

Electronic Supplementary Information (ESI)

A Computational Investigation of Ring-Shift Isomerization of *sym*-Octahydrophenanthrene into *sym*-Octahydroanthracene Catalyzed by Acidic Zeolites

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Fig. S1 The terminology used in definition of the *S*-value for the level/model combination in an ONIOM scheme. (Blue: silicon; red: oxygen; pink: aluminum; white: hydrogen.)

$$S(\text{level}) = E(\text{level, real}) - E(\text{level, model})$$

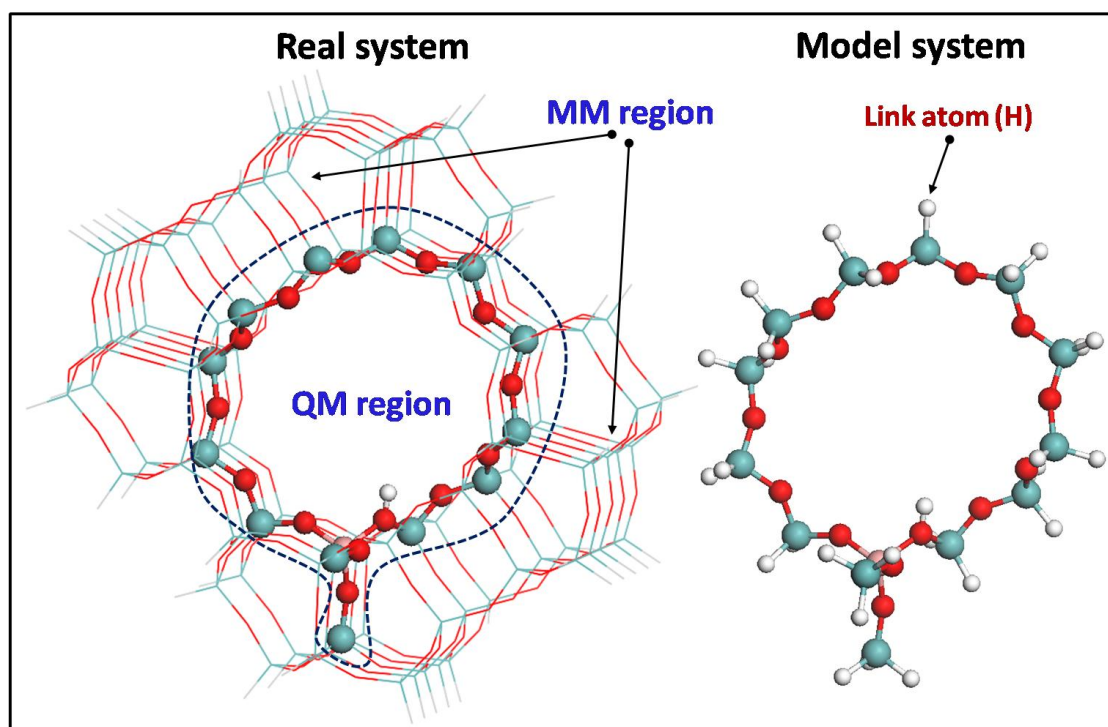
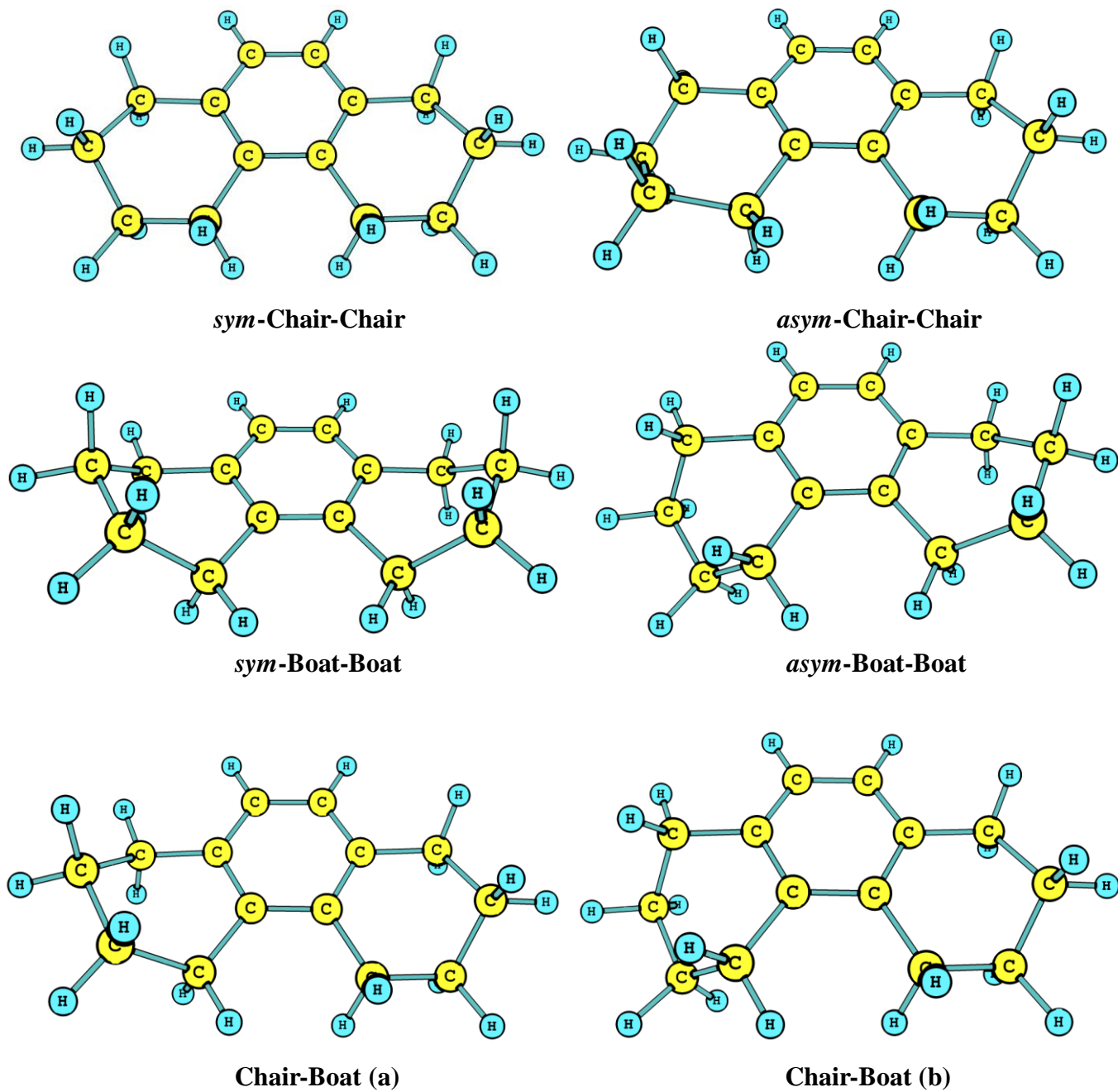
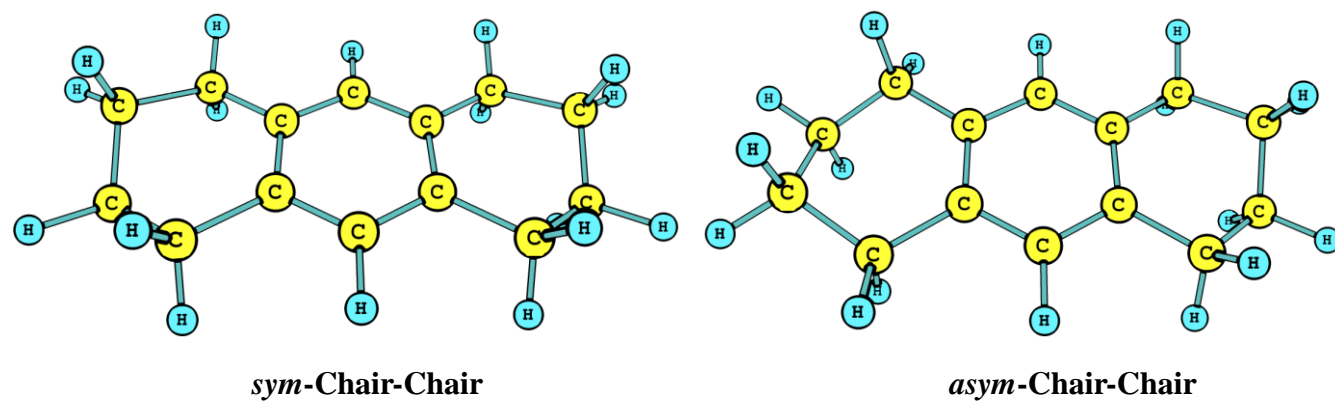


Fig. S2 Optimized geometries of *sym*-OHP and *sym*-OHA molecular configurations in the gas phase.

(a) Gas phase structures of *sym*-OHP conformers



(b) Gas phase structures of *sym*-OHA conformers



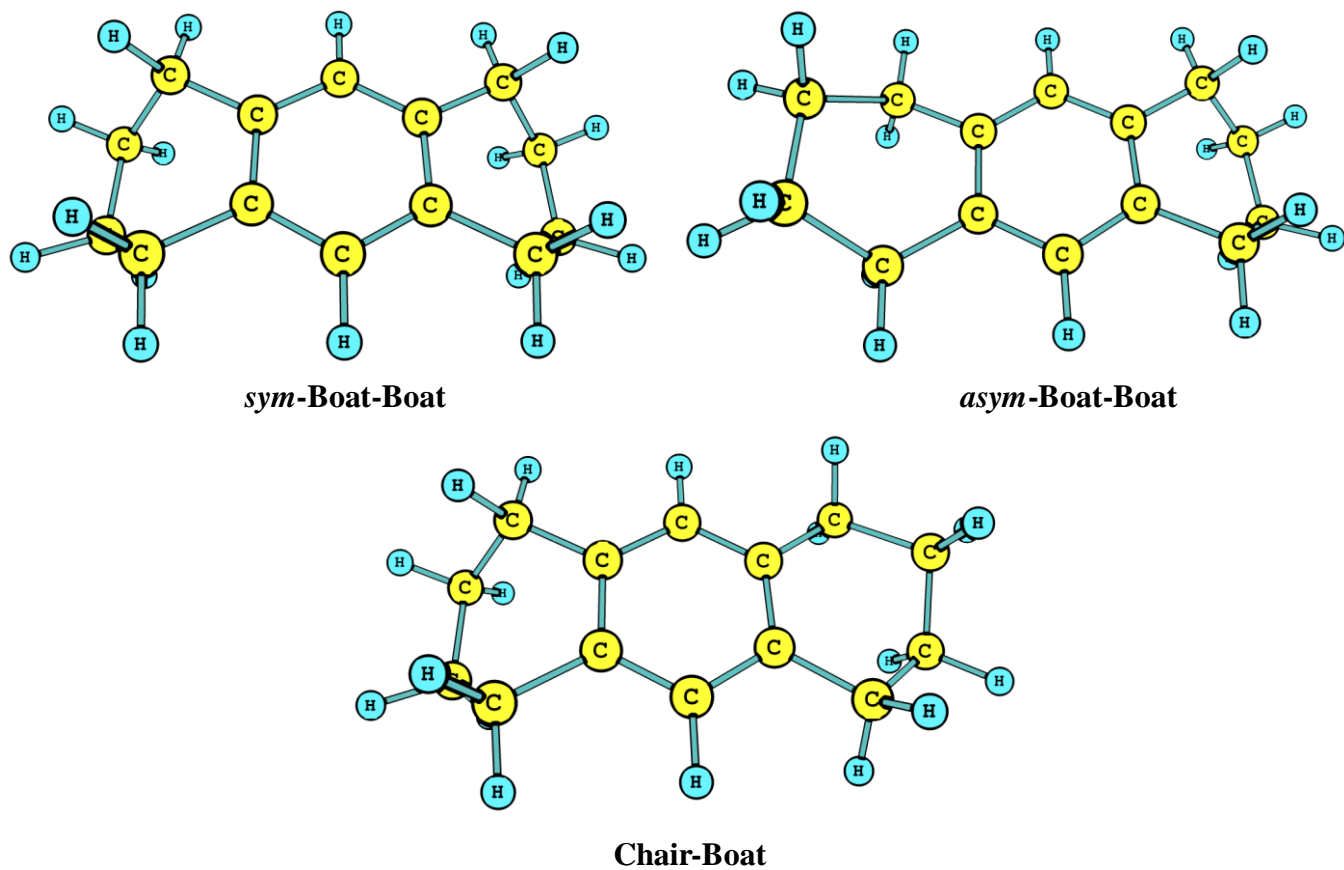
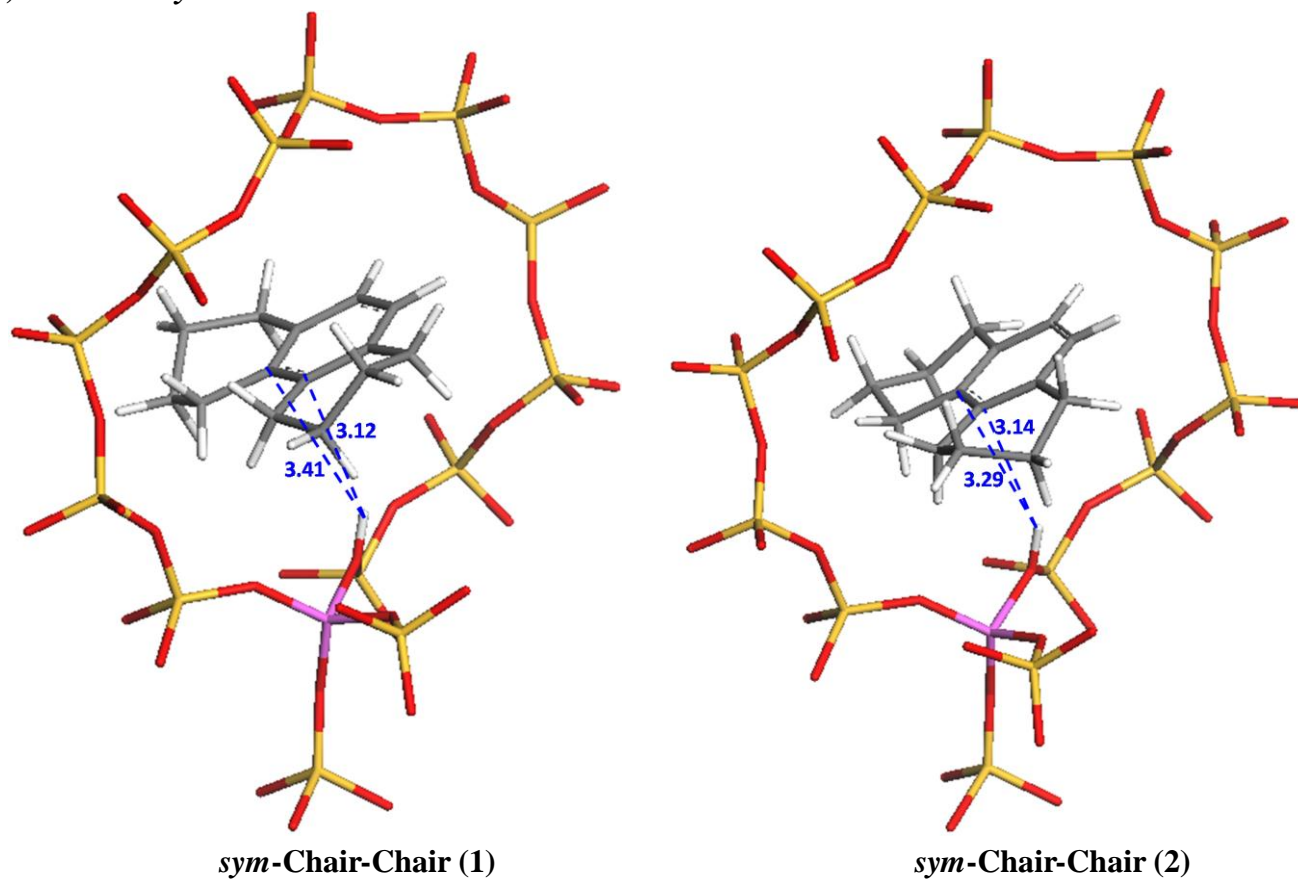
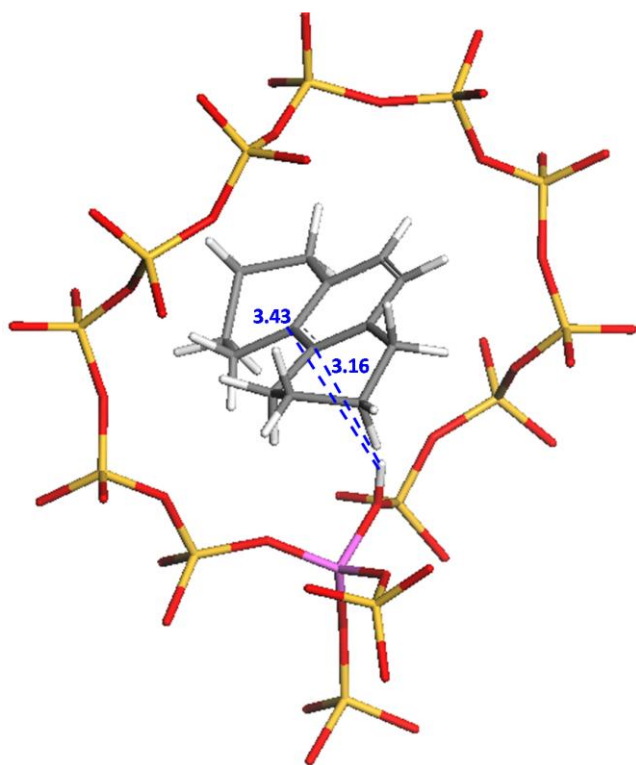
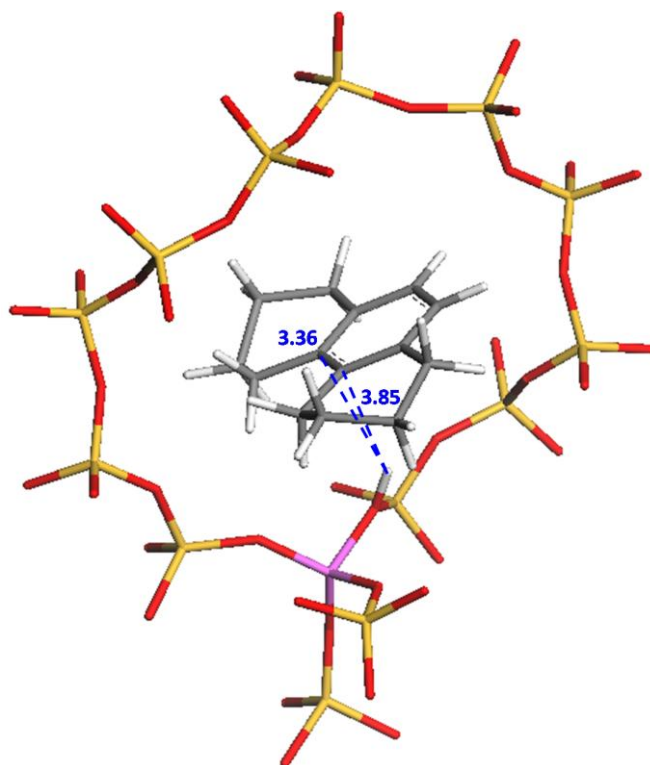


Fig. S3 All the possible adsorbed structures of *sym*-OHP and *sym*-OHA over the 120T Al-H-MOR.
(a) Adsorbed *sym*-OHP structures

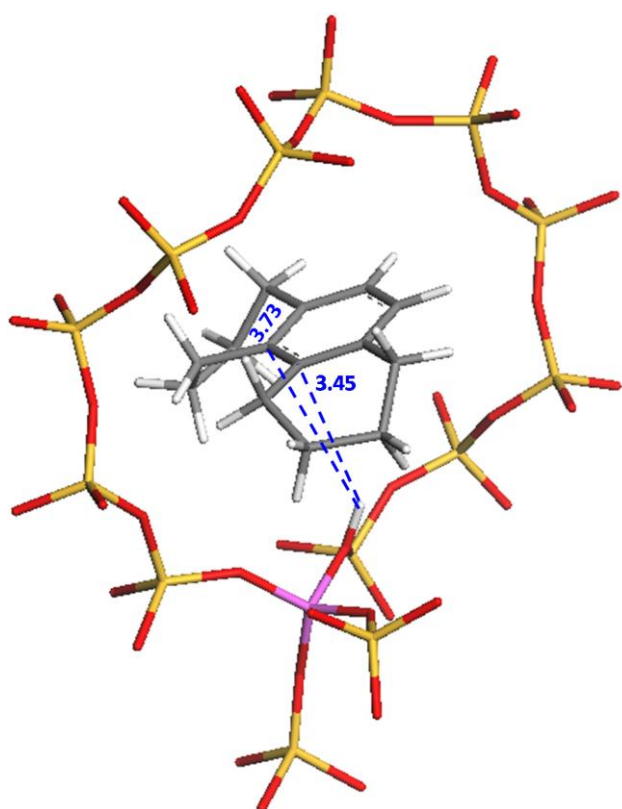




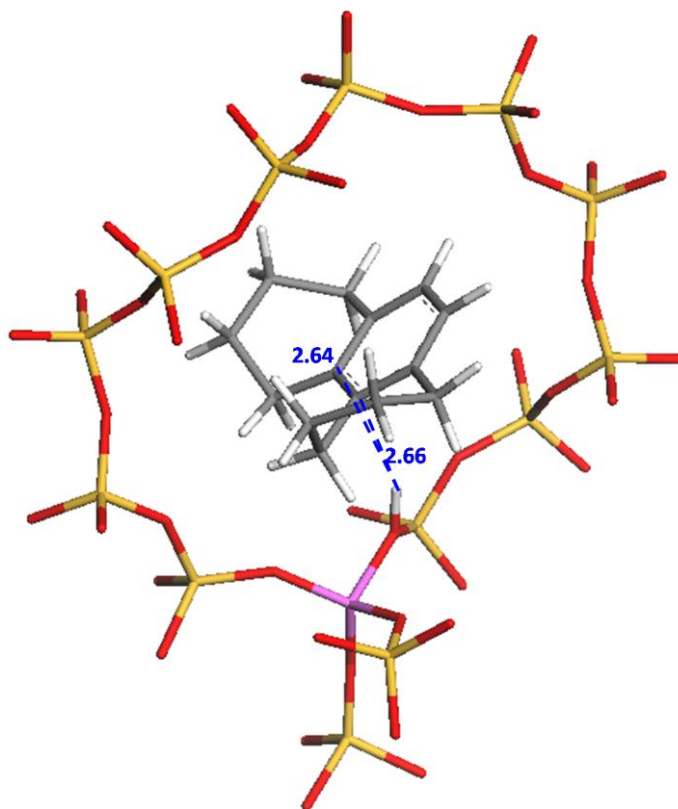
asym-Chair-Chair (1)



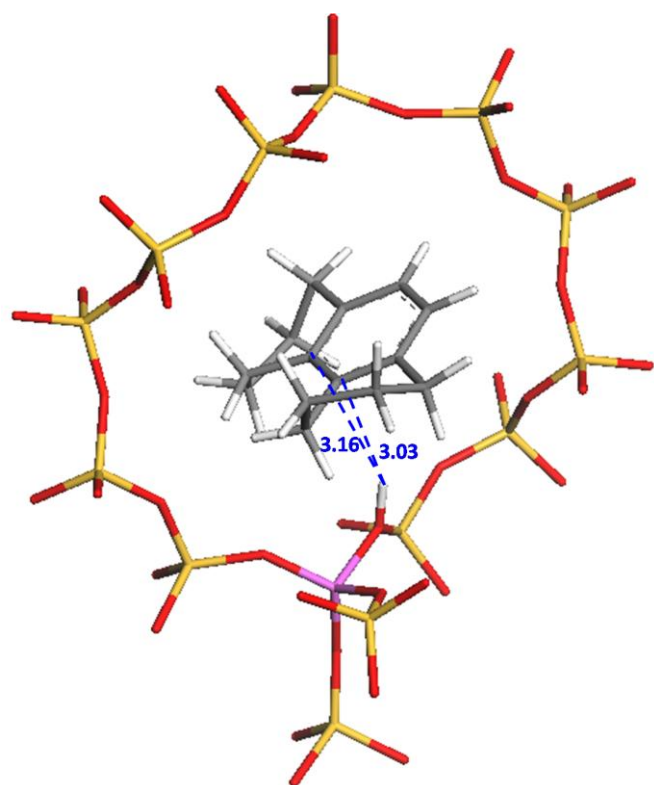
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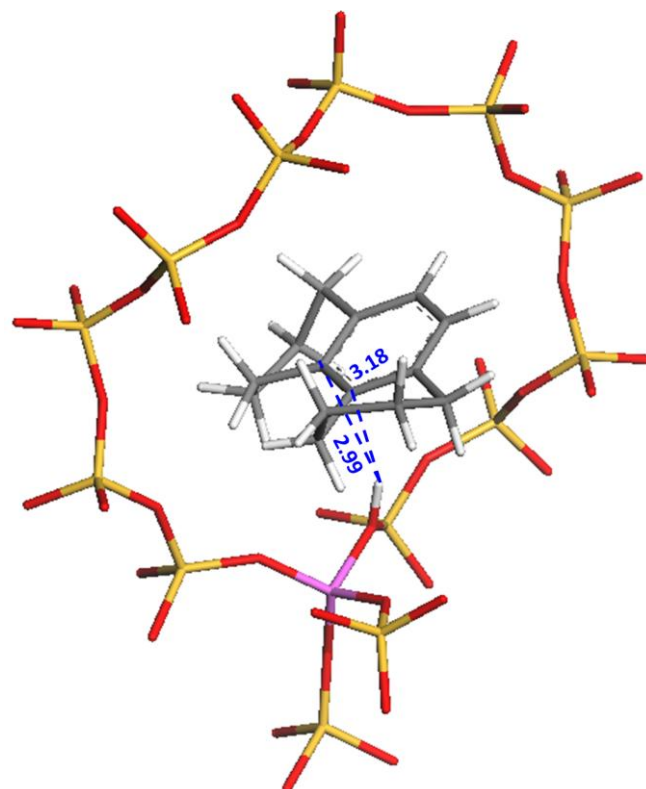
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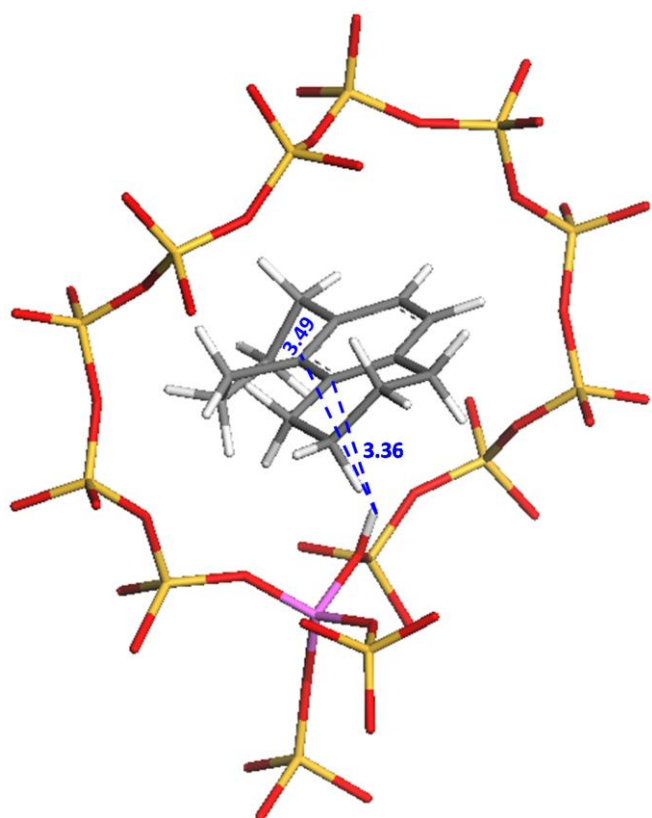
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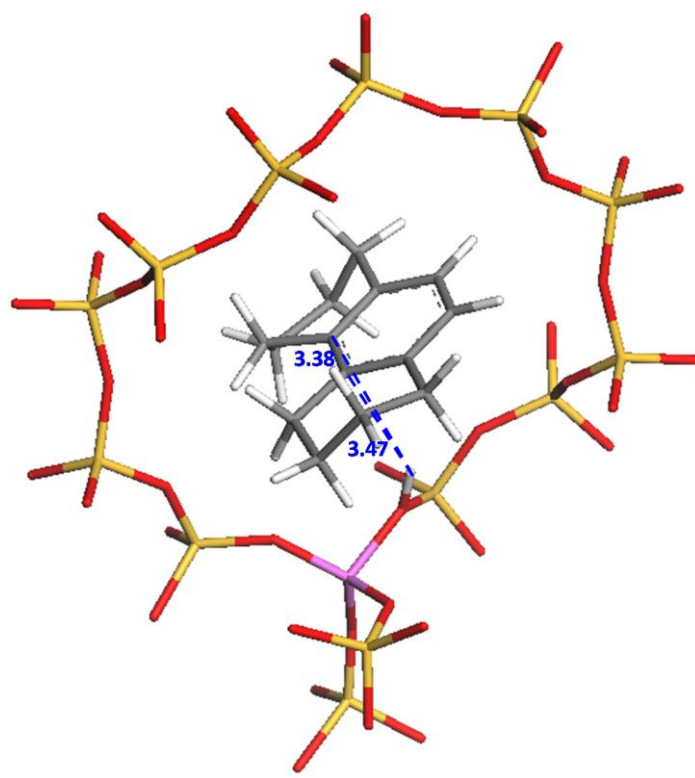
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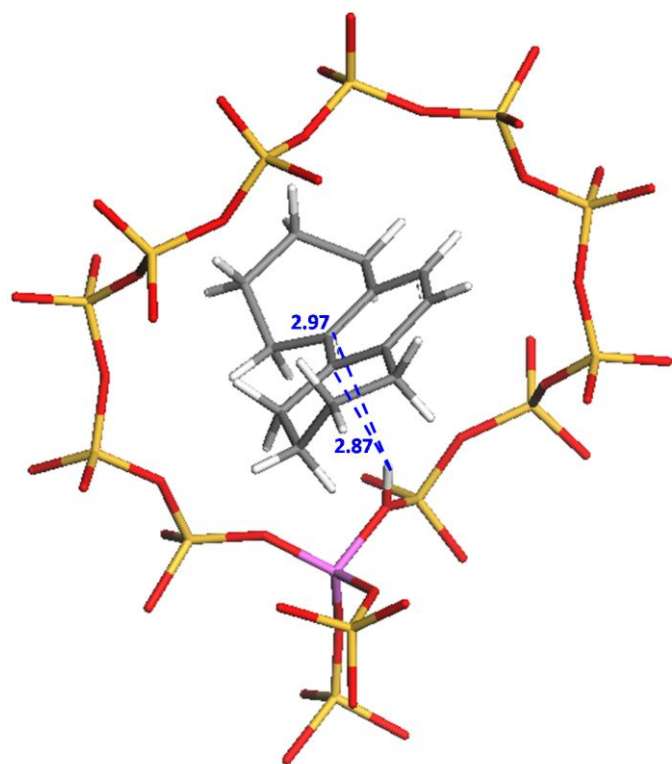
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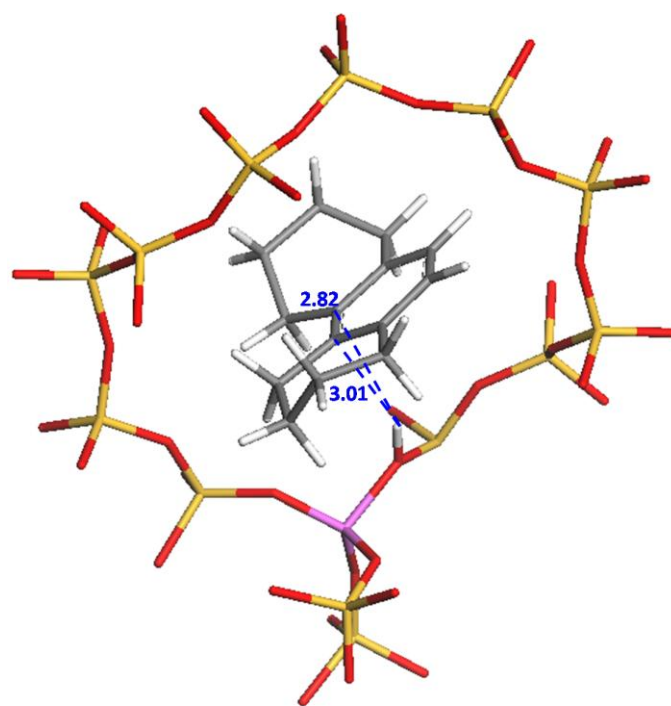
Chair-Boat (1)



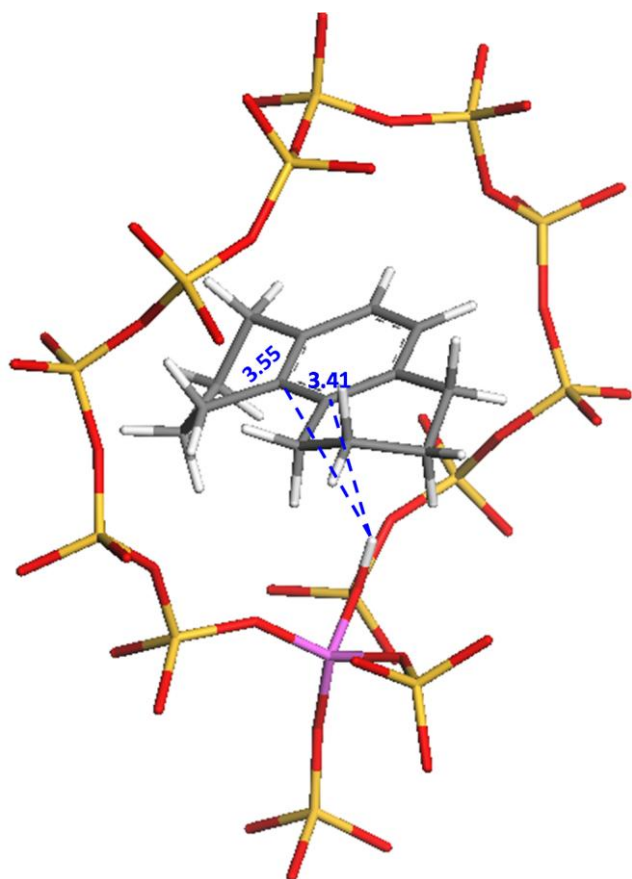
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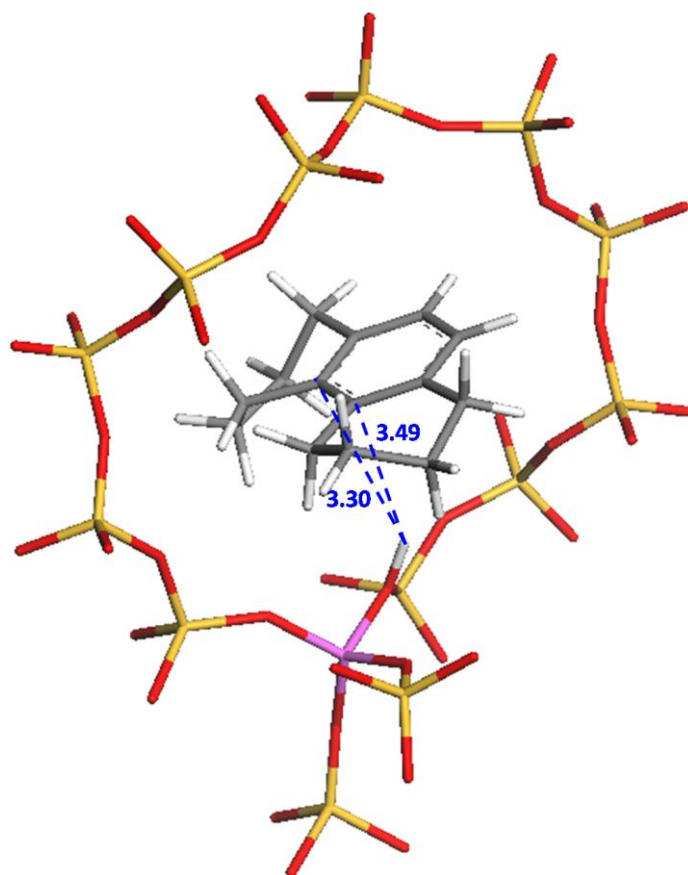
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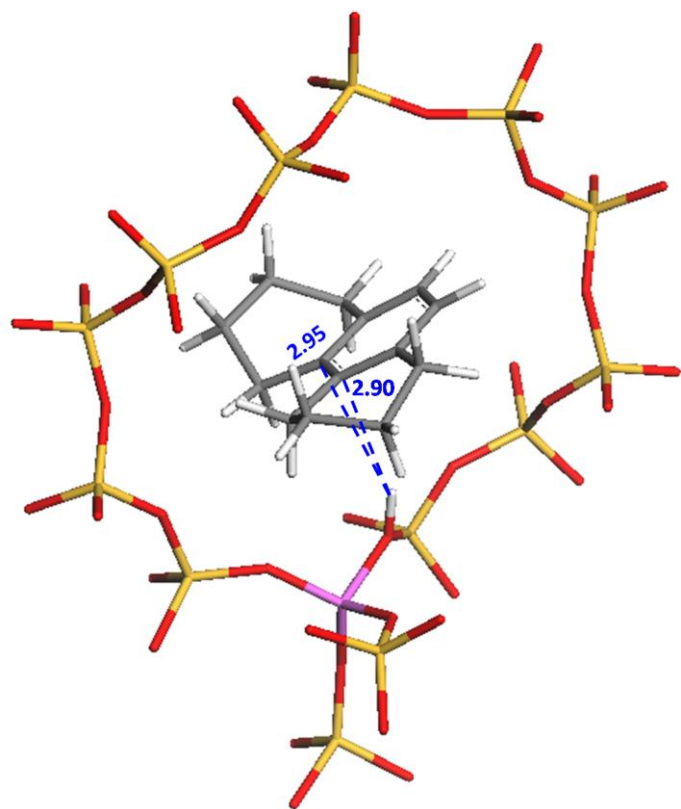
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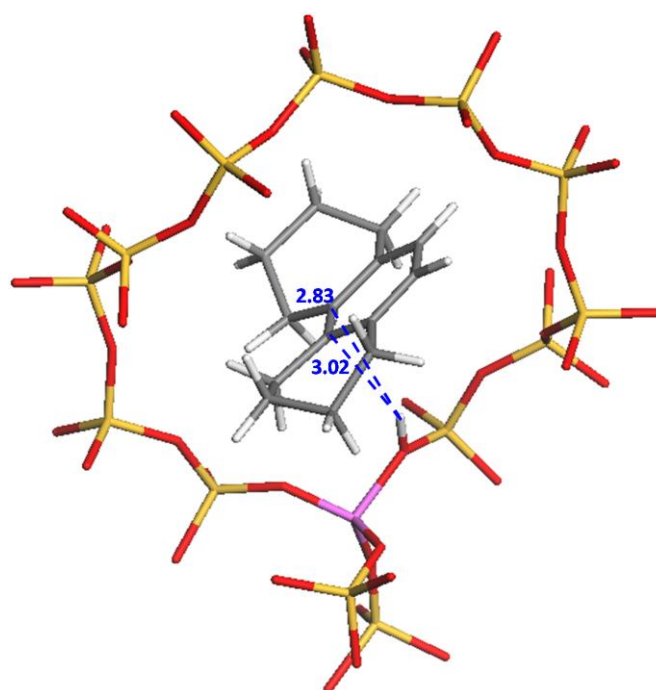
Chair-Boat (5)



Chair-Boat (6)

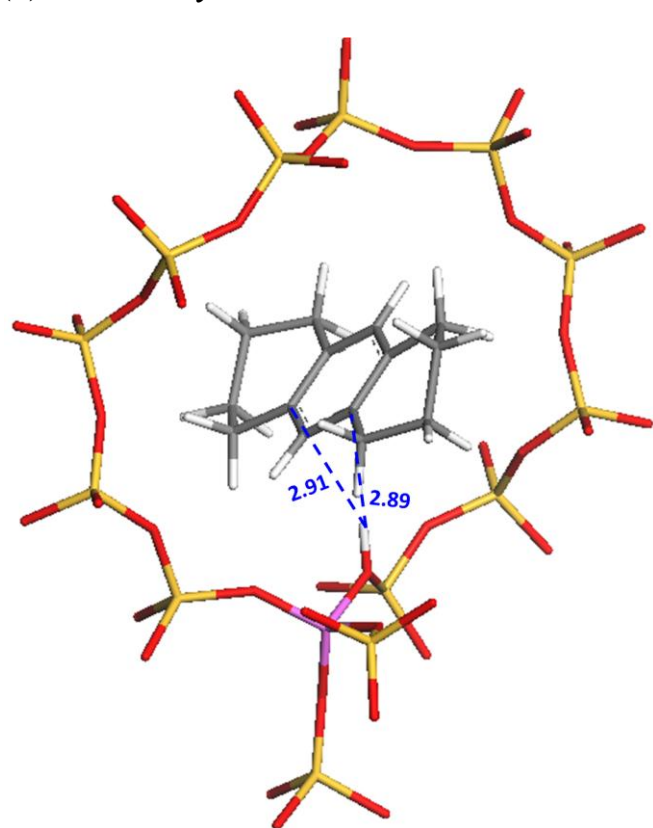


Chair-Boat (7)

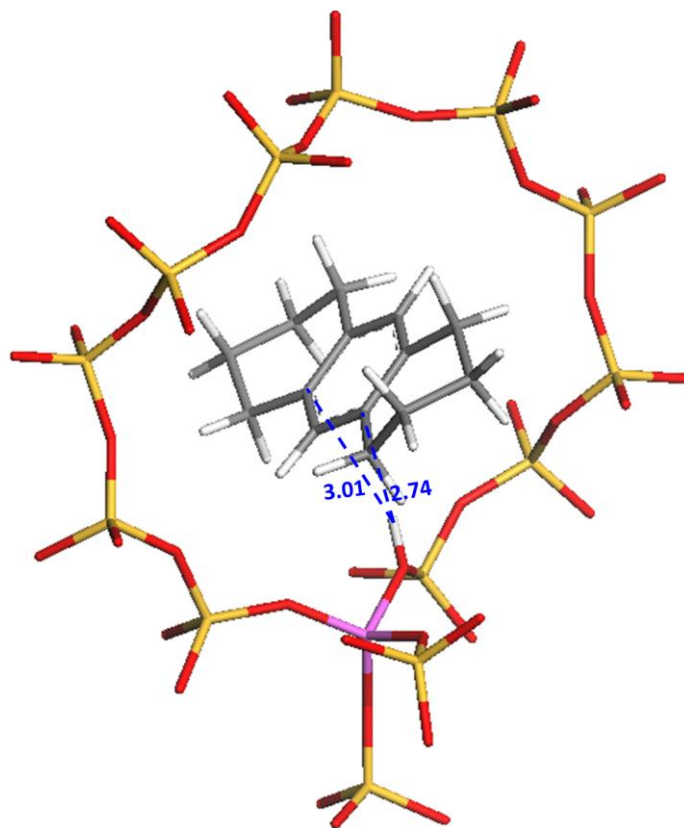


Chair-Boat (8)

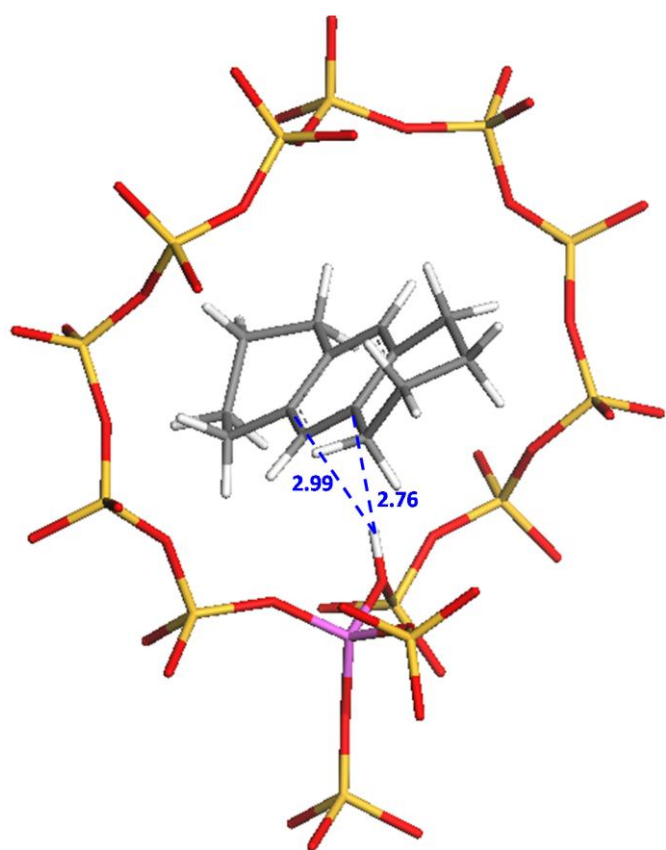
(b) Adsorbed *sym*-OHA structures



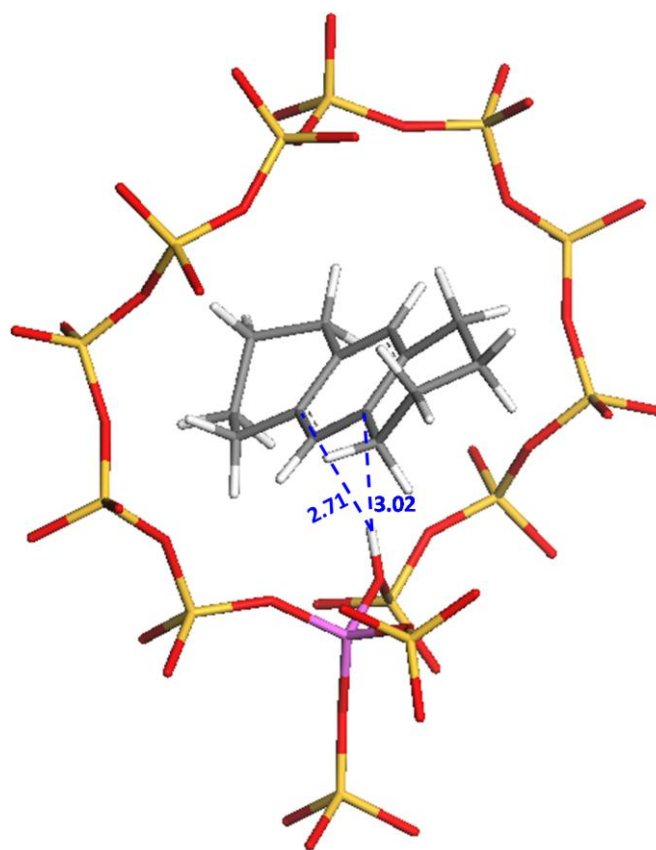
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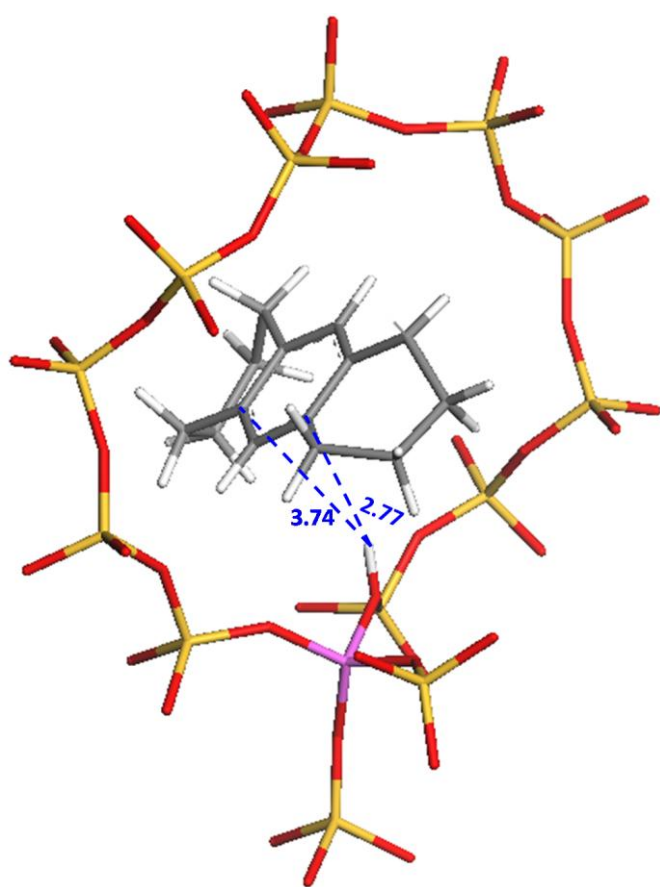
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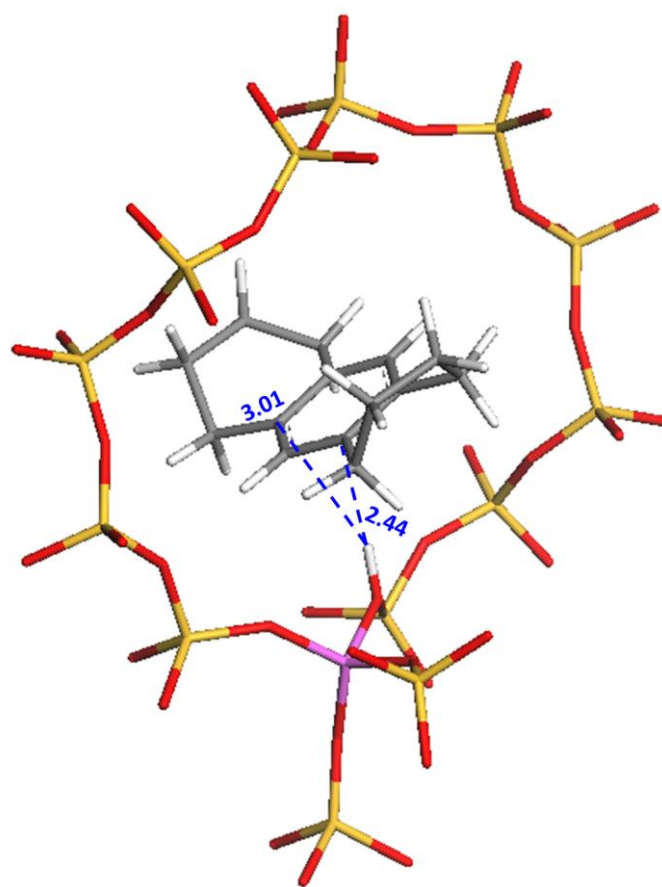
asym-Chair-Chair (1)



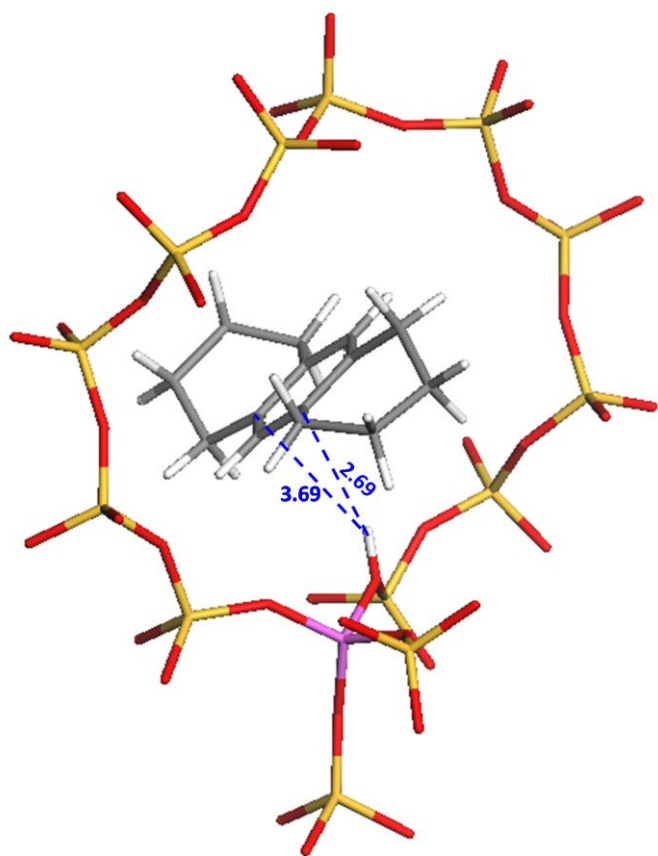
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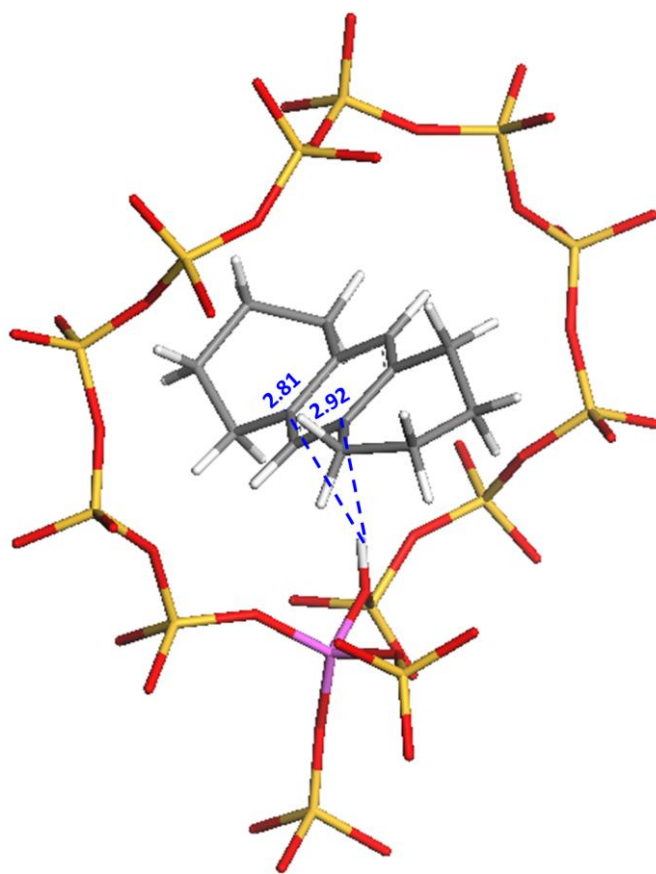
sym-Boat-Boat (1)



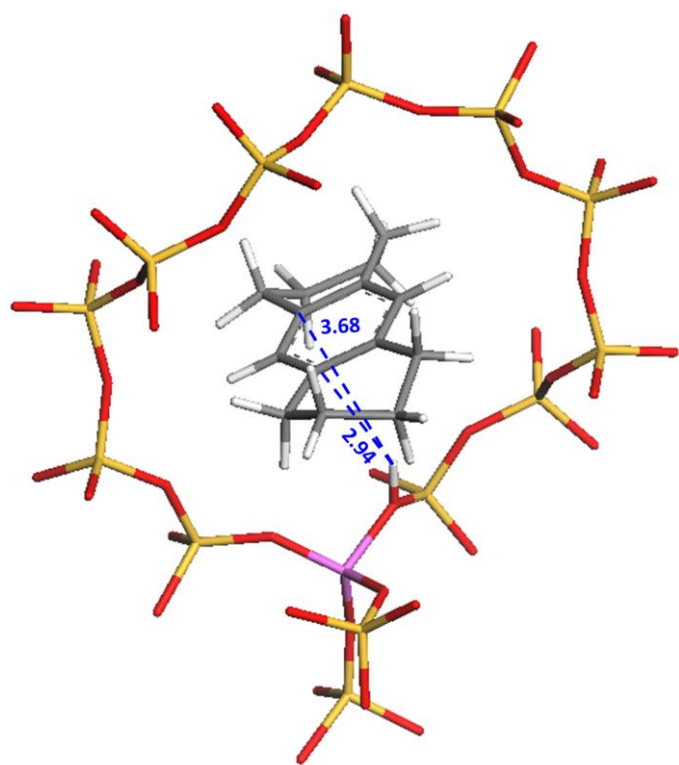
sym-Boat-Boat (2)



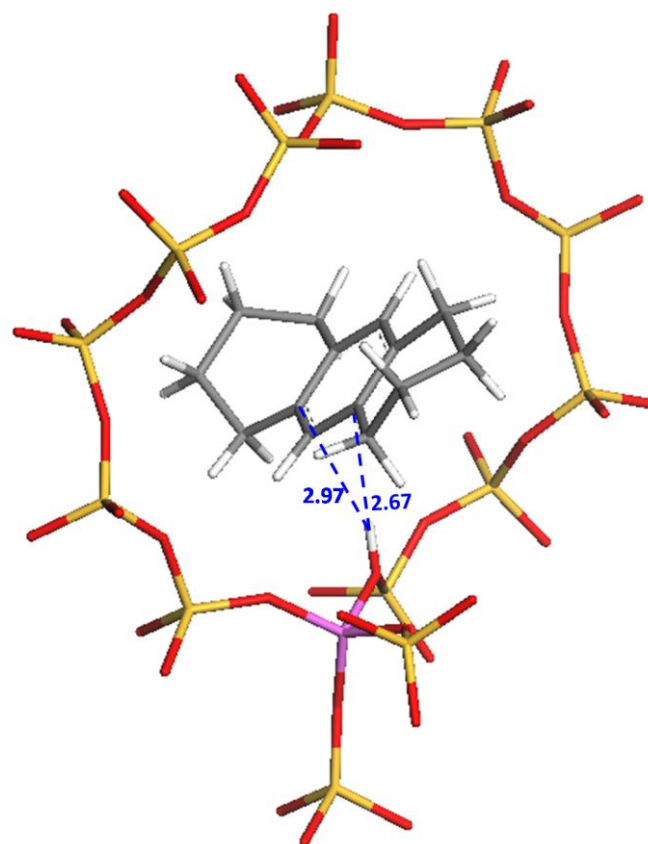
***asym-Boat-Boat* (1)**



***asym-Boat-Boat* (2)**



Chair-Boat (1)



Chair-Boat (2)

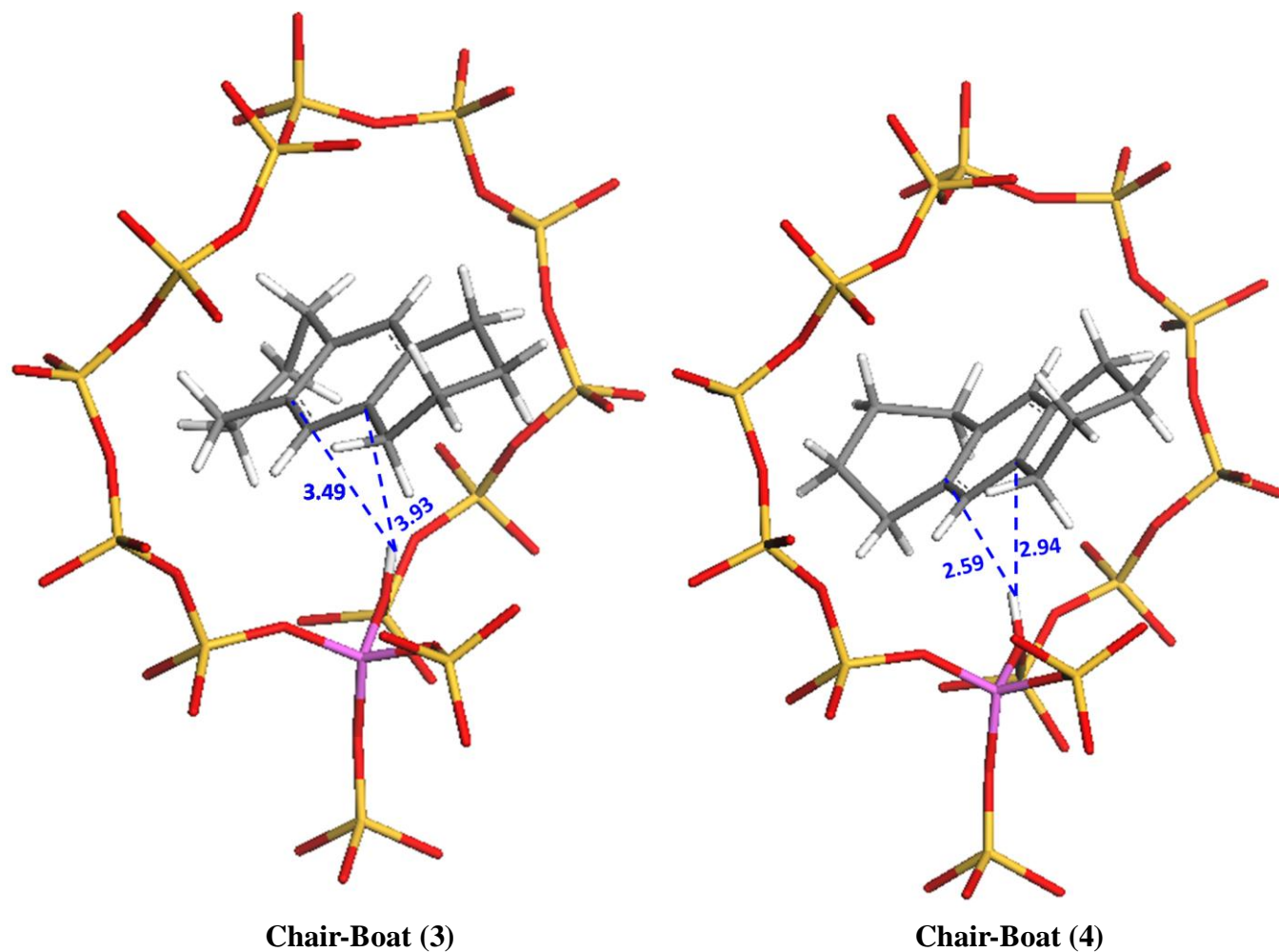
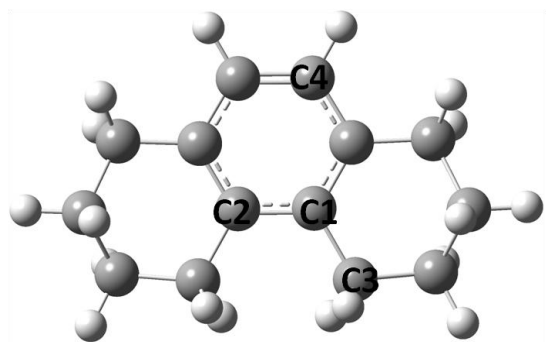
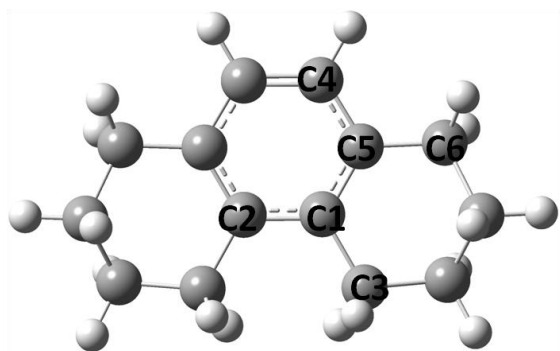
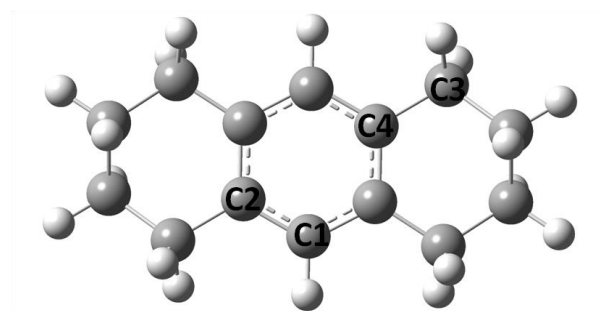


Fig. S4 Atom label reference structures.

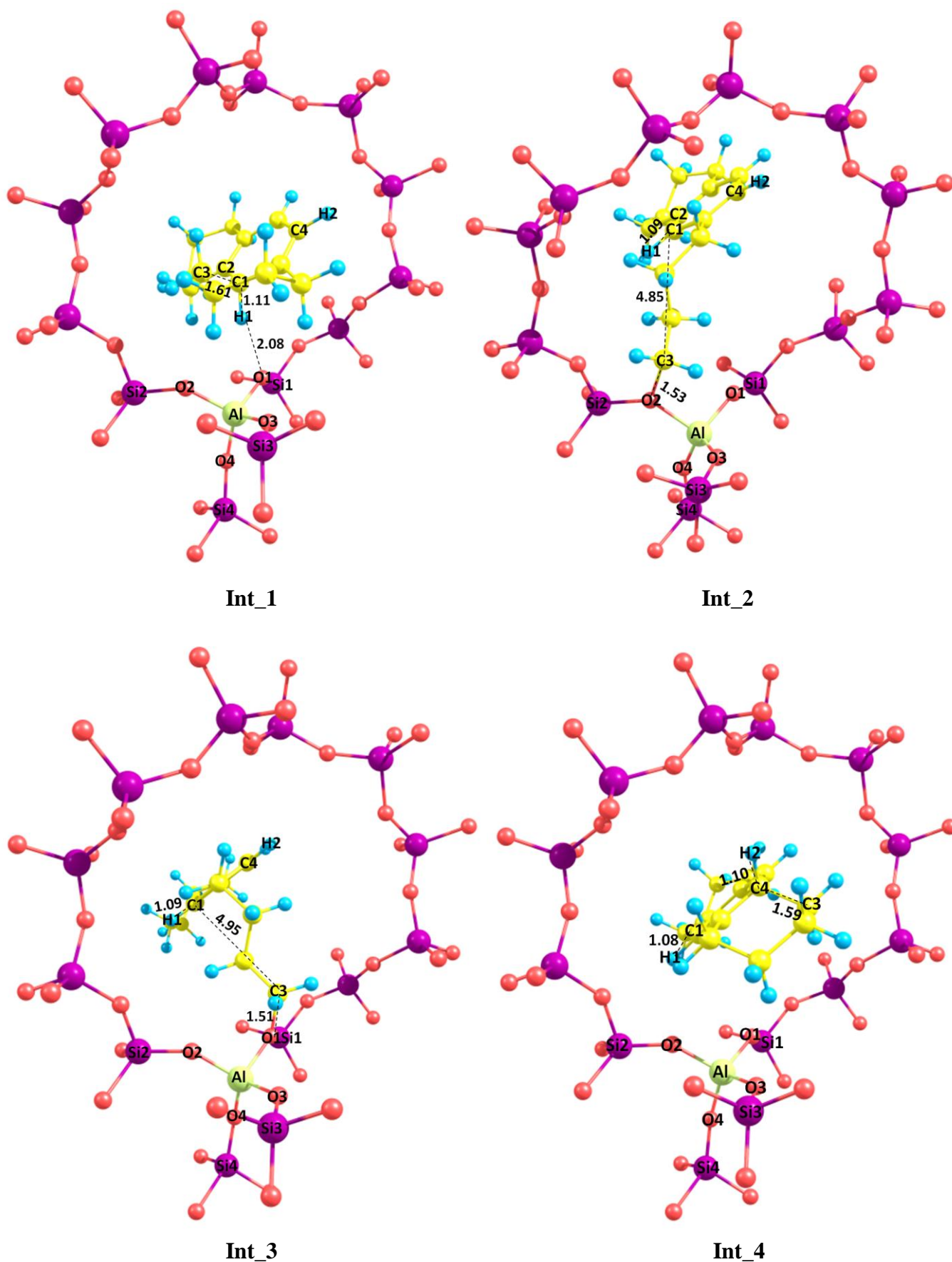


(a) reference structures for the “six-membered ring” mechanism



(b) reference structures for the “five-membered ring” mechanism

Fig. S5 Optimized geometries of all the intermediate species included in the “six-membered ring” mechanism of ring-shift isomerization of *sym*-OHP into *sym*-OHA catalyzed by the 120T Al-H-MOR. Only the adsorbates and 14T quantum region are shown for clarity.



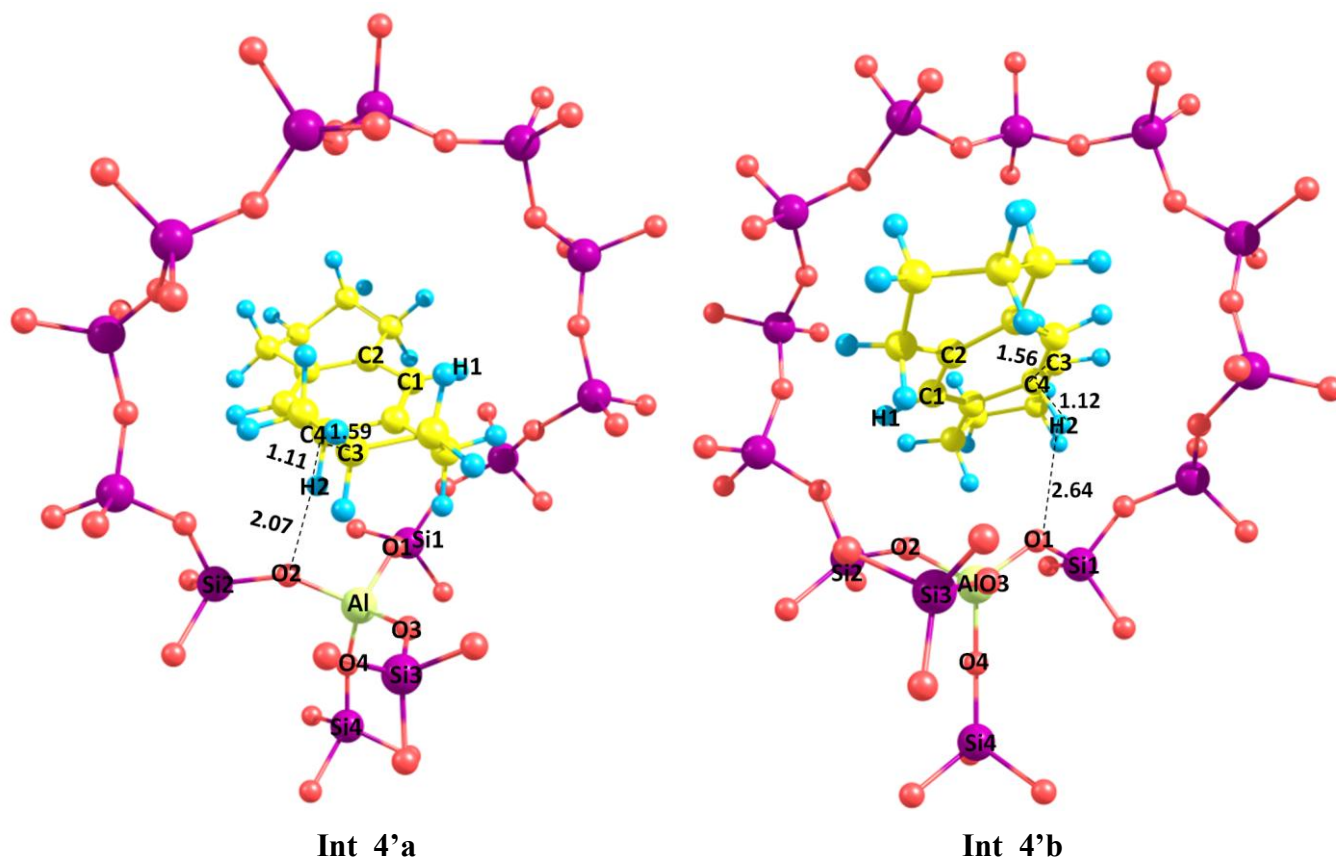
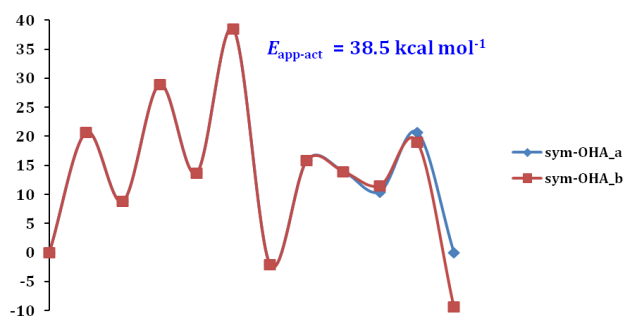
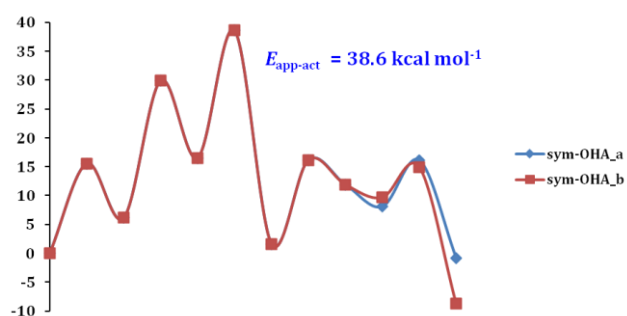


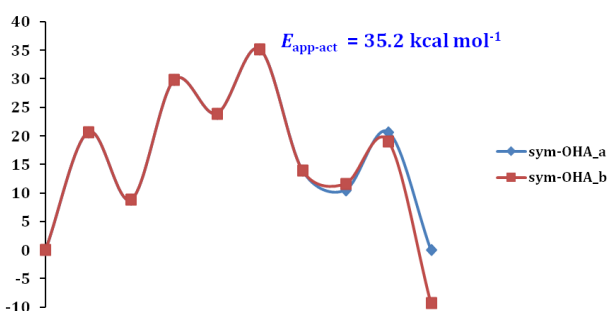
Fig. S6 Energy profiles based on the “six-membered ring” and “five-membered ring” mechanisms with the 120T Al-H-MOR starting and ending with the adsorbed states calculated with the B3PW91 and PBE functionals.



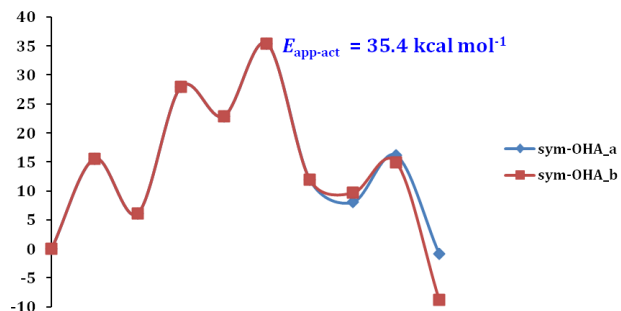
(a) with B3PW91 functional (six-membered ring mechanism)



(b) with PBE functional (six-membered ring mechanism)



(c) with B3PW91 functional (five-membered ring mechanism)



(d) with PBE functional (five-membered ring mechanism)

Fig. S7 Energy profiles for the proposed “six-membered ring” and “five-membered ring” mechanisms with the 120T Al-H-MOR starting and ending with the adsorbed states computed with 6-311g(d,p) and 6-311+g(d,p) basis sets.

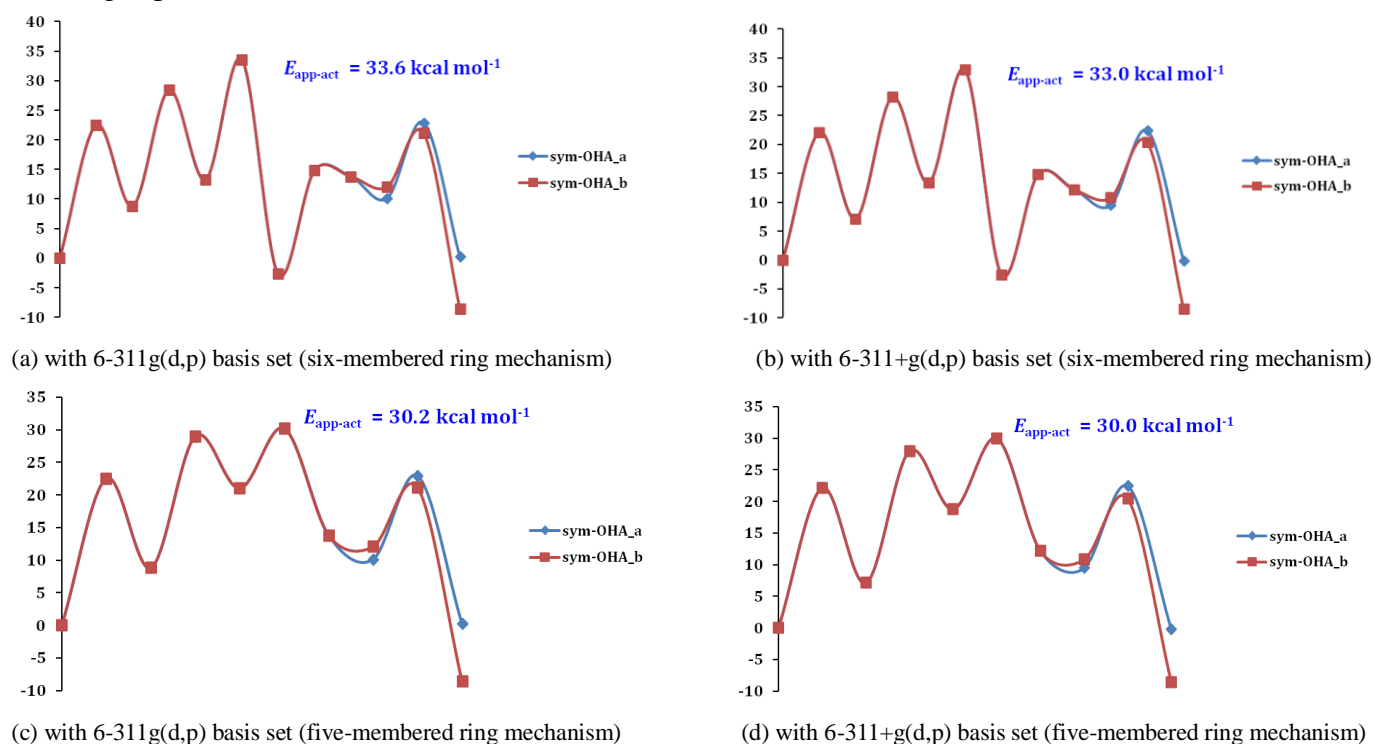
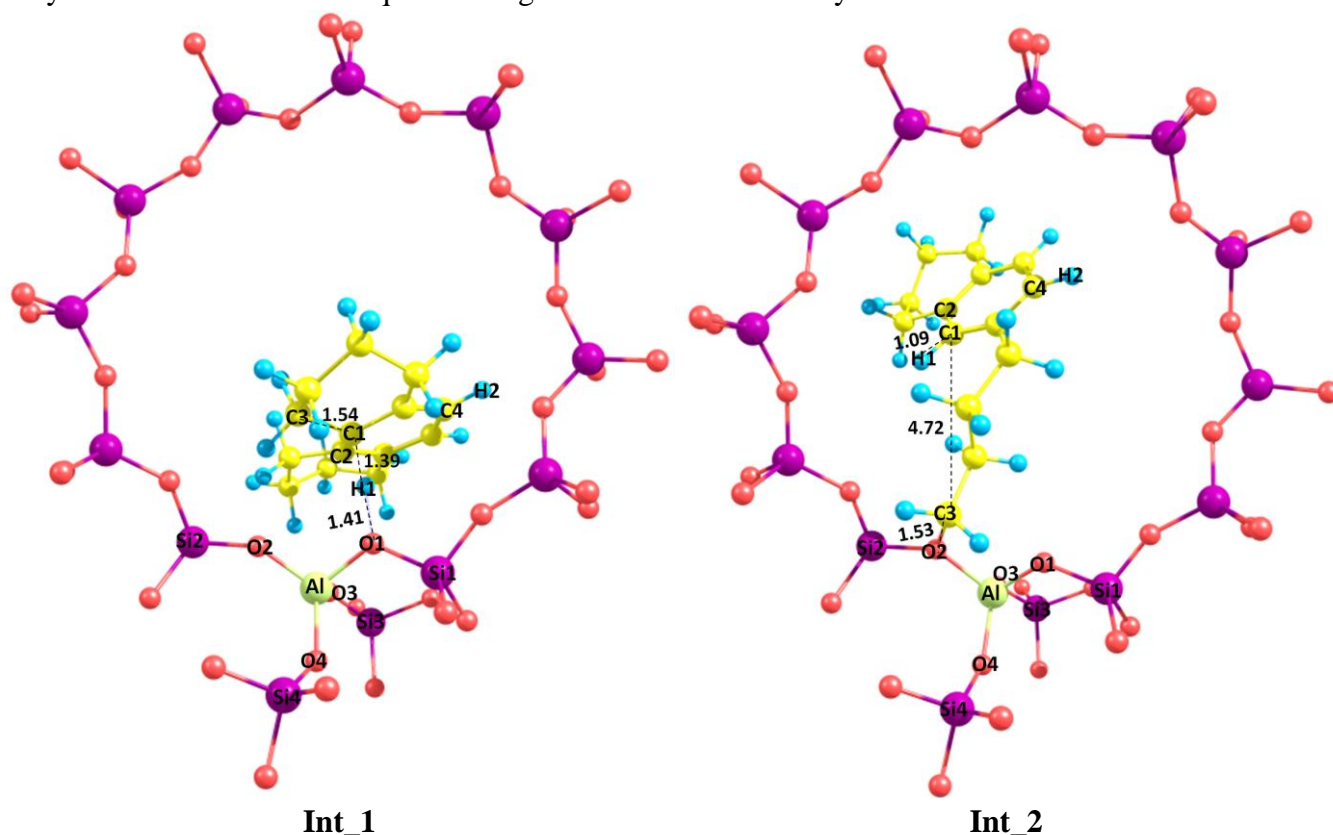
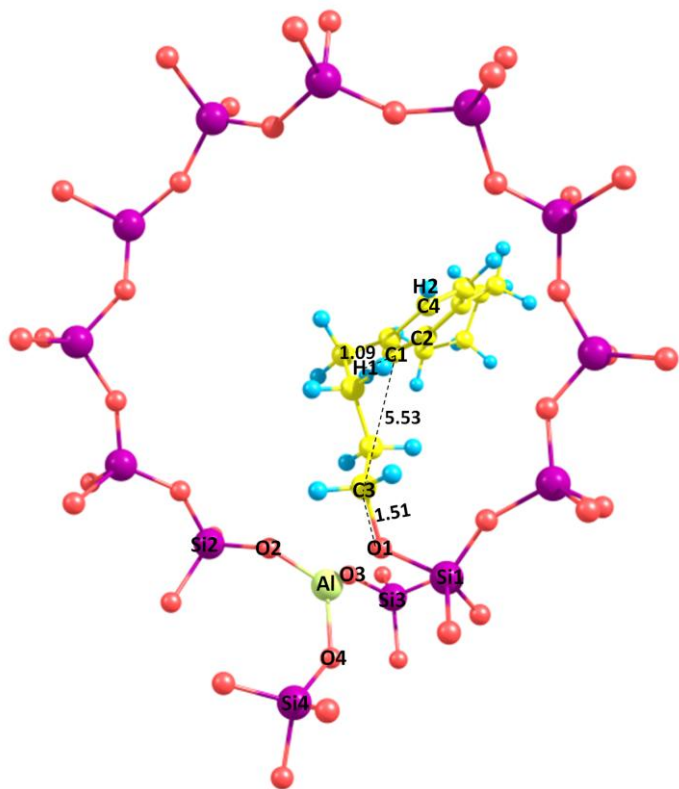
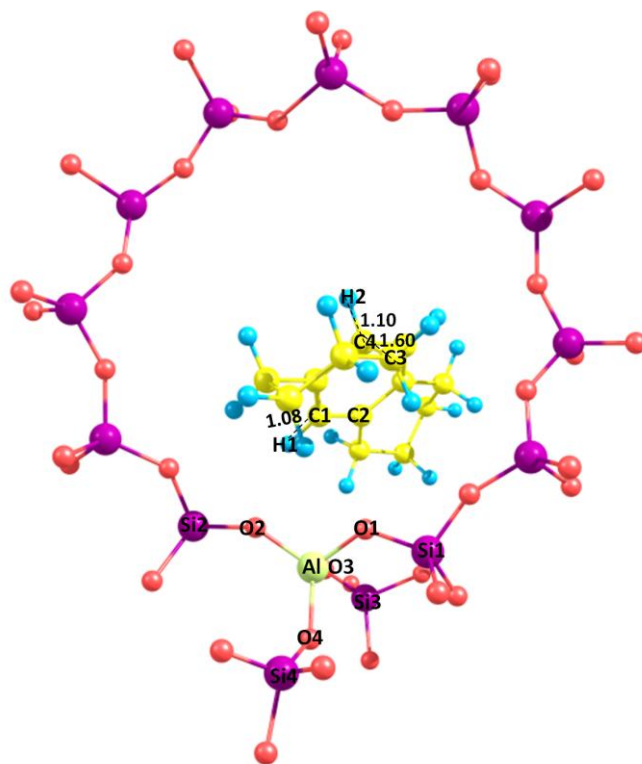


Fig. S8 Optimized geometries of all the stationary points and transition states included in the both mechanisms of ring-shift isomerization of *sym*-OHP into *sym*-OHA catalyzed by the 140T Al-H-FAU. Only the adsorbates and 14T quantum region are shown for clarity.

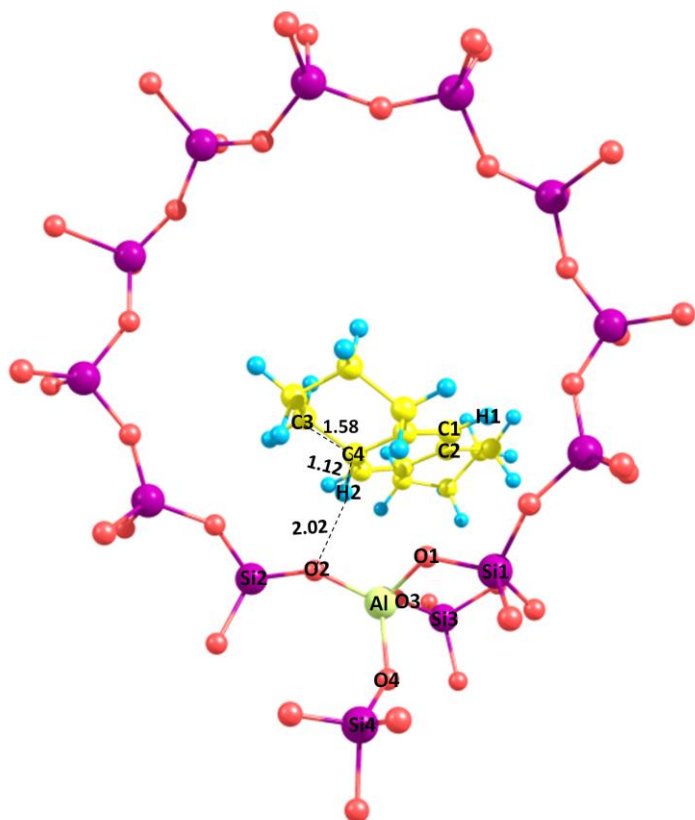




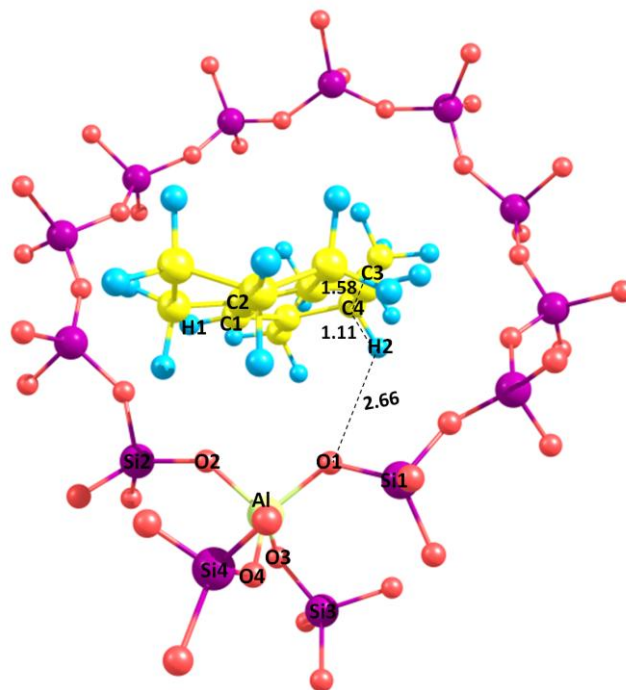
Int_3



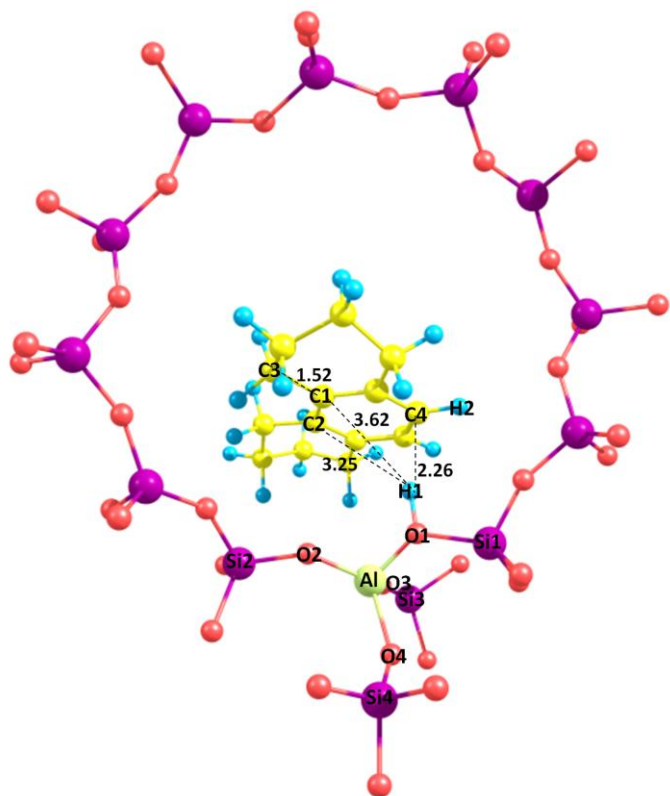
Int_4



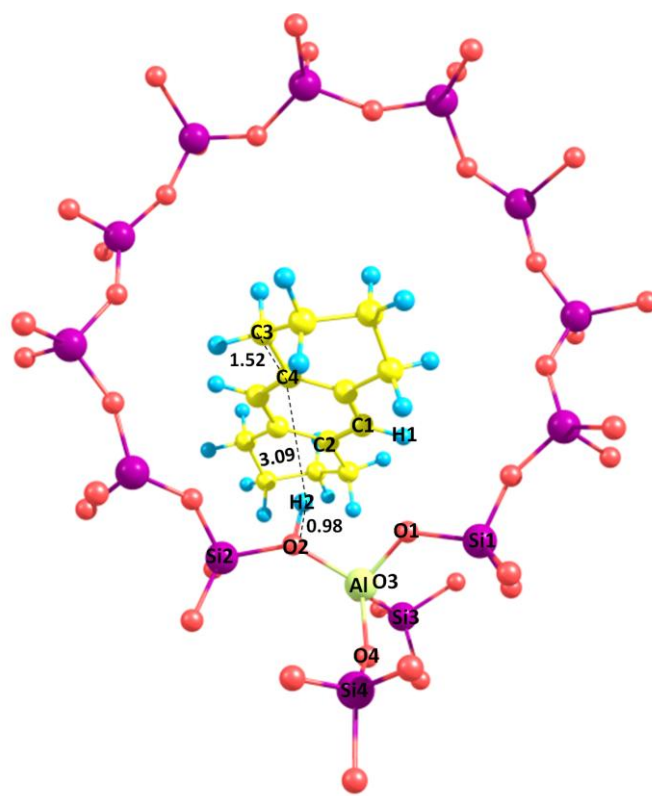
Int_4'a



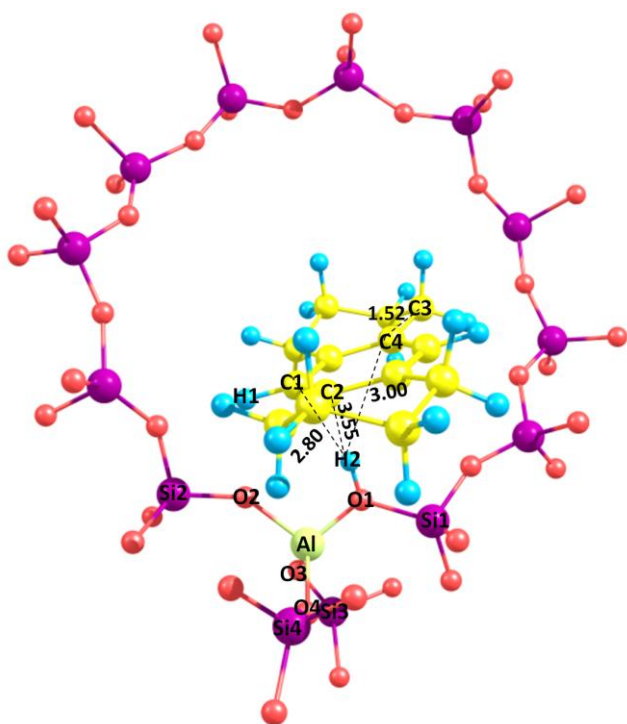
Int_4'b



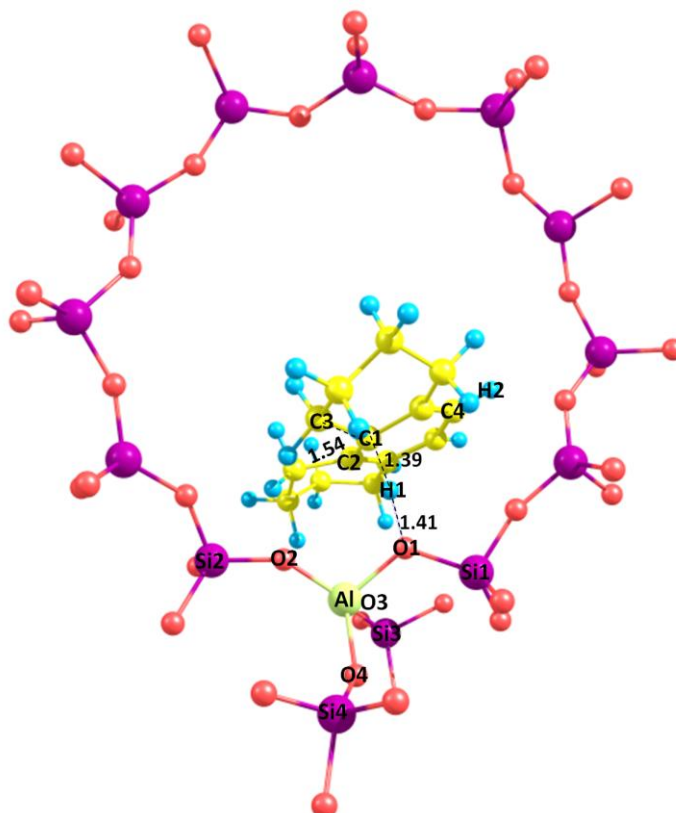
Ads_sym-OHP



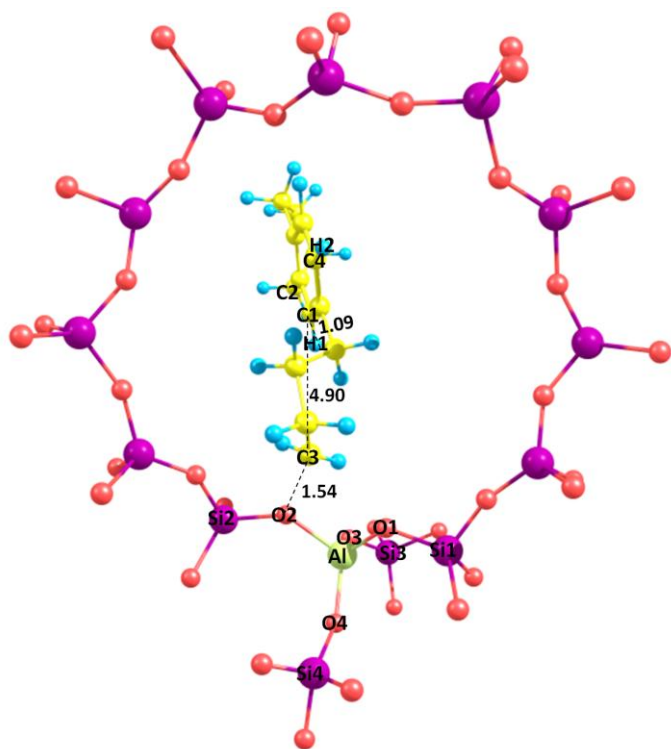
Ads_sym-OHA_a



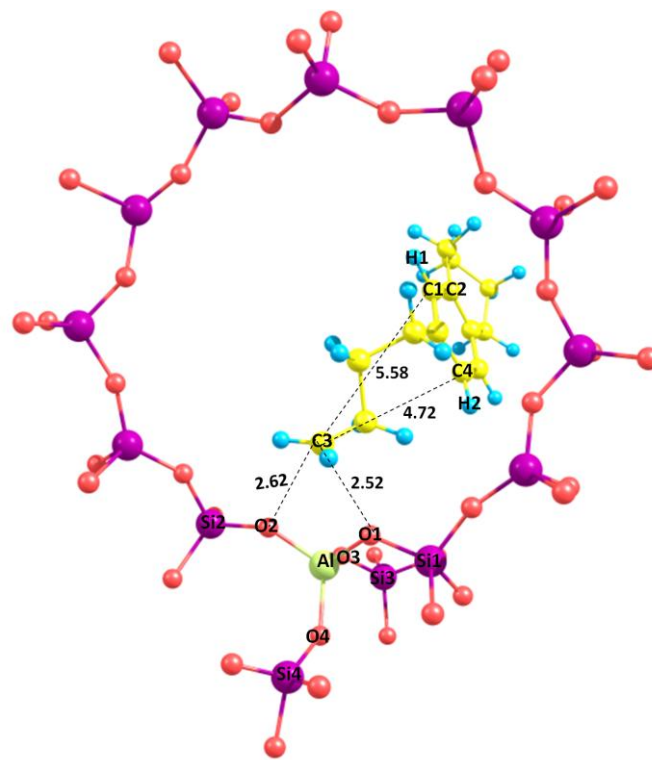
Ads_sym-OHA_b



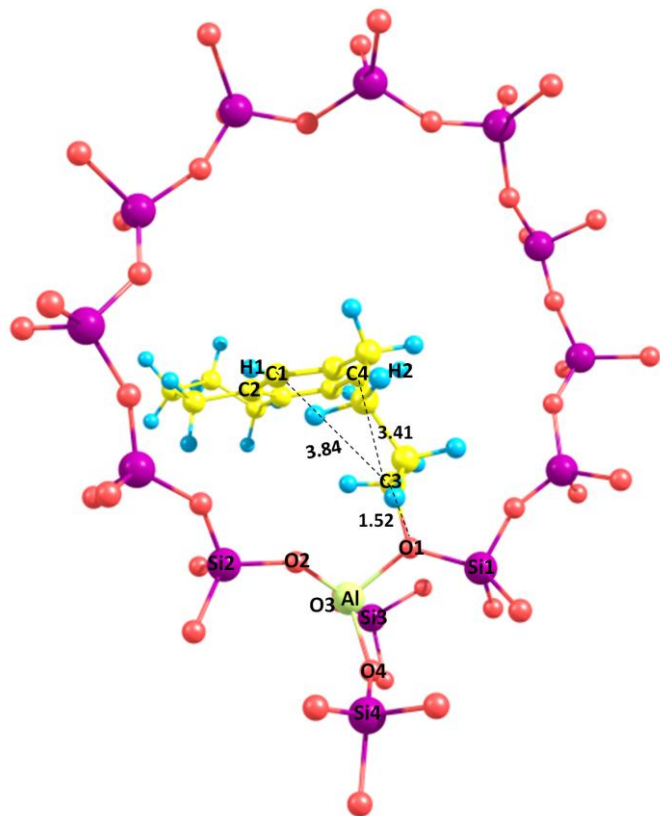
TS_1



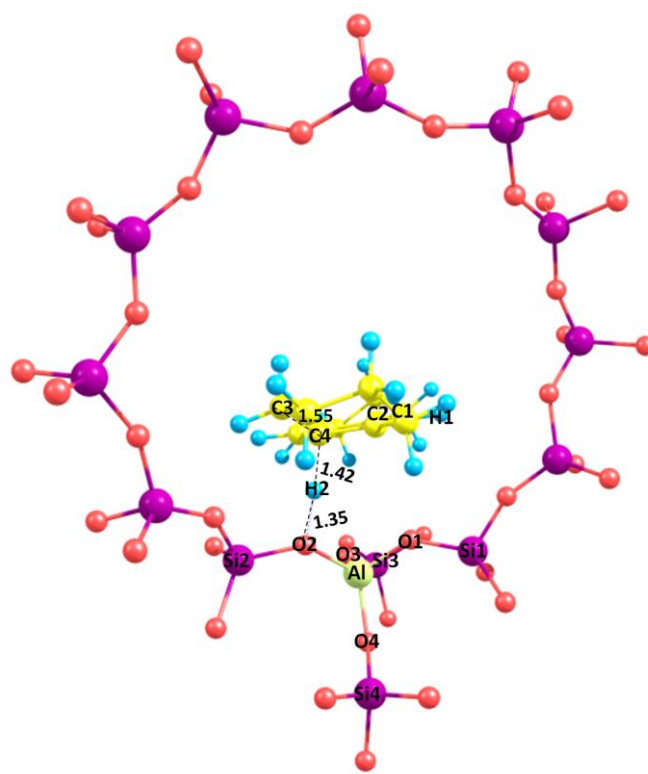
TS_2



TS_3



TS_4



TS_5a

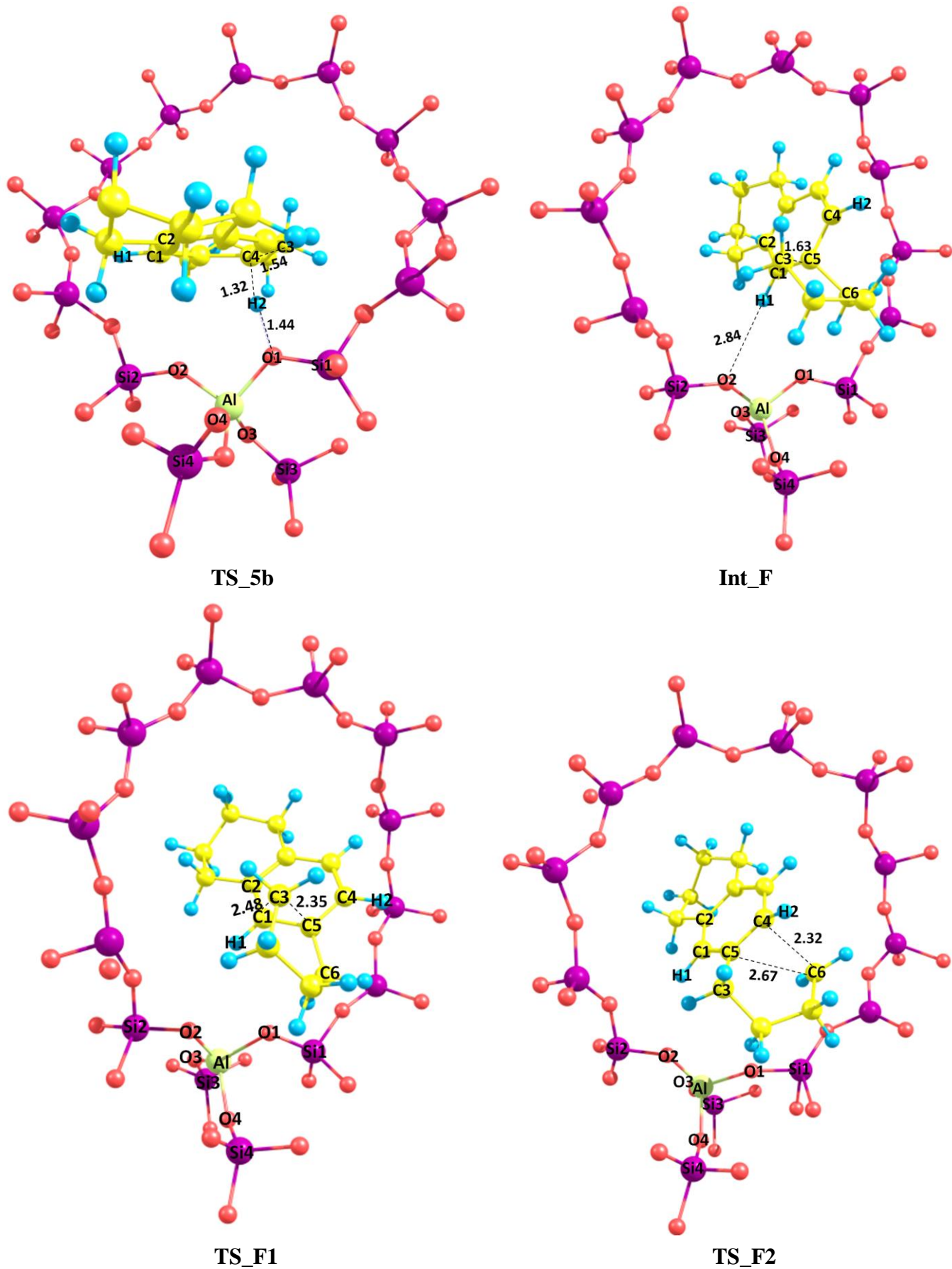


Fig. S9 Relative energy profiles for ring-shift isomerization of *sym*-OHP into *sym*-OHA in the “six-membered ring” mechanism catalyzed by the 120T B-H-MOR, Ga-H-MOR, and 140T Al-H-FAU.

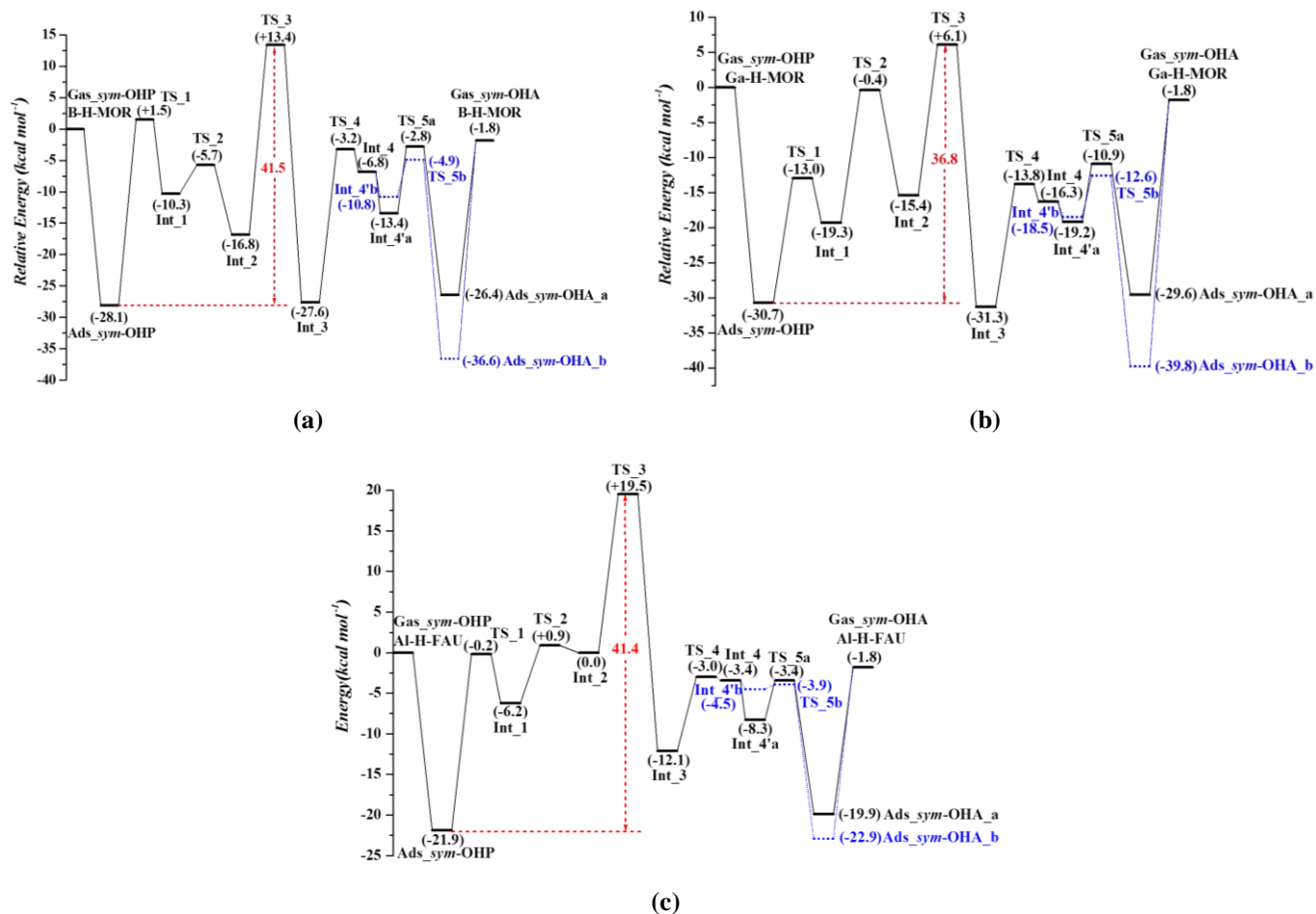


Fig. S10 Calculated equilibrium compositions (%) of the *sym*-OHP and *sym*-OHA conformers in the temperature range of 175 to 325 °C.

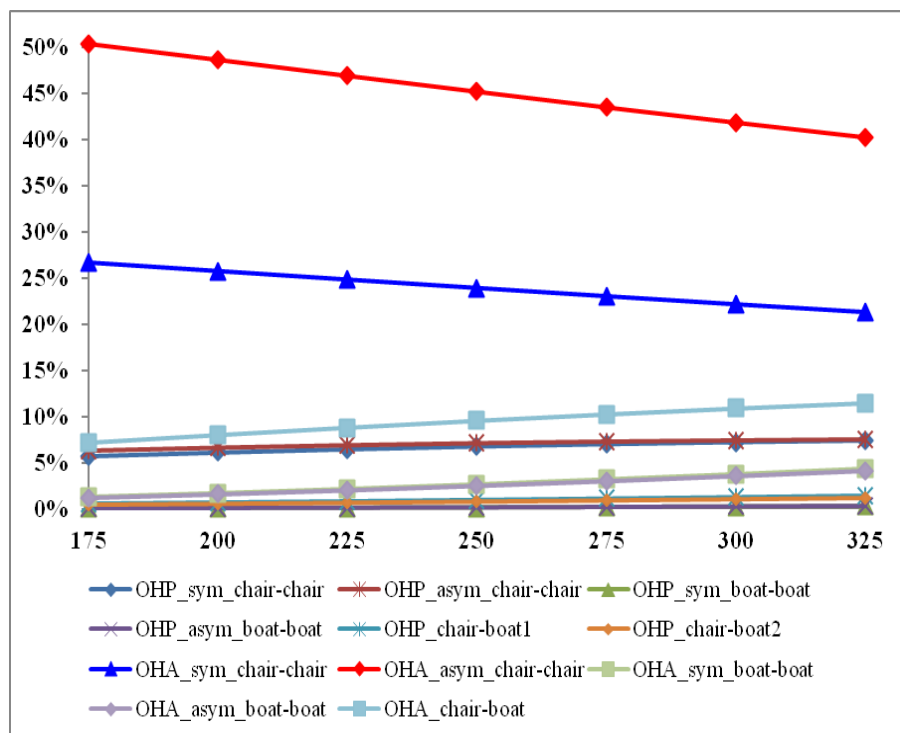


Table S1 Key geometric parameters of the optimized *sym*-OHP and *sym*-OHA adsorption states with both the DFT(B3LYP) and ONIOM(B3LYP:UFF) approaches.

Geometric parameter	<i>sym</i> -OHP		<i>sym</i> -OHA	
	DFT(B3LYP)	ONIOM(B3LYP:UFF)	DFT(B3LYP)	ONIOM(B3LYP:UFF)
C ₁ -C ₂	1.42	1.42	1.41	1.40
C ₁ -C ₃	1.52	1.52	3.83	3.83
C ₁ -H ₁	3.17	3.12	1.09	1.09
C ₂ -H ₁	3.45	3.41	2.15	2.15
C ₄ -H ₂	1.08	1.08	3.78	3.74
O ₁ -H ₁	0.98	0.97	3.27	3.22
O ₁ -Al	1.84	1.80	1.84	1.80
O ₁ -Si ₁	1.68	1.67	1.68	1.67
O ₂ -Al	1.68	1.65	1.68	1.66
O ₂ -Si ₂	1.59	1.57	1.59	1.57
Si ₁ -O ₁ -Al	129.1	125.8	128.4	125.2
Si ₂ -O ₂ -Al	148.1	145.9	148.9	146.7
Si ₃ -O ₃ -Al	132.5	131.5	132.6	131.5
Si ₄ -O ₄ -Al	156.8	154.0	156.8	154.0

Table S2 The evaluations of the ONIOM(DFT/UFF) energies on the adsorbed reactant (*sym*-OHP), intermediate species, and the adsorbed product (*sym*-OHA) over the 120T Al-H-MOR. Energies are given in Hartree.

Species	ONIOM(DFT:UFF)
	ΔS -value
<i>sym</i> -OHP	0.03958330
Int_1	0.04049951
Int_2	0.04040031
Int_3	0.03918137
Int_4	0.04004935
Int_4'a	0.04272292
Int_4'b	0.04417378
<i>sym</i> -OHA_a	0.03998476
<i>sym</i> -OHA_b	0.03977902

Table S3 The adsorption stability of all the possible adsorbed structures of *sym*-OHP and *sym*-OHA over the 120T Al-H-MOR. Energies are given in kcal mol⁻¹.

<i>sym</i> -OHP					
Structure	Relative Energy	Structure	Relative Energy	Structure	Relative Energy
<i>sym</i> -Chair-Chair(1)	0.29	<i>sym</i> -Boat-Boat(1)	6.11	Chair-Boat(1)	3.06
<i>sym</i> -Chair-Chair(2)	1.19	<i>sym</i> -Boat-Boat(2)	5.39	Chair-Boat(2)	2.95
asym-Chair-Chair(1)	0.18	asym-Boat-Boat(1)	5.12	Chair-Boat(3)	3.16
asym-Chair-Chair(2)	0	asym-Boat-Boat(2)	5.05	Chair-Boat(4)	3.17
Chair-Boat(5)	3.34	Chair-Boat(6)	3.01	Chair-Boat(7)	3.55

Chair-Boat(8)	3.54				
<i>sym</i>-OHA					
Structure	Relative Energy	Structure	Relative Energy	Structure	Relative Energy
sym-Chair-Chair(1)	0	sym-Boat-Boat(1)	6.46	Chair-Boat(1)	3.15
sym-Chair-Chair(2)	0.57	sym-Boat-Boat(2)	6.09	Chair-Boat(2)	2.64
asym-Chair-Chair(1)	0.30	asym-Boat-Boat(1)	6.08	Chair-Boat(3)	3.28
asym-Chair-Chair(2)	0.18	asym-Boat-Boat(2)	5.33	Chair-Boat(4)	2.68

Table S4 Imaginary vibrational modes for all the transition states created in the “six-membered ring” and “five-membered ring” mechanisms of ring-shift isomerization of *sym*-OHP into *sym*-OHA over different acidic zeolite catalysts.

Transition States	Al-H-MOR	B-H-MOR	Ga-H-MOR	Al-H-FAU
	imaginary vibrational frequency (cm ⁻¹)			
TS_1	-1431.84	-1508.27	-1379.66	-1233.68
TS_2	-158.71	-169.16	-133.42	-168.97
TS_3	-249.36	-289.39	-230.28	-207.27
TS_4	-111.88	-304.16	-206.64	-99.81
TS_5a	-1388.36	-889.62	-1332.95	-1315.41
TS_5b	-1220.18	-998.05	-1216.68	-883.45
TS_F1	-286.07	-273.15	-289.53	-301.21
TS_F2	-296.20	-300.78	-299.75	-310.98