Stereoelectronic and conformational effects in carbohydrate derived oxocarbenium, iminium and ammonium ions

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Appendix

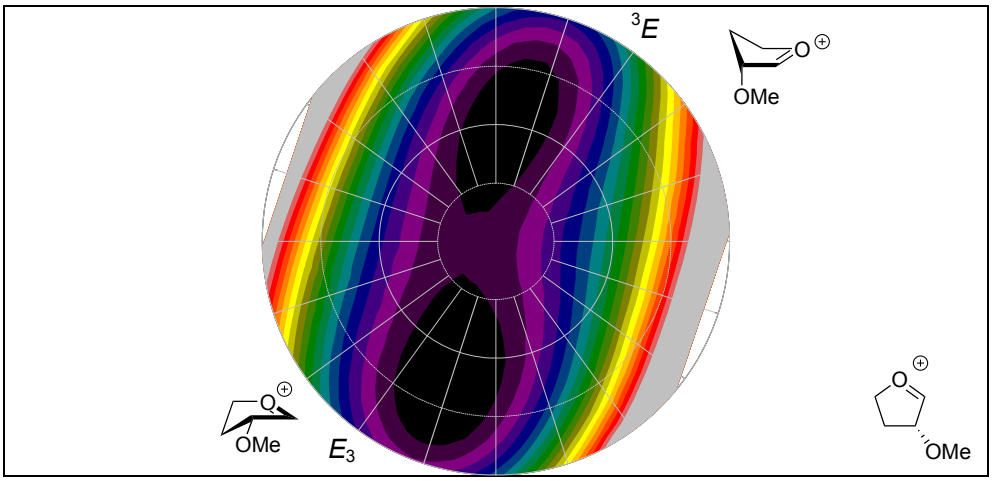
This Appendix provides additional free energy surface (FES) maps that have been calculated for mono- and disubstituted tetrahydrofuranyl oxocarbenium ions (“stripped pentofuranosyl oxocarbenium ions”, Schemes A.1-A.9). The maps are reported alongside the *C*-allylation reactions, described by Woerpel and co-workers, in which they occur as possible intermediates. Overall, there is good to excellent agreement between the calculated lowest energy oxocarbenium ions and the experimentally observed product

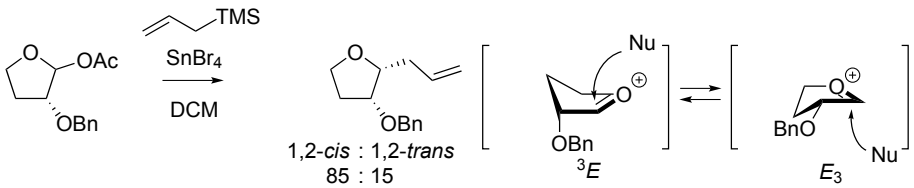
ratio's, taking into account the inside attack model as described in Chapters 1-3. The FES maps provide a clear picture on the influence of the different single ring substituents.

Figures A.1-A.4 depict the FES maps that have been calculated for the two possible anomers of the four D–furanosyl triflates. The most favorable structures are depicted in these Figures and the differences in energy between the α- and β-anomers have been determined based on the energies of their lowest energy conformers.

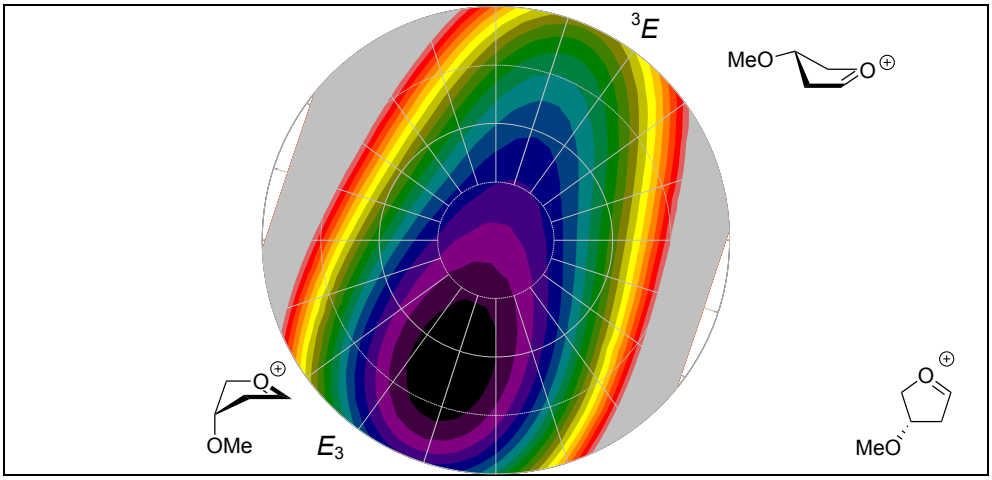
For the results of the *C*-allylation reactions see: Larsen, C. H.; Ridgway, B. H.; Shaw, J. T.; Smith, D. M.; Woerpel, K. A., *J. Am. Chem. Soc.* **2005**, *127*, 10879-10884, 10.1021/ja0524043.

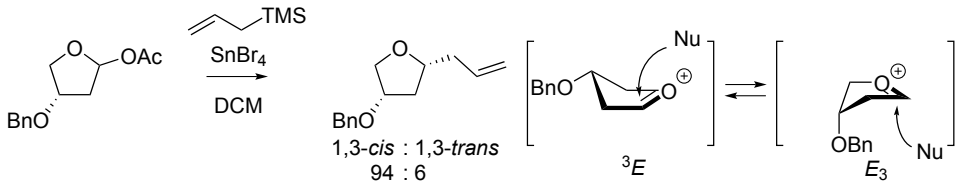
Scheme A.1 (*R*)-4-methoxy-3,4-dihydro-2H-furan-1-ium.



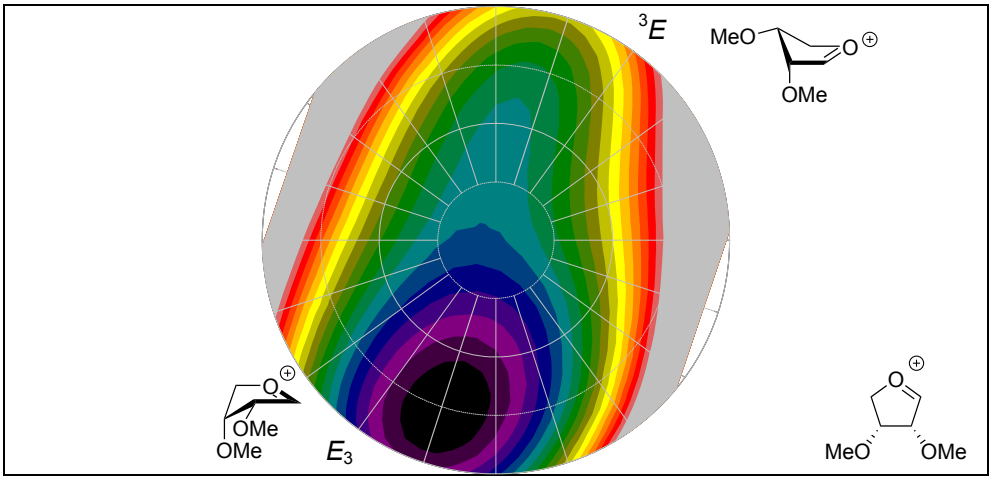


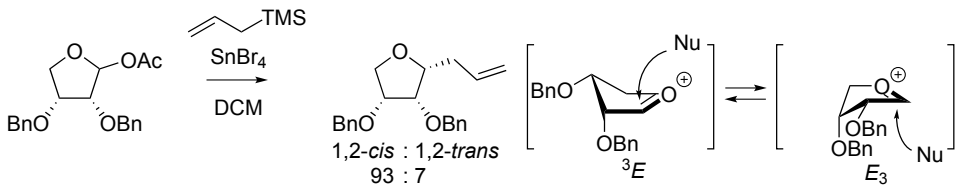
Scheme A.2 (*S*)-3-methoxy-3,4-dihydro-2H-furan-1-ium.



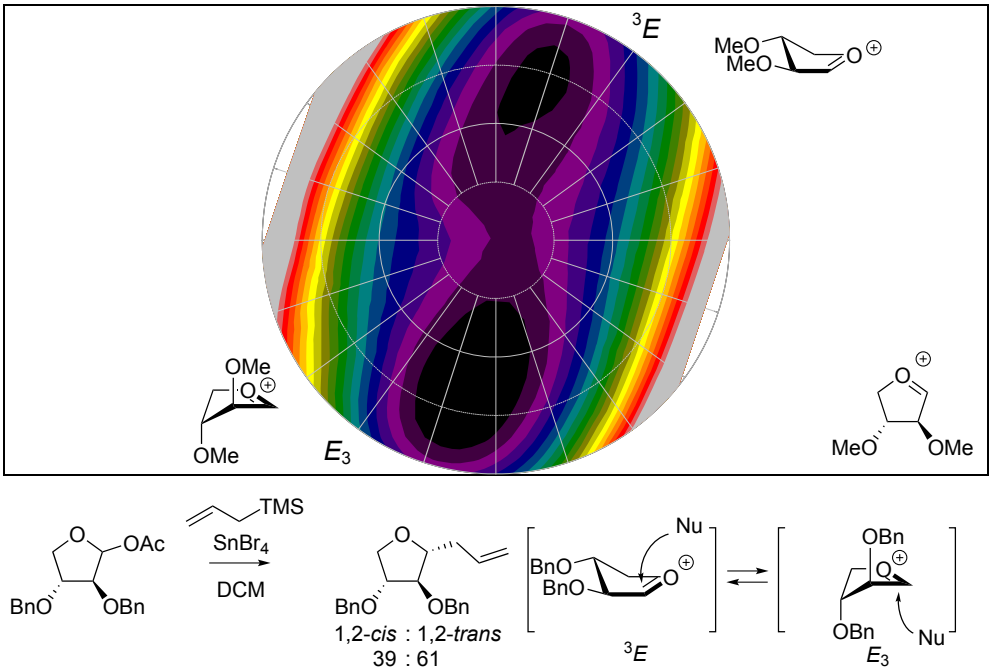


Scheme A.3 (3*R*,4*R*)-3,4-dimethoxy-3,4-dihydro-2H-furan-1-ium.

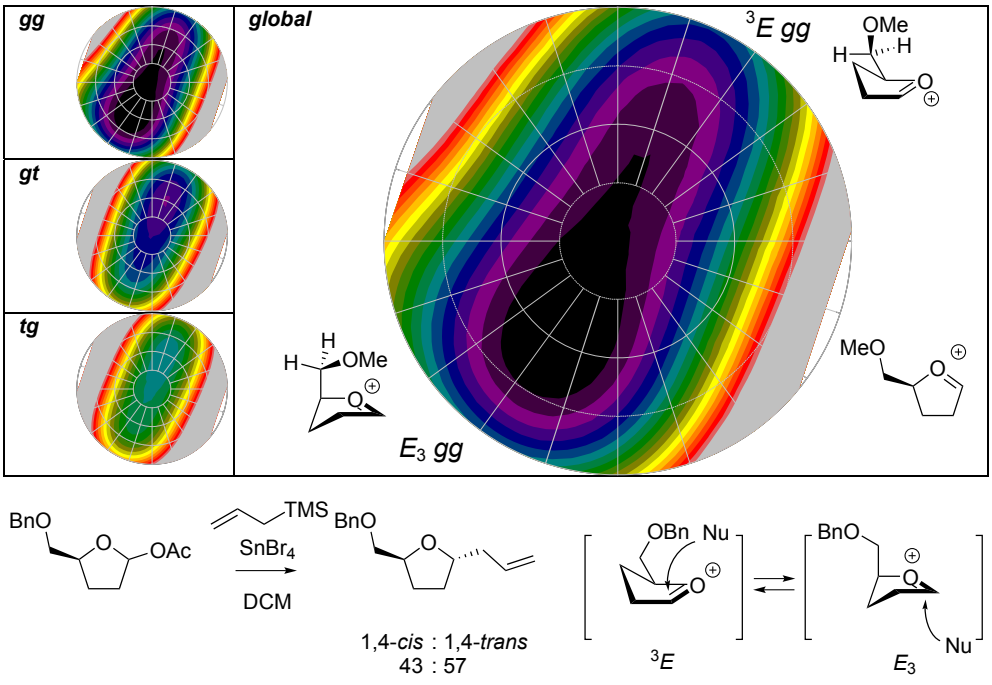




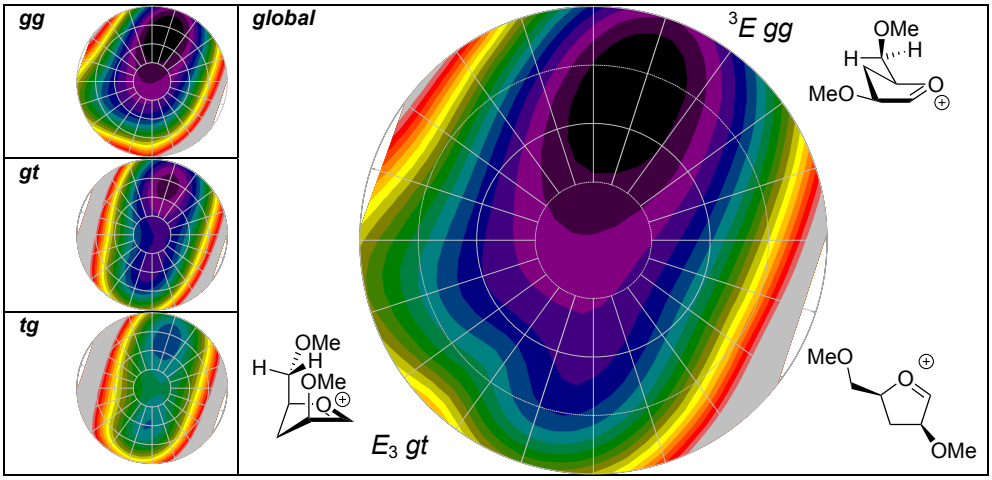
Scheme A.4 (3*R*,4*S*)-3,4-dimethoxy-3,4-dihydro-2H-furan-1-ium.



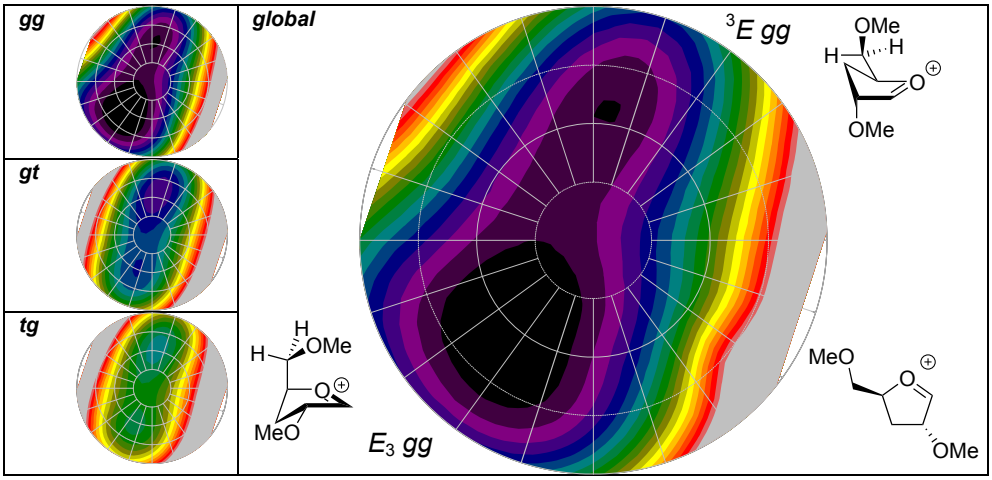
Scheme A.5 (*S*)-2-(methoxymethyl)-3,4-dihydro-2H-furan-1-ium.



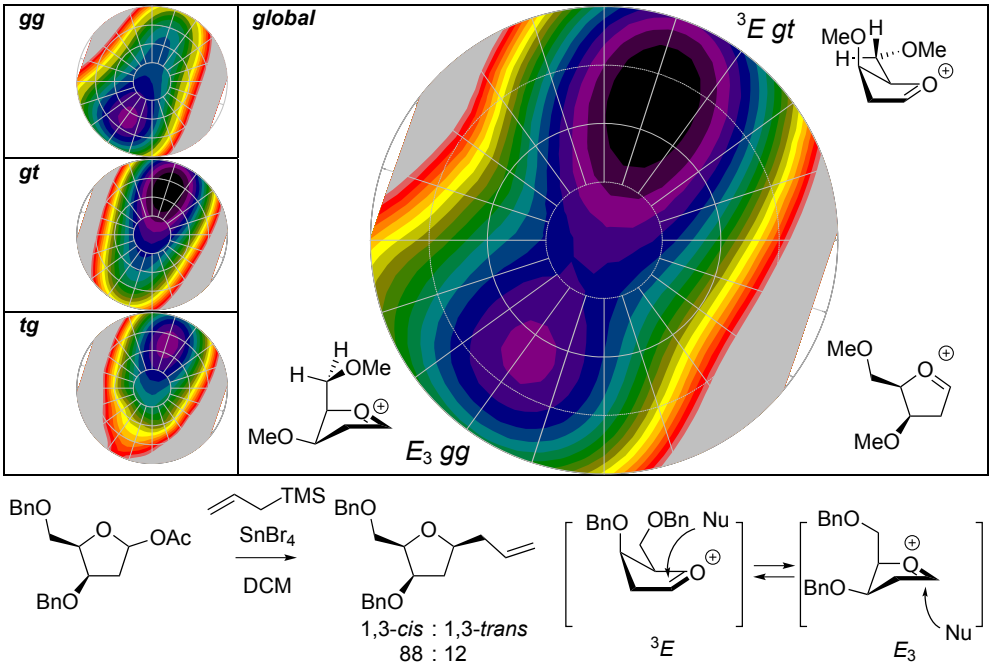
Scheme A.6 (2*S*,4*S*)-4-methoxy-2-(methoxymethyl)-3,4-dihydro-2H-furan-1-ium.



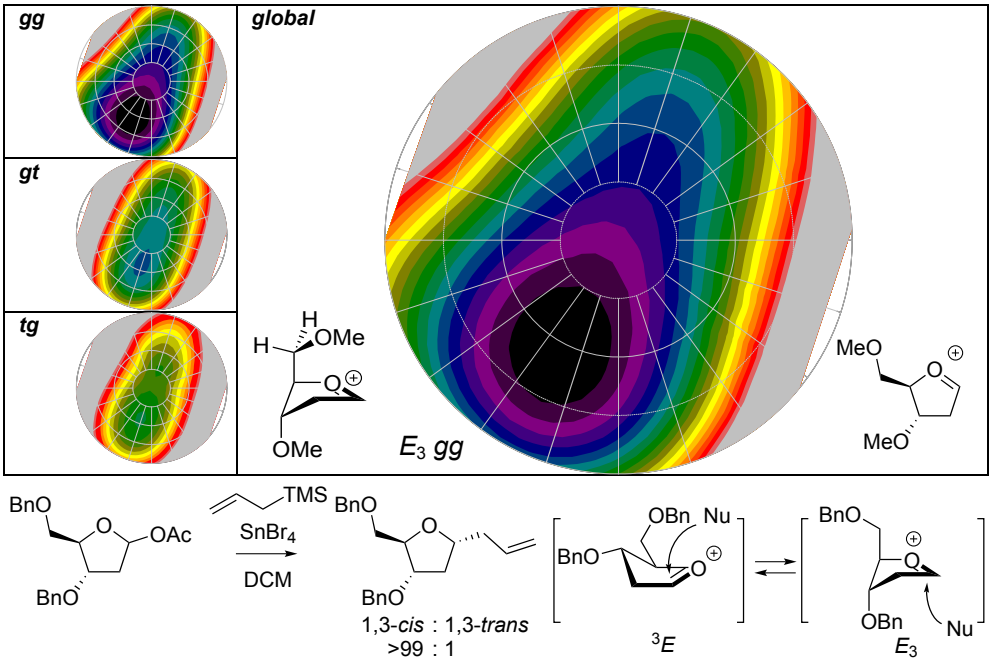
Scheme A.7 (2*S*,4*R*)-4-methoxy-2-(methoxymethyl)-3,4-dihydro-2H-furan-1-ium.



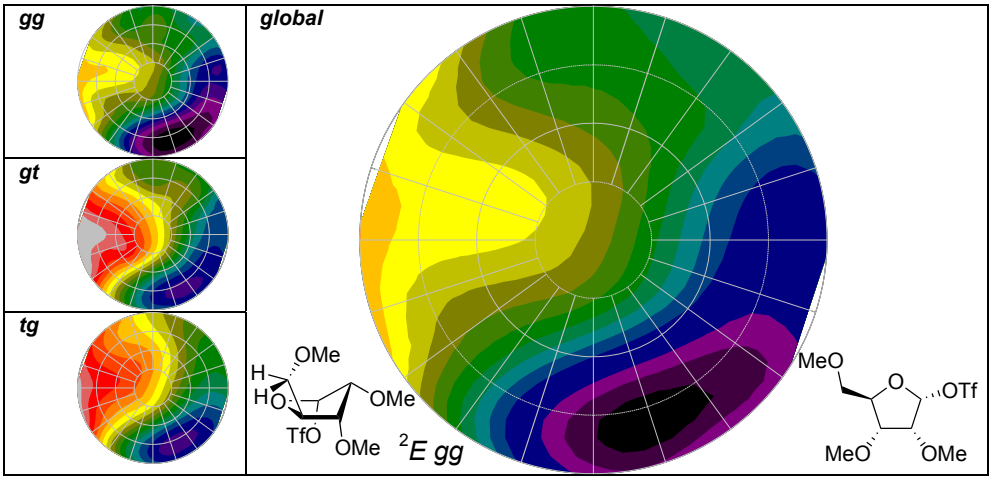
Scheme A.8 (2*R*,3*R*)-3-methoxy-2-(methoxymethyl)-3,4-dihydro-2H-furan-1-ium.



Scheme A.9 (2*R*,3*R*)-3-methoxy-2-(methoxymethyl)-3,4-dihydro-2H-furan-1-ium.



(α)



(β)

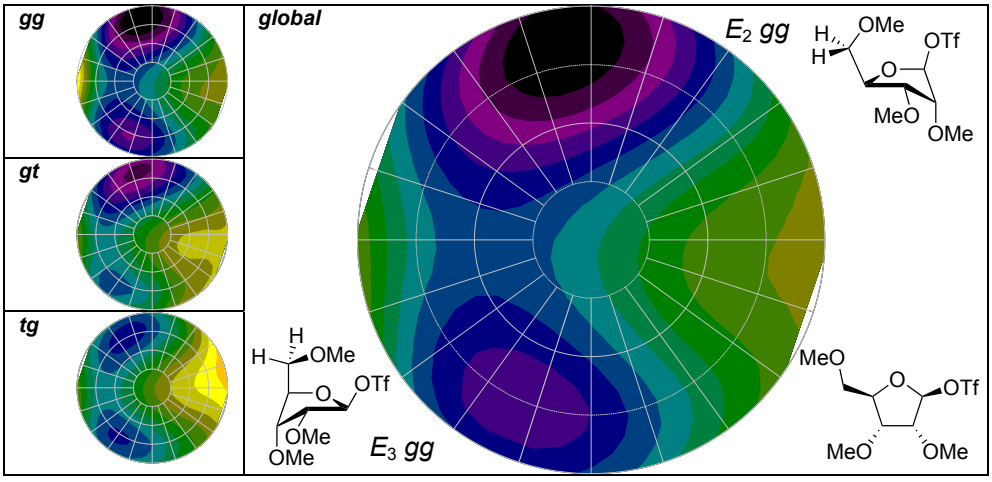
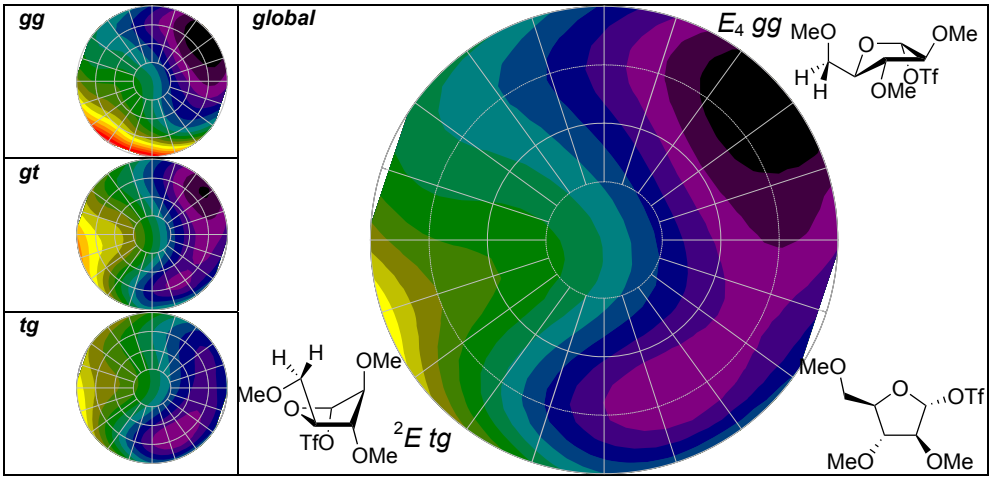


Figure A.1 2,3,5-Tri-*O*-benzyl-D-ribofuranosyl triflate (α : β = 1.0 : 0.0 kcal/mol).

(α)



(β)

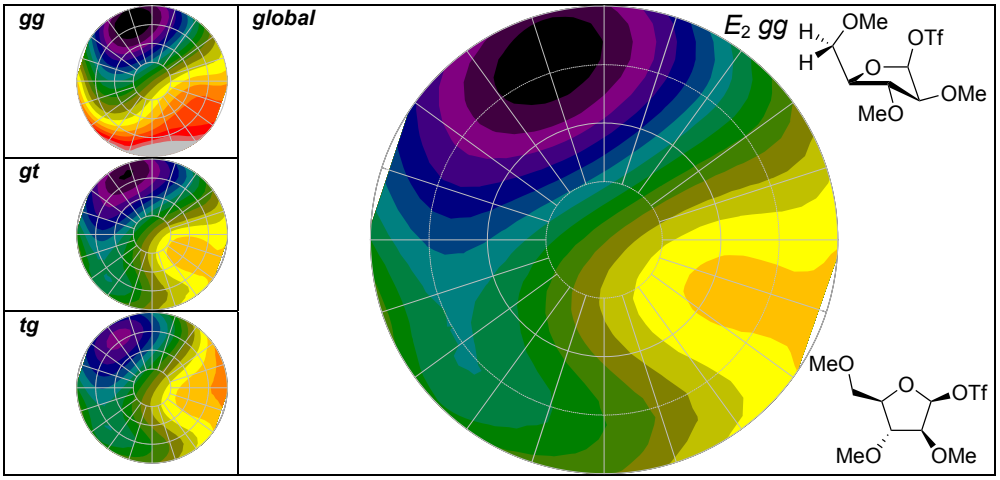
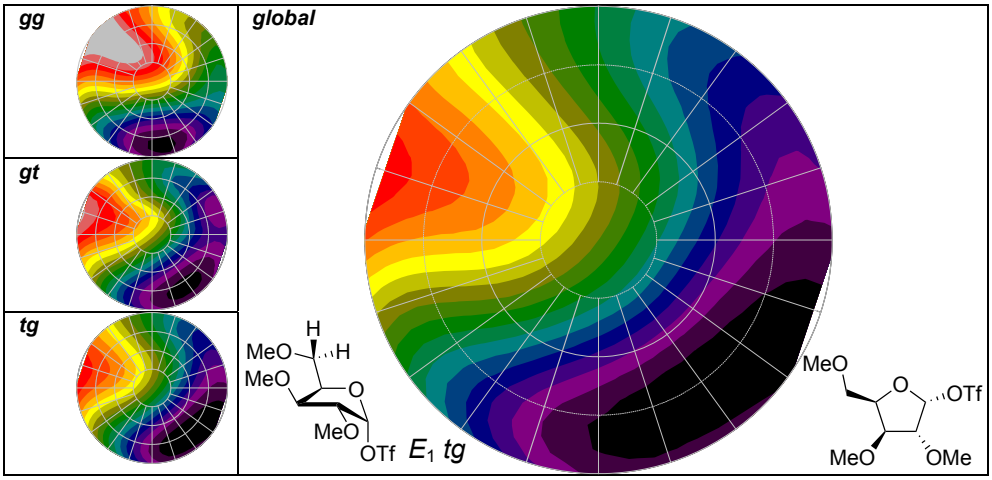


Figure A.2 2,3,5-Tri-*O*-benzyl-D-arabinofuranosyl triflate (α : β = 0.0 : 1.0 kcal/mol).

(α)



(β)

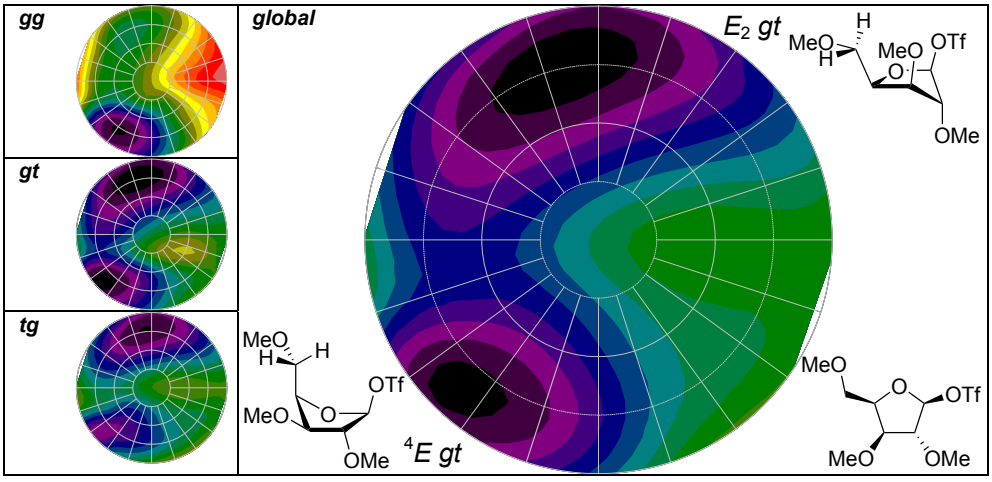
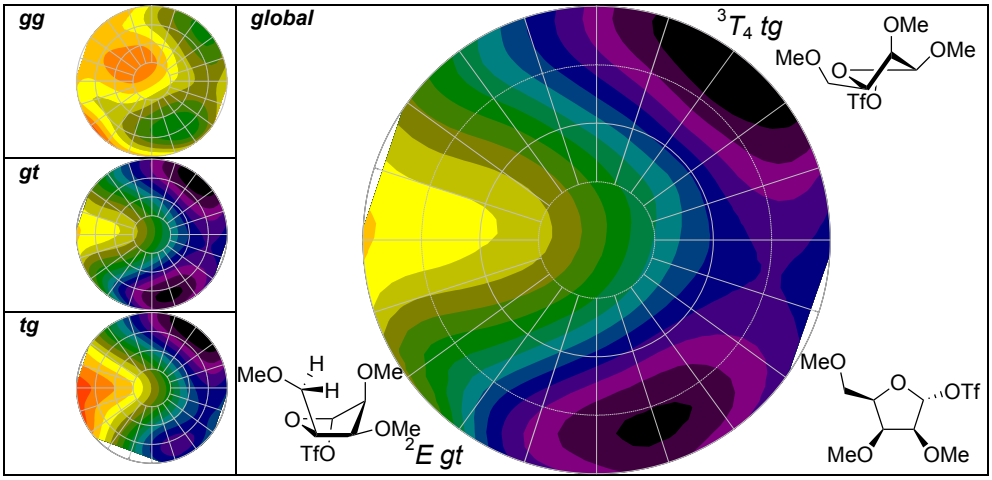


Figure A.3 2,3,5-Tri-*O*-benzyl-D-xylofuranosyl triflate (α : β = 0.6 : 0.0 kcal/mol).

(α)



(β)

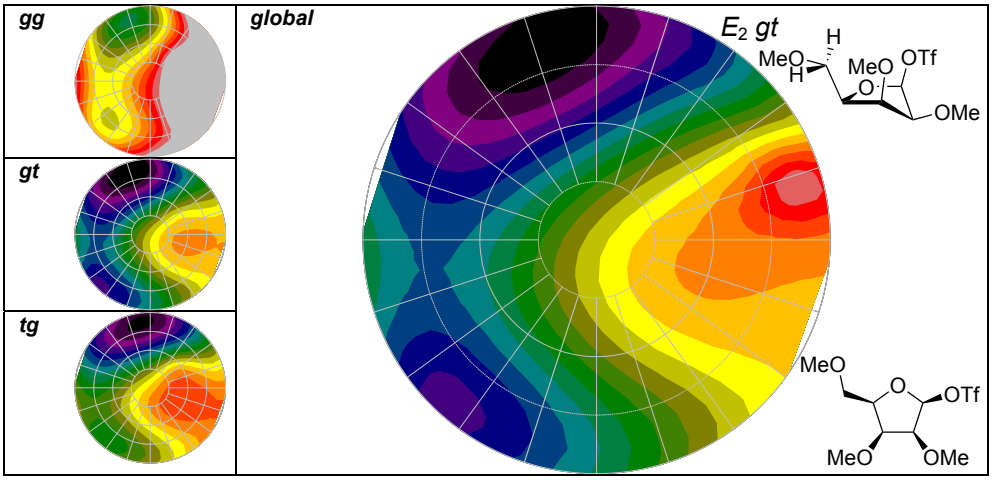


Figure A.4 2,3,5-Tri-*O*-benzyl-D-lyxofuranosyl triflate (α : β = 0.0 : 1.0 kcal/mol).