Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPLEMENTARY MATERIAL

Modeling the mechanism of glycosylation reactions between ethanol, 1,2-ethanediol and methoxymethanol

Luis Miguel Azofra,[†,*] Ibon Alkorta,[†] Alejandro Toro-Labbé[‡] and José Elguero[†]

[†]Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006, Madrid, Spain

[‡]Laboratorio de Química Teórica Computacional, QTC, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, E-6094411, Santiago de Chile, Chile

*Author to whom correspondence should be addressed.

Fax: +34 91 564 48 53

e-mail: luisazofra@iqm.csic.es

URL: http://are.iqm.csic.es

Table SI1. Cartesian coordinates of all the TS structures for the hydroxylic interchange. Optimized at B3LYP/6-311+G(d,p) computational level.

$CH_3CH_2OH + OH^-$ 'in-out'

C	0.057468000	-0.645718000	0.024080000
H	0.073909000	-1.546279000	-0.557425000
H	0.116146000	-0.715763000	1.093265000
O	-1.920460000	-0.826011000	0.123981000
H	-2.059641000	-1.686810000	0.537008000
O	2.051874000	-0.763270000	0.113926000
H	2.359151000	-0.701105000	-0.798810000
C	-0.006374000	0.707243000	-0.631431000
H	-1.020314000	1.107529000	-0.556225000
H	0.704368000	1.383372000	-0.151501000
H	0.260105000	0.641265000	-1.691902000

$CH_3CH_2OH + OH^-$ 'out-out'

C	-0.034430000	-0.267801000	0.000000000
H	0.883330000	-0.822898000	0.000000000
H	-0.974647000	-0.785476000	0.000000000
O	-0.017254000	-0.383587000	-1.996297000
H	0.094589000	-1.325298000	-2.174503000
O	-0.017254000	-0.383587000	1.996297000
H	0.094589000	-1.325298000	2.174503000
C	-0.024751000	1.232981000	0.000000000

H	-0.525544000	1.601505000	-0.897991000
H	-0.525544000	1.601505000	0.897991000
H	1.000366000	1.612727000	0.000000000

$CH_2OHCH_2OH + OH^-$ 'in-out'

C	0.086747000	-0.567978000	-0.071502000
H	0.327240000	-1.410865000	-0.696346000
H	-0.060898000	-0.724070000	0.977893000
O	-1.798365000	-0.714020000	-0.397895000
H	-1.918008000	-1.654102000	-0.563175000
O	2.047329000	-0.662367000	0.594781000
H	2.612455000	-0.692474000	-0.187377000
C	0.177784000	0.829875000	-0.656637000
H	-0.174878000	1.545988000	0.100944000
H	1.215987000	1.066041000	-0.880282000
O	-0.577807000	0.961095000	-1.859449000
H	-1.355480000	0.389926000	-1.654751000

$CH_2OHCH_2OH + OH^-$ 'out-out'

C	0.037218000	-0.565681000	-0.024444000
H	1.090024000	-0.681607000	-0.213950000
H	-0.567073000	-1.432933000	0.153381000
O	-0.186913000	-1.030798000	-2.034935000
H	-0.208705000	-1.995093000	-2.061038000
O	0.256514000	-0.365812000	1.869777000
H	1.152414000	-0.681069000	2.024599000
C	-0.600378000	0.791612000	-0.267499000
H	-0.412129000	1.076252000	-1.300919000
H	-1.688120000	0.695621000	-0.133239000
O	-0.078483000	1.804770000	0.590407000
H	0.138859000	1.280156000	1.397860000

$CH_3OCH_2OH + OH^-$ 'in-in'

C	-0.033785000	-0.628295000	0.000000000
H	-0.680619000	-1.480880000	0.000000000
H	1.034451000	-0.709881000	0.000000000
O	-0.653817000	0.575687000	0.000000000
C	0.255841000	1.664594000	0.000000000
H	0.876411000	1.623733000	-0.901639000
H	-0.340612000	2.580345000	0.000000000
H	0.876411000	1.623733000	0.901639000
O	0.215925000	-0.825866000	1.981499000
H	-0.654809000	-0.626580000	2.346455000
O	0.215925000	-0.825866000	-1.981499000
H	-0.654809000	-0.626580000	-2.346455000

$CH_3OCH_2OH + OH^-$ 'in-out'

C	-0.099477000	-0.508887000	-0.074008000
H	-0.804251000	-1.313379000	-0.090257000
H	0.962514000	-0.651965000	-0.093516000
O	-0.630954000	0.725984000	-0.074661000
C	0.327246000	1.751850000	0.129877000
H	1.065569000	1.743735000	-0.681329000

H	-0.215266000	2.700091000	0.120065000
H	0.810557000	1.602352000	1.099834000
O	0.018274000	-0.649673000	1.932245000
H	0.594706000	-1.405305000	2.100012000
O	0.166649000	-0.763518000	-2.071405000
H	-0.644218000	-0.408899000	-2.455499000

$CH_3OCH_2OH + OH^-$ 'in-out'

C	0.094411000	-0.595783000	0.000000000
H	0.782158000	-1.414924000	0.000000000
H	-0.971364000	-0.705793000	0.000000000
O	0.650025000	0.614947000	0.000000000
C	-0.293627000	1.672832000	0.000000000
H	-0.909764000	1.614461000	0.903665000
H	0.275281000	2.605002000	0.000000000
H	-0.909764000	1.614461000	-0.903665000
O	-0.068869000	-0.753001000	-2.031144000
H	-0.649174000	-1.506547000	-2.199069000
O	-0.068869000	-0.753001000	2.031144000
H	-0.649174000	-1.506547000	2.199069000

Table SI2. Cartesian coordinates of all the TS structures for the model glycosylation reactions. Optimized at B3LYP/6-311+G(d,p) computational level.

$CH_3CH_2OH + CH_2OHCH_2O^-$

C	0.05254700	-0.26901400	0.00000000
H	-0.78721500	-0.94607700	0.00000000
H	1.05868200	-0.65953200	0.00000000
O	0.05254700	-0.38743500	1.98062900
H	0.07237700	-1.33948200	2.15010200
O	0.05254700	-0.38743500	-1.98062900
C	-0.15575200	1.22068900	0.00000000
H	0.29505800	1.65568300	0.90157200
H	0.29505800	1.65568300	-0.90157200
H	-1.22786700	1.46211600	0.00000000
C	0.24542751	-1.78189656	-2.23197352
H	-0.55532024	-2.33791312	-1.79089685
H	1.17508862	-2.09595764	-1.80536381
C	0.26760609	-2.03136248	-3.75147175
H	1.20754054	-2.46097689	-4.02869854
H	-0.52286861	-2.70293284	-4.01423209
O	0.08845521	-0.79133241	-4.44076878
H	-0.00559721	-0.08052527	-3.80240575

$CH_3CH_2OH + CH_3OCH_2O^-$

C	0.05254700	-0.26901400	0.00000000
H	-0.78721500	-0.94607700	0.00000000
H	1.05868200	-0.65953200	0.00000000
O	0.05254700	-0.38743500	1.98062900
H	0.07237700	-1.33948200	2.15010200
O	0.05254700	-0.38743500	-1.98062900
C	-0.15575200	1.22068900	0.00000000
H	0.29505800	1.65568300	0.90157200

H	0.29505800	1.65568300	-0.90157200
H	-1.22786700	1.46211600	0.00000000
C	0.24542751	-1.78189656	-2.23197352
H	-0.55532024	-2.33791312	-1.79089685
H	1.17508862	-2.09595764	-1.80536381
O	0.26602191	-2.01354349	-3.64293616
C	0.45887976	-3.40788047	-3.89498818
H	-0.34183996	-3.96411348	-3.45413359
H	0.47421660	-3.58068505	-4.95083067
H	1.38856886	-3.72215753	-3.46859854

$CH_2OHCH_2OH + CH_3CH_2O^-$

C	0.34966100	0.54336500	-0.00663500
H	0.47544900	0.84928600	-1.03683100
H	0.68166200	1.19517000	0.78508800
O	2.33613200	-0.02002400	-0.11002200
O	-1.39955400	1.28622900	0.13851500
H	-1.47865400	1.82125400	-0.66044500
C	-0.04729100	-0.89658300	0.28068500
H	0.69354800	-1.55761700	-0.17986700
H	-0.02168900	-1.05697800	1.37470900
O	-1.33583500	-1.21769700	-0.24335200
H	-1.78571900	-0.33647300	-0.17857300
C	3.04429491	1.21660125	0.00898760
H	2.80133363	1.67826908	0.94318920
H	2.76435384	1.86658494	-0.79354227
C	4.55951998	0.94840393	-0.05235717
H	4.80248032	0.48673567	-0.98655881
H	4.83946131	0.29842034	0.75017270
H	5.08940413	1.87371093	0.03669197

$CH_2OHCH_2OH + CH_2OHCH_2O^-$

C	0.34966100	0.54336500	-0.00663500
H	0.47544900	0.84928600	-1.03683100
H	0.68166200	1.19517000	0.78508800
O	2.33613200	-0.02002400	-0.11002200
O	-1.39955400	1.28622900	0.13851500
H	-1.47865400	1.82125400	-0.66044500
C	-0.04729100	-0.89658300	0.28068500
H	0.69354800	-1.55761700	-0.17986700
H	-0.02168900	-1.05697800	1.37470900
O	-1.33583500	-1.21769700	-0.24335200
H	-1.78571900	-0.33647300	-0.17857300
C	3.04429491	1.21660125	0.00898760
H	2.80133363	1.67826908	0.94318920
H	2.76435384	1.86658494	-0.79354227
C	4.55951998	0.94840393	-0.05235717
H	5.01841636	1.28584141	0.85342982
H	4.98143671	1.47415837	-0.88330154
O	4.78935268	-0.45424792	-0.20934349
H	3.94789081	-0.91523977	-0.24141279

$CH_2OHCH_2OH + CH_3OCH_2O^-$

C	0.34966100	0.54336500	-0.00663500
H	0.47544900	0.84928600	-1.03683100

H	0.68166200	1.19517000	0.78508800
O	2.33613200	-0.02002400	-0.11002200
O	-1.39955400	1.28622900	0.13851500
H	-1.47865400	1.82125400	-0.66044500
C	-0.04729100	-0.89658300	0.28068500
H	0.69354800	-1.55761700	-0.17986700
H	-0.02168900	-1.05697800	1.37470900
O	-1.33583500	-1.21769700	-0.24335200
H	-1.78571900	-0.33647300	-0.17857300
C	3.04429491	1.21660125	0.00898760
H	2.80133363	1.67826908	0.94318920
H	2.76435384	1.86658494	-0.79354227
O	4.45128962	0.96756088	-0.04797540
C	5.16007670	2.20383331	0.07098402
H	4.91739808	2.66563050	1.00519515
H	6.21276738	2.01696227	0.02830432
H	4.88041559	2.85394980	-0.73153589

$CH_3OCH_2OH + CH_3CH_2O^-$

C	-0.00036600	-0.62508300	0.02985700
H	-0.00074800	-1.48133900	0.68195800
H	-0.00036700	-0.70520100	-1.04479800
O	0.00006000	0.58272500	0.65110200
C	0.00111900	1.67221500	-0.25916700
H	-0.90528900	1.63403400	-0.88372200
H	0.00148000	2.59210400	0.34151100
H	0.90795100	1.63281100	-0.88301900
O	1.96695100	-0.83341200	-0.21102600
O	-1.96785300	-0.83209100	-0.21108700
H	-2.33110800	-0.64497100	0.66581900
C	2.50402114	-0.55935240	1.08564165
H	2.23645898	0.43400053	1.37985322
H	2.10750759	-1.25930107	1.79115484
C	4.03817672	-0.68649419	1.04319618
H	4.44004003	-0.48142672	2.01342977
H	4.30573861	-1.67984756	0.74898585
H	4.43469035	0.01345301	0.33768157

$CH_3OCH_2OH + CH_2OHCH_2O^-$

C	-0.00036600	-0.62508300	0.02985700
H	-0.00074800	-1.48133900	0.68195800
H	-0.00036700	-0.70520100	-1.04479800
O	0.00006000	0.58272500	0.65110200
C	0.00111900	1.67221500	-0.25916700
H	-0.90528900	1.63403400	-0.88372200
H	0.00148000	2.59210400	0.34151100
H	0.90795100	1.63281100	-0.88301900
O	1.96695100	-0.83341200	-0.21102600
O	-1.96785300	-0.83209100	-0.21108700
H	-2.33110800	-0.64497100	0.66581900
C	2.50402114	-0.55935240	1.08564165
H	2.23645898	0.43400053	1.37985322
H	2.10750759	-1.25930107	1.79115484
C	4.03817672	-0.68649419	1.04319618
H	4.48124039	0.24796671	1.31774564
H	4.35228964	-1.44533394	1.72904989

O	4.45082157	-1.03926307	-0.27974688
H	3.67942962	-1.11800286	-0.84574556

$CH_3OCH_2OH + CH_3OCH_2O^-$

C	-0.00036600	-0.62508300	0.02985700
H	-0.00074800	-1.48133900	0.68195800
H	-0.00036700	-0.70520100	-1.04479800
O	0.00006000	0.58272500	0.65110200
C	0.00111900	1.67221500	-0.25916700
H	-0.90528900	1.63403400	-0.88372200
H	0.00148000	2.59210400	0.34151100
H	0.90795100	1.63281100	-0.88301900
O	1.96695100	-0.83341200	-0.21102600
O	-1.96785300	-0.83209100	-0.21108700
H	-2.33110800	-0.64497100	0.66581900
C	2.50402114	-0.55935240	1.08564165
H	2.23645898	0.43400053	1.37985322
H	2.10750759	-1.25930107	1.79115484
O	3.92859418	-0.67741263	1.04622800
C	4.46632759	-0.40346461	2.34264431
H	4.07007587	-1.10339359	3.04832412
H	5.53224206	-0.49192645	2.31263004
H	4.19902463	0.58990825	2.63702414

Table SI3. Cartesian coordinates of all the TS structures for the model glycosylation reactions with a bare H_2O molecule. Optimized at B3LYP/6-311+G(d,p) computational level.

$CH_3CH_2OH + CH_2OHCH_2O^- + H_2O$

C	0.05254700	-0.26901400	0.00000000
H	-0.78721500	-0.94607700	0.00000000
H	1.05868200	-0.65953200	0.00000000
O	0.05254700	-0.38743500	1.98062900
H	0.07237700	-1.33948200	2.15010200
O	0.05254700	-0.38743500	-1.98062900
C	-0.15575200	1.22068900	0.00000000
H	0.29505800	1.65568300	0.90157200
H	0.29505800	1.65568300	-0.90157200
H	-1.22786700	1.46211600	0.00000000
C	0.24542751	-1.78189656	-2.23197352
H	-0.55532024	-2.33791312	-1.79089685
H	1.17508862	-2.09595764	-1.80536381
C	0.26760609	-2.03136248	-3.75147175
H	1.20754054	-2.46097689	-4.02869854
H	-0.52286861	-2.70293284	-4.01423209
O	0.08845521	-0.79133241	-4.44076878
H	-0.00559721	-0.08052527	-3.80240575
O	-0.38200652	-0.46800740	4.83075473
H	-0.29903673	-0.49875626	3.83467716
H	-0.28529234	-1.35696960	5.18002909

$CH_3CH_2OH + CH_3OCH_2O^- + H_2O$

C	0.216395000	-0.361766000	0.119161000
H	-0.530062000	-1.138562000	0.248343000
H	1.252023000	-0.631922000	0.018022000
O	0.466499000	-0.448042000	2.108644000
H	0.733480000	-1.350229000	2.258931000
O	-0.011395000	-0.530596000	-1.836506000
C	-0.187359000	1.098479000	0.134992000
H	0.287839000	1.594385000	0.949422000
H	0.080100000	1.578062000	-0.805045000
H	-1.292377000	1.193421000	0.265084000
C	0.236372000	-1.775522000	-2.148115000
H	-0.493125000	-2.520398000	-1.654746000
H	1.221087000	-2.086017000	-1.889194000
O	-0.526624000	-0.273521000	4.605947000
H	-0.132976000	-0.307714000	3.704117000
O	0.100995000	-1.980117000	-3.603885000
C	0.379845000	-3.327164000	-3.961040000
H	-0.344296000	-4.032984000	-3.482877000
H	0.247940000	-3.356521000	-5.102284000
H	1.381608000	-3.629921000	-3.715685000
H	-1.233280000	-0.936035000	4.542553000

$CH_2OHCH_2OH + CH_3CH_2O^- + H_2O$

C	0.34966100	0.54336500	-0.00663500
H	0.47544900	0.84928600	-1.03683100
H	0.68166200	1.19517000	0.78508800
O	2.33613200	-0.02002400	-0.11002200
O	-1.39955400	1.28622900	0.13851500
H	-1.47865400	1.82125400	-0.66044500
C	-0.04729100	-0.89658300	0.28068500
H	0.69354800	-1.55761700	-0.17986700
H	-0.02168900	-1.05697800	1.37470900
O	-1.33583500	-1.21769700	-0.24335200
H	-1.78571900	-0.33647300	-0.17857300
C	3.04429491	1.21660125	0.00898760
H	2.80133363	1.67826908	0.94318920
H	2.76435384	1.86658494	-0.79354227
C	4.55951998	0.94840393	-0.05235717
H	4.80248032	0.48673567	-0.98655881
H	4.83946131	0.29842034	0.75017270
O	-4.07409800	2.35280784	0.64879007
H	-3.13915924	1.99906450	0.62130996
H	5.08940413	1.87371093	0.03669197
H	-4.05701461	3.30970100	0.57353291

$CH_2OHCH_2OH + CH_2OHCH_2O^- + H_2O$

C	0.34966100	0.54336500	-0.00663500
H	0.47544900	0.84928600	-1.03683100
H	0.68166200	1.19517000	0.78508800
O	2.33613200	-0.02002400	-0.11002200
O	-1.39955400	1.28622900	0.13851500
H	-1.47865400	1.82125400	-0.66044500
C	-0.04729100	-0.89658300	0.28068500
H	0.69354800	-1.55761700	-0.17986700
H	-0.02168900	-1.05697800	1.37470900
O	-1.33583500	-1.21769700	-0.24335200

H	-1.78571900	-0.33647300	-0.17857300
C	3.04429491	1.21660125	0.00898760
H	2.80133363	1.67826908	0.94318920
H	2.76435384	1.86658494	-0.79354227
C	4.55951998	0.94840393	-0.05235717
H	5.01841636	1.28584141	0.85342982
H	4.98143671	1.47415837	-0.88330154
O	4.78935268	-0.45424792	-0.20934349
H	3.94789081	-0.91523977	-0.24141279
O	-4.07409800	2.35280784	0.64879007
H	-3.13915924	1.99906450	0.62130996
H	-4.05701461	3.30970100	0.57353291

$CH_2OHCH_2OH + CH_3OCH_2O^- + H_2O$

C	0.34966100	0.54336500	-0.00663500
H	0.47544900	0.84928600	-1.03683100
H	0.68166200	1.19517000	0.78508800
O	2.33613200	-0.02002400	-0.11002200
O	-1.39955400	1.28622900	0.13851500
H	-1.47865400	1.82125400	-0.66044500
C	-0.04729100	-0.89658300	0.28068500
H	0.69354800	-1.55761700	-0.17986700
H	-0.02168900	-1.05697800	1.37470900
O	-1.33583500	-1.21769700	-0.24335200
H	-1.78571900	-0.33647300	-0.17857300
C	3.04429491	1.21660125	0.00898760
H	2.80133363	1.67826908	0.94318920
H	2.76435384	1.86658494	-0.79354227
O	-4.07409800	2.35280784	0.64879007
H	-3.13915924	1.99906450	0.62130996
O	4.45128962	0.96756088	-0.04797540
C	5.16007670	2.20383331	0.07098402
H	4.91739808	2.66563050	1.00519515
H	6.21276738	2.01696227	0.02830432
H	4.88041559	2.85394980	-0.73153589
H	-4.05701461	3.30970100	0.57353291

$CH_3OCH_2OH + CH_3CH_2O^- + H_2O$

C	0.05989200	-0.50925000	0.05863800
H	0.07242400	-1.32629300	0.75461100
H	0.08400400	-0.64737000	-1.00429600
O	-0.07580200	0.71575800	0.60673700
C	-0.24178600	1.74510300	-0.35669300
H	-1.12840000	1.53132900	-0.96181100
H	-0.37713400	2.67833100	0.19473500
H	0.65145600	1.81692100	-0.98777400
O	2.01264900	-0.59257400	-0.07966200
O	-1.91975900	-0.88967900	-0.28489400
H	-2.34815700	-0.74382400	0.56743300
C	2.62413300	-0.52948100	1.14491800
H	2.53284200	0.47303500	1.62428700
H	2.17316500	-1.23973800	1.88427600
C	4.12346800	-0.86416100	1.05356700
H	4.61130000	-0.81466300	2.03837200
H	4.25985100	-1.87090800	0.64441500
H	4.62431700	-0.15971200	0.38051100

O	-2.83207773	0.43894496	-2.33782676
H	-2.49301675	-0.05483483	-1.57485941
H	-2.33417841	0.15450489	-3.15708869

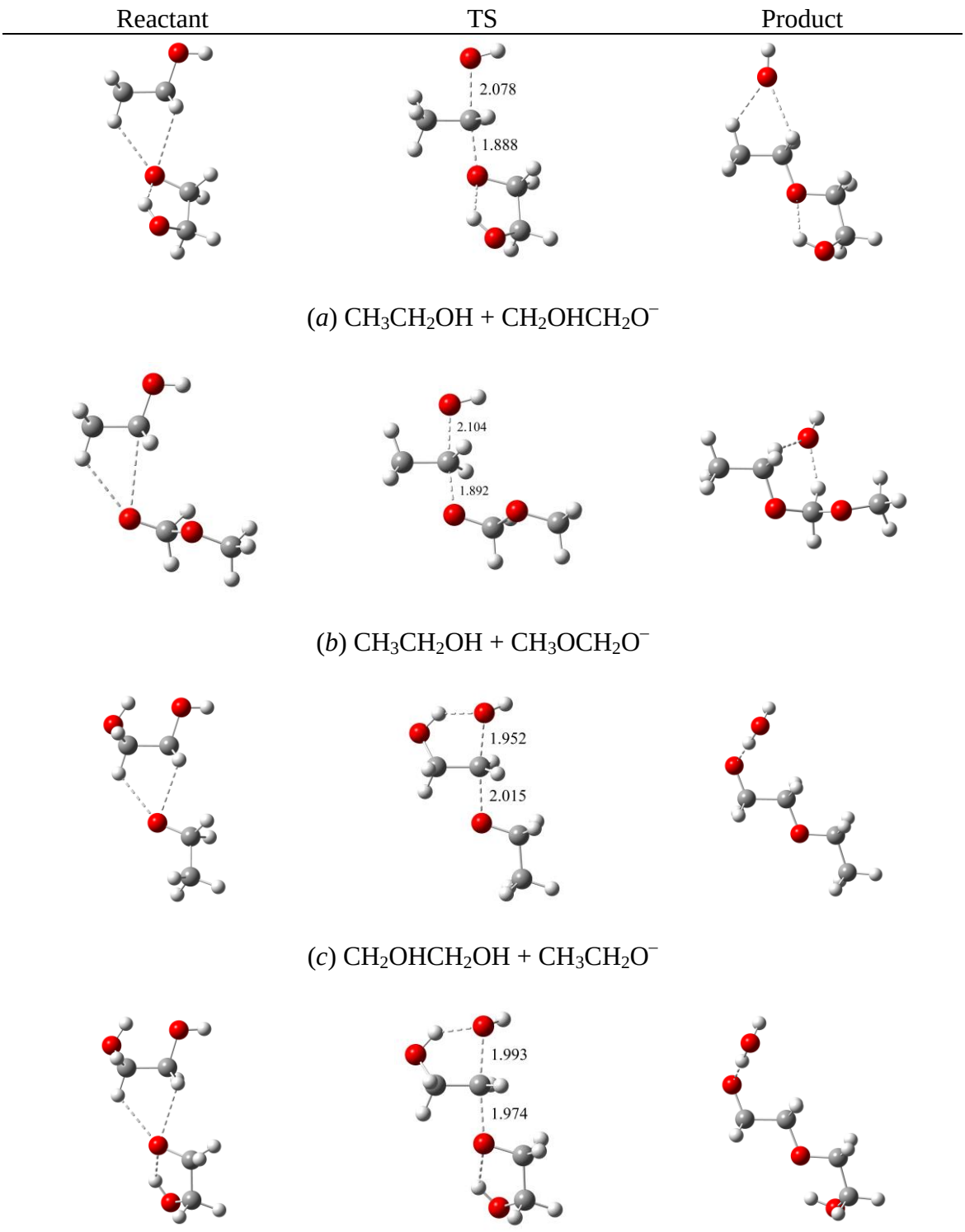
$CH_3OCH_2OH + CH_2OHCH_2O^- + H_2O$

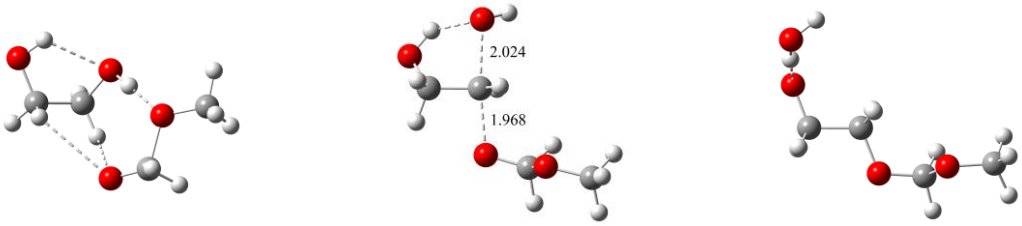
C	-0.00036600	-0.62508300	0.02985700
H	-0.00074800	-1.48133900	0.68195800
H	-0.00036700	-0.70520100	-1.04479800
O	0.00006000	0.58272500	0.65110200
C	0.00111900	1.67221500	-0.25916700
H	-0.90528900	1.63403400	-0.88372200
H	0.00148000	2.59210400	0.34151100
H	0.90795100	1.63281100	-0.88301900
O	1.96695100	-0.83341200	-0.21102600
O	-1.96785300	-0.83209100	-0.21108700
H	-2.33110800	-0.64497100	0.66581900
C	2.50402114	-0.55935240	1.08564165
H	2.23645898	0.43400053	1.37985322
H	2.10750759	-1.25930107	1.79115484
O	-4.45602141	-1.04790509	-0.74283861
H	-3.51778179	-0.99516586	-0.40089565
C	4.03817672	-0.68649419	1.04319618
H	4.48124039	0.24796671	1.31774564
H	4.35228964	-1.44533394	1.72904989
O	4.45082157	-1.03926307	-0.27974688
H	3.67942962	-1.11800286	-0.84574556
H	-5.20487151	-1.25913762	-0.18051811

$CH_3OCH_2OH + CH_3OCH_2O^- + H_2O$

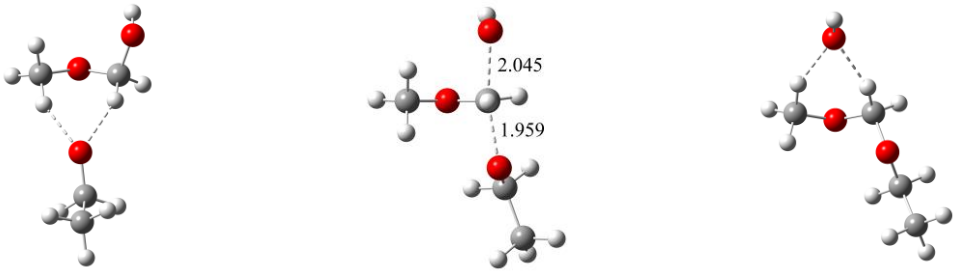
C	0.39313200	-0.49016200	-0.08308100
H	0.62881200	-1.40914800	0.41642000
H	0.26865300	-0.43665600	-1.14622900
O	0.06352700	0.53633400	0.71262800
C	-0.57210300	1.60805500	0.02252700
H	-1.47361100	1.21681100	-0.45703600
H	-0.82469900	2.35982000	0.77319100
H	0.11220500	2.04248400	-0.71578700
O	2.27050900	-0.10226200	-0.40628400
O	-1.59442700	-1.21266900	-0.40755400
H	-1.90605800	-1.56032400	0.43660400
C	2.97431600	0.12818400	0.69025300
H	3.93588200	0.64984900	0.47535500
H	2.42851200	0.71507100	1.46524700
O	3.36505600	-1.13415100	1.37561100
C	4.02095000	-0.89044900	2.58513300
H	3.38934900	-0.33520800	3.30148300
H	4.28283100	-1.85415700	3.03305700
H	4.95324600	-0.31057200	2.44939000
O	-3.89386893	-0.05190709	-1.17819004
H	-3.12967002	-0.61893113	-0.87080793
H	-3.83965833	0.07411014	-2.52055310

Figure SI1. Stationary points (minima and TS) for all the model glycoylation reactions, calculated at B3LYP/6-311+G(d,p) computational level. All minima and TS present C_1 symmetry. The C···O distances in the penta-coordinated TS are shown in Å.

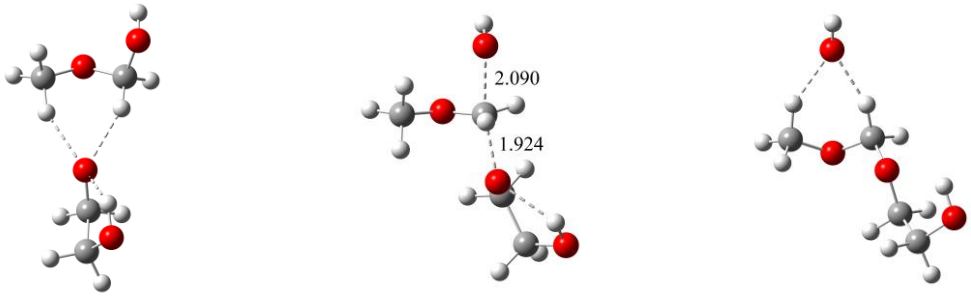




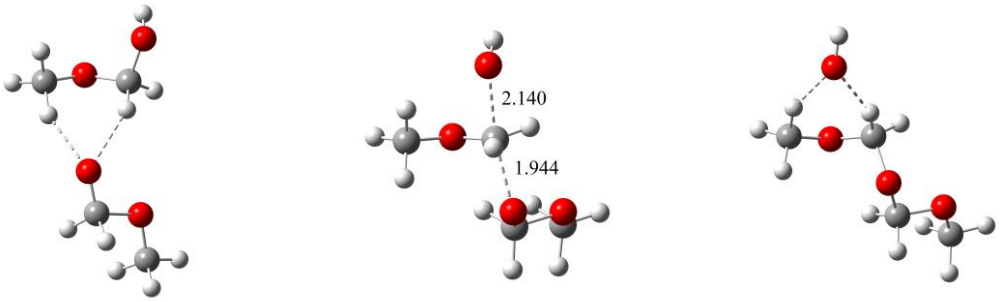
(*e*) $CH_2OHCH_2OH + CH_3OCH_2O^-$



(*f*) $CH_3OCH_2OH + CH_3CH_2O^-$

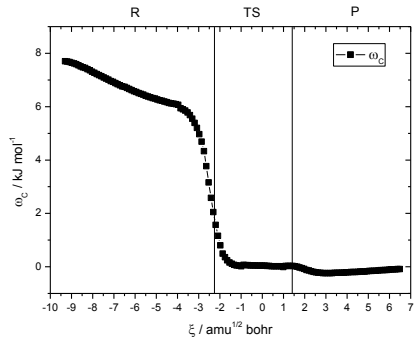


(*g*) $CH_3OCH_2OH + CH_2OHCH_2O^-$

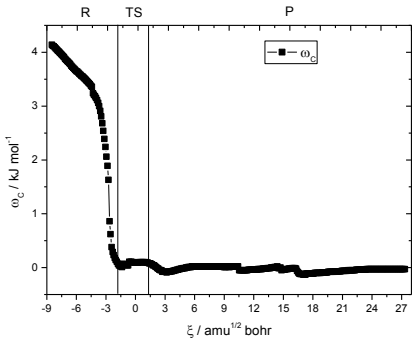


(*h*) $CH_3OCH_2OH + CH_3OCH_2O^-$

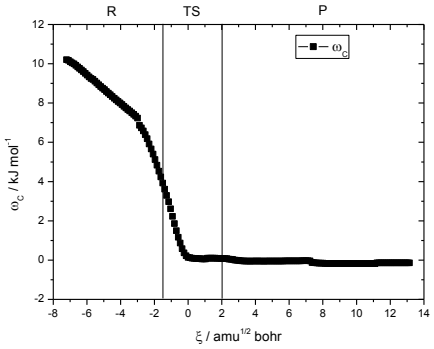
Figure SI2. Local electrophilicity index in kJ mol^{-1} in the reactive carbon atom of the substrates *vs*. the reaction coordinate in $amu^{½}$ bohr of all the glycosylation reaction models, calculated at B3LYP/6-311+G(d,p) computational level.



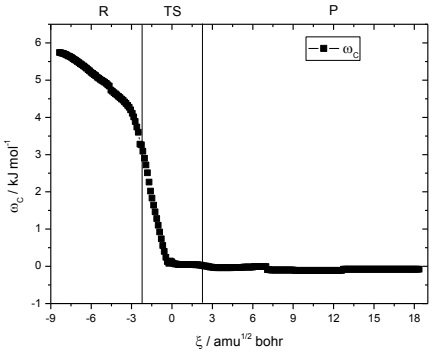
(*a*) $CH_3CH_2OH + CH_2OHCH_2O^-$



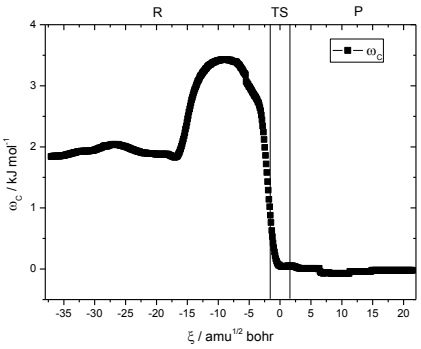
(*b*) $CH_3CH_2OH + CH_3OCH_2O^-$



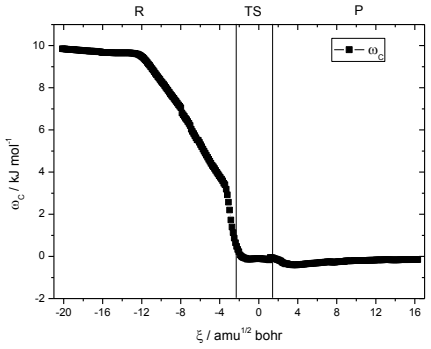
(*c*) $CH_2OHCH_2OH + CH_3CH_2O^-$



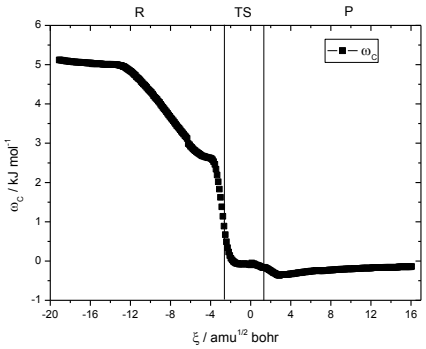
(*d*) $CH_2OHCH_2OH + CH_2OHCH_2O^-$



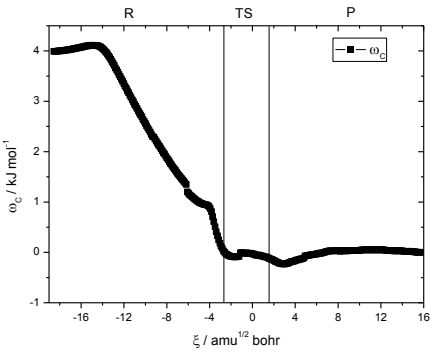
(*e*) $CH_2OHCH_2OH + CH_3OCH_2O^-$



(*f*) $CH_3OCH_2OH + CH_3CH_2O^-$

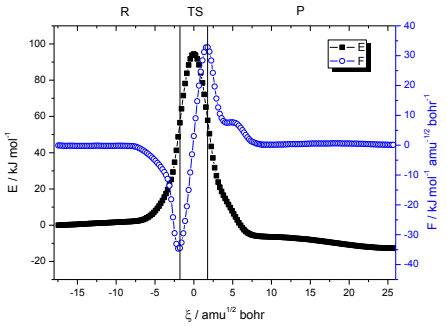


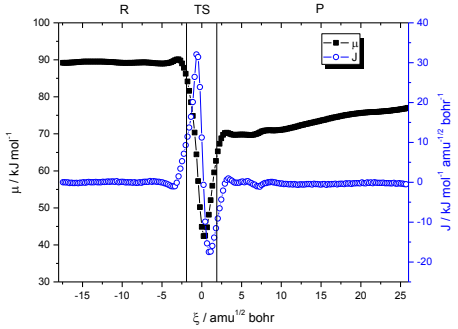
(*g*) $CH_3OCH_2OH + CH_2OHCH_2O^-$



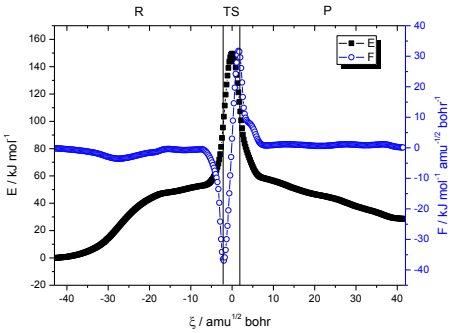
(*h*) $CH_3OCH_2OH + CH_3OCH_2O^-$

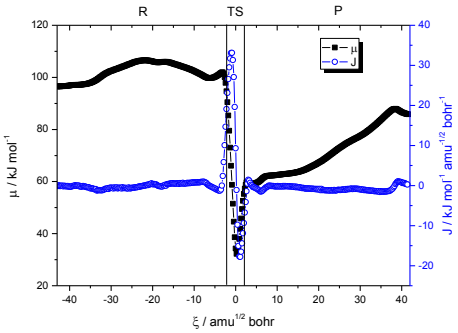
Figure SI3. Energy (black squares) in kJ mol^{-1} and reaction force (blue circles) in kJ mol^{-1} $amu^{-½}$ $bohr^{-1}$ profiles *vs.* the reaction coordinate in $amu^{½}$ bohr (left). Electronic chemical potential (black squares) in kJ mol^{-1} and REF (blue circles) in kJ mol^{-1} $amu^{-½}$ $bohr^{-1}$ profiles *vs.* the reaction coordinate in $amu^{½}$ bohr (right) of all the glycosylation reaction models in presence of one H_2O molecule, calculated at B3LYP/6-311+G(d,p) computational level.



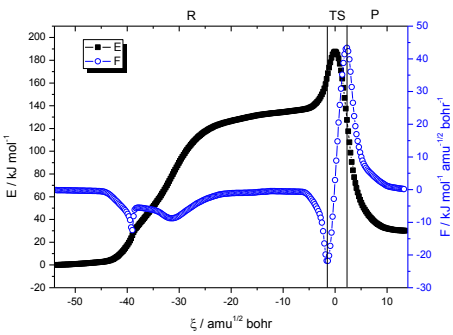


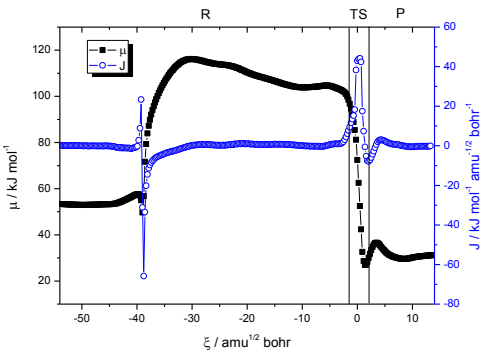
(*a*) $CH_3CH_2OH + CH_2OHCH_2O^- + H_2O$



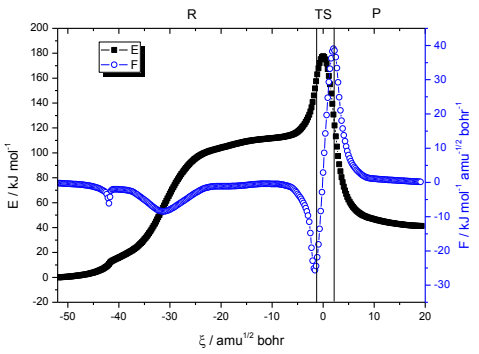


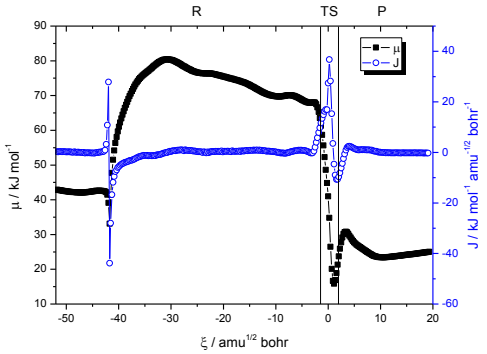
(*b*) $CH_3CH_2OH + CH_3OCH_2O^- + H_2O$



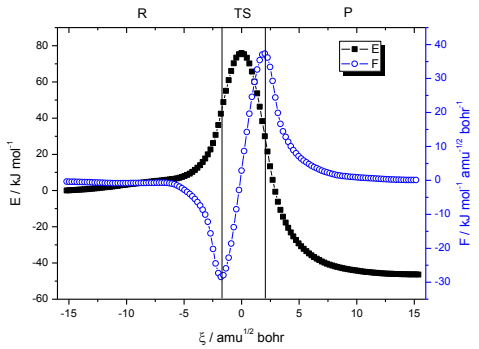


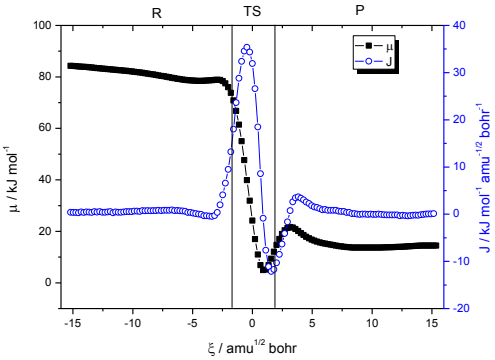
(*c*) $CH_2OHCH_2OH + CH_3CH_2O^- + H_2O$



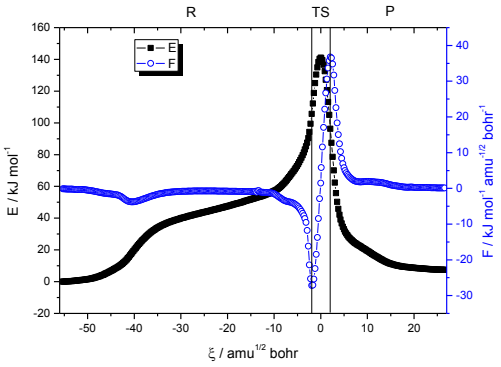


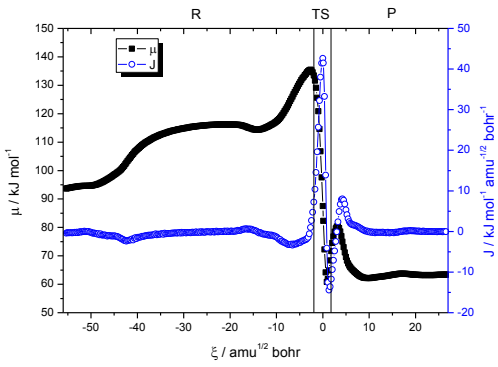
(*d*) $CH_2OHCH_2OH + CH_2OHCH_2O^- + H_2O$



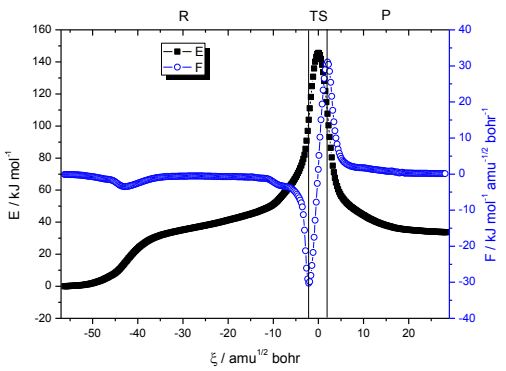


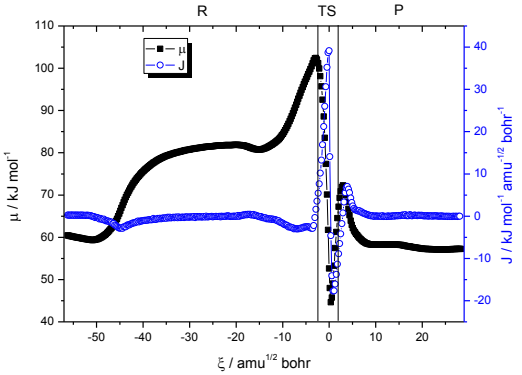
(*e*) $CH_2OHCH_2OH + CH_3OCH_2O^- + H_2O$



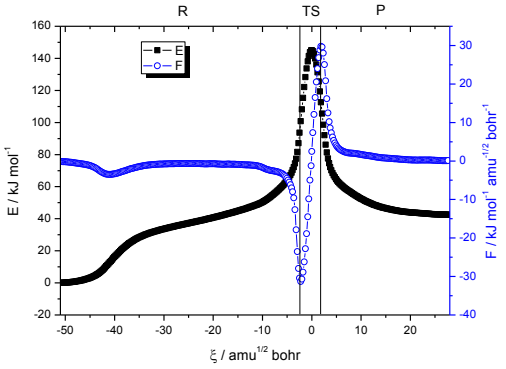


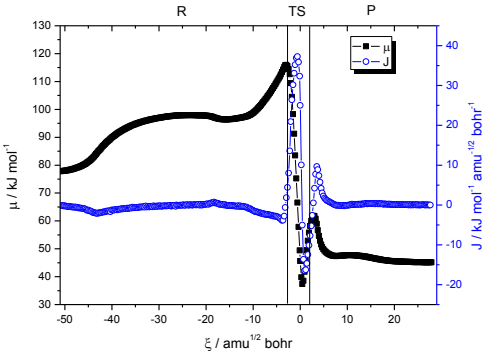
(*f*) $CH_3OCH_2OH + CH_3CH_2O^- + H_2O$





(*g*) $CH_3OCH_2OH + CH_2OHCH_2O^- + H_2O$





(*h*) $CH_3OCH_2OH + CH_3OCH_2O^- + H_2O$