



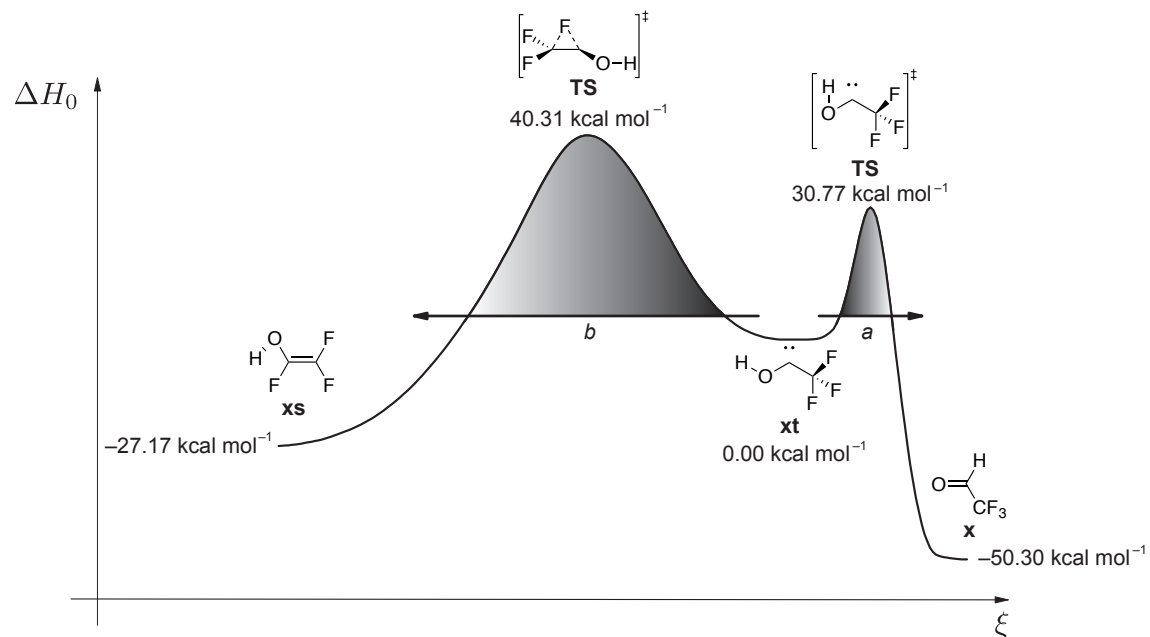
Presented by

Henrik Quanz

December 4th, 2015

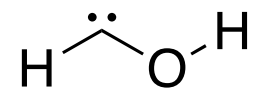
Institute of Organic Chemistry

Justus-Liebig University Giessen

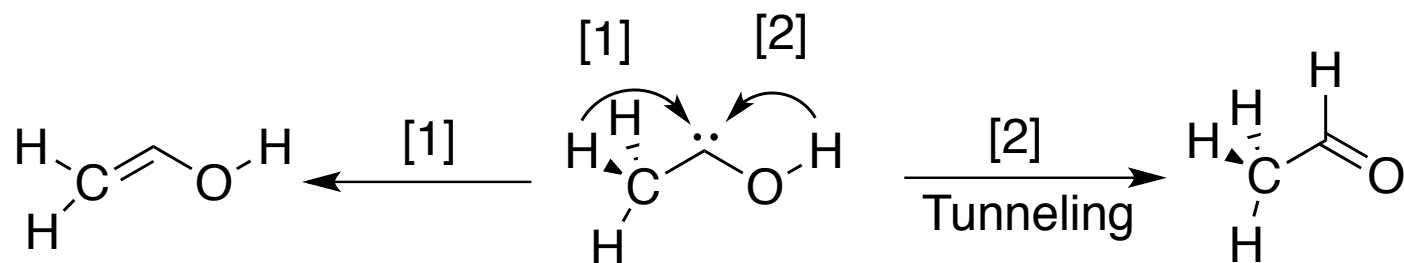




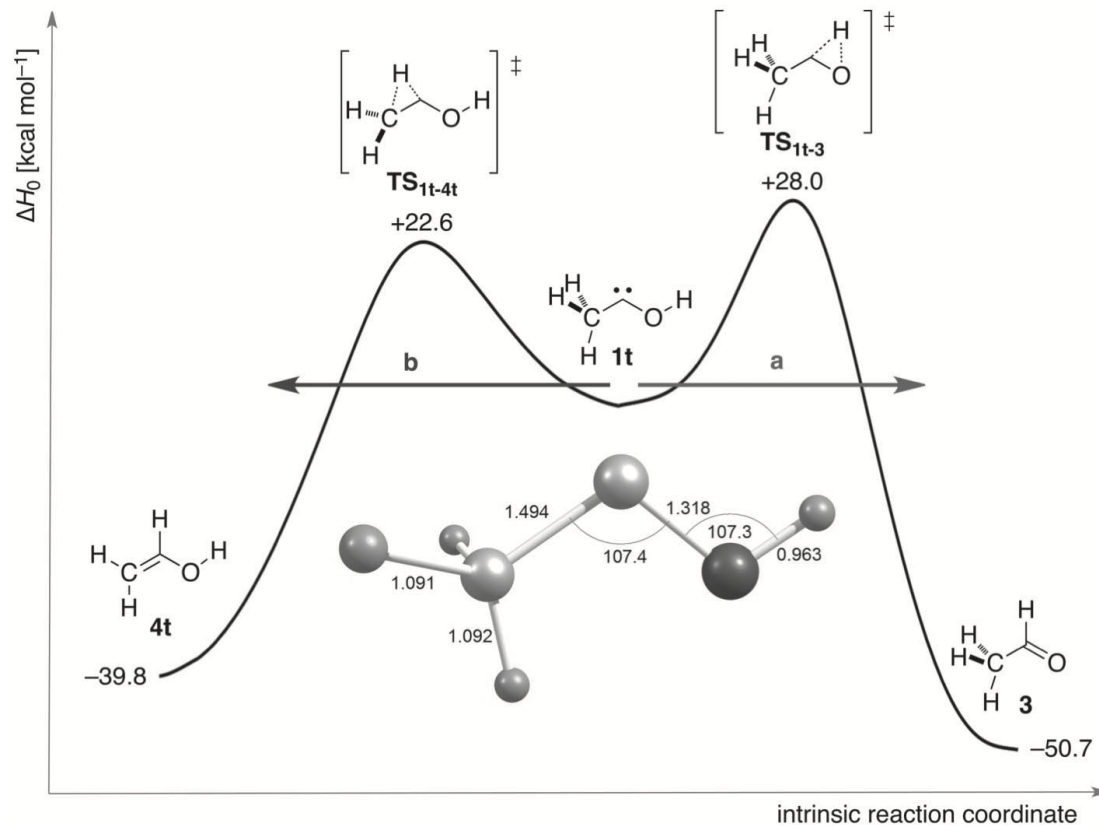
thermodynamic
temperature
pressure
solvent
tunneling
light
kinetics
equilibrium
catalysis
side products
mixture
dynamic effects
complexes
moisture
impurities
phase
spin
gravity
time
long range interactions



Nature **2008**, 453, 906-909.

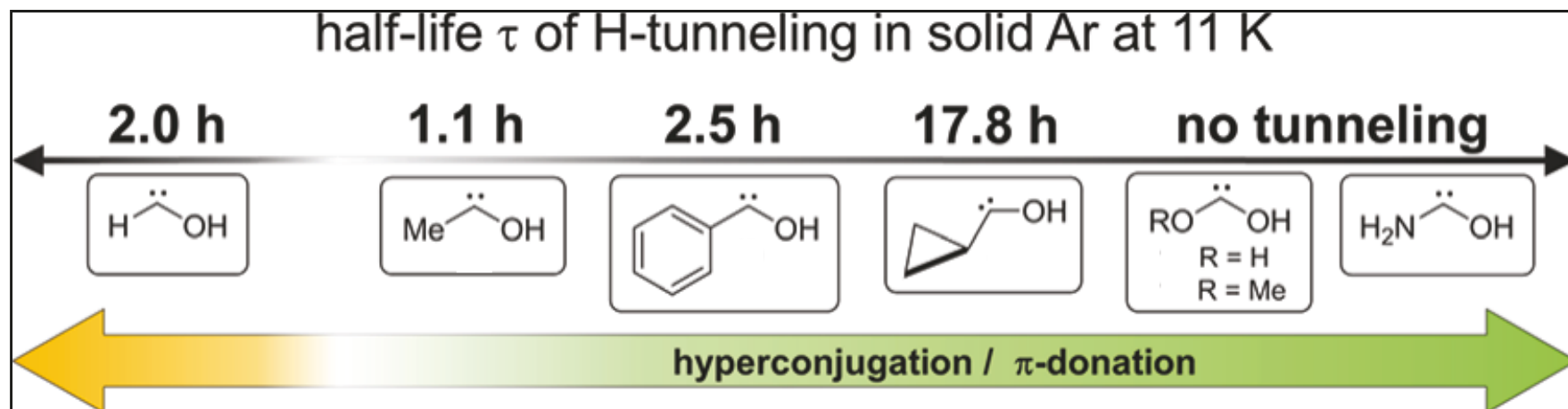


Science **2011**, 332, 1300-1303



$$\kappa(x) = \sqrt{\frac{2m(V(x) - E)}{\hbar^2}}$$

$$\ln |T|^2 \approx -2 \int_{\text{barrier}} \kappa(x) dx$$



Influence of CF₃-Group?

Gerbig D; Reisenauer H P; Wu C-H; Ley D; Allen W D; Schreiner P R. *J Am Chem Soc* **2010**, 132, 7273–7275.

Schreiner P R; Reisenauer H P; Ley D; Gerbig D; Wu C-H; Allen W D. *Science* **2011**, 332, 1300–1303.

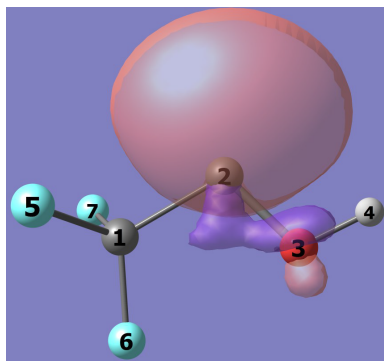
Gerbig D; Ley D; Schreiner P R. *Org Lett* **2011**, 13, 3526–3529.

Schreiner P R; Reisenauer H P; Pickard IV F C; Simmonett A C; Allen W D; Matyus E; Csaszar A G. *Nature* **2008**, 453, 906–909.

Schreiner P R; Reisenauer H P. *Angew Chem, Int Ed Engl* **2008**, 47, 7071–7074.

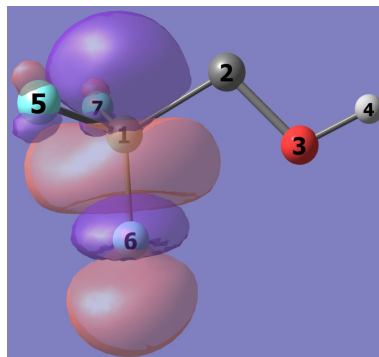


- Hyperconjugation influences half life



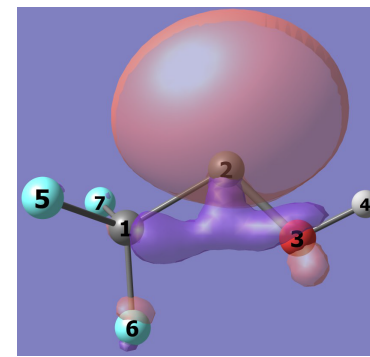
LP-C2

+



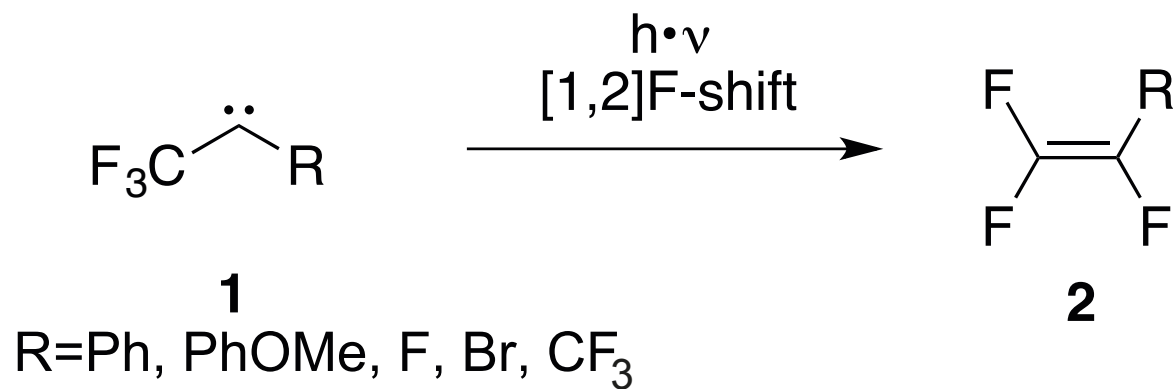
anti-C1-F6

=



NLMO

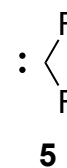
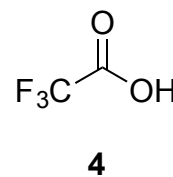
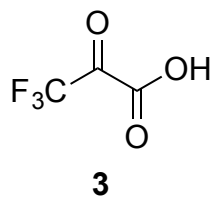
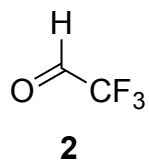
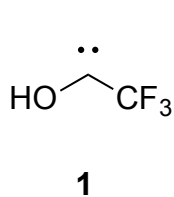
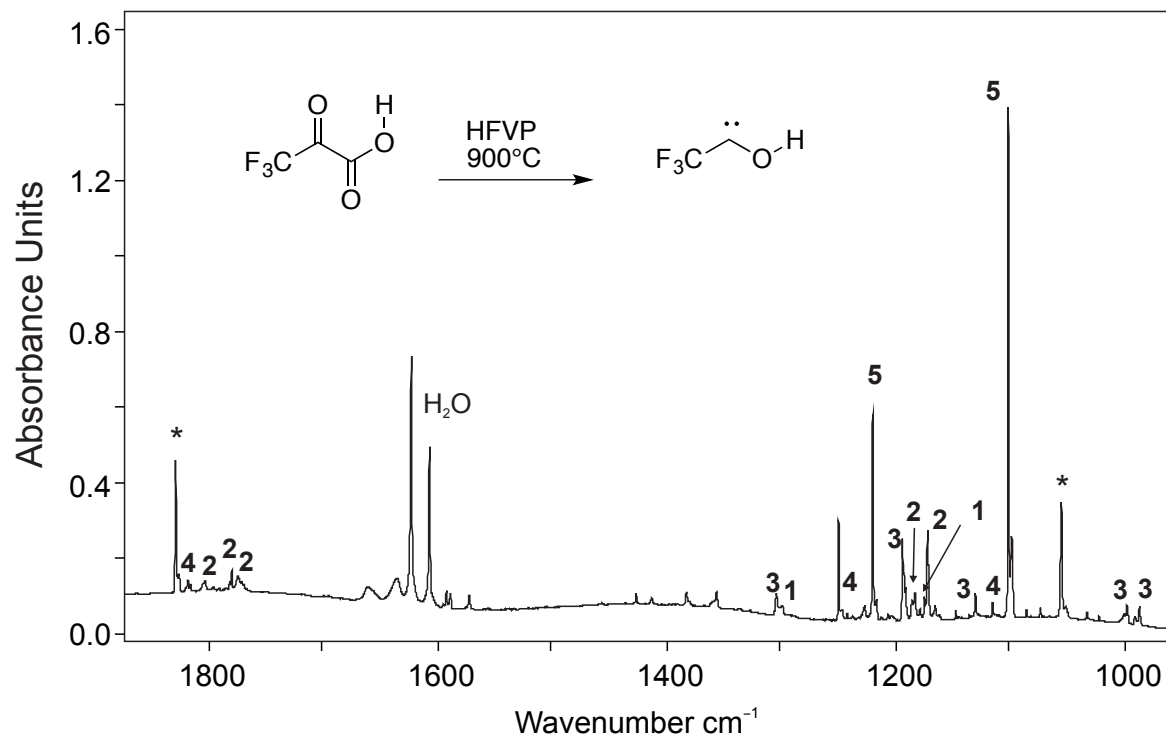
- Trifluoromethylhydroxycarbene: SOPT analysis: 6.28 kcal/mol
 - Bond Length: 1-6: 1.33 Å
- Inductive Effects
 - Singlet-Triplett Gap splits (MeCOH: 30.64 kcal/mol; F₃CCOH: 22.7 kcal/mol)
 - "It is now well established that σ -electron-withdrawing substituents favor the singlet versus the triplet state."
- Mesomeric Effect?
 - F₃C Carbenes to be predicted linear

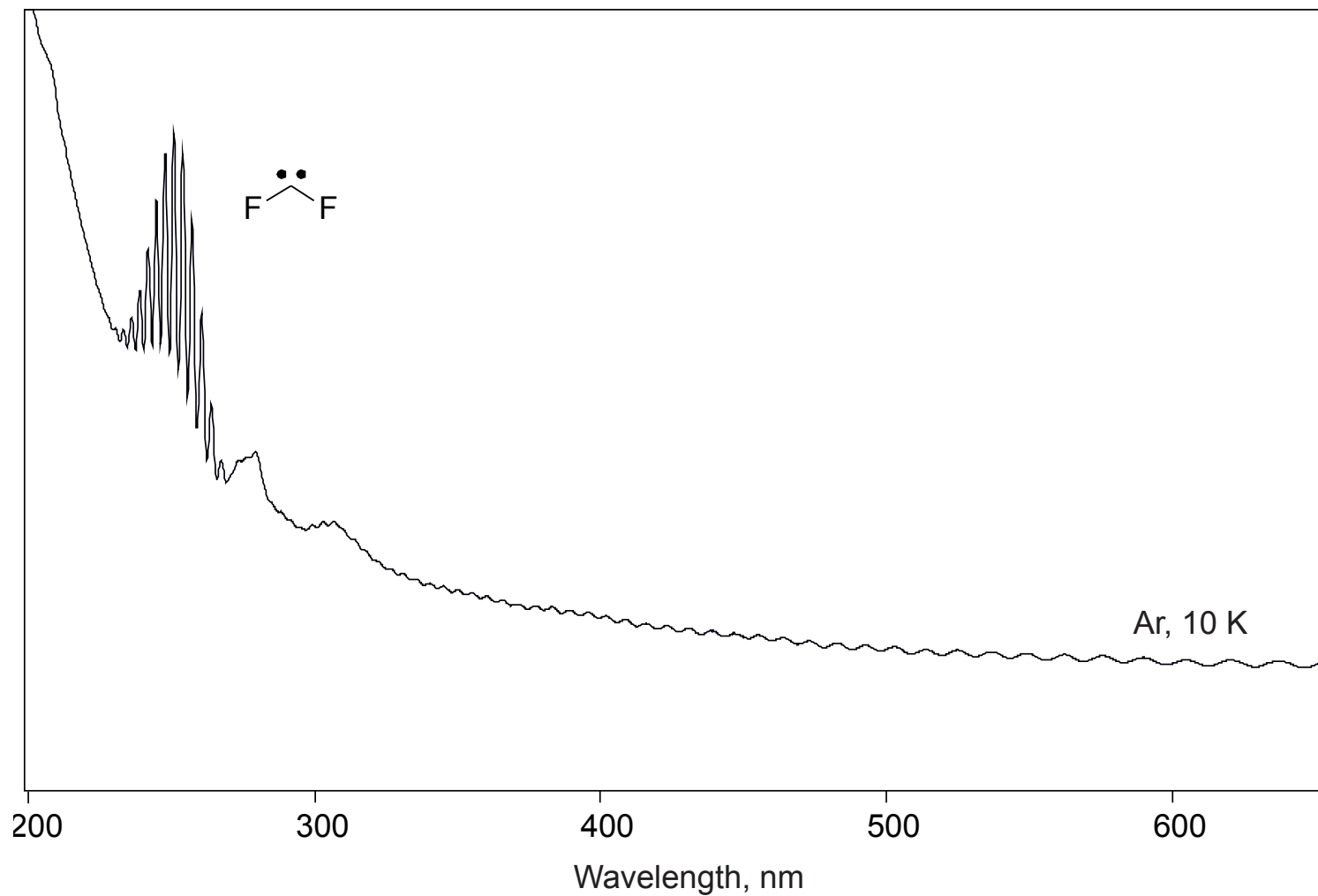


W. W. Sander, *J. Org. Chem.* **1988**, 53, 121.

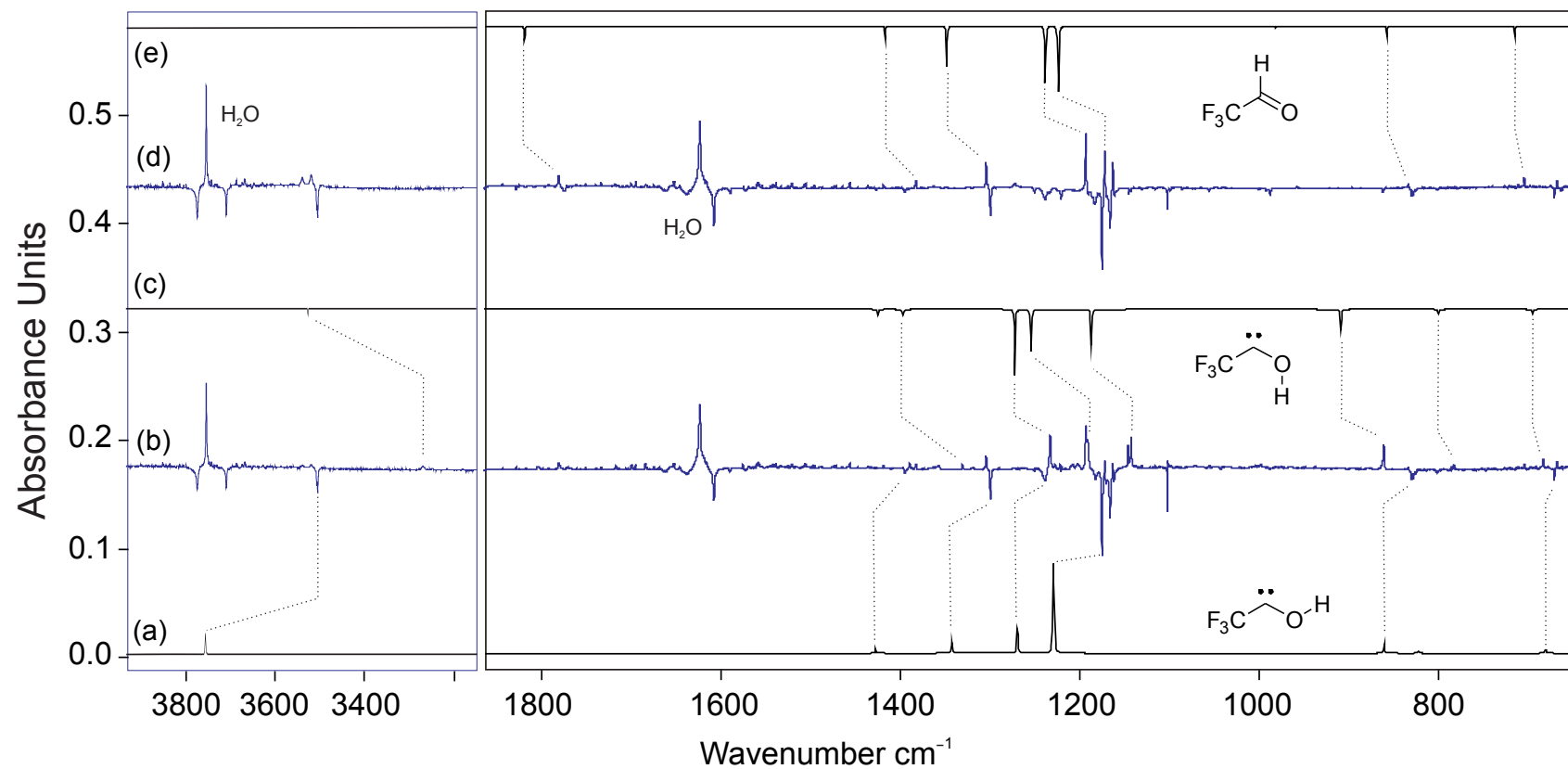
J. E. O'Gara, W. P. Dailey, *J. Am. Chem. Soc.* **1992**, 114, 3581.

A. K. Mal'tsev, P. S. Zuev, O. M. Nefedov, *Izv. Akad. Nauk USSR, Ser. Khim.* **1985**, 957.

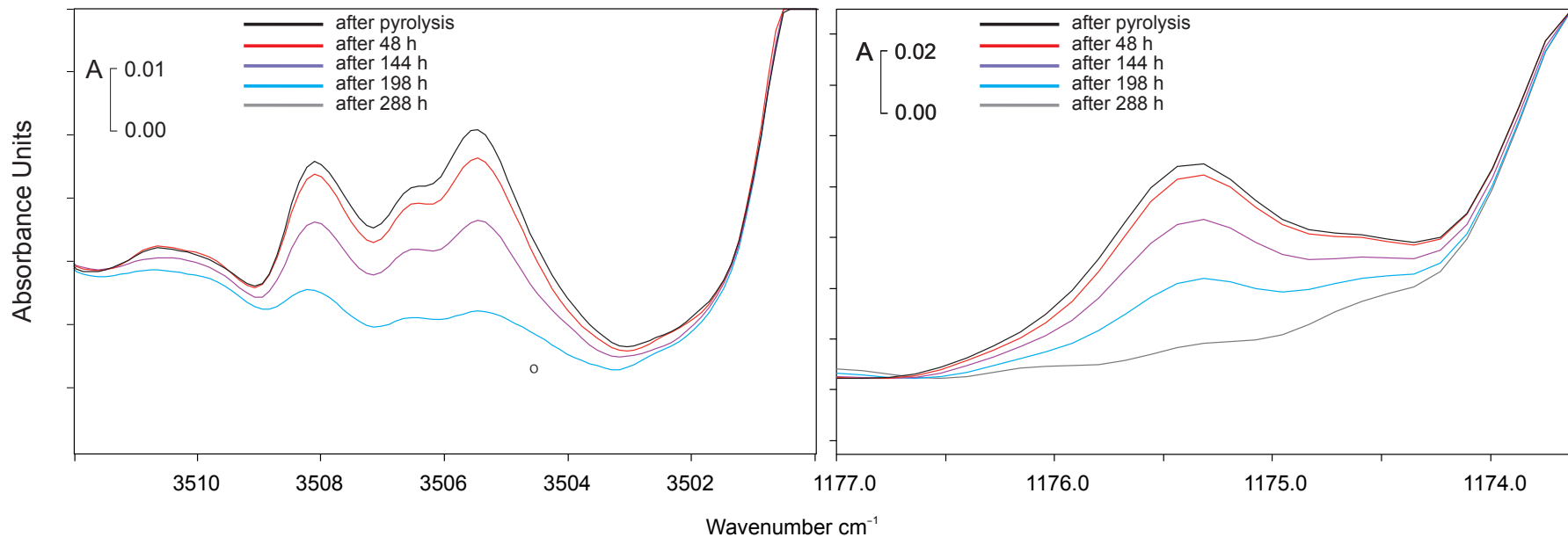




K. Mal'tsev, P. S. Zuev, O. M. Nefedov, *Izv. Akad. Nauk USSR, Ser. Khim.* **1985**, 957.



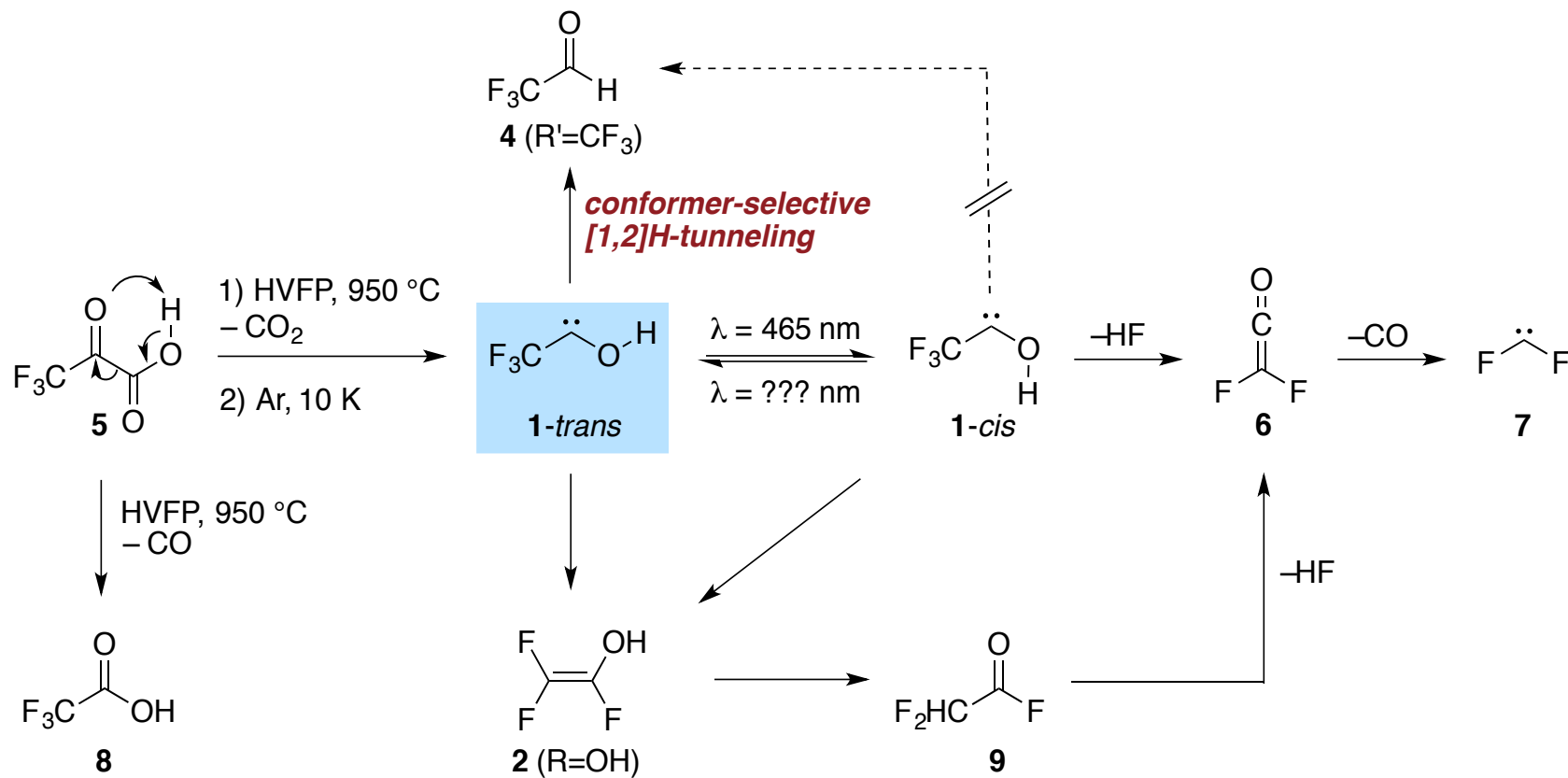
Spectra computed at: CCSD(T)/cc-pVTZ

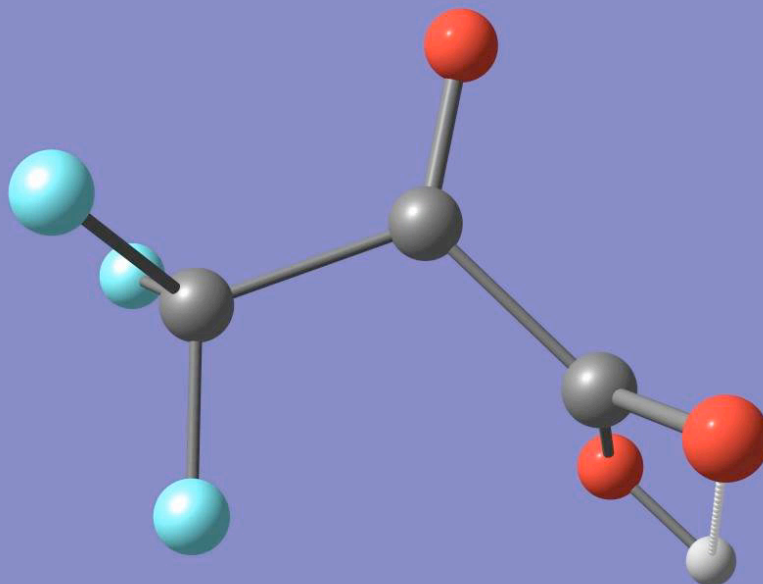


Experimental half-life:
6 days $\pm$ 11 h at 10 K

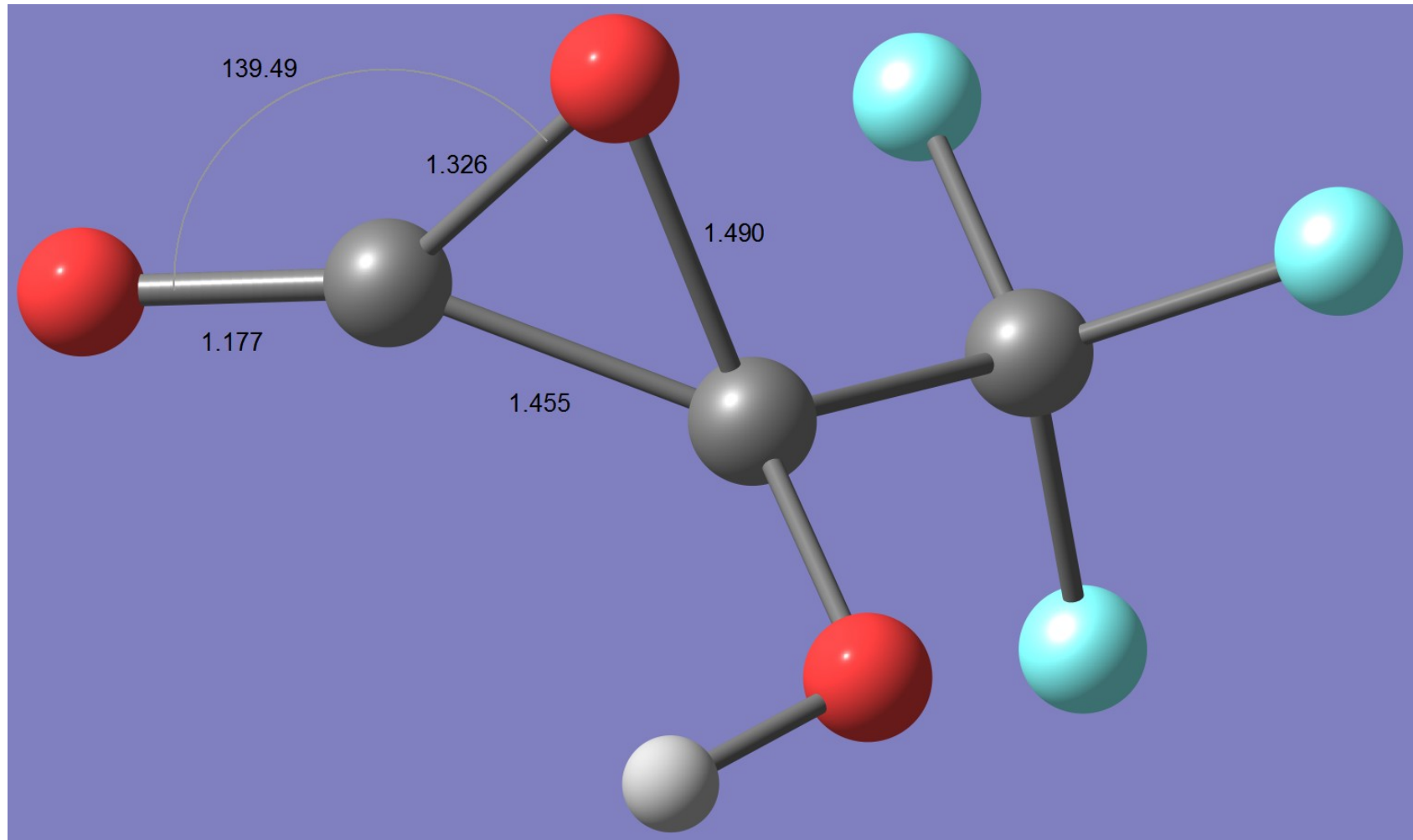
attempt energy: 4 kcal/mol

Method	Half-Life
MP2/cc-pVTZ	1.58 h
MP2/cc-pVTZ//CCSD(T)/cc-pVTZ	166 s
M06-2X/cc-pVTZ	1.1 d
M06-2X/cc-pVTZ//CCSD(T)/cc-pVTZ	108 m
M06-2X/6-311++G(d,p)	7.15 d

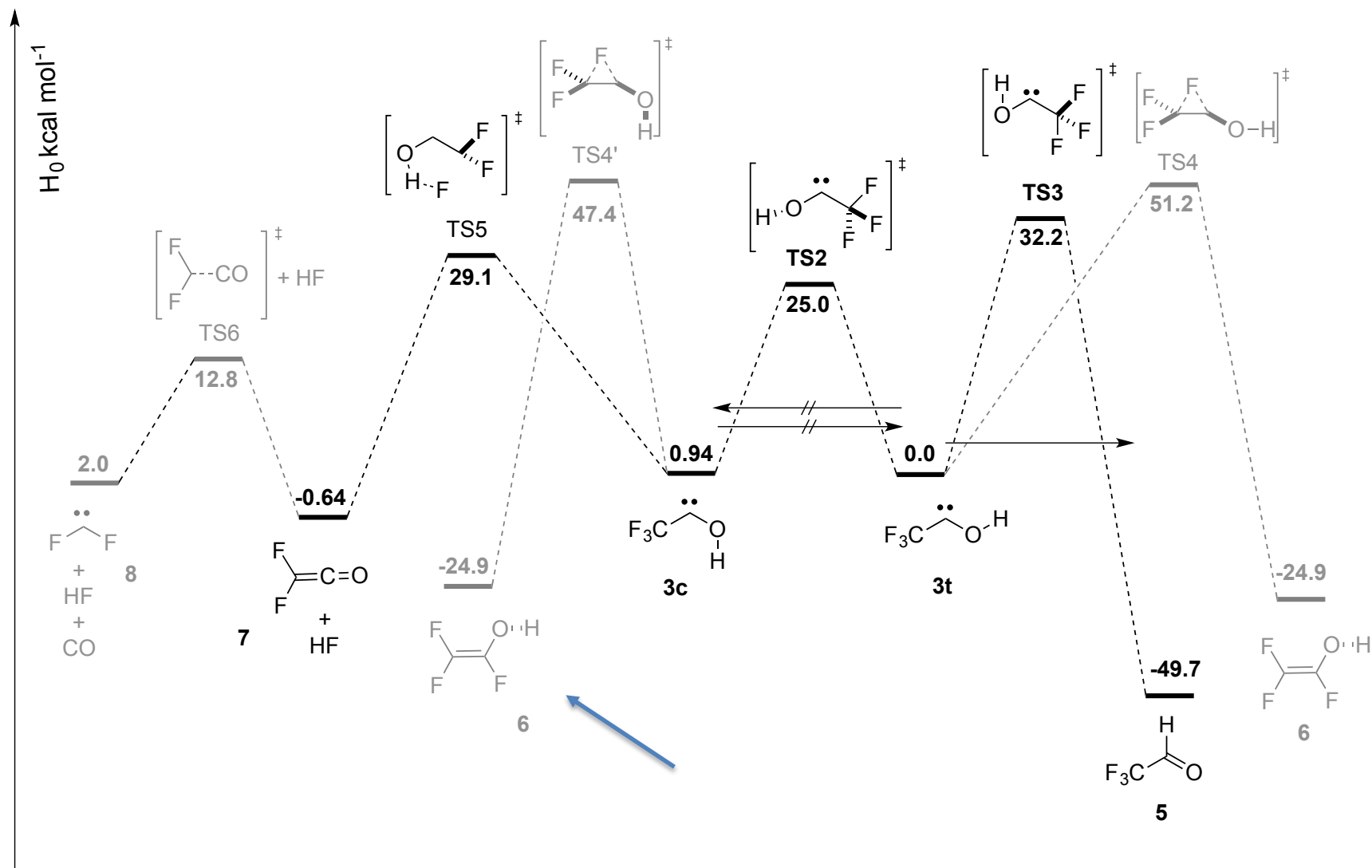




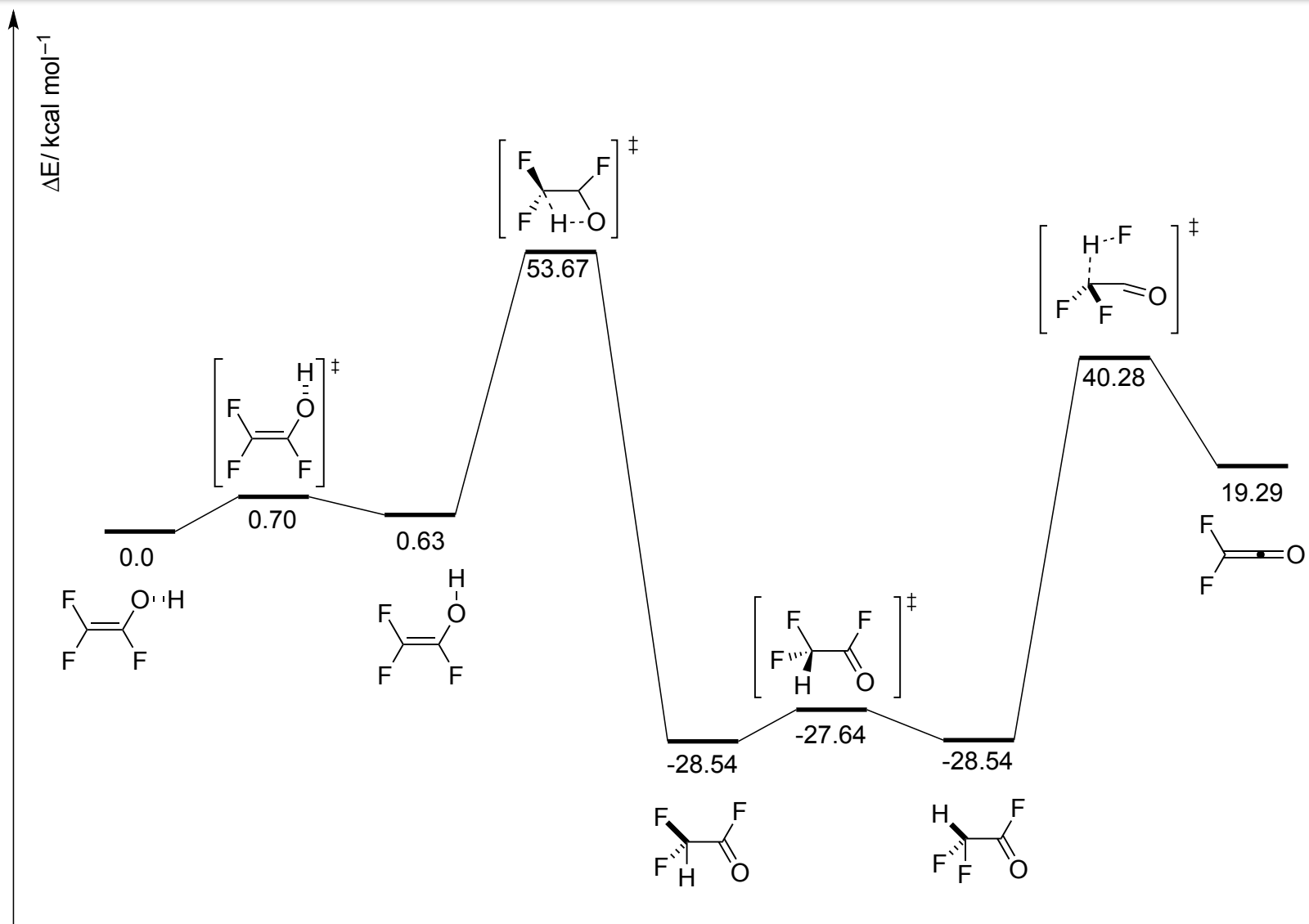
Energies in kcal/mol are computed at the M062X/cc-pVTZ level of theory



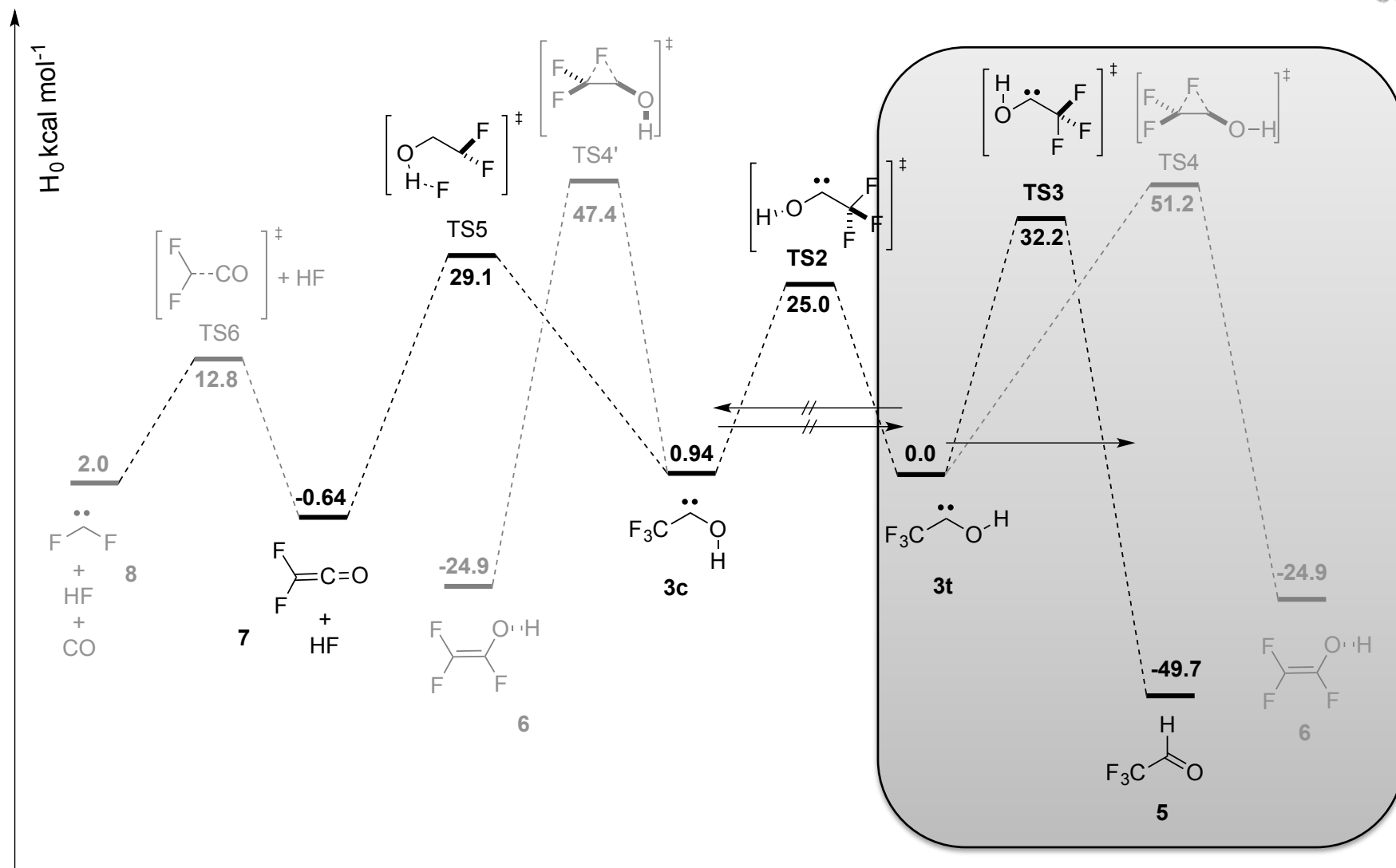
compared to: Trifluoromethyl propylene oxide: CO: 1.402 Å; 1.42 Å; C-C: 1.46 Å



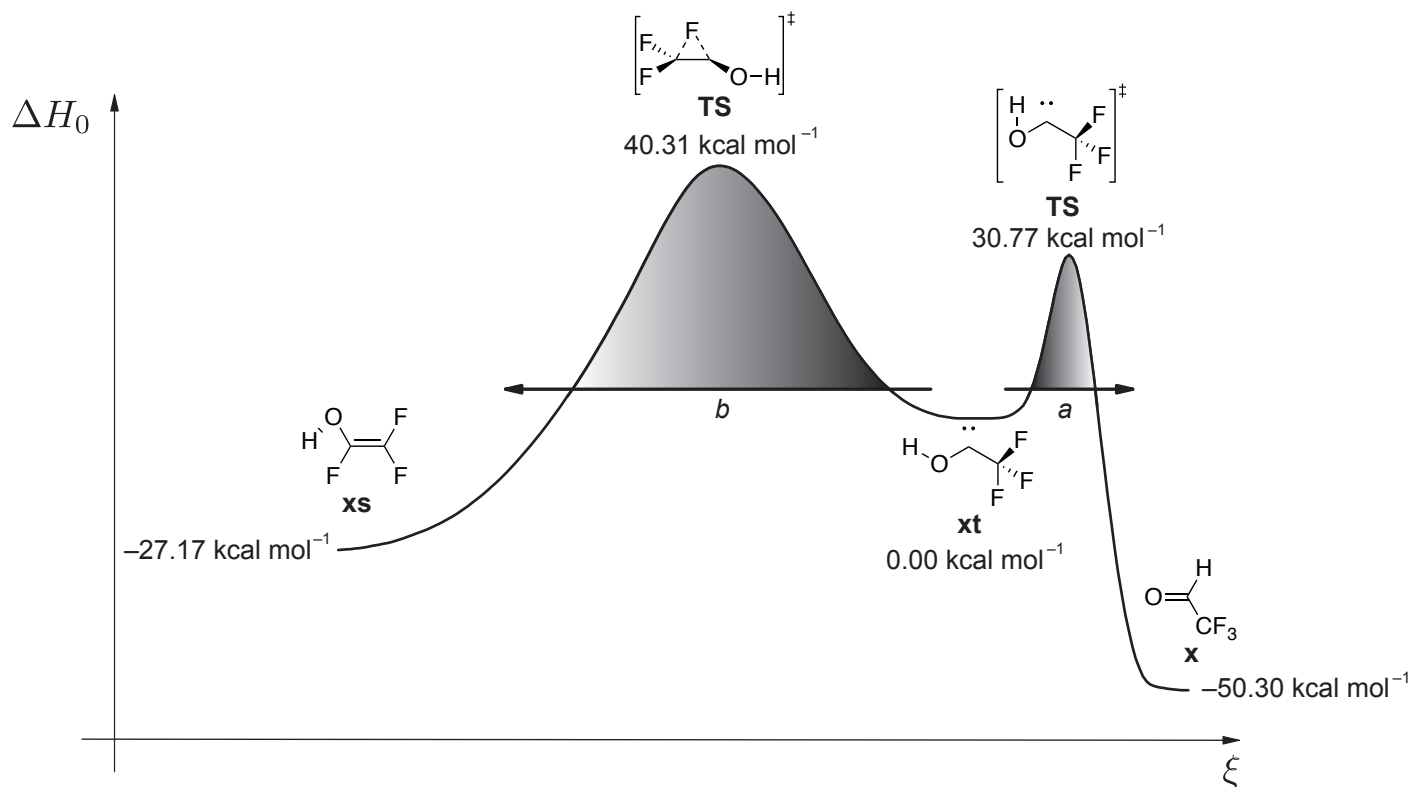
Energies are computed at the M06-2X/cc-pVTZ



Energies are computed at the B3-LYP/cc-pVTZ

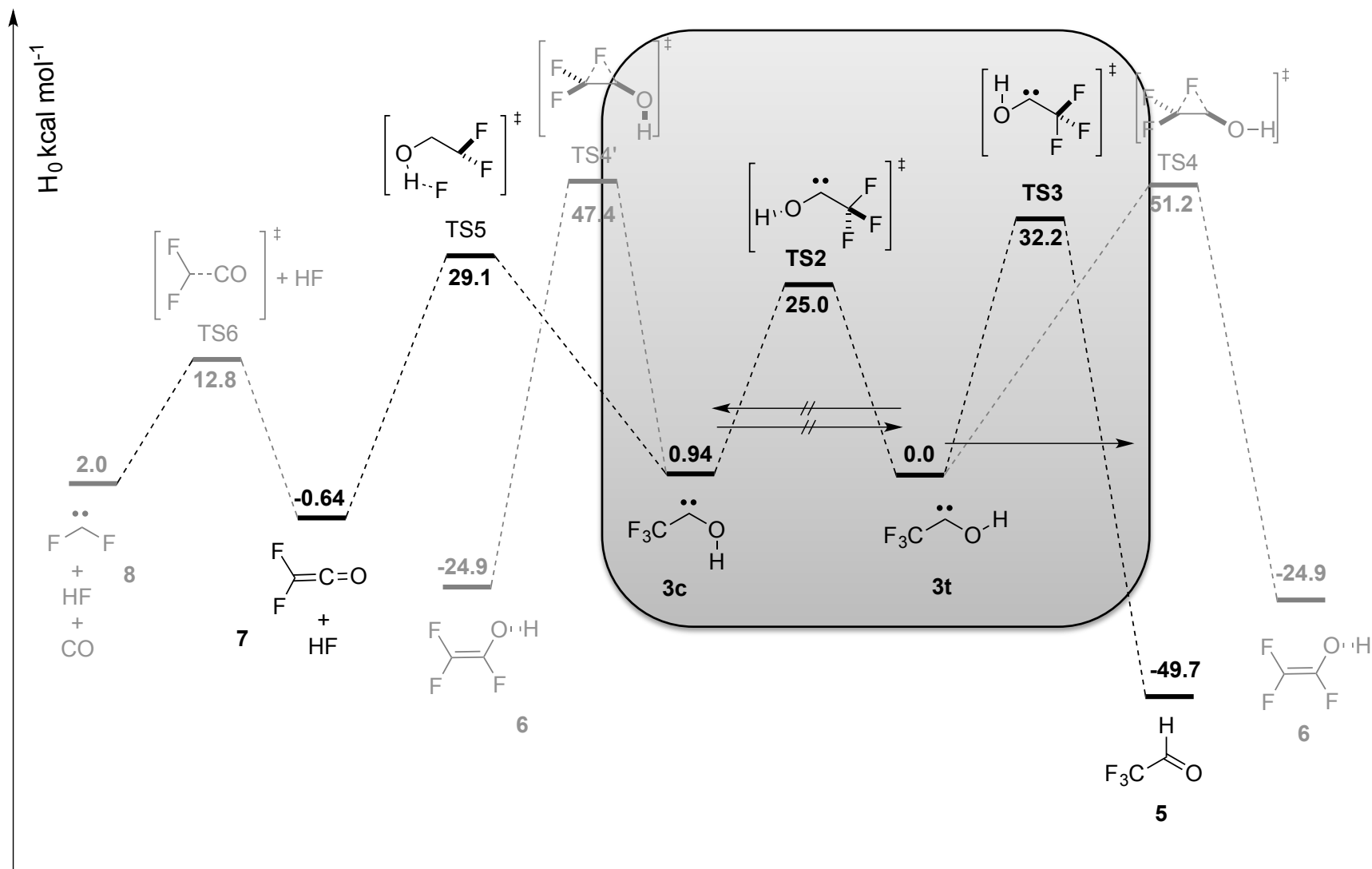


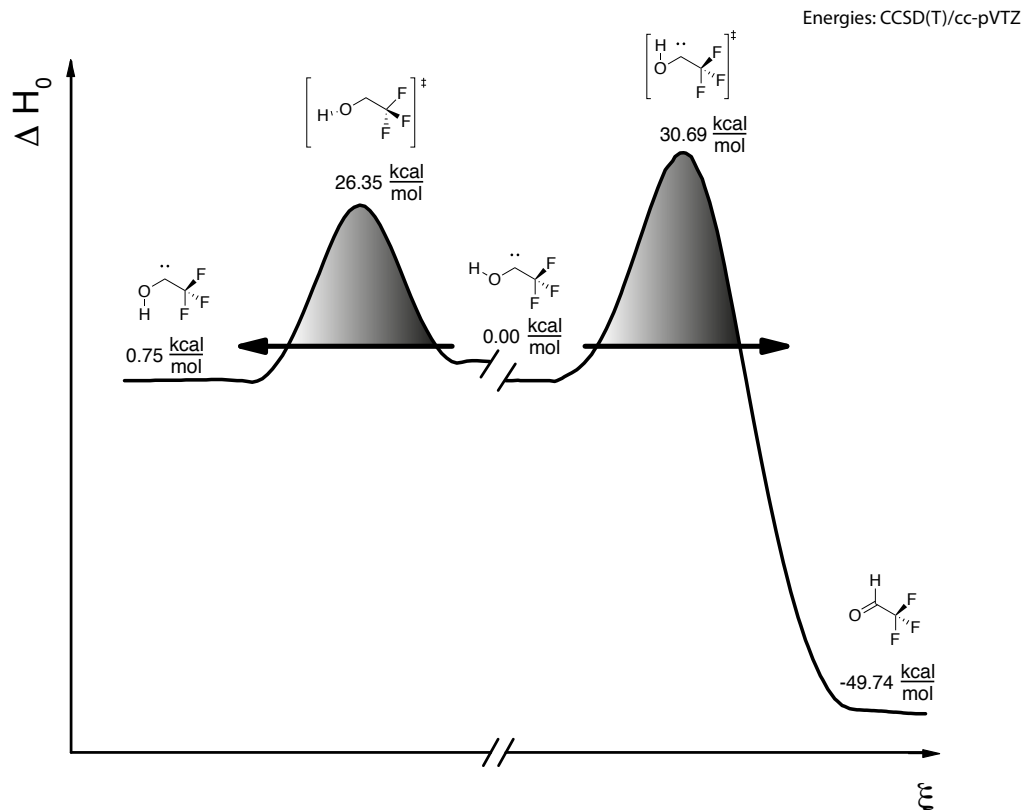
Energies are computed at the M06-2X/cc-pVTZ



Method	Half-Lives F-shift	Half-Lives H-shift
B3-LYP/cc-pVTZ	3.67 h	4.53 h
B3-LYP/cc-pVTZ//CCSD(T)/cc-pVTZ	21.5 d	810 s

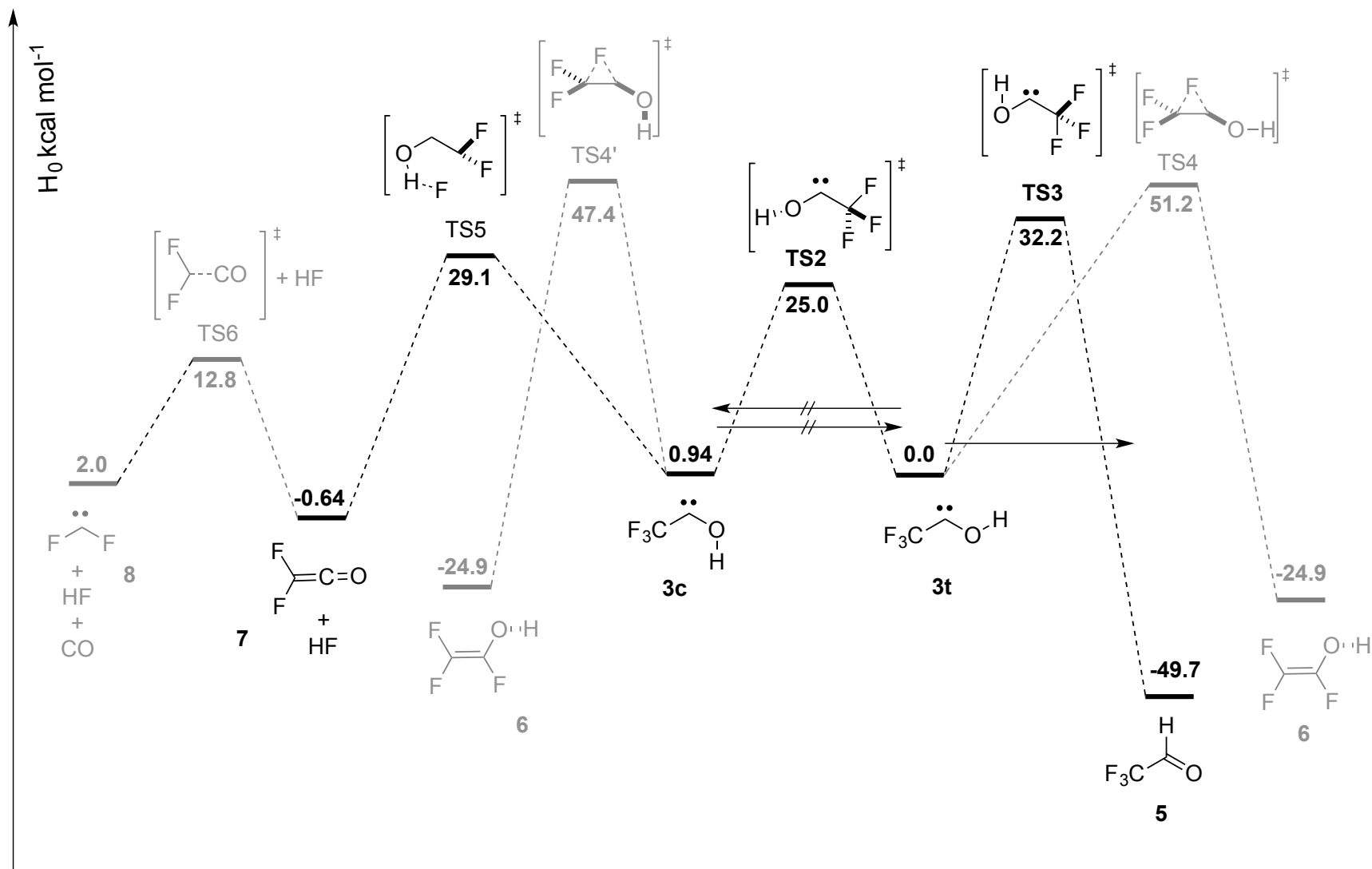
IRC computed at the B3-LYP/cc-pVTZ

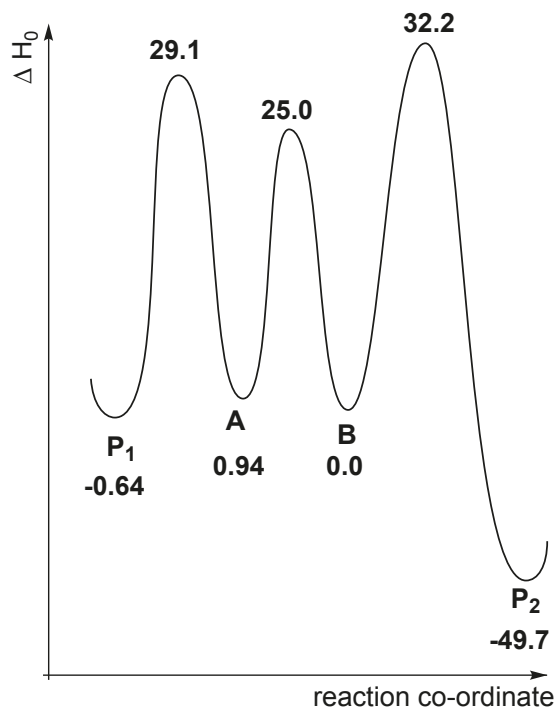




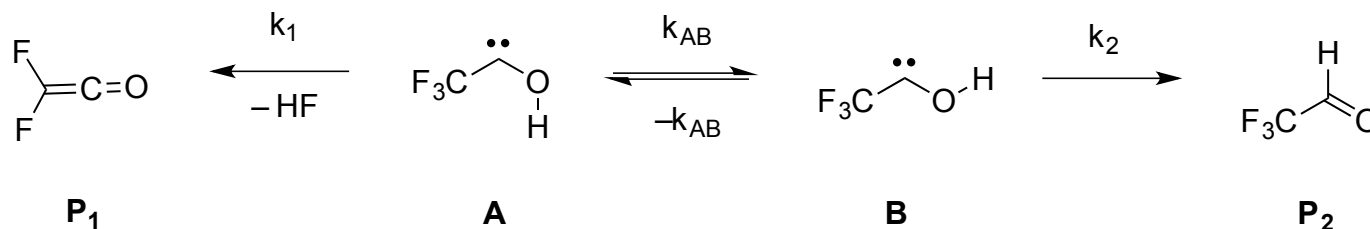
Method	Half-Lives isomerisation	Half-Lives H-shift
M06-2X/6-311++G(d,p)	1190 y	7.15 d
B3LYP/cc-pVTZ	41200 y	4.53 h

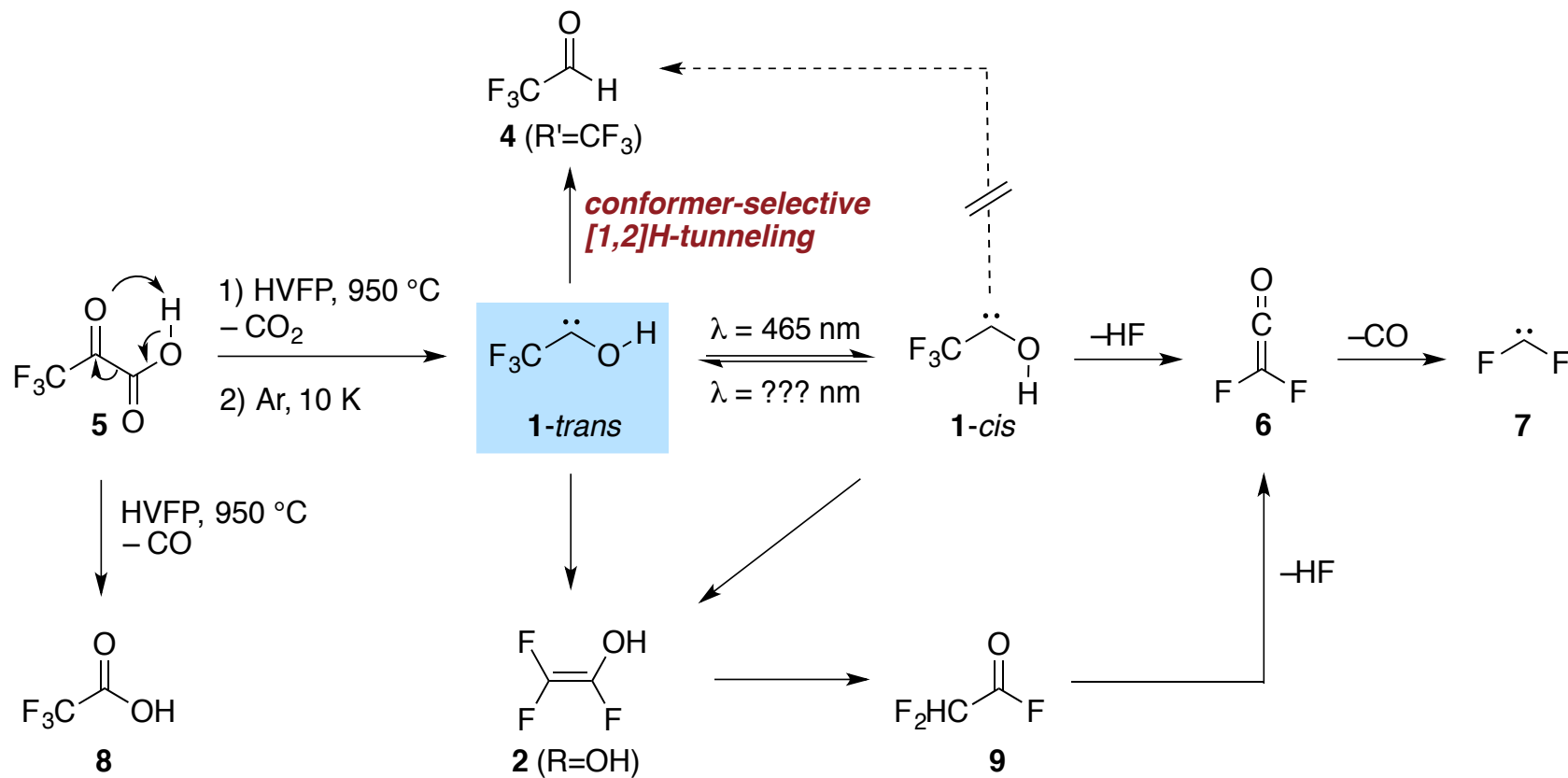
IRC computed at the M06-2x/6-311++G(d,p)





- Applicable when
 - irreversible reaction of same order
 - k_{AB} order of magnitude faster than k_x
 - the equilibrium between the A and B is no more than 10:1 in favor of either species
 - calculation gives 7:1 for P1 in this case

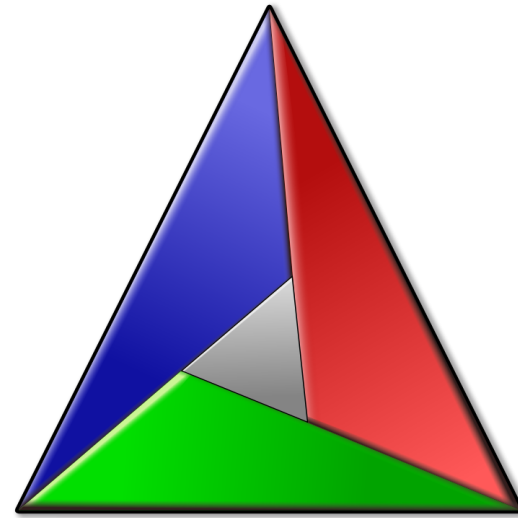








- CMake (before GNU Autotools)
 - opensource by Kiteware
 - popular software uses it like KDE or LLVM and PSI4
 - easy to configure and maintain
 - it just works everytime!
 - Windows version
 - supports different IDEs
- Source control with mercurial
 - tracks changes of source code
 - different forks possible
 - merging capability
 - GUIs available
 - pull and request from server
 - alternative: git





- make projection is needed to generate the ZPVEs along IRC
- added support for MP2
- added support for gaussian checkpoint files
- added support for high level single points
 - **highLevelInput:**
 "%1%\n
 %2%\n
 *CFOUR(CALC=CCSD(T),BASIS=%7%\n
 MEMORY_SIZE=%3%,MEM_UNIT=MB,ABCDTYPE=AOBASIS\n
 CC_PROG=ECC,SCF_MAXCYC=300,CC_MAXCYC=100\n
 COORDINATES=CARTESIAN,CHARGE=%5%,MULTIPLICITY=%6%)"
 - **highLevelHarvestRegex:** 'CCSD\.(T) energy\s+([+-]\d+\.\d+)'
- added boost option reading from command lines
- support for isotopes
 - 1 x y z
 1(iso=2) x y z





- I want to thank you all for your attention and I like to thank you all for your overall kindness. Thanks go especially to

Prof. Dr. Peter R. **Schreiner**, Ph.D.

Dr. Arthur Mardyukov

Dr. Dennis Gerbig and Jan P. Wagner

Jan Schümann and Christian Eschmann

and again the whole group!
