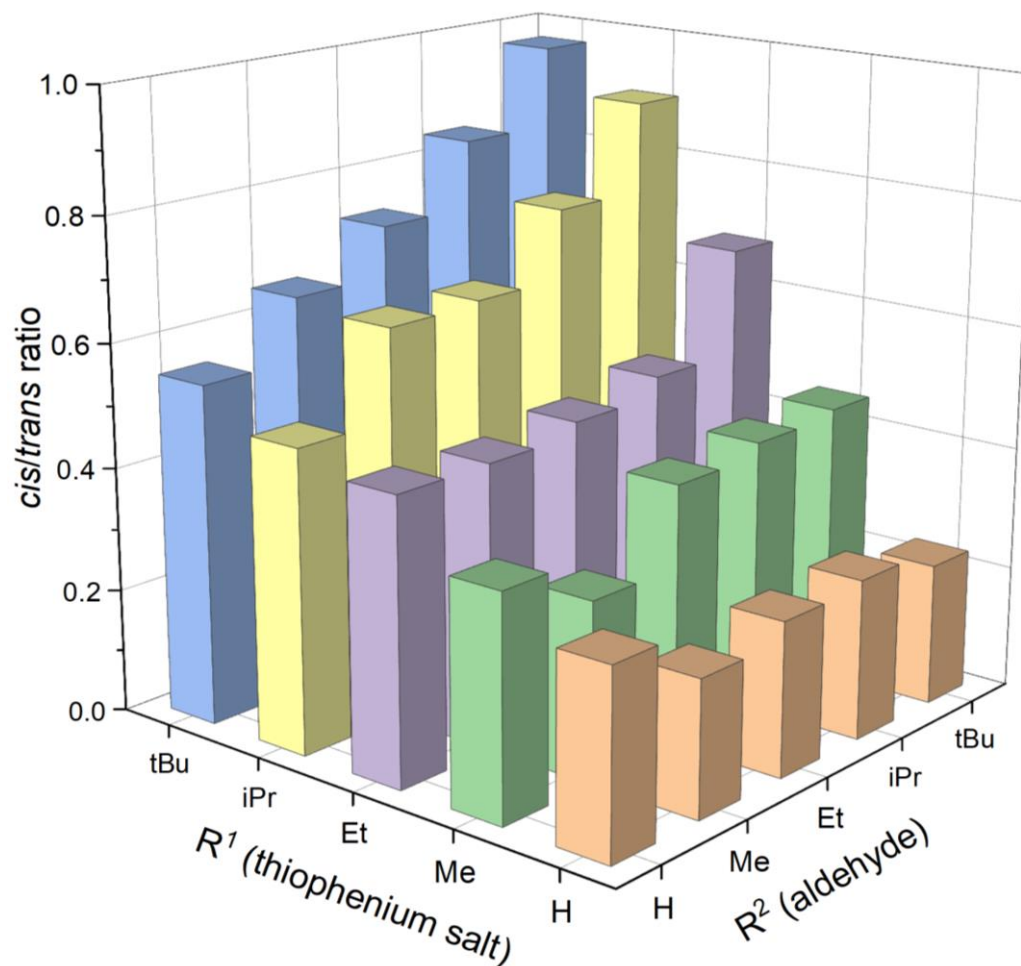


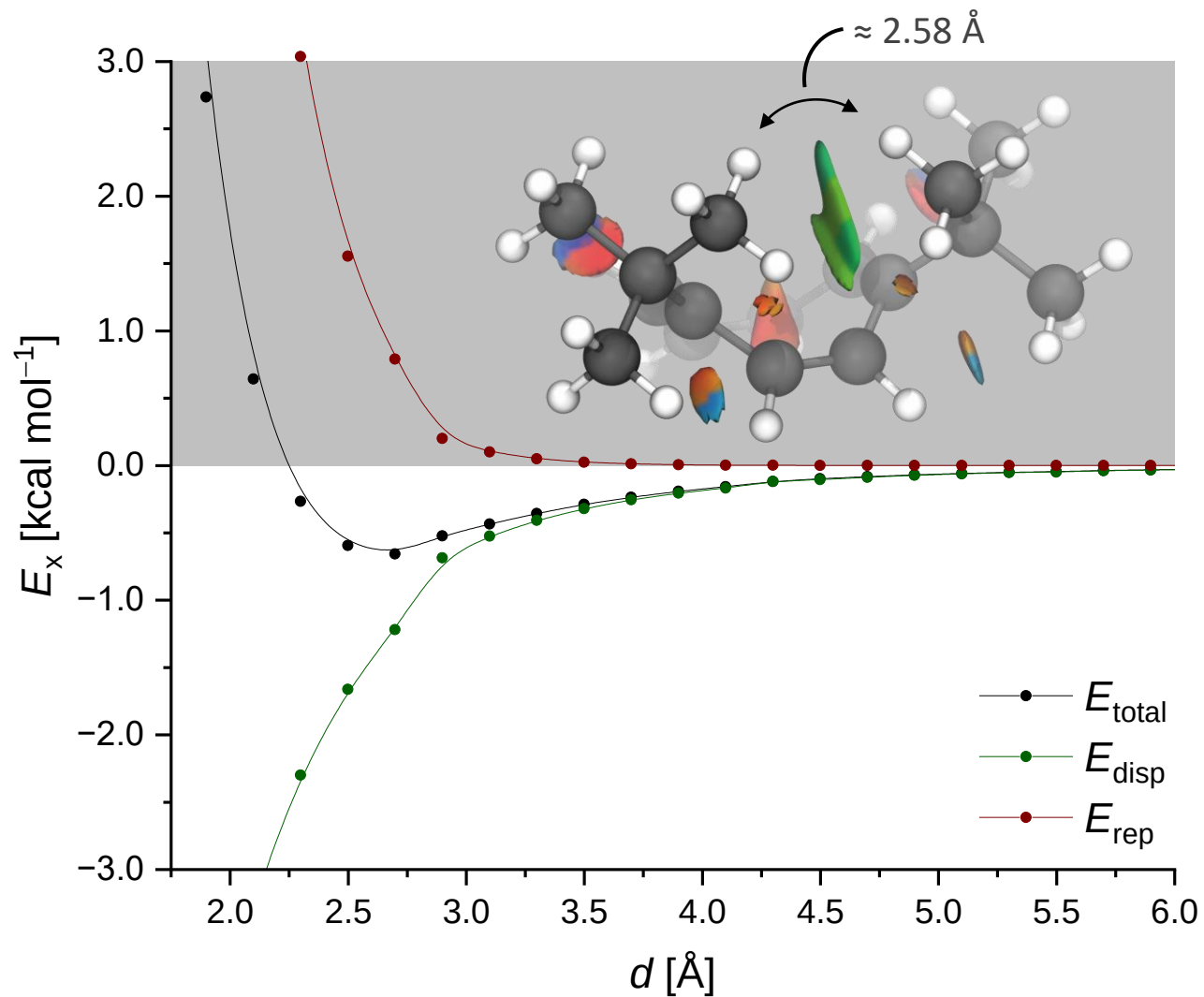
London Dispersion Interactions - From Structure to Reactivity

Seminar talk presented by
Lars Rummel

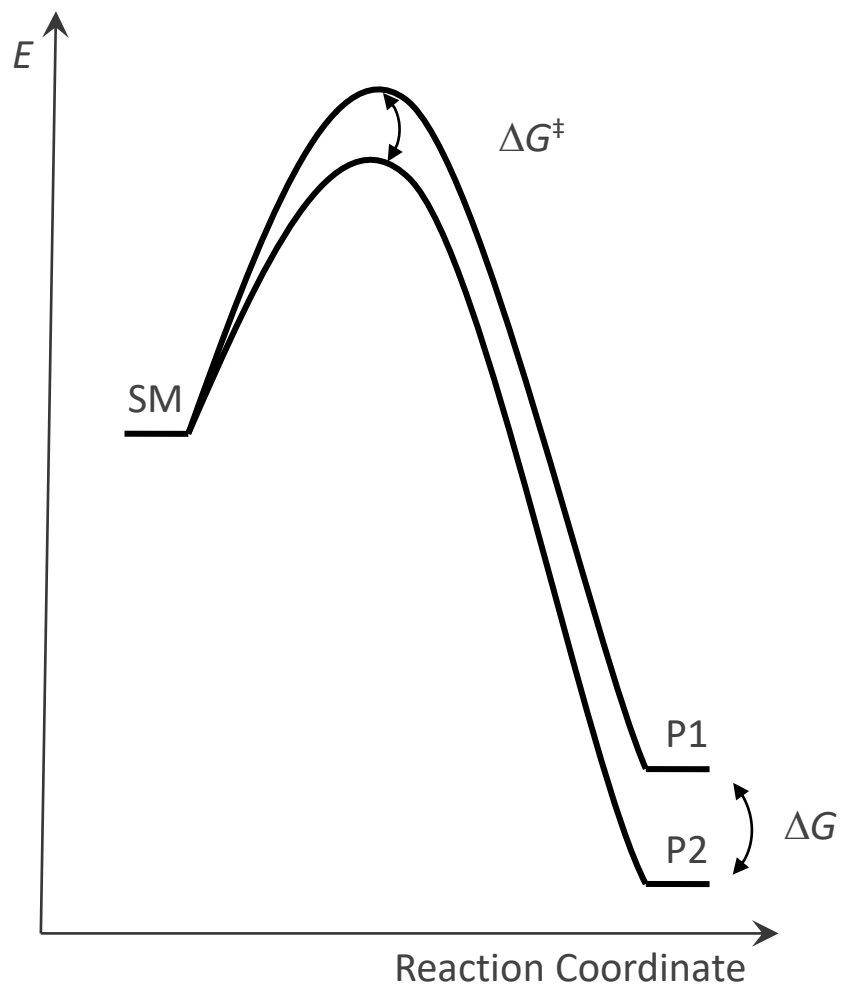
August 05th, 2022

*Institute of Organic Chemistry
Justus-Liebig University Giessen*

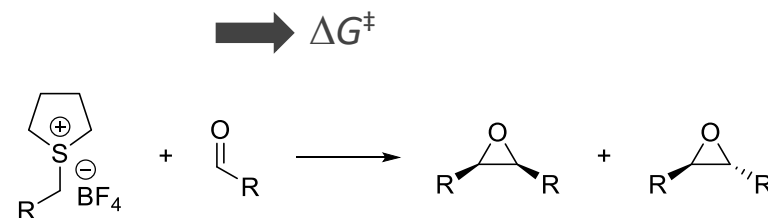




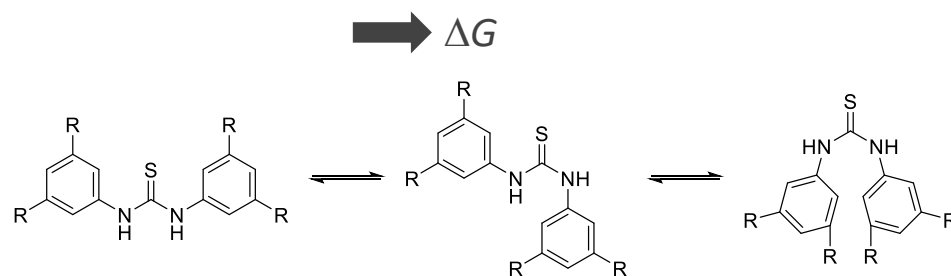
SAPT0/def2-QZVPP, 1,6-COT optimized with B3LYP(D3)/def2-QZVPP.

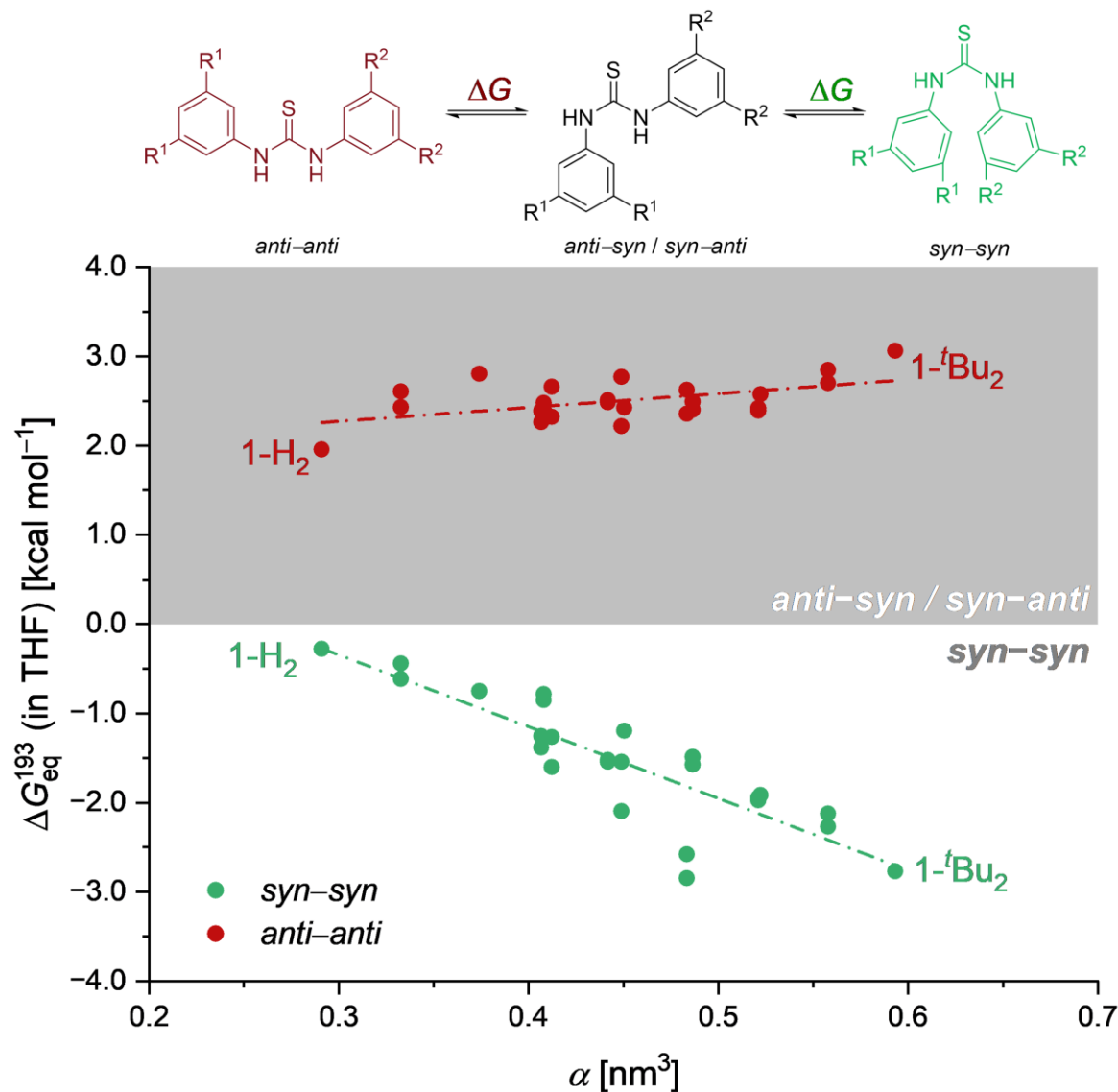


Irreversible Reaction

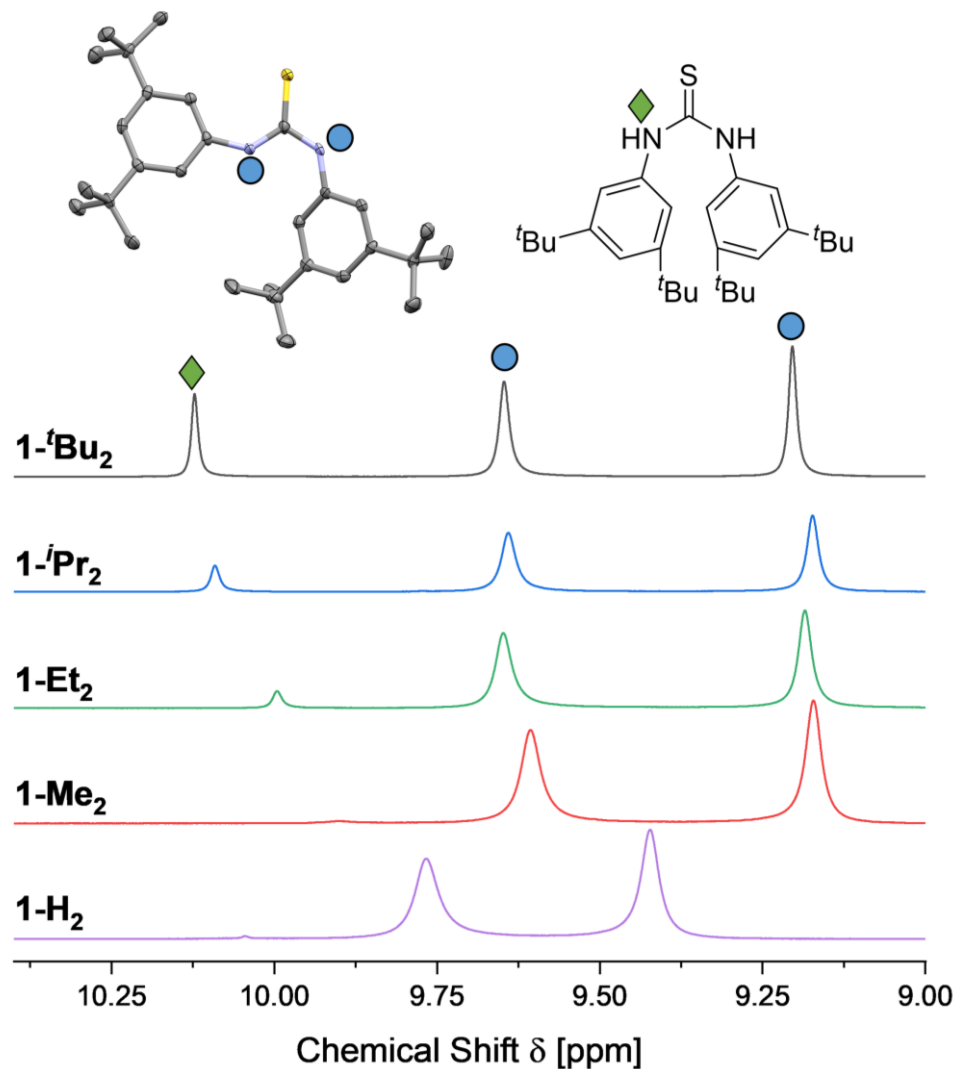


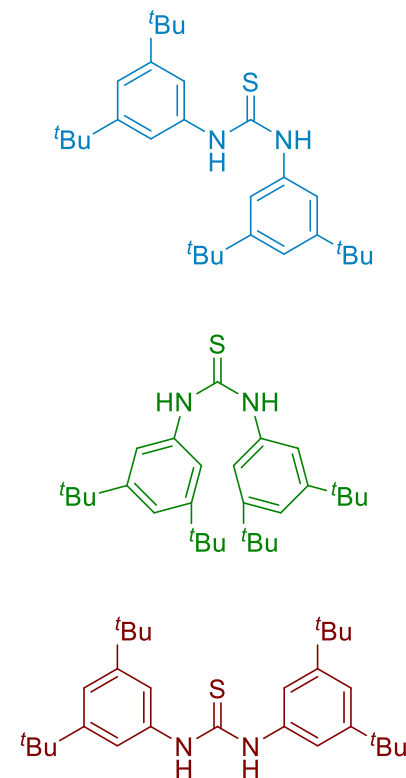
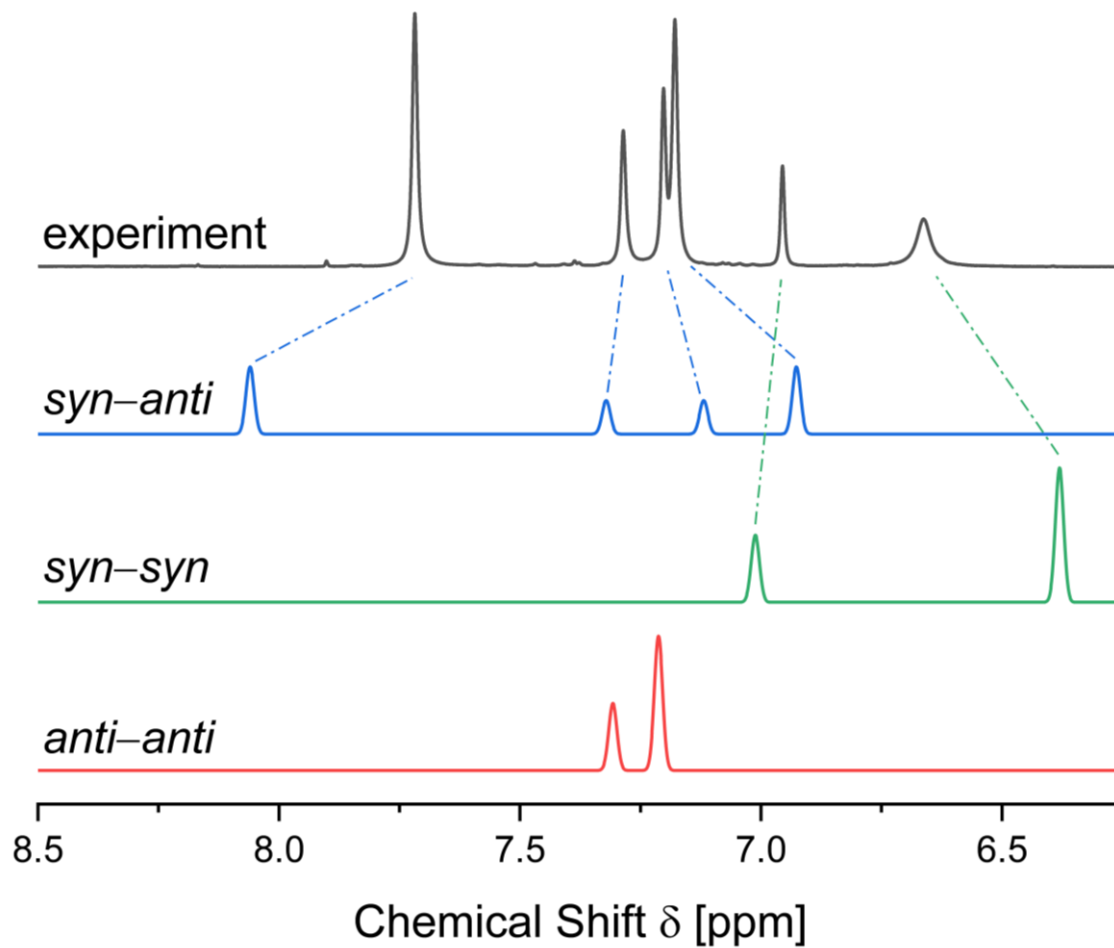
Reversible Reaction



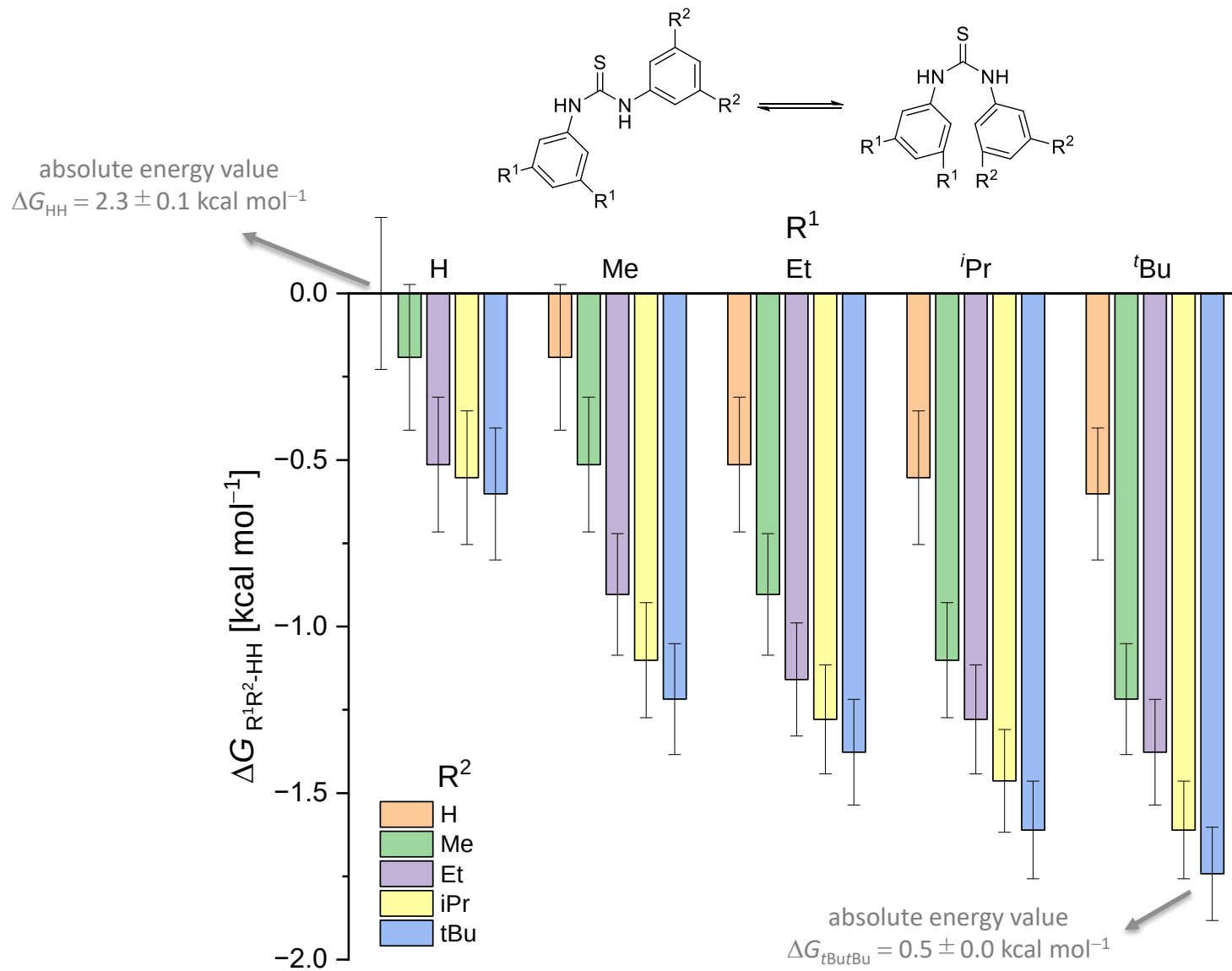


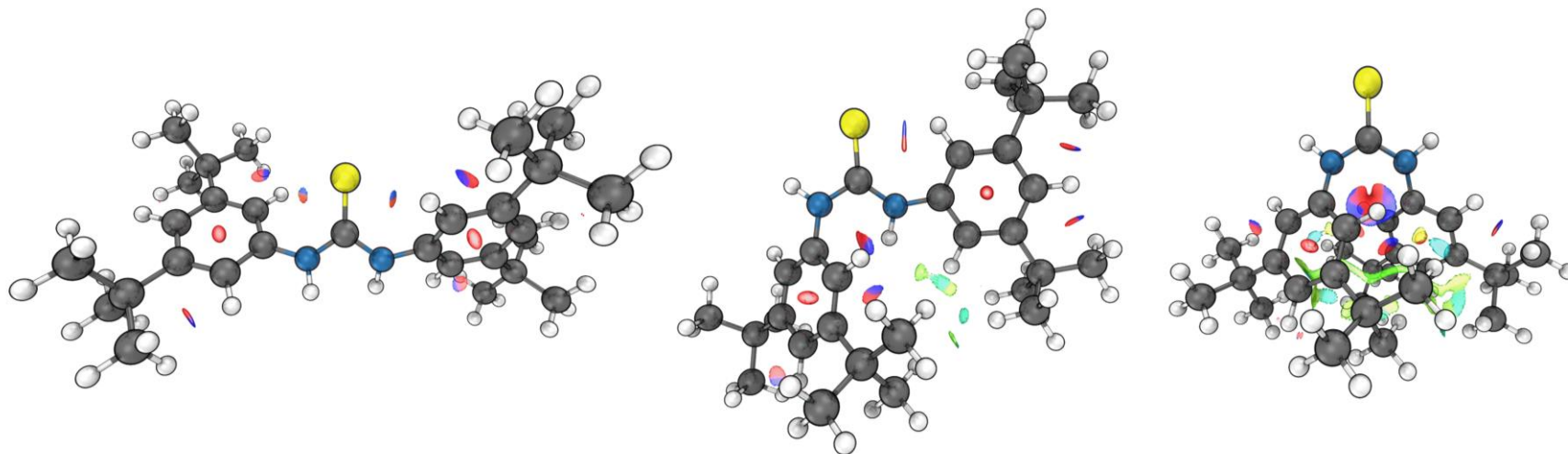
DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3(BJ)/def2-TZVPP, PCM model THF





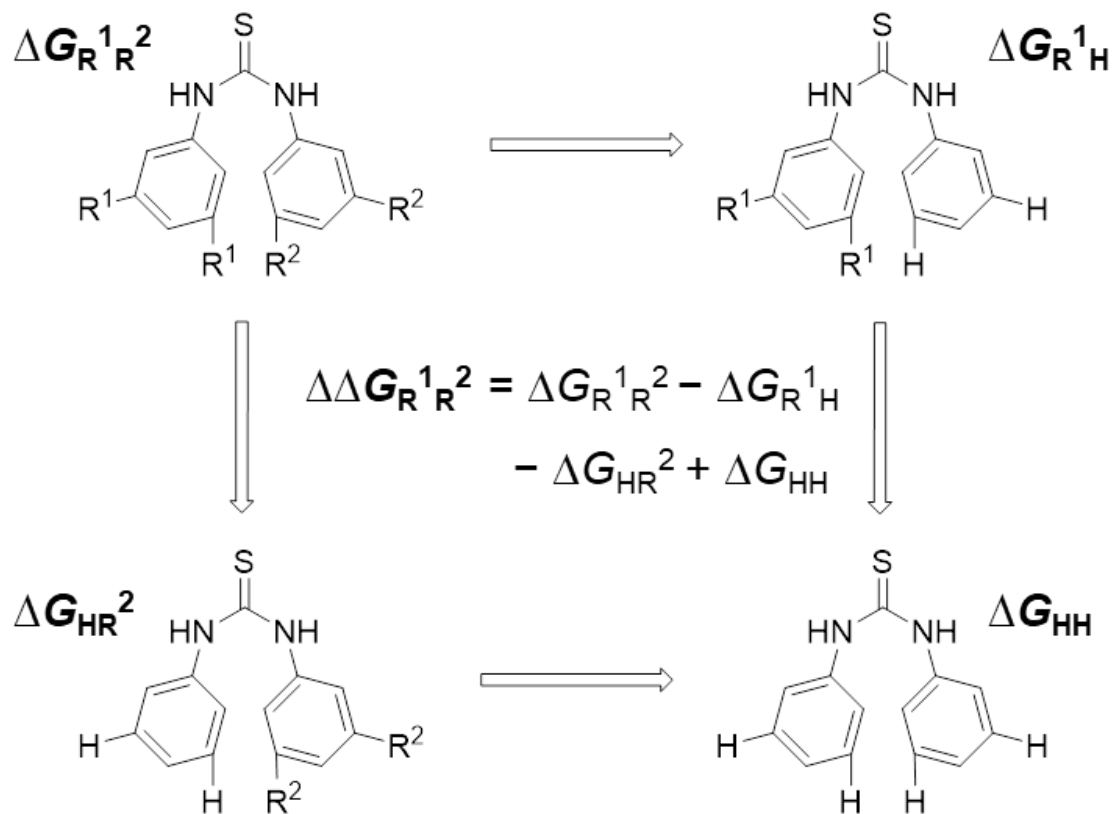
B3LYP-D3(BJ)/def2-TZVPP, SMD model THF

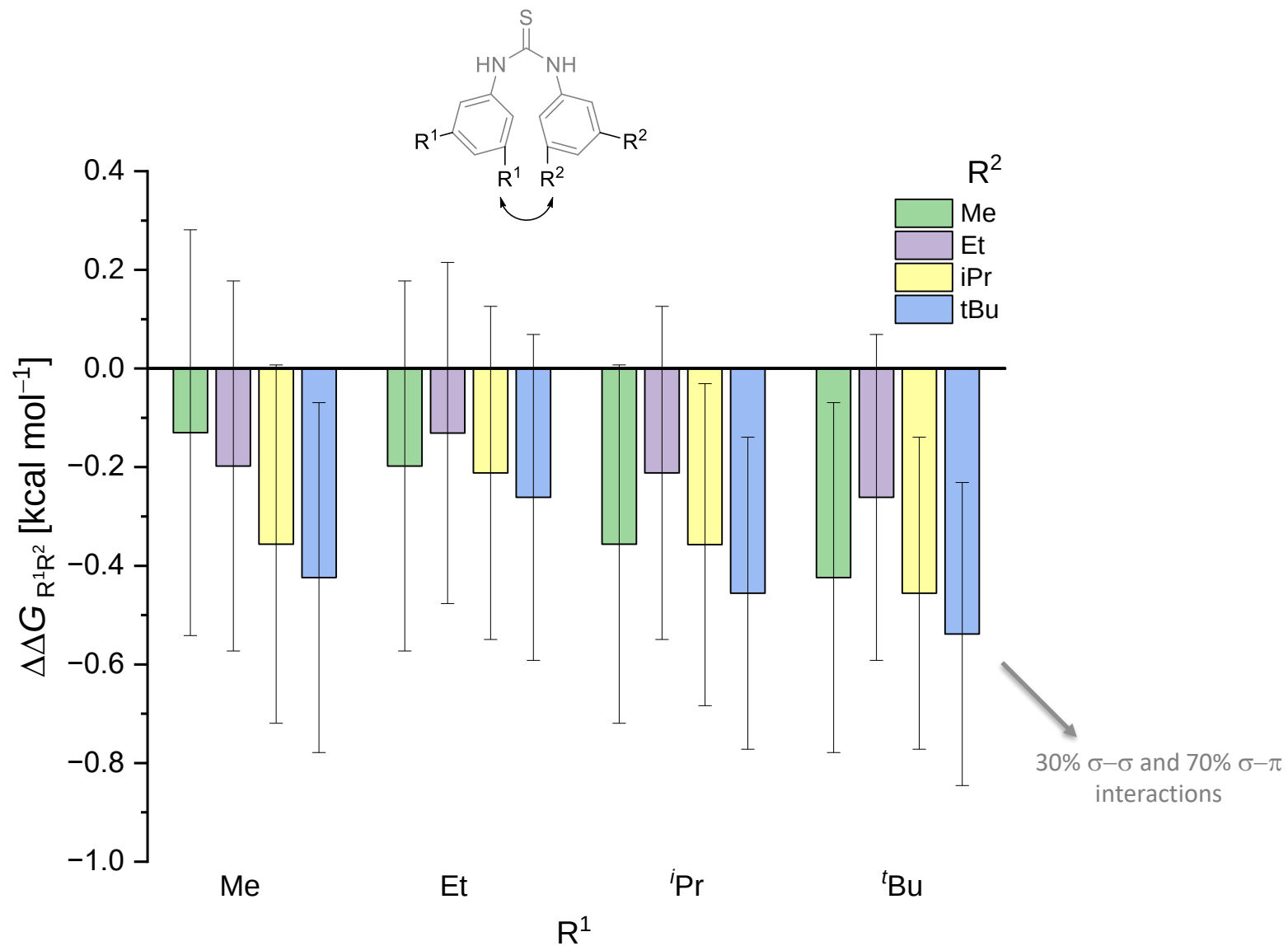


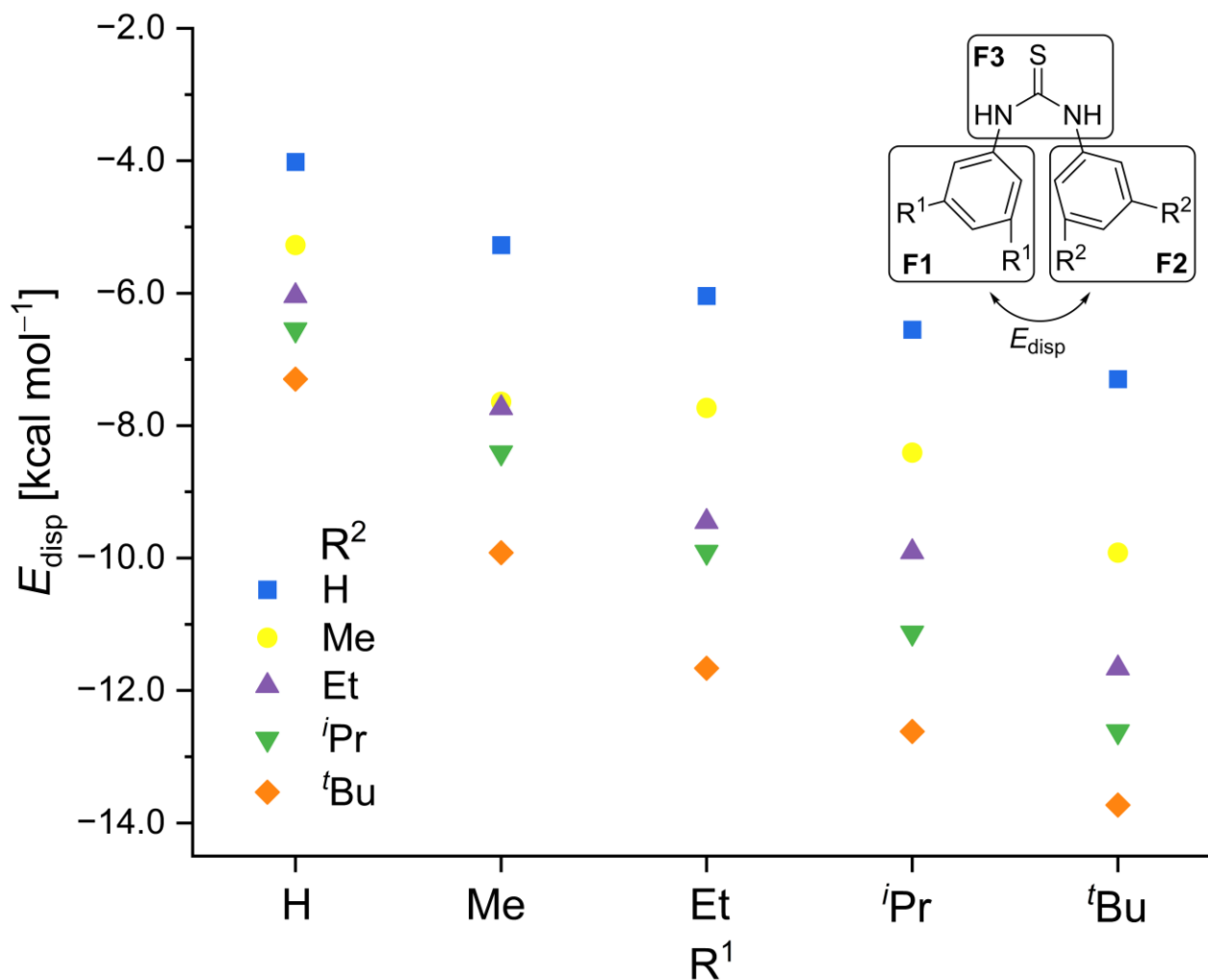


B3LYP-D3(BJ)/def2-TZVPP, isovalue s of 0.2, ranging from $\text{sign}(\lambda_2)\rho = -0.05$ a.u. to $+0.05$ a.u.

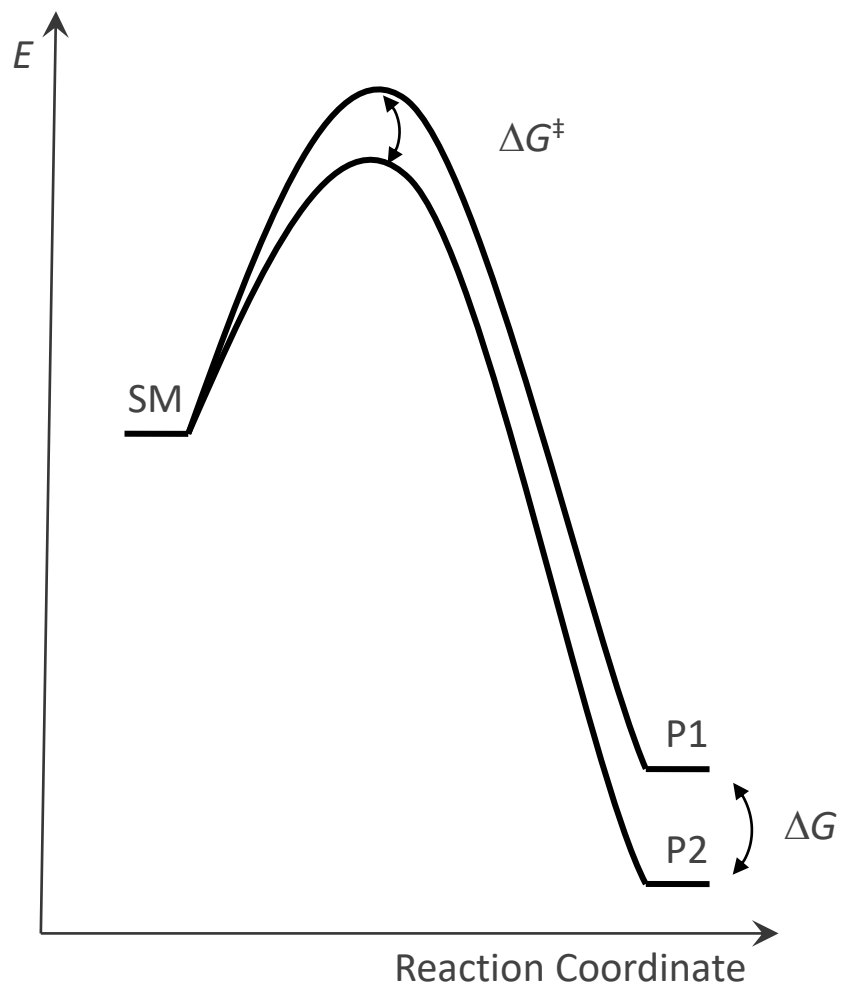
E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* **2010**, 132, 6498-6506; L. Rummel, M. H. J. Domanski, H. Hausmann, J. Becker, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2022**, 61, e202204393.



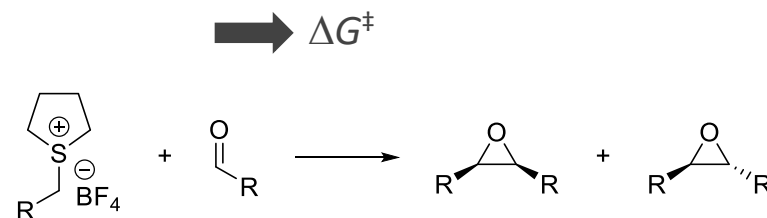




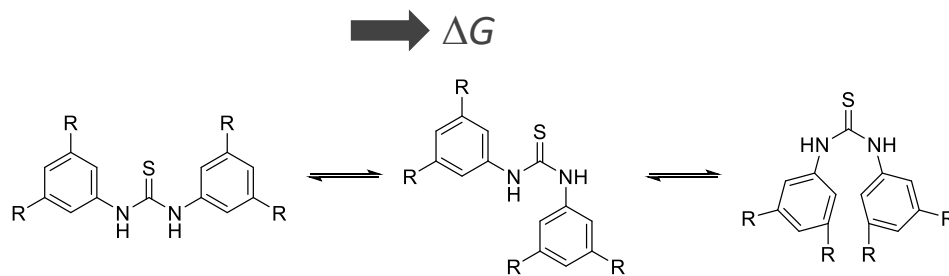
DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3(BJ)/def2-TZVPP



Irreversible Reaction

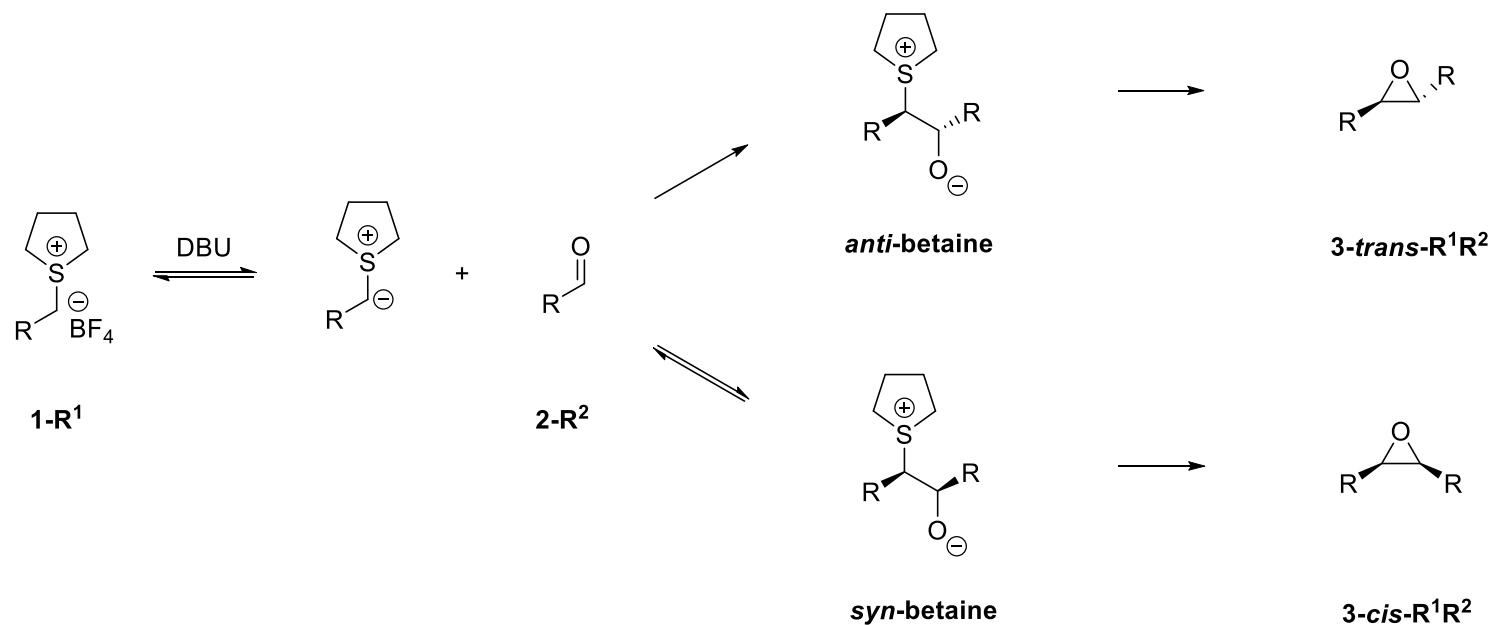


Reversible Reaction



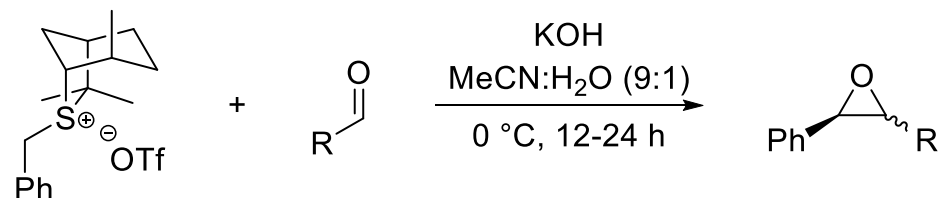
$$\Delta\Delta G_{t\text{Bu}t\text{Bu-HH}} = -1.7 \text{ kcal mol}^{-1}$$

30% σ - σ and 70% σ - π





1. Stability of the Carbonyl Group.

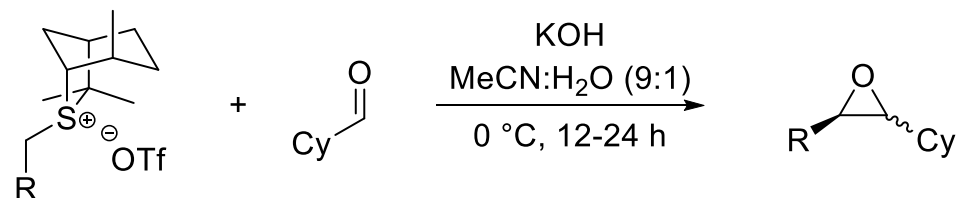


Entry	R	dr [<i>trans</i> : <i>cis</i>]
1	Ph	>95:5
2	Cy	93:7
3	n-Bu	91:9

Aromatic aldehydes strongly favor *trans*-epoxides



2. Stability of the Ylide.

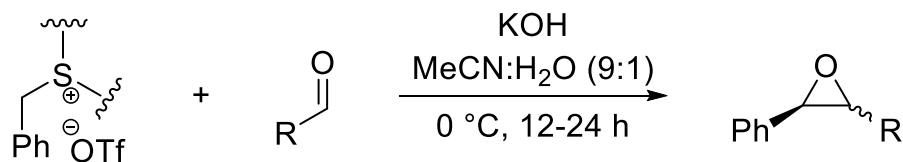


Entry	R	dr [<i>trans</i> : <i>cis</i>]
1	<i>p</i> -CN Ph	>95:5
2	<i>p</i> -H Ph	93:7
3	<i>p</i> -OMe Ph	67:33

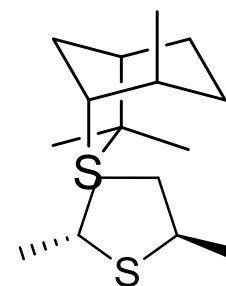
EWGs favor *trans*-epoxides



3. Steric Hindrance of the Ylide/Aldehyde.



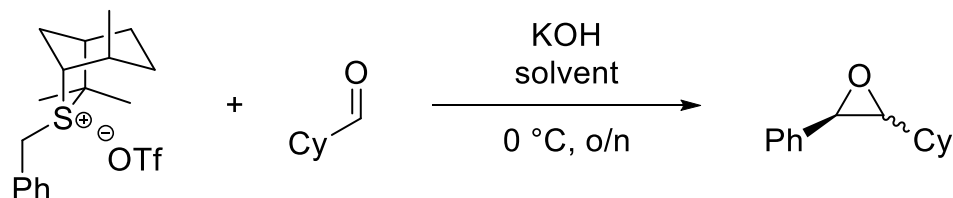
Entry	R	dr [<i>trans</i> : <i>cis</i>]
1	Cy	93:7
2	<i>n</i> -Bu	91:9
3	TIPS-propargyl aldehyde	60:40
4	Cy	75:25
5	<i>n</i> -Bu	70:30
6	TIPS-propargyl aldehyde	Not reported



Steric bulk at every position favors *trans*-epoxides

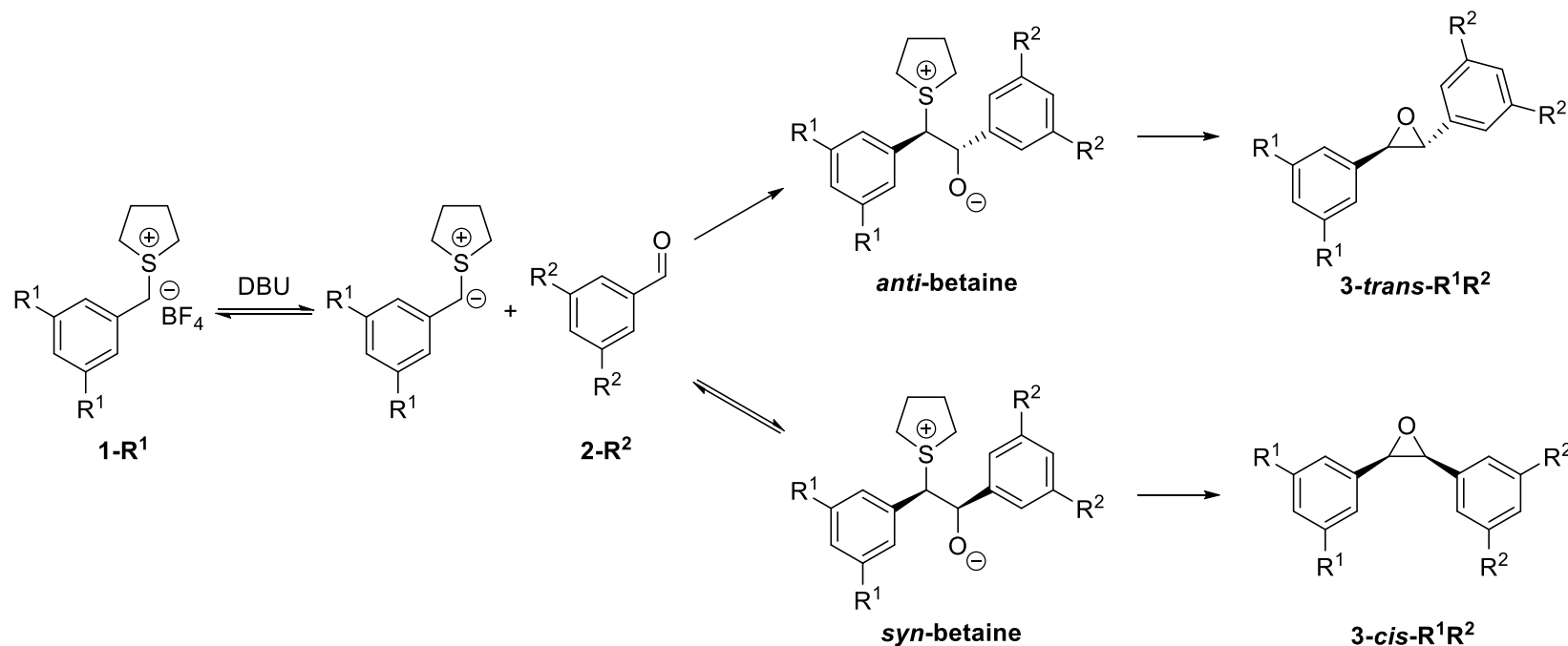


4. Solvation Effects.



Entry	solvent	dr [<i>trans:cis</i>]
1	MeCN	>95:5
2	MeCN- ^t BuOH (9:1)	91:9
3	MeCN-H ₂ O (9:1)	73:27

Aprotic (less protic) solvents favor *trans*-epoxides



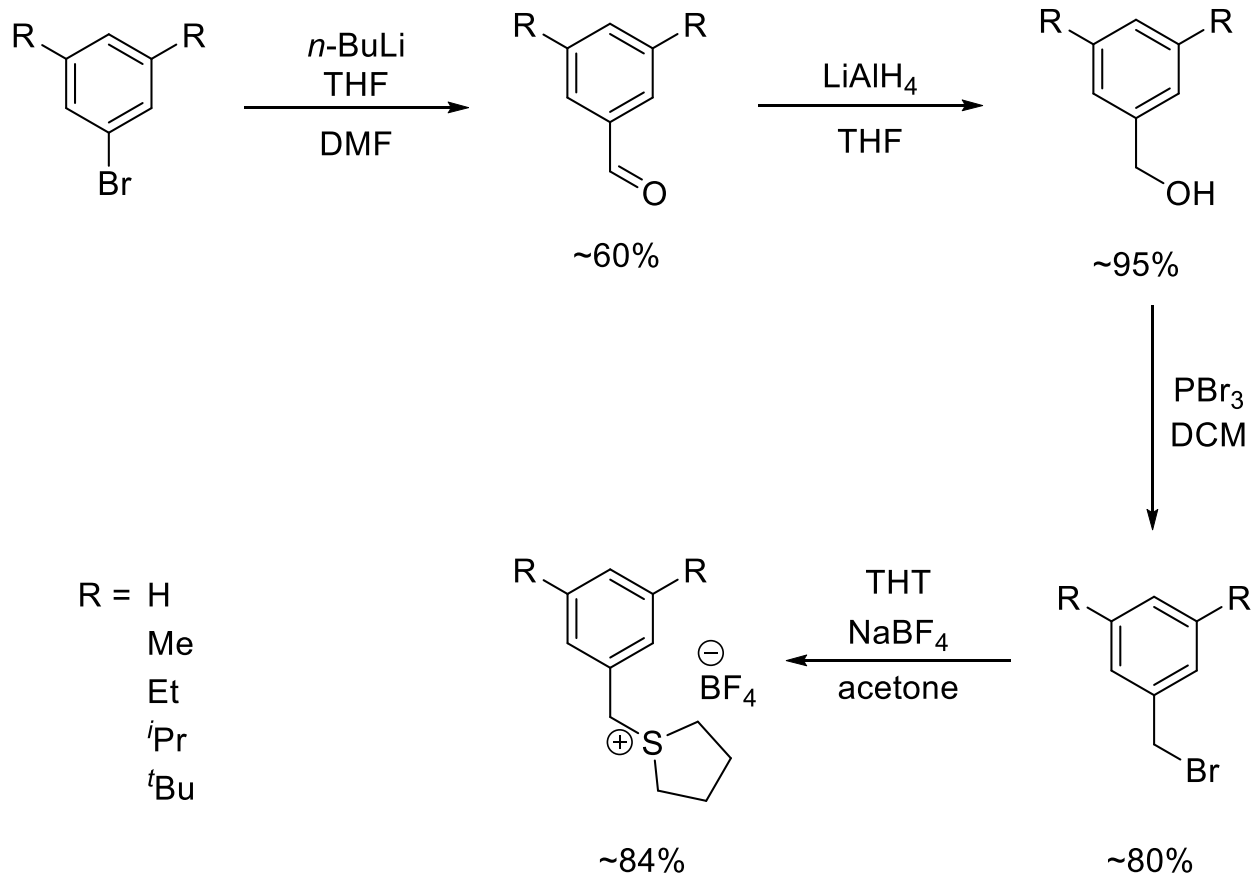
1. Stability of the Carbonyl Group.
2. Stability of the Ylide.
3. Steric Hindrance of the Ylide/Aldehyde.
4. Solvation Effects.

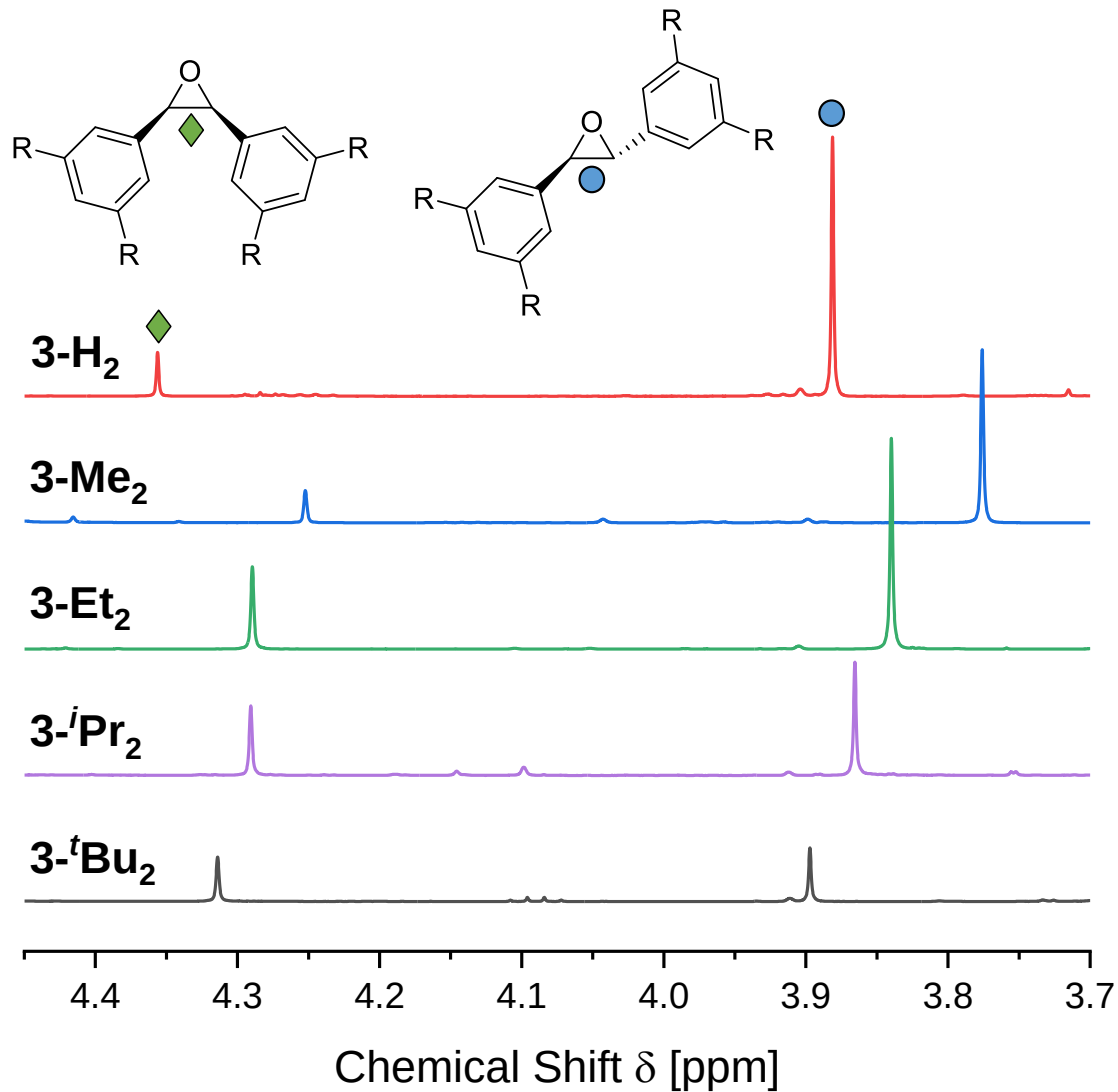
Aromatic Aldehydes

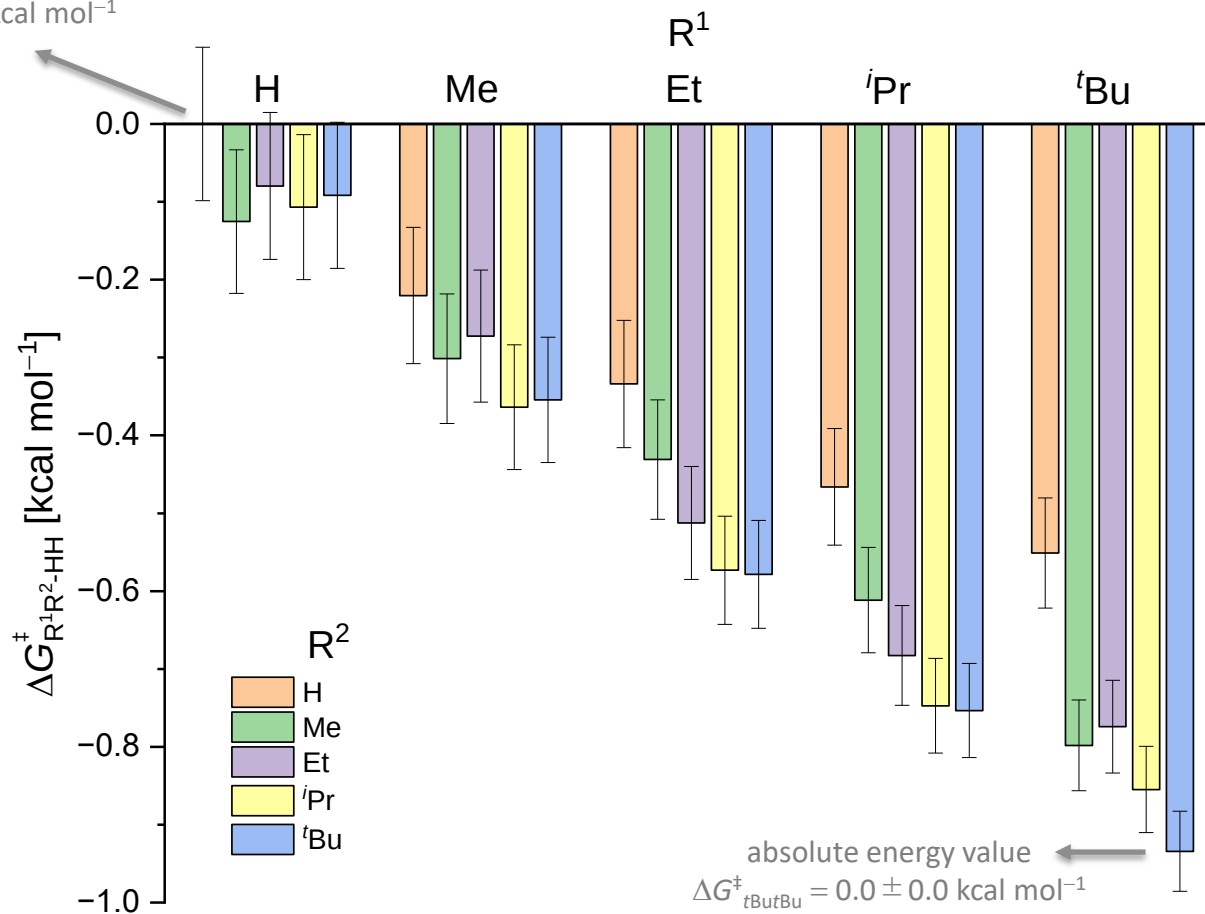
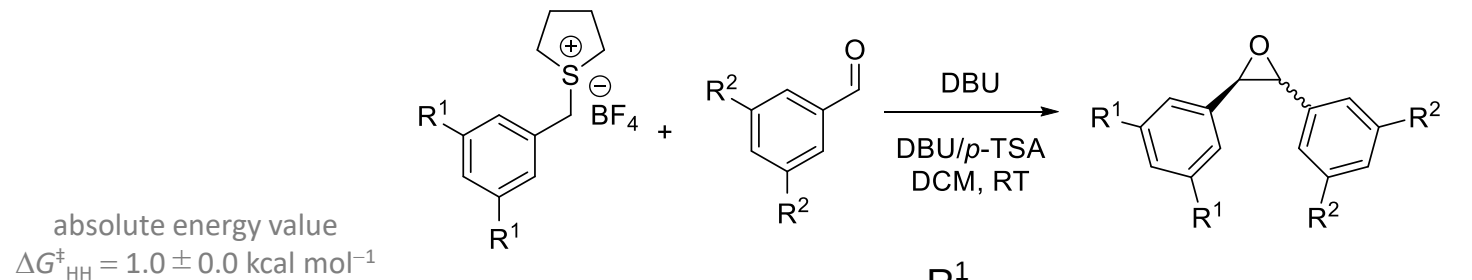
Aromatic Ylides with EWG?

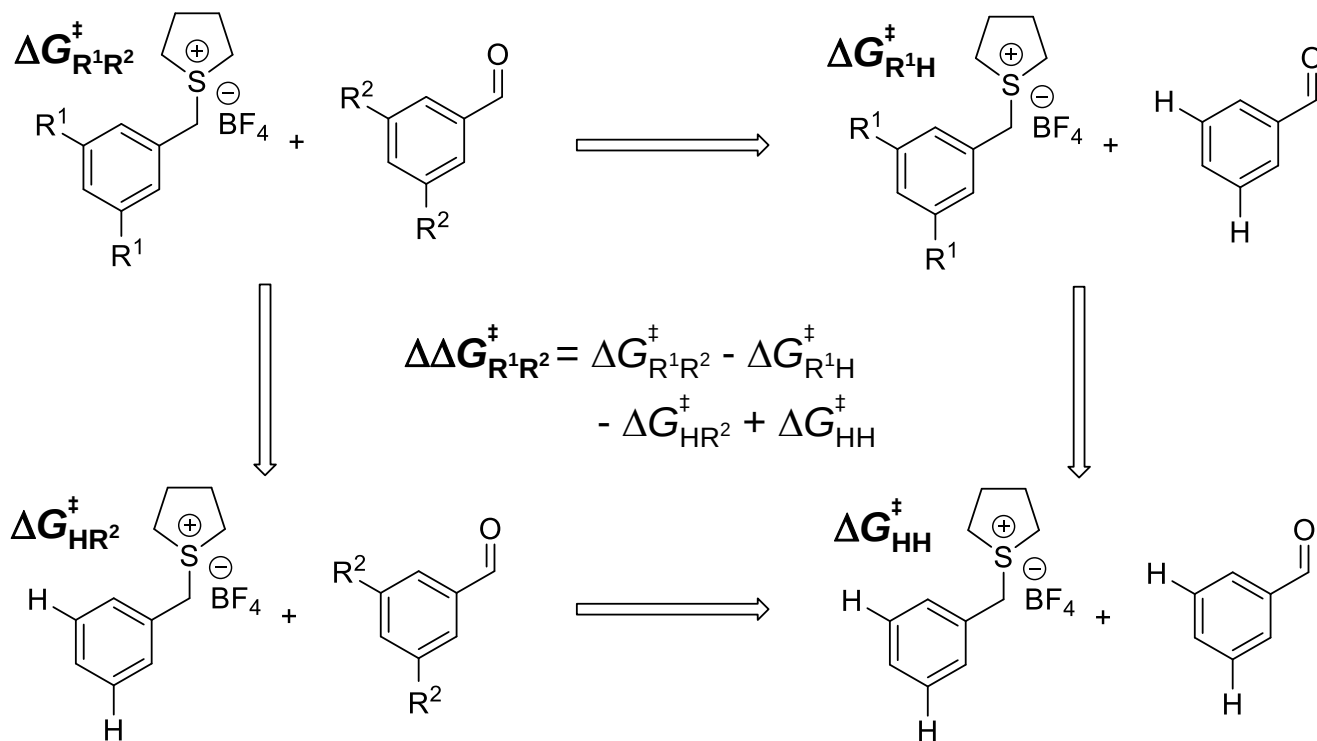
Steric Bulk

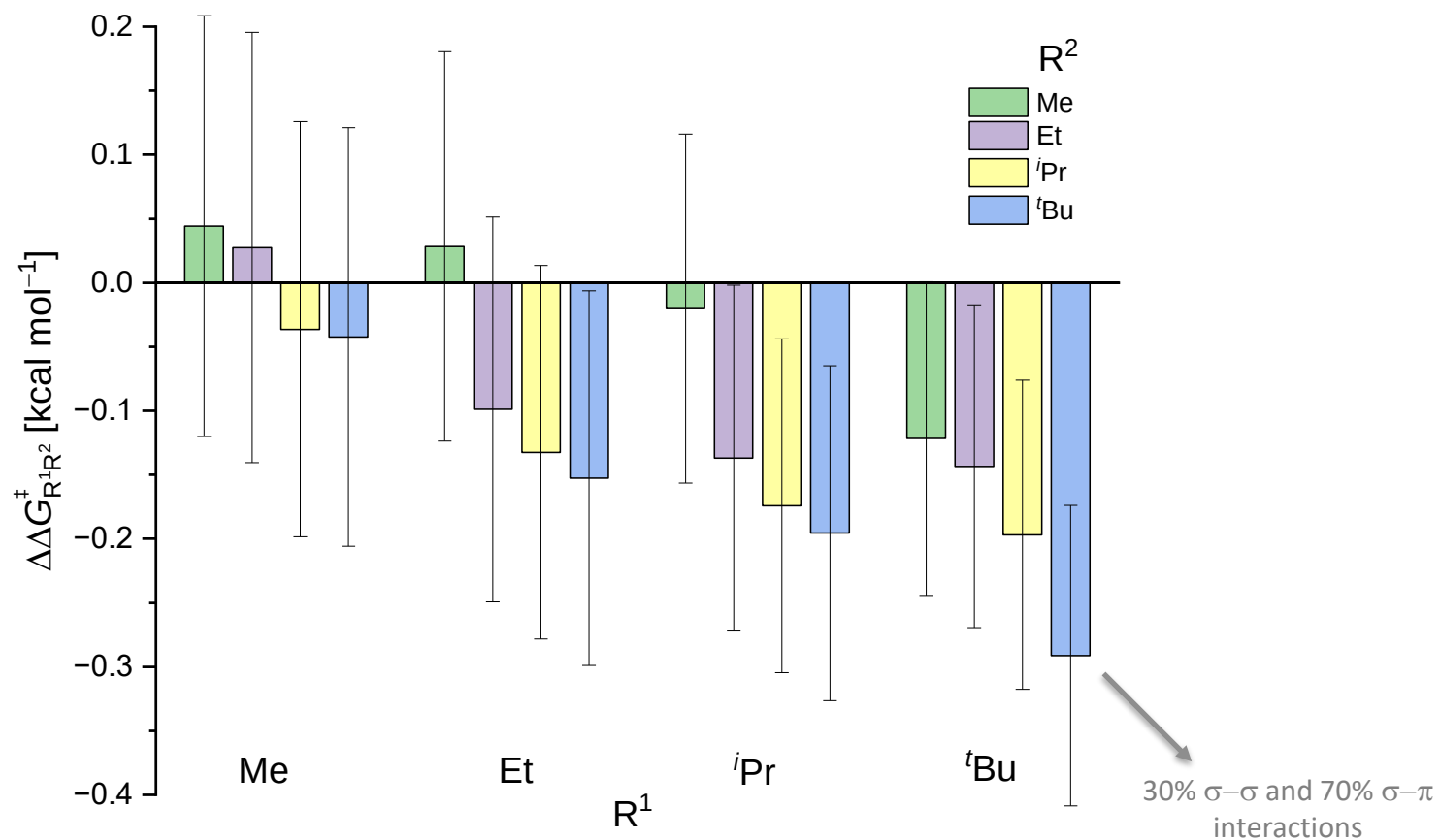
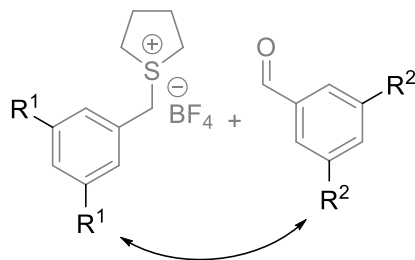
DCM

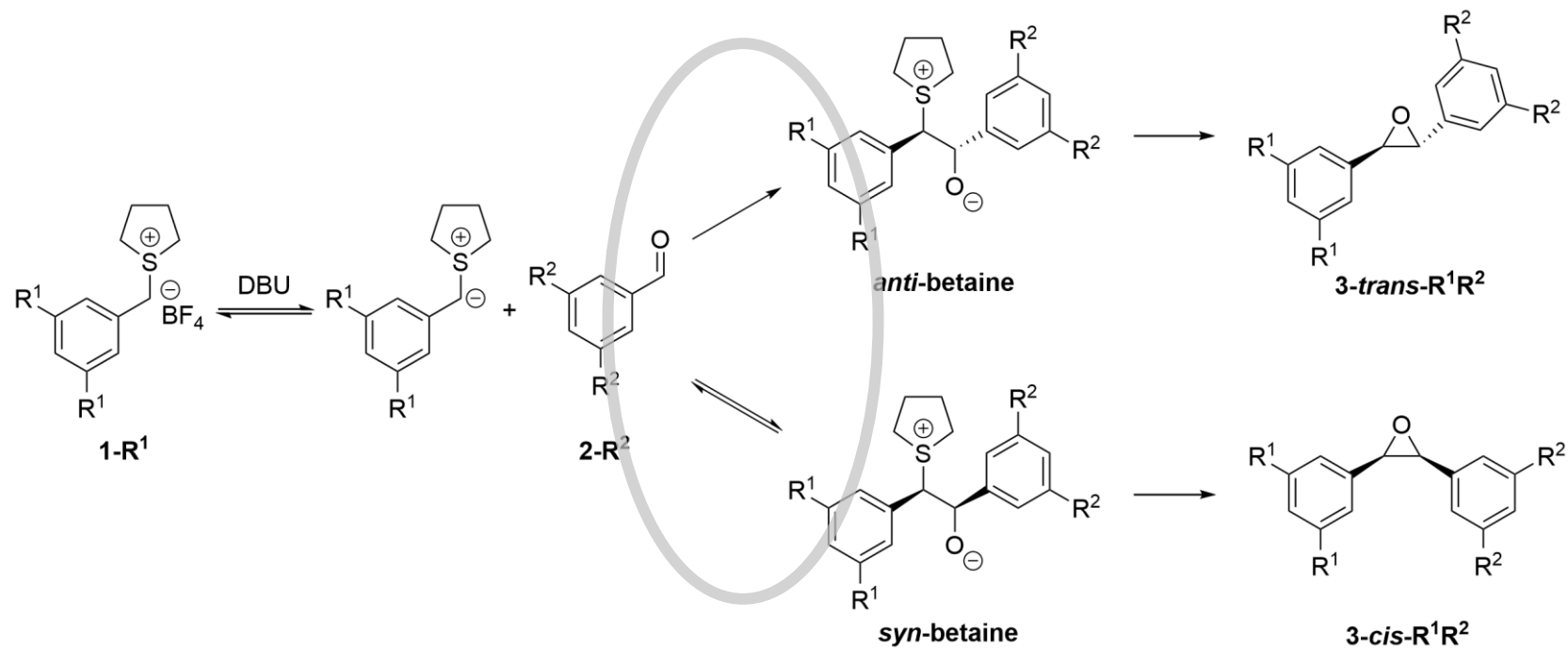


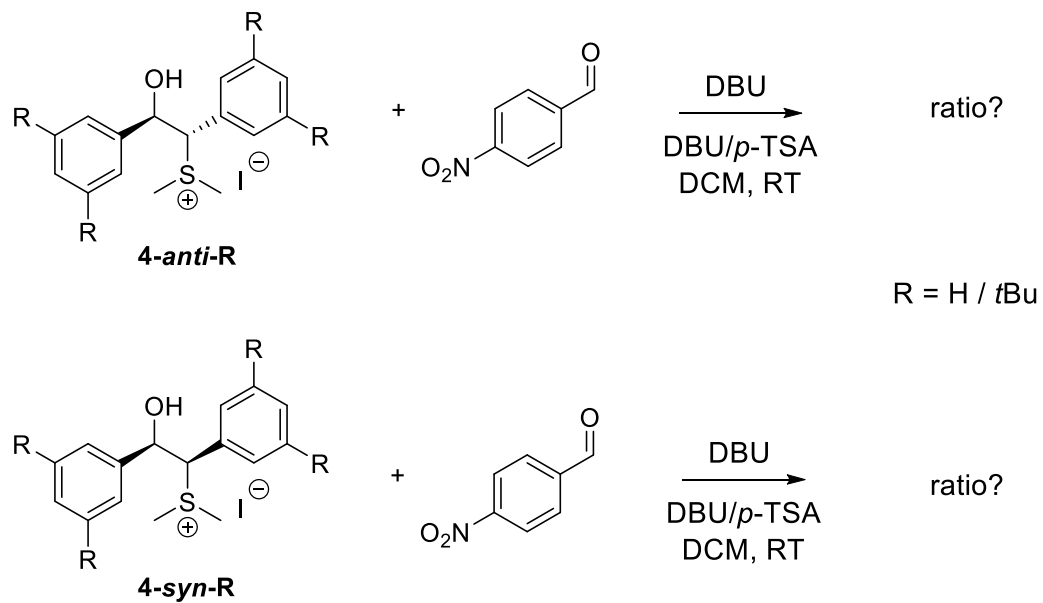


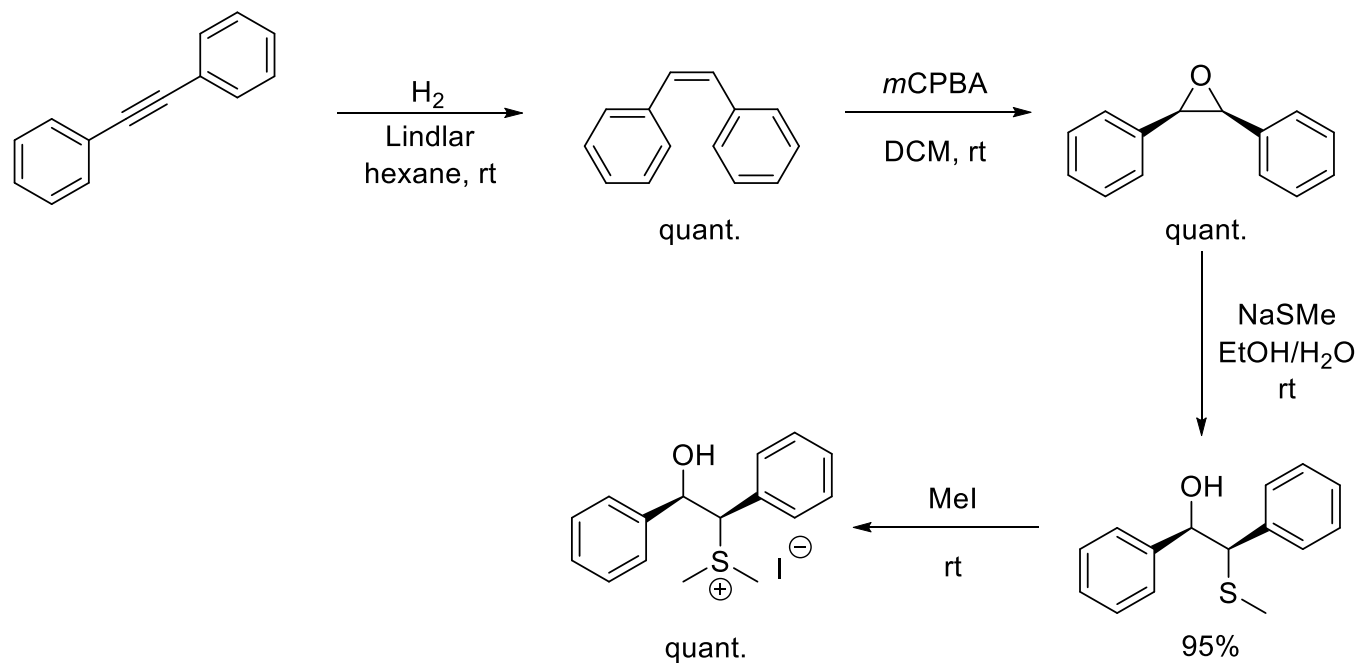


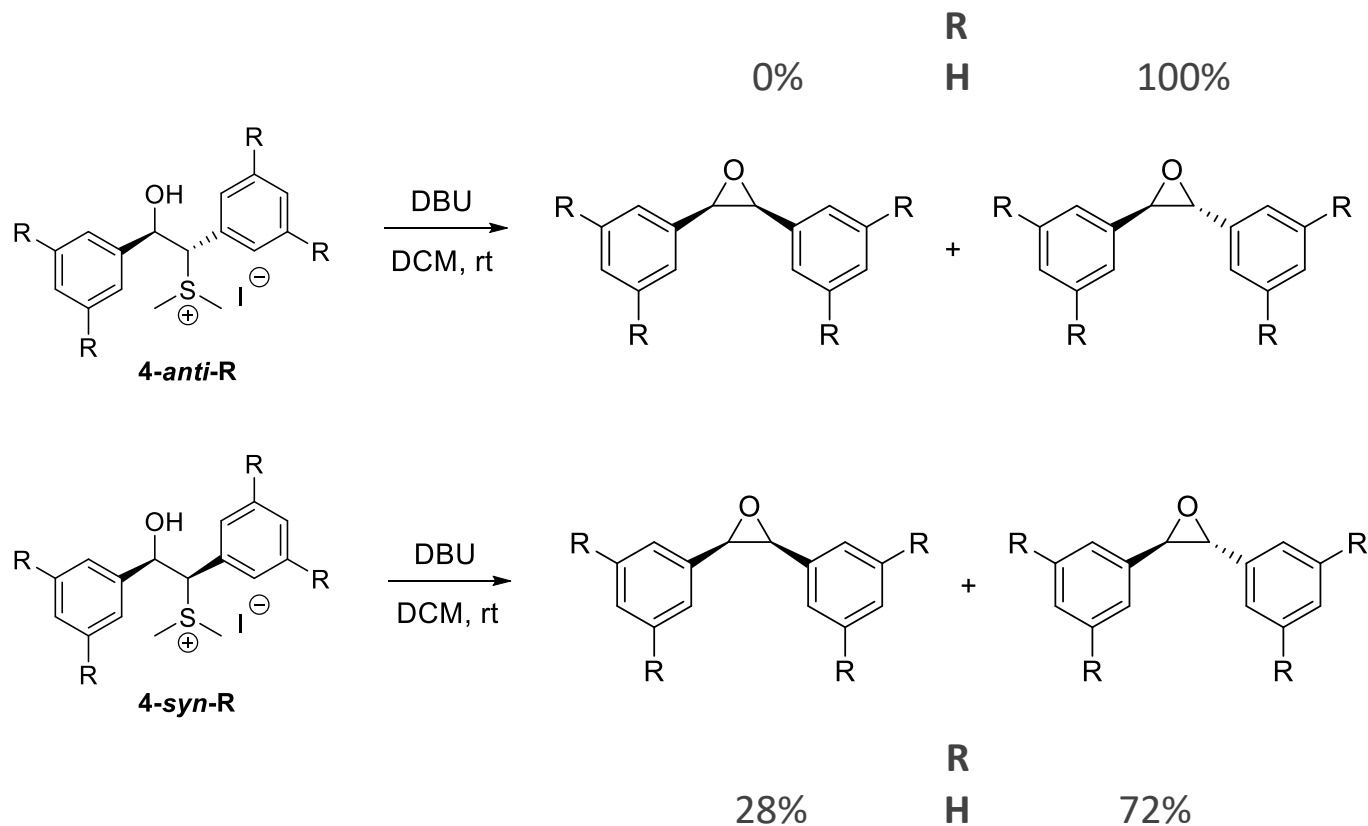


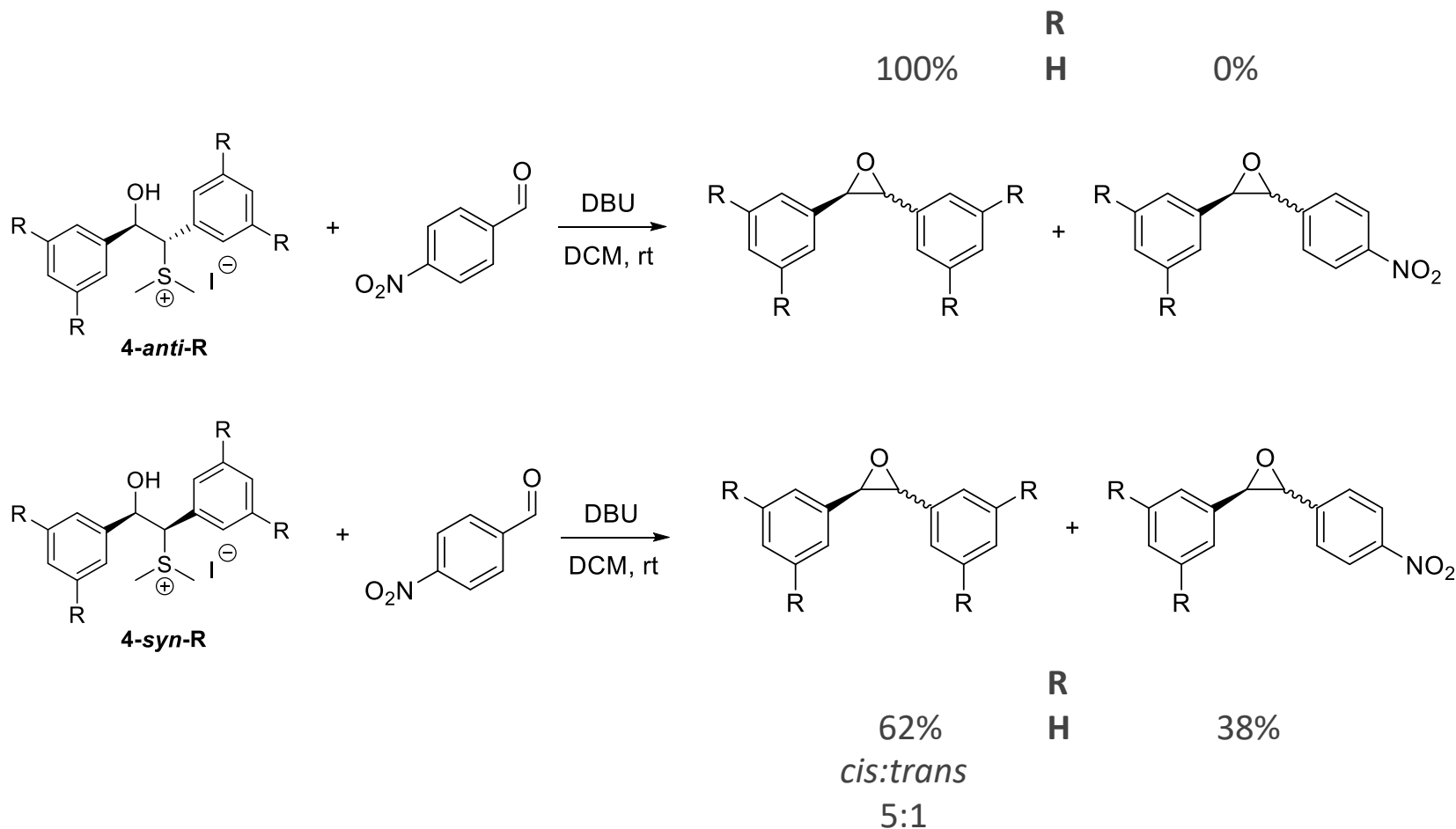






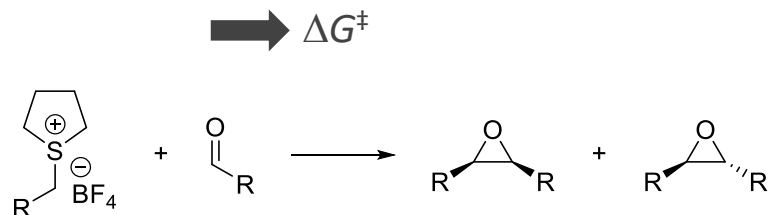








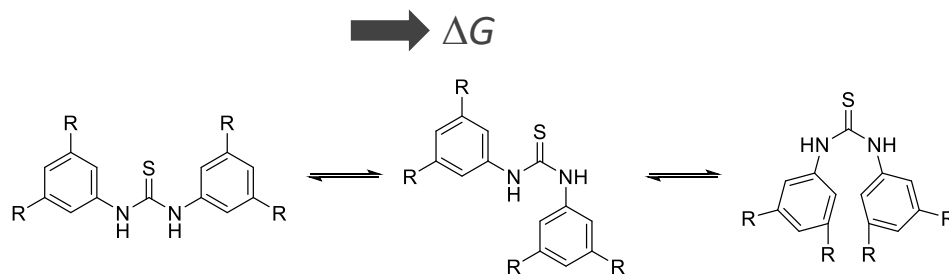
Irreversible Reaction



$$\Delta\Delta G^\ddagger_{t\text{Bu}t\text{Bu-HH}} = -1.0 \text{ kcal mol}^{-1}$$

30% σ - σ and 70% σ - π

Reversible Reaction



$$\Delta\Delta G_{t\text{Bu}t\text{Bu-HH}} = -1.7 \text{ kcal mol}^{-1}$$

30% σ - σ and 70% σ - π



Prof. Dr. Peter R. Schreiner, PhD.

Dispersion Subgroup:

Marvin Domanski, Ephrath Solel, PhD., Finn M. Wilming, Henrik König, Jan M. Schümann

Dr. Dennis Gerbig, and Dr. Bastian Bernhardt

Salome Wagner, Valeria Malynych, Anna Shurando

The PRS Group

