

## Supplementary Information

### Sodium Cubane and Double-Cubane Aggregates of Hybridised Salicylaldimines and their Transmetallation to Nickel for Catalytic Ethylene Oligomerisation

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#### Materials and characterization methods

All the starting materials were used as purchased from Sigma–Aldrich and Alfa Aesar. All reactions were carried out in an atmosphere of dry, pure argon gas, using standard Schlenk protocols and glovebox. All the solvents used are dried through M3RAUN solvent purification system 800 series. NiCl<sub>2</sub>(DME) was prepared according to literature method.<sup>1</sup> All NMR spectra were measured on ACF300 MHz FT NMR spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer. Mass spectra were obtained using Bruker amaZon X ion trap mass spectrometer and Finnigan LCQ quadrupole ion trap mass spectrometer. Ethylene oligomerization were carried out using parr 5000 multi reactor heater system. Oligomer products were analysed by shimadzu GC-2010 with a flame ionisation detector. The products were quantified, using nonane as internal standard.

#### 1. Synthesis

##### Synthesis of ligands (HL<sup>1</sup> -HL<sup>4</sup>)

**Synthesis of HL<sup>1</sup>** 5.22ml of 2-hydroxybenzaldehyde (50mmol) was dissolved in 50mL of methanol. 6.29ml of N',N'-dimethylpropane-1,3-diamine (50mmol) was added into the reaction. MgSO<sub>4</sub> and several drops of formic acid were added. The resulting solution was stirred overnight at room temperature. The solvent was removed under reduced pressure. Dichloromethane was used to dissolve the product. After filtration, the liquid part was collected. Solvent was removed to afford the product. (Yield: 9.1g, 88%). <sup>1</sup>HNMR (300MHz, DMSO-d<sup>6</sup>): δ (ppm) = 13.5 (b, 1H, -OH), 8.54 (s, 1H, PhCH=N), 7.44 (d, 1H, Ph-H), 7.34 (t, 1H, Ph-H), 6.89 (t, 2H, Ph-H), 3.60 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.29 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.13 (s, 6H, CH<sub>3</sub>), 1.78-1.73 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>). ESI-MS (m/z): 207 ([MH]<sup>+</sup>).

**Synthesis of HL<sup>2</sup>** 5.22ml of 2-hydroxybenzaldehyde (50mmol) was dissolved in 50mL of methanol. 4.32 ml of 3-methoxypropan-1-amine (50mmol) was added into the reaction. MgSO<sub>4</sub> and several drops of formic acid were added. The resulting solution was stirred overnight at room temperature. The solvent was removed under reduced pressure. Dichloromethane was used to dissolve the product. After filtration, the liquid part was collected. Solvent was removed to afford the product. (Yield: 8.5g, 89%). <sup>1</sup>HNMR (300MHz, DMSO-d<sup>6</sup>): δ (ppm) = 13.6 (b, 1H, -

*OH*), 8.56 (s, 1H, PhCH=N), 7.68 (m, 1H, Ph-*H*), 7.45 (m, 1H, Ph-*H*), 6.89 (m, 2H, Ph-*H*), 3.64 (t, 2H, NCH<sub>2</sub>), 3.41 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 3.25 (s, 3H, OCH<sub>3</sub>), 1.87 (m, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O). ESI-MS (*m/z*): 194 ([MH]<sup>+</sup>).

**Synthesis of HL<sup>3</sup>** 5.22ml of 2-hydroxybenzaldehyde (50mmol) was dissolved in 50mL of methanol. 6.27ml of 2-(methylthio)aniline (50mmol) was added into the reaction. MgSO<sub>4</sub> and several drops of formic acid were added. The resulting solution was stirred overnight at room temperature. The solvent was removed under reduced pressure. Dichloromethane was used to dissolve the product. After filtration, the liquid part was collected. Solvent was removed to afford the product (Yield: 11.5g, 95%). <sup>1</sup>H NMR (300MHz, DMSO-d<sup>6</sup>): δ (ppm) = 12.97 (b, 1H, -OH), 8.97 (s, 1H, PhCH=N), 7.68 (m, 1H, Ph-*H*), 7.43 (m, 2H, Ph-*H*), 7.34 (m, 2H, Ph-*H*), 7.27 (m, 1H, Ph-*H*), 6.97 (m, 2H, Ph-*H*), 2.48 (s, 3H, SCH<sub>3</sub>). ESI-MS (*m/z*): 244 ([MH]<sup>+</sup>).

**Synthesis of HL<sup>4</sup>** 5.22ml of 2-hydroxybenzaldehyde (50mmol) was dissolved in 50mL of methanol. 5.63ml of 2-methoxyaniline (50mmol) was added into the reaction. MgSO<sub>4</sub> and several drops of formic acid were added. The resulting solution was stirred overnight at room temperature. The solvent was removed under reduced pressure. Dichloromethane was used to dissolve the product. After filtration, the liquid part was collected. Solvent was removed to afford the product. (Yield: 11g, 97%). <sup>1</sup>H NMR (300MHz, DMSO-d<sup>6</sup>): δ (ppm) = 13.79 (b, 1H, -OH), 8.95 (s, 1H, PhCH=N), 7.62 (m, 1H, Ph-*H*), 7.30 (m, 2H, Ph-*H*), 7.29 (m, 1H, Ph-*H*), 7.14 (m, 1H, Ph-*H*), 7.03 (m, 1H, Ph-*H*), 6.96 (m, 2H, Ph-*H*), 3.85 (s, 3H, OCH<sub>3</sub>). ESI-MS (*m/z*): 228 ([MH]<sup>+</sup>).

#### Synthesis of sodium complexes (1 -4)

**Synthesis of 1** 0.206g HL<sup>1</sup> (1mmol) was dissolved in 5ml dried THF and 0.024g (1mmol) NaH was added into the reaction. The reaction was kept at room temperature overnight. After overnight reaction, the solvent was removed to afford solid. The solid was washed with ether. 0.1033g (Yield: 45%) white solid was obtained. The white solid was dissolved in THF and Hexane was laying on the top of the solution. after 72hrs the yellow crystal was obtained. <sup>1</sup>H NMR (300MHz, DMSO-d<sup>6</sup>): δ (ppm) = 8.44 (s, 1H, PhCH=N), 7.35 (d, 1H, Ph-*H*), 6.74 (t, 1H, Ph-*H*), 6.08 (d, 1H, Ph-*H*), 5.80 (t, 1H, Ph-*H*), 3.35 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.20 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.11 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 1.63 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>). ESI-MS (*m/z*): 935 ([L<sup>1</sup>]<sub>4</sub>Na<sub>5</sub>]<sup>+</sup>), 707 ([L<sup>1</sup>]<sub>3</sub>Na<sub>4</sub>]<sup>+</sup>), 479 ([L<sup>1</sup>]<sub>2</sub>Na<sub>3</sub>]<sup>+</sup>). Anal. Calcd. For C<sub>48</sub>H<sub>68</sub>N<sub>8</sub>O<sub>4</sub>Na<sub>4</sub>: C, 63.14; H, 7.51; N, 12.27. Found: C, 63.16; H, 7.35; N, 12.21.

**Synthesis of 2** 0.193g HL<sup>2</sup> (1mmol) was dissolved in 5ml dried THF and 0.024g (1mmol) NaH was added into the reaction. The reaction was kept at room temperature overnight. After overnight reaction, the solvent was removed to afford solid. The solid was washed with ether. . 0.082g (Yield: 38%) white solid was obtained. <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>): δ (ppm) = 8.46 (s, 1H, PhCH=N), 7.25 (m, 1H, Ph-*H*), 6.74 (m, 1H, Ph-*H*), 6.08 (m, 1H, Ph-*H*), 5.82 (m, 1H, Ph-*H*), 3.40-3.38 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.23 (s, 3H, OCH<sub>3</sub>), 1.75 (m, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). ESI-MS (*m/z*): 216 ([L<sup>2</sup>NaH]<sup>+</sup>), 453 ([L<sup>2</sup>]<sub>2</sub>Na<sub>3</sub>]<sup>+</sup>), 668 ([L<sup>2</sup>]<sub>3</sub>Na<sub>4</sub>]<sup>+</sup>), 883 ([L<sup>2</sup>]<sub>4</sub>Na<sub>5</sub>]<sup>+</sup>), 1098 ([L<sup>2</sup>]<sub>5</sub>Na<sub>6</sub>]<sup>+</sup>), 1313 ([L<sup>2</sup>]<sub>6</sub>Na<sub>7</sub>]<sup>+</sup>). Anal. Calcd. For C<sub>66</sub>H<sub>84</sub>N<sub>6</sub>O<sub>12</sub>Na<sub>6</sub>: C, 61.39; H, 6.56; N, 6.51. Found: C, 61.48; H, 6.17; N, 6.30.

**Synthesis of 3** 0.243g HL<sup>3</sup> (1 mmol) was dissolved in 5ml dried THF and 0.024g (1mmol) NaH was added into the reaction. The reaction was kept at room temperature overnight. After overnight reaction, the solvent was removed to afford solid. The solid was washed with ether. 0.164g (Yield: 62%) yellow solid was obtained. The yellow solid was dissolved in THF and Hexane was laying on the top of the solution. after 72hrs the yellow crystal was obtained. <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>): δ (ppm) = 8.71 (s, 1H, PhCH=N), 7.55 (m, 1H, Ph-*H*), 7.10 (m, 3H, Ph-*H*), 6.85

(m, 2H, Ph-H), 6.18 (m, 1H, Ph-H), 5.92 (m, 1H, Ph-H), 2.35 (s, 3H, SCH<sub>3</sub>). ESI-MS (m/z): 266 ([L<sup>3</sup>NaH]<sup>+</sup>), 288 ([L<sup>3</sup>Na<sub>2</sub>]<sup>+</sup>), 533 ([L<sup>3</sup>]<sub>2</sub>Na<sub>3</sub>]<sup>+</sup>), 818 ([L<sup>3</sup>]<sub>3</sub>Na<sub>4</sub>]<sup>+</sup>), 1083 ([L<sup>3</sup>]<sub>4</sub>Na<sub>5</sub>]<sup>+</sup>), 1348 ([L<sup>3</sup>]<sub>5</sub>Na<sub>6</sub>]<sup>+</sup>). Anal. Calcd. For C<sub>84</sub>H<sub>72</sub>N<sub>6</sub>O<sub>6</sub>S<sub>6</sub>Na<sub>6</sub>: C, 63.38; H, 4.56; N, 5.28; S, 12.09. Found: C,63.14; H, 4.76; N, 5.27; S, 12.24.

**Synthesis of 4** 0.227g HL<sup>4</sup> (1mmol) was dissolved in 5ml dried THF and 0.024g (1mmol) NaH was added into the reaction. The reaction was kept at room temperature overnight. After overnight reaction, the solvent was removed to afford solid. The solid was washed with ether. 0.108g (Yield: 43%) yellow solid was obtained. The yellow solid was dissolved in THF and Hexane was laying on the top of the solution. after 72hrs the yellow crystal was obtained. <sup>1</sup>HNMR (300 MHz, DMSO-d<sup>6</sup>): δ (ppm) = 8.40 (s, 1H, PhCH=N), 7.25 (m, 1H, Ph-H), 6.99-6.87 (m, 5H, Ph-H), 6.21 (m, 1H, Ph-H), 5.97 (m, 1H, Ph-H), 3.78 (s, 3H, OCH<sub>3</sub>). ESI-MS (m/z): 521 ([L<sup>4</sup>]<sub>2</sub>Na<sub>3</sub>]<sup>+</sup>), 770 ([L<sup>4</sup>]<sub>3</sub>Na<sub>4</sub>]<sup>+</sup>), 1019 ([L<sup>4</sup>]<sub>4</sub>Na<sub>5</sub>]<sup>+</sup>). Anal. Calcd. For C<sub>56</sub>H<sub>48</sub>N<sub>4</sub>O<sub>8</sub>Na<sub>4</sub>: C, 67.46; H, 4.85; N, 5.62. Found: C,67.55; H,5.26; N, 5.68.

### Synthesis of nickel complexes (5-16)

**Synthesis of 5** HL<sup>1</sup> (0.248g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.088g, 0.4mmol) was added. After overnight reaction, the solvent was removed to afford yellow solid. The solid was recrystallized using tetrahydrofuran/ether. 0.09g (Yield: 96%) yellow solid complex was obtained. ESI-MS(m/z): 491 ([L<sup>1</sup>]<sub>2</sub>NiNa]<sup>+</sup>). Anal. Calcd. For C<sub>24</sub>H<sub>34</sub>N<sub>4</sub>NiO<sub>2</sub>: C, 61.43; H, 7.30; N, 11.94. Found: C,61.02; H, 6.95; N, 12.09.

**Synthesis of 6** HL<sup>1</sup> (0.248g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.132g, 0.6mmol) was added. After overnight reaction, the solvent was removed to afford yellow solid. The solid was recrystallized using tetrahydrofuran/ether. 0.140g (44%) yellow solid complex was obtained. ESI-MS(m/z): 491 ([L<sup>1</sup>]<sub>2</sub>NiNa]<sup>+</sup>), 961 ([L<sup>1</sup>]<sub>4</sub>Ni<sub>2</sub>Na]<sup>+</sup>). Anal. Calcd. For C<sub>24</sub>H<sub>34</sub>ClN<sub>4</sub>NaNiO<sub>2</sub>: C, 54.63; H, 6.49; N, 10.62. Found: C,54.44; H, 6.36; N, 10.62.

**Synthesis of 7** HL<sup>1</sup> (0.248 g, 1.2 mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.264 g, 1.2 mmol) was added. After overnight reaction, the solvent was removed to afford green solid. The solid was recrystallized using tetrahydrofuran/ether. 0.239 g (45%) light green solid complex was obtained. ESI-MS(m/z): 263 ([L<sup>1</sup>Ni]<sup>+</sup>), 843 ([L<sup>1</sup>]<sub>3</sub>Ni<sub>3</sub>Cl(OH)]<sup>+</sup>). Anal. Calcd. For C<sub>36</sub>H<sub>52</sub>N<sub>6</sub>Ni<sub>3</sub>Cl<sub>2</sub>O<sub>4</sub>: C, 49.14; H, 5.96; N, 9.55. Found: C,49.53; H, 5.71; N, 9.54.

**Synthesis of 8** HL<sup>2</sup> (0.233g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.088g, 0.4mmol) was added. After overnight reaction, the solvent was removed to afford dark green solid. The solid was recrystallized using tetrahydrofuran/ether. 0.09g(51%) green solid complex was obtained. ESI-MS(m/z): 465 ([L<sup>2</sup>]<sub>2</sub>NiNa]<sup>+</sup>). Anal. Calcd. For C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>NiO<sub>4</sub>: C, 59.62; H, 6.37; N, 6.32. Found: C,59.46; H, 6.04; N, 6.33.

**Synthesis of 9** HL<sup>2</sup> (0.233g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.132g, 0.6mmol) was added. After overnight reaction, the solvent was removed to afford green solid. The solid was recrystallized using

tetrahydrofuran/ether. 0.140 g (67%) green solid was obtained. ESI-MS(m/z): 694 ( $[(L^2)_3Ni_2]^+$ ), 822 ( $[(L^2)_3Ni_3Cl_2]^+$ ). Anal. Calcd. For  $C_{37}H_{50}N_3Ni_3Cl_3O_7$ : C, 47.72; H, 5.41; N, 4.51. Found: C, 48.35; H, 5.1; N, 4.53.

**Synthesis of 10** HL<sup>2</sup> (0.233g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.264g, 1.2mmol) was added. After overnight reaction, the solvent was removed to afford light green solid. The solid was recrystallized using tetrahydrofuran/ether. 0.290g(67%) light green solid was obtained. ESI-MS(m/z): 537 ( $[(L^2)_2Ni_2Cl]^+$ ), 667 ( $[(L^2)_2Ni_3Cl_3]^+$ ), 822 ( $[(L^2)_3Ni_3Cl_2]^+$ ), 952 ( $[(L^2)_3Ni_4Cl_4]^+$ ). Anal. Calcd. For  $C_{44}H_{56}Cl_4N_4Ni_4O_8$ : C, 46.13; H, 4.93; N, 4.89. Found: C, 46.18; H, 5.33; N, 4.94.

**Synthesis of 11** HL<sup>3</sup> (0.293g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.088g, 0.4mmol) was added. After overnight reaction, the solvent was removed to afford brown solid. The solid was recrystallized using tetrahydrofuran/ether. 0.290g(67%) brown solid was obtained. ESI-MS(m/z): 565 ( $[(L^3)_2NiNa]^+$ ). Anal. Calcd. For  $C_{28}H_{24}N_2NiO_2S_2$ : C, 61.90; H, 4.45; N, 5.16; S, 11.80. Found: C, 62.38; H, 4.58; N, 5.17; S, 11.69.

**Synthesis of 12** HL<sup>3</sup> (0.293g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.132g, 0.6mmol) was added. After overnight reaction, the solvent was removed to afford earth yellow solid. The solid was recrystallized using tetrahydrofuran/ether. 0.250g (100%) earth yellow solid was obtained. ESI-MS(m/z): 543 ( $[(L^3)_2NiH]^+$ ), 637 ( $[(L^3)_2Ni_2Cl]^+$ ), 844 ( $[(L^3)_3Ni_2]^+$ ). Anal. Calcd. For  $C_{42}H_{36}ClN_3Ni_2O_3S_3$ : C, 57.34; H, 4.12; N, 4.78; S, 10.93. Found: C, 57.21; H, 3.97; N, 4.66; S, 10.31.

**Synthesis of 13** HL<sup>3</sup> (0.293g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.264g, 1.2mmol) was added. After overnight reaction, the reaction is filtered to get the green solid. The solid was recrystallized using acetonitrile/ether. 0.290g(86%) green solid was obtained. ESI-MS(m/z): 543 ( $[(L^3)_2NiH]^+$ ), 637 ( $[(L^3)_2Ni_2Cl]^+$ ), 844 ( $[(L^3)_3Ni_2]^+$ ), 974 ( $[(L^3)_3Ni_3Cl_2]^+$ ). Anal. Calcd. For  $C_{32}H_{30}Cl_4N_4Ni_3O_2S_2 \cdot CH_3CN$ : C, 43.45; H, 3.42; N, 6.33; S, 7.25. Found: C, 43.4; H, 3.58; N, 6.04; S, 6.85.

**Synthesis of 14** HL<sup>4</sup> (0.272g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.044g, 0.2mmol) was added. After overnight reaction, the solvent was removed to afford earth yellow solid. The solid was recrystallized using tetrahydrofuran/ether. 0.100g (32%) earth yellow solid was obtained. ESI-MS(m/z): 533 ( $[(L^4)_2NiNa]^+$ ), 782 ( $[(L^4)_3NiNa_2]^+$ ), 1031 ( $[(L^4)_4NiNa_3]^+$ ), 1280 ( $[(L^4)_5NiNa_4]^+$ ), 1530 ( $[(L^4)_6NiNa_5]^+$ ). Anal. Calcd. For  $C_{84}H_{72}ClN_6Na_5NiO_{12}$ : C, 64.4; H, 4.63; N, 5.36. Found: C, 64.1; H, 4.52; N, 5.31.

**Synthesis of 15** HL<sup>4</sup> (0.272g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.132g, 0.6mmol) was added. After overnight reaction, the solvent was removed to afford earth yellow solid. The solid was recrystallized using tetrahydrofuran/ether. 0.250g (82 %) yellow solid was obtained. ESI-MS (m/z): 533 ( $[(L^4)_2NiNa]^+$ ). Anal. Calcd. For  $C_{28}H_{24}N_2NiO_4$ : C, 65.79; H, 4.73; N, 5.48. Found: C, 65.85; H, 4.48; N, 5.4.

**Synthesis of 16** HL<sup>4</sup> (0.272g, 1.2mmol) was dissolved in 5ml dried THF. 0.0288g(1.2mmol) NaH was added into the reaction. The reaction was kept at room temperature for 1 hr. NiCl<sub>2</sub>(DME) (0.264g, 1.2mmol) was added. After

overnight reaction, the solvent was removed to afford earth yellow solid. The solid was recrystallized using tetrahydrofuran/ether. 0.331g (86%) earth yellow solid was obtained. ESI-MS (*m/z*): 511 ( $[(L^4)_2NiH]^+$ ), 605 ( $[(L^4)_2Ni_2Cl]^+$ ), 796 ( $[(L^4)_3Ni_2]^+$ ). Anal. Calcd. For  $C_{42}H_{36}Cl_3N_3Ni_3O_6$ : C, 52.48; H, 3.78; N, 4.37. Found: C, 52.2; H, 4.19; N, 4.26.

## 2. Crystallographic information

**Table S1.** Crystallographic data and refinement parameters for complexes **1**, **3**, **4**, **7**.

Compound	<b>1</b>	<b>3</b>	<b>4</b>	<b>7</b>
Empirical formula	$C_{48}H_{68}N_8Na_4O_4$	$C_{84}H_{72}N_6Na_6O_6S_6$	$C_{56}H_{48}N_4Na_4O_8$	$C_{37}H_{54}Cl_4N_6Ni_3O_4$
Formula weight	913.06	1591.78	996.94	964.79
Temperature / K	100(2)	223(2)	100(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Triclinic	Monoclinic	Monoclinic
Space group	$I4_1/a$	$P-1$	Cc	$P2_1/c$
<i>a</i> / Å	20.2549(14)	12.5133(8)	16.3906(9)	11.031(8)
<i>b</i> / Å	20.2549(14)	13.8309(9)	16.5378(9)	17.991(14)
<i>c</i> / Å	12.4783(9)	25.5673(16)	18.1746(11)	21.829(17)
$\alpha$ / °	90	84.192(2)	90	90
$\beta$ / °	90	84.067(2)	100.2930(10)	94.77(2)
$\gamma$ / °	90	65.0260(10)	90	90
Volume / Å <sup>3</sup>	5119.4(6)	3981.6(4)	100.2930(10)	4317(6)
Z	4	2	4	4
Density (calculated) / Mg/m <sup>3</sup>	1.185	1.328	1.366	1.484
Absorption coefficient / mm <sup>-1</sup>	0.105	0.262	0.122	1.587
F(000)	1952	1656	2080	2008
Crystal size / mm <sup>3</sup>	0.60 x 0.60 x 0.48	0.60 x 0.54 x 0.20	0.44 x 0.16 x 0.14	0.30 x 0.26 x 0.06
Theta range for data collection / °	1.92 to 27.50	0.80 to 27.50	1.76 to 27.50	1.47 to 25.00
Reflections collected	25665	52330	16970	25122
Independent reflections	2952 [ $R_{(int)} = 0.0348$ ]	18232 [ $R_{(int)} = 0.0369$ ]	10146 [ $R_{(int)} = 0.0459$ ]	7582 [ $R_{(int)} = 0.0950$ ]
Data / restraints / parameters	2952 / 0 / 145	18232 / 0 / 979	10146 / 2 / 653	7582 / 125 / 540
Flack parameter			-0.2(3)	
GOF	1.043	1.084	1.025	1.056

Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1033	R1 = 0.0609, wR2 = 0.1358	R1 = 0.0618, wR2 = 0.1185	R1 = 0.0680, wR2 = 0.1469
R indices (all data)	R1 = 0.0441, wR2 = 0.1055	R1 = 0.0784, wR2 = 0.1446	R1 = 0.0770, wR2 = 0.1262	R1 = 0.1142, wR2 = 0.1691
Largest diff. peak and hole / e.Å <sup>-3</sup>	0.367 and -0.245	0.808 and -0.384	0.320 and -0.267	0.614 and -0.560

**Table S2.** Crystallographic data and refinement parameters for complexes **8**, **9**, **12**, **13**.

Compound	<b>8</b>	<b>9</b>	<b>12</b>	<b>13</b>
Empirical formula	C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> NiO <sub>4</sub>	C <sub>37</sub> H <sub>50</sub> Cl <sub>3</sub> N <sub>3</sub> Ni <sub>3</sub> O <sub>7</sub>	C <sub>42</sub> H <sub>36</sub> ClN <sub>3</sub> Ni <sub>2</sub> O <sub>3</sub> S <sub>3</sub>	C <sub>32.5</sub> H <sub>32.75</sub> Cl <sub>4</sub> N <sub>3.25</sub> Ni <sub>3</sub> O <sub>2.5</sub> S <sub>2</sub>
Formula weight	443.17	931.28	879.79	890.92
Temperature / K	223(2)	100(2)	223(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /c	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	11.5049(11)	18.722(2)	12.3237(8)	12.2929(14)
<i>b</i> / Å	7.3081(7)	10.9768(13)	13.6103(9)	13.6662(16)
<i>c</i> / Å	13.8761(14)	20.175(2)	13.7343(9)	22.289(3)
$\alpha$ / °	90	90	60.4860(10)	96.290(2)
$\beta$ / °	111.595(2)	104.568(3)	79.9780(10)	95.839(2)
$\gamma$ / °	90	90	79.0150(10)	98.850(2)
Volume / Å <sup>3</sup>	1084.80(18)	4012.7(8)	1959.3(2)	3650.7(7)
Z	2	4	2	4
Density (calculated) / Mg/m <sup>3</sup>	1.357	1.542	1.491	1.621
Absorption coefficient / mm <sup>-1</sup>	0.924	1.643	1.233	1.975
F(000)	468	1936	908	1818
Crystal size / mm <sup>3</sup>	0.30 x 0.22 x 0.20	0.28 x 0.26 x 0.10	0.18 x 0.10 x 0.06	0.16 x 0.10 x 0.08
Theta range for data collection / °	1.98 to 27.49	2.09 to 27.50	1.69 to 27.50	1.68 to 27.49
Reflections collected	7397	28117	25496	48584
Independent reflections	2491 [R <sub>(int)</sub> = 0.0343]	9204 [R <sub>(int)</sub> = 0.0516]	8969 [R <sub>(int)</sub> = 0.0893]	16709 [R <sub>(int)</sub> = 0.0330]
Data / restraints /	2491 / 0 / 134	9204 / 0 / 481	8969 / 7 / 501	16709 / 33 / 886

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parameters				
GOF	1.066	1.022	1.039	1.049
Final R indices	$R1 = 0.0418, wR2 =$	$R1 = 0.0461, wR2 =$	$R1 = 0.0754, wR2 =$	$R1 = 0.0349, wR2 =$
$[I > 2\sigma(I)]$	0.1079	0.1029	0.1304	0.0886
R indices (all data)	$R1 = 0.0514, wR2 =$	$R1 = 0.0670, wR2 =$	$R1 = 0.1339, wR2 =$	$R1 = 0.0423, wR2 =$
	0.1144	0.1111	0.1487	0.0918
Largest diff. peak and hole / $e.\text{\AA}^{-3}$	0.267 and -0.419	0.834 and -0.353	0.692 and -0.392	0.931 and -0.673

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Diffraction measurements were conducted at 100(2)–223(2) K on a Bruker AXS APEX CCD diffractometer by using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). (Table S1 and S2) The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.<sup>2</sup> Structure solutions and refinements were performed by using the programs SHELXS-97<sup>3a</sup> and SHELXL-97<sup>3b</sup>.

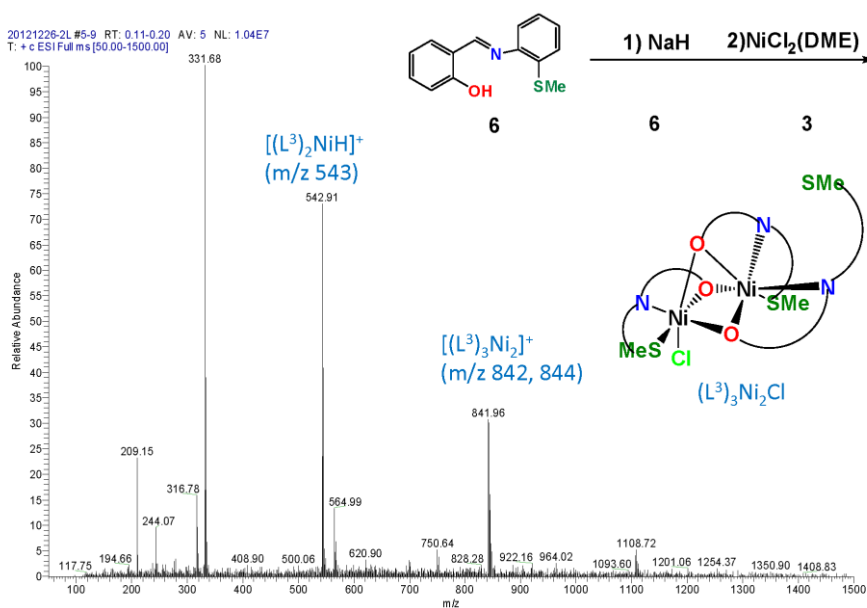
CCDC No.: 918631 (1), 918624 (3), 918629 (4), 918625 (7), 918627 (8), 918626 (9), 918628 (12) and 918630 (13).

### 3. Ethylene oligomerisation

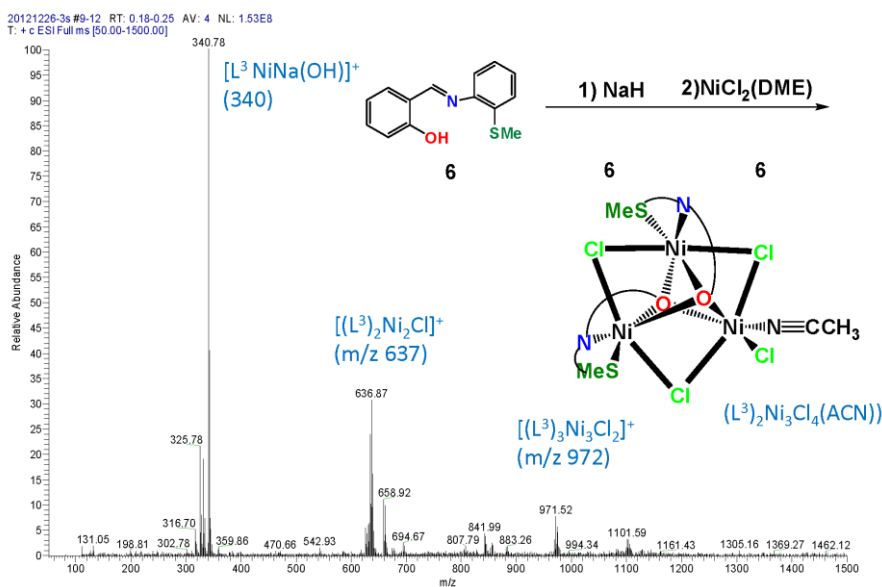
All catalytic reactions were carried out in a magnetically stirred (200 rpm) 100 mL stainless steel autoclave. A 100mL teflon container was used to protect the inner walls of the autoclave from corrosion. 0.01mmol of catalysts (metal based) were dissolve in 30ml toluene in 100ml stainless-steel autoclave in glovebox. 0.1ml internal standard and 13 equivalent cocatalyst were introduced into the reactor. The reactor was purged with ethylene for 3 times. All catalytic tests were started between 25 and 30 °C, and no cooling of the reactor was done during the reaction. After purging the reactor with ethylene, the reactor was pressurized to 10 bar. A temperature increase was observed, which resulted solely from the exothermicity of the reaction. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene. The pressure was maintained at 10 bar for 30 mins. Acidified MeOH was introduced to terminate the reaction. GC analysis of the product was performed immediately after the termination of the reaction.

### 4. ESI-MS spectra of the reaction products from the direct reaction between sodium complex and Ni(II) precursor and from an one-pot reaction

Ligand HL<sup>3</sup> was selected for the transmetallation under different conditions. Reaction 1 (HL<sup>3</sup>/NaH/Ni=6/6/3) and 2 (HL<sup>3</sup>/NaH/Ni=6/6/6) are the one-pot reaction where ligand HL<sup>3</sup> was mixed with NaH for 30 mins and then NiCl<sub>2</sub>(DME) was added. Reaction 3 ((L<sup>3</sup>)<sub>6</sub>Na<sub>6</sub>/Ni = 1:3) and 4 ((L<sup>3</sup>)<sub>6</sub>Na<sub>6</sub>/Ni = 1:6) are the direct reaction between sodium complex (L<sup>3</sup>)<sub>6</sub>Na<sub>6</sub> (single crystals) and NiCl<sub>2</sub>(DME).

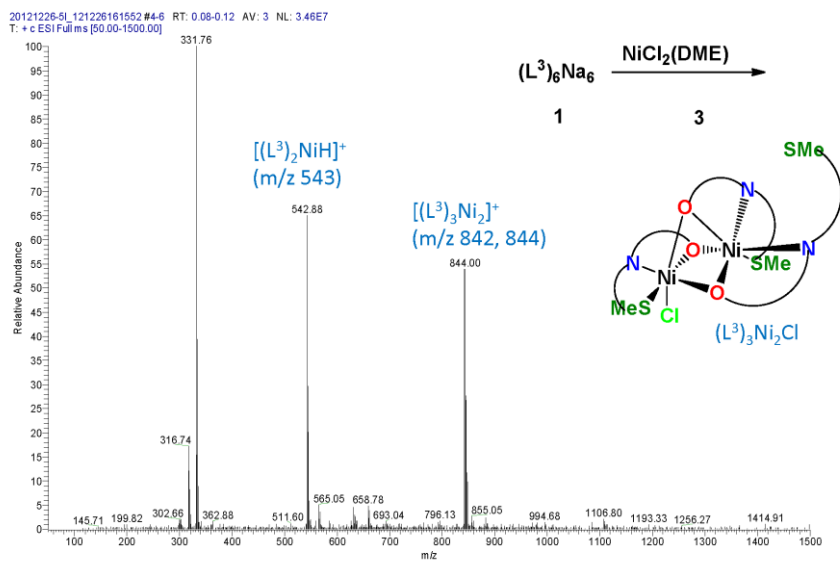


**Figure S1** The ESI-MS spectrum of the product obtained from reaction 1

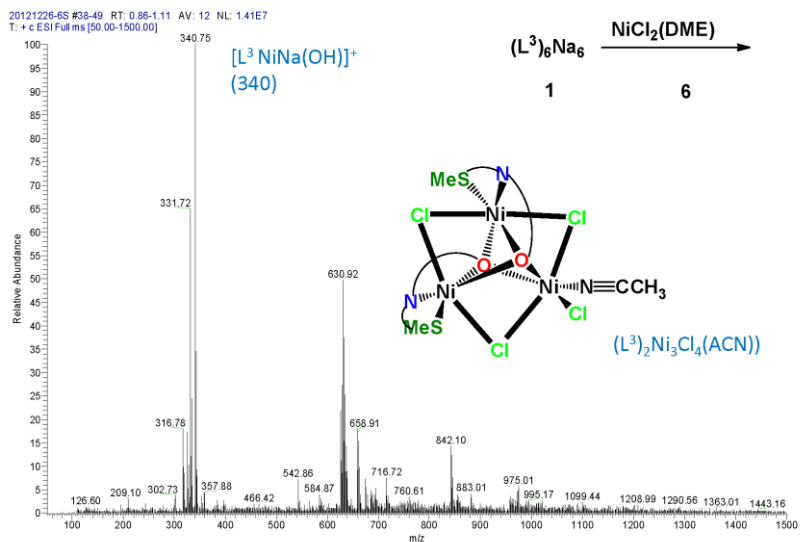


**Figure S2** The ESI-MS spectrum of the product obtained from reaction 2





**Figure S3** The ESI-MS spectrum of the product obtained from reaction 3



**Figure S4** The ESI-MS spectrum of the product obtained from reaction 4

**Table S3** Ethylene oligomerisation catalysed by hybrid-ligand supported Ni(II) with EtAlCl<sub>2</sub> as co-catalyst.

Complex	Formula	Activity (g·g <sup>-1</sup> (Ni)·h <sup>-1</sup> )	Selectivity(%)		1-butene <sup>a</sup> (%)
			C <sub>4</sub>	C <sub>6</sub>	
5	(L <sup>1</sup> ) <sub>2</sub> Ni	13053	99	1	36
6	(L <sup>1</sup> ) <sub>4</sub> Ni <sub>2</sub> NaCl	15104	99	1	26
7	[(L <sup>1</sup> ) <sub>3</sub> Ni <sub>3</sub> Cl(OH)]Cl	11915	98	2	33
8	(L <sup>2</sup> ) <sub>2</sub> Ni	8751	99	1	40
9	(L <sup>2</sup> ) <sub>3</sub> Ni <sub>3</sub> Cl <sub>3</sub> (THF)	10022	98	2	43
10	(L <sup>2</sup> ) <sub>4</sub> Ni <sub>4</sub> Cl <sub>4</sub>	7675	98	2	55
11	(L <sup>3</sup> ) <sub>2</sub> Ni	2065	98	2	90
12	(L <sup>3</sup> ) <sub>3</sub> Ni <sub>2</sub> Cl	9742	98	2	41
13	(L <sup>3</sup> ) <sub>2</sub> Ni <sub>3</sub> Cl <sub>4</sub>	2463	98	2	82
14	(L <sup>4</sup> ) <sub>6</sub> NiNa <sub>5</sub> Cl	6764	98	2	56
15	(L <sup>4</sup> ) <sub>2</sub> Ni	7728	99	1	60
16	(L <sup>4</sup> ) <sub>3</sub> Ni <sub>3</sub> Cl <sub>3</sub>	1539	98	2	87

Conditions: r.t., 10 bar of C<sub>2</sub>H<sub>4</sub>, 30 mL of toluene, 0.01 mmol of catalyst (metal based), 13 equiv of EtAlCl<sub>2</sub>.<sup>a</sup> among the C<sub>4</sub> products

## References

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2. SADABS: Area-Detection Absorption Correction: Bruker AXS Inc., Madison, WI, 1995.
3. (a) G. M. Sheldrick, SHELXS-97 Program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.