Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Radical routes to interstellar glycolaldehyde. The possibility of stereoselectivity in gas-phase polymerization reactions involving CH_2O and $^{\cdot}CH_2OH$.

Tianfang Wang and John H. Bowie*

Department of Chemistry, The University of Adelaide, South Australia, 5005

* Corresponding author. e-mail: john.bowie@adelaide.edu.au

Table S1 Energies and Selected Geometries of Minima and Transition States for Reaction between Formaldehyde and Hydroxymethylene. **Level of theory used CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). Relative energies in kJ mol^{-1} with respect to [A+B] (0 kJ mol^{-1}).**

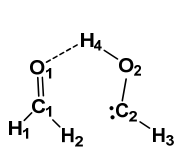
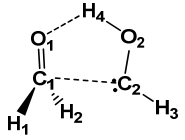
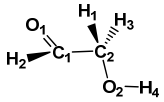
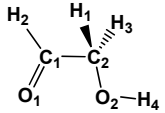
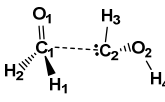
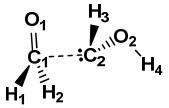
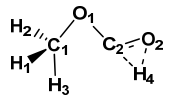
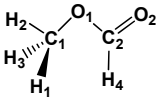
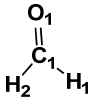
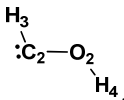
								
	1	**TS 1/2**	**TS 6/2**	**2**	**3**	**TS 3/4**	**TS 7/8**	**8**
State	^{1}A	^{1}A	^{1}A	^{1}A'	^{1}A	^{1}A	^{1}A	^{1}A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_S	C_1
Energy (Hartree)	-228.54230	-228.54079	-228.63714	-228.64510	-228.53204	-228.52803	-228.54010	-228.66226
Energy Relative to [A+B]	-34	-30	-283	-304	-7	3	-28	-349
Gibbs free energy (Hartree 298 K)	-228.57134	-228.56897	-228.66338	-228.67167	-228.56394	-228.55567	-228.56748	-228.68890
Gibbs free energy relative to [A+B]	2	8	-240	-262	21	43	12	-307
Dipole Moment (Debye)	2.64	2.35	1.88	2.94	3.27	3.33	3.20	2.02
Bond Length (Å)								
C_1C_2	3.328	3.081	1.527	1.507	2.839	2.256	2.332	—
C_1O_1	1.218	1.217	1.206	1.208	1.212	1.226	1.437	1.430
C_2O_2	1.299	1.297	1.425	1.402	1.305	1.304	1.290	1.198
C_2O_1	—	—	—	—	3.118	2.524	1.315	1.343
C_1H_1	1.098	1.098	—	—	1.099	1.097	1.085	1.089
C_2H_3	1.109	1.108	1.097	1.101	1.106	1.104	—	—
C_1H_3	—	—	—	—	—	—	1.086	1.089
C_2H_1	—	—	1.091	1.101	—	—	—	—
C_2H_4	—	—	—	—	—	—	1.242	1.102
O_2H_4	0.984	0.984	—	—	0.966	0.966	1.223	—
Bond Angle (°)								
$O_1C_1C_2$	72.9	78.4	121.3	121.8	91.6	87.7	30.5	31.3
$H_1C_1C_2$	166.9	126.6	—	—	88.5	96.3	120.6	94.2
$H_2C_1C_2$	47.9	67.9	117.9	116.7	90.7	94.4	120.6	94.1
$O_2C_2C_1$	79.2	83.2	108.7	112.0	139.5	119.9	149.6	156.4
$H_4O_2C_2$	106.9	107.6	107.4	106.0	108.2	108.6	59.2	—
$H_3C_2O_2$	103.7	103.6	111.8	107.8	103.2	104.9	—	—

Table S1 Continued.

$O_1C_2C_1$	—	—	—	—	—	—	33.7	33.6
$H_3C_1C_2$	47.9	172.8	—	—	—	—	79.5	94.1
Dihedral Angle (^{o})								
$O_2C_1C_2O_1$	0.0	12.4	76.9	0.0	74.0	75.1	0.0	0.0
$H_1C_1C_2O_1$	-180.0	-119.8	-166.1	122.5	-122.0	-122.6	-72.2	-124.7
$H_2C_1C_2O_1$	180.0	131.7	176.5	180.0	121.9	122.1	72.2	0.0
$H_3C_1C_2O_1$	180.0	175.4	-45.1	-122.5	-32.7	-38.2	180.0	124.8
$H_4O_2C_2C_1$	0.0	1.9	60.9	0.0	-78.9	-68.2	180.0	-180.0



, **[A], State** $^1A_1$, **Symmetry** C_{2V}, **Dipole Moment** 2.89, **Energy** -114.30646 Hartree, **C_1H_1** 1.100 Å, **C_1O_1** 1.209 Å, **$H_2C_1H_1$** 116.5^o, **$C_1H_1H_2O_1$** 0.0^o.



, **[B], State** $^1A'$, **Symmetry** C_S, **Dipole Moment** 1.30, **Energy** -114.22286 Hartree, **C_2H_3** 1.107 Å, **C_2O_2** 1.308 Å, **O_2H_4** 0.966 Å, **$H_3C_3O_2$** 102.4^o, **$H_4O_2C_2$** 107.8^o, **$H_3C_2O_2H_4$** 180.0^o.

Table S1 Continued.

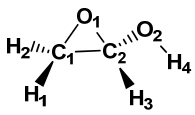
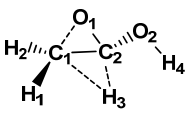
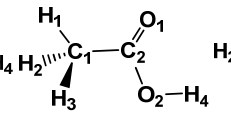
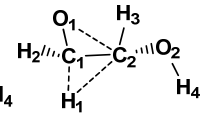
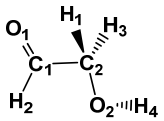
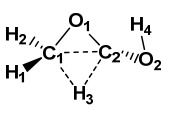
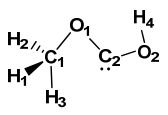
							
	4	**TS4/5**	**5**	**TS 4/6**	**6**	**TS 4/7**	**7**
State	^1A	^1A	^1A	^1A	^1A	^1A	^1A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-228.61495	-228.51035	-228.68823	-228.53294	-228.64021	-228.52009	-228.59506
Energy Relative to [A+B]	-225	50	-417	-10	-291	24	-173
Gibbs free energy (Hartree 298 K)	-228.64098	-228.53661	-228.71529	-228.55920	-228.66771	-228.54608	-228.62204
Gibbs free energy relative to [A+B]	-181	93	-376	34	-251	68	-131
Dipole Moment (Debye)	2.15	5.48	2.01	7.29	2.21	2.93	2.89
Bond Length (Å)							
C_1C_2	1.458	1.418	1.498	1.454	1.515	1.855	2.330
C_1O_1	1.454	2.234	2.416	1.303	1.210	1.404	1.435
C_2O_2	1.374	1.398	1.354	1.287	1.412	1.338	1.314
C_2O_1	1.411	1.312	1.207	2.313	2.402	1.413	1.323
C_1H_1	1.082	1.080	1.084	1.171	2.117	1.084	1.086
C_2H_3	1.082	1.185	2.126	1.086	1.092	1.272	—
C_1H_3	—	1.850	1.088	—	—	1.381	1.085
C_2H_1	—	—	—	1.894	1.091	—	—
Bond Angle (^{o})							
$O_1C_1C_2$	58.0	33.6	—	113.9	123.3	49.1	30.9
$H_1C_1C_2$	121.0	115.0	109.6	91.7	—	130.9	120.8
$H_2C_1C_2$	118.6	125.7	109.6	109.7	114.8	107.3	120.8
$O_2C_2C_1$	123.5	117.1	109.5	126.7	112.5	110.4	141.6
$H_4O_2C_2$	108.2	104.2	106.0	109.0	108.9	109.0	110.3
$H_3C_2O_2$	109.7	103.3	109.5	114.1	109.0	114.9	—
$O_1C_2C_1$	60.9	109.7	126.2	31.0	—	48.6	33.8
Dihedral Angle (^{o})							
$O_2C_1C_2O_1$	105.5	138.9	180.0	137.4	164.8	100.2	0.0
$H_1C_1C_2O_1$	-101.7	-60.1	0.1	-121.3	-78.0	-88.1	-72.5
$H_2C_1C_2O_1$	102.2	119.7	121.2	136.7	-179.3	108.9	72.5
$H_3C_1C_2O_1$	-104.1	-116.1	-121.0	-40.1	38.5	-154.1	180.0
$H_4O_2C_2C_1$	34.2	128.3	180.0	1.4	77.4	54.1	0.0

Table S2 Energies and Selected Geometries of Minima and Transition States for Nucleophilic Attack of Water on Oxiran-2-ol to form methyl formate. **Level of theory used CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). Relative energies in kJ mol^{-1} with respect to [4+A] (0 kJ mol^{-1}).**

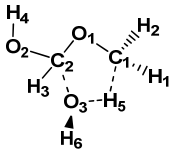
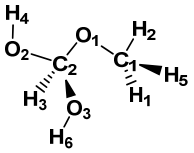
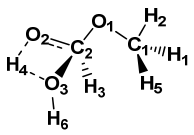
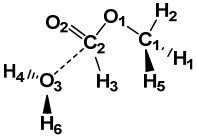
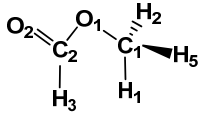
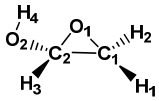
					
	TS [4+A]/B	**B**	**TS B/C**	**C**	**D**
State	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A
Symmetry	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-304.85262	-304.96273	-304.89952	-304.97102	-228.66226
Energy Relative to [4+A]	191	-98	67	-120	-124 **[D+A]**
Gibbs free energy (Hartree 298 K)	-304.88169	-304.99175	-304.92844	-305.00355	-228.68890
Gibbs free energy relative to [4+A]	229	-60	106	-91	-126 **[D+A]**
Dipole Moment (Debye)	3.28	1.39	4.38	3.03	
Bond Length (Å)					
C_1C_2	2.339	2.339	2.313	2.350	
C_1O_1	1.536	1.420	1.426	1.432	
C_2O_2	1.301	1.378	1.290	1.201	
C_2O_1	1.248	1.380	1.330	1.340	
C_1H_1	1.093	1.093	1.090	1.089	
C_2H_3	1.080	1.096	1.098	1.100	
C_1H_2	1.087	1.085	1.084	1.084	
O_2H_4	0.969	0.965	1.234	2.694	
C_2O_3	2.268	1.405	1.771	2.963	
C_1H_5	1.518	1.088	1.089	1.087	See structure **8** in
O_3H_5	1.126	2.492	2.709	2.604	**SupplementaryTable 1**
O_3H_6	0.961	0.962	0.967	0.959	
Bond Angle (^{o})					
$O_1C_1C_2$	36.9	32.8	31.6	30.9	
$H_1C_1C_2$	94.8	89.8	90.2	86.2	
$H_2C_1C_2$	130.1	138.8	137.6	134.2	
$O_2C_2C_1$	154.6	142.7	151.6	154.8	
$H_4O_2C_2$	108.6	106.6	80.0	72.7	
$H_3C_2O_2$	115.3	106.5	121.1	124.1	

Table S2 Continued.

$O_1C_2C_1$	36.9	33.9	34.2	33.2	
$O_3C_2O_1$	88.7	107.2	106.4	75.6	
$H_5C_1O_1$	85.9	111.2	109.4	109.4	
$H_6O_3C_2$	129.1	107.4	110.6	126.7	
Dihedral Angle (^{o})					
$O_2C_1C_2O_1$	34.3	8.0	7.2	19.0	See structure **8** in
$H_1C_1C_2O_1$	-110.5	-130.8	-132.4	-144.0	**SupplementaryTable 1**
$H_2C_1C_2O_1$	8.5	-11.0	-12.2	-30.5	
$H_3C_1C_2O_1$	-157.4	-128.0	-149.2	-170.7	
$H_4O_2C_2C_1$	10.0	-56.9	-109.3	-64.2	
$O_3C_1C_2O_1$	121.1	121.4	110.5	87.3	
$H_5C_1C_2O_1$	125.4	119.8	117.4	106.0	
$H_6O_3C_2C_1$	-105.0	-152.2	-106.3	-158.7	



, **4**, see structure **4** in **Table 1**.

, **[A]**, **State** $^1A_1$, **Symmetry** C_{2V}, **Dipole Moment** 2.02, **Energy** -76.31028 Hartree, **Gibbs free energy** -76.32792 **Hartree**, **O_3H_5** 0.959 Å, **$H_5O_3H_6$** 104.5^o.

Table S3 Energies and Selected Geometries of Minima and Transition States for the Interconversion of $^{\cdot}CH_2CHO$ to $CH_3{}^{\cdot}CO$.

Level of theory used –CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).

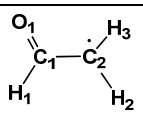
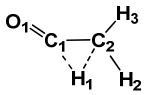
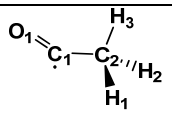
	 A	 TS A/B	 B
State	^{2}A	^{2}A	^{2}A
Symmetry	C_1	C_1	C_S
Energy (Hartree)	-152.87694	-152.81424	-152.89084
Energy Relative to A	0	165	-36
Gibbs free energy (Hartree 298 K)	-152.90193	-152.83891	-152.91647
Gibbs free energy relative to A	0	165	-38
Dipole Moment (Debye)	2.87	3.54	3.04
Bond Length (Å)			
C_1C_2	1.458	1.386	1.507
C_1O_1	1.190	1.193	1.184
C_1H_1	1.108	1.263	2.117
C_2H_1	—	1.497	1.087
C_2H_2	1.079	1.077	1.089
C_2H_3	1.078	1.090	1.087
O_2H_4	—	—	—
C_2O_2	—	—	—
Bond Angle (^{o})			
$O_1C_1C_2$	123.9	145.3	128.4
$H_1C_1C_2$	114.7	68.6	—
$H_2C_2C_1$	120.8	117.9	108.4
$H_3C_2C_1$	118.8	121.5	111.1
$H_1C_2C_1$		51.8	108.3
Dihedral Angle (^{o})			
$H_1C_1C_2O_1$	180.0	128.2	-121.7
$H_2C_2C_1O_1$	180.0	167.4	-121.9
$H_3C_2C_1O_1$	0.0	-8.5	-0.1

Table S4 Energies and Selected Geometries of Minima and Transition States for the Interconversion of $^{\cdot}CH_2OH$ to CH_3O^{-}.

Level of theory used –CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).

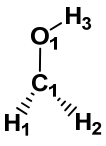
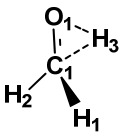
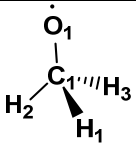
	 **A**	 **TS A/B**	 **B**
State	^{2}A	^{2}A'	^{2}A
Symmetry	C_1	C_S	C_1
Energy (Hartree)	-114.84812	-114.78575	-114.83503
Energy Relative to A	0	164	34
Gibbs free energy (Hartree 298 K)	-114.87107	-114.80858	-114.85794
Gibbs free energy relative to A	0	164	34
Dipole Moment (Debye)	1.61	2.00	1.93
Bond Length (Å)			
C_1O_1	1.362	1.369	1.371
C_1H_1	1.075	1.085	1.099
C_1H_2	1.079	1.085	1.099
C_1H_3	—	1.232	1.099
O_1H_3	0.959	1.219	—
C_2O_2	—	—	—
C_2H_4	—	—	—
Bond Angle (^{o})			
$H_1C_1O_1$	113.3	118.1	104.9
$H_2C_1O_1$	118.6	118.1	104.9
$H_3C_1O_1$	—	55.6	104.9
$H_3O_1C_1$	109.3	56.5	—
$H_4C_2O_2$	—	—	—
Dihedral Angle (^{o})			
$H_2C_1O_1H_1$	151.0	154.3	116.5
$H_3C_1O_1H_1$	174.4	-102.8	-116.5

Table S5 Energies and Selected Geometries of Minima and Transition States for Reaction between doublet HCHO and $^{\cdot}CH_2OH$.
Level of theory used –CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). Relative energies in kJ mol^{-1} with respect to [A+B] (0 kJ mol^{-1}).

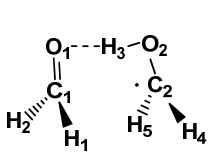
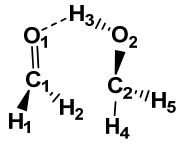
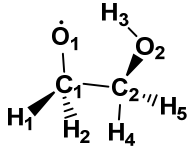
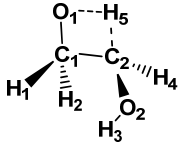
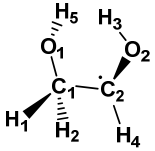
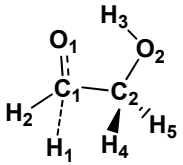
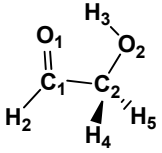
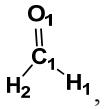
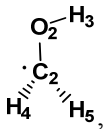
							
	9	**TS 9/10**	**10**	**TS 10/11**	**11**	**TS 10/[2+C]**	**2**
State	^{2}A	^{2}A	^{2}A	^{2}A	^{1}A	^{1}A	^{1}A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-229.162601	-229.14674	-229.16596	-229.12052	-229.18269	-229.13142	-228.64510
Energy Relative to [A+B]	-21	21	-30	89	-74	61	25 **[2+C]**
Gibbs free energy (Hartree 298 K)	-229.19395	-229.17452	-229.19354	-229.14802	-229.21035	-229.15873	-228.67167
Gibbs free energy relative to [A+B]	12	63	13	133	-31	105	71 **[2+C]**
Dipole Moment (Debye)	3.42	2.17	1.72	1.82	1.66	2.41	2.21
Bond Length (Å)							
C_1C_2	3.552	1.962	1.519	1.495	1.485	1.520	
C_1O_1	1.214	1.225	1.374	1.429	1.430	1.211	
C_2O_2	1.356	1.336	1.411	1.377	1.358	1.395	
O_1H_3	1.900	2.290	2.415	—	2.272	2.109	
O_2H_3	0.970	0.969	0.963	0.962	0.967	0.969	
C_1H_1	1.098	1.106	1.101	1.092	1.095	1.588	
C_1H_2	1.098	1.106	1.096	1.089	1.091	1.107	
C_2H_4	1.076	1.082	1.089	1.085	1.079	1.090	
C_2H_5	1.081	1.084	1.094	1.281	—	1.100	
O_1H_5	—	—	—	1.331	0.963	—	See structure **2** in **Supplementary Table 1**
Bond Angle (^{o})							
$O_1C_1C_2$	70.6	101.1	112.2	89.1	110.4	120.4	
$H_1C_1O_1$	121.3	121.2	103.8	112.9	104.1	98.7	
$H_2C_1O_1$	121.0	121.6	111.2	112.7	112.0	121.5	
$O_2C_2C_1$	64.5	103.6	111.0	121.0	116.6	110.9	
$H_3O_2C_2$	108.5	107.4	106.9	109.2	106.8	105.7	
$H_4C_2O_2$	114.1	113.0	107.1	111.0	113.5	109.9	
$H_5C_2O_2$	118.4	118.0	111.2	113.9	—	112.1	
$H_5O_1C_1$	—	—	—	84.1	107.3	—	

Table S5 Continued.

Dihedral Angle (°)							
$O_2C_2C_1O_1$	59.0	54.2	57.5	112.1	48.8	22.3	
$H_1C_1C_2O_1$	-156.6	-122.3	-114.6	-114.8	-115.4	-104.6	
$H_2C_1C_2O_1$	124.2	123.7	126.4	114.9	124.4	163.2	See structure **2** in
$H_3O_2C_2C_1$	-34.5	-53.4	-53.0	-26.5	-25.0	-21.7	**Supplementary**
$H_4C_2C_1O_1$	152.1	173.4	175.8	-105.7	-164.6	145.1	**Table 1**
$H_5C_2C_1O_1$	-71.0	-65.9	-65.6	-1.8	—	-98.8	
$H_5O_1C_1C_2$	—	—	—	1.7	65.0	—	



, **[A],** See structure **A** in **Supplementary Table 1.**



, **[B], State** ^{2}A, **Symmetry** C_1, **Dipole Moment** 1.30, **Energy** -114.84812 Hartree, **C_2H_4** 1.075 Å, **C_2H_4** 1.079 Å, **C_2O_2** 1.362 Å, **O_2H_3** 0.959 Å, **$H_3O_2C_2$** 109.3°, **$H_4C_2O_2$** 113.3°, **$H_5C_2O_2$** 118.6°, **$H_5C_2O_2H_4$** 151.0°, **$H_3O_2C_2H_4$** -174.4°.

, **[C]**, **Energy** -0.49982 Hartree.

Table S6 Energies and Selected Geometries of Minima and Transition States for Reaction between HCHO and $^{\cdot}CH(OH)CH_2OH$.
Level of theory used – CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). Relative energies in kJ mol^{-1} with respect to [A+11] (0 kJ mol^{-1}).

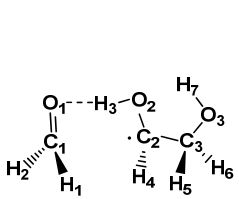
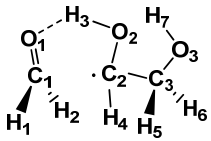
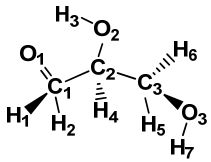
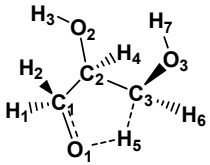
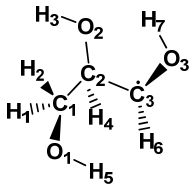
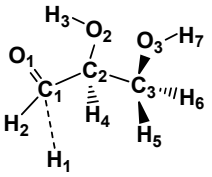
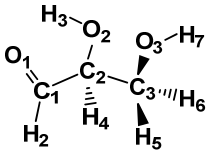
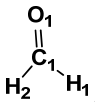
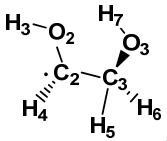
							
	B	**TS B/12**	**12**	**TS 12/14**	**14**	**TS 12/[13+C]**	**13**
State	^2A	^2A	^2A	^2A	^2A	^2A	^2A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-343.49510	-343.48318	-343.49535	-343.46952	-343.51334	-343.46668	-342.98028
Energy Relative to [A+11]	-16	16	-16	52	-63	59	24 **[13+C]**
Gibbs free energy (Hartree 298 K)	-343.53102	-343.51440	-343.52655	-343.50011	-343.54537	-343.49747	-343.01044
Gibbs free energy relative to [A+11]	18	61	30	99	-20	106	72 **[13+C]**
Dipole Moment (Debye)	3.35	2.00	1.18	3.86	1.63	2.06	2.66
Bond Length (Å)							
C_1C_2	3.494	1.947	1.534	1.528	1.533	1.527	1.509
C_1O_1	1.215	1.231	1.377	1.403	1.410	1.208	1.212
C_2O_2	1.362	1.343	1.421	1.415	1.435	1.401	1.404
C_2C_3	1.483	1.495	1.517	1.526	1.483	1.516	—
C_3O_3	1.422	1.405	1.412	1.381	1.354	1.414	1.410
O_1H_3	1.877	2.018	2.495	—	—	2.021	2.057
O_2H_3	0.971	0.977	0.962	0.961	0.962	0.973	0.970
C_1H_1	1.098	1.105	1.091	1.093	1.091	1.635	—
C_2H_4	1.084	1.089	1.095	1.092	1.093	1.102	1.100
C_3H_5	1.088	1.089	1.089	1.221	—	1.091	1.090
O_1H_5	—	—	—	1.361	0.963	—	—
Bond Angle (^{o})							
$O_1C_1C_2$	72.0	100.7	108.1	103.1	111.7	119.9	121.7
$H_1C_1O_1$	121.3	121.4	113.2	108.6	106.1	102.6	—
$H_2C_1O_1$	121.0	121.2	107.6	112.4	112.0	122.1	121.7

Table S6 Continued

$O_2C_2C_1$	66.4	101.4	111.2	115.6	109.1	109.2	110.3
$H_3O_2C_2$	109.0	106.1	109.3	109.5	108.8	105.2	106.1
$H_4C_2C_1$	81.4	94.0	108.5	110.1	108.7	104.3	107.4
$C_3C_2C_1$	148.5	110.3	111.7	100.8	111.8	114.5	110.2
$H_5C_3C_2$	109.8	109.8	110.2	94.7	—	110.4	110.3
$H_5O_1C_1$	—	—	—	—	107.2	—	—
Dihedral Angle (°)							
$O_2C_2C_1O_1$	53.9	46.6	64.4	-156.3	177.5	19.1	5.9
$H_1C_1C_2O_1$	-157.5	-122.0	-124.2	-117.3	-117.4	-108.0	—
$C_3C_2C_1O_1$	149.5	166.7	-178.3	-39.3	-65.0	141.1	126.2
$O_3C_3C_2O_2$	57.8	45.4	59.8	37.8	39.2	56.5	61.8
$H_5C_3C_2O_2$	176.5	165.4	178.7	152.3	—	175.0	-179.9
$H_5O_1C_1C_2$	—	—	—	—	60.1	—	106.1



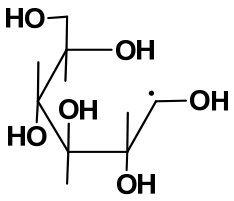
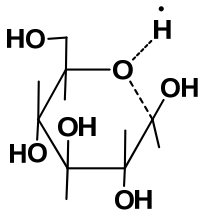
, **[A],** See structure **A** in **Supplementary Table 1.**



, **[11],** See structure **11** in **Supplementary Table 5.**

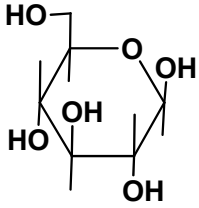
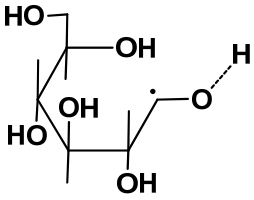

, **[C]**, **Energy** -0.49982 Hartree.

Table S7 Energies, Electronic Dipole Moments and Cartesian Coordinates of Minima and Transition States for the glucose cyclisation reactions. Level of theory used – MP2/6-31+G(d). Relative energies in kJ mol^{-1} with respect to 15 (0 kJ mol^{-1}).

		
	15	**TS 15/16**
Energy (Hartree)	-685.52800	-685.46115
Energy Relative to 15	0	176
Gibbs Free energy (Hartree, 298 K)	-685.567461	-685.498403
Gibbs Free energy Relative to 15	0	181
Dipole Moment (Debye)	5.01	4.88

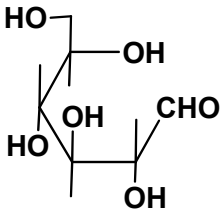
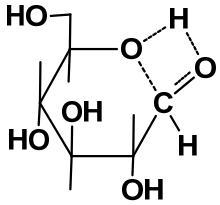
Coordinates	C	-0.074934	-0.093251	-0.088197	C	-0.016334	-0.075500	-0.119714
	C	-0.137629	0.035589	1.443521	C	-0.003981	0.110624	1.409004
	C	1.112763	-0.104368	2.308277	C	1.364192	0.051849	2.078046
	C	2.204406	0.852354	-0.765367	C	2.376595	0.686646	-0.315983
	C	0.718575	0.943538	-0.904241	C	0.977516	0.850514	-0.844978
	H	0.753503	-0.251212	3.340411	H	1.289269	0.485771	3.083555
	H	-0.821874	-0.764703	1.757058	H	-0.647569	-0.672336	1.840476
	H	-1.120366	0.014861	-0.412592	H	-1.025204	0.184399	-0.460690
	H	2.798340	1.759243	-0.705242	H	3.066395	1.497427	-0.556476
	H	0.477051	0.721351	-1.959963	H	0.968118	0.568174	-1.909165
	O	2.724136	-0.220095	-1.494379	O	2.871809	-0.597320	-0.505717
	O	0.284512	2.274219	-0.639529	H	3.480995	-0.808041	0.242571
	H	-0.254137	2.248130	0.178345	O	0.593806	2.215316	-0.788782
	O	0.336237	-1.432431	-0.394377	H	0.283297	2.386664	0.125572
	H	1.141176	-1.400312	-0.947044	O	0.200243	-1.446075	-0.464411
	O	-0.765143	1.295543	1.772575	H	1.154608	-1.549762	-0.657230
	H	-0.100283	1.804966	2.282058	O	-0.597921	1.407371	1.614655
	C	2.045473	-1.255181	2.000790	H	-0.475611	1.677460	2.544724
	H	2.511425	-1.125661	1.022209	C	1.940038	-1.367473	2.210849
	O	1.813863	1.148027	2.252203	H	1.540051	-2.035700	1.445188
	H	2.593290	1.051771	2.834661	O	2.272570	0.977742	1.382713
	O	3.040915	-1.179390	3.045982	H	2.839416	1.623538	2.137999
	H	3.734250	-1.839334	2.869957	O	3.376062	-1.282232	2.103238
	H	1.508926	-2.209801	2.034349	H	3.754977	-2.122753	2.420938
	H	3.697353	-0.202310	-1.460021	H	1.663383	-1.762453	3.197242

Table S7 Continued.

	 **16**	 **TS 15/[17+A]**
Energy (Hartree)	-685.03697	-685.48706
Energy Relative to 15	-19 **[16+A]**	107 **[17+A]**
Gibbs Free energy (Hartree, 298 K)	-685.074473	-685.526521
Gibbs Free energy Relative to 15	-14 **[16+A]**	107 **[17+A]**
Dipole Moment (Debye)	4.61	4.31

Coordinates						
C	-0.027433	-0.063723	-0.136165	C	0.079227	0.141189	-0.078835
C	-0.140119	-0.156176	1.387319	C	0.005696	-0.137440	1.441125
C	1.205029	-0.014088	2.097890	C	1.275951	-0.071372	2.300710
C	2.160146	1.143834	0.171494	C	1.784781	2.117504	-0.233780
C	0.818803	1.138786	-0.568823	C	0.407188	1.594396	-0.534480
H	1.021650	0.288843	3.137759	H	0.997432	-0.487238	3.282978
H	-0.605965	-1.117114	1.650306	H	-0.385990	-1.158319	1.531425
H	-1.039520	0.031258	-0.548271	H	-0.944941	-0.023706	-0.448926
H	1.018752	1.073414	-1.645103	H	1.865791	3.063834	0.316885
O	0.126110	2.362982	-0.370612	H	0.395240	1.550492	-1.644985
H	-0.262307	2.332435	0.528674	O	2.796858	1.591835	-0.738752
O	0.598330	-1.288312	-0.585337	H	2.580892	1.134357	-2.145095
H	0.284732	-1.482638	-1.488130	O	-0.598158	2.504681	-0.137822
O	-1.020886	0.932503	1.734168	H	-1.037817	2.136073	0.653014
H	-1.036463	1.025814	2.705436	O	0.949671	-0.833150	-0.633091
C	2.020707	-1.315638	2.168381	H	1.331326	-0.505855	-1.467273
H	2.069187	-1.832823	1.206476	O	-0.972670	0.751579	2.016626
O	1.959031	1.095698	1.582109	H	-0.496350	1.339621	2.630713
O	3.318686	-1.063555	2.685863	C	2.502710	-0.840919	1.826972
H	3.736481	-0.428403	2.070778	H	2.876407	-0.444987	0.881425
H	1.531345	-1.988005	2.881403	O	1.589741	1.318040	2.478652
O	3.035725	0.127261	-0.282534	H	2.419983	1.353033	2.985810
H	2.492499	-0.650505	-0.524678	O	3.467658	-0.650034	2.879302
H	2.667304	2.097223	0.015481	H	4.347825	-0.885589	2.550535
				H	2.263448	-1.904764	1.704465

Table S7 Continued.

		
	17	**TS 17/16**
Energy (Hartree)	-685.01847	-684.95944
Energy Relative to 15	30 **[17+A]**	185 **[TS 17/16 + A]**
Gibbs Free energy (Hartree, 298 K)	-685.05689	-684.99663
Gibbs Free energy Relative to 15	32 **[17+A]**	191 **[TS 17/16 + A]**
Dipole Moment (Debye)	2.93	5.25

Coordinates						
C	-0.119944	-0.097707	-0.120861	C -0.011323	-0.145808	-0.044767
C	-0.121495	0.027222	1.414079	C -0.001315	0.141403	1.461930
C	1.173531	-0.113458	2.199263	C 1.386161	0.100891	2.098665
C	2.128384	0.942605	-0.784170	C 2.272549	0.822264	-0.377296
C	0.619726	0.979856	-0.939724	C 0.828323	0.864215	-0.832308
H	0.890811	-0.078992	3.265001	H 1.386385	0.728048	2.999972
H	-0.805410	-0.754200	1.770715	H -0.628167	-0.617799	1.950676
H	-1.175405	-0.003100	-0.408160	H -1.050437	-0.081811	-0.387232
H	2.624173	1.901496	-0.564362	H 2.794204	1.776521	-0.527426
H	0.429683	0.726611	-1.994716	H 0.841674	0.541617	-1.881485
O	2.771304	-0.094476	-0.968524	O 2.963838	-0.310752	-0.607314
O	0.115314	2.289101	-0.725575	O 0.305333	2.183947	-0.826584
H	-0.342044	2.283270	0.141135	H -0.031889	2.368537	0.073357
O	0.294178	-1.411596	-0.497201	O 0.459601	-1.472260	-0.273149
H	1.219335	-1.350979	-0.814945	H 1.408226	-1.397042	-0.545777
O	-0.707911	1.307716	1.754284	O -0.604055	1.441435	1.618607
H	-0.024942	1.813665	2.239298	H -0.711846	1.641524	2.567018
C	1.990917	-1.376053	2.014050	C 1.818132	-1.296125	2.516610
H	2.403683	-1.440601	1.007190	H 1.888894	-1.962310	1.652329
O	1.961718	1.049897	1.897827	O 2.420744	0.699808	1.251330
H	2.809679	0.933937	2.374062	H 3.104993	-0.119410	0.737440
O	3.056499	-1.228819	2.977154	O 3.080226	-1.141520	3.171751
H	3.766821	-1.857852	2.758744	H 3.484768	-2.020222	3.283981
H	1.385599	-2.264482	2.228813	H 1.061710	-1.696371	3.206922

$\dot{H}$, **[A]**, **Energy** -0.49823 Hartree.

Table S8 Energies, Electronic Dipole Moments and Cartesian Coordinates of Minima and Transition States for the glucose/water cyclisation reactions. Level of theory used – MP2/6-31+G(d). Relative energies in kJ mol^{-1} with respect to [17+A] (0 kJ mol^{-1})

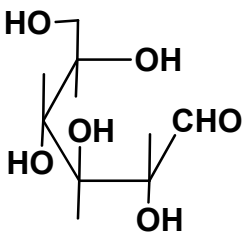
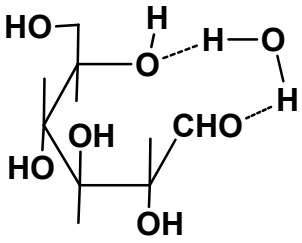
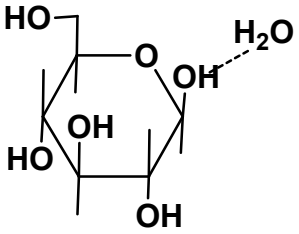
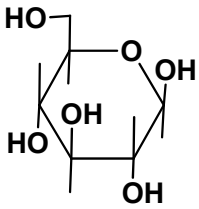
		
	17	**TS [17+A]/18**
Energy (Hartree)	-685.01847	-761.19365
Energy Relative to [17+A]	0 **[17+A]**	35
Gibbs Free energy (Hartree, 298 K)	-685.05689	-761.23106
Gibbs Free energy Relative to [17+A]	0 **[17+A]**	84
Dipole Moment (Debye)	2.93	2.75
Coordinates	See structure **17** in **Supplementary Table 7**	C -0.164858 -0.080499 -0.030955 C -0.078166 0.176516 1.478167 C 1.308912 -0.028308 2.076197 C 2.261897 0.445589 -0.369277 C 0.848411 0.760603 -0.816748 H 1.367135 0.509758 3.031208 H -0.775013 -0.511347 1.975830 H -1.173049 0.202492 -0.352993 H 2.966519 1.251047 -0.619125 H 0.791399 0.468108 -1.872128 O 2.668350 -0.802089 -0.621641 O 0.590906 2.155386 -0.766920 H 0.293109 2.373384 0.140393 O 0.002552 -1.471667 -0.288253 H 0.948858 -1.615065 -0.519103 O -0.512650 1.539979 1.661283 H -0.576104 1.739333 2.614085 C 1.704754 -1.475051 2.379683 H 1.875835 -2.055448 1.471005 O 2.295963 0.692052 1.239972 H 3.298271 0.276739 1.404806 O 2.833810 -1.512890 3.246141 H 3.632574 -1.441173 2.679862 H 0.873283 -1.933418 2.925449 H 3.680721 -0.883318 0.075064 O 4.328255 -0.648790 1.086141 H 5.237750 -0.344296 0.915002

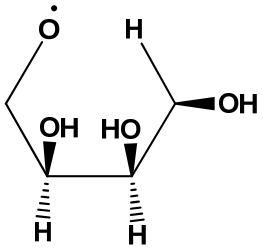
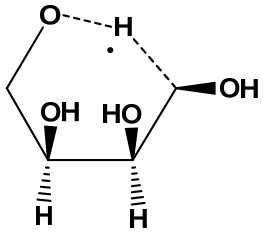
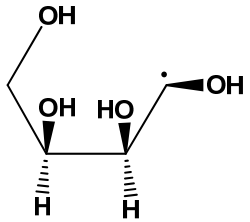
Table S8 Continued.

	 **18**	 **16**
Energy (Hartree)	-761.23460	-685.03697
Energy Relative to [17+A]	-72	-49 **[16+A]**
Gibbs Free energy (Hartree, 298 K)	-761.27370	-685.074473
Gibbs Free energy Relative to [17+A]	-28	-46 **[16+A]**
Dipole Moment (Debye)	3.57	4.61

Coordinates	C	-0.232015	-0.064774	-0.034189	See structure **16** in **Supplementary Table 7**
	C	-0.119449	0.170888	1.475751	
	C	1.294297	-0.029818	2.019430	
	C	2.217220	0.455863	-0.216643	
	C	0.831952	0.738729	-0.787826	
	H	1.377027	0.503895	2.975901	
	H	-0.809542	-0.515517	1.985079	
	H	-1.221944	0.275355	-0.356442	
	H	2.936998	1.181269	-0.609905	
	H	0.831835	0.435674	-1.840384	
	O	2.567644	-0.869491	-0.589529	
	O	0.576484	2.137067	-0.766405	
	H	0.274158	2.362719	0.138344	
	O	-0.151804	-1.462410	-0.316165	
	H	0.778497	-1.674779	-0.533959	
	O	-0.549955	1.536548	1.671875	
	H	-0.485335	1.760366	2.619186	
	C	1.658837	-1.483830	2.333207	
	H	1.711180	-2.102132	1.435195	
	O	2.281662	0.651768	1.199116	
	H	4.225234	0.308533	1.431046	
	O	2.868980	-1.556599	3.084879	
	H	3.620934	-1.430748	2.472863	
	H	0.877720	-1.893723	2.982267	
	H	3.487467	-1.025071	-0.281370	
	O	4.775481	-0.460751	1.165842	
	H	5.705986	-0.230387	1.332938	

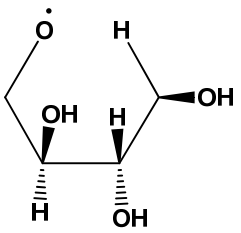
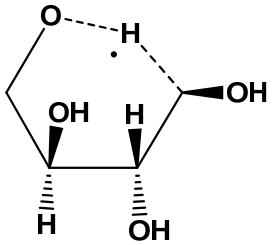
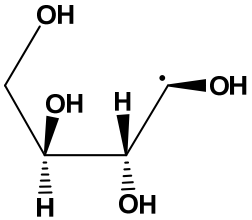
H_2O, **[A], State** $^1A_1$, **Symmetry** C_{2V}, **Dipole Moment** 2.33, **Energy** -76.18854 Hartree, **Gibbs free energy** -76.20620 Hartree, **OH** 0.971 Å, **HOH** 105.5°.

Table S9 Energies, Electronic Dipole Moments and Cartesian Coordinates of Minima and Transition States for the H Transfer Reactions of D and F. Level of theory used – MP2/6-311+G(d). Relative energies in kJ mol^{-1} with respect to D (0 kJ mol^{-1}).

	 D	 TS	
Energy (Hartree)	-457.367238	-457.34613	-457.38444
Energy Relative to D	0	56	-44
Gibbs Free energy (Hartree, 298 K)	-457.401167	-457.37891	-457.41805
Gibbs Free energy Relative to D	0	60	-43
Dipole Moment (Debye)	1.27	2.62	4.04

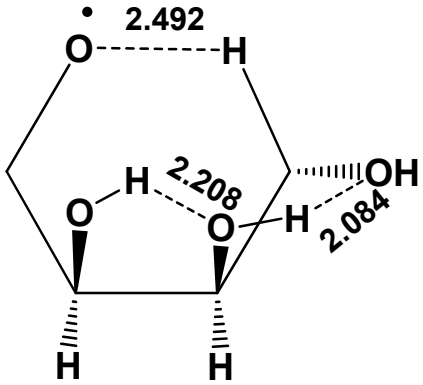
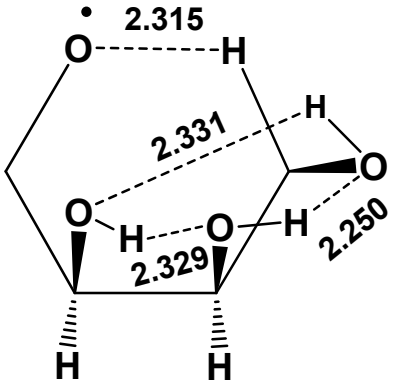
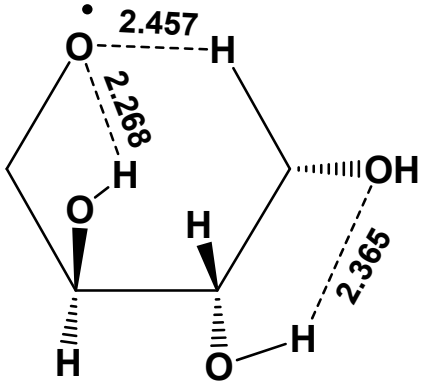
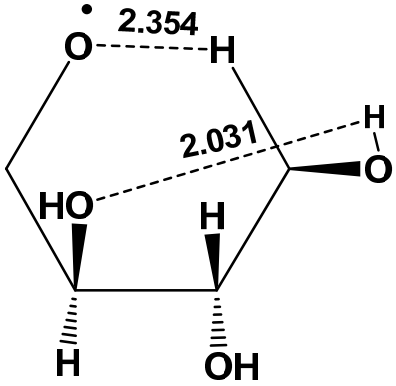
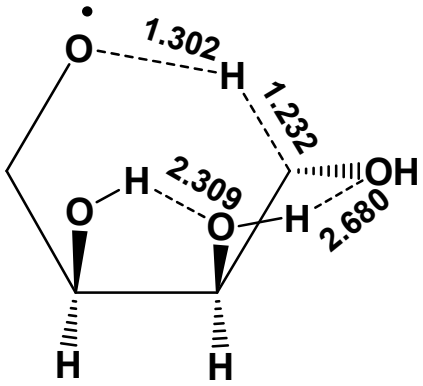
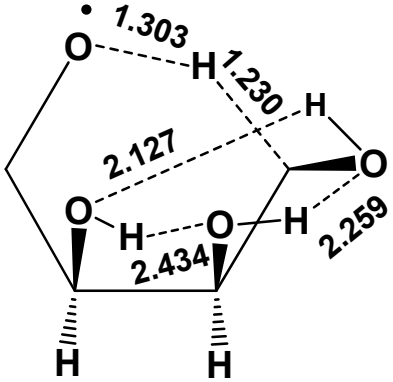
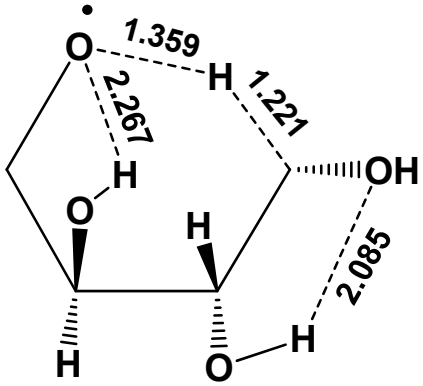
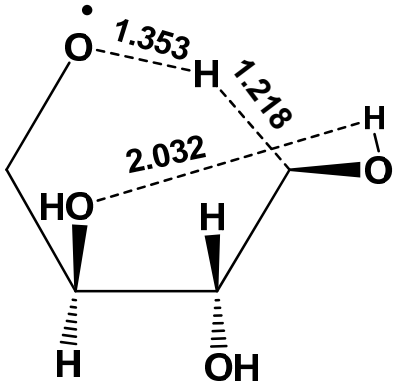
Coordinates	C	0.211348	-0.892052	-1.312047	C	0.214669	-0.890065	-1.326386	C	0.207431	-0.798371	-1.323510
	H	0.049941	1.860065	-1.537202	H	0.308675	1.813080	-1.705877	H	0.129904	1.685684	-1.641494
	C	1.186236	-0.197219	-0.350346	C	1.201773	-0.215532	-0.372057	C	1.251880	-0.154277	-0.408981
	C	0.754819	1.178351	0.144072	C	0.652299	1.139393	0.055026	C	0.903055	1.226440	0.035667
	O	0.738535	2.126441	-0.912661	O	0.778135	2.126895	-0.915756	O	0.504423	2.150045	-0.869350
	H	-0.208013	1.133352	0.663903	H	-0.544672	0.902276	0.212110	H	-1.386914	0.766518	0.219076
	H	1.503841	1.541961	0.852657	H	1.043607	1.520944	0.999723	H	1.383909	1.668845	0.902792
	C	-1.221358	-0.964868	-0.810533	C	-1.165856	-0.936128	-0.682958	C	-1.178156	-0.940045	-0.712978
	H	-1.296718	-1.514060	0.140548	H	-1.142186	-1.653293	0.151377	H	-1.092051	-1.542851	0.202876
	H	-1.826185	-1.532188	-1.538218	H	-1.888166	-1.290353	-1.429058	H	-1.805708	-1.485691	-1.419605
	O	-1.857859	0.253618	-0.700901	O	-1.609466	0.327641	-0.271725	O	-1.852446	0.280743	-0.472601
	O	2.440513	-0.087289	-1.022927	O	2.459980	0.085654	-1.028970	O	2.457075	-0.195790	-1.216658
	H	2.552788	0.843111	-1.263153	H	2.627535	0.855305	-1.172244	H	3.093159	0.437269	-0.863338
	H	1.334903	-0.852022	0.519387	H	1.336507	-0.847895	0.514697	H	1.392710	-0.784373	0.479838
	H	0.576117	-1.922183	-1.448446	H	0.550065	-1.914287	-1.539970	H	0.568933	-1.809517	-1.562747
	O	0.165250	-0.227571	-2.566948	O	0.133849	-0.137490	-2.535834	O	0.095177	-0.031321	-2.524763
	H	1.070673	-0.206073	-2.902531	H	0.994021	-0.217850	-2.968038	H	0.962251	-0.065595	-2.951010

Table S9 Continued.

	 F	 TS	
Energy (Hartree)	-457.36126	-457.34530	-457.38197
Energy Relative to F	16	58	-38
Gibbs Free energy (Hartree, 298 K)	-457.39673	-457.37848	-457.41608
Gibbs Free energy Relative to F	13	61	-38
Dipole Moment (Debye)	3.62	2.45	2.58

Coordinates	C	-0.054940	-1.174262	-0.591902	C	2.421221	-0.426394	-1.353006	C	2.382573	-0.391840	-1.314481
	H	-1.052385	1.323964	-0.051217	H	-0.652461	1.597170	-0.572200	H	-0.906381	1.333181	-0.470584
	C	0.960679	-0.046055	-0.764492	C	1.007362	-0.182034	-0.820771	C	0.954817	-0.160268	-0.805526
	C	0.839601	1.084251	0.258845	C	1.008427	1.000937	0.140543	C	0.826922	0.972314	0.169675
	O	-0.286069	1.907595	0.020957	O	-0.215314	1.621566	0.291137	O	-0.423551	1.470622	0.358464
	H	0.839278	0.675105	1.277493	H	1.417900	0.760605	1.121842	H	1.411133	0.954339	1.082899
	H	1.716807	1.731876	0.165068	H	1.850788	1.744256	-0.337907	H	2.667539	2.227305	-0.635851
	C	0.123177	-1.947269	0.716760	C	2.944588	0.874088	-1.966530	C	2.996685	0.840558	-1.972016
	H	1.157365	-2.297438	0.824103	H	2.301370	1.198893	-2.792064	H	2.283176	1.295679	-2.665807
	H	-0.507515	-2.857584	0.685987	H	3.961922	0.701163	-2.343623	H	3.893049	0.547442	-2.521931
	O	-0.316458	-1.295318	1.847087	O	3.055042	1.843303	-0.960275	O	3.443832	1.771799	-0.987276
	H	0.108541	-1.883681	-1.416030	H	2.402182	-1.224376	-2.103562	H	2.336067	-1.198711	-2.057900
	O	-1.346580	-0.580184	-0.693340	O	3.257343	-0.858659	-0.293207	O	3.198310	-0.848310	-0.249691
	H	-2.013536	-1.177832	-0.336774	H	3.662328	-0.069725	0.093869	H	3.692023	-0.080889	0.073729
	O	2.229781	-0.693320	-0.669621	O	0.127312	0.181047	-1.889162	O	0.072085	0.163165	-1.893127
	H	2.907174	-0.111045	-1.029292	H	-0.328402	-0.599545	-2.218142	H	-0.253053	-0.650587	-2.291597
	H	0.810649	0.385503	-1.763844	H	0.649029	-1.081797	-0.303709	H	0.619261	-1.097466	-0.328338

Table S10 H-bonding Characteristics Changes from Reactants to Transition States of the H transfer reactions for C, D, E and F Structures in Scheme 5.

C	D	E	F
			
Reactant	**Reactant**	**Reactant**	**Reactant**
			
TS	**TS**	**TS**	**TS**