

## Tetracosanuclear nickel complexes as effective catalysts for cycloaddition of carbon dioxide with epoxides

Guan-Lin Liu<sup>†</sup>, En-Hsu Wu<sup>†</sup>, Yu-Ching Hung, Wei-Chi Chou, Chia-Hsin Hung, Chu-Chieh Lin\* and Bao-Tsan Ko\*

*Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan*

<sup>†</sup>G.-L. Liu and E.-H. Wu contributed equally to this work.

### Experimental

#### General conditions

Nickel(II) acetate tetrahydrate, 5-fluorosalicylaldehyde, 5-chlorosalicylaldehyde, 2'-hydroxyacetophenone, 2'-hydroxy-5'-methoxyacetophenone, N,N'-diethylethylenediamine, 5'-bromo-2'-hydroxyacetophenone, N,N,2,2-tetramethyl-1,3-propanediamine, 3-(dimethyl-amino)-1-propylamine, tetrabutylammonium chloride, tetrabutylammonium bromide, toluene, methanol (MeOH), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), diethyl ether, *n*-hexane, and carbon dioxide (CO<sub>2</sub>, 99.95%) were purchased and used without further purification. Deuterated solvents (Deuterated chloroform and Deuterated benzene) were dried over 4 Å molecular sieves. Cyclohexene oxide (CHO) was purified by distillation over calcium hydride (CaH<sub>2</sub>) at least four times prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 400 or 600 spectrometers (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C, 600 MHz for <sup>1</sup>H, and 150 MHz for <sup>13</sup>C) and the chemical shift referenced internally residuary solvent signal relative to tetramethylsilane (TMS, δ = 0.0 ppm). <sup>1</sup>H NMR and <sup>13</sup>C NMR assignments were confirmed by DEPT, HSQC, and COSY. The Fourier transform IR (FT-IR) spectra were recorded on a Nicolet iS 5 FT-IR Spectrometer in the range 4,000–500 cm<sup>-1</sup>. Microanalyses were performed using a Heraeus CHNO-RAPID instrument. Mass analyses were performed by utilizing the positive electron spray ionization (ESI<sup>+</sup>) technique with a Thermo Finnigan TSQ Quantum

mass spectrometer for newly prepared complexes upon dissolving in CH<sub>2</sub>Cl<sub>2</sub> solvent.

### Synthesis of NNO-Schiff-base ligand precursors L<sup>1</sup>H–L<sup>6</sup>H.

#### Synthesis of ligand precursors L<sup>1</sup>H

A mixture of 5-fluorosalicylaldehyde (1.40 g, 10.0 mmol) and N,N,2,2-tetramethyl-1,3-propanediamine (1.30 g, 10.0 mmol) was dissolved in methanol (50 mL), and the solution was stirred for 2 h. The mixture was dried under vacuum to yield yellow oil-like liquid. Yield: 2.43 g (96%). Anal. Calc. for C<sub>14</sub>H<sub>21</sub>FN<sub>2</sub>O: C, 66.64; H, 8.39; N, 11.10%; Found: C, 66.29; H, 8.28; N, 11.05%. ESI-MS (m/z): 253.17 [100%, (L<sup>1</sup>H<sub>2</sub>)<sup>+</sup>]. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 13.44 (s, 1H, ArOH), 8.25 (s, 1H, HC=N), 7.00 (ddd, *J* = 8.8, 8.3, 3.1 Hz, 1H, ArH), 6.93 (dd, *J* = 8.4, 3.1 Hz, 1H, ArH), 6.88 (dd, *J* = 9.0, 4.5 Hz, 1H, ArH), 3.46 (d, *J* = 1.2 Hz, 2H, C=NCH<sub>2</sub>), 2.29 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.18 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 0.92 (s, 6H, CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 163.96 (d, *J* = 1.9 Hz, HC=N), 157.41 (s, ArCOH), 155.24 (d, *J* = 236.3 Hz, ArCF), 119.05 (d, *J* = 23.2 Hz, ArC), 118.48 (d, *J* = 7.1 Hz, ArCC=N), 117.91 (d, *J* = 7.3 Hz, ArC), 116.18 (d, *J* = 23.1 Hz, ArC), 68.38 (C=NCH<sub>2</sub>), 68.33 (CH<sub>2</sub>CH<sub>2</sub>N) 48.80 (N(CH<sub>3</sub>)<sub>2</sub>), 37.16 (C(CH<sub>3</sub>)<sub>2</sub>), 24.48 (C(CH<sub>3</sub>)<sub>2</sub>).

#### Synthesis of ligand precursors L<sup>2</sup>H

A mixture of 5-fluorosalicylaldehyde (1.40 g, 10.0 mmol) and 3-(dimethylamino)-1-propylamine (1.02 g, 10.0 mmol) was dissolved in methanol (50 mL), and the solution was stirred for 2 h. The mixture was dried under vacuum to yield yellow oil-like liquid. Yield: 2.09 g (93%). Anal. Calc. for C<sub>12</sub>H<sub>17</sub>FN<sub>2</sub>O: C, 64.26; H, 7.64; N, 12.49%; Found: C, 64.54; H, 7.62; N, 11.82%. ESI-MS (m/z): 225.08 [100%, (L<sup>2</sup>H<sub>2</sub>)<sup>+</sup>]. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 13.26 (s, 1H, ArOH), 8.27 (s, 1H, HC=N), 6.99 (td, *J* = 8.6, 3.1 Hz, 1H, ArH), 6.92 (dd, *J* = 8.4, 3.1 Hz, 1H, ArH), 6.88 (m, 1H, ArH), 3.63 (t, *J* = 6.7 Hz, 2H, C=NCH<sub>2</sub>), 2.33 (m, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 2.21 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 1.84 (p, *J* = 6.9 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 163.81 (d, *J* = 1.9 Hz, HC=N), 157.18 (s, ArCOH), 155.18 (d, *J* = 236.3 Hz, ArCF), 118.98 (d,

$J = 23.2$  Hz, ArC), 118.40 (d,  $J = 7.1$  Hz, ArCC=N), 117.86 (d,  $J = 7.3$  Hz, ArC), 116.13 (d,  $J = 23.1$  Hz, ArC), 57.38 (C=NCH<sub>2</sub>), 56.99 (CH<sub>2</sub>CH<sub>2</sub>N) 45.40 (N(CH<sub>3</sub>)<sub>2</sub>), 28.63 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

### Synthesis of ligand precursors L<sup>3</sup>H

A mixture of 5-chlorosalicylaldehyde (1.57 g, 10.0 mmol) and 3-(dimethylamino)-1-propylamine (1.02 g, 10.0 mmol) was dissolved in methanol (50 mL), and the solution was stirred for 24 h. The mixture was dried under vacuum to yield yellow oil-like liquid. Yield: 2.36 g (98%). Anal. Calc. for C<sub>12</sub>H<sub>17</sub>ClN<sub>2</sub>O: C, 59.87; H, 7.12; N, 11.64%; Found: C, 59.49; H, 7.11; N, 11.48%. ESI-MS (m/z): 241.2 [100%, (L<sup>3</sup>H<sub>2</sub>)<sup>+</sup>]. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  13.52 (s, 1H, ArOH), 8.25 (s, 1H, CH=N), 7.22-7.16 (m, 2H, ArH), 6.87 (d,  $J = 8.8$  Hz, 1H, ArH), 3.62 (d,  $J = 8.8$  Hz, 2H, C=NCH<sub>2</sub>), 2.32 (t,  $J = 7.2$  Hz, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 2.20 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 1.83 (p,  $J = 7.0$  Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  163.71 (CH=N), 159.89, 131.84, 130.16, 122.85, 119.39, 118.51 (ArC), 57.21 (C=NCH<sub>2</sub>), 56.94 (CH<sub>2</sub>NMe<sub>2</sub>), 45.39 (N(CH<sub>3</sub>)<sub>2</sub>), 28.59 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

### Synthesis of ligand precursors L<sup>4</sup>H

A mixture of 2'-hydroxy-5'-methoxyacetophenone (1.66 g, 10.0 mmol) and 3-(dimethylamino)-1-propylamine (1.02 g, 10.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 12 h. After cooling to room temperature, the mixture was dried under vacuum to yield orange oil-like liquid. Yield: 2.45 g (98%). Anal. Calc. for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 67.17; H, 8.86; N, 11.19%; Found: C, 66.46; H, 8.94; N, 11.13%. ESI-MS (m/z): 251.2 [100%, (L<sup>4</sup>H<sub>2</sub>)<sup>+</sup>]. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm) :  $\delta$  15.92 (s, 1H, ArOH), 7.03 (d,  $J = 3.0$  Hz, 1H, ArH), 6.92 (dd,  $J = 9.0, 3.0$  Hz, 1H, ArH), 6.87 (d,  $J = 8.9$  Hz, 1H, ArH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.60 (t,  $J = 6.9$  Hz, 2H, C=NCH<sub>2</sub>), 2.41 (t,  $J = 7.1$  Hz, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 2.32 (s, 3H, N=C(CH<sub>3</sub>)), 2.24 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 1.92 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, ppm) :  $\delta$  170.80 (C=N), 157.92, 150.46, 118.95, 118.84, 118.80, 112.22 (ArC), 57.13 (CH<sub>2</sub>NMe<sub>2</sub>), 55.84 (OCH<sub>3</sub>), 47.22 (C=NCH<sub>2</sub>), 45.34 (N(CH<sub>3</sub>)<sub>2</sub>), 28.30

(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.19 (N=C(CH<sub>3</sub>)).

### Synthesis of ligand precursors L<sup>5</sup>H

A mixture of 5'-bromo-2'-hydroxyacetophenone (2.15 g, 10.0 mmol) and N,N,2,2-Tetramethyl-1,3-propanediamine (1.30 g, 10.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 12 h. After cooling to room temperature, the mixture was dried under vacuum to yield orange oil-like liquid. Yield: 3.17 g (97%). Anal. Calc. for C<sub>15</sub>H<sub>23</sub>BrN<sub>2</sub>O: C, 55.05; H, 7.08; N, 8.56%; Found: C, 54.93; H, 7.13; N, 8.62%. ESI-MS (m/z): 327.2 [100%, (L<sup>5</sup>H<sub>2</sub>)<sup>+</sup>]. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm) : δ 17.02 (s, 1H, ArOH), 7.53 (d, *J* = 2.4 Hz, 1H, ArH), 7.27 (dd, *J* = 8.7, 2.3 Hz, 1H, ArH), 6.75 (dd, *J* = 8.9, 2.4 Hz, 1H, ArH), 3.37 (s, 2H, C=NCH<sub>2</sub>), 2.28 (d, *J* = 2.4 Hz, 3H, N=C(CH<sub>3</sub>)), 2.23 (d, *J* = 2.2 Hz, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.20 (d, *J* = 2.2 Hz, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 0.96 (d, *J* = 2.2 Hz, 6H, C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, ppm) : δ 170.91 (C=N), 164.67, 135.14, 130.18, 121.15, 119.71, 107.40 (ArC), 67.87 (CH<sub>2</sub>NMe<sub>2</sub>), 57.24 (C=NCH<sub>2</sub>), 48.63 (N(CH<sub>3</sub>)<sub>2</sub>), 36.73 (C(CH<sub>3</sub>)<sub>2</sub>), 24.40 (C(CH<sub>3</sub>)<sub>2</sub>), 14.30 (N=C(CH<sub>3</sub>)).

### Synthesis of ligand precursors L<sup>6</sup>H

A mixture of 2'-hydroxy-5'-methoxyacetophenone (1.66 g, 10.0 mmol) and N,N,2,2-Tetramethyl-1,3-propanediamine (1.30 g, 10.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 12 h. After cooling to room temperature, the mixture was dried under vacuum to yield orange oil-like liquid. Yield: 2.67 g (96%). Anal. Calc. for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.03; H, 9.41; N, 10.06%; Found: C, 68.85; H, 9.38; N, 10.04%. ESI-MS (m/z): 279.2 [100%, (L<sup>6</sup>H<sub>2</sub>)<sup>+</sup>]. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm) : δ 16.10 (s, 1H, ArOH), 7.04 (d, *J* = 3.0 Hz, 1H, ArH), 6.92 (dd, *J* = 9.0, 3.0 Hz, 1H, ArH), 6.87 (d, *J* = 8.9 Hz, 1H, ArH), 3.77 (s, 3H, OCH<sub>3</sub>), 3.40 (s, 2H, C=NCH<sub>2</sub>), 2.32 (s, 3H, N=C(CH<sub>3</sub>)), 2.28 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.26 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 1.00 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, ppm) : δ 170.90 (C=N), 158.26, 150.58, 119.11, 118.99, 115.96, 112.48 (ArC), 68.15

(CH<sub>2</sub>NMe<sub>2</sub>), 58.14 (C=NCH<sub>2</sub>), 56.09 (OCH<sub>3</sub>), 48.79 (N(CH<sub>3</sub>)<sub>2</sub>), 36.84 (C(CH<sub>3</sub>)<sub>2</sub>), 24.61 (C(CH<sub>3</sub>)<sub>2</sub>), 14.55 (N=C(CH<sub>3</sub>)).

### Synthesis of [(L<sup>1</sup>)<sub>2</sub>Ni<sub>2</sub>(OAc)<sub>2</sub>(H<sub>2</sub>O)] (1)

A mixture of L<sup>1</sup>H (0.252 g, 1.0 mmol) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.249 g, 1.0 mmol) was dissolved in methanol (50 mL), and the solution was heated under reflux for 24 h. The solution was then cooled to room temperature, and the volatile materials were removed under vacuum. The residue was recrystallized with CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 0.223 g (59%). IR (cm<sup>-1</sup>, neat): 1,640 (ν<sub>C=N</sub>), 1,540 (ν<sub>asymmetric monodentate acetate</sub>), 1,410 (ν<sub>symmetric monodentate acetate</sub>). Anal. Calc. for C<sub>32</sub>H<sub>48</sub>F<sub>2</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>7</sub>: C, 50.83; H, 6.40; N, 7.41%; Found: C, 50.37; H, 6.69; N, 7.16%.

### Synthesis of [(L<sup>2</sup>)<sub>2</sub>Ni<sub>2</sub>(OAc)<sub>2</sub>(H<sub>2</sub>O)] (2)

A mixture of L<sup>2</sup>H (0.224 g, 1.0 mmol) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.249 g, 1.0 mmol) was dissolved in methanol (50 mL), and the solution was heated under reflux for 24 h. The solution was then cooled to room temperature and the volatile materials were removed under vacuum. The residue was recrystallized with CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 0.242 g (69%). IR (cm<sup>-1</sup>, neat): 1,637 (ν<sub>C=N</sub>), 1,550 (ν<sub>asymmetric monodentate acetate</sub>), 1,413 (ν<sub>symmetric monodentate acetate</sub>). Anal. Calc. for C<sub>28</sub>H<sub>40</sub>F<sub>2</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>7</sub>: C, 48.04; H, 5.76; N, 8.00%; Found: C, 47.78; H, 5.78; N, 8.08%.

### Synthesis of [(L<sup>2</sup>)Ni<sub>3</sub>(OAc)<sub>4</sub>(OH)]<sub>8</sub> (3)

A mixture of L<sup>2</sup>H (0.224 g, 1.0 mmol) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.747 g, 3.0 mmol) was dissolved in methanol (50 mL), and the solution was heated under reflux for 24 h. The solution was then cooled to room temperature and the volatile materials were removed under vacuum. The residue was recrystallized with CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 0.387 g (59%). IR

( $\text{cm}^{-1}$ , neat): 1,650 ( $\nu_{\text{C=N}}$ ), 1,573 ( $\nu_{\text{asymmetric bridging bidentate acetate}}$ ), 1,417 ( $\nu_{\text{symmetric bridging bidentate acetate}}$ ). Anal. Calc. for  $\text{C}_{160}\text{H}_{232}\text{F}_8\text{N}_{16}\text{Ni}_{24}\text{O}_{80}$ : C, 36.81; H, 4.48; N, 4.29%; Found: C, 36.17; H, 5.18; N, 3.60%.

#### Synthesis of $[(\text{L}^3)\text{Ni}_3(\text{OAc})_4(\text{OH})]_8$ (4)

A mixture of  $\text{L}^3\text{H}$  (1.20 g, 5.0 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3.73 g, 15.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 48 h. The solution was then cooled to room temperature and the volatile materials were removed under vacuum. The residue was recrystallized with  $\text{CH}_2\text{Cl}_2$  and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 2.04 g (61%). IR ( $\text{cm}^{-1}$ , neat): 1,636 ( $\nu_{\text{C=N}}$ ), 1,563 ( $\nu_{\text{asymmetric bridging bidentate acetate}}$ ), 1,470 ( $\nu_{\text{symmetric bridging bidentate acetate}}$ ). Anal. Calc. for  $\text{C}_{160}\text{H}_{232}\text{Cl}_8\text{N}_{16}\text{Ni}_{24}\text{O}_{80}$ : C, 35.91; H, 4.37; N, 4.19%; Found: C, 35.90; H, 5.17; N, 4.12%.

#### Synthesis of $[(\text{L}^4)\text{Ni}_3(\text{OAc})_4(\text{OH})]_8$ (5)

A mixture of  $\text{L}^4\text{H}$  (1.25 g, 5.0 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3.73 g, 15.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 48 h. The solution was then cooled to room temperature and the volatile materials were removed under vacuum. The residue was recrystallized with  $\text{CH}_2\text{Cl}_2$  and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 0.38 g (11%). IR ( $\text{cm}^{-1}$ , neat): 1,612 ( $\nu_{\text{C=N}}$ ), 1,556 ( $\nu_{\text{asymmetric bridging bidentate acetate}}$ ), 1,387 ( $\nu_{\text{symmetric bridging bidentate acetate}}$ ). Anal. Calc. for  $\text{C}_{176}\text{H}_{272}\text{N}_{16}\text{Ni}_{24}\text{O}_{88}$ : C, 38.94; H, 5.05; N, 4.13%; Found: C, 38.57; H, 5.38; N, 3.95%.

#### Synthesis of $[(\text{L}^5)\text{Ni}_3(\text{OAc})_4(\text{OH})]_8$ (6)

A mixture of  $\text{L}^5\text{H}$  (1.64 g, 5.0 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3.73 g, 15.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 48 h. The

solution was then cooled to room temperature and the volatile materials were removed under vacuum. The residue was recrystallized with CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 0.34 g (9%). IR (cm<sup>-1</sup>, neat): 1,614 (ν<sub>C=N</sub>), 1,576 (ν<sub>asymmetric bridging bidentate acetate</sub>), 1,390 (ν<sub>symmetric bridging bidentate acetate</sub>). Anal. Calc. for C<sub>184</sub>H<sub>280</sub>Br<sub>8</sub>N<sub>16</sub>Ni<sub>24</sub>O<sub>80</sub>: C, 36.56; H, 4.67; N, 3.71%; Found: C, 36.56; H, 4.97; N, 3.63%.

### Synthesis of [(L<sup>6</sup>)Ni<sub>3</sub>(OAc)<sub>4</sub>(OH)]<sub>8</sub> (7)

A mixture of L<sup>6</sup>H (1.39 g, 5.0 mmol) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (3.73 g, 15.0 mmol) was dissolved in toluene (50 mL), and the solution was heated under reflux with dean-stark trap for 48 h. The solution was then cooled to room temperature and the volatile materials were removed under vacuum. The residue was recrystallized with CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane, and the resulting precipitate was collected by filtration and dried under vacuum to give green solids. Yield: 0.53 g (15%). IR (cm<sup>-1</sup>, neat): 1,614 (ν<sub>C=N</sub>), 1,583 (ν<sub>asymmetric bridging bidentate acetate</sub>), 1,456 (ν<sub>symmetric bridging bidentate acetate</sub>). Anal. Calc. for C<sub>192</sub>H<sub>304</sub>N<sub>16</sub>Ni<sub>24</sub>O<sub>88</sub>: C, 40.79; H, 5.42; N, 3.96%; Found: C, 40.92; H, 5.89; N, 3.76%.

### Cycloaddition of CO<sub>2</sub> and CHO catalyzed by nickel complexes 1-7 in the presence of quaternary ammonium Salt (<sup>n</sup>Bu<sub>4</sub>NX, X = Cl, Br)

A representative procedure for the cycloaddition of cyclohexene oxide with CO<sub>2</sub> (Table S4, entry 3) was exemplified. [(L<sup>2</sup>)Ni<sub>3</sub>(O<sub>2</sub>Ac)<sub>4</sub>(OH)]<sub>8</sub> (**3**) (21.8 mg, 0.00417 mmol) was dissolved in 50.0 mmol of neat CHO with the addition of <sup>n</sup>Bu<sub>4</sub>NBr (cocatalyst, 64.5 mg, 0.2 mmol) under a dry nitrogen atmosphere. The mixture was added to the 100 mL autoclave with a magnetic stirrer under CO<sub>2</sub> atmosphere. CO<sub>2</sub> was then charged into the autoclave until reaching the reacting pressure 300 psi, and the stirrer was started. The reaction was carried out at 60 °C for 24 h. The reactor was placed into ice water and excess CO<sub>2</sub> was released after the reaction. <sup>1</sup>H NMR spectroscopic studies were employed to analyze the CHO conversion (18%) and the

coupling selectivity (Fig. S8). The spectral characteristics of the product were referenced on the basis of the previous literature reports.<sup>S1</sup>

### **X-ray crystallographic studies**

Suitable crystals of nickel complexes **1–7** were mounted onto glass fiber by using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas to collect diffraction data at 150 K using Bruker APEX2 diffractometer, and intensity data were collected with a combination of  $\phi$  and  $\omega$  scans. All the data were corrected by Lorentz and polarization effects, and the program APEX2<sup>S2</sup> in SADABS<sup>S3</sup> was conducted for the absorption correction. The space group determination was based on a check of the Laue symmetry and systematic absences, and was verified by utilizing the structure solution. The structure was solved and refined with SHELXTL package.<sup>S4</sup> All non-H atoms were located from successive Fourier maps, and hydrogen atoms were treated as a riding model on their parent C atoms. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H-atoms. Drawing of the molecular structure was performed by using Oak Ridge Thermal Ellipsoid Plots (ORTEP).<sup>S5</sup> Crystallographic data of nickel complexes **1–3** and **5–7** were illustrated in Table S7. In addition, the majority of crystallographic data generally revealed the presence of highly disordered solvent molecules, thus the SQUEEZE subroutine in the PLATON program<sup>S6</sup> (for complexes **2**, **3** and **5–7**) was applied to data refinement. According to the solvent mask results calculated by the crystallographic program, the masked molecules types and quantities were added to the formula and presented in Table S7. Moreover, several zero-intensity reflections of complex **2** in the crystallographic data were omitted and refined.

### **Reference:**

S1 C.-Y. Li, Y.-C. Su, C.-H. Lin, H.-Y. Huang, C.-Y. Tsai, T.-Y. Lee, B.-T. Ko, *Dalton Trans.* 2017, **46**, 15399–15406.

S2 Bruker AXS, *APEX2, V2010.3*; Bruker AXS Inc.: Madison, WI 2010.

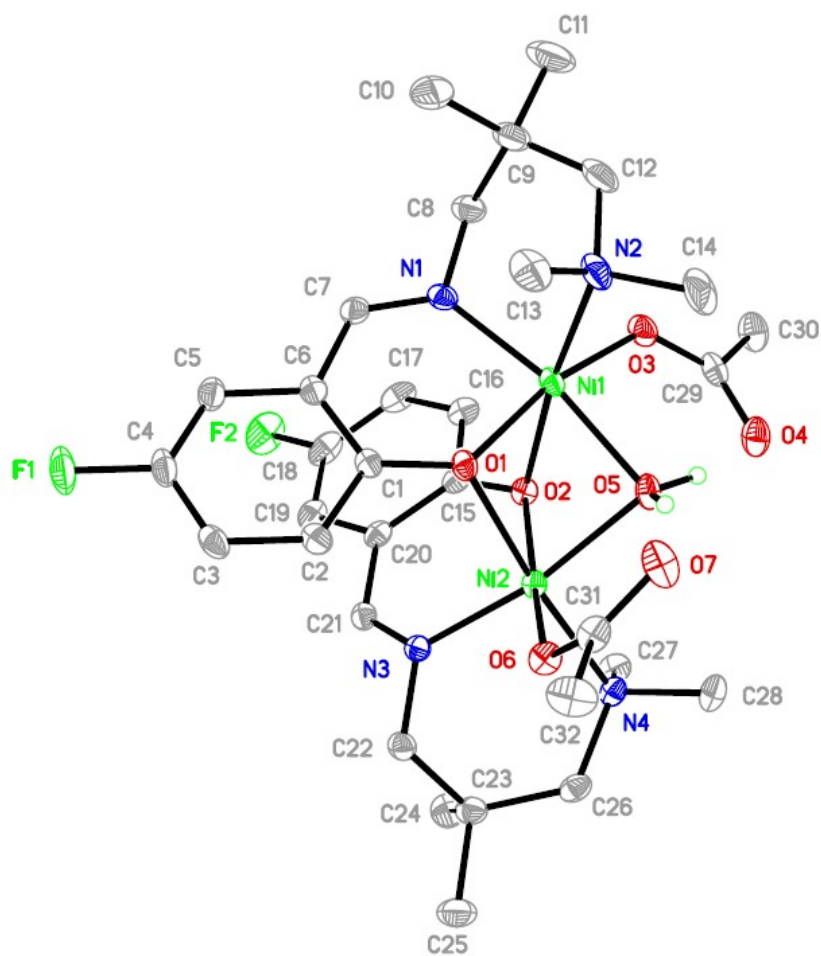


S3 *SADABS V2008/1, SAINT+V7.60A*; Bruker AXS Inc.: Madison, WI 2008.

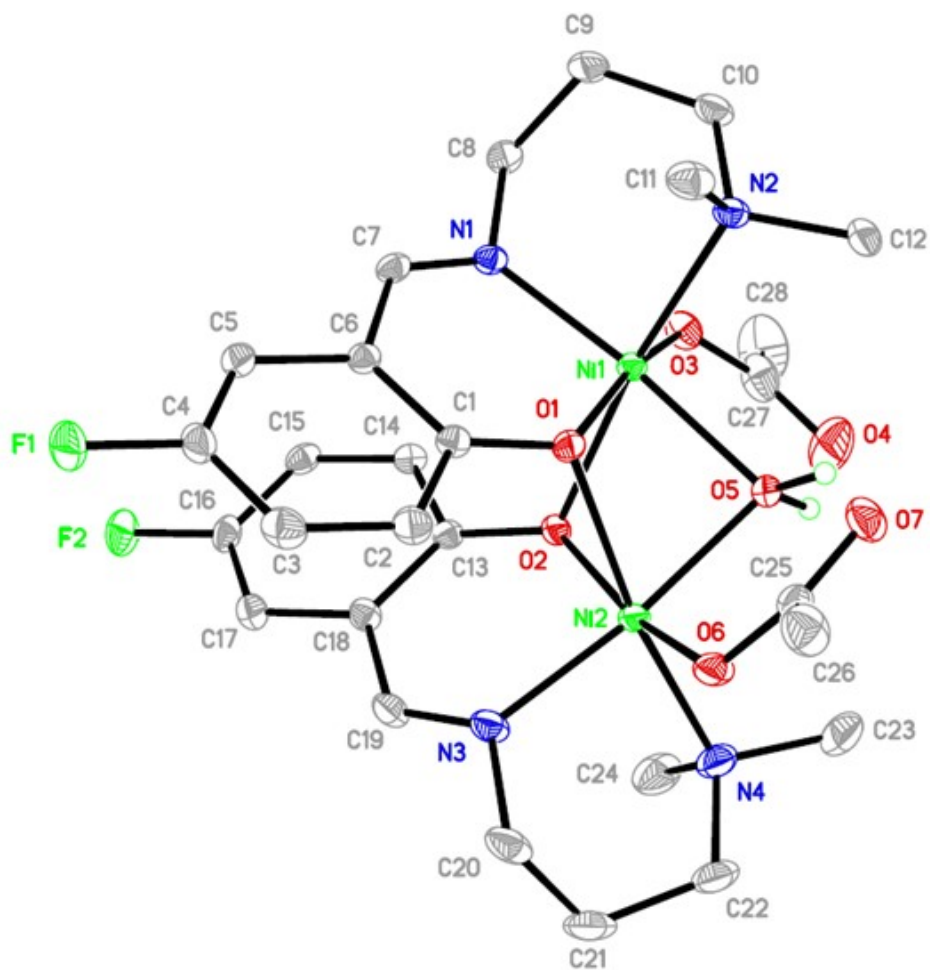
S4 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.

S5 Burnett, M. N. & Johnson, C. K.(1996) ORTEPIII, Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.

S6 A. Spek, *Acta Crystallogr. C*, 2015, **71**, 9–18.

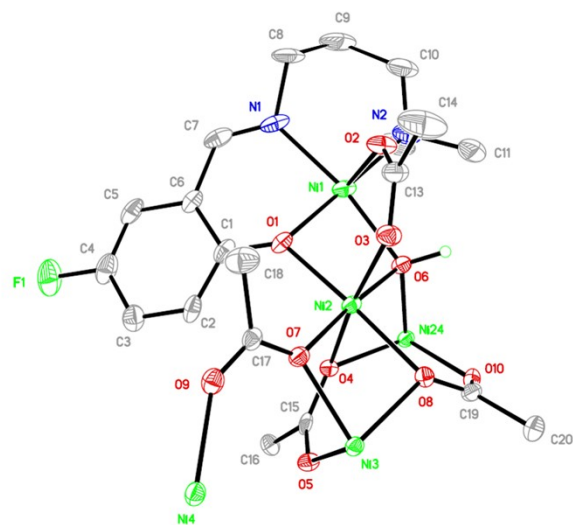


**Fig. S1** ORTEP drawing of complex **1** with probability ellipsoids drawn at level 30%. Hydrogen atoms (except that of the coordinated water) are omitted for clarity.

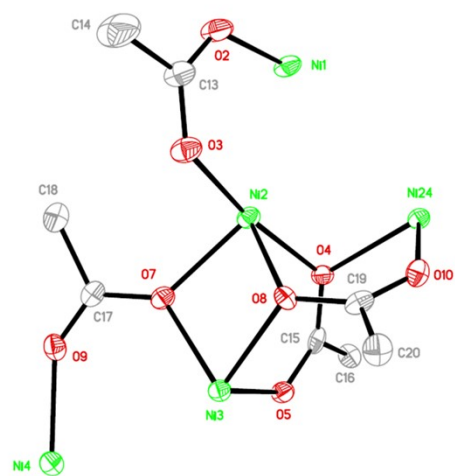


**Fig. S2** ORTEP drawing of complex **2** with probability ellipsoids drawn at level 30%. Hydrogen atoms (except that of the coordinated water) are omitted for clarity.

(a)

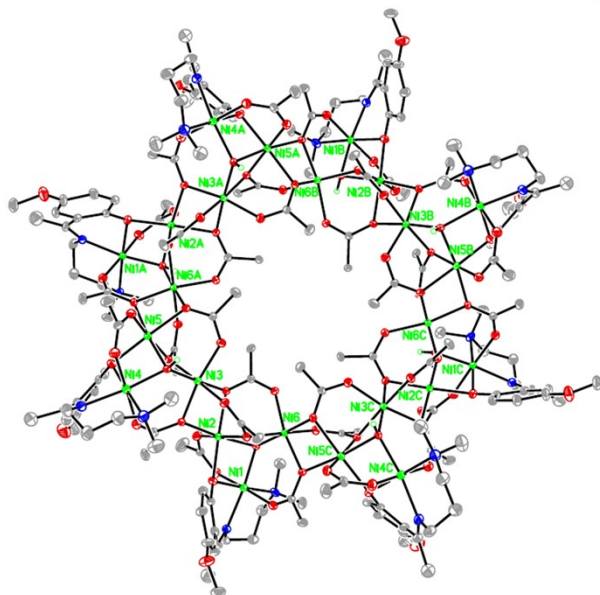


(b)

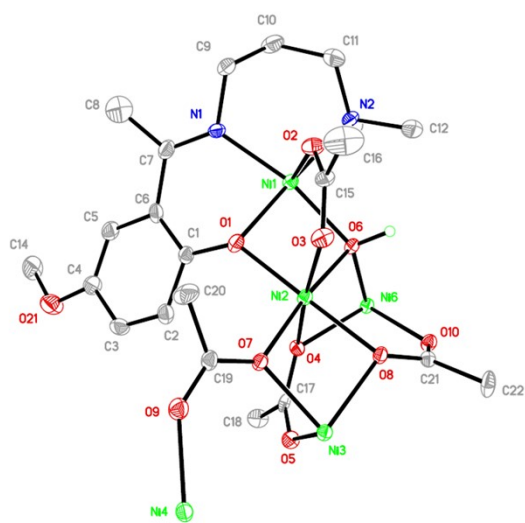


**Fig. S3** (a) A repeating unit of complex **3**. (b) Bonding modes of acetates and nickel ions at one repeating unit of complex **3**.

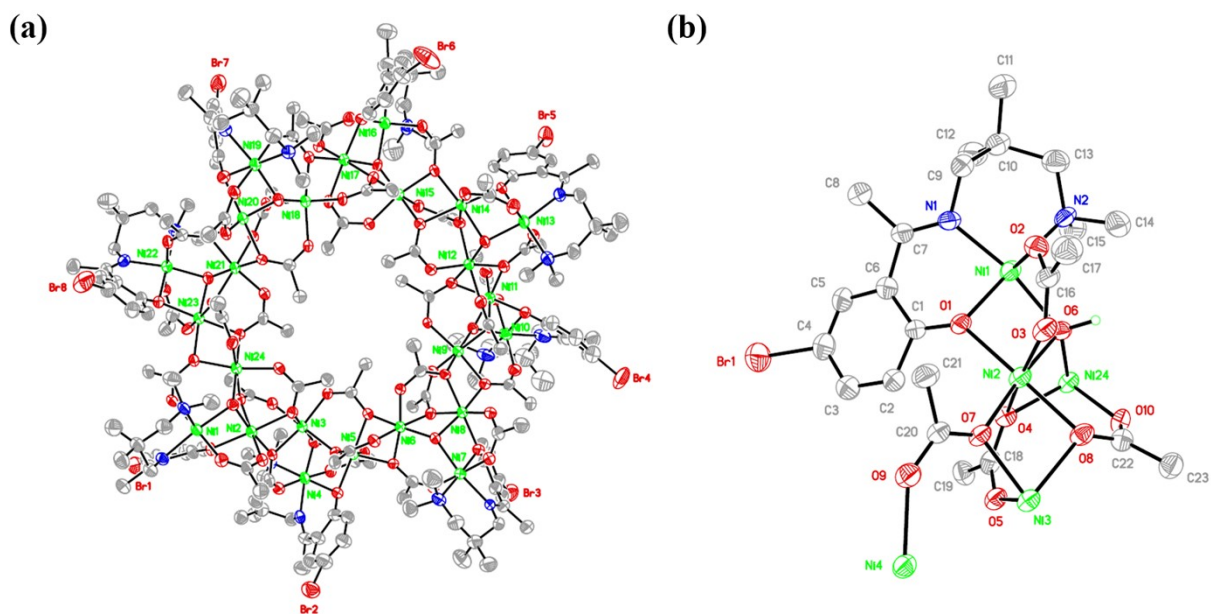
(a)



(b)

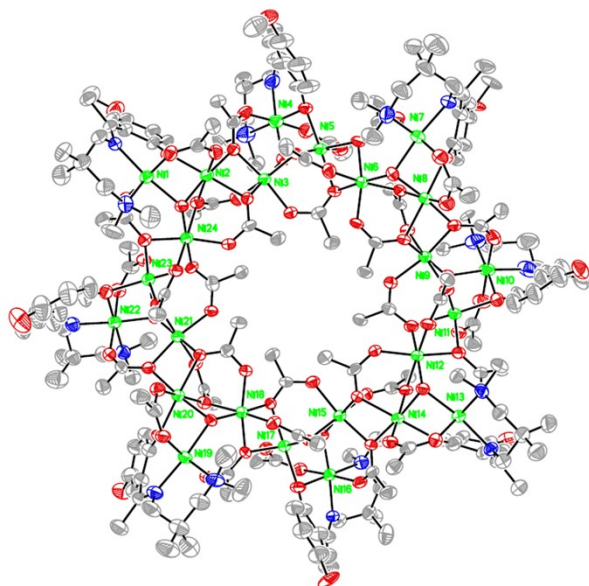


**Fig. S4** (a) ORTEP drawing of complex **5** with probability ellipsoids drawn at level 30%. (b) A repeating unit of complex **5**.

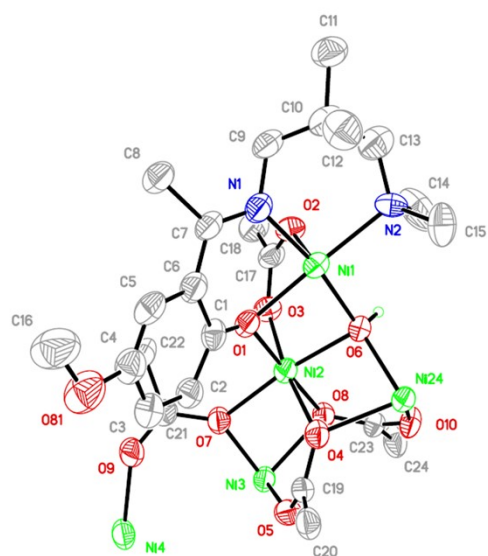


**Fig. S5** (a) ORTEP drawing of complex **6** with probability ellipsoids drawn at level 30%. (b) A repeating unit of complex **6**.

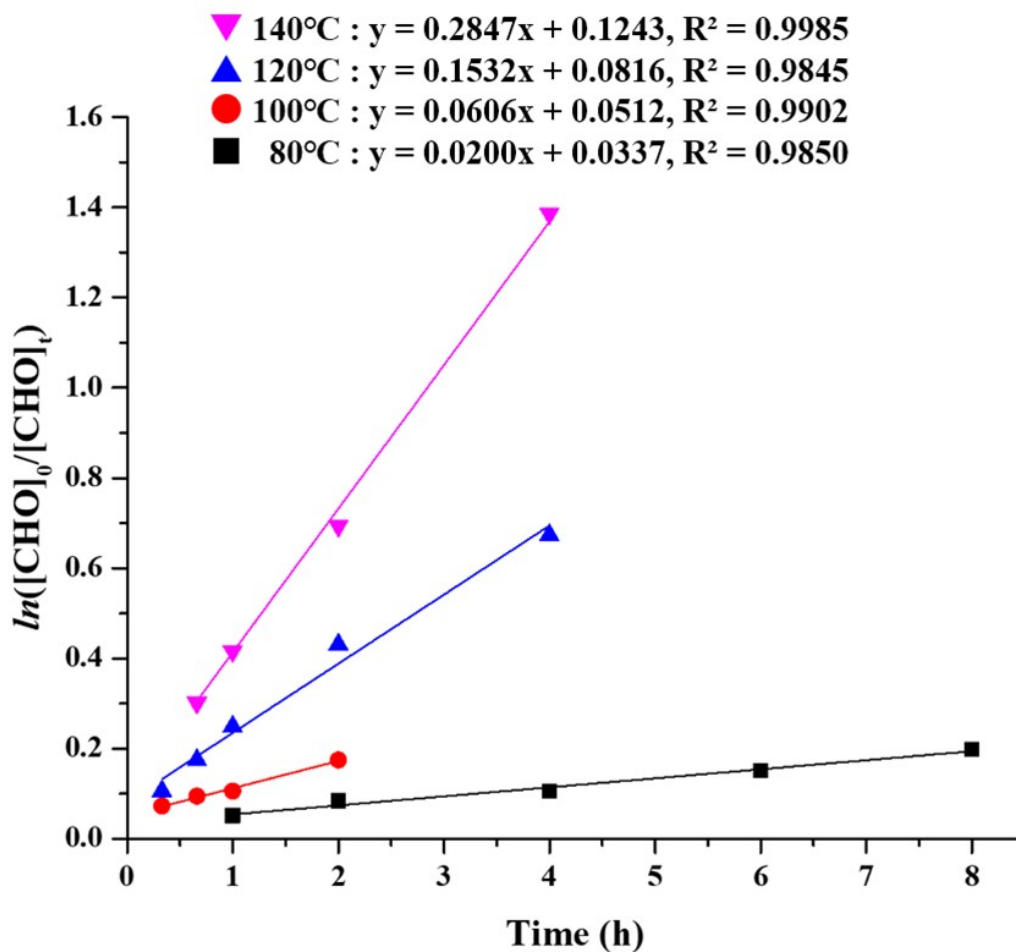
(a)



(b)

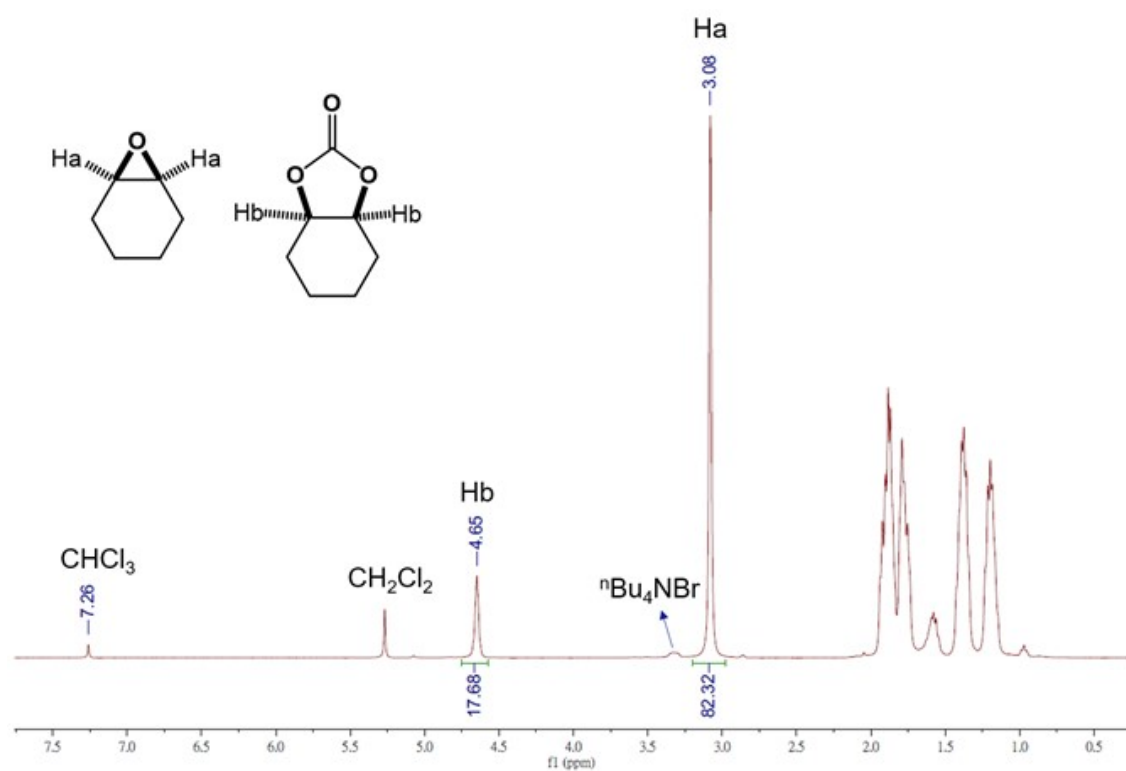


**Fig. S6** (a) ORTEP drawing of complex 7 with probability ellipsoids drawn at level 30%. (b) A repeating unit of complex 7.



**Fig. S7** Kinetic plots of  $\ln([\text{CHO}]_0/[\text{CHO}]_t)$  versus time for  $\text{CO}_2/\text{CHO}$  cycloaddition by complex **3** ( $[\text{CHO}]_0/[\mathbf{3}]_0 = 12000$ ) at 80, 100, 120 and 140 °C, under initial  $\text{CO}_2$  pressure of 300 psi.





**Fig. S8** <sup>1</sup>H NMR spectrum of the methine region of crude sample produced by cycloaddition of cyclohexene oxide and CO<sub>2</sub> using tetracosanuclear nickel complex **3** in the presence of nBu<sub>4</sub>NBr (0.4 mol%) at 60 °C and 300 psi CO<sub>2</sub> (400 MHz, CDCl<sub>3</sub>).

**Table S1** Selected bond lengths (Å) and bond angles (°) for dinickel complexes **1** and **2**

	<b>1</b>	<b>2</b>
Ni-N(aldimine)	2.0105(14)	2.007(2)
Ni-N(amine)	2.1270(15)	2.151(2)
Ni-O(phenoxy)	2.0797(12)	2.1035(17)
Ni-O(carboxylate)	2.0416(13)	2.0319(19)
Ni-O(water)	2.0963(13)	2.0796(18)
O(1)-Ni(1)-O(3)	166.57(5)	166.65(7)
O(2)-Ni(1)-N(2)	173.91(6)	172.34(7)
O(5)-Ni(1)-N(1)	168.84(5)	171.44(8)
O(1)-Ni(2)-N(4)	174.20(5)	171.79(9)
O(2)-Ni(2)-O(6)	167.03(5)	164.18(7)
O(5)-Ni(2)-N(3)	168.45(5)	172.29(8)
Ni(1)···Ni(2)	2.8568(3)	2.8849(4)

**Table S2** Selected bond lengths (Å) and bond angles (°) for tetracosanuclear nickel complexes **3** and **5–7**

	<b>3</b>	<b>5</b>	<b>6</b>	<b>7</b>
Ni-N(aldimine)	2.051(7)	2.075(7)	2.050(9)	2.023(11)
Ni-N(amine)	2.166(8)	2.198(7)	2.175(9)	2.172(11)
Ni-O(phenoxy)	2.043(6)	2.043(5)	2.053(6)	2.051(8)
Ni-O(carboxylate)	2.076(5)	2.073(5)	2.072(7)	2.078(8)
Ni-O(hydroxy)	2.027(5)	2.027(5)	2.028(6)	2.026(7)
O(1)-Ni(1)-N(2)	177.9(3)	176.7(2)	176.4(3)	177.4(3)
O(2)-Ni(1)-O(79)	178.5(2)	176.9(2)	178.4(3)	179.0(3)
O(6)-Ni(1)-N(1)	169.0(3)	168.1(2)	168.6(3)	170.7(4)
O(1)-Ni(2)-O(8)	176.3(2)	177.4(2)	177.3(3)	179.0(3)
O(3)-Ni(2)-O(4)	170.9(2)	172.3(2)	171.2(3)	172.2(3)
O(6)-Ni(2)-O(7)	175.5(2)	173.41(18)	173.9(2)	172.8(3)
O(5)-Ni(3)-O(14)	173.2(2)	174.55(19)	172.6(3)	172.9(3)
O(7)-Ni(3)-O(20)	170.6(2)	170.3(2)	169.0(2)	171.3(3)
O(8)-Ni(3)-O(16)	173.2(2)	173.34(19)	173.7(3)	174.1(3)
Ni(1)⋯Ni(2)	2.9959(14)	2.9843(12)	3.0146(17)	2.985(2)
Ni(2)⋯Ni(3)	3.0944(13)	3.0931(12)	3.1184(17)	3.090(2)

**Table S3** Cycloaddition reaction of CO<sub>2</sub> and CHO catalyzed by dinuclear nickel complexes **1** and **2**

Entry	[CHO]:[Cocat.]:[Cat.]	Cat.	Cocat.	Time (h)	Temp (°C)	%CHO <sup>a</sup> Conv.	%CHC <sup>a</sup> (% <i>cis</i> )	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )
1	1000:0:1	<b>1</b>	-	24	120	1	>99(32)	10	<1
2	1000:1:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NCl	24	120	72	>99(84)	720	30
3	1000:1:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	24	120	71	>99(98)	710	30
4	1000:2:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	24	120	88	>99(>99)	880	37
5	1000:4:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	24	120	96	>99(>99)	960	40
6	1000:4:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	4	80	15	>99(>99)	90	23
7	1000:4:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	4	100	23	>99(>99)	230	58
8	1000:4:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	4	120	63	>99(>99)	630	158
9	1000:4:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	4	140	75	>99(>99)	750	188
10	1000:4:1	<b>1</b>	<i>n</i> Bu <sub>4</sub> NBr	24	140	99	>99(>99)	990	41
11	1000:4:1	<b>2</b>	<i>n</i> Bu <sub>4</sub> NBr	4	120	50	>99(98)	500	125

Reaction conditions: 50.0 mmol CHO,  $p\text{CO}_2^0 = 300$  psi. <sup>a</sup>Based on <sup>1</sup>H NMR analysis of the reaction mixture.

<sup>b</sup>TON = number of moles of CHO consumed per mole of catalyst. <sup>c</sup>TOF = TON per hour.

**Table S4** Cycloaddition reaction of CO<sub>2</sub> and alicyclic epoxides catalyzed by tetracosanuclear Ni complexes **3**

Entry	epoxide	% epoxide <sup>a</sup> Conv.	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )
1	VCHO	97	11640	485
2	CPO	>99	12000	500
3 <sup>d</sup>	CHO	18	2160	90

Reaction conditions: [epoxide]:[<sup>n</sup>Bu<sub>4</sub>NBr]:[Ni-ion] = 1000:4:2, 0.00417 mmol catalyst, 50.0 mmol alicyclic epoxide, *p*CO<sub>2</sub><sup>0</sup> = 300 psi, 140 °C, 24 h. <sup>a</sup>Based on <sup>1</sup>H NMR analysis of the reaction mixture. <sup>b</sup>TON = number of moles of alicyclic epoxide consumed per mole of catalyst. <sup>c</sup>TOF = TON per hour. <sup>d</sup>T = 60 °C.

**Table S5** Kinetic studies of CO<sub>2</sub>/CHO copolymerization catalyzed by tetracosanuclear nickel complex **3** at various temperatures (80, 100, 120 and 140 °C)

Entry	Temp (°C)	Time/h	CHO Conv. (%) <sup>a</sup>	ln([CHO] <sub>0</sub> /[CHO] <sub>t</sub> )
1	80	1	5	0.0513
2	80	2	8	0.0834
3	80	4	10	0.1054
4	80	6	14	0.1508
5	80	8	18	0.1985
6	100	0.33	7	0.0726
7	100	0.66	9	0.0943
8	100	1	10	0.1054
9	100	2	16	0.1744
10	120	0.33	10	0.1054
11	120	0.66	16	0.1744
12	120	1	22	0.2485
13	120	2	35	0.4308
14	120	4	49	0.6733
15	140	0.33	20	0.2231
16	140	0.66	26	0.3011
17	140	1	34	0.4155
18	140	2	50	0.6931

Reaction conditions: [CHO]:[<sup>n</sup>Bu<sub>4</sub>NBr]:[**3**] = 12000:4:1, 0.00417 mmol catalyst, 50.0 mmol CHO, *p*CO<sub>2</sub><sup>0</sup> = 300 psi.

<sup>a</sup>Based on <sup>1</sup>H NMR analysis of the reaction mixture.

**Table S6** Kinetic parameters for CO<sub>2</sub>/CHO copolymerization catalyzed by complex **3** at various reaction temperatures

Entry	Temp (°C)	Temp (K)	Temp <sup>-1</sup> (K <sup>-1</sup> )	Observed rate coefficient, <i>k</i> <sub>obs</sub> (h <sup>-1</sup> )	ln[ <i>k</i> <sub>obs</sub> ]	R·[ln( <i>h</i> · <i>k</i> <sub>obs</sub> / <i>k</i> <sub>B</sub> ·T)]
1	80	353.15	0.00283	0.0200	-3.9120	-278.839
2	100	373.15	0.00268	0.0606	-2.8035	-270.080
3	120	393.15	0.00254	0.1532	-1.8760	-262.803
4	140	413.15	0.00242	0.2847	-1.2563	-258.064

Reaction conditions: [CHO]:[<sup>n</sup>Bu<sub>4</sub>NBr]:[**3**] = 12000:4:1, 0.00417 mmol catalyst, 50.0 mmol CHO, *p*CO<sub>2</sub><sup>0</sup> = 300 psi.

**Table S7** Crystallographic data of nickel complexes **1–3** and **5–7**

	<b>1</b>	<b>2</b> ·0.25[C <sub>6</sub> H <sub>14</sub> ]·0.5[CH <sub>2</sub> C l <sub>2</sub> ]·0.25[H <sub>2</sub> O]	<b>3</b> ·10[C <sub>6</sub> H <sub>14</sub> ]·3[CH <sub>2</sub> Cl <sub>2</sub> ]·0.5 [H <sub>2</sub> O]
formula	C <sub>34</sub> H <sub>52</sub> F <sub>2</sub> N <sub>4</sub> Ni <sub>2</sub> O <sub>9</sub>	C <sub>30</sub> H <sub>45</sub> ClF <sub>2</sub> N <sub>4</sub> Ni <sub>2</sub> O <sub>7.25</sub>	C <sub>223</sub> H <sub>379</sub> Cl <sub>6</sub> F <sub>8</sub> N <sub>16</sub> Ni <sub>24</sub> O <sub>80.5</sub>
Formula weight	816.21	768.57	6346.14
Temp (K)	150.0	150.15	150.0
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a (Å)	14.7730(5)	12.1743(8)	24.8794(10)
b (Å)	12.7347(5)	17.2045(12)	26.4236(10)
c (Å)	20.8529(8)	18.9504(13)	43.2603(17)
α (deg)	90	107.870(2)	90
β (deg)	92.829(2)°	107.105(3)	93.397(2)
γ (deg)	90	99.032(2)	90
<i>V</i> (Å <sup>3</sup> )	3918.3(3)	3474.7(4)	28389.5(19)
<i>Z</i>	4	4	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.384	1.469	1.485
μ (Mo Kα)(mm <sup>-1</sup> )	1.025	1.221	1.689
<i>F</i> (000)	1720	1608	13276
Reflections collected	61192	71803	342711
No. of parameters	492	799	2641
Indep. reflns ( <i>R</i> <sub>ini</sub> )	8099 (0.0486)	16506 (0.0445)	49878 (0.0607)
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0283	0.0398	0.0832
w <i>R</i> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0699	0.1071	0.2130
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.038	1.034	1.063



**Table S7** Crystallographic data of nickel complexes **1–3** and **5–7** (Cont'd)

	5·58[CH <sub>2</sub> Cl <sub>2</sub> ]	6·0.5[H <sub>2</sub> O]·10[CH <sub>2</sub> Cl <sub>2</sub> ]·9[C <sub>6</sub> H <sub>14</sub> ]	7·12[C <sub>6</sub> H <sub>14</sub> ]·0.5[H <sub>2</sub> O]
formula	C <sub>234</sub> H <sub>388</sub> Cl <sub>116</sub> N <sub>16</sub> Ni <sub>24</sub> O <sub>88</sub>	C <sub>248</sub> H <sub>427</sub> Br <sub>8</sub> Cl <sub>20</sub> N <sub>16</sub> Ni <sub>24</sub> O <sub>80.5</sub>	C <sub>250.5</sub> H <sub>424</sub> N <sub>16</sub> Ni <sub>24</sub> O <sub>88.5</sub>
Formula weight	10354.82	7678.35	6437.07
Temp (K)	150.0	150.0	150.0
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	<i>I4/m</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
a (Å)	24.8850(12)	33.816(4)	33.427(5)
b (Å)	24.8850(12)	26.775(4)	26.526(4)
c (Å)	73.876(6)	36.089(5)	35.933(5)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	90	90.081(7)	90.278(6)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	45749(6)	32676(8)	31861(8)
<i>Z</i>	4	4	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.503	1.561	1.342
$\mu$ (Mo K $\alpha$ )(mm <sup>-1</sup> )	1.700	2.562	1.455
<i>F</i> (000)	21008	15852	13580
Reflections collected	318236	296033	347437
No. of parameters	701	2938	2848
Indep. reflns ( <i>R</i> <sub>int</sub> )	20267 (0.0525)	57357 (0.1287)	55965 (0.1589)
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0846	0.0875	0.1080
w <i>R</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.2303	0.2525	0.3204
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.128	1.009	1.090