

Supplementary Information: A New Mechanistic Proposal for the Aromatic Cycle of the MTO Process based on a Computational Investigation for H-SSZ-13

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S1. Original pairing mechanism

Figure S1 summarizes the investigation of the original pairing mechanism. Formation of the products was studied both via singlet and triplet states. It turns out that coadsorbed propene and the antiaromatic singlet pentamethylcyclopentadienyl cation (o3.s) react spontaneously in a 2+2 cycloaddition to form structure o2.s . It was therefore not possible to obtain a local minimum for o3.s . The free energy sketched in Fig. S1 for o3.s was estimated based on the singlet-triplet splitting of the adsorbed isolated pentamethylcyclopentadienyl cation (40 kJ/mol at the PBE-D3 level of theory) and the computed stability of o3.t (110 kJ/mol).

Structure o2.s can be formed from o1.s with a barrier of 218 kJ/mol, given relative to heptaMB⁺. Formation of o3.t from o2.s was studied with an NEB and unconstrained spin and the result is sketched in Fig. S1: The formation of o3.t is simply uphill in energy, with a crossover in stability from singlet to triplet occurring at some point. Rate constants for this inter system crossing (ISC) were not obtained.

In the triplet state, coadsorbed propene and the triplet pentamethylcyclopentadienyl cation (o3.t) are stable. The initial state (o1.t) is already high in free energy with 144 kJ/mol and the highest barrier is 290 kJ/mol, which leads to an intermediate state (o4.t), where propene is still weakly adsorbed. Dissociation of propene to give o3.t then occurs with a much lower barrier. While singlet states were computed in the same manner as everything else in the main text (i.e. with ab-initio corrections), triplet states were computed only at the periodic PBE-D3 level of theory (with free energy corrections).

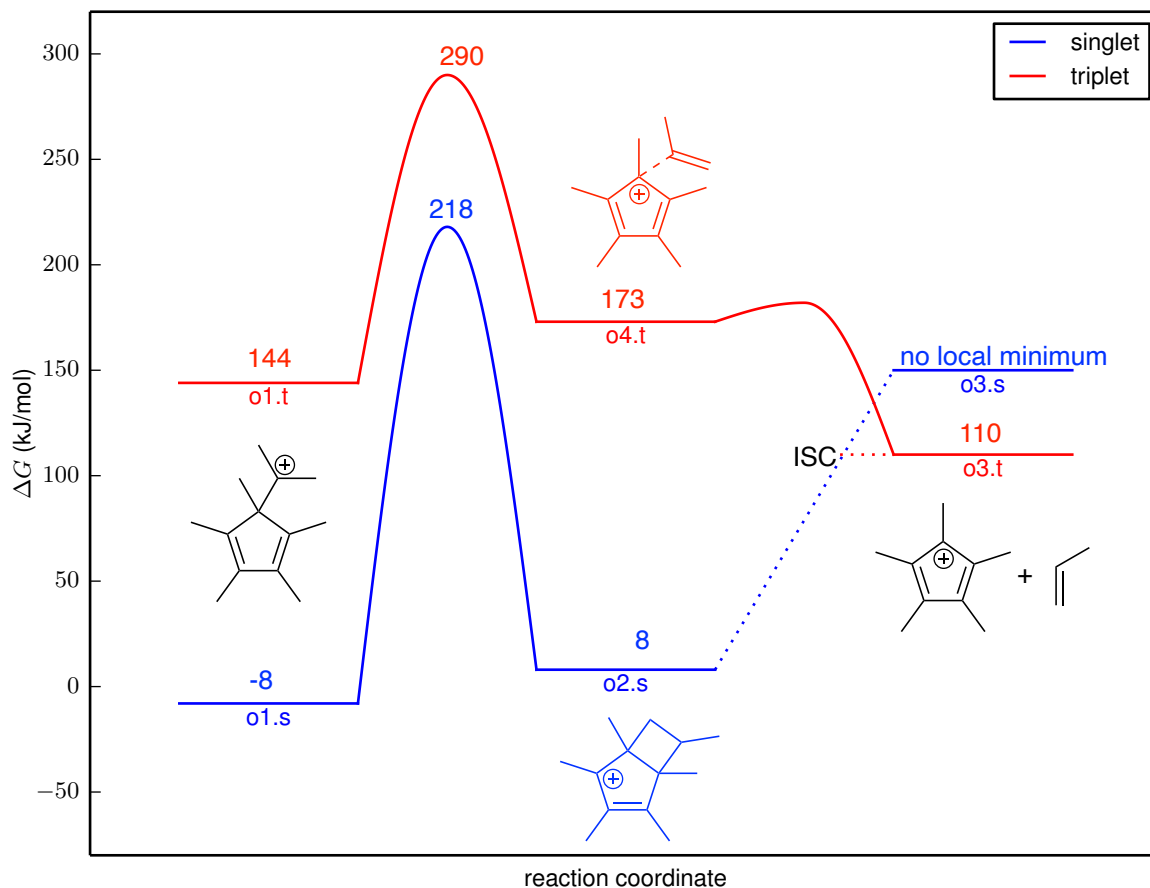


Figure S1. Summary of the computed reactivity for the original pairing mechanism at the PBE-D3 level of theory. The final state corresponds to the co-adsorbed pentamethylcyclopentadienyl cation and propene (rather than propene in the gas phase). All free energies are given relative to heptaMB⁺.

One may ask the question, whether an adsorbed hydrocarbon in a zeolite actually behaves according to the Hückel-rule and can be classified as antiaromatic. We have therefore analyzed the atomic structure of the adsorbed pentamethyl cyclopentadienyl cation (structure o3 in Fig. S1, but without co-adsorbed propylene) in terms of the C-C distances and the electronic structure in terms of the shape and eigenvalues of the orbitals (see Fig. S2.) We now compare those to the results

expected from the literature for the isolated cyclopentadienyl and pentamethyl cyclopentadienyl cation (refs. 64 and 67 in the main text). Our results are found to agree with the literature and general expectations according to the following points: 1) Triplet ground state. 2) Nearly identical C-C bond distances in the triplet state, about 143 pm with the largest variation of 1.3 pm. 4) In the triplet state, nearly degenerate singly-occupied orbitals with a large band gap to the next unoccupied orbital. 5) Distortion of the 5-ring in the singlet state, giving one long, two short and two intermediate C-C bond distances, which differ significantly, up to 20 pm. 6) Small band gap in the singlet state (in empirical single-electron theories, with identical C-C bond lengths, one would expect HOMO and LUMO to be degenerate.) The plots of the frontier orbital densities (not showing the sign, i.e. the nodal structure) are in line with the expected π and π^* -orbitals. In contrast to the discussed properties of the antiaromatic pentamethyl cyclopentadienyl cation, all other zeolites structures, in particular those involved in the new mechanism proposed in the main text, have a band gap > 1 eV.

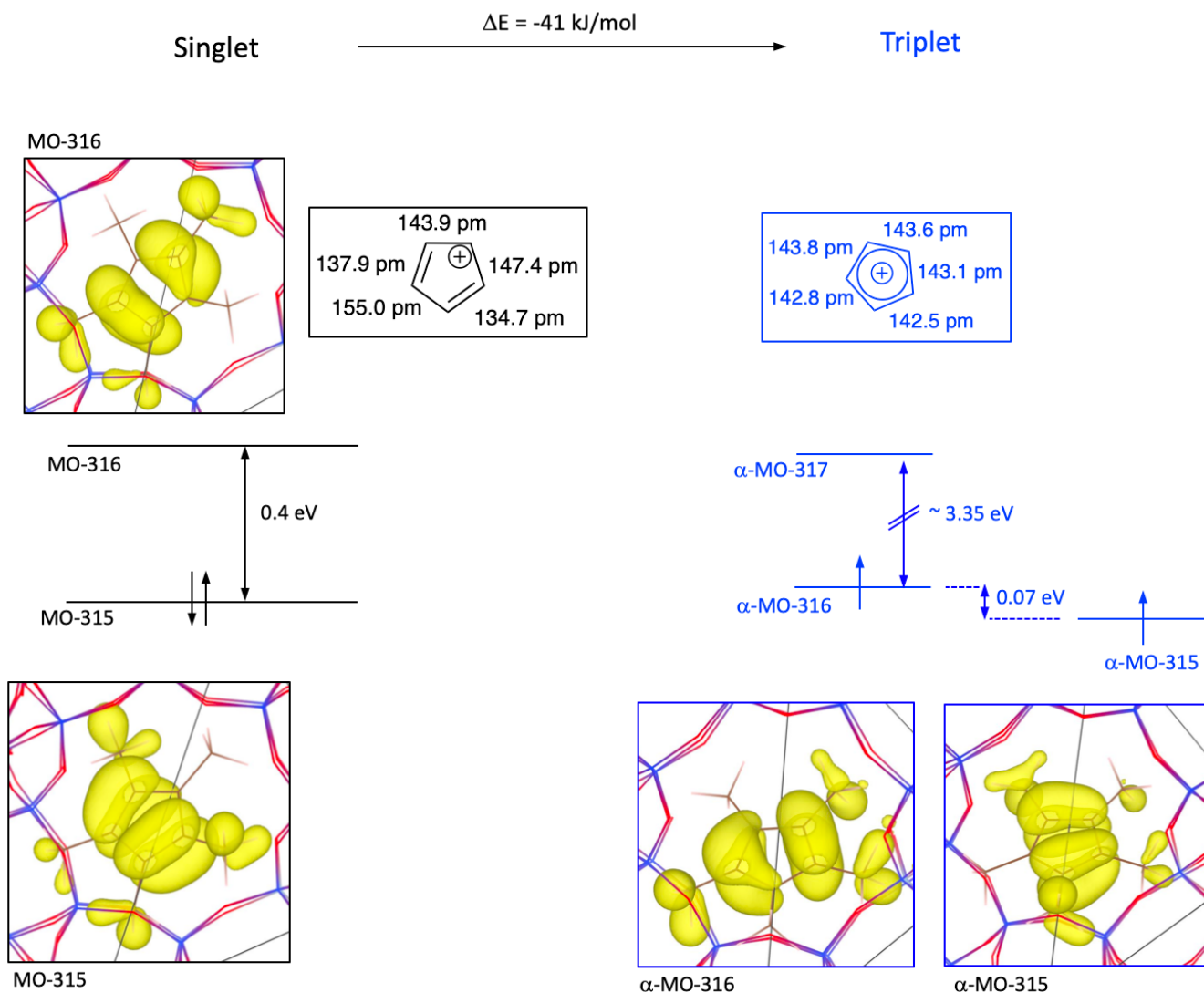


Figure S2. Analysis of the structure of the adsorbed pentamethyl cyclopentadienyl cation in both triplet and singlet state. The plots show the structure of the zeolite and adsorbate as a wire-model and also show the density of the frontier orbitals, thus not showing the sign of the orbitals, which is generally technically not easy to visualize for a complex Bloch wave function with different values at different k-points. However, since we perform calculations only at the Γ -point, the Bloch wave functions can be chosen to be real and the plot shows the density of these orbitals. The orbital diagram is shown schematically and the actual separation of the orbital energies is indicated. The bond lengths are shown together with the most representative Lewis structure using the same orientation as also used in the orbital density plots. Orbitals and orbital energies were obtained at the PBE-level using periodic DFT as in all other calculations.

S2. Computed reaction free energies

Table S1 lists the computed free energies discussed in the main text, which are referenced to heptaMB⁺, structure 1, see also Fig. 1.

Table S1. Data shown in Fig. 1 in the main main text. Reaction Gibbs free energies in kJ/mol computed using DFT and ab initio calculations on cluster models as stated in the main text.

structure	ΔG
1	0
TS_1-2	120
2	70
TS_2-3	126
3	28
TS_3-4	71
4	56
TS_4-5	109
5	48
TS_5-6r	127
6r	19
TS_6r-7r	91
7r	43
TS_7r-7r'	115
7r'	59
TS_7r'-8r	69
8r	-27
TS_8r-9r	80
9r	-26
TS_9r-10r	75
10r	-31
TS_10r-12	24
12	-155
5rot	52
TS_5-6	91
6	29
TS_6-7	142
7	-8
TS_7-8	84
8	-66
TS_8-9	63
9	-52
TS_9-10	17
10	-19
TS_10-11	39
11	-84

S3. Computed total energies

Tables S2 and S3 list the computed total energies and Table S4 lists the harmonic frequencies. Table S5 lists the D3-contribution (zero damping). Variations of the D3-correction relative to heptaMB+ for structures with the same number of atoms (i.e. before propene elimination) are relatively small, generally less than 10 kJ/mol and no systematic difference is observed between antiaromatic structure as proposed in the original mechanism and the structures proposed in the revised paring mechanism

Table S2. Total energies in kJ/mol. The model (PBC or 46T cluster) is stated in the first row, but this is identical for molecules. Corrections to the free energies resulting from nuclear motion are labeled ΔG_{harm} and CC-final/46T refers to the final ab initio energy obtained for the cluster as described in the main text. Additionally, the CBS-extrapolated HF and correlation energies are given.

	PBC	PBC	46T	46T	46T	46T
mol	PBE-D3	ΔG_{harm}	PBE-D3	CC-final/46T	HF/CBS(234)	MP2-corr/CBS(23)
water	-1372.372	-72.771	-1372.372	-200499.822	-199711.264	-755.364
methanol	-2917.361	-28.782	-2917.361	-303507.373	-302195.517	-1225.819
ethene	-3085.950	-24.510	-3085.950	-206025.997	-204972.383	-948.664
propene	-4699.841	22.565	-4699.841	-309102.069	-307511.884	-1440.602
1	-101841.745	584.074	-119769.140	-50412879.576	-50342427.767	-67839.690
TS_1-2	-101730.209	591.373	-119678.575	-50412788.141	-50342283.112	-67893.389
2	-101742.271	592.068	-119688.631	-50412836.465	-50342377.453	-67839.815
TS_2-3	-101709.689	589.302	-119651.699	-50412772.935	-50342288.235	-67866.840
3	-101800.978	576.864	-119710.913	-50412827.173	-50342382.689	-67834.523
TS_3-4	-101762.012	576.393	-119680.608	-50412792.259	-50342376.592	-67787.783
4	-101772.765	574.135	-119693.642	-50412807.256	-50342382.491	-67799.205
TS_4-5	-101726.743	585.973	-119647.693	-50412766.094	-50342309.489	-67838.889
5	-101782.822	575.975	-119705.788	-50412819.271	-50342400.721	-67790.888
TS_5-6r	-101692.380	576.380	-119628.250	-50412753.137	-50342316.660	-67818.764
6r	-101833.254	587.977	-119758.233	-50412862.180	-50342461.573	-67771.478
TS_6r-7r	-101743.682	569.277	-119691.134	-50412793.479	-50342328.452	-67846.956
7r	-101758.071	568.621	-119707.438	-50412843.014	-50342420.220	-67798.115
TS_7r-7r'	-104760.198	686.591	-122695.747	-50716411.279	-50644575.924	-69136.168
7r'	-101775.952	585.567	-119717.800	-50412836.251	-50342362.924	-67856.899
TS_7r'-8r	-101775.803	584.976	-119717.011	-50412825.010	-50342345.565	-67865.649
8r	-101879.902	588.437	-119797.828	-50412901.160	-50342496.608	-67785.565
TS_8r-9r	-101765.071	591.961	-119686.292	-50412801.371	-50342325.967	-67877.142
9r	-101869.894	578.850	-119796.085	-50412898.934	-50342478.463	-67801.442
TS_9r-10r	-101771.230	592.496	-119688.025	-50412802.549	-50342329.153	-67874.379
10r	-101872.438	581.861	-119793.668	-50412902.126	-50342473.025	-67817.536
TS_10r-12	-101824.636	565.034	-119763.021	-50412847.846	-50342398.622	-67845.280
12	-97105.692	394.419	-115049.885	-50103782.564	-50035095.848	-66212.868
5rot	-101782.646	579.504	-119706.421	-50412819.635	-50342400.288	-67791.118
TS_5-6	-101744.011	579.610	-119663.592	-50412776.598	-50342317.691	-67846.279
6	-101805.831	590.244	-119714.691	-50412838.127	-50342400.880	-67816.433
TS_6-7	-101683.998	560.723	-119622.903	-50412726.220	-50342265.446	-67845.508
7	-96963.655	398.396	-114912.515	-50103643.889	-50034912.489	-66241.799
TS_7-8	-96911.536	410.700	-114861.684	-50103565.806	-50034760.482	-66329.728

8	-97051.489	405.077	-114984.513	-50103693.120	-50034994.588	-66204.908
TS_8-9	-96925.034	406.463	-114866.973	-50103574.290	-50034848.959	-66239.504
9	-97046.597	402.027	-114972.305	-50103667.890	-50034971.717	-66197.739
TS_9-10	-96980.229	402.448	-114921.720	-50103615.879	-50034877.296	-66251.605
10	-96988.624	405.396	-114931.973	-50103656.207	-50034946.311	-66216.237
TS_10-11	-96963.574	420.109	-114909.240	-50103615.113	-50034863.288	-66263.076
11	-97089.037	402.322	-115024.633	-50103710.757	-50035004.807	-66218.221
01.s	-101838.565	570.809	-119759.969	-50412868.044	-50342431.411	-67829.342
01.t	-101696.143	582.679				
03.t	-101684.313	536.830				
TS_01.t-04.t	-101530.529	563.189				
TS_04.t-03.t	-101629.944	554.239				
TS_01.s-02.s	-101612.587	577.184	-119533.571	-50412647.794	-50342203.937	-67823.498
02.s	-101838.959	592.670	-119744.410	-50412858.413	-50342433.170	-67808.926

Table S3. Total energies for molecules and 46T cluster models in kJ/mol.

structure	CCSD(T)/cc-pVDZ	MP2/cc-pVDZ	MP2/cc-pVTZ	HF/cc-pVDZ	HF/cc-pVTZ	HF/cc-pVQZ
water	-200170.775	-200137.363	-200373.813	-199605.134	-199684.499	-199704.514
methanol	-303036.011	-302949.974	-303289.637	-302058.555	-302162.899	-302187.749
ethene	-205720.861	-205615.911	-205836.534	-204893.271	-204954.841	-204968.493
propene	-308645.817	-308496.234	-308825.478	-307398.249	-307486.391	-307506.165
1	-50380499.975	-50377887.856	-50401684.468	-50328910.738	-50339433.689	-50341764.566
TS_1-2	-50380407.828	-50377796.187	-50401595.339	-50328763.097	-50339290.187	-50341620.568
2	-50380428.554	-50377809.357	-50401634.754	-50328818.377	-50339379.779	-50341714.720
TS_2-3	-50380355.895	-50377738.034	-50401567.574	-50328732.469	-50339289.259	-50341624.764
3	-50380423.250	-50377813.288	-50401631.085	-50328835.659	-50339383.790	-50341718.824
TS_3-4	-50380390.118	-50377762.234	-50401578.823	-50328832.328	-50339378.559	-50341712.975
4	-50380409.829	-50377784.268	-50401595.988	-50328842.958	-50339384.307	-50341718.575
TS_4-5	-50380374.142	-50377756.426	-50401563.455	-50328781.554	-50339313.904	-50341646.155
5	-50380426.157	-50377798.495	-50401608.246	-50328863.838	-50339404.389	-50341737.496
TS_5-6r	-50380347.955	-50377730.242	-50401549.700	-50328771.115	-50339318.977	-50341653.261
6r	-50380475.807	-50377846.678	-50401652.625	-50328927.265	-50339466.944	-50341798.975
TS_6r-7r	-50380389.846	-50377771.774	-50401594.252	-50328781.171	-50339334.364	-50341666.727
7r	-50380419.565	-50377794.886	-50401634.064	-50328844.834	-50339420.561	-50341757.406
TS_7r-7r'	-50683552.439	-50680853.252	-50705007.777	-50630921.158	-50641561.705	-50643910.551
7r'	-50380444.576	-50377828.148	-50401640.839	-50328824.821	-50339370.184	-50341701.347
TS_7r'-8r	-50380436.807	-50377823.011	-50401631.905	-50328812.322	-50339352.911	-50341683.788
8r	-50380500.343	-50377881.357	-50401697.655	-50328953.034	-50339499.421	-50341833.332
TS_8r-9r	-50380426.753	-50377828.490	-50401621.873	-50328814.102	-50339333.695	-50341663.313
9r	-50380517.701	-50377898.672	-50401700.349	-50328951.739	-50339485.429	-50341816.200
TS_9r-10r	-50380430.038	-50377831.021	-50401622.949	-50328817.777	-50339337.054	-50341666.552
10r	-50380513.396	-50377901.831	-50401707.396	-50328939.142	-50339476.481	-50341809.559
TS_10r-12	-50380437.254	-50377833.310	-50401660.570	-50328849.700	-50339403.934	-50341736.713

12	-50071796.312	-50069322.464	-50092847.532	-50021592.743	-50032111.152	-50034436.117
5rot	-50380426.104	-50377797.875	-50401608.102	-50328863.753	-50339404.242	-50341737.172
TS_5-6	-50380380.016	-50377767.387	-50401580.053	-50328784.718	-50339322.992	-50341654.997
6	-50380441.691	-50377820.878	-50401630.207	-50328871.223	-50339403.930	-50341737.026
TS_6-7	-50380280.753	-50377665.487	-50401518.682	-50328689.532	-50339264.153	-50341601.936
7	-50071669.998	-50069180.397	-50092691.149	-50021430.518	-50031928.438	-50034252.010
TS_7-8	-50071631.473	-50069155.876	-50092630.371	-50021326.091	-50031782.107	-50034100.183
8	-50071736.837	-50069243.213	-50092736.512	-50021533.345	-50032011.616	-50034333.570
TS_8-9	-50071620.651	-50069134.824	-50092626.023	-50021388.044	-50031865.845	-50034187.862
9	-50071734.767	-50069236.333	-50092709.048	-50021531.205	-50031990.601	-50034310.503
TS_9-10	-50071642.388	-50069155.410	-50092668.504	-50021392.191	-50031894.939	-50034217.720
10	-50071672.051	-50069178.392	-50092703.233	-50021443.619	-50031962.985	-50034287.166
TS_10-11	-50071643.119	-50069154.370	-50092665.182	-50021388.424	-50031882.737	-50034204.010
11	-50071764.380	-50069276.650	-50092761.631	-50021553.353	-50032023.387	-50034343.996
01.s	-50380469.407	-50377862.115	-50401675.120	-50328896.030	-50339434.891	-50341768.028
TS_01.s- 02.s	-50380231.898	-50377611.539	-50401438.958	-50328654.892	-50339205.638	-50341540.436
02.s	-50380456.755	-50377840.438	-50401653.479	-50328890.936	-50339432.530	-50341768.299

Table S4. Computed harmonic frequencies. Note that structure 7r contains a spurious imaginary frequency, which was replaced by 12 cm⁻¹ in the calculation of Gibbs free energies.

structure	Harmonic frequency (1/cm)
water	1577.5,3700.3,3815.6
methanol	295.5,1010.5,1055.3,1128.2,1324.6,1419.0,1439.6,1452.1,2918.9,2970.5,3044.0,3728.2
ethene	805.1,932.2,936.5,1029.0,1197.8,1340.2,1419.7,1638.7,3050.9,3065.0,3123.5,3153.2
propene	193.9,417.5,568.8,897.9,912.5,913.9,988.8,1024.0,1154.3,1284.8,1349.6,1395.5,1420.7,1437.2,1659.3,2946.8,2997.6,3030.5,3048.8,3054.9,3138.6
1	20.8,49.4,61.9,74.1,82.8,93.5,106.0,131.8,154.6,168.9,175.4,191.2,197.5,206.0,208.2,225.8,254.2,261.9,285.8,290.1,300.6,320.0,331.0,355.1,363.2,380.1,382.9,411.1,429.0,440.4,466.8,535.8,540.7,555.3,567.4,571.4,591.6,599.5,634.4,658.8,677.7,684.5,785.4,800.6,849.3,929.8,936.1,949.0,954.4,972.6,984.0,994.0,998.3,1020.4,1029.2,1039.2,1069.6,1075.8,1080.9,1093.1,1094.9,1107.0,1213.2,1263.5,1323.2,1330.0,1333.7,1344.6,1348.2,1358.1,1359.7,1365.7,1374.1,1384.9,1397.5,1400.1,1414.6,1417.7,1422.4,1424.7,1427.2,1435.3,1448.3,1454.2,1459.6,1459.9,1467.5,1486.1,1525.2,1591.5,2948.7,2970.3,2976.1,2988.7,2990.5,2995.6,2996.3,3018.7,3034.2,3047.0,3054.6,3057.7,3077.0,3084.4,3084.5,3085.7,3103.1,3159.1,3169.1,3173.7,3194.6
TS_1-2	930.8i,39.7,63.8,67.2,90.7,98.4,103.5,117.8,141.8,156.7,184.5,203.0,212.0,227.7,253.1,270.6,275.7,277.8,311.9,324.6,334.6,335.2,341.3,349.3,360.5,368.4,383.1,422.3,439.1,475.6,488.7,532.2,554.0,570.1,584.6,591.6,593.9,636.0,642.1,650.4,688.3,719.6,735.7,769.3,791.0,905.3,908.4,927.5,935.6,947.9,954.9,969.4,975.3,991.7,1006.4,1021.9,1029.2,1068.0,1075.7,1078.2,1100.8,1104.5,1114.5,1136.1,1218.2,1252.4,1269.9,1340.7,1344.2,1354.1,1357.6,1360.4,1367.0,1373.9,1383.0,1392.7,1409.3,1416.0,1421.0,1423.6,1429.9,1431.7,1437.8,1438.6,1443.8,1457.0,1464.8,1470.0,1533.7,1588.8,1655.4,2959.2,2965.8,2975.6,2977.9,2979.3,2982.3,3013.0,3032.0,3038.0,3050.5,3052.6,3057.9,3071.5,3077.6,3096.0,3127.9,3145.8,3155.8,3165.5,3191.5
2	43.6,50.4,61.6,71.7,89.2,91.5,119.3,138.5,144.7,152.9,182.2,193.2,233.6,243.9,246.4,269.7,279.0,312.6,314.7,321.5,336.8,347.4,354.3,358.7,367.1,374.1,381.5,422.3,436.3,474.5,521.6,538.4,548.2,552.0,582.3,588.7,599.2,614.9,624.4,671.9,705.6,710.4,743.1,756.2,782.2,840.6,858.3,895.9,904.4,922.5,947.3,960.1,976.8,994.1,1001.9,1023.3,1029.2,1068.5,1074.7,1076.7,1103.5,1117.1,1129.0,1135.0,1214.2,1237.5,1260.1,1333.0,1338.9,1354.8,1358.2,1361.3,1368.0,1372.4,1394.4,1414.7,1419.6,1423.9,1425.3,1430.7,1432.9,1437.7,1440.0,1446.2,1453.4,1466.2,1469.3,1580.5,1619.3,1668.3,2960.9,2961.7,2967.9,2972.1,2974.5,2979.0,3011.9,3020.2,3020.8,3035.5,3038.4,3062.7,3066.7,3080.8,3084.6,3143.0,3151.4,3159.1,3159.8,3173.1,3173.5

TS_2-3	1102.9i,52.0,70.4,80.4,89.3,101.2,108.7,117.9,134.4,160.8,172.5,191.6,199.6,220.3,247.7,257.7,275.9,287.2,295.3,312.1,324.9,338.5,351.0,355.7,357.7,373.9,385.6,414.0,418.4,437.2,491.9,524.5,560.7,573.3,579.3,583.1,597.5,632.9,656.5,664.6,695.7,703.6,715.6,755.3,791.9,888.0,889.6,908.4,919.9,938.9,952.4,962.6,978.8,992.0,997.9,1018.3,1023.8,1047.9,1072.6,1078.7,1104.4,1116.1,1120.8,1133.4,1201.8,1222.6,1244.5,1264.7,1319.0,1335.3,1345.6,1349.2,1357.2,1365.2,1375.8,1397.9,1409.9,1418.0,1420.5,1424.9,1425.2,1432.6,1435.2,1437.8,1445.2,1449.6,1465.1,1469.3,1539.2,1620.8,1642.2,2963.8,2966.1,2968.0,2971.8,2984.1,2990.4,3011.8,3024.1,3026.3,3045.8,3059.9,3074.8,3081.2,3088.5,3098.0,3105.7,3112.5,3167.7,3169.2,3171.2
3	24.8,46.0,56.3,62.1,78.5,91.1,98.9,115.9,132.2,162.6,177.5,192.5,196.5,214.2,224.4,227.7,261.7,274.9,288.8,296.0,311.2,314.2,334.3,341.2,358.6,372.1,383.6,415.3,436.1,445.5,477.0,514.2,533.7,562.3,574.0,575.7,599.2,636.1,658.4,661.8,682.3,704.2,731.4,776.4,834.6,889.5,915.7,929.4,932.1,962.2,968.8,973.9,983.8,1005.6,1016.9,1045.9,1050.4,1055.7,1067.6,1108.2,1116.0,1131.1,1157.5,1180.8,1225.7,1259.0,1280.0,1324.3,1336.7,1350.8,1358.1,1366.4,1370.5,1375.9,1388.8,1395.4,1412.3,1414.1,1417.7,1426.2,1435.4,1436.7,1439.4,1441.1,1447.5,1456.2,1465.5,1472.6,1495.2,1624.8,2963.4,2966.3,2982.9,2985.3,2989.0,2990.8,3003.7,3044.9,3048.8,3049.8,3052.6,3054.4,3059.8,3087.0,3089.1,3103.4,3106.4,3107.2,3109.9,3131.6,3181.8
TS_3-4	96.4i,36.6,52.1,57.3,65.9,72.2,77.5,79.7,110.0,122.8,138.2,158.2,179.5,190.3,240.7,263.2,281.3,283.5,287.4,303.3,311.6,322.7,329.0,340.3,350.7,373.7,384.4,394.4,446.4,464.5,522.5,530.3,543.8,548.4,563.4,591.4,626.8,635.6,660.8,663.1,703.1,718.2,747.5,774.3,780.4,823.7,860.0,884.3,922.6,936.2,968.9,982.4,990.4,1005.6,1016.9,1027.0,1054.6,1057.5,1069.1,1100.4,1102.9,1116.0,1120.0,1176.9,1224.7,1256.7,1267.5,1281.5,1298.1,1316.6,1327.1,1347.0,1361.3,1369.0,1371.3,1377.3,1383.7,1403.6,1415.2,1416.4,1419.6,1424.9,1432.5,1436.5,1441.8,1443.8,1457.8,1469.6,1589.6,1657.9,2896.0,2930.2,2939.9,2977.1,2978.7,2981.0,2984.8,2994.4,2999.6,3016.7,3028.4,3049.4,3054.7,3085.1,3091.6,3109.3,3110.8,3119.2,3126.7,3149.1,3187.1
4	33.8,52.1,62.2,69.6,76.8,100.5,112.9,121.1,138.7,143.8,164.6,169.4,181.3,188.9,208.4,245.5,265.4,283.6,287.5,295.4,315.3,316.9,322.1,323.2,352.8,374.9,377.5,386.7,441.0,458.3,523.4,531.8,540.1,561.9,564.5,595.0,630.5,637.2,658.4,660.4,693.9,698.2,712.1,751.4,775.4,843.5,869.7,877.3,919.8,939.6,973.0,983.2,996.1,1009.2,1020.4,1025.8,1044.7,1052.9,1067.9,1095.2,1102.2,1132.3,1158.9,1196.8,1235.4,1262.8,1270.5,1282.0,1287.2,1326.8,1327.4,1345.3,1363.4,1370.0,1374.7,1375.5,1388.9,1403.5,1415.9,1417.7,1420.2,1422.2,1427.8,1435.7,1439.2,1444.6,1458.3,1466.7,1635.4,1647.8,2855.5,2901.9,2930.7,2976.3,2983.9,2984.5,2984.8,2987.2,3007.4,3016.2,3034.2,3059.1,3061.5,3083.7,3084.5,3092.5,3112.5,3122.2,3144.9,3150.8,3179.4
TS_4-5	449.0i,49.3,67.3,73.5,81.7,93.7,101.9,121.7,153.1,164.9,174.1,189.4,201.4,208.7,212.7,216.1,236.2,239.7,266.2,278.9,287.5,309.5,316.6,320.2,325.6,356.1,375.5,395.0,415.7,448.5,476.3,534.6,545.2,547.8,556.3,562.7,619.5,633.7,639.3,660.4,696.7,704.0,717.0,782.7,844.0,872.9,882.4,895.6,921.2,933.3,941.5,980.2,998.0,1019.0,1029.4,1059.1,1070.8,1082.3,1095.5,1096.7,1104.5,1140.7,1168.5,1189.4,1231.8,1268.0,1291.9,1318.8,1344.3,1349.4,1359.6,1361.9,1365.5,1375.6,1381.0,1396.5,1404.2,1410.6,1415.4,1422.6,1423.5,1428.1,1429.2,1435.5,1441.1,1442.7,1455.4,1462.9,1627.8,1640.1,1970.9,2949.7,2974.6,2979.2,2979.9,2984.1,2988.0,3012.8,3028.9,3053.6,3056.1,3065.8,3069.9,3079.5,3093.3,3096.8,3116.4,3126.8,3168.6,3177.5,3191.0
5	34.0,49.4,55.7,68.0,79.8,82.3,98.0,111.8,150.5,154.5,161.3,199.3,208.9,217.9,228.7,241.6,255.3,273.1,274.0,283.7,290.3,316.9,331.1,331.8,343.6,350.3,375.0,386.5,393.9,442.5,528.3,533.7,534.6,548.8,557.7,586.0,600.2,632.0,633.9,666.9,669.8,709.0,762.9,821.2,843.8,884.7,900.5,911.3,922.5,935.3,938.2,947.7,981.7,1016.0,1024.1,1047.9,1051.4,1080.6,1089.6,1094.4,1110.6,1149.9,1156.5,1190.7,1238.8,1270.8,1289.3,1305.2,1324.3,1334.1,1350.6,1357.5,1364.4,1368.0,1378.1,1393.3,1407.2,1416.2,1422.8,1423.3,1428.9,1435.6,1439.9,1443.4,1447.0,1456.8,1462.2,1477.9,1588.3,1637.2,2893.5,2962.5,2962.6,2972.3,2975.4,2981.0,2982.4,2991.3,3017.6,3024.0,3049.9,3059.5,3064.7,3066.7,3069.9,3076.4,3088.5,3106.8,3146.2,3172.6,3211.2
TS_5-6r	363.7i,18.4,32.1,63.6,66.5,85.9,86.7,113.1,120.5,136.2,174.9,182.9,193.0,195.4,202.0,225.5,226.7,249.9,270.7,285.9,298.9,305.3,310.9,324.9,348.3,373.5,379.3,393.2,442.7,467.1,510.8,544.6,554.2,556.3,594.0,608.7,638.4,651.3,660.3,684.6,697.4,710.8,786.8,836.2,852.7,884.7,892.8,899.9,918.2,937.8,949.8,956.1,994.3,1018.1,1038.0,1044.2,1075.7,1087.1,1090.5,1099.8,1107.8,1120.2,1140.5,1160.2,1210.6,1228.2,1273.5,1290.5,1297.0,1341.0,1351.1,1359.4,1361.7,1369.2,1377.4,1385.0,1404.9,1411.8,1418.3,1419.2,1423.9,1428.9,1437.4,1439.6,1444.3,1445.5,1451.8,1455.4,1639.1,1650.2,2430.8,2958.7,2975.3,2978.8,2983.1,2992.7,3007.2,3012.6,3036.2,3041.8,3050.7,3059.4,3081.3,3085.4,3090.6,3108.7,3116.7,3142.3,3152.1,3178.8,3213.8
6r	43.4,52.3,63.4,65.4,78.6,84.6,93.3,98.5,107.9,132.0,140.6,200.3,202.7,208.5,226.0,242.8,250.8,271.2,275.4,287.9,307.1,311.1,336.0,356.0,369.4,401.7,413.8,432.2,468.2,494.0,538.2,553.2,555.2,594.2,609.5,636.6,653.4,665.7,674.3,706.0,742.7,780.8,835.7,866.7,884.5,915.0,930.5,948.2,953.4,963.6,966.7,994.8,1012.0,1022.5,1042.4,1061.6,1083.9,1094.4,1105.5,1122.3,1133.4,1163.6,1191.6,1213.6,1227.6,1238.9,1291.3,1329.4,1333.4,1345.3,1350.5,1359.3,1362.5,1370.1,1372.1,1386.7,1405.5,1411.3,1416.8,1428.3,1433.4,1435.0,1438.9,1444.8,1451.6,1458.9,1464.2,1475.2,1506.3,1604.9,2927.1,2942.5,2955.8,2979.2,2985.4,2985.6,2989.7,2999.5,3051.3,3060.4,3062.1,3063.2,3064.9,3074.5,3082.1,3084.0,3085.2,3087.8,3114.1,3128.2,3237.7
TS_6r-7r	857.1i,4.0,47.3,60.9,68.4,74.6,84.4,90.5,95.8,120.3,141.4,150.6,160.1,189.4,218.8,227.3,237.3,251.3,272.2,282.8,304.5,314.6,346.7,355.5,388.2,403.8,415.9,462.2,469.6,484.2,537.3,568.7,581.7,588.3,598.6,637.2,643.6,670.4,674.5,708.0,713.9,746.7,793.1,864.6,874.8,882.1,888.1,913.3,948.1,959.1,963.5,979.3,985.2,998.0,1003.3,101

	9.6,1056.8,1082.6,1096.7,1104.4,1107.5,1121.3,1161.4,1195.9,1212.9,1256.9,1288.0,1302.5,1308.1,1329.7,1340.6,1344.6,1349.3,1357.7,1364.8,1370.3,1395.3,1402.7,1414.7,1431.4,1433.2,1433.8,1435.5,1437.5,1446.6,1454.0,1459.5,1467.9,1517.5,1572.0,1613.6,2960.7,2962.8,2967.8,2976.7,2984.2,2986.8,2991.2,3009.0,3033.5,3041.1,3057.8,3061.6,3073.4,3080.9,3093.6,3094.5,3099.9,3113.1,3141.8,3236.6
7r	36.3i,38.6,46.8,65.4,73.8,78.3,85.7,88.0,104.5,115.5,130.8,163.9,167.0,201.0,220.3,236.1,243.6,253.5,281.2,305.7,313.4,325.9,356.7,358.3,388.1,405.6,445.9,454.1,472.0,508.2,544.5,569.0,575.9,596.4,609.1,620.7,636.8,668.9,696.2,699.9,721.1,729.8,783.6,810.5,844.3,860.5,868.6,875.2,909.3,949.2,952.0,955.4,969.8,988.3,995.1,1019.5,1038.9,1079.9,1090.3,1105.6,1108.6,1146.4,1161.9,1192.8,1205.0,1244.2,1292.4,1299.7,1305.6,1334.2,1344.7,1346.0,1353.2,1359.8,1367.5,1370.8,1403.9,1420.3,1429.2,1435.7,1436.3,1439.5,1440.3,1445.2,1451.1,1460.6,1470.2,1454.6,1612.0,1634.2,2930.8,2933.1,2971.7,2981.6,2992.8,2999.1,3000.5,3020.2,3020.2,3052.8,3055.5,3067.8,3074.5,3078.7,3082.8,3087.1,3111.3,3135.5,3136.8,3175.5,3227.7
TS _{7r-7r'}	216.3i,58.4,60.6,63.3,79.8,88.8,91.0,93.5,104.1,119.4,124.4,134.4,137.1,141.0,151.3,169.7,182.4,194.7,198.8,225.1,231.2,249.5,256.5,272.9,281.8,291.5,317.6,321.6,352.6,363.7,394.8,402.0,409.2,444.0,448.9,467.4,495.2,531.4,568.1,581.2,592.7,632.7,634.7,666.0,679.0,687.4,705.6,729.6,780.5,815.0,839.7,851.4,872.8,896.2,905.3,940.2,947.8,952.8,958.4,980.5,995.7,1003.0,1017.5,1020.9,1042.2,1062.4,1079.4,1091.0,1102.7,1105.7,1143.1,1144.7,1193.3,1217.3,1251.0,1256.9,1294.4,1296.3,1303.8,1333.6,1343.6,1349.2,1355.9,1365.0,1370.4,1377.0,1397.0,1407.5,1414.1,1426.6,1429.2,1429.9,1432.8,1436.6,1437.7,1439.5,1442.3,1445.7,1457.1,1463.0,1517.3,1534.7,1621.7,1639.7,2670.9,2927.2,2951.5,2973.0,2977.5,2981.5,2985.4,2999.6,3030.8,3032.2,3042.9,3056.9,3062.2,3070.8,3079.0,3081.7,3096.9,3119.2,3119.4,3128.2,3144.9,3146.0,3146.5,3228.0,3239.6
7r'	36.6,48.4,65.0,69.0,79.4,84.7,87.3,104.2,123.6,150.6,176.9,181.5,205.5,221.7,234.2,247.7,256.2,276.2,291.5,292.2,305.8,322.0,348.9,352.7,418.1,432.6,442.2,455.2,479.1,506.1,544.9,579.0,595.1,611.5,638.2,657.4,669.1,680.9,709.6,718.1,728.9,742.9,815.5,844.2,848.2,864.6,894.0,918.6,938.7,949.1,960.2,964.6,986.9,998.3,1010.6,1023.5,1038.8,1072.9,1100.2,1114.8,1136.5,1158.6,1194.5,1210.6,1229.2,1282.0,1297.0,1300.3,1312.1,1327.1,1345.7,1351.3,1364.1,1372.9,1374.7,1392.2,1399.3,1423.2,1424.5,1429.1,1430.9,1436.9,1437.9,1441.4,1452.4,1457.4,1459.2,1530.4,1554.0,1649.4,1958.1,2966.7,2972.3,2974.9,2980.9,2984.5,2989.8,3009.6,3023.9,3035.8,3041.6,3046.1,3052.6,3059.6,3061.9,3071.6,3081.4,3101.5,3149.8,3158.1,3160.0
TS _{7r'-8r}	219.3i,34.0,49.7,54.4,68.8,81.3,87.7,91.5,103.6,142.9,145.9,175.8,184.9,209.2,223.3,233.1,253.1,268.3,279.6,290.2,302.3,321.2,341.2,353.0,419.7,432.0,443.5,455.0,477.9,505.2,543.8,571.6,591.6,605.6,634.3,645.8,662.3,678.6,689.7,710.9,716.2,730.6,818.7,847.8,867.5,871.5,896.1,918.0,937.5,959.9,960.6,982.8,986.2,999.3,1023.5,1038.6,1047.5,1074.4,1109.5,1114.6,1134.9,1160.4,1194.3,1206.2,1224.8,1245.5,1283.0,1307.0,1327.8,1333.2,1341.1,1347.0,1354.4,1363.8,1373.8,1375.9,1394.3,1415.9,1424.9,1426.8,1430.2,1430.4,1437.4,1438.8,1444.1,1452.6,1457.8,1461.7,1543.7,1610.1,1650.0,2968.2,2972.5,2974.8,2984.8,2985.7,2992.0,3007.9,3024.0,3037.1,3040.8,3045.3,3046.7,3062.9,3063.3,3074.0,3075.6,3103.0,3147.4,3152.1,3156.3
8r	40.4,56.1,64.7,70.5,75.9,91.7,99.3,106.8,124.5,137.2,149.0,164.8,211.8,216.3,234.0,247.1,255.0,266.3,268.9,299.8,319.0,322.2,332.1,351.3,376.4,379.9,408.9,433.5,453.2,476.3,506.8,527.6,545.3,578.2,585.1,629.2,647.2,651.8,683.8,693.2,695.7,801.3,861.4,865.5,891.2,907.8,912.3,941.2,947.1,966.4,970.9,982.7,995.9,1016.0,1020.3,1059.5,1080.7,1105.2,1106.5,1125.6,1133.5,1155.4,1175.4,1223.8,1238.9,1268.4,1308.7,1332.9,1336.3,1347.0,1353.6,1361.1,1369.5,1376.2,1377.9,1389.3,1398.6,1416.6,1431.7,1434.8,1437.0,1441.7,1445.9,1452.3,1456.6,1457.2,1467.8,1469.7,1523.1,1605.6,2911.9,2938.3,2941.9,2971.8,2983.7,2987.8,2995.1,3004.6,3011.7,3037.6,3043.5,3043.7,3074.4,3077.2,3098.5,3102.4,3113.9,3115.1,3119.9,3130.3,3156.6
TS _{8r-gr}	453.8i,38.5,53.5,66.5,68.0,75.3,86.0,97.8,101.7,111.6,131.0,161.3,186.8,207.7,212.2,217.2,244.6,257.4,276.4,295.8,309.2,333.1,346.6,367.9,371.7,383.5,407.0,434.3,467.5,479.7,499.5,506.7,521.2,555.9,558.0,611.4,627.6,656.3,662.8,700.9,702.3,720.3,834.8,883.7,913.5,916.7,926.9,935.9,952.1,981.1,997.9,1012.6,1025.7,1035.8,1037.4,1058.8,1068.4,1093.5,1108.1,1146.3,1159.0,1189.4,1206.5,1233.3,1252.8,1266.7,1270.8,1315.0,1347.9,1351.1,1360.0,1363.3,1373.9,1378.7,1379.6,1407.4,1411.0,1414.8,1424.9,1432.1,1440.0,1443.8,1446.7,1454.2,1457.6,1461.1,1465.2,1478.8,1567.8,1591.5,2951.2,2968.2,2970.6,2972.5,2974.3,2983.1,3019.2,3024.6,3037.3,3044.6,3047.6,3064.7,3068.9,3086.2,3087.0,3104.5,3109.9,3111.8,3128.5,3153.2,3168.4
gr	26.5,41.2,61.8,64.6,70.1,80.3,82.6,109.8,125.9,133.2,153.4,182.9,188.1,205.4,225.8,233.3,258.0,258.2,269.7,277.6,292.1,302.6,312.7,335.0,374.6,390.7,405.1,432.0,444.4,462.4,504.9,527.5,562.5,564.7,589.9,606.4,625.2,656.5,678.1,712.6,714.7,798.1,821.2,877.5,903.3,912.5,936.8,954.8,969.1,978.5,982.8,1000.8,1021.8,1024.1,1031.4,1050.8,1067.7,1081.8,1099.2,1119.4,1124.6,1149.5,1181.8,1218.0,1246.2,1271.2,1319.8,1326.0,1329.1,1346.9,1352.0,1364.0,1368.0,1368.9,1374.2,1391.1,1413.2,1425.1,1430.7,1433.6,1434.3,1439.1,1443.0,1452.9,1453.6,1459.0,1463.0,1477.6,1513.8,1616.8,2829.6,2956.4,2977.6,2978.2,2984.2,2990.5,2994.0,3003.9,3020.2,3043.3,3048.8,3058.6,3065.8,3072.0,3085.0,3085.3,3094.6,3102.6,3114.5,3115.4,3215.0
TS _{gr-10r}	423.0i,38.4,55.3,67.3,70.9,77.4,89.3,90.2,106.1,127.6,147.5,163.6,183.1,198.6,224.3,240.5,257.4,261.1,278.4,304.7,327.4,337.9,341.3,359.8,369.4,381.3,411.4,428.3,437.2,461.6,496.0,521.0,524.0,543.7,563.4,590.7,623.2,648.4,652.9,681.3,704.2,707.3,820.4,833.6,884.0,922.7,931.5,942.0,947.1,959.5,983.7,1004.7,1023.5,1026.5,1043.3,1049.2,1069.4,1089.0,1101.9,1129.1,1148.0,1175.8,1204.4,1217.0,1252.0,1267.7,1275.4,1299.7,1346.9,1356.5,1359.3,1364.9,1371.5,1376.4,1378.8,1390.8,1402.5,1409.0,1421.3,1429.5,1437.7,1444.2,1448.4,1448.8,1455.4,1459.8,146

	2.8,1472.6,1543.3,1609.8,2944.8,2958.9,2973.0,2977.8,2983.8,2989.8,3013.4,3035.0,3045.7,3051.7,3056.1,3059.8,3078.4,3080.4,3087.5,3091.8,3104.3,3109.5,3128.0,3169.0,3198.2
10r	49.6,54.3,57.1,67.8,76.1,77.9,88.3,94.4,109.3,127.3,137.9,161.4,188.4,209.3,239.3,250.7,261.9,271.4,304.4,313.5,316.0,326.7,347.1,357.9,368.5,372.7,389.9,417.1,433.8,450.8,471.1,531.7,533.5,567.8,569.3,581.9,631.0,651.8,655.0,705.5,719.6,733.1,827.4,838.4,884.9,893.8,914.8,935.5,949.5,969.9,985.5,991.3,1001.0,1022.8,1036.9,1044.4,1052.7,1070.7,1115.0,1121.0,1138.4,1163.8,1176.9,1219.7,1253.1,1269.6,1298.6,1312.8,1333.8,1340.8,1350.9,1364.8,1372.7,1377.5,1379.4,1398.0,1401.7,1421.3,1424.7,1429.7,1430.8,1432.4,1436.3,1448.5,1450.0,1458.5,1468.2,1472.9,1552.3,1597.5,2945.6,2964.8,2970.7,2981.3,2995.7,2997.9,3000.4,3014.4,3030.2,3033.2,3047.0,3065.2,3078.5,3078.7,3084.2,3085.6,3090.7,3105.6,3110.8,3120.4,3150.0
TS_10r-12	404.4i,43.4,52.2,55.8,60.3,81.2,88.4,99.2,117.7,135.5,137.8,151.4,169.5,182.5,187.3,207.9,215.7,227.4,245.7,273.8,285.4,302.9,310.3,333.0,342.5,345.5,377.6,434.4,465.3,483.5,504.1,516.5,530.9,542.8,576.7,586.6,649.1,656.6,664.1,704.4,712.1,727.1,779.6,801.2,847.2,851.8,872.2,917.4,927.6,932.6,958.3,973.8,974.9,998.5,1007.8,1009.5,1026.4,1028.2,1061.9,1067.5,1073.6,1168.7,1196.1,1209.2,1219.3,1251.3,1262.5,1287.7,1318.0,1335.9,1349.1,1354.5,1359.4,1364.3,1371.5,1386.7,1395.8,1413.2,1421.3,1423.0,1424.8,1440.0,1442.7,1446.6,1451.8,1452.4,1464.1,1482.6,1577.3,1580.4,1592.4,2906.8,2955.4,2959.1,2962.0,2996.9,3002.3,3009.3,3012.8,3021.6,3022.2,3051.3,3063.4,3069.9,3070.2,3071.3,3074.8,3108.7,3112.8,3121.5,3141.1
12	19.5,42.4,45.3,54.8,58.6,64.8,76.9,107.9,136.3,150.7,182.6,215.3,242.2,259.3,288.4,309.7,312.5,316.9,331.7,357.1,362.8,466.8,484.2,500.5,512.3,517.6,546.0,598.4,626.7,648.7,704.5,715.9,725.5,727.8,781.6,789.4,850.9,914.4,921.0,971.2,982.8,995.3,1008.4,1026.0,1028.4,1037.3,1060.3,1063.5,1165.8,1203.9,1247.7,1259.4,1329.0,1353.7,1354.1,1360.7,1364.9,1394.1,1417.8,1423.9,1425.0,1438.0,1441.0,1441.9,1455.1,1458.7,1480.2,1581.8,1599.1,2946.7,2951.0,2953.8,2969.4,2993.4,3004.4,3005.5,3030.1,3046.1,3054.2,3069.9,3095.3,3110.3,3123.9,3697.8
5rot	42.2,53.3,59.1,72.4,79.4,89.6,100.3,116.1,150.2,160.9,166.9,198.9,206.1,216.2,224.5,242.6,256.8,271.3,276.8,287.6,292.8,319.0,329.6,334.6,346.9,353.6,373.1,388.1,395.9,442.9,528.5,535.1,535.8,549.8,559.2,586.6,600.6,630.4,635.5,664.8,671.2,704.1,762.5,821.0,843.1,885.4,901.5,910.3,922.2,935.8,938.6,948.3,982.1,1015.7,1023.9,1047.6,1051.7,1080.6,1089.5,1095.0,1110.4,1150.9,1155.9,1190.3,1238.3,1273.2,1290.2,1305.0,1324.7,1333.3,1350.4,1357.4,1364.0,1367.8,1378.1,1393.1,1406.9,1416.6,1423.1,1423.2,1428.9,1435.1,1439.6,1444.1,1446.7,1455.9,1462.6,1479.3,1588.7,1636.8,2894.9,2959.1,2961.7,2967.5,2972.7,2980.6,2981.1,2993.0,3018.9,3023.4,3047.9,3059.4,3064.7,3068.4,3071.6,3075.0,3091.2,3106.7,3147.3,3168.9,3210.7
TS_5-6	181.ii,36.5,57.1,69.3,75.0,80.7,94.3,101.0,135.2,154.9,168.7,183.3,194.3,197.7,212.3,230.3,237.4,252.9,277.4,278.8,284.8,292.5,313.6,316.5,323.2,328.7,334.4,372.5,372.8,378.5,413.4,526.6,534.0,548.6,552.1,565.2,586.5,627.3,629.9,664.3,669.9,701.0,702.7,807.8,822.2,866.4,884.8,907.2,925.2,935.3,938.7,958.1,986.9,996.5,1016.7,1025.0,1069.5,1085.4,1091.2,1092.6,1105.9,1140.7,1163.9,1186.5,1219.7,1299.9,1318.8,1339.2,1343.7,1349.7,1359.4,1365.3,1373.5,1387.8,1397.7,1404.5,1412.3,1417.0,1418.2,1421.7,1423.4,1429.9,1430.5,1433.2,1440.2,1441.7,1450.0,1530.1,1613.4,1642.1,2958.1,2963.1,2970.6,2973.4,2973.8,2982.1,3021.5,3031.0,3033.3,3035.3,3037.5,3044.3,3062.3,3080.9,3088.1,3090.2,3095.6,3110.3,3155.6,3177.6,3192.9
6	37.0,55.1,66.3,75.4,92.1,95.3,107.0,116.0,151.8,155.0,166.0,188.6,199.3,226.9,243.2,247.0,270.3,280.6,289.9,306.2,309.0,319.7,325.4,348.2,353.0,374.1,375.6,397.8,436.7,462.1,534.1,538.9,548.4,558.9,581.9,595.2,615.8,635.1,647.8,660.4,684.2,715.6,765.4,842.4,858.3,909.2,914.7,925.8,944.6,946.0,954.5,958.6,979.4,1015.8,1048.4,1061.8,1084.4,1091.0,1111.0,1114.6,1116.3,1156.9,1160.3,1191.8,1243.9,1290.5,1319.5,1322.9,1337.6,1344.0,1357.6,1365.6,1372.2,1383.0,1392.1,1395.2,1401.6,1413.7,1428.9,1429.6,1435.2,1441.0,1443.0,1447.4,1451.1,1460.4,1467.8,1479.7,1521.2,1625.1,2945.8,2967.1,2983.8,2994.1,3003.2,3004.7,3007.9,3018.7,3037.1,3038.1,3057.1,3069.1,3073.3,3081.7,3085.3,3088.7,3095.1,3097.5,3100.6,3160.0,3202.9
TS_6-7	690.9i,53.2,71.1,74.6,77.4,99.0,104.6,106.8,119.5,124.9,130.8,141.3,149.2,152.4,180.1,190.1,201.3,221.4,242.2,261.1,272.5,280.3,297.5,317.6,329.1,330.6,347.0,357.8,394.8,422.1,521.6,527.3,548.7,563.3,565.1,588.6,591.0,624.6,636.5,654.9,684.2,687.9,724.7,757.8,799.1,824.4,852.9,902.1,915.4,918.8,926.9,934.5,945.0,995.7,1009.5,1018.1,1025.2,1039.0,1056.8,1066.2,1081.5,1094.1,1138.1,1150.3,1182.9,1220.4,1272.6,1317.8,1328.0,1333.6,1336.3,1359.7,1369.6,1374.8,1379.5,1388.8,1398.6,1407.5,1417.1,1420.1,1423.3,1432.6,1434.2,1435.0,1439.4,1441.3,1445.8,1573.8,1597.1,1638.2,1642.9,2956.3,2957.6,2960.9,2979.4,2984.0,3000.8,3012.1,3026.8,3036.7,3046.5,3048.3,3060.4,3065.2,3071.8,3091.8,3096.5,3118.5,3146.1,3160.7,3199.6
7	33.0,57.8,71.5,72.9,82.2,89.5,98.9,104.6,133.5,160.0,166.1,171.8,194.6,244.6,267.3,289.1,294.3,303.0,316.3,331.4,355.6,399.1,514.7,536.0,554.5,558.4,562.5,591.4,597.4,619.7,630.2,694.5,698.0,716.0,756.4,790.5,797.7,817.4,896.6,925.0,947.1,989.4,1011.2,1023.7,1037.3,1067.6,1080.7,1089.5,1118.6,1138.1,1219.1,1308.9,1321.6,1355.1,1362.6,1375.5,1381.7,1398.8,1414.0,1422.3,1423.6,1425.2,1431.3,1435.4,1439.4,1443.5,1612.6,1615.6,1670.5,2962.3,2967.1,2974.3,2977.3,3017.0,3029.3,3040.8,3044.0,3049.4,3055.7,3056.6,3071.4,3086.8,3125.1,3192.6
TS_7-8	887.3i,56.9,67.1,75.9,94.4,114.3,130.2,139.1,146.7,156.1,170.1,174.1,214.6,251.6,280.9,294.4,309.9,319.6,334.3,336.7,345.3,413.5,482.6,537.6,543.5,569.1,573.5,584.5,608.1,625.6,633.1,677.9,700.9,706.1,737.3,820.3,838.6,846.7,934.3,943.4,950.2,967.1,1000.1,1020.3,1023.0,1046.3,1060.0,1083.5,1094.1,1150.5,1204.1,1322.8,1331.5,1337.2,1354.6,1357.3,1365.2,1375.9,1407.1,1409.9,1422.6,1429.0,1430.8,1438.7,1443.6,1448.3,1461.2,1484.8,1565.4,1649.1,2935.2,2943.2,2969.5,2974.1,3026.4,3036.2,3049.4,3056.0,3068.7,3097.3,3100.4,3126.6,3158.4,3261.6

8	56.0,60.0,64.2,73.3,77.2,85.2,106.3,117.1,123.8,131.2,143.9,191.1,214.2,245.9,259.1,286.5,300.2,304.4,327.9,346.7,371.3,413.5,516.1,527.8,539.0,564.2,574.0,597.9,614.7,627.6,652.9,671.6,695.2,699.8,818.8,843.6,921.2,932.5,950.2,971.3,980.8,991.2,1017.5,1034.5,1049.2,1087.5,1121.8,1127.9,1149.2,1188.0,1218.4,1296.2,1323.7,1326.4,1354.6,1357.7,1378.4,1383.9,1393.5,1407.7,1423.9,1433.7,1436.8,1440.2,1448.9,1453.3,1482.0,1526.4,1631.8,2948.0,2950.7,2968.3,2975.3,2991.9,3022.5,3030.8,3036.2,3088.0,3088.2,3089.5,3098.5,3121.5,3131.8,3212.7
TS_8-9	372.7i,47.9,56.9,58.2,71.5,80.4,88.0,124.0,131.0,160.7,164.9,203.3,239.6,277.2,282.5,291.3,304.8,335.4,348.2,373.7,389.5,458.6,503.0,541.3,544.2,565.3,592.7,600.9,634.6,637.2,644.9,675.8,684.3,712.1,796.2,820.3,879.9,908.6,918.6,926.1,952.2,973.3,1000.9,1023.5,1043.5,1063.3,1074.0,1088.9,1104.3,1156.8,1173.3,1210.1,1286.6,1313.1,1328.2,1365.0,1369.0,1374.6,1380.9,1405.2,1410.4,1413.8,1421.1,1424.5,1435.3,1438.2,1453.3,1632.3,1641.3,1698.8,2950.4,2962.1,2977.5,2994.1,3014.0,3028.8,3051.9,3061.5,3081.2,3081.5,3092.8,3110.1,3143.7,3173.7
9	34.4,39.2,47.7,55.0,60.0,70.4,95.2,102.4,112.9,161.2,171.6,199.9,253.2,270.1,317.2,328.8,356.2,374.5,379.3,391.5,438.0,463.8,488.2,502.3,533.9,559.6,606.1,634.1,636.8,654.4,660.3,679.4,691.5,760.3,831.7,879.5,907.0,955.9,963.1,972.8,975.1,997.9,1024.0,1039.4,1079.2,1093.4,1094.8,1144.4,1169.2,1207.0,1227.7,1304.2,1315.1,1319.0,1328.1,1342.2,1361.5,1372.9,1385.5,1393.8,1406.0,1415.9,1428.2,1429.7,1439.4,1448.4,1471.6,1513.8,1595.4,2855.6,2937.1,2961.4,2965.9,2979.7,2983.2,3011.3,3013.7,3048.8,3054.2,3072.6,3084.2,3087.6,3100.6,3180.5
TS_9-10	960.1i,35.1,56.6,65.7,76.2,83.5,94.7,97.6,110.3,113.1,128.2,199.4,240.6,264.2,302.8,329.1,349.4,355.1,382.2,385.8,438.2,461.0,497.2,502.0,558.9,569.4,592.7,611.0,646.2,659.0,673.6,696.3,702.0,717.2,822.9,857.3,886.3,893.5,928.8,947.6,959.9,975.3,988.0,1006.5,1020.8,1047.1,1063.4,1099.6,1123.5,1183.3,1187.9,1225.7,1286.0,1302.3,1332.5,1342.4,1355.1,1363.2,1372.7,1397.7,1407.5,1411.5,1417.3,1425.9,1432.9,1437.3,1451.6,1525.3,1584.0,1618.3,2908.9,2956.5,2964.5,2980.7,3017.9,3022.3,3029.6,3041.2,3051.7,3068.1,3076.9,3122.7,3141.4,3163.8
10	33.1,48.0,57.6,65.7,68.6,78.7,87.0,108.4,123.9,148.0,216.7,246.2,253.4,282.6,314.7,326.8,353.8,359.3,375.0,390.4,441.4,473.9,499.8,541.3,569.3,584.1,603.0,613.5,630.9,687.2,695.8,707.4,712.1,730.2,802.4,823.3,845.8,860.1,876.2,914.8,956.0,978.6,988.4,1013.0,1019.8,1057.2,1059.3,1098.4,1178.5,1187.0,1206.9,1224.2,1292.1,1326.6,1338.8,1356.3,1363.1,1366.0,1391.3,1403.6,1415.6,1420.4,1429.4,1435.7,1442.3,1448.7,1547.9,1611.6,1633.6,2728.4,2876.1,2951.7,2960.6,2976.3,3007.9,3015.1,3024.2,3033.5,3053.5,3075.5,3087.9,3123.1,3142.2,3161.5
TS_10-11	232.7i,51.1,55.7,59.9,81.8,90.0,100.5,124.6,146.9,216.7,219.0,228.6,251.6,260.0,275.0,327.4,335.4,358.8,381.0,396.1,448.5,482.1,502.0,549.6,565.8,572.3,603.2,604.7,640.9,665.3,693.9,710.4,727.8,736.9,774.2,844.5,875.1,885.7,898.9,971.2,986.8,991.2,996.1,1023.1,1035.7,1065.3,1073.2,1116.6,1157.9,1181.6,1191.2,1230.6,1294.7,1343.8,1351.0,1355.2,1361.2,1372.7,1385.7,1396.0,1414.8,1417.8,1428.5,1436.8,1447.3,1450.4,1493.2,1548.6,1665.8,1696.0,2919.8,2968.0,2973.9,2976.6,2986.3,3023.5,3027.7,3034.4,3070.5,3078.5,3108.3,3115.5,3116.4,3157.1
11	30.3,46.0,52.9,58.8,66.6,81.7,111.0,120.9,125.6,147.3,160.1,215.6,262.8,277.8,312.9,318.6,325.2,340.3,372.9,377.1,424.9,448.0,472.1,506.7,523.7,534.0,569.5,600.3,638.9,641.3,647.2,668.0,712.6,746.0,844.9,860.5,896.0,949.1,974.8,983.3,992.4,1016.5,1028.4,1054.4,1064.0,1066.0,1097.7,1124.9,1169.4,1222.7,1245.4,1252.8,1324.0,1339.3,1357.5,1360.4,1365.8,1388.5,1401.2,1407.7,1416.1,1423.3,1430.8,1434.7,1442.9,1460.3,1469.3,1520.6,1609.9,2548.2,2958.3,2960.9,2961.8,2982.2,2982.9,3007.1,3015.9,3036.8,3052.2,3070.5,3074.8,3092.7,3104.1,3139.9
01.s	36.7,57.7,62.5,66.6,82.1,88.4,96.6,123.1,138.1,145.8,147.1,162.1,166.4,170.8,175.9,203.1,220.5,234.8,261.0,265.8,281.5,296.9,311.6,328.7,344.8,360.8,369.8,410.1,428.8,446.0,483.4,538.9,546.3,555.3,557.2,579.1,598.8,624.2,638.2,657.2,668.3,685.0,687.6,801.0,817.0,918.0,931.4,947.3,951.1,956.6,961.3,993.3,1020.2,1026.3,1038.9,1060.6,1065.9,1073.5,1098.2,1104.1,1158.8,1161.7,1172.3,1219.3,1320.4,1326.5,1337.9,1340.8,1352.4,1359.9,1363.9,1366.5,1372.0,1380.5,1385.2,1396.7,1409.9,1412.9,1419.9,1428.4,1433.0,1436.5,1441.4,1444.8,1449.6,1455.8,1457.4,1469.8,1500.7,1543.9,2894.8,2933.9,2970.1,2981.9,2988.1,2995.7,3002.6,3031.7,3034.9,3042.0,3053.5,3058.8,3062.4,3073.1,3074.0,3079.3,3084.8,3089.7,3092.5,3092.9,3164.0
01.t	59.1,65.2,74.1,78.1,90.1,95.1,108.6,121.8,136.4,147.3,158.1,181.3,194.2,200.7,210.9,219.9,232.9,274.0,277.4,307.9,315.2,329.6,345.8,360.5,372.1,376.4,380.0,398.4,401.9,445.1,453.4,482.8,515.2,538.6,572.7,576.3,581.5,583.3,630.1,648.7,655.9,694.9,733.2,774.5,882.9,885.8,924.1,938.9,941.3,949.2,965.9,972.9,979.0,983.0,1015.7,1050.3,1062.0,1088.5,1103.1,1108.3,1120.6,1123.5,1205.2,1239.6,1269.5,1315.8,1326.1,1328.5,1337.1,1345.5,1354.2,1362.8,1367.8,1374.3,1386.5,1393.1,1402.5,1407.1,1415.7,1424.9,1426.4,1428.3,1432.5,1438.0,1440.6,1454.4,1461.3,1463.8,1470.3,1484.0,2942.0,2949.8,2952.0,2970.4,2971.4,2991.6,2995.4,3001.0,3012.0,3015.8,3025.3,3031.5,3069.5,3085.4,3094.9,3101.2,3112.4,3117.5,3132.7,3167.7,3179.7
03.t	37.9,53.2,64.9,66.7,72.9,78.3,91.8,95.2,100.3,114.4,118.6,124.5,134.2,150.6,161.2,164.5,175.9,180.7,187.4,200.0,222.1,266.3,271.1,299.8,316.8,320.7,334.4,348.0,355.3,376.2,420.8,520.2,535.4,552.2,559.8,562.6,589.2,595.5,607.8,609.4,626.6,659.8,713.0,804.1,822.5,913.1,919.9,922.6,928.1,938.0,955.1,961.5,963.0,970.7,989.8,1008.3,1012.7,1063.9,1068.7,1088.1,1117.5,1165.0,1188.0,1190.5,1284.7,1334.0,1339.5,1341.1,1342.3,1345.3,1348.2,1373.0,1378.6,1380.0,1389.6,1398.5,1404.4,1409.3,1411.6,1414.0,1420.2,1421.0,1426.1,1430.4,1451.9,1456.9,1473.0,1479.9,1501.2,1629.3,2940.8,2943.8,2948.2,2954.0,2963.6,2973.0,2996.3,2998.2,3017.3,3021.5,3022.6,3024.8,3043.3,3062.1,3064.7,3071.1,3083.9,3117.5,3159.7,3185.5,3204.2
TS_01.t-04.t	1358.0i,40.6,62.7,67.9,76.8,81.8,110.6,117.7,123.7,132.9,140.7,148.5,161.6,179.0,188.6,235.8,244.6,246.8,258.2,267.6,279.4,297.3,304.8,321.1,323.7,335.5,362.2,376.5,403.3,417.3,478.7,514.7,528.9,536.0,554.1,560.2,570.0,583.2,604.1,618.3,625.9,662.9,701.6,726.7,788.7,836.7,878.9,904.4,917.8,929.9,950.5,956.6,987.2,990.5,1006.6

	2,1009.2,1049.0,1066.3,1073.8,1082.9,1098.7,1119.3,1147.0,1154.9,1211.0,1264.6,1288.6,1319.6,1343.4,1349.8,1351.0,1356.8,1360.7,1367.2,1371.5,1391.9,1403.3,1409.9,1412.2,1418.6,1419.6,1423.0,1430.7,1438.4,1439.8,1449.2,1452.3,1458.0,1468.6,1488.7,2101.2,2943.9,2945.8,2959.4,2969.2,2979.1,2981.2,2999.8,3006.8,3017.3,3025.0,3054.8,3059.4,3069.6,3083.3,3089.6,3093.8,3107.3,3152.7,3175.2,3189.2
TS_04.t-03.t	342.5i,15.9,58.7,64.3,76.1,81.2,87.4,100.0,116.5,125.0,129.2,141.5,152.8,159.9,178.4,189.2,221.4,232.7,254.2,263.2,267.3,278.2,289.4,297.8,311.8,316.6,330.0,375.0,378.3,401.5,430.3,485.5,529.0,530.4,547.5,555.6,565.5,591.2,612.8,615.9,628.7,659.2,705.0,799.1,817.3,836.9,896.7,916.6,925.2,930.8,945.2,955.2,960.4,988.7,998.1,1007.8,1048.6,1057.0,1070.2,1079.9,1121.5,1155.2,1156.7,1175.6,1196.3,1320.0,1334.4,1342.4,1346.1,1354.7,1359.5,1368.4,1376.0,1378.6,1383.6,1395.6,1405.9,1409.9,1414.5,1417.8,1421.4,1423.3,1431.0,1434.5,1443.8,1445.7,1463.5,1467.8,1472.5,1496.2,2940.1,2949.9,2960.0,2966.2,2977.1,2981.1,2986.8,3007.1,3012.6,3019.8,3026.8,3048.9,3064.8,3074.8,3075.3,3077.2,3100.2,3106.5,3176.1,3179.0,3188.9
TS_01.s-02.s	815.0i,60.5,68.4,74.9,80.5,82.6,97.9,114.7,124.0,129.6,135.2,153.6,160.9,197.2,202.6,227.2,255.4,260.8,263.7,267.4,278.0,303.1,308.7,312.3,334.4,338.3,358.5,374.1,416.7,419.4,512.6,523.3,528.0,560.5,563.2,570.2,581.0,597.3,626.0,640.1,661.5,689.4,707.6,765.8,810.3,846.2,899.4,920.2,929.9,947.2,978.2,983.1,989.3,1003.0,1011.7,1020.9,1057.1,1065.6,1080.0,1090.7,1103.5,1108.5,1144.6,1157.5,1210.9,1267.8,1300.8,1327.7,1335.4,1356.8,1364.3,1364.6,1369.9,1372.5,1377.8,1410.7,1413.3,1414.9,1415.7,1423.6,1427.8,1431.6,1435.2,1437.5,1450.5,1457.4,1459.2,1464.2,1576.9,1620.0,2348.5,2944.4,2959.4,2964.7,2966.3,2977.3,2993.7,3006.1,3006.8,3014.0,3044.6,3049.4,3076.8,3088.8,3093.9,3098.0,3108.7,3117.9,3181.5,3191.5,3196.1

Table S5. D3-correction (zero damping) to periodic structures in eV.

mol	D3
water	0.000
methanol	-0.015
ethene	-0.013
propene	-0.040
1	-8.376
TS_1-2	-8.422
2	-8.418
TS_2-3	-8.423
3	-8.351
TS_3-4	-8.387
4	-8.405
TS_4-5	-8.392
5	-8.380
TS_5-6r	-8.362
6r	-8.375
TS_6r-7r	-8.362
7r	-8.369
TS_7r-7r'	-8.956
7r'	-8.403
TS_7r'-8r	-8.399
8r	-8.352
TS_8r-9r	-8.362
9r	-8.383
TS_9r-10r	-8.359
10r	-8.419
TS_10r-12	-8.453

12	-7.575
5rot	-8.379
TS_5-6	-8.426
6	-8.422
TS_6-7	-8.442
7	-7.640
TS_7-8	-7.718
8	-7.663
TS_8-9	-7.548
9	-7.575
TS_9-10	-7.570
10	-7.579
TS_10-11	-7.611
11	-7.579
01.s	-8.341
01.t	-8.355
03.t	-8.474
TS_01.t-04.t	-8.395
TS_04.t-03.t	-8.442
TS_01.s-02.s	-8.430
02.s	-8.396
04.t	-8.404