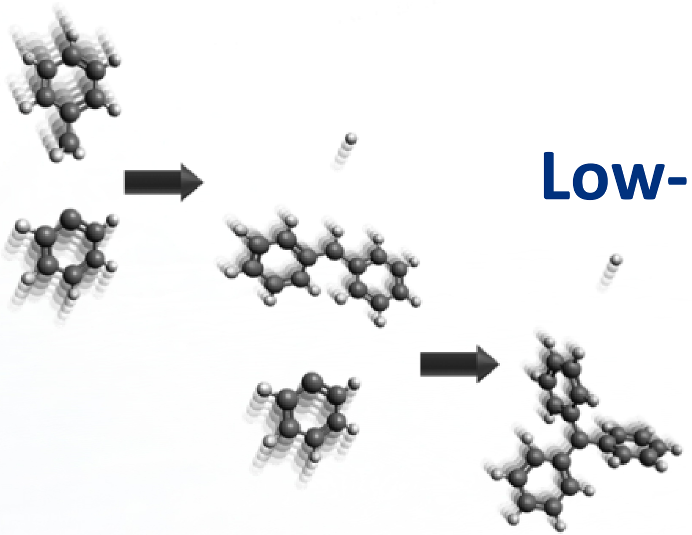
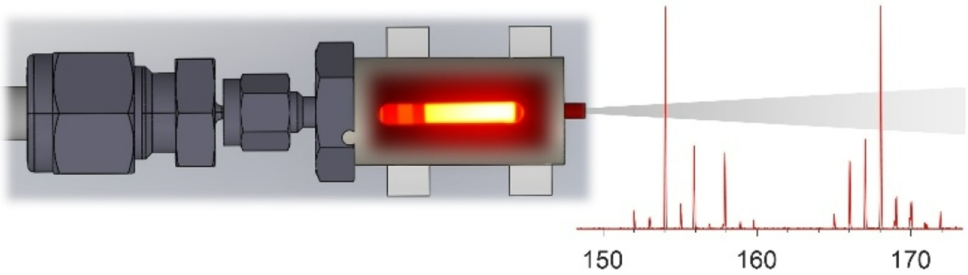
SAND2022-11233C



# Radical-radical chain reactions: Low-pressure gas-phase aromatic growth



**David Couch**, Myrsini San Marchi, Angie Zhang, Craig Taatjes, Nils Hansen

Combustion Research Facility, Sandia National Laboratories

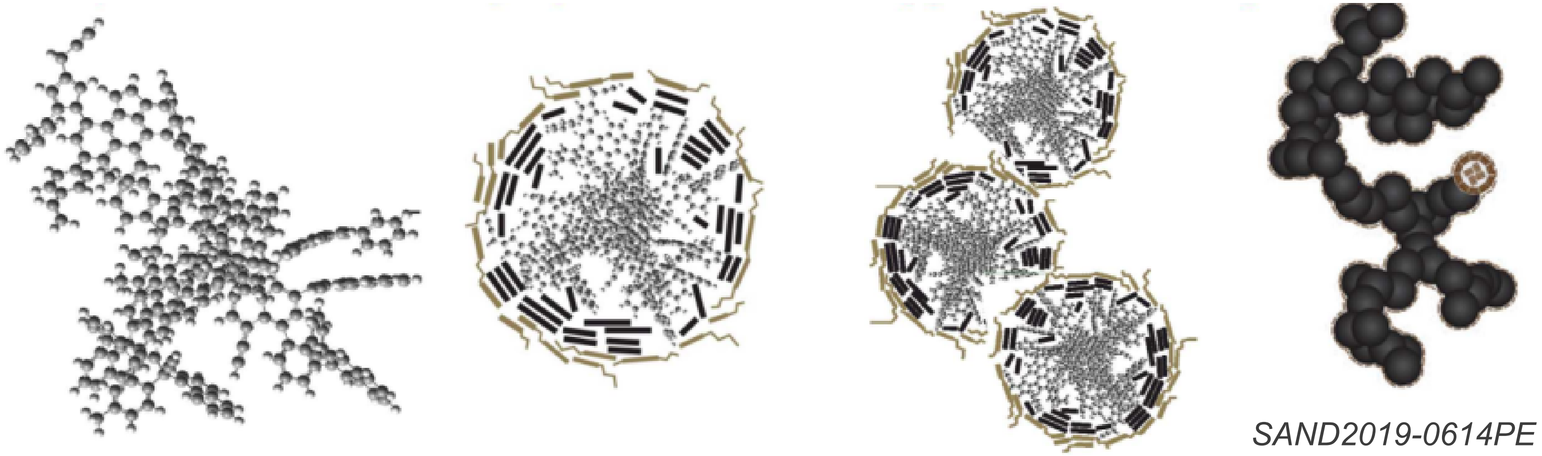
August 21, 2022

# Soot forms fast. What about nanomaterials?

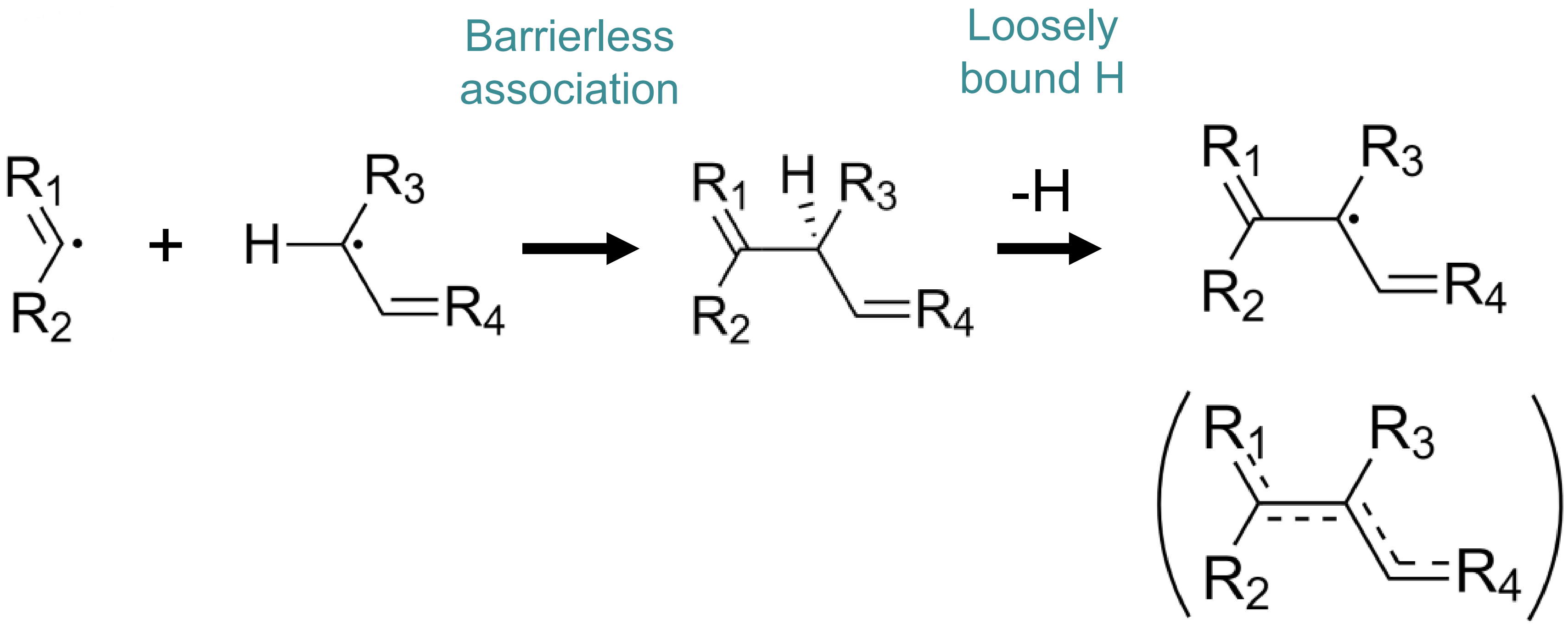
- In flames and engines, soot particles form in nanoseconds
- Gas phase reactions produce an aromatic jumble
- Flat polycyclic aromatic hydrocarbons (PAHs) stick to the young “particle”

2 big questions in the soot formation community:

- What reactions lead to a particle forming so fast?
- Can we use these reactions to quickly grow useful nanomaterials?

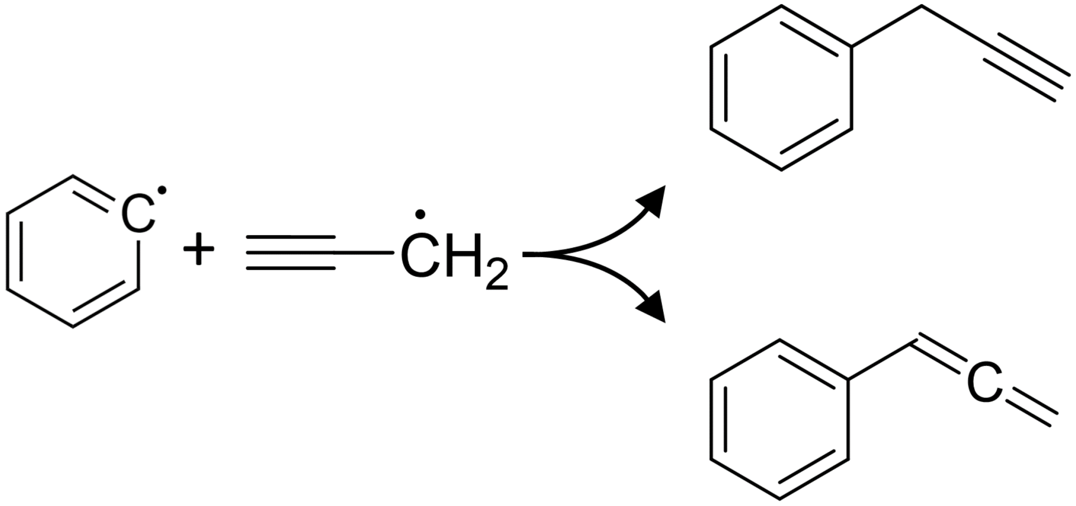


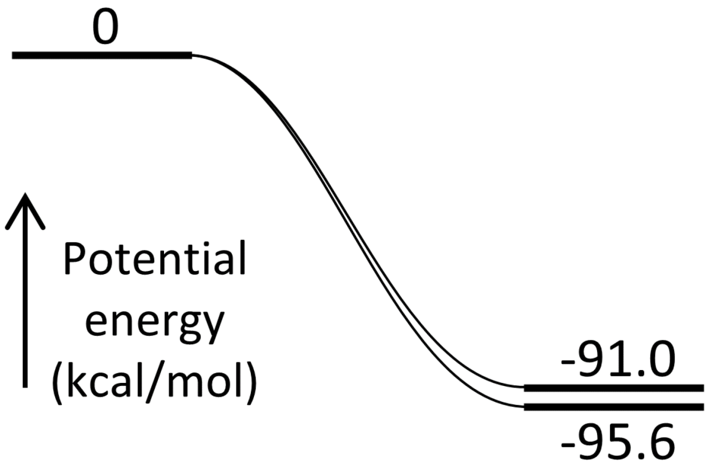
# $\sigma + \pi$ reactions are good radical-propagating candidates



Highly conjugated radical

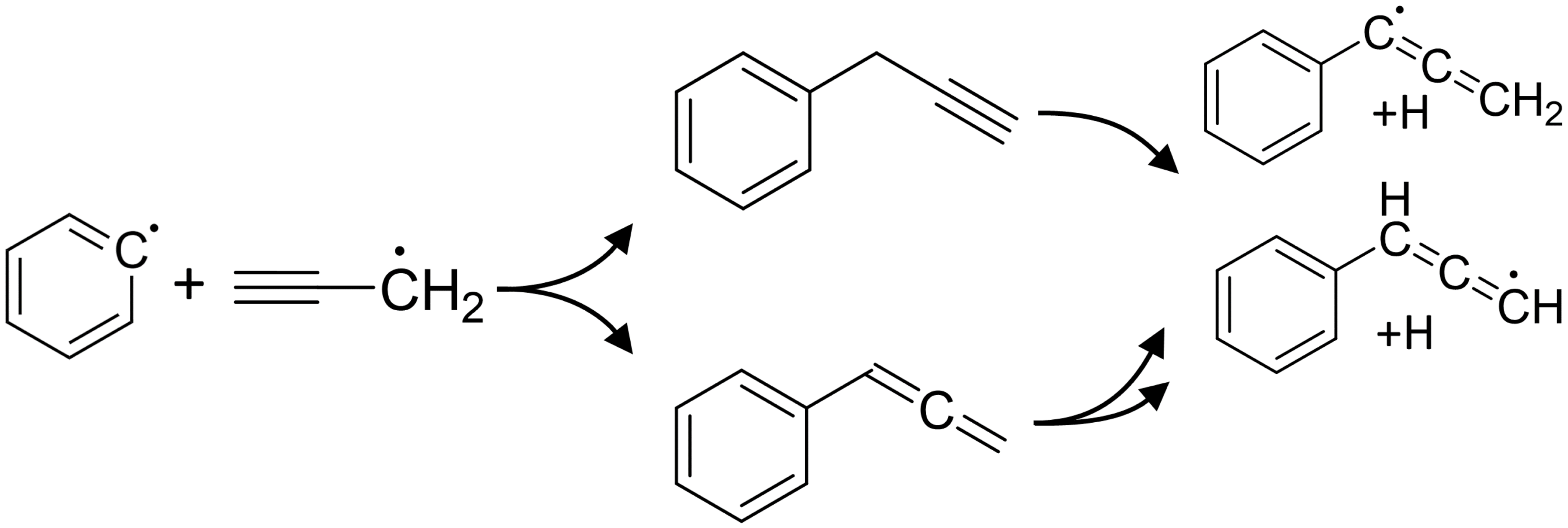
# Phenyl + propargyl

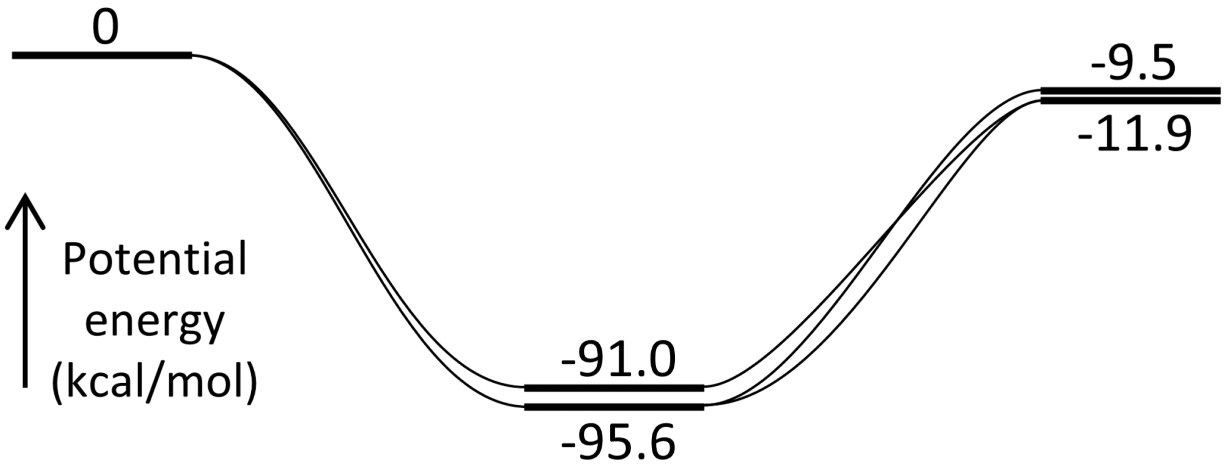




*Energies from Morozov et al., PCCP **2020**, 22, 6868-6880*

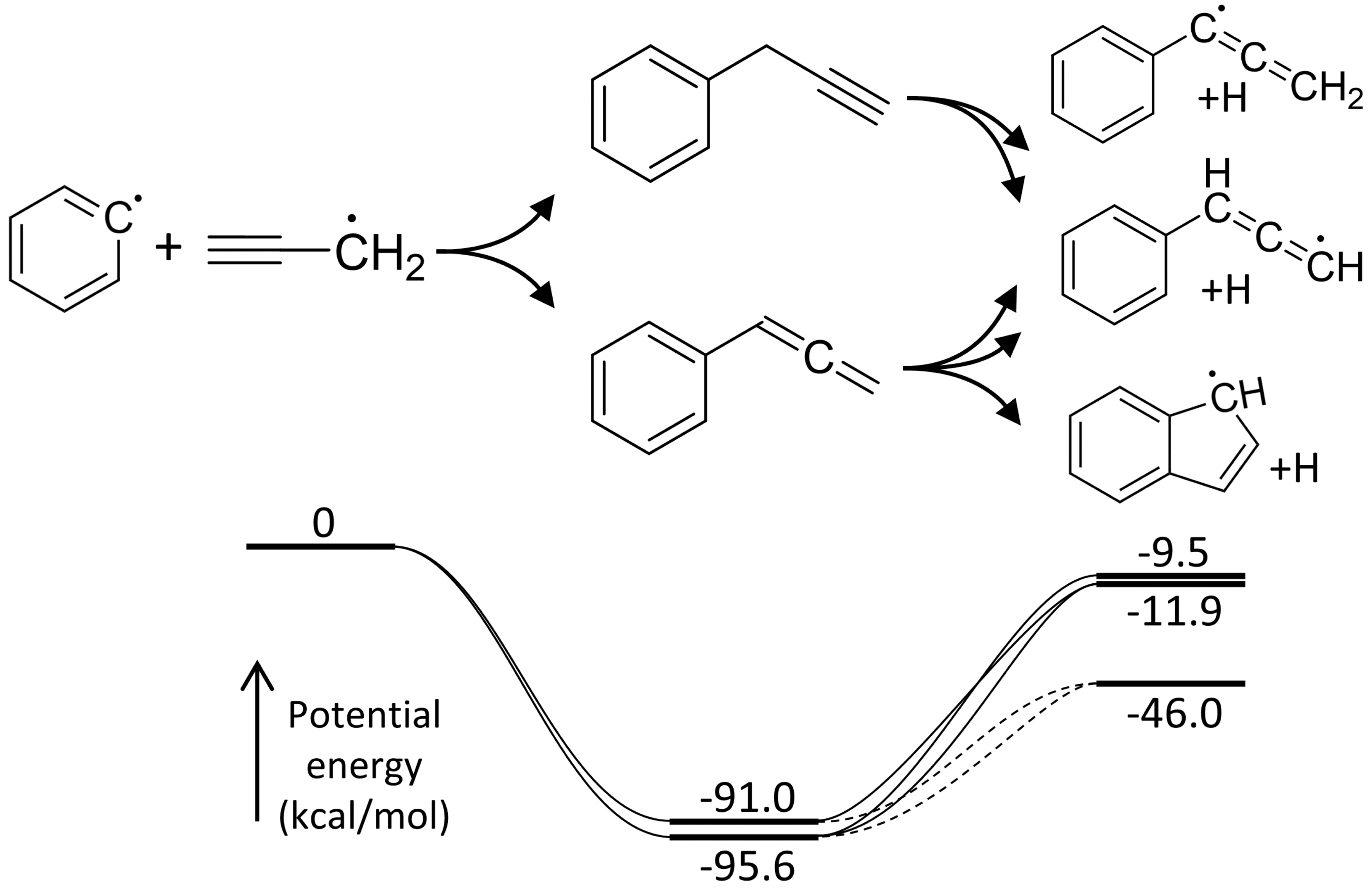
# Phenyl + propargyl





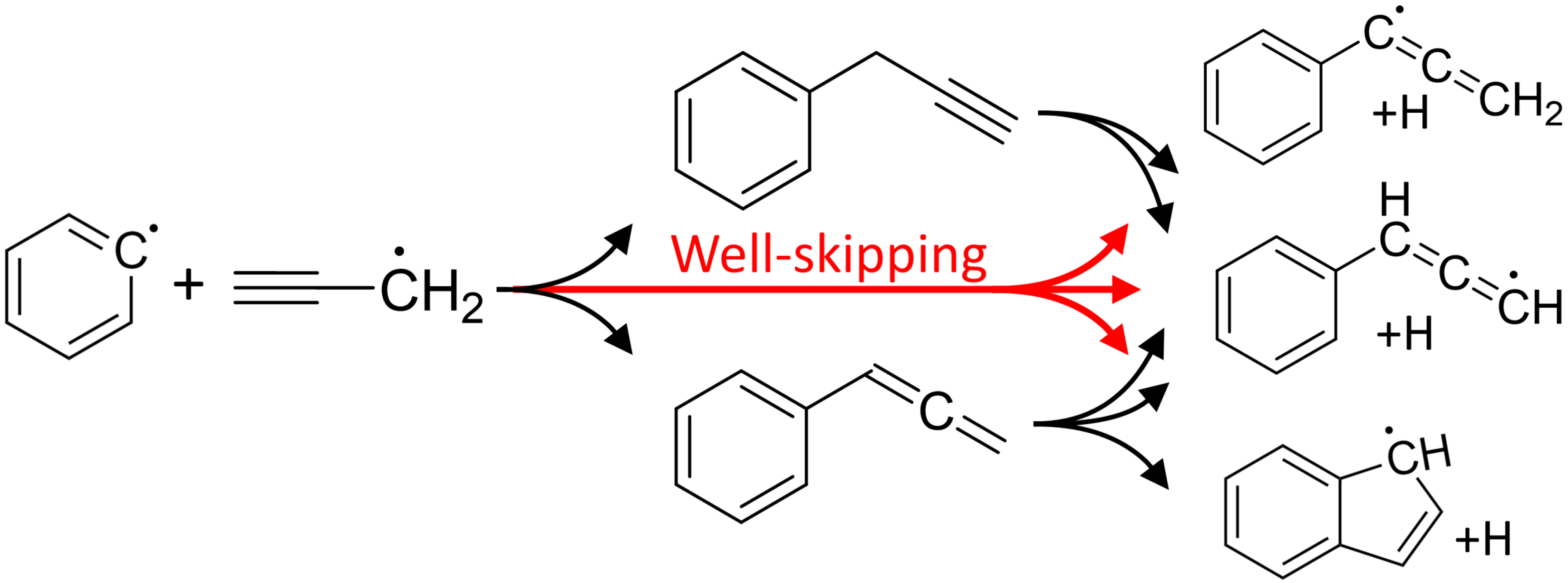
*Energies from Morozov et al., PCCP* ***2020****, 22, 6868-6880*

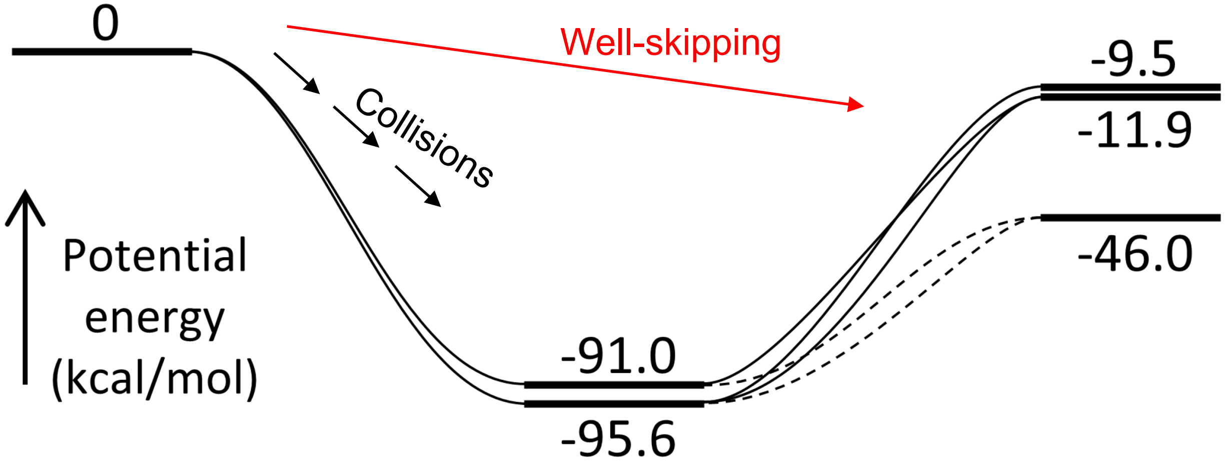
# Phenyl + propargyl



*Energies from Morozov et al., PCCP* ***2020****, 22, 6868-6880*

# Phenyl + propargyl



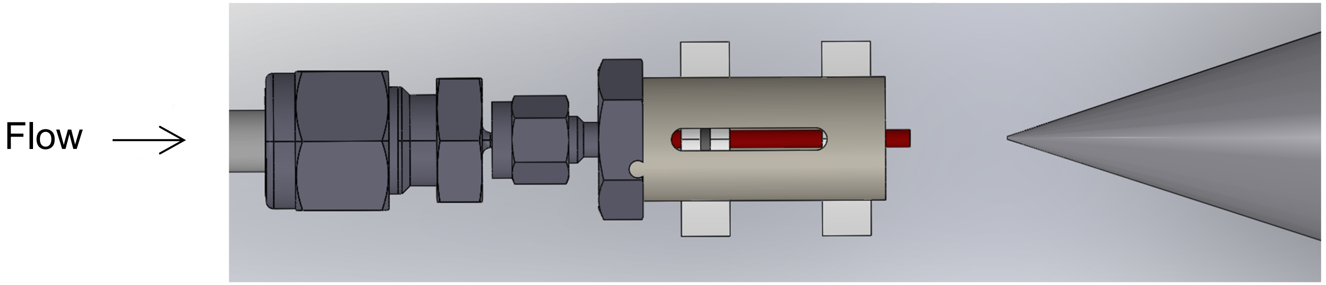


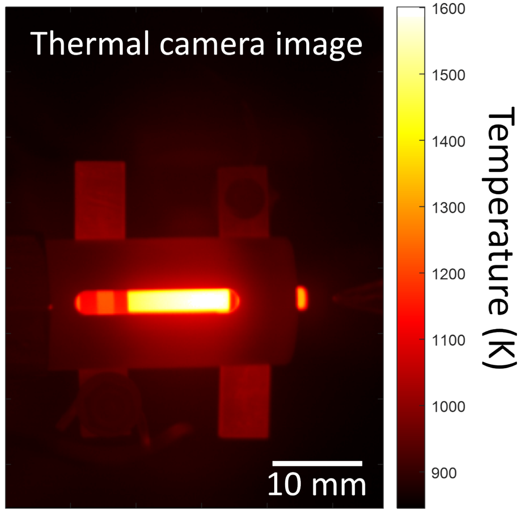
*Energies from Morozov et al., PCCP **2020**, 22, 6868-6880*

# Apparatus

- Flash pyrolysis ($\sim 100\ \mu s$)

30 Torr, 1600 K silicon carbide tube



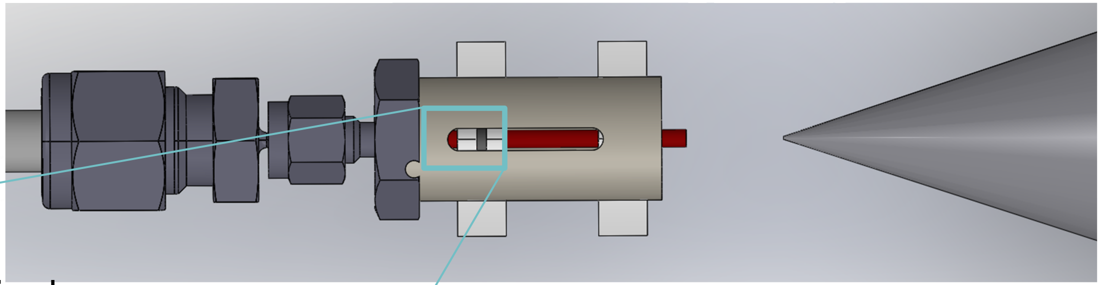


# Apparatus

- Flash pyrolysis (~100 $\mu s$)

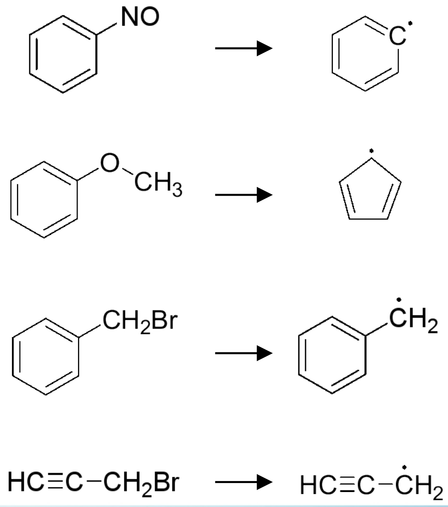
30 Torr, 1600 K silicon carbide tube

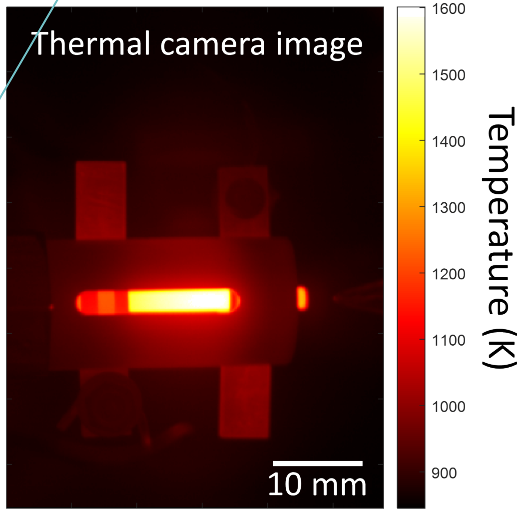
Gas flow (99.8% Helium) →



Commercially available

Desired radicals



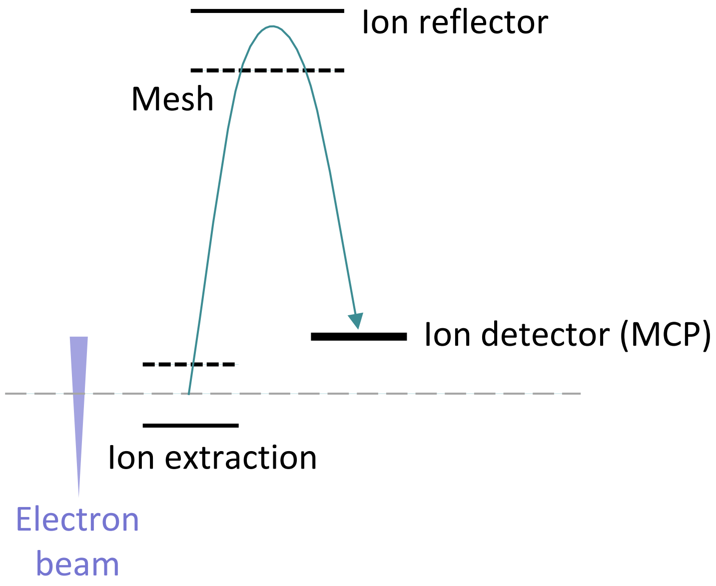


# Apparatus

- Flash pyrolysis ($\sim$100 $\mu s$) followed by electron-ionization mass spectrometry

- Flash pyrolysis ($\sim$100 $\mu s$) followed by electron-ionization mass spectrometry

Reflectron mass spectrometer



# Apparatus

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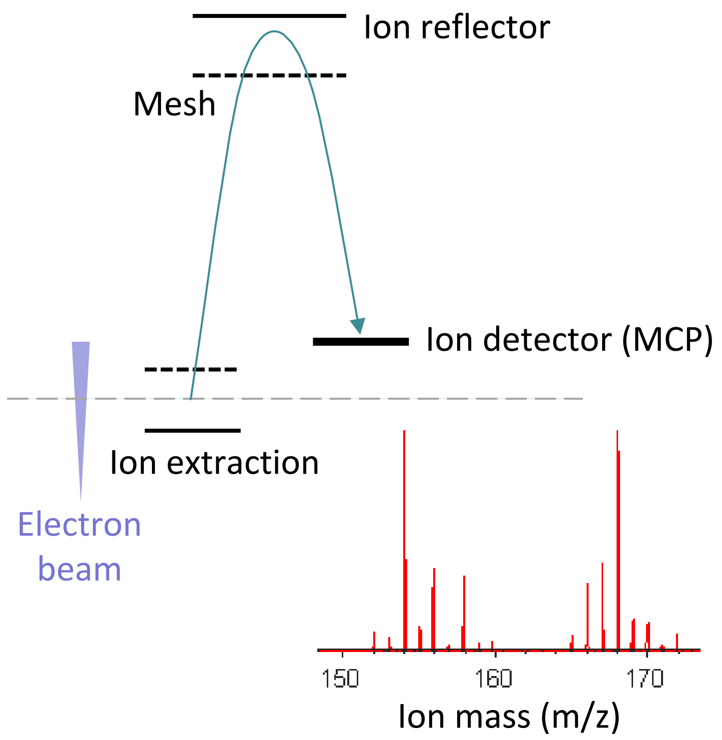
Reflectron mass spectrometer



# Apparatus

- Flash pyrolysis (~100 $\mu s$) followed by electron-ionization mass spectrometry

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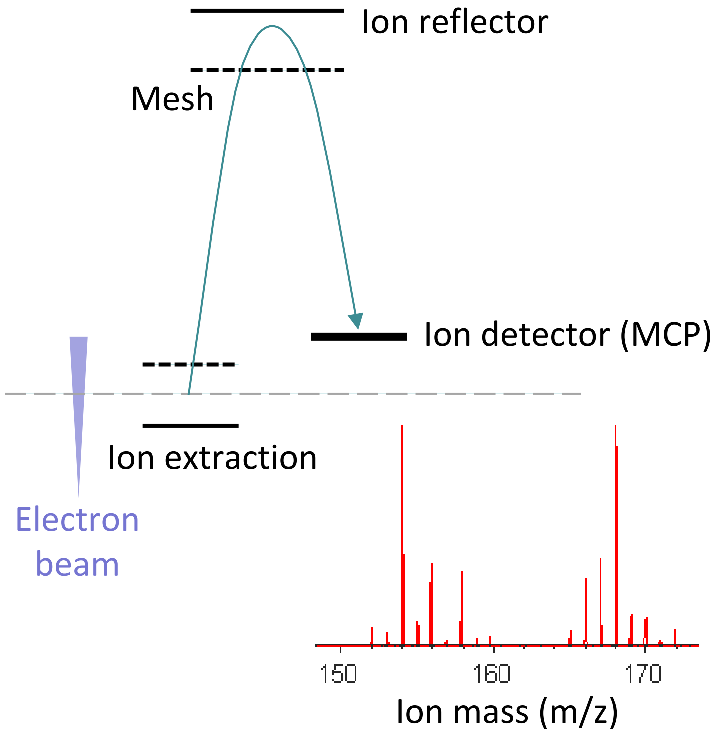
Reflectron mass spectrometer

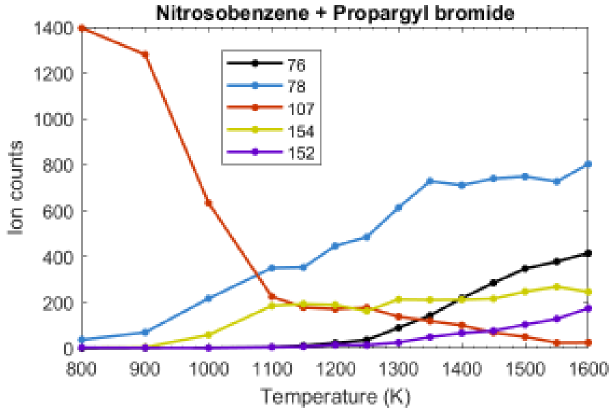

Ion reflector

Mesh

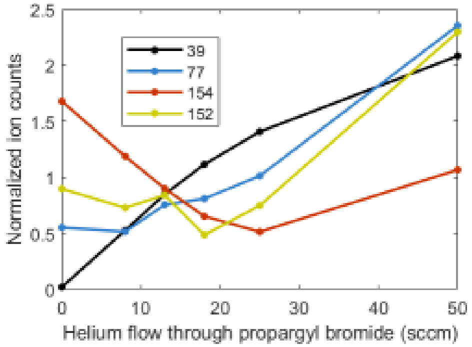
Ion detector (MCP)

Ion extraction

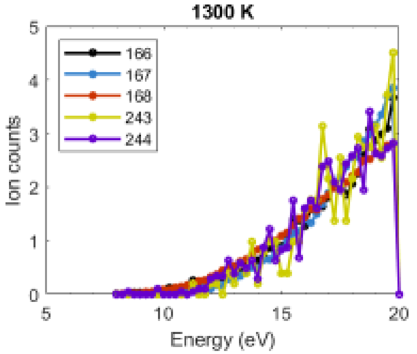
Electron beam



Temperature

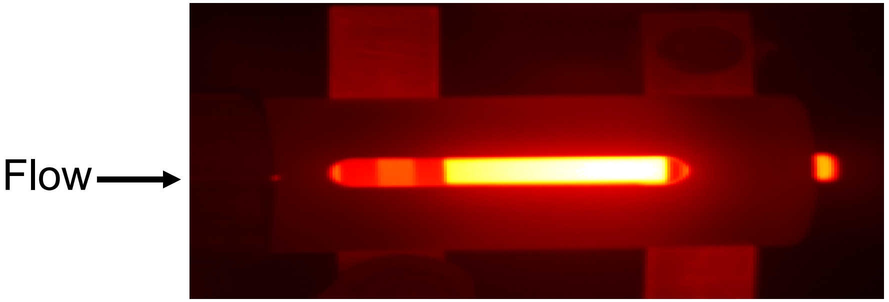


Reactant concentration

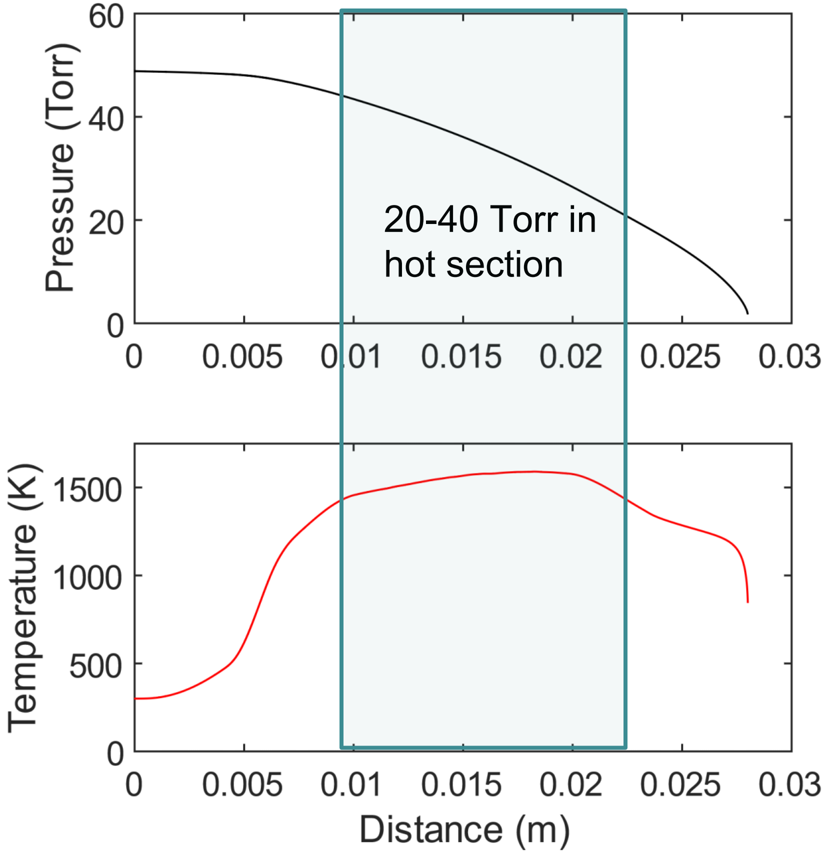


Electron energy

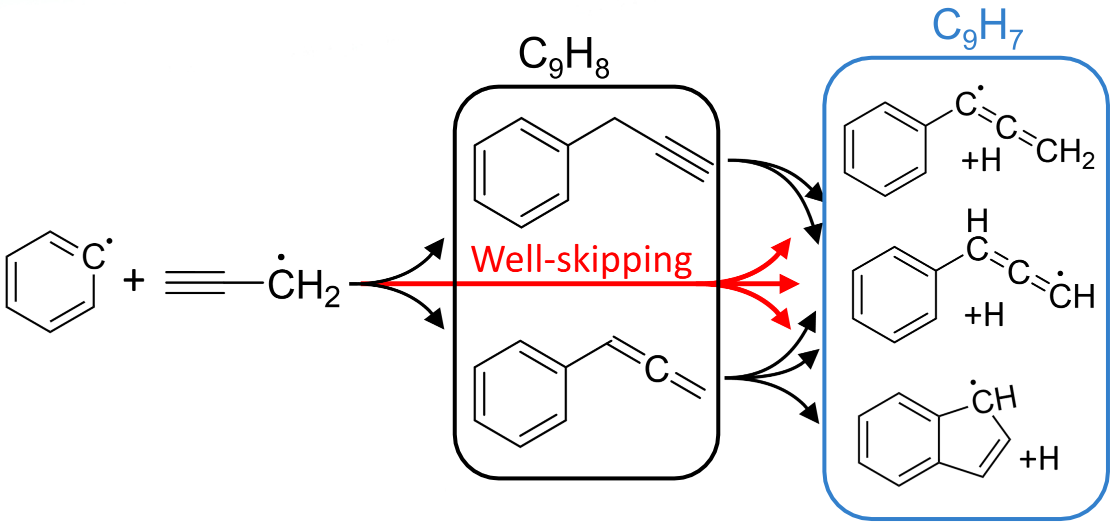
# Flow simulation allows comparison to models

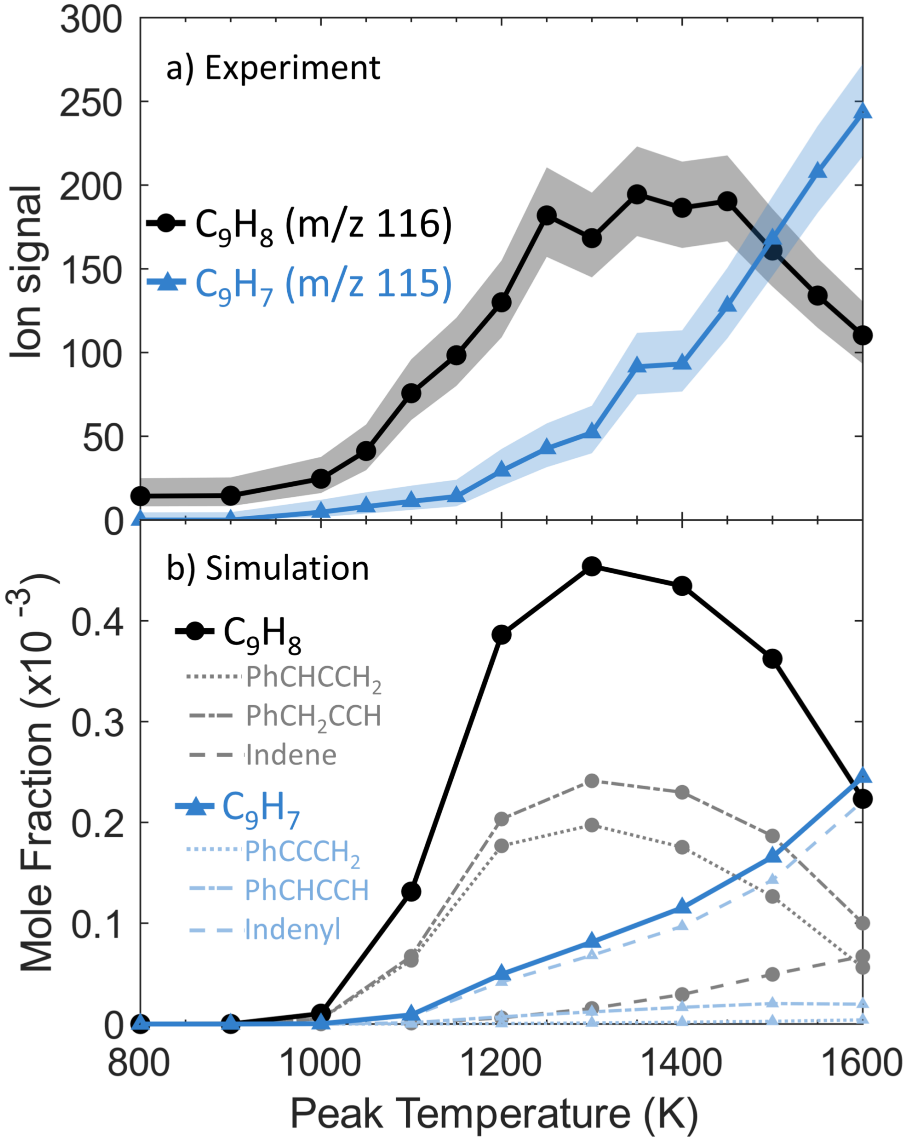


- Reactor has varying pressure and temperature
- Flow properties and chemical kinetics and are solved simultaneously
- We simulate the flow using a boundary-layer model
  - *Weddle, et al., Int. J. Chem. Kin.* ***2018****, 50, 473-480*



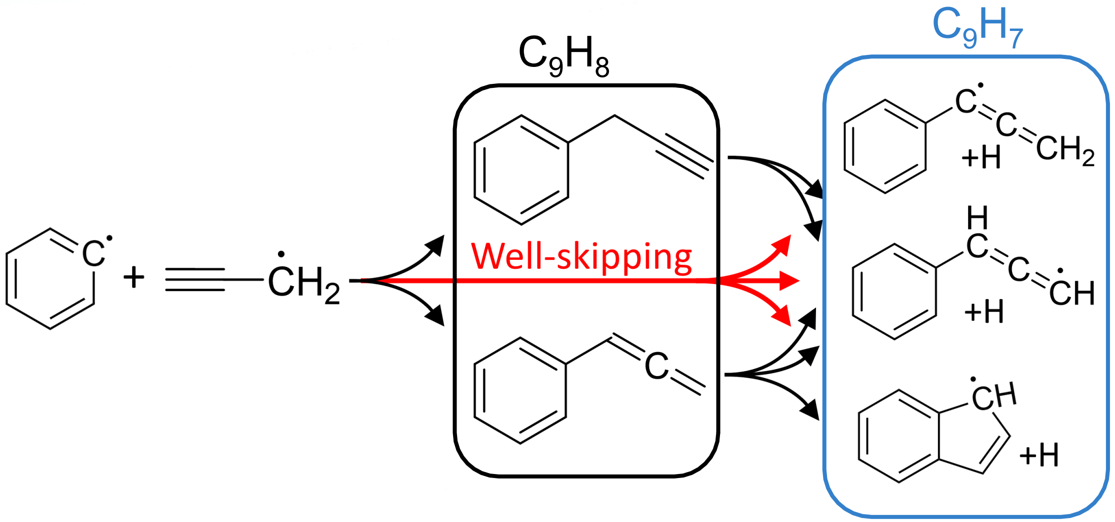
# Phenyl + Propargyl
# Agreement between experiment and simulation



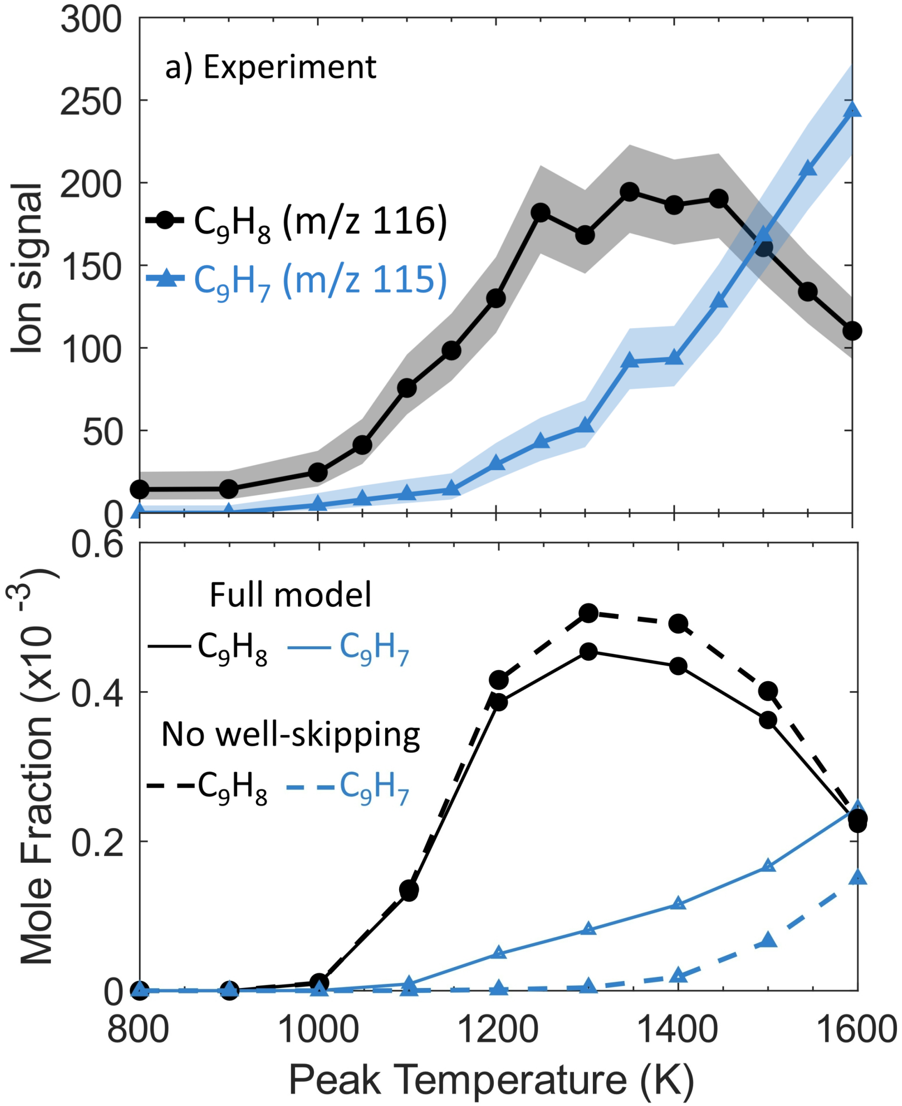


- The experiment cannot distinguish isomers
- The simulation mostly agrees with experiment
- $C_9H_7$ is mostly indenyl radical according to simulation

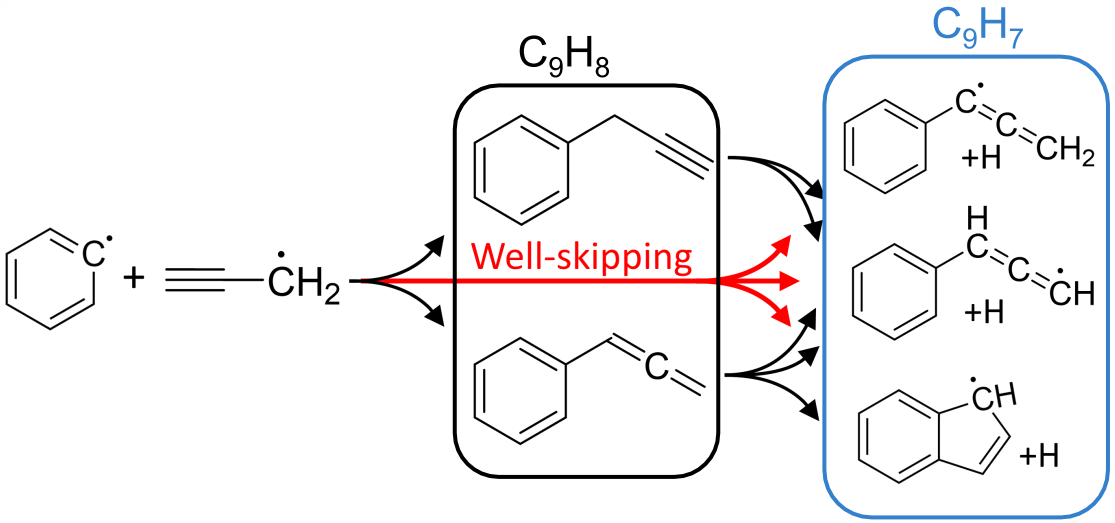
# Phenyl + Propargyl
## Large role of well-skipping at 30 Torr

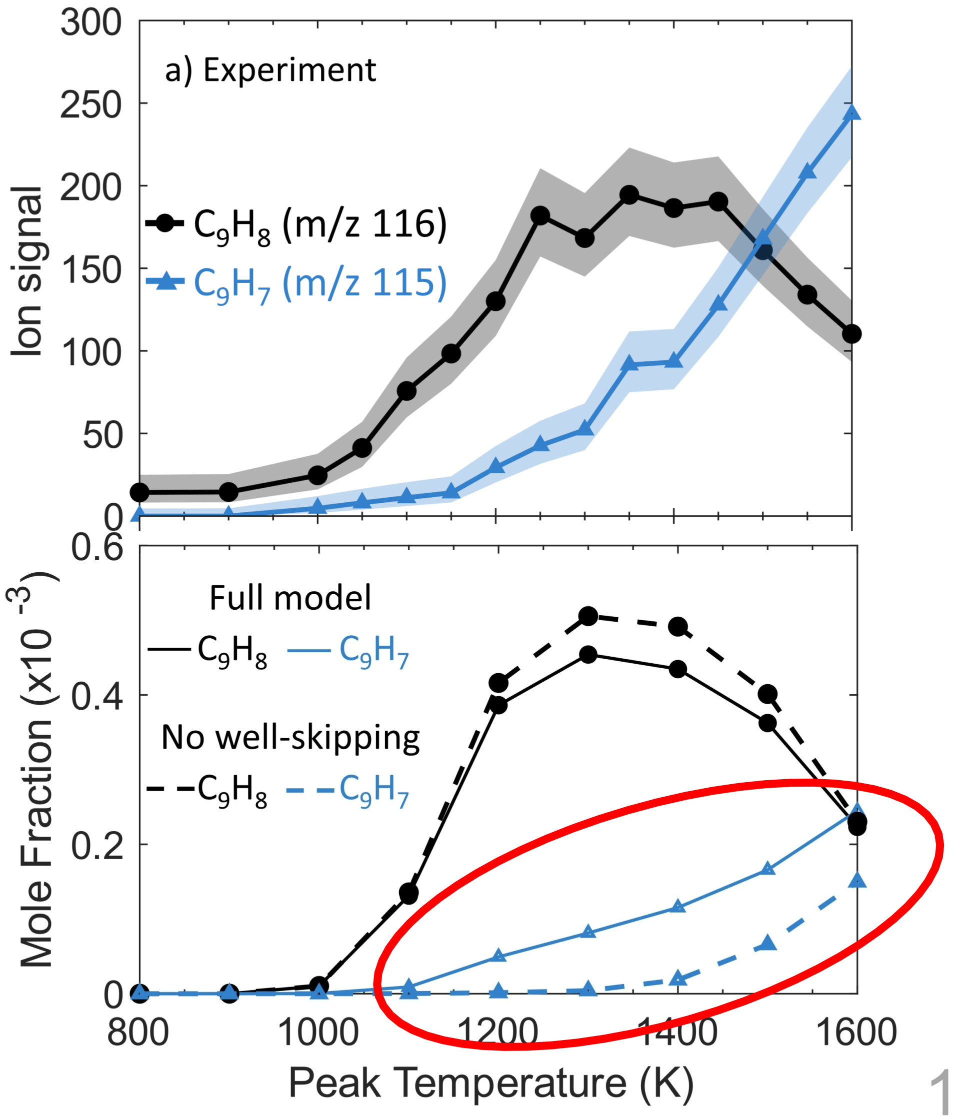


- We cut well-skipping from the simulation



# Phenyl + Propargyl
# Large role of well-skipping at 30 Torr

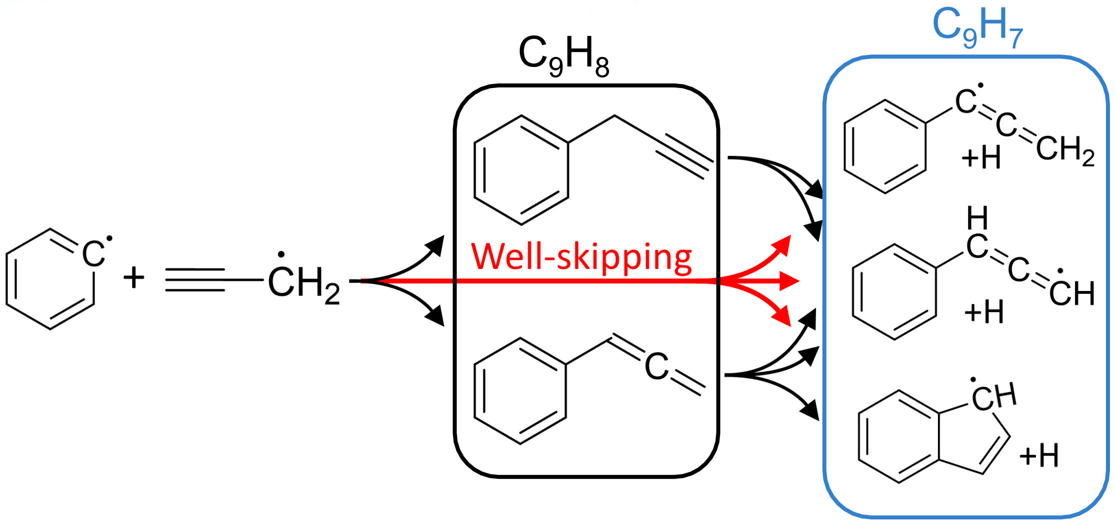


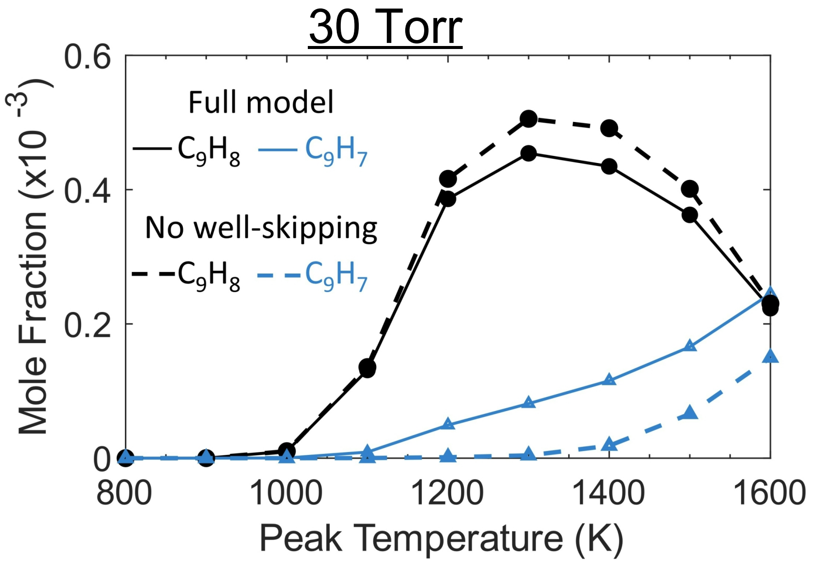


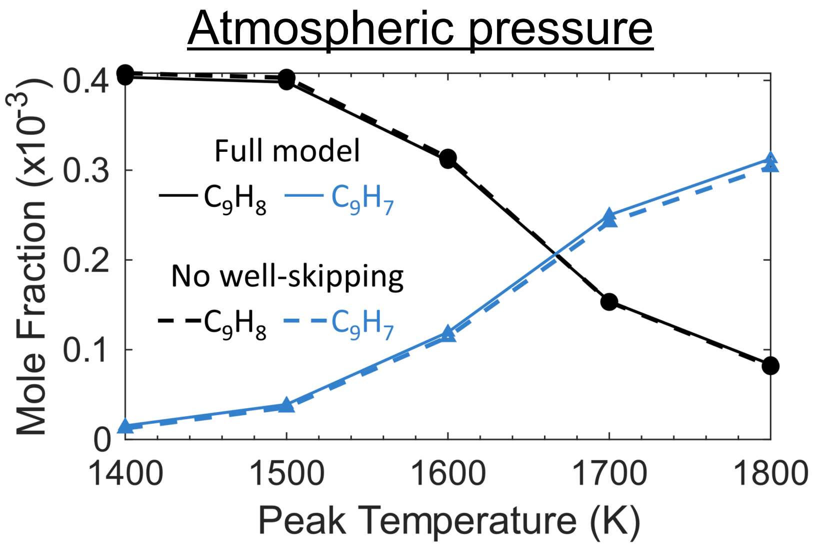
- We cut well-skipping from the simulation
- $C_9H_7$ yield changes, no longer agrees with experiment
- Conclusion – well-skipping is the dominant source of $C_9H_7$ here
  - Though $C_9H_8$ yield is higher

# Phenyl + Propargyl

## Small role of well-skipping at atmospheric pressure



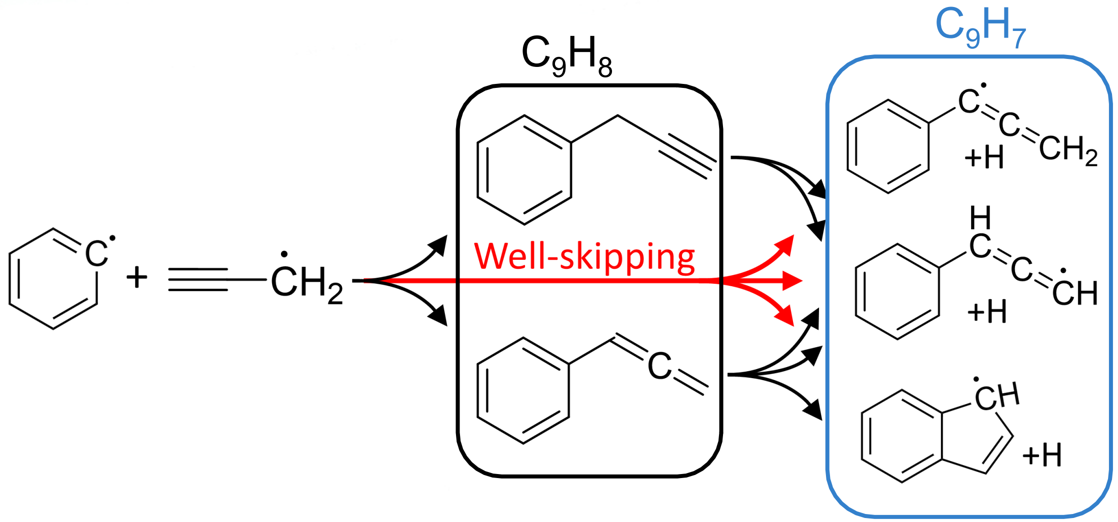

30 Torr


Atmospheric pressure

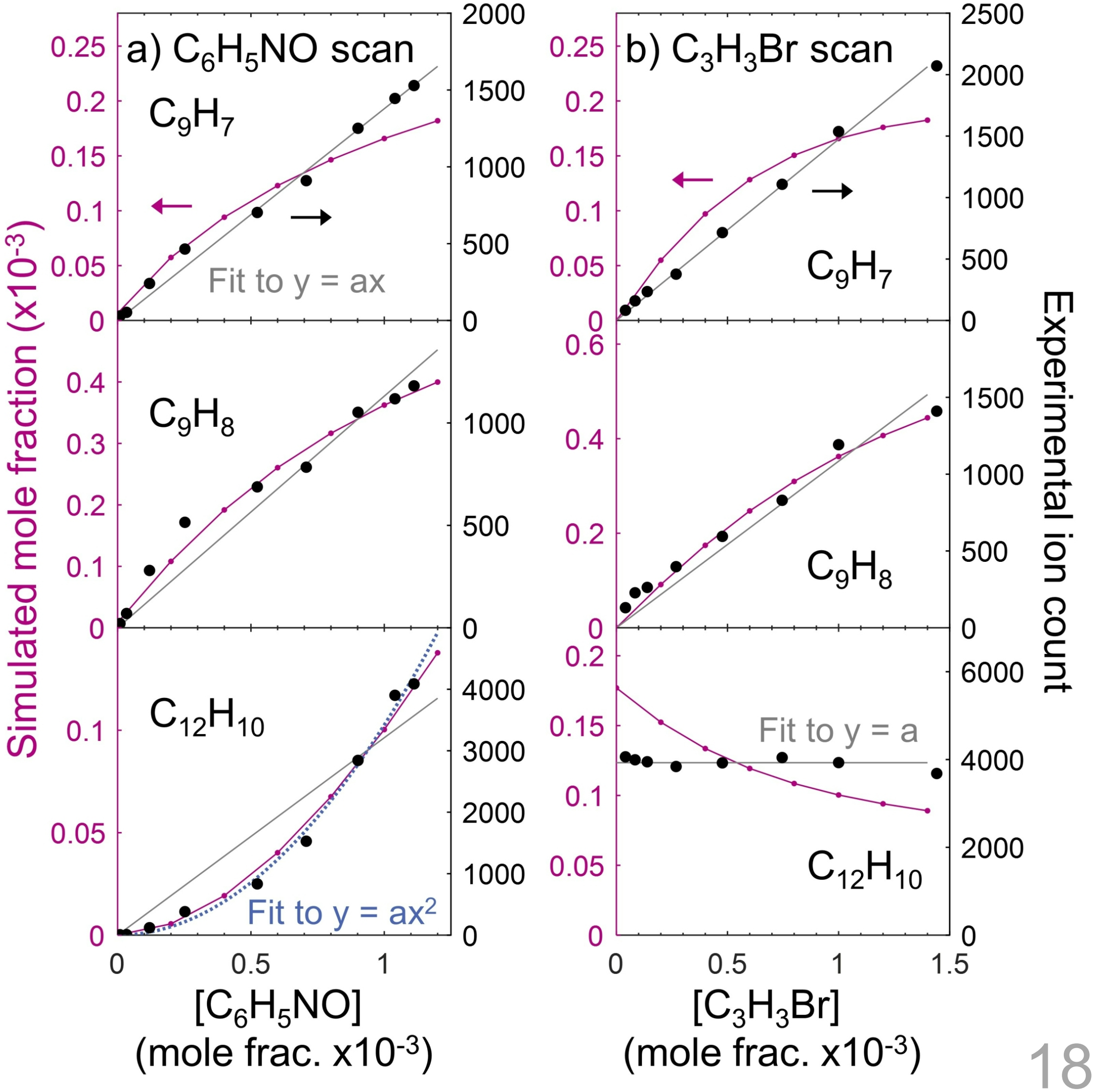
- At 30 Torr (low pressure flames), well-skipping is significant
- Well-skipping is inconsequential at atmospheric pressure

# Phenyl + Propargyl

# Concentration scans consistent with proposed mechanism

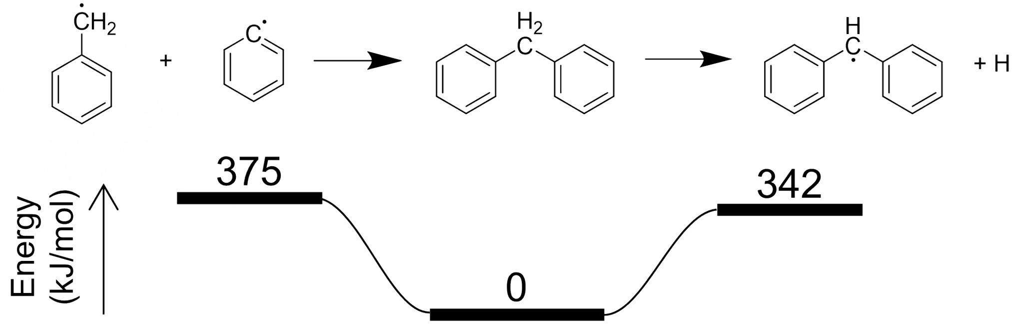


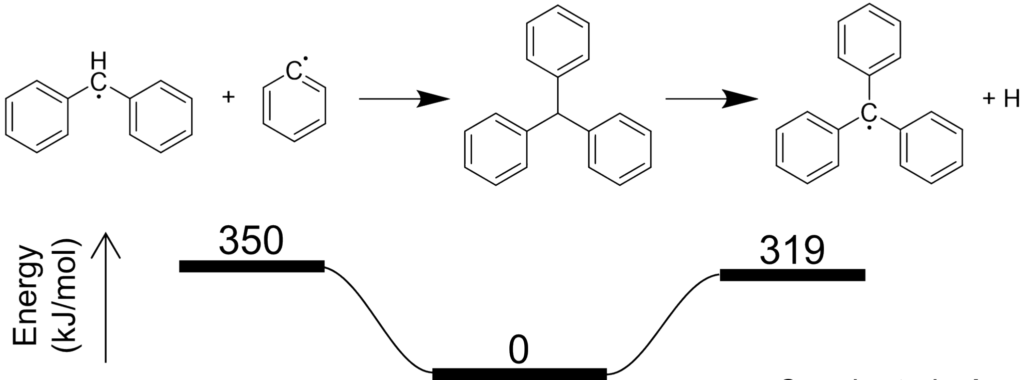
- We scanned each precursor concentration to test for 1st or 2nd order reaction behavior
- As expected, $C_9H_7$ and $C_9H_8$ are 1st order in both reactants
- Biphenyl ($C_{12}H_{10}$) is 2nd order vs phenyl, invariant with propargyl



# Phenyl + Benzyl
# Observation of chain reaction

- Chain reaction – the product becomes the reactant

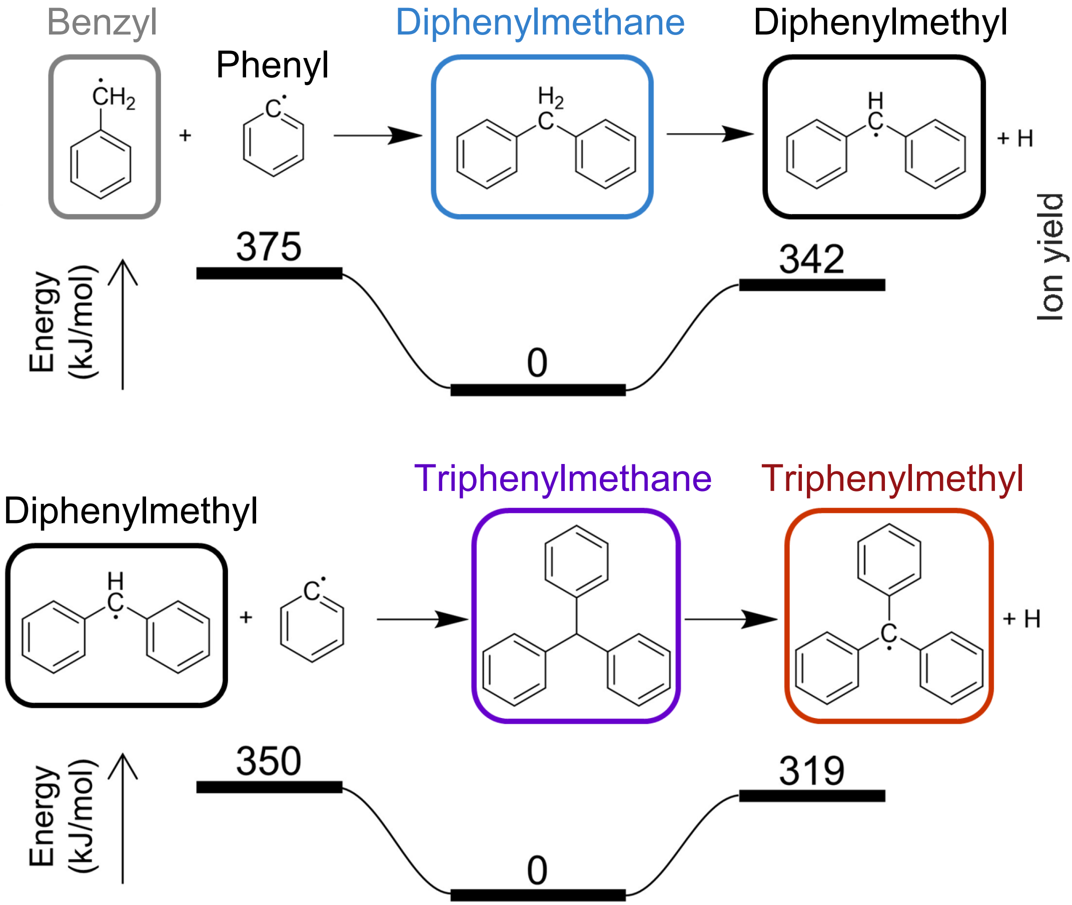


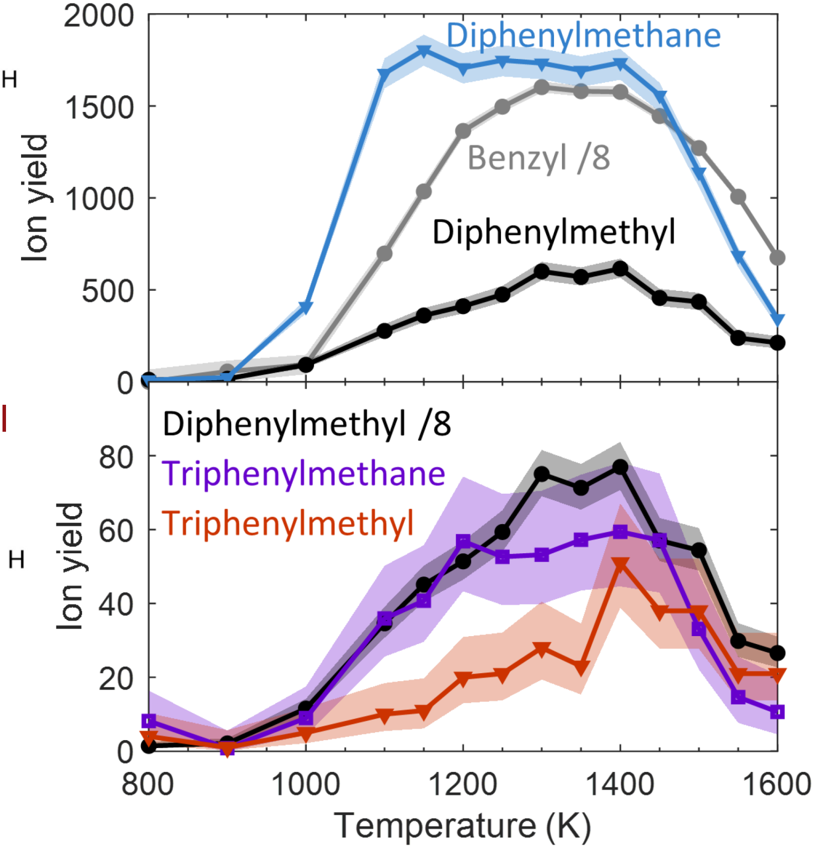


*Couch et al., Ange. Chem. Int. Ed.* ***2021****, 60, 27230-27235*

# Phenyl + Benzyl
# Observation of chain reaction

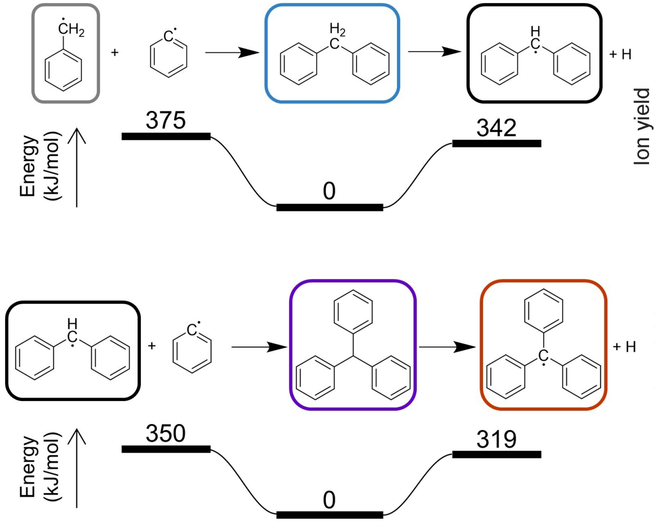
- Chain reaction – the product becomes the reactant

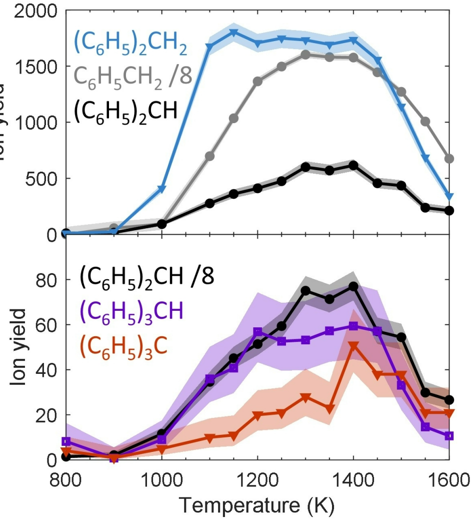


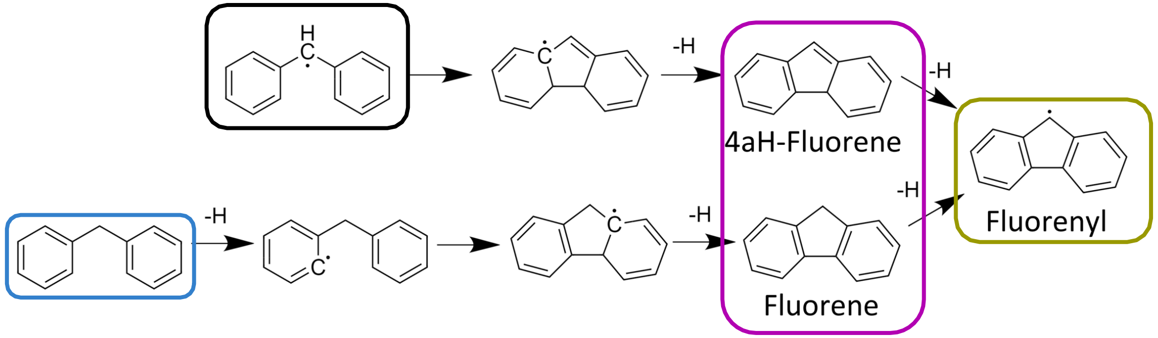


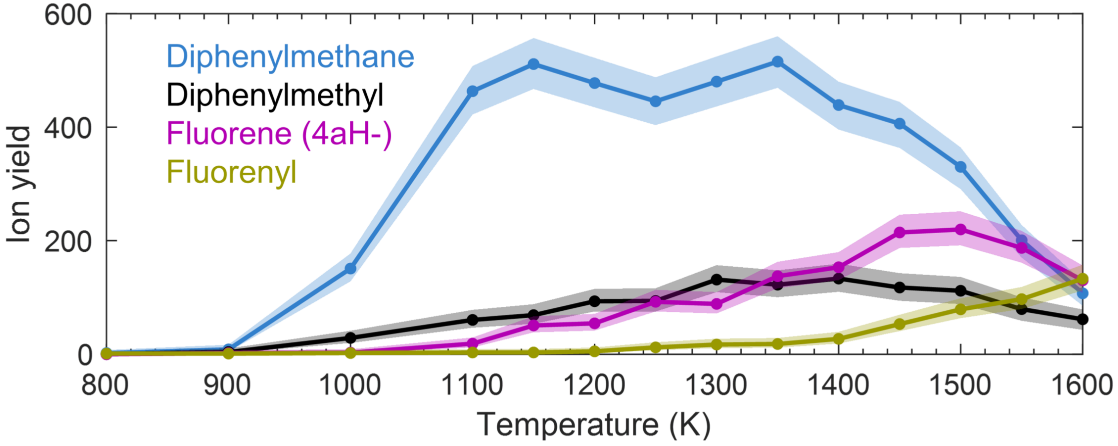
# Phenyl + Benzyl
# Decomposition to another stable radical

- Chain reaction – the product becomes the reactant
- Decomposition competes with further growth
  - 5-member-ring radicals are quite stable







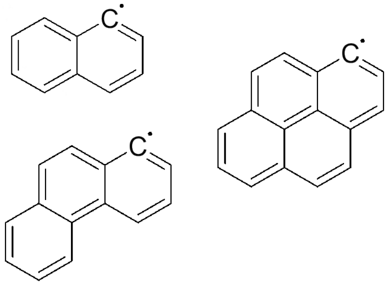


*Couch et al., Ange. Chem. Int. Ed.* ***2021****, 60, 27230-27235*

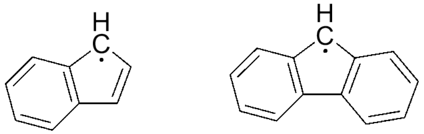
# Phenyl + Cyclopentadienyl

- Surrogate for polycyclic $\sigma + \pi$ reactions

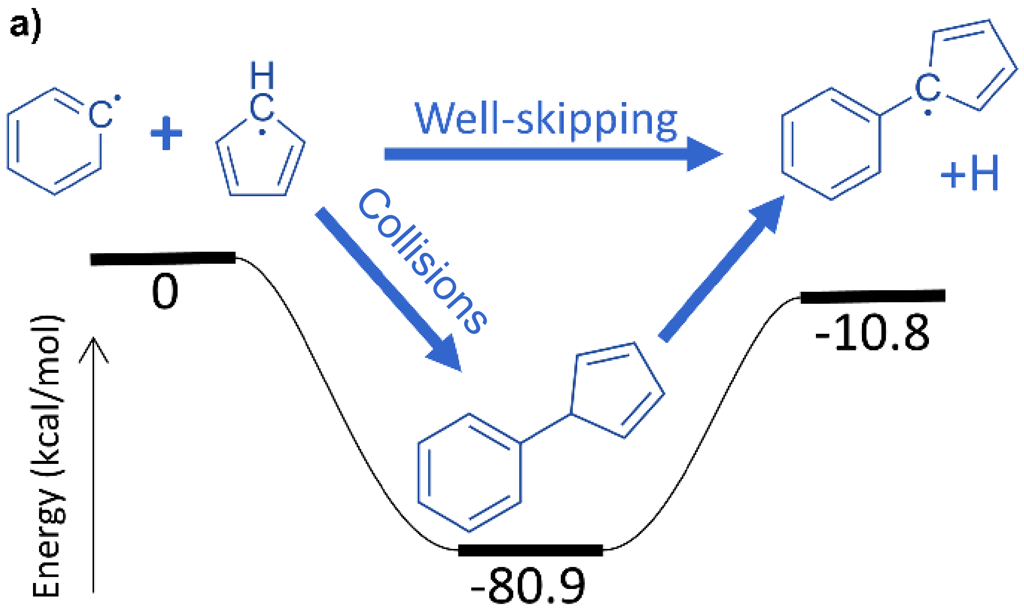
Aryl $\sigma$ radicals

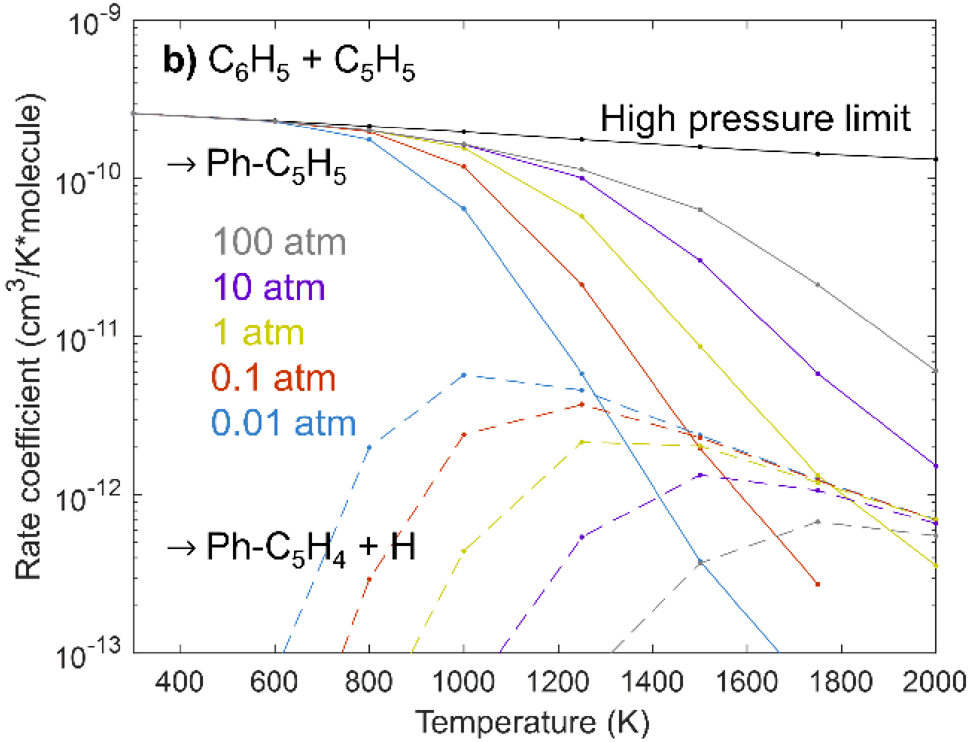


Resonance-stabilized $\pi$ radicals

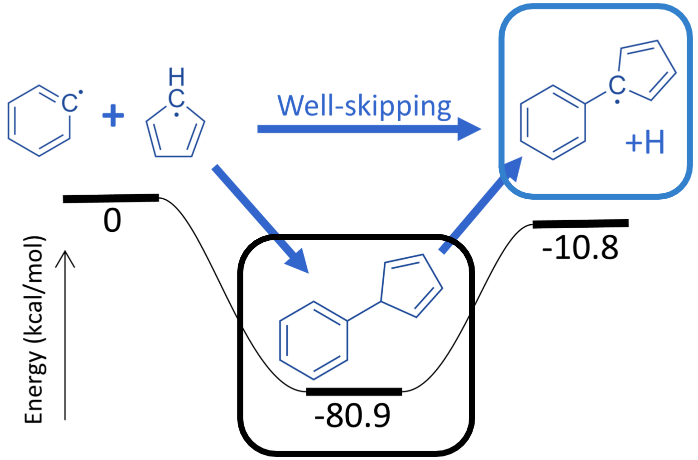


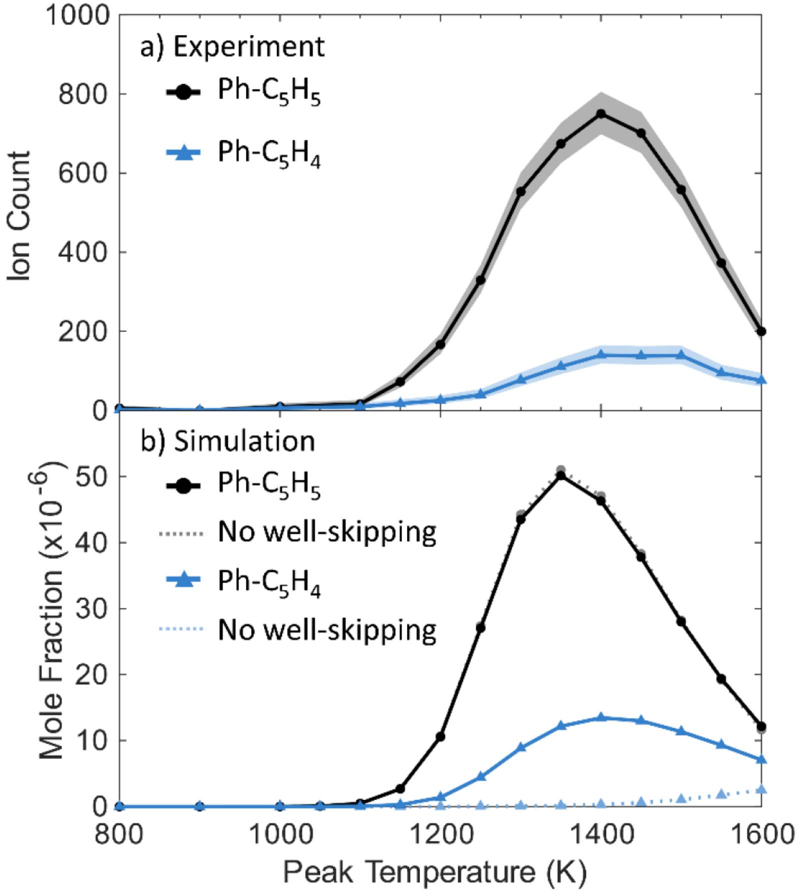
# Phenyl + Cyclopentadienyl
# Calculation of rates





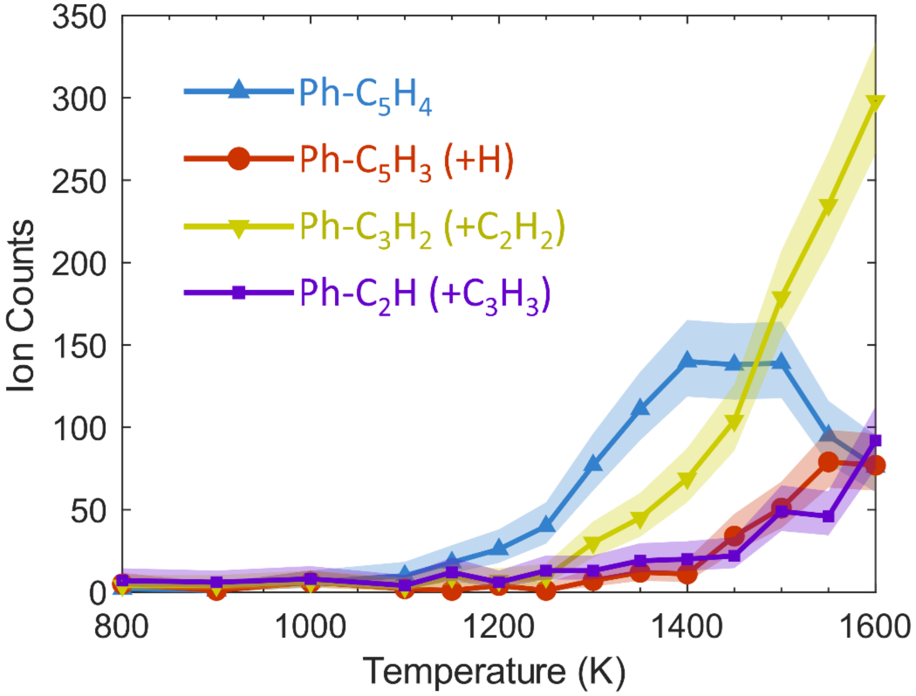
# Phenyl + Cyclopentadienyl
# Calculation of rates

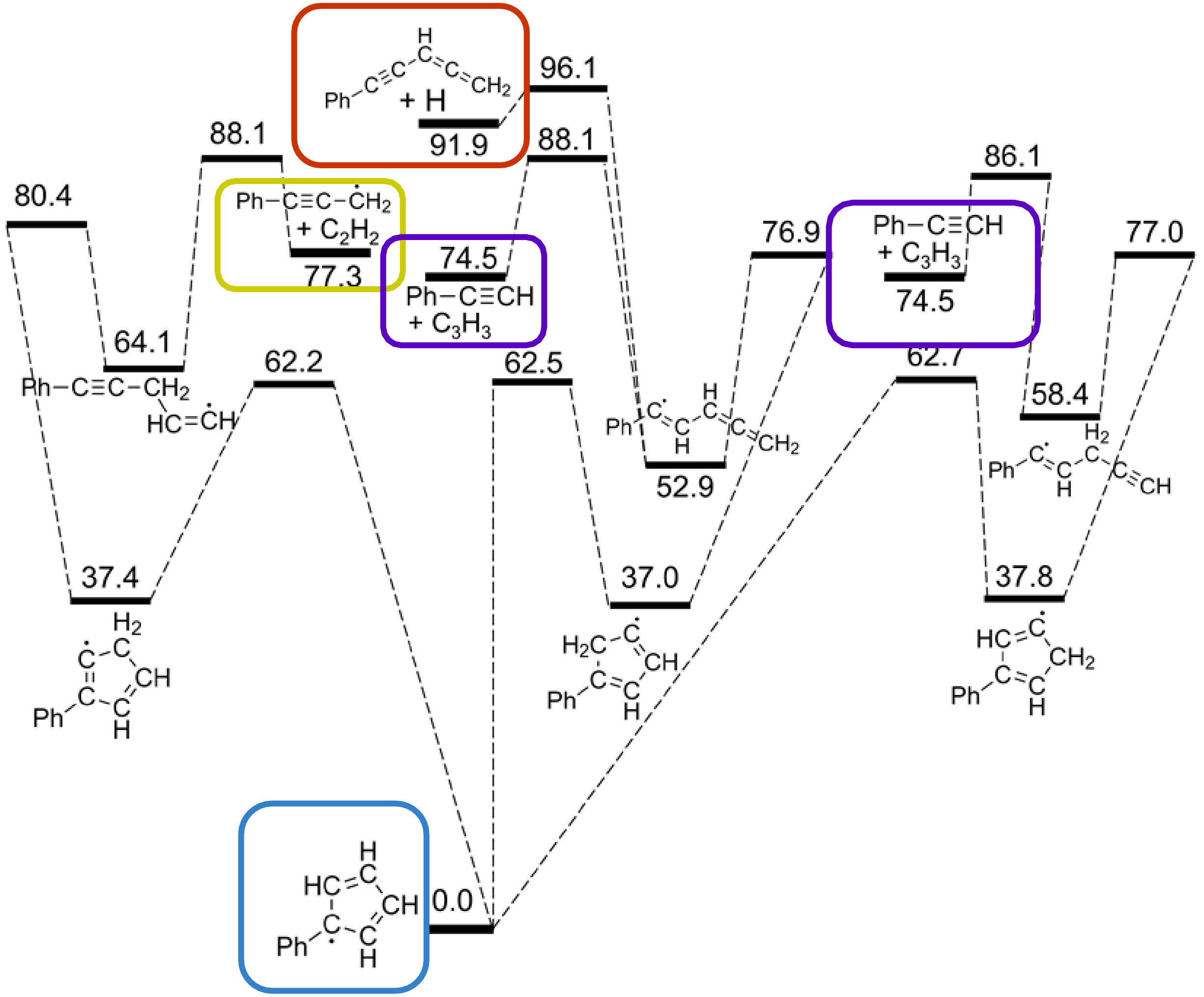




- Good agreement between simulation and experiment
- Ph-$C_5H_4$ radical comes from well-skipping, not sequential steps

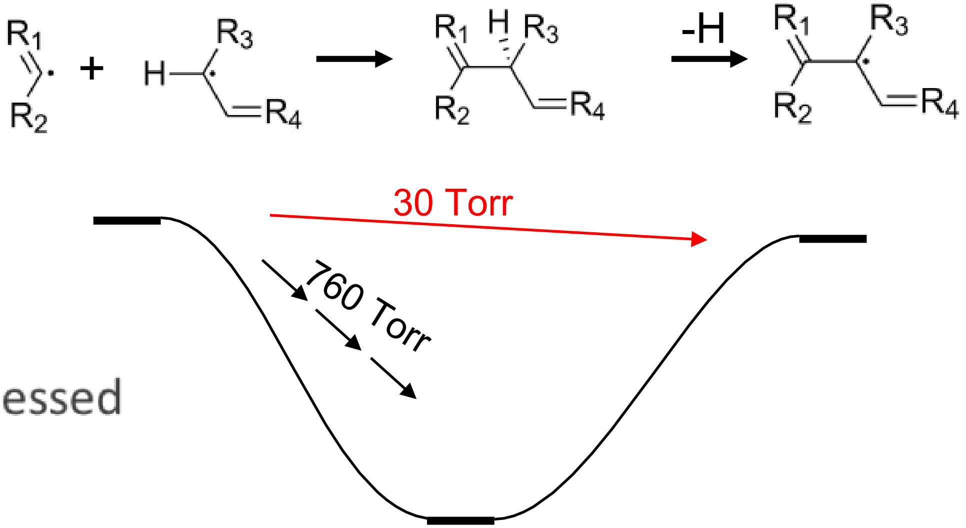
# Phenyl + Cyclopentadienyl
# Product decomposition





- 62 kcal/mol for isomerization
- 3 or more competing pathways after isomerization

# Summary



- We studied three $\sigma$-radical + $\pi$-radical reactions
  - All three showed well-skipping behavior at 30 Torr
  - Chain reaction and 5-member-ring radicals are observed
  - At atmospheric pressure and higher, well-skipping is suppressed but low-barrier H loss is still possible
  - The simulation is successfully modeling the experiment

- How can we utilize soot chemistry for carbon materials?
  - Grow nanotubes from larger radicals or PAHs
  - Use carbon particles as nucleation site for other materials

# Acknowledgements

## Sandia

Dr. Nils Hansen

Dr. Craig Taatjes

Angie Zhang

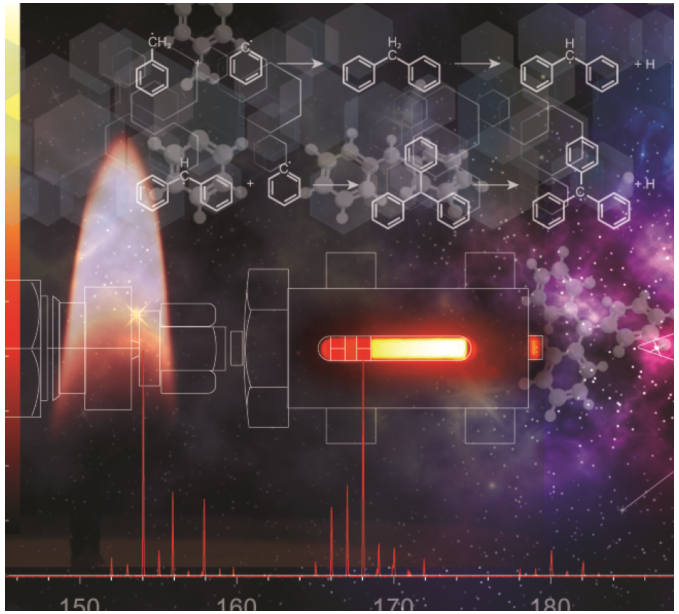
Myrsini San Marchi (UCLA)

## Lawrence Livermore

Dr. Goutham Kukkadapu

## Argonne

Dr. Ahren Jasper



*Ange. Chem. Int. Ed.* ***2021****, 60, 27230-27235*

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