

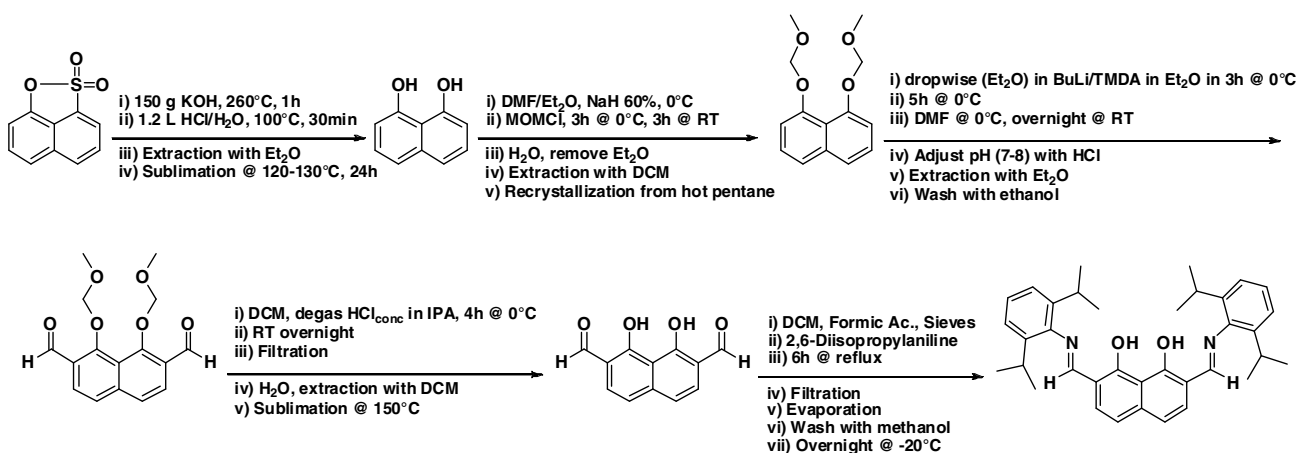
## Supporting Information

### Neutral Bimetallic Ni(II) Phenoxyiminato Catalysts for Highly Branched Polyethylenes and Ethylene-Norbornene Copolymerizations

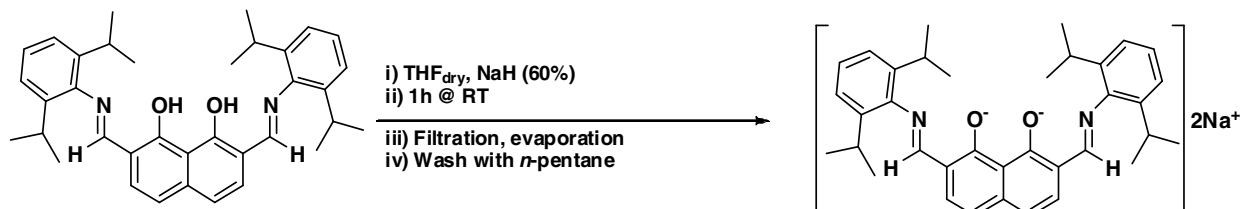
Brandon A. Rodriguez, Massimiliano Delferro, and Tobin J. Marks\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

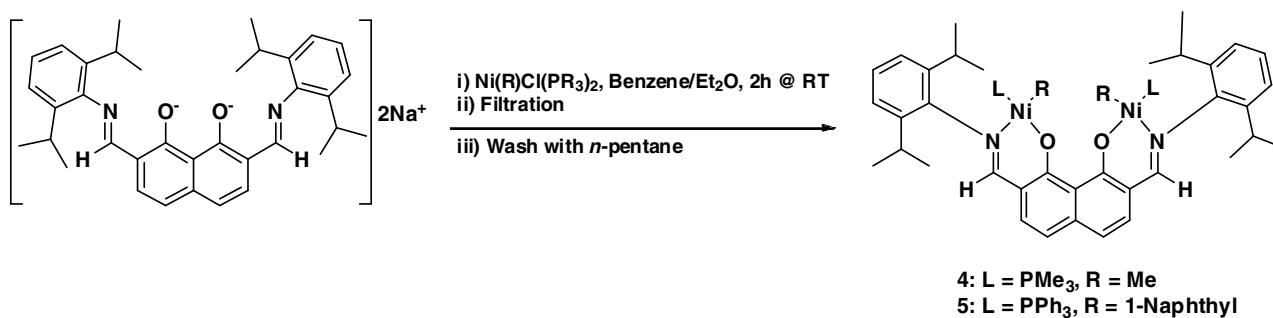
t-marks@northwestern.edu



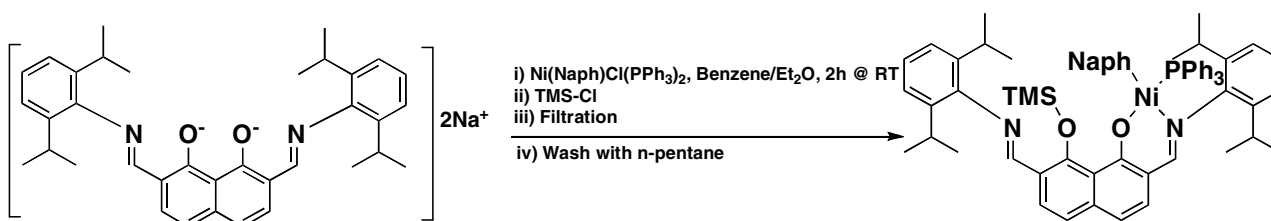
**Scheme S1.** Synthesis of ligand for bimetallic catalysts.



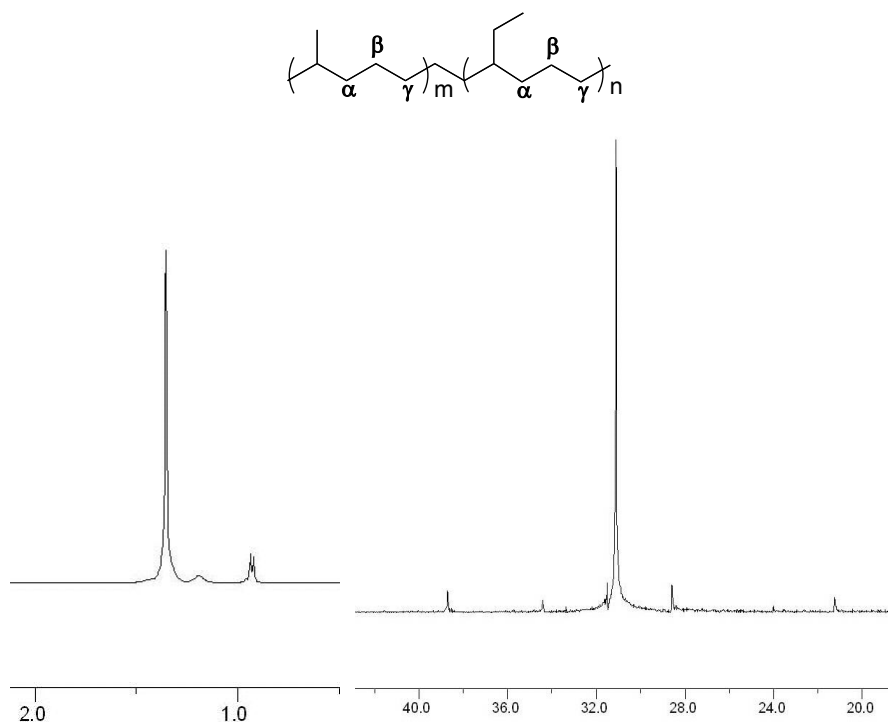
**Scheme S2.** Synthesis of ligand disodium salt.



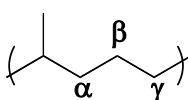
**Scheme S3.** Synthesis of binuclear complexes FI<sup>2</sup>-Ni<sub>2</sub>-A and FI<sup>2</sup>-Ni<sub>2</sub>-B.

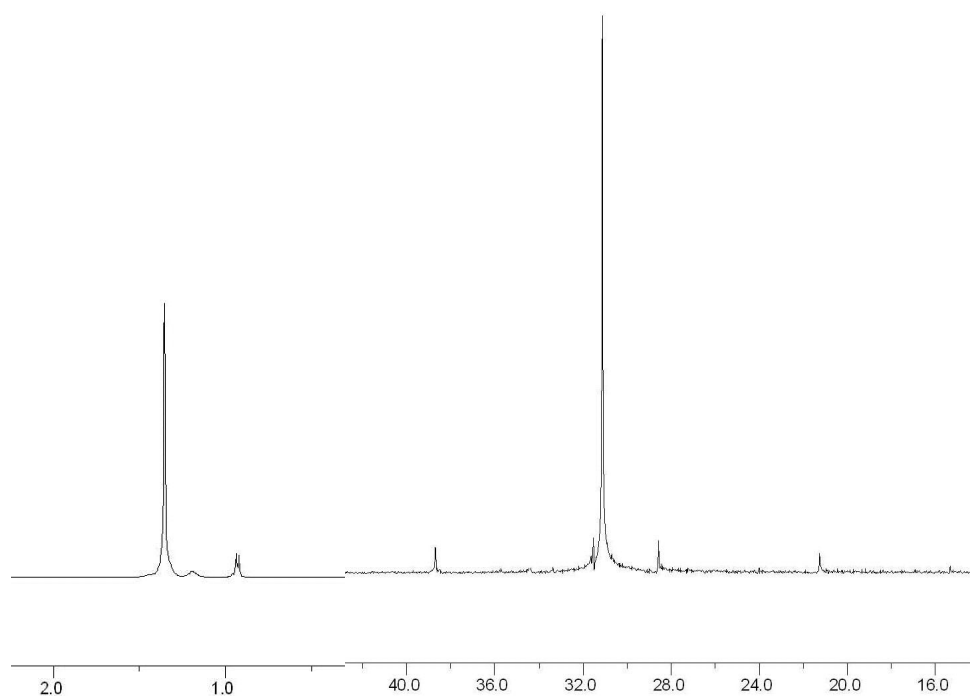


**Scheme S4.** Synthesis of monometallic complex with binuclear ligand,  $\text{FI}^2\text{TMS-Ni}$

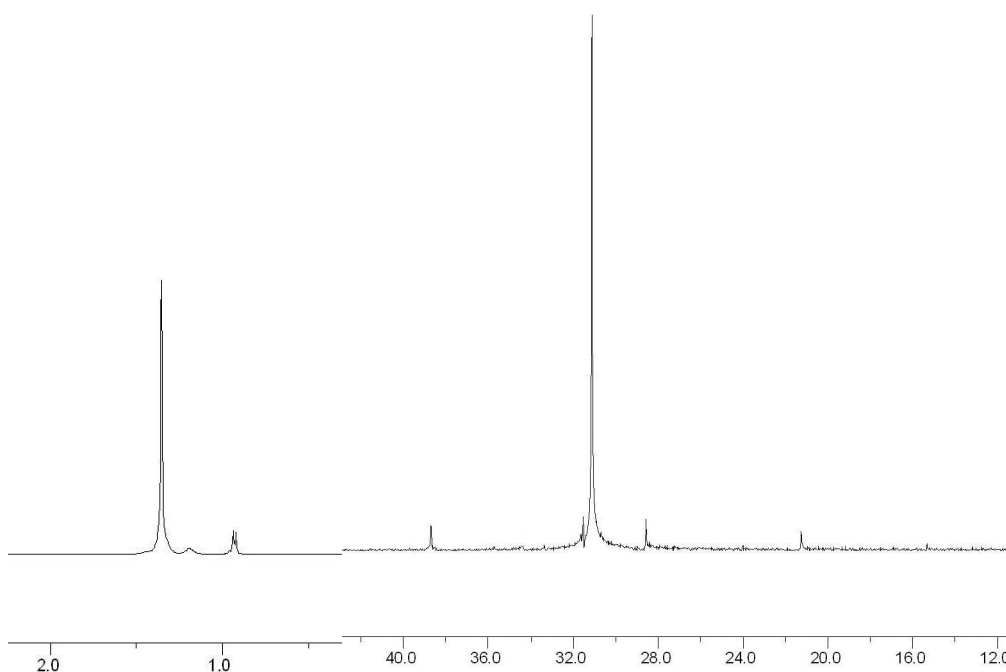
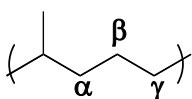


**Scheme S4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polyethylenes obtained from the monometallic catalysts at  $130^\circ\text{C}$  at 400 MHz in tetrachloroethane. In the  $^{13}\text{C}$  spectrum, there are five resonances observed other than the polyethylene homopolymer backbone: methyl branches, ethyl branches, and carbons  $\alpha$ ,  $\beta$ , and  $\gamma$  to the branch at  $\delta$  21.0, 34.2, 39.0, 28.2, and 31.5 ppm, respectively.

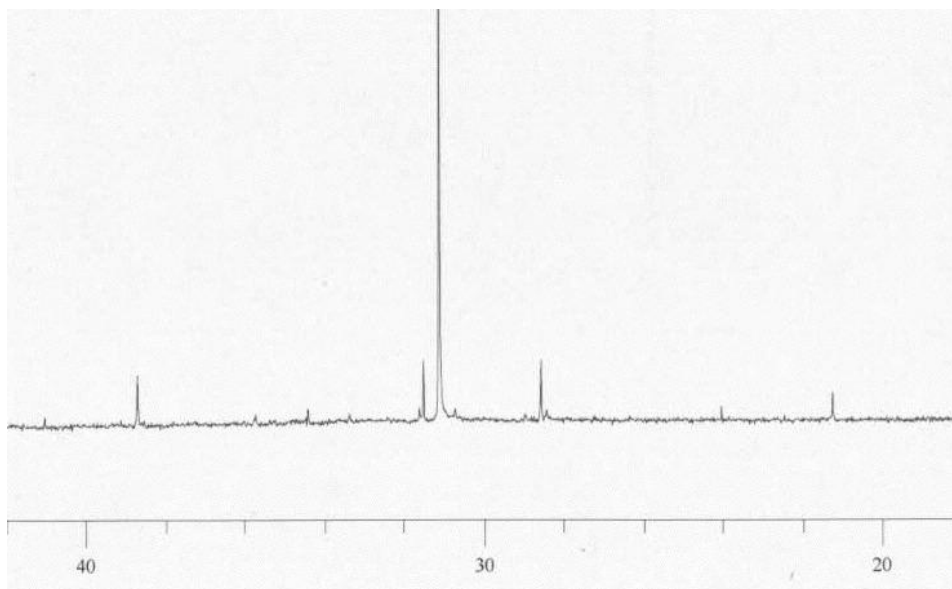




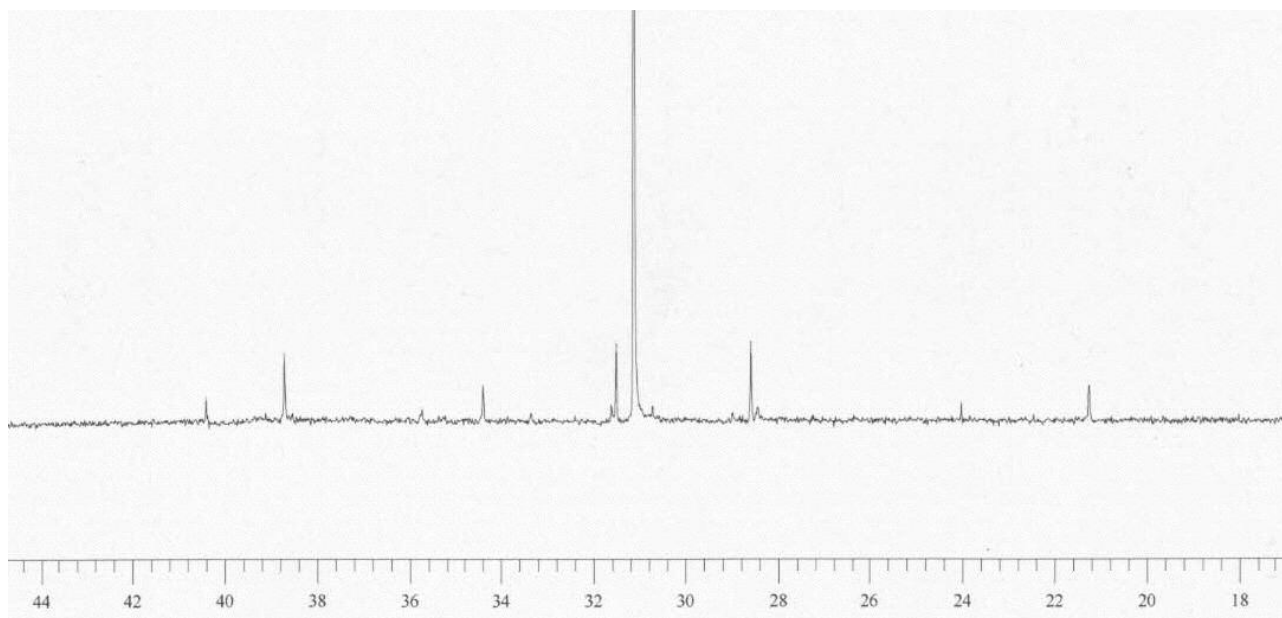
**Scheme S5.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polyethylenes obtained from the bimetallic catalysts at  $130^\circ\text{C}$  at 400 MHz in tetrachloroethane. In the  $^{13}\text{C}$  spectrum, there are four peaks observed other than the polyethylene homopolymer backbone: methyl branches, and the carbons  $\alpha$ ,  $\beta$ , and  $\gamma$  to the branch at  $\delta$  21.0, 39.0, 28.2, and 31.5 ppm, respectively. The absence of significant ethyl branch carbon signals indicates that methyls are the predominant branching mode.



**Scheme S6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polyethylenes obtained from the bimetallic catalysts without using a cocatalyst at  $130^\circ\text{C}$  at 400 MHz in tetrachloroethane. In the  $^{13}\text{C}$  spectra, there are four peaks observed other than the polyethylene homopolymer backbone: methyl branches, and the carbons  $\alpha$ ,  $\beta$ , and  $\gamma$  to the branch at  $\delta$  21.0, 39.0, 28.2, and 31.5 ppm, respectively. The absence of significant ethyl branch carbon signals indicates that methyls are the predominant branching mode.



**Scheme S7.**  $^{13}\text{C}$  NMR spectrum of poly(co-norbornene)ethylenes obtained from the monometallic catalysts at  $130^\circ\text{C}$  at 400 MHz in tetrachloroethane. Smaller signals at  $\delta$  41.0, 35.8, and 33.0 ppm correspond to co-enriched norbornene.



**Scheme S8.**  $^{13}\text{C}$  NMR spectrum of poly(co-norbornene)ethylenes obtained from the bimetallic catalysts at  $130^\circ\text{C}$  at 400 Mhz in tetrachloroethane. Note the significant increase of peaks at  $\delta$  41.0, 35.8, and 33.0 ppm relative polyethylene signals.

**Materials and Methods.** All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum line ( $10^{-5}$  Torr), or in a nitrogen-filled Vacuum Atmospheres glove box with a high capacity recirculator ( $<1$  ppm  $O_2$ ). Argon and ethylene (Matheson, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Ether solvents were purified by distillation from Na/K alloy/benzophenone ketyl. Hydrocarbon solvents (*n*-pentane and toluene) were dried using activated alumina columns according to the method described by Grubbs,<sup>S1</sup> and were additionally vacuum-transferred from Na/K alloy immediately before vacuum line manipulations. All solvents for high-vacuum line manipulations were stored *in vacuo* over Na/K alloy in Teflon-valve sealed bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all  $\geq 99$  atom %D), were freeze pump-thaw degassed, dried over Na/K alloy and were stored in resealable flasks. Other non-halogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from  $CaH_2$  and stored over activated Davison 4A molecular sieves. The reagents *trans*-[NiMeCl(PMe<sub>3</sub>)<sub>2</sub>],<sup>S2</sup> *trans*-[Ni(Naph)Cl(PPh<sub>3</sub>)<sub>2</sub>] (Naph = 1-naphthyl),<sup>S3</sup> 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene,<sup>S4</sup> salicylaldimine and salicylaldiminate sodium salt<sup>S5</sup> were prepared according to literature procedures. [Ni(cod)<sub>2</sub>] (cod = 1,5-cyclooctadiene) was purchased from Aldrich.

**Physical and Analytical Measurements.** NMR spectra were recorded on Varian <sup>UNITY</sup>Inova-500 (FT, 500 MHz, <sup>1</sup>H; 125 MHz, <sup>13</sup>C), <sup>UNITY</sup>Inova-400 (FT, 400 MHz, <sup>1</sup>H; 100 MHz, <sup>13</sup>C) and Mercury-400 (FT 400 MHz, <sup>1</sup>H; 100 MHz, <sup>13</sup>C; 162 MHz, <sup>31</sup>P). Chemical shifts ( $\delta$ ) for <sup>1</sup>H and <sup>13</sup>C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. Chemical shifts ( $\delta$ ) for <sup>31</sup>P spectra were reported relative to an external 85% H<sub>3</sub>PO<sub>4</sub> standard. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J.Young). Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. <sup>13</sup>C NMR assays of polymer microstructure were conducted in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 130°C. Signals were assigned according to the literature for polyethylene. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 10 °C/min. GPC measurements were performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10  $\mu$ m mixed columns was used. Samples were prepared at 160 °C. Molecular weights were determined by GPC using narrow polystyrene standards and are not corrected.

**Synthesis of 2,7-Di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalenediolate disodium salt (1).**

To a solution of 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene (1.0g, 1.87 mmol) in THF dry (30 mL) was added NaH (0.224, 9.35 mmol). The resulting mixture was stirred at rt for 1 h, filtered, and the filtrate evaporated. The yellow residue was washed with pentane (30 mL) and dried *in vacuo*. This salt was immediately used without further purification for the following synthesis. Yield, 83%.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C, 500 MHz):  $\delta$  = 8.13 (s, 2H,  $\text{HC}=\text{N}$ ), 7.53-6.75 (m, 10H, Ph) 3.07 (sept, 4H,  $^3J_{\text{HH}}$  = 6.8 Hz,  $\text{CHMe}_2$ ), 1.34 (s, 12H,  $\text{CHMe}_2$ ).

**Synthesis of {2,7-Di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalenediolato}bis[(methyl)-(trimethylphosphine)Ni(II)] (2).** A solution of **1** (0.900 g, 1.55 mmol) in  $\text{Et}_2\text{O}$  (25 mL) was added dropwise at rt to a stirring solution of *trans*-[NiMeCl(PMe<sub>3</sub>)<sub>2</sub>] (0.815 g, 3.12 mmol) in benzene (25 mL). A rapid color change from yellow to dark red was observed, and after 1 h the mixture became dark orange. After this time, the reaction mixture was filtered by cannula. The volatiles were then removed from the filtrate *in vacuo* and the residue was washed with pentane. A light orange powder of **2** was obtained. Yield, 73%.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C, 500 MHz):  $\delta$  7.65 (d,  $^4J_{\text{PH}}$  = 8.0 Hz, 2H,  $\text{HC}=\text{N}$ ), 7.13-6.43 (m, 10H, Ph), 4.13 (sept, 2H,  $^3J_{\text{HH}}$  = 6.5 Hz,  $\text{CHMe}_2$ ), 3.73 (sept, 2H,  $^3J_{\text{HH}}$  = 6.5 Hz,  $\text{CHMe}_2$ ), 1.56 (d,  $^3J_{\text{HH}}$  = 6.5 Hz, 6H,  $\text{CHMe}_2$ ), 1.31 (d,  $^3J_{\text{HH}}$  = 6.5 Hz, 6H,  $\text{CHMe}_2$ ), 1.15 (d,  $^3J_{\text{HH}}$  = 6.5 Hz, 6H,  $\text{CHMe}_2$ ), 1.08 (d,  $^3J_{\text{HH}}$  = 6.5 Hz, 6H,  $\text{CHMe}_2$ ), 1.06 (d,  $^2J_{\text{PH}}$  = 9.5 Hz, 18H, PMe<sub>3</sub>), -1.15 (d,  $^3J_{\text{PH}}$  = 7.3 Hz, 6H, NiMe).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C, 125 MHz):  $\delta$  170.33, 163.93, 150.17, 145.26, 141.96, 133.50, 125.96, 123.91, 123.02, 115.97, 113.51, 28.47, 24.45, 14.15, -12.23.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C, 162 MHz):  $\delta$  -7.58. Anal. Found: C, 63.12; H, 7.71; N, 3.29. Calcd. for  $\text{C}_{44}\text{H}_{64}\text{N}_2\text{Ni}_2\text{O}_2\text{P}_2$ : C, 63.49; H, 7.75; N, 3.37.

**Synthesis of {2,7-Di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalenediolato}bis[(1-naphthyl)-(triphenylphosphine)Ni(II)] (3).** A solution of **1** (0.800 g, 1.38 mmol) in  $\text{Et}_2\text{O}$  (25 mL) was added dropwise at rt to a stirring solution of *trans*-[Ni(Naph)Cl(PPh<sub>3</sub>)<sub>2</sub>] (2.06 g, 2.76 mmol) in benzene (25 mL). A rapid color change from yellow to dark pink was observed, and after 2 h the mixture became dark purple. After this time, the reaction mixture was filtered by cannula. The volatiles were next removed *in vacuo* from the filtrate and the residue was washed with pentane. A purple powder of **3** was obtained. Yield, 74%.

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , 25°C, 500 MHz):  $\delta$  11.07 (d,  $^3J_{\text{PH}}$  = 14.0 Hz, 2H, Naph-H), 10.16 (d,  $^4J_{\text{PH}}$  = 8.0 Hz, 2H, Naph-H), 8.90 (d,  $^4J_{\text{PH}}$  = 8.0 Hz, 2H, Naph-H), 7.88 (d,  $^4J_{\text{PH}}$  = 6.6 Hz, 2H,  $\text{HC}=\text{N}$ ), 7.53-6.24 (m, 48H, Ph), 3.09 (sept, 2H,  $^3J_{\text{HH}}$  = 6.9 Hz,  $\text{CHMe}_2$ ), 1.22 (d,  $^3J_{\text{HH}}$  = 6.9 Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$

NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 125 MHz):  $\delta$  177.47, 159.34, 152.28, 144.14, 140.62, 137.41, 134.14, 130.37, 129.91, 123.86, 122.50, 118.79, 113.20, 28.08, 22.96. <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 162 MHz):  $\delta$  33.2. Anal. Found: C, 77.16; H, 6.01; N, 2.11. Calcd. for C<sub>92</sub>H<sub>86</sub>N<sub>2</sub>Ni<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 77.33; H, 5.92; N, 1.96.

**Synthesis of {2,7-Di-[(2,6-diisopropylphenyl)imino]-1-naphthalenato}(1-naphthyl)-(triphenylphosphine)-Trimethylsilane Ni(II).** A solution of **1** (0.800 g, 1.38 mmol) in Et<sub>2</sub>O (25 mL) was added dropwise at rt to a stirring solution of *trans*-[Ni(Naph)Cl(PPh<sub>3</sub>)<sub>2</sub>] (1.03 g, 1.38 mmol) in benzene (25 mL). A rapid color change from yellow to dark pink was observed, and after 2 h the mixture became dark red. After this time, 1 equivalent of trimethylsilane-chloride was added to react with the second Na<sup>+</sup> site. The reaction mixture was then filtered by cannula. The volatiles were next removed from the filtrate *in vacuo* from the filtrate and the residue was washed with pentane. A red powder was obtained. Yield, 78%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, 500 MHz):  $\delta$  = 13.98 (s, 1H, OH), 8.13-8.22 (d, 2H, HC=N), 7.53-6.75 (m, 10H, Ph) 3.07 (m, 4H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 1.34 (s, 12H, CHMe<sub>2</sub>). <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 162 MHz):  $\delta$  31.0. Anal. Found: C, 78.16; H, 6.19; N, 2.77. Calcd. for C<sub>64</sub>H<sub>63</sub>N<sub>2</sub>NiO<sub>2</sub>P: C, 78.29; H, 6.47; N, 2.85.

**Synthesis of {[2-(*t*-Butyl)-6-(2,6-diisopropylphenyl)imino]phenolato}(methyl)-(trimethylphosphine)Ni(II) (4).** A solution of the salicylaldiminate sodium salt (0.400 g, 1.11 mmol) in Et<sub>2</sub>O (30 mL) was added dropwise at rt to a solution of *trans*-[NiMeCl(PMe<sub>3</sub>)<sub>2</sub>] (0.290 g, 1.11 mmol) in Et<sub>2</sub>O (25 mL). The orange mixture was stirred for 2 h at rt. After this time, the reaction mixture was filtered by cannula. The filtrate was then evaporated *in vacuo* and the solid residue was washed with pentane. A yellow-orange microcrystalline powder of **4** was obtained. Yield, 74%.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 500 MHz):  $\delta$  7.84 (d, <sup>4</sup>J<sub>PH</sub> = 8.8 Hz, 1H, HC=N), 7.42-6.56 (m, 6H, Ph), 3.96 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, CHMe<sub>2</sub>), 1.51 (s, 9H, CMe<sub>3</sub>), 1.32 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H, CHMe<sub>2</sub>), 0.97 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H, CHMe<sub>2</sub>), 0.95 (d, <sup>2</sup>J<sub>PH</sub> = 9.1 Hz, 9H, PMe<sub>3</sub>), -1.10 (d, <sup>3</sup>J<sub>PH</sub> = 7 Hz, 3H, NiMe). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 125 MHz):  $\delta$  166.25, 149.49, 141.45, 140.62, 133.690, 126.220, 123.45, 120.19, 35.23, 29.80, 28.32, 22.45, 14.15, -17.32. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 162 MHz):  $\delta$  -12.57. Anal. Found: C, 66.53; H, 8.63; N, 2.91. Calcd. for C<sub>27</sub>H<sub>42</sub>NNiOP: C, 66.69; H, 8.71; N, 2.88.

**Synthesis of {[2-(*t*-Butyl)-6-(2,6-diisopropylphenyl)imino]phenolato}(1-naphthyl)-(triphenylphosphine)Ni(II) (5).** A solution of the salicylaldiminate sodium salt (0.500 g, 1.39 mmol) in benzene (30 mL) was added dropwise at rt to a stirring solution of *trans*-

[Ni(Naph)Cl(PPh<sub>3</sub>)<sub>2</sub>] (1.037 g, 1.39 mmol) in benzene (25 mL). The orange mixture was stirred for 2 h at rt. After this time, the reaction mixture was filtered by cannula filtration. The filtrate was then evaporated *in vacuo* and the solid residue was washed with ethanol. A yellow-orange microcrystalline powder of **5** was obtained. Yield, 75%.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 500 MHz): δ 10.47 (d, <sup>4</sup>J<sub>PH</sub> = 8.8 Hz, 1H, NiC-CH<sub>naph</sub>), 7.96 (d, <sup>4</sup>J<sub>PH</sub> = 8.8 Hz, 1H, HC=N), 7.69-6.55 (m, 24H, Ph), 5.56 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, CHMe<sub>2</sub>), 2.98 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, CHMe<sub>2</sub>), 1.68 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 3H, CHMe<sub>2</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 3H, CHMe<sub>2</sub>), 0.90 (s, 9H, CMe<sub>3</sub>), 0.85 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 3H, CHMe<sub>2</sub>), -0.07 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 3H, CHMe<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 125 MHz): δ 167.11, 165.13, 150.59, 141.56, 140.51, 136.42, 134.82, 133.42, 132.16, 131.73, 129.55, 127.51, 125.79, 123.71, 122.18, 121.56, 120.70, 114.20, 34.67, 30.02, 28.45, 24.45, 21.43. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 162 MHz): δ 24.21. Anal. Found: C, 77.78; H, 6.81; N, 1.86. Calcd. for C<sub>51</sub>H<sub>52</sub>NNiOP: C, 78.07; H, 6.68; N, 1.79.

**General procedure for Polymerization of Ethylene by Ni complexes.** A 200 mL glass pressure vessel was equipped with a large magnetic stirbar, and was heated to the required temperature, with the temperature monitored by thermocouple. At no time was the temperature allowed to deviate more than 2°C. Next, 25 mL of toluene was injected into the reactor and the reactor was pressurized with ethylene to 1.0 atm. For single component trials, 20 μmol of catalyst solution was then injected and the pressure brought to 7.0 atm for 2 h with rapid stirring. For cocatalyst-activated trials, a solution of 10 μmol of catalyst in [Ni(cod)<sub>2</sub>] was injected, after which the pressure was increased to 7.0 atm and rapid stirring maintained for 40 min. After the desired run time, the reactor was vented, and the reaction mixture was quenched with 10% HCl in ethanol. The precipitated polymer was stirred overnight, filtered, and dried under vacuum at 80°C overnight.

**General procedure for Copolymerization of Ethylene and Norbornene by Ni complexes.** A 200 mL glass pressure vessel was equipped with a large magnetic stirbar and heated to the required temperature. Next, 25 mL of toluene was injected into the reactor along with 225 eq. of norbornene. The reactor was then pressurized with ethylene to 1.0 atm. Next, 20 μmol of catalyst solution was injected and the pressure brought to 7.0 atm for 1.5 h with rapid stirring. After the desired run time, the reactor was vented, and the reaction mixture was quenched with 10% HCl in ethanol. The precipitated polymer was stirred overnight, filtered, and dried under vacuum at 80°C overnight.

## References

- S1 Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* 1996, 15, 1518-1520.
- S2 Klein, H.-F.; Karsch, H. H., *Chem. Ber.* 1973, 106, 1433.

- S<sup>3</sup> Van Soolingen, J.; Verkruijsse, H.D.; Keegstra, M.A.; Brandsma, L., *Synth. Commun.* 20 (1990) 3153.
- S<sup>4</sup> Salata, M.R.; Marks, T.J., *JACS*, 2008, *130*, 12.
- S<sup>5</sup> Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* 1998, *17*, 3149.