Supplementary information

Supplementary Table 1 Optimized geometries of 128T ONIOM model of H-[Al]-MFI zeolite (B3LYP/6-31G(d,p):MNDO level of theory) with different models of relaxation. Distances are in Å and angles in degrees.

Parameters	Models			
	12T/5T (Supplementary Fig. 1c)	30T/5T (Supplementary Fig. 1d)	30T/8T (Supplementary Fig. 1e)	30T/24T (Supplementary Fig. 1f)
H-[Al]-MFI				
O1-H1	0.973	0.970	0.969	0.969
Si1-O1	1.653	1.658	1.682	1.674
Si2-O2	1.582	1.578	1.579	1.591
Al-O1	1.801	1.798	1.804	1.845
Al-O2	1.663	1.668	1.673	1.701
<Al-O>	1.698	1.703	1.709	1.739
Al···H1	2.308	2.389	2.404	2.395
∠Si1-O1-Al	133.8	130.7	128.1	128.8
∠Si2-O2-Al	130.2	127.0	133.5	141.0
H-[B]-MFI				
O1-H1	0.970	0.969	0.969	0.969
Si1-O1	1.656	1.667	1.687	1.667
Si2-O2	1.607	1.602	1.605	1.603
B-O1	1.782	1.732	1.714	1.745
B-O2	1.402	1.411	1.418	1.412
<B-O>	1.491	1.488	1.487	1.492
B···H1	2.195	2.238	2.223	2.204
∠Si1-O1-B	137.6	134.5	135.8	134.9
∠Si2-O2-B	149.2	148.1	147.9	150.6

Supplementary Table 2 Comparison of the adsorption energy, ΔE_{ads} (in kcal/mol) of the N-bond complexes over the H-[Al]-MFI zeolite in the ONIOM2(B3LYP/6-31G(d,p)) and ONIOM2(B3LYP/6-31G(d,p):UFF) schemes.

Model	Method	Adsorption energy (kcal/mol)
H-[Al]-MFI		
12T:128T	B3LYP/6-31G(d,p):MNDO	-27.73
12T:128T	B3LYP/6-31G(d,p):UFF[a]	-40.33
12T:128T	MP2/6-311G(d,p):HF/6-31G(d)[a]	-46.25
12T:128T	B3LYP/6-31G(d,p):UFF	-43.53
H-[B]-MFI		
12T:128T	B3LYP/6-31G(d,p):MNDO	-19.54
12T:128T	B3LYP/6-31G(d,p):UFF[a]	-35.69
12T:128T	MP2/6-311G(d,p):HF/6-31G(d)[a]	-34.10
12T:128T	B3LYP/6-31G(d,p):UFF	-34.79

[a] Single point calculation at the B3LYP/6-31G(d,p):MNDO optimization.

Supplementary Table 2 Optimized geometries for the Beckmann rearrangement of cyclohexanone oxime on the 128T ONIOM model of H-[Al]-MFI zeolite (B3LYP/6-31G(d,p):MNDO level of theory). Distances are in Å and angles in degrees.

	Adsorption steps of the Beckmann rearrangement on H-[Al]-MFI zeolite						
Parameters	N-bound complex	1,2 H-shift TS complex	O-bound complex	Rearrangement TS	Enol-amide complex	Tautomerization TS	Keto-amide complex
Distances							
O1-H1	1.775	0.996	1.984	3.089	1.754	1.513	-
N1-H1	1.035	1.876	-	-	-	-	-
N1-O3	1.373	1.453	1.535	2.545	2.261	-	-
O3-H1	2.018	1.935	0.989	0.966	1.002	1.045	0.985
O3-H2	0.986	0.976	1.063	0.976	1.081	1.218	-
O2-H2	1.941	1.962	1.435	1.994	1.398	2.240	2.015
N-O1	2.732	2.689	-	-	-	-	-
O2-O3	2.794	2.763	2.480	2.875	2.437	2.826	-
N-C1	1.285	1.273	1.280	1.187	1.242	1.266	1.296
N-C2	-	-	2.338	1.995	1.465	1.462	1.474
C1-C2	1.488	1.504	1.504	1.864	2.360	-	-
C1-C3	1.497	1.502	1.505	1.465	1.500	1.483	1.499
N-H2	-	-	-	-	2.383	1.414	1.025
C1-O3					1.469	1.422	1.317
Angles							
N-H1-O3	-	44.8	-	-	-	-	
H1-O3-H2	-	81.0	103.0	103.7	97.6	107.0	-
C2-N-C1	-	-	-	-	-	-	-
C2-N-O3	-	-	-	151.6	-	-	-
N-C1-O3	-	-	-	-	112.8	102.3	115.6
N-H2-O3	-	-	-	-	70.3	105.2	-
N-C1-O3-H2	-	-	-	-	33.9	3.8	-

Supplementary Table 3 Optimized geometries for the Beckmann rearrangement of cyclohexanone oxime on the 128T ONIOM model of H-[B]-MFI zeolite (B3LYP/6-31G(d,p):MNDO level of theory). Distances are in Å and angles in degrees.

	Adsorption steps of the Beckmann rearrangement on H-[Al]-MFI zeolite						
Parameters	N-bound complex	1,2 H-shift TS complex	O-bound complex	Rearrangement TS	Enol-amide complex	Tautomerization TS	Keto-amide complex
Distances							
O1-H1	1.764	0.990	1.042	1.960	1.022	1.466	-
N1-H1	1.043	1.946	-	-	-	-	-
N1-O3	1.378	1.440	1.465	2.522	2.256	-	-
O3-H1	2.047	1.874	1.510	0.980	1.562	1.062	0.973
O3-H2	0.983	0.975	0.972	0.965	0.976	1.213	-
O2-H2	2.749	2.791	2.414	-	2.523	2.488	1.764
N-O1	2.784	2.717	-	-	-	-	-
O2-O3	3.218	2.953	2.796	2.923	2.893	2.876	-
N-C1	1.288	1.274	1.283	1.188	1.257	1.267	1.291
N-C2	-	-	2.361	1.999	1.460	1.461	1.474
C1-C2	1.484	1.498	1.500	1.841	2.346	-	-
C1-C3	1.501	1.505	1.513	1.467	1.509	1.483	1.495
N-H2	-	-	-	-	2.194	1.406	1.038
C1-O3					1.402	1.418	1.321
Angles							
N-H1-O3	-	44.2	-	-	-	-	-
H1-O3-H2	-	116.9	107.5	105.6	105.9	107.7	-
C2-N-C1	-	-	-	64.8	-	-	-
C2-N-O3	-	-	-	149.1	-	-	-
N-C1-O3	-	-	-	-	115.9	102.2	116.1
N-H2-O3	-	-	-	-	80.8	105.8	-
N-C1-O3-H2	-	-	-	-	1.6	1.4	-

Supplementary Table 4 Comparison of the adsorption energy, ΔE_{ads} (in kcal/mol) along the Beckmann rearrangement of clyclohexanone oxime on the H-[Al]-MFI zeolite in the bare cluster, ONIOM and e-ONIOM models.

Geometry/method	ΔE_{ads}		
	12T model[a]	ONIOM energies[b]	e-ONIOM energies[c]
N-bound complex	-32.50	-46.25	-50.67
1,2 H-shift TS complex	-19.37	-17.88	-19.21
O-bound complex	-21.02	-28.50	-31.51
Rearrangement TS	5.25	-9.54	-15.36
Enol-amide complex	-53.09	-56.63	-59.86
Tautomerization TS	-25.14	-36.69	-40.91
Keto-amide complex	-80.64	-85.02	-90.50

[a]Energies obtained from single point calculations at MP2/6-311G(d,p)//B3LYP/6-31G(d,p) level of theory.

[b]Energies obtained from single point calculations at MP2/6-311G(d,p):HF/6-31G(d)//B3LYP/6-31G(d,p):MNDO level of theory.

[c]Energies obtained from single point calculations at MP2/6-311G(d,p):HF/6-31G(d):electrostatic potentials//B3LYP/6-31G(d,p):MNDO level of theory.

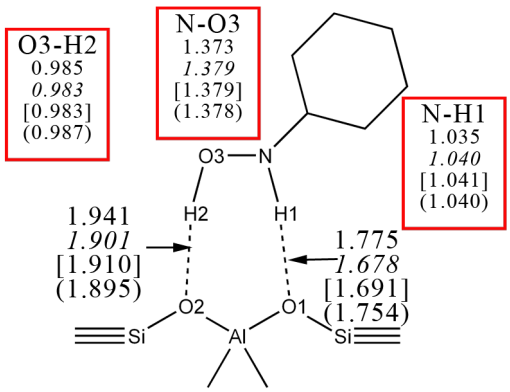
Supplementary Table 5 Comparison of the adsorption energy, ΔE_{ads} (in kcal/mol) along the Beckmann rearrangement of clyclohexanone oxime on the H-[B]-MFI zeolite in the bare cluster, ONIOM and e-ONIOM models.

Geometry/method	ΔE_{ads}		
	12T model[a]	ONIOM energies[b]	e-ONIOM energies[c]
N-bound complex	-18.22	-34.10	-39.91
1,2 H-shift TS complex	-13.62	-13.40	-15.59
O-bound complex	-15.15	-17.57	-18.91
Rearrangement TS	17.52	-4.09	-11.45
Enol-amide complex	-48.36	-50.49	-52.19
Tautomerization TS	-19.94	-26.86	-31.77
Keto-amide complex	-73.07	-77.82	-84.65

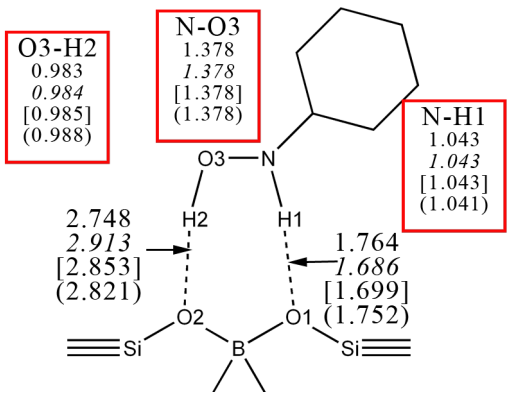
[a]Energies obtained from single point calculations at MP2/6-311G(d,p)//B3LYP/6-31G(d,p) level of theory.

[b]Energies obtained from single point calculations at MP2/6-311G(d,p):HF/6-31G(d)//B3LYP/6-31G(d,p):MNDO level of theory.

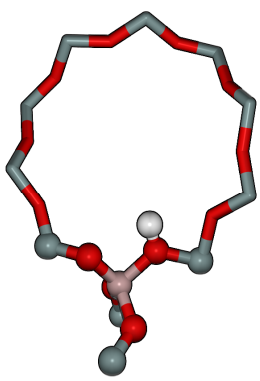
[c]Energies obtained from single point calculations at MP2/6-311G(d,p):HF/6-31G(d):electrostatic potentials//B3LYP/6-31G(d,p):MNDO level of theory



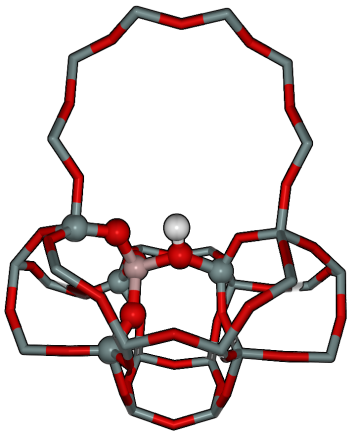
a



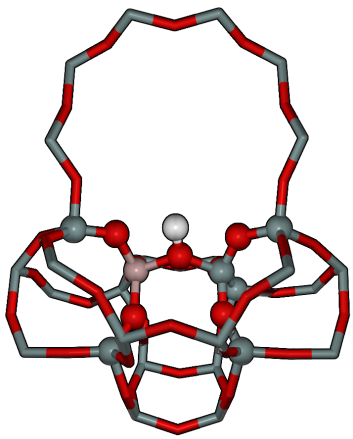
b



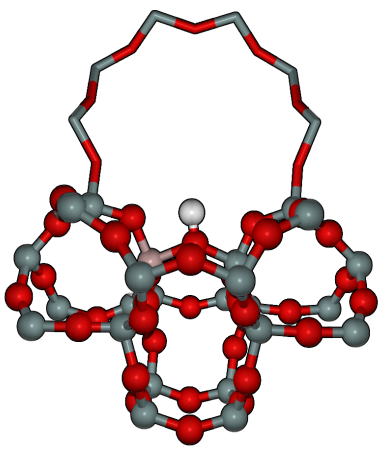
c



d

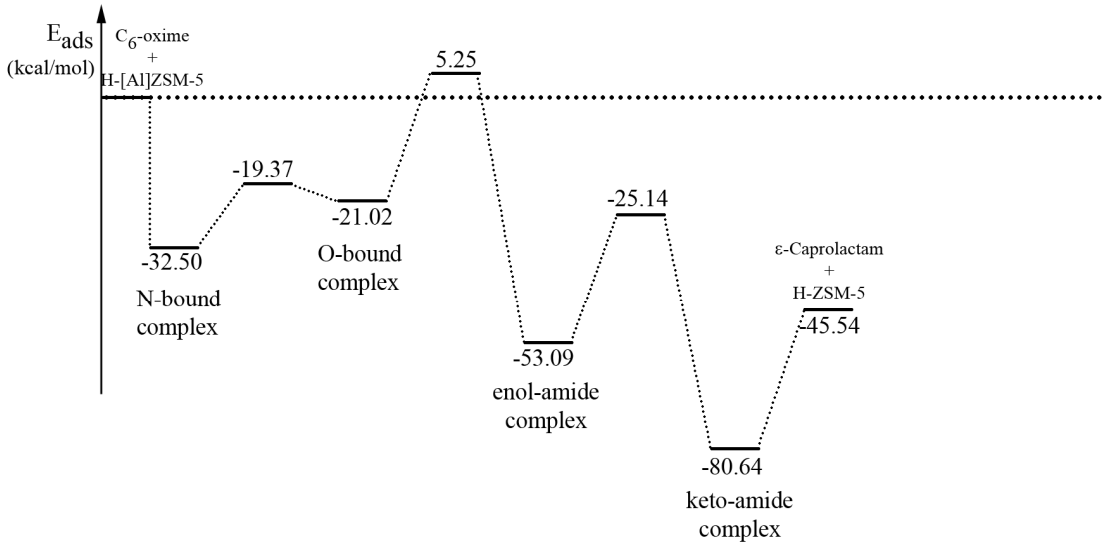


e

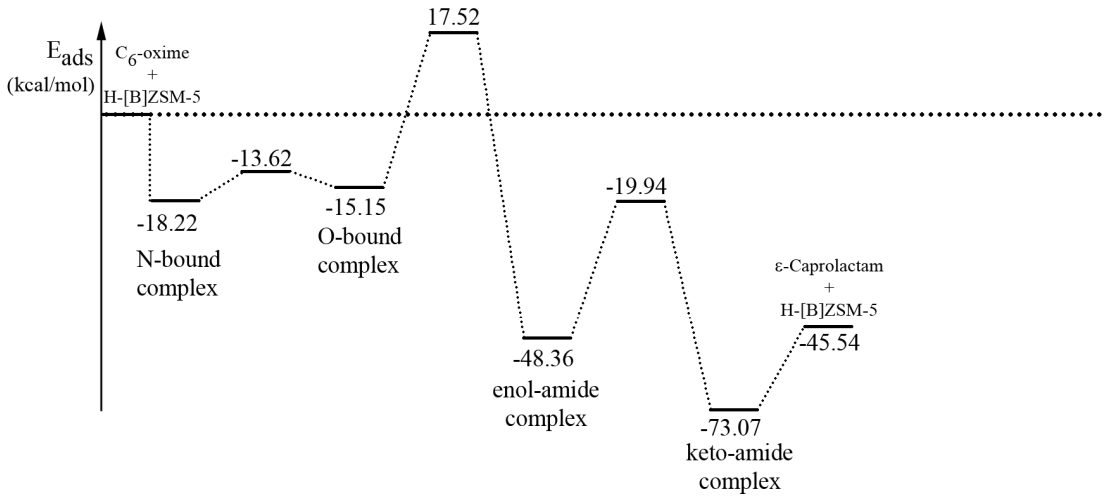


f

Supplementary Figure 1. The N-bound complexes at the ONIOM2(B3LYP/6-31G(d,p):MNDO) level of theory: a) H-[Al]-MFI zeolite and b) H-[B]-MFI zeolite (Distances are in Å). The geometrical structures obtained from ONIOM2 scheme with different degree of relaxation in QM region: 5T, 8T and 30T atoms are shown. The nomenclature "nT/mT" is designated in which the "n" refers to number of T atoms in QM region and the "m" refers the degree of relaxation of T atoms in optimization (presented as bonds and sticks): c) 12T/5T, d) *30T/5T*, e) [30T/8T] and f) (30T/24T), respectively.



A



B

Supplementary Figure 2. Energetic profile along the pathway of the Beckmann rearrangement of cyclohexanone oxime molecules on bare cluster models at the MP2/6-311G(d,p)//B3LYP level of theory: (a) 12T H-[Al]-MFI, (b) 12T H-[B]-MFI. The energetic changes are in kcal/mol