Theoretical and Experimental Investigations towards Mercapto Carbenes

Seminar talk presented by
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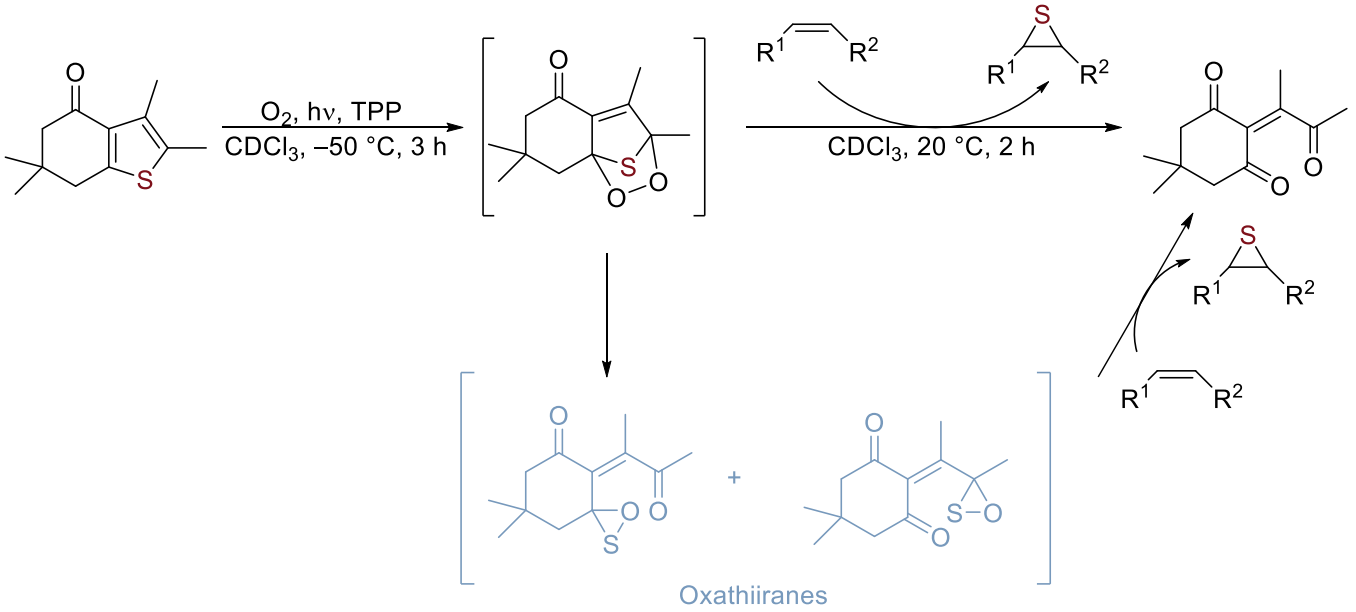
27.03.2020

Institute of Organic Chemistry, Justus-Liebig-University Giessen

Mercapto Carbenes – Oxathiiranes



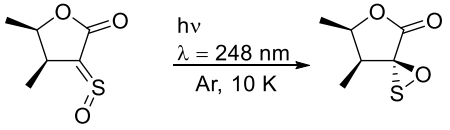
- Reactivity of the alkene and diastereoselectivity of the episulfidation parallels to epoxidations with dimethyldioxirane

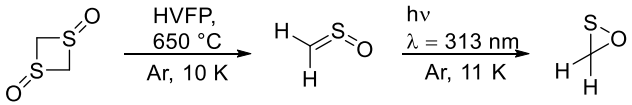
- Similar influence of the ring strain in the alkene compared to epoxidations with *m*CPBA

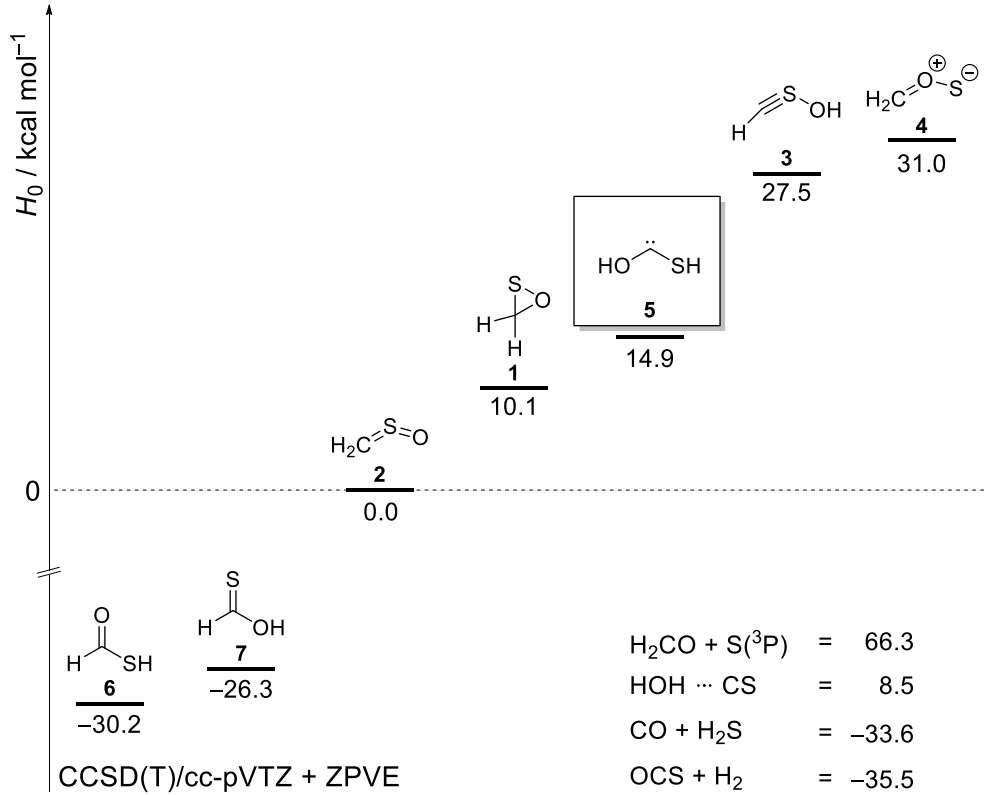
→ episulfidation should involve an analogous intermediate

W. Adam, S. Weinkötz, *J. Chem. Soc. Chem. Commun.* **1996**, 177-178; W. Adam, B. Fröhling, K. Peters, S. Weinkötz, *J. Am. Chem. Soc.* **1998**, *120*, 8914-8919; K. J. Shea, J.-S. Kim, *J. Am. Chem. Soc.* **1992**, *114*, 3044-3051.

Mercapto Carbenes – Hydroxy Mercapto Methylene

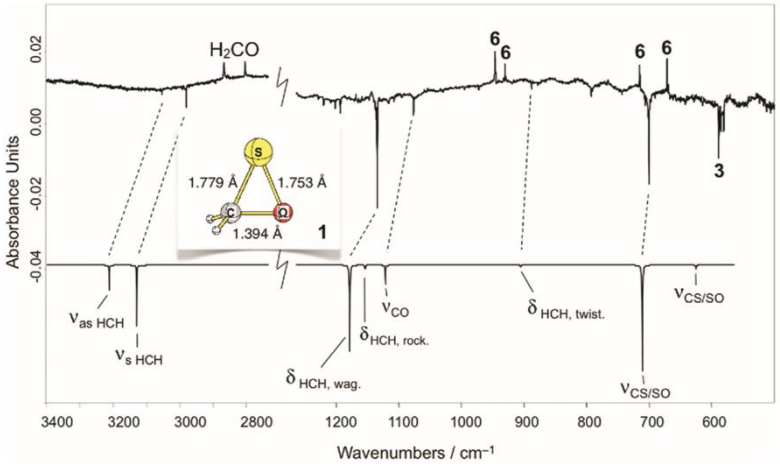


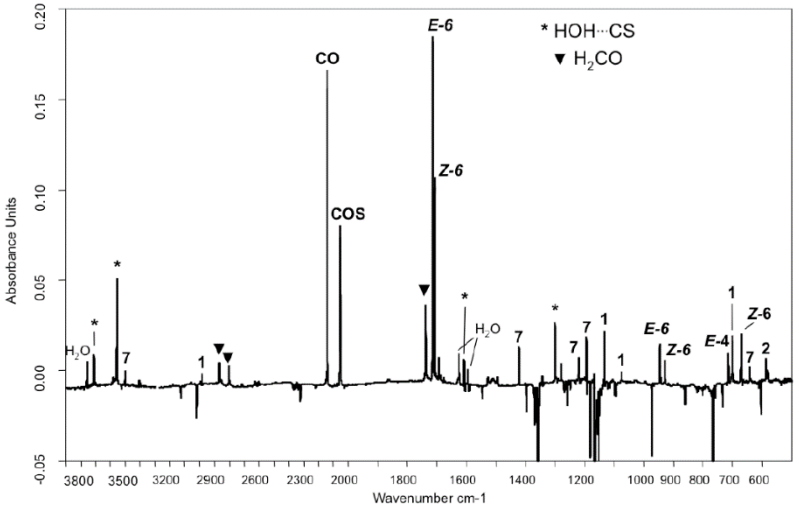




$H_2CO + S(^3P)$	=	66.3
HOH ··· CS	=	8.5
$CO + H_2S$	=	–33.6
$OCS + H_2$	=	–35.5

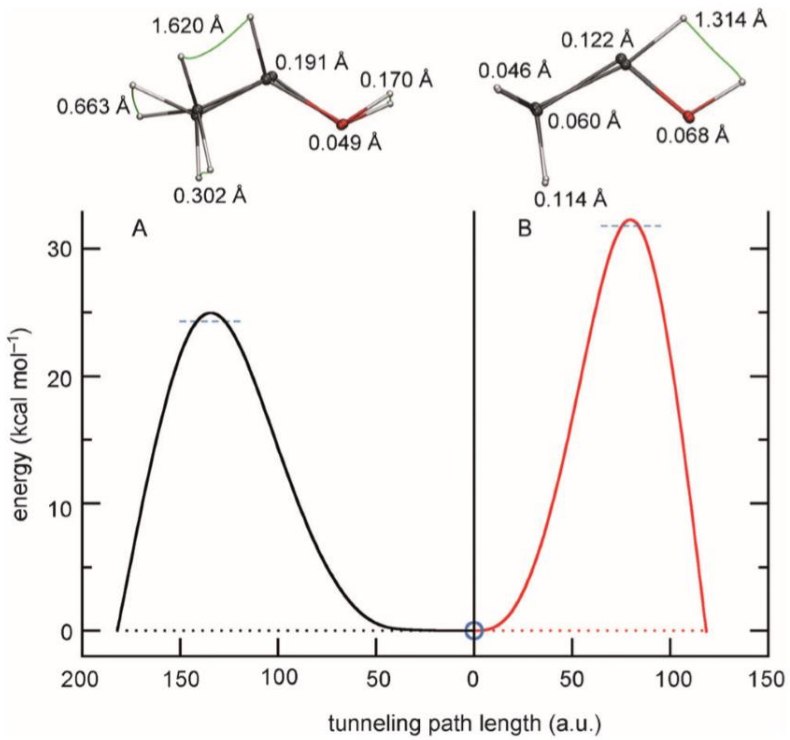
- Conversion of **1** to **6** with λ > 360 nm

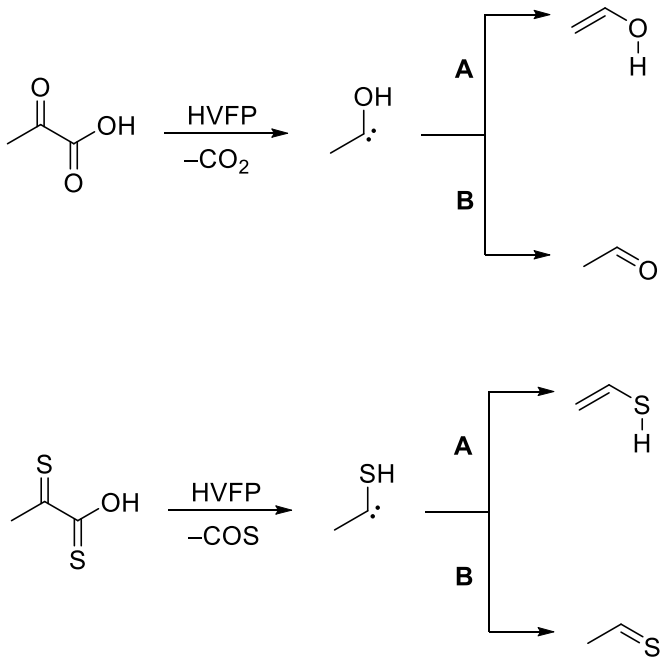




O. C. M. O'Sullivan, S. G. Collins, A. R. Maguire, M. Böhm, W. Sander, *Eur. J. Org. Chem.* **2006**, *13*, 2918-2924; P. R. Schreiner, H. Reisenauer, J. Romanski, G. Mloston, *J. Am. Chem. Soc.* **2010**, *132*, 7240-7241.

Mercapto Carbenes – Methyl Mercapto Methylene



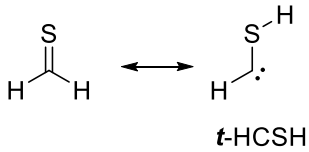


CCSD(T)-F12/cc-pVTZ (rates: B3LYP/cc-pVTZ)

	Route A			Route B		
	$\Delta^{\ddagger}H$ [kcal mol^{-1}]	$t_{1/2}$	L [a.u.]	$\Delta^{\ddagger}H$ [kcal mol^{-1}]	$t_{1/2}$	L [a.u.]
H_3C-C-OH	25.0	139 d	182	32.1	3 h	121
H_3C-C-SH	21.5	10 h	172	30.6	221 d	141

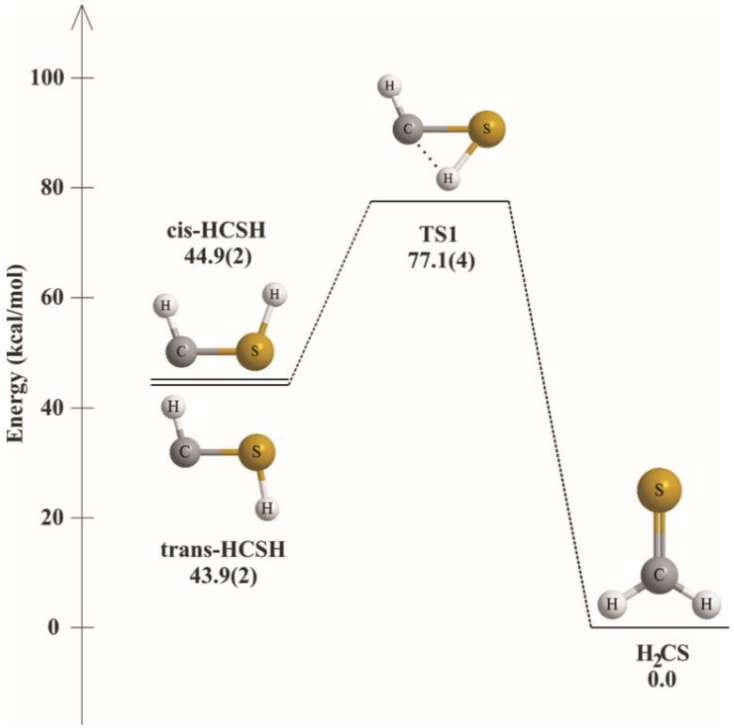
P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, *332*(6035), 1300-1303; J. Kästner, *Chem. Eur. J.* **2013**, *19*, 8207-8212.

- H_2CS is a congener of formaldehyde and a tautomer of mercapto methylene

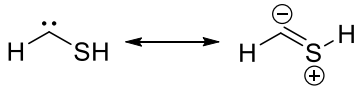


t-HCSH

- Kaiser, Lee *et al.* 1998: First evidence for mercapto methylene: (crossed molecular beam experiments with atomic carbon and H_2S followed bei TOF-MS analysis (1998))



- Tunneling process is to slow to be observable (> 10^4 h)
- Bond order?:

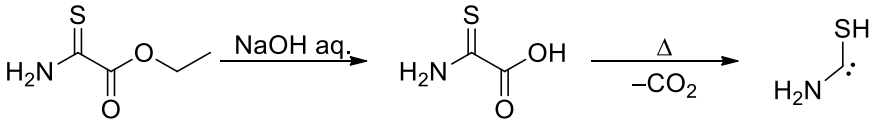


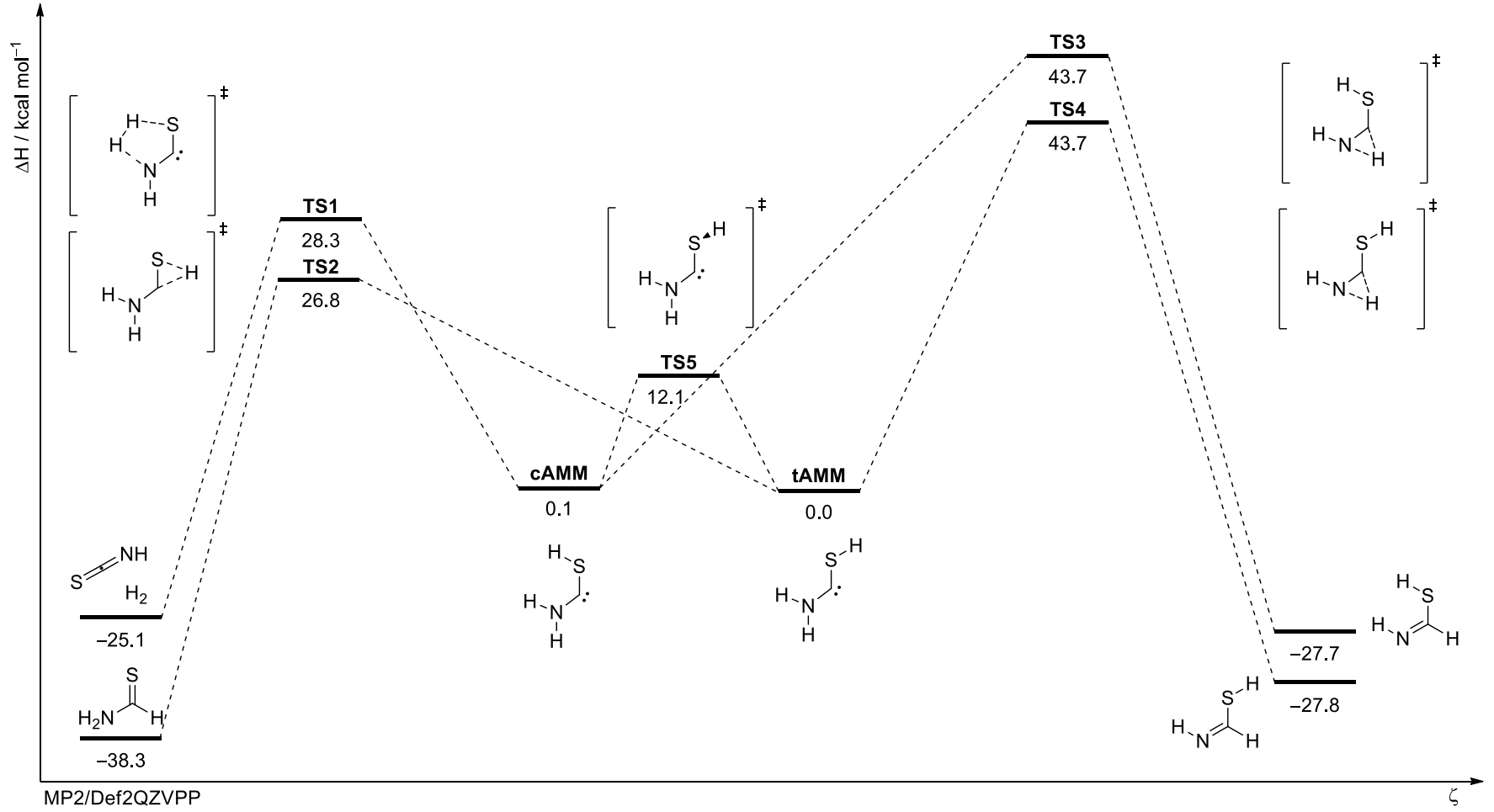
- "it is not a true carbene and it is better represented as an ylide with a negatively charged carbon atom and a positively charged sulfur"

	B3LYP/Def2QZVPP	
	$\Delta^{\ddagger}H$ [kcal mol^{-1}]	$t_{1/2}$
H-C-SH	32.0	17149 d
D-C-SD	34.0	$2.4 \cdot 10^{14}$ d

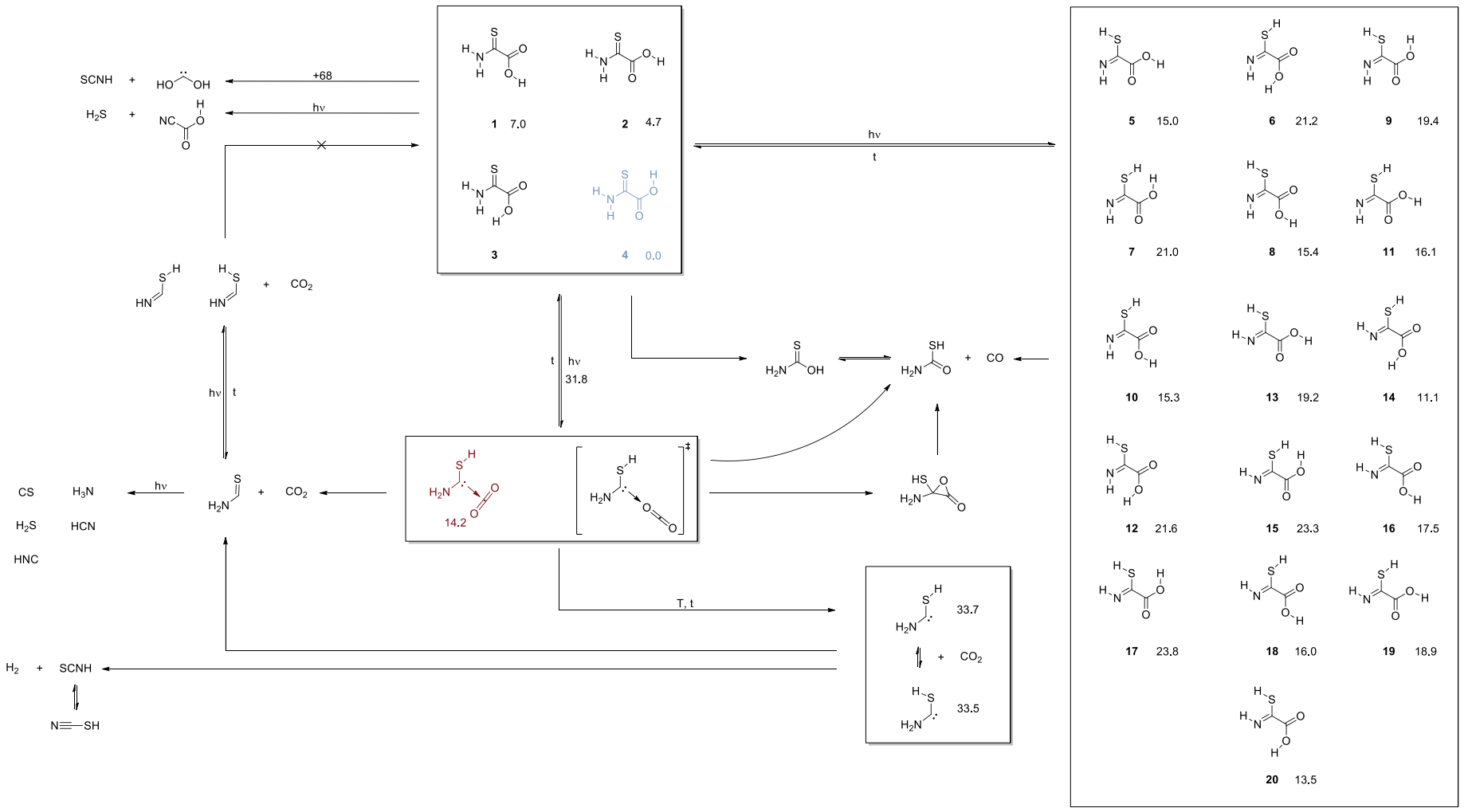
J. Sarka, A. G. Császár, P. R. Schreiner, *Collect. Czech. Chem. Commun.* **2011**, *76(6)*, 645-667; D. R. Johnson, F. X. Powell, *Science* **1970**, *169(3946)*, 679-680; M. W. Sinclair, N. Fourikis, J. C. Ribes, B. J. Robinson, R. D. Brown, P. D Godfrey, *Aust. J. Phys.* **1973**, *26*, 85-91; D. Despois, *Earth, Moon and Planets* **1998**, *79*, 103-124; L. M. Woodney, M. F. A'Hearn, *Earth, Moon and Planets* **1997**, *78*, 69-70; N. Marcelino, J. Cernicharo, E. Roueff, N. Gerin, R. Mauersberger, *Astrophys. J.* **2005**, *620*, 308-320; R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee, *Sience* **1998**, *279*, 1181-1184. Image: Wikipedia.

Amino Mercapto Methylene



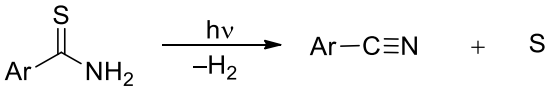


Amino Mercapto Methylene

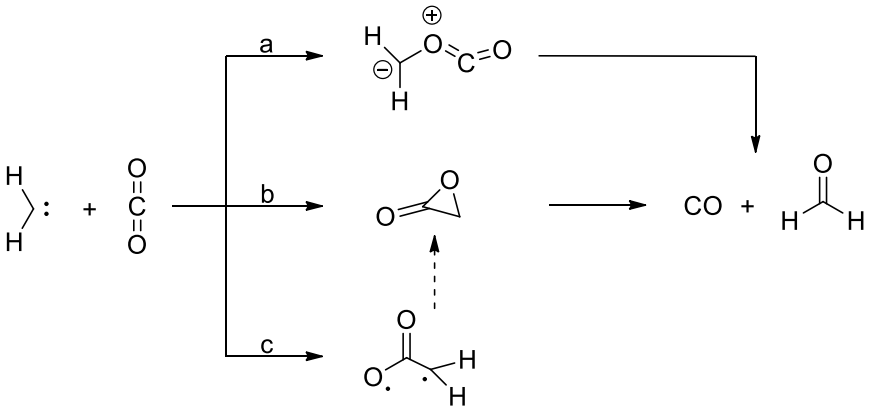


MP2/Def2QZVPP

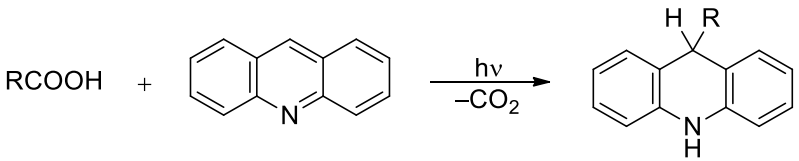
Formation of Nitriles



Oxygen abstraction

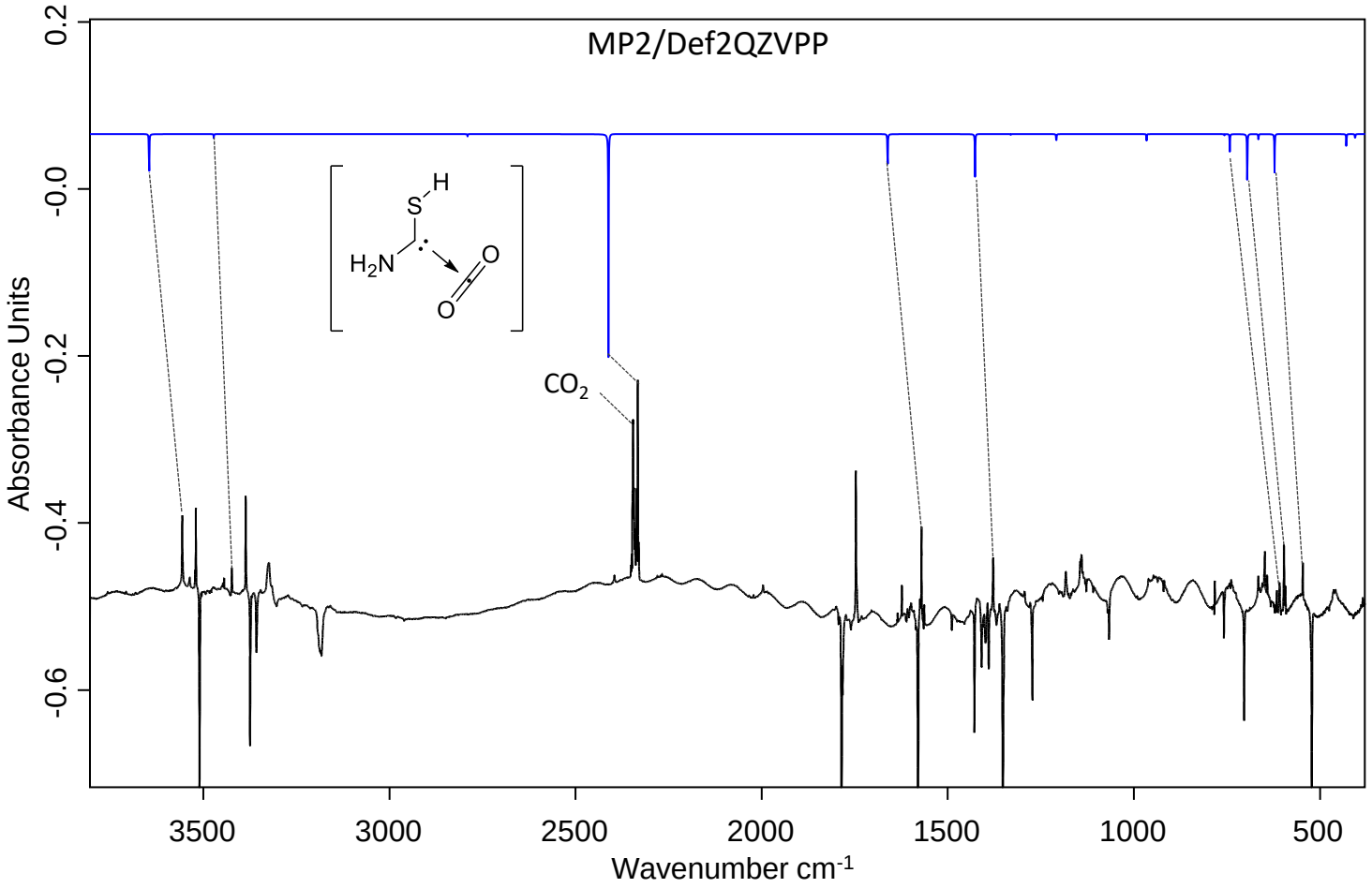


Photodecarboxylation



G. Crank, A. Mursyidi, *J. Photoch. Photobio A* **1990**, *53*, 30-310; G. B. Kistiakowsky,K. J. Sauer, *J. Am. Chem. Soc.* **1958**, *86*, 1066; D. Kovacs, J. E. Jackson, *J. Phys. Chem. A.* **2001**, *105*, 7579; L. Farkas, O. H. Wansbrough-Jones, *Z. Phys. Chem.* **1932**, *18(1)*, 124-145; R. Noyori, M. Katô, M. Kawanisi, H. Nozaki, *Tetrahedron.* **1969**, *25*, 1125-1136.

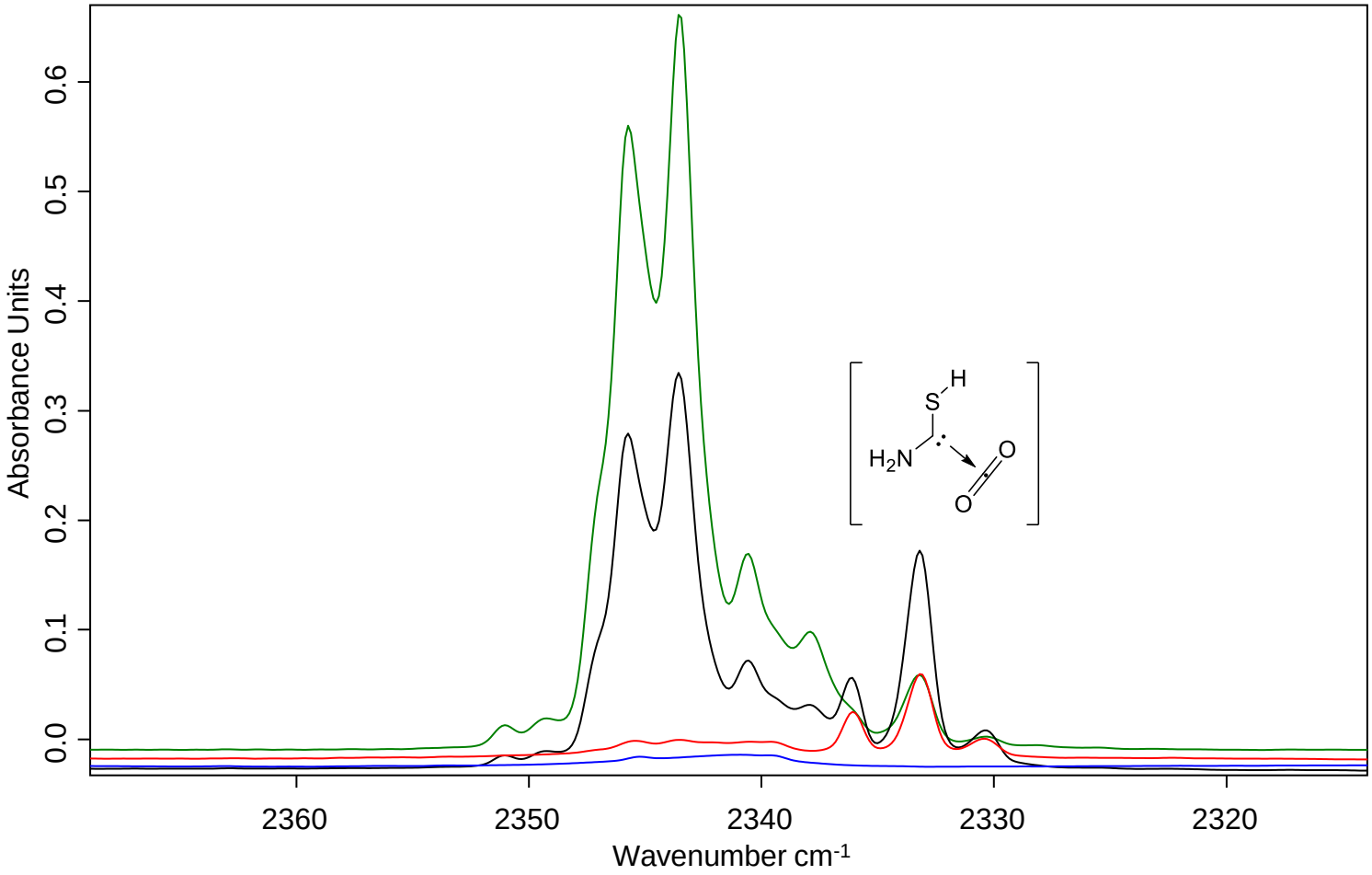
Amino Mercapto Methylene



UV/VIS:

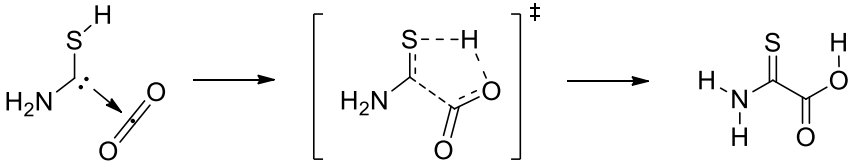
- With 300 nm irradiation, a species forms that absorbs at 254 nm
- With 254 nm irradiation, this species reacts further immediately

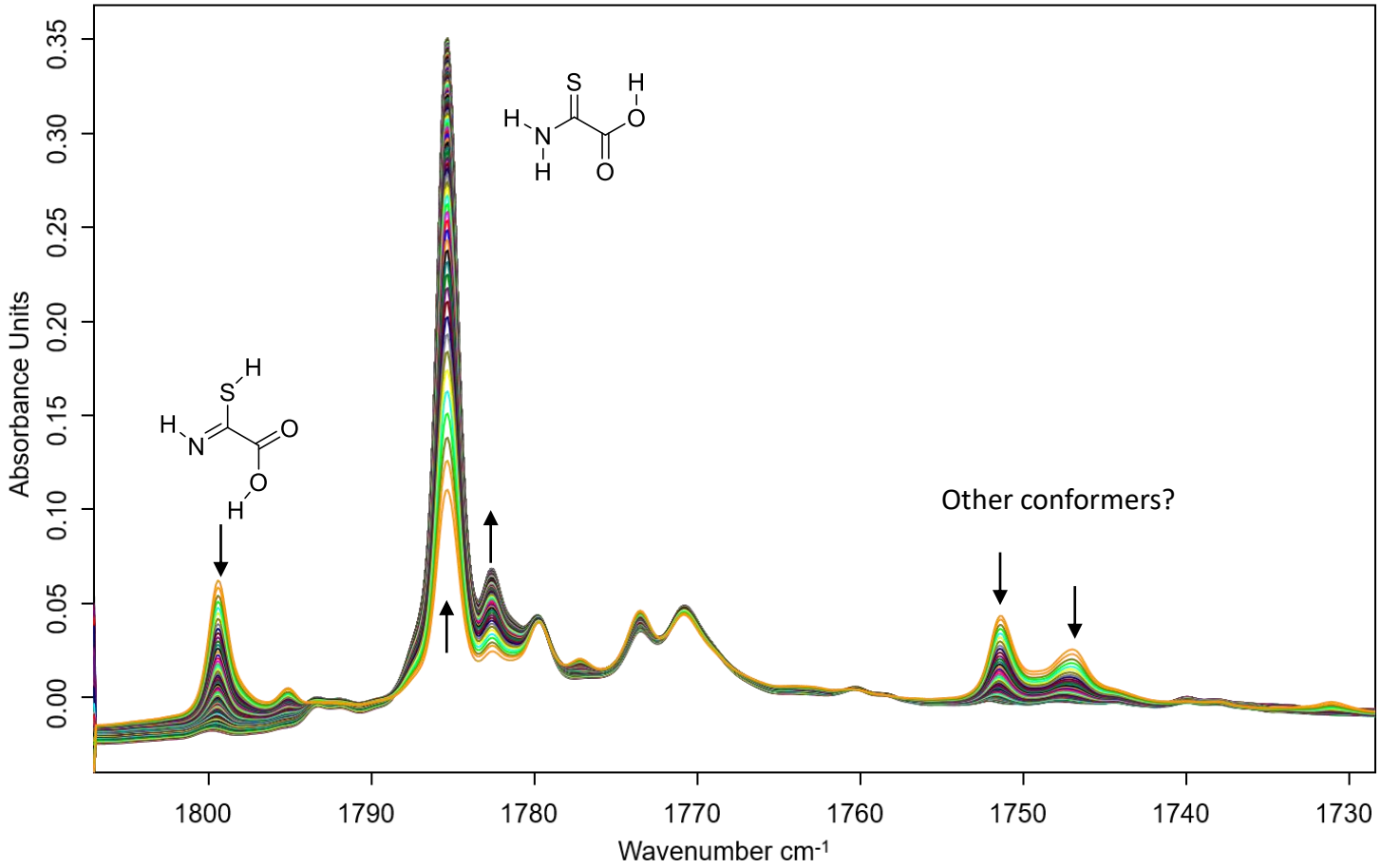
Amino Mercapto Methylene



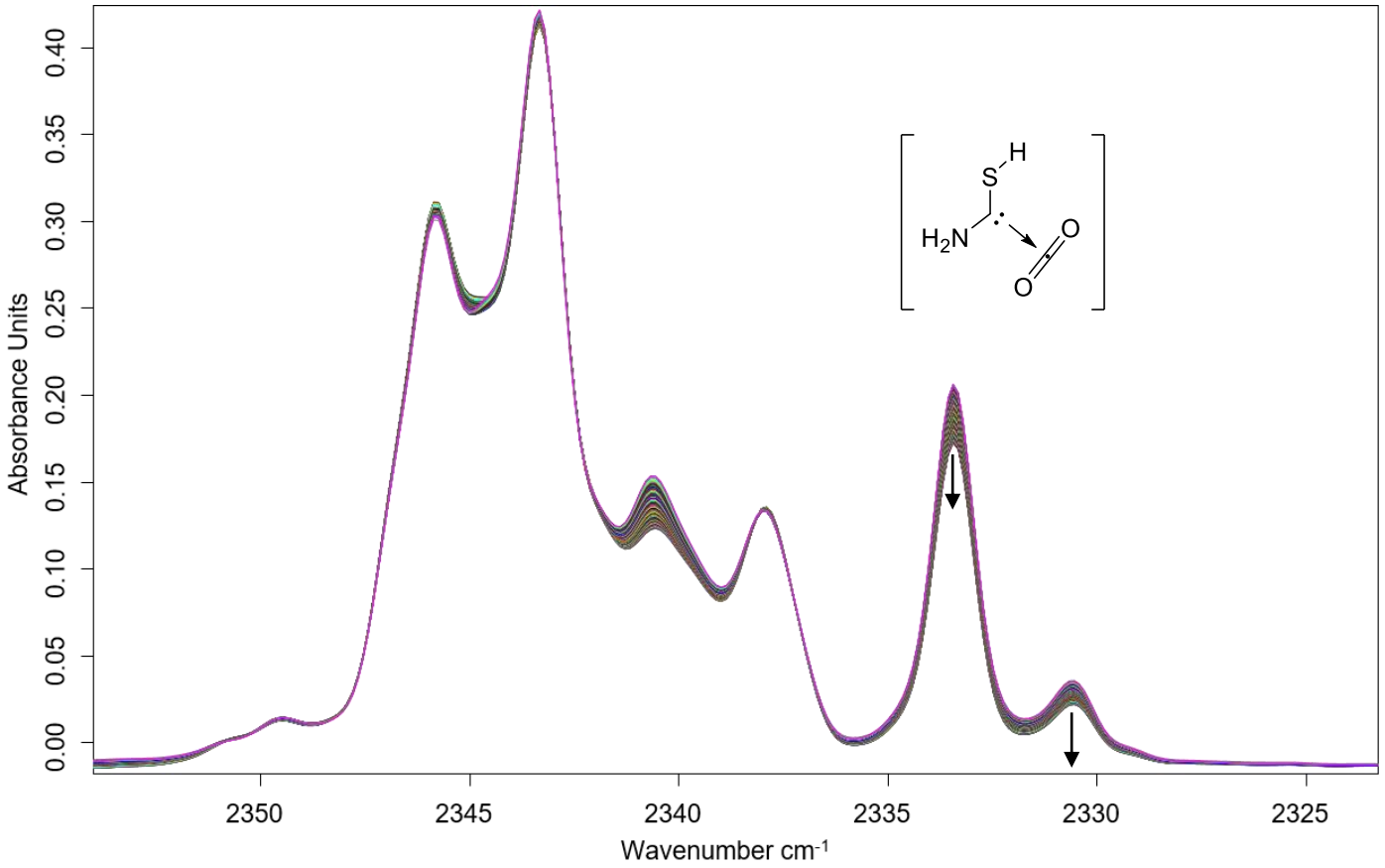
Amino Mercapto Methylene

Carbonyl Ene Reaction

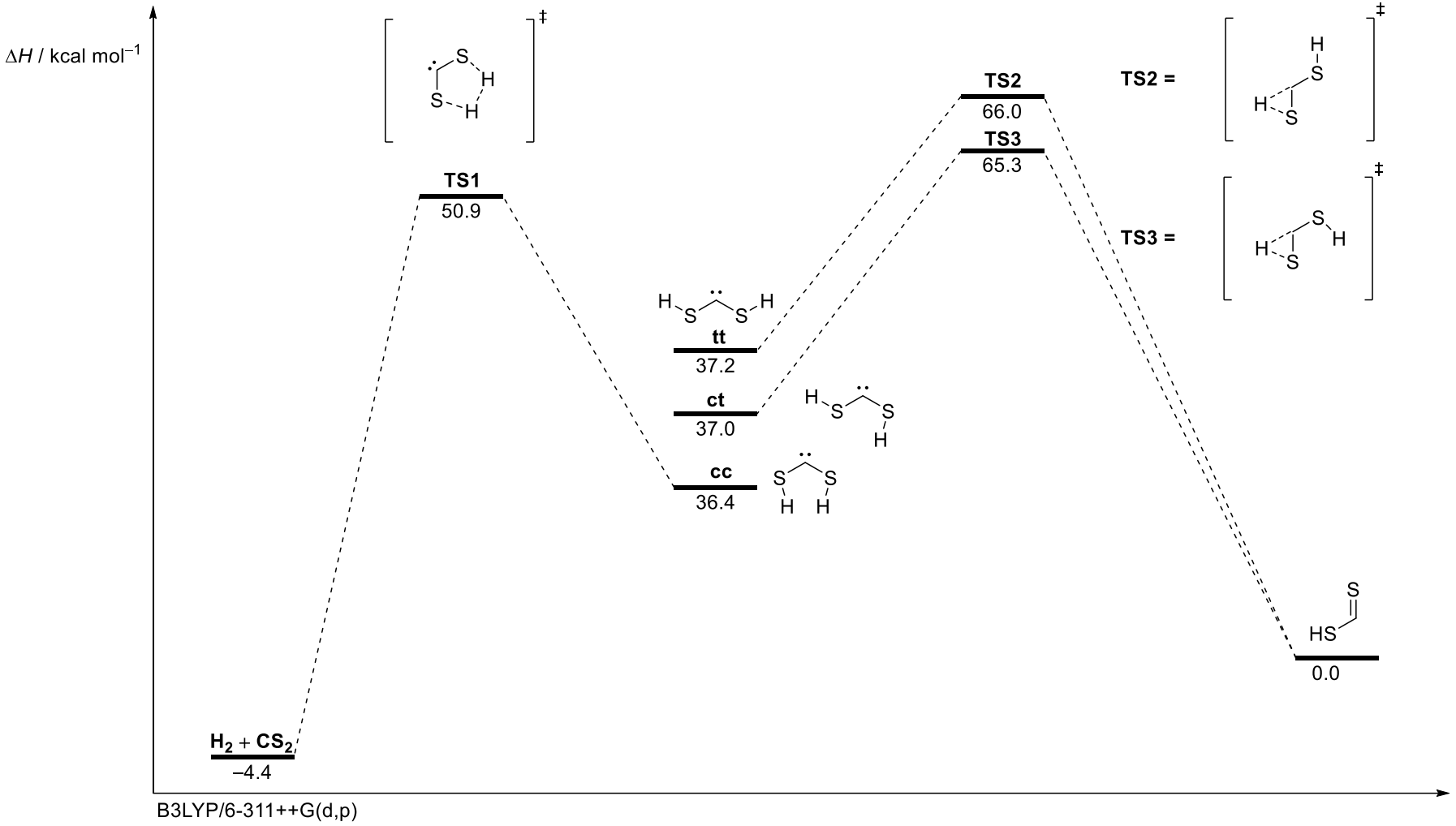




Amino Mercapto Methylene

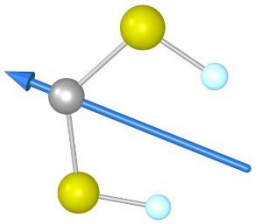


Dimercapto Methylene

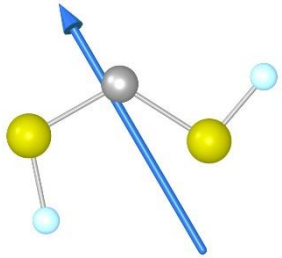


Dimercapto Methylene

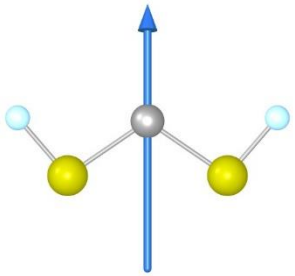
cc: 0.301944 Debye

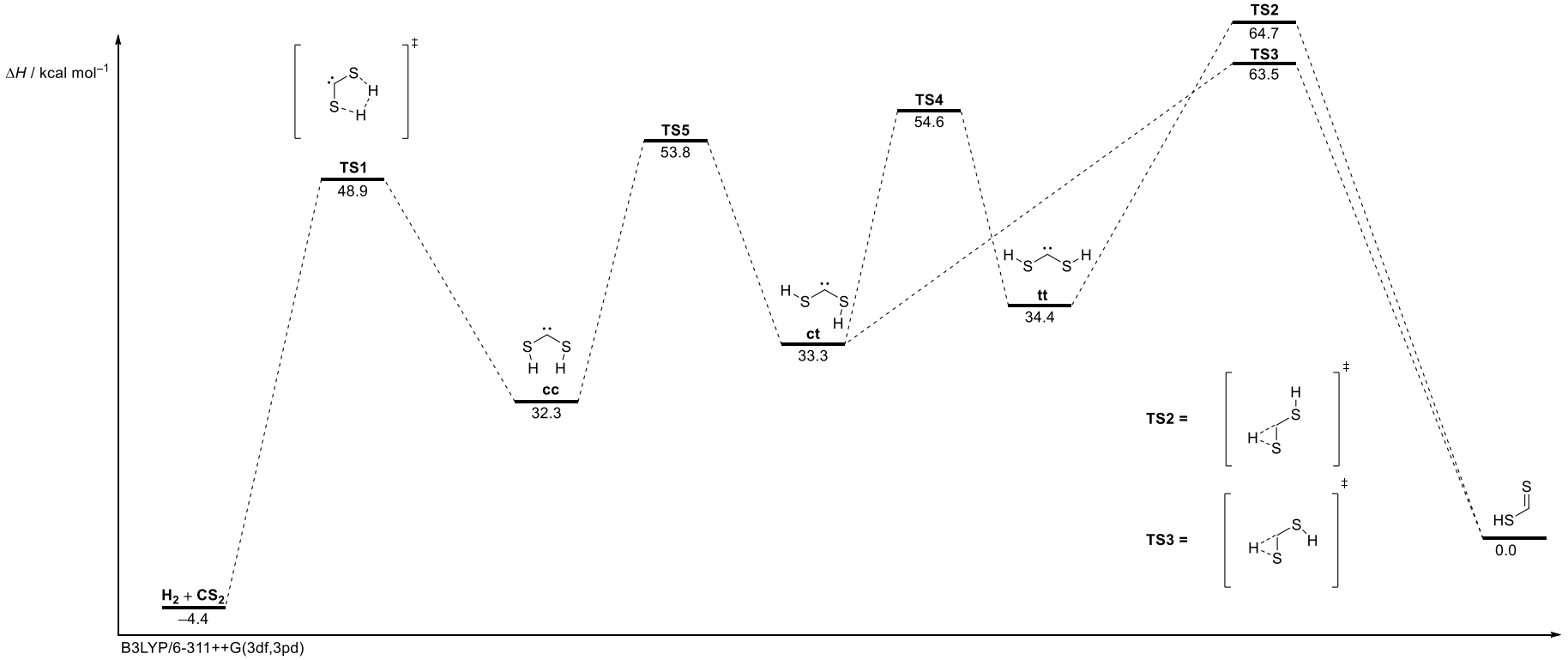


ct: 0.202086 Debye

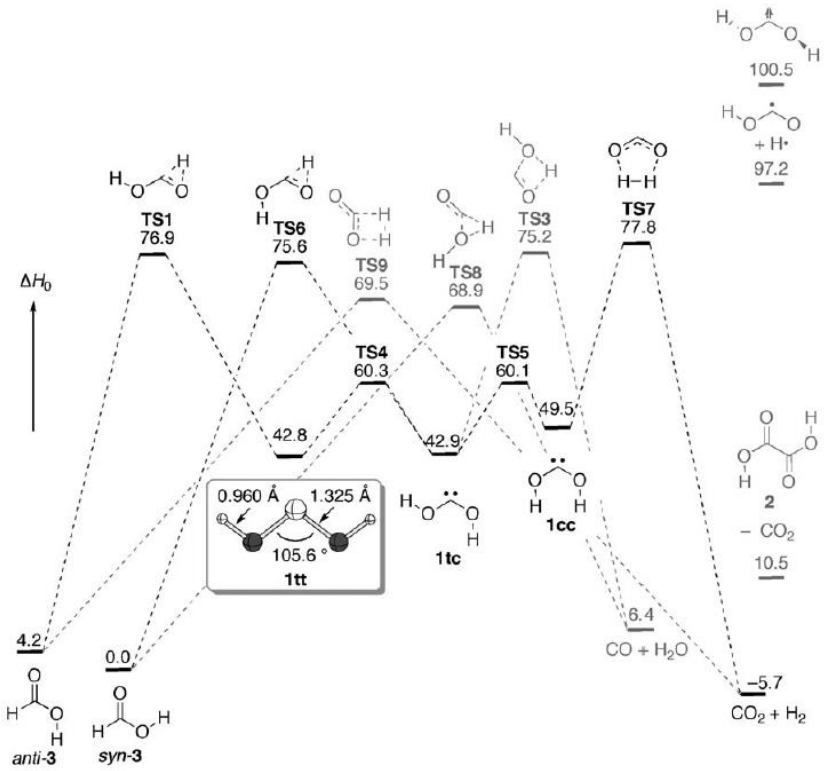


tt: 0.284863 Debye





Dimercapto Methylene



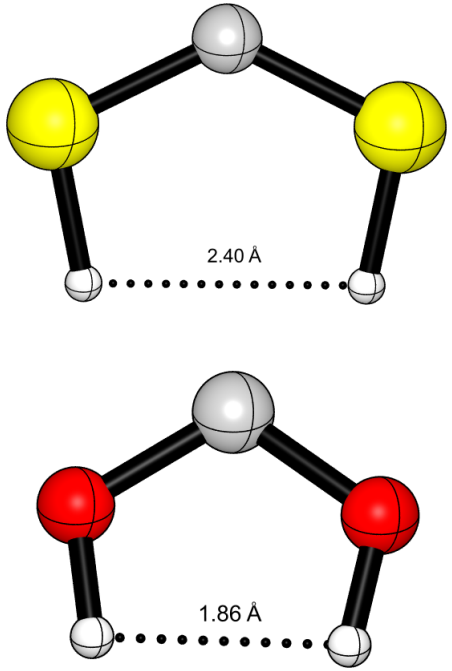
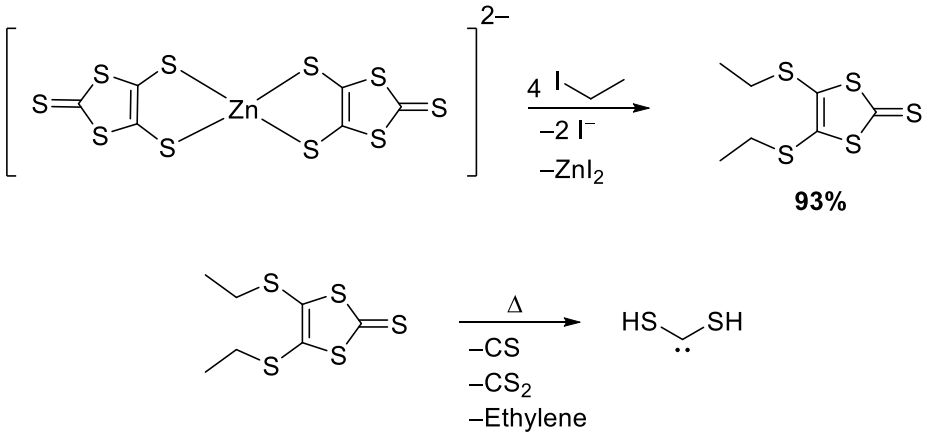


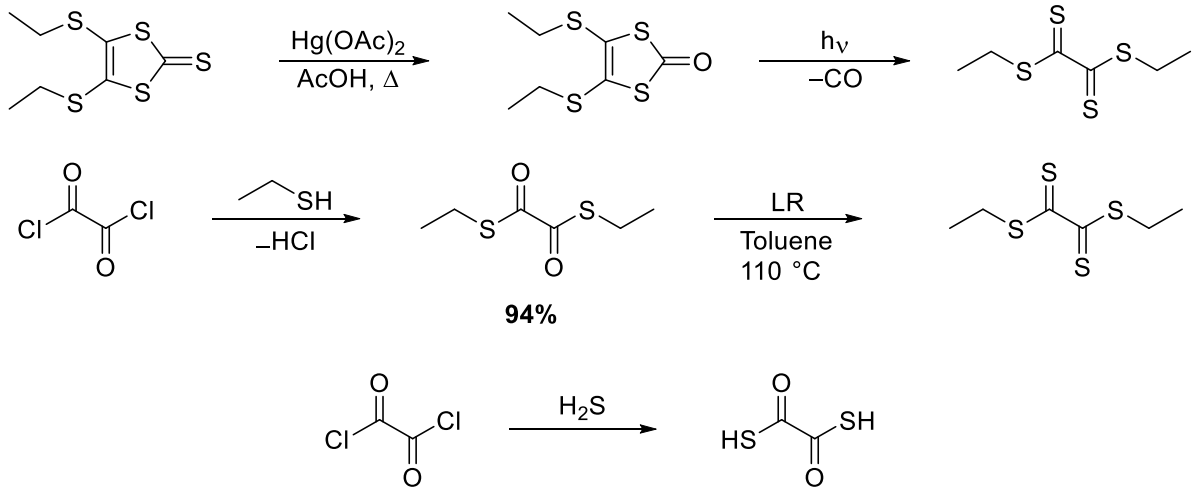
Figure 5. Potential energy hypersurface (ΔH_0) of **1** and related species at the CCSD(T)/cc-pVTZ + ZPVE level in kcal mol^{-1}. The main reaction pathways are highlighted.

	HF/6-311++G(d,p) /kcal mol^{-1}	B3LYP/6-311++G(3df,3dp) /kcal mol^{-1}	B3LYP-D3/6-311++G(3df,3dp) /kcal mol^{-1}
cc	0	0	0
ct	-1.0	1.0	1.3
tt	-1.5	2.1	2.6

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

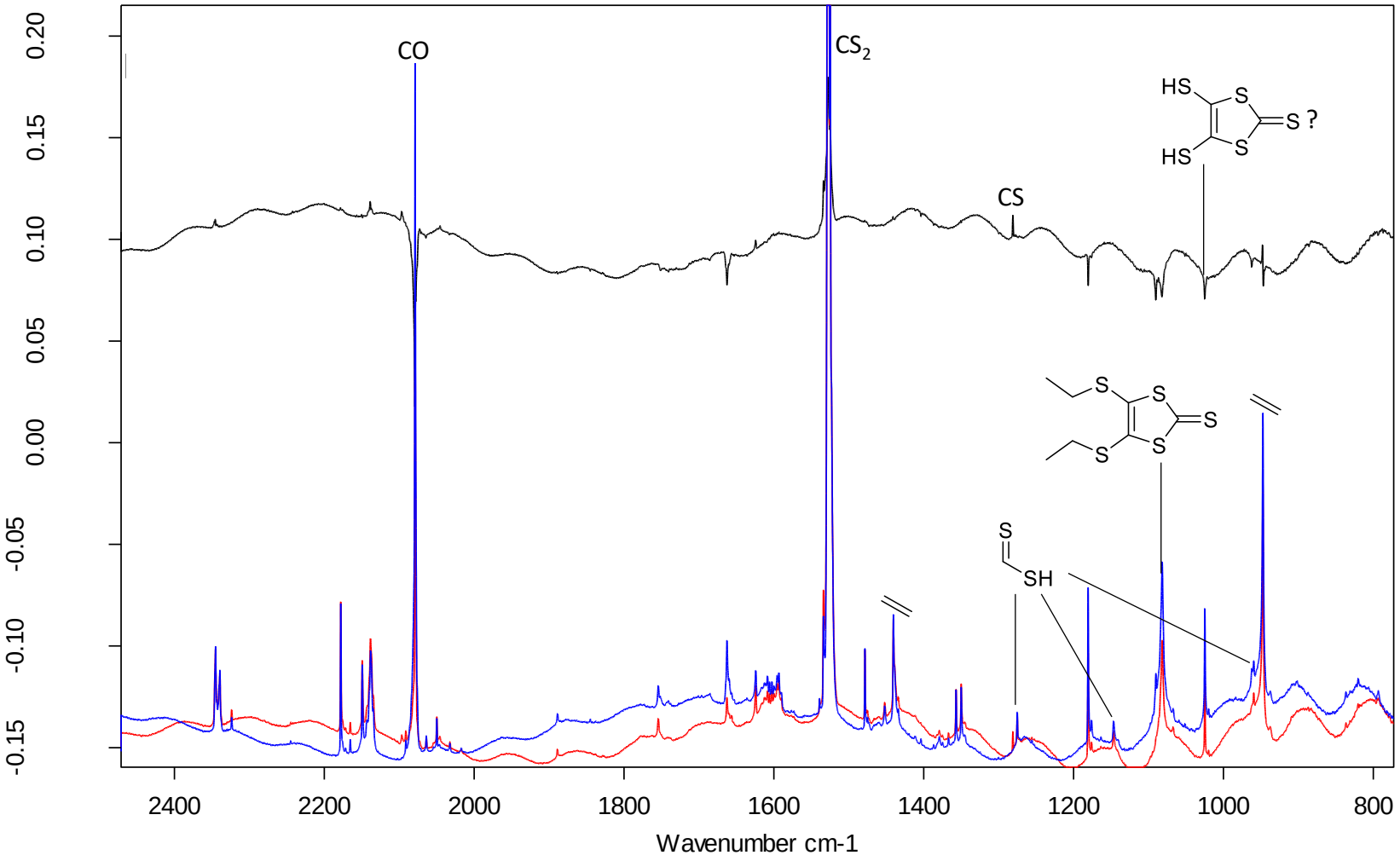
Precursor Synthesis



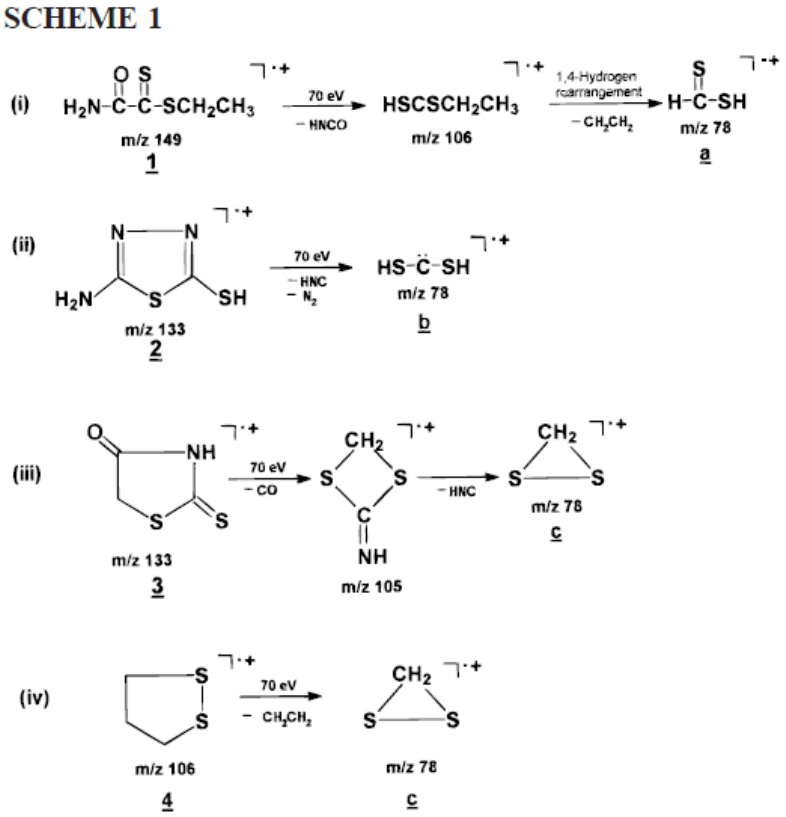


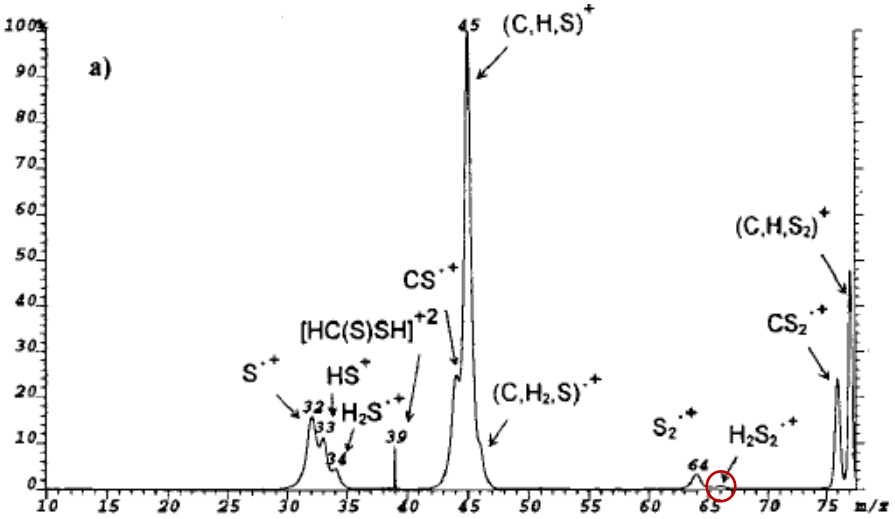
E. A. Ignatenko, A. A. Gorbunov, E. V. Shklyaeva, G. G. Abashev, *Chem. Heterocycl. Compd.* **2014**, *50(5)*, 691-698; P. Jeroschewski, P. Hansen, *Sulfur Reports* **1986**, *7(1)*, 1-44.

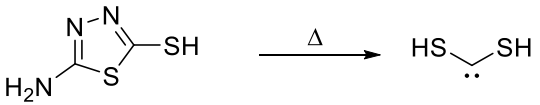
Dimercapto Methylene



Dimercapto Methylene



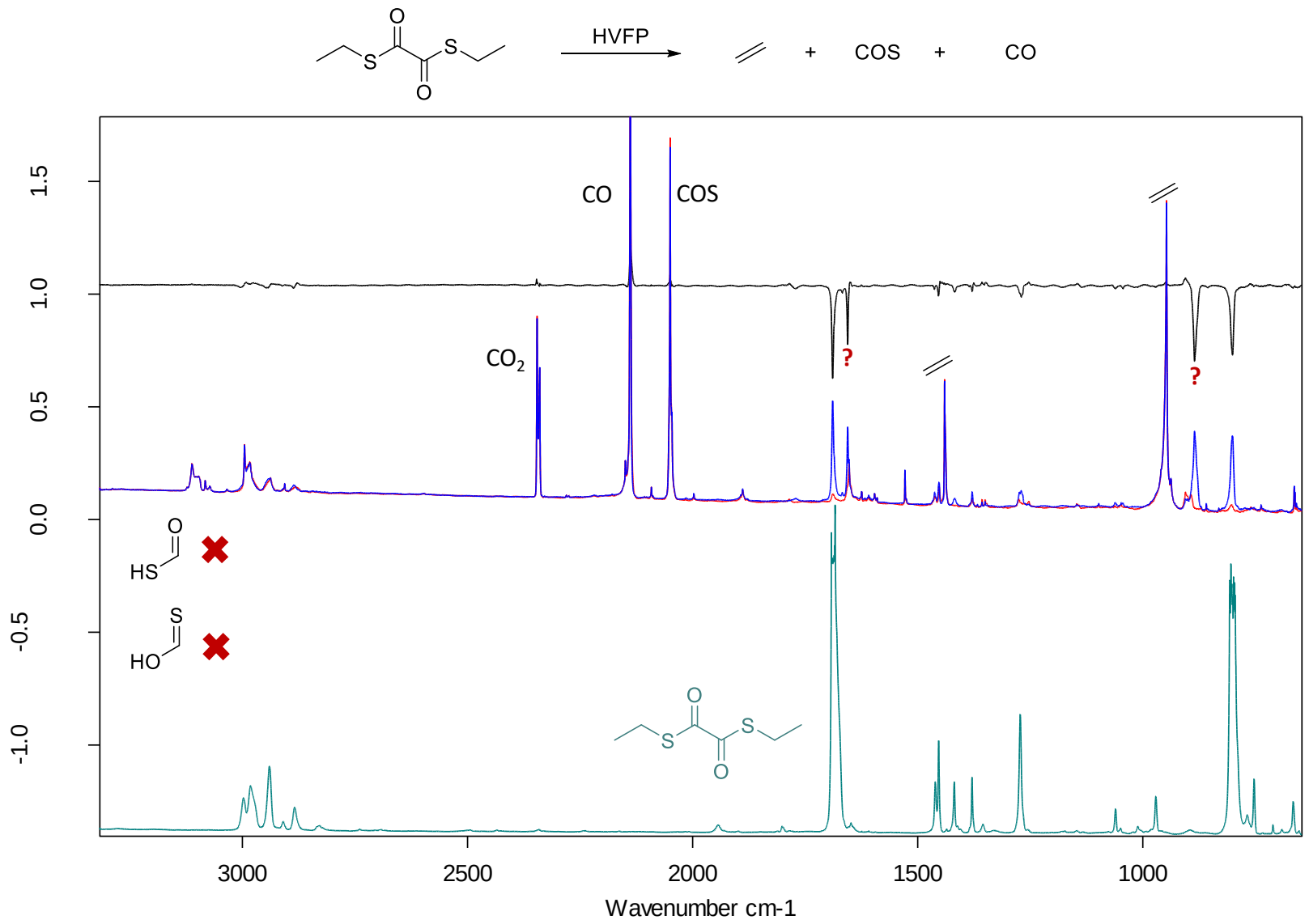




mp: 235 °C
Source Temperature: 250 °C
Cost: > 1€/g

S. Vivekananda, R. Srinivas, *J. Phys. Chem. A* **1999**, *103*, 5123-5128.

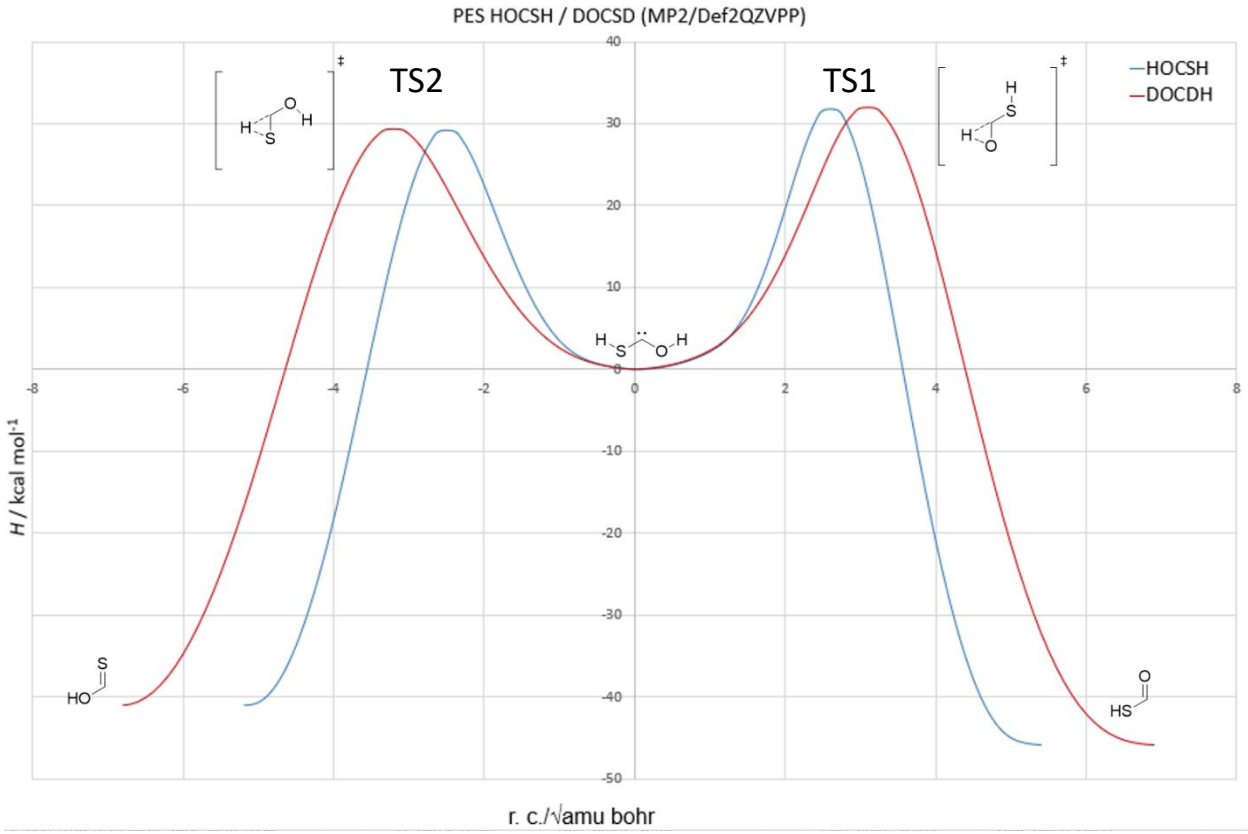
Mercapto Hydroxy Methylene



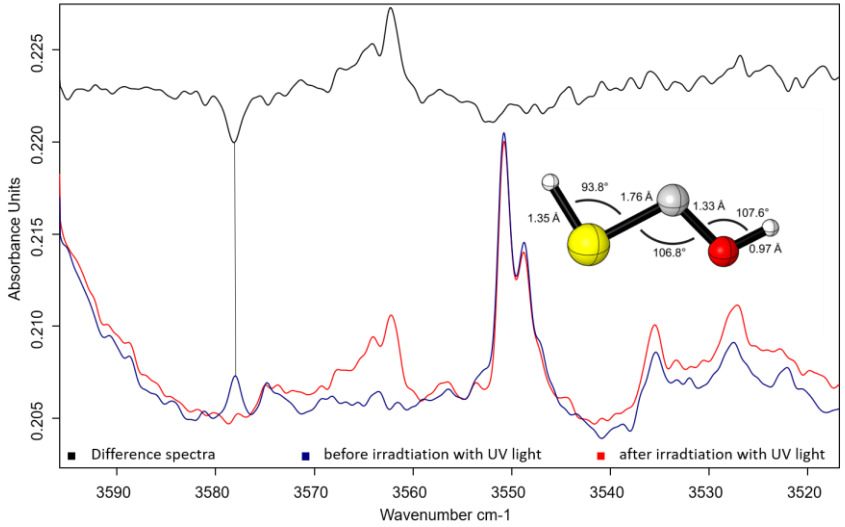
Hydroxy Mercapto Methylene

	Route B (via TS2)		Route A (via TS1)	
	electr. Barrier [kcal mol^{-1}] (total barrier)	$\tau_{1/2}$	electr. Barrier [kcal mol^{-1}] (total barrier)	$\tau_{1/2}$
HO-C-SH	29.5 (26.7) 33.4[a]	61 d	32.1 (28.4) 27.0[a]	6 d
DO-C-SD	29.5 (27.5)	1.8 10^{10} d	31.1 (29.3)	1.4 10^{8} d

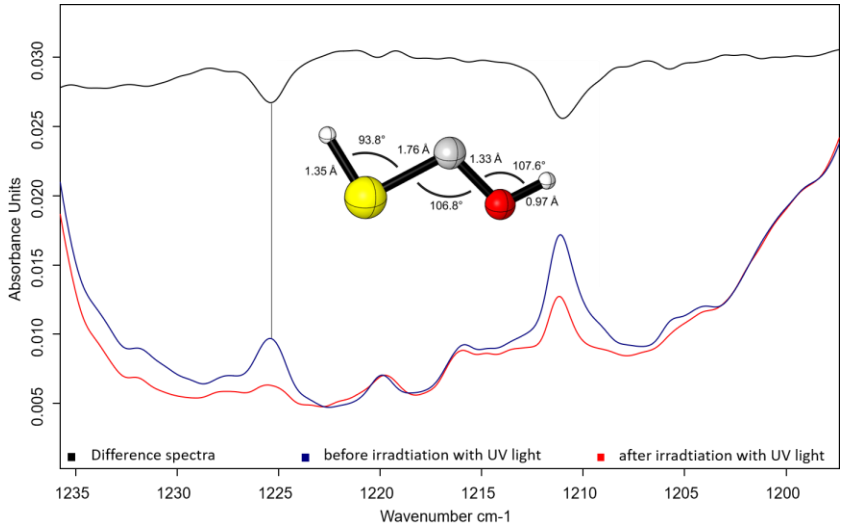
[a]CCSD(T)/cc-pVDZ



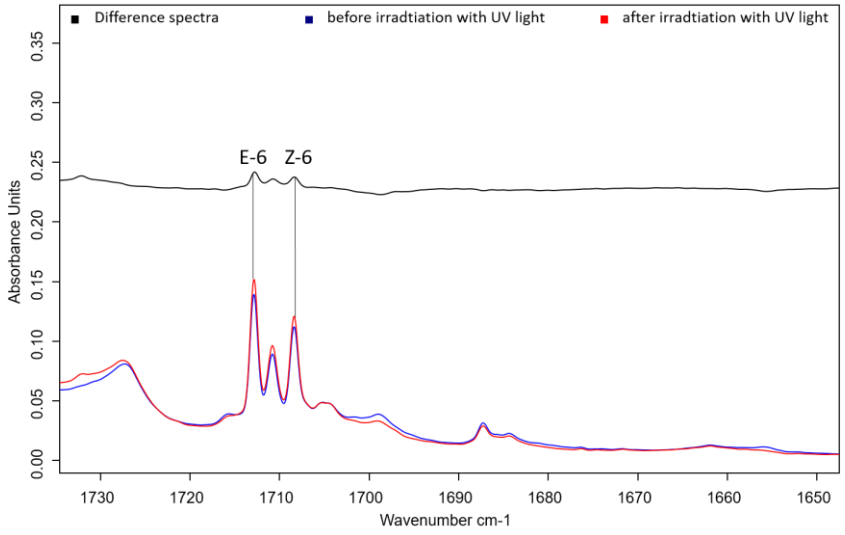
Hydroxy Mercapto Methylene

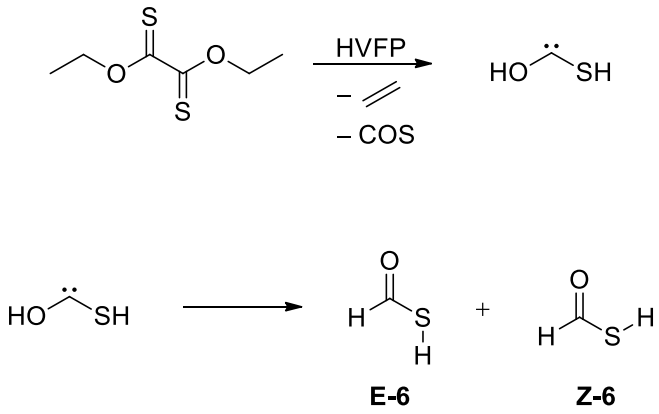


OH str.: 3578.0 cm^{-1} (CCSD(T)/cc-pVTZ: 3821.0 cm^{-1})



CO str.: 1225.4 cm^{-1} (CCSD(T)/cc-pVTZ: 1260.9 cm^{-1})

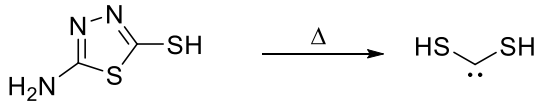




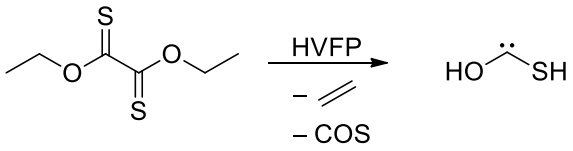
E-6 **Z-6**

- Precursor synthesis for Mercapto Methylene, Methyl Mercapto Methylene

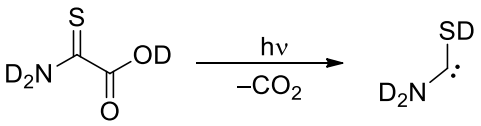
- Precursor test for Dimercapto Methylene



- High level IRC computations for Hydroxy Mercapto Methylene
- Better spectra



- Deuteration of 2-Amino-2-Thioxoacetic Acid
- Identification of isomerization products (computationally)



Acknowledgement

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- Lab 204/205
- PRS group