

**COMPUTATIONAL ANALYSIS OF THE
ENANTIOSELECTIVITY OF DIELS-ALDER REACTIONS
INVOLVING CHIRAL CATIONIC OXAZABOROLIDINIUM
CATALYST**

NASR Y.M. OMAR

**THESIS SUBMITTED IN FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY**

**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2011

***To the soul of my mother
To my father and all family members***

UNIVERSITI MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: Nasr Y.M. Omar (I.C/Passport No: K134998)

Registration/Matric No: SHC040017

Name of Degree: PhD

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

Computational Analysis of the Enantioselectivity of Diels-Alder Reactions Involving Chiral Cationic Oxazaborolidinium Catalyst

Field of Study: Computational Organic Chemistry

I do solemnly and sincerely declare that:

- (1) I am the sole author/writer of this Work;
- (2) This Work is original;
- (3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
- (4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
- (5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
- (6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature

Date 24/2/2011

Subscribed and solemnly declared before,

Witness's Signature

Date 24/2/2011

Name: Dr. Richard Wong Chee Seng
Designation: Associate Professor

Abstract

This thesis is divided into six chapters. In the first chapter, the results of standard high-performance computing (HPC) benchmarks are presented in order to assess the performance characteristics of the various hardware and software components of an own built commodity-class Linux cluster. Introductions to enantioselective synthesis and quantum mechanical methods are provided in the second chapter. The third chapter gives insights into the enantioselectivity and mechanism of the organocatalytic Diels-Alder reaction using density functional theory (DFT) at the B3LYP/6-31G(d) level of theory. The fourth chapter attempts to rationalize the enantioselectivity and mechanism of the organocatalytic Diels-Alder reaction using various aspects of DFT. The organocatalytic solid-phase Diels-Alder reaction in terms of enantioselectivity and mechanism is theoretically investigated in the fifth chapter using the hybrid method ONIOM(QM:MM). The sixth chapter deals with the same organocatalyst but as applied to cyanosilylation of aldehydes. The mechanism and enantioselectivity of this reaction are also investigated by means of DFT at the B3LYP/6-31G(d) level of theory.

Abstrak

Tesis ini dibahagikan kepada 6 bab. Di dalam bab yang pertama, keputusan tanda aras *high performance computing* (HPC) diberikan untuk menilai karakteristik komponen peralatan dan perisian kluster Linux *commodity class* yang dibina untuk tujuan komputasi. Pengenalan kepada sintesis *enantio* terpilih dan kaedah-kaedah mekanik kuantum diberikan di dalam bab 2. Bab 3 pula menjelaskan isu-isu berkaitan pemilihan *enantio* dan mekanisma pemangkinan organik tindakbalas Diels-Alder yang dikaji dengan teori *density functional* (DFT) pada tahap teori B3LYP/6-31G(d). Di dalam bab 4, perbincangan untuk merasionalisasi pemilihan *enantio* dan mekanisma pemangkinan organik untuk tindakbalas Diel-Alder dari pelbagai aspek DFT di ketengahkan. Pemangkinan organik dalam keadaan pepejal bagi tindakbalas Diels- Alder yang sama dibincangkan dalam bab 5 menggunakan kaedah hibrid ONIOM(QM:MM). Bab 6 pula membincangkan penggunaan pemangkin organik yang sama tetapi tindakbalas yang dikaji adalah pen-sianosililiasian aldehyd. Mekanisma dan pemilihan *enantio* bagi tindakbalas ini juga dikaji menggunakan DFT pada tahap B3LYP/6-31G(d).

Acknowledgements

First and foremost, my most sincere and profound appreciation to my supervisors Professor Dr. Noorsaadah Abd. Rahman and Professor Dr. Sharifuddin M. Zain for their instrumental role in assisting me to complete this thesis. Their valuable guidance was essential during the course of my work.

My gratitude also goes out to the Malaysian government for the valuable financial aid provided which greatly contributed towards the successful completion of my thesis.

A special word of thanks goes to the Department of Chemistry, Centre for Information Technology and MIMOS Berhad for providing computer facilities.

My heartfelt thanks also go out to all my family members who have been instrumental in providing moral encouragements for my success. I wish to take this opportunity to express my cordial gratitude to them for all that they have done for me.

I would also like to take this opportunity to thank my friends and colleagues who have, in more ways than one, assisted and encouraged me in my endeavor to complete this work.

Contents

Abstract iv

Abstrak v

Acknowledgements vi

List of Figures ix

List of Schemes xiv

List of Tables xv

1 Performance Analysis of a Commodity-Class Linux Cluster for Computational Chemistry Applications

- 1.1 Introduction 1
- 1.2 Cluster Software and Hardware 5
- 1.3 Benchmark Results and Analysis 6
 - 1.3.1 Compilers, processor, and memory performance 7
 - 1.3.2 Network performance 11
 - 1.3.3 Disk storage and parallel I/O performance 24
- 1.4 Conclusion 34
- 1.5 References 34

2 Enantioselective Synthesis and Theoretical Backgrounds

- 2.1 Enantioselective Synthesis 40
 - 2.1.1 Stereochemistry and stereoisomerism 40
 - 2.1.2 Selective synthesis of enantiomers 43
 - 2.1.3 Enantioselective organocatalysis 44
 - 2.1.4 Enantioselective organocatalytic Diels-Alder reactions 46
- 2.2 Theoretical Backgrounds 47
 - 2.2.1 The Schrödinger equation and the potential energy surface 47
 - 2.2.2 The Hartree-Fock method 51
 - 2.2.3 Basis sets and the Roothaan-Hall equations 55
 - 2.2.4 Density functional theory and the Kohn-Sham equations 59
 - 2.2.5 Geometry optimization and vibrational frequencies 65
 - 2.2.6 Thermochemical quantities 69
 - 2.2.7 Molecular mechanics 73
 - 2.2.8 Classical molecular dynamics 75
 - 2.2.9 Periodic boundary conditions 77
 - 2.2.10 Hybrid quantum mechanics/molecular mechanics (QM/MM) methods 78
- 2.3 References 80

3 Enantioselective Organocatalytic Diels-Alder Reactions: A Density Functional Theory and Kinetic Isotope Effects Study

- 3.1 Introduction 88
- 3.2 Computational Details 90
- 3.3 Results and Discussion 92
 - 3.3.1 Description of the studied reactions and stereochemical nomenclature 92
 - 3.3.2 Geometries and energetics of stationary points 98
 - 3.3.3 Kinetic isotope effects 112
 - 3.3.4 Preliminary data and further investigations 116

- 3.4 Conclusion 123
- 3.5 References 124

4 Density Functional Theory Investigation of the Enantioselectivity and Mechanism of an Organocatalytic Diels-Alder Reaction

- 4.1 Introduction 129
- 4.2 Computational Details 130
- 4.3 Results and Discussion 132
 - 4.3.1 Reaction force analysis along the intrinsic reaction coordinate 132
 - 4.3.2 Natural population analysis (NPA) 136
 - 4.3.3 Topological analysis of the electron localization function 140
 - 4.3.4 Bond order analysis 143
 - 4.3.5 Analysis of the global and local reactivity indices 148
- 4.4 Conclusion 152
- 4.5 References 154

5 An ONIOM Study on the Enantioselectivity of Diels-Alder Reaction Catalyzed by SiO₂-Immobilized Chiral Oxazaborolidinium Cation

- 5.1 Introduction 161
- 5.2 Methods and Computational Details 163
 - 5.2.1 Preparation of amorphous silica bulk and surface 163
 - 5.2.2 ONIOM models and details of the calculations 166
- 5.3 Results and Discussion 170
 - 5.3.1 Characterization of the amorphous silica bulk and surface 170
 - 5.3.2 Diels-Alder reaction on the silica surface 172
 - 5.3.3 Limitations of the study and future recommendations 177
- 5.4 Conclusion 178
- 5.5 References 179

6 A DFT Investigation on the Enantioselective Cyanosilylation of Aldehydes Catalyzed by Chiral Oxazaborolidinium Cation

- 6.1 Introduction 184
- 6.2 Computational Details 185
- 6.3 Results and Discussion 186
- 6.4 Conclusion 197
- 6.5 References 197

List of Figures

- 1.1 Bandwidths for MTU 1500, 8160, and 9000 with and without interrupt coalescence (IC) at 8 MB socket buffer size 16
- 1.2 Latencies for MTU 1500, 8160, and 9000 for message sizes less than 2 KB 17
- 1.3 Latencies for MTU 1500, 8160, and 9000 for message sizes in the range of 2 KB to 128 KB 17
- 1.4 Latencies for MTU 1500, 8160, and 9000 for message sizes greater than 128 KB 18
- 1.5 Bandwidths for raw TCP, MPICH, and TCGMSG-MPICH 20
- 1.6 Bandwidths for MPICH, ARMCI, and GA libraries 23
- 1.7 Bandwidths for NFS, PVFS2, and Lustre using the POSIX IO and MPI-IO interfaces. Shown is the average of access patterns ‘write’, ‘read/write’, and ‘random read/write’. In the case of MPI-IO, this includes access methods ‘individual file pointer’ and ‘explicit offset’ 32
- 2.1 Chiral molecules with no asymmetric carbon atoms (**1** and **2**) vs. achiral molecules with asymmetric carbon atoms (**3** and **4**) 41
- 2.2 *R* vs. *S* stereochemical assignments 43
- 2.3 A simple molecular coordinate system showing position vectors (**R** and **r**) and their magnitudes (R and r) 48
- 2.4 A model potential energy surface showing important stationary points 50
- 2.5 Radial behavior of STO and GTO 57
- 2.6 Relationship between computed energies and thermochemical quantities along a reaction path at 298.15 K and 1 atm pressure. U , E_0 , E_{298} , H_{298} , and G_{298} are given by Eqs. 2-50, 2-58, 2-62, 2-63, and 2-64, respectively. TS = transition state. Note: the “transition state” term is used to denote a Boltzmann average on the Gibbs free energy surface while the “transition structure” term is used to describe the first-order saddle point on the potential energy surface 71
- 2.7 The relationship between percent enantiomeric excess, relative reaction rate and relative energy at 298.15 K 74
- 2.8 Periodic boundary conditions in two dimensions. The simulation box (in blue) is surrounded by eight periodic images. Arrows indicate that if during the simulation an atom (or a molecule) steps outside the boundary of the box, its image simultaneously enters the box 77
- 2.9 The ONIOM layers and models. (a) ONIOM layers, (b) three-layer ONIOM model, and (c) two-layer ONIOM model 79
- 3.1 Corey’s enantioselective Diels-Alder reaction of benzoquinone using chiral oxazaborolidinium catalyst 92
- 3.2 Asynchronous bond formation at the transition state 93
- 3.3 Uncatalyzed Diels-Alder reaction with four possible reaction pathways. Diene addition to the less substituted double bond. Transition states are as shown in Figure 3.10 96

- 3.4 Uncatalyzed Diels-Alder reaction with four possible reaction pathways. Diene addition to the methyl substituted double bond. Transition states are as shown in Figure 3.11 96
- 3.5 Catalyzed Diels-Alder reaction with eight possible reaction pathways. The catalyst is coordinated *syn* to the HC=CH double bond that undergoes the [4+2]-cycloaddition. Transition states are as shown in Figure 3.13. In brackets are the transition states involving the *s-trans* diene 97
- 3.6 Catalyzed Diels-Alder reaction with eight possible reaction pathways. The catalyst is coordinated *anti* to the HC=CH double bond that undergoes the [4+2]-cycloaddition. Transition states are as shown in Figure 3.14. In brackets are the transition states involving the *s-trans* diene 97
- 3.7 Reactants B3LYP/6-31G(d) optimized structures. Relative free energies are in kcal/mol at 178.15 K with relative free energies at 298.15 K given in brackets. Distances are in angstroms. For names see text. Color code: carbon in grey, hydrogen in white, oxygen in red, nitrogen in blue, and boron in pink 99
- 3.8 Relative Gibbs free energies for the coordination between **R3** and catalyst **R4** at 178.15 K and 298.15 K 100
- 3.9 Products B3LYP/6-31G(d) optimized structures. Relative free energies are in kcal/mol at 178.15 K with relative free energies at 298.15 K given in brackets. For names see text 100
- 3.10 B3LYP/6-31G(d) optimized transition structures for the uncatalyzed Reaction 3-B. Relative free energies are in kcal/mol at 178.15 K with relative free energies at 298.15 K given in brackets. Distances are in angstroms. **TS1** = *endo* transition state involving the *s-cis* diene, **TS2** = *endo* transition state involving the *s-trans* diene, **TS3** = *exo* transition state involving the *s-cis* diene, and **TS4** = *exo* transition state involving the *s-trans* diene 101
- 3.11 B3LYP/6-31G(d) optimized transition structures for the uncatalyzed Reaction 3-C. Relative free energies are in kcal/mol at 178.15 K with relative free energies at 298.15 K given in brackets. These energies are relative to **TS1**. Distances are in angstroms. **TS5** = *endo* transition state involving the *s-cis* diene, **TS6** = *endo* transition state involving the *s-trans* diene, **TS7** = *exo* transition state involving the *s-cis* diene, and **TS8** = *exo* transition state involving the *s-trans* diene 102
- 3.12 Reaction energy diagram for the uncatalyzed Reaction 3-B at 178.15 K and 298.15 K showing activation free energies and relative rates. Free energies are in kcal/mol. **TS1** and **TS3** are as shown in Figure 3.10 103
- 3.13 B3LYP/6-31G(d) optimized transition structures for the catalyzed Reaction 3-D. Relative free energies are in kcal/mol at 178.15 K with relative free energies at 298.15 K given in brackets. Distances are in angstroms. **TS9** = *endo* transition state involving the *s-cis* diene attack to the front face, **TS10** = *endo* transition state involving the *s-trans* diene attack to the front face, **TS11** = *exo* transition state involving the *s-cis* diene attack to the front face, **TS12** = *endo* transition state involving the *s-cis* diene attack to the rear face, **TS13** =

- endo* transition state involving the *s-trans* diene attack to the rear face, **TS14** = *exo* transition state involving the *s-cis* diene attack to the rear face, and **TS15** = *exo* transition state involving the *s-trans* diene attack to the rear face. The *exo* transition state involving the *s-trans* diene attack to the front face could not be located 105
- 3.14 B3LYP/6-31G(d) optimized transition structures for the catalyzed Reaction 3-E. Relative free energies are in kcal/mol at 178.15 K with relative free energies at 298.15 K given in brackets. These energies are relative to **TS9**. Distances are in angstroms. **TS16** = *endo* transition state involving the *s-cis* diene attack to the front face, **TS17** = *endo* transition state involving the *s-trans* diene attack to the front face, **TS18** = *exo* transition state involving the *s-cis* diene attack to the front face, **TS19** = *exo* transition state involving the *s-trans* diene attack to the front face, **TS20** = *endo* transition state involving the *s-cis* diene attack to the rear face, **TS21** = *endo* transition state involving the *s-trans* diene attack to the rear face, and **TS22** = *exo* transition state involving the *s-cis* diene attack to the rear face. The *exo* transition state involving the *s-trans* diene attack to the rear face could not be located 107
- 3.15 Reaction energy diagram for the catalyzed Reaction 3-D at 178.15 K and 298.15 K showing activation free energies and relative rates. Free energies are in kcal/mol. **TS9** and **TS14** are as shown in Figure 3.13 110
- 3.16 Experimental ²H and ¹³C (italicized numbers) KIEs at 298 K for the uncatalyzed Diels-Alder reaction between isoprene and maleic anhydride 114
- 3.17 Experimental ²H and ¹³C (italicized numbers) KIEs at 298 K for the Lewis acid catalyzed Diels-Alder reaction of isoprene and methyl vinyl ketone 114
- 3.18 B3LYP/6-31G(d) computed ²H and ¹³C (italicized numbers) KIEs at 298 K for the uncatalyzed Reaction 3-B (**TS1** and **TS3**) and the catalyzed Reaction 3-D (**TS9** and **TS14**) 115
- 3.19 Catalyzed Diels-Alder reaction with eight possible reaction pathways. The catalyst is coordinated *syn* to the HC=CH double bond that undergoes the [4+2]-cycloaddition 117
- 3.20 Catalyzed Diels-Alder reaction with eight possible reaction pathways. The catalyst is coordinated *anti* to the HC=CH double bond that undergoes the [4+2]-cycloaddition 117
- 3.21 B3LYP/6-31G(d) optimized structures for Danishefsky diene and products. Relative free energies are in kcal/mol at 298.15 K. For names see text 118
- 3.22 B3LYP/6-31G(d) optimized transition structures for the catalyzed Reaction 3-F. Relative free energies are in kcal/mol at 298.15 K. Distances are in angstroms. **TS23** = *endo* transition state involving the *s-cis* diene attack to the front face, **TS24** = *exo* transition state involving the *s-cis* diene attack to the front face, **TS25** = *endo* transition state involving the *s-cis* diene attack to the rear face, and **TS26** = *exo* transition state involving the *s-cis* diene attack to the rear face. For all transition structures, the carbon atom attached to the OMe group has the *R* configuration 119

- 3.23 Reaction energy diagram for the catalyzed Reaction 3-F at 298.15 K showing activation free energy (kcal/mol) and relative rate. **TS23** and **TS24** are as shown in Figure 3.22 121
- 3.24 B3LYP/6-31G(d) computed ^2H and ^{13}C (italicized numbers) KIEs at 298 K for Reaction 3-F (**TS23** and **TS24**) 122
- 4.1 Second-order Gonzalez-Schlegel reaction path following algorithm 133
- 4.2 B3LYP/6-31G(d) IRC for the *endo* (starting from **TS9**) and the *exo* (starting from **TS14**) channels of the Diels-Alder reaction between **14** and **15** in the presence of catalyst **16** 134
- 4.3 Reaction force profiles associated with the internal coordinate R1 for the *endo* and the *exo* channels of the Diels-Alder reaction between **14** and **15** in the presence of catalyst **16** 135
- 4.4 Reaction force profiles associated with all Cartesian coordinates for the *endo* and the *exo* channels of the Diels-Alder reaction between **14** and **15** in the presence of catalyst **16** 135
- 5.1 Building amorphous silica bulk and surface. (a) β -Cristobalite unit cell, (b) β -cristobalite supercell, (c) created bulk amorphous silica, (d) final amorphous silica surface, and (e) final amorphous silica surface with silanol groups (top view). The two hydrogen atoms with the '+' sign indicate where the functionalization of the surface will take place. Silicon, oxygen and hydrogen atoms are displayed in yellow, red and white, respectively 164
- 5.2 Amino silica surface. (a) 3-Aminopropyltrimethoxysilane to be attached to the silica surface, (b) UFF optimized amino silica surface (top view), and (c) UFF optimized amino silica surface (side view). Hydrogens were used to fill out the valence that resulted from removing the periodic boundary conditions. Hydrogens were added using the HyperChem program 167
- 5.3 ONIOM(B3LYP/6-31G(d):UFF) optimized amino silica-immobilized catalyst **16**. (a) Top view and (b) side view. The QM layer is in the ball-and-stick representation and the MM layer is in the wireframe representation 168
- 5.4 Silanol groups on the surface of silica 171
- 5.5 Catalyzed Diels-Alder reaction with catalyst immobilized on amino SiO_2 surface having four possible reaction pathways. The catalyst is coordinated *syn* to the $\text{HC}=\text{CH}$ double bond that undergoes the [4+2]-cycloaddition. The dotted line indicates the partitioning into MM and QM regions 173
- 5.6 ONIOM(B3LYP/6-31G(d):UFF) optimized transition structures for the catalyzed Reaction 5-A. Relative free energies are in kcal/mol and distances are in angstroms. **TS27** = *endo* transition state involving the *s-cis* diene attack to the front face, **TS28** = *endo* transition state involving the *s-cis* diene attack to the rear face, **TS29** = *exo* transition state involving the *s-cis* diene attack to the front face and **TS30** = *exo* transition state involving the *s-cis* diene attack to the rear face 175
- 6.1 Corey's enantioselective cyanosilylation of benzaldehyde using chiral oxazaborolidinium catalyst 187
- 6.2 Modeled enantioselective cyanosilylation of benzaldehyde using chiral oxazaborolidinium catalyst **16** 187
- 6.3 B3LYP/6-31G(d) optimized transition state structure for the isomerization from $\text{Me}_3\text{POH}_3\text{SiCN}$ to $\text{Me}_3\text{POH}_3\text{SiNC}$. Color code: carbon in grey, hydrogen in white, oxygen in red, nitrogen in blue, silicon in yellow and

phosphorus in orange. Arrows indicate displacement vectors. Distances are in angstroms 188

- 6.4 Possible transition states of the cyanosilylation of aldehydes. Products have either the *R* or the *S* configuration 189
- 6.5 B3LYP/6-31G(d) optimized first transition structures for Reaction 6-B (isocyanide path). Relative free energies are in kcal/mol at 273.15 K. Distances are in angstroms. **TS31** = transition state having the *R* configuration and **TS32** = transition state having the *S* configuration. Color code: carbon in grey, hydrogen in white, oxygen in red, nitrogen in blue, silicon in yellow, boron in pink and phosphorus in orange 190
- 6.6 B3LYP/6-31G(d) optimized first transition structures for Reaction 6-B (cyanide path). Relative free energies are in kcal/mol at 273.15 K. Distances are in angstroms. **TS33** = transition state having the *R* configuration and **TS34** = transition state having the *S* configuration 191
- 6.7 B3LYP/6-31G(d) optimized intermediates for Reaction 6-B (isocyanide path). Relative free energies are in kcal/mol at 273.15 K. Distances are in angstroms. **Int1** = intermediate having the *R* configuration and **Int2** = intermediate having the *S* configuration 192
- 6.8 B3LYP/6-31G(d) optimized intermediates for Reaction 6-B (cyanide path). Relative free energies are in kcal/mol at 273.15 K. Distances are in angstroms. **Int3** = intermediate having the *R* configuration and **Int4** = intermediate having the *S* configuration 193
- 6.9 B3LYP/6-31G(d) optimized second transition structures for Reaction 6-B (isocyanide path). Relative free energies are in kcal/mol at 273.15 K. Distances are in angstroms. **TS35** = transition state having the *R* configuration and **TS36** = transition state having the *S* configuration 194
- 6.10 B3LYP/6-31G(d) optimized second transition structures for Reaction 6-B (cyanide path). Relative free energies are in kcal/mol at 273.15 K. Distances are in angstroms. **TS37** = transition state having the *R* configuration and **TS38** = transition state having the *S* configuration 195

List of Schemes

- 1.1 Layered structure of the test cluster 7
- 2.1 Typical chiral organocatalysts 46
- 2.2 The direct SCF method for the solution of the Roothaan-Hall equations for a closed-shell molecular system. The one-electron integrals need only to be evaluated once since they remain constant throughout the iterative calculation 60
- 2.3 DFT exchange-correlation energy functionals with their corresponding physical ingredients 64

List of Tables

- 1.1 HPL benchmark results using different BLAS libraries 9
- 1.2 CPU times in seconds for NWChem and GAMESS-UK calculations using different BLAS libraries 10
- 1.3 Latency numbers for MPICH, ARMCI, and GA operations 24
- 1.4 Wall times (in seconds) for NWChem direct and semi-direct algorithms using different filesystems 33
- 4.1 Natural population analysis of the charge (e) transferred from **14** to **15** along the IRC. Points are as illustrated in Figures 4.3 and 4.4 139
- 4.2 Electron populations for the valence ELF basins of the reacting complex (**14-15-16**) along the IRC. Points and carbon numbers are as illustrated in Figure 4.3 142
- 4.3 Computed Mayer bond orders, BO, for the reacting complex (**14-15-16**) along the IRC. The corresponding bond lengths (Å) are given in brackets. Points and carbon numbers are as illustrated in Figure 4.3 145
- 4.4 Computed electrostatic (and exchange) interaction energies (eV) for atomic pairs involved in the reaction between diene **14** and dienophile **15** in the presence of catalyst **16** along the IRC. Points and carbon numbers are as illustrated in Figure 4.3 146
- 4.5 Calculated deviations in bond lengths, B, (Å) and dihedral angle, D, (degrees) from the reactants for the *endo* and *exo* transition state structures of the reaction between diene **14** and dienophile **15** in the presence of catalyst **16**. Carbon numbers are as illustrated in Figure 4.3 147
- 4.6 Computed electronic chemical potential, μ , chemical hardness, η , global electrophilicity, ω , and local electrophilicity, ω_k , for **14**, **15**, and complex **15-16**. All values are in eV. Local electrophilicities are calculated for only **15** and complex **15-16**. Carbon numbers are as illustrated in Figure 4.3 149
- 5.1 Morse potential parameters for silica 163
- 6.1 B3LYP/6-31G(d) calculated activation free energies (kcal/mol) 196