Radical Stability

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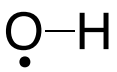
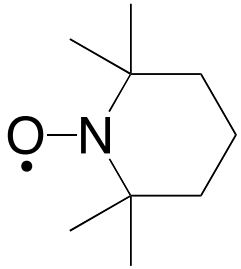
2020

Radical Stability - Some Terminology

hydroxyl
"transient"

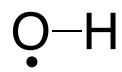


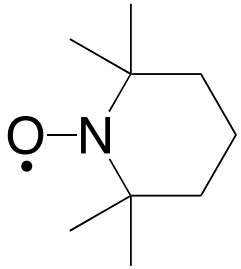


TEMPO
(tetramethylpiperidine-1-oxyl)
"persistent"

Radical Stability - Some Terminology

hydroxyl
"transient"





TEMPO
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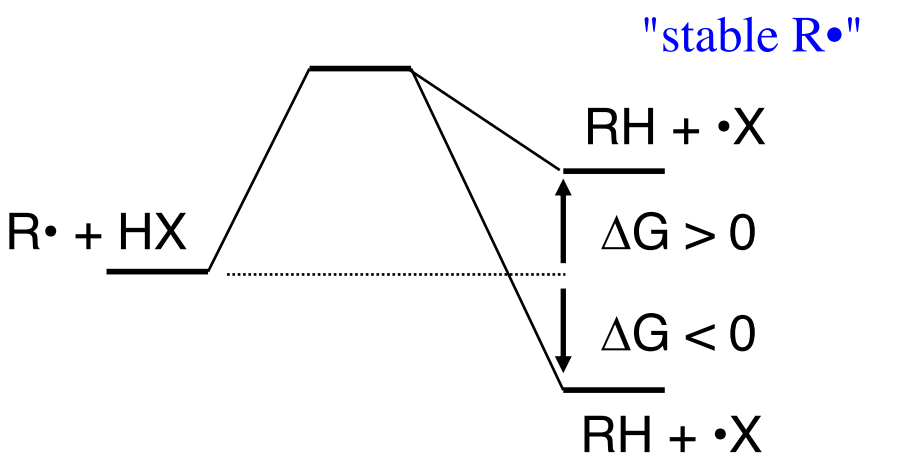
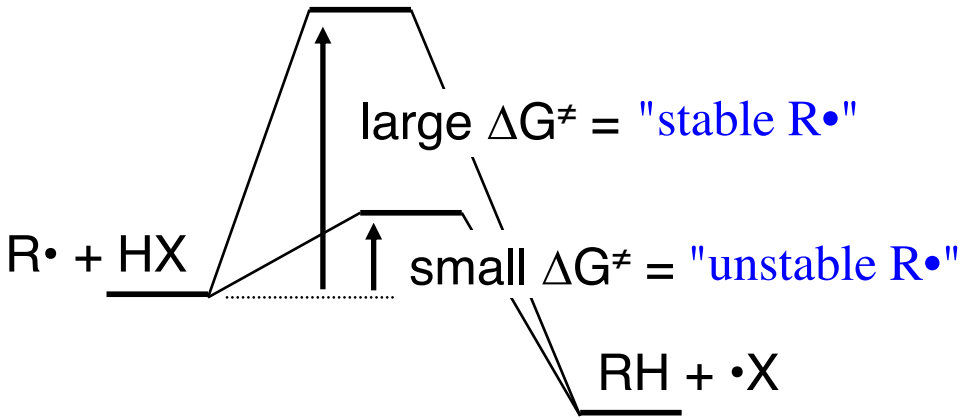
"persistent"

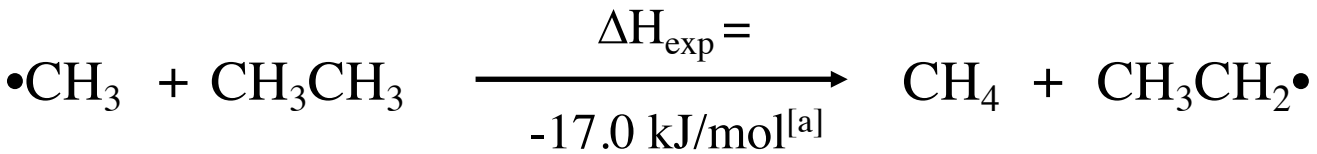
Thermodynamics



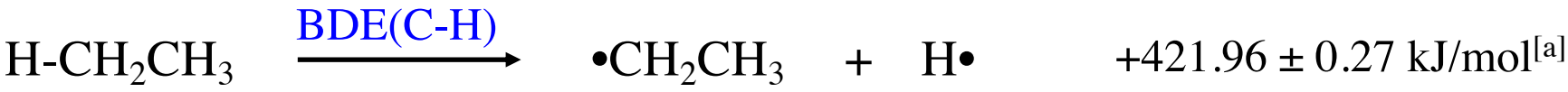
Kinetics



Radical Stability - Some Definitions



Radical stabilization energy
(RSE) = -17.0 kJ/mol



[a] ATcT database, 1.122p (2020)

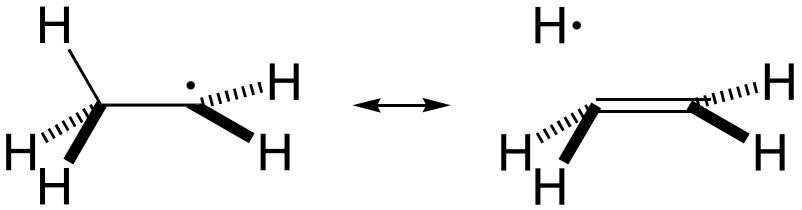
Radical Stability - Some Definitions

$$\bullet CH_3 + R\text{-}H \xrightarrow{\Delta H_{rxn}} CH_4 + R\bullet$$

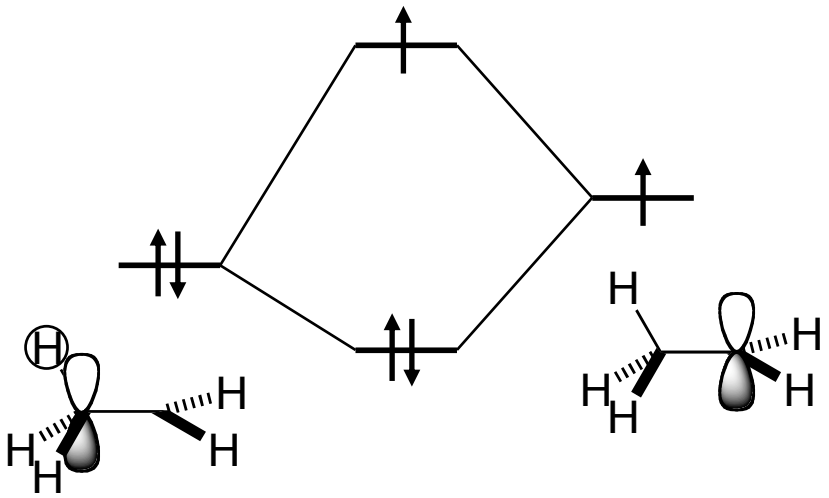
$$\bullet CH_3 + CH_3CH_3 \xrightarrow[-17.0\ kJ/mol]{\Delta H_{exp} =} CH_4 + CH_3CH_2\bullet$$

Radical stabilization energy
(RSE) = -17.0 kJ/mol

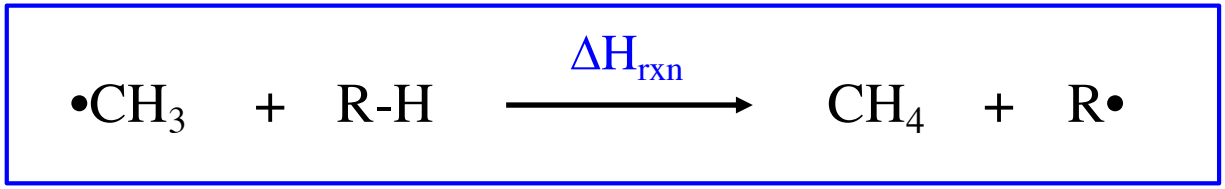
VB Theory

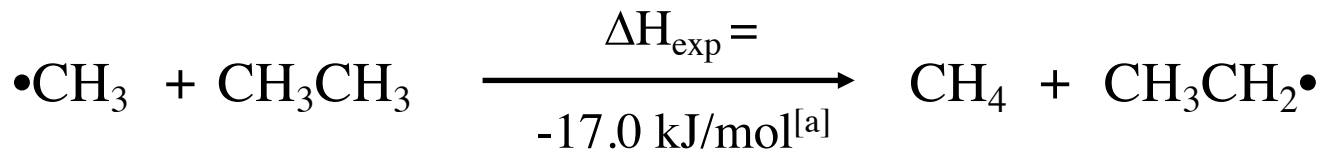


MO Theory



Radical Stability - Some Definitions





Radical stabilization energy
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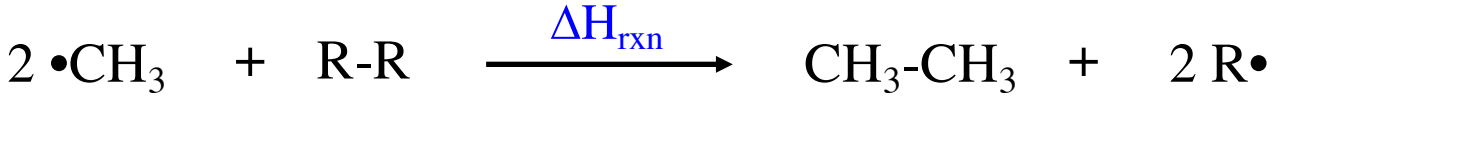
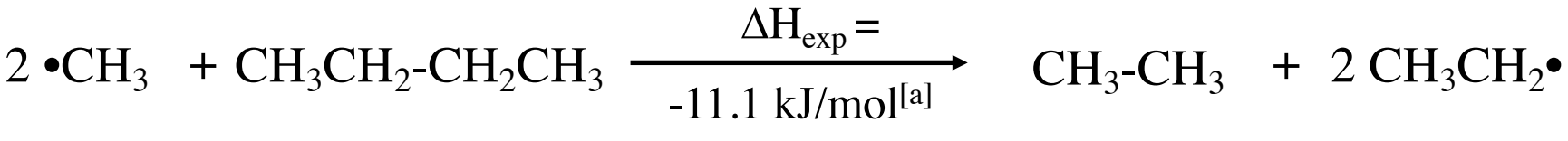


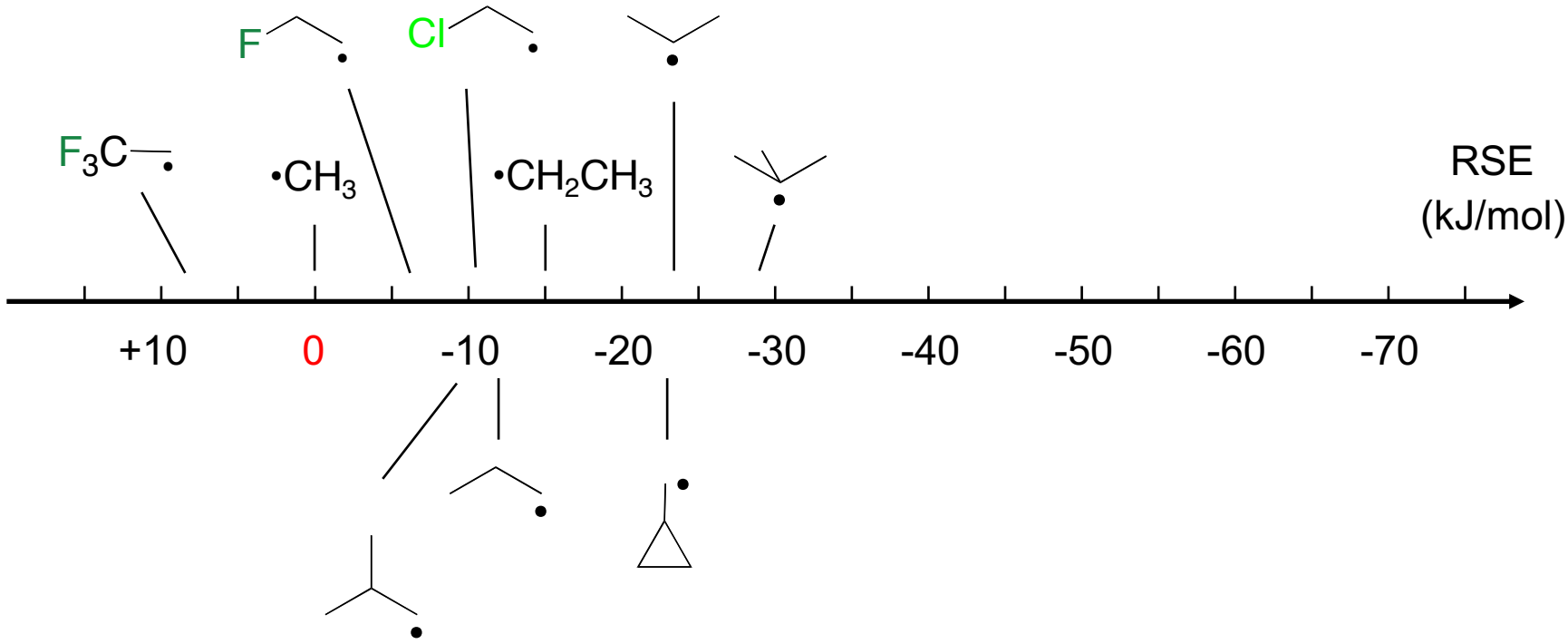


Two radicals involved!
RSE = -5.6 kJ/mol

[a] ATcT database, 1.122p (2020)

Mechanisms of Radical Stabilization I

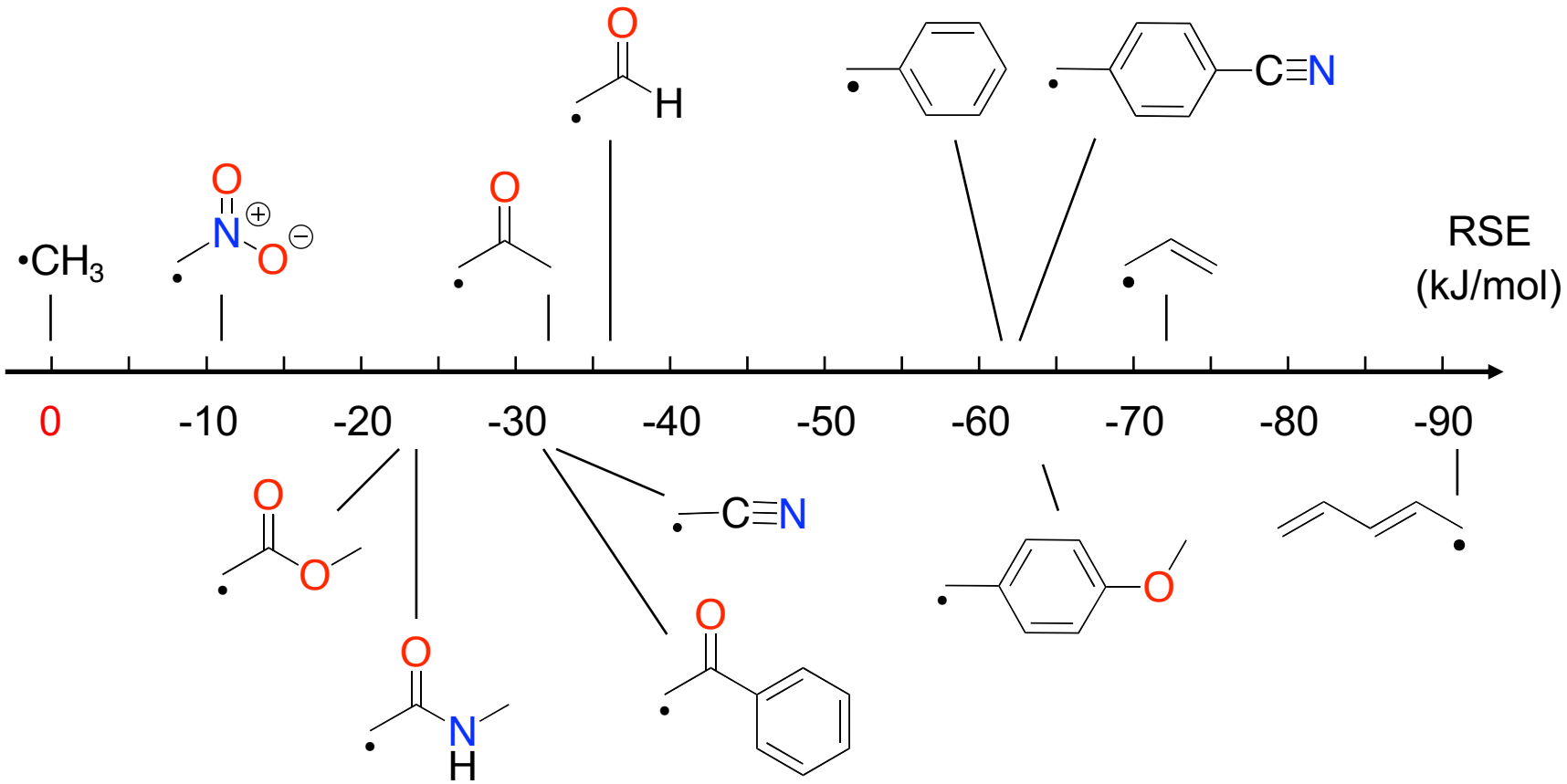
- Inductive Effects -



ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

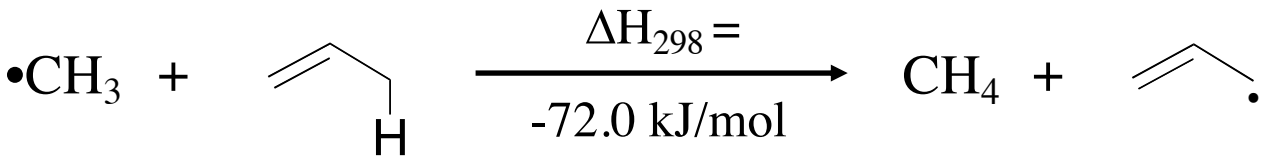
Mechanisms of Radical Stabilization II

- Resonance Stabilization -

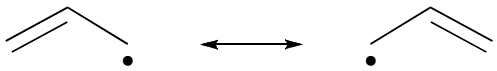


ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

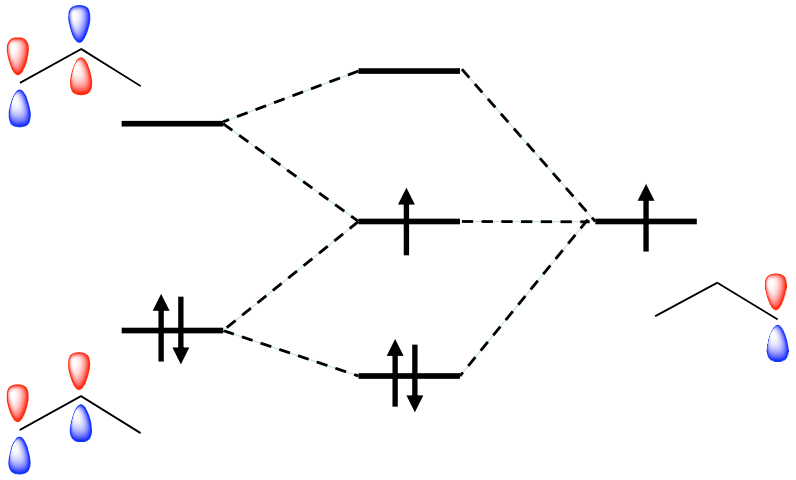
Resonance Stabilization



VB Theory

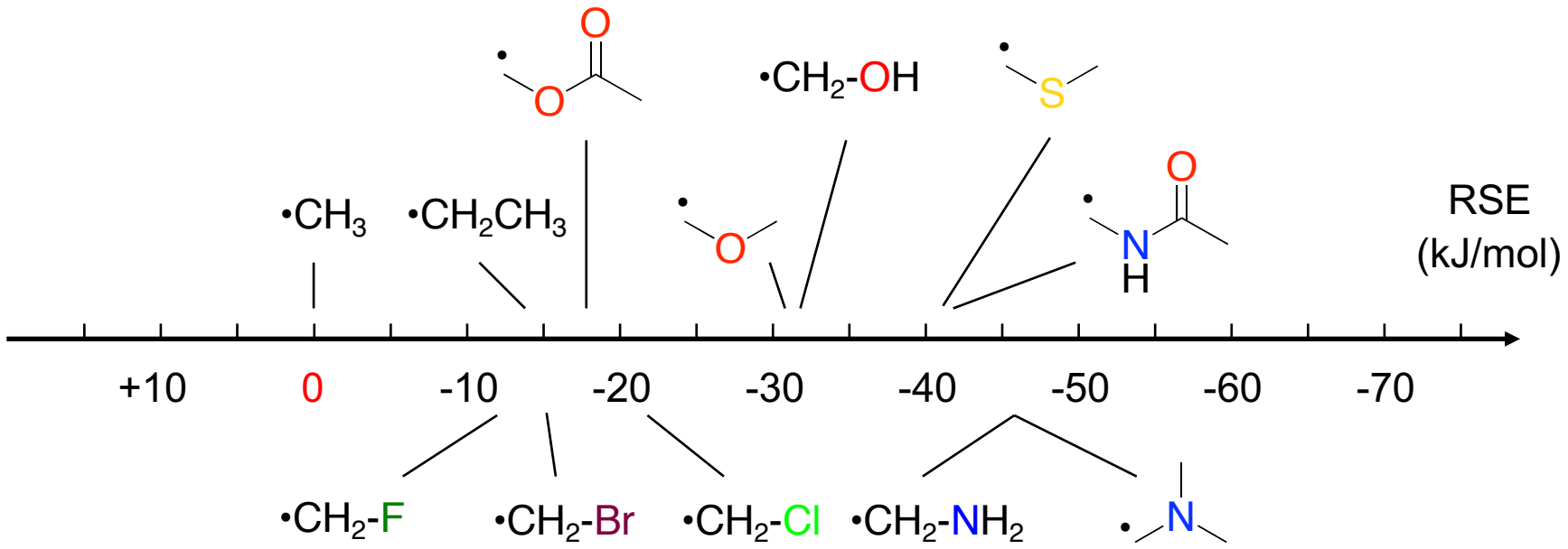


MO Theory



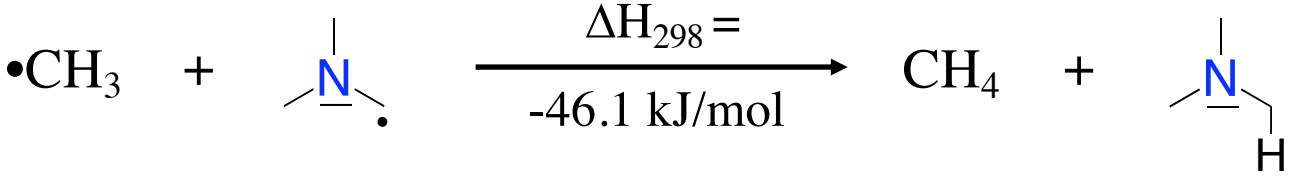
Mechanisms of Radical Stabilization III

- Lone Pair Donors -

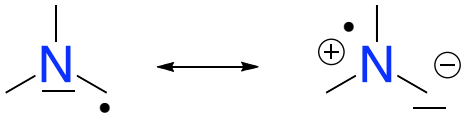


ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

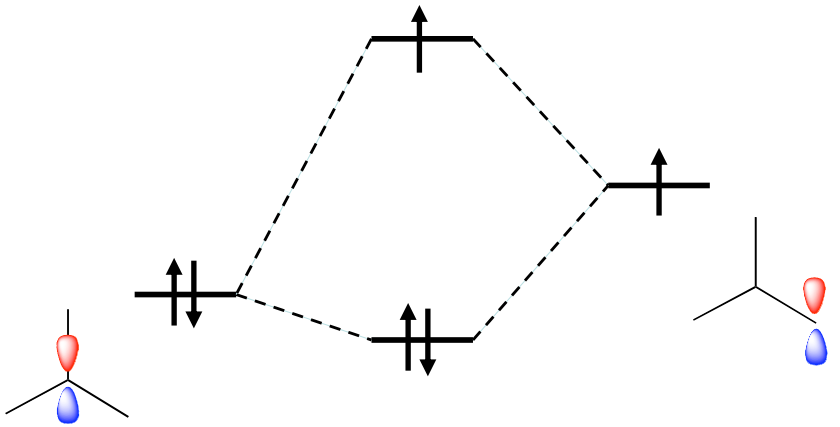
Lone-Pair Stabilization



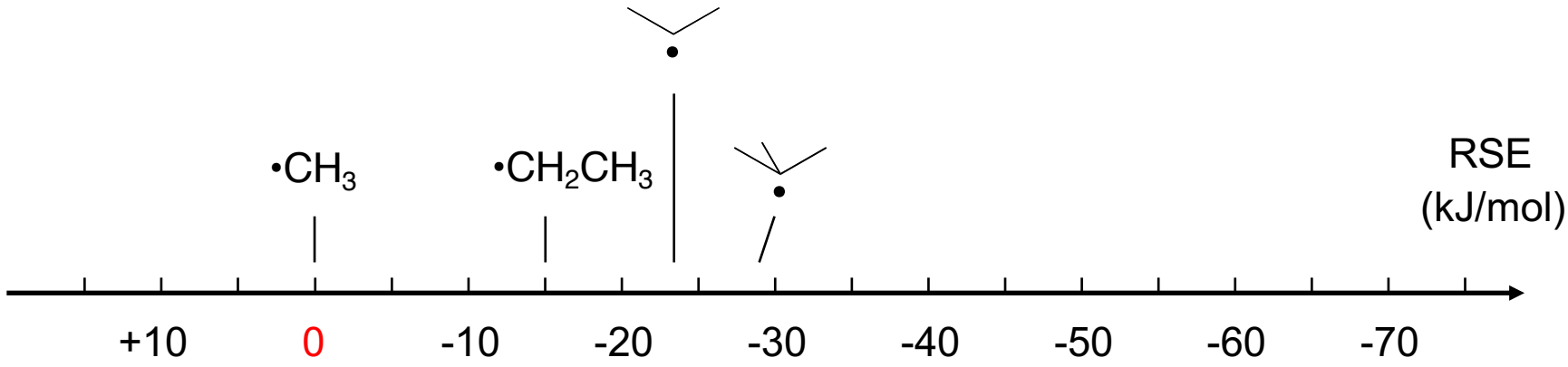
VB Theory



MO Theory

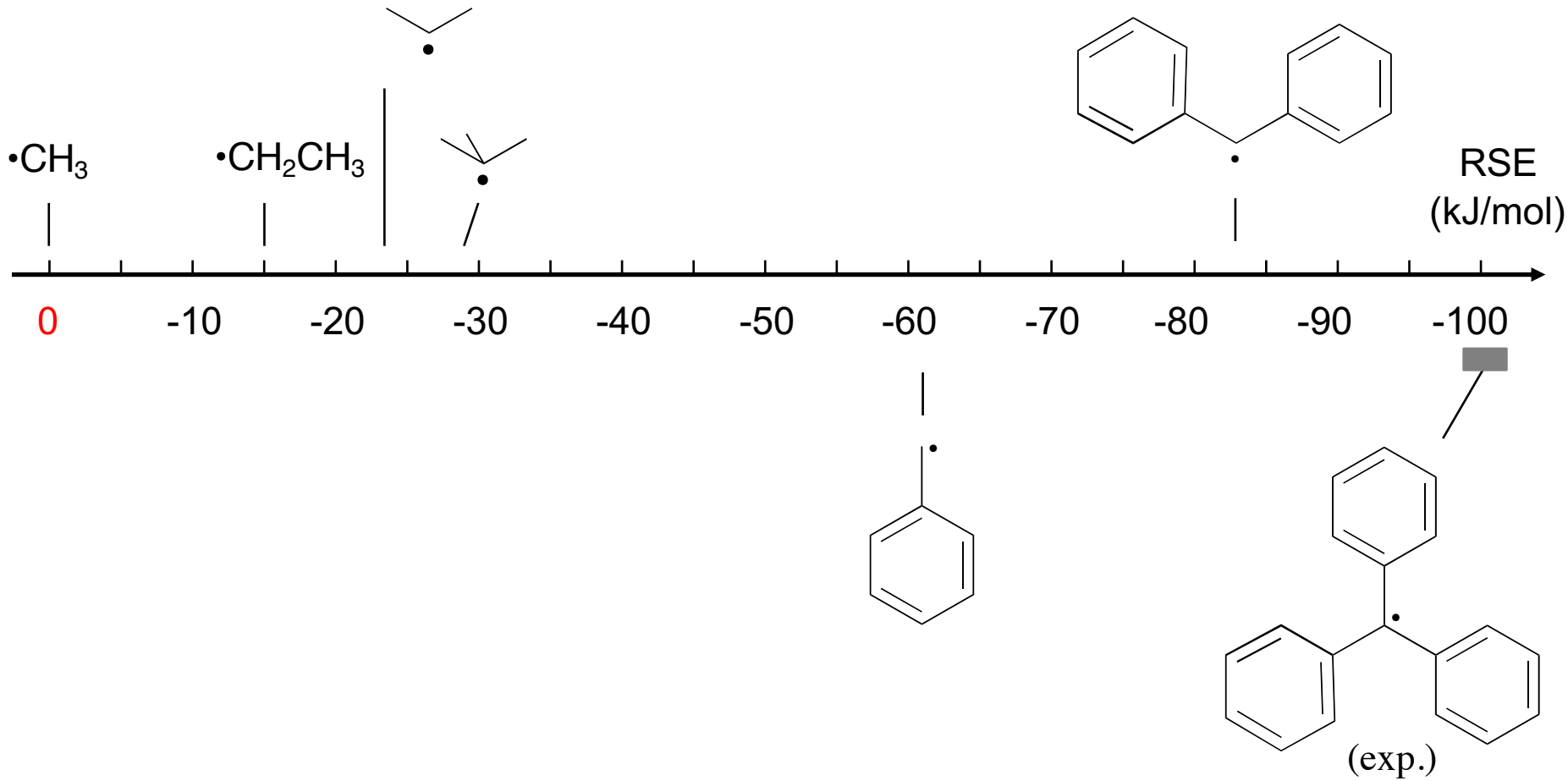


Multiple Substituents - Saturation



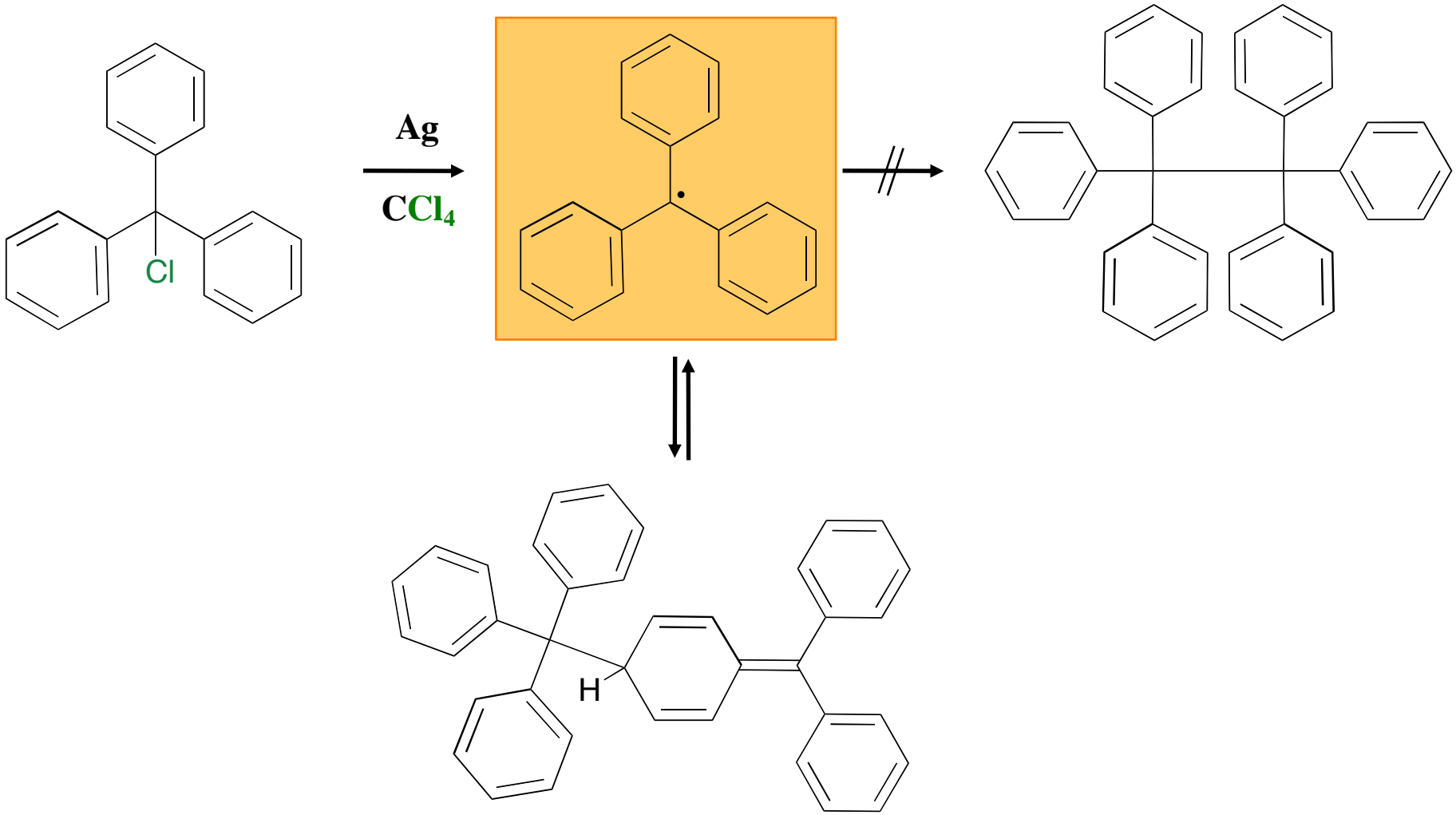
ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

Multiple Substituents – Saturation II



ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

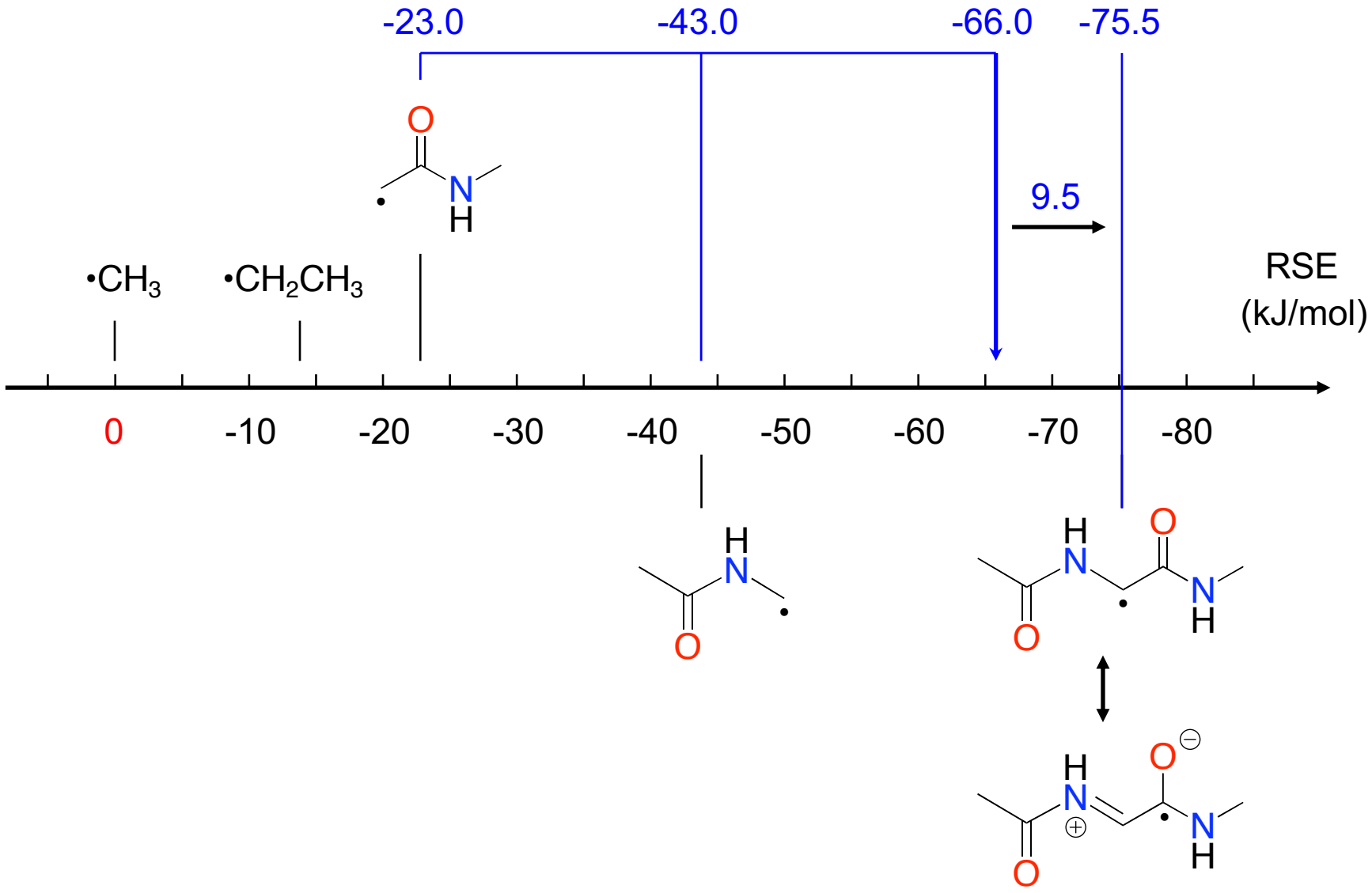
The Triphenylmethyl Radical



M. Gomberg, „Triphenylmethyl, ein Fall von dreiwerthigem Kohlenstoff“, *Ber. Dt. Chem. Ges.* **1900**, *33*, 3150.

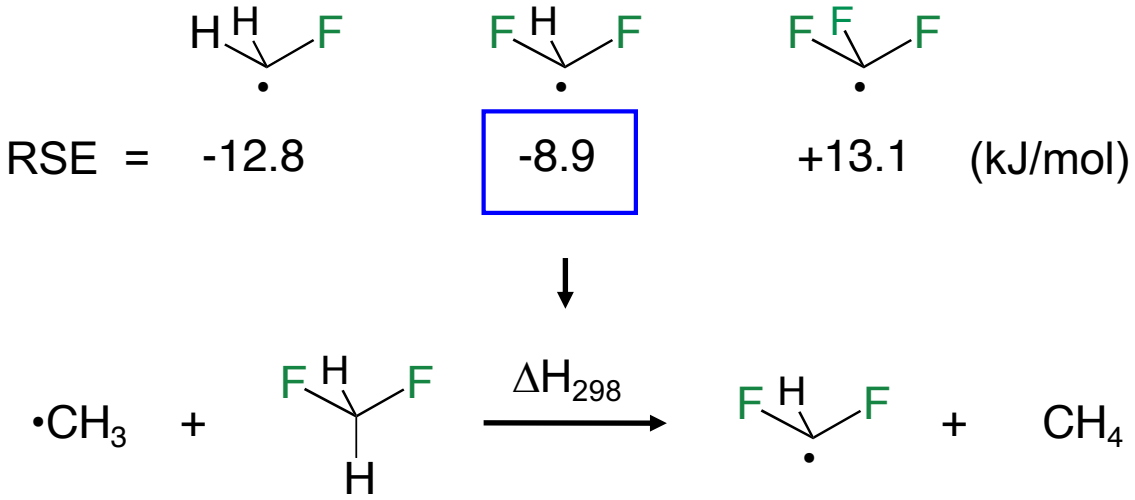
J. M. McBride, „The Hexaphenylethane Riddle“, *Tetrahedron* **1974**, *30*, 2009.

Multiple Substitution – Synergistic Effects

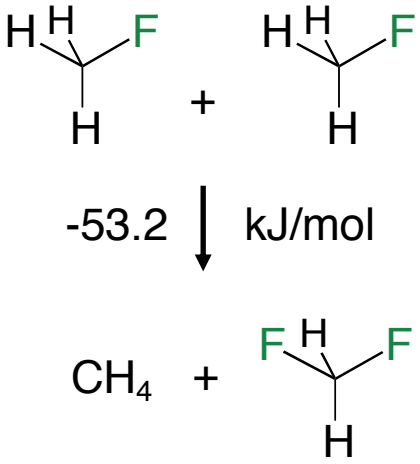


ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

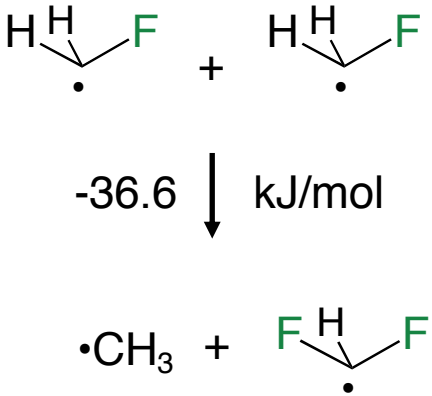
The Interpretation of Radical Stability



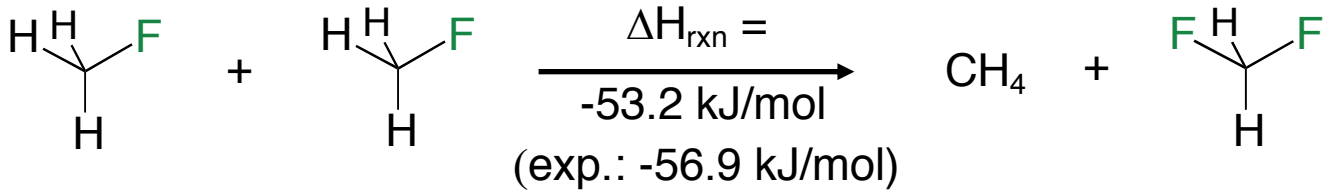
anomeric effect 1



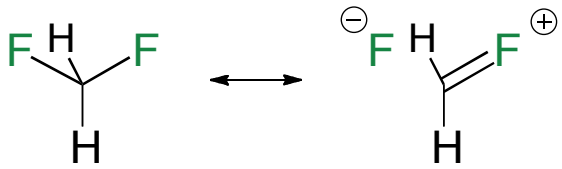
anomeric effect 2



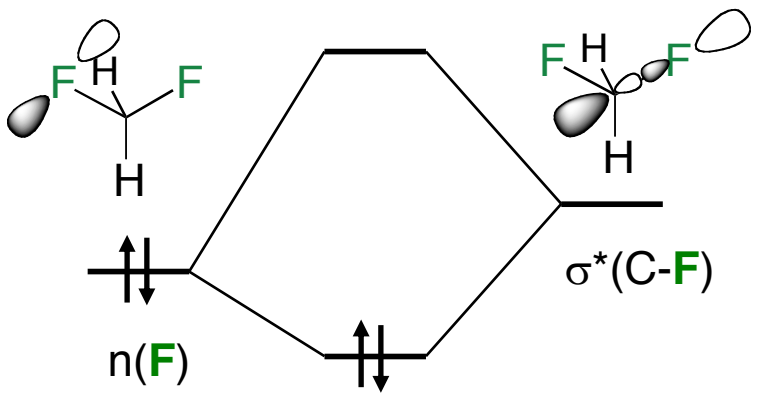
The Anomeric Effect



VB Theory

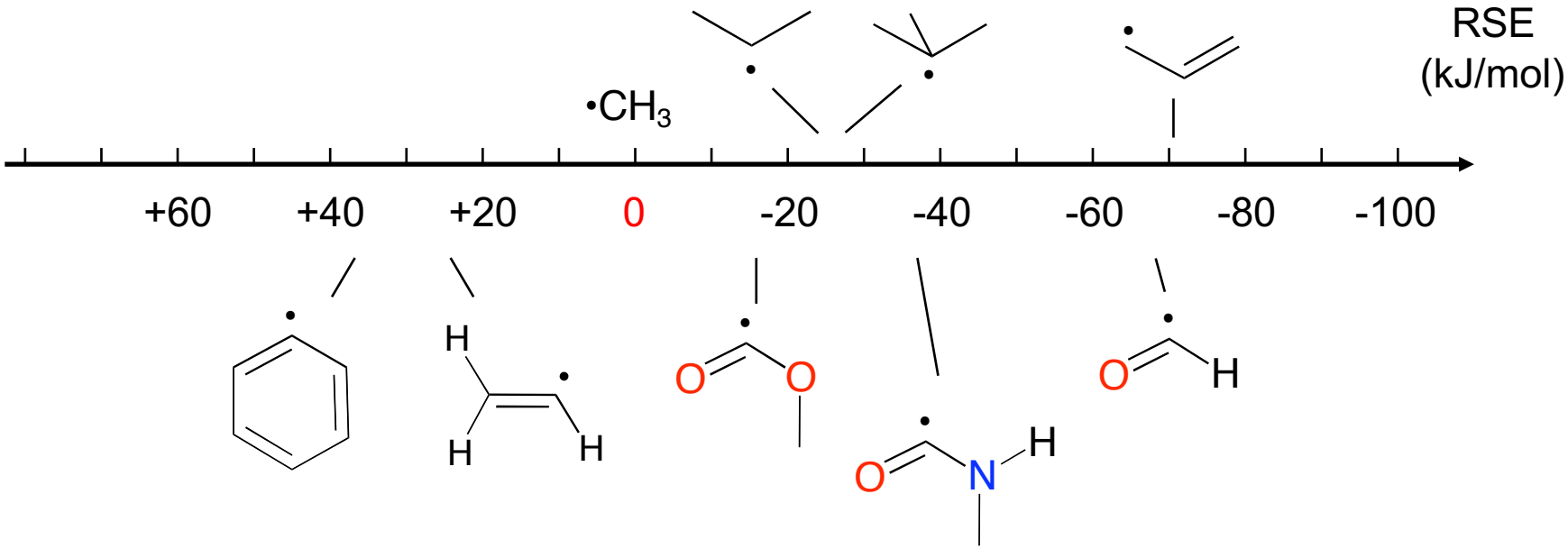


MO Theory



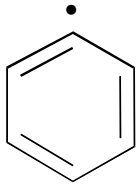
ΔH$_{298}$(G3(MP2)-RAD) [kJ/mol]

Stability of σ-Radicals

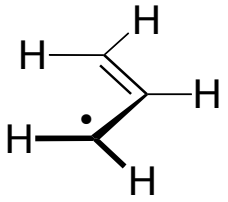


ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

σ-Radicals vs. π-Radicals

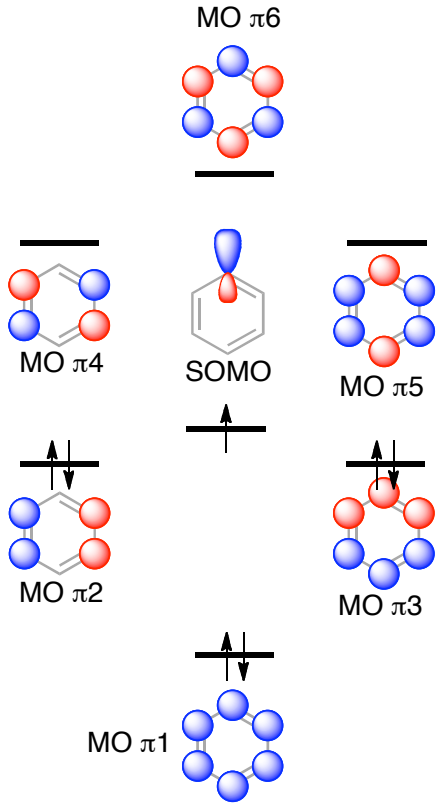


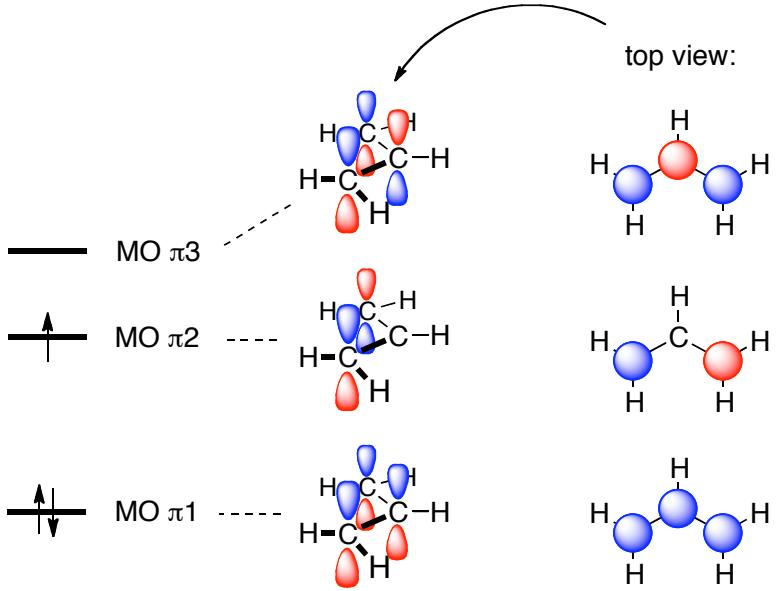
+37.0



-72.0

RSE
(kJ/mol)





The Stability of Carbon-Centered Radicals

$$\bullet CH_3 + R\text{-}H \xrightarrow{\Delta H_{rxn}} CH_4 + R\bullet$$

$$\bullet CH_3 + CH_3CH_3 \xrightarrow[-17.0\ kJ/mol^{[a]}]{\Delta H_{exp} =} CH_4 + CH_3CH_2\bullet$$

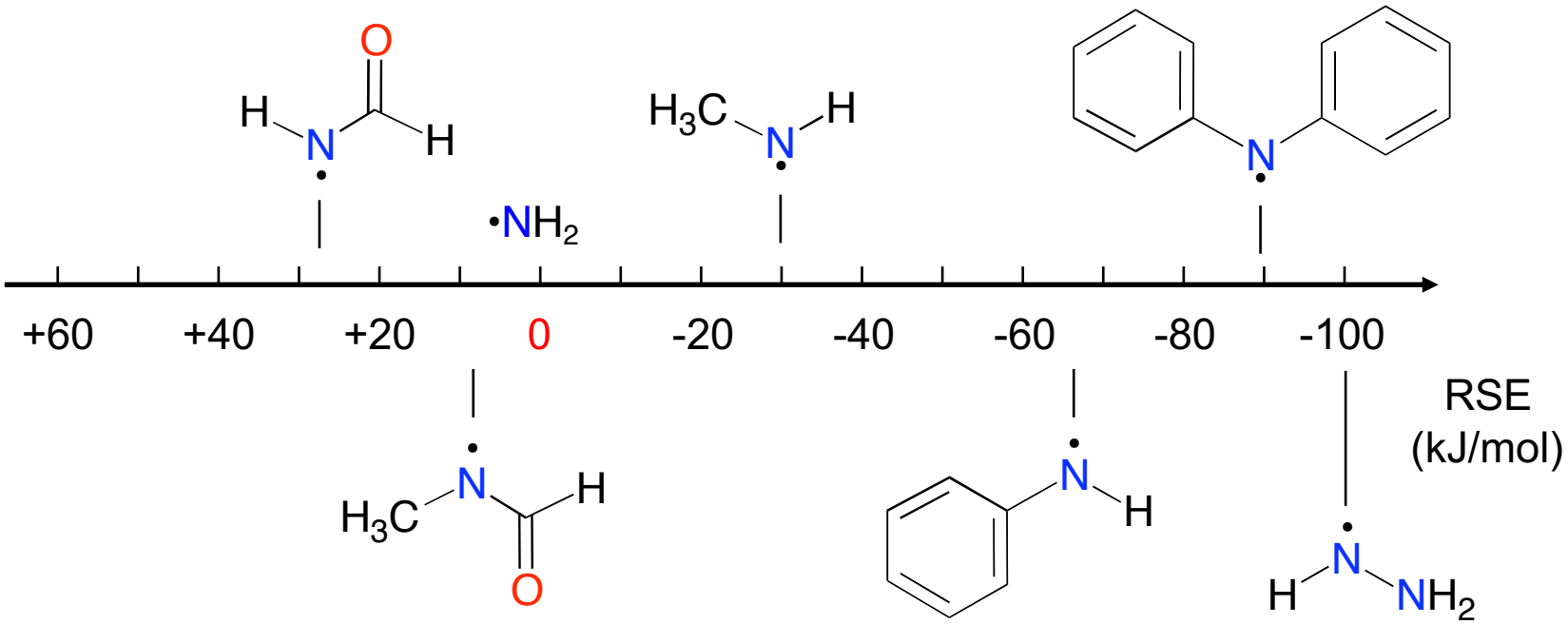
. . . and the Stability of Nitrogen-Centered Radicals

$$\bullet NH_2 + R_2N\text{-}H \xrightarrow{\Delta H_{rxn}} H_3N + R_2N\bullet$$

$$\bullet NH_2 + CH_3NH_2 \xrightarrow[-33.4\ kJ/mol^{[a]}]{\Delta H_{exp} =} H_3N + CH_3NH\bullet$$

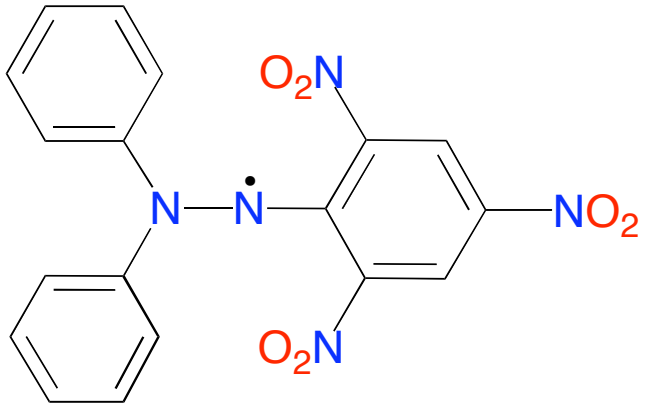
[a] ATcT database, 1.122p (2020)

The Stability of Nitrogen-Centered Radicals



ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

DPPH - A Persistent Nitrogen-Centered Radical



1,1-Diphenyl-2-picrylhydrazyl (DPPH)

- stable solid with mp = 130 °C
- EPR standard at g = 2.0036
- radical trap

The Stability of Carbon-Centered Radicals

$$\bullet CH_3 + R\text{-}H \xrightarrow{\Delta H_{rxn}} CH_4 + R\bullet$$

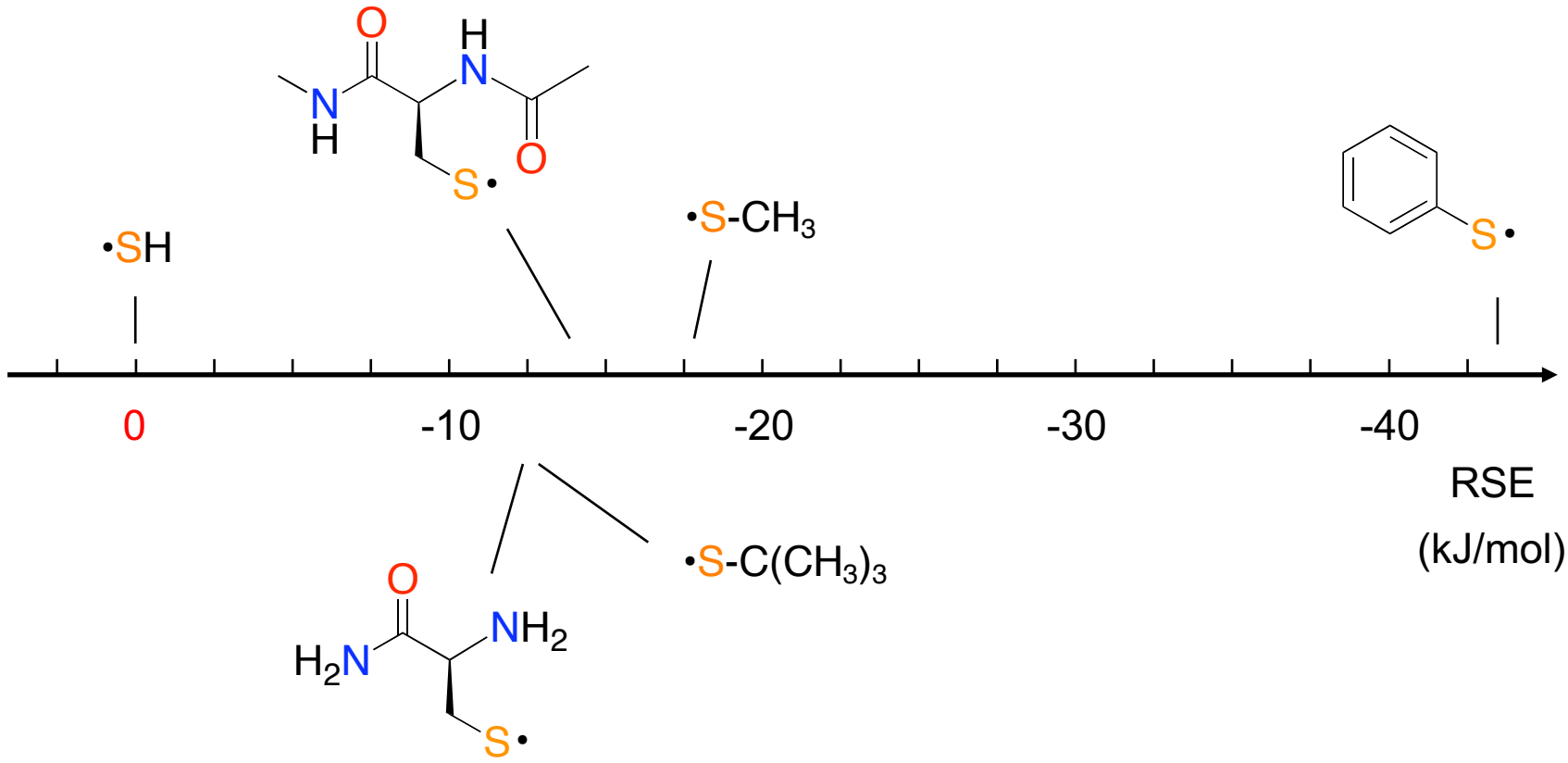
$$\bullet CH_3 + CH_3CH_3 \xrightarrow[-17.0\ kJ/mol^{[a]}]{\Delta H_{exp} =} CH_4 + CH_3CH_2\bullet$$

. . . and the Stability of Sulfur-Centered Radicals

$$\bullet SH + RS\text{-}H \xrightarrow{\Delta H_{rxn}} H_2S + RS\bullet$$

$$\bullet SH + CH_3SH \xrightarrow[-15.5\ kJ/mol]{\Delta H_{exp} =} H_2S + CH_3S\bullet$$

The Stability of Sulfur-Centered Radicals



ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

The Stability of Carbon-Centered Radicals

$$\bullet CH_3 + R\text{-}H \xrightarrow{\Delta H_{rxn}} CH_4 + R\bullet$$

$$\bullet CH_3 + CH_3CH_3 \xrightarrow[-17.0\ kJ/mol^{[a]}]{\Delta H_{exp} =} CH_4 + CH_3CH_2\bullet$$

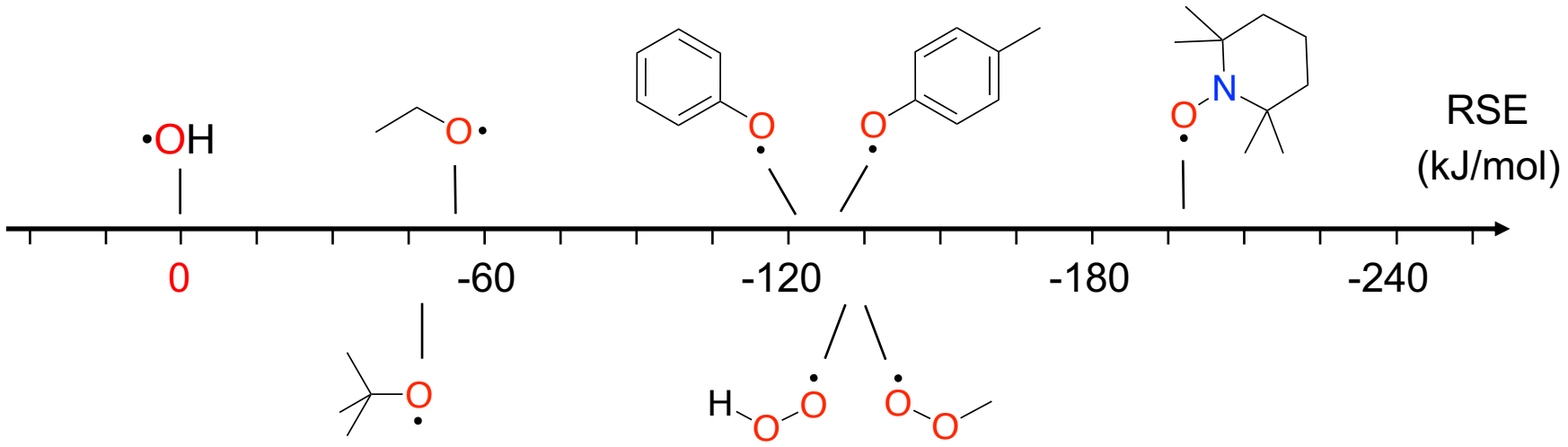
…. and the Stability of Oxygen-Centered Radicals

$$\bullet OH + RO\text{-}H \xrightarrow{\Delta H_{rxn}} H_2O + RO\bullet$$

$$\bullet OH + CH_3OH \xrightarrow[-56.9\ kJ/mol^{[a]}]{\Delta H_{exp} =} H_2O + CH_3O\bullet$$

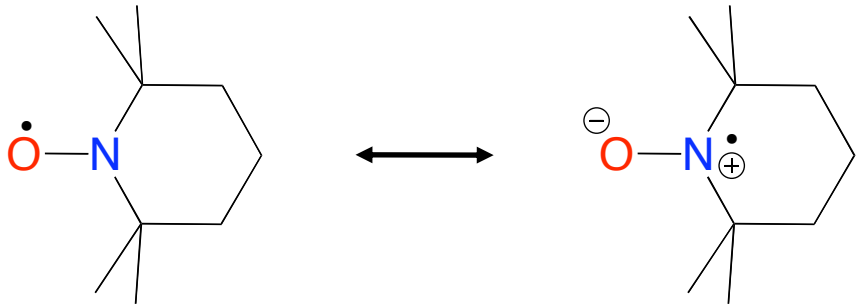
[a] ATcT database, 1.122p (2020)

The Stability of Oxygen-Centered Radicals



ΔH_{298}(G3B3-D3) [kJ/mol]

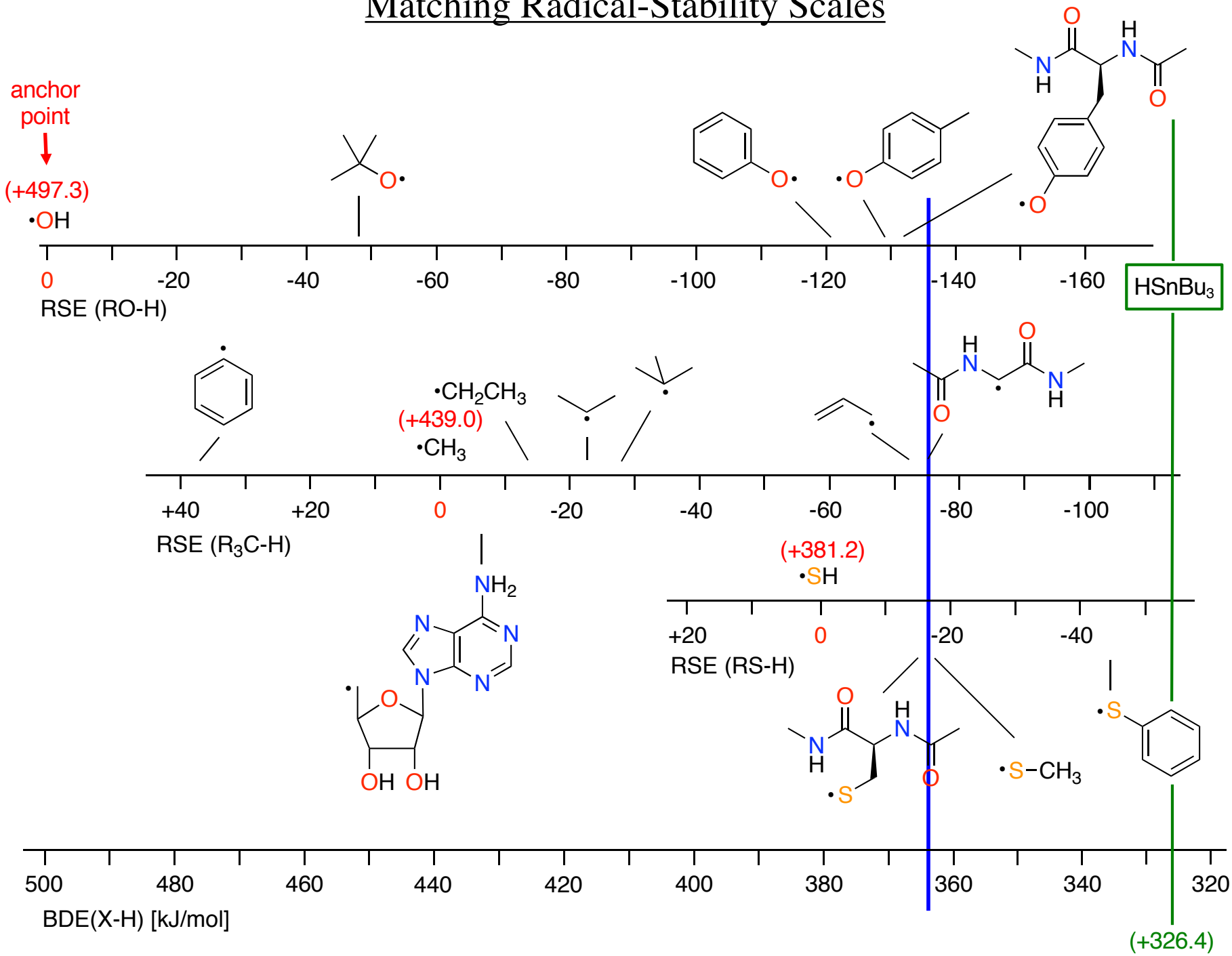
TEMPO - A Persistent Oxygen-Centered Radical



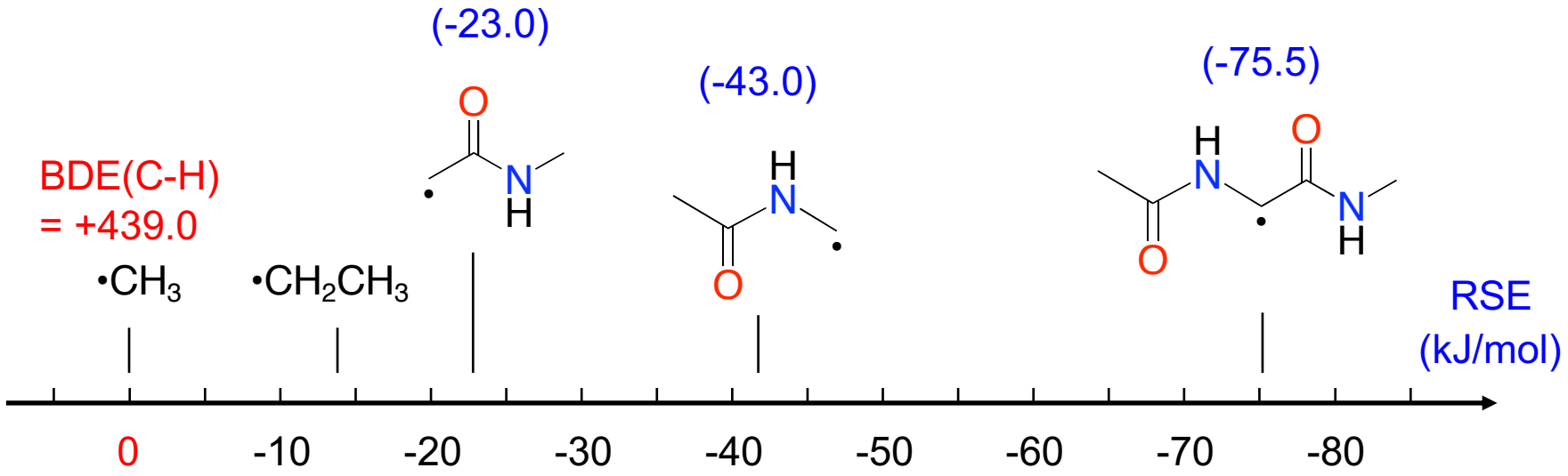
(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO)

- stable solid with mp = 36 °C
- mediator for living radical polymerization
- radical trap
- catalyst for oxidation reactions

Matching Radical-Stability Scales



Calculating Bond Dissociation Energies (BDE)

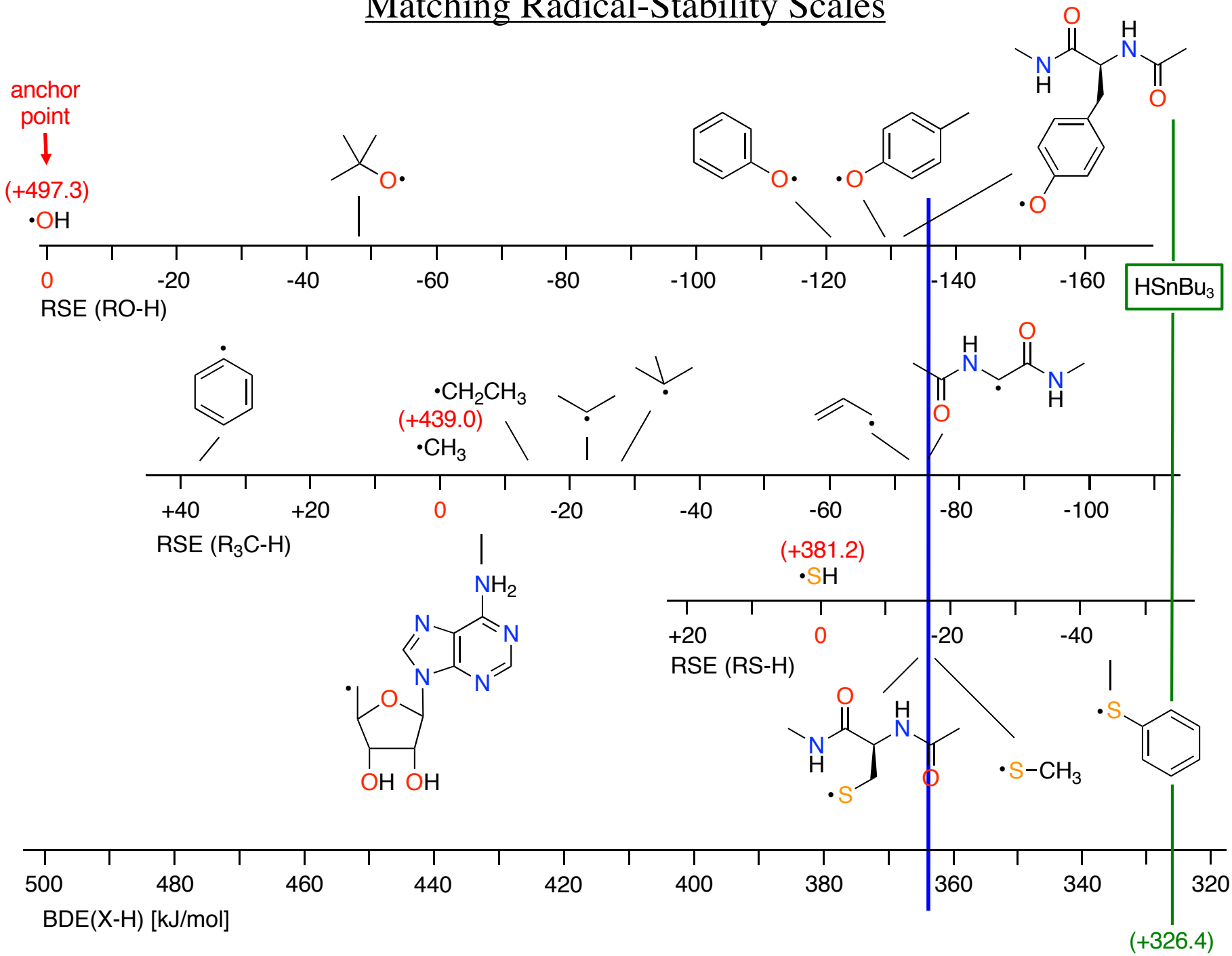


$$BDE(R\text{-}H) = BDE(CH_3\text{-}H) + RSE(R\bullet)$$

$$BDE(Gly\text{-}H) = +439.0 - 75.5 = +363.5 \text{ kJ/mol}$$

ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

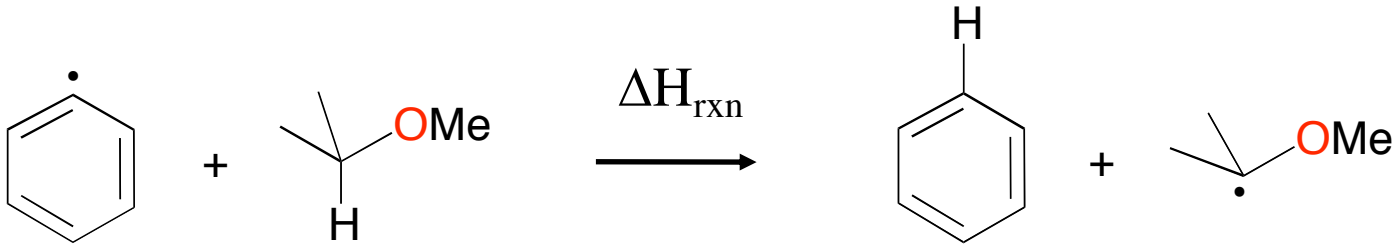
Matching Radical-Stability Scales



Calculating Hydrogen-Transfer Reaction Energies

$$\bullet R_1 + R_2\text{-}H \xrightarrow{\Delta H_{rxn}} R_1\text{-}H + R_2\bullet$$

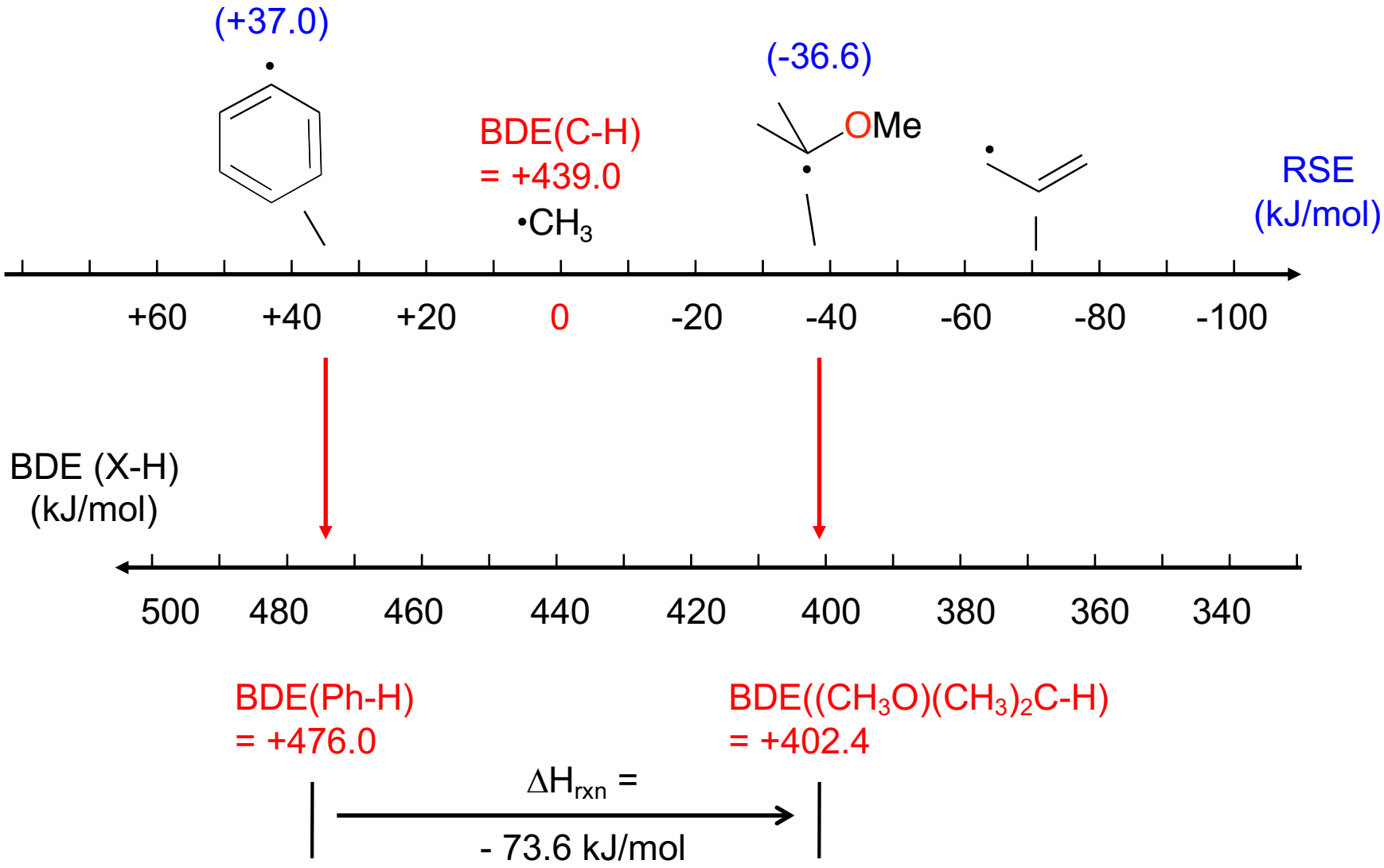
$$\Delta H_{rxn} = BDE(R_2\text{-}H) - BDE(R_1\text{-}H)$$



$$\Delta H_{rxn} = BDE((CH_3O)(CH_3)_2C\text{-}H) - BDE(Ph\text{-}H)$$

ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

Calculating Hydrogen-Transfer Reaction Energies

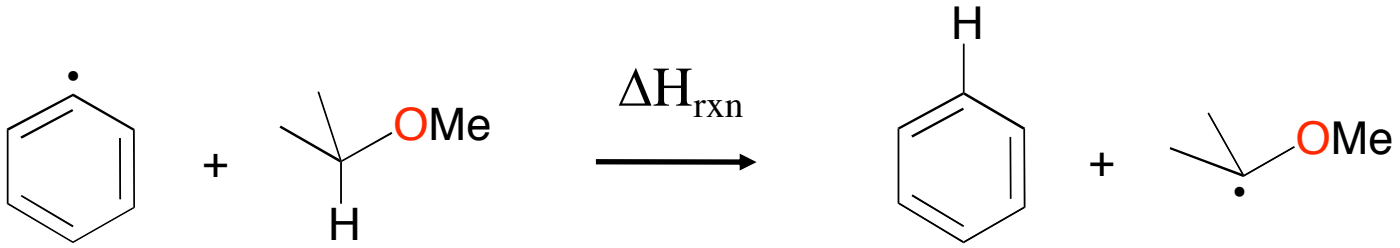


ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

Calculating Hydrogen-Transfer Reaction Energies

$$\bullet R_1 + R_2\text{-}H \xrightarrow{\Delta H_{rxn}} R_1\text{-}H + R_2\bullet$$

$$\Delta H_{rxn} = BDE(R_2\text{-}H) - BDE(R_1\text{-}H)$$



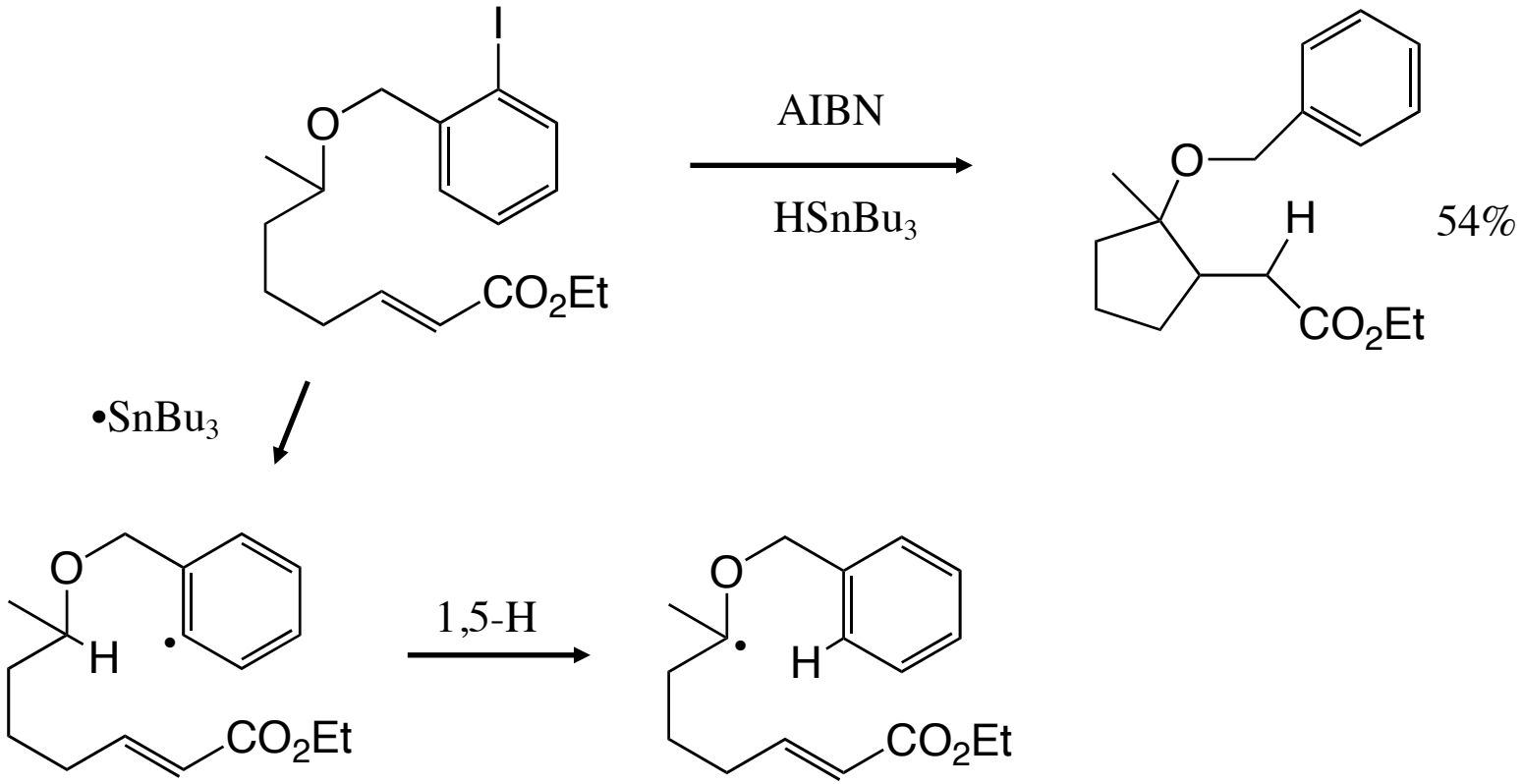
$$\Delta H_{rxn} = BDE((CH_3O)(CH_3)_2C\text{-}H) - BDE(Ph\text{-}H)$$

$$\Delta H_{rxn} = 402.4 - 476.0 = -73.6 \text{ kJ/mol}$$

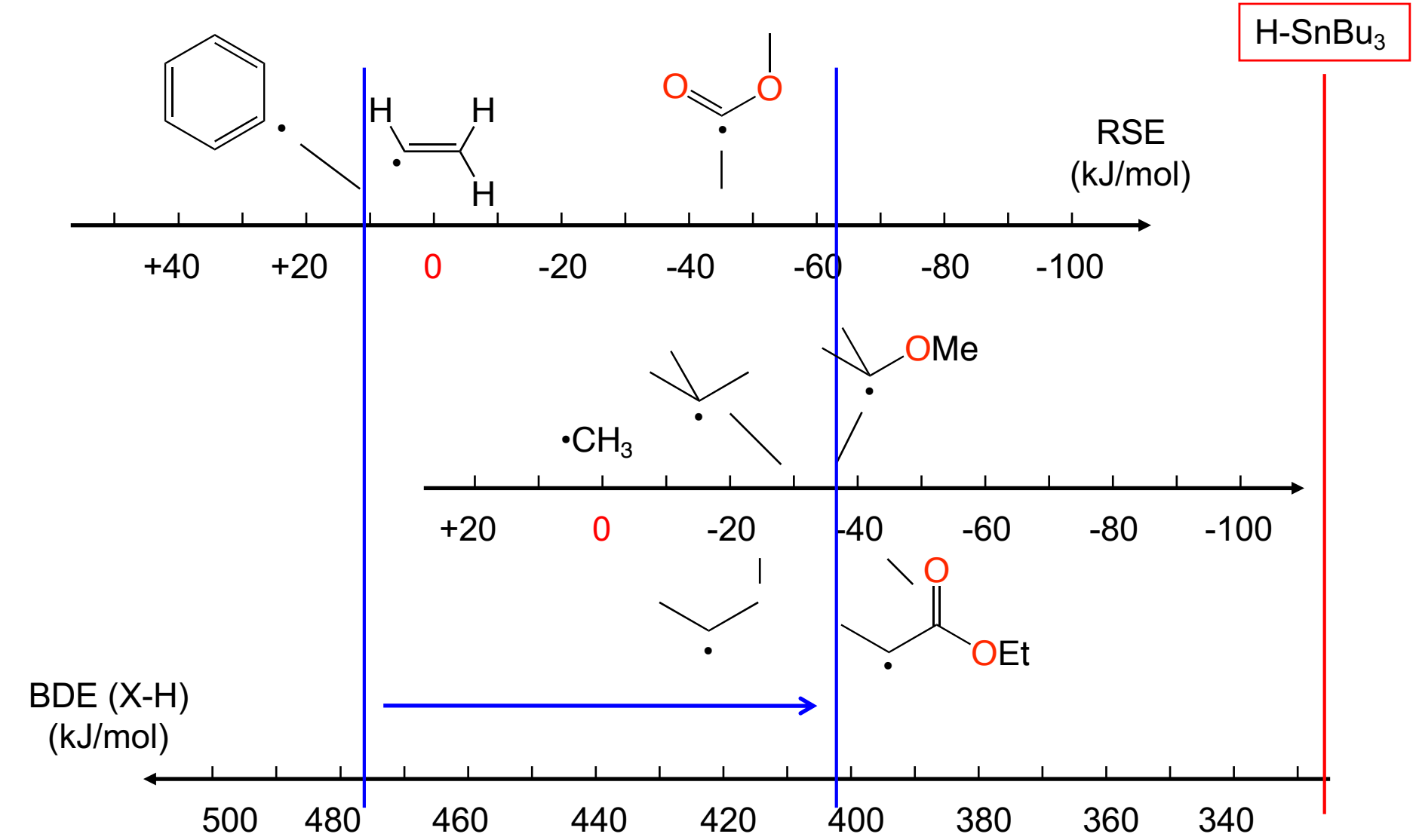
ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

Protecting Group/Radical Translocating (PRT) Reactions

D. P. Curran et al., *J. Am. Chem. Soc.* **1988**, *110*, 5900.



Matching Radical-Stability Scales



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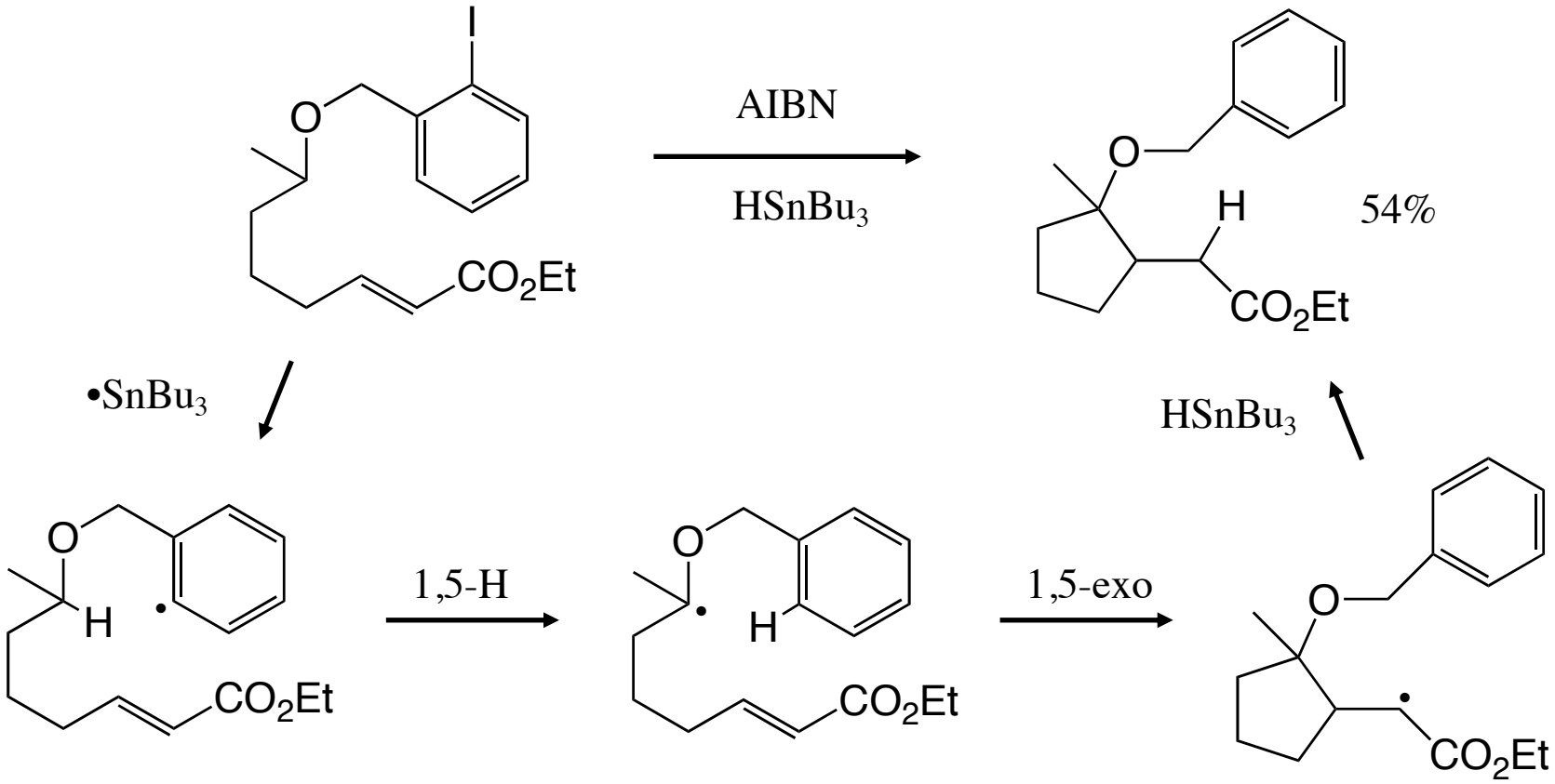

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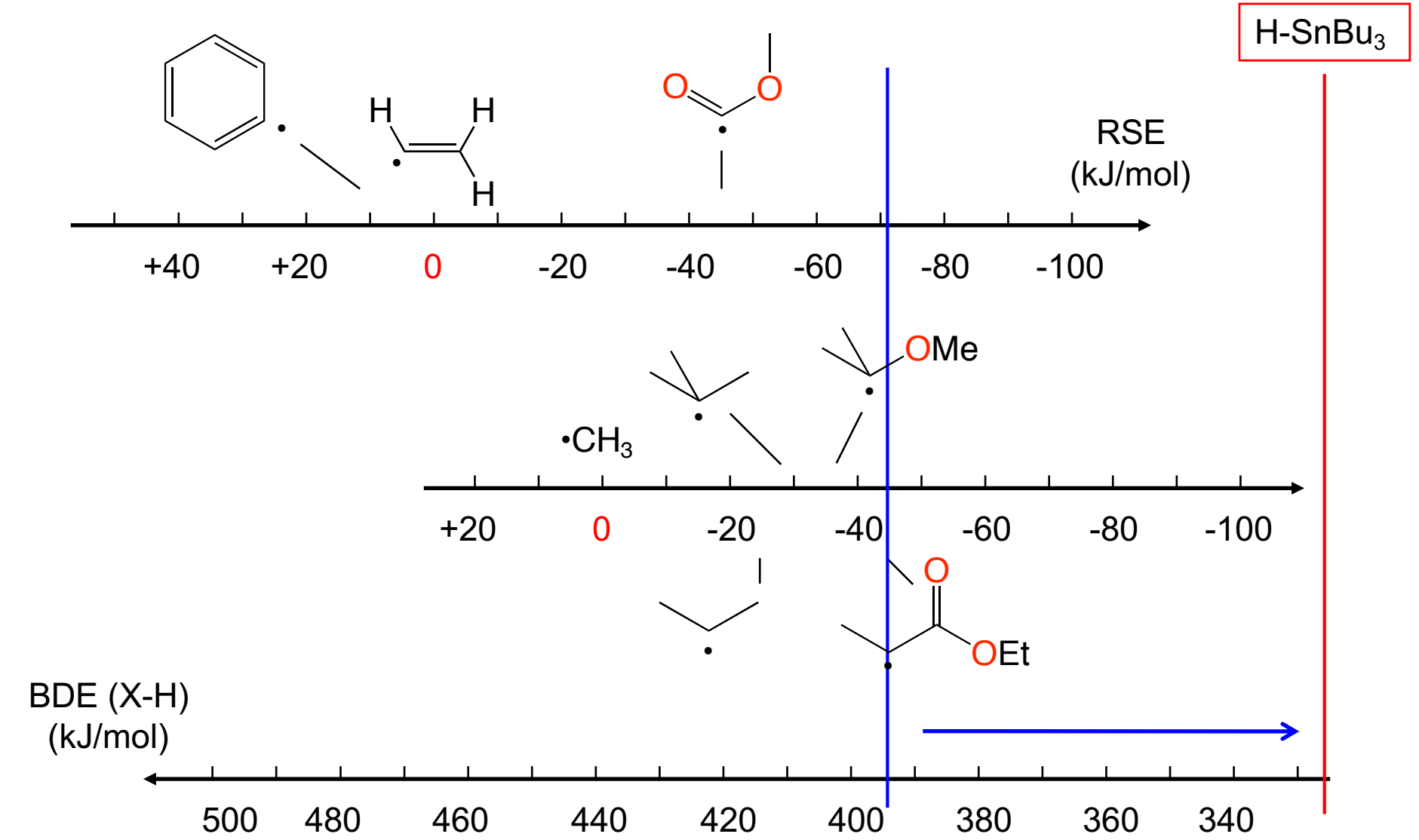

ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

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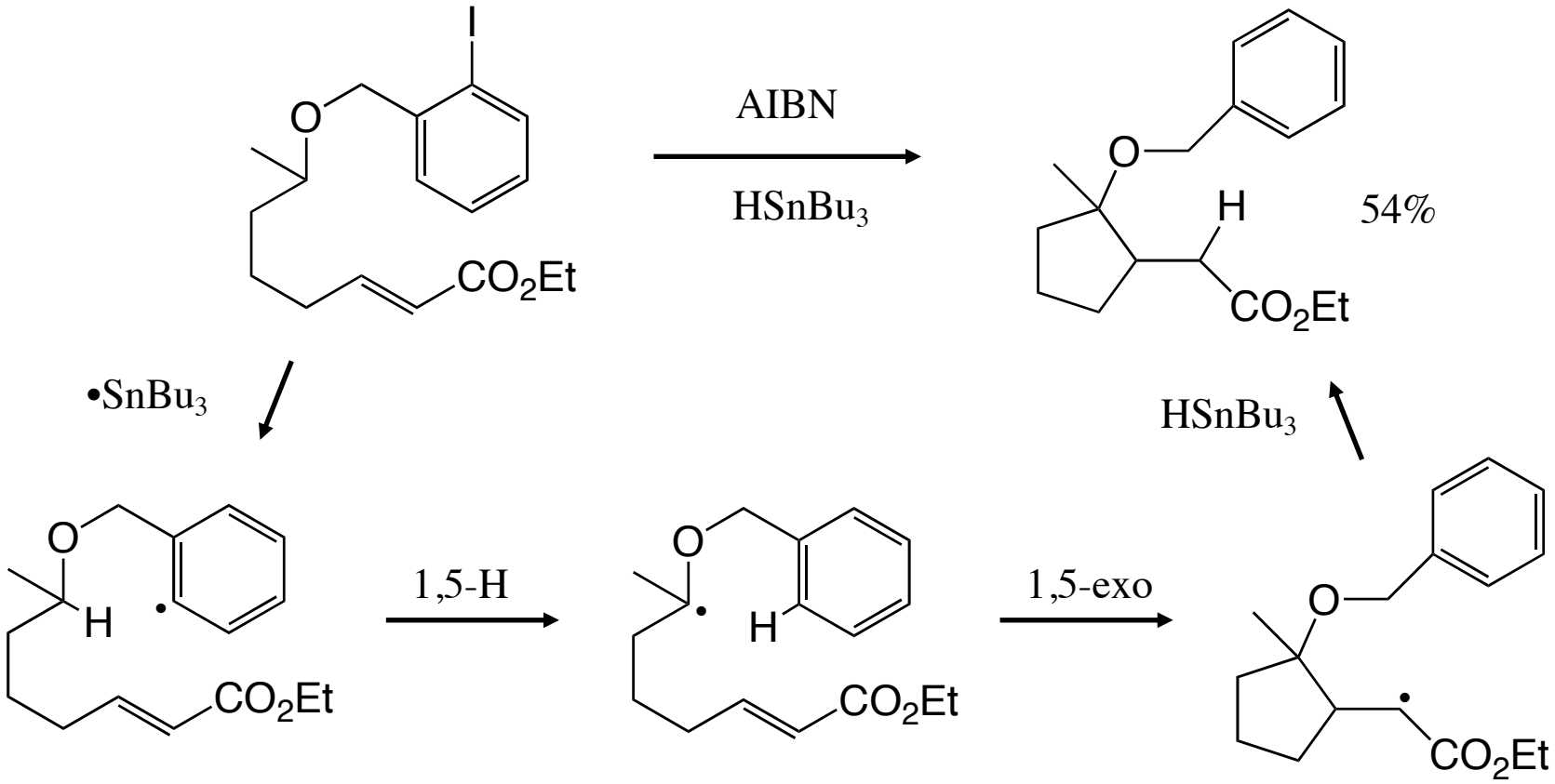

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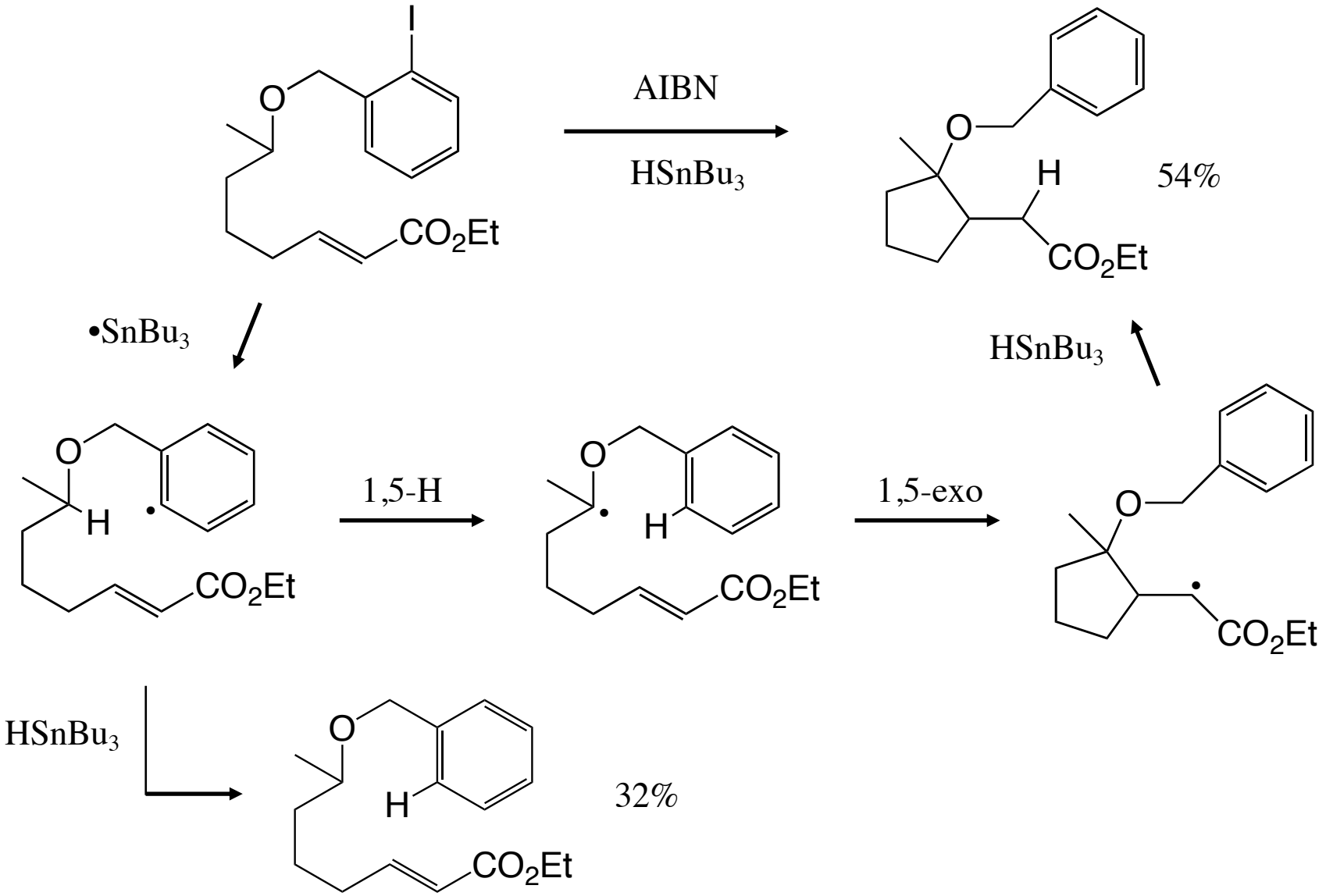

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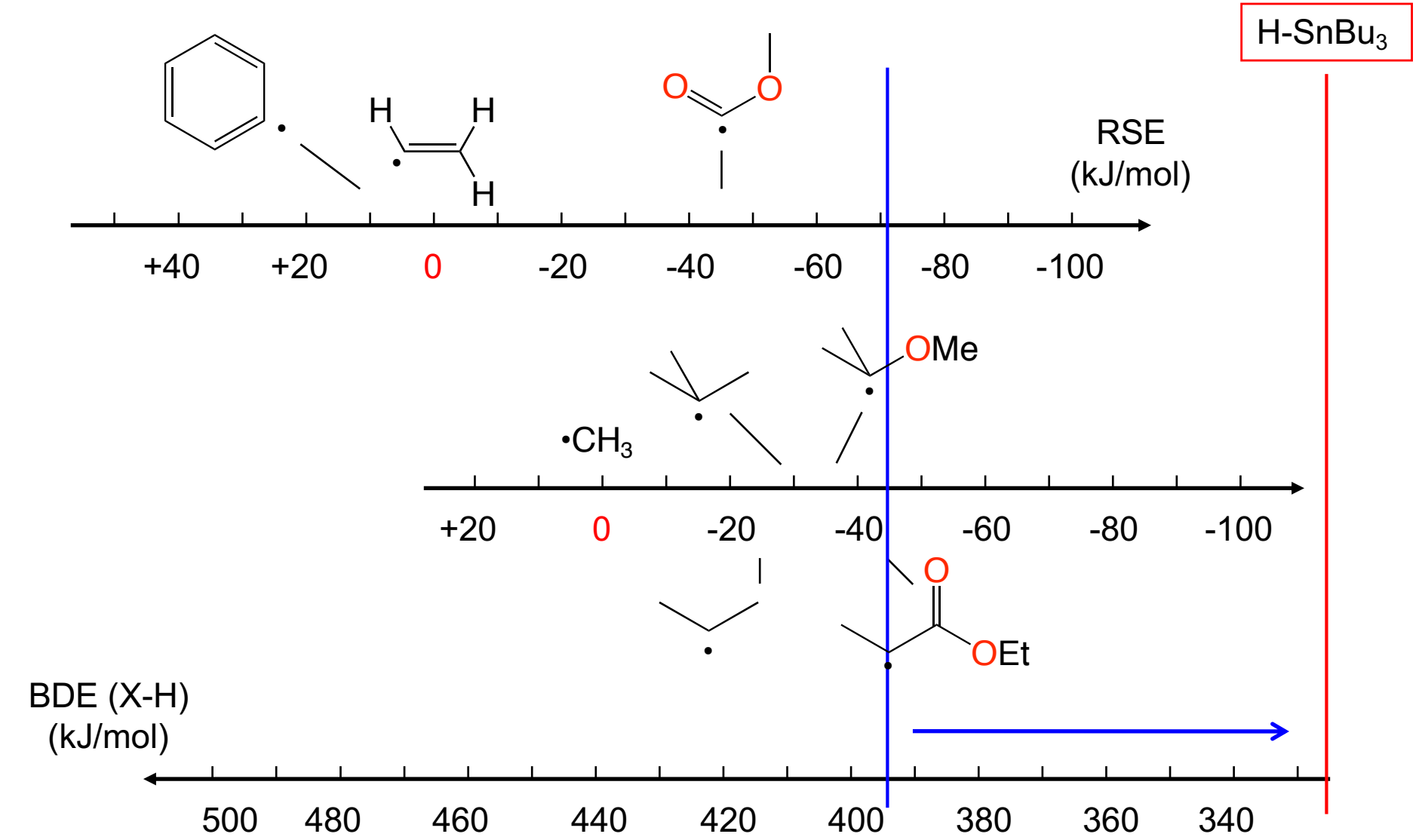

ΔH_{298}(G3(MP2)-RAD) [kJ/mol]

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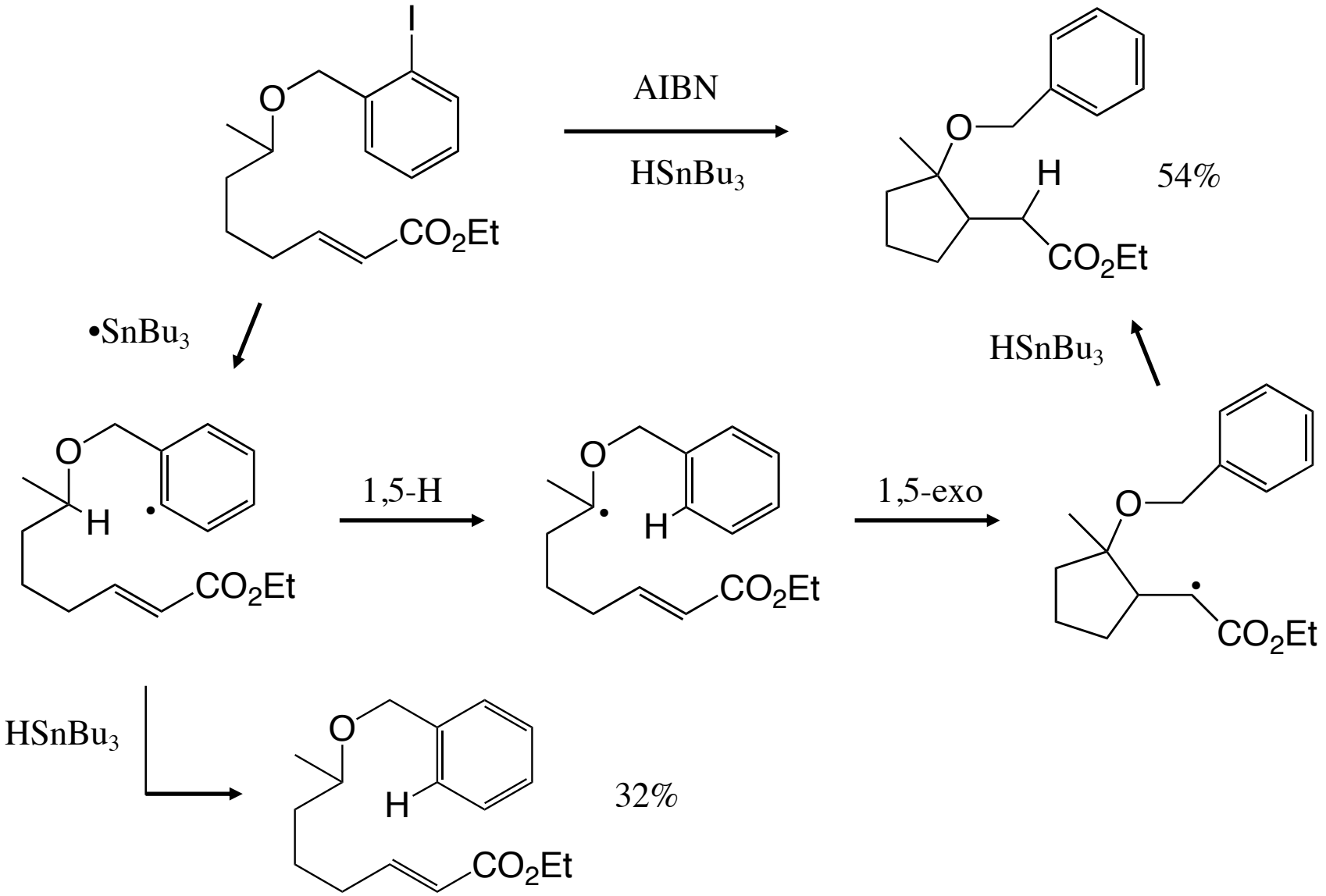

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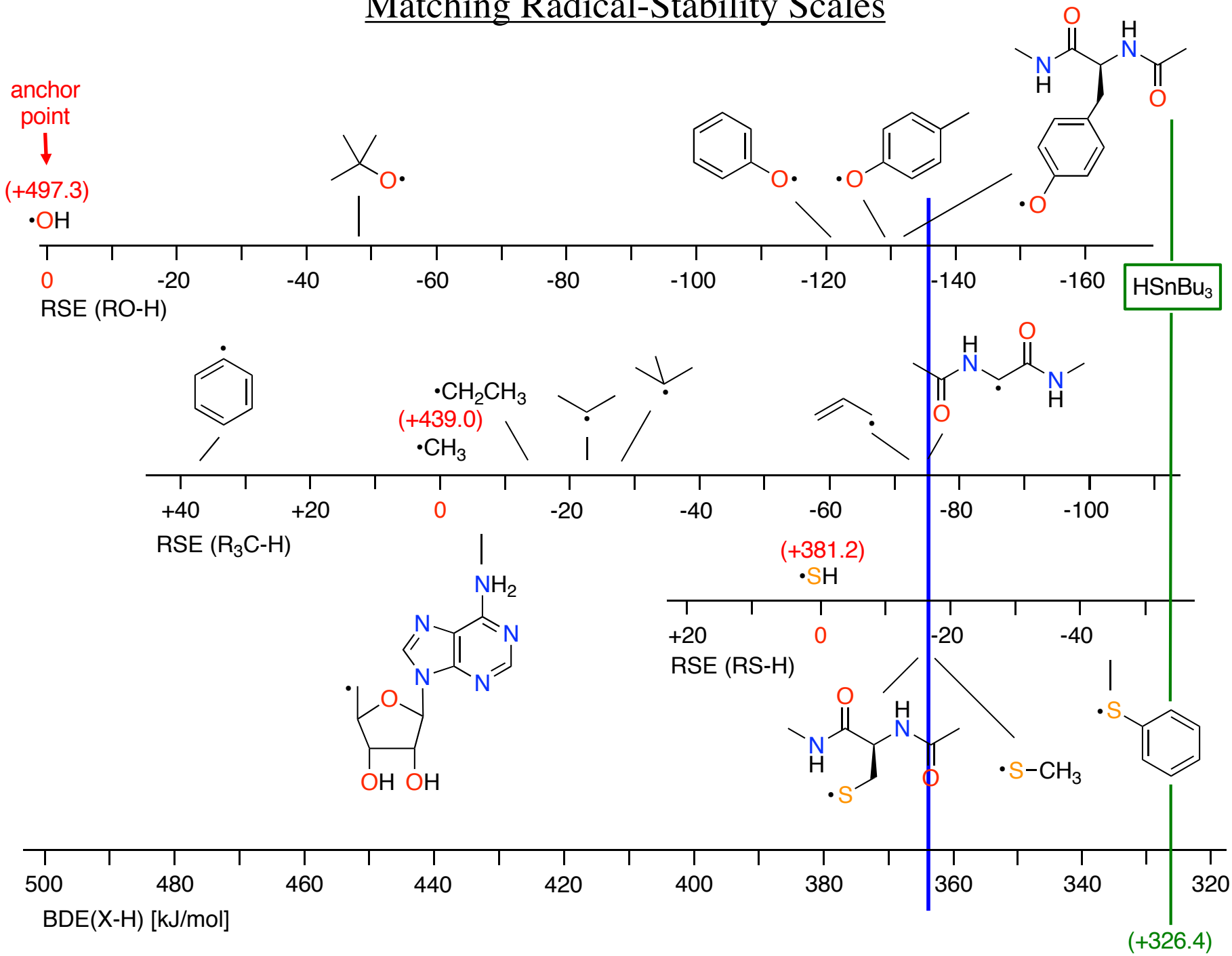

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