Well-defined Al-containing Lewis Acids for Organic Transformations

LIU ZHIZHOU

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2016
Well-defined Al-containing Lewis Acids for Organic Transformations

LIU ZHIZHOU

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of

Doctor of Philosophy

2016
ACKNOWLEDGMENTS

First and foremost, I would like to thank my supervisor Nanyang Assistant Professor Dr. Vidovic Dragoslav for not hesitating even for a moment to give me the chance to be a part of his research group in the summer of 2012. Yet, still, it was one of the most important turning points in my life’s path. I started to face my life cheerfully and determinedly. His endless knowledge, insights, instructions and enthusiasm are truly inspirational.

I also thank all my coworkers from Dr. Vidovic Dragoslav’s research group for their valuable suggestions and help in the lab for the last four years. It is really a precious and wonderful experience working with them. They are: Dr. M. Senthilkumar, Dr. Zhu Di, Dr. Madelyn Tay, Dr. Alexey Smarun, Dr. B. Murugesapandian, Dr. Chitra Gurnani, Nemanja Djordjevic, Gordana Ilic and Monika Bjelcic.

I would like to thank the CBC technical support staff: Dr. Li Yongxin, Dr. Ganguly Rakesh, Ms Goh Ee Ling, Ong Yiren Derek, Ms Zhu Wenwei and Ms Pui Pang Yi for their assistance with common laboratory instruments. I would also like to thank the School of Physical and Mathematical Sciences of Nanyang Technological University for the financial support.

Also I would like to thank all my friends I met in NTU and Singapore, who brought me joy and support in the last four years. It’s a great memory to live in this beautiful tropical isle.

And most of all, I would like to thank my family for their love and encouragement. They always supported my decision and allowed me to determine my life’s path freely.
TABLE OF CONTENTS

ABSTRACT ......................................................................................................................................................... x

PUBLICATIONS .................................................................................................................................................. xi

ABBREVIATIONS ........................................................................................................................................... xii

Chapter 1 Introduction ........................................................................................................................................... 1

1.1 Lewis acid catalysts applied in organic synthesis .................................................................................. 2

1.1.1 Lewis acids used for C-C bond formation ......................................................................................... 4

1.1.2 Lewis acids used in oxidation and reduction reactions .................................................................. 10

1.1.3 Lewis acids used for polymerizations ............................................................................................. 12

1.2 Aluminum based Lewis acids ............................................................................................................. 13

1.3 HBA activity ........................................................................................................................................... 15

1.4 β-Diketiminato Ligands ....................................................................................................................... 17

1.5 Research objective .............................................................................................................................. 21

Chapter 2 Synthesis and characterization of β-diketiminate-supported aluminum compounds ................................................................. 27

2.1 Synthesis of β-diketiminato ligands ...................................................................................................... 28

2.2 Synthesis of LAI(Cl)₂ precursors ......................................................................................................... 31

2.3 Synthesis of LAI(OTf)₂ ......................................................................................................................... 35

2.4 Synthesis of the cationic aluminum complexes ................................................................................... 42

2.5 Summary ................................................................................................................................................ 50

2.6 Experimental section .......................................................................................................................... 50
Chapter 3 Application in organic transformations ............................................................. 63

3.1 Diels-Alder reactions involving 2,3-dimethylbutadiene............................................. 64

3.2 Diels-Alder reactions of 1,3-cyclohexadiene and isoprene .................................... 70

3.3 Michael polymerizations involving dienophiles....................................................... 75

3.4 Summary ................................................................................................................ 83

3.5 Experimental section .............................................................................................. 84

Chapter 4 Pursuing the active species in an NCN pincer aluminum-based Lewis acid system for catalytic Diels-Alder cycloadditions ................................................................ 92

4.1 Synthesis of bis(imino)aryl NCN pincer ligand ..................................................... 93

4.2 Synthesis of NCN pincer ligand supported aluminum complexes ....................... 94

4.3 Identification for the active species of Diels-Alder cycloadditions ....................... 101

4.4 Catalytic application in Diels-Alder cycloadditions ............................................ 110

4.5 Summary .............................................................................................................. 115

4.6 Experimental Section ........................................................................................... 116

Appendix .......................................................................................................................... 122

TABLE OF SCHEMES

Scheme 1.1 Lewis acid and Lewis base............................................................................. 2

Scheme 1.2 Possible mechanism for Aldol reactions in the presence of Lewis acid ....... 6

Scheme 1.3 Ene reaction catalyzed by chiral aluminum complexes. ............................... 7
Scheme 1.4 Asymmetric Diels-Alder reaction catalyzed by boron Lewis acid.................9

Scheme 1.5 Reduction catalyzed by zinc Lewis acid..................................................11

Scheme 1.6 Reductions catalyzed by chiral zinc Lewis acid........................................11

Scheme 1.7 Immortal copolymerization of ε-caprolactone and L-Lactide.......................13

Scheme 1.8 Michael additions catalyzed by chiral aluminum complex..........................14

Scheme 1.9 Tandem reactions catalyzed by aluminum triflate....................................15

Scheme 1.10 Proposed proton release mechanism. .......................................................16

Scheme 1.11 β-difunctional, monoanionic, chelating ligands. .......................................17

Scheme 1.12 Bonding modes of β-diketiminato III ligands to metals.............................18

Scheme 1.13 Group 13 compounds supported by β-diketiminato III ligands ...............19

Scheme 1.14 Synthetic route to β-diketiminato ligands..............................................20

Scheme 1.15 Synthetic route to β-diketiminato ligands..............................................20

Scheme 1.16 Synthetic route to β-diketiminato ligands..............................................21

Scheme 2.1 β-Diketiminato Ligands used. ......................................................................29

Scheme 2.2 synthesis of LH ligands 1a – 1d ...............................................................29

Scheme 2.3 Synthesis of asymmetric LH ligands 1e and 1f........................................30

Scheme 2.4 Attempted synthesis of complexes 2 via Potassium Salt Elimination...........31

Scheme 2.5 Synthesis of compound 2 via Lithium Salt Elimination, LiHMDS as a base.32
Scheme 2.6 Synthesis of compound 2 via Lithium Salt Elimination, n-BuLi as a base.....32

Scheme 2.7 Synthesis of aluminum bistriflate complexes.................................................36

Scheme 2.8 Formation of cationic compounds.................................................................42

Scheme 2.9 Proposed reaction of 3d with CD₃CN ..............................................................44

Scheme 3.1 Proposed dienophile-to-enolate side reaction ..................................................70

Scheme 3.2 Scope of substrates for polymerization............................................................81

Scheme 3.3 Proposed mechanism for Michael polymerization..........................................82

Scheme 3.4 Reactivity of poly-12.......................................................................................83

Scheme 4.1 General synthesis of Ligand 45........................................................................94

Scheme 4.2 General synthesis of Ligand 45........................................................................94

Scheme 4.3 Synthetic approaches to LAlCl₂ compounds...................................................96

Scheme 4.4 Synthetic approaches to LAl(OTf)₂ compounds .............................................98

Scheme 4.6 Formation of active species.........................................................................109

Scheme 4.7 Synthesis of pyridium cation and catalysis for Diels-Alder cycloaddition. 114

TABLE OF FIGURES

Figure 2.1 Molecular structure for 2c. .............................................................................33

Figure 2.2 Molecular structure for 2f. .............................................................................34

Figure 2.3 Molecular structure for 3a. .............................................................................38
Figure 2.4 Molecular structure for 3b. ................................................................. 38
Figure 2.5 Molecular structure for 3c. ................................................................. 39
Figure 2.6 Molecular structure for 3d. ................................................................. 39
Figure 2.7 Molecular structure for 3e. ................................................................. 40
Figure 2.8 Molecular structure for 3f. ................................................................. 40
Figure 2.9 Reaction between 3c and DMAP ......................................................... 43
Figure 2.10 Coordination between 3b and chalcone ............................................. 45
Figure 2.11 Structure for ([LAl(OTf)₂Na][BAr₄Cl₄])ₙ. ............................................. 47
Figure 2.12 Structure for ([LAl(OTf)₂Li][B(C₆F₅)₄]) ............................................. 49
Figure 3.1 ¹H NMR of 13, 41 and poly-12 ......................................................... 78
Figure 3.2 ¹³C NMR of 13, 41 and poly-12 ......................................................... 79
Figure 4.1 Molecular structure for 47. ............................................................... 97
Figure 4.2 Molecular structure for 48. ............................................................... 99
Figure 4.3 Reactions between 46 or 47 and NaBAR₄ .......................................... 104
Figure 4.4 Molecular structure for 49. ............................................................... 106
Figure 4.5 Molecular structure for 50. ............................................................... 108
Figure 4.6 ¹H NMR for the formation of active species ....................................... 110
Figure 4.7 ¹H NMR for reaction of 50 and dbpy ............................................... 113
TABLE OF TABLES

Table 1.1 IED Diels-Alder Reactions with Various Dienophiles ............................................. 4

Table 1.2 Ene reaction with trisubstituted olefins ................................................................. 8

Table 1.3 Reaction of methacrolein with cyclopentadiene. ................................................. 10

Table 1.4 Lewis-Acid-Catayzed Aldol Polymerization. ..................................................... 12

Table 2.1 Summary of the crystallographic data for compounds 2c, 2f .................. 35

Table 2.2 $^{27}$Al NMR (ppm) for complexes 2 and 3 ............................................................ 36

Table 2.3 Al-N bond lengths (Å) for complexes 2 and 3 ..................................................... 37

Table 2.4 Summary of the crystallographic data for compounds 3a- 3f ....................... 41

Table 2.5 $^{19}$F NMR (ppm) for 3 and 3+ DMAP ................................................................. 44

Table 2.6 Summary of the crystallographic data for compounds 6, 7 ......................... 49

Table 3.1 Diels-Alder reaction by different catalytic systems ............................................. 65

Table 3.2 Diels-Alder reactions involving 2,3-dimethylbutadiene ..................................... 67

Table 3.3 Selected Diels–Alder transformations in the presence of a pyridine base. ....... 69

Table 3.4 Diels-Alder reactions involving 1,3-cyclohexadiene ........................................ 71

Table 3.5 Diels-Alder reactions involving isoprene ............................................................ 73

Table 3.6 Diels-Alder reactions involving isoprene by asymmetric catalysts ................. 74
Table 3.7 Competition between Diels-Alder cycloaddition and dienophile polymerization
.................................................................................................................................................76

Table 4.1 Summary of crystallographic data for 47 – 50.............................................................99

Table 4.2. Screening of potential (pre)catalysts for Diels Alder cycization between
2,3-dimethylbutadiene and 1,3-diphenyl-2-propenone.........................................................102

Table 4.3 Catalytic activity of 47/THF system under different heating times..................103

Table 4.4 50 or HBA catalyzed Diels-Alder reactions of dienophiles 5 and 9-14 with dienes
4, 23 or 32. The results are listed as: time (h), yield (%), trans/cis or endo:exo, and/or
para:meta ratios for each run.................................................................................................111

Table 4.5 Pyridium catalyzed Diels-Alder reaction...............................................................115
ABSTRACT

This thesis focuses on designing and catalytic applications of aluminum based Lewis acids. It contains four parts:

Chapter 1 gives a brief introduction of the development of Lewis acid chemistry and its increasing influence on modern synthetic organic chemistry. Aluminum compounds are widely used as efficient and powerful Lewis acid catalysts. Hence, we proposed our strategy to prepare various Al-based Lewis acids and investigate their potential applications.

Chapter 2 describes the design, synthesis and characterization of a series of aluminum bistriflate complexes supported by β-diketiminate ligands. Several approaches to cationic aluminum complexes were also illustrated in this chapter.

Chapter 3 focuses on the catalytic application of these aluminum bistriflate complexes on Diels-Alder transformations. Less reactive dienes such as 2,3-dimethylbutadiene, 1,3-cyclohexadiene and isoprene and a series of dienophiles were examined. A competition between Diels-Alder reaction and Michael polymerization was also described when cyclic dienophiles were used.

Chapter 4 describes the synthesis of several aluminum compounds stabilized by an NCN pincer ligand. Several experiments indicated that the cationic aluminum complex 50 was the active species for Diels-Alder catalytic reactions.
PUBLICATIONS


## ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xyl</td>
<td>2,6-dimethylphenyl</td>
</tr>
<tr>
<td>Mes</td>
<td>1,3,5-trimethylphenyl</td>
</tr>
<tr>
<td>Dip</td>
<td>2,6-diisopropylphenyl</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>OTf</td>
<td>trifluoromethanesulfonate</td>
</tr>
<tr>
<td>dbpy</td>
<td>2,6-di-tertbutylpyridine</td>
</tr>
<tr>
<td>Equiv</td>
<td>equivalent</td>
</tr>
<tr>
<td>HRMS</td>
<td>high–resolution mass spectrometry</td>
</tr>
<tr>
<td>'Pr</td>
<td>isopropyl</td>
</tr>
<tr>
<td>IR</td>
<td>infrared Spectroscopy</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>η</td>
<td>eta</td>
</tr>
<tr>
<td>β</td>
<td>beta</td>
</tr>
<tr>
<td>'Bu</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>π</td>
<td>pi</td>
</tr>
<tr>
<td>σ</td>
<td>sigma</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction
1.1 Lewis acid catalysts applied in organic synthesis

The concept of Lewis acid was given by Gilbert N. Lewis in 1923, where an acid is described as a molecule or ion capable of coordinating with a lone pair of electrons and a base as a molecule or ion having a lone pair of electrons to share.$^1$ It can be then concluded that all Lewis acids are electron deficient while Lewis bases are electron rich. It is a much more general concept than that given by Brønsted, where acid is simply described as a proton donor and a base as a proton acceptor.$^2$ According to these two definitions, all the Brønsted acids can be considered as Lewis acids. Nevertheless, the Lewis acid definition has expanded the application of acids to a much wider range. Besides the classic acids, many metallic and nonmetallic species that lack electron density can be also considered as acids. For example, boron trifluoride, which has no protons to donate, can accept the lone pair from ammonia as it possesses an empty p orbital i.e. the central B is electron deficient. In this case, boron trifluoride acts as a Lewis acid and ammonia acts as a Lewis base to form an adduct (Scheme 1.1).

In the following decades, the chemistry of Lewis acids has attracted more and more attention and played an extremely important role in modern synthetic organic chemistry. Many Lewis acids have been found to be quite suitable for the catalysis of a variety of...
useful and powerful organic transformations, which include, but are not limited to alklylation, Friedel-Crafts reactions, Ene reactions, Aldol reactions and cycloaddition reactions. The most common mode of Lewis acid catalytic activity is their ability to lower the LUMOs of electrophilic substrates by binding to a heteroatom (e.g. O, N, etc.). Traditionally, the Diels-Alder reaction, Mukaiyama aldol synthesis and Friedel–Crafts reaction are usually catalyzed by common Lewis acids such as BF$_3$·Et$_2$O, AlCl$_3$ and TiCl$_4$. When dissolved in solution, these Lewis acids usually exist as dimers, trimers or oligomers, and can activate various kinds of functional groups efficiently. However, as a disadvantage, they usually provide relatively low regio-, stereo-, and chemoselectivities. One of the strategies to improve on these selectivities, is to modify these Lewis acids with a supporting ligand. Research showed that binding organic ligands to these Lewis acids led not only to the formation of monomeric structures but it also to improved selectivities. For example, as a common used Lewis acid, TiCl$_4$ is a respectable catalyst for the usual Diels-Alder cycloadditions. However, when two of the chloride atoms were replaced by (R,R)-3-Aza-3-benzyl-1,5-dihydroxy-1,5-diphenylpentane ligand (L), the resulting L-TiCl$_2$ complex was proved to be an excellent chiral Lewis acid catalyst for the synthesis of a series of asymmetric tetrahydroquinoline derivatives via inverse electron demand (IED) Diels-Alder reactions between electron-poor diene benzylidene aniline and several electron-rich dienophiles. This Ti-based Lewis acid produced moderate yields and at times high enantioselectivities (up to 92%) for these IED Diels-Alder reactions as shown in Table 1.1.
Table 1.1 IED Diels-Alder Reactions with Various Dienophiles

<table>
<thead>
<tr>
<th></th>
<th>dienophile</th>
<th>T °C</th>
<th>Conversion %</th>
<th>a/b</th>
<th>a</th>
<th>b</th>
<th>ee %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dihydropyran (n=2)</td>
<td>0</td>
<td>60</td>
<td>0.25</td>
<td>92</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>dihydrofuran (n=1)</td>
<td>0</td>
<td>50</td>
<td>2.33</td>
<td>82</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>dihydrofuran (n=1)</td>
<td>-40</td>
<td>60</td>
<td>2.33</td>
<td>56</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ethylvinyl ether</td>
<td>35</td>
<td>65</td>
<td>0.67</td>
<td>90</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>cyclopentadiene</td>
<td>35</td>
<td>58</td>
<td></td>
<td></td>
<td></td>
<td>21</td>
</tr>
</tbody>
</table>

Over the years, various Lewis acids supported by different ligands have been prepared and studied, among which, many have been applied in chemical industry. In these cases, Lewis acid catalysts showed both high activities and good selectivity. There is no doubt that, the discovery that Lewis acid can be used as catalysts for so many organic reactions is one of the most significant events in chemistry in the past century.

1.1.1 Lewis acids used for C-C bond formation
Since discovered by Borodin \(^{21}\) and Wurtz \(^{22-24}\) in 1872, Aldol addition has been widely applied in the formation of carbon-carbon bonds. Due to this great significance to organic synthetic chemistry, a large amount of work has been undertaken to investigate this kind of reactions in the past years. These reactions can easily occur in the presence of a strong base such as LDA (lithium diisopropylamide) or NaOH. However, when the unsymmetrical carbonyl compounds were used for the addition, the formation of crossed products was observed. In contrast, when Lewis acids are used as catalysts, this problem can be solved.\(^{25}\)

Recently, Aldol reactions have been widely applied in the synthesis of a wide variety of compounds that contain stereoselective carbon-carbon bonds. One method is to use asymmetric modified electrophiles or enolates \(^{26}\) as substrates, the other method is to use chiral Lewis acids as catalysts for these Aldol reactions. In the latter case, Lewis acids usually coordinate i.e. activate aldehydes followed by the addition of various substrates such as silyl enol ether.\(^{27}\)

For example, Fu\(^{28}\) and coworker reported a planar chiral Lewis acid based on boron, which can catalyze Aldol reactions between a wide range of different dienophiles and aldehydes, resulting in high yields and stereoselectivities. The proposed mechanism for the catalytic reaction is shown in Scheme 1.2. The designed chiral Lewis acid can activate and organize the aldehydes via a \(\pi\)-interaction, following with the highly stereoselective addition to dienphiles.
Nowadays, the Ene reactions is one of the most valuable tools for the organic synthesis. However, the carbonyl-Ene reaction usually requires high temperature or highly activated reagents as it is a group transfer reaction. Also the enophile and the ene in this reaction can be modified by various functional groups, allowing for a valuable access to useful carbon-carbon bonds formation. As a result, various catalysts have been investigated to catalyze the Ene reactions in the past decades. Among those, Lewis acids have revealed their potential for these reactions as they showed both high activity and selectivity. For example, one of the methods to prepare chiral alcohols is the Ene reaction between aldehyde and alkene catalyzed by chiral Lewis acids. In 1988, Yamamoto and coworker used a chiral aluminum Lewis acid based on BINOL as catalyst and successfully synthesized a series of chiral alcohols with high yields and enantioselectivity up to 88% as shown in Scheme 1.3.
Subsequently, Mikami and other researchers reported that titanium complexes based on BINOL can also catalyze the asymmetric carbonyl-ene reactions. After that, a lot of other metal cations have also been explored as efficient catalysts for these reactions. Evans and coworkers reported a series of chiral scandium-pybox compounds and used them as attractive Lewis acid catalysts for the ene reaction of 1, 1- disubstituted olefins and N-phenyl glyoxamide at the beginning of this century. As shown in the Table 1.2, in the presence of 4Å molecular sieves, 5 mol% of the scadium-pybox compounds can catalyze the reaction efficiently, affording both high yields and excellent enantioselectivities (up to 99%).
Table 1.2 Ene reaction with trisubstituted olefins

<table>
<thead>
<tr>
<th>olefin</th>
<th>product</th>
<th>ee %</th>
<th>yield %</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>H(Me)</td>
<td>94</td>
<td>78</td>
<td>13:1</td>
</tr>
<tr>
<td>Et</td>
<td></td>
<td>99</td>
<td>76</td>
<td>24:1</td>
</tr>
<tr>
<td>n = 1</td>
<td>n(H₂C)</td>
<td>98</td>
<td>82</td>
<td>9.3:1</td>
</tr>
<tr>
<td>2</td>
<td>r(H₂C)</td>
<td>98</td>
<td>78</td>
<td>9.3:1</td>
</tr>
<tr>
<td></td>
<td>Me</td>
<td>96</td>
<td>58</td>
<td>9:1</td>
</tr>
</tbody>
</table>

It was first reported 1942 by Wassermann\textsuperscript{42} that Diels-Alder reactions can be catalyzed by Brønsted acids. However, not much attention was paid to this area for a long time. In contrast, the Lewis acid catalyzed Diels-Alder reactions have been well-developed and widely used in organic synthesis and industry, although the first Lewis acid catalyzed reactions were discovered almost two decades after the ones catalyzed by Brønsted acids.\textsuperscript{43} Yate and Eaton\textsuperscript{44} pointed out that the simple Lewis acids such as AlCl\textsubscript{3} and BF\textsubscript{3}.OEt\textsubscript{2} allow Diels-Alder reaction to run in quite mild conditions. This discovery promoted the development of the Diels-Alder reactions, making this type of C-C bond formation a powerful tool to form six-membered ring.\textsuperscript{45} In the catalytic process, a Lewis acid first
activates the substrates by coordinating to the oxygen atom of the carbonyl group of dienophiles, lowering the energy of LUMO. However, because Lewis acids such as AlCl$_3$ and BF$_3$·OEt$_3$ are usually corrosive and non-recyclable, it is important to modify these particular Lewis acids with different ligands. Furthermore, the introduction of chiral ligands makes it possible to catalyze asymmetric Diels-Alder reactions.$^{46,47}$ Kelly $^{48}$ prepared a chiral boron Lewis acid through the reaction of a disubstituted 1, 1'-binaphthol and juglone in 1986. This complex can react with a variety of dienes stoichiometrically to give Diels-Alder products with high enantioselectivities up to 98% (Scheme 1.4).

![Scheme 1.4 Asymmetric Diels-Alder reaction catalyzed by boron Lewis acid.](image)

$^{(90 \%)} > 95 \%$ ee

More recently, E. P. Kündig $^{49}$ and coworker reported a series of chiral indenyl ruthenium complexes which can be used as efficient Lewis acid catalysts for asymmetric Diles-Alder reactions between methacrolein with cyclopentadiene. They showed unprecedented high
exo selectivity (>99%) as well as high enantioselectivity up to 97% as shown in Table 1.3. Also, these ruthenium Lewis acid catalysts are room-temperature stable and can be recovered.

Table 1.3 Reaction of methacrolein with cyclopentadiene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>exo: endo</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[CpFe((R,R)-biphop-F)][SbF$_6$]</td>
<td>1</td>
<td>85</td>
<td>98: 2</td>
<td>97 (R)</td>
</tr>
<tr>
<td>2</td>
<td>(S,S)-a</td>
<td>22</td>
<td>91</td>
<td>97: 3</td>
<td>92 (S)</td>
</tr>
<tr>
<td>3</td>
<td>(S,S)-b</td>
<td>22</td>
<td>87</td>
<td>97: 3</td>
<td>97 (S)</td>
</tr>
<tr>
<td>4</td>
<td>(S,S)-c</td>
<td>2.5</td>
<td>85</td>
<td>99.7: 0.3</td>
<td>88 (S)</td>
</tr>
<tr>
<td>5</td>
<td>(S,S)-d</td>
<td>4</td>
<td>80</td>
<td>99.8: 0.2</td>
<td>95 (S)</td>
</tr>
</tbody>
</table>

1.1.2 Lewis acids used in oxidation and reduction reactions

Lewis acids are also widely used in catalytic enantioselective oxidation and reduction reactions. Mikami$^{50}$ reported a series of chiral diamine–Zn–diol Lewis acid catalytic systems which are prepared by mixing chiral diamines, ZnEt$_2$ and achiral diols in situ. When polymethylhydrosiloxane (PMHS) was used as the source of hydride and in the presence of 3 Å molecular sieves, ortho-multisubstituted benzophenones can be reduced to the corresponding optically active alcohols via hydrosilylation using 10 mol% of the
diamine–Zn–diol compounds. As shown in Scheme 1.5, both high yield and excellent enantioselectivity (97% and 96%, respectively) can be obtained for this reaction under mild reaction conditions.

Scheme 1.5 Reduction catalyzed by zinc Lewis acid

Cozzi and coworker also reported the application of zinc Lewis acid catalysts for the enantioselective reductions. When catecholborane was used as the source of hydride, a series of aromatic methyl ketones can be reduced to corresponding chiral alcohols by adding 4 mol% of chiral iminoxazoline (IMOX) ligand and Zn(OTf)$_2$ in situ. These catalytic reductions are performed in dichloromethane at -15°C with high enantioselectivities up to 93% ee and moderate yield as shown in Scheme 1.6.

Scheme 1.6 Reductions catalyzed by chiral zinc Lewis acid.
1.1.3 Lewis acids used for polymerizations

Another important application of Lewis acids is the catalysis of a wide range of polymerization reactions.\textsuperscript{52-55} For example, in the presence of Lewis acids such as rare-earth metal triflates, bis(silylketene acetal)s and dialdehydes can be polymerized via Mukaiyama aldol reaction, affording poly(hydroxy ester)s as products with high molecular weights and unique chain structure as shown in Table 1.4.\textsuperscript{56}

\begin{table}[h]
\centering
\caption{Lewis-Acid-Catayzed Aldol Polymerization.}
\begin{tabular}{lll}
\hline
LA (mol \%) & Yield (%) & Mn \\
\hline
Sc(OTf)\textsubscript{3} (10) & 50 & 55 700 \\
Yb(OTf)\textsubscript{3} (20) & 15 & 11 300 \\
TiCl\textsubscript{4} (200) & 29 & 2 700 \\
\hline
\end{tabular}
\end{table}

Recently, Cui’s group\textsuperscript{57} reported a series of multinuclear aluminum complexes that can initiate the ring-opening polymerization of \(\varepsilon\)-caprolactone and L-Lactide efficiently. Moreover, with addition of excess isopropyl alcohol, these complexes can also catalyze the
copolymers. The copolymerization of the two monomers with narrow molecular weight distributions and the copolymerization process shows “immortal” characters (Scheme 1.7).

![Scheme 1.7 Immortal copolymerization of ε-caprolactone and L-Lactide.]

**1.2 Aluminum based Lewis acids**

It is not surprising that with the development of Lewis acid chemistry, a wide variety of Lewis acids based on various metals have been well investigated and documented. Arguably, the most important Lewis acids are compounds incorporating group 13 elements. This is because they are capable of accepting an additional electron lone pair in their three-coordinate, neutral state. Among these, aluminum-based Lewis acids are plausibly the most appealing because of their inexpensiveness and availability. As aluminum is the most abundant metallic element in the Earth’s crust (about 8.3% by weight).

So far, aluminum Lewis acids have been found increasing important applications in both academia and industry. In 1986 Shibasaki and coworkers reported the synthesis of a heterobimetallic complex through the reaction of (R)-BINOL and lithium aluminum hydride. This chiral aluminum complex can used as an efficient catalyst for asymmetric Michael addition reactions of a range of malonic esters and cyclic enones with good reactivity and enantioselectivity up to 99% as indicated in Scheme 1.8.
Scheme 1.8 Michael additions catalyzed by chiral aluminum complex.

Wang and co-workers reported the preparation of several polysubstituted indanes through an unprecedented formal [2 + 3]-cycloaddition promoted by AlCl₃. When 1,2-DCE was used as solvent, in the presence of two equivs of AlCl₃, a large amount of 1,1-cyclopropanes can react with N-benzylic sulfonamides to form highly functionalized and stereoslective indane compounds with high yields. AlCl₃ also can be used as an efficient Lewis acid catalyst to promote the Silane Reduction of Glycopyranoside to prepare SGLT-2 inhibitor Empagliflozin.

However, non-recyclable and corrosive properties of aluminum trichloride limit its wide-spread use. This could be avoided by the replacement of halogens with triflates (OTf;
Tf = O$_2$SCF$_3$) substituents, affording both higher stability and Lewis acidity. Al(OTf)$_3$ is evidently the most common triflate containing aluminum species that has been investigated in a variety of organic transformations. For example, Williams$^{62}$ reported that Al(OTf)$_3$ can promote the conversion of 3,4,6-Tri-O-acetyl-D-galactal to chiral bridged benzopyrans or 1-O-aryl-2-deoxy derivatives depending on different reaction conditions as shown in Scheme 1.9. These reactions are processed in a tandem fashion with high yields and stereoselectivity. It revealed a new and efficient approach to the synthesis of chiral chromenes, chromans and benzopyrans.

Scheme 1.9 Tandem reactions catalyzed by aluminum triflate.

As a cheap and non-toxic Lewis acid, Al(OTf)$_3$ was also found to be an efficient catalyst to construct a variety of tetrahydropyrido [1,2-a]indol-6-one skeletons via an intramolecular reaction following by protonation and Mannich-type nucleophilic addition of indoles.$^{63}$

1.3 HBA activity

As already indicated, a large portion of Lewis acid catalytic systems, including the Al-based ones, were usually prepared and used in situ. This could be a big problem because in certain reaction conditions these Lewis acids are capable of generating hidden Brønsted
acids (HBAs) which also can catalyze the target organic transformations.\textsuperscript{64-70} For instance, Pizzo\textsuperscript{71} and co-workers reported that AlCl$_3$·2THF can be used as a reactive Lewis acid catalytic system for Diels-Alder transformations. But in this work all experimental procedures were performed at a benchtop without any attempts to eliminate the influence of air/moisture. As AlCl$_3$ is quite air- and moisture-sensitive\textsuperscript{72}, it can be concluded that hydrolysis of AlCl$_3$ cannot be avoided in this particular setting, resulting in the formation of a Bronsted acid. Therefore, the observed catalytic activity might have been performed by an HBA (presumably HCl).

In 2011 Hintermann\textsuperscript{73} and co-workers reported a useful strategy to generate HBA and suggested several important control experiments to minimize the possibility of HBA activity. Oestreich\textsuperscript{74} also reported an efficient Lewis acid catalyst for Diels-Alder reaction. Although the ferrocene-stabilized silicon cation used for the catalysis was deactivated in the presence of common hindered base dbpy (2,6-di-tertbutylpyridine) (Scheme 1.10), the Lewis acid activity was demonstrated by a serious of comparative experiments.

![Scheme 1.10 Proposed proton release mechanism.](image)

Hence, it is very meaningful to characterize the designed Lewis acids in order to identify the active species in corresponding Lewis acid catalysis.
1.4 β-Diketiminato Ligands

It is quite important to select a proper supporting ligand for Lewis acid catalyst because it can impact both the reactivity and selectivity of the resulting complex via its electronic and steric properties. In the past decades, various ligands have been investigated and documented to support aluminum-based Lewis acids, providing them with better stability, activity and selectivity. Perhaps the most outstanding representatives are the β-difunctional, monoanionic, chelating ligands as shown in Scheme 1.11.

![Scheme 1.11 β-difunctional, monoanionic, chelating ligands.](image)

In the past five decades, large amount of experimental evidence have been generated on the research of β-diketonato I and β-enaminoketonato II ligands, which are widely used as chelating ligands in coordination chemistry. However, β-diketiminato III ligands, which are also referred as “nacnac” ligands, have demonstrated their wide appeal in the new century. This is due to the possibility of various substituents on nitrogen, which might be hydrogen, alkyl, silyl or aryl groups.

The studies on β-diketiminato III ligands stared in the mid-1960s, focusing on the synthesis and structures of homoleptic M(II) β-diketiminates where M = Ni, Co, Cu. In the mid-1990s people recognized that β-diketiminato III ligands can act as useful cyclopentadienyl-like spectator ligands because they can form strong metal-ligand bonds.
and possess exceptional and tunable steric demands.\textsuperscript{77a,b} Since then, \(\beta\)-diketiminato III gained significantly increasing attentions and, hence, developed rapidly as an important ligand choice.\textsuperscript{78} This class of ligands can coordinate to metals in a variety of bonding modes, as shown in Scheme 1.12.

The most common bonding mode is structure A, where both the two nitrogen atoms of the ligand coordinate to the metal in a N,N-chelating fashion and the resulting MNCCCN six-membered metallacyclic ring is planar. When the metal possesses empty d orbitals with appropriate symmetry, it can bond to the \(\beta\)-diketiminato III ligand in mode B, where the
MNCCCN ring lies in a boat fashion. In a binuclear complex, the β-diketiminato III ligand may adopt the type C binding mode, with one of the nitrogen is additionally bonded to the M centre of another molecule. In this instance, the metallacyclic rings could be in many conformations. In mode D both nitrogen atoms of the β-diketiminato III binuclear complex are four-coordinate. An example of a complex in which M is bound at the γ-C of the ligand backbone (type E) would be [GeC(C(Me)N(C₆H₃Pr₂-2,6))₂Cl₃]. Type F is different from C as both of the nitrogen atoms are three-coordinate and function as terminal ligands. Type G is a tautomer of type A or type B. Beside these, other bonding modes are also listed.

The β-diketiminato III ligands are widely used to support group 13 compounds. For example, a large amount of neutral boron and aluminum complexes supported by nacnac ligands have been reported as shown in Scheme 1.13. These ligands are also used to stabilize monocationic boron complexes. However, there are quite few examples were reported using nacnac ligands to stabilize dicationic boron complexes and cationic aluminum complexes.  

![Scheme 1.13 Group 13 compounds supported by β-diketiminato III ligands](image-url)
The β-diketiminato III ligands can be prepared using several synthetic routes, most of which involving the condensation reaction of a primary amine with either a β-diketone or 1,1,3,3-tetraethoxypropane. In 1968 McGeachin reported the first synthetic route using a β-diketone to form β-diketiminato ligand as shown in Scheme 1.14.

An alternative procedure involved converting a 1,3-diketone into a ketoketal and then into the β-diketimine through the condensation with aniline as shown below.

These ligands can also be prepared from a β-diacetal such as 1,1,3,3-tetraalkoxypropane. In hot aqueous ethanol 1,1,3,3-tetraethoxypropane was treated with an aromatic amine hydrochloride for 1h, after which β-diketimine hydrochloride can be crystallized at ambient temperature. Then, the desired β-diketimine can be obtained by adding aqueous sodium hydroxide.
In 1997 Dip-substituted β-diketimine was first reported as a supporting ligand for Ni(II) and Pd(II) catalysts used in ethylene polymerization. Since then, it started to play an important part in many fields as a useful and common supporting ligand. Various metal complexes based on this kind of ligands have been investigated and widely used as catalysts for wide range of organic reactions.

1.5 Research objective

Based on all above mentioned observations, it is not surprising that aluminum Lewis acids have extensively been used for the catalysis of organic transformations including Diels–Alder cycloadditions. However, a recent book by Yamamoto and Ishihara indicated that Al-catalyzed Diels-Alder reactions involving less reactive dienes and dienophiles were not well documented. Moreover, most of these Al-based catalytic systems were not well structurally characterized, lacking of identification of the active species. Hence, we synthesized several aluminum complexes based on different ligands and used them for the catalysis of a handful of Diels-Alder reactions involving less reactive dienes and dienophiles. Additional experiments were also performed to gain evidence against HBA activity.
Reference

1 Lewis, G.N. Valence and the Structure of Atoms and Molecules 1923, 142.


21 Borodin observed the dimerization of acetaldehyde to 3-hydroxybutanal under acidic conditions.


75 Holm, R. H.; Everett, G. W.; Chakravorty, A. Prog. Inorg. Chem. 1966, 7, 83.


Chapter 2

Synthesis and characterization of β-diketiminate-supported aluminum compounds
The importance of Lewis acids in various catalytic and stoichiometric organic transformations has been extensively reported. Arguably, the most widely used Lewis acids are simple group 13 trihalides such as BF\(_3\)·OEt\(_2\) and AlCl\(_3\). However, their applications are limited because these compounds are usually non-recyclable and corrosive. In recent years, a quantity of reports have surfaced describing the use of triflate substrates in place of halogens in order not only to increase stability but also to enhance the activity of the target Lewis acids. Examples include LiOTf, B(OTf)\(_3\) and Sc(OTf)\(_3\). However, the majority of reaction conditions have been optimized simply by employing different triflate-containing metal compounds. Only a handful of reports investigated catalytic properties of metal triflate together with organic ligands of which the majority had been prepared and used in situ. As it is the case with many other elements, Al(OTf)\(_3\) is the most common triflate containing aluminum species that has been investigated in a variety of organic transformations. Few compounds containing “Al-OTf” fragment(s) have been reported but predominantly for structural information. In fact, structural information on aluminum compounds containing triflate substituents is generally limited and only one of these compounds has been explored as a catalyst but with limited success. Thus we set to explore the influence of triflate substituents on Lewis acidic properties of several β-diketiminate-supported aluminum compounds and their potential application as Lewis acid catalysts.

2.1 Synthesis of β-diketiminato ligands

A series of symmetric and asymmetric monoanionic β-diketiminato ligands with different substituents at nitrogen atoms were screened in this chapter as summarized in Scheme 2.1.
Scheme 2.1 β-Diketiminato Ligands used.

The corresponding LH ligands were synthesized though condensation of 2,4-pentanedione and a series of anilines. As shown in Scheme 2.2, the symmetric LH ligands 1a - 1d can be synthesized by simple reflux of the two reagents in toluene together with 1 equiv of para-toluenesulfonic acid monohydrate. The water generated can be removed by the use of a Dean–Stark apparatus. After workup, all these four ligands can be isolated as colorless crystals with high yield (> 85%).

Scheme 2.2 synthesis of LH ligands 1a – 1d
Two asymmetric LH ligands 1e and 1f were prepared by a two-step method as shown in Scheme 2.3. In the first step, 2-(2,6-Diisopropylphenylimido)-2-pentene-4-one was synthesized from 2,4-pentanedione and 2,6-diisopropylaniline by dehydration in toluene catalyzed by concentrated H$_2$SO$_4$. Then, the resulting β-ketoamine was subsequently treated with corresponding anilines in the presence of 1 equiv of para-toluenesulfonic acid monohydrate with water removed by a Dean-Stark apparatus. After work up the desired β-diketimines were recrystallized from cold ethanol in good yield (~ 80%).

![Scheme 2.3 Synthesis of asymmetric LH ligands 1e and 1f]

In order to study the catalytic properties of aluminum bitriflates incorporating nacnac L$^-$ ligands, it was necessary to prepare aluminum dichloro complexes as precursors to the aluminum bistriflate complexes. For this purpose several strategies were carried out to optimize the synthesis of the aforementioned complexes and the most important results are summarized in the following section.
2.2 Synthesis of \( \text{LAICl}_2 \) precursors.

In order to find a convenient and a high-yield method to prepare the aluminum dichloro complexes (\( \text{LAICl}_2 \)), a variety of salt elimination approaches such as potassium and lithium salt eliminations were examined. As shown in Scheme 2.4, the LH ligands were first treated with potassium bis(trimethylsilyl)amide (KHMDS) in toluene at room temperature\(^3\,^4\). After stirring the reaction mixture overnight a volatile oil \( \text{HN(SiMe}_3\text{)}_2 \) was formed as a by-product. After removing \( \text{HN(SiMe}_3\text{)}_2 \) under reduced pressure, 1.05 equiv of \( \text{AlCl}_3 \) was added at low temperature. Unfortunately, NMR spectroscopic analysis showed that besides the desired aluminum dichloro compounds several unidentified impurities were also present in the crude reaction mixture. Several attempts have been made to purify the desired product but all of them were unsuccessful.

![Scheme 2.4 Attempted synthesis of complexes 2 via Potassium Salt Elimination.](image)

Since the potassium salt elimination method appeared not to be an ideal approach for the synthesis of aluminum dichloro complexes, we decided to switch to lithium salt elimination. As shown in Scheme 2.5, LiHMDS was used as a base to deprotonate the LH ligand instead of KHMDS. As before, the elimination was carried out in toluene at room temperature. After stirring overnight the side product \( \text{HN(SiMe}_3\text{)}_2 \) was removed from the reaction mixture by vacuum and the resulted lithium salt was re-dissolved in toluene before 1.05 equiv of \( \text{AlCl}_3 \) was added to the reaction mixture. To our delight, after lithium chloride was
filtered away and toluene was removed under reduced pressure, pure product can be obtained by washing with hexane in good yield.

Scheme 2.5 Synthesis of compound 2 via Lithium Salt Elimination, LiHMDS as a base.

Inspired by this achievement, we decided to investigate a more convenient strategy to synthesize aluminum dichloride complexes as the abovementioned method was time consuming due to reaction times and the need to remove the by-product (HN(SiMe$_3$)$_2$). Therefore, the use of a more reactive base n-butyl lithium (°BuLi) that does not produce a potentially reactive by-product was our choice. As shown in Scheme 2.6, the lithium salt elimination can be completed in 1 hour when the ligands were treated with °BuLi in toluene at 0 °C. AlCl$_3$ was subsequently added without any extra treatment of the reaction mixture. Six aluminum dichloride complexes 2a-2f were synthesized using this method in high yields (> 80%).

Scheme 2.6 Synthesis of compound 2 via Lithium Salt Elimination, °BuLi as a base.
$^1$H NMR spectroscopic identifications of 2a-2f revealed a dramatic $\gamma$-H chemical shift from ~4.8 ppm to 5.4 ppm compared to their LH ligands, indicating the formation of new compounds. $^{27}$Al NMR spectroscopic identifications of 2a-2f revealed the presence of a $\delta_{\text{Al}}$ signal around 103 ppm for all six precursors (Table 2.2), while the other multinuclear NMR data were consistent with the reported values. $^{5,6}$ Moreover, crystals of compounds 2c and 2f suitable for X-ray analysis were grown from a toluene/hexane solvent mixture. Molecular structures of these compounds are shown in Figure 2.1 and Figure 2.2, with the crystallographic data summarized in Table 2.1.

![Molecular structure for 2c](image)

Figure 2.1 Molecular structure for 2c.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.8582(12), Al1-N2 1.8633(12), Al1-Cl1 2.1299(6), Al1-Cl2 2.1295(6), N1-Al1-N2 98.94(5), Cl1-Al1-Cl2 106.54(2).
Figure 2.2 Molecular structure for 2f.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.860(7), Al1–N2 1.846(9), Al1-Cl1 2.124(7), Al1-Cl2 2.116(9), N1-Al1-N2 99.31(8), Cl1-Al1-Cl2 109.10(3).

The central aluminum atoms of both the two complexes are four-coordinate, adopting distorted tetrahedral geometries. The Al-Cl bond lengths for 2c (2.1299(6) and 2.1295(6) Å) and 2f (2.124(7) and 2.116(9) Å) are similar with that reported by Kemp (2.1253(10) and 2.1146(7) Å for \(\text{DipDAB-AlCl}_2\))\(^7\) and Jordan (2.124(2) and 2.113(2) Å for \(\{\text{Me}_2\text{NC(NiPr)}_2\}\text{AlCl}_2\))\(^8\), but shorter than that reported by Dagorne (2.174(1) Å for (bis-phenol imidazolinium)Al(CH\(_3\))(Cl))\(^9\) and Roesky (2.1531(11) Å for [(3,5-\(\text{Bu}_2\)-N-CH=C(SiMe\(_3\))-pz)AlCl(3,5-\(\text{Bu}_2\)pz)]\(^10\).
Table 2.1 Summary of the crystallographic data for compounds 2c, 2f

<table>
<thead>
<tr>
<th></th>
<th>2c</th>
<th>2f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{C}<em>{25}\text{H}</em>{29}\text{AlCl}_2\text{N}_2$</td>
<td>$\text{C}<em>{25}\text{H}</em>{33}\text{AlCl}_2\text{N}_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>431.36</td>
<td>459.41</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\ -1$</td>
<td>$P\ 1\ 2\ 1/n\ 1$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>7.9153(7)</td>
<td>11.8734(18)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>8.6925(7)</td>
<td>15.792(2)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>18.0519(14)</td>
<td>15.792(2)</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>93.343(2)</td>
<td>108.616(4)</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>1139.58(16)</td>
<td>2550.3(6)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$D_c$/g cm$^{-3}$</td>
<td>1.257</td>
<td>1.197</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>456</td>
<td>976</td>
</tr>
<tr>
<td>Crystal size/ mm</td>
<td>0.200 x 0.380 x 0.400</td>
<td>0.010 x 0.020 x 0.240</td>
</tr>
<tr>
<td>θ range/°</td>
<td>2.80 to 30.94</td>
<td>2.69 to 25.07</td>
</tr>
<tr>
<td>No. of reflns collected</td>
<td>28389</td>
<td>30483</td>
</tr>
<tr>
<td>No. of indep reflns</td>
<td>7218</td>
<td>4514</td>
</tr>
<tr>
<td>$R1$ [$I&gt;2\sigma (I)$]</td>
<td>0.0420</td>
<td>0.0597</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.1157</td>
<td>0.1526</td>
</tr>
<tr>
<td>Peak and hole/e Å$^{-3}$</td>
<td>0.495 and -0.420</td>
<td>0.380 and -0.402</td>
</tr>
</tbody>
</table>

All the six aluminum dichloro complexes were well characterized by $^1\text{H}$, $^{13}\text{C}$ and $^{27}\text{Al}$ NMR spectroscopic analysis and used as precursors for the preparation of target aluminum bistriflate complexes.

### 2.3 Synthesis of LAl(OTf)$_2$

The target aluminum bistriflate complexes were synthesized using the triflate-for-chloride exchange procedure between pre-prepared aluminum dichloro complexes and silver triflate (AgOTf), which seemed to be the most appropriate reagent for this kind of exchange.$^{11}$ As shown in Scheme 2.7, complexes 2a-2f can react with two equiv of silver triflate, in the absence of light, in a non-coordination solvent such as 1,2-difluorobenzene, affording aluminum bistriflate complexes 3a-3f. The substrates exchange was clearly supported by
$^{27}$Al NMR spectroscopy as an upfield $\delta_{\text{Al}}$ signal around 60 ppm displaced the original $\delta_{\text{Al}}$ signal of LAICl$_2$ precursors around 103 ppm as shown in Table 2.2. These complexes were also identified by the presence of a $\delta_{\text{F}}$ signal around -77.3 ppm, which is different from the $\delta_{\text{F}}$ value observed for a free triflate anion at $\sim$ -79 ppm.$^{12}$

\[
\begin{align*}
\text{Scheme 2.7 Synthesis of aluminum bistriflate complexes}
\end{align*}
\]

Table 2.2 $^{27}$Al NMR (ppm) for complexes 2 and 3

|   | 2a | 102 | 3a | 64 | 2b | 101 | 3b | 64 | 2c | 101 | 3c | 63 | 2d | 102 | 3d | 56 | 2e | 102 | 3e | 66 | 2f | 102 | 3f | 64 |

Complex 3a was quite difficult to isolate and purify possibly due to more-than-expected air/moisture sensitivity, even though we managed to obtain few crystals that were used for single crystal X-ray and NMR spectroscopic analyses. The other complexes 3b-3f were all prepared in good yield and characterized by multinuclear NMR spectroscopic analysis. Crystals for these complexes were grown from a concentrated 1,2-difluorobenzene solution which was layered with $n$-hexane. The molecular structures of compounds 3a-3f are shown in Figure 2.3-2.8, together with the selected bond lengths and angles, while the
crystallographic data are summarized in Table 2.4. Crystallographic characterizations of 3a through 3f showed that these bistriflate compounds, reminiscent of the dichloro precursors, were four-coordinate. This might be a bit unusual considering (i) possible multidentate nature of triflate substrates\textsuperscript{11} and (ii) the ability of similar Al-based complexes to expand the coordination number to six.\textsuperscript{13} The Al-N bond lengths and the N1-Al1-N2 bond angles for 3c, 3d and 3f have shortened (~ 0.03 Å, Table 2.3) and widened (~ 3°), respectively, with reference to complexes 2c, 2d\textsuperscript{14} and 2f, potentially hinting at a decrease in electron density at the aluminum centers after the ligand exchange. In addition, the Al-N bond lengths for complexes 3a – 3d decreased gradually by ~ 0.02 Å, which might be due to the increasing electron donating group on N-aryl ring.

| 2a     | -      | 3a       | 1.826(4)   | 1.828(4)   |
| 2b     | -      | 3b       | 1.8306(16) | 1.8322(16) |
| 2c     | 1.8582(12) | 3c       | 1.8350(19) | 1.8377(19) |
| 2d     | 1.8663(9)  | 3d       | 1.841(3)   | 1.853(3)   |
| 2e     | -      | 3e       | 1.830(6)   | 1.843(6)   |
| 2f     | 1.846(9)  | 3f       | 1.8363(10) | 1.8399(10) |

Furthermore, the values for the Al-O (i.e. Al-OTf) bond in 3a (1.767(3) and 1.755(4) Å), 3b (1.7570(14) and 1.7611(14) Å), 3c (1.7605(17) and 1.7652(19)Å), 3d (1.765(3) and 1.769(3)Å), 3e (1 1.756(5) and 1.768(5) Å), and 3f (1.7686(9) and 1.7630(9) Å) provide additional evidence for the electron deficiency at the central aluminum atoms as these Al-O bond lengths are the shortest with respect to the other crystallographically elucidated triflate-containing aluminum compounds with Al-OTf bond lengths ranging from 1.807(10) to 2.074(4) Å.\textsuperscript{15a,b,c,d}
Figure 2.3 Molecular structure for 3a.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.826(4), Al1-N2 1.828(4), Al1-O1 1.767(3), Al1-O4 1.755(4); N1-Al1-N2 101.82(17), O1-Al1-O4 101.77(17).

Figure 2.4 Molecular structure for 3b.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.8306(16), Al1-N2 1.8322(16), Al1-O1 1.7570(14), Al1-O4 1.7611(14); N1-Al1-N2 101.53(7), O1-Al1-O4 109.28(7).
Figure 2.5 Molecular structure for 3c.
Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.8350(19), Al1-N2 1.8377(19), Al1-O1 1.7605(17), Al1-O4 1.7652(19); N1-Al1-N2 102.14(8), O1-Al1-O4 105.38(10).

Figure 2.6 Molecular structure for 3d.
Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.853(3), Al1-N2 1.841(3), Al1-O1 1.765(3), Al1-O4 1.769(3); N1-Al1-N2 101.3(1), O1-Al1-O4 106.1(1).
Figure 2.7 Molecular structure for 3e. Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.830(6), Al1-N2 1.843(6), Al1-O1 1.756(5), Al1-O4 1.768(5); N1-Al1-N2 100.7(3), O1-Al1-O4 103.2(2).

Figure 2.8 Molecular structure for 3f. Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.8399(10), Al1-N2 1.8363(10), Al1-O1 1.7686(9), Al1-O4 1.7630(9); N1-Al1-N2 101.64(5), O1-Al1-O4 109.71(4).
Table 2.4 Summary of the crystallographic data for compounds 3a-3f

<table>
<thead>
<tr>
<th></th>
<th>3a</th>
<th>3b</th>
<th>3c</th>
<th>3d</th>
<th>3e</th>
<th>3f</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C_{19}H_{17}AlF_{6}N_{2}O_{6}S_{2}</td>
<td>C_{23}H_{25}AlF_{6}N_{2}O_{6}S_{2}</td>
<td>C_{25}H_{29}AlF_{6}N_{2}O_{6}S_{2}</td>
<td>C_{124}H_{164}Al_{4}F_{24}N_{8}O_{24}S_{8}</td>
<td>C_{25}H_{29}AlF_{6}N_{2}O_{6}S_{2}</td>
<td>C_{27}H_{33}AlF_{6}N_{2}O_{6}S_{2}</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>574.45</td>
<td>630.55</td>
<td>658.60</td>
<td>2971.02</td>
<td>658.60</td>
<td>686.65</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P -1</td>
<td>P -1</td>
<td>C 1 2/c 1</td>
<td>P 1 21/c 1</td>
<td>P -1</td>
<td>P -1</td>
</tr>
<tr>
<td><strong>a /Å</strong></td>
<td>9.885(2)</td>
<td>9.4142(3)</td>
<td>35.666(6)</td>
<td>36.0533(16)</td>
<td>10.5596(10)</td>
<td>9.3172(3)</td>
</tr>
<tr>
<td><strong>b /Å</strong></td>
<td>11.505(3)</td>
<td>11.1193(3)</td>
<td>11.6490(17)</td>
<td>19.9087(8)</td>
<td>15.4198(17)</td>
<td>12.1746(4)</td>
</tr>
<tr>
<td><strong>c /Å</strong></td>
<td>12.865(3)</td>
<td>15.5284(5)</td>
<td>14.667(3)</td>
<td>19.2748(7)</td>
<td>19.116(2)</td>
<td>15.5472(4)</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>92.182(7)°</td>
<td>72.923(2)</td>
<td>92.590(10)</td>
<td>90.427(2)</td>
<td>96.852(5)</td>
<td>74.1182(13)</td>
</tr>
<tr>
<td><strong>V /Å³</strong></td>
<td>1181.3(5)</td>
<td>1405.07(7)</td>
<td>6087.5(17)</td>
<td>13834.6(10)</td>
<td>3087.0(6)</td>
<td>1588.64(9)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td><strong>Dc/ g cm⁻³</strong></td>
<td>1.615</td>
<td>1.490</td>
<td>1.437</td>
<td>1.426</td>
<td>1.417</td>
<td>1.435</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>584</td>
<td>648</td>
<td>2720</td>
<td>6208</td>
<td>6830</td>
<td>6678</td>
</tr>
<tr>
<td><strong>Crystal size/ mm</strong></td>
<td></td>
<td></td>
<td></td>
<td>0.180 x 0.220 x 0.360</td>
<td>0.40 x 0.40 x 0.18</td>
<td>0.240 x 0.300 x 0.400</td>
</tr>
<tr>
<td><strong>θ range/°</strong></td>
<td>1.78 to 29.00°</td>
<td>1.39 to 28.39</td>
<td>2.78 to 27.09</td>
<td>1.52 to 26.45</td>
<td>1.66 to 26.07</td>
<td>1.36 to 31.13</td>
</tr>
<tr>
<td><strong>No. of reflns collected</strong></td>
<td>18967</td>
<td>27133</td>
<td>52291</td>
<td>167728</td>
<td>27133</td>
<td>52291</td>
</tr>
<tr>
<td><strong>No. of indep reflns</strong></td>
<td>6253</td>
<td>6830</td>
<td>6678</td>
<td>6208</td>
<td>6830</td>
<td>6678</td>
</tr>
<tr>
<td><strong>R1 [I &gt; 2σ (I)]</strong></td>
<td>0.0663</td>
<td>0.0397</td>
<td>0.0425</td>
<td>0.0659</td>
<td>0.0397</td>
<td>0.0425</td>
</tr>
<tr>
<td><strong>wR2 (all data)</strong></td>
<td>0.2381</td>
<td>0.1199</td>
<td>0.1271</td>
<td>0.2659</td>
<td>0.2659</td>
<td>0.1143</td>
</tr>
<tr>
<td><strong>Peak and hole/e Å⁻³</strong></td>
<td>0.578 and -0.968</td>
<td>0.415 and -0.410</td>
<td>0.461 and -0.434</td>
<td>1.219 and -0.718</td>
<td>0.375 and -0.570</td>
<td>0.641 and -0.538</td>
</tr>
</tbody>
</table>
2.4 Synthesis of the cationic aluminum complexes

In general, one of the efficient approaches to increase the Lewis acidities of compounds is to make them cationic. After the synthesis of the aluminum bistriflate complexes 3a-3f, we made several attempts to synthesize the cationic aluminum complexes as summarized in Scheme 2.8.

![Scheme 2.8 Formation of cationic compounds](image)

Triflate group is considered to be one of the best leaving groups. Initially, a neutral nucleophilic reagent was added to the bistriflate complexes in order to promote the dissociation of the triflate substrates. First, we treated the aluminum bistriflate complex 3d with 2 equiv of N-heterocyclic carbene, but this attempt was unsuccessful as multinuclear NMR spectroscopic analysis revealed the formation of unidentified and inseparable impurities.

Then, we tried another nucleophile 4-dimethylaminopyridine (DMAP) to perform ligand exchange at the aluminum center. When 2 equiv of DMAP was added into the CD₂Cl₂ solution of complexes 3c, ¹H NMR clearly revealed that aluminum coordinate to DMAP as
shown in Figure 2.9. The $\delta_H$ signal of free DMAP $H_1$ at 8.20 ppm was replaced by an upfield signal at 7.77 ppm, which indicated the coordination of DMAP at the Al center has occurred.

Even though no valuable structural information was obtained due to the hydrolysis in the recrystallization step, this coordination can also be confirmed by the upfield shift of $\delta_F$ signal from $\sim$-77.3 ppm to $\sim$-78.4 ppm (Table 2.5). This $\delta_F$ signal is similar with that of the free triflate anion which is usually at around -79 ppm, suggesting that the new formed aluminum had a positive charge, with triflate groups replaced by DMAP. However, no crystal was obtained and we cannot confirm the structure.

Figure 2.9 Reaction between 3c and DMAP
Table 2.5 $^{19}$F NMR (ppm) for 3 and 3+ DMAP

<table>
<thead>
<tr>
<th></th>
<th>$^{19}$F NMR (ppm)</th>
<th>3b + 2 DMAP</th>
<th>3c + 2 DMAP</th>
<th>3d + 2 DMAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>-77.29</td>
<td>-78.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>-77.28</td>
<td>-78.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>-77.28</td>
<td>-78.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Additionally, when dissolved in a coordinating solvent such as CD$_3$CN, the values for $\delta_{\text{Al}}$ of 3b dramatically shift further upfield in comparison to the CD$_2$Cl$_2$-dissolved system suggesting acetonitrile coordination to aluminum centers in 3. In fact, the value for $\delta_{\text{F}}$ of 3 in CD$_3$CN around -79.04 ppm (vs -77.28 ppm in CD$_2$Cl$_2$) indicated that the triflate substituents were no longer bound to the aluminum center, affording cationic compounds as shown in Scheme 2.9.

![Scheme 2.9 Proposed reaction of 3d with CD$_3$CN](image)

As all the methods above failed to provide the desired cationic aluminum compounds, we decided to investigate whether these neutral aluminum bistriflates (3) would be able to catalyze Diels-Alder reactions. We investigated the [4 + 2]-cycloaddition of 2,3-dimethylbutadiene (4), which is 250 times less reactive than cyclopentadiene, and chalcone (5). Unfortunately, no targeted cycloaddition product was obtained when 5 mol% Dip$^\text{LAl(OTf)}_2$ was used as catalyst. Nevertheless when the aluminum bistriflate complexes were mixed with the dienophile, an obvious color change was observed. $^1$H NMR spectroscopy also clearly revealed the coordination between chalcone and the aluminum.
centre (Figure 2.10). With this information in hand, we decided to activate the aluminum bistriflate complex further by adding 1 equiv of sodium tetrakis[3,5-bischlorophenyl] borate (NaBAR\textsubscript{Cl}\textsubscript{4}). To our delight, the new formed catalytic system showed quite good activity and excellent endo/exo selectivity for the Diels-Alder transformation. It is, however, worth noting that this cycloaddition cannot be catalyzed by using NaBAR\textsubscript{Cl}\textsubscript{4} only.

![Figure 2.10 Coordination between 3b and chalcone](image)

Even though we obtained this initially exciting result, it was of paramount importance to gather more spectroscopic information about (i.e. identify) the active species before we started to expend its catalytic properties. Multinuclear NMR spectroscopic analysis clearly suggested interaction between the bistriflate complex and NaBAR\textsubscript{Cl}\textsubscript{4}. For example, the \textsuperscript{19}F signal shifted downfield from δ = -77.2 ppm to -76.5 ppm, which suggested that the triflate ligands of new formed compound possessed a higher “degree of coordination”.\textsuperscript{12} Furthermore, the \textsuperscript{27}Al NMR signal originally assigned to the initial bistriflate compounds disappeared presumably due to signal broadening. Also, no free or protonated
β-diketiminate ligand signals were found in $^1$H NMR spectroscopy which suggested that no decomposition or hydrolysis occurred in this process. On the other hand, lack of any precipitate formation (NaOTf) implied that the formation of an uncharged aluminum compound was most likely outcome for this reaction. Fortunately, after several trials, we successfully obtained a few crystals suitable for single crystal X-ray diffraction analysis. The crystal structure (Figure 2.11) shows that both triflate ligands were still bound to the aluminum center, while they were also coordinate to an sodium ion using different oxygen atoms, forming a [LAl(OTf)$_2$Na]$^+$ unit 6. The crystallographic data are summarized in Table 2.6

One of the OTf ligands and one of the aryl substituents were further coordinated to a second Na ion belonging to a different cationic unit, and vice versa, effectively creating a dimeric [LAl(OTf)$_2$Na]$_2$$^{2+}$ fragment. Each sodium cation was further weakly coordinated by two Cl atoms found on two distinct [BAr$^{Cl}_4$]$^-$ anions, resulting in the formation of a 2-dimensional coordination polymer. To the best of our knowledge, this is the first example of a coordination polymer that involves a tetraaryl borate anion. Nevertheless, we do not expect that this particular solid-state structure is retained in solution, as the Na ion is weakly coordinated to the anion and the aryl substituent.
Figure 2.11 Structure for ([LAl(OTf)$_2$Na][Bar$_4$Cl$_4$])$_n$.

The ellipsoids (apart from the CF$_3$ and non-bonding Dip groups) have been drawn at 50% probability level. All hydrogen atoms and [Bar$_4$Cl$_4$]- (apart from coordinating Cl atoms) anions have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.814(3), Al1-N2 1.849(3), Al1-O1 1.772(3), Al1-O4 1.770(3), S1-O1 1.497(2), S1-O2 1.417(3), S1-O3 1.419(3), S2-O4 1.485(3), S2-O5 1.425(3), S2-O6 1.427(3), Na1-O2 2.368(3), Na1-O6 2.334(3), Na1-O3 2.251(3), Na1-Cl2 2.867(3), Na1-Cl7 3.033(2), N1-Al1-N2 105.2(2), O1-Al1-O4 106.3(1).

Compared with its precursor 3d, no drastic structural change has occurred in 6 because the role of Na might be just to keep two OTf ligands together. For example, the average value of Al-N bond lengths (~1.832 Å) and Al-O bond lengths (~1.771 Å) are virtually identical to the same parameters obtained for 3d.
With this information in hand we decided to investigate the influence of the alkali metal and the anion on the overall structural and reactivity properties of the Lewis acidic system. For this purpose we mixed $\text{DipLAl(OTf)}_2$ with either KBAr$^{\text{Cl}}_4$ or LiB$(C_6F_5)_4$-Et$_2$O. First of all, as it was the case using NaBAr$^{\text{Cl}}_4$ there was no visible elimination of MOTf ($M = \text{Li or K}$) suggesting that no aluminum-based cationic species has formed. Then, it was not surprising that there was absolutely no change in the reaction rates regarding the cycloaddition between 4 and 5. This provided additional evidence that the central Al is responsible for the observed catalytic activity. On one occasion we were fortunate enough to obtain few crystals from the reaction between $\text{xylLAl(OTf)}_2$ and LiB$(C_6F_5)_4$-Et$_2$O suitable for single crystal X-ray diffraction. Molecular structure of the new compound 7 is shown in Figure 2.12 with the crystallographic data summarized in Table 2.6. Again, both triflate ligands were still coordinated to the Al center while the lithium cation is bridging between two triflates forming familiar $[\text{xylLAl(OTf)}_2\text{Li}]^+$ unit 7. However, in this case due to the presence of OEt$_2$ molecules the solid state structure is not polymeric. Considering these information it can be concluded that the role of the alkali metal is presumably to “tie-up” the two triflate ligands in order to alleviate steric congestion at the Al center leading to a higher catalytic activity in comparison to $\text{xylLAl(OTf)}_2$. 
Figure 2.12 Structure for \([\text{LAI(OTf)}_2\text{Li}][\text{B(C}_6\text{F}_5)_4]\)

All hydrogen atoms and \([\text{B(C}_6\text{F}_5)_4]\)- anions have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.817(3), Al1-N2 1.822(3), Al1-O1 1.770(3), Al1-O4 1.755(3), Li2-O2 2.031(7), Li2-O5 2.018(8); N1-Al1-N2 102.08(15), O1-Al1-O4 104.03(13).

Table 2.6 Summary of the crystallographic data for compounds 6, 7

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{110}H_{106}Al_2B_2Cl_16F_{12}N_4Na_2O_{12}S_4</td>
<td>C_{102}H_{70}Al_2B_2F_{52}Li_2N_4O_{14}S_4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2720.98</td>
<td>2781.32</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2/n</td>
<td>P -1</td>
</tr>
<tr>
<td>a /Å</td>
<td>17.2647(11)</td>
<td>12.5725(6)</td>
</tr>
<tr>
<td>b /Å</td>
<td>20.3414(15)</td>
<td>15.7968(7)</td>
</tr>
<tr>
<td>c /Å</td>
<td>18.7463(13)</td>
<td>16.9105(7)</td>
</tr>
<tr>
<td>β/°</td>
<td>90.972(2)</td>
<td>98.387(2)</td>
</tr>
<tr>
<td>V / Å³</td>
<td>6582.5(8)</td>
<td>2894.1(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Dc/ g cm⁻³</td>
<td>1.373</td>
<td>2.27843</td>
</tr>
<tr>
<td>F(000)</td>
<td>2784</td>
<td>1396</td>
</tr>
<tr>
<td>Crystal size/ mm</td>
<td>0.400 x 0.280 x 0.240</td>
<td>0.220 x 0.300 x 0.420</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>θ range/°</td>
<td>1.59 to 29.19</td>
<td>1.62 to 29.40</td>
</tr>
<tr>
<td>No. of reflns collected</td>
<td>17754</td>
<td>94461</td>
</tr>
<tr>
<td>No. of indep reflns</td>
<td>17754</td>
<td>15850</td>
</tr>
<tr>
<td>R1 [I &gt;2σ (I)]</td>
<td>0.0637</td>
<td>0.0692</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.1677</td>
<td>0.1702</td>
</tr>
<tr>
<td>Peak and hole/e Å⁻³</td>
<td>0.961 and -0.738</td>
<td>0.572 and -0.479</td>
</tr>
</tbody>
</table>

2.5 Summary

In summary, we have prepared a series of β-diketiminate supported aluminum dichloro compounds. The corresponding aluminum bistriflate compounds were subsequently synthesized via triflate-for-chloride exchange using silver triflate. When these aluminum bistriflate compounds were combined with NaBArCl₄, (or any other alkali borate salt) they formed quite active Lewis acid systems capable of catalyzing Diels-Alder transformation. Further information about the catalysis will be discussed in next chapter.

2.6 Experimental section

All operations were performed under argon or oxygen-free nitrogen pressure using standard Schlenk line and glovebox techniques. All glassware involving sensitive reaction was oven- and vacuum-dried and argon flow-degassed before use. All solvents were dried, distilled under nitrogen atmosphere, degassed under argon and stored with 4Å molecular sieves prior to use. The starting materials 2,4-pentanedione, TsOH•H₂O, amines, AlCl₃ and silver triflate were obtained from commercial source and used without further purification. ¹H, ¹³C, ¹¹B, ¹⁹F and ²⁷Al NMR spectra were measured on Bruker AV 300, 400, 500 MHz, JEOL ECA400 MHz, JEOL ECA400 SL, BBFO1 400MHz or BBFO2 400MHz
spectrometers at 298 K unless otherwise stated. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal, sept = septet. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OptiMelt Stanford Research System. X-ray data was collected on diffractometer Bruker X8 CCD and Bruker Kappa CCD, equipped with a liquid nitrogen-cooling stream. Nacnac ligands were prepared according to the literature, and the analytical and spectroscopic data are in accordance with those reported.2,17

**Preparation of [CH(MeCNR)2]H (1a - 1d).**

2,4-pentanedione (10.0 g, 100 mmol) was mixed with substituent aniline (200 mmol) in 400 mL toluene containing TsOH•H2O (20 g). The reaction mixture was left to reflux overnight with water removed by a Dean-Stark apparatus. After which, the solution was cooled to ambient temperature and the solid was filtered off by Buchner funnel. The filtrate was neutralized by 1 equiv of Na2CO3 (10.6 g) following by extraction with 200 mL dichloromethane twice. The combined organic layers were dried with MgSO4. Removal of volatiles via rotary evaporator afforded brown oil. The oil was re-dissolved in 30 mL ethanol and kept under -30°C overnight. Pure product was obtained as colorless crystals. β-diketiminate ligand 1a - 1d were prepared following this procedure.

**Synthesis of 1a.** Yield 81%. 1H NMR (400 MHz, CDCl3, 25 °C): δ 1.80 (s, 6H, CH3 on backbone) 4.78 (s, 1H, γ-H), 6.89 (m, 6H, ArH), 7.09 (m, 4H, ArH), 13.17 (br s, 1H, NH).
Synthesis of 1b. Yield 85%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.70 (s, 6H, CH$_3$ on backbone), 2.16 (s, 12H, ArCH$_3$), 4.88 (s, 1H, $\gamma$-H), 6.93 (t, 2H, J$_{H-H}$ = 7.36, p-ArH), 7.03 (d, 4H, J$_{H-H}$ = 7.36, m-ArH), 12.10 (s, 1H, NH).

Synthesis of 1c. Yield 87%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.68 (s, 6H, CH$_3$ on backbone), 2.12 (s, 12H, m-ArCH$_3$), 2.26 (s, 6H, p-ArCH$_3$), 4.85 (s, 1H, $\gamma$-H), 6.85 (t, 4H, m-ArH), 12.11 (s, 1H, NH).

Synthesis of 1d. Yield 89%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.11 (d, 12H, J$_{H-H}$ = 6.95, CH(CH$_3$)$_2$), 1.20 (d, 12H, J$_{H-H}$ = 6.95, CH(CH$_3$)$_2$), 1.71 (s, 6H, CH$_3$ on backbone), 3.08 (sept, 4H, JH-H = 6.95, CH(CH$_3$)$_2$), 4.87 (s, 1H, $\gamma$-H), 7.10 (m, 6H, ArH), 12.10 (s, 1H, NH).

Synthesis of asymmetric $\beta$-diketiminate ligands (1e-1f).

2-(2,6-Diisopropylphenylimido)-2-pentene-4-one. 2,4-pentanedione (10.0 g, 100 mmol, 2 equivs) was mixed with 2,6-Diisopropylaniline (8.8 g, 50 mmol) in 400 mL toluene containing catalytic amount of conc. H$_2$SO$_4$. The reaction mixture was left to reflux overnight with water removed by a Dean-Stark apparatus. After cooled to ambient temperate, volatiles were removed under reduced pressure, affording a pale brown oil. The oil was then stirred with 30 mL petroleum ether at -20 °C, forming a white solid which was then washed by cold hexane and dried in vacuo. Yield: 11.3g, 87%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.14 (d, 3H, J$_{H-H}$ = 6.95, CH(CH$_3$)$_2$), 1.20 (d, 3H, J$_{H-H}$ = 6.95, CH(CH$_3$)$_2$), 2.11 (s, 6H, CH$_3$ on backbone), 3.01 (sept, 2H, J$_{H-H}$ = 6.95, CH(CH$_3$)$_2$), 5.20 (s, 1H, $\gamma$-H), 7.16-7.29 (t, 3H, ArH), 12.05 (s, 1H, NH).
500 mL round bottomed flask in 100 mL toluene. The solution was brought to reflux overnight with water removed by a Dean-Stark apparatus. After which the reaction mixture was cooled down to room temperature and reduced under vacuo to give yellow oil. The oil was treated with diethyl ether, water and Na₂CO₃. The water layer was separated and extracted with 200 mL ether. The organic layers were combined and dried over Na₂SO₄. The solvent was evaporated, yielding a yellow solid, which was recrystallized in cold ethanol. Asymmetric β-diketiminate ligands 1e-1f were prepared following this procedure.

**Synthesis of 1e.** Yield 75%. \(^1\)H NMR (400 MHz, CDCl₃, 25 °C): \(\delta\) 1.14(d, 6H, J_H-H = 6.95, CH(CH₃)₂), 1.21(d, 6H, J_H-H = 6.95, CH(CH₃)₂), 2.08(s, 6H, CH₃ on backbone), 2.98 (sept, 2H, J_H-H = 6.95, CH(CH₃)₂), 4.89 (s, 1H, γ-H), 6.94-7.29 (m, 8H, ArH), 12.70 (s, 1H, NH).

**Synthesis of 1f.** Yield 80%. \(^1\)H NMR (400 MHz, CDCl₃, 25 °C): \(\delta\) 1.11(d, 6H, J_H-H = 7.04, CH(CH₃)₂), 1.21(d, 6H, J_H-H = 7.04, CH(CH₃)₂), 1.70(s, 6H, CH₃ on backbone), 2.15(s, 6H, ArCH₃), 3.08 (sept, 2H, J_H-H = 7.04, CH(CH₃)₂), 4.88 (s, 1H, γ-H), 6.91-7.14 (m, 6H, ArH), 12.25 (s, 1H, NH).

**Synthesis of 2a.** \(^n\)BuLi solution in cyclohexane (2M, 0.53 mL, 1.05 mmol) was added dropwise to 20 mL toluene solution of ligand 1a (0.25 g, 1.0 mmol) at 0 °C. The reaction solution was allowed to warm to ambient temperature and left to stir for 1 hour, after which, the solution was added slowly to AlCl₃ (0.14g, 1.05 equiv). The reaction mixture was warmed to room temperature and left to stir for 5 hours. Then the solution was filtered to remove the precipitate (LiCl), after that, the solvent was evaporated under reduced pressure. The residue was washed by cold hexane, affording the designated product 2a 0.30 g as white solid, yield 86%. \(^1\)H NMR (400 MHz, CDCl₃, 25 °C): \(\delta\) 1.91(s, 6H, CH₃ on backbone), 5.21 (s, 1H, γ-H), 7.20-7.42 (m, 10H, ArH). \(^13\)C NMR (100 MHz, CDCl₃,
25 °C): δ 23.3 (s, 2C, CH₃, on backbone), 98.4 (s, 1C, γ-C), 126.8 (s, 2C, ArC), 127.1 (s, 2C, ArC), 129.4 (s, 2C, ArC), 142.4 (s, 2C, ArC), 171.0 (s, 2C, CN). ²⁷Al NMR (104 Hz, DCM, 25 °C): δ 99 (sharp, s).

**Synthesis of 2b.** Following the same procedure described for the synthesis of 2a, treatment of 1b (0.31 g, 1.00 mmol) with "BuLi (2.0 M in cyclohexane, 0.53 mL, 1.05 mmol) and then *in situ* adding AlCl₃ (0.14 g, 1.05 mmol) yielded complex 2b (0.34 g, 84%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.81 (s, 6H, CH₃ on backbone), 2.32 (s, 12H, ArCH₃), 5.37 (s, 1H, γ-H), 7.11 (b, 6H, ArH). ²⁷Al NMR (104 Hz, DCM, 25 °C): δ 98 (sharp, s).

**Synthesis of 2c.** Following the same procedure described for the synthesis of 2a, treatment of 1c (0.33 g, 1.00 mmol) with "BuLi (2.0 M in cyclohexane, 0.53 mL, 1.05 mmol) and then *in situ* adding AlCl₃ (0.14 g, 1.05 mmol) yielded complex 2c (0.35 g, 81%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.80 (s, 6H, CH₃ on backbone), 2.26 (s, 18H, ArCH₃), 5.33 (s, 1H, γ-H), 6.92 (b, 4H, ArH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 18.4 (s, 2C, ArCH₃), 20.5 (s, 4C, ArCH₃), 22.6 (s, 2C, CH₃, on backbone), 97.8 (s, 1C, γ-C), 129.3 (s, 2C, ArC), 133.4 (s, 2C, ArC), 136.1 (s, 2C, ArC), 137.2 (s, 2C, ArC), 171.8 (s, 2C, CN). ²⁷Al NMR (104 Hz, DCM, 25 °C): δ 98 (sharp, s).

**Synthesis of 2d.** Following the same procedure described for the synthesis of 2a, treatment of 1d (0.42 g, 1.00 mmol) with "BuLi (2.0 M in cyclohexane, 0.53 mL, 1.05 mmol) and then *in situ* adding AlCl₃ (0.14 g, 1.05 mmol) yielded complex 2d (0.44 g, 85%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.16 (d, 12H, J_H-H = 6.88, CH(CH₃)₂), 1.19 (d, 12H, J_H-H = 6.88, CH(CH₃)₂), 1.89 (s, 6H, CH₃ on backbone), 3.20 (sept, 4H, J_H-H = 6.88, CH(CH₃)₂), 5.41 (s, 1H, γ-H), 7.21-7.32 (m, 6H, ArH). ²⁷Al NMR (104 Hz, DCM, 25 °C): δ 99 (sharp, s).
Synthesis of 2e. Following the same procedure described for the synthesis of 2a, treatment of 1e (0.33 g, 1.00 mmol) with "BuLi (2.0 M in cyclohexane, 0.53 mL, 1.05 mmol) and then in situ adding AlCl₃ (0.14 g, 1.05 mmol) yielded complex 2e (0.37 g, 86%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.17(d, 6H, J_H-H = 6.84, CH(CH₃)₂), 1.27(d, 6H, J_H-H = 6.84, CH(CH₃)₂), 1.88(s, 3H, CH₃ on backbone), 1.98(s, 3H, CH₃ on backbone), 3.09 (sept, 2H, J_H-H = 6.84, CH(CH(CH₃)₂)), 5.37 (s, 1H, γ-H), 7.16-7.42 (m, 8H, ArH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 23.4(s, 2C, CH(CH₃)₂), 23.8 (s, 2C, CH(CH₃)₂), 24.8 (s, 1C, CH₃, on backbone), 24.9 (s, 1C, CH₃, on backbone), 28.3 (s, 2C, CH(CH₃)₂), 99.3 (s, 1C, γ-C), 124.5 (s, 1C, ArC), 126.5 (s, 1C, ArC), 127.0 (s, 1C, ArC), 127.8 (s, 1C, ArC), 129.5 (s, 1C, ArC), 137.7 (s, 1C, ArC), 142.8 (s, 1C, ArC), 144.6 (s, 1C, ArC), 170.4(s, 1C, CN), 172.4 (s, 1C, CN). ²⁷Al NMR (104 Hz, DCM, 25 °C): δ 102 (sharp, s).

Synthesis of 2f. Following the same procedure described for the synthesis of 2a, treatment of 1f (0.36 g, 1.00 mmol) with "BuLi (2.0 M in cyclohexane, 0.53 mL, 1.05 mmol) and then in situ adding AlCl₃ (0.14 g, 1.05 mmol) yielded complex 2b (0.42 g, 91%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.15(d, 6H, J_H-H = 6.84, CH(CH₃)₂), 1.17(d, 6H, J_H-H = 6.84, CH(CH₃)₂), 1.83(s, 3H, CH₃ on backbone), 1.89(s, 3H, CH₃ on backbone), 2.31(s, 6H, ArCH₃), 3.18 (sept, 2H, J_H-H = 6.84, CH(CH₃)₂), 5.41 (s, 1H, γ-H), 7.11-7.31 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 18.9(s, 2C, ArCH₃), 23.1(s, 2C, CH(CH₃)₂), 23.9 (s, 2C, CH(CH₃)₂), 24.7 (s, 1C, CH₃, on backbone), 24.9 (s, 1C, CH₃, on backbone), 28.3 (s, 2C, CH(CH₃)₂), 99.3 (s, 1C, γ-C), 124.6 (s, 1C, ArC), 127.0 (s, 1C, ArC), 127.9 (s, 1C, ArC), 129.0 (s, 1C, ArC), 134.0 (s, 1C, ArC), 137.4 (s, 1C, ArC), 140.9 (s, 1C, ArC), 144.7 (s, 1C, ArC), 171.4(s, 1C, CN), 172.4 (s, 1C, CN). ²⁷Al NMR (104 Hz, DCM, 25 °C): δ 101 (sharp, s).
**Synthesis of 3a.** Compound 2a (0.34 g, 1.00 mmol) and 2.1 equiv of AgOTf (0.54 g, 2.10 mmol) were mixed in 20 mL 1,2-difluorobenzene. The reaction mixture was left to stir overnight in the absence of light. After filtration, the clear solution obtained was concentrated to 5 mL and transferred to a smaller Schlenk flask, following by layering with 10 mL hexane. Colorless crystals were grown in 2 days. After dryness under vacuum, product 3a was obtained as white solid. Yield: 0.35g, 61%. $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ 2.04 (s, 6H, C$_3$H$_3$ on backbone), 5.47 (s, 1H, γ-H), 7.22-7.49 (m, 10H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ 23.5 (s, 2C, C$_3$H$_3$, on backbone), 100.1 (s, 1C, γ-C), 111.4 (s, 2C, CF$_3$), 126.1 (s, 2C, ArC), 128.3 (s, 2C, ArC), 130.0 (s, 2C, ArC), 140.0 (s, 2C, ArC), 174.0 (s,2C, CN). $^{27}$Al NMR (104 Hz, CDCl$_3$, 25°C): $\delta$ 64 (sharp, s). $^{19}$F NMR (376 Hz, CDCl$_3$, 25°C): $\delta$ -77.29 (sharp, s).

**Synthesis of 3b.** Complex 3b was prepared by treatment of 2b (0.70 g, 1.74 mmol) and AgOTf (0.90 g, 3.50 mmol) following the same procedure described for 3a. Yield: 0.72 g, 66%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.94 (6H, s, CH$_3$ on backbone), 2.26 (12H, s, ortho-CH$_3$), 5.60 (1H, s, γ-CH), 7.18-7.19 (6H, m, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ 18.1 (s, CH$_3$ on backbone), 23.0 (s, CH$_3$ on R), 99.8 (s, γ-C), 128.2 (s, ArC), 129.4 (s, ArC), 133.6 (s, ArC), 137.7 (s, ArC), 175.0 (s, CN). $^{27}$Al NMR (104 Hz, DCM, 25 °C): $\delta$ 65 (sharp, s). $^{19}$F NMR (376 Hz, DCM, 25 °C): $\delta$ -77.29 (sharp, s). HRMS (ESI) calculated for C$_{23}$H$_{26}$N$_2$O$_6$F$_6$AlS$_2$ [ M + H]: 631.0952; Found:631.0957.

**Synthesis of 3c.** Complex 3c was prepared by treatment of 2c (0.70 g, 1.62 mmol) and AgOTf (0.91 g, 3.50 mmol) following the same procedure described for 3a. Yield: 0.62 g, 58%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.91 (s, 6H, CH$_3$ on backbone), 2.20 (s, 12H, ortho-CH$_3$), 2.29 (s, 6H, p-CH$_3$), 5.57 (s, 1H, γ-H), 6.97 (s, 4H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ 18.0 (s, p-CH$_3$), 20.9 (s, ortho-CH$_3$), 22.9 (s, CH$_3$ on backbone),
99.7 (s, γ-C), 130.0 (s, ArC), 133.1 (s, ArC), 135.2 (s, ArC), 137.8 (s, ArC), 175.1 (s, CN).

$^{27}$Al NMR (104 Hz, DCM, 25 °C): δ 61 (sharp, s). $^{19}$F NMR (376 Hz, DCM, 25 °C): δ -77.28 (sharp, s). HRMS (ESI) calculated for C$_{25}$H$_{30}$N$_2$O$_6$F$_6$AlS$_2$ [M + H]: 659.1265; Found: 659.1271.

Synthesis of 3d. Complex 3d was prepared by treatment of 2d (0.60 g, 1.16 mmol) and AgOTf (0.62 g, 2.41 mmol) following the same procedure described for 3a. Yield: 0.54 g, 63%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.16 (d, 12H, J$_{H-H}$ = 6.88, CH(CH$_3$)$_2$), 1.23 (d, 12H, J$_{H-H}$ = 6.88, CH(CH$_3$)$_2$), 2.00 (s, 6H, CH$_3$ on backbone), 3.03 (m, 4H, J$_{H-H}$ = 6.88, CH(CH$_3$)$_2$), 5.77 (s, 1H, γ-H), 7.24-7.34 (m, 6H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): δ 24.1 (s, CH$_3$ on backbone), 24.5 (s, CH(CH$_3$)$_2$), 24.6 (s, CH(CH$_3$)$_2$), 28.3 (s, CH(CH$_3$)$_2$), 100.7 (s, γ-C), 124.9 (s, ArC), 128.5 (s, ArC), 136.4 (s, ArC), 144.2 (s, ArC), 176.1 (s, CN). $^{27}$Al NMR (104 Hz, DCM, 25 °C): δ 59 (sharp, s). $^{19}$F NMR (376 Hz, DCM, 25 °C): δ -77.28 (sharp, s). HRMS (ESI) calculated for C$_{31}$H$_{42}$N$_2$O$_6$F$_6$AlS$_2$ [M + H]: 743.2204; Found: 743.2175.

Synthesis of 3e. Complex 3e was prepared by treatment of 2e (0.50 g, 1.16 mmol) and AgOTf (0.62 g, 2.41 mmol) following the same procedure described for 3a. Yield: 0.47 g, 62%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.19 (d, 6H, J$_{H-H}$ = 6.84, CH(CH$_3$)$_2$), 1.22 (d, 6H, J$_{H-H}$ = 6.84, CH(CH$_3$)$_2$), 1.98 (s, 3H, CH$_3$ on backbone), 2.11 (s, 3H, CH$_3$ on backbone), 2.84 (sept, 2H, J$_{H-H}$ = 6.84, CH(CH$_3$)$_2$), 5.63 (s, 1H, γ-H), 7.16-7.47 (m, 8H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): δ 23.5 (s, 2C, CH(CH$_3$)$_2$), 23.6 (s, 2C, CH(CH$_3$)$_2$), 24.0 (s, 1C, CH$_3$, on backbone), 24.5 (s, 1C, CH$_3$, on backbone), 28.4 (s, 2C, CH(CH$_3$)$_2$), 100.0 (s, 1C, γ-C), 124.9 (s, 1C, ArC), 125.7 (s, 1C, ArC), 128.1 (s, 1C, ArC), 128.8 (s, 1C, ArC), 130.0 (s, 1C, ArC), 135.4 (s, 1C, ArC), 140.5 (s, 1C, ArC), 143.9 (s,
1C, ArC), 173.5 (s, 1C, CN), 174.9 (s, 1C, CN). $^{27}$Al NMR (104 Hz, DCM, 25 °C): $\delta$ 66 (sharp, s). $^{19}$F NMR (376 Hz, DCM, 25 °C): $\delta$ -77.40 (sharp, s).

**Synthesis of 3f.** Complex 3f was prepared by treatment of 2f (0.53 g, 1.16 mmol) and AgOTf (0.62 g, 2.41 mmol) following the same procedure described for 3a. Yield: 0.44g, 56%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.15 (d, 6H, J$_{H-H}$ = 6.84, CH(C$_2$H$_3$)$_2$), 1.19 (d, 6H, J$_{H-H}$ = 6.84, CH(CH$_3$)$_2$), 1.99 (s, 3H, CH$_3$ on backbone), 2.01 (s, 3H, CH$_3$ on backbone), 2.26 (s, 6H, ArCH$_3$), 2.97 (sept, 2H, J$_{H-H}$ = 6.84, CH(CH$_3$)$_2$), 5.74 (s, 1H, $\gamma$-H), 7.14-7.33 (m, 6H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ 18.4 (s, 2C, ArCH$_3$), 23.3 (s, 2C, CH(CH$_3$)$_2$), 23.8 (s, 2C, CH(CH$_3$)$_2$), 24.3 (s, 1C, CH$_3$, on backbone), 24.5 (s, 1C, CH$_3$, on backbone), 28.2 (s, 2C, CH(CH$_3$)$_2$), 100.7 (s, 1C, $\gamma$-C), 124.9 (s, 1C, ArC), 127.8 (s, 1C, ArC), 128.7 (s, 1C, ArC), 128.9 (s, 1C, ArC), 129.4 (s, 1C, ArC), 133.5 (s, 1C, ArC), 138.9 (s, 1C, ArC), 144.0 (s, 1C, ArC), 180.0 (s, 1C, CN), 180.5 (s, 1C, CN). $^{27}$Al NMR (104 Hz, DCM, 25 °C): $\delta$ 64 (sharp, s). $^{19}$F NMR (376 Hz, DCM, 25 °C): $\delta$ -77.01 (sharp, s).

General procedure for the formation of LAl(OTf)$_2$/NaBAr$^\text{Cl}_4$.

15 mg (0.024 mmol) of NaBAr$^\text{Cl}_4$ was dissolved in 1 mL of DCM-d$_2$ in a J. Young NMR tube followed by the addition of 1 equiv of LAl(OTf)$_2$. Multinuclear NMR was recorded right away. Even though these systems showed to be quite stable in DCM they appear to be extremely air/moisture sensitive and the most efficient results are achieved if used in situ. A small batch of crystals was obtained by layering this solution with hexane.

3b + NaBAr$^\text{Cl}_4$. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 1.91 (s, 6H, CH$_3$ on backbone), 2.14 (s, 12H, ortho-CH$_3$), 5.69 (s, 1H, $\gamma$-H), 6.97 (m, 6H, ArH), 7.03 (m, 12H, BAr$^\text{Cl}_4$H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 17.6 (s, CH$_3$ on backbone), 22.8 (s, CH$_3$ on R), 101.1 (s,
γ-C, 123.1 [BarCl₄ (p-CH)], 128.7 (s, ArC), 129.5 (s, ArC), 132.9 (q, J_{BC} = 4 Hz, BarCl₄), 133.0 [BarCl₄ (m-CH)], 134.0 (s, ArC), 137.0 (s, ArC), 163.9 (q, J_{BC} = 49 Hz, BarCl₄), 176.7 (s, CN). ¹⁹F NMR (376 Hz, DCM, 25 °C): δ -75.93 (sharp, s). ¹¹B NMR (128 Hz, DCM, 25 °C): δ -6.9.

**3c** + NaBarCl₄. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 1.88 (s, 6H, CH₃ on backbone), 2.09 (m, 18H, Ar-CH₃), 5.68 (s, 1H, γ-H), 6.82 (m, 3H, BarCl₄H), 6.97 (m, 4H, ArH), 7.04 (m, 9H, BarCl₄H). ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C): δ 17.5 (s, p-CH₃), 20.5 (s, ortho-CH₃), 22.7 (s, CH₃ on backbone), 101.1 (s, γ-C), 123.1 [BarCl₄ (p-CH)], 125.3 (s, ArC), 129.2 (s, ArC), 132.9 (q, J_{BC} = 4 Hz, BarCl₄), 133.3 [BarCl₄ (m-CH)], 134.6 (s, ArC), 138.8 (s, ArC), 163.8 (q, J_{BC} = 49 Hz, BarCl₄), 176.8 (s, CN). ¹⁹F NMR (376 Hz, DCM, 25 °C): δ -75.90 (sharp, s). ¹¹B NMR (128 Hz, DCM, 25 °C): δ -6.9.

**3d** + NaBarCl₄. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ (d, 12H, J_{HH} = 7.00, CH(CH₃)₂), 1.30 (d, 12H, J_{HH} = 6.32, CH(CH₃)₂), 2.00 (s, 6H, CH₃ on backbone), 2.87 (m, 4H, J_{HH} = 6.52, CH(CH₃)₂), 5.74 (s, 1H, γ-H), 7.04-7.10 (m, 12H, BarCl₄H), 7.43-7.45 (m, 6H, ArH). ¹³C NMR (100 MHz, Cd₂Cl₂, 25 °C): δ 24.2 (s, CH₃ on backbone), 24.4 (s, CH(CH₃)₂), 24.6 (s, CH(CH₃)₂), 28.7 (s, CH(CH₃)₂), 101.1 (s, γ-C), 123.1 [BarCl₄ (p-CH)], 125.3 (s, ArC), 129.2 (s, ArC), 132.9 [BarCl₄ (m-CH)], 133.0 (q, J_{BC} = 4 Hz, BarCl₄), 135.8 (s, ArC), 144.1 (s, ArC), 163.9 (q, J_{BC} = 49 Hz, BarCl₄), 176.8 (s, CN). ¹⁹F NMR (376 Hz, DCM, 25 °C): δ -76.50 (sharp, s). ¹¹B NMR (128 Hz, DCM, 25 °C): δ -7.0.

**3b** + LiBC₆F₅. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 1.05(t, 12H, J_{HH} = 7.32, CH₂CH₃), 1.91(s, 6H, ArCH₃), 2.18 (s, 6H, CH₃ on backbone), 3.38 (q, 8H, J_{HH} = 7.32, CH₂CH₃), 5.71 (s, 1H, γ-H), 7.19 (m, 6H, ArH). ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C): δ 14.4 (CH₂CH₃), 17.6 (CH₃ on backbone), 22.7 (ArCH₃), 65.5 (CH₂CH₃), 100.7 (γ-C), 128.5(ArC),
129.5 (ArC), 133.6 (ArC), 135.1 (BAr^F_4), 137.1 (s, ArC), 137.5 (BAr^F_4), 147.0 (BAr^F_4), 149.3 (BAr^F_4), 176.3 (CN). $^{11}$B NMR (128 Hz, DCM, 25 °C): $\delta$ –17.6.
References


12 It is generally accepted that the signal for non-coordinated triflate anion is observed at around $\delta_F = -79$ ppm, whereas the coordinated anion is found at about 1-2 ppm downfield shifted from this value. See for example: Hayashida, T.; Kondo, H.; Terasawa, J.; Kirchner, K.; Sunda, Y.; Nagashima, H. J. Organomet. Chem. 2007, 692, 382.


Chapter 3

Application in organic transformations
Ever since the elegant applications in the total synthesis of a large range of complex natural products in the 1950s, Diels-Alder cycloadditions have been at the frontline in organic synthesis for its power and effectiveness.\textsuperscript{1} It was considered to be a useful and powerful synthetic reaction as it can increase the molecular complexity (molecular size, topology, stereochemistry, functionality, and appendages) and widely used to synthesize numerous natural products and biologically active molecules.\textsuperscript{2-5} The reactivity of normal Diels-Alder reaction depends on the energy difference between the HOMO of the diene and the LUMO of dienophile.\textsuperscript{6} The most common dienophiles usually contain electron withdrawing substituents such as carbonyl, cyano or nitro groups as they can lower the corresponding LUMO energy. This effect can be dramatically enhanced by coordinating to Lewis acids, which are the most widely used catalysts for Diels-Alder reaction. Herein, we examined the β-diketiminate supported Al bis(triflate) systems which were discussed in Chapter 2 as Lewis acid catalysts for a series of Diels-Alder reactions involving three dienes and several dienophiles.

3.1 Diels-Alder reactions involving 2,3-dimethylbutadiene.

As mentioned in Chapter II, when activated by 1 equiv of NaBAR\textsuperscript{Cl}\textsubscript{4}, \textsubscript{Dip}LA(OTf)\textsubscript{2} (3d) (5 mol\%) is capable of efficiently catalyzing the Diels-Alder reaction between 2,3-dimethylbutadiene (4) and chalcone (5) in dichloromethane where 2 equiv of diene was used (entry 2, Table 3.1). After that, other species including KBAR\textsuperscript{Cl}\textsubscript{4}, NaBAR\textsuperscript{CF\textsubscript{3}}\textsubscript{4} and LiB(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}·Et\textsubscript{2}O were also used to activate the aluminum bistriflate complex in order to increase the catalytic activity. As shown in Table 3.1, KBAR\textsuperscript{Cl}\textsubscript{4} and NaBAR\textsuperscript{CF\textsubscript{3}}\textsubscript{4} showed similar ability to activate the aluminum bistriflate complex while introducing LiB(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}·Et\textsubscript{2}O led to decreased activity presumably due to the presence of coordinating Et\textsubscript{2}O.
Table 3.1 Diels-Alder reaction by different catalytic systems

<table>
<thead>
<tr>
<th>#</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Endo/exo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3d</td>
<td>24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>3d + NaBArCl4</td>
<td>6</td>
<td>80</td>
<td>99 : 1</td>
</tr>
<tr>
<td>3</td>
<td>3d + KBarCl4</td>
<td>6</td>
<td>78</td>
<td>99 : 1</td>
</tr>
<tr>
<td>4</td>
<td>3d + KBarCF3Cl4</td>
<td>6</td>
<td>80</td>
<td>99 : 1</td>
</tr>
<tr>
<td>5</td>
<td>3d + LiB(C6F5)4·Et2O</td>
<td>24</td>
<td>22</td>
<td>99 : 1</td>
</tr>
</tbody>
</table>

With all this information in hand, we decided to furthermore expand the catalytic properties of this series of aluminum bistriflate complexes. Complexes 3b-3d combined with NaBArCl4 were used to catalyze the Diels-Alder cycloadditions between 4 and several different dienophiles as summarized in Table 3.2. When enones 3-buten-2-one (9) and ethyl vinyl ketone (10) were used, all the three catalytic systems were proved to be excellent catalysts for the cycloadditions with the corresponding trans adducts (where applicable) as the only observable isomers (entry 1, 2, Table 3.2). To be noticed, decent yields were also gained when the catalyst loadings were reduced to 1 mol%. When benzalacetone (11) was used for the cycloaddition, 3d still acted as a good catalyst while catalyst loadings of 15% were required for 3b and 3c to afford decent yields (entry 3, Table 3.2). To our surprise, a quite different result was observed when 5 was examined as a dienophile, because 3b and 3c can complete the catalysis in 3h while 3d required more than 18h to achieve good conversion.
After that we decided to examine whether these catalytic systems can also catalyze the Diels-Alder cycloaddition reactions involving cyclic enones. Similar to the runs involving dienophiles 5 and 11, when cyclic dienophiles were used for the Diels-Alder cycloadditions, 3b/3c also performed quite differently in comparison to 3d. A higher catalyst loading was required to catalyze the Diels-Alder reaction between diene 4 and 2-cyclopenten-1-one (12) for the system containing 3d, affording good isolated yield of the desired cycloadduct (entry 5, Table 3.2). In contrast, when 3b or 3c was used for this particular transformation, no cycloadduct formation was observed even when 15 mol% catalyst loading was used. However, the reaction mixture became jelly, suggesting an occurrence of a different transformation. After workup with methanol a white solid was successfully isolated and analyzed by multinuclear NMR spectroscopy. The $^1$HNMR spectra revealed that this unexpected product resembled oligomeric/polymeric material. This part of work will be discussed in more detail in section 3.3. Furthermore, Diels-Alder cycloaddition involving 2-cyclohexen-1-one (13) can also be catalyzed by 3d resulting in the formation of the desired adduct in good yields (87% in 24h). Nevertheless, when 3b or 3c was used, a dramatically decrease in activity was observed (~20% in 24h, entry 6, Table 3.2). In addition, large amount of white precipitate was observed during the reaction, which also seemed to be of a polymeric character. All these three catalytic systems were also compatible with the Diels-Alder cycloadditions involving crotonaldehyde in good isolated yields (> 80% in 24h, entry 7, Table 3.2). A catalyst loading of 10% in the case of 3d and additional amount of diene were required for cycloaddition reaction involving ethyl crotonate which is considered to be a much less reactive dienophile. On the other hand, 3b and 3c did not show any activity for this transformation under same reaction conditions (entry 8, Table 3.2).
Table 3.2 Diels-Alder reactions involving 2,3-dimethylbutadiene

\[
\begin{align*}
\text{Entry} & \quad \text{Dienophile} & \quad \text{Adduct} & \quad 3b/\text{NaBAr}^4 & \quad 3c/\text{NaBAr}^4 & \quad 3d/\text{NaBAr}^4 & \quad \text{HBA} \\
1 & \quad & \quad & 5\% & 5\% & 5\% & 1\% \\
& \quad \quad \quad & \quad \quad & 1h & 1h & 1h & 1h \\
& \quad \quad \quad \quad \quad 9 & \quad \quad \quad \quad \quad 16 & \quad \quad \quad \quad \quad 98\% & 94\% & 96\% & 90\% \\
2 & \quad \quad \quad \quad \quad 5\% & 5\% & 5\% & 1\% \\
& \quad \quad \quad \quad \quad 10 & \quad \quad \quad \quad \quad 17 & \quad \quad \quad \quad \quad 91\% & 92\% & 96\% & 89\% \\
3 & \quad \quad \quad \quad \quad 15\% & 15\% & 5\% & 1\% \\
& \quad \quad \quad \quad \quad 11 & \quad \quad \quad \quad \quad 18 & \quad \quad \quad \quad \quad 99: 1 & 99: 1 & 99: 1 \\
4 & \quad \quad \quad \quad \quad 5\% & 5\% & 5\% & 1\% \\
& \quad \quad \quad \quad \quad 5 & \quad \quad \quad \quad \quad 8 & \quad \quad \quad \quad \quad 97\% & 96\% & 86\% & 33\% \\
5 & \quad \quad \quad \quad \quad 10\% & 10\% & 10\% & 1\% \\
& \quad \quad \quad \quad \quad 12 & \quad \quad \quad \quad \quad 19 & \quad \quad \quad \quad \quad 24h & 24h & 1h & 12h \\
6 & \quad \quad \quad \quad \quad 5\% & 5\% & 5\% & 1\% \\
& \quad \quad \quad \quad \quad 13 & \quad \quad \quad \quad \quad 20 & \quad \quad \quad \quad \quad 24h & 24h & 24h & 12h \\
7 & \quad \quad \quad \quad \quad 5\% & 5\% & 5\% & 1\% \\
& \quad \quad \quad \quad \quad 14 & \quad \quad \quad \quad \quad 21 & \quad \quad \quad \quad \quad 96: 4 & 97: 3 & 96: 4 & 91: 9 \\
8 & \quad \quad \quad \quad \quad 10\% & 10\% & 5\% & 1\% \\
& \quad \quad \quad \quad \quad 15 & \quad \quad \quad \quad \quad 22 & \quad \quad \quad \quad \quad 24h & 24h & 24h & 24h \\
\end{align*}
\]

\(^a\) 4 equiv of diene was used.

As more and more evidences revealed that various organic transformations catalyzed by Lewis acids can also be catalyzed by HBA, which usually generated by the hydrolysis of
the metal compounds, it is necessary to perform additional experiments to demonstrate that the catalytic activity was afforded by the aluminum bistriflate compound rather than an HBA. The most prominent approaches to gather evidence against HBA catalysis are (i) investigation of the same transformations using an in-situ generated source of HOTf by mixing AgOTf and \( \text{tBuCl} \), and (ii) addition of a proton source (e.g. dbpy: 2,6-\( \text{tBu}_2 \)-py) to the examined catalytic systems. Therefore, rigorous steps have to be taken in order to minimize the possibility of the presence and subsequent reactivity of an HBA.

As already mentioned, an HBA was prepared by mixing AgOTf and 1 equiv of \( \text{tBuCl} \) in CD\(_2\)Cl\(_2\) following the procedure described by Hintermann\(^7\) et al. It was also suggested that 1 mol % of the HBA system was more than enough for this purpose as higher amounts and the use of triflic acid could result in false negative observations. Although the target Diels-Alder transformations involving 3-buten-2-one (9) and ethyl vinyl ketone (10) occurred with same reaction rates, the transformations involving other dienophiles were dramatically different with respect to the aluminum-based Lewis acid systems as shown in Table 3.2 (longer reaction times and lower yields). For instance, when the less reactive dienophiles were used, only the swift polymerization of 2,3-dimethylbutadiene was observed (entry 5, 6 and 8, Table 3.2).
Table 3.3 Selected Diels–Alder transformations in the presence of a pyridine base.

As anticipated, introducing equimolar amounts of the proton source (dbpy) to the HBA system completely quenched its catalytic activity (entry 1 and 2, Table 3.3) and stoichiometric amounts of pyridinium cation ([dbpy-H]$^+$) were formed. On the other hand, when 3d/NaBAr$^{14}_4$ and equimolar amounts of dbpy were mixed in DCM-d$_2$ solution the formation [dbpy-H]$^+$ was limited to less than 10%. The formed system showed only subtle effect on the isolated yields when used to catalyze the reactions between diene 4 and 9 presumably due to the dienophile-to-enolate side reaction (Schem 3.1).
Therefore, the aforementioned evidence strongly indicated that the investigated Diels-Alder cycloadditions were most likely catalyzed by our aluminum-based Lewis acid systems rather than an HBA.

### 3.2 Diels-Alder reactions of 1,3-cyclohexadiene and isoprene

Inspired by these achievements, we decided to investigate the Diels-Alder reactions involving less reactive dienes, 1,3-cyclohexadiene (23) and isoprene (32). The results were summarized in Table 3.4 and Table 3.5. When 1,3-cyclohexadiene was used, the high reactive dienophiles 9 and 10 were also quite suitable for the targeted Diels-Alder cycloaddtions resulting good isolated yields (entries 1 and 2, Table 3.4). However, the less reactive dienphiles demanded higher catalyst loadings or longer reaction times in order to obtain decent yields. For example, in the case of 11 15 mol% of 3d was required in order to obtain quantitative yield, while 3b and 3c did not show good catalytic activities for this reaction. Only about 40% yields were obtained even after 15 mol% of catalyst loadings were used and the reaction times were extended to 24h (entries 3, Table 3.4). In contrast, 3b and 3c showed better activities for the cycloaddition involving 5 than 3d (84% in 12h, 60% in 12h and 16% in 60h respectively, entries 4, Table 3.4). In most of the cases, the cyclic dienophiles showed no activities under the investigated reaction conditions. Only when catalyzed by 3d and extra amount of diene were used, cycloaddition product of 13 can be
obtained (81% in 24h, entries 5,6, Table 3.4). For 14 all the three catalytic systems showed mild activities and selectivities (entries 7, Table 3.4). There was then no surprise that no activity was observed for the quite unreactive dienophile 15 even when extra amounts of the diene and higher catalyst loading were used (entries 8, Table 3.4).

Table 3.4 Diels-Alder reactions involving 1,3-cyclohexadiene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dienophile</th>
<th>Adduct</th>
<th>3b/NaBAR$_4^+$</th>
<th>3c/NaBAR$_4^+$</th>
<th>3d/NaBAR$_4^+$</th>
<th>HBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>96%</td>
<td>92%</td>
<td>98%</td>
<td>92%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C$_1$Et</td>
<td>10</td>
<td>94%</td>
<td>90%</td>
<td>98%</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C$_1$Ph</td>
<td>11</td>
<td>40%</td>
<td>37%</td>
<td>94%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>99:1</td>
<td>99:1</td>
<td>99:1</td>
<td>99:1</td>
</tr>
<tr>
<td>4</td>
<td>C$_1$Ph</td>
<td>5</td>
<td>98:2</td>
<td>99:1</td>
<td>99:1</td>
<td>99:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C$_1$Ph</td>
<td>12</td>
<td>15%</td>
<td>15%</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>15%</td>
<td>15%</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>13</td>
<td>15%</td>
<td>15%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29</td>
<td>15%</td>
<td>15%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td>7</td>
<td>C$_1$Me</td>
<td>14</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>95:5</td>
<td>95:5</td>
<td>95:5</td>
<td></td>
</tr>
</tbody>
</table>
Similar results were obtained when isoprene (32) was examined to react with these dienophiles. For the reactive dienophiles 9 and 10, all the catalytic systems including HBA can afford acceptable isolated yields in 2h with para : meta ratios > 97 : 3 (entries 1,2, Table 3.5). 10 mol% of 3d was required to obtain cycloaddition product 35 while 3b and 3c did not show any activity at all (entry 3, Table 3.5). In contrast, 3b and 3c showed much higher activities than 3d in the cycloaddition reaction between 5 and isoprene. For this reaction HBA also showed some catalytic activity but much lower para : meta ratio (88 : 12, entry 4, Table 3.5). For cyclic dienophiles 12, 13 and less reactive ethyl crotanate 15, no cycloaddition product was obtained via the catalysis of all these catalytic systems even when extra amount of diene and catalyst loadings were used (entries 5, 6 and 8, Table 3.5). For aldehyde 14 all the catalytic systems showed mild activities with para : meta ratios > 96 : 4 (entry 7, Table 3.5).
**Table 3.5 Diels-Alder reactions involving isoprene**

\[ \text{Dienophile} + \text{R}_{1}\text{R}_2\text{R}_3 \rightarrow \text{Adduct} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dienophile</th>
<th>Adduct</th>
<th>3b/NaBAR(^{14})</th>
<th>3c/NaBAR(^{14})</th>
<th>3d/NaBAR(^{14})</th>
<th>HBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>55%</td>
<td>5%</td>
<td>55%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>82%</td>
<td>84%</td>
<td>77%</td>
<td>83%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>99:1</td>
<td>99:1</td>
<td>99:1</td>
<td>97:3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>5%</td>
<td>5%</td>
<td>55%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>82%</td>
<td>74%</td>
<td>78%</td>
<td>82%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>98:2</td>
<td>97:3</td>
<td>98:2</td>
<td>97:3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>15%</td>
<td>15%</td>
<td>10%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11</td>
<td>24h</td>
<td>24h</td>
<td>12h</td>
<td>10h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>97.3%</td>
<td>53%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>15%</td>
<td>15%</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>76%</td>
<td>98%</td>
<td>39%</td>
<td>29%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>99:1</td>
<td>99:1</td>
<td>99:1</td>
<td>88:12</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>15%</td>
<td>15%</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13</td>
<td>15%</td>
<td>15%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14</td>
<td>82%</td>
<td>69%</td>
<td>80%</td>
<td>28%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>96:4</td>
<td>96:4</td>
<td>96:4</td>
<td>96:4</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>15%</td>
<td>15%</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
<td>24h</td>
</tr>
</tbody>
</table>

\(^a\)4 equiv of diene was used.
In order to increase the para : meta ratios of the cycloaddition products, we decided to use the asymmetric aluminum bistriflate compounds to catalyze the Diels-Alder reactions involving isoprene. As shown in Table 3.6, compounds 3e ([Dip-Ph]LAI(OTf)2)/NaBAR"Cl"4 and 3f ([Dip-Xyl]LAI(OTf)2)/NaBAR"Cl"4 were examined. However, for the reactive dienophiles 9 and 10, no significant increase in para : meta ratios were observed while the activities were acceptable (entries 1 and 2, Table 3.6). In contrast, for the less reactive dienophiles 5 and 11, para : meta ratios slightly increased but resulting dramatically decrease in activities (entries 3 and 4, Table 3.6). Thus, as these asymmetric compounds did not show promising improvements with respect to selectivity and reaction rates we decided not to further investigate their catalytic activity.

Table 3.6 Diels-Alder reactions involving isoprene by asymmetric catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dienophile</th>
<th>Adduct</th>
<th>3e/NaBAR&quot;Cl&quot;4</th>
<th>3f/NaBAR&quot;Cl&quot;4</th>
<th>HBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>33</td>
<td>5%</td>
<td>5%</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>1h</td>
<td>1h</td>
<td>77%</td>
<td>77%</td>
<td>83%</td>
</tr>
<tr>
<td></td>
<td>2h</td>
<td>1h</td>
<td>98:2</td>
<td>98:2</td>
<td>97:3</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>34</td>
<td>5%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>2h</td>
<td>1h</td>
<td>82%</td>
<td>82%</td>
<td>82%</td>
</tr>
<tr>
<td></td>
<td>2h</td>
<td>1h</td>
<td>98:2</td>
<td>98:2</td>
<td>97:3</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>35</td>
<td>15%</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>24h</td>
<td>-</td>
<td>-</td>
<td>53%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>97:3</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>36</td>
<td>15%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>12h</td>
<td>50%</td>
<td>29%</td>
<td>99:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>88:12</td>
</tr>
</tbody>
</table>
3.3 Michael polymerizations involving dienophiles.

As aforementioned, when 3b and 3c were used to catalyze the Diels-Alder reactions involving 2-cyclopenten-1-one (12), the reaction mixture became jelly without any cycloaddition product formed. However, according to the initial $^1$H NMR spectrum it was quite evident that 12 was actually consumed while diene 4 was not. Indeed, excluding 4 from the reaction mixture had no influence on the consumption of dienophile 12. Closer examination of the $^1$H NMR spectrum revealed the presence of a set of broad peaks from 1.0 to 3.5 ppm suggesting the formation of an oligomeric or polymeric material. This also occurred when 2-cyclohexen-1-one (13) was used for Diels-Alder reaction, where large amount of precipitate was formed during the reaction. However, when 3d was used to catalyze these reactions, Diels-Alder adducts were obtained as the only products. In summary, as shown in Table 3.7, there is a competition between Diels-Alder cycloaddition and dienophile polymerization. For 5 membered ring dienophile 12, the reaction was dominated by polymerization when catalyzed by 3b or 3c, while Diels-Alder cycloaddition played the dominant role when catalyzed by 3d (entry 1, Table 3.7). This might be due to the higher steric hindrance of isopropyl groups at 3d with respect to the methyl groups found at ortho positions at 3b/3c. It is thought that due to these steric factors the dienophile can be more activated by 3b/3c than by 3d leading to self-polymerization of the substrate. In the case of 3d the dioneophile might not be as strongly bound to the central Al but effectively enough for the Diels-Alder cycloaddition. When less reactive six-membered ring dienophile 2-cyclohexen-1-one (13) was used, both polymerization and Diels-Alder cycloaddition were obtained under the catalysis of 3b and 3c. but only Diels-Alder transformation was observed when 3d was used as catalyst. The fact that the use of 13 resulted in both polymerization and cycloaddition suggest that the higher ring strain of 12 in comparison to 13 plays an important role in the observed polymerization.
Table 3.7 Competition between Diels-Alder cycloaddition and dienophile polymerization

\[
\begin{array}{c|c|c|c|c}
\text{Entry} & \text{Dienophile} & 3b & 3c & 3d \\
\hline
1 & \begin{array}{c}
\text{Dienophile polymerization} \\
\text{12}
\end{array} & \begin{array}{c}
\text{polymerization} \\
\text{92%}
\end{array} & \begin{array}{c}
\text{polymerization} \\
\text{99:1}
\end{array} & 2h^a \\
2 & \begin{array}{c}
\text{24h} \\
\text{23%} \\
\text{99:1}
\end{array} & \begin{array}{c}
\text{24h} \\
\text{21%} \\
\text{99:1}
\end{array} & \begin{array}{c}
\text{24h} \\
\text{87%} \\
\text{99:1}
\end{array}
\end{array}
\]

\(^a10\%\) of catalyst used.

As shown in Table 3.4 and 3.5, entries 5 and 6, when 1,3-cyclohexadiene or isoprene was used for these Diels-Alder reactions, polymerization was also favored under the catalysis of 3b or 3c/NaBAR\text{Cl}_4. Hence, we want to study whether a more reactive diene would favor Diels-Alder cycloaddition rather than dienophile polymerization. For this purpose we chose cyclopentadiene, which is 500 more reactive than 1,3-cyclohexadiene. Under the same reaction conditions already described in Table 3.7, \(^1\text{H}\) NMR clearly revealed the formation of Diels-Alder adduct and the absence of polymerization of 12 when cyclopentadiene was introduced in the reaction mixture. Thus, based on the nature of the diene it is possible to control whether Diels-Alder cyclization or dienophile polymerization will occur for 12.
In order to gather more information on the polymer properties and the mechanism insights of this reaction a clean polymer sample(s) was required. This was achieved by combining compound 3b with 1 equiv of NaBAR\textsuperscript{Cl\textsubscript{4}} in DCM following by the addition of 20 equiv of 2-cyclopenten-1-one or 2-cyclohexen-1-one. After several hours methanol was added to the reaction mixture in order to precipitate the product and remove the catalyst and unreacted starting materials. After filtration and dryness under vacuum, individual polymers (poly-12 (polymer based on 12) and poly-13 (polymer based on 13)) were obtained as white solids in moderate yields (56% in 3h for poly-12 and 50% in 6h for poly-13). Unfortunately, complete conversion cannot be reached by extending the reaction times or increasing the catalyst loadings. Poly-12 was analyzed by gel permeation chromatography (GPC) and multinuclear NMR spectroscopy. Apart from IR spectroscopy poly-13 was not further characterized due to its insolubility in common organic solvents.

As shown in Figure 3.1, \textsuperscript{1}H NMR of the polymer is quite different with its monomer or cyclopentanone. The HC=CH signal at 6.1 and 7.7 ppm disappeared while the alkyl peaks were replaced by broad peaks around 1.0 to 3.5 ppm. More evidence for the existence of an oligomeric/polymeric material was acquired from the \textsuperscript{13}C NMR spectrum as it also contained broad signals. In fact, a broad signal at $\delta$ 220 ppm suggested that the carbonyl group was still intact as shown in Figure 3.2. More evidence for the presence of a carbonyl fragment was gathered from IR spectroscopy which revealed the presence of a strong band at ~ 1730 cm\textsuperscript{-1}. On the other hand, the absence of any signals associated with an alkene group implied that the C=C double bond of the monomeric dienophile was presumably involved in the formation of this new material. This was also supported by the observation that cyclopentanone (41) and cyclohexanone (44) lacking of C=C, cannot polymerize under the same reaction conditions. To examine the molar mass of the prepared and purified polymeric material, gel permeation chromatography (GPC) was employed. This analysis indicated that the average molecular weight of the purified polymers ranged from 30–40
kDa with polydispersity index of 1.5-2. Finally, to further investigate the chemical structure (i.e. the repeating unit) of the polymer, MALDI-TOF mass spectrometry was used. This study indicated that the polymer chains were composed of a structural repeat unit with molar mass of 82 g/mol. Considering the nature of the monomer and structural knowledge acquired from other analyses, this weight fits very well to the proposed structure of the polymer repeat unit (C$_5$H$_6$O) presented in Scheme 3.4.

![Figure 3.1 H NMR of 13, 41 and poly-12](image-url)
Based on our knowledge this appears to be the first time that cyclopentenone was polymerized via Michael addition polymerization. In order to gather more information on the mechanism, polymerization of 13 was attempted with several different reagents. Firstly, in the absence of NaBArCl4 compound 3b succeeded in polymerizing this substrate but slow conversion rates were observed (36% of the substrate converted in 3h). This is in agreement that the addition of NaBArCl4 dramatically enhances the Lewis acidity of these aluminium bistriflate compounds. Then, most common Lewis acids, such as AlCl3, B(C6F5)3 and BF3OEt2, were not adequate catalysts for polymerization of 13 as no conceivable transformation of cyclopentenone was detected under the reaction conditions used for 3b/NaBArCl4. The same inactivity was observed when a soluble source of HOTf (tBuCl/AgOTf) was mixed with cyclopentenone.

Since we did not find another type of catalyst capable to catalyze this polymerization, we decided to figure out the optimized reaction conditions using 3b/NaBArCl4 system. First, we
examined the influence of different catalyst loadings on the reaction activity. It was not surprised when 1 mol% of catalyst loading was used, the Al-dienophile coordination did occur, but no polymerization product was obtained. However, to our surprise, when the catalyst loading was increased to 10 mol%, a decrease in isolated yield (28%, 3h) was obtained. Meanwhile, the obtained polymer has a lower molecule weight of about 23000. This could be possibly due to a higher catalyst/monomer ratio resulting in lower molecule weights and higher content of oligomer, which is washed away by methanol. We were also interested in investigating the solvent influence to the catalysis. We found that beside of DCM, non-coordinate solvents such as chloroform, fluorobenzene and 1,2-difluorobenzene were also quite suitable for the polymerization. It is also worth mentioning that polymerization cannot occur when the catalyst was mixed with neat 2-cyclopenten-1-one. 

It was strange that the quite reactive 3-buten-2-one (9) did not afford any polymeric material when catalyzed by 3b/NaBAR\textsuperscript{Cl\_4} system as self-polymerization can readily occur when fresh distilled 3-buten-2-one was stored at room temperature. Then, we attempted to polymerize several different substrates using 3b/NaBAR\textsuperscript{Cl\_4} to investigate the role of the carbonyl and the alkene groups as well as the importance of the cyclic nature of substrate 13. As shown in Scheme 3.2, other non-cyclic dienphiles 10, 11, 5, 14, 15 were not suitable to the polymerization, which indicated a strained framework was possibly required for the polymerization. As aforementioned, cyclopentanone and cyclohexanone cannot be polymerized due to lack of C=C double bond. Then, we examined another substrate cyclopentene (42), which possesses both strained framework and C=C double bond, but lack of a carbonyl group. Yet again, even this substrate was not polymerized by the catalytic system. With this information in hand, we decided to expand the scope of substrates for polymerization. However, replacing one of the vinylic protons with a methyl group at of 2-cyclopenten-1-one resulted in the catalytic inertness of this new substrate (43) with
respect to the desired polymerization. On the other hand, introducing cyclohexenone (13) or cycloheptenone (45) into a DCM solution containing 5% (mol) of 3b/NaBAR\textsubscript{4} resulted in the consumption of the substrate, albeit longer reaction times were required, and the formation of an oligomeric/polymeric material in the yields of 50% and 23%, respectively. Unfortunately, high insolubility of these materials in most common organic solvents prevented their further characterization. Nevertheless, the sole formation of these presumably oligomeric/polymeric materials suggested that, besides the presence of the carbonyl and alkene groups, the cyclic nature of the substrate played a pivotal role in their ability to form polymeric materials with catalytic amounts of 3b/NaBAR\textsubscript{4}. One can only assume that alleviation of ring strain as these materials are polymerized (e.g. cyclopentenone →polymeric cyclopentanone) is one of the most prominent driving forces behind the observed reactivity of cyclic dienophiles. This would also explain slower reaction rates and lower isolated yields for transformation of 13 and 45 due to a lesser degree of ring strain in comparison to 12.

Scheme 3.2 Scope of substrates for polymerization
Considering the abovementioned evidence it was proposed that the polymerization of cyclic dienophiles, or at least of 12, occurs via the Michael addition polymerization mechanism that is summarized in Scheme 3.3. Once the first molecule of substrate coordinates to the aluminium centre its \( \beta \) position becomes electrophilic enough (A, Scheme 3.4) for an attack by another molecule of 12. The substrate polarization i.e. the site of the nucleophilic attack is consistent with several examples of Michael addition, which mechanism involved an Al-activated cyclopentenone. However, in this case 12 is dramatically more activated by the Al system than in the case of the most common Lewis and Brønsted acids allowing the subsequent molecule of the same substrate to act as a Michael donor. This would presumably yield the formation of a very reactive carbocation (B, Scheme 3.3) that would then sequentially react with other molecules of the dienophile leading to the observed polymerization. It is also noteworthy that the reason for inability of 3b/NaBArCl\(_4\) to perform similar polymerization could be found in the fact that the \( \text{iPr} \) substituents on 3d prevent as strong coordination of 12 as in the case of 3b. This would then lead to less polarized substrate 12 when 3d was used in comparison to 3b, which is not sufficient for the polymerization but is adequate for the Diels Alder cycloaddition.

\[
\begin{align*}
\text{L-Al} & \quad + \quad \text{cyclic dienophile} \\
\text{L-Al: 3b/NaBArCl}_4 & \quad \rightarrow \quad \text{reactive carbocation (B)} \quad \rightarrow \quad \text{polymer}
\end{align*}
\]

Scheme 3.3 Proposed mechanism for Michael polymerization
Our next aim was to investigate whether this polymer can be possibly modified in order to afford potential applications. The presence of carbonyl group provided the polymer the possibility to react with amines. As shown in Scheme 3.5, 1.2 equiv of benzylamine was mixed with the polymer in dry DCM with 4Å molecule sieves. The reaction mixture was set up to reflux overnight. After removal of the volatiles, the residue was examined by $^1$H NMR. To our disappointment, the lack of aromatic signal suggested that the polymer cannot be modified by this method.

![Scheme 3.4 Reactivity of poly-12](image)

**3.4 Summary**

In summary, when combined with NaBAr$^{+}$Cl$_4$ β-diketiminate-supported aluminum bistriflate complexes 3b-3d, can form quite active Lewis acid systems capable of performing a series of Diels-Alder reactions. Several additional experiments were also performed to demonstrate that these cycloadditions were indeed catalyzed by the Lewis acid systems rather than an HBA. A subtle reduction in steric hindrance of Lewis acid catalyst 3d, achieved by replacing the $^t$Pr substituents with Me groups, to form catalyst 3b resulted in unprecedented chemistry of cyclic dienophiles. 3b/ NaBAr$^{+}$Cl$_4$ was unexpectedly shown to polymerize cyclic dienophiles. After several experimental studies it is believed that the
Michael addition polymerization mechanism most adequately describes the polymer formation.

3.5 Experimental section

General procedure for aluminum-catalyzed Diels-Alder reactions

3d (12 mg, 0.016 mmol) and NaBArCl₄ (10 mg, 0.016 mol) was dissolved in 1 mL DCM-d₂ in a J. Young NMR tube. To this solution the diene 2,3-dimethyl-1,3-butadiene (52 mg, 72 μL, 0.64 mmol) and a dienophile (0.5 equiv with respect to the diene) was added. The reaction mixture was left for the time indicated in Tables 3.1-3.6 in the main text. After reaction completion, the corresponding products were purified by flash column chromatography on silica gel using hexane/ethyl acetate mixtures affording analytically pure Diels-Alder products. The trans/cis ratio (if applicable) was determined by ¹H NMR.

General procedure for tBuCl/AgOTf-catalyzed Diels-Alder reactions

The acid system was generated based on the reported procedure to which system 100 equiv of the dienophile and 200 equiv of the diene were added. The reaction mixture was left for the time indicated in Table 3.2 and 3.4-3.6 in the main text before purifying the products using already described technique(s).

General procedure for the catalytic reactions with 2,6-tBu₂-C₆H₃N

These reactions were conducted in the exactly same manner as already described for aluminium- and tBuCl/AgOTf-catalyzed reactions except for the addition of 1 equiv of the pyridine base before addition of the organic substrates. The reaction mixture was left for the time indicated in Table 3.3 in the main text before purification step(s).
General procedure for aluminum-catalyzed Michael polymerization

**3b** (56 mg, 0.088 mmol) and 1 equiv of NaBAR$_4^{Cl}$ (56 mg, 0.088 mmol) was dissolved in 2 mL DCM in a 10 mL round-bottomed flask containing a stir bar in glovebox. To this solution 2-cyclopenten-1-one (150 μL, 1.78 mmol) was added. The reaction mixture was left to stir for 3h before added in to 20 mL methanol to precipitate the polymer. After filtration the crude product was re-dissolved in 0.5 mL THF and then precipitated with another 20 mL methanol. Repeat twice. The obtained polymer was dried under vacuum at 40 °C overnight. Yield: 87 mg, 59%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 1.0 -3.5 ppm (broad, aliphatic). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 20-25, 38-40, 49-51 (all aliphatic), 119-121 (carbonyl). FTIR (KBr pellets): 1728 cm$^{-1}$ (C=O stretch). GPC: $M_n = 26000$, $M_w = 36000$, $M_w/M_n$(PDI) =1.38.

The polymerization of 2-cyclohexen-1-one and 2-cyclohepten-1-one have been attempted using the same procedure yielding insoluble materials in the yields of 50% (6 h) and 23% (24 h), respectively. Due to poor solubilitythese materials have been characterized by FTIR only.

2-cyclohexen-1-one: FTIR (KBr pellets): 1707 cm$^{-1}$ (C=O stretch).

2-cyclohepten-1-one: FTIR (KBr pellets): 1681 cm$^{-1}$ (C=O stretch).

NMR data for Diels-Alder products

**1-(3,4-Dimethylcyclohex-3-en-1-yl)ethanone (16)**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.49-1.57 (m, 1H), 1.60 (s, 3H), 1.62 (s, 3H), 1.87-1.94 (m, 1H), 1.98-2.12 (m, 4H), 2.17 (s, 3H), 2.52-2.58 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.9, 19.1, 25.4, 28.0, 31.3, 33.4, 48.4, 124.1, 125.5, 212.0 ppm. The analytical and spectroscopic data are in accordance with those reported.$^9$
1-(3,4-Dimethylcyclohex-3-en-1-yl)ethanone (17)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.03 (t, $J = 7.3$ Hz, 3H), 1.45-1.58 (m, 1H), 1.59 (s, 3H), 1.62 (s, 3H), 1.82-1.90 (m, 1H), 1.95-2.17 (m, 4H), 2.49 (dq, $J_{H-H} = 7.2$ Hz, $J = 4.0$ Hz, 2H), 2.54-2.61 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 7.9, 18.9, 19.2, 25.7, 31.4, 33.5, 33.9, 47.5, 124.2, 125.5, 214.6 ppm. The analytical and spectroscopic data are in accordance with those reported.$^9,^{10}$

1-(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)ethanone (18)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.61 (s, 3H), 1.63 (s, 3H), 1.81 (s, 3H), 2.03-2.12 (m, 1H), 2.13-2.21 (m, 2H), 2.22-2.30 (m, 1H), 2.87-3.00 (m, 2H), 7.10-7.17 (m, 3H), 7.21-7.26 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.8, 18.8, 29.7, 35.1, 40.5, 43.6, 54.1, 123.9, 125.6, 126.7, 127.5, 128.7, 144.3, 212.3 ppm. The analytical and spectroscopic data are in accordance with those reported.$^{11}$

(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)phenylmethanone (8)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.70 (bs, 6H), 2.24-2.38 (m, 4H), 3.31 (ddd, $J = 14.4$ Hz, $J = 9.6$ Hz, $J = 7.1$ Hz, 1H), 4.02 (dt, $J = 10.7$ Hz, $J = 5.6$ Hz, 1H), 7.04-7.10 (m, 1H), 7.13-7.25 (m, 4H), 7.35-7.42 (m, 2H), 7.46-7.51 (m, 1H), 7.81-7.87 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.8, 18.9, 37.1, 40.8, 43.2, 47.5, 124.2, 125.8, 126.3, 127.5, 128.2, 128.4, 128.6, 132.8, 137.5, 144.8, 203.6 ppm. The analytical and spectroscopic data are in accordance with those reported.$^{12}$

5,6-dimethyl-2,3,3a,4,7,7a-hexahydro-1H-inden-1-one (19)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.57 (bs, 3H), 1.60 (bs, 3H), 1.66-1.78 (m, 3H), 1.95-2.33 (m, 6H), 2.40-2.466 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.9, 19.4, 26.4, 27.9, 32.8, 33.0, 34.4, 47.8, 123.5, 124.1, 220.1 ppm.
6,7-Dimethyl-3,4,4a,5,8,8a-hexahydro-2H-naphthalen-1-one (20)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.59 (bd, $J = 1.6$ Hz, 3H), 1.62 (bd, $J_{H-H} = 0.7$ Hz, 3H), 1.68-1.78 (m, 2H), 1.81-1.94 (m, 4H), 1.97-2.06 (m, 1H), 2.20-2.22 (m, 1H), 2.31-2.46 (m, 3H), 2.68 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.9, 19.3, 24.2, 28.4, 30.2, 34.1, 36.6, 39.9, 49.3, 122.9, 123.6, 213.3 ppm. The analytical and spectroscopic data are in accordance with those reported.$^{13}$

4,6-dimethylcyclohex-3-ene-1-carbaldehyde (21)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.99 (d, $J = 6.2$ Hz, 3H), 1.56 (s, 3H), 1.59 (s, 3H), 1.63 (m, 1H), 2.01 (m, 3H), 2.17 (m, 2H), 9.61 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.7, 18.9, 19.6, 28.8, 30.4, 39.0, 53.6, 122.6, 125.2, 205.4 ppm.

ethyl 3,4,6-trimethylcyclohex-3-ene-1-carboxylate (22)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.92 (d, $J = 6.3$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.59 (bs, 6H), 1.71-1.73 (m, 1H), 1.88-2.27 (m, 5H), 4.10-4.18 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.4, 18.6, 18.8, 19.6, 31.5, 35.1, 40.1, 48.0, 60.1, 123.6, 125.0, 176.3 ppm.

endo-1-(Bicyclo[2.2.2]oct-5-en-2-yl)ethanone (24)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.18-1.38 (m, 2H), 1.44-1.55 (m, 1H), 1.57-1.61 (m, 1H), 1.62-1.68 (m, 2H), 2.12 (s, 3H), 2.51-2.63 (m, 1H), 2.71 (ddd, $J_{H-H} = 8.7$ Hz, $J = 6.9$ Hz, $J = 2.1$ Hz, 1H), 2.88-2.92 (m, 1H), 6.11 (ddd, $J_{H-H} = 8.3$ Hz, $J = 6.5$ Hz, $J = 1.1$ Hz, 1H), 6.26 (ddd, $J = 8.5$ Hz, $J = 6.8$ Hz, $J = 1.1$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 24.6, 26.0, 28.4, 28.8, 29.7, 32.2, 51.7, 131.2, 135.3, 209.9 ppm. The analytical and spectroscopic data are in accordance with those reported.$^{14}$
endo-1-(Bicyclo[2.2.2]oct-5-en-2-yl)propan-1-one (25)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.02 (t, $J_{H-H} = 7.3$ Hz, 3H), 1.21-1.35 (m, 2H), 1.44-1.53 (m, 1H), 1.54-1.62 (m, 1H), 1.62-1.67 (m, 2H), 2.33-2.51 (m, 2H), 2.55-2.61 (m, 1H), 2.68 (dt, $J = 7.7$ Hz, $J = 2.1$ Hz, 1H), 2.84-2.89 (m, 1H), 6.10 (ddd, $J = 7.9$ Hz, $J = 6.5$ Hz, $J = 1.0$ Hz, 1H), 6.27 (ddd, $J = 8.0$ Hz, $J = 6.7$ Hz, $J = 1.1$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.2, 24.6, 26.1, 29.0, 29.7, 32.3, 34.0, 50.6, 131.3, 135.1, 212.6 ppm. The analytical and spectroscopic data are in accordance with those reported.\(^{10}\)

endo-1-(3-Phenylbicyclo[2.2.2]oct-5-en-2-yl)ethanone (26)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.97-1.10 (m, 1H), 1.43-1.49 (m, 1H), 1.67-1.79 (m, 2H), 2.02 (s, 3H), 2.50-2.56 (m, 1H), 2.94 (dd, $J = 6.8$ Hz, $J = 1.8$ Hz, 1H), 2.99-3.05 (m, 1H), 3.12 (ddd, $J = 6.7$ Hz, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H), 6.12 (ddd, $J = 7.6$ Hz, $J = 6.8$ Hz, $J = 0.9$ Hz, 1H), 6.48 (ddd, $J = 8.0$ Hz, $J = 6.8$ Hz, $J = 1.2$ Hz, 1H), 7.22-7.40 (m, 5H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.5, 26.1, 28.5, 32.7, 37.3, 45.6, 56.6, 126.5, 128.2, 128.6, 131.6, 136.1, 142.8, 209.0 ppm. The analytical and spectroscopic data are in accordance with those reported.\(^{15}\)

deo-Phenyl-(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (27)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.08-1.18 (m, 1H), 1.47 (ddddd, $J = 11.3$ Hz, $J = 11.3$ Hz, $J = 3.4$ Hz, $J = 3.4$ Hz, 1H), 1.80-1.95 (m, 2H), 2.55-2.71 (m, 1H), 2.96-3.01 (m, 1H), 3.48 (ddd, $J = 6.5$ Hz, $J = 4.0$ Hz, $J = 2.0$ Hz, 1H), 3.80 (dd, $J = 6.5$ Hz, $J = 1.6$ Hz, 1H), 6.11 (ddd, $J = 8.9$ Hz, $J = 7.7$ Hz, $J = 0.8$ Hz, 1H), 6.58 (dd, $J = 9.1$ Hz, $J = 8.0$ Hz, $J = 1.0$ Hz, 1H), 7.19-7.24 (m, 1H), 7.27-7.36 (m, 4H), 7.36-7.43 (m, 2H), 7.48-7.53 (m, 1H), 7.85-7.90 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.6, 26.6, 34.7, 36.6, 44.8, 51.1, 126.3, 128.3, 128.6, 128.6, 130.8, 132.8, 136.4, 136.6, 143.0, 200.9 ppm. The analytical and spectroscopic data are in accordance with those reported.\(^{15}\)
4,4a,6,7,8,8a-hexahydro-1,4-ethanonaphthalen-5(1H)-one (29)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.28 (m, 1H), 1.45-1.59 (m, 3H), 1.71-1.80 (m, 4H), 2.05-2.09 (m, 1H), 2.34-2.45 (m, 4H), 3.08 (m, 1H), 6.11 (m, 1H), 6.24 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 20.8, 24.0, 26.0, 29.6, 31.2, 35.9, 38.8, 42.2, 52.9, 133.1, 134.5, 214.5 ppm.

3-methylbicyclo[2.2.2]oct-5-ene-2-carbaldehyde (30)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.08 (d, $J_{H-H} = 6.92$ Hz, 3H), 1.25-1.32 (m, 1H), 1.53-1.55 (m, 2H), 1.75-1.94 (m, 3H), 2.32 (m, 1H), 2.81 (m, 1H), 6.08 (m, 1H), 6.40 (m, 1H), 9.40 (d, $J = 2.00$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 18.4, 19.7, 25.6, 31.4, 32.3, 35.6, 59.7, 130.2, 137.8, 203.7 ppm.

1-(4-methylcyclohex-3-en-1-yl)ethan-1-one (33)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.57 (m, 1H), 1.65 (s, 3H), 1.94-1.98 (m, 3H), 2.15 (bs, 5H), 2.51 (m, 1H), 5.38 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.4, 25.0, 27., 28.0, 29.5, 47.3, 119.3, 133.9, 211.9 ppm.

1-(4-methylcyclohex-3-en-1-yl)propan-1-one (34)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.02 (t, $J_{H-H} = 7.3$ Hz, 3H), 1.56-1.61 (m, 1H), 1.64 (bs, 3H), 1.90-1.99 (m, 3H), 2.11-2.1 (m, 2H), 2.45-2.54 (m, 3H), 5.38 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 7.8, 23.4, 25.2, 27.3, 29.6, 33.9, 46.3, 119.4, 133.8, 214.5 ppm.

1-(5-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (35)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.69 (s, 3H), 1.84 (s, 3H), 2.20-2.26 (m, 4H), 2.96-3.04 (m, 2H), 5.46 (m, 1H), 7.18-7.30 (m, 5H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.1, 28.8, 29.7, 38.6, 43.0, 53.0, 118.9, 126.5, 127.4, 128.6, 133.8, 144.1, 121.2 ppm.
(5-methyl-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-yl)(phenyl)methanone (36)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.74 (s, 3H), 2.28-2.38 (m, 4H), 3.32 (m, 1H), 3.93 (m, 1H), 5.50 (m, 1H), 7.04-7.10 (m, 1H), 7.16-7.19 (m, 4H), 7.36-7.42 (m, 2H), 7.46-7.52 (m, 1H), 7.79-7.81 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.2, 30.8, 38.9, 42.8, 46.6, 119.3, 126.2, 127.5, 128.0, 128.4, 128.5, 132.7, 134.1, 137.4, 144.7, 203.7 ppm.

4,6-dimethylcyclohex-3-ene-1-carbaldehyde (39)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.00 (d, $J_{H-H} = 6.3$ Hz, 3H), 1.62 (s, 3H), 1.66-1.69 (m, 1H), 2.00-2.20 (m, 5H), 5.35 (m, 1H), 9.60 (s, 1H), $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 19.7, 23.4, 24.1, 28.4, 37.0, 52.4, 117.8, 133.5, 205.4 ppm.
References


Chapter 4
Pursuing the active species in an NCN pincer aluminum-based Lewis acid system for catalytic Diels-Alder cycloadditions
After identifying a series of well-defined \( \beta \)-diketiminate-stabilized aluminium bis(triflate) systems capable of catalyzing several difficult Diels Alder transformations we decided to investigate the role of the ligand on the overall catalytic activity. Various pincer ligands have been extensively used to support numerous transition metal complexes including Ru, Os, Ni, Pd and Pt. \textsuperscript{1–6} Theses complexes showed good stability and were widely investigated as Heck-coupling and C–C bond formation catalysts. More recently, a series of lanthanide complexes based on bis(imino)aryl NCN pincer ligands were reported as efficient catalysts for diene polymerization with excellent cis-1,4 selectivities. \textsuperscript{7} However, with respect to the aluminum chemistry, there is only a single report describing the preparation of diethylaluminum complexes stabilized by these NCN pincer ligands and their role as L-lactide polymerization catalysts. \textsuperscript{8} Besides which, Beck and Schmidt\textsuperscript{9} reported that monodentate analogues of the current ligand family can used to support aluminum halide derived Lewis acids. Hence, we decide to prepare an aluminum bistriflate complex based on this type of pincer ligand and extend its potential applications in catalysis.

### 4.1 Synthesis of bis(imino)aryl NCN pincer ligand

At the beginning, pincer ligand \( \text{C}_6\text{H}_3[\text{CHNC}_6\text{H}_3(\text{i-Pr})_2]_2\text{Br} \) (45) was synthesized following the procedure reported by Elsevier\textsuperscript{10} as shown in Scheme 4.1. This procedure involved condensation of \( \text{C}_6\text{H}_3(\text{CHO})_2\text{Br} \) and excess of 2,6-diisopropylaniline in reflux toluene in the presence of 4Å molecular sieves for 16h, which was then followed by THF extraction. However, this method required long reaction time and harsh reaction conditions. Moreover, the final product obtained with this method contained few impurities causing the appearance of a green color.
Thus, we tried another method provided by Cui’s group as shown in Scheme 4.2. This reaction was performed at room temperature by mixing the two reagents in methanol with catalytic amount of formic acid. Pure product (yellow color) can be easily obtained by simple filtration resulting in excellent isolated yields (> 90%) and, more importantly, the entire procedure takes around 2 h.

4.2 Synthesis of NCN pincer ligand supported aluminum complexes

In order to synthesize the target aluminum bistriflate complex, the corresponding aluminum dichloride precursor needed to be prepared first. The initial synthetic procedure was similar to that used in synthesis of the nacnac LAlCl$_2$ in Chapter II. The free ligand (45) was debrominated by $n$BuLi in toluene at -78°C followed by addition of 1 equiv of AlCl$_3$ as shown in Scheme 4.3. However, after several tries we unable to isolate pure samples.
According to $^1$H NMR spectroscopy numerous species were present in the reaction mixture and it was impossible to determine whether the dichloride aluminum compound was actually formed. Then, we tried other non-coordinating solvents, such as benzene and hexane, but no improvement in terms of purity was achieved. This might be due to the low solubility of the lithium salt, formed in the initial step, in these solvent media. Thus, we decided to use coordinating solvents to perform this reaction in order to stabilize and solubilize the lithium salt, although the introduction of a coordinating molecule might cause the decrease in Lewis acidity of the target aluminum complex. We first chose diethyl ether as a solvent for this reaction. However, we still could not isolate a pure sample of the desired aluminum dichloride compound. Then we tried another commonly used coordination solvent THF, which to our delight, was quite suitable for this reaction. As shown in Scheme 4.3, after removing all volatiles under reduced pressure and extraction with DCM, the target dichloride aluminum complex 46 was isolated, as a THF adduct. The presence of bound THF was confirmed by $^1$H NMR spectroscopy as a set of signals at 1.89 and 3.92 ppm was downfield shifted from the same signals observed for free THF (1.85 and 3.76 ppm). $^{27}$Al NMR spectroscopic identification of this dichloride complex revealed the presence of a signal at $\delta_{\text{Al}} \sim 97$ ppm. The coordinated THF can be easily removed by exposing 46 under reduced pressure overnight affording THF-free analogue 47. The $^1$H NMR spectrum of 47 was quite similar to that of 46 except for the absence of THF signals. The formation of 47 can also be confirmed by $^{27}$Al NMR spectroscopy as the aluminum signal shifted downfield to $\delta_{\text{Al}} \sim 106$ ppm. Crystals of 47 suitable for single crystal X-ray diffraction were obtained from a toluene/hexane solvent mixture. Molecular structure is shown in Figure 4.1 with the crystallographic data summarized in Table 4.1. It is worth noting that a crop of crystals obtained from a toluene/hexane solvent mixture of 46 revealed the same structure as 47, which suggested a weak coordination between of THF at the aluminum center.
As shown in Figure 4.1, the monoanionic bis(imino)aryl NCN pincer ligand coordinates to the aluminum atom in a tridentate fashion. The geometry around the central Al atom can be described as a distorted trigonal bipyramid with one carbon atom and two chloride atoms in the equatorial position and two nitrogen atoms in the apical position. The Al-C bond length 1.943(3) Å is shorter than those observed in diethylaluminum complex (2,6-(2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)₂C<sub>6</sub>H<sub>3</sub>)AlEt<sub>2</sub> (1.977(7) Å) stabilized by the same NCN pincer ligand but similar to those observed in cationic aryl aluminum complex [(2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)₂Al][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1.9412(12) Å).<sup>11</sup>

The two Al-N bonds have quite different lengths even though only one set of proton and carbon signals were observed in the NMR experiments in solution. The value for the short Al-N bond length of 2.139(2) Å is comparable to the same bond distance of 2.1862(19) Å for (2,6-(2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH)₂C<sub>6</sub>H<sub>3</sub>)AlEt<sub>2</sub> but considerably longer than that reported for {3,5-Bu<sub>1</sub>₂-2-(O)C<sub>6</sub>H<sub>2</sub>CH=N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}AlMe<sub>2</sub> (1.972(3) Å ).<sup>12</sup> On the other hand the long Al-N bond distance of 2.502 Å is apparently longer than typical Al-N coordination bonds. Nevertheless, this bond distance is shorter than the sum of the van der Waals radii for N and Al atoms [r<sub>v</sub>(N) + r<sub>m</sub>(Al) = 1.55 + 1.43 = 2.98 Å], suggesting that the imine N
atom indeed coordinates to the Al atom. The Al-Cl bond lengths of 2.1250(11) and 2.1384(11) Å are similar with that for compound 2c (2.1299(6) and 2.1295(6) Å) and 2f (2.124(7) and 2.116(9) Å) discussed in Chapter 2, which are stabilized by β-diketiminato ligands.

Figure 4.1 Molecular structure for 47.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-C1 1.943(3), Al1-N1 2.139(2), **Al1-N2 2.1637**, Al1-Cl1 1.943(3), Al1-Cl2 2.1250(11), C1-Al1-N1 80.37(10), Cl1-Al1-N1 102.72(7), Cl1-Al1-Cl2 109.78(5).

Our next aim was to prepare bistriflate aluminum compound by replacing the Cl ligands with OTf in order to enhance the Lewis acidic properties of the aluminum center. For this purpose, dichloride precursor 46 or 47 was mixed with AgOTf in DCM or 1,2-difluorobenzene in the absence of light as shown in Scheme 4.4. However, after numerous tries no clean sample of the target bistriflate compound was obtained even though the formation of AgCl precipitate was observed. According to $^1$H and $^{19}$F NMR
spectroscopy numerous species were present in the reaction mixture and it was difficult to determine whether the bistriflate aluminum compound has actually formed. On one occasion, before we even isolated 46 (or 47) we added AgOTf to the reaction mixture in THF, left it to stir overnight and layered the resulting solution with hexane after filtration. Fortunately several crystals suitable for single crystal X-ray diffraction were obtained and the resulting molecular structure is shown in Figure 4.2 with the crystallographic data summarized in Table 4.1.

![Scheme 4.4 Synthetic approaches to LAl(OTf)$_2$ compounds](image-url)
Figure 4.2 Molecular structure for 48.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-C1 2.052(4), Al1-N1 2.122(3), Al1-O1 1.882(3), Al1-O4 1.920(3), Al1-O7 1.977(3), Al1-O8 1.960(3), O1-S1 1.479(3), O4-S2 1.477(3), C1-Al1-N1 82.03(14), Cl1-Al1-O1 169.54(14), Cl1-Al1-O4 103.60(14).

Table 4.1 Summary of crystallographic data for 47 – 50

<table>
<thead>
<tr>
<th></th>
<th>47</th>
<th>48</th>
<th>49</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{32}H_{39}AlCl_{2} N_{2}</td>
<td>C_{98}H_{134}Al_{2}F_{12}N_{4}O_{10}S_{4}</td>
<td>C_{92}H_{98}Al_{2}BCl_{2}O_{4}N_{4}Na</td>
<td>C_{64.36}H_{68.91}Al_{2}B_{11.82}Cl_{11.82}N_{2}O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>549.53</td>
<td>2058.26</td>
<td>2056.50</td>
<td>1343.31</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
<td>P 1 21/c 1</td>
<td>C 1 2/c 1</td>
<td>P -1</td>
</tr>
<tr>
<td>a /Å</td>
<td>9.5204(11)</td>
<td>9.7628(8)</td>
<td>16.9979(7)</td>
<td>14.2999(7)</td>
</tr>
<tr>
<td>b /Å</td>
<td>25.954(3)</td>
<td>27.367(2)</td>
<td>27.9699(11)</td>
<td>16.7422(9)</td>
</tr>
<tr>
<td>c /Å</td>
<td>12.6419(16)</td>
<td>19.2292(14)</td>
<td>20.6231(9)</td>
<td>17.0542(9)</td>
</tr>
<tr>
<td>β /°</td>
<td>98.612(5)</td>
<td>101.133(3)</td>
<td>92.6642(16)</td>
<td>104.6772(19)</td>
</tr>
<tr>
<td>V / Å³</td>
<td>3088.5(6)</td>
<td>5040.9(7)</td>
<td>9794.2(7)</td>
<td>3280.3(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Dc/ g cm⁻³</td>
<td>1.182</td>
<td>1.356</td>
<td>1.395</td>
<td>1.360</td>
</tr>
</tbody>
</table>
As shown in Figure 4.2, the central aluminum is six-coordinate, adopting a distorted octahedral geometry. The monoanionic bis(imino)aryl NCN pincer ligand coordinates to the aluminum atom in a bidentate fashion with only one imine N atom forming a coordination bond. Besides the two triflate ligands, the metal center is further supported by two THF molecules. The Al-N bond length of 2.122(3) Å is a bit shorter than the shorter Al-N bond length of its precursor 46 (2.139(2) Å), potentially hinting at a decrease in electron density at the aluminum center after the ligand exchange. The Al-OTf bond lengths of 1.882(3) and 1.920(3) Å were longer than those observed for bistriflate aluminum complexes 3a - 3f (1.755(4) to 1.769(3) Å) stabilized by Nacnac ligands which is presumably due to the presence of coordinated THF molecules which not only increase the electron density at the aluminum center but also increase the coordination number from 4 to 6. Unfortunately, we were never able to isolate enough pure samples of 48 in order to perform further analysis, such as multinuclear NMR spectroscopy, because this compound appeared to be extremely air/moisture sensitive. As a result we were not able investigate its catalytic properties for Diels Alder transformations.
4.3 Identification for the active species of Diels-Alder cycloadditions

Nevertheless, both 46 and 47 could potentially be used as Lewis acid catalysts simply because of the presence of the aluminum center. Hence, we then focused our attention on investigating the potential catalytic properties of 46 or 47 for Diels Alder reaction between 2,3-dimethylbutadiene (4) and 1,3-diphenyl-2-propenone (5) which has already been proven to be quite suitable for the β-diketiminate bistriflate aluminum catalytic systems. Unfortunately, both 46 and 47 showed no catalytic activity with respect to the target cycloaddition as no formation of adduct 8 or consumption of the starting materials was observed (entry 1, Table 4.2). In our experience the addition of borates such as NaBAR\textsubscript{Cl}\textsubscript{4} could dramatically increase the catalytic properties of the aluminum compounds. As a result when 47 was mixed with 1 equiv of NaBAR\textsubscript{Cl}\textsubscript{4} in CD\textsubscript{2}Cl\textsubscript{2}, we did observe the formation of the target Diels-Alder cycloadduct via \textsuperscript{1}H NMR spectroscopy as 22% conversion of the starting materials could be achieved in 3h at room temperature (entry 3, Table 4.2). This is, however, a much slower conversion rate than in the case of β-diketiminate bistriflate aluminum compounds as discussed in chapter 3. Nevertheless, the slower catalytic performance was understandable as OTf was less nucleophilic and a much better leaving group than Cl. Due to the presence of THF coordination at aluminum center, 46 is also thought to be less Lewis acidic than 47, and potentially even a worst catalyst than its THF-free analogue. However, to our surprise, when 46 was mixed with 1 equiv of NaBAR\textsubscript{Cl}\textsubscript{4} and used for the catalysis, it showed a much higher catalytic activity than 47 under the same reaction conditions. Complete conversion of starting materials was achieved in 3h (entry 2, table 4.2) which was comparable to the β-diketiminate aluminum catalytic systems. This suggested that the reactions between 46 or 47 and NaBAR\textsubscript{Cl}\textsubscript{4} form different species due to the presence of THF. It was then meaningful to investigate the role of THF in this particular catalytic process.
Table 4.2. Screening of potential (pre)catalysts for Diels Alder cycization between 2,3-dimethylbutadiene and 1,3-diphenyl-2-propenone.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>#</th>
<th>Pre-catalyst</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Trans/cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46 or 47</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>46/NaBAr&lt;sub&gt;Cl&lt;/sub&gt;&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3</td>
<td>99</td>
<td>99:1</td>
</tr>
<tr>
<td>3</td>
<td>47/NaBAr&lt;sub&gt;Cl&lt;/sub&gt;&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3</td>
<td>22</td>
<td>99:1</td>
</tr>
<tr>
<td>4</td>
<td>47/THF/NaBAr&lt;sub&gt;Cl&lt;/sub&gt;&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3</td>
<td>30</td>
<td>99:1</td>
</tr>
<tr>
<td>5</td>
<td>47/THF/NaBAr&lt;sub&gt;Cl&lt;/sub&gt;&lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;a&lt;/sup&gt;</td>
<td>3</td>
<td>97</td>
<td>99:1</td>
</tr>
<tr>
<td>6</td>
<td>49</td>
<td>4</td>
<td>11</td>
<td>99:1</td>
</tr>
<tr>
<td>7</td>
<td>49/THF&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1</td>
<td>12</td>
<td>99:1</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>3</td>
<td>99&lt;sup&gt;b&lt;/sup&gt;</td>
<td>99:1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Heat up to 50°C for 6h before adding NaBAr<sub>Cl</sub><sub>4</sub> or substrates. <sup>b</sup>The same % conversion was observed even with the addition of 1 equiv (with respect to the catalyst) of dbpy.

Since the only difference between 46 and 47 was the presence of a bound THF, it seems that 47 can readily converted to 46 by simple addition of 1 equiv of THF. However no coordinated THF signal was observed by <sup>1</sup>H NMR spectroscopy when 1 equiv of THF was added to the CD<sub>2</sub>Cl<sub>2</sub> solution of 47 and even more surprisingly was the fact that this resulting mixture did not show any increase in catalytic activity when 1 equiv of NaBAr<sub>Cl</sub><sub>4</sub> was added. Furthermore, the catalytic activity still remained quite sluggish even when THF was used as solvent. This indicated that THF could not coordinate to aluminum center by simply mixing the aluminum compound and THF together. This might be due the fact that
in order for THF to coordinate to the dichloroaluminum moiety in 47 one of the imine N must de-coordinate. As 46 (precursor to 47) is formed in THF it might be possible that THF coordination precedes the formation of the bonds between central Al and the pincer NCN ligand resulting in only one imine N coordination as in the case of 48. Even though there is no spectroscopic evidence to suggest asymmetric coordination of the pincer ligand in 46 this simply could be explain by rapid (on the NMR time scale) coordination/de-coordination between the two imine N atoms. This hypothesis is further supported by the fact that the catalytic activity of the 47/THF system can be increased by heating the reaction mixture to 60 °C for 6 h before the addition of NaBArCl\textsubscript{4} (entries 4,5, Table 4.2). Different heating times were also examined as shown in Table 4.3 which showed longer heating time did not increase the reaction rates. As these reactions were performed in situ they do not give a clear picture about the true role of THF in the catalysis. Therefore, it was important to identify the major species of the two catalytic systems.

<table>
<thead>
<tr>
<th>#</th>
<th>Temperature</th>
<th>Time(h)</th>
<th>Conversion(%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>r.t.</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>60 °C</td>
<td>1</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>60 °C</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>60 °C</td>
<td>12</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>60 °C</td>
<td>24</td>
<td>52</td>
</tr>
</tbody>
</table>

\textsuperscript{a}5% of LAlCl\textsubscript{2} was mixed with 1 equiv of THF in CD2Cl2 following by heat up for x h and then added 1 equiv of NaBArCl\textsubscript{4} before used for the Diels-Alder reaction between 4 and 5, reaction time: 1 h.
As shown in Figure 4.3, when mixed with 1 equiv of NaBAR\(^{\text{Cl}}_4\) in CD\(_2\)Cl\(_2\), 46 and 47 acted quite differently. The \(^1\)H NMR spectrum of the mixture of 47 and NaBAR\(^{\text{Cl}}_4\) gave a set of quite broad signals, which is in the contrast in comparison to the most signals of the 46/NaBAR\(^{\text{Cl}}_4\) mixture. Besides, a new set of signals were observed at the aromatic region as well as at 2.58 ppm which should be identified as the \(^\text{iPr}\) protons. This suggested that a second species was formed which processed a quite different structure. The \(^1\)H NMR spectru also clearly showed the presence of THF coordination as the signals for this molecule were downfield shifted (2.05 and 4.04 ppm) compared to free THF (1.82 and 3.69 ppm).

![Figure 4.3 Reactions between 46 or 47 and NaBAR\(^{\text{Cl}}_4\)](image)

With this information in hand, we tried to obtain crystalline samples for both reactions in order to figure out what exactly happened in these two cases. Stirring 47 and 1 equiv of NaBAR\(^{\text{Cl}}_4\) in DCM for 5 min and layering the resulting solution with hexane afforded a crop of colorless crystals, suitable for single crystal X-ray diffraction, which were identified as
complex 49 (Scheme 4.5). Molecular structure is shown in Figure 4.4 with the crystallographic data summarized in Table 4.1. It is not surprising that both two Cl atoms were still bonded to aluminum center as this also occurred in the β-diketiminate case. This complex is essentially a dimer of 47 supported by a Na cation. The monoanionic bis(imino)aryl NCN pincer ligand coordinates to the aluminum atom in a tridentate fashion. Compared with 47, 49 has a slightly shorter Al-C bond (1.936(3) Å) and longer Al-Cl bonds (2.1500(13) and 2.1583(13) Å). The most important distinction between 47 and 49 is that both nitrogen atoms in 49 coordinate to the aluminum center with similar bond lengths (2.182(3) and 2.237(3) Å), which are quite different in 47 (2.139(2) and 2.502 Å). This might be due to the presence of Na cation as it shifts electron density away from the AlCl₂ moiety causing the Al center to be more electron deficient, resulting in a more efficient Al-N bonding.

Scheme 4.5 Reactions between aluminum dichloride complexes and NaBAR₄Cl
Figure 4.4 Molecular structure for 49.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms, the \(^{1}\text{Pr}\) groups of the Dip substituents, the counter ion and solvent molecules have been removed for clarity.

Selected bond lengths (Å) and angles (°): Al1-C1 1.936(3), Al-Na1 3.5707(10), Al1-N1 2.237(3), Al1-N2 2.182(3), Al1-Cl1 2.1500(13), Al1-Cl2 2.1583(13), Na1-Cl1 2.9622(9), Na1-Cl2 2.8838(9), N2-Al1-N1 155.29(11), C1-Al1-N1 76.71(13), Cl1-Al1-N1 95.42(9), Cl1-Al1-Cl2 103.13(5).

We then used the dimer 49 to investigate its catalytic properties towards the initial Diels Alder reaction, hoping to shed light on the active species. However, the activity of the new compound was the lowest (~ 11% conversion in 4h; entry 6, Table 4.2) with respect to all systems containing NaBAr\(^{Cl}\)\(^{4}\). This suggested that 49 was not the active species in the 47/NaBAr\(^{Cl}\)\(^{4}\) system which is reported to produce high catalytic activity. When 1 equiv of THF was added into the DCM solution of 49 followed by heating the resulting solution to 60 °C for 6h, a slight promotion in catalytic activity was observed (~ 12% conversion in 1h; entry 7, Table 4.2). The lower increase in catalytic activity than that of the
LAiCl$_2$/THF/NaBar$_{\text{Cl}_4}$ system might be due to the presence of Na cation resulting in difficulty in formation of the true active species which was still unknown.

On the other hand, when 46 reacted with 1 equiv of NaBar$_{\text{Cl}_4}$ in DCM, another species 50 was obtained by layering the resulting solution with hexane. Crystal structure showed that the new species was a mononuclear cationic aluminum compound. As shown in Figure 4.5 the central aluminum was also five coordinate, with one of the Cl ligands replaced by a THF molecule. Both nitrogen atoms are coordinated to the aluminum center and the Al-N bond lengths were 2.182(3) and 2.237(3) Å. The Al-Cl bond length was 2.1185(11) Å, which were a bit shorter than that of 46 (1.943(3) and 2.1250(11) Å) and 49 (2.1500(13) and 2.1583(13) Å), revealing a decrease in electron density at the aluminum center. The Al-C bond length 1.932(3) Å was also shorter than that of 46 (1.943(3) Å) and 49 (1.936(3) Å), which also suggested that the cationic aluminum complex was more Lewis acidic than its dichloride precursor. Consequently, complex 50 appears to be a better Lewis acid catalyst than 49.
Figure 4.5 Molecular structure for 50.

Thermal ellipsoids have been drawn at 50% probability level. All hydrogen atoms, the \(^{\text{i}}\)Pr groups of the Dip substituents, the counter ion and solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1-C1 1.932(3), Al1-N1 2.181(2), Al1-N2 2.213(2), Al1-Cl1 2.1185(11), Al-O1 1.844(2), N2-Al1-N1 154.69(9), C1-Al1-N1 78.32(10), Cl1-Al1-N1 96.81(7), O1-Al1-C1 112.23(11)

When 50 was used for the same Diels-Alder reaction, complete conversion of starting materials was observed in 3h, which was similar with the 46/NaBAr\(^{\text{Cl}}\)_4 system. This suggested that we formed a more Lewis acidic system, in comparison to 46/47/49. It was then important to investigate whether the coordinated THF played any role in the catalysis process or just stabilized the cationic species. For this purpose 5 equiv of 1,3-diphenyl-2-propenone (5) was mixed with 50 in CD\(_2\)Cl\(_2\). \(^1\)H NMR spectroscopy clearly revealed a complete de-coordination of THF and coordination of the dienophile (Scheme
4.6, Figure 4.6). This observation suggested that the active species was free cation [LAlCl]⁺ (51) while 50 its pre-catalyst. When 47/NaBArCl₄ was mixed with 5 in CD₂Cl₂, the formation of 51 was also observed, but in a lower conversion (~30%). This might be the reason why 47/NaBArCl₄ system also showed some activity with respect to the attempted Diels-Alder transformation.

Scheme 4.6 Formation of active species
4.4 Catalytic application in Diels-Alder cycloadditions

As monocationic aluminum complex 50 was determined to be the most prominent pre-catalyst, we decided to investigate its catalytic property for several other Diels Alder reactions as summarized in Table 4.4. Almost all dienophiles were quite suitable for the target Diels Alder reactions with diene 4. For example, complete substrates conversion can be observed within 1h for the reactive dienophiles 9 and 10 when 5% of 50 was used (entries 1 and 2, Table 4.4). Longer reaction times were required for the difficult dienophiles such as 11, 5 and 14 (entries 3, 4 and 7, Table 4.4). However, 50 showed lower catalytic activities for the cycloadditions involving cyclic dienophiles. Only 41% isolated yield was obtained for 13 in 24h while no formation of the target Diels Alder adduct was observed even though a 10% catalyst loading was used (entries 5 and 6, Table 4.4) for 12. Unlike what happened in the Nacnac case, no formation of polymers was observed. For
much less reactive dienophile 15, extra amount of diene and longer reaction times were required to approach decent conversion (entries 8, Table 4.4). Additionally, less reactive dienes (23 and 32) were also examined for Diels Alder transformations. For 9 complete substrate conversion was observed in 1 h while for 5 longer reaction times were required to achieve excellent isolated yields of > 97% (entries 9-12, Table 4.4). Considering these observations the catalytic activity of cation 50 is comparable with those for the ferrocenyl-stabilized silylium cation15 and β-diketiminate supported Al-based systems with respect to the attempted Diels Alder cycloadditions.

Table 4.4 50 or HBA catalyzed Diels-Alder reactions of dienophiles 5 and 9-14 with dienes 4, 23 or 32. The results are listed as: time (h), yield (%), trans/cis or endo:exo, and/or para:meta ratios for each run.

<table>
<thead>
<tr>
<th>#</th>
<th>Diene</th>
<th>Dienophile</th>
<th>Adduct</th>
<th>50</th>
<th>HBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>9</td>
<td>16</td>
<td>1 h</td>
<td>96 % 90 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 h</td>
<td>-    -</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>10</td>
<td>17</td>
<td>1 h</td>
<td>98 % 89 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 h</td>
<td>-    -</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>11</td>
<td>18</td>
<td>24 h</td>
<td>72 % 58 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24 h</td>
<td>-    -</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>5</td>
<td>8</td>
<td>3 h</td>
<td>99:1 99:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24 h</td>
<td>98 % 33 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>99:1 99:1</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>12</td>
<td>19</td>
<td>1 h</td>
<td>-    1 h^a</td>
</tr>
</tbody>
</table>

111
Even though detailed investigations on the nature of the catalytic species were undertaken it still did not rule out the presence of an HBA. However, as discussed in Chapter III, an HBA (HOTf generated by AgOTf/tBuCl) showed quite different catalytic property for the abovementioned catalytic cycloadditions, suggesting the absence of HBA activity. Additionally, when 4 and 5 (entry 8, Table 4.2) were cyclized by 50 in the presence of 1 equiv of dbpy no loss of catalytic activity was observed, which provided additional evidence against HBA activity. Therefore, the investigated Diels Alder cycloadditions were indeed catalyzed by Lewis acidic complex 50 rather than an HBA. It is worth noting that
when 50 was mixed with equimolar amounts of dbpy in CD$_2$Cl$_2$, less than 10% ($^1$H NMR spectroscopy) of the corresponding pyridium cation [dbpy-H]$^+$ was formed as shown in Figure 4.7. This is important because if large amounts of the [dbpy-H]$^+$ are produced, especially if excess (with respect to catalyst) quantities of dbpy are used$^{16}$, then [dbpy-H]$^+$ could actually act as a proton source because the pKa value for [dbpy-H]$^+$ varies from 0.9 (DMSO) to 5 (H$_2$O) suggesting that this pyridinium cation could be a quite potent proton donor. Thus, we believe that when using dbpy to potentially gather evidence against an HBA activity it is crucial to determine the amount of [dbpy-H]$^+$ that has been produced under the established reaction conditions as large quantities of this pyridinium cation could, in fact, be the source of HBA activity.

Figure 4.7 $^1$H NMR for reaction of 50 and dbpy

In order to provide more evidence for this hypothesis, we prepared pyridium cation through the reaction between dbpy and HOTf in hexane and used it for the catalysis of a simple
Diels-Alder cycloaddition as shown in Scheme 4.7. Excess amount of dbpy was used for the preparation of pyridium in order to make sure one of the starting materials, HOTf was consumed completely as trace amount of HOTf might result in catalytic activity.

Scheme 4.7 Synthesis of pyridium cation and catalysis for Diels-Alder cycloaddition

As shown in Table 4.5, even the simplest Diels-Alder reaction did not occur at room temperature without any addition of catalyst (pyridium). When 10% of pyridium was added into this reaction mixture, also no formation of cycloadduct was observed by ¹H NMR spectroscopy. This is in agreement to the conclusion that HBA activity can be avoided by the addition of dbpy with the formation of small amounts of the corresponding protonated pyridine. However, when 50% of pyridium of used for this reaction, about 50% starting materials conversion was observed in 6h, although the activity became much lower in the following reaction times (77% conversion in 24h, entries3, 4, Table 4.5). When stoichiometric amount of pyridium was used, about 67% conversion was obtained in 2h while it took 12h to achieve complete conversion (entries 5, 6, Table 4.5). Although we still have not figure out the reason for the dramatic decrease in activity, there is enough evidence to demonstrate that even this particular pyridinium cation could be considered as a source of protons. Thus, it is critical to consider the effect of the formation of pyridinium cation when carrying out such experiments for avoiding HBA activity.
Table 4.5 Pyridium catalyzed Diels-Alder reaction

<table>
<thead>
<tr>
<th>#</th>
<th>Pyridium (%)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>10%</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>50%</td>
<td>6</td>
<td>51%</td>
</tr>
<tr>
<td>4</td>
<td>50%</td>
<td>24</td>
<td>77%</td>
</tr>
<tr>
<td>5</td>
<td>100%</td>
<td>2</td>
<td>67%</td>
</tr>
<tr>
<td>6</td>
<td>100%</td>
<td>12</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

4.5 Summary

Several aluminum complexes stabilized by bis(imino)phenyl NCN pincer ligand were prepared, fully characterized and used for the catalysis of a series of Diels Alder transformations. The mononuclear cationic compound 50 appears to be the most prominent pre-catalyst. Several control experiments were performed to show that cation 51 is most likely to be the active species in the catalysis process rather than an HBA. Lastly, the control experiment using dbpy should be carefully examined as the presence of large quantities of the corresponding pyridinium cation could serve as a proton source.
4.6 Experimental Section

All manipulations were carried out using standard Schlenk techniques and a dry-box. CH$_2$Cl$_2$, CD$_2$Cl$_2$ and CDCl$_3$ were distilled over CaH$_2$ while THF, toluene and $n$-hexane were distilled over sodium. All solvents were stored over 4 Å molecular sieves. Ligand 45 was prepared according to reported synthetic procedures. All other chemicals were purchased from commercial sources and used without further purification. The NMR spectra were recorded on a Bruker Avance III 400 or JEOL ECA400 (1$^H$ NMR at 400 MHz; 13$^C$ NMR at 100 MHz, 11$^B$ NMR at 128 MHz and 27$^Al$ NMR at 104 MHz) instrument. Tetramethysilane was used as reference for 1$^H$ and 13$^C$ NMR, while 11$^B$ and 27$^Al$ NMR spectra were recorded with respect to Et$_2$O-BF$_3$, and AlCl$_3$/D$_2$O, respectively. Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using the electro spray ionization (ESI) mode.

**Synthesis of ligand 45.** 2-Bromobenzene-1,3-dialdehyde (10.0 g, 46.9 mmol) and 2,6-diisopropylaniline (22.1 mL, 117.3 mmol) was dissolved in 200 mL methanol in a 500 mL round-bottomed flask with a stirrer bar. To this solution, 1 drop of formic acid was added. The reaction mixture was left to stir for 2h and then filtered. The obtained yellow solid was washed by cold methanol and dried under vacuum. Yield 23 g, 92%. 1$^H$ NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.20 (d, 3$^J$H-H = 6.92 Hz, 24H, CH(C$_3$H$_3$)$_2$), 2.95 (sept, J$^H$H = 6.92 Hz, 4H, C$_3$H(CH$_3$)$_2$), 7.12-7.21 (m, 6H, Ph), 7.58 (t, 3$^J$H-H = 7.72 Hz, 1H, Ph), 8.39 (d, 3$^J$H-H = 7.72 Hz, 2H, Ph), 8.70 (s, 2H, C=CH) ppm.

**Synthesis of LAlCl$_2$(THF), 46.** $^n$BuLi (0.52 mL, 1.05 mmol, 2M in cyclohexane) was added dropwise to a THF (20 mL) solution of 2,6-(2,6-$^i$Pr$_2$-C$_8$H$_3$N=CH)$_2$-C$_8$H$_3$-1-Br (45) ( 0.53 g, 1.00 mmol) at – 78°C. The mixture was stirred for 30 min before AlCl$_3$ (0.13, 1.00
mmol) was added. The solution was allowed to warm to room temperature gradually and stir overnight. The solvent was removed under reduced pressure and the residue was extracted by dichloromethane. After evaporation of most of the dichloromethane, 10 mL n-hexane was added. The red powder formed was dried under vacuum for 5 min. Yield: 0.46 g, (74%).

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.16 (d, $^3$J$_{H-H}$ = 6.50 Hz; 24H, CH(C$_H$3)$_2$), 1.89 (b, 4H, THF), 3.16 (sept, $^3$J$_{H-H}$ = 6.50 Hz, 4H, CH(CH$_3$)$_2$), 3.92 (b, 4H, THF), 7.19-7.24 (m, 6H, Ph), 7.60 (t, $^3$J$_{H-H}$ = 7.48 Hz, 1H, Ph), 7.74 (d, $^3$J$_{H-H}$ = 7.48 Hz, 2H, Ph), 8.34 (s, 2H, CH=N) ppm.

$^{13}$C NMR (100.5 MHz, CDCl$_3$, 25 °C): $\delta$ 24.5 (CH(C$_H$3)$_2$), 25.5 (THF), 28.2 (CH(CH$_3$)$_2$), 69.5 (THF), 123.7 ($p$-N-C$_6$H$_3$), 126.7 ($m$-N-C$_6$H$_3$), 131.0 ($p$-Al-C$_6$H$_3$), 132.3 ($m$-Al-C$_6$H$_3$), 139.7 ($o$-N-C$_6$H$_3$), 140.9 (C=N-C), 143.7 ($o$-Al-C$_6$H$_3$), 168.4 (C=N-C) ppm. $^{27}$Al NMR (104.2 MHz, CDCl$_3$, 25 °C): $\delta$ 97 ppm. HRMS (ESI) calculated for C$_{36}$H$_{48}$N$_2$OCl$_2$Al [M + H]: 621.2959; Found: 621.2927. MP: ~191°C (onset of decomposition).

**Synthesis of LAlCl$_2$, 47.** nBuLi (0.52 mL, 1.05 mmol, 2M in cyclohexane) was added dropwise to a THF (20 mL) solution of 2,6-(2,6-iPr$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (45) (0.53 g, 1.00 mmol) at –78°C. The mixture was stirred for 30 min before AlCl$_3$ (0.13, 1.00 mmol) was added. The solution was allowed to warm to room temperature gradually and stir overnight. The solvent was removed under reduced pressure and the residue was extracted by toluene. After evaporation of toluene, 10 mL n-hexane was added to wash the crude product. The red powder obtained was dried under vacuum for about 15 h. Yield: 0.41 g, (75%). Crystals were grown in toluene/n-hexane mixed solution. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 1.16 (d, $^3$J$_{H-H}$ = 6.52 Hz, 24H, CH(CH$_3$)$_2$), 3.16 (sept, J$_{H-H}$ = 6.52 Hz, 4H, CH(CH$_3$)$_2$), 7.19-7.23 (m, 6H, Ph), 7.60 (t, $^3$J$_{H-H}$ = 7.48 Hz, 1H, Ph), 7.74 (d, $^3$J$_{H-H}$ = 7.48 Hz, 2H, Ph), 8.34 (s, 2H, CH=N) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$, 25 °C): $\delta$ 25.5 (CH(CH$_3$)$_2$), 28.2 (CH(CH$_3$)$_2$), 123.7 ($p$-N-C$_6$H$_3$), 126.7 ($m$-N-C$_6$H$_3$), 131.0 ($p$-Al-C$_6$H$_3$),
132.3 (m-Al-C₆H₃), 139.8 (o-N-C₆H₃), 140.9 (C=N-C), 143.7 (o-Al-C₆H₃), 168.4 (C=N-C) ppm. ²⁷Al NMR (104.2 MHz, CDCl₃, 25 °C): δ 106 ppm. HRMS (ESI) calculated for C₃₂H₄₀N₂Cl₂Al [M + H]: 549.2384; Found: 549.2371. MP: ~ 190°C (onset of decomposition).

**Synthesis of LAl(OTf)₂(THF)₂, 48.** nBuLi (0.52 mL, 1.05 mmol, 2M in cyclohexane) was added dropwise to a 20 mL THF solution containing 45 (0.53 g, 1.00 mmol) at –78°C. The mixture was stirred for 30 min before AlCl₃ (0.13, 1.00 mmol) was added. The solution was gradually allowed to warm to room temperature and stir for 15h. This reaction mixture was then transferred to another flask that contained AgOTf (0.77 g, 3.0 mmol) and left to stir overnight in the absence of light. After filtration, the solution was concentrated and layered with n-hexane. Few yellow crystals were obtained at -15°C after 1 day. The product appeared to be generally unstable presumably due to high air/moisture sensitivity and, thus, it was possible only to obtain single crystal X-ray analysis.

**Synthesis of [LAlCl₂NaCl₂Al][NaBAR⁺Cl₄⁻], 49.** 47 (0.55g, 1.00 mmol) and NaBAR⁺Cl₄⁻ (0.62g, 1.00 mmol) were dissolved in 5 mL of CH₂Cl₂ and left to stir for 5 min. After filtration, the solution was layered with 5 mL n-pentane. Colorless crystals were obtained after 1 day. Yield: 0.61g, 71%. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 1.12 (broad, 48H, CH(C₆H₃)₂), 2.99 (sept, J_H-H = 6.84 Hz, 8H, CH(CH₃)₂), 6.97-7.21 (m, 24H, Ph), 7.64 (t, 3J_H-H = 7.58 Hz, 2H, Ph), 7.83 (d, 3J_H-H = 7.58 Hz, 4H, Ph), 8.42 (s, 4H, C=O) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂, 25 °C): δ 25.5 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 123.1 (p-N-C₆H₃), 124.2 (p-C, Ar⁺), 127.6 (m-N-C₆H₃), 132.1 (m-Al-C₆H₃), 132.9 (m-C, Ar⁺), 133.0 (o-C, Ar⁺), 133.1 (p-Al-C₆H₃), 139.2 (o-N-C₆H₃), 140.9 (C=N-C), 142.2 (o-Al-C₆H₃), 164.0 (q, 1J_BC = 49 Hz, B-C), 170.0 (C=N-C) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂, 25 °C): δ -7.9 ppm. ²⁷Al NMR (104.2 MHz, CD₂Cl₂, 25 °C): no signal observed.
HRMS (ESI): (the only signal observed was actually for LAICl$_2$) calculated for C$_{32}$H$_{40}$N$_2$Cl$_2$Al [M + H]: 549.2384; Found: 549.2372. MP: ~ 254°C (onset of decomposition).

**Synthesis of [LAICl(THF)][BAr$_4$Cl]$_4$, 50.** A fresh sample of 46 (0.62 g, 1.00 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$ followed by the addition of NaBAr$_4$Cl$_4$ (0.62 g, 1 mmol). After it was left to stir for 6 h, the solution was filtered and layered with 5 mL pentane. Colorless crystals were obtained after 1 day. Yield: 0.73 g, 62%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): δ 1.10 (broad, 24H, CH(CH$_3$)$_2$), 2.10 (b, 4H, THF), 2.56 (sept, J$_{H-H}$ = 6.88 Hz, 4H, CH(CH$_3$)$_2$), 4.07 (b, 4H, THF), 6.94-7.34 (m, 18H, Ph), 7.71 (t, $^3$J$_{H-H}$ = 7.32 Hz, 1H, Ph), 7.91 (d, $^3$J$_{H-H}$ = 7.32 Hz, 2H, Ph), 8.59 (s, 2H, CH=N) ppm. $^{13}$C NMR (100.5 MHz, CD$_2$Cl$_2$, 25 °C): δ 25.2 (CH(CH$_3$)$_2$), 25.8 (THF), 29.1 (CH(CH$_3$)$_2$), 75.5 (THF), 123.0 (p-N-C$_6$H$_3$), 124.3 (p-C, Ar$^{Cl}$), 128.2 (m-N-C$_6$H$_3$), 132.9 (m-C, Ar$^{Cl}$), 133.1 (o-C, Ar$^{Cl}$), 134.0 (m-Al-C$_6$H$_3$), 134.4 (p-Al-C$_6$H$_3$), 139.0 (o-N-C$_6$H$_3$), 140.1 (C=N-C), 142.2 (o-Al-C$_6$H$_3$), 164.0 (q, $^1$J$_{BC}$ = 48 Hz, B-C), 173.3 (C=N-C) ppm. $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 25 °C): δ -7.9 ppm. $^{27}$Al NMR (104.2 MHz, CD$_2$Cl$_2$, 25 °C): no signal observed. HRMS (ESI): (the only signal observed was due to ligand L) calculated for C$_{32}$H$_{31}$N$_2$ [M + H]: 453.3270; Found: 453.3269. MP: ~ 156°C (onset of decomposition).

**Synthesis of pyridium.** dbpy (0.86 mL, 2 equiv, 4.00 mmol) was dissolved in 100 mL hexane. To this solution a mixture of 300 mg HOTf and 5 mL hexane was added slowly while vigorous stirring. The reaction mixture was left to stir overnight. After filtration and dry under vacuum, pure product was obtained as white solid. Yield: 510 mg, 75%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.16 (s, 18H, C(CH$_3$)$_3$), 7.77 (dd, $^3$J$_{H-H}$ = 8.24 Hz, 2H, m-ArH), 8.39 (t, $^3$J$_{H-H}$ = 8.24 Hz, 1H, p-ArH), 12.46 (br, 1H, NH) ppm. $^{13}$C NMR (100.5
MHz, CDCl$_3$, 25 °C): $\delta$ 29.1 (C(CH$_3$)$_3$), 37.2 (C(CH$_3$)$_3$), 119.0 (CF$_3$), 122.1 (CH), 147.8 (CH), 164.9 (C) ppm. $^{19}$F NMR (376.4 MHz, CDCl$_3$, 25 °C): $\delta$ -78.08 ppm.

General procedure for Diels-Alder cycloadditions. A precatalyst, usually 50, (0.017 mmol, 0.05 equiv) was dissolved in 1 mL CD$_2$Cl$_2$ in a J. Young NMR tube. To this solution a diene (0.68 mmol, 2 equiv) and a dienophile (0.34 mmol, 1 equiv) was added. The reaction mixture was left for the time indicated in Table 4.2-4.5. Then, the crude mixture was purified by flash column chromatography on silica gel using $n$-hexane/ethyl acetate solvent mixture affording the corresponding Diels-Alder products. The endo:exo ratio is determined by GLC analysis of the reaction mixture prior to workup.
References

7 Gao, W.; Cui, D. J. Am. Chem. Soc. 2008, 130, 4984.
16 Schneider, A. E.; Manolikakes, G. J. Org. Chem. 2015, 80, 6193.
Appendix
1. NMR Spectrum

Figure S1. $^1$H-NMR spectrum of 3a.

Figure S2. $^{13}$C-NMR spectrum of 3a.
Figure S3. $^{27}$Al-NMR spectrum of 3a.

Figure S4. $^1$H-NMR spectrum of 3b.
Figure S5. $^{13}$C-NMR spectrum of 3b.

Figure S6. $^{27}$Al-NMR spectrum of 3b.
Figure S7. $^1$H-NMR spectrum of 3c.

Figure S8. $^{13}$C-NMR spectrum of 3c.
Figure S9. $^{27}$Al-NMR spectrum of 3c.

Figure S10. $^1$H-NMR spectrum of 3d.
Figure S11. $^{13}$C-NMR spectrum of 3d.

Figure S12. $^{27}$Al-NMR spectrum of 3d.
Figure S13. $^1$H-NMR spectrum of 3e.

Figure S14. $^{13}$C-NMR spectrum of 3e.
Figure S15. $^{27}$Al-NMR spectrum of 3e.

Figure S16. $^1$H-NMR spectrum of 3f.
Figure S17. $^{13}$C-NMR spectrum of 3f.

Figure S18. $^{27}$Al-NMR spectrum of 3f.
Figure S19. $^1$H-NMR spectrum of 3b + NaBAR$^{+}\text{Cl}^{-}_4$.

Figure S20. $^{13}$C-NMR spectrum of 3b + NaBAR$^{+}\text{Cl}^{-}_4$. 
Figure S21. $^1$H-NMR spectrum of 3c + NaBAr$_4$Cl$_4$.

Figure S22. $^{13}$C-NMR spectrum of 3c + NaBAr$_4$Cl$_4$. 
Figure S23. $^1$H-NMR spectrum of 3d + NaBAR$^{+}$Cl.$^{-4}$.

Figure S24. $^{13}$C-NMR spectrum of 3d + NaBAR$^{+}$Cl.$^{-4}$. 
Figure S25. $^1$H-NMR spectrum of 46.

Figure S26. $^{13}$C-NMR spectrum of 46.
Figure S27. $^{27}\text{Al}$-NMR spectrum of 46.

Figure S28. $^1\text{H}$-NMR spectrum of 47.
Figure S29. $^{13}$C-NMR spectrum of 47.

Figure S30. $^{27}$Al-NMR spectrum of 47.
Figure S31. $^1$H-NMR spectrum of 49.

Figure S32. $^{13}$C-NMR spectrum of 49.
Figure S33. $^1$H-NMR spectrum of 50.

Figure S34. $^{13}$C-NMR spectrum of 50.
Figure S35. $^1$H-NMR spectrum of pyridium.

Figure S36. $^1$H-NMR spectrum of poly-12.
Figure S37. $^{13}$C-NMR spectrum of poly-12

2. Spectrum for polymers.

Figure S38. A typical gel permeation chromatogram for poly(cyclopentanone).
Figure S39. A typical MALDI-tof mass spectrum of poly(cyclopentanone).

Figure S40. The FTIR spectrum for poly(cyclopentanone).
Figure S41. The FTIR spectrum for the polymerization of 2-cyclohexen-1-one.

Figure S42. The FTIR spectrum for the polymerization of 2-cyclohepten-1-one.