

DFT study on the propylene reaction on Kaminsky  
catalyst in  $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$   
And MD simulation on the binding of propylene with  
the catalyst

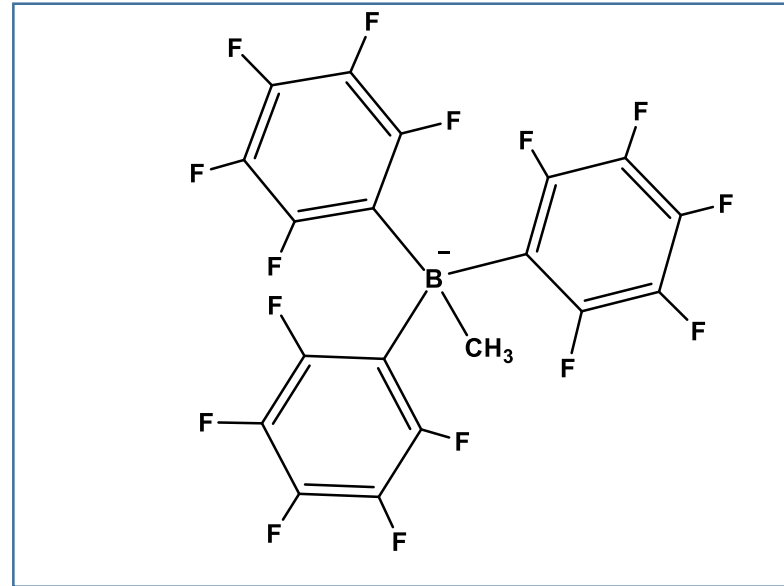
23/10/2014

K. S. Sandhya

# Outline

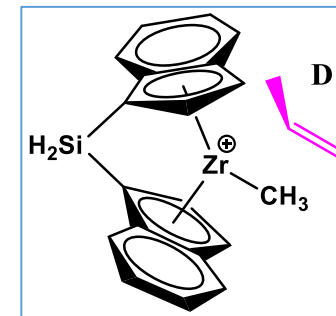
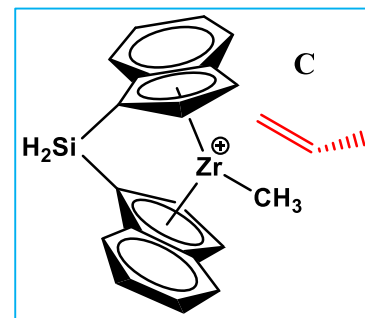
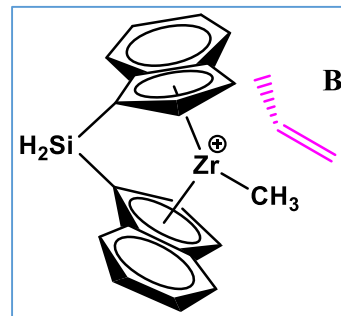
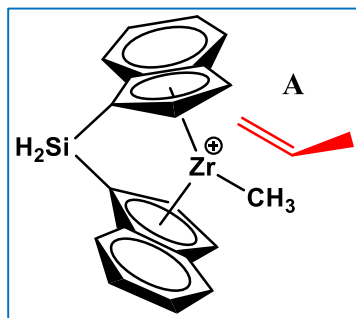
- Reaction mechanism of first insertion of four different mode of propylene attack in the presence of counter anion (CA).
- Second insertion of propylene in the presence of CA.
- Force field parameter development for the binding of propylene.
- Two different method for atomic charge generation (CHelpG, NPA).
- Comparing the geometry from DFT and from MD.
- MD simulation of binding of propylene with A mode of attack using two different atomic charges.
- Implementation of the force filed parameters for the C and B mode of attack for MD simulation.
- Future plan

# DFT study on the propylene reaction on Kaminsky catalyst in $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$



Counter anion : co-catalyst

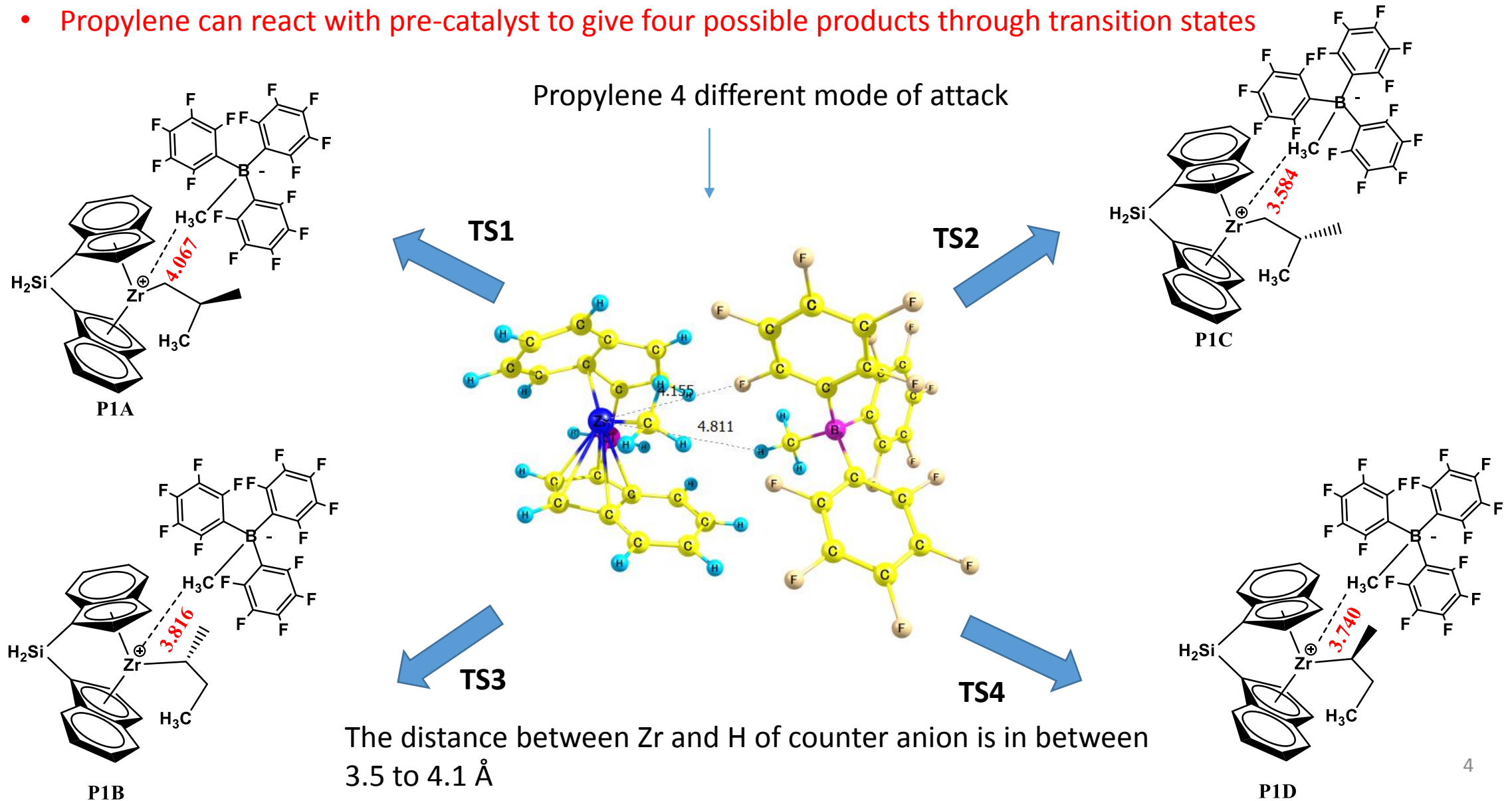
We have considered four different mode of propylene attack to the pre-catalyst (without propylene) along with counter anion.



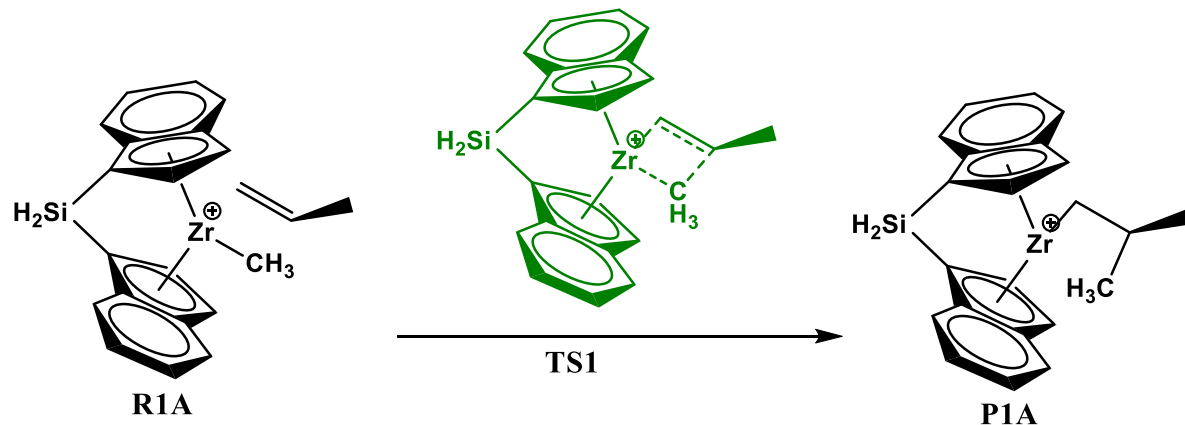
The four mode of propylene attack to the pre-catalyst.

# Reaction mechanism scheme

- Propylene can react with pre-catalyst to give four possible products through transition states



## Four centered transition state



## Method

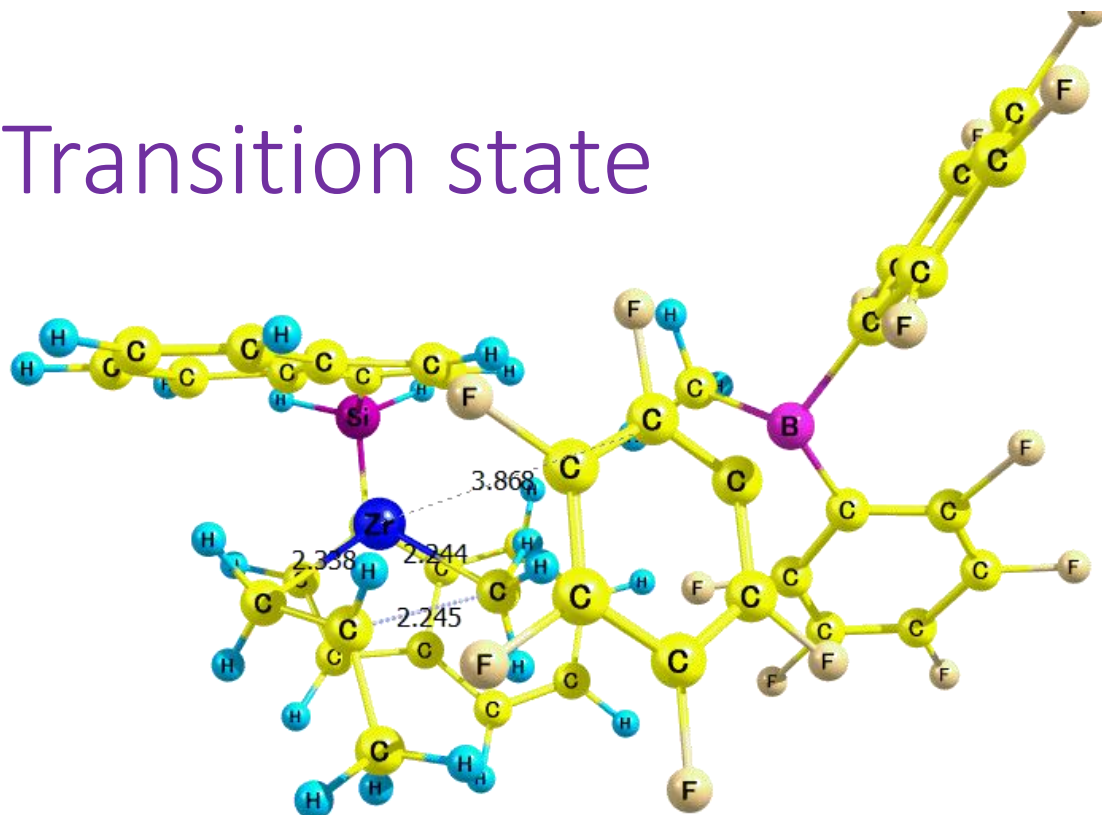
For **A** attack M06/6-31++ G (d,p)

LanL2DZ

Activation barrier 4.25 [kcal/mol]

Method M06/6-31G(d,p) , LanL2DZ for Zr  
SP calc. M06/def2\_TZVPP

## Transition state



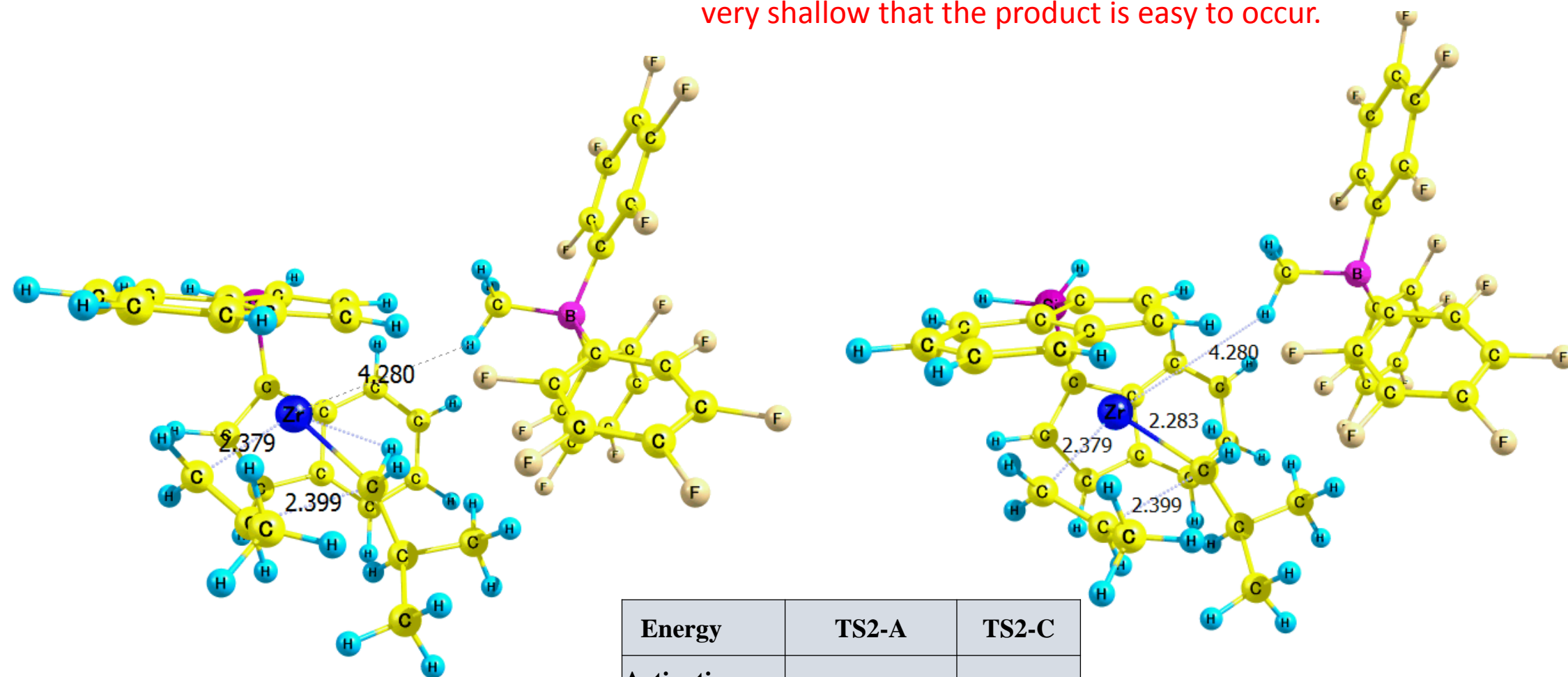
Animation of first insetion

Energy [kcal/mol]	<b>A</b>	<b>C</b>	<b>B</b>	<b>D</b>
Activation barrier	5.40	3.94	9.92	22.50
Activation barrier	4.75	5.75	8.86	20.61

- A and C mode of propylene attack is favorable compared to B and D mode of approach.

## Second Insertion of propylene attack

- Activation barrier for the second insertion is very shallow that the product is easy to occur.



Energy	TS2-A	TS2-C
Activation barrier [kcal/mol]	2.2	2.9

## Overall energy profile for the insertion of propylene in the presence of counter anion.

Method : M06/6-31G (d,p) LanL2DZ

Complex name	Relative energy [ kcal/mol ]	
	A-A	C-C
<b>Intl</b>	0	0
<b>Rea1</b>	-25.28	-25.47
<b>TS1</b>	-15.88	-21.52
<b>Pdt1</b>	-30.98	-37.71
<b>Rea2</b>	-39.98	-40.62
<b>TS2</b>	-39.31	-38.1
<b>Pdt2</b>	-57.63	-77.72

A-A -> First and second insertion by A style approach of propylene  
C-C -> First and second insertion by C style approach of propylene

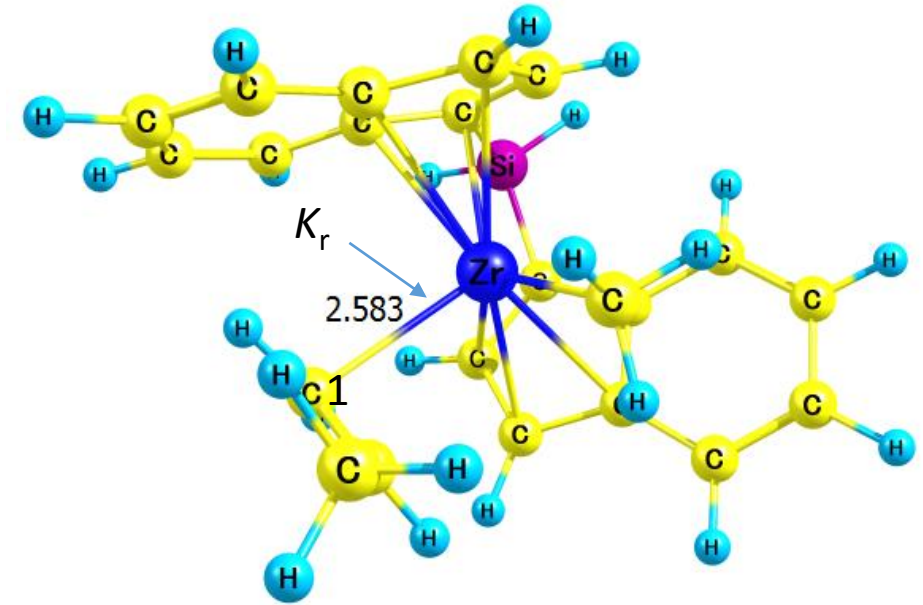
Intl = Initial geometry without propylene attack  
TS means transition states  
Rea means reactants  
Pdt means products

- This table clearly explain the polymerization of Propylene is taking place with decrease in energy of reaction. That is as reaction is proceeds the polymer become more stabilized compared to initial complex.

# Force field parameter development using DFT

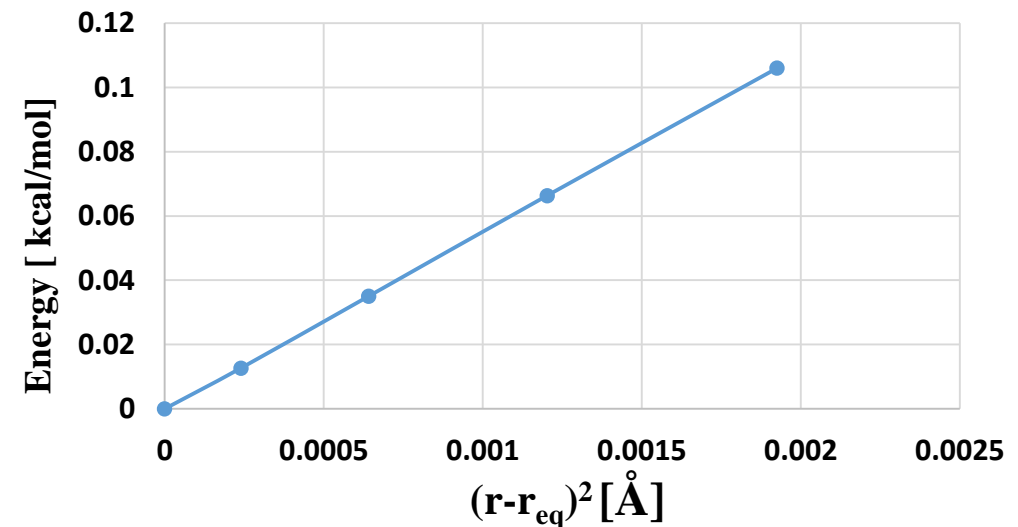
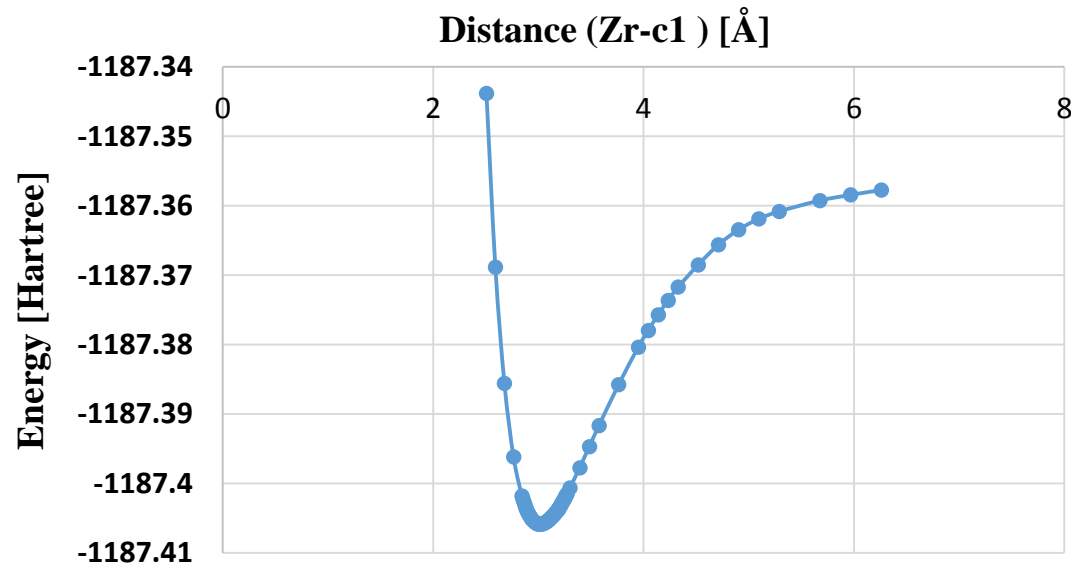
Force field parameters are created using the equation given below

$$E_{\text{total}} = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_{\theta} (\theta - \theta_{\text{eq}})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \sum_{i < j} \left[ \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right]$$



One example for finding the force constant for bond between zr-c1.

M06/6-31++ G(d,p), LanL2DZ for Zr





# Force field parameters created

Bond	K1	Distance [Å]
zr-c2	204	2.58
zr-c9	258	3.011
c9-ha	396	1.094
c2-hb	396	1.091
c2-hd	399	1.093
c9-c2	590	1.324
c9-c3	314	1.481
zr-cp	219	2.43
c4-ha	367	1.099
zr-c4	150	2.242

Angle	K2	Angle [°]
si-c5-z	r 7.50	98.85
zr-c2-h	b 1.28	103.1
zr-c2-h	d 2.09	86.42
zr-c9-h	a 3.96	95.58
zr-c2-c	9 4.18	94.29
zr-c9-c	2 0.03	59.07
zr-c9-c	3 2.09	117.71

Dihedral angle	Multiplicity	K3	$\phi$ [°]	Periodicity, n
c4-zr-c2-c9	1	51	360	1
c4-zr-c9-c3	1	58	360	1

## Other parameters taken from Previous papers <sup>a,b</sup>

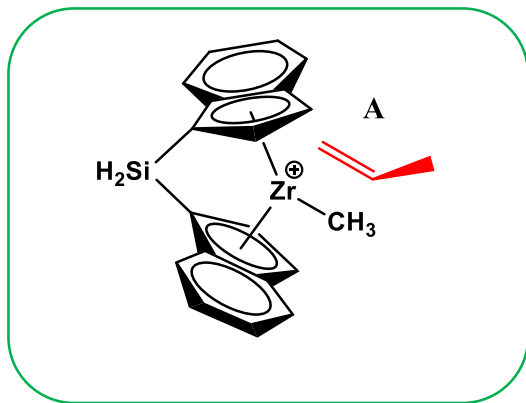
Bond	K1	Distance [Å]
c3-hc	345	1.09
c4-hc	340	1.09
zr-c5	137	2.38
zr-c4	200	2.26
si-c5	506	1.90

Angle	K2	Angle [°]
hc-c4-hc	35	109.5
si-c3-hc	35	109.5
c3-si-c3	40	109.5
zr-c4-hc	150	109.5
si-c5-c5	40	126.0
c5-c3-c3	70	109.5
c5-si-c5	70	109.5
c3-si-c5	22	109.5

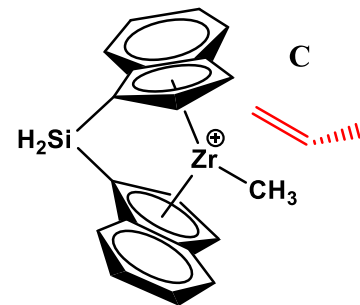
Atom type	Vander Waals depth, $\epsilon$ [kcal/mol]	Vander Waals radius, [Å]
zr	1.000	0.000
si	1.908	0.086
c4	1.910	0.130

a. Bosnich et. al., J. Am. Chem. Soc., 1995, 117, 1352-1368

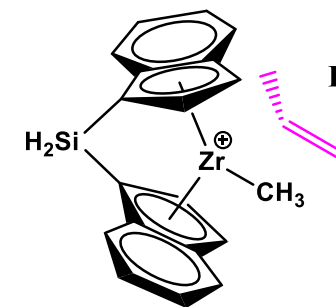
b. Brintzinger et.al., J. Mol. Struc., 1999, 485-486, 409-419



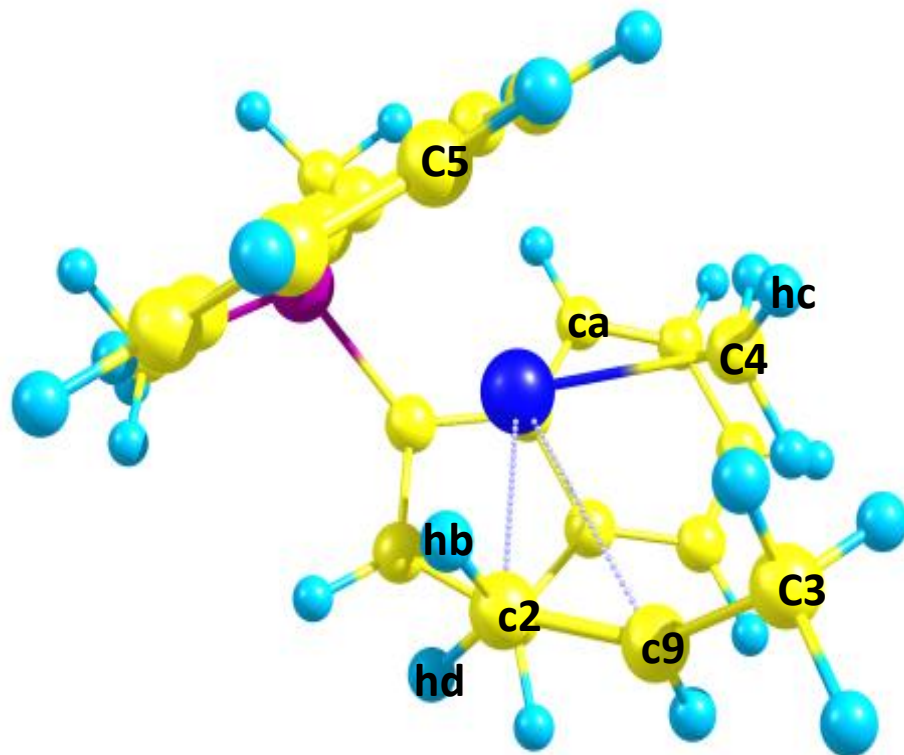
Parameters used to  
DFT optimized structure  
of C mode of attack



And



Force field parameters are created for this complex  
Atom types used for this complex



Solvent **Pentane**

Atomic charges from two method

1. CHelpG M06/6-31++G(d,p)
2. NPA M06/6-31++G(d,p)

New script has written for the  
extraction of atomic charge calculated  
from the Gaussian 09 out put gesp file  
to prepin file.

# Structural comparison between DFT optimized geometry and MD minimized geometry

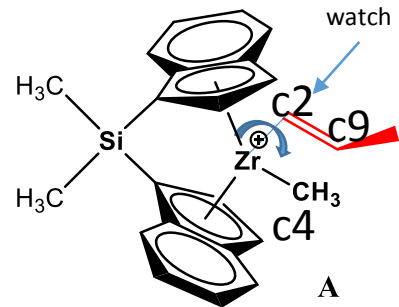
Structural Parameters of A	DFT	MD (atomic charge from CHelpG)	MD (atomic charge from NPA)
zr-c2	2.589	2.616	2.648
zr-c9	3.010	3.017	3.039
zr-c4	2.243	2.299	2.358
zr-cp	2.430	2.43	2.410
zr-c2-hb	104	104	104
zr-c2-hb	85	80	73
zr-c9-ha	95	95	125
zr-c9-c3	119	120	89
c4-zr-c2-c9	20	19	20

Atom type	Atomic charges	
	NPA	CHelpG
zr	0.937	1.237
c4:	-0.456	-1.123
c2 :	-0.226	-0.584
c9 :	0.75	-0.025
si :	0.666	1.850

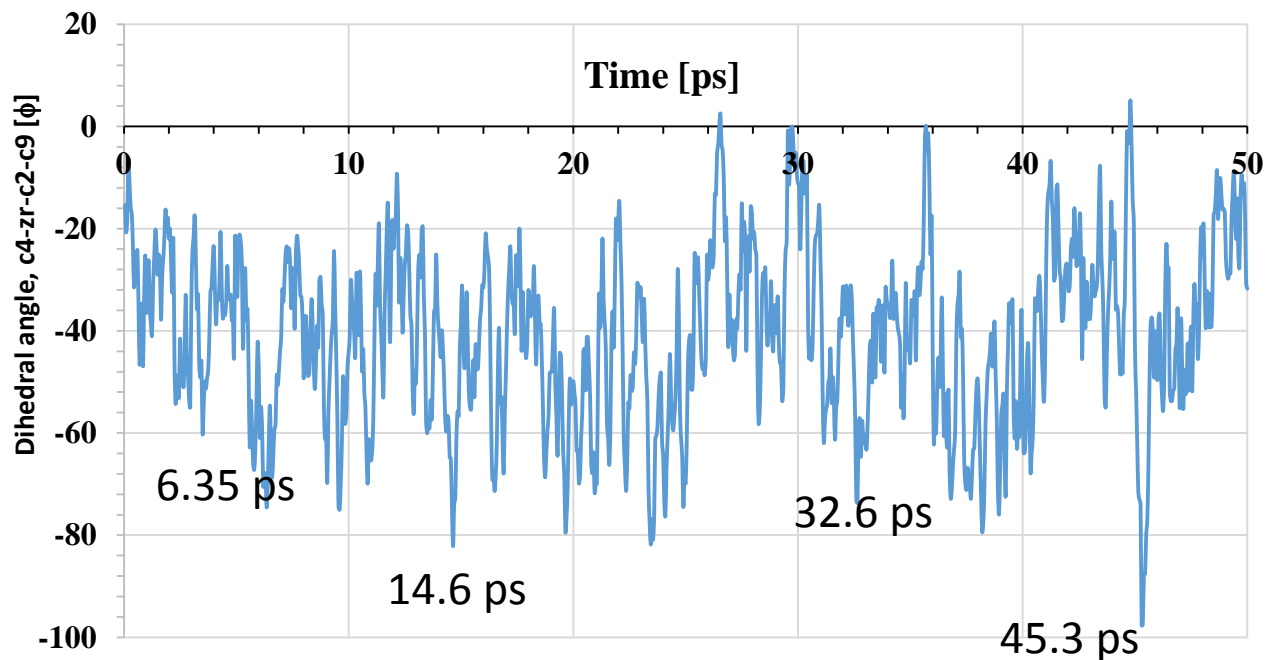
**MD minimized Geometry obtained using CHelpG atomic charges is more similar to DFT structure.**

# MD simulation of propylene bonded activated complex, A – CHelpG method for atomic charge

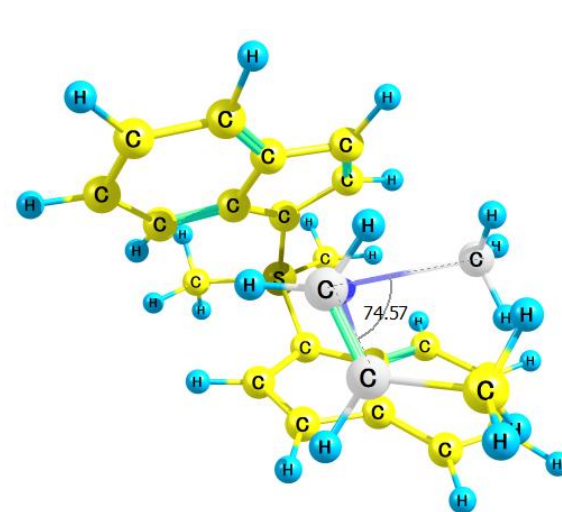
c9-c2-zr-c4



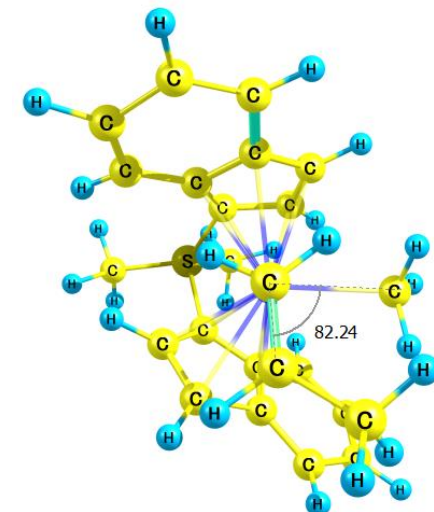
MD -> Dt = 0.001, NSTLIM = 50000  
TEMP = 300 K Pressure = 1 atm



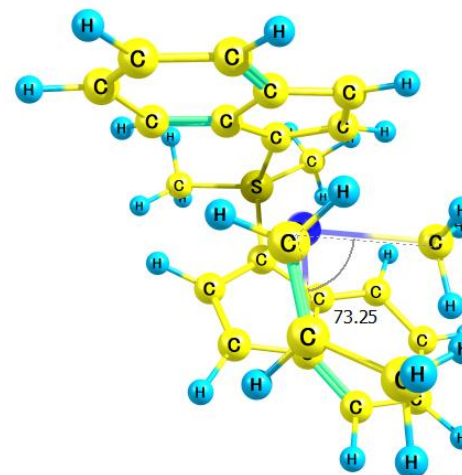
Various metastable structures during MD simulation



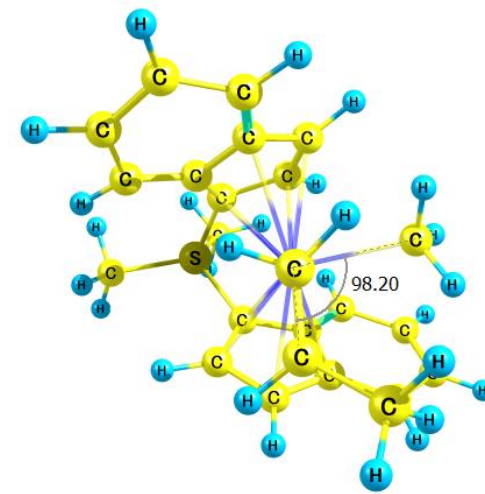
6.35 ps



14.6ps



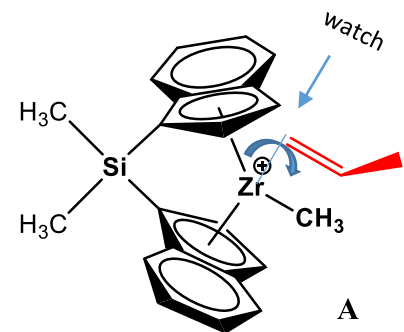
32.6 ps



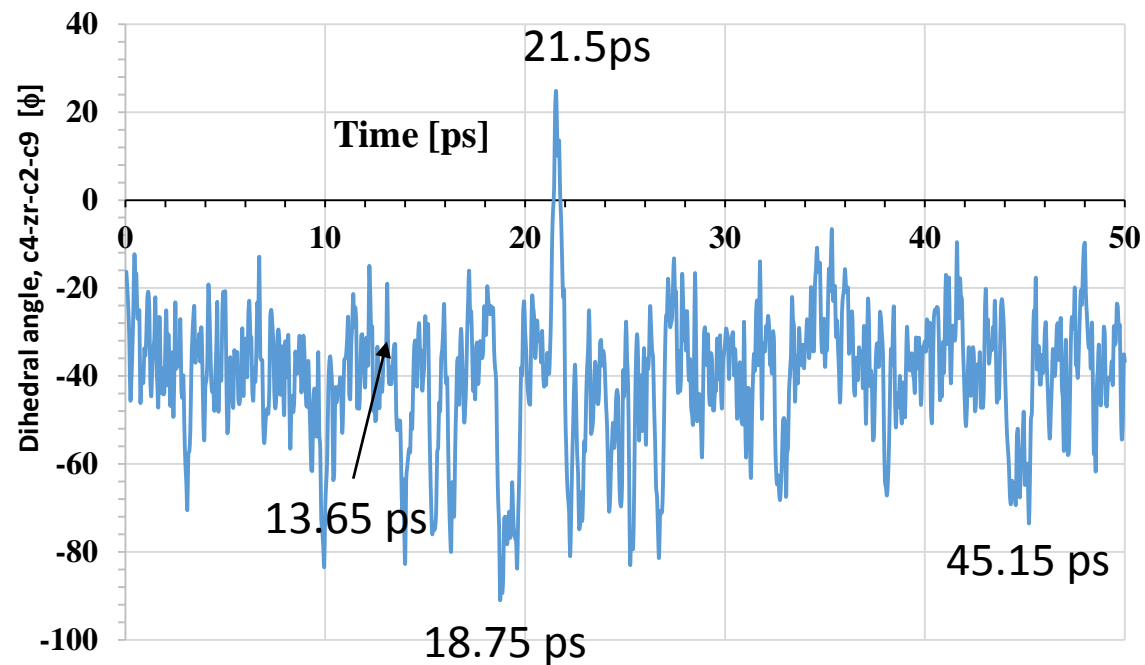
45.3 ps <sup>12</sup>

**This Figures clearly indicate that various rotations possible for the Propylene when it bound to the reactive pre-catalyst.**

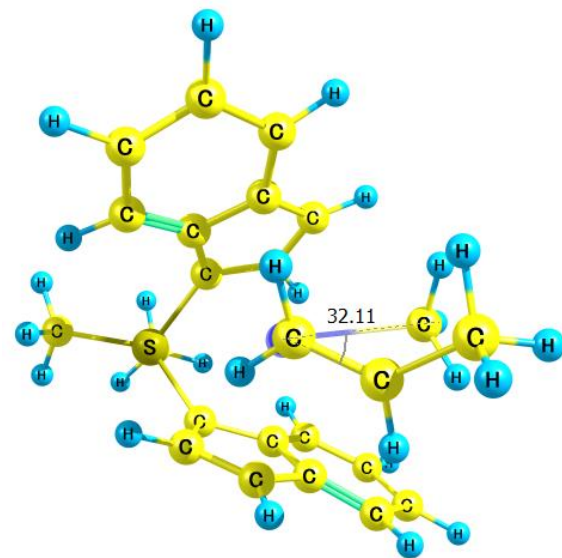
# MD simulation of propylene bonded activated complex, A



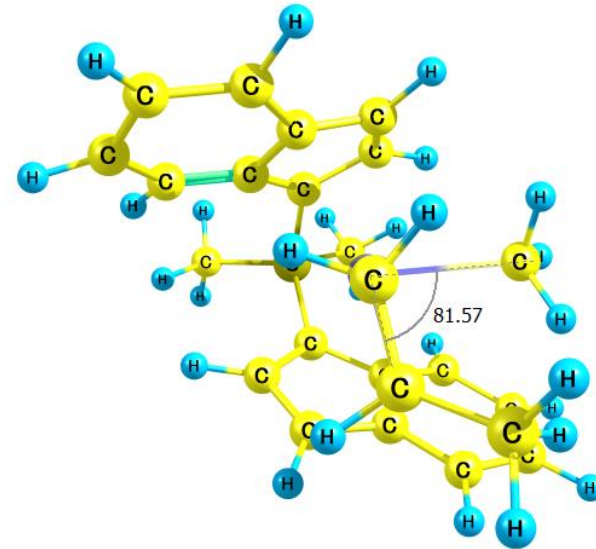
NPA method used for atomic charge



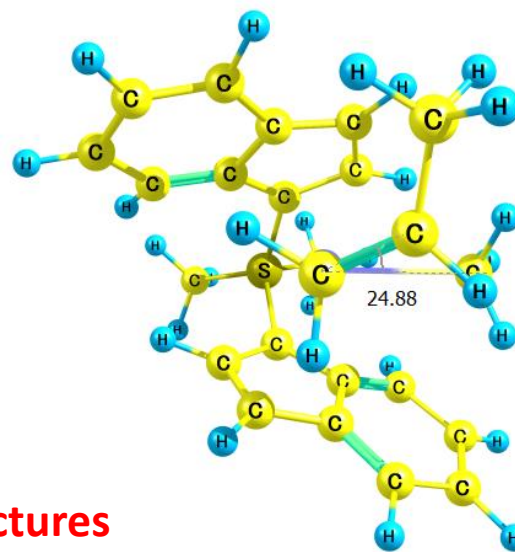
## Various metastable structures during MD simulation



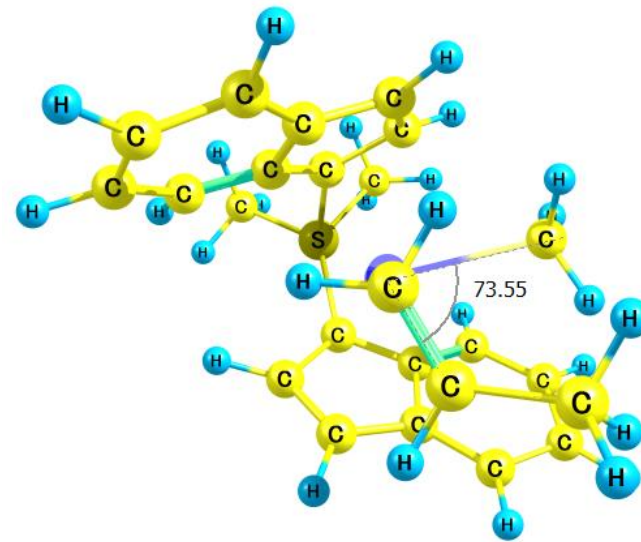
13.65 ps



18.75 ps



21.5 ps



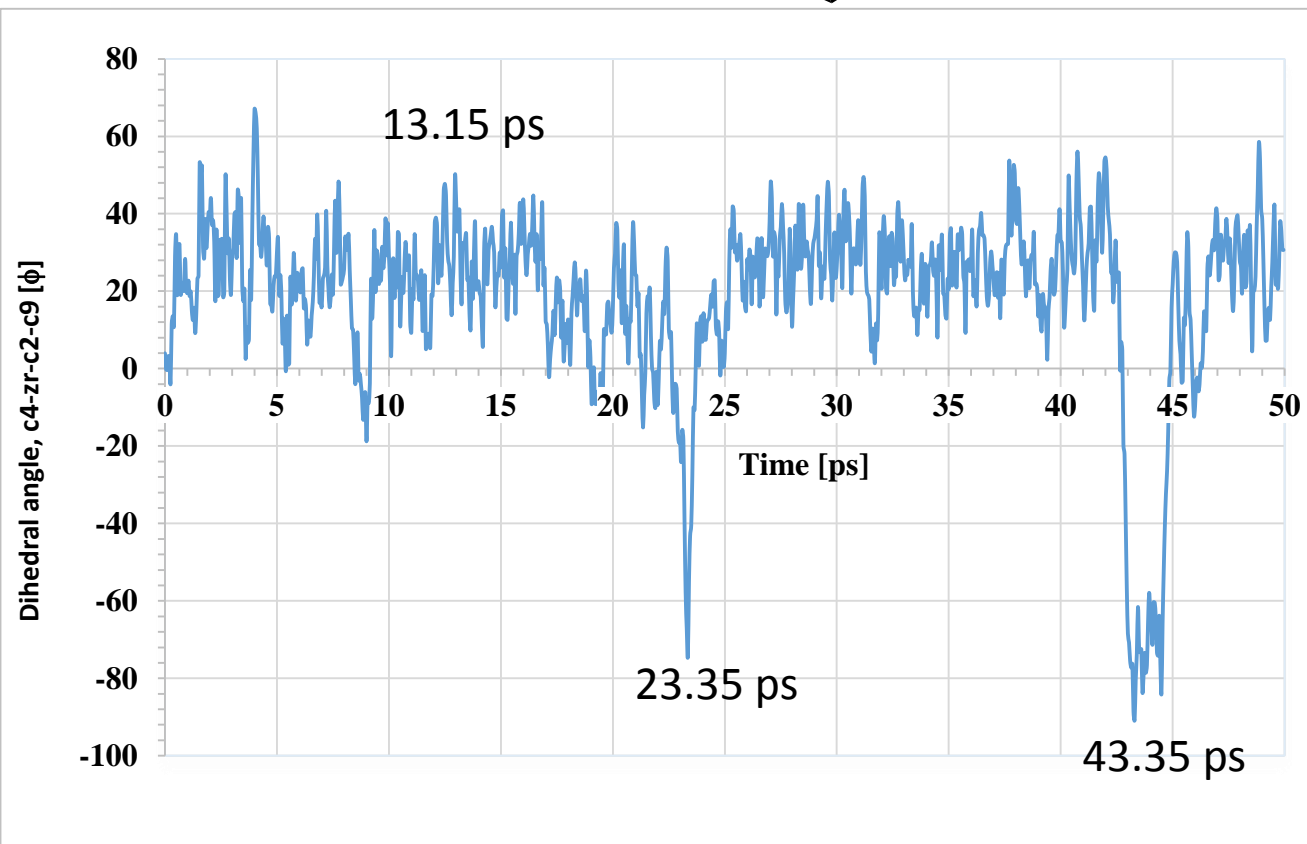
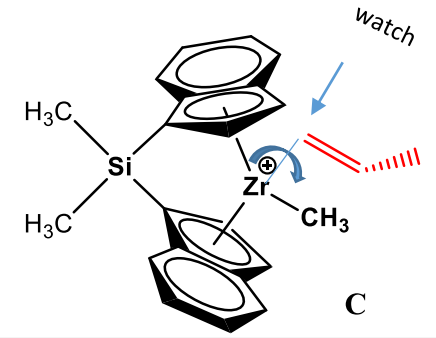
45.15 ps

13

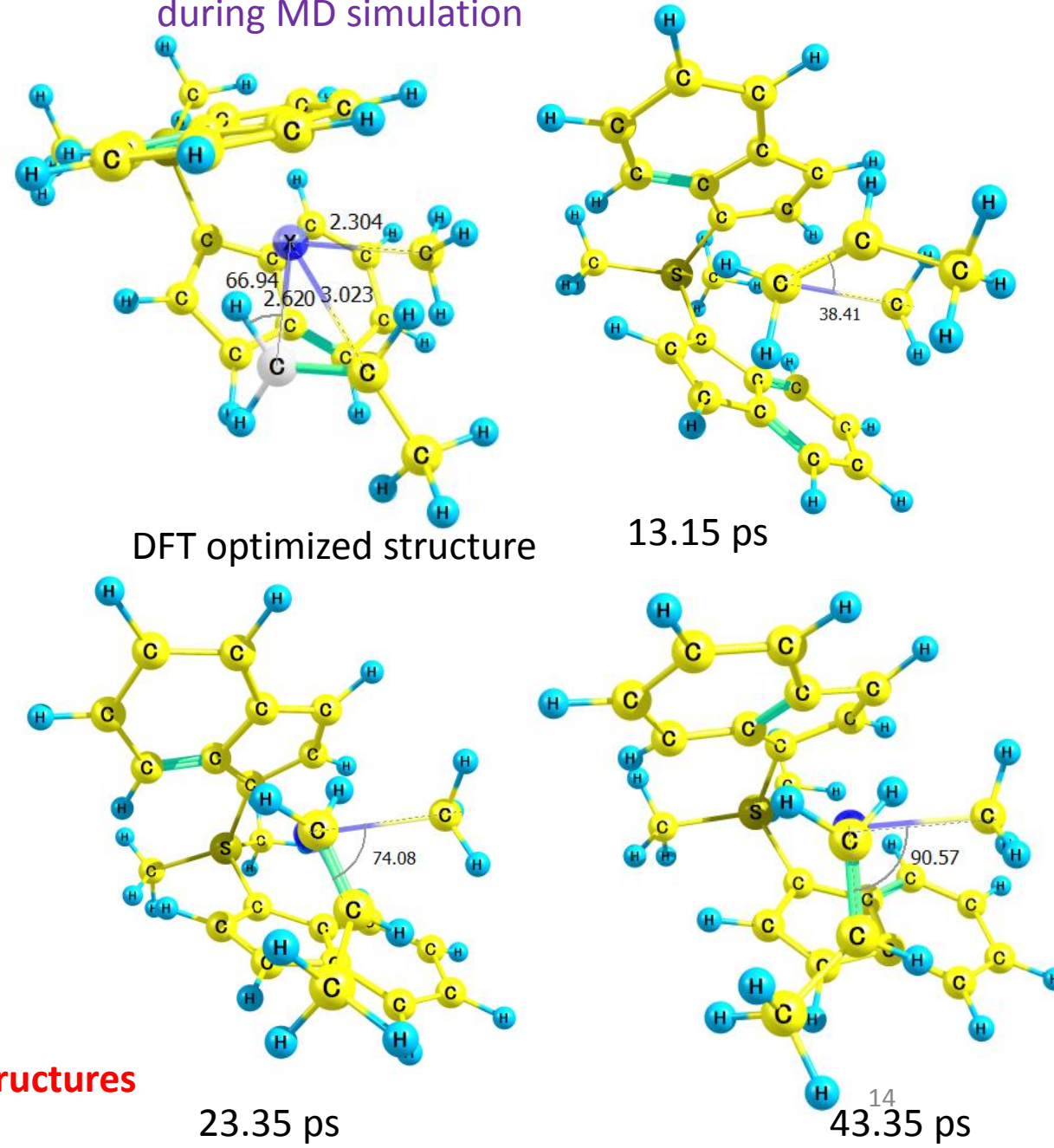
In this figure also clearly shed the presence of metastable structures

# MD simulation of propylene bonded activated complex, C

Atomic charge : CHelpG method

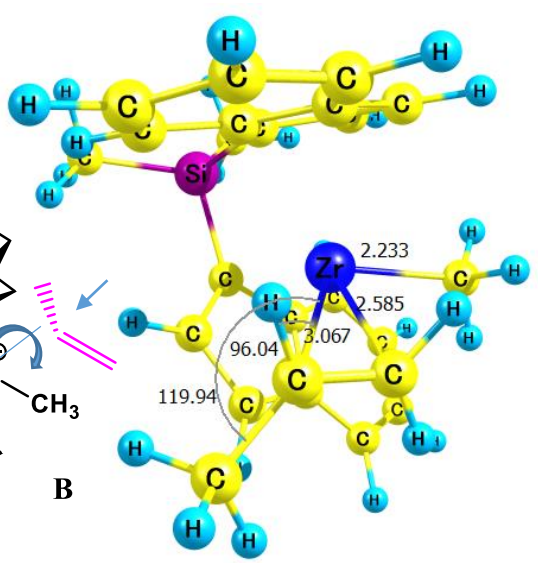
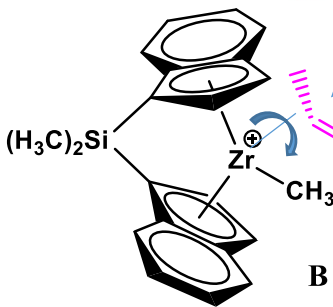


- Various metastable structures are seen during MD simulation

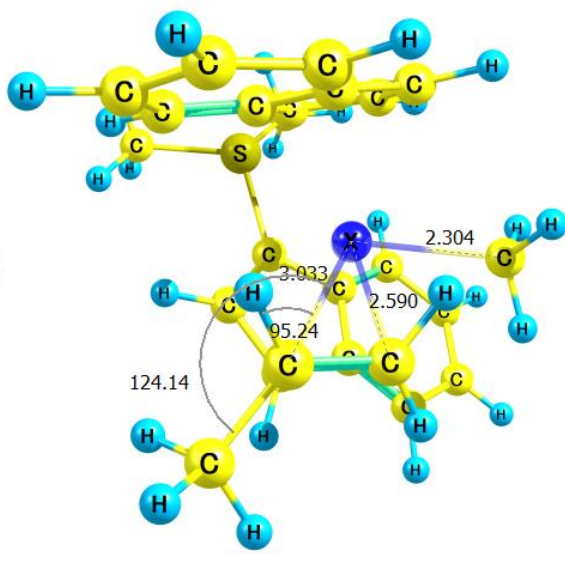


**In the C mode of approach of propylene also shows metastable structures in MD simulation**

# MD simulation of propylene bonded activated complex, B

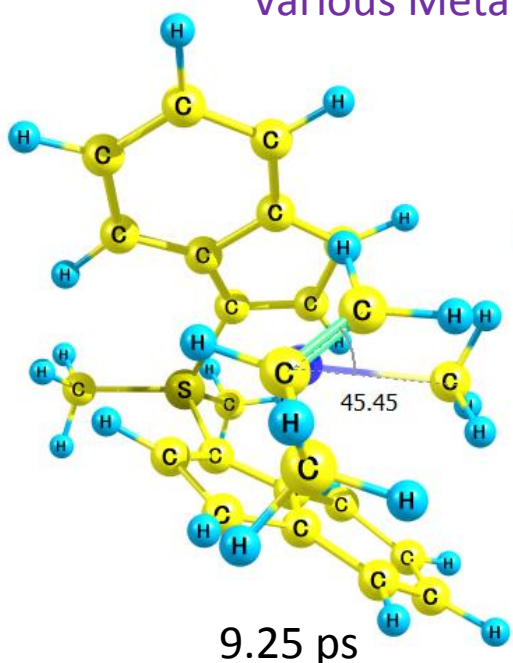


DFT optimized structure

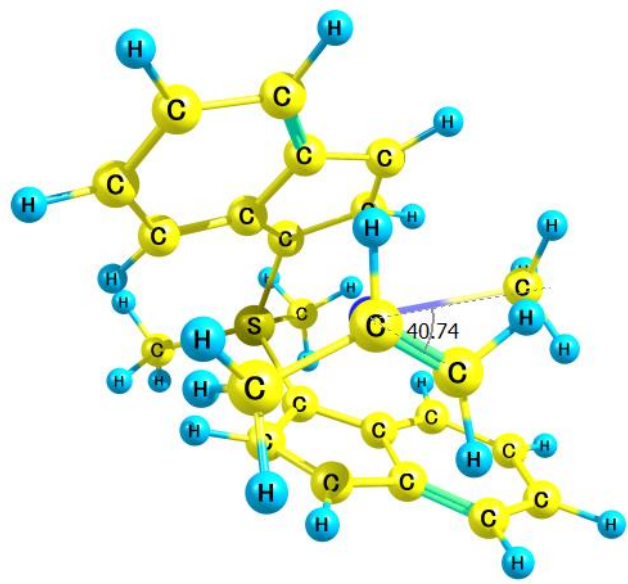


MD minimized structure

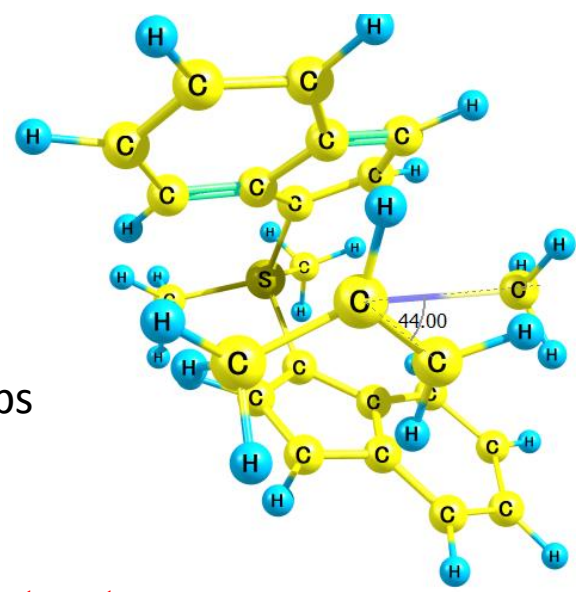
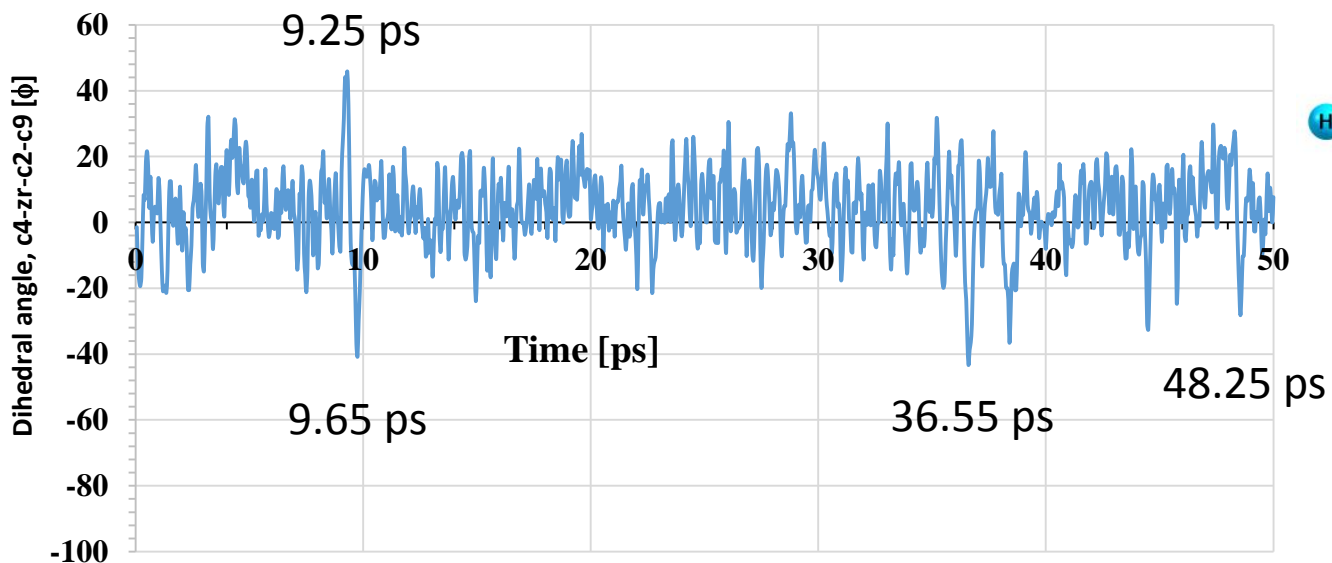
## Various Meta stable structures



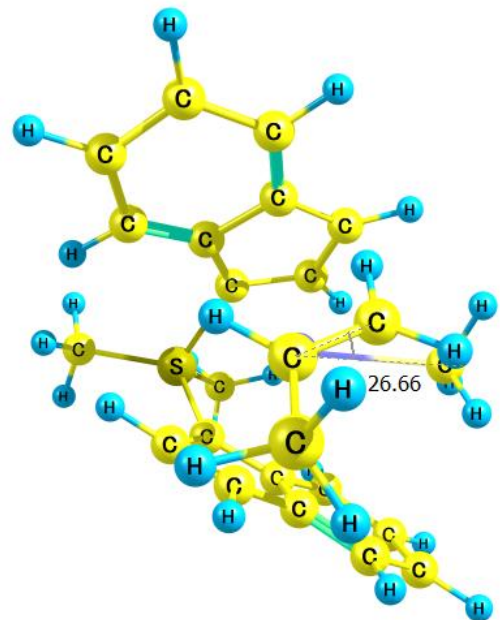
9.25 ps



9.65 ps



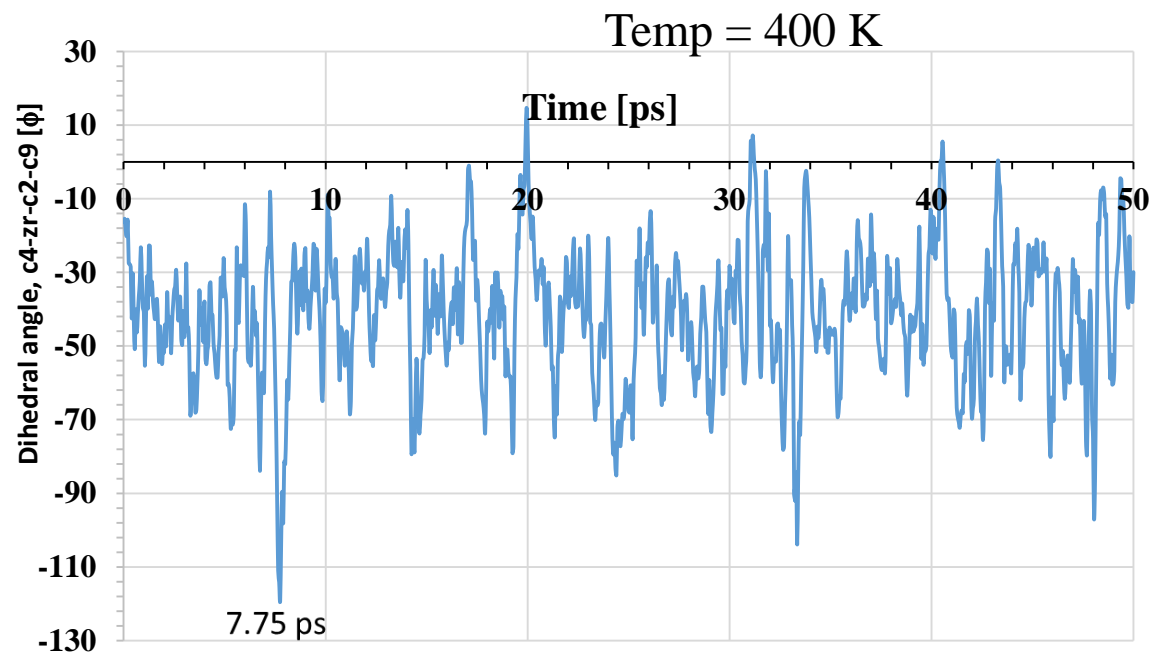
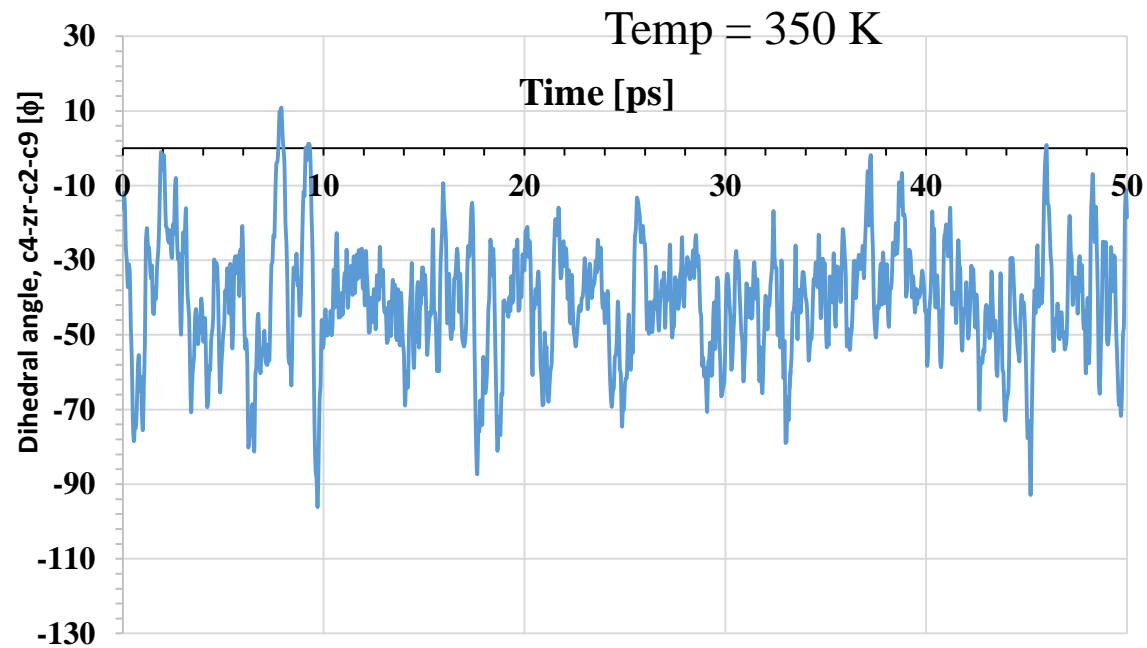
36.55 ps



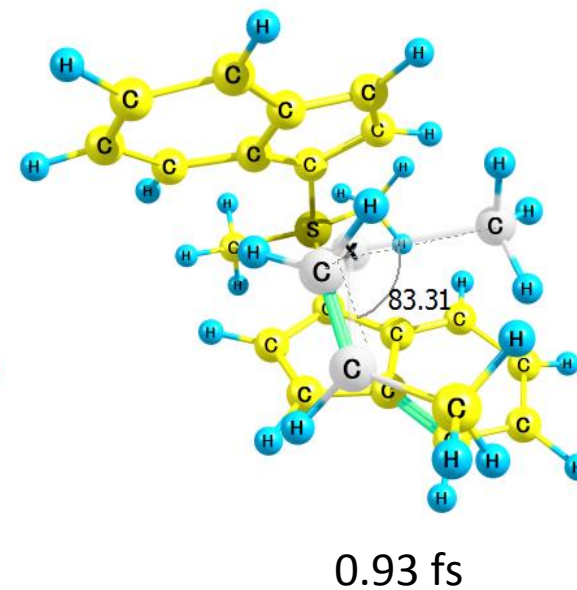
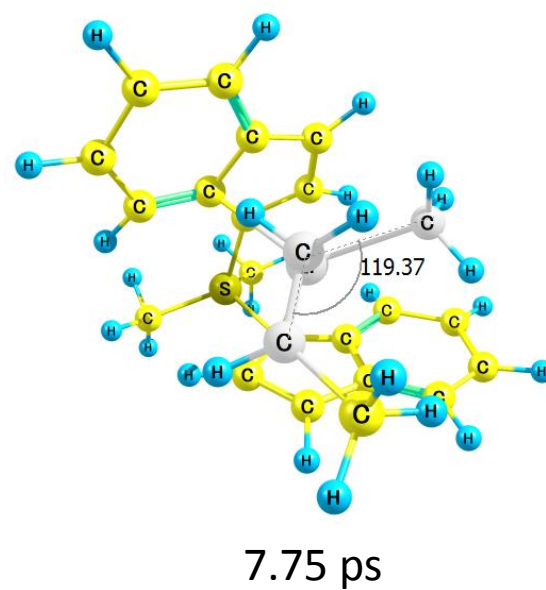
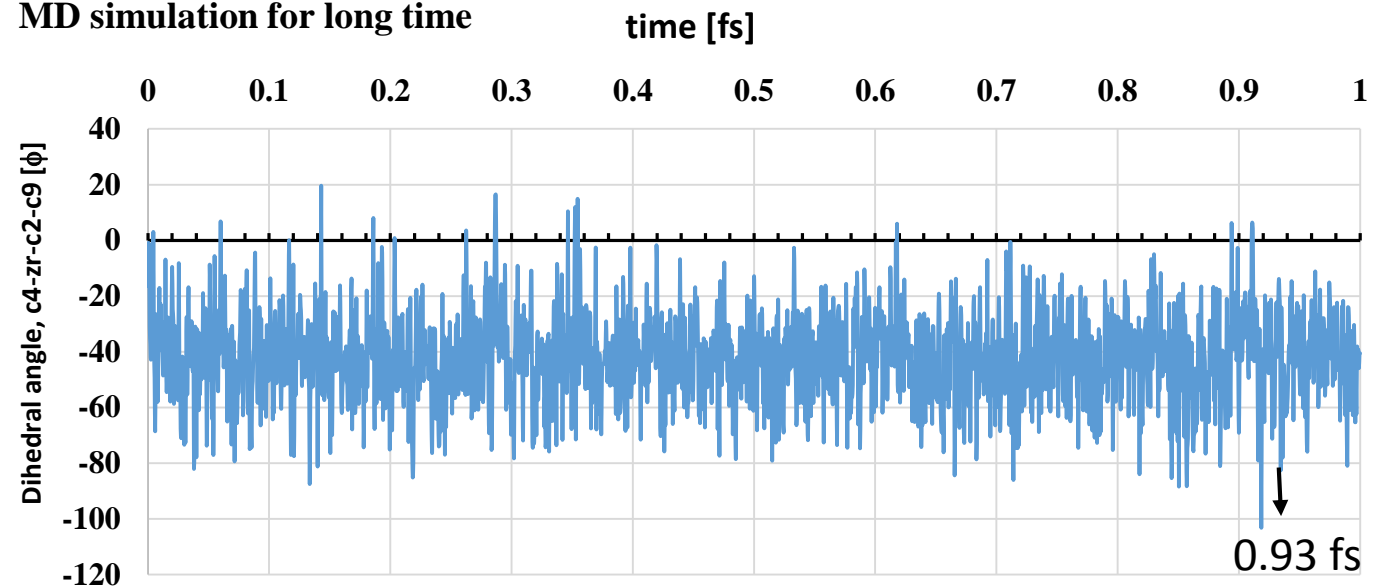
48.25 ps

- In the case of B approach of propylene, various metastable structures are possible, but it always keep its initial position even after 50 ps

# MD simulation at 350 K and 400 K



# MD simulation for long time

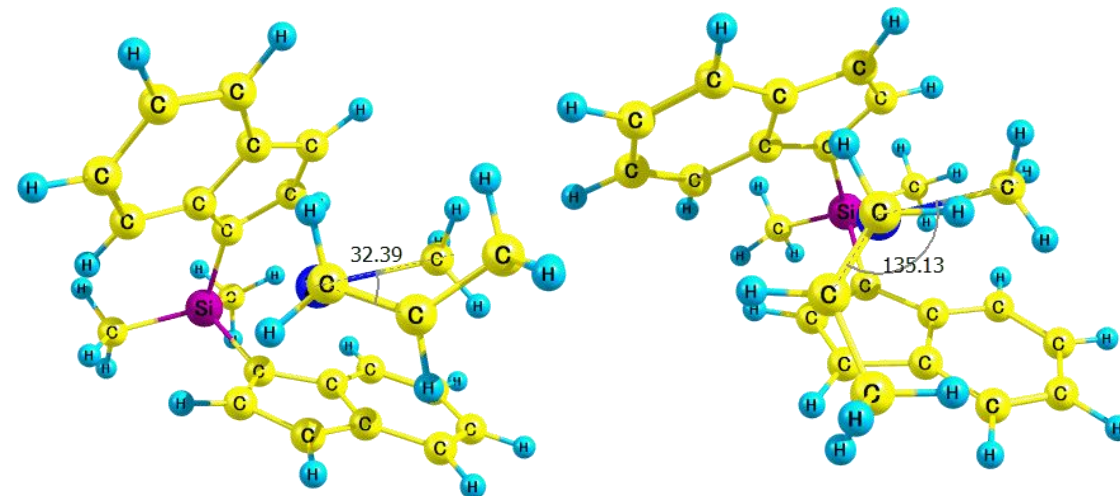


- At various temperature (upto 400 K) as well as at long run time also flipping of propylene occurs



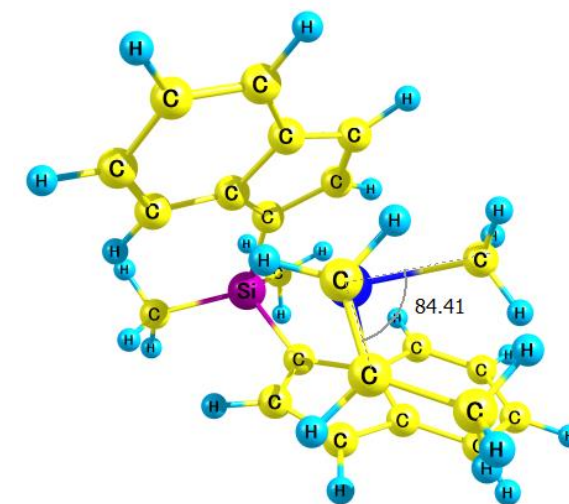
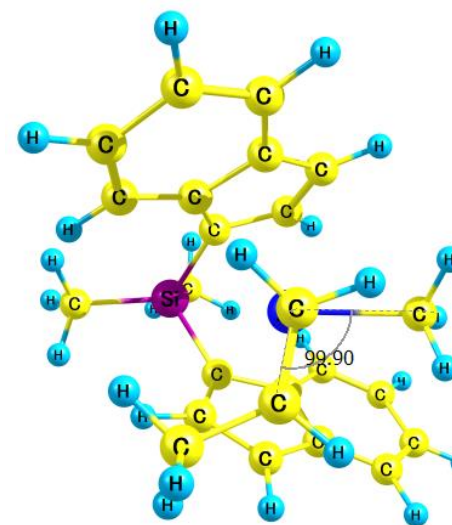
# DFT studies on rotation of propylene

Complex name	Relative energy [kcal/mol]	Complex name	Relative energy in [kcal/mol]
<b>A</b>	0	<b>C</b>	0
<b>TS1</b>	0.83	<b>TS1</b>	2.43
<b>Metastate</b>	-0.27	<b>Metastate</b>	0.13
<b>TS2</b>	2.35	<b>TS2</b>	2.35
<b>B</b>	0.59	<b>D</b>	0.41



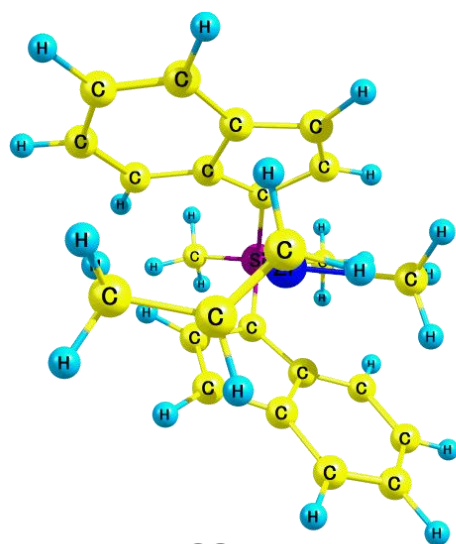
meta TS1

meta TS2

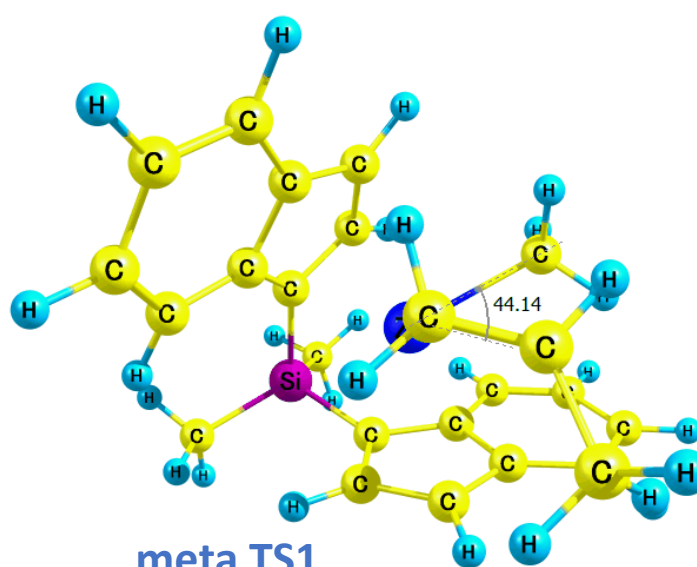


meta state

meta state



meta TS2

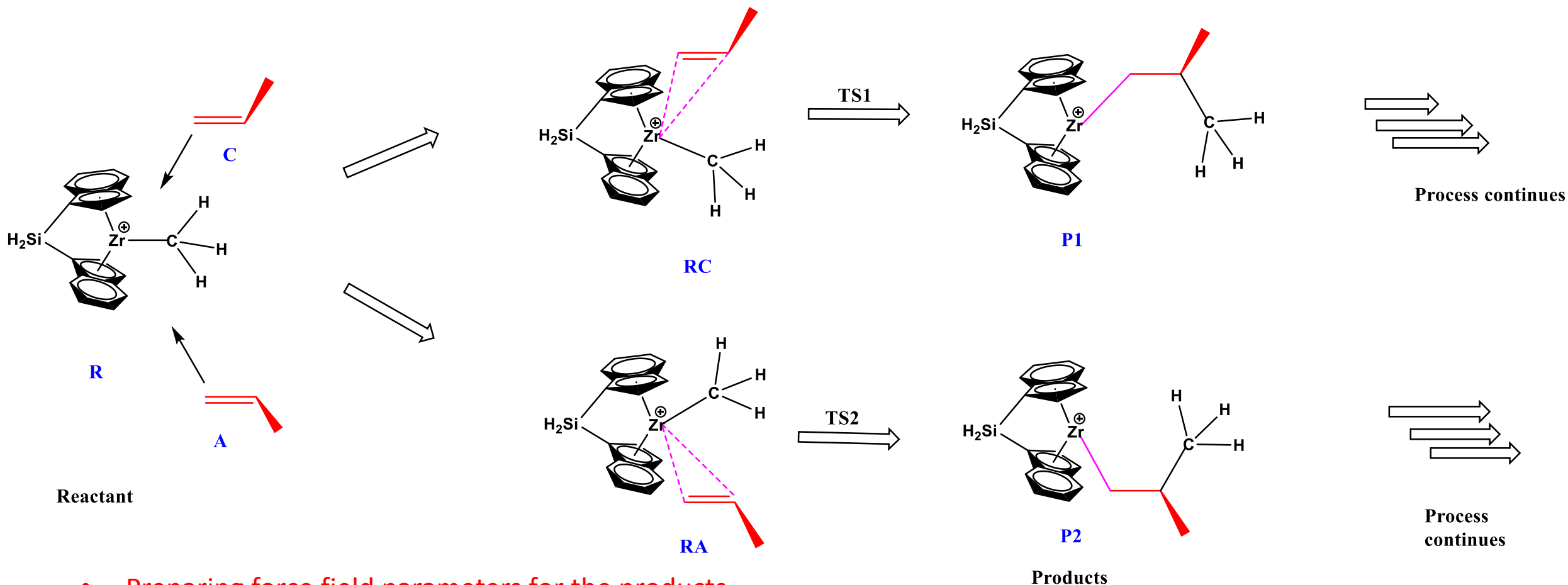


meta TS1

- Rotation between A to B or C to D is easy since activation barrier is less than 3 kcal/mol from DFT results

# Future plan

## REACTION SCHEME FOR MC/MD



- Preparing force field parameters for the products
- Writing a paper regarding the force field development of intermediate state for MD simulation and the DFT studies on the metastable state. Target time- one month.
- Force field parameter for C mode attack of propylene and use of **Merz-Singh-Kollman (MK)** method to assign atomic charge to A mode of attack.

# Conclusions

- DFT studies on the reaction mechanism of four different attack of propylene in the presence of the counter anion show a decrease in the activation barrier.
- Numerous force field parameters are developed and successfully implemented for MD simulation.
- Various metastable structures are observed in MD simulation.
- TS's for the metastable structures confirm that activation barrier is very less (3 kcal/mol).

Thank you