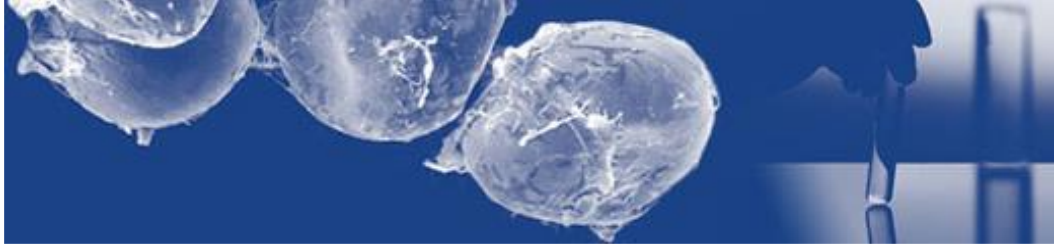


Novel Matrix-Isolated Carbenes

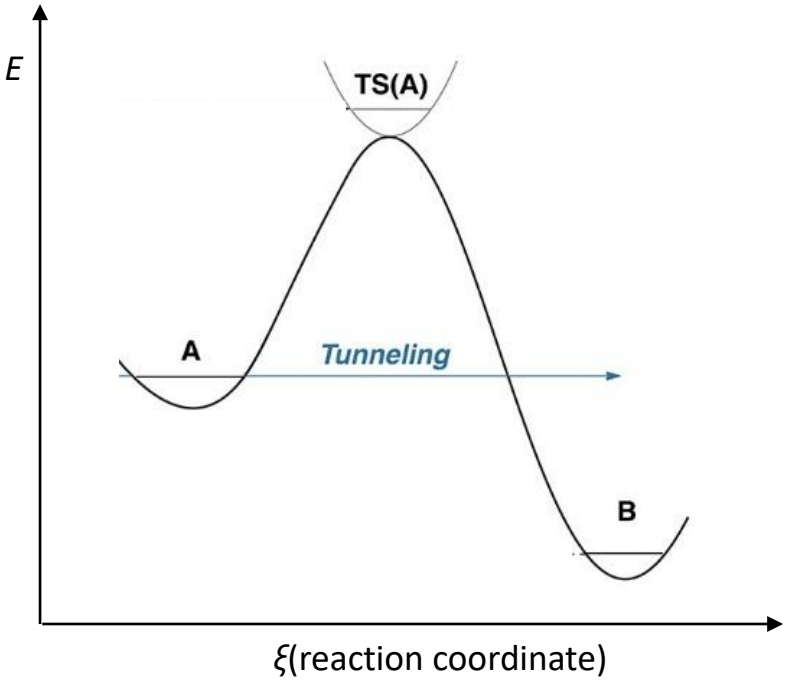
Group Seminar by

Bastian Bernhardt

9th July 2021

QMT in chemical reactions:

- Low masses
- Small and narrow activation barriers



P. R. Schreiner, *Trends Chem.* **2020**, *2*, 980–989.

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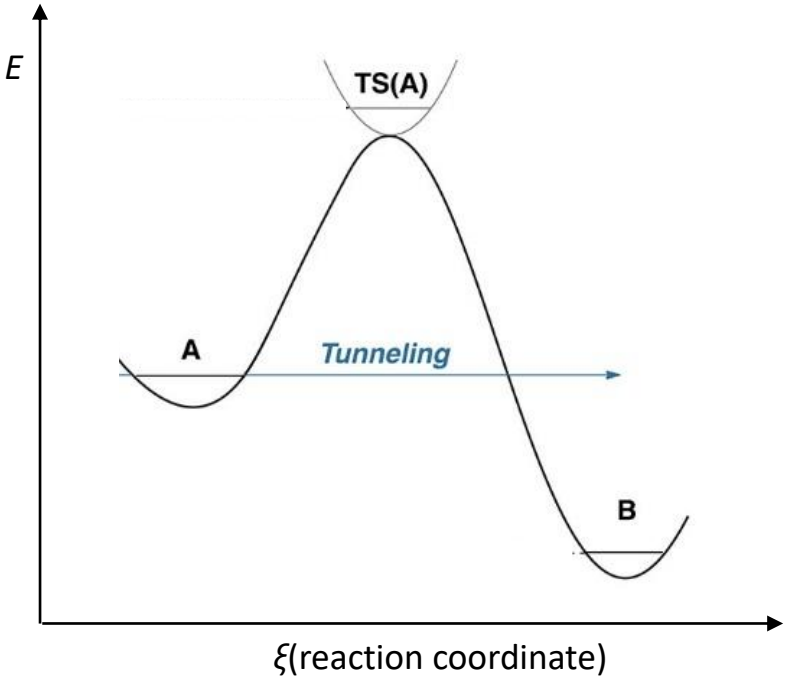
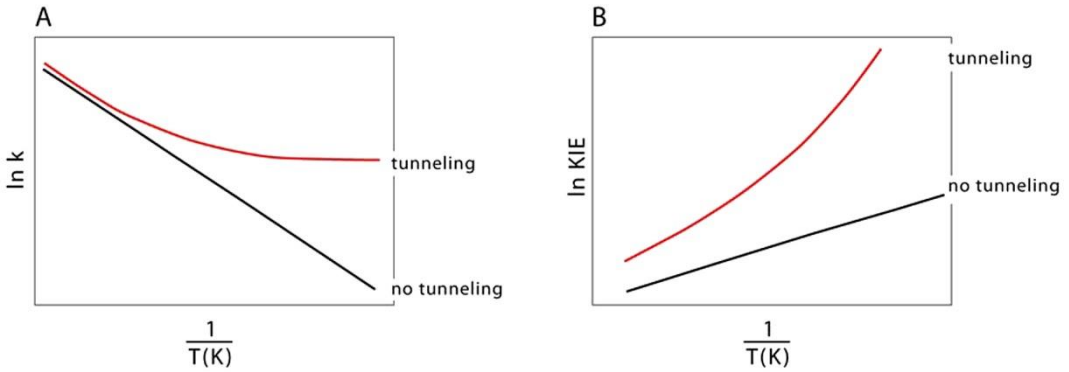
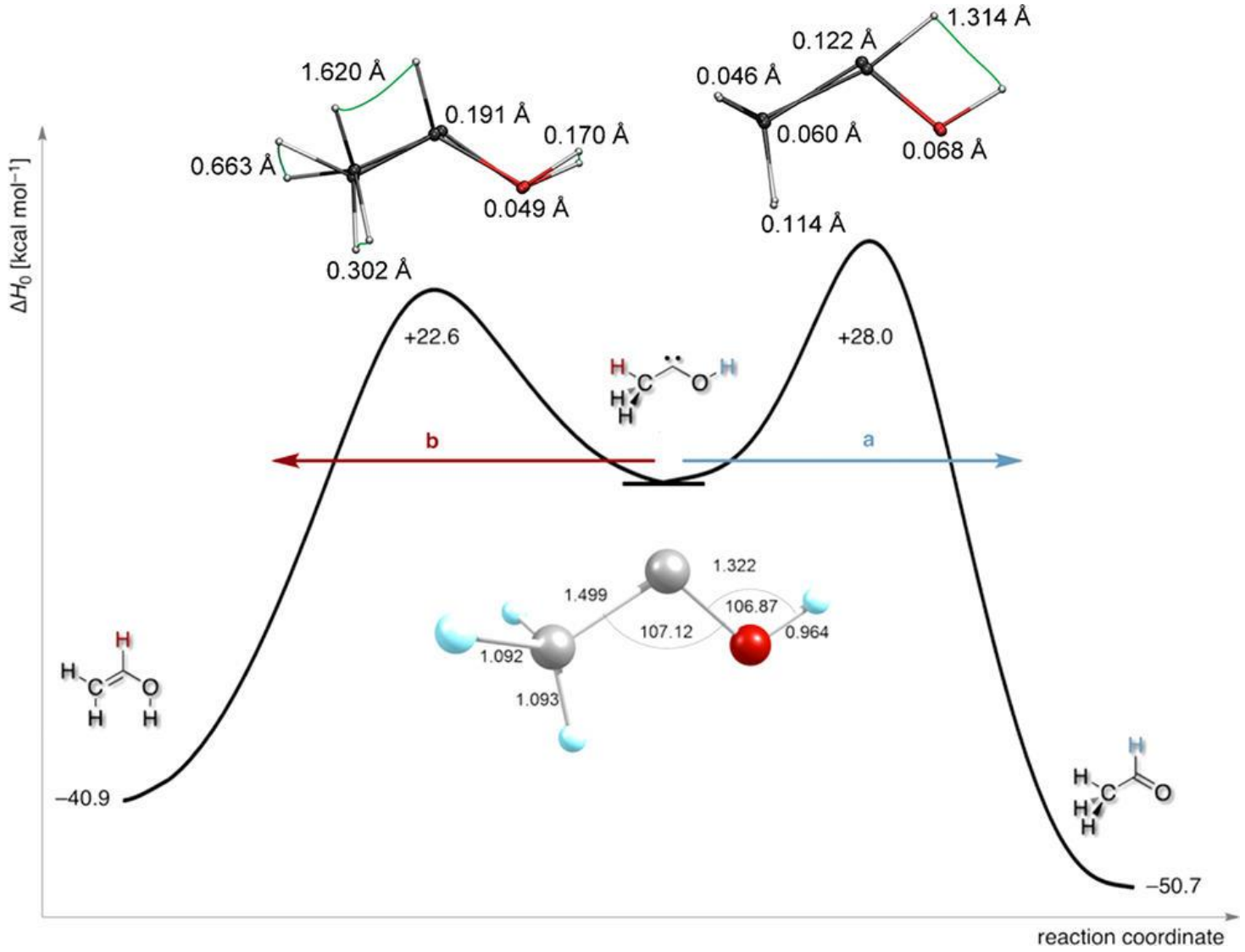


- T independence
- Large KIE



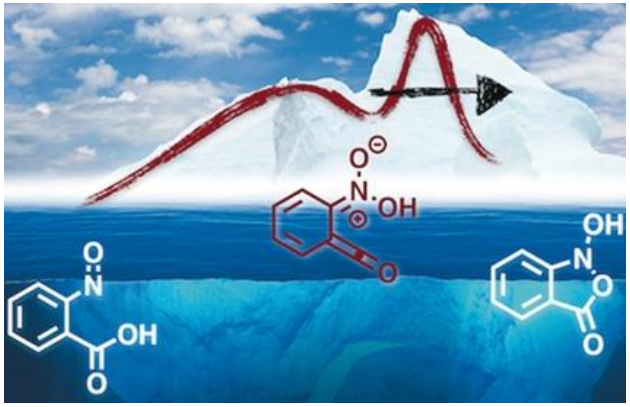
E. M. Greer, K. Kwon, A. Greer, C. Doubleday, *Tetrahedron* **2016**, *72*, 7357–7373.

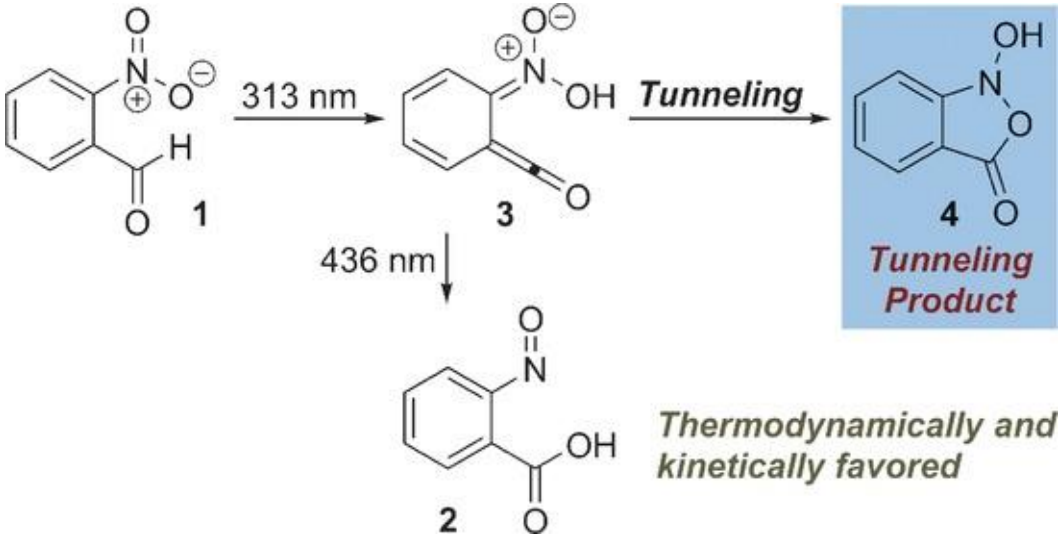
Tunneling Control



P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, *332*, 1300–1304; P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 15276–15283.

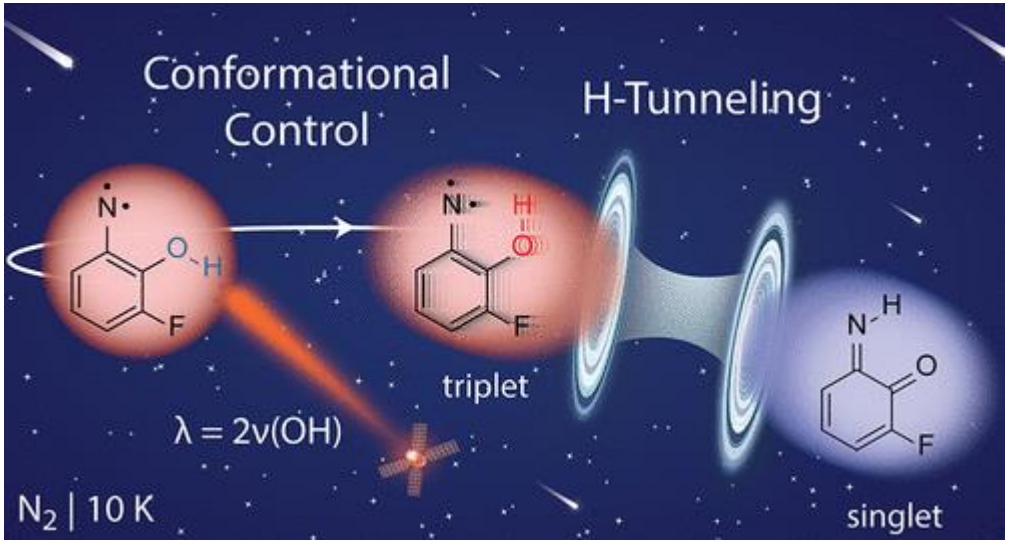
Tunneling Product





D. Gerbig, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2017**, *129*, 9573–9576.

Switching on H-Tunneling through Conformational Control



J. P. L. Roque, C. M. Nunes, L. P. Viegas, N. A. M. Pereira, T. M. V. D. Pinho e Melo, P. R. Schreiner, R. Fausto, *J. Am. Chem. Soc.* **2021**, *143*, 8266–8271.

How to influence/control QMT?

- Selecting only specific conformers (*e.g.* by NIR excitation)

A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2016**, *9*, 71–76; A. K. Eckhardt, F. R. Erb, P. R. Schreiner, *Chem. Sci.* **2019**, *10*, 802-808; P. R. Schreiner, H. P. Reisenauer, F. C. Pickard IV, A. C. Simmonett, W. D. Allen, E. Mátyus, A. G. Császár, *Nature* **2008**, *453*, 906–909; M. M. Linden, J. P. Wagner, B. Bernhardt, M. A. Bartlett, W. D. Allen, P. R. Schreiner, *J. Phys. Chem. Lett.* **2018**, *9*, 1663–1667.

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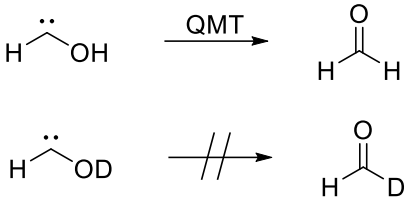

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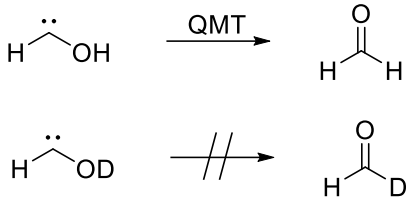
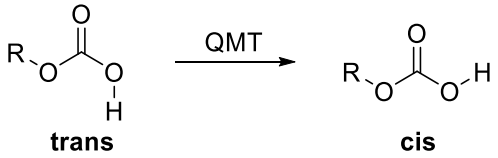


- (Remote) molecular structure



trans **cis**

$t_{1/2}$: R = H < CH_3 < CD_3

in contrast to

$t_{1/2}$: formic acid > acetic acid

A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2016**, *9*, 71–76; A. K. Eckhardt, F. R. Erb, P. R. Schreiner, *Chem. Sci.* **2019**, *10*, 802-808; P. R. Schreiner, H. P. Reisenauer, F. C. Pickard IV, A. C. Simmonett, W. D. Allen, E. Mátyus, A. G. Császár, *Nature* **2008**, *453*, 906–909; M. M. Linden, J. P. Wagner, B. Bernhardt, M. A. Bartlett, W. D. Allen, P. R. Schreiner, *J. Phys. Chem. Lett.* **2018**, *9*, 1663–1667.

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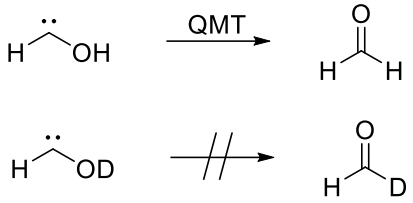
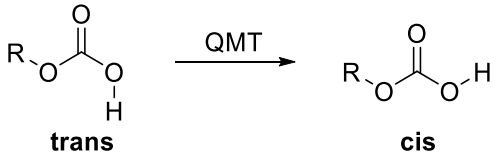


- (Remote) molecular structure
- Matrix material



trans **cis**

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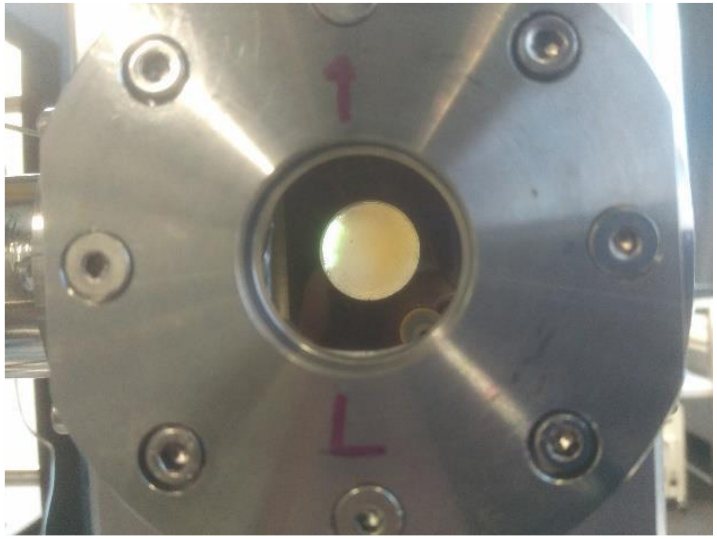
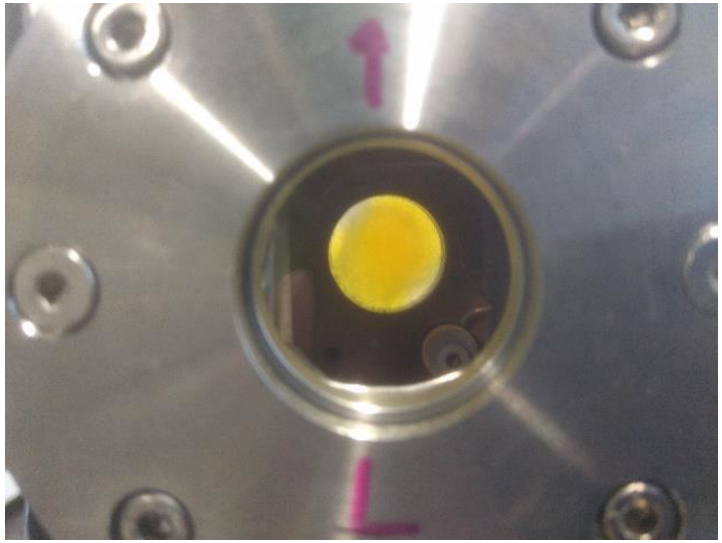
- Temperature, light

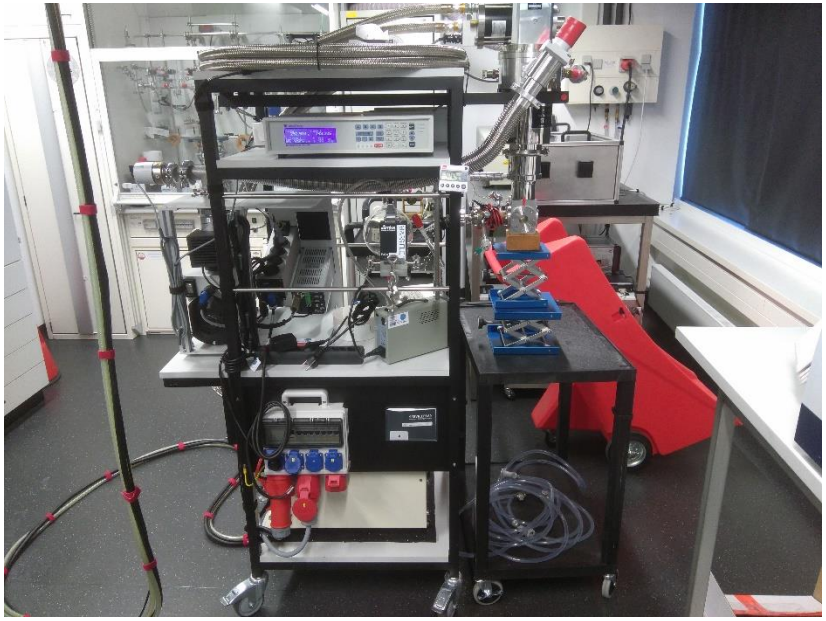
A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2016**, *9*, 71–76; A. K. Eckhardt, F. R. Erb, P. R. Schreiner, *Chem. Sci.* **2019**, *10*, 802-808; P. R. Schreiner, H. P. Reisenauer, F. C. Pickard IV, A. C. Simmonett, W. D. Allen, E. Mátyus, A. G. Császár, *Nature* **2008**, *453*, 906–909; M. M. Linden, J. P. Wagner, B. Bernhardt, M. A. Bartlett, W. D. Allen, P. R. Schreiner, *J. Phys. Chem. Lett.* **2018**, *9*, 1663–1667.

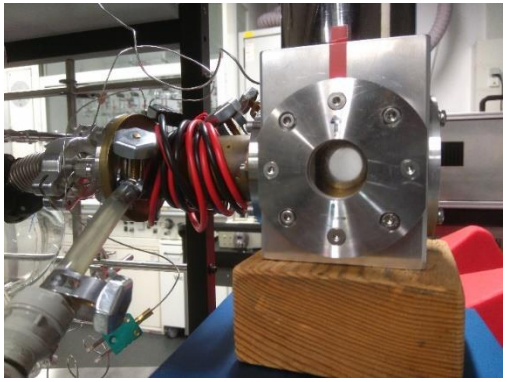
- Reactive species are trapped on a cold window (3-20 K)
- Co-condensation with matrix host (Ar, N_2, …)
- Generation of intermediates by pyrolysis or photolysis
- Characterization by IR, UV/Vis, or VCD

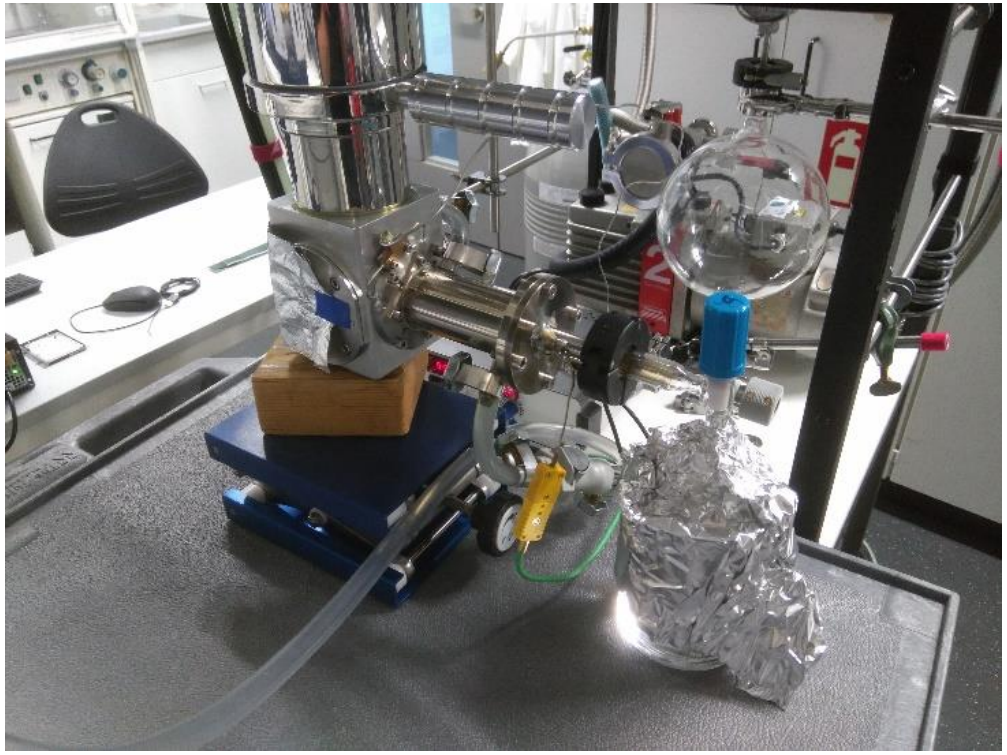




Matrix Apparatus

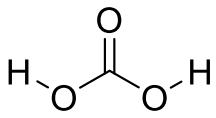




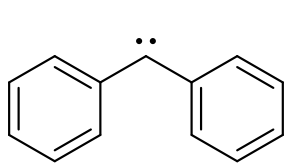


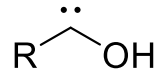
Examples

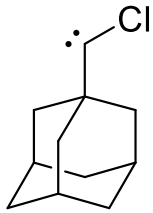
- Unstable Molecules



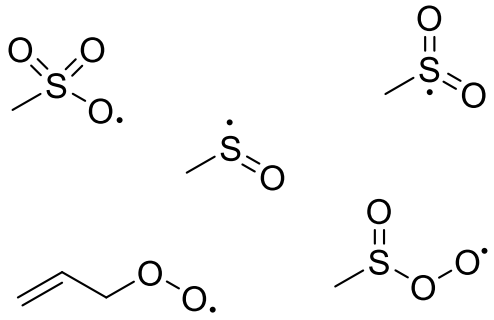
- Carbenes



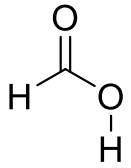


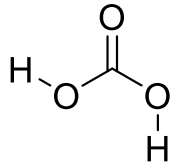


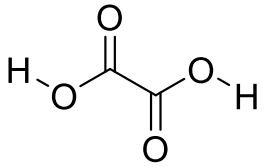
- Radicals



- High-energy conformers







H. P. Reisenauer, J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2014**, *53*, 11766-11771; A. Mardyukov, P. R. Schreiner, *Acc. Chem. Res.* **2018**, *51*, 475-483; G. Yao, P. Rempala, C. Bashore, R. S. Sheridan, *Tetrahedron. Lett.* **1999**, *40*, 17-20; W. W. Sander, *J. Org. Chem.* **1989**, *54*, 333-339; M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, *J. Am. Chem. Soc.* **1997**, *119*, 11715-11716.

Examples

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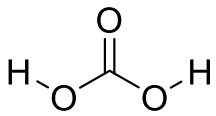

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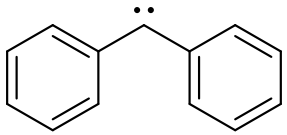

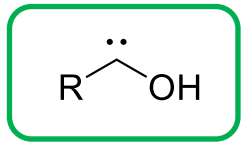

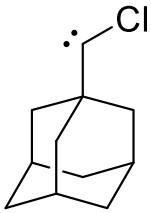

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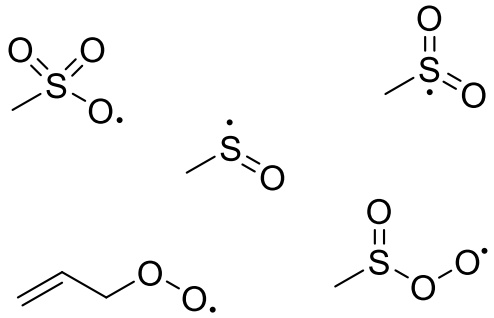

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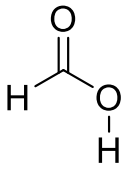

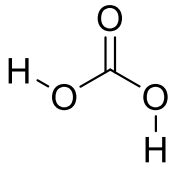

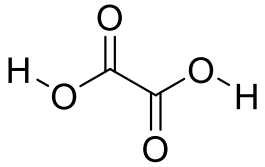

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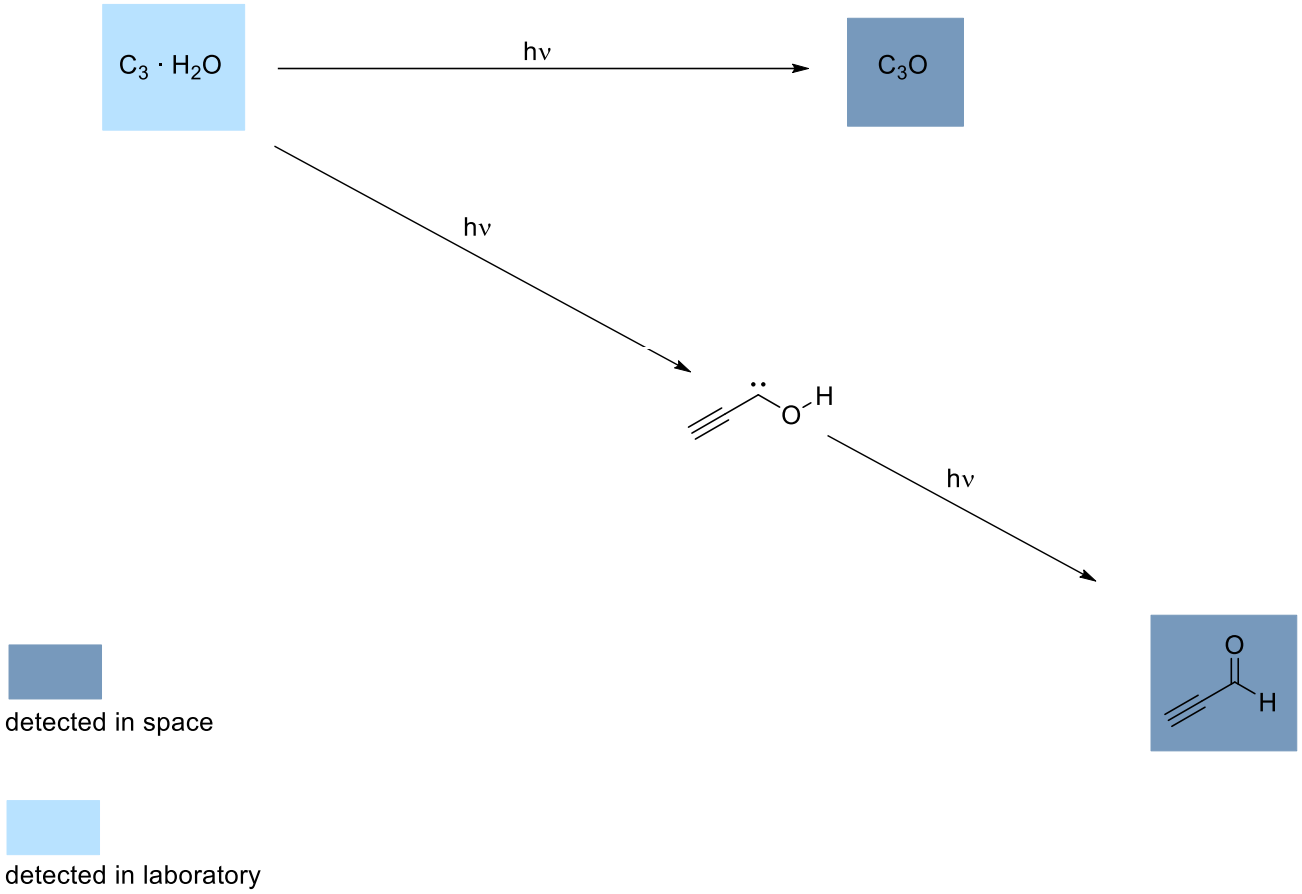
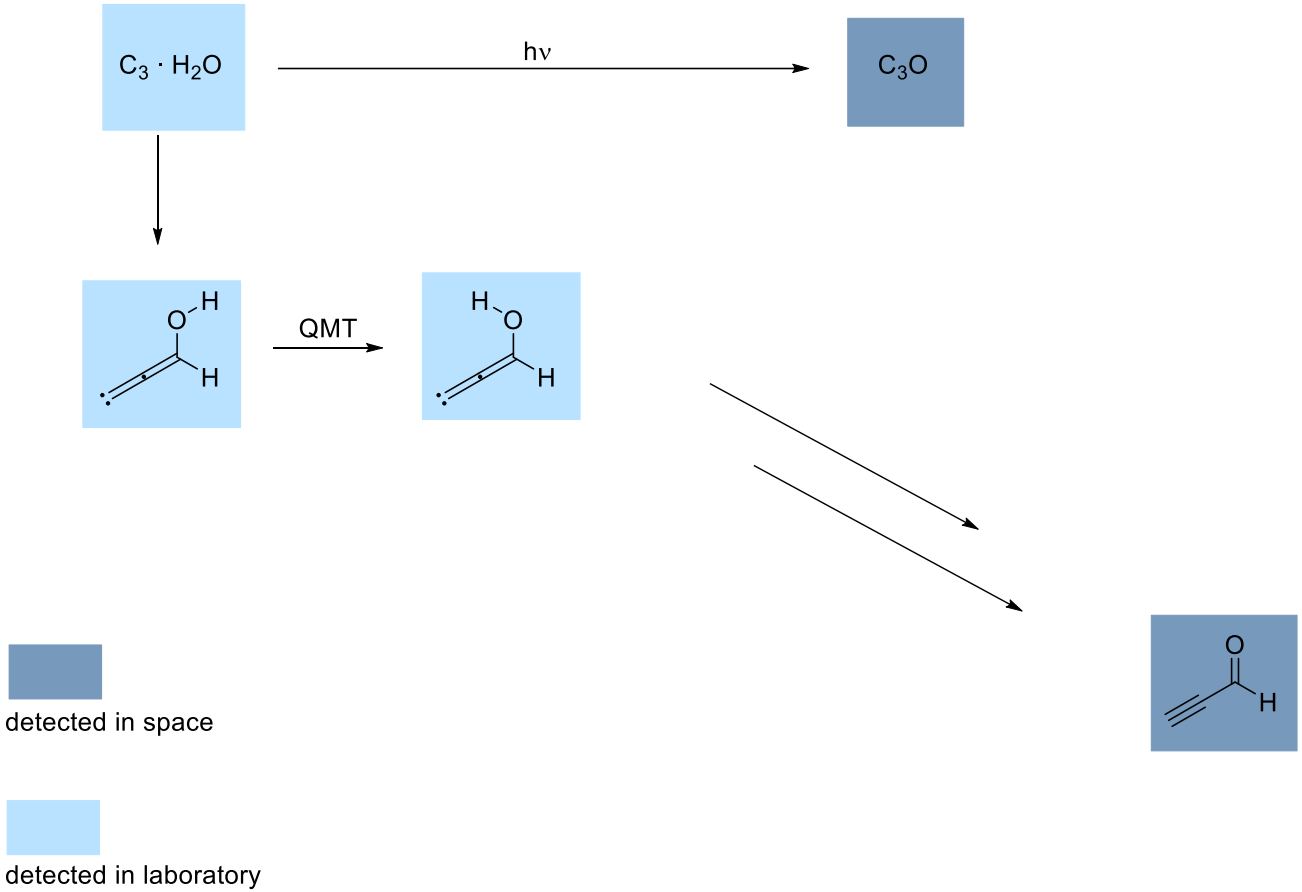
The C_3H_2O Potential Energy Surface



B. J. Ortman, R. H. Hauge, J. L. Margrave, Z. H. Kafafi, *J. Phys. Chem.* **1990**, *94*, 7973–7977.

The C_3H_2O Potential Energy Surface



R. Liu, X. Zhou, P. Pulay, *J. Phys. Chem.* **1992**, *96*, 5748–5752; J. Szczepanski, S. Ekern, M. Vala, *J. Phys. Chem.* **1995**, *99*, 8002–8012.

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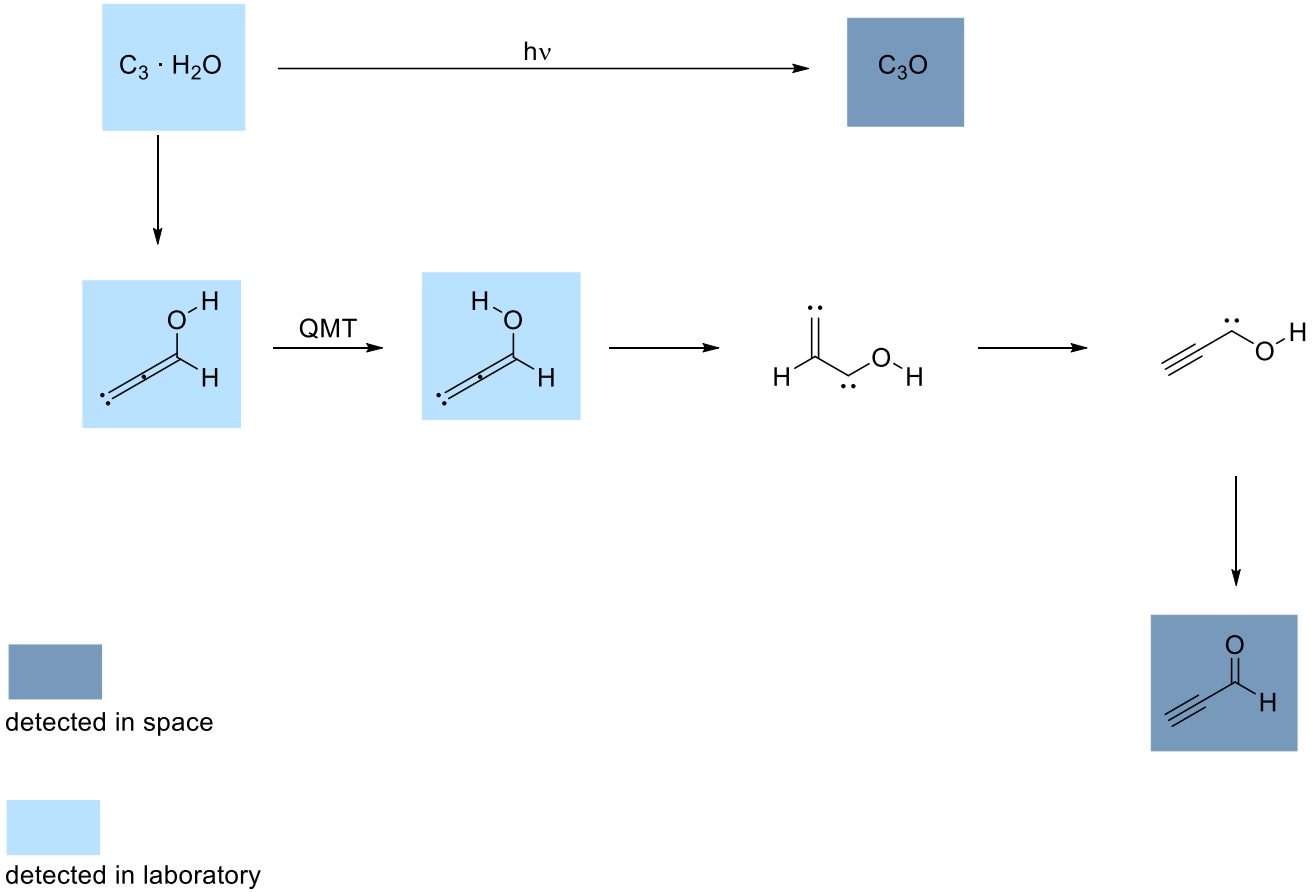

S. Ekern, J. Szczepanski, M. Vala, *J. Phys. Chem.* **1996**, *100*, 16109–16115.

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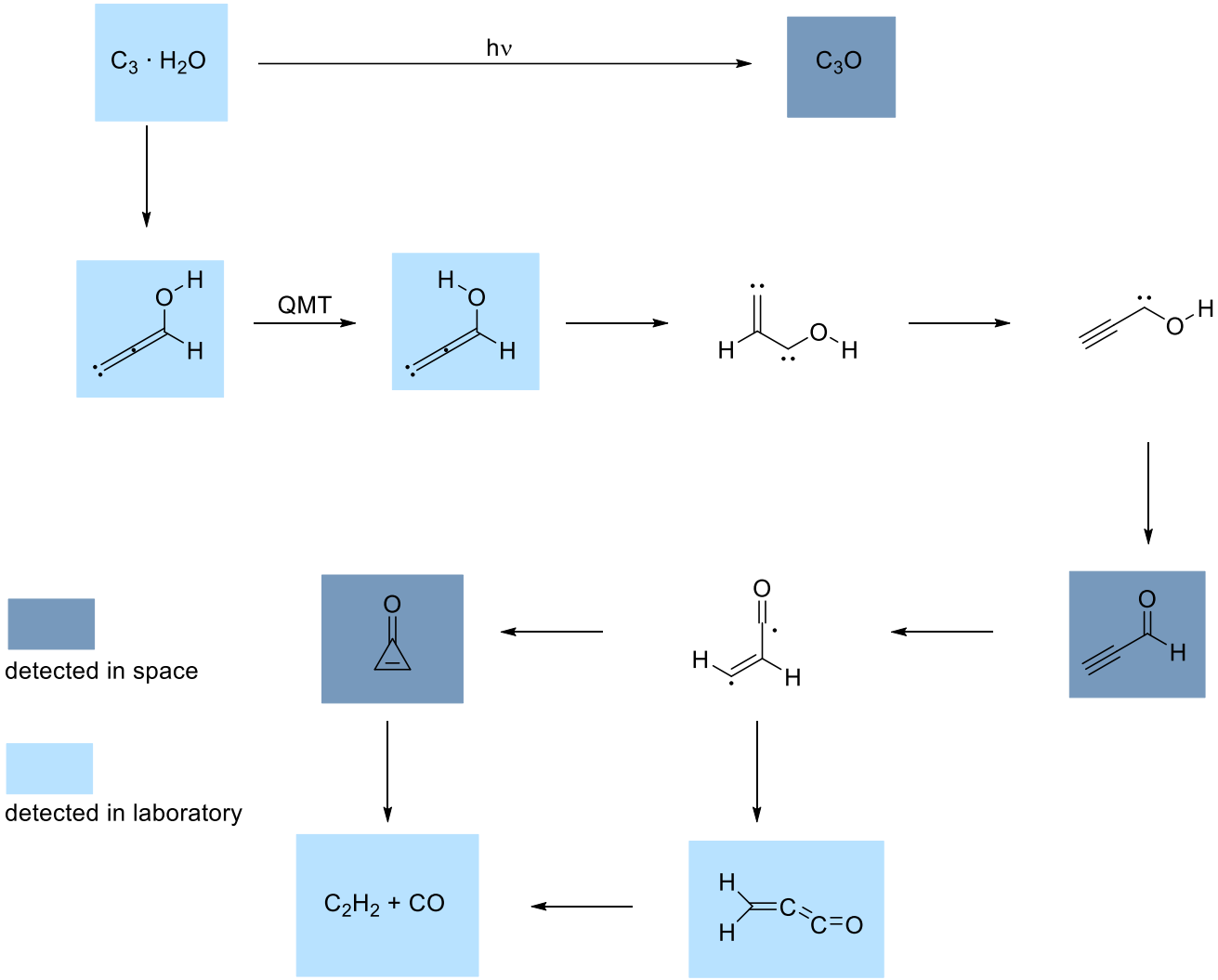
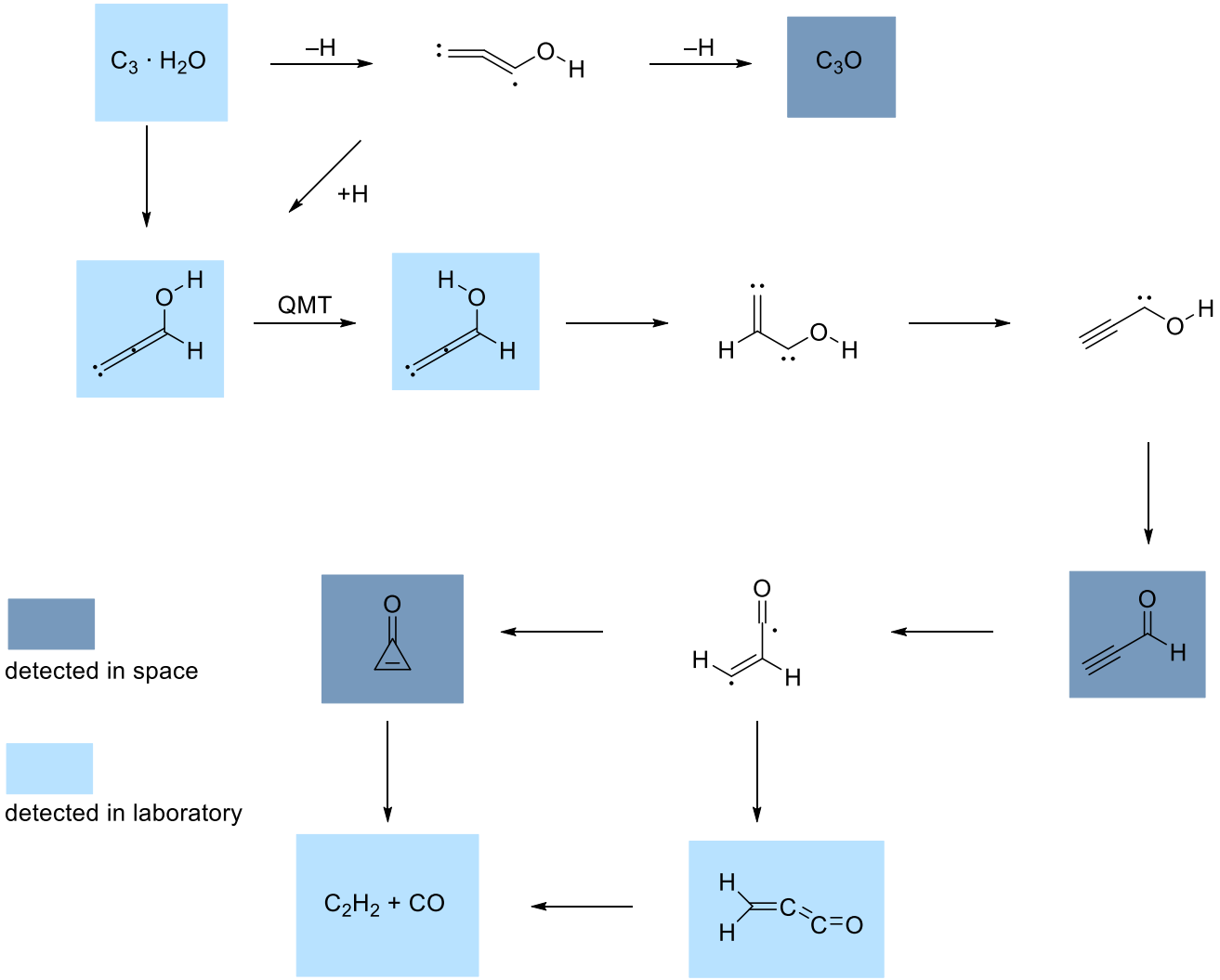


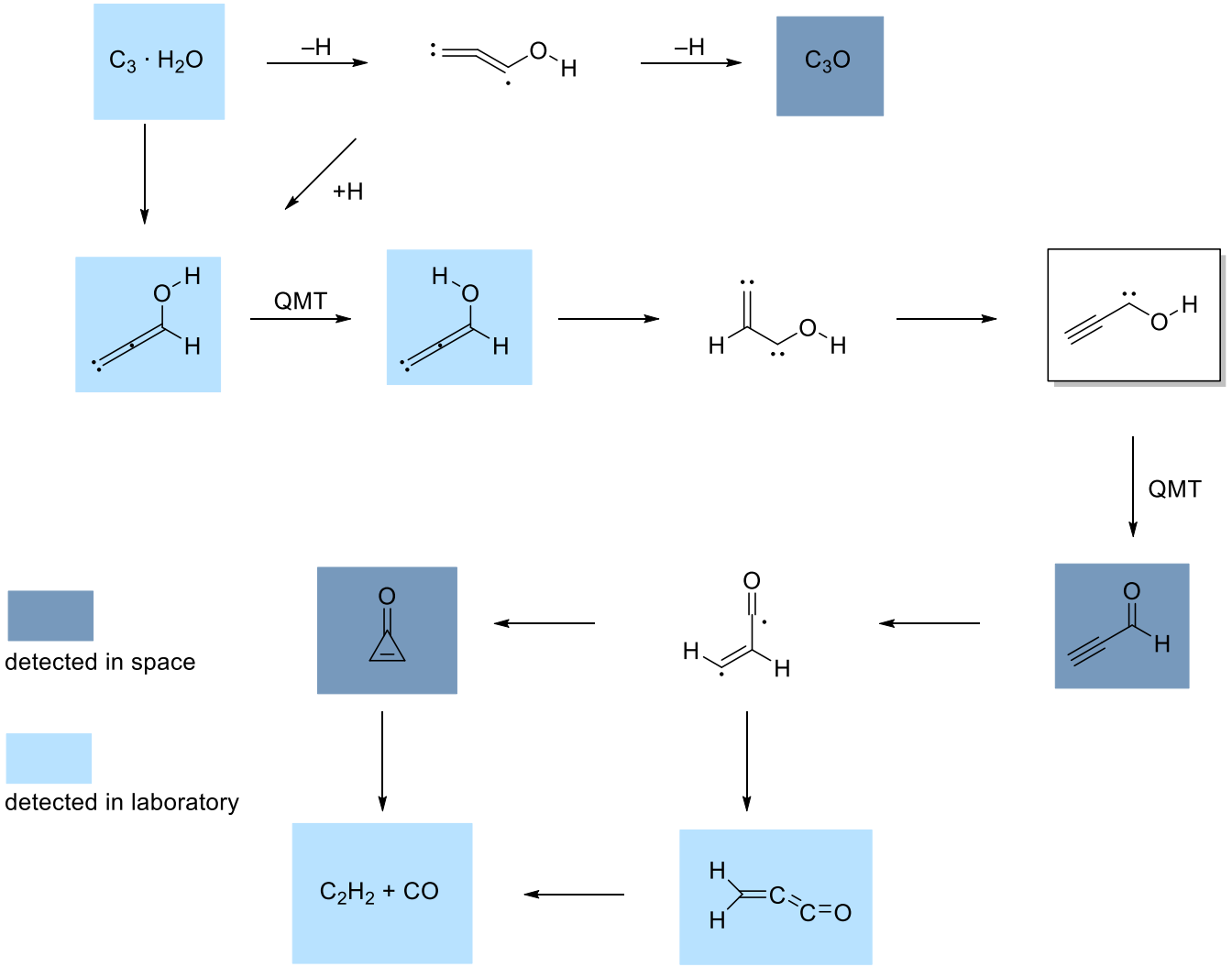
S. Ekern, J. Szczepanski, M. Vala, *J. Phys. Chem.* **1996**, *100*, 16109–16115.

The C_3H_2O Potential Energy Surface



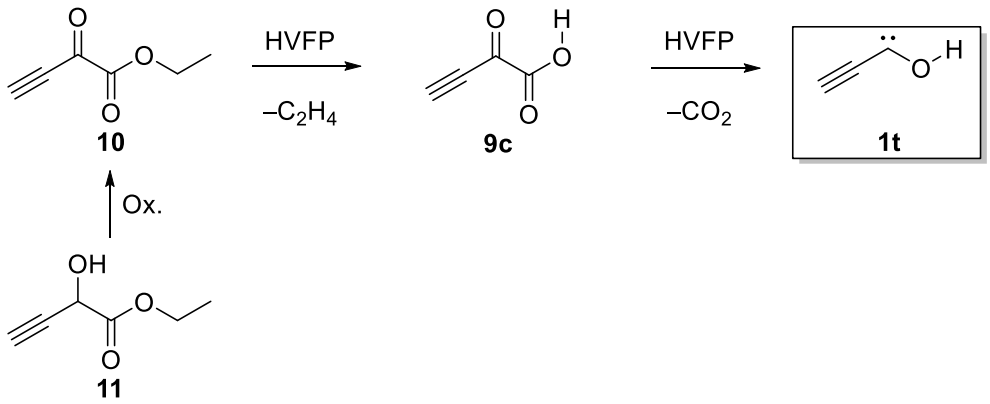
S. Ekern, M. Vala, *J. Phys. Chem. A* **1997**, *101*, 3601–3606.

The C_3H_2O Potential Energy Surface



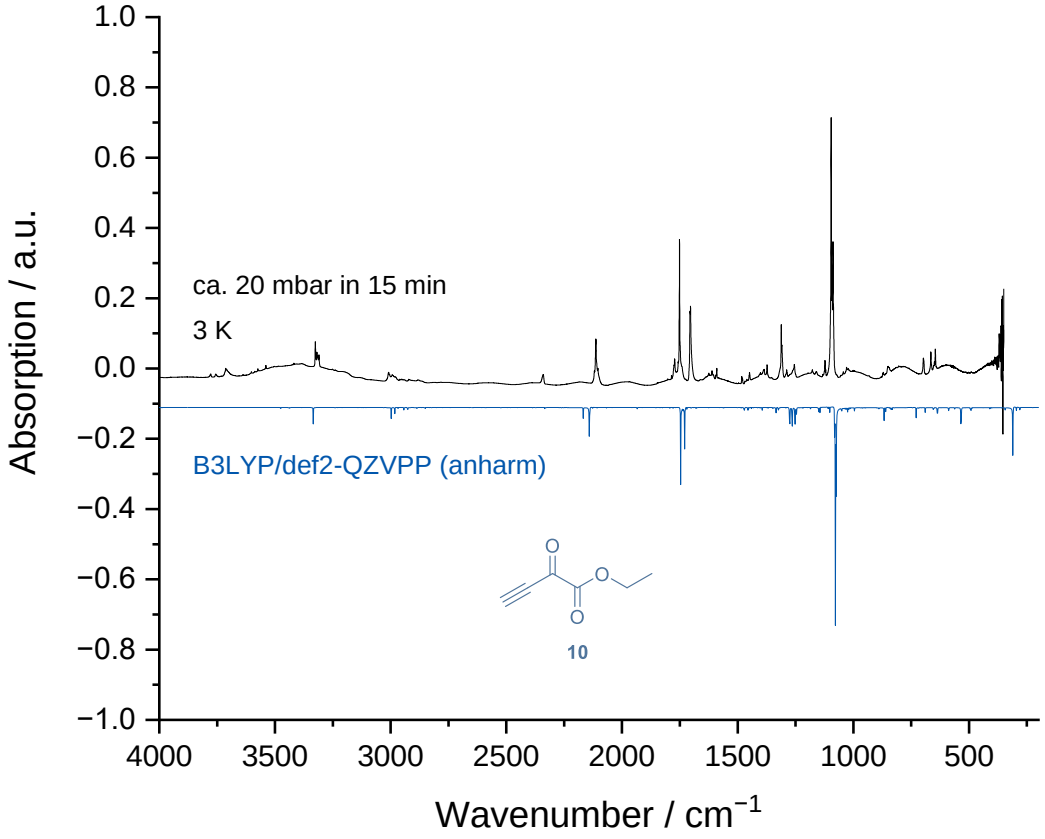
B. Bernhardt, M. Ruth, A. K. Eckhardt, P. R. Schreiner, *J. Am. Chem. Soc.* **2021**, *143*, 3741-3745.

Ethynylhydroxycarbene – Reaction Scheme

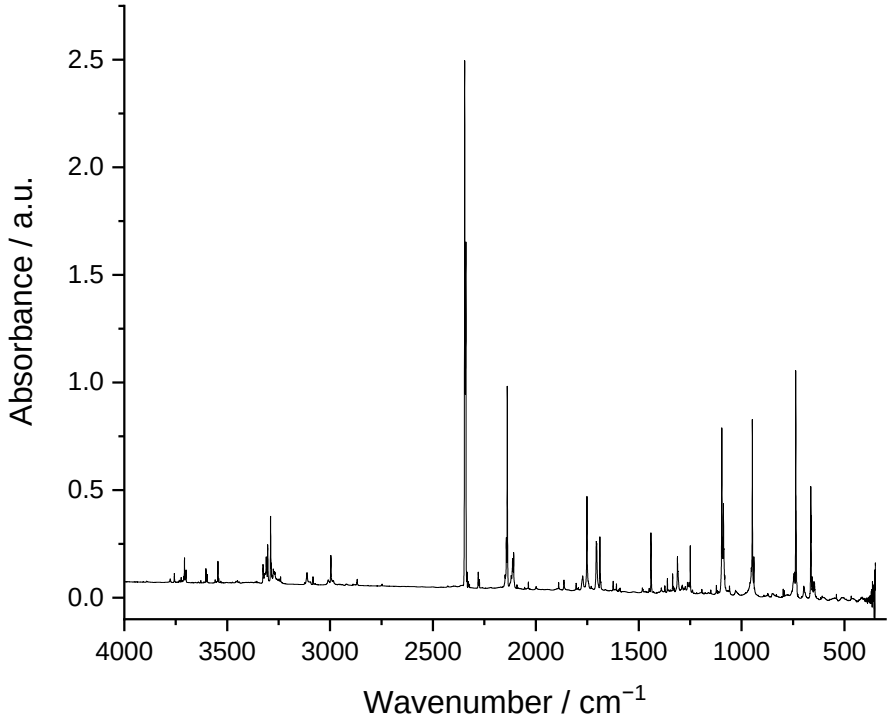


B. Bernhardt, M. Ruth, A. K. Eckhardt, P. R. Schreiner, *J. Am. Chem. Soc.* **2021**, *143*, 3741-3745.

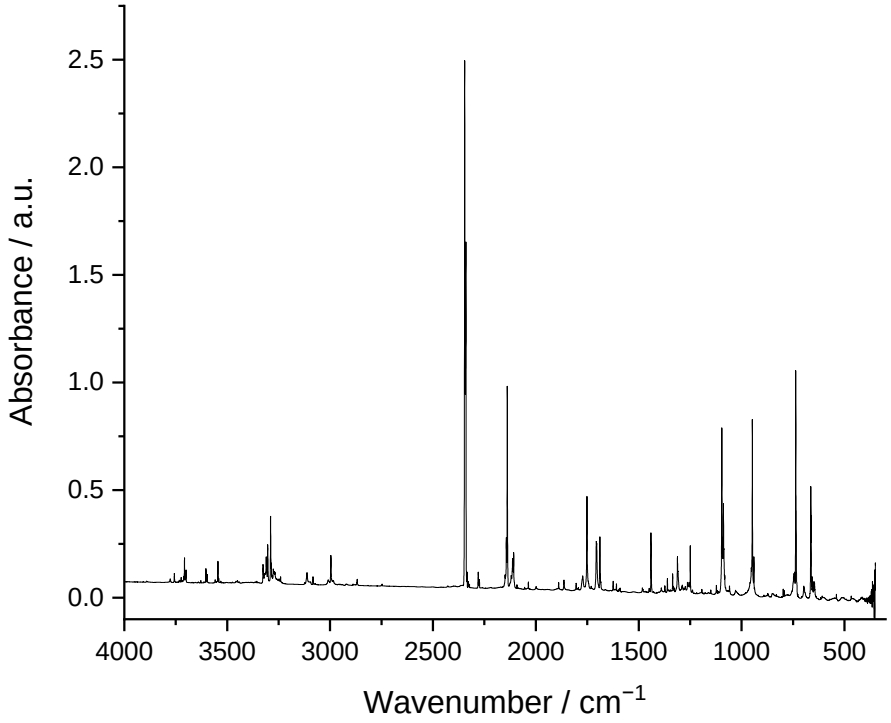
Ethynylhydroxycarbene – Precursor

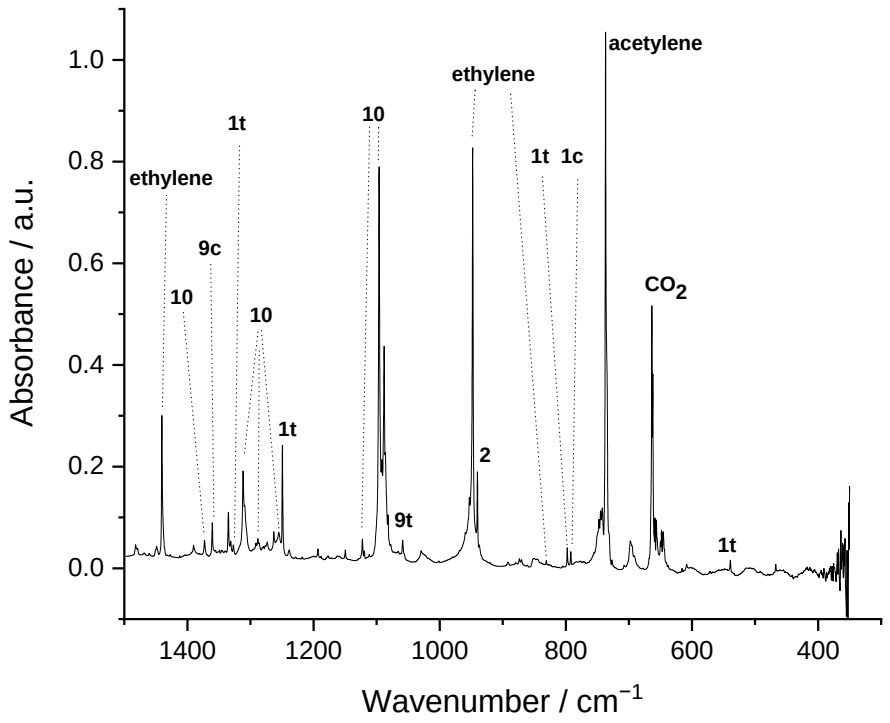


Ethynylhydroxycarbene – Pyrolysis Spectrum

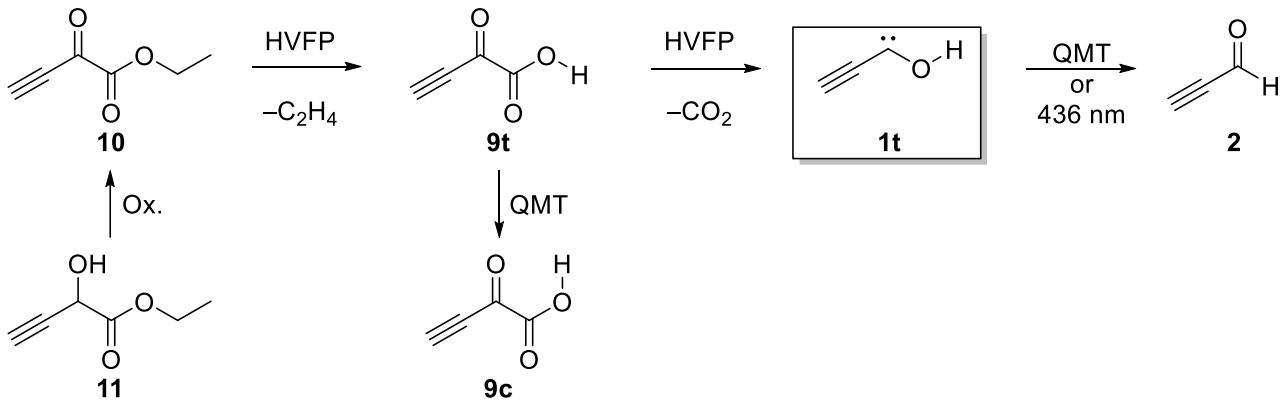


Ethynylhydroxycarbene – Pyrolysis Spectrum

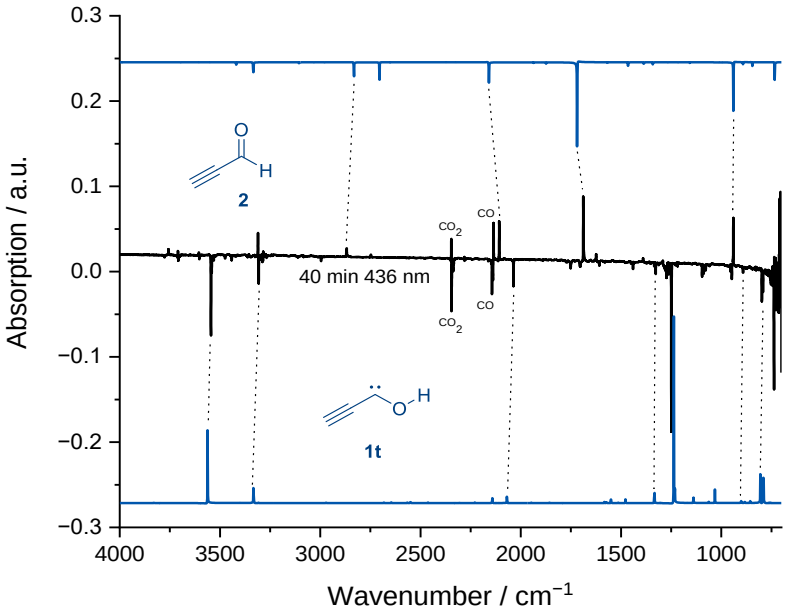


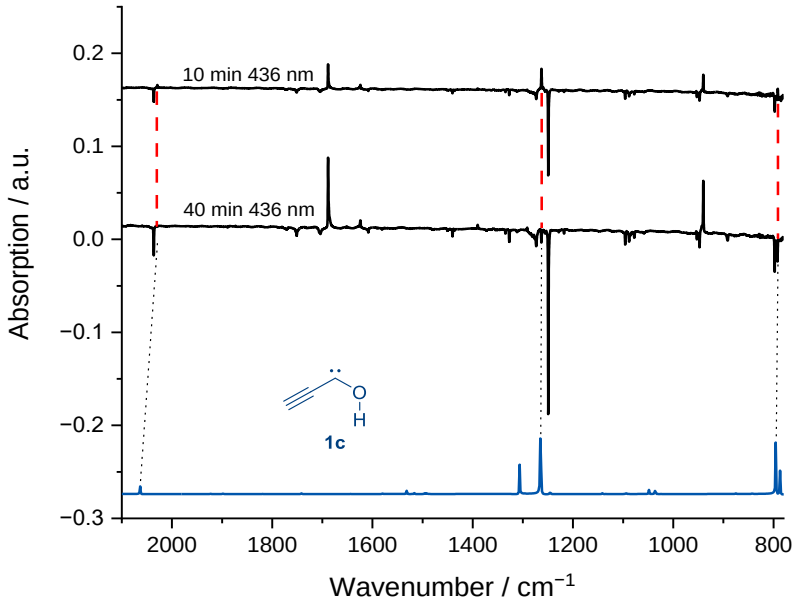


Ethynylhydroxycarbene – Reaction Scheme



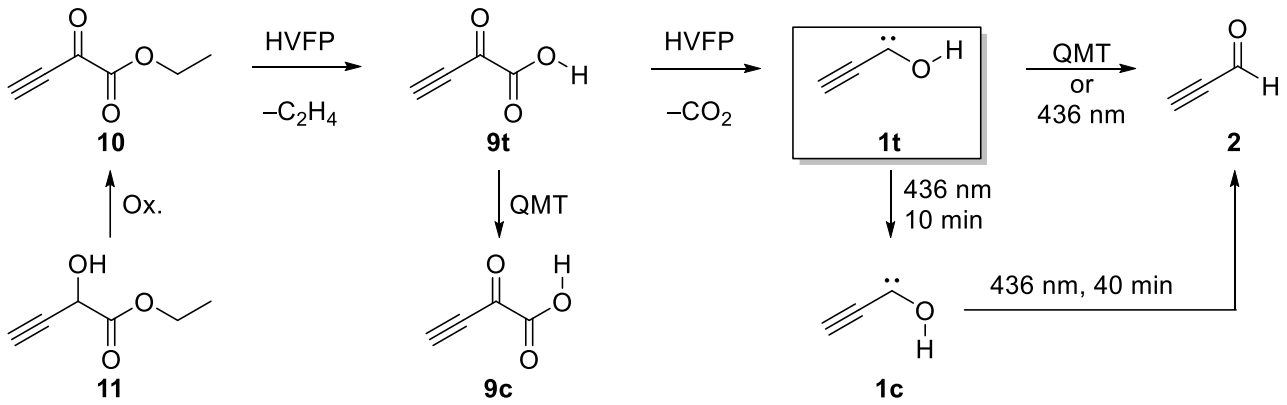
Ethynylhydroxycarbene – Photochemistry



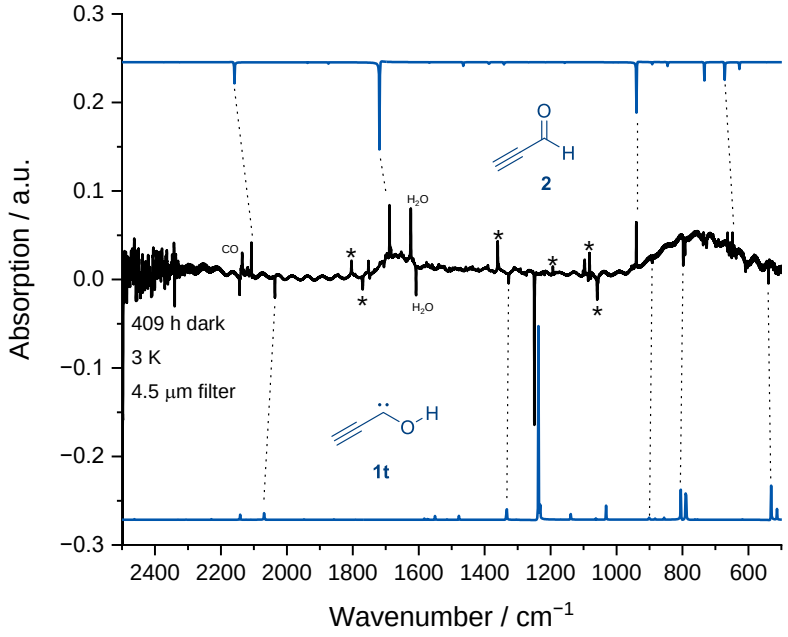


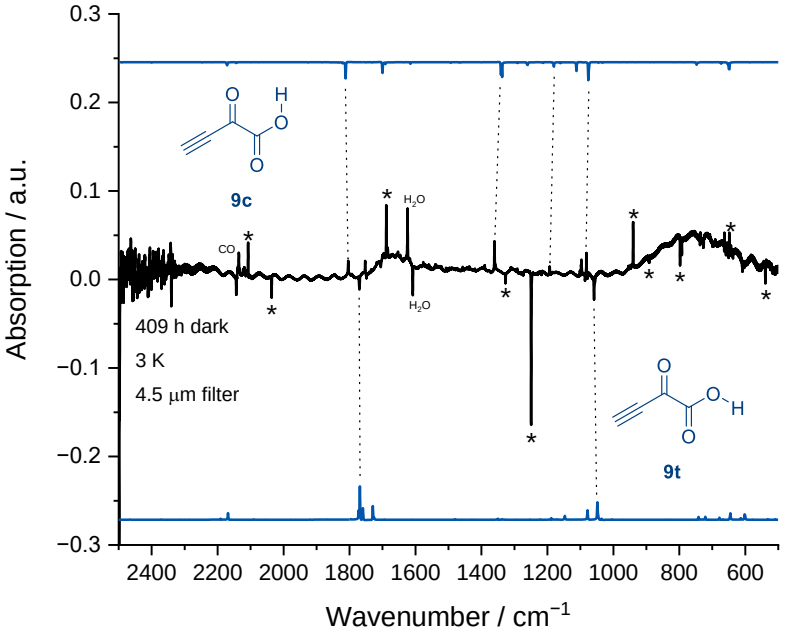
B3LYP/def2-QZVPP

Ethynylhydroxycarbene – Reaction Scheme



Ethynylhydroxycarbene – QMT

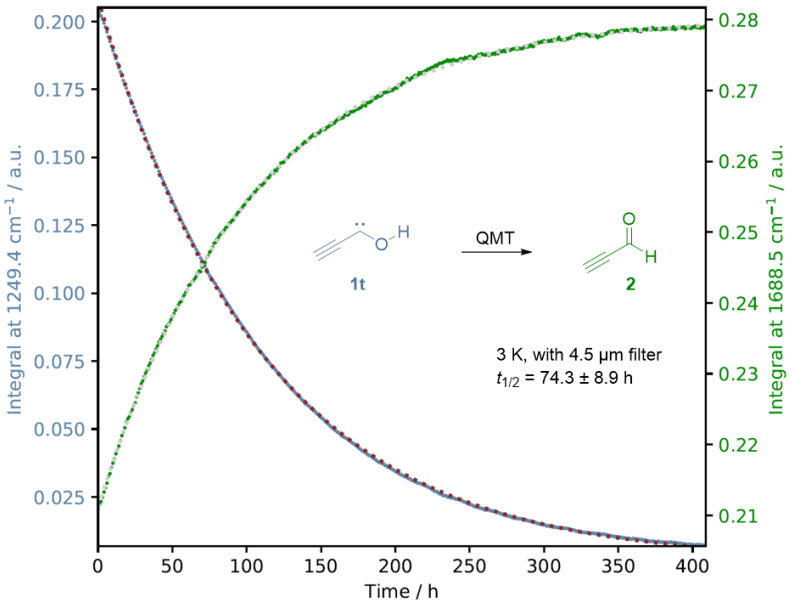


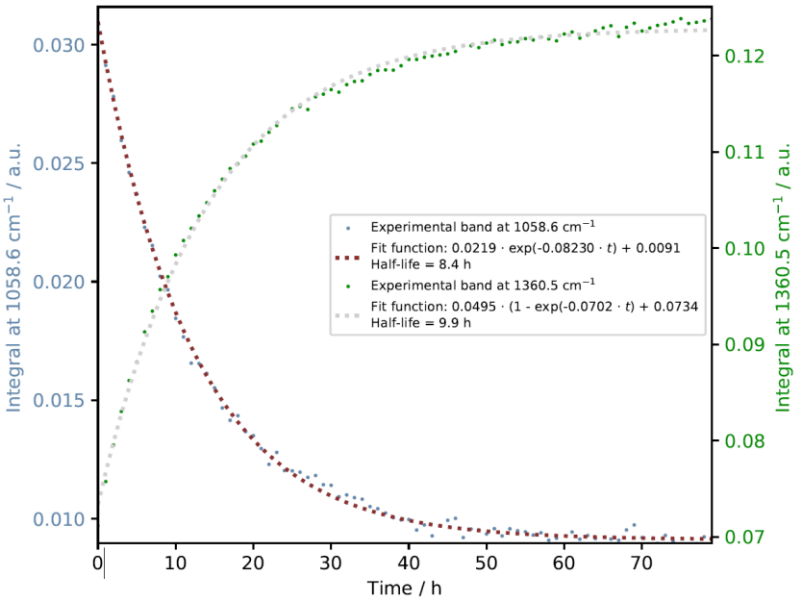


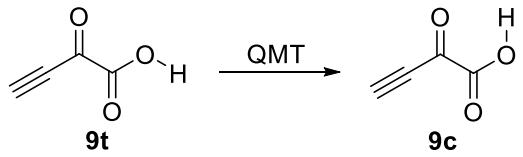
B3LYP/def2-QZVPP

Ethynylhydroxycarbene – Kinetic Analyses

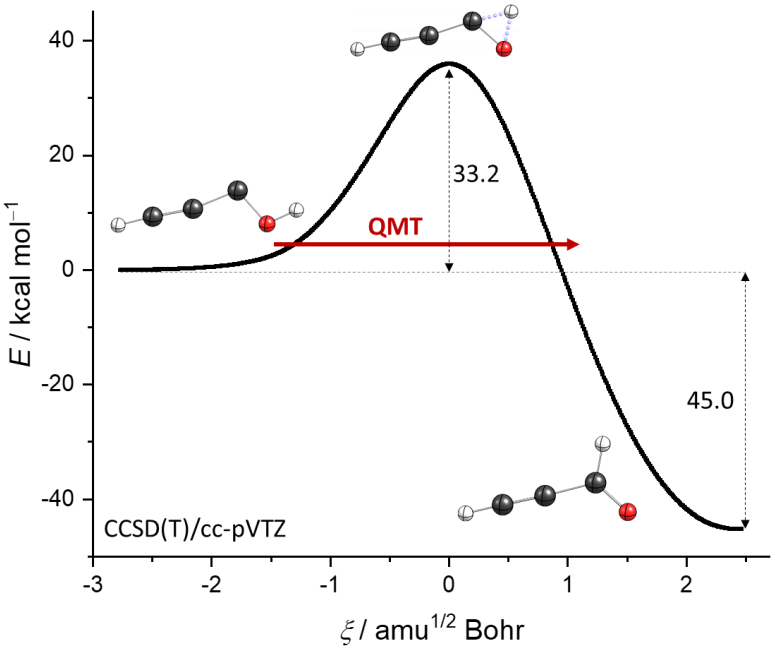
CVT/SCT//B3LYP/def2-QZVPP: 62.1 h

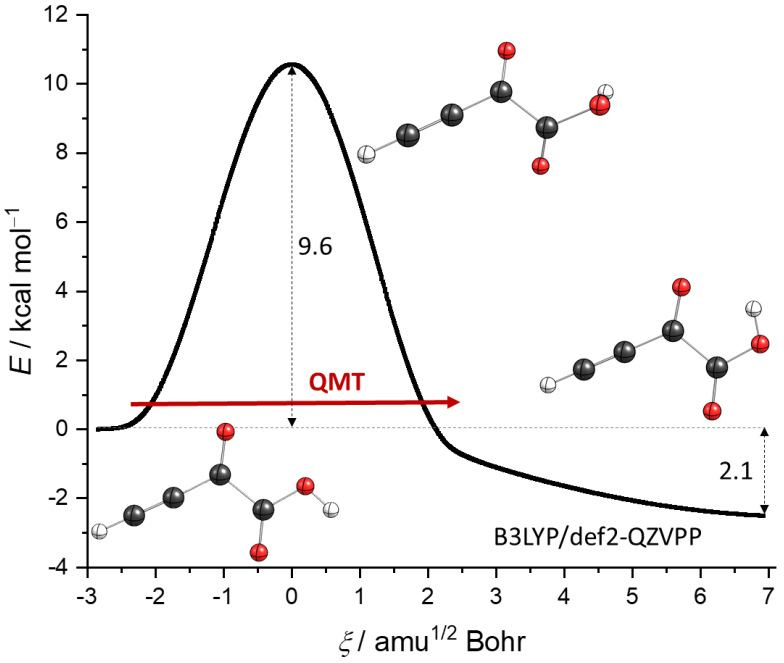




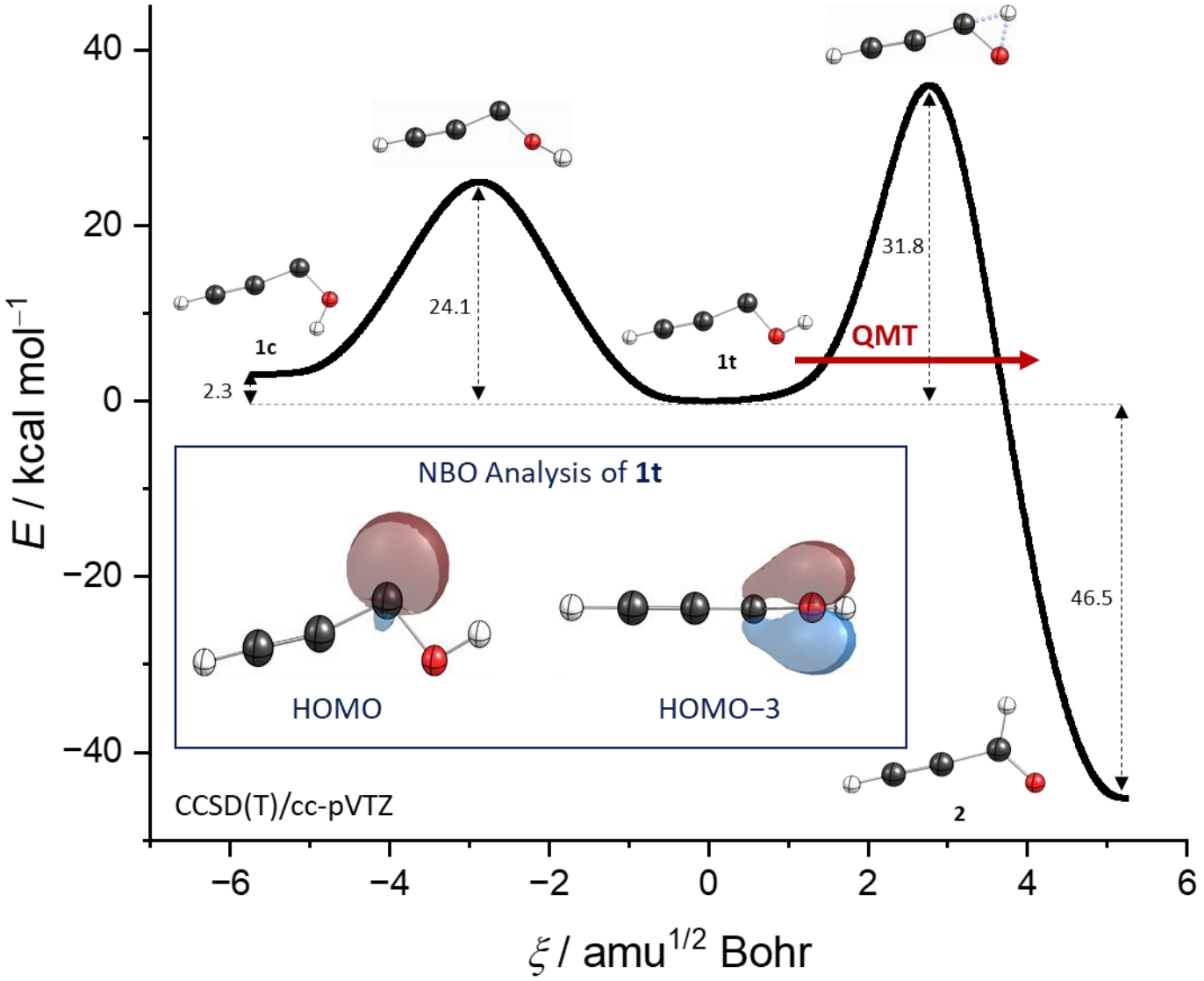


Ethynylhydroxycarbene – Kinetic Analyses

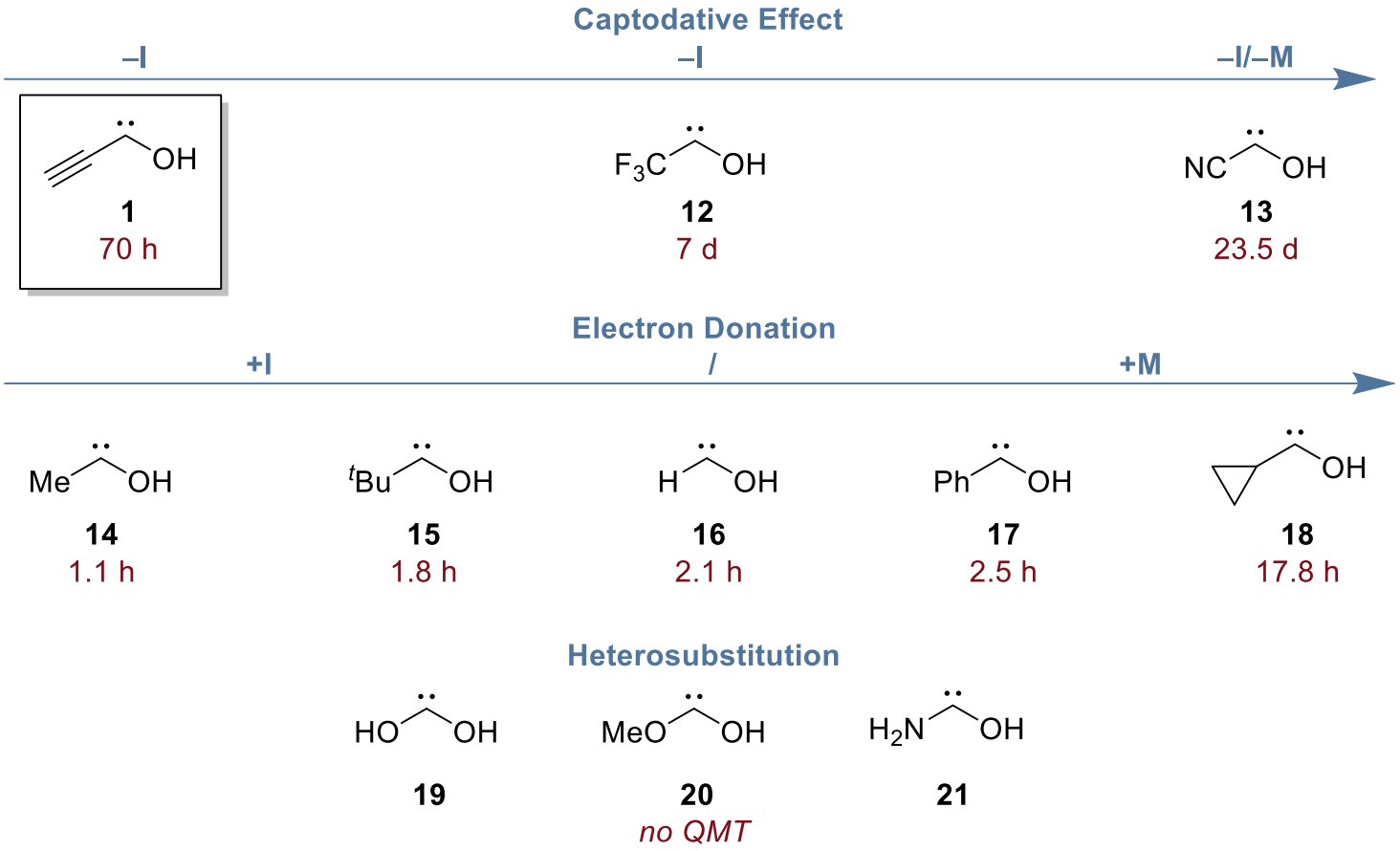




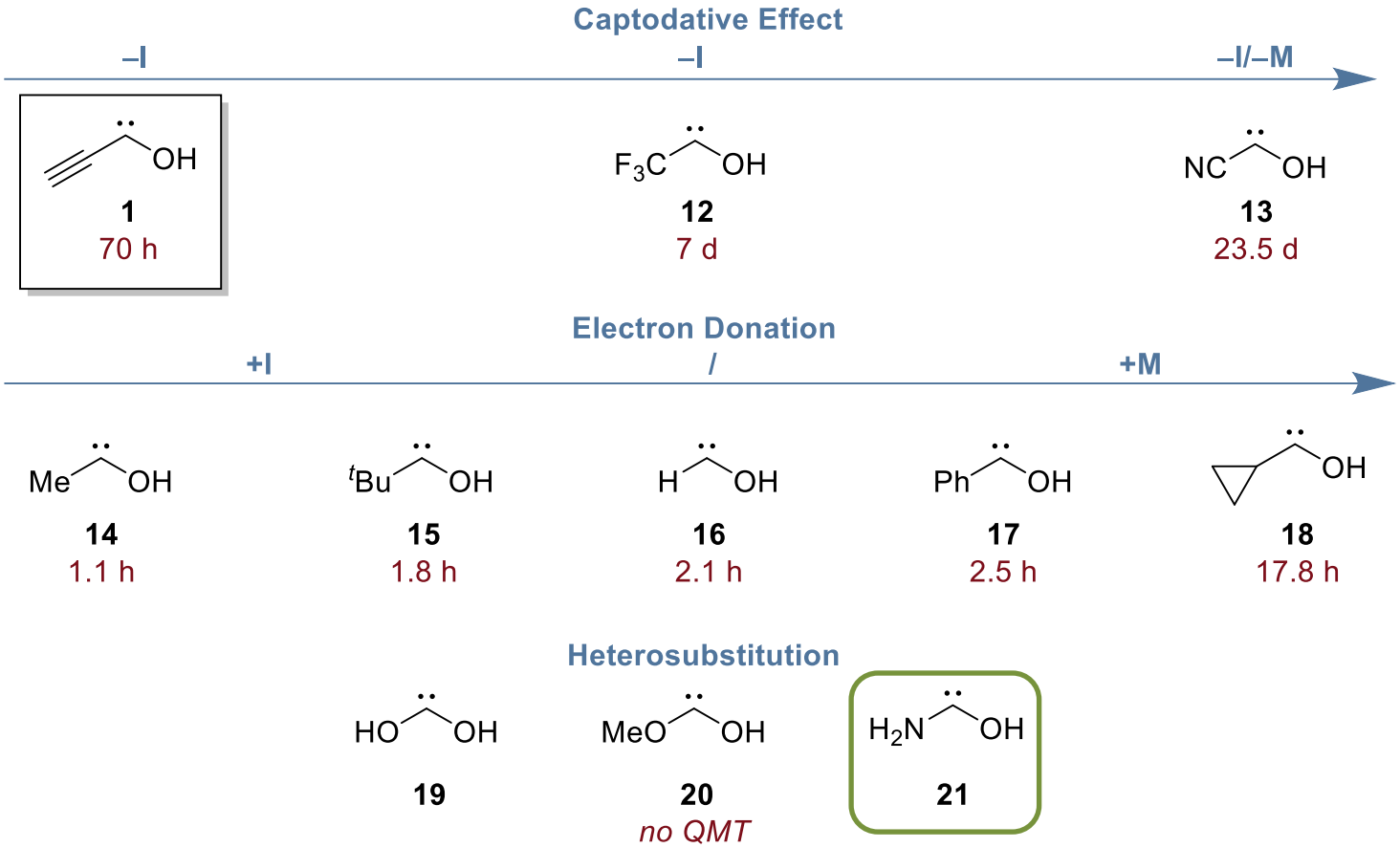
Ethynylhydroxycarbene – Potential Energy Surface



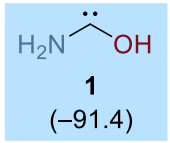
QMT Half-Lives of Hydroxycarbenes



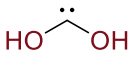
QMT Half-Lives of Hydroxycarbenes



Aminohydroxymethylene

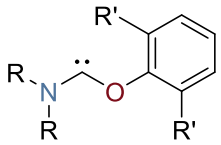


1
(–91.4)



known
(–88.4)

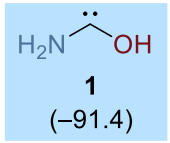
unknown
(–91.2)



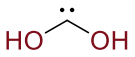
a) R = ^{i}Pr, R' = ^{t}Bu
b) R = ^{i}Pr, R' = Me
c) R = Me, R' = ^{t}Bu

P. R. Schreiner, H. P. Reisenauer, *Angew. Chem. Int. Ed.* **2008**, *120*, 7179-7182; A. K. Eckhardt, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2018**, *57*, 5248-5252; B. Bernhardt, M. Ruth, H. P. Reisenauer, P. R. Schreiner, *manuscript in preparation*.

Aminohydroxymethylene

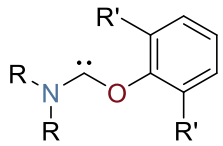


1
(–91.4)



known
(–88.4)

unknown
(–91.2)



a) R = ^{i}Pr, R' = ^{t}Bu
b) R = ^{i}Pr, R' = Me
c) R = Me, R' = ^{t}Bu

isodesmic stabilization / kcal mol^{-1}

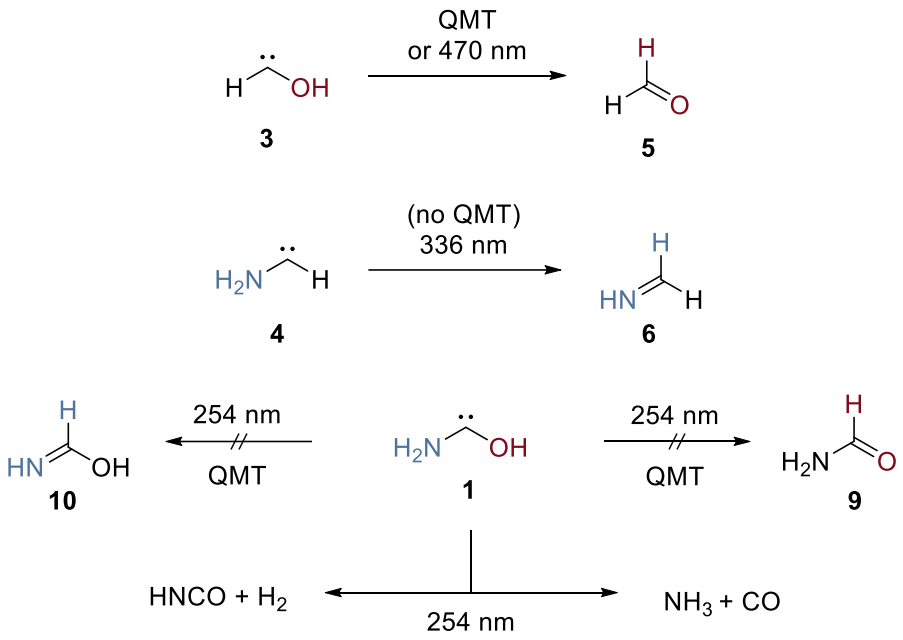
B3LYP/6-311+G(d,p)

$\Delta_r H^\circ_{0K} = \sum_i \nu_i \Delta_f H^\circ_{0K}$

19	H, H	0.0	–45.6	Cl, Cl	**23**
20	H, Cl	–25.0	–59.9	F, F	**24**
21	H, F	–29.7	–66.1	HS, SH	**25**
22	H, SH	–44.5	–81.8	H_2N, SH	**26**
9	H, OH	–50.4	–88.4	HO, OH	**27**
1	H, NH_2	–63.6	–91.2	H_2N, NH_2	**28**
			–91.4	H_2N, OH	**29**

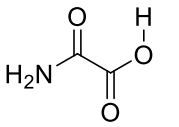
P. R. Schreiner, H. P. Reisenauer, *Angew. Chem. Int. Ed.* **2008**, *120*, 7179-7182; A. K. Eckhardt, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2018**, *57*, 5248-5252; B. Bernhardt, M. Ruth, H. P. Reisenauer, P. R. Schreiner, *manuscript in preparation*.

Aminohydroxymethylene



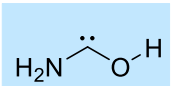
B. Bernhardt, M. Ruth, H. P. Reisenauer, P. R. Schreiner, *manuscript in preparation*.

Aminohydroxymethylene – Reaction Scheme



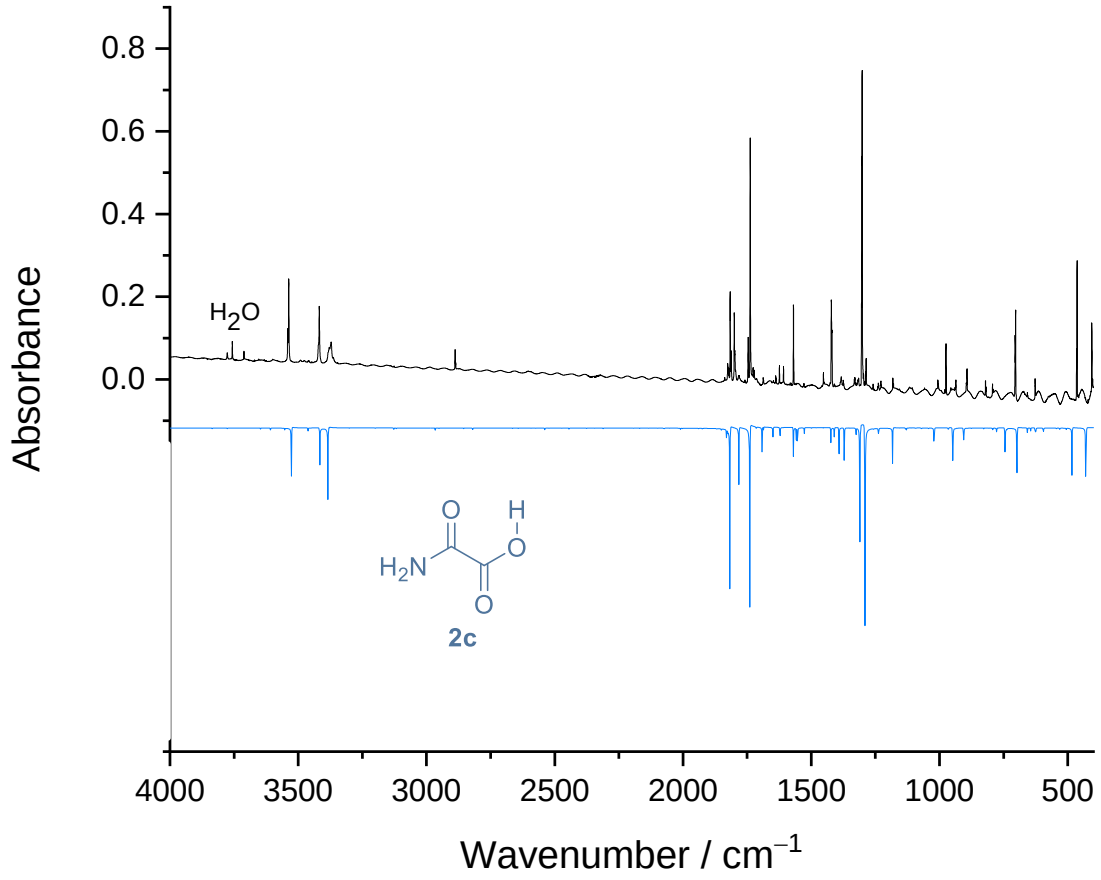
2c

FVP | $-CO_2$



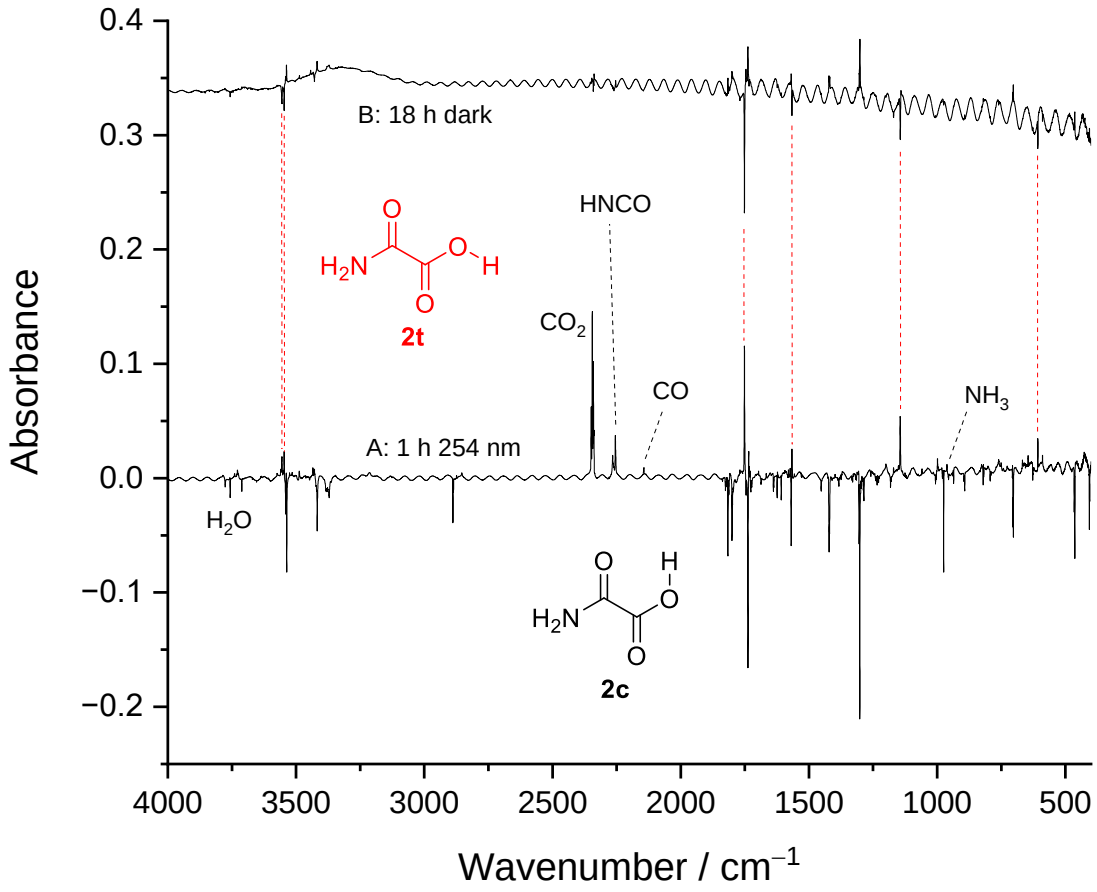
1t

Aminohydroxymethylene – Precursor

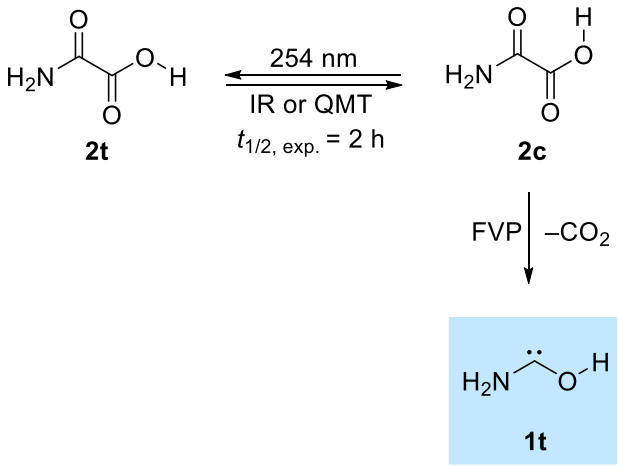


B3LYP/6-311++G(3df,3pd)

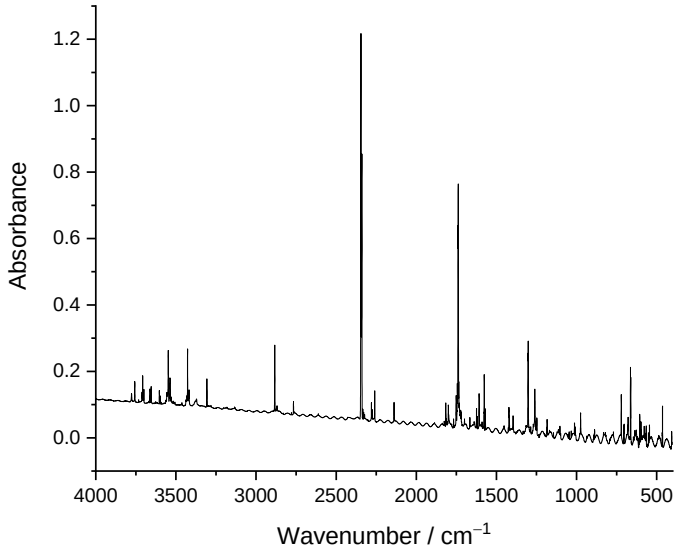
Aminohydroxymethylene – Photolysis



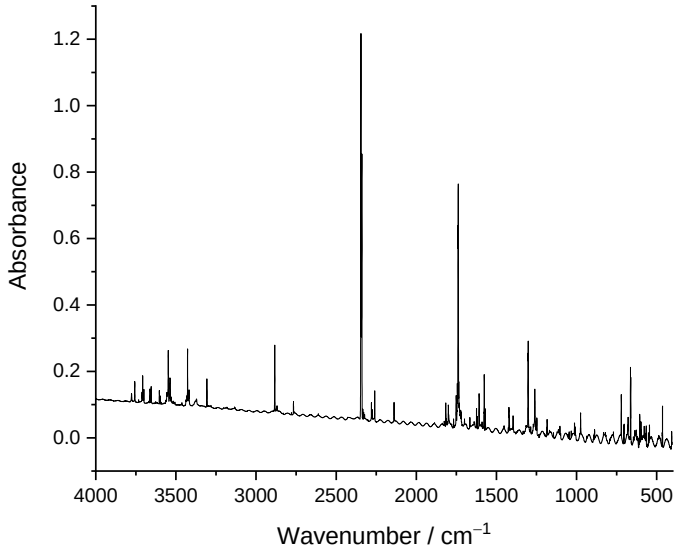
Aminohydroxymethylene – Reaction Scheme

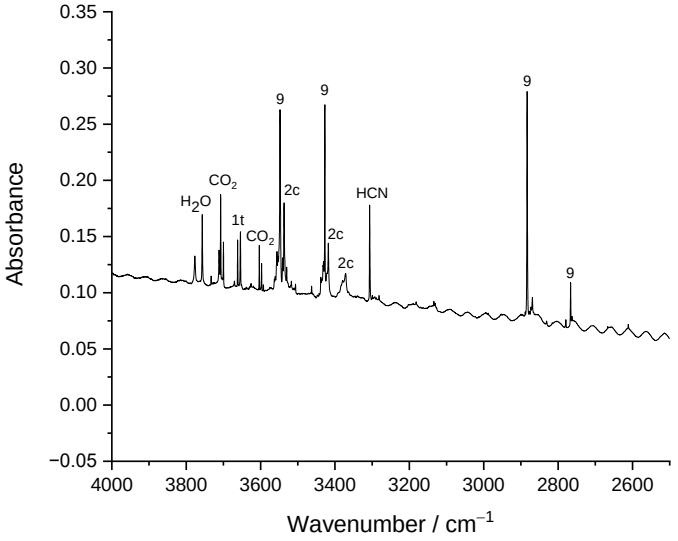


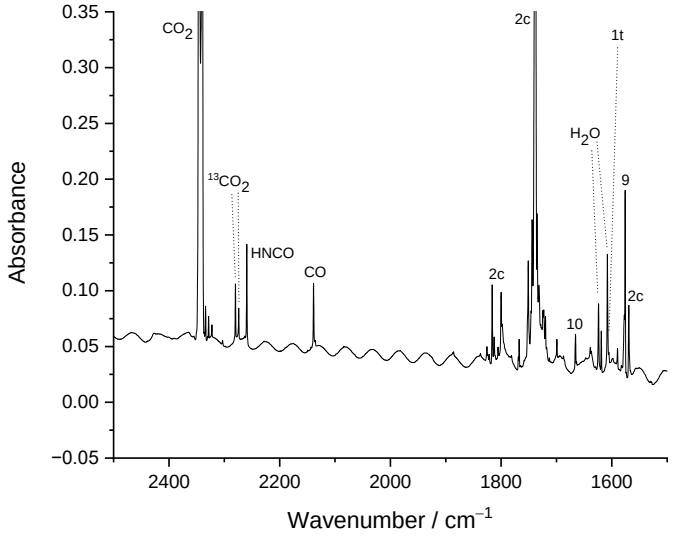
Aminohydroxymethylene – Pyrolysis

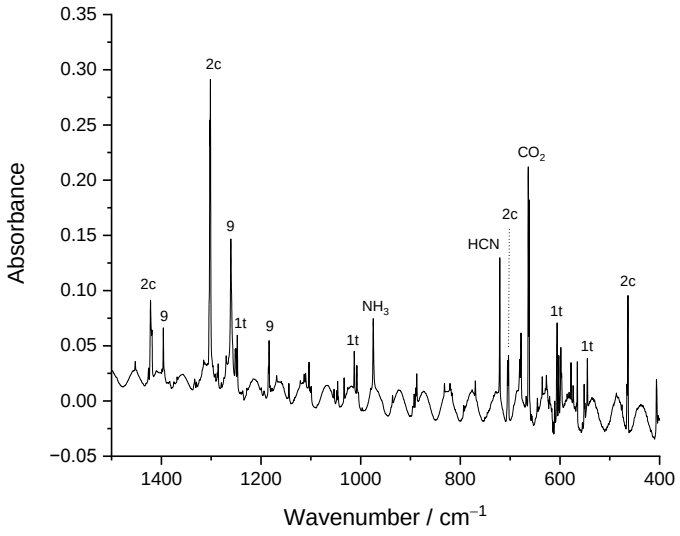


Aminohydroxymethylene – Pyrolysis

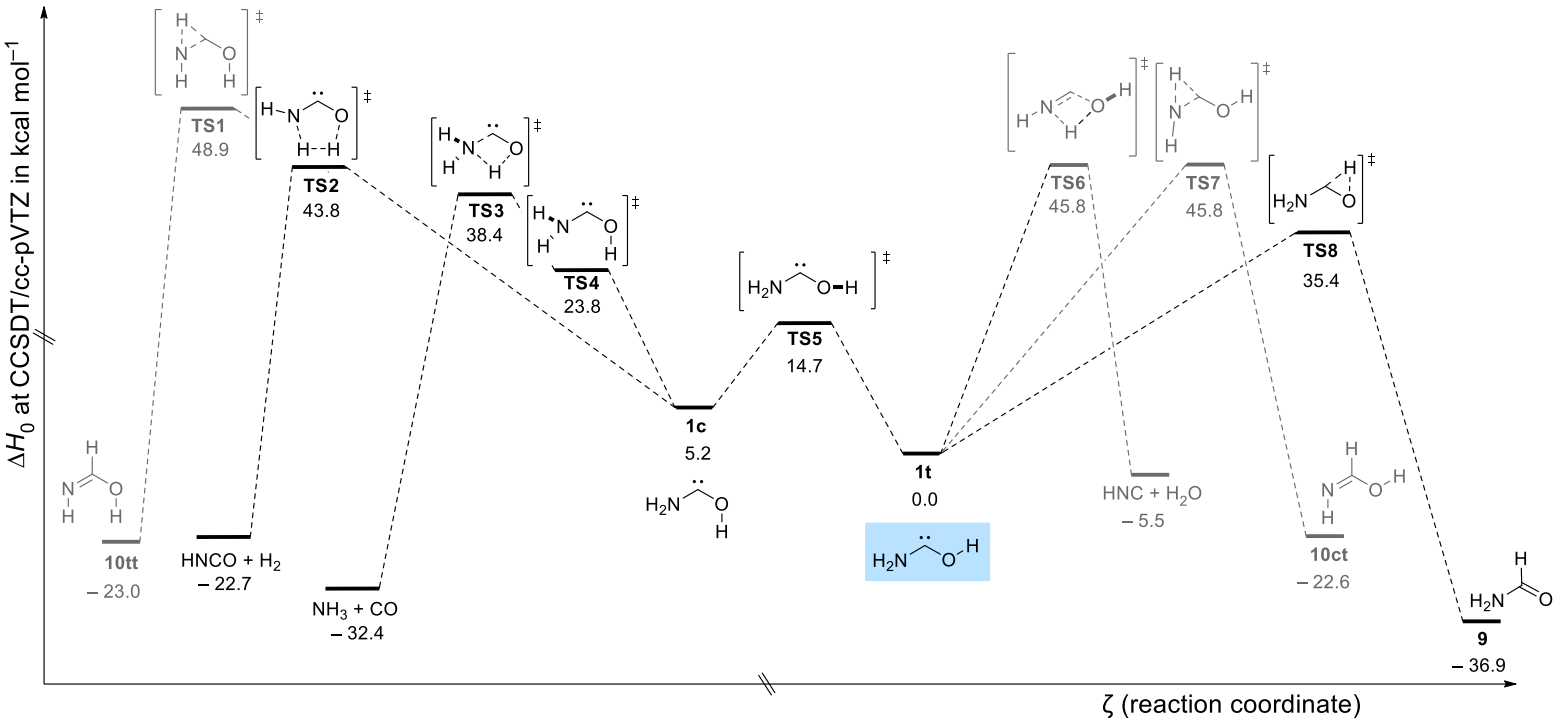




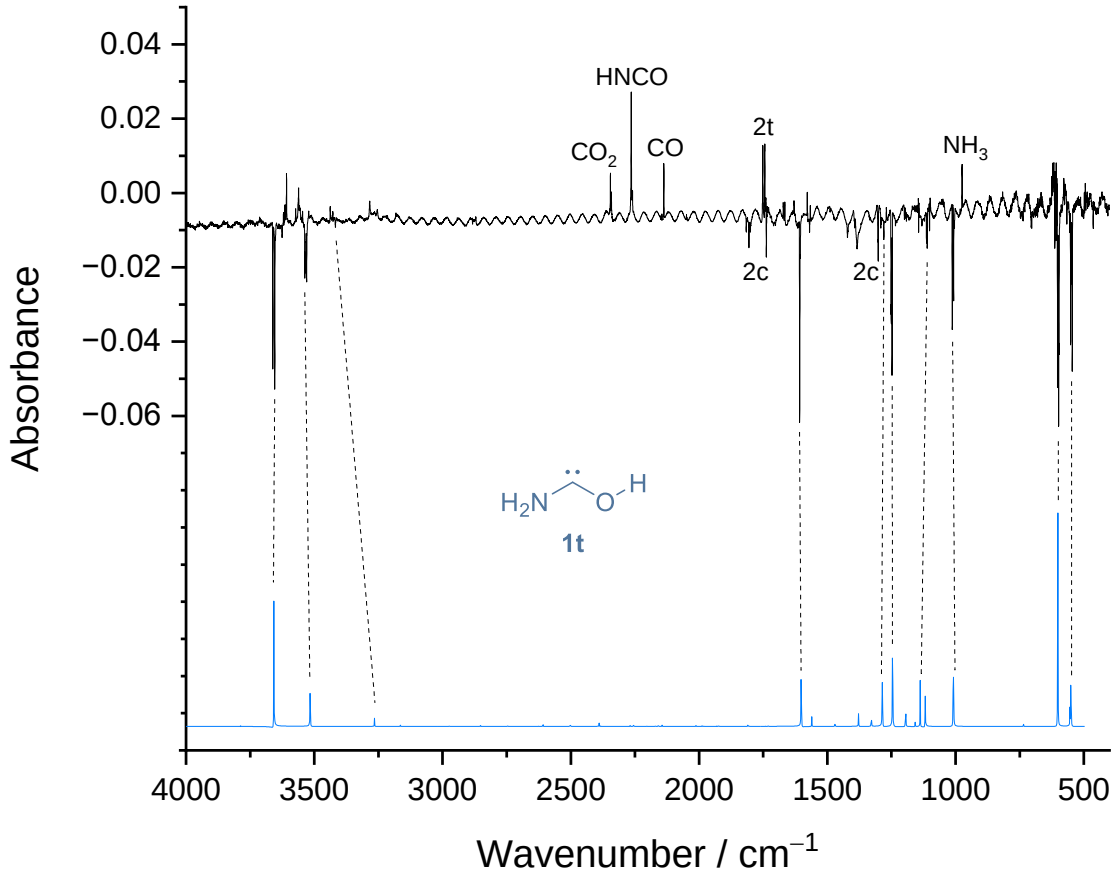




Aminohydroxymethylene – Potential Energy Surface

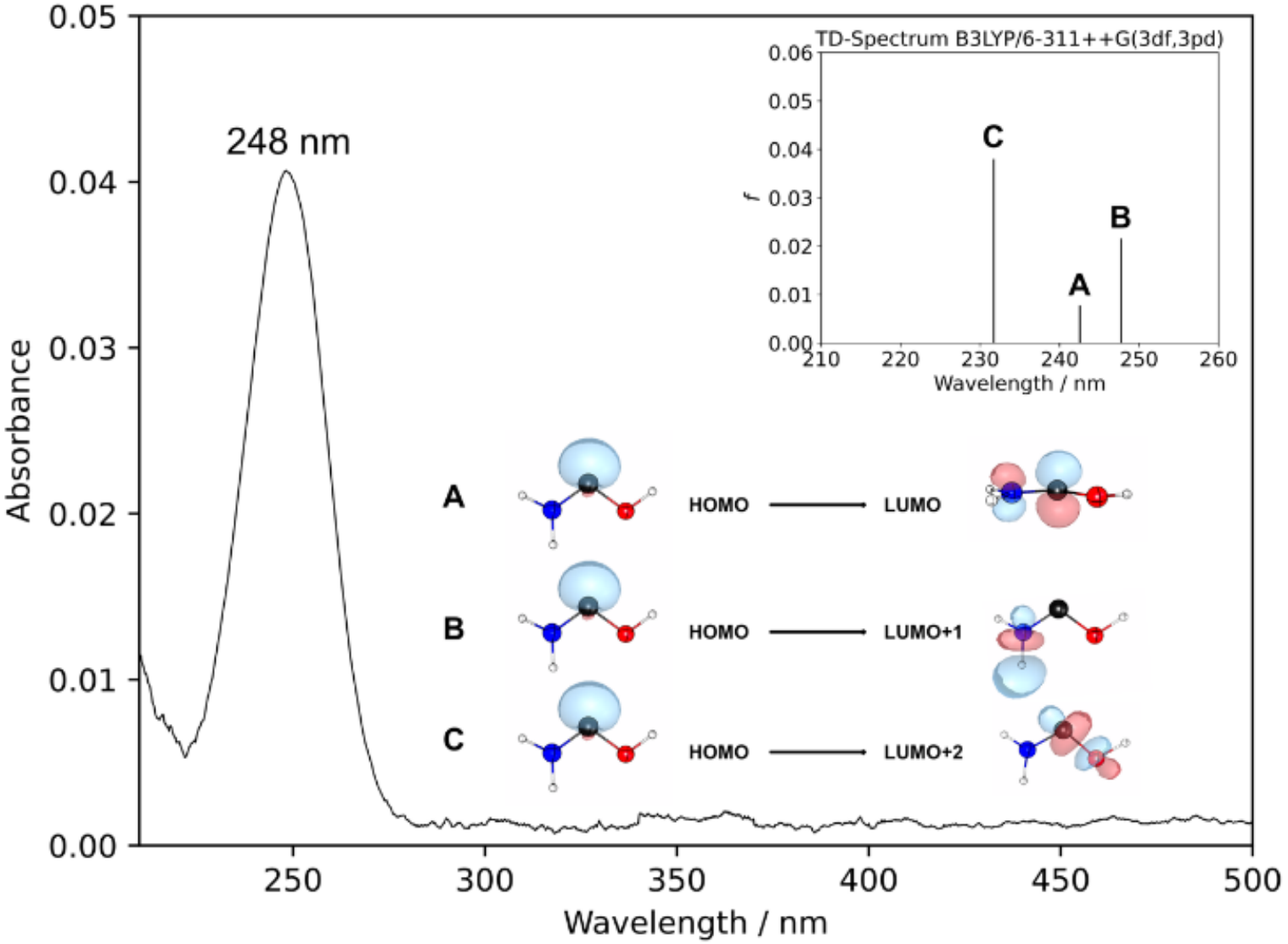


15 min 254 nm

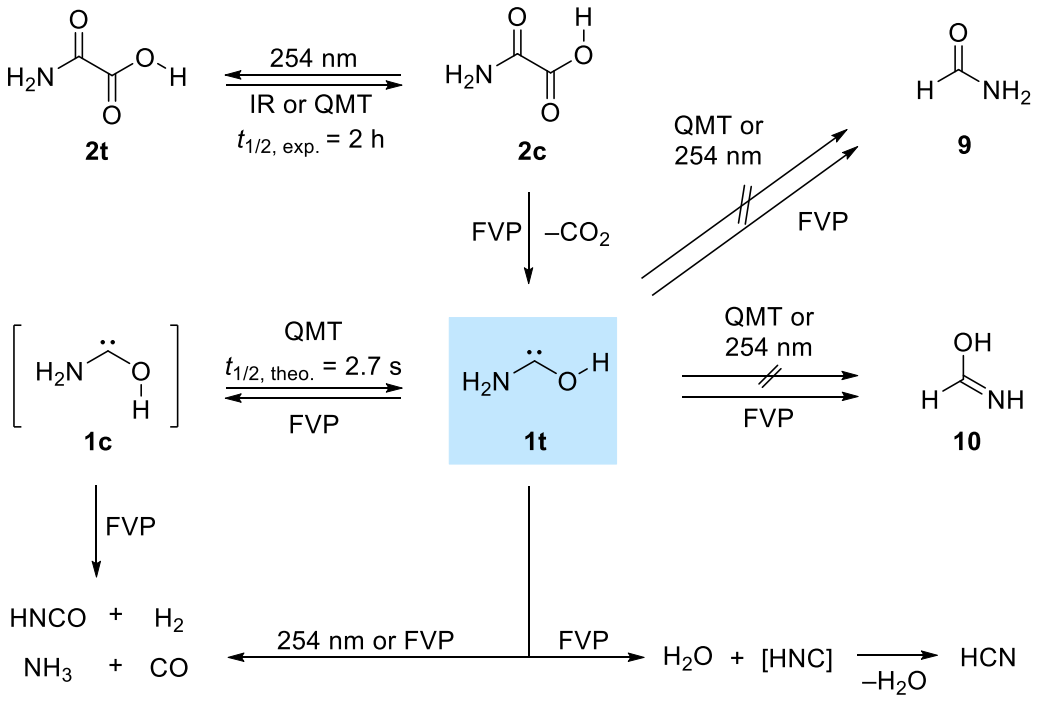


B3LYP/6-311++G(3df,3pd)

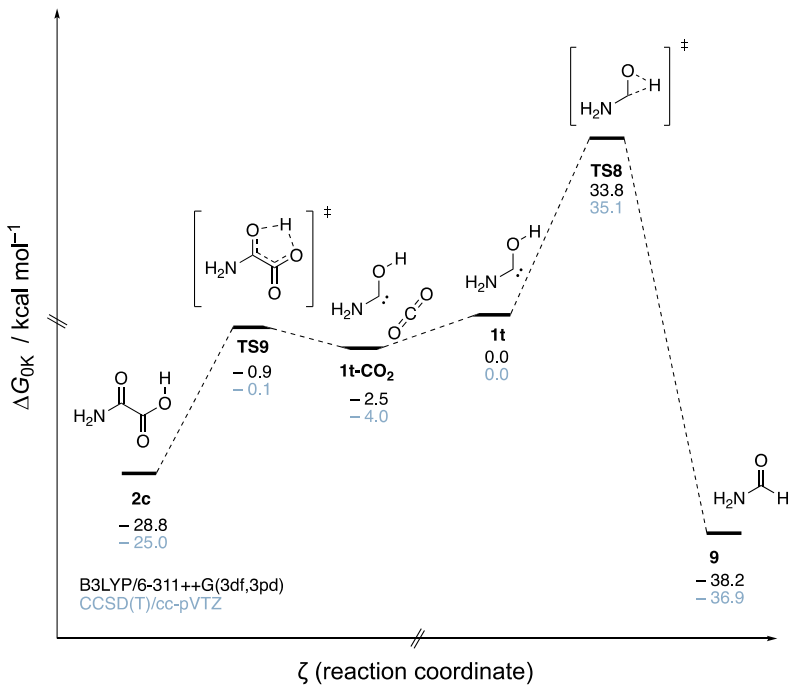
Aminohydroxymethylene – Matrix UV/Vis Spectrum

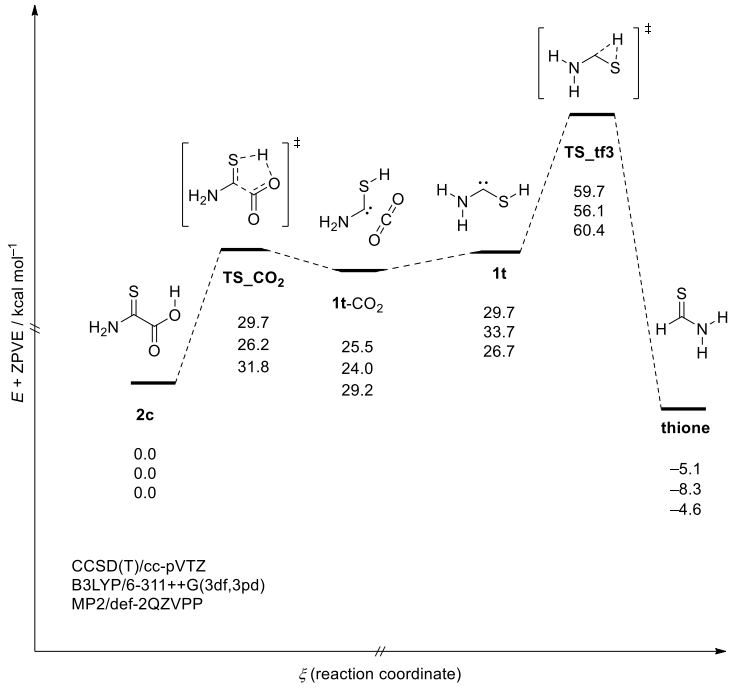


Aminohydroxymethylene – Reaction Scheme



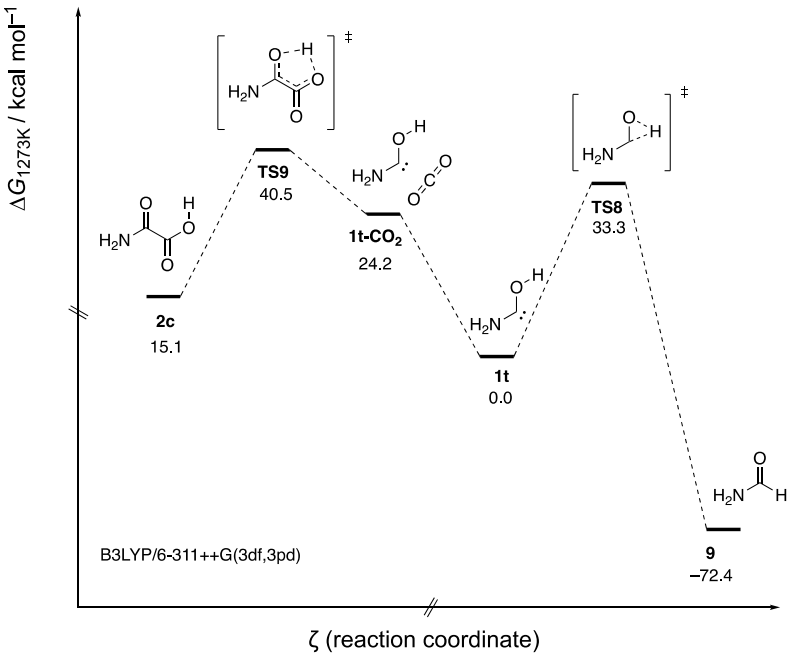
PES at 0 K

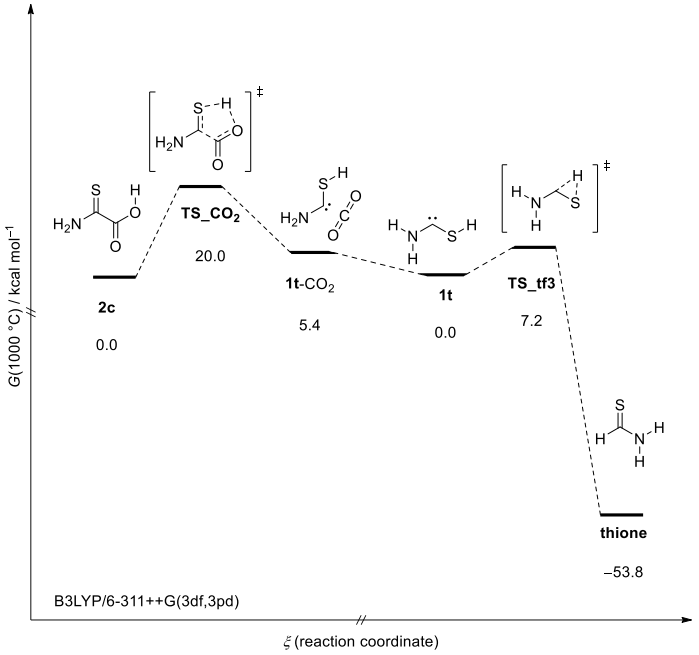




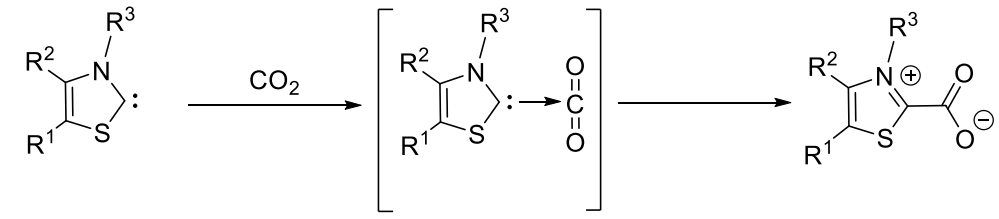
B. Bernhardt, M. Schauermann, E. Solel, A. K. Eckhardt, P. R. Schreiner, *manuscript in preparation*.

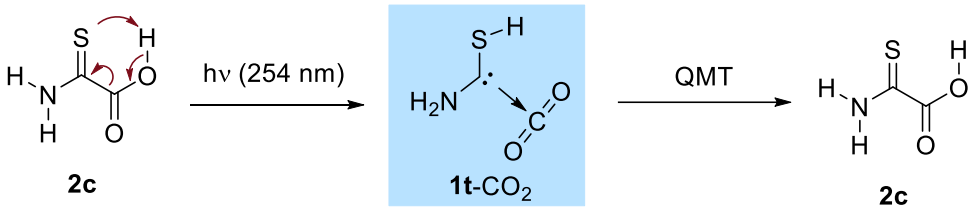
PES at 1000 °C


ΔG1273K / kcal mol−1
TS9
40.5
1t-CO2
24.2
TS8
33.3
2c
15.1
1t
0.0
9
−72.4
B3LYP/6-311++G(3df,3pd)
ζ (reaction coordinate)


G(1000 °C) / kcal mol−1
TS_CO2
20.0
1t-CO2
5.4
1t
0.0
TS_tf3
7.2
2c
0.0
thione
−53.8
B3LYP/6-311++G(3df,3pd)
ξ (reaction coordinate)

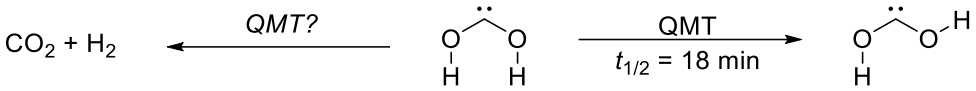
Aminomercaptomethylene

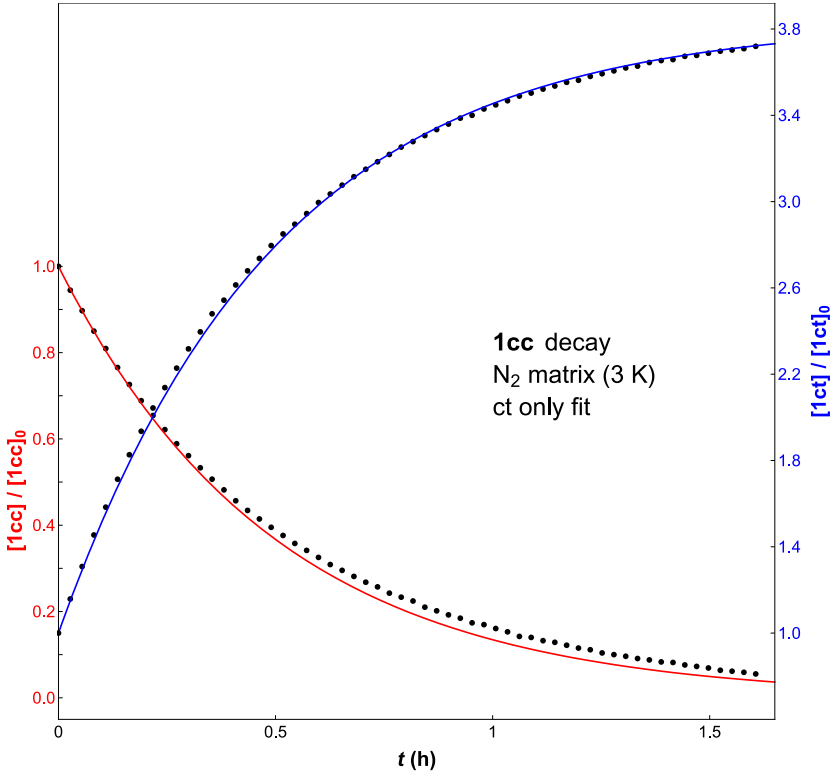


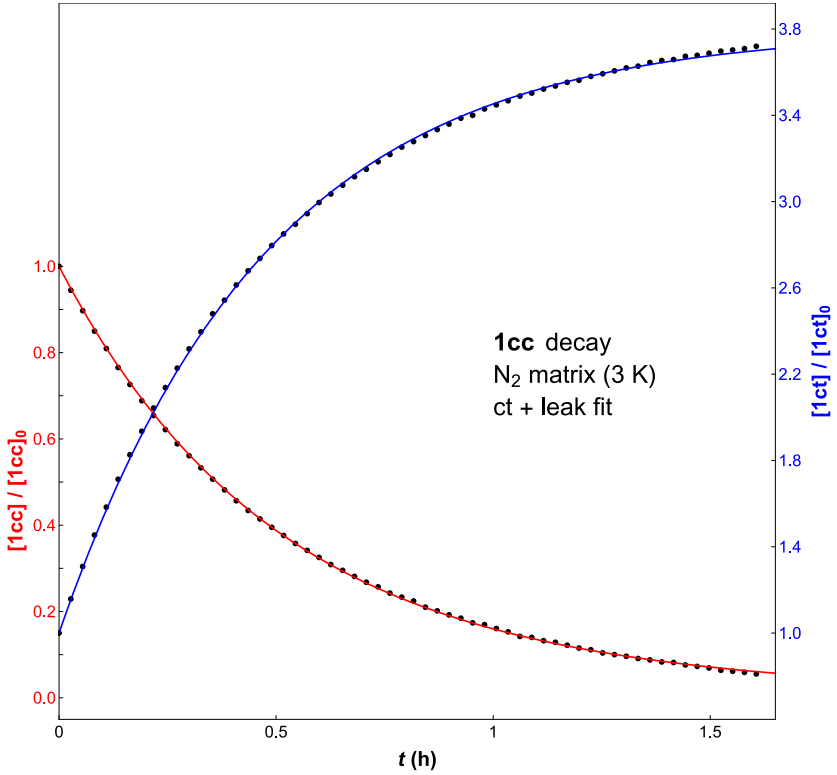


This work

Dihydroxycarbene

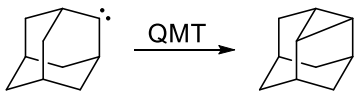


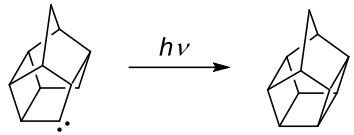


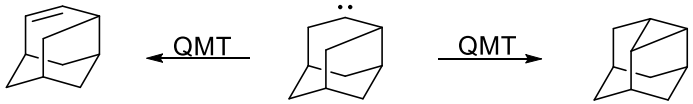


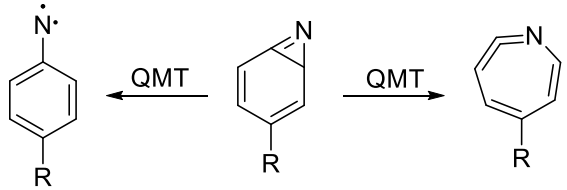
H. Quanz, B. Bernhardt, F. R. Erb, M. A. Bartlett, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2020**, *142*, 19457-19461.

Outlook









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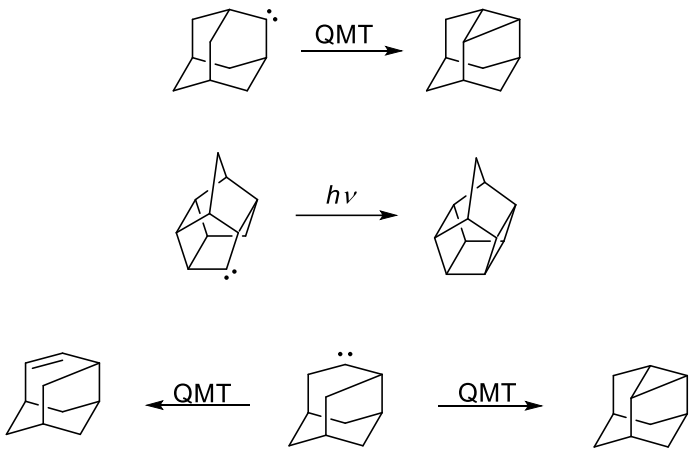
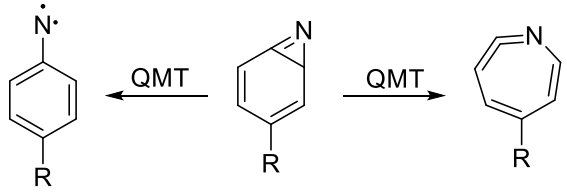
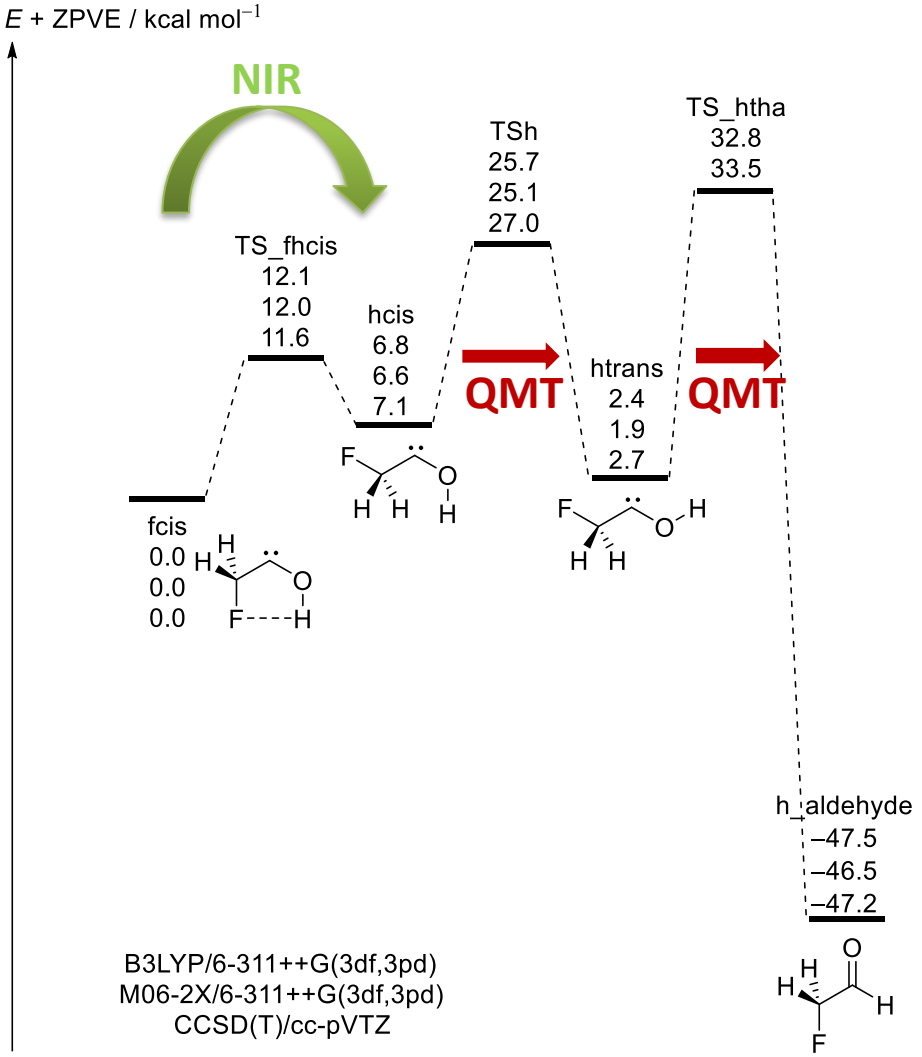

QMT
hν
QMT
QMT


N
QMT
N
QMT
N
R
R
R


E + ZPVE / kcal mol−1
NIR
TS_fhcis
12.1
12.0
11.6
hcis
6.8
6.6
7.1
TSh
25.7
25.1
27.0
QMT
htrans
2.4
1.9
2.7
TS_htha
32.8
33.5
QMT
fcis
0.0
0.0
0.0
h_aldehyde
–47.5
–46.5
–47.2
B3LYP/6-311++G(3df,3pd)
M06-2X/6-311++G(3df,3pd)
CCSD(T)/cc-pVTZ

Outlook

Pos	+/-	Name	TUR ITA	WAL CH	DEN FIN	BEL RUS	ENG KRO	AUT MKD	NIE UKR	P	B	S	G
			0:3	-:-	-:-	-:-	-:-	-:-	-:-				
1		Bastian	$0:3_4$	-:-	-:-	-:-	-:-	-:-	-:-	4	0	1,00	4
2		Akkad	$2:4_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Alex	$1:3_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Artur	$0:2_2$	-:-	-:-	-:-				2	0		2
2		Eschi	$0:1_2$							2	0		2
2		Felix	$0:2_2$	-:-	-:-	-:-				2	0		2
2		Fred	$1:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Friedhelm	$0:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Jan	$0:4_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Lars	$0:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Maggus	$1:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Mika	$0:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Paul	$1:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		prs	$0:1_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		quanzi	$0:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Raffi	$1:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
2		Yakiniku	$1:2_2$	-:-	-:-	-:-	-:-	-:-	-:-	2	0		2
18		Finn								0	0		0

9	▼1	Alex	1:3	$2:0_2$	2	15		88
9	▲1	Yakiniku	$2:0_3$	$1:0_3$	6	15		88
11	▼1	quanzi	$3:1_3$	$2:0_2$	5	18		87
12	▼3	prs	$2:1_2$	0:1	2	15		86
13	▲2	Akkad	$2:1_2$	$2:1_4$	6	18	1,00	82
14	▼1	Simon	$4:1_2$	$2:0_2$	4	21	0,33	82
15	▲1	Bastian	$2:0_3$	$1:0_3$	6	15		77
15	▼1	Raffi	2:4	6:7	0	15		77
17		Friedhelm			0	21	0,33	62
18		Jan			0	18		29
19		Finn			0	0		0

Acknowledgement

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- PRS Group