Electronic Supplementary Information – Ab initio insight into furan conversion to levulinate ester in reaction with methylal and methanol

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Table S1. The bond lengths (unit: Å), bond angles (unit: degree), and dipole moment (μ) of 2-methoxymethyl-furan (MMF), optimized by using different methods such as pseudo-atomic orbital-double zeta polarization (PAO-DZP) method with supercell modeling without (Vac.) and with 25 and 40 methanol solvent molecules (Met-25 and Met-40) using PBE exchange-correlation functional as implemented in SIESTA package and all-electron atomic orbital B3LYP/6-311+G* method with cluster modeling without (Vac.) and with methanol solvent effect (Met.) as implemented in NWChem package.

	PBE/DZP			B3LYP/6-311+G*	
	Vac.	Met-25	Met-40	Vac.	Met.
O1–C1	1.365	1.371	1.359	1.361	1.365
O1–C4	1.369	1.376	1.365	1.374	1.377
C1–C2	1.354	1.357	1.352	1.359	1.359
C2–C3	1.407	1.409	1.403	1.432	1.434
C3–C4	1.362	1.362	1.359	1.363	1.363
C4–C5	1.470	1.474	1.463	1.493	1.491
C5–O2	1.421	1.417	1.418	1.425	1.436
O2–C6	1.413	1.426	1.405	1.417	1.426
C1–H1	1.071	1.071	1.073	1.078	1.078
C2–H2	1.067	1.070	1.068	1.080	1.080
C3–H3	1.077	1.079	1.068	1.080	1.081
C5–H4	1.101	1.104	1.100	1.099	1.097
C5–H5	1.088	1.091	1.084	1.091	1.090
C6–H6	1.098	1.098	1.098	1.090	1.090
C6–H7	1.098	1.098	1.094	1.099	1.095
C6–H8	1.120	1.117	1.121	1.096	1.096
C1–O1–C4	105.6	106.1	105.7	107.3	107.4
O1–C1–C2	110.8	110.1	110.7	110.5	110.3
C1–C2–C3	106.8	107.1	106.8	106.0	106.2
C2–C3–C4	106.1	106.5	106.1	106.9	106.9
C3–C4–C5	127.6	127.7	128.4	133.3	133.0
C4–C5–O2	110.6	109.2	110.1	115.0	114.5
C5–O2–C6	110.2	108.8	108.5	114.2	113.9
μ (D)				1.29	1.27

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Table S2. The bond lengths (unit: Å), bond angles (unit: degree), and dipole moment (μ) of methyl levulinate (MLA), optimized by using different methods such as PBE/DZP with supercell modeling and B3LYP/6-311+G* method with cluster modeling.

	PBE/DZP			B3LYP/6-311+G*	
	Vac.	Met-25	Met-40	Vac.	Met.
C1–C2	1.518	1.503	1.508	1.513	1.509
C2–C3	1.537	1.537	1.537	1.532	1.521
C3–C4	1.545	1.550	1.551	1.546	1.549
C4–C5	1.523	1.507	1.520	1.524	1.517
C5–O3	1.381	1.336	1.366	1.356	1.343
C6–O3	1.436	1.448	1.433	1.432	1.448
C2–O1	1.212	1.232	1.220	1.211	1.221
C5–O2	1.208	1.226	1.212	1.203	1.216
C1–H1	1.092	1.095	1.120	1.095	1.093
C1–H2	1.097	1.107	1.129	1.089	1.090
C1–H3	1.103	1.111	1.120	1.094	1.094
C3–H4	1.107	1.125	1.115	1.098	1.096
C3–H5	1.116	1.125	1.109	1.092	1.092
C4–H6	1.090	1.102	1.095	1.092	1.088
C4–H7	1.120	1.097	1.093	1.091	1.091
C6–H8	1.099	1.115	1.108	1.091	1.089
C6–H9	1.131	1.100	1.098	1.093	1.089
C6–H10	1.096	1.104	1.098	1.088	1.087
C1–C2–C3	116.8	118.9	115.5	118.0	117.8
O1–C2–C3	120.6	119.8	121.5	119.9	120.7
C2–C3–C4	112.1	112.8	113.7	116.4	114.9
C3–C4–C5	106.1	110.4	110.0	112.6	111.2
C4–C5–O3	121.1	119.3	117.1	119.3	120.4
O2–C5–O3	118.3	118.9	120.1	118.6	117.8
C5–O3–C6	123.0	120.3	118.7	122.3	122.2
μ (D)				5.68	6.51

Table S3. The bond lengths (unit: Å) and bond angles (unit: degree) of furan, DMM, MMF and MLA optimized by using PBE/6-311+G* method with cluster modeling.

Furan		DMM		MMF		MLA	
O−C1	1.404	C1−O1	1.471	O1–C1	1.401	C1–C2	1.556
C1−C2	1.385	C2−O1	1.449	O1–C4	1.418	C2–C3	1.576
C2−C3	1.464	C2−O2	1.449	C1–C2	1.386	C3–C4	1.590
C1−H1	1.096	C3−O2	1.471	C2–C3	1.459	C4–C5	1.566
C2−H2	1.099	C1−H3	1.118	C3–C4	1.391	C5–O3	1.404
C1−O−C1	106.3	C1−H4	1.109	C4–C5	1.522	C6–O3	1.484
C1−C2−C3	106.4	C1−H5	1.114	C5–O2	1.479	C2–O1	1.235
C1−C2−H2	126.4	C2−H1	1.115	O2–C6	1.464	C5–O2	1.227
O−C1−C2	110.4	C2−H2	1.115	C1–H1	1.097	C1–H1	1.115
O−C1−H1	115.1	C3−H6	1.118	C2–H2	1.099	C1–H2	1.110
		C3−H7	1.109	C3–H3	1.100	C1–H3	1.114
		C3−H8	1.114	C5–H4	1.118	C3–H4	1.118
		C1−O1−C2	114.2	C5–H5	1.111	C3–H5	1.111
		O1−C2−O2	114.9	C6–H6	1.119	C4–H6	1.111
		C3−O2−C2	114.2	C6–H7	1.110	C4–H7	1.111
		H1−C2−O2	111.0	C6–H8	1.116	C6–H8	1.111
		H2−C2−O2	104.5	C1–O1–C4	106.8	C6–H9	1.112
		H6−C3−O2	110.8	O1–C1–C2	110.5	C6–H10	1.107
		H7−C3−O2	105.8	C1–C2–C3	106.3	C1–C2–C3	118.2
		H8−C3−O2	111.6	C2–C3–C4	107.3	O1–C2–C3	120.0
		H3−C1−O1	110.8	C3–C4–C5	133.7	C2–C3–C4	116.9
		H4−C1−O1	105.8	C4–C5–O2	115.3	C3–C4–C5	113.2
		H5−C1−O1	111.6	C5–O2–C6	114.4	C4–C5–O3	120.0
						O2–C5–O3	117.7
						C5–O3–C6	122.6

Table S4. The bond lengths (unit: Å), bond angles (unit: degree), and dipole moment (μ) of methanol, optimized by using different methods such as PBE/DZP with supercell modeling and B3LYP/6-311+G* method with cluster modeling, in comparison with the experimental (Exp.) values.

	PBE/DZP			B3LYP/6-311+G*		
	Vac.	Met-25	Met-40	Vac.	Met.	Exp.[a]
C–O	1.410	1.437	1.423	1.422	1.432	1.425
C–H	1.085	1.109	1.104	1.095	1.093	1.094
O–H	0.970	0.991	0.979	0.964	0.966	0.945
C–O–H	114.1	109.5	107.1	109.5	108.8	108.5
H–C–H	104.6	110.0	107.6	108.5	108.9	108.6
μ (D)				1.97	2.01	1.70

[a] D. R. Lide, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 2005.

Table S5. The bond length (unit: Å), bond angle (unit: degree), and dipole moment (μ) of water molecule, optimized by using different methods such as PBE/DZP with supercell modeling and B3LYP/6-311+G* method with cluster modeling, in comparison with the experimental (Exp.) values.

	PBE/DZP			B3LYP/6-311+G*		
	Vac.	Met-25	Met-40	Vac.	Met.	Exp.[a]
O–H	0.969	0.996	0.969	0.964	0.965	0.957
H–O–H	105.3	106.3	104.8	107.0	106.3	104.5
μ (D)				2.35	2.37	1.85

[a] D. R. Lide, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 2005.

Table S6. Fukui indices for electrophilic attack (f^-), nucleophilic attack (f^+) and radical attack (f^0), and corresponding atomic charges in Mulliken (Mull.) and Hirshfeld (Hirsh.) approaches for reactant molecules.

	f^-		Atomic charge		f^+		Atomic charge		f^0	
	Mull.	Hirsh.	Mull.	Hirsh.	Mull.	Hirsh.	Mull.	Hirsh.	Mull.	Hirsh.
Furan										
O	0.050	0.073	-0.430	-0.1027	0.070	0.128	-0.442	-0.1228	0.060	0.100
C1	0.204	0.203	0.145	0.0269	0.226	0.180	0.102	-0.0114	0.215	0.192
C2	0.100	0.130	-0.134	-0.0675	0.082	0.120	-0.152	-0.0925	0.091	0.125
C3	0.100	0.129	-0.140	-0.0671	0.081	0.120	-0.158	-0.0921	0.091	0.125
C4	0.201	0.202	0.202	0.0273	0.225	0.181	0.159	-0.0110	0.213	0.192
H1	0.091	0.073	0.118	0.0766	0.084	0.079	0.101	0.0615	0.088	0.076
H2	0.082	0.058	0.109	0.0650	0.074	0.057	0.093	0.0535	0.078	0.057
H3	0.081	0.058	0.109	0.0653	0.074	0.057	0.094	0.0539	0.078	0.057
H4	0.091	0.073	0.121	0.0767	0.084	0.079	0.103	0.0616	0.087	0.076
DMM										
O1	0.208	0.196	-0.532	-0.1505	-0.022	0.041	-0.551	-0.1742	0.093	0.118
O2	0.215	0.202	-0.531	-0.1493	-0.019	0.040	-0.551	-0.1735	0.098	0.121
C1	-0.066	0.052	0.043	-0.0138	-0.160	0.082	0.066	-0.0272	-0.113	0.067
C2	-0.050	0.054	0.379	0.0880	-0.109	0.060	0.395	0.0766	-0.080	0.057
C3	-0.068	0.051	0.071	-0.0135	-0.157	0.085	0.094	-0.0270	-0.113	0.068
H1	0.112	0.063	0.075	0.0425	0.183	0.084	0.045	0.0278	0.148	0.074
H2	0.113	0.064	0.078	0.0423	0.179	0.082	0.049	0.0276	0.146	0.073
H3	0.095	0.055	0.070	0.0402	0.184	0.089	0.042	0.0258	0.139	0.072
H4	0.092	0.051	0.097	0.0501	0.152	0.077	0.072	0.0373	0.122	0.064
H5	0.083	0.054	0.091	0.0372	0.213	0.096	0.061	0.0222	0.148	0.075
H6	0.095	0.055	0.071	0.0401	0.191	0.092	0.042	0.0254	0.143	0.074
H7	0.090	0.050	0.097	0.0503	0.160	0.081	0.072	0.0372	0.125	0.065
H8	0.080	0.052	0.091	0.0375	0.206	0.094	0.062	0.0229	0.143	0.073
MMF										
O1	0.045	0.059	-0.439	-0.0866	0.065	0.105	-0.450	-0.1031	0.055	0.082
O2	0.039	0.048	-0.585	-0.1983	0.007	0.041	-0.589	-0.2072	0.023	0.045
C1	0.194	0.191	0.139	0.0303	0.203	0.162	0.099	-0.0050	0.198	0.176
C2	0.094	0.122	-0.141	-0.0673	0.063	0.101	-0.157	-0.0897	0.079	0.112
C3	0.112	0.121	-0.170	-0.0649	0.109	0.119	-0.192	-0.0889	0.111	0.120
C4	0.141	0.150	0.327	0.0664	0.141	0.124	0.299	0.0390	0.141	0.137
C5	0.002	0.029	0.076	0.0187	0.032	0.046	0.072	0.0112	0.017	0.037
C6	-0.011	0.012	0.061	-0.0250	-0.008	0.015	0.063	-0.0277	-0.010	0.014
H1	0.086	0.069	0.119	0.0772	0.077	0.072	0.102	0.0632	0.082	0.070
H2	0.077	0.055	0.109	0.0656	0.067	0.049	0.095	0.0552	0.072	0.052
H3	0.078	0.055	0.107	0.0656	0.073	0.057	0.092	0.0544	0.075	0.056
H4	0.047	0.028	0.106	0.0466	0.062	0.038	0.095	0.0400	0.055	0.033
H5	0.020	0.012	0.079	0.0395	0.024	0.014	0.074	0.0369	0.022	0.013
H6	0.020	0.013	0.099	0.0494	0.020	0.014	0.095	0.0467	0.020	0.014
H7	0.041	0.026	0.118	0.0582	0.051	0.033	0.109	0.0523	0.046	0.029
H8	0.015	0.010	0.095	0.0264	0.014	0.010	0.092	0.0244	0.014	0.010
Methanol										
C	-0.014	0.128	0.040	-0.0046	-0.026	0.121	0.044	-0.0295	-0.020	0.124
O	0.509	0.448	-0.538	-0.2318	-0.222	0.199	-0.567	-0.2966	0.143	0.324
H1	0.092	0.062	0.102	0.0522	0.071	0.052	0.085	0.0409	0.081	0.057
H2	0.157	0.118	0.096	0.0523	0.141	0.087	0.067	0.0319	0.149	0.102
H3	0.162	0.122	0.095	0.0516	0.129	0.082	0.066	0.0312	0.146	0.102
H4	0.094	0.123	0.305	0.1809	0.906	0.459	0.205	0.1226	0.500	0.291
Water										
O	0.697	0.639	-0.456	-0.2482	-0.242	0.287	-0.502	-0.3408	0.227	0.463
H1	0.152	0.181	0.278	0.1743	0.621	0.357	0.201	0.1206	0.387	0.269
H2	0.152	0.181	0.278	0.1743	0.621	0.356	0.201	0.1206	0.386	0.269

Table S7. DFT total energies of molecules calculated with PBE/DZP method using supercells in vacuum and methanol solvent environments (Met-25 and Met-40) and with B3LYP/6-311+G* method using clusters in vacuum and solvent environments without and with zero-point correction (ZPC) and thermal correction (TC). The energy differences of ΔE_1 and ΔE_2 are referred to the reaction energies for $C_4H_4O+C_3H_8O_2 \rightarrow C_6H_8O_2+CH_3OH$ and $C_6H_8O_2+H_2O \rightarrow C_6H_{10}O_3$, respectively.

		Furan (C_4H_4O)	DMM ($C_3H_8O_2$)	MET (CH_3OH)	MMF ($C_6H_8O_2$)	Water (H_2O)	MLA ($C_6H_{10}O_3$)	solvent	ΔE_1 (kJ/mol)	ΔE_2 (kJ/mol)
PBE/DZP (eV)										
Vacuum		-1116.511504	-1461.958595	-653.232490	-1925.012689	-466.607448	-2393.240475		21.716	-156.442
Solvent	Met-25	-17477.691119	-17821.743282	-17013.583295	-18286.135812	-16820.541130	-18755.880581	-16353.896127	-27.488	-299.279
	Met-40	-27281.240279	-27626.745245	-26817.649889	-28090.375946	-26630.528813	-28558.180946	-26163.836435	-3.892	-107.422
B3LYP/6-311+G* (Ha)										
DFT	Vacuum	-230.082826	-269.633227	-115.755316	-383.958677	-76.444553	-460.459392		5.412	-147.550
Energy	Solvent	-230.089110	-269.641666	-115.765187	-383.968136	-76.459057	-460.484793		-6.691	-151.328
	Vacuum	-229.939961	-269.399847	-115.649704	-383.689360	-76.399303	-460.138118		1.954	-129.930
	ZPC	0.069568	0.113422	0.051143	0.130852	0.021208	0.155788			
Corrected	TC	0.073297	0.119958	0.054469	0.138465	0.024042	0.165486			
Energy	Solvent	-229.946198	-269.409095	-115.660241	-383.699260	-76.414159	-460.163326		-11.055	-131.117
	ZPC	0.069604	0.112984	0.050752	0.130603	0.021032	0.155888			
	TC	0.073308	0.119587	0.054194	0.138273	0.023866	0.165579			

Table S8. Harmonic frequencies (unit: cm^{-1}) along the normal modes and symmetry in furan, calculated with B3LYP/6-311+G* in comparison with the previous calculation and experiment.

Mode	Symmetry	This work	MP2/cc-PVTZ[a]	Exp.[b]
ν_1	A_1	3282.840	3325.5	3169.4
ν_2	A_1	3248.905	3300.5	3139.84
ν_3	A_1	1509.751	1510.1	1490.55
ν_4	A_1	1412.854	1421.4	1384.51
ν_5	A_1	1165.745	1165.5	1140.2
ν_6	A_1	1083.103	1114.3	1067.22
ν_7	A_1	1012.600	1025.7	994.68
ν_8	A_1	887.224	878.8	870.43
ν_9	A_2	870.994	868.2	864
ν_{10}	A_2	721.437	726.4	721.5
ν_{11}	A_2	610.875	613.4	599.6
ν_{12}	B_1	834.438	838.7	837.59
ν_{13}	B_1	748.526	761.3	744.65
ν_{14}	B_1	617.769	631.7	602.85
ν_{15}	B_2	3277.013	3318.2	3160.75
ν_{16}	B_2	3238.049	3290.2	3130.15
ν_{17}	B_2	1591.085	1578.1	1557.5
ν_{18}	B_2	1289.070	1292.2	1266.7
ν_{19}	B_2	1195.650	1248.4	1180.97
ν_{20}	B_2	1058.382	1066.4	1042.5
ν_{21}	B_2	894.929	884.3	873

[a] A. Mellouki, J. Liévin, M. Herman, *Chem. Phys.* 271 (2001) 239–266.
[b] T. D. Klots, R. D. Chirico, W. V. Steele, *Spectrochim. Acta* 50A (1994) 765;
A. Mellouki, M. Herman, J. Demaison, B. Lemoine, L. Margulés, *J. Mol. Spectrosc.* 198 (1999) 348.

Table S9. Harmonic frequencies (ω) in DMM, MMF, and MLA, calculated with B3LYP/6-311+G* and cluster modeling.

DMM		MMF		MLA	
No	ω (cm^{-1})	No	ω (cm^{-1})	No	ω (cm^{-1})
1	0.000	1	0.000	1	0.000
2	0.000	2	0.000	2	0.000
3	0.000	3	0.000	3	0.000
4	0.000	4	0.000	4	0.000
5	0.000	5	0.000	5	0.000
6	0.000	6	0.000	6	0.000
7	94.205	7	50.226	7	21.768
8	133.190	8	99.164	8	24.743
9	155.671	9	145.460	9	84.012
10	206.434	10	226.186	10	107.993
11	316.883	11	299.517	11	156.128
12	452.720	12	366.383	12	170.809
13	598.685	13	457.516	13	188.433
14	924.065	14	612.326	14	257.781
15	934.942	15	638.106	15	330.276
16	1058.517	16	735.385	16	405.230
17	1131.719	17	760.523	17	479.269
18	1160.777	18	820.374	18	509.419
19	1181.595	19	871.908	19	547.203
20	1182.240	20	904.949	20	568.515
21	1217.462	21	908.881	21	716.716
22	1257.461	22	940.972	22	741.770
23	1348.805	23	982.163	23	749.888
24	1436.893	24	1037.267	24	893.932
25	1476.466	25	1103.949	25	920.375
26	1490.001	26	1116.163	26	995.035
27	1500.052	27	1171.472	27	1053.645
28	1501.322	28	1181.547	28	1057.322
29	1509.292	29	1199.193	29	1087.215
30	1520.121	30	1235.401	30	1135.515
31	1526.874	31	1257.313	31	1172.981
32	3000.824	32	1334.611	32	1202.804
33	3001.682	33	1400.850	33	1222.737
34	3017.193	34	1423.043	34	1252.582
35	3067.706	35	1482.268	35	1276.654
36	3070.206	36	1489.486	36	1358.111
37	3070.474	37	1503.510	37	1377.536
38	3132.693	38	1519.752	38	1398.649
39	3133.058	39	1523.303	39	1476.425
		40	1625.014	40	1485.095
		41	2990.414	41	1490.833
		42	3003.151	42	1495.132
		43	3050.396	43	1503.364
		44	3109.232	44	1519.731
		45	3124.986	45	1520.485
		46	3237.144	46	1779.531
		47	3248.507	47	1797.916
		48	3276.877	48	3023.669
				49	3036.004
				50	3041.946
				51	3076.493
				52	3095.420
				53	3096.795
				54	3114.919
				55	3120.575
				56	3143.340
				57	3154.650

Table S10. Cartesian coordinates of atoms in Furan, DMM, MMF and MLA, optimized with B3LYP/6-311+G* and cluster modeling (unit: Å).

	x	*y*	*z*
Furan			
C	0.0000	-1.0949	0.2920
C	0.0000	-0.7179	-1.0128
C	0.0000	0.7179	-1.0128
C	0.0000	1.0949	0.2920
O	0.0000	0.0000	1.1041
H	0.0000	-2.0484	0.7941
H	0.0000	-1.3740	-1.8701
H	0.0000	1.3740	-1.8701
H	0.0000	2.0484	0.7941
DMM			
C	0.5118	-1.8442	-0.2900
C	-0.9399	0.0015	0.0292
C	0.5496	1.8292	0.2679
O	-0.1653	-1.0009	0.6343
O	-0.1873	0.9944	-0.6177
H	-1.5395	0.4312	0.8397
H	-1.5882	-0.4205	-0.7471
H	-0.2018	-2.3440	-0.9578
H	1.0376	-2.5955	0.2983
H	1.2314	-1.2845	-0.8946
H	-0.1203	2.3379	0.9731
H	1.0521	2.5738	-0.3486
H	1.2939	1.2605	0.8329
MMF			
C	-0.6672	-2.0167	-0.4442
C	0.6688	-2.2540	-0.3733
C	1.2491	-1.0781	0.2031
C	0.2277	-0.2081	0.4402
C	0.1702	1.1766	0.9942
C	-0.6395	2.3641	-0.9114
O	-0.9572	-0.7801	0.0443
O	0.3962	2.2154	0.0447
H	-1.5094	-2.5930	-0.7913
H	1.1779	-3.1536	-0.6854
H	2.2937	-0.8993	0.4110
H	-0.7984	1.3277	1.4909
H	-1.6088	2.5361	-0.4238
H	-0.3837	3.2345	-1.5156
H	0.9580	1.3001	1.7385
H	-0.7246	1.4876	-1.5634
MLA			
C	-0.1751	0.3334	-1.1738
C	-1.1390	-0.6723	-0.5037
C	-0.4907	-1.8532	0.2257
C	0.6060	-2.6137	-0.4868
C	0.7701	0.9917	-0.1752
C	-0.8176	2.8276	0.0964
H	-0.7624	1.0697	-1.7256
H	0.4572	-0.1800	-1.8992
H	-1.7778	-1.0952	-1.2898
H	-1.8021	-0.1811	0.2112
H	0.3683	-2.7760	-1.5429
H	0.7688	-3.5707	0.0075
H	1.5310	-2.0307	-0.4449
H	-1.6902	2.1870	0.2360
H	-0.7936	3.2143	-0.9252
H	-0.8767	3.6630	0.7907
O	-0.8832	-2.1710	1.3260
O	1.8274	0.5001	0.1225
O	0.4013	2.1505	0.4236

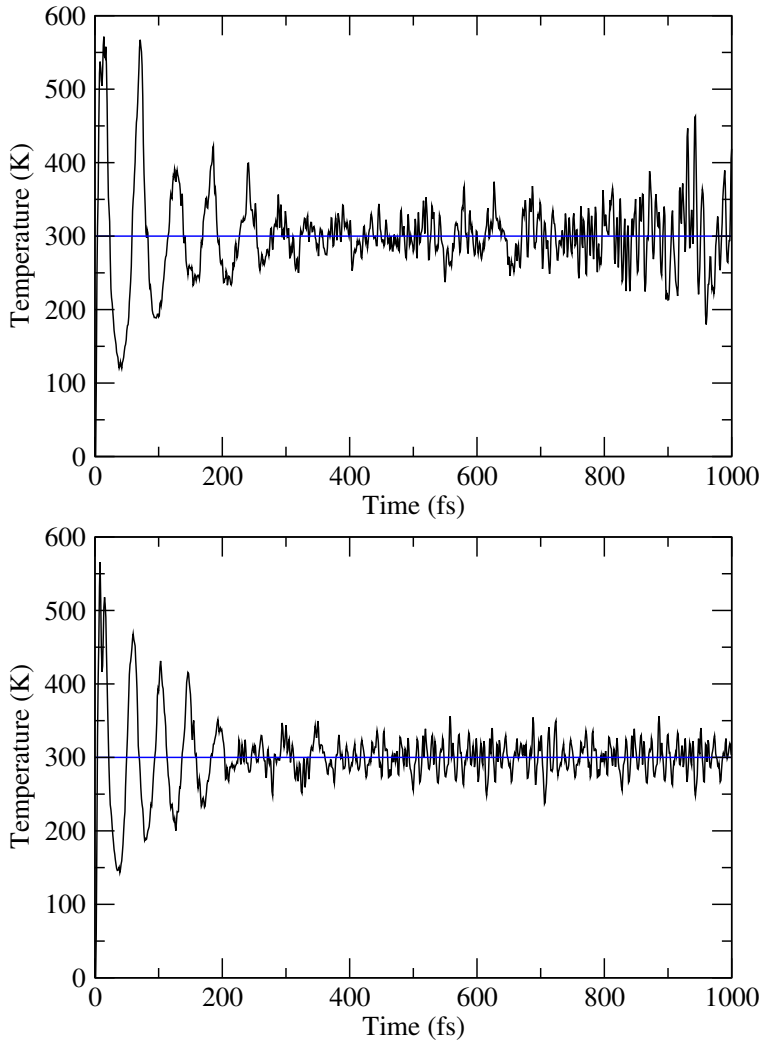

Fig. S1 Temperature fluctuation during *NVT* equilibration of 1 ps in AIMD for 25 methanol plus one furan molecules included in the supercell with a lattice constant of 12 Å (top panel) and for 40 methanol plus one furan molecules included in the supercell with a lattice constant of 14 Å (bottom panel).

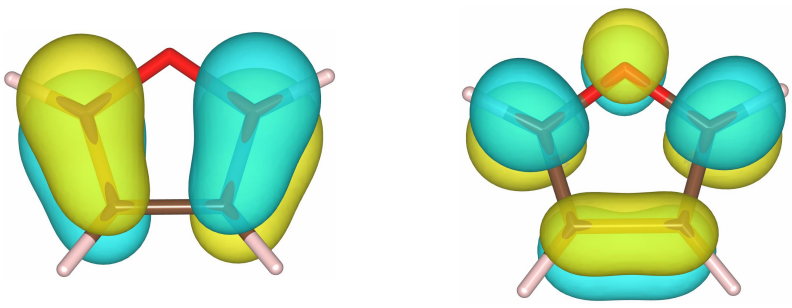

Fig. S2 HOMO and LUMO of furan.

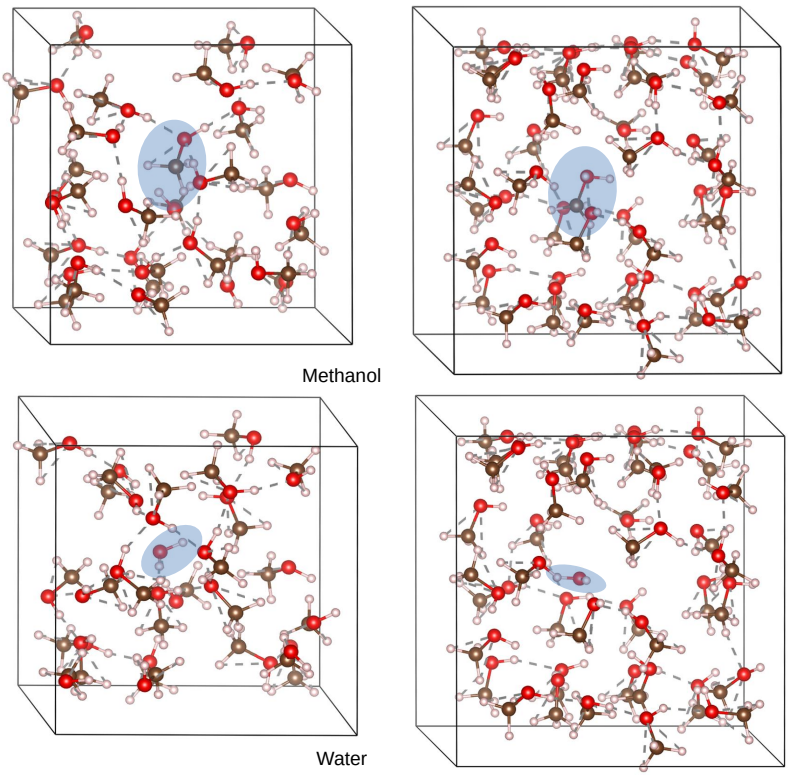

Fig. S3 Configurations of 26 and 41 methanol molecules (top panel) and 25 and 40 methanol plus one water molecules (bottom panel) included in the supercells with lattice constant of 12 and 14 Å, respectively.

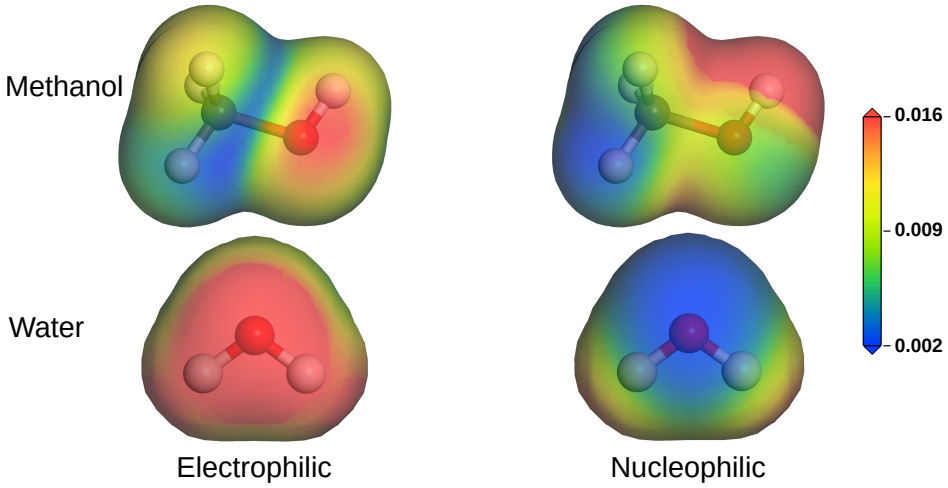

Fig. S4 Isodensity surface view of Fukui functions depicting the chemical reactivity to electrophilic and nucleophilic attack for methanol and water molecules, mapped on isosurface of total electron density at the value of $0.2|e|$ Å^{-3}.

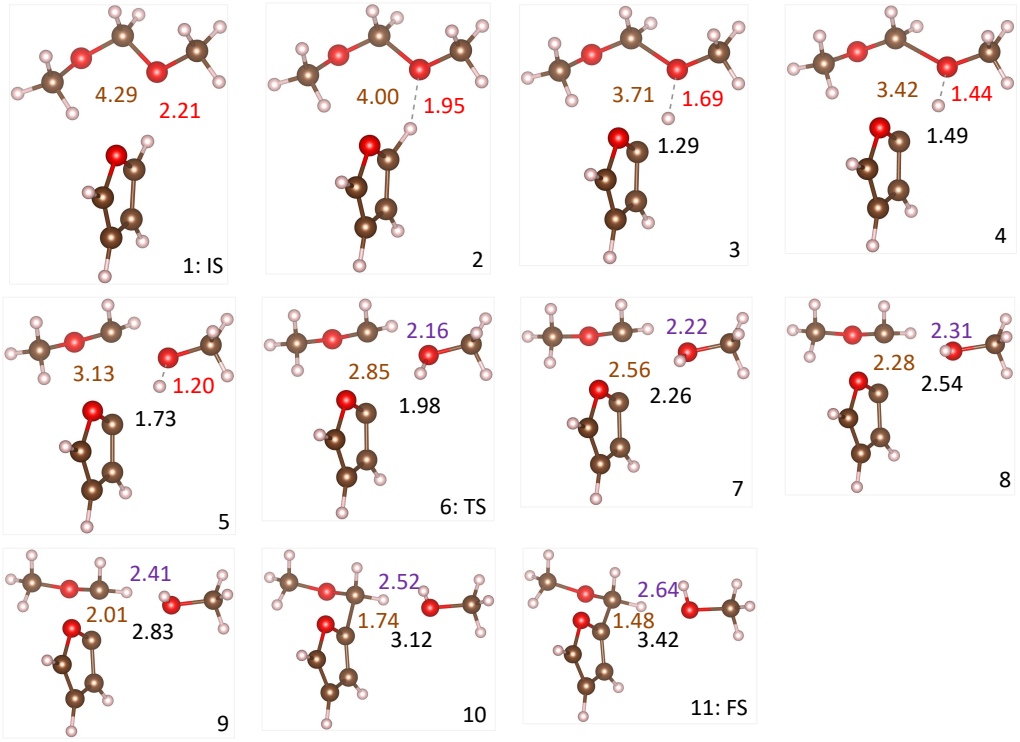

Fig. S5 Geometries of reactant or product molecules during NEB run for reaction of furan + DMM to MMF + methanol, implemented with PBE/DZP and 30 Å supercell in vacuum. IS, TS and FS mean the initial state, transition state and final state, respectively.

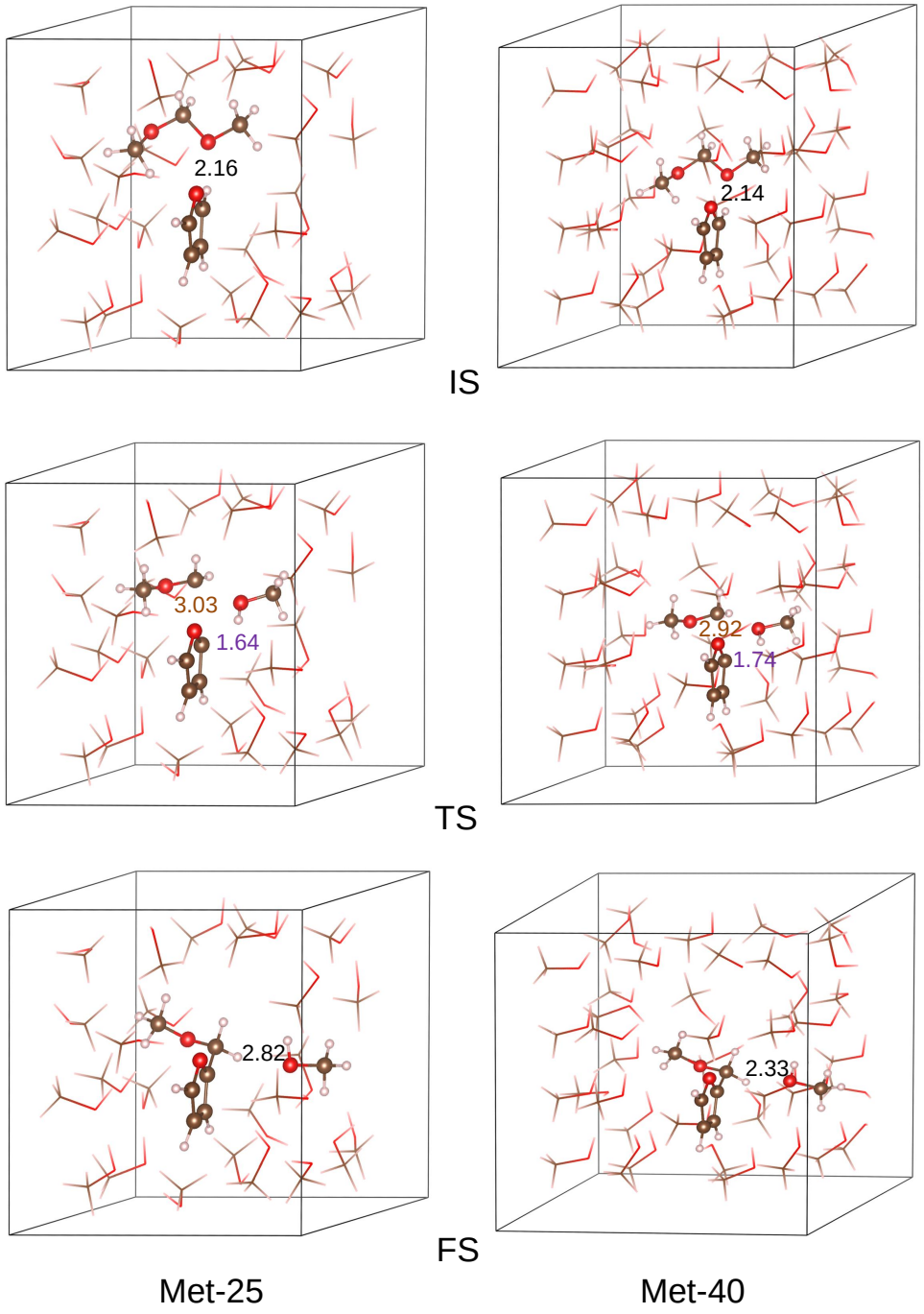

Fig. S6 Geometries of reactant or product molecules during NEB run for reaction of furan + DMM to MMF + methanol, implemented with PBE/DZP method and Met-25 and Met-40 supercell models. IS, TS and FS mean the initial state, transition state and final state, respectively.

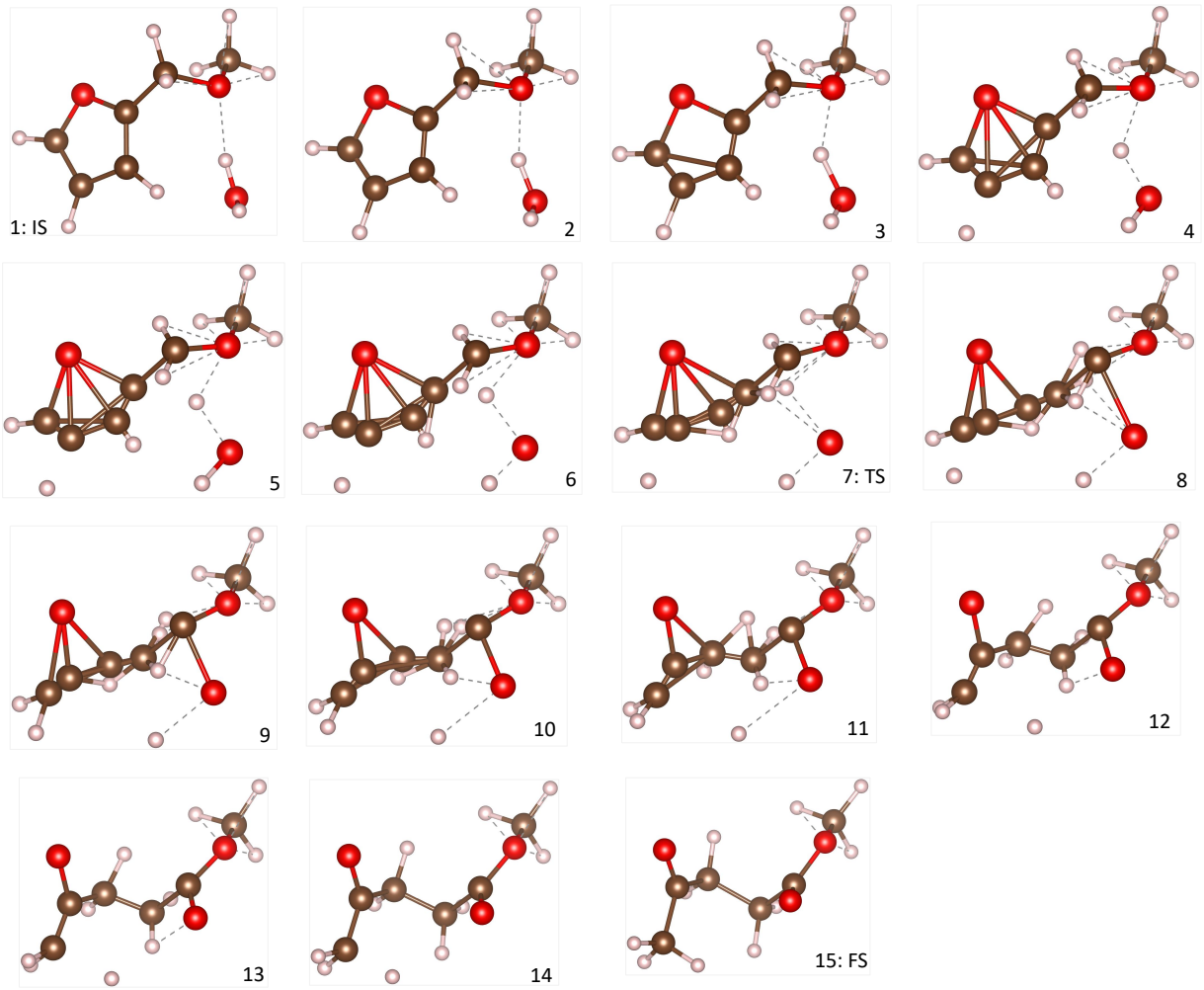

Fig. S7 Geometries of reactant or product molecules during NEB run for reaction of MMF + water to MLA, implemented with PBE/DZP and 30 Å supercell in vacuum. IS, TS and FS mean the initial state, transition state and final state, respectively.

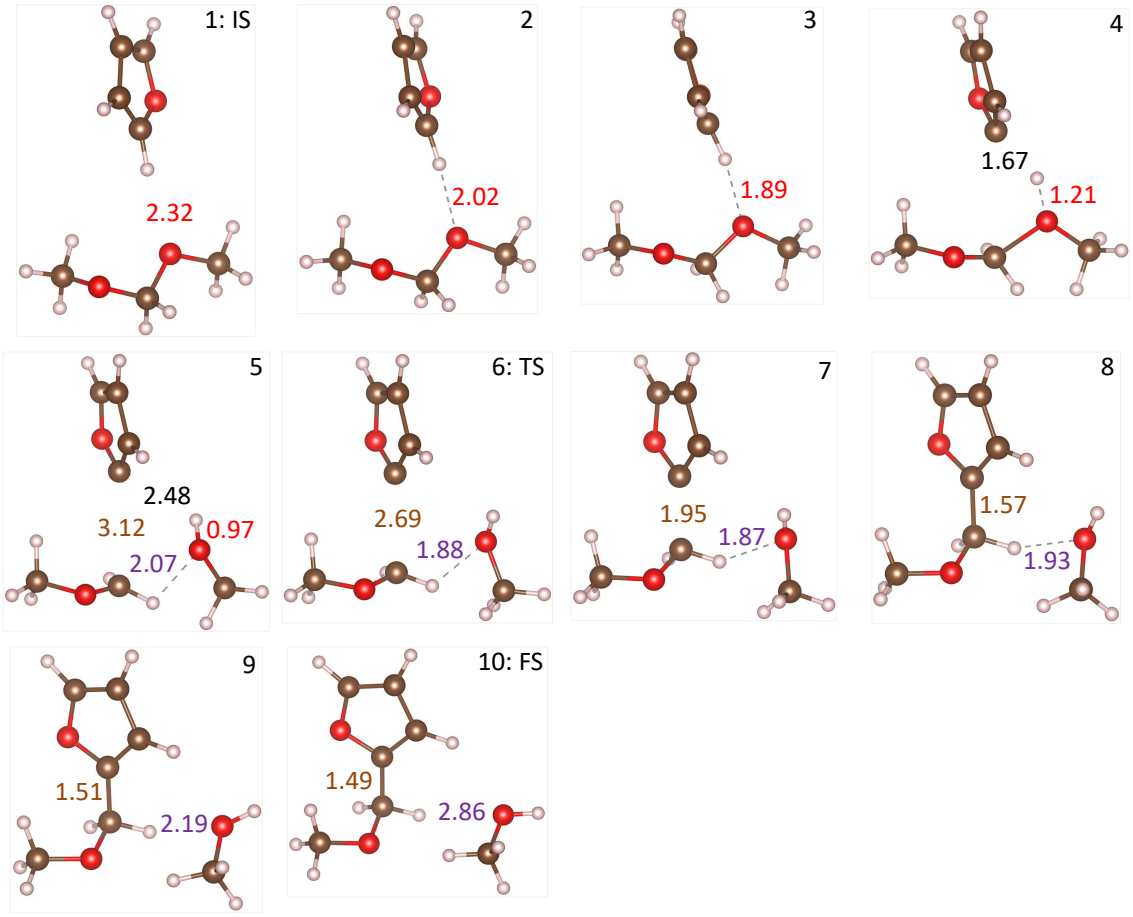

Fig. S8 Geometries of reactant or product molecules during NEB run for reaction of furan + DMM to MMF + methanol, implemented with B3LYP/6-311+G* cluster in vacuum. IS, TS and FS mean the initial state, transition state and final state, respectively.

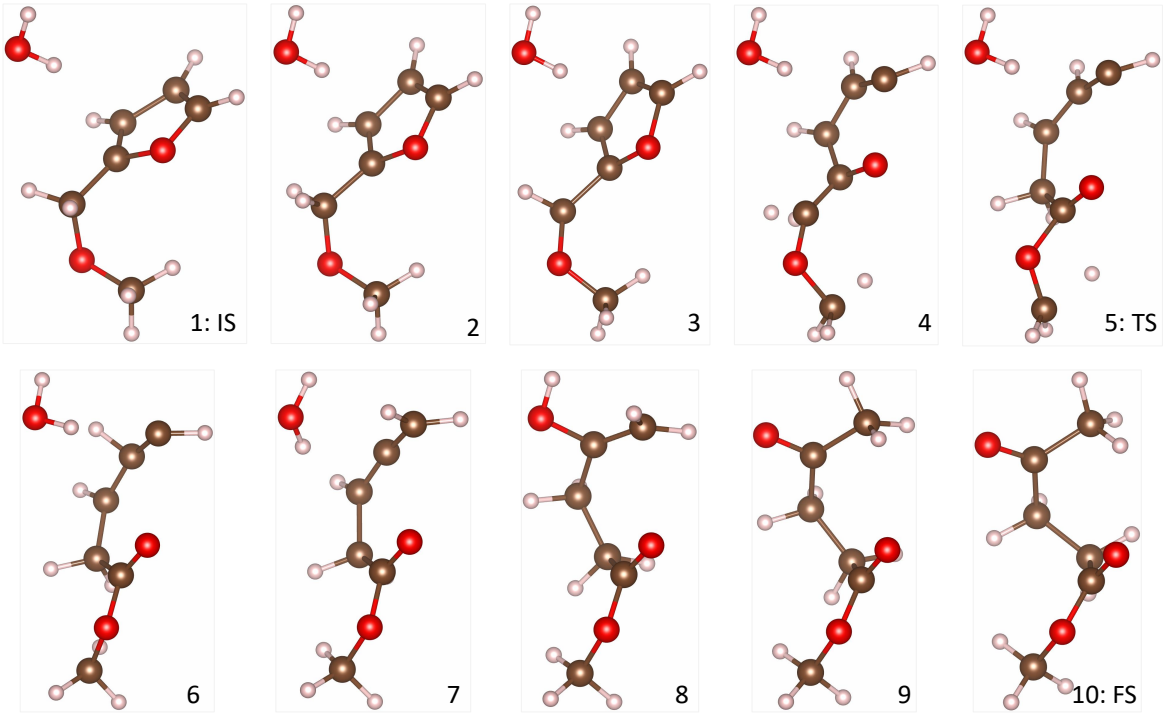

Fig. S9 Geometries of reactant or product molecules during NEB run for reaction of MMF + water to MLA, implemented with B3LYP/6-311+G* cluster in vacuum. IS, TS and FS mean the initial state, transition state and final state, respectively.

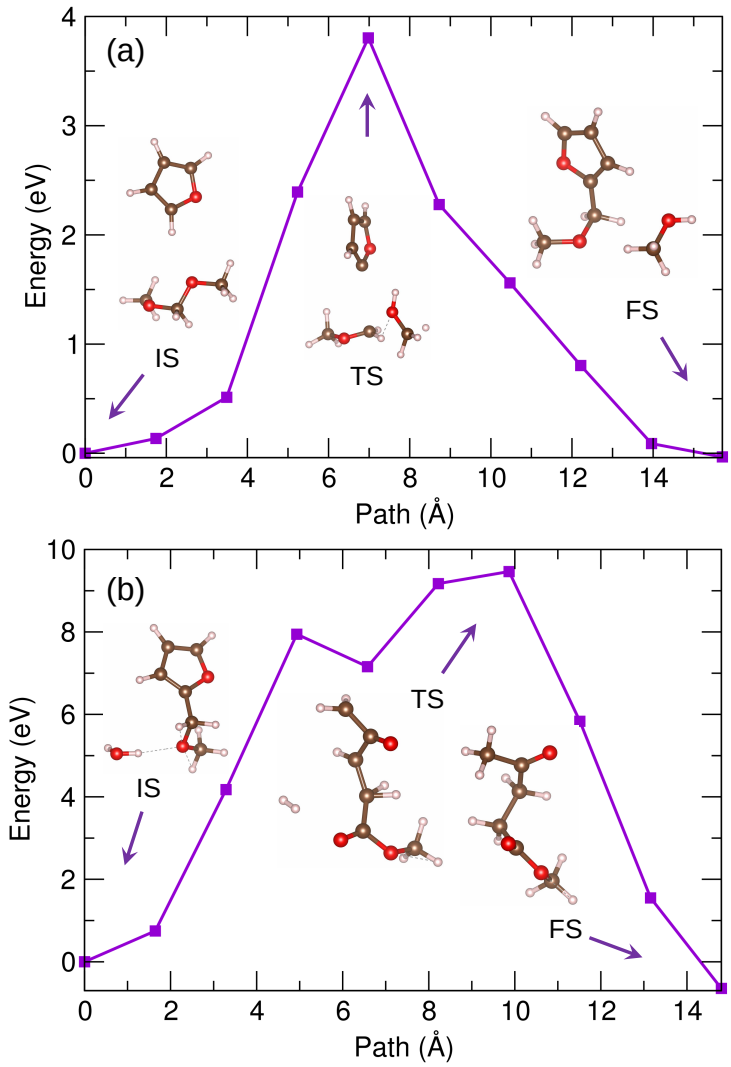

Fig. S10 Energy profile for reactions of (a) furan + DMM to MMF + methanol and (b) MMF + water to MLA calculated with PBE/6-311+G* cluster models in vacuum environment, together with geometries of molecules corresponding to IS, TS and FS.

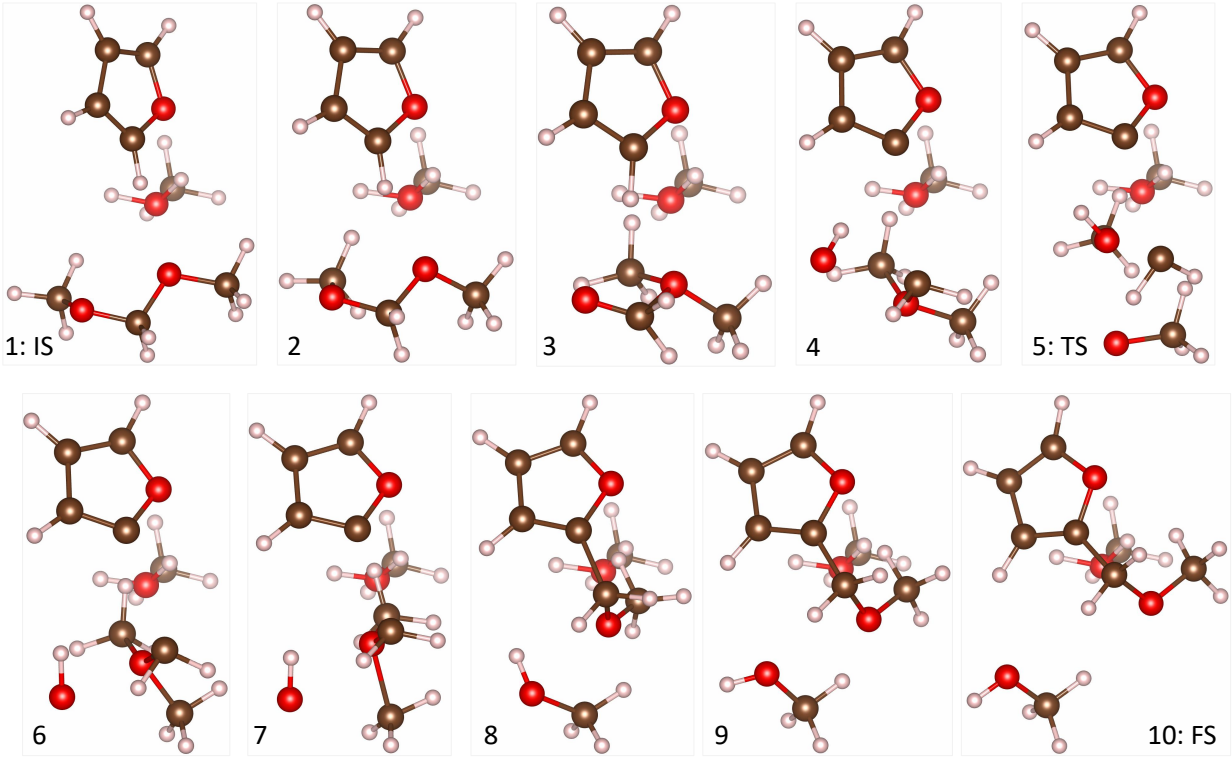

Fig. S11 Geometries of reactant or product molecules during NEB run for reaction of furan + DMM to MMF + methanol with a protonated methanol molecule, implemented with B3LYP/6-311+G* cluster in vacuum. IS, TS and FS mean the initial state, transition state and final state, respectively.

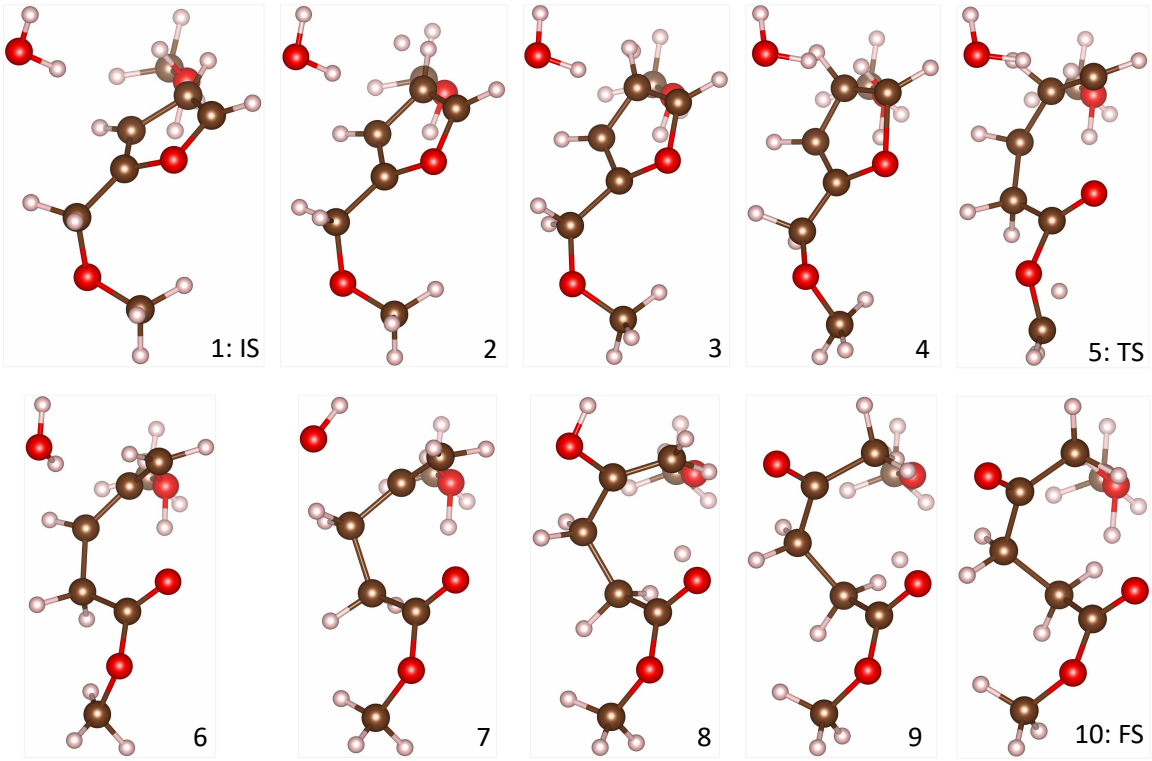

Fig. S12 Geometries of reactant or product molecules during NEB run for reaction of MMF + water to MLA with a protonated methanol molecule, implemented with B3LYP/6-311+G* cluster in vacuum. IS, TS and FS mean the initial state, transition state and final state, respectively.