A Combined Computational and Experimental Study of Methane Activation during Oxidative Coupling of Methane (OCM) by Surface Metal Oxide Catalysts

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Table S1. Calculated values for $\mu O\,(T, p)$ in eV, referenced to 300K, 101325Pa (1atm) highlighted in red.

	1.00 E-10	**0.1**	**0.15**	**0.2**	**0.25**	**0.3**	**0.35**	**0.4**	**1**	**1.00E +10**
300	-0.30	-0.03	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01	0.00	0.30
350	-0.41	-0.10	-0.09	-0.09	-0.08	-0.08	-0.08	-0.08	-0.06	0.29
400	-0.52	-0.16	-0.16	-0.15	-0.15	-0.14	-0.14	-0.14	-0.12	0.27
450	-0.63	-0.23	-0.22	-0.22	-0.21	-0.21	-0.21	-0.21	-0.19	0.26
500	-0.75	-0.30	-0.29	-0.29	-0.28	-0.28	-0.28	-0.27	-0.25	0.24
600	-0.98	-0.44	-0.43	-0.43	-0.42	-0.42	-0.41	-0.41	-0.38	0.21
700	-0.98	-0.59	-0.58	-0.57	-0.56	-0.56	-0.55	-0.55	-0.52	0.17
800	-1.21	-0.74	-0.72	-0.71	-0.71	-0.70	-0.69	-0.69	-0.66	0.13
900	-1.45	-0.89	-0.87	-0.86	-0.85	-0.85	-0.84	-0.83	-0.80	0.09
1000	-1.69	-1.04	-1.02	-1.01	-1.00	-0.99	-0.99	-0.98	-0.94	0.05
1100	-1.93	-1.20	-1.18	-1.16	-1.15	-1.14	-1.14	-1.13	-1.09	0.00
1200	-2.18	-1.35	-1.33	-1.32	-1.31	-1.30	-1.29	-1.28	-1.23	-0.04
1300	-2.43	-1.51	-1.49	-1.47	-1.46	-1.45	-1.44	-1.44	-1.38	-0.09

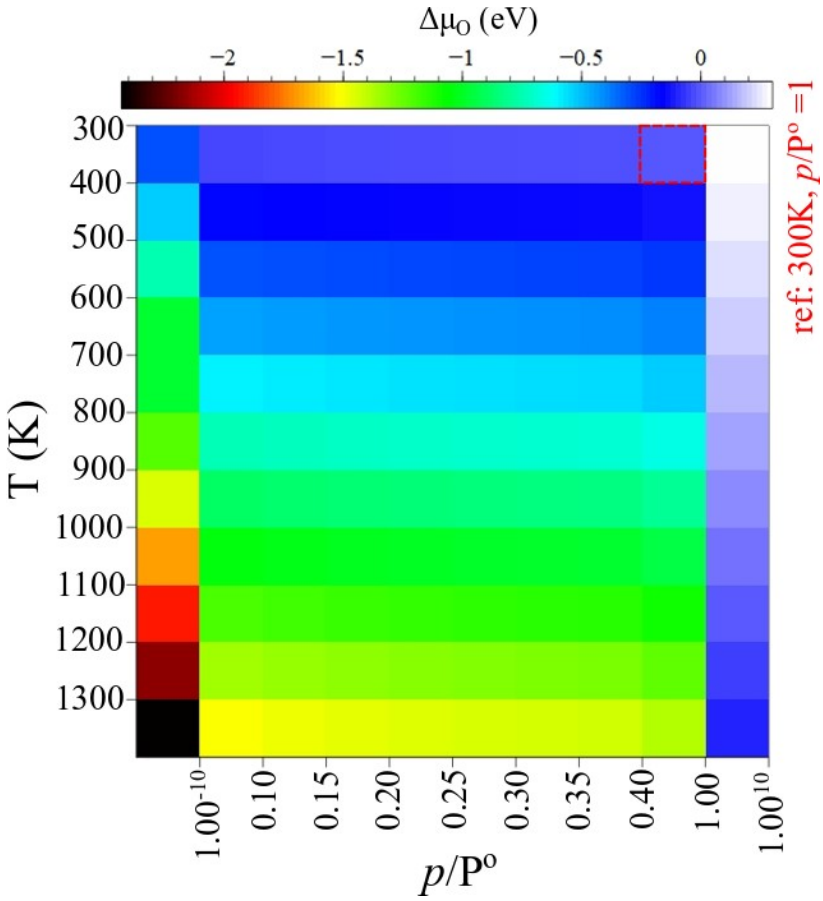


Figure S1. *μO(T,P) taken from table S1, calculated according to eq(4) shown in experimental section.*

The positive values for "O_2 balance" in **Table S2** indicate that oxygen needs to be added into the system to form the respective Mn_aO_b cluster, while a negative value signifies release of O_2 from the solid to the gas-phase.

Table S2. Calculated parameters from general stoichiometry equation for various Mn_aO_b clusters.

Cluster Stoichiometry	a = Mn atoms in the cluster	b = O atoms in the cluster	Fraction of Mn_2O_3 = (a/32)	O_2 balance = b – 48(a/32)
MnO	1	1	0.03125	-0.5
MnO_2	1	2	0.03125	0.5
MnO_3	1	3	0.03125	1.5
Mn_2O	2	1	0.0625	-2
Mn_2O_2	2	2	0.0625	-1
Mn_2O_3	2	3	0.0625	0
Mn_2O_4	2	4	0.0625	1
Mn_2O_5	2	5	0.0625	2

Bader charge-oxidation state correlation using bulk reference compounds. Often, calculated values of Bader charges, especially transitional metals, are reported in the literature as misnomers for formal oxidation states. While Bader charge and oxidation state are indirectly related, Bader charges cannot be explicitly used as oxidation state. To ascertain oxidation state of a metal center from its Bader charge, the calculated data needs to be calibrated with compounds where formal oxidation state is experimentally known. Using the calibrated correlation then, one can back out oxidation state of a metal center from its Bader charge value, which has been demonstrated implicitly in various literature reports.[10] This approach of data calibration was used to generate linear correlations, shown below, for both Mn and W centers, so their formal oxidation state under various conditions could be ascertained from the Bader charge calculation. Reference compounds used for each case are labelled on the plot in **Figure S2.**

oxidation state		calculated Bader charge
Mn	3	1.61
	2.67	1.51
	2	1.43
	0	0
W	6	2.56
	4	2.01
	0	0

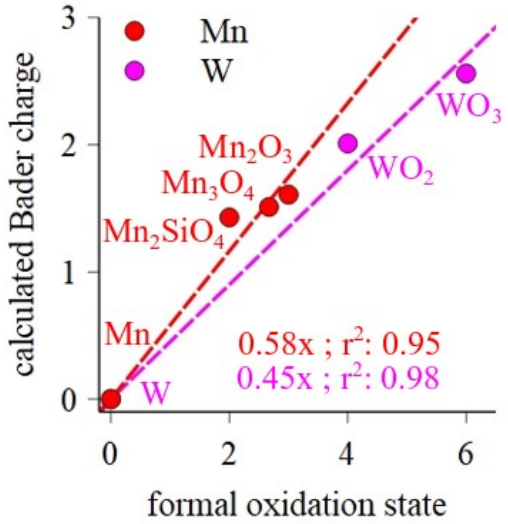


Figure S2. Linear correlation of calculated Bader charge values with formal oxidation state of transition metals using bulk reference compounds.

Table S3. Summary of various pathways studied for CH_4 dissociation over Na_2WO_4 surface sites.

CH_4 dissociation pathways over Na_2WO_4/SiO_2 catalyst`			
	TS	Final	Descriptor

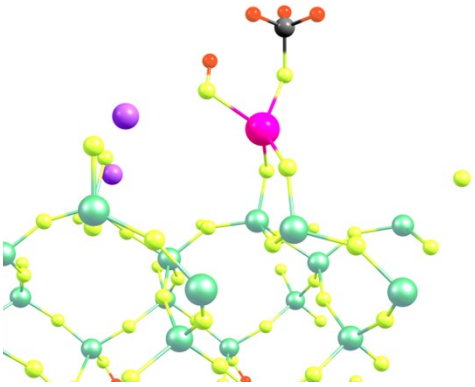
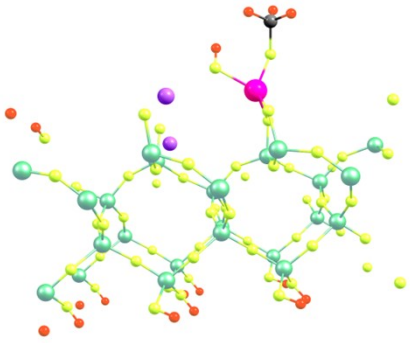
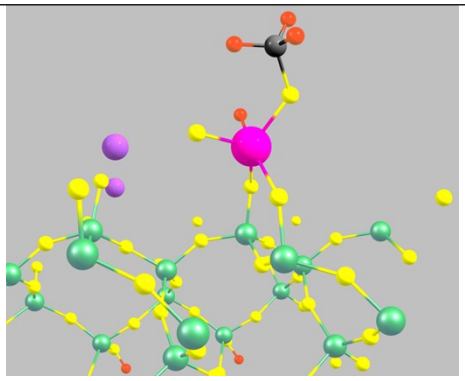
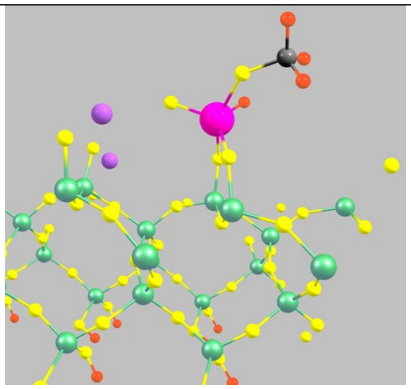
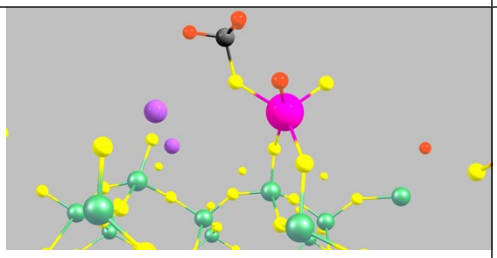
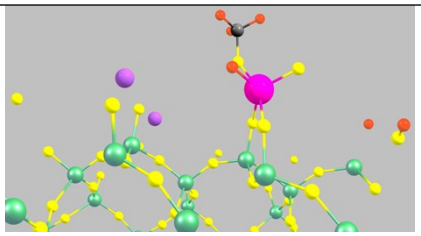
1			W_OCH3_OH_N a
2			b_H_W_OCH3
3			H_W_OCH3
4	Shown in main file-dominant pathway		

Table S4. Summary of various pathways studied for CH_4 dissociation over Mn_2O_5-Na_2WO_4 surface sites.

CH_4 dissociation pathways over Mn_2O_5-Na_2WO_4/SiO_2 catalyst`: WO_5 moiety			
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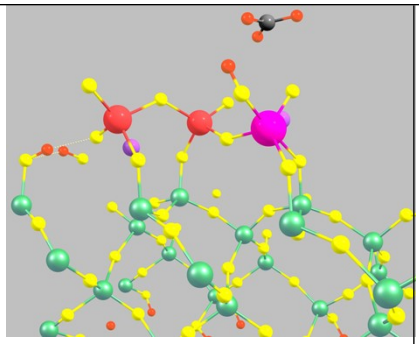
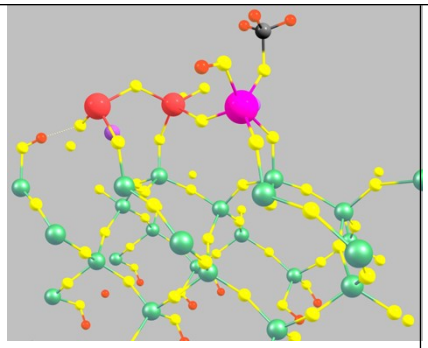
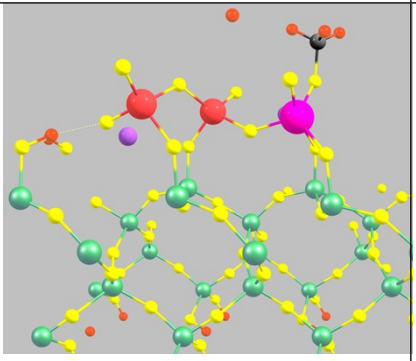
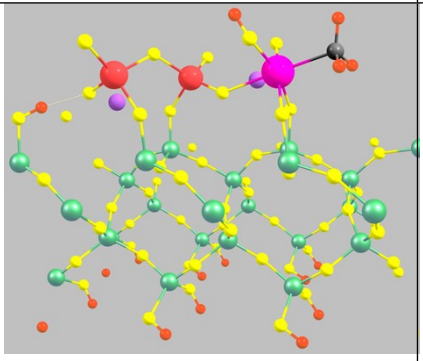
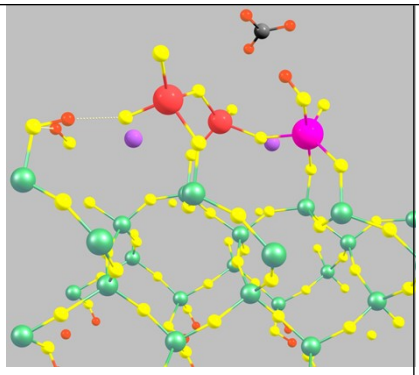
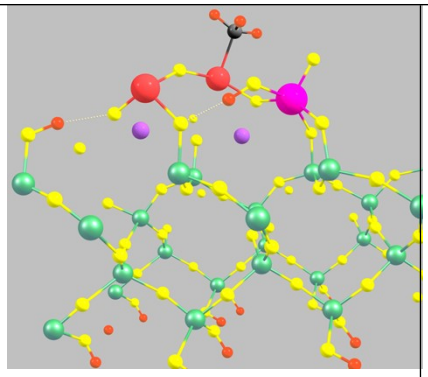
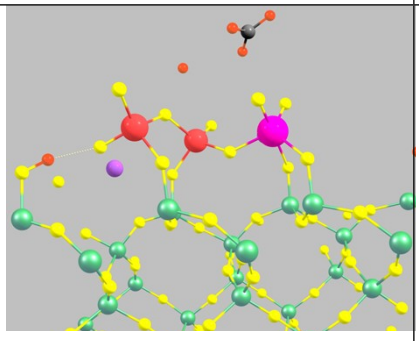
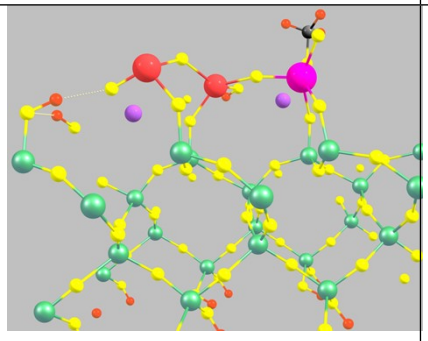
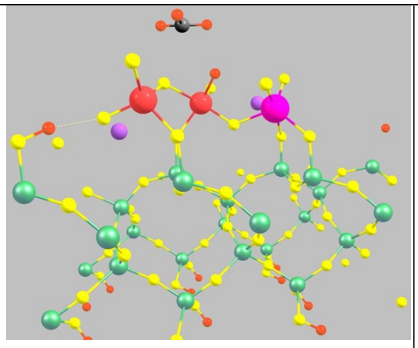
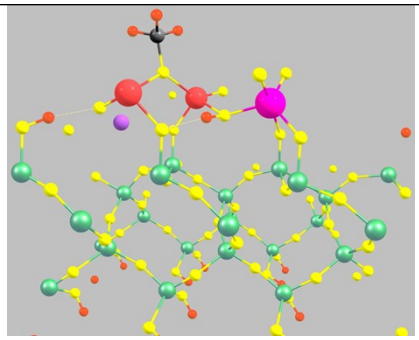
1			WO_CH3_OH
2			W_CH3_OH
W-O-Mn moiety			
3			W_CH3_OH_b
4			W_OCH3_OH_Mn1

5			b_Mn1_OCH3_Mn1_OH_W
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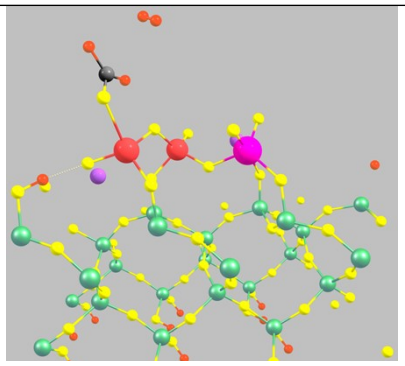
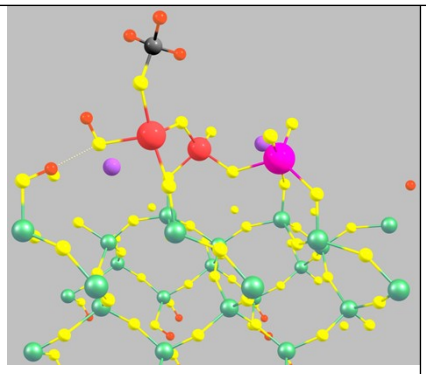
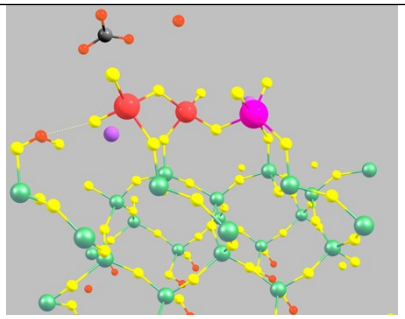
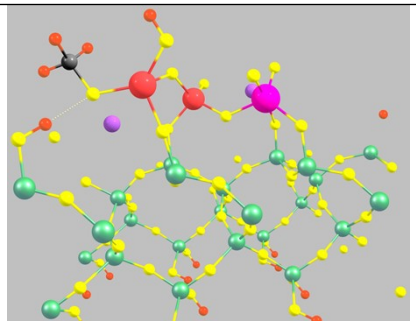
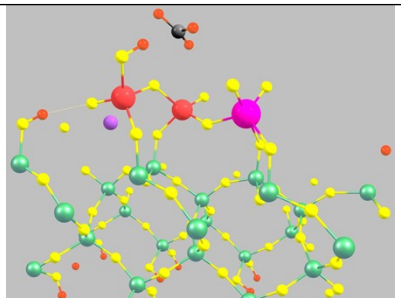
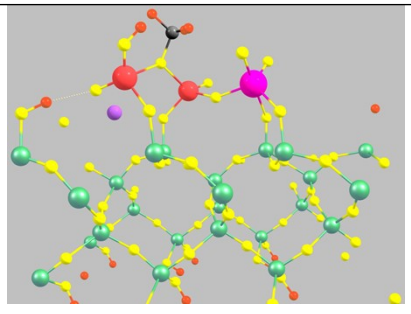
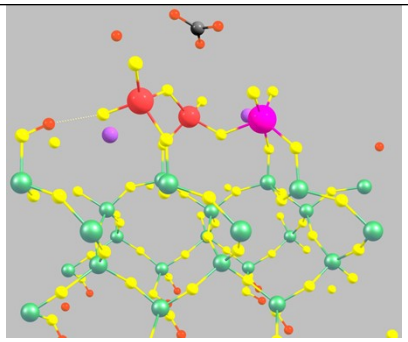
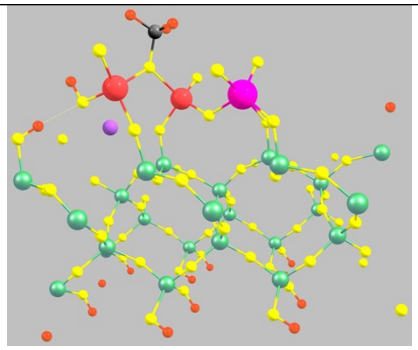
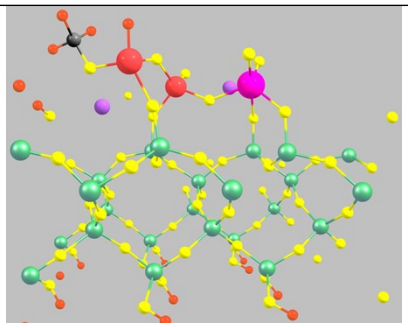
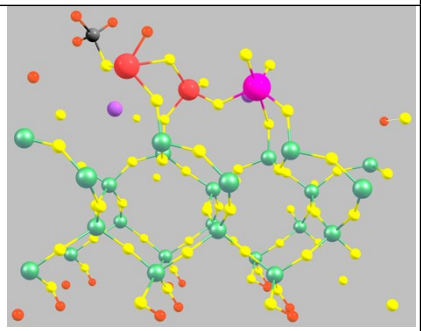
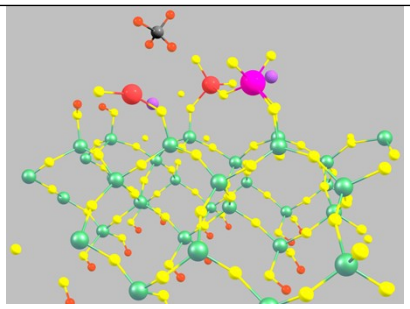
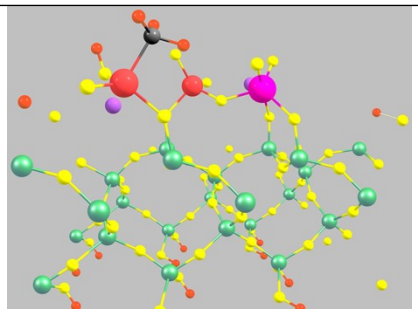
6			Mn2_OCH3_OH
7			B_Mn2_OCH3_OH
8			B_Mn2_OCH3_Mn1-2_OH
9	Shown in main file-dominant pathway		

10			Mn1-2_OCH3_Mn2_OH
11			Mn2_H_OCH3
12			Mn2_CH3_OH

Optimized POSCAR of Mn_2O_5-Na_2WO_4/SiO_2

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     0.0000000000000000   10.1387000000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000   28.0000000000000000
   Si   O    H    W    Na   Mn
    24    64    14     1     2     2
Selective dynamics
Direct
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0.5169524158426810	0.1248384898947137	0.4317339619186455	T	T	T
0.4829403232376848	0.3737579362334742	0.4317242006050535	T	T	T
0.8491731693124009	0.1259435548661472	0.4321572716972852	T	T	T
0.8137210852486447	0.3743426602613980	0.4318925443226291	T	T	T
0.1922798097670295	0.6245441425204703	0.4274528860832518	T	T	T
0.1389926864801154	0.8754875263136341	0.4270224076210525	T	T	T
0.5302757977268016	0.6224270907924492	0.4250225326535784	T	T	T
0.4743103305639451	0.8737873167745747	0.4280163025467374	T	T	T
0.8594128970590660	0.6240826046018739	0.4269585622579868	T	T	T
0.8049510725429343	0.8752011898692018	0.4266663023177699	T	T	T
0.0616032809748930	0.0039326235984447	0.4940455304121585	T	T	T
0.2280709629079354	0.9672279799837966	0.5028427626915075	T	T	T
0.3947098838713288	0.0093422901673748	0.4919525105781233	T	T	T
0.5615106165227814	0.9641065381969085	0.5036895347212393	T	T	T
0.7273815352718955	0.0063650597205651	0.4922616925852594	T	T	T
0.8941599358585250	0.9615052963847148	0.5018467150671952	T	T	T
0.1002320491231714	0.5346066241777052	0.5023932943485079	T	T	T
0.2675647616818182	0.5017716045951133	0.4974564198453635	T	T	T
0.4339100437087140	0.5403055021549932	0.4987769517201244	T	T	T
0.6017375003938525	0.4934152900152711	0.4928190843512539	T	T	T
0.7698725258062638	0.5399169756135649	0.5033104127433106	T	T	T
0.9338526294576042	0.4906856437137179	0.4928655380493154	T	T	T

0.9995672101362985	0.7494565638228394	0.4937632176999003	T	T	T
0.9950564357315343	0.8876849337344197	0.5741062019086840	T	T	T
0.3314026214241181	0.7547103754511255	0.4933317241002513	T	T	T
0.3335550461648111	0.8978344377817749	0.5728907284468079	T	T	T
0.6642584483457057	0.7505253120245214	0.5020192184169403	T	T	T
0.6667260139778293	0.9155092641003364	0.5765014802014008	T	T	T
0.9833161514753925	0.6038030177681009	0.5719337283023265	T	T	T
0.3482760058060350	0.6226518790011610	0.5748812569596282	T	T	T
0.3600077287429926	0.7148893706922479	0.6647031200187925	T	T	T
0.4571564998027569	0.9316070491133459	0.6429528523372738	T	T	T
0.6734925507395602	0.5792829089434477	0.5757751142218268	T	T	T
0.9366136240000031	0.1554933079999969	0.2701178570000025	F	F	F
0.9751808259999990	0.4167210789999984	0.2840807139999981	F	F	F
0.2699736980000011	0.1554696359999994	0.2701382139999993	F	F	F
0.3085132819999998	0.4167220650000019	0.2840807139999981	F	F	F
0.6032976070000018	0.1554785129999985	0.2701307139999969	F	F	F
0.6418325879999998	0.4167329140000007	0.2840771429999975	F	F	F
0.9366418990000014	0.6554676639999997	0.2701389289999980	F	F	F
0.9751663600000029	0.9167309420000009	0.2840775000000022	F	F	F
0.2699644919999997	0.6554765400000022	0.2701314290000028	F	F	F
0.3085152550000032	0.9167191060000022	0.2840810710000028	F	F	F
0.6033081269999983	0.6554686500000031	0.2701385709999968	F	F	F
0.6418470540000030	0.9167210789999984	0.2840807139999981	F	F	F
0.9370657765877155	0.8861482815335364	0.5901160927725044	T	T	T
0.0012684999754811	0.6897596956007064	0.5852640079882363	T	T	T
0.4064800213067699	0.7980229958050487	0.6157519282677413	T	T	T
0.3975635739783385	0.5015493057527109	0.6377618729824945	T	T	T
0.8313157653449252	0.5842250477547424	0.5875029276123769	T	T	T
0.6008541985120175	0.6352965010988001	0.6230112561895851	T	T	T
0.7345182862766747	0.8721123825800773	0.6253228052671211	T	T	T