COMPUTATIONAL AND MECHANISTIC STUDIES ON THE FORMATION OF CYCLIC SYSTEMS

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COMPUTATIONAL AND MECHANISTIC STUDIES ON THE FORMATION OF CYCLIC SYSTEMS

submitted by **ÖZLEM SARI** in partial fulfillment of the requirements for the degree of **Doctor of Philosophy in Department of Chemistry, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver _____
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Cihangir Tanyeli _____
Head of Department, **Chemistry**

Prof. Dr. Metin Balcı _____
Supervisor, **Chemistry Dept., METU**

Prof. Dr. Safiye Sağ Erdem
Co-Supervisor **Chemistry Dept**., **Marmara University** _____

Examining Committee Members:

Prof. Dr. Canan Ünaleroğlu _____
Chemistry Dept., Hacettepe University

Prof. Dr. Metin Balcı _____
Chemistry Dept., METU

Prof. Dr. Metin Zora _____
Chemistry Dept., METU

Doç. Dr. Yavuz Dede _____
Chemistry Dept., Gazi University

Prof. Dr. Özdemir Doğan _____
Chemistry Dept., METU

Date: June 19, 2017

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Özlem Sarı

Signature:

ABSTRACT

COMPUTATIONAL AND MECHANISTIC STUDIES ON THE FORMATION OF CYCLIC SYSTEMS

Sarı, Özlem
PhD, Department of Chemistry
Supervisor: Prof. Dr. Metin Balcı
Co-supervisor: Prof. Dr. Safiye Sağ Erdem
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Nowadays, computational chemistry has become an important tool in life sciences especially in organic chemistry. Development of various computational techniques let us to understand the nature of the organic molecules, elucidate the reaction mechanisms and design new catalysts. Computational chemistry can also provide valuable molecular insights into the geometrical and electronic properties of molecules. This study presents a combined experimental and computational analysis of various reactions and transformations; such as intramolecular cyclization, hydroamination, bromination, propargyl-allene isomerization, epoxidation and asymmetric allylic arylation.

In the first part of the study, density functional theory calculations were carried out to assess the mechanism of the formation of pyrrolotrizaepine and pyrrolotrizaepinone derivatives. In the second part, the reaction of *N*-propargyl carbaldeyde with different types of amines such as primary amines, alkyl amines and bulky amines were evaluated. In the next part, experimentally observed regioselectivities and stereoselectivities of bromination and epoxidation reactions were examined by means of theoretical calculations. After that, intramolecular cyclization reaction of *O*-propargylated pyrazole derivatives for the construction of

benzopyrazoloxazepines and benzopyrazoloxasocines were studied with density functional theory calculations. In the final part of the study, enantioselectivity observed in the rhodium catalyzed asymmetric allylic arylation reaction was theoretically investigated.

Keywords: Density functional theory, pyrrolotrizaepine, pyrrolopyrazine, asymmetric allylic arylation, benzopyrazoloxazepine.

ÖZ

HALKALI SİSTEMLERİN OLUŞUMU ÜZERİNE HESAPSAL VE MEKANİSTİK ÇALIŞMALAR

Sarı, Özlem
Doktora, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Metin Balcı
Ortak Tez Yöneticisi: Prof. Dr. Safiye Sağ Erdem
Haziran 2017, 365 sayfa

Günümüzde, hesaplamalı kimya fen bilimleri alanında özellikle organik kimyada önemli bir araç olmaya başlamıştır. Çok sayıda hesaplamalı tekniklerin gelişmesi, organik moleküllerin doğasını anlamamıza, reaksiyon mekanizmalarını aydınlatmamıza ve yeni katalizörler tasarlanmamıza izin vermiştir. Hesaplamalı kimya aynı zamanda moleküllerin geometrik ve elektronik özelliklerine de moleküler kavrayış sağlar. Bu çalışma, molekül içi halkalaşma, hidroaminasyon, brominasyon, propagil-allen izomerizasyonu, epoksidasyon ve asimetrik alilik arilasyon gibi birçok reaksiyon ve dönüşümün deneysel ve hesapsal olarak analizini sunmaktadır.

Çalışmanın ilk bölümünde, yoğunluk fonksiyoneli teorisi hesaplamaları, pirolotriazepin ve pirolotriazepinon türevlerinin oluşum mekanizmalarını değerlendirmek için uygulandı. İkinci bölümde, *N*-propargil karbaldehitin birincil aminler, alkil aminler ve hacimli aminler gibi değişik türde aminlerle verdiği reaksiyonları değerlendirildi. Bir sonraki bölümde, brominasyon ve epoksidasyon reaksiyonlarında deneysel olarak gözlenen yer seçicilik ve stereoseçimlilik teorik hesaplamalar yardımıyla incelendi. Bundan sonra, *O*-propargillenmiş pirazol türevlerinin molekül içi halkalaşma reaksiyonu ile benzopirazolokzazepin ve

benzopirazolokzazosinlerin tasarımı, yoğunluk fonksiyoneli teorisi hesaplamaları ile çalışıldı. Çalışmanın son bölümünde, rodyum katalizli asimetrik alilik arilasyon reaksiyonunda gözlenen enantiyoseçicilik teorik olarak incelendi.

Anahtar Kelimeler: Yoğunluk fonksiyoneli teorisi, pirolotriazepin, pirolopirazin, asimetrik alilik arilasyon, benzopirazolokzazepin

To my family…

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LIST OF ABBREVIATIONS

ATR	Attenuated total reflectance
AAA	Asymmetric allylic alkylation
B3LYP	Becke-3-parameter functional and Lee, Yang, Parr correlation functional
Boc	*tert*-Butyloxycarbonyl
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
CNS	Central nervous system
CCK_1	Cholecystokinin A receptor
DCC	*N*, *N*′-Dicyclohexylcarbodiimide
DFT	Density functional theory
DIBAL	Diisobutylaluminium hydride
DIPA	Diisopropylamine
DKR	Dynamic Kinetic Resolution
DMDO	Dimethyldioxirane
DMF	Dimethylformamide
DMP	2,2 Dimethoxypropane
DYKAT	Dynamic kinetic asymmetric transformation
IRC	Intrinsic Reaction Coordinate
KR	Kinetic Resolution
m-CPBA	*m*-Chloroperoxybenzoic acid
NBO	Natural bond orbital
PC	Product complex
PCM	Polarizable continuum model
PPA	Polyphosphoric acid
RC	Reactant complex
RHF	Restricted Hartree–Fock

SMD	Solvation model density
TBAF	Tetra(n-butyl)ammonium fluoride
TBAC	Tetrabutylammonium cyanoborohydride
TS	Transition state
ϕ	Pyramidalization angle

CHAPTER 1

DESIGN AND SYNTHESIS OF PYRROLOTRIAZEPINE DERIVATIVES: AN EXPERIMENTAL AND COMPUTATIONAL STUDY

1.1 Introduction

Nitrogen-containing seven-membered heterocycles constitute an important class among organic compounds and are highly useful in synthetic chemistry due to their broad range of pharmacological activities. Thus, construction of these molecules has long been a topic of interest and investigation.[1a-d]

1.1.1 Triazepines

Triazepines are seven-membered heterocyclic compounds containing three nitrogen atoms (Figure 1).[1e-h]

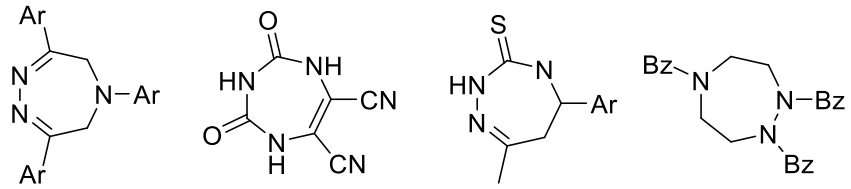
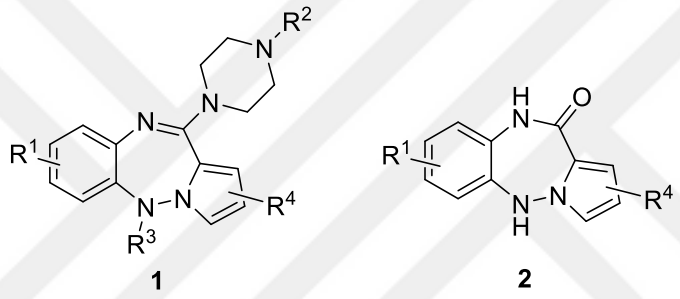


Figure 1. Examples of triazepine derivatives

Triazepine derivatives have a wide range of biological activities including antibacterial, psychotropic, antiviral, antisecretory, anticancer, cholecystokinin (CCK_2) receptor antagonist, analgesic, and anti-inflammatory activities.[2]

Benzotriazepines and benzotrizapinones, a class of triazepine derivatives, have received much attention from synthetic organic chemists because of their CNS (central nervous system) activity and their usage as psychoactive agents.[3] Fischer *et al.*[4] reported that structures **1** and **2** can be utilized as neuroleptic agents to treat psychotic disturbances, like schizophrenia (Figure 2).



1 **2**

Figure 2. Biologically active triazepine derivatives

Synthesis of benzotriazepinone derivatives **3-5** were reported and subjected to ptosis test using clozapine as a reference drug to evaluate their antipsychotic activity (Figure 3).[5] It was found that benzotriazepinones **3** and **5** showed the same antipsychotic activity as the reference drug clozapine, however; they leaded to complete ptosis in mice. On the other hand, benzotriazepinone **4** also showed the same antipsychotic activity as clozapine but with lesser side effects.[5]

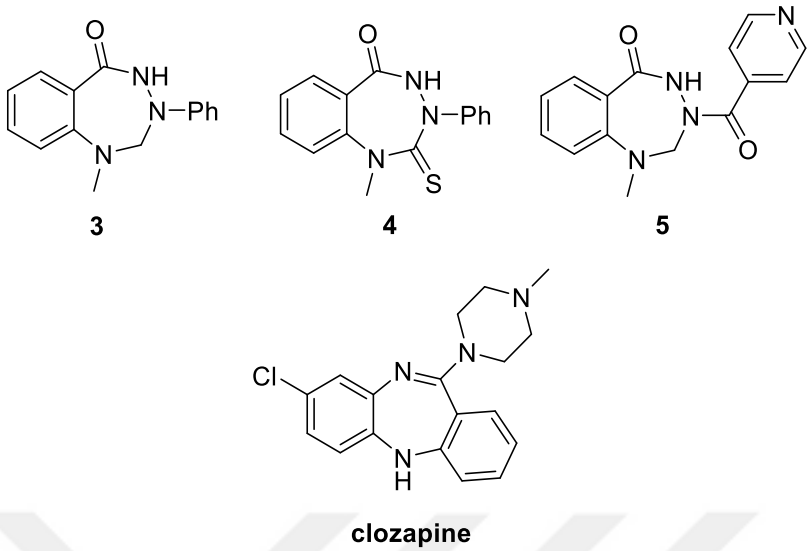
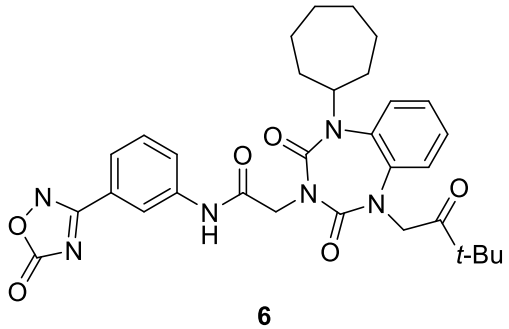


Figure 3. Structures of benzotriazepinones **3**–**5** and clozapine

Compound **6** is a CCK_2 receptor antagonist that displays better selectivity than CCK_1 receptors (Figure 4).[6] Therefore, the development of reliable and efficient methods to synthesize triazepines and triazepinones is of great value.

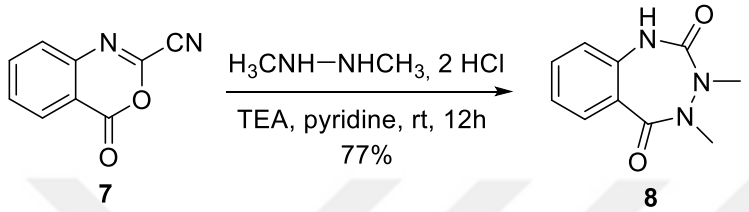


6

Figure 4. Structure of triazepine derivative **6**

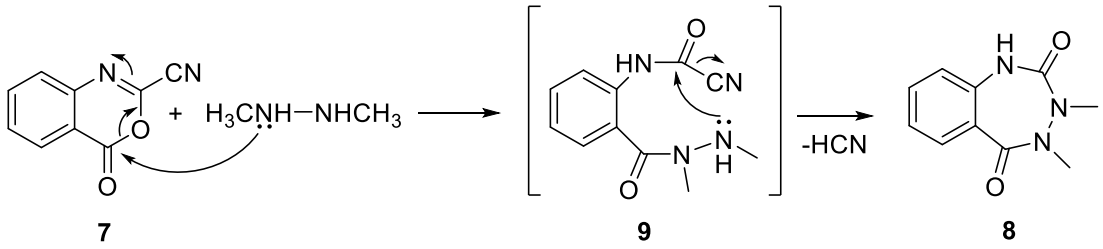
1.1.1.1 Synthesis of Triazepine and Triazepinone Derivatives

Besson *et al.*[7] reported the one-pot synthesis of 1,3,4-benzotriazepine-2,5-dione (**8**) by the reaction of benzoxazinone **7** with 1,2-dimethylhydrazine dihydrochloride (Scheme 1).



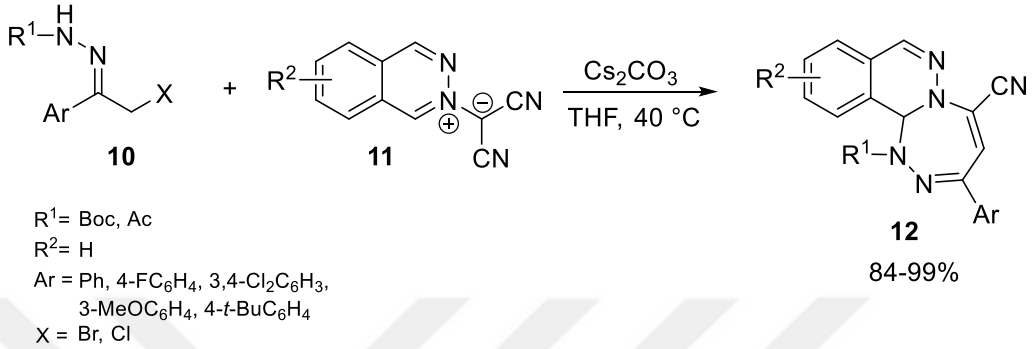
Scheme 1. Synthesis of 1,3,4-benzotriazepine-2,5-dione (**8**)

Proposed mechanism is illustrated in Scheme 2. The reaction started with the nucleophilic attack of 1,2-dimethylhydrazine nitrogen atom to the carbonyl group of the benzoxazinone. The following ring opening gave the intermediate **9**. Cyclization and elimination of hydrogen cyanide afforded the corresponding product **8**.[7]



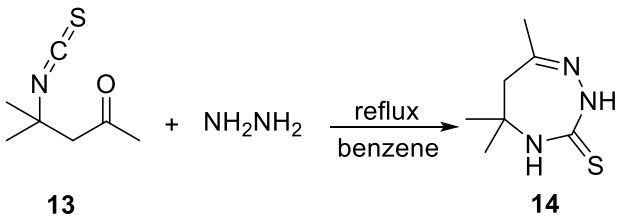
Scheme 2. Proposed mechanism for the formation of 1,3,4-benzotriazepine-2,5-dione (**8**)

In 2016, Guo and co-workers reported a catalyst-free [4 + 3] cycloaddition reaction between phthalazinium dicyanomethanides **11** and in situ formed azoalkenes **10** yielding various 1,2,4-triazepine derivatives **12** (Scheme 3).[2]



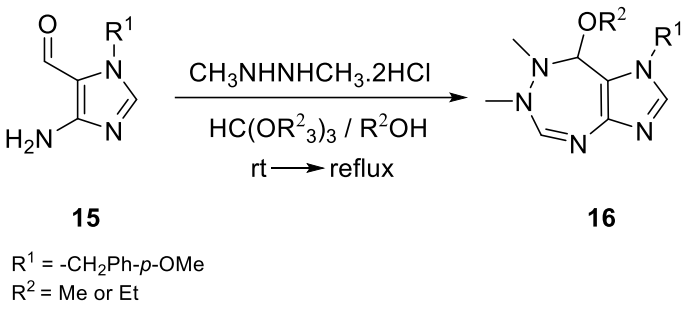
Scheme 3. Synthesis of 1,2,4-triazepine derivatives

Synthesis of 5,5,7-trimethyl-triazepine-3-thione (**14**) was described by Zigeuner *et. al.* Treatment of 4-methyl-4-isothiocyanatopentan-2-one (**13**) with hydrazine hydrate in benzene yielded the corresponding triazepine **14** (Scheme 4).[8]



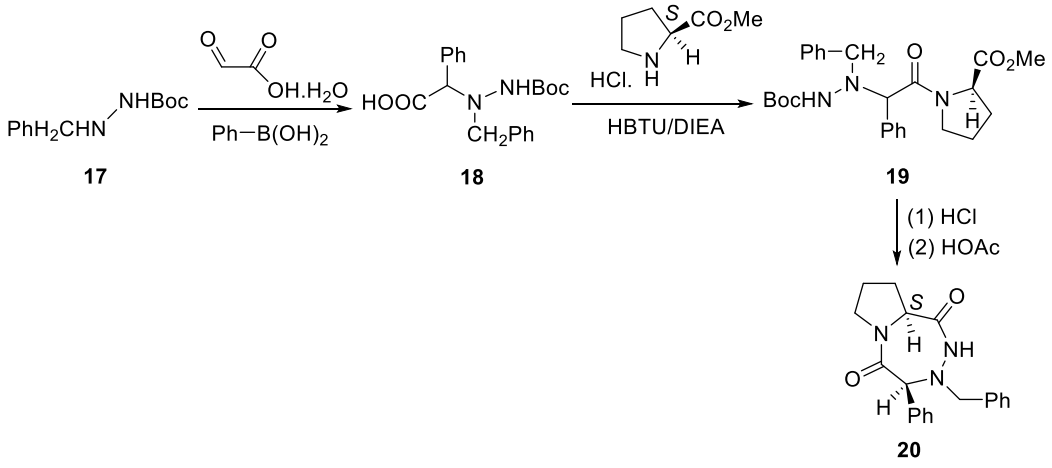
Scheme 4. Synthesis of 5,5,7-trimethyl-triazepine-3-thione (**14**)

Imidazo-trizaepine derivatives were synthesized by Hosmane *et al.*[9] in 2004 starting from the reaction of **15** with 1,2-dimethylhydrazine dihydrochloride and trimethyl or triethyl orthoformate (Scheme 5).



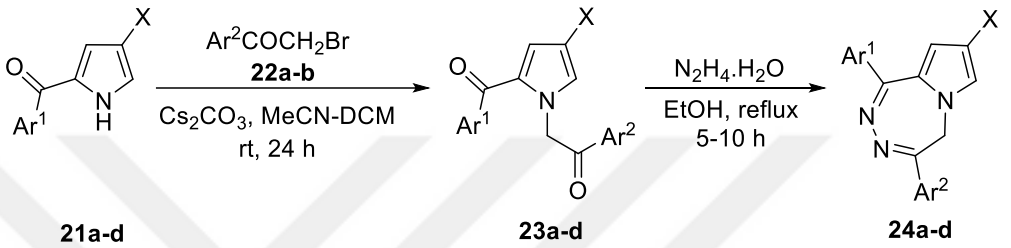
Scheme 5. Synthesis of imidazo-trizaepine derivatives

Short and efficient synthesis of 4,5-bridged 1,2,5-triazepine-3,6-dione **20** was demonstrated by Neogi *et al.*[10] Hydrazine derivative **17** was subjected to Petasis multicomponent condensation reaction with glyoxylic acid monohydrate and boronic acid. The following coupling reaction with *L*-proline methyl ester hydrochloride and deprotection of the Boc (*tert*-butyloxycarbonyl) group gave the compound **19** which then cyclized in presence of acetic acid to give the corresponding product **20** (Scheme 6).



Scheme 6. Synthesis of 4,5-bridged 1,2,5-triazepine-3,6-dione **20**

In 2016, Földesi *et al.*[11] developed a new synthetic method for the preparation of pyrrolotriazepine derivatives **24a-d** (Scheme 7). Starting material **21a-d** was treated with bromo-phenylethanone derivatives **22a** and **22b** in presence of Cs_2CO_3 to obtain 1,5-diketones (**23a–d**), which were then reacted with hydrazine monohydrate at reflux temperature of ethanol to give the target pyrrolotriazepine derivatives **24a-d**.

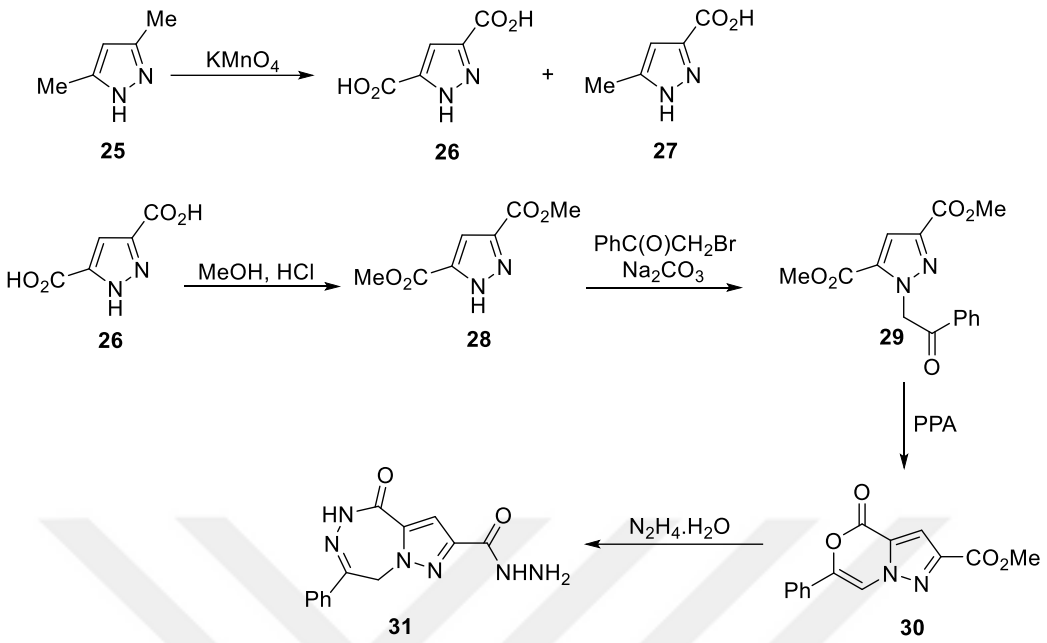


21a-d **23a-d** **24a-d**

23-24	X	Ar^1	Ar^2	Yield of **23** (%)	Yield of **24** (%)
a	H	C_6H_5	C_6H_5	83	61
b	H	3-ClC_6H_4	C_6H_5	87	67
c	H	4-FC_6H_4	4-MeC_6H_4	89	60
d	Br	C_6H_5	C_6H_5	79	64

Scheme 7. Synthesis of pyrrolotriazepine derivative **24a-d**

In 2016, synthesis of pyrazolotriazepine derivative **31** was reported (Scheme 8). Oxidation of 3,5-dimethylpyrazole (**25)** gave a mixture of compounds **26** and **27**. Compound **26** was submitted to esterification reaction to give **28,** which subsequently subjected to the alkylation reaction to furnish the compound **29**. Treatment of **29** with polyphosphoric acid (PPA) afforded oxazine derivative **30**. Finally, compound **30** was reacted with hydrazine monohydrate at reflux temperature of isopropyl alcohol to give the target pyrazolotriazepine derivative **31** in 57% yield.[12]



Scheme 8. Synthesis of pyrazolotriazepine derivative **31**

1.1.2 Allenes

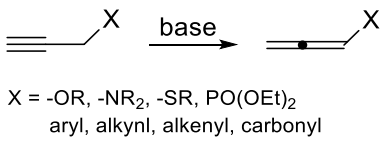
Allenes have attracted much attention from synthetic organic chemists because of the fascinating features of the cumulenic double bond system.[13] The reactivity of allenes compared to those of alkenes and alkynes are very different.[14] Since many allenes are axially chiral, they can show synthetic potential in regio- and stereoselective transformations and the acidity of their hydrogen atoms allows easy functionalization. Allenic structures also play an important role in hydrocarbon chemistry, and extremely bent allenes are being studied due to their interesting electronic nature.[15] In addition, these species can be found in many natural compounds and pharmacologically active structures.[16]

1.1.2.1 Synthesis of Allenes

Synthetic methods for the preparation of allenes have been intensively studied in the past decades. These methods may include classical reaction types such as; addition, elimination, substitution and rearrangement as well as new synthetic strategies.[16] We have mainly focused on the formation of allenes via isomerization of alkynes.

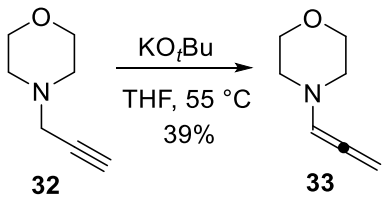
1.1.2.1.1 Propargyl-allene Isomerization

The base-catalyzed propargyl-allene isomerization is one of the earliest methods for the formation of allenes. Strong bases like alkali metal amides are used for the simple alkynes at high temperature. In order to facilitate the isomerization, weaker bases such as NaOH or TBAF (tetra-n-butyl-ammonium fluoride) are found to be sufficient for the alkynes having activated *a*-hydrogen. The activation groups may also contain alkene, alkyne, arene or carbonyl group, or groups including nitrogen, oxygen, sulfur, or phosphorus atom (Scheme 9).[16] We have mainly focused on the formation of allenes via isomerization of *N*-substituted alkynes.



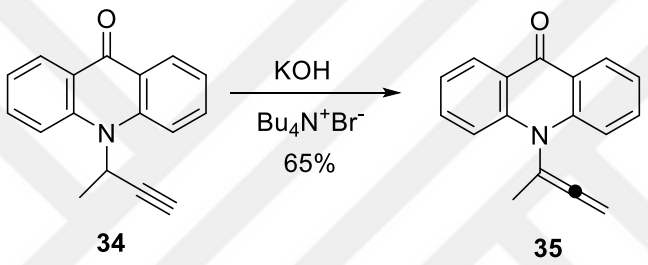
Scheme 9. Isomerization of alkynes to corresponding allenes

Alkyl-substituted propargylic amine **32** was treated with KO*t*Bu to give the isomerization product **33** in a low yield (Scheme 10).[17]



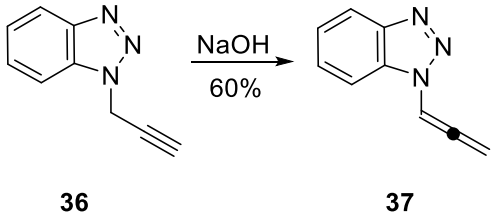
Scheme 10. Isomerization of *N*-substituted alkyne **32** to allene **33**

Arylamine with a propargyl group **34** was reacted with KOH in presence of a phase transfer catalyst to lead allenic structure **35** in 65% yield (Scheme 11).[18]



Scheme 11. Isomerization of *N*-substituted alkyne **34** to allene **35**

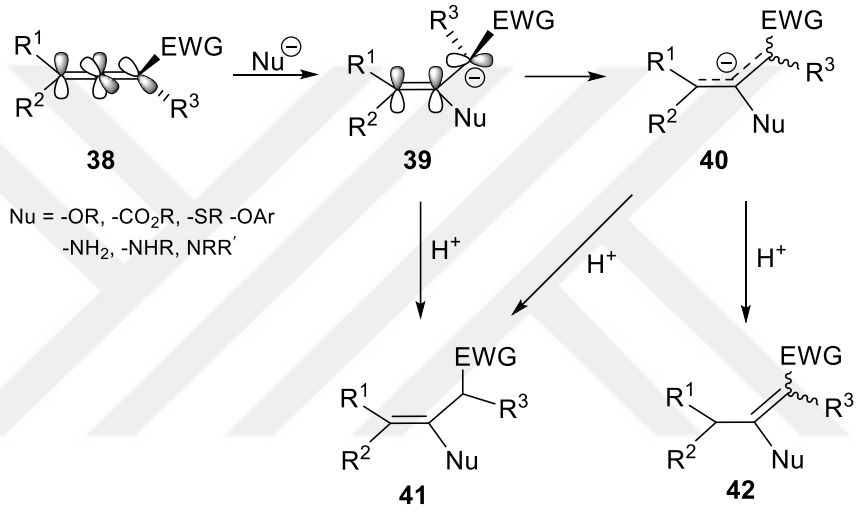
Nitrogen atom may also be the part of the aromatic ring in heteroaromatic systems for the isomerization reactions shown in Scheme 12.[19]



Scheme 12. Isomerization of *N*-substituted alkyne **36** to allene **37**

1.1.2.2 Nucleophilic Addition of Allenes

The nucleophilic addition reaction of allenes having an electron withdrawing group afforded such products **41** and **42** shown in Scheme 13. For example, using hydrogen halides as a nucleophile leads to kinetically favored product **41** whereas, nucleophiles such as lithium aluminum hydride-aluminum trichloride or azide yield to thermodynamically favored product **42**.[19]

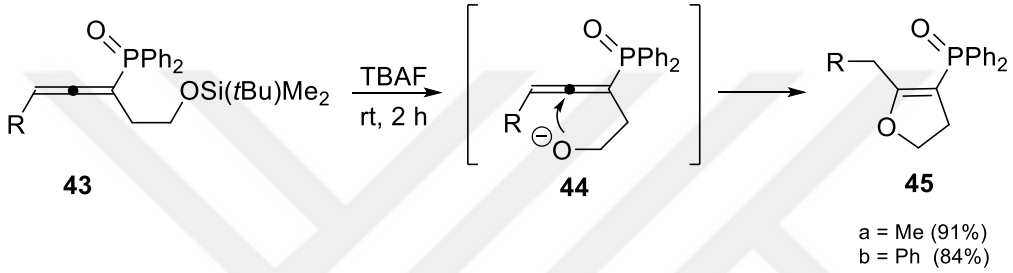


Scheme 13. Nucleophilic addition reaction of electron deficient allenes

According to the proposed mechanism, nucleophilic attack on the central carbon atom of the allene gave firstly the intermediate **39**. This intermediate needs a 90° rotation of the C-C single bond in order to form the allylic carbanion **40**, which can lead to both products **41** and **42**. On the other hand, intermediate **39** can only form the product **41** by proton transfer.[19]

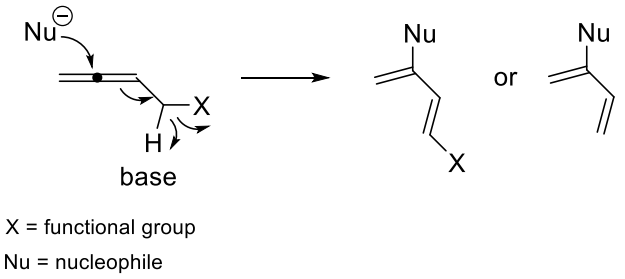
1.1.2.2.1 Nucleophilic Addition of Allenes Including Ring Closure

Intramolecular cyclization of allenes have previously been used for the construction of heterocyclic compounds. For instance, silyl ether derivatives were reacted with tetrabutylammonium fluoride (TBAF) to yield intermediate **44**, the subsequent intramolecular cyclization via a nucleophilic attack of the alkoxide group afforded to dihydrofurans **45a** and **45b** (Scheme 14).[20]



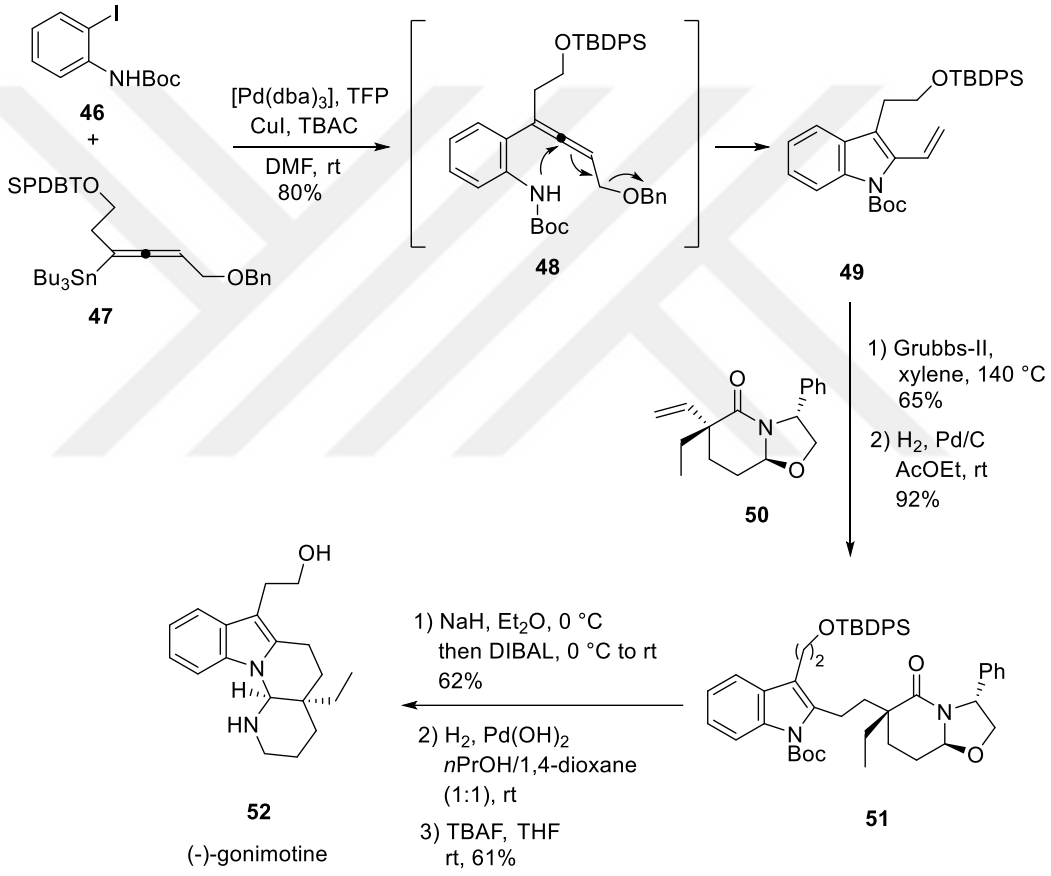
Scheme 14. Synthesis of dihydrofurans via intramolecular cyclization of allenes

It has been proposed that an addition/elimination or isomerization of allenic skeleton can take place via bases, acids, and nucleophiles to give 1,3-conjugated dienes. Thus, an existing nucleophile may also lead to the ring closure after building up the allene skeleton (Scheme 15).[21]



Scheme 15. Addition/elimination or isomerization of the allenic skeleton to 1,3-dienes.

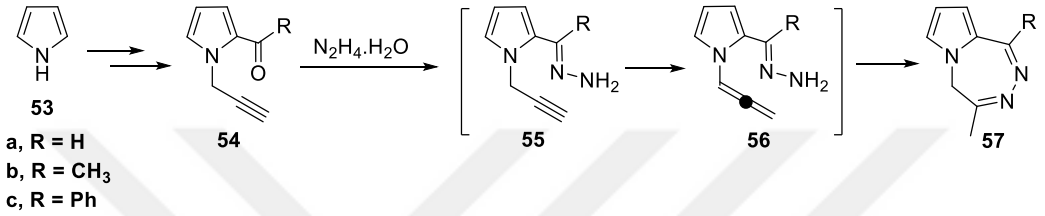
A stereoselective synthesis of (-)-goniomitine was achieved by utilizing an intramolecular cyclization of allenes. Stille coupling reaction of an *N*-acyl-2-iodoaniline (**46**) with allene derivative **47** was applied to generate precursor **48**. After several steps shown in Scheme 16, the natural product **52** was successfully synthesized.[21]



Scheme 16. Total synthesis of (-)-goniomitine **52** by intramolecular allene cyclization. TBAC = tetrabutylammonium cyanoborohydride

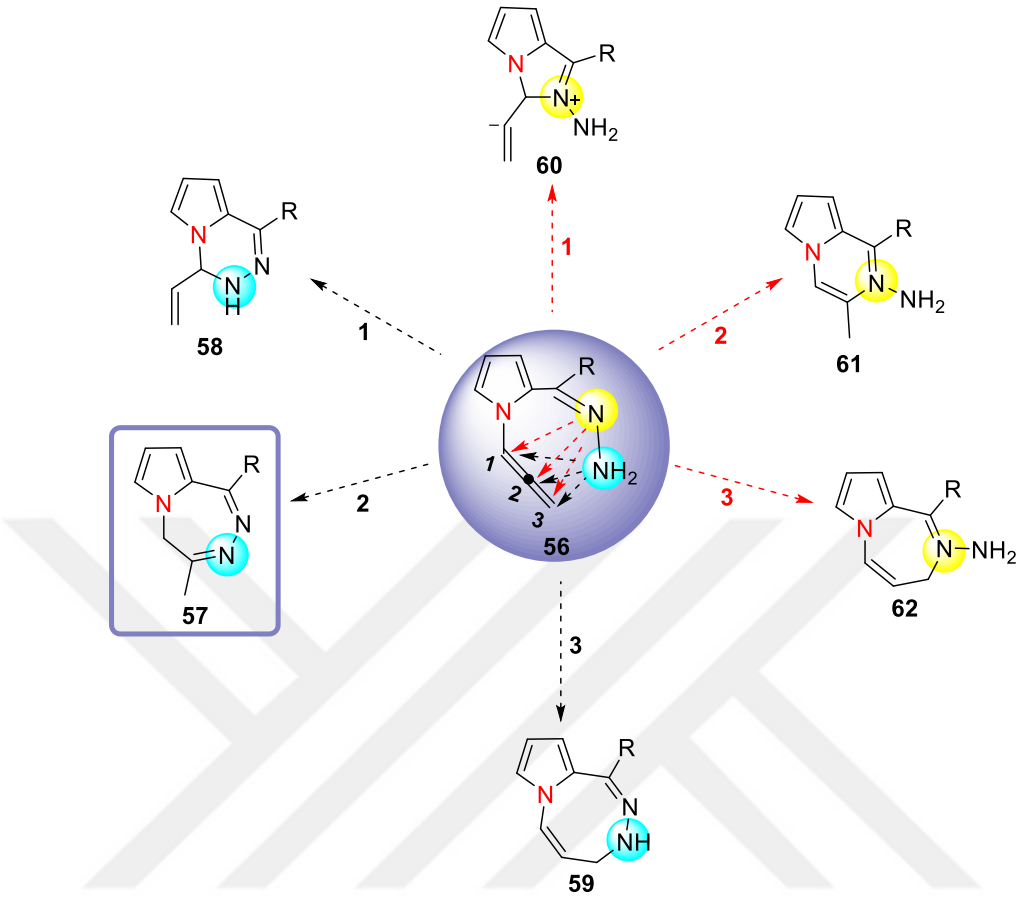
1.1.3 Objective of the Study

Our objective was to synthesize pyrolotrizepine derivatives **57a-c** via metal free cyclization of pyrrole hydrazone derivatives **55** and **56**, formed by the reaction of acylpyrroles **54** with hydrazine monohydrate (Scheme 17). Base catalyzed propargyl-allene isomerization was proposed during the cyclization.



Scheme 17. Synthesis of pyrrolotriazepine derivatives **56a-c**

Six possible nucleophilic attacks to the carbon atoms of allene unit were possible as depicted in Scheme 18. Therefore, six cyclization products can be obtained theoretically. However, only pyrrolotriazepine derivatives **57a-c** was observed. Our goal was to apply theoretical calculations to enlighten the mechanism for the formation of triazepine derivatives **57a-c**. DFT (density functional theory) calculations have been carried out. Comparison of computational and experimental study will be helpful in rationalizing the mechanism.

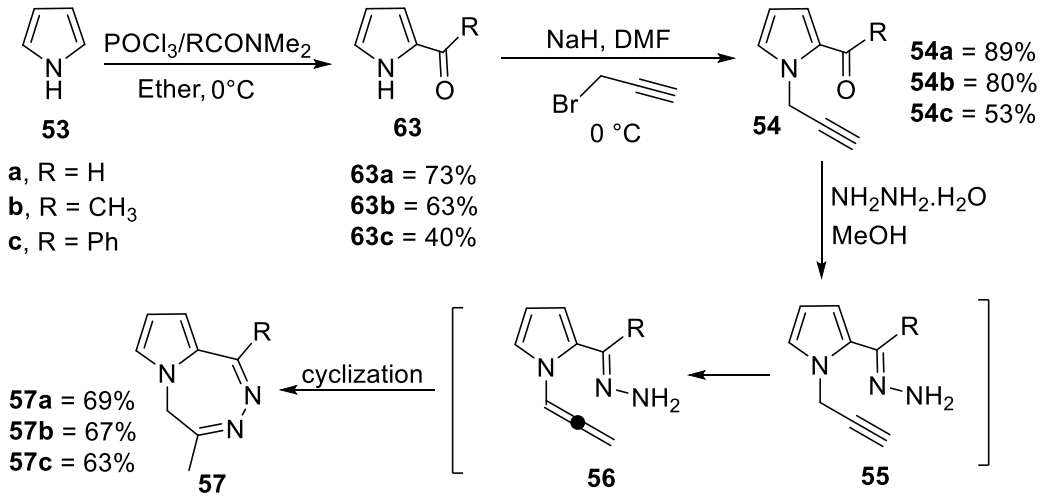


Scheme 18. Possible cyclization products

1.2 Results and Discussion

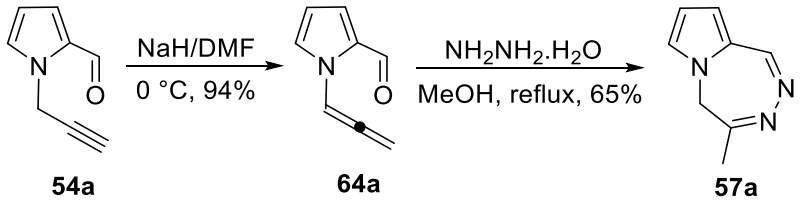
1.2.1 Synthesis of Pyrrole-Fused Triazepines

For the synthesis of triazepine derivatives, pyrrole (**53**) was subjected to Vilsmeier reaction to give the pyrrole carbonyl compounds **63a-c**. Treatment of **63a-c** with propargyl bromide in presence of NaH yielded the alkyne derivatives **54a-c**. Heating of **54a-c** with hydrazine monohydrate at reflux temperature of methanol afforded the target cyclization products **57a-c** (Scheme 19).[1b]



Scheme 19. Synthesis of pyrrole fused triazepines **57a-c**

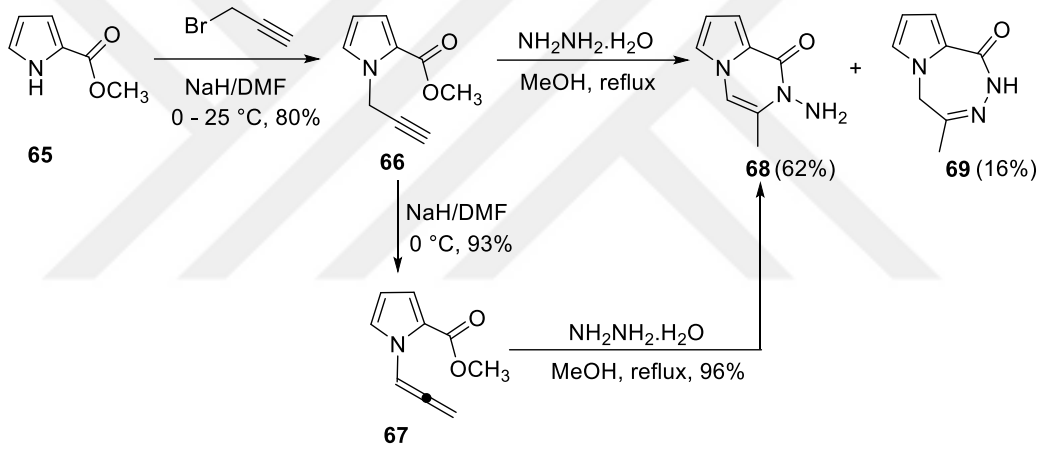
During the cyclization, propargyl-allene isomerization was proposed as shown in Scheme 19. To support our proposal, *N*-allene carbaldeyhde **64a** was synthesized independently by our group and subjected to the intramolecular cyclization reaction under the same reaction conditions (Scheme 20). Same cyclization product was observed in 65% yield, which supports that the mechanism proceeds through the allenic structure **64a** as an intermediate.[1b]



Scheme 20. Base catalyzed isomerization of **54a** to allene **64a** and its reaction with hydrazine monohydrate

1.2.2 Synthesis of Pyrrole-Fused Triazepinones and Pyrazinones

After synthesis of the pyrrolotriazepine derivatives, we turned our attention to the construction of pyrrolotriazepinone derivatives by intramolecular cyclization of propargyl ester **66** with hydrazine monohydrate. First, pyrrole carboxylate **65** and propargyl bromide were reacted to generate the key compound **66**. The cyclization reaction of propargyl ester **66** was carried out with hydrazine monohydrate. However, the expected triazepinone derivative **69** was obtained only in 16% yield. Interestingly, pyrrolopyrazinone derivative **68** was observed as the major product in 62% yield (Scheme 21).[1b]



Scheme 21. Reaction of propargyl ester **56** with hydrazine monohydrate

Finally, propargyl ester **66** was converted to corresponding allene **67** in order to see whether the mechanism proceeds through an allenic intermediate or not. Reaction of compound **66** with NaH in DMF yielded to the allene **67**, which then submitted to the cyclization reaction with hydrazine monohydrate. Again, pyrrolopyrazinone derivative **68** was obtained in 96% yield (Scheme 21). It should be also noted that, intramolecular cyclization involves the nucleophilic attack of the less reactive nitrogen atom onto the central carbon of allene.[1b]

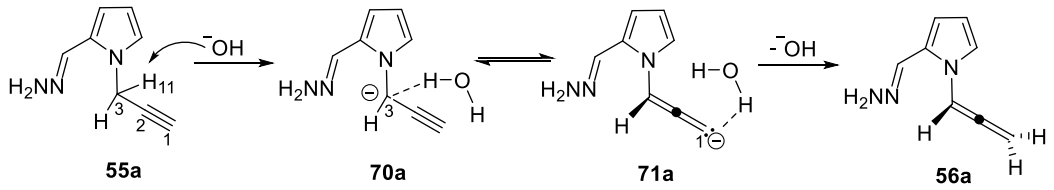
1.2.3 Theoretical Calculations for the Formation of Triazepine, Triazepinone and Pyrazinone Derivatives

1.2.3.1 Propargyl-Allene Isomerizaton

Prototropic isomerization reactions often include two-stage transformations involving the formation of carbanions as an intermediate. In the unsubstituted MeC≡CH, it is clear that the most acidic proton is located at the sp-hybridized carbon atom. Therefore, a base is expected to abstract a proton from this carbon atom. However, proton abstraction from the sp^3-hybridized carbon atom can be also observed in the case of a formation of relative stable anion.[22] In the light of these observations, we first explored the propargyl-allene isomerization from **55a** to **56a**.

It has been shown that, in heteropropargyl systems, propargyl isomer is less stable than the corresponding allene isomer. For example, alkylpropargyl ethers can easily undergo base catalyzed isomerization to alkyl allenyl ethers.[23] Therefore, we first compared the energies of **55a** and **56a** by using DFT calculations. According to the results, allene isomer **56a** is calculated to be 8.43 (gas phase) and 7.43 kcal/mol (methanol) more stable than the propargyl isomer **55a**.

Vitkoskaya *et al*.[22] suggested a mechanism for the propargyl-allene isomerization. According to their proposed mechanism, hydroxide ion abstracts a proton from the sp^3-hybridized carbon atom. We also proposed that hydroxide ion, which can be formed by the reaction of hydrazine with water, abstracts one of the methylenic proton (H11) (Scheme 22). Carbanion **70a** can be stabilized by intermolecular hydrogen bonding interaction and also the inductive effect of pyrrole nitrogen as well as conjugation with propargyl group. In the next step, carbanion **71a** abstracts a proton from water.[1b]



Scheme 22. Proposed mechanism for the propargyl-allene isomerization

We have carried out quantum mechanical calculations to characterize transition states for this process. The potential energy surface for the propargyl-allene isomerization is displayed in Figure 5. Calculations were performed at PCM[24a,b]/RHF/6-31+G(d)//RHF/6-31+G(d) level in methanol, since B3LYP[25a-c] could not optimize the proposed transition states.[1b]

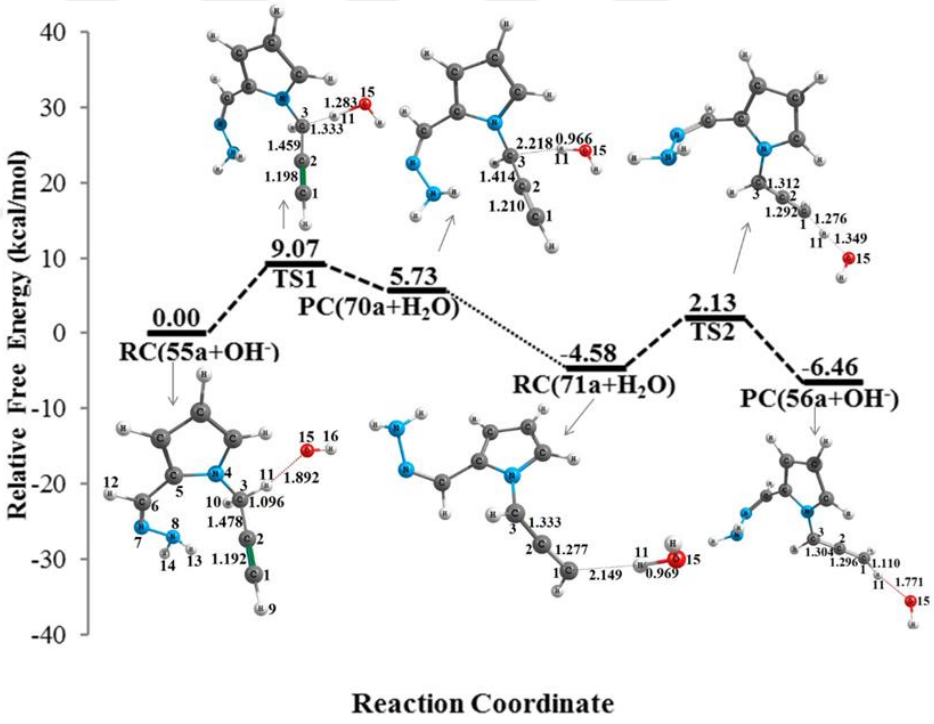
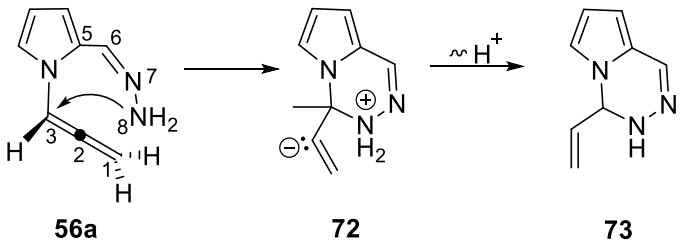


Figure 5. Potential energy surface for the propargyl-allene isomerization at PCM/RHF/6-31+G(d)// RHF/6-31+G(d) level in methanol. Distances are given in angstroms.

As can be seen from Figure 5, hydroxide ion abstracts a proton attached to the sp^3-hybridized carbon atom. The C3-H11 bond is 1.096 Å for reactant complex **RC(55a+OH$^-$)** and is elongated in **TS1** (1.333 Å). The Gibbs free energy of activation was found to be 9.07 kcal/mol in methanol. **RC(70a+OH$^-$)** is calculated to be more stable than **PC(71a+OH$^-$)** because of the intermolecular interactions of water with different carbon atoms. Second step includes the abstraction of H11 by carbanion **71a**, which takes place through **TS2** and has a low free energy of activation of 6.71 kcal/mol. As a result, free energy change of overall reaction is calculated to be -6.46 kcal/mol, which indicates a slightly exergonic reaction. The small activation barriers in Figure 5 show that our initial computational results are consistent with the experimental observations. [1b]

1.2.3.2 Formation of 73 from 56a

There are three electrophilic centers in **56a**, namely, C1, C2 and C3. Calculated Mulliken charges of C1, C2 and C3 in **56a** (-0.60, 0.22, and -0.16 at B3LYP/6-31+G(d,p)) showed that C2 is much more electrophilic than C1 and C3. Since, the most electrophilic carbon is the central carbon atom, we assume that nucleophiles exclusively attack this carbon atom of allene moiety. On the other hand, nucleophilic attack of N8 on C3 would form a stable six-membered structure **73** (Scheme 23). Therefore, we also consider this mechanism. The potential energy surface is given in Figure 6. First step needs an activation energy of 51.82 kcal/mol. Solvent methanol decreases the barrier to 41.78 kcal/mol, which is still quite high. Since, proton transfer step has also high barrier (39.23 kcal/mol in methanol), we assume that the reaction is not facile.[1b]



Scheme 23. Proposed mechanism for the formation of **73**

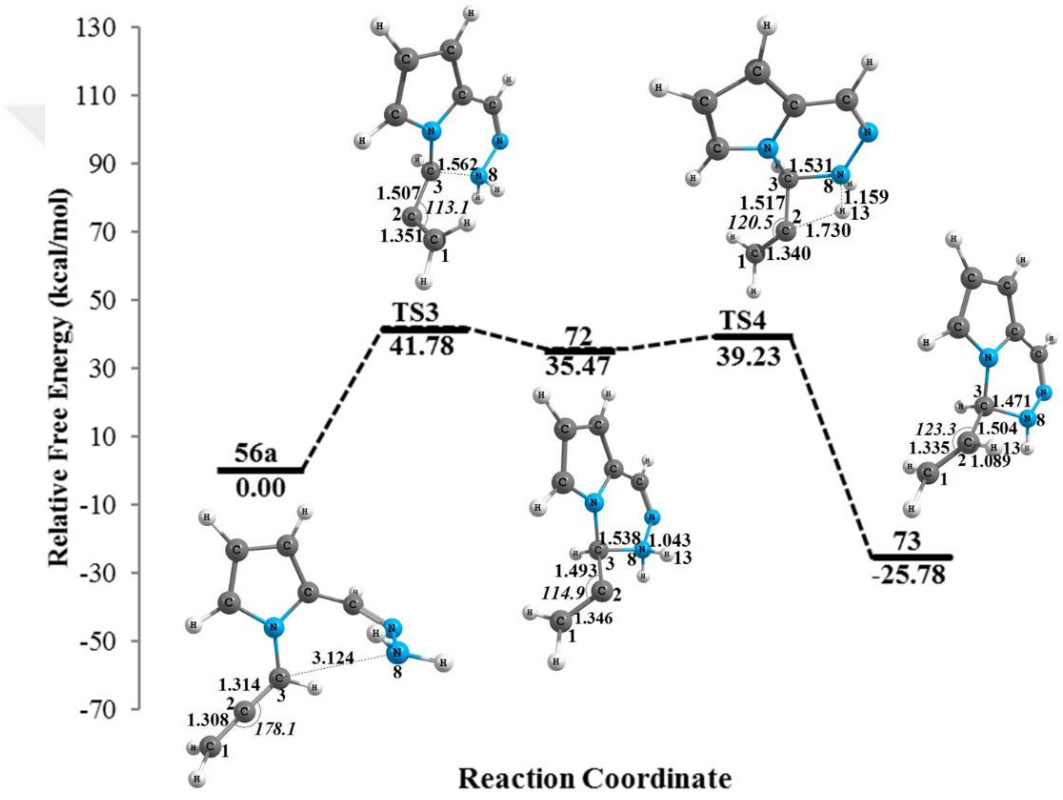
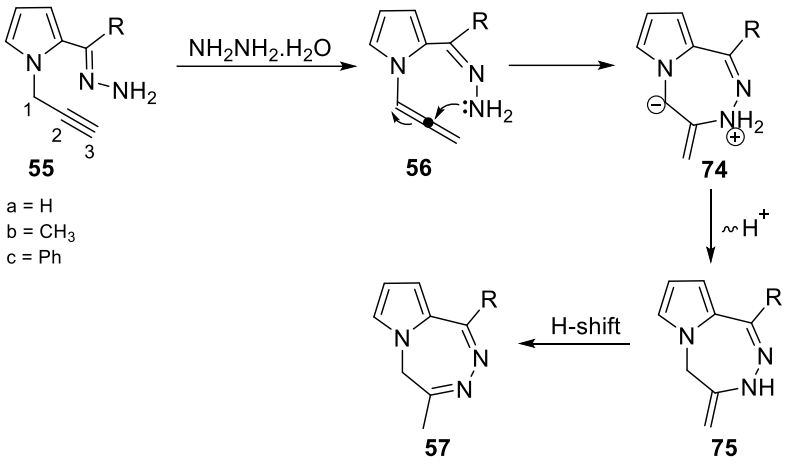


Figure 6. Potential energy surface for the formation of **73** at PCM/B3LYP/6-31+G(d,p)// B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms; angles are given in degrees.

1.2.3.3 Formation of 57a from 55a

As we mentioned above, alkyne derivative **55a** first undergoes an isomerization reaction under the basic conditions to generate the corresponding allene **56a** (Scheme 24). After the formation of allene, nucleophilic attack of N8 on the most electrophilic carbon C2 take place via **TS5** with an activation energy of 30.46 (in gas phase) and 28.65 kcal/mol in methanol. The potential energy surface is illustrated in Figure 7. Bond distance C2−N8 is calculated as 4.226, 1.788, and 1.520 Å in structures **56a**, **TS5**, and **74a**, respectively. Next step involves the transfer of a proton in **74a** from N8 to C3, resulting in the formation of intermediate **75a** through **TS6**. Explicit usage of solvent molecules in the proton transfer steps plays a crucial role because the solvent serves as the proton conduit. This step was investigated with the assistance of methanol; thus, the reaction proceeds through six-membered transition state instead of unfavorable four-membered transition state. Final step involves methanol-assisted 1,3-H shift from N8 to C1 via **TS7**. Overall, cyclization step (**TS5**) seems to be the rate-determining step when the activation barrier is evaluated. This mechanism can be consired as a plausible mechanism since it has reasonable activation energies and supports all experimental findings.[1b]



Scheme 24. Mechanism for the formation of pyrrolotriazepine derivatives **57a-c**

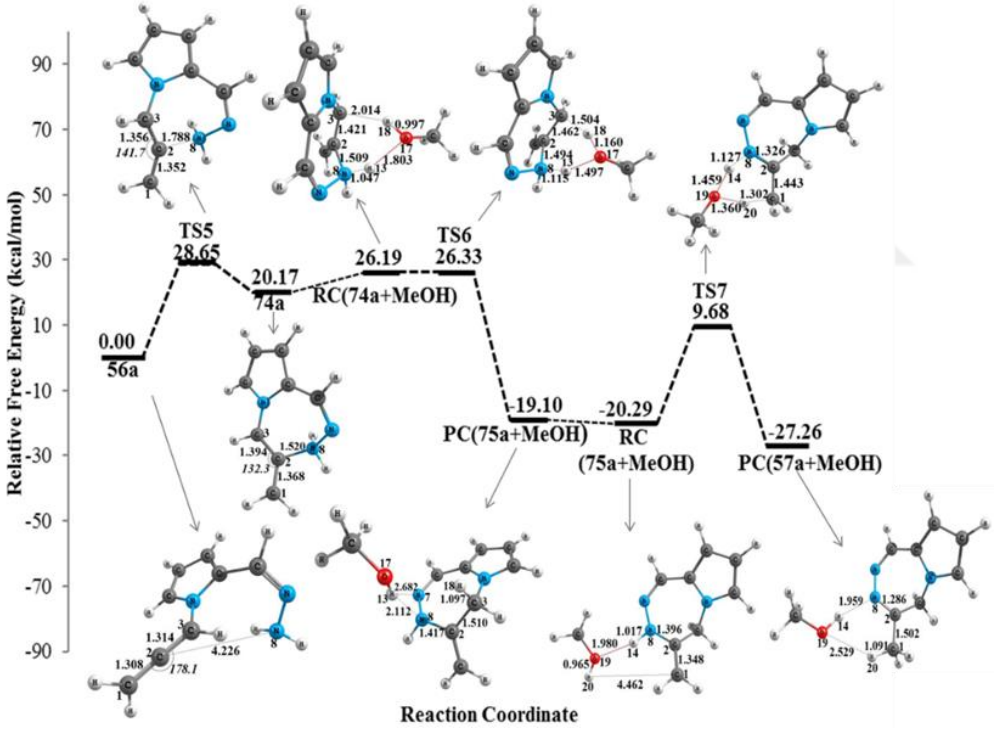


Figure 7. Potential energy surface for the formation of **57a** at PCM/B3LYP/6-31+G(d,p)// B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms; angles are given in degrees.

1.2.3.4 Formation of 69 from 78

After examining the formation of pyrrolotriazepine **57a**, we focused on the formation of the pyrrolotriazepinone **69** and pyrrolopyrazinone **68** starting from hydrazide **76** (Figure 8). Mulliken charges of C1, C2 and C3 (-0.69, 0.31, and -0.06) were calculated at B3LYP/6-31+G(d,p) level in **76**. It was found that C2 carbon is much more electrophilic than C1 and C3. Since C1 is less electrophilic than C2 and C3, nucleophilic attack of N8 on C1 that give rise to eight-membered product, was not taken into account. However, the nucleophilic attack of N8 on the C3 was considered due to the formation of a stable six-membered ring product **78**. The first step involving cyclization from **76** to **77** was found to have an activation energy of 46.26 kcal/mol in methanol (Figure 9). Next step includes the proton transfer from N8 to C2 via **TS9**. **TS9** is calculated to be 3.23 kcal/mol less stable than **TS8**. Therefore, the path from **76** to **78** is not plausible, since both transition states **TS8** and **TS9** require high activation barriers.[1b]

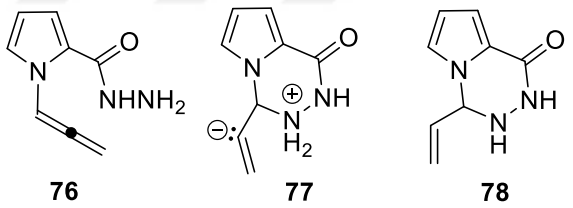


Figure 8. Structures of **76**–**78**

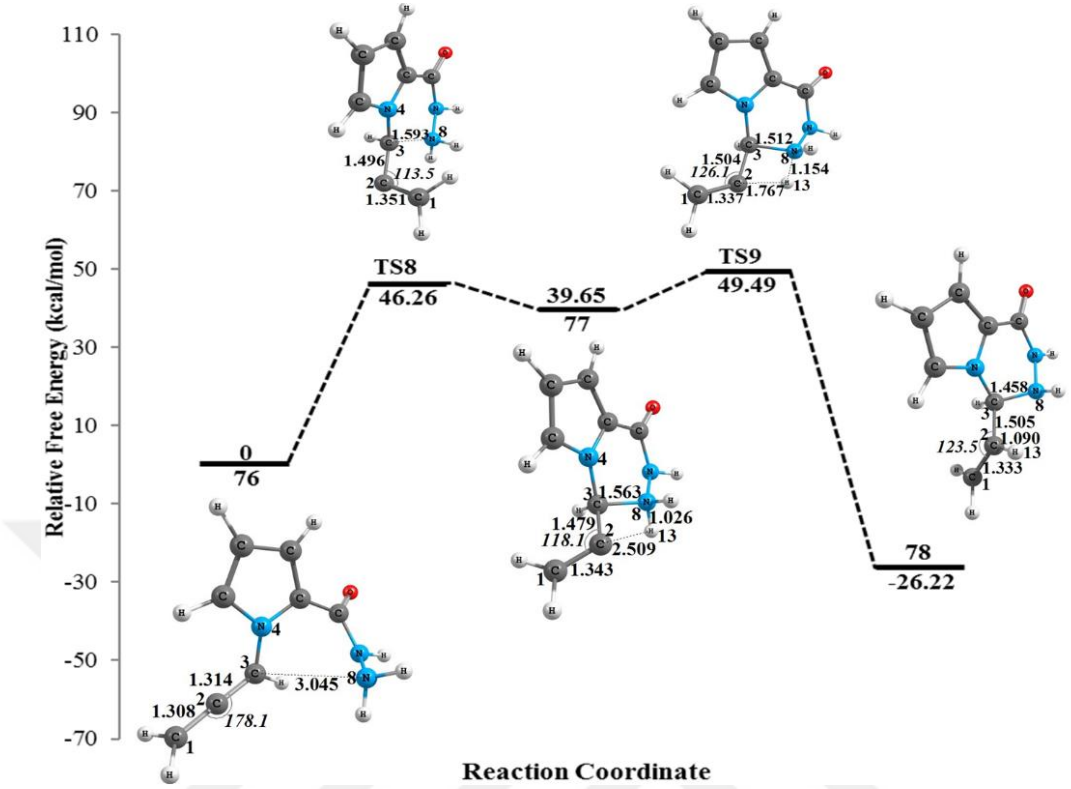


Figure 9. Potential energy surface for the formation of **78** at PCM/B3LYP/6-31+G(d,p)// B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms; angles are given in degrees.

1.2.3.5 Formation of 69 from 76

This pathway starts with the intramolecular cyclization of **76** through **TS10** to form seven-membered ring intermediate **79** (Figure 10). The potential energy surface is given in Figure 11. The Gibbs activation energy of this step was calculated to be 34.03 and 31.63 kcal/mol in the gas phase and methanol, respectively. The C5-N4-C3-C2 dihedral angle changes from -11.2° in **76** to -164.3 in **79**. While the N8-C2 bond forms, the C1−C2−C3 angle gradually changes from 178.2° in **76** to 143.2° and 136.7° in **TS10** and **79**, respectively. The second step involves the proton

transfer from N8 to C3 with the assistance of methanol. The energy of **TS11** is 34.00 kcal/mol (in methanol) higher than the initial reactant **76**. The third step is the 1,3-H shift from N8 to C1. The Gibbs activation energy is predicted to be quite high (50.02 kcal/mol in the gas phase). This path is also more feasible with the assistance of methanol. Explicit consideration of methanol lowers the activation barrier to 34.18 and 29.91 kcal/mol in the gas phase and methanol, respectively. Second step seems to be the rate-determining step when the overall reaction profile is considered.[1b]

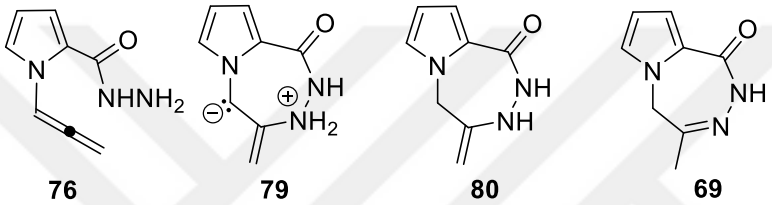


Figure 10. Structures of **69**, **76**, **79** and **80**

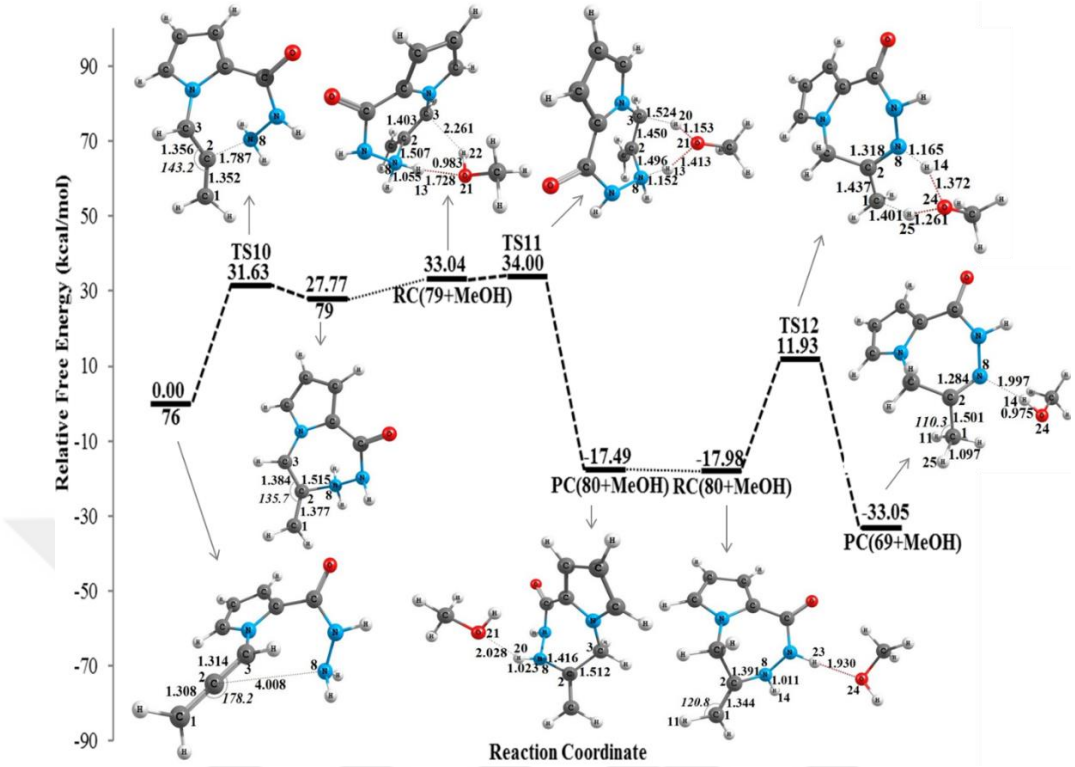


Figure 11. Potential energy surface for the formation of **69** at PCM/B3LYP/6-31+G(d,p)// B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms; angles are given in degrees.

1.2.3.6 Formation of pyrrolopyrazinone 68 from 76

The initial stage of this pathway started with the nucleophilic attack of N7 on the most electrophilic carbon C2 of the allene unit. Mulliken charges showed that N8 (-0.67) is more nucleophilic than N7 (-0.24), since lone pair electrons of N7 are in conjugation with carbonyl group. However, this pathway leads to the formation of experimentally observed product **57**. Therefore, we also modeled this reaction by using density functional theory. Initial step includes cyclization which is suggested to occur via **TS13**. This step requires a Gibbs free activation energy of 32.89 kcal/mol in methanol and was found to be endergonic (Figure 13). The distance

between the C2 and N7 was found to be 3.200, 1.827 and 1.495 Å in structures **76**, **TS13**, and **81**, respectively (Figure 12, 13). The second step was the proton transfer from **N8** to **C1**, which takes place through **TS14** and modeled with the assistance of methanol. The Gibbs free energy with respect to the initial reactant **76** was calculated to be 33.70 kcal/mol in methanol. The overall reaction is quite exergonic by 37.26 kcal/mol.[1b]

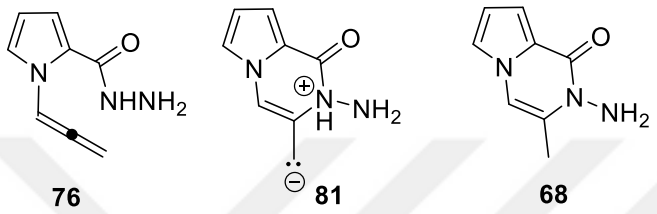


Figure 12. Structures of **68**, **76** and **81**

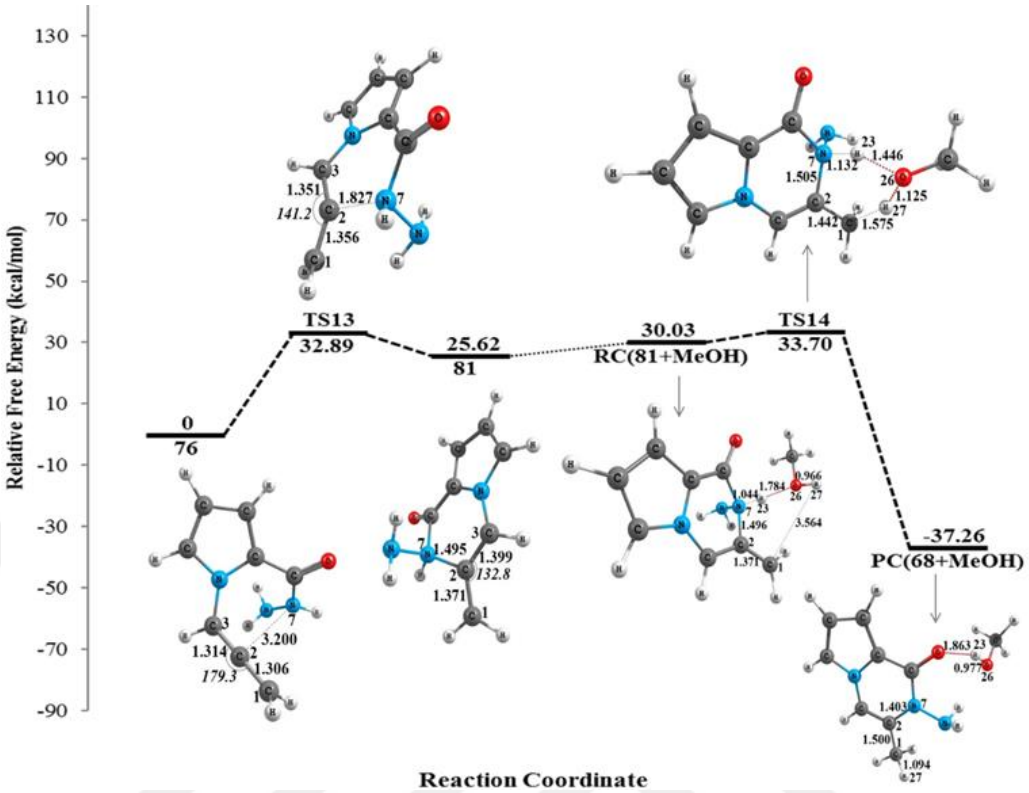


Figure 13. Potential energy surface for the formation of **68** at PCM/B3LYP/6-31+G(d,p)// B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms; angles are given in degrees.

The synthesis of pyrrolotriazepines **57a-c**, pyrrolotiazepinone **69** and pyrrolopyrazinone **68** were accomplished starting from pyrrole. Formation of possible cyclization products were investigated with DFT calculations. The results showed that the reaction proceeds through base catalyzed propargyl-allene isomerization. Calculated activation barriers for the cyclization reactions were examined in the light of experimental findings.

CHAPTER 2

A COMBINED EXPERIMENTAL AND THEORETICAL STUDY FOR THE FORMATION OF INDOLIZINE, PYRROLO[1,2,A]PYRAZINE, PYRROLO[1,2-A]PYRAZINONE

2.1 Introduction

Indolizines are aromatic systems, possessing a bridgehead nitrogen atom shared by an electron-excessive and an electron-deficient ring.[26] Indolizines have attracted considerable interest because of their observed pharmaceutical activities such as antitumor, anti-inflammatory and CNS (central nervous system) activity.[27] Indolizines can be shown as a prototype molecule for the azaindolizines as shown in Figure 14, which have an additional nitrogen atom instead of –CH group.[28]

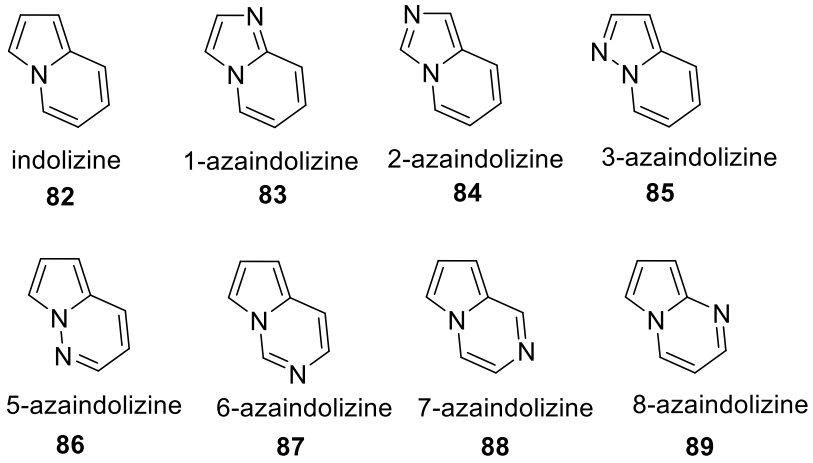


Figure 14. Structures of indolizine derivatives **82**–**89**

Azaindolizine derivatives have previously been used in different areas, for instance; material science, pharmaceutical and agricultural chemistry.[29] For example, 6-azaindolizines (**87**) are found in the marine alkaloid hinckdentine **91**, some analogues of which have cataleptogenic activity (Figure 15).[27] These compounds are also found in variolins **90,** that are isolated from the Antarctic sponge *Kirkpatrickia* V*arialosa*, having antiviral and antitumor activity.[27]

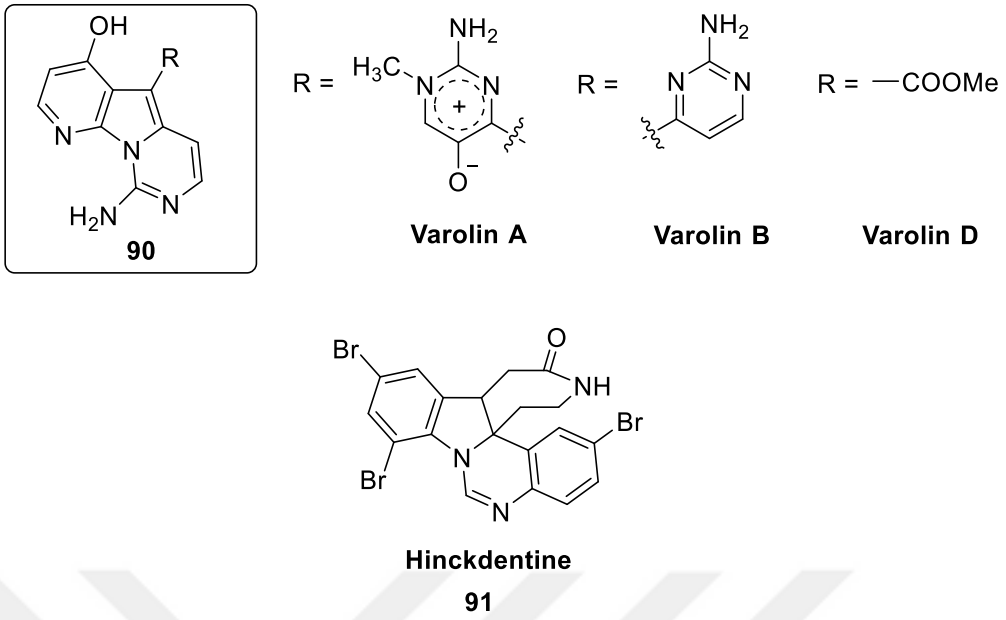
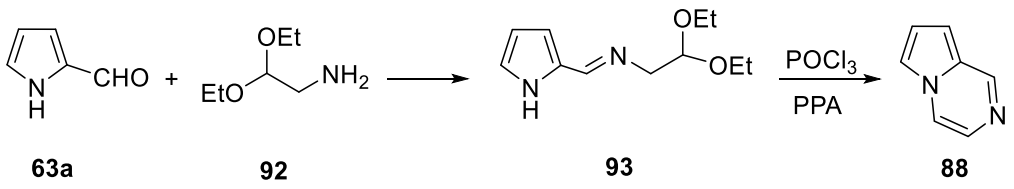


Figure 15. Structures of azaindolizine derivatives **90** and **91**

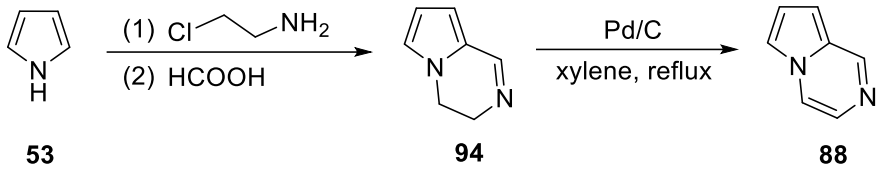
2.1.1 Synthesis of 7-azaindolizines

Hertz and Tocker[30] synthesized 7-azaindolizine (**88**) starting from pyrrole carbaldehyde **63a** (Scheme 25). For this purpose, they first synthesized aldimine derivative **93** by condensation of **63a** with aminoethylacetal **92** in 90% yield. Reaction of **93** with polyphosphoric acid and phosphorus oxychloride led to the cyclization product **88** in an overall yield of 18%.



Scheme 25. Synthesis of 7-azaindolizine (**88**)

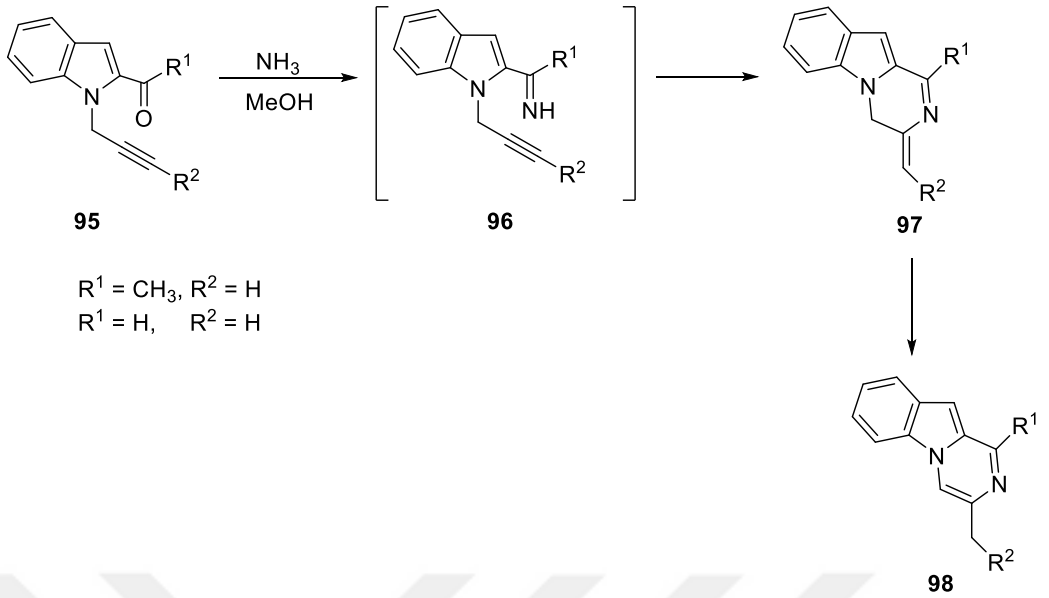
Minquez *et al.*[31] used different types of acids in order to improve the yield of the cyclization product. Finally, compound **88** was synthesized starting from the reaction of pyrrole with 2-chloroethanamine (Scheme 26).



53 **94** **88**

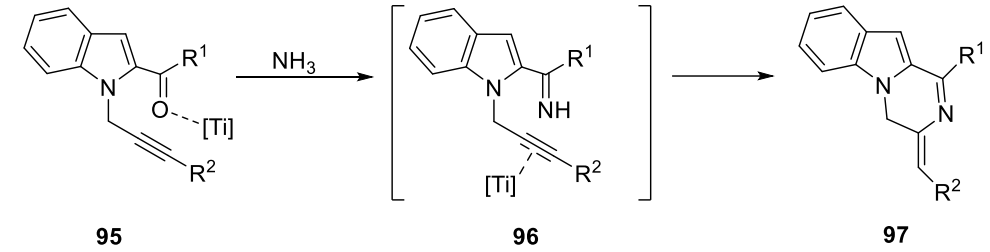
Scheme 26. Synthesis of 7-azaindolizine (**88**) starting from pyrrole

Arcadi *et al.*[32] synthesized pyrazinoindole derivative **98** from the reaction of 2-carbonyl-*N*-propargylindoles **95** and ammonia in methanol (Scheme 27). The reaction operated well in the case of *N*-propargylindole-2-carbaldehydes; however, the yields and selectivity were poor in the case of 2-acetyl-*N*-propargylindoles. In addition, the reaction did not work with 2-benzoyl-*N*-propargylindoles. According to the proposed mechanism, the first step is the formation of an imine intermediate **96**. 6-*exo*-*dig* cyclization of **96** results in the formation of 3,4-dihydropyrazinoindole **97** which then give pyrazinoindole **98** by partial isomerization (Scheme 27).



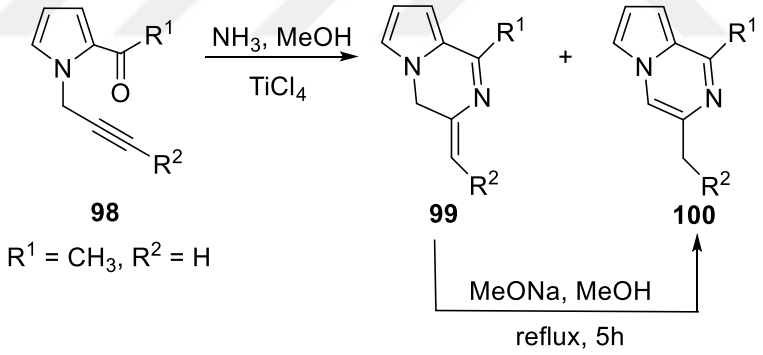
Scheme 27. Synthesis of pyrazinoindole **98** starting from 2-carbonyl-*N*-propargylindoles **95**

A different approach was also applied in order to increase the efficiency of the methodology for annulation of 2-acetyl and 2-benzoyl derivatives. Therefore, 2 M of ammonia was added to the solution of corresponding alkynyl indole in methanol and heated in a multi-mode microwave oven at 150 ℃. The yields of the products were increased in a shorter reaction time. Their proposed mechanism started with the formation of imine intermediate (Scheme 28). To activate the ketone moiety, Lewis acid catalysts were used. Titanium tetrachloride was found as the optimal choice due to the good yields and shorter reaction time. Titanium tetrachloride can also coordinate to the alkyne moiety as well as the carbonyl oxygen, activate the cyclization to produce exclusively the dihydropyrazino derivatives **97**.



Scheme 28. A different approach for the synthesis of **97**

A similar procedure was applied for the synthesis of pyrrolo-pyrazine derivatives starting from 2-acetyl-*N*-propargylpyrroles **98** (Scheme 29). Compound **98** was dissolved in a mixture of 2 M of ammonia and methanol in a sealed microwave tube. To this solution, titanium tetrachloride was added. The resulting mixture was heated in multi-mode microwave oven at 130 °C, to form the isomeric compounds **99** and **100**. Furthermore, they noted that the isomer **99** was converted to the pyrrolo-pyrazine derivative **100** in quantitative yield by treatment with MeONa in methanol for 5 h.

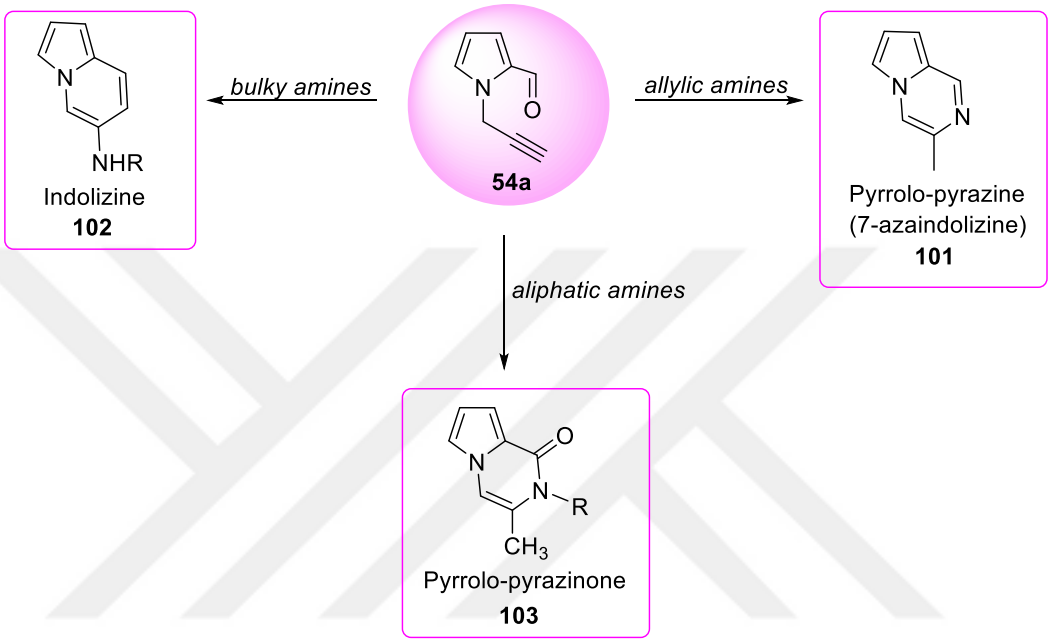


Scheme 29. Synthesis of pyrrolo-pyrazine derivative **100**

2.1.2 Objective of the Study

Our goal was to understand the effects of different types of amines in the cyclization of *N*-propargyl carbaldeyde and establish the formation mechanism of the products

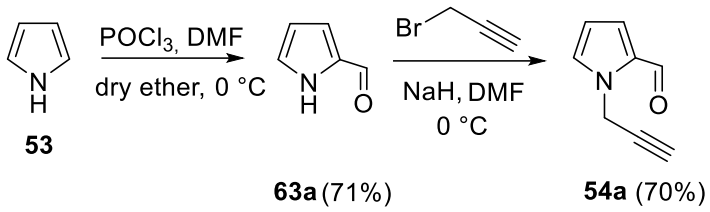
by means of theoretical calculations. We observed an interesting reactivity pattern in the cyclization reactions, which leads to the different skeletons such as indolizine **102**, 7-azaindolizine **101** and pyrrolo-pyrazinone **103** derivatives (Scheme 30). The experimental results were supported by quantum chemical calculations in order to understand the factors controlling the cyclization reaction.



Scheme 30. Different skeletons obtained from *N*-propargyl carbaldehyde

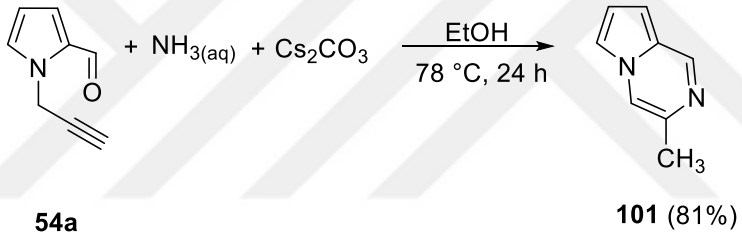
2.2 Results and Discussion

The starting material, *N*-propargyl carbaldeyde **54a**, was prepared by Vilsmeier reaction as previously described in Chapter 1 (Scheme 31).[1b]



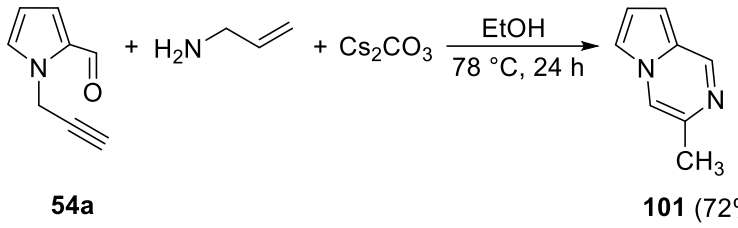
Scheme 31. Synthesis of *N*-propargyl carbaldeyde **54a**

We next examined the reaction of *N*-propargyl carbaldeyde **54a** with different types of amine derivatives to understand the role of those amines in the cyclization process. For this purpose, the reaction was first performed with ammonia in presence of cesium carbonate at reflux temperature of ethanol shown in Scheme 32. Cyclization product 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**) was obtained in 81% yield.



Scheme 32. The reaction of *N*-propargyl carbaldeyde **54a** with ammonia

We then explored the reaction of compound **54a** with allyl amine under the same reaction conditions (Scheme 33). Interestingly, same cyclization product **101** was formed in 72% yield, which shows the removal of allyl unit during the reaction.



Scheme 33. The reaction of *N*-propargyl carbaldeyde **44a** with allyl amine

In order to determine the fate of allyl group and understand the reaction mechanism, side product should be detected. For this purpose, a sample was taken from reaction medium and analyzed with Mass Spectroscopy. Diallyl amine was detected as the side product (Figure 16).

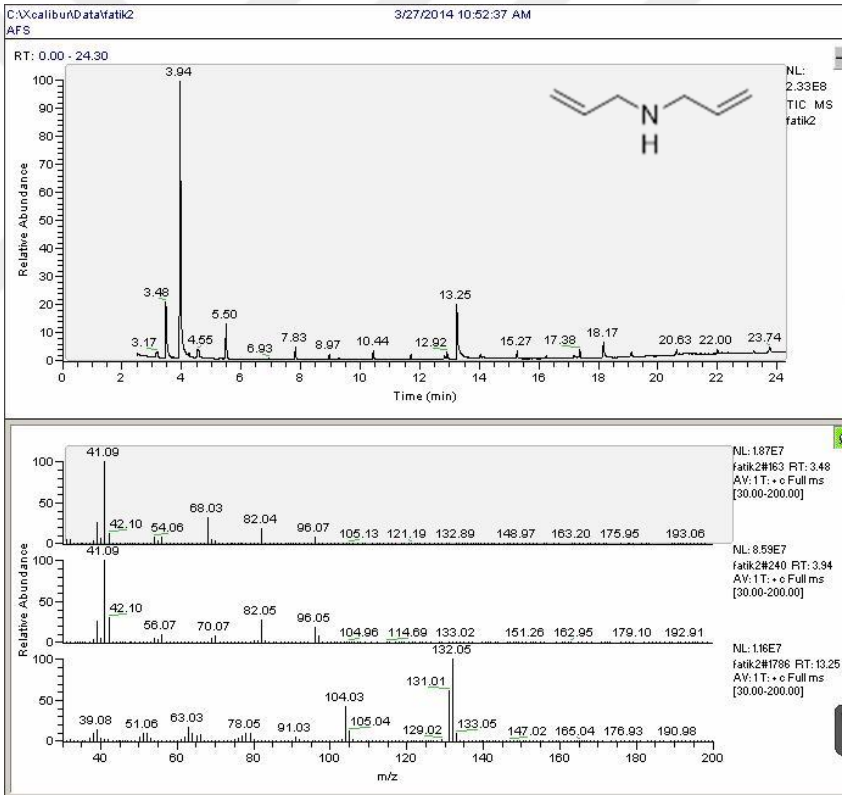
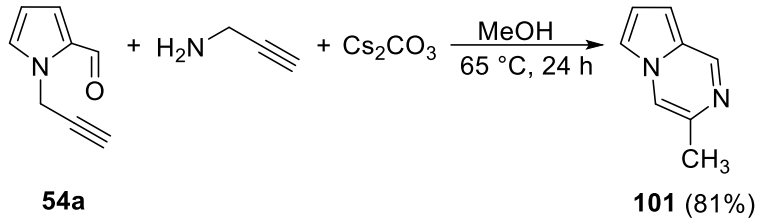


Figure 16. Mass Spectroscopy analysis of the reaction of *N*-propargyl carbaldeyde **54a** with allyl amine[33]

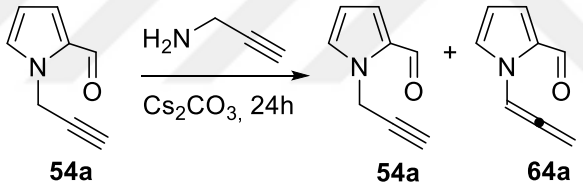
Product **101** was also obtained by using propargyl amine as depicted in Scheme 34. Based on these results, we propose that the cyclization occurs with the removal of both allyl and propargyl units.



54a **101** (81%)

Scheme 34. The reaction of *N*-propargyl carbaldeyde **54a** with propargyl amine

Solvent effect has been also evaluated. Polar protic solvents like methanol and ethanol were used for the cyclization reaction. Compound **54a** was treated with propargyl amine in dry aprotic solvents such as acetonitrile, THF and DMF (Scheme 35).



54a **54a** **64a**

Solvent	Temperature	Ratio	
dry THF	65 °C	92%	8%
dry MeCN	81 °C	36%	64%
dry DMF	65 °C	–	100%

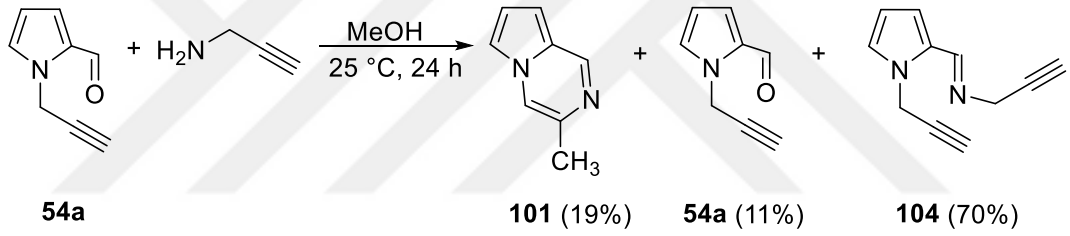
Scheme 35. Treatment of compound **54a** with propargyl amine in dry aprotic solvents

Using aprotic solvents led to the recovery of starting material **54a** and formation of *N*-propargyl allene **64a** in different ratios. Interestingly, any trace of the expected product, 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**), was not observed. Firstly, we

proposed that cyclization occurs via allene intermediate. Secondly, this result confirmed the pivotal role of the solvent in the mechanism.

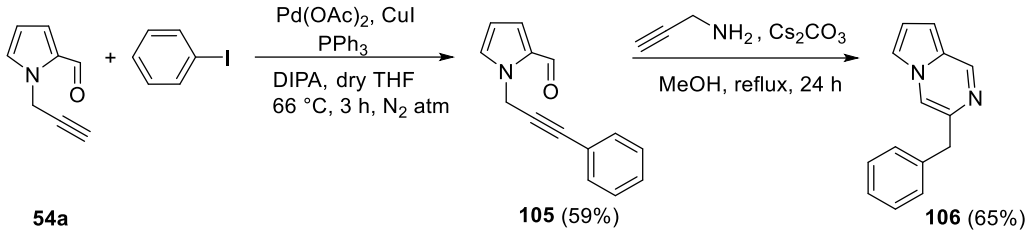
NaH can be used as a base for the propargyl-allene isomerization in DMF[1b]; however, the target product only formed in polar protic solvents. Therefore, a mild base such as Cs_2CO_3 was preferred for the cyclization.

In order to understand the details of the mechanism, a similar procedure was applied without using a base (Cs_2CO_3) at 25 °C (Scheme 36). Cyclization product **101** and imine derivative **104** were obtained in 19% and 70% yield, respectively, indicating that the reaction mechanism proceeds through imine (aldimine) intermediate. In addition, formation of product **101** shows that propargyl amine acts as a base as well as a nucleophile.



Scheme 36. The reaction of **54a** with propargyl amine without using base at 25 °C

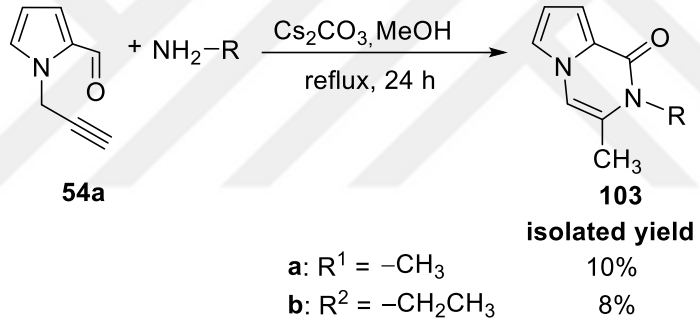
In order to test the generality of this cyclization reaction we decided to functionalize the alkyne moiety. The functionalization of the alkyne moiety was accomplished by Sonagashira cross-coupling reaction. *N*-propargyl carbaldeyde **54a** was treated with iodobenzene in presence of copper(I) iodide (CuI), palladium acetate ($Pd(OAc)_2$), triphenylphosphine (PPh_3) and diisopropylamine (DIPA) in dry tetrahydrofuran (THF) under nitrogen atmosphere (Scheme 37). After the completion of the reaction, the corresponding coupling product **105** was purified by column chromatography. Heating **105** with propargyl amine at reflux temperature of methanol afforded the pyrrolo-pyrazine derivative **106** in 65% yield.



Scheme 37. Synthesis of pyrrolo-pyrazine derivative **106**

2.2.1 Aliphatic Amines

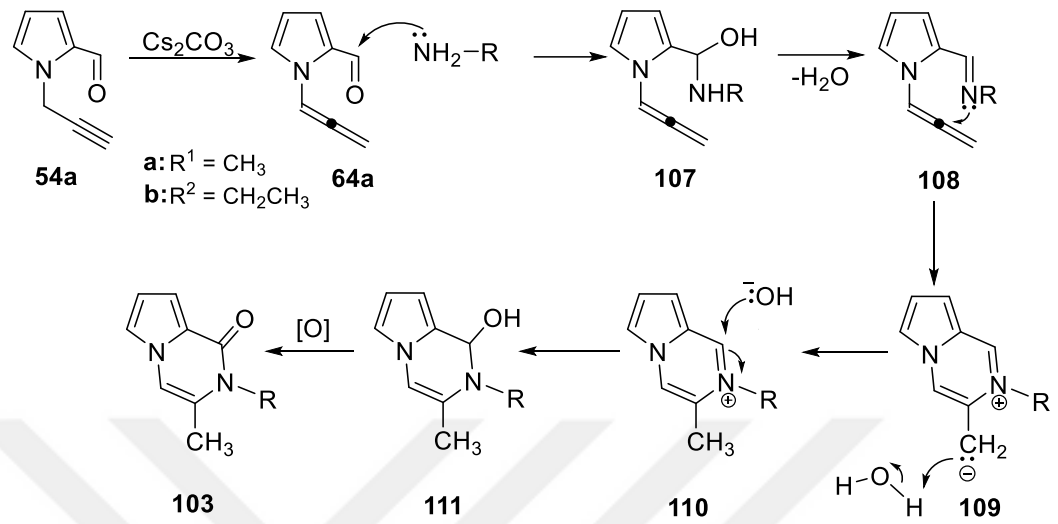
When *N*-propargyl carbaldeyde **54a** was treated with aliphatic amines such as methyl and ethylamine, unexpected cyclization products were obtained in low yields (Scheme 38).



Scheme 38. Treatment of *N*-propargyl carbaldeyde **54a** with aliphatic amines

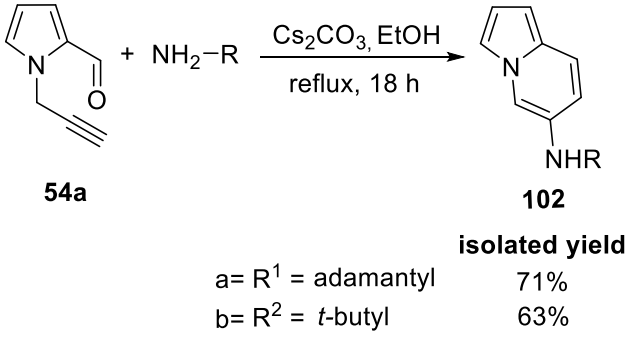
Proposed mechanism for the formation of pyrrolo-pyrazinone derivatives **103a-b** is depicted in Scheme 39. The reaction starts with a base-catalyzed propargyl-allene isomerization to form *N*-allene carbaldehyde **64a**. Then, nitrogen atom of the amine attacks the carbonyl carbon of **64a** to generate hemiaminal **107**. After elimination of water molecule, intramolecular cyclization takes place to form zwitter ionic intermediate **109**. Hydroxide ion, which is formed by the abstraction of proton by carbanion, would attack the iminium carbon of **110**. Final step includes the

oxidation of **111** with oxygen present in the environment, to give the desired product **103a-b**.



Scheme 39. Proposed mechanism for the formation of pyrrolo-pyrazinone derivatives **103a-b**

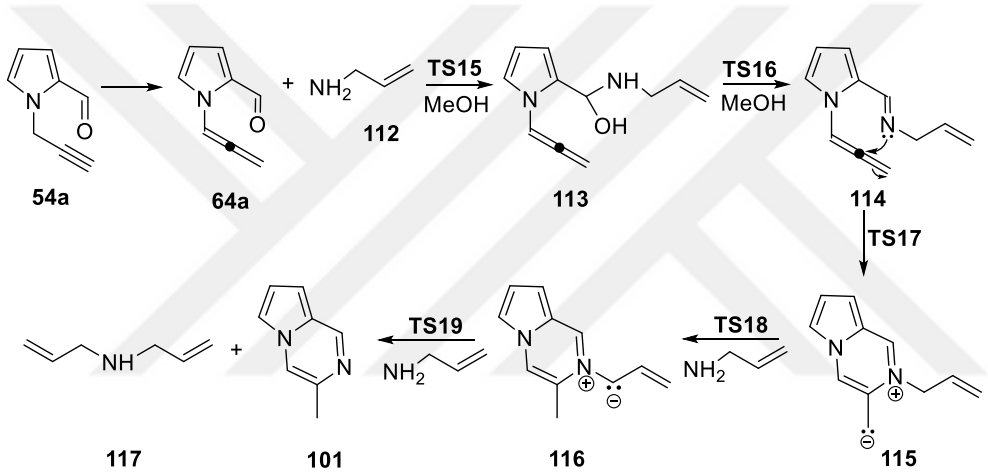
Our group also investigated the effect of amines substituted with bulky groups.[34] Treatment of **54a** with adamantyl and *tert*-butyl amine at reflux temperature of ethanol produced a different skeleton shown in Scheme 40.



Scheme 40. Treatment of *N*-propargyl carbaldeyde **54a** with bulky amines

2.2.2 Theoretical Calculations

Formation of 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**) and indolizine derivative **102a** were investigated by means of theoretical calculations in an effort to understand the reaction mechanism. All calculations were performed at conductor-like polarizable continuum model[35] (CPCM)/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol solvent. Proposed mechanism for the formation of compound **101** is given in Scheme 41. Our previous computational work demonstrated that propargyl-allene isomerization was feasible in presence of a base (Chapter 1).[1b] Therefore, this step was not modeled in the present study.



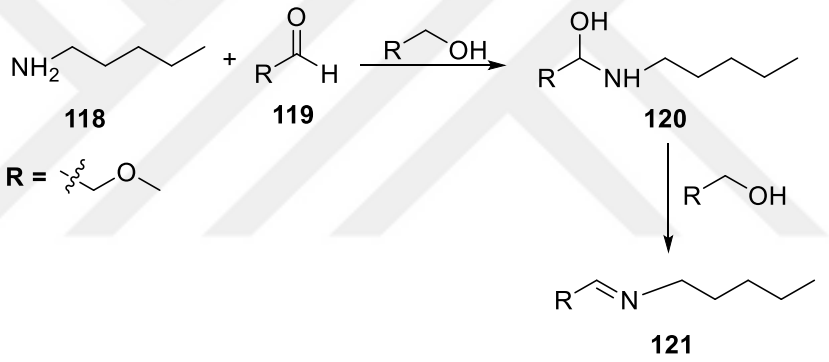
Scheme 41. Proposed mechanism for the formation of 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**)

2.2.2.1 Imine formation

As mentioned in the Chapter 2, cyclization occurs via the imine intermediate based on the NMR analysis of the crude product. Cyclization product **101** could not be observed in dry THF, DMF and acetonitrile. For this purpose, imine formation from *N*-propargyl pyrrole and allyl amine, has been investigated with and without the explicit solvent molecules. Imine formation mechanism includes two steps. First

step is the nucleophilic attack of lone pair electrons of nitrogen of allyl amine to the carbonyl carbon of aldehyde **64a** resulting the tetrahedral intermediate; hemiaminal **113**. Second step is the elimination of water to give imine **114** (Scheme 41).

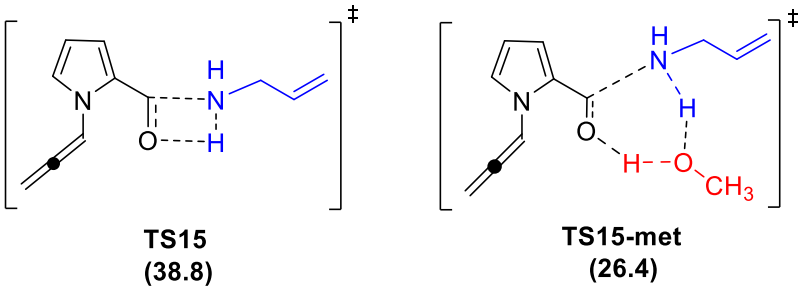
Wang *et al.*[36] also modeled the imine formation reaction starting from 2-methoxy-acetaldehyde **119** and pentyl amine **118** (Scheme 42). They calculated the Gibbs free activation energy for the alcohol catalyzed (21.0 kcal/mol) and non-catalyzed (32.5 kcal/mol) hemiaminal formation using TPSSTPSS(IEFPCM, toluene)/ LanL2DZ/ 6-31++G(d,p)//TPSSTPSS/LanL2DZ/6-31G(d,p) method. According to their calculations, catalyst lowers the activation barrier compared to the reaction without catalyst. They also modeled the direct dehydration and indirect dehydration of hemiaminal **120**. Activation barrier of alcohol assisted dehydration step was approximately 15 kcal/mol less than the direct dehydration step.



Scheme 42. Imine formation reaction starting from 2-methoxy-acetaldehyde **119** and pentyl amine **118**

According to our calculations, the first step proceeded with 26.4 kcal/mol free activation barrier with respect to **RC(64a+112+MeOH)** with the assistance of methanol. Without explicit methanol, the barrier was calculated to be 38.8 kcal/mol (Scheme 43). The lowering of the barrier by methanol can be attributed to three factors; (1) the formation of the more stable six-membered ring transition state instead of less stable four-membered ring transition state, (2) activation of carbonyl group by hydrogen bonding with methanol, and (3) enhancement of the

nucleophilicity of allyl amine due to the intermolecular NH---O bonding with methanol. Optimized geometries are shown in Figure 17.



Scheme 43. Methanol-catalyzed and non-catalyzed transition states for the formation of hemiaminal **113** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. The values in parenthesis represent the activation barriers of the corresponding step in kcal/mol.

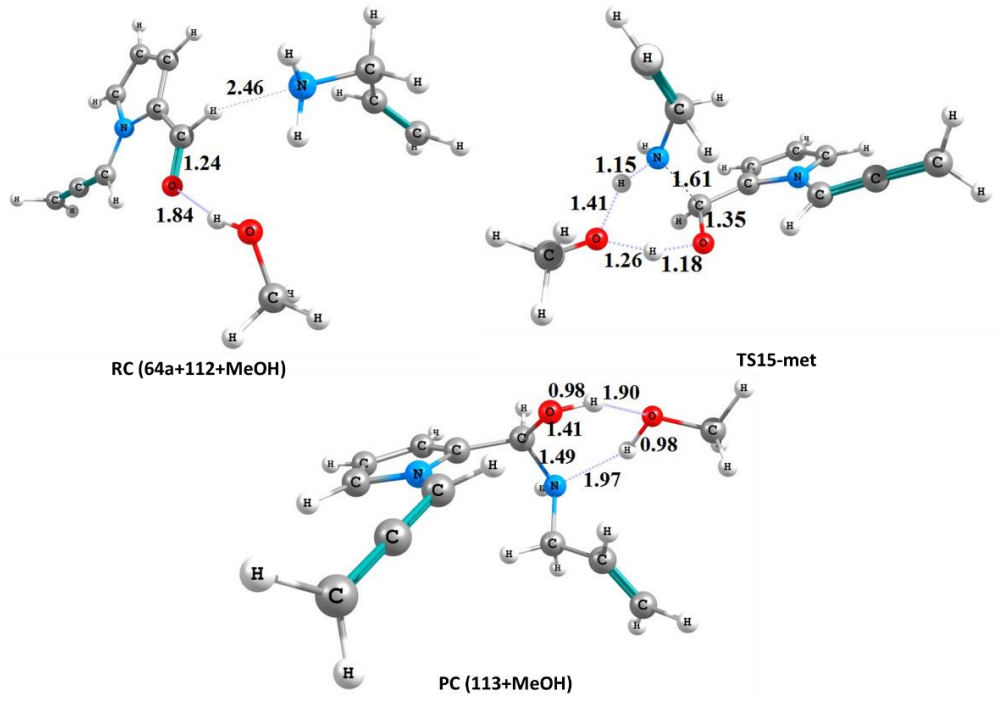
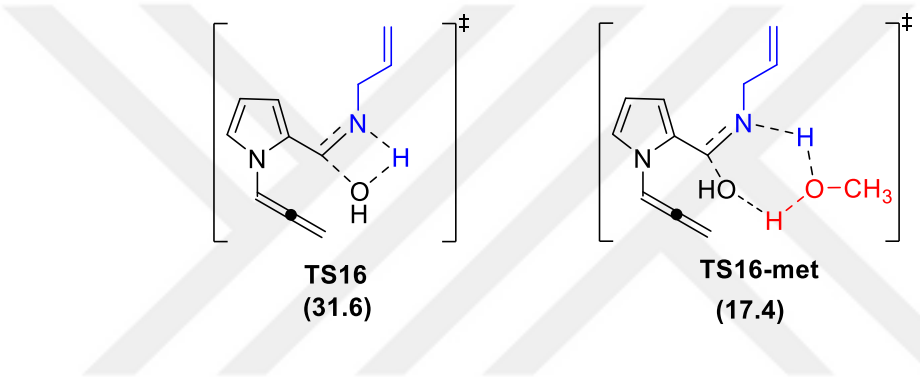


Figure 17. Optimized geometries for the stationary points for the formation of hemiaminal **113** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms

Second step gave rise to the imine formation through 28.1 kcal/mol free energy barrier with respect to the **RC(64a+112+MeOH)**. However, the free energy barrier for the formation of imine from heminal-H_2O complex was low (17.4 kcal/mol with respect to the **RC(113+MeOH)**) with the explicit effect of methanol (Scheme 44). The non-catalyzed barrier (with respect to the **RC(64a+112)**) was calculated to be 31.6 kcal/mol indicating that the methanol has a stabilizing effect on the transition state. Therefore, we also suggest a dehydration reaction, which takes place through methanol molecule via hydrogen-bond network. Optimized geometries are shown in Figure 18. Potential energy profile of the overall mechanism for the formation of pyrrolo-pyrazine **101** is given in Figure 19.



Scheme 44. Methanol-catalyzed and non-catalyzed transition states for the formation of **114** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. The values in parenthesis represent the activation barriers of the corresponding step in kcal/mol.

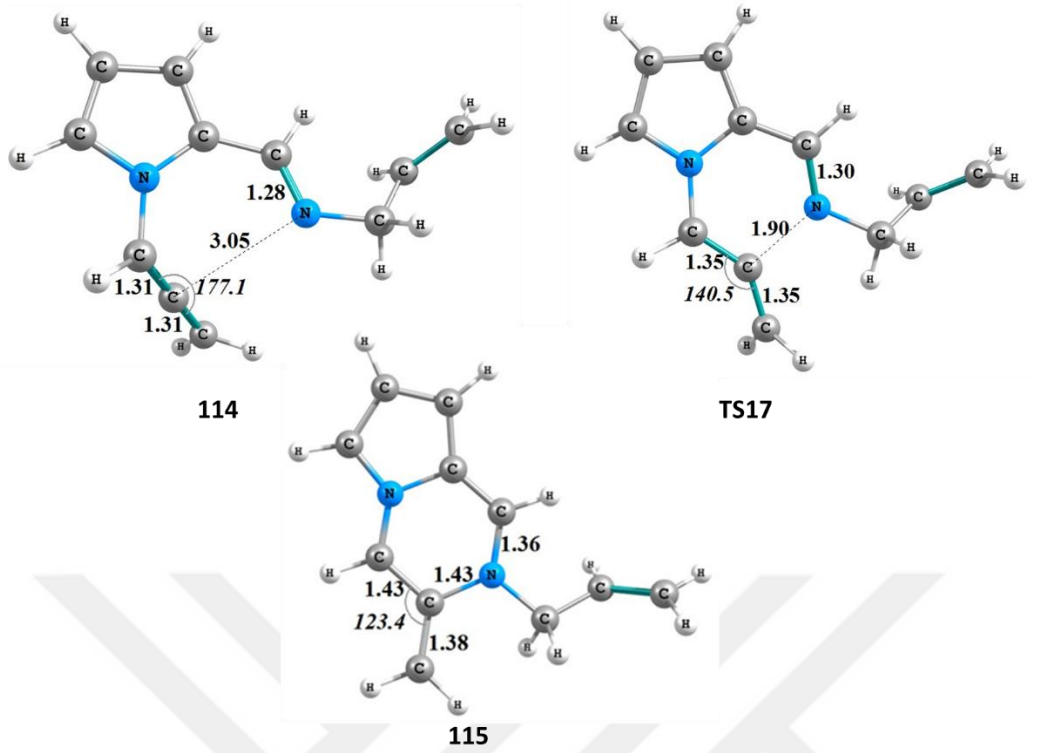


Figure 18. Optimized geometries of the stationary points for the formation of **114** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms

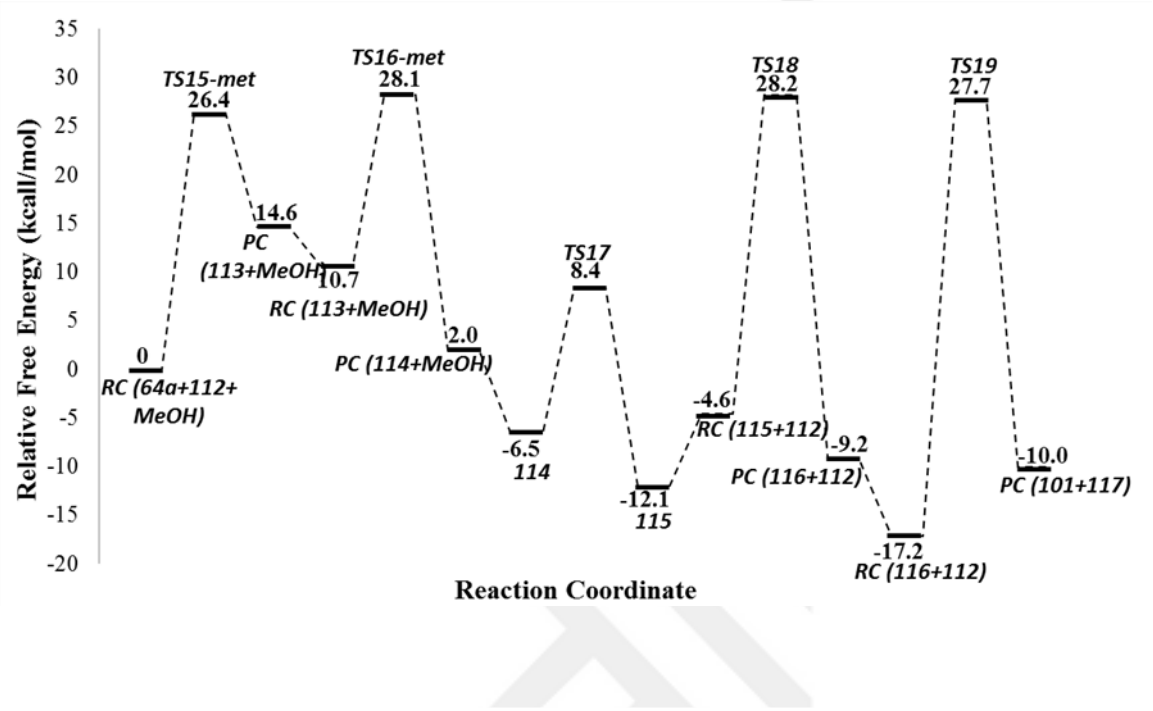


Figure 19. Potential energy profile and relative Gibbs free energies (kcal/mol) in methanol related to formation of 3-methyl-pyrrolo[1,2-*a*]pyrazine at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. The effect of methanol was taken into account both implicitly and explicitly

2.2.2.2 Cyclization Reaction

Cyclization reaction occurs via the nucleophilic attack of imine nitrogen atom on the central carbon C2 of the allene moiety, since it is more electropositive as supported in our previous study.[1b] The calculated energy barrier for this step in methanol via transition state **TS17** was 14.9 kcal/mol (Figure 19). Optimized geometries are shown in Figure 20.

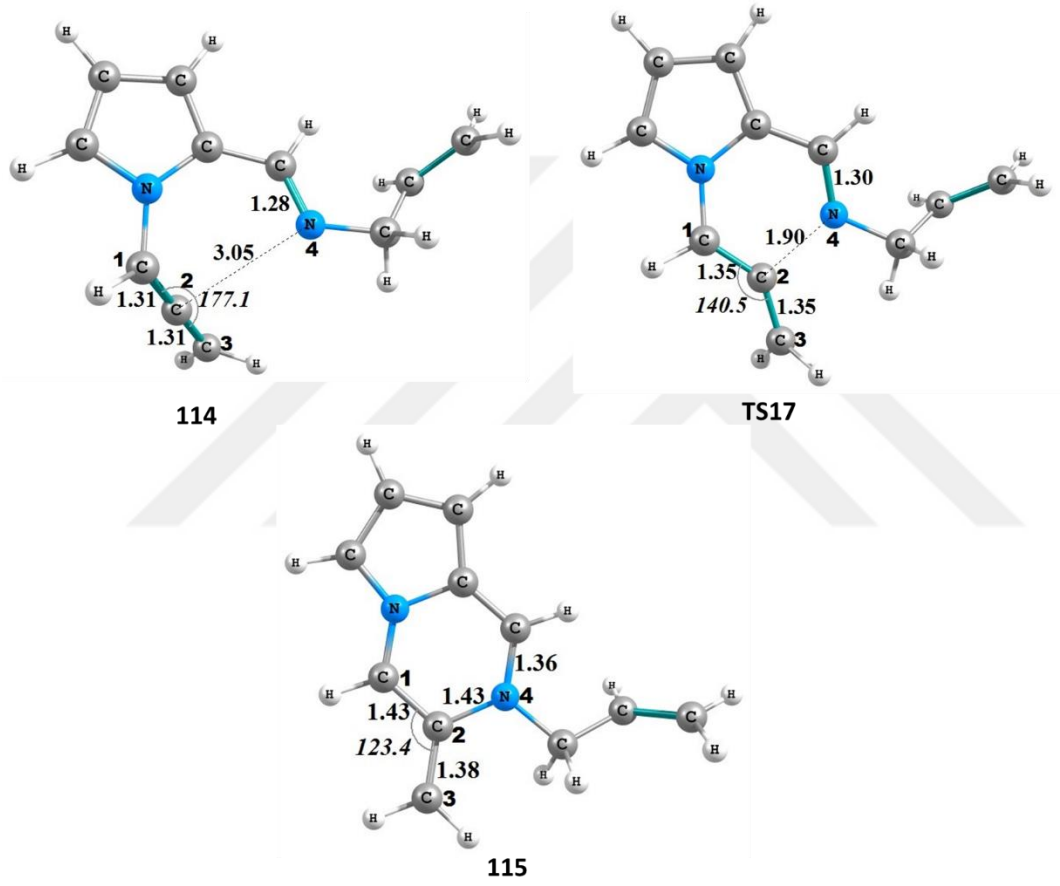
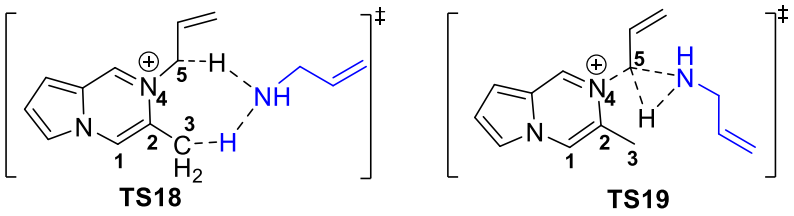


Figure 20. Optimized geometries of the stationary points for the formation of **115** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol..
Distances are given in angstroms; angles are in degrees

The next step is the proton transfer from C5-carbon to the C3-carbon atom, since these protons are acidic due to the inductive electron-withdrawing effect of the iminium group as well as the mesomeric electron-withdrawing effect of the ethylene group. Proposed transition state for the formation of **116** is shown in Scheme 45. Optimized geometries are shown in Figure 21.



Scheme 45. Transition states for the formation of **116** and **101**

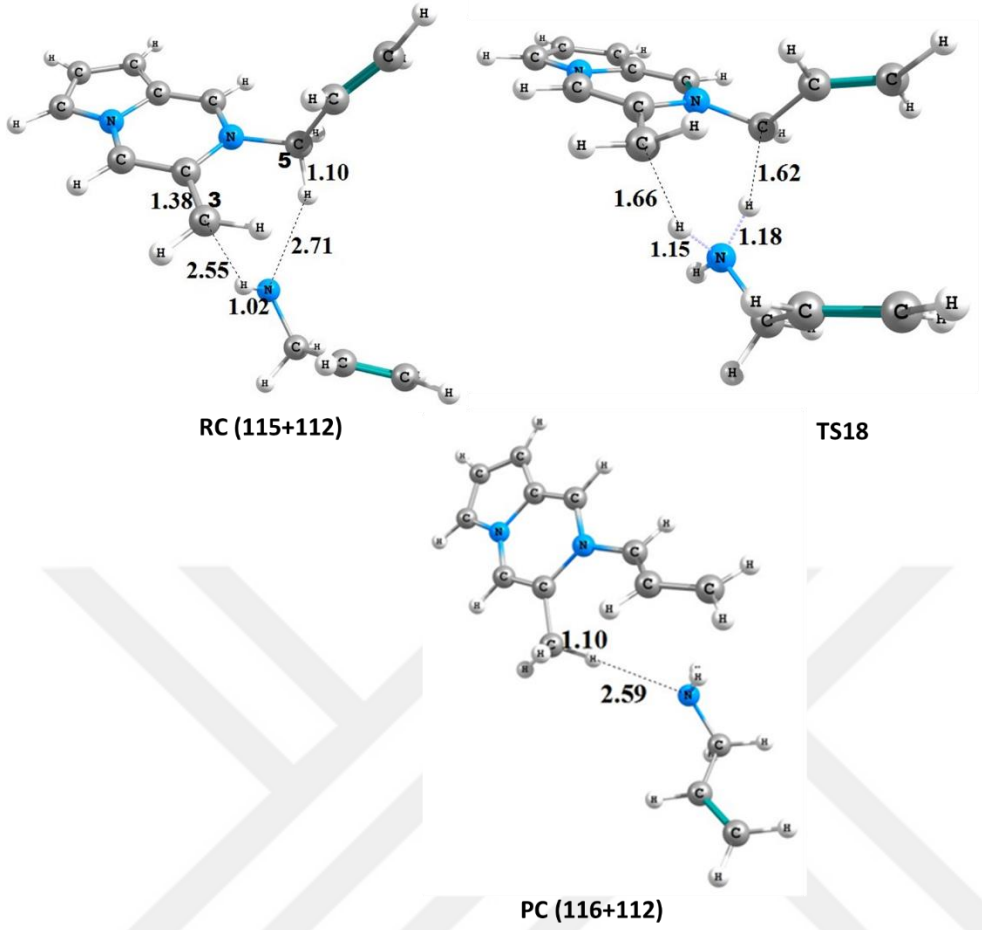


Figure 21. Optimized geometries of the stationary points of the formation of **116** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms.

As mentioned above, diallylamine was observed as a side product, which can be attributed to the deprotonation followed by S_N2 type reaction between **116** and allylamine (Scheme 41). For this purpose, this step was also modeled with the assistance of allyl amine. Proton abstraction from allyl amine to C5 and S_N2 reaction of allyl amine with **116** occur in a concerted way as shown in Scheme 45. Optimized geometries are shown in Figure 22. It is likely that methanol can also catalyze this step giving rise to allyl methyl ether; however, we could not observe allyl methyl ether in GC.

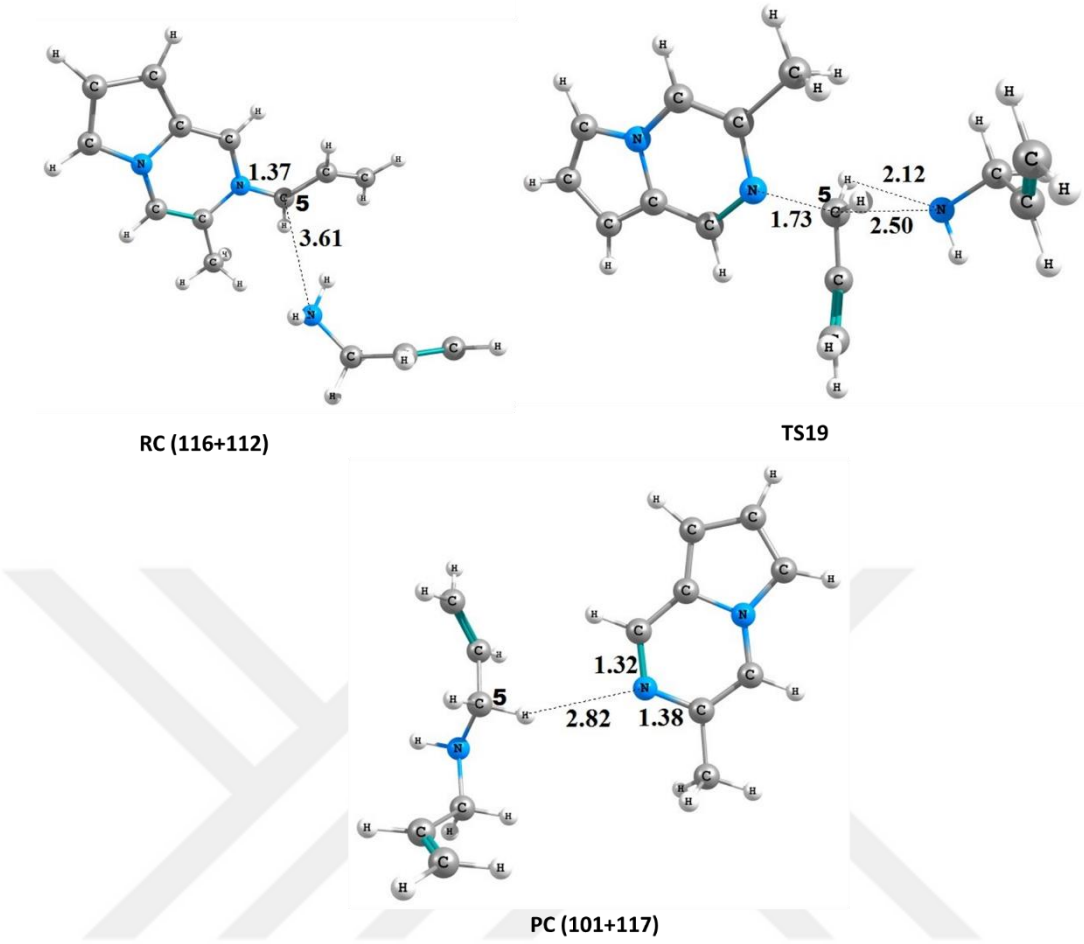
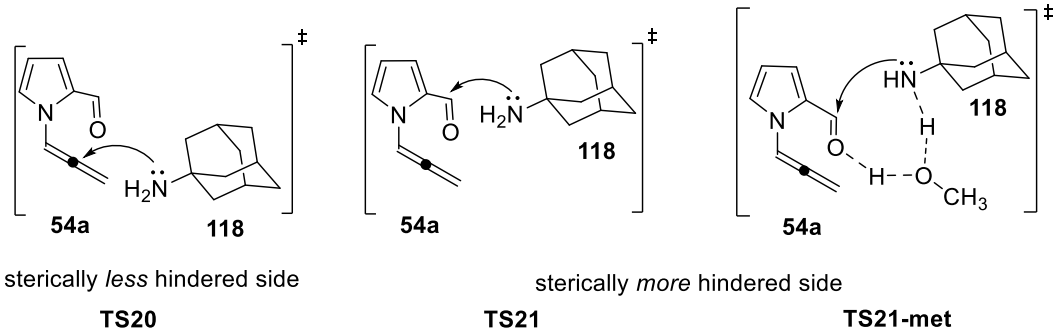


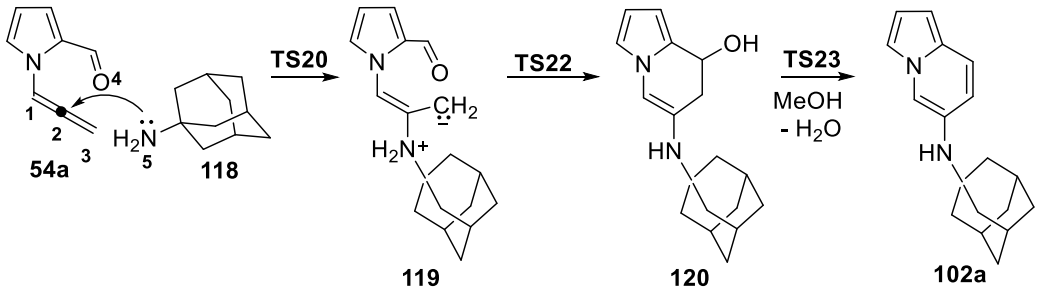
Figure 22. Optimized geometries of the stationary points of the formation of 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**) at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms.

As mentioned above, when the reaction was performed in presence of bulky amines such as adamantyl amine, cyclization product **102a** exhibiting a different skeleton, indolizine, was formed. Formation of **102a** reveals that a different cyclization mechanism occurs with bulky amines. In order to clarify the mechanism, two competing pathways were modeled: nucleophilic attack at the center carbon of allene moiety (**TS20**) and aldehyde carbonyl carbon (**TS21 and TS21-met**) (Scheme 46).



Scheme 46. Possible transition states for the reaction of **54a** with **118**

According to the gas phase optimizations, **TS21** was found to be 12.6 kcal/mol higher in energy than **TS20**. In **TS20**, bulky adamantyl group approach from the sterically less crowded side; thus, there is no steric repulsion between the allyl moiety and adamantyl group. The other reason for this preference is that **TS21** forms a four-membered ring. Therefore, methanol assisted transition state **TS21-met**, which leads to the relatively more stable six-membered ring, was also modeled. **TS21-met** was found to be less stable (5.4 kcal/mol) than **TS20**. Combining the computational results with the experimental observations, we propose that adamantyl amine preferentially attacks to the sterically less hindered central carbon atom in allene moiety, which affords indolizine derivative **102a**. Proposed mechanism is depicted in Scheme 47 and potential energy profile is given in Figure 23.



Scheme 47. Proposed mechanism for the formation of **102a**.

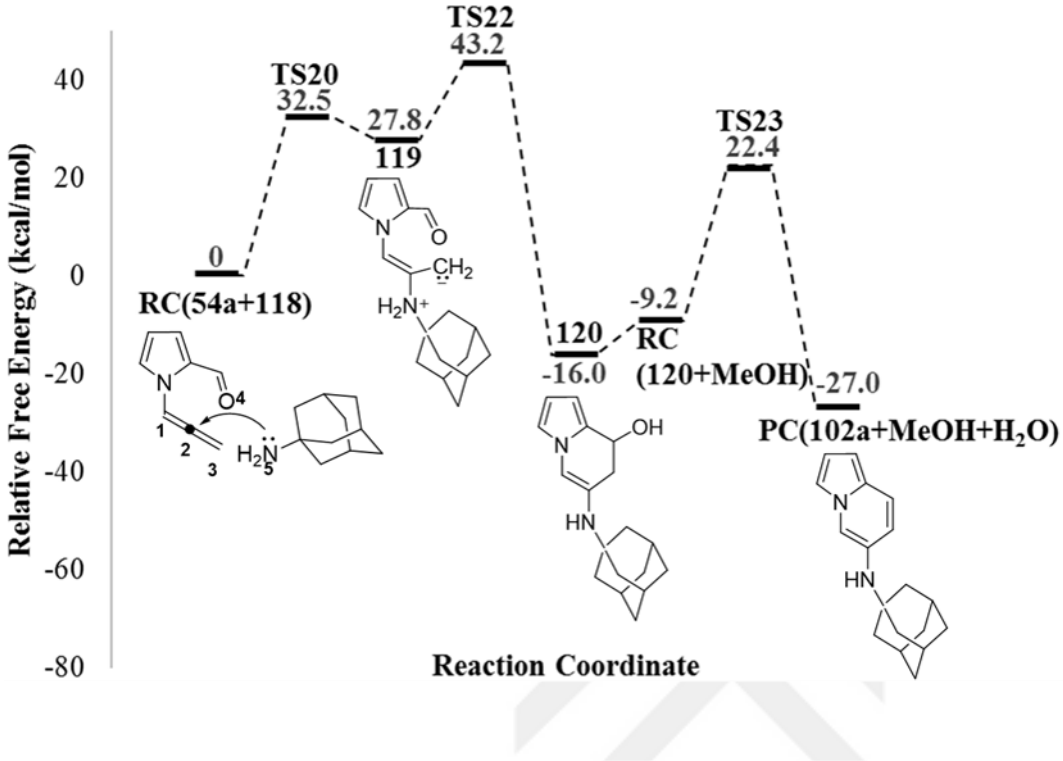


Figure 23. Potential energy profile and relative Gibbs free energies (kcal/mol) in methanol related to formation of indolizine derivative **102a** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol.

In the first step of the reaction, nucleophilic attack of the N5 nitrogen atom on C2 carbon atom takes place. C2-N5 bond distance (1.81Å) in **TS20** is only slightly longer than the C2-N5 bond distance (1.52 Å) in the product indicating a product-like transition state. The C1-C2-C3 angle changes from 177.9° in **RC(54a+118)** to 139.0 and 132.5° in **TS20** and **119**, respectively. Optimized structures are depicted in Figure 24. The potential energy profile for this step shows that the activation barrier is 32.5 kcal/mol, and the reaction is considerably endergonic by 27.8 kcal/mol in methanol.

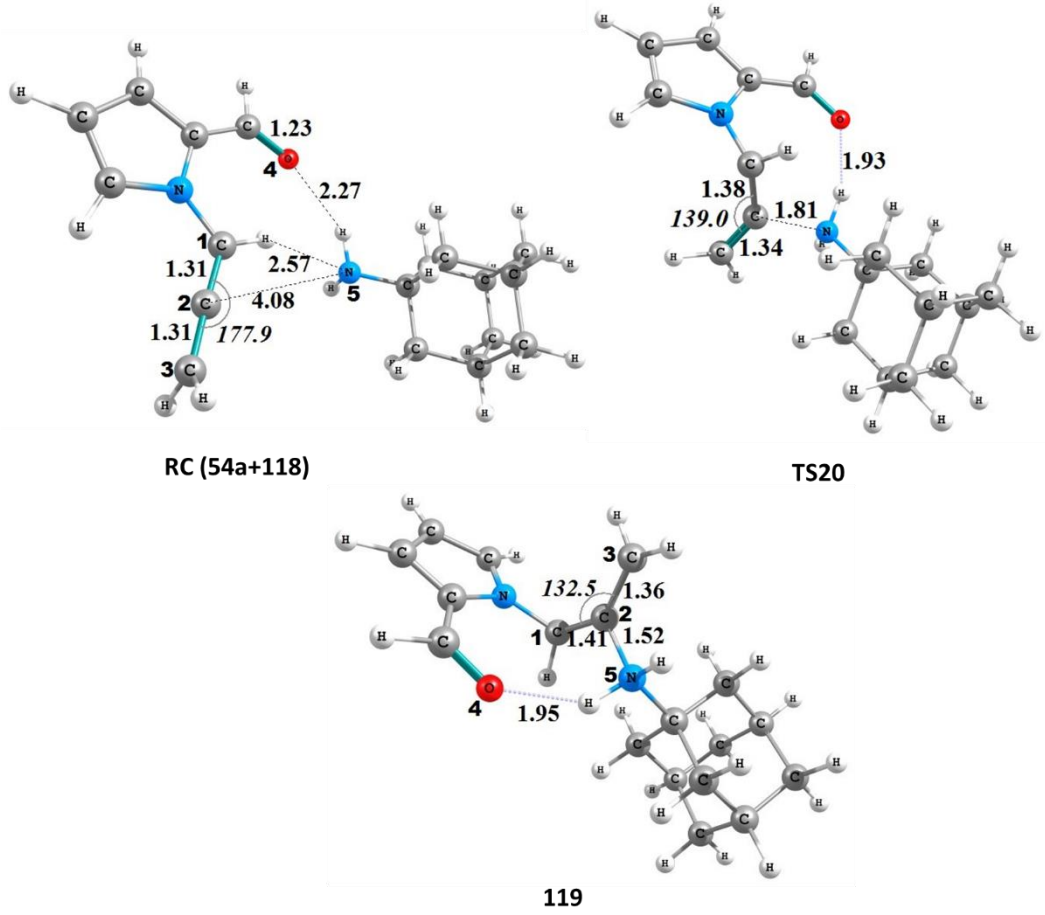


Figure 24. Optimized geometries of the stationary points of the first step for the formation of **101** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms, angles are given in degrees.

In the next step, negatively charged C3 carbon atom attacks the carbonly carbon to form six-membered heterocyclic intermediate **120**, through transition state **TS22** with an activation energy of 15.4 kcal/mol with respect to **119**. Optimized geometries are shown in Figure 25.

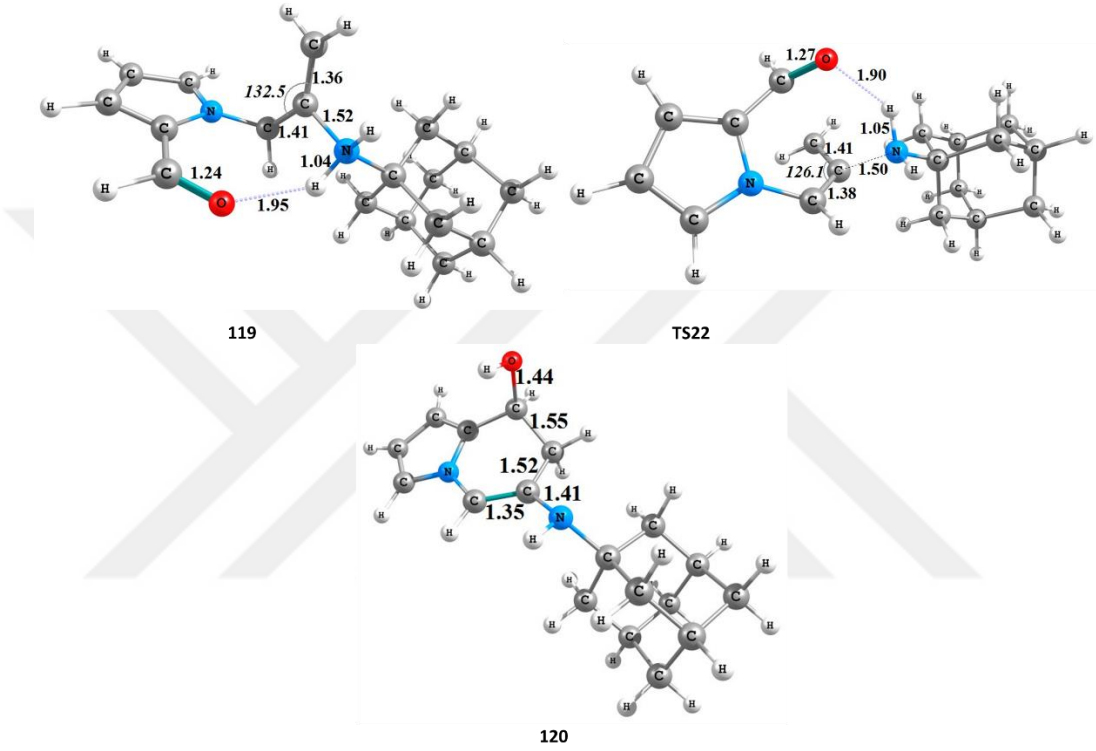


Figure 25. Optimized geometries of the stationary points of the second step for the formation of **120** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms, angles are given in degrees

The third step involves the water elimination from **RC(120+MeOH)**, which proceeds through transition state **TS23** and has an free energy of activation of 31.6 kcal/mol with respect to **120**. This step is also more feasible with the assistance of methanol and strongly exergonic with an energy of 27.0 kcal/mol. Optimized geometries are shown in Figure 26.

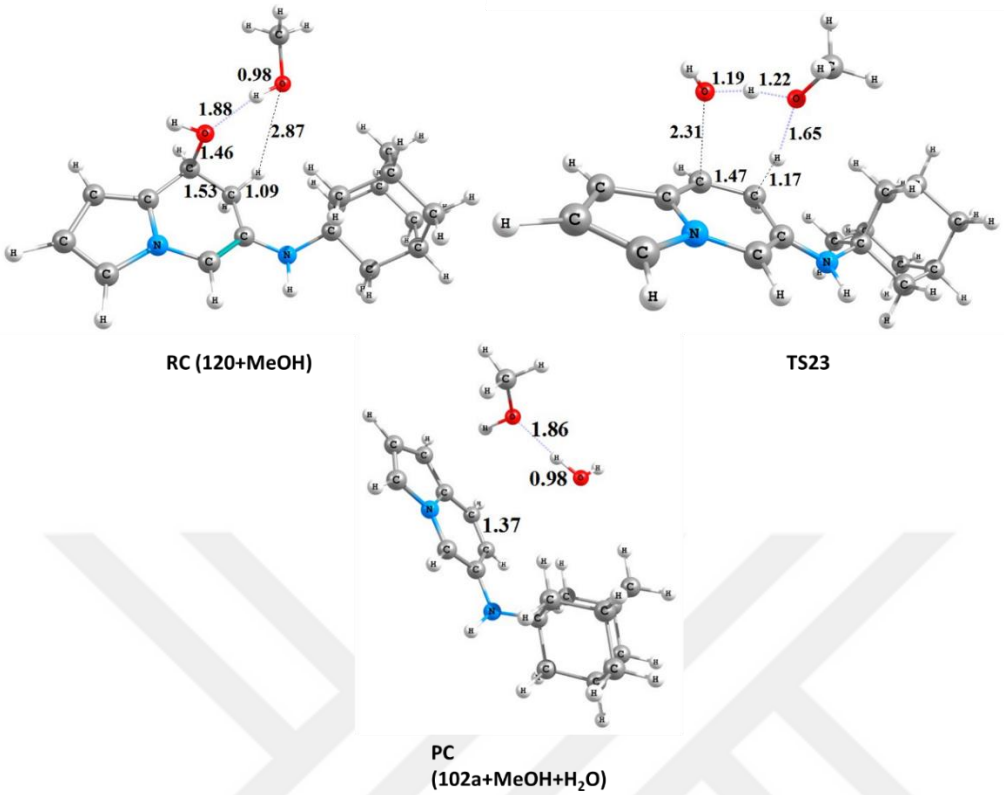


Figure 26. Optimized geometries of the stationary points for the formation of indolizine derivative **102a** at CPCM/B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level in methanol. Distances are given in angstroms.

We herein described a combined experimantal and theoretical study for the formation of 7-aza indolizine **101**, indolizine **102** and pyrrolopyrazinone **103**. The reaction of *N*-propargyl carbaldeyde **54a** with various amines yielded different skeletons. To provide mechanistic insights into the cyclization reactions, we performed DFT calculations. According to the results obtained from theoretical calculations, the first step is base-catalyzed propargyl-allene isomerization. The second step involved nucleophilic attack on either carbonyl carbon or center carbon of allene unit. The results showed that, bulky amines prefer to attack on center carbon of allene, while the aliphatic amines or allylic amines prefer to attack on carbonyl carbon.

CHAPTER 3

UNEXPECTED REGIOSELECTIVITY OBSERVED IN THE BROMINATION AND EPOXIDATION REACTIONS OF *P*-BENZOQUINONE-FUSED NORBORNADIENE: AN EXPERIMANTAL AND COMPUTATIONAL STUDY

3.1 Introduction

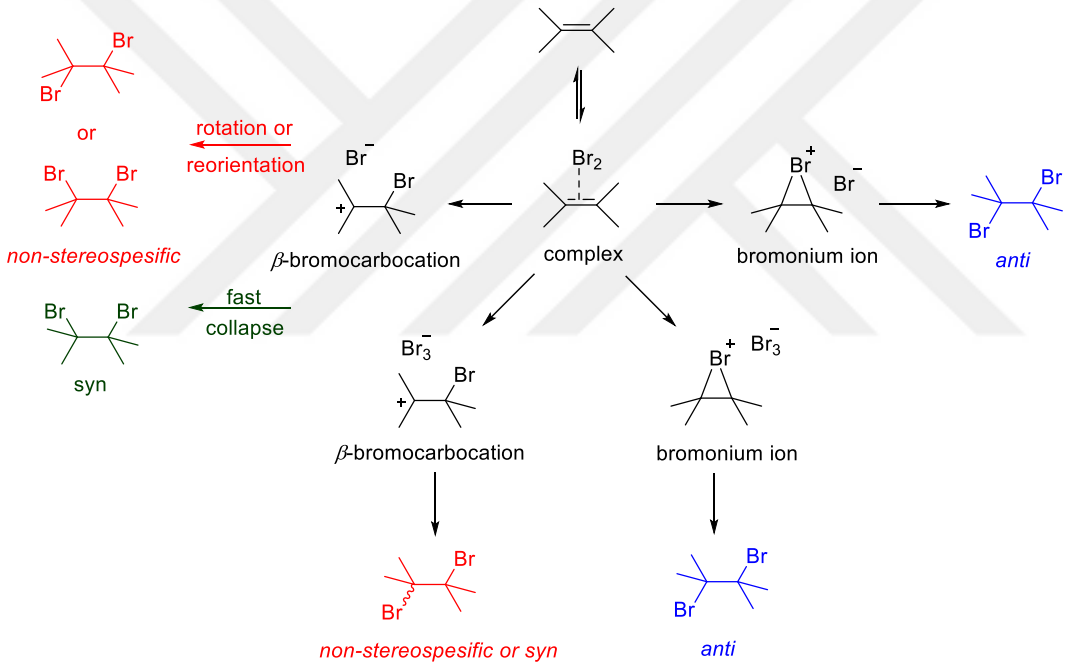
3.1.1 Bromination of Alkenes

Bromination of olefins is synthetically important process in organic chemistry.[37] Bromo-organics are utilized as pharmaceuticals, agrochemicals, polymers, fire retardants, insecticides and dyes.[38]

The mechanism of electrophilic bromination of olefins in both protic and aprotic solvents have been studied intensively over the last decade.[39] The proposed mechanism for the bromination starts with the formation of a complex between the alkene and Br_2. The next step is the generation of bridged intermediate or β-bromocarbocation (Scheme 48). The relative stability of the potential carbocation determines the formation of the possible intermediates.[40]

Bromination of aliphatic systems generally proceeds through bridged intermediate; however, styrenes are borderline cases. In styrenes, electron-donating substituents attached to the phenyl ring, stabilize the carbocation formed whereas, electron-withdrawing groups favor the bridged intermediate.[40]

In the final step, bromide or tribromide can attack either bridged ion or open carbocation. When the reaction proceeds through a bridged bromonium ion, bromide attacks from the backside, which results in the formation of an *anti*-addition product. However, an open bromocarbocation, having a free C–C rotation, can lead to the both *anti*- and *syn*-addition products. When the carbocation is an ion pair which collapses faster than rotation, *syn* addition is favored (Scheme 48). Stereochemical studies on bromination show that *anti* addition is favored for olefins without bearing substituents that can stabilize a cationic intermediate. On the other hand, *syn* addition can be preferred when the alkene is conjugated with an aryl group.[40]



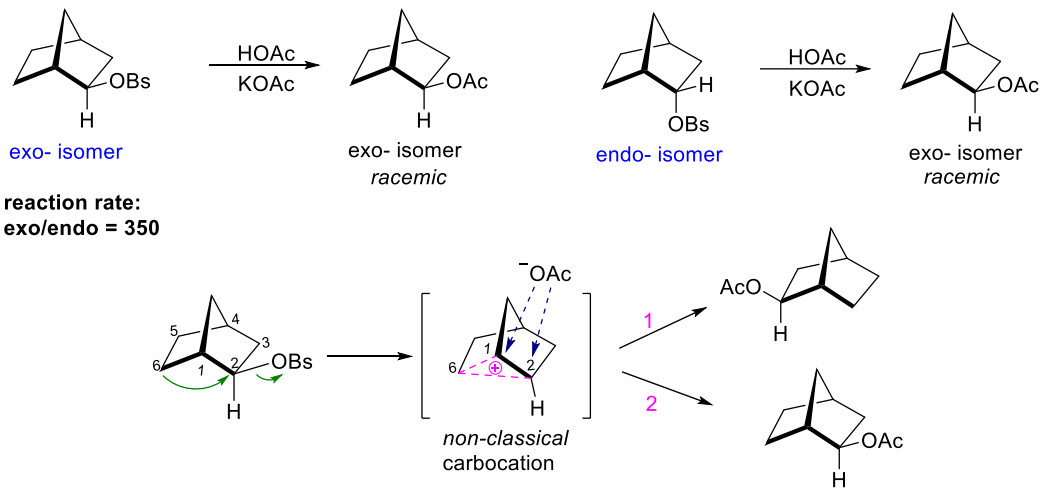
Scheme 48. Possible products for the bromination reaction

3.1.2 Non-Classical Carbocations

Carbocations are intermediates that contain a vacant orbital having a positive charge. Carbocations can be divided into two main groups: classical (trivalent)

carbenium ions and non-classical (pentacoordinate (or higher)) carbonium ions. Classical carbenium ions, which are electron deficient systems, involve the formation of two-electron, two-center bonds. For instance, CH_3^+ can be classified as classical carbenium ion. On the other hand, non-classical carbonium ions involve the formation of two-electron, three (or multi)-center bonds. For example, CH_5^+ can be considered as non-classical carbonium ion. Since two electrons are shared among three or more atoms, non-classical carbonium ions are also known as electron deficient species.[41]

Numerous studies on bridged systems, mostly norbornyl cation, have been performed to find whether its structure is classical or non-classical. The solvolysis in acetic acid of *exo- and endo*-2-norbornyl sulfonates yielded to exclusively *exo*-acetate product (Scheme 49). Besides, enantiomerically pure *exo*-brosylate (*p*-bromobenzenesulfonate) resulted in the formation of completely racemic *exo*-product, and similarly the *endo*-brosylate furnished 93% racemic product. This outcome shows that the reaction proceeds through an achiral species. According to Winstein, C1–C6 σ-bond electrons assisted to the solvolysis of *exo*-brosylate in acetic acid. He also proposed that the reaction proceeds through non-classical carbonium ion as an intermediate. Formation of racemic products can now be explained since the intermediate is achiral. It is also interesting to note that, *exo*-brosylate was found to be 350 times more reactive than *endo*-brosylate. The bridged ion can be observed only from the *exo*-brosylate, since both leaving group and C1–C6 σ-bond have *anti* orientation.[40]



Scheme 49. Solvolysis of *exo*- and *endo*-2-norbornyl sulfonates in acetic acid

3.1.3 Pyramidalization of Double Bond

The pyramidalized alkenes are the ones in which one or both sp^2 carbon atoms of the double bond are not coplanar with their attached atoms.[42]

Margetic *et al.*[43] defined the pyramidalization angle (ϕ) by using the butterfly-bending angle (ψ) which is specified as $\psi = 180° - [D1]$. The dihedral angle (*D1*) can be either C1–C2–C3–C4 or C5–C3–C2–C6 (Figure 27).

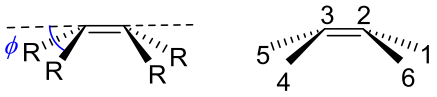


Figure 27. Representation of pyramidalization angle (ϕ)

For instance, the direction of pyramidalization in norbornene (**121**) and norbornadiene (**122**) is *endo* and pyramidalization angles are calculated as 7° and 2.4°, respectively (Figure 28). Furthermore, the double bond of *syn*-sesquinorbornene (**123**) is strongly pyramidalized in the *endo* direction about 16–

18°. However, *exo* pyramidalization is observed in the double bonds of bicyclo[2.2.2]octadienes.[42]

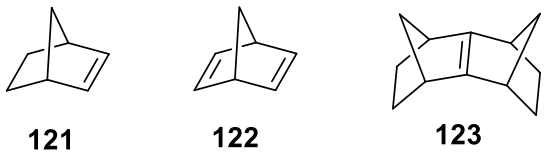


Figure 28. Structures of norbornene (**121**) and norbornadiene (**122**) and *syn*-sesquinorbornene (**123**)

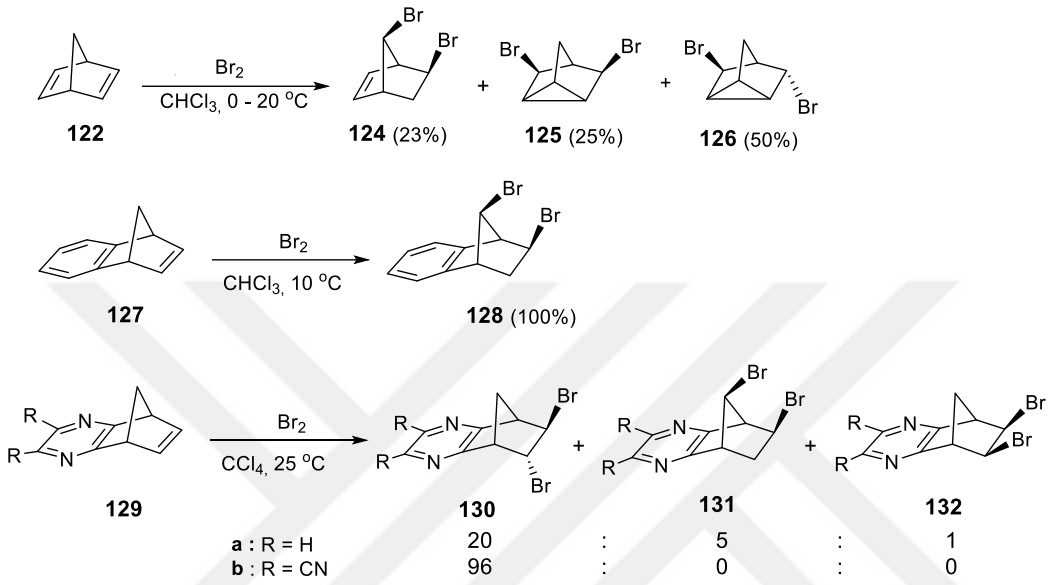
Because of the pyramidalization, electron density on the two faces of the double bond are not equivalent. This unusual behavior give rise to a π-facial stereoselectivity in electrophilic addition reactions to double bonds.[44] For example, adducts formed in the bromination reaction of norbornadiene and benzonorbornadiene can be affected from the double bond pyramidalization. *exo*-Attack is observed since the double bonds of these molecules are pyramidalized in the *endo* direction.[45]

3.1.4 Bromination of Strained Cyclic Compounds

The mechanism of the electrophilic bromination of alkenes is well known in literature; however, the bromination of strained bicyclic systems is more complicated. For example, treatment of norbornadiene (**122**) with bromine in chloroform led to formation of the products **124**–**126** which were derived from Wagner-Meerwein rearrangement and homoallylic conjugation (Scheme 50).[46] When the bromination was performed with benzonorbornadiene (**127**) at 10 °C, only the rearranged product **128** was obtained.[47]

Kobayashi and Miki[48] reported a bromination reaction of norbornadiene-fused pyrazine derivatives **129a** yielding *trans- and cis*-rearranged products **130-132a** in

a ratio of 20:1:5, respectively. However, the reaction of dicyanopyrazine derivative **129b** with bromine afforded exclusively *trans*-product **130b**. These results show that charge density on the ring affects the structure of products obtained in the bromination reactions.



Scheme 50. Reaction of norbornadiene and benzonorbornadiene derivatives **122**, **127** and **129** with bromine

3.1.5 Epoxidation of Alkenes

Epoxidation is a powerful methodology for the construction of oxirane rings.[49] Peracids such as *m*-chloroperoxybenzoic acid (*m*–CPBA) and dioxiranes have been utilized as an effective oxidizing agents for alkenes.[50,51] According to the experimental results, dimethyldioxirane (DMDO) is found to be more reactive than peracids in the epoxidation of alkenes.[51] For instance, epoxidation of cyclohexene with DMDO is 74 times faster than epoxidation with perbenzoic acid.[51] The proposed mechanism for the epoxidation does not include ionic intermediates and the reaction is assumed to be a concerted process (Figure 29).[40] Electron releasing

groups attached to the alkenes increase the rate of the epoxidation. Unconjugated alkenes are more reactive than alkenes having aromatic groups since the reaction does not include carbocation character in the transition state. On the other hand, electron-withdrawing groups attached to the peroxy acids increase the rate of the epoxidation, which shows that the peroxy acids have electrophilic character in the reaction.[40]

In 1950, Bartlett suggested the "butterfly" transition structure in which the peroxy acid and C=C bond axis lie in the same plane.[49,52,53] Recent high-level calculations by Bach *et al.* and Houk *et al.* demonstrated that transition states having a spiro geometry (in which peroxy acid plane is approximately perpendicular to the C=C bond axis) are found to be more stable than its planar counterpart (Figure 29).[52,53]

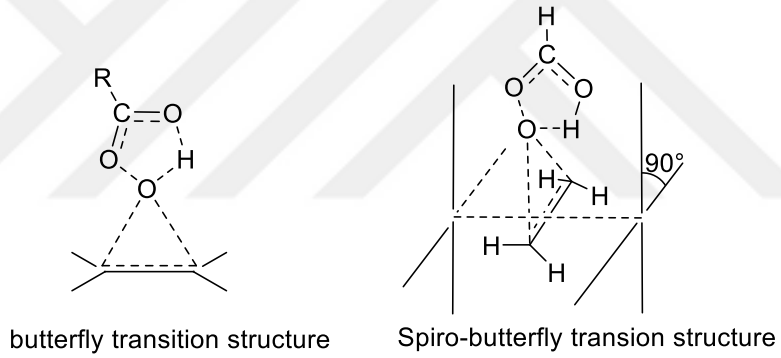
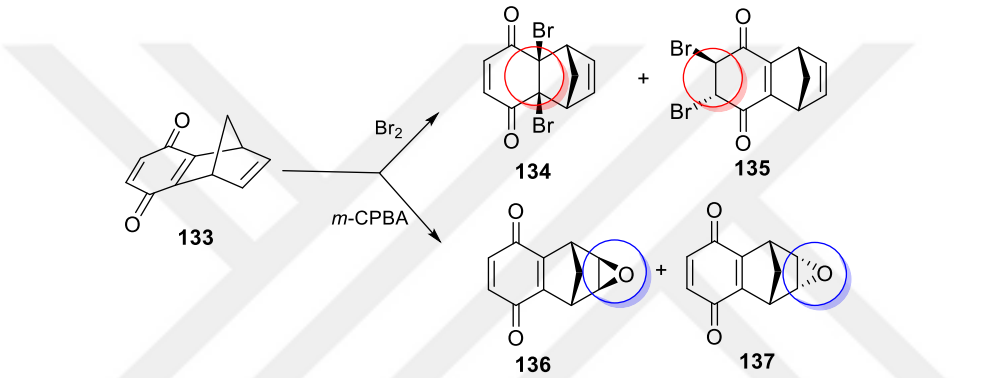


Figure 29. Proposed transition structures for the epoxidation of olefins

3.1.6 Objective of the Study

In this part, regioselectiviy and stereoselectivity of bromination and epoxidation of *p*-benzoquinone-fused norbornadiene **133** were studied (Scheme 51). The reaction of compound **133** with bromine was investigated at various temperatures (-78, -50, 0, 25, and 77 °C) by Essiz *et al.*[54] At room temperature, the major products **134** and

135 were obtained by the attack of the bromine on the double bonds of *p*-benzoquinone unit. However, minor product **140** (2% yield) was obtained by the attack of the bromine on the double bond of the norbornene unit (Scheme 51). On the other hand, the epoxidation reaction of compound **133** with *m*-CPBA or DMDO (dimethyldioxirane) yielded the products derived from the epoxidation of the double bond of norbornadiene unit. We herein theoretically investigated the mechanism of bromination and epoxidation reactions as well as the effect of double bond pyramidalization on the outcome of the bromination.[54]

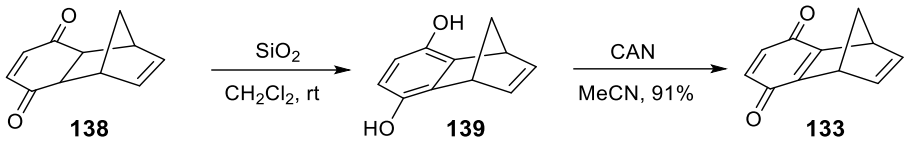


Scheme 51. Bromination and epoxidation of *p*-benzoquinone-fused norbornadiene **133**

3.2 Results and Discussion

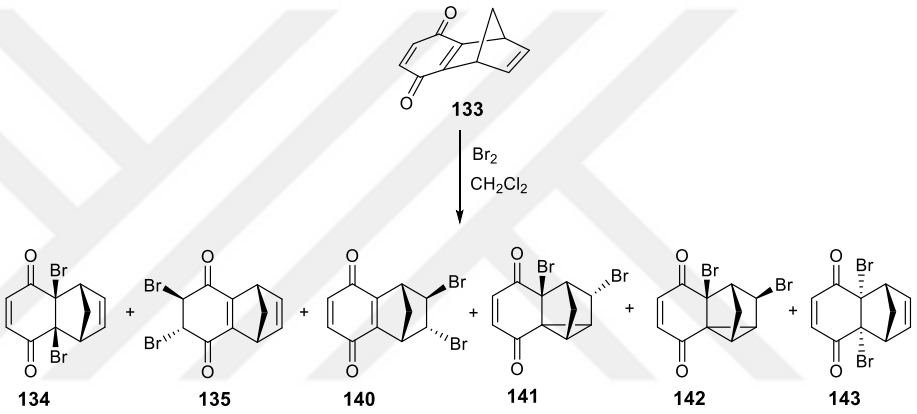
3.2.1 Bromination of *p*-Benzoquinone-Fused Norbornadiene 133

The key structure, (1*R*,4*S*)-1,4-methanonaphthalene-5,8(1*H*,4*H*)-dione (**133**), was synthesized by starting from enedion **138** as described in Scheme 52.[54]



Scheme 52. Synthesis of *p*-benzoquinone-fused norbornadiene **133**

Treatment of compound **133** with bromine at various temperatures, resulted in the formation of different products as shown in Scheme 53. Formation of two major products (**134** and **135**) and four minor products (**140**-**143**) were observed at room temperature.[54]

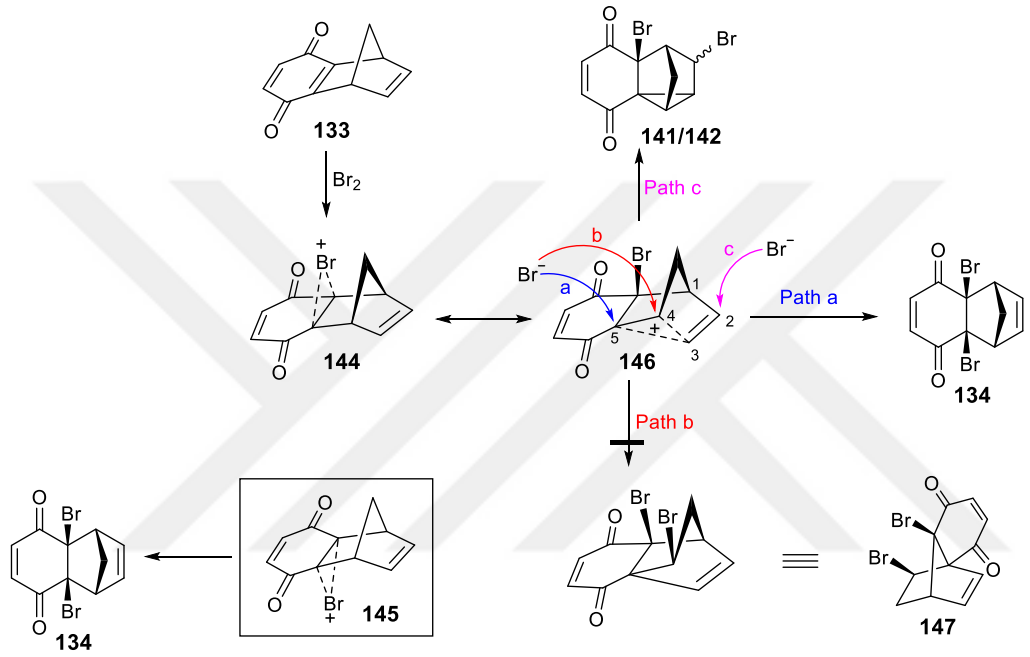


Temperature	Yields in %					
	134	**135**	**140**	**141**	**142**	**143**
77 °C	50	50	-	-	-	-
25 °C	47	45	2	2	1	1
0 °C	44	42	8	2	1	1
-50 °C	-	-	63	17	13	-
-78 °C	-	-	64	15	14	-

Scheme 53. Addition of bromine to **133** at various temperatures

As mentioned above, in bromination reactions, *anti* addition is favored over *syn* addition. Therefore, formation of syn products **134** and **143** is unexepected. In addition, *exo* attack is mainly observed due to pyrimidalization of the double bond in **133**. The mechanism for the formation of **134** is thought to proceed by electrophilic attack of bromine from the *exo* face of the double bond. After the

formation of corresponding bromonium ion **144**, non-classical carbocation **146** is formed by an alkyl shift (Scheme 54). The bromide ion can either attack to the C5 (path a) or C4 (path b) to generate the **134** and **147**, respectively. Compound **134** was the major product for the bromination reaction; however, compound **147** was not observed. We also assume that the minor product **143** was formed via intermediate **145**.[54]



Scheme 54. Proposed mechanisms for formation of **134**, **141** and **142**

It should be also noted that one of the stereoisomer **134** was observed as the major product while the other isomer **143** was the minor product. This can be attributed to the *endo*-pyrimidalization in **133**. DFT calculations were carried out in order to calculate the pyrimidalization angle in **122** and **133** at M06-2X[55]/6-31+G(d,p) level (Figure 30). The dihedral angle C1-C2-C3-H3 is 176.7 in **122** and 176.9 in **133**, indicating that the degree of pyrimidalization is very close in these compounds.[54]

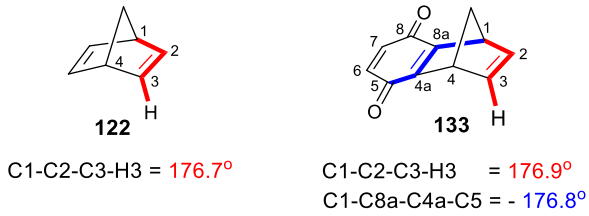


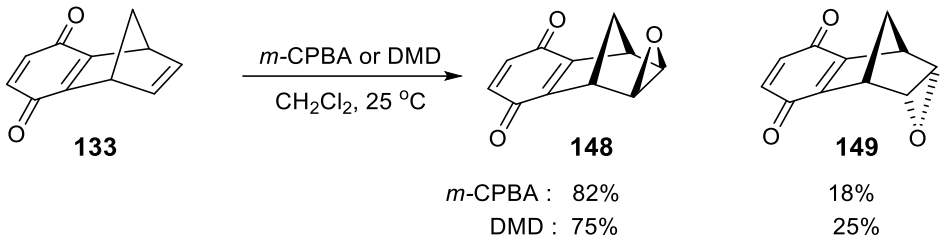
Figure 30. Pyramidalization angles of compound **122** and **133** at the M06-2X/6-31+G(d,p) level.

In order to understand the regio- and stereoselectivity of bromination, the reaction was also carried out at various temperatures. In this case, compounds **140**, **141** and **142** were observed with yields of 63%, 17%, and 13% at -50°C and 64%, 15%, and 14% at -78°C, respectively (Scheme 53). The major product **140** was formed by the *anti* attack of bromine to norbornene double bond. However, when the reaction temperature was increased to 0 °C, the product distribution changed and the results were found very similar to the results obtained at 25°C.

Bromination reaction was also investigated at 77 °C. The high temperature bromination gave a mixture of **134** and **135** in the same ratio (Scheme 53). Rearranged products were not observed since the bromination at high temperature follows a different reaction mechanism, which proceeds through radicals. It is widely known that the radicals have a low tendency for rearrangements.[54]

3.2.2 Epoxidation of *p*-Benzoquinone-fused Norbornadiene 133

To elucidate the regio- and stereoselectivity, starting material **133** was submitted to the epoxidation reaction with *m*-chloroperbenzoic acid (m-CPBA) and dimethyldioxirane (DMDO) by Essiz *et al.*[54] Two epoxides were formed as depicted in Scheme 55. It is interesting to note that epoxidation was only observed in norbornene double bond.

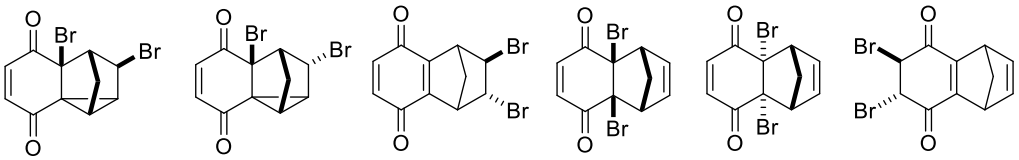


Scheme 55. Epoxidation of *p*-benzoquinone-fused norbornadiene **133**

3.2.3 Theoretical Calculations on Bromination and Epoxidation of 133

The regio- and stereoselectivity in bromination and epoxidation of **133** were studied by means of theoretical calculations. Compound **133** has three double bonds which can undergo epoxidation and bromination reactions from *endo*- and the *exo*-faces. Firstly, the relative energies of possible bromination products were calculated as shown in Table 1. Calculations indicate that compound **142** is thermodynamically most stable product; however, it was observed in only 1% yield. On the other hand, one of the major product **134** was clearly found as the less stable product.[54]

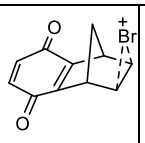
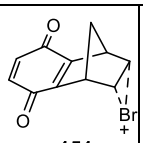
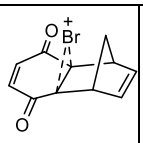
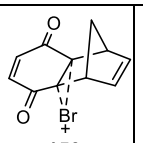
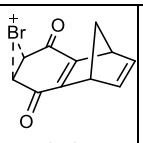
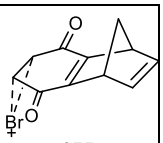
Table 1. Calculated relative enthalpies of six possible products using M06-2X/6-31+G(d,p) level in kcal/mol



In order to understand the formation of the major products, relative energies of possible bromonium ions were also calculated (Table 2). According to the calculations, bromonium-cation complexes **150**, **151** and **152** were found as thermodynamically most stable intermediates. Unfortunately, only the formation of

152 was in agreement with the experimental results at room temperature. However, compound **140** derived from bromonium ions **150** and **151**, was observed as the minor product.[54]

Table 2. Calculated relative enthalpies of six possible bromine-cation complexes using M06-2X/6-31+G(d,p) level in kcal/mol

Bromine-cation Complexes	 **150**	 **151**	 **152**	 **153**	 **154**	 **155**
Energy Differences	-3.5	-1.0	0.0	6.7	18.3	18.9

Natural Bond Orbital (NBO) analysis was also performed to show the charge distribution in **133.** Based on the results, negative charges are mainly located on the C2–C3 and C6–C7 carbon atoms (Figure 31). Thus, bromine is expected to attack on more negatively charged double bond in **133**. Formation of one of the major products **135**, which is derived from the addition of bromine to the quinoid double bond, is in agreement with the NBO analyses. However, the formation of the other major product **134** cannot be explained with the charge distribution.

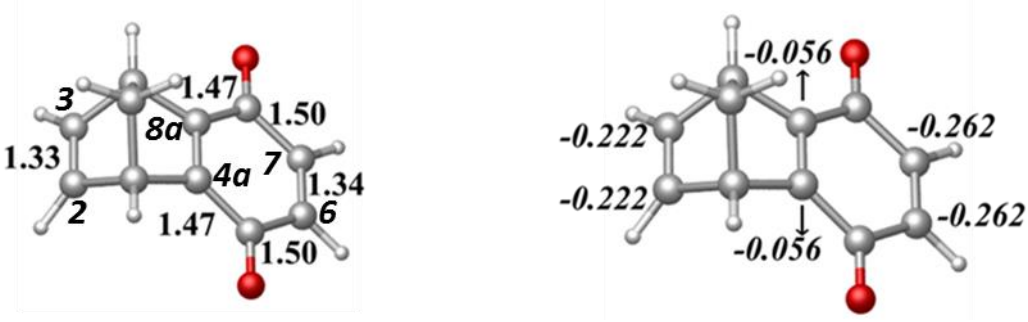


Figure 31. Geometry optimized structure of **133** and NBO analysis using M06-2X method and a basis set 6-31+G(d,p). Distances are given in Å. (carbon, grey; oxygen, red; hydrogen, white).

In addition, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) analyses of **133** have been carried out using M06-2X method (Figure 32). HOMO is mainly located over norbornene double bond whereas LUMO is located over the benzoquinone ring.

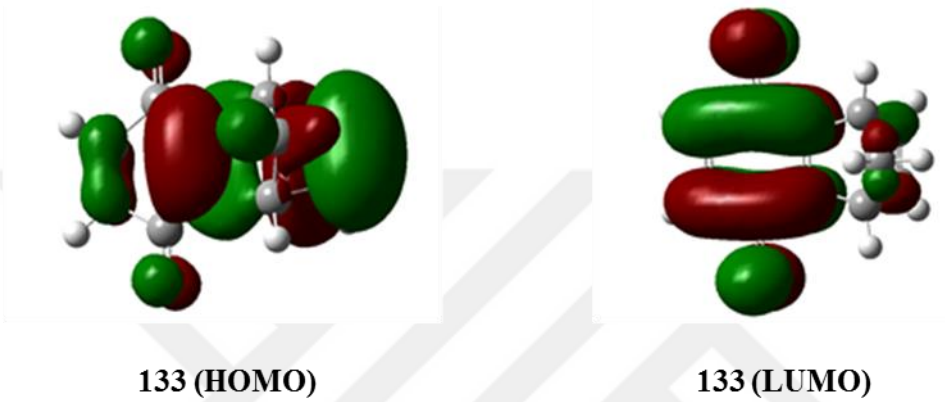


Figure 32. The calculated highest occupied (HOMO) and lowest unoccupied (LUMO) MOs of **133**

We have also located the transition structures corresponding to the formation of non-classical carbocations **156** and **157** via sigma bond participation (Figure 33).

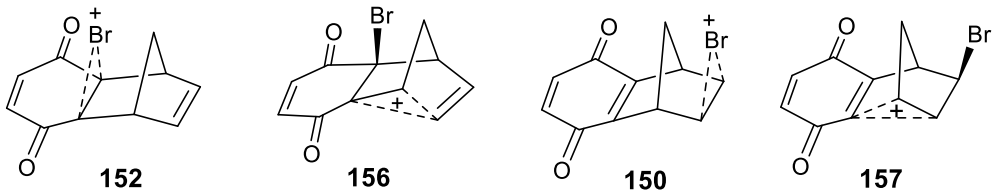


Figure 33. The structures of bromonium ions **152** and **150**, and non-classical carbocations **156** and **157**

Optimized geometries of bromonium ion complexes (**152** and **150**), transition states, and non-classical carbocations are depicted in Figure 34. **TS24** requires an

activation free energy of 0.44 kcal/mol with respect to the energy of **152**. On the other hand, the activation barrier associated with **TS25** is 2.92 kcal/mol. Therefore, the formation of non-classical carbocation **156** is energetically more favorable than the formation of **157**. These calculated energies are in good agreement with the experimental results.

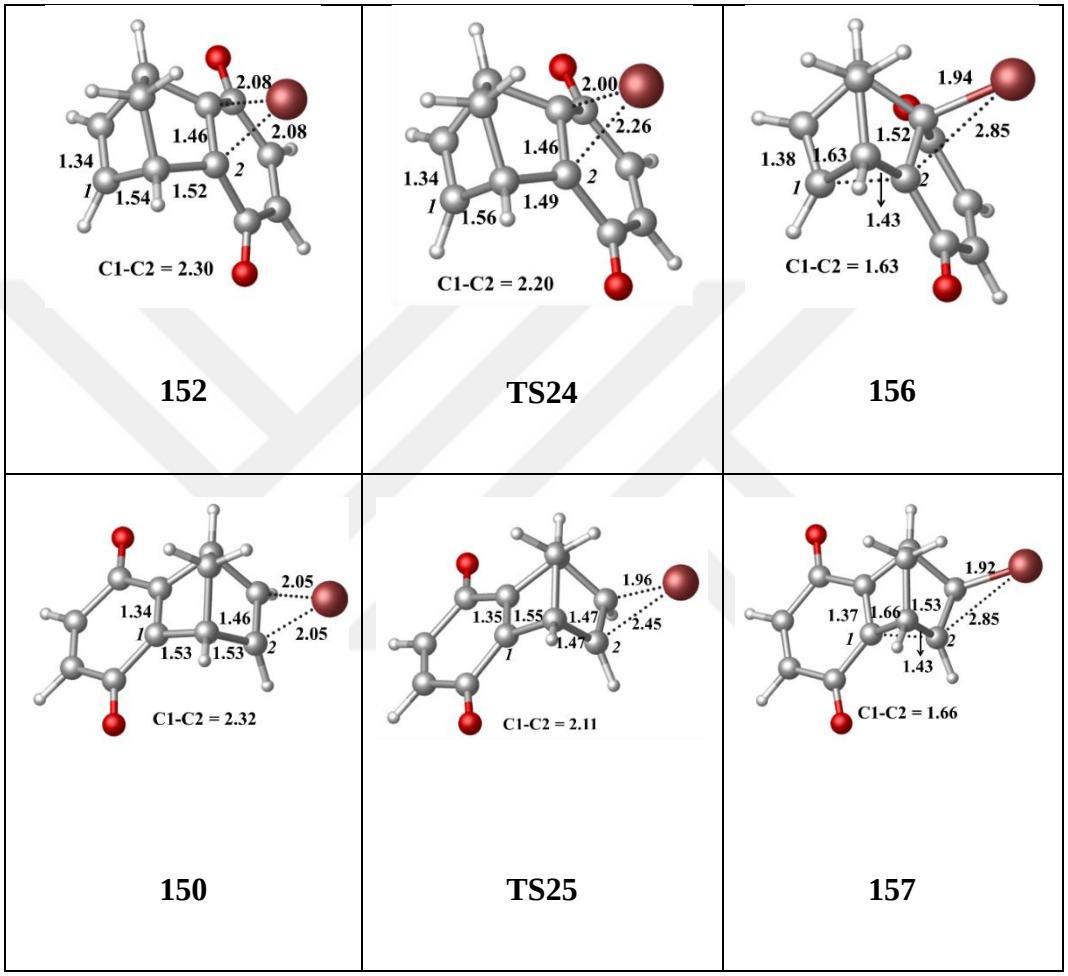
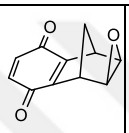
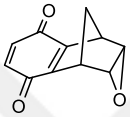
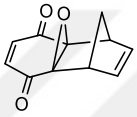
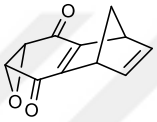
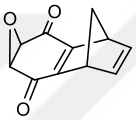
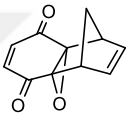


Figure 34. Optimized geometries of bromonium ion complexes (**152** and **150**), transition structures (**TS24** and **TS25**), and non-classical carbocations (**156** and **157**) at the CPCM/M06-2X/6-31+G(d,p)//M06-2X/6-31+G(d,p) level in DCM. Distances are given in Å. (carbon, grey; oxygen, red; bromine, dark red; hydrogen, white).

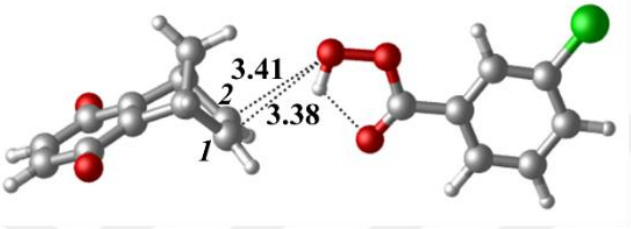
As mentioned above, bromination of **133** took place on the quinoid double bonds; however, epoxidation of **133** with *m*-CPBA led to a 4:1 mixture of **148** and **149**. In order to explain the experimentally observed regioselectivity and stereoselectivity, we first calculated the relative enthalpies of the six possible epoxides at B3LYP/6-31+G(d,p) level (Table 3).

Table 3. Relative energies of **148**, **149**, and **158-161** and activation barriers of each step for the formation of possible epoxides (in kcal/mol) at B3LYP/6-31+G(d,p) level. (Activation barriers are calculated with respect to the reactant complex of each step)

Epoxides	 **148**	 **149**	 **158**	 **159**	 **160**	 **161**
Relative Energies	-10.2	-6.8	-2.6	0.0	-0.4	+1.4
Activa-tion energies in Gas Phase	16.5	18.8	22.9	23.1	23.5	26.7
Activa-tion energies in CH_2Cl_2 (CPCM)	14.0	15.9	22.7	22.1	22.5	26.5

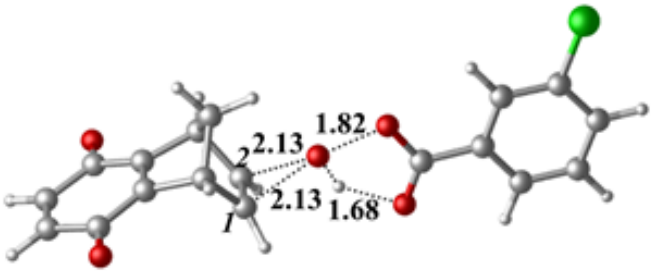
Structures **148** and **149** was found to be more stable than the other products. DFT calculatios accurately describes the observed product distribution. Furthermore, transition states for the epoxidation reaction were modeled using B3LYP/6-31+G(d,p) method in gas phase and DCM. Six different transition state arrangements are possible, differing in regiochemistry and stereochemistry (endo vs exo attack to the three different double bonds). Optimized geometries are depicted in Figure 35. The stereochemical outcome (formation of major product **148**) is largely dictated by the *endo*-pyramidalization of the double bond in **133**.

Therefore, attack from the *exo*-face is mainly preferred. The predicted energy barriers for the epoxidation of norbornene double bond in DCM via **TS26** and **TS27** are lower than other possible transition states (**TS28-31**). The results of our calculations indicate that formation of structures **148** and **149** is both kinetically and thermodynamically more favorable than the formation of other possible epoxides. The computational results described herein correlates well with experimental data.[54]



C1-C2 = 1.34

RC1 (133+162)

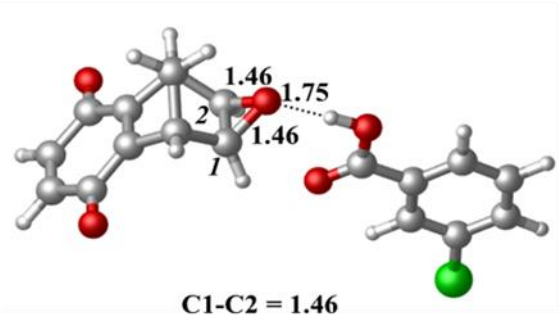


C1-C2 = 1.37

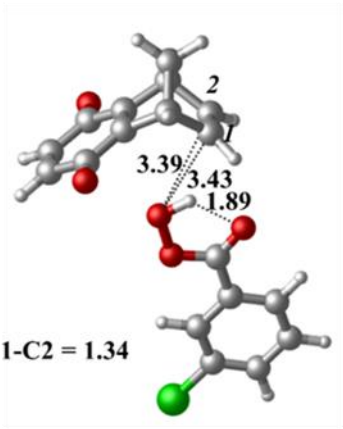
TS26

Figure 35. Optimized geometries for stationary points of epoxidation reactions at B3LYP/6-31+G(d,p) level in gas phase. Distances are given in angstroms; angels are in degrees. (carbon, grey; oxygen, red; chlorine, green; hydrogen, white)

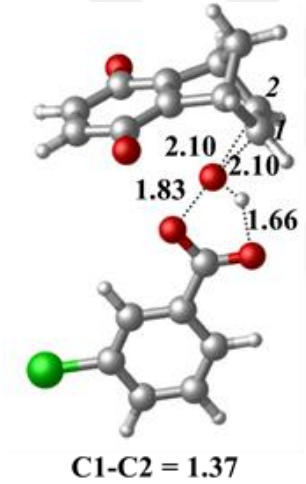
Figure 35 (continued)



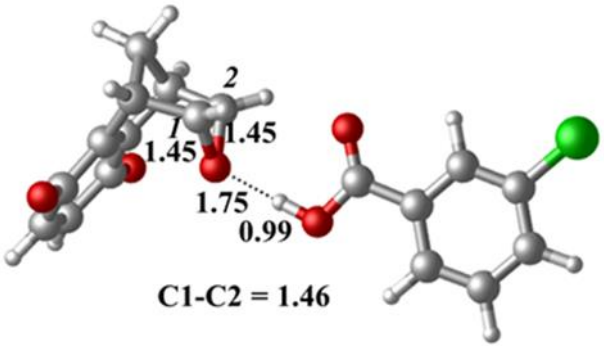
PC (148+163)



RC2 (133+162)

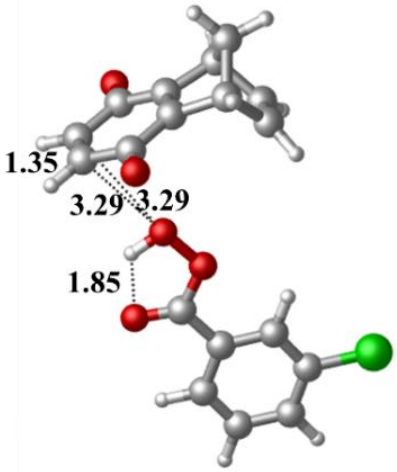


TS27

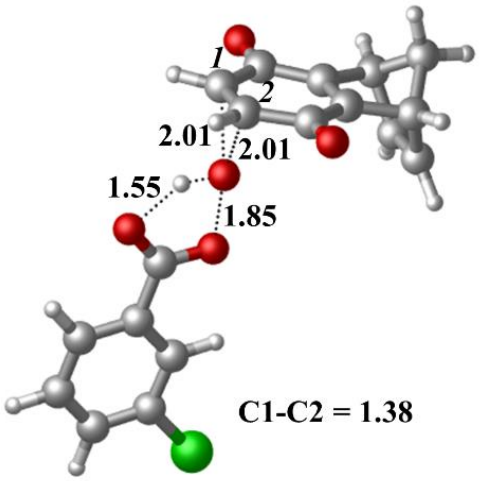


PC(149+163)

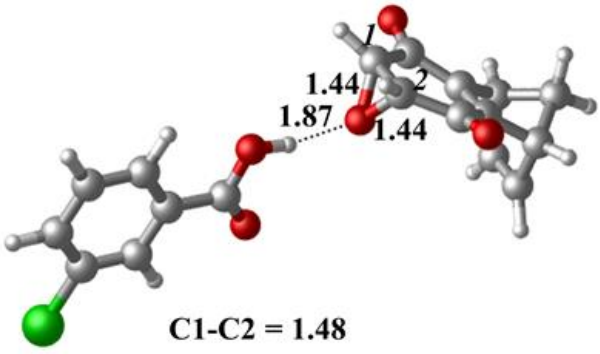
Figure 35 (continued)



RC3 (133+162)

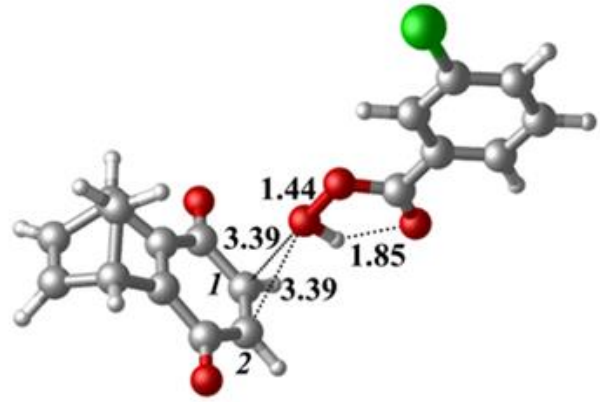


TS28

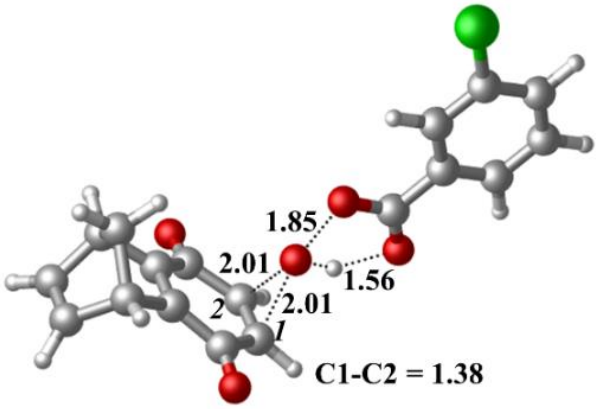


PC (159+163)

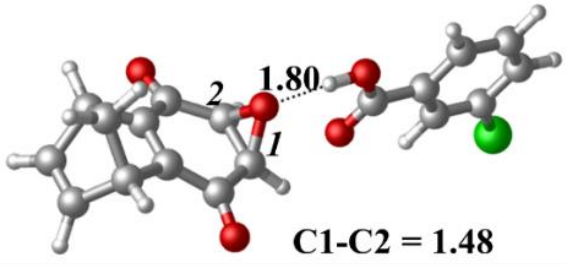
Figure 35 (continued)



RC4 (133+162)

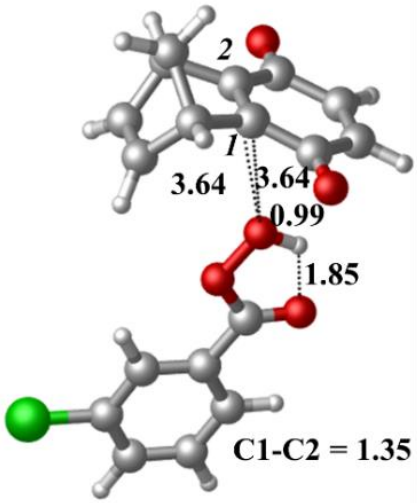


TS29

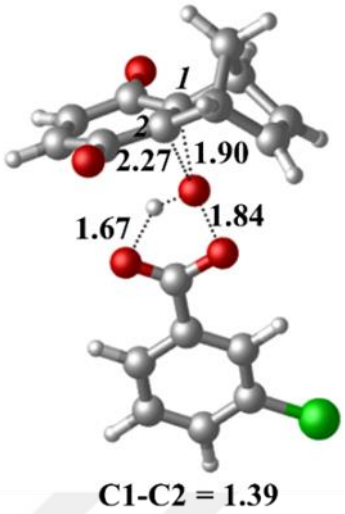


PC (34+163)

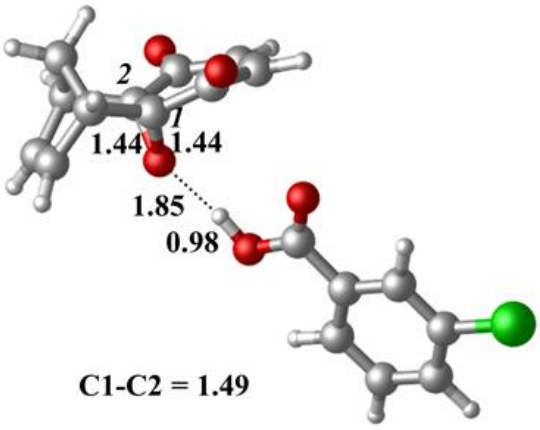
Figure 35 (continued)



RC5 (133+162)

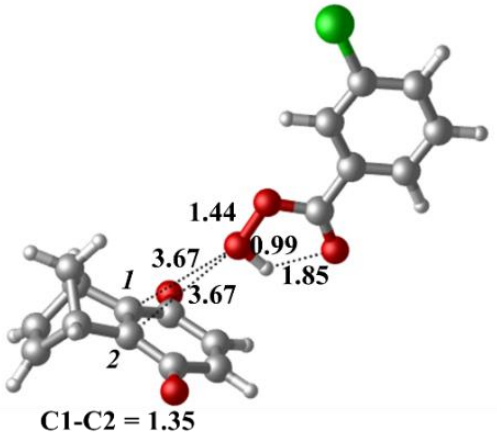


TS30

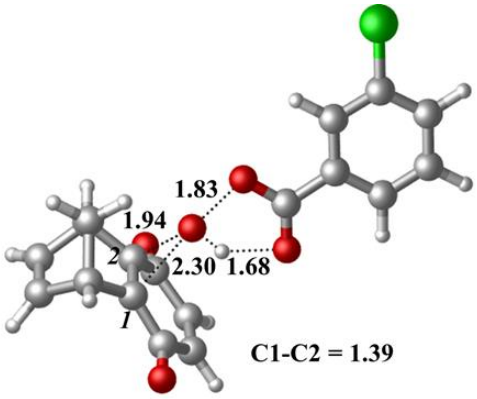


PC (161+163)

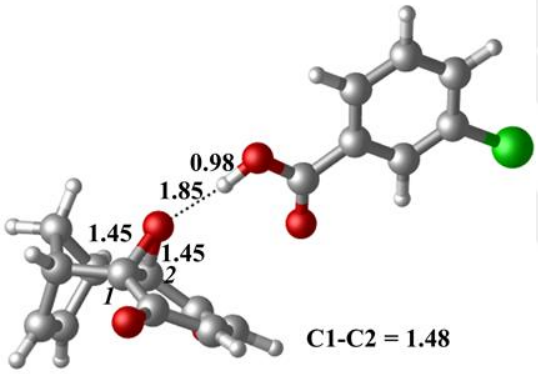
Figure 35 (continued)



RC6 (133+162)



TS31



PC(158+163)

We herein described the regioselectivity and stereoselectivity observed in the epoxidation and bromination of norbornadiene **133**. At room temperature, the major products **134** and **135** were formed by the attack of bromine on the double bonds of *p*-benzoquinone unit. However, epoxidation of **133** took place from only the norbornadiene unit. To understand these results, relative energies of products and intermediates were calculated. In addition, activation barriers for the formation of products and intermediates (non-classical carbocations) were computed. Computational results are good agreement with experimental observations.

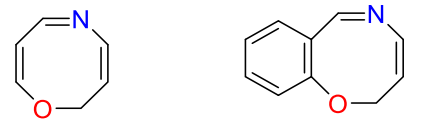
CHAPTER 4

COMPUTATIONAL MODELING OF THE MECHANISM FOR THE FORMATION OF BENZO-PYRAZOLO-OXAZOCINES AND BENZO-PYRAZOLO-OXAZEPINES VIA GOLD CATALYSIS

4.1 Introduction

4.1.1 Benzoxazocines and Benzoxazepines

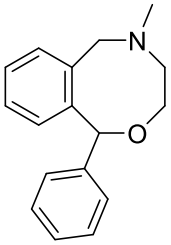
1,5-Oxazocine is eight-membered unsaturated heterocyclic system having one oxygen atom, one nitrogen atom and six carbon atoms. Benzoxazocine is heterocyclic compound that composed of a benzene ring fused to an oxazocine ring (Figure 36).[56]



Oxazocine Benzoxazocine

Figure 36. Structures of oxazocine and benzoxazocine

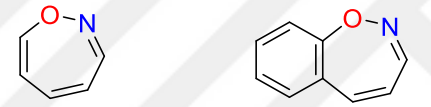
Oxazocine derivatives are of great interest in various aspects because of their biological properties. It was noted that dibenz[*b*,*f*][1,5]oxazocines are effective as neurotropic agents, such as antidepressants, analgesics, and sedatives. For instance, the benzoxazocine nefopam is utilized as a non-opioid analgesic (Figure 37).[57]



Nefopam

Figure 37. Structure of Nefopam

1,2-Oxazepine, on the other hand, is a seven-membered unsaturated heterocyclic system having one oxygen atom, one nitrogen atom and five carbon atoms.[57,58] Benzoxazepine is a heterocyclic compound that composed of a benzene ring fused to an oxazepine ring (Figure 38).[57]



Oxazepine Benzoxazepine

Figure 38. Strucutures of oxazepine and benzoxazepine

Synthesis of 1,4-oxazepines has attracted much attention from synthetic organic chemists due to their biological properties such as histone deacetylase inhibitions and antitumor activity. Besides their applications in medicinal chemistry, 1,4-oxapines have also been utilized for the synthesis of secoiridoids and monoterpenoid alkaloids.[59] In particular, benzoxazepine derivatives are valuable materials that serve as core structural components for various drugs like amoxapine, loxapine, and sintamil (Figure 39).[59] In addition, compounds that include this core act as a non-nucleoside HIV-1 reverse transcriptase inhibitor, a histamine receptor agonist, calcium antagonists, antidepressants and analgesics. For example,

benzo[*b*][1,4]oxazepine derivatives show antidepressive and anxiolytic activity and they are utilized for the treatment of bronchial asthma and allergic bronchitis. Tetrahydrobenzo[*b*][1,4]oxazepines, on the other hand, show anticancer activity against breast cancer cells.[60]

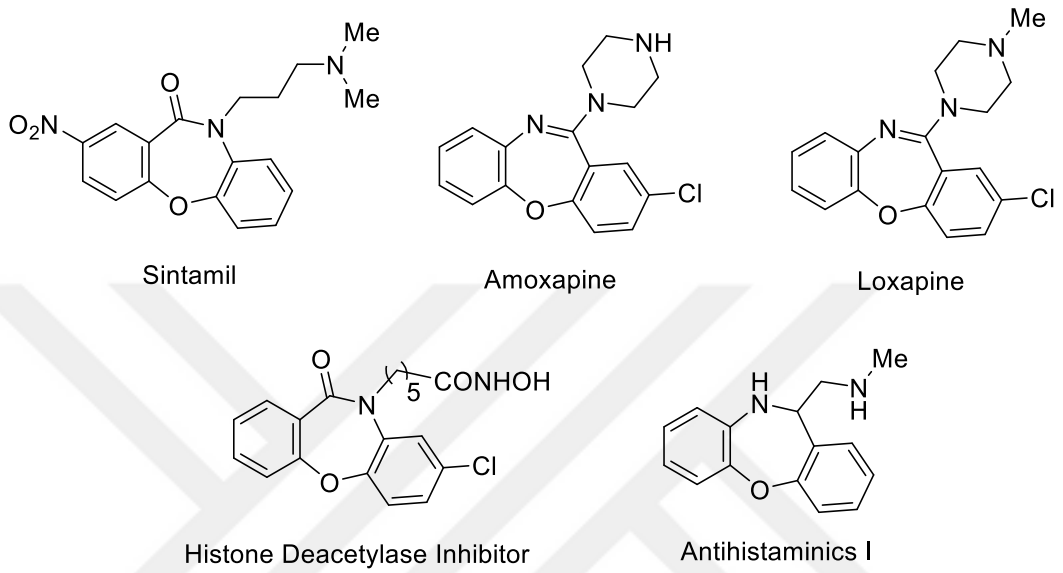
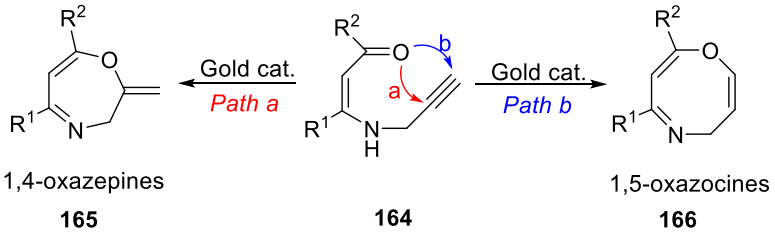


Figure 39. Structures of 1,4-oxazepine derivatives

Due to their unique biological properties, synthesis of these compounds have been examined by number of researchers, and several synthetic methods have been reported. However, the preparation of these compounds often requires multiple steps and can be challenging.[59]

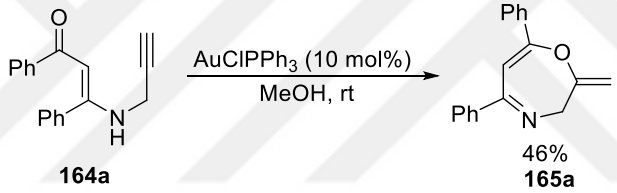
4.1.2 Synthesis of Benzoxazocines and Benzoxazepines

Gold-catalyzed cyclization reaction of *N*-propargylic *β*-enaminone **164** lead to two possible cycloadducts as shown in Scheme 56. The authors proposed that the rection can take place through either 7-*exo*-dig pathway to provide 1,4-oxazepines **165** or 8-*endo*-dig pathway to give 1,5-oxazocines **166**.[59]



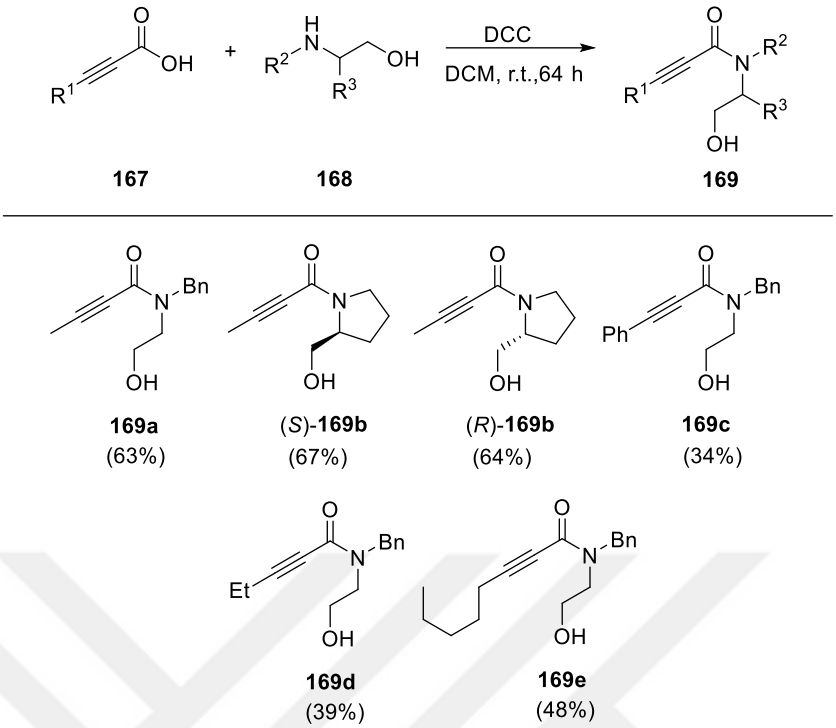
Scheme 56. Synthetic approach for the formation of oxazepine and oxazocine derivatives **165** and **166**

As shown in Scheme 57, the cyclization reaction of **164a** (1 equiv) in presence of $AuClPPh_3$ as a catalyst (10 mol %) resulted in the formation of 1,4-oxazepine derivative **165a** in 46% yield. However, any trace amount of 1,5-oxazocine derivatives were not observed.[59]



Scheme 57. Synthesis of 1,4-oxazepine derivative **165a**

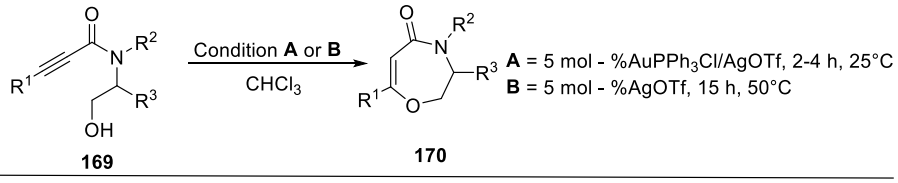
Recently, the synthesis of oxazepines using cycloisomerization of hydroxypropargylamides with a gold or silver catalyst has been reported.[61] Hydroxypropargylamides **169** were prepared from the coupling reaction of amino alcohols **168** with 3-substituted propiolic acids **167** according to the procedure shown in Scheme 58.



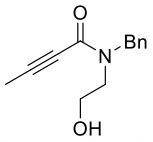
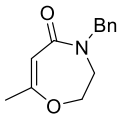
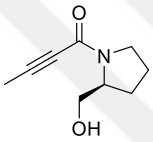
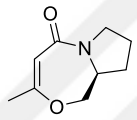
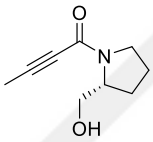
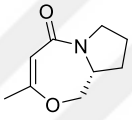
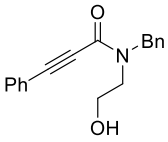
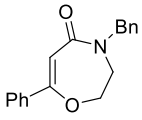
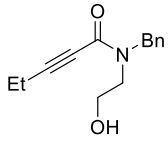
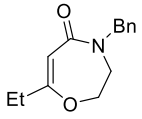
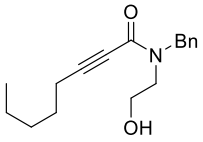
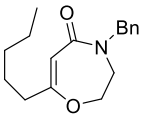
Scheme 58. Synthesis of hydroxypropargylamides **169**

Treatment of hydroxypropargylamides **169** with gold and silver catalysts in $CHCl_3$ furnished the target oxazepine derivatives **170** in good to high yields (Table 4). The reaction was thought to proceed through 7-*endo-dig* cycloisomerization.[61]

Table 4. Cyclization of hydroxypropargylamides **169** with gold and silver catalysts



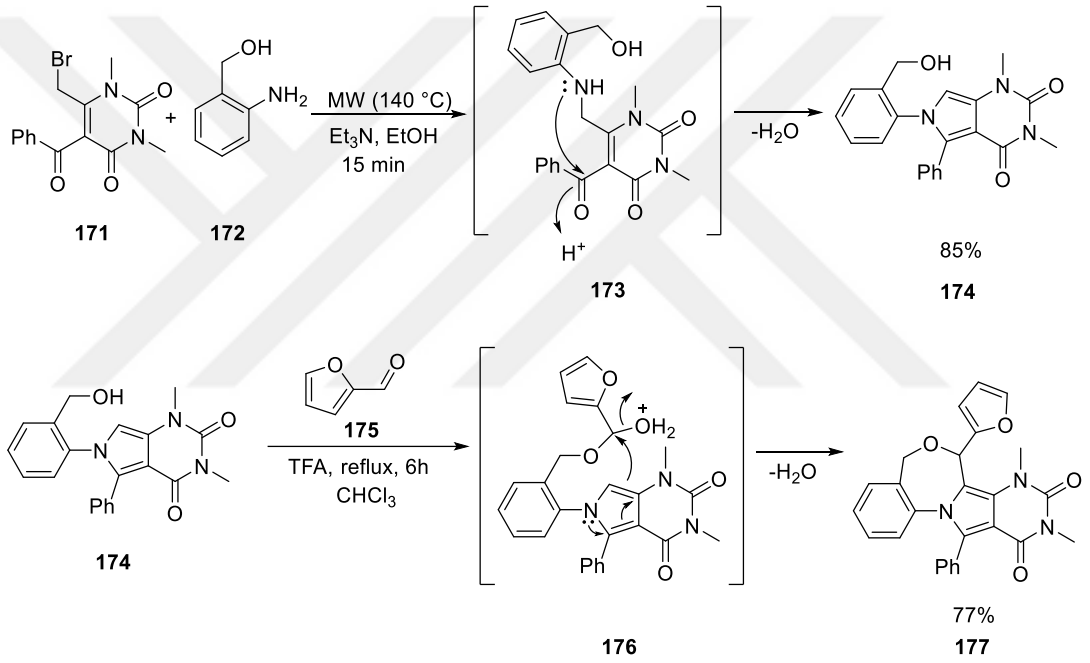
169 **170**

Starting Material	Oxazepine	Yield (%)[a]	
		Conditions A	Conditions B
 **169a**	 **170a**	96	91
 **(*S*)-169b**	 **(*S*)-170b**	95	89
 **(*R*)-169b**	 **(*R*)-170b**	96	–
 **169c**	 **170c**	73	74[b]
 **169d**	 **170d**	84	86
 **169e**	 **170e**	90	86

[a] Yield of isolated product. [b] 20 mol-% of AgOTf was utilized, and the reaction was perfomed for 20 h.

Sun and Chung *et al.*[62] reported an efficient synthesis of 1,4-oxazepine derivative **177**. The key structure, pyrrole derivative **174**, was obtained by the reaction of compound **171** with *o*-amino phenyl methanol **172** under the microwave irradiation at 140 °C (Scheme 59). The cyclization of intermediate **173** was thought to proceed by nucleophilic attack of aniline nitrogen on carbonyl carbon attached to the phenyl ring.

Pyrrolo-1,4-oxazepine dione **177** was synthesized by the reaction of compound **174** with aldehyde **175** at reflux temperature of chloroform (Scheme 59).[62]

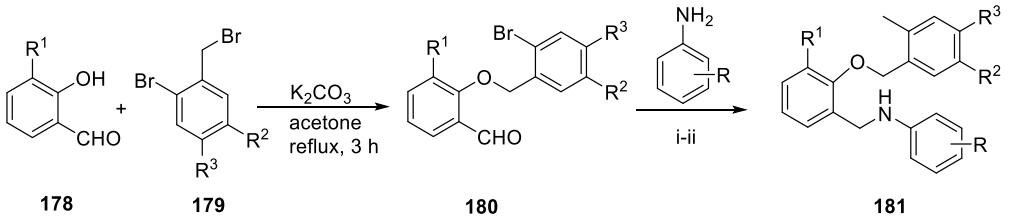


171 172 173 174 174 175 176 177

Scheme 59. Synthesis of 1,4-oxazepine derivative **177**

Mitra *et al.*[57] developed a synthetic approach for the preparation of dibenz[*b,f*][1, 5]oxazocines **182** using Pd catalyst. Treatment of salicyl aldehyde derivatives **178** with compound **179** in presence of anhydrous potassium carbonate led to the formation of key structures **180a-d** in 92-95% yield. Afterward, compounds **180a-**

d were converted into the amine derivatives **181** from the reaction with substituted anilines and followed by $NaBH_4$ reduction (Scheme 61).

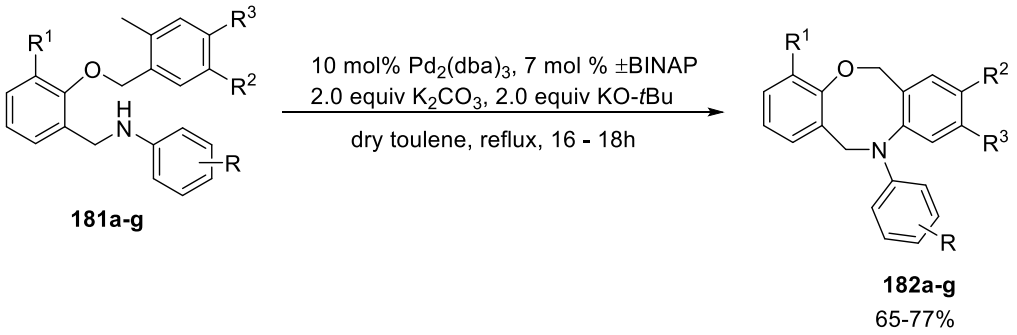


180a = $R^1 = R^2 = R^3$ = H, 93%
180b = $R^1 = R^3$ = H, R^2 = OMe, 92%
180c = R^1 = OMe, $R^2 = R^3$ = H, 95%
180d = R^1 = OMe, $R^2 + R^3$ = O-CH_2-O, 93%

181a = R = $R^1 = R^2 = R^3$ = H, 72%
181b = R = $R^1 = R^3$ = H, R^2 = OMe, 68%
181c = R = 4-OMe, $R^1 = R^2 = R^3$ = H, 74%
181d = R = 4-OMe, R^1 = OMe, $R^2 = R^3$ = H, 75%
181e = R = 2-OMe, R^1 = OMe, $R^2 = R^3$ = H, 74%
181f = R = H, R^1 = OMe, $R^2 + R^3$ = O-CH_2-O, 72%
181g = R = 4-OMe, R^1 = OMe, $R^2 + R^3$ = O-CH_2-O, 71%
181h = R = 4-NO_2, R^1 = OMe, $R^2 + R^3$ = O-CH_2-O, 48%

Scheme 60. Synthesis of amine derivatives **181**. Conditions: (i) EtOH, 25 °C, 12 h (ii) $NaBH_4$, EtOH, 0 °C, 2 h.

Synthesis of the target dibenz[*b,f*][1, 5]oxazocines **182a-g** was reached by the reaction of compounds **181a-g** with $Pd_2(dba)_3$, ±BINAP, and KO-*t*Bu in presence of K_2CO_3 in dry toluene (Scheme 61).[57]

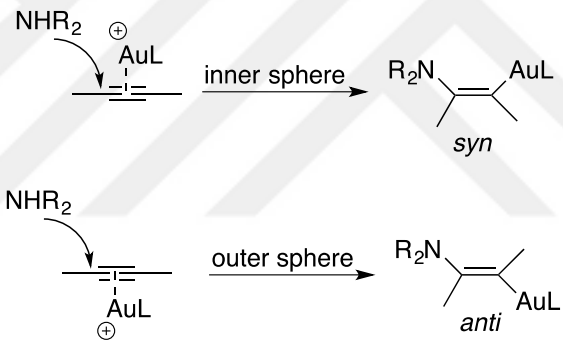


Scheme 61. Intramolecular cyclization of amine derivatives **181a-g**

4.1.3 Gold–Catalyzed Intramolecular Cyclization

Transition metal-catalyzed intramolecular cyclizations have attracted much attention from synthetic organic chemists and led to the construction of biologically important heterocycles.[63] In particular, Au catalysts are highly effective species for the electrophilic activation of triple bonds for the nucleophilic attack.[64] Gold catalyzed intramolecular cyclization reactions have been examined by a number of researchers from both experimental and theoretical viewpoints.[63]

Due to their large π-acidic character, gold catalysts activate the C-C multiple bond to the nucleophilic attack.[64] Two mechanisms are plausible: inner sphere and outer sphere (Scheme 62).[65]



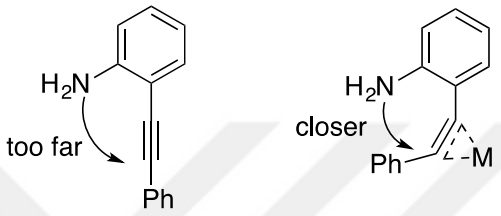
Scheme 62. Short representation of inner and outer sphere mechanism

Recently, outer sphere mechanism is the most widely proposed process for the gold-catalyzed reactions in particular for the intramolecular hydroamination reactions.[65]

4.1.3.1 Gold-Catalyzed Hydroamination Reactions

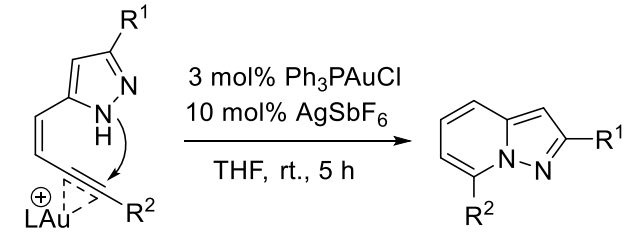
Intramolecular hydroamination reactions, addition of an N-H bond across an unsaturated C-C bond, represent highly desirable synthetic route for the organic

synthesis.[66] The reaction proceeds via the nucleophilic attack of the nitrogen lone pair electrons on an carbon atom in alkyne moiety.[67] Recently, Au(I) and Au(III) catalysts were shown to efficiently catalyze the hydroamination of alkynes.[68] Preliminary mechanistic analysis showed that the coordination of C-C multiple bond to the metal is the key step for the hydroamination reactions because it decreases the bond angles at the alkyne carbons, making it possible for the –NH group to attack the C-C multiple bond (Scheme 63).[66]



Scheme 63. Intramolecular hydroamination of alkynes with and without metal catalyst

Wu *et al.*[69] synthesized pyrazolo[1,5-*a*]pyridines **184** via an Au(I)-catalyzed cyclization of alkynylpyrazoles **183** in good to excellent yields (Scheme 64).



183

R^1 = Me, Ph

R^2 = H, alkyl, Ph

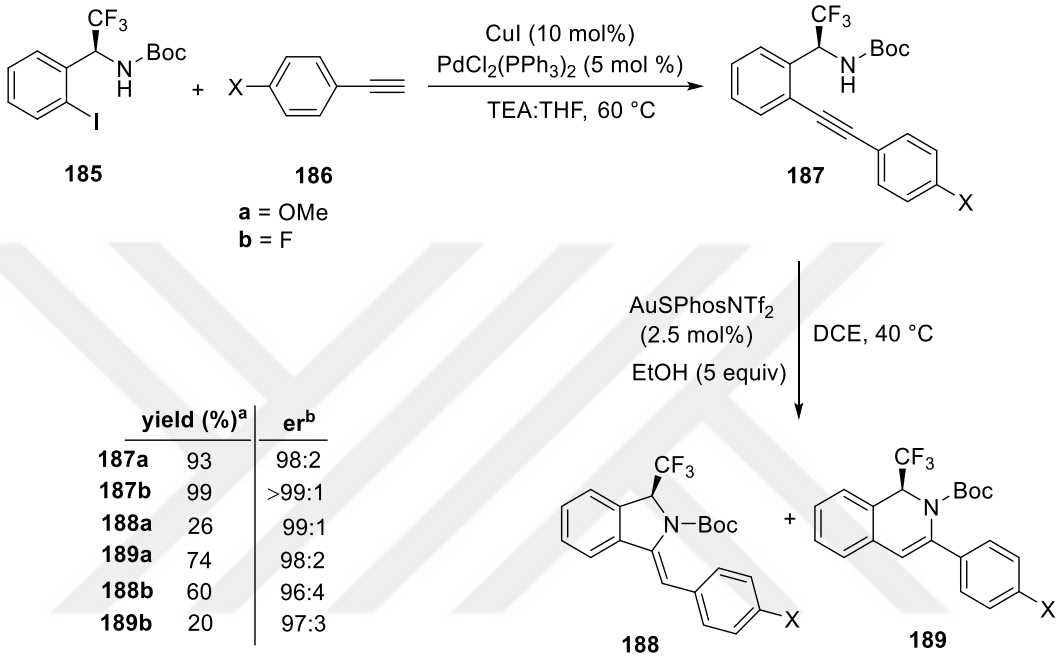
184

86-99%

Scheme 64. Synthesis of pyrazolo[1,5-*a*]pyridines via Au(I)-catalyzed 6-*endo-dig* cyclization.

Catalán and Fustero *et al.*[70] reported the synthesis of an enantiomerically pure

isoindoline and dihydroisoquinoline derivatives using the intramolecular hydroamination reaction of alkynyl carbamate (±)-**187** with gold-catalyst (Scheme 65). For the construction of the **188** and **189**, first they synthesized compound **187** by Sonogashira cross-coupling reaction. Next, compound **187** underwent an intramolecular cyclization reaction to give desired skeletons **188** and **189**.



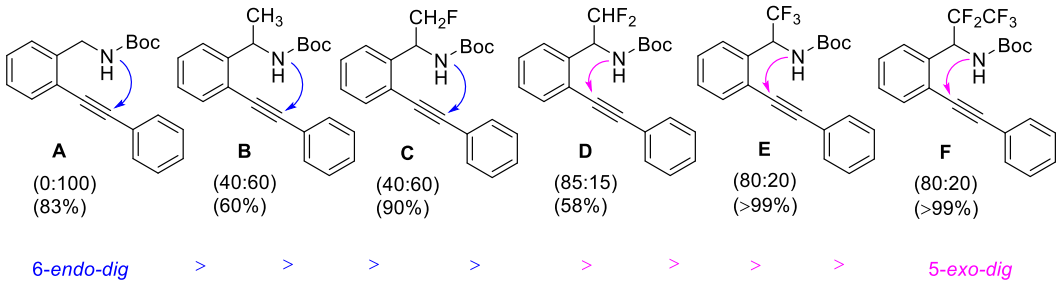
	yield (%)[a]	er[b]
187a	93	98:2
187b	99	>99:1
188a	26	99:1
189a	74	98:2
188b	60	96:4
189b	20	97:3

a) Isolated yield b) Determined by chiral HPLC analysis

Scheme 65. Synthesis of isoindoline **188** and dihydroisoquinoline **189** via intramolecular hydroamination

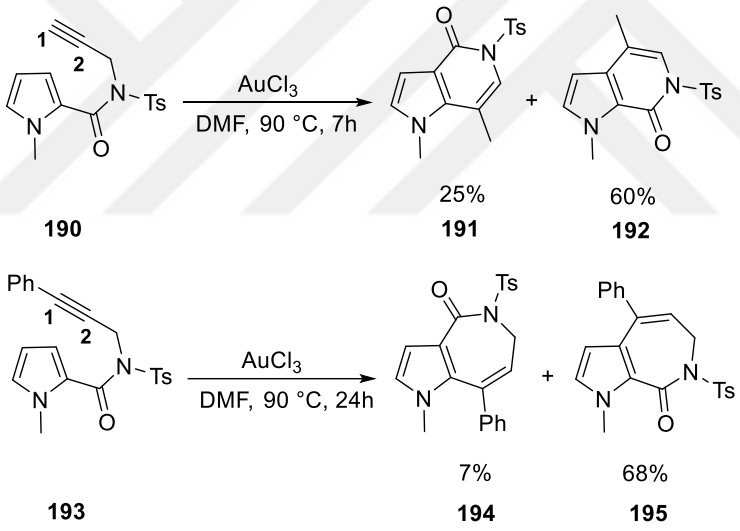
They also observed that electron-donating alkyne substitution (-OMe) favors the 6-*endo-dig* cyclization product **189**, while electron-withdrawing alkyne substitution (-F) favors the 5-*exo-dig* product **188**.

In addition, *α*-substitution effect on regioselectivity was also investigated by the replacement of one or more hydrogen atoms by fluorine. They found that introduction of fluorine atoms at the *α*-position favors the 5-*exo-dig* product (Scheme 66).[70]



Scheme 66. α-Substitution effect on regioselectivity

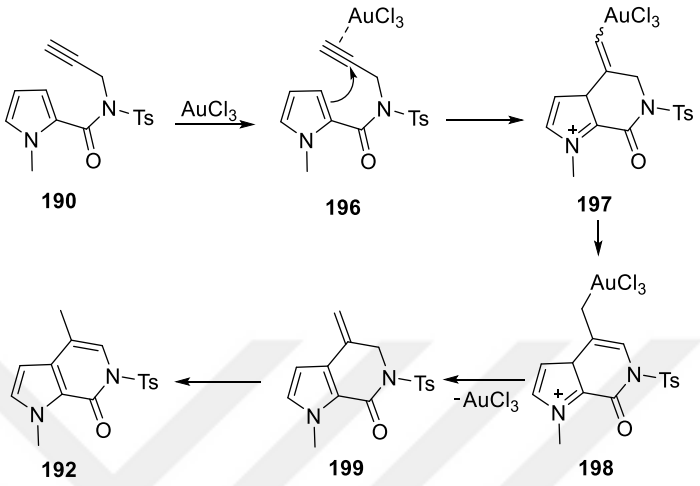
Broggini *et al.*[71] investigated the intramolecular cyclization of terminal and internal alkynes **190** and **193** with $AuCl_3$ catalyst (Scheme 67). Cyclization of terminal alkynes lead to pyrrolopyridinones **191** and **192**, on the other hand, cyclization of internal alkynes resulted in the formation of pyrroloazepinones **194** and **195**.



Scheme 67. Synthesis of pyrrolopyridinones and pyrroloazepinones via intramolecular hydroamination

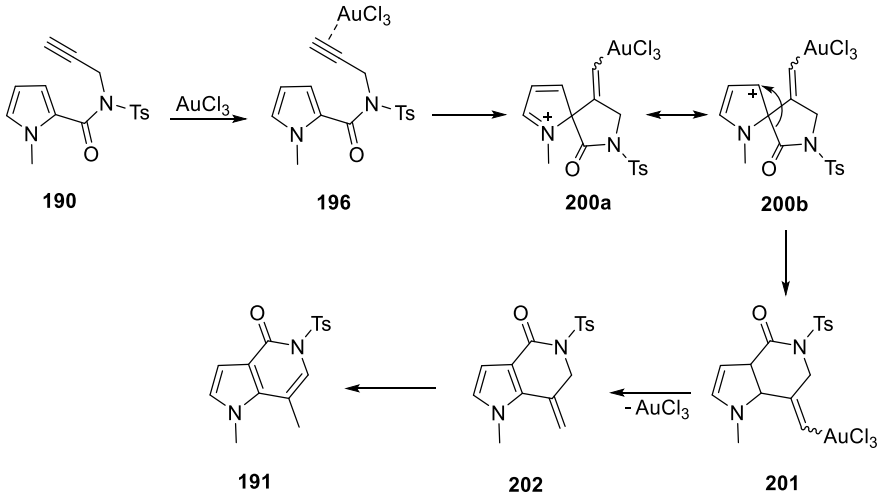
For the formation of pyrrolopyridinone **192,** they proposed the mechanism shown in Scheme 68. In the first step, $AuCl_3$ coordinates to the triple bond to form the intermediate **196**. 6-*exo-dig* cyclization involves an intramolecular nucleophilic

attack of pyrrole's β-carbon on internal carbon of alkyne that leads to six-membered intermediate **197**. Pyrrolopyridinone **192** can be obtained by series of protodeauration steps.[71]



Scheme 68. Proposed mechanism for the formation of pyrrolopyridinone **192**

A similar mechanism was suggested for the formation of pyrrolopyridinones **191** (Scheme 69).



Scheme 69. Proposed mechanism for the formation of pyrrolopyridinone **191**

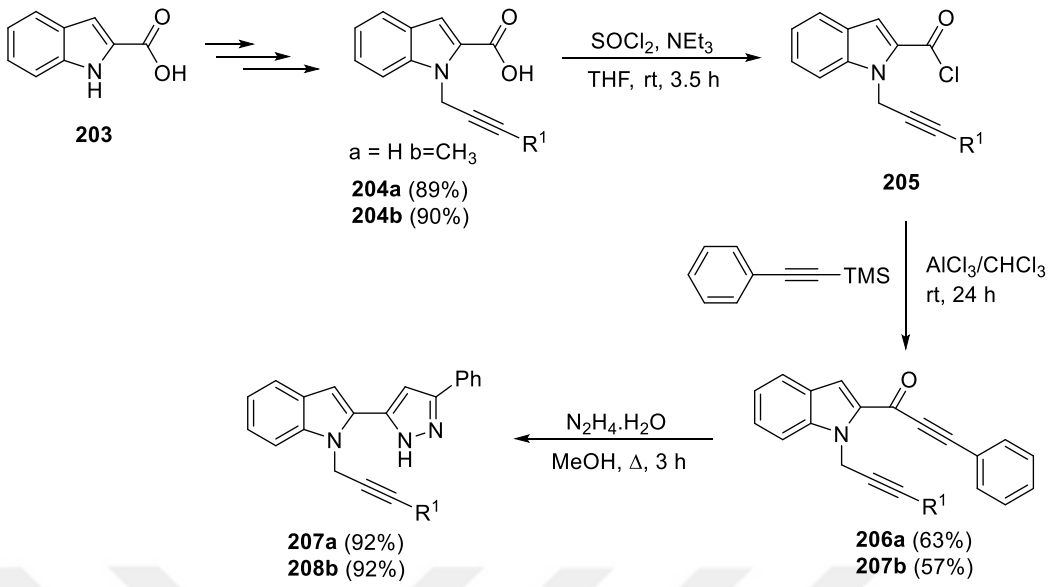
In this case, 6-*exo*-*dig* cyclization involves an intramolecular nucleophilic attack of pyrrole's α-carbon on internal carbon of alkyne to form spiro 5,5-ring intermediate **200a** or **200b**. Carbonyl carbon migration and subsequent protodeauration steps lead to the pyrrolopyridinone **191**.[71]

On the other hand, phenyl substituted alkyne **193** follows a very different reaction route to form the pyrroloazepinones **194** and **195**. In this case, 7-*endo*-*dig* cyclization was observed. One can infer that substituent effect is significant for the intramolecular cyclization.[71]

In terminal alkyne **190**, C2 is more electropositive than the terminal alkyne carbon C1. The bond distance between the C1 and gold was found to be 2.25 Å, while C2 and gold bond distance was calculated as 2.44 Å. According to the NBO analysis, the calculated charge on terminal carbon C1 and internal carbon C2 is −0.21 and +0.06, respectively.[63]

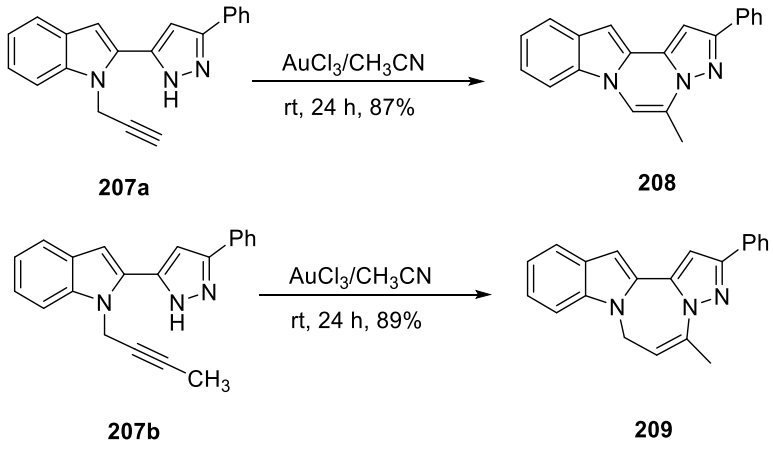
On the other hand, in phenyl substituted alkyne **193**, C1 is more electropositive than C2. The bond distance between the C1 and gold was found to be 2.52 Å, while C2 and gold bond distance was calculated as 2.21 Å which support the experimental result that the nucleophilic attack on the C2 is less favored.[63]

Recently, Balci *et al*.[72,73] reported the formation of pyrazolopyrazinoindole **208** and pyrazolodiazepinoindole **209** by $AuCl_3$ catalyzed hydroamination reaction. The key structures *N*-propargyl-α,β-alkynyl ketones **207a** and **207b** were synthesized starting from carboxylic acid derivative **203** according to the procedure shown in Scheme 70.



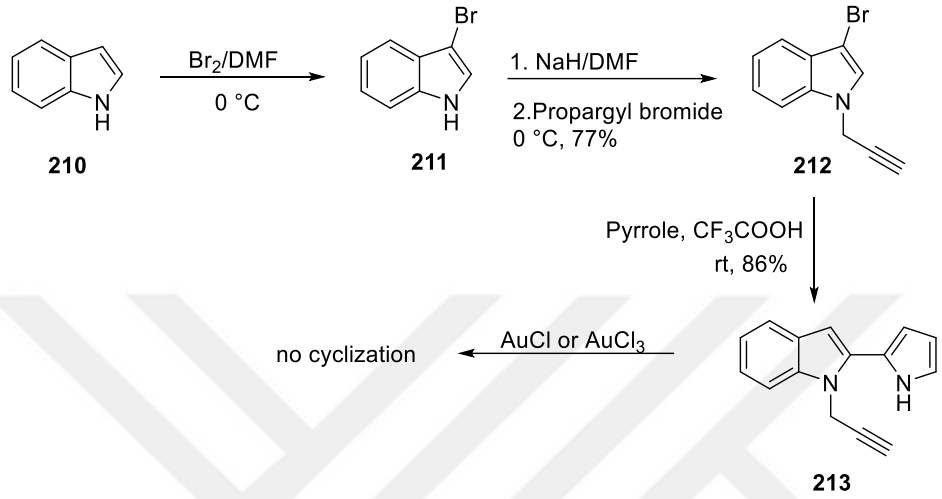
Scheme 70. Synthesis of *N*-propargyl *α,β*-alkynyl ketones **207a** and **207b**

Afterward, terminal and internal alkynes **207a** and **207b** were subjected to the intramolecular cyclization reaction with gold catalyst. 6-*exo*-dig and 7-*endo*-dig cylization products **208** and **209** were obtained in 87% and 89% yield, respectively (Scheme 71).[69]



Scheme 71. Synthesis of compound **208** and **209**

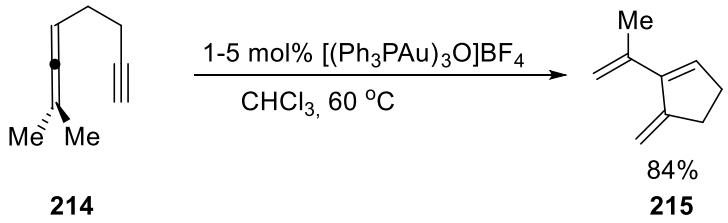
Next, they turned their attention to the intramolecular cyclization of pyrrole derivative **213**. However, they could not observe the cyclization products using AuCl and $AuCl_3$ catalyst. This result can be attributed to the reactivity difference between pyrrole and pyrazole ring.[72]



Scheme 72. Reaction of pyrrole derivative **213** with gold catalyst

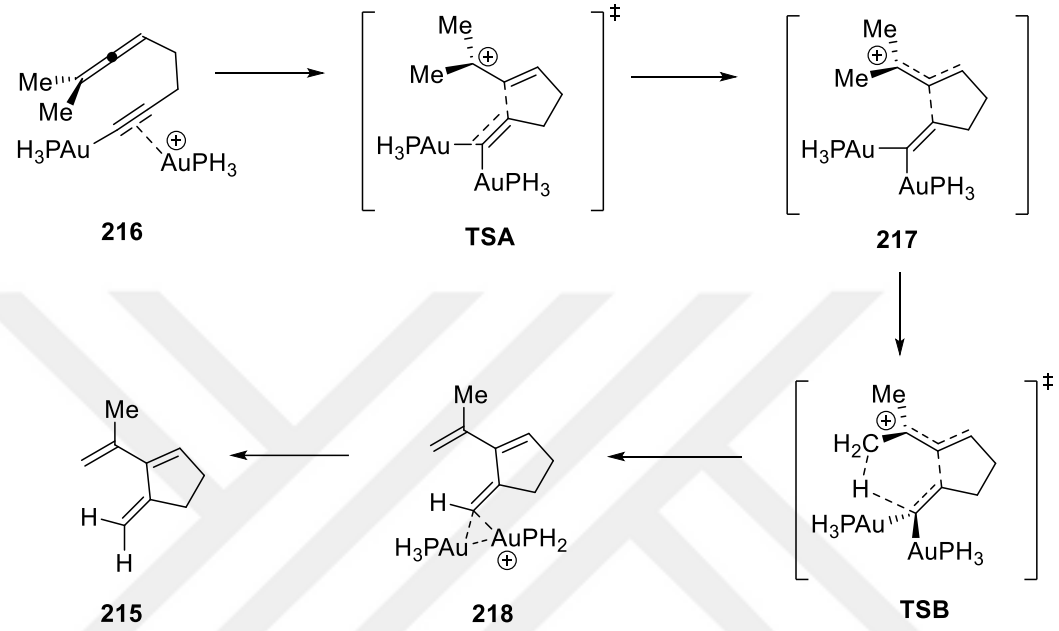
4.1.4 Dual Gold Catalysis

In 2008; Houk, Toste and co-workers[74] reported a gold(I)-catalyzed rearrangement of allenynes to cross-conjugated trienes. Only terminal alkynes gave the product shown in Scheme 73.



Scheme 73. Rearrangement of **214** to triene **215**

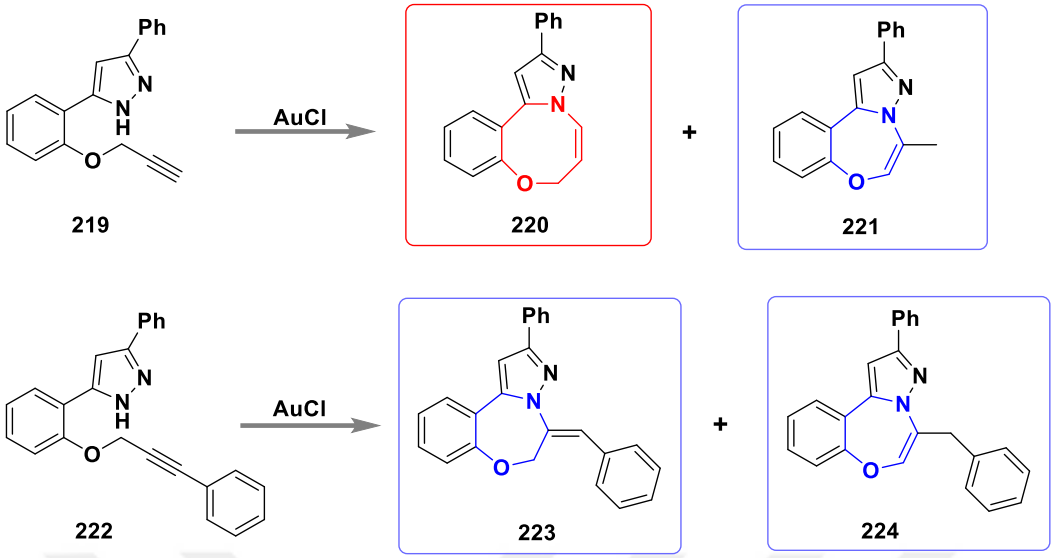
According to the combined experimental and theoretical results, they proposed a mechanism which shown Scheme 74. The intermediate includes two gold complexes, one σ-bonded and one π-coordinated. Such complexes can activate the organic structures by the formation of σ, π-activated alkyne complexes.



Scheme 74. Proposed mechanism for the formation of triene **215**

4.1.5 Objective of the Study

Our research group constructed benzene fused oxazepine and oxazocine derivatives that might have important biological activities (Scheme 75). The outcome of the intramolecular hydroamination gave 7-*exo*-*dig* or 8-*endo*-*dig* processes, depending on the substitution of the alkyne.[56] In this study, formation of the products **220/221** and **223/224** were investigated by performing DFT calculations.

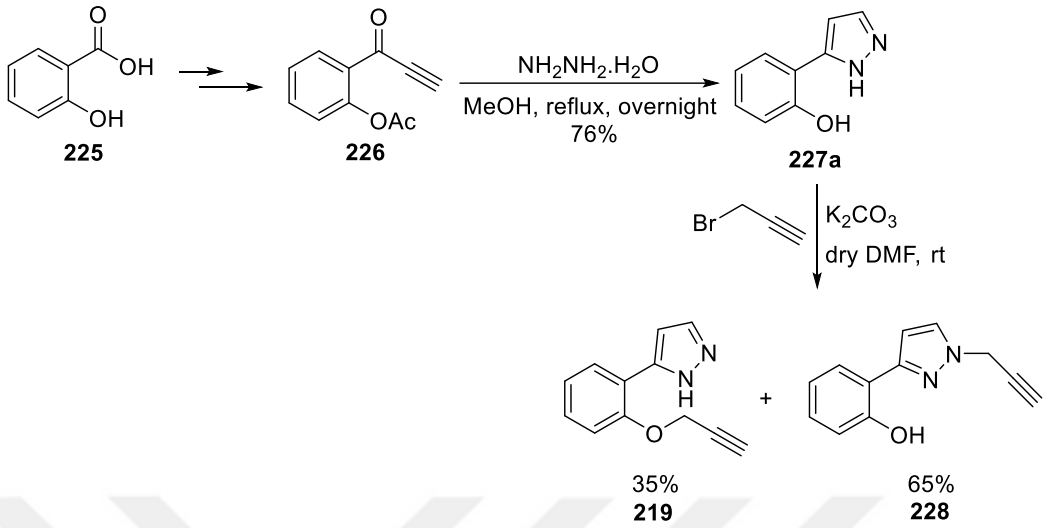


Scheme 75. Construction of benzene fused oxazepine and oxazocine derivatives **220/221** and **223/224**

The calculations provide insights into the gold-catalyzed intramolecular hydroamination reactions as well as the allene chemistry. The experimental results were analyzed in the light of theoretical findings to determine the most plausible mechanism.

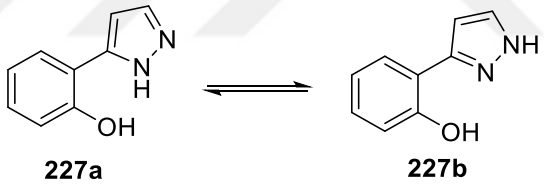
4.2 Results and Discussion

Salicylic acid (**225**) was used as the starting material. After several steps, alkyne derivative **226** was synthesized by our group.[56] Heating of **216** with hydrazine monohydrate at the reflux temperature of methanol afforded the key structure **227a** in 76% yield. Treatment of phenol derivative **227a** with propargyl bromide in presence of K_2CO_3 yielded to *O*- and *N*-propargylated products **219** and **228** in 35% and 65% yield, respectively. The propargyl group was regiospecifically bonded to one of the nitrogen atoms (Scheme 76).[56]



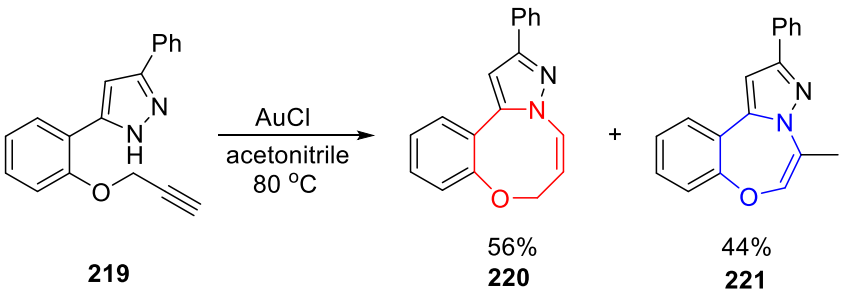
Scheme 76. Synthesis of *O*-propargylated compound **219**

These results show that there might be a tautomerie between the pyrazole derivatives **227a** and **227b** (Scheme 77).[56]



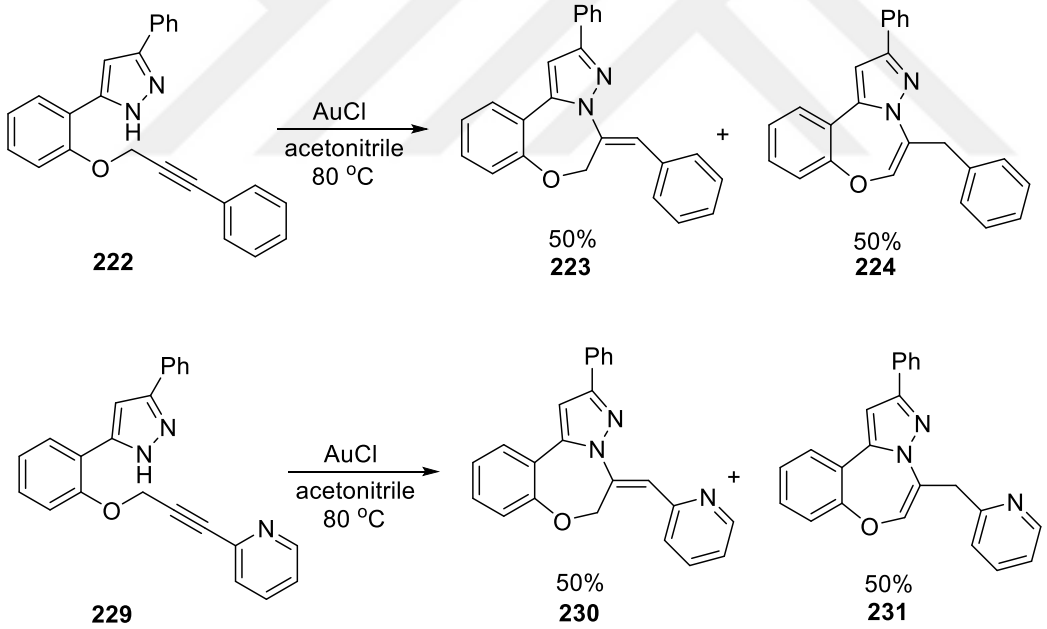
Scheme 77. Tautomerie between the pyrazole derivatives **227a** and **227b**

Treatment of *O*-propargylated compound **219** with AuCl in acetonitrile afforded the eight-membered oxazocine and seven-membered oxazepine derivatives **220** and **221** (Scheme 78).[56]



Scheme 78. Synthesis of oxazocine **220** and oxazepine **221**

Compounds **222** and **229** were synthesized by Sonogashira coupling reaction of pyrazole derivative **219**. To test the effect of substituents and the generality of this cyclization reaction, phenyl and pyridine substituted *O*-propargylated compounds **222** and **229** were submitted to cyclization reaction under the same reaction conditions. Unfortunately, the expected products with 8-membered oxazocine rings were not observed in both cases (Scheme 79).[56]



Scheme 79. Intramolecular cyclization of compound **222** and **229**

This outcome confirmed the important role of the substituent on the alkyne moiety. In order to understand the pivotal role of the substituents on the intramolecular

hydroamination reaction, NBO analyses were applied. Besides, Gibbs free activation barriers were calculated to enlighten the mechanism.

4.2.1 Theoretical Calculations

4.2.1.1 Application of the NBO Analysis

First of all, NBO analyses were applied to understand the reactivity difference between the terminal and internal alkynes toward intramolecular hydroamination reaction. NBO atomic charges and some selected bond lengths (Å) are shown in Figure 40.

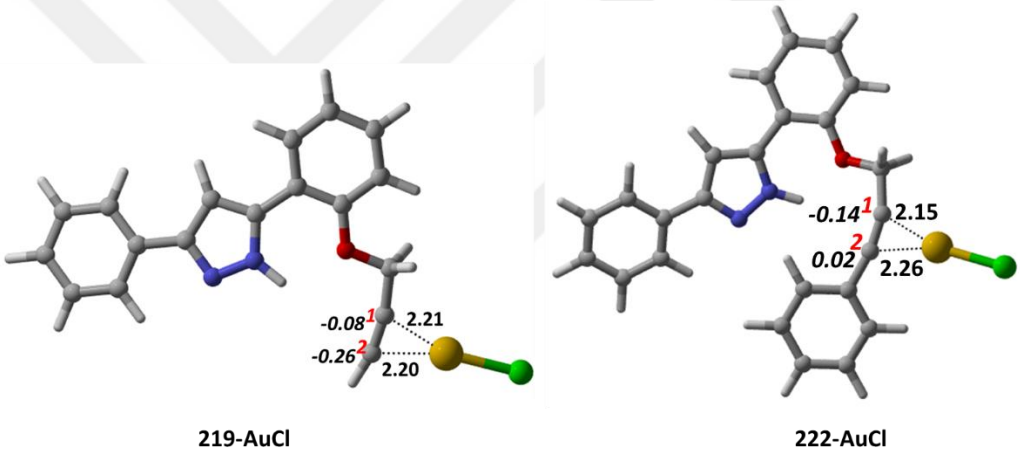


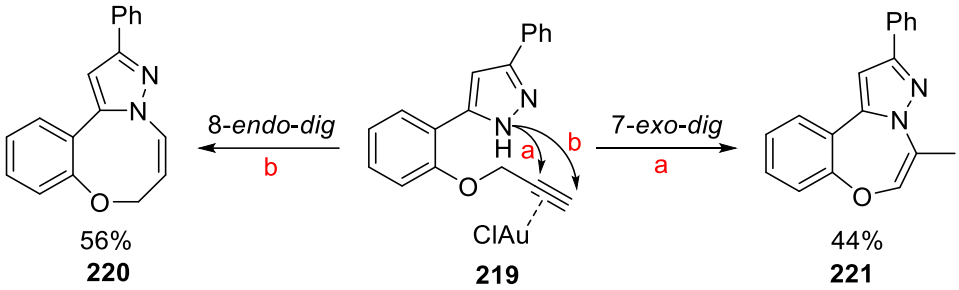
Figure 40. NBO atomic charges of **219** and **222** at M06/6-31G(d)/LANL2DZ(f) level. Distances are given in italics. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue; gold, yellow; chlorine, green).

In terminal alkyne **219**, AuCl coordinates to the C1 and C2 in almost symmetrical way. The C1 carbon atom was found to be more electropositive due to the inductive effect of the oxygen. In the case of internal alkyne **222**, AuCl didn't coordinate symmetrically to the carbon atoms due to the electronic as well as steric effects of the bulky phenyl group. In this case, both inductive effect of the oxygen and the

coordination of the gold(I)chloride affect the relative charge distribution. AuCl coordinates more closely to C-1 because of two reasons, (1) Positive charge can be more stabilized by the phenyl group, and (2) Due to the steric repulsion between the phenyl group and the gold atom. Therefore, the C1-Au distance is shorter than the C2-Au distance. According to this outcome, C2 was found to be more electropositive in internal alkynes; thus, -NH should preferentially attack the C2 carbon atom leading to the formation of an 8-membered ring. However, formation of an 8-membered oxazocine ring was not observed. The experimental results were not in agreement with NBO analysis; therefore, we turned our attention to locate the transition states related to the formation of the products.

4.2.1.2 Modeling the Reaction Mechanisms of Gold-catalyzed Intramolecular Hydroamination Reaction

The initial step for the intramolecular cyclization includes the coordination of AuCl to the C-C triple bond. After the activation of triple bond, nucleophilic attack of –NH group to the C-C multiple bond takes place. The *O*-propargylated compound **219** may undergo 8-*endo-dig* and 7-*exo-dig* processes shown in Scheme 80.



Scheme 80. Initial steps for the hydroamination of **209**

Calculations were performed at SMD[75]-M06[55a]/6-31G(d) (C,N,H,O)/LANL2DZ(f) [76](Au) levels of theory. Optimized geometries for 7-*exo-dig* mechanism are shown in Figure 41. In order to reach the transition state **TS32**, 17.9 kcal/mol of activation

energy is required in acetonitrile. Bond distance of C−N is predicted as 2.04 and 1.52 Å in **TS32** and **PC(232+AuCl)**, respectively. Intramolecular hydrogen bond NH···O (2.23 Å) in **RC(219+AuCl)**, stabilizes the system.

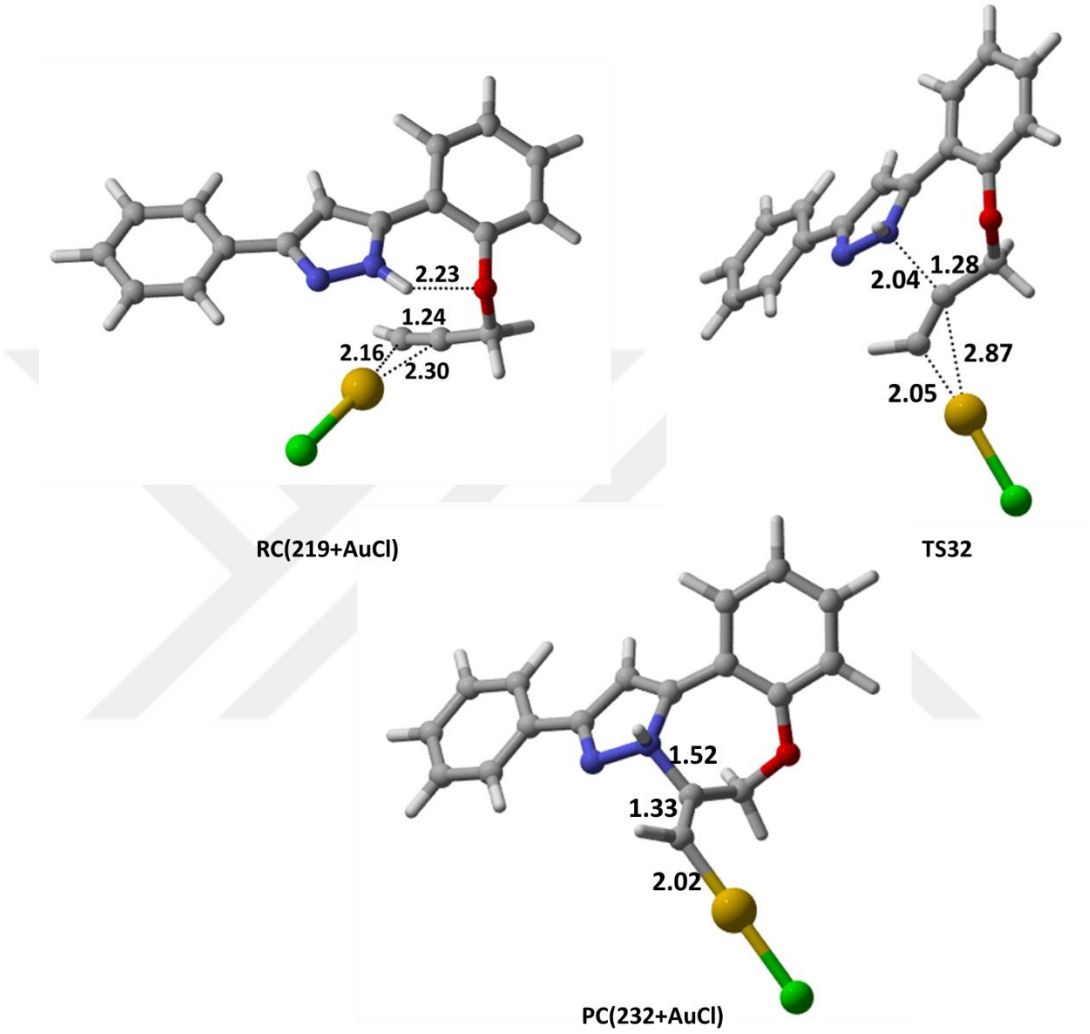


Figure 41. Optimized geometries for the 7-*exo-dig* reaction pathway at SMD(MeCN)/M06/6-31G(d)/LANL2DZ(f) level. Distances are given in angstroms. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue; gold, yellow; chlorine, green)

Optimized geometries for 8-*endo-dig* cyclization are shown in Figure 42. In order to reach the **TS33**, 16.2 kcal/mol of activation energy is required in acetonitrile.

This small barrier difference is in agreement with the experimental result, since the ratio of 7- and 8-membered products is quite close by 44% and 56%. The $\Delta\Delta G^{\neq}$ value, which shows the difference between the Gibbs free energies of the transition states in these two paths, was calculated as 1.3 kcal/mol. On the basis of results obtained, both 7- and 8-membered products can be formed as experimentally observed.

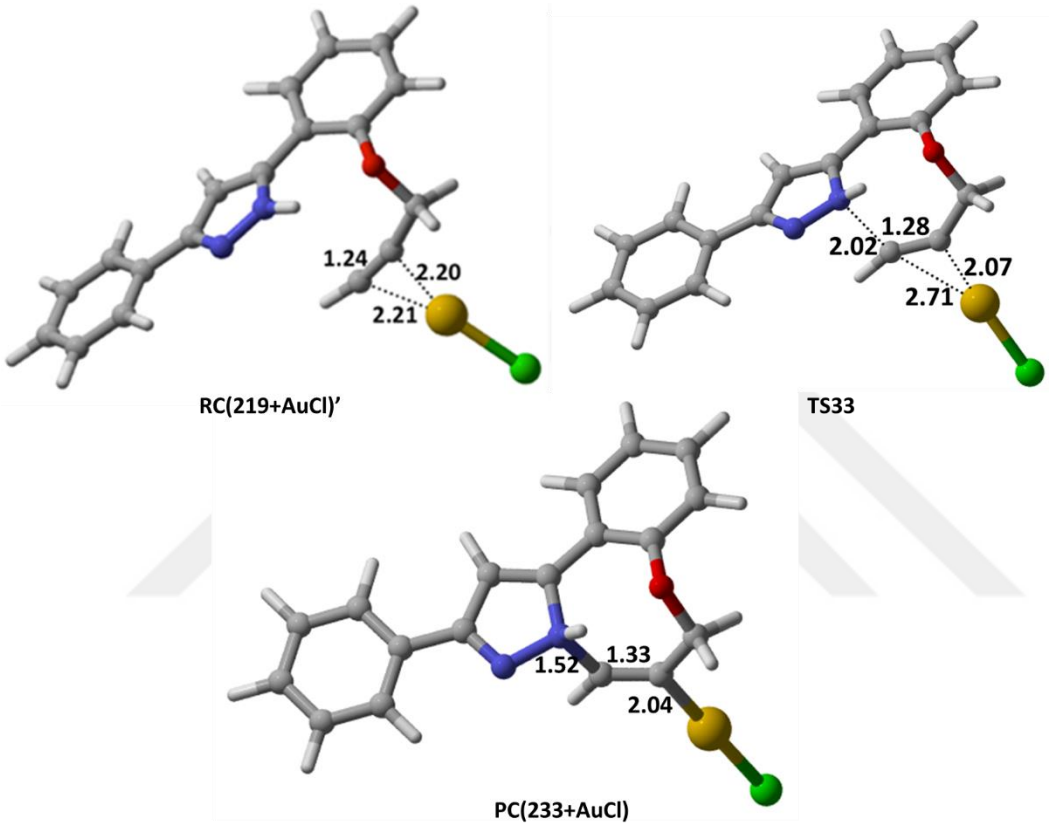
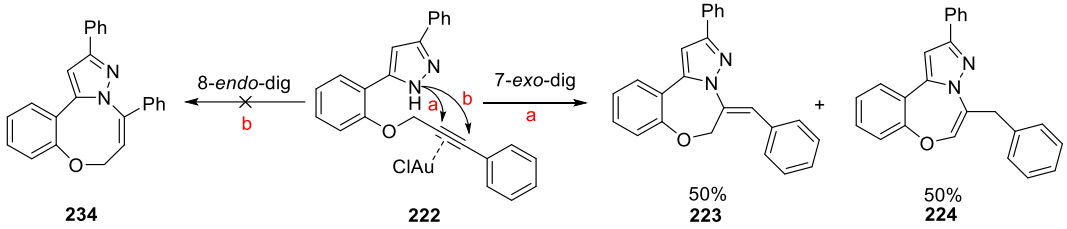


Figure 42. Optimized geometries for the 8-*endo-dig* reaction at SMD(MeCN)/M06/6-31G(d)/LANL2DZ(f) level. Distances are given in angstroms. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue; gold, yellow; chlorine, green)

In the case of internal alkynes, *O*-propargylated compound couldn't follow the path b leading to oxacozine derivative shown in Scheme 81.



Scheme 81. Initial step for the hydroamination of **222**

In order to understand the formation of the products, both pathways were modeled. To reach transition state **TS34** leading to the 8-membered ring product, an activation barrier of 30.8 kcal/mol is required. As it can be observed in Figure 43, there is no π-π stacking interaction, which results in a relatively high energy barrier.

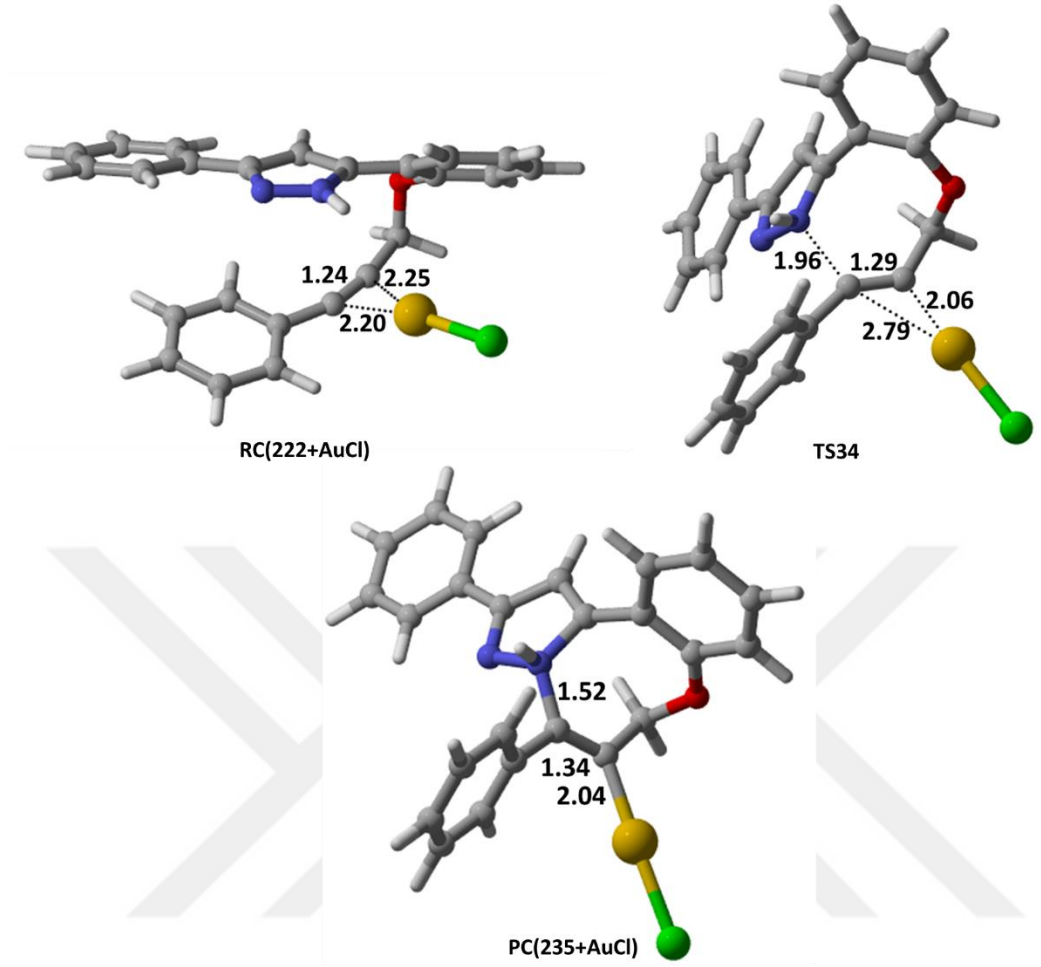


Figure 43. Optimized geometries for the 8-*endo-dig* reaction pathway at SMD(MeCN)/M06/6-31G(d)/LANL2DZ(f) level. Distances are given in angstroms. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue; gold, yellow; chlorine, green)

Geometry of the transition state **TS35** leading to the 7-membered product is shown in Figure 44. The π-π stacking interaction between the two aromatic groups, stabilize the transition state. We found that transition state leading to the formation of an 8-membered ring (**TS34**) is 5.5 kcal/mol less stable than the **TS35**. This theoretical result is in good agreement with the experimental finding.

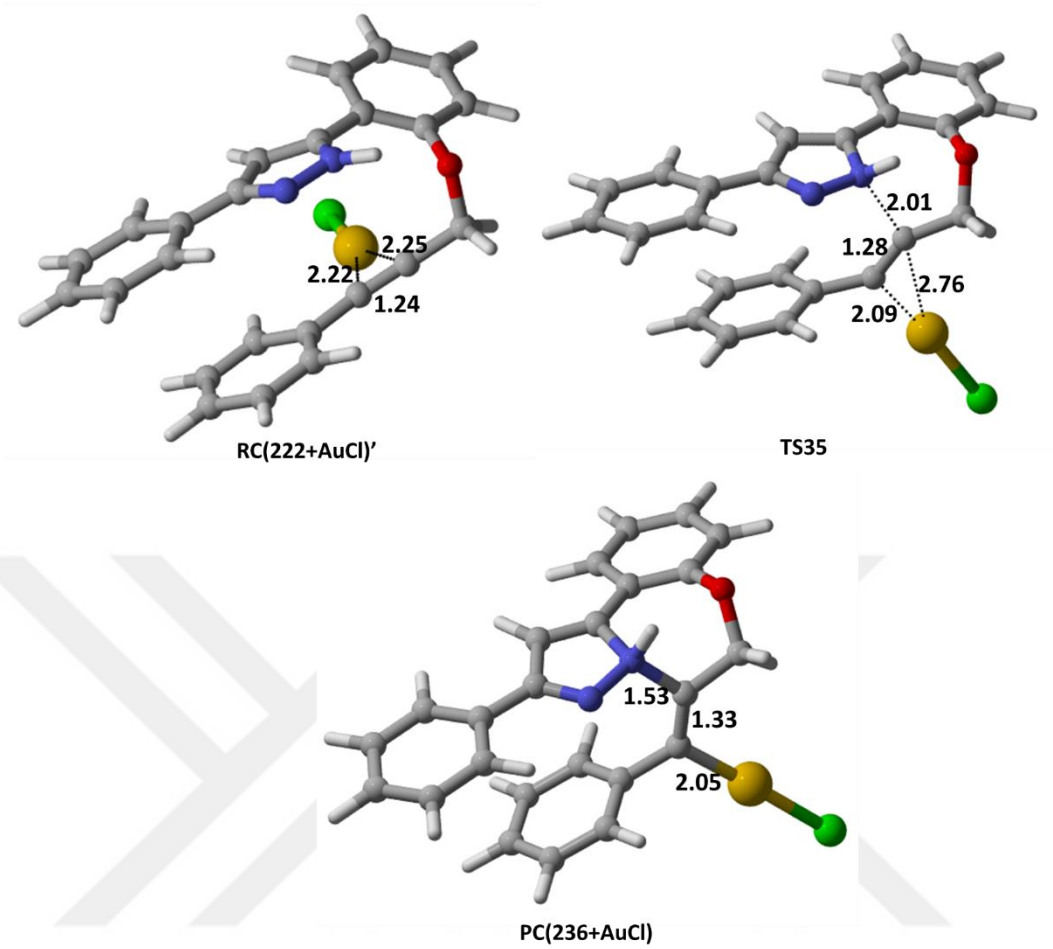


Figure 44. Optimized geometries for the 7-*exo-dig* reaction pathway at SMD(MeCN)/M06/6-31G(d)/LANL2DZ(f) level. Distances are given in angstroms. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue; gold, yellow; chlorine, green)

In addition, transition state calculation including both σ- and π-activation was carried out for the terminal alkyne. Reactant complex, transition state and product complex geometries are shown in Figure 45. The activation barrier corresponding to the cyclization step was predicted to be 30.5 kcal/mol in acetonitrile. Since the corresponding transition state is not stable, this path is not considered as a plausible mechanism.

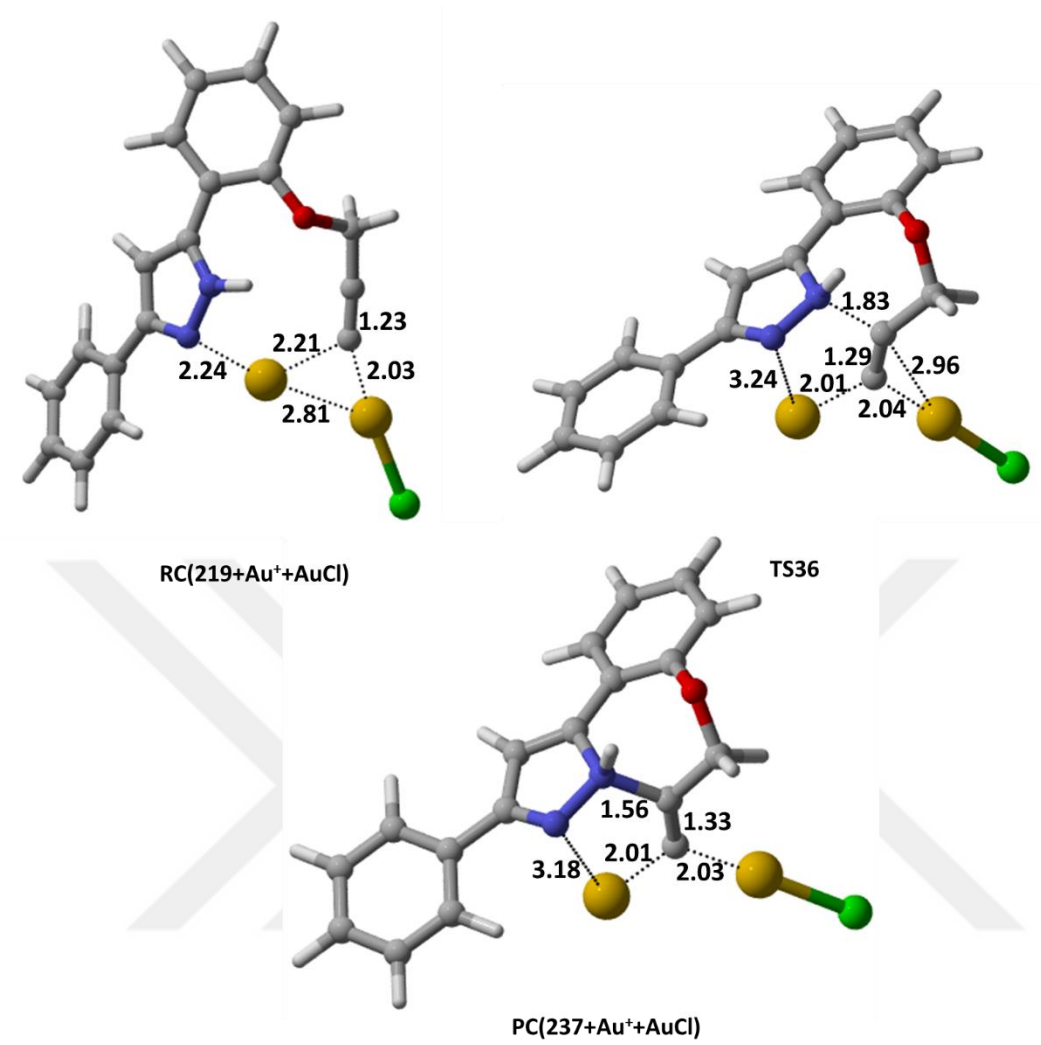
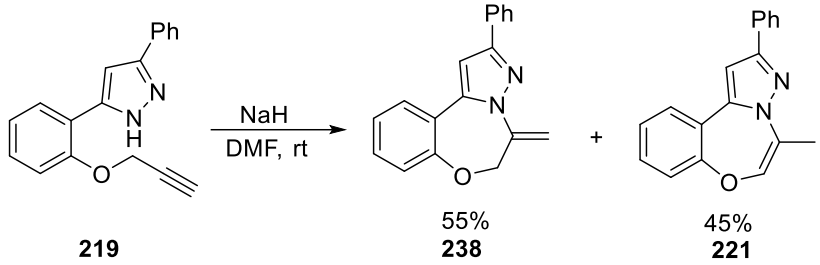


Figure 45. Optimized geometries for the dual gold catalysis at SMD(MeCN)/M06/6-31G(d)/LANL2DZ(f) level. Distances are given in angstroms. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue; gold, yellow; chlorine, green)

4.2.1.3 Intramolecular Cyclization Reaction of *O*-propargylated Compound under Basic Condition

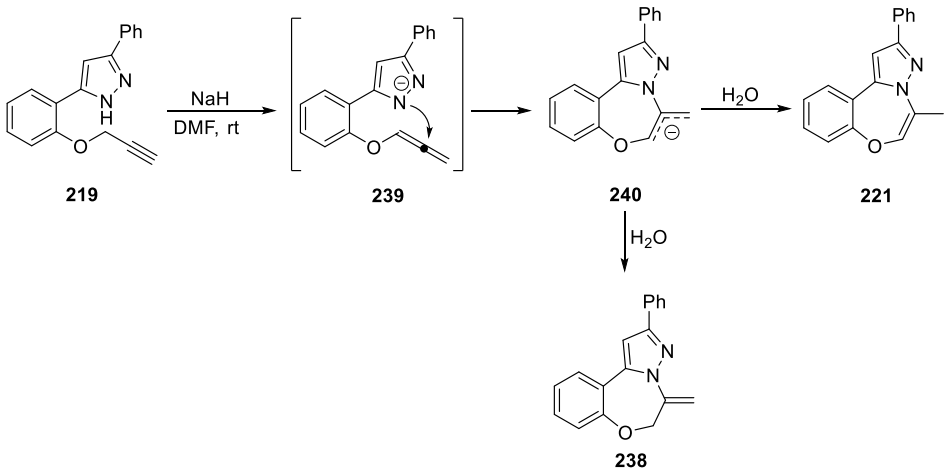
The second part of the study includes the investigation of the base-catalyzed

intramolecular cyclization. Alkyne derivative **219** was treated with NaH in dry DMF at room temperature for 18 h (Scheme 82). The reaction afforded only seven-membered ring products **238** and **221**. Eight-membered ring system was not observed under the basic condition.



Scheme 82. Intramolecular cyclization of **209** under basic condition

A plausible mechanism for the intramolecular cyclization of terminal alkyne with NaH is shown in Scheme 83. Since the central carbon atom of the allene unit is more electropositive, nucleophilic attack takes place on this carbon leading exclusively to formation of a seven-membered cyclic structure **240**. After the formation of intermediate **240**, proton abstraction from H_2O present in DMF takes place which results in the formation of two possible products **238** and **221**.



Scheme 83. Proposed mechanism for the intramolecular cyclization of **219** under the basic condition

Formation of seven-membered structures was also computationally investigated in an effort to clarify the mechanism. Optimized geometries for the first step were shown in Figure 46. The Gibbs free activation barrier associated with the cyclization step was found to be 19.8 kcal/mol in DMF. This step has a higher activation barrier compared to the proton abstraction step.

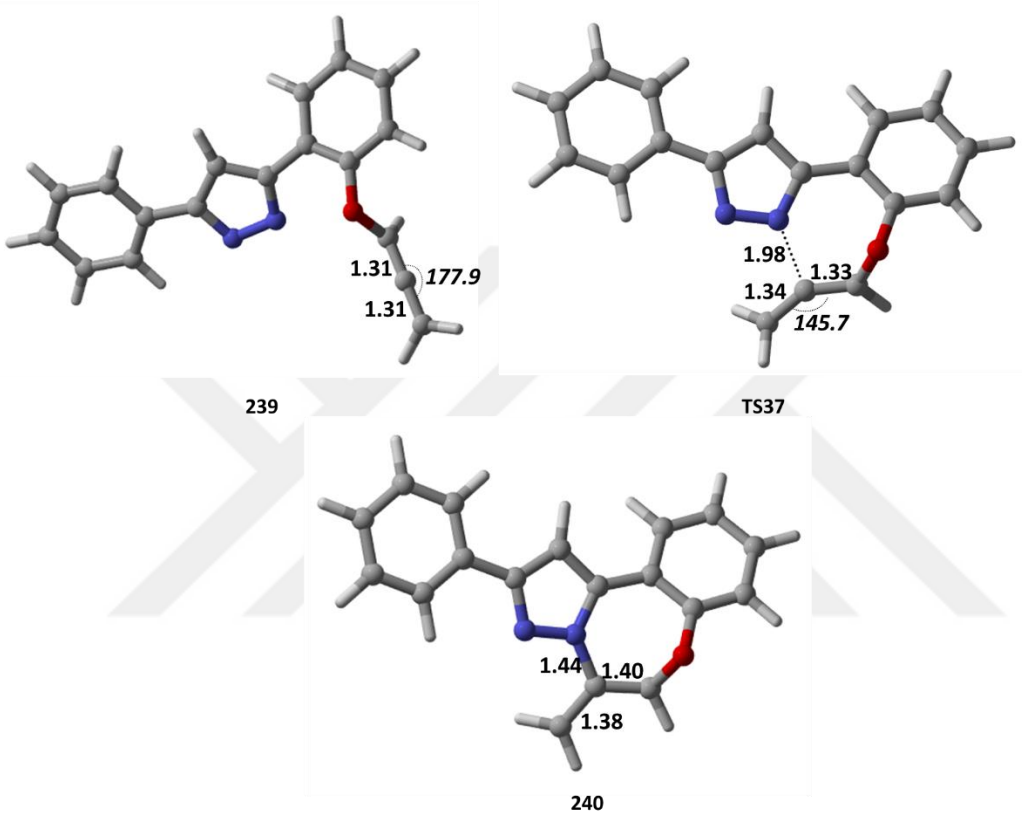


Figure 46. Optimized geometries for the intramolecular cyclization reaction of O-propargylated compound under basic conditions using SMD-M06/6-31+G(d) method. Distances are given in angstroms; angles are in degrees. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue)

The potential energy profile was generated relative to the energies of the initial reactants shown in Figure 47.

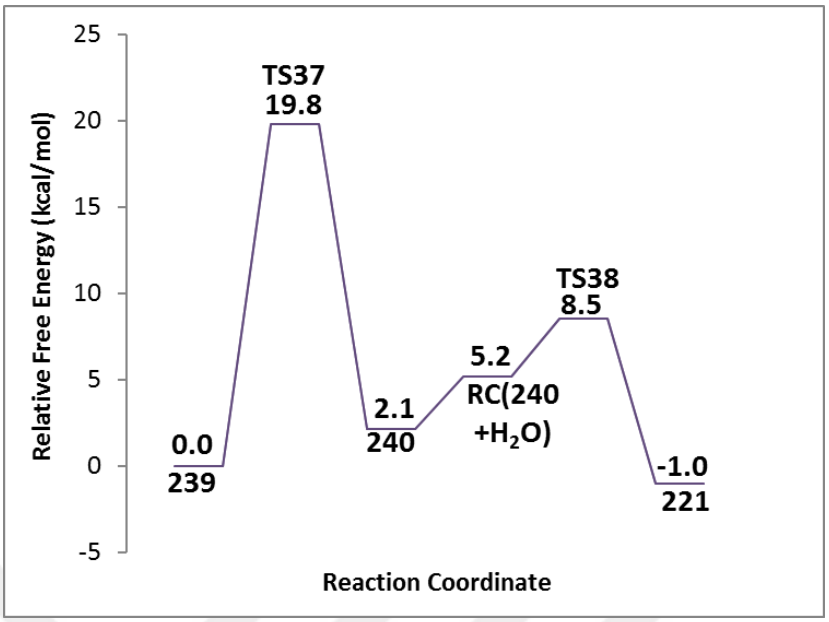


Figure 47. Potential energy profile related to formation of 7-membered oxazepine derivative **211** at the SMD-M06/6-31+G(d) level in DMF

The second step includes the proton abstraction from water having an activation barrier of 8.5 kcal/mol with respect to the reactant complex of the first step (Figure 47). Optimized geometries for this step are shown in Figure 48. Unfortunately, the product could only be optimized without water.

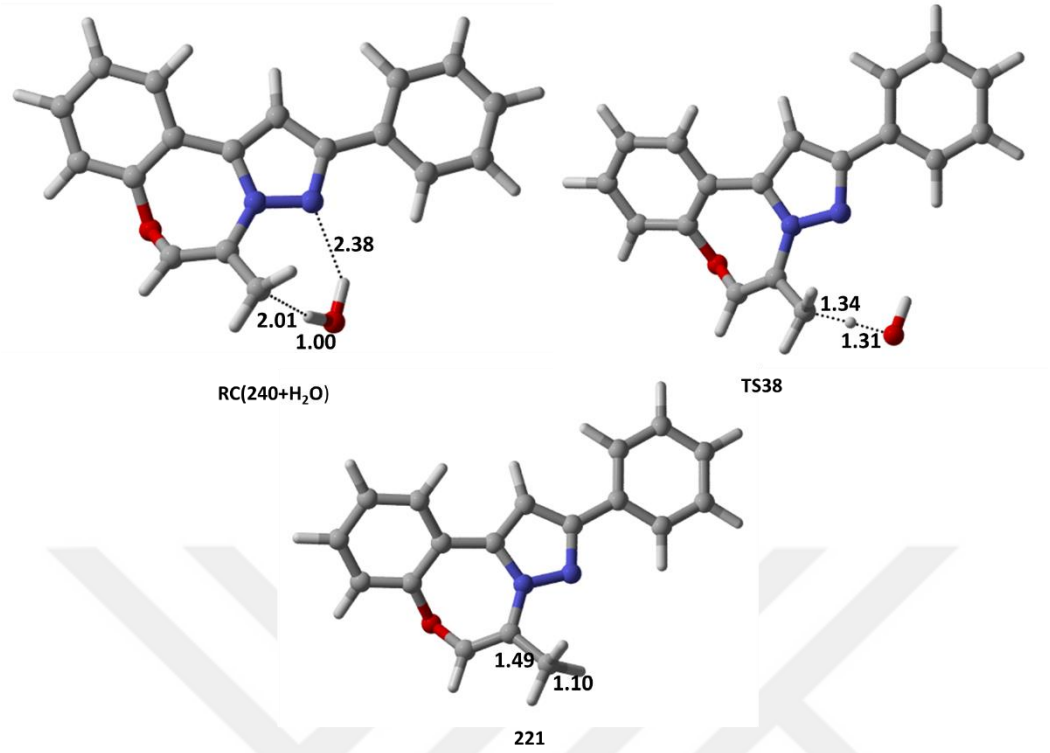


Figure 48. Optimized geometries for the proton transfer step using SMD-M06/6-31+G(d) method. Distances are given in angstroms; angles are in degrees. (carbon, grey; hydrogen, light grey; oxygen, red; nitrogen, blue)

In this part, our research group described the synthesis of benzene fused oxazepine and oxzocine derivatives via gold catalysis. In the case of terminal alkynes, both 7-*exo-dig* and 8-*endo-dig* cyclizations occurred. On the other hand, in the case of internal alkynes only the 7-*exo-dig* cyclization was observed. To understand these results, NBO analysis were performed. However, we could not explain the formation of products by means of NBO analysis. The formation of experimentally observed products can be explained with the calculated activation barriers for the cyclization reactions.

CHAPTER 5

COMPUTATIONAL MODELING OF THE RHODIUM-CATALYZED ASYMMETRIC ALLYLIC ARYLATION OF RACEMIC HALIDES WITH ARYLBORONIC ACIDS

5.1 Introduction

Computational methods have been used in order to model the synthetic reactions since 40 years.[77] The rise of modern quantum chemical calculations, fast and inexpensive computers make it possible to calculate the energies, reactivity and electronic properties of the molecules.[78] In particular, computational chemistry has become an important tool for the simulations of catalytic reactions.[77] The main objective of asymmetric catalysis is to form enantiomerically pure organic compounds under mild conditions.[79]

In asymmetric reactions, after the generation of chirality, the reaction may follow two pathways, which leads to *R*- or *S*-product. If the pathways are isoenergetic, then the product will be a racemate. On the other hand, if chiral compounds are utilized to obtain non-degenerate diastereomeric pathways, it would lead to the desired chiral products (Figure 49).[80]

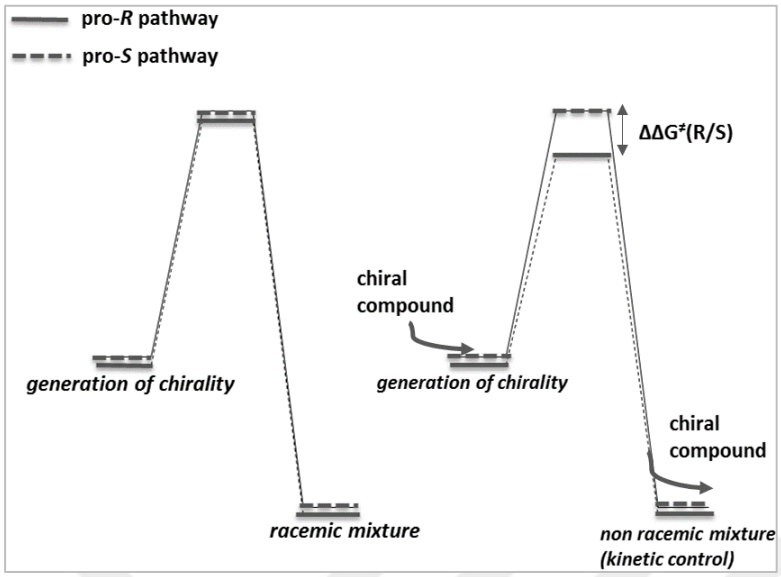


Figure 49. Enantiomeric and diastereomeric pathways in asymmetric reactions[80]

The most common methods for the enantioselective reactions are those involving chiral compounds as a substrate. In order to achieve chiral products starting from non-chiral substrates, chiral compounds are mostly used; as chiral auxiliaries, as chiral reagents and as chiral catalysts.[85]

Enantioselectivity can be expressed by enantiomeric excess (% ee) which is the excess of one enantiomer over the other in the reaction mixture.[80] The experimental enantiomeric excess can be calculated using the following equation;

$$\% \, ee = \frac{[R] - [S]}{[R] + [S]} \times 100$$

In equation given above, $[R]$ and $[S]$ refers to the experimentally determined product concentrations.

Enantiomeric excess can be also calculated using Boltzmann distribution of the transition states which leads to each enantiomer. In equation given below,

$\Delta\Delta G^{\neq}_{R/S}$, refers to the free energy difference between the pro-*S* and pro-*R* transition states. T represents the temperature and R is the gas constant.

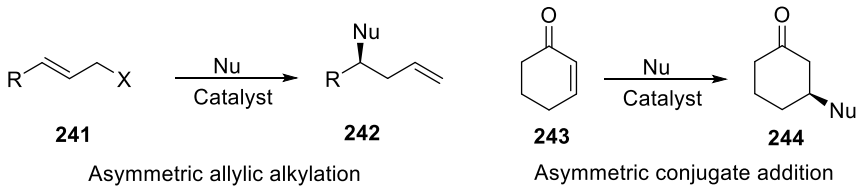
$$\frac{[S]}{[R]} = e^{-\Delta\Delta G^{\neq}_{R/S}/RT}$$

Collectively, the computational enantiomeric excess can be calculated using the following equation;[80]

$$\%\, ee = \frac{1 - e^{-\Delta\Delta G^{\neq}_{R/S}/RT}}{1 + e^{-\Delta\Delta G^{\neq}_{R/S}/RT}} \times 100$$

5.1.1 Enantioselective catalysis methods

The search for new and efficient methods for the synthesis of enantiopure compounds has been an important area of research in the pharmaceutical and agricultural industries. One of the most widely used approaches for obtaining single enantiomers using enantioselective catalysis is to convert pro-chiral substrates to desired enantio-enriched products (Scheme 84).[81,82]



Scheme 84. Asymmetric reactions starting from pro-chiral substrates

The second widely used strategy is the transformation of racemic mixtures into an enantio-enriched products.[81,82] These strategies to obtain enantiomerically-enriched molecules are shown in Figure 50.[81]

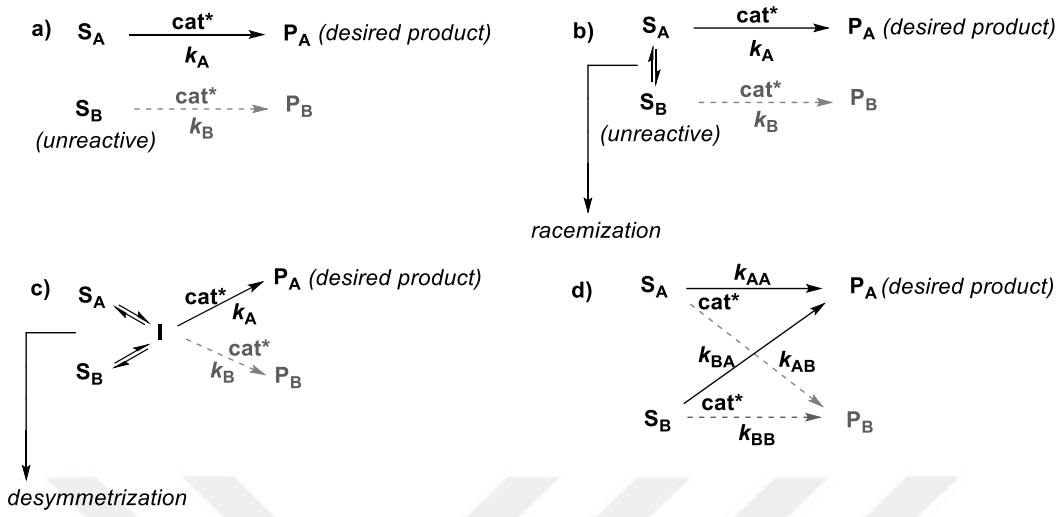


Figure 50. Strategies to obtain enantio-enriched products starting from asymmetric reactions of racemic substrates[81]

In kinetic resolution (KR), one of the enantiomer of a racemate is converted into the corresponding product at a higher reaction rate ($k_A \gg k_B$) while the other enantiomer remains unchanged. Therefore, a major disadvantage of this method is the maximum theoretical yield of 50% (Figure 50a).[81]

Dynamic kinetic resolution (DKR) has recently become an alternative method to the kinetic resolution. In DKR, slowly reacting enantiomer undergoes racemization and converts into more reactive enantiomer. Thus**,** DKR overcomes the drawback of kinetic resolution and leads to 100% theoretical yield (Figure 50b).[81]

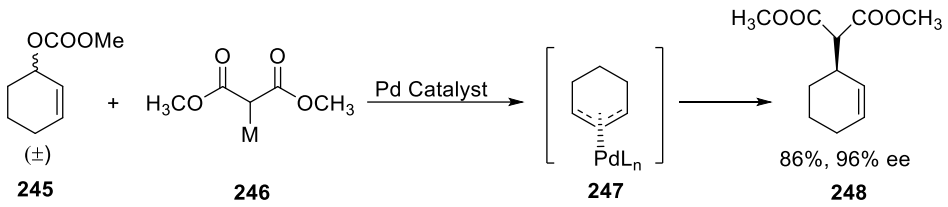
In dynamic kinetic asymmetric transformation (DYKAT), both enantiomers of starting material are converted into a common pseudo-prochiral (meso or C2-symmetrical) intermediate (I). The new stereogenic center is formed by the subsequent enantioselective step (Figure 50c).[81]

Recently, Ito and co-workers proposed another method which is called direct enantioconvergent transformation (DET).[81] In this case, each enantiomer follows a different reaction pathway to form the same enantiomer of the desired product (Figure 50d). The reaction rate of the two pathways should be similar ($k_{AA} \approx k_{BA}$) in order to prevent the KR.[81,83]

5.1.2 Asymmetric allylic substitution using stabilized and non-stabilized nucleophiles

Asymmetric allylic substitution is probably the most powerful method to generate chiral centers in starting materials since it allows the synthesis of natural products. In particular, transition-metal-catalyzed asymmetric allylic alkylation (AAA) reactions are probably the most powerful method to form carbon–carbon bonds.[82,84] These catalysts involve different metals such as Pd, Ir, and Ru are generally used with 'soft' stabilized nucleophiles, for instance malonates. Cu-based catalysts, on the other hand, are used with 'hard' non-stabilized nucleophiles such as organometallic molecules (RMgX, R_2Zn, R_3Al, RLi).[85]

Recently, palladium-catalyzed AAA reactions have been reported in which the racemic starting materials were converted to enantio-enriched products with good yields and enantioselectivities (Scheme 85).[82]



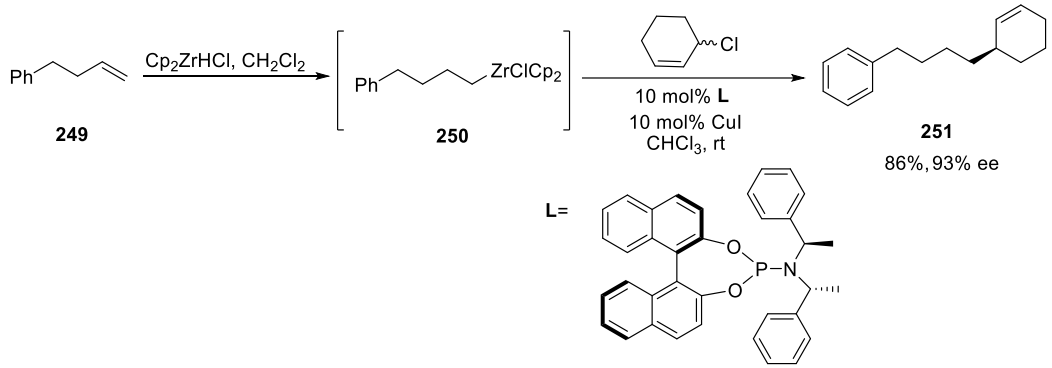
Scheme 85. Pd-catalyzed asymmetric allylic alkylation

Although asymmetric reactions with palladium catalysts and stabilized (soft) nucleophiles have been intensively studied, reactions with non-stabilized (hard) carbon nucleophiles are documented in a few instances.[84]

The asymmetric allylic substitution reactions with stabilized and non-stabilized nucleophiles follow different reaction mechanisms (Scheme 86). Stabilized nucleophiles directly attack to the allylic carbon; however, non-stabilized nucleophiles attack to the transition metal first. In the case of non-stabilized nucleophiles bond formation is likely to occur in the reductive elimination step while in the case of stabilized nucleophiles, bond formation occurs outside of the coordination sphere of the transition metal; therefore, the stereochemistry can be determined when the π-allyl intermediate undergoes a nucleophilic attack. [82,86,87]

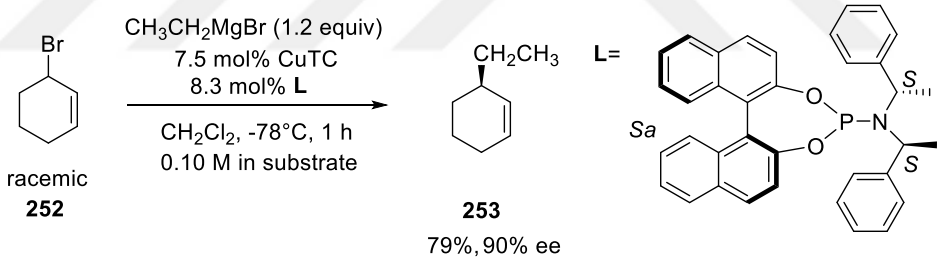
Scheme 86. Reaction mechanisms for stabilized and non-stabilized nucleophiles in asymmetric allylic substitution

Fletcher *et al.*[82] reported a copper-catalyzed asymmetric allylic alkylation of cyclic allylic chlorides with non-stabilized nucleophiles (Scheme 87). The coupling reaction of racemic 3-chloro-cyclohexene with alkylzirconium species **250** formed in situ from alkene **249** and Schwartz reagent (Cp_2ZrHCl) led to the product **251** in 86% yield and 93% enantiomeric excess.



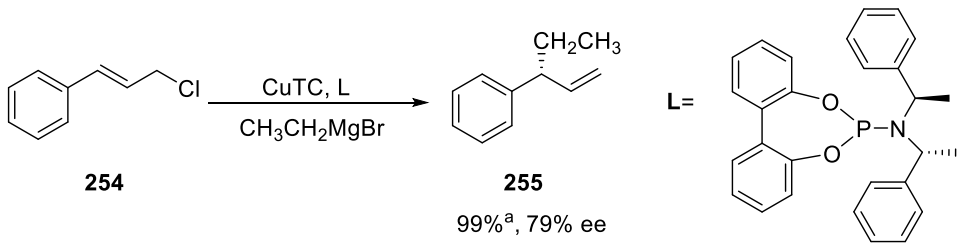
Scheme 87. Cu-catalyzed asymmetric allylic alkylation of cyclic allylic chlorides with non-stabilized nucleophiles

Alexakis *et al.*[88] demonstrated a copper catalyzed asymmetric allylic alkylation reaction of bromocyclohexene **252** with primary alkyl Grignard reagent as the non-stabilized nucleophile in presence of copper(I) thiophene-2-carboxylate (CuTC) and axial chiral ligand **L**. The product **253** was formed in good yield and enantioselectivity (Scheme 88).



Scheme 88. Cu-catalyzed asymmetric allylic alkylation reaction of bromocyclohexene **252** with primary alkyl Grignard reagent

Alexakis *et al.*[89] also reported a copper-catalyzed asymmetric allylic alkylation reaction shown in Scheme 89. Allylic chloride **254** was reacted with Grignard reagent in presence of CuTC and biphenol ligand **L** to give the product **255**.

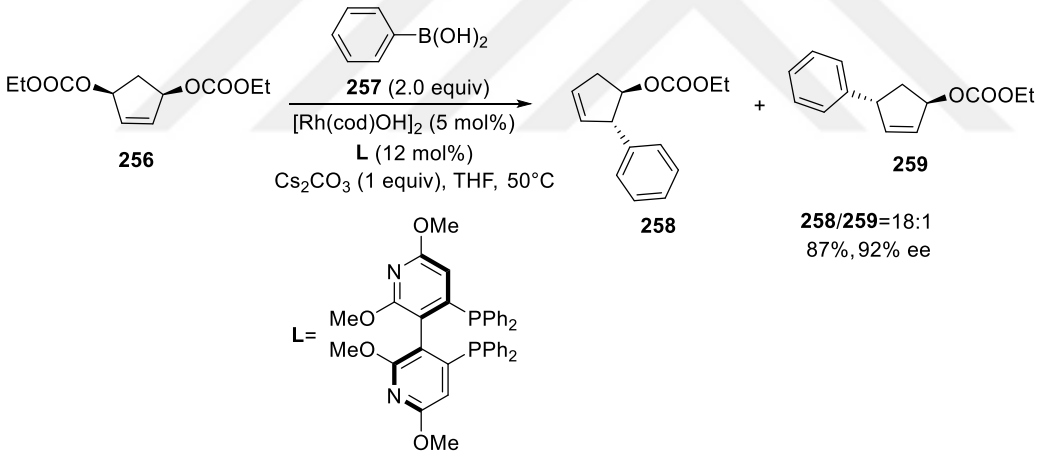


254 **255**

99%[a], 79% ee

Scheme 89. Cu-catalyzed asymmetric allylic alkylation of allylic chloride **254** [a] yields after chromatographic isolation on silica gel.

In 2006 Lautens *et al.*[84] described a rhodium-catalyzed asymmetric allylic substitution with phenyl boronic acid **257** as the non-stabilized nucleophile (Scheme 90). The rhodium(I) catalyst generated in situ from the reaction of $[Rh(cod)OH]_2$ with Xyl-P-PHOS ligand **L**. Subsquent S_N2' allylic substitution led to the desired products in good yields and enantioselectivities.



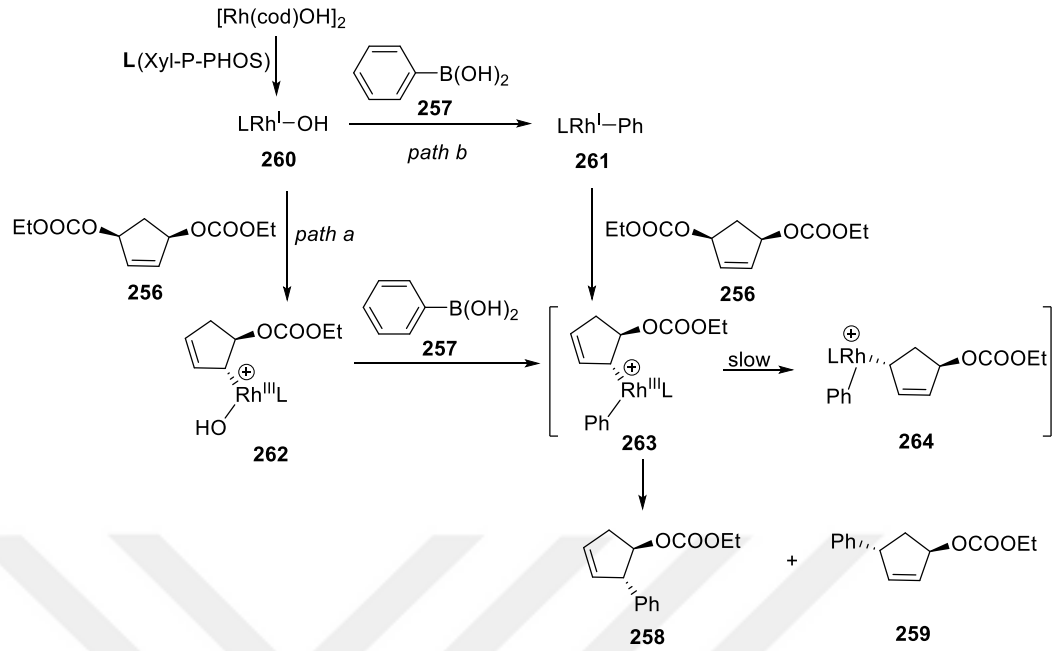
256 **258** **259**

258/**259**=18:1

87%, 92% ee

Scheme 90. Rh-catalyzed asymmetric allylic substitution with phenyl boronic acids

Two mechanisms were proposed for Rh-catalyzed asymmetric allylic substitution reaction (Scheme 91).[84]

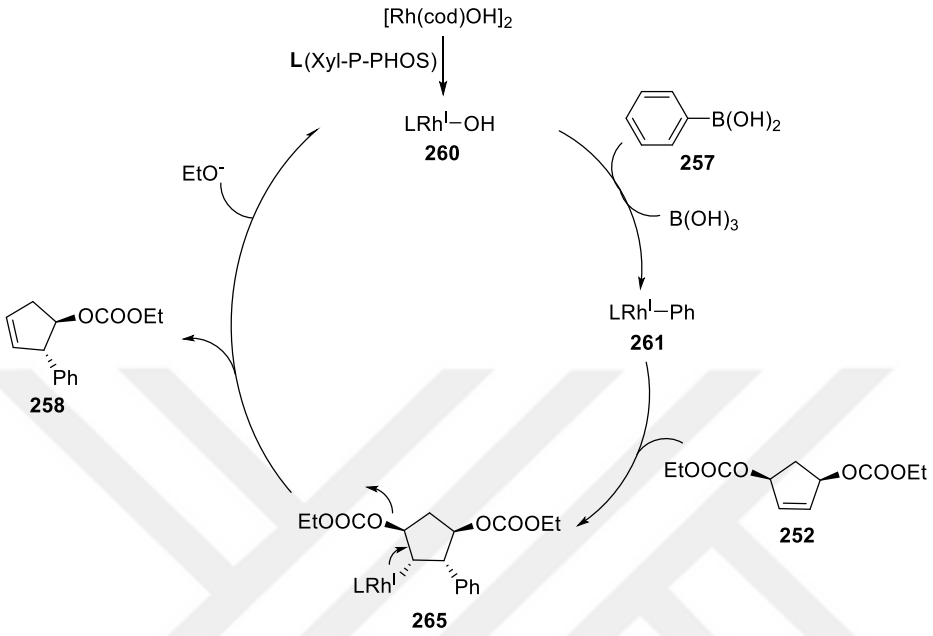


Scheme 91. Proposed mechanism for the Rh-catalyzed asymmetric allylic substitution reaction

The mechanism first starts with the ligand exchange process between ligand **L** and Rh(cod)OH_2 to form Rh(I)-OH species **260**. The second step involves the generation of the cationic rhodium(III) complex **262** from the reaction of meso compound **256** with **260**. Addition of phenylboronic acid (**257**) led to the formation of σ-enyl complex **263**. The final step of the mechanism is the C−C bond forming reductive elimination which results in the formation of the desired product **258**. On the other hand if the reaction follows path b, addition of phenylboronic acid (**257**) to Rh(I) complex **260** could give the Rh-Ph species **261**. Complex **261** is then reacted with meso compound **256** to yield σ-enyl complex **263**. Subsequent reductive elimination afforded the desired product **258**.[84]

Another possible mechanism that shown in Scheme 92 was also suggested. According to the mechanism, the catalytic cycle starts with the ligand exchange process to form Rh(I) complex **260**. Addition of phenyl boronic acid would lead to

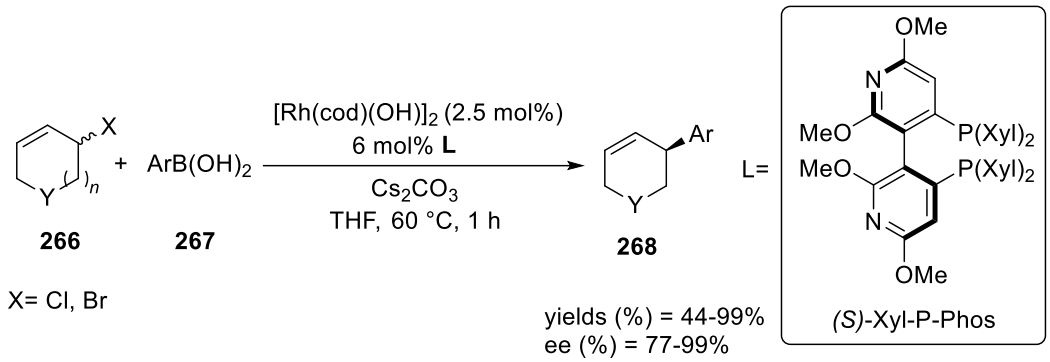
Rh-Ph complex **261** followed by carborhodation which would form intermediate **265**. Elimination of alkoxy group yields to the desired product **258**.[84]



Scheme 92. Proposed catalytic cycle for the Rh-catalyzed asymmetric allylic substitution

5.1.3 Objective of the Study

Fletcher *et al.*[90] reported an highly enantioselective rhodium catalyzed asymmetric allylic arylation using stabilized nucleophiles **267** that allows the conversion of racemic halides **266** into single-enantiomers (Scheme 93).



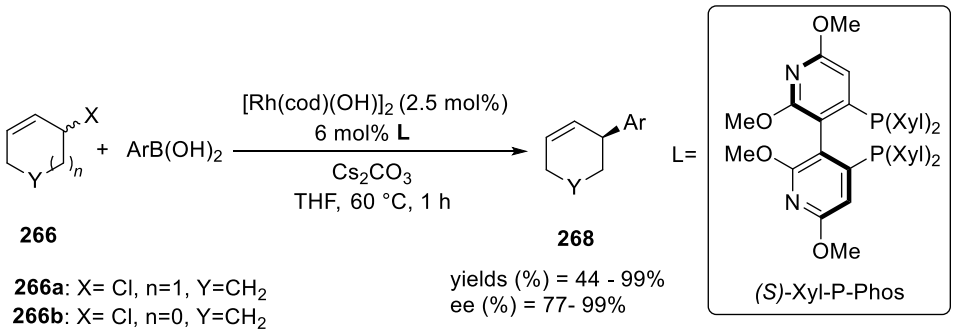
Scheme 93. Rh-catalyzed AAA of racemic halides with stabilized nucleophiles

They proposed that the transformation of both enantiomers of racemic halides into a single enantiomer of the desired product occurs via dynamic kinetic asymmetric transformation (DYKAT).[90] Understanding the stereo-selectivity in this study is complex because the substrate is racemic and synthesis of target compound is challenging. Besides, the halide ion co-product formed in the reaction media hinders the configuration of the remaining starting material so that the mechanism remains unclear.[90] We herein theoretically explored the reaction mechanism and the enantioselectivity observed in the rhodium catalyzed asymmetric allylic arylation reaction. Mechanistic analysis based on theoretical calculations will contribute to a better understanding of rhodium catalyzed asymmetric alllylic arylation reactions.

5.2 Results and Discussion

Fletcher *et al.*[90] described an asymmetric allylic arylation reaction of racemic halides using non-stabilized nucleophiles and Rh catalysts (Scheme 94). In the reaction, a variety of nucleophiles and electrophiles can be used to obtain enantio-enriched products in good yields and excellent enantioselectivities. They proposed that the reaction follows dynamic kinetic asymmetric transformation pathway whereas the detailed mechanism of the formation of enantio-enriched products remains unclear. We herein theoretically investigated the reaction mechanism of

the Rh-catalyzed asymmetric allylic arylation. The results were evaluated in the light of experimental findings to find the most plausible mechanism.

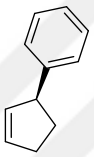
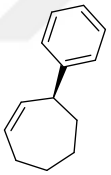
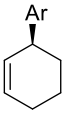
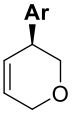


266

266a: X= Cl, n=1, Y=CH_2
266b: X= Cl, n=0, Y=CH_2
266c: X= Cl, n=2, Y=CH_2
266d: X= Br, n=1, Y=CH_2
266e: X= Cl, n=1, Y=O

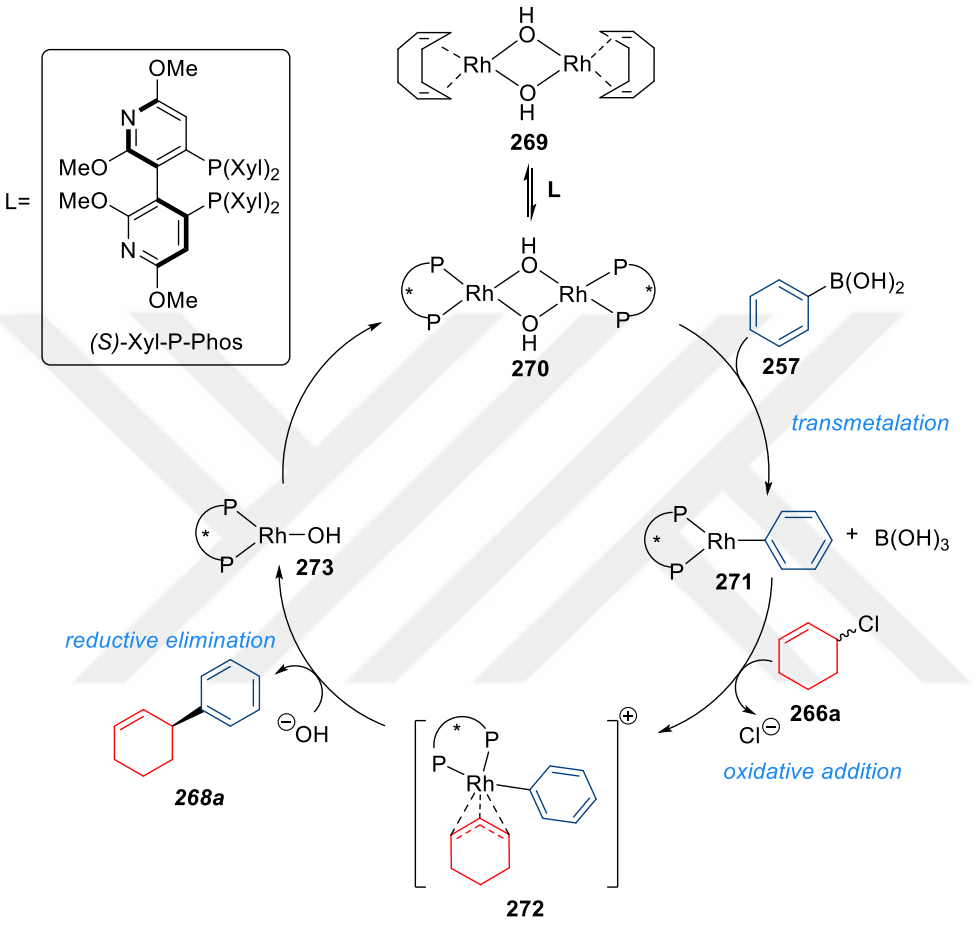
268

yields (%) = 44 - 99%
ee (%) = 77- 99%

Allylic halide	Boronic acid	Product		Yield (%)[a]	ee (%)[b]
266a	Ar = Ph		**268a**	99	99
	Ar = 4-MePh		**268b**	58	>94
	Ar = 4-F_3CPh		**268c**	60	96
	Ar = 4-FPh		**268d**	54	>99
266b	Ar = Ph		**268e**	67	>99
266c	Ar = Ph		**268f**	62	97
266d	Ar = 2-MePh		**268g**	45	>99
	Ar = 3-NO_2Ph		**268h**	51	96
	Ar = 2-OMe		**268i**	80	74
	Ar = 4-TBSOPh		**268j**	40	99
266e	Ar = Ph		**268k**	99	96
	Ar = 2-Naphth		**268l**	90	98

Scheme 94. Rh-catalyzed asymmetric allylic arylation of allylic halides. [a] = Isolated yield, [b] = Enantiomeric excess determined by HPLC using a chiral non-racemic stationary

Proposed catalytic cycle for the asymmetric allylic arylation (AAA) of racemic halides catalyzed by Rh(I)/(*S*)-Xyl-P-Phos (2,2′,6,6′-tetramethoxy-4,4′-bis(di(3,5-methyl) phenyl phos-phino)-3,3′-bipyridine) is illustrated in Scheme 95.

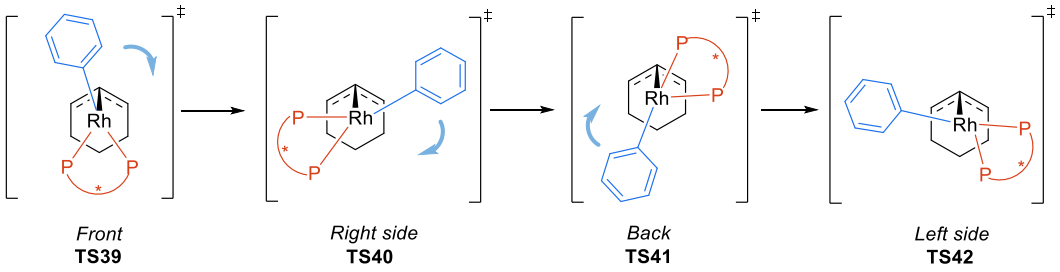


Scheme 95. Proposed catalytic cycle for Rh-catalyzed asymmetric allylic arylation

The reaction is initiated by ligand exchange process in which the cyclooctadiene ligand substitutes with (*S*)-Xyl-P-Phos **L**. The second step is the transmetalation of a phenyl group from boron to Rh(I)-OH complex **270** to generate Rh(I)-Ar complex **271**. Subsequent oxidative addition of racemic 3-chlorocyclohex-1-ene (**266a**) to the complex **271** would yield the η3-allyl-Rh(III) intermediate **272**. And the final

step is the reductive elimination that is associated with C−C bond formation, generating the product **268a**.

There are four potential binding orientations between the catalyst and the substrate: namely, front, right side, back, left side and two absolute configurations of chlorocyclohexene **266a** (S and R) (Scheme 96). Therefore, all eight possible transition states corresponding to the oxidative addition were located in order to gain insight into the origin of the stereoselectivity. Geometry optimizations and frequency calculations were performed using the dispersion-corrected ωB97XD[91] functional with the LANL2DZ(f) pseudopotential for Rh and 6-31G(d) basis set for all other atoms. Single-point energies in the solvent THF were evaluated for all optimized structures using SMD-ωB97XD/6-311G(d,p)(C,N,H,O), 6-311+G(d,p)(Cl) and LANL2TZ(f)[92] (Rh) levels of theory. The Gibbs free energy corrections were also calculated using Grimme's quasiharmonic approximation[93] in which the vibrational entropies were corrected by recomputing all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}. The Gibbs free energies were also evaluated at 333 K and a concentration of 1.0 mol/L.



Scheme 96. Simplified models for the Rh(I)-catalyzed oxidative addition. Chlorine atoms are omitted for clarity. Possible orientations are given according to the position of phenyl group with respect to the cyclohexene.

The calculated relative free energies ($\Delta\Delta G^{\ddagger}$) of each transition state mode for the oxidative addition step are shown in Figure 51.

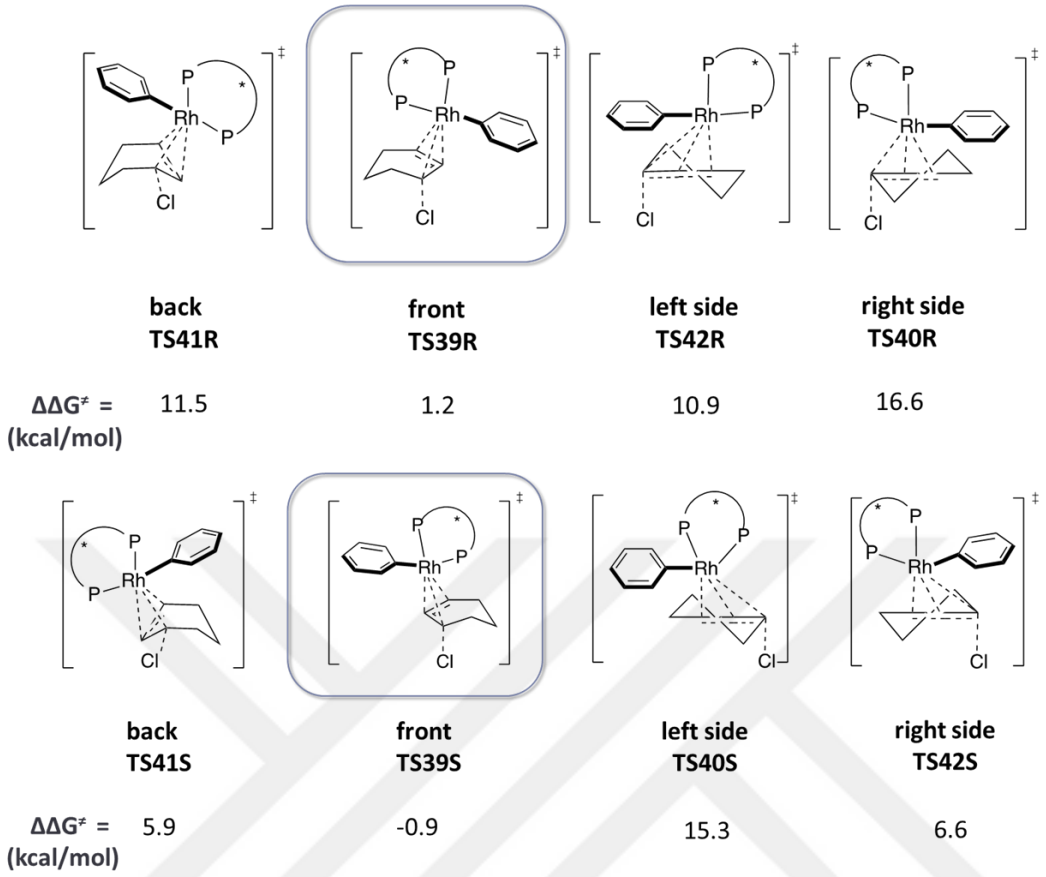


Figure 51. Simplified models of possible transition states for the oxidative addition step. $\Delta\Delta G^{\neq}$ energy values are calculated relative to the reactant complex of **TS39R** at SMD-ωB97XD/6-311+G(d,p)/LANL2TZ(f)//ωB97XD/6-31G(d)/LANL2DZ(f) level of theory.

According to the calculations, **TS39**, in which the phenyl group positioned in front of the cyclohexene, is found to be the most stable transition state for both S and R enantiomer of 3-chloro-cycloehexene (Figure 52). In **TS39**, Rh-phenyl fragment is positioned far away from the cyclohexene which shows that direction of approach of the phenyl group is critical.

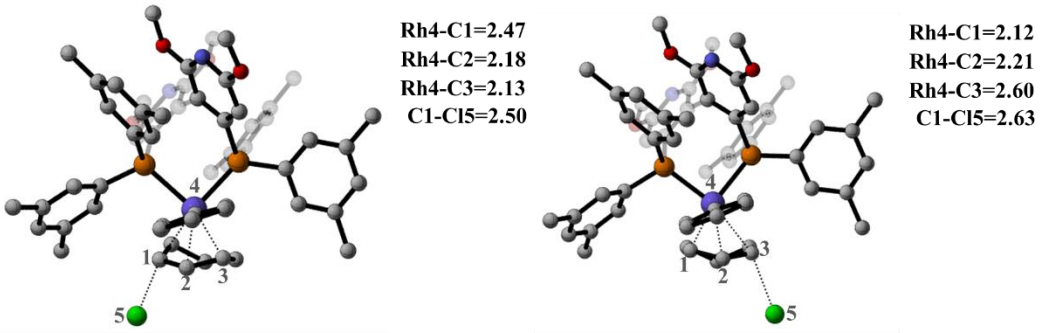


Figure 52. Most stable transition state geometries for the oxidative addition obtained at the ωB97XD/6-31G(d)/LANL2DZ(f) level of theory. The bond distances are given in angstrom. The hydrogen atoms are omitted for clarity.

Dissociation of the chloride via **TS39** would lead to the intermediate **274**. Optimized structure of **274** is depicted in Figure 53. The intermediate indicates η^3 coordination of the allyl unit, since C1 − C2 bond length (1.40 Å) and C2−C3 bond length (1.41 Å) are of partial double bond character, and the Rh4– C1, Rh4 – C2 and Rh4 – C3 bond lengths are 2.19, 2.18 and 2.21 Å, respectively.

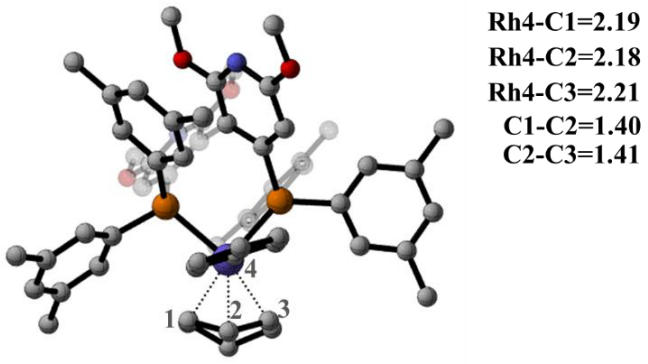
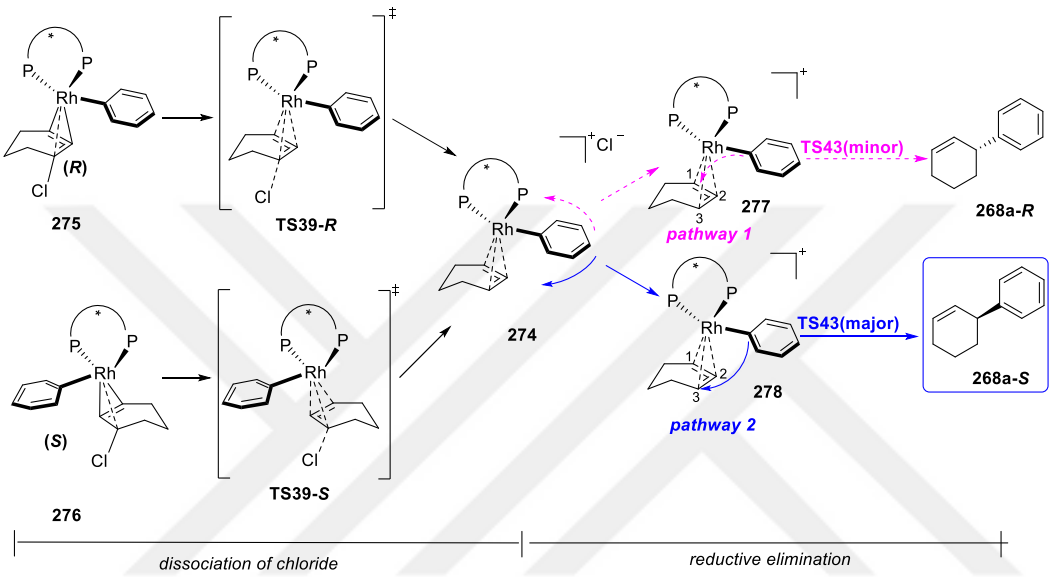


Figure 53. Optimized geometry of the η^3-allyl intermediate **274** obtained at the ωB97XD/6-31G(d)/LANL2DZ(f) level of theory. The bond distances are given in angstrom. The hydrogen atoms are omitted for clarity.

The reaction continues with the reductive elimination starting from the cationic Rh(III)-allyl intermediate **274**. This step may follow two distinct pathways: Rh(I)/(*S*)-Xyl-P-Phos/phenyl unit undergoes clock-wise (**TS43(minor)**) or anticlockwise (**TS43(major)**) rotations to form new C−C bond. The possible pathways for the competitive reductive elimination are depicted in Scheme 97.



Scheme 97. Proposed reaction mechanism for the oxidative addition/reductive elimination process. The blue arrow in **274** represents the clockwise rotation, whereas the pink arrow represents the counterclockwise rotation of the of the Rh(I)/(S)-Xyl-P-Phos/phenyl unit. Hydrogen atoms are omitted for clarity

TS43(major) is the lowest energy transition state, leading to the desired stereo product, *S*, which is in agreement with the experimental results (Figure 54).

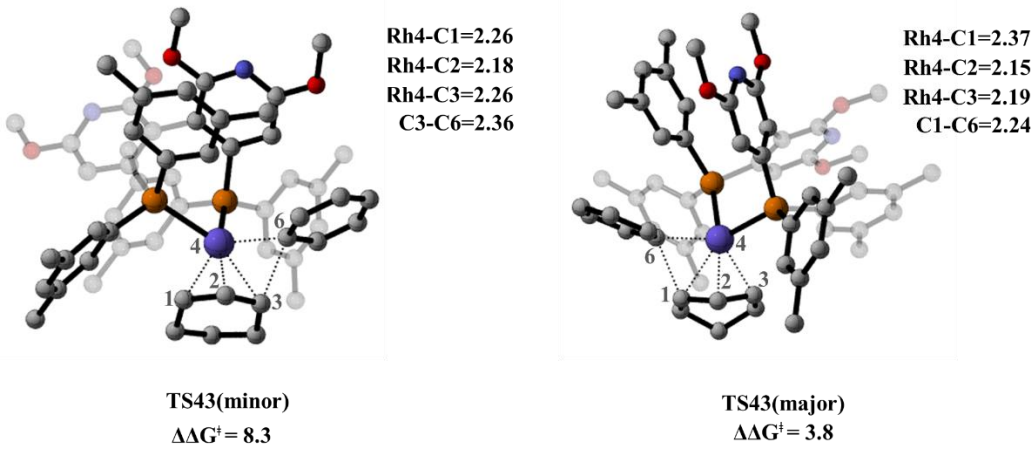


Figure 54. Transition state geometries for reductive elimination obtained at the SMD(THF)-ωB97XD/6-311+G(d,p)/LANL2TZ(f)//ωB97XD/6-31G(d)/LANL2-DZ(f) level of theory. The bond distances are given in angstrom. Relative Gibbs free energies are shown in kcal/mol with respect to reactant complex of the **TS39R**. The hydrogen atoms are omitted for clarity (carbon, gray; oxygen, red; nitrogen, blue; rhodium, purple; phosphorus, orange).

Comparison of the reductive elimination transition states reveals that the position of the phenyl group attached to the rhodium center is critical. In the lower energy transition state **TS43(major)**, phenyl group is located on the sterically less hindered side to avoid the unfavorable interaction with the xylene group of the ligand (Figure 55).

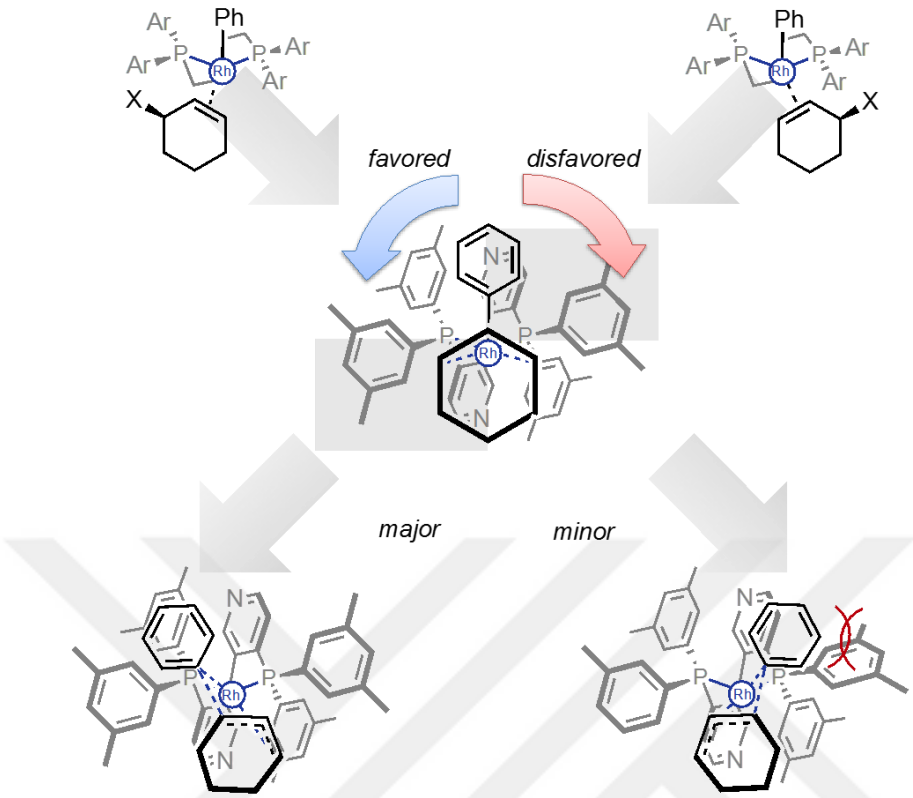


Figure 55. Proposed model for explaining the rate- and stereoselectivity-determining step for the asymmetric allylic arylation and critical transition states.

According to the mechanistic analysis, both enantiomers of the racemic substrate are converted into the same intermediate which then undergoes a reductive elimination to afford the target product. When the overall reaction profile is considered, reductive elimination step is found to be the rate-limiting and selectivity determining step (Figure 56). The computational enantiomeric excess (≈99%) in the solvent is in good agreement with the experimental enantiomeric excess which is (99%). A detailed mechanistic analysis based on theoretical calculations help to determine the reaction pathway.

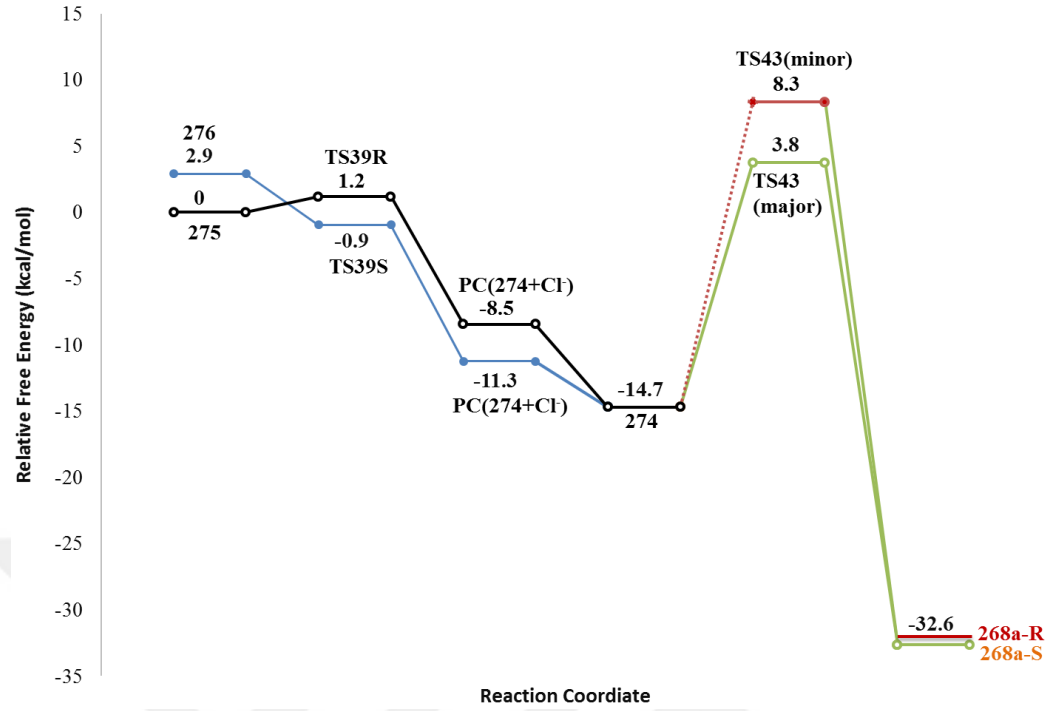


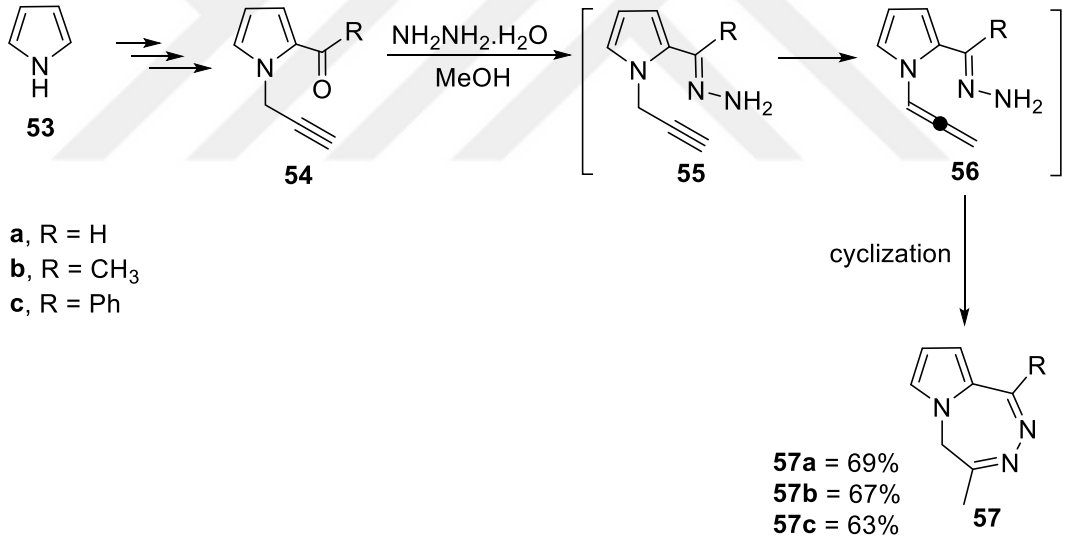
Figure 56. Computed free energy profile of the most favorable pathway for Rh-catalyzed asymmetric allylic arylation using SMD(THF)-ωB97XD/6-311+G(d,p)/LANL2TZ(f)//ωB97XD/6-31G(d)/LANL2DZ(f) level of theory. Gibbs free energies are given in kcal/mol.

We herein theoretically explain the enantioselectivity observed in the rhodium catalyzed asymmetric allylic arylation of racemic halides. Experimental results showed that transmetallation step was too fast; therefore, this step was not modeled. All possible transition states for the oxidative addition and reductive elimination steps were located. Based on the results, reductive elimination step is found to be the rate- and stereo determining step.

CHAPTER 6

CONCLUSION

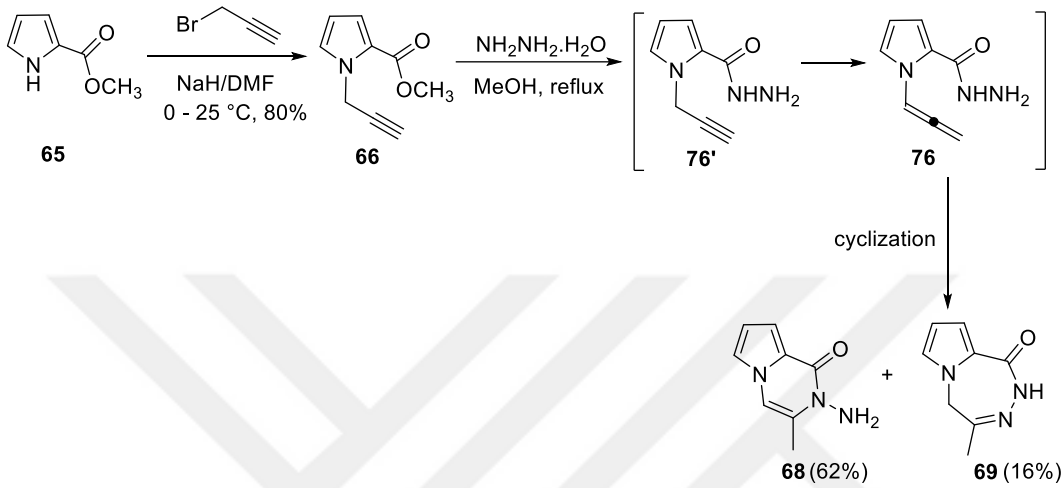
Our group designed a new synthetic approach for the synthesis of pyrrolotrizapine derivatives **57** via metal free cyclization method. For this purpose, key compound **54** was obtained starting from pyrrole. *N*-propargyl carbaldeyhe **54** was then submitted to the cyclization reaction with hydrazine monohydrate to afford the desired skeleton **57** (Scheme 98).



Scheme 98. Synthesis of pyrrolotriazepine derivatives **57** starting from pyrrole

A similar synthetic approach was applied starting from pyrrole ester **65** for the construction of pyrrolotriazepinone derivatives **69** (Scheme 99). However, target

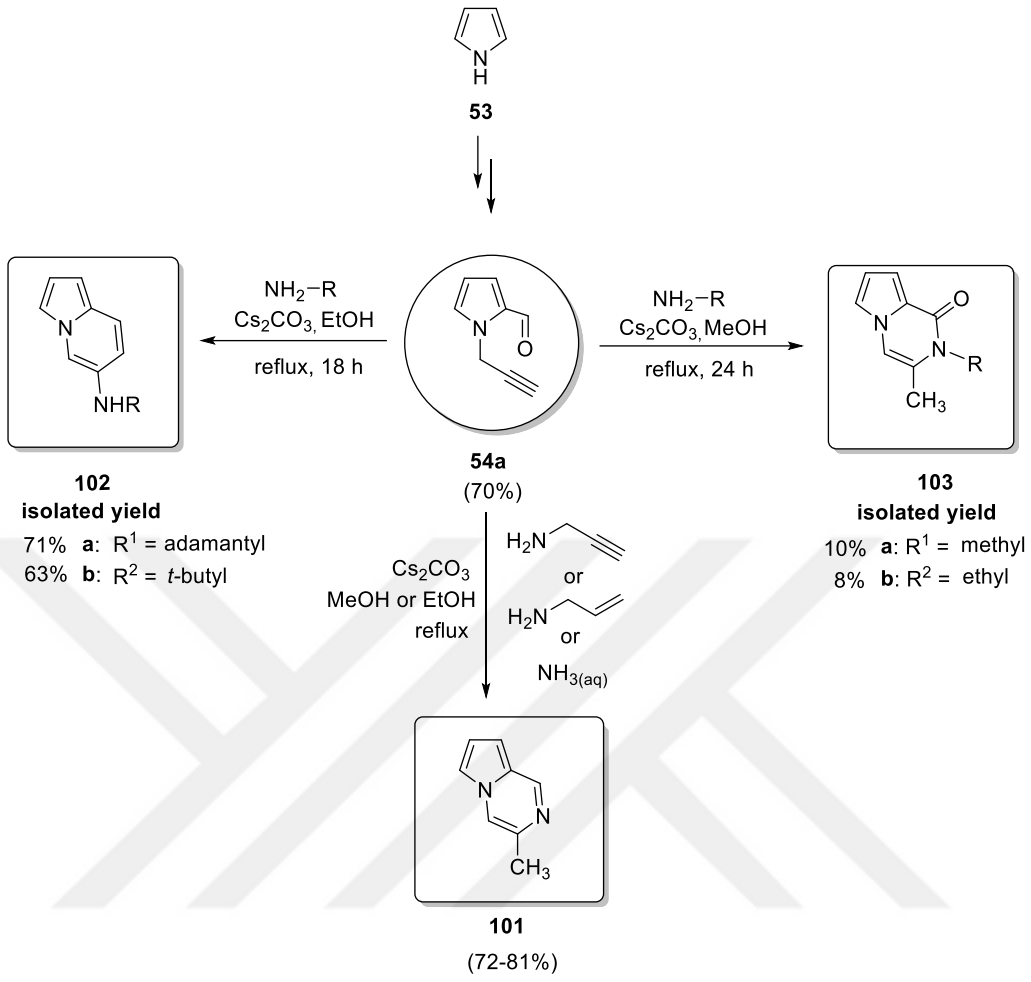
product **69** was observed in 16% yield. Interestingly, pyrrolopyrazinone derivative **68** was obtained as the major product.



Scheme 99. Synthesis of pyrrolotriazepinone derivatives **69** starting from pyrrole ester **65**

The potential energy profiles along the reaction pathways were investigated by means of DFT calculations. Base-catalyzed propargyl-allene isomerization was suggested during the cyclization process. Calculated transition state energies are in good agreement with the experimental findings.

In the second part of the study, the reaction of *N*-propargyl carbaldeyde **54a** with different types of amines were investigated (Scheme 100). Intramolecular cyclization was achieved by using primary amines such as ammonia, propargyl or allyl amine. Each case, formation of the same product **101** was observed. We next examined the reaction of *N*-propargyl carbaldeyde **54a** with alkyl amine such as methyl and ethyl amine. A different skeleton which is pyrrolo-pyrazinones **103** were formed in poor yields. In the final case, the reaction of **54a** with bulky amines (adamantyl or *tert*-butyl amine) led to the formation of indolizine derivatives **102**.

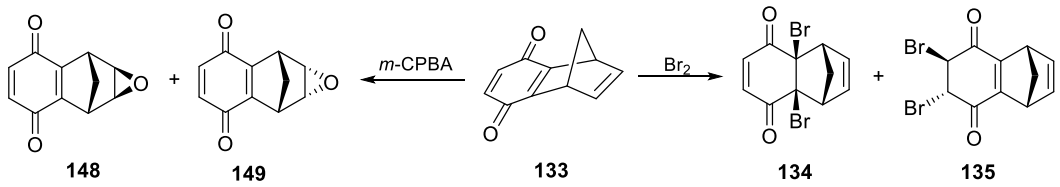


Scheme 100. The reaction of key compound **54a** with different types of amines

To understand the main factors causing this difference in reactivity, the reaction mechanisms have been studied by means of computational methods. Based on the computational analysis and experimental results, we proposed that propargyl-allene isomerization takes place during the reaction. After the formation of allene intermediate, two competing pathways were investigated. The first pathway involves the nucleophilic attack of amine at aldehyde carbonyl carbon which then leads to formation of imine. The second pathway involves the nucleophilic attack at the center carbon of allene moiety. According to the computational results, the reaction with primary amines follow the first pathway while bulky amines follow

the second pathway. These theoretical predictions are in line with the experimental findings.

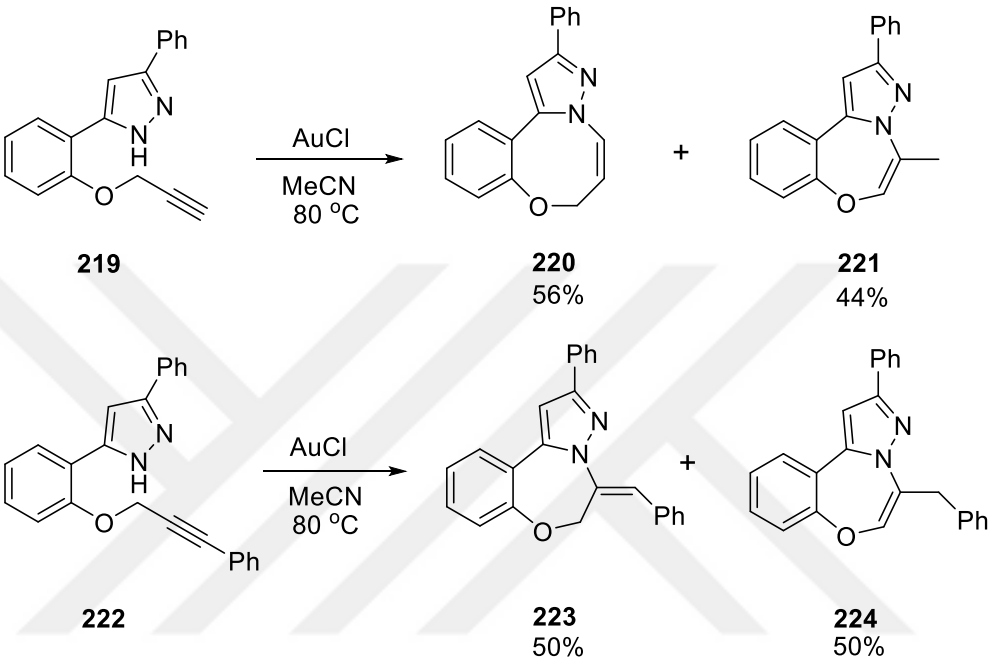
In the next part of the study, regioselectiviy and stereoselectivity of the bromination and epoxidation reaction of norbornadiene derivative **133** were investigated (Scheme 101). Compound **133** underwent epoxidation from the double bond of the norbornene unit, whereas the opposite regioselectivity was observed for the addition of bromide. Experimentally observed regioselectivities and stereoselectivities were investigated with a detailed computational analysis. For the bromination reaction, relative energies of possible bromonium ions and products were calculated. In addition, transition states for the formations of non-classical carbocations via sigma bond participation were located. Experimantally observed products were rationalized with the theoretical calculations. In the case of epoxidation, it was found that formation of the compounds **148** and **149** is both kinetically and thermodynamically more favorable than the formation of other possible epoxides.



Scheme 101. Bromination and epoxidation reaction of **133**

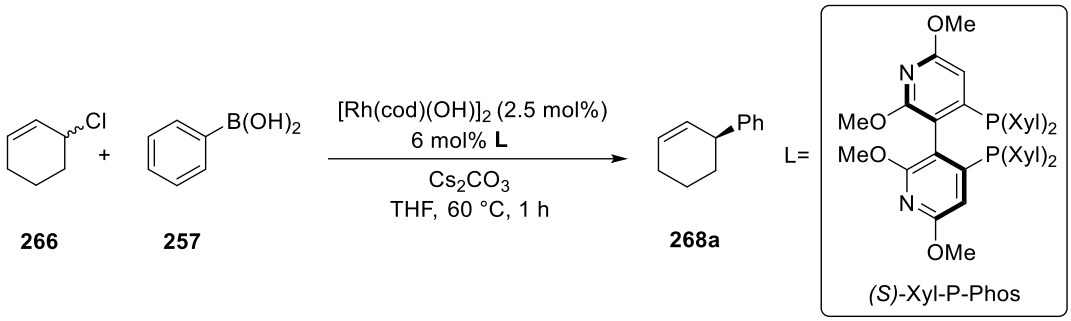
In the next part of the study, our research group synthesized benzoxazepines and benzoxazocines that might have important biological activities (Scheme 102). Terminal alkynes undergo intramolecular cyclization through both 7-*exo-dig* and 8-*endo-dig* processes; however, internal alkynes undergo only 7-*exo-dig* cyclization. In order to elucidate the mechanism, Gibbs free activation barriers for the formation of the products **220/221** and **223/224** were calculated. In the case of terminal

alkynes, when we compare the activation barriers, the reaction may follow both pathways (7-*exo*-*dig* and 8-*endo*-*dig*). However, in the case of internal alkynes, we proposed that π-π stacking interaction favors the 7-*exo*-*dig* cyclization which is responsible for the formation of only benzoxazepine derivatives **223** and **224**.



Scheme 102. Hydroamination reaction of terminal and internal alkynes **219** and **222** with AuCl

In the final part of the study, enantioselectivity observed in the Rh-catalyzed asymmetric allylic arylation reaction was investigated by means of DFT calculations (Scheme 103). The Gibbs free activation barriers for the possible oxidative additon and reductive elimination steps were calculated. According to the computational results, both enantiomers are converted into a common intermediate which then undergoes a reductive elimination to give the desired product. We proposed that the reductive elimination step is both rate-limiting and selectivity determining step.



266 257 268a

Scheme 103. Rh-catalyzed AAA of racemic halides

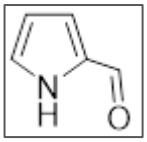
CHAPTER 7

EXPERIMENTAL

7.1 General Methods

All reagents were commercially available and used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400 MHz and 100 MHz NMR instrument, respectively, using $CDCl_3$ as the solvent and TMS as an internal standard. The coupling constants, *J*, were reported in hertz (Hz) and chemical shifts, δ, were reported in parts per million (ppm). The peak patterns of ^{1}H NMR are designated as follows: s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; bq, broad quartet; and m, multiplet. Purification of the reaction products was performed by coulumn chromatography using silica gel (60-mesh). TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates. Melting points were measured using melting point apparatus and were uncorrected. High resolution Mass spectra were recorded by LC-MS TOF electrospray ionization technique. Evaporation of solvents was performed at reduced pressure, using a rotary vacuum evaporator

7.2 Synthesis of 1*H*-pyrrole-2-carbaldehyde (63a)

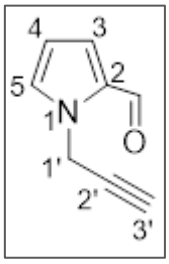


To a solution of $POCl_3$ (26.1 g, 0.17 mol) and DMF (13.6 g, 0.19 mol) in dry ether (70 mL) at 0 °C was added pyrrole (11.6 g, 0.17 mol) dropwise in an ice bath. The reaction mixture was stirred at room temperature for 16 h. After removal of the solvent, the saturated solution of Na_2CO_3

was added until a basic medium was obtained. The reaction mixture was extracted with EtOAc (5 × 100 mL) and washed with brine (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was evaporated and the crude product was purified over silica gel eluting with hexane/EtOAc (3/1) to give **63a**[1b] as a colorless solid. (11.30 g, 70%).

7.3 Synthesis of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a)

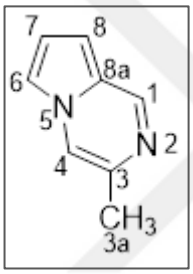
To a stirred mixture of 1*H*-pyrrole-2-carbaldehyde (9.3 g, 0.098 mol) in DMF (50 mL) was added NaH (3.95 g, 0.165 mol) at 0 °C portionwise. The reaction mixture was stirred at 0 °C for 20 minutes and propargyl bromide (15 g, 0.126 mol) in DMF (20 mL) was added to the reaction flask dropwise over a period of 30 minutes. After stirring for 16 h at room temperature, solvent was removed. The resulting mixture was diluted with water (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed with brine (4 × 50 mL) and dried over $MgSO_4$ and filtered. The solvent was evaporated and the crude product was purified over silica gel eluting with hexane/EtOAc (5/1) to give **54a**[1b] as a light orange liquid. (9.13 g, isolated yield: 70%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (bd, J = 0.8 Hz, 1H, −CHO), 7.26 (bs, 1H, H-5, -CH), 6.96 (dd, $J_{3,4}$ = 4.0 Hz, $J_{3,5}$ =1.7 Hz, 1H, H-3, -CH), 6.28 (dd, $J_{4,3}$ = 4.0 Hz, $J_{4,5}$ =2.7 Hz, 1H, H-4, -CH), 5.21 (d, $J_{1',3'}$ = 2.6 Hz, 2H, H-1', -CH_2), 2.47 (t, $J_{3',1'}$ = 2.6 Hz, 1H, H-3',-CH). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.6, 131.1, 130.4, 125.0, 110.1, 77.5, 74.4, 38.1

7.4 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Propargylamine

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.666 g, 5.0 mmol) in methanol (15 mL) was added propargylamine (0.32 mL, 5.0 mmol) and Cs_2CO_3 (1.63 g, 5.0 mmol). The mixture was stirred at reflux temperature of methanol for 24 h. After completion of reaction, solvent was removed. The mixture was diluted with water (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine (3 × 50 mL) and dried over $MgSO_4$ and filtered. The solvent was evaporated to give the product 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**)[94] as a brown solid (0.535 g, crude yield: 81%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H, H-1, -CH), 7.64 (bq, $J_{4,3a}$ = 1.0 Hz, 1H, H-4, -CH), 7.35-7.30 (m, 1H, H-6, -CH), 6.81 (dd, $J_{7,8}$ = 4.1 Hz, $J_{7,6}$ = 2.4 Hz, 1H, H-7, -CH), 6.73 (bd, $J_{8,7}$ = 4.1 Hz, 1H, H-8, -CH), 2.40 (bd, $J_{3a,4}$ = 1.0 Hz, 3H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 135.2, 127.3, 114.9, 114.5, 114.1, 103.0, 20.7.

7.5 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Ammonia Solution.

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1.0 mmol) in ethanol (10 mL) was added ammonia solution (32%) (0.255 g, 15.0 mmol) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at reflux temperature of ethanol. After completion of the reaction, solvent was removed.The mixture was diluted with water (15 mL) and extracted with EtOAc (3 × 15 mL). The collected organic layers were combined and washed with brine (15 mL), dried over $MgSO_4$.

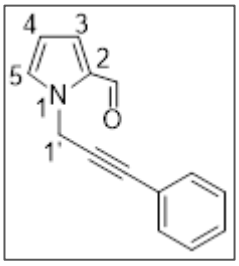
The solvent was removed by vacuum to give the product **101**[94] as a brown solid. (0.107 g, crude yield: 81%).

7.6 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Allylamine

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1.0 mmol) in methanol (10 mL) was added allylamine (0.058 g, 1.0 mmol) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at reflux temperature of methanol. After stirring for 24 h, solvent was removed. The mixture was diluted with water (15 mL) and extracted with EtOAc (3 × 15 mL). The collected organic layers were washed with brine (15 mL) and dried over $MgSO_4$. The solvent was removed by vacuum to give the product **101**[94] as a brown solid. (0.095 g, crude yield: 72%).

7.7 Synthesis of 1-(3-Phenylprop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (105)

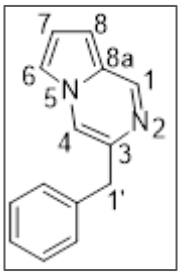
Cuprous iodide (3.8 mg, 0.02 mmol) of palladium acetate (4.5 mg, 0.02 mmol), and triphenylphosphine (13.1 mg, 0.05 mmol) were placed in a two necked round bottom flask under nitrogen atmosphere. In another flask, 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.266 g, 2.0 mmol) and iodobenzene (0.24 mL, 2.18 mmol) and diisopropylamine (1 mL, 7.0 mmol) were dissolved in dry THF (20 mL), and then added to the mixture prepared above. The mixture was heated and stirred at the reflux temperature of THF and then filtered through celite. The crude product was purified by column chromatography eluting with hexane/EtOAc (5/1) to give **105**[95a,95b] as a yellowish liquid (0.246 g, isolated yield: 59%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (bs, 1H, -CHO), 7.47-7.42 (m, 2H, Ar-H), 7.36 (bs, 1H, Ar-H), 7.34-7.28 (m, 3H, Ar-H), 6.98 (dd, $J_{3,4}$ = 4.0 Hz, $J_{3,5}$ = 1.7 Hz, 1H, H-3, -CH), 6.29 (dd, $J_{4,3}$ = 4.0 Hz, $J_{4,5}$ = 2.6 Hz, 1H, H-4), 5.43 (bs, 2H, H-1', -CH_2). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.6, 131.8, 131.2, 130.4, 128.8, 128.4, 125.0, 122.2, 110.1, 86.1, 82.7, 39.0.

7.8 Synthesis of 3-Benzylpyrrolo[1,2-*a*]pyrazine (106)

To a solution of 1-(3-phenylprop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.163 g, 0.78 mmol) in methanol (10 mL) was added propargylamine (0.08 mL, 1.2 mmol) and Cs_2CO_3 (0.254 g, 0.78 mmol). The reaction mixture was heated at the reflux temperature of methanol for 24 h during stirring. After completion of the reaction, solvent was removed. The resulting mixture was purified over silica gel eluting with hexane/EtOAc (3/1) to give **106**[96] as a brown solid (crude yield: 0.105 g 65%; isolated yield: 0.052 g, 32%).

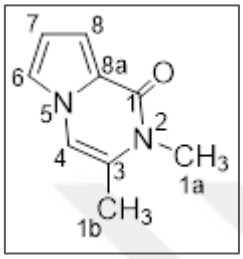


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H, H-1, -CH), 7.43 (s, 1H, H-4, -CH), 7.27 – 7.20 (m, 5H, Ar-H, -CH), 7.19 – 7.13 (m, Ar-H,-CH), 6.74, (dd, $J_{7,8}$ = 3.8 Hz, $J_{7,6}$ = 2.5 Hz, 1H, H7, -CH), 6.68 (d, $J_{8,7}$ = 3.8 Hz, 1H, H8, -CH), 3.96 (s, 2H, H-1', -CH_2) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 138.8, 138.4, 129.2, 128.7, 126.6, 115.9, 115.1, 103.8, 40.8

7.9 Synthesis of 2,3-Dimethylpyrrolo[1,2-*a*]pyrazin-1(*2H*)-one (103a)

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1.0 mmol) in methanol (10 mL) was added excess methylamine (0.9 mL, 40%) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at reflux temperature of

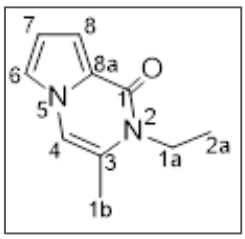
methanol for 24 h, and then solvent was removed. The mixture was diluted with water (15 mL) and extracted with EtOAc (3 × 15 mL). The collected organic layers were washed with brine (15 mL). Solvent was dried over $MgSO_4$ and removed by vacuum. The resulting mixture was purified over silica gel eluting with hexane/EtOAc (3/1) to give **103a**[97] as a light brown solid (0.017 g; isolated yield: 10%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (bd, $J_{8,7}$ = 3.9 Hz, 1H, H-8, -CH), 6.99 (dd, $J_{6,7}$ = 2.4 Hz, $J_{6,8}$= 1.5 Hz, 1H, H-6, -CH), 6.82 (bs, 1H, H-4, -CH), 6.50 (dd, $J_{7,8}$ = 3.9 Hz, $J_{7,6}$ =2.4 Hz, 1H, H-7, -CH), 3.45 (s, 3H, H-1a, -CH_3), 2.22 (bd, $J_{1b,4}$ = 1.1 Hz, 3H, H-1b, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 124.7, 123.1, 117.2, 112.1, 109.7, 105.9, 29.2, 17.4.

7.10 Synthesis of 2-Ethyl-3-methylpyrrolo[1,2-*a*]pyrazin-1(2*H*)-one (103b)

To a solution of 1-(prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1.0 mmol) in methanol (10 mL) was added excess aqueous ethylamine (1 mL, 70%) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at reflux temperature of methanol for 24 h, solvent was removed. The mixture was diluted with water (15 mL) and extracted with EtOAc (3 × 15 mL). The collected organic layers were washed with brine (15 mL). Solvent was dried with $MgSO_4$ and removed by vacuum. The resulting mixture was purified over silica gel eluting with hexane/EtOAc (3/1) to give **103b**[97] as a brown solid. (0.014 g; isolated yield: 8%).

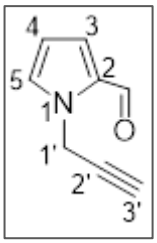


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (bd, $J_{8,7}$ = 4.0, 1H, H-8, -CH), 6.99 (dd, $J_{6,7}$ = 2.5, $J_{6,8}$ = 1.5 Hz, 1H, H-6, -CH), 6.80 (bs, 1H, H-4, -CH), 6.51 (dd, $J_{7,8}$ = 4.0, $J_{7,6}$ =2.5 Hz, 1H, H-7, -CH), 4.02 (q, $J_{1a,2a}$= 7.1 Hz, 2H, H-1a, -CH_2), 2.25 (bd, $J_{1b,4}$ = 1.1 Hz, 3H, H-1b, -CH_3), 1.28 (t, $J_{2a,1a}$ = 7.1 Hz, 3H, H-2a,

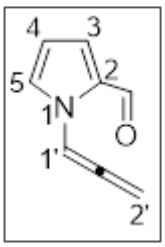
-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 124.2, 123.4, 117.1, 112.0, 109.5, 106.1, 37.5, 16.9, 14.5

7.11 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Propargylamine in Dry THF

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1 mmol) in dry THF (10 mL) was added propargylamine (0.064 mL, 1.0 mmol) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at reflux temperature of THF for 24 h. After completion of reaction, solvent was removed. The resulting mixture was extracted with ethyl acetate (3 × 15 mL). The combined extracts were washed with brine (3 × 15 mL) and dried over $MgSO_4$. The solvent was evaporated to give a mixture of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**)[1b] (92%) and 1-(propa-1,2-dienyl)-1*H*-pyrrole-2-carbaldehyde (**64a**)[1b] (8%). 3-Methyl-pyrrolo[1,2-*a*]pyrazine (**101**) was not observed. The ratio was calculated from the ^{1}H-NMR spectrum.



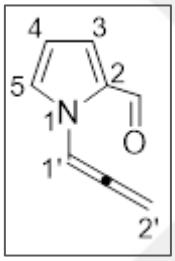
1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (bd, J = 1.0 Hz, 1H, -CHO), 7.27 (bs, 1H, H-5, -CH), 6.96 (dd, $J_{3,4}$ = 4.0 Hz, $J_{3,5}$ =1.7 Hz, 1H, H-3, -CH), 6.28 (dd, $J_{4,3}$ = 4.0 Hz, $J_{4,5}$ =2.6 Hz, 1H, H-4, -CH), 5.20 (d, $J_{1',3'}$ = 2.6 Hz, 2H, H-1', -CH_2), 2.48 (t, $J_{3',1'}$ = 2.6 Hz, 1H, H-3', -CH).



1-(Propa-1,2-dienyl)-1*H*-pyrrole-2-carbaldehyde (64a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, J = 1.0 Hz, 1H, -CHO), 8.14 (t, $J_{1',2'}$ = 6.6 Hz, 1H, H-1', -CH), 7.23 –7.21 (m, 1H, H-5, -CH), 6.98 (dd, $J_{3,4}$ = 4.0 Hz, $J_{3,5}$ = 1.6 Hz, 1H, H-3, -CH), 6.32 (dd, $J_{4,3}$ = 4.0 Hz, $J_{4,5}$ = 2.7 Hz 1H, H-4, -CH), 5.53 (d, $J_{2',1'}$ = 6.6 Hz, 2H, H-2', -CH_2).

7.12 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Propargylamine in Dry DMF

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1 mmol) in dry DMF (10 mL) was added propargylamine (0.064 mL, 1.0 mmol) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at 65 °C for 24 h. After completion of reaction, solvent was removed. The mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 × 15 mL). The combined extracts were washed with brine (5 × 15 mL) and dried over $MgSO_4$. The solvent was evaporated to give the product 1-(propa-1,2-dien-1-yl)-1*H*-pyrrole-2-carbaldehyde (**64a**).[1b] 3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**) was not observed.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 0.9 Hz, 1H, -CHO), 8.15 (t, $J_{1'2'}$ = 6.6 Hz, 1H, H-1', -CH), 7.24 –7.21 (m, 1H, H-5, -CH), 6.99 (dd, $J_{3,4}$ = 3.9 Hz, $J_{3,5}$ = 1.6 Hz, 1H, H-3, -CH), 6.32 (dd, $J_{4,3}$ = 3.9 Hz, $J_{4,5}$ = 2.8 Hz 1H, H-4, -CH), 5.53 (d, $J_{2',1'}$ = 6.6 Hz, 2H, H-2', -CH_2).

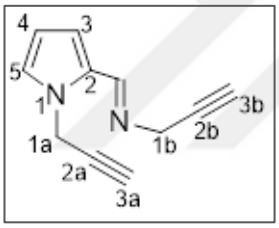
7.13 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Propargylamine in Dry Acetonitrile

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**) (0.133 g, 1 mmol) in dry acetonitrile (10 mL) was added propargylamine (0.064 mL, 1.0 mmol) and Cs_2CO_3 (0.326 g, 1.0 mmol). The mixture was stirred at reflux temperature of acetonitrile for 24 h. After completion of reaction, the mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 × 15 mL). The combined extracts were washed with brine (3 × 15 mL) and dried over $MgSO_4$. The solvent was evaporated to give the product mixture 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54a**)[1] (34%) and 1-(propa-1,2-dienyl)-1*H*-pyrrole-2-carbaldehyde (**64a**)[1] (64%).

3-methyl-pyrrolo[1,2-*a*]pyrazine (**101**) was not observed. The ratio was calculated from the ^{1}H-NMR spectrum.

7.14 Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (54a) with Propargylamine in the absence of a base (Cs_2CO_3)

To a solution of 1-(prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (**54**a) (0.266 g, 2.0 mmol) in methanol (10 mL) was added propargylamine (0.128 mL, 2.0 mmol). The mixture was stirred at room temperature for 24 h. After completion of reaction, the solvent was evaporated to give the crude product. The ^{1}H NMR spectral analysis of the residue afforded the formation of three products; **101**[94] (19%), **54a**[1b] (11%) and (E)-N-(prop-2-yn-1-yl)-1-(1-(prop-2-yn-1-yl)-1H-pyrrol-2-yl)methanimine **(104**) (70%). The ratio was calculated from the ^{1}H-NMR spectrum.



(E)-N-(prop-2-yn-1-yl)-1-(1-(prop-2-yn-1-yl)-1H-pyrrol-2-yl)methanimine (80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (bt J = 1.4 Hz, 1H, N=CH), 7.07-7.04 (m, 1H, H-5, -CH), 6.54 dd, $J_{3,4}$ = 3.7 Hz, $J_{3,5}$ =1.7 Hz, 1H, H-3, -CH), 6.21 (dd, $J_{4,3}$ = 3.7 Hz, $J_{4,5}$ =2.8 Hz, 1H, H-4, -CH), 5.31 (d, $J_{1a,3b}$ = 2.5 Hz, 2H, H-1a, -CH_2), 4.43–4.40 (m, 2H, H-1b, - CH_2), 2.48 (t, $J_{3a,1a}$ = 2.5 Hz, 1H, H-3a, -CH), 2.38 (t, $J_{3b,1b}$ = 2.6 Hz, 1H, H-3b, -CH).

7.15 Theoretical Methods

All calculations were performed with the Gaussian 09[98] program package. Geometry optimization and frequency calculations were carried out with the hybrid density functional B3LYP (Becke-3-parameter-Lee-Yang-Parr) method using the 6-31+G(d,p) basis set in the gas phase (except otherwise indicated). Solvent effects were considered by single-point energy calculations on the gas-phase stationary

points employing the polarizable continuum model (PCM) at the same level of theory (except otherwise indicated). In order to identify all of the stationary points as minima (no imaginary frequency) or transition states (one imaginary frequency), harmonic vibrational frequency calculations were performed using analytical second derivatives at 25 °C and 1 atm. The intrinsic reaction coordinate[99] (IRC) calculations were followed to ensure that all of the transition states were connected the corresponding reactants and products on the potential energy surface. Natural bond orbital[100] (NBO) analyses were performed to obtain the charge distribution of some selected stationary points. The optimized geometry structures are illustrated by Chemcraft[101] or CYLview[102].

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APPENDIX A

SPECTRAL DATA

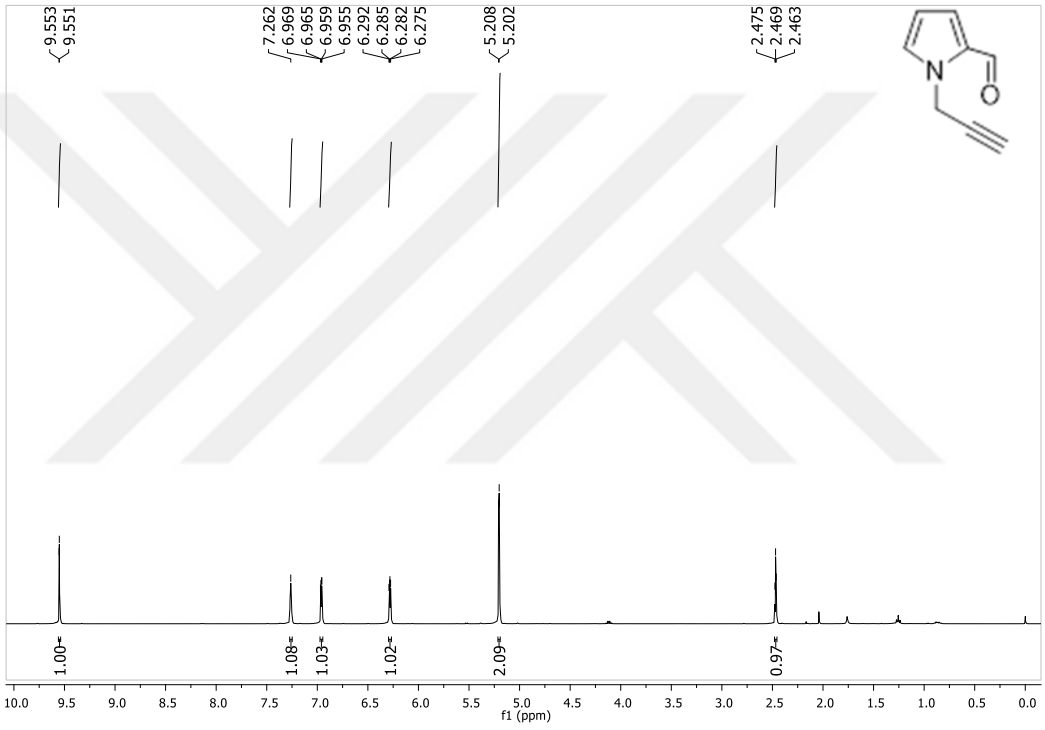

Figure 57. ^{1}H-NMR Spectrum of Compound **54a**

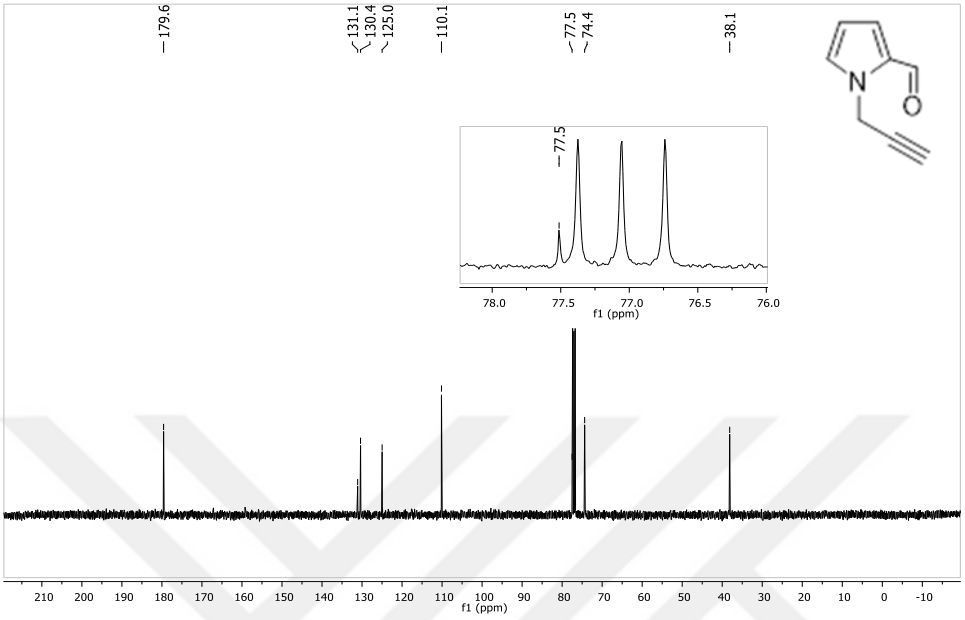

Figure 58. ^{13}C-NMR Spectrum of Compound **54a**

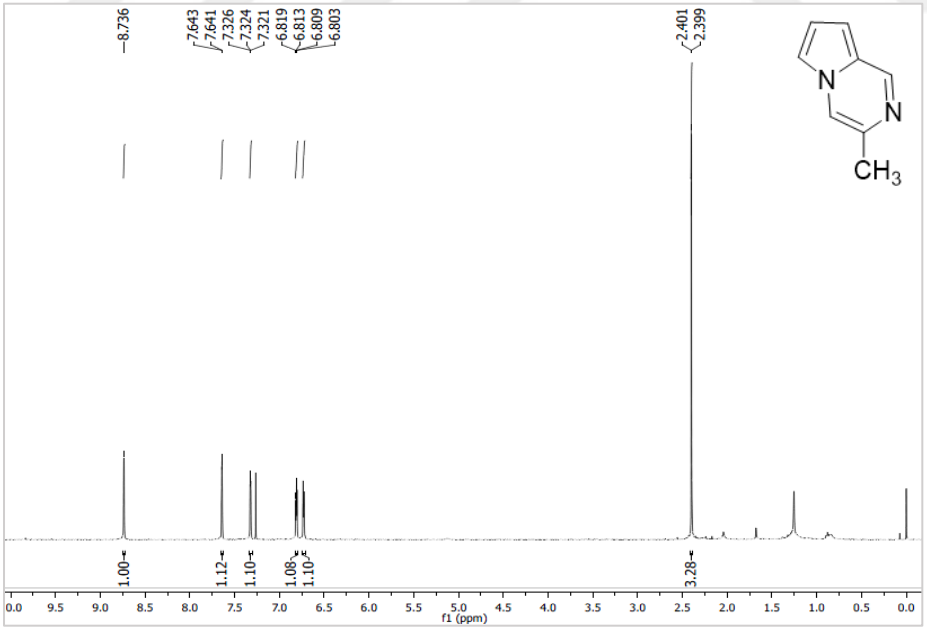

Figure 59. ^{1}H-NMR Spectrum of Compound **101**

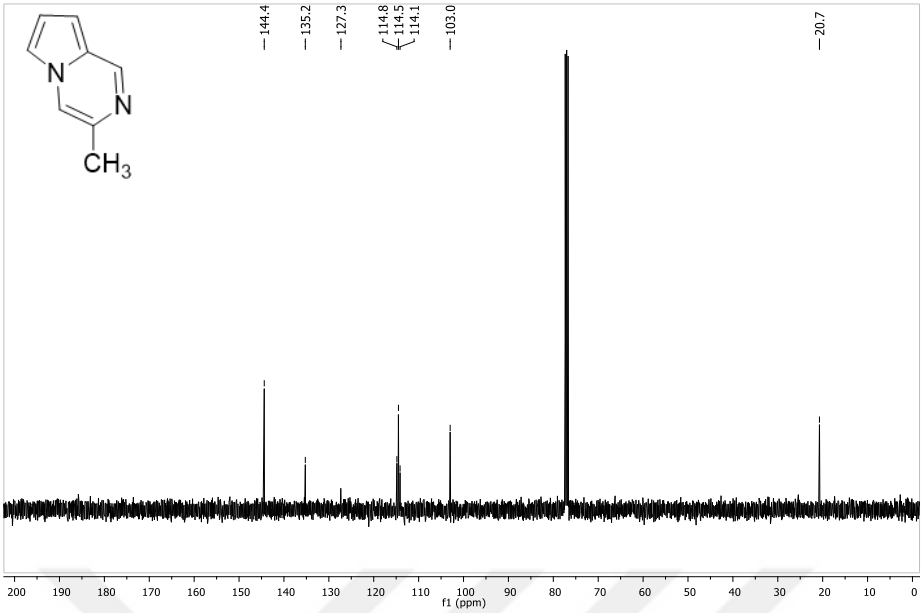

Figure 60. ^{13}C-NMR Spectrum of Compound **101**

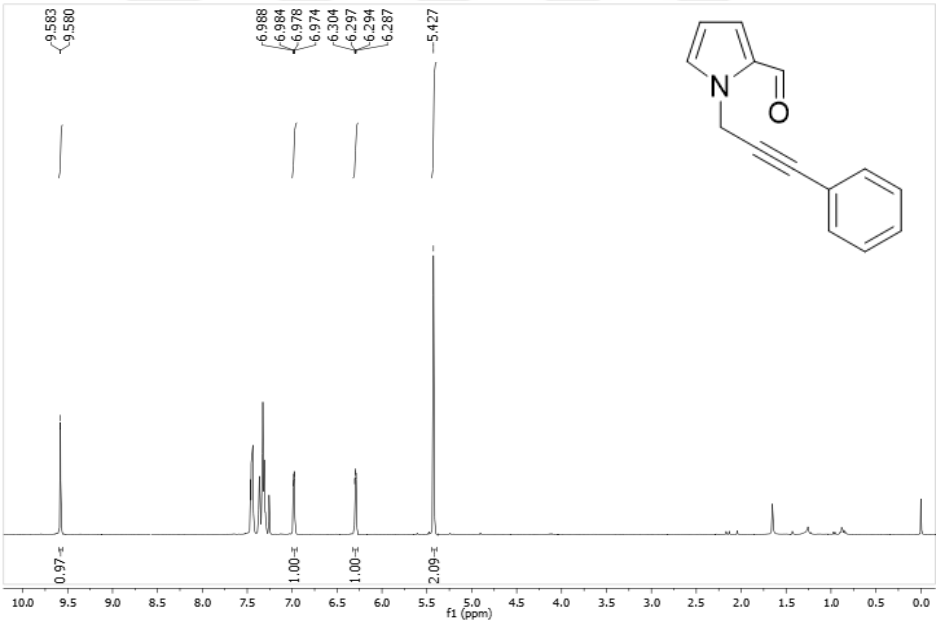

Figure 61. ^{1}H-NMR Spectrum of Compound **105**

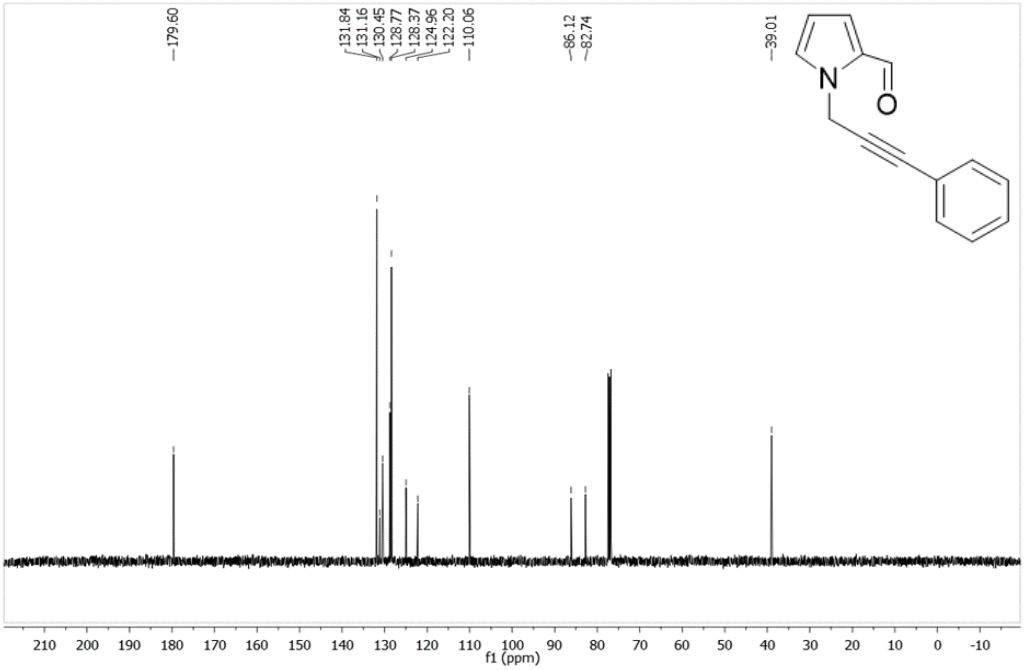

Figure 62. ^{13}C-NMR Spectrum of Compound **105**

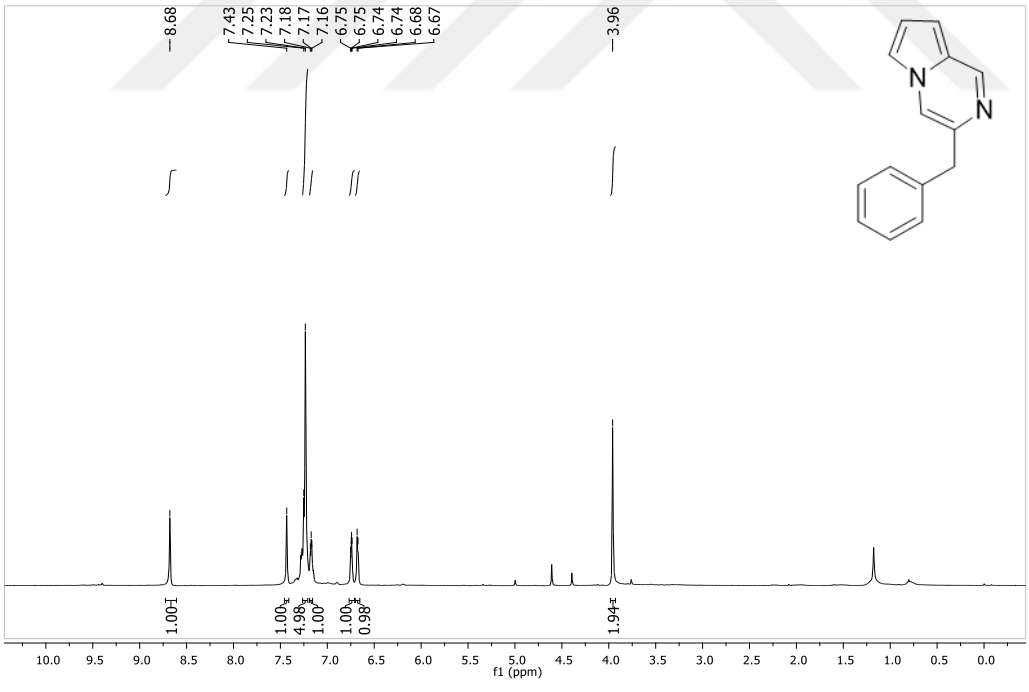

Figure 63. ^{1}H-NMR Spectrum of Compound **106**

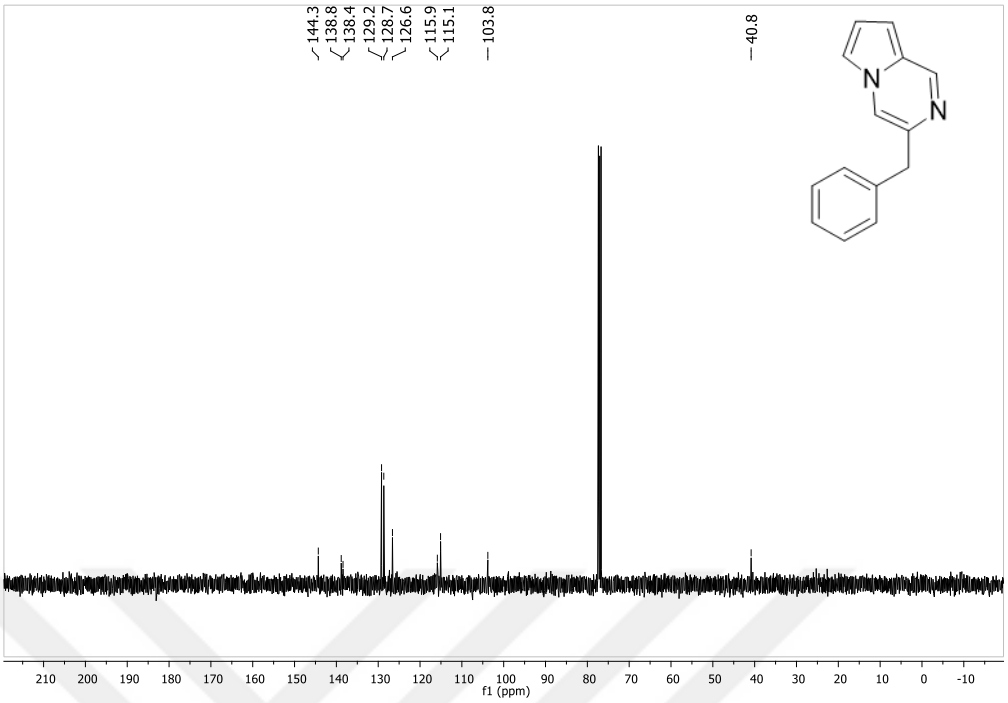

Figure 64. ^{13}C-NMR Spectrum of Compound **106**

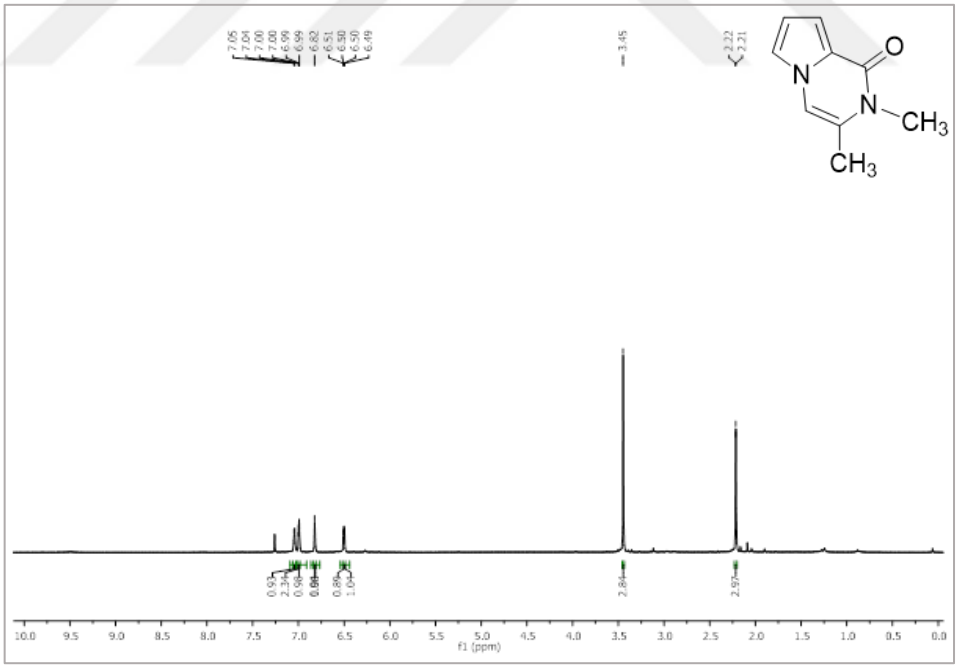

Figure 65. ^{1}H-NMR Spectrum of Compound **103a**

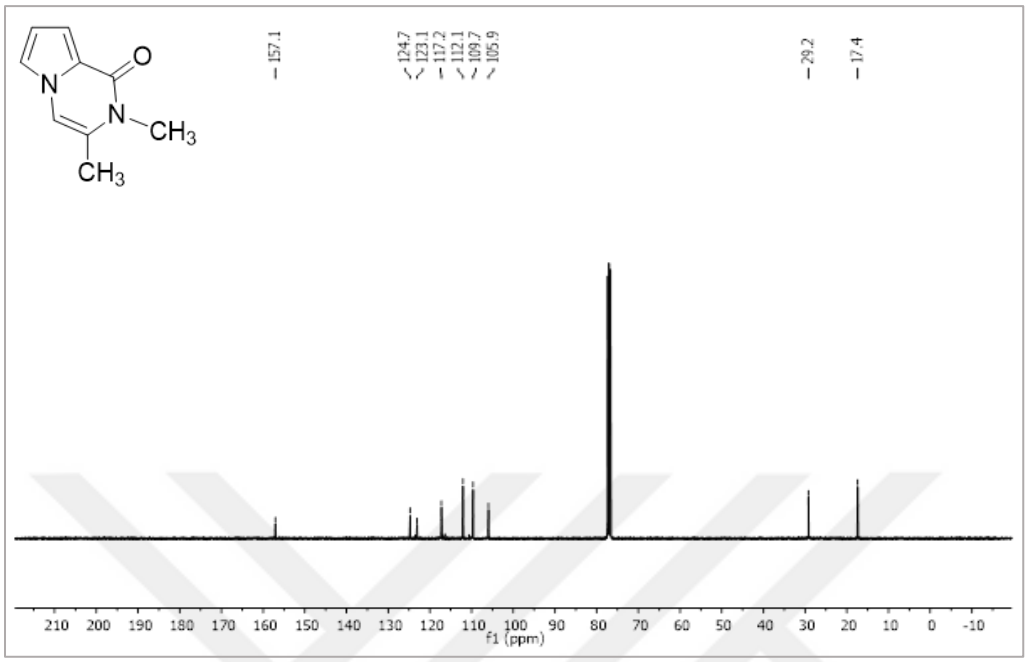

Figure 66. ^{13}C-NMR Spectrum of Compound **103a**

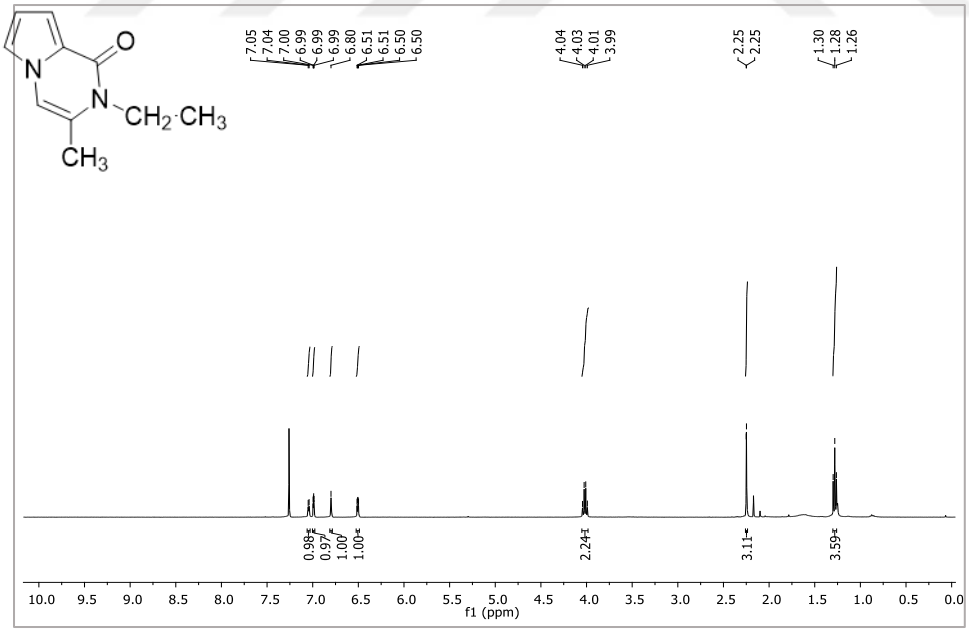

Figure 67. ^{1}H-NMR Spectrum of Compound **103b**

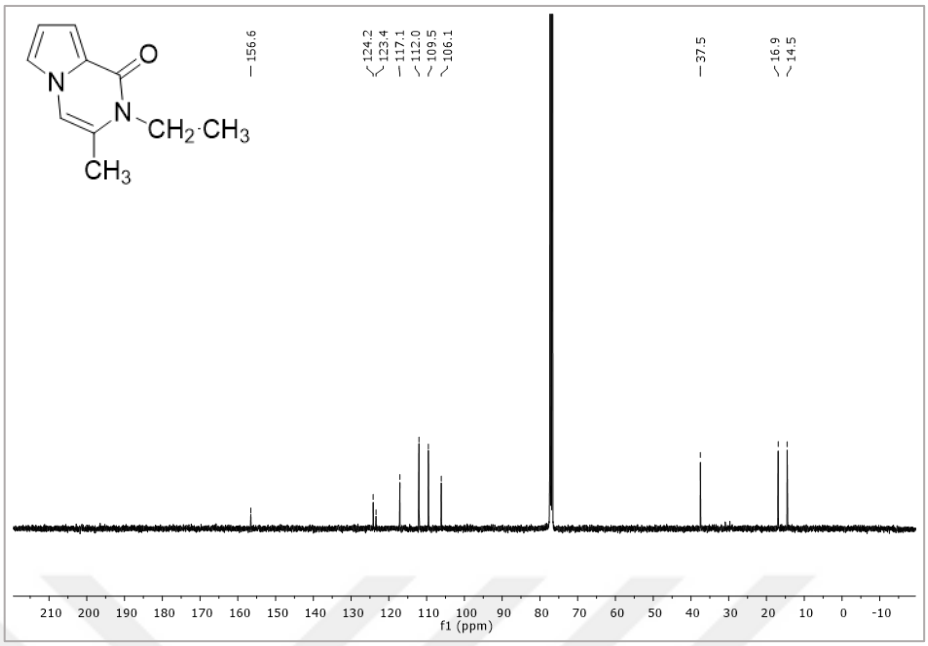

Figure 68. ^{13}C-NMR Spectrum of Compound **103b**

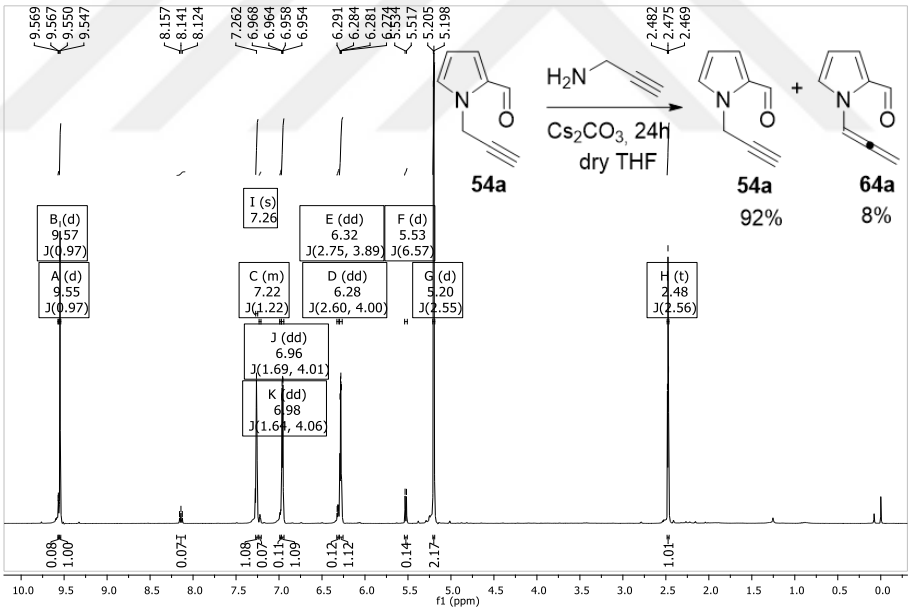

Figure 69. ^{1}H-NMR Spectrum of the Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde with Propargylamine in Dry THF

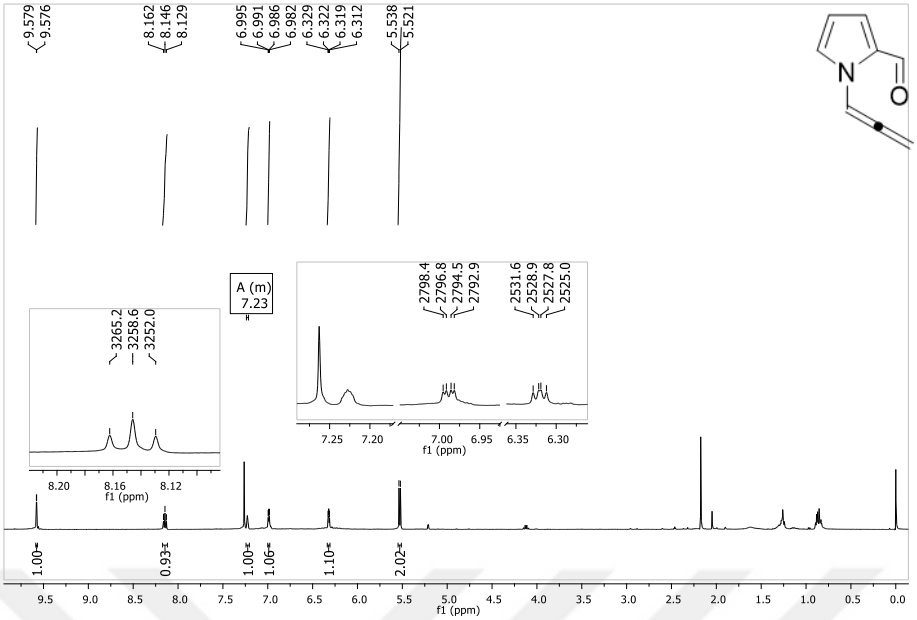

Figure 70. [1]H-NMR Spectrum of the Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde with Propargylamine in Dry DMF

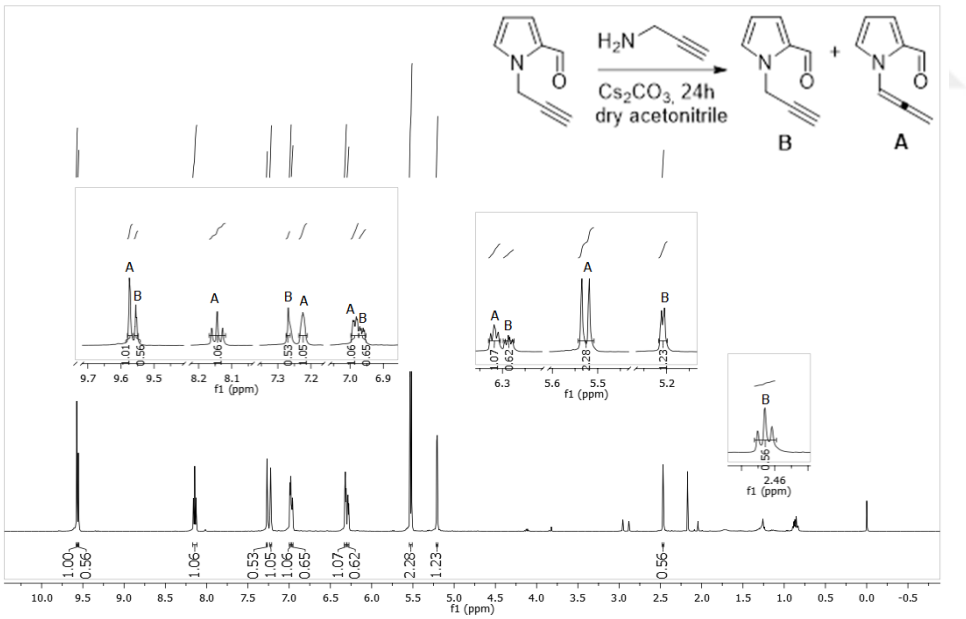

Figure 71. [1]H-NMR Spectrum of the Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde with Propargylamine in Dry Acetonitrile

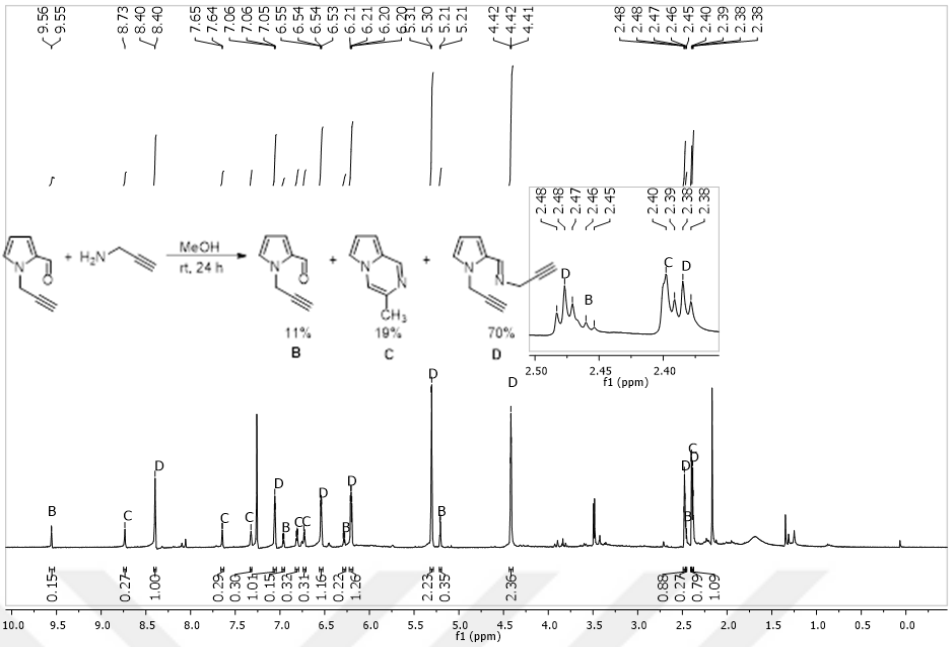

Figure 72. ^{1}H-NMR Spectrum of the Reaction of 1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde with Propargylamine without Using Base (Cs_2CO_3)

APPENDIX B

COMPUTATIONAL RESULTS

The following tables and cartesian coordinates are related to Chapter 1.

Absolute Energies of the Structures

Energies are given in terms of ZPE-corrected total energy (Eel+ZPE), enthalpy (Eel+H) and Gibbs free-energy (Eel+G) as extracted from Gaussian output of each structure.

Table S1. Absolute energies of optimized structures in gas phase **(**RHF/6-31+G(d))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (*i*)
RC (55a+OH^-)	-546.629055	-546.615484	-546.668613	—
TS1	-546.623966	-546.610898	-546.663521	-1616.9
PC (70a+H_2O)	-546.638944	-546.624833	-546.680548	—
RC (71a+H_2O)	-546.651214	-546.637018	-546.694440	—
TS2	-546.628378	-546.615127	-546.669226	-1351.8
PC (56a+OH^-)	-546.627991	-546.614014	-546.669680	—

[a]Eel = Total electronic energy
[b]ZPE = Zero-point energy correction
[c]H = Enthalpy correction
[d]G = Gibbs free energy correction

Table S2. Single point energies in methanol (PCM/RHF/6-31+G(d)//RHF/6-31+G(d))

Compound No	Eel[a] (au)	Eel+G[b] (au)
RC (55a+OH^-)	-546.913239	-546.768882
TS1	-546.892538	-546.754434
PC (70a+H_2O)	-546.899865	-546.759745
RC (71a+H_2O)	-546.914658	-546.776186
TS2	-546.901582	-546.765489
PC (56a+OH^-)	-546.918899	-546.779170

[a]Eel = Total electronic energy
[b]G = Gibbs free energy correction extracted from the corresponding gas phase frequency calculation and added to single point energy Eel.

Table S3. Absolute energies of optimized structures in gas phase (B3LYP/6-31+G(d,p))

Compound No	Eel+ZPE (au)	Eel+H (au)	Eel+G (au)	Imaginary Frequency (*i*)
55a	-474.264934	-474.253578	-474.301576	—
56a (Fig.2)	-474.277952	-474.266549	-474.314694	—
TS3	-474.198804	-474.189528	-474.232119	-191.6
72	-474.212432	-474.202530	-474.246835	—
TS4	-474.212392	-474.202809	-474.246341	-886.7
73	-474.320443	-474.310656	-474.354577	—
56a (Fig.3)	-474.277951	-474.266548	-474.314694	—
TS5	-474.232388	-474.222476	-474.266154	-431.9
MeOH	-115.683636	-115.679355	-115.706401	—
74a	-474.242452	-474.232504	-474.276259	—
RC(74a+MeOH)	-589.941018	-589.926985	-589.981479	—
TS6	-589.941430	-589.928302	-589.980711	-1047.2
PC(75a+MeOH)	-590.011104	-589.996579	-590.054058	—
75a	-474.322505	-474.312817	-474.356413	—
RC (75a+MeOH)	-590.012959	-589.998114	-590.056371	—
TS7	-589.966099	-589.953094	-590.004819	-1410.4
57a	-474.327677	-474.317896	-474.361392	—
PC(57a+MeOH)	-590.020342	-590.005697	-590.064080	—
76 (Fig.4)	-549.517748	-549.505311	-549.555628	—

Table S3 (continued)

TS8	-549.430683	-549.420272	-549.465418	-228.8
77	-549.445705	-549.434648	-549.481409	—
TS9	-549.438104	-549.427466	-549.473258	-1151.0
78	-549.561898	-549.550894	-549.597774	—
76 (Fig.5)	-549.517748	-549.505309	-549.555635	—
TS10	-549.466089	-549.454982	-549.501397	-373.5
79	-549.469676	-549.458668	-549.504826	—
RC(79+MeOH)	-665.170580	-665.155449	-665.211868	—
79	-549.567408	-549.556440	-549.602832	—
TS11	-665.167181	-665.152929	-665.207771	-1141.3
80	-549.561935	-549.551234	-549.597088	—
PC(80+MeOH)	-665.253790	-665.238310	-665.297411	—
RC(80+MeOH)	-665.252650	-665.236827	-665.296130	—
TS12	-665.208768	-665.194636	-665.249019	-1711.0
69	-549.582996	-549.572211	-549.618182	—
PC(69+MeOH)	-665.273464	-665.257750	-665.318524	—
76 (Fig.6)	-549.516305	-549.503813	-549.553972	—
TS13	-549.468480	-549.457391	-549.503831	-420.7
81	-549.478449	-549.466985	-549.514086	—
RC(81+MeOH)	-665.175175	-665.158978	-665.218834	—
TS14	-665.171034	-665.156330	-665.211864	-903.7
PC(68+MeOH)	-665.286768	-665.271199	-665.329712	—
68	-549.591719	-549.580445	-549.627266	—

Table S4. Single point energies in methanol (PCM/B3LYP/631+G(d,p)//B3LYP/6-31+G(d,p))

Compound No	Eel (au)	Eel+G (au)
55a	-474.432730	-474.310359
56a (Fig.2)	-474.443875	-474.322208
TS3	-474.382965	-474.255631
72	-474.392306	-474.265686
TS4	-474.382761	-474.259687
73	-474.491211	-474.363291
56a (Fig.3)	-474.443875	-474.322208
TS5	-474.401282	-474.276552
74a	-474.416981	-474.290062
MeOH	-115.740785	-115.712311
RC(74a+MeOH)	-590.166954	-589.992791
TS6	-590.163074	-589.992566
PC(75a+MeOH)	-590.237688	-590.064956
RC (75a+MeOH)	-590.238615	-590.066859
75a	-474.493556	-474.364959
TS7	-590.188922	-590.019099
57a	-474.500751	-474.373212
PC(57a+MeOH)	-590.248614	-590.077960
76 (Fig.4)	-549.696448	-549.570434
TS8	-549.627258	-549.496715
77	-549.637140	-549.507252
TS9	-549.618217	-549.491564
78	-549.743322	-549.612216
76 (Fig.5)	-549.696452	-549.570443
TS10	-549.647934	-549.520041
79	-549.656593	-549.526189
TS11	-665.401646	-665.228567
80	-549.742347	-549.61014
PC(80+MeOH)	-665.487674	-665.310630
RC(80+MeOH)	-665.487652	-665.311407
TS12	-665.436535	-665.263745
69	-549.763811	-549.631898
PC(58+MeOH)	-665.510456	-665.335421
76 (Fig.6)	-549.6944675	-549.568376
TS13	-549.6437598	-549.515960

Table S4 (continued)

81	-549.656646	-549.527553
RC(81+MeOH)	-665.407182	-665.232825
TS14	-665.398795	-665.226982
PC(68+MeOH)	-665.517729	-665.340069
68	-549.769934	-549.638719

Cartesian Coordinates for the Optimized Structures Given in Paths

Structure No: RC (55a+OH^-) (RHF/6-31+G(d))

	X	Y	Z
C	0.626644	-1.052326	-0.445479
H	1.686592	-1.222045	-0.665351
C	0.227941	-1.920786	0.682592
C	-0.104382	-2.640550	1.572369
H	-0.367600	-3.272157	2.377547
O	3.550601	-0.923855	-0.799917
H	4.335578	-1.427078	-0.972548
H	0.037358	-1.297187	-1.315621
C	1.596624	1.110514	0.067923
C	1.229995	2.380687	0.431159
C	-0.177876	2.396037	0.454332
C	-0.638192	1.146205	0.100526
N	0.483561	0.364415	-0.130634
H	2.560748	0.650517	-0.089609
H	1.896063	3.193237	0.642425
H	-0.810268	3.232538	0.684376
C	-2.087136	0.936962	-0.009853
H	-2.596689	1.822971	0.334427
N	-2.900410	0.059085	-0.412532
N	-2.441681	-1.149842	-0.933892
H	-1.918248	-1.658607	-0.246931
H	-3.260344	-1.687413	-1.131389

Structure No: TS1 (RHF/6-31+G(d))

	X	Y	Z
C	0.971123	-0.659739	-0.494170
H	2.163211	-0.270783	-0.946631
C	1.184877	-1.623960	0.579840
C	1.422669	-2.412708	1.449321
H	1.664814	-3.097552	2.216215
O	3.293519	0.204578	-1.323857
H	3.943953	-0.481437	-1.238002
H	0.402318	-1.105454	-1.297154
C	0.969728	1.581786	0.493719
C	0.117772	2.609918	0.799874
C	-1.170300	2.177690	0.415693
C	-1.056075	0.895617	-0.073482

N	0.272587	0.543584	-0.017310
H	2.036194	1.514894	0.548505
H	0.392094	3.560621	1.212950
H	-2.087079	2.733731	0.474494
C	-2.225973	0.186115	-0.633274
H	-2.935020	0.866151	-1.077447
N	-2.625102	-1.009574	-0.635009
N	-1.861976	-2.020356	-0.112575
H	-1.235303	-1.742048	0.618332
H	-2.474816	-2.738629	0.208715

Structure No: PC (70a+H_2O) (RHF/6-31+G(d))

	X	Y	Z
C	0.961277	-0.424349	-0.486458
H	2.985355	0.261314	-1.081769
C	1.435527	-1.237042	0.568991
C	1.890773	-1.919224	1.458789
H	2.361273	-2.471474	2.225977
O	3.941048	0.404521	-1.097172
H	4.251746	-0.145853	-0.391034
H	0.584456	-0.955301	-1.342735
C	0.502394	1.834950	0.356786
C	-0.544192	2.684214	0.610751
C	-1.710925	1.963768	0.282544
C	-1.325546	0.699769	-0.117247
N	0.045897	0.640352	-0.073876
H	1.557317	1.996516	0.427952
H	-0.474515	3.694941	0.962955
H	-2.725282	2.313177	0.328796
C	-2.343161	-0.281611	-0.550570
H	-3.230144	0.217443	-0.908338
N	-2.474771	-1.535539	-0.523257
N	-1.476891	-2.377551	-0.114637
H	-0.796720	-1.977344	0.501897
H	-1.898398	-3.183272	0.294556

Structure No: RC (71a+H_2O) (RHF/6-31+G(d))

	X	Y	Z
C	-0.902246	-0.851349	-0.365404
C	-2.016715	-1.096585	0.323436
C	-3.146494	-1.258385	0.896742

H	-3.195339	-1.917072	1.755337
H	-0.597896	-1.419474	-1.224408
C	-0.453403	1.557611	0.003589
C	0.619252	2.359792	0.293274
C	1.743145	1.505946	0.391060
C	1.299289	0.220011	0.169438
N	-0.047943	0.272046	-0.060466
H	-1.482231	1.800070	-0.160223
H	0.601473	3.424564	0.418626
H	2.741117	1.802368	0.650417
C	1.978190	-1.082973	0.276725
H	1.388442	-1.872138	0.708046
N	3.147677	-1.418592	-0.056717
N	3.962523	-0.534073	-0.733390
H	3.752341	0.429264	-0.578452
H	4.909674	-0.732543	-0.492961
O	-5.334546	0.260684	-0.686150
H	-4.752151	-0.202326	-0.066031
H	-4.850976	0.241735	-1.500299

Structure No: TS2 (RHF/6-31+G(d))

	X	**Y**	**Z**
C	0.595710	-0.782516	-0.138159
C	1.829699	-0.736596	-0.582691
C	3.071469	-0.669842	-0.932243
H	3.293987	-0.816832	-1.982961
H	0.122892	-1.681277	0.206314
C	0.232793	1.618285	0.356573
C	-0.790445	2.521773	0.280407
C	-1.930193	1.805520	-0.170376
C	-1.545306	0.501630	-0.344012
N	-0.220300	0.397061	-0.018563
H	1.257927	1.743619	0.635940
H	-0.732324	3.564502	0.522096
H	-2.916709	2.192023	-0.340595
C	-2.379467	-0.632574	-0.812965
H	-2.730258	-0.608213	-1.830982
N	-2.776997	-1.616961	-0.136575
N	-2.355329	-1.748217	1.162115
H	-2.150450	-0.873724	1.610666
H	-3.043819	-2.259773	1.670930
O	5.103880	-0.155948	0.644161
H	4.036203	-0.434237	-0.131239

H	4.994335	-0.555776	1.498495

Structure No: PC (56a+OH^-) (RHF/6-31+G(d))

	X	Y	Z
C	0.529030	-0.795669	-0.193158
C	1.767127	-0.763357	-0.601856
C	3.014061	-0.716333	-0.951767
H	3.259068	-0.817711	-1.998680
H	0.031036	-1.701500	0.091649
C	0.231998	1.604445	0.328240
C	-0.774329	2.525291	0.281623
C	-1.942016	1.832382	-0.136318
C	-1.593809	0.521525	-0.318393
N	-0.259092	0.390339	-0.031639
H	1.266443	1.709671	0.580950
H	-0.688979	3.565707	0.523839
H	-2.924412	2.240175	-0.276805
C	-2.467690	-0.591936	-0.761912
H	-2.894383	-0.525551	-1.748364
N	-2.820431	-1.600096	-0.095550
N	-2.310420	-1.781147	1.163934
H	-2.090198	-0.924778	1.639485
H	-2.952945	-2.330046	1.693440
O	5.330895	-0.136647	0.635376
H	3.848215	-0.558505	-0.236451
H	5.642374	-0.326036	1.511959

Structure No: 55a (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.103434	0.518159	0.210768
C	1.497720	1.803871	-0.137879
C	0.328229	2.567382	-0.390526
C	-0.754039	1.738989	-0.171108
N	-0.290453	0.489601	0.174307
H	2.524082	2.131472	-0.234394
H	0.280564	3.599321	-0.709054
H	-1.814822	1.930358	-0.231372
C	1.961710	-0.622649	0.566409
H	2.759344	-0.432170	1.281882
N	1.950242	-1.823032	0.093603
N	0.994085	-2.156809	-0.841345

C	-1.117200	-0.556940	0.794048
H	-1.210262	-0.359256	1.870294
C	-2.451050	-0.650732	0.199525
C	-3.564259	-0.751061	-0.261107
H	0.702594	-1.394803	-1.456863
H	1.299807	-2.969686	-1.360887
H	-0.603009	-1.513865	0.669265
H	-4.542690	-0.841797	-0.675602

Structure No: 56a (Fig.S1) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.056927	0.544564	-0.317127
C	1.422699	1.861766	-0.092783
C	0.269140	2.570667	0.345231
C	-0.778863	1.677253	0.364205
N	-0.309553	0.441215	-0.033948
H	2.422664	2.255553	-0.212815
H	0.214216	3.614557	0.620669
H	-1.820501	1.809692	0.614053
C	-1.102312	-0.705084	-0.281278
C	-2.411677	-0.747929	-0.184557
C	-3.714064	-0.832038	-0.097260
H	-4.357346	-0.637213	-0.954427
H	-0.536437	-1.590405	-0.549642
H	-4.208268	-1.100511	0.835673
C	1.891798	-0.570168	-0.800323
N	2.106862	-1.707754	-0.231080
N	1.465476	-1.993542	0.946709
H	1.964650	-2.716815	1.447140
H	1.233718	-1.191851	1.534943
H	2.445921	-0.416630	-1.724011

Structure No: TS3 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.218096	0.557374	0.049513
C	-2.450854	-0.074238	0.255868
C	-2.243275	-1.454595	0.075429
C	-0.897313	-1.641940	-0.246465
N	-0.284605	-0.430760	-0.242059
H	-3.371092	0.416989	0.542063
H	-2.978527	-2.240176	0.174312

H	-0.340129	-2.536277	-0.480068
C	1.060917	-0.083956	-0.725398
C	2.171771	-1.082128	-0.523797
C	2.349504	-1.421060	0.771414
H	3.135598	-2.113047	1.073698
H	0.967308	0.285203	-1.753738
H	1.733061	-1.080079	1.634358
C	-0.792585	1.916407	0.085347
N	0.441308	2.338776	0.065068
N	1.373607	1.209570	0.093133
H	2.279854	1.548380	-0.238969
H	1.520421	0.894154	1.064096
H	-1.539078	2.706574	0.119789

Structure No: 72 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.390666	0.266178	0.067661
C	2.439848	-0.656794	-0.024599
C	1.858765	-1.935984	-0.101005
C	0.472399	-1.773783	-0.048501
N	0.202151	-0.449274	0.047159
H	3.492665	-0.411838	-0.062621
H	2.375717	-2.879572	-0.200085
H	-0.331189	-2.494232	-0.077743
C	-1.096180	0.177268	0.299768
C	-2.226151	-0.376280	-0.504552
C	-3.108820	-1.115909	0.192579
H	-3.981134	-1.557344	-0.290112
H	-1.229915	0.301803	1.390478
H	-3.032067	-1.335134	1.270652
C	1.334870	1.685417	0.141903
N	0.260598	2.415256	0.044034
N	-0.913989	1.597104	-0.263893
H	-1.737223	2.133284	0.020248
H	-1.041917	1.432441	-1.285352
H	2.251345	2.248304	0.303904

Structure No: TS4 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.382906	0.308827	-0.004020
C	2.453364	-0.577320	-0.153613

C	1.927328	-1.882726	-0.072676
C	0.552420	-1.768987	0.121122
N	0.235041	-0.446817	0.165763
H	3.482052	-0.295274	-0.331866
H	2.473071	-2.810744	-0.164643
H	-0.213273	-2.524106	0.215635
C	-1.071086	0.129094	0.462912
C	-2.169669	-0.314565	-0.484157
C	-3.073565	-1.225750	-0.097923
H	-3.885463	-1.521655	-0.760787
H	-1.253613	0.110596	1.546433
H	-3.069025	-1.730313	0.876885
C	1.280002	1.730866	-0.034353
N	0.172464	2.408500	-0.006123
N	-1.001671	1.574131	-0.037738
H	-1.744425	2.100517	0.425063
H	-1.507090	1.194257	-1.009180
H	2.186728	2.329383	-0.074607

Structure No: 73 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.423261	0.332659	0.048102
C	2.505097	-0.540973	0.011842
C	1.979675	-1.857286	-0.049481
C	0.595911	-1.758558	-0.040419
N	0.269584	-0.427506	-0.012724
H	3.547702	-0.254097	0.009761
H	2.543058	-2.778085	-0.105878
H	-0.167579	-2.521530	-0.062487
C	-1.025915	0.196578	0.250584
C	-2.164242	-0.546318	-0.393898
C	-3.224200	-0.994188	0.282067
H	-4.043937	-1.499607	-0.219173
H	-1.177954	0.235485	1.346093
H	-3.307259	-0.871480	1.359597
C	1.269518	1.762371	0.145206
N	0.131484	2.361601	-0.009986
N	-0.942536	1.542652	-0.336399
H	-1.802613	2.060762	-0.202079
H	-2.086949	-0.668743	-1.472756
H	2.131186	2.394351	0.336673

Structure No: 56a (Fig.2) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.056996	0.544499	-0.316973
C	-1.422961	1.861625	-0.092355
C	-0.269372	2.570658	0.345273
C	0.778784	1.677382	0.363819
N	0.309537	0.441350	-0.034390
H	-2.423054	2.255184	-0.212033
H	-0.214448	3.614516	0.620827
H	1.820527	1.810002	0.613102
C	-1.891894	-0.570237	-0.800148
H	-2.445961	-0.416738	-1.723886
N	-2.106678	-1.707929	-0.231054
N	-1.464852	-1.993741	0.946646
C	1.102295	-0.705061	-0.281491
H	0.536317	-1.590315	-0.549788
C	2.411636	-0.747792	-0.184701
C	3.713981	-0.831800	-0.096920
H	4.207925	-1.100074	0.836181
H	4.357507	-0.636997	-0.953903
H	-1.233687	-1.191929	1.534989
H	-1.964013	-2.717050	1.447080

Structure No: TS5 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.086076	0.635897	-0.173685
C	2.456090	0.624338	0.097727
C	2.830793	-0.717741	0.321194
C	1.686040	-1.490412	0.160325
N	0.626418	-0.678795	-0.130176
H	3.091257	1.498474	0.152761
H	3.815850	-1.087431	0.568329
H	1.549869	-2.561569	0.200855
C	0.222232	1.765872	-0.442129
H	0.673078	2.620292	-0.945779
N	-1.017330	1.953574	-0.121488
N	-1.591985	0.888499	0.641251
C	-0.650871	-1.126912	-0.624643
H	-0.622672	-1.776479	-1.489782
C	-1.827700	-0.729722	-0.081492
C	-3.104673	-1.136325	0.097046
H	-3.952905	-0.460278	0.032911

H	-3.312994	-2.194779	0.204504
H	-1.029714	0.687047	1.476368
H	-2.519409	1.181801	0.946675

Structure No: 74a (B3LYP/6-31+G(d,p))

	X	Y	Z
C	0.997852	0.660272	-0.143569
C	2.411426	0.787410	-0.166165
C	2.950353	-0.477066	0.043305
C	1.881328	-1.373408	0.179634
N	0.696120	-0.706539	0.062215
H	2.942594	1.722688	-0.277846
H	3.996837	-0.740907	0.105398
H	1.884448	-2.444748	0.316835
C	-0.553966	-1.345244	0.004396
C	-1.775870	-0.674742	-0.007984
C	-3.014876	-1.027044	-0.467335
H	-3.914451	-0.517415	-0.135866
C	0.067652	1.708399	-0.325473
N	-1.207352	1.829344	-0.051777
N	-1.723720	0.674796	0.689612
H	-1.188665	0.570793	1.561412
H	-2.679840	0.935046	0.932856
H	-0.518564	-2.402374	-0.213953
H	-3.135573	-1.876718	-1.126481
H	0.474492	2.618970	-0.763548

Structure No: RC (74a+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.534403	-0.372591	-0.459902
C	2.837565	0.141949	-0.663360
C	3.067040	1.104936	0.317005
C	1.914617	1.162405	1.111153
N	0.991540	0.274608	0.655371
H	3.500781	-0.158979	-1.462901
H	3.955007	1.705449	0.454874
H	1.701859	1.762888	1.983967
C	-0.279120	0.056871	1.284215
C	-1.090444	-1.041633	0.892266
C	-1.827309	-1.899962	1.643342
H	-2.633608	-2.494186	1.222292

C	0.921783	-1.358716	-1.277668
N	-0.285009	-1.828509	-1.418030
N	-1.300551	-1.156092	-0.598135
H	-1.490679	-0.194216	-0.966615
H	-2.138344	-1.716197	-0.754070
H	-0.238987	0.241649	2.352631
H	-1.670225	-1.965190	2.712907
O	-1.685830	1.581464	-0.724443
H	-1.290809	1.397064	0.172590
C	-2.804624	2.457741	-0.615532
H	-3.580502	2.051828	0.047674
H	-2.499084	3.443728	-0.243711
H	-3.224860	2.579993	-1.616910
H	1.610774	-1.841581	-1.970740

Structure No: TS6 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.484792	-0.391954	-0.486708
C	2.834858	-0.039071	-0.702873
C	3.172335	0.937729	0.236486
C	2.030966	1.159225	1.015143
N	1.021291	0.360659	0.587530
H	3.467514	-0.462352	-1.471308
H	4.124845	1.433379	0.358641
H	1.878986	1.826695	1.851490
C	-0.325158	0.369612	1.151383
C	-1.070956	-0.874121	0.963459
C	-1.636614	-1.679682	1.876476
H	-2.359444	-2.446465	1.609693
C	0.769898	-1.349942	-1.266815
N	-0.456669	-1.771662	-1.341186
N	-1.422842	-1.104095	-0.469961
H	-1.668794	-0.086670	-0.853435
H	-2.248823	-1.698111	-0.528266
H	-0.268305	0.655098	2.200829
H	-1.402802	-1.564308	2.928607
O	-1.645575	1.409687	-0.823011
H	-1.093900	1.221925	0.179668
C	-2.806511	2.206536	-0.662612
H	-3.334009	1.985164	0.279410
H	-2.546605	3.273795	-0.665153
H	-3.499409	2.025181	-1.493505
H	1.401227	-1.865136	-1.990895

Structure No: PC (75a+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.348453	-0.652135	0.573849
C	2.589170	-1.295414	0.609710
C	3.317428	-0.892497	-0.530477
C	2.505517	-0.021372	-1.242138
N	1.320903	0.121735	-0.571617
H	2.919934	-1.960670	1.395710
H	4.317498	-1.193975	-0.807939
H	2.674234	0.492631	-2.177629
C	0.162663	0.866830	-1.056890
C	-0.506923	1.663283	0.037794
C	-0.529153	3.005631	0.040699
H	-1.023263	3.567648	0.827848
C	0.306407	-0.747894	1.571671
N	-0.795366	-0.109450	1.794966
N	-1.261633	0.912535	0.972916
H	-2.544181	-0.253809	-0.232938
H	-1.887913	1.484742	1.526894
H	0.513868	1.547901	-1.833475
H	-0.078967	3.573551	-0.765432
O	-2.857692	-0.703835	-1.035843
H	-0.562458	0.173696	-1.500408
C	-3.494301	-1.925000	-0.676742
H	-4.386827	-1.757485	-0.057754
H	-3.806021	-2.408658	-1.605996
H	-2.814643	-2.601703	-0.141017
H	0.497379	-1.515520	2.320170

Structure No: 75a (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-0.999150	0.718761	0.006476
C	-2.353450	0.779592	-0.329565
C	-2.864858	-0.538257	-0.298284
C	-1.820643	-1.372638	0.069024
N	-0.696862	-0.607931	0.249089
H	-2.888408	1.681829	-0.592874
H	-3.875489	-0.851294	-0.519427
H	-1.793147	-2.440799	0.229888
C	0.577465	-1.075943	0.775074

H	0.562818	-2.166340	0.757963
H	0.680984	-0.748626	1.817836
C	1.757968	-0.581646	-0.028412
C	2.566501	-1.428099	-0.694303
H	2.412079	-2.499351	-0.645141
C	-0.056540	1.814862	0.063154
N	1.237094	1.876636	0.088822
N	2.055715	0.780957	0.086908
H	3.413598	-1.072974	-1.273335
H	2.993287	1.051316	-0.172748
H	-0.521123	2.798803	0.045119

Structure No: RC (75a+MeOH) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.624793	-0.946822	0.030339
C	2.812392	-1.566487	-0.365394
C	3.817873	-0.573037	-0.422798
C	3.230547	0.625229	-0.047651
N	1.906161	0.391783	0.222413
H	2.915315	-2.614841	-0.610308
H	4.851968	-0.707496	-0.707531
H	3.650276	1.614814	0.062091
C	0.965165	1.348968	0.785975
H	1.426849	2.335959	0.737145
H	0.789715	1.102698	1.841523
C	-0.353212	1.377962	0.046900
C	-0.769881	2.481904	-0.605605
H	-0.182494	3.392293	-0.587824
C	0.319281	-1.550541	0.191592
N	-0.880671	-1.062358	0.259647
N	-1.181214	0.264266	0.197988
H	-4.846670	0.758210	-0.040395
H	-1.713077	2.502331	-1.141961
C	-4.516399	-1.193380	-0.032057
H	-5.307544	-1.499258	-0.727570
H	-4.856505	-1.341996	0.999993
H	-3.628051	-1.803997	-0.198504
O	-4.119215	0.165446	-0.264764
H	-2.173493	0.397343	0.019142
H	0.334151	-2.638243	0.224167

Structure No: TS7 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.881389	0.769700	0.009706
C	3.148840	0.895325	0.584553
C	3.690641	-0.401847	0.708572
C	2.762516	-1.292501	0.182909
N	1.672144	-0.580695	-0.230771
H	3.599030	1.824373	0.905889
H	4.651127	-0.668734	1.125957
H	2.807702	-2.364371	0.054330
C	0.524449	-1.067551	-0.979303
H	0.592910	-2.152205	-1.059191
H	0.537730	-0.638462	-1.990718
C	-0.752646	-0.681695	-0.266312
C	-1.746936	-1.633492	0.165821
H	-1.574309	-2.655244	-0.169574
C	0.917482	1.784067	-0.331792
N	-0.377345	1.734170	-0.454388
N	-1.080665	0.598084	-0.153560
H	-2.820233	-0.987684	-0.189207
H	-1.950246	-1.600798	1.241971
C	-4.433816	0.214039	0.813039
H	-4.020110	-0.260088	1.725424
H	-5.376865	-0.302324	0.576282
H	-4.676315	1.255291	1.072570
O	-3.542758	0.161455	-0.272960
H	-2.200523	0.698424	-0.074916
H	1.321721	2.782993	-0.487254

Structure No: 57a (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.046505	0.707813	-0.023425
C	-2.363169	0.597890	-0.469166
C	-2.732170	-0.763922	-0.374190
C	-1.648186	-1.454759	0.152223
N	-0.633213	-0.562000	0.357905
H	-2.967888	1.412633	-0.842774
H	-3.681676	-1.200742	-0.649877
H	-1.533300	-2.497852	0.410109
C	0.667670	-0.786063	0.975589
H	0.764278	-1.846974	1.213347
H	0.734041	-0.211837	1.908893
C	1.738147	-0.332982	-0.006289

C	2.630903	-1.370585	-0.624928
H	3.221725	-1.886203	0.143469
C	-0.184721	1.853421	0.185001
N	1.113471	1.922451	0.148447
N	1.866187	0.892369	-0.366334
H	3.309139	-0.904028	-1.341000
H	2.033312	-2.134692	-1.138626
H	-0.676563	2.795071	0.427440

Structure No: PC (57a+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.685538	-0.935233	0.085554
C	2.779582	-1.429562	-0.624795
C	3.578055	-0.324816	-0.997585
C	2.976111	0.817629	-0.484961
N	1.832296	0.443379	0.162474
H	2.952731	-2.469596	-0.864350
H	4.494404	-0.348986	-1.570194
H	3.284854	1.852705	-0.516797
C	0.921499	1.264709	0.948420
H	1.246648	2.304553	0.887296
H	0.956126	0.950329	1.999883
C	-0.481737	1.092163	0.388623
C	-1.139600	2.270744	-0.269224
H	-1.243809	3.097908	0.445048
C	0.598216	-1.601826	0.766958
N	-0.604931	-1.178232	1.020649
N	-1.099237	-0.034818	0.426335
H	-2.125995	2.007738	-0.653947
H	-0.514738	2.636490	-1.094321
C	-4.661441	-1.009124	-0.561966
H	-4.251098	-1.830164	-1.168407
H	-5.626600	-0.719080	-0.987348
H	-4.832402	-1.381320	0.458805
O	-3.828075	0.138582	-0.580486
H	-2.952961	-0.085211	-0.205635
H	0.803209	-2.604424	1.141508

Structure No: 76 (Fig.4) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	0.839548	0.637328	-0.094106

C	1.156119	1.953372	0.201541
C	-0.054812	2.642280	0.464651
C	-1.083854	1.737920	0.298023
N	-0.549991	0.513499	-0.035310
H	2.162107	2.345714	0.235919
H	-0.166469	3.682365	0.736554
H	-2.154201	1.865746	0.357000
C	-1.296446	-0.619351	-0.431395
C	-2.601797	-0.733579	-0.340287
C	-3.900556	-0.878258	-0.279268
H	-4.549022	-0.566191	-1.097327
H	-0.699835	-1.420536	-0.852297
H	-4.387378	-1.314122	0.592360
C	1.826067	-0.416979	-0.399047
O	2.848284	-0.176982	-1.038017
N	1.595090	-1.718228	0.045435
H	2.394760	-2.316793	-0.150637
N	0.879283	-1.938302	1.241174
H	0.330182	-2.788200	1.163241
H	1.507286	-2.007311	2.039557

Structure No: TS8 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.077881	0.415753	-0.035174
C	1.685391	1.646822	0.202302
C	0.687522	2.634761	0.080322
C	-0.510932	1.992374	-0.217644
N	-0.276946	0.651503	-0.275928
H	2.726313	1.782633	0.458711
H	0.811423	3.700869	0.205491
H	-1.503430	2.379063	-0.390743
C	-1.205200	-0.385773	-0.724793
C	-2.668840	-0.211627	-0.471170
C	-2.979042	-0.099989	0.839192
H	-4.012528	-0.002753	1.171707
H	-0.944442	-0.670363	-1.750704
H	-2.258688	-0.054216	1.687428
C	1.620306	-0.923279	0.037255
N	2.788937	-1.229233	0.220046
N	0.675801	-1.979909	-0.157182
H	0.976264	-2.860309	0.254471
N	-0.699577	-1.664058	0.080944
H	-1.303479	-2.418323	-0.262311

H	-0.940392	-1.489749	1.069002

Structure No: 77 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.073611	0.525981	0.056041
C	-1.520978	1.838617	-0.074623
C	-0.380675	2.664997	-0.121879
C	0.740160	1.844821	-0.029709
N	0.322211	0.553939	0.074448
H	-2.558488	2.132281	-0.145228
H	-0.361821	3.740130	-0.228390
H	1.794401	2.074927	-0.046491
C	1.168555	-0.612120	0.323076
C	2.450383	-0.682582	-0.410512
C	3.542175	-0.160153	0.172231
H	4.514568	-0.209955	-0.317952
H	1.155587	-0.864235	1.397022
H	3.560106	0.341324	1.152220
C	-1.813487	-0.715928	0.081999
O	-3.029083	-0.843556	0.084792
N	-1.010547	-1.893911	0.142860
H	-1.488849	-2.715689	-0.217022
N	0.342953	-1.767935	-0.330260
H	0.878135	-2.615630	-0.113886
H	0.481571	-1.601153	-1.347694

Structure No: TS9 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.106613	0.464918	0.013493
C	-1.661545	1.733759	-0.119721
C	-0.598426	2.661201	-0.094458
C	0.585479	1.944343	0.051266
N	0.281232	0.617879	0.100315
H	-2.716467	1.938198	-0.233417
H	-0.672573	3.735568	-0.184033
H	1.607819	2.283023	0.109047
C	1.132748	-0.532044	0.407959
C	2.539545	-0.819430	-0.041177
C	3.552489	0.052610	-0.067849
H	4.541828	-0.270082	-0.388442
H	1.012441	-0.791422	1.469441

H	3.495540	1.105851	0.225809
C	-1.745968	-0.846011	0.046346
O	-2.950222	-1.053494	0.034086
N	-0.847240	-1.949403	0.134822
H	-1.232630	-2.829031	-0.195632
N	0.479857	-1.676021	-0.333826
H	1.487378	-2.227293	-0.225245
H	0.495238	-1.420124	-1.334559

Structure No: 78 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.166979	0.400571	0.022949
C	1.788621	1.639797	0.083836
C	0.769730	2.621314	0.052681
C	-0.449078	1.960121	-0.031830
N	-0.206481	0.613652	-0.033002
H	2.856383	1.793862	0.141461
H	0.899875	3.693616	0.094002
H	-1.456782	2.345217	-0.080109
C	-1.146158	-0.514851	-0.221843
C	-2.496866	-0.207121	0.365081
C	-3.619785	-0.163988	-0.352583
H	-4.578655	0.048191	0.110058
H	-1.230426	-0.726361	-1.294138
H	-3.619735	-0.343103	-1.424912
C	1.712353	-0.957184	-0.066870
O	2.901023	-1.230541	-0.207968
N	0.731777	-1.938647	-0.058788
H	1.018519	-2.907388	-0.101882
N	-0.579776	-1.698368	0.412902
H	-2.518024	-0.016976	1.437928
H	-0.552754	-1.551143	1.425017

Structure No: 76 (Fig.5) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-0.839980	0.637020	-0.094000
C	-1.157360	1.952916	0.201640
C	0.053124	2.642602	0.464519
C	1.082748	1.738954	0.297413
N	0.549655	0.514132	-0.035535
H	-2.163645	2.344447	0.236402

H	0.164140	3.682774	0.736345
H	2.153018	1.867529	0.355893
C	1.296718	-0.618066	-0.432592
C	2.602330	-0.731160	-0.342704
C	3.900678	-0.877477	-0.277281
H	4.383370	-1.314786	0.595937
C	-1.826177	-0.417830	-0.398050
N	-1.594009	-1.719128	0.045179
H	-2.393563	-2.317986	-0.150420
N	-0.876135	-1.940160	1.239370
H	-1.502719	-2.010044	2.038787
H	-0.327042	-2.789887	1.159736
O	-2.849497	-0.177894	-1.035280
H	0.700555	-1.418895	-0.854822
H	4.552801	-0.565659	-1.092391

Structure No: TS10 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.111426	0.267342	-0.008755
C	2.429386	-0.005196	0.342620
C	2.578178	-1.409678	0.359771
C	1.351319	-1.955435	0.006319
N	0.451557	-0.946394	-0.208978
H	3.175706	0.742521	0.570677
H	3.472257	-1.966174	0.603149
H	1.049205	-2.984086	-0.127694
C	-0.849608	-1.115205	-0.802389
C	-1.983474	-0.731545	-0.166267
C	-3.295716	-1.022916	-0.023126
H	-4.062508	-0.260825	0.092077
C	0.479617	1.576867	-0.202327
N	-0.824953	1.763080	0.304431
H	-1.398988	2.401152	-0.235685
N	-1.557851	0.670729	0.856992
H	-1.003260	0.284420	1.626391
H	-2.425967	1.020782	1.269998
O	1.036600	2.545840	-0.699119
H	-0.880022	-1.592886	-1.773305
H	-3.627257	-2.048934	-0.134847

Structure No: 79 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**

C	1.011302	0.389996	-0.038539
C	2.409814	0.450666	0.047586
C	2.888630	-0.863570	0.117529
C	1.781056	-1.708060	0.069727
N	0.634862	-0.969625	-0.027570
H	2.975370	1.370416	0.085963
H	3.917707	-1.180338	0.210867
H	1.721664	-2.786799	0.078279
C	-0.637343	-1.563262	-0.270248
C	-1.822946	-0.882202	-0.056486
C	-3.104432	-0.952917	-0.555218
H	-3.951959	-0.585258	0.018654
C	0.144175	1.545382	-0.162681
N	-1.172549	1.509811	0.414753
H	-1.877876	1.899508	-0.207223
N	-1.633241	0.243638	0.938723
H	-0.957825	-0.036413	1.661273
H	-2.526655	0.428106	1.402662
O	0.477299	2.618451	-0.645592
H	-0.622953	-2.467702	-0.861226
H	-3.320905	-1.572084	-1.415878

Structure No: RC (79+MeOH) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-0.212658	1.114280	0.428055
C	0.007891	2.356861	-0.159791
C	-1.092460	2.628629	-1.005157
C	-1.962526	1.552664	-0.901443
N	-1.431095	0.636116	-0.036781
H	0.867958	2.982571	0.032644
H	-1.244765	3.506861	-1.616368
H	-2.920238	1.376487	-1.370370
C	-2.063678	-0.623215	0.370672
C	-1.219162	-1.808447	-0.038491
C	-1.672670	-2.787677	-0.832658
H	-1.052578	-3.643383	-1.077591
C	0.629314	0.406585	1.404148
N	0.408693	-0.964821	1.521620
H	1.008235	-1.411889	2.206216
N	0.123341	-1.785642	0.410550
H	1.654476	0.338866	-1.444393
H	0.805263	-1.640665	-0.337945

O	1.445385	0.980504	2.122189
H	-2.201788	-0.610060	1.457534
H	-2.663228	-2.736991	-1.270298
O	2.078874	-0.531530	-1.460125
H	-3.047766	-0.676145	-0.096634
C	3.478789	-0.374631	-1.203011
H	3.912843	-1.376525	-1.211847
H	3.963016	0.223410	-1.984735
H	3.660868	0.085808	-0.224392

Structure No: TS11 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-1.477489	0.044233	-0.118325
C	-2.696136	-0.603390	-0.369311
C	-2.627098	-1.878187	0.206238
C	-1.373653	-1.982365	0.805894
N	-0.676938	-0.827393	0.623894
H	-3.509738	-0.162837	-0.926263
H	-3.387909	-2.645730	0.195171
H	-0.931749	-2.796420	1.362836
C	0.675167	-0.659675	1.159876
C	1.223263	0.681577	1.115718
C	1.838691	1.415839	2.061469
H	2.438102	2.290212	1.820207
C	-1.204832	1.398829	-0.569829
N	0.115814	1.887084	-0.768266
H	0.161044	2.881483	-0.566287
N	1.277024	1.180375	-0.294107
H	1.525734	0.242585	-0.915200
H	2.058871	1.826664	-0.408426
O	-2.093153	2.188318	-0.878748
H	0.735670	-1.103371	2.152271
H	1.789126	1.122602	3.103478
O	1.789042	-1.130225	-1.122635
H	1.451321	-1.223731	-0.024209
C	3.098516	-1.629239	-1.360194
H	3.084031	-2.724933	-1.403795
H	3.461304	-1.254035	-2.323682
H	3.807196	-1.323435	-0.574910

Structure No: 80 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.088091	0.226173	-0.029068
C	-2.345579	-0.173444	-0.468537
C	-2.401874	-1.581457	-0.376022
C	-1.182086	-2.007650	0.130618
N	-0.384555	-0.916638	0.338310
H	-3.115803	0.500131	-0.815393
H	-3.231535	-2.220382	-0.643388
H	-0.828065	-3.001417	0.366052
C	0.956337	-0.942989	0.927918
H	1.195088	-1.974960	1.187689
H	0.949450	-0.352570	1.851271
C	1.983806	-0.397559	-0.035466
C	3.035163	-1.107281	-0.467370
H	3.158855	-2.145527	-0.182539
C	-0.564220	1.588875	0.104922
N	0.827555	1.710811	0.207238
H	1.141872	2.666951	0.329076
N	1.729991	0.911104	-0.510123
H	3.778603	-0.672218	-1.127325
O	-1.278450	2.582893	0.197567
H	1.607465	0.971886	-1.515935

Structure No: PC (80+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-0.212658	1.114280	0.428055
C	0.007891	2.356861	-0.159791
C	-1.092460	2.628629	-1.005157
C	-1.962526	1.552664	-0.901443
N	-1.431095	0.636116	-0.036781
H	0.867958	2.982571	0.032644
H	-1.244765	3.506861	-1.616368
H	-2.920238	1.376487	-1.370370
C	-2.063678	-0.623215	0.370672
C	-1.219162	-1.808447	-0.038491
C	-1.672670	-2.787677	-0.832658
H	-1.052578	-3.643383	-1.077591
C	0.629314	0.406585	1.404148
N	0.408693	-0.964821	1.521620
H	1.008235	-1.411889	2.206216
N	0.123341	-1.785642	0.410550
H	1.654476	0.338866	-1.444393

H	0.805263	-1.640665	-0.337945
O	1.445385	0.980504	2.122189
H	-2.201788	-0.610060	1.457534
H	-2.663228	-2.736991	-1.270298
O	2.078874	-0.531530	-1.460125
H	-3.047766	-0.676145	-0.096634
C	3.478789	-0.374631	-1.203011
H	3.912843	-1.376525	-1.211847
H	3.963016	0.223410	-1.984735
H	3.660868	0.085808	-0.224392

Structure No: RC (80+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.008216	-1.076081	-0.049139
C	1.791669	-2.158877	-0.426996
C	3.145682	-1.777489	-0.286284
C	3.155670	-0.474773	0.189474
N	1.863935	-0.044815	0.328458
H	1.402213	-3.105601	-0.772519
H	4.018629	-2.376284	-0.504546
H	3.982037	0.172137	0.448368
C	1.461424	1.237196	0.912398
H	2.361439	1.772131	1.217214
H	0.864396	1.039890	1.811019
C	0.658690	2.080617	-0.053752
C	0.932748	3.369799	-0.318039
H	1.812992	3.845919	0.096674
C	-0.457580	-0.981631	0.001420
N	-0.977031	0.302824	-0.012349
H	-1.989727	0.401358	0.087107
N	-0.315868	1.331598	-0.705030
H	-4.560612	1.096121	0.324717
H	0.308802	3.962991	-0.979653
O	-1.193468	-1.960492	0.141754
C	-4.471079	-0.876629	0.137906
H	-4.846950	-1.057373	1.151721
H	-3.652751	-1.570113	-0.062402
H	-5.278670	-1.029672	-0.587755
O	-3.917719	0.446492	0.016067
H	-0.882185	1.780445	-1.412001

Structure No: TS12 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.837548	0.440527	0.099134
C	3.061064	0.382641	0.758981
C	3.483200	-0.963770	0.757557
C	2.514907	-1.699105	0.087771
N	1.519654	-0.851007	-0.310218
H	3.564843	1.236351	1.188046
H	4.389739	-1.362960	1.189576
H	2.465140	-2.753883	-0.142362
C	0.337780	-1.215990	-1.081487
H	0.362867	-2.290066	-1.261926
H	0.351105	-0.687831	-2.044085
C	-0.911414	-0.843120	-0.311936
C	-1.907802	-1.773973	0.140799
H	-1.763280	-2.796901	-0.201556
C	1.026093	1.625190	-0.164719
N	-0.301674	1.441009	-0.601880
H	-0.783707	2.331867	-0.662201
N	-1.157629	0.438583	-0.127214
H	-3.017350	-0.980396	-0.179620
H	-2.107667	-1.739835	1.215207
O	1.463728	2.769211	-0.087822
C	-4.497124	0.236964	0.879242
H	-5.424725	-0.301149	0.644408
H	-4.748807	1.287402	1.070005
H	-4.081824	-0.186352	1.809647
O	-3.587195	0.143834	-0.202020
H	-2.306569	0.603106	-0.023272

Structure No: 69 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.103525	0.242029	-0.020434
C	-2.382737	-0.112132	-0.438423
C	-2.488304	-1.516361	-0.338624
C	-1.276982	-1.987815	0.149706
N	-0.440397	-0.922584	0.335363
H	-3.130638	0.587953	-0.780383
H	-3.345780	-2.124769	-0.588887
H	-0.954961	-2.991622	0.388376
C	0.899400	-0.955370	0.898992

H	1.165604	-1.997945	1.080825
H	0.903692	-0.423361	1.861183
C	1.907072	-0.293522	-0.022184
C	3.011347	-1.126501	-0.607399
H	3.575787	-1.634907	0.184782
C	-0.535202	1.584473	0.069058
N	0.856273	1.747781	0.225983
H	1.086037	2.729193	0.112741
N	1.881985	0.959347	-0.296090
H	3.691572	-0.499491	-1.186182
H	2.602549	-1.905752	-1.263168
O	-1.233165	2.595010	0.023721

Structure No: PC (69+MeOH) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	1.716428	0.641681	0.066117
C	2.810176	0.976914	0.858481
C	3.500845	-0.217598	1.155476
C	2.821752	-1.254406	0.529298
N	1.740641	-0.732412	-0.124351
H	3.050941	1.980513	1.176703
H	4.394195	-0.321777	1.754627
H	3.032674	-2.313786	0.490917
C	0.795513	-1.455557	-0.959610
H	1.052967	-2.515162	-0.926395
H	0.882807	-1.107715	-1.998721
C	-0.631933	-1.234652	-0.495909
C	-1.415581	-2.404528	0.023814
H	-1.430537	-3.210581	-0.720788
C	0.720818	1.541261	-0.507073
N	-0.475115	1.009084	-1.038721
H	-1.103986	1.773198	-1.262065
N	-1.201584	-0.085647	-0.563761
H	-2.441636	-2.118126	0.261326
H	-0.939415	-2.810179	0.925645
O	0.885584	2.756450	-0.566638
C	-4.440386	0.853616	1.177340
H	-5.468736	0.624606	1.469411
H	-4.415145	1.883171	0.791063
H	-3.807571	0.801382	2.075524
O	-4.059480	-0.098037	0.194232
H	-3.128769	0.049593	-0.057776

Structure No: 76 (Fig.6) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-0.751307	-0.458341	-0.250797
C	-2.065543	-0.839238	-0.460371
C	-2.900542	0.260860	-0.127809
C	-2.075186	1.293563	0.260219
N	-0.762854	0.862986	0.195803
H	-2.370802	-1.822863	-0.787633
H	-3.980071	0.293972	-0.167440
H	-2.298844	2.313905	0.536484
C	0.329247	1.760020	0.332499
C	1.467954	1.679229	-0.318219
C	2.598473	1.617126	-0.969138
H	2.729718	2.130841	-1.919607
C	0.432333	-1.347336	-0.392012
N	1.354683	-1.373793	0.635119
H	2.068485	-2.084231	0.526899
N	1.132169	-0.973971	1.966500
H	1.198364	0.038027	2.036614
H	0.210312	-1.268901	2.281054
O	0.572362	-2.077051	-1.371040
H	0.141743	2.574012	1.028965
H	3.441639	1.039798	-0.595214

Structure No: TS13 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.001894	0.471206	-0.038657
C	2.369170	0.727936	0.140664
C	3.010111	-0.510472	0.268342
C	2.035167	-1.504202	0.142121
N	0.818093	-0.920856	-0.036837
H	2.807527	1.713825	0.194436
H	4.061987	-0.684922	0.444894
H	2.128322	-2.580478	0.157532
C	-0.366738	-1.588120	-0.425704
C	-1.598166	-1.042024	-0.324747
C	-2.902602	-1.391852	-0.202459
H	-3.701252	-0.848219	-0.700600
C	-0.077340	1.361561	-0.326838
N	-1.406906	0.753847	-0.051204
H	-2.077756	1.245967	-0.646582

N	-1.824541	1.010079	1.314548
H	-2.501620	0.251715	1.492426
H	-1.009139	0.815980	1.899598
O	-0.031819	2.491036	-0.783413
H	-0.224247	-2.570724	-0.855586
H	-3.164776	-2.317130	0.299318

Structure No: 81 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	0.975982	0.487439	-0.160496
C	2.360759	0.811955	-0.162619
C	3.046704	-0.369211	0.071603
C	2.097857	-1.407490	0.201673
N	0.848813	-0.899148	0.057150
H	2.759353	1.807764	-0.287027
H	4.117298	-0.495878	0.151407
H	2.242347	-2.466348	0.358586
C	-0.362699	-1.597907	0.026492
C	-1.543461	-0.909675	-0.270808
C	-2.765772	-1.316416	-0.739249
C	-0.146051	1.310697	-0.321047
N	-1.478982	0.541773	0.083106
H	-2.206669	1.053259	-0.422316
N	-1.704182	0.821875	1.503602
H	-2.457420	0.187841	1.778629
H	-0.863076	0.494679	1.981121
O	-0.299183	2.471316	-0.632952
H	-0.293778	-2.671146	-0.067617
H	-2.928891	-2.345764	-1.032517
H	-3.615165	-0.642779	-0.776953

Structure No: RC (81+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.386892	-0.752453	-0.106130
C	-2.444471	-1.698830	-0.189464
C	-3.628169	-0.976537	-0.179924
C	-3.301730	0.395719	-0.104765
N	-1.952936	0.535895	-0.065127
H	-2.311218	-2.770146	-0.213072
H	-4.633564	-1.372559	-0.214466

H	-3.942678	1.265158	-0.103194
C	-1.209403	1.720465	-0.071456
C	0.185285	1.651069	-0.177110
C	1.120717	2.566806	-0.585724
C	0.001626	-0.942592	-0.042369
N	0.759735	0.373281	0.346445
H	1.726084	0.233432	-0.022191
N	0.897349	0.349434	1.806192
H	1.414843	1.202866	2.027401
H	-0.047727	0.493281	2.166449
O	0.696984	-1.932454	-0.173862
H	-1.750912	2.622913	-0.313509
O	3.419158	-0.026100	-0.522077
H	3.504459	0.072498	-1.479631
C	3.974086	-1.295106	-0.121783
H	5.032573	-1.353806	-0.396970
H	3.880776	-1.341648	0.963655
H	3.412138	-2.125103	-0.558695
H	0.808767	3.529015	-0.973377
H	2.182001	2.391015	-0.455116

Structure No: TS14 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-1.604624	-0.591212	-0.077743
C	-2.858342	-1.156836	-0.359715
C	-3.753871	-0.096641	-0.547128
C	-3.036390	1.094443	-0.384242
N	-1.742176	0.793105	-0.100443
H	-3.061165	-2.216673	-0.407462
H	-4.807090	-0.166025	-0.778345
H	-3.358436	2.122935	-0.461608
C	-0.675964	1.682822	0.115305
C	0.588890	1.252931	0.353653
C	1.836057	1.970279	0.262638
C	-0.356368	-1.207321	0.223604
N	0.780036	-0.226087	0.555541
H	1.618157	-0.448218	-0.172440
N	1.287401	-0.565426	1.875596
H	2.286421	-0.370547	1.865128
H	0.852561	0.080828	2.533201
O	-0.082915	-2.384307	0.249765
H	-0.904312	2.732326	-0.007673

O	2.649404	-0.094785	-1.122356
H	2.513535	0.948622	-0.725628
C	3.990715	-0.561378	-1.089935
H	4.536746	-0.170399	-0.217722
H	3.995214	-1.655445	-1.042735
H	4.523102	-0.249882	-1.997055
H	1.716026	3.013252	-0.029933
H	2.499892	1.878303	1.129513

Structure No: PC (68+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	1.044347	-0.975688	0.281253
C	1.502045	-2.288248	0.342526
C	2.825632	-2.285713	-0.147156
C	3.152853	-0.979839	-0.497780
N	2.070664	-0.185098	-0.236626
H	0.928760	-3.128804	0.703711
H	3.482433	-3.139295	-0.239760
H	4.061337	-0.562953	-0.907279
C	1.909304	1.186781	-0.417484
C	0.740061	1.781352	-0.085270
C	0.512039	3.253720	-0.256338
C	-0.218371	-0.376765	0.641286
N	-0.308013	1.004815	0.432203
H	-2.894458	-0.760687	0.445587
N	-1.498797	1.676749	0.795528
H	-2.269904	1.286991	0.246582
H	-1.697754	1.437061	1.766131
O	-1.173801	-1.013531	1.113156
H	2.747724	1.732244	-0.826114
O	-3.620464	-0.276575	0.005090
H	0.270006	3.730673	0.697442
C	-4.384885	-1.159832	-0.804675
H	-3.770932	-1.647616	-1.574755
H	-4.880994	-1.935188	-0.204916
H	-5.154249	-0.562736	-1.301211
H	1.412179	3.716574	-0.668231
H	-0.327941	3.450063	-0.928959

Structure No: 68 (B3LYP/6-31+G(d,p))

	X	Y	Z

C	1.040501	0.531830	-0.000502
C	2.357443	0.977440	-0.000243
C	3.181358	-0.169716	0.000211
C	2.357955	-1.289983	0.000426
N	1.057397	-0.863226	-0.000026
H	2.660985	2.013645	-0.000480
H	4.262184	-0.189690	0.000384
H	2.595520	-2.343782	0.000771
C	-0.120190	-1.610725	0.000015
C	-1.320110	-0.985702	-0.000130
C	-2.619057	-1.735440	-0.000125
C	-0.220454	1.241621	-0.000275
N	-1.361426	0.414966	-0.000542
N	-2.626958	1.043409	0.000604
H	-2.653220	1.663562	0.810188
H	-2.654358	1.664071	-0.808540
O	-0.344207	2.467471	0.000183
H	-0.020682	-2.686604	0.000017
H	-3.222349	-1.485973	-0.877953
H	-2.420447	-2.809891	-0.000834
H	-3.221742	-1.487089	0.878460

The following tables and cartesian coordinates are related to Chapter 2.

1. Absolute Energies of the Structures

Energies are given in terms of ZPE-corrected total energy (Eel+ZPE), enthalpy (Eel+H) and Gibbs free-energy (Eel+G) as extracted from Gaussian output of each structure.

Table S5. Absolute energies of optimized structures for the formation of imine **114** in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
RC(64a+112 +MeOH)	-727.733043	-727.711495	-727.788785	–
TS15-met	-727.694594	-727.676148	-727.741599	-990.3
PC(113+Me OH)	-727.716566	-727.697106	-727.765385	–
RC(113+Me OH)	-727.719181	-727.698877	-727.770366	–
TS16-met	-727.690466	-727.670638	-727.739420	-686.3
PC(114+Me OH)	-727.732178	-727.710797	-727.784297	–

[a]Eel = Total electronic energy
[b]ZPE = Zero point energy correction
[c]H = Enthalpy correction
[d]G = Gibbs free energy correction

Table S6. Single point energies in methanol (CPCM/B3LYP/6-31+G(d,p)//B3LYP/6 31+G(d,p))

Compound No	Eel[a] (au)	Eel+G[b] (au)
RC(64a+112+MeOH)	-728.024054	-727.797887
TS15-met	-727.988038	-727.755847
PC(113+MeOH)	-728.011257	-727.774602
RC(113+MeOH)	-728.013551	-727.780891
TS16-met	-727.980990	-727.753026
PC(114+MeOH)	-728.023779	-727.794764

Table S7. Absolute energies of optimized structures for the formation of **114** without assistance of methanol in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
RC(64a+112)	-612.039100	-612.022037	-612.088105	–
TS15	-611.978269	-611.963249	-612.020771	-1560.2
113 (Product of TS15)	-612.025204	-612.009887	-612.067707	–
113 (Reactant of TS16)	-612.022157	-612.006480	-612.066317	–
TS16	-611.963218	-611.947337	-612.006879	-453.0
PC(114+Me-OH)	-612.037761	-612.020491	-612.084936	–

Table S8. Single point energies for the formation of **114** without assistance of methanol (CPCM/B3LYP/6-31+G(d,p)//B3LYP/6 31+G(d,p))

Compound No	Eel[a] (au)	Eel+G[b] (au)
RC(64a+112)	-612.275959	-612.096732
TS15	-612.218688	-612.035034
113 (Product of TS15)	-612.264641	-612.075855
113 (Reactant of TS16)	-612.261986	-612.075456
TS16	-612.207630	-612.025010
PC(114+MeOH)	-612.275823	-612.096148

Table S9. Absolute energies of optimized structures for the formation of **101** in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
114	-535.609487	-535.595502	-535.650482	–
TS17	-535.588372	-535.575658	-535.626516	-443.4
115	-535.620224	-535.607816	-535.657578	–
RC(115+112)	-708.797633	-708.778017	-708.848542	–
TS18	-708.752340	-708.734507	-708.797930	-1131.7
PC(116+112)	-708.809236	-708.789705	-708.859752	–
RC(116+112)	-708.819021	-708.799326	-708.871080	–
TS19	-708.737100	-708.718311	-708.784614	-483.8
PC(101+117)	-708.809236	-708.789705	-708.859752	–

Table S10. Single point energies in methanol (CPCM/B3LYP/6-31+G(d,p)//B3LYP/6 31+G(d,p))

Compound No	Eel[a] (au)	Eel+G[b] (au)
114	-535.818209	-535.657285
TS17	-535.797023	-535.633612
115	-535.833559	-535.666199
RC(115+112)	-709.111580	-708.859132
TS18	-709.060555	-708.809138
PC(116+112)	-709.123073	-708.869703
RC(116+112)	-709.132816	-708.881057
TS19	-709.062752	-708.809555
PC(101+117)	-709.123073	-708.869703

Table S11. Absolute energies of optimized structures for the methanol assisted hemiaminal formation in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
RC(54a+118+ MeOH)	-1000.411008	-1000.385951	-1000.470732	–
TS21-met	-1000.366905	-1000.344787	-1000.417416	-646.7
Product Complex of TS21-met	-1000.386381	-1000.363270	-1000.438592	–

Table S12. Absolute energies of optimized structures for the hemiaminal formation without methanol assistance in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
RC(54a+118)	-884.715977	-884.695627	-884.767050	–
TS21	-884.648248	-884.629737	-884.693486	-1590.8
Product Complex of TS21	-884.696986	-884.678114	-884.742679	–

Table S13. Single point energies in methanol (CPCM/B3LYP/6-31+G(d,p)//B3LYP/6 31+G(d,p))

Compound No	Eel[a] (au)	Eel+G[b] (au)
RC(54a+118)	-885.113692	-884.774666
TS21	-885.049184	-884.706296
Product Complex of TS21	-885.097666	-884.750189

Table S14. Absolute energies of optimized structures for the formation of **102a** in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
RC(54a+118)	-884.715536	-884.695058	-884.767904	–
TS20	-884.667586	-884.649033	-884.713578	-322.0
119(Product of TS20)	-884.670733	-884.652188	-884.716451	–
119 (Reactant of TS22)	-884.670731	-884.652186	-884.716454	–
TS22	-884.644089	-884.626677	-884.687862	-296.8
120	-884.747009	-884.729335	-884.790990	–
RC(120+Me-OH)	-1000.440245	-1000.417712	-1000.492856	–
TS23	-1000.383774	-1000.361693	-1000.434258	-842.1
PC(102a+Me-OH+H_2O)	-1000.463986	-1000.439849	-1000.519502	–

Table S15. Single point energies for the formation of **102a** in methanol (CPCM/B3LYP/6-31+G(d,p)//B3LYP/6 31+G(d,p))

Compound No	Eel[a] (au)	Eel+G[b] (au)
RC(54a+118)	-885.113517	-884.776194
Ts20	-885.069640	-884.724461
119(Product of TS20)	-885.079908	-884.731964
119 (Reactant of TS22)	-885.079904	-884.731963
Ts22	-885.056550	-884.707292
120	-885.154170	-884.801766
RC(120+MeOH)	-1000.900128	-1000.503252
Ts23	-1000.842544	-1000.452853
PC(102a+MeOH+H_2O)	-1000.922135	-1000.531561

2. Cartesian Coordinates for the Optimized Structures Given in Paths

Structure No: RC (64a+112+MeOH)

	X	Y	Z
C	-3.423746	-1.607099	-0.001605
C	-2.619364	-2.706226	-0.267337
C	-1.311525	-2.221740	-0.464595
C	-1.340510	-0.832699	-0.316154
N	-2.661053	-0.472396	-0.029227
H	-4.482208	-1.547528	0.205223
H	-2.951858	-3.733451	-0.311094
H	-0.423604	-2.795451	-0.693062
C	-3.120108	0.853130	0.196682
H	-2.337318	1.599262	0.113482
C	-4.363789	1.165496	0.479474
C	-5.589802	1.521981	0.762444
H	-5.940997	1.588997	1.791203
H	-6.306673	1.768898	-0.019408
C	-0.206864	0.047581	-0.441101
O	-0.224442	1.281867	-0.316641
N	3.149156	-0.620495	-1.175179
C	4.246334	-1.295572	-0.465776
H	5.231119	-0.821516	-0.613801
H	4.321434	-2.314976	-0.870099
C	3.957684	-1.382371	1.008816
C	4.783781	-0.971965	1.975314
H	2.991740	-1.815529	1.269469
H	4.527294	-1.072058	3.026077
H	5.747695	-0.521771	1.746828
O	2.352141	2.317534	-0.764645
H	1.420663	2.065600	-0.597743
C	2.690142	3.434471	0.045005
H	2.084968	4.317673	-0.204359
H	2.573189	3.218684	1.116617
H	3.740079	3.672969	-0.146391
H	0.742832	-0.469925	-0.668093
H	3.124521	0.377085	-0.950313
H	3.285414	-0.691850	-2.180413

Structure No: TS15-met

	X	Y	Z

C	-3.094675	-0.694637	0.275003
C	-2.967564	-1.990934	0.721960
C	-1.629804	-2.393726	0.456286
C	-0.970341	-1.330639	-0.137341
N	-1.883783	-0.284329	-0.247158
H	-3.946054	-0.031695	0.253414
H	-3.751971	-2.587891	1.165402
H	-1.192832	-3.362986	0.659529
C	-1.646716	0.977309	-0.855870
H	-0.729947	1.006613	-1.436235
C	-2.453859	2.008703	-0.755817
C	-3.233891	3.057910	-0.699527
H	-3.114273	3.817980	0.071387
H	-4.034564	3.213835	-1.421498
C	0.474455	-1.297965	-0.538652
O	0.827399	-0.394639	-1.483176
N	1.420105	-1.062015	0.738516
C	1.055813	0.033102	1.691336
H	1.537028	-0.189398	2.648895
H	-0.029035	-0.008721	1.845551
C	1.475710	1.397347	1.215249
C	2.214176	2.232965	1.948953
H	1.119900	1.696723	0.233303
H	2.467049	3.226329	1.591397
H	2.588787	1.956652	2.932464
O	3.145329	-0.685325	-1.002088
H	2.002469	-0.442804	-1.471734
C	4.185919	0.239854	-1.223356
H	4.438256	0.291357	-2.292350
H	3.923742	1.256561	-0.887293
H	5.091682	-0.069134	-0.682858
H	0.766548	-2.333090	-0.792283
H	2.408641	-0.868052	0.187198
H	1.463161	-1.943910	1.248984

Structure No: PC(113+MeOH)

	X	**Y**	**Z**
C	-3.212893	-0.766234	0.227006
C	-3.076951	-2.042641	0.720587
C	-1.708821	-2.405484	0.568237
C	-1.040381	-1.340642	-0.007187
N	-1.977569	-0.329049	-0.216889

H	-4.079974	-0.131830	0.125370
H	-3.872103	-2.654314	1.123055
H	-1.255557	-3.350299	0.838583
C	-1.741234	0.931108	-0.823181
H	-0.794825	0.995239	-1.346635
C	-2.583129	1.939716	-0.797168
C	-3.397169	2.963908	-0.815340
H	-3.357725	3.738579	-0.050682
H	-4.148348	3.083082	-1.595330
C	0.446891	-1.286788	-0.266383
O	0.725612	-0.514693	-1.415128
N	1.290950	-0.835686	0.874385
C	0.930835	0.438846	1.544474
H	1.257859	0.364331	2.586800
H	-0.160713	0.575524	1.561537
C	1.584010	1.641398	0.911924
C	2.360403	2.505846	1.570940
H	1.376942	1.799188	-0.144547
H	2.787812	3.375674	1.080527
H	2.589968	2.378406	2.627183
O	3.454863	-0.909407	-0.949703
H	1.689271	-0.579044	-1.580799
C	4.660335	-0.152440	-0.988457
H	5.064355	-0.236403	-2.000298
H	4.484368	0.907692	-0.763792
H	5.404333	-0.546719	-0.283612
H	0.757177	-2.329634	-0.424007
H	3.010675	-0.822231	-0.076302
H	1.277641	-1.580851	1.566411

Structure No: RC(113+MeOH)

	X	**Y**	**Z**
C	-3.259433	-0.483883	0.209675
C	-3.448106	-1.769684	-0.242842
C	-2.184848	-2.241966	-0.699014
C	-1.258249	-1.234482	-0.509781
N	-1.928766	-0.146974	0.046673
H	-3.953511	0.234991	0.617482
H	-4.386873	-2.305223	-0.254843
H	-1.964403	-3.218610	-1.108728
C	-1.358890	1.102105	0.404884
H	-0.419456	1.353829	-0.080166
C	-1.916766	1.955658	1.234362

C	-2.444070	2.839484	2.041086
H	-2.214931	2.846267	3.105627
H	-3.132001	3.603647	1.681599
C	0.209409	-1.298417	-0.808379
O	0.582614	-0.318864	-1.855817
N	1.050594	-1.144117	0.329921
C	2.489167	-1.360823	0.128924
H	2.969490	-0.550445	-0.437215
H	2.591911	-2.279286	-0.466301
C	3.179813	-1.541025	1.453576
C	4.204178	-0.794772	1.875495
H	2.784377	-2.335727	2.085709
H	4.677189	-0.968681	2.837699
H	4.602351	0.017023	1.270851
O	1.659556	2.080895	-0.871806
C	2.046698	3.143701	-1.730986
H	2.921426	2.881309	-2.343158
H	1.230355	3.455361	-2.398870
H	2.313429	3.993004	-1.096677
H	0.404616	-2.291512	-1.231195
H	1.402896	1.301578	-1.398069
H	0.873442	-0.289463	0.848459
H	-0.043875	-0.402066	-2.589375

Structure No: TS16-met

	X	**Y**	**Z**
C	3.244842	-0.389651	-0.148996
C	3.386021	-1.767544	-0.225780
C	2.087851	-2.307207	-0.246546
C	1.174359	-1.247592	-0.190276
N	1.915696	-0.066628	-0.128538
H	3.988096	0.390826	-0.084021
H	4.321522	-2.307355	-0.251985
H	1.813720	-3.352036	-0.302720
C	1.408758	1.263227	0.007715
H	0.537916	1.358530	0.673581
C	1.990290	2.295129	-0.557174
C	2.542895	3.358384	-1.081865
H	2.231821	3.738717	-2.052979
H	3.331832	3.903769	-0.566849
C	-0.239178	-1.429633	-0.300773
O	-0.908773	-1.512259	1.905036
N	-1.162472	-0.542643	-0.626970

C	-2.574260	-0.944883	-0.727514
H	-3.048711	-0.798119	0.248162
H	-2.596271	-2.017256	-0.952590
C	-3.282889	-0.166549	-1.802681
C	-4.372536	0.574745	-1.589444
H	-2.861320	-0.241715	-2.804805
H	-4.866967	1.103584	-2.398814
H	-4.806663	0.675655	-0.597527
O	-1.062828	0.879188	1.625616
C	-1.808130	1.658777	2.523829
H	-2.811571	1.235973	2.709746
H	-1.310043	1.755085	3.504417
H	-1.948599	2.676687	2.128911
H	-0.534177	-2.469498	-0.387817
H	-0.990503	-0.310402	1.897848
H	-1.061367	0.399392	-0.220021
H	-0.236623	-1.795597	2.537835

Structure No: PC(114+MeOH)

	X	**Y**	**Z**
C	-3.622189	-0.284099	0.074107
C	-3.928105	-1.630550	0.119133
C	-2.713359	-2.333426	-0.044009
C	-1.683508	-1.402033	-0.172213
N	-2.266581	-0.134833	-0.100913
H	-4.259138	0.585606	0.132511
H	-4.915486	-2.050613	0.246664
H	-2.576576	-3.406361	-0.055561
C	-1.604819	1.108085	-0.264982
H	-0.576761	1.038844	-0.595962
C	-2.165443	2.277069	-0.053070
C	-2.687968	3.461451	0.132400
H	-2.628764	3.967435	1.094980
H	-3.200345	3.990776	-0.669933
C	-0.289727	-1.763259	-0.312364
O	4.027181	1.041837	-1.541919
N	0.754646	-1.014993	-0.270411
C	2.054155	-1.690430	-0.432745
H	2.638408	-1.139468	-1.177179
H	1.905876	-2.718440	-0.804242
C	2.817034	-1.732695	0.869921
C	4.024520	-1.189846	1.051520
H	2.325642	-2.260007	1.688688

H	4.539297	-1.275335	2.004961
H	4.526625	-0.642880	0.256696
O	1.726065	1.661491	-0.109266
C	1.874358	2.221899	1.193624
H	2.544456	1.618303	1.818335
H	2.306012	3.218597	1.072819
H	0.903707	2.319534	1.696852
H	-0.172869	-2.847222	-0.461685
H	3.232753	1.382963	-1.075855
H	1.338703	0.757567	-0.040392
H	4.176351	1.629859	-2.290877

Structure No: RC(64a+112) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	3.555728	-0.923960	-0.199943
C	3.222873	-2.269921	-0.239881
C	1.825618	-2.354290	-0.076131
C	1.329934	-1.056023	0.060762
N	2.419340	-0.184002	-0.018834
H	4.515702	-0.436590	-0.286371
H	3.917793	-3.086734	-0.372400
H	1.219956	-3.250259	-0.056428
C	2.346178	1.231818	0.076924
H	1.336965	1.601910	0.223197
C	3.385078	2.031048	-0.001460
C	4.391106	2.863535	-0.073537
H	4.715929	3.284431	-1.024064
H	4.941322	3.171210	0.814596
C	-0.054976	-0.693045	0.248399
H	-0.739680	-1.560848	0.282623
O	-0.509901	0.447810	0.367479
N	-3.390139	-0.710467	0.652606
C	-4.343452	-0.426031	-0.429946
H	-5.055146	-1.258087	-0.498722
H	-3.774083	-0.420564	-1.368590
H	-2.624715	-0.035856	0.653136
H	-3.854906	-0.649800	1.555234
C	-5.100562	0.872542	-0.288694
C	-6.430751	0.976289	-0.199341
H	-4.487265	1.773864	-0.234241
H	-6.925586	1.936356	-0.082122
H	-7.072132	0.097990	-0.244997

Structure No: TS15 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	2.093348	-0.930779	-1.131674
C	1.524549	-2.148380	-1.437582
C	0.456616	-2.351987	-0.520900
C	0.394979	-1.251002	0.317356
N	1.411662	-0.379548	-0.066243
H	2.942206	-0.417013	-1.556670
H	1.853536	-2.822595	-2.215900
H	-0.195515	-3.213778	-0.463675
C	1.730232	0.849731	0.569307
H	1.239642	0.963421	1.534070
C	2.541173	1.753485	0.068115
C	3.357219	2.674961	-0.377447
H	3.004630	3.506076	-0.986736
H	4.423636	2.648167	-0.156450
C	-0.595588	-1.007457	1.410893
H	-0.979128	-1.991625	1.736869
O	-0.299252	-0.129373	2.413398
N	-1.914289	-0.213647	0.938678
C	-1.960371	0.441656	-0.389657
H	-1.889512	-0.317197	-1.176592
H	-1.071322	1.077722	-0.459361
H	-1.455650	0.363385	1.906215
H	-2.764769	-0.755956	1.104087
C	-3.210793	1.262748	-0.538349
C	-4.132786	1.060450	-1.483673
H	-3.340814	2.070486	0.181694
H	-5.014839	1.689098	-1.559683
H	-4.031170	0.266601	-2.220430

Structure No: 113 (product of TS15) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	2.219434	-0.640377	-1.109603
C	1.840861	-1.871079	-1.592523
C	0.726502	-2.299497	-0.816304
C	0.447473	-1.318439	0.116435
N	1.374959	-0.293939	-0.069391
H	3.030966	0.014248	-1.388162
H	2.321571	-2.411468	-2.395842
H	0.181872	-3.228594	-0.921482

C	1.492313	0.891150	0.699600
H	0.947834	0.861468	1.636237
C	2.212473	1.935518	0.356468
C	2.929443	2.991232	0.067324
H	2.510874	3.832956	-0.482879
H	3.974893	3.070993	0.363230
C	-0.728539	-1.328306	1.064783
H	-0.972293	-2.388302	1.221458
O	-0.350790	-0.732315	2.305635
N	-1.977418	-0.719589	0.603362
C	-1.897506	0.574379	-0.091270
H	-1.344703	0.512550	-1.041417
H	-1.346785	1.264347	0.559201
H	-1.173059	-0.622655	2.805944
H	-2.492007	-1.386024	0.034372
C	-3.278960	1.117088	-0.333341
C	-3.760861	1.450550	-1.534079
H	-3.902962	1.228914	0.553109
H	-4.763536	1.850464	-1.653949
H	-3.164933	1.340993	-2.437634

Structure No: 113 (reactant of TS16) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	2.888181	-0.498674	-0.581176
C	2.881045	-1.874251	-0.581312
C	1.554124	-2.282658	-0.266114
C	0.783569	-1.148037	-0.080339
N	1.615754	-0.049374	-0.275385
H	3.670723	0.209453	-0.807274
H	3.724426	-2.512172	-0.805001
H	1.190092	-3.298627	-0.184552
C	1.239905	1.317372	-0.237003
H	0.233251	1.521039	-0.584300
C	2.043788	2.295561	0.113496
C	2.818672	3.298526	0.435606
H	3.455792	3.787854	-0.299625
H	2.858651	3.680767	1.454207
C	-0.639659	-1.140318	0.414497
H	-1.044301	-2.124787	0.143989
O	-0.691885	-0.996144	1.858392
N	-1.518319	-0.147766	-0.159681
C	-2.948243	-0.509892	-0.125118
H	-3.320380	-0.674638	0.897522

H	-3.052926	-1.457015	-0.671310
H	0.041870	-1.495648	2.243621
1	-1.401841	0.719857	0.359714
C	-3.768481	0.548287	-0.809380
C	-4.783546	1.203984	-0.239578
H	-3.482690	0.772283	-1.836967
H	-5.353675	1.953143	-0.781298
H	-5.082101	1.008228	0.788117

Structure No: TS16 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	2.933183	-0.488200	-0.246565
C	2.982187	-1.873860	-0.216628
C	1.652499	-2.330580	-0.205529
C	0.807933	-1.213769	-0.212257
N	1.626024	-0.080805	-0.248314
H	3.727964	0.240970	-0.295371
H	3.881443	-2.472796	-0.215792
H	1.311961	-3.356227	-0.167580
C	1.197701	1.269444	-0.321768
H	0.171005	1.401418	-0.639625
C	1.965659	2.303040	-0.067076
C	2.694910	3.359245	0.181540
H	3.296319	3.835095	-0.591770
H	2.726835	3.803713	1.175159
C	-0.609489	-1.284628	-0.154456
H	-0.999231	-2.295751	-0.265888
O	-0.832511	-0.509976	2.019884
N	-1.487932	-0.279412	-0.237593
C	-2.922736	-0.626184	-0.231373
H	-3.215130	-0.883689	0.793156
H	-3.055871	-1.509901	-0.868163
H	-0.479906	-0.525910	2.921247
H	-1.266201	0.348439	0.580021
C	-3.749932	0.511558	-0.762299
C	-4.721456	1.113810	-0.072126
H	-3.519884	0.836960	-1.776802
H	-5.306731	1.921665	-0.501461
H	-4.961885	0.818086	0.946372

Structure No: 114 (B3LYP/6-31+G(d,p))

	X	Y	Z

C	-3.040042	-0.641610	0.085011
C	-3.093127	-2.022713	0.060483
C	-1.762189	-2.481330	-0.043136
C	-0.918701	-1.370065	-0.084205
N	-1.730500	-0.236340	-0.002233
H	-3.829258	0.091519	0.157396
H	-3.991010	-2.621942	0.108730
H	-1.427322	-3.508833	-0.090645
C	-1.299063	1.115668	0.023264
H	-0.240463	1.263445	-0.141622
C	-2.098817	2.138942	0.218533
C	-2.856399	3.189168	0.399438
H	-3.039429	3.596739	1.392676
H	-3.328580	3.701717	-0.437583
C	0.518772	-1.467268	-0.189646
H	0.847343	-2.518131	-0.179266
O	1.790534	2.298052	-0.994096
N	1.393487	-0.530583	-0.291948
C	2.797162	-0.949588	-0.370458
H	3.214315	-0.585453	-1.317608
H	2.878748	-2.050705	-0.371610
H	2.462815	2.619191	-0.380994
H	1.656877	1.358757	-0.756999
C	3.600386	-0.388264	0.777256
C	4.695892	0.363425	0.639422
H	3.237492	-0.640243	1.773740
H	5.251034	0.722300	1.501255
H	5.079004	0.637492	-0.341204

Structure No: 114 (reactant of TS17) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-0.761932	-0.890149	0.080379
C	-1.252118	-2.158825	0.384105
C	-2.656546	-2.149204	0.216069
C	-2.999033	-0.872312	-0.183705
N	-1.860200	-0.102229	-0.264301
H	-0.635842	-3.001234	0.668707
H	-3.340835	-2.972216	0.365375
H	-3.964109	-0.433923	-0.393554
C	-1.924428	1.284515	-0.594095
C	-1.339272	2.243211	0.080362
C	-0.727348	3.218081	0.696451

H	0.284908	3.500389	0.414581
C	0.650340	-0.552947	0.036594
N	1.156397	0.546607	-0.380338
H	-2.537131	1.509602	-1.463906
H	-1.196961	3.762721	1.512528
H	1.276702	-1.387204	0.383840
C	2.616128	0.691240	-0.413541
H	2.926089	0.645394	-1.466945
H	2.831748	1.717702	-0.084674
C	3.446183	-0.264838	0.406500
C	4.362734	-1.099974	-0.091811
H	3.281443	-0.238899	1.484734
H	4.958250	-1.744317	0.549197
H	4.554113	-1.161449	-1.161258

Structure No: TS17 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.137039	-0.874861	-0.039660
C	-2.076522	-1.915435	-0.019736
C	-3.347384	-1.324375	0.067827
C	-3.168447	0.058940	0.088223
N	-1.832721	0.334545	0.029768
H	-1.842067	-2.970506	-0.050241
H	-4.299960	-1.832620	0.117562
H	-3.892785	0.859188	0.133212
C	-1.251980	1.609729	-0.120292
C	0.057639	1.908191	-0.018591
C	0.877048	2.973829	0.106873
H	1.693589	3.172802	-0.580370
C	0.274660	-0.878498	-0.154747
N	0.946948	0.226418	-0.082238
H	-1.960899	2.385620	-0.383377
H	0.734718	3.670452	0.927526
H	0.775135	-1.840242	-0.301766
C	2.397222	0.296419	-0.188116
H	2.691881	0.355363	-1.244939
H	2.662942	1.262695	0.271936
C	3.111329	-0.833913	0.496358
C	3.947210	-1.682501	-0.110146
H	2.917226	-0.936753	1.564143
H	4.456214	-2.468624	0.439762
H	4.162002	-1.609268	-1.174116

Structure No: 115 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-1.159344	-0.838923	-0.027010
C	-2.149821	-1.866897	-0.049917
C	-3.378509	-1.227302	-0.023579
C	-3.182645	0.171464	0.013239
N	-1.839749	0.416408	0.008374
H	-1.951909	-2.928212	-0.073964
H	-4.349511	-1.704570	-0.028478
H	-3.895525	0.981242	0.033025
C	-1.143461	1.580205	0.010937
C	0.280395	1.622676	-0.016983
C	1.001907	2.791908	-0.079926
H	2.077055	2.837654	-0.150061
C	0.210091	-0.814214	-0.015780
N	0.919369	0.340895	0.032674
H	-1.716279	2.496866	-0.001259
H	0.465864	3.732490	-0.092090
H	0.777647	-1.734985	-0.038785
C	2.390195	0.326298	0.075212
H	2.775400	0.677962	-0.891291
H	2.677826	1.075287	0.824812
C	2.996373	-0.997001	0.443015
C	3.862900	-1.659693	-0.327531
H	2.742266	-1.387648	1.428395
H	4.328595	-2.582250	0.005891
H	4.142743	-1.296081	-1.313596

Structure No: RC(115+112) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-2.728794	0.049403	-0.637301
C	-3.994913	-0.070544	-1.283397
C	-4.708160	-1.022539	-0.573184
C	-3.918832	-1.499583	0.497758
N	-2.717839	-0.855214	0.466131
H	-4.309778	0.483898	-2.154975
H	-5.712487	-1.363038	-0.787204
H	-4.136295	-2.233840	1.258115
C	-1.632611	-0.944933	1.279040
C	-0.451418	-0.179404	1.070206
C	0.668115	-0.282869	1.869796

H	1.516429	0.380118	1.797665
C	-1.601429	0.802236	-0.838620
N	-0.504214	0.705726	-0.052229
H	-1.697983	-1.632162	2.110848
H	0.638766	-0.960332	2.714208
H	-1.552012	1.513924	-1.653564
C	0.658708	1.558678	-0.363962
C	3.812257	-1.987027	-0.739146
H	4.263287	-2.034429	-1.737014
H	3.898822	-2.997148	-0.297942
H	1.955337	-1.487570	0.031557
H	0.602823	1.822298	-1.423327
H	1.554771	0.941490	-0.242933
N	2.412748	-1.546962	-0.881402
C	4.595477	-1.030143	0.119078
C	5.706779	-0.393520	-0.259254
H	4.210180	-0.876940	1.128403
H	6.241478	0.270155	0.414343
H	6.121430	-0.516489	-1.257624
H	1.888284	-2.224689	-1.429922
C	0.700328	2.802938	0.484912
C	0.849949	4.033723	-0.011353
H	0.609554	2.653176	1.558970
H	0.895342	4.904388	0.635929
H	0.944451	4.213847	-1.080470

Structure No: TS18 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	2.824610	0.529739	0.407841
C	4.123301	0.837728	0.869248
C	4.964069	-0.176535	0.401143
C	4.200790	-1.092025	-0.338783
N	2.904953	-0.664300	-0.333407
H	4.392455	1.694617	1.469410
H	6.029063	-0.258291	0.570642
H	4.488375	-1.992204	-0.860671
C	1.779809	-1.170216	-0.942659
C	0.520127	-0.604632	-0.783612
C	-0.677648	-1.260374	-1.228460
H	-1.435594	-0.631453	-1.692680
C	1.579432	1.141917	0.490417
N	0.456430	0.609923	-0.027026
H	1.909779	-2.069832	-1.528176

H	-0.469392	-2.148969	-1.825516
H	1.471184	2.092864	0.995927
C	-0.826346	1.214442	0.340824
C	-3.509548	-1.348589	1.276038
H	-3.912394	-0.678291	2.044429
H	-3.670141	-2.379577	1.618666
H	-1.546323	-1.499925	0.169004
H	-0.657611	1.856534	1.209376
H	-1.679263	-0.029898	0.930789
N	-2.046256	-1.126462	1.140304
C	-4.233970	-1.138462	-0.025193
C	-5.212171	-0.247857	-0.200995
H	-3.927970	-1.778851	-0.851276
H	-5.723936	-0.147318	-1.153191
H	-5.529130	0.417870	0.598520
H	-1.541552	-1.497187	1.946771
C	-1.550382	1.892643	-0.733596
C	-2.393697	2.936418	-0.585105
H	-1.426849	1.485455	-1.737083
H	-2.946183	3.337523	-1.428395
H	-2.560659	3.407631	0.381719

Structure No: PC(116+112) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	3.330707	0.426149	0.378351
C	4.652911	0.596828	0.809219
C	5.347282	-0.594601	0.492699
C	4.472563	-1.478419	-0.120683
N	3.242344	-0.855292	-0.189672
H	5.052819	1.479404	1.286387
H	6.391098	-0.796259	0.691270
H	4.614013	-2.478445	-0.501185
C	2.035136	-1.286298	-0.679464
C	0.910590	-0.522609	-0.657805
C	-0.402552	-1.126546	-1.068635
H	-0.757883	-0.764197	-2.037886
C	2.190910	1.235432	0.340983
N	0.974701	0.803321	-0.123295
H	2.002331	-2.299880	-1.058513
H	-0.278508	-2.209175	-1.152532
H	2.231781	2.260829	0.678208
C	-0.127400	1.625251	0.046134
C	-4.647356	-0.756320	1.363020

H	-5.268348	0.054421	1.779469
H	-4.664136	-1.577252	2.093271
H	-1.186630	-0.931208	-0.328753
H	0.024399	2.370886	0.819133
H	-3.163423	0.464469	0.600020
N	-3.239586	-0.385843	1.157616
C	-5.261395	-1.239794	0.076888
C	-6.384321	-0.756120	-0.461843
H	-4.717568	-2.040104	-0.425061
H	-6.789381	-1.151786	-1.388843
H	-6.939065	0.052834	0.009158
H	-2.783036	-0.199560	2.046502
C	-1.218646	1.788630	-0.846184
C	-2.241330	2.676797	-0.678116
H	-1.242333	1.184510	-1.747562
H	-3.022362	2.772740	-1.423441
H	-2.288568	3.342186	0.180423

Structure No: RC(116+112) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	2.831155	0.522365	-0.572612
C	3.905750	0.841806	-1.410561
C	4.769940	-0.281055	-1.425110
C	4.240784	-1.267449	-0.610089
N	3.055485	-0.777457	-0.091591
H	4.034907	1.771786	-1.944550
H	5.694319	-0.367164	-1.979940
H	4.593682	-2.255549	-0.357095
C	2.166984	-1.326818	0.800057
C	1.041518	-0.683903	1.198280
C	0.065913	-1.328918	2.136471
C	1.690141	1.206027	-0.126130
N	0.752188	0.620300	0.685071
H	2.399177	-2.316898	1.171488
H	1.530389	2.238523	-0.391016
C	-0.441621	1.221318	1.001549
C	-4.245522	-1.524457	-0.161805
H	-4.389471	-2.612843	-0.147838
H	-4.677687	-1.138766	0.768773
H	-0.970182	0.811985	1.846328
H	-2.601266	-0.276591	-0.169633
H	-0.055969	-0.751223	3.060943
H	0.435701	-2.319438	2.412212

H	-0.921065	-1.445443	1.670910
N	-2.793574	-1.276398	-0.129355
C	-4.972970	-0.927835	-1.342058
C	-5.951328	-0.021046	-1.258479
H	-4.641746	-1.267450	-2.325568
H	-6.432949	0.386368	-2.142784
H	-6.304264	0.345769	-0.296662
C	-0.958628	2.344130	0.301249
C	-1.989577	3.133656	0.709729
H	-0.522791	2.558943	-0.675725
H	-2.389675	3.906801	0.063761
H	-2.453185	3.012405	1.685172
H	-2.341851	-1.693258	-0.940599

Structure No: TS19 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-2.734503	0.638135	-0.028401
C	-3.939344	1.353415	0.021178
C	-4.971945	0.408995	0.140110
C	-4.409707	-0.868637	0.161298
N	-3.056718	-0.734495	0.058852
H	-4.034450	2.428664	-0.020237
H	-6.030465	0.618670	0.206373
H	-4.871435	-1.841512	0.242135
C	-2.047149	-1.675834	0.017956
C	-0.742942	-1.293860	-0.085246
C	0.360440	-2.314351	-0.131532
C	-1.383046	0.973685	-0.157827
N	-0.415512	0.060039	-0.177913
H	-2.346137	-2.715368	0.060520
H	-1.071897	2.007982	-0.253052
C	1.215881	0.500833	0.201748
C	4.222349	-0.342677	1.092055
H	5.192186	-0.301990	1.635524
H	3.785921	-1.320137	1.356832
H	1.757778	-0.084782	-0.531290
H	1.310536	0.124939	1.212989
H	0.958343	-2.216715	-1.042931
H	-0.064595	-3.320390	-0.107543
H	1.042983	-2.211428	0.717465
N	3.322749	0.714735	1.528110
C	4.537522	-0.347440	-0.390126
C	4.303630	-1.351707	-1.246508

H	4.961336	0.583196	-0.774825
H	4.537386	-1.275781	-2.306031
H	3.890128	-2.300350	-0.905075
C	1.381721	1.964817	0.079205
C	1.497742	2.624063	-1.089461
H	1.372834	2.516170	1.015830
H	1.622862	3.702204	-1.119124
H	1.524525	2.100136	-2.042435
H	3.764638	1.607920	1.284842

Structure No: PC(101+117) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	2.721206	0.683592	0.173693
C	3.570647	1.770029	0.410306
C	4.886630	1.271865	0.410504
C	4.841350	-0.102109	0.176744
N	3.530473	-0.461026	0.033007
H	3.256072	2.792574	0.561776
H	5.791767	1.843461	0.563899
H	5.631902	-0.834243	0.103898
C	2.945335	-1.689275	-0.210936
C	1.584998	-1.777081	-0.312814
C	0.896574	-3.087941	-0.578802
C	1.324606	0.490951	0.051111
N	0.762297	-0.675025	-0.180409
H	3.614284	-2.535444	-0.310733
H	0.667368	1.353013	0.151205
C	-2.677962	1.031937	-0.118815
C	-4.320593	-0.732442	-0.688993
H	-5.080185	-0.946691	-1.452582
H	-3.504172	-1.449329	-0.839668
H	-2.934818	1.104060	0.951750
H	-1.897355	0.263147	-0.207616
H	0.195935	-3.320631	0.230540
H	1.611437	-3.910989	-0.667584
H	0.313928	-3.030516	-1.504699
N	-3.798211	0.610997	-0.968130
C	-4.921876	-0.928940	0.685156
C	-4.485380	-1.800362	1.599358
H	-5.772814	-0.287676	0.925510
H	-4.958975	-1.896833	2.572518
H	-3.636540	-2.451849	1.401213
C	-2.130215	2.347692	-0.600049

C	-1.987781	3.438934	0.159477
H	-1.846268	2.376866	-1.651996
H	-1.576909	4.362275	-0.239400
H	-2.275607	3.443422	1.208973
H	-4.546193	1.299662	-0.923897

Structure No: RC(54a+118+MeOH) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-4.837812	-2.042576	-0.227311
C	-3.822127	-2.880856	-0.664484
C	-2.651368	-2.101691	-0.746665
C	-2.973344	-0.799055	-0.357568
N	-4.335243	-0.784543	-0.039763
H	-5.880856	-2.246863	-0.035020
H	-3.928209	-3.931473	-0.893896
H	-1.665362	-2.423353	-1.053232
C	-5.062935	0.352179	0.403759
H	-4.455353	1.247078	0.484638
C	-6.344009	0.342147	0.692082
C	-7.617083	0.377271	0.989407
H	-7.972554	0.178565	1.999528
H	-8.371577	0.609769	0.239144
C	-2.055242	0.310312	-0.305307
O	-2.333468	1.471463	0.033297
N	1.291694	0.507329	-1.179612
O	-0.051249	3.108297	-0.148926
C	-0.332318	4.467578	-0.447024
H	0.624932	4.978529	-0.583668
H	-0.917959	4.575649	-1.371490
H	-0.874023	4.963068	0.371266
H	-0.892183	2.619319	-0.034088
C	2.826983	-1.394731	-0.928691
H	1.957007	-2.020270	-0.690678
H	2.970309	-1.445011	-2.018329
C	4.085547	-1.917015	-0.203629
H	4.278639	-2.953344	-0.510740
C	2.526015	0.062166	-0.515460
C	2.314600	0.107952	1.014131
H	1.442179	-0.506421	1.271414
H	2.083730	1.136829	1.320452
C	3.853257	-1.862495	1.321730
H	4.735208	-2.247953	1.851236
H	3.007407	-2.506599	1.597958

C	3.571581	-0.405961	1.748046
H	3.400439	-0.365351	2.831667
C	4.783704	0.476981	1.382202
H	4.604835	1.513025	1.699647
H	5.678637	0.128094	1.915362
C	5.297476	-1.033607	-0.568676
H	5.486623	-1.080550	-1.649919
H	6.201034	-1.408586	-0.069188
C	3.758587	0.935853	-0.868525
H	3.913273	0.918971	-1.957290
H	3.552594	1.978297	-0.590121
C	5.020655	0.423620	-0.142046
H	5.879168	1.055617	-0.405348
H	1.071332	1.472760	-0.920488
H	-1.021606	0.056241	-0.603211
H	1.421911	0.497943	-2.190768

Structure No: TS21-met (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-3.487151	-0.939583	-0.924569
C	-3.337642	-0.635495	-2.259441
C	-2.422273	0.449243	-2.339448
C	-2.020827	0.768972	-1.054478
N	-2.692145	-0.086033	-0.183380
H	-4.120589	-1.658140	-0.427296
H	-3.846158	-1.121569	-3.080147
H	-2.085310	0.947386	-3.239365
C	-2.664348	-0.033882	1.235518
H	-2.177753	0.855617	1.622673
C	-3.190704	-0.947163	2.019708
C	-3.717644	-1.818300	2.841990
H	-3.144419	-2.659373	3.229947
H	-4.752308	-1.737302	3.173116
C	-1.017041	1.817879	-0.684073
O	-1.088310	2.301119	0.580235
N	0.511142	1.384603	-0.968441
O	0.970374	3.493488	0.310893
C	1.859169	3.945744	1.298503
H	2.841961	4.183687	0.862414
H	1.485203	4.863173	1.779281
H	2.024010	3.201784	2.100234
H	-0.194117	2.999602	0.646761
C	0.636437	-1.133995	-1.223193

H	-0.426521	-1.273393	-1.009958
H	0.730245	-1.001772	-2.310246
C	1.429083	-2.381476	-0.770366
H	1.026714	-3.260438	-1.288861
C	1.179058	0.115414	-0.496723
C	1.034486	-0.059949	1.028392
H	-0.018687	-0.168199	1.297351
H	1.405915	0.833913	1.541746
C	1.270221	-2.557186	0.754635
H	1.807701	-3.455129	1.086813
H	0.212597	-2.702532	1.009586
C	1.824512	-1.310667	1.476187
H	1.706356	-1.428161	2.560354
C	3.318096	-1.137559	1.131997
H	3.729188	-0.264783	1.656040
H	3.887805	-2.012784	1.470483
C	2.921778	-2.209177	-1.116520
H	3.050049	-2.104799	-2.202524
H	3.484849	-3.101335	-0.813131
C	2.681383	0.281126	-0.842291
H	2.797295	0.427355	-1.926052
H	3.073607	1.179439	-0.349733
C	3.473733	-0.963997	-0.392877
H	4.531795	-0.822837	-0.646491
H	1.003424	2.273242	-0.478778
H	-1.092202	2.610386	-1.449256
H	0.647910	1.450428	-1.978935

Structure No: Product Complex of TS21-met (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-3.670085	-0.422365	-0.940883
C	-3.500807	0.008683	-2.235597
C	-2.427256	0.942809	-2.226582
C	-1.955091	1.049148	-0.932065
N	-2.736291	0.210550	-0.137335
H	-4.393950	-1.092463	-0.503278
H	-4.093938	-0.294596	-3.086953
H	-2.029794	1.479525	-3.078183
C	-2.663403	0.053815	1.269976
H	-2.054372	0.800401	1.764641
C	-3.289630	-0.883028	1.946733
C	-3.910932	-1.782966	2.665508
H	-3.450905	-2.740421	2.906928

H	-4.915581	-1.612400	3.050980
C	-0.756764	1.879662	-0.523254
O	-0.852378	2.254165	0.833896
N	0.605054	1.355125	-0.837201
O	1.554640	3.653308	0.506446
C	2.791115	3.866987	1.175754
H	3.614187	4.020716	0.464988
H	2.683568	4.771767	1.779097
H	3.048937	3.032644	1.843158
H	-0.127355	2.885829	1.013569
C	0.355248	-1.172380	-1.145695
H	-0.689554	-1.188743	-0.825839
H	0.351844	-1.025685	-2.234369
C	1.023341	-2.519528	-0.791876
H	0.462759	-3.331791	-1.272055
C	1.112602	0.002538	-0.471324
C	1.115353	-0.209468	1.058972
H	0.092517	-0.191046	1.443851
H	1.652061	0.617222	1.541373
C	1.003893	-2.709832	0.739222
H	1.455016	-3.675185	1.005651
H	-0.031657	-2.727036	1.102862
C	1.782561	-1.558664	1.409858
H	1.766058	-1.687640	2.499631
C	3.241225	-1.567148	0.908252
H	3.814555	-0.766802	1.395624
H	3.727462	-2.515381	1.173487
C	2.480812	-2.526277	-1.294291
H	2.504941	-2.411931	-2.386589
H	2.959011	-3.487328	-1.062599
C	2.581994	-0.031316	-0.967059
H	2.604582	0.129739	-2.055014
H	3.136465	0.797983	-0.508808
C	3.255189	-1.374516	-0.622063
H	4.291032	-1.360338	-0.985103
H	1.575330	2.826282	-0.031033
H	-0.809809	2.775957	-1.158491
H	0.740955	1.474291	-1.840037

Structure No: RC(54a+118) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	5.445628	1.108622	0.391954
C	4.945410	2.401993	0.402418

C	3.579952	2.319004	0.060958
C	3.271065	0.974513	-0.151890
N	4.441531	0.240471	0.058462
H	6.439882	0.739633	0.596467
H	5.510651	3.293965	0.631840
H	2.874410	3.134080	-0.027548
C	4.556424	-1.170490	-0.059510
H	3.624278	-1.656521	-0.327952
C	5.670212	-1.838991	0.132629
C	6.756712	-2.543984	0.314482
H	7.019707	-2.944606	1.292520
H	7.439667	-2.760757	-0.505777
C	1.975621	0.450298	-0.521765
H	1.196834	1.226946	-0.634758
O	1.685943	-0.733760	-0.710477
N	-1.221061	0.343688	-1.396843
H	-0.531708	-0.391071	-1.230302
H	-1.404638	0.358614	-2.398853
C	-3.449190	1.244640	-0.916643
H	-2.962960	2.191310	-0.649909
H	-3.680401	1.294203	-1.990950
C	-4.746090	1.048162	-0.103952
H	-5.430499	1.883194	-0.302943
C	-2.462875	0.085212	-0.656724
C	-2.142117	0.039947	0.853363
H	-1.645822	0.975797	1.140085
H	-1.432272	-0.775096	1.052265
C	-4.401869	1.006363	1.400408
H	-5.317881	0.885323	1.994471
H	-3.942907	1.955609	1.708137
C	-3.432664	-0.163371	1.674704
H	-3.181785	-0.191552	2.743138
C	-4.103854	-1.491859	1.265283
H	-3.430911	-2.334493	1.474492
H	-5.013607	-1.653668	1.859303
C	-5.416612	-0.280799	-0.512810
H	-5.685406	-0.255598	-1.577737
H	-6.350222	-0.420845	0.048867
C	-3.154865	-1.246634	-1.051673
H	-3.380184	-1.231908	-2.127842
H	-2.459779	-2.080371	-0.881005
C	-4.451111	-1.452994	-0.237964
H	-4.923948	-2.399020	-0.533132

Structure No: TS21 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-3.044940	-0.129569	1.598149
C	-2.561584	-1.228805	2.275216
C	-1.820904	-2.000878	1.339580
C	-1.854309	-1.347999	0.118338
N	-2.625427	-0.198867	0.285431
H	-3.681643	0.679879	1.921464
H	-2.741103	-1.460108	3.315895
H	-1.316553	-2.939619	1.527598
C	-2.980328	0.723520	-0.734191
H	-2.759994	0.351531	-1.731974
C	-3.530822	1.895050	-0.512183
C	-4.097058	3.063887	-0.346574
H	-3.509230	3.974709	-0.239394
H	-5.180269	3.174211	-0.309787
C	-1.211195	-1.793182	-1.156999
H	-1.112801	-2.891898	-1.106109
O	-1.683102	-1.302303	-2.340213
N	0.311768	-1.286601	-1.447696
H	-0.416070	-0.896104	-2.361615
H	0.810104	-2.112221	-1.788622
C	1.765078	-1.277579	0.603414
H	0.918635	-1.519879	1.253800
H	2.210500	-2.227535	0.273594
C	2.812289	-0.442717	1.374474
H	3.150028	-1.014037	2.248237
C	1.266950	-0.485058	-0.626424
C	0.637896	0.844908	-0.164547
H	-0.218676	0.653353	0.486148
H	0.269143	1.400690	-1.035838
C	2.169333	0.882636	1.835519
H	2.897672	1.473972	2.405824
H	1.323804	0.679618	2.505241
C	1.689796	1.677804	0.602387
H	1.224947	2.616776	0.927094
C	2.890734	1.982011	-0.315284
H	2.563945	2.567022	-1.185176
H	3.631558	2.590195	0.220134
C	4.012850	-0.140254	0.454290
H	4.491914	-1.076018	0.135644
H	4.770809	0.436159	1.000582
C	2.477088	-0.173404	-1.541994
H	2.924967	-1.114017	-1.894233

H	2.130643	0.371848	-2.429040
C	3.529409	0.655811	-0.776328
H	4.376412	0.861085	-1.442977

Structure No: Product Complex of TS21 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	3.289741	-0.598181	-1.467321
C	2.942042	-1.905332	-1.723029
C	2.009566	-2.296401	-0.719188
C	1.803172	-1.217527	0.117046
N	2.598660	-0.171639	-0.348783
H	3.956394	0.075406	-1.984077
H	3.308866	-2.508458	-2.541665
H	1.536128	-3.263161	-0.612444
C	2.709109	1.106438	0.251854
H	1.865961	1.355376	0.892357
C	3.696912	1.949395	0.047399
C	4.648464	2.827393	-0.141019
H	4.600999	3.558032	-0.947547
H	5.528582	2.860995	0.499513
C	0.971525	-1.172506	1.367363
H	0.438704	-2.130507	1.417900
O	1.761999	-1.174180	2.561618
N	0.068980	-0.011613	1.455076
H	2.382140	-0.431599	2.526905
H	-0.212208	0.026885	2.433888
C	-1.998565	-1.247566	0.632671
H	-1.421053	-2.072090	0.196774
H	-2.229811	-1.526221	1.670772
C	-3.303641	-1.061067	-0.173037
H	-3.877216	-1.996819	-0.151498
C	-1.159647	0.057762	0.621766
C	-0.834002	0.427774	-0.845553
H	-0.219421	-0.352536	-1.306454
H	-0.245462	1.353589	-0.858483
C	-2.950414	-0.700506	-1.631431
H	-3.867812	-0.585920	-2.224303
H	-2.371402	-1.512407	-2.091424
C	-2.137028	0.610594	-1.654935
H	-1.878845	0.864688	-2.690938
C	-2.977771	1.745879	-1.036466
H	-2.419007	2.690873	-1.069780
H	-3.897763	1.896856	-1.617025

C	-4.139372	0.075308	0.450685
H	-4.411123	-0.178871	1.484256
H	-5.078321	0.202632	-0.104389
C	-2.021316	1.193554	1.223882
H	-2.260047	0.953700	2.270684
H	-1.433404	2.120181	1.232505
C	-3.324562	1.385052	0.422763
H	-3.909625	2.195204	0.876776

Structure No: RC (54a+118) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	5.168173	0.785674	0.275001
C	6.119777	-0.213345	0.419803
C	5.448483	-1.442702	0.274485
C	4.097445	-1.170559	0.042760
N	3.944501	0.218354	0.047002
H	5.269263	1.860089	0.317843
H	7.172424	-0.058268	0.608415
H	5.877140	-2.434515	0.327101
C	3.070362	-2.164540	-0.165437
C	2.726040	0.928720	-0.148232
H	1.846509	0.311360	-0.304695
C	2.644666	2.239401	-0.143718
H	3.467419	-3.198718	-0.114806
O	1.874857	-1.974931	-0.380170
C	2.516557	3.540660	-0.147662
H	2.609095	4.119768	-1.065372
H	2.304169	4.095358	0.765226
N	-0.585287	-0.097101	-1.023396
H	-0.602576	0.008251	-2.036810
H	-0.108702	-0.976663	-0.827256
C	-3.955637	1.130490	1.324416
H	-4.959299	1.189439	1.767077
H	-3.361022	1.939869	1.769151
C	-4.038832	1.314416	-0.206166
H	-4.490218	2.288279	-0.436861
C	-3.313048	-0.235879	1.645613
H	-3.247639	-0.365188	2.733896
C	-4.177481	-1.363019	1.041332
H	-5.183506	-1.344724	1.482173
H	-3.741291	-2.342442	1.280600
C	-4.902181	0.186210	-0.810281
H	-4.986605	0.316593	-1.897829

H	-5.921361	0.232390	-0.402896
C	-4.264201	-1.181946	-0.488932
H	-4.873869	-1.985512	-0.922930
C	-2.841160	-1.231716	-1.085632
H	-2.374089	-2.205095	-0.880795
H	-2.883622	-1.121081	-2.178892
C	-2.617011	1.254814	-0.802493
H	-1.989172	2.056714	-0.394700
C	-1.894421	-0.286961	1.040253
H	-1.262438	0.501115	1.468369
H	-1.414867	-1.247364	1.275953
C	-1.954342	-0.104785	-0.492424
H	-2.658221	1.401427	-1.891947

Structure No: TS20 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	-4.317514	-1.289323	0.712601
C	-5.545478	-0.660591	0.487411
C	-5.255310	0.649618	0.081613
C	-3.856620	0.789174	0.054140
N	-3.301936	-0.430215	0.452145
H	-4.093415	-2.289733	1.053732
H	-6.520503	-1.109516	0.613909
H	-5.961998	1.428973	-0.174116
C	-3.152657	1.972986	-0.348617
C	-1.894486	-0.705288	0.615830
H	-1.436896	-0.115339	1.400472
C	-1.165080	-1.122710	-0.474752
H	-3.840756	2.804945	-0.600140
O	-1.931378	2.162716	-0.448476
C	-1.153588	-2.133669	-1.360003
H	-0.686773	-2.066682	-2.338134
H	-1.669840	-3.055599	-1.116774
N	0.071014	0.112293	-0.946977
H	0.106745	0.109092	-1.967417
H	-0.436504	0.966455	-0.667944
C	3.621204	-1.291286	1.089829
H	4.641500	-1.335132	1.492652
H	3.123143	-2.226978	1.375572
C	3.665291	-1.160611	-0.447520
H	4.192455	-2.021343	-0.877346
C	2.867203	-0.084366	1.686414
H	2.825553	-0.177162	2.778566

C	3.596024	1.220122	1.302071
H	4.615451	1.215959	1.709327
H	3.079741	2.084931	1.739215
C	4.394472	0.143256	-0.833554
H	4.451696	0.236555	-1.926492
H	5.426852	0.121311	-0.460870
C	3.642131	1.350237	-0.234860
H	4.149902	2.281765	-0.514429
C	2.199347	1.377470	-0.785889
H	1.652381	2.240248	-0.384023
H	2.215307	1.485455	-1.879579
C	2.222230	-1.131709	-0.997864
H	1.695109	-2.059093	-0.750694
C	1.425441	-0.055679	1.133725
H	0.890641	-0.969940	1.415587
H	0.873291	0.790775	1.562117
C	1.462998	0.071555	-0.403358
H	2.240751	-1.051346	-2.094857

Structure No: 119 (Product od TS 20) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	4.021228	-1.590846	-0.579086
C	5.323706	-1.078457	-0.535561
C	5.204528	0.301185	-0.319678
C	3.832951	0.601428	-0.227488
N	3.126506	-0.594708	-0.392030
H	3.667465	-2.600091	-0.735146
H	6.234052	-1.649519	-0.651704
H	6.007218	1.023294	-0.236897
C	3.280160	1.908736	-0.022071
C	1.685496	-0.694530	-0.394614
H	1.270190	-0.148583	-1.233739
C	1.071254	-0.502501	0.863933
H	4.064970	2.687502	0.053260
O	2.091905	2.261425	0.074927
C	1.359307	-0.972132	2.112210
H	0.920666	-0.545702	3.009111
H	2.113395	-1.737711	2.244594
N	-0.040002	0.536100	0.840112
H	-0.160328	0.844527	1.807555
H	0.397987	1.333189	0.337998
C	-3.423423	-1.566669	-0.935215
H	-4.439792	-1.784058	-1.288228

H	-2.813605	-2.455248	-1.141761
C	-3.440986	-1.275226	0.580040
H	-3.837349	-2.142879	1.120922
C	-2.852633	-0.345159	-1.685236
H	-2.825098	-0.550600	-2.761974
C	-3.734657	0.890321	-1.411708
H	-4.755983	0.713030	-1.772005
H	-3.349003	1.760661	-1.959071
C	-4.322016	-0.039168	0.858953
H	-4.357525	0.165645	1.937467
H	-5.353658	-0.230693	0.537410
C	-3.753570	1.180478	0.103621
H	-4.368088	2.065826	0.307072
C	-2.311851	1.452208	0.586347
H	-1.895956	2.327965	0.070364
H	-2.316405	1.677204	1.662711
C	-2.000058	-1.003423	1.067664
H	-1.357461	-1.873446	0.900416
C	-1.409970	-0.076546	-1.199975
H	-0.772189	-0.942612	-1.400638
H	-0.983761	0.780142	-1.738442
C	-1.434794	0.211945	0.312202
H	-1.998547	-0.808861	2.148717

Structure No: 119 (Reactant od TS22) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	4.021234	-1.590505	-0.579510
C	5.323660	-1.078020	-0.535619
C	5.204333	0.301546	-0.319408
C	3.832720	0.601663	-0.227345
N	3.126395	-0.594505	-0.392365
H	3.667578	-2.599737	-0.735893
H	6.234071	-1.648976	-0.651778
H	6.006961	1.023693	-0.236328
C	3.279789	1.908822	-0.021416
C	1.685433	-0.694472	-0.395027
H	1.270062	-0.148183	-1.233908
C	1.071156	-0.503097	0.863591
H	4.064482	2.687670	0.054136
O	2.091482	2.261383	0.075658
C	1.359018	-0.973537	2.111595
H	0.920296	-0.547621	3.008697
H	2.112893	-1.739393	2.243538

N	-0.039868	0.535658	0.840217
H	-0.160108	0.843820	1.807739
H	0.398118	1.332900	0.338327
C	-3.423586	-1.566653	-0.934843
H	-4.440002	-1.783874	-1.287805
H	-2.813959	-2.455417	-1.141176
C	-3.441153	-1.274823	0.580345
H	-3.837787	-2.142208	1.121458
C	-2.852459	-0.345473	-1.685127
H	-2.824865	-0.551237	-2.761805
C	-3.734181	0.890345	-1.412027
H	-4.755546	0.713295	-1.772327
H	-3.348197	1.760402	-1.959600
C	-4.321881	-0.038435	0.858826
H	-4.357465	0.166723	1.937272
H	-5.353534	-0.229823	0.537233
C	-3.753104	1.180887	0.103221
H	-4.367439	2.066417	0.306461
C	-2.311357	1.452382	0.586003
H	-1.895189	2.327860	0.069779
H	-2.315963	1.677701	1.662288
C	-2.000204	-1.003248	1.067979
H	-1.357760	-1.873426	0.900909
C	-1.409778	-0.077086	-1.199804
H	-0.772108	-0.943302	-1.400206
H	-0.983344	0.779349	-1.738486
C	-1.434640	0.211821	0.312272
H	-1.998739	-0.808480	2.149005

Structure No: TS22 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	4.540002	-1.592991	-0.101918
C	5.638011	-0.787824	0.125591
C	5.162043	0.557685	0.210823
C	3.795105	0.537318	0.012767
N	3.421585	-0.793500	-0.180072
H	4.453570	-2.664870	-0.204882
H	6.660285	-1.122663	0.232298
H	5.758506	1.443532	0.384552
C	2.779044	1.634925	0.045682
C	2.067256	-1.127333	-0.430413
H	1.836954	-1.567610	-1.397324
C	1.152002	-0.377182	0.274975

H	2.966020	2.390843	0.825620
O	2.056688	1.931482	-0.951528
C	1.427830	0.424348	1.399808
H	0.712632	1.154947	1.748977
H	2.131368	0.051327	2.134210
N	0.027672	0.101023	-0.590679
H	0.363999	1.072886	-0.817251
H	0.142836	-0.389889	-1.482593
C	-3.707981	-0.633438	1.545852
H	-4.782297	-0.720421	1.752107
H	-3.180850	-0.947615	2.455818
C	-3.352093	0.828789	1.202764
H	-3.609337	1.480520	2.046111
C	-3.323290	-1.548038	0.363871
H	-3.567165	-2.589546	0.604508
C	-4.095658	-1.107831	-0.898191
H	-5.175615	-1.203095	-0.729176
H	-3.846818	-1.762847	-1.743762
C	-4.126673	1.270890	-0.054658
H	-3.896768	2.317213	-0.294743
H	-5.207145	1.214684	0.128541
C	-3.743688	0.356472	-1.236001
H	-4.278810	0.669531	-2.140435
C	-2.225517	0.468968	-1.490973
H	-1.944445	-0.162416	-2.346203
H	-1.956137	1.502251	-1.746669
C	-1.829180	0.932397	0.951343
H	-1.289514	0.621482	1.848883
C	-1.803487	-1.440544	0.103399
H	-1.232348	-1.765390	0.980298
H	-1.516452	-2.096982	-0.729866
C	-1.453083	0.020021	-0.230434
H	-1.544621	1.969812	0.732739

Structure No: 120 (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	4.149306	-1.867759	-0.167840
C	5.284895	-1.378013	0.449567
C	5.029310	-0.020210	0.796201
C	3.742996	0.280144	0.385686
N	3.213837	-0.856693	-0.204451
H	3.921890	-2.846190	-0.565595
H	6.192628	-1.935111	0.634382

H	5.709728	0.666046	1.281554
C	2.922085	1.532134	0.371711
C	1.905774	-0.914677	-0.728392
H	1.696208	-1.768339	-1.363659
C	1.014975	0.068842	-0.478238
H	3.191218	2.160584	1.224372
O	3.203261	2.363350	-0.772007
C	1.416510	1.195775	0.457439
H	0.852449	2.099191	0.219077
H	1.188028	0.919004	1.496822
N	-0.214797	0.138844	-1.171740
H	3.178250	1.812851	-1.567105
H	-0.201477	-0.512480	-1.952531
C	-3.344554	-0.187775	1.856777
H	-4.341832	-0.271457	2.308529
H	-2.620531	-0.163009	2.682301
C	-3.246676	1.109442	1.026014
H	-3.431066	1.976321	1.673208
C	-3.071721	-1.403494	0.946318
H	-3.136920	-2.328435	1.533713
C	-4.113474	-1.435686	-0.191900
H	-5.123866	-1.541316	0.224583
H	-3.940784	-2.308007	-0.836722
C	-4.291788	1.076962	-0.106128
H	-4.247853	2.006563	-0.689064
H	-5.303755	1.010065	0.314773
C	-4.014874	-0.135966	-1.018395
H	-4.745839	-0.160572	-1.836544
C	-2.597169	-0.008954	-1.610997
H	-2.397245	-0.858766	-2.280651
H	-2.507839	0.904099	-2.212602
C	-1.827605	1.228427	0.426754
H	-1.101475	1.274100	1.244600
C	-1.655671	-1.281646	0.341607
H	-0.897836	-1.286782	1.135429
H	-1.444631	-2.146450	-0.303348
C	-1.532228	0.019401	-0.490070
H	-1.727353	2.154554	-0.152821

Structure No: RC(120+MeOH) (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-4.521433	-1.877300	0.646033
C	-5.594800	-1.036818	0.402364

C	-5.076008	0.155244	-0.174000
C	-3.699201	0.005542	-0.262707
N	-3.373892	-1.238444	0.241407
H	-4.482810	-2.877015	1.053847
H	-6.631878	-1.261278	0.607999
H	-5.639224	1.022044	-0.493559
C	-2.593902	0.915439	-0.670877
C	-2.051510	-1.733915	0.266694
H	-1.911967	-2.652708	0.824405
C	-1.062987	-1.114164	-0.414601
H	-2.947219	1.612895	-1.439088
O	-2.123081	1.710270	0.463185
C	-1.378561	0.143383	-1.200398
H	-1.566950	-0.148373	-2.243427
N	0.195348	-1.714523	-0.573252
H	-2.869169	1.853696	1.061052
H	0.183747	-2.654720	-0.192052
C	3.323185	1.255355	0.080003
H	4.303188	1.696638	0.307624
H	2.634207	2.079658	-0.139577
C	2.809498	0.458541	1.298245
H	2.727384	1.126143	2.165237
C	3.440152	0.314993	-1.138779
H	3.803470	0.879220	-2.007294
C	4.417799	-0.833128	-0.819151
H	5.415886	-0.431555	-0.598982
H	4.522878	-1.495299	-1.689338
C	3.785898	-0.691438	1.616173
H	3.438277	-1.253378	2.494027
H	4.777255	-0.290083	1.865561
C	3.889798	-1.627415	0.393101
H	4.569414	-2.459828	0.617296
C	2.493512	-2.194370	0.063860
H	2.550267	-2.874409	-0.797145
H	2.120248	-2.777463	0.918824
C	1.414108	-0.121754	0.978958
H	0.710217	0.696091	0.796557
C	2.048596	-0.269412	-1.467509
H	1.372701	0.546078	-1.741295
H	2.102736	-0.947006	-2.329280
C	1.494798	-1.054983	-0.252635
H	1.030301	-0.689989	1.837464
C	0.030409	4.721416	0.303740
H	-0.808405	5.210962	-0.212910
H	-0.090386	4.870217	1.387039

H	0.956309	5.213260	-0.006947
O	0.144069	3.348972	-0.038839
H	-0.529490	0.828080	-1.221239
H	-0.675187	2.883651	0.212266

Structure No: TS23 (B3LYP/6-31+G(d,p))

	X	Y	Z
C	4.417456	-1.793739	-0.915620
C	5.528160	-1.273128	-0.220799
C	5.051075	-0.377739	0.730097
C	3.639672	-0.344906	0.610441
N	3.290007	-1.240110	-0.419228
H	4.374761	-2.530956	-1.704691
H	6.558772	-1.535471	-0.413941
H	5.624866	0.227386	1.417482
C	2.638309	0.376502	1.244118
C	1.959143	-1.542614	-0.735033
H	1.821134	-2.339116	-1.456051
C	0.931523	-0.941898	-0.063286
H	2.872345	0.924288	2.143206
O	2.983269	2.596044	0.707472
C	1.225060	0.191855	0.868739
H	0.594739	0.179844	1.759319
N	-0.354525	-1.423635	-0.225734
H	3.675587	2.654284	0.035477
H	-0.394753	-2.171427	-0.907002
C	-3.580928	1.347547	0.774121
H	-4.593356	1.759897	0.877972
H	-2.886270	2.092470	1.182001
C	-3.263327	1.090213	-0.713889
H	-3.337984	2.030754	-1.273442
C	-3.467553	0.023832	1.560731
H	-3.684725	0.203639	2.621265
C	-4.466851	-1.002494	0.992668
H	-5.493710	-0.628004	1.094863
H	-4.409571	-1.942089	1.558775
C	-4.262126	0.062905	-1.283385
H	-4.059181	-0.113070	-2.348529
H	-5.287339	0.449751	-1.212926
C	-4.142022	-1.256953	-0.493271
H	-4.835161	-2.002382	-0.903670
C	-2.702837	-1.795370	-0.611769
H	-2.605244	-2.743109	-0.064879

H	-2.470164	-1.998393	-1.667652
C	-1.821522	0.547983	-0.844313
H	-1.112213	1.294548	-0.474166
C	-2.027586	-0.522860	1.435480
H	-1.341344	0.206758	1.873844
H	-1.916321	-1.459906	1.996006
C	-1.678330	-0.775026	-0.053172
H	-1.580071	0.361195	-1.899530
C	0.790167	2.987097	-1.614931
H	1.029619	4.044065	-1.818393
H	1.528760	2.372406	-2.163891
H	-0.195944	2.786792	-2.059039
O	0.783484	2.723077	-0.234745
H	0.918935	1.185040	0.332501
H	1.916542	2.776813	0.206458

Structure No: PC (102a+MeOH+H_2O) (B3LYP/6-31+G(d,p))

	X	Y	Z
C	3.752819	-1.234253	-1.470686
C	4.897430	-0.890337	-0.765758
C	4.557238	-0.750043	0.601101
C	3.187324	-1.025946	0.717612
N	2.709775	-1.314934	-0.573995
H	3.594170	-1.417763	-2.522762
H	5.879331	-0.761569	-1.200776
H	5.224664	-0.533634	1.423600
C	2.259181	-1.082380	1.788944
C	1.372303	-1.569965	-0.814810
H	1.098104	-1.729472	-1.851071
C	0.470051	-1.612424	0.217598
H	2.619894	-0.899242	2.795848
O	0.645270	2.760415	0.786089
C	0.942770	-1.378344	1.553812
H	0.238692	-1.460579	2.372579
N	-0.892213	-1.955887	0.000298
H	0.629776	3.341582	1.555609
H	-0.973929	-2.518810	-0.842857
C	-2.890493	1.924090	0.026462
H	-3.689204	2.677457	-0.014022
H	-1.942699	2.452911	0.180397
C	-2.841781	1.136073	-1.299104
H	-2.653653	1.826082	-2.131865

C	-3.147187	0.946107	1.192577
H	-3.177328	1.501794	2.138735
C	-4.489391	0.218370	0.974800
H	-5.312830	0.944653	0.945502
H	-4.692680	-0.463761	1.811673
C	-4.180921	0.402769	-1.520115
H	-4.160157	-0.147409	-2.471234
H	-5.002408	1.128425	-1.588739
C	-4.433011	-0.571113	-0.349759
H	-5.381194	-1.101859	-0.506185
C	-3.284565	-1.598882	-0.276210
H	-3.450830	-2.310256	0.542338
H	-3.245621	-2.183234	-1.208017
C	-1.695434	0.102862	-1.226948
H	-0.738072	0.617663	-1.086861
C	-1.998062	-0.085409	1.259155
H	-1.052519	0.441111	1.425943
H	-2.154425	-0.778176	2.096706
C	-1.932152	-0.886603	-0.058135
H	-1.635708	-0.459360	-2.171320
C	3.978447	2.992686	-0.853597
H	3.565201	4.002852	-0.895843
H	5.070008	3.061275	-0.767283
H	3.721578	2.465616	-1.780511
O	3.406377	2.357170	0.290162
H	3.744810	1.447422	0.359058
H	1.593537	2.587801	0.615601

Structure No: 102a (B3LYP/6-31+G(d,p))

	X	**Y**	**Z**
C	-4.369101	-1.501379	0.096505
C	-5.452674	-0.788498	0.594741
C	-5.096873	0.574914	0.668468
C	-3.781452	0.686781	0.208974
N	-3.348665	-0.610370	-0.139736
H	-4.242458	-2.555277	-0.101629
H	-6.403586	-1.221619	0.874080
H	-5.713560	1.395037	1.007528
C	-2.870076	1.754128	0.010306
C	-2.071330	-0.847626	-0.611908
H	-1.828298	-1.882552	-0.824528
C	-1.191027	0.186131	-0.810060

H	-3.198737	2.762319	0.241776
C	-1.616502	1.522532	-0.495123
H	-0.943980	2.345721	-0.702248
N	0.080572	-0.034655	-1.411754
H	0.054513	-0.888859	-1.962363
C	2.892474	0.234755	1.918932
H	3.837847	0.230097	2.477625
H	2.095547	0.463060	2.639176
C	2.647958	-1.147323	1.278421
H	2.610961	-1.916917	2.060306
C	2.933833	1.312031	0.814883
H	3.098014	2.297904	1.268394
C	4.078520	0.996677	-0.169489
H	5.042418	1.002261	0.356639
H	4.132748	1.770342	-0.947013
C	3.789772	-1.464446	0.289472
H	3.636467	-2.455575	-0.158850
H	4.750443	-1.499501	0.820348
C	3.831809	-0.384176	-0.811733
H	4.636371	-0.611434	-1.522799
C	2.485180	-0.358657	-1.563155
H	2.498568	0.396191	-2.359020
H	2.308123	-1.332082	-2.044582
C	1.303544	-1.126831	0.518376
H	0.476565	-0.928382	1.211306
C	1.586764	1.327879	0.059405
H	0.780134	1.572433	0.759690
H	1.592567	2.101495	-0.719036
C	1.322891	-0.046671	-0.593624
H	1.113724	-2.110817	0.065296

The following tables and cartesian coordinates are related to Chapter 3.

1. Absolute Energies of the Structures

Energies are given in terms of ZPE-corrected total energy (E_{el}+ZPE), enthalpy (E_{el}+H) and Gibbs free-energy (E_{el}+G) as extracted from Gaussian output of each structure.

Table S16. Absolute energies of optimized structures in gas phase **(**M06-2X/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
150	-3145.488235	-3145.476179	-3145.527181	–
151	-3145.484007	-3145.472113	-3145.522511	–
152	-3145.482840	-3145.470596	-3145.520904	–
153	-3145.472026	-3145.459898	-3145.509863	–
155	-3145.452427	-3145.440505	-3145.491053	–
154	-3145.452709	-3145.441403	-3145.490359	-89.02
142	-5717.639869	-5717.626814	-5717.679815	–
141	-5717.635703	-5717.622680	-5717.675564	–
140	-5717.633438	-5717.620021	-5717.674888	–
134	-5717.620399	-5717.607044	-5717.660154	–
143	-5717.618702	-5717.605332	-5717.658496	–
135	-5717.609557	-5717.596166	-5717.650932	–
122	-271.242809	-271.237024	-271.270916	–
133	-573.979907	-573.969656	-574.014882	–

[a]E_{el} = Total electronic energy
[b]ZPE = Zero-point energy correction
[c]H = Enthalpy correction
[d]G = Gibbs free energy correction

Table S17. Absolute energies of optimized structures in DCM **(**CPCM/M06-2X/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
152	-3145.551940	-3145.539744	-3145.589917	–
TS24	-3145.551927	-3145.540272	-3145.589214	-176.2
156	-3145.571880	-3145.559680	-3145.609806	–
150	-3145.565399	-3145.553479	-3145.603813	–
TS25	-3145.560954	-3145.549302	-3145.599162	-280.5
157	-3145.567762	-3145.555564	-3145.606674	–

Table S18. Absolute energies of optimized structures in gas phase **(**B3LYP/6-31+G(d,p))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (i)
RC1(133+162)	-1529.689795	-1529.668461	-1529.745016	-5.8
TS26	-1529.665857	-1529.644818	-1529.718719	-402.3
PC(148+163)	-1529.781100	-1529.760982	-1529.831992	-0.9
148	-649.426286	-649.415494	-649.461973	–
RC2(133+162)	-1529.689580	-1529.667428	-1529.746242	–
TS27	-1529.663958	-1529.642985	-1529.716329	-423.2
PC(149+163)	-1529.775957	-1529.754899	-1529.829447	–
149	-649.420964	-649.410138	-649.456671	–
RC4(133+162)	-1529.688512	-1529.666192	-1529.748053	–
TS29	-1529.658231	-1529.637294	-1529.710591	-481.0
PC(160+163)	-1529.764214	-1529.742987	-1529.818263	–
160	-649.410818	-649.399860	-649.446717	–
RC3(133+162)	-1529.688145	-1529.665865	-1529.746740	–
TS28	-1529.657761	-1529.636832	-1529.709934	-483.4
PC(159+163)	-1529.759022	-1529.737562	-1529.815260	–
159	-649.410227	-649.399259	-649.446175	–
RC5(133+162)	-1529.688145	-1529.665866	-1529.746730	–
TS30	-1529.651791	-1529.630660	-1529.704226	-464.2
PC(161+163)	-1529.758319	-1529.737089	-1529.811768	–
161	-649.407829	-649.396979	-649.443194	–
RC6(133+162)	-1529.688476	-1529.666199	-1529.746899	–
TS31	-1529.657692	-1529.636545	-1529.710405	-442.9
PC(158+163)	-1529.764710	-1529.743545	-1529.817804	–
158	-649.414256	-649.403464	-649.449542	–

Table S19. Single point energies in DCM (CPCM/B3LYP/6-31+G(d,p)//B3LYP/6 31+G(d,p))

Compound No	Eel[a] (au)	Eel+G[b] (au)
RC1(133+162)	-1529.973342	-1529.758471
TS26	-1529.952763	-1529.736204
PC(148+163)	-1530.068388	-1529.845774
RC2(133+162)	-1529.973151	-1529.759553
TS27	-1529.951027	-1529.734142
PC(149+163)	-1530.063282	-1529.843576
RC4(133+162)	-1529.972327	-1529.761759
TS29	-1529.942238	-1529.725948
PC(160+163)	-1530.049582	-1529.830840
RC3(133+162)	-1529.972462	-1529.760922
TS28	-1529.942123	-1529.725681
PC(159+163)	-1530.047810	-1529.831634
RC5(133+162)	-1529.972462	-1529.760912
TS30	-1529.934621	-1529.718739
PC(161+163)	-1530.043287	-1529.824755
RC6(133+162)	-1529.972211	-1529.760498
TS31	-1529.940173	-1529.724331
PC(158+163)	-1530.049466	-1529.830213

[a]Eel = Total electronic energy

[b]G = Gibbs free energy correction extracted from the corresponding gas phase frequency calculation and added to single point energy E_{el}.

2. Cartesian Coordinates for the Optimized Structures Given in Paths

Structure No: 122 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	1.238264	0.668476	-0.520540
C	-0.001123	1.119818	0.274234
C	0.001123	-1.119818	0.274234
C	1.240144	-0.666246	-0.519678
C	0.000000	0.000000	1.351148
H	-0.901402	-0.000918	1.969606
H	0.901401	0.000918	1.969607
C	-1.240144	0.666246	-0.519679
C	-1.238263	-0.668476	-0.520541
H	-0.001991	2.155089	0.615394
H	0.001990	-2.155089	0.615393
H	-1.930670	1.333855	-1.020510
H	-1.927097	-1.337340	-1.022027
H	1.930670	-1.333855	-1.020509
H	1.927098	1.337340	-1.022026

Structure No: 133 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.176216	-0.040944	0.672262
C	0.292947	-1.492542	1.130148
C	0.292947	-1.492542	-1.130148
C	0.176216	-0.040944	-0.672262
C	1.242134	-1.994730	0.000000
H	1.361925	-3.080244	0.000000
H	2.214512	-1.494170	0.000000
C	-0.997800	-2.196062	0.667195
H	-1.764971	-2.561638	1.338015
C	-0.997800	-2.196062	-0.667195
H	-1.764971	-2.561638	-1.338015
H	0.586505	-1.639509	2.168194
H	0.586505	-1.639509	-2.168194
C	0.006631	1.191382	-1.463050
C	0.006631	1.191382	1.463050
O	-0.026025	1.201608	-2.680027

O	-0.026025	1.201608	2.680027
C	-0.127846	2.453902	-0.669705
H	-0.228835	3.365263	-1.252101
C	-0.127846	2.453902	0.669705
H	-0.228835	3.365263	1.252101

Structure No: 150 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	1.110022	0.665261	0.371386
C	1.113848	-0.677260	0.335003
C	2.301520	-1.460104	-0.097582
C	3.512352	-0.646318	-0.411001
C	3.501741	0.695907	-0.392438
C	2.270911	1.477300	-0.077478
H	4.402381	-1.213434	-0.666517
H	4.380518	1.284110	-0.639060
O	2.261495	-2.666745	-0.196411
O	2.190957	2.680749	-0.193119
C	-1.020556	-0.720399	-0.548598
C	-0.291326	-1.163084	0.715909
C	-0.298701	1.123484	0.771984
C	-1.022667	0.739904	-0.513612
C	-0.658000	-0.045162	1.725672
H	0.004171	-0.064380	2.590777
H	-1.693578	-0.057461	2.065819
H	-0.392829	-2.210100	0.992738
H	-0.406667	2.154956	1.099819
Br	-2.941988	-0.000166	-0.306677
H	-1.031442	1.364499	-1.402544
H	-1.027466	-1.301567	-1.466587

Structure No: 151 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.634979	0.669429	0.822454
C	0.635101	-0.669526	0.822613
C	1.634586	-1.459931	0.060005
C	2.759807	-0.671222	-0.520448
C	2.759689	0.671215	-0.520568
C	1.634077	1.459774	0.059305
H	3.557454	-1.250463	-0.976225
H	3.557286	1.250526	-0.976346

O	1.492584	-2.651155	-0.115385
O	1.492928	2.651310	-0.114643
C	-1.820123	-0.730753	0.476962
C	-0.670079	-1.147325	1.414504
C	-0.670106	1.147163	1.414606
C	-1.820155	0.730679	0.477049
C	-0.904497	-0.000138	2.458917
H	-0.155144	-0.000167	3.251990
H	-1.905809	-0.000175	2.900831
H	-0.717949	-2.186535	1.733331
H	-0.717972	2.186351	1.733509
H	-2.715834	1.331635	0.344369
H	-2.715788	-1.331710	0.344201
Br	-1.346000	0.000089	-1.380223

Structure No: 152 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.205978	-0.024443	0.726707
C	0.205290	-0.055275	-0.730428
C	-0.835753	-0.883147	-1.471260
C	-1.919015	-1.475877	-0.642580
C	-1.915611	-1.452050	0.700197
C	-0.826818	-0.831874	1.501197
H	-2.704410	-1.977061	-1.200973
H	-2.697883	-1.933562	1.280014
O	-0.705820	-1.072942	-2.652341
O	-0.686001	-0.986377	2.686135
C	2.106748	-1.340851	-0.649847
C	1.660327	0.055060	-1.146381
C	1.664028	0.099269	1.133120
C	2.110122	-1.313900	0.690505
C	2.263627	0.932097	-0.024064
H	1.961698	1.979697	-0.043912
H	3.351621	0.869230	-0.025010
H	1.844933	0.290812	-2.191516
H	1.851731	0.376413	2.167599
H	2.333223	-2.118586	1.380849
H	2.325759	-2.172135	-1.309175
Br	-0.727018	1.683020	-0.024321

Structure No: 153 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.056060	-0.729364	-0.265245
C	-0.056135	0.729779	-0.263854
C	1.253976	1.488725	-0.453600
C	2.496952	0.671915	-0.473393
C	2.497051	-0.670627	-0.474600
C	1.254170	-1.487628	-0.456831
H	3.419660	1.242864	-0.525375
H	3.419846	-1.241350	-0.527505
O	1.226585	2.677108	-0.635095
O	1.227177	-2.675961	-0.638713
C	-2.557523	0.667584	-0.145257
C	-1.363346	1.144108	-0.956946
C	-1.363260	-1.142492	-0.959087
C	-2.557449	-0.667577	-0.146476
C	-1.303631	0.001819	-2.030480
H	-0.393648	0.002437	-2.642592
H	-2.179208	0.002417	-2.680905
H	-1.353054	2.181770	-1.285736
H	-1.352901	-2.179524	-1.289854
H	-3.230784	-1.335039	0.377580
H	-3.230939	1.334021	0.379999
Br	-0.119930	-0.001549	1.661127

Structure No: 154 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.917433	-0.677812	-0.000383
C	2.268285	-1.131510	0.532932
C	2.268401	1.131839	0.532213
C	0.917476	0.677981	-0.000726
C	2.471902	0.000480	1.585995
H	3.477998	0.000564	2.006396
H	1.721213	0.000765	2.381905
C	3.306853	-0.666271	-0.511311
H	3.887045	-1.343218	-1.125100
C	3.306778	0.665787	-0.511883
H	3.886946	1.342256	-1.126220
H	2.324173	-2.170120	0.853100
H	2.324433	2.170644	0.851719
C	-0.151565	1.497540	-0.571327
C	-0.151288	-1.497504	-0.571391
O	-0.125363	2.686484	-0.761341

O	-0.124850	-2.686439	-0.761420
C	-1.414067	0.730435	-0.996611
C	-1.414030	-0.730684	-0.996441
Br	-2.438582	-0.000072	0.589859
H	-2.113460	1.280449	-1.625711
H	-2.113358	-1.280857	-1.625473

Structure No: 155 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.975582	0.677748	-0.447086
C	2.352080	1.131775	0.017011
C	2.352015	-1.131830	0.017067
C	0.975566	-0.677768	-0.447118
C	3.189673	-0.000068	-0.652330
H	4.229202	-0.000088	-0.323102
H	3.129101	-0.000092	-1.744220
C	2.458023	0.666804	1.485174
H	2.499247	1.341392	2.330890
C	2.457894	-0.666776	1.485215
H	2.499014	-1.341317	2.330973
H	2.600823	2.169925	-0.193812
H	2.600714	-2.170005	-0.193684
C	-0.189354	-1.504277	-0.760839
C	-0.189319	1.504292	-0.760790
O	-0.216333	-2.703498	-0.868683
O	-0.216247	2.703507	-0.868705
C	-1.499101	-0.730186	-0.979806
C	-1.499083	0.730236	-0.979778
Br	-2.222894	0.000010	0.765195
H	-2.300034	-1.278241	-1.475052
H	-2.300002	1.278322	-1.475010

Structure No: 142 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.540334	0.921511	-0.535055
C	-0.716723	-0.374519	0.216852
C	-1.154579	-0.115311	1.649055
C	-2.150852	0.988519	1.804304
C	-2.351488	1.925069	0.863650
C	-1.574651	1.973276	-0.415119
H	-2.679087	1.009643	2.753375

H	-3.068617	2.728850	1.004615
O	-0.737792	-0.748693	2.591728
O	-1.728991	2.866250	-1.222650
C	1.531445	0.178037	0.472538
C	0.666925	-0.981150	-0.053831
C	0.439402	0.676107	-1.650333
C	0.943519	1.285642	-0.373930
C	0.788579	-0.811483	-1.585555
H	0.085788	-1.438904	-2.134288
H	1.803180	-1.012159	-1.934874
H	0.854055	-1.962878	0.376564
H	0.381187	1.252512	-2.564814
H	1.428371	0.333706	1.545312
Br	3.434978	-0.076863	0.189890
Br	-2.166552	-1.470792	-0.534361
H	1.246999	2.322494	-0.297510

Structure No: 141 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.450173	0.990953	0.573890
C	0.504258	-0.401410	0.000707
C	0.112818	-0.484904	-1.469625
C	0.371884	0.757550	-2.259072
C	0.764419	1.921983	-1.718267
C	0.898308	2.137812	-0.245649
H	0.238942	0.646470	-3.331643
H	0.976050	2.791252	-2.334874
O	-0.277896	-1.503400	-1.989018
O	1.246568	3.205054	0.217599
C	-1.551152	-0.228985	1.227474
C	-0.298292	-1.116705	1.100084
C	0.430673	0.861003	2.075507
C	-0.859970	1.108385	1.352821
C	0.450471	-0.642209	2.376856
H	1.453376	-1.058309	2.464018
H	-0.114443	-0.881850	3.282259
H	-0.454934	-2.185242	0.964063
H	0.891239	1.616080	2.700100
Br	2.377300	-1.031540	-0.061862
H	-1.390902	2.051776	1.384689
H	-2.144669	-0.491002	2.103639
Br	-2.801459	-0.269124	-0.256687

Structure No: 140 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	1.400508	-0.213603	0.889796
C	0.936162	-1.325542	0.293893
C	1.718626	-2.060683	-0.720450
C	3.131971	-1.610937	-0.895878
C	3.610450	-0.525522	-0.272481
C	2.772148	0.290749	0.658609
H	3.733699	-2.202493	-1.579637
H	4.630720	-0.178801	-0.407977
O	1.240189	-2.956897	-1.389602
O	3.206574	1.286479	1.202709
C	-1.202319	-0.344299	-0.197092
C	-0.530698	-1.465145	0.633231
C	0.242540	0.433015	1.614383
C	-0.710672	0.947709	0.501300
C	-0.543724	-0.830847	2.043783
H	-0.004182	-1.427502	2.782119
H	-1.553491	-0.612155	2.402663
H	-0.968267	-2.452004	0.491679
H	0.492171	1.182696	2.364095
H	-1.531919	1.521981	0.925049
H	-0.949794	-0.388167	-1.254112
Br	-3.140035	-0.477463	-0.139636
Br	0.157950	2.138904	-0.761030

Structure No: 134 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.787803	0.283415	-0.126995
C	0.787953	0.283134	-0.126946
C	1.414946	0.980170	1.079174
C	0.669267	0.896999	2.364270
C	-0.669075	0.897196	2.364217
C	-1.414609	0.980701	1.079060
H	1.257250	0.963665	3.274805
H	-1.257110	0.964004	3.274709
O	2.469896	1.564629	0.990064
O	-2.469554	1.565176	0.989990
C	0.669691	2.397005	-1.340233
C	1.126304	0.951935	-1.486824
C	-1.125828	0.952356	-1.486886

C	-0.668681	2.397243	-1.340179
C	0.000161	0.381152	-2.370383
H	-0.000039	-0.711320	-2.428977
H	0.000274	0.815589	-3.371509
H	2.160727	0.793063	-1.785512
H	-2.160291	0.793879	-1.785636
H	-1.334074	3.232280	-1.157296
H	1.335396	3.231804	-1.157401
Br	1.634216	-1.479286	-0.033567
Br	-1.634754	-1.478693	-0.033669

Structure No: 143 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.787787	0.216786	0.325419
C	0.788011	0.217139	0.324902
C	1.398394	1.577929	-0.034885
C	0.667657	2.399934	-1.037031
C	-0.669394	2.399514	-1.036618
C	-1.398901	1.577384	-0.033703
H	1.260938	3.073860	-1.647453
H	-1.263498	3.073001	-1.646727
O	2.427579	1.963564	0.469097
O	-2.429012	1.961656	0.469428
C	0.669151	-1.651138	1.934064
C	1.128814	-0.211318	1.775703
C	-1.127449	-0.212021	1.776379
C	-0.666764	-1.651562	1.934392
C	0.000674	0.529847	2.524638
H	0.000284	1.615489	2.369365
H	0.001062	0.312984	3.594015
H	2.161026	0.020937	2.032766
H	-2.159647	0.019570	2.034092
H	-1.326300	-2.510524	1.940628
H	1.329238	-2.509679	1.939952
Br	-1.661164	-0.938126	-0.983056
Br	1.660990	-0.937656	-0.983926

Structure No: 135 (M06-2X/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	1.003038	-0.732351	-0.543258
C	1.115494	-0.281836	0.721623

C	0.037205	0.425788	1.430540
C	-1.111098	0.882277	0.530585
C	-1.435057	-0.097998	-0.580690
C	-0.201703	-0.546217	-1.366374
H	-1.982349	1.125521	1.136496
O	0.047948	0.675103	2.614493
O	-0.249181	-0.745795	-2.558792
C	3.459134	0.279829	0.317769
C	2.533122	-0.589881	1.190474
C	2.350510	-1.329026	-0.935821
C	3.351571	-0.157553	-0.938041
C	2.718031	-1.946581	0.445901
H	2.014782	-2.716972	0.775103
H	3.745857	-2.313135	0.484932
H	2.691508	-0.553026	2.266906
H	2.342600	-1.970159	-1.815507
H	3.812561	0.244766	-1.831145
H	4.026652	1.124831	0.686580
H	-2.185774	0.290615	-1.266868
Br	-2.204145	-1.695450	0.236970
Br	-0.532354	2.549576	-0.308923

Structure No: 152 (M06-2X/6-31+G(d,p) level in DCM)

	X	**Y**	**Z**
C	-0.204613	-0.049276	-0.728980
C	-0.203319	-0.034755	0.730173
C	0.847455	-0.825622	1.492392
C	1.941622	-1.420580	0.683422
C	1.940309	-1.434123	-0.658818
C	0.843878	-0.856441	-1.477136
H	2.738312	-1.889236	1.252223
H	2.735820	-1.914319	-1.219537
O	0.728104	-0.984880	2.681966
O	0.720408	-1.041658	-2.662507
C	-2.098240	-1.345822	0.685481
C	-1.662393	0.065370	1.140161
C	-1.664670	0.042630	-1.137853
C	-2.099417	-1.359197	-0.654471
C	-2.270295	0.904572	-0.006664
H	-1.975647	1.953711	-0.017316
H	-3.356950	0.830912	-0.004856
H	-1.851208	0.335810	2.175146
H	-1.855595	0.292635	-2.177546

H	-2.306425	-2.187411	-1.320231
H	-2.303624	-2.160471	1.368242
Br	0.696152	1.680861	-0.017658

Structure No: TS24 (M06-2X/6-31+G(d,p) level in DCM)

	X	Y	Z
C	-0.193900	-0.325096	0.593425
C	-0.258188	0.467145	-0.631711
C	0.824637	1.478766	-0.962271
C	1.851483	1.697084	0.085552
C	1.830852	1.079357	1.277386
C	0.757594	0.135807	1.687723
H	2.628168	2.411540	-0.168271
H	2.586769	1.278774	2.030221
O	0.771177	2.093705	-1.999237
O	0.594788	-0.236328	2.822965
C	-2.112641	1.468204	0.003578
C	-1.668220	0.472717	-1.106705
C	-1.662970	-0.640101	0.886603
C	-2.153345	0.790856	1.162877
C	-2.240015	-0.843271	-0.533689
H	-1.898869	-1.744112	-1.043438
H	-3.329060	-0.815020	-0.524003
H	-1.847716	0.770700	-2.135413
H	-1.844724	-1.389184	1.651880
H	-2.424493	1.167304	2.141674
H	-2.294204	2.518760	-0.182763
Br	0.789848	-1.535617	-0.661038

Structure No: 156 (M06-2X/6-31+G(d,p) level in DCM)

	X	Y	Z
C	-0.330676	0.239768	0.365484
C	0.985952	0.170004	-0.392317
C	1.546781	-1.176699	-0.776419
C	1.066863	-2.303616	0.063164
C	0.196380	-2.144831	1.075038
C	-0.362135	-0.818218	1.460886
H	1.488446	-3.276223	-0.171170
H	-0.093866	-2.981270	1.703397
O	2.362456	-1.292530	-1.660821
O	-0.794367	-0.574803	2.563080

C	1.981175	1.093969	0.518869
C	1.298054	1.468256	-0.911681
C	-0.237064	1.718756	0.793821
C	1.126392	1.656081	1.441729
C	0.149535	2.415916	-0.539253
H	-0.649097	2.404507	-1.282477
H	0.492005	3.438499	-0.383269
H	2.015809	1.619205	-1.710329
H	-1.058476	2.119969	1.379361
H	1.382993	1.992837	2.442850
H	3.032610	0.861731	0.611213
Br	-1.819505	-0.147340	-0.811530

Structure No: 150 (M06-2X/6-31+G(d,p) level in DCM)

	X	Y	Z
C	1.101409	0.665069	0.335373
C	1.104887	-0.678358	0.289533
C	2.306482	-1.455581	-0.094824
C	3.513259	-0.643401	-0.424281
C	3.502404	0.696899	-0.400151
C	2.273419	1.474474	-0.071228
H	4.405671	-1.206460	-0.678630
H	4.382853	1.283377	-0.643037
O	2.305630	-2.670451	-0.134006
O	2.229829	2.687823	-0.133613
C	-1.047698	-0.717075	-0.580602
C	-0.296764	-1.164686	0.671638
C	-0.304758	1.118766	0.739895
C	-1.050484	0.742162	-0.537831
C	-0.650395	-0.053929	1.693637
H	0.024938	-0.077239	2.547536
H	-1.680869	-0.069295	2.045564
H	-0.401477	-2.210476	0.947082
H	-0.417165	2.145372	1.077369
Br	-2.947498	0.000345	-0.284500
H	-1.075115	1.368679	-1.423265
H	-1.070613	-1.291072	-1.501122

Structure No: TS25 (M06-2X/6-31+G(d,p) level in DCM)

	X	Y	Z
C	-1.168404	-0.675674	0.341627

C	-1.056830	0.669184	0.335511
C	-2.194076	1.542998	-0.065331
C	-3.443514	0.830601	-0.449927
C	-3.530303	-0.507679	-0.474128
C	-2.377654	-1.389660	-0.134744
H	-4.285064	1.463190	-0.713788
H	-4.444801	-1.018333	-0.759009
O	-2.091060	2.752058	-0.070178
O	-2.413358	-2.598107	-0.241064
C	1.097158	0.465411	-0.526082
C	0.374363	1.020805	0.715850
C	0.173648	-1.260421	0.862557
C	0.770618	-0.966316	-0.448331
C	0.628227	-0.088822	1.765820
H	-0.024884	0.009965	2.632562
H	1.666740	-0.170133	2.087224
H	0.586071	2.055159	0.972641
H	0.149010	-2.290911	1.203385
Br	2.997980	0.044520	-0.334846
H	0.852941	-1.664018	-1.278588
H	0.966606	0.982709	-1.471790

Structure No: 157 (M06-2X/6-31+G(d,p) level in DCM)

	X	**Y**	**Z**
C	-1.095694	-0.664643	0.150591
C	-0.985783	0.695000	0.224600
C	-2.155019	1.584278	-0.094255
C	-3.421536	0.878249	-0.402831
C	-3.510281	-0.460887	-0.465341
C	-2.355197	-1.365836	-0.206295
H	-4.278886	1.514859	-0.597021
H	-4.445495	-0.956186	-0.707082
O	-2.020907	2.786930	-0.087230
O	-2.424436	-2.572593	-0.273820
C	1.115349	0.184362	-0.524745
C	0.436938	1.002578	0.609341
C	0.105166	-1.216407	1.147964
C	0.441557	-1.156419	-0.237272
C	0.582376	0.066487	1.834286
H	-0.055603	0.360618	2.667072
H	1.614637	-0.033185	2.177402
H	0.720228	2.046412	0.708898
H	-0.162610	-2.143193	1.645129

Br	3.024561	0.047551	-0.365727
H	0.456603	-2.015937	-0.900415
H	0.906968	0.567040	-1.521402

Structure No: RC1(133+162) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	4.372907	-0.381440	0.614009
C	2.975133	-0.908859	0.953089
C	3.002160	-0.437618	-1.266152
C	4.389067	-0.100317	-0.709793
C	2.716535	-1.695052	-0.376852
H	1.690963	-2.061518	-0.467090
H	3.427635	-2.510913	-0.541309
C	2.001201	0.267044	0.716193
C	2.016926	0.545251	-0.594734
H	2.882832	-1.435817	1.901525
H	2.934639	-0.533475	-2.348749
C	5.561890	0.485822	-1.377059
C	5.527074	-0.123213	1.488996
O	5.583564	0.771357	-2.572080
O	5.519440	-0.348026	2.697075
C	6.751300	0.722148	-0.502190
H	7.624687	1.137096	-0.997274
C	6.735341	0.442396	0.813736
H	7.594991	0.615775	1.454857
C	-6.685611	1.210295	0.245177
C	-6.279084	-0.101916	-0.008637
C	-4.930661	-0.440689	-0.083013
C	-3.969987	0.565421	0.102753
C	-4.361929	1.886799	0.358398
C	-5.717877	2.201231	0.427915
H	-7.742272	1.448505	0.298201
H	-4.633707	-1.463183	-0.280909
H	-3.600256	2.645490	0.498326
H	-6.028680	3.222234	0.625427
Cl	-7.491159	-1.350213	-0.238566
C	-2.514484	0.280309	0.037730
O	-1.616523	1.092121	0.187245
O	-2.254720	-1.027183	-0.215037
O	-0.839146	-1.284010	-0.273521
H	-0.457646	-0.386628	-0.104229
H	1.472702	0.790575	1.504106
H	1.503487	1.345739	-1.114117

Structure No: TS26 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	4.109507	-0.341725	0.676489
C	2.666942	-0.594430	1.136080
C	2.667259	-0.591177	-1.138086
C	4.109696	-0.339797	-0.677375
C	2.244803	-1.579009	-0.002477
H	1.180922	-1.810933	-0.002961
H	2.842233	-2.494192	-0.003702
C	1.904433	0.662099	0.686264
C	1.904647	0.664080	-0.684879
H	2.536844	-0.895192	2.173642
H	2.537446	-0.888967	-2.176540
C	5.323681	-0.064762	-1.466254
C	5.323275	-0.068921	1.466476
O	5.326795	-0.019706	-2.692962
O	5.326054	-0.027337	2.693308
C	6.568461	0.164560	-0.672366
H	7.470339	0.339450	-1.251933
C	6.568273	0.162658	0.673583
H	7.469989	0.335911	1.253893
C	-6.704897	0.668554	0.000901
C	-5.961654	-0.513399	-0.000543
C	-4.569340	-0.495575	-0.000594
C	-3.906975	0.739756	0.000843
C	-4.637457	1.934923	0.002302
C	-6.031451	1.893091	0.002321
H	-7.788678	0.628326	0.000909
H	-4.001563	-1.418060	-0.001715
H	-4.101021	2.876925	0.003395
H	-6.602811	2.816395	0.003445
Cl	-6.802659	-2.059136	-0.002336
C	-2.408062	0.808497	0.000863
O	-1.806310	1.899568	0.002164
O	-1.792425	-0.339042	-0.000555
O	-0.028970	0.095202	-0.000046
H	-0.363889	1.044329	0.001099
H	1.618548	1.470744	1.346650
H	1.618849	1.474578	-1.343027

Structure No: PC (148+163) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-3.865884	-0.025547	-0.678359
C	-3.126342	-1.278249	-1.142862
C	-3.126210	-1.279804	1.141050
C	-3.865798	-0.026486	0.678364
C	-3.559069	-2.245193	-0.001535
H	-3.022362	-3.193366	-0.002208
H	-4.637042	-2.420578	-0.001592
C	-1.658638	-0.982741	-0.731569
C	-1.658524	-0.983749	0.729946
H	-3.289992	-1.581231	-2.176263
H	-3.289699	-1.584203	2.174061
C	-4.442832	1.078557	1.465903
C	-4.442996	1.080574	-1.464320
O	-4.419934	1.104637	2.693303
O	-4.420210	1.108335	-2.691688
C	-5.068549	2.179566	0.674494
H	-5.517060	2.980463	1.255247
C	-5.068618	2.180500	-0.671339
H	-5.517183	2.982206	-1.250933
C	6.397129	-0.196537	0.001030
C	5.523768	0.893789	0.000210
C	4.144255	0.714463	-0.000301
C	3.625527	-0.587885	0.000014
C	4.488306	-1.692663	0.000837
C	5.868843	-1.489832	0.001340
H	7.469357	-0.033078	0.001413
H	3.465190	1.559015	-0.000935
H	4.075722	-2.694543	0.001076
H	6.542617	-2.341174	0.001977
Cl	6.182386	2.524262	-0.000175
C	2.140489	-0.745652	-0.000547
O	1.737965	-2.023803	-0.000247
O	1.360695	0.197177	-0.001219
O	-1.002398	-2.059353	-0.001573
H	0.745218	-2.044393	-0.000746
H	-1.001787	-0.357197	-1.326960
H	-1.001631	-0.358962	1.326091

Structure No: 148 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.232485	-0.678755	0.253458

C	1.202875	-1.141593	0.488824
C	1.202875	1.141594	0.488823
C	-0.232483	0.678756	0.253450
C	1.668083	0.000001	1.439308
H	2.740958	0.000001	1.629218
H	1.115172	0.000001	2.381350
C	1.929043	-0.731983	-0.824617
C	1.929046	0.731982	-0.824619
H	1.330265	-2.174235	0.811926
H	1.330264	2.174236	0.811922
C	-1.450613	1.464406	-0.013179
C	-1.450619	-1.464407	-0.013147
O	-1.457496	2.692007	-0.056869
O	-1.457492	-2.692007	-0.056885
C	-2.698668	0.672816	-0.231316
H	-3.601718	1.253475	-0.396732
C	-2.698669	-0.672816	-0.231311
H	-3.601720	-1.253475	-0.396727
O	3.159370	0.000000	-0.651176
H	1.860704	-1.346755	-1.717781
H	1.860702	1.346755	-1.717782

Structure No: RC2(133+162) (B3LYP/6-31+G(d,p) level in gas phase)

	X	**Y**	**Z**
C	3.678210	0.178281	0.602810
C	4.020591	-1.239991	1.069711
C	3.762335	-1.311594	-1.182831
C	3.523973	0.135642	-0.740305
C	4.895203	-1.662733	-0.159290
H	5.151875	-2.725492	-0.155010
H	5.795858	-1.052580	-0.281546
C	2.781586	-2.114632	0.772000
C	2.629076	-2.157550	-0.558773
H	4.444665	-1.320489	2.069570
H	3.950045	-1.457544	-2.245608
C	3.147320	1.319797	-1.529059
C	3.482689	1.412016	1.380971
O	2.995597	1.293470	-2.748148
O	3.612044	1.462804	2.601962
C	2.968072	2.581892	-0.749868
H	2.701723	3.459687	-1.331653
C	3.121972	2.624316	0.585794
H	2.988360	3.538589	1.156904

C	-5.948490	-0.742214	-0.046827
C	-5.216958	0.446713	0.007106
C	-3.825537	0.439188	0.055972
C	-3.156025	-0.794271	0.050041
C	-3.875800	-1.995931	-0.003971
C	-5.268184	-1.962476	-0.052050
H	-7.031823	-0.709401	-0.084127
H	-3.274345	1.370530	0.097138
H	-3.334905	-2.935470	-0.007792
H	-5.832107	-2.888907	-0.094115
Cl	-6.067403	1.981972	0.013406
C	-1.675292	-0.881354	0.099162
O	-1.015383	-1.907403	0.086892
O	-1.086193	0.339166	0.163536
O	0.348786	0.229404	0.202926
H	0.477399	-0.751641	0.181807
H	2.153535	-2.562292	1.533259
H	1.848346	-2.648631	-1.127648

Structure No: TS27 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	3.228950	0.445647	0.674886
C	3.811134	-0.886388	1.136778
C	3.811190	-0.886012	-1.136966
C	3.228999	0.445879	-0.674666
C	4.876515	-1.070726	-0.000102
H	5.343700	-2.060090	-0.000255
H	5.644282	-0.291382	0.000045
C	2.836600	-1.993657	0.686521
C	2.836642	-1.993376	-0.687210
H	4.130459	-0.936786	2.176286
H	4.130581	-0.936040	-2.176473
C	2.635873	1.537309	-1.466026
C	2.635675	1.536760	1.466571
O	2.616992	1.536683	-2.693349
O	2.616546	1.535633	2.693891
C	2.060231	2.662780	-0.672410
H	1.637362	3.478458	-1.251622
C	2.060154	2.662536	0.673298
H	1.637216	3.478001	1.252758
C	-5.625302	-0.461320	0.000129
C	-4.678652	0.565003	-0.000044
C	-3.313059	0.293157	-0.000134

C	-2.887319	-1.042215	-0.000041
C	-3.823698	-2.083951	0.000139
C	-5.186716	-1.788177	0.000219
H	-6.683626	-0.223885	0.000193
H	-2.586236	1.096321	-0.000274
H	-3.468785	-3.108255	0.000218
H	-5.917015	-2.591670	0.000354
Cl	-5.223255	2.238257	-0.000152
C	-1.425534	-1.381038	-0.000134
O	-1.031580	-2.564094	0.000126
O	-0.611510	-0.366213	-0.000519
O	1.052184	-1.129997	-0.000413
H	0.531505	-1.994598	-0.000369
H	2.382296	-2.715145	1.352943
H	2.382447	-2.714649	-1.353941

Structure No: PC (149+163) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	3.931745	0.324425	-0.672673
C	3.076761	1.406489	-1.297235
C	2.939339	1.629849	0.967192
C	3.850064	0.457154	0.671892
C	3.311729	2.543948	-0.247729
H	2.623536	3.386732	-0.372400
H	4.342327	2.910306	-0.221458
C	1.583000	1.091338	-0.944971
C	1.494510	1.236156	0.509019
H	3.257638	1.621091	-2.349611
H	2.996119	2.047724	1.971355
C	4.471412	-0.507017	1.597256
C	4.647505	-0.794288	-1.311365
O	4.361358	-0.426036	2.817546
O	4.684664	-0.954261	-2.528344
C	5.255652	-1.604025	0.956626
H	5.747756	-2.291726	1.638426
C	5.336603	-1.736034	-0.380199
H	5.898471	-2.537590	-0.851118
C	-6.169980	-1.316525	0.008025
C	-5.804319	0.031292	0.041905
C	-4.468081	0.417681	0.026097
C	-3.473055	-0.568537	-0.025008
C	-3.823344	-1.925398	-0.059393
C	-5.169922	-2.290669	-0.042642

H	-7.218114	-1.594905	0.021287
H	-4.182609	1.462709	0.052779
H	-3.045568	-2.678680	-0.098407
H	-5.448129	-3.339774	-0.068914
Cl	-7.058445	1.262352	0.105839
C	-2.048702	-0.120481	-0.040183
O	-1.170902	-1.131385	-0.092461
O	-1.709737	1.054912	-0.008745
O	1.364127	-0.074457	-0.107966
H	-0.251772	-0.757203	-0.098444
H	0.780279	1.323782	-1.636987
H	0.612061	1.585202	1.034308

Structure No: 149 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.116879	-0.676975	-0.363203
C	-1.308125	-1.139196	-0.578484
C	-1.308192	1.139148	-0.578547
C	0.116869	0.676938	-0.363116
C	-1.796964	-0.000105	-1.532421
H	-2.883602	-0.000145	-1.671063
H	-1.301419	-0.000120	-2.508394
C	-2.126389	-0.733403	0.698538
C	-2.126377	0.733522	0.698214
H	-1.440359	-2.173964	-0.892152
H	-1.440342	2.173889	-0.892328
C	1.323949	1.463711	-0.056173
C	1.324106	-1.463689	-0.056556
O	1.326714	2.691031	-0.007573
O	1.326821	-2.690981	-0.007408
C	2.565490	0.672856	0.193983
H	3.463957	1.253347	0.383234
C	2.565531	-0.672755	0.193930
H	3.464028	-1.253200	0.383166
O	-1.412675	-0.000083	1.709241
H	-2.935047	-1.365941	1.053126
H	-2.934758	1.366082	1.053330

Structure No: RC3(133+162) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z

C	-3.578993	0.296366	0.676658
C	-3.678198	1.754963	1.134149
C	-3.678314	1.755142	-1.133605
C	-3.579065	0.296473	-0.676354
C	-4.628415	2.268536	0.000361
H	-4.743168	3.355682	0.000453
H	-5.608465	1.780163	0.000373
C	-2.378349	2.449029	0.669334
C	-2.378417	2.449134	-0.668814
H	-3.969576	1.907203	2.172487
H	-3.969799	1.907545	-2.171889
C	-3.448220	-0.936919	-1.465127
C	-3.448061	-0.937153	1.465220
O	-3.434407	-0.954353	-2.693868
O	-3.434097	-0.954781	2.693956
C	-3.342665	-2.201491	-0.672846
C	-3.342598	-2.201599	0.672726
C	5.977832	-0.009600	0.000065
C	4.901044	0.880449	-0.000337
C	3.585452	0.424981	-0.000345
C	3.349659	-0.958503	0.000064
C	4.419280	-1.864590	0.000471
C	5.727398	-1.384102	0.000468
H	6.993545	0.370376	0.000062
H	2.762653	1.129149	-0.000660
H	4.210368	-2.928376	0.000785
H	6.560759	-2.079461	0.000781
Cl	5.210864	2.608034	-0.000841
C	1.976140	-1.517685	0.000086
O	1.681198	-2.701723	0.000474
O	1.018402	-0.554412	-0.000389
O	-0.298125	-1.137807	-0.000351
H	-0.070606	-2.100782	0.000041
H	-1.603491	2.799251	1.340480
H	-1.603628	2.799459	-1.339984
H	-3.270123	-3.116284	-1.254782
H	-3.270000	-3.116485	1.254509

Structure No: TS28 (B3LYP/6-31+G(d,p) level in gas phase)

	X	**Y**	**Z**
C	-3.532124	0.107770	0.678468
C	-4.203051	1.406120	1.134152
C	-4.203015	1.406111	-1.134190

C	-3.532105	0.107763	-0.678475
C	-5.278119	1.502126	-0.000036
H	-5.811510	2.455943	-0.000049
H	-5.987202	0.667666	-0.000045
C	-3.278034	2.552712	0.669031
C	-3.278013	2.552706	-0.669048
H	-4.530675	1.429242	2.172371
H	-4.530605	1.429227	-2.172420
C	-2.955122	-0.977522	-1.478534
C	-2.955132	-0.977489	1.478551
O	-3.026015	-1.044333	-2.700304
O	-3.026025	-1.044276	2.700323
C	-2.269372	-2.055724	-0.691551
C	-2.269372	-2.055702	0.691591
C	5.982243	-0.065672	-0.000022
C	4.996710	0.923713	-0.000001
C	3.642909	0.598724	0.000012
C	3.271048	-0.752833	0.000007
C	4.246558	-1.758171	-0.000013
C	5.596699	-1.408863	-0.000028
H	7.030448	0.213020	-0.000034
H	2.884662	1.372486	0.000026
H	3.932796	-2.795756	-0.000017
H	6.358104	-2.182805	-0.000044
Cl	5.475880	2.615911	0.000007
C	1.826000	-1.142955	0.000014
O	1.474022	-2.345156	0.000024
O	0.964403	-0.173944	0.000006
O	-0.651724	-1.081997	0.000007
H	-0.011169	-1.891222	0.000019
H	-2.699697	3.175851	1.340092
H	-2.699654	3.175840	-1.340096
H	-1.877502	-2.889626	-1.265774
H	-1.877493	-2.889587	1.265832

Structure No: PC (159+163) (B3LYP/6-31+G(d,p) level in gas phase)

	X	**Y**	**Z**
C	4.113187	-0.130685	-0.679525
C	5.196553	0.799044	-1.235458
C	5.240745	0.990869	1.022915
C	4.138739	-0.014956	0.673947
C	6.256857	0.598148	-0.101287
H	7.097483	1.292363	-0.176985

H	6.618273	-0.432264	-0.020811
C	4.751265	2.234478	-0.882446
C	4.777359	2.347822	0.450850
H	5.490119	0.613119	-2.267420
H	5.574443	0.980191	2.059374
C	3.265552	-0.777022	1.574530
C	3.212699	-1.035071	-1.404290
O	3.431136	-0.859070	2.783316
O	3.335935	-1.323110	-2.586368
C	2.115605	-1.502776	0.901595
C	2.090572	-1.632275	-0.576613
C	-6.533159	-0.823854	-0.069282
C	-6.067479	0.492785	-0.035562
C	-4.706403	0.777533	0.005417
C	-3.787764	-0.281400	0.013109
C	-4.238897	-1.607991	-0.020296
C	-5.608726	-1.871039	-0.061293
H	-7.599027	-1.021917	-0.101235
H	-4.343423	1.798364	0.031292
H	-3.520492	-2.418905	-0.014312
H	-5.964146	-2.896608	-0.087490
Cl	-7.226309	1.815408	-0.045460
C	-2.334734	0.063379	0.056972
O	-1.533835	-1.023106	0.064607
O	-1.905402	1.201853	0.083257
O	1.267147	-0.658095	0.097294
H	-0.597040	-0.727803	0.088543
H	4.422634	2.965305	-1.611276
H	4.474470	3.191926	1.058332
H	1.593161	-2.225078	1.525294
H	1.549117	-2.450322	-1.047021

Structure No: 159 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.248638	-0.678801	-0.210668
C	-1.712152	-1.133201	-0.215272
C	-1.712226	1.133103	-0.215421
C	-0.248678	0.678777	-0.210662
C	-2.287370	-0.000131	-1.129840
H	-3.379560	-0.000173	-1.173212
H	-1.864735	-0.000182	-2.139875
C	-2.311858	-0.669254	1.129342
C	-2.312006	0.669329	1.129206

H	-1.880088	-2.171350	-0.497969
H	-1.880202	2.171201	-0.498281
C	0.972797	1.494197	-0.249574
C	0.972863	-1.494184	-0.249494
O	0.981952	2.694773	-0.486799
O	0.982080	-2.694740	-0.486820
C	2.262494	0.742833	0.010331
C	2.262521	-0.742738	0.010325
O	2.292051	0.000042	1.238148
H	-2.607312	-1.339753	1.927254
H	-2.607579	1.339931	1.926989
H	3.172138	1.291922	-0.225383
H	3.172194	-1.291775	-0.225398

Structure No: RC4(133+162) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	3.517554	0.194560	0.676381
C	3.816387	1.625752	1.133369
C	3.816170	1.625032	-1.134473
C	3.517396	0.194133	-0.676520
C	3.036982	2.373885	-0.000718
H	3.216992	3.452245	-0.001081
H	1.963409	2.161571	-0.000552
C	5.254835	1.944403	0.668524
C	5.254708	1.943970	-0.670095
H	3.576406	1.850264	2.171673
H	3.575995	1.848888	-2.172874
C	3.300175	-1.026653	-1.464952
C	3.300539	-1.025726	1.465644
O	3.330705	-1.052940	-2.693214
O	3.331391	-1.051231	2.693914
C	3.038975	-2.268943	-0.672142
C	3.039139	-2.268518	0.673688
C	-6.228642	-0.055450	-0.000382
C	-5.223461	0.914836	0.000025
C	-3.876670	0.561935	0.000180
C	-3.535573	-0.799496	-0.000079
C	-4.532433	-1.785187	-0.000484
C	-5.873612	-1.406690	-0.000635
H	-7.270573	0.245571	-0.000497
H	-3.110536	1.327486	0.000495
H	-4.242499	-2.829828	-0.000677
H	-6.651101	-2.163965	-0.000952

Cl	-5.665468	2.613110	0.000347
C	-2.123364	-1.250991	0.000068
O	-1.736730	-2.408197	-0.000109
O	-1.242310	-0.216215	0.000451
O	0.114768	-0.696949	0.000630
H	-0.037395	-1.674798	0.000449
H	6.094946	2.079435	1.339248
H	6.094695	2.078574	-1.341061
H	2.862536	-3.169984	-1.253363
H	2.862847	-3.169190	1.255523

Structure No: TS29 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-3.373696	0.201937	-0.678323
C	-4.072063	1.485256	-1.134240
C	-4.071365	1.486341	1.133477
C	-3.373282	0.202587	0.678350
C	-3.541286	2.426613	-0.000994
H	-4.026241	3.405926	-0.001315
H	-2.452388	2.536365	-0.001381
C	-5.541388	1.372374	-0.669036
C	-5.540977	1.373017	0.669285
H	-3.907992	1.767734	-2.173021
H	-3.906655	1.769808	2.171886
C	-2.846365	-0.908447	1.476915
C	-2.847362	-0.909904	-1.476181
O	-2.952853	-0.991895	2.695121
O	-2.954635	-0.994441	-2.694251
C	-2.163361	-1.990168	0.692248
C	-2.163987	-1.990955	-0.690981
C	6.097626	-0.018906	-0.000031
C	5.112953	0.971340	-0.000236
C	3.758891	0.647407	-0.000222
C	3.385835	-0.703828	-0.000007
C	4.360535	-1.709985	0.000195
C	5.710954	-1.361768	0.000186
H	7.146066	0.258898	-0.000043
H	3.001509	1.421993	-0.000376
H	4.045955	-2.747319	0.000354
H	6.471707	-2.136343	0.000345
Cl	5.593423	2.663069	-0.000520
C	1.940574	-1.093063	0.000004
O	1.587456	-2.294599	0.000035

O	1.079479	-0.123007	-0.000015
O	-0.537866	-1.027887	0.000015
H	0.099682	-1.838779	0.000030
H	-6.383559	1.259818	-1.341067
H	-6.382736	1.261107	1.341939
H	-1.779301	-2.827254	1.267091
H	-1.780308	-2.828584	-1.265286

Structure No: PC (160+163) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-3.943035	0.015630	-0.679005
C	-5.379947	0.288462	-1.132818
C	-5.379839	0.289935	1.132839
C	-3.942976	0.016357	0.679164
C	-5.774293	1.293637	-0.000629
H	-6.839654	1.536914	-0.000710
H	-5.172741	2.208395	-0.001247
C	-6.221277	-0.922261	-0.668081
C	-6.221309	-0.921295	0.669817
H	-5.495941	0.591811	-2.172311
H	-5.495633	0.594649	2.171953
C	-2.769933	-0.328436	1.492320
C	-2.770126	-0.330297	-1.491869
O	-2.820806	-0.574999	2.689292
O	-2.821225	-0.578813	-2.688424
C	-1.454890	-0.387653	0.741356
C	-1.455017	-0.388768	-0.740969
C	6.509040	0.868175	0.000053
C	5.917806	-0.397681	0.000404
C	4.534930	-0.548882	0.000049
C	3.724260	0.594956	-0.000676
C	4.301826	1.872342	-0.001045
C	5.691088	2.000669	-0.000677
H	7.589625	0.961946	0.000362
H	4.074773	-1.530064	0.000358
H	3.664882	2.748784	-0.001661
H	6.145041	2.986833	-0.000970
Cl	6.942193	-1.826080	0.001366
C	2.245815	0.398702	-0.001029
O	1.552028	1.548014	-0.001806
O	1.705867	-0.699044	-0.000378
O	-1.139925	0.815210	-0.000719
H	0.589092	1.328166	-0.001365

H	-6.664340	-1.646079	-1.341205
H	-6.664421	-1.644147	1.343952
H	-0.613916	-0.828188	1.270823
H	-0.614295	-0.830150	-1.270155

Structure No: 160 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-0.232819	0.678774	0.127162
C	-1.674674	1.132763	0.373976
C	-1.674799	-1.132688	0.374025
C	-0.232905	-0.678791	0.127151
C	-2.086341	0.000068	1.371668
H	-3.155769	0.000137	1.596708
H	-1.499992	0.000016	2.296178
C	-2.495460	0.669016	-0.851052
C	-2.495777	-0.668910	-0.850856
H	-1.796151	2.172044	0.676035
H	-1.796277	-2.171953	0.676129
C	0.946115	-1.489094	-0.206233
C	0.946161	1.488980	-0.206592
O	0.895681	-2.679582	-0.484903
O	0.895873	2.679635	-0.484680
C	2.264858	-0.743392	-0.208991
C	2.264848	0.743202	-0.209010
O	2.547862	-0.000029	0.985578
H	-2.926393	1.342579	-1.581787
H	-2.926981	-1.342471	-1.581431
H	3.105529	-1.292613	-0.628615
H	3.105458	1.292496	-0.628663

Structure No: RC5(133+162) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-3.577672	0.298171	0.675809
C	-3.675562	1.757471	1.131381
C	-3.673174	1.754822	-1.136366
C	-3.576227	0.296612	-0.677194
C	-4.623901	2.270793	-0.004092
H	-4.737327	3.358078	-0.005476
H	-5.604546	1.783614	-0.004554
C	-2.374359	2.449376	0.667145
C	-2.372954	2.447824	-0.671004

H	-3.967903	1.911360	2.169207
H	-3.963325	1.906283	-2.175161
C	-3.446100	-0.937902	-1.464353
C	-3.449365	-0.934562	1.465997
O	-3.430793	-0.956808	-2.693050
O	-3.436946	-0.950746	2.694769
C	-3.343293	-2.201657	-0.670416
C	-3.344762	-2.200093	0.675138
C	5.975705	-0.008757	-0.001079
C	4.898335	0.880584	0.000522
C	3.583043	0.424249	0.001068
C	3.348156	-0.959387	-0.000021
C	4.418370	-1.864772	-0.001628
C	5.726171	-1.383422	-0.002148
H	6.991170	0.371882	-0.001476
H	2.759782	1.127874	0.002326
H	4.210154	-2.928694	-0.002444
H	6.559987	-2.078234	-0.003389
Cl	5.207017	2.608373	0.001862
C	1.975007	-1.519465	0.000505
O	1.680830	-2.703693	-0.000188
O	1.016627	-0.556830	0.001873
O	-0.299497	-1.141178	0.002646
H	-0.071269	-2.103992	0.001434
H	-1.599823	2.799515	1.338706
H	-1.597013	2.796403	-1.341755
H	-3.271325	-3.117290	-1.251131
H	-3.274124	-3.114418	1.258069

Structure No: TS30 (B3LYP/6-31+G(d,p) level in gas phase)

	X	**Y**	**Z**
C	3.198429	0.073426	-0.628362
C	3.820686	1.387850	-1.094687
C	3.142303	1.708664	1.051794
C	2.754838	0.262803	0.678605
C	4.500905	1.756618	0.272494
H	4.950884	2.752982	0.262003
H	5.233343	1.016593	0.614669
C	2.721450	2.461182	-1.103400
C	2.328601	2.652715	0.161180
H	4.439150	1.304287	-1.987116
H	3.148604	1.909374	2.121926
C	2.650449	-0.894810	1.618452

C	3.301748	-1.270332	-1.229633
O	2.577708	-0.751097	2.829383
O	3.693925	-1.451313	-2.378060
C	2.683301	-2.243288	0.979791
C	2.975731	-2.412473	-0.323799
C	-5.620015	-0.820905	-0.106382
C	-4.978935	0.417675	-0.037971
C	-3.590020	0.516311	-0.033255
C	-2.827159	-0.657716	-0.098056
C	-3.454006	-1.908509	-0.167353
C	-4.846566	-1.983015	-0.171151
H	-6.703405	-0.871755	-0.108943
H	-3.102166	1.482056	0.019355
H	-2.840960	-2.801097	-0.217631
H	-5.338589	-2.949389	-0.224896
Cl	-5.946005	1.884582	0.043875
C	-1.327860	-0.601893	-0.098071
O	-0.633549	-1.634369	-0.138919
O	-0.810981	0.593483	-0.056474
O	1.005646	0.300695	-0.068078
H	0.738736	-0.674721	-0.113793
H	2.293112	2.878850	-2.006145
H	1.511051	3.268104	0.514750
H	2.474603	-3.081630	1.637550
H	3.012451	-3.396559	-0.781601

Structure No: PC (161+163) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	3.224084	-0.336448	0.556005
C	4.573132	-0.938864	0.048633
C	3.779089	0.252466	-1.715380
C	2.704411	0.443862	-0.598041
C	5.045707	0.285488	-0.800426
H	5.975559	0.099912	-1.344011
H	5.136866	1.210257	-0.217902
C	4.261858	-1.920957	-1.073562
C	3.792437	-1.217397	-2.114663
H	5.216904	-1.283788	0.857063
H	3.701323	0.992691	-2.510707
C	1.987749	1.737879	-0.333010
C	2.986645	0.164575	1.954259
O	1.920243	2.624328	-1.167371
O	3.640262	-0.237808	2.904925

C	1.461504	1.912139	1.051628
C	1.932450	1.204051	2.097699
C	-5.706932	-1.167198	0.149540
C	-5.228726	0.113416	-0.138827
C	-3.864437	0.377377	-0.203301
C	-2.956363	-0.665719	0.026627
C	-3.419956	-1.956514	0.316587
C	-4.792768	-2.198892	0.376217
H	-6.775064	-1.350002	0.194409
H	-3.491732	1.369700	-0.428718
H	-2.709138	-2.755288	0.491554
H	-5.158558	-3.196246	0.600123
Cl	-6.374272	1.415721	-0.425252
C	-1.500548	-0.346591	-0.049649
O	-0.709899	-1.408048	0.187729
O	-1.060597	0.764330	-0.300513
O	2.023292	-0.741869	-0.136096
H	0.227346	-1.123932	0.111746
H	4.324131	-2.999080	-0.982872
H	3.394400	-1.605821	-3.044781
H	0.731770	2.705649	1.177531
H	1.606407	1.405194	3.114450

Structure No: 161 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	0.066496	-0.743905	-0.229386
C	1.447055	-1.135416	0.389296
C	1.447224	1.135317	0.388566
C	0.066564	0.743511	-0.230017
C	1.536255	0.000294	1.458695
H	2.479536	0.000396	2.011216
H	0.695507	0.000570	2.163188
C	2.539097	-0.671040	-0.565981
C	2.539176	0.670176	-0.566423
H	1.483771	-2.168291	0.734245
H	1.483991	2.168406	0.732831
C	-1.215400	1.476897	0.028262
C	-1.215887	-1.476629	0.028408
O	-1.245539	2.645659	0.383138
O	-1.246833	-2.645402	0.383140
C	-2.462779	0.674127	-0.130480
C	-2.462968	-0.673271	-0.130619
O	0.076146	-0.000400	-1.460253

H	3.125659	-1.328198	-1.197251
H	3.125865	1.326800	-1.198134
H	-3.386590	1.245084	-0.167983
H	-3.386931	-1.243986	-0.168250

Structure No: RC6(133+162) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	3.630884	0.147055	0.676650
C	4.199142	1.494067	1.133594
C	4.198828	1.493846	-1.134066
C	3.630705	0.146926	-0.676688
C	3.578747	2.378721	-0.000234
H	3.963574	3.401985	-0.000387
H	2.484302	2.378530	-0.000049
C	5.672179	1.528935	0.668835
C	5.671992	1.528801	-0.669722
H	4.007175	1.760680	2.171946
H	4.006572	1.760243	-2.172418
C	3.192217	-1.013018	-1.465341
C	3.192492	-1.012694	1.465624
O	3.222938	-1.046756	-2.693226
O	3.223341	-1.046171	2.693515
C	2.700813	-2.184094	-0.672758
C	2.700989	-2.183950	0.673383
C	-6.327032	-0.210860	-0.000262
C	-5.416181	0.848479	-0.000006
C	-4.042456	0.621870	0.000105
C	-3.576353	-0.701873	-0.000032
C	-4.477414	-1.775838	-0.000283
C	-5.847940	-1.523239	-0.000403
H	-7.392479	-0.008128	-0.000349
H	-3.350362	1.454958	0.000306
H	-4.091943	-2.789119	-0.000384
H	-6.551796	-2.349438	-0.000601
Cl	-6.013796	2.498478	0.000163
C	-2.127963	-1.019583	0.000097
O	-1.635387	-2.135995	0.000071
O	-1.348198	0.092998	0.000234
O	0.047967	-0.257377	0.000424
H	-0.008929	-1.245195	0.000273
H	6.522270	1.499331	1.339880
H	6.521897	1.499067	-1.340997
H	2.358365	-3.036107	-1.253826

H	2.358704	-3.035833	1.254743

Structure No: TS31 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	-2.679533	-0.378742	0.579204
C	-3.075486	-1.854263	0.700188
C	-3.663461	-1.193714	-1.391679
C	-3.071437	0.021651	-0.692741
C	-2.785923	-2.318694	-0.761380
H	-3.197372	-3.309932	-0.962054
H	-1.733915	-2.271080	-1.040923
C	-4.619473	-1.835922	0.639164
C	-4.970565	-1.442722	-0.594161
H	-2.620754	-2.395871	1.527197
H	-3.753616	-1.127721	-2.474098
C	-3.173123	1.447592	-1.063140
C	-2.571744	0.609810	1.690989
O	-3.568119	1.813094	-2.165796
O	-2.532711	0.272187	2.864905
C	-2.830879	2.424202	0.012709
C	-2.558988	2.042655	1.275565
C	5.742289	0.758825	-0.069931
C	5.100566	-0.481105	-0.047564
C	3.711692	-0.579535	-0.061769
C	2.949441	0.596155	-0.098518
C	3.576987	1.848340	-0.121477
C	4.969491	1.922577	-0.107065
H	6.825634	0.809435	-0.058470
H	3.223478	-1.546369	-0.044145
H	2.964442	2.742229	-0.150382
H	5.461988	2.890045	-0.124752
Cl	6.066832	-1.950045	-0.000507
C	1.450162	0.540954	-0.116118
O	0.756038	1.573653	-0.124899
O	0.934996	-0.656699	-0.123970
O	-0.874338	-0.368826	-0.128832
H	-0.623630	0.609377	-0.139962
H	-5.266284	-2.057912	1.479339
H	-5.963753	-1.256781	-0.984903
H	-2.839349	3.468988	-0.283329
H	-2.340050	2.760696	2.060198

Structure No: PC (158+163) (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z
C	2.658934	0.433855	-0.565087
C	3.681573	0.531395	-1.723828
C	4.458523	-1.145033	-0.398370
C	3.165691	-0.655417	0.295952
C	4.063985	-0.965451	-1.890538
H	4.926892	-1.085794	-2.547744
H	3.245073	-1.605554	-2.220696
C	4.955974	1.040909	-1.028673
C	5.415408	0.050621	-0.245468
H	3.343615	1.084767	-2.599018
H	4.827250	-2.115773	-0.069252
C	2.968996	-0.572868	1.785701
C	1.989002	1.616185	0.078501
O	3.617383	-1.264285	2.556889
O	1.925230	2.699846	-0.476602
C	1.961454	0.413617	2.255391
C	1.497973	1.406650	1.470166
C	-5.804118	-1.081445	-0.176964
C	-5.290415	0.213774	-0.075421
C	-3.919322	0.448977	-0.070295
C	-3.040602	-0.639089	-0.168348
C	-3.539967	-1.944824	-0.271227
C	-4.918951	-2.157710	-0.274888
H	-6.876968	-1.240771	-0.179586
H	-3.519517	1.453454	0.005391
H	-2.851415	-2.777809	-0.347830
H	-5.312174	-3.166500	-0.354595
Cl	-6.399460	1.572207	0.048110
C	-1.576301	-0.350845	-0.161200
O	-0.815713	-1.455467	-0.260129
O	-1.105294	0.772055	-0.074498
O	1.933219	-0.820425	-0.457318
H	0.129544	-1.186830	-0.262957
H	5.347973	2.046274	-1.125492
H	6.261401	0.077911	0.430914
H	1.662867	0.322821	3.296081
H	0.800669	2.152678	1.837783

Structure No: 158 (B3LYP/6-31+G(d,p) level in gas phase)

	X	Y	Z

C	0.080513	-0.739087	0.453303
C	1.545927	-1.136703	0.148700
C	1.546325	1.136374	0.148983
C	0.080797	0.739177	0.453342
C	2.302814	-0.000383	0.890456
H	3.365775	-0.000509	0.642719
H	2.164433	-0.000485	1.972223
C	1.753550	-0.671811	-1.303455
C	1.753966	0.671767	-1.303283
H	1.806483	-2.169814	0.376059
H	1.807278	2.169331	0.376602
C	-1.125288	1.473678	-0.053620
C	-1.125732	-1.473474	-0.053775
O	-1.081868	2.648336	-0.387180
O	-1.082365	-2.648192	-0.387094
C	-2.378800	0.673883	-0.159415
C	-2.378978	-0.673411	-0.159706
O	-0.152538	-0.000086	1.674618
H	1.819679	-1.334396	-2.158352
H	1.820417	1.334559	-2.157993
H	-3.290069	1.245971	-0.311293
H	-3.290400	-1.245188	-0.311897

The following tables and cartesian coordinates are related to Chapter 4.

1. Absolute Energies of the Structures

Energies are given in terms of ZPE-corrected total energy (E_{el}+ZPE), enthalpy (E_{el}+H) and Gibbs free-energy (E_{el}+G) as extracted from Gaussian output of each structure.

Table S20. Absolute energies of optimized structures in acetonitrile (SMD/M06/6-31G(d)/LANL2DZ(f)(Au))

Compound No	Eel+G[d] (au)	Eel+H[c] (au)	Eel[a]+ZPE[b] (au)	Imaginary Frequency (i)
RC(219+AuCl)	-1473.811252	-1473.736854	-1473.758701	–
TS32	-1473.782693	-1473.708782	-1473.729739	-406.5
PC(232+AuCl)	-1473.794512	-1473.721271	-1473.741892	–
RC(219+AuCl)'	-1473.810662	-1473.732419	-1473.754713	–
TS33	-1473.784790	-1473.710555	-1473.731533	-495.5
PC(233+AuCl)	-1473.796937	-1473.725110	-1473.745632	–
RC(222+AuCl)	-1704.621988	-1704.537372	-1704.563732	–
TS34	-1704.572921	-1704.488556	-1704.513239	-460.2
PC(235+AuCl)	-1704.582444	-1704.498890	-1704.524204	–
RC(222+AuCl)'	-1704.595536	-1704.513081	-1704.538335	–
TS35	-1704.581703	-1704.499737	-1704.525027	-462.3
PC(236+AuCl)	-1704.622990	-1704.541008	-1704.567009	–
RC(219+Au^++AuCl)	-1608.706237	-1608.624612	-1608.648323	–
TS36	-1608.657653	-1608.578051	-1608.600613	-322.2
PC(237+Au^++AuCl)	-1608.658069	-1608.579401	-1608.602005	–

[a]E_{el} = Total electronic energy
[b]ZPE = Zero-point energy correction
[c]H = Enthalpy correction
[d]G = Gibbs free energy correction

Table S21. Absolute energies of optimized structures in DMF (SMD/M06/6-31+G(d))

Compound No	Eel+G[d] (au)	Eel+H[c] (au)	Eel[a]+ZPE[b] (au)	Imaginary Frequency (i)
239	-877.704881	-877.637475	-877.655913	–
TS37	-877.673330	-877.611241	-877.628418	-401.5
240	-877.701527	-877.640281	-877.657351	–
RC(240+H_2O)	-954.087422	-954.022952	-954.041910	-14.7
TS38	-954.084612	-954.017683	-954.037083	-1694.0
221	-878.223566	-878.165015	-878.181177	-8.4
OH^-	-75.879077	-75.859514	-75.862819	–
221+OH^-	-954.102643	-954.024529	-954.043996	–

2. Cartesian Coordinates for the Optimized Structures Given in Paths

Structure No: RC(219+AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	4.694596	1.119937	0.307300
C	3.339735	0.938450	0.563652
C	2.404564	1.943749	0.273658
C	2.881022	3.141565	-0.277504
C	4.230899	3.325990	-0.540541
C	5.142006	2.312842	-0.247645
H	5.391689	0.321191	0.557214
H	2.170145	3.939097	-0.489648
H	4.575903	4.266865	-0.964834
H	6.203748	2.454512	-0.440506
C	0.969735	1.778617	0.497168
C	-0.108499	2.376639	-0.135057
C	-1.254071	1.820271	0.474025
N	0.429169	0.941036	1.420420
N	-0.908260	0.946423	1.428074
H	-0.060282	3.098142	-0.942529
C	-2.666509	2.080778	0.173038
C	-3.028406	3.023389	-0.796392
C	-3.680114	1.387498	0.848102
C	-4.367093	3.265866	-1.084889
H	-2.256055	3.575388	-1.331092
C	-5.016961	1.631669	0.558880
H	-3.410105	0.654806	1.607357
C	-5.367241	2.571416	-0.409072
H	-4.629028	4.003081	-1.842459
H	-5.792302	1.084486	1.093386
H	-6.415393	2.761842	-0.634721
O	2.908203	-0.234961	1.151603
C	2.976400	-1.386956	0.328018
Au	-0.190372	-1.981803	-0.332912
C	1.986101	-1.354474	-0.755166
C	1.263080	-1.230689	-1.750386
H	0.934100	-1.026618	-2.757337
H	3.974516	-1.498054	-0.124186
H	2.805902	-2.251178	0.978269
H	0.936646	0.312676	2.033246
Cl	-2.099857	-2.879158	0.720145

Structure No: TS32 ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	-1.542759	4.793070	0.122548
C	-1.405257	3.408811	0.164755
C	-2.522130	2.572125	-0.007866
C	-3.764587	3.171240	-0.271700
C	-3.898558	4.548519	-0.332168
C	-2.785556	5.362183	-0.117947
H	-0.654477	5.404488	0.267749
H	-4.638031	2.532743	-0.393517
H	-4.873500	4.990924	-0.525324
H	-2.883823	6.445499	-0.151302
C	-2.459937	1.125368	0.134612
C	-3.265407	0.141604	-0.348481
C	-2.794478	-1.076608	0.245765
N	-1.480032	0.483488	0.924347
N	-1.768407	-0.863883	1.043297
H	-4.079701	0.263814	-1.052823
C	-3.334617	-2.423695	0.048698
C	-4.474199	-2.626998	-0.737065
C	-2.719432	-3.525408	0.657928
C	-4.989607	-3.907070	-0.908675
H	-4.966963	-1.783163	-1.217238
C	-3.236646	-4.801447	0.485113
H	-1.831537	-3.369290	1.268094
C	-4.373610	-4.996110	-0.298611
H	-5.877635	-4.053142	-1.520995
H	-2.750749	-5.650197	0.963433
H	-4.779021	-5.997697	-0.432751
O	-0.150042	2.918423	0.400967
C	0.317640	1.911202	-0.480761
Au	3.081167	-0.455240	-0.003923
C	0.413589	0.597546	0.160346
C	1.084637	-0.450093	0.467319
H	0.659446	-1.326373	0.954433
H	-0.294284	1.875078	-1.393434
H	1.340262	2.178012	-0.785254
H	-1.229240	0.917026	1.817916
Cl	5.405407	-0.593753	-0.492538

Structure No: PC(232+AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	0.196820	4.443133	-0.411934
C	-0.210644	3.103691	-0.410048
C	-1.480004	2.769906	0.110904
C	-2.316699	3.809888	0.563078
C	-1.909546	5.129610	0.543052
C	-0.636203	5.441483	0.058859
H	1.181668	4.670366	-0.815590
H	-3.294221	3.542259	0.961930
H	-2.569767	5.910740	0.912797
H	-0.294896	6.474846	0.042159
C	-2.014841	1.419562	0.187141
C	-3.227385	0.909854	-0.078862
C	-3.167909	-0.514521	0.196173
N	-1.203371	0.304027	0.703609
N	-1.999301	-0.901082	0.631950
H	-4.069445	1.462329	-0.478954
C	-4.249564	-1.477348	0.002625
C	-5.514905	-1.054573	-0.419267
C	-4.019839	-2.839256	0.244326
C	-6.535621	-1.981867	-0.594758
H	-5.711842	-0.001274	-0.610494
C	-5.040969	-3.759640	0.066801
H	-3.033761	-3.165164	0.570533
C	-6.301003	-3.332224	-0.352853
H	-7.517738	-1.646455	-0.922096
H	-4.856462	-4.815477	0.255623
H	-7.101185	-4.057293	-0.491154
O	0.679716	2.247921	-0.954926
C	0.316245	0.883232	-1.187706
Au	2.965457	-0.947276	0.146472
C	0.165495	0.123050	0.078475
C	1.061325	-0.612226	0.734572
H	0.720665	-1.043790	1.682761
H	-0.587655	0.845427	-1.815780
H	1.148954	0.463895	-1.759010
H	-1.047216	0.471371	1.712365
Cl	5.238484	-1.344208	-0.500551

Structure No: RC(219+AuCl)' ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z

C	0.770661	4.166036	0.215966
C	0.007856	3.062771	0.583854
C	-1.217470	2.781946	-0.041514
C	-1.650973	3.660687	-1.045124
C	-0.891936	4.759720	-1.419666
C	0.324407	5.014500	-0.789403
H	1.709485	4.354973	0.735334
H	-2.608496	3.475535	-1.530156
H	-1.255224	5.425815	-2.199792
H	0.920223	5.881077	-1.069653
C	-2.032298	1.613756	0.286380
C	-3.030902	0.988208	-0.443723
C	-3.444302	-0.104196	0.346933
N	-1.913255	0.886991	1.429677
N	-2.749922	-0.154409	1.491277
H	-3.390433	1.279749	-1.423661
C	-4.477081	-1.104418	0.053163
C	-5.205771	-1.053579	-1.140559
C	-4.751465	-2.131631	0.965084
C	-6.182791	-2.004825	-1.414903
H	-5.010308	-0.262469	-1.863909
C	-5.727788	-3.080853	0.689803
H	-4.188485	-2.175834	1.896227
C	-6.448068	-3.022532	-0.502182
H	-6.739903	-1.949693	-2.349095
H	-5.927257	-3.872331	1.410876
H	-7.213307	-3.766831	-0.716877
H	-1.257594	1.061806	2.183559
C	1.217835	0.285555	0.539315
C	0.629987	-0.601107	-0.091760
C	1.583125	1.464231	1.346054
H	2.364603	2.044305	0.834329
H	1.986716	1.138263	2.311584
O	0.441406	2.257719	1.620340
Au	2.786851	-1.097067	-0.138037
H	-0.060576	-1.265010	-0.586265
Cl	4.869538	-2.120971	-0.527250

Structure No: TS33 ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	**Y**	**Z**
C	0.830493	4.261410	0.296275

C	0.123783	3.104032	0.602741
C	-1.031735	2.751855	-0.115941
C	-1.453757	3.610114	-1.142583
C	-0.747511	4.762140	-1.452088
C	0.399701	5.090068	-0.732145
H	1.715020	4.502845	0.883977
H	-2.351581	3.364654	-1.707003
H	-1.095448	5.408736	-2.254926
H	0.956707	5.995168	-0.966680
C	-1.807513	1.551927	0.173685
C	-2.916236	1.030328	-0.425094
C	-3.246063	-0.150213	0.315705
N	-1.452621	0.635670	1.180693
N	-2.403049	-0.351878	1.311443
H	-3.433796	1.421726	-1.292845
C	-4.358905	-1.068391	0.062332
C	-5.346404	-0.746365	-0.874995
C	-4.447325	-2.280975	0.758095
C	-6.401891	-1.619687	-1.111725
H	-5.295725	0.195504	-1.419220
C	-5.502139	-3.150859	0.519438
H	-3.675920	-2.536856	1.482274
C	-6.482231	-2.823554	-0.416992
H	-7.164907	-1.357879	-1.842676
H	-5.559084	-4.092352	1.063135
H	-7.306990	-3.508780	-0.605526
H	-1.037267	0.968010	2.052699
C	1.275073	0.231149	0.660157
C	0.149250	-0.328860	0.428660
C	1.669331	1.486540	1.352612
H	2.406243	2.037897	0.750744
H	2.145762	1.239390	2.309147
O	0.554328	2.323906	1.653881
Au	2.699982	-1.074104	-0.092290
H	-0.444626	-1.115414	-0.015325
Cl	4.421327	-2.500600	-0.894805

Structure No: PC(233+AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	**Y**	**Z**
C	0.905753	4.032615	0.511865
C	0.139733	2.888982	0.704407
C	-0.931777	2.594829	-0.158026

C	-1.220249	3.484274	-1.204374
C	-0.454406	4.622520	-1.395007
C	0.611622	4.895712	-0.537079
H	1.722836	4.237103	1.201765
H	-2.046951	3.260632	-1.876596
H	-0.685449	5.298519	-2.215182
H	1.214100	5.790010	-0.683480
C	-1.765301	1.427531	0.039035
C	-2.980956	1.072339	-0.409276
C	-3.304841	-0.202693	0.203989
N	-1.304643	0.322066	0.896059
N	-2.362230	-0.642860	0.993926
H	-3.609464	1.650270	-1.076844
C	-4.539385	-0.959109	0.010693
C	-5.572480	-0.447847	-0.783144
C	-4.691757	-2.212912	0.619759
C	-6.739777	-1.180147	-0.964305
H	-5.472223	0.524637	-1.261150
C	-5.857826	-2.939430	0.435398
H	-3.886396	-2.611799	1.233506
C	-6.883830	-2.424432	-0.357508
H	-7.538683	-0.776680	-1.583277
H	-5.969683	-3.913062	0.908784
H	-7.798484	-2.996647	-0.502872
H	-1.083166	0.681553	1.839751
C	1.177199	0.004347	0.662796
C	-0.062330	-0.368634	0.352559
C	1.503268	1.159149	1.552465
H	2.353187	1.728072	1.147584
H	1.798653	0.800650	2.547696
O	0.403990	2.068245	1.773080
Au	2.768397	-1.033717	-0.079668
H	-0.371569	-1.168049	-0.314526
Cl	4.653538	-2.224974	-0.952436

Structure No: RC(222+AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	3.071601	2.614584	-0.958577
C	1.723774	2.323521	-0.771767
C	1.176547	2.227664	0.519119
C	2.025874	2.462084	1.610885
C	3.371995	2.750370	1.426733

C	3.898575	2.823816	0.139102
H	3.458990	2.683472	-1.974426
H	1.617342	2.426096	2.620577
H	4.007908	2.931029	2.291157
H	4.950451	3.058843	-0.012753
C	-0.218883	1.841875	0.731604
C	-1.383635	2.044027	0.011191
C	-2.397095	1.391686	0.747777
N	-0.589306	1.106128	1.816181
N	-1.895632	0.813698	1.846027
H	-1.479110	2.600373	-0.912303
C	-3.822470	1.265534	0.423868
C	-4.305510	1.641035	-0.835600
C	-4.720095	0.731908	1.357200
C	-5.651367	1.488773	-1.152185
H	-3.618906	2.044528	-1.579971
C	-6.064605	0.582004	1.040222
H	-4.349664	0.431028	2.336181
C	-6.536850	0.960048	-0.215960
H	-6.009089	1.784692	-2.137410
H	-6.750235	0.167779	1.778188
H	-7.590610	0.842194	-0.463880
H	0.020817	0.729045	2.534714
C	0.642070	-0.228264	-1.788995
C	0.017623	-1.102126	-1.161881
C	1.110033	0.924614	-2.570173
H	0.510865	0.995824	-3.486278
H	2.162400	0.798710	-2.862491
O	0.913039	2.142860	-1.867172
Au	1.988386	-1.033883	-0.182058
C	-1.073347	-1.898826	-0.675010
C	-0.885610	-2.956548	0.223127
C	-2.369184	-1.538263	-1.075667
C	-1.987131	-3.645121	0.714217
H	0.125343	-3.223289	0.531576
C	-3.463740	-2.225258	-0.569852
H	-2.504038	-0.704686	-1.764559
C	-3.274120	-3.277290	0.324812
H	-1.842323	-4.466047	1.413710
H	-4.468404	-1.927067	-0.866840
H	-4.134586	-3.811791	0.723465
Cl	3.858467	-1.380983	1.208864

Structure No: TS34 ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	0.618733	4.476680	0.179945
C	0.008910	3.258522	-0.147528
C	-1.200137	2.905459	0.482760
C	-1.763742	3.809690	1.400746
C	-1.158720	5.014916	1.712837
C	0.048335	5.343149	1.095592
H	1.552235	4.722452	-0.323337
H	-2.702467	3.528990	1.877833
H	-1.618699	5.689504	2.431520
H	0.547669	6.282897	1.325247
C	-1.943600	1.652228	0.284713
C	-3.106861	1.364904	-0.341565
C	-3.368506	-0.027472	-0.071425
N	-1.512996	0.452829	0.916215
N	-2.452485	-0.555223	0.708600
H	-3.686440	2.039388	-0.961029
C	-4.486217	-0.827344	-0.574290
C	-5.578297	-0.212554	-1.196091
C	-4.474278	-2.220930	-0.428653
C	-6.641360	-0.978523	-1.661535
H	-5.607144	0.870116	-1.308821
C	-5.536753	-2.981825	-0.895426
H	-3.619728	-2.699375	0.047796
C	-6.622768	-2.362555	-1.513425
H	-7.487424	-0.490792	-2.142416
H	-5.517455	-4.064242	-0.781340
H	-7.454767	-2.961494	-1.880130
H	-1.303556	0.570172	1.914770
C	0.796647	0.230606	-0.577109
C	0.255447	-0.280791	0.480344
C	0.277032	1.271384	-1.523345
H	-0.809942	1.202521	-1.644768
H	0.724020	1.141634	-2.512939
O	0.670021	2.571238	-1.112457
Au	2.717891	-0.489437	-0.818929
C	0.407708	-1.259749	1.537305
C	0.839540	-0.864477	2.810253
C	0.133700	-2.609430	1.276947
C	1.010060	-1.815773	3.807888
H	1.048468	0.188213	3.001562
C	0.310172	-3.554908	2.278849
H	-0.208839	-2.900996	0.284545

C	0.746911	-3.158521	3.541995
H	1.353531	-1.510157	4.794248
H	0.105036	-4.604149	2.075204
H	0.883269	-3.902645	4.324899
Cl	4.944432	-1.254459	-1.180013

Structure No: PC(235+AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	0.845310	4.128051	0.189298
C	0.100659	2.993418	-0.151579
C	-1.003268	2.633477	0.649805
C	-1.332289	3.438886	1.754049
C	-0.588557	4.559624	2.080655
C	0.508196	4.899759	1.287948
H	1.692803	4.385442	-0.443300
H	-2.193861	3.153433	2.357111
H	-0.858420	5.162055	2.945104
H	1.106984	5.776365	1.529171
C	-1.868657	1.483892	0.384525
C	-3.136315	1.352605	-0.024620
C	-3.441607	-0.068807	-0.052942
N	-1.420986	0.119894	0.754509
N	-2.449875	-0.813187	0.358046
H	-3.784946	2.164103	-0.332672
C	-4.696485	-0.664515	-0.502754
C	-5.764634	0.148527	-0.897879
C	-4.837468	-2.059219	-0.532762
C	-6.958496	-0.426773	-1.316446
H	-5.668362	1.232461	-0.876837
C	-6.029708	-2.627419	-0.953334
H	-4.003281	-2.687628	-0.225397
C	-7.092198	-1.812041	-1.344748
H	-7.787379	0.209413	-1.620349
H	-6.134821	-3.710273	-0.976808
H	-8.027923	-2.260250	-1.674460
H	-1.473050	0.116474	1.790544
C	0.668346	0.075699	-0.611437
C	-0.017007	-0.364827	0.448549
C	0.076282	1.053159	-1.589465
H	-1.018810	1.008389	-1.665117
H	0.462318	0.866150	-2.596003
O	0.499124	2.383672	-1.290454

Au	2.632741	-0.408287	-0.877079
C	0.421747	-1.338622	1.470817
C	0.430434	-0.998676	2.828991
C	0.849896	-2.614154	1.086159
C	0.867432	-1.913159	3.781796
H	0.127628	0.001950	3.147284
C	1.289607	-3.525547	2.040074
H	0.826152	-2.887235	0.031646
C	1.299314	-3.177280	3.388961
H	0.880716	-1.631780	4.833263
H	1.617799	-4.515808	1.728608
H	1.643841	-3.892136	4.134346
Cl	4.950938	-0.912302	-1.220182

Structure No: RC(222+AuCl)' ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	-1.967361	4.279316	-0.101292
C	-1.008826	3.387846	-0.564565
C	0.161654	3.145533	0.182716
C	0.335155	3.820400	1.401106
C	-0.622533	4.710821	1.858114
C	-1.774837	4.940897	1.106071
H	-2.855906	4.448279	-0.706203
H	1.227939	3.625121	1.993323
H	-0.475153	5.223013	2.806387
H	-2.530162	5.637114	1.465307
C	1.169932	2.211183	-0.267387
C	2.408604	1.888901	0.143190
C	2.848779	0.769164	-0.665343
N	0.844027	1.266510	-1.354710
N	1.958692	0.385968	-1.541647
H	2.965381	2.370260	0.938596
C	4.108763	0.045727	-0.519380
C	4.977210	0.344122	0.536561
C	4.415812	-1.008053	-1.391630
C	6.128757	-0.410320	0.726063
H	4.748698	1.154098	1.226824
C	5.567897	-1.755769	-1.199877
H	3.738082	-1.241627	-2.210905
C	6.423075	-1.461708	-0.137784
H	6.795197	-0.178330	1.554421
H	5.799929	-2.575775	-1.876789

H	7.323542	-2.054107	0.015134
O	-1.187983	2.812211	-1.796031
C	-1.545846	1.423588	-1.805727
Au	-2.524136	-1.269029	-0.030929
C	-0.506254	0.595511	-1.114702
C	-0.665498	-0.468191	-0.326655
C	0.436714	-1.155832	0.378904
C	0.852782	-0.693900	1.633293
C	1.057622	-2.286995	-0.166159
C	1.900431	-1.319801	2.304535
H	0.355656	0.170670	2.077169
C	2.106088	-2.906795	0.505933
H	0.726211	-2.660695	-1.135885
C	2.537981	-2.422139	1.739857
H	2.224165	-0.938359	3.272326
H	2.593299	-3.772645	0.058349
H	3.367011	-2.902887	2.257588
H	-2.523471	1.268301	-1.327467
H	-1.630166	1.176480	-2.872350
Cl	-4.669797	-2.258807	0.367912
H	0.751301	1.798025	-2.239220

Structure No: TS35 ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	-2.134934	4.241058	-0.038256
C	-1.120746	3.415707	-0.504254
C	0.068440	3.241327	0.224742
C	0.209769	3.936050	1.434652
C	-0.798746	4.766384	1.899421
C	-1.975035	4.917703	1.165496
H	-3.037806	4.346692	-0.636947
H	1.125454	3.818302	2.011832
H	-0.668741	5.296975	2.840321
H	-2.768771	5.566777	1.530047
C	1.116868	2.345666	-0.234712
C	2.285673	1.940183	0.330260
C	2.844777	0.975793	-0.571556
N	0.964573	1.573544	-1.415680
N	2.078319	0.786889	-1.626927
H	2.697855	2.270026	1.276442
C	4.081115	0.214071	-0.391744
C	4.765505	0.246678	0.828149

C	4.563667	-0.599084	-1.425523
C	5.908671	-0.522956	1.012468
H	4.395192	0.864372	1.645438
C	5.706021	-1.365103	-1.239300
H	4.029809	-0.629145	-2.373963
C	6.379332	-1.332392	-0.018417
H	6.430837	-0.493526	1.967188
H	6.072316	-1.994656	-2.048484
H	7.273099	-1.936595	0.128131
O	-1.269803	2.822974	-1.738241
C	-1.660888	1.458503	-1.749745
Au	-2.478418	-1.332075	-0.036007
C	-0.722292	0.550039	-1.038160
C	-0.580985	-0.510155	-0.329263
C	0.536010	-1.258875	0.259233
C	0.853367	-1.079409	1.610336
C	1.261550	-2.178167	-0.505278
C	1.909265	-1.785342	2.177144
H	0.275247	-0.371730	2.205406
C	2.306629	-2.892005	0.073445
H	1.007517	-2.319753	-1.555636
C	2.639382	-2.693134	1.411679
H	2.160479	-1.626276	3.224894
H	2.869828	-3.602799	-0.529887
H	3.466170	-3.243768	1.857922
H	-2.655038	1.336027	-1.293454
H	-1.731223	1.188452	-2.810550
Cl	-4.564506	-2.387893	0.387559
H	0.653086	2.056661	-2.263389

Structure No: PC(236+AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	4.089925	1.532770	0.814952
C	2.715748	1.679481	0.972075
C	1.897343	2.043191	-0.110881
C	2.507394	2.264859	-1.352157
C	3.879370	2.119723	-1.512578
C	4.673869	1.753801	-0.427574
H	4.690693	1.254182	1.679976
H	1.884704	2.552501	-2.198703
H	4.331770	2.298005	-2.486246
H	5.750423	1.646223	-0.545895

C	0.440387	2.095818	0.002432
C	-0.536921	1.740467	-0.913976
C	-1.760271	1.873147	-0.220919
N	-0.227917	2.435450	1.133813
N	-1.555917	2.305726	1.030098
H	-0.368360	1.385163	-1.925177
C	-3.113294	1.540914	-0.680104
C	-3.333546	1.039833	-1.968514
C	-4.207259	1.680582	0.183912
C	-4.614829	0.690548	-2.382971
H	-2.495880	0.918148	-2.654987
C	-5.485863	1.329532	-0.230641
H	-4.039581	2.061084	1.190761
C	-5.695480	0.830349	-1.515468
H	-4.767085	0.300545	-3.388468
H	-6.324049	1.440971	0.456035
H	-6.697542	0.552572	-1.838809
O	2.150800	1.489158	2.215563
C	2.011227	0.133489	2.625025
Au	1.390283	-1.277992	-0.189332
C	0.937872	-0.559843	1.895367
C	-0.119908	-1.007818	1.419875
C	-1.502652	-1.348033	1.227099
C	-1.974588	-1.859678	0.011870
C	-2.401511	-1.098033	2.276791
C	-3.328664	-2.124886	-0.149634
H	-1.270594	-2.039268	-0.801607
C	-3.751472	-1.370671	2.106716
H	-2.028972	-0.685747	3.213350
C	-4.216871	-1.883023	0.895741
H	-3.691963	-2.520644	-1.096291
H	-4.447280	-1.174859	2.920468
H	-5.278423	-2.087681	0.765161
H	2.964964	-0.403030	2.522061
H	1.749187	0.159451	3.689830
Cl	2.508278	-1.828388	-2.190249
H	0.185296	2.705762	2.019510

Structure No: RC(219+Au++AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	Y	Z
C	-4.296105	-3.506649	0.266710
C	-3.537377	-2.410106	-0.133969

C	-4.069711	-1.107585	-0.058583
C	-5.381198	-0.947170	0.405500
C	-6.141032	-2.041535	0.792514
C	-5.593962	-3.322149	0.728839
H	-3.861902	-4.503281	0.197990
H	-5.799960	0.057083	0.461253
H	-7.159501	-1.897104	1.146906
H	-6.184283	-4.185812	1.029554
C	-3.246659	0.065244	-0.336512
C	-3.239984	1.325785	0.257119
C	-2.116571	1.986435	-0.256937
N	-2.214176	0.058243	-1.199810
N	-1.476947	1.194427	-1.152383
H	-3.949596	1.694991	0.987818
C	-1.606378	3.322084	0.064217
C	-2.078473	4.003448	1.191477
C	-0.642406	3.935449	-0.746996
C	-1.592972	5.268152	1.504572
H	-2.822761	3.536652	1.835674
C	-0.157369	5.197958	-0.429136
H	-0.282171	3.424134	-1.638900
C	-0.629812	5.868446	0.697481
H	-1.967204	5.784914	2.386717
H	0.589162	5.664315	-1.069945
H	-0.249884	6.858453	0.944102
O	-2.276553	-2.575409	-0.634927
C	-1.302723	-3.231212	0.200614
Au	2.808847	-1.023385	0.274451
C	-0.087898	-2.425275	0.200858
C	0.891856	-1.680938	0.150283
H	-1.704441	-3.345340	1.218100
H	-1.111293	-4.237659	-0.197442
H	-1.867935	-0.740792	-1.721995
Au	0.515731	0.387128	-0.522567
Cl	5.103122	-0.459644	0.504579

Structure No: TS36 ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	**Y**	**Z**
C	1.829017	4.609785	0.098497
C	0.882772	3.698404	0.549180
C	-0.224710	3.355771	-0.249708
C	-0.351899	3.964046	-1.506965

C	0.589680	4.877916	-1.953708
C	1.683943	5.200455	-1.151439
H	2.669946	4.849311	0.746530
H	-1.203534	3.709352	-2.135963
H	0.472029	5.339624	-2.931849
H	2.427052	5.914353	-1.501439
C	-1.203238	2.376730	0.186603
C	-2.255668	1.787495	-0.429039
C	-2.766079	0.809448	0.501843
N	-1.034115	1.679844	1.426104
N	-2.083903	0.797391	1.626633
H	-2.633458	2.005467	-1.421000
C	-3.929173	-0.061099	0.304253
C	-4.626918	-0.046695	-0.908297
C	-4.348033	-0.921058	1.327940
C	-5.727252	-0.876467	-1.092861
H	-4.309928	0.612043	-1.715360
C	-5.448155	-1.745755	1.140488
H	-3.802878	-0.934420	2.270207
C	-6.140838	-1.725785	-0.070179
H	-6.263897	-0.857888	-2.039658
H	-5.768958	-2.408239	1.942470
H	-7.002980	-2.374356	-0.215429
O	1.014010	3.197196	1.822306
C	1.463313	1.845762	1.940206
Au	2.430244	-1.173095	0.087839
C	0.597128	0.870723	1.220031
C	0.688860	-0.197571	0.498867
H	2.488279	1.747126	1.554478
H	1.477467	1.657365	3.021345
H	-0.871510	2.266835	2.251954
Au	-0.709341	-1.252791	-0.483505
Cl	4.459326	-2.337204	-0.408855

Structure No: PC(237+Au++AuCl) ((SMD/M06/6-31G(d)/LANL2DZ(f)(Au) level in acetonitrile)

	X	**Y**	**Z**
C	1.585565	4.596647	0.148546
C	0.695304	3.622170	0.581746
C	-0.408292	3.258104	-0.217102
C	-0.588550	3.904554	-1.449746
C	0.299332	4.878394	-1.875627
C	1.389467	5.223448	-1.076259

H	2.424248	4.855917	0.791605
H	-1.434159	3.624682	-2.076078
H	0.146421	5.367149	-2.835385
H	2.092049	5.984175	-1.410873
C	-1.346097	2.238316	0.199659
C	-2.511713	1.775157	-0.287280
C	-2.909819	0.669356	0.562263
N	-1.015097	1.383197	1.347166
N	-2.063405	0.435561	1.530572
H	-3.043634	2.142897	-1.157284
C	-4.107111	-0.151822	0.397121
C	-5.151896	0.273408	-0.430606
C	-4.210098	-1.378958	1.067721
C	-6.285930	-0.516278	-0.580888
H	-5.088246	1.228387	-0.949380
C	-5.342166	-2.164774	0.910718
H	-3.389509	-1.711707	1.701420
C	-6.382126	-1.734331	0.086412
H	-7.097616	-0.178613	-1.222318
H	-5.414810	-3.119061	1.428989
H	-7.269312	-2.352957	-0.036938
O	0.867775	3.091006	1.833499
C	1.341095	1.737133	1.898736
Au	2.568251	-0.983461	0.121334
C	0.421464	0.798845	1.174250
C	0.702774	-0.246707	0.407511
H	2.352325	1.658944	1.476043
H	1.389471	1.526112	2.975598
H	-0.983601	1.957721	2.206836
Au	-0.591116	-1.375191	-0.630215
Cl	4.740166	-1.929734	-0.270934

Structure No: 239 ((SMD/M06/6-31+G(d)) level in DMF)

	X	**Y**	**Z**
C	4.016100	-1.207970	-0.273783
C	2.804524	-0.523239	-0.242565
C	1.599685	-1.161222	0.090476
C	1.669242	-2.541373	0.346006
C	2.870240	-3.240696	0.302129
C	4.056188	-2.570379	0.004123
H	4.920785	-0.659482	-0.537986
H	0.750213	-3.066419	0.608254
H	2.881887	-4.308700	0.515869

H	5.004554	-3.104992	-0.022777
C	0.309039	-0.466664	0.179380
C	-0.948429	-0.966034	-0.183742
C	-1.832022	0.062793	0.173741
N	0.175188	0.770015	0.722485
N	-1.134481	1.088997	0.722605
H	-1.170203	-1.921578	-0.651321
C	-3.288957	0.117433	0.020646
C	-3.992073	-0.938912	-0.580841
C	-4.028409	1.223844	0.470724
C	-5.375536	-0.892707	-0.725345
H	-3.447471	-1.811703	-0.942101
C	-5.411450	1.269590	0.326521
H	-3.504083	2.054219	0.942227
C	-6.096224	0.212224	-0.272885
H	-5.894042	-1.726718	-1.198236
H	-5.960159	2.140560	0.685133
H	-7.179028	0.249241	-0.386126
O	2.789169	0.803061	-0.630390
C	3.379410	1.680753	0.240236
C	3.771328	2.878336	-0.124604
C	4.147492	4.087671	-0.446722
H	3.460306	4.936673	-0.402408
H	5.166021	4.307544	-0.776733
H	3.472041	1.333089	1.272716

Structure No: TS37 ((SMD/M06/6-31+G(d)) level in DMF)

	X	**Y**	**Z**
C	4.440897	-0.560499	-0.444594
C	3.151592	-0.035962	-0.423584
C	2.055678	-0.801421	0.021131
C	2.325412	-2.109813	0.456069
C	3.611077	-2.637591	0.440345
C	4.677637	-1.862586	-0.014525
H	5.250894	0.072451	-0.806159
H	1.500430	-2.724296	0.816643
H	3.780320	-3.656392	0.786537
H	5.688623	-2.267235	-0.031286
C	0.679751	-0.306660	-0.005648
C	-0.511566	-1.040854	0.028335
C	-1.520218	-0.067940	-0.044320
N	0.355789	1.011015	-0.098946
N	-0.966353	1.164802	-0.108578

H	-0.622541	-2.120545	0.068538
C	-2.974873	-0.255289	-0.058175
C	-3.536007	-1.525520	0.142381
C	-3.845703	0.825024	-0.269855
C	-4.915318	-1.710206	0.131385
H	-2.884475	-2.382257	0.315273
C	-5.224670	0.640192	-0.278698
H	-3.429026	1.818580	-0.429997
C	-5.769373	-0.628273	-0.079097
H	-5.326355	-2.707065	0.289396
H	-5.880012	1.494623	-0.446474
H	-6.849102	-0.771936	-0.087565
O	2.962191	1.236435	-0.909727
C	2.693197	2.167111	0.095195
C	1.458914	2.584838	0.377489
C	0.711286	3.590380	0.856352
H	-0.102041	3.423487	1.563643
H	0.833144	4.600229	0.462654
H	3.570277	2.508561	0.648170

Structure No: 240 ((SMD/M06/6-31+G(d)) level in DMF)

	X	Y	Z
C	-4.413564	-0.595120	0.624367
C	-3.160911	-0.005088	0.475413
C	-2.110842	-0.698611	-0.151751
C	-2.370767	-1.979062	-0.660743
C	-3.626590	-2.562463	-0.532190
C	-4.646892	-1.873065	0.122982
H	-5.198253	-0.033113	1.129514
H	-1.571847	-2.522314	-1.165494
H	-3.806699	-3.555668	-0.940829
H	-5.631146	-2.326626	0.234975
C	-0.741356	-0.182835	-0.149196
C	0.420739	-0.935640	-0.102046
C	1.473058	-0.002110	-0.048770
N	-0.345701	1.134652	-0.127254
N	0.997634	1.245119	-0.067148
H	0.478305	-2.017958	-0.062114
C	2.915495	-0.260669	0.038171
C	3.402888	-1.573552	0.015575
C	3.833589	0.793203	0.146729
C	4.768856	-1.827534	0.099131
H	2.707524	-2.408174	-0.069910

C	5.198473	0.538291	0.228040
H	3.469004	1.819239	0.168469
C	5.673807	-0.772900	0.205413
H	5.126773	-2.856271	0.080405
H	5.897360	1.369958	0.311478
H	6.742978	-0.970667	0.270102
O	-2.934691	1.232970	0.980551
C	-2.515314	2.154391	-0.040177
C	-1.150158	2.324226	-0.276720
C	-0.521237	3.477938	-0.713738
H	0.408062	3.443848	-1.279962
H	-1.111854	4.394100	-0.763191
H	-3.171857	3.025097	-0.079980

Structure No: RC(240+H_2O) ((SMD/M06/6-31+G(d)) level in DMF)

	X	Y	Z
C	4.538855	-0.539836	-0.599097
C	3.240438	-0.062875	-0.450418
C	2.229141	-0.876783	0.085719
C	2.567742	-2.174609	0.491676
C	3.866553	-2.652849	0.355027
C	4.852669	-1.835973	-0.198402
H	5.291736	0.119231	-1.029520
H	1.796579	-2.813804	0.921613
H	4.108857	-3.663521	0.679605
H	5.870873	-2.205968	-0.311788
C	0.834810	-0.440023	0.119402
C	-0.295708	-1.229917	-0.003518
C	-1.384216	-0.340770	0.078573
N	0.389793	0.852862	0.264603
N	-0.958274	0.914248	0.244651
H	-0.309516	-2.302179	-0.166080
C	-2.819934	-0.637745	0.001170
C	-3.272760	-1.958665	-0.109644
C	-3.767941	0.394316	0.048089
C	-4.634659	-2.240225	-0.172013
H	-2.555083	-2.778111	-0.144005
C	-5.127916	0.111660	-0.014166
H	-3.430733	1.426446	0.138569
C	-5.568965	-1.207122	-0.124393
H	-4.966533	-3.274475	-0.255921
H	-5.849743	0.926799	0.024817

H	-6.634519	-1.428027	-0.171468
O	2.925447	1.191394	-0.883185
C	2.470146	2.020216	0.172488
C	1.159538	2.029933	0.581394
C	0.495776	3.067306	1.269978
H	-0.250773	2.793587	2.021126
H	1.120806	3.929347	1.524884
H	3.171715	2.807338	0.443815
O	-1.341146	3.699997	-1.007843
H	-0.714000	3.625477	-0.234056
H	-1.646138	2.780734	-1.069323

Structure No: TS38 ((SMD/M06/6-31+G(d)) level in DMF)

	X	Y	Z
C	4.545888	-0.565521	-0.538265
C	3.229697	-0.121999	-0.482457
C	2.213093	-0.928296	0.049332
C	2.561117	-2.195225	0.536800
C	3.875110	-2.646119	0.484289
C	4.869345	-1.831158	-0.056972
H	5.302172	0.089804	-0.967780
H	1.784663	-2.829152	0.964475
H	4.124159	-3.633579	0.869171
H	5.900445	-2.178629	-0.100842
C	0.815760	-0.505520	0.037419
C	-0.321386	-1.286375	-0.051799
C	-1.401646	-0.382530	0.018498
N	0.382084	0.794048	0.151275
N	-0.965073	0.872100	0.151946
H	-0.350225	-2.363124	-0.178094
C	-2.838904	-0.674849	-0.040035
C	-3.296145	-1.998462	-0.027509
C	-3.780892	0.361326	-0.104682
C	-4.658534	-2.279725	-0.076621
H	-2.581194	-2.819163	0.028239
C	-5.141772	0.078778	-0.151629
H	-3.438258	1.395456	-0.119036
C	-5.587789	-1.242806	-0.138260
H	-4.994515	-3.315919	-0.064100
H	-5.860115	0.896348	-0.201949
H	-6.653893	-1.462985	-0.175275
O	2.909753	1.097578	-1.023258
C	2.411027	2.014232	-0.093898

C	1.161092	1.960256	0.413890
C	0.514228	3.025362	1.168003
H	-0.018320	2.648148	2.053369
H	1.255337	3.780657	1.466910
H	3.098602	2.823670	0.147017
O	-1.211201	4.321726	-0.370188
H	-0.378166	3.667603	0.393405
H	-1.713914	3.595189	-0.767113

Structure No: 221 ((SMD/M06/6-31+G(d)) level in DMF)

	X	Y	Z
C	4.448614	-0.534225	-0.492176
C	3.151731	-0.038594	-0.489225
C	2.091894	-0.765828	0.067610
C	2.378429	-2.014142	0.637381
C	3.672213	-2.520608	0.636527
C	4.709256	-1.781566	0.068485
H	5.238756	0.060575	-0.947303
H	1.568759	-2.586006	1.089648
H	3.871415	-3.492758	1.084081
H	5.724934	-2.173487	0.063593
C	0.714873	-0.284807	0.017321
C	-0.463346	-1.002197	-0.029300
C	-1.494095	-0.037019	-0.007802
N	0.352805	1.038933	0.059808
N	-0.989252	1.197231	0.056771
H	-0.552079	-2.081199	-0.086156
C	-2.943654	-0.263255	-0.053002
C	-3.451929	-1.567526	-0.089503
C	-3.843972	0.810890	-0.061157
C	-4.824109	-1.794289	-0.133732
H	-2.770131	-2.417174	-0.082981
C	-5.215175	0.582398	-0.104396
H	-3.463235	1.830927	-0.034865
C	-5.712119	-0.720370	-0.141506
H	-5.200090	-2.816143	-0.162206
H	-5.901297	1.428496	-0.110570
H	-6.786314	-0.896752	-0.176211
O	2.908990	1.162185	-1.125398
C	2.416394	2.171266	-0.325614
C	1.189892	2.169055	0.205774
C	0.647512	3.314043	0.987527
H	0.299683	2.988667	1.977006

H	1.423821	4.076005	1.119970
H	3.098719	3.008302	-0.182631
H	-0.204188	3.780566	0.476481

The following tables and cartesian coordinates are related to Chapter 5.

1. Absolute Energies of the Structures

Energies are given in terms of ZPE-corrected total energy (E_{el}+ZPE), enthalpy (E_{el}+H) and Gibbs free-energy (E_{el}+G) as extracted from Gaussian output of each structure.

Table S22. Absolute energies of optimized structures in gas phase (ωB97XD/6-31G(d)/LANL2DZ(f))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (*i*)
276	-3909.624466	-3909.554615	-3909.729263	–
TS39S	-3909.597477	-3909.527239	-3909.703110	-183.3
PC(274+Cl$^-$)	-3909.606540	-3909.535693	-3909.713457	–
274	-3449.266770	-3449.198599	-3449.367662	–
275	-3909.626773	-3909.556303	-3909.734007	–
TS39R	-3909.607379	-3909.537748	-3909.710395	-176.3
PC(274+Cl$^-$)	-3909.608815	-3909.538888	-3909.711493	–
274	-3449.266530	-3449.198519	-3449.366600	–
TS41S	-3909.600619	-3909.530306	-3909.705827	-218.5
TS41R	-3909.586633	-3909.516379	-3909.692262	-123.6
TS43minor	-3449.235254	-3449.166946	-3449.337908	–
TS43major	-3449.243367	-3449.175968	-3449.343137	-155.6
268a-S	-3449.299049	-3449.231018	-3449.399963	–
268a-R	-3449.299581	-3449.231835	-3449.400836	–

[a]E_{el} = Total electronic energy
[b]ZPE = Zero point energy correction
[c]H = Enthalpy correction
[d]G = Gibbs free energy correction

Table S23. Absolute energies of transition states in THF (SMD-ωB97XD/6-31G(d)/LANL2DZ(f))

Compound No	Eel[a]+ZPE[b] (au)	Eel+H[c] (au)	Eel+G[d] (au)	Imaginary Frequency (*i*)
TS42S	-3909.664167	-3909.593509	-3909.771052	-216.2
TS42R	-3909.658798	-3909.589192	-3909.761165	-214.2
TS40S	-3909.651568	-3909.581747	-3909.755373	-202.2
TS40R	-3909.650373	-3909.581263	-3909.751135	-211.9

Table S24. Single point energies in THF (SMD-ωB97XD/6-311+G(d,p)/LANL2TZ(f)//ωB97XD/6-31G(d)/LANL2DZ(f))

Compound No	Eel[e] (au) (gas)	Eel[f] (au) (THF)	Eel+G[g] (au)
276	-3910.730183	-3911.537732	-3910.537553
TS39S	-3910.702421	-3911.541746	-3910.543105
PC(274+Cl$^-$)	-3910.711195	-3911.414268	-3910.417150
274	-3450.372646	-3451.175971	-3450.173031
275	-3910.731402	-3911.540218	-3910.542338
TS39R	-3910.712466	-3911.540045	-3910.539719
PC(274+Cl$^-$)	-3910.715153	-3911.412776	-3910.411542
274	-3450.372584	-3451.176023	-3450.172586
TS41S	-3910.704569	-3911.529805	-3910.532188
TS41R	-3910.690897	-3911.521236	-3910.523363
TS42S-THF	-3910.765335	-3911.525530	-3910.531097
TS42R-THF	-3910.762158	-3911.522944	-3910.524249
TS40S-THF	-3910.754173	-3911.514687	-3910.517230
TS40R-THF	-3910.754998	-3911.516190	-3910.515244
TS43minor	-3450.339748	-3451.138354	-3450.137554
TS43major	-3450.349030	-3451.147532	-3450.143895
268a-S	-3450.406131	-3451.206098	-3450.201856

[e]Eel = Total electronic energy in gas phase (ωB97XD/6-31G(d)/LANL2DZ(f))

[f]Eel = Total electronic energy in THF (SMD-ωB97XD/6-311+G(d,p)/LANL2TZ(f)//ωB97XD/6-31G(d)/LANL2DZ(f))

[g]G = Gibbs free energy correction was calculated at 333 K and the at a concentration of 1.0 mol/L using Thrular's quasiharmonic approximation in which the vibrational entropies were corrected by recomputing all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}. Calculated Gibbs free energy correction was added to single point energy E_{el} in THF.

Table S25. Single point energies in THF

(SMD-ωB97XD/6-311G(d,p)(C,H,P,N,O)/6-311+G(d,p)(Cl)/LANL2TZ(f)
//ωB97XD /6-31G(d)/LANL2DZ(f))

Compound No	Eel[e] (au) (gas)	Eel[f] (au) (THF)	Eel+G[g] (au)
276	-3910.730186	-3911.514460	-3910.514449
TS39S	-3910.702421	-3911.519251	-3910.52061
PC(274+Cl$^-$)	-3910.711195	-3911.534156	-3910.537038
274	-3450.372646	-3451.153993	-3450.151053
275	-3910.731402	-3911.516984	-3910.519104
TS39R	-3910.712466	-3911.517563	-3910.517237
PC(274+Cl$^-$)	-3910.715153	-3911.533819	-3910.532585
274	-3450.372584	-3451.154039	-3450.150602
TS43minor	-3450.339748	-3451.115181	-3450.114381
TS43major	-3450.349030	-3451.125289	-3450.121652
268a-S	-3450.406131	-3451.183889	-3450.179647
268a-R	-3450.407236	-3451.185745	-3450.180652

[e]Eel = Total electronic energy in gas phase (ωB97XD/6-31G(d)/LANL2DZ(f))
[f]Eel = Total electronic energy in THF
(SMD-ωB97XD/6-311G(d,p)(C,H,P,N,O)/6-311+G(d,p)(Cl)/LANL2TZ(f)
//ωB97XD /6-31G(d)/LANL2DZ(f))
[e]G = Gibbs free energy correction was calculated at 333 K and the at a concentration of 1.0 mol/L using Thrular's quasiharmonic approximation in which the vibrational entropies were corrected by recomputing all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}. Calculated Gibbs free energy correction was added to single point energy E_{el} in THF.

Cartesian Coordinates for the Optimized Structures Given in Paths

Structure No: 276 (reactant complex of TS39S)

	X	Y	Z
Rh	0.628732	1.391331	-0.846922
C	0.093004	1.087071	-2.730247
C	0.768229	0.131333	-3.500150
H	1.624244	-0.393344	-3.088292
C	0.337461	-0.189002	-4.786756
H	0.869989	-0.947896	-5.354512
C	-0.770202	0.449617	-5.338943
C	-1.426613	1.427996	-4.596861
H	-2.289597	1.940342	-5.014464
C	-0.992268	1.754993	-3.312852
H	-1.533036	2.508237	-2.746897
H	-1.109885	0.196789	-6.339409
P	-1.613952	0.747236	-0.164117
P	1.572508	-0.717481	-0.103202
C	-2.615751	-0.597453	-0.916242
C	-2.234852	-1.195982	-2.112330
H	-1.315992	-0.898490	-2.601634
C	-3.013247	-2.203740	-2.689528
C	-4.187539	-2.589143	-2.050094
H	-4.805248	-3.368424	-2.494530
C	-4.596562	-2.001426	-0.847590
C	-3.794230	-1.015490	-0.283891
H	-4.088104	-0.564701	0.661062
C	-2.553511	-2.845432	-3.973553
H	-1.608704	-3.379604	-3.820522
H	-3.291810	-3.557948	-4.355533
H	-2.373889	-2.085100	-4.741336
C	-5.892168	-2.404192	-0.187241
H	-6.724015	-1.784740	-0.544143
H	-6.145399	-3.447713	-0.401912
H	-5.834729	-2.284311	0.899315
C	-2.797590	2.158207	-0.164486
C	-2.382973	3.362795	0.415401
H	-1.416787	3.416682	0.903863
C	-3.173634	4.505961	0.368147
C	-4.398570	4.439534	-0.301238
H	-5.026646	5.327556	-0.350168
C	-4.825564	3.266793	-0.917878

C	-4.016947	2.128278	-0.840473
H	-4.350534	1.216018	-1.323651
C	-2.699556	5.796637	0.988095
H	-2.305559	6.476207	0.222716
H	-3.516678	6.317190	1.498660
H	-1.901796	5.619778	1.715909
C	-6.124246	3.220070	-1.684320
H	-6.818921	3.994000	-1.343509
H	-5.950294	3.379168	-2.755291
H	-6.615938	2.248287	-1.573789
C	2.013467	-0.423610	1.660427
C	2.630282	-1.363510	2.485189
H	2.878385	-2.346681	2.098141
C	2.929480	-1.063811	3.813918
C	2.590357	0.195771	4.313069
H	2.814001	0.431188	5.352255
C	1.971066	1.158020	3.516256
C	1.696134	0.827831	2.190665
H	1.179528	1.566511	1.577170
C	3.628727	-2.078670	4.683913
H	3.302887	-3.096503	4.446140
H	4.714372	-2.037436	4.535218
H	3.434642	-1.898759	5.746139
C	1.571932	2.505341	4.062923
H	2.099564	2.730191	4.994944
H	1.796159	3.304214	3.347031
H	0.495620	2.541940	4.267883
C	3.105481	-1.432979	-0.811276
C	3.847107	-0.609629	-1.657850
H	3.452968	0.368289	-1.920323
C	5.072053	-1.025125	-2.185575
C	5.533488	-2.297605	-1.855884
H	6.484327	-2.638879	-2.262267
C	4.802638	-3.156053	-1.028500
C	3.588514	-2.711594	-0.511009
H	3.002123	-3.381546	0.112370
C	5.849887	-0.123057	-3.110339
H	6.927711	-0.283528	-3.007541
H	5.585332	-0.316858	-4.156855
H	5.639939	0.932077	-2.908414
C	5.334443	-4.526076	-0.687770
H	6.108520	-4.464519	0.086571
H	4.541366	-5.180611	-0.313762
H	5.784963	-5.005933	-1.562712

C	-0.678380	-2.139300	0.839932
C	0.399553	-2.127431	-0.056487
C	0.463150	-3.091280	-1.063045
H	1.246448	-3.100369	-1.810399
C	-0.534038	-4.060077	-1.104827
N	-1.511845	-4.151352	-0.214234
C	-1.576323	-3.214345	0.720236
O	-0.488035	-4.956302	-2.109163
C	-1.560854	-5.881836	-2.189551
H	-1.366985	-6.470514	-3.087052
H	-1.590241	-6.530761	-1.308943
H	-2.520253	-5.362117	-2.276660
O	-2.576334	-3.276322	1.613401
C	-3.480675	-4.359471	1.488146
H	-4.234923	-4.197764	2.259688
H	-3.943585	-4.370023	0.497557
H	-2.973193	-5.315697	1.649918
C	-0.959105	-1.100274	1.866769
C	-0.722498	-1.401828	3.216745
N	-0.957629	-0.577209	4.229067
C	-1.467708	0.609954	3.939231
C	-1.775232	1.032799	2.648379
H	-2.211164	2.012247	2.504459
C	-1.506879	0.166456	1.591815
O	-0.197585	-2.607017	3.487159
C	0.068544	-2.901691	4.846783
H	0.525991	-3.892107	4.843634
H	0.754399	-2.166803	5.278477
H	-0.854176	-2.913000	5.435309
O	-1.692475	1.481349	4.943089
C	-1.299817	1.072474	6.243852
H	-1.550536	1.908063	6.898438
H	-1.837771	0.172167	6.554882
H	-0.224481	0.869190	6.282329
C	2.115716	2.715343	-1.572238
C	0.924375	3.442557	-1.241396
C	0.912328	4.299806	0.023477
C	2.301737	4.837064	0.376651
C	3.287591	3.676382	0.485091
C	3.415617	2.919615	-0.833117
H	2.644459	5.537934	-0.393937
H	2.264989	5.386477	1.325271
H	4.275490	4.013423	0.811526
H	2.934000	2.959956	1.238382

H	0.568285	3.715756	0.893277
H	0.191523	5.117304	-0.088022
H	0.304866	3.806911	-2.058442
H	2.269956	2.482579	-2.625057
H	3.959253	1.987074	-0.680453
Cl	4.572711	3.868440	-1.937412

Structure No: TS39S

	X	Y	Z
Rh	0.433250	1.671108	-0.504639
C	0.012027	1.504511	-2.438700
C	0.867200	0.805499	-3.294399
H	1.797219	0.386057	-2.925511
C	0.535314	0.630629	-4.637960
H	1.205785	0.068175	-5.281917
C	-0.640345	1.170404	-5.151897
C	-1.472910	1.906573	-4.312964
H	-2.386643	2.348156	-4.701411
C	-1.147512	2.080354	-2.969248
H	-1.821393	2.645254	-2.331716
H	-0.894944	1.033031	-6.198581
P	-1.658147	0.568041	0.023242
P	1.711191	-0.402546	-0.162414
C	-2.500295	-0.690850	-1.020468
C	-2.087162	-0.999244	-2.312212
H	-1.202869	-0.539120	-2.730447
C	-2.788920	-1.929139	-3.084712
C	-3.907340	-2.547821	-2.534472
H	-4.460666	-3.273562	-3.128508
C	-4.338558	-2.263217	-1.234157
C	-3.624710	-1.333634	-0.486081
H	-3.944419	-1.110646	0.528954
C	-2.312810	-2.233246	-4.481993
H	-1.286925	-2.618012	-4.467692
H	-2.952035	-2.972915	-4.974279
H	-2.304978	-1.323141	-5.091758
C	-5.561284	-2.931247	-0.656012
H	-6.456973	-2.318173	-0.812028
H	-5.744121	-3.904124	-1.123627
H	-5.451901	-3.086796	0.421933
C	-3.003344	1.801041	0.260178
C	-2.886492	2.806264	1.228417

H	-2.044736	2.810908	1.909764
C	-3.818633	3.833146	1.328584
C	-4.881693	3.860952	0.421475
H	-5.616256	4.661320	0.487006
C	-5.012525	2.894375	-0.570520
C	-4.067514	1.865248	-0.640436
H	-4.171571	1.113591	-1.416261
C	-3.664213	4.914190	2.368795
H	-3.325311	5.850592	1.910223
H	-4.614702	5.120678	2.871612
H	-2.931713	4.632597	3.131070
C	-6.136647	2.950899	-1.574734
H	-6.908520	3.663823	-1.270976
H	-5.764054	3.261262	-2.558004
H	-6.607689	1.970177	-1.699022
C	2.097956	-0.548870	1.631964
C	2.826422	-1.617705	2.154879
H	3.185624	-2.404671	1.499699
C	3.100106	-1.698433	3.519242
C	2.628921	-0.688652	4.361436
H	2.837924	-0.747579	5.428122
C	1.899799	0.392675	3.869799
C	1.644787	0.442806	2.500880
H	1.048710	1.267290	2.122339
C	3.912453	-2.847071	4.063099
H	3.669526	-3.782088	3.547790
H	4.984902	-2.665424	3.926021
H	3.736175	-2.992589	5.133485
C	1.368749	1.472920	4.777540
H	1.875473	1.465432	5.747172
H	1.509542	2.463347	4.330937
H	0.295015	1.343133	4.956700
C	3.331870	-0.752299	-0.947811
C	4.047262	0.350626	-1.407130
H	3.591321	1.330816	-1.349610
C	5.329071	0.220252	-1.945231
C	5.880600	-1.056797	-2.018900
H	6.876552	-1.181158	-2.440896
C	5.186136	-2.186959	-1.575445
C	3.910965	-2.023862	-1.039106
H	3.361774	-2.901997	-0.710741
C	6.067239	1.430670	-2.458806
H	7.145305	1.337146	-2.295439
H	5.905942	1.553871	-3.536237

H	5.725108	2.349773	-1.973101
C	5.818739	-3.553840	-1.662997
H	6.593730	-3.676272	-0.896974
H	5.078096	-4.346202	-1.518636
H	6.294875	-3.708591	-2.636788
C	-0.339826	-2.291006	0.325311
C	0.703410	-1.897173	-0.523651
C	0.885952	-2.559910	-1.736861
H	1.643015	-2.266909	-2.452610
C	0.055319	-3.639055	-2.024646
N	-0.879467	-4.090391	-1.199561
C	-1.074121	-3.424203	-0.071776
O	0.227111	-4.256292	-3.207698
C	-0.657909	-5.326380	-3.505530
H	-0.387135	-5.654474	-4.509576
H	-0.537230	-6.146435	-2.791458
H	-1.699195	-4.990257	-3.482526
O	-2.045975	-3.838846	0.753282
C	-2.794643	-4.972582	0.348693
H	-3.555157	-5.105689	1.119244
H	-3.262912	-4.803931	-0.625058
H	-2.158507	-5.860951	0.287159
C	-0.753490	-1.593418	1.570031
C	-0.499769	-2.205036	2.808358
N	-0.851708	-1.703035	3.984646
C	-1.505387	-0.551775	3.983858
C	-1.850829	0.148862	2.829228
H	-2.422068	1.060561	2.925725
C	-1.458269	-0.376865	1.601762
O	0.162802	-3.369160	2.785134
C	0.442930	-3.978021	4.034300
H	0.991832	-4.889474	3.794059
H	1.052975	-3.320294	4.660642
H	-0.480278	-4.221604	4.568427
O	-1.854297	-0.001675	5.161399
C	-1.454013	-0.691524	6.336551
H	-1.800006	-0.073692	7.165699
H	-1.911626	-1.683864	6.386051
H	-0.365741	-0.803123	6.373594
C	1.074353	3.688293	-1.125646
C	-0.051108	3.718024	-0.257779
C	0.206196	3.957430	1.230935
C	1.633208	4.437027	1.516838
C	2.665722	3.529903	0.848963

C	2.351840	3.424246	-0.621739
H	1.776055	5.442118	1.105571
H	1.802106	4.482872	2.598619
H	3.665397	3.958154	0.938165
H	2.689740	2.538915	1.320867
H	0.025630	3.031630	1.808064
H	-0.528421	4.677005	1.610366
H	-1.004339	4.060852	-0.652209
H	0.956213	3.839496	-2.191335
H	3.130477	3.156352	-1.317316
Cl	3.606384	5.651822	-1.220096

Structure No: PC(274+Cl^-) Product Complex of TS39S

	X	Y	Z
Rh	0.320526	1.739452	-0.560159
C	0.041905	1.417594	-2.504998
C	1.016947	0.786573	-3.275252
H	1.971639	0.505227	-2.843589
C	0.775852	0.524725	-4.625102
H	1.540034	0.021569	-5.210406
C	-0.418896	0.916935	-5.220704
C	-1.368858	1.597128	-4.462261
H	-2.297838	1.929062	-4.917579
C	-1.138612	1.854191	-3.113095
H	-1.896878	2.373957	-2.533780
H	-0.598191	0.715843	-6.272495
P	-1.742430	0.506100	-0.047661
P	1.717054	-0.201614	-0.078012
C	-2.472002	-0.837107	-1.067836
C	-2.003054	-1.158493	-2.337145
H	-1.128069	-0.668449	-2.739881
C	-2.633222	-2.142759	-3.103994
C	-3.732037	-2.806577	-2.567065
H	-4.227169	-3.578007	-3.154729
C	-4.213948	-2.513836	-1.286345
C	-3.574537	-1.525857	-0.545803
H	-3.936026	-1.293705	0.453062
C	-2.104512	-2.451443	-4.481050
H	-1.037585	-2.696205	-4.440827
H	-2.635401	-3.291791	-4.939163
H	-2.208349	-1.580529	-5.137830
C	-5.410845	-3.236726	-0.720380

H	-6.332753	-2.667890	-0.890406
H	-5.541309	-4.219217	-1.185199
H	-5.307963	-3.382192	0.359657
C	-3.164413	1.666195	0.084958
C	-3.168660	2.701618	1.029934
H	-2.372855	2.775420	1.761482
C	-4.162903	3.673105	1.040216
C	-5.166310	3.613766	0.067492
H	-5.946070	4.372748	0.062939
C	-5.179473	2.614451	-0.898756
C	-4.172127	1.642948	-0.879184
H	-4.185739	0.868109	-1.638770
C	-4.146500	4.787328	2.056101
H	-3.950967	5.752439	1.574579
H	-5.110393	4.869475	2.569587
H	-3.373657	4.628245	2.814164
C	-6.246695	2.560014	-1.963015
H	-7.000364	3.339033	-1.816688
H	-5.811416	2.696177	-2.959560
H	-6.756042	1.590245	-1.959860
C	2.001389	-0.226487	1.741457
C	2.801471	-1.192453	2.351605
H	3.278849	-1.962257	1.754125
C	3.011533	-1.180826	3.730033
C	2.407123	-0.181812	4.495400
H	2.572112	-0.164442	5.571266
C	1.606935	0.801026	3.914344
C	1.416712	0.758807	2.535513
H	0.771384	1.506151	2.085754
C	3.904524	-2.216611	4.366125
H	3.759543	-3.199087	3.904964
H	4.960256	-1.949253	4.241575
H	3.710785	-2.311650	5.439151
C	0.939153	1.872786	4.737982
H	1.422110	1.985996	5.713226
H	0.982120	2.841545	4.228327
H	-0.117938	1.638836	4.911038
C	3.393461	-0.544750	-0.735074
C	4.215527	0.516409	-1.124354
H	3.855839	1.541196	-1.122791
C	5.539280	0.283359	-1.522845
C	6.008737	-1.029487	-1.526535
H	7.033399	-1.216674	-1.844528
C	5.212904	-2.106500	-1.134895

C	3.905217	-1.851391	-0.736804
H	3.278945	-2.687219	-0.440383
C	6.447691	1.414524	-1.926416
H	7.238910	1.544077	-1.177696
H	6.937112	1.191480	-2.881545
H	5.912422	2.368644	-2.012472
C	5.765032	-3.510494	-1.135198
H	6.534413	-3.630005	-0.363265
H	4.981364	-4.250452	-0.945428
H	6.230271	-3.750640	-2.097268
C	-0.239943	-2.202830	0.410895
C	0.783572	-1.750556	-0.431718
C	1.022808	-2.417974	-1.632436
H	1.769325	-2.089275	-2.343223
C	0.281302	-3.563892	-1.905127
N	-0.629080	-4.066685	-1.081770
C	-0.889463	-3.391459	0.026157
O	0.518786	-4.192448	-3.069610
C	-0.267262	-5.341207	-3.351013
H	0.056276	-5.677991	-4.336332
H	-0.097798	-6.124972	-2.606830
H	-1.333008	-5.092691	-3.364427
O	-1.848340	-3.851244	0.842836
C	-2.517600	-5.037062	0.446239
H	-3.273711	-5.211183	1.212893
H	-2.988167	-4.908892	-0.532800
H	-1.823538	-5.881535	0.399673
C	-0.741154	-1.503238	1.620214
C	-0.488742	-2.049941	2.888495
N	-0.935434	-1.541466	4.029338
C	-1.685661	-0.452821	3.959570
C	-2.036819	0.178929	2.766670
H	-2.691086	1.037516	2.805457
C	-1.543356	-0.351131	1.578466
O	0.273481	-3.148994	2.932550
C	0.559369	-3.688259	4.212705
H	1.212245	-4.541595	4.025902
H	1.067130	-2.950633	4.840793
H	-0.356286	-4.014416	4.714748
O	-2.134359	0.101791	5.099970
C	-1.722550	-0.506626	6.316030
H	-2.151450	0.109788	7.106489
H	-2.096130	-1.532071	6.389727
H	-0.631038	-0.522028	6.395248

C	0.660949	3.771594	-1.267412
C	-0.427203	3.775513	-0.371224
C	-0.139663	4.060548	1.101134
C	1.291069	4.576802	1.304250
C	2.324537	3.666513	0.635347
C	1.888113	3.287162	-0.767727
H	1.366620	5.574912	0.857888
H	1.501653	4.682743	2.373962
H	3.282693	4.183537	0.491481
H	2.536088	2.785808	1.253204
H	-0.290547	3.161321	1.721537
H	-0.876606	4.784773	1.469178
H	-1.423491	4.001193	-0.742769
H	0.509617	3.893008	-2.333819
H	2.700757	3.158286	-1.481718
Cl	4.646315	4.450620	-1.823595

Structure No: 274 (Product of TS39S without chloride)

	X	Y	Z
Rh	0.193792	-0.569865	-1.934523
C	0.571761	1.250050	-2.662117
C	-0.453648	2.164651	-2.887821
H	-1.489812	1.903141	-2.702889
C	-0.150224	3.446152	-3.354206
H	-0.955041	4.159263	-3.507056
C	1.165599	3.808003	-3.623838
C	2.182652	2.873807	-3.441768
H	3.213866	3.136768	-3.658535
C	1.889998	1.596895	-2.969164
H	2.700293	0.890125	-2.812387
H	1.395060	4.804882	-3.986633
P	1.713064	-0.126979	-0.062766
P	-1.741592	-0.011002	-0.567444
C	2.068219	1.524308	0.652748
C	1.654246	2.716834	0.067757
H	1.026911	2.711064	-0.811980
C	2.012499	3.946587	0.626340
C	2.782721	3.954556	1.785898
H	3.063301	4.907359	2.230848
C	3.203437	2.769637	2.399338
C	2.838535	1.557646	1.822339
H	3.154068	0.629769	2.292958

C	1.556497	5.220475	-0.037430
H	0.469173	5.223534	-0.170231
H	1.834362	6.102120	0.547869
H	2.005009	5.319663	-1.032252
C	4.047562	2.795072	3.648853
H	5.108210	2.655754	3.409776
H	3.951419	3.748759	4.176393
H	3.758339	1.994008	4.336410
C	3.403865	-0.732292	-0.458740
C	3.654768	-2.081656	-0.740688
H	2.864876	-2.817766	-0.648964
C	4.907489	-2.514567	-1.163699
C	5.921370	-1.565912	-1.328307
H	6.904625	-1.893458	-1.659969
C	5.699113	-0.214574	-1.083475
C	4.433945	0.191215	-0.644503
H	4.265497	1.245175	-0.449475
C	5.165115	-3.970456	-1.459279
H	5.354292	-4.126962	-2.527411
H	6.044532	-4.333541	-0.917656
H	4.314143	-4.595679	-1.171820
C	6.785223	0.809117	-1.299149
H	7.776645	0.348138	-1.287073
H	6.662939	1.307015	-2.268296
H	6.759364	1.583512	-0.526549
C	-2.255495	-1.519817	0.344304
C	-3.346188	-1.502361	1.215096
H	-3.907354	-0.586758	1.370459
C	-3.725613	-2.651502	1.906400
C	-2.987892	-3.823240	1.718386
H	-3.274995	-4.722012	2.260490
C	-1.894515	-3.871734	0.855634
C	-1.547569	-2.707523	0.172434
H	-0.679704	-2.734569	-0.477772
C	-4.922683	-2.628106	2.822548
H	-5.020402	-1.658992	3.321567
H	-5.846864	-2.804036	2.260018
H	-4.854373	-3.402927	3.592001
C	-1.075021	-5.125025	0.681619
H	-1.594172	-6.001963	1.078196
H	-0.860481	-5.313131	-0.376315
H	-0.113917	-5.039733	1.202431
C	-3.332641	0.573798	-1.265011
C	-3.649030	0.207942	-2.571543

H	-2.923058	-0.336397	-3.161670
C	-4.886232	0.524530	-3.136379
C	-5.809801	1.215569	-2.356231
H	-6.778166	1.470714	-2.782078
C	-5.528314	1.588697	-1.038948
C	-4.284941	1.262282	-0.502518
H	-4.060805	1.561007	0.516788
C	-5.192830	0.151358	-4.564442
H	-6.265490	0.002747	-4.717404
H	-4.867850	0.940825	-5.252299
H	-4.679151	-0.770994	-4.853763
C	-6.561927	2.311019	-0.212320
H	-7.360126	1.625886	0.095572
H	-6.122740	2.741051	0.692260
H	-7.028369	3.121811	-0.780670
C	-0.580438	0.846032	1.853835
C	-1.325776	1.217439	0.729070
C	-1.655123	2.556452	0.528446
H	-2.187572	2.907313	-0.345634
C	-1.282990	3.472679	1.511175
N	-0.655772	3.136300	2.629962
C	-0.303371	1.869545	2.783179
O	-1.589913	4.759812	1.298485
C	-1.173989	5.697135	2.286055
H	-1.465397	6.672368	1.896731
H	-1.670348	5.504214	3.241094
H	-0.091154	5.651075	2.432920
O	0.378402	1.522508	3.878537
C	0.660339	2.548860	4.820590
H	1.243675	2.066700	5.605128
H	1.233854	3.354870	4.354999
H	-0.263605	2.962137	5.234597
C	-0.019358	-0.504385	2.103867
C	-0.550510	-1.287353	3.144061
N	-0.107414	-2.491233	3.480324
C	0.920265	-2.977549	2.801834
C	1.563978	-2.295869	1.766534
H	2.431533	-2.748520	1.310272
C	1.076700	-1.043210	1.409353
O	-1.586970	-0.775830	3.814020
C	-2.128842	-1.556920	4.870283
H	-2.955840	-0.968589	5.267959
H	-2.490059	-2.518259	4.494153
H	-1.380637	-1.735144	5.647404

O	1.378530	-4.202269	3.098753
C	0.716746	-4.908648	4.142565
H	1.227357	-5.868992	4.209185
H	0.796061	-4.369955	5.090571
H	-0.341131	-5.054479	3.904320
C	0.640209	-1.162035	-3.987768
C	1.533462	-1.828922	-3.132965
C	1.137368	-3.203100	-2.607056
C	-0.063775	-3.777299	-3.369034
C	-1.234599	-2.788052	-3.440921
C	-0.739834	-1.383843	-3.768592
H	0.261214	-4.015573	-4.388246
H	-0.387860	-4.714317	-2.906035
H	-1.930569	-3.102250	-4.227892
H	-1.813235	-2.803582	-2.510304
H	0.912027	-3.169136	-1.528241
H	1.999924	-3.873940	-2.689824
H	2.591207	-1.586360	-3.169806
H	0.978223	-0.335525	-4.602535
H	-1.415638	-0.739167	-4.323139

Structure No: 275

	X	Y	Z
Rh	0.772252	-1.215180	-1.083548
C	0.693119	-0.319616	-2.844607
C	-0.488669	-0.291741	-3.594055
H	-1.367161	-0.830130	-3.252483
C	-0.567962	0.441480	-4.779124
H	-1.505471	0.463836	-5.329104
C	0.538898	1.137787	-5.255310
C	1.733577	1.080974	-4.540347
H	2.611582	1.609923	-4.901942
C	1.813220	0.353738	-3.355426
H	2.749271	0.340599	-2.803426
H	0.475656	1.705848	-6.179167
P	1.410290	0.883821	0.055495
P	-1.529808	-0.980506	-0.337537
C	0.964624	2.579232	-0.497351
C	0.308495	2.781536	-1.708240
H	0.027105	1.935700	-2.321553
C	-0.023929	4.068427	-2.137561
C	0.306598	5.148630	-1.323588

H	0.052266	6.156964	-1.647306
C	0.952419	4.973247	-0.095120
C	1.272569	3.680816	0.309768
H	1.762571	3.527522	1.268600
C	-0.724261	4.248670	-3.459838
H	-1.667274	3.691090	-3.480960
H	-0.940883	5.302965	-3.660556
H	-0.106746	3.860225	-4.277048
C	1.313087	6.155404	0.770299
H	1.152433	5.932296	1.830225
H	2.369005	6.424865	0.647847
H	0.716002	7.036597	0.514016
C	3.231638	0.991249	0.285159
C	3.887265	-0.098380	0.866421
H	3.306489	-0.936012	1.244294
C	5.276384	-0.160918	0.947839
C	6.017876	0.897893	0.422635
H	7.104760	0.859807	0.468723
C	5.397154	1.993280	-0.177055
C	4.002142	2.028940	-0.243014
H	3.519535	2.876352	-0.719665
C	5.947012	-1.382505	1.523881
H	6.070571	-2.153779	0.752664
H	6.939879	-1.148285	1.919731
H	5.351679	-1.818605	2.332623
C	6.218155	3.132808	-0.727894
H	5.654677	3.707065	-1.469397
H	6.514397	3.823877	0.070583
H	7.134509	2.768899	-1.203500
C	-1.667188	-1.692757	1.355140
C	-2.861397	-1.756313	2.075081
H	-3.775513	-1.356719	1.646989
C	-2.899004	-2.321520	3.347987
C	-1.713883	-2.816309	3.900311
H	-1.736550	-3.253843	4.897122
C	-0.506084	-2.767360	3.207556
C	-0.506760	-2.208055	1.930305
H	0.437087	-2.148365	1.392056
C	-4.200811	-2.422228	4.103773
H	-4.686772	-3.387657	3.918480
H	-4.045093	-2.335964	5.184221
H	-4.899039	-1.637088	3.797454
C	0.779801	-3.265374	3.817006
H	0.588906	-3.941404	4.656274

H	1.383757	-3.805174	3.079439
H	1.383696	-2.428833	4.189006
C	-2.916962	-1.818617	-1.199538
C	-2.574566	-2.894358	-2.014219
H	-1.524050	-3.128680	-2.161629
C	-3.554678	-3.661024	-2.652397
C	-4.889218	-3.318157	-2.462725
H	-5.664154	-3.899345	-2.959946
C	-5.264785	-2.236906	-1.656267
C	-4.269536	-1.495809	-1.027440
H	-4.552129	-0.644045	-0.414424
C	-3.150088	-4.824775	-3.521713
H	-2.650807	-5.599887	-2.929011
H	-4.015218	-5.280724	-4.012067
H	-2.446259	-4.507186	-4.298833
C	-6.722876	-1.896327	-1.472947
H	-7.244661	-2.685448	-0.918891
H	-6.847806	-0.959630	-0.921840
H	-7.227447	-1.787745	-2.439242
C	-1.590817	1.570779	0.868214
C	-2.079571	0.763207	-0.168070
C	-2.832429	1.344686	-1.189118
H	-3.193200	0.782244	-2.040728
C	-3.113399	2.704784	-1.100867
N	-2.737092	3.473434	-0.088079
C	-1.992171	2.917887	0.856099
O	-3.816584	3.260419	-2.106599
C	-4.047625	4.658496	-2.026639
H	-4.576076	4.917076	-2.945026
H	-4.658257	4.908159	-1.153443
H	-3.103358	5.207955	-1.962962
O	-1.574593	3.687003	1.872995
C	-1.948934	5.053119	1.842095
H	-1.479239	5.500873	2.719030
H	-1.588368	5.534697	0.928737
H	-3.036167	5.165406	1.897538
C	-0.672870	1.118493	1.945013
C	-1.186057	0.948911	3.239997
N	-0.474560	0.565645	4.291735
C	0.817970	0.351112	4.100133
C	1.464777	0.516890	2.877999
H	2.531614	0.351583	2.826043
C	0.704005	0.891436	1.773218
O	-2.498959	1.170780	3.406299

C	-3.026648	0.971514	4.705284
H	-4.100277	1.139357	4.608973
H	-2.829555	-0.045557	5.056038
H	-2.596067	1.680932	5.419094
O	1.566011	-0.069986	5.139696
C	0.881548	-0.325958	6.355898
H	1.644025	-0.684900	7.048260
H	0.413768	0.582690	6.746197
H	0.106872	-1.087060	6.215414
C	2.304436	-2.437844	-1.922625
C	3.396259	-2.833002	-0.980099
C	2.885340	-3.610188	0.227058
C	1.973275	-4.760471	-0.199615
C	0.739722	-4.263664	-0.969487
C	1.044155	-3.116245	-1.940751
H	2.557484	-5.438205	-0.831688
H	1.657088	-5.334213	0.679394
H	0.305997	-5.102202	-1.528630
H	-0.031160	-3.965190	-0.246085
H	2.323289	-2.904245	0.858264
H	3.725721	-3.970182	0.829239
H	3.991463	-1.971343	-0.684667
H	2.668094	-2.022769	-2.858646
H	0.550677	-3.189757	-2.910145
Cl	4.658517	-3.881480	-1.857630

Structure No: TS39R

	X	**Y**	**Z**
Rh	0.743626	-1.199273	-1.217310
C	0.732131	-0.028954	-2.828140
C	-0.414793	0.226396	-3.581627
H	-1.352311	-0.263593	-3.343575
C	-0.380605	1.123993	-4.651308
H	-1.293293	1.322242	-5.207160
C	0.805856	1.757550	-5.004562
C	1.966723	1.471635	-4.288056
H	2.906402	1.946664	-4.556334
C	1.932523	0.584122	-3.216288
H	2.846759	0.394040	-2.659524
H	0.830128	2.456433	-5.835549
P	1.536555	0.670483	0.206380
P	-1.556663	-0.844391	-0.513754

C	1.222994	2.456786	-0.084382
C	0.673114	2.916860	-1.276782
H	0.354538	2.217333	-2.037264
C	0.497135	4.284353	-1.503782
C	0.875677	5.180288	-0.508287
H	0.741268	6.248113	-0.673910
C	1.422938	4.743877	0.703579
C	1.589304	3.377868	0.904918
H	2.009664	3.023527	1.843063
C	-0.089993	4.745204	-2.813283
H	-1.062859	4.273687	-2.990826
H	-0.222228	5.831655	-2.837165
H	0.560046	4.459336	-3.647668
C	1.850916	5.728748	1.763161
H	1.686255	5.324076	2.766907
H	2.918934	5.960366	1.672990
H	1.301693	6.672164	1.680374
C	3.363756	0.645112	0.420061
C	4.003732	-0.500284	0.900770
H	3.423081	-1.341567	1.260824
C	5.391616	-0.636316	0.874306
C	6.146083	0.418525	0.362821
H	7.229280	0.323629	0.321776
C	5.542494	1.577698	-0.125038
C	4.150782	1.678765	-0.100060
H	3.685299	2.571980	-0.503164
C	6.026734	-1.930332	1.310999
H	5.870536	-2.701650	0.543167
H	7.103292	-1.814599	1.466731
H	5.583677	-2.294795	2.244423
C	6.380312	2.712451	-0.659882
H	5.802760	3.348946	-1.337194
H	6.746957	3.345843	0.157036
H	7.254034	2.339188	-1.203237
C	-2.005849	-1.703477	1.055363
C	-3.244617	-1.503588	1.670663
H	-3.963798	-0.813838	1.241602
C	-3.570076	-2.161680	2.853238
C	-2.621043	-3.006117	3.437085
H	-2.860392	-3.505061	4.374585
C	-1.376462	-3.219235	2.851267
C	-1.095123	-2.573343	1.646723
H	-0.132380	-2.742320	1.182944
C	-4.927590	-1.971789	3.482458

H	-5.650952	-2.686995	3.072794
H	-4.892397	-2.125128	4.565810
H	-5.314932	-0.965575	3.293327
C	-0.327991	-4.085329	3.501703
H	-0.734499	-4.633940	4.356684
H	0.079266	-4.815722	2.794112
H	0.509854	-3.474442	3.858912
C	-2.965925	-1.342318	-1.588246
C	-2.738200	-2.359538	-2.510861
H	-1.737653	-2.760346	-2.620635
C	-3.767883	-2.861737	-3.311837
C	-5.040533	-2.318580	-3.169781
H	-5.851365	-2.691492	-3.792973
C	-5.303629	-1.297036	-2.251140
C	-4.259624	-0.818343	-1.465725
H	-4.459823	-0.011462	-0.767541
C	-3.478065	-3.951942	-4.312246
H	-3.029733	-4.824240	-3.824128
H	-4.387593	-4.280723	-4.823089
H	-2.769612	-3.605659	-5.073350
C	-6.697192	-0.738681	-2.104581
H	-7.327852	-1.411881	-1.511674
H	-6.686196	0.233735	-1.603349
H	-7.179439	-0.611975	-3.079266
C	-1.394843	1.504678	1.043899
C	-1.884249	0.927457	-0.135998
C	-2.505353	1.737643	-1.085330
H	-2.854877	1.360757	-2.037232
C	-2.678621	3.085391	-0.782449
N	-2.310119	3.638016	0.364827
C	-1.673348	2.870280	1.236381
O	-3.267149	3.857403	-1.714142
C	-3.387925	5.240565	-1.416564
H	-3.845134	5.687017	-2.300166
H	-4.020921	5.401014	-0.538795
H	-2.406634	5.687448	-1.229892
O	-1.245941	3.422299	2.379764
C	-1.511585	4.801830	2.569605
H	-1.030922	5.059850	3.514055
H	-1.092647	5.395405	1.752415
H	-2.588232	4.988634	2.629879
C	-0.579903	0.793200	2.060521
C	-1.146513	0.503690	3.311893
N	-0.525929	-0.144374	4.288182

C	0.725723	-0.518442	4.070090
C	1.432694	-0.233650	2.902222
H	2.473520	-0.515989	2.842769
C	0.765741	0.427828	1.875134
O	-2.411260	0.899773	3.514248
C	-2.971826	0.636626	4.788991
H	-3.998053	1.002174	4.733566
H	-2.959178	-0.434768	5.007543
H	-2.423928	1.164993	5.575344
O	1.368033	-1.219314	5.021612
C	0.631549	-1.533057	6.194379
H	1.306358	-2.128736	6.809699
H	0.333764	-0.624804	6.726732
H	-0.267535	-2.107569	5.949563
C	2.047404	-2.490327	-2.395290
C	2.824450	-2.528501	-1.225586
C	2.239990	-3.218734	-0.021065
C	1.471031	-4.479681	-0.418959
C	0.376430	-4.195157	-1.460950
C	0.715076	-3.003679	-2.352769
H	2.216508	-5.165474	-0.830665
H	1.036507	-4.948245	0.470973
H	0.247550	-5.080733	-2.096385
H	-0.590452	-4.031938	-0.967646
H	1.562946	-2.509840	0.515866
H	3.033803	-3.453060	0.690950
H	3.680394	-1.880703	-1.124154
H	2.449895	-2.033877	-3.291130
H	0.168978	-2.952770	-3.293511
Cl	4.681288	-4.179593	-1.524756

Structure No: PC(274+Cl^-) (Product complex of TS39R)

	X	**Y**	**Z**
Rh	0.703726	-1.130042	-1.314487
C	0.672451	0.166096	-2.833872
C	-0.484868	0.476698	-3.547329
H	-1.424000	-0.018469	-3.325729
C	-0.455045	1.438838	-4.559771
H	-1.372958	1.680932	-5.088693
C	0.733977	2.078864	-4.891760
C	1.903282	1.735427	-4.215383
H	2.844616	2.213948	-4.470347

C	1.875643	0.784015	-3.199934
H	2.796205	0.545776	-2.673140
H	0.753790	2.827011	-5.678477
P	1.541298	0.613162	0.200714
P	-1.590168	-0.791083	-0.564191
C	1.219200	2.415002	0.044011
C	0.663292	2.978290	-1.099557
H	0.323122	2.348957	-1.909579
C	0.511614	4.362735	-1.215306
C	0.918623	5.169454	-0.157067
H	0.804245	6.249380	-0.236823
C	1.471814	4.627905	1.008765
C	1.615889	3.247776	1.098218
H	2.045814	2.814185	1.997679
C	-0.081930	4.935626	-2.476830
H	-1.064801	4.495600	-2.677992
H	-0.195902	6.022313	-2.411730
H	0.553692	4.707552	-3.339685
C	1.931742	5.517409	2.137026
H	1.773044	5.037468	3.107960
H	3.002534	5.736485	2.049550
H	1.398783	6.473645	2.137294
C	3.372879	0.584257	0.346726
C	4.048951	-0.564523	0.763851
H	3.501357	-1.442755	1.083873
C	5.443016	-0.649335	0.736512
C	6.156223	0.449603	0.260749
H	7.242061	0.393965	0.216461
C	5.513431	1.604645	-0.185242
C	4.121434	1.664224	-0.139653
H	3.627187	2.561300	-0.495777
C	6.128991	-1.922658	1.146127
H	5.980910	-2.688050	0.366381
H	7.202501	-1.768103	1.289486
H	5.710494	-2.313682	2.080483
C	6.315850	2.776241	-0.694772
H	5.675683	3.517033	-1.183497
H	6.840665	3.278200	0.126814
H	7.072758	2.451898	-1.416526
C	-2.018429	-1.763409	0.942208
C	-3.245974	-1.578728	1.584744
H	-3.953492	-0.845214	1.212295
C	-3.574002	-2.309051	2.722700
C	-2.640130	-3.216809	3.231667

H	-2.881427	-3.774890	4.134700
C	-1.409462	-3.420374	2.614440
C	-1.122825	-2.695627	1.456133
H	-0.169661	-2.858526	0.971251
C	-4.917277	-2.129841	3.384321
H	-5.651897	-2.831937	2.972164
H	-4.859889	-2.311210	4.462378
H	-5.303614	-1.117544	3.229611
C	-0.379809	-4.364599	3.180459
H	-0.782534	-4.942877	4.017331
H	-0.027843	-5.070642	2.420558
H	0.496015	-3.811781	3.540701
C	-3.033616	-1.189219	-1.634940
C	-2.868438	-2.191013	-2.587158
H	-1.892731	-2.641303	-2.718310
C	-3.932362	-2.623117	-3.383569
C	-5.176656	-2.027085	-3.204931
H	-6.013254	-2.345205	-3.824274
C	-5.379138	-1.025265	-2.250434
C	-4.301643	-0.616554	-1.470146
H	-4.457008	0.170903	-0.739517
C	-3.709516	-3.698061	-4.417250
H	-3.293079	-4.602333	-3.960160
H	-4.641829	-3.971442	-4.919365
H	-3.000091	-3.363582	-5.182689
C	-6.744684	-0.414004	-2.058464
H	-7.382480	-1.066362	-1.450114
H	-6.680443	0.554010	-1.552776
H	-7.250379	-0.262914	-3.017479
C	-1.358197	1.423837	1.169016
C	-1.871992	0.951812	-0.046294
C	-2.491196	1.842786	-0.921653
H	-2.854438	1.548438	-1.897369
C	-2.644521	3.163282	-0.507923
N	-2.255480	3.615344	0.675716
C	-1.616472	2.773725	1.474027
O	-3.234547	4.014638	-1.365491
C	-3.333187	5.371405	-0.956280
H	-3.804691	5.890177	-1.791467
H	-3.944680	5.466750	-0.054293
H	-2.342803	5.792177	-0.757461
O	-1.165117	3.228414	2.649526
C	-1.412489	4.591268	2.953627
H	-0.922126	4.765486	3.912061

H	-0.992191	5.245153	2.184457
H	-2.486239	4.784440	3.037911
C	-0.532545	0.622470	2.106605
C	-1.072686	0.244477	3.345994
N	-0.438355	-0.484406	4.253844
C	0.800983	-0.860372	3.976181
C	1.482799	-0.500465	2.812996
H	2.515571	-0.796271	2.702656
C	0.801955	0.249586	1.859840
O	-2.326004	0.639897	3.609698
C	-2.857137	0.293528	4.877453
H	-3.881590	0.667990	4.873382
H	-2.846514	-0.790070	5.023524
H	-2.285569	0.764539	5.683099
O	1.456074	-1.637815	4.854054
C	0.748040	-2.029786	6.021126
H	1.437864	-2.663289	6.579033
H	0.462821	-1.159247	6.619255
H	-0.156029	-2.589259	5.760175
C	1.865300	-2.364606	-2.701061
C	2.600338	-2.267370	-1.515643
C	2.186697	-3.128777	-0.347615
C	1.492971	-4.410231	-0.810905
C	0.293935	-4.113249	-1.720382
C	0.550170	-2.890034	-2.593734
H	2.260527	-4.978163	-1.346759
H	1.178612	-5.003622	0.054513
H	0.107756	-4.971709	-2.378770
H	-0.622508	-3.977473	-1.132042
H	1.514608	-2.549451	0.335495
H	3.082378	-3.368093	0.229995
H	3.567763	-1.783006	-1.498510
H	2.207278	-1.866326	-3.600410
H	-0.067445	-2.793022	-3.484332
Cl	4.997227	-4.087501	-1.502799

Structure No: 274 (Product of TS39-R without chloride)

	X	Y	Z
Rh	0.207922	-0.561352	-1.932843
C	0.594125	1.261774	-2.649093
C	-0.428116	2.180112	-2.874117
H	-1.465639	1.920160	-2.695314

C	-0.119696	3.463929	-3.330705
H	-0.922307	4.179670	-3.482893
C	1.198262	3.824857	-3.591027
C	2.212384	2.887403	-3.409528
H	3.245308	3.149267	-3.619362
C	1.914627	1.607966	-2.946941
H	2.723057	0.899012	-2.790988
H	1.431687	4.823672	-3.945931
P	1.712810	-0.127717	-0.048572
P	-1.739138	-0.008880	-0.578041
C	2.059988	1.519100	0.680445
C	1.649183	2.714202	0.098595
H	1.028639	2.712008	-0.786015
C	2.002316	3.941290	0.666163
C	2.764939	3.943669	1.830795
H	3.041885	4.894351	2.282499
C	3.183041	2.755920	2.440550
C	2.822759	1.546627	1.855042
H	3.136220	0.616515	2.322622
C	1.549001	5.218281	0.006552
H	0.461723	5.223714	-0.126699
H	1.828074	6.097368	0.595113
H	1.998020	5.319995	-0.987773
C	4.020625	2.775789	3.694530
H	3.728519	1.971255	4.376820
H	5.082450	2.638214	3.459811
H	3.921312	3.726911	4.226102
C	3.407832	-0.725318	-0.438802
C	3.667978	-2.069160	-0.723999
H	2.883976	-2.812099	-0.635248
C	4.923824	-2.491728	-1.157757
C	5.926816	-1.536765	-1.324816
H	6.910014	-1.853043	-1.667737
C	5.695902	-0.185279	-1.070422
C	4.432143	0.208697	-0.626624
H	4.254052	1.260563	-0.430208
C	5.172908	-3.943700	-1.481167
H	4.998240	-4.141593	-2.545874
H	6.206303	-4.228301	-1.263213
H	4.513246	-4.600953	-0.906354
C	6.795929	0.829675	-1.253621
H	6.408424	1.851301	-1.206372
H	7.556511	0.725023	-0.471590
H	7.298587	0.699211	-2.217367

C	-2.262471	-1.523310	0.319391
C	-3.360405	-1.511384	1.181277
H	-3.922354	-0.596746	1.338692
C	-3.746194	-2.664897	1.861586
C	-3.007723	-3.835891	1.671673
H	-3.299968	-4.738144	2.205150
C	-1.907036	-3.878975	0.818121
C	-1.553431	-2.710136	0.146188
H	-0.679418	-2.733223	-0.495812
C	-4.950552	-2.647028	2.768288
H	-5.869733	-2.824571	2.198110
H	-4.885967	-3.423339	3.536560
H	-5.055114	-1.679329	3.268634
C	-1.087453	-5.131831	0.641323
H	-1.606610	-6.009605	1.036030
H	-0.873270	-5.317739	-0.417081
H	-0.126241	-5.047839	1.162055
C	-3.322155	0.586160	-1.285224
C	-3.621070	0.248834	-2.602247
H	-2.886857	-0.281911	-3.195090
C	-4.851032	0.580526	-3.177475
C	-5.782167	1.257939	-2.396726
H	-6.743064	1.527047	-2.830459
C	-5.517447	1.603609	-1.067193
C	-4.283447	1.262865	-0.521299
H	-4.070443	1.543172	0.505587
C	-5.135908	0.223312	-4.614344
H	-4.913151	-0.830907	-4.811109
H	-6.184444	0.398544	-4.869301
H	-4.521749	0.823658	-5.295448
C	-6.559717	2.315032	-0.242166
H	-7.368573	1.629713	0.036016
H	-6.132903	2.720917	0.679377
H	-7.009784	3.142408	-0.799750
C	-0.594842	0.829640	1.857731
C	-1.333120	1.209633	0.731205
C	-1.662545	2.549869	0.539525
H	-2.190729	2.907046	-0.334613
C	-1.296620	3.458512	1.531627
N	-0.675948	3.113581	2.651476
C	-0.324421	1.845707	2.797056
0	-1.602566	4.747196	1.327191
C	-1.191734	5.676912	2.324058
H	-1.482756	6.654963	1.941559

H	-1.691543	5.475638	3.275552
H	-0.109388	5.630899	2.474687
O	0.349883	1.489857	3.894218
C	0.627501	2.509049	4.845309
H	1.203928	2.020026	5.630724
H	1.206596	3.316581	4.389332
H	-0.298296	2.921927	5.255525
C	-0.035513	-0.522641	2.101238
C	-0.574611	-1.313794	3.131148
N	-0.134604	-2.520668	3.460728
C	0.898086	-3.001748	2.786144
C	1.549994	-2.311674	1.761633
H	2.421341	-2.760506	1.309031
C	1.065944	-1.055887	1.411080
O	-1.615377	-0.807002	3.797881
C	-2.164914	-1.596133	4.844204
H	-2.994399	-1.010597	5.240790
H	-2.523848	-2.554351	4.458109
H	-1.422061	-1.780794	5.624931
O	1.353785	-4.229050	3.076317
C	0.684389	-4.943595	4.109707
H	1.194447	-5.904489	4.172442
H	0.756980	-4.412268	5.062389
H	-0.371758	-5.087385	3.862745
C	0.671404	-1.147683	-3.983940
C	1.558543	-1.813985	-3.121986
C	1.161455	-3.189956	-2.601346
C	-0.032072	-3.766006	-3.373996
C	-1.204250	-2.779132	-3.456964
C	-0.709775	-1.373652	-3.778608
H	0.302728	-4.003598	-4.390192
H	-0.358535	-4.703748	-2.914157
H	-1.891227	-3.094140	-4.251438
H	-1.792812	-2.796092	-2.532667
H	0.927874	-3.158140	-1.524118
H	2.025934	-3.859166	-2.677675
H	2.615911	-1.568791	-3.150333
H	1.013278	-0.319022	-4.593703
H	-1.382590	-0.730568	-4.338537

Structure No: TS41S

	X	**Y**	**Z**

Rh	0.783097	-1.239318	-0.811281
C	2.694988	-1.250032	-1.553699
C	2.642439	-0.908227	-2.918980
C	3.970062	-1.399179	-1.001263
C	3.789025	-0.693625	-3.679476
H	1.675745	-0.821666	-3.418980
C	5.127591	-1.199502	-1.756429
H	4.090249	-1.665927	0.044161
C	5.046245	-0.837844	-3.096191
H	3.699563	-0.430284	-4.730891
H	6.099194	-1.324831	-1.284372
H	5.947542	-0.680805	-3.681851
C	-1.039844	1.571666	1.485711
C	0.098213	0.848348	1.877296
C	-1.536219	1.309437	-0.986452
C	-1.254471	2.115794	0.124146
C	-1.199932	3.499876	-0.099021
C	-1.559891	3.280638	-2.326878
C	-1.696397	1.895799	-2.237769
C	-2.036398	1.757109	2.458111
C	-0.925676	0.544894	4.015808
C	0.163200	0.334675	3.168706
P	-1.515821	-0.521231	-0.758332
P	1.417706	0.461033	0.632824
N	-1.341412	4.072305	-1.287384
N	-1.992551	1.256803	3.684378
O	-0.869571	-0.009665	5.237135
O	-1.657900	3.831571	-3.551398
C	-2.001395	0.168632	6.076666
H	-2.901526	-0.244377	5.611115
H	-2.168891	1.228333	6.291073
H	-1.768030	-0.372124	6.994182
C	-1.486186	5.238331	-3.637465
H	-0.504152	5.537271	-3.257295
H	-2.258389	5.765498	-3.069263
H	-1.570696	5.474216	-4.698776
O	-0.972976	4.283032	0.964357
O	-3.109129	2.478026	2.102293
C	-0.937635	5.681197	0.736974
H	-1.901609	6.043169	0.366097
H	-0.161616	5.939821	0.011093
H	-0.715599	6.127181	1.707183
C	-4.119687	2.653129	3.081231
H	-3.739183	3.211447	3.941955

H	-4.501465	1.687666	3.425226
H	-4.908857	3.218131	2.583362
H	-1.922775	1.327608	-3.129971
H	1.015207	-0.212019	3.545652
C	1.789424	2.099062	-0.083735
C	2.023224	3.211301	0.730587
C	1.801002	2.242567	-1.467951
C	2.278486	4.458802	0.168381
H	1.993013	3.105248	1.812409
C	2.024684	3.488062	-2.056258
H	1.621235	1.379218	-2.100803
C	2.264611	4.580065	-1.225050
H	2.443407	5.556823	-1.671789
C	2.890266	0.035019	1.632115
C	4.068435	0.771083	1.560657
C	2.885526	-1.170846	2.345619
C	5.233982	0.321977	2.191761
H	4.107861	1.687839	0.981155
C	4.024246	-1.633998	2.993619
H	1.988949	-1.780591	2.373572
C	5.195596	-0.873428	2.901779
H	6.100245	-1.235026	3.387157
C	-2.272640	-1.188172	-2.287926
C	-3.490489	-1.867809	-2.297847
C	-1.520292	-1.124085	-3.465408
C	-3.965881	-2.464380	-3.467949
H	-4.073876	-1.950617	-1.385813
C	-1.974738	-1.702460	-4.648727
H	-0.551328	-0.627541	-3.458540
C	-3.200053	-2.370411	-4.630246
H	-3.561905	-2.840190	-5.542649
C	-2.760652	-0.797621	0.544227
C	-3.988777	-0.128138	0.523196
C	-2.468952	-1.679250	1.581181
C	-4.924205	-0.341872	1.530941
H	-4.210537	0.575250	-0.275956
C	-3.379322	-1.890409	2.619948
H	-1.531340	-2.221812	1.602824
C	-4.597551	-1.215590	2.574479
H	-5.320225	-1.375177	3.373271
C	1.971484	3.624953	-3.556366
H	2.332335	4.604280	-3.885791
H	0.943971	3.501590	-3.919401
H	2.583910	2.855595	-4.039060

C	2.577227	5.647925	1.046881
H	2.050775	5.574119	2.003649
H	2.282095	6.586252	0.566395
H	3.650091	5.714722	1.263893
C	6.504141	1.126757	2.074832
H	6.759466	1.298414	1.023316
H	7.347618	0.617801	2.550298
H	6.392995	2.108648	2.549012
C	4.004797	-2.934968	3.754947
H	4.772605	-3.621303	3.381162
H	3.035856	-3.434696	3.666893
H	4.202628	-2.769897	4.820051
C	-1.133467	-1.625685	-5.898414
H	-0.945861	-0.584267	-6.182965
H	-1.621047	-2.122618	-6.741930
H	-0.158598	-2.102815	-5.744126
C	-5.292929	-3.180851	-3.469886
H	-5.338487	-3.935563	-4.260576
H	-6.115334	-2.474680	-3.636710
H	-5.474295	-3.678917	-2.512696
C	-3.005926	-2.808709	3.753362
H	-2.546770	-3.726969	3.368962
H	-3.875779	-3.068210	4.365159
H	-2.263011	-2.327961	4.402112
C	-6.266007	0.345941	1.484691
H	-6.682454	0.483774	2.487760
H	-6.988261	-0.244451	0.908138
H	-6.188855	1.328925	1.008983
C	0.531312	-3.405805	-1.901167
C	-0.104619	-3.251756	-0.680602
C	0.713611	-3.235341	0.496661
C	2.059838	-3.906292	0.499399
C	2.204448	-4.839467	-0.702810
C	1.834481	-4.159085	-2.026596
H	2.852267	-3.155407	0.519321
H	2.127793	-4.477597	1.429106
H	3.226321	-5.228715	-0.753762
H	1.529227	-5.686826	-0.537624
H	2.641719	-3.512272	-2.383297
H	1.689013	-4.925491	-2.799052
H	0.339420	-2.804255	1.410932
H	-1.181312	-3.175781	-0.595740
H	-0.069890	-3.287003	-2.799980
Cl	-0.647514	-5.077327	1.710303

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	X	Y	Z
P	1.651672	-0.003901	-0.780909
P	-1.585702	0.051289	0.271351
C	1.778411	0.287599	1.024263
C	1.026610	1.301468	1.633560
C	1.102588	1.376842	3.034007
C	2.386303	-0.488379	3.195895
C	2.452171	-0.648605	1.809943
H	2.977037	-1.514371	1.411002
C	-1.083754	1.841085	0.314777
C	0.128664	2.228459	0.905060
C	0.482869	3.581512	0.784445
C	-1.375979	4.101631	-0.396389
C	-1.861372	2.797872	-0.330940
H	-2.808295	2.569376	-0.798738
C	3.325680	-0.484022	-1.356986
C	4.494536	-0.355651	-0.616345
H	4.461247	0.009087	0.405350
C	5.730721	-0.713669	-1.167111
C	5.771196	-1.173931	-2.478198
H	6.727711	-1.458512	-2.912491
C	4.611687	-1.293555	-3.252942
C	3.395742	-0.948264	-2.677866
H	2.480888	-1.045480	-3.261119
C	1.545478	1.621134	-1.626675
C	2.564061	2.568834	-1.497623
H	3.412754	2.365061	-0.850148
C	2.501070	3.775142	-2.188390
C	1.393160	4.022649	-3.005466
H	1.329949	4.970555	-3.537712
C	0.368901	3.090588	-3.157998
C	0.470064	1.878254	-2.472148
H	-0.321545	1.137212	-2.573706
C	-3.355481	0.163616	-0.193685
C	-3.664965	0.422674	-1.529674
H	-2.866247	0.561812	-2.254214
C	-4.985929	0.472441	-1.966704
C	-6.000981	0.253246	-1.035351
H	-7.038104	0.282834	-1.365464
C	-5.721092	-0.014395	0.303872

C	-4.388923	-0.054657	0.715808
H	-4.166254	-0.275796	1.754375
C	-1.597691	-0.337256	2.060683
C	-1.046185	-1.529452	2.511639
H	-0.659911	-2.235519	1.793438
C	-0.940354	-1.813852	3.874016
C	-1.456317	-0.888489	4.777712
H	-1.381123	-1.089583	5.845071
C	-2.060277	0.300299	4.351875
C	-2.105478	0.578546	2.988738
H	-2.520208	1.524308	2.649386
C	-5.297337	0.700056	-3.422552
H	-5.260624	-0.252151	-3.965065
H	-6.294159	1.130379	-3.559633
H	-4.568303	1.372549	-3.886214
C	-6.838151	-0.278541	1.282568
H	-6.473284	-0.274965	2.313992
H	-7.627162	0.476618	1.199539
H	-7.299204	-1.255739	1.096259
C	4.691462	-1.800379	-4.670621
H	3.700294	-1.864940	-5.129420
H	5.307199	-1.140023	-5.291876
H	5.143999	-2.797432	-4.704774
C	6.977540	-0.632415	-0.324012
H	7.880907	-0.752570	-0.929107
H	7.042727	0.327965	0.198745
H	6.973367	-1.421292	0.436393
C	-0.855272	3.399495	-3.981397
H	-0.636233	4.122501	-4.773298
H	-1.261327	2.495819	-4.447734
H	-1.640185	3.826751	-3.345057
C	3.620072	4.781107	-2.081340
H	4.361196	4.626730	-2.874752
H	3.247005	5.806383	-2.176222
H	4.141078	4.693571	-1.122975
C	-2.652430	1.269420	5.344418
H	-3.726740	1.090731	5.472968
H	-2.183917	1.171783	6.328810
H	-2.527518	2.303213	5.007184
C	-0.255465	-3.082935	4.313734
H	-0.125535	-3.114211	5.399938
H	-0.837940	-3.964495	4.021482
H	0.731535	-3.180308	3.845533
O	-2.112014	4.996701	-1.081610

O	1.654506	3.951538	1.319663
O	0.442623	2.383294	3.630504
O	2.993507	-1.409811	3.951502
N	-0.237807	4.497339	0.151931
N	1.765261	0.521497	3.795678
C	-1.552830	6.290837	-1.247682
H	-0.583896	6.232927	-1.753563
H	-2.268817	6.840262	-1.859815
H	-1.417155	6.789474	-0.283514
C	2.019820	5.314568	1.189020
H	3.008389	5.394308	1.642935
H	2.056976	5.610474	0.136832
H	1.311086	5.963291	1.712886
C	0.572409	2.482731	5.038675
H	-0.051435	3.329602	5.328073
H	0.228307	1.568306	5.529760
H	1.613494	2.664184	5.322815
C	2.839169	-1.302558	5.356407
H	1.779971	-1.298655	5.633714
H	3.334870	-2.182142	5.767228
H	3.305163	-0.388636	5.738231
Rh	-0.275831	-1.473452	-1.088949
C	-2.066199	-2.301814	-1.605862
C	-2.337514	-2.165240	-2.977150
C	-3.085449	-2.831367	-0.809439
C	-3.563724	-2.535285	-3.525544
H	-1.567280	-1.779014	-3.646700
C	-4.317119	-3.203771	-1.346997
H	-2.945766	-2.922193	0.265890
C	-4.563809	-3.058290	-2.708422
H	-3.734288	-2.423106	-4.593920
H	-5.091097	-3.596793	-0.692609
H	-5.521859	-3.349545	-3.129536
C	0.550515	-3.449777	-2.225520
C	1.282818	-3.017322	-1.132087
C	0.691335	-3.203145	0.153147
C	-0.249203	-4.351203	0.400808
C	-0.193613	-5.347426	-0.759140
C	-0.326578	-4.677300	-2.133726
H	-1.268403	-3.995361	0.568136
H	0.089556	-4.833001	1.322804
H	-0.969979	-6.109711	-0.639335
H	0.780204	-5.846720	-0.701056
H	-1.367946	-4.460452	-2.381988

H	0.034158	-5.370036	-2.905774
H	1.100139	-2.665204	0.994152
H	2.260286	-2.572140	-1.225541
H	0.893057	-3.157522	-3.217163
Cl	2.961494	-4.299795	1.136537

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	X	Y	Z
Rh	-1.356828	0.755885	-0.281317
C	-2.794582	-0.068551	-1.497389
C	-2.567106	0.385913	-2.808471
C	-3.921211	-0.871292	-1.290556
C	-3.423382	0.063536	-3.860259
H	-1.700619	1.011270	-3.023269
C	-4.782343	-1.201009	-2.339933
H	-4.157556	-1.235474	-0.296720
C	-4.540470	-0.738843	-3.630088
H	-3.213569	0.436962	-4.859913
H	-5.653914	-1.819315	-2.137681
H	-5.211677	-0.996986	-4.444502
C	1.895759	-1.197948	1.098263
C	0.561372	-1.494279	1.412745
C	2.109387	0.318966	-0.927006
C	2.388155	-0.883385	-0.263994
C	3.207741	-1.803790	-0.938348
C	3.386263	-0.485334	-2.777332
C	2.623991	0.531717	-2.202644
C	2.810726	-1.175943	2.166118
C	1.216545	-1.642077	3.708912
C	0.216589	-1.730424	2.741267
P	0.928545	1.506411	-0.146142
P	-0.753101	-1.418218	0.102051
N	3.687923	-1.620550	-2.162480
N	2.489078	-1.389654	3.435155
O	0.851145	-1.820822	4.988932
O	3.827907	-0.286654	-4.030437
C	1.856863	-1.642387	5.980762
H	2.314054	-0.651010	5.906697
H	2.638464	-2.403665	5.893225
H	1.344135	-1.747218	6.937779
C	4.557017	-1.347231	-4.638837
H	3.973602	-2.273113	-4.654620

H	5.501641	-1.527459	-4.116321
H	4.755708	-1.015405	-5.658793
O	3.506309	-2.940113	-0.298084
O	4.086726	-0.900327	1.869924
C	4.344664	-3.868309	-0.973578
H	5.334411	-3.438349	-1.158209
H	3.905861	-4.178222	-1.925888
H	4.432606	-4.723466	-0.302526
C	5.011010	-0.847852	2.948068
H	5.126487	-1.831662	3.414610
H	4.693146	-0.128314	3.707065
H	5.957095	-0.535269	2.504321
H	2.455037	1.442167	-2.761125
H	-0.790807	-1.968390	3.052763
C	-0.058658	-2.484429	-1.210800
C	0.453825	-3.754798	-0.932648
C	0.021492	-1.976800	-2.505964
C	1.023145	-4.526453	-1.944322
H	0.423058	-4.144654	0.082136
C	0.614057	-2.716066	-3.530938
H	-0.358093	-0.981643	-2.715403
C	1.102491	-3.988480	-3.233178
H	1.567785	-4.576546	-4.022319
C	-2.137976	-2.366822	0.840604
C	-2.560696	-3.601742	0.360365
C	-2.879940	-1.734242	1.849213
C	-3.706375	-4.218515	0.881007
H	-2.026311	-4.091624	-0.447752
C	-4.010125	-2.332262	2.396026
H	-2.585572	-0.746738	2.194766
C	-4.412129	-3.577165	1.894779
H	-5.306291	-4.046518	2.301052
C	1.102273	3.044930	-1.121046
C	1.574405	4.234312	-0.573002
C	0.612383	3.043933	-2.435154
C	1.577534	5.417301	-1.324298
H	1.941734	4.262503	0.448690
C	0.612056	4.202224	-3.204675
H	0.215783	2.126445	-2.863968
C	1.098582	5.383394	-2.631061
H	1.094576	6.298780	-3.220019
C	1.694001	1.850995	1.474619
C	3.054937	2.155771	1.587353
C	0.906335	1.754367	2.619503

C	3.628208	2.375031	2.836768
H	3.674653	2.206968	0.695369
C	1.461517	1.953945	3.886951
H	-0.143179	1.485219	2.530332
C	2.817557	2.263347	3.973734
H	3.265161	2.412348	4.954750
C	0.757548	-2.115557	-4.905866
H	-0.180901	-1.656473	-5.236507
H	1.049891	-2.867244	-5.645398
H	1.522303	-1.328872	-4.907492
C	1.537452	-5.911729	-1.648913
H	1.979860	-5.965647	-0.648860
H	2.293447	-6.222801	-2.376615
H	0.723414	-6.646529	-1.685421
C	-4.161947	-5.543365	0.324591
H	-4.381463	-5.461825	-0.746333
H	-5.064646	-5.900353	0.829211
H	-3.384557	-6.307992	0.437923
C	-4.791759	-1.657164	3.492907
H	-4.613169	-2.145989	4.458591
H	-5.868651	-1.705670	3.298779
H	-4.514480	-0.603531	3.594587
C	0.068360	4.199564	-4.609857
H	-0.174492	3.184774	-4.940102
H	0.790764	4.623342	-5.316452
H	-0.845246	4.802386	-4.676190
C	2.107307	6.690578	-0.716076
H	1.637604	6.889739	0.253515
H	1.924337	7.551076	-1.366443
H	3.188160	6.621125	-0.544483
C	0.604227	1.804772	5.117325
H	-0.231955	2.513482	5.101749
H	1.179103	1.983054	6.031132
H	0.175009	0.797640	5.176210
C	5.088643	2.724485	2.965092
H	5.222974	3.807052	3.081491
H	5.649795	2.414560	2.077979
H	5.539107	2.245495	3.840707
C	-3.964992	1.759224	0.520075
C	-2.674448	1.970683	1.056512
C	-1.769184	2.851574	0.434451
C	-2.208260	3.696541	-0.750463
C	-3.726209	3.900606	-0.747869
C	-4.456177	2.562769	-0.643661

H	-1.915471	3.222528	-1.695954
H	-1.685503	4.658492	-0.722254
H	-4.034578	4.423045	-1.659449
H	-4.012443	4.524749	0.107023
H	-4.296551	1.969378	-1.554108
H	-5.534805	2.697655	-0.542422
H	-0.949152	3.235498	1.034024
H	-2.457048	1.558238	2.037156
H	-4.508845	0.866923	0.798334
Cl	-5.389294	2.770630	2.338943

Structure No: TS42R

	X	**Y**	**Z**
Rh	-1.268871	1.067952	-0.156013
C	-2.762320	0.437702	-1.488008
C	-2.508825	0.958881	-2.769387
C	-3.847576	-0.433209	-1.356604
C	-3.263538	0.576252	-3.877383
H	-1.694322	1.667774	-2.915651
C	-4.612637	-0.817406	-2.460974
H	-4.117226	-0.827465	-0.381436
C	-4.316723	-0.326682	-3.729201
H	-3.030327	0.986921	-4.856970
H	-5.443125	-1.506186	-2.323687
H	-4.908295	-0.627860	-4.589547
C	1.846138	-1.397884	0.902618
C	0.526628	-1.527843	1.362567
C	1.818898	0.129503	-1.111630
C	2.154442	-1.089211	-0.511767
C	2.690311	-2.080887	-1.353448
C	2.418038	-0.815302	-3.219788
C	1.928691	0.269305	-2.493704
C	2.868883	-1.565738	1.848773
C	1.404115	-1.905027	3.549625
C	0.296478	-1.793942	2.708014
P	1.050187	1.489500	-0.124997
P	-0.882701	-1.212498	0.195854
N	2.833908	-1.946994	-2.664683
N	2.660161	-1.809826	3.136933
O	1.162845	-2.118117	4.853508
O	2.472442	-0.690182	-4.555157
C	2.287792	-2.140403	5.726211

H	2.850833	-1.203821	5.667113
H	2.954854	-2.975464	5.491030
H	1.873961	-2.265080	6.727762
C	2.915690	-1.821794	-5.297064
H	2.324367	-2.710385	-5.057440
H	3.972029	-2.030955	-5.100540
H	2.778615	-1.555041	-6.345860
O	3.057323	-3.234136	-0.783511
O	4.129270	-1.448850	1.415438
C	3.586667	-4.241448	-1.635836
H	4.532771	-3.918344	-2.081953
H	2.883909	-4.493490	-2.434042
H	3.757219	-5.106708	-0.994120
C	5.163699	-1.607873	2.377371
H	5.152320	-2.616175	2.803339
H	5.067667	-0.877576	3.185743
H	6.095684	-1.446586	1.833982
H	1.643519	1.174744	-3.014341
H	-0.694446	-1.913030	3.124962
C	-0.534314	-2.399284	-1.153987
C	-0.114291	-3.703296	-0.860221
C	-0.696636	-2.011922	-2.479703
C	0.128734	-4.617708	-1.880218
H	0.030796	-4.008600	0.173088
C	-0.449271	-2.909224	-3.523459
H	-1.009985	-1.001514	-2.714731
C	-0.038606	-4.201687	-3.207889
H	0.161871	-4.908790	-4.011104
C	-2.324179	-1.948938	1.063672
C	-2.951860	-3.117284	0.632135
C	-2.874325	-1.241535	2.136839
C	-4.109967	-3.583319	1.261431
H	-2.564558	-3.669231	-0.217466
C	-4.028704	-1.681189	2.782459
H	-2.403634	-0.322051	2.470239
C	-4.635245	-2.855399	2.329270
H	-5.543075	-3.206027	2.816543
C	1.597457	2.972127	-1.079464
C	0.700075	4.000555	-1.347385
C	2.913619	3.091002	-1.554975
C	1.084776	5.145774	-2.055499
H	-0.325047	3.927647	-1.015374
C	3.324077	4.213621	-2.266779
H	3.625692	2.284972	-1.412026

C	2.397836	5.237546	-2.502852
H	2.712276	6.118696	-3.059190
C	2.042868	1.581536	1.423282
C	3.435946	1.704840	1.438387
C	1.356043	1.509006	2.632842
C	4.133306	1.770692	2.642456
H	3.999966	1.723178	0.512827
C	2.029802	1.558497	3.855498
H	0.281560	1.372943	2.624640
C	3.416475	1.694112	3.841295
H	3.957133	1.731548	4.785319
C	-0.626210	-2.453429	-4.948961
H	-1.678855	-2.224793	-5.154139
H	-0.301024	-3.217485	-5.661674
H	-0.053612	-1.538701	-5.139901
C	0.552956	-6.028563	-1.561852
H	1.031568	-6.086777	-0.579254
H	1.255970	-6.414076	-2.307738
H	-0.311160	-6.704677	-1.548900
C	-4.765671	-4.858272	0.796370
H	-5.842454	-4.848090	0.992882
H	-4.343220	-5.726423	1.317436
H	-4.613058	-5.014326	-0.276299
C	-4.633117	-0.873148	3.901211
H	-5.187276	-1.508852	4.598986
H	-5.336993	-0.129730	3.505751
H	-3.864329	-0.333790	4.464165
C	4.726855	4.315600	-2.809313
H	5.150619	5.309887	-2.631685
H	4.738249	4.145976	-3.892961
H	5.389242	3.575385	-2.350026
C	0.081611	6.242280	-2.305709
H	-0.847679	5.838737	-2.723235
H	0.471189	6.990023	-3.003215
H	-0.178742	6.754890	-1.372042
C	1.261454	1.432984	5.145664
H	0.487630	2.205419	5.222355
H	1.919965	1.528781	6.014352
H	0.757964	0.461067	5.208566
C	5.632275	1.930316	2.646199
H	6.076993	1.524871	3.560567
H	5.911081	2.989929	2.587002
H	6.087481	1.423821	1.788838
C	-3.753822	2.520925	0.107271

C	-2.418607	2.973903	-0.017927
C	-1.511910	2.872718	1.063151
C	-2.017064	2.513487	2.455982
C	-3.541949	2.594230	2.584152
C	-4.257366	1.953267	1.396743
H	-1.684141	1.509251	2.736076
H	-1.549899	3.195229	3.176100
H	-3.859729	2.117768	3.517407
H	-3.847168	3.645216	2.629161
H	-4.086945	0.869037	1.369901
H	-5.337492	2.101243	1.456299
H	-0.632580	3.509474	1.045831
H	-2.174889	3.524564	-0.920817
H	-4.331864	2.357885	-0.789402
Cl	-5.020700	4.675027	0.127956

Structure No: TS40S

	X	**Y**	**Z**
P	1.528970	0.333374	-0.713301
P	-1.591751	-0.355831	0.331512
C	0.986374	1.521389	-2.002452
C	-0.047849	1.160333	-2.861470
H	-0.547623	0.203134	-2.725265
C	-0.482078	2.032229	-3.863110
C	0.171882	3.255238	-4.006966
H	-0.157637	3.944320	-4.782768
C	1.235574	3.626506	-3.176323
C	1.633752	2.748970	-2.170272
H	2.443482	3.034028	-1.503592
C	-1.682277	1.686856	-4.705342
H	-1.617101	2.134450	-5.702348
H	-1.794497	0.603863	-4.821292
H	-2.596852	2.065839	-4.231206
C	1.942616	4.942709	-3.376228
H	2.405758	5.292962	-2.448283
H	2.737656	4.848485	-4.126707
H	1.252086	5.715567	-3.729603
C	3.278607	0.168833	-1.223865
C	4.329016	0.938468	-0.733526
H	4.160300	1.666512	0.054851
C	5.623108	0.784470	-1.248104
C	5.832423	-0.137533	-2.270539

H	6.835321	-0.265839	-2.673678
C	4.786143	-0.904785	-2.797693
C	3.512800	-0.741469	-2.261999
H	2.688449	-1.338401	-2.649085
C	6.753808	1.610538	-0.690935
H	6.890778	1.416590	0.379063
H	7.698043	1.390407	-1.197761
H	6.550803	2.681796	-0.803886
C	5.047185	-1.901615	-3.896950
H	4.125222	-2.399535	-4.212930
H	5.487062	-1.415671	-4.775385
H	5.752945	-2.672288	-3.565948
C	-1.607220	-0.215406	2.163693
C	-2.493517	0.661285	2.801422
H	-3.198241	1.245244	2.214580
C	-2.470912	0.812644	4.185237
C	-1.522569	0.094641	4.924550
H	-1.479469	0.232607	6.003608
C	-0.625430	-0.778209	4.313472
C	-0.691893	-0.933054	2.926049
H	0.006478	-1.597336	2.433229
C	-3.446417	1.733874	4.871321
H	-3.004527	2.195968	5.760061
H	-3.779290	2.530683	4.198838
H	-4.338355	1.184395	5.197849
C	0.431316	-1.512994	5.097058
H	0.321139	-1.347883	6.173147
H	0.383710	-2.592178	4.911605
H	1.434818	-1.181861	4.802825
C	-3.274659	-0.940022	-0.108885
C	-4.225296	-1.309192	0.836451
H	-4.020346	-1.197931	1.896891
C	-5.451617	-1.859392	0.441238
C	-5.703023	-2.029107	-0.916470
H	-6.647269	-2.468884	-1.232820
C	-4.763904	-1.662821	-1.889157
C	-3.554231	-1.124750	-1.469553
H	-2.803747	-0.869668	-2.212950
C	-6.449958	-2.299504	1.481870
H	-6.564104	-1.546035	2.268994
H	-7.434083	-2.482517	1.039579
H	-6.122531	-3.227902	1.965736
C	-5.052277	-1.871671	-3.352771
H	-5.807292	-1.161655	-3.712231

H	-4.149991	-1.736293	-3.956967
H	-5.437215	-2.880396	-3.537883
C	-0.699660	2.351307	0.312912
C	-1.685103	1.449363	-0.119166
C	-2.685159	1.903867	-0.973968
H	-3.479921	1.268500	-1.337268
C	-2.639621	3.228608	-1.402408
N	-1.716169	4.098260	-1.018123
C	-0.781057	3.663310	-0.183221
O	-3.587140	3.623750	-2.268699
C	-3.467941	4.934485	-2.810847
H	-4.286830	5.028986	-3.525257
H	-3.562121	5.697486	-2.032080
H	-2.509104	5.061663	-3.322998
O	0.179205	4.515856	0.196454
C	0.099842	5.848712	-0.290963
H	0.996217	6.347328	0.080337
H	0.079753	5.874423	-1.383788
H	-0.792439	6.353538	0.093078
C	0.404890	2.005274	1.241107
C	0.366611	2.481413	2.565434
N	1.247062	2.158741	3.503057
C	2.229051	1.328371	3.171587
C	2.418770	0.831036	1.883698
H	3.250281	0.165092	1.686799
C	1.493431	1.192986	0.903436
O	-0.637705	3.304178	2.887430
C	-0.680439	3.795820	4.220265
H	-1.596454	4.384392	4.284134
H	-0.705179	2.978010	4.945445
H	0.185297	4.432079	4.431148
O	3.095161	0.936066	4.117880
C	2.864647	1.395811	5.445436
H	3.631970	0.916151	6.054398
H	2.963605	2.483816	5.510114
H	1.871382	1.104241	5.800402
C	1.909346	-2.555877	0.858138
C	0.840682	-3.476274	0.745043
C	1.094586	-4.758672	-0.017669
C	1.966334	-4.511136	-1.246026
C	3.286570	-3.841887	-0.863904
C	3.135824	-2.784021	0.190375
H	1.413326	-3.866893	-1.941551
H	2.168056	-5.451417	-1.769135

H	3.773692	-3.395750	-1.737628
H	3.988383	-4.586434	-0.477113
H	3.880251	-2.000484	0.212580
H	1.609945	-5.447554	0.669445
H	0.152986	-5.234429	-0.299480
Cl	4.496920	-3.683241	2.039110
Rh	0.221893	-1.659102	-0.376886
H	0.141477	-3.555237	1.573422
H	1.930985	-1.834458	1.669084
C	-1.176829	-3.064090	-0.876918
C	-2.092079	-3.767974	-0.084537
C	-1.213420	-3.291913	-2.259555
C	-3.018045	-4.645295	-0.645454
H	-2.101179	-3.618278	0.993252
C	-2.134116	-4.173440	-2.829204
H	-0.523756	-2.762072	-2.917487
C	-3.044325	-4.854986	-2.023746
H	-3.723945	-5.165966	-0.002500
H	-2.141396	-4.323450	-3.906624
H	-3.766270	-5.537649	-2.463788

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	X	**Y**	**Z**
P	1.617896	0.209738	-0.578781
P	-1.599249	-0.220347	0.171298
C	1.505809	0.784648	1.162251
C	0.535685	1.707330	1.559844
C	0.441915	1.968979	2.941644
C	2.032115	0.437914	3.468727
C	2.249692	0.111047	2.134380
H	2.970493	-0.658933	1.893173
C	-1.485965	1.635710	0.021939
C	-0.440085	2.336346	0.640390
C	-0.331580	3.706218	0.352279
C	-2.146454	3.694627	-1.001760
C	-2.370450	2.334886	-0.794348
H	-3.207635	1.867538	-1.292099
C	3.416291	0.054393	-0.947492
C	4.445558	0.458745	-0.097716
H	4.227668	0.898502	0.869311
C	5.784607	0.319151	-0.477686
C	6.075511	-0.225545	-1.726229

H	7.114857	-0.355513	-2.021269
C	5.063451	-0.602529	-2.612683
C	3.737964	-0.443228	-2.215803
H	2.946450	-0.701517	-2.916172
C	1.273007	1.630648	-1.688702
C	2.070578	2.778228	-1.643491
H	2.873214	2.855032	-0.914525
C	1.842805	3.833213	-2.523836
C	0.793414	3.723720	-3.443437
H	0.598927	4.550249	-4.125078
C	-0.010917	2.586601	-3.509751
C	0.255034	1.531533	-2.633221
H	-0.358064	0.633115	-2.666280
C	-3.334954	-0.513437	-0.355976
C	-3.618743	-0.414756	-1.724145
H	-2.825434	-0.165545	-2.423486
C	-4.896028	-0.657238	-2.213848
C	-5.901102	-1.018433	-1.308390
H	-6.901906	-1.223632	-1.684598
C	-5.645344	-1.136822	0.053527
C	-4.350730	-0.878869	0.521377
H	-4.150949	-0.995081	1.581498
C	-1.637539	-0.418433	1.993553
C	-0.816303	-1.370970	2.585119
H	-0.151643	-1.949098	1.953282
C	-0.806458	-1.560059	3.969662
C	-1.647111	-0.767772	4.748557
H	-1.651678	-0.901340	5.828932
C	-2.480518	0.204558	4.180554
C	-2.459125	0.379183	2.799155
H	-3.084105	1.146674	2.349675
C	-5.186794	-0.579982	-3.689419
H	-4.304913	-0.258857	-4.252437
H	-5.494501	-1.558387	-4.076636
H	-5.999213	0.125275	-3.899738
C	-6.720254	-1.561347	1.021500
H	-6.466308	-2.518499	1.492358
H	-6.843749	-0.827058	1.825974
H	-7.685800	-1.680181	0.520452
C	5.395622	-1.211293	-3.949249
H	5.546773	-2.292744	-3.845201
H	4.588066	-1.057182	-4.672158
H	6.315688	-0.788437	-4.365615
C	6.883872	0.778795	0.445674

H	7.051100	1.858641	0.347068
H	6.634400	0.580045	1.493133
H	7.829210	0.276116	0.219317
C	-1.187997	2.520549	-4.447855
H	-0.990001	3.052349	-5.384198
H	-1.448793	1.484989	-4.690040
H	-2.067356	2.985131	-3.982944
C	2.721856	5.057851	-2.502652
H	3.523045	4.974371	-3.247761
H	2.152593	5.963189	-2.738386
H	3.194060	5.193291	-1.524412
C	-3.392030	1.039900	5.043154
H	-4.367177	0.552187	5.166696
H	-2.971455	1.189233	6.042745
H	-3.570087	2.022172	4.594158
C	0.124469	-2.575058	4.581158
H	-0.057567	-2.693013	5.653826
H	0.003894	-3.556405	4.107849
H	1.170602	-2.275612	4.447106
O	-2.987308	4.332179	-1.832588
O	0.699609	4.359547	0.901193
O	-0.463153	2.874558	3.328272
O	2.738855	-0.233166	4.393058
N	-1.152768	4.374748	-0.447084
N	1.171951	1.367484	3.868696
C	-2.692950	5.690444	-2.140062
H	-1.702039	5.785927	-2.595137
H	-3.459676	6.000365	-2.851242
H	-2.739028	6.319049	-1.245456
C	0.830024	5.742961	0.602251
H	1.753299	6.059632	1.089415
H	0.895641	5.912311	-0.475732
H	-0.015205	6.312198	1.002194
C	-0.569100	3.136868	4.721822
H	-1.404112	3.830791	4.825103
H	-0.764253	2.219714	5.283572
H	0.346816	3.599782	5.102929
C	2.446711	0.041614	5.759524
H	1.392304	-0.147079	5.983725
H	3.077362	-0.637304	6.334880
H	2.687371	1.078613	6.013089
C	1.834811	-2.932337	-1.202658
C	0.732669	-3.774366	-1.397021
C	0.459729	-4.876148	-0.407307

C	0.644185	-4.422848	1.037660
C	1.948551	-3.644691	1.260528
C	2.455102	-2.894889	0.069891
H	-0.209418	-3.791364	1.299049
H	0.616880	-5.286438	1.709537
H	1.845674	-2.928199	2.086101
H	2.759828	-4.315759	1.558905
H	3.238201	-2.168951	0.239488
H	1.169823	-5.681142	-0.648581
H	-0.545522	-5.280029	-0.552174
Cl	4.530926	-4.287961	-0.558040
Rh	0.110042	-1.626933	-0.823678
H	0.442015	-3.975212	-2.421882
H	2.357996	-2.498278	-2.044499
C	-1.515384	-2.777314	-1.458182
C	-1.773536	-2.777882	-2.838839
C	-2.431845	-3.449424	-0.640273
C	-2.901823	-3.394653	-3.375349
H	-1.073687	-2.291971	-3.518316
C	-3.569360	-4.063364	-1.167474
H	-2.279013	-3.476288	0.437063
C	-3.812235	-4.039786	-2.538354
H	-3.071453	-3.370027	-4.449561
H	-4.270301	-4.558573	-0.499278
H	-4.697813	-4.516067	-2.950483

Structure No: TS43minor

	X	**Y**	**Z**
C	1.052032	0.926118	1.861075
C	1.863804	0.147654	1.024544
C	-1.281575	1.133148	0.856198
C	-0.123406	1.695518	1.401543
C	-0.078768	3.104993	1.456102
C	-2.122791	3.340140	0.497848
C	-2.295272	1.963757	0.372903
C	1.393356	0.955888	3.223279
C	3.185940	-0.398367	2.939989
C	2.954665	-0.519887	1.567676
P	-1.405878	-0.643256	0.419057
P	1.496466	0.078338	-0.798581
N	-1.048484	3.903346	1.038261
N	2.429853	0.323486	3.755800

O	4.238495	-1.060578	3.435275
O	-3.100022	4.126501	0.023019
C	4.481646	-0.950351	4.831791
H	3.650858	-1.370732	5.406642
H	4.623713	0.093392	5.124592
H	5.391866	-1.521644	5.012839
C	-2.952902	5.529821	0.203770
H	-2.057652	5.900484	-0.303324
H	-2.886954	5.781549	1.266013
H	-3.847246	5.971717	-0.235116
O	1.039830	3.651938	1.939802
O	0.578103	1.645932	4.031083
C	1.114305	5.069857	1.977008
H	0.341348	5.484146	2.630341
H	1.000606	5.491474	0.974467
H	2.105100	5.293063	2.373273
C	0.969977	1.803097	5.387681
H	1.947571	2.288007	5.458115
H	1.014030	0.838592	5.900180
H	0.202672	2.433871	5.836465
H	-3.185779	1.585071	-0.113085
H	3.638823	-1.115970	0.982480
C	1.648510	1.860410	-1.179920
C	2.784464	2.569227	-0.774239
C	0.585791	2.537885	-1.763791
C	2.868329	3.943495	-0.980758
H	3.601975	2.052499	-0.277261
C	0.638233	3.916579	-1.973425
H	-0.324217	1.999887	-1.991486
C	1.788986	4.597756	-1.585578
H	1.844998	5.674248	-1.736626
C	2.992291	-0.704798	-1.502408
C	3.774530	-0.049838	-2.452269
C	3.260195	-2.044826	-1.196968
C	4.828662	-0.712637	-3.089105
H	3.566092	0.983208	-2.712619
C	4.307968	-2.724790	-1.812891
H	2.638033	-2.572538	-0.478064
C	5.077072	-2.044024	-2.760647
H	5.890174	-2.569173	-3.257672
C	-3.075743	-1.212538	0.899602
C	-3.389354	-2.535968	0.569209
C	-3.983169	-0.451495	1.627517
C	-4.612129	-3.092544	0.926245

H	-2.673151	-3.140252	0.016140
C	-5.220034	-0.988855	2.001817
H	-3.746670	0.569160	1.909578
C	-5.520352	-2.297784	1.634588
H	-6.484395	-2.719185	1.912697
C	-0.454142	-1.693200	1.575865
C	-0.533159	-1.501497	2.954271
C	0.296392	-2.748994	1.065428
C	0.184578	-2.321422	3.821733
H	-1.122275	-0.680712	3.357182
C	0.999999	-3.604157	1.914020
H	0.355015	-2.896194	-0.009674
C	0.939368	-3.369075	3.285516
H	1.499283	-4.014903	3.959142
C	-0.539443	4.628141	-2.588865
H	-0.580281	4.458298	-3.671604
H	-0.482136	5.708690	-2.428010
H	-1.481203	4.265192	-2.162886
6	4.095366	4.710063	-0.557509
H	4.851723	4.708820	-1.351008
H	4.551123	4.267619	0.333414
H	3.855994	5.754407	-0.335524
C	5.690700	0.008894	-4.093393
H	5.143759	0.820380	-4.582420
H	6.056229	-0.672595	-4.867102
H	6.566576	0.449789	-3.603286
C	4.610994	-4.158084	-1.457860
H	5.366937	-4.209390	-0.665612
H	5.000998	-4.708019	-2.319283
H	3.718888	-4.678091	-1.095783
C	-6.191425	-0.167529	2.811200
H	-7.227786	-0.435570	2.585469
H	-6.065835	0.902182	2.619411
H	-6.035595	-0.331527	3.883924
C	-4.951459	-4.518181	0.573062
H	-4.959921	-5.149778	1.468536
H	-4.223458	-4.941302	-0.125807
H	-5.943083	-4.588707	0.114324
C	1.846961	-4.718808	1.355770
H	1.594135	-4.925945	0.310222
H	1.715758	-5.646436	1.921415
H	2.911672	-4.457384	1.399285
C	0.193203	-2.052756	5.303414
H	1.100421	-1.498456	5.573639

H	0.184051	-2.981662	5.881801
H	-0.667929	-1.450444	5.607350
C	-0.300304	-1.247532	-3.889456
C	-1.645053	-1.659553	-3.678952
C	-1.967193	-3.096320	-3.344046
C	-0.911753	-3.798101	-2.484949
C	0.523778	-3.411200	-2.862031
C	0.696825	-1.948924	-3.208967
H	-1.085190	-3.533984	-1.437432
H	-1.035904	-4.883156	-2.560559
H	1.216806	-3.687901	-2.061002
H	0.851193	-3.976031	-3.747734
H	1.719002	-1.610742	-3.335652
H	-2.074821	-3.608040	-4.311854
H	-2.949121	-3.152727	-2.862387
Rh	-0.579050	-0.760424	-1.778553
H	-0.075589	-0.358093	-4.471460
C	-2.503405	-0.025103	-2.362385
C	-2.378076	1.200466	-3.028691
C	-3.771305	-0.420834	-1.943045
C	-3.458958	2.072156	-3.125898
H	-1.438964	1.482920	-3.494425
C	-4.859989	0.444656	-2.053610
H	-3.928117	-1.399205	-1.508044
C	-4.703170	1.706369	-2.617493
H	-3.328339	3.032955	-3.615205
H	-5.830674	0.122732	-1.687976
H	-5.545665	2.386379	-2.689851
H	-2.399429	-1.176258	-4.285326

Structure No: TS43major

	X	**Y**	**Z**
Rh	-0.394156	0.013573	-1.914861
C	-1.945338	-1.355191	-2.444469
C	-1.332733	-2.579336	-2.740190
C	-3.312305	-1.318916	-2.188010
C	-2.067373	-3.761785	-2.685162
H	-0.277278	-2.618088	-3.002259
C	-4.046355	-2.503294	-2.139810
H	-3.816336	-0.374404	-2.013345
C	-3.426331	-3.726699	-2.376654
H	-1.578110	-4.709279	-2.890947

H	-5.109467	-2.463813	-1.920641
H	-4.001787	-4.646817	-2.346070
C	0.590677	0.700360	2.050979
C	-0.542334	1.254426	1.439294
C	1.414403	-1.206075	0.605822
C	0.985147	-0.708018	1.837589
C	0.807671	-1.652109	2.868063
C	1.282551	-3.408630	1.508958
C	1.535445	-2.580979	0.414725
C	1.334297	1.540760	2.893094
C	-0.049766	3.305590	2.552351
C	-0.881015	2.577295	1.696628
P	1.667212	-0.077225	-0.822810
P	-1.486359	0.226499	0.223854
N	0.969982	-2.957526	2.716815
N	1.028293	2.807713	3.139585
O	-0.374234	4.588842	2.768400
O	1.373817	-4.730965	1.312417
C	0.494873	5.346388	3.603470
H	1.494816	5.410923	3.163213
H	0.572902	4.898019	4.597179
H	0.042792	6.335848	3.666728
C	1.122795	-5.572919	2.432692
H	0.123964	-5.393430	2.840140
H	1.863351	-5.404434	3.219599
H	1.202074	-6.590114	2.049580
O	0.432330	-1.182979	4.060476
O	2.432296	1.021817	3.449705
C	0.250995	-2.131911	5.103751
H	1.193144	-2.634925	5.338543
H	-0.492783	-2.880958	4.819842
H	-0.094025	-1.554529	5.961463
C	3.203275	1.876160	4.283585
H	2.630877	2.183338	5.163387
H	3.521168	2.767692	3.735867
H	4.067637	1.283268	4.583202
H	1.830753	-3.021122	-0.529073
H	-1.754327	3.058646	1.278899
C	-1.954442	-1.219347	1.237655
C	-2.412185	-1.022663	2.546639
C	-1.859714	-2.508152	0.724738
C	-2.784017	-2.105885	3.336464
H	-2.468319	-0.018668	2.960092
C	-2.218191	-3.612668	1.501880

H	-1.483319	-2.669175	-0.277456
C	-2.676016	-3.393283	2.797938
H	-2.954722	-4.246640	3.413729
C	-3.056041	1.142228	-0.009829
C	-4.280408	0.632593	0.418303
C	-3.033622	2.347818	-0.719523
C	-5.472924	1.312936	0.150977
H	-4.322741	-0.312302	0.950132
C	-4.204262	3.045762	-1.001292
H	-2.086721	2.751824	-1.064274
C	-5.417207	2.510422	-0.558528
H	-6.341281	3.041881	-0.776167
C	3.045736	-0.895765	-1.726358
C	3.161127	-0.802119	-3.112534
C	4.057789	-1.553870	-1.013528
C	4.252992	-1.346627	-3.792383
H	2.404807	-0.293929	-3.693253
C	5.155778	-2.110756	-1.664492
H	3.983120	-1.665332	0.063457
C	5.237633	-1.997887	-3.054110
H	6.090816	-2.432491	-3.571224
C	2.446599	1.453729	-0.190542
C	3.674327	1.433104	0.475603
C	1.794927	2.668604	-0.387748
C	4.246138	2.613275	0.944355
H	4.194245	0.496237	0.644064
C	2.340620	3.865173	0.076833
H	0.825801	2.679810	-0.872158
C	3.565520	3.816941	0.739263
H	4.005752	4.741251	1.108331
C	-2.100131	-5.000037	0.925353
H	-2.846238	-5.155434	0.138113
H	-2.251651	-5.768115	1.689706
H	-1.113038	-5.151471	0.475345
C	-3.302037	-1.891344	4.736291
H	-2.846147	-1.008678	5.195277
H	-3.094826	-2.754307	5.376587
H	-4.387738	-1.739133	4.733063
C	-6.784996	0.756568	0.642667
H	-7.633966	1.218406	0.131139
H	-6.905309	0.939031	1.716696
H	-6.840808	-0.325601	0.486983
C	-4.168143	4.320232	-1.805381
H	-4.885538	5.053801	-1.425515

H	-4.425705	4.125096	-2.853639
H	-3.174098	4.777805	-1.785343
C	6.224455	-2.841850	-0.892052
H	6.116479	-2.687285	0.185176
H	7.224086	-2.505694	-1.185625
H	6.172023	-3.919924	-1.081312
C	4.373284	-1.208257	-5.289022
H	3.401748	-1.016313	-5.755004
H	4.791149	-2.113349	-5.739827
H	5.036618	-0.375725	-5.550600
C	1.590416	5.160157	-0.104537
H	1.167880	5.236738	-1.112207
H	2.240363	6.025476	0.053928
H	0.758318	5.229067	0.606202
C	5.586253	2.589825	1.635264
H	5.677336	3.401736	2.363285
H	6.398969	2.706755	0.908949
H	5.744991	1.642421	2.159308
C	-1.449727	0.153397	-4.027081
C	-0.033884	0.294590	-4.018522
C	0.495611	1.415567	-3.338259
C	-0.288162	2.719962	-3.311634
C	-1.530692	2.658122	-4.203361
C	-2.346340	1.380765	-3.978294
H	-0.570772	2.984989	-2.288973
H	0.378135	3.521551	-3.652611
H	-2.158232	3.537647	-4.029300
H	-1.212332	2.692971	-5.251967
H	-2.888651	1.437187	-3.030793
H	-3.107495	1.280453	-4.759460
H	1.575237	1.524302	-3.291258
H	0.585931	-0.486777	-4.446358
H	-1.838750	-0.679079	-4.597800

Structure No: 268a-S

	X	**Y**	**Z**
Rh	0.858049	1.315063	0.696032
C	3.258556	1.725473	2.373883
C	2.894192	1.253042	3.646030
C	4.032731	0.891621	1.560898
C	3.303063	0.005521	4.094649
H	2.305502	1.888276	4.303713

C	4.438846	-0.367137	2.009834
H	4.362667	1.216578	0.580621
C	4.084496	-0.810785	3.274648
H	3.025444	-0.326502	5.090678
H	5.045854	-0.989640	1.360122
H	4.416977	-1.782782	3.625933
C	-1.253949	-1.303610	-1.619819
C	0.027986	-0.855994	-1.956890
C	-1.641663	-0.891273	0.859943
C	-1.585634	-1.744059	-0.246263
C	-1.711433	-3.122475	0.017470
C	-1.840161	-2.813387	2.261650
C	-1.752726	-1.427202	2.141714
C	-2.200978	-1.334835	-2.653270
C	-0.725578	-0.545287	-4.191327
C	0.315615	-0.477924	-3.261615
P	-1.356405	0.922082	0.702381
P	1.227340	-0.585626	-0.596254
N	-1.848937	-3.643503	1.226775
N	-1.949293	-0.963870	-3.902377
O	-0.454185	-0.137265	-5.439142
O	-1.914918	-3.319655	3.500692
C	-1.532294	-0.125085	-6.368577
H	-2.333998	0.533878	-6.021499
H	-1.936768	-1.130115	-6.514525
H	-1.105872	0.251637	-7.297919
C	-1.947406	-4.737718	3.622451
H	-1.055823	-5.186102	3.173962
H	-2.835763	-5.152011	3.138400
H	-1.974196	-4.933005	4.694275
O	-1.657592	-3.944534	-1.034495
O	-3.434726	-1.736588	-2.333969
C	-1.775961	-5.337897	-0.777290
H	-2.756073	-5.572597	-0.353018
H	-0.999304	-5.671839	-0.084175
H	-1.657722	-5.820116	-1.747594
C	-4.398282	-1.766706	-3.378755
H	-4.104362	-2.473872	-4.159144
H	-4.519914	-0.775499	-3.824119
H	-5.325799	-2.089439	-2.905767
H	-1.769784	-0.816515	3.035328
H	1.289368	-0.126779	-3.576566
C	1.434648	-2.200522	0.202068
C	1.539454	-3.374602	-0.551473

C	1.459977	-2.252453	1.593136
C	1.679341	-4.605006	0.083610
H	1.490656	-3.330679	-1.636991
C	1.575240	-3.479024	2.252923
H	1.364710	-1.334546	2.169123
C	1.686316	-4.635283	1.483558
H	1.777329	-5.596593	1.985910
C	2.809259	-0.178390	-1.403428
C	3.921676	-1.016075	-1.349722
C	2.930559	1.093201	-1.976455
C	5.154661	-0.590808	-1.850008
H	3.839095	-1.999910	-0.897448
C	4.149604	1.544537	-2.477136
H	2.061544	1.746157	-2.025629
C	5.251786	0.690096	-2.397391
H	6.213489	1.032228	-2.774997
C	-2.440252	1.580048	2.037019
C	-2.088253	2.687783	2.801946
C	-3.695293	0.987705	2.252315
C	-2.960061	3.221348	3.758104
H	-1.126463	3.164198	2.675454
C	-4.582036	1.496235	3.194241
H	-3.979328	0.094652	1.704770
C	-4.199003	2.617964	3.937355
H	-4.886624	3.021183	4.677945
C	-2.180666	1.481290	-0.838914
C	-3.546455	1.290700	-1.061736
C	-1.408646	2.099524	-1.821647
C	-4.136479	1.703395	-2.254562
H	-4.166835	0.808572	-0.314825
C	-1.968462	2.504457	-3.032593
H	-0.344882	2.234935	-1.649923
C	-3.332756	2.298966	-3.230031
H	-3.786331	2.612740	-4.168300
C	1.533369	-3.531326	3.758240
H	2.269864	-2.849675	4.196019
H	1.735794	-4.538751	4.133027
H	0.547415	-3.223226	4.124308
C	1.832800	-5.872994	-0.718009
H	1.349889	-5.784198	-1.695827
H	1.396814	-6.731953	-0.198609
H	2.891591	-6.098537	-0.890979
C	6.355447	-1.501564	-1.814198
H	7.270089	-0.947428	-1.582231

H	6.502477	-1.984539	-2.787102
H	6.236686	-2.292400	-1.067532
C	4.285731	2.933089	-3.047351
H	4.772983	2.915656	-4.027274
H	4.895320	3.564600	-2.390215
H	3.309575	3.413973	-3.163986
C	-5.921830	0.846401	3.428922
H	-6.134481	0.082074	2.676217
H	-6.727671	1.586908	3.398260
H	-5.956350	0.365985	4.413090
C	-2.549736	4.432122	4.557940
H	-1.572803	4.282882	5.030586
H	-3.273825	4.654856	5.345991
H	-2.472627	5.317078	3.915978
C	-1.096219	3.097548	-4.109634
H	-0.310224	3.728643	-3.681218
H	-1.677637	3.709442	-4.805393
H	-0.605700	2.305139	-4.687940
C	-5.618935	1.532002	-2.471379
H	-5.859800	1.435820	-3.534522
H	-6.169860	2.398069	-2.086679
H	-5.996522	0.644110	-1.954914
C	2.805977	3.128533	1.952293
C	1.284220	3.133128	1.879182
C	0.588399	3.604746	0.787213
C	1.271059	4.341528	-0.349893
C	2.666196	4.812936	0.067072
C	3.447474	3.640464	0.653552
H	1.345960	3.709151	-1.243502
H	0.640934	5.191322	-0.634757
H	3.195508	5.227996	-0.796472
H	2.576185	5.617502	0.807992
H	3.462430	2.849581	-0.104624
H	4.491570	3.907271	0.847008
H	-0.483401	3.760443	0.867441
H	0.773112	2.940324	2.819329
H	3.087466	3.820760	2.758966

Structure No: 268a-R

	X	**Y**	**Z**
C	1.581921	1.511713	-0.989492
C	2.159572	0.593666	-0.100642

C	-0.895983	1.035814	-1.268972
C	0.381596	1.220219	-1.807790
C	0.504940	1.037865	-3.197492
C	-1.675746	0.446702	-3.440526
C	-1.944578	0.617376	-2.082357
C	2.188831	2.776304	-1.067354
C	3.777704	2.252626	0.464213
C	3.286629	0.955523	0.627266
P	-1.101121	1.040508	0.548800
P	1.362796	-1.052450	0.164425
N	-0.492071	0.676091	-3.993614
N	3.252040	3.141841	-0.364185
O	4.831467	2.602280	1.214344
O	-2.685345	0.021338	-4.216710
C	5.287714	3.946552	1.107462
H	4.493185	4.647457	1.380539
H	5.622773	4.166169	0.090337
H	6.119817	4.023705	1.806805
C	-2.423776	-0.105530	-5.610232
H	-1.607953	-0.810432	-5.793993
H	-2.161409	0.861577	-6.047877
H	-3.351624	-0.477624	-6.044613
O	1.717627	1.223410	-3.726353
O	1.621595	3.669336	-1.883424
C	1.862957	0.999907	-5.122161
H	1.242934	1.693049	-5.697148
H	1.585058	-0.026244	-5.379029
H	2.918824	1.172587	-5.330981
C	2.230997	4.951078	-1.965221
H	3.241587	4.874799	-2.376115
H	2.281751	5.420647	-0.979224
H	1.594315	5.531447	-2.633059
H	-2.930737	0.393401	-1.699040
H	3.790071	0.289848	1.313385
C	1.355113	-1.724605	-1.531316
C	2.525415	-1.640001	-2.295626
C	0.192749	-2.248457	-2.089432
C	2.547650	-2.099341	-3.607864
H	3.422870	-1.198194	-1.869674
C	0.187285	-2.698214	-3.413713
H	-0.727175	-2.259928	-1.510839
C	1.367932	-2.622954	-4.147515
H	1.371103	-2.969168	-5.179465
C	2.613906	-2.011049	1.088976

C	3.237045	-3.130713	0.547328
C	2.861750	-1.660373	2.424726
C	4.124069	-3.895241	1.316261
H	3.036953	-3.427446	-0.477468
C	3.746068	-2.395533	3.204918
H	2.334734	-0.817262	2.867098
C	4.365528	-3.513792	2.632122
H	5.046764	-4.106440	3.239213
C	-2.826117	1.487866	0.933162
C	-3.300440	1.085908	2.184211
C	-3.640442	2.254453	0.101687
C	-4.591153	1.402010	2.599419
H	-2.653257	0.517009	2.849783
C	-4.937278	2.594068	0.496185
H	-3.278686	2.586261	-0.867306
C	-5.397438	2.149595	1.736338
H	-6.412285	2.395582	2.042836
C	-0.188693	2.476412	1.203048
C	-0.417507	3.747524	0.671492
C	0.714327	2.307979	2.248844
C	0.269561	4.851962	1.167117
H	-1.121816	3.879834	-0.145864
C	1.431564	3.396530	2.749459
H	0.885431	1.313523	2.655657
C	1.195951	4.654226	2.196016
H	1.747227	5.510854	2.578984
C	-1.081919	-3.220030	-4.035501
H	-1.433148	-4.126426	-3.529688
H	-0.936906	-3.464808	-5.091545
H	-1.877520	-2.471916	-3.963440
C	3.810546	-2.037111	-4.428071
H	4.359152	-2.984510	-4.371098
H	4.476909	-1.245570	-4.072849
H	3.591821	-1.850413	-5.484071
C	4.811950	-5.092064	0.710655
H	4.140358	-5.643719	0.045623
H	5.169201	-5.781182	1.480892
H	5.679186	-4.779890	0.117108
C	4.035228	-2.005781	4.631821
H	5.030384	-1.554887	4.717650
H	4.013487	-2.877076	5.294115
H	3.307918	-1.277479	5.002927
C	-5.809605	3.440665	-0.395526
H	-6.871240	3.252624	-0.211456

H	-5.607158	3.247050	-1.453264
H	-5.627900	4.506483	-0.214501
C	-5.108803	0.946611	3.940086
H	-5.204665	1.790674	4.632033
H	-4.436520	0.215340	4.399709
H	-6.097735	0.486357	3.845884
C	2.476296	3.191881	3.816539
H	2.144512	2.464367	4.564471
H	2.709753	4.126620	4.334293
H	3.404767	2.812008	3.372710
C	0.001967	6.230105	0.617150
H	0.868338	6.887192	0.740117
H	-0.841812	6.698968	1.136753
H	-0.248058	6.189785	-0.447640
C	-0.899465	-3.399106	1.307635
C	-2.392964	-3.718050	1.369675
C	-2.908029	-3.702353	2.822337
C	-2.288490	-2.585664	3.666259
C	-0.777699	-2.784485	3.764980
C	-0.166822	-3.020635	2.408761
H	-2.497916	-1.604257	3.212732
H	-2.738419	-2.561409	4.663737
H	-0.292811	-1.926082	4.245632
H	-0.556911	-3.656612	4.397421
H	0.909915	-3.132460	2.382097
H	-2.647064	-4.659270	3.290101
H	-4.000486	-3.642634	2.828160
Rh	-0.637337	-1.142124	1.190263
H	-0.369919	-3.771062	0.431958
C	-3.208351	-2.871131	0.392945
C	-3.155308	-3.171291	-0.974909
C	-4.049942	-1.836781	0.804382
C	-3.917892	-2.465132	-1.895292
H	-2.525760	-3.991315	-1.314378
C	-4.813807	-1.120113	-0.117430
H	-4.150620	-1.591094	1.855578
C	-4.753286	-1.432900	-1.468446
H	-3.877352	-2.726217	-2.947544
H	-5.456393	-0.318938	0.234512
H	-5.349168	-0.881430	-2.188921
H	-2.477499	-4.751800	1.009182

CURRICULUM VITAE

Personal Information

Name Surname	Özlem SARI
Nationality:	Turkish (TC)
Date and Place of Birth:	8 June 1986, Akçakoca
Marital Status:	Single
Email:	ozlemsari86@gmail.com; sari.ozlem@metu.edu.tr

Education

Degree	Institution	Years
PhD	METU	2011-2017
Visiting researcher	University of Oxford	2015-2016 (8 months)
MS	Marmara University	2009-2011
BS	Marmara University	2004-2009

Foreign Language

English (fluent)

Work Experience

Year	Place	Enrollment
2010−Present	Ahi Evran University	Research and Teaching Assistant

Publications

1. Çalışkan, R.; Sari, O.; Balci, M., Functionalization of oxabenzonorbornadiene: Manganese(III)-mediated oxidative addition of dimedone, *J Phys Org Chem.* **2017**, DOI: 10.1002/poc.3720
2. Essiz, S.E.; Dalkilic, E.; Sari, O.; Dastan, A.; Balci, M., Unexpected regioselectivity observed in the bromination and epoxidation reactions of *p*-benzoquinone-fused norbornadiene: An experimental and computational study, *Tetrahedron*, **2017**, *73*, 1640–1649. DOI: 10.1016/j.tet.2017.02.017
3. Sari, O.; Erdem, S.S.; Kaufmann, D.E., Mechanisms of the Reaction between Polyhalogenated Nitrobutadienes and Electron-Deficient Anilines: Computational Modeling, *J. Org. Chem*., **2014**, *79*, 2123–2138 DOI: 10.1021/jo402858j
4. Menges, N.; Sari, O.; Abdullayev, Y.; Erdem, S.S.; Balci, M., Design and Synthesis of Pyrrolotriazepine Derivatives: An Experimental and Computational Study, *J. Org. Chem*. **2013**, *78*, 5184–5195. DOI: 10.1021/jo4001228

Professional Meetings and Activities

1. **Sari O**., Mengeş N., Erdem S.S., Balci M., Pirolo-Pirazin, İndolizin Türevlerinin Sentezi ve Oluşum Mekanizmalarının Hesapsal Olarak Modellenmesi, 2. Ulusal Hesaplamalı Kimya Kongresi, Poster Presentation, 2-5 June 2015, Kars
2. **Sari O**., Menges N., Abdullayev Y., Erdem S.S., Balci M., Pirolotriazepin Turevlerinin Sentezi ve Reaksiyon Mekanizmasinin DFT Yöntemi ile Modellenmesi, 1st National Computational Chemistry Workshop with International Participation, Oral Presantation, 29-31 May 2014, Van-TURKEY

3. **Sari O**., Menges N., Erdem S.S., Balci M ,7-Azaindolizin Turevlerinin Sentezi ve Reaksiyon Mekanizmasinin DFT Metodu ile Modellenmesi, 1st National Computational Chemistry Workshop with International Participation, Poster Presentation, 29-31 May 2014, Van-TURKEY
4. **Sari O**., Menges N., Erdem S.S., Balci M., Azaindolizin Turevlerinin Sentezi ve Reaksiyon Mekanizmasinin DFT Yontemi ile Modellenmesi, 2. Ilac Kongresi Uretimi, Teknolojisi, Standartizasyonu Kongresi, Poster Presentation, 21-23 March 2014, Antalya-TURKEY
5. Workshop: Ilac Arastirmalarinda Uygulamali Molekuler Modelleme ve Simulasyon Teknikleri, Hacettepe University, 20-22 Februrary 2013, Ankara-TURKEY
6. **Sari O**., Erdem S.S., Balci M., Menges N., Modeling the Reaction Mechanism for the Formation of Triazepine Derivatives: A Computational (DFT) Study Chemical Physics Congress X. Poster Presentation, TOBB ETU, 10-12 October 2012, Ankara-TURKEY.
7. WATOC 2011 Satellite Meeting: Simulations in Organic Chemistry, 15-16 July 2011,Vigo-SPAIN
8. Workshop: Introduction to Gaussian: Theory and Practice,11-15 July 2011, Santiago de Compostela-SPAIN
9. **Sari O**., Erdem S.S., Kaufmann D.E., Polihalojenlenmis Nitrobutadienlerin Elektronca Eksik Anilinlerle Verdigi Reaksiyon Mekanizmasinin DFT Metodu ile Modellenmesi, 25th National Chemistry Congress with International Participation, Oral Presantation, 26 June-02 July 2011, Erzurum-TURKEY
10. **Sari O**., Erdem S.S., Kaufmann D.E., Modeling the Mechanism of the Reaction between Polyhalogenated Nitrobutadienes and Electron Deficient Anilines, Chemical Physics Congress IX, Poster Presentation, 14-16 October 2010, Izmir- TURKEY