Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Theoretical Comparison of Removing Formate from Fructose with Methylglucoside into Levulinate Catalyzed by Brønsted Acid in Methanol Solution

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Catalogue

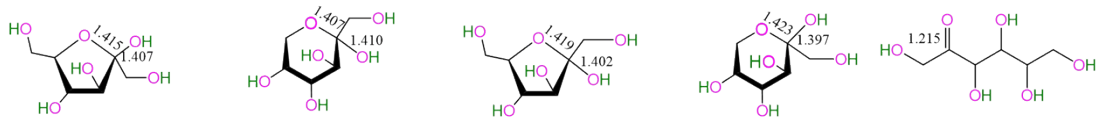


Figure S1. The geometric structures and the relative Gibbs free energy (ΔG, kJ mol^{-1}) relative to *β*-D-fructofuranoses for five configurations of fructose at PBE0/6-311++G(d,p) level in methanol solution under ambient temperature and pressure (453.15 K and 25 atm). For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

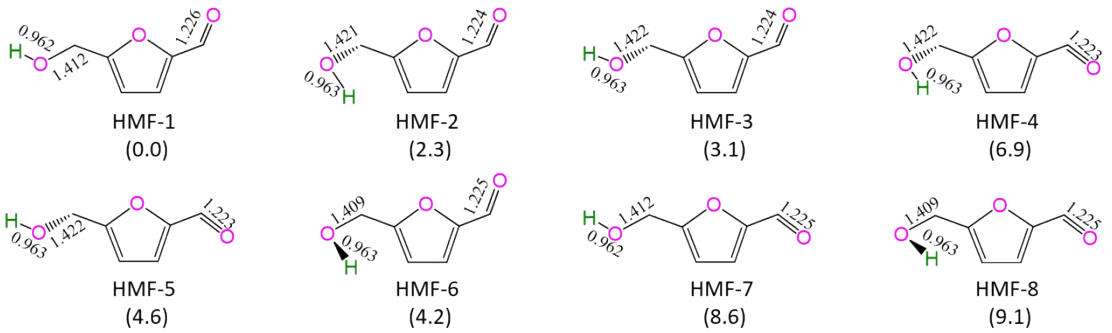
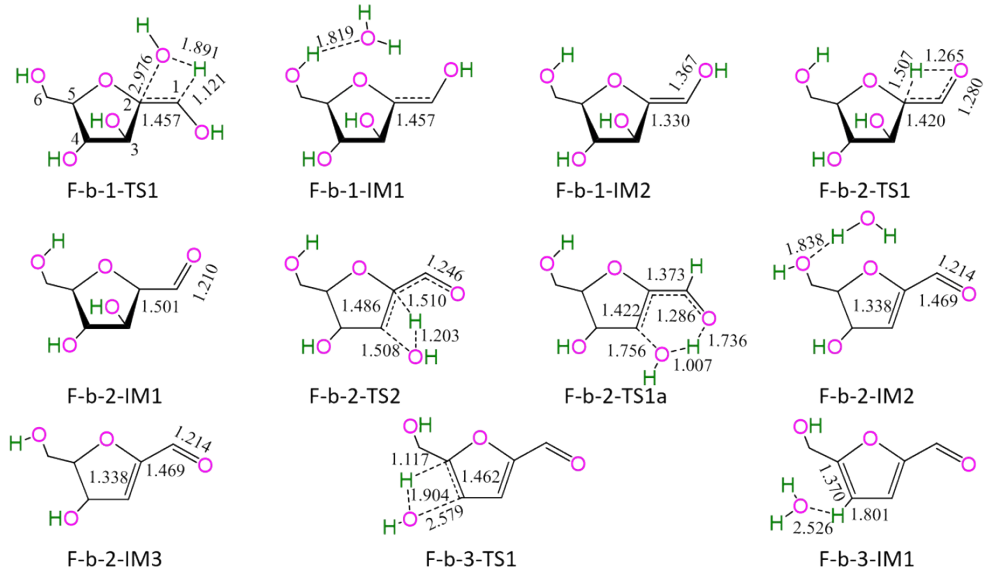


Figure S2. The geometric structures and the relative Gibbs free energy (Δ*G*, kJ mol^{-1}) relative to HMF-1 for five tautomers of HMF at PBE0/6-311++G(d,p) level in methanol solution under ambient temperature and pressure (453.15 K and 25 atm). For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



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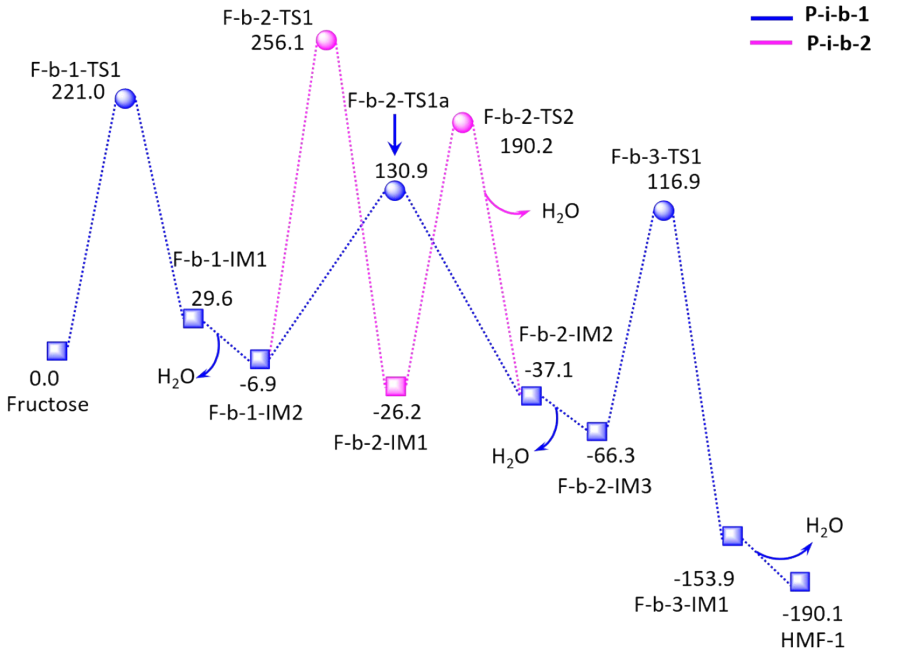
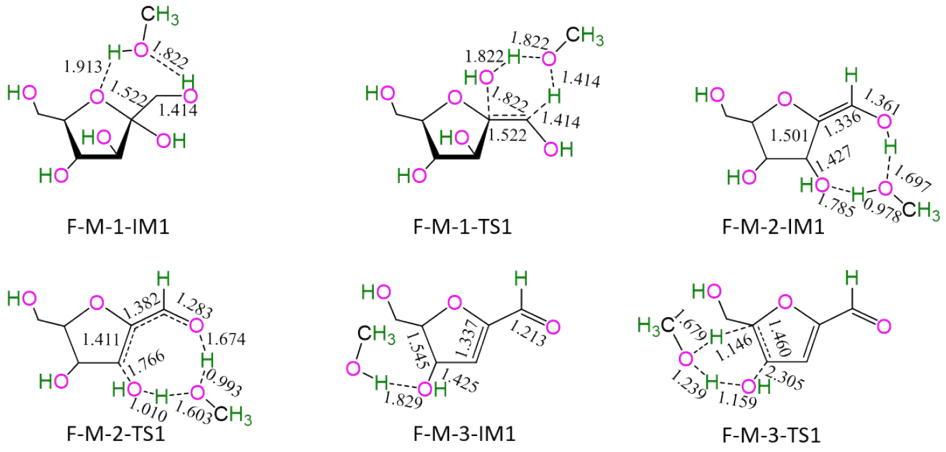


(b)

Figure S3. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the dehydration of fructose to HMF in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



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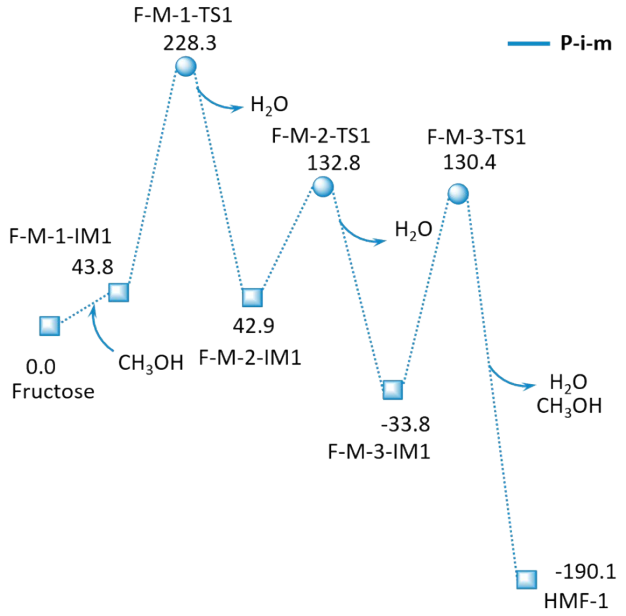
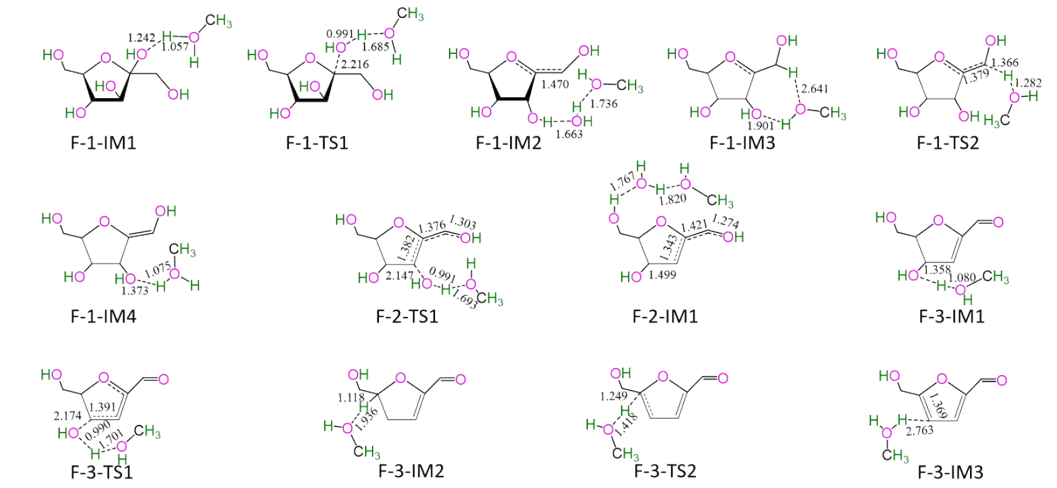


(b)

Figure S4. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the dehydration of fructose to HMF in the presence of explicit CH_3OH in methanol solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



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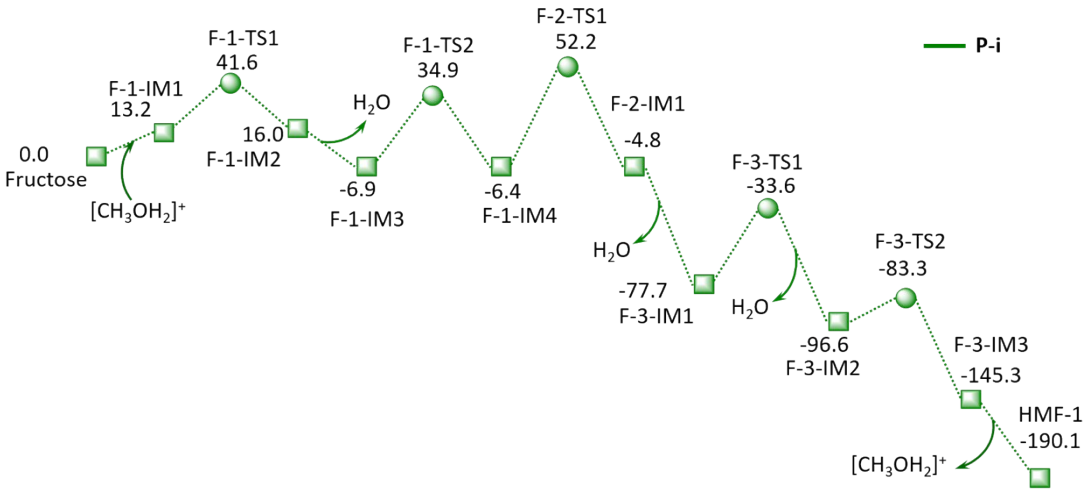
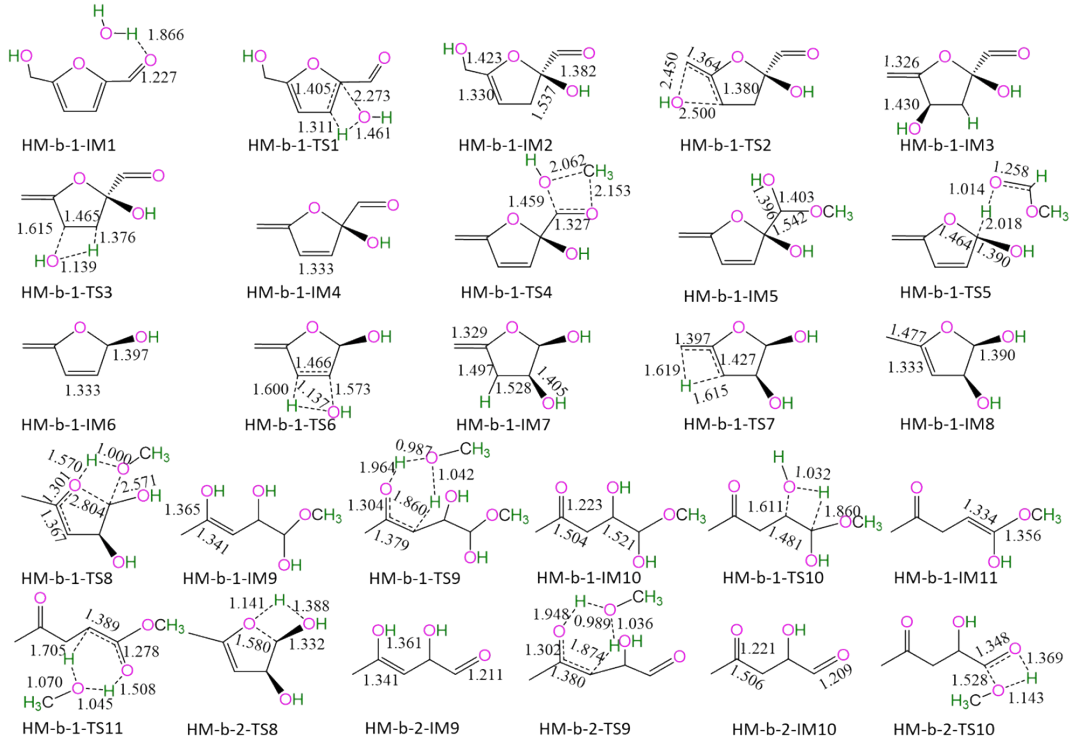
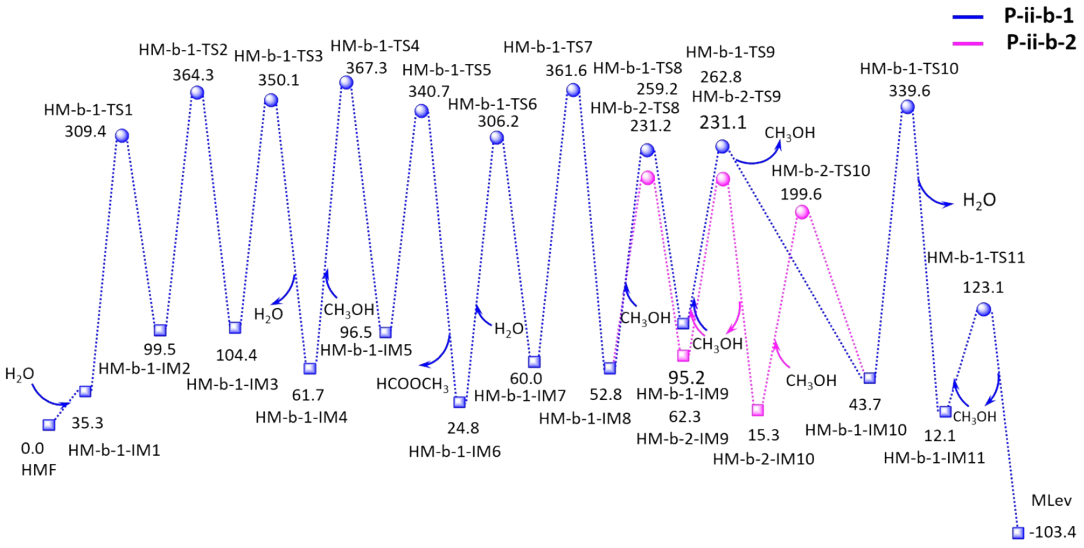


(b)

Figure S5. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the dehydration of fructose to HMF catalyzed by $[CH_3OH_2]^+$. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

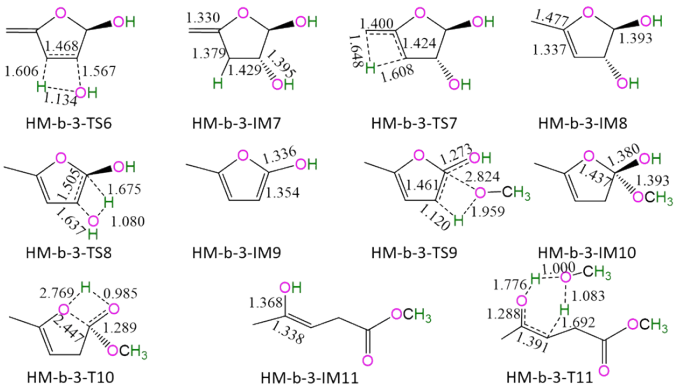


(a)

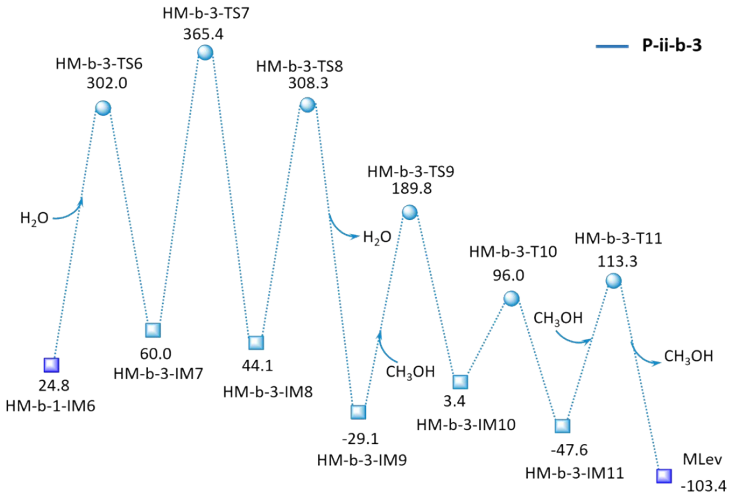


(b)

Figure S6. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the first and second conversion pathway of HMF with methanol to MF and MLev in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

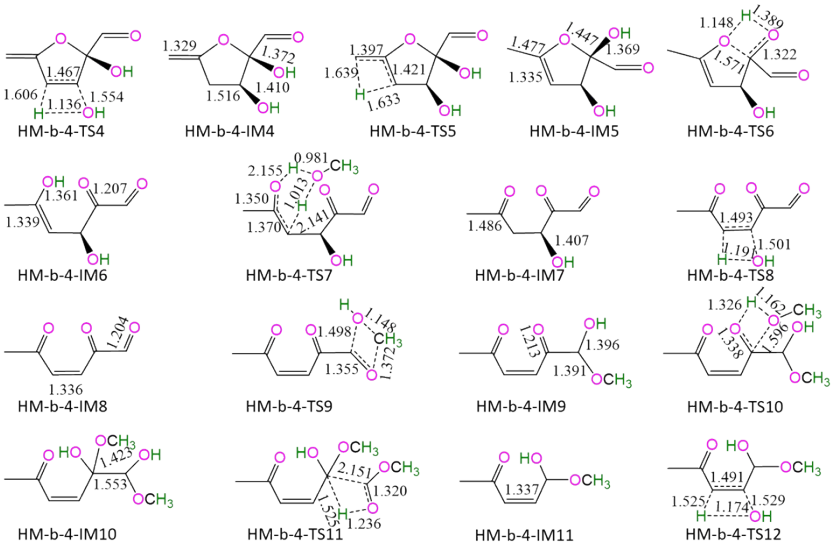


(a)



(b)

Figure S7. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the third conversion pathway of HMF with methanol to MF and MLev in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



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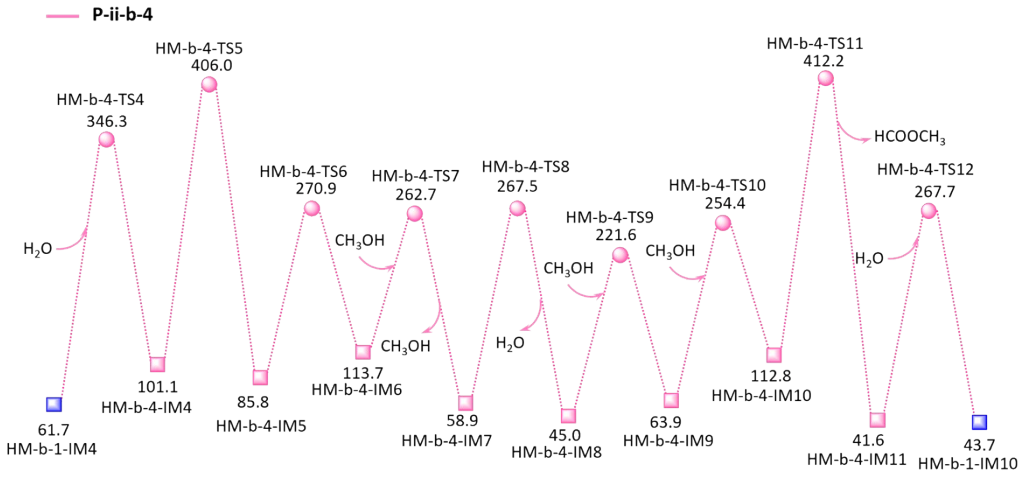
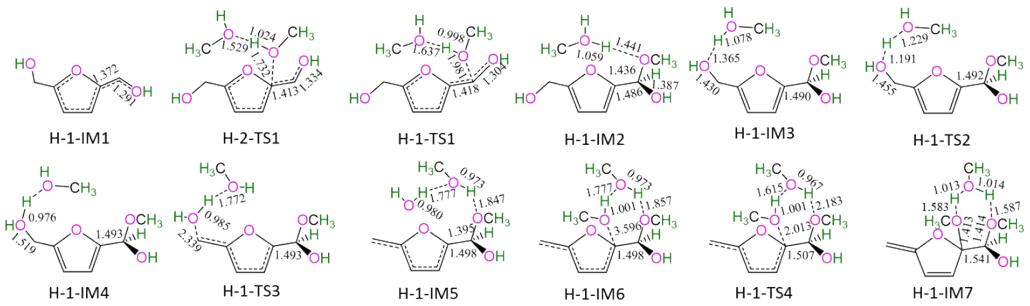


(b)

Figure S8. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the forth conversion pathway of HMF with methanol to MF and MLev in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



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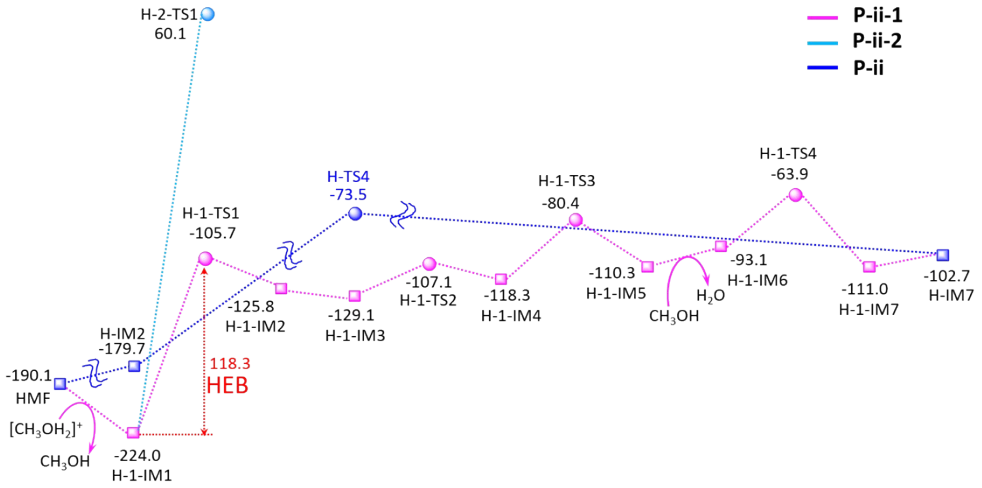


(b)

Figure S9. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the conversion of HMF through protonation of the carbonyl oxygen with CH_3OH to both MLev and MF catalyzed by $[CH_3OH_2]^+$ in methanol solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

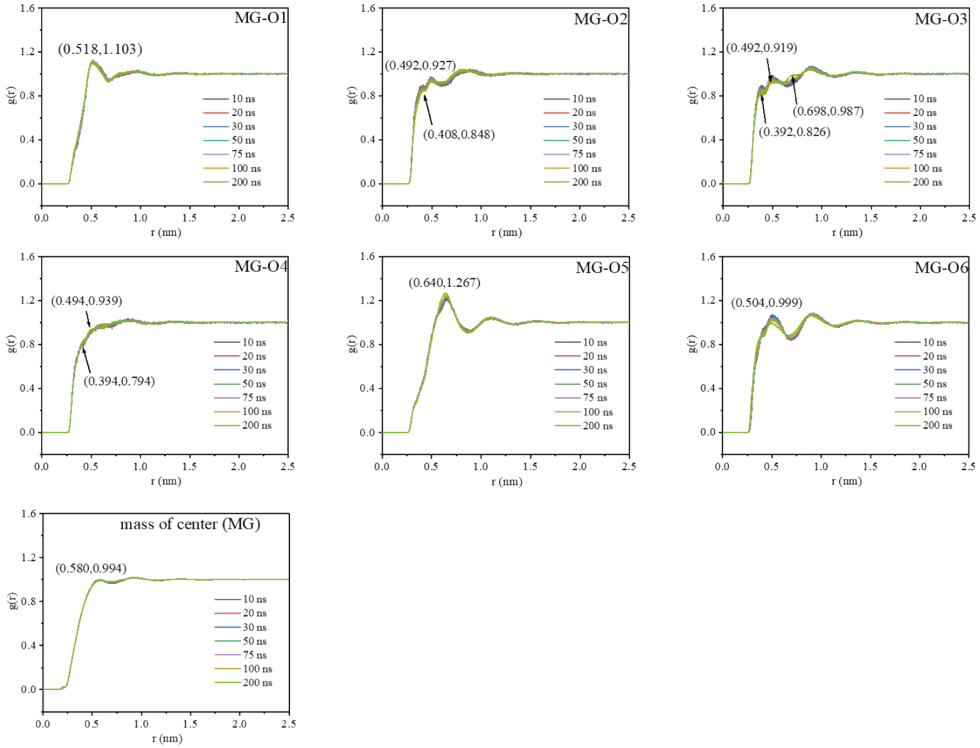
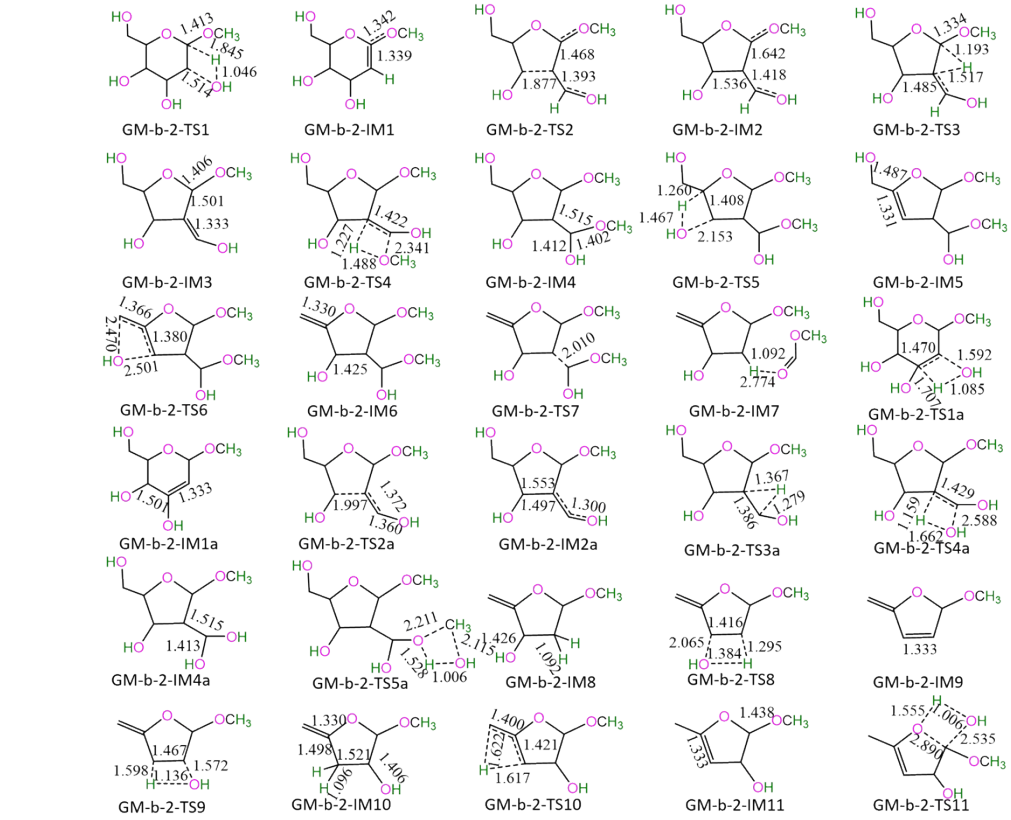
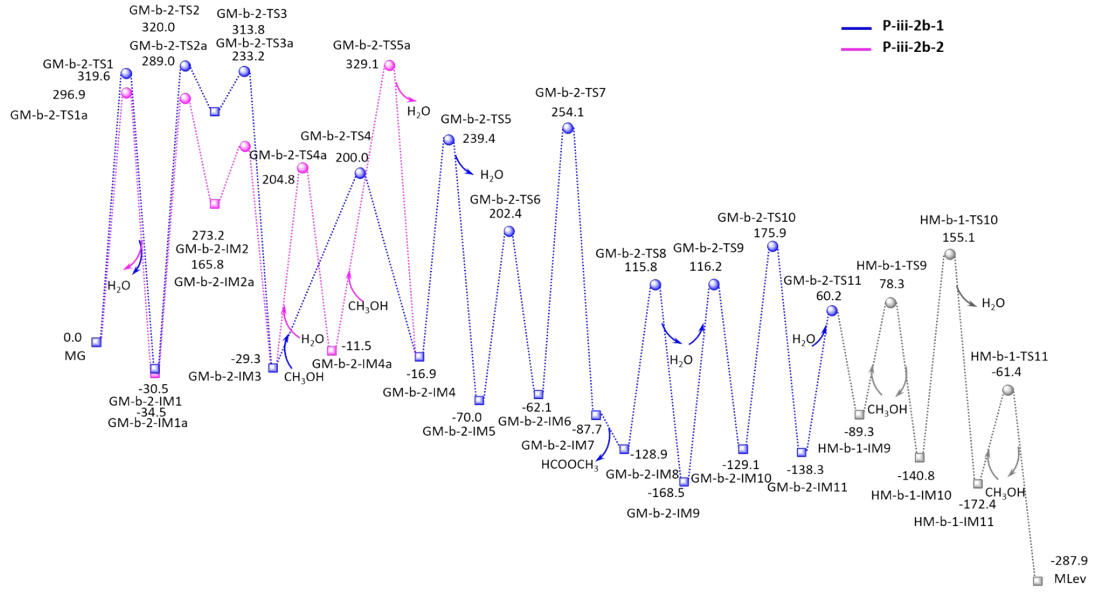


Figure S10. The radial distribution functions (RDF) of solvent molecules with respect to six-type oxygen of methyl glucoside, i.e., (a) the –O1CH_3 group, (b) the –O2H group, (c) the –O3H group, (d) the –O4H group, (e) the –O5 group, (f) the –O6H group, (g) the center of MG mass.

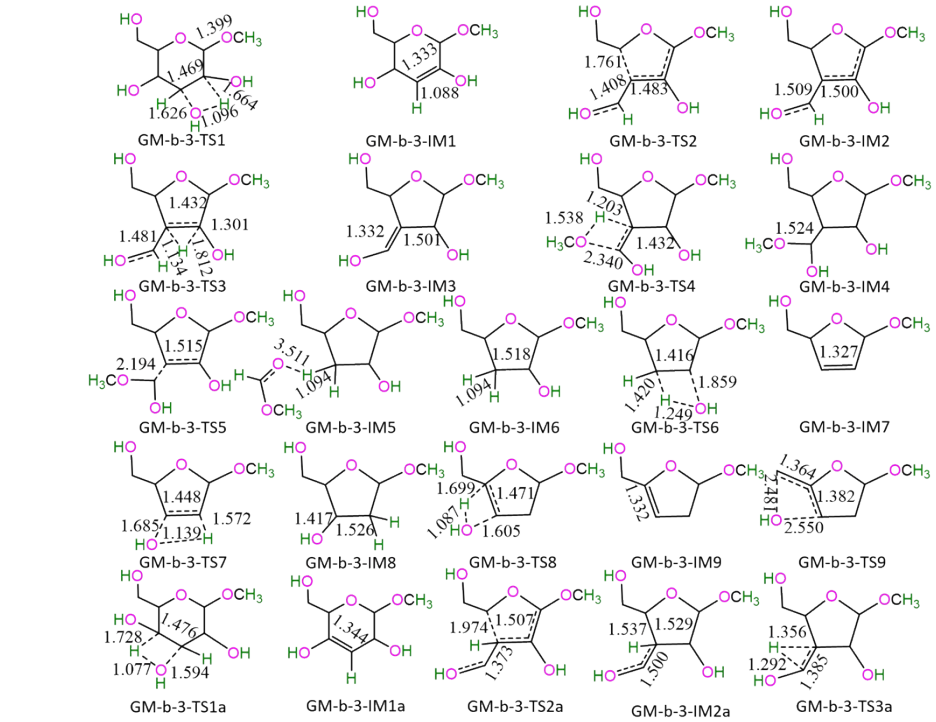


(a)

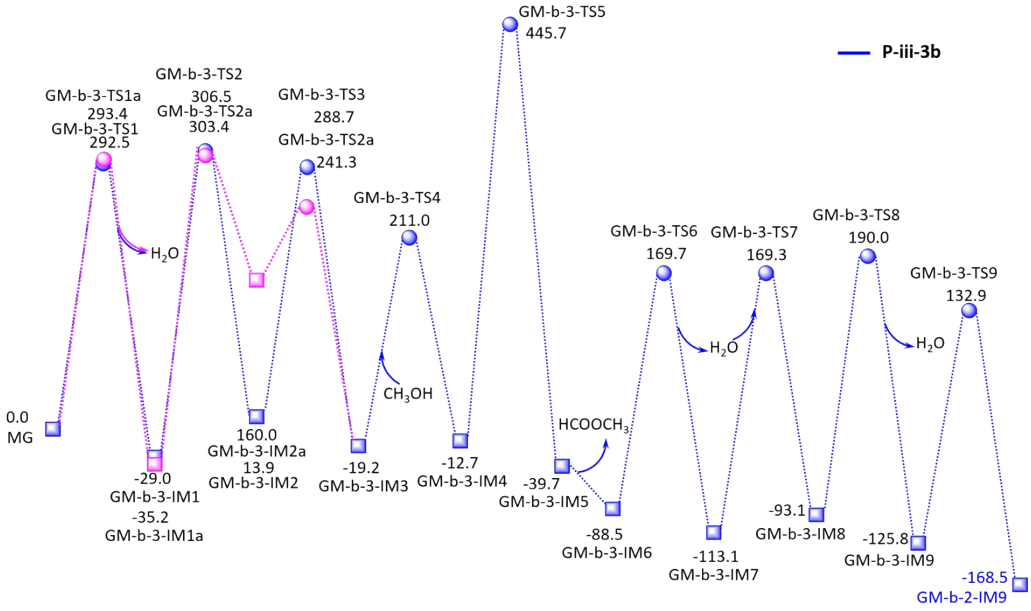


(b)

Figure S11. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the dehydration of MG through –O2H group with methanol to MF and MLev in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

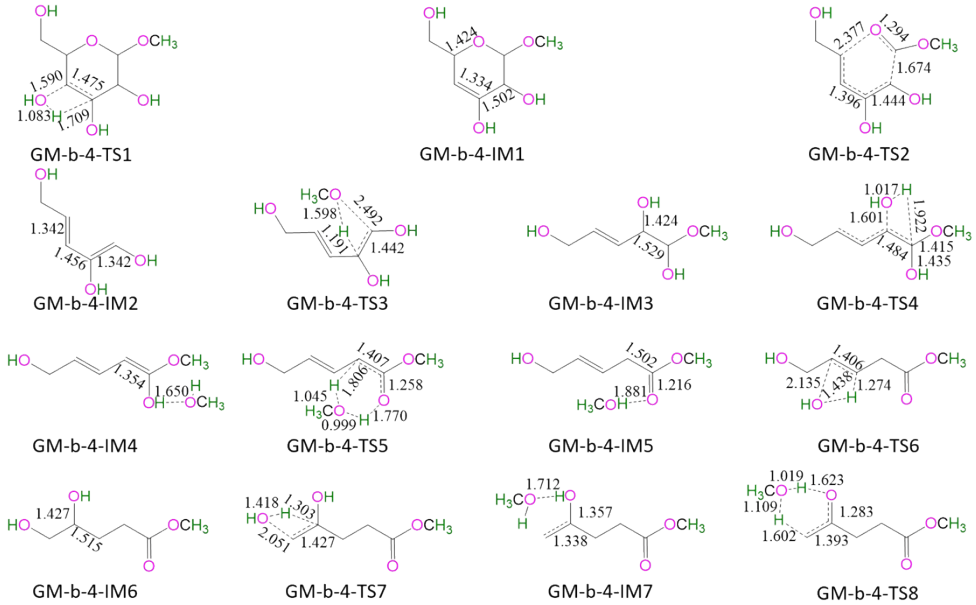


(a)

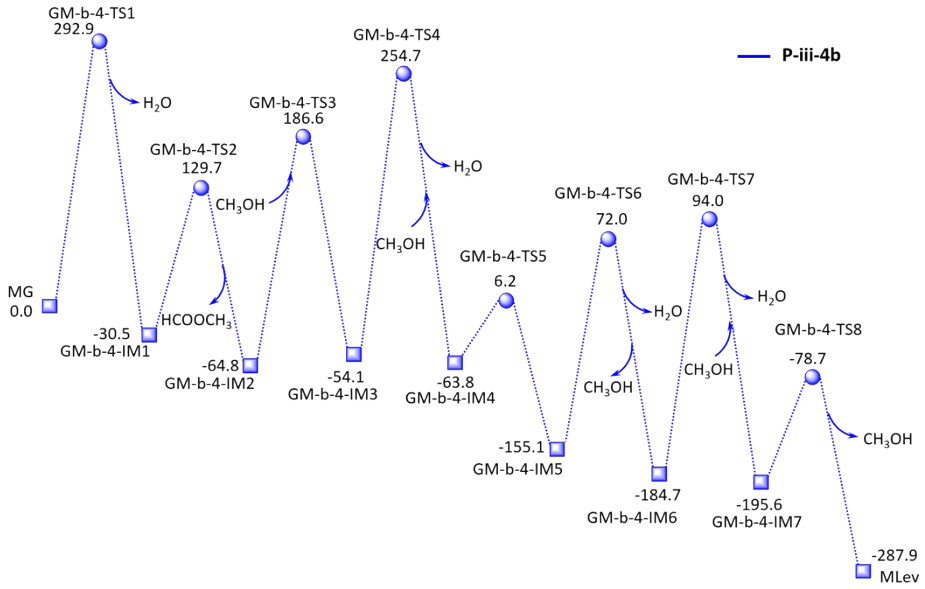


(b)

Figure S12. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (Gr, kJ mol^{-1}) relative to the reactants for the dehydration of MG through −O3H group with methanol to MF and MLev in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



(a)



(b)

Figure S13. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (Gr, kJ mol^{-1}) relative to the reactants for the dehydration of MG through −O4H group with methanol to MF and MLev in the absence of catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

NOTES: Evaluation of rate constants:

The rate constants *k*(T) were evaluated according to conventional transition state theory *k'*(T), including the tunneling correction *κ*(T) based on Wigner's formulation as follows:[1]

$$k^{'} = \frac{k_B T}{hc^0} \bullet e^{\frac{-\Delta G^{\neq}}{RT}}$$

$$\kappa\ (T)\ = 1 + \frac{1}{24}\left|\frac{w^{\neq} h}{k_B T}\right|^2$$

$$k = \kappa\ (T)\ \times k^{'}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$k = A \bullet e^{\frac{-E_a}{RT}}$$

where k_B is Boltzmann's constant, T is the absolute temperature, *h* is Planck's constant, c^0 is the standard concentration (1 mol dm^{-3}), $\Delta G^{\neq}$ is the activation Gibbs free energy barrier and $\omega^{\neq}$ is the imaginary frequency of the TS.

References:

1. E. Wigner, *J. Chem. Phys*., 1937, **5**, 720–723.

The equations for calculating TOF according to the energetic span model:

The efficiency of catalyst can be determined by the turnover frequency (TOF) of the catalytic cycle. Based on the transition state theory (TST), the TOF can be calculated by Eqs. (i) and (ii) proposed by Kozuch et al., in which δE (the energetic span) is defined as the energy difference between the summit and trough of the catalytic cycle.[2-7]

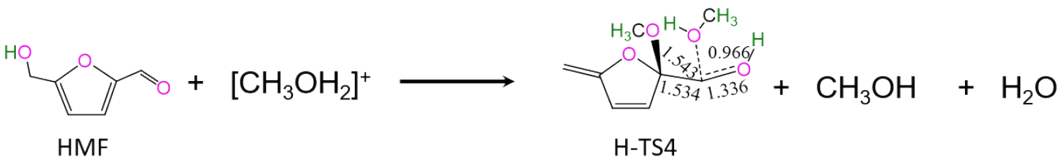
$$\mathrm{TOF} = \frac{k_\mathrm{B}T}{h} e^{-\delta E/RT}$$

$$\delta E = \begin{pmatrix} G_{\mathrm{DTS}} - G_{\mathrm{DI}} & \text{if DTS appears after DI} \\ G_{\mathrm{DTS}} - G_{\mathrm{DI}} + \Delta G_r & \text{if DTS appears before DI} \end{pmatrix}$$

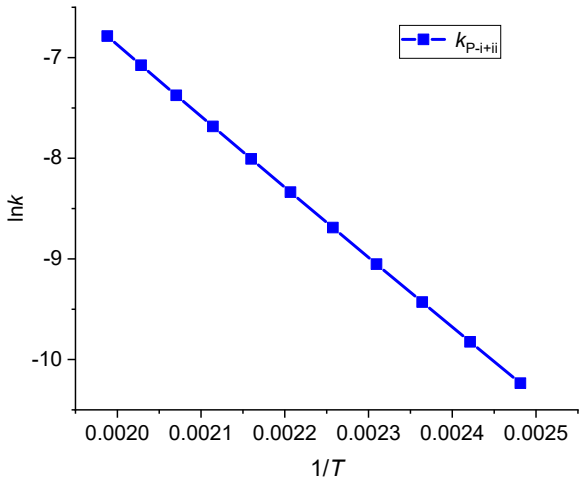
where k_B is the Boltzmann constant, T is the absolute temperature, and h is the Planck constant. G_{DTS} and G_{DI} are the Gibbs free energies of the determining transition state (DTS) and the determining intermediate (DI), and ΔG_r is the global free energy of the whole cycle.

References:

2. C. Amatore and A. Jutand, *J. Organomet. Chem.*, 1999, **576**, 254-278.
3. S. Kozuch and S. Shaik, *J. Am. Chem. Soc*., 2006, **128**, 3355-3365.
4. S. Kozuch and S. Shaik, *J. Phys. Chem. A*, 2008, **112**, 6032-6041.
5. S. Kozuch and S. Shaik, *Acc. Chem. Res.*, 2011, **44**, 101-110.
6. A. Uhe, S. Kozuch and S. Shaik, *J. Comput. Chem.*, 2011, **32**, 978-985.
7. S. Kozuch, *ACS Catal.*, 2015, **5**, 5242-5255.

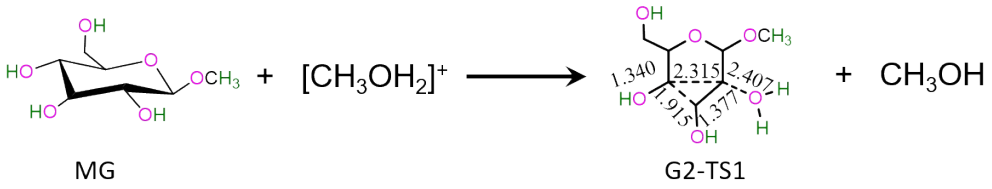


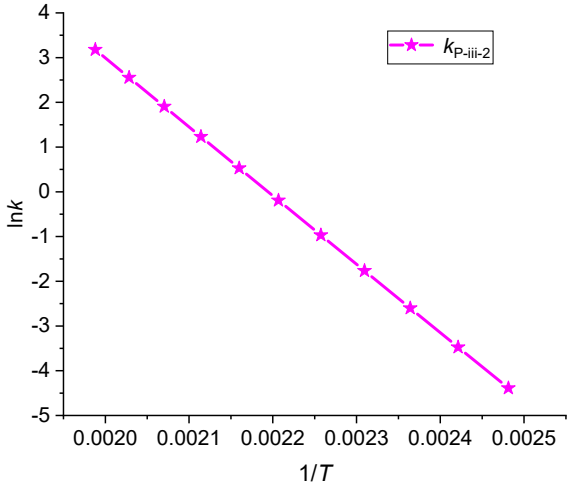
HMF H-TS4



$$k_{\text{P-i+ii}} = 1.21\times10^{3}\exp(-58113/RT)$$

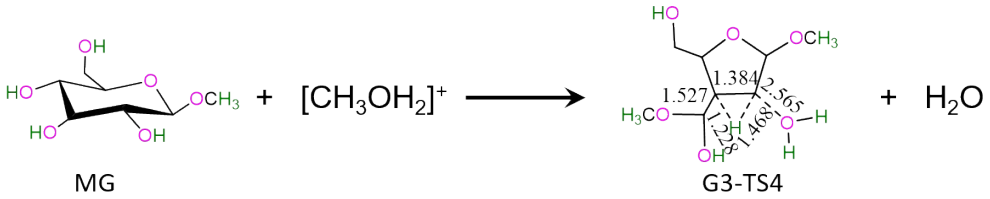
Figure S14. Arrhenius plots of rate constants for the crucial reaction step for **P-i+ii** of fructose to MLev and MF through HMF in the presence of $[CH_3OH_2]^+$ in methanol solution.

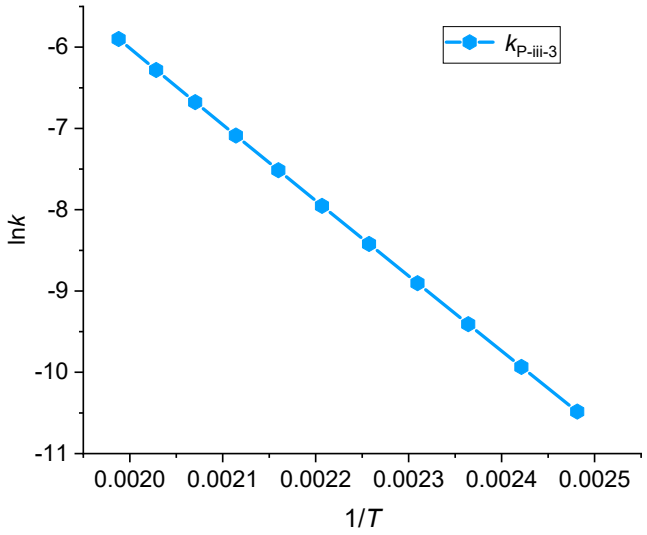




$$k_{\text{P-iii-2}} = 4.18\times10^{14}\, exp(-127537 / RT)$$

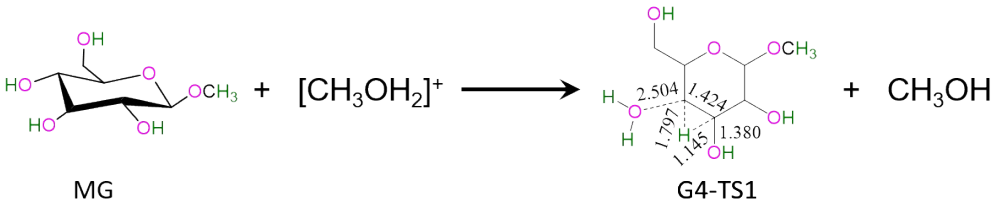
Figure S15. Arrhenius plots of rate constants for the crucial reaction step for **P-iii-2** of MG with methanol to MLev and MF through −O2H protonated in the presence of $[CH_3OH_2]^+$ in methanol solution.

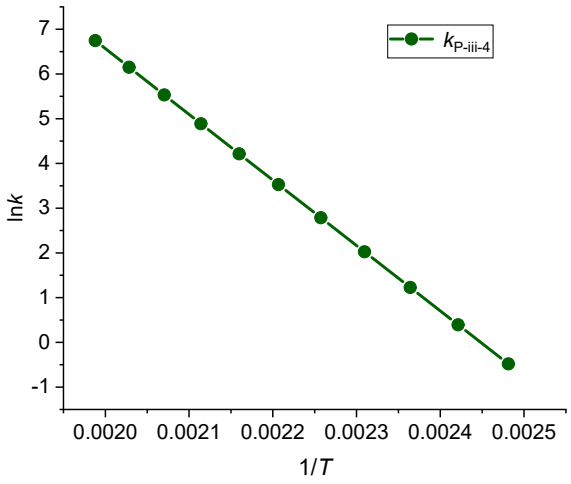




$$k_{\mathrm{P-iii-3}} = 2.86\times10^{5}\, exp(-77254 / RT)$$

Figure S16. Arrhenius plots of rate constants for the crucial reaction step for **P-iii-3** of MG with methanol to MLev and MF through −O3H protonated in the presence of $[CH_3OH_2]^+$ in methanol solution.





$$k_{\text{P-iii-4}} = 3.49\times10^{15}\, exp(-131635 / RT)$$

Figure S17. Arrhenius plots of rate constants for the crucial reaction step for **P-iii-4** of MG with methanol to MLev and MF through −O4H protonated in the presence of $[CH_3OH_2]^+$ in methanol solution.

Table S1. The proportion of rate constants ($k_{P\text{-}iii\text{-}2}$, $k_{P\text{-}iii\text{-}3}$ and $k_{P\text{-}iii\text{-}4}$) for the dehydration of MG with methanol to MF and MLev catalyzed by $[CH_3OH)_4]^+$ under the temperature range of 403 − 503 K.

$k_{P\text{-}iii\text{-}4}$=3.49× 10^15 exp(−131635/RT)	$k_{P\text{-}iii\text{-}2}$=4.18× 10^14 exp(−127537/RT)	$k_{P\text{-}iii\text{-}3}$=2.86× 10^5 exp(−77254/RT)	$k_{P\text{-}iii\text{-}2}/k_{P\text{-}iii\text{-}2}+k_{P\text{-}iii\text{-}3}+k_{P\text{-}iii\text{-}4}$	$k_{P\text{-}iii\text{-}3}/k_{P\text{-}iii\text{-}2}+k_{P\text{-}iii\text{-}3}+k_{P\text{-}iii\text{-}4}$	$k_{P\text{-}iii\text{-}4}/k_{P\text{-}iii\text{-}2}+k_{P\text{-}iii\text{-}3}+k_{P\text{-}iii\text{-}4}$
3.02E-02	1.23E-02	2.77E-05	28.90%	0.07%	71.03%
7.83E-02	3.09E-02	4.84E-05	28.31%	0.04%	71.65%
1.94E-01	7.44E-02	8.25E-05	27.74%	0.03%	72.23%
4.60E-01	1.72E-01	1.37E-04	27.21%	0.02%	72.77%
1.05E+00	3.82E-01	2.22E-04	26.70%	0.02%	73.28%
2.34E+00	8.31E-01	3.56E-04	26.22%	0.01%	73.77%
4.91E+00	1.71E+00	5.50E-04	25.77%	0.01%	74.22%
1.01E+01	3.44E+00	8.41E-04	25.35%	0.01%	74.65%
2.03E+01	6.73E+00	1.26E-03	24.94%	0.00%	75.05%
3.94E+01	1.28E+01	1.87E-03	24.56%	0.00%	75.44%
7.46E+01	2.38E+01	2.71E-03	24.19%	0.00%	75.81%

Table S2. The proportion of rate constants $k_{P\text{-iii-}2}$, $k_{P\text{-iii-}4}$ and $k_{P\text{-i+ii}}$ under the temperature range of 403 − 503 K.

T	$k_{P\text{-i+ii}}$=1.21× 10^3 exp(-58113/RT)	$k_{P\text{-iii-}4}$=3.49× 10^15 exp(-131635/RT)	$k_{P\text{-iii}}$-2=4.18× 10^14 exp(-127537/RT)	$k_{P\text{-iii-}4}/k_{P\text{-i+ii}}$	$k_{P\text{-iii-}2}/k_{P\text{-i+ii}}$
405	3.87E-05	3.67E-02	1.48E-02	9.49E+02	3.84E+02
415	5.86E-05	9.41E-02	3.70E-02	1.61E+03	6.31E+02
425	8.71E-05	2.31E-01	8.82E-02	2.65E+03	1.01E+03
435	1.27E-04	5.44E-01	2.02E-01	4.28E+03	1.59E+03
445	1.82E-04	1.23E+00	4.47E-01	6.76E+03	2.45E+03
455	2.58E-04	2.69E+00	9.53E-01	1.05E+04	3.70E+03
465	3.59E-04	5.69E+00	1.97E+00	1.59E+04	5.49E+03
475	4.92E-04	1.17E+01	3.94E+00	2.37E+04	8.01E+03
485	6.66E-04	2.32E+01	7.67E+00	3.48E+04	1.15E+04
495	8.92E-04	4.48E+01	1.45E+01	5.03E+04	1.63E+04
505	1.18E-03	8.45E+01	2.68E+01	7.16E+04	2.28E+04

Table S3. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) relative to *β*-D-fructofuranoses for five configurations of fructose at PBE0/6-311++G(d,p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
β-D-fructofuranoses	0.19778	-686.49060	0.13320	-686.55518	0.0	0.0
β-D-fructopyranoses	0.19920	-686.48846	0.13918	-686.54848	5.6	17.6
α-D-fructofuranoses	0.19832	-686.48681	0.13576	-686.54937	10.0	15.2
α-D-fructopyranoses	0.19768	-686.48785	0.13539	-686.55014	7.2	13.2
D-fructoketose	0.19483	-686.48160	0.12709	-686.54934	23.6	15.3

Table S4. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) relative to HMF-1 for eight tautomers of 5-hydroxymethylfurfural at PBE0/6-311++G(d,p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
HMF-1	0.11257	-457.40525	0.05813	-457.45969	0.0	0.0
HMF-2	0.11317	-457.40574	0.06010	-457.45881	-1.3	2.3
HMF-3	0.11275	-457.40530	0.05955	-457.45850	-0.1	3.1
HMF-4	0.11295	-457.40411	0.06001	-457.45705	3.0	6.9
HMF-5	0.11237	-457.40382	0.05825	-457.45794	3.8	4.6
HMF-6	0.11320	-457.40546	0.06057	-457.45808	-0.5	4.2
HMF-7	0.11256	-457.40334	0.05948	-457.45642	5.0	8.6
HMF-8	0.11300	-457.40377	0.06053	-457.45624	3.9	9.1

Table S5. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of fructose to HMF-1 in the absence of catalyst at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
β-D-fructofuranoses	0.19778	-686.49060	0.13320	-686.55518	0.0	0.0
F-b-1-TS1	0.19001	-686.40492	0.12012	-686.47481	225.0	211.0
F-b-1-IM1	0.19387	-686.47406	0.12402	-686.54391	43.4	29.6
F-b-1-IM2	0.16909	-610.10664	0.10724	-610.16849		
F-b-1-IM2 + H_2O	0.19042	-686.47133	0.10397	-686.55779	50.6	-6.9
F-b-2-TS1	0.16643	-610.05644	0.10683	-610.11604		
F-b-2-TS1 + H_2O	0.18777	-686.42113	0.10356	-686.50534	182.4	130.8
F-b-2-TS1a	0.16307	-610.00744	0.10217	-610.06834		
F-b-2-TS1a + H_2O	0.18440	-686.37212	0.09889	-686.45764	311.1	256.1
F-b-2-IM1	0.16827	-610.11297	0.10538	-610.17587		
F-b-2-IM1 + H_2O	0.18960	-686.47766	0.10210	-686.56517	34.0	-26.2
F-b-2-TS2a	0.16268	-610.03380	0.10304	-610.09343		
F-b-2-TS2a + H_2O	0.18401	-686.39849	0.09976	-686.48273	241.8	190.2
F-b-2-IM2	0.16452	-610.11099	0.09551	-610.18001		
F-b-2-IM2 + H_2O	0.18585	-686.47568	0.09223	-686.56931	39.2	-37.1
F-b-2-IM3	0.14023	-533.74449	0.08291	-533.80182		
F-b-2-IM3 + 2*H_2O	0.18290	-686.47386	0.07635	-686.58041	44.0	-66.3
F-b-3-TS1	0.13452	-533.67207	0.07454	-533.73205		
F-b-3-TS1 + 2*H_2O	0.17718	-686.40144	0.06798	-686.51064	234.1	116.9
F-b-3-IM1	0.13578	-533.76794	0.06852	-533.83520		
F-b-3-IM1 + 2*H_2O	0.17844	-686.49731	0.06196	-686.61379	-17.6	-153.9
HMF-1	0.11257	-457.40525	0.05813	-457.45969		
HMF-1 + 3*H_2O	0.17657	-686.49931	0.04829	-686.62759	-22.9	-190.1

Table S6. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with ZPE and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of fructose to HMF-1 in the presence of explicit CH_3OH at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
β-D-fructofuranoses	0.19778	-686.49060	0.13320	-686.55518	0.0	0.0
F-M-1-IM1	0.25246	-802.07990	0.17687	-802.15550		
F-M-1-IM1 - CH_3OH	0.20108	-686.49572	0.15832	-686.53848	-13.4	43.8
F-M-1-TS1	0.24244	-802.00585	0.16305	-802.08525		
F-M-1-TS1 - CH_3OH	0.19106	-686.42167	0.14450	-686.46823	181.0	228.3
F-M-2-IM1	0.22349	-725.69439	0.15131	-725.76657		
F-M-2-IM1 - CH_3OH + H_2O	0.19344	-686.47489	0.12948	-686.53885	41.3	42.9
F-M-2-TS2	0.22135	-725.66326	0.15231	-725.73231		
F-M-2-TS2 - CH_3OH + H_2O	0.19130	-686.44377	0.13048	-686.50458	123.0	132.8
F-M-3-IM1	0.19365	-649.33285	0.12003	-649.40647		
F-M-3-IM1 - CH_3OH + 2*H_2O	0.18493	-686.47803	0.09492	-686.56804	33.0	-33.8
F-M-3-TS3	0.18437	-649.27351	0.11394	-649.34395		
F-M-3-TS3 - CH_3OH + 2*H_2O	0.17565	-686.41870	0.08883	-686.50552	188.8	130.4
HMF-1	0.11257	-457.40525	0.05813	-457.45969		
HMF-1 + 3*H_2O	0.17657	-686.49931	0.04829	-686.62759	-22.9	-190.1

Table S7. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of fructose to HMF-1 catalyzed by $[CH_3OH_2]^+$ at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
β-D-fructofuranoses	0.19778	-686.49060	0.13320	-686.55518	0.0	0.0
F-1-IM1	0.26414	-802.49289	0.18746	-802.56956		
F-1-IM1 - $[CH_3OH_2]^+$	0.20035	-686.50688	0.15710	-686.55013	-42.7	13.2
F-1-TS1	0.26100	-802.47972	0.18195	-802.55877		
F-1-TS1 - $[CH_3OH_2]^+$	0.19722	-686.49371	0.15159	-686.53934	-8.2	41.6
F-1-IM2	0.25911	-802.48312	0.17373	-802.56850		
F-1-IM2 - $[CH_3OH_2]^+$	0.19532	-686.49712	0.14337	-686.54907	-17.1	16.0
F-1-IM3	0.23477	-726.11017	0.15701	-726.18792		
F-1-IM3 - $[CH_3OH_2]^+ + H_2O$	0.19231	-686.48885	0.12337	-686.55779	4.6	-6.9
F-1-TS2	0.23022	-726.09891	0.15712	-726.17201		
F-1-TS2 - $[CH_3OH_2]^+ + H_2O$	0.18776	-686.47760	0.12348	-686.54188	34.2	34.9
F-1-IM4	0.23500	-726.11384	0.16110	-726.18774		
F-1-IM4 - $[CH_3OH_2]^+ + H_2O$	0.19255	-686.49252	0.12746	-686.55761	-5.0	-6.4
F-2-TS1	0.23252	-726.09006	0.15715	-726.16543		
F-2-TS1 - $[CH_3OH_2]^+ + H_2O$	0.19007	-686.46874	0.12351	-686.53530	57.4	52.2
F-2-IM1	0.23229	-726.10963	0.15480	-726.18712		
F-2-IM1 - $[CH_3OH_2]^+ + H_2O$	0.18984	-686.48831	0.12116	-686.55699	6.0	-4.8
F-3-IM1	0.20643	-649.75575	0.13660	-649.82559		
F-3-IM1 - $[CH_3OH_2]^+ + 2*H_2O$	0.18531	-686.49912	0.09968	-686.58476	-22.4	-77.7
F-3-TS1	0.20335	-649.73526	0.12978	-649.80882		
F-3-TS1 - $[CH_3OH_2]^+ + 2*H_2O$	0.18222	-686.47863	0.09286	-686.56799	31.4	-33.6
F-3-IM2	0.17726	-573.37373	0.10750	-573.44349		
F-3-IM2 - $[CH_3OH_2]^+ + 3*H_2O$	0.17747	-686.48179	0.06730	-686.59196	23.1	-96.6
F-3-TS2	0.17454	-573.37304	0.10914	-573.43844		
F-3-TS2 - $[CH_3OH_2]^+ + 3*H_2O$	0.17475	-686.48109	0.06894	-686.58690	25.0	-83.3
F-3-IM3	0.18084	-573.39460	0.11341	-573.46203		
F-3-IM3 - $[CH_3OH_2]^+ + 3*H_2O$	0.18105	-686.50266	0.07321	-686.61050	-31.7	-145.3
HMF-1	0.11257	-457.40525	0.05813	-457.45969		
HMF-1 + $3*H_2O$	0.17657	-686.49931	0.04829	-686.62759	-22.9	-190.1

Table S8. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with ZPE and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the first and second conversion of HMF-1 with methanol to MF and MLev in the presence of CH_3OH at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
HMF-1	0.11257	-457.40525	0.05813	-457.45969	0.0	0.0
HM-b-1-IM1	0.13733	-533.77293	0.07471	-533.83556		
HM-b-1-IM1 - H_2O	0.11600	-457.40825	0.07799	-457.44626	-7.9	35.3
HM-b-1-TS1	0.13367	-533.67471	0.07725	-533.73113		
HM-b-1-TS1 - H_2O	0.11234	-457.31002	0.08053	-457.34183	250.0	309.4
HM-b-1-IM2	0.13938	-533.75321	0.08147	-533.81111		
HM-b-1-IM2 - H_2O	0.11804	-457.38852	0.08475	-457.42181	43.9	99.5
HM-b-1-TS2	0.13311	-533.65197	0.07486	-533.71022		
HM-b-1-TS2 - H_2O	0.11178	-457.28728	0.07814	-457.32092	309.7	364.3
HM-b-1-IM3	0.13912	-533.75315	0.08304	-533.80923		
HM-b-1-IM3 - H_2O	0.11778	-457.38847	0.08632	-457.41993	44.1	104.4
HM-b-1-TS3	0.13150	-533.65931	0.07518	-533.71563		
HM-b-1-TS3 - H_2O	0.11017	-457.29462	0.07846	-457.32633	290.4	350.1
HM-b-1-IM4	0.11069	-457.38404	0.05854	-457.43619	55.7	61.7
HM-b-1-TS4	0.16388	-572.87730	0.10438	-572.93680		
HM-b-1-TS4 - CH_3OH	0.11250	-457.29311	0.08583	-457.31978	294.4	367.3
HM-b-1-IM5	0.16719	-572.97899	0.10623	-573.03995		
HM-b-1-IM5 - CH_3OH	0.11581	-457.39480	0.08768	-457.42293	27.4	96.5
HM-b-1-TS5	0.16186	-572.88223	0.09714	-572.94695		
HM-b-1-TS5 - CH_3OH	0.11047	-457.29805	0.07859	-457.32993	281.5	340.7
HM-b-1-IM6	0.10233	-344.16375	0.05630	-344.20978		
HM-b-1-IM6 - CH_3OH - $HCOOCH_3$	0.11271	-457.39871	0.06118	-457.45024	17.2	24.8
HM-b-1-TS6	0.12332	-420.44208	0.07348	-420.49192		
HM-b-1-TS6 - CH_3OH - $HCOOCH_3$ + H_2O	0.11237	-457.31235	0.08164	-457.34308	243.9	306.2
HM-b-1-IM7	0.13078	-420.53531	0.08040	-420.58569		
HM-b-1-IM7 - CH_3OH - $HCOOCH_3$ + H_2O	0.11983	-457.40557	0.08856	-457.43685	-0.8	60.0
HM-b-1-TS7	0.12355	-420.42084	0.07360	-420.47080		
HM-b-1-TS7 - CH_3OH - $HCOOCH_3$ + H_2O	0.11260	-457.29111	0.08176	-457.32196	299.7	361.6
HM-b-1-IM8	0.13038	-420.53719	0.07914	-420.58843		
HM-b-1-IM8 - CH_3OH - $HCOOCH_3$ + H_2O	0.11943	-457.40746	0.08730	-457.43959	-5.8	52.8
HM-b-1-TS8	0.17936	-536.06245	0.11499	-536.12682		
HM-b-1-TS8 - 2*CH_3OH - $HCOOCH_3$ + H_2O	0.11703	-457.34853	0.10460	-457.36096	148.9	259.2
HM-b-1-IM9	0.18468	-536.12704	0.12242	-536.18930		
HM-b-1-IM9 - 2*CH_3OH - $HCOOCH_3$ + H_2O	0.12235	-457.41312	0.11203	-457.42344	-20.7	95.2

Continued from **Table S8**

Species	ZPE	E_c	G_0	G_c	E_r	G_r
HM-b-1-TS9	0.23616	-651.67085	0.16452	-651.74249		
HM-b-1-TS9 - 3*CH_3OH - $HCOOCH_3$ + H_2O	0.12244	-457.37275	0.13558	-457.35961	85.3	262.8
HM-b-1-IM10	0.18412	-536.14594	0.12116	-536.20890		
HM-b-1-IM10 - 2*CH_3OH - $HCOOCH_3$ + H_2O	0.12179	-457.43202	0.11077	-457.44304	-70.3	43.7
HM-b-1-TS10	0.17750	-536.03112	0.11243	-536.09620		
HM-b-1-TS10 - 2*CH_3OH - $HCOOCH_3$ + H_2O	0.11517	-457.31720	0.10203	-457.33034	231.2	339.6
HM-b-1-IM11	0.15510	-459.77067	0.09415	-459.83163		
HM-b-1-IM11 - 2*CH_3OH - $HCOOCH_3$	0.11410	-457.42144	0.08048	-457.45507	-42.5	12.1
HM-b-1-TS11	0.20496	-575.33764	0.13623	-575.40637		
HM-b-1-TS11 - 3*CH_3OH - $HCOOCH_3$	0.11258	-457.40422	0.10401	-457.41279	2.7	123.1
HM-b-2-TS8	0.12475	-420.47005	0.07435	-420.52045		
HM-b-2-TS8 - CH_3OH - $HCOOCH_3$ + H_2O	0.11380	-457.34032	0.08251	-457.37161	170.5	231.2
HM-b-2-IM9	0.12735	-420.52957	0.07213	-420.58479		
HM-b-2-IM9 - CH_3OH - $HCOOCH_3$ + H_2O	0.11640	-457.39984	0.08029	-457.43595	14.2	62.3
HM-b-2-TS9	0.17949	-536.07366	0.11560	-536.13754		
HM-b-2-TS9 - 2*CH_3OH - $HCOOCH_3$ + H_2O	0.11715	-457.35974	0.10521	-457.37168	119.5	231.1
HM-b-2-IM10	0.12723	-420.54779	0.07230	-420.60272		
HM-b-2-IM10 - CH_3OH - $HCOOCH_3$ + H_2O	0.11628	-457.41806	0.08046	-457.45387	-33.6	15.3
HM-b-2-TS10	0.17836	-536.08574	0.11458	-536.14953		
HM-b-2-TS10 - 2*CH_3OH - $HCOOCH_3$ + H_2O	0.11603	-457.37182	0.10418	-457.38367	87.8	199.6
Mlev	0.15586	-459.81561	0.09582	-459.87564		
MLev - 2*CH_3OH + $HCOOCH_3$	0.11485	-457.46637	0.08215	-457.49908	-160.5	-103.4

Table S9. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with ZPE and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the third conversion of HMF-1 with methanol to MF and MLev in the presence of CH_3OH at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
HM-b-3-TS6	0.12345	-420.44370	0.07363	-420.49352		
HM-b-3-TS6 - CH_3OH - $HCOOCH_3$ + H_2O	0.11250	-457.31397	0.08179	-457.34468	239.7	302.0
HM-b-3-IM7	0.13050	-420.53510	0.07994	-420.58567		
HM-b-3-IM7 - CH_3OH - $HCOOCH_3$ + H_2O	0.11955	-457.40537	0.08810	-457.43683	-0.3	60.0
HM-b-3-TS7	0.12380	-420.41914	0.07358	-420.46937		
HM-b-3-TS7 - CH_3OH - $HCOOCH_3$ + H_2O	0.11285	-457.28941	0.08173	-457.32053	304.1	365.4
HM-b-3-IM8	0.13002	-420.54042	0.07869	-420.59174		
HM-b-3-IM8 - CH_3OH - $HCOOCH_3$ + H_2O	0.11907	-457.41069	0.08685	-457.44290	-14.3	44.1
HM-b-3-TS8	0.12281	-420.43862	0.07034	-420.49110		
HM-b-3-TS8 - CH_3OH - $HCOOCH_3$ + H_2O	0.11186	-457.30889	0.07849	-457.34226	253.0	308.3
HM-b-3-IM9	0.10148	-344.18265	0.05380	-344.23032		
HM-b-3-IM9 - CH_3OH - $HCOOCH_3$	0.11186	-457.41760	0.05868	-457.47078	-32.4	-29.1
HM-b-3-TS9	0.15189	-459.70546	0.09338	-459.76397		
HM-b-3-TS9 - 2*CH_3OH - $HCOOCH_3$	0.11089	-457.35622	0.07971	-457.38741	128.7	189.8
HM-b-3-IM10	0.15734	-459.78005	0.10243	-459.83496		
HM-b-3-IM10 - 2*CH_3OH - $HCOOCH_3$	0.11634	-457.43082	0.08875	-457.45840	-67.1	3.4
HM-b-3-TS10	0.15578	-459.74565	0.10174	-459.79969		
HM-b-3-TS10 - 2*CH_3OH - $HCOOCH_3$	0.11478	-457.39642	0.08807	-457.42313	23.2	96.0
HM-b-3-IM11	0.15658	-459.79500	0.09721	-459.85437		
HM-b-3-IM11 - 2*CH_3OH - $HCOOCH_3$	0.11557	-457.44577	0.08354	-457.47781	-106.4	-47.6
HM-b-3-TS11	0.20653	-575.34264	0.13904	-575.41013		
HM-b-3-TS11 - 3*CH_3OH - $HCOOCH_3$	0.11414	-457.40922	0.10682	-457.41655	-10.4	113.3

Table S10. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with ZPE and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the forth conversion of HMF-1 with methanol to MF and MLev in the presence of CH_3OH at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
HM-b-4-TS4	0.13150	-533.66117	0.07558	-533.71708		
HM-b-4-TS4 - H_2O	0.11016	-457.29649	0.07886	-457.32779	285.6	346.3
HM-b-4-IM4	0.13868	-533.75401	0.08222	-533.81047		
HM-b-4-IM4 - H_2O	0.11735	-457.38933	0.08550	-457.42118	41.8	101.1
HM-b-4-TS5	0.13177	-533.63787	0.07530	-533.69434		
HM-b-4-TS5 - H_2O	0.11044	-457.27319	0.07858	-457.30504	346.7	406.0
HM-b-4-IM5	0.13875	-533.75889	0.08132	-533.81632		
HM-b-4-IM5 - H_2O	0.11741	-457.39420	0.08460	-457.42702	29.0	85.8
HM-b-4-TS6	0.13340	-533.68916	0.07673	-533.74582		
HM-b-4-TS6 - H_2O	0.11207	-457.32447	0.08001	-457.35652	212.1	270.9
HM-b-4-IM6	0.13678	-533.74566	0.07678	-533.80567		
HM-b-4-IM6 - H_2O	0.11545	-457.38098	0.08005	-457.41637	63.7	113.7
HM-b-4-TS7	0.19024	-649.29800	0.12228	-649.36595		
HM-b-4-TS7 - H2O - CH_3OH	0.11752	-457.34912	0.10701	-457.35963	147.4	262.7
HM-b-4-IM7	0.13665	-533.76620	0.07628	-533.82657		
HM-b-4-IM7 - H_2O	0.11532	-457.40151	0.07956	-457.43727	9.8	58.9
HM-b-4-TS8	0.13163	-533.68939	0.07391	-533.74711		
HM-b-4-TS8 - H_2O	0.11029	-457.32471	0.07719	-457.35781	211.5	267.5
HM-b-4-IM8	0.10890	-457.38647	0.05280	-457.44257	49.3	45.0
HM-b-4-TS9	0.16024	-572.92794	0.09587	-572.99231		
HM-b-4-TS9 - CH_3OH	0.10885	-457.34376	0.07732	-457.37529	161.5	221.6
HM-b-4-IM9	0.16532	-572.98835	0.10129	-573.05238		
HM-b-4-IM9 - CH_3OH	0.11394	-457.40416	0.08274	-457.43536	2.9	63.9
HM-b-4-TS10	0.21525	-688.52338	0.14179	-688.59684		
HM-b-4-TS10 - 2*CH_3OH	0.11248	-457.35501	0.10469	-457.36280	131.9	254.4
HM-b-4-IM10	0.22098	-688.57823	0.14843	-688.65078		
HM-b-4-IM10 - 2*CH_3OH	0.11821	-457.40986	0.11133	-457.41674	-12.1	112.8
HM-b-4-TS11	0.21311	-688.46435	0.14073	-688.53673		
HM-b-4-TS11 - 2*CH_3OH	0.11034	-457.29598	0.10363	-457.30269	286.9	412.2
HM-b-4-IM11	0.15646	-459.76143	0.09746	-459.82043		
HM-b-4-IM11 - 2*CH_3OH + $HCOOCH_3$	0.11546	-457.41219	0.08379	-457.44386	-18.2	41.6
HM-b-4-TS12	0.17871	-536.06181	0.11694	-536.12358		
HM-b-4-TS12 - 2*CH_3OH + $HCOOCH_3$ - H_2O	0.11638	-457.34789	0.10655	-457.35772	150.6	267.7

Table S11. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with ZPE and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of HMF-1 with methanol to MF and MLev catalyzed by $[CH_3OH_2]^+$ at PBE0/6-311++G (d, p) level in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
β-D-fructofuranoses	0.19778	-686.49060	0.13320	-686.55518	0.0	0.0
HMF-1	0.11257	-457.40525	0.05813	-457.45969		
HMF-1 + 3*H_2O	0.17657	-686.49931	0.04829	-686.62759	-22.9	-190.1
H-IM1	0.17891	-573.41110	0.11207	-573.47794		
H-IM1 + 3*H_2O - $[CH_3OH_2]^+$	0.17912	-686.51916	0.07187	-686.62641	-75.0	-187.0
H-IM2	0.12658	-457.80507	0.07351	-457.85815		
H-IM2 + 3*H_2O - $[CH_3OH_2]^+$ + CH_3OH	0.17818	-686.49732	0.05186	-686.62363	-17.6	-179.7
H-TS1	0.11921	-457.78468	0.05994	-457.84396		
H-TS1 + 3*H_2O - $[CH_3OH_2]^+$ + CH_3OH	0.17081	-686.47693	0.03829	-686.60945	35.9	-142.5
H-IM3	0.09643	-381.41896	0.04795	-381.46744		
H-IM3 + 4*H_2O - $[CH_3OH_2]^+$ + CH_3OH	0.16935	-686.47589	0.02302	-686.62223	38.6	-176.0
H-TS2	0.15071	-496.99847	0.09420	-497.05498		
H-TS2 + 4*H_2O - $[CH_3OH_2]^+$	0.17225	-686.47121	0.05072	-686.59274	50.9	-98.6
H-IM4	0.15130	-496.99843	0.09390	-497.05582		
H-IM4 + 4*H_2O - $[CH_3OH_2]^+$	0.17284	-686.47117	0.05042	-686.59359	51.0	-100.9
H-TS3	0.14804	-496.99603	0.09306	-497.05101		
H-TS3 + 4*H_2O - $[CH_3OH_2]^+$	0.16958	-686.46878	0.04959	-686.58877	57.3	-88.2
H-IM5	0.15231	-496.99810	0.09634	-497.05407		
H-IM5 + 4*H_2O - $[CH_3OH_2]^+$	0.17385	-686.47085	0.05286	-686.59184	51.9	-96.3
H-TS4	0.20799	-612.57889	0.14445	-612.66243		
H-TS4 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17815	-686.46745	0.08242	-686.58318	60.8	-73.5
H-IM6	0.20867	-612.61014	0.14438	-612.67443		
H-IM6 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17883	-686.49870	0.08235	-686.59518	-21.3	-105.0
H-TS5	0.25751	-728.20449	0.18139	-728.28061		
H-TS5 + 4*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH	0.17628	-686.50886	0.10081	-686.58433	-47.9	-76.6
H-IM7	0.26212	-728.21615	0.18769	-728.29058		
H-IM7 + 4*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH	0.18089	-686.52053	0.10711	-686.59431	-78.6	-102.7
H-TS6	0.25707	-728.20889	0.18070	-728.28526		
H-TS6 + 4*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH	0.17584	-686.51327	0.10012	-686.58899	-59.5	-88.8
H-IM8	0.20720	-612.63814	0.14125	-612.70409		
H-IM8 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17736	-686.52670	0.07922	-686.62484	-94.8	-182.9
H-TS7	0.20610	-612.61840	0.14092	-612.68359		
H-TS7 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17626	-686.50696	0.07889	-686.60433	-43.0	-129.1
H-IM9	0.20639	-612.63404	0.13577	-612.70466		
H-IM9 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17654	-686.52260	0.07374	-686.62541	-84.0	-184.4
H-TS8	0.20202	-612.63362	0.13431	-612.70133		
H-TS8 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17218	-686.52218	0.07228	-686.62207	-82.9	-175.6

Continued from **Table S11**

Species	ZPE	E_c	G_0	G_c	E_r	G_r
H-IM10	0.14264	-383.83069	0.09218	-383.88115		
H-IM10 + 4*H_2O - $[CH_3OH_2]^+$ - CH_3OH + $HCOOCH_3$	0.17456	-686.53839	0.05358	-686.65937	-125.5	-273.6
H-TS9	0.22127	-575.77679	0.15146	-575.84660		
H-TS9 + 3*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH + $HCOOCH_3$	0.18048	-686.53561	0.09759	-686.61851	-118.2	-166.3
H-IM11	0.16728	-460.19133	0.10609	-460.25252		
H-IM11 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH + $HCOOCH_3$	0.17788	-686.53434	0.07077	-686.64144	-114.8	-226.5
H-IM12	0.22350	-575.78382	0.15476	-575.85256		
H-IM12 + 3*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH + $HCOOCH_3$	0.18271	-686.54265	0.10089	-686.62447	-136.6	-181.9
H-TS10	0.22108	-575.77843	0.15291	-575.84660		
H-TS10 + 3*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH + $HCOOCH_3$	0.18029	-686.53725	0.09904	-686.61850	-122.5	-166.3
H-IM13	0.16920	-460.20480	0.11036	-460.26363		
H-IM13 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH + $HCOOCH_3$	0.17979	-686.54781	0.07504	-686.65256	-150.2	-255.7
H-TS11	0.21764	-575.79857	0.14711	-575.86910		
H-TS11 + 3*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH + $HCOOCH_3$	0.17685	-686.55739	0.09324	-686.64100	-175.4	-225.3
H-IM14	0.16876	-460.22374	0.10849	-460.28401		
H-IM14 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH + $HCOOCH_3$	0.17935	-686.56675	0.07317	-686.67293	-199.9	-309.2
MLev	0.15586	-459.81561	0.09582	-459.87564		
MLev - 2*CH_3OH + $HCOOCH_3$+3*H_2O	0.17885	-686.560434	0.072315	-686.66697	-183.3	-293.5

Table S12. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of MG through –O2H group with methanol to MF and MLev in the absence of catalyst in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
MG	0.22553	-725.71623	0.15673	-725.78503	0.0	0.0
GM-b-2-TS1	0.22087	-725.59559	0.15316	-725.66330	316.8	319.6
GM-b-2-IM1	0.19721	-649.34324	0.13312	-649.40733		
GM-b-2-IM1 + H_2O	0.21855	-725.70792	0.12984	-725.79663	21.8	-30.5
GM-b-2-TS2	0.19338	-649.20959	0.12910	-649.27386		
GM-b-2-TS2 + H_2O	0.21471	-725.57427	0.12582	-725.66316	372.7	320.0
GM-b-2-IM2	0.19465	-649.22510	0.12808	-649.29167		
GM-b-2-IM2 + H_2O	0.21599	-725.58978	0.12480	-725.68096	332.0	273.2
GM-b-2-TS3	0.19091	-649.21076	0.12544	-649.27623		
GM-b-2-TS3 + H_2O	0.21225	-725.57544	0.12216	-725.66553	369.6	313.8
GM-b-2-IM3	0.19724	-649.34150	0.13184	-649.40690		
GM-b-2-IM3 + H_2O	0.21857	-725.70619	0.12856	-725.79620	26.4	-29.3
GM-b-2-TS4	0.24568	-764.86020	0.16928	-764.93660		
GM-b-2-TS4 + H_2O - CH_3OH	0.21562	-725.64070	0.14745	-725.70888	198.3	200.0
GM-b-2-IM4	0.25438	-764.94605	0.18125	-765.01918		
GM-b-2-IM4 + H_2O - CH_3OH	0.22433	-725.72655	0.15942	-725.79146	-27.1	-16.9
GM-b-2-TS5	0.24386	-764.84560	0.16789	-764.92157		
GM-b-2-TS5 + H_2O - CH_3OH	0.21381	-725.62610	0.14606	-725.69385	236.6	239.4
GM-b-2-IM5	0.22519	-688.57946	0.15452	-688.65013		
GM-b-2-IM5 + 2*H_2O - CH_3OH	0.21647	-725.72464	0.12941	-725.81171	-22.1	-70.0
GM-b-2-TS6	0.21943	-688.47603	0.14907	-688.54638		
GM-b-2-TS6 + 2*H_2O - CH_3OH	0.21071	-725.62121	0.12396	-725.70796	249.5	202.4
GM-b-2-IM6	0.22476	-688.57822	0.15586	-688.64712		
GM-b-2-IM6 + 2*H_2O - CH_3OH	0.21604	-725.72341	0.13075	-725.80869	-18.8	-62.1
GM-b-2-TS7	0.21095	-688.46663	0.15092	-688.52666		
GM-b-2-TS7 + 2*H_2O - CH_3OH	0.20223	-725.61182	0.12581	-725.68824	274.2	254.1
GM-b-2-IM7	0.22130	-688.57764	0.14210	-688.65684		
GM-b-2-IM7 + 2*H_2O - CH_3OH	0.21258	-725.72283	0.11699	-725.81842	-17.3	-87.7
GM-b-2-IM8	0.15865	-459.76004	0.10363	-459.81506		
GM-b-2-IM8 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.21170	-725.72437	0.10195	-725.83412	-21.4	-128.9
GM-b-2-TS8	0.14885	-459.66497	0.09195	-459.72187		
GM-b-2-TS8 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20190	-725.62930	0.09028	-725.74093	228.2	115.8
GM-b-2-IM9	0.13008	-383.38968	0.07892	-383.44085		
GM-b-2-IM9 + 3*H_2O - CH_3OH + $HCOOCH_3$	0.20446	-725.71870	0.07396	-725.84920	-6.5	-168.5
GM-b-2-TS9	0.15125	-459.66747	0.09701	-459.72172		
GM-b-2-TS9 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20430	-725.63180	0.09533	-725.74077	221.7	116.2
GM-b-2-IM10	0.15864	-459.76009	0.10358	-459.81514		
GM-b-2-IM10 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.21168	-725.72441	0.10190	-725.83420	-21.5	-129.1
GM-b-2-TS10	0.15148	-459.64347	0.09596	-459.69899		
GM-b-2-TS10 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20453	-725.60779	0.09428	-725.71804	284.7	175.9
GM-b-2-IM11	0.15841	-459.76300	0.10276	-459.81865		
GM-b-2-IM11 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.21146	-725.72732	0.10108	-725.83771	-29.1	-138.3
GM-b-2-TS11	0.17894	-536.06896	0.11556	-536.13235		
GM-b-2-TS11 + H_2O - CH_3OH + $HCOOCH_3$	0.21065	-725.66860	0.11716	-725.76210	125.1	60.2

Continued from **Table S12**

Species	ZPE	E_c	G_0	G_c	E_r	G_r
HM-b-1-IM9	0.18468	-536.12704	0.12242	-536.18930		
HM-b-1-IM9 + H_2O - CH_3OH + $HCOOCH_3$	0.21639	-725.72668	0.12402	-725.81906	-27.4	-89.3
HM-b-1-TS9	0.23616	-651.67085	0.16452	-651.74249		
HM-b-1-TS9 + H_2O - 2*CH_3OH + $HCOOCH_3$	0.21649	-725.68631	0.14757	-725.75522	78.6	78.3
HM-b-1-IM10	0.18412	-536.14594	0.12116	-536.20890		
HM-b-1-IM10 + H_2O - CH_3OH + $HCOOCH_3$	0.21584	-725.74558	0.12276	-725.83866	-77.1	-140.8
HM-b-1-TS10	0.17750	-536.03112	0.11243	-536.09620		
HM-b-1-TS10 + H_2O - CH_3OH + $HCOOCH_3$	0.20922	-725.63076	0.11403	-725.72595	224.4	155.1
HM-b-1-IM11	0.15510	-459.77067	0.09415	-459.83163		
HM-b-1-IM11 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20815	-725.73500	0.09247	-725.85068	-49.3	-172.4
HM-b-1-TS11	0.20496	-575.33764	0.13623	-575.40637		
HM-b-1-TS11 + 2*H_2O - 2*CH_3OH + $HCOOCH_3$	0.20663	-725.71778	0.11600	-725.80841	-4.0	-61.4
GM-b-2-TS1a	0.21869	-725.60350	0.15026	-725.67194	296.0	296.9
GM-b-2-IM1a	0.19752	-649.34488	0.13353	-649.40886		
GM-b-2-IM1a + H_2O	0.21885	-725.70956	0.13025	-725.79816	17.5	-34.5
GM-b-2-TS2a	0.19497	-649.22285	0.13217	-649.28565		
GM-b-2-TS2a + H_2O	0.21630	-725.58754	0.12889	-725.67495	337.9	289.0
GM-b-2-IM2a	0.19661	-649.26921	0.13325	-649.33257		
GM-b-2-IM2a + H_2O	0.21794	-725.63390	0.12997	-725.72187	216.2	165.8
GM-b-2-TS3a	0.19304	-649.24188	0.12803	-649.30690		
GM-b-2-TS3a+ H_2O	0.21437	-725.60657	0.12475	-725.69620	287.9	233.2
GM-b-2-TS4a	0.21899	-725.63486	0.14681	-725.70704	213.6	204.8
GM-b-2-IM4a	0.22646	-725.72037	0.15740	-725.78943	-10.8	-11.5
GM-b-2-TS5a	0.27493	-841.19658	0.19478	-841.27672		
GM-b-2-TS5a - CH_3OH	0.22354	-725.61240	0.17623	-725.65971	272.6	329.1
MLev	0.15586	-459.81561	0.09582	-459.87564		
Mlev + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20890	-725.77993	0.09414	-725.89469	-167.2	-287.9

Table S13. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of MG through –O3H group with methanol to MF and MLev in the absence of catalyst in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
MG	0.22553	-725.71623	0.15673	-725.78503	0.0	0.0
GM-b-3-TS1	0.21797	-725.60402	0.14836	-725.67363	294.6	292.5
GM-b-3-IM1	0.19688	-649.34171	0.13181	-649.40677		
GM-b-3-IM1 + H_2O	0.21821	-725.70639	0.12853	-725.79607	25.8	-29.0
GM-b-3-TS2	0.19422	-649.21530	0.13052	-649.27900		
GM-b-3-TS2 + H_2O	0.21555	-725.57999	0.12725	-725.66830	357.7	306.5
GM-b-3-IM2	0.19706	-649.32658	0.13319	-649.39045		
GM-b-3-IM2 + H_2O	0.21839	-725.69127	0.12991	-725.77975	65.6	13.9
GM-b-3-TS3	0.19210	-649.22042	0.12675	-649.28578		
GM-b-3-TS3 + H_2O	0.21344	-725.58511	0.12347	-725.67508	344.3	288.7
GM-b-3-IM3	0.19791	-649.33736	0.13221	-649.40305		
GM-b-3-IM3 + H_2O	0.21924	-725.70205	0.12894	-725.79235	37.2	-19.2
GM-b-3-TS4	0.24624	-764.85697	0.17081	-764.93240		
GM-b-3-TS4 + H_2O - CH_3OH	0.21619	-725.63747	0.14898	-725.70468	206.8	211.0
GM-b-3-IM4	0.25389	-764.94428	0.18057	-765.01760		
GM-b-3-IM4 + H_2O - CH_3OH	0.22384	-725.72478	0.15874	-725.78988	-22.4	-12.7
GM-b-3-TS5	0.24499	-764.76669	0.16868	-764.84299		
GM-b-3-TS5 + H_2O - CH_3OH	0.21494	-725.54719	0.14685	-725.61527	443.8	445.7
GM-b-3-IM5	0.25083	-764.95236	0.17533	-765.02786		
GM-b-3-IM5 + H_2O - CH_3OH	0.22077	-725.73286	0.15350	-725.80014	-43.7	-39.7
GM-b-3-IM6	0.18814	-536.13047	0.12962	-536.18899		
GM-b-3-IM6 + H_2O - CH_3OH + $HCOOCH_3$	0.21986	-725.73011	0.13122	-725.81875	-36.4	-88.5
GM-b-3-TS6	0.17828	-536.02876	0.11640	-536.09063		
GM-b-3-TS6 + H_2O - CH_3OH + $HCOOCH_3$	0.20999	-725.62840	0.11800	-725.72039	230.6	169.7
GM-b-3-IM7	0.15918	-459.75323	0.10333	-459.80908		
GM-b-3-IM7 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.21222	-725.71756	0.10165	-725.82813	-3.5	-113.1
GM-b-3-TS7	0.18013	-536.03199	0.12131	-536.09081		
GM-b-3-TS7 + H_2O - CH_3OH + $HCOOCH_3$	0.21185	-725.63163	0.12291	-725.72056	222.1	169.3
GM-b-3-IM8	0.18748	-536.13008	0.12682	-536.19074		
GM-b-3-IM8 + H_2O - CH_3OH + $HCOOCH_3$	0.21920	-725.72972	0.12842	-725.82050	-35.4	-93.1
GM-b-3-TS8	0.18048	-536.02287	0.12045	-536.08290		
GM-b-3-TS8 + H_2O - CH_3OH + $HCOOCH_3$	0.21220	-725.62251	0.12205	-725.71266	246.1	190.0
GM-b-3-IM9	0.15920	-459.75835	0.10364	-459.81391		
GM-b-3-IM9 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.21224	-725.72268	0.10196	-725.83296	-16.9	-125.8
GM-b-3-TS9	0.15310	-459.65920	0.09695	-459.71534		
GM-b-3-TS9 + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20615	-725.62352	0.09528	-725.73440	243.4	132.9
GM-b-3-TS1a	0.21839	-725.60306	0.14816	-725.67328	297.1	293.4
GM-b-3-IM1a	0.19714	-649.34479	0.13279	-649.40914		
GM-b-3-IM1a + H_2O	0.21847	-725.70947	0.12952	-725.79843	17.7	-35.2
GM-b-3-TS2a	0.19477	-649.21654	0.13113	-649.28018		
GM-b-3-TS2a + H_2O	0.21610	-725.58123	0.12785	-725.66947	354.5	303.4
GM-b-3-IM2a	0.19578	-649.26647	0.12746	-649.33478		
GM-b-3-IM2a + H_2O	0.21711	-725.63115	0.12418	-725.72408	223.4	160.0
GM-b-3-TS3a	0.19207	-649.23940	0.12763	-649.30384		
GM-b-3-TS3a + H_2O	0.21340	-725.60408	0.12435	-725.69314	294.5	241.3

Table S14. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of MG through –O4H group with methanol to MF and MLev in the absence of catalyst in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
MG	0.22553	-725.71623	0.15673	-725.78503	0.0	0.0
GM-b-4-TS1	0.21819	-725.60490	0.14963	-725.67346	292.3	292.9
GM-b-4-IM1	0.19765	-649.34314	0.13342	-649.40737		
GM-b-4-IM1 + H_2O	0.21899	-725.70783	0.13015	-725.79667	22.1	-30.5
GM-b-4-TS2	0.19355	-649.28208	0.12929	-649.34633		
GM-b-4-TS2 + H_2O	0.21488	-725.64676	0.12602	-725.73563	182.4	129.7
GM-b-4-IM2	0.12853	-420.50848	0.07407	-420.56294		
GM-b-4-IM2 + H_2O + $HCOOCH_3$	0.21162	-725.69231	0.09422	-725.80971	62.8	-64.8
GM-b-4-TS3	0.17739	-536.01831	0.11149	-536.08420		
GM-b-4-TS3 + H_2O + $HCOOCH_3$ - CH_3OH	0.20910	-725.61795	0.11309	-725.71396	258.0	186.6
GM-b-4-IM3	0.18497	-536.11227	0.12135	-536.17589		
GM-b-4-IM3 + H_2O + $HCOOCH_3$ - CH_3OH	0.21668	-725.71191	0.12295	-725.80564	11.4	-54.1
GM-b-4-TS4	0.17957	-535.99442	0.11573	-536.05825		
GM-b-4-TS4 + H_2O + $HCOOCH_3$ - CH_3OH	0.21128	-725.59406	0.11733	-725.68801	320.8	254.7
GM-b-4-IM4	0.20977	-575.33331	0.13577	-575.40730		
GM-b-4-IM4 + 2*H_2O + $HCOOCH_3$ - 2*CH_3OH	0.21143	-725.71345	0.11554	-725.80934	7.3	-63.8
GM-b-4-TS5	0.20834	-575.31289	0.14059	-575.38063		
GM-b-4-TS5 + 2*H_2O + $HCOOCH_3$ - 2*CH_3OH	0.21000	-725.69303	0.12036	-725.78267	60.9	6.2
GM-b-4-IM5	0.21033	-575.36883	0.13707	-575.44209		
GM-b-4-IM5 + 2*H_2O + $HCOOCH_3$ - 2*CH_3OH	0.21199	-725.74897	0.11684	-725.84413	-86.0	-155.1
GM-b-4-TS6	0.17619	-536.06398	0.11231	-536.12786		
GM-b-4-TS6 + H_2O + $HCOOCH_3$ - CH_3OH	0.20791	-725.66362	0.11391	-725.75761	138.1	72.0
GM-b-4-IM6	0.18516	-536.16144	0.12097	-536.22562		
GM-b-4-IM6 + H_2O + $HCOOCH_3$ - CH_3OH	0.21687	-725.76108	0.12257	-725.85538	-117.7	-184.7
GM-b-4-TS7	0.17571	-536.05432	0.11054	-536.11949		
GM-b-4-TS7 + H_2O + $HCOOCH_3$ - CH_3OH	0.20742	-725.65396	0.11214	-725.74925	163.5	94.0
GM-b-4-IM7	0.21015	-575.38254	0.13518	-575.45751		
GM-b-4-IM7 + 2*H_2O + $HCOOCH_3$ - 2*CH_3OH	0.21181	-725.76268	0.11495	-725.85954	-121.9	-195.6
GM-b-4-TS8	0.20575	-575.34308	0.13587	-575.41296		
GM-b-4-TS8 + 2*H_2O + $HCOOCH_3$ - 2*CH_3OH	0.20741	-725.72322	0.11564	-725.81499	-18.3	-78.7
MLev	0.15586	-459.81561	0.09582	-459.87564		
Mlev + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20890	-725.77993	0.09414	-725.89469	-167.2	-287.9

Table S15. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of MG through –O2H protonated with methanol to MF and MLev catalyzed by $[CH_3OH_2]^+$ in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
MG	0.22553	-725.71623	0.15673	-725.78503	0.0	0.0
G2-IM1	0.23841	-726.11572	0.16858	-726.18555		
G2-IM1 - $[CH_3OH_2]^+ + CH_3OH$	0.22600	-725.71391	0.15677	-725.78314	6.1	5.0
G2-TS1	0.23288	-726.07299	0.16104	-726.14484		
G2-TS1 - $[CH_3OH_2]^+ + CH_3OH$	0.22048	-725.67118	0.14923	-725.74243	118.3	111.9
G2-IM2	0.21066	-649.74458	0.14403	-649.81121		
G2-IM2 - $[CH_3OH_2]^+ + CH_3OH + H_2O$	0.21959	-725.70745	0.12894	-725.79810	23.1	-34.3
G2-TS2	0.26548	-765.32989	0.19257	-765.40280		
G2-TS2 - $[CH_3OH_2]^+ + H_2O$	0.22302	-725.70857	0.15893	-725.77267	20.1	32.5
G2-IM3	0.26681	-765.35228	0.19314	-765.42595		
G2-IM3 - $[CH_3OH_2]^+ + H_2O$	0.22436	-725.73096	0.15950	-725.79582	-38.7	-28.3
G2-TS3	0.26388	-765.35372	0.19307	-765.42453		
G2-TS3 - $[CH_3OH_2]^+ + H_2O$	0.22143	-725.73240	0.15943	-725.79440	-42.4	-24.6
G2-IM4	0.26639	-765.35172	0.19302	-765.42510		
G2-IM4 - $[CH_3OH_2]^+ + H_2O$	0.22394	-725.73041	0.15938	-725.79497	-37.2	-26.1
G2-TS4	0.25821	-765.31109	0.17869	-765.39061		
G2-TS4 - $[CH_3OH_2]^+ + H_2O$	0.21575	-725.68977	0.14505	-725.76048	69.5	64.5
G2-IM5	0.23471	-688.94039	0.16447	-689.01063		
G2-IM5 - $[CH_3OH_2]^+ + 2*H_2O$	0.21358	-725.68376	0.12755	-725.76980	85.3	40.0
G2-TS5	0.23445	-688.93893	0.16462	-689.00875		
G2-TS5 - $[CH_3OH_2]^+ + 2*H_2O$	0.21332	-725.68230	0.12770	-725.76792	89.1	44.9
G2-IM6	0.23376	-688.99208	0.15680	-689.06904		
G2-IM6 - $[CH_3OH_2]^+ + 2*H_2O$	0.21264	-725.73546	0.11988	-725.82821	-50.5	-113.4
G2-IM7	0.17321	-460.15575	0.11775	-460.21121		
G2-IM7 - $[CH_3OH_2]^+ + 2*H_2O + HCOOCH_3$	0.21385	-725.71826	0.10426	-725.82786	-5.3	-112.4
G2-TS6	0.21990	-575.70460	0.14883	-575.77567		
G2-TS6 - $[CH_3OH_2]^+ + 2*H_2O + HCOOCH_3 - CH_3OH$	0.20916	-725.68292	0.11679	-725.77529	87.5	25.6
G2-IM8	0.14363	-383.75767	0.09364	-383.80766		
G2-IM8 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3$	0.20560	-725.68487	0.07687	-725.81360	82.3	-75.0
G2-TS7	0.19140	-499.33362	0.13306	-499.39196		
G2-TS7 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3 - CH_3OH$	0.20200	-725.67663	0.09774	-725.78089	104.0	10.9
G2-IM9	0.19658	-499.38987	0.13215	-499.45430		
G2-IM9 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3 - CH_3OH$	0.20717	-725.73289	0.09683	-725.84322	-43.7	-152.8
G2-TS8	0.19183	-499.38919	0.12818	-499.45285		
G2-TS8 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3 - CH_3OH$	0.20243	-725.73220	0.09286	-725.84178	-41.9	-149.0
G2-IM10	0.14235	-383.81956	0.09075	-383.87116		
G2-IM10 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3$	0.20433	-725.74676	0.07398	-725.87711	-80.1	-241.7
G2-TS9	0.13899	-383.78699	0.08816	-383.83781		
G2-TS9 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3$	0.20096	-725.71419	0.07139	-725.84376	5.4	-154.2
G2-IM11	0.14227	-383.83262	0.09103	-383.88386		
G2-IM11 - $[CH_3OH_2]^+ + 3*H_2O + HCOOCH_3$	0.20424	-725.75982	0.07426	-725.88981	-114.4	-275.1

Continued from **Table S15**

Species	ZPE	E_c	G_0	G_c	E_r	G_r
G2-IM12	0.21976	-575.78501	0.14431	-575.86046		
G2-IM12 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.20902	-725.76333	0.11227	-725.86008	-123.7	-197.0
G2-TS10	0.22127	-575.77679	0.15146	-575.84660		
G2-TS10 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.21053	-725.75511	0.11942	-725.84623	-102.1	-160.7
G2-IM13	0.22363	-575.78326	0.15616	-575.85073		
G2-IM13 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.21289	-725.76159	0.12412	-725.85036	-119.1	-171.5
H-TS10	0.22108	-575.77843	0.15291	-575.84660		
H-TS10 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.21034	-725.75675	0.12087	-725.84622	-106.4	-160.6
H-IM13	0.16920	-460.20480	0.11036	-460.26363		
H-IM13 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.20984	-725.76731	0.09687	-725.88028	-134.1	-250.1
H-TS11	0.21764	-575.79857	0.14711	-575.86910		
H-TS11 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.20690	-725.77689	0.11507	-725.86872	-159.3	-219.7
H-IM14	0.16876	-460.22374	0.10849	-460.28401		
H-IM14 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.20940	-725.78625	0.09500	-725.90065	-183.8	-303.6
MLev	0.15586	-459.81561	0.09582	-459.87564		
MLev + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20890	-725.77993	0.09414	-725.89469	-167.2	-287.9

Table S16. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of MG through –O3H protonated with methanol to MF and MLev catalyzed by $[CH_3OH_2]^+$ in methanol solution.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
MG	0.22553	-725.71623	0.15673	-725.78503	0.0	0.0
G3-IM1	0.23904	-726.11574	0.16998	-726.18480		
G3-IM1 - $[CH_3OH_2]^+ + CH_3OH$	0.22664	-725.71392	0.15816	-725.78239	6.1	6.9
G3-TS1	0.23176	-726.07902	0.15698	-726.15380		
G3-TS1 - $[CH_3OH_2]^+ + CH_3OH$	0.21936	-725.67720	0.14516	-725.75139	102.5	88.3
G3-IM2	0.21075	-649.73968	0.14404	-649.80639		
G3-IM2 - $[CH_3OH_2]^+ + CH_3OH + H_2O$	0.21968	-725.70255	0.12894	-725.79328	35.9	-21.7
G3-TS2	0.26665	-765.34326	0.19568	-765.41423		
G3-TS2 - $[CH_3OH_2]^+ + H_2O$	0.22420	-725.72195	0.16204	-725.78410	-15.0	2.4
G3-IM3	0.26722	-765.34992	0.19373	-765.42342		
G3-IM3 - $[CH_3OH_2]^+ + H_2O$	0.22477	-725.72861	0.16008	-725.79329	-32.5	-21.7
G3-TS3	0.26382	-765.34959	0.19255	-765.42087		
G3-TS3 - $[CH_3OH_2]^+ + H_2O$	0.22137	-725.72828	0.15891	-725.79074	-31.6	-15.0
G3-IM4	0.26713	-765.35006	0.19504	-765.42214		
G3-IM4 - $[CH_3OH_2]^+ + H_2O$	0.22467	-725.72874	0.16140	-725.79201	-32.8	-18.3
G3-TS4	0.25847	-765.29659	0.18142	-765.37364		
G3-TS4 - $[CH_3OH_2]^+ + H_2O$	0.21601	-725.67527	0.14777	-725.74351	107.5	109.0
G3-IM5	0.23575	-688.95353	0.16537	-689.02391		
G3-IM5 - $[CH_3OH_2]^+ + 2*H_2O$	0.21463	-725.69690	0.12845	-725.78308	50.8	5.1
G3-TS5	0.23611	-688.93196	0.16716	-689.00091		
G3-TS5 - $[CH_3OH_2]^+ + 2*H_2O$	0.21498	-725.67533	0.13024	-725.76008	107.4	65.5

Table S17. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the dehydration of MG through –O4H protonated with methanol to MF and MLev catalyzed by $[CH_3OH_2]^+$ in methanol solution.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
MG	0.22553	-725.71623	0.15673	-725.78503	0.0	0.0
G4-IM1	0.23902	-726.11474	0.16957	-726.18418		
G4-IM1 + CH_3OH - $[CH_3OH_2]^+$	0.22662	-725.71292	0.15776	-725.78177	8.7	8.6
G4-TS1	0.23024	-726.07199	0.15590	-726.14632		
G4-TS1 + CH_3OH - $[CH_3OH_2]^+$	0.21783	-725.67017	0.14409	-725.74391	120.9	108.0
G4-IM2	0.21043	-649.76945	0.14604	-649.83384		
G4-IM2 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.21936	-725.73232	0.13095	-725.82073	-42.2	-93.7
G4-TS2	0.25927	-765.33698	0.18357	-765.41269		
G4-TS2 - $[CH_3OH_2]^+$ + H_2O	0.21682	-725.71567	0.14993	-725.78256	1.5	6.5
G4-IM3	0.26464	-765.34624	0.18993	-765.42096		
G4-IM3 - $[CH_3OH_2]^+$ + H_2O	0.22219	-725.72493	0.15629	-725.79083	-22.8	-15.2
G4-IM4	0.21092	-649.73938	0.14599	-649.80432		
G4-IM4 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.21985	-725.70225	0.13090	-725.79121	36.7	-16.2
G4-TS3	0.20849	-649.72226	0.14480	-649.78595		
G4-TS3 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.21742	-725.68514	0.12971	-725.77284	81.7	32.0
G4-IM5	0.20825	-649.74293	0.13999	-649.81120		
G4-IM5 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.21718	-725.70580	0.12490	-725.79809	27.4	-34.3
G4-TS4	0.20562	-649.72635	0.13745	-649.79453		
G4-TS4 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.21455	-725.68922	0.12236	-725.78142	70.9	9.5
G4-IM6	0.20454	-649.73578	0.12946	-649.81086		
G4-IM6 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.21347	-725.69865	0.11437	-725.79775	46.2	-33.4
G4-TS5	0.20068	-649.72403	0.12728	-649.79743		
G4-TS5 + CH_3OH - $[CH_3OH_2]^+$ + H_2O	0.20961	-725.68691	0.11219	-725.78432	77.0	1.9
G4-IM7	0.14172	-420.90499	0.08631	-420.96039		
G4-IM7 + CH_3OH - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21242	-725.68700	0.09465	-725.80476	76.8	-51.8
G4-TS6	0.19430	-536.49504	0.13098	-536.55837		
G4-TS6 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21361	-725.69287	0.12076	-725.78571	61.4	-1.8
G4-IM8	0.19819	-536.51614	0.13442	-536.57990		
G4-IM8 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21750	-725.71396	0.12421	-725.80725	6.0	-58.3
G4-TS7	0.19435	-536.51377	0.13199	-536.57612		
G4-TS7 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21366	-725.71159	0.12178	-725.80347	12.2	-48.4
G4-IM9	0.19787	-536.51590	0.13316	-536.58062		
G4-IM9 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21718	-725.71372	0.12294	-725.80796	6.6	-60.2
G4-TS8	0.19083	-536.49947	0.12203	-536.56827		
G4-TS8 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21015	-725.69729	0.11182	-725.79561	49.7	-27.8
G4-IM10	0.16728	-460.13478	0.10671	-460.19535		
G4-IM10 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.20793	-725.69729	0.09322	-725.81199	49.7	-70.8
G4-TS9	0.16598	-460.12303	0.10750	-460.18151		
G4-TS9 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.20662	-725.68554	0.09401	-725.79815	80.6	-34.4
G4-IM11	0.17037	-460.18200	0.11142	-460.24095		
G4-IM11 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.21101	-725.74451	0.09793	-725.85759	-74.2	-190.5
G4-IM12	0.22341	-575.78781	0.15314	-575.85807		
G4-IM12 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.21267	-725.76613	0.12110	-725.85770	-131.0	-190.8

Continued from **Table S17**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
G4-TS10	0.21895	-575.74595	0.14884	-575.81606		
G4-TS10 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$ - CH_3OH	0.20821	-725.72428	0.11680	-725.81569	-21.1	-80.5
G4-IM13	0.16567	-460.16565	0.10497	-460.22635		
G4-IM13 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.20632	-725.72816	0.09148	-725.84300	-31.3	-152.2
G4-TS11	0.19064	-536.52436	0.12506	-536.58994		
G4-TS11 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.20996	-725.72218	0.11485	-725.81729	-15.6	-84.7
G4-IM14	0.19943	-536.56670	0.13619	-536.62995		
G4-IM14 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH^3$	0.21874	-725.76453	0.12598	-725.85729	-126.8	-189.7
G4-TS12	0.19553	-536.56655	0.13326	-536.62882		
G4-TS12 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21484	-725.76437	0.12304	-725.85617	-126.4	-186.8
G4-IM15	0.19921	-536.56645	0.13592	-536.62975		
G4-IM15 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21853	-725.76428	0.12570	-725.85710	-126.1	-189.2
G4-TS13	0.19101	-536.51467	0.12682	-536.57886		
G4-TS13 - $[CH_3OH_2]^+$ + H_2O + $HCOOCH_3$	0.21032	-725.71249	0.11661	-725.80620	9.8	-55.6
H-IM14	0.16876	-460.22374	0.10849	-460.28401		
H-IM14 - $[CH_3OH_2]^+$ + 2*H_2O + $HCOOCH_3$	0.20940	-725.78625	0.09500	-725.90065	-183.8	-303.6
MLev	0.15586	-459.81561	0.09582	-459.87564		
MLev + 2*H_2O - CH_3OH + $HCOOCH_3$	0.20890	-725.77993	0.09414	-725.89469	-167.2	-287.9

Table S18. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) for the conversion of HMF through protonation of the carbonyl oxygen with CH_3OH to both MLev and MF catalyzed by $[CH_3OH_2]^+$ in methanol solution.

Species	ZPE	E_c	G_0	G_c	E_r	G_r
CH_3OH	0.05138	-115.58419	0.01855	-115.61702		
$[CH_3OH_2]^+$	0.06379	-115.98600	0.03036	-116.01943		
H_2O	0.02133	-76.36469	-0.00328	-76.38930		
$HCOOCH_3$	0.06177	-228.81914	0.02343	-228.85748		
β-D-fructofuranoses	0.19778	-686.49060	0.13320	-686.55518	0.0	0.0
HMF-1	0.11257	-457.40525	0.05813	-457.45969		
HMF-1 + 3*H_2O	0.17657	-686.49931	0.04829	-686.62759	-22.9	-190.1
H-1-IM1	0.12537	-457.81959	0.06996	-457.87500		
H-1-IM1 + 3*H_2O - $[CH_3OH_2]^+$ + CH_3OH	0.17696	-686.51183	0.04831	-686.64049	-55.7	-224.0
H-2-TS1	0.23193	-688.92643	0.15751	-689.00085		
H-2-TS1 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.18076	-686.45030	0.09876	-686.53229	105.8	60.1
H-1-TS1	0.23350	-688.98874	0.15826	-689.06398		
H-1-TS1 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.18232	-686.51261	0.09951	-686.59543	-57.8	-105.7
H-1-IM2	0.23506	-688.99690	0.16033	-689.07163		
H-1-IM2 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.18389	-686.52078	0.10158	-686.60308	-79.2	-125.8
H-1-IM3	0.23556	-688.99825	0.16092	-689.07289		
H-1-IM3 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.18438	-686.52212	0.10217	-686.60434	-82.8	-129.1
H-1-TS2	0.23189	-689.00286	0.16022	-689.06453		
H-1-TS2 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.18071	-686.52673	0.10147	-686.59598	-94.9	-107.1
H-1-IM4	0.23524	-689.01192	0.15799	-689.06877		
H-1-IM4 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.18406	-686.53580	0.09924	-686.60022	-118.7	-118.3
H-1-TS3	0.23025	-688.97854	0.15443	-689.05435		
H-1-TS3 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17907	-686.50241	0.09568	-686.58580	-31.0	-80.4
H-1-IM5	0.23022	-688.98270	0.14717	-689.06575		
H-1-IM5 + 3*H_2O - $[CH_3OH_2]^+$ - CH_3OH	0.17905	-686.50657	0.08843	-686.59719	-41.9	-110.3
H-1-IM6	0.25988	-728.20289	0.17586	-728.28691		
H-1-IM6 + 4*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH	0.17865	-686.50726	0.09528	-686.59064	-43.7	-93.1
H-1-TS4	0.25986	-728.19798	0.18205	-728.27579		
H-1-TS4 + 4*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH	0.17863	-686.50235	0.10147	-686.57952	-30.9	-63.9
H-1-IM7	0.26220	-728.21700	0.18546	-728.29373		
H-1-IM7 + 4*H_2O - $[CH_3OH_2]^+$ - 2*CH_3OH	0.18097	-686.52137	0.10488	-686.59746	-80.8	-111.0