Supporting Information of "Understanding the importance of carbenium ions in the conversion of biomass-derived alcohols with first principles calculations"

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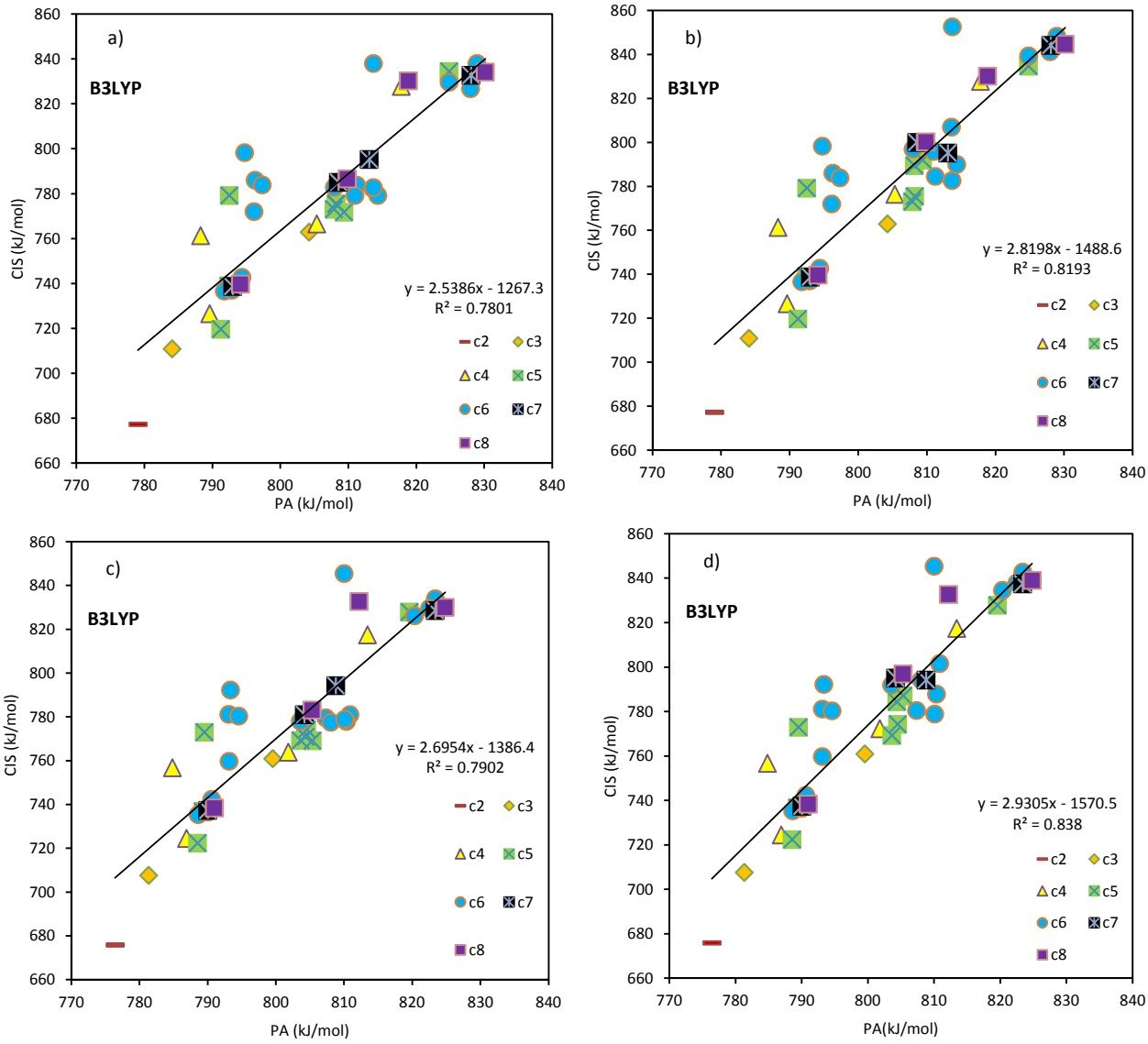
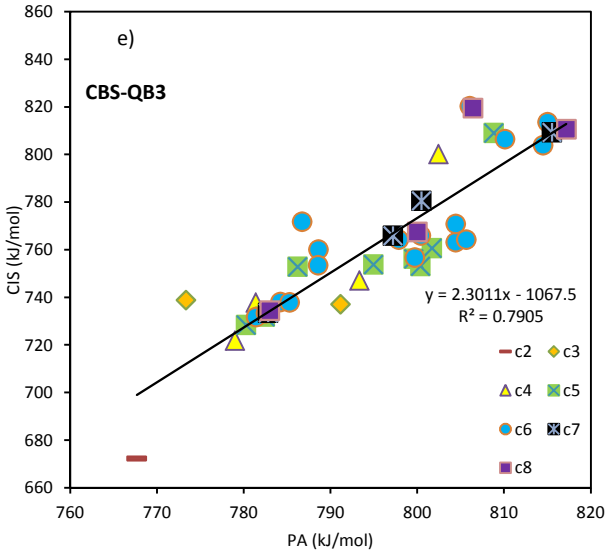
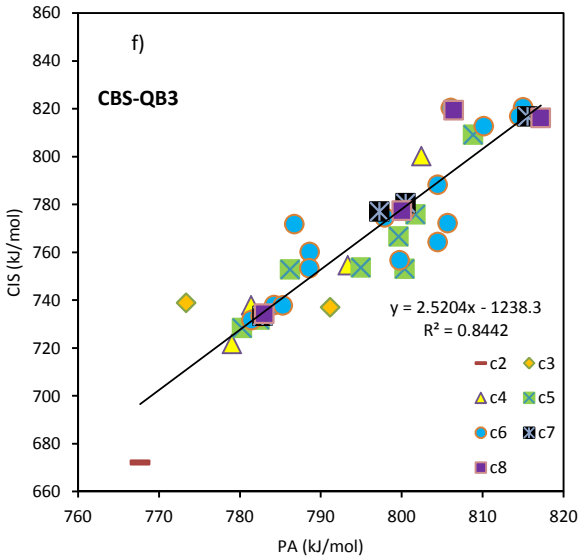
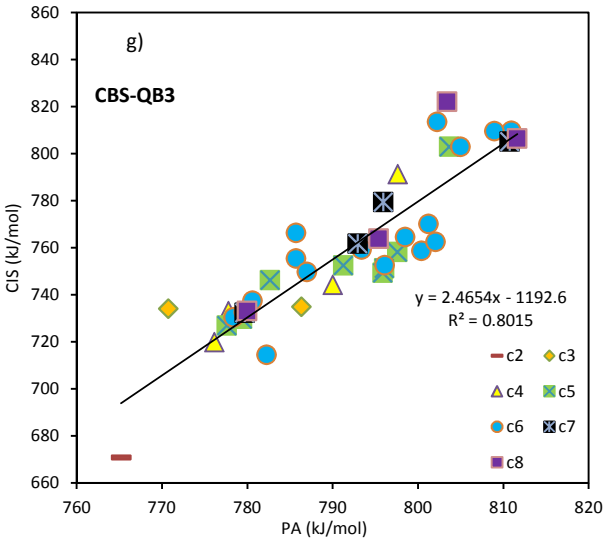
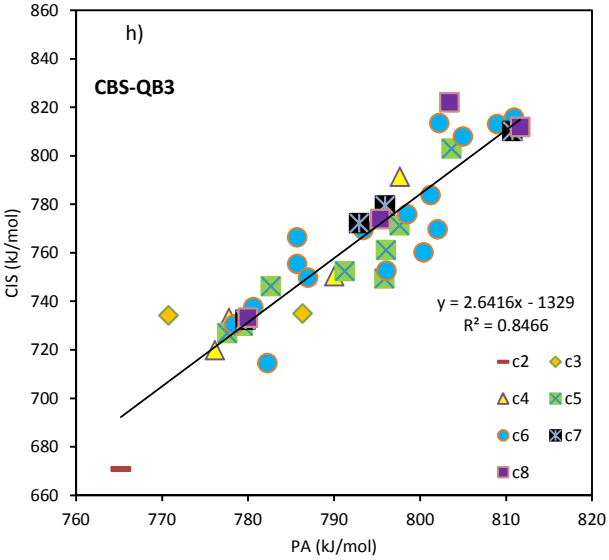
S01: CIS vs PA for the complete set of alcohols investigated using B3LYP/6-311G*, CBS-QB3 and G4 methods. Three sets of four graphs correspond to calculations for higher- and lower-stability alkene isomers, in terms of Gibbs Free Energy (G) and Enthalpy (H), respectively, at the three levels of theory considered. (a) CIS vs. PA considering the less stable alkene isomers in terms of Gibbs free energy. (b) CIS vs. PA considering for the most stable alkene isomers in terms of Gibbs free energy. (c) CIS vs. PA for the less stable alkene isomers & (d) CIS vs. PA for most stable isomers, both calculated in terms of enthalpy. Remaining data presented in (e)-(h) and (i)-(l) follow an identical format for the CBS-QB3 and G4 computational methods, respectively.

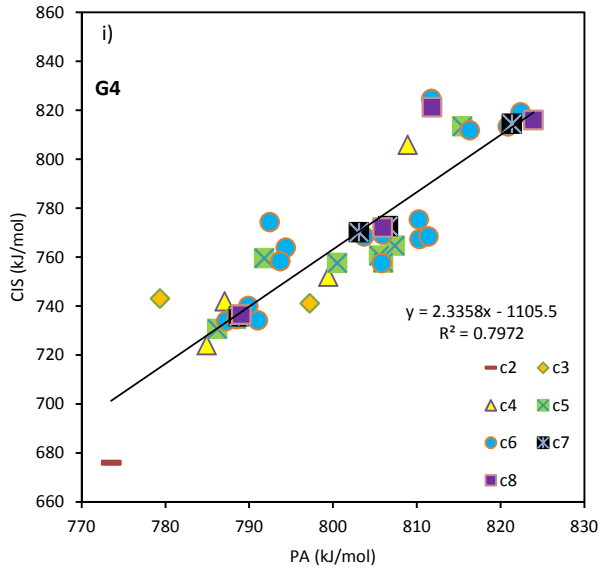


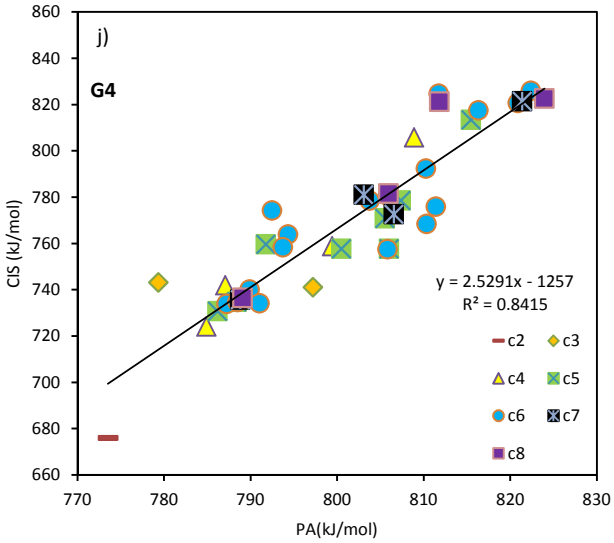

e)
CBS-QB3
CIS (kJ/mol)
PA (kJ/mol)
y = 2.3011x - 1067.5
R² = 0.7905
c2
c3
c4
c5
c6
c7
c8

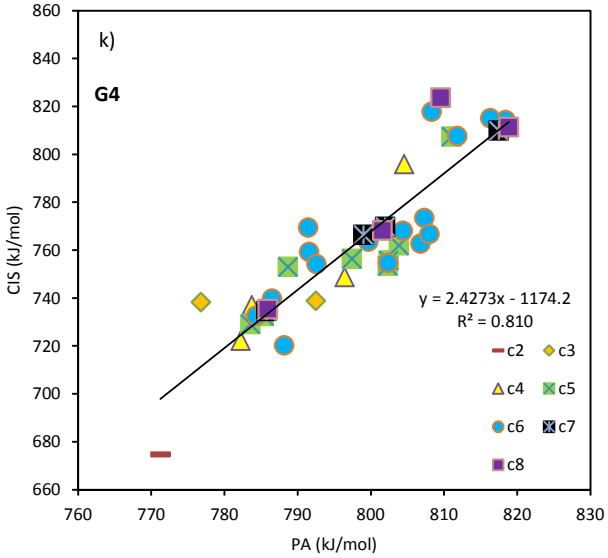

f)
CBS-QB3
CIS (kJ/mol)
PA (kJ/mol)
y = 2.5204x - 1238.3
R² = 0.8442
c2
c3
c4
c5
c6
c7
c8

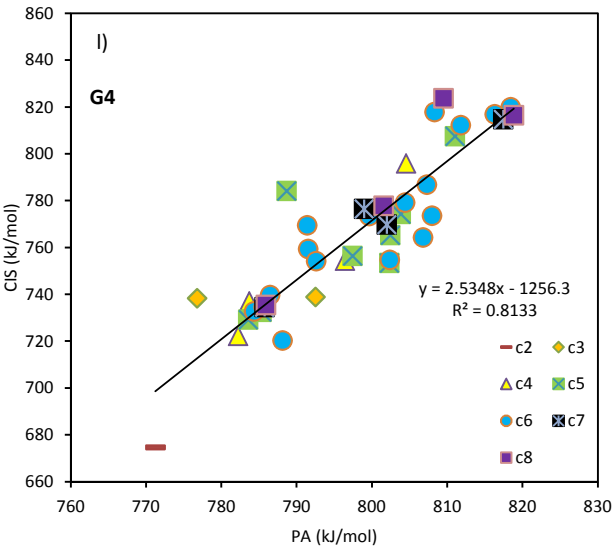

g)
CBS-QB3
CIS (kJ/mol)
PA (kJ/mol)
y = 2.4654x - 1192.6
R² = 0.8015
c2
c3
c4
c5
c6
c7
c8


h)
CBS-QB3
CIS (kJ/mol)
PA (kJ/mol)
y = 2.6416x - 1329
R² = 0.8466
c2
c3
c4
c5
c6
c7
c8

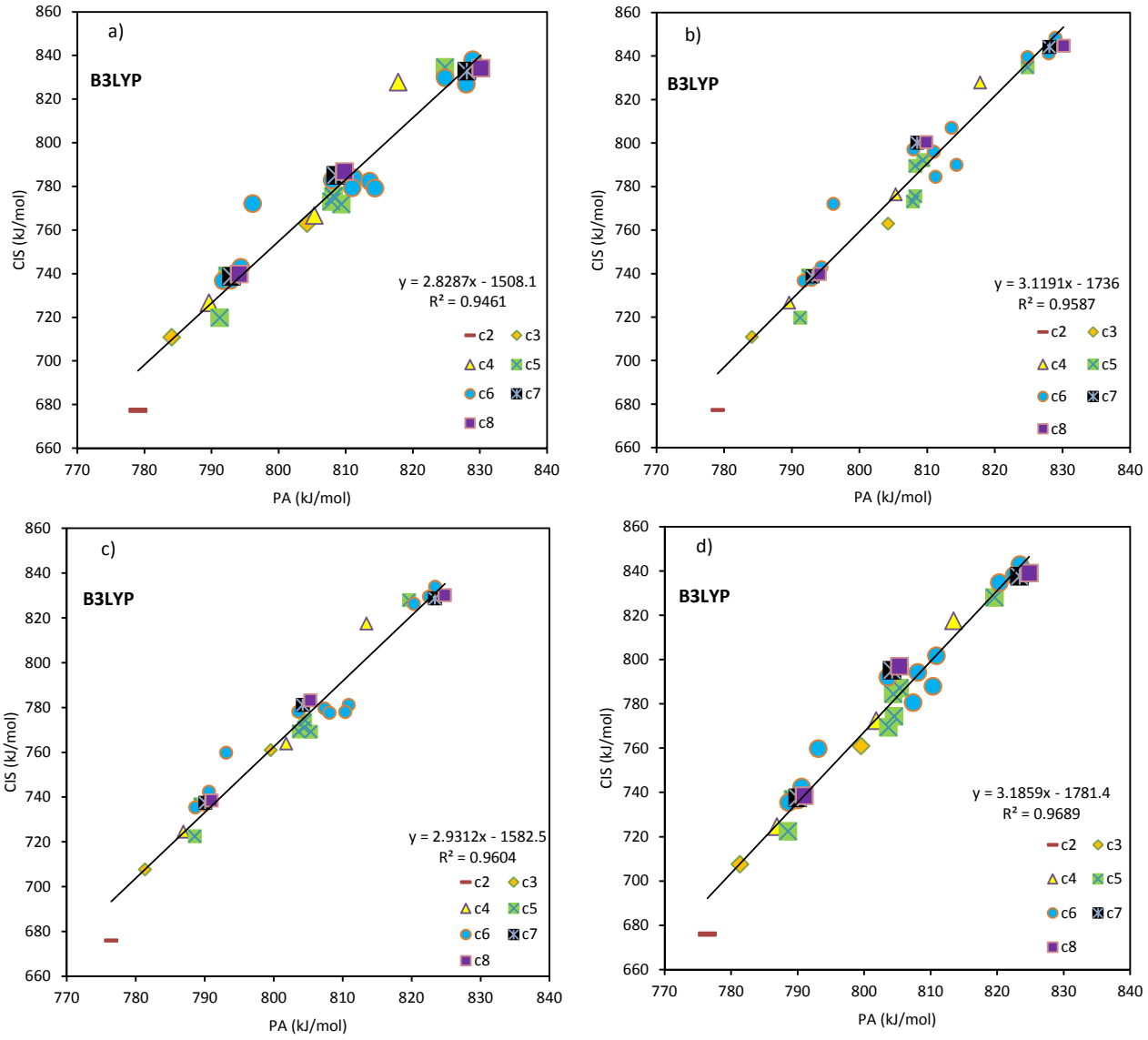

i)
G4
y = 2.3358x - 1105.5
R² = 0.7972
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

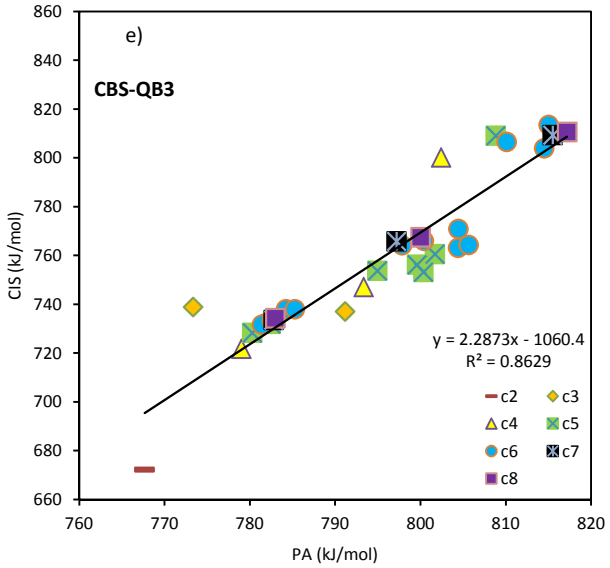

j)
G4
y = 2.5291x - 1257
R² = 0.8415
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA(kJ/mol)

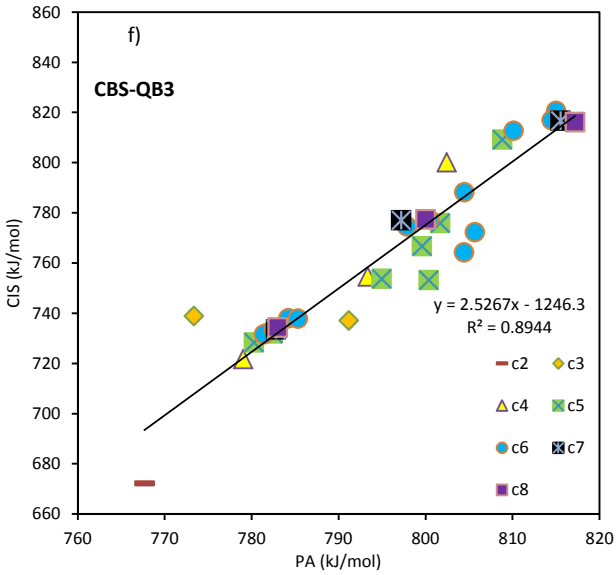

k)
G4
y = 2.4273x - 1174.2
R² = 0.810
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

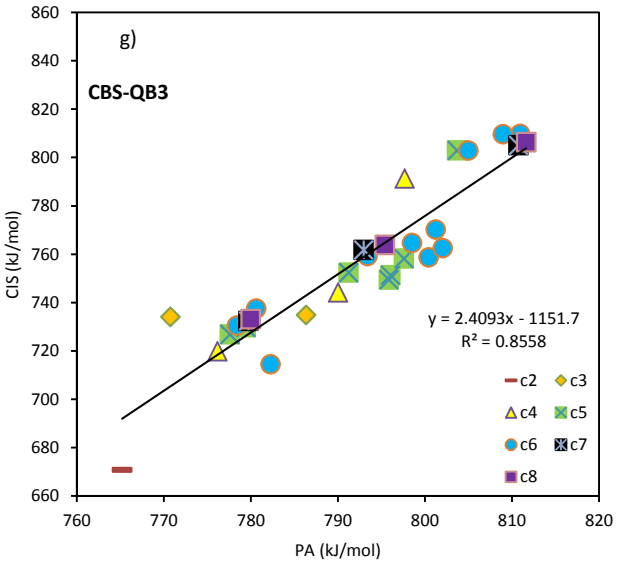

l)
G4
y = 2.5348x - 1256.3
R² = 0.8133
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

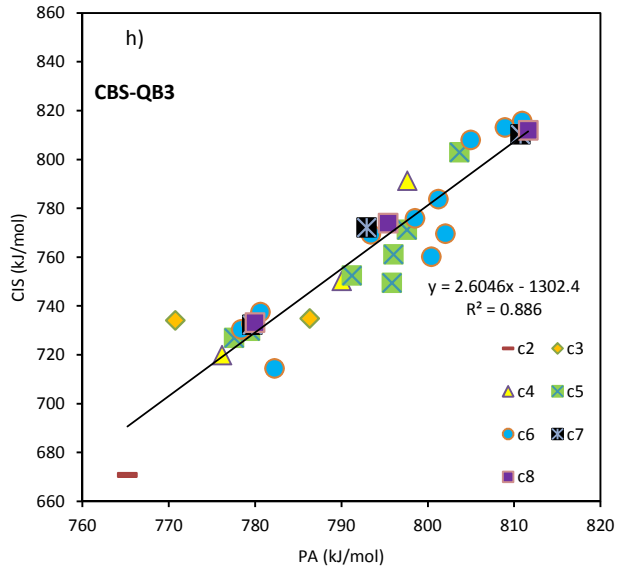
S02: CIS vs. PA for alcohols that did not undergo carbenium ion rearrangement investigated using B3LYP, CBS-QB3 and G4 methods. A total of 11 points corresponding to alcohols that restructured were omitted. The graphs are presented as in S01. (a) CIS vs. PA calculated for less-stable alkene isomers & (b) most stable isomers in terms of Gibbs free energy (B3LYP). (c) CIS vs. PA for less stable & (d) less stable alkene isomers, both calculated in terms of enthalpy (B3LYP). Remaining data presented in (e)-(h) and (i)-(l) follow an identical format for the CBS-QB3 and G4 computational methods, respectively.

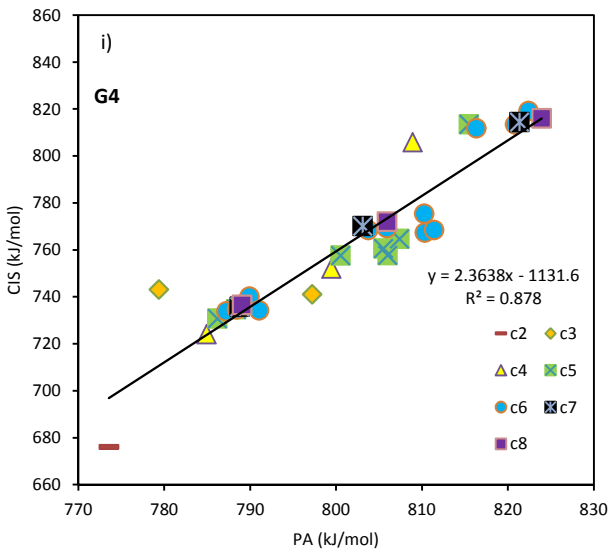


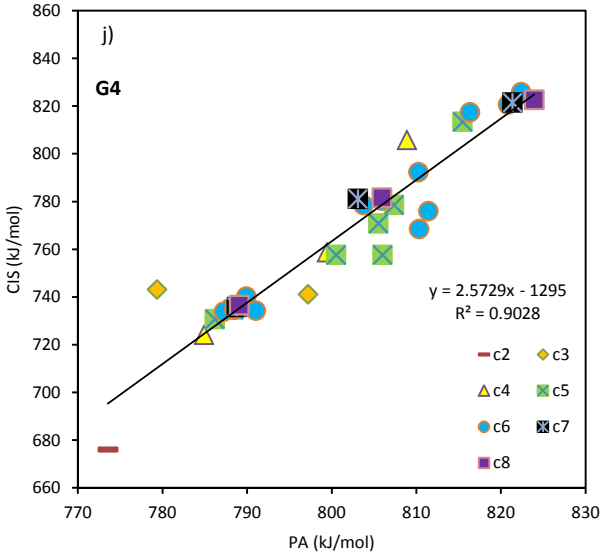

e)
CBS-QB3
y = 2.2873x - 1060.4
R² = 0.8629
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820

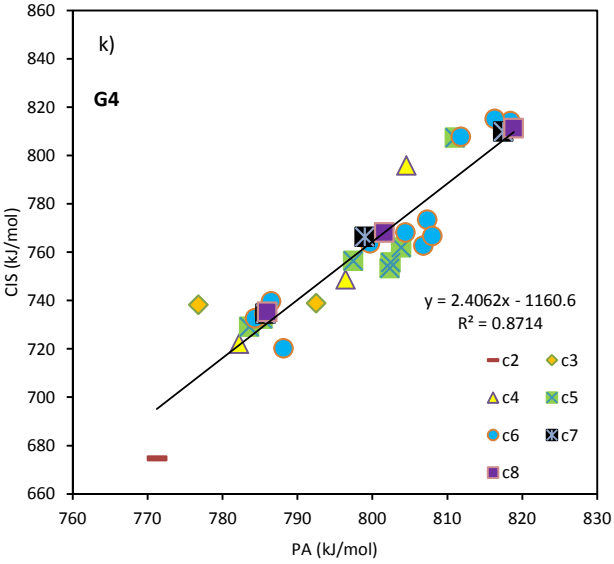

f)
CBS-QB3
y = 2.5267x - 1246.3
R² = 0.8944
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820

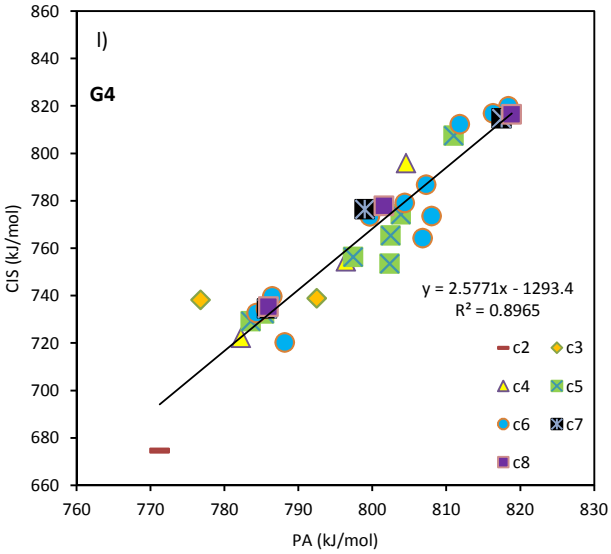

g)
CBS-QB3
y = 2.4093x - 1151.7
R² = 0.8558
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820


h)
CBS-QB3
y = 2.6046x - 1302.4
R² = 0.886
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820

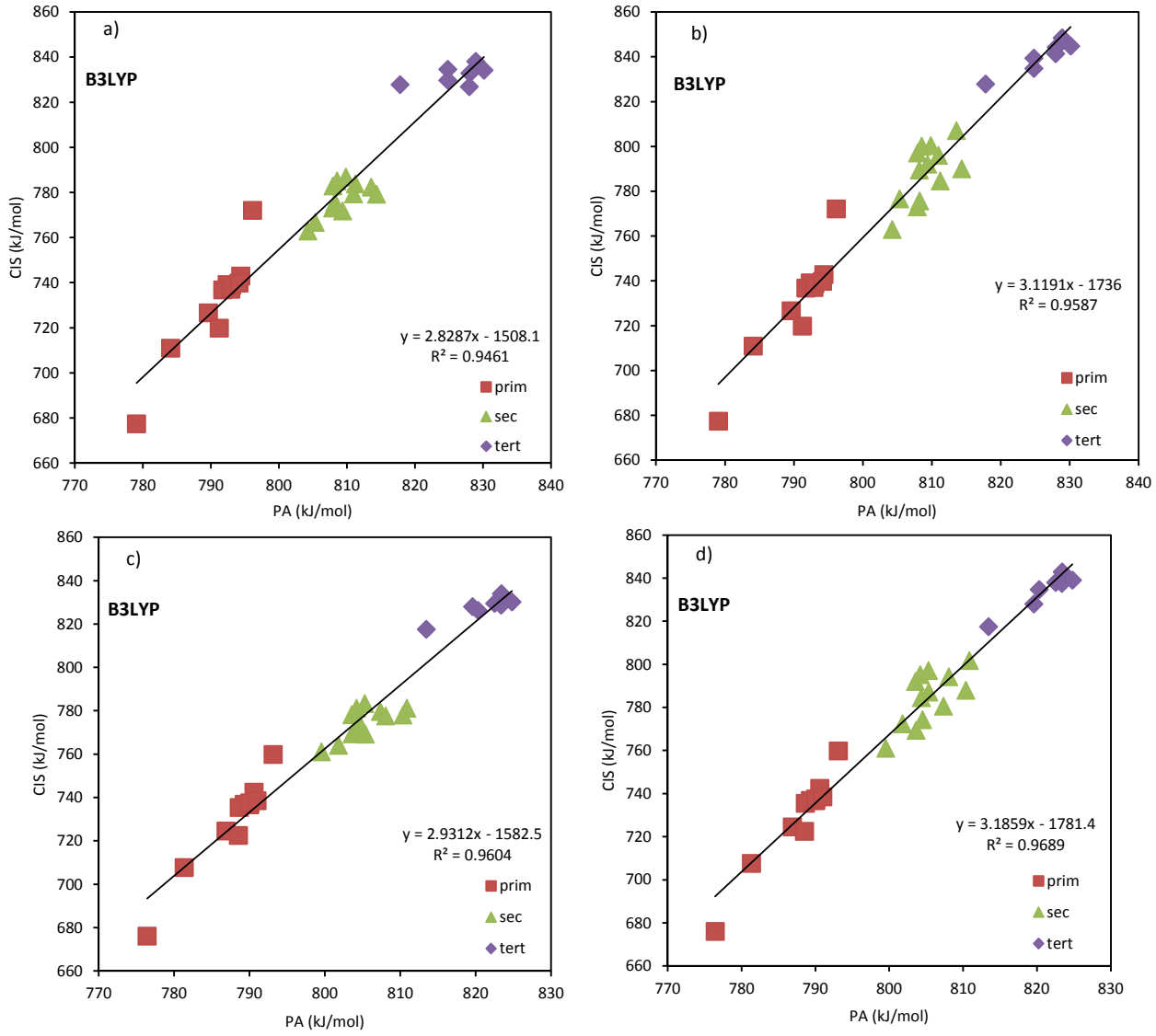

i)
G4
y = 2.3638x - 1131.6
R² = 0.878
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

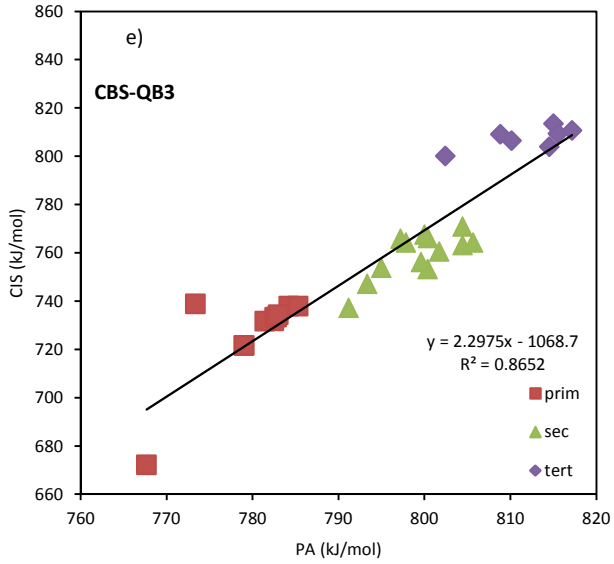

j)
G4
y = 2.5729x - 1295
R² = 0.9028
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

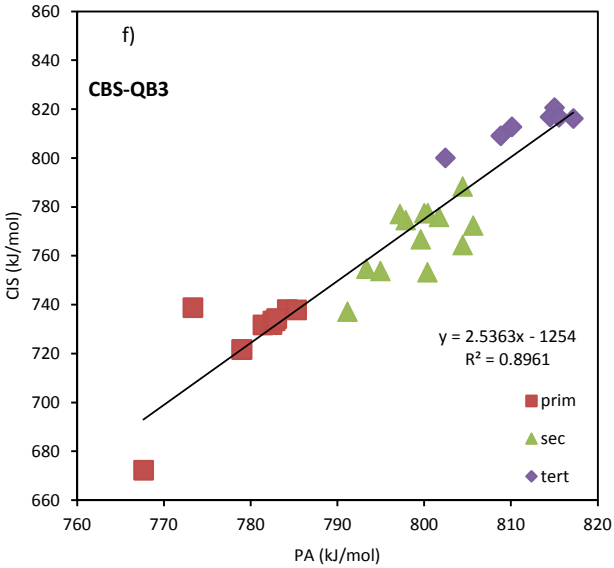

k)
G4
y = 2.4062x - 1160.6
R² = 0.8714
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

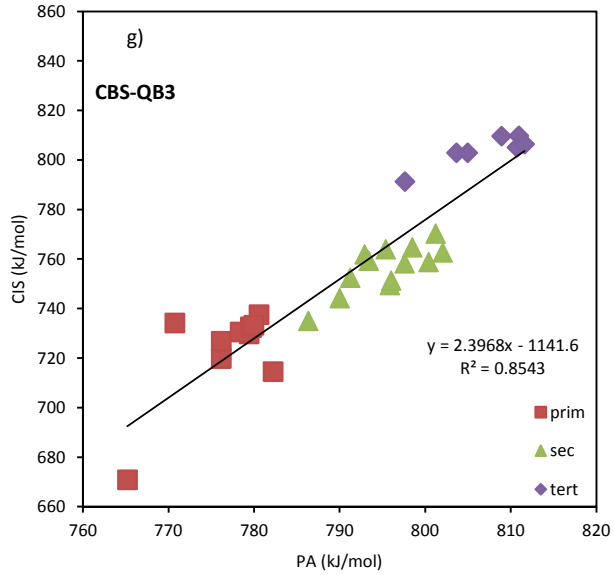

l)
G4
y = 2.5771x - 1293.4
R² = 0.8965
c2
c3
c4
c5
c6
c7
c8
CIS (kJ/mol)
PA (kJ/mol)

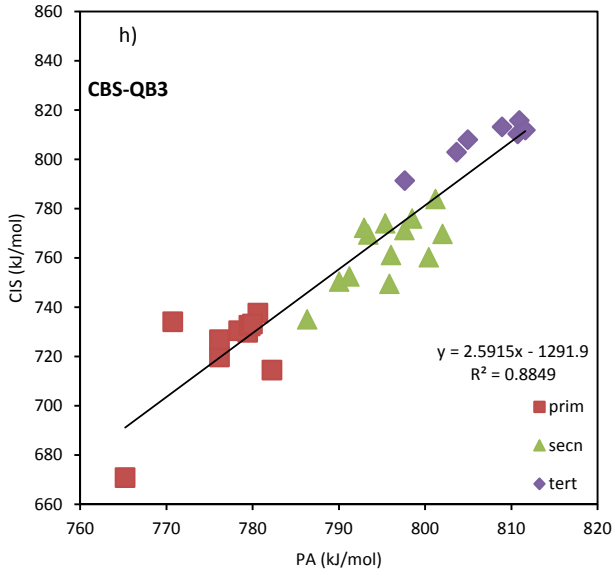
S03: Computational results presented in S02 re-plotted in terms of degree of alcohol substitution – Primary, Secondary and Tertiary alcohols.

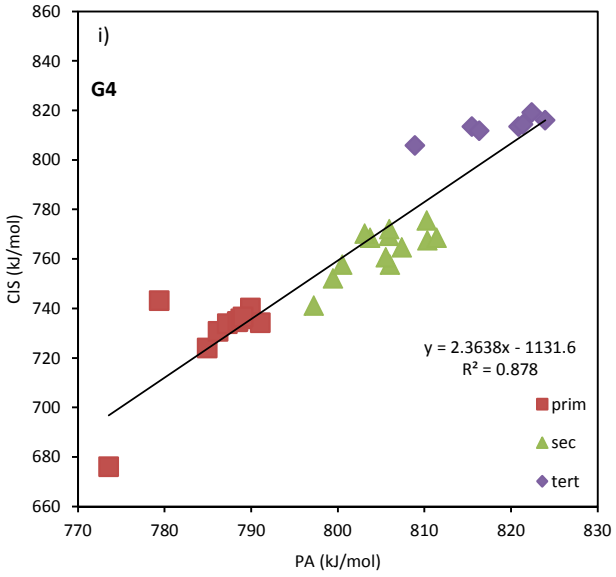


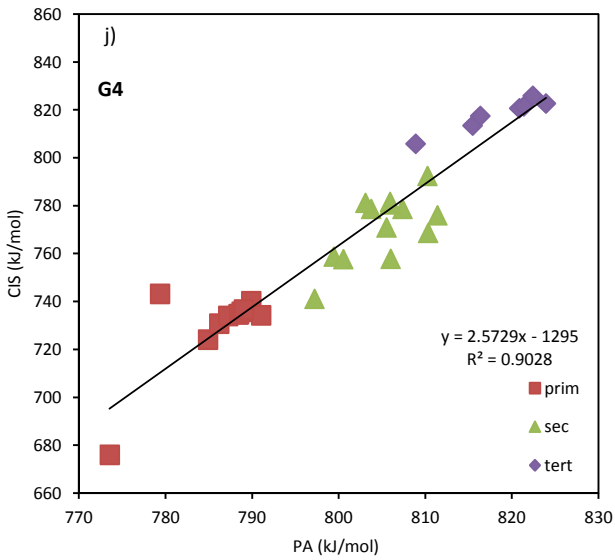

e)
CBS-QB3
y = 2.2975x - 1068.7
R² = 0.8652
prim
sec
tert
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820

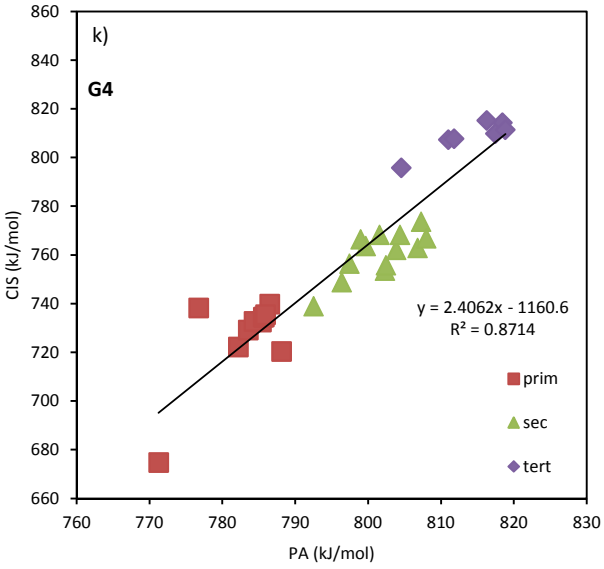

f)
CBS-QB3
y = 2.5363x - 1254
R² = 0.8961
prim
sec
tert
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820

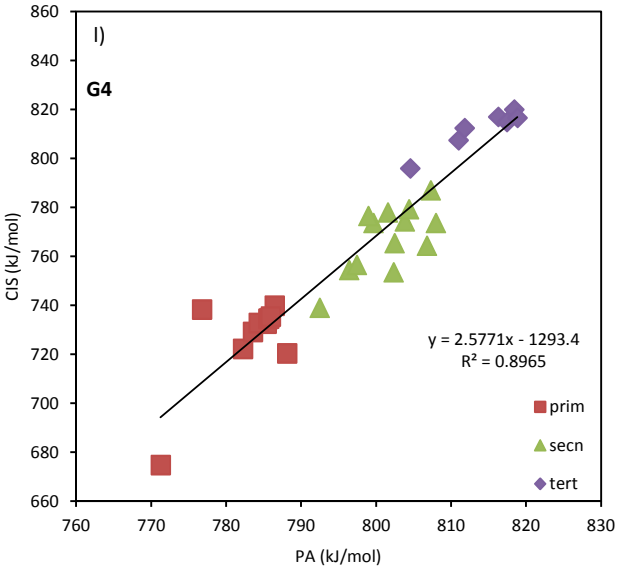

g)
CBS-QB3
y = 2.3968x - 1141.6
R² = 0.8543
prim
sec
tert
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820


h)
CBS-QB3
y = 2.5915x - 1291.9
R² = 0.8849
prim
secn
tert
CIS (kJ/mol)
PA (kJ/mol)
660
680
700
720
740
760
780
800
820
840
860
760
770
780
790
800
810
820

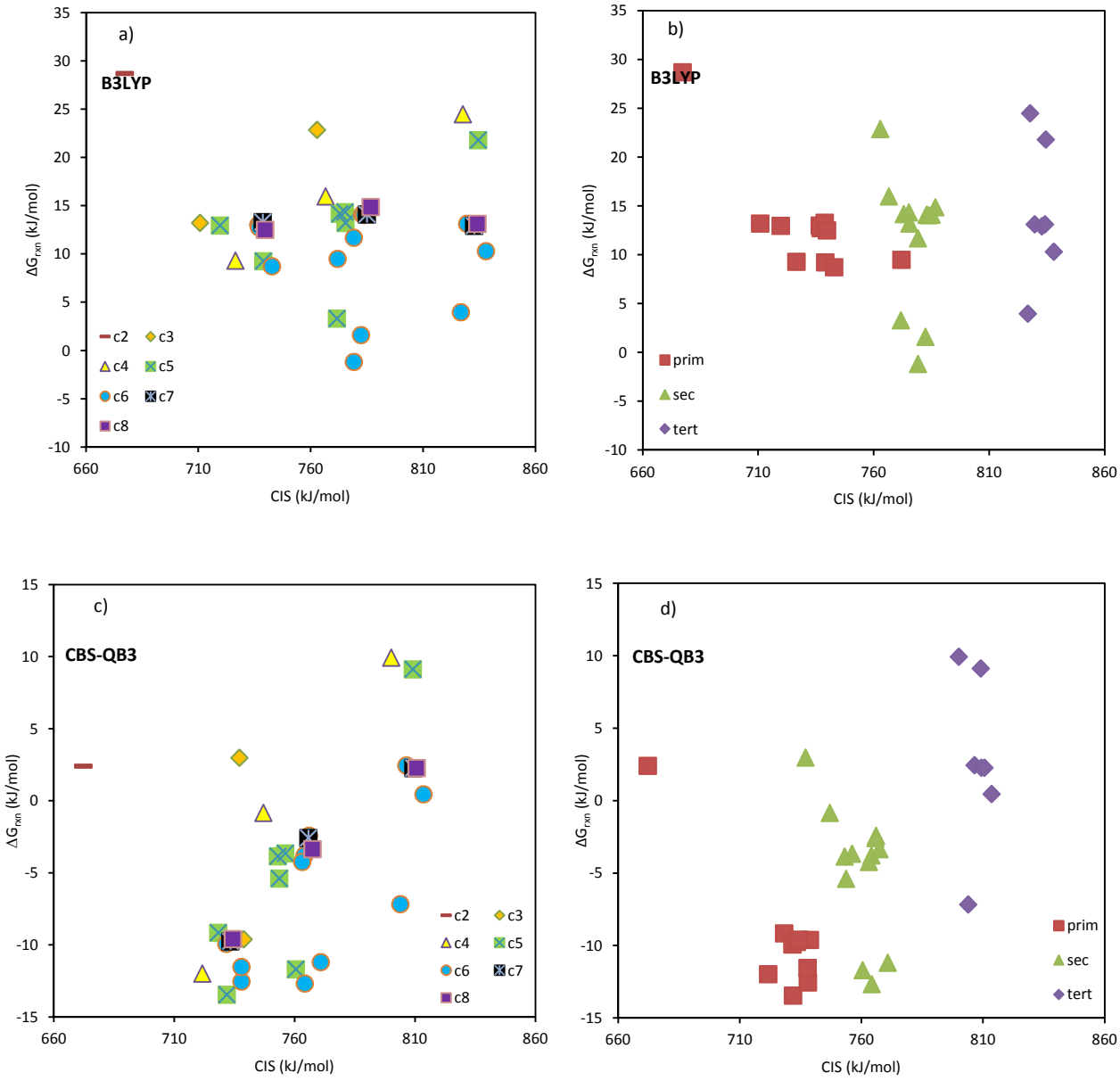

i)
G4
y = 2.3638x - 1131.6
R² = 0.878
prim
sec
tert
CIS (kJ/mol)
PA (kJ/mol)

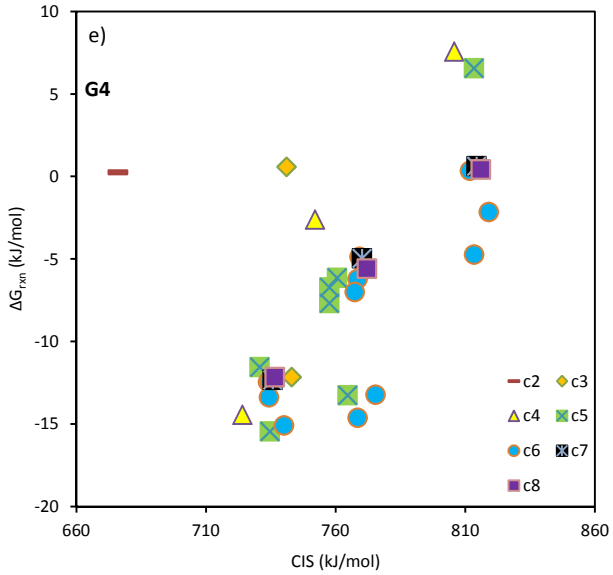

j)
G4
y = 2.5729x - 1295
R² = 0.9028
prim
sec
tert
CIS (kJ/mol)
PA (kJ/mol)

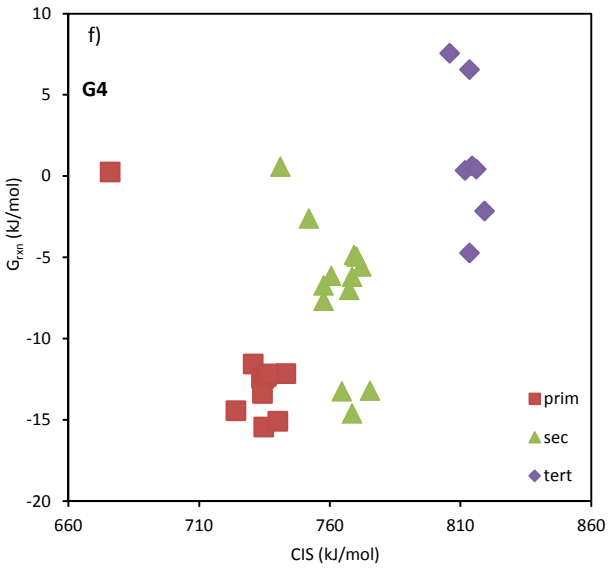

k)
G4
y = 2.4062x - 1160.6
R² = 0.8714
prim
sec
tert
CIS (kJ/mol)
PA (kJ/mol)


l)
G4
y = 2.5771x - 1293.4
R² = 0.8965
prim
secn
tert
CIS (kJ/mol)
PA (kJ/mol)

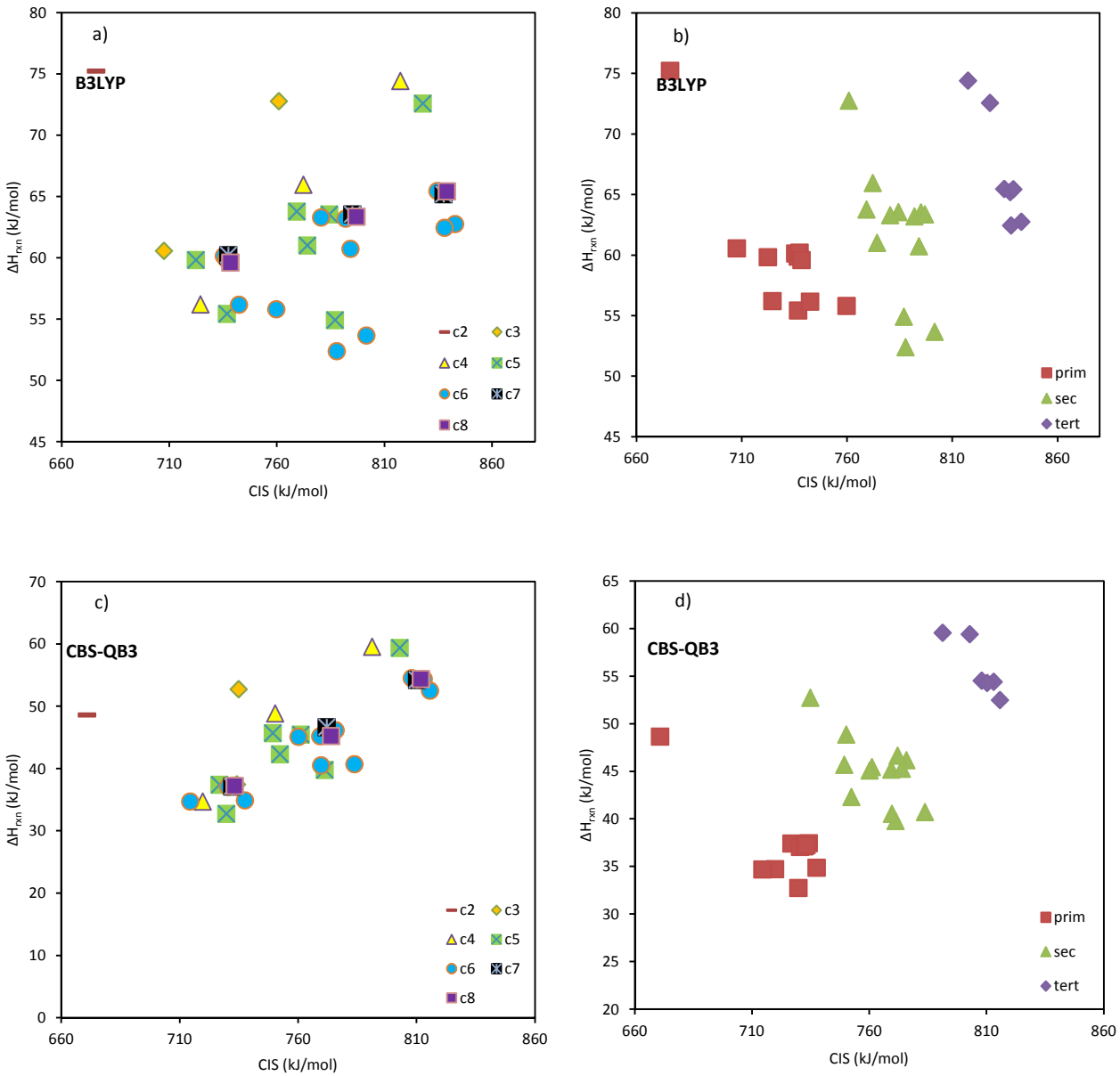
S04: Computational results for alcohol dehydration ΔG_{rxn} vs CIS for alcohols that did not undergo rearrangement, investigated using B3LYP/6-311G*, CBS-QB3 and G4 methods. Included are plots differentiating alcohols as Primary, Secondary and Tertiary. (a) ΔG_{rxn} vs CIS calculated for most stable alkene isomers & (b) differentiated by degree of alcohol substitution, in terms of Gibbs free energy, utilizing the B3LYP/6-311G* method. Figures S04(c,d) and S04(e,f) present computational data in the same format for CBS-QB3 and G4 methods, respectively.

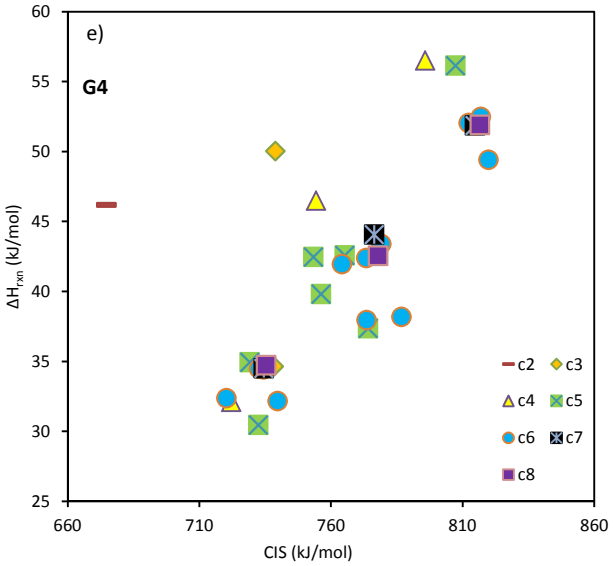


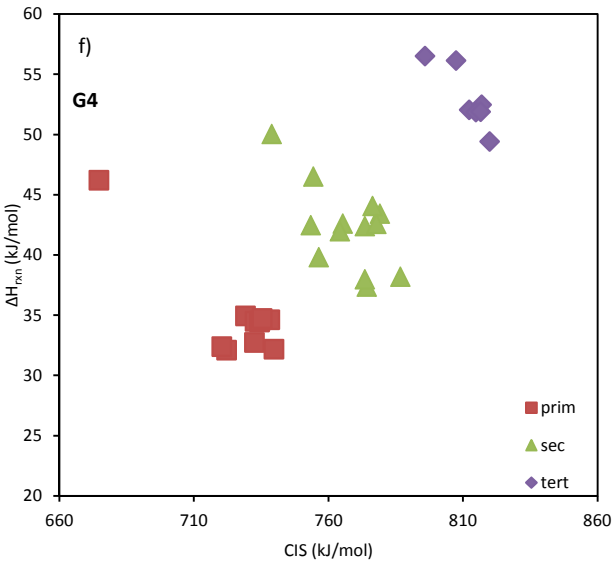

e)
G4
10
5
0
-5
-10
-15
-20
660
710
760
810
860
ΔG_rxn (kJ/mol)
CIS (kJ/mol)
c2
c3
c4
c5
c6
c7
c8


f)
G4
10
5
0
-5
-10
-15
-20
660
710
760
810
860
G_rxn (kJ/mol)
CIS (kJ/mol)
prim
sec
tert

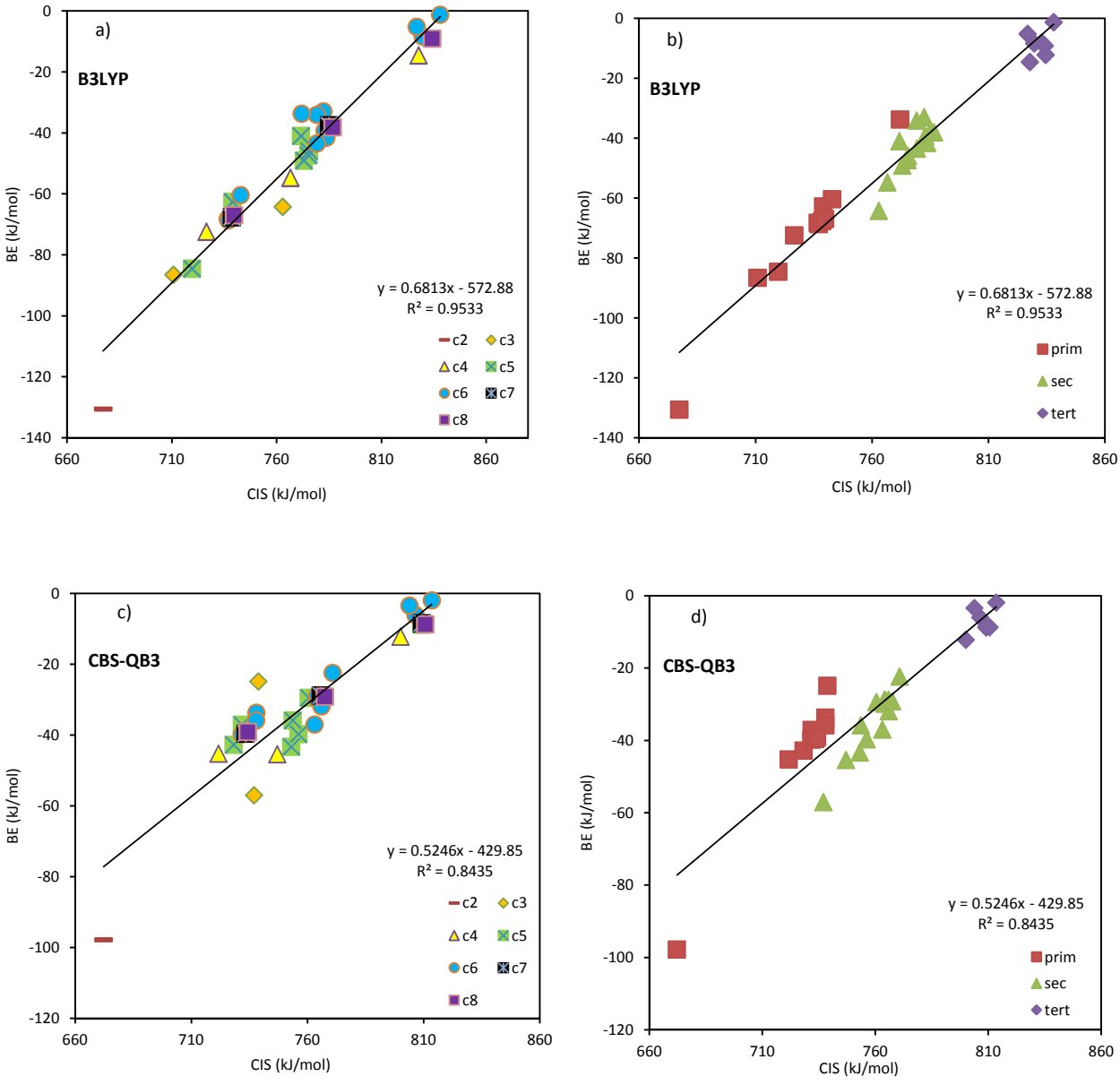
S05: Computational results for alcohol dehydration ΔH_{rxn} vs CIS for alcohols that did not undergo rearrangement, investigated using B3LYP/6-311G*, CBS-QB3 and G4 methods. Included are plots differentiating alcohols as Primary, Secondary and Tertiary. (a) ΔH_{rxn} vs CIS calculated for most stable alkene isomers & (b) differentiated by degree of alcohol substitution, in terms of enthalpy, utilizing the B3LYP/6-311G* method. Figures S05(c,d) and S05(e,f) present computational data in the same format for CBS-QB3 and G4 methods, respectively.

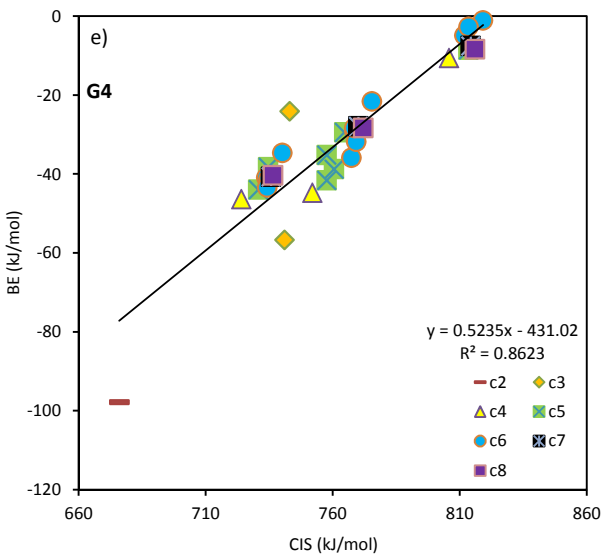


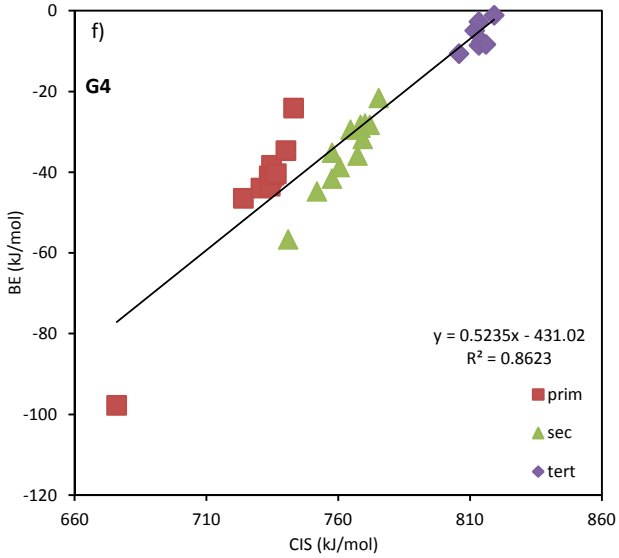

e)
G4
60
55
50
45
40
35
30
25
660
710
760
810
860
CIS (kJ/mol)
ΔHrxn (kJ/mol)
c2
c3
c4
c5
c6
c7
c8


f)
G4
60
55
50
45
40
35
30
25
20
660
710
760
810
860
CIS (kJ/mol)
ΔHrxn (kJ/mol)
prim
sec
tert

S06: Computational results for BE_{H_2O} vs. CIS for structures that did not undergo rearrangement, investigated using B3LYP/6-311G*, CBS-QB3 and G4 methods. Included are plots differentiating alcohols as Primary, Secondary and Tertiary. (a) BE_{H_2O} vs. CIS for lower-energy alkenes (more stable) & (b) differentiated by degree of alcohol substitution.




e)
G4
BE (kJ/mol)
CIS (kJ/mol)
0
-20
-40
-60
-80
-100
-120
660
710
760
810
860
y = 0.5235x - 431.02
R² = 0.8623
c2
c3
c4
c5
c6
c7
c8


f)
G4
BE (kJ/mol)
CIS (kJ/mol)
0
-20
-40
-60
-80
-100
-120
660
710
760
810
860
y = 0.5235x - 431.02
R² = 0.8623
prim
sec
tert

S07: Tabulated computational results (kJ/mol) for all reported values calculated at the B3LYP/6-311G* level of theory. First five columns of this table report CIS, PA and ΔG_{rxn} values calculated in terms of Gibbs free energy at 298 K. The next five columns correspond to the same quantities calculated in terms of calculated enthalpies at the same temperature. The binding energies of water (BE_{H_2O}) were calculated using eq. 8 of the manuscript. Note that values of CIS, ΔG_{rxn} and ΔH_{rxn} corresponding to more stable alkene isomers are denoted by superscript "+", while those of less stable alkenes by "-".

	Gibbs Free Energy					Enthalpy					
Species	**CIS^+**	**CIS^-**	**PA**	**ΔG^+_{rxn}**	**ΔG^-_{rxn}**	**CIS^+**	**CIS^-**	**PA**	**ΔH^+_{rxn}**	**ΔH^-_{rxn}**	**BE**
Ethanol	677.3	677.3	779.1	28.7	28.7	675.9	675.9	776.4	75.2	75.2	-130.5
1-prop	710.8	710.8	784.1	13.2	13.2	707.6	707.6	781.3	60.6	60.6	-86.5
2-prop	762.9	762.9	804.2	22.9	22.9	760.9	760.9	799.5	72.8	72.8	-64.3
1-butanol	726.6	726.6	789.6	9.3	9.3	724.5	724.5	786.9	56.2	56.2	-72.4
isobutanol	761.3	761.3	788.3	2.0	2.0	756.8	756.8	784.8	50.7	50.7	-29.0
2-butanol	766.6	776.5	805.3	25.8	16.0	772.3	763.9	801.8	74.3	66.0	-54.8
tert-butanol	827.8	827.8	817.8	24.5	24.5	817.4	817.4	813.4	74.4	74.4	-14.6
1-pentanol	719.7	719.7	791.2	13.0	13.0	722.4	722.4	788.5	59.8	59.8	-84.5
3-methyl-1-Butanol	739.0	739.0	792.4	9.2	9.2	736.8	736.8	789.3	55.4	55.4	-62.7
2-Methyl-1-butanol	779.2	779.2	792.5	1.3	1.3	773.0	773.0	789.5	48.4	48.4	-14.6
3-pentanol	773.0	773.0	807.9	14.2	14.2	769.3	769.3	803.6	63.8	63.8	-49.1
2-pentanol	775.3	789.4	808.2	28.5	14.3	784.4	770.9	804.4	77.1	63.6	-47.3
3-Methyl-2-butanol	771.7	792.0	809.4	23.6	3.3	787.0	769.2	805.4	72.8	54.9	-41.0
Cyclopentanol	775.5	775.5	808.2	13.2	13.2	774.2	774.2	804.5	61.0	61.0	-46.0
2-methyl-2-butanol	834.5	834.7	824.8	22.0	21.8	827.9	827.9	819.6	72.6	72.6	-12.1
1-hexanol	736.7	736.7	791.8	13.0	13.0	735.4	735.4	788.6	60.2	60.2	-68.1
2-Hexanol	782.9	797.0	808.0	28.2	14.1	791.9	778.1	803.6	77.1	63.2	-39.3
3-Hexanol	783.7	784.5	811.2	14.8	14.0	780.5	779.5	807.4	64.3	63.3	-41.6
2-Methyl-1-pentanol	786.0	786.0	796.3	-0.1	-0.1	781.2	781.2	793.1	48.9	48.9	-10.2
3-Methyl-1-pentanol	742.8	742.8	794.4	8.7	8.7	742.4	742.4	790.6	56.2	56.2	-60.4
4-Methyl-1-pentanol	737.0	737.0	792.9	12.7	12.7	736.6	736.6	790.0	59.9	59.9	-68.7
2-Methyl-2-pentanol	829.7	839.4	824.8	22.8	13.1	834.6	826.2	820.3	73.9	65.5	-8.3
3-Methyl-2-pentanol	782.3	807.0	813.6	26.2	1.6	801.6	781.1	810.9	74.2	53.7	-32.9
4-Methyl-2-pentanol	779.2	796.0	811.0	28.4	11.7	794.2	777.6	808.1	77.3	60.7	-43.5
2-Methyl-3-pentanol	779.2	790.0	814.3	9.6	-1.2	787.9	778.0	810.4	62.3	52.4	-34.1
3-Methyl-3-pentanol	838.0	848.3	828.9	20.6	10.3	842.8	833.9	823.4	71.6	62.8	-1.3
2,3-Dimethyl-1-butanol	783.9	783.9	797.3	-2.0	-2.0	780.3	780.3	794.6	46.1	46.1	-11.5
3,3-Dimethyl-1-butanol	772.0	772.0	796.1	9.5	9.5	759.8	759.8	793.1	55.8	55.8	-33.7
2,3-Dimethyl-2-butanol	826.8	841.2	828.0	18.4	4.0	837.9	829.5	822.5	70.9	62.5	-5.2
3,3-Dimethyl-2-butanol	838.0	852.6	813.7	22.8	3.0	845.5	845.5	810.0	71.5	71.5	16.0
Cyclohexanol	782.7	782.7	813.7	-8.0	-8.0	778.9	778.9	810.1	40.3	40.3	-23.0
2-Ethyl-1-butanol	798.2	798.2	794.8	-0.7	-0.7	792.3	792.3	793.3	47.5	47.5	4.1
1-heptanol	738.7	738.7	793.0	13.3	13.3	737.4	737.4	790.0	60.2	60.2	-67.6
2-heptanol	785.1	800.1	808.5	29.1	14.1	795.1	781.1	804.2	77.6	63.5	-37.6
2-Methylhexan-2-ol	832.8	844.1	828.1	24.3	12.9	837.5	828.6	823.4	74.1	65.2	-8.2
Cycloheptanol	795.3	795.3	813.1	2.9	2.9	794.2	794.2	808.8	52.2	52.2	-20.7
1-octanol	739.7	739.7	794.1	12.5	12.5	738.4	738.4	791.0	59.6	59.6	-66.9
2-octanol	786.7	800.4	809.9	28.6	14.9	797.0	783.2	805.3	77.1	63.4	-38.1
2-Methylheptan-2-ol	834.2	844.7	830.1	23.6	13.1	839.0	830.0	824.8	74.4	65.4	-9.1
cyclooctanol	830.3	830.3	818.8	0.2	0.2	832.8	832.8	812.2	47.8	47.8	11.2

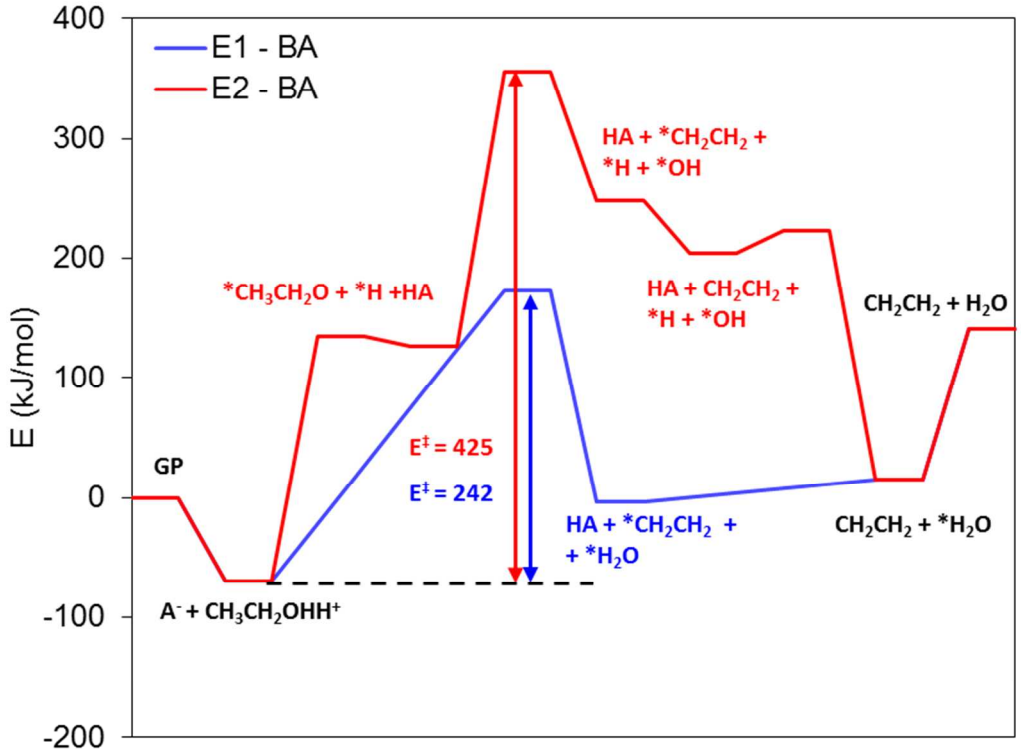
S08: Tabulated computational results (kJ/mol) for all reported values calculated at the CBS-QB3 level of theory. First five columns of this table report CIS, PA and ΔG_{rxn} values calculated in terms of Gibbs free energy at 298 K. The next five columns correspond to the same quantities calculated in terms of calculated enthalpies at the same temperature. The binding energies of water (BE_{H_2O}) were calculated using eq. 8 of the manuscript. Note that values of CIS, ΔG_{rxn} and ΔH_{rxn} corresponding to more stable alkene isomers are denoted by superscript "+", while those of less stable alkenes by "-".

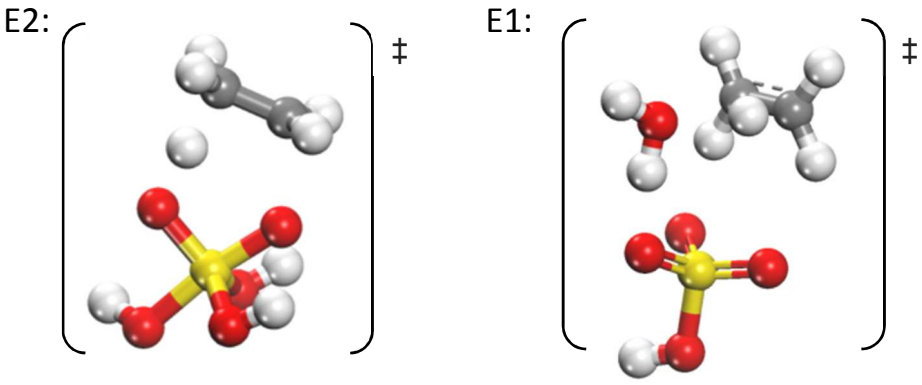
	Gibbs Free Energy					Enthalpy					
Species	**CIS^+**	**CIS^-**	**PA**	**ΔG^+_{rxn}**	**ΔG^-_{rxn}**	**CIS^+**	**CIS^-**	**PA**	**ΔH^+_{rxn}**	**ΔH^-_{rxn}**	**BE**
Ethanol	672.2	672.2	767.7	2.4	2.4	670.9	670.9	765.2	48.6	48.6	-97.9
1-prop	738.8	738.8	773.4	-9.6	-9.6	734.1	734.1	770.7	37.5	37.5	-24.9
2-prop	737.1	737.1	791.2	3.0	3.0	734.9	734.9	786.3	52.7	52.7	-57.1
1-butanol	721.7	721.7	779.0	-12.0	-12.0	719.8	719.8	776.2	34.7	34.7	-45.3
isobutanol	737.8	737.8	781.4	-19.2	-19.2	733.1	733.1	777.8	29.4	29.4	-24.4
2-butanol	747.1	754.6	793.3	-0.8	6.7	744.1	750.3	790.0	48.9	55.0	-45.4
tert-butanol	800.1	800.1	802.4	9.9	9.9	791.3	791.3	797.6	59.6	59.6	-12.3
1-pentanol	728.3	728.3	780.3	-9.2	-9.2	726.8	726.8	777.6	37.4	37.4	-42.8
3-methyl-1-Butanol	731.9	731.9	782.5	-13.5	-13.5	729.8	729.8	779.4	32.7	32.7	-37.1
2-Methyl-1-butanol	752.8	752.8	786.2	-20.0	-20.0	746.2	746.2	782.7	27.3	27.3	-13.5
3-pentanol	753.1	753.1	800.4	-3.9	-3.9	749.4	749.4	795.9	45.7	45.7	-43.4
2-pentanol	756.2	766.6	799.6	-3.7	6.8	751.2	761.1	796.0	45.5	55.3	-39.8
3-Methyl-2-butanol	760.5	775.8	801.7	-11.7	3.6	758.1	771.2	797.6	39.8	52.9	-29.5
Cyclopentanol	753.7	753.7	795.0	-5.4	-5.4	752.4	752.4	791.2	42.3	42.3	-35.9
2-methyl-2-butanol	809.1	809.1	808.8	9.1	9.1	802.9	802.9	803.7	59.4	59.4	-8.9
1-hexanol	731.7	731.7	781.4	-9.9	-9.9	730.5	730.5	778.4	37.1	37.1	-39.8
2-Hexanol	764.2	774.6	797.9	-3.8	6.6	759.2	769.4	793.4	45.2	55.3	-29.9
3-Hexanol	763.1	764.3	804.4	-4.2	-3.1	758.7	760.1	800.4	45.1	46.5	-37.1
2-Methyl-1-pentanol	760.1	760.1	788.6	-19.4	-19.4	755.5	755.5	785.7	29.2	29.2	-9.1
3-Methyl-1-pentanol	738.0	738.0	784.2	-12.5	-12.5	737.6	737.6	780.6	34.9	34.9	-33.7
4-Methyl-1-pentanol	733.3	733.3	782.6	-9.7	-9.7	732.6	732.6	779.6	37.3	37.3	-39.6
2-Methyl-2-pentanol	806.5	812.7	810.1	2.4	8.7	802.9	808.0	805.0	54.5	59.7	-6.1
3-Methyl-2-pentanol	770.8	788.2	804.4	-11.2	6.2	770.2	783.8	801.2	40.7	54.3	-22.4
4-Methyl-2-pentanol	766.0	777.4	800.4	-2.4	9.0	764.6	775.8	798.5	46.2	57.4	-32.0
2-Methyl-3-pentanol	764.2	772.2	805.7	-12.7	-4.7	762.5	769.7	802.0	40.5	47.7	-28.7
3-Methyl-3-pentanol	813.5	820.6	815.0	0.5	7.5	809.7	815.7	810.9	52.5	58.5	-1.9
2,3-Dimethyl-1-butanol	753.4	753.4	788.6	-20.5	-20.5	749.8	749.8	787.0	27.4	27.4	-14.6
3,3-Dimethyl-1-butanol	737.9	737.9	785.3	-11.5	-11.5	714.5	714.5	782.2	34.7	34.7	-35.9
2,3-Dimethyl-2-butanol	803.9	816.9	814.5	-7.2	5.8	809.6	813.1	808.9	54.4	57.9	-3.4
3,3-Dimethyl-2-butanol	820.3	820.3	806.1	3.6	3.6	813.5	813.5	802.2	52.3	52.3	10.7
Cyclohexanol	756.7	756.7	799.7	-23.4	-23.4	752.6	752.6	796.1	24.6	24.6	-19.6
2-Ethyl-1-butanol	771.8	771.8	786.7	-19.0	-19.0	766.4	766.4	785.7	28.8	28.8	4.0
1-heptanol	733.5	733.5	782.8	-9.7	-9.7	732.3	732.3	779.7	37.1	37.1	-39.6
2-heptanol	765.8	777.1	797.2	-2.6	8.7	761.8	772.1	792.9	46.6	57.0	-28.8
2-Methylhexan-2-ol	809.3	816.7	815.5	2.3	9.7	805.1	810.2	810.7	54.3	59.4	-8.5
Cycloheptanol	780.4	780.4	800.5	-13.2	-13.2	779.4	779.4	795.9	36.0	36.0	-6.9
1-octanol	734.3	734.3	783.0	-9.6	-9.6	733.2	733.2	780.0	37.2	37.2	-39.1
2-octanol	767.5	777.4	800.0	-3.3	6.6	763.8	773.9	795.4	45.3	55.3	-29.2
2-Methylheptan-2-ol	810.6	816.2	817.2	2.3	7.8	806.4	811.9	811.6	54.4	59.9	-8.8
Cyclooctanol	819.4	819.4	806.4	-18.7	-18.7	822.1	822.1	803.4	28.6	28.6	31.7

S09: Tabulated computational results (kJ/mol) for all reported values calculated at the G4 level of theory. First five columns of this table report CIS, PA and ΔG_{rxn} values calculated in terms of Gibbs free energy at 298 K. The next five columns correspond to the same quantities calculated in terms of calculated enthalpies at the same temperature. The binding energies of water (BE_{H_2O}) were calculated using eq. 8 of the manuscript. Note that values of CIS, ΔG_{rxn} and ΔH_{rxn} corresponding to more stable alkene isomers are denoted by superscript "+", while those of less stable alkenes by "-".

	Gibbs Free Energy					Enthalpy					
Species	**CIS^+**	**CIS^-**	**PA**	**ΔG^+_{rxn}**	**ΔG^-_{rxn}**	**CIS^+**	**CIS^-**	**PA**	**ΔH^+_{rxn}**	**ΔH^-_{rxn}**	**BE**
Ethanol	676.0	676.0	773.5	0.3	0.3	674.7	674.7	771.3	46.2	46.2	-97.8
1-prop	743.1	743.1	779.4	-12.1	-12.1	738.2	738.2	776.8	34.6	34.7	-24.1
2-prop	741.1	741.1	797.2	0.6	0.6	738.9	738.9	792.5	50.0	50.1	-56.7
1-butanol	724.0	724.0	784.9	-14.4	-14.4	722.1	722.1	782.2	32.1	32.1	-46.4
isobutanol	741.9	741.9	787.1	-21.8	-21.8	736.9	736.9	783.7	26.4	26.4	-23.4
2-butanol	752.0	758.7	799.4	-2.6	4.1	748.7	754.3	796.4	46.5	52.1	-44.8
tert-butanol	805.8	805.8	808.9	7.6	7.6	795.8	795.8	804.6	56.5	56.5	-10.6
1-pentanol	730.7	730.7	786.2	-11.6	-11.6	729.1	729.1	783.6	34.9	34.9	-43.9
3-methyl-1-Butanol	734.7	734.7	788.4	-15.4	-15.4	732.4	732.4	785.4	30.5	30.5	-38.3
2-Methyl-1-butanol	759.6	759.6	791.8	-22.3	-22.3	753.0	784.1	788.7	24.6	55.7	-9.9
3-pentanol	757.7	757.7	806.0	-6.7	-6.7	753.4	753.4	802.3	42.5	42.5	-41.6
2-pentanol	760.6	770.8	805.5	-6.2	4.0	755.7	765.3	802.5	42.6	52.2	-38.8
3-Methyl-2-butanol	764.6	778.5	807.4	-13.3	0.6	762.0	774.2	803.9	37.3	49.6	-29.5
Cyclopentanol	757.6	757.6	800.5	-7.7	-7.7	756.3	756.3	797.4	39.8	39.8	-35.2
2-methyl-2-butanol	813.4	813.4	815.5	6.5	6.6	807.3	807.4	811.0	56.1	56.2	-8.6
1-hexanol	733.9	733.9	787.2	-12.4	-12.4	732.7	732.7	784.3	34.5	34.5	-40.9
2-Hexanol	768.5	778.6	803.7	-6.2	3.9	763.6	773.5	799.7	42.4	52.3	-29.1
3-Hexanol	767.4	768.5	810.3	-7.0	-5.9	762.8	764.2	806.8	41.9	43.4	-35.9
2-Methyl-1-pentanol	763.9	763.9	794.3	-22.3	-22.3	759.3	759.3	791.6	26.3	26.3	-8.2
3-Methyl-1-pentanol	740.1	740.1	789.9	-15.1	-15.1	739.7	739.7	786.5	32.2	32.2	-34.7
4-Methyl-1-pentanol	734.7	734.7	788.5	-12.5	-12.5	734.4	734.4	785.6	34.4	34.4	-41.3
2-Methyl-2-pentanol	811.8	817.5	816.3	0.3	6.1	807.7	812.3	811.8	52.1	56.6	-4.9
3-Methyl-2-pentanol	775.4	792.3	810.3	-13.2	3.7	773.5	786.8	807.3	38.2	51.5	-21.6
4-Methyl-2-pentanol	769.3	780.5	805.9	-4.9	6.3	768.1	779.1	804.4	43.4	54.4	-31.8
2-Methyl-3-pentanol	768.5	775.9	811.4	-14.6	-7.2	766.8	773.5	808.0	38.0	44.7	-28.3
3-Methyl-3-pentanol	819.1	825.9	822.4	-2.1	4.6	814.3	819.9	818.4	49.4	55.0	-1.1
2,3-Dimethyl-1-butanol	758.3	758.3	793.7	-22.3	-22.3	754.2	754.2	792.6	24.8	24.8	-13.0
3,3-Dimethyl-1-butanol	734.2	734.2	791.0	-13.4	-13.4	720.3	720.3	788.1	32.4	32.4	-43.4
2,3-Dimethyl-2-butanol	813.4	820.7	820.8	-4.7	2.5	815.1	816.9	816.3	52.5	54.2	-2.7
3,3-Dimethyl-2-butanol	824.7	824.7	811.7	0.5	0.5	817.8	817.8	808.3	49.0	49.0	12.5
Cyclohexanol	757.6	757.6	805.8	-26.1	-26.1	754.7	754.7	802.4	21.8	21.8	-22.1
2-Ethyl-1-butanol	774.3	774.3	792.5	-22.0	-22.0	769.5	769.5	791.4	25.7	25.7	3.9
1-heptanol	735.7	735.7	788.8	-12.3	-12.3	734.5	734.5	785.8	34.5	34.5	-40.8
2-heptanol	770.2	781.1	803.1	-5.0	6.0	766.3	776.4	799.0	44.1	54.1	-28.0
2-Methylhexan-2-ol	814.4	821.4	821.4	0.6	7.6	809.9	814.7	817.5	51.9	56.7	-7.6
Cycloheptanol	772.6	772.6	806.6	-16.7	-16.7	769.7	769.7	802.0	32.9	32.9	-17.3
1-octanol	736.6	736.6	789.1	-12.2	-12.2	735.4	735.4	785.9	34.7	34.7	-40.3
2-octanol	772.0	781.6	805.9	-5.6	3.9	768.2	777.8	801.6	42.6	52.3	-28.3
2-Methylheptan-2-ol	816.0	822.6	823.9	0.4	7.0	811.4	816.5	818.8	51.9	57.1	-8.3
cyclooctanol	821.2	821.2	811.8	-21.4	-21.4	823.7	823.7	809.5	25.9	25.9	30.8

S10: Energy profile of the H_2SO_4-catalyzed alcohol dehydration reaction evolving via the E1 (blue) and E2 (red) mechanisms, along with states shared by both mechanisms (black). All calculations were performed at the B3LYP/6-311G* level of theory. The asterisk (*) denotes an adsorbed state of relevant reaction species and the reported energies were referenced to the gas phase species. Molecular model representations of relevant transition states for the E2 and E1 mechanisms are shown below.





S11: Energy profile of the $Al(OH)_3$-catalyzed alcohol dehydration reaction evolving via the E1 (blue) and E2 (red) mechanisms, along with states shared by both mechanisms (black). All calculations were performed at the B3LYP/6-311G* level of theory. The asterisk (*) denotes an adsorbed state of relevant reaction species and the reported energies were referenced to the gas phase species. Molecular model representations of relevant transition states for the E2 and E1 mechanisms are shown below.