Chain Walking Alkenes to Access Remote Sites for Hydroamination

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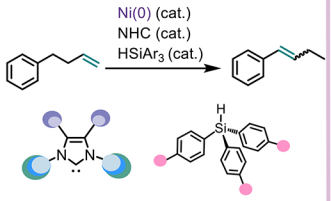
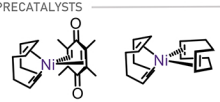
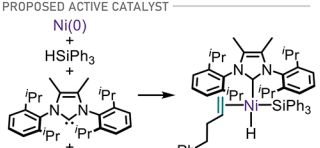
ALKENE ISOMERIZATION



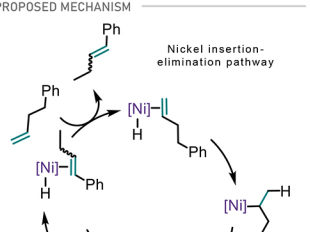
Ni(0) PRECATALYSTS



PROPOSED ACTIVE CATALYST



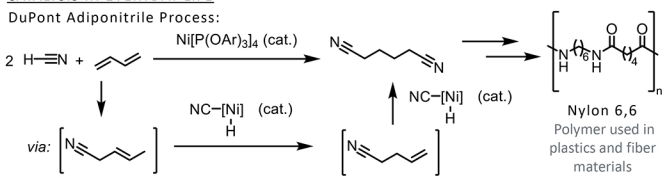
PROPOSED MECHANISM



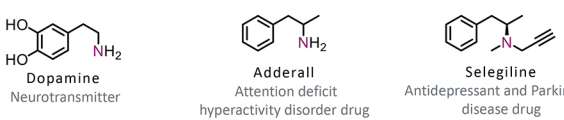
REMOTE FUNCTIONALIZATION

CATALYSIS IN EVERYDAY LIFE

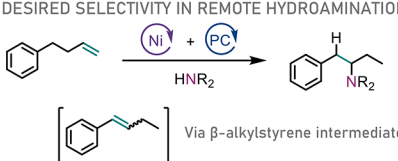
DuPont Adiponitrile Process:



EXAMPLES OF BIOACTIVE AMINE MOLECULES



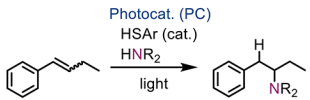
OUR HYPOTHESIS: USE DUAL CATALYSIS TO ACHIEVE DESIRED SELECTIVITY IN REMOTE HYDROAMINATION



ADVANTAGES FOR THIS APPROACH

- Thermodynamic driving force for site-selectivity
- Atom-economical synthesis
- Specialized catalyst for each task
- Functionalization step triggered by light
- Functionalization catalyst can be easily switched

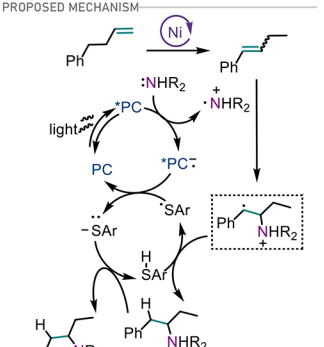
HYDROAMINATION



β-selective (Anti-Markovnikov) addition of 2° amines
Driven by aminium radical cation
Inspired by work from the Knowles lab

PHOTOCATALYSTS

PROPOSED MECHANISM



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REFERENCES

[1] Larsen, Grotjahn. The Value and Application of Transition Metal Catalyzed Alkene Isomerization in Industry. In Applied Homogeneous Catalysis with Organometallic Compounds. 3rd Ed.; Wiley: Weinheim, 2018; p 1365. [2] Tullo. The chemical industry is bracing for a nylon 6,6 shortage. *Chemical & Engineering News*, 2018. [3] Sommer, Juliá-Hernández, Martin, Marek. *ACS Cent. Sci.* 2018, 153. [4] Xiao, He, Ye, Zhu. *Chem* 2018, 1645. [5] Kawamura, Chang, Martin, Smith, Morris, Cook. *Organometallics* 2022, 486. [6] Musacchio, Lainhart, Zhang, Naguib, Sherwood, Knowles. *Science* 2017, 727. [7] Tran, Li, Apolinar, Derosa, Joannou, Wisniewski, Eastgate, Engle. *Angew. Chem. Int. Ed.* 2020, 7409. [8] Romano, Fiorito, Mazet. *J. Am. Chem. Soc.* 2019, 16983.