuLi (1.6 M, 7.8 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. After that, the
reaction mixture A was transferred to the resulting suspension and stirred at room temperature overnight. The solution was filtered over celite and the solvent was removed under vacuum. The ligand was isolated by recrystallization (THF/hexane) as a white solid L5 (0.5 g, 17% yield, 74% purity without further purification). $^{31}$P NMR (202 MHz, CDCl$_3$): δ 50.53.

L6: N-methylbenzamide (1.01 g, 7.4 mmol) was dissolved in THF (20 mL) at -10 °C under nitrogen. A solution of 4.7 mL n-BuLi (1.6 M, 7.52 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. Di-tert-butylchlorophosphane (1.37 g, 7.58 mmol) in THF (20 mL) was added and the clear solution was refluxed for 12 h. The mixture was evaporated to dryness and subsequently suspended in CHCl$_3$ (40 mL). After that, the suspension was filtered through Celite. The solvent was removed under vacuum and crystallized (THF/ether) to remove white solid. The product was isolated by removed the solvent as a yellow viscous liquid L6. (1.6 g, 78% yield, 83% content without further purification). $^{31}$P NMR (202 MHz, CDCl$_3$): δ 95.59.

Pd1: A mixture of L1 (168.4 mg, 0.46 mmol) and (COD)PdMeCl (122.4 mg, 0.46 mmol) in 15 mL of CH$_2$Cl$_2$ was stirred at room temperature for 12 h. The resulting mixture was evaporated and the residue was washed by Et$_2$O. The solid was collected by filtration to give Pd1 as a white solid (200 mg, 83.4%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.08-7.84 (m, 2H), 7.69-7.53 (m, 3H), 7.52-7.34 (m, 4H), 7.02-6.97 (m, 2H), 6.95-6.87 (m, 2H), 4.30 (d, J = 19.08 Hz, 2H, -CH$_2$-), 3.73 (s, 6H, OMe), 0.80 (s, 3H, Pd-CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): it cannot be characterized due to a very poor solubility. $^{31}$P NMR (202 MHz, CDCl$_3$): δ 24.64.

**Elemental analysis:** Anal. Calcd for C$_{23}$H$_{24}$ClO$_3$Pd:C, 52.99; H, 4.64. Found: C, 53.06; H, 4.68.
**Pd2**: Similar procedure was employed with mixing **L2** (379.4 mg, 1.0 mmol) and (COD)PdMeCl (265 mg, 1.0 mmol). **Pd2** was obtained as a gray solid (450 mg, 83.9%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.66-7.55 (m, 4H), 7.51-7.46 (m, 3H), 7.45-7.40 (m, 2H), 3.81 (s, 6H, OMe), 2.93 (d, $J = 7.51$, 3H, NMe), 0.81 (d, $J = 2.86$ Hz, 3H, Pd-Me). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 180.56 (d, $J = 11.13$ Hz), 160.83 (d, $J = 4.40$ Hz), 135.24 (d, $J = 12.04$ Hz), 134.48 (d, $J = 2.56$ Hz), 133.22 (d, $J = 4.14$ Hz), 131.42 (s), 128.70 (s), 127.57 (s), 121.45 (d, $J = 11.30$ Hz), 115.24 (d, $J = 51.99$ Hz), 111.79 (d, $J = 9.61$ Hz), 55.99 (s, OMe), 37.31 (d, $J = 5.03$ Hz, NMe), -5.18 (s, Pd-Me). $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 88.80.

Elemental analysis: Anal. Calcd for C$_{23}$H$_{25}$ClNO$_3$PPd: C, 51.51; H, 4.70; N, 2.61. Found: C, 51.70; H, 4.64; N, 2.65.

**Pd3**: Similar procedure was employed with mixing **L3** (227.7 mg, 0.5 mmol) and (COD)PdMeCl (132.5 mg, 0.5 mmol). **Pd3** was obtained as a white solid (250 mg, 81.7%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.04-7.94 (m, 2H), 7.83-7.70 (m, 4H), 7.69-7.56 (m, 2H), 7.53-7.47 (m, 1H), 7.47-7.41 (m, 4H), 2.74 (d, $J = 7.31$ Hz, NMe), 1.06 (d, $J = 3.15$ Hz, Pd-Me). $^{13}$C NMR (125 MHz, CDCl$_3$): it cannot be characterized due to a very poor solubility. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 88.30.

Elemental analysis: Anal. Calcd for C$_{23}$H$_{19}$ClF$_6$NOPPd: C, 45.12; H, 3.31; N, 2.29. Found: C, 45.30; H, 3.29; N, 2.20.
Pd4: Similar procedure was employed with mixing L4 (136.6 mg, 0.3 mmol) and (COD)PdMeCl (79.5 mg, 0.3 mmol). Pd4 was obtained as a white solid (150 mg, 81.7%). $^1$H NMR (500 MHz, CDCl3): δ 8.00-7.93 (m, 2H), 7.65-7.59 (m, 2H), 7.58-7.53 (m, 2H), 7.44-7.38 (m, 4H), 7.38-7.34 (m, 1H), 7.32-7.28 (t, 2H), 7.15-7.11 (m, 2H), 6.81 (d, $J = 8.89$ Hz, 1H), 6.54 (d, $J = 10.41$ Hz, 1H), 4.00 (s, 3H, OMe), 3.53 (s, 3H, OMe), 2.77 (d, $J = 4.79$ Hz, 3H, NMe), 0.75 (d, $J = 3.20$ Hz, 3H, Pd-Me).

$^{13}$C NMR (125 MHz, CDCl3): δ 179.29 (d, $J = 11.54$ Hz), 157.67 (d, $J = 71.45$ Hz), 140.77 (d, $J = 19.24$ Hz), 134.70 (d, $J = 16.46$ Hz), 134.35 (d, $J = 8.60$ Hz), 133.64 (d, $J = 10.85$ Hz), 132.28 (d, $J = 53.36$ Hz), 129.18 (d, $J = 51.92$ Hz), 128.37 (s), 128.06 (s), 127.03 (d, $J = 11.40$ Hz), 126.05 (d, $J = 51.28$ Hz), 116.63 (d, $J = 4.76$ Hz), 105.09 (s), 103.77 (s), 56.75 (s), 55.99 (s), 36.28 (d, $J = 4.18$ Hz, NMe), -4.52 (s, Pd-Me).

$^{31}$P NMR (202 MHz, CDCl3): δ 93.24.

Elemental analysis: Anal. Calcd for C$_{29}$H$_{29}$ClNO$_3$PPd: C, 56.88; H, 4.77; N, 2.29.

Found: C, 56.71; H, 4.68; N, 2.21.

Pd5: Similar procedure was employed with mixing L5 (129.3 mg, 0.25 mmol actually) and (COD)PdMeCl (66.3 mg, 0.25 mmol). Pd5 was obtained as a white solid (80 mg, 54.4%). $^1$H NMR (500 MHz, CDCl3): δ 7.80-7.73 (m, 1H), 7.62-7.54 (m, 6H), 7.52-7.43 (m, 7H), 7.26-7.20 (m, 2H), 7.01 (t, 1H), 2.96 (d, $J = 5.35$ Hz, 3H, NMe), 0.59 (s, 3H, Pd-Me).

$^{13}$C NMR (125 MHz, CDCl3): δ 180.44 (d, $J = 12.23$ Hz), 160.83 (dd, $J = 9.31$ Hz, $J = 7.93$ Hz), 158.87 (dd, $J = 8.96$ Hz, $J = 10.00$ Hz), 137.28 (d, $J = 20.36$ Hz), 134.70 (d, $J = 5.30$ Hz), 133.77 (d, $J = 9.91$ Hz), 133.27 (d, $J = 4.34$ Hz), 132.95 (d, $J = 4.65$ Hz), 131.77, 131.50 (d, $J = 3.72$ Hz), 131.42 (s), 130.61 (d, $J = 12.70$ Hz), 129.45 (d, $J = 10.84$ Hz), 128.59 (s), 128.52 (d, $J = 6.20$ Hz), 128.15 (s), 127.72 (s), 127.53 (d, $J = 3.41$ Hz), 126.39 (d, $J = 45.85$ Hz), 113.17 (dd, $J = 3.80$ Hz, $J = 4.70$ Hz), 111.32 (dd, $J = 3.36$ Hz, $J = 4.47$ Hz), 35.77 (NMe), -5.20 (d, $J = 3.39$ Hz, Pd-Me).

$^{31}$P NMR (202 MHz, CDCl3): δ 83.23.

$^{19}$F NMR (470 MHz, CDCl3): δ -108.46, -113.76.

Elemental analysis: Anal. Calcd for C$_{27}$H$_{29}$ClF$_2$NOPPd: C, 55.12; H, 3.94; N, 2.38.

Found: C, 55.00; H, 3.89; N, 2.31.
**Pd6**: Similar procedure was employed with mixing L6 (100 mg, 0.28 mmol actually) and (COD)PdMeCl (74 mg, 0.28 mmol). **Pd6** was obtained as a white solid (100 mg, 81.8%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.49-7.40 (m, 3H), 7.35-7.29 (m, 2H), 3.19 (d, $J = 3.33$ Hz, 3H, $NMe$), 1.56 (d, $J = 15.07$ Hz, 18H, -(CH$_2$)$_3$), 1.03 (d, $J = 1.20$ Hz, 3H, Pd-Me). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 182.77 (d, $J = 7.04$ Hz), 133.23 (d, $J = 4.14$ Hz), 131.25 (s), 128.97 (s), 126.74 (s), 40.94 (d, $J = 8.60$ Hz), 40.47 (d, $J = 4.02$ Hz), 30.12 (d, $J = 6.52$ Hz, $NMe$), -7.49 (s, Pd-Me). $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 138.2.

Elemental analysis: Anal. Calcd for C$_{17}$H$_{29}$ClNOPPd: C, 46.80; H, 6.70; N, 3.21. Found: C, 46.74; H, 6.64; N, 3.19.

**Ni1**: A mixture of L1 (182.2 mg, 0.5 mmol), [Ni(allyl)Cl]$_2$ (67.5 mg, 0.25 mmol), and NaBAF (443 mg, 0.5 mmol) in 15 mL CH$_2$Cl$_2$ was stirred at room temperature for 12 h. The resulting mixture was filtrated and evaporated. The resulting solid was recrystallized from CH$_2$Cl$_2$ and hexane solution to give **Ni1** as a bright yellow solid (450 mg, 67.8%)$^{12}$. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.13-8.04 (m, 2H), 7.84-7.78 (m, 1H), 7.76-7.69 (m, 9H), 7.65-7.52 (m, 8H), 7.26-7.16 (m, 2H), 7.11-7.03 (m, 4H), 5.83 (br, 1H, allyl-CH$_2$), 4.24 (d, $J = 12.94$Hz, 2H, -CH$_2$), 4.13-3.89 (m, 1.69H, allyl-CH$_2$), 3.83 (s, 6H, OMe), 3.03-2.53 (m, 1.69H, allyl-CH$_2$). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta$ 213.76 (d, $J = 11.44$ Hz), 162.17 (dd, $J = 49.40$ Hz, $J = 50.95$ Hz), 160.77 (s), 137.95 (s), 135.21 (s), 133.41 (d, $J = 4.06$ Hz), 131.29 (s), 130.09 (s), 129.66 (br), 129.41 (br), 129.16 (br), 128.91 (br), 128.25 (s), 126.09 (s), 123.92 (s), 122.19 (d, $J = 11.96$Hz), 121.76 (s), 117.88 (br), 116.99 (s), 112.05 (d, $J = 4.17$), 56.36 (s, OMe), 44.03 (d, $J = 27.28$, -CH$_2$). $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 15.49.

Elemental analysis: Anal. Calcd for C$_{57}$H$_{38}$BF$_{24}$NiO$_3$P: C, 51.58; H, 2.89. Found: C, 51.44; H, 2.88.
Ni2: Similar procedure was employed with mixing L2 (124.6 mg, 0.328 mmol), [Ni(allyl)Cl]2 (44 mg, 0.164 mmol) and NaBAF (291 mg, 0.328 mmol). Ni2 was obtained as a bright yellow solid (300 mg, 68.2%). 1H NMR (500 MHz, CDCl3): δ 7.78-7.64 (m, 8H), 7.64-7.56 (m, 3H), 7.54-7.41 (m, 7H), 7.22-7.01 (m, 6H), 5.55 (br, 1H, allyl-CH-), 4.87-4.39 (m, 0.64H, allyl -CH2-), 3.57-3.08 (m, 1.52H, allyl -CH2-), 3.87 (s, 6H, OMe), 2.90 (d, J = 3.35, 3H, NMe), 2.41-2.72 (m, 0.71H, allyl -CH2-). 13C NMR (125 MHz, CDCl3): δ 185.81 (d, J = 17.51), 161.84 (dd, J = 52.98, J = 52.98), 135.79 (s), 134.94 (s), 133.38 (s), 132.07 (s), 129.43 (s), 129.04 (d, J = 26.29), 127.59 (s), 125.77 (s), 123.60 (s), 122.54 (d, J = 12.45), 121.43 (s), 117.60 (d, J = 6.21), 116.70 (s), 112.22 (d, J = 8.37), 56.13 (s, OMe), 36.11 (d, J = 2.87, NMe). 31P NMR (202 MHz, CDCl3): δ 86.37.

Ni3: Similar procedure was employed with mixing L3 (149.5 mg, 0.328 mmol), [Ni(allyl)Cl]2 (44 mg, 0.164 mmol) and NaBAF (291 mg, 0.328 mmol) Ni3 was obtained as a bright yellow solid (390 mg, 83.8%). 1H NMR (125 MHz, CDCl3): δ 8.10-7.89 (m, 2H), 7.85-7.71 (m, 3H), 7.70-7.66 (m, 8H), 7.65-7.59 (m, 2H), 7.53-7.46 (m, 6H), 7.41-7.31 (m, 3H), 5.83 (br, 0.78H, allyl-CH-), 4.97-4.80 (m, 0.78H, allyl -CH2-), 3.82-3.60 (m, 0.34H, allyl -CH2-), 3.55-3.44 (m, 0.48H, allyl -CH2-), 3.39-3.27 (m, 0.31H, allyl -CH2-), 2.80 (d, J = 4.81, 3H, NMe), 2.51-2.31 (m, 0.28H, allyl -CH2-), 2.15-2.01 (m, 0.44H, allyl -CH2-). 13C NMR (125 MHz, CDCl3): δ 186.74 (d, J = 19.40), 161.82 (dd, J = 51.68, J = 45.70), 134.92 (s), 134.63 (s), 133.94 (d, J = 28.06), 132.90 (d, J = 9.62), 130.41 (d, J = 5.00), 129.55 (s), 129.16 (br), 128.92 (br), 127.91 (s), 127.41 (s), 125.74 (s), 123.57 (s), 121.41 (s), 117.62 (br), 36.37 (s, NMe). 31P NMR (202 MHz, CDCl3): δ 90.34, 89.11.
Elemental analysis: Anal. Calcd for C54H28BF30NNiOP: C, 47.09; H, 2.05; N, 1.02. Found: C, 47.20; H, 2.09; N, 1.05.
Ni4: Similar procedure was employed with mixing L4 (99.6 mg, 0.219 mmol), [Ni(allyl)Cl]2 (29.3 mg, 0.11 mmol) and NaBAF (193.7 mg, 0.219 mmol). Ni4 was obtained as a bright yellow solid (210 mg, 67.7%). ¹H NMR (500 MHz, CDCl₃): δ 7.78-7.66 (m, 9H), 7.65-7.42 (m, 16H), 7.42-7.29 (m, 2H), 6.72 (m, 2H), 5.35 (br, 0.4H, allyl-CH⁻), 4.57-4.39 (m, 0.78H, allyl -CH₂⁻), 4.25 (br, 0.35H, allyl-CH⁻), 3.75 (s, 3H, OMe), 3.36 (s, 3H, OMe), 3.16 (s, 3H, NMe), 2.86-2.76 (m, 0.38H, allyl -CH₂⁻), 2.53-2.31 (m, 0.83H, allyl -CH₂⁻), 1.45-1.35 (m, 0.46H, allyl -CH₂⁻). ¹³C NMR (125 MHz, CDCl₃): δ 161.84 (dd, J = 49.60, J = 44.70), 134.94 (s), 134.92 (s), 134.04 (s), 133.79 (d, J = 3.80), 131.34 (s), 130.47 (d, J = 9.70), 130.20 (d, J = 16.02), 129.64 (d, J = 2.89), 129.28 (s), 129.15 (br), 128.90 (s), 128.22 (br), 127.94 (s), 126.25 (s), 125.85 (s), 125.77 (s), 123.61 (s), 121.44 (s), 117.60 (br), 105.15 (s), 56.25 (s, OMe), 35.58 (s, NMe). ³¹P NMR (202 MHz, CDCl₃): δ 91.82, 90.66.

Elemental analysis: Anal. Calcd for C₆₃H₄₃BF₂₄NNiO₃P: C, 53.34; H, 3.06; N, 0.99. Found: C, 53.20; H, 3.01; N, 0.94.

Ni5: Similar procedure was employed with mixing L5 (160 mg, 0.28 mmol, actually), [Ni(allyl)Cl]₂ (26.5 mg, 0.14 mmol) and NaBAF (175.4 mg, 0.28 mmol). Ni5 was obtained as a bright yellow solid (150 mg, 38.3%). ¹H NMR (500 MHz, CDCl₃): δ 7.84-7.76 (m, 1H), 7.72-7.67 (m, 11H), 7.66-7.57 (m, 6H), 7.55-7.46 (m, 11H), 5.38 (br, 0.39H, allyl-CH⁻), 4.81-4.71 (m, 0.35H, allyl -CH₂⁻), 4.60-4.53 (m, 0.31H, allyl -CH₂⁻), 4.35 (br, 0.41H, allyl-CH⁻), 3.37-3.29 (m, 0.43H, allyl -CH₂⁻), 3.12 (s, 3H, NMe), 3.07-3.00 (m, 1H, allyl -CH₂⁻), 2.72-2.65 (m, 0.39H, allyl -CH₂⁻), 2.49-2.41 (m, 0.34H, allyl -CH₂⁻), 1.60-1.52 (m, 0.38H, allyl -CH₂⁻), 1.48-1.40 (m, 0.46H, allyl -CH₂⁻). ¹³C NMR (125 MHz, CDCl₃): δ 161.84 (dd, J = 49.60, J = 50.16), 136.40 (s), 136.24 (s), 134.96 (s), 133.79 (3), 133.11 (s), 131.98 (q), 130.73 (br), 130.14 (d, J = 11.24), 129.56 (s), 129.43 (m), 129.15 (br), 128.90 (br), 128.64 (br), 127.94 (s), 127.74 (s), 127.57 (s), 127.39 (s), 126.25 (s), 125.85 (s), 125.77 (s), 123.61 (s), 121.44 (s), 117.60 (br), 105.15 (s), 56.25 (s, OMe), 35.58 (s, NMe).
126.76 (s), 125.84 (s), 125.22 (s), 124.85 (s), 123.61 (s), 121.44 (s), 117.59 (br), 35.58 (s, NMe). $^{31}$P NMR (202 MHz, CDCl$_3$): δ 90.98, 89.83.

Elemental analysis: Anal. Calcd for C$_{61}$H$_{37}$BF$_{26}$NNiOP: C, 52.54; H, 2.67; N, 1.00. Found: C, 52.40; H, 2.60; N, 0.97.

Ni6: Similar procedure was employed with mixing L6 (100 mg, 0.28 mmol, actually), [Ni(allyl)Cl]$_2$ (26.5 mg, 0.14 mmol) and NaBAF (175.4 mg, 0.28 mmol). Ni6 was obtained as a bright yellow solid (180 mg, 51.8%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.73-7.67 (m, 89H), 7.62-7.58 (m, 1H), 7.53-7.46 (m, 6H), 7.35-7.29 (m, 2H), 5.63 (br, 1H, allyl-CH$_{-}$), 4.78-4.72 (m, 1H, allyl -CH$_{2-}$), 3.59 (dd, J = 6.84, J = 6.40, 1H, allyl -CH$_{2-}$), 3.31 (m, 1H, allyl -CH$_{2-}$), 3.29 (d, J = 2.45, 1H, NMe), 2.02 (d, J = 12.92, 1H, allyl -CH$_{2-}$), 1.55 (d, J = 17.84, 9H), 1.36 (d, J = 16.29, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 188.11 (d, J = 11.19), 161.85 (dd, J = 48.99, J = 48.99), 134.93 (s), 133.32 (s), 130.12 (s), 129.61 (s), 129.44 (br), 129.18 (br), 128.93 (br), 128.68 (br), 127.94 (s), 126.81 (s), 125.77 (s), 123.61 (s), 121.44 (s), 117.63 (br), 117.22 (s), 79.33 (d, J = 19.48), 46.48 (d, J = 2.22 ), 39.70 (d, J = 3.68), 39.36 (dd, J = 7.26, J = 6.99), 29.39 (dd, J = 5.96, J = 6.77). $^{31}$P NMR (202 MHz, CDCl$_3$): δ 146.16.

Elemental analysis: Anal. Calcd for C$_{51}$H$_{43}$BF$_{24}$NNiOP: C, 49.31; H, 3.49; N, 1.13. Found: C, 49.17; H, 3.43; N, 1.10.
General produces for the polymerization

Homopolymerization of ethylene: In a typical experiment, a 150 mL glass pressure reactor connected with a high pressure gas line was added 48 mL of toluene, then adjusted to the desired polymerization temperature. The desired amount of catalyst in 2 mL of CH₂Cl₂ was injected into the polymerization system via syringe under N₂. With a rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After the desired amount of time, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.

Copolymerization of ethylene and polar monomers: a 150 mL glass pressure reactor connected with a high pressure gas line was added 17 mL of toluene, then adjusted to the desired polymerization temperature. The desired amount of polar monomers and catalyst in 2 mL of CH₂Cl₂ was injected into the polymerization system respectively via syringe under N₂. With a rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After the desired amount of time, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.
NMR figures of ligands and catalysts

Figure S1. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Chlorobis(2,6-dimethoxyphenyl)phosphine

Figure S2. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of L1
**Figure S3.** $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of L1

**Figure S4.** $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of L1
Figure S5. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of L2

Figure S6. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of L2
Figure S7. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of L2

Figure S8. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Chlorobis(2-(trifluoromethyl)phenyl)phosphine
Figure S9. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of L3

Figure S10. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of L3
Figure S11. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of L3

Figure S12. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of (2’, 6’-dimethoxybiphenyl-2-yl)phenylphosphine chloride
Figure S13. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of L4

Figure S14. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of L4
Figure S15. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of L4

Figure S16. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of L5
Figure S17. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of L6

Figure S18. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Pd1
Figure S19. $^{31}$P NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Pd1

Figure S20. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Pd2
**Figure S21.** $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Pd2

**Figure S22.** $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Pd2
Figure S23. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Pd3

Figure S24. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Pd3
Figure S25. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Pd4

Figure S26. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Pd4
Figure S27. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Pd4

Figure S28. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Pd5
Figure S29. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Pd5

Figure S30. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Pd5
Figure S31. $^{19}$F NMR spectrum (470 MHz, 298 K, CDCl$_3$) of Pd5

Figure S32. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Pd6
**Figure S33.** $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Pd6

**Figure S34.** $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Pd6
Figure S35. $^1$H NMR spectrum (500 MHz, 298 K, (CD$_3$)$_2$SO) of NaBAr$_4$F$_4$

Figure S36. $^{13}$C NMR spectrum (125 MHz, 298 K, (CD$_3$)$_2$SO) of NaBAr$_4$F$_4$
Figure S37. $^1$H NMR spectrum (500 MHz, 298 K, CD$_2$Cl$_2$) of Ni1

Figure S38. $^{13}$C NMR spectrum (125 MHz, 298 K, CD$_2$Cl$_2$) of Ni1
Figure S39. $^{31}$P NMR spectrum (202 MHz, 298 K, CD$_2$Cl$_2$) of Ni1

Figure S40. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Ni2
Figure S41. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Ni2

Figure S42. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ni2
Figure S43. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Ni3

Figure S44. $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Ni3
Figure S45. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl₃) of Ni₃

Figure S46. $^{31}$P NMR spectra (202 MHz, C₂D₂Cl₄) of Ni₃ at 298K, 319K, 350K
Figure S47. COSY spectrum (400 MHz, CDCl$_3$) of Ni3

Figure S48. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Ni4
**Figure S49.** $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Ni4

**Figure S50.** $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ni4
Figure S51. $^1$H NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ni5

Figure S52. $^{31}$C NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ni5
Figure S53. $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ni5

Figure S54. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Ni6
**Figure S55.** $^{13}$C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of Ni6

**Figure S56.** $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ni6
**Figure S57.** $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of Ligands and catalysts

**Figure S58.** $^{31}$P NMR spectrum (202 MHz, 298 K, CDCl$_3$) of Ligands and catalysts
NMR Spectra of polymers

Figure S59. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of ethylene oligomer (Pd 1, 80 °C) from table 1, entry 1.

Figure S60. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of ethylene oligomer (Pd 1, 30 °C) from table 1, entry 2.
**Figure S61.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of ethylene oligomer (Ni 1, 80 °C) from table 1, entry 13

**Figure S62.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of ethylene oligomer (Ni 1, 30 °C) from table 1, entry 14
Figure S63. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of ethylene oligomer (Ni 3, 80 °C) from table 1, entry 17.

Figure S64. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of ethylene oligomer (Ni 3, 30 °C) from table 1, entry 18.
Figure S65. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of PMA

Figure S66. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 3.
Figure S67. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 4.

Figure S68. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 5.
**Figure S69.** $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 8.

**Figure S70.** $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 10.
Figure S71. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 11.

Figure S72. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-methyl acrylate copolymer from table 2, entry 13.
**Figure S73-H.** $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 14.

**Figure S73-C.** $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 14.
Figure S74. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene- acrylic acid copolymer from table 2, entry 15.

Figure S75. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 16.
Figure S76. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 17.
GPC traces and DSC data of (co)polymers

Figure S77. GPC trace of the polymer from table 1, entry 3.

Figure S78. GPC trace of the polymer from table 1, entry 4.
Figure S79. GPC trace of the polymer from table 1, entry 5.

Figure S80. GPC trace of the polymer from table 1, entry 6.
Figure S81. GPC trace of the polymer from table 1, entry 7.

Figure S82. GPC trace of the polymer from table 1, entry 8.
Figure S83. GPC trace of the polymer from table 1, entry 9.

Figure S84. GPC trace of the polymer from table 1, entry 10.
Figure S85. GPC trace of the polymer from table 1, entry 11.

Figure S86. GPC trace of the polymer from table 1, entry 12.
Figure S87. GPC trace of the polymer from table 1, entry 15

Figure S88. GPC trace of the polymer from table 1, entry 16
Figure S89. GPC trace of the polymer from table 1, entry 19

Figure S90. GPC trace of the polymer from table 1, entry 20
Figure S91. GPC trace of the polymer from table 1, entry 22

Figure S92. GPC trace of the polymer from table 1, entry 23
Figure S93. GPC trace of the polymer from table 1, entry 24

Figure S94. GPC trace of the polymer from table 2, entry 3
Figure S95. GPC trace of the polymer from table 2, entry 4

Figure S96. GPC trace of the polymer from table 2, entry 5
**Figure S97.** GPC trace of the polymer from table 2, entry 8

**Figure S98.** GPC trace of the polymer from table 2, entry 10
Figure S99. GPC trace of the polymer from table 2, entry 11

Figure S100. GPC trace of the polymer from table 2, entry 13
Figure S101. GPC trace of the polymer from table 2, entry 14

Figure S102. GPC trace of the polymer from table 2, entry 15
Figure S103. GPC trace of the polymer from table 2, entry 16

Figure S104. GPC trace of the polymer from table 2, entry 17
Figure S105. DSC data of the polymer from table 1, entry 7

Figure S106. DSC data of the polymer from table 1, entry 8
**Figure S107.** DSC data of the polymer from table 1, entry 9

**Figure S108.** DSC data of the polymer from table 1, entry 10
Figure S109. DSC data of the polymer from table 1, entry 12

Figure S110. DSC data of the polymer from table 1, entry 22
Figure S111. DSC data of the polymer from table 1, entry 23

Figure S112. DSC data of the polymer from table 1, entry 24
Figure S113. DSC data of the polymer from table 2, entry 4

Figure S114. DSC data of the polymer from table 2, entry 8
Figure S115. DSC data of the polymer from table 2, entry 10

Figure S116. DSC data of the polymer from table 2, entry 14
Figure S117. DSC data of the polymer from table 2, entry 16

Figure S118. DSC data of the polymer from table 2, entry 17
X-ray Crystallography

**Figure S119.** Molecular structures of catalysts Pd2. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg) for Pd2: Pd1-P1 = 2.1850(8), Pd1-C23 = 2.033(4), Pd1-O1 = 2.189(2), Pd1-C11 = 2.3590(8), C23-Pd1-C11 = 91.49(12), O1-Pd1-P1 = 80.29(7).

**Figure S120.** Molecular structures of catalysts Ni6. Hydrogen atoms and the BArF4 groups were omitted for clarity. Selected bond lengths (Å) and angles (deg) for Ni6: Ni1-P1 = 2.1707(10), Ni1-C17 = 1.998(4), Ni1-C18 = 2.014(4), Ni1-C19 = 2.034(4), Ni1-O1 = 1.894(2), O1-Ni1-P1 = 86.13(7), C17-Ni1-C19 = 72.73(17).
**Table S1. Crystallographic data for Pd2 and Ni6**

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<th>Ni6</th>
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<td><strong>Formula</strong></td>
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<td>5317.25(19)</td>
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<td><strong>Data / restraints / parameters</strong></td>
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<tr>
<td><strong>GOF (on F²)</strong></td>
<td>0.996</td>
<td>1.003</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole (e Å⁻³)</strong></td>
<td>4.511 / −0.669</td>
<td>1.073 / −0.733</td>
</tr>
<tr>
<td><strong>CCDC No.</strong></td>
<td>1973964</td>
<td>1973963</td>
</tr>
</tbody>
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Reference


