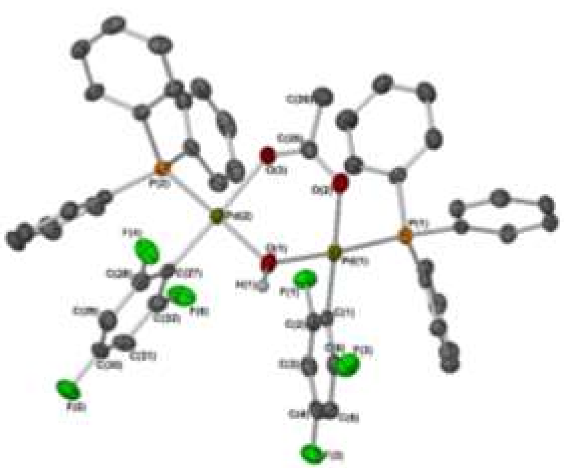
“Advance Educational Techniques In Science & Humanities”
Nandurbar, 2nd June 2020

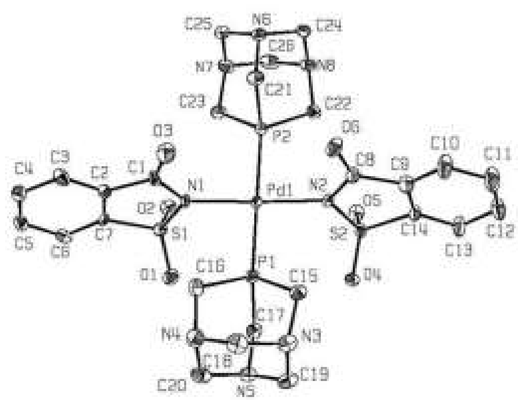
INSTITUTE OF CHEMICAL TECHNOLOGY

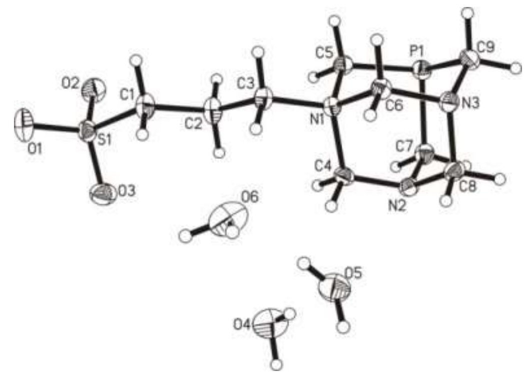
Virtual Seminar on

Latest Trends and Future Challenges in Chemical Sciences: An Organometallic Perspective

-Dr. Anant R. Kapdi

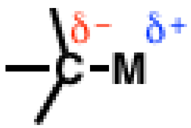






Introduction

"Organometallics" are compounds with a carbon-metal bond



Carbon has an electronegativity of 2.6.

Most metals (M) have electronegativities ≤ 2.0

Therefore organometallics have **dipoles** where the carbon is **negative** (i.e. nucleophilic)

This means that organometallic compounds tend to act as carbon-based nucleophiles as well as bases

Common Examples of Organometallic Compounds

$H_3C–Li$	$H_3C–Mg–Cl$	$H_3C–Cu^{\ominus}–CH_3$ $Li^{\oplus}$
organolithium	organomagnesium "Grignard" reagents	organocuprate "Gilman" reagents

Wurtz reagent **R-Na** Wittig Reagent **$R_2C=PR_3$** Simon-Smith reagent **$IZnCH_2I$**

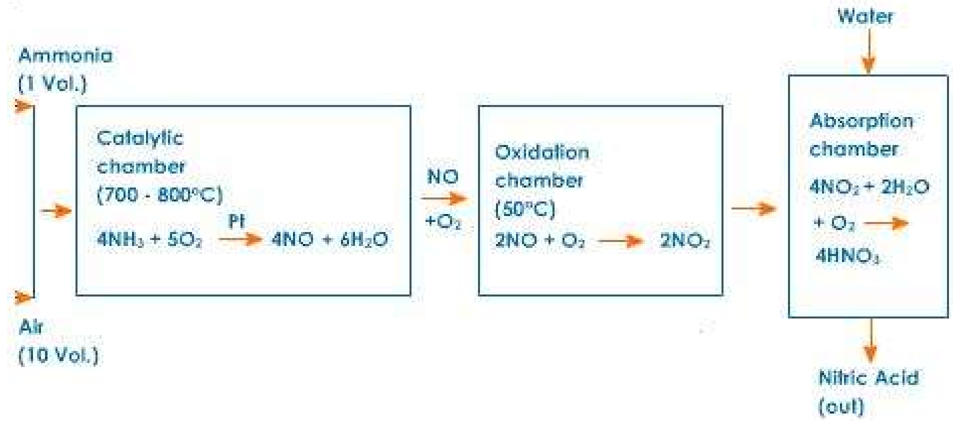
Lombardo's reagent **Cl_3TiCH_2ZnBr** Trimethyl Aluminium **Me_3Al**

Nobel Prizes in Chemistry related to Metals

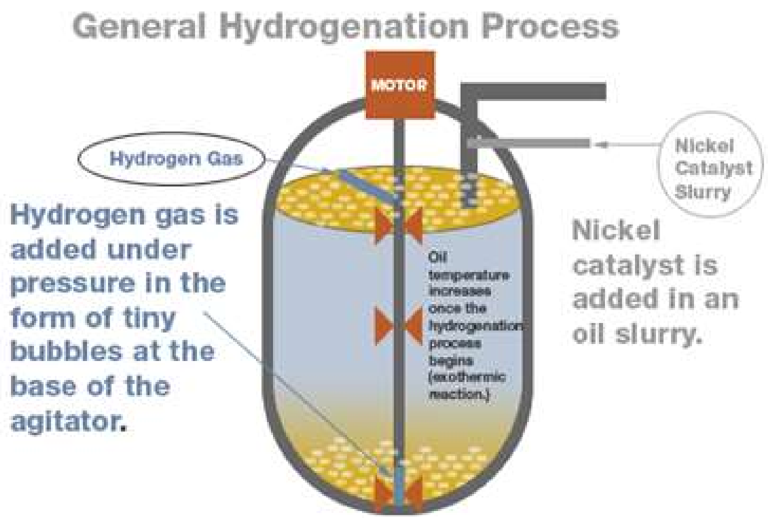
Historical Significance

1760 - Cacodyl – tetramethyldiarsine
1827 – "Zeise's salt"
1863 - 1st metal-carbonyl, $[PtCl_2(CO)_2]$
1890 – L. Mond, (impure) Ni + xs CO ——> $Ni(CO)_4$
1899 –> Grignard reagent discovery
1900 – M catalysts; organic hydrogenation
(food industry, margerine) Ni, Fe

Wilhelm Ostwald: 1909 (Pt/Rh for the preparation of nitric acid from ammonia)



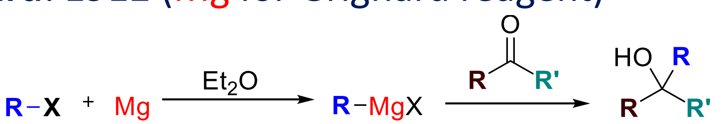
Paul Sabatier: 1912 (Ni as hydrogenation catalyst)



Alfred Werner: 1913 (Co amine complexes geometry)

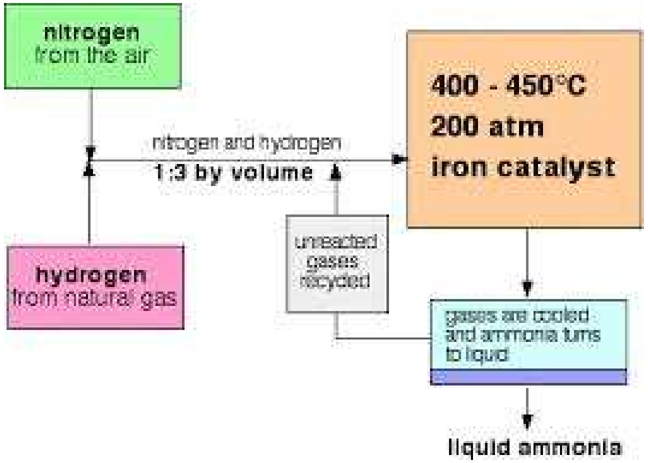
Educación Química 2015;26:330–45

Victor Grignard: 1912 (Mg for Grignard reagent)



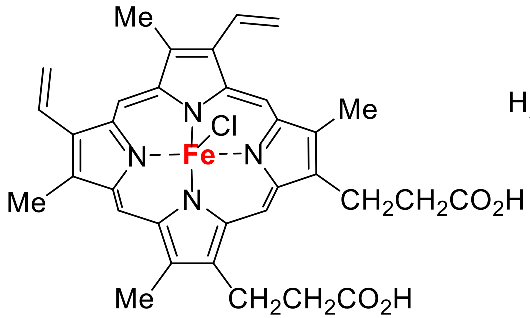
Nobel Prizes in Chemistry related to Metals

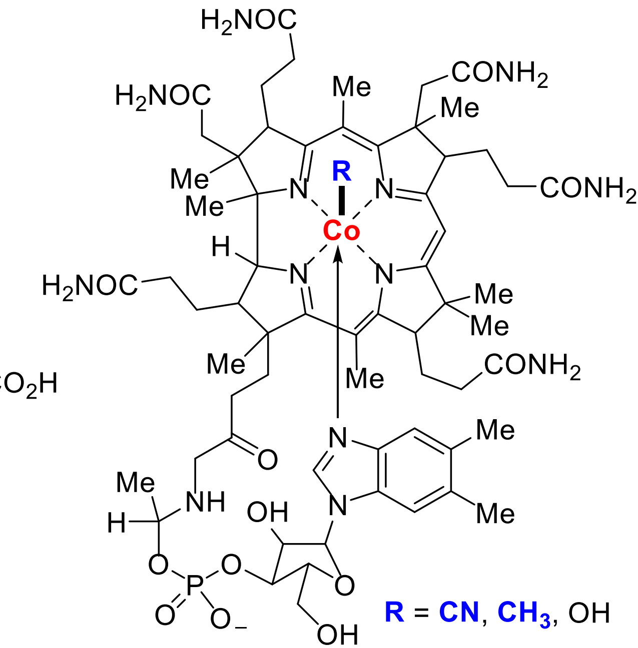
Fritz Haber: 1918 (**Os** for the production of ammonia; **Fe** or **Ru** have also been used)



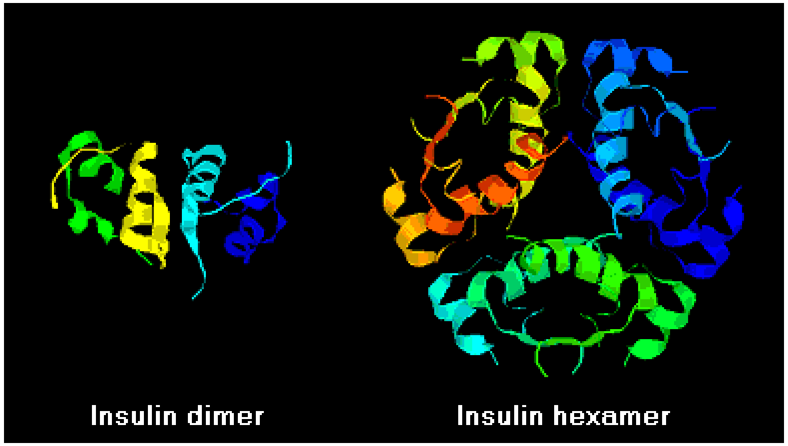
Hans Fischer: 1930 (**Fe** in Haemin structure)

Dorothy Hodgkin 1964 (Co in Cobalamin complex)



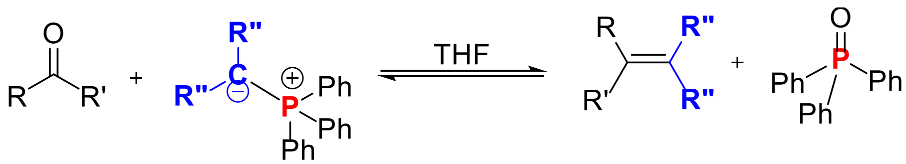


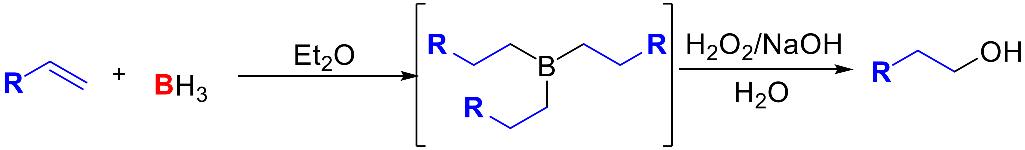
Frederick Sanger: 1958 (**Zn** in Insulin and other protein structures elucidation)



Georg Wittig: 1979 (**P** in Wittig reaction)

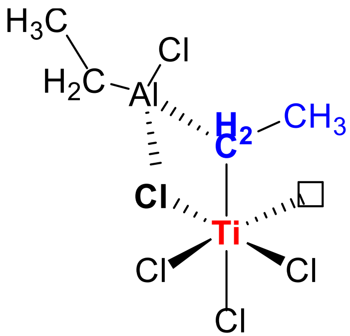
Herbert C. Brown 1979 (B for hydroboration)



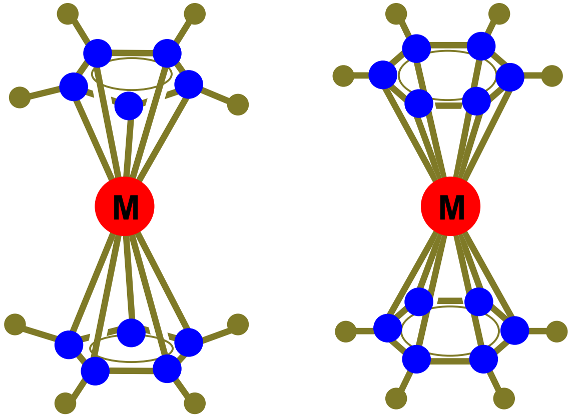


Nobel Prizes in Chemistry related to Metals

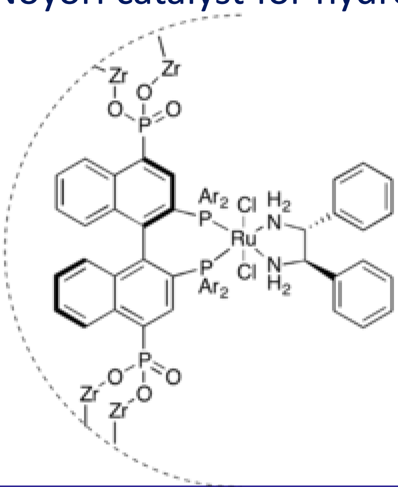
Karl Ziegler and Giullio Natta: 1963
(**Ti** – Ziegler polymerisation, **V**- Natta catalyst)



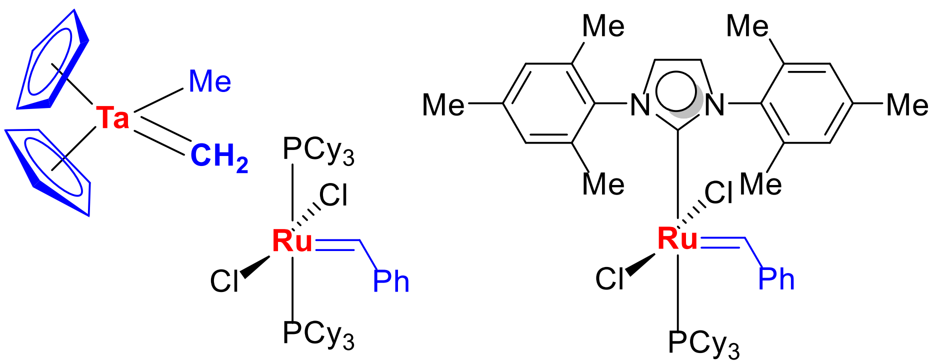
Ernst Otto Fischer and Geoffrey Wilkinson: 1973
(**Ni**, **Fe** based Sandwich compounds)



William Knowles, Ryoji Noyori, Barry Sharpless: 2001 (**Ti**-Sharpless Epoxidation, **Os**-Sharpless Dihydroxylation, **Rh**-Knowles Hydrogenation, **Ru**-Noyori catalyst for hydrogenation)

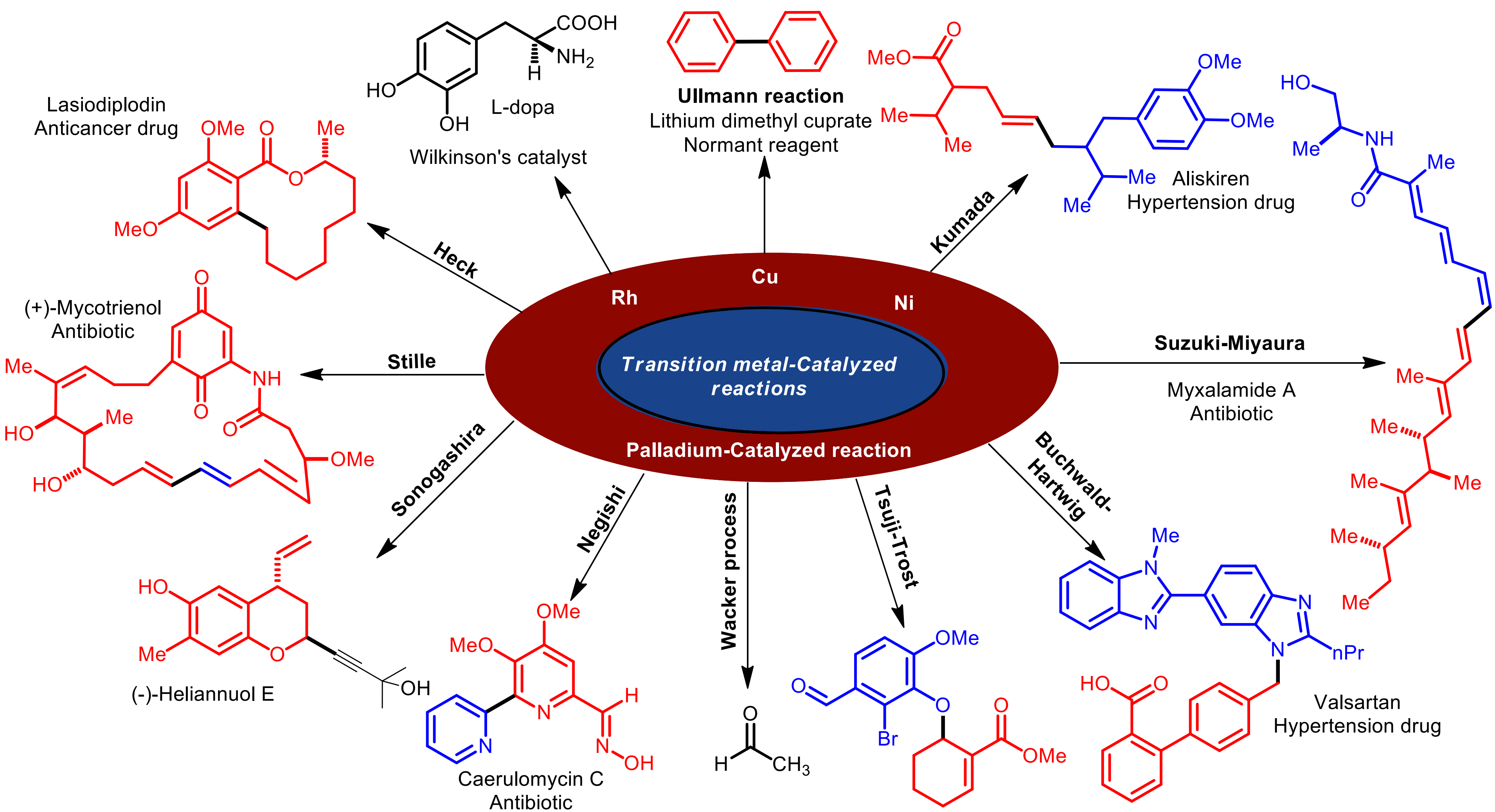


Yves Chauvin, Richard Schrock and Robert Grubbs: 2005 (**Mo-** Schrock catalyst, **Ru**-Grubbs Catalyst)



Nobel Prizes in Chemistry related to Metals

Richard Heck, Akira Suzuki, Eichii Negishi: 2010 (**Pd**, **Ni** for cross-coupling reactions)

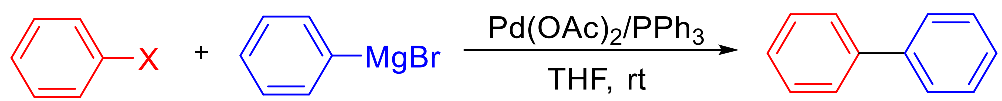


Chem. Asian. J. 2018, **13**, 2991-3013.

New Trends in Coupling Processes

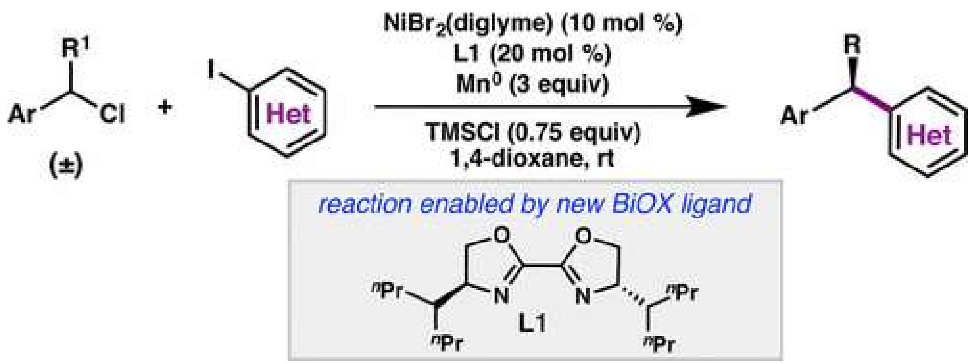
Traditional cross-coupling

Electrophile + Nucleophile —Pd/Ni→ Electrophile—Nucleophile

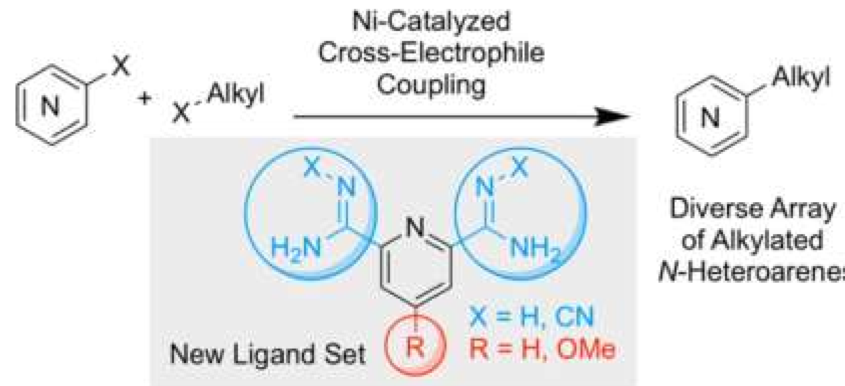


New trends in cross-coupling

Electrophile + Electrophile —Pd/Ni→ Electrophile—Electrophile

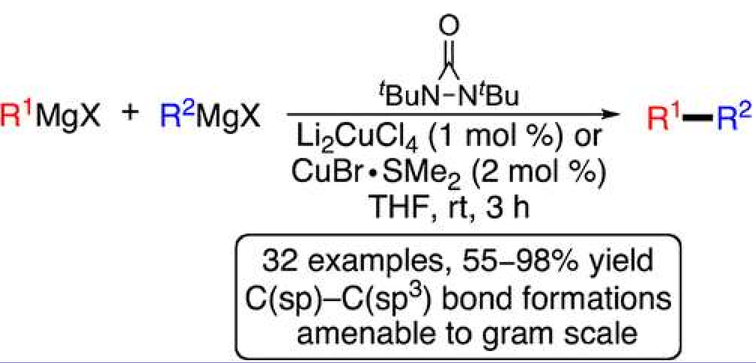


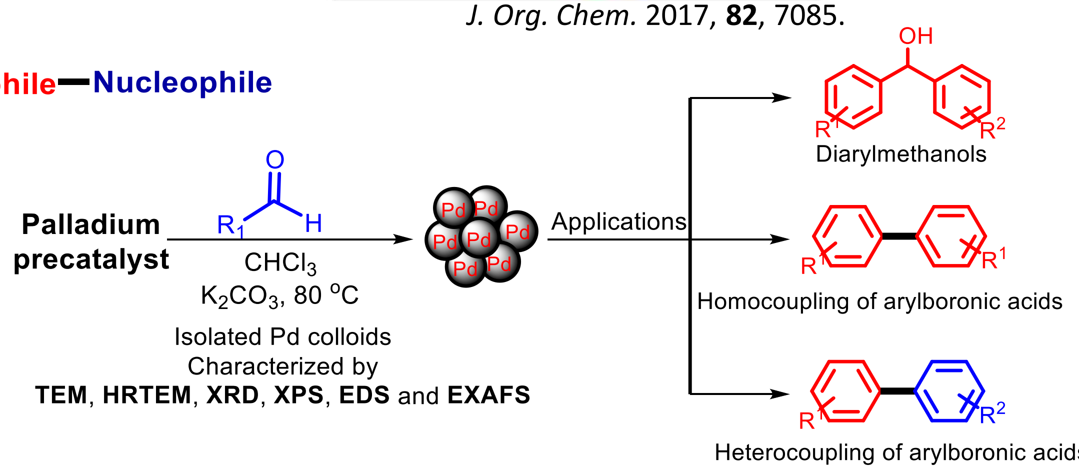
J. Am. Chem. Soc. 2017, **139**, 5684.



J. Org. Chem. 2017, **82**, 7085.

Nucleophile + Nucleophile —Pd/Ni→ Nucleophile—Nucleophile



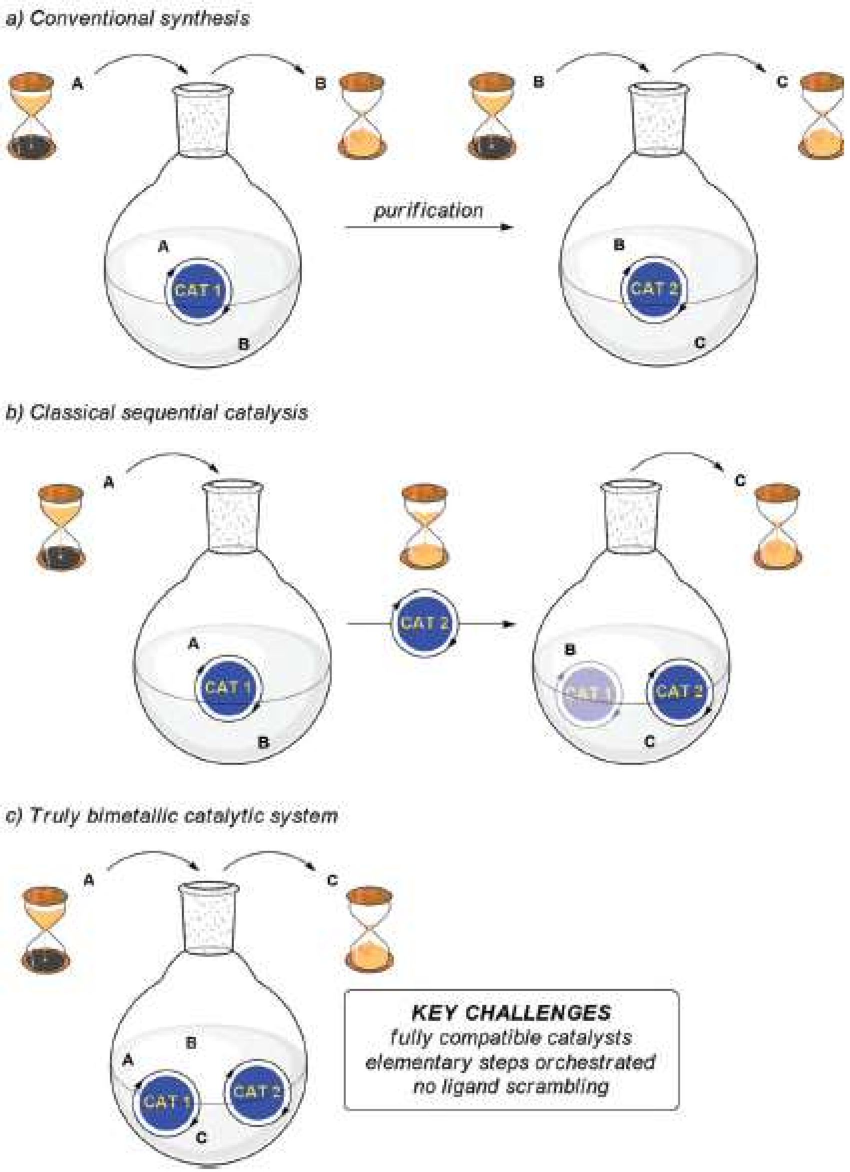


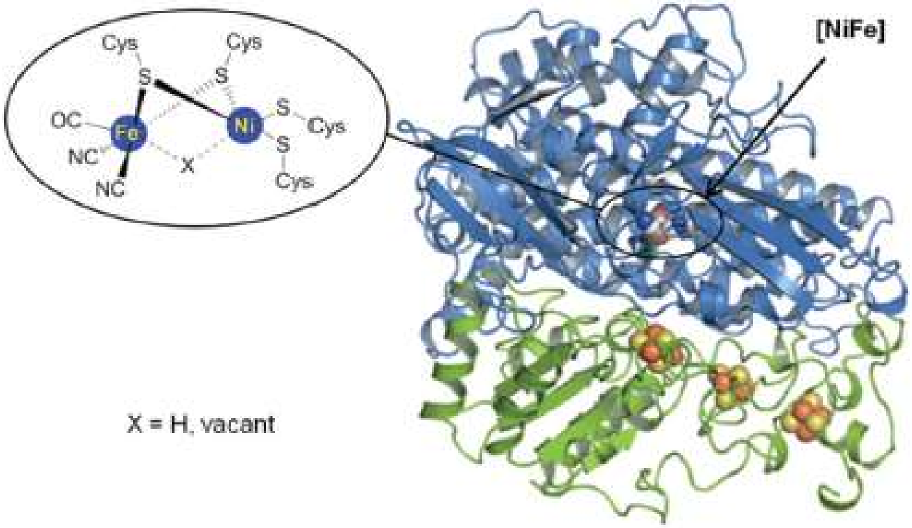
Isolated Pd colloids
Characterized by
TEM, **HRTEM**, **XRD**, **XPS**, **EDS** and **EXAFS**

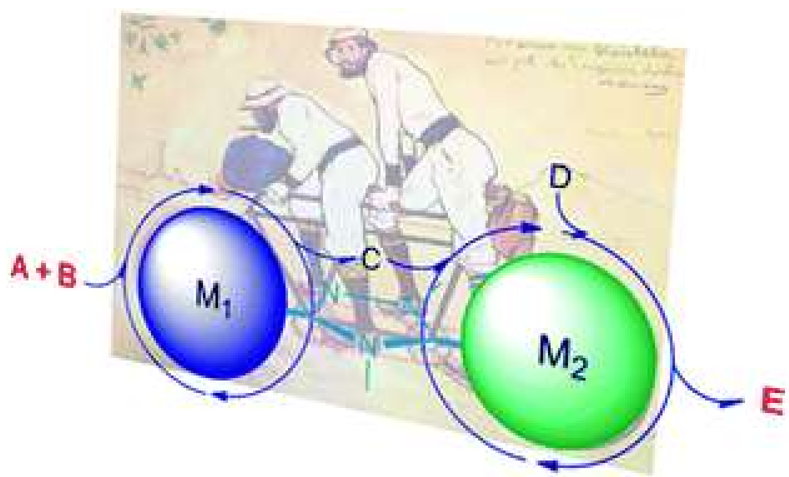
Org. Lett. 2014, **16**, 6144-6147.

ACS Omega, 2017, **2**, 204-217.
Chem. Asian J., 2018 , **13**, 2489

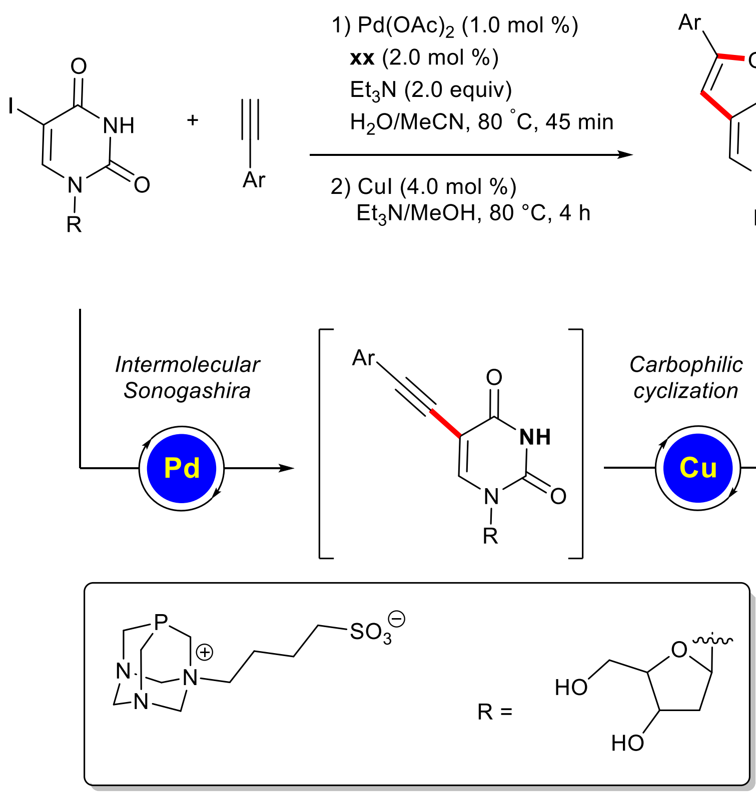
Bio-inspired Multiple Bond Formation: Multi-metal Catalysis

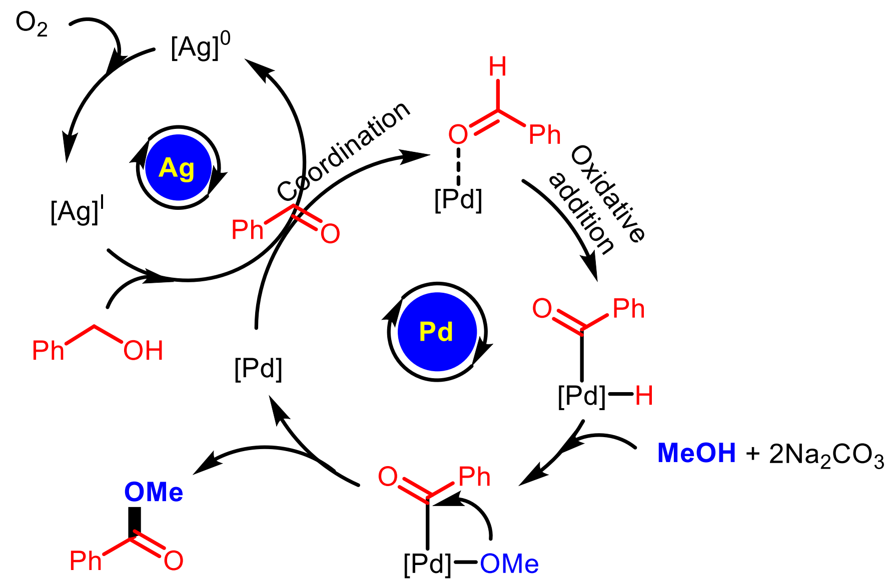


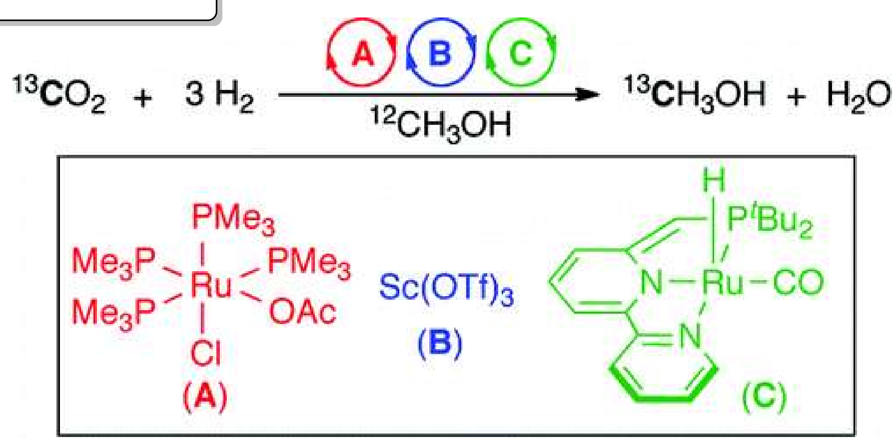




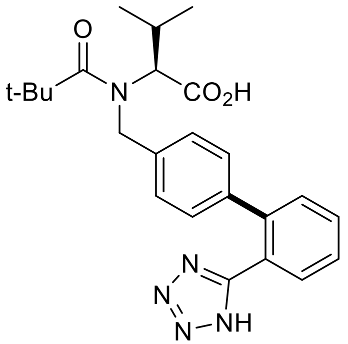
Bio-inspired Multiple Bond Formation: Multi-metal Catalysis



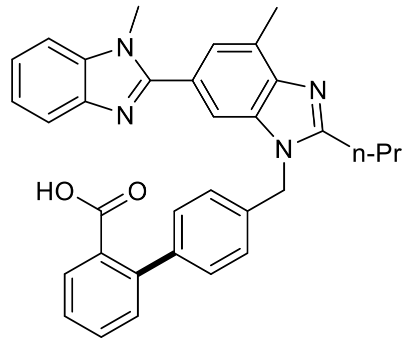




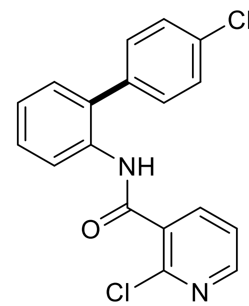
C-H Bond functionalization as Greener alternative for Cross-coupling



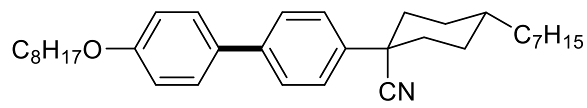
Diovan (Valsartan, Novartis)



Micardis (Telmisartan, Boehringer)

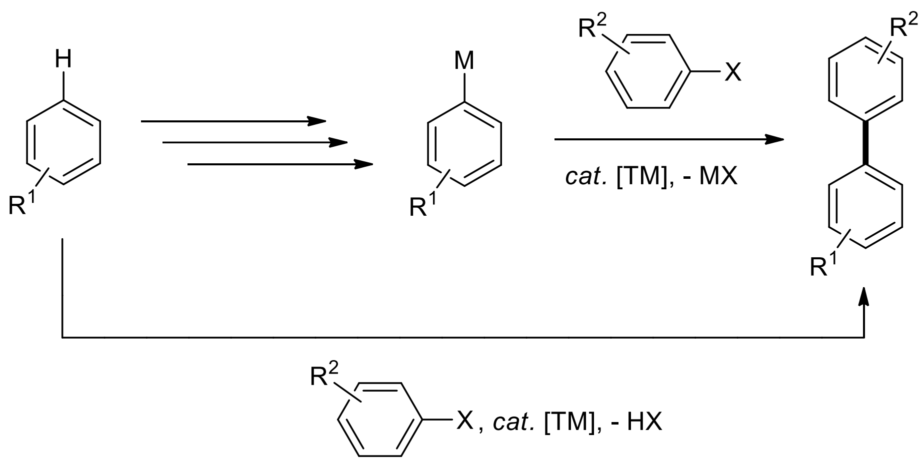


Boscalid (BASF)



NCB 807 (Liquid crystal, Merck)

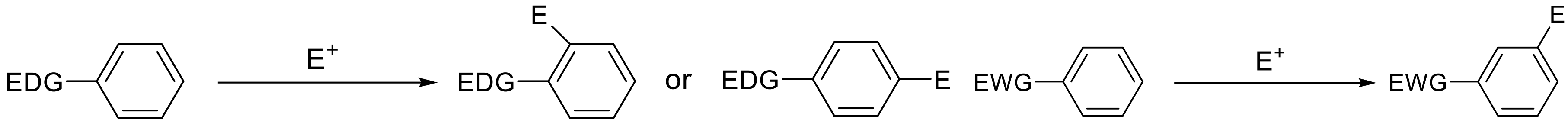
(a) traditional cross-coupling



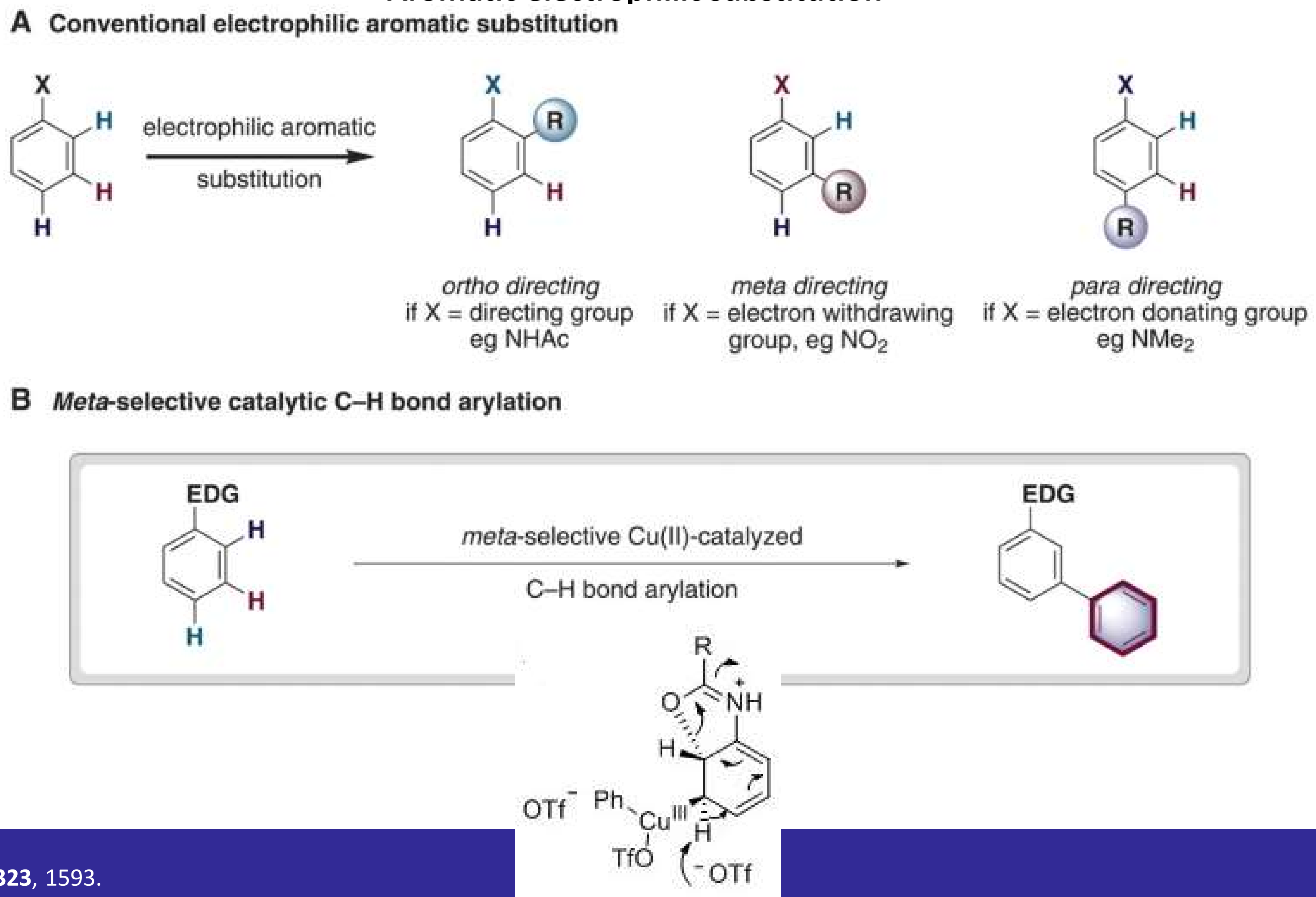
(b) direct arylation

Science, 2000, **287**, 1942.; *J. Chem. Soc., Dalton Trans.,* 2001, **17**, 2437.
Acc. Chem. Res., 2002, **35**, 826.;*Chem. Rev.,* 2002, **102**, 1731.

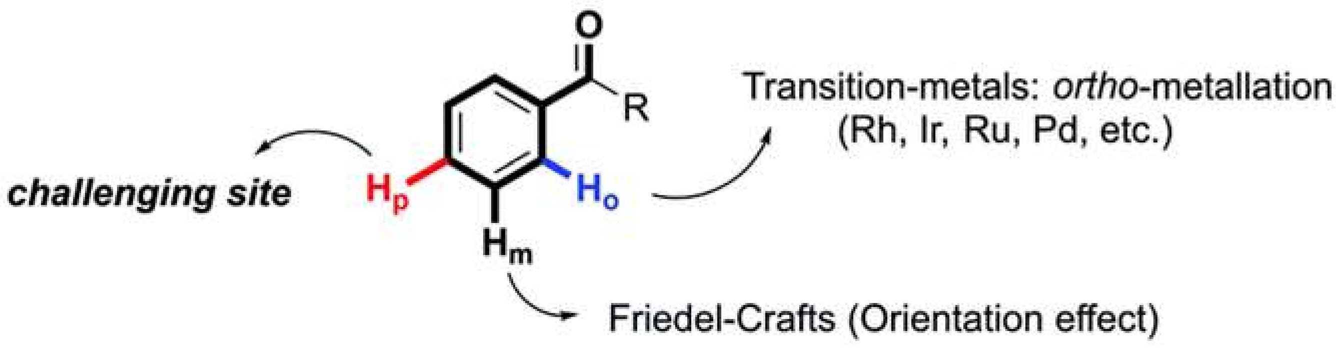
Challenging basic fundamentals of Organic Chemistry

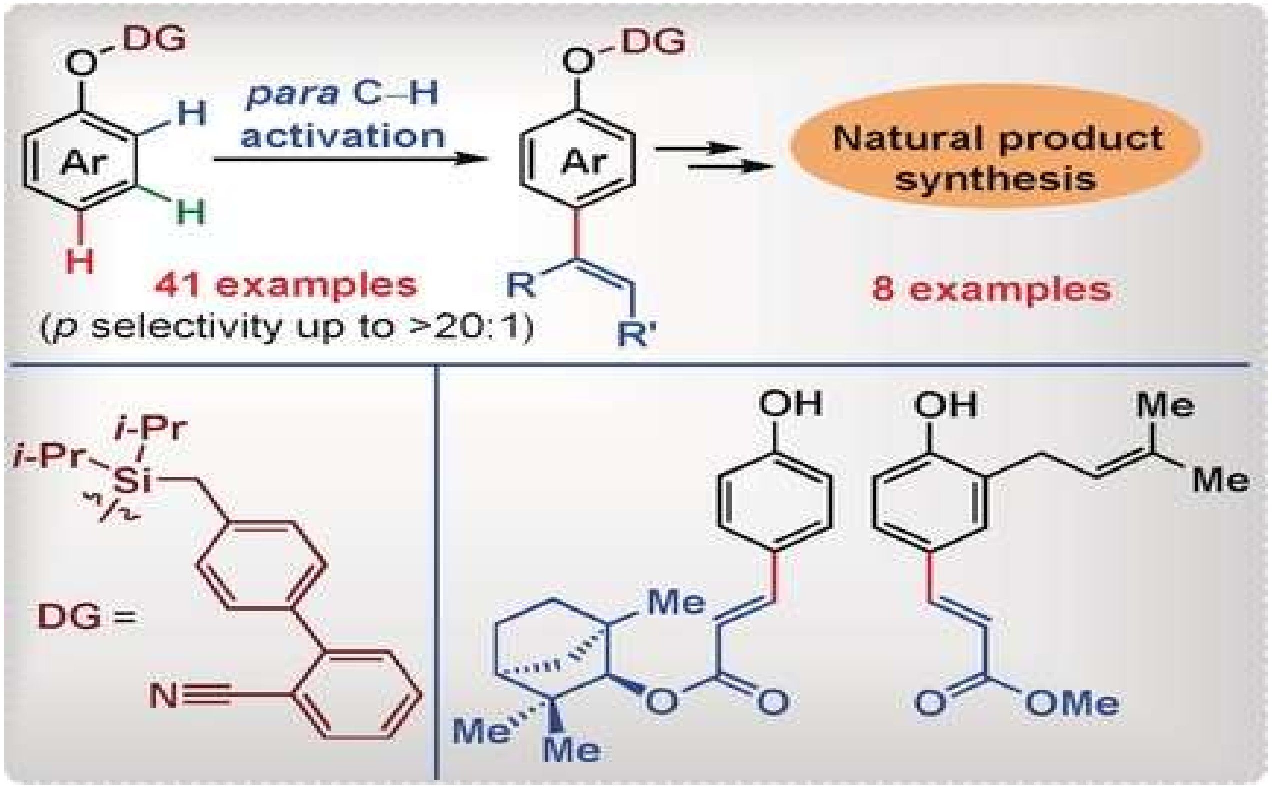


Aromatic electrophilic substitution

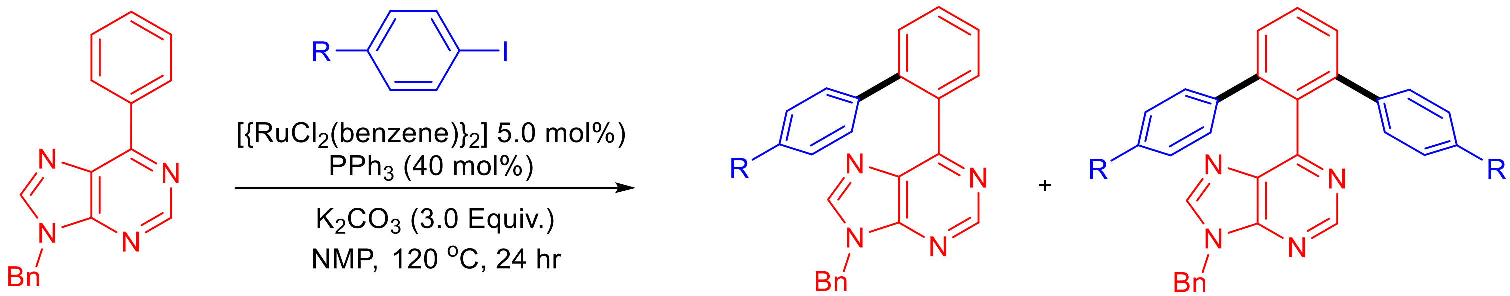


C-H Bond functionalization as Greener alternative for Cross-coupling

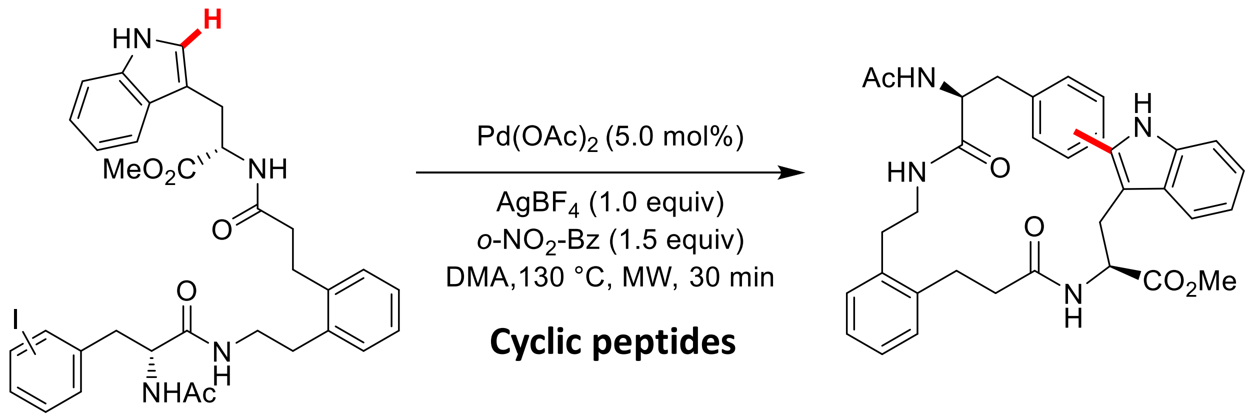




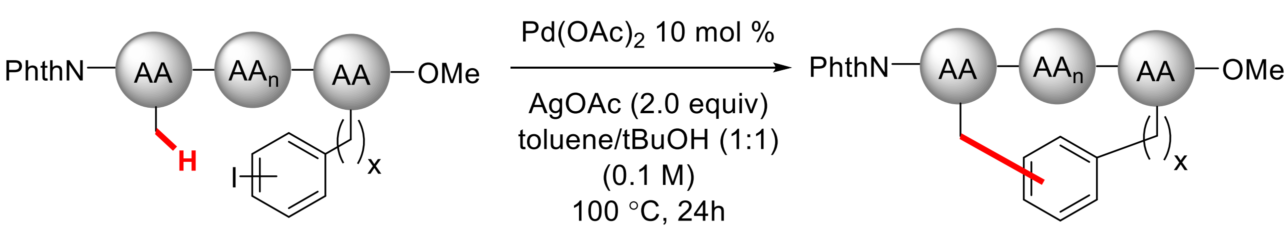
Applications: Bio-active molecules modification



Nucleosides



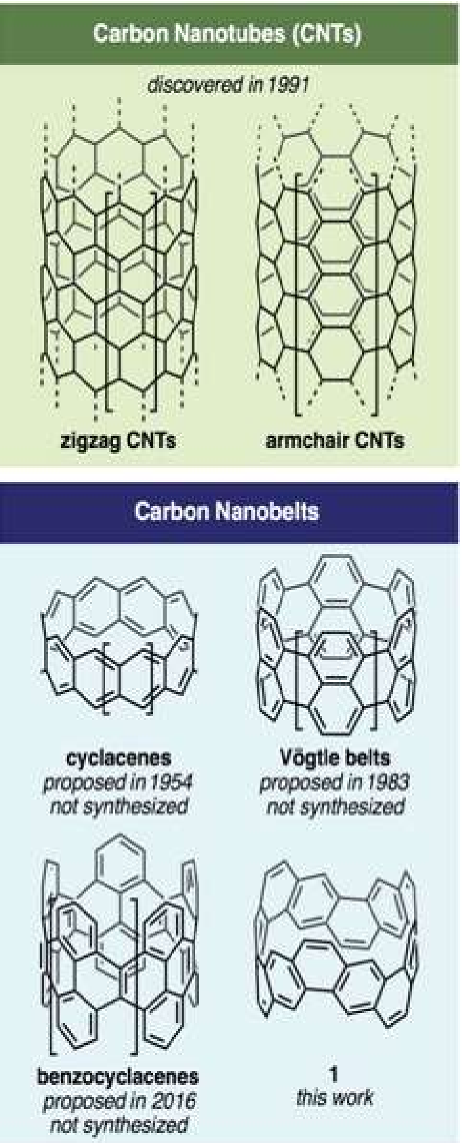
Cyclic peptides

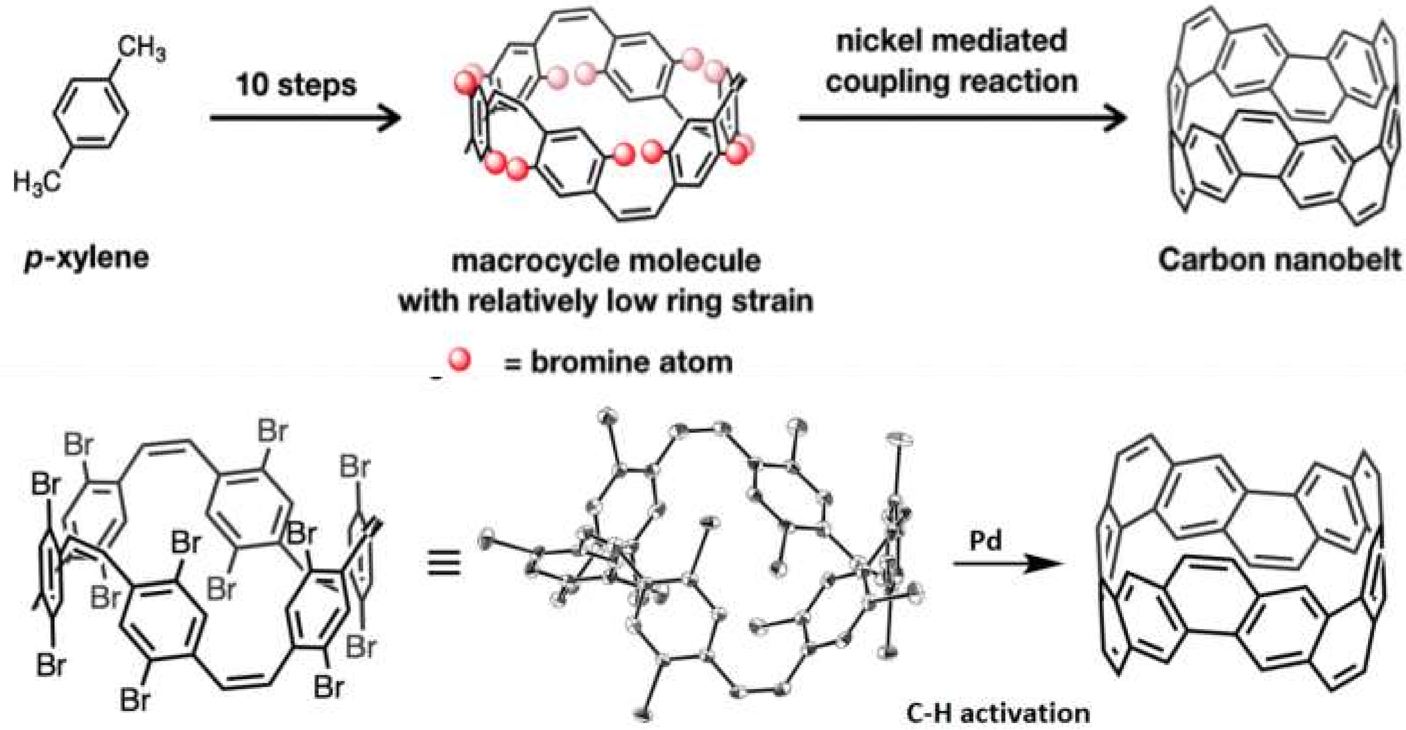


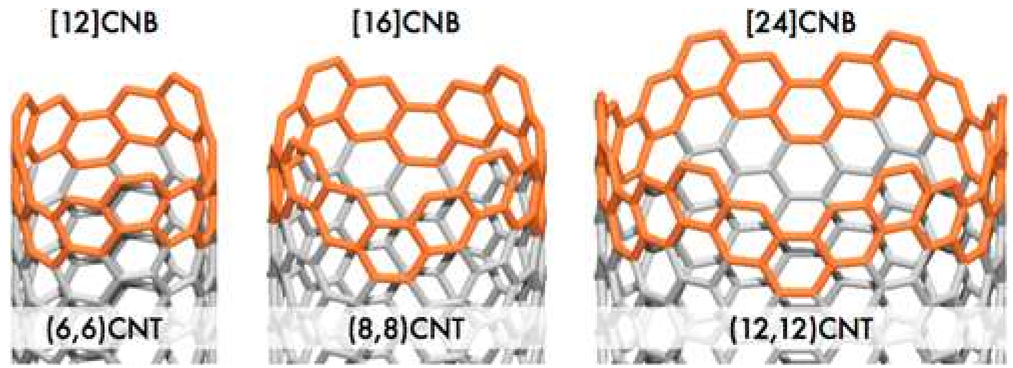
Tripeptides

C-H Bond functionalization as Greener alternative for Cross-coupling

Applications: Carbon Belt



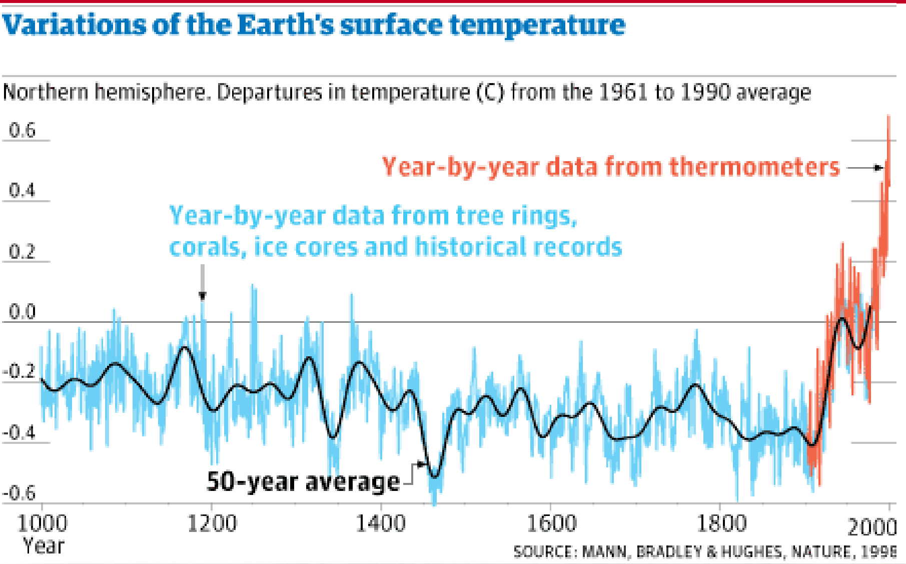


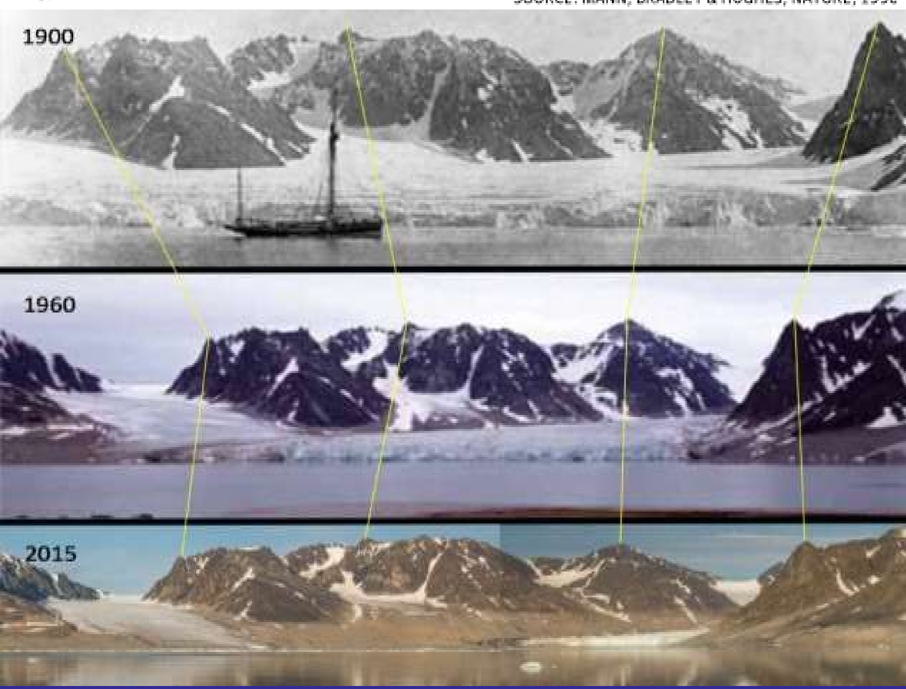


Future Challenges in Chemistry

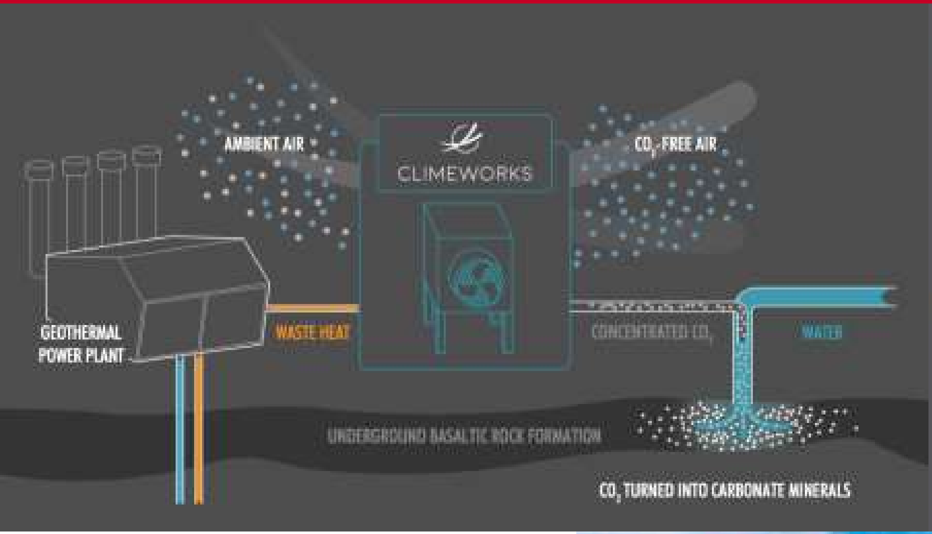
Can Organometallic Chemistry Provide the solution?

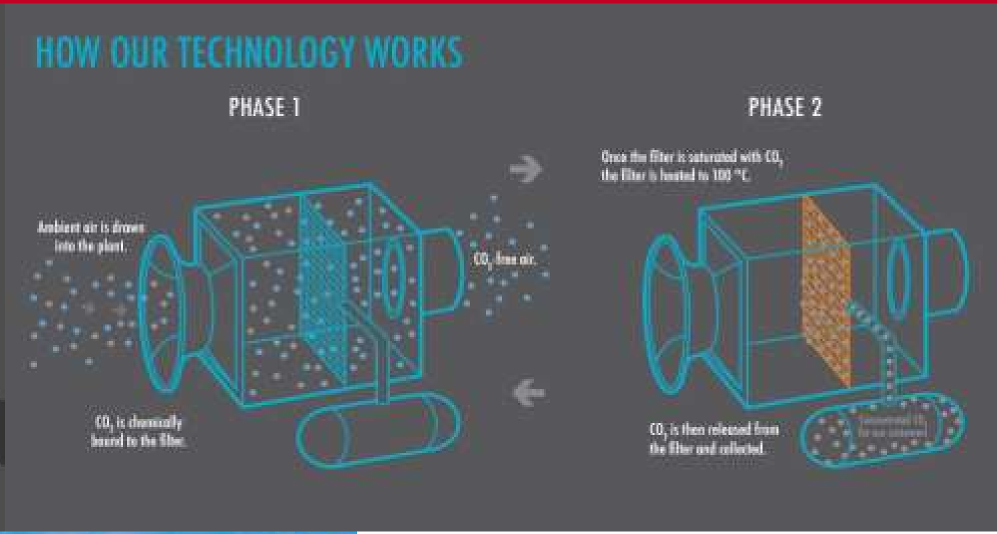
Environment: Carbon Dioxide Sequestration and Utilization

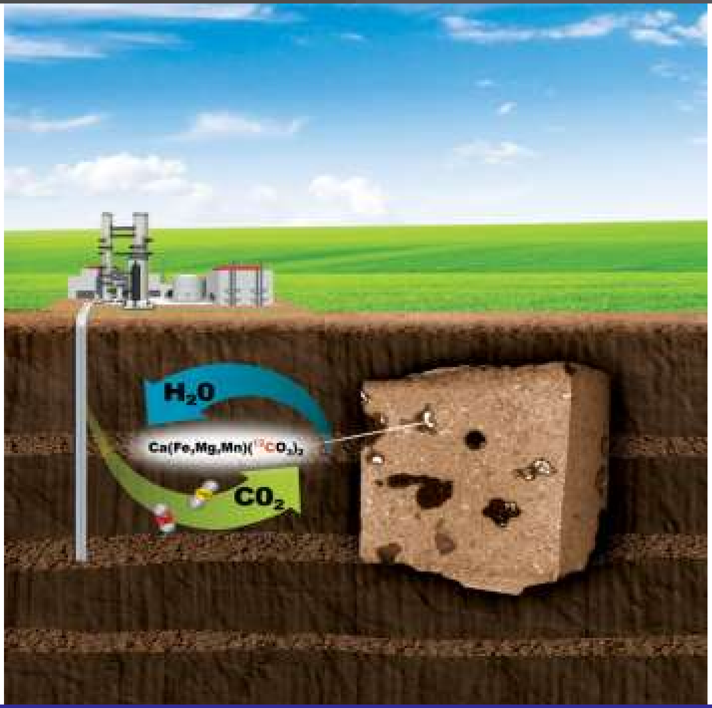


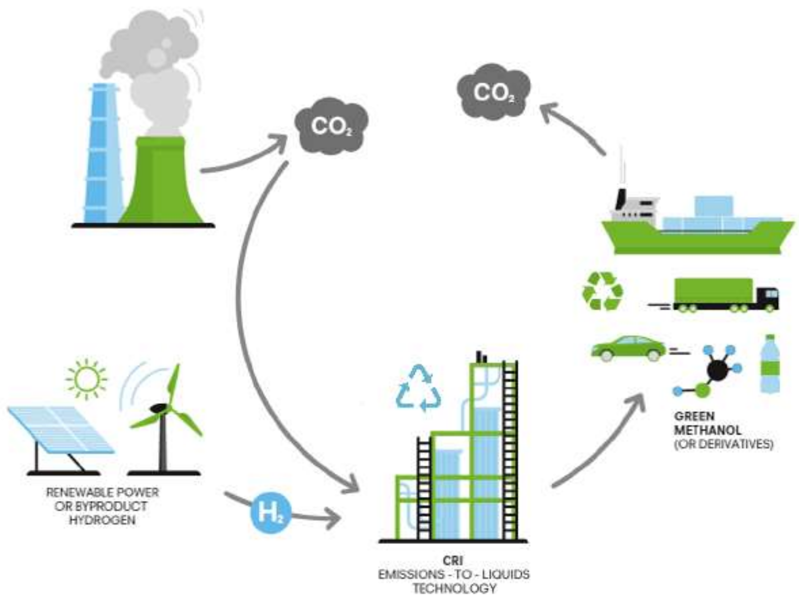


Environment: Carbon Dioxide Sequestration and Utilization

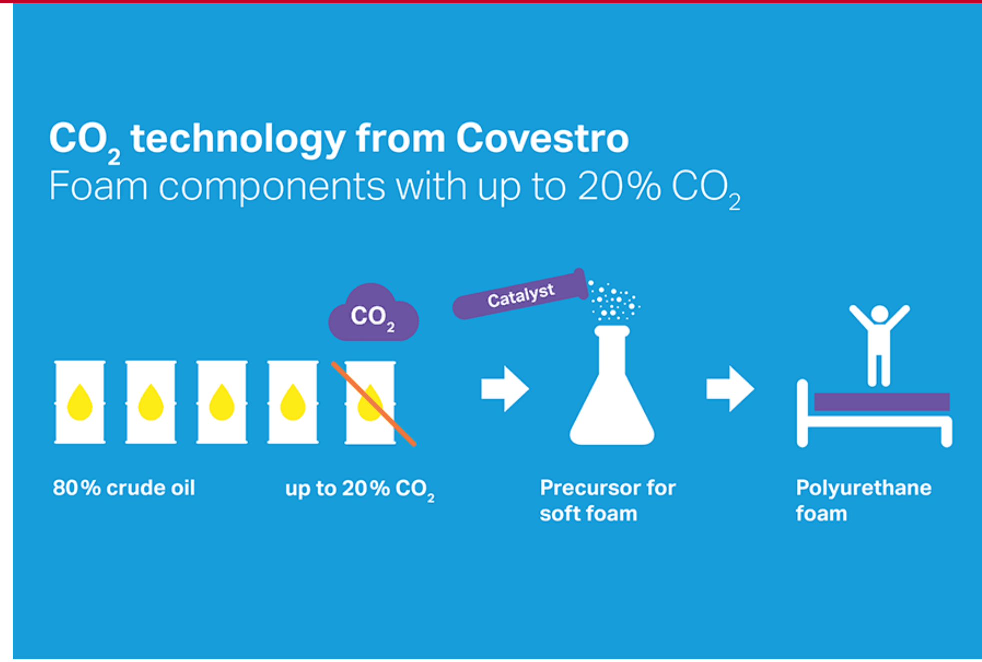


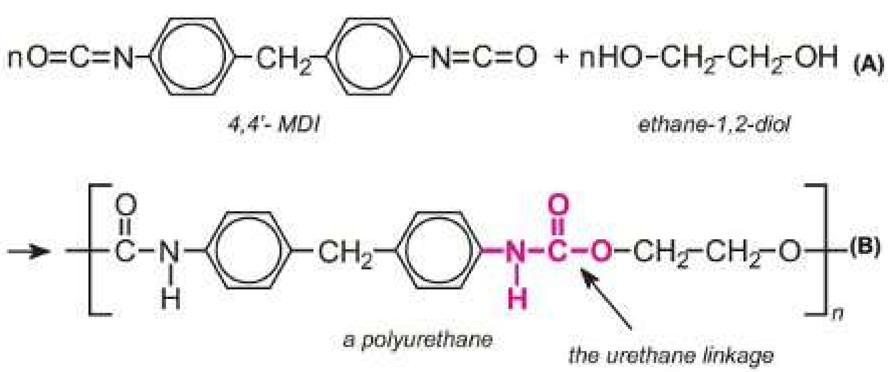




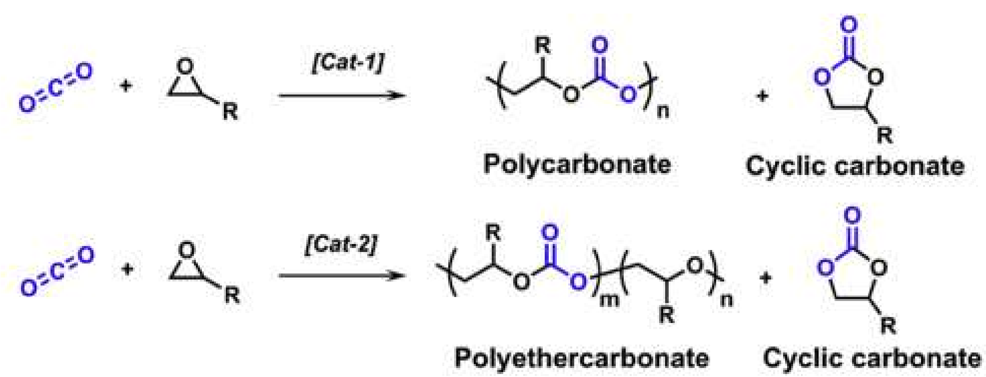


Carbon cycling International (2 million litres per year)





Bayer MaterialScience

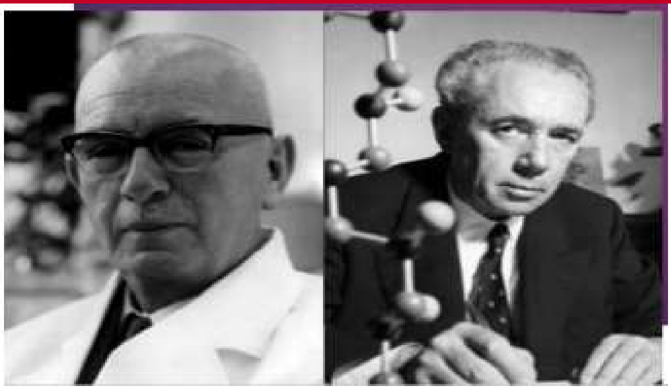


BASF: The Chemical Company

Sakamura et.al. *Green Chem.*, **2004**, *6*, 524 – 525.

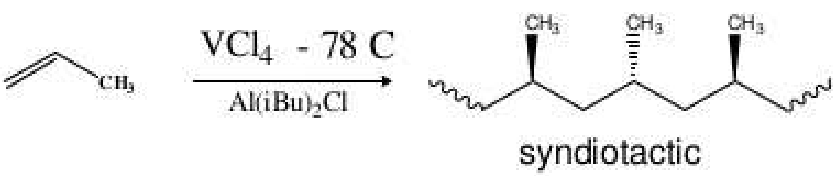
Sun et.al. *Ind. Eng. Chem. Res.* ***2019****, 58, 872–878*

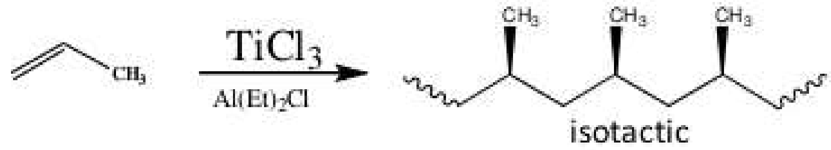
Ziegler-Natta Polymerization



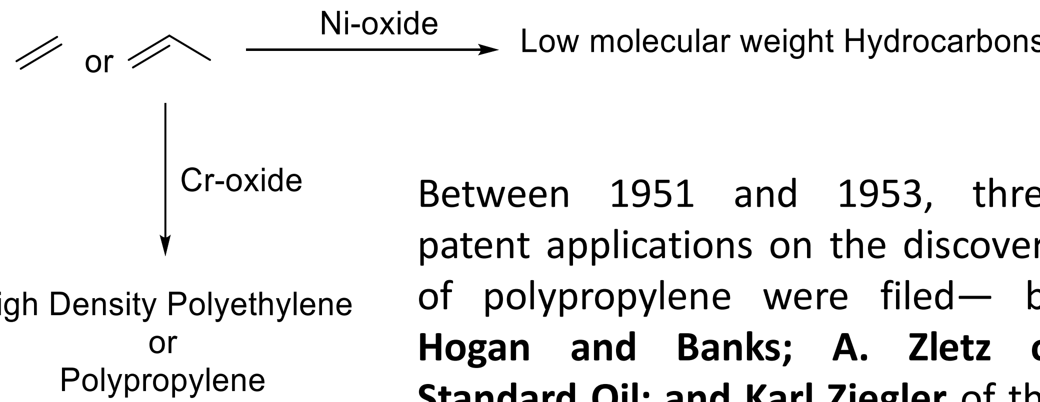
Karl Ziegler Guilio Natta

Karl Ziegler: 1951 discovery of polyethylene synthesis
Karl Ziegler + Guillio Natta: Isotactic polymer (1952: Ti)
Karl Ziegler + Guillio Natta: Syndiotactic polymer (1955: V)

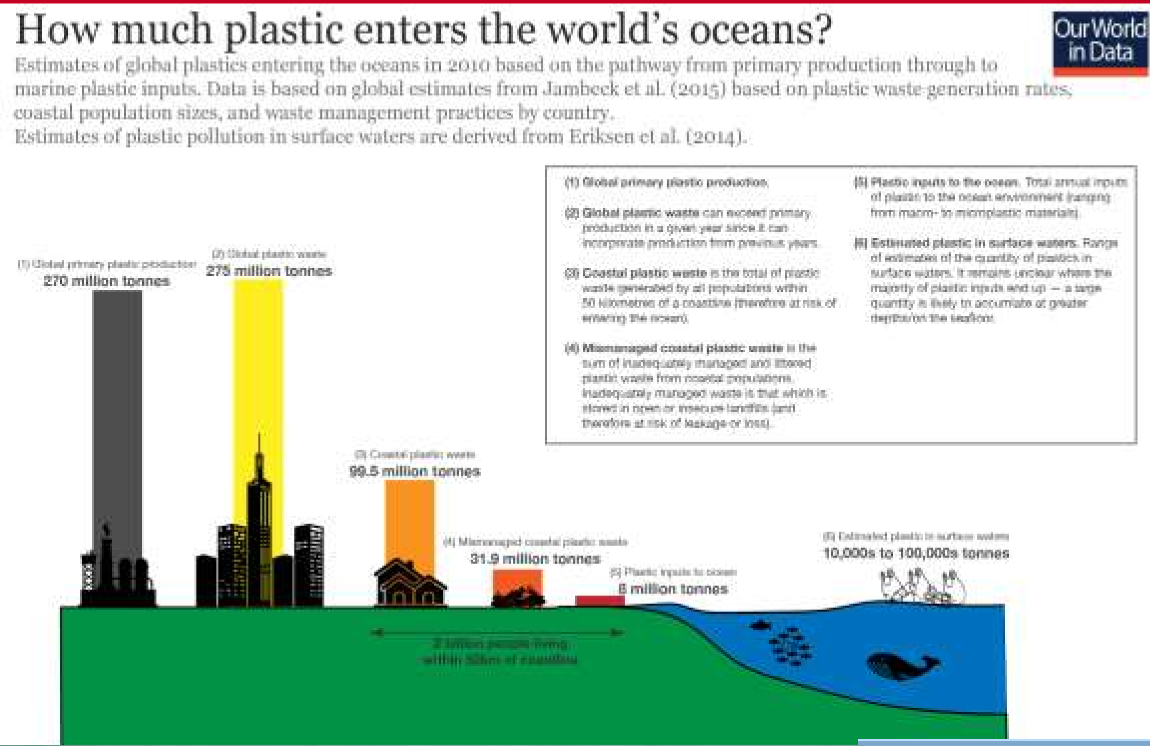


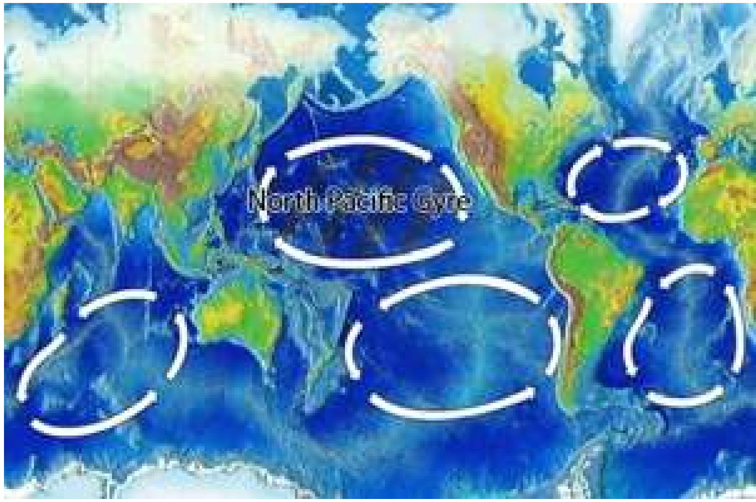


In 1983, patent awarded to **J. Paul Hogan, Robert L. Banks**



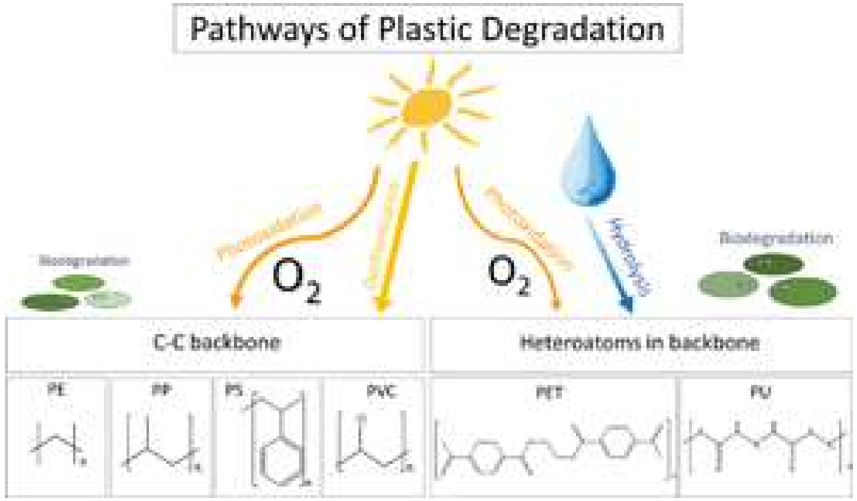
Between 1951 and 1953, three patent applications on the discovery of polypropylene were filed— by **Hogan and Banks; A. Zletz of Standard Oil; and Karl Ziegler** of the Max Planck Institute.

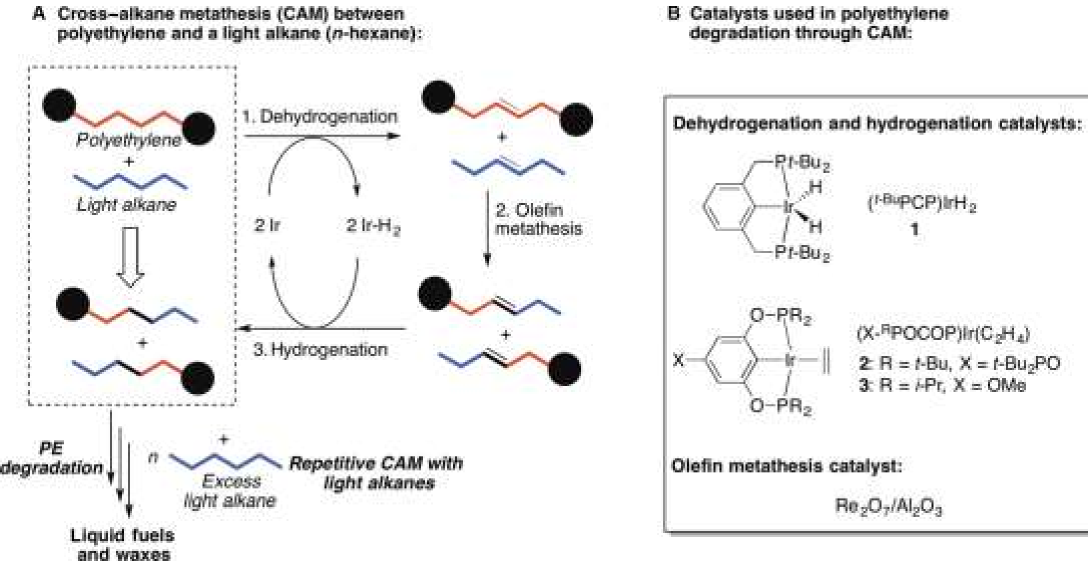




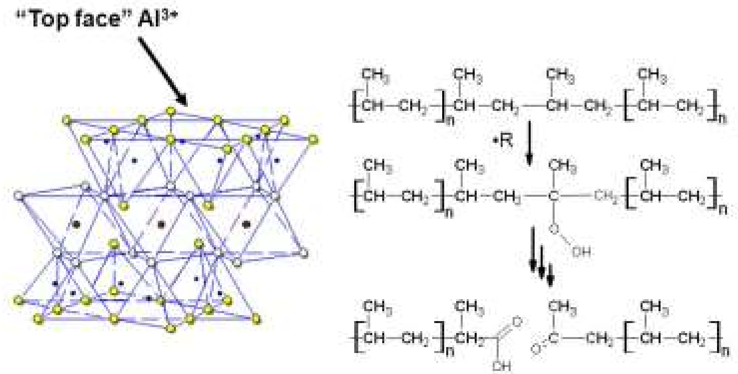
The North Pacific Gyre.

Environment: Polymer Degradation





Aluminum Catalyzed Polypropylene Thermal Degradation



Science Advances , **2016,** 2, e1501591.

Thank you

Inspire awardee or CSIR NET or UGC NET JRF interested in joining our research group can have a look at our website and can contact me on the email id given below.

My website: https://kapdigroupresearch.com/
Email id: ar.kapdi@ictmumbai.edu.in