# **Supplementary Information**

## Aza-cyclophane Supported Macrocyclic α-Diimine Nickel Catalyst for Ethylene Polymerization

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### Contents

Supplementary Methods	2
Supplementary Tables	7
Supplementary Figures	8
Supplementary References	39

#### **Supplementary Methods**

General Procedures: 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 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz) or a Bruker AV500 (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz). The molecular weights ( $M_n$ ) and molecular weight distributions ( $M_w/M_n$ ) of polyethylenes were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 µm Mixed-B LS type columns at 150 °C. Melting points ( $T_m$ ) of polyethylenes and copolymers were measured through DSC analyses, which were carried out on a Mettler TOPEM TM DSC Instruments under nitrogen atmosphere at heating and cooling rates of 10 °C/min (temperature range: 20-160 °C). Elemental analysis was performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry. Mass spectra of the ligands and complexes were recorded on an Acquity UPLC & Quattro Premier. Infrared spectra were recorded on a Bruker VERTEX 70 Fourier Transform Infrared Spectrometer, Germany (wave number range: 4000-400 cm<sup>-1</sup>, resolution: 2cm<sup>-1</sup>, scan number: 32 times). Stress/strain experiments were performed at 5 mm/min by means of an Electromechanical Universal Testing Machine (E43.104) at room temperature. Polymers were meltpressed at 200 °C to obtain the test specimens, which have 15-mm gauge length, 2-mm width and thickness of 1 mm. At least three specimens of each polymer were tested.

**X-Ray diffraction**:<sup>1-4</sup> Data collections were performed at -100 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å).The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. All structures were solved by direct methods and refined by full-matrix least-squares procedures on  $F^2$  using Olex2. 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.

**Materials:** Pre-ligand<sup>5</sup>, **L-open**<sup>6</sup> and **L-closed**<sup>7</sup> were prepared using literature procedure. All other reagents were commercially available and used as received.

#### **Preparation of Ligands and Catalysts**



**2,6-Bis(4-nitrophenyl)-4-methylaniline:** To a mixture of 2,6-dibromo-4-methylaniline (22.6 mmol, 6.0 g), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nitrobenzene (54.2 mmol, 13.5 g), and Na<sub>2</sub>CO<sub>3</sub> (113.2 mmol, 12 g) were added toluene (250 mL), EtOH (50 mL) and H<sub>2</sub>O (50 mL) at room temperature under N<sub>2</sub> atmosphere. The suspension was degassed under reduced pressure, followed by the refilling of N<sub>2</sub> gas. After that, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.4 mmol, 0.52 g) was added to the suspension. After stirring for 48 h at 90 °C, the organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was filtered through Celite pad, and evaporated. The residue was purified by column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1/2, R<sub>f</sub> = 0.35) to afford the title compound as an orange solid in 98.8% yield.

<sup>1</sup>**H** NMR (500 MHz, 298 K, CDCl<sub>3</sub>, 7.26 ppm): δ = 8.34-8.32 (d, *J* = 8.7 Hz, 4H, aryl-*H*), 7.71-7.69 (d, *J* = 8.7 Hz, 4H, aryl-*H*), 7.00 (s, 2H, aryl-*H*), 3.67 (s, 2H, -NH<sub>2</sub>), 2.33 (s, 3H, aryl-CH<sub>3</sub>) ppm.



**Preparation of pre-ligand:** ZnCl<sub>2</sub> (0.277 g, 2.0 mmol) and acenaphthenequinone (0.237 g, 1.3 mmol) were suspended in glacial acetic acid (5 mL). 2,6-Bis(4-nitrophenyl)-4-methylaniline (1.00 g, 2.9 mmol) was added, and the reaction mixture was refluxed under stirring overnight. The solution was allowed to cool to room temperature the next morning, and a bright orange-red solid precipitated. The solid was separated by filtration and washed with acetic acid ( $3 \times 5$  mL) and diethyl ether ( $5 \times 6$  mL), to remove remaining acetic acid. Drying under vacuum gave bright orange-red, poorly soluble solid. According to the reported literature, the solid is zinc diimine complex. Next the product of the previous step was suspended in methylene chloride (30 mL), and a solution of potassium oxalate (0.922 g, 5 mmol) in water (5 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water ( $3 \times 20$  mL) and dried with MgSO<sub>4</sub>. After filtration the solvent was removed under vacuum to give the crude product as an dark orange powder. The powder was purified by hot washing with methanol reflux to afford the title compound as an orange solid (0.7 g). The total yield of two steps is 63.6%.

<sup>1</sup>**H** NMR (500 MHz, 298 K, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 7.84-7.82 (d, *J* = 8.6 Hz, 8H, aryl-*H*), 7.57-7.55 (d, *J* = 8.6 Hz, 8H, aryl-*H*), 7.29 (s, 4H, aryl-*H*), 7.70-7.68 (d, *J* = 8.2 Hz, 2H, An-*H*), 7.27-7.25 (m, 2H, An-*H*), 6.68-6.66 (d, *J* = 7.2 Hz, 2H, An-*H*), 2.53 (s, 6H, aryl-*Me*) ppm.

<sup>13</sup>**C NMR** (125 MHz, 298 K, CDCl<sub>3</sub>, 77.16 ppm): δ = 161.69 (N=*C*), 146.70, 146.24, 144.40, 140.24, 135.70, 132.44, 130.29, 129.65, 129.60, 128.76, 127.86, 123.10, 122.62, 21.09 (aryl-*Me*) ppm.



**Preparation of Ligand L-open:** The pre-ligand (300 mg, 0.4 mmol), ammonium chloride (323 mg, 6.0 mmol), and Zn powder (400 mg, 6.1 mmol) were mixed with dry methanol (3 mL) under N<sub>2</sub> atmosphere and stirred for 1 h at room temperature. The solution gradually changes from a gray suspension to a purplish-red suspension. The reaction mixture was quenched with drop-by-drop water and filtered through a celite bed. The filtrate was extracted with ethyl acetate, dried over anhydrous MgSO<sub>4</sub> followed by vacuum evaporation. The crude compound was purified by column chromatography (hexane/ethyl acetate = 1/1, Rf = 0.20) to afford **L-open** as a red solid in 62.2% yield.

<sup>1</sup>**H** NMR (500 MHz, 298 K, CDCl<sub>3</sub>, 7.26 ppm):  $\delta = 7.09-7.07$  (d, J = 8.3 Hz, 8H, aryl-*H*), 7.03 (s, 4H, aryl-*H*), 6.35-6.33 (d, J = 8.3 Hz, 8H, aryl-*H*), 7.69-7.68 (d, J = 8.3 Hz, 2H, An-*H*), 7.28-7.26 (t, J = 7.8 Hz, 2H, An-*H*), 6.75-6.74 (d, J = 7.2 Hz, 2H, An-*H*), 5.41 (br, -NH<sub>2</sub>), 2.41 (s, 6H, aryl-*Me*) ppm.

<sup>13</sup>**C** NMR (125 MHz, 298 K, CDCl<sub>3</sub>, 77.16 ppm): δ = 161.56 (N=*C*), 144.64, 140.35, 133.48, 131.63, 131.03, 130.98, 130.67, 130.50, 130.16, 128.24, 127.72, 122.94, 115.20, 21.00 (aryl-*Me*) ppm.

**Elemental analysis:** Anal. Calcd for C<sub>50</sub>H<sub>40</sub>N<sub>6</sub>: C, 82.84; H, 5.56; N, 11.59. Found: C, 82.93; H, 5.60; N, 12.07.

MALDI-TOF-MS (m/z): Calcd for C<sub>50</sub>H<sub>40</sub>N<sub>6</sub>: 724.33, found: 725.3 [M+H]<sup>+</sup>.



**Preparation of Ligand L-closed:** Lithium aluminum hydride (202 mg, 5.3 mmol) was added to dry THF (5 mL) to form a 1M solution. The lithium aluminum hydride solution was slowly added to a solution of pre-ligand (300 mg, 0.4 mmol) in dry THF (3 mL) under N<sub>2</sub> atmosphere at room temperature. At the beginning of the drop, the color of the solution deepened from orange to dark green, and when the drop was completed, it was a brown suspension. The reaction mixture was stirred for 5 h at room temperature and the brown suspension quenched with water (5 mL). After extraction with DCM (3×15 mL), the combined organic layers were washed with brine (20 mL), dried with MgSO<sub>4</sub> followed by vacuum evaporation. The crude compound was purified by column chromatography (hexane/ethyl acetate = 1/4, R<sub>f</sub> = 0.80) to afford the product as a reddish brown solid in 19.5% yield.

<sup>1</sup>**H** NMR (500 MHz, 298 K, CDCl<sub>3</sub>, 7.26 ppm):  $\delta = 7.17-7.14$  (m, 8H, aryl-*H*), 6.47 (m, 8H, aryl-*H*), 6.08 (s, 4H, aryl-*H*), 5.81 (s, 4H, -N*H*), 7.88-7.87 (d, J = 8.2 Hz, 2H, An-*H*), 7.45-7.42(m, 2H, An-*H*),

6.69 (m, 2H, An-*H*), 2.45 (s, 6H, aryl-*Me*) ppm.

<sup>13</sup>**C NMR** (125 MHz, 298 K, CDCl<sub>3</sub>, 77.16 ppm): δ = 171.32 (N=*C*), 146.50, 145.81, 140.04, 133.14, 131.85, 131.22, 131.04, 130.28, 130.15, 128.49, 128.31, 128.23, 123.64, 116.34, 115.39, 21.03 (aryl-*Me*) ppm.

**Elemental analysis:** Anal. Calcd for C<sub>50</sub>H<sub>36</sub>N<sub>6</sub>: C, 83.31; H, 5.03; N, 11.66. Found: C, 83.16; H, 5.01; N, 11.73.

MALDI-TOF-MS (m/z): Calcd for C<sub>50</sub>H<sub>36</sub>N<sub>6</sub>: 720.30, found: 721.3 [M+H]<sup>+</sup>.



**Preparation of Ni-open**: To a solution of ligand L-open (120 mg, 0.17 mmol) in dry dichloromethane (25 mL) was added 51 mg (0.17 mmol) of NiBr<sub>2</sub>(DME). After stirring the mixture for 24 h at room temperature, the insoluble solid powder was filtered, the solvent was evaporated, and the brown solid powder was washed with ether (10 mL  $\times$  2) and dried under vacuum to obtain **Ni-open** (90 mg, 57.6% yield).

**Elemental analysis:** Anal. Calcd for C<sub>50</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>6</sub>Ni: C, 63.66; H, 4.27; N, 8.91. Found: C, 63.90; H, 4.24; N, 8.95.

MALDI-TOF-MS (m/z): Calcd for C<sub>50</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>6</sub>Ni: 940.10, found: 724.3 [M-Ni-2Br]<sup>+</sup>.



**Preparation of Ni-closed**: To a solution of ligand L-closed (200 mg, 0.28 mmol) in dry THF (35 mL) was added 95 mg (0.31 mmol) of NiBr<sub>2</sub>(DME). After stirring the mixture for 3 days at room temperature, the insoluble solid powder was filtered, the solvent was evaporated, and the green powder was washed with ether (10 mL  $\times$  2) and dried under vacuum to obtain **Ni-closed** (157 mg, 60.5% yield).

**Elemental analysis:** Anal. Calcd for C<sub>50</sub>H<sub>36</sub>Br<sub>2</sub>N<sub>6</sub>Ni: C, 63.93; H, 3.86; N, 8.95. Found: C, 63.70; H, 4.90; N, 8.89.

**MALDI-TOF-MS** (m/z): Calcd for C<sub>50</sub>H<sub>36</sub>Br<sub>2</sub>N<sub>6</sub>Ni: 936.07, found: 778.2 [M-2Br]<sup>+</sup>, 718.3 [M-Ni-2Br-2H]<sup>+</sup>.

#### **General Procedure for Ethylene Polymerization**

#### A general procedure for ethylene polymerization using Ni catalyst

In a typical experiment, a 350 mL glass pressure reactor connected with a high-pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature 98 mL of Toluene ( $CH_2Cl_2$ ) and Al reagents was added to the reactor under N<sub>2</sub> atmosphere, then the desired amount of Ni catalyst in 2 mL of  $CH_2Cl_2$  was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and kept constant at 8 bar of ethylene. After specific time, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL acidic EtOH (10% HCl in EtOH) to the reactor and dried in a vacuum oven at 50 °C to constant weight for at least 48 h.

#### A general procedure for effect of the Bu<sub>2</sub>Mg on ethylene polymerization using Ni catalyst

In a typical experiment, a 50 mL glass pressure reactor connected with a high-pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature 18 mL of *n*-hexane and the mixture of DEAC and Bu<sub>2</sub>Mg was added to the reactor under N<sub>2</sub> atmosphere, then the desired amount of Ni catalyst in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and kept constant at 8 bar of ethylene. After specific time, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL acidic EtOH (10% HCl in EtOH) to the reactor and dried in a vacuum oven at 50 °C to constant weight for at least 48 h.

#### The specific information of Al reagents used in ethylene polymerization

The MAO (from Albemarle Corporation, USA) used in this polymerization is a toluene solution with a concentration of 2 mol·L<sup>-1</sup>. The MMAO used in this polymerization is a heptane solution with a concentration of 1.5 mol·L<sup>-1</sup>. The DEAC (from Energy Chemical, EnergySeal) used in this polymerization is a toluene solution with a concentration of 1.0 mol·L<sup>-1</sup>. The EAD (from Energy Chemical, EnergySeal) used in this polymerization is a toluene solution with a concentration of 1.8 mol·L<sup>-1</sup>. The EASC (from Aladdin) used in this polymerization is a toluene solution with a concentration of 0.4 mol·L<sup>-1</sup>. The TEA (from Energy Chemical, EnergySeal) used in this polymerization is a toluene solution with a concentration of 1.0 mol·L<sup>-1</sup>.

Both DEAC and Bu<sub>2</sub>Mg used in mixture is a hexanes solution of 1.0 mol·L<sup>-1</sup> (from Energy Chemical, EnergySeal).

	Ni-closed
Formula	C50H36Br2N6Ni
Formula weight	938.34
Crystal dimensions (mm <sup>3</sup> )	$0.30 \times 0.08 \times 0.06$
Crystal system	monoclinic
Space group	P 1 21/n 1
a (Å)	11.8543(4)
b (Å)	22.0339(8)
c (Å)	17.7751(7)
α (°)	90
β (°)	102.6380(10)
γ (°)	90
Volume (Å <sup>3</sup> )	4530.3(3)
Ζ	4
<i>T</i> (K)	173(2)
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.371
$\mu (\mathrm{mm}^{-1})$	2.232
F(000)	1888
No. of rflns. collected	118654
No. of indep. rflns. $/R_{int}$	13263 / 0.1138
No. of obsd. rflns. $[I_0 > 2\sigma(I_0)]$	7810
Data / restraints / parameters	13263 / 0 / 534
$R_1 / wR_2 [I_0 > 2\sigma(I_0)]$	0.0523 / 0.1145
$R_1 / wR_2$ (all data)	0.1139 / 0.1376
GOF (on $F^2$ )	1.021
Largest diff. peak and hole (e $Å^{-3}$ )	0.522 / -0.636
CCDC No.	2300226

Supplementary Table 1. Crystallographic data for Ni-closed.

# **Supplementary Figures**

NMR figures of ligands and complexes



Figure S1. <sup>1</sup>H NMR spectrum of 2,6-Bis(4-nitrophenyl)-4-methylaniline in CDCl<sub>3</sub>.



- 2.53







3800 3500 3200 2900 2600 2300 2000 1700 1400 1100 800 500 **Figure S4.** Infrared spectrum of **pre-ligand** solid powder.



Figure S6. <sup>13</sup>C NMR spectrum of L-closed in CDCl<sub>3</sub>.



Figure S7. MALDI-TOF spectrum of L-open in CH<sub>2</sub>Cl<sub>2</sub>.



Figure S8. Infrared spectrum of L-open solid powder.



Figure S10. <sup>13</sup>C NMR spectrum of L-closed in CDCl<sub>3</sub>.



Figure S11. MALDI-TOF spectrum of L-closed in  $CH_2Cl_2$ .



Figure S12. Infrared spectrum of L-closed solid powder.



Figure S13. <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of L-closed in CDCl<sub>3</sub>.



Figure S14. MALDI-TOF spectrum of Ni-open in CH<sub>2</sub>Cl<sub>2</sub>.



Figure S15. MALDI-TOF spectrum of Ni-closed in CH<sub>2</sub>Cl<sub>2</sub>.

### NMR figures of polymers



**Figure S16.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niclosed** from table 1, entry 1.



**Figure S17.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niclosed** from table 1, entry 2.



**Figure S18.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 1, entry 3.



**Figure S19.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 1, entry 4.



**Figure S20.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niclosed** from table 1, entry 5.



**Figure S21.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niclosed** from table 1, entry 6.



**Figure S22.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niclosed** from table 2, entry 1.



**Figure S23.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 2, entry 2.



**Figure S24.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 2, entry 3.



**Figure S25.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 2, entry 4.



**Figure S26.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 2, entry 5.



**Figure S27.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niclosed** from table 2, entry 6.



**Figure S28.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 2, entry 7.



**Figure S29.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niopen** from table 2, entry 8.



**Figure S31.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Niopen** from table 2, entry 10.



**Figure S33.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 3, entry 2.



**Figure S35.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 3, entry 4.



**Figure S36.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni-closed** from table 3, entry 5.



**closed** from Table 2.

#### **GPC figures of polymers**



Figure S38. GPC trace of the polymer from table 1, entry 1.



Figure S39. GPC trace of the polymer from table 1, entry 3.



Figure S40. GPC trace of the polymer from table 1, entry 4.



Figure S41. GPC trace of the polymer from table 1, entry 6.



Figure S42. GPC trace of the polymer from table 2, entry 2.



Figure S43. GPC trace of the polymer from table 2, entry 4.



Figure S44. GPC trace of the polymer from table 2, entry 5.



Figure S45. GPC trace of the polymer from table 3, entry 5.

# DSC traces of polymers



Figure S46. DSC data of the polymer from table 1, entry 1.



Figure S47. DSC data of the polymer from table 1, entry 2.



Figure S48. DSC data of the polymer from table 1, entry 3.



**Figure S49.** DSC data of the polymer from table 1, entry 4.



Figure S50. DSC data of the polymer from table 1, entry 5.



Figure S51. DSC data of the polymer from table 1, entry 6.



Figure S52. DSC data of the polymer from table 2, entry 1.



Figure S54. DSC data of the polymer from table 2, entry 4.



Figure S55. DSC data of the polymer from table 2, entry 5.



Figure S56. DSC data of the polymer from table 2, entry 6.



Figure S57. DSC data of the polymer from table 2, entry 7.



Figure S58. DSC data of the polymer from table 2, entry 8.



Figure S59. DSC data of the polymer from table 2, entry 9.



Figure S60. DSC data of the polymer from table 2, entry 10.



**Figure S61.** DSC data of the polymer from table 3, entry 1.



Figure S62. DSC data of the polymer from table 3, entry 2.



**Figure S63.** DSC data of the polymer from table 3, entry 3.



**Figure S64.** DSC data of the polymer from table 3, entry 4.





**Figure S66.** The photograph of the polymer products from Table 3 entry 3 (500 equiv. Et<sub>2</sub>AlCl, 150 equiv. Bu<sub>2</sub>Mg).



**Figure S67.** The photograph of the polymer products from Table 3 entry 1 (500 equiv. Et<sub>2</sub>AlCl, 0 equiv. Bu<sub>2</sub>Mg).



**Figure S68.** The photograph of the catalytic system. (left: 0.3  $\mu$ mol cat./500 equiv. Et<sub>2</sub>AlCl/150 equiv. Bu<sub>2</sub>Mg; right: 0.3  $\mu$ mol cat./500 equiv. Et<sub>2</sub>AlCl/0 equiv. Bu<sub>2</sub>Mg).



**Figure S69.** The photograph of the catalytic system after 4h. (left: 0.3  $\mu$ mol cat./500 equiv. Et<sub>2</sub>AlCl/150 equiv. Bu<sub>2</sub>Mg; right: 0.3  $\mu$ mol cat./500 equiv. Et<sub>2</sub>AlCl/0 equiv. Bu<sub>2</sub>Mg).

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