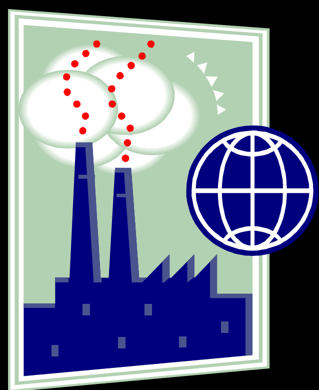
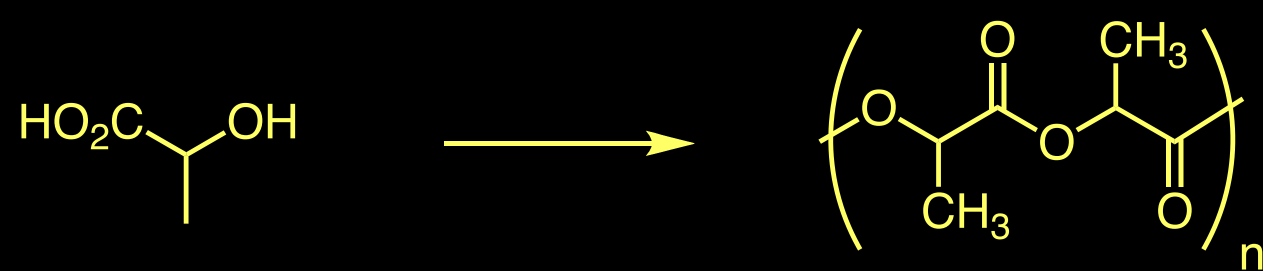
Smith Group Research



Invention of Catalytic Reactions

Z = BX_2, aryl, OH, ...

Materials From Renewable Resources



Commodity Materials
Biological Applications

Polylactic Acid

Energy

Developing New Chemistry for Old Fuels

$upport

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National Science Foundation
WHERE DISCOVERIES BEGIN

NATIONAL INSTITUTES OF HEALTH

MICHIGAN ECONOMIC DEVELOPMENT CORPORATION

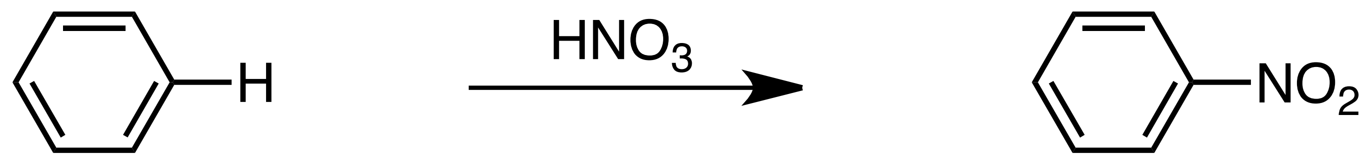
MERCK

ACS Green Chemistry Institute
PHARMACEUTICAL ROUNDTABLE

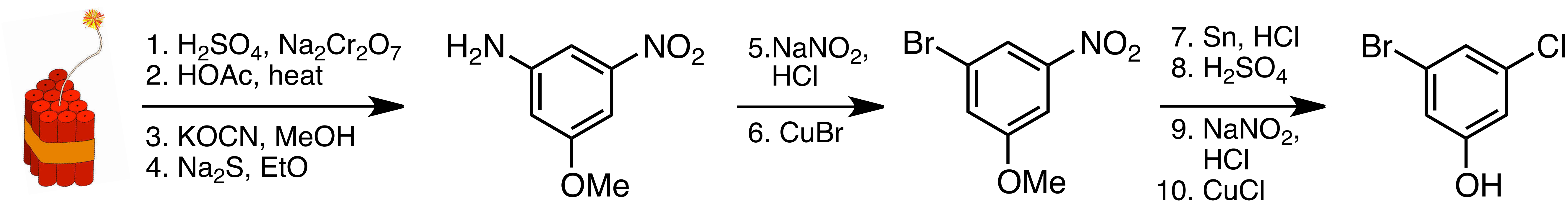
DOW

BoroPharm, Inc.
Your Bridge to Discovery

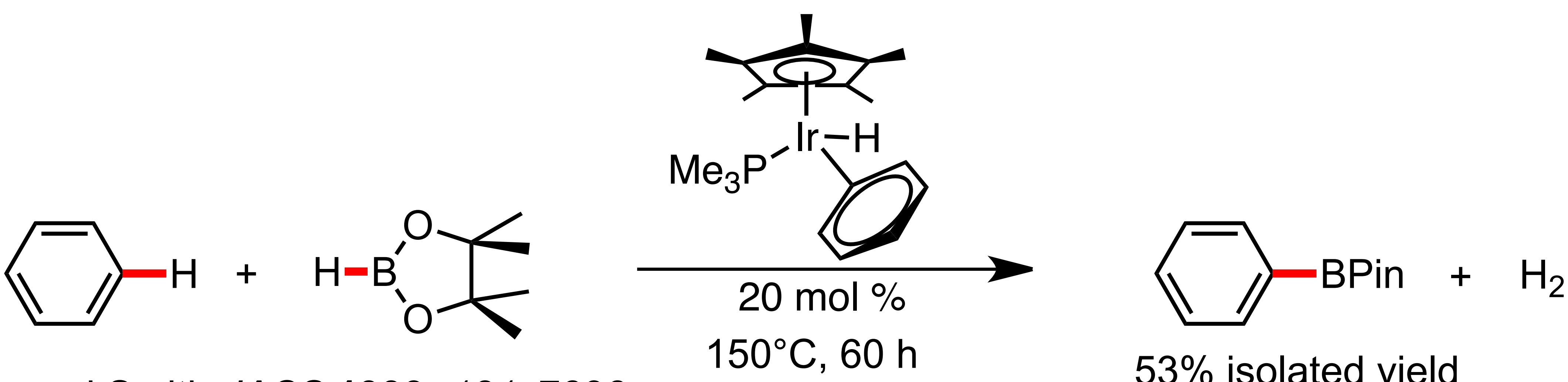
C-H Activation: A Chemical "Holy Grail"



Faraday, M. *Philos. Trans. Roy. Soc. (London)* **1825**, *115*, 440-466.

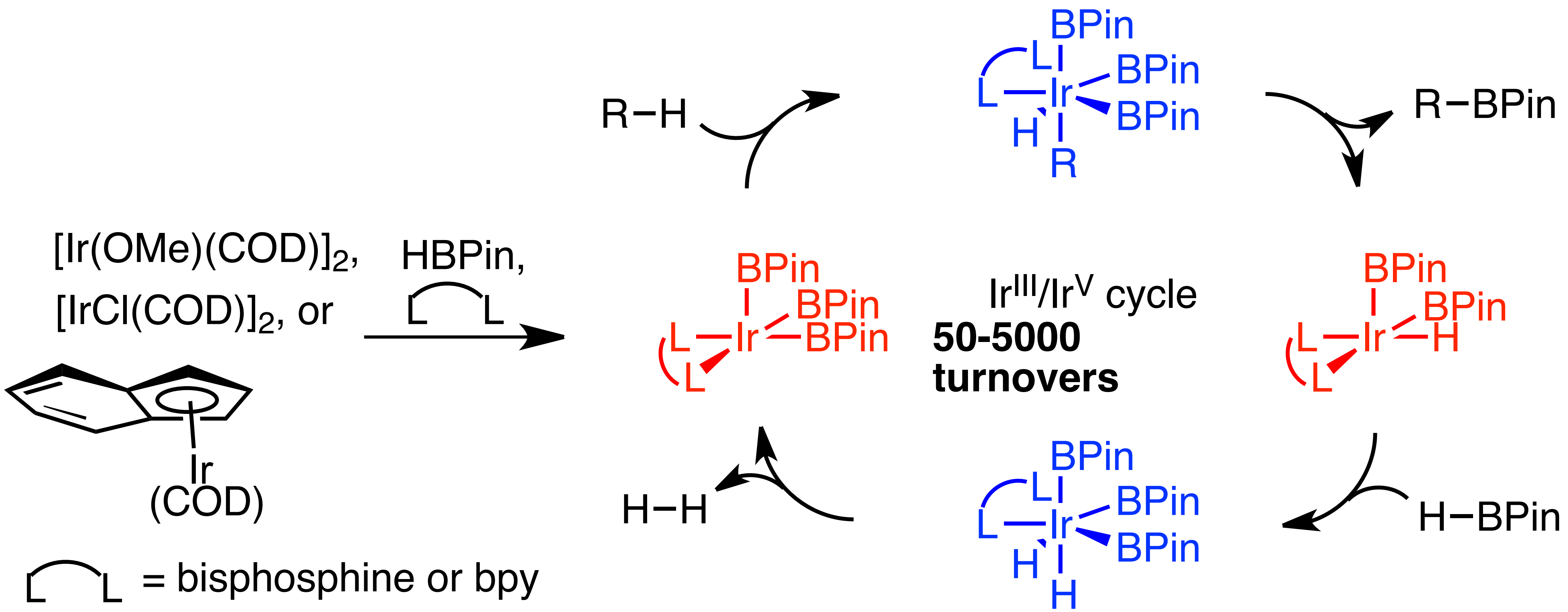


Hodgson, H. H.; Wignall, J. S. *J. Chem. Soc.* **1926**, 2077.



Iverson and Smith *JACS* **1999**, *121*, 7696.

Great Things Can Have Modest Beginnings



Cho, J.-Y.; Iverson, C. N.; and Smith, M. R., III *JACS* **2000**, *122*, 12868.

Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III *Science* **2002**, *295*, 305-308.

Maleczka, R. E., Jr.; Shi, F.; Holmes, D.; Smith, M. R., III *JACS* **2003**, *125*, 7792-7793.

Chotana, G. A.; Rak, M. A.; Smith, M. R., III *JACS* **2005**, *127*, 10539-10544.

Paul, S.; et al. *JACS* **2006**, *128*, 15552-15553.

Holmes, D.; Chotana, G. A.; Maleczka, R. E.; Smith, M. R., III *Org. Lett.* **2006**, *8*, 1407-1410.

Shi, F.; Smith, M. R., III; Maleczka, R. E., Jr. *Org. Lett.* **2006**, *8*, 1411-1414.

Chotana, G. A.; Kallepalli, V. A.; Maleczka, R. E., Jr.; Smith, M. R., III *Tetrahedron* **2008**, *64*, 6103-6114.

Chotana, G. A.; *Chem. Commun.* **2009**, 5731-5733.

Vanchura, B. A., et al. *Chem. Commun.* **2010**, *46*, 7724-7726.

Roosen, P. C., et al. *JACS* **2012**, *134*, 11350-11353.

Boron is a Portal to Molecular Diversity

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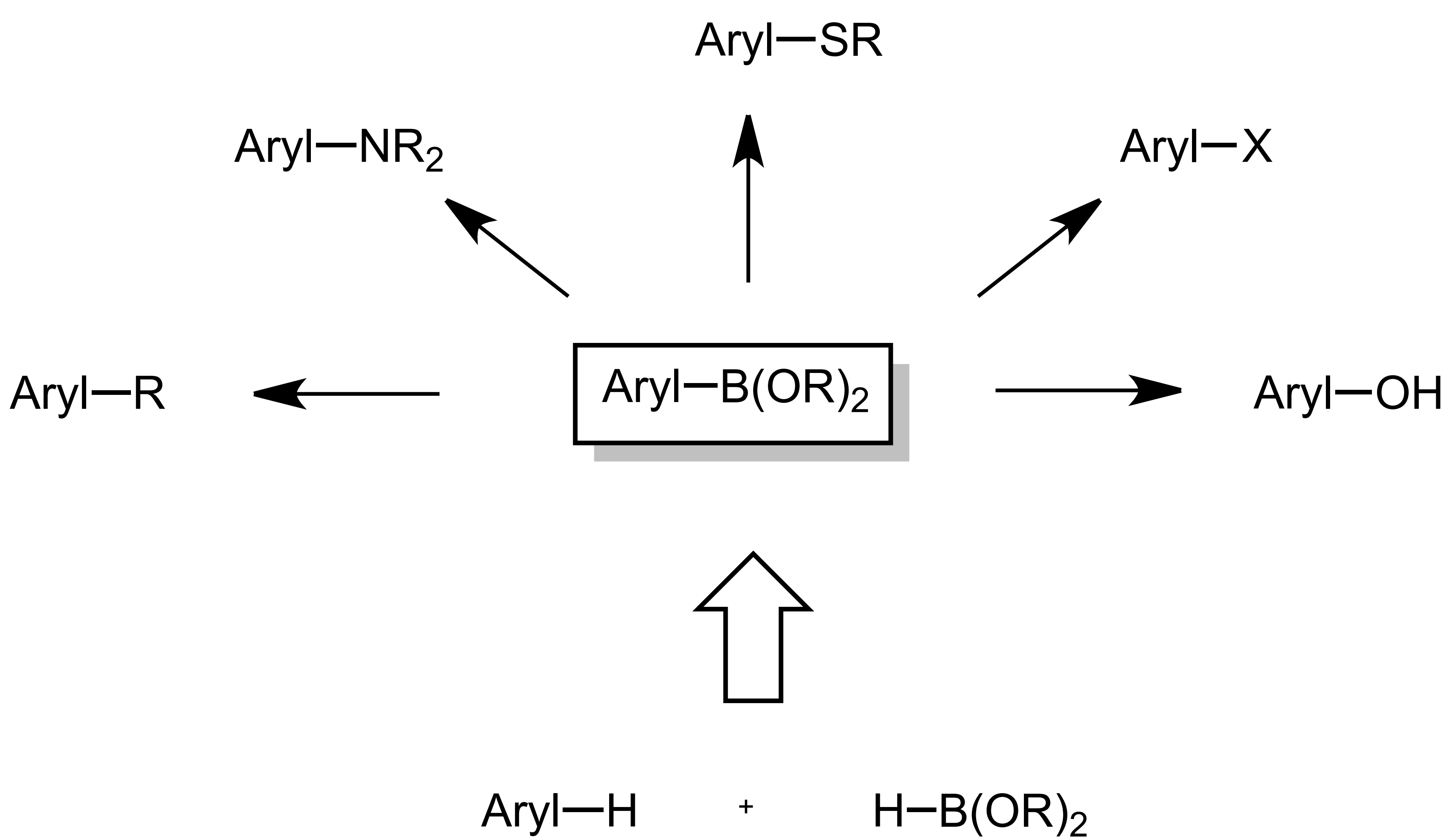
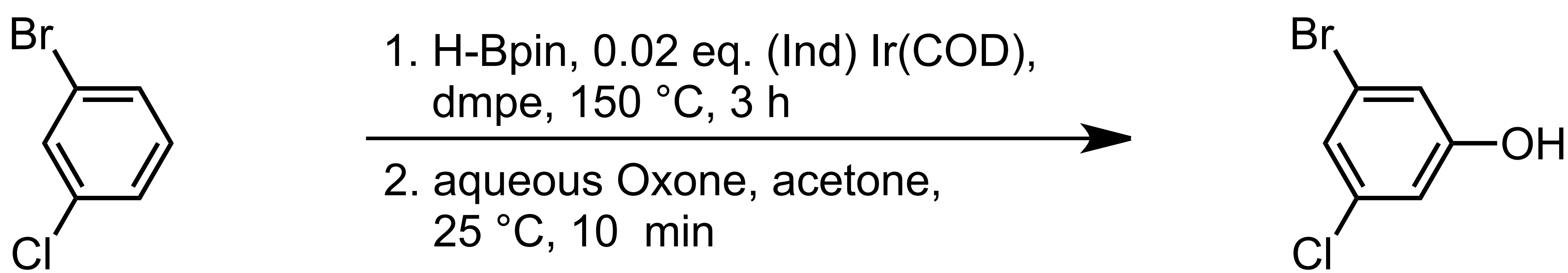
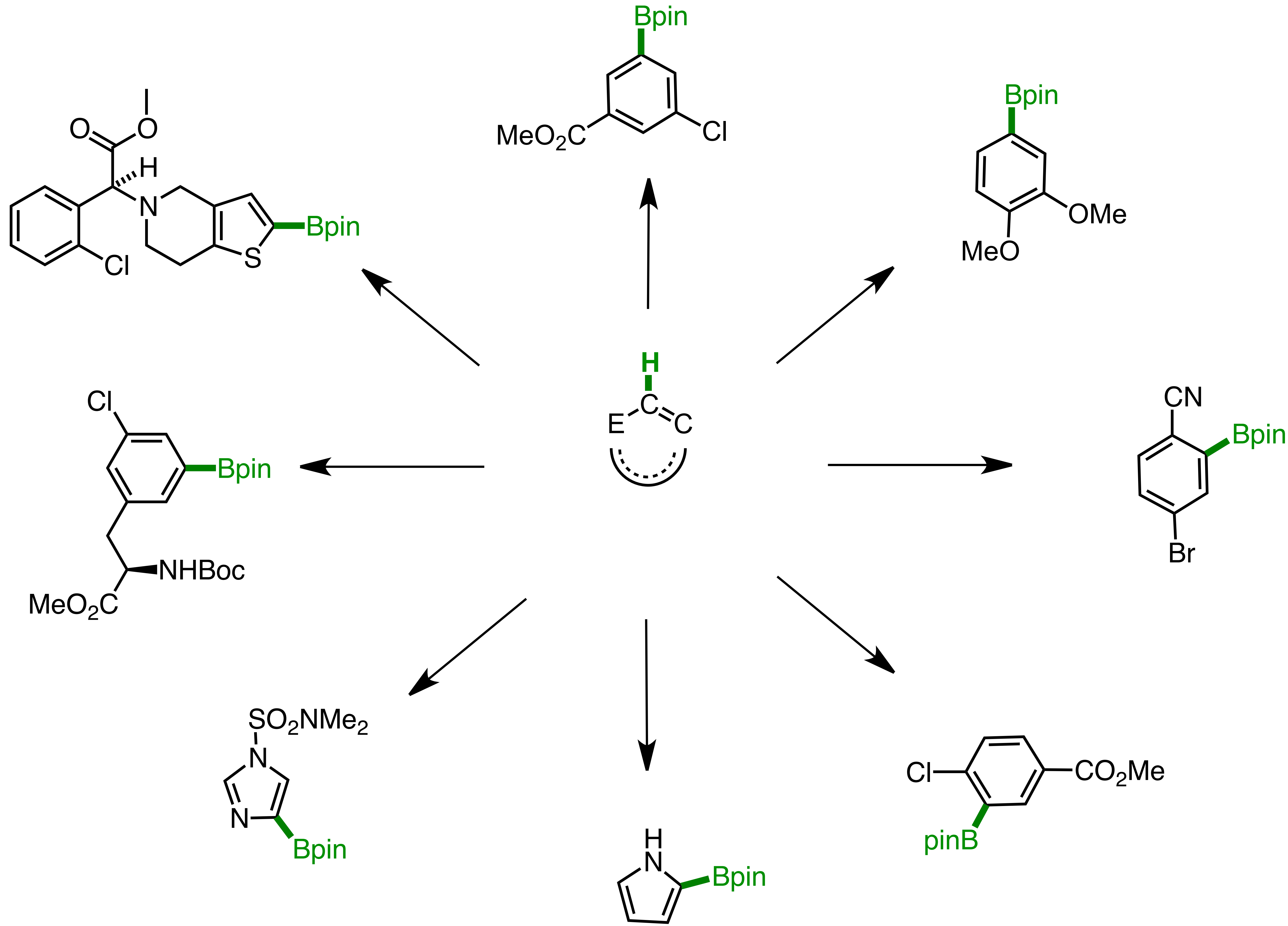




one-pot, 79% yield
previous synthesis, 10 steps from TNT

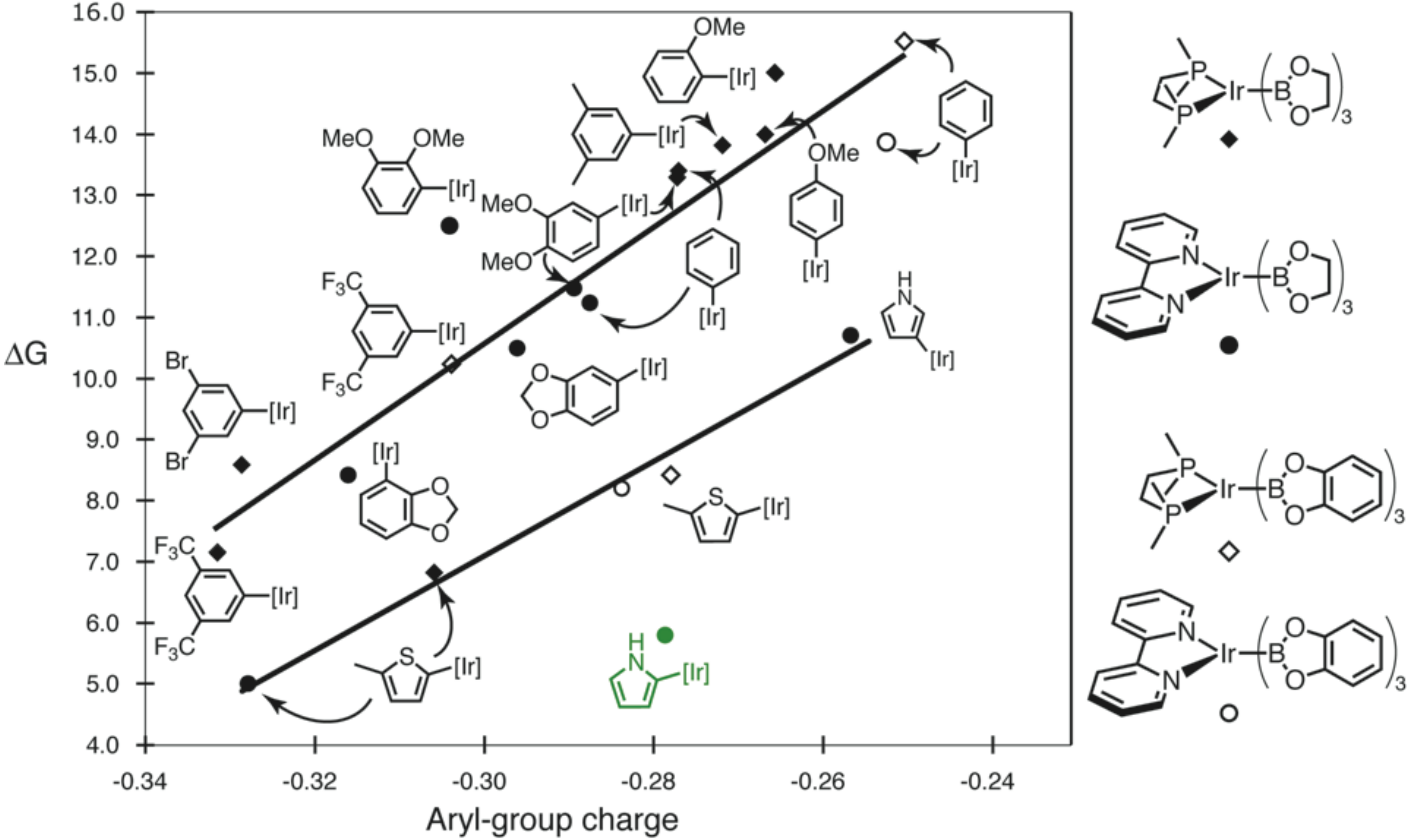
Maleczka, R. E.; Shi, F.; Holmes, D.; Smith, M. R. *J. Am. Chem. Soc.* **2003**, 125, 7792-7793.

Broad Scope of C–H Functionalization

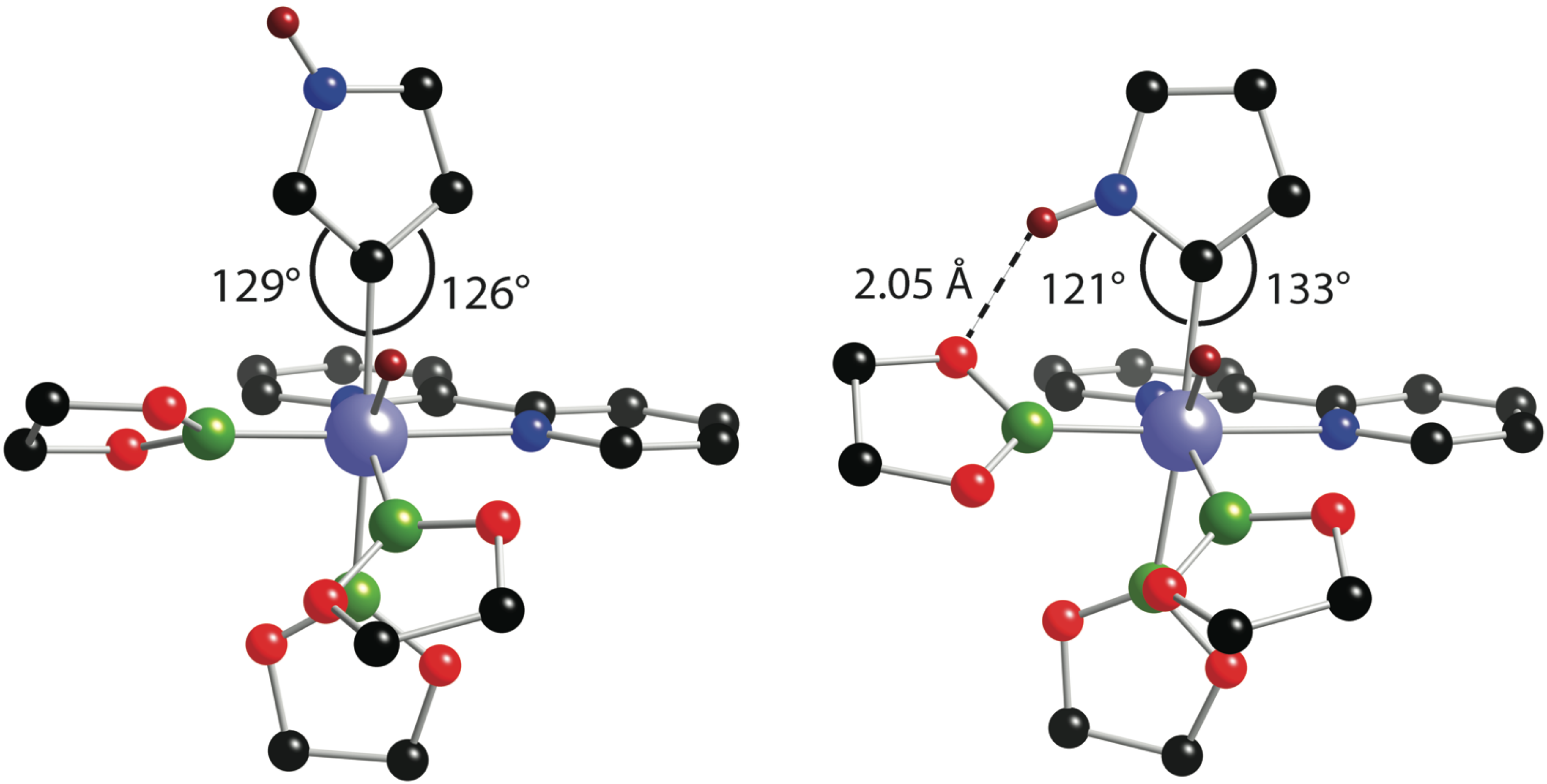


Power to the People

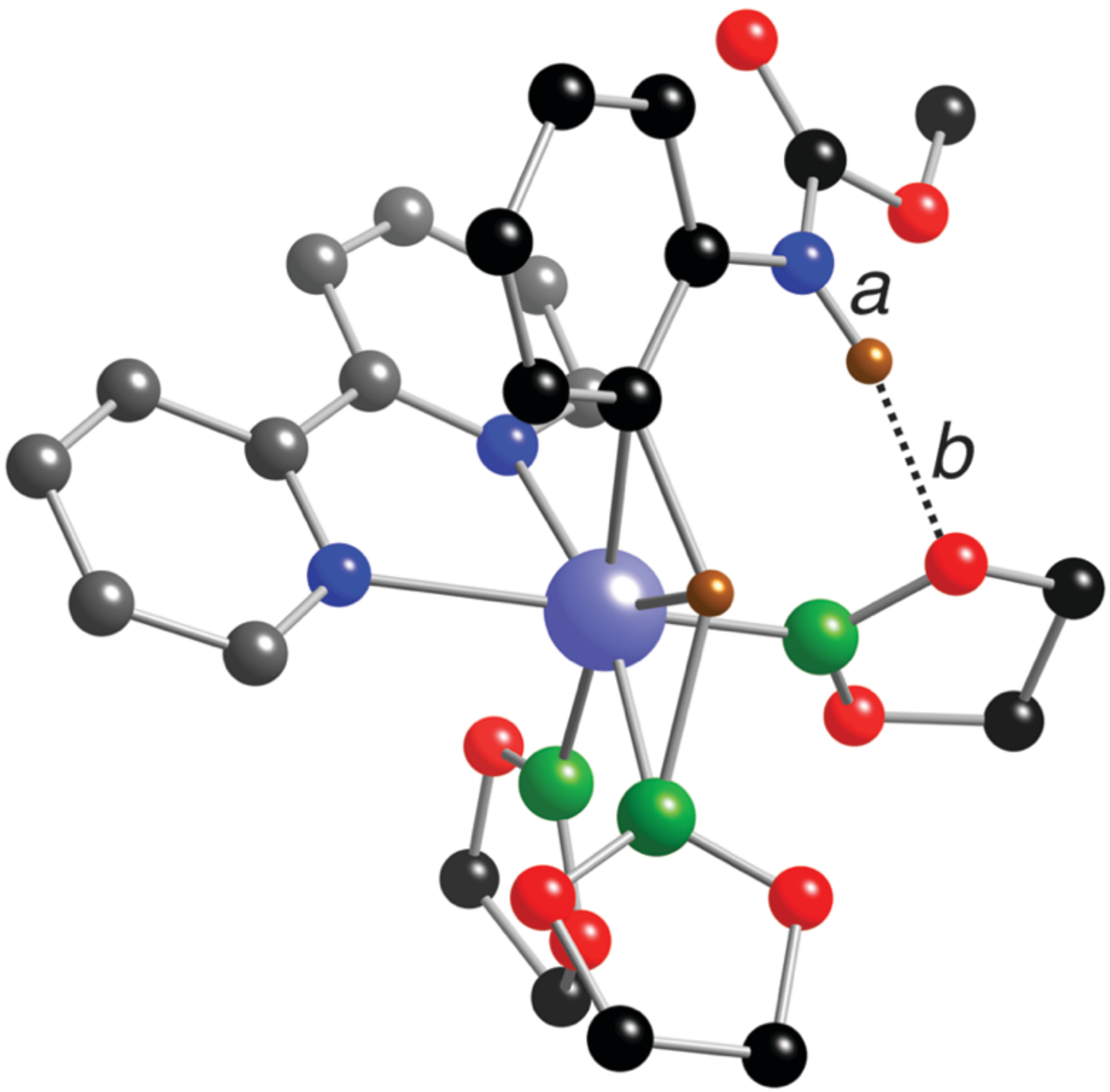
Pyrrole Is The Biggest Outlier



N···H···O Bonding in the Transition State



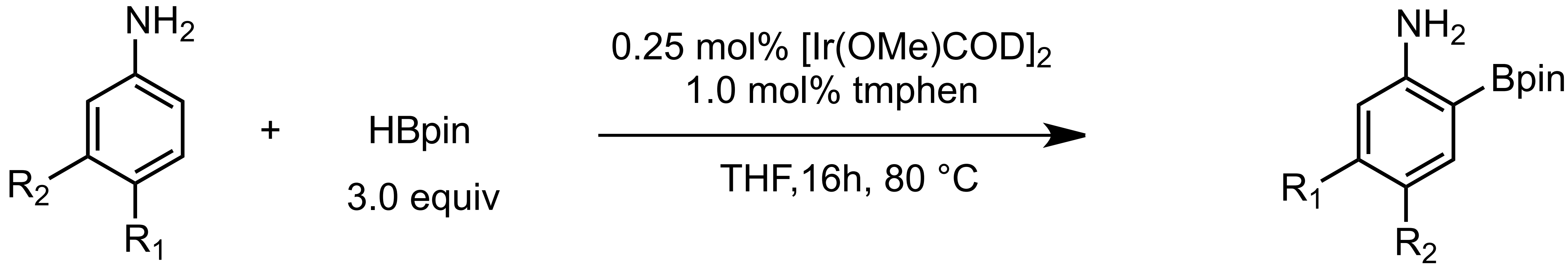
Calculated Transition State

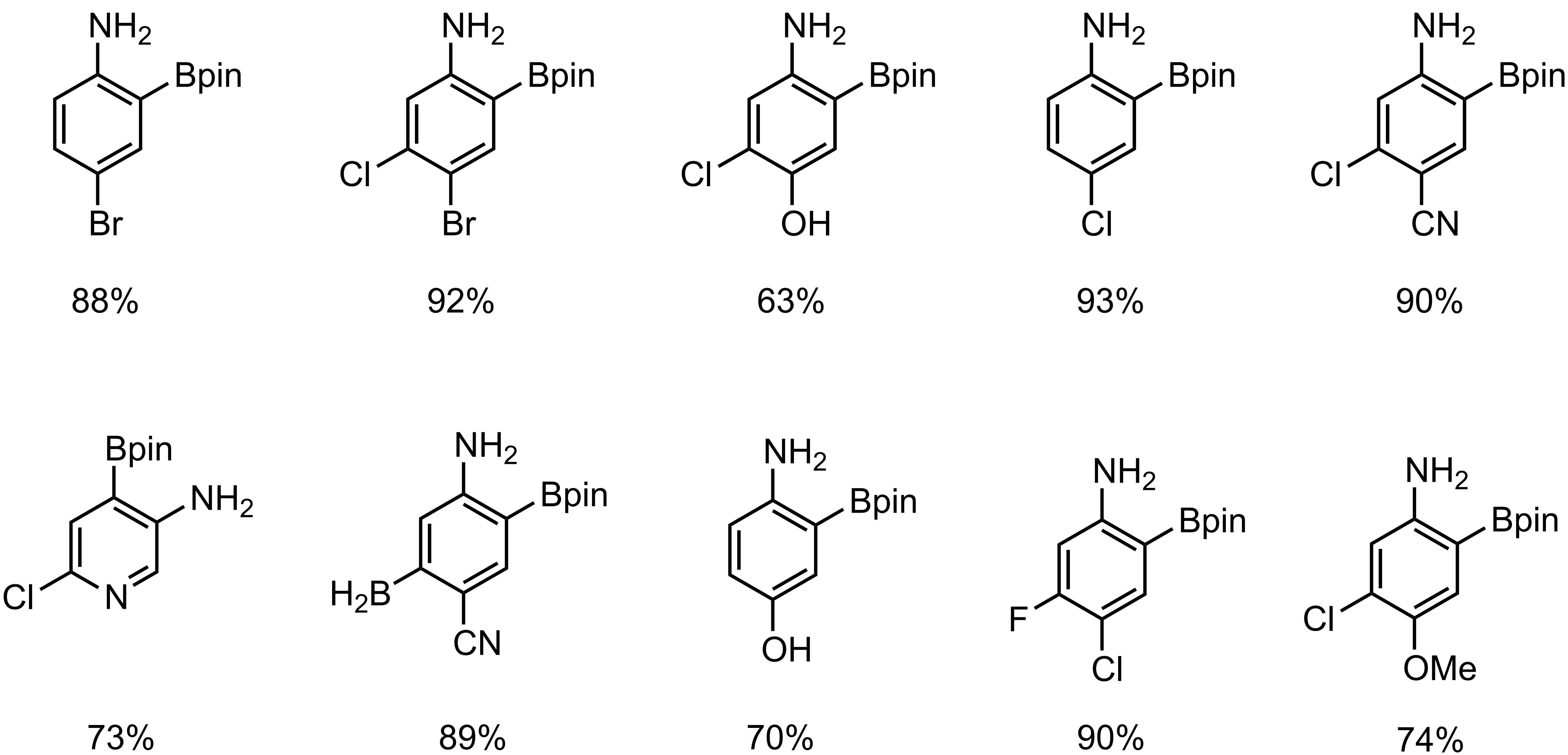


$a = 1.021$ Å $\quad b = 1.897$ Å

	o:*m*:*p*
$\Delta H^{\ddagger}$ (theory)	>99:<1:<1
$\Delta G^{\ddagger}$ (theory)	88:8:4
Experiment	90:5:5

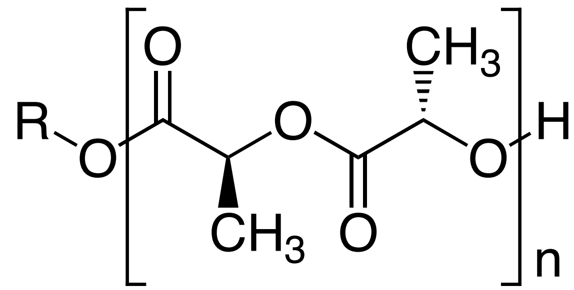
Reaction Scope





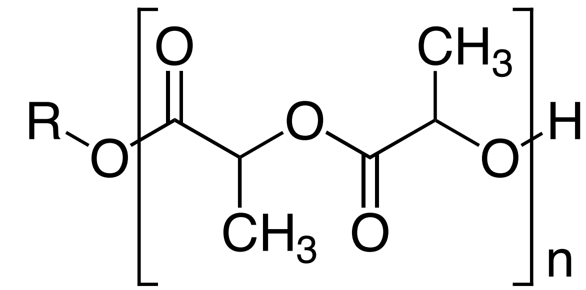
Sean Preshlock and Don Plattner

Poly(lactic) Acid: A Renewable Commodity Plastic



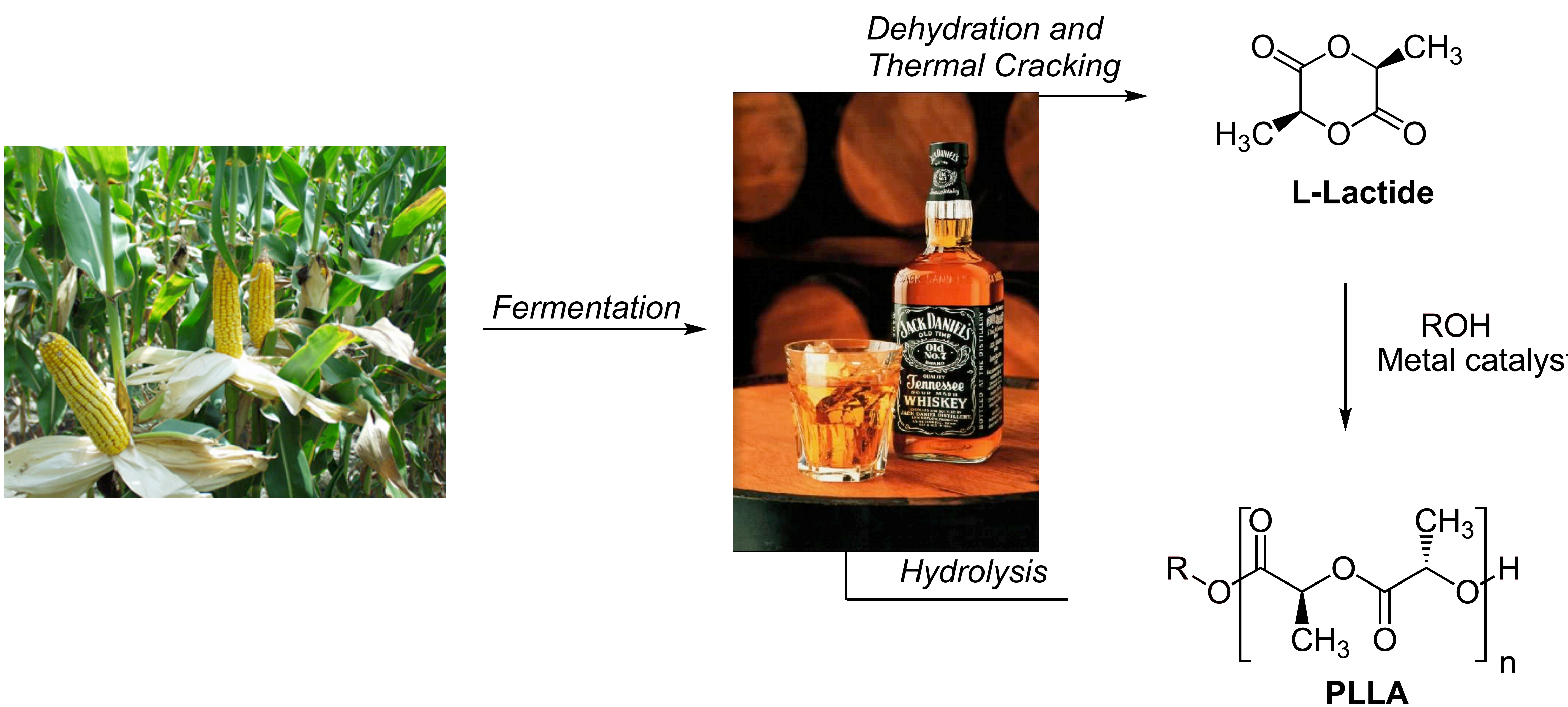
poly(*L*-lactide) (PLLA)

crystalline (T_m = 180 °C)



poly(*rac*-lactide) (PLA)

glassy T_g (~55 °C):



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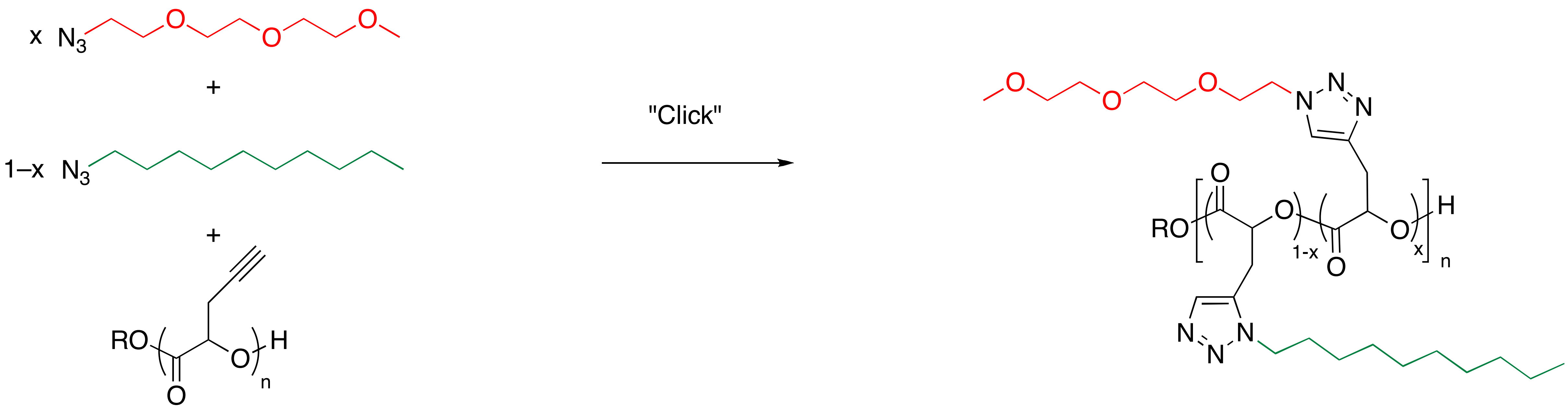
Degradable Single Molecule Micelles



Degradable Amphiphilic Polymer

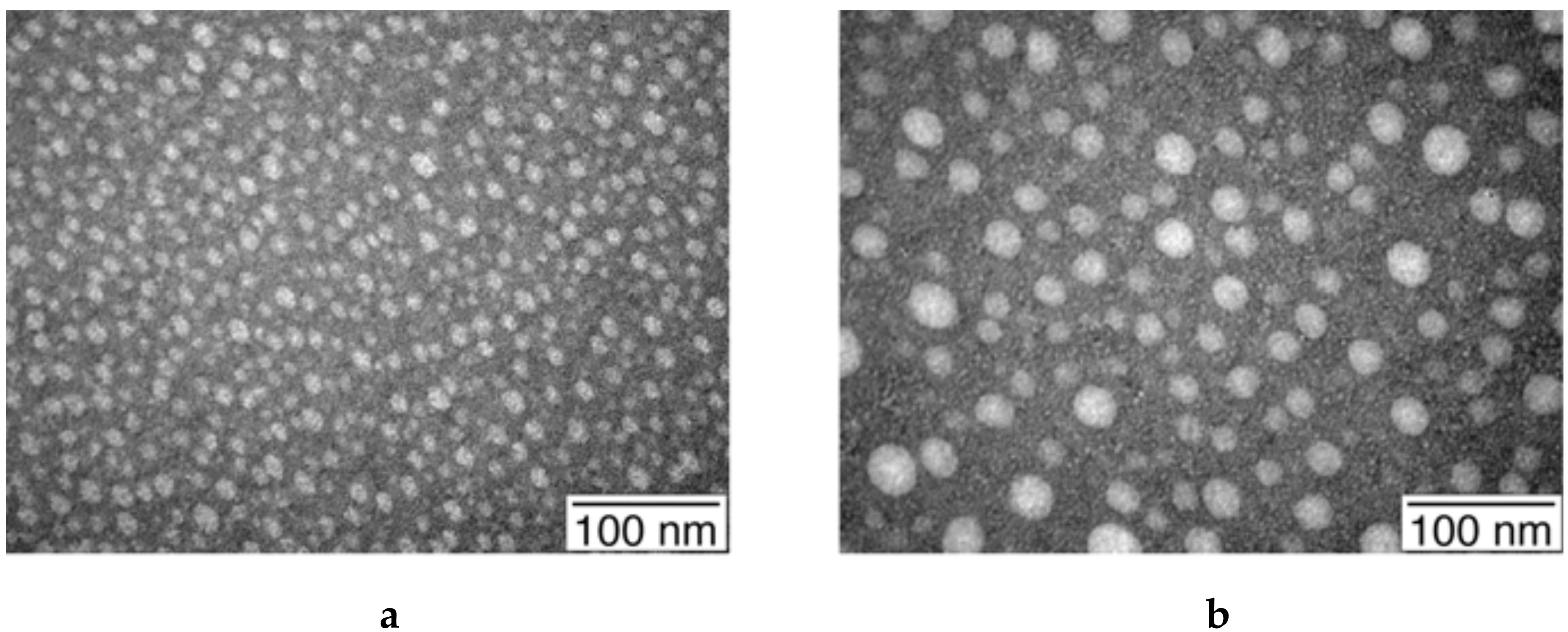


Figure 17. TEM images of polymer nanomicelles (**a**) M_n ~ 43,0000, diameter ~ 10 nm (**b**) M_n~ 260,000, diameter ~ 30 nm.

Functional Nanoparticle Applications

Well-defined

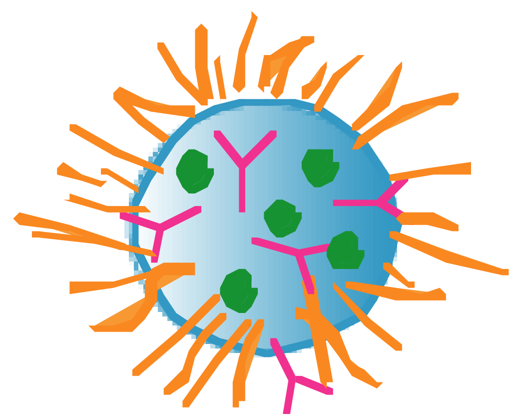
Easily Synthesized

Controllable Release

Drug Screening
(Labeling)

Drug Delivery
(Therapy)

Gene Delivery
(Transfection--siRNA or DNA)



Detection
(Imaging)

Stimuli-responsive

Degradable

Cross-linkable

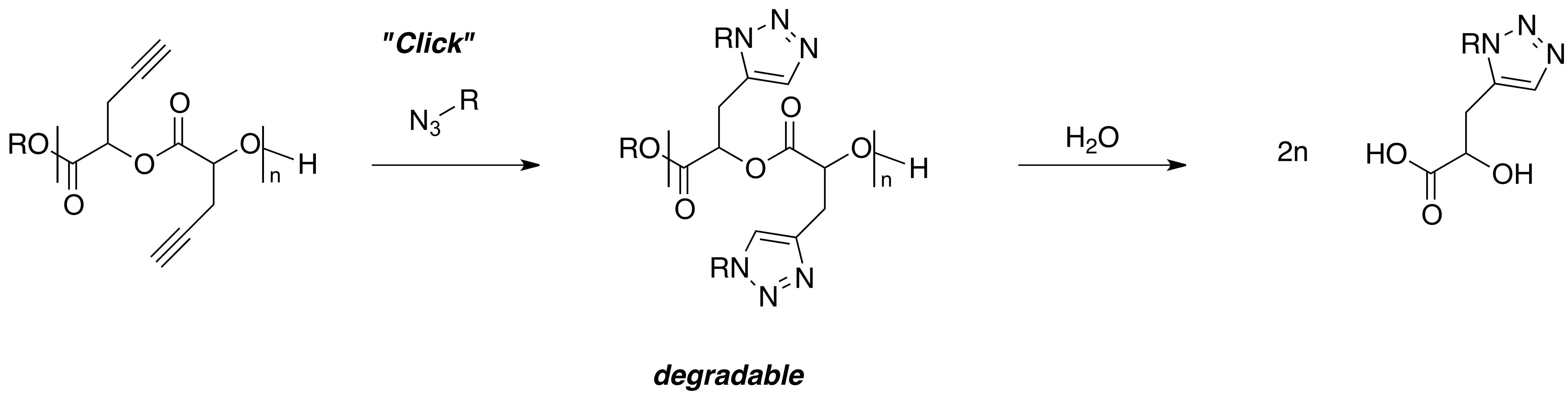
Biocompatible

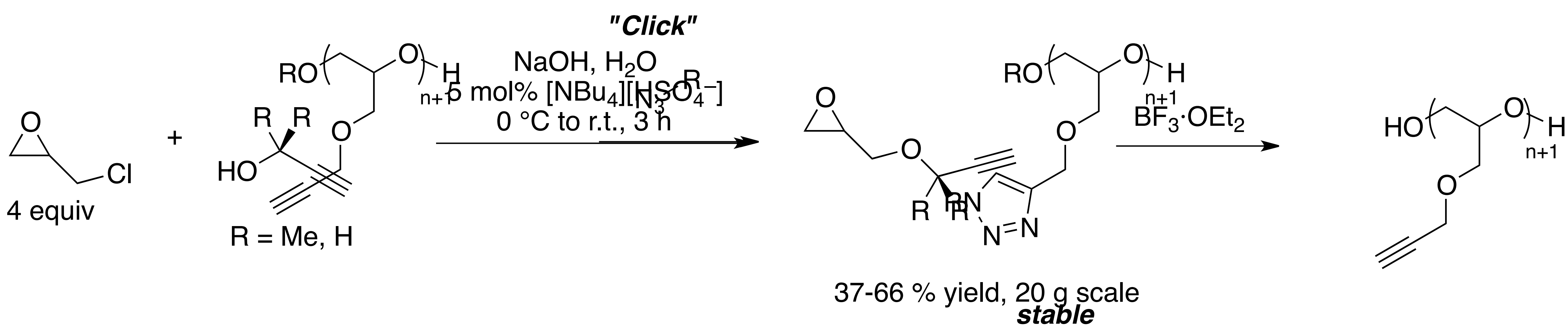
Diagnosis
(Devices and Labeling)

Diagnosis/Monitoring
(Disease Markers)

Liu, Y. Y.; Miyoshi, H.; Nakamura, M. Int. J. Cancer 2007, 120, 2527-2537.

From Degradable to Nondegradable Nanomicelles



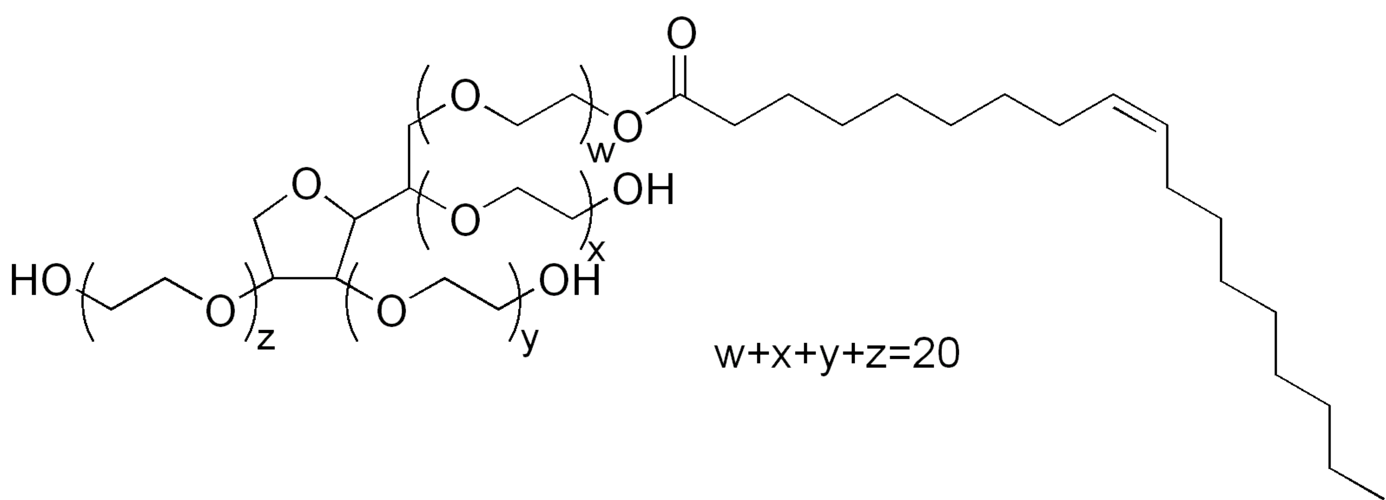


Marie Le Gaillard

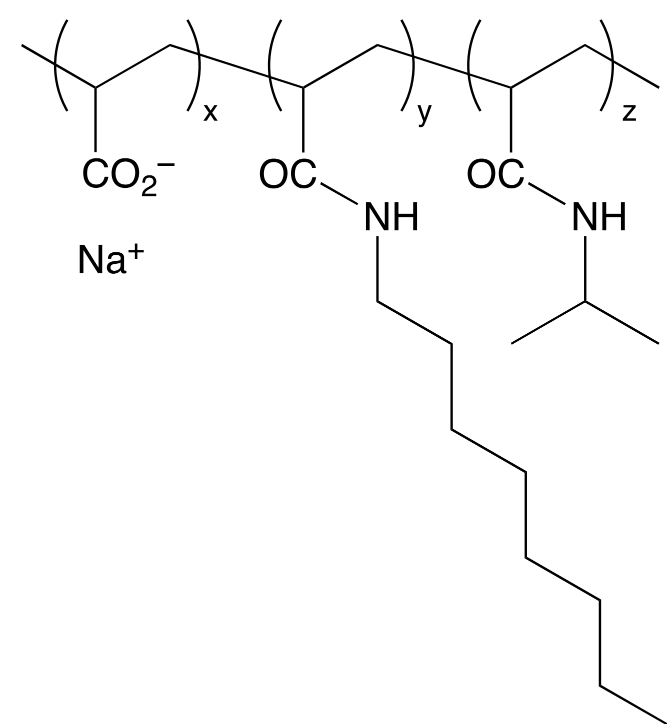
A Simple Market Analysis

Membrane proteins are projected to have a $30 billion annual market...

...That buys a lot of beer.



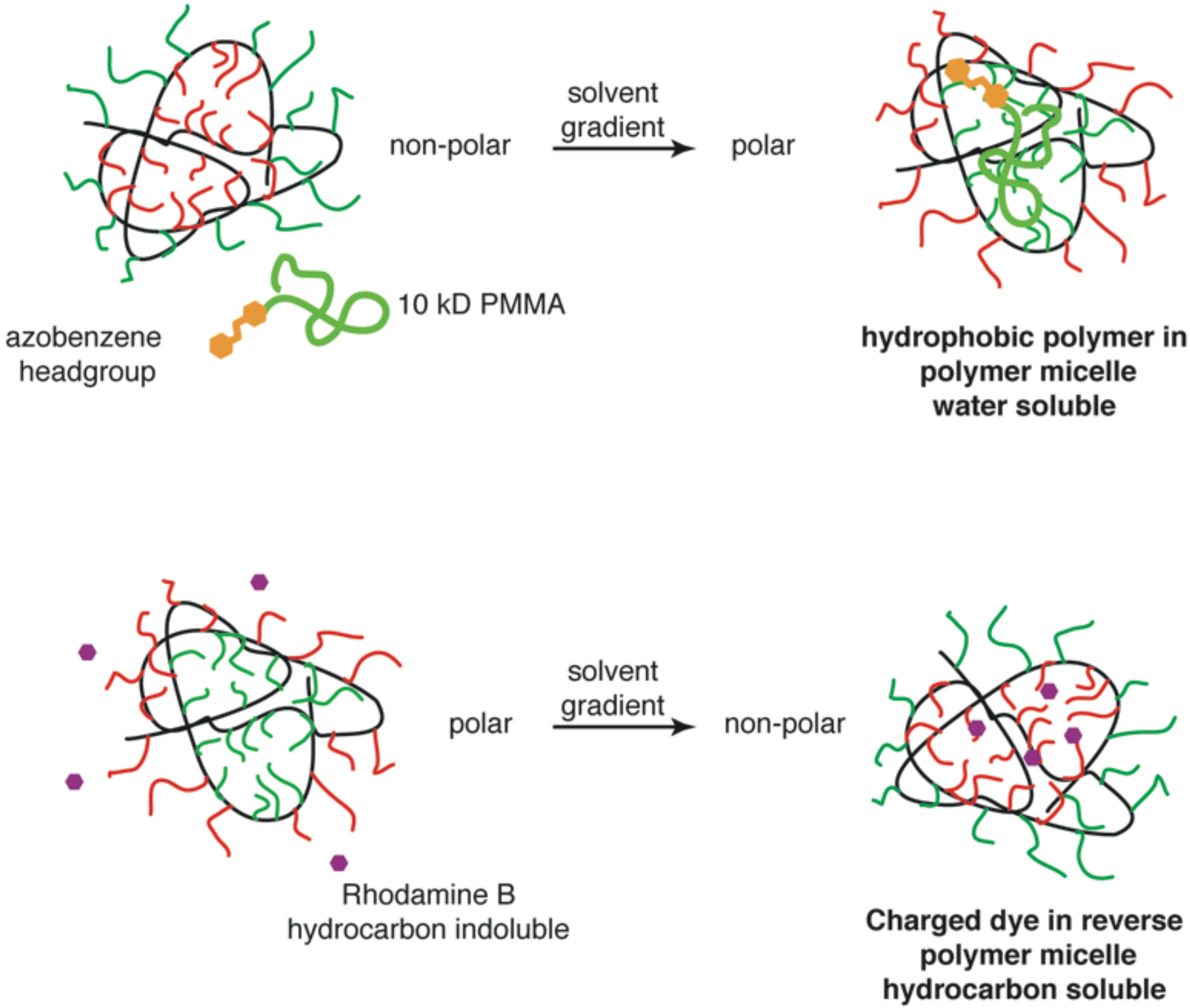
Tween-80



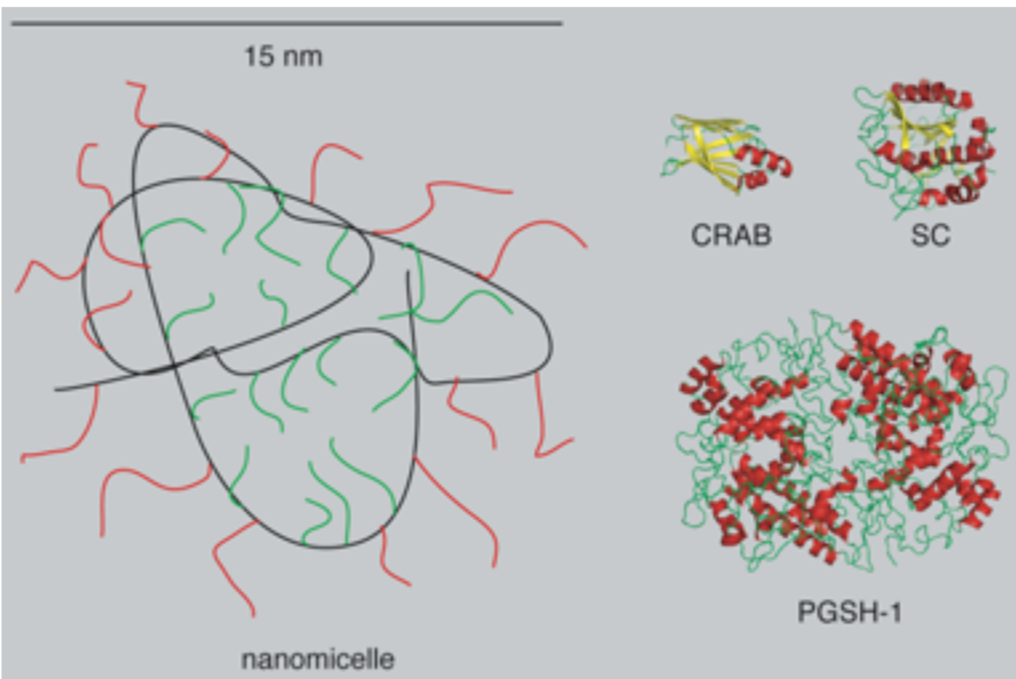
Amphipol

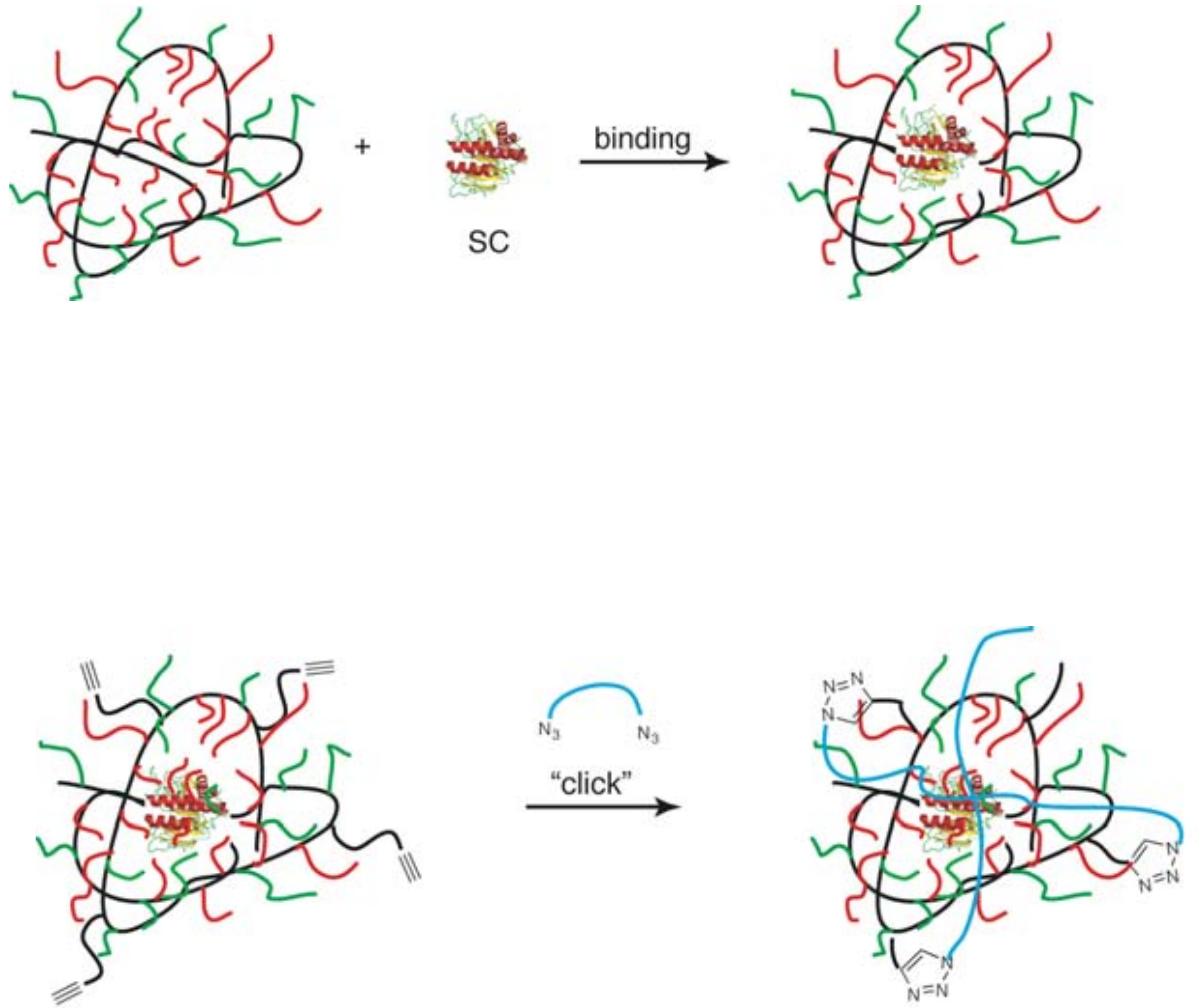
Poorly degradable

Encapsulation of Non-Polar and Polar Species in Nanomicelles



Enhancing Protein Solubility with Degradable and Tailorable Micelles





Sustainability is an Old Problem

By 1853 New York omnibuses carried 120,000 passengers per day.

Culver Pictures

In 2009, the New York Subway carries 4,300,000 passengers per day

Fossil Fuels: Key to 20th Century Sustainability

Growth is the biggest challenge to sustainability

The Energy Problem

By 2050 Earth's population is predicted to increase by 50% while energy demand is predicted to increase by at least 100%

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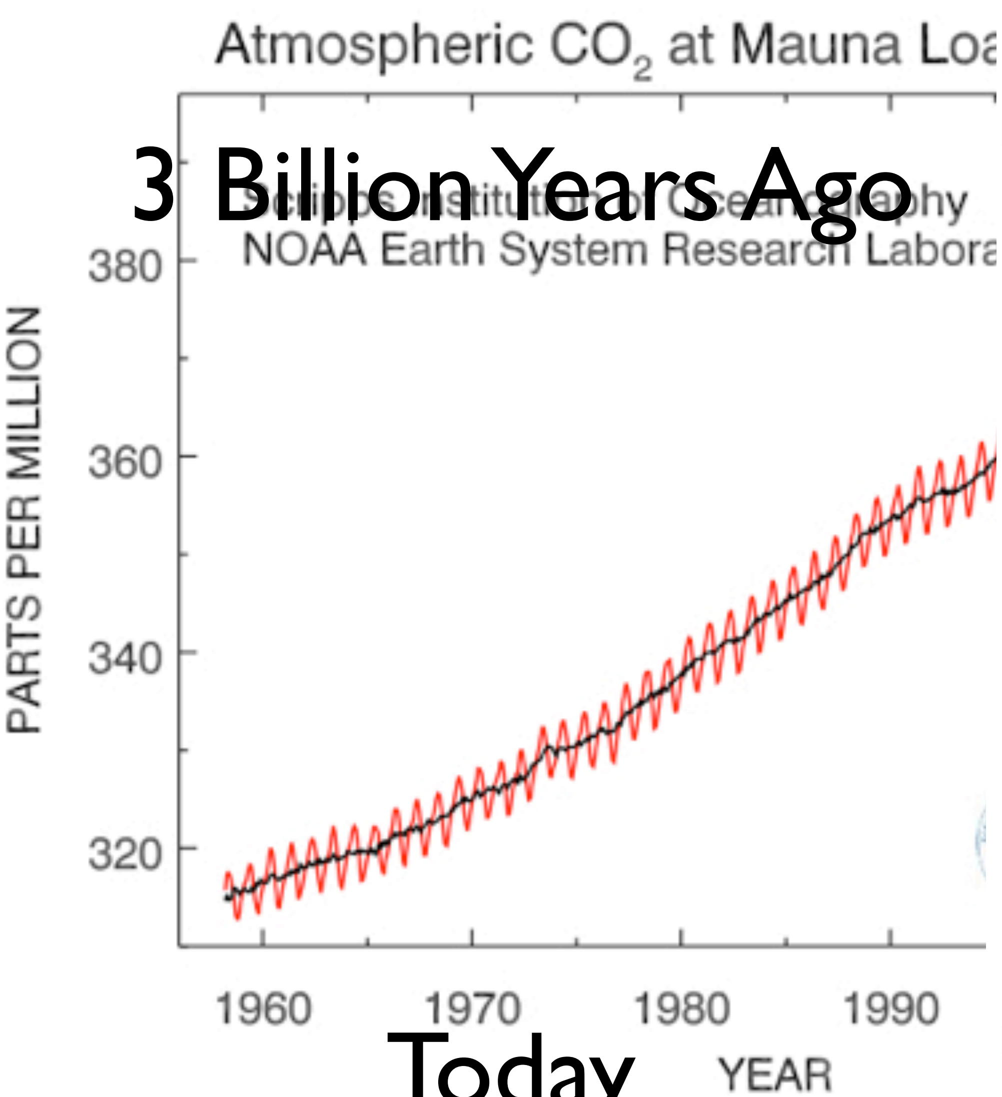
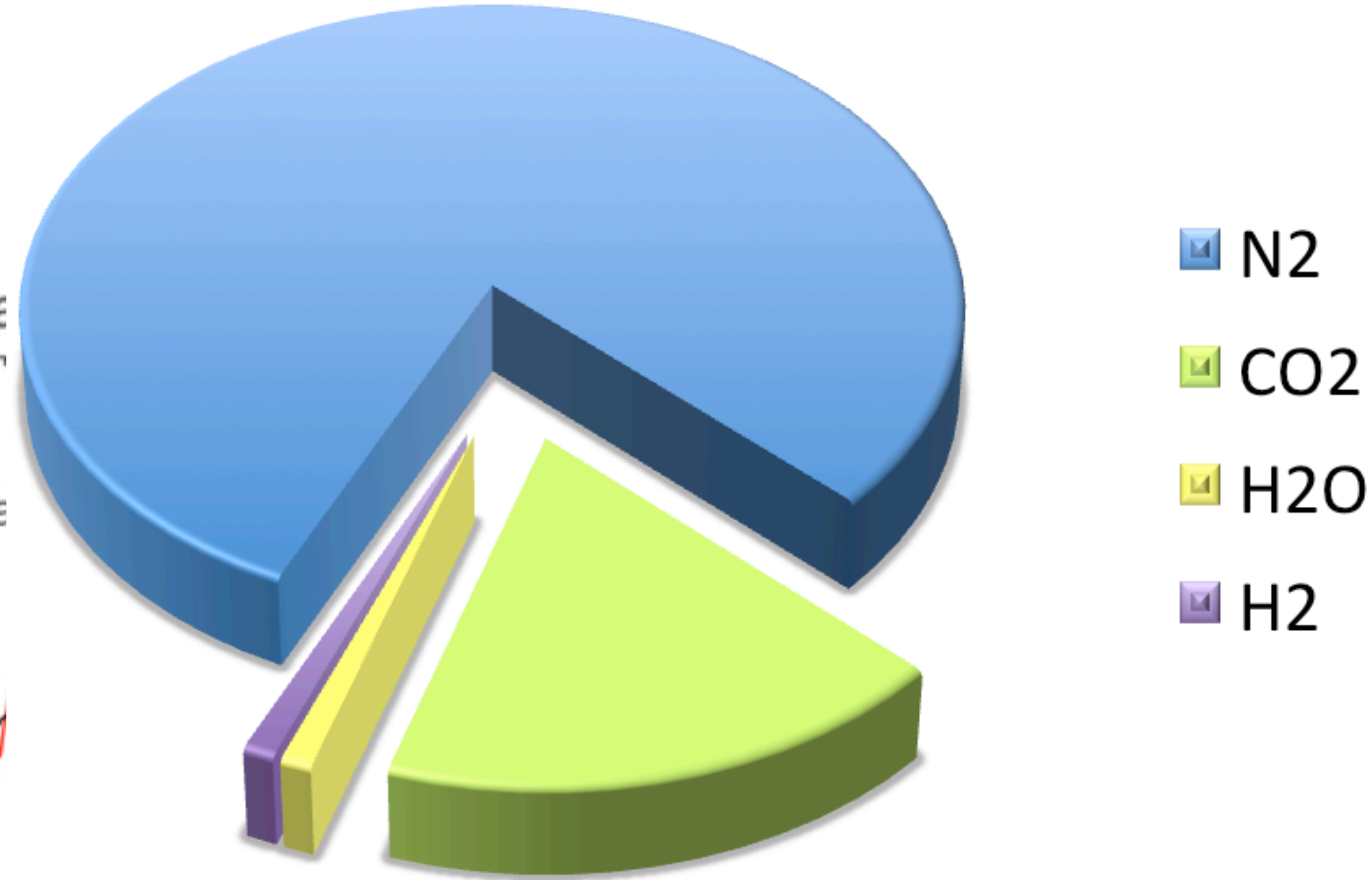
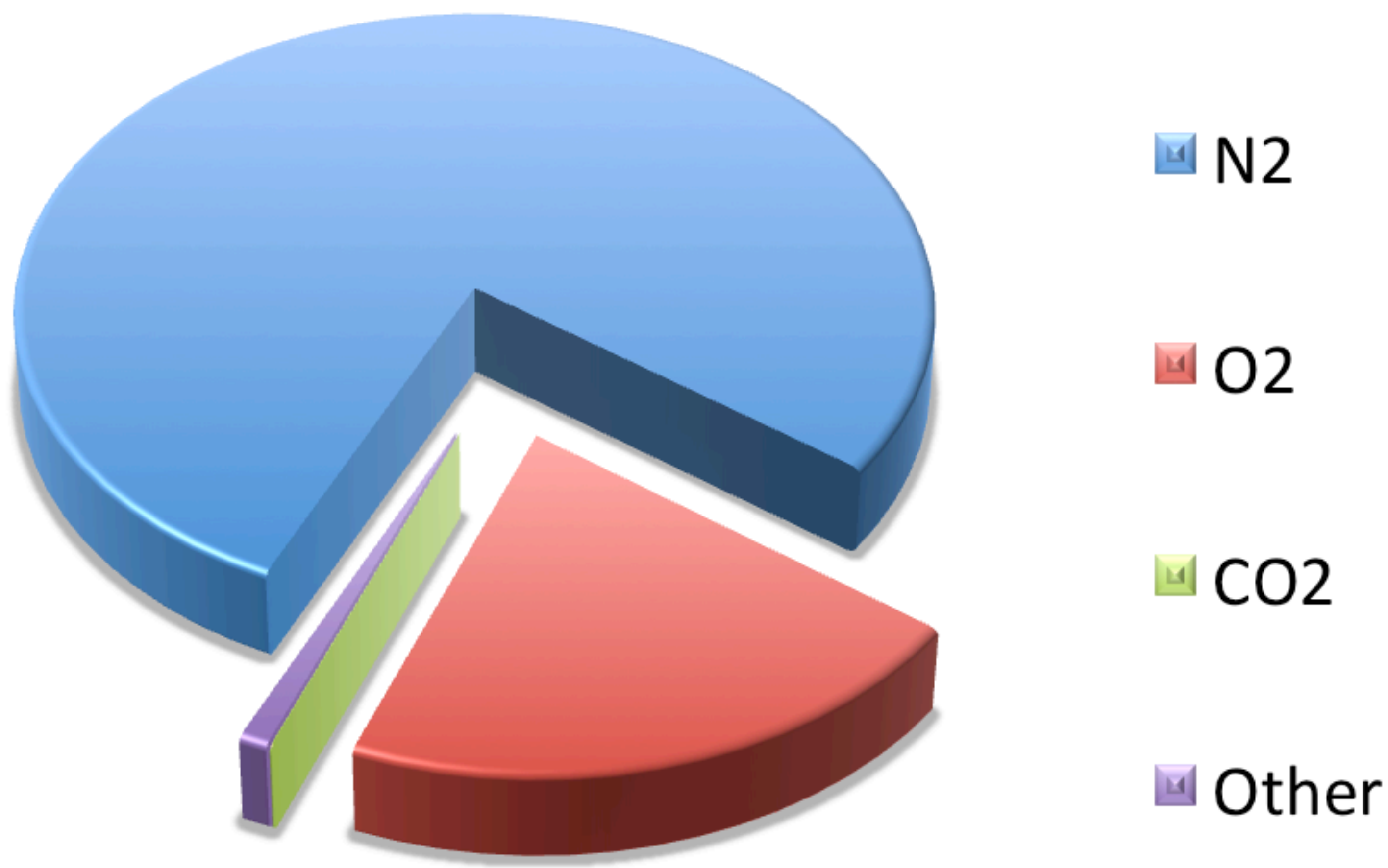
The Problem with CO_2 Recycling

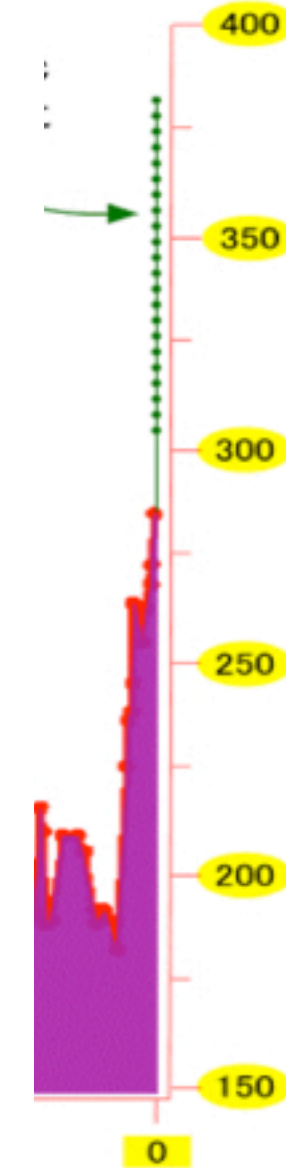


3 Billion Years Ago



Today





Carbon-Free Fuels

Disadvantages of carbon-based fuels

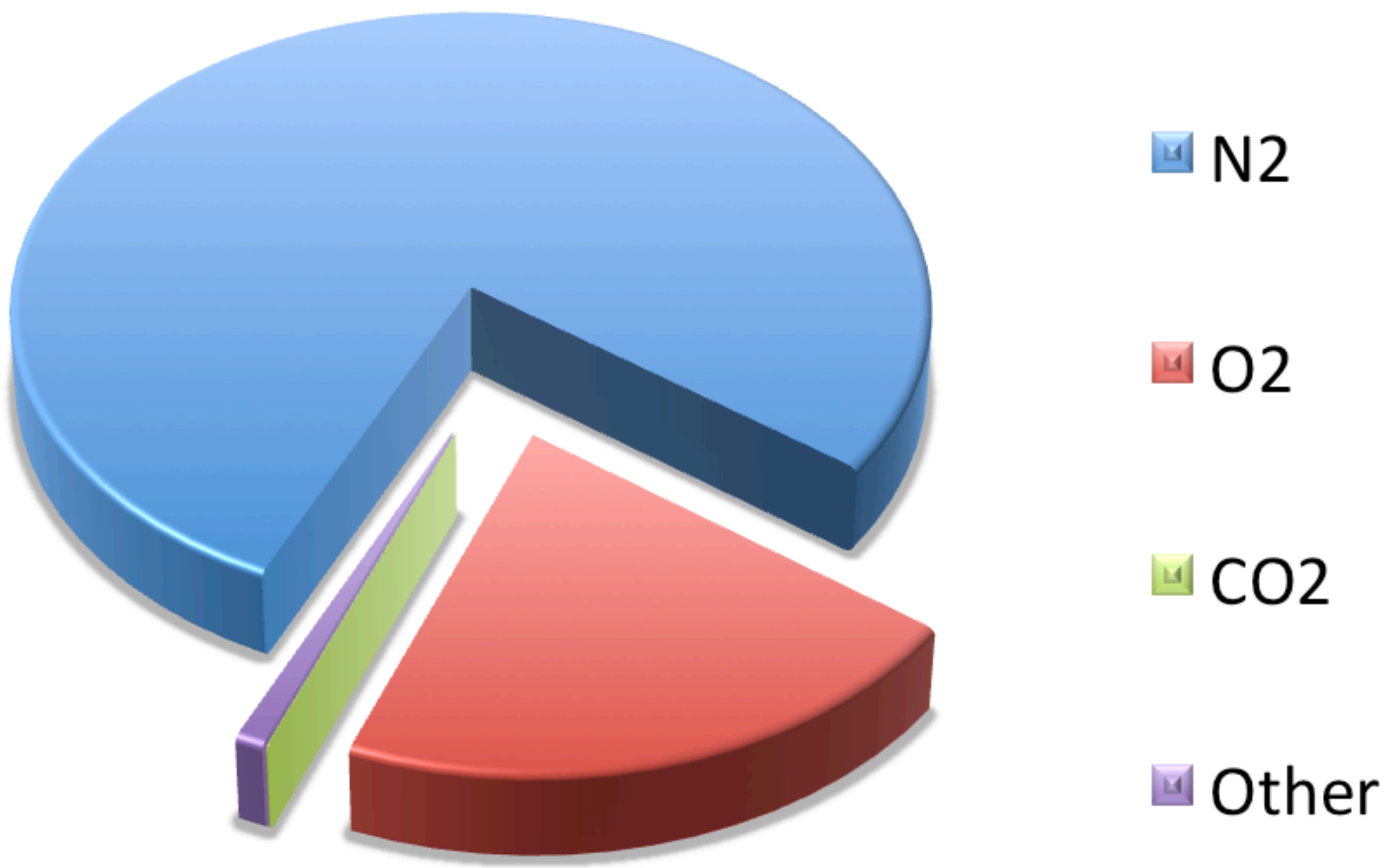
CO_2 recycling required for carbon neutrality

Low CO_2 concentration hampers atmospheric recovery

Onboard CO_2 recovery impractical for transportation applications

One possible solution: Avoid carbon!

Carbon-Free Fuels

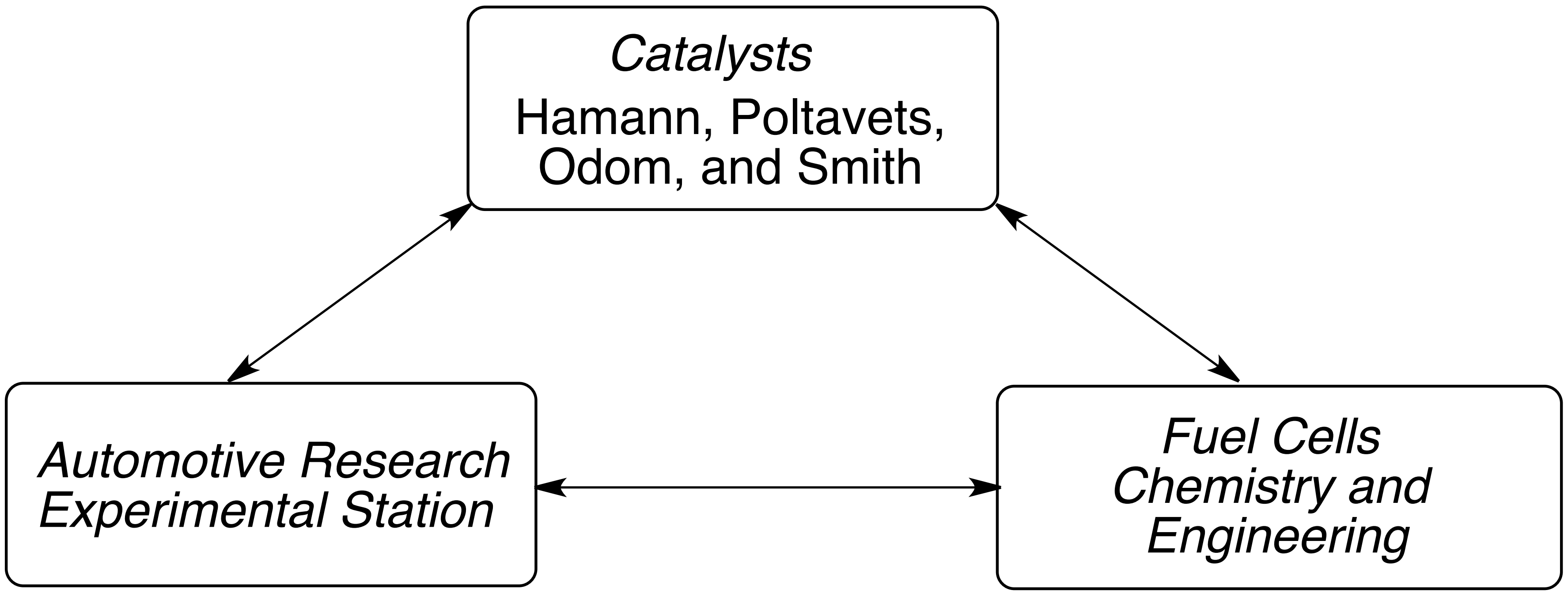


Carbon Free Fuels: Research Team

MSU Research Team
Professor Thomas Hamann-Energy conversion chemistry
Professor Aaron Odom-Nitrogen chemistry, catalysis
Professor Viktor Poltavets-Solid-state chemistry, catalysis
Professor Milton Smith-Catalysis
Professor Daniel Nocera (Harvard/MSU)-Energy science

Dr. James Boncella (Los Alamos)-Fuel cells, nitrogen chemistry

Targeted agencies for center funding:
DOE (ARPA-E), NSF



Ammonia: A Hydrogen Dense Fuel

Advantages

Haber-Bosch process is well-established and is the second largest industrial chemical process. Approximately 1-2% of global energy is dedicated to ammonia production.

$$1/2\ N_2 + 3/2\ H_2 \rightleftharpoons NH_3$$

ΔH°_{rxn} = -11 kcal/mol,
ΔS°_{rxn} = -24 cal/mol·K

T (°C)	K_{eq}
25	7.1
160	1.0
450	0.01

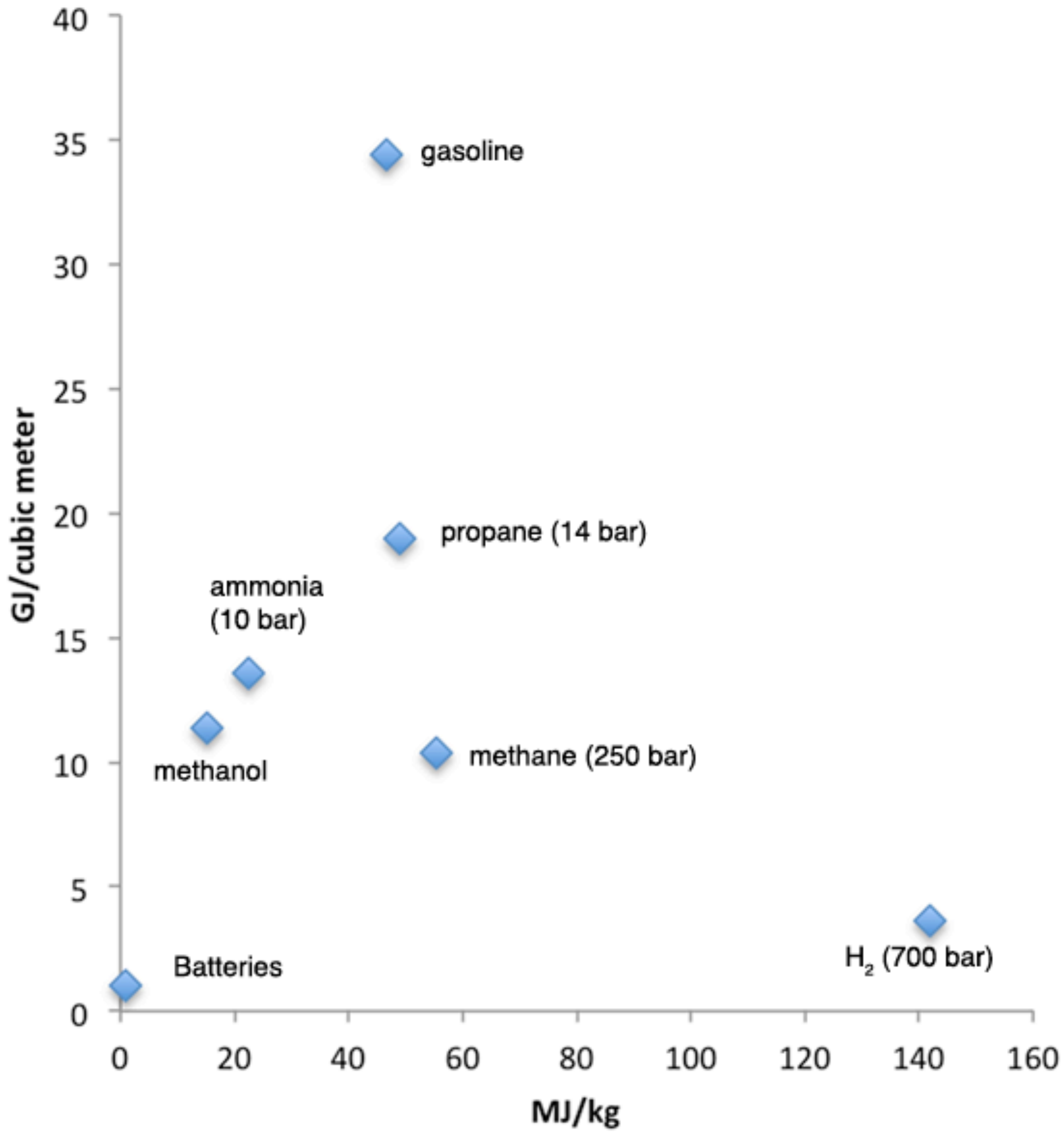
$$NH_3 \longrightarrow 1/_2\ N_2 + 3/_2\ H_2 \qquad 0.077\ V$$

- By mass, liquid NH_3 energy density is 40% of gasoline, 94% of methanol
- Liquid NH_3 is an efficient H_2 carrier

$$2\ NH_3 + 3/2\ O_2 \longrightarrow N_2 + 3\ H_2O$$

Releases 87% of the energy of H_2 oxidation!

Ammonia: A Hydrogen Dense Fuel



Ammonia: A Hydrogen Dense Fuel

Advantages

Synthesized from nitrogen, the most abundant gas in the atmosphere

Can be used as fuel in internal combustion engines

Produces less NOx emissions than gasoline

Ammonia is non-flammable

Ammonia: A Hydrogen Dense Fuel

Challenges

Carbon-neutral H_2 production does not meet energy needs

Current Haber-Bosch process requires high pressure of N_2 and H_2.

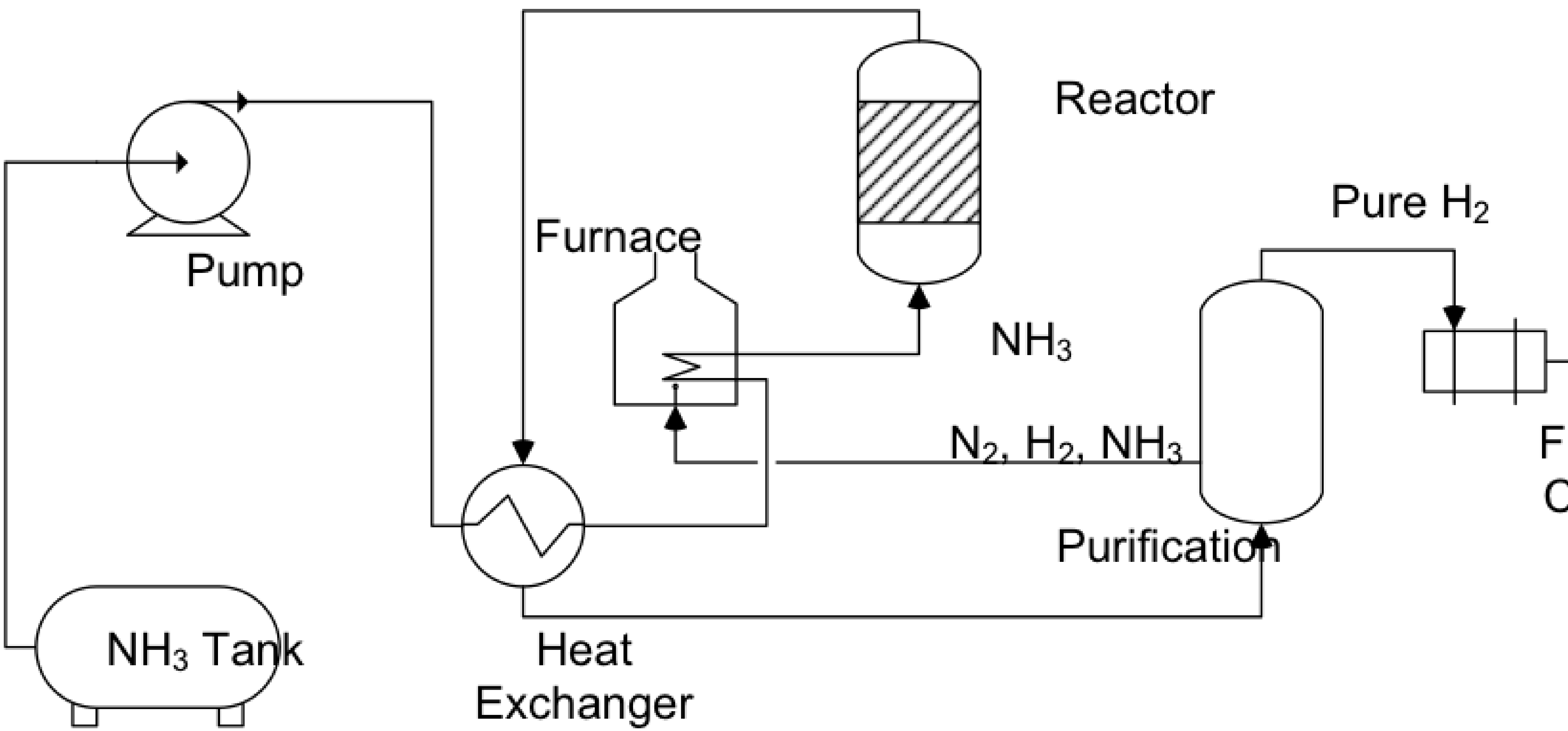
Like gasoline, ammonia is toxic.

Ammonia cracking to N_2 and H_2 is inefficient

Fundamental research is needed to address these challenges

Current Cracking Technology: Reverse Haber-Bosch

$$NH_3 \underset{\text{catalyst}}{\overset{T > 500\ °C}{\rightleftharpoons}} 1/2\ N_2 + 3/2\ H_2$$



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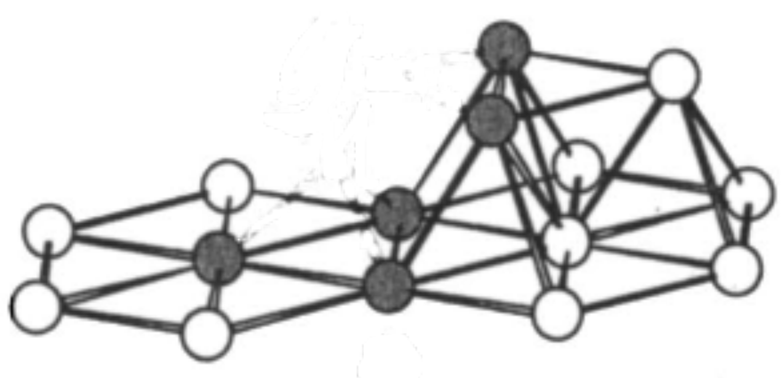
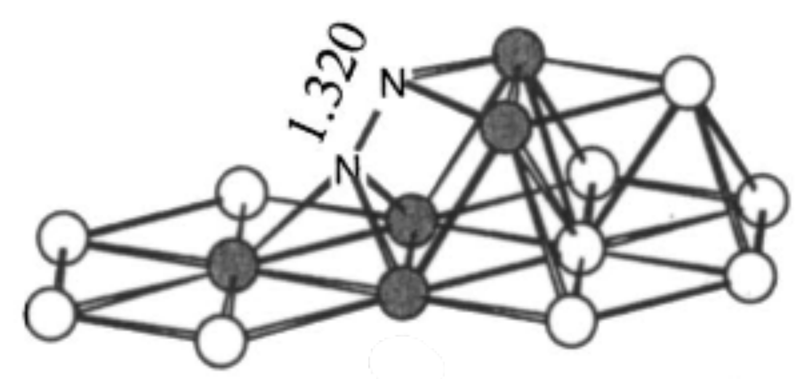
Carbon Free Fuels: Proposed Research

New catalysts for ammonia synthesis

Improve current Haber-Bosch by synthesizing nano-structures that increase active sites for catalysis.

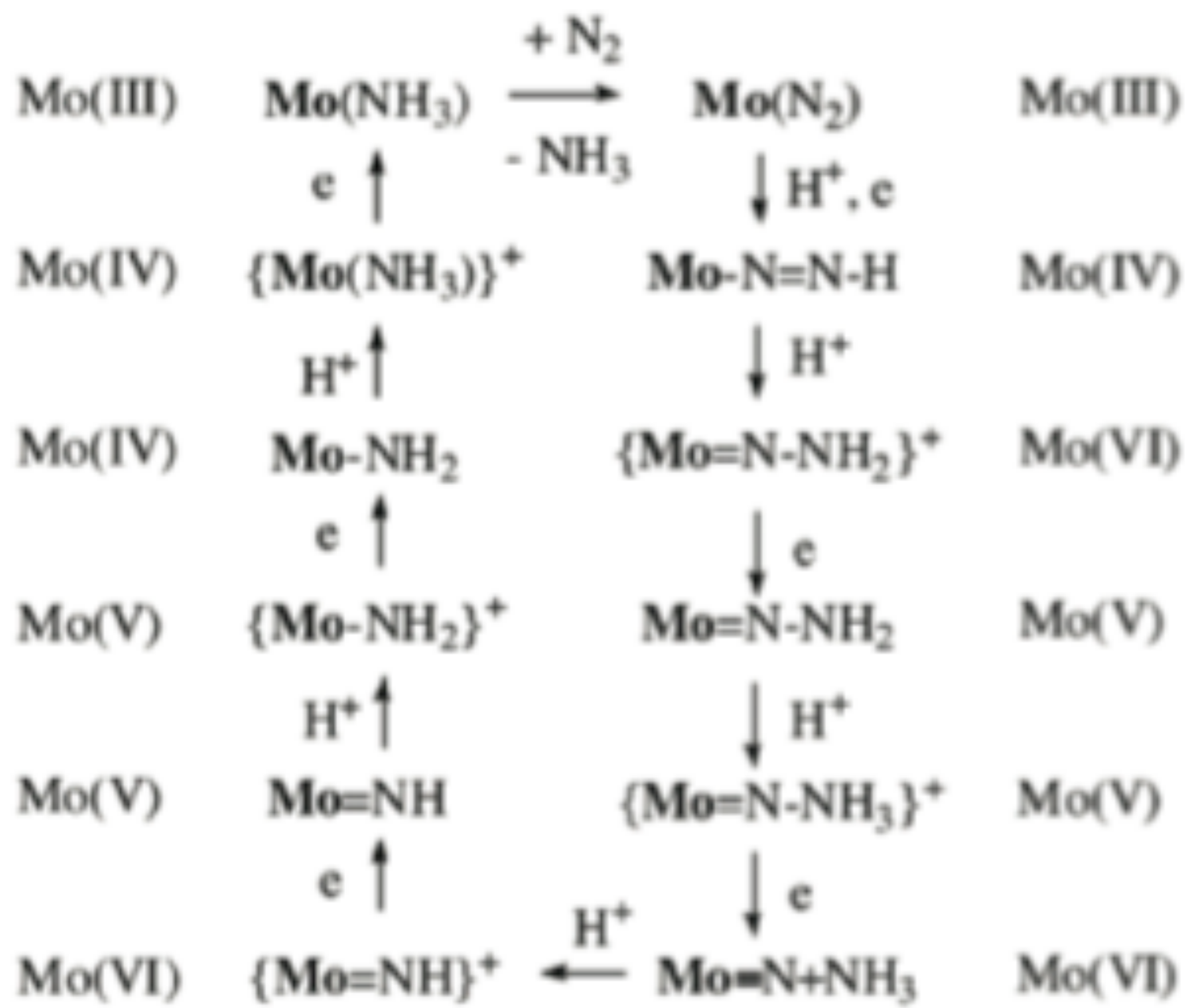




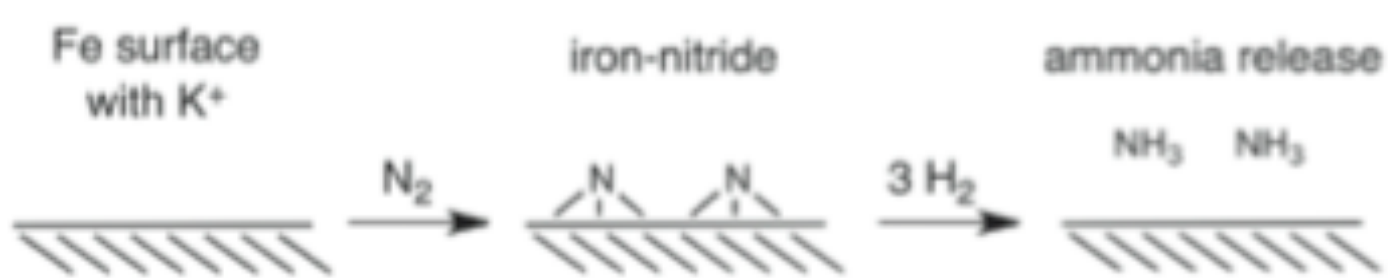
Develop ammonia synthesis where water is the hydrogen source instead of hydrogen gas.

$$N_2 + 3\,H_2O + \text{electrical energy} \longrightarrow 2\,NH_3 + 3/2\,O_2$$

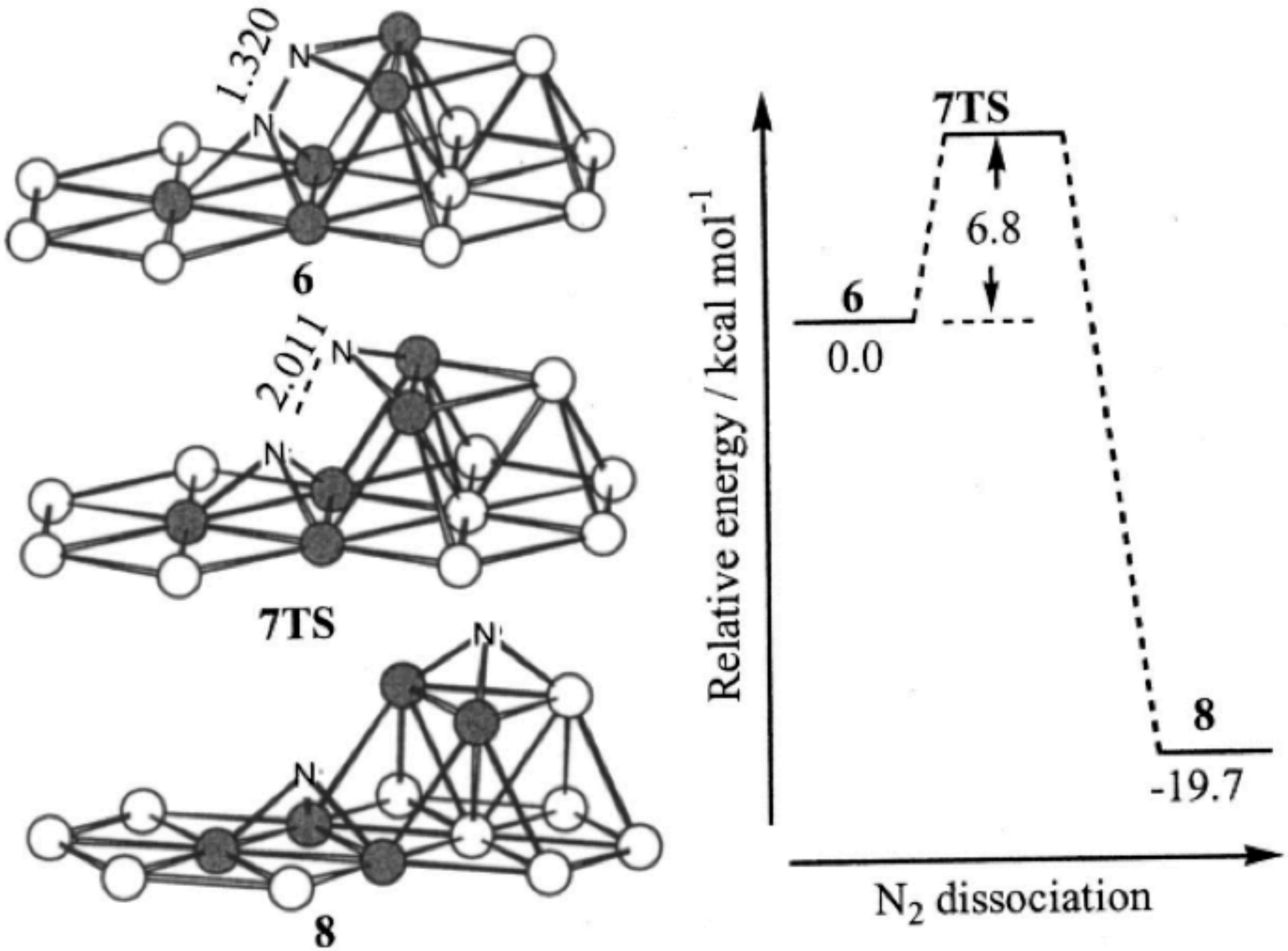
Ammonia Synthesis



a



Computational Studies of Haber-Bosch

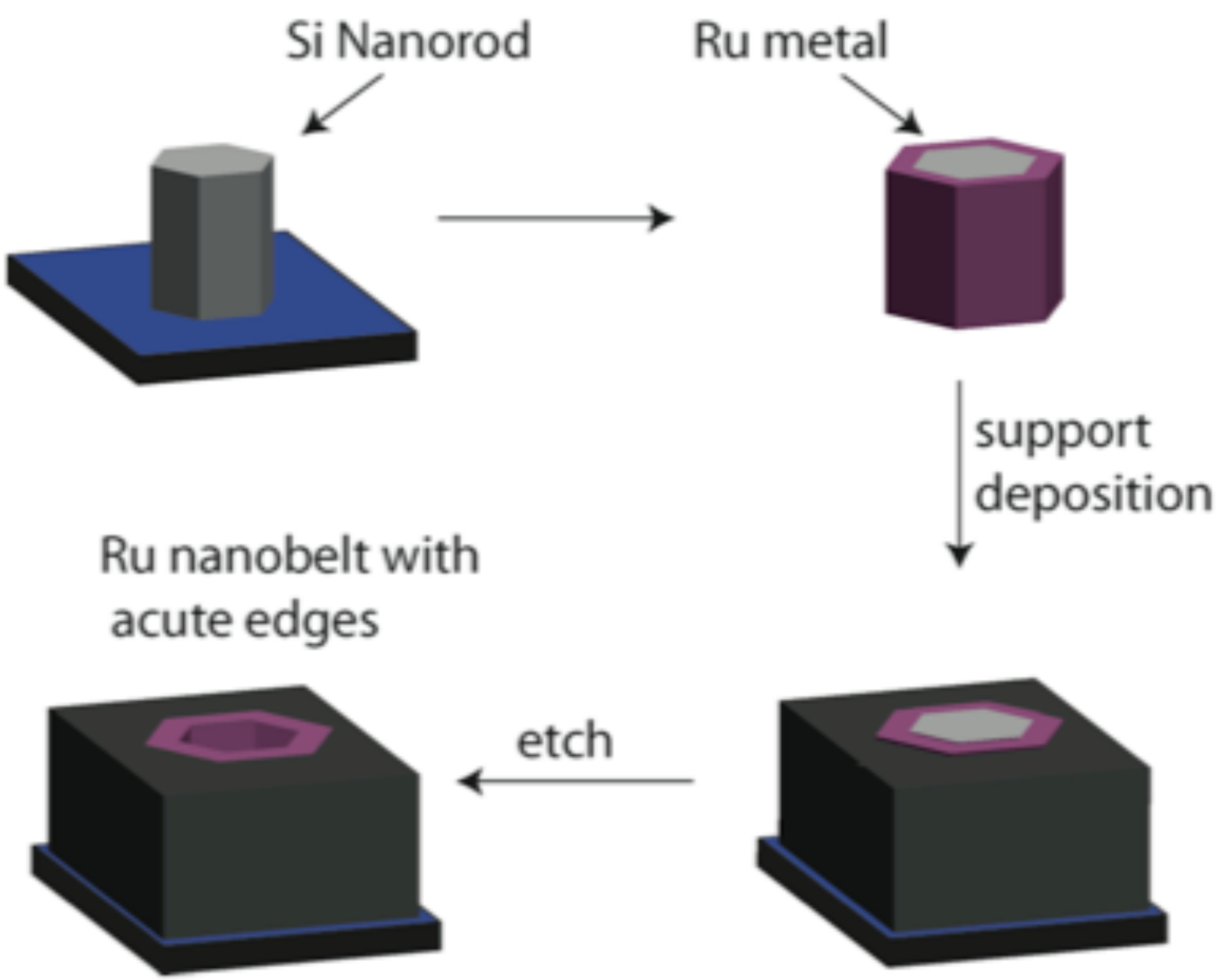


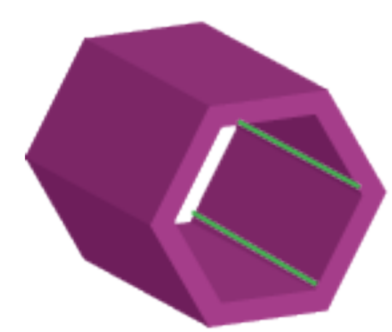
Cao, Z. X.; Wan, H. L.; Zhang, Q. N., *J. Chem. Phys.* **2003,** *119*, 9178-9182.

Carbon Free Fuels: Proposed Research

New catalysts for ammonia synthesis

Improve current Haber-Bosch by synthesizing nano-structures that increase active sites for catalysis.





Carbon Free Fuels: Proposed Research

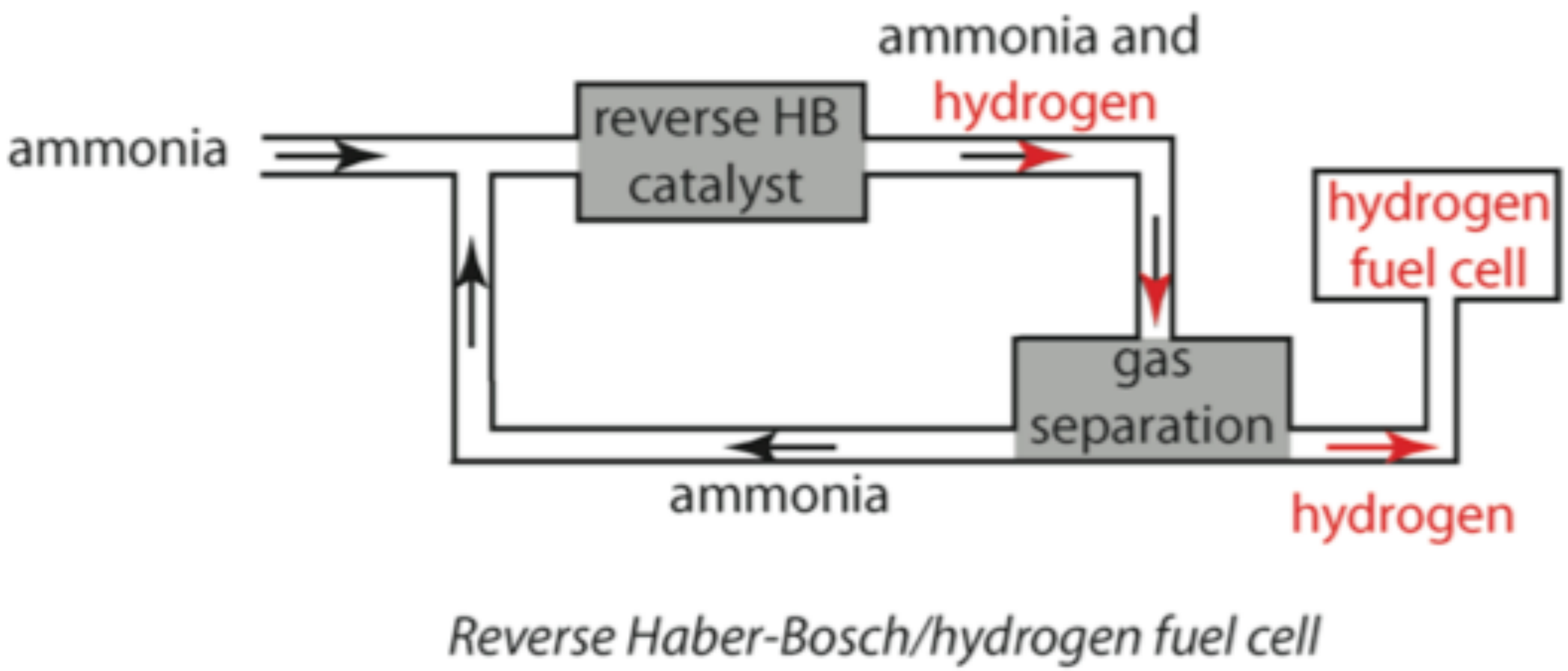
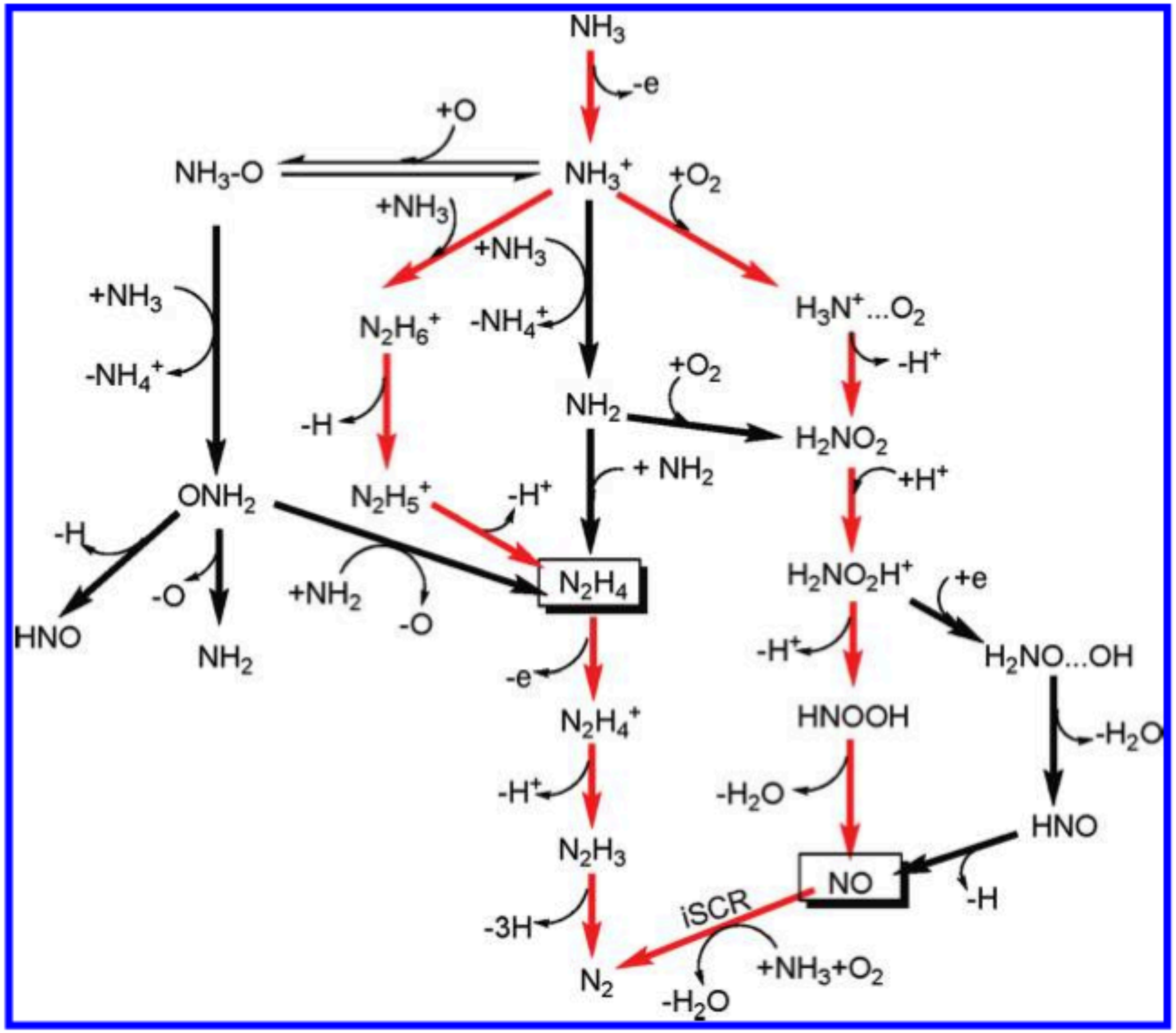


Figure 3. Hydrogen synthesis from ammonia feeding a hydrogen fuel cell.

Upgrading NH_3 by Selective Oxidation to Hydrazine



R. M. Yuan, G. Fu, X. Xu, H. L. Wan, *J. Phys. Chem. C* **2011**, *115*, 21218-21229.

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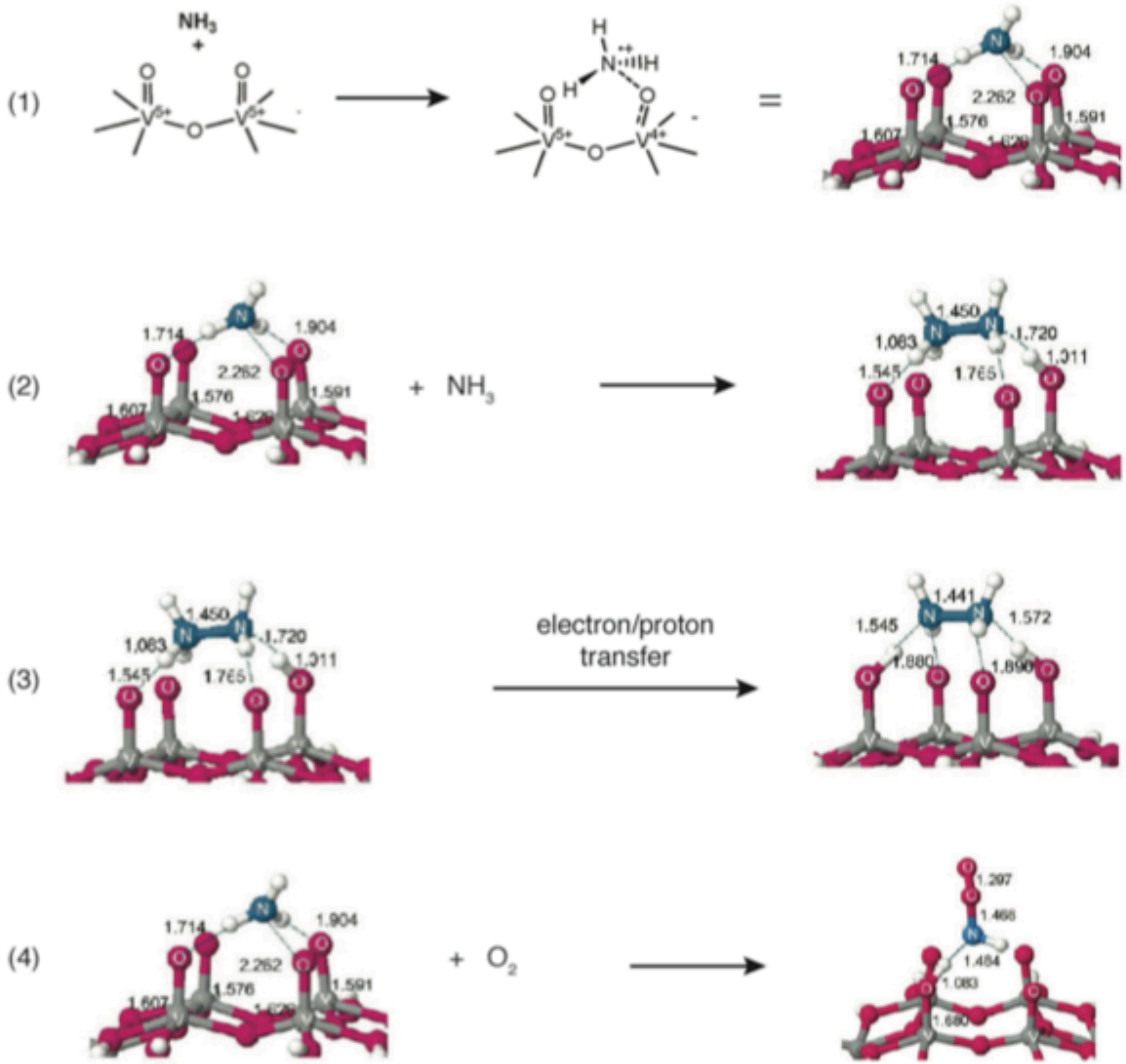
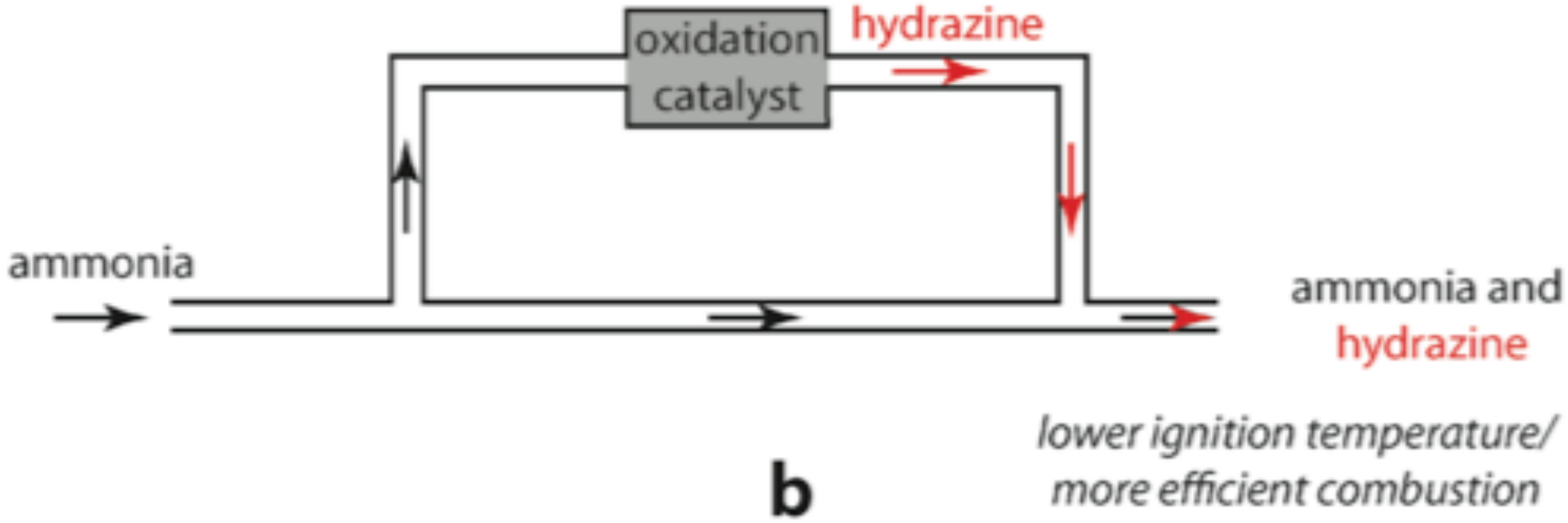


R. M. Yuan, G. Fu, X. Xu, H. L. Wan, *J. Phys. Chem. C* **2011**, *115*, 21218-21229.

Upgrading NH_3 by Selective Oxidation to Hydrazine



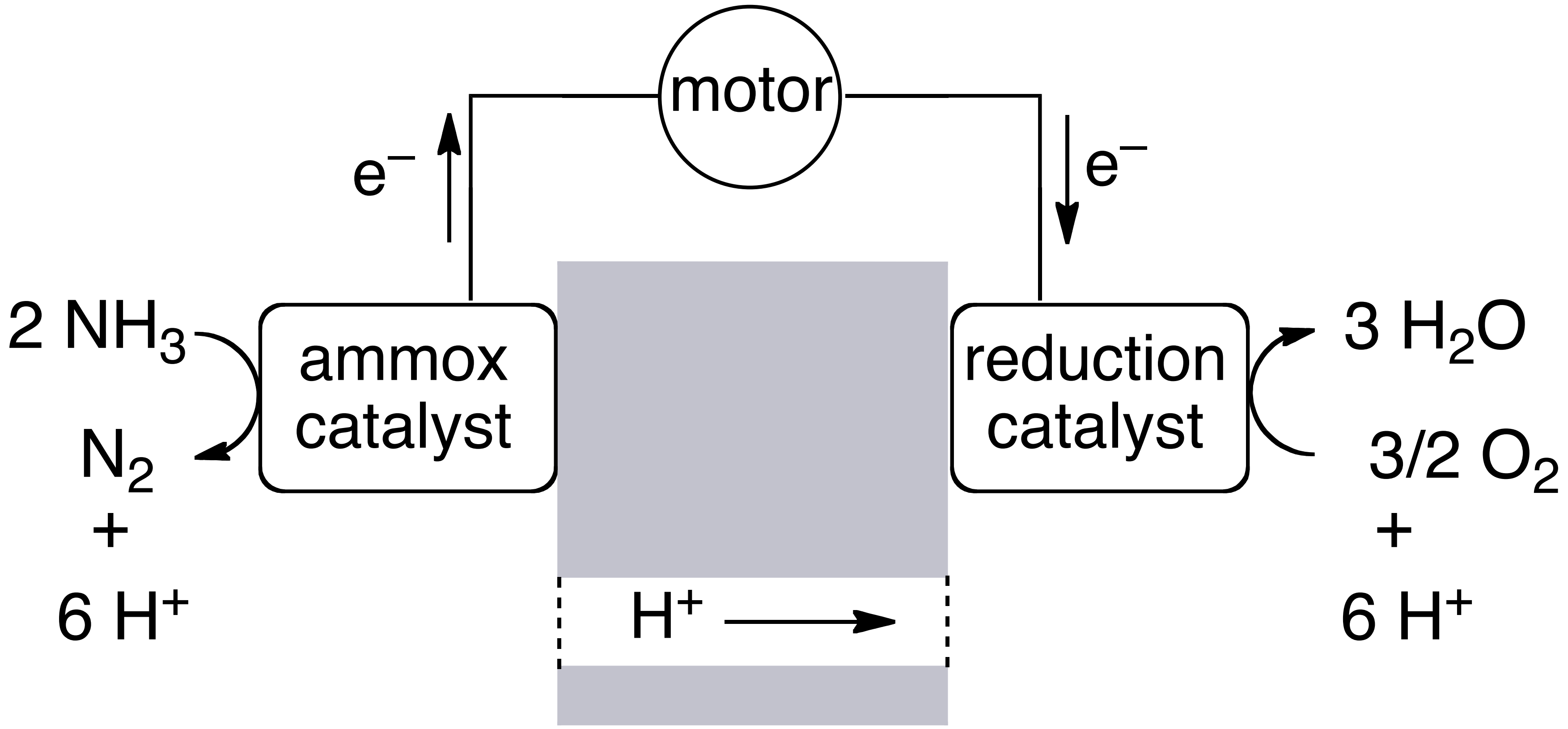
Proposed Research: Ammonia to Energy

Develop catalysts for ammonia oxidation

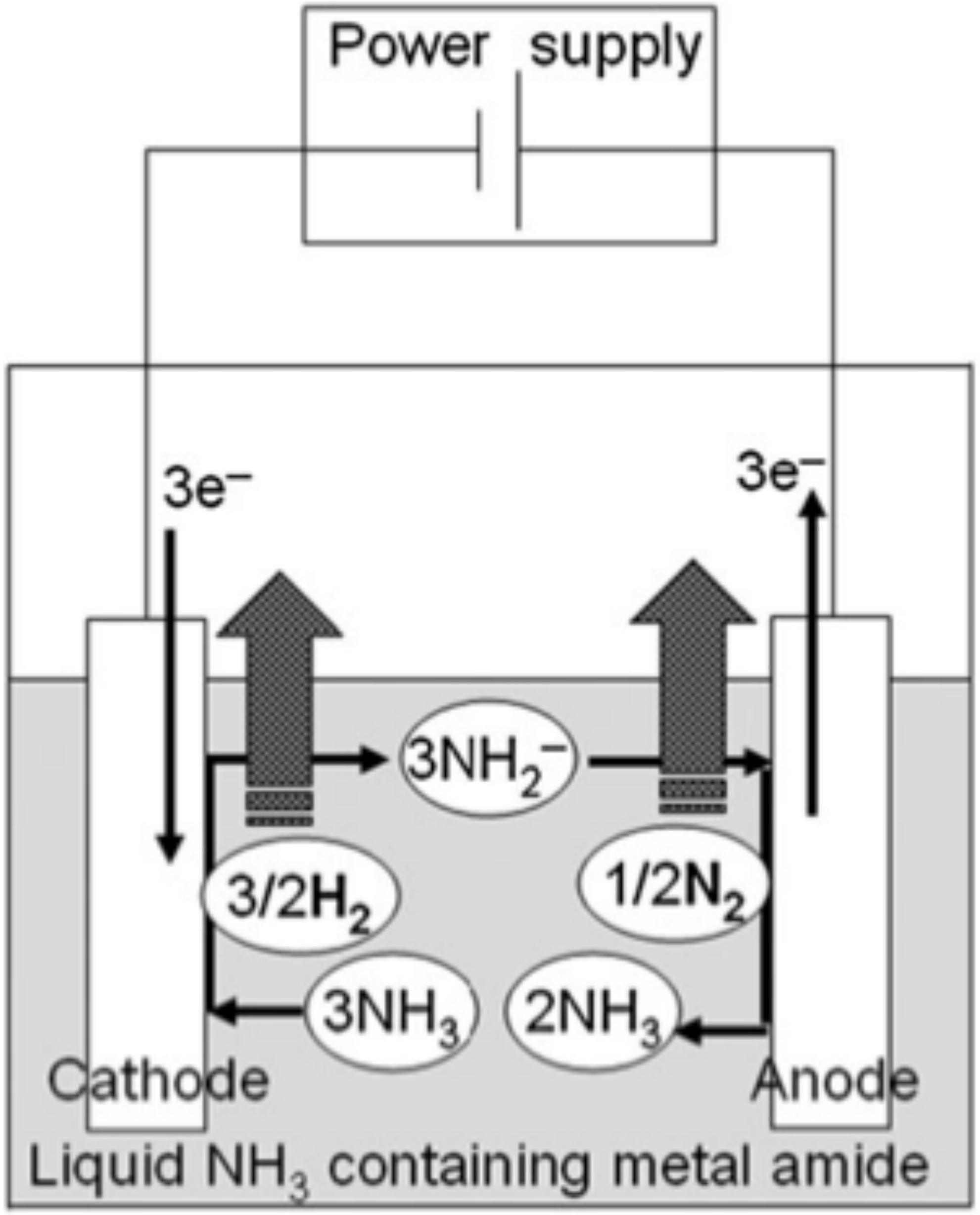
$$NH_3 \longrightarrow 1/2\ N_2 + 3\ H^+ + 3\ e^-$$

$$H_2O \xrightarrow{\text{PS-II}} 1/2\ O_2 + 2\ H^+ + 2\ e^-$$

- **Design new ammonia fuel cells**



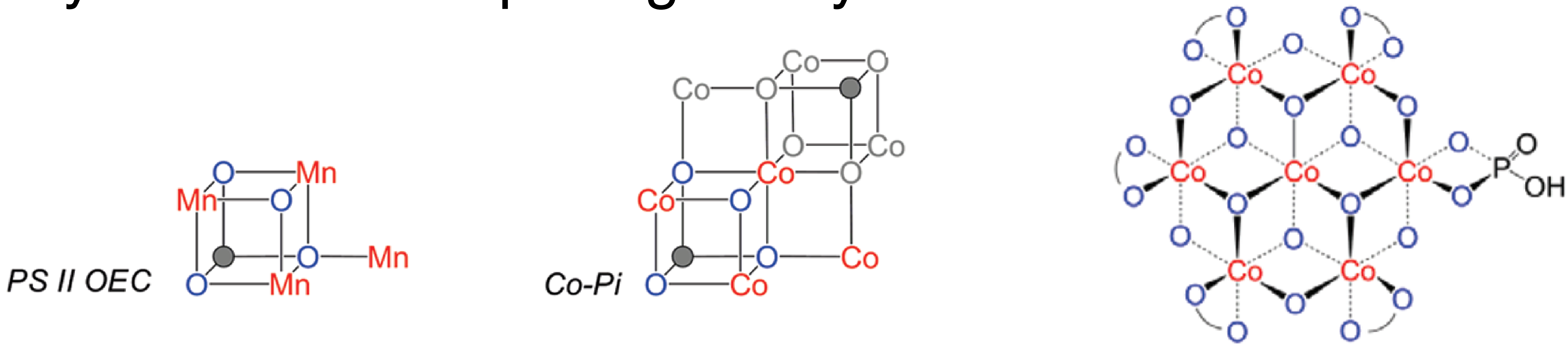
Proposed Research: Ammonia to Energy

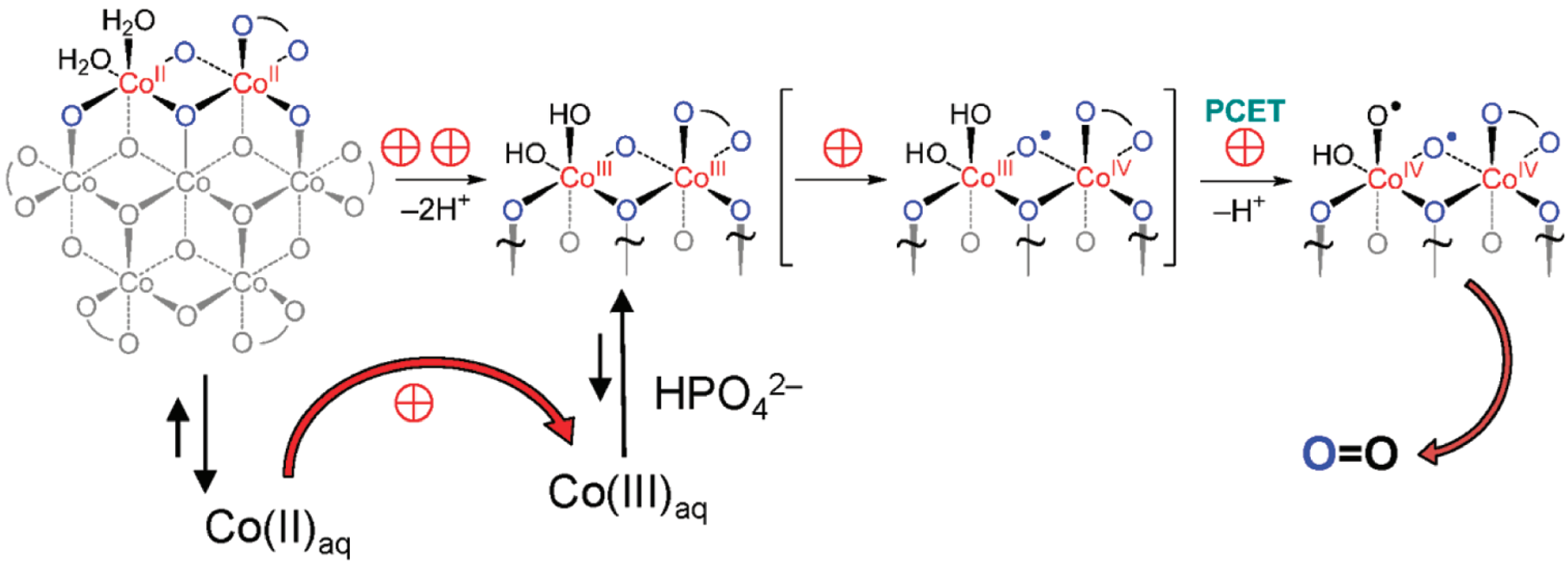


Electrolysis at 2 V potential!

Hanada, N.; Hino, S.; Ichikawa, T.; Suzuki, H.; Takai, K.; Kojima, Y., *Chem. Commun.* **2010,** *46*, 7775-7777.

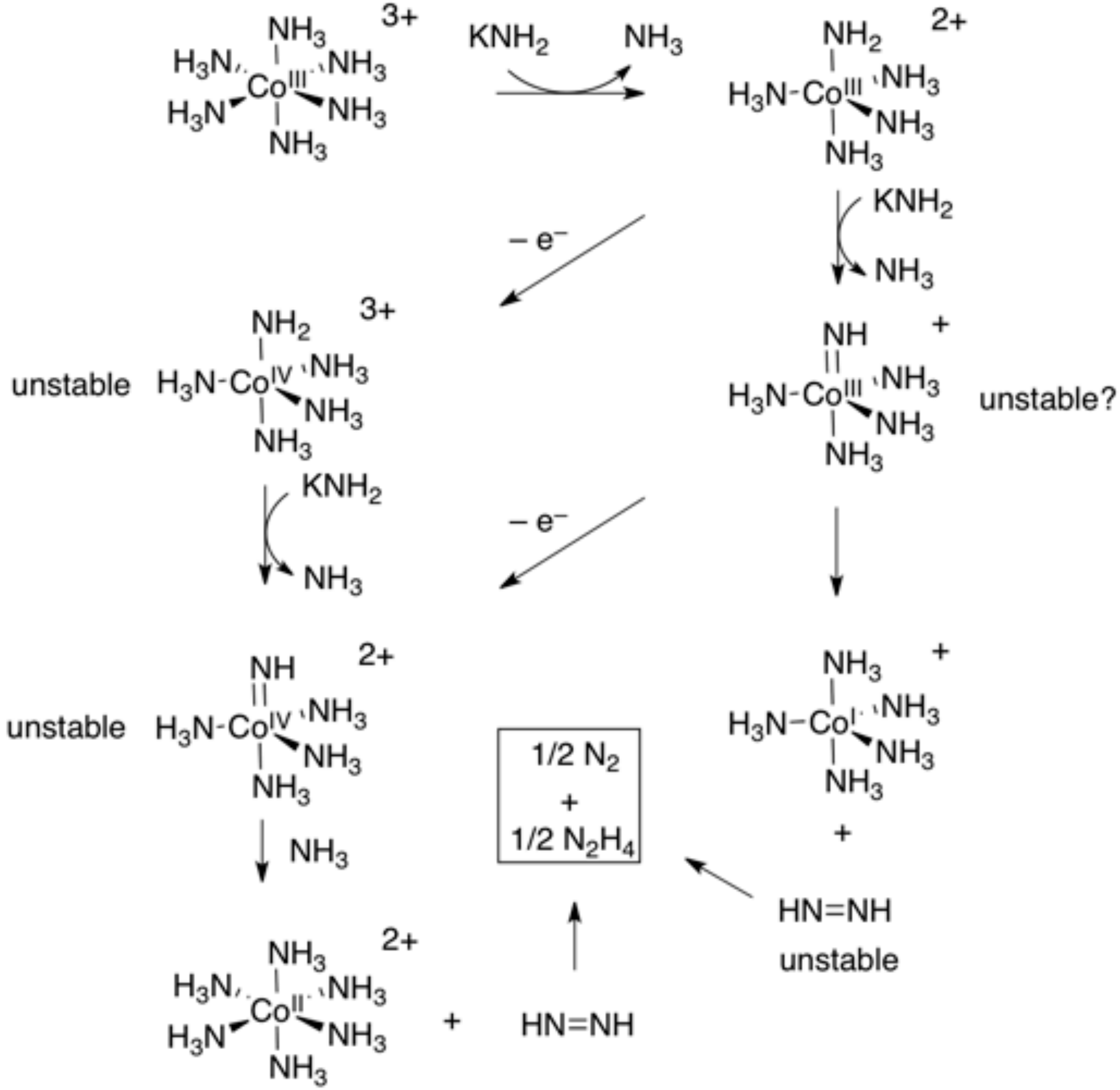
A synthetic water splitting catalyst:





Nocera and coworkers, J. Am. Chem. Soc. 2011, 133, 5174–5177
Nocera and coworkers, *Acc. Chem. Res.*, **2011**, *45*, 767-776.

Proposed Research: Metal Catalyzed Oxidation



Proposed Research: Metal Catalyzed Oxidation

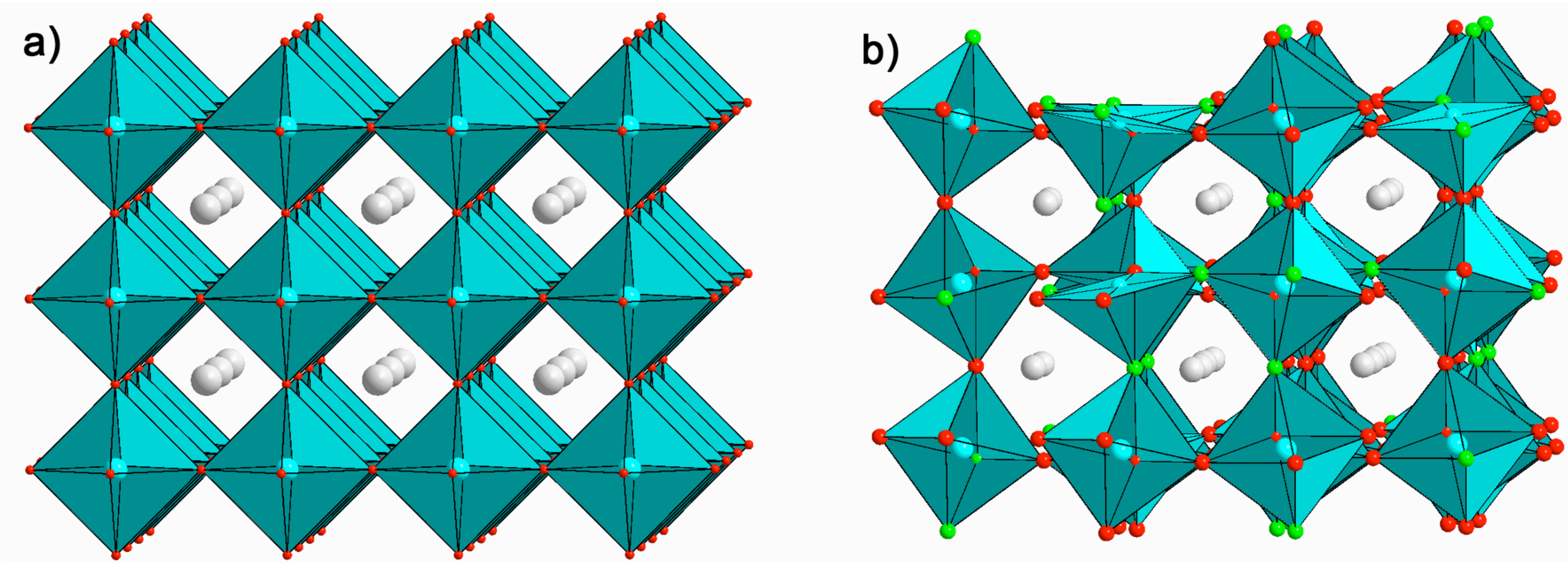


Figure 10. Crystal structure models of a) AMO_3 perovskite and b) $AMO_{3-x-y}N_y$ anion deficient oxynitride perovskite. The A cations are shown as light grey spheres, the B cations are situated in the octahedra and the square pyramids, and the O and N atoms are represented by red and green spheres respectively.

Impacts: Local and Global

Complements MSU's efforts in Biofuels making us the leader in fuel research

Significant IP opportunities in energy and agricultural sectors

Elimination of CO_2 emission at the tailpipe of transportation vehicles

Hydrogen storage from Earth abundant feedstocks

Off-grid synthesis of fuel and fertilizer for third-world countries by converting electrical energy (from solar, wind, etc.) to fuel