

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY ( Leave Blank)	2. REPORT DATE 09-27-04	3. REPORT TYPE AND DATES COVERED Final report: 07/01/01-06/30/04	
4. TITLE AND SUBTITLE Design of Nanoscale Polymeric Materials with Transition Metal Catalysis		5. FUNDING NUMBERS DAAD190110686	
6. AUTHOR(S) Zhibin Guan		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, Irvine 516 Rowland Hall, Department of Chemistry University of California, Irvine, CA 92697-2025			
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER  42395-CH-H  o \	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The ARO grant provided partial support to the research efforts in PI's laboratory on development of highly efficient catalytic syntheses of polymeric materials having complex topologies and functionalities from simple commercial olefinic monomers. In the past three years, we have made significant progress in both developing new polymeric materials and designing new catalysts. Specifically, the following accomplishments were achieved in this laboratory: (1) successfully demonstrated a new strategy of one-pot synthesis of hyperbranched polymers via direct free radical polymerization of commercial divinyl monomers by using a cobalt chain transfer catalyst; (2) developed a highly efficient one-pot synthesis of amphiphilic dendritic molecular nanocarriers that can be used for drug delivery and scaffold for multivalent ligands; (3) developed new N <sup>^</sup> P based and bisazaferrocene ligands for late transition metal polymerization catalysts; and (4) developed a novel family of cyclophane-based late transition metal complexes that are highly active and stable catalysts for olefin polymerization.			
14. SUBJECT TERMS nanomaterial, polymers, dendrimers, hyperbranched polymers, polymer topology, polymer architecture, amphiphilic dendrimers, drug delivery, polymerization catalysis, chain walking		15. NUMBER OF PAGES  66	
17. SECURITY CLASSIFICATION OR REPORT <b>UNCLASSIFIED</b>		16. PRICE CODE	
		20. LIMITATION OF ABSTRACT  <b>UL</b>	
18. SECURITY CLASSIFICATION ON THIS PAGE <b>UNCLASSIFIED</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>UNCLASSIFIED</b>		

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

**REPORT DOCUMENTATION PAGE (SF298)**  
**(Continuation Sheet)**

**Papers submitted but not published:**

1. "Ligand Electronic Effects on Late Transition Metal Polymerization Catalysts" Popeney, C.; Guan, Zhibin. Manuscript submitted to *JACS*.

**Papers published in peer-reviewed journals:**

1. "Transition Metal Catalyzed One-pot Synthesis of Water-Soluble Dendritic Molecular Nanocarriers" Chen, G. and Guan, Zhibin. *J. Am. Chem. Soc.* **2004**, *126*, 2662. (This work was highlighted by *Chemical & Engineering News* **2004**, March 1, page 27).
2. "Cyclophane-Based Highly Active Late-Transition-Metal Catalysts for Ethylene Polymerization" Camacho, D.; Salo, E. V.; Ziller, J. W.; Guan, Zhibin. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821.
3. "Synthesis and Structure of *m*-Terphenyl-Based Cyclophanes with Nitrogen Intra-Annular Functional Groups" Camacho, D.; Salo, E. V. Guan, Zhibin. *Org. Lett.* **2004**, *6*, 865.
4. "Synthesis of Functional Olefin Copolymers with Controllable Topology Using a Chain Walking Catalyst" Chen, G.; Ma, S.; Guan, Zhibin. *J. Am. Chem. Soc.* **2003**, *125*, 6697.
5. "Late-Transition-Metal Complexes with Bisazaferrocene Ligands for Ethylene Oligomerization" Salo, E.; Guan, Zhibin. *Organometallics* **2003**, *22*, 5033.
6. "Control of Polymer Topology through Late-Transition-Metal Catalysis" Guan, Zhibin. *J. Polym. Soc. Part A: Polym. Chem.* **2003**, *41*, 3680.
7. "Control of Polymer Topology through Transition Metal Catalysis: Synthesis of Hyperbranched Polymers by Cobalt-Mediated Free Radical Polymerization" Guan, Zhibin. *J. Am. Chem. Soc.* **2002**, *124*, 5616.
8. "Synthesis of New Phosphine-imine Ligands and Their Influence on the Thermal Stability of Late Transition Metal Polymerization Catalysts" Guan, Zhibin and Marshall, W. *Organometallics* **2002**, *21*, 3580.
9. "Control of Polymer Topology by Chain Walking Catalysts" Guan, Zhibin. *Chem. Eur. J.* **2002**, *8*, 3086.

**Papers published in conference proceedings:**

1. "Control of Polymer Topology through Transition-Metal Catalysis: Synthesis of Functional Olefin Copolymers Using a Chain Walking Catalyst" Guan, Zhibin; Chen, Guanghui; Ma, Sharon X. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2003**, *44*(2), 14.
2. Synthesis of New Late Transition Metal Catalysts Containing Nitrogen-phosphine Ligands for Olefin Polymerization. *Polym. Preprints (American Chemical Society)* **2002**, *43*(1), 295.
3. "Tuning Polymer Topology by Late Transition Metal Catalyst: From Linear to Hyperbranched to Dendritic" Guan, Zhibin; Cotts, Patricia M. *Polym. Mater. Sci. Eng.* **2001**, *84*, 382.

**Papers presented in conference meetings (only list invited talks):**

1. "Chain Walking - A New Strategy to Control Polymer Topology", Presented at the **International Workshop on Branched Polymers for Performance**, Williamsburg, Virginia, May 23-26, 2004.

2. "Chain Walking - A New Strategy to Control Polymer Topology", Presented at the **Advances in Polyolefins Conference**, Sonoma Valley, CA, October 5-8, 2003.
3. "New Polymeric Materials Design at the Interfaces with Catalysis and Biology", Presented at the **7th International Symposium on Polymers for Advanced Technologies Conference**, Fort Lauderdale, FL, September 21-23, 2003.
4. "Chain Walking - A New Strategy to Control Polymer Topology", Presented at the **3<sup>rd</sup> International Symposium on Dendrimer and Hyperbranched Polymers**, Berlin, Germany, September 17-21, 2003.
5. "Control of Polymer Topology by Transition Metal Catalysis", Tutorial Lecture presented at the **226<sup>th</sup> American Chemical Society National Meeting**, New York City, September 7, 2003.
6. "Chain Walking - A New Strategy to Control Polymer Topology", Presented at the **DOD Multidisciplinary University Research Initiative (MURI) Workshop**, Baltimore, Maryland, May 27-28, 2003.
7. "New Polymeric Materials Design at the Interfaces with Catalysis and Biology", Presented at the **US-Japan Symposium on Advanced Polymer Chemistry for the 21<sup>st</sup> Century**, Nagoya City, Japan, December 7-10, 2002.
8. "Synthesis of Transition Metal Complexes Containing New Phosphine-Nitrogen Ligands for Olefin Polymerization" Presented at the **223<sup>rd</sup> American Chemical Society National Meeting**, Orlando, FL, April 7-11, 2002.
9. "Chain Walking: A New Strategy to Control Polymer Topology" Presented at the **ACS Physical and Materials Chemistry Symposium**, Spokane, WA, June 19-22, 2002.

**Scientific personnel supported by this grant:**

Chris Popeney, 3<sup>rd</sup> yr graduate student; Guanghui Chen, 5<sup>th</sup> yr graduate student

## Final Report for “Design of Nanoscale Polymeric Materials with Transition Metal Catalysis”

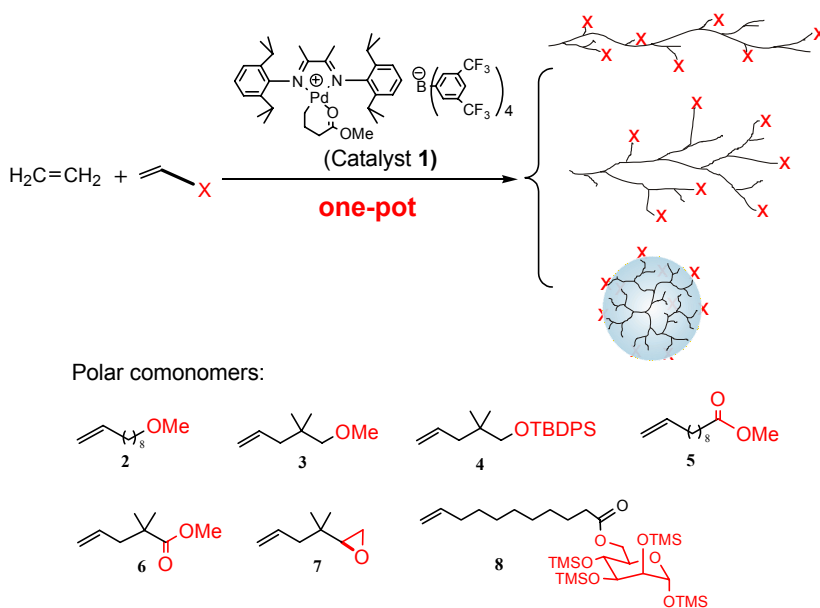
### a. Introduction.

With partial support from the ARO (Grant #: DAAD19-01-1-0686), my students and I have been engaged in development of highly efficient catalytic synthesis of polymeric materials having controlled branching topology and functionality. For many applications, polymeric materials are very sensitive to feedstock prices and environmental regulations, which provides the driving force to design catalytic routes that can transform simple commercial monomers into new polymers with improved and/or new structures and properties. My group has been exploring a new concept of synthesizing dendritic polymers through transition metal catalyzed one-pot polymerization of simple commercial monomers.<sup>1,2</sup> We demonstrated that polymers having various topologies could be prepared from transition-metal catalyzed polymerization of simple olefinic monomers. In one strategy, polyethylene topologies were successfully controlled from linear to hyperbranched to dendritic by controlling the competition between chain walking and insertion using the Brookhart palladium-bisimine chain walking catalyst.<sup>3</sup> In parallel to polymer synthesis, new ligands and their transition metal complexes were also explored to enhance our capability in polymer synthesis. In this report, the progress we made in both polymer synthesis and catalyst design during the funding period will be summarized.

### b. Progress in One-Pot Catalytic Polymer Syntheses

#### b.1. One-pot synthesis of functional polymers having controllable topology.

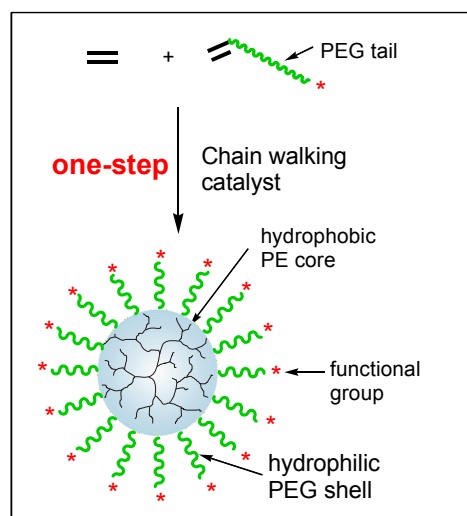
Following our previous success in controlling polyethylene branching topology using a Pd- $\alpha$ -diimine chain walking catalyst, we demonstrated for the first time that the branching topology of ethylene polar copolymers can be controlled by simply changing ethylene pressure and the comonomer concentrations using the chain walking catalyst.<sup>4</sup> For ethylene copolymerization with the ether and ester comonomers, the copolymer topology becomes more dendritic as the concentrations of ethylene and comonomers are decreasing. This provides a simple route to access a wide variety of functional polymers with controllable topologies for many potential applications. As a few examples, we synthesized dendritic copolymers containing multiple hydroxyl, epoxide and mannose groups.<sup>4</sup> Although these polymers are not perfect dendrimers because of their polydisperse nature in molecular weight and branching length distribution, their branching topology and globular structure resemble those of dendrimers and many chemical and physical properties of these dendritic polymers made by the chain walking catalyst are also similar to dendrimers made of the same building block. Whereas perfect dendrimers have beautiful structural



precision and uniformity, the multi-step syntheses involved in their preparations sometimes limit their general applications. Our approach offers a simple one-pot process for making functional polymers with tunable topologies starting with simple olefinic monomers. Due to the ease of synthesis and the availability of many olefinic monomers, these functional dendritic polymers may find many general applications in which polymer structural precision and uniformity are not critical.

### b.2. One-pot synthesis of functional polymers having controllable topology.

Amphiphilic soft nanoparticles have many potential applications including drug delivery and presenting multivalent ligands. Developing efficient synthesis of this type of soft nanoparticles is challenging and needed. Using the Brookhart chain walking catalyst, we demonstrated that copolymerization of ethylene and a comonomer with a polyethylene glycol (PEG) tail afforded, in one step, amphiphilic copolymer having hydrophobic core and hydrophilic shell.<sup>5</sup> Light scattering, fluorescence and UV/Vis spectroscopic studies with Nile Red in aqueous solution showed unimolecular micellar properties for the copolymers. The unimolecular micellar properties coupled with the good water solubility and biocompatibility of the PEG moieties make these molecular nanocarriers promising candidates for a variety of biomedical applications such as delivering hydrophobic drugs and as stable three-dimensional scaffold to present multivalent antigens. One-step synthesis of fluorophilic-lipophilic type of unimolecular micelles are also developed with the same copolymerization strategy which will be explored for fluorous and CO<sub>2</sub> applications.

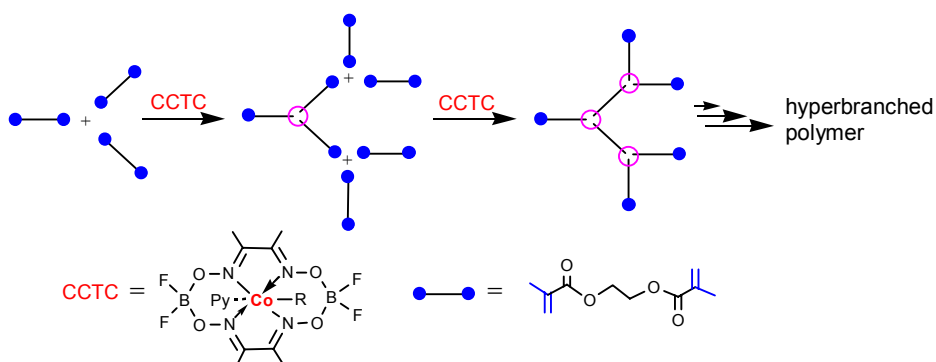


### b.3. One-pot synthesis of hyperbranched polymer by radical polymerization.

Following our success in controlling polyolefin branching topology using a Pd- $\alpha$ -diimine chain walking catalyst, we developed a new approach for the synthesis of hyperbranched polymers by direct free radical polymerization of divinyl monomers controlled by a cobalt chain transfer catalyst (CCTC).<sup>6</sup> By controlling the competition between propagation and chain transfer with CCTC, the free radical polymerization of ethylene glycol dimethacrylate afforded soluble hyperbranched polymers in one pot. The structure of the hyperbranched polymers was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR. The molecular weight and intrinsic viscosity of the hyperbranched polymers were measured by matrix-assisted laser desorption ionization (MALDI) mass spectrometry and size exclusion chromatography (SEC) equipped with triple detectors. The intrinsic viscosities of the hyperbranched polymers are much lower than those of their linear analogs and do not show molecular weight dependence. The unique structure and properties of these hyperbranched

polymers combined with the commercial availability of many divinyl monomers and the robustness of free radical

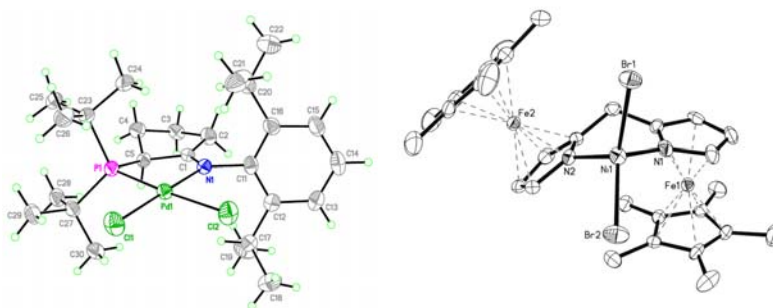
polymerization make this new approach attractive for the preparation of new functional materials.



## c. Progress in Development of New Polymerization Catalysts

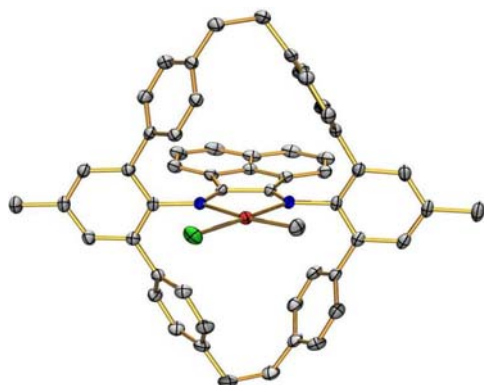
### c.1. New N<sup>^</sup>P ligands and bisazaferrocene ligands for Ni(II) and Pd(II) catalysts.

In parallel to our polymer synthesis, we spent significant amount of efforts on developing better late transition metal olefin polymerization catalysts. Whereas the Ni(II)- and Pd(II)- $\alpha$ -



bisimine catalysts exhibit excellent activity and good functional group tolerance, one severe limitation is their relatively low thermal stability. The catalysts decompose rapidly at temperatures about 50 °C for Pd(II)-  $\alpha$ -bisimine and 70 °C for Ni(II)-  $\alpha$ -bisimine catalysts, which is significantly lower than the decomposition temperatures of early transition metal such as Ziegler-Natta and single-site metallocene catalysts. For practical applications, significantly higher thermal stability is desired for process and economic considerations. With the attempt to address this critical issue in late-transition-metal polymerization catalysis, we have synthesized a few new family of chelating ligands and tested their complexes with late-transition metals for olefin polymerizations. We have successfully prepared new Pd(II) and Ni(II) catalysts containing new P<sup>^</sup>N ligands<sup>7</sup> and bisazaferrocene ligands,<sup>8</sup> which exhibit significantly higher thermal stability than the current  $\alpha$ -diimine counterparts. In the P<sup>^</sup>N ligands, we used a better  $\sigma$ -donating phosphine to replace one imine site of the bisimine ligands with the purpose to increase the binding strength of the ligand to the metal center. The stronger binding ability of the phosphine led to an improvement of the catalyst thermal stability. We also developed novel  $C_2$ -symmetric and unsymmetric bisazaferrocene complexes with late-transition-metal Ni(II) and Pd(II). In these complexes, the two  $sp^2$  hybridized nitrogen atoms in the azaferrocene rings coordinate to the transition metals with the azaferrocene architecture presenting pentamethyl or pentaphenyl cyclopentadiene ( $Cp^*$  or  $Cp^0$ ) rings above and below the coordination plane for the purpose of blocking the associative chain transfer processes of ethylene from the axial faces. The complexes were prepared, fully characterized, and tested for ethylene polymerization.

**c.2. New cyclophane ligands for Ni(II) and Pd(II) catalysts.** A major breakthrough in our catalyst development is the discovery of new cyclophane-based catalysts that show extremely high activity and high thermal stability for ethylene polymerization.<sup>9</sup> In our ligand design, we strategically position metal binding sites at the core of cyclophanes to chelate transition metals. The cyclophane framework shields all directions of the catalytic metal center except leaving two



X-Ray crystal structure of the cyclophane- $\alpha$ -diimine-Pd(Me)Cl

*cis* coordination sites open in the front: one for monomer entry and the other for the growing polymer chain. The well-defined cavity and sterically hindered microenvironment of cyclophanes offer great opportunities for tuning the catalytic properties. A key strategy in our ligand synthesis is the use of the *cis*- $\alpha$ -diimine as a template to facilitate the cyclization by ring closing metathesis (RCM).<sup>10</sup> The Ni(II)-cyclophane catalyst has a productivity of 42,000 kg PE/(mol Ni·h) and is thermally stable up to 90 °C, the temperature suitable for industrial gas phase olefin polymerization processes. A patent has been filed for this family of catalysts and we are currently developing a

series of new cyclophane-based ligands for olefin polymerization catalysis.

**d. Summary.** Significant progress has been made in the last three years on developing highly efficient synthesis of functional polymeric materials having complex molecular structure and architecture through transition metal polymerization catalysis. Important breakthroughs were made in one-pot synthesis of highly functional polymers having controllable branching topologies including amphiphilic dendritic nanocarriers. The development of highly active and stable new catalysts will further enhance our capability in new polymer design. The transition metal catalyzed polymerization will ultimately lead to highly efficient routes toward complex and multifunctional polymeric materials from simple monomeric building blocks. This will open the door for producing functional materials for many practical applications including biomedical and nanotechnological applications.

The ARO fund has also provided for research and education activities to be conducted by undergraduate students and Ph.D. students. The multi-disciplinary research activity encompassed many areas including organic synthesis, organometallic, computer modeling, and polymer synthesis and polymer property studies, which provided great opportunities to train graduate and undergraduate students, especially for minority and women students currently working on this project. During the funding period, I maintained constant interactions through emails and discussions at national meetings with the program manager for this grant, Dr. Douglas Kiserow, at the Army Research Office. I presented our work at the DOD MURI Workshop on Polymer Branching Topology held on May 27-28, 2003, and the International Workshop on Branched Polymers for Performance held on May 23-26, 2004. I also visited the Army Research Laboratory on May 29, 2003 for discussing potential collaborations.

## e. Bibliography

1. "Control of Polymer Topology by Chain Walking Catalysts" Guan, Zhibin. *Chem. Eur. J.* **2002**, *8*(14), 3086.
2. "Control of Polymer Topology through Late-Transition-Metal Catalysis" Guan, Zhibin. *J. Polym. Soc. Part A: Polym. Chem.* **2003**, *41*, 3680.
3. "Chain Walking – A New Strategy to Control Polymer Topology" Guan, Zhibin; Cotts, P. M.; McCord, E. F. and McLain, S. J. *Science* **1999**, *283*, 2059.
4. "Synthesis of Functional Olefin Copolymers with Controllable Topology Using a Chain Walking Catalyst" Chen, G.; Ma, S.; Guan, Zhibin. *J. Am. Chem. Soc.* **2003**, *125*, 6697.
5. "Transition Metal Catalyzed One-pot Synthesis of Water-Soluble Dendritic Molecular Nanocarriers" Chen, G. and Guan, Zhibin. *J. Am. Chem. Soc.* **2004**, *126*, 2662.
6. "Control of Polymer Topology through Transition Metal Catalysis: Synthesis of Hyperbranched Polymers by Cobalt-Mediated Free Radical Polymerization" Guan, Zhibin. *J. Am. Chem. Soc.* **2002**, *124*, 5616.
7. "Synthesis of New Phosphine-imine Ligands and Their Influence on the Thermal Stability of Late Transition Metal Polymerization Catalysts" Guan, Zhibin and Marshall, W. *Organometallics* **2002**, *21*, 3580.
8. "Late-Transition-Metal Complexes with Bisazaferrocene Ligands for Ethylene Oligomerization" Salo, E.; Guan, Zhibin. *Organometallics* **2003**, *22*, 5033.
9. "The First Cyclophane-Based Highly Active Late-Transition-Metal Catalyst for Ethylene Polymerization" Camacho, D.; Salo, E. V.; Ziller, J. W.; Guan, Zhibin. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821.
10. "Synthesis and Structure of *m*-Terphenyl-Based Cyclophanes with Nitrogen Intra-Annular Functionality" Camacho, D.; Salo, E. V. Guan, Zhibin. *Org. Lett.* **2004**, *6*, 865.