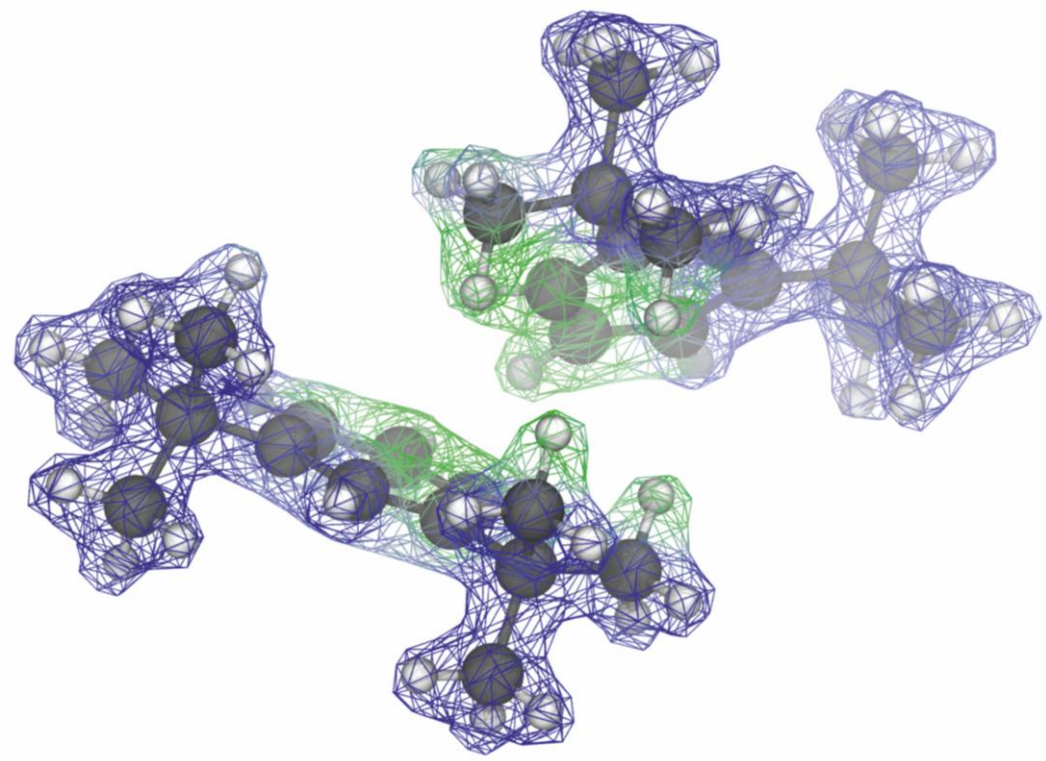
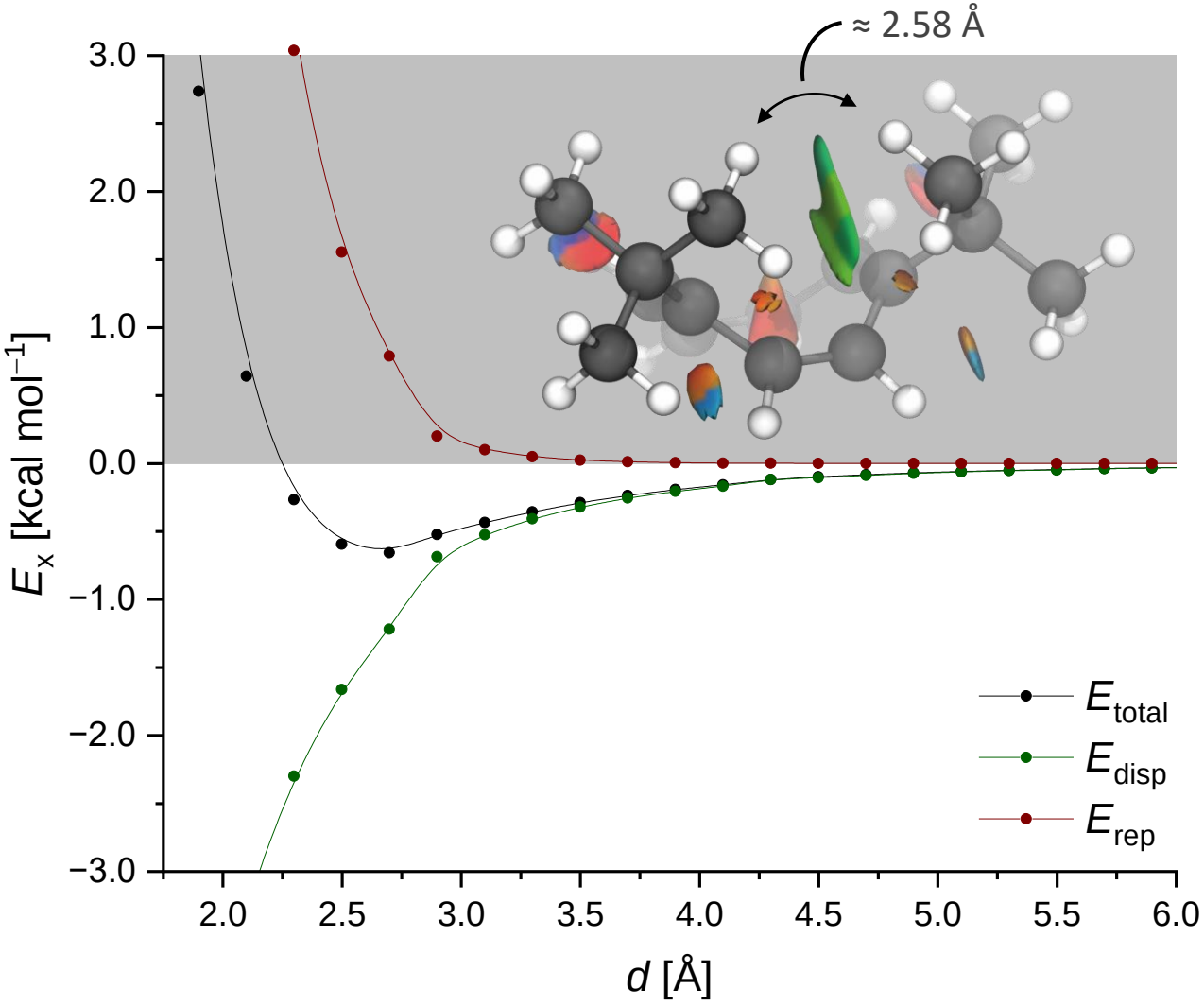
Elucidation of London Dispersion Interactions

Seminar talk presented by
Lars Rummel

February 12th, 2021

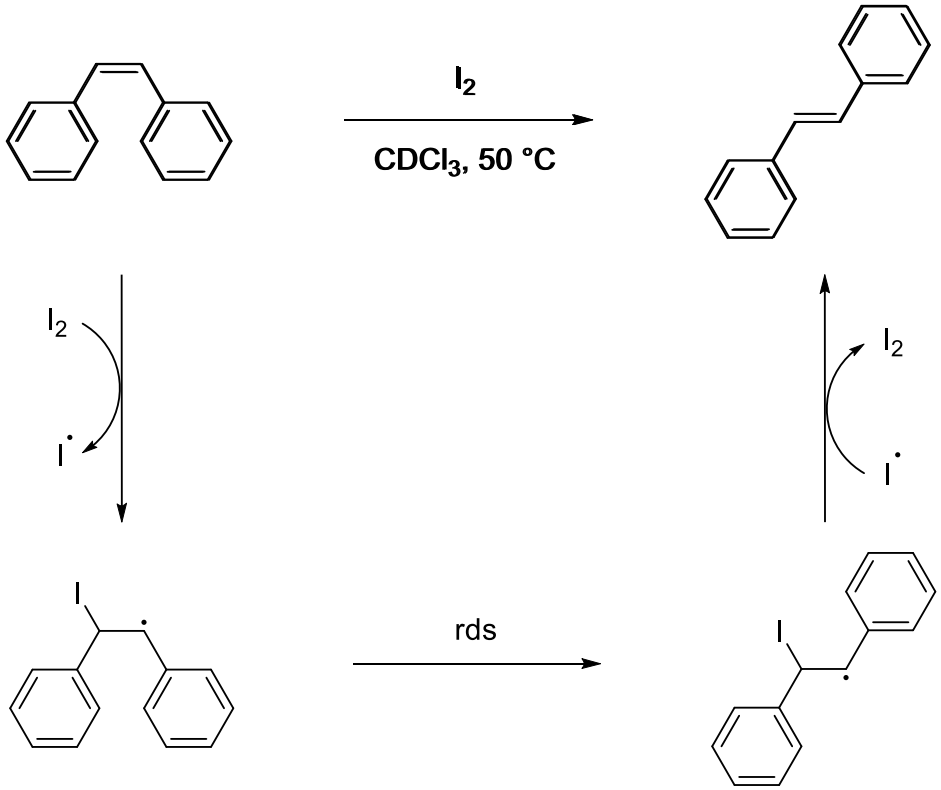
Institute of Organic Chemistry
Justus-Liebig University Giessen



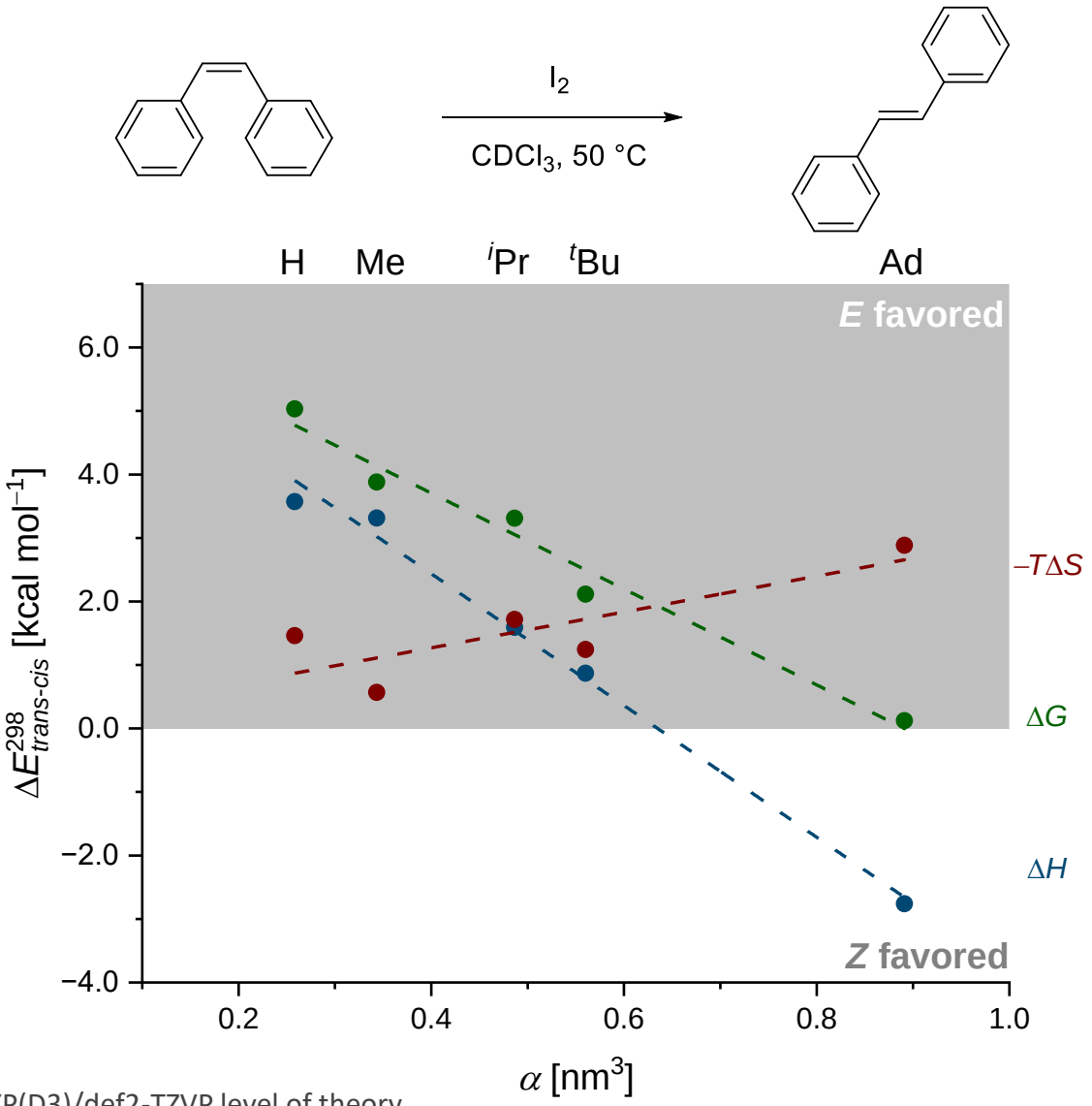


*Computations on a SAPT0/def2-QZVPP level of theory. 1,6-COT optimized with B3LYP(D3)/def2-QZVPP.

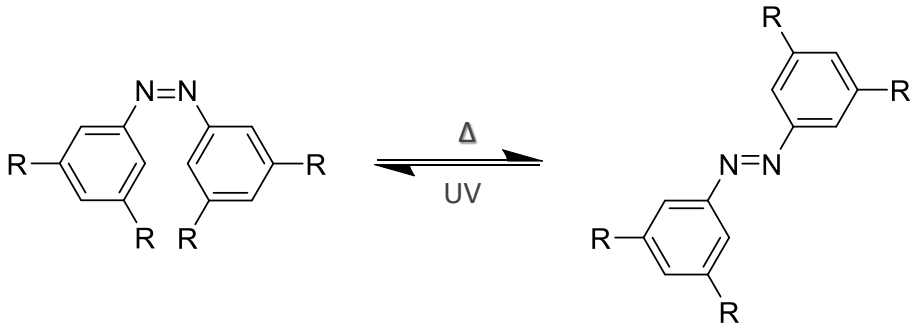
J. M. Schümann, J. P. Wagner, A. K. Eckhardt, H. Quanz, P. R. Schreiner, *J. Am. Chem. Soc.* **2021**, 143, 1, 41-45.

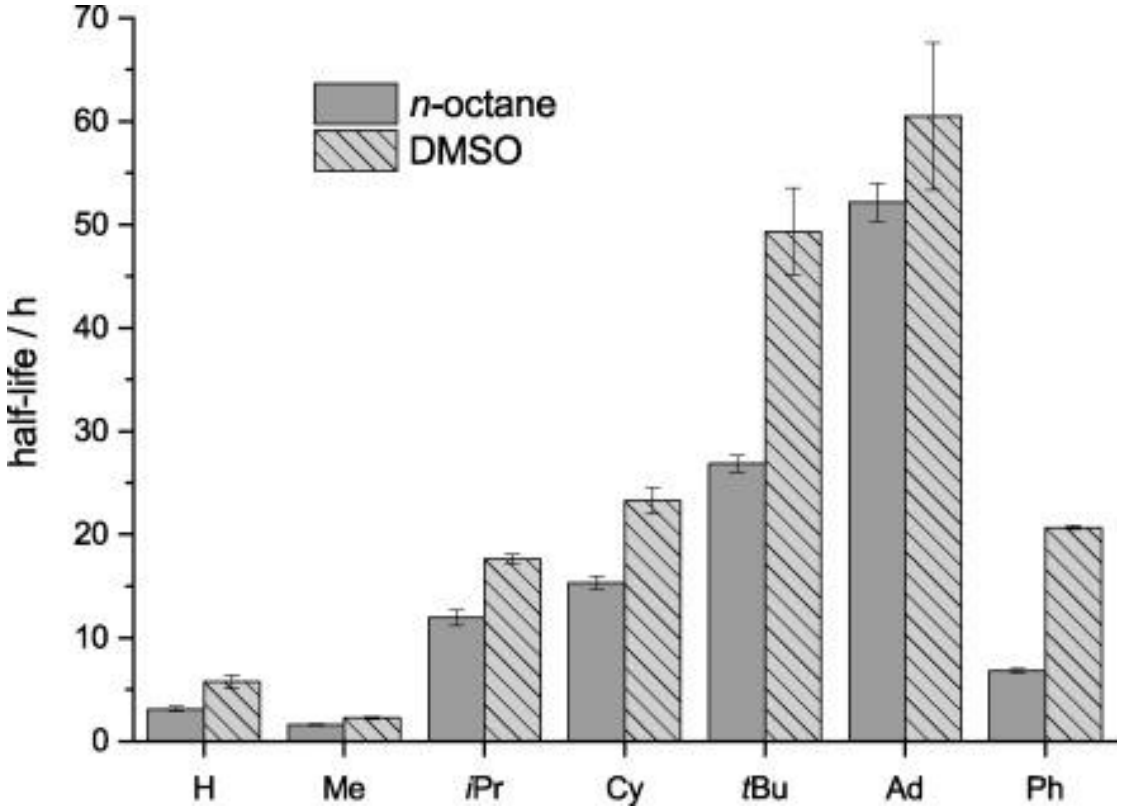


S. S. Hepperle, Q. Li, A. L. L. East, *J. Phys. Chem. A* **2005**, *109*, 10975-10981.
S. Yamashita, *Bull. Chem. Soc. Jpn.* **1961**, *34*, 487-489

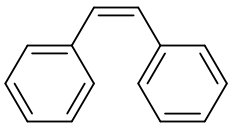


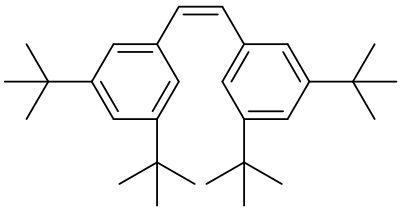
*Computations on a B3LYP(D3)/def2-TZVP level of theory.

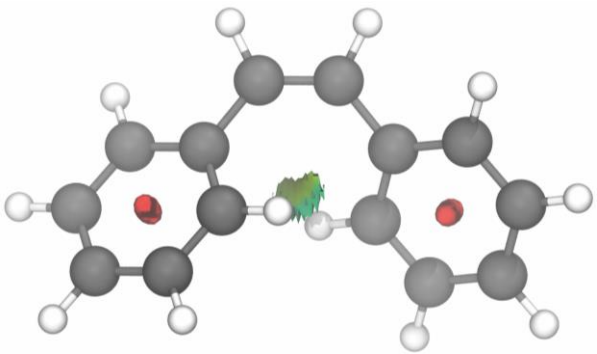

N=N
R
R
R
R
Δ
UV
N=N
R
R
R
R


n-octane
DMSO
half-life / h
0
10
20
30
40
50
60
70
H
Me
iPr
Cy
tBu
Ad
Ph

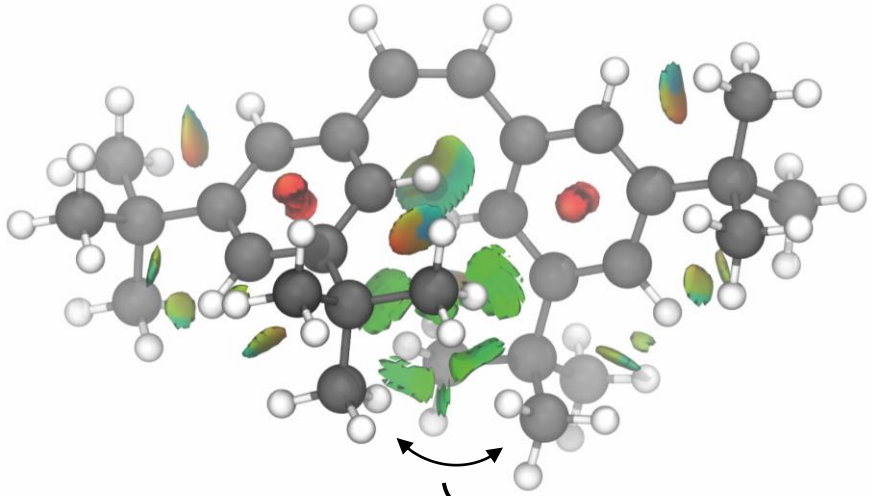
Non-Covalent Interaction Plots





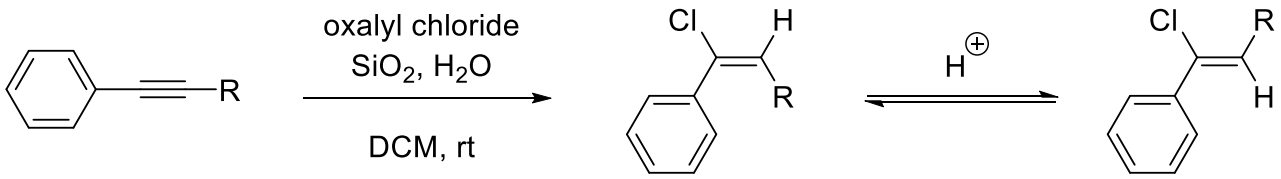


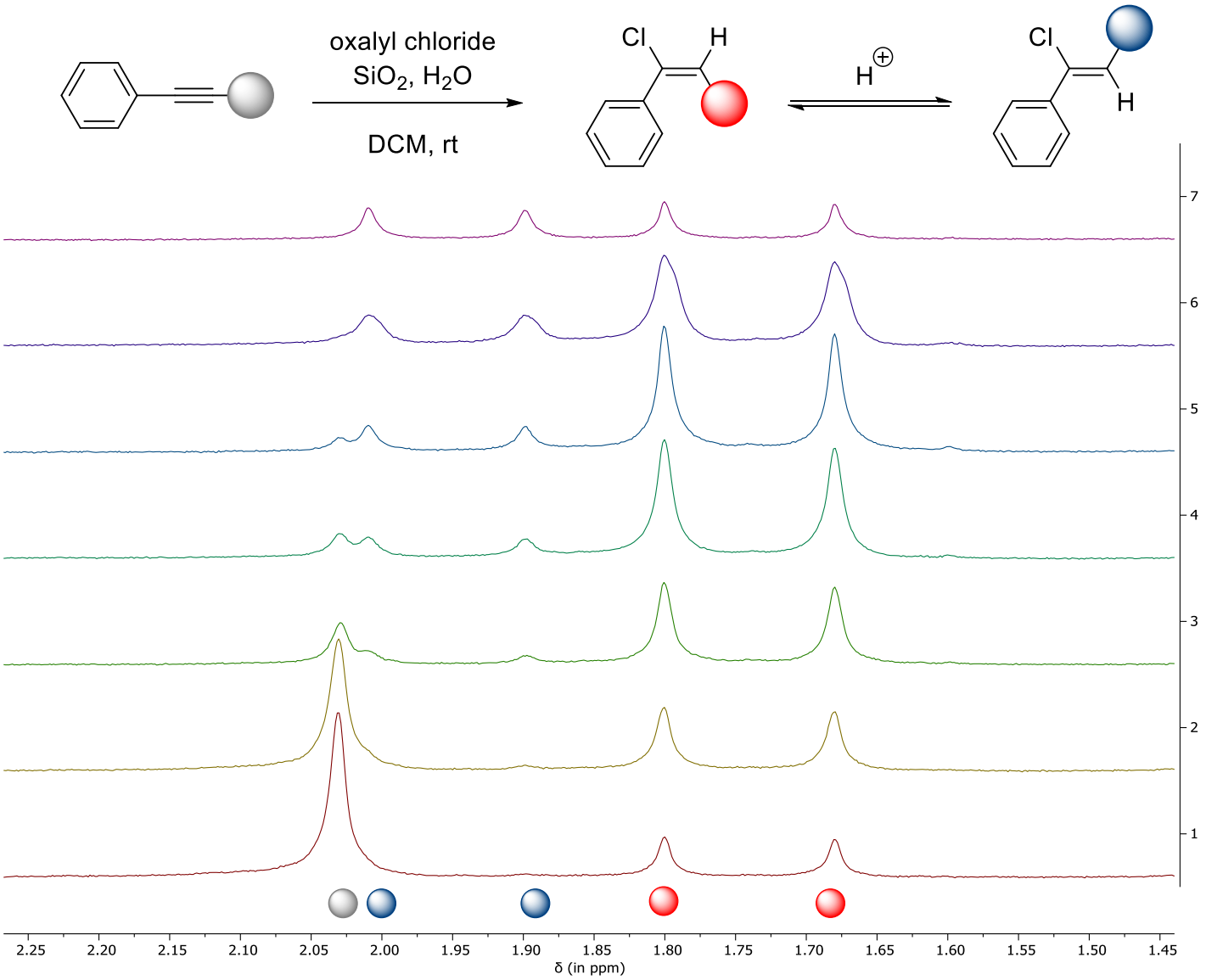
$R_{C-C} = 1.34$ Å



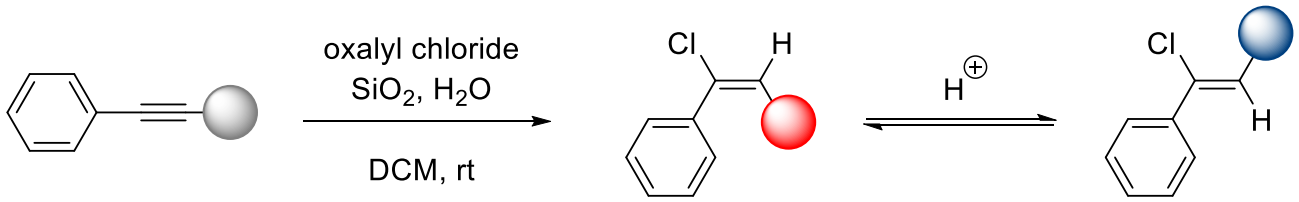
≈ 2.35 Å

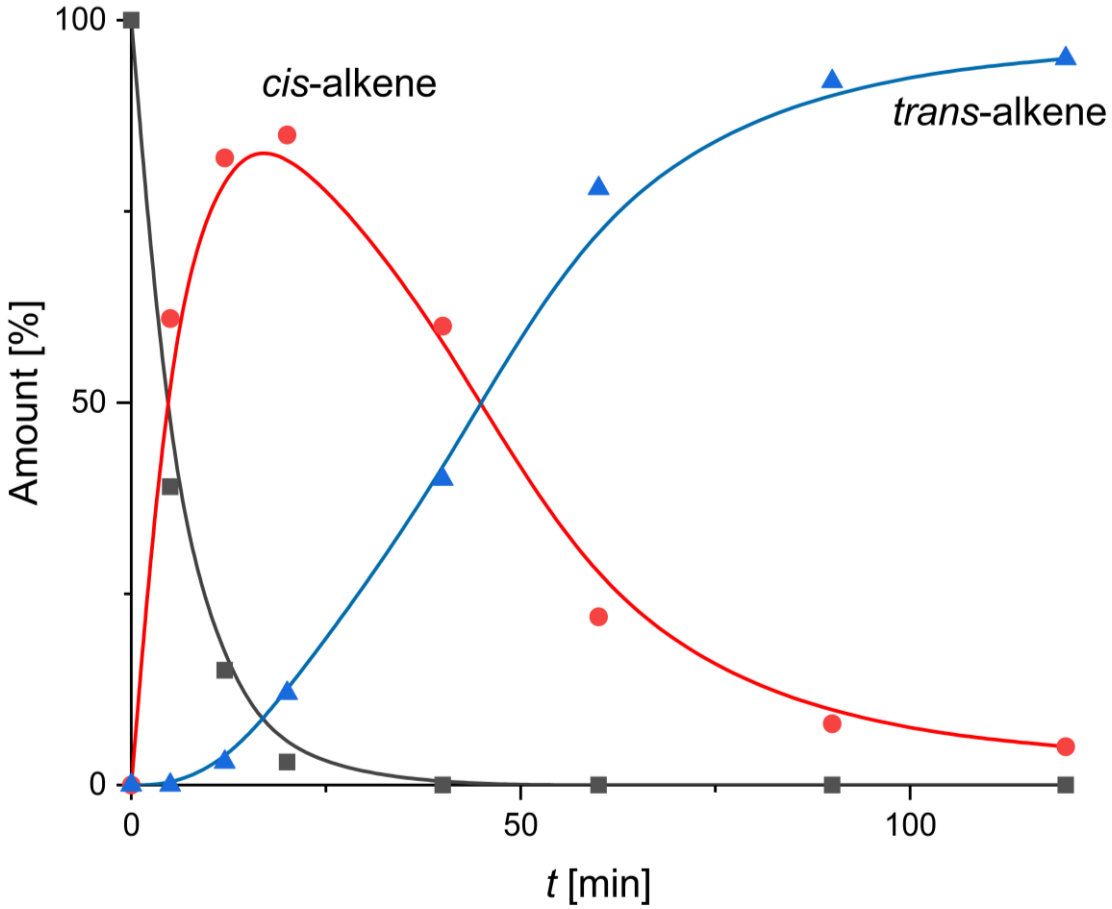
*Non-covalent interaction (NCI) plots (s = 0.3 Å/-5 < ρ < +5 Å) depicted separately with and without interaction/structure. Repulsion is color-coded red, “strong” attraction blue and weak interactions in green.


R
oxalyl chloride
SiO2, H2O
DCM, rt
Cl
H
R
H⊕
Cl
R
H

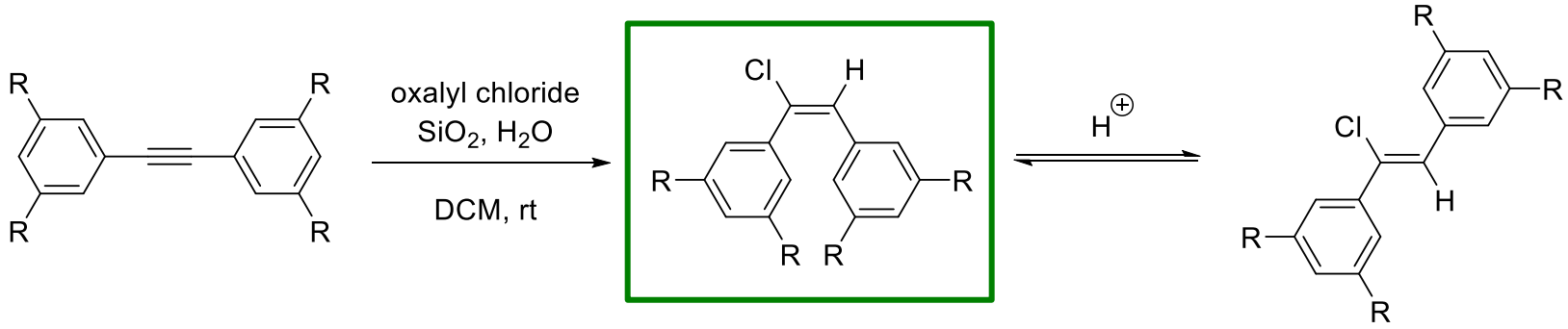


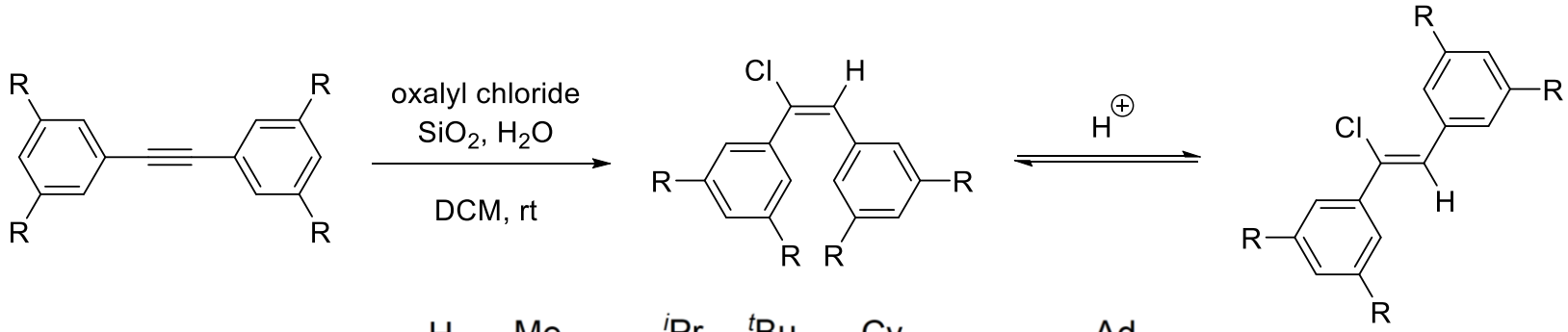
P. Kropp, K. Daus, S. Crawford, M. Tubergen, K. Kepler, S. Craig, V. Wilson, *J. Am. Chem. Soc.* **1990**, 112, 20, 7433-7434.
N. Pienta, S. Crawford, P. Kropp, *J. Chem. Educ*. **1993**, 70, 8, 682.

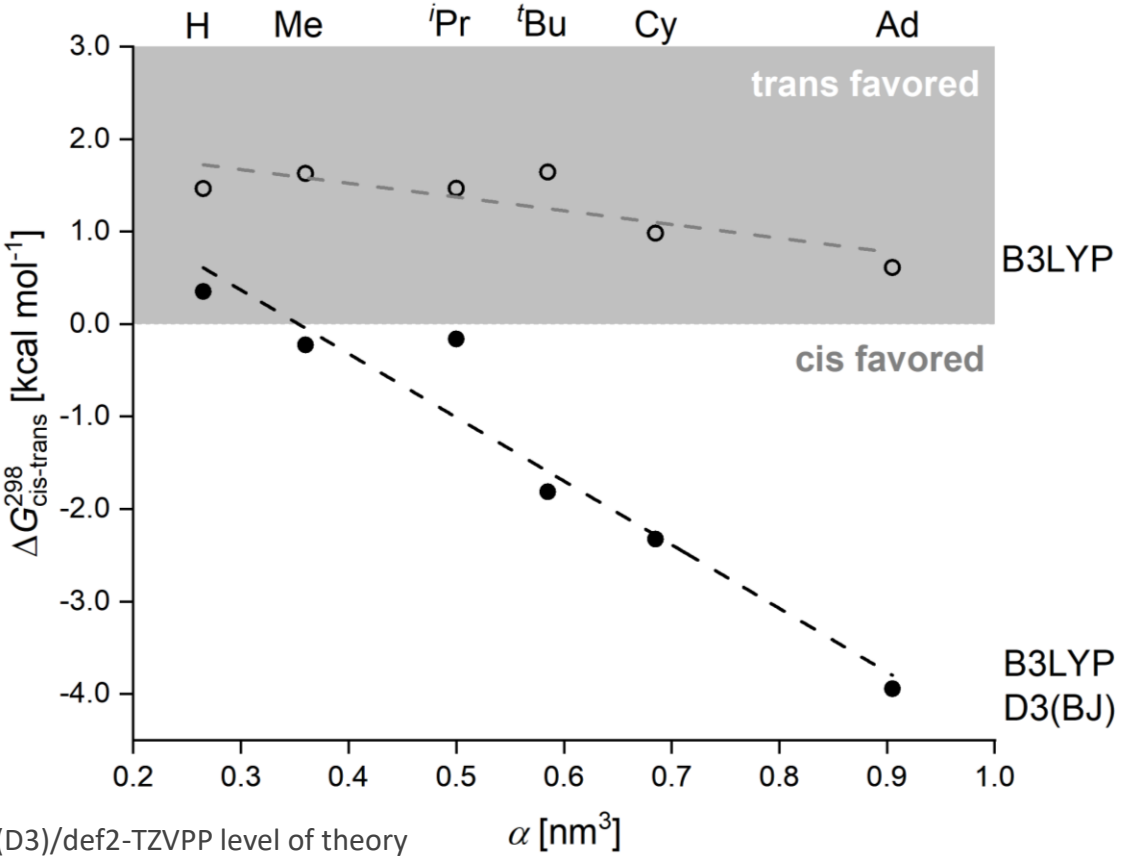




P. Kropp, K. Daus, S. Crawford, M. Tubergen, K. Kepler, S. Craig, V. Wilson, *J. Am. Chem. Soc.* **1990**, 112, 20, 7433-7434.
N. Pienta, S. Crawford, P. Kropp, *J. Chem. Educ*. **1993**, 70, 8, 682.

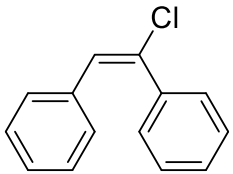

R
R
R
R
oxalyl chloride
SiO2, H2O
DCM, rt
Cl
H
R
R
R
R
H⊕
R
R
Cl
H
R
R

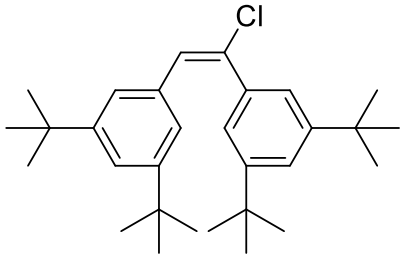


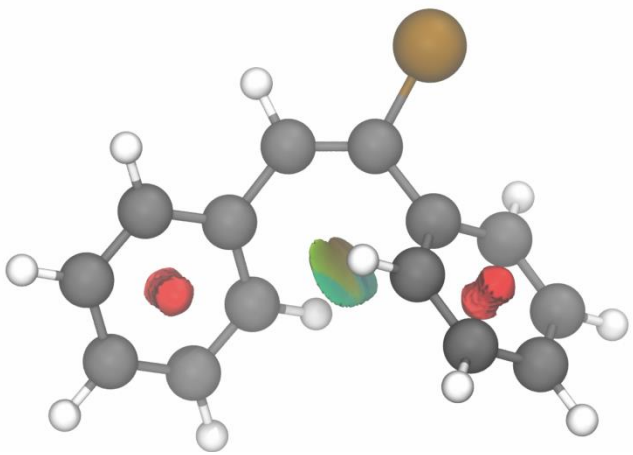


*Computations on a B3LYP(D3)/def2-TZVPP level of theory

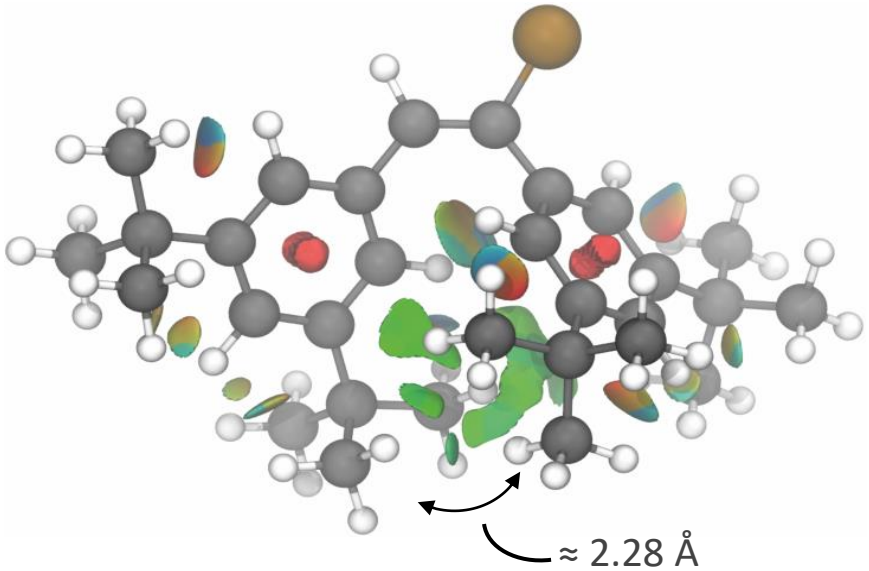
Non-Covalent Interaction Plots





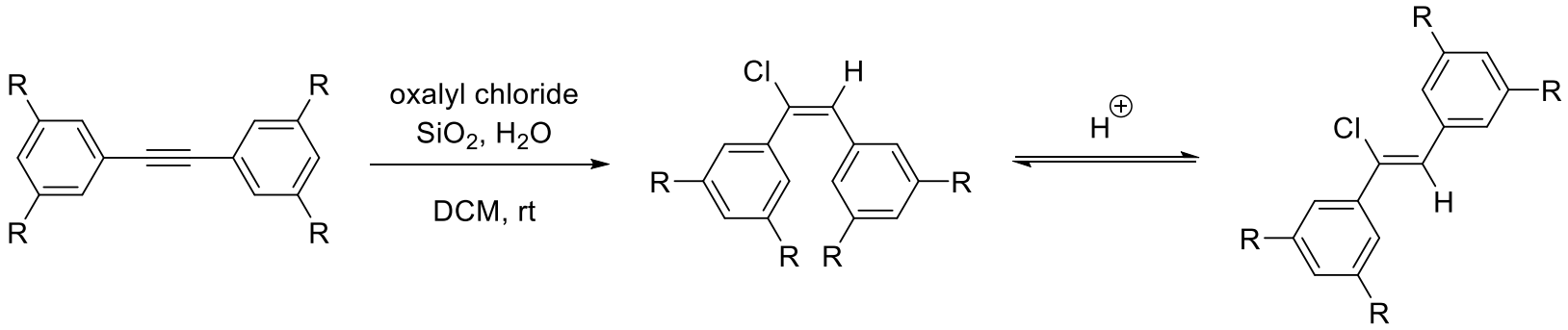


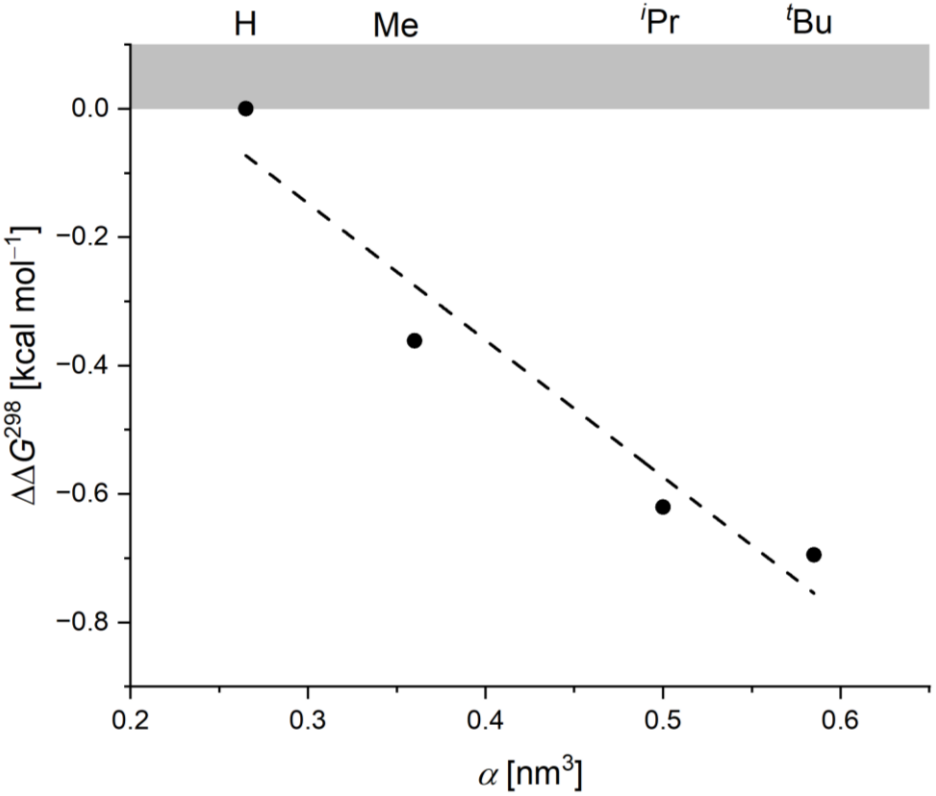
$R_{C-C} = 1.34$ Å

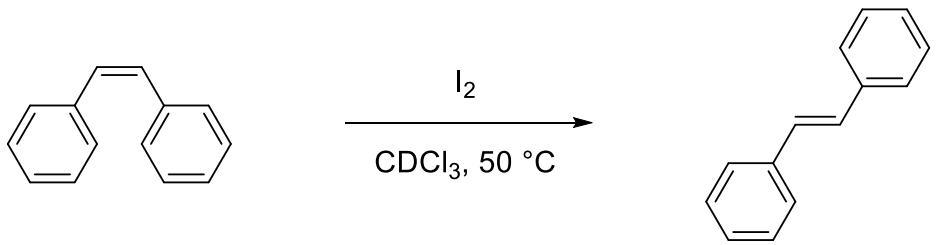


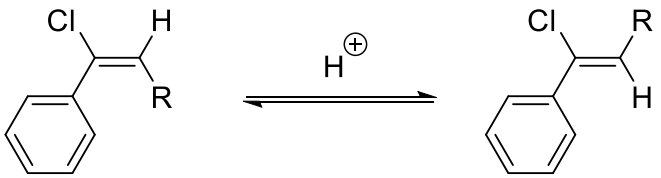
≈ 2.28 Å

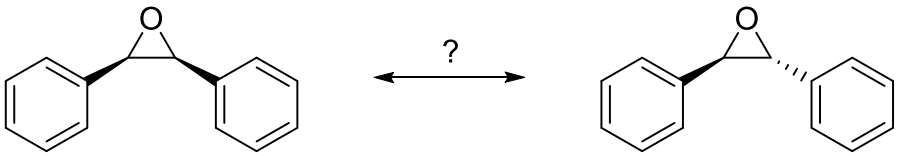
*Non-covalent interaction (NCI) plots (s = 0.3 Å/-5 < ρ < +5 Å) depicted separately with and without interaction/structure. Repulsion is color-coded red, “strong” attraction blue and weak interactions in green.

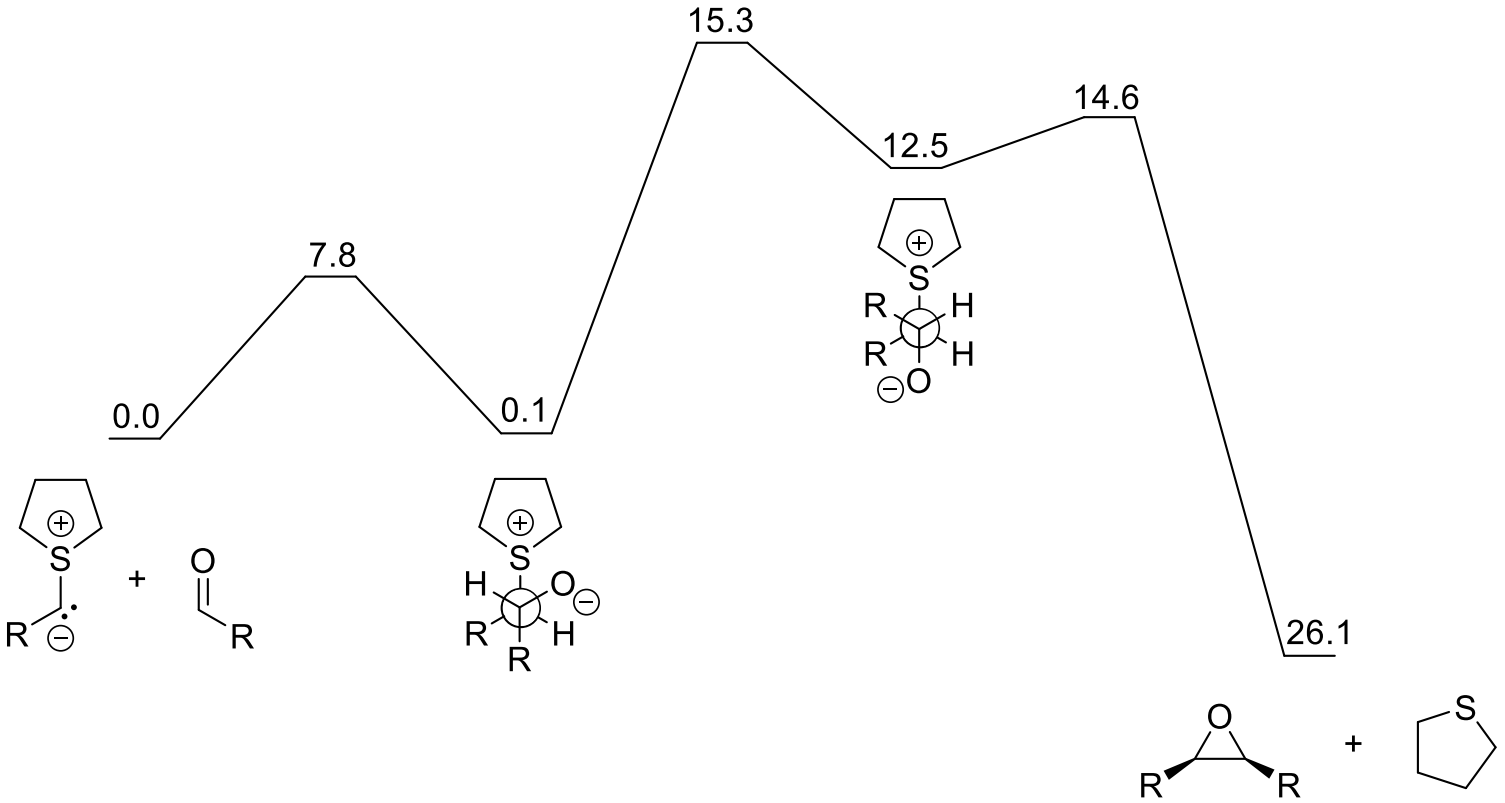

R
R
R
R
oxalyl chloride
SiO_2, H_2O
DCM, rt
Cl
H
R
R
R
R
H⊕
R
R
Cl
H
R
R


H
Me
iPr
tBu
0.0
−0.2
−0.4
−0.6
−0.8
ΔΔG298 [kcal mol−1]
0.2
0.3
0.4
0.5
0.6
α [nm3]


I2
CDCl3, 50 °C

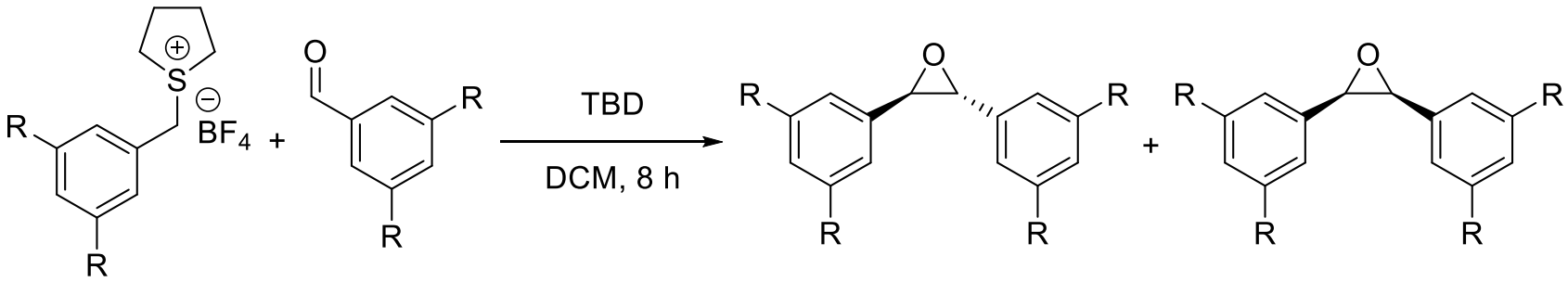

Cl
H
R
H⊕
Cl
R
H


O
?
O



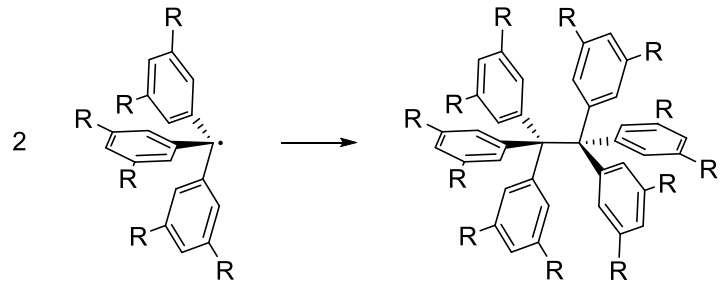
* ΔG_{298} given in kcal mol^{-1} for R = Ph. Computations on a B3LYP(D3)/def2-SVP level of theory

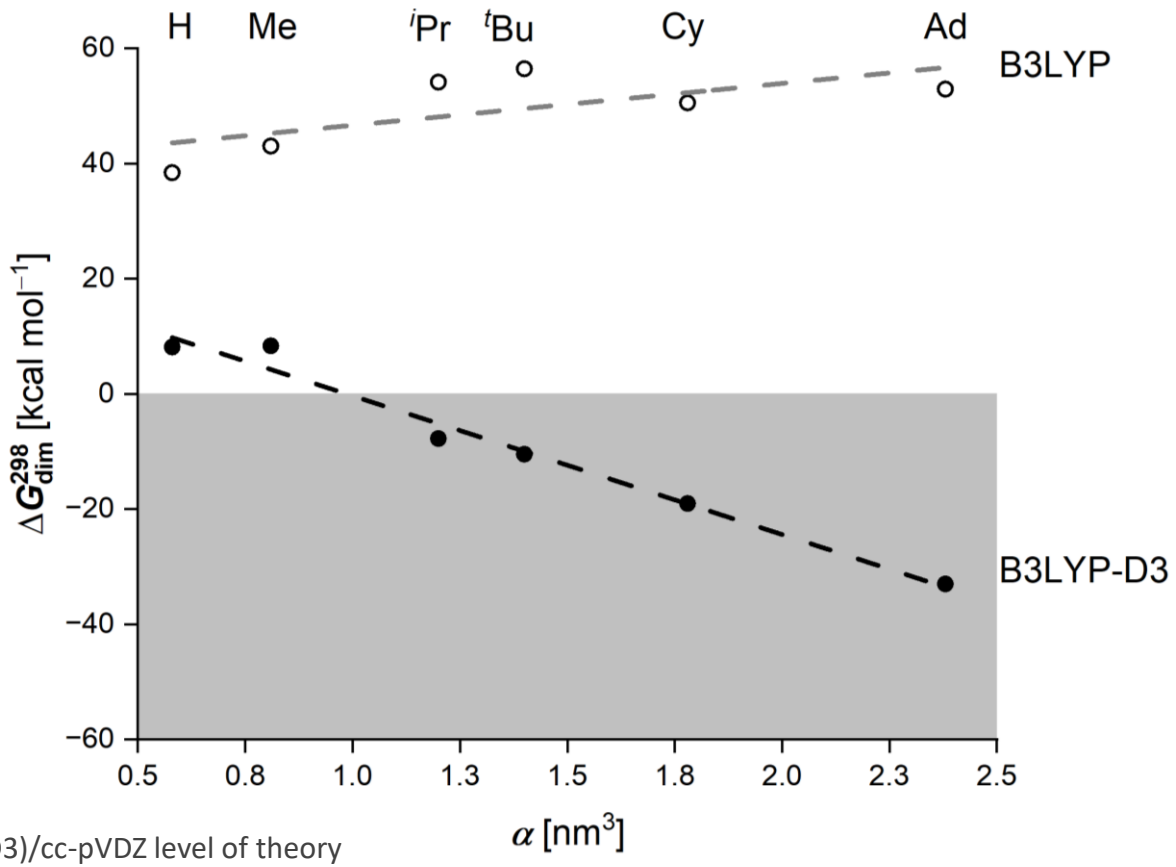
A. W. Johnson, Robert B. LaCount, *J. Am. Chem. Soc.* **1961**, 83, 2, 417-423.
V. Aggarwal, J. Richardson, *Chem. Commun.* **2003**, 2644-2651



R	*cis*-Epoxide	*trans*-Epoxide	ΔG^{298} [kcal mol^{-1}]
H	0.30	1	0.7
Me	0.28	1	0.8
*t*Bu	0.90	1	0.1

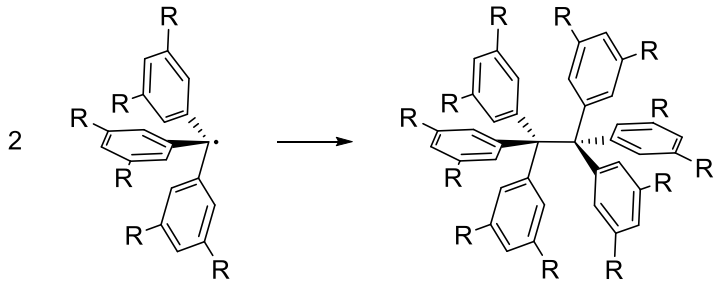
$\Delta\Delta G^{298} =$ 0.6 kcal mol^{-1}

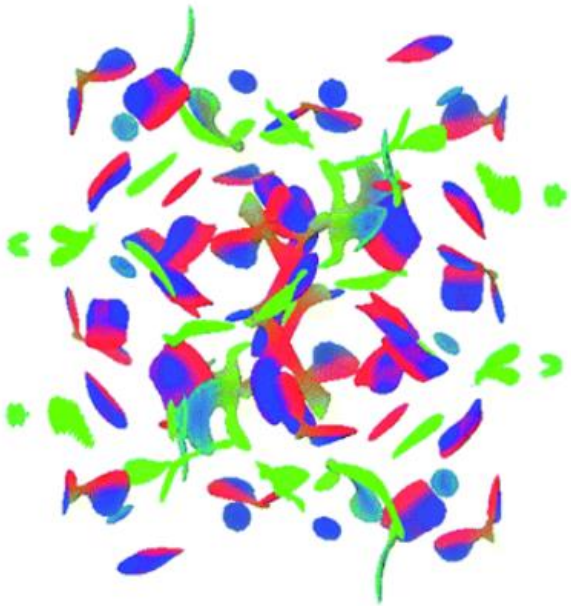


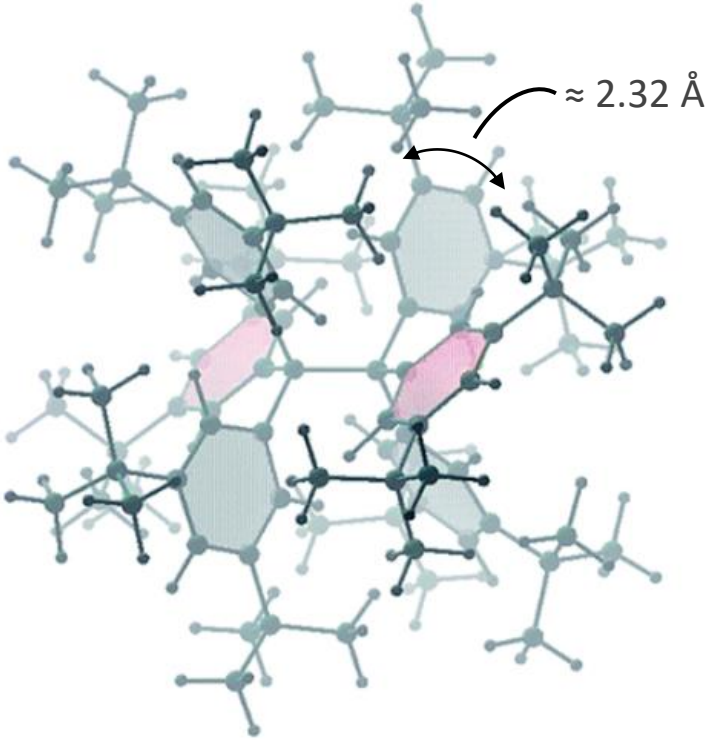


*Computations on a B3LYP(D3)/cc-pVDZ level of theory

S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2017**, *8*, 405-410.

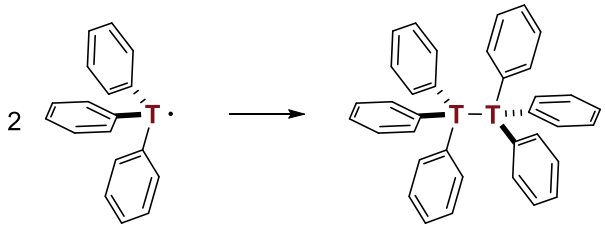


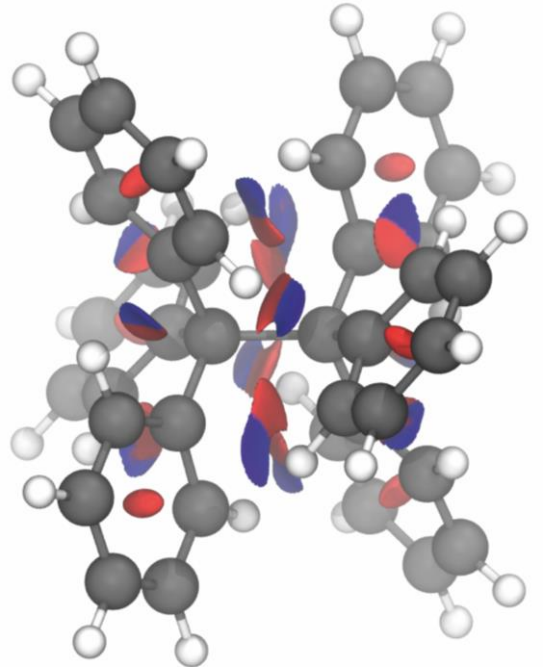




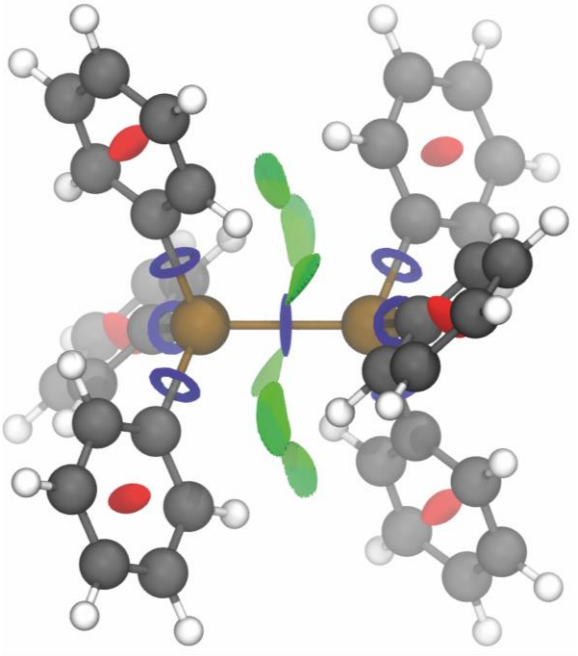
*Computations on a B3LYP(D3)/cc-pVDZ level of theory

S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2017**, *8*, 405-410.



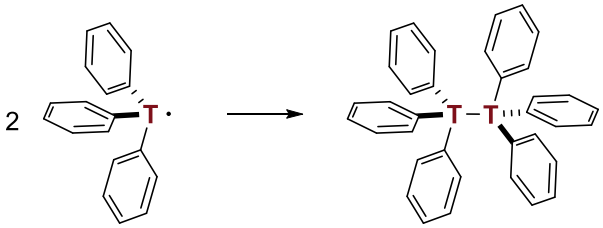


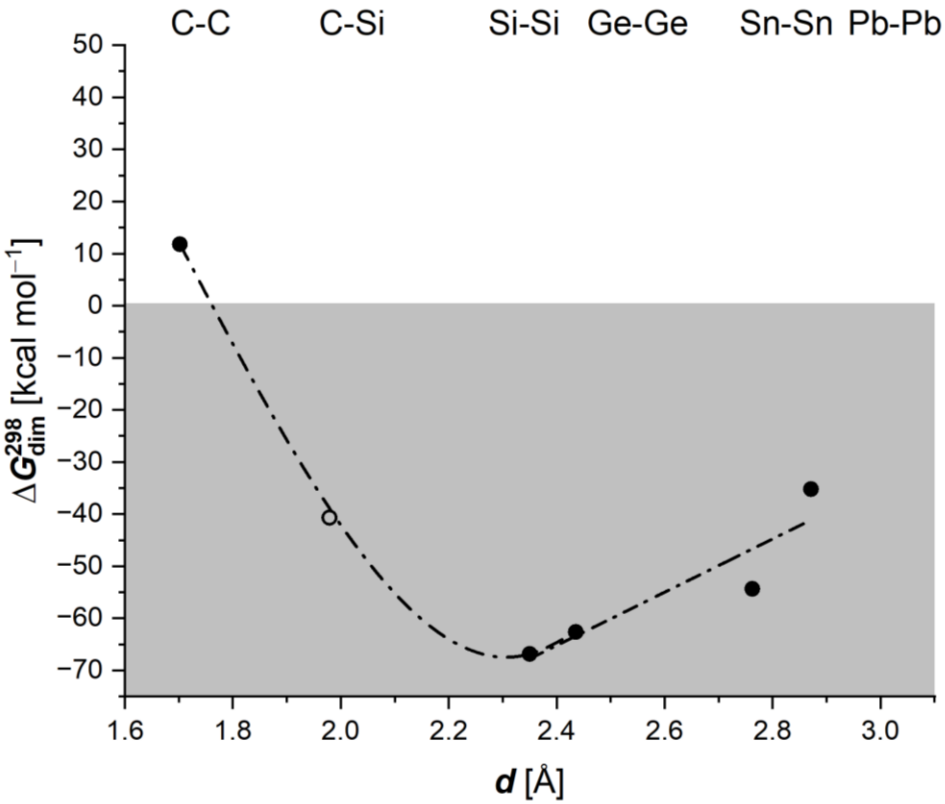
$R_{C-C} = 1.70$ Å



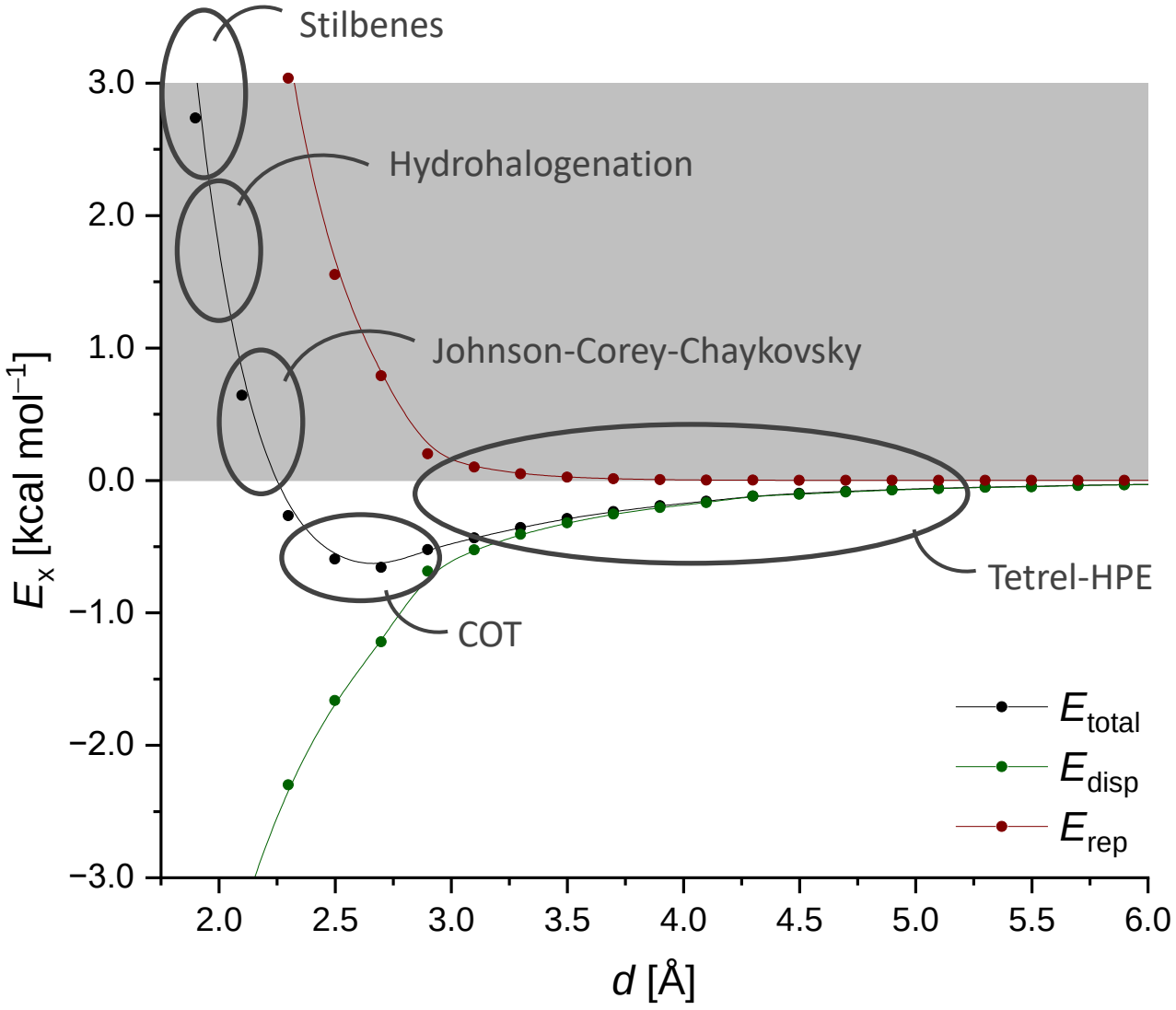
$R_{Pb-Pb} = 2.86$ Å

*Computations on a B3LYP(D3)/def2-TZVP level of theory





*Computations on a B3LYP(D3)/def2-TZVP level of theory


Stilbenes
Hydrohalogenation
Johnson-Corey-Chaykovsky
Tetrel-HPE
COT
E_{total}
E_{disp}
E_{rep}
E_x [kcal mol^{-1}]
d [Å]
3.0
2.0
1.0
0.0
−1.0
−2.0
−3.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0

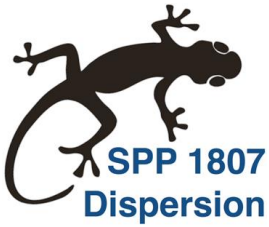
Prof. Dr. Peter R. Schreiner, PhD.

Dispersion Subgroup:
Jan M. Schümann, Finn M. Wilming, Henrik König, Christian Eschmann, Ephrath Solel, PhD.

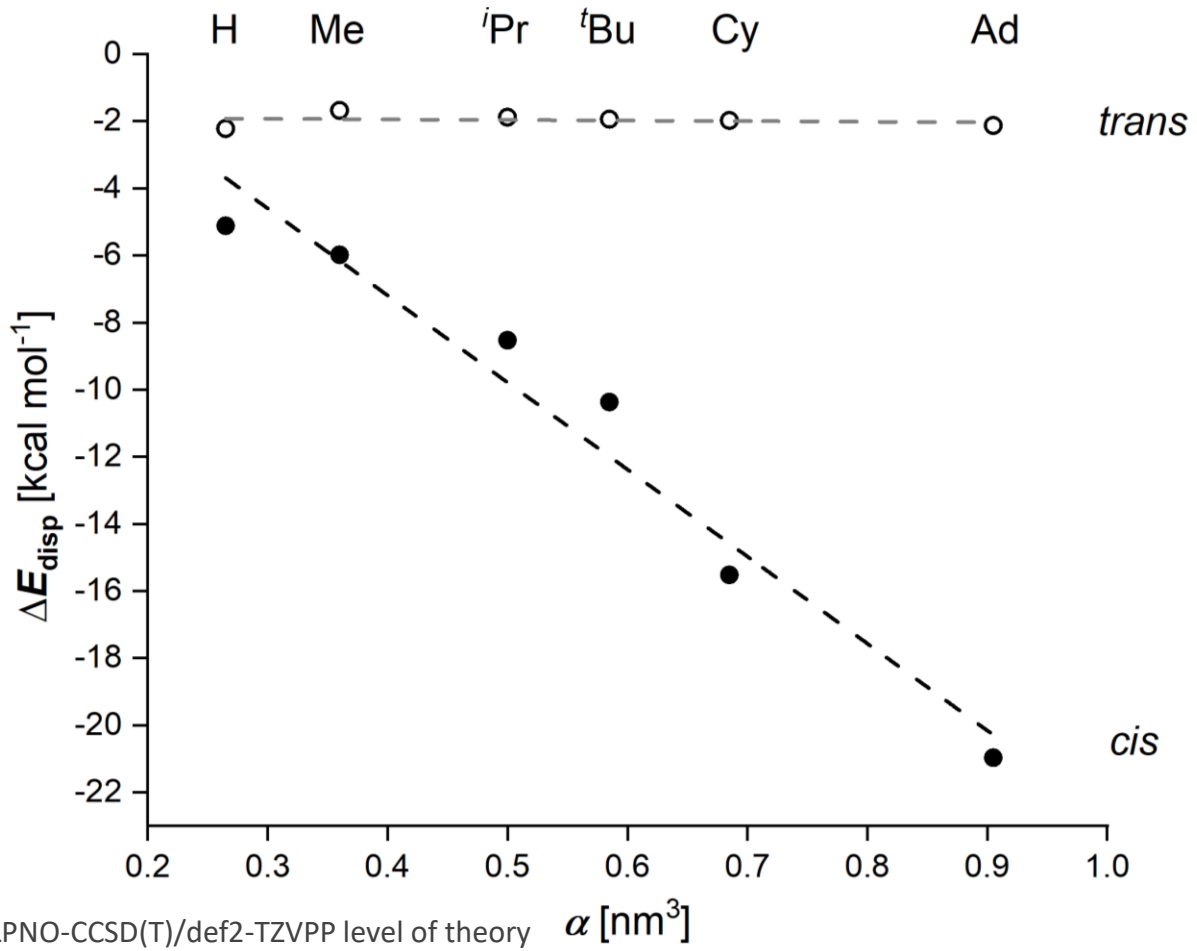
Dr. Dennis Gerbig, Henrik Quanz and Bastian Bernhardt

Kai Hanke, Marvin Domanski

The PRS Group

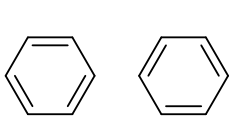


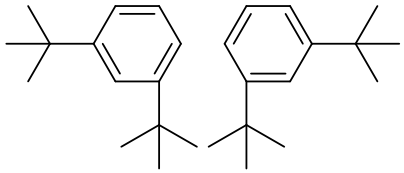
Local Energy Decomposition Analysis

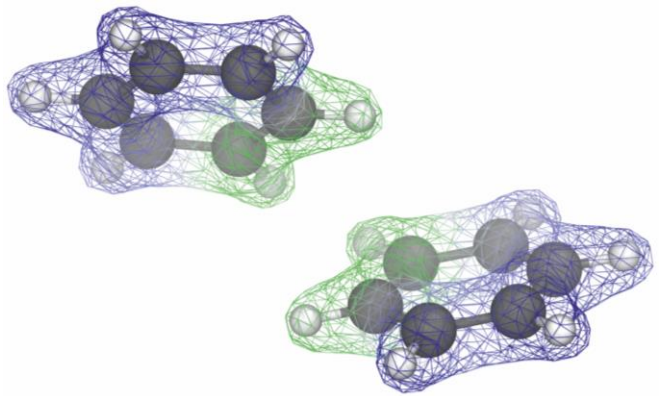


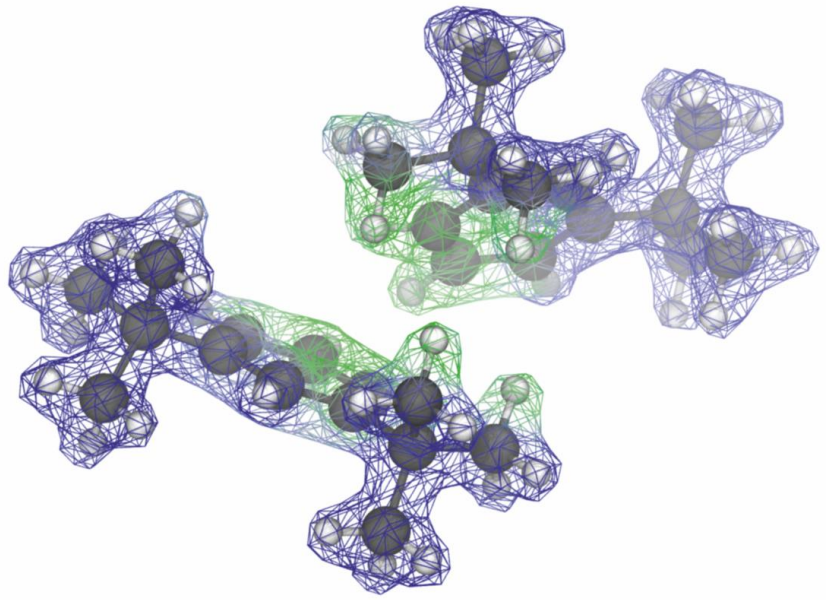
*Computations on a DLPNO-CCSD(T)/def2-TZVPP level of theory

Dispersion Interaction Density Plots

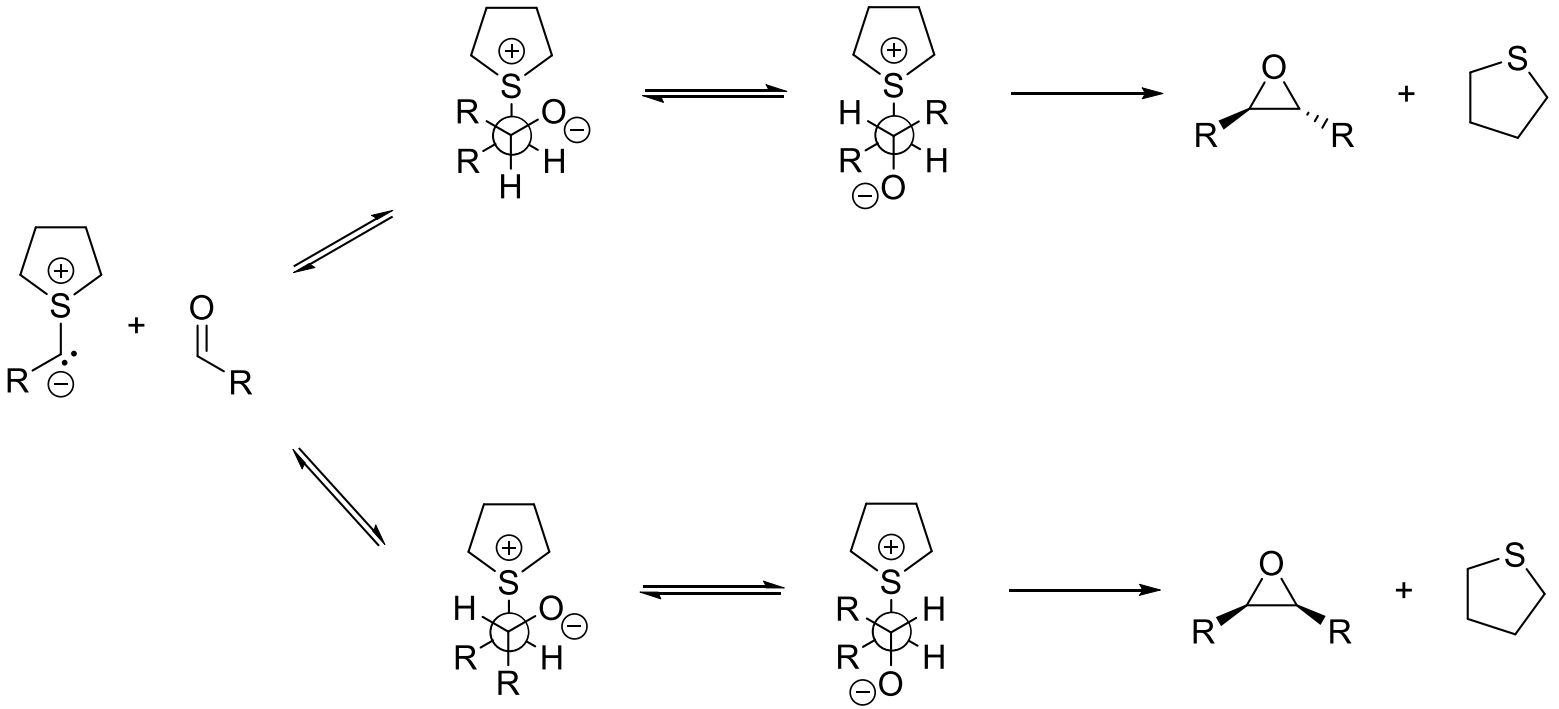






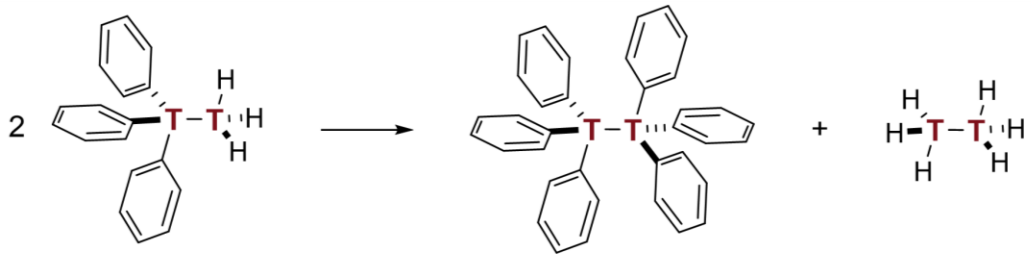


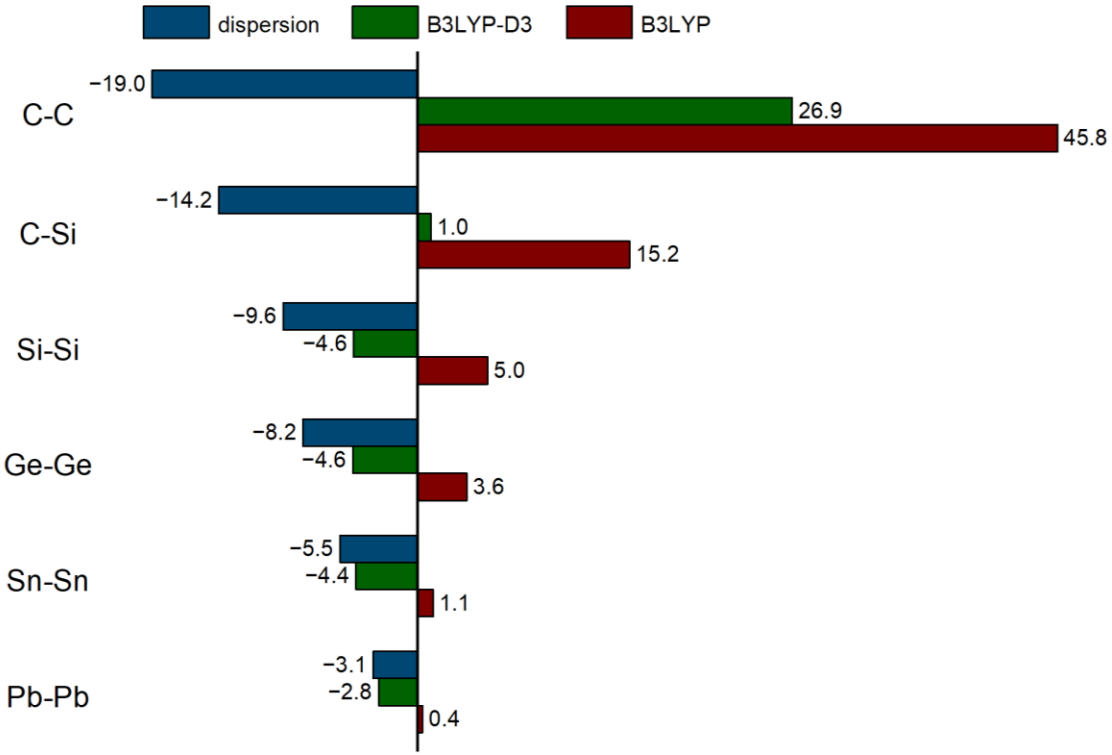
*Computations on a DLPNO-CCSD(T)/def2-TZVPP level of theory



A. W. Johnson, Robert B. LaCount, *J. Am. Chem. Soc.* **1961**, 83, 2, 417-423.
V. Aggarwal, J. Richardson, *Chem. Commun.* **2003**, 2644-2651

London Dispersion Effects on Thermodynamic Stability





*ΔG_{298} given in kcal mol^{-1}. Computations on a B3LYP(D3)/def2-TZVP level of theory