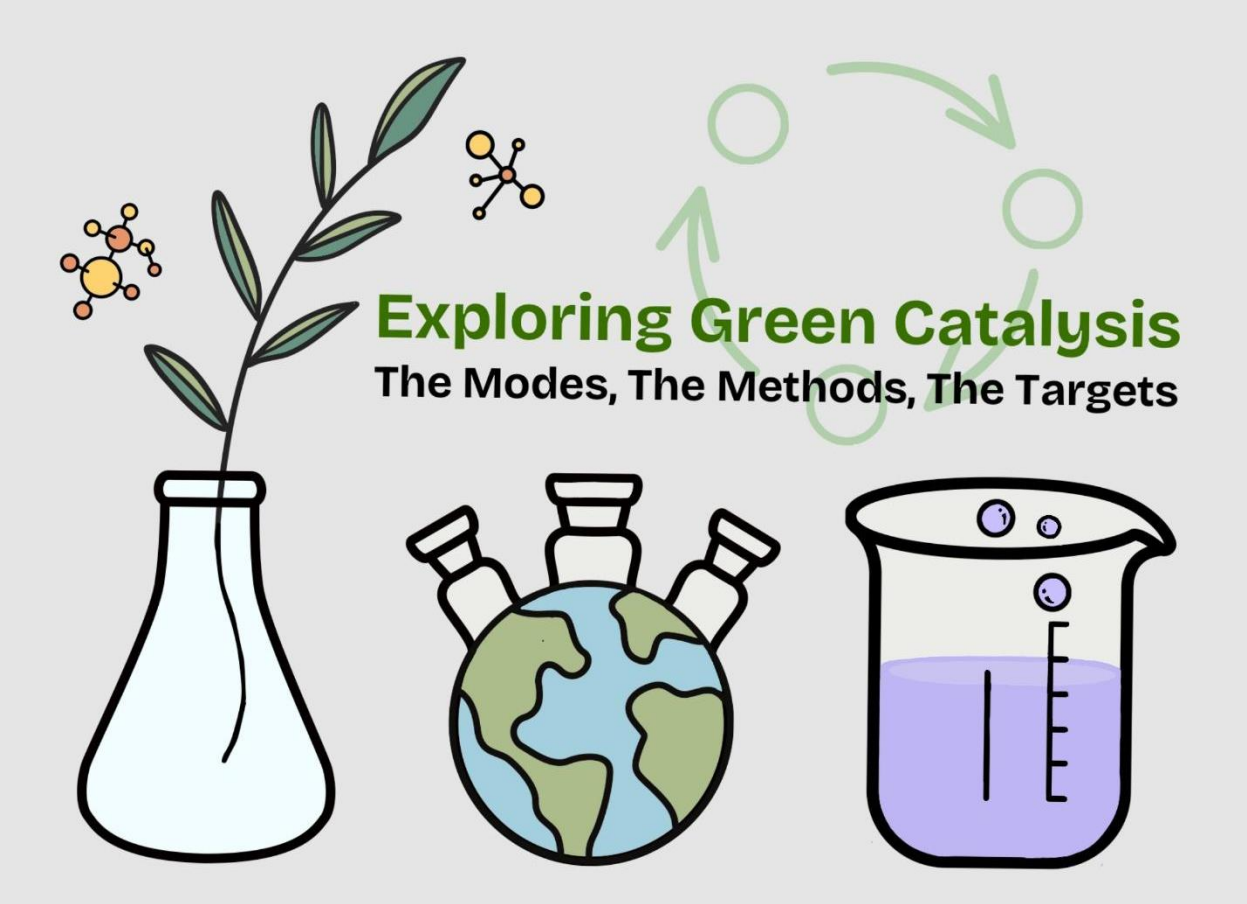

Symposium Workbook

June 18th, 2025

CSC 2025

Exploring Green Catalysis – The Modes, The Methods, The Targets

Contents

Welcome to the Exploring Green Catalysis Symposium at CSC2025

Description:

In this interactive symposium we will explore key components that influence inorganic chemistry's impact on society – addressing global challenges, sustainability initiatives, and the importance of scientific communication. During this morning-long session, participants will collaboratively investigate the components of green catalysis design, apply their synthetic knowledge, and communicate sustainability considerations through a series of engaging, sustainability-focused activities.

Organizers:

Marissa L. Clapson (University of Prince Edward Island), Jaelyn Bjornerud-Brown (BSc. Candidate, University of Victoria), Kristen Perry (MSc. Candidate, University of Toronto), Megan Ftizgerald (MSc. Candidate, Memorial University of Newfoundland), Connor S. Durfy (PhD. Candidate, University of British Columbia), Emma Davy (PhD. Research Scientist Carbon Engineering).

Comments from the Organizational Team:

As organizers, we set out to challenge the conventional structure of chemistry symposia by creating a space that prioritizes active participation, meaningful connection, and shared learning. Rather than focusing on talks, we've designed this session to foster engagement in gamified activities that highlight key concepts in green catalysis. Our goal is to create an environment where participants exchange ideas, collaborate, problem-solve, and enjoy themselves while doing so.

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Symposium Schedule:

8:00 – 8:05 AM	Opening remarks and introductions
8:05 – 8:30 AM	**Activity 1 – Green laboratories** At activity 1, you will have the opportunity to position yourself as various stakeholders in a teaching lab (instructor, student, and more!). You will consider a classic laboratory experiment and consider how to modernize the experiment and the lab itself through a lens of sustainability and green chemistry. You will get to contribute a group assessment and see the work of others using our interactive poster
8:30 – 9:00 AM	Flash talks
9:00 – 9:30 AM	Green chemistry panel discussion
9:30 – 10:00 AM	Coffee break – activities remain open
10:00 – 11:00 AM	**Activity 2 - Breakout by Design (of Catalysts!)** In this green inorganic chemistry escape room activity participants will solve a series of hands-on puzzles focused on dissociative substitution reactions and cross coupling methods. Throughout the three puzzles, participants will explore second-year inorganic chemistry principles in ligand design, process design, green chemistry applications, and mechanistic considerations. The puzzles provided participants with a scaffolded view on catalyst design, highlighting the cyclical nature of green chemistry design and implementation. **Activity 3 - Sustainability Survivor** This activity aims to promote discussion and create connections between green chemistry metrics and waste reduction practices. In addition to general knowledge questions pertaining to green chemistry and catalysis, teams will be tasked with answering short, trivia-like questions by finding corresponding answers on tiles, eventually solving a puzzle. First team to finish their puzzle, wins!
11:00 – 11:40 AM	Discussions in green design

Presenters and Panel Speakers:

Zhen Dai (Graduate student, McGill University)
Organocatalytic Peptide Coacervates as Green Microreactors for Aldol Additions in Water

Nelson Rutajoga (Graduate student, University of Ottawa)
Diagnostic Hydrogen Generating Method for Evaluating Remediation Ability of Novel TiO2-Based Catalysts Under Visible Light

Dr. Gillian Thomas (Assistant Professor, University of Leeds)
Expedited Reaction Optimization: Transfer Learning meets High-Throughput Experimentation

Dr. Marissa L. Clapson (Assistant Professor, University of Prince Edward Island)
Lead symposium organizer and session chair

Activity 1 - Our Role: Exploring Individuals' Roles in Developing Sustainable Alternatives.

Activity Leads: Dr. Emma Davy, Connor S. Durfy, and Julia Pitsiaeli

Overview of the Activity:

Green chemistry and lessons in this field are becoming of increasing important in the undergraduate classroom and the graduate/industry research space. While new teaching materials can be developed for undergraduate students, an effective method for teaching green chemistry can be to adapt existing teaching materials and practices.

This activity will focus on adaptation. Here, you will adopt a persona that you would find in an undergraduate teaching lab: an undergraduate student, a graduate student teaching assistant, a teaching faculty member, health and safety personnel, or a lab technician. You will consider a classic organic transformation: the Friedel-Crafts reaction.

Here, positioning yourself as these stakeholders, you will think about how this particular lab could be made more "green" or "sustainable". Please note that this does not have to be changes to the experiment or the space (although those suggestions are welcome), they can be lessons that could be incorporated based on the existing experiment paradigm.

Learning Objectives:

- To challenge one's definition of **green chemistry** and **sustainability** and to position this definition across various stakeholders in an undergraduate teaching laboratory.
- To adopt a perspective outside your own (i.e., if you are faculty, consider being a student) when considering these green chemistry considerations.
- To collaborate with a group in creating definitions of **green chemistry** and **sustainability**.
- To adapt existing resources to be "greener" through changes to chemistry, infrastructure, policies and mindset.

Station Procedure:

1) Arrive to the station and draw a **stakeholder** from the card pile (student, teaching assistant, lab technician, faculty or lab director, health and safety professional) and receive a copy of the current undergraduate lab.

2) Receive and read the undergraduate lab experiment.

3) Consider:

    a) What is your definition of **sustainable** and **green chemistry**? How long have you had this definition? Do you think it can change? How does this align with definitions from the Canadian Society for Chemistry/American Chemical Society?

4) Consider:
    a) What are the "non-sustainable" elements of this experiment?
    b) What changes would you make to make the experiment procedure itself more sustainable?
    c) What changes would you make to make the experimental space itself more sustainable?
    d) What changes would you made beyond the experiment procedure and space in in the interest of sustainability?
5) Use the coloured post-its to write your suggestions and label the poster:
    - Yellow: Experimental Procedure
    - Pink: Experimental Space
    - Green: Beyond Procedure and Space
6) Reflect:
    a) What sustainability concerns most directly impact your **stakeholder**?
    b) Which of your suggested changes can your **stakeholder** reasonably contribute to?
    c) How do the perspectives of other **stakeholders** affect the changes you prioritize?

References:

1. The UN's 17 Goals for Sustainable development (https://sdgs.un.org/goals)
2. The 12 principles of Green Chemistry (https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html)
3. Dicks, A. Teaching Greener & More Sustainable Analytical Chemistry to Undergraduates: Some Strategies & Tips. *Green Analytical Chemistry*. **2023**, *7*, 100082.
4. Dicks, A., D'eon, J., Morra, B., Chisu, C.K., Quinlan, K.B., Cannon, A. A Systems Thinking Department: Fostering a Culture of Green Chemistry Practice Among Students. *J. Chem. Educ.* **2019**, *96*, 2836.
5. Mercer, S. M.; Andraos, J.; Jessop, P. G. Choosing the Greenest Synthesis: A Multivariate Metric Green Chemistry Exercise. *J. Chem. Educ.* **2012**, *89* (2), 215-220.
6. Aubrecht, K. B.; Bourgeois, M.; Brush, E. J., MacKellar, J.; Wissinger, J. E. Integrating Green Chemistry in the Curriculum: Building Student Skills in Systems Thinking, Safety, and Sustainability. *J. Chem. Educ.* **2019**, *96* (12), 2872-2880.

Activity 2 – A Sustainability Puzzle: Leveraging Second-Year Inorganic Principles for Sustainable Catalyst Design

Activity Leads: Kristen L. Perry, Jaelyn Bjornerud-Brown, and Connor S. Durfy

Overview of the Activity:

When designing catalysts, there are many intersecting contributors that must be kept in mind. As we strive for creating more green-focused chemistry and catalysts, it is important to consider factors such as metal choice, ligand selection, reaction conditions, and overall sustainability. Green catalysis aims to reduce environmental impact while maintaining or improving reaction efficiency. This escape room activity is designed to reinforce these principles through a fun, collaborative, and challenge-based experience. Participants will apply their knowledge of catalysis and green chemistry concepts to solve a series of puzzles that highlight key aspects of sustainable catalyst design.

Get together in a team of 4–5 people. Using the provided information within the workbook plus your personal experience, work with your team to get through the three different puzzles within this 'escape room.' Each puzzle will have a code or answer that can be inputted into the corresponding virtual lock (Flippity QR code below), which will allow your group to progress to the next puzzle. Good luck and think green!

Overall Learning Objectives:

- To be able to analyze the interconnected components of catalyst design.
- To recognize the role of catalysis in green chemistry.
- To demonstrate collaborative problem solving in a team context

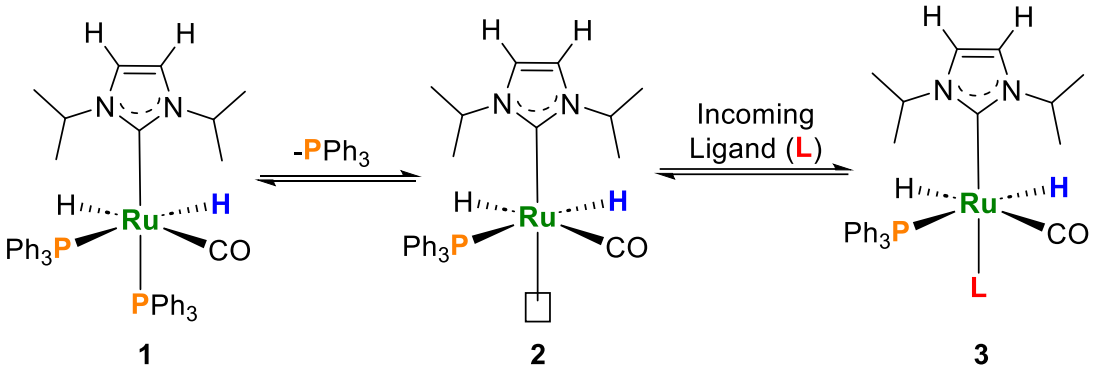
QR Code for the Virtual Lock

Puzzle 1: Dissociative Mechanisms.

Overview of Puzzle 1:

The objective of this first puzzle is to understand how different properties of a complex can influence the rates of dissociative mechanisms. The two properties being examined in this puzzle are the steric bulk of the dissociating ligand (phosphines) and the electronic properties of the *trans* N-heterocyclic carbene (NHC) ligand, which affect ligand lability through the Trans Effect. To complete this puzzle, you must rank the donicity of the NHC ligands and steric size of the phosphine ligands, then use this information to determine which ligand combination will result in the fastest and slowest phosphine dissociation reactions. Solving this will provide the combination needed to move into the next puzzle.

The general reaction can be observed below:



Note: This puzzle is based on the metal complex above, however for simplicity, we will only be modeling the *trans* NHC – Metal – phosphine bonds.

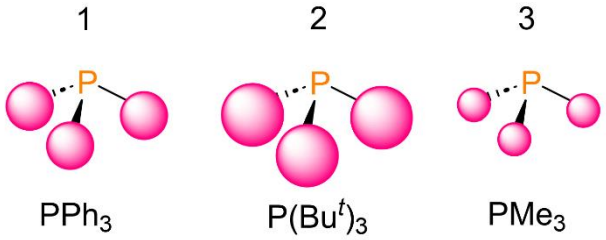
Learning Objectives:

By the end of this activity, you should be able to:

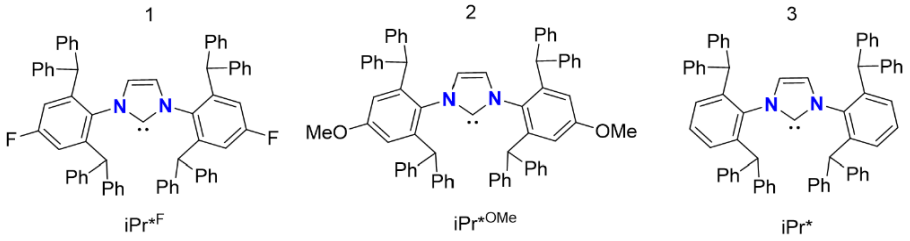
- Explain how steric and electronic properties affect ligand dissociation.
- Understand the trans effect and its' role in substitution mechanisms.
- Predict relative reactivity in dissociative pathways.
- Apply these ideas to rational catalyst design in green chemistry

Station Procedure:

1) At the station, there should be several different puzzle pieces
   a. A dowel representing the axial bond,
   b. A green bead representing the metal center,
   c. Three different phosphine groups of varying size,



   d. Three laminated NHC ligands.



2) Review the lab notes. They provide some valuable information on the topics listed below that may be beneficial for the puzzle.
   a. Phosphine and NHC ligands.
   b. Steric and electronic effects.
   c. Dissociative substitution mechanisms.
3) With this information, consider the different ligands:
   a. Which NHC ligand would be the most donating? The least? How would this impact the bond length between it and the metal? How does this in turn impact dissociation of the phosphine?
   b. *As the steric bulk on the phosphines increases, how does this impact the rate of dissociation?*
4) Model the substitution using the provided pieces:
   a. The laminated NHC ligands are attached via Velcro and can be switched out.
   b. The phosphines are represented by different 3D models that can be attached to the bottom of the dowel.
      a. Each phosphine model includes balls representing the R groups. Assume that as the size of the balls increases, so does the cone angle (i.e., steric bulk).
5) Slide the metal bead along the dowel to represent the bond length based on the NHC bond strength. Move the bead to one of the marked positions on the dowel that corresponds to the appropriate bond length
   a. Hint: stronger bonds have shorter bond lengths.

6) To unlock the code on Flippity (lock #1), provide the ligand combination that would result in the *fastest phosphine dissociation* (corresponding phosphine number followed by the NHC number) then the combination that would result in the *slowest dissociation* (again, phosphine number followed by NHC number).

References:

1. Occhipinti, G.; Nascimento, D. L.; Foscato, M.; Fogg, D. E.; Jensen, V. R. The Janus Face of High Trans-Effect Carbenes in Olefin Metathesis: Gateway to Both Productivity and Decomposition. *Chem. Sci.* **2022**, *13* (18), 5107–5117. https://doi.org/10.1039/d2sc00855f.

2. Blanco, C. O.; Nascimento, D. L.; Fogg, D. E. Routes to High-Performing Ruthenium–Iodide Catalysts for Olefin Metathesis: Ligand Lability Is Key to Efficient Halide Exchange. *Organometallics* **2021**, *40* (12), 1811–1816. https://doi.org/10.1021/acs.organomet.1c00253.

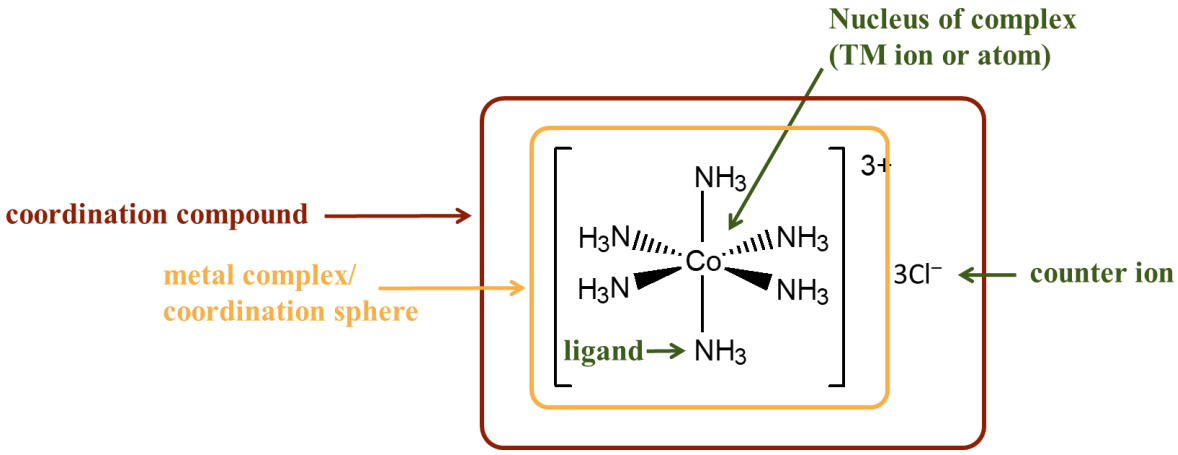
3. Nelson, D. J.; Collado, A.; Manzini, S.; Meiries, S.; Slawin, A. M. Z.; Cordes, D. B.; Nolan, S. P. Methoxy-Functionalized N-Heterocyclic Carbenes. *Organometallics* **2014**, *33* (8), 2048–2058. https://doi.org/10.1021/om5001919.

4. Richens, D. T. Ligand Substitution Reactions at Inorganic Centers. *Chem. Rev.* **2005**, *105* (6), 1961–2002. https://doi.org/10.1021/cr030705u.

5. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*, 5th ed.; New York [Etc.]: Pearson, 2018.

6. Jover, J.; Cirera, J. Computational Assessment on the Tolman Cone Angles for P-Ligands. *Dalton Trans.* **2019**, *48* (40), 15036–15048. https://doi.org/10.1039/c9dt02876e.

Lab Notes for Puzzle 1



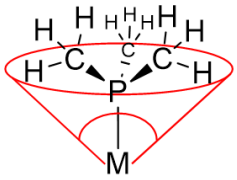
Coordination Complex: A central metal atom or ion bound to the surrounding ligands (molecules or ions).

Coordination Sphere: Includes the central metal and any directly bound ligands.

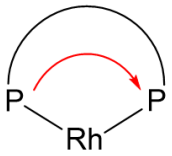
Phosphines and Bite/Cone Angle

Phosphine ligands have the general formula PR_3, where R can be various alkyl or aryl groups. They are common ligands in coordination and organometallic chemistry. One way to describe the size of a phosphine ligand is by its *cone angle*, which is a measure of how much space the ligand takes up around the metal center. Larger cone angles indicate bulkier ligands, which can impact how easily other molecules can approach the metal and participate in reactions.

Cone Angle: a measure of the steric bulk of a ligand bound to a metal
-ligands with bigger functional groups will have larger cone angles



Bite Angle: a measure of the angle on a central atom between two bonds to a bidentate ligand
-ligands forming 5-membered rings with the metal will have smaller bite angles than a 6-membered ring



N-Heterocyclic Carbenes (NHC)

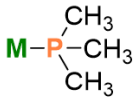
Carbenes are molecules that contain a carbon atom with only two bonds and a lone pair of electrons, making them highly reactive. *N-Heterocyclic carbenes (NHCs)* are a relatively stable class of carbenes in which the reactive carbon is part of a ring structure that typically includes nitrogen atoms. NHCs are strong electron-donating ligands that form stable bonds with metal

centers. Their electronic properties can be tuned by changing the groups attached to the ring, allowing chemists to adjust how much electron density is donated to the metal. This tunability makes NHCs versatile ligands in many metal-catalyzed reactions.

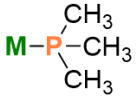
Two major components affecting the donicity of a ligand are the inductive effect, related to the electron donating properties of peripheral functional groups, and hyper conjugation, related to the ability of neighbouring sigma bonds to share electron density with adjacent atoms. An example of each is provided below:

Inductive Effect: Addition of an electron withdrawing or donating group to a molecule results in a permanent dipole in the bond

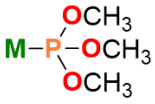
Hyperconjugation: the ability of neighbouring σ-bonds to share electron donicity with adjacent donors.



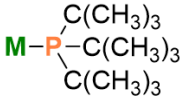
Exhanging methyl groups to methoxy groups increases the strength of the M-P bond.



Exhanging methyl groups on P to *tert*butyl groups increases strength of the M-P bond



OCH_3 is an EDG increasing electron donicity on P

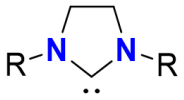


^{t}Bu has a number of σ-bonding interactions that can share electrons donicity with P

Note: For the sake of Puzzle 1 in Activity 2, on iPr*^{F} we will only account for the *inductive effect* of fluorine atoms.

Below are examples of common NHC ligand classes:

Imidazolylidene



imidazolinylidene

thiazolylidene (X=S)
Oxazolylidene (X=O)

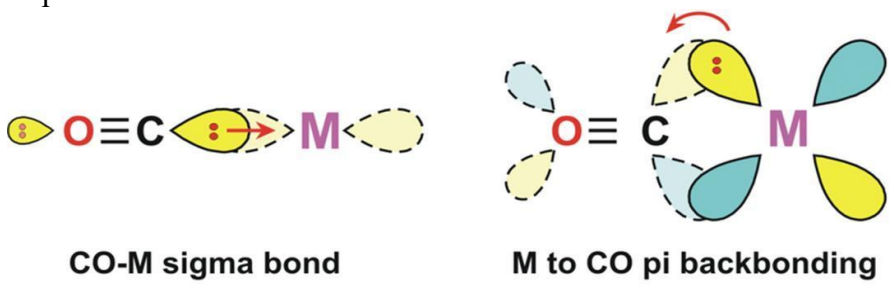
<u>Back Bonding and the Tolman Electronic Parameter:</u>

Back bonding happens when a metal donates electron density from its d-orbitals back into a ligand's empty antibonding orbitals.

- This typically involves ligands with π-bonds, like CO, because they have empty π* orbitals capable of accepting electron density.
- It can also happen with phosphines, where the metal donates into the ligand's empty σ* orbitals.

Why It Matters:

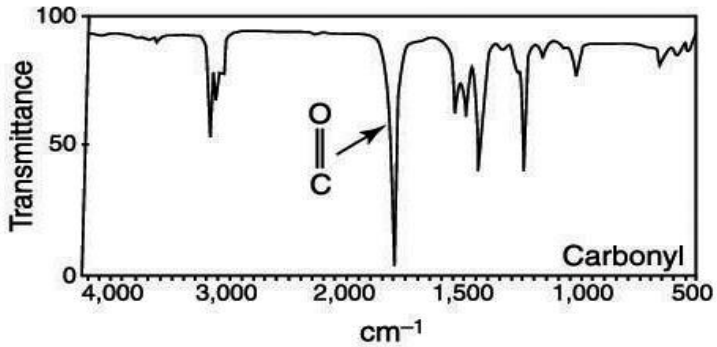
- Ligands can donate electrons to the metal (σ donation).
- The metal can then donate electrons back to the ligand (π back bonding).
- This 2-way sharing affects bond strength, reactivity, and spectroscopic properties in metal complexes.



Note: π-Donor ligands have filled pi-orbitals that can donate electron density into the metal's empty orbitals (e.g., halides, OH^-). *π-Acceptor ligands* have empty π* orbitals (σ* orbitals of the appropriate symmetry) that can accept electron density from the metal (e.g., CO, CN^-, NO^+, PR_3).

The Tolman Electronic Parameter is one method to analyze the comparative donicity of a ligand. Utilizing the corresponding metal carbonyl complex, the IR stretching frequency of the CO ligand *trans* to the ligand of interest is compared to that of free CO and other ligand species. A longer CO bond length would indicate that the CO is bound to the metal center:

- A ligand donates electrons to the metal (ex. the carbon of CO engages in sigma bonding with the metal).
- The metal back donates electrons into the CO ligand's π* orbitals. This weakens the C≡O bond pi-bond. As a result:
    - The C–O bond length increases.
    - The IR stretching frequency of C–O decreases.



Free CO: C–O stretch ~2143 cm^{-1}
Metal–CO complex with strong back bonding: ~1850–2000 cm^{-1}

Phosphorus Ligands (L)	CO, cm^{-1}
$P(t\text{-Bu})_3$	2056
PCy_3	
$P(i\text{-Pr})_3$	2059
$P(NMe_2)_3$	2062
PMe_3	2064
$PPhMe_2$	2065
PBz_3	2066
PPh_2Me	2067
PPh_3	2069
$PPh_2(OEt)$	2072
$P(p\text{-}C_6H_4Cl)_3$	2073
$PPh(OEt)_2$	2074
$P(OEt)_3$	2077
PH_3	2083
PCl_3	2097
PF_3	2111

CO stretching frequencies measured for $Ni(CO)_3L$ where L are PR_3 Ligands of different σ donor abilities. [ν(CO) =2143 cm^{-1}]

Comparing to donicity of different phosphine ligands utilizing a $Ni(PR_3)(CO)_3$ species, we can compare the difference in *trans*-carbonyl stretching frequencies to rank the relative ligand donicity. In this list, PF_3 is considered the *Weakest donor*, whereas $P(t\text{-Bu})_3$ is considered the *strongest donor*.

Key Terms:

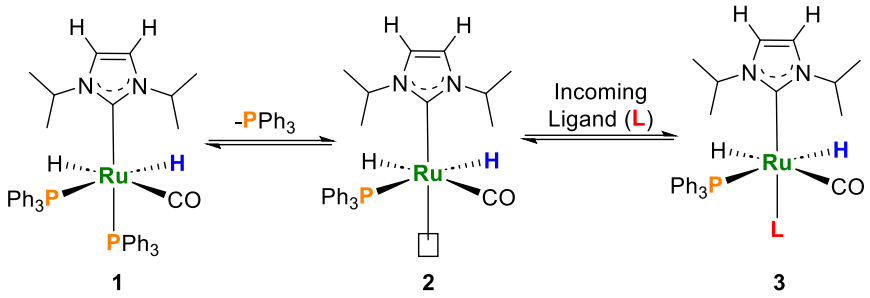
- *Donicity*: How well a ligand shares electron density with the metal.
- *Trans Effect:* Strong donor ligands increase the lability of ligands *trans* to them (making them more likely to dissociate).
- *Tolman Electronic Parameter (TEP):* A metric that correlates a ligands electron donating ability with the IR stretching frequency of a CO ligand *trans* to it.
- Stronger donor ligands → greater back bonding → longer CO bonds → lower IR frequency.

Dissociative Mechanisms:

In coordination and organometallic chemistry, reactions often involve the exchange of ligands. There are two main mechanistic pathways:

- *Associative (A)* – where a new ligand binds to a metal center before the old one leaves. It is common for 16-electron complexes. The mechanism is similar to an S_N2 reaction.
- *Dissociative (D)* – where a ligand leaves first, creating a vacant site for an incoming ligand to bind. It is common for 18-electron complexes. These undergo mechanisms that are similar to an S_N1 reaction.

A sample dissociative mechanism utilizing Grubbs catalyst:



Dissociative mechanisms proceed in two steps. The initial ruthenium (Ru) complex contains four neutral ligands (NHC, 2 PPh_3, and CO). These ligands do not effect the oxidation state of the metal. The complex also has two anionic ligands (2 H), these ligands do impact the oxidation state of the metal. Two anionic ligands result in +2 oxidation state at the metal, Ru(II). Ru(II) has six d-electrons. Each metal-ligand bond hosts two electrons. This results in a total of 10 + 8 = 18 electrons for the complex. This complex is completely saturated and cannot bind an incoming ligand, therefore in order to exchange ligands, a ligand must first dissociate from the metal center.

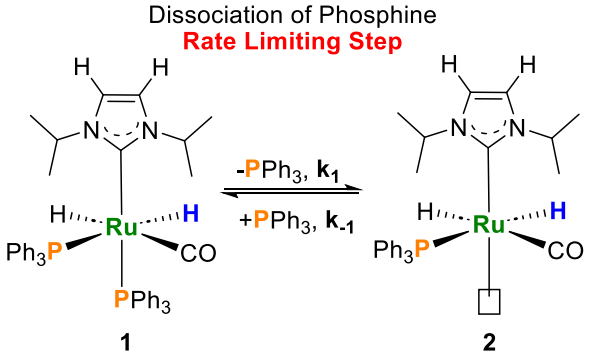
Neutral ligand are often the first to dissociate from the metal center in a ligand exchange mechanism. Here, the phosphine ligands are the most labile. Since the NHC is a strong donor, the *trans* phosphine ligand will be the one to dissociate from the metal, noting that phosphine dissociation is a reversible reaction. The reaction is pushed in the forward direction based on the effects of the *trans* ligand (donicity), the steric size of the phosphine (cone angle), and the binding strength of the incoming ligand (L). The general mechanism proceeds as follows:

1. *Dissociation of ligand (PR_3):* The ligand leaves, resulting in a lower coordination number
2. *Association or new ligand:* A new ligand binds to the now-vacant coordination site.

The rate of a dissociative reaction mechanism is controlled by how fast the ligand leaves. There are several methods to increase the rate of ligand dissociation:

$$\text{Rate} = k_1[L_nRu\text{-}PPh_3] = k_1[1]$$

1. Weaken the Ru-PR_3 bond by increasing the donor strength of the trans ligand
2. Weaken the Ru-P bond by increasing the cone angle of the phosphine.



References:

1. S. Vanicek, M. Podewitz, C. Hassenrück, M. Pittracher, H. Kopacka, K. Wurst, T. Müller, K. R. Liedl, R. F. Winter, B. Bildstein, *Chem. Eur. J.* **2018**, *24*, 3165.

2. Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An Overview of N-Heterocyclic Carbenes. *Nature* **2014**, *510* (7506), 485–496. https://doi.org/10.1038/nature13384.

3. Ligand Substitution Reactions. *Springer eBooks* **2007**, 121–134. https://doi.org/10.1007/978-3-540-46129-6_7.

4. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*, 5th ed.; New York [Etc.]: Pearson, 2018.

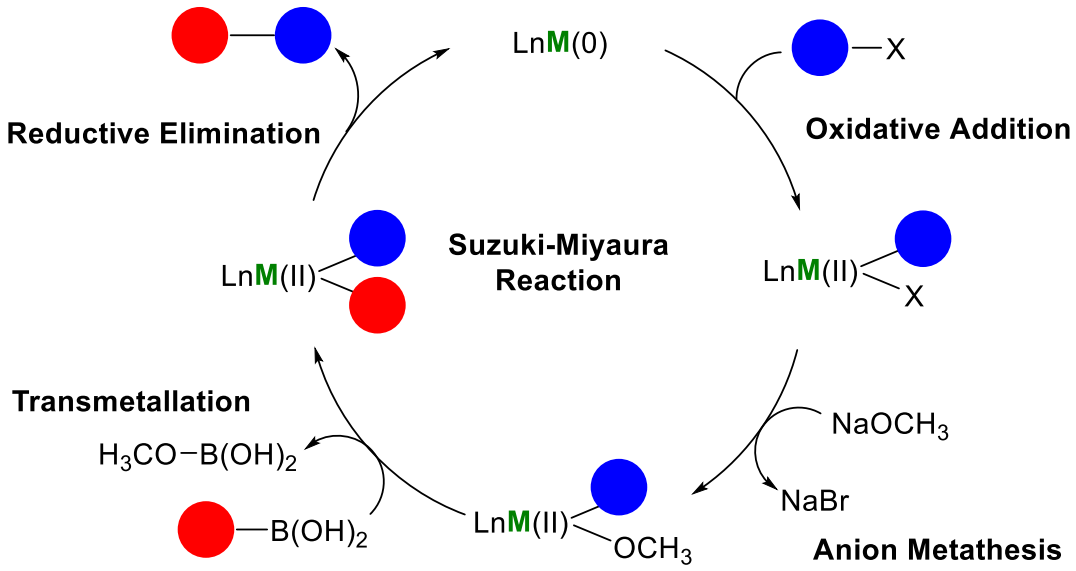
5. Jover, J.; Cirera, J. Computational Assessment on the Tolman Cone Angles for P-Ligands. *Dalton Trans.* **2019**, *48* (40), 15036–15048. https://doi.org/10.1039/c9dt02876e.

Puzzle 2: Considerations in Experimental Design for Suzuki-Miyaura Cross Coupling.

Overview of Puzzle 2:

The objective of this second puzzle is to evaluate the compatibility of different catalyst selections, exploring the relationship between metal-ligand selection and experimental parameters, to better understand the balance required to make the "greenest" functional catalyst. In order to complete this puzzle, you must optimize a Suzuki-Miyaura cross coupling reaction for the greenest overall experimental design. Once you have found the correct pathway, this will provide you with the information necessary to unlock the next puzzle.

The general reaction can be observed below.



Learning Objectives:

Through this puzzle, the following learning objectives will be emphasized:

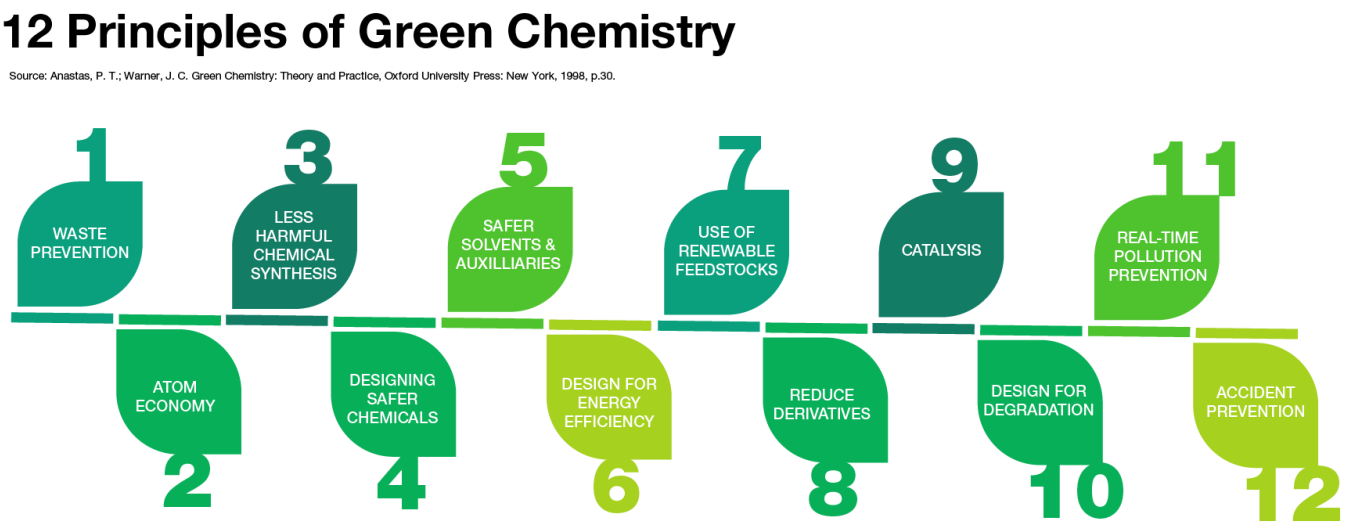
- To challenge one's perception of **green chemistry** in the context of reaction optimization.
- To expand one's understanding on the interdependence of reaction design challenges.
- To emphasize significant **barriers to sustainability** in relevant chemical reaction conditions.

Station Procedure:

1) Puzzle 2 features a table of reaction conditions for Suzuki-Miyaura cross coupling. Using the erasable marker provided you must evaluate the choices in each column and circle the greenest choice on the sheet protector.
2) In order to construct a reasonable set of reaction conditions the pathway must be connected by one common colour (e.g. if you pick one tile with **orange**, **purple**, and **red**, and a second tile with **blue** and **purple**, your common colour is **purple**, and every subsequent tile must contain this colour). Note, you will be able to choose your metal only after you've decided on a reaction pathway.
3) Review the lab notebook for help regarding green considerations for reaction conditions and to see relevant examples of optimized Suzuki-Miyaura cross coupling reactions with various catalyst designs.
4) With this information, consider the different choices:
    a. What type of ligand would have the lowest cost and toxicity of those listed?
    b. Which solvents are the safest to handle? Which have the lowest environmental impact and are most easily recycled?
    c. What reaction conditions are the least energy intensive? Which are the least hazardous to employ?
    d. Which additives pose a potential risk to safety?
    e. How might catalyst loading impact overall cost and product purification?
5) Once you've circled a choice of ligand, solvent, reaction conditions, temperature, additives, time, and catalyst loading, remove the top sheet from the sheet protector to reveal the metal colours and overall greenness of each choice (ranked by number of leaves on each tile). Circle the metal which corresponds to your chosen colour and review your pathway.
6) Edit your pathway as needed to reach the "greenest" pathway with the most possible total number of leaves. Note, exclamation points represent hazardous conditions and/or reagents, these should not be featured along your route.
7) To unlock the code on Flippity (lock #2), provide the metal identity and number of leaves along your pathway (eg. Co27).

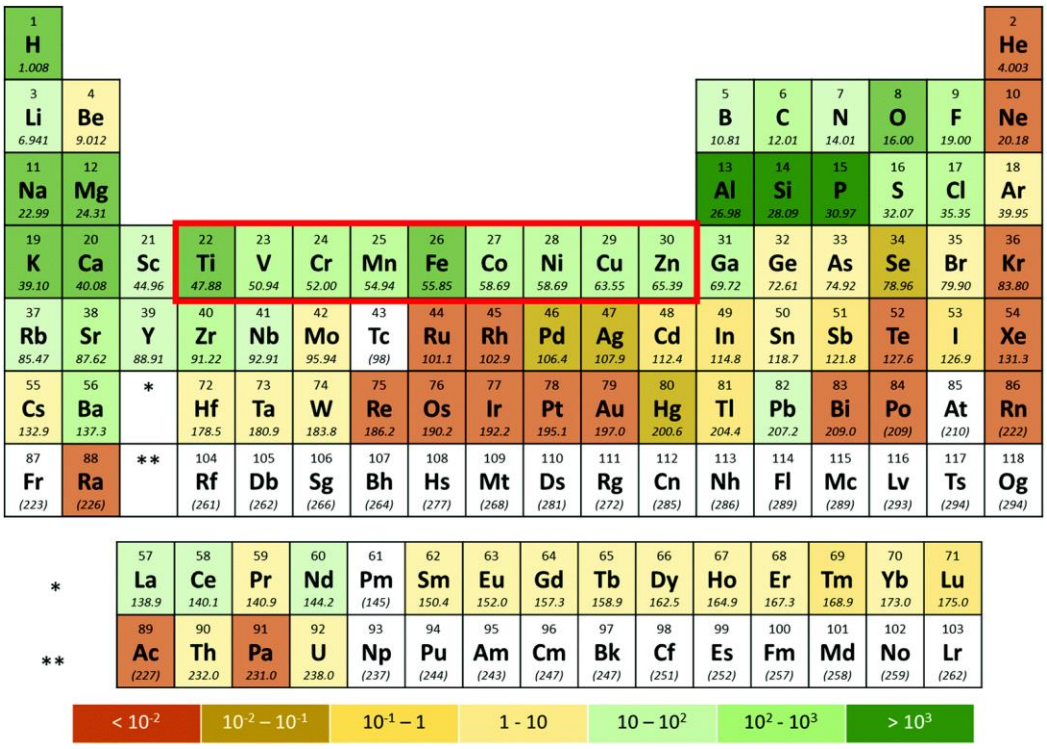
Lab Notes for Puzzle 2

Green chemistry considerations:



Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, 1st ed.; Oxford University Press, **1998**; Vol. 1.

Transition metal abundance:

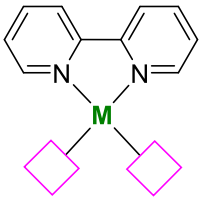
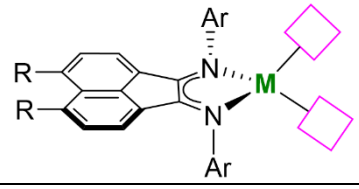
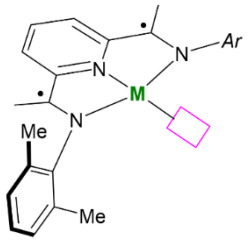
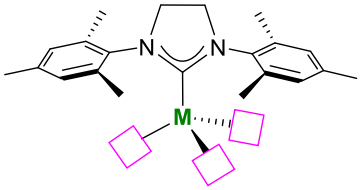
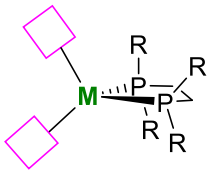


Elemental abundance (in mg per kg of Earth's crust).

Gourdon, L.; Cariou, K.; Gasser, G. *Chem. Soc. Rev.* **2022**, *51*, 1167-1195.

Ligand considerations; toxicity, recyclability, and disposal:

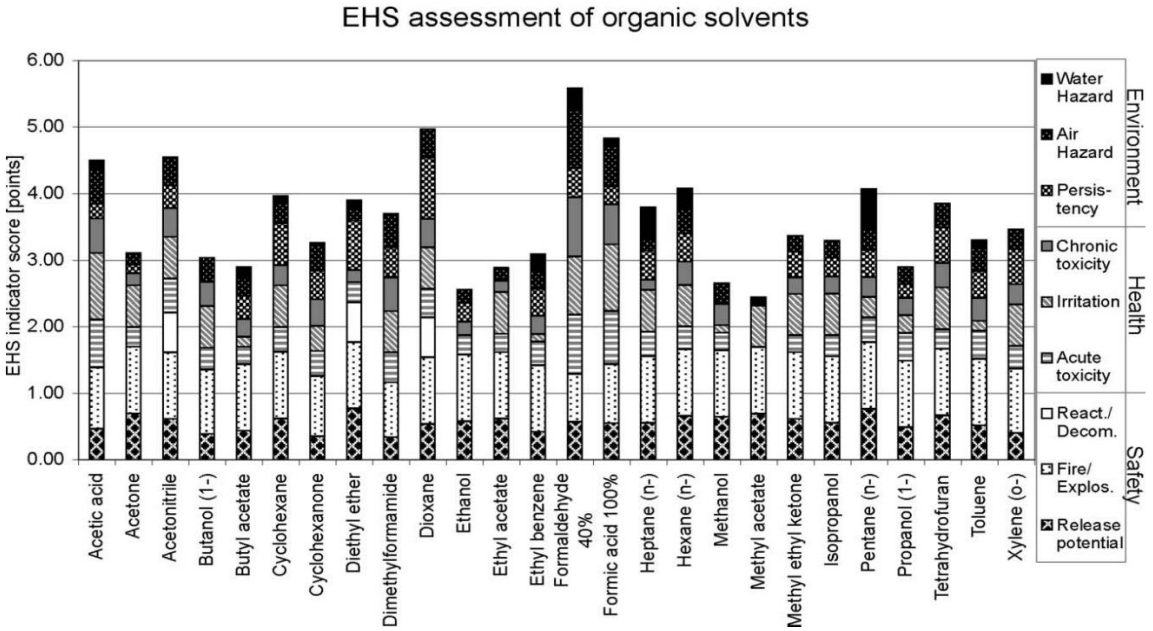
Cost, Environmental Impact, Ethical Sourcing are estimated based on related known ligand motifs and their synthesis. Solvent, work-up, waste disposal is not taken into consideration in cost.

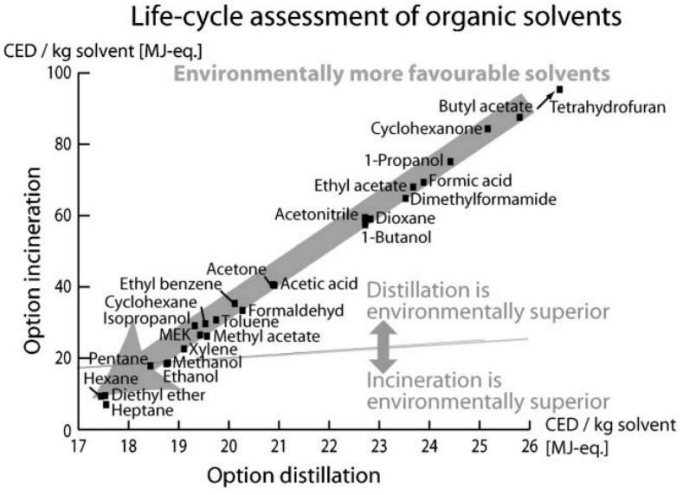
Common Ligands	Considerations
2,2'-Bipyridine (bipy) 	Synthetic steps: Commercially available Cost: $10.12/1g Hazardous reagents: N/A
Bis(imino)acenaphthenes (BIAN) 	Synthetic steps: • 15% molar excess of the aniline with acenaphthenequinone + 3-fold molar excess of $ZnCl_2$ in refluxing acetic acid **80-95% yield for simple derivatives.** • Reference: Cenini et al. *Organometallics* **2002** Cost: $3.12/1g Hazardous reagents: N/A
Substituted bis(imino)pyridine 	Synthetic steps: • Schiff-base condensation of 2 equiv of the desired aniline with 2,6-diacetylpyridine **~60% yield.** • Reference: Bennett et al. *J. Am. Chem. Soc.* **1998** Cost: $50.71/1g Hazardous reagents: 97% formic acid
N-Heterocyclic carbenes (NHCs) 	Synthetic steps: • Deprotonation of dimesitylimidazolium cation to give IMes" **89% yield.** • Reference: Ison et al. *J. Chem. Educ.* **2012** Cost: $154.05/1g Hazardous reagents: N/A
Common *bis*(phosphine) 	Synthetic steps: • For the synthesis of symmetric 1,2-bis(dichlorophosphino)ethane derivatives, reacted with appropriate Grignard reagent **60-70% yield.** • Reference: Leight et al. *J. Organomet. Chem.* **1979** Cost: $251.54/1g Hazardous reagents: Grignard reagent

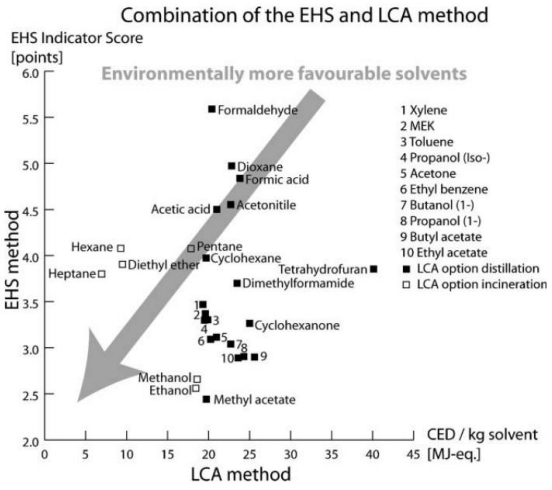
Solvent considerations:

Two methods for evaluating solvent greenness are the EHS assessment method (focused on identifying hazards) and the life-cycle assessment (LCA) method (focused on quantifying emissions produced and resources required in the production, use, potential recycling, and disposal of the solvent). By using both methods, we can obtain a full view of how green a solvent is. See below for the EHS score and LCA of common organic solvents and five binary solvent mixtures (in performing the LCA the cumulative energy demand (CED) method was used) as well as the combination of these methods.

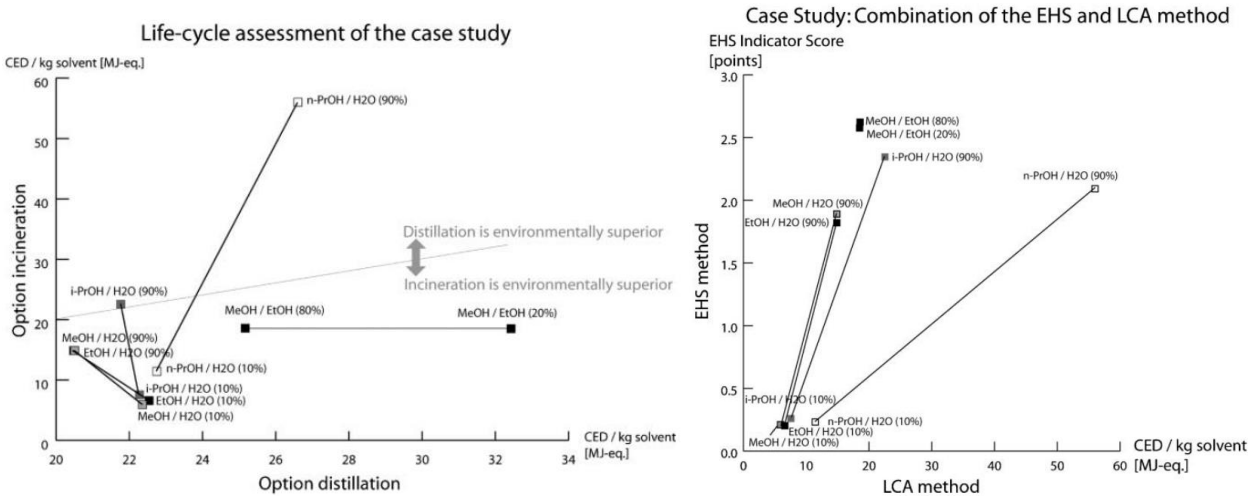
Organic solvents:







Aqueous solvent mixtures:

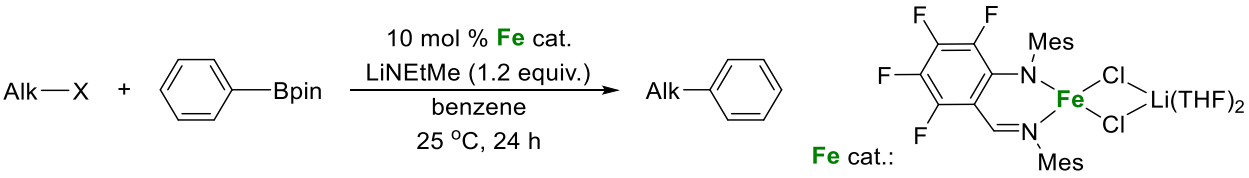


Capello, C.; Fischer, U.; Hungerbuhler, K. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.* **2007**, *9*, 927-934.

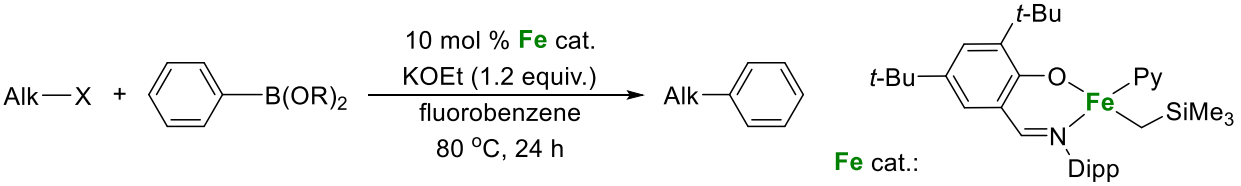
Notes on Suzuki-Miyaura Cross Coupling Reactions

Shown below are select examples of optimized reaction conditions for the Suzuki-Miyaura cross coupling of aryl/alkyl halides and aryl boronic acids/boronates.

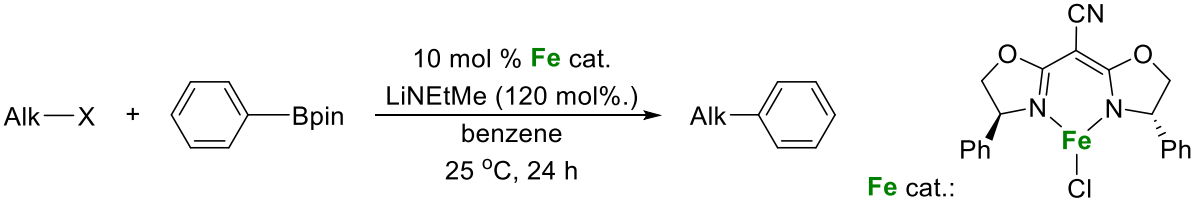
Iron catalyzed SMC:



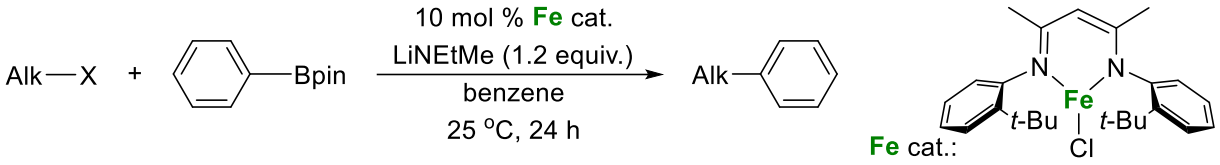
Chen, D.; Lepori, C.; Guillot, R.; Gil, R.; Bezzenine, S.; Hannedouche, J. *Angew. Chem. Int. Ed.* **2024**, *63*, e202408419.



Peterson, P. O.; Joannou, M. V.; Simmons, E. M.; Wisniewski, S. R.; Kim, J.; Chirik, P. J. *ACS Catal.* **2023**, *13*, 2443-2448.

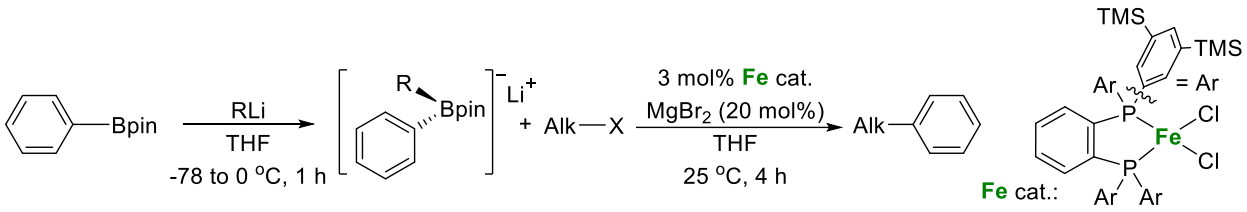


Crockett, M. P.; Tyrol, C. C.; Wong, A. S.; Li, B.; Byers, J. A. *Org. Lett.* **2018**, *20*, 5233-5237.

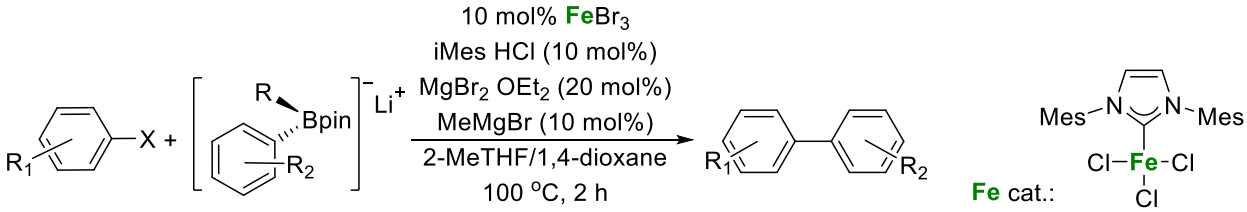


Crockett, M. P.; Wong, A. S.; Li, B.; Byers, J. A. *Angew. Chem. Int. Ed.* **2020**, *59*, 5392-5397.

Alternative strategies for SMC using iron catalysts involve pre-activation of the boronic coupling partner:

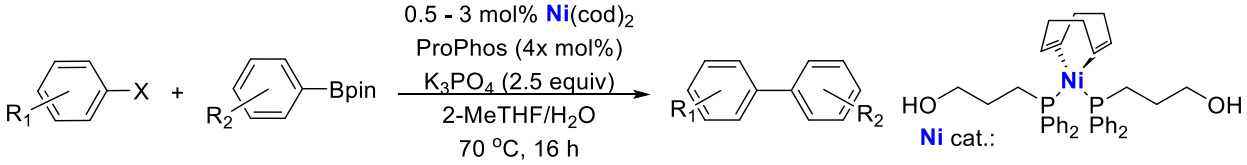


Hatakeyama, T.; Hashimoto, T.; Kondo, Y.; Fujiwara, Y.; Seike, H.; Takaya, H.; Tamada, Y.; Ono, T.; Nakamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 10674-10676.

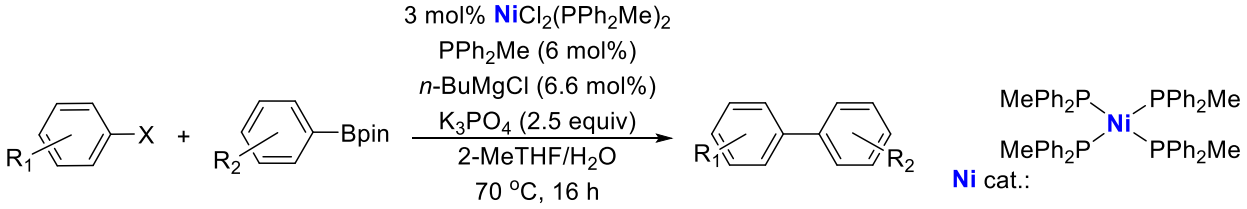


Rowsell, B. J. S.; O'Brien, H. M.; Athavan, G.; Daley-Dee, P. R.; Krieger, J.; Richards, E.; Heaton, K.; Fairlamb, I. J. S.; Bedford, R. B. *Nat. Catal.* **2024**, *7*, 1186-1198.

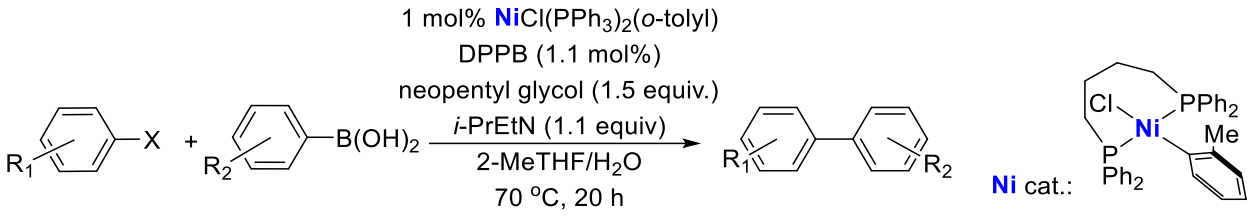
Nickel catalyzed SMC:



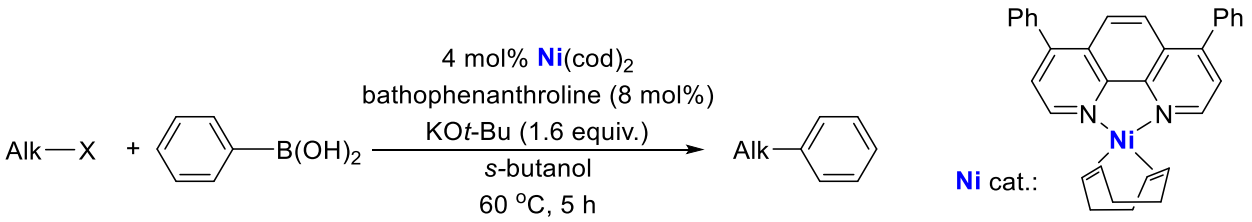
Yang, J.; Neary, M. C.; Diao, T. *J. Am. Chem. Soc.* **2024**, *146*, 6360-6368.



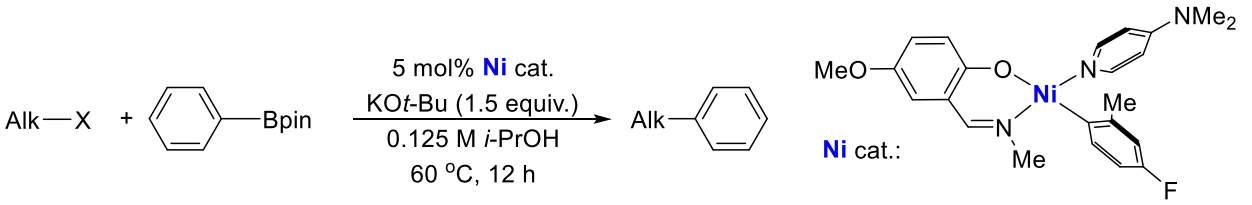
Haibach, M. C.; Ickes, A. R.; Tcyrulnikov, S.; Shekhar, S.; Monfette, S.; Swiatowiec, R.; Kotecki, B. J.; Wang, J.; Wall, A. L.; Henry, R. F.; Hansen, E. C. *Chem. Sci.* **2022**, *13*, 12906-12912



Guo, X.; Dang, H.; Wisniewski, S. R.; Simmons, E. M. *Organometallics*, **2022**, *41*, 1269-1274.

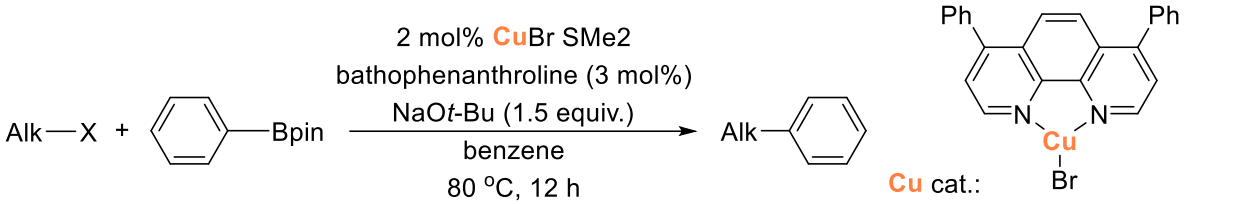


Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1340-1341.

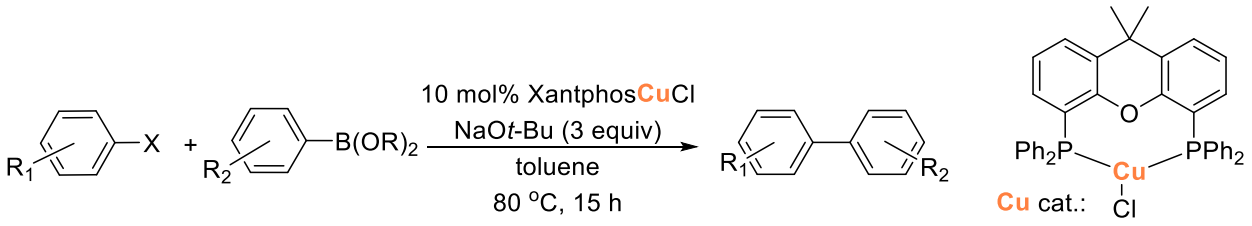


Mills, L. R.; Simmons, E. M.; Lee, H.; Nester, E.; Kim, J.; Wisniewski, S. R.; Pecoraro, M. V.; Chirik, P. J. *J. Am. Chem. Soc.* **2024**, *146*, 10124-10141.

Copper catalyzed SMC:

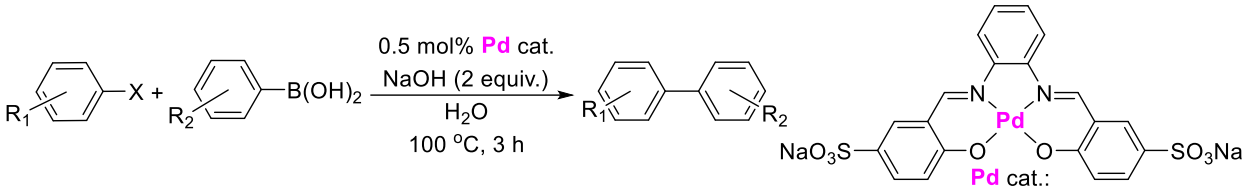


Zhou, Y.; Qiu, L.; Li, J.; Xie, W. *J. Am. Chem. Soc.* **2023**, *145*, 28146-28155.

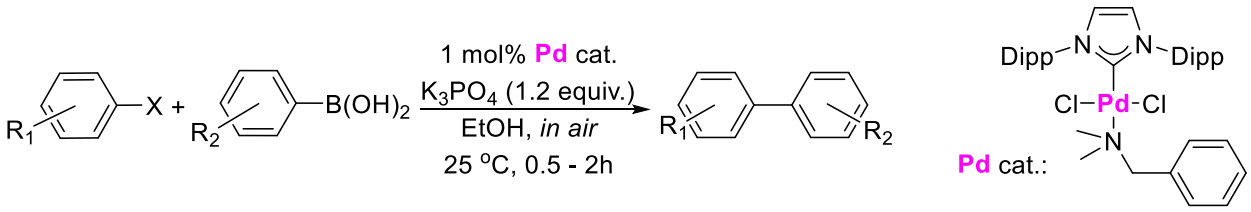


Zhou, Y.; You, W.; Smith, K. B.; Brown, M. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 3475-3479.

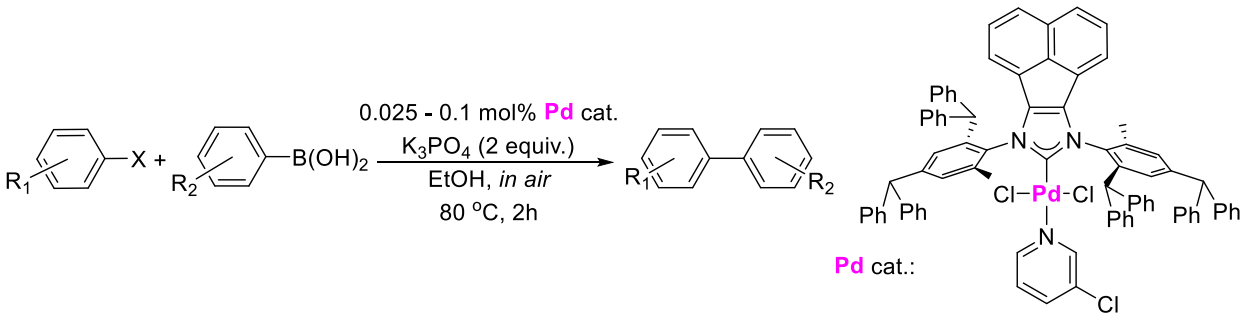
Palladium catalyzed SMC:



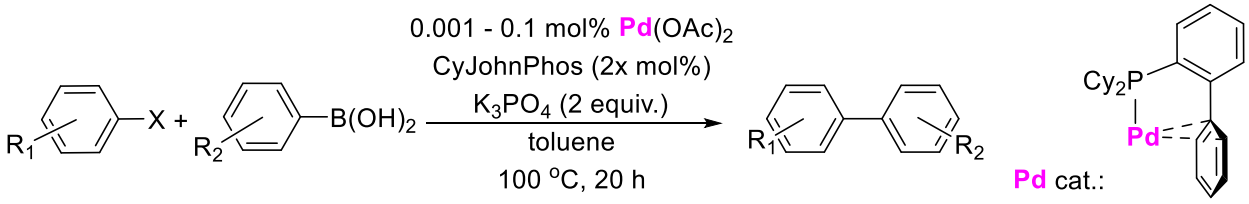
Liu, Y.-S.; Gu, N.-N.; Liu, P.; Ma, X.-W.; Liu, Y.; Xie, J.-W.; Dai, B. *Tetrahedron* **2015**, *71*, 7985-7989.



Chen, M.-T.; Kao, Z.-L. *Dalton Trans.* **2017**, *46*, 16394-16398.



Ouyang, J.-S.; Li, Y.-F.; Huang, F.-D.; Lu, D.-D.; Liu, F.-S. *ChemCatChem*. **2017**, *10*, 371-375.



Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550-9561.

References:

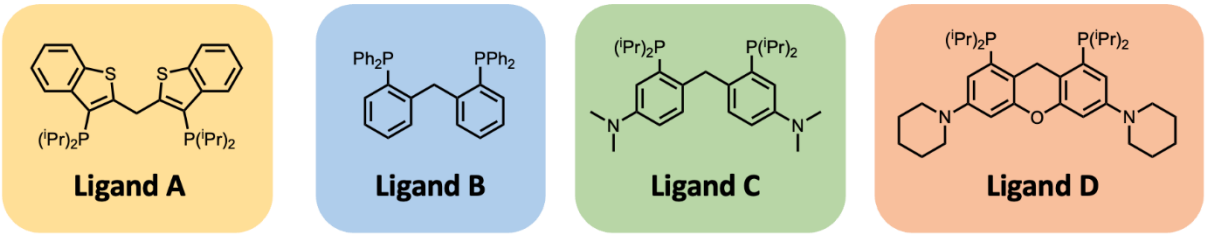
1. Gasperini, M.; Ragaini, F.; Cenini, S. *Organometallics* **2002**, *21*, 2950-2957.
2. Small, B. L.; Brookhart, M.; Bennett, A. M. *J. Am. Chem. Soc.* **1998**, *120*, 4049-4050.
3. Ison, E. A.; Ison, A. *J. Chem. Educ.* **2012**, *89*, 1575-1577.

Puzzle 3: Green Catalyst Design for N_2O Reduction.

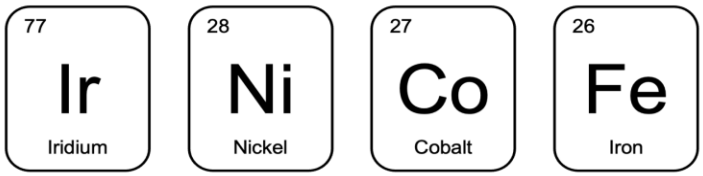
Overview of Puzzle 3:

The objective of this third puzzle is to come up with the greenest and most efficient catalyst design for nitrous oxide (N_2O) reduction. You will have the choice of four metals (iridium, nickel, cobalt, and iron) and the choice of four ligands (A, B, C, and D). You have been left the lab notes of a previous student that highlight their synthesis and observations about these four ligands, as well as information about the corresponding metal complexes.

In this puzzle, there are four L shaped puzzle pieces representing the four ligands the previous student had been working with:



As well as four game pieces (wooden pegs) on the lefthand side of the board representing the four metals:



Learning objectives:

By the end of this puzzle, the aim is:

- To think about balance between improved reactivity with a ligand versus greenness of the ligands, as well as with metals.
- To emphasize the idea that even though a combination might be the greenest, it may not have the desired reactivity.
- To illustrate that ligand and organometallic complex design is a cyclical process.

Station Procedure:

Puzzle #3a *(virtual lock number 3):*

1) Your first task will be to rank the ligands based on their donor strength. To do this, arrange the L shaped pieces in the puzzle board from 1 (the best donor) to 4 (the weakest donor).
2) Once you are sure of your answer, head to the virtual lock (#3) and put in the letters of the ligands in order to unlock the first part of this puzzle! (Note: put the letter of the ligand you have put in the #1 spot first, followed by the #2 spot, then so on. An example of formatting would be "ABCD" inputted into the answer field).

Puzzle #3b *(virtual lock number 4)*:

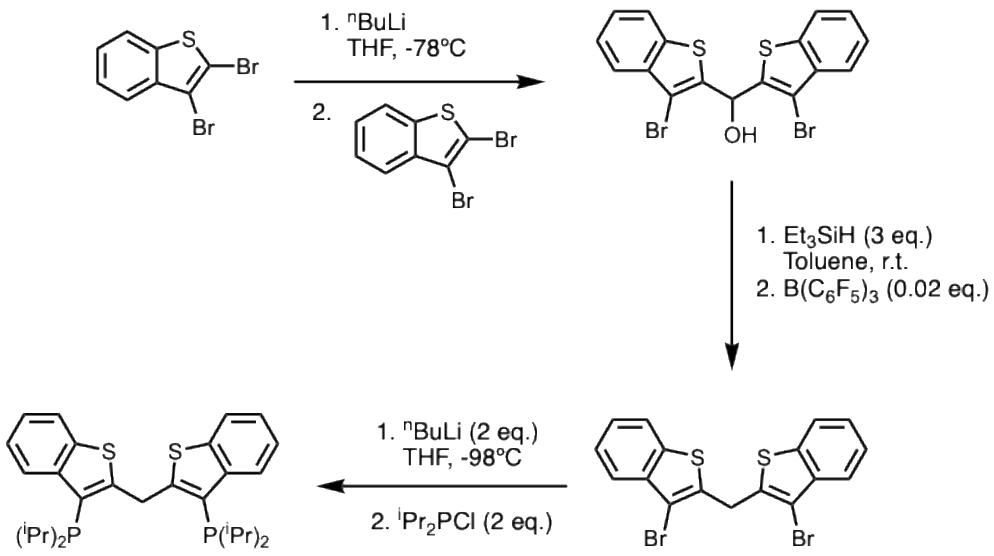
3) Once you have the outside of your maze completed, you will need to choose one of the ligands for your catalyst design, ensuring that it is the greenest and most effective option! To make your choice of ligand, take one of the four square pieces corresponding to your ligand of choice and place it in the middle of your puzzle (**ensuring the letter is near the top of the board**).
4) To make your choice of metal, choose the game piece on the lefthand side of the board corresponding to your metal of choice and move it through your now completed maze! ****You may only change directions with your piece if you hit a wall in the maze****
5) If you have chosen the correct metal, your piece should make it to one of the outcomes on the right side of the board. If you have chosen an incorrect metal, your piece will run into a wall.
6) Once you have the correct ligand in place and you are travelling through the maze with the correct metal, your piece will make it to the slot on the right indicating the correct option! To unlock virtual lock #4, input your metal choice and ligand choice in the following format: [Metal], [Ligand Letter] (ex. If the answer was zinc metal with ligand E, you would input "Zinc, E" into the answer field).

References:

1) Smith, J. D.; Chih, E.; Piers, W. E.; Spasyuk, D. M. Tuning Iridium (I) PCcarbeneP Frameworks for Facile Cooperative N2O Reduction. *Polyhedron* **2018**, *155*, 281–290. https://doi.org/10.1016/j.poly.2018.08.054.
2) Hoffbauer, M. R.; Iluc, V. M. [2+2] Cycloadditions with an Iron Carbene: A Critical Step in Enyne Metathesis. *J. Am. Chem. Soc.* **2021**, *143* (15), 5592–5597. https://doi.org/10.1021/jacs.0c12175.
3) Smith, J. D.; Borau-Garcia, J.; Piers, W. E.; Spasyuk, D. Systematic Dismantling of a Carefully Designed PCcarbeneP Pincer Ligand via C–C Bond Activations at an Iridium Centre. *Can. J. Chem.* **2016**, *94* (4), 293–296. https://doi.org/10.1139/cjc-2015-0251.

Lab Notes for Puzzle 3

Ligand A Synthesis

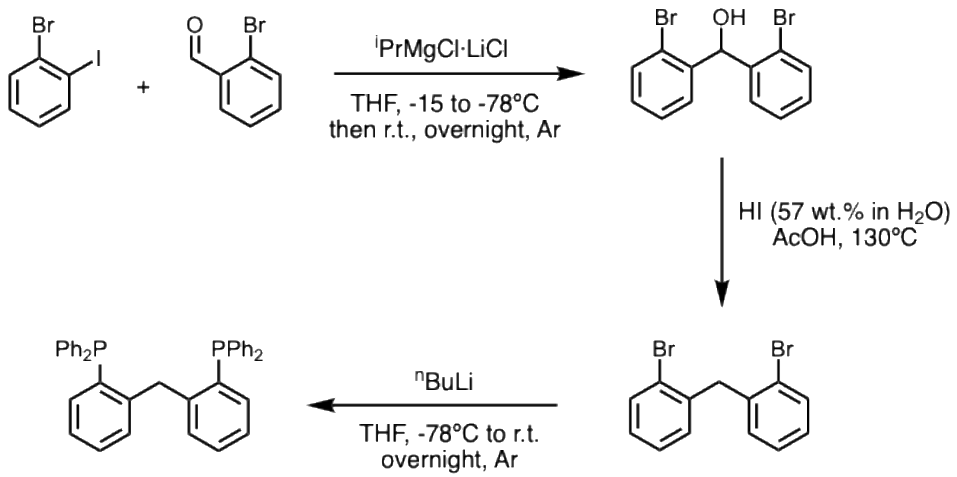


Doyle, L. E.; Piers, W. E.; Borau-Garcia, J. Ligand Cooperation in the Formal Hydrogenation of N2O Using a PCsp2P Iridium Pincer Complex. *J. Am. Chem. Soc*. **2015**, *137* (6), 2187–2190. https://doi.org/10.1021/ja512602m.

Notes:

- During testing this ligand was used in a catalyst design, and it was found that the catalytic hydrogenation of N_2O was difficult due to slow kinetic behaviour of the reaction.
- CO stretching frequency of associated carbonyl complex: 2048 cm^{-1}.

Ligand B Synthesis

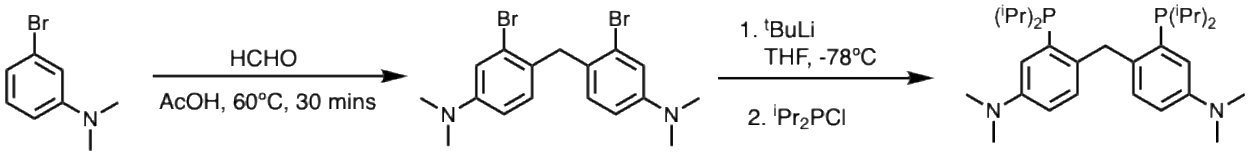


Zhao, K.; Wang, H.; Li, T.; Liu, S.; Benassi, E.; Li, X.; Yao, Y.; Wang, X.; Cui, X.; Shi, F. Identification of a Potent Palladium-Aryldiphosphine Catalytic System for High-Performance Carbonylation of Alkenes. *Nat. Commun.* **2024**, *15* (1), 2016. https://doi.org/10.1038/s41467-024-46286-9.

Notes:

- This ligand has been previously used in a catalyst design with iron as the metal to achieve [2+2] cycloadditions.
- CO stretching frequency of the corresponding carbonyl complex: 2004 cm^{-1}.

Ligand C Synthesis

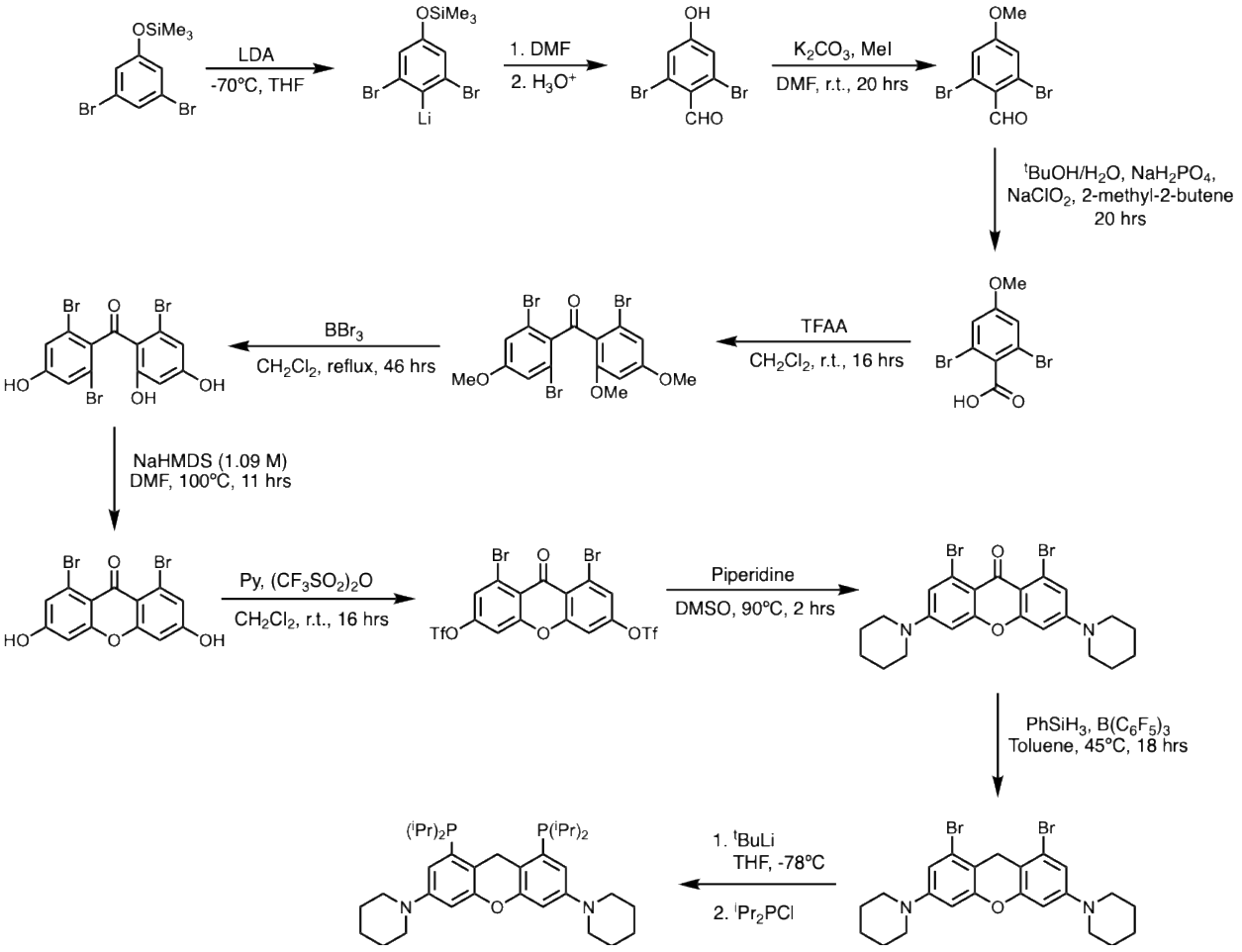


1) Smith, J. D.; Borau-Garcia, J.; Piers, W. E.; Spasyuk, D. Systematic Dismantling of a Carefully Designed PCcarbeneP Pincer Ligand via C–C Bond Activations at an Iridium Centre. *Can. J. Chem.* **2016**, *94* (4), 293–296. https://doi.org/10.1139/cjc-2015-0251.
2) Lukinavičius, G.; Umezawa, K.; Olivier, N.; Honigmann, A.; Yang, G.; Plass, T.; Mueller, V.; Reymond, L.; Corrêa Jr, I. R.; Luo, Z.-G.; Schultz, C.; Lemke, E. A.; Heppenstall, P.; Eggeling, C.; Manley, S.; Johnsson, K. A Near-Infrared Fluorophore for Live-Cell Super-Resolution Microscopy of Cellular Proteins. *Nat. Chem.* **2013**, *5* (2), 132–139. https://doi.org/10.1038/nchem.1546.

Notes:

- This ligand is very reactive! When it was used in catalyst testing, after 18 hours complete ligand breakdown was observed due to cleavage of the $C_{aryl} - C_{anchor}$ bonds.
- CO stretching frequency of the corresponding carbonyl complex: 1963 cm^{-1}.

Ligand D Synthesis



1) Da˛browski, M.; Kubicka, J.; Luliński, S.; Serwatowski, J. A Study on the Metalation of Alkoxydibromobenzenes. *Tetrahedron Lett.* **2005**, *46* (24), 4175–4178. https://doi.org/10.1016/j.tetlet.2005.04.065.
2) Sugawara, S.; Abe, M.; Fujiwara, Y.; Wakioka, M.; Ozawa, F.; Yamamoto, Y. 1,8-Disubstituted Xanthylidene-Based Remote Carbenes: Photolytic Generation and Isolation of Low-Coordinate Palladium(II) Complex. *Eur. J. Inorg. Chem.* **2015**, *2015* (3), 534–541. https://doi.org/10.1002/ejic.201403017.
3) Smith, J. D.; Logan, J. R.; Doyle, L. E.; Burford, R. J.; Sugawara, S.; Ohnita, C.; Yamamoto, Y.; Piers, W. E.; Spasyuk, D. M.; Borau-Garcia, J. Cationic Mono and Dicarbonyl Pincer Complexes of Rhodium and Iridium to Assess the Donor Properties of PCcarbeneP Ligands. *Dalton Trans.* **2016**, *45* (32), 12669–12679. https://doi.org/10.1039/C6DT02615J.

Notes:

- The synthesis of this ligand took so long!
- CO stretching frequency of the corresponding carbonyl complex: 1974 cm^{-1}.

Activity 3 - Keywords: A Waste and Hazard Reduction Puzzle

Activity Lead: Megan Fitzgerald

Overview of the Activity:

Waste and hazard reduction are both hallmarks of greener and more sustainable chemistry. This activity addresses many of the 12 principles of green chemistry through the scope of a trivia-style question to answer matching game. Participants form four groups of 4-6 people, preferably containing individuals for multiple different backgrounds. Team 1 and team 2 will "battle" each other; team 3 and team 4 will "battle" as well. Each team will have a question board, as well as a shared basket of answer tiles. The questions on each individual question board will contain questions pertaining to toxicology, atom economy, E-factor, VOC emissions, catalysis and more!

Teams must find the tiles that list an answer to each question. With some questions, the answer will be obvious, however, with other questions, the answer could be more open-ended. To help participants to answer their questions and form their board, each tile has a corresponding letter on the other side of the listed answer, which helps each team to form a phrase on their question board. Form your team's correct keyword/phrase first to win! Consult this workbook regarding any information needed to find the answer corresponding to each question.

Learning Objectives:

- To expose participants to some metrics that would be relevant to chemical safety – such as LD50 and solvent flash points.
- To expose participants to some questions and metrics that pertain to reaction efficiency – such as atom economy, turnover number and turnover frequency.
- To expose participants to some questions and metrics that pertain to waste reduction – such as E-factor and atom economy.

Activity 3 Lab Notes

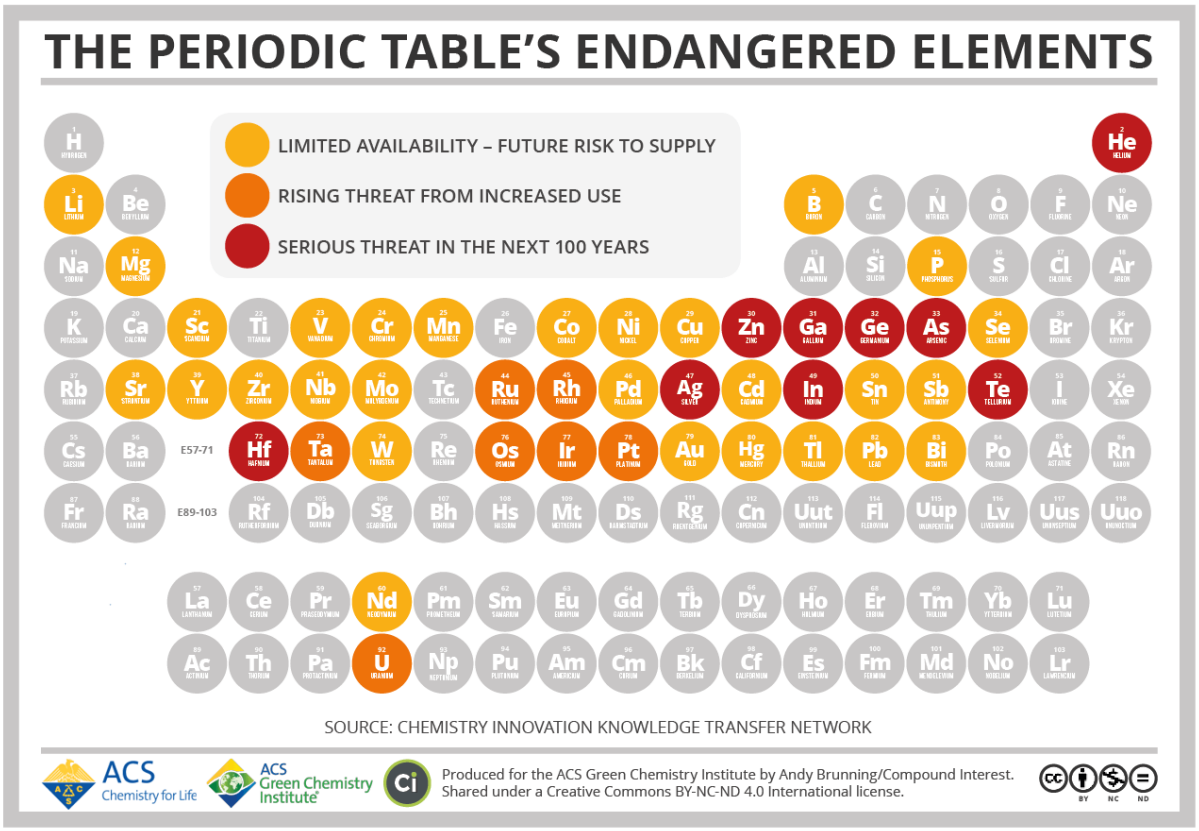


Figure 1: Periodic table of endangered elements
The Periodic Table of Endangered Elements. American Chemical Society, Compound Interest: https://www.acs.org/green-chemistry-sustainability/research-innovation/endangered-elements.html

Equation 1: Atom economy

$$Atom\ economy\ (\%) = \frac{molar\ mass\ of\ all\ desired\ products}{molar\ mass\ of\ all\ reactants}$$

Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 8

Equation 2: Turnover number

$$Turnover\ number = \frac{amount\ of\ product}{amount\ of\ catalyst}$$

Equation 3: Turnover Frequency

$$Turnover\ frequency = \frac{amount\ of\ product}{(amount\ of\ catalyst) * (time(s))}$$

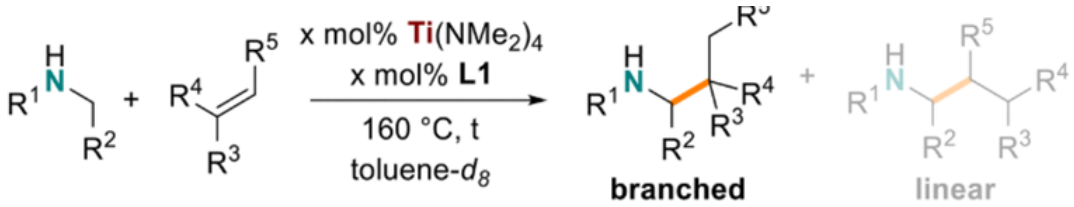
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 102

Equation 4: E-Factor

$$E - factor = \frac{mass\ of\ waste\ (kg)}{mass\ of\ products\ (kg)}$$

Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 85

Reaction Schemes:



Scheme 1.1: General reaction scheme for titanium-catalyzed intermolecular hydroaminoalkylation of internal alkenes. L1 indicates a ligand on the Ti catalyst.

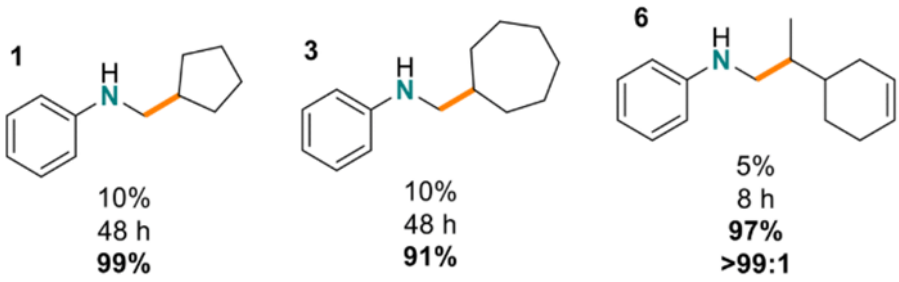
Reaction Conditions	Reactant Amounts (mmol)
Amine	0.5
Alkene	0.5
0.7 mL toluene-d8	-
1,3,5-trimethoxybenzene (internal standard for NMR analysis)	0.17

Reference: Manßen, M.; Scott, S. S.; Deng, D.; Zheng, C. H. M.; Schafer, L. L. Accessing Secondary Amine Containing Fine Chemicals and Polymers with an Earth-Abundant Hydroaminoalkylation Catalyst. *Green Chem.* **2023**, *25* (7), 2629–2639. https://doi.org/10.1039/D3GC00011G.

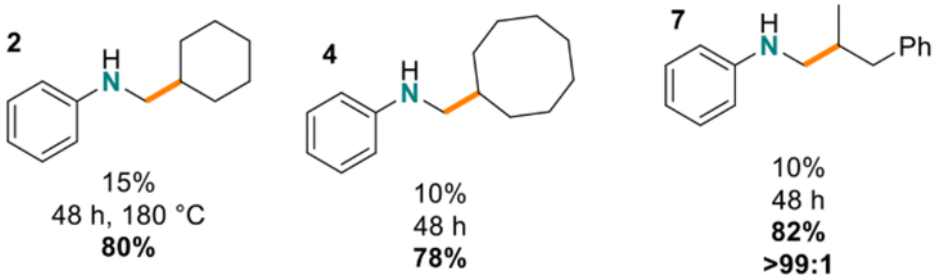
Information listed as:

- Catalyst loading (mol%)
- Reaction time (h)
- **% Yield**

Substrate Group A (1, 3, 6):



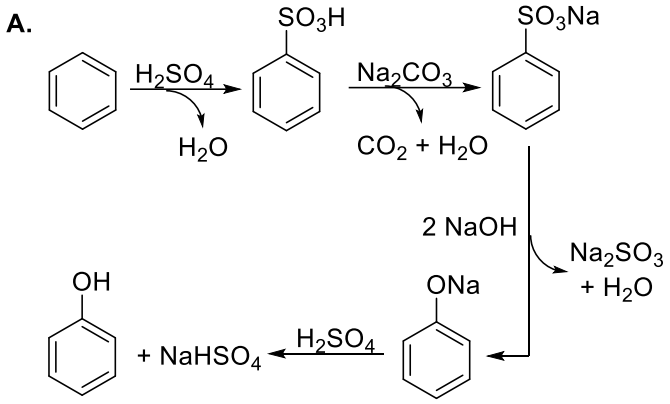
Substrate group B (2, 4, 7):



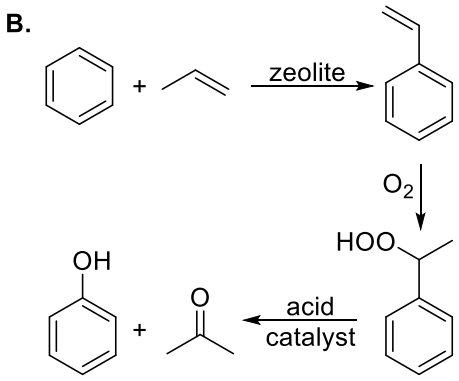
Reference: Manßen, M.; Scott, S. S.; Deng, D.; Zheng, C. H. M.; Schafer, L. L. Accessing Secondary Amine Containing Fine Chemicals and Polymers with an Earth-Abundant Hydroaminoalkylation Catalyst. *Green Chem.* **2023**, *25* (7), 2629–2639. https://doi.org/10.1039/D3GC00011G.

LD50 Data:

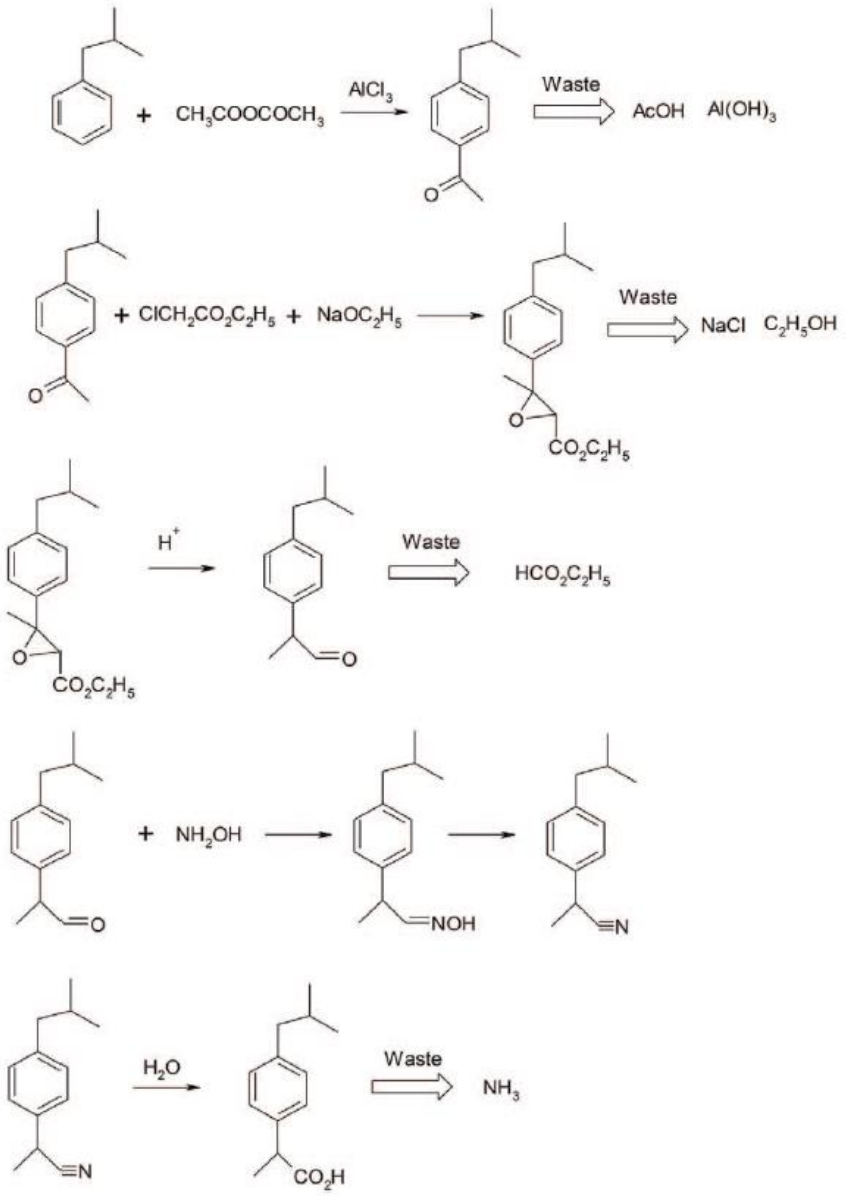
Chemical Name	Chemical Formula	LD50	SDS
Potassium Hydroxide	KOH	ORAL 333 mg/kg (rat, male)	*Potassium Hydroxide* (CAS RN: 1310-58-3). P5958, rev. 6.9; MilliporeSigma Canada Ltd.: Oakville, ON, May 5th, 2025. https://www.sigmaaldrich.com/CA/en/sds/sigald/p5958?userType=undefined
Ammonium Hydroxide	NH_4OH	ORAL 350 mg/kg (rat)	*Ammonium Hydroxide* (CAS RN: 1336-21-6). A667-212, rev. 9; AquaPhoenix Scientific: Hanover, PA, December 31st, 2014. https://www.fishersci.ca/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-a/S25164.pdf
Potassium Carbonate (anhydrous)	K_2CO_3	ORAL 2000 mg/kg (rat, male and female)	*Potassium Carbonate (anhydrous), ACS Grade* (CAS RN: 584-08-7). P208-3, rev. 7; Fischer Scientific Company: Fair Lawn, NJ, May 12th, 2011. https://www.fishersci.com/store/msds?partNumber=P208500&productDescription=POT+CARBONATE+ANHY+CR+ACS+500G&vendorId=VN00033897&countryCode=US&language=en
Triethylamine	$N(CH_2CH_3)_3$	ORAL 460 mg/kg (rat)	*Triethylamine* (CAS RN: 121-44-8). BP616-500, rev. 8; Fischer Scientific Company: Fair Lawn, NJ, February 16th, 2024 https://www.fishersci.com/store/msds?partNumber=O4884100&productDescription=TRIETHYLAMINE+HPLC+100ML&vendorId=VN00033897&countryCode=US&language=en
Hydrochloric acid	HCl	ORAL 238 mg/kg (rat)	*Hydrochloric acid* (CAS RN: 7647-01-0). A481-212, rev. 8; Fischer Scientific Company: Fair Lawn, NJ, October 13th, 2023 https://www.fishersci.com/store/msds?partNumber=A481212&productDescription=HYDROCHLORIC+ACID+NF%2FFCC+21%2F2L&vendorId=VN00033897&countryCode=US&language=en
Formic acid	HCOOH	ORAL 738 mg/kg (rat)	*Formic acid* (CAS RN: 64-18-6). AC147930000, rev. 7; Fischer Scientific Company: Fair Lawn, NJ, October 25th, 2022 https://www.fishersci.com/store/msds?partNumber=AC147930250&productDescription=FORMIC+ACID+98%25+25ML&vendorId=VN00033901&countryCode=US&language=en
Glacial acetic acid	CH_3COOH	ORAL 3310 mg/kg (rat)	*Acetic acid* (CAS RN: 64-19-7). W200603, rev. 8.9; MilliporeSigma Canada Ltd.: Oakville, ON, January 8th, 2023 https://www.sigmaaldrich.com/CA/en/sds/aldrich/w200603?userType=undefined
Citric acid, Anhydrous	$C_6H_8O_7$	ORAL 6730 mg/kg (rat)	*Citric acid, anhydrous* (CAS RN: 77-92-9). S25255, rev. 8.9; Fischer Science Education: Hanover, PA, December 14th, 2014 https://www.fishersci.ca/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-c/S25255.pdf



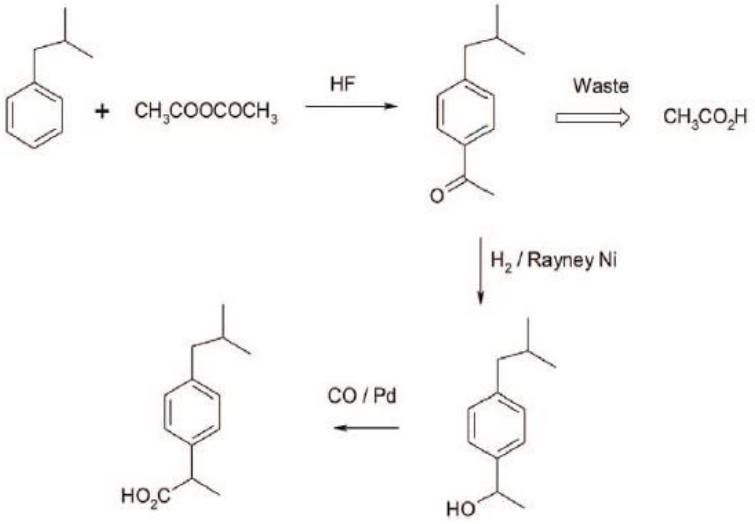
Scheme 1.1: Sulfonation route to phenol.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 30



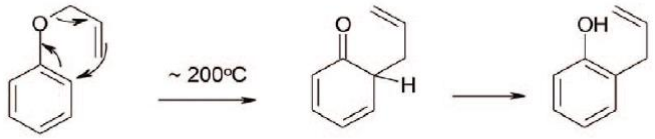
Scheme 1.2: Cumene route to phenol.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 31



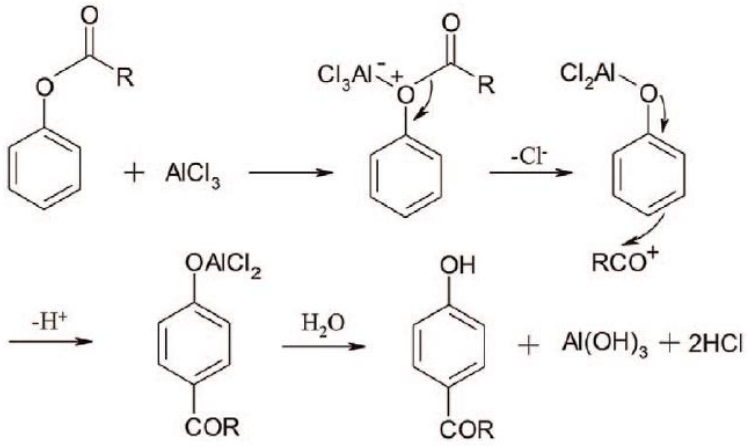
Scheme 2.1: Original Boots route to Ibuprofen synthesis.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 32



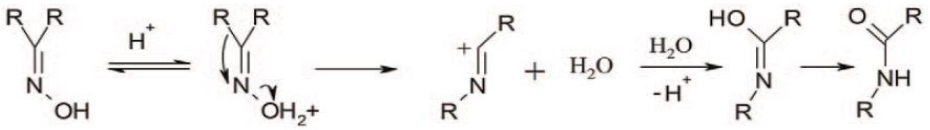
Scheme 2.2: Current manufacturing route to Ibuprofen.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 33



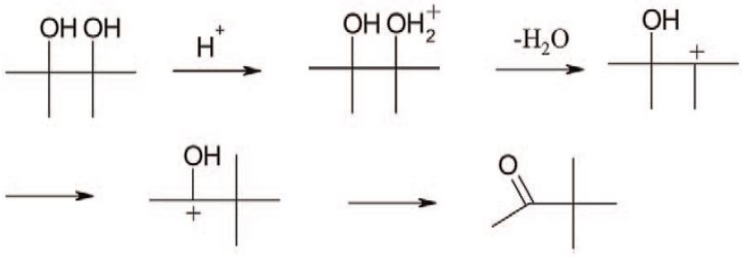
Scheme 3.1: Claisen rearrangement.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 11



Scheme 3.2: Fries rearrangement.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 11



Scheme 3.3: Beckmann rearrangement.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 12.



Scheme 3.4: Pinacol rearrangement.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 12

Other important information:
Many enzymatic processes occur in the synthesis of products undergoing degradation at the end-of-life stages. To reduce a material's impact on the environment past that stage, "design for degradation" - one of the principles of green chemistry – addresses this issue. Common household products, like plastics, polymers or surfactants, are all disposed of eventually, and thus must be designed to degrade in a way that does not cause harm to the environment. Studies on common household surfactants revealed that two sulfonated alkylbenzenes (found in household cleaners) had significantly differing rates of degradation. The branched isomer had a much slower rate of degradation, whereas the linear sulfonated alkylbenzene had a much faster rate of degradation. Thus, linear alkanes are favoured to increase rates of degradation. In addition, pertaining to polymer sizes, rates of degradation tend to decrease as polymer molecular weight increases. Finally, as some bacteria and bacterial enzymes performing reactions require an aqueous environment, any material that is not water-soluble will be slower to degrade.

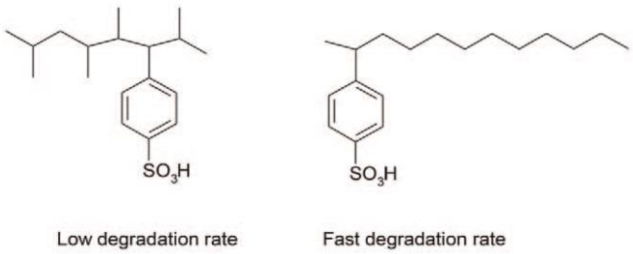


Figure 2: Relative degradation rates of sulfonated alkylbenzenes.
Reference: Lancaster, M. *Green Chemistry: An Introductory Text*, 4th ed.; Royal Society of Chemistry: La Vergne, UNITED KINGDOM, 2025; pg. 55-59.