Transition-Metal-Catalyzed Carboxylation through the Fixation of Carbon Dioxide

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Supervisor: Zhang-Jie Shi

Fudan University

2019-06-14

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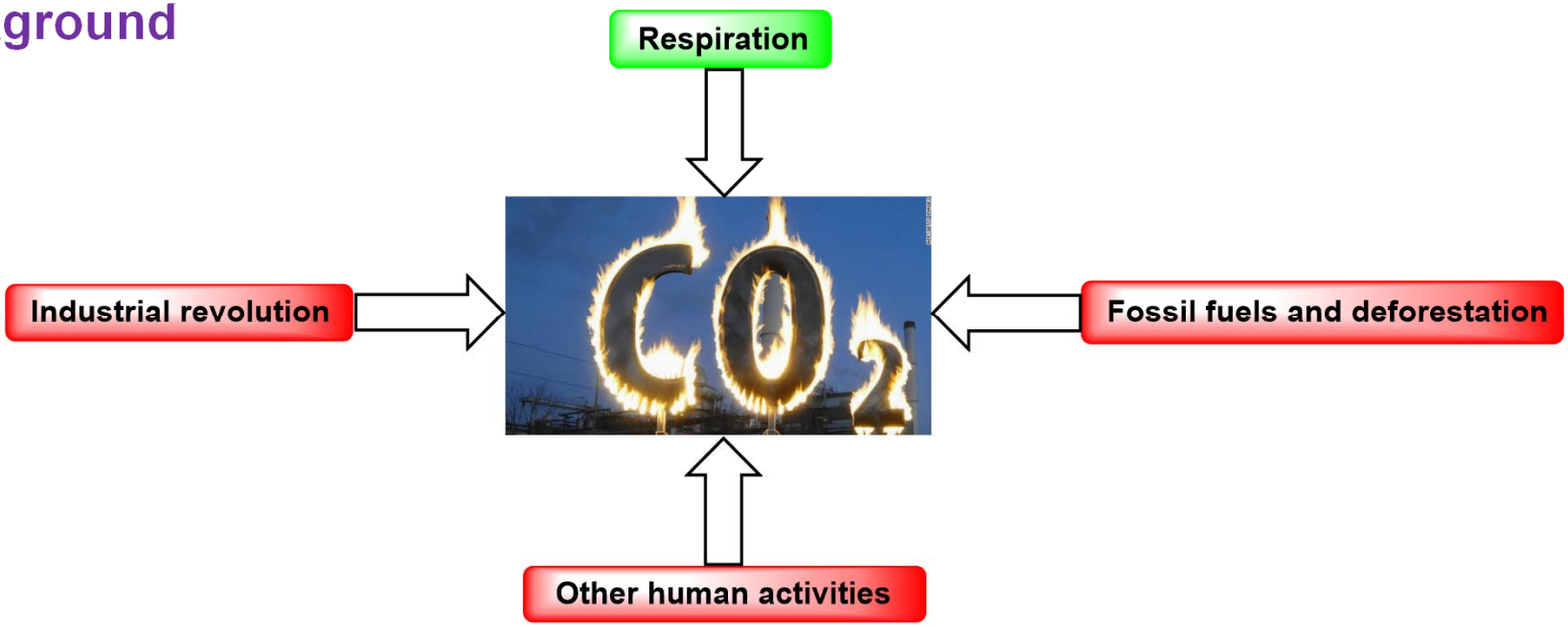
Introduction

Background



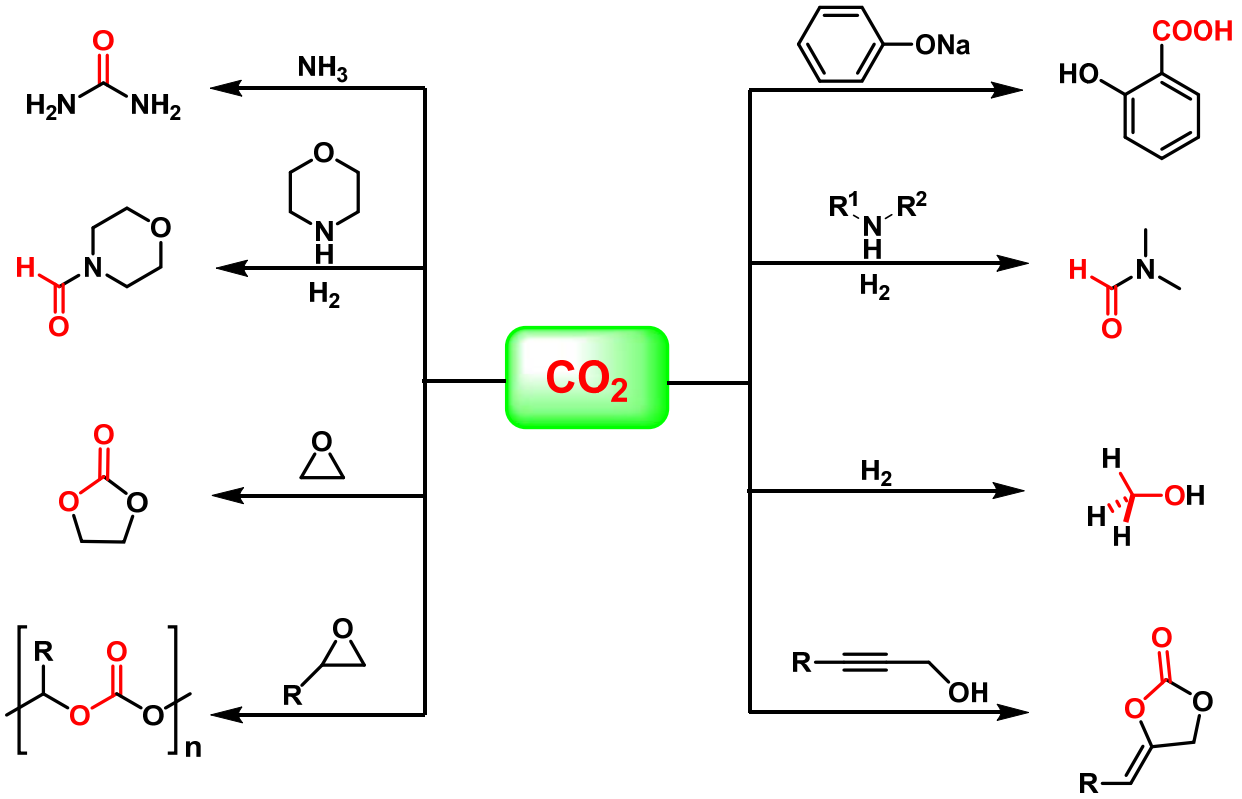
- Abundant
- Inexpensive C1 feedstock
- Greenhouse gas

- ➢ Capture
- ➢ Storage
- ➢ Added-value products

Bardow, A. et al. *Chem. Soc. Rev.* **2014**, *43*, 7982.

Introduction

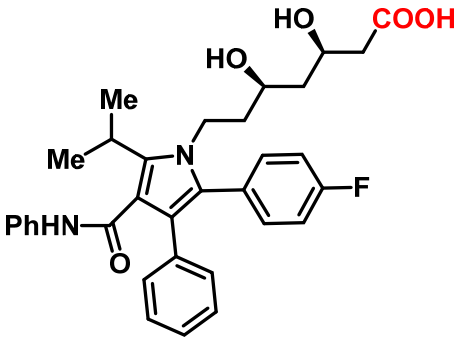
CO_2 fixation into chemicals



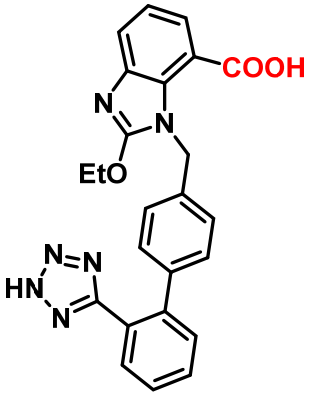
Ding, K. L. et al. *Angew. Chem. Int. Ed.* **2012**, *51*, 13041.
Beller, M. et al. *Nat. Commun.* **2015**, *6*, 5933.
Ding, K. L. et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 6186.

Introduction

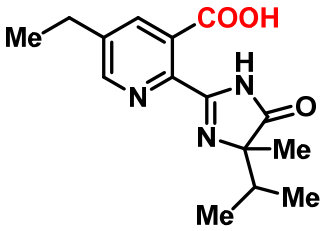
Carboxylic acids in human life



Lipitor
Hypercholesterolemia



Blopress
Hypertension



Imazethapyr
Herbicide

nylon

agrochemicals

pharmaceuticals

cosmetics

Maag, H. et al. *Prodrugs of Carboxylic Acids, Springer*, New York, **2007**.
Martin, R. et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 15948.

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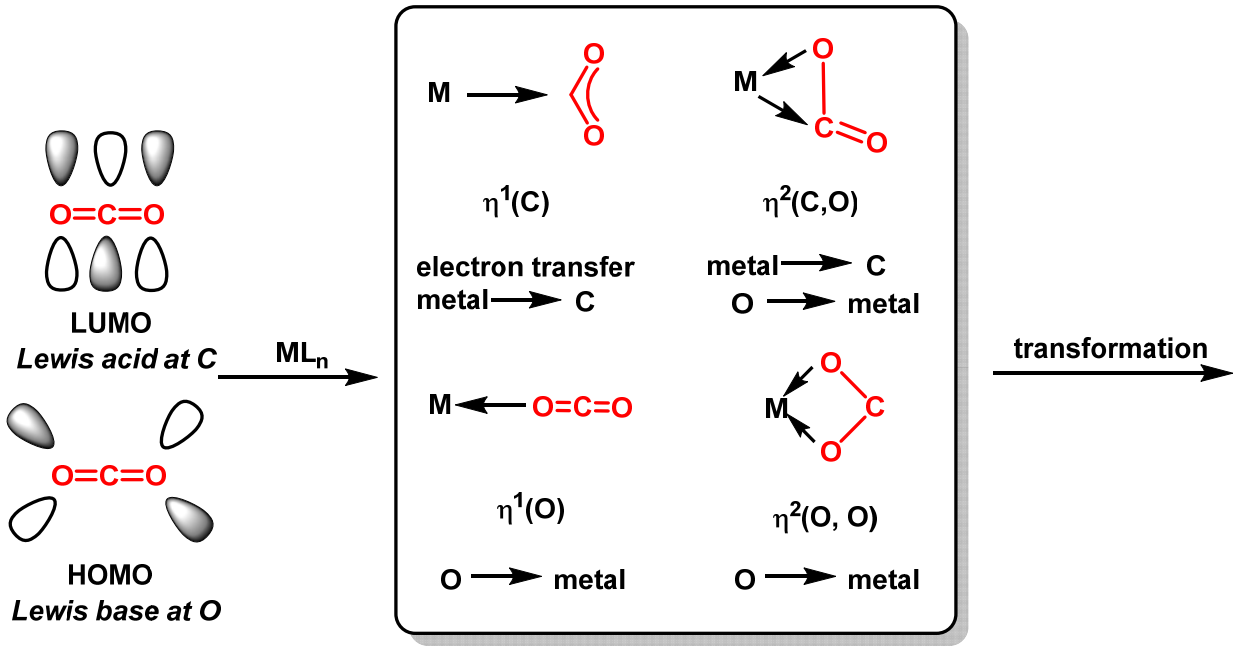
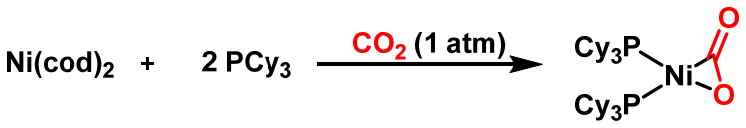
The Coordination Mode of CO_2 with Transition Metals

Binding modes to transition metals



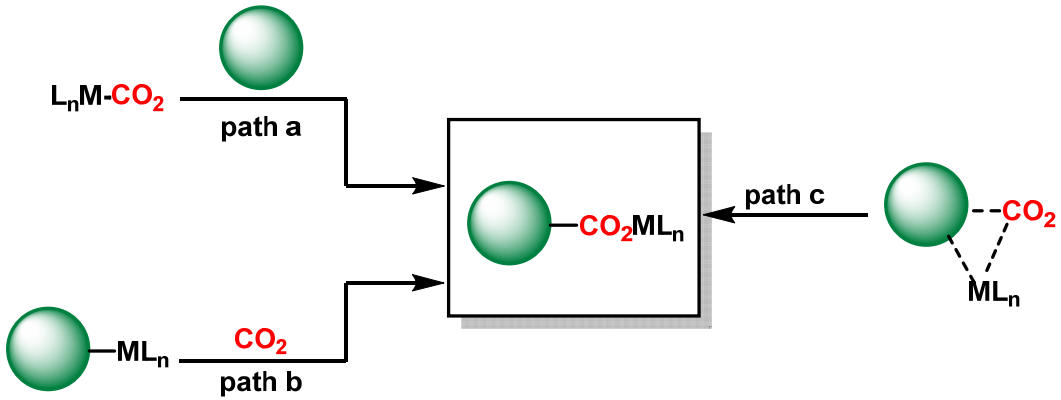
1975年实现首例过渡金属-CO_2配合物Ni(CO_2)(PCy_3)$_2$的合成与表征



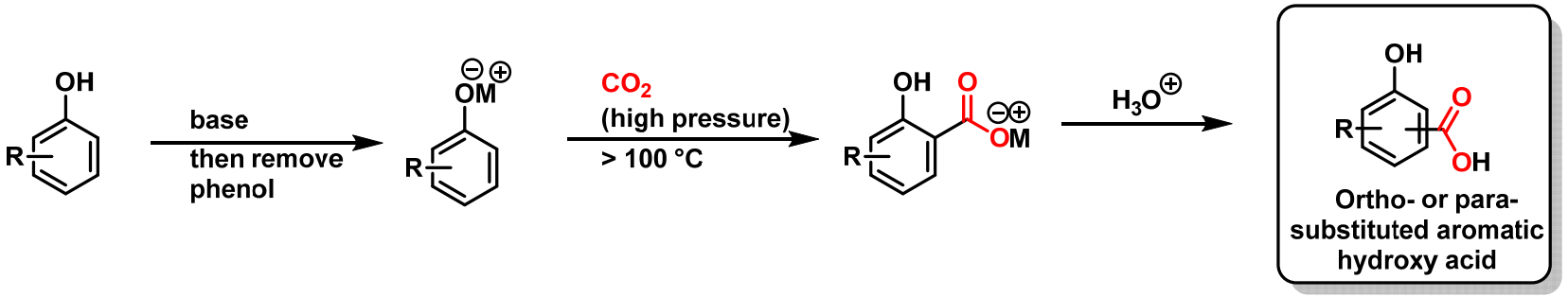
Gibson, D. H. et al. *Chem. Rev.* **1996**, *96*, 2063.
Mori, M. et al. *Eur. J. Org. Chem.* **2007**, *2017*, 4981.
Albano, V. G. et al. *J. Chem. Soc, Chem. Commun*, **1975**, *15*, 636.

The Coordination Mode of CO_2 with Transition Metals

Common catalytic strategy when converting CO_2 into RCO_2H.



Kolbe-Schmitt reaction



R = H, alkyl, aryl, OH, *O*-alkyl, NR_2; base: alkali metal hydroxides (e.g., NaOH, KOH, CsOH), K_2CO_3, $KHCO_3$

Kolbe, H. et al. *Ann. Chem.* **1860**, *113*, 125.
Lindsey, A. S. et al. *Chem. Rev.* **1957**, *57*, 583.

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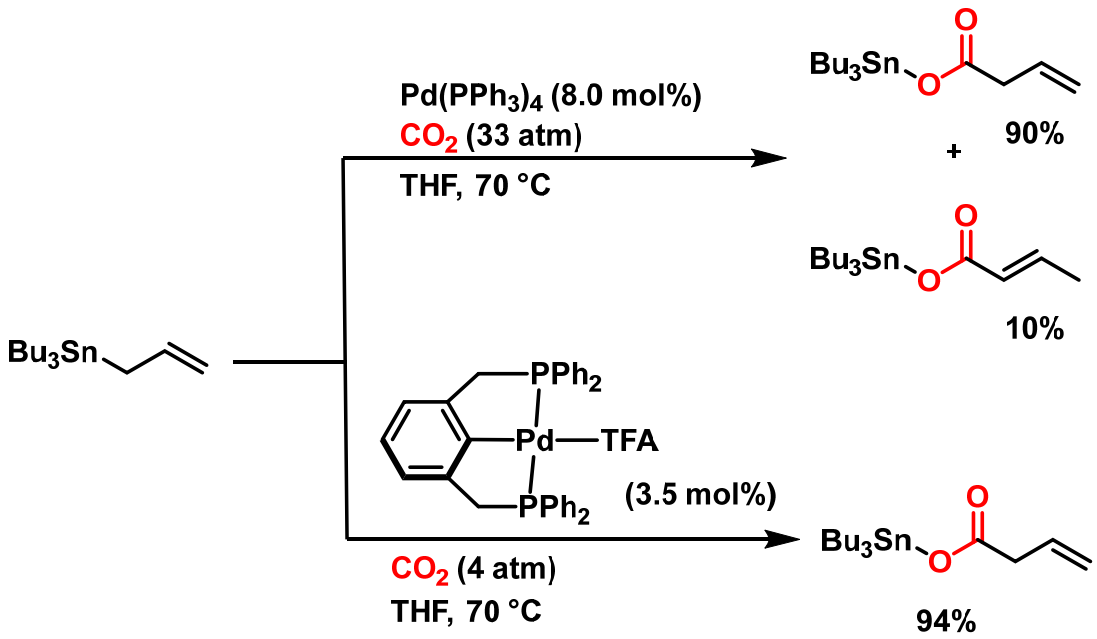
Pd-catalyzed Carboxylation of Organotin Reagents



Nicholas, M. et al. *J. Am. Chem. Soc.* **1997**, *119*, 5057.
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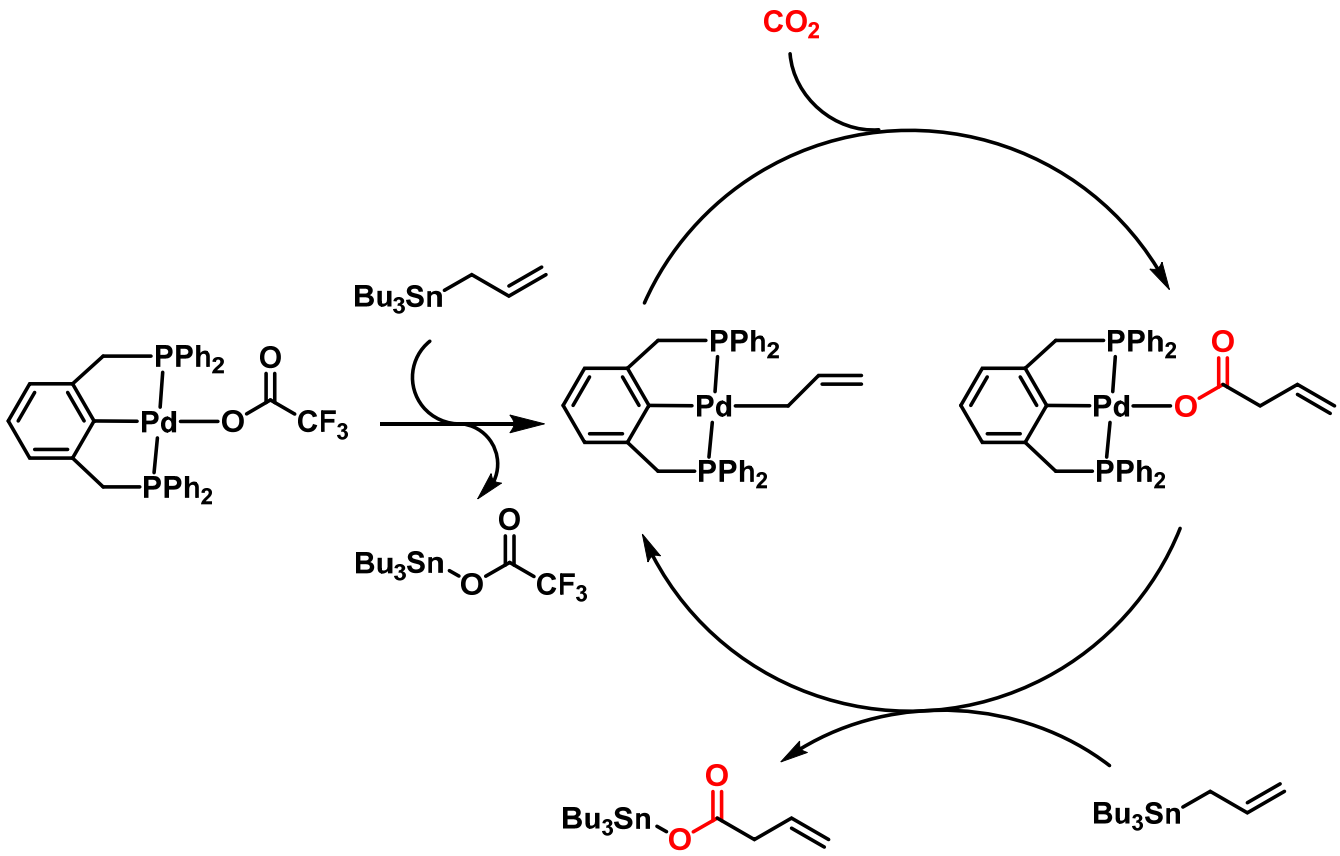
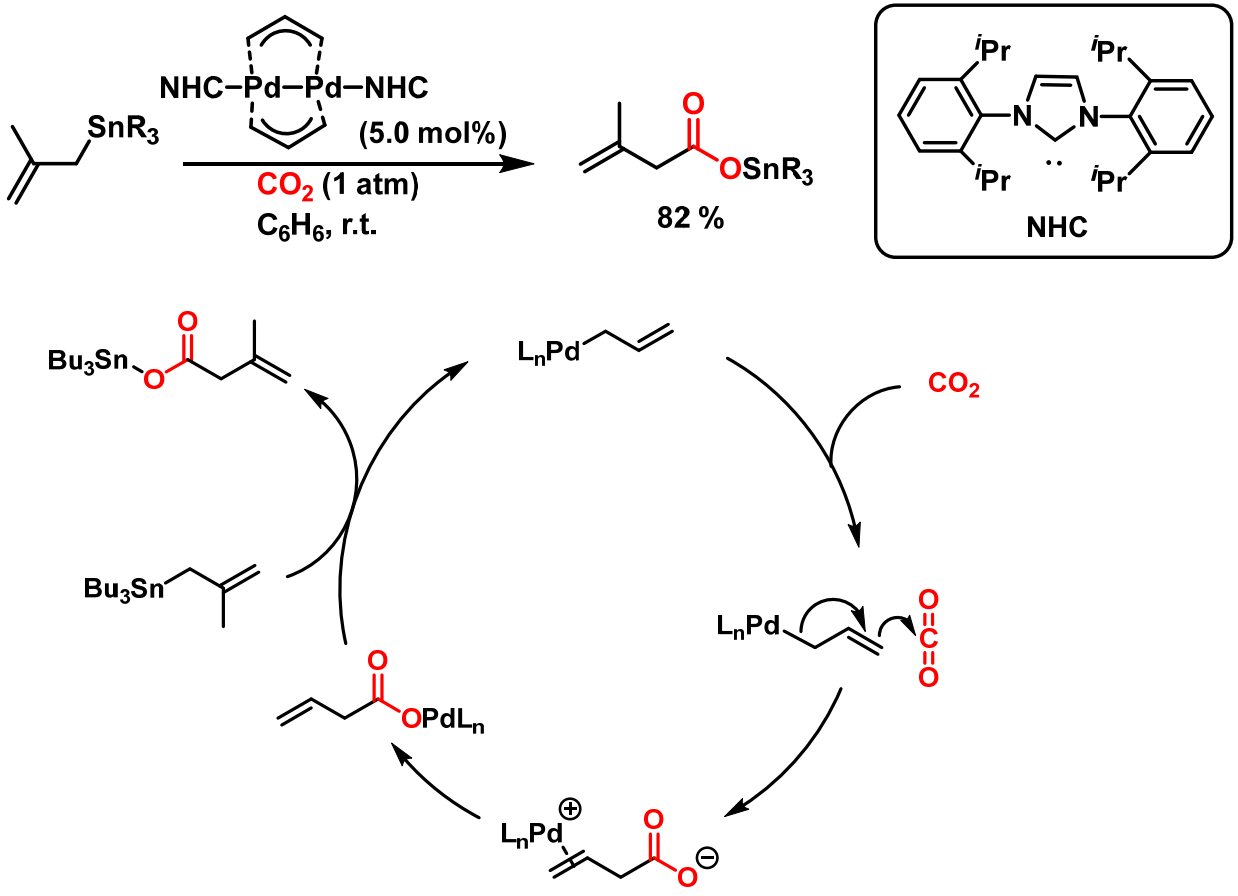
Pd-catalyzed Carboxylation of Organotin Reagents



Wendt, O. F. et al. *Dalton Trans.*, **2007**, 488.

Pd-catalyzed Carboxylation of Organotin Reagents



Hazari, N. et al. *Chem. Commun.* **2011**, *47*, 1069.
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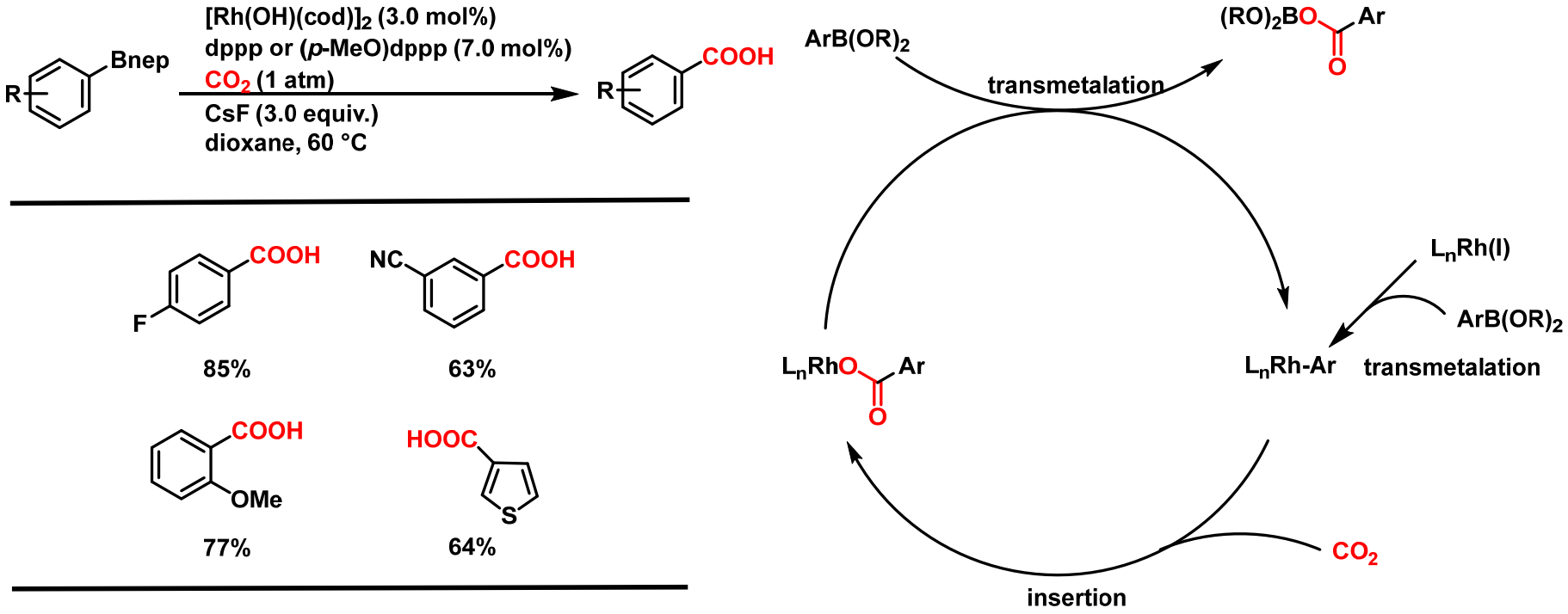
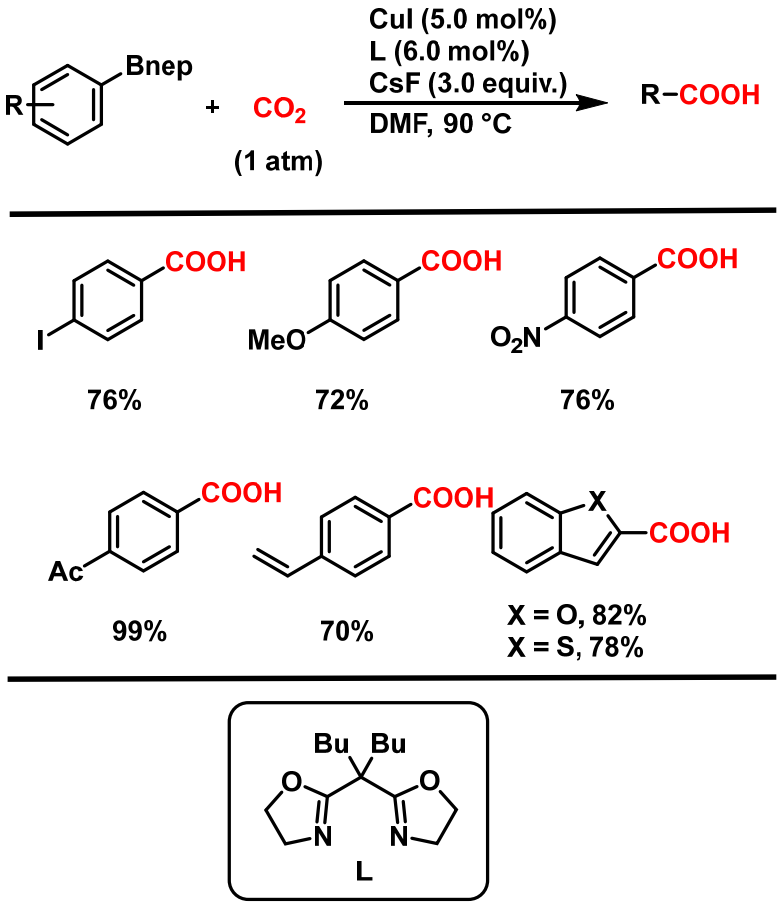
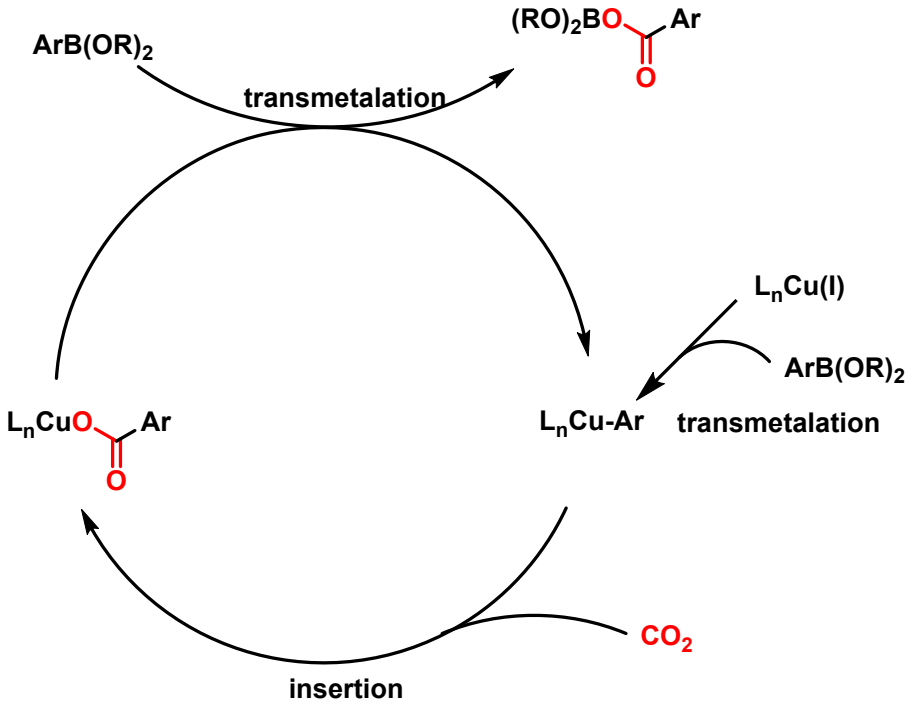
Rh-catalyzed Carboxylation of Organoboron Reagents



Iwasawa, N. et al. *J. Am. Chem. Soc.* **2006**, *128*, 8706.

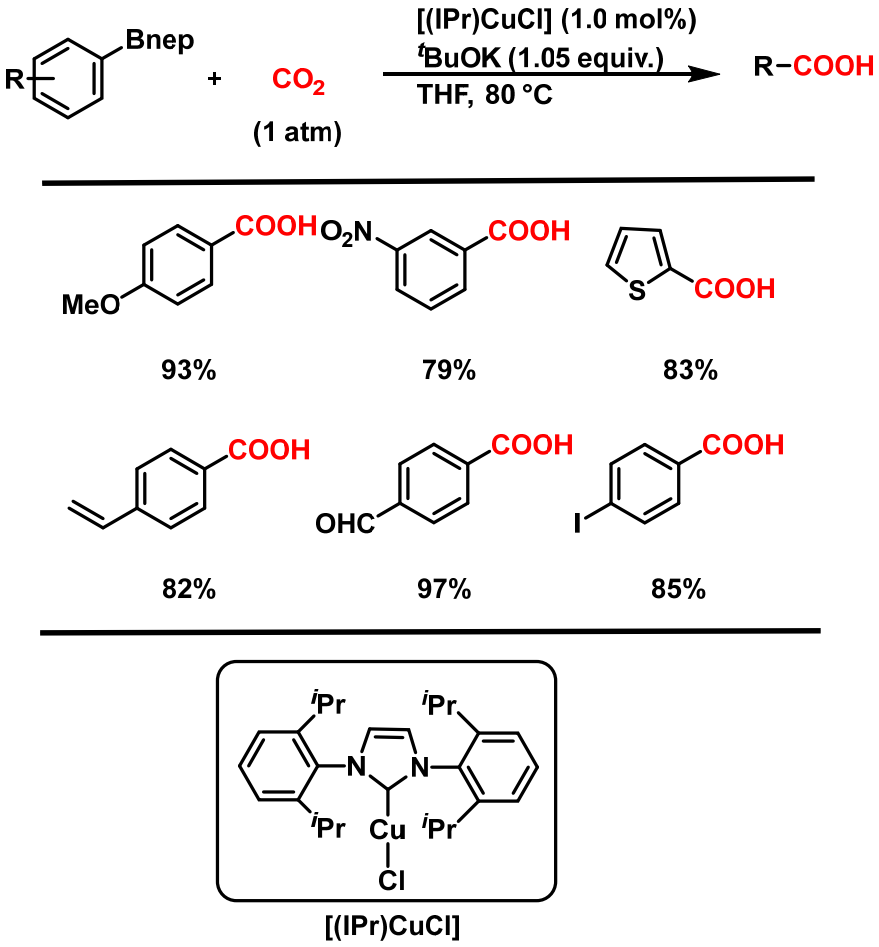
Cu-catalyzed Carboxylation of Organoboron Reagents

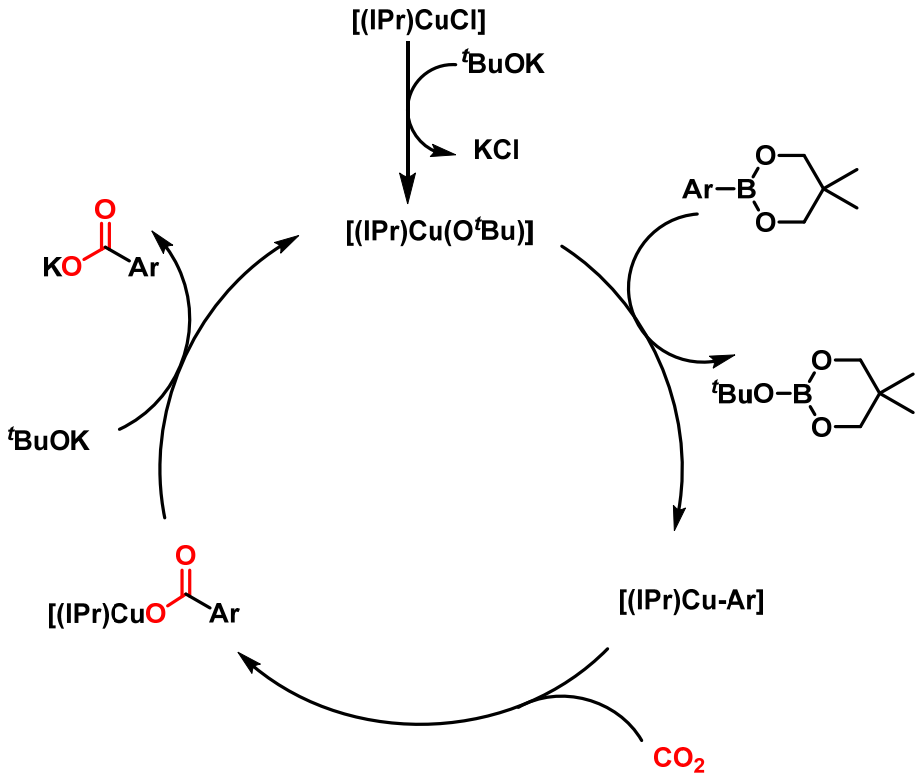




Iwasawa, N. et al. *Org. Lett.* **2008**, *10*, 2697.

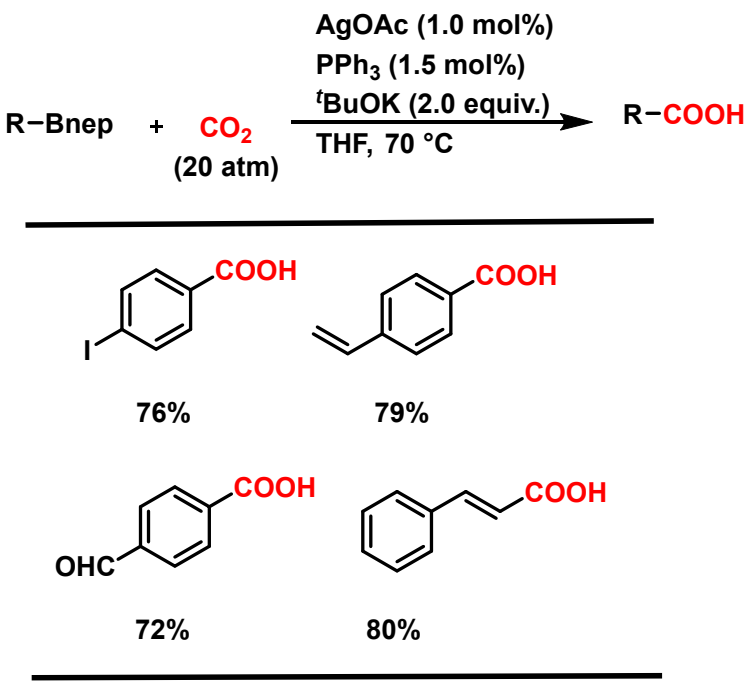
Cu-catalyzed Carboxylation of Organoboron Reagents

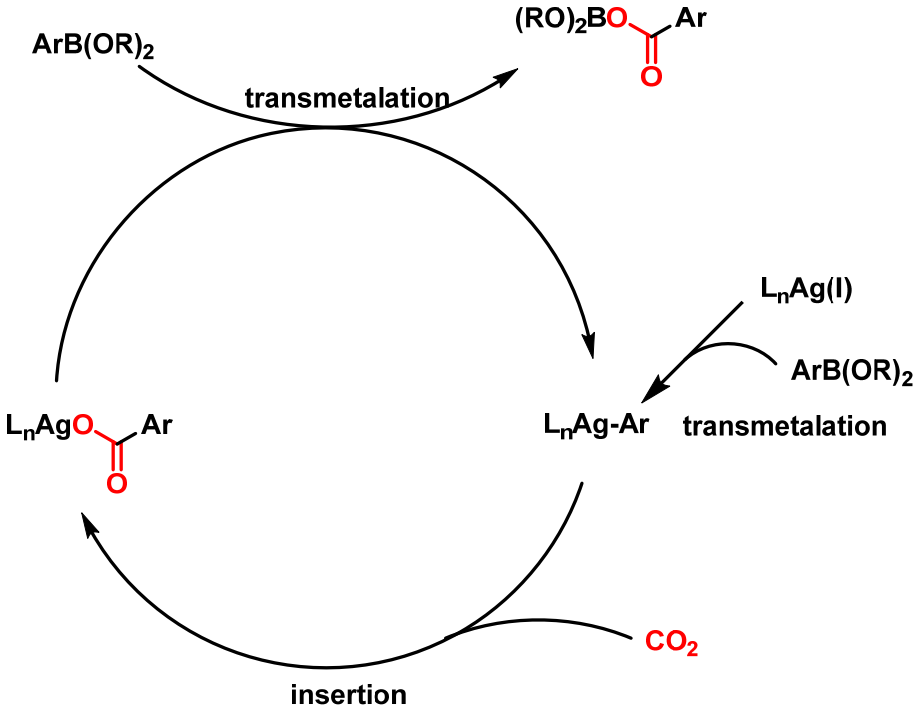




Hou, Z. et al. *Angew. Chem. Int. Ed.* **2008**, *47*, 5792.

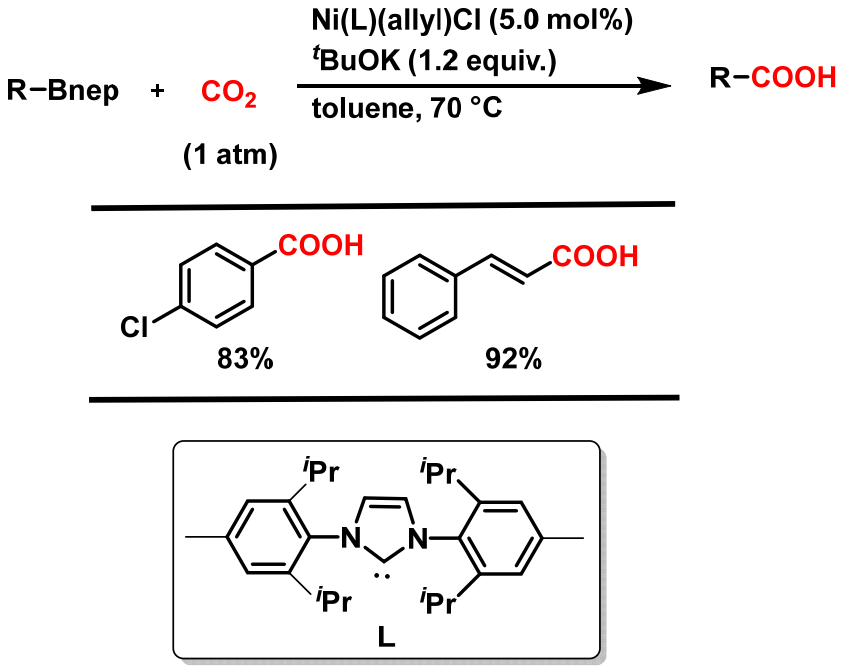
Ag-catalyzed Carboxylation of Organoboron Reagents

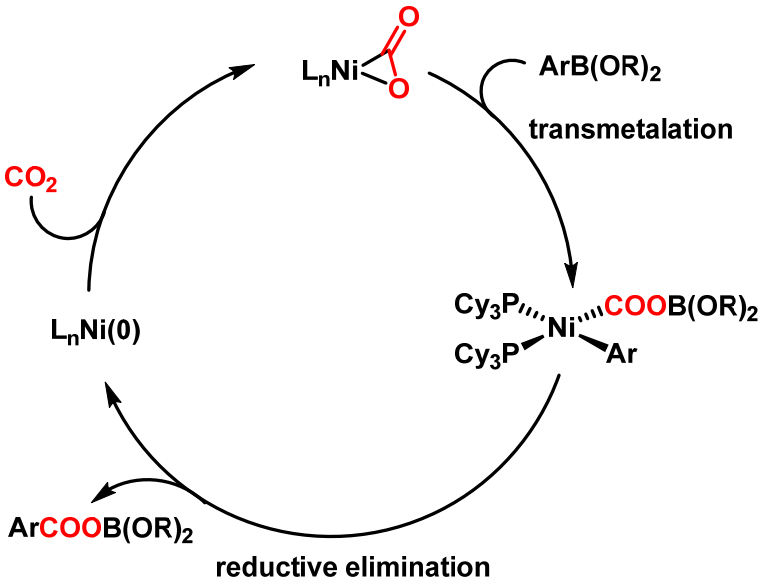




Lu, X.-B. et al. *Chem. Commun.* **2012**, *48*, 6292.

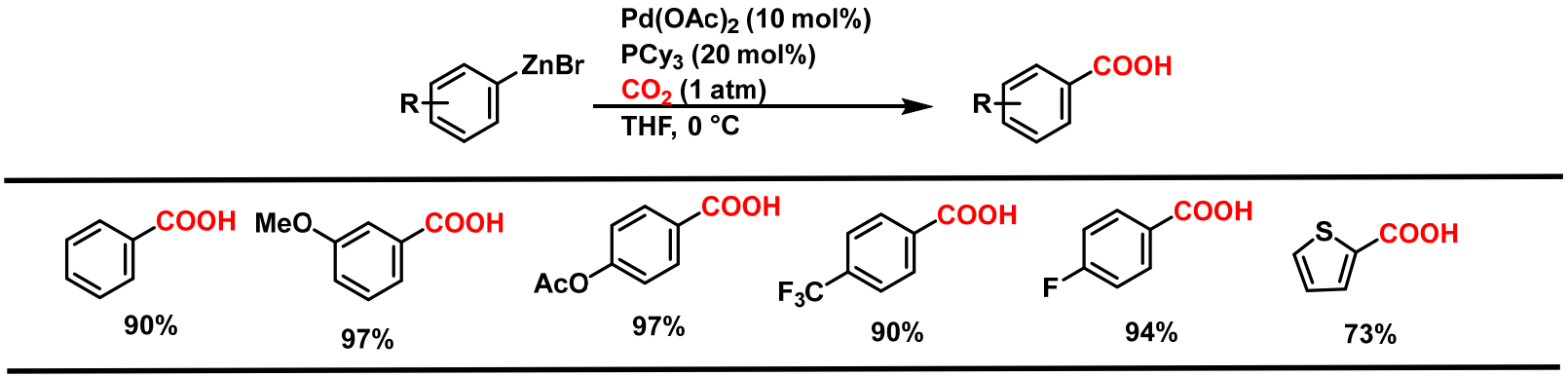
Ni-catalyzed Carboxylation of Organoboron Reagents



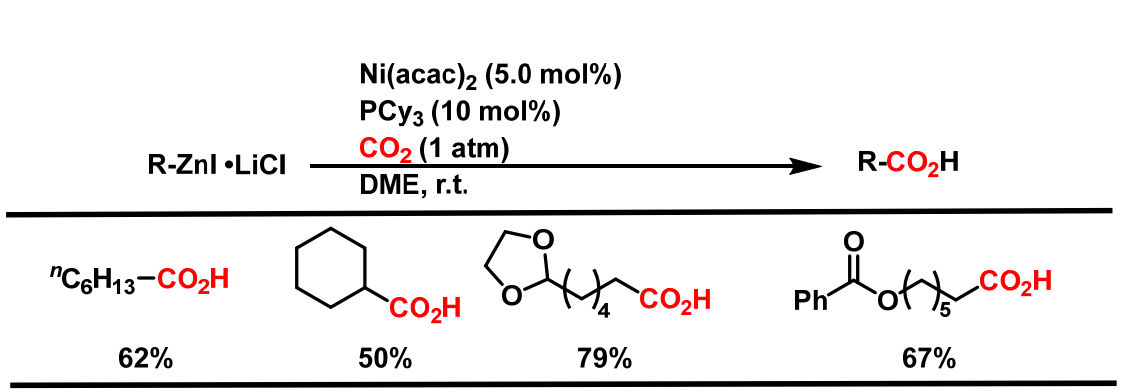


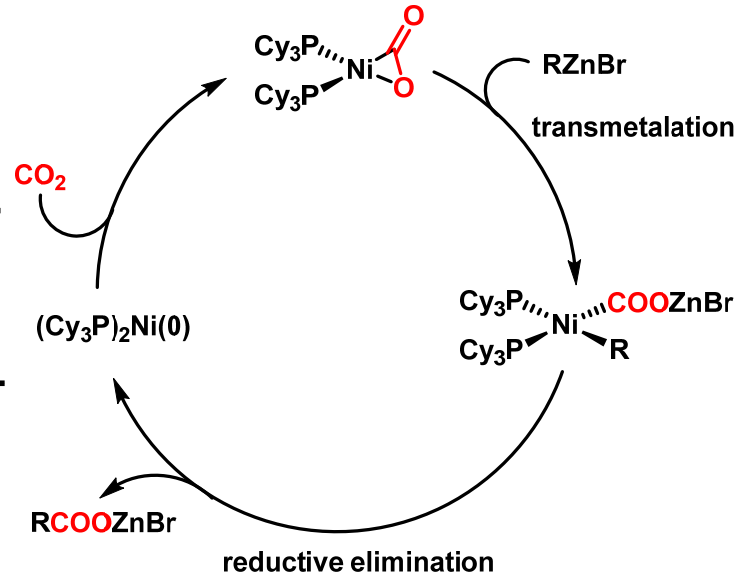
Nolan, S. P. et al. *Chem. Commun.* **2014**, *50*, 8010.

Pd/Ni Carboxylation of Organozinc Reagents



Dong, V. M. et al. *J. Am. Chem. Soc.* **2008**, *130*, 7826.





Oshima, K. et al. *Org. Lett.* **2008**, *10*, 2681.

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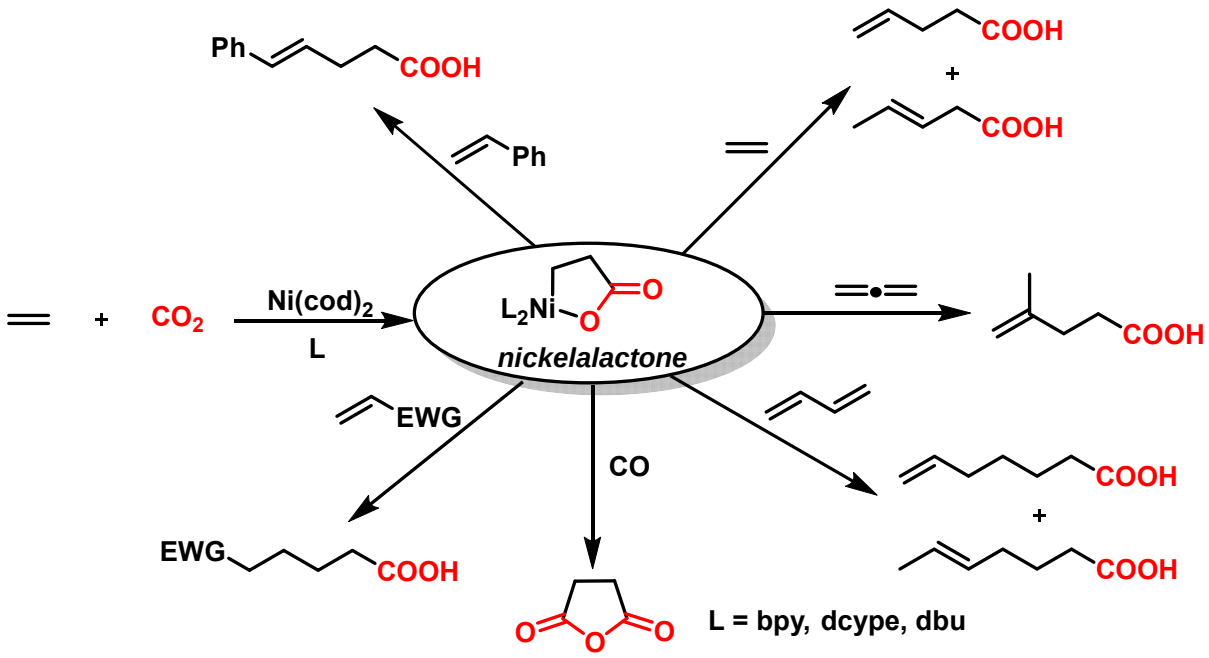
Carboxylation of Alkenes

Nickelalactone formation and reactivity



Hoberg, H. et al. *Angew. Chem. Int. Ed.* **1987**, *26*, 771.
Hoberg, H. et al. *J. Organomet. Chem.* **1982**, *236*, C28.
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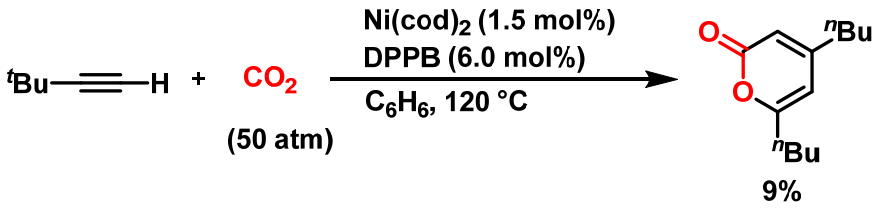
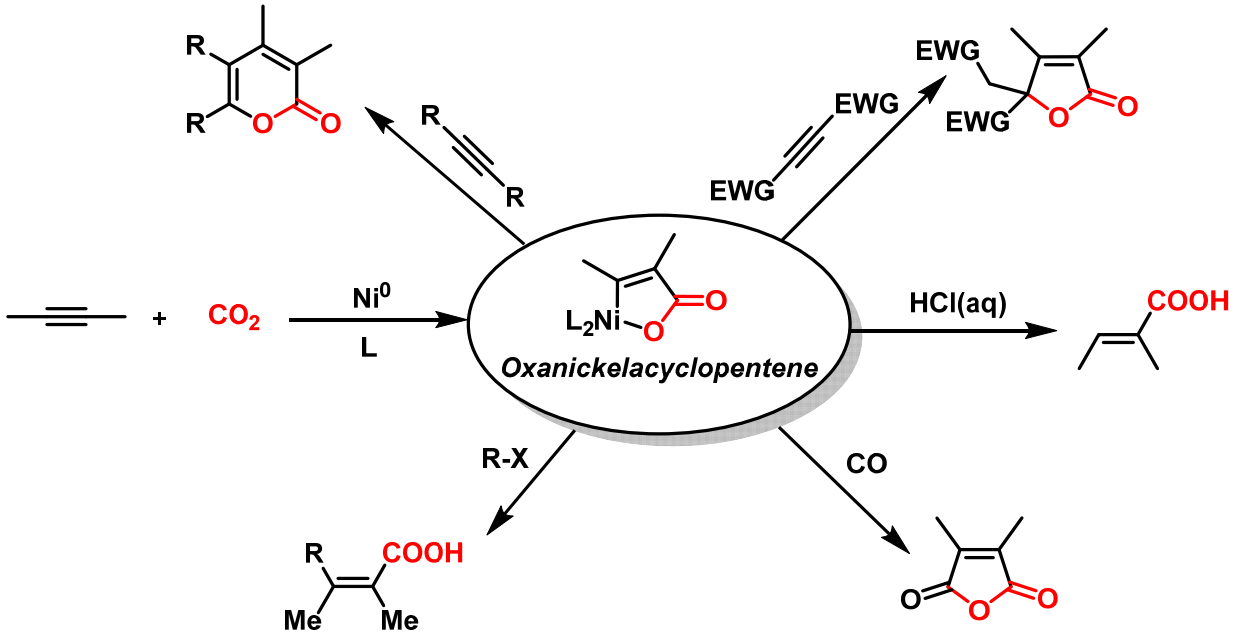
Carboxylation of Alkynes



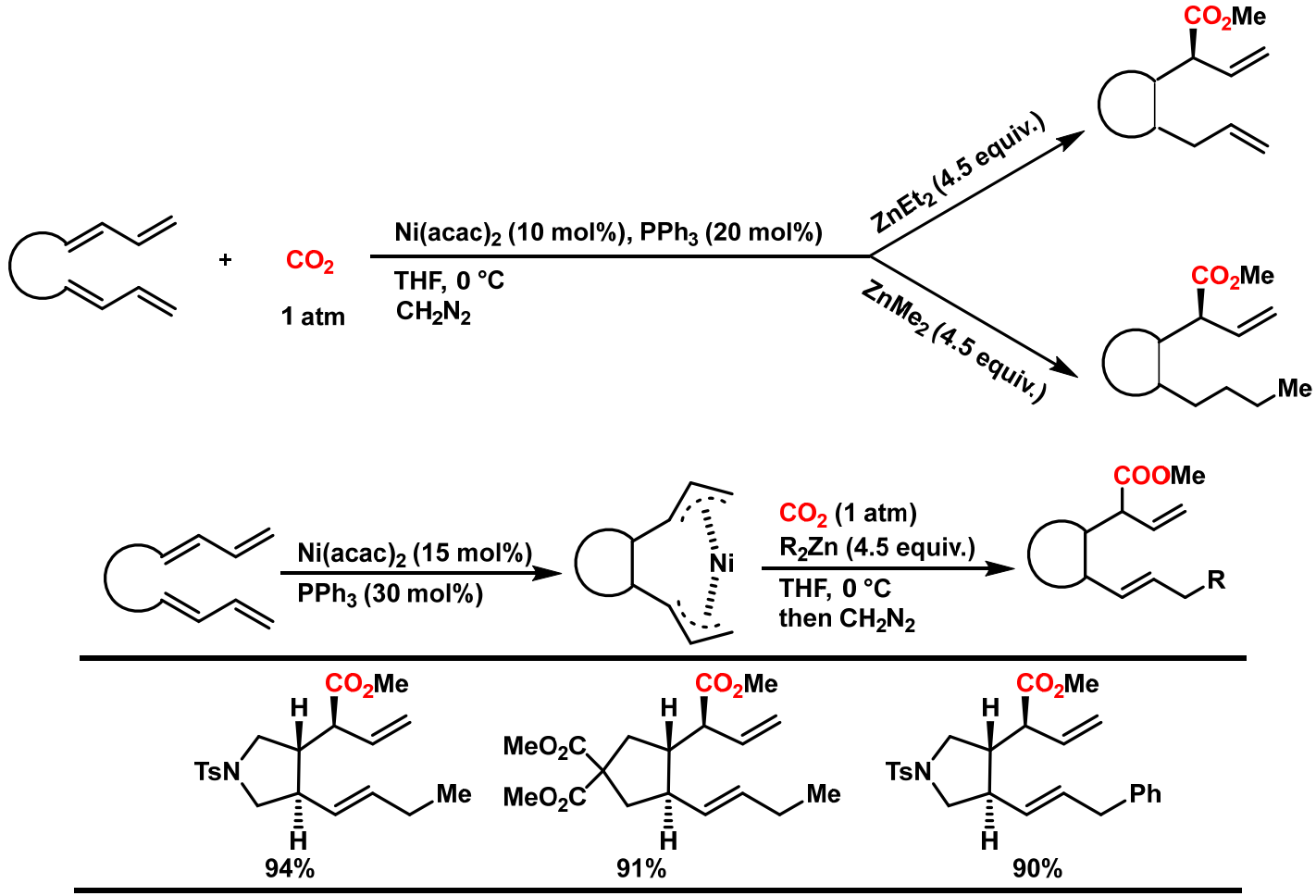
Inoue, Y. et al. *Chem. Lett.* **1977**, *6*, 855.

Oxanickelacyclopentenes formation and reactivity



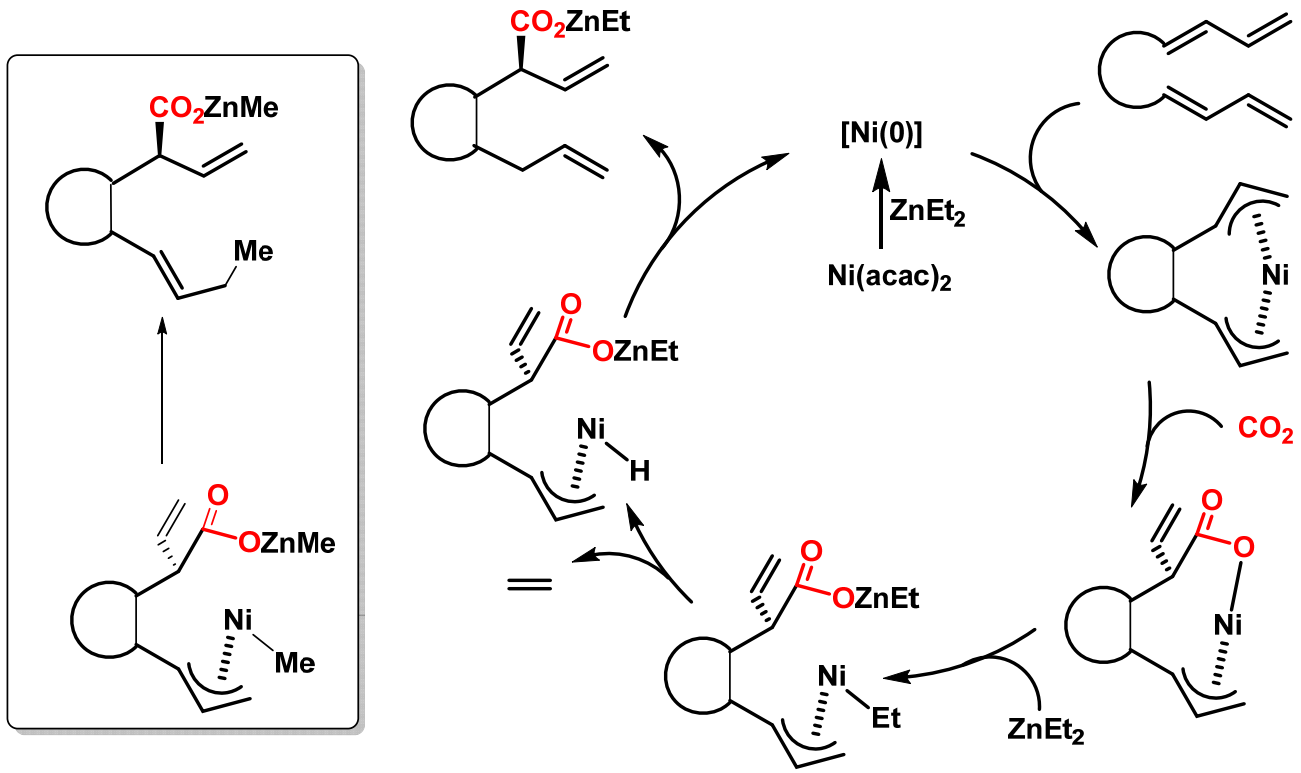
Hoberg, H. et al. *Angew. Chem. Int. Ed.* **1982**, *21*, 76.

Ni-catalyzed Carboxylation of 1,3-dienes with CO_2



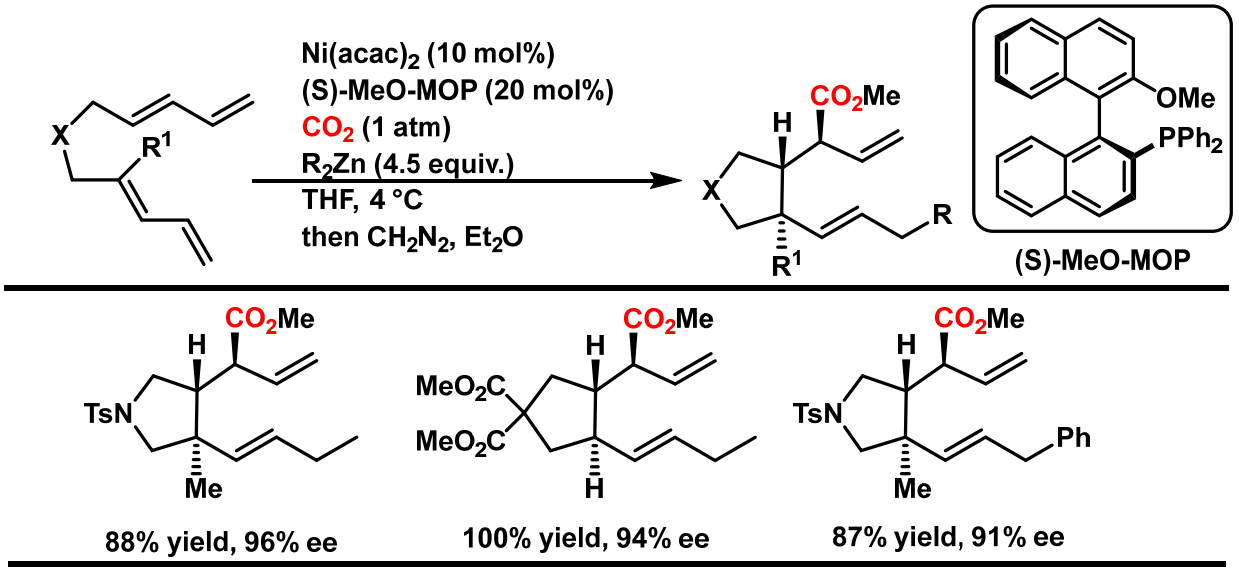
Mori, M. et al. *J. Am. Chem. Soc.* **2002**, *124*, 10008.

Ni-catalyzed Carboxylation of 1,3-dienes with CO_2



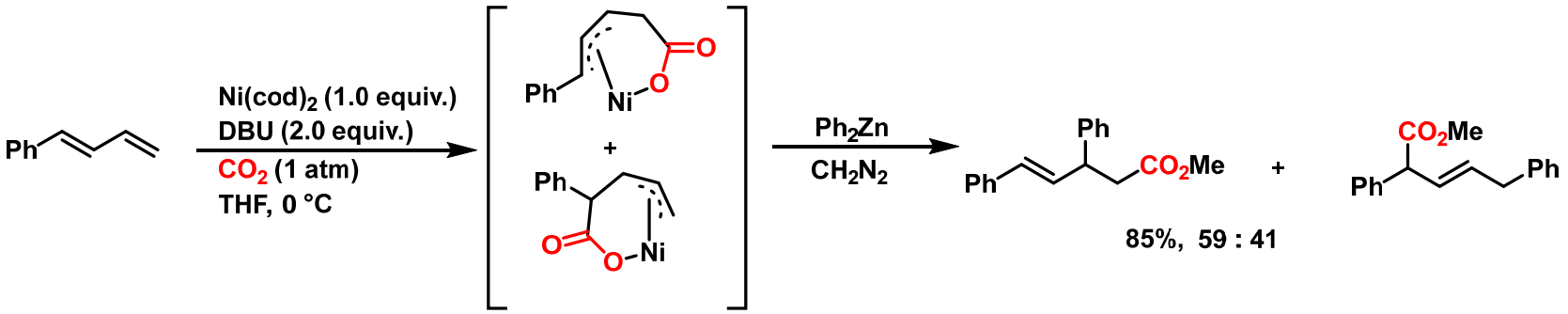
Mori, M. et al. *J. Am. Chem. Soc.* **2002**, *124*, 10008.

Ni-catalyzed Carboxylation of 1,3-dienes with CO_2

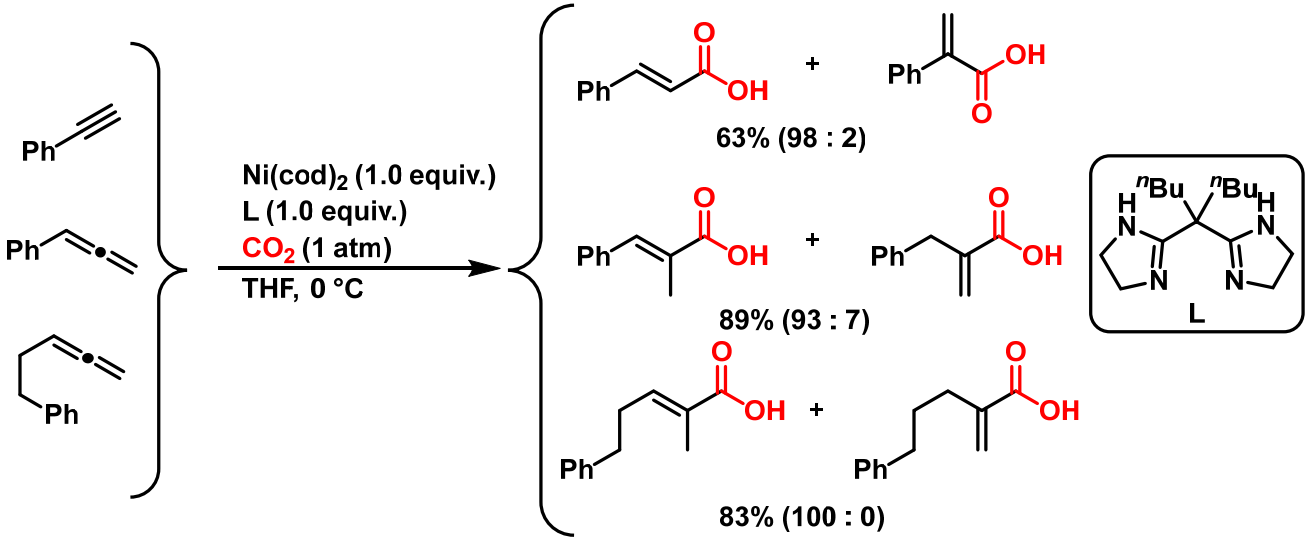


Mori, M. et al. *J. Am.. Chem. Soc.* **2004**, *126*, 5956.

Ni-catalyzed Carboxylation of Alkenes and Alkynes

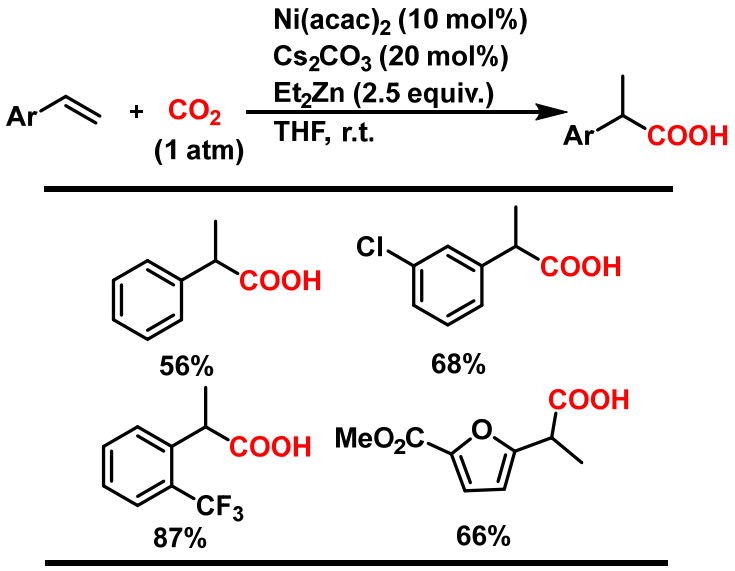


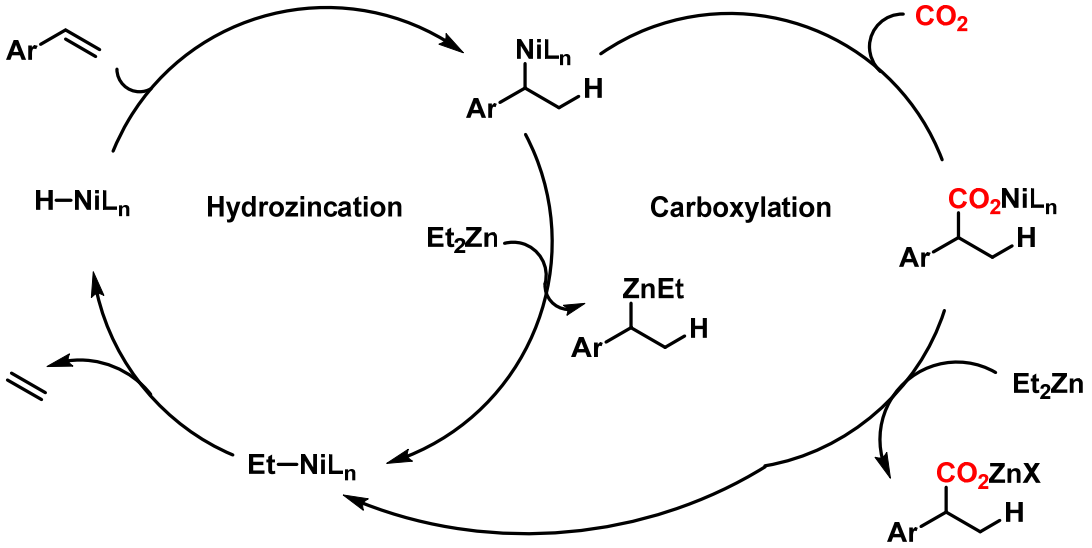
Mori, M. et al. *J. Am. Chem. Soc.* **2001**, *123*, 2895.



Iwasawa, N. et al. *Chem. Commun.* **2004**, 2568.

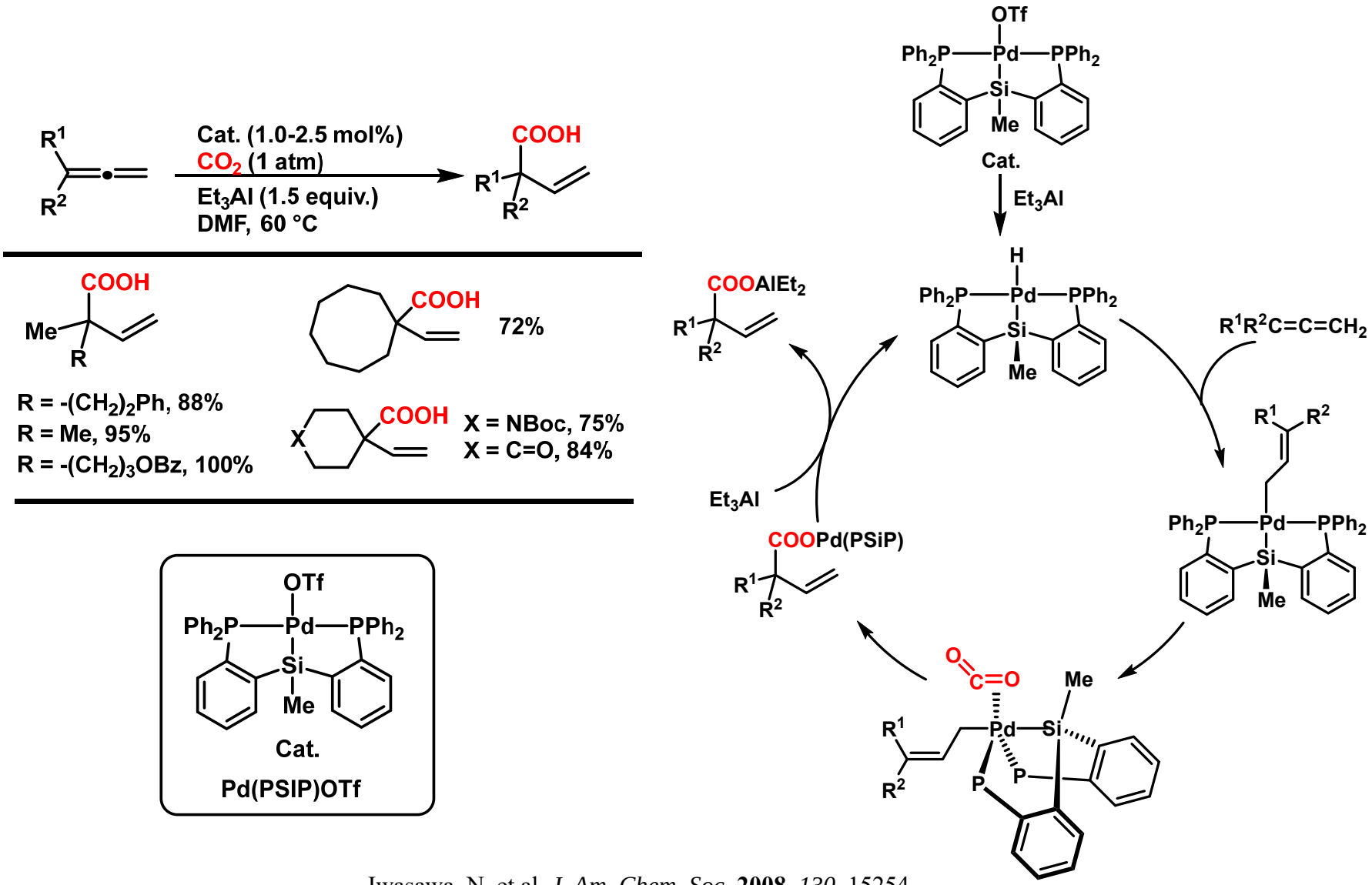
Ni-catalyzed Hydrocarboxylation of Styrene





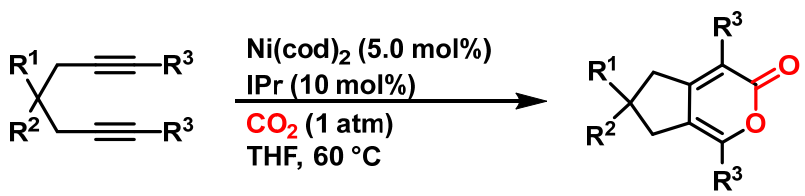
Rovis, T. et al. *J. Am. Chem. Soc.* **2008**, *130*, 14936.

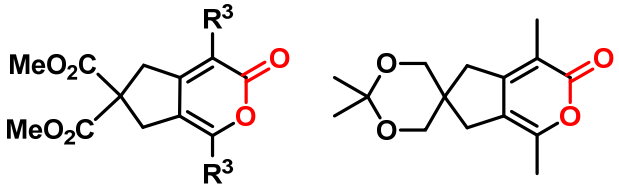
Pd-catalyzed Hydrocarboxylation of Allenes



Iwasawa, N. et al. *J. Am. Chem. Soc.* **2008**, *130*, 15254.

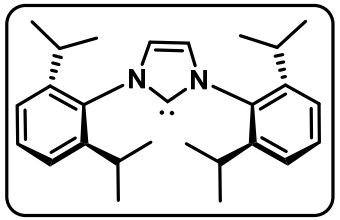
Ni-catalyzed Carboxylation of Diacetylene



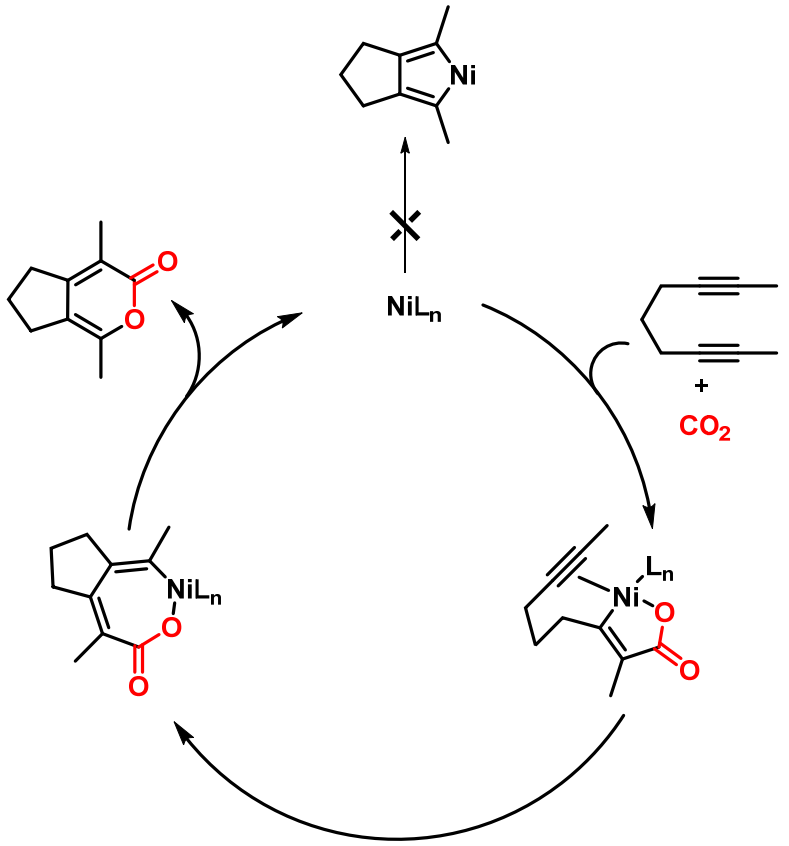


R = Me, 93%
R = Et, 94%
R = ^{i}Pr, 86%

96%

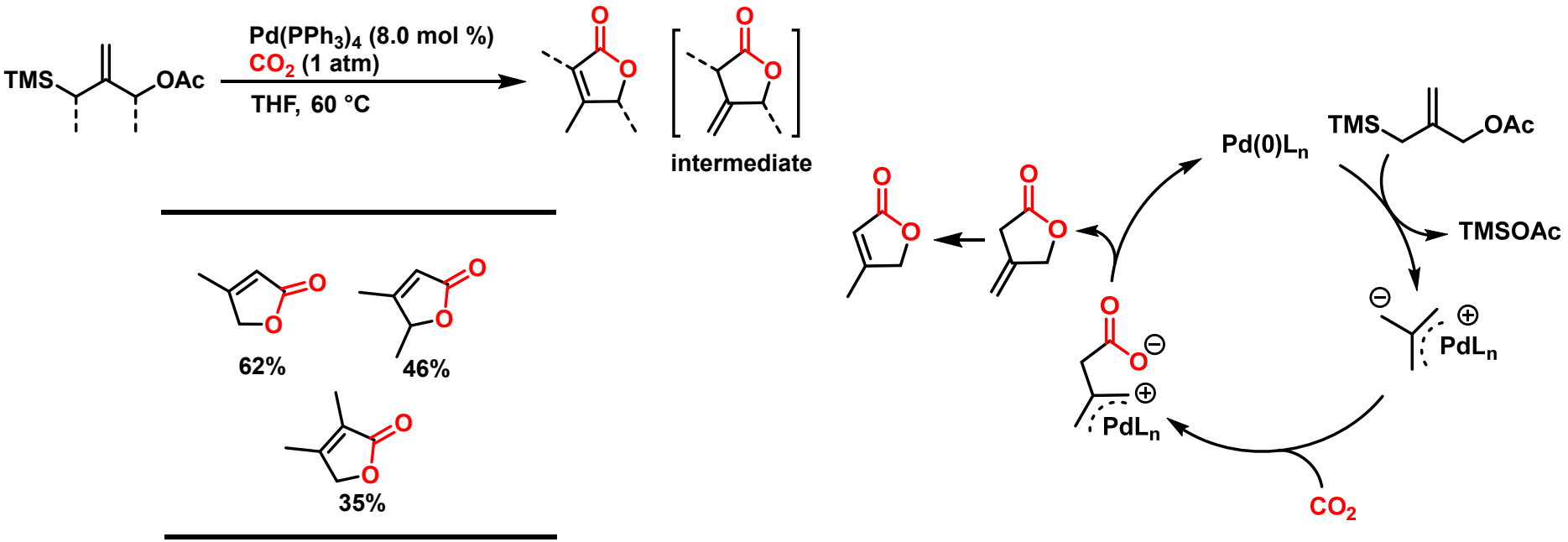


IPr



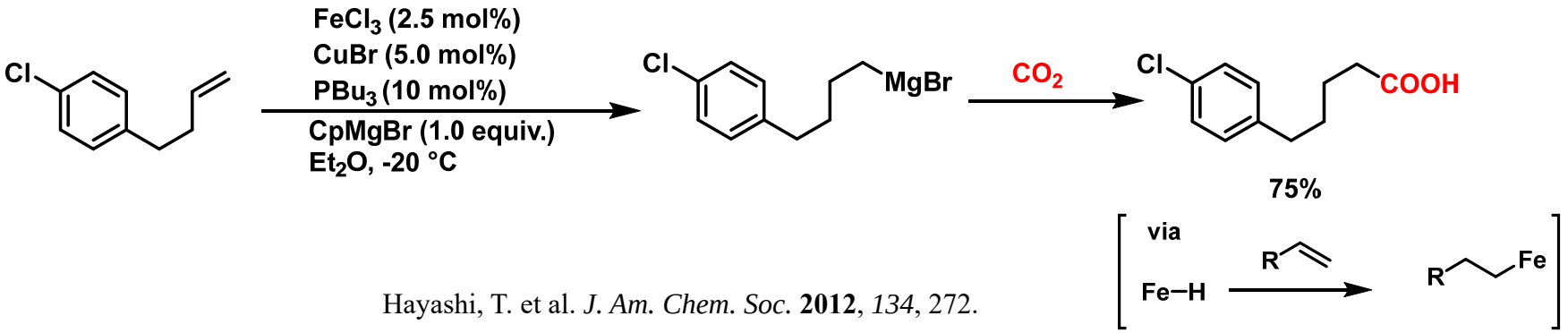
Tekavec, T. N. et al. *J. Am. Chem. Soc.* **2002**, *124*, 15188.
Louie, J. et al. *Chem. Commun.* **2004**, 112.

Pd-catalyzed Carboxylation of Allyl Acetate

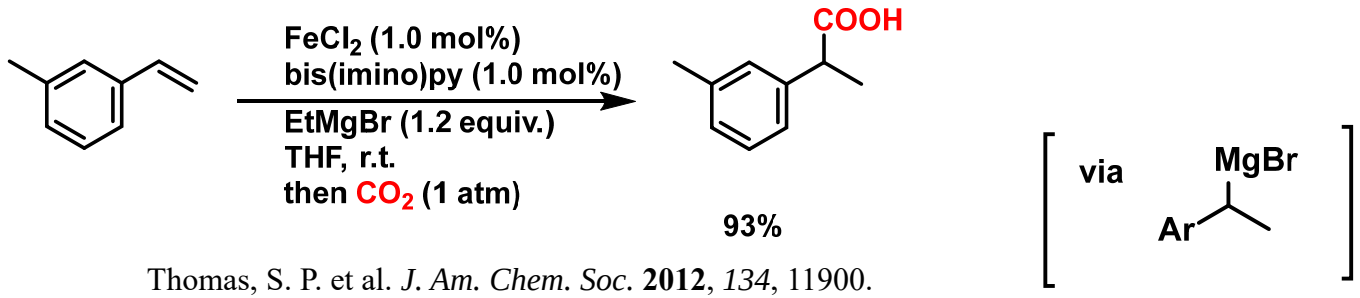


Worthy, A. D. et al. *Org. Lett.* **2007**, *9*, 3817.

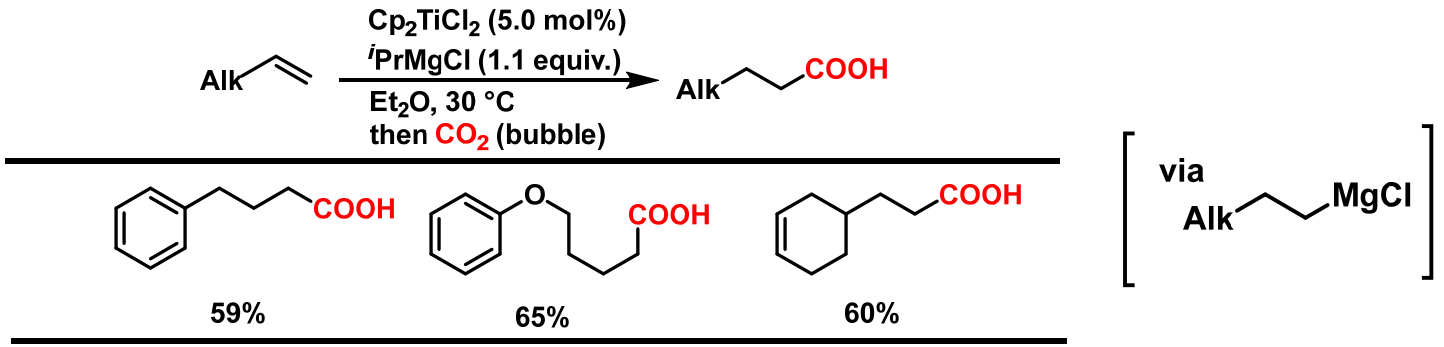
Fe/Ti-catalyzed Carboxylation of Olefins



Hayashi, T. et al. *J. Am. Chem. Soc.* **2012**, *134*, 272.

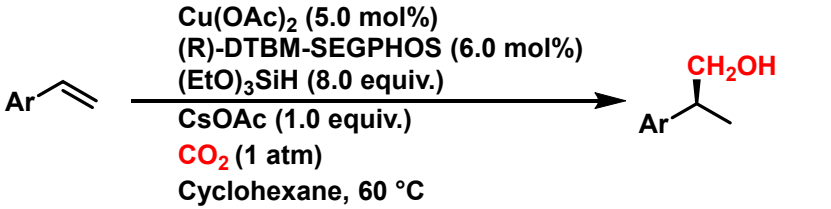


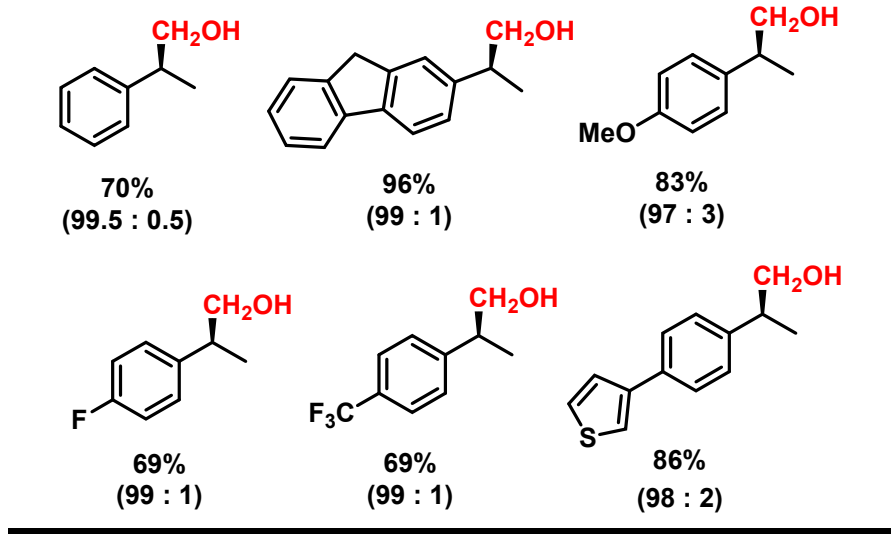
Thomas, S. P. et al. *J. Am. Chem. Soc.* **2012**, *134*, 11900.

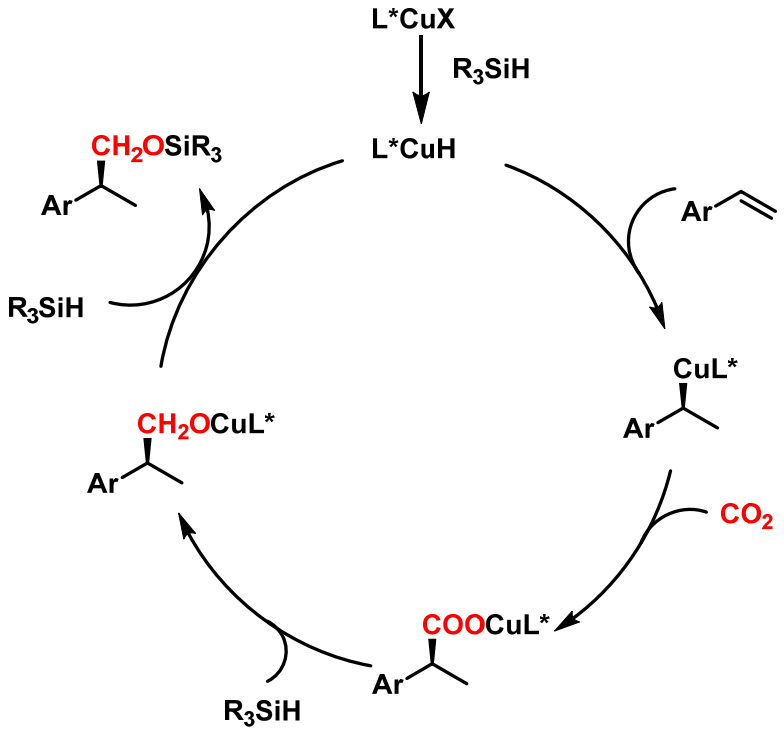


Xi, C. et al. *Org. Lett.* **2016**, *18*, 2050.

Cu-catalyzed Enantioselective Hydroxymethylation of Styrenes







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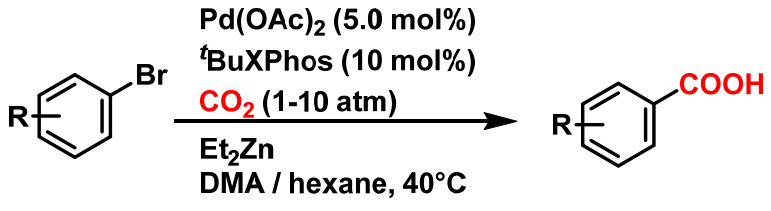
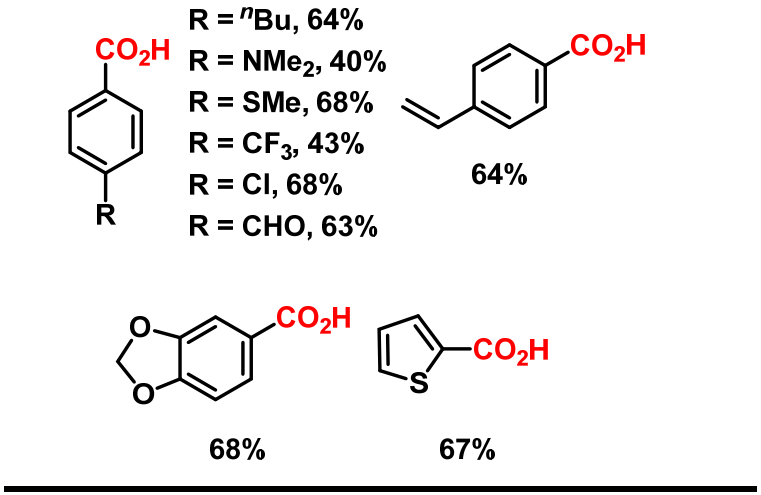
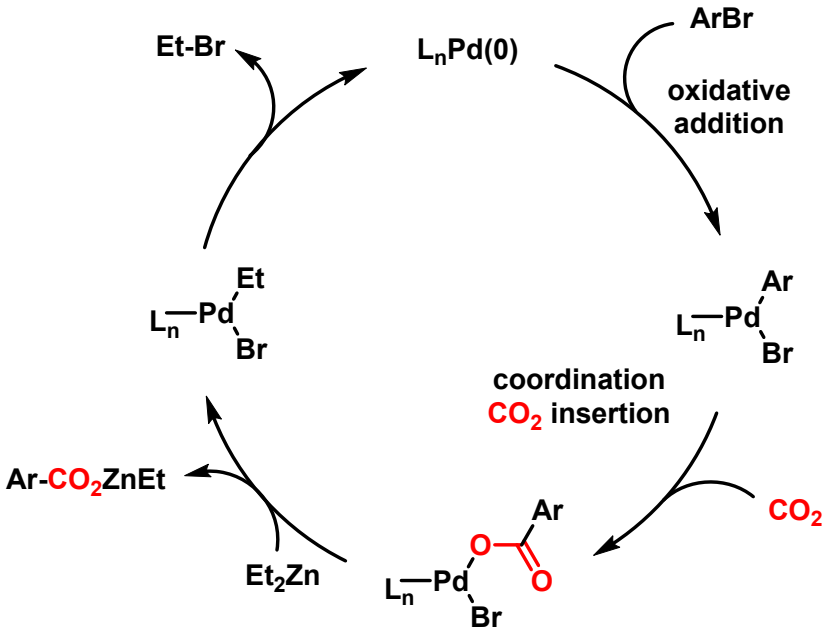
Pd-catalyzed Carboxylation of Aryl Bromides

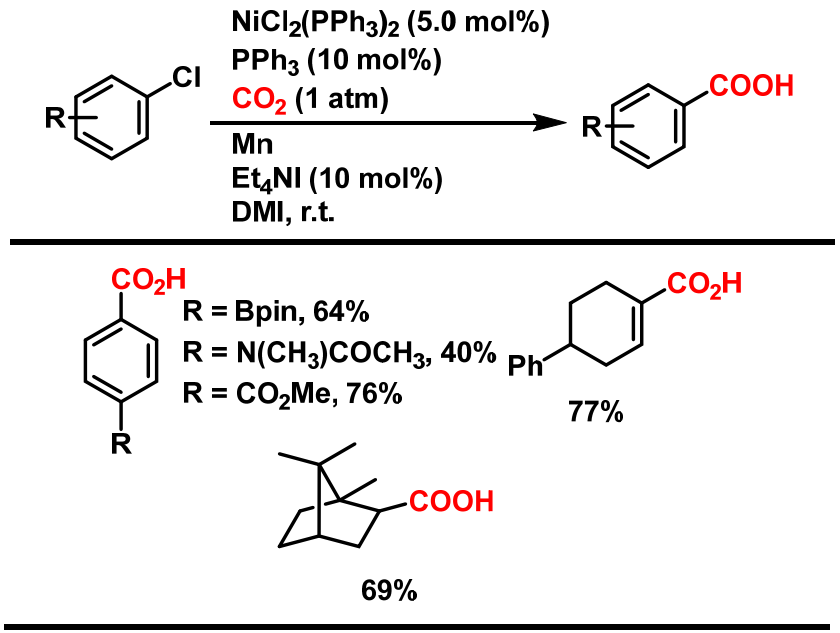


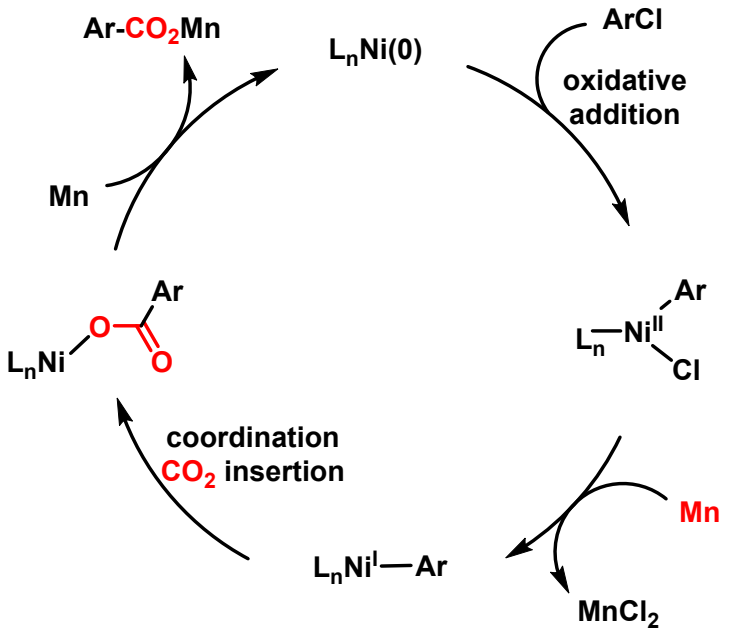




Martin, R. et al. *J. Am. Chem. Soc.* **2009**, *131*, 15974.

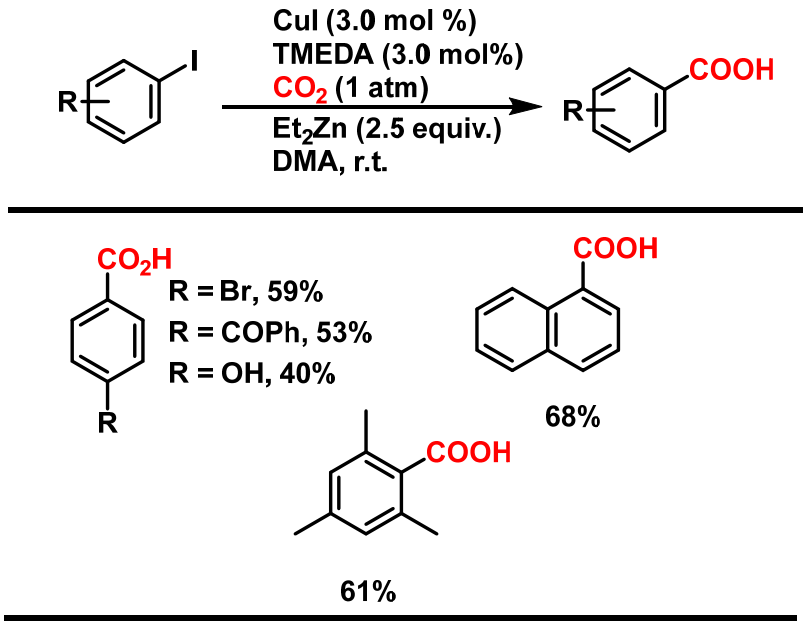
Ni-catalyzed Carboxylation of Aryl Chlorides

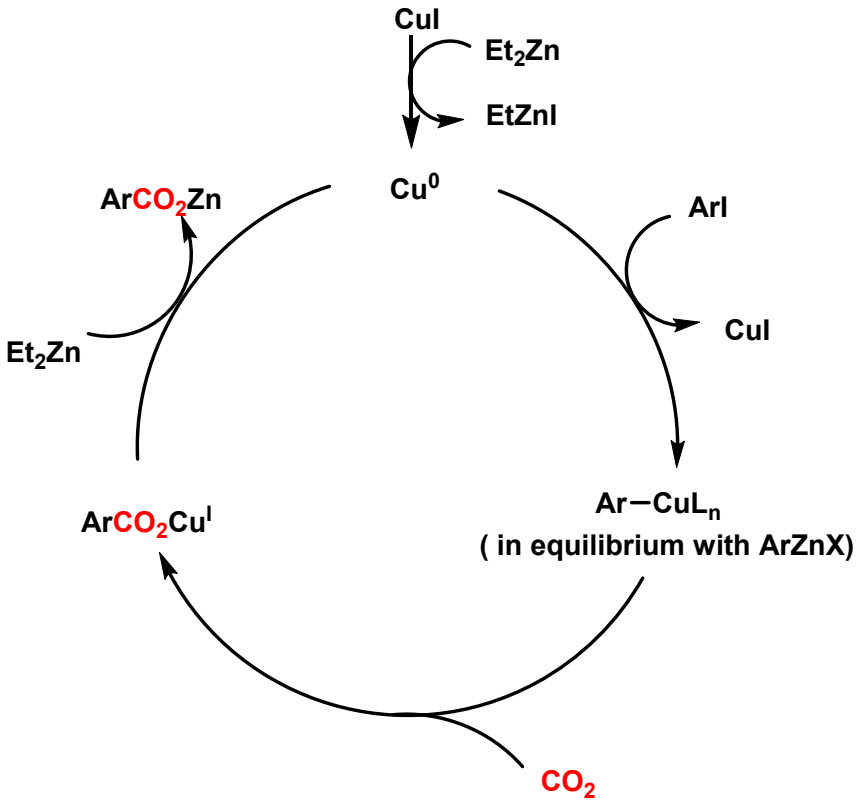




Tsuji, Y. et al. *J. Am. Chem. Soc.* **2012**, *134*, 9106.

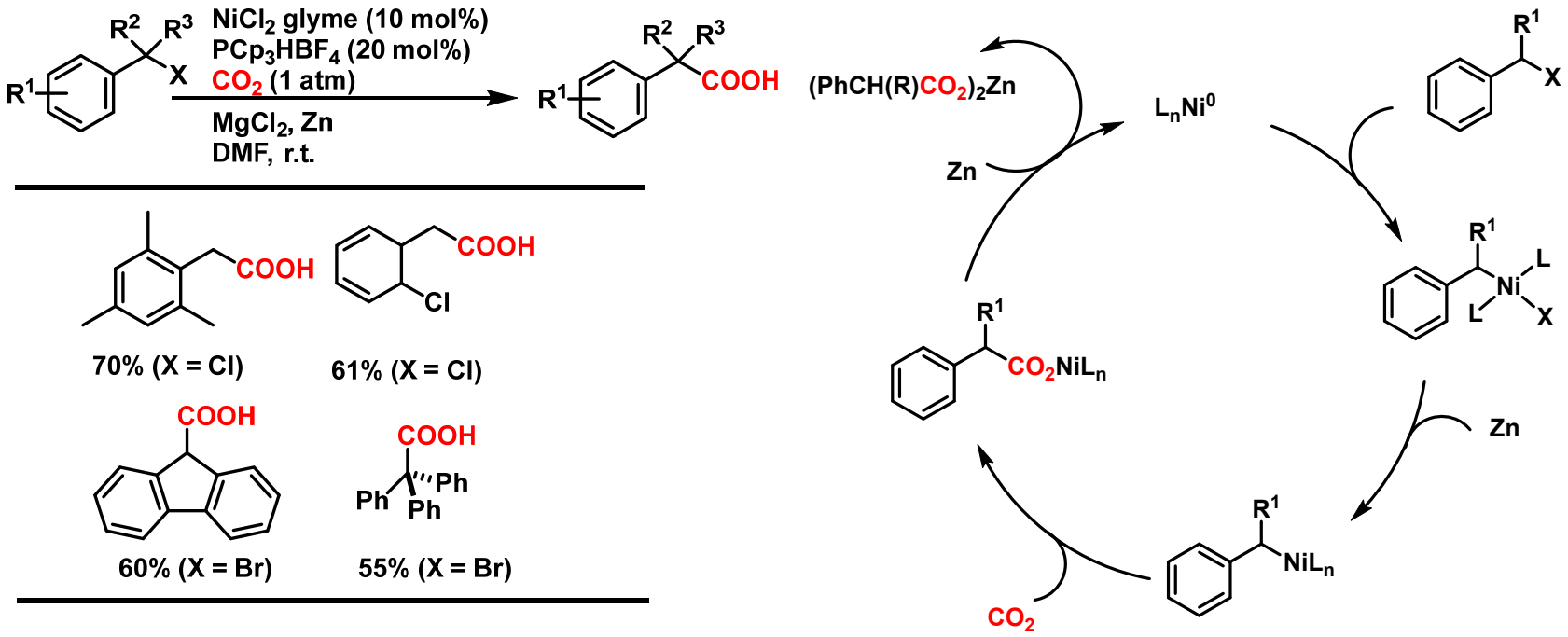
Cu-catalyzed Carboxylation of Aryl Iodides





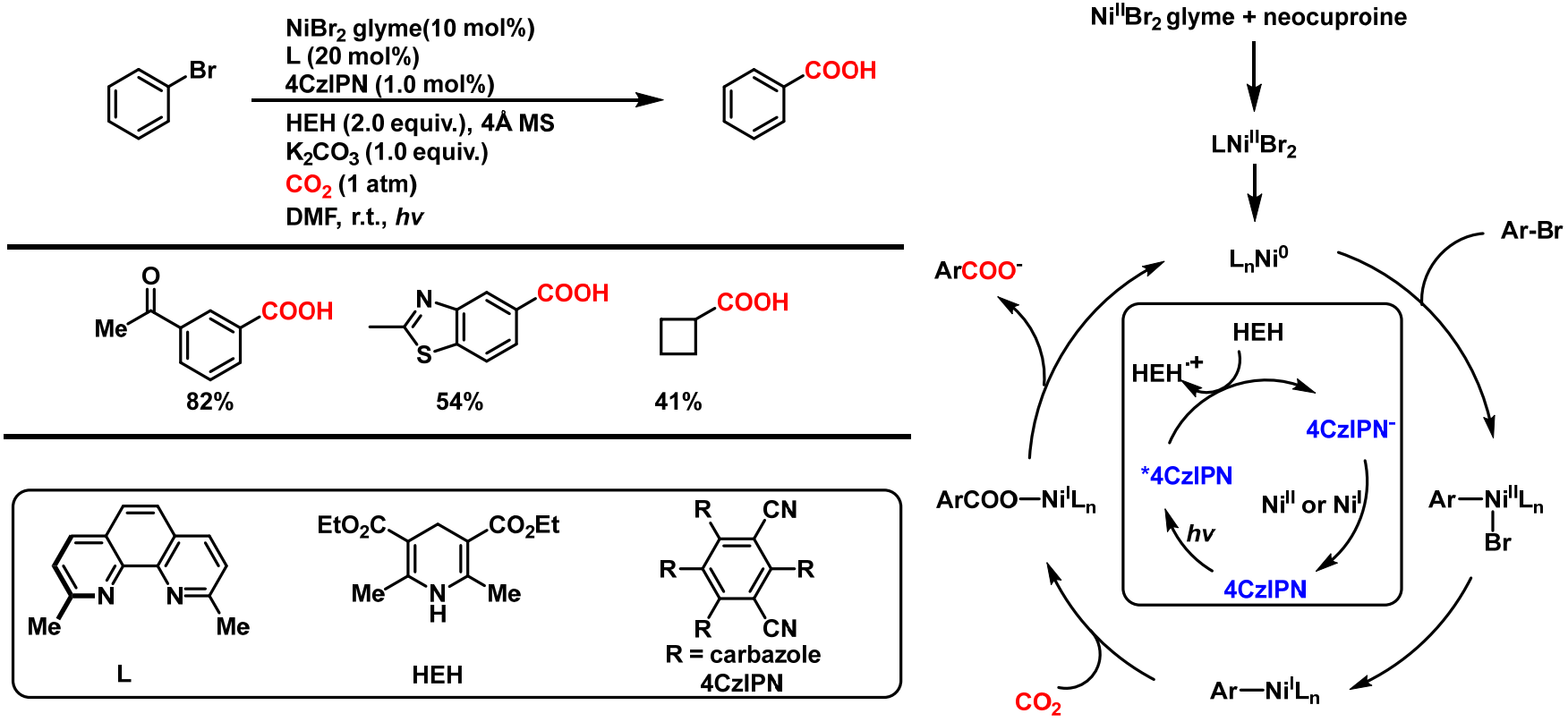
Daugulis, O. et al. *ACS Catal.* **2013**, *3*, 2417.

Ni-catalyzed Carboxylation of Benzyl Halides



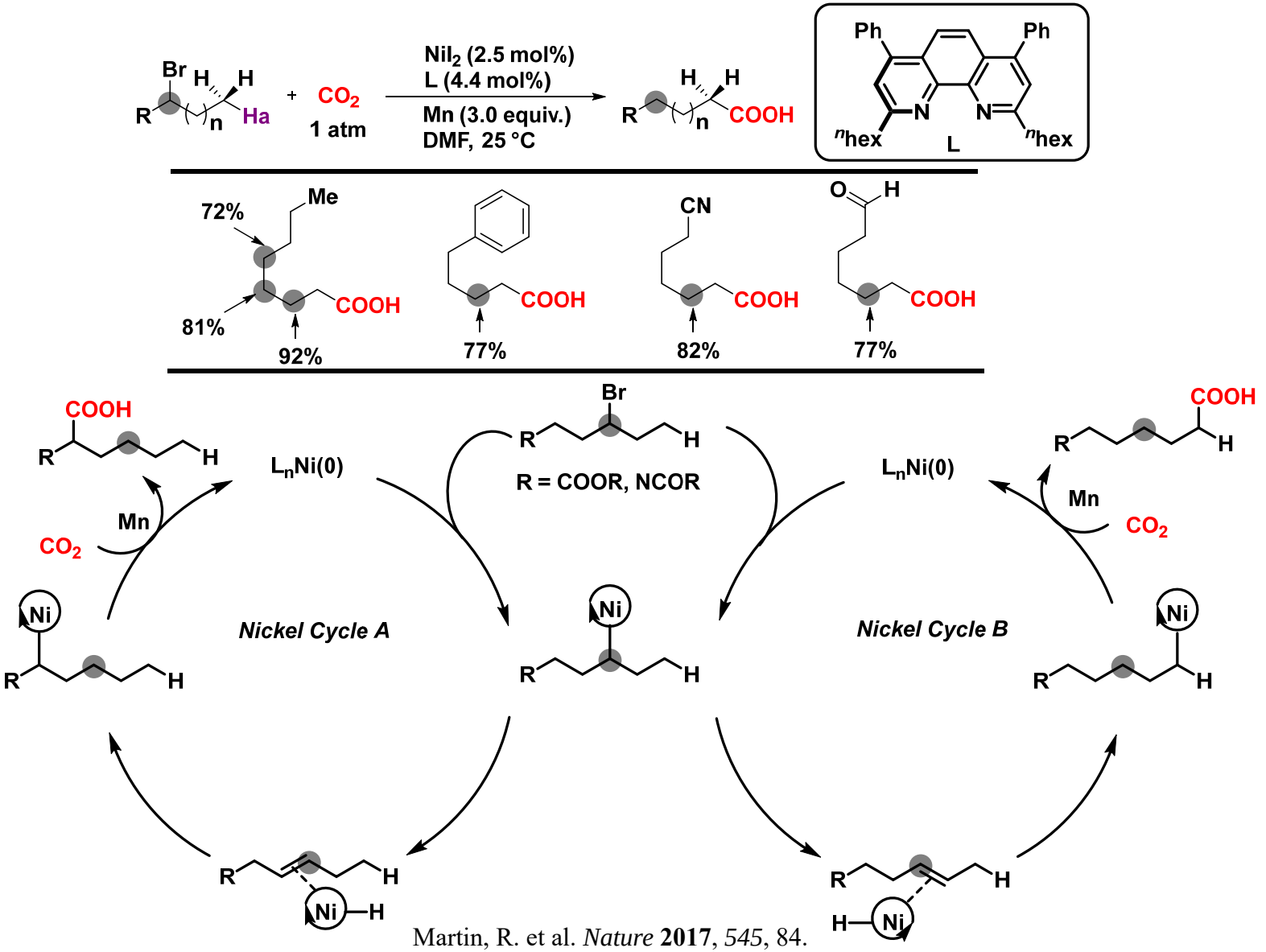
Martin, R . et al. *J. Am. Chem. Soc.* **2013**, *135*, 1221.

Ni-catalyzed Carboxylation of Bromides by Photoredox Catalysis



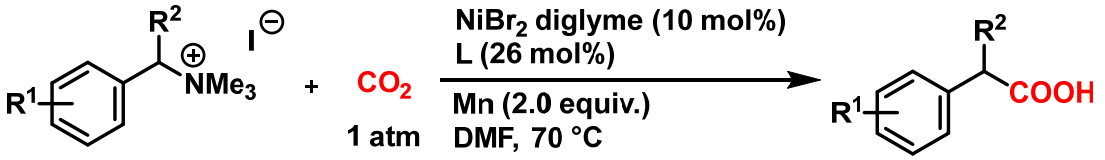
König, B. et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 13426.

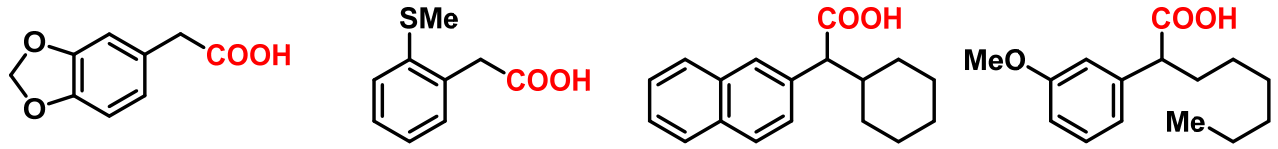
Ni-catalyzed Remote Carboxylation of Halogenated Hydrocarbons

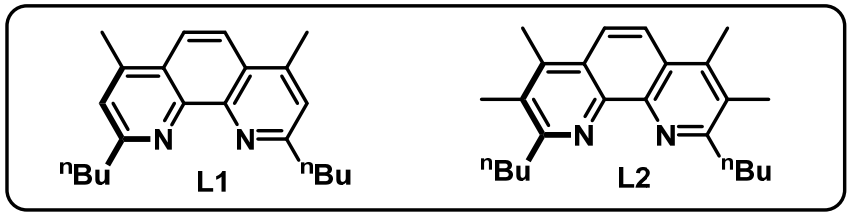


Martin, R. et al. *Nature* **2017**, *545*, 84.

Ni-catalyzed Carboxylations of C-N Electrophiles



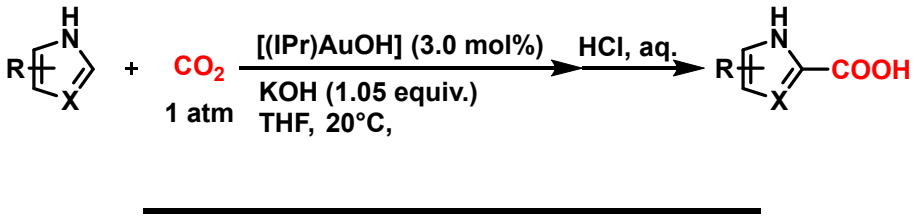


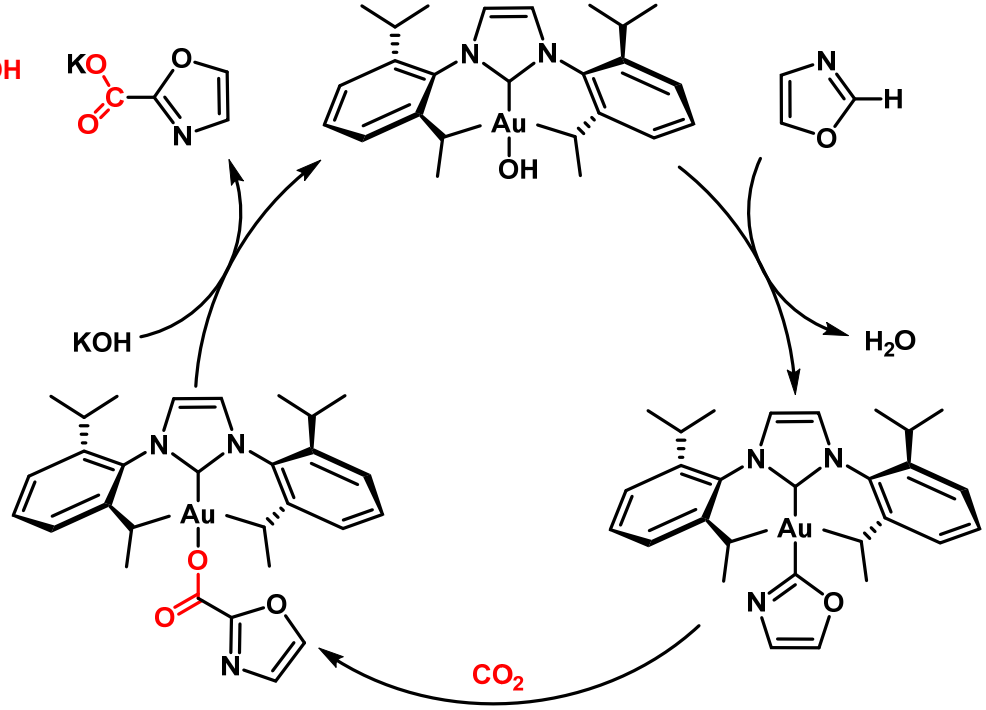


Martin, R. et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 5053.

Contents

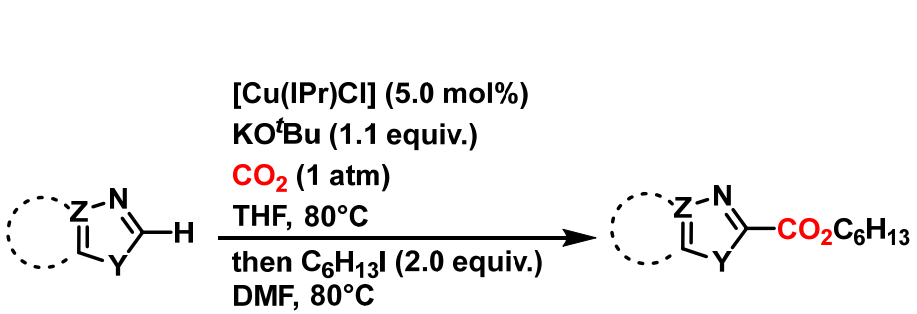
Au-catalyzed Carboxylation of Acidic sp^2 C-H Bonds

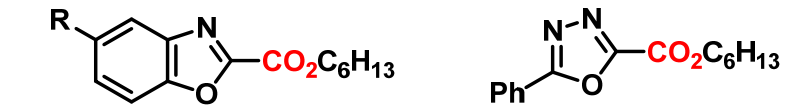




Nolan, S. P. et al. *J. Am. Chem. Soc.* **2010**, *132*, 8858.

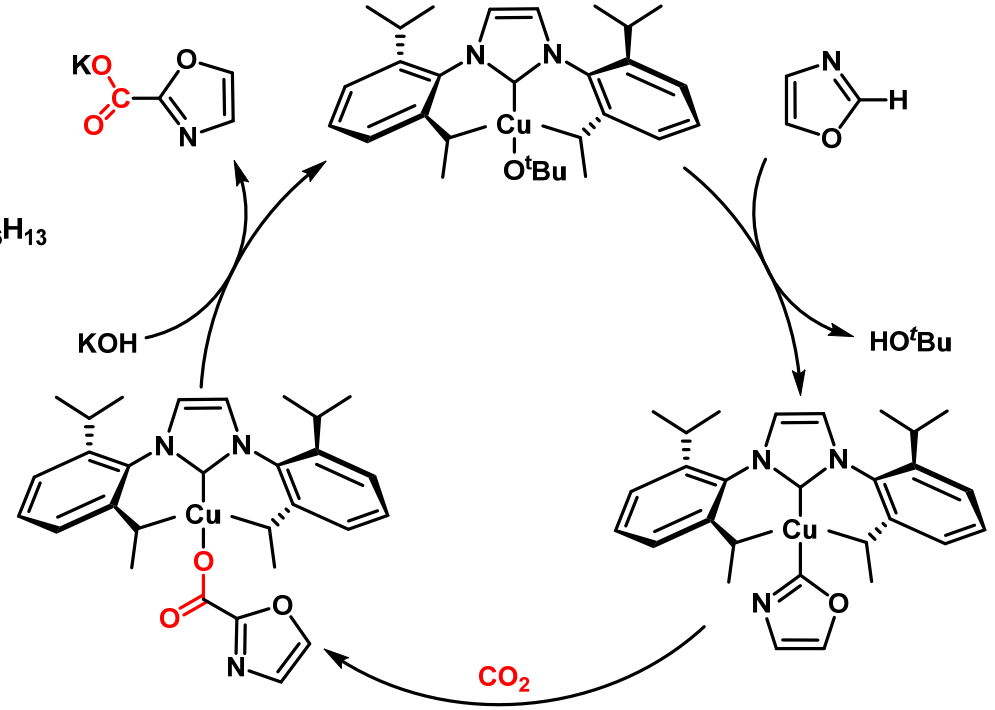
Cu-catalyzed Carboxylation of Acidic sp^2 C-H Bonds





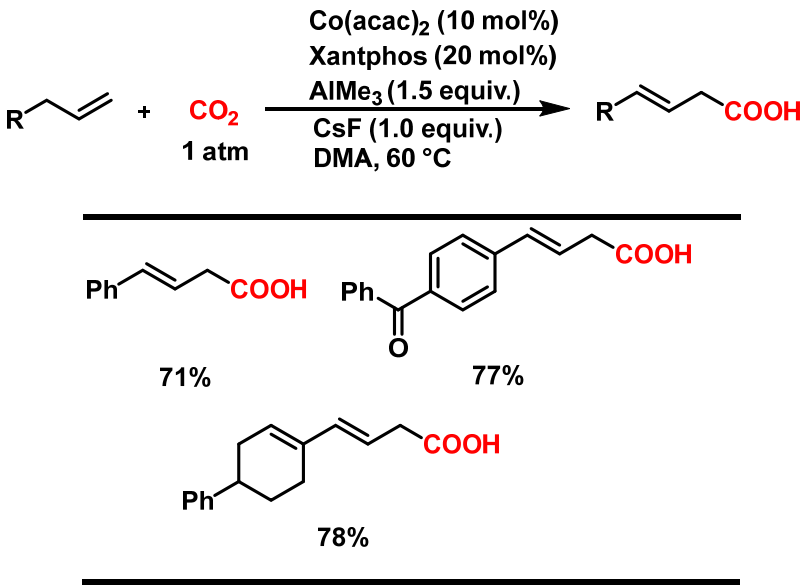
R = Me, 87%
R = Br, 62%
R = NO_2, 50%

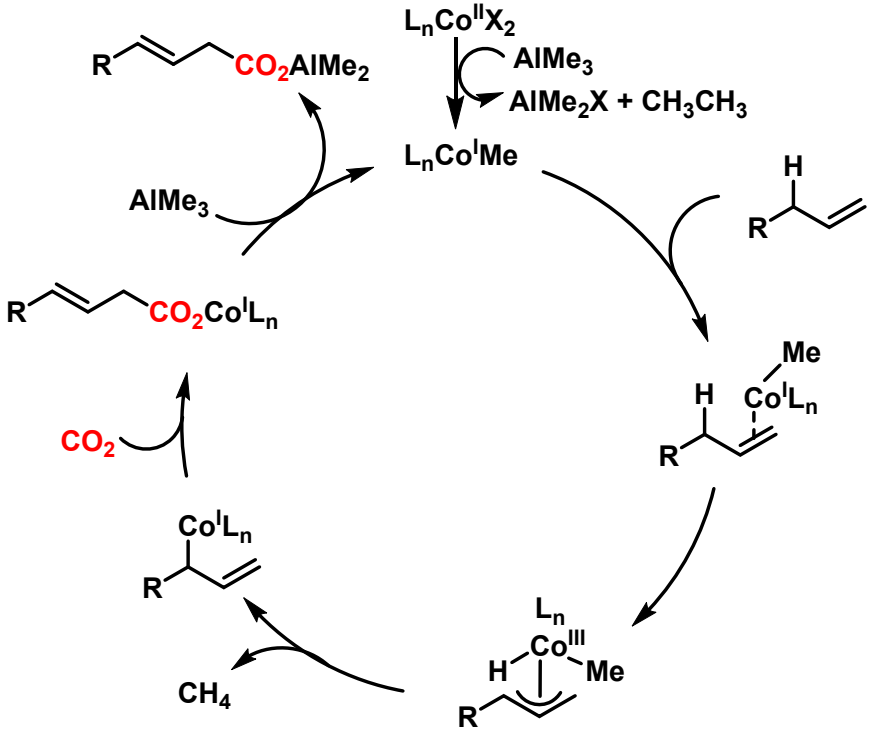
38%



Hou, Z. et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 8670.

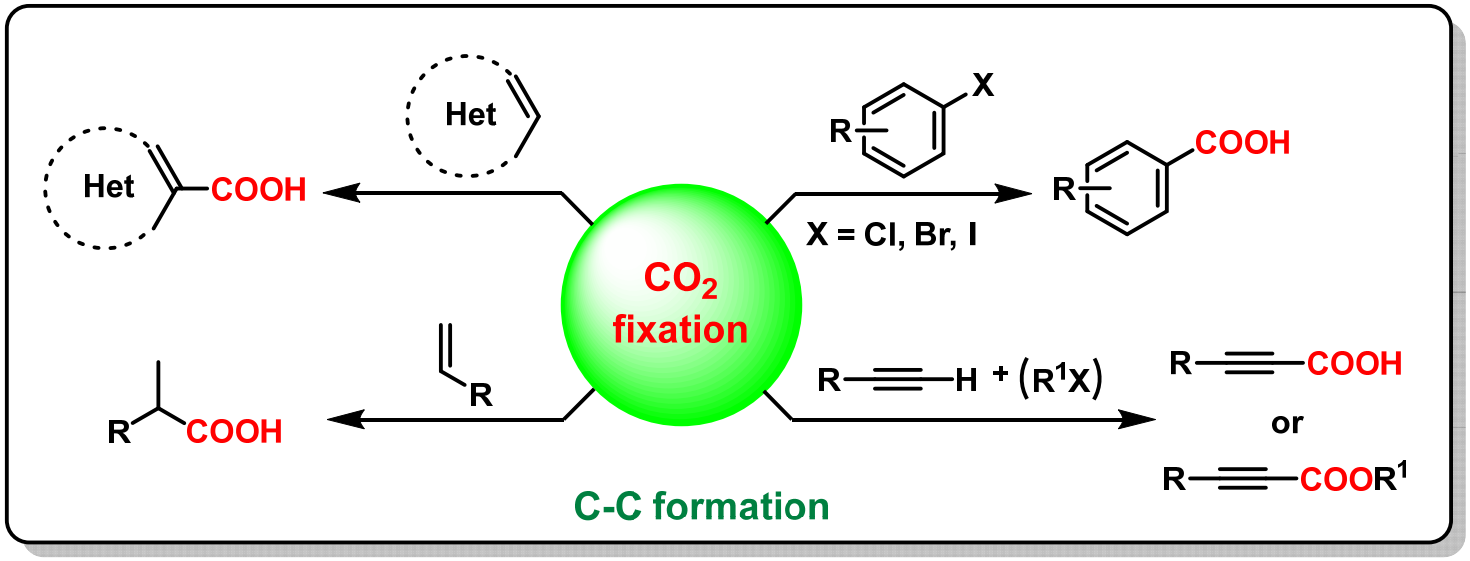
Cobalt-catalyzed Carboxylation of Allylic sp^3 C-H Bonds





Sato, Y. et al. *J. Am. Chem. Soc.* **2017**, *139*, 6094.

Summary

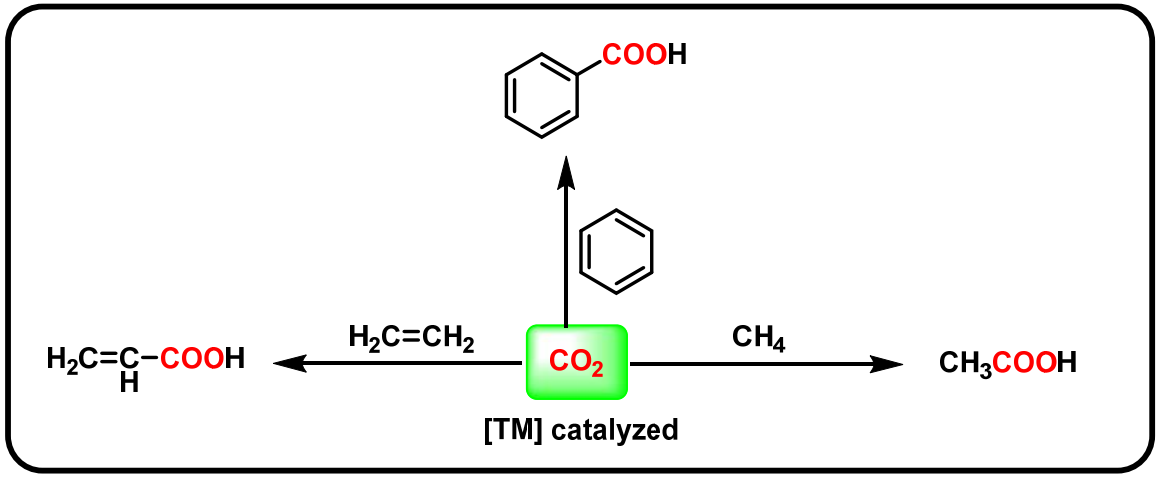

Het
Het
COOH
X
R
COOH
R
X = Cl, Br, I
CO_2 fixation
R
R
COOH
R—≡—H + (R^1X)
R—≡—COOH
or
R—≡—COOR^1
C-C formation

Prospect

★ **Research the unique role exerted by the additives and coordinating solvents (e.g., CsF, DMF)**

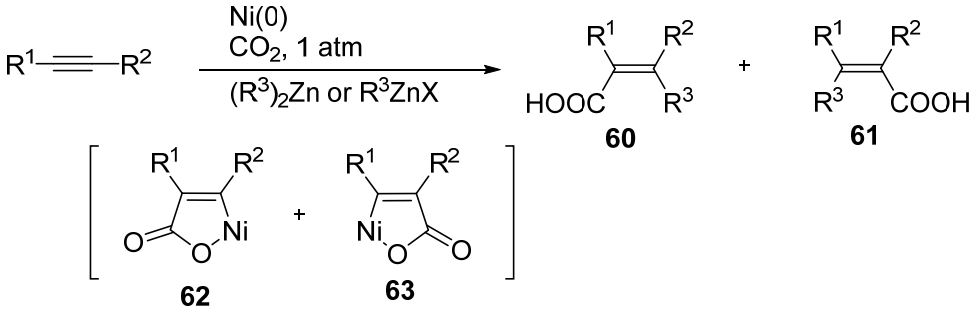
★ **Design new and efficient ligand**

★ **Employment of no reducing agent reaction**



Acknowledgement

- Thanks to Professor Zhang-Jie Shi and Hua-Yi Fang for their great help.
- Thanks to all the members of the research team for their help.
- Thanks to all the teachers in the Department of Chemistry for their help.
- Thanks to all the teachers and classmates present.


Ni(0)
CO2, 1 atm
(R3)2Zn or R3ZnX
R1
R2
HOOC
R3
COOH
60
61
62
63

Hoberg, H. et al. *Angew. Chem. Int. Ed.* **1987**, *26*, 771.
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3. Kolbe, H., Lautemann, E. Liebigs Ann. Chem. 1860, 115, 178.
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5. Lindsey, A. S., Jeskey, H. The Kolbe-Schmitt reaction. Chem. Rev. 1957, 57, 583-620.
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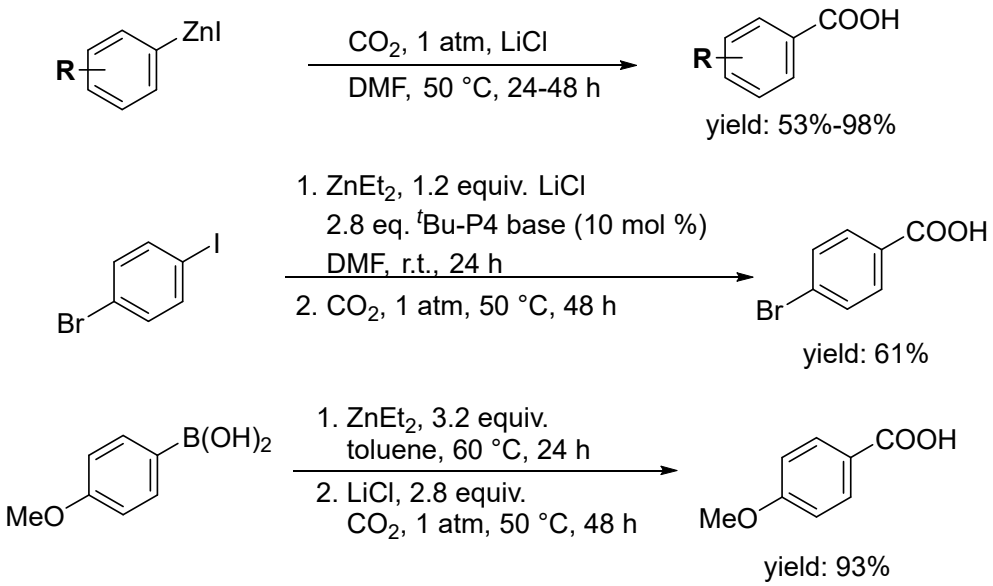
of metal centers in carboxylation reactions. Gazz. Chim. Ital. 1995, 125, 509-538.
7. Schmitt, R. German Patent 29939, 1884, 233
8. Schmitt, R. J. Prakt. Chem./Chem.-Ztg. 1885, 31, 397

Transition-metal-catalyzed carboxylation of organometallic reagents

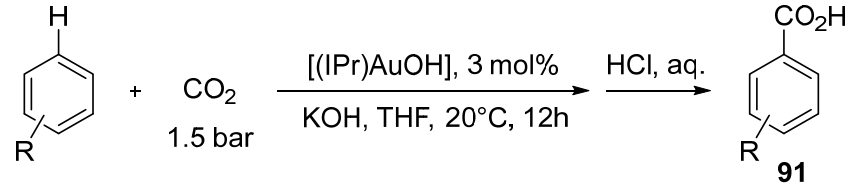
Organozinc reagents

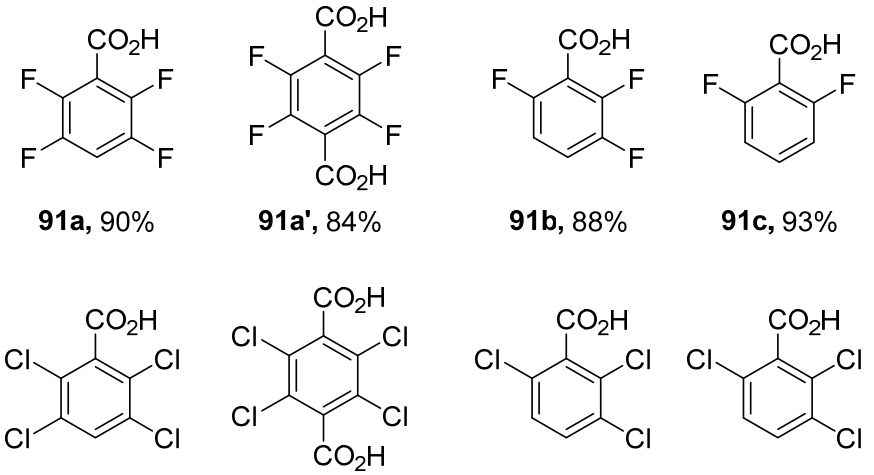


Carboxylation of aromatic zinc compounds in transitionmetal-free process.

Kondo, Y. et al. *Org. Lett.* **2009**, *11*, 2035.

Metal(NHC)-catalyzed carboxylation of C–H bonds

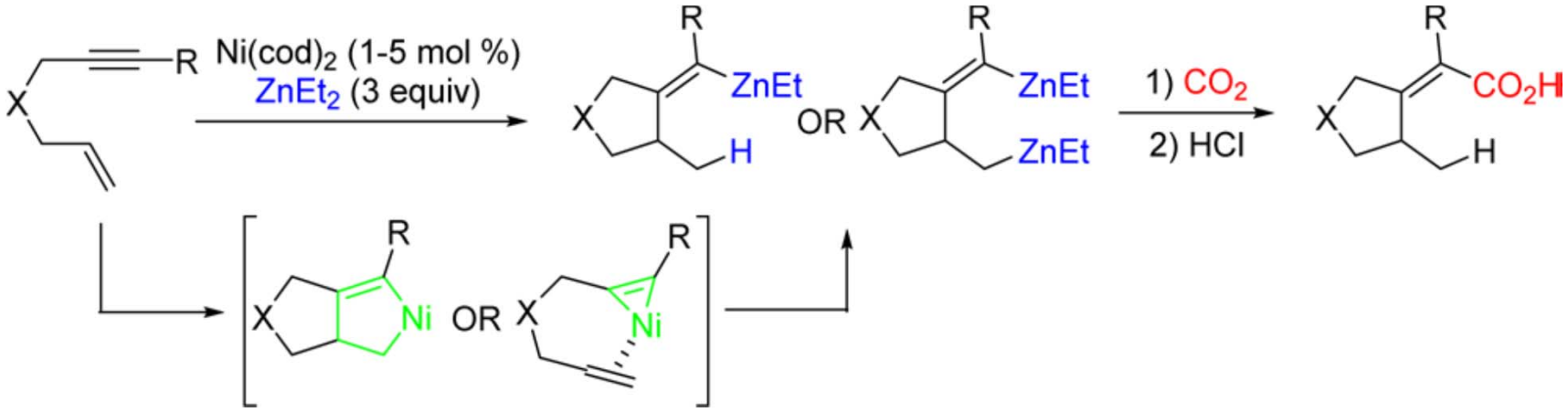




Carboxylation of arenes catalyzed by [(IPr)AuOH].

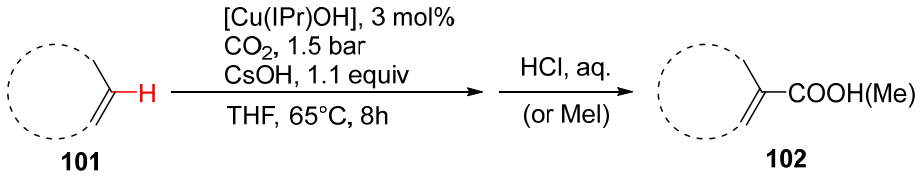
Nolan, S. P. et al. *Chem. Commun.* **2010**, *46*, 2742.

Transition-metal-catalyzed carboxylation with CO_2 via oxidative cycloaddition

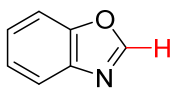


Ma, S. M. et al. *ACS Catal.* **2017**, *7*, 4504.

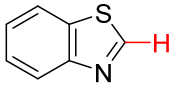
Metal(NHC)-catalyzed carboxylation of C–H bonds



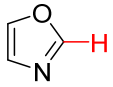
101 **102**



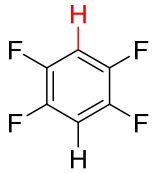
101a, pK_a = 24.8



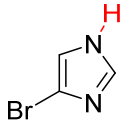
101b, pK_a = 27.3



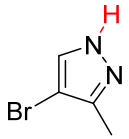
101c, pK_a = 27.7



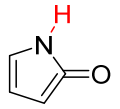
101d, pK_a = 23.1



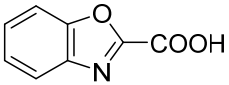
101e, pK_a = 18.6



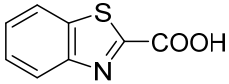
101f, pK_a = 19.8



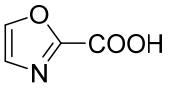
101g, pK_a = 18.6



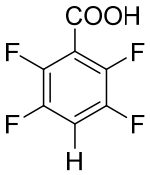
102a, 90%



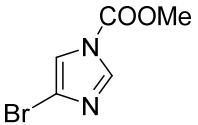
102b, 82%



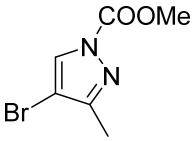
102c, 77%



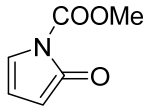
102d, 93%



102e, 88%



102f, 85%

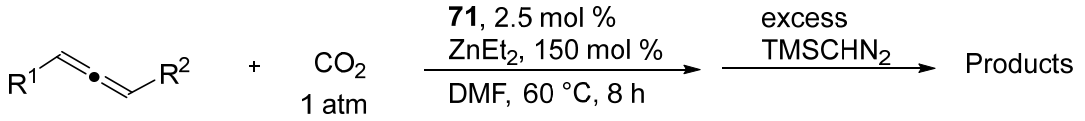


102g, 90%

Reactions of various substrates in Nolan *et al.*'s NHC-Cu system.

Nolan, S. P. et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 8674

Transition-metal-catalyzed reductive hydrocarboxylation of unsaturated compounds



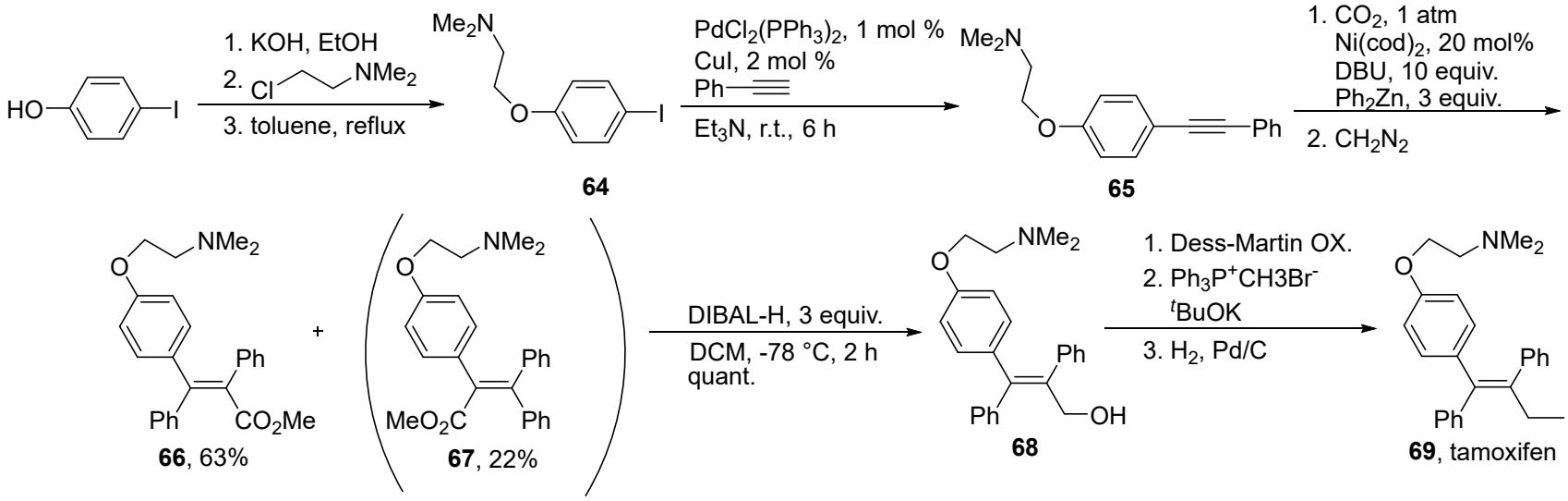
allene	COOMe / R^1 / R^2	R^2 / R^1 / COOMe	R^1 / COOMe / R^2
78a, $R^1 = CH_2CH_2Ph$, $R^2 = H$	**79a**, 65%	**80a**, 3%	**81a**, 1%
78a, $R^1 = Ph$, $R^2 = H$	**79b**, 54%	**80b**, 2%	**81b**, 7%
78a, $R^1 = CH_2CH_2Ph$, $R^2 = CH_2CH_2Ph$	**79c**, 51%		**81c**, 6%

Carboxylation of mono- or disubstituted allenes.

Iwasawa, N. et al. *J. Am. Chem. Soc.* **2008**, *130*, 15254.

Transition-metal-catalyzed carboxylation with CO_2 via oxidative cycloaddition

Nickel-catalyzed carboxylation via oxidative cycloaddition

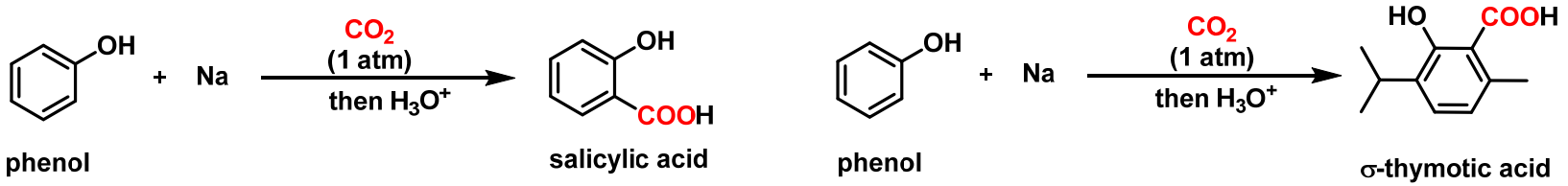


Synthesis of Tamoxifen via Ni-catalyzed arylative carboxylation.

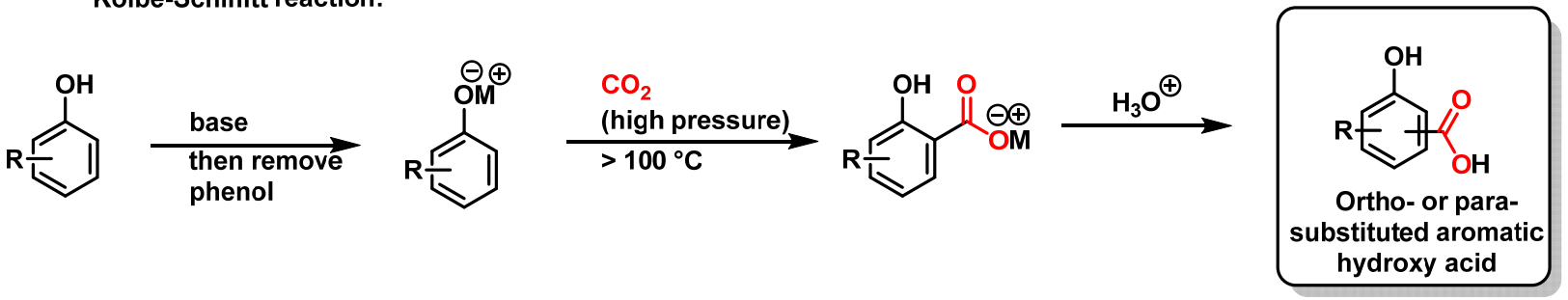
Sato, Y. et al. *Synlett* **2006**, 3182.

Introduction

Kolbe & Lautemann (1860)



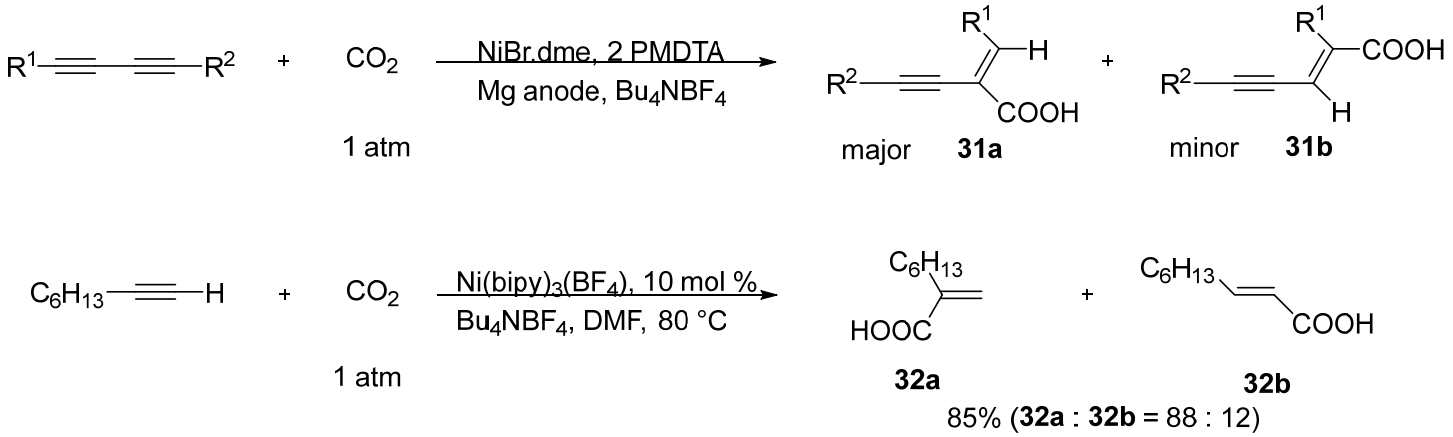
Kolbe-Schmitt reaction:



R = H, alkyl, aryl, OH, *O*-alkyl, NR_2; base: alkali metal hydroxides (e.g., NaOH, KOH, CsOH), K_2CO_3, $KHCO_3$

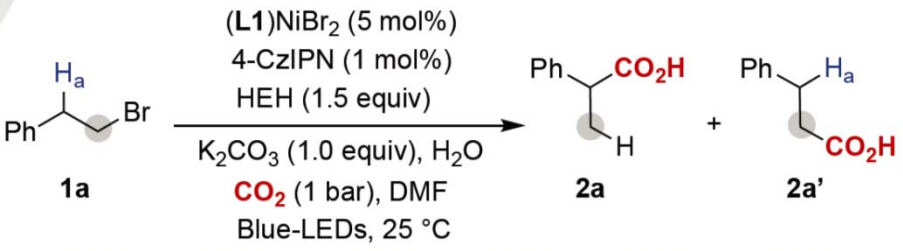
Transition-metal-catalyzed carboxylation with CO_2 via oxidative cycloaddition

Nickel-catalyzed carboxylation via oxidative cycloaddition

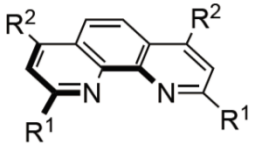


Electrochemical carboxylation of alkynes in the presence of nickel catalyst.

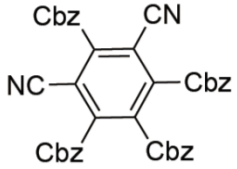
J. Perichon, et al. *J. Am. Chem. Soc.* **1991**, *113*, 8447.
J. Perichon, et al. *J. Organomet. Chem.* **1988**, *352*, 239.
J. Perichon, et al. *J. Chem. Soc.,Chem. Commun.* **1991**, 549.
J. Perichon, et al. *J. Org. Chem.* **1993**, *58*, 2578.



entry	deviation from standard conditions	yield (%)[a],[b]	2a:2a'
1	***none***	***66 (56)***	***90:10***
2	(**L2**)$NiBr_2$ instead of (**L1**)$NiBr_2$	36	70:30
3	(**L3**)$NiBr_2$ instead of (**L1**)$NiBr_2$	28	71:29
4	(**L4**)$NiBr_2$ instead of (**L1**)$NiBr_2$	30	62:38
5	(**L5**)$NiBr_2$ instead of (**L1**)$NiBr_2$	42	72:28
6	(**L6**)$NiBr_2$ instead of (**L1**)$NiBr_2$	55	85:15
7	$NiBr_2$·glyme/**L1** instead of (**L1**)$NiBr_2$	58	90:10
8	using HEH (1.0 equiv)	59	90:10
9	using 4Å MS instead of H_2O	50	85:15
10	using LiBr (1.0 equiv)	61	84:16
11	Cs_2CO_3 instead of K_2CO_3	35	42:58
12	no (**L1**)$NiBr_2$, no 4-CzIPN or no light	0	—



R^1=Me; R^2=H (**L1**)
R^1=Me; R^2=Me (**L2**)
R^1=Me; R^2=OMe (**L3**)
R^1=Me; R^2=Ph (**L4**)
R^1=Me; R^2=4-F-C_6H_4 (**L5**)
R^1=Et; R^2=H (**L6**)



4-CzIPN

Martin, R. *Chem. Eur. J.* 10.1002/chem.201902095

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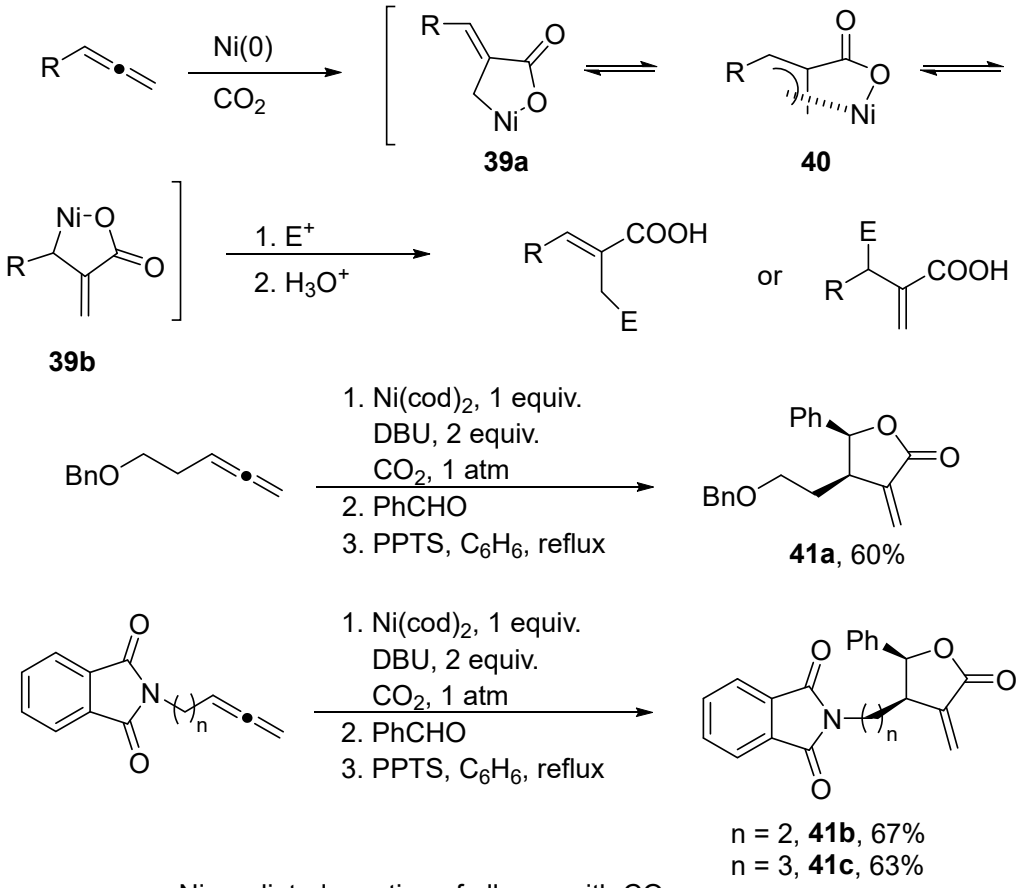

Ni-mediated reaction of allenes with CO_2.

Mori, M. et al. *Org. Lett.* **2003**, *5*, 2599.
Mori, M. et al. *Synthesis* **2004**, 791.

Transition-metal-catalyzed carboxylation with CO_2 via oxidative cycloaddition

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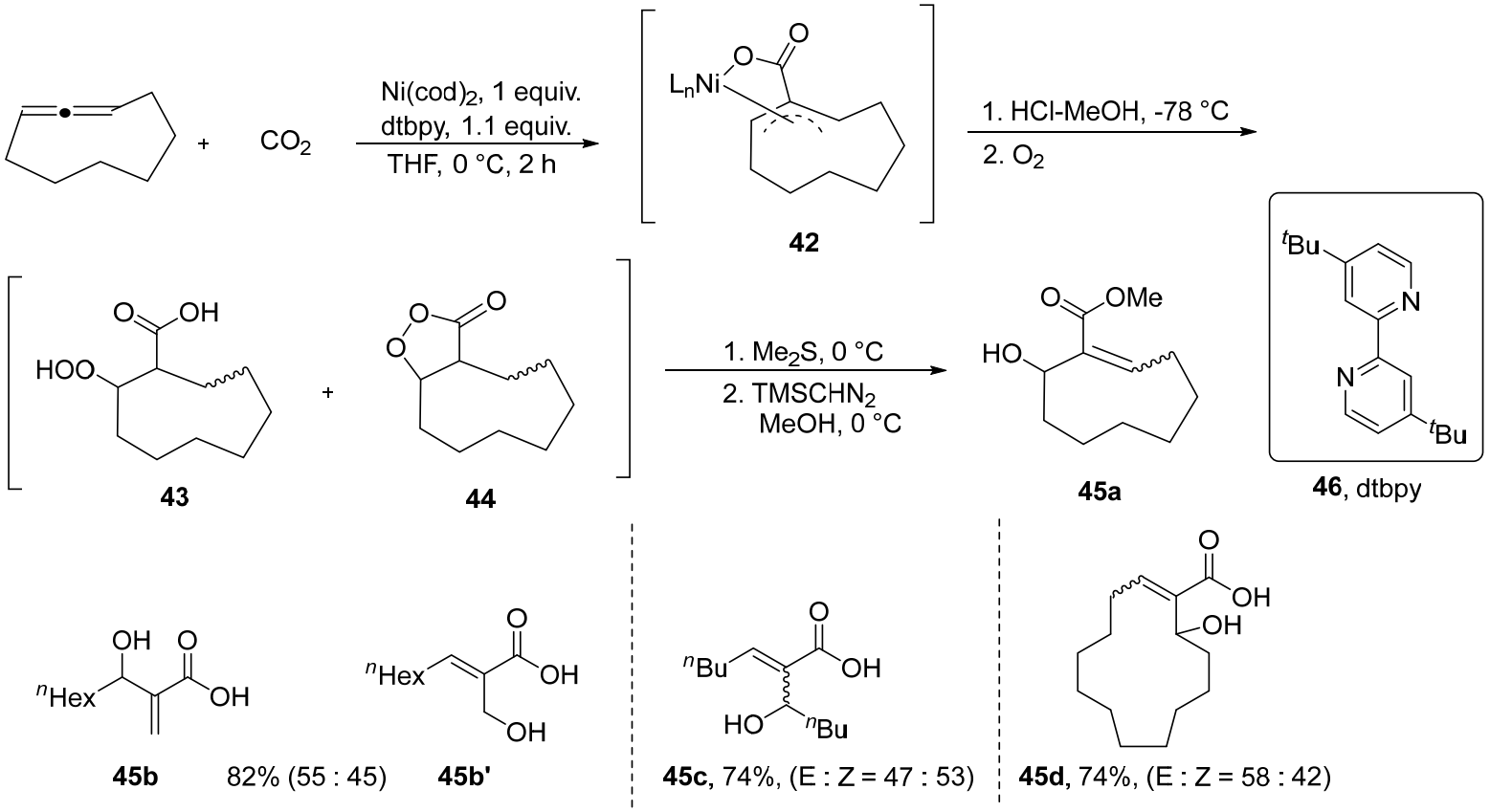
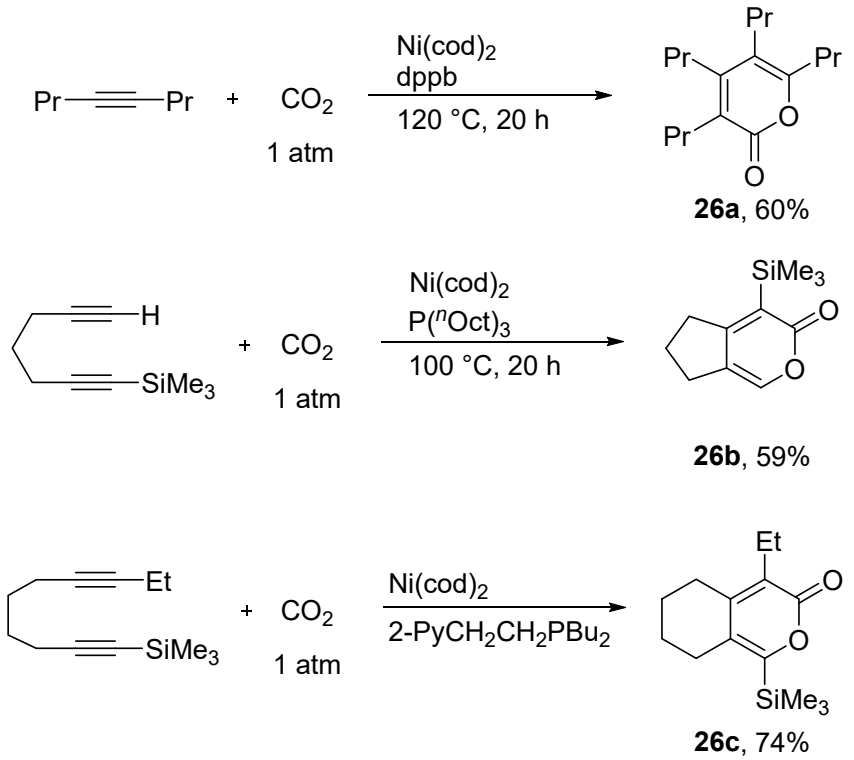


Ni-mediated hydroxycarboxylation of 1,2-dienes.

Iwasawa, N. et al. *Org. Lett.* **2007**, *9*, 1251.

Transition-metal-catalyzed carboxylation with CO_2 via oxidative cycloaddition

Nickel-catalyzed carboxylation via oxidative cycloaddition



Nickel-catalyzed carboxylative cyclization of diynes

T. Saegusa, et al. *Synth. Commun.* **1987**, *17*, 147.
T. Saegusa, et al. *J. Org. Chem.* **1988**, *53*, 3140.
T. Saegusa, et al. *J. Org. Chem.* **1990**, *55*, 2978.

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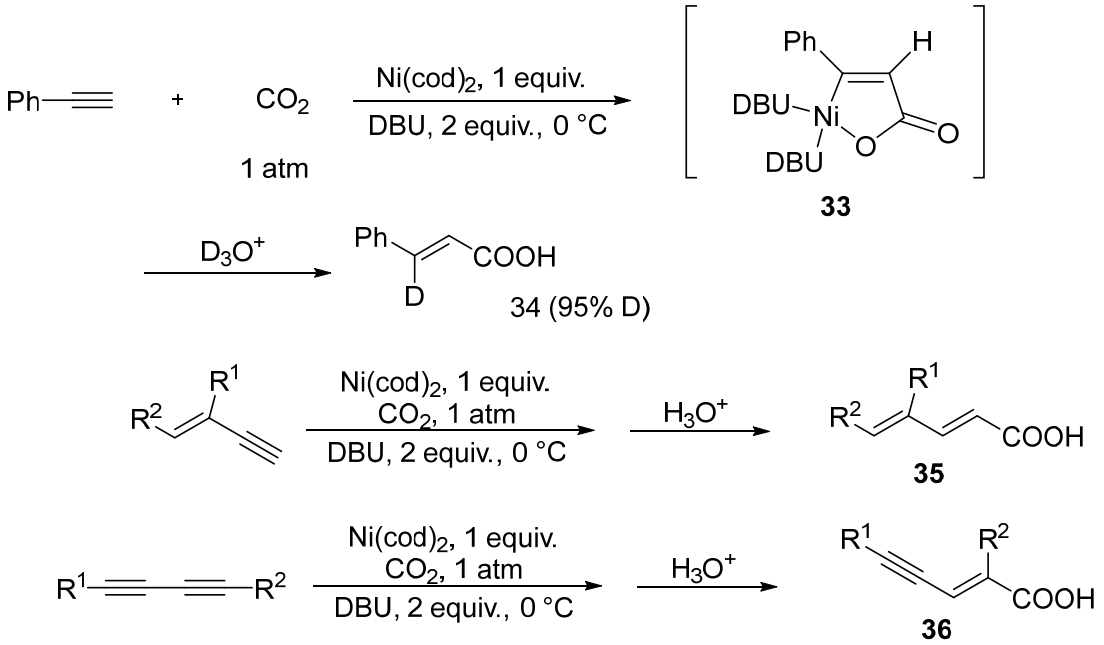
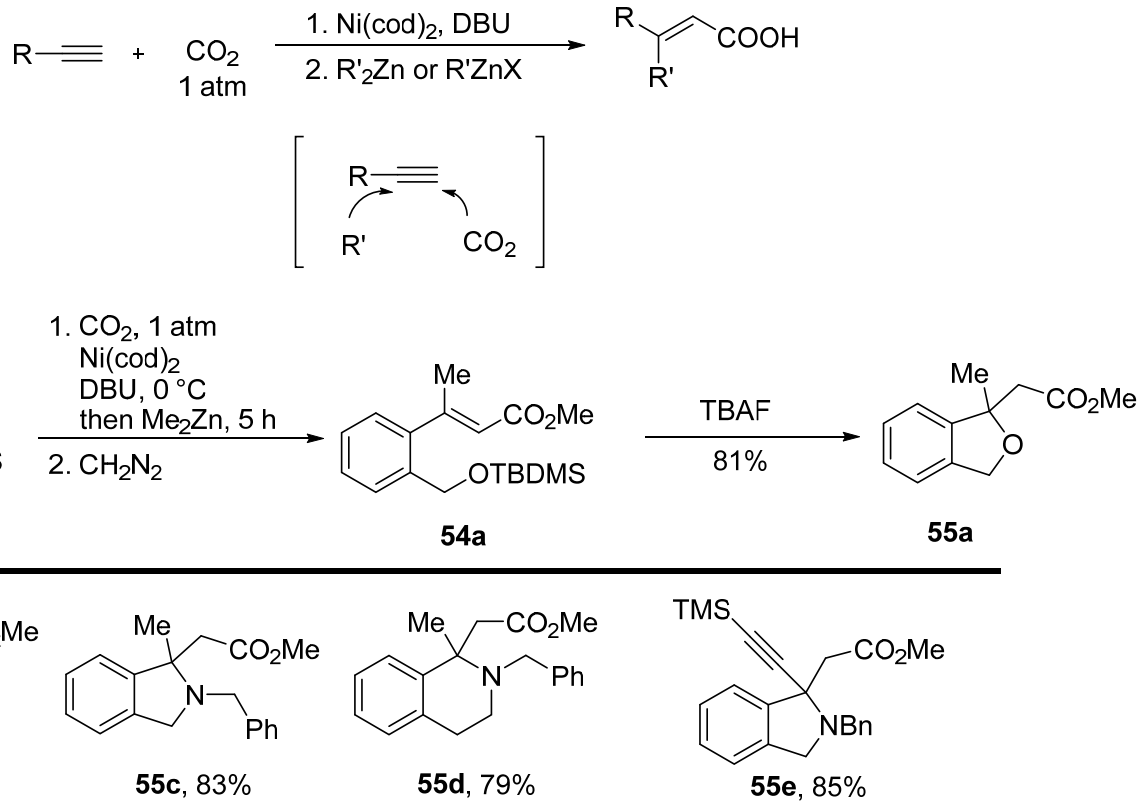


Nickel(0)-mediated carboxylation of various substituted alkynes.

Yamamoto, Y. et al. *J. Org. Chem.* **1999**, *64*, 3975.

Transition-metal-catalyzed carboxylation with CO_2 via oxidative cycloaddition

Nickel-catalyzed carboxylation via oxidative cycloaddition



Synthesis of heterocycles using Ni-mediated carboxylations.

Mori, M. et al. *Org. Lett.* **2001**, *3*, 3345.

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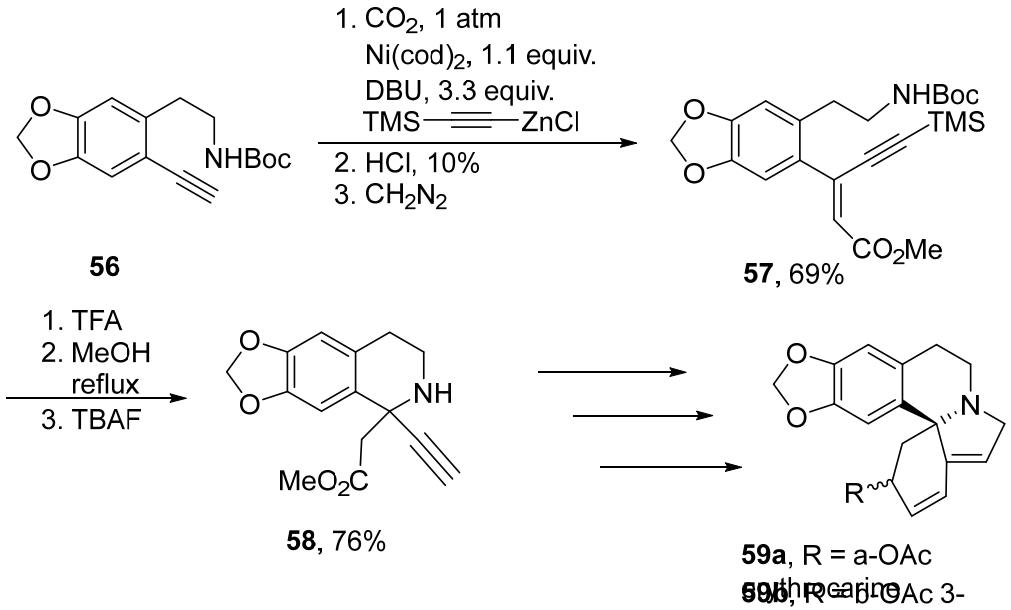


56

57, 69%

58, 76%

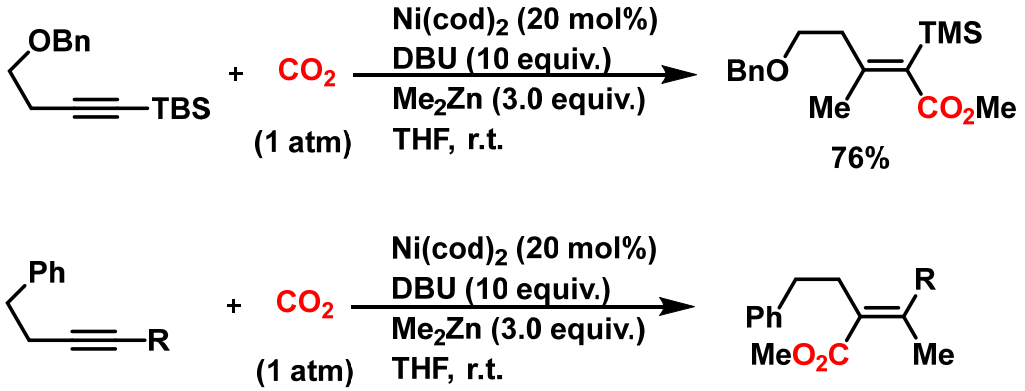
59a, R = a-OAc erythrocarine

59b, R = b-OAc 3-epierythrocarine

The synthesis of bioactive erythrina alkaloid.

Mori, M. et al. *Org. Lett.* **2003**, *5*, 2323.

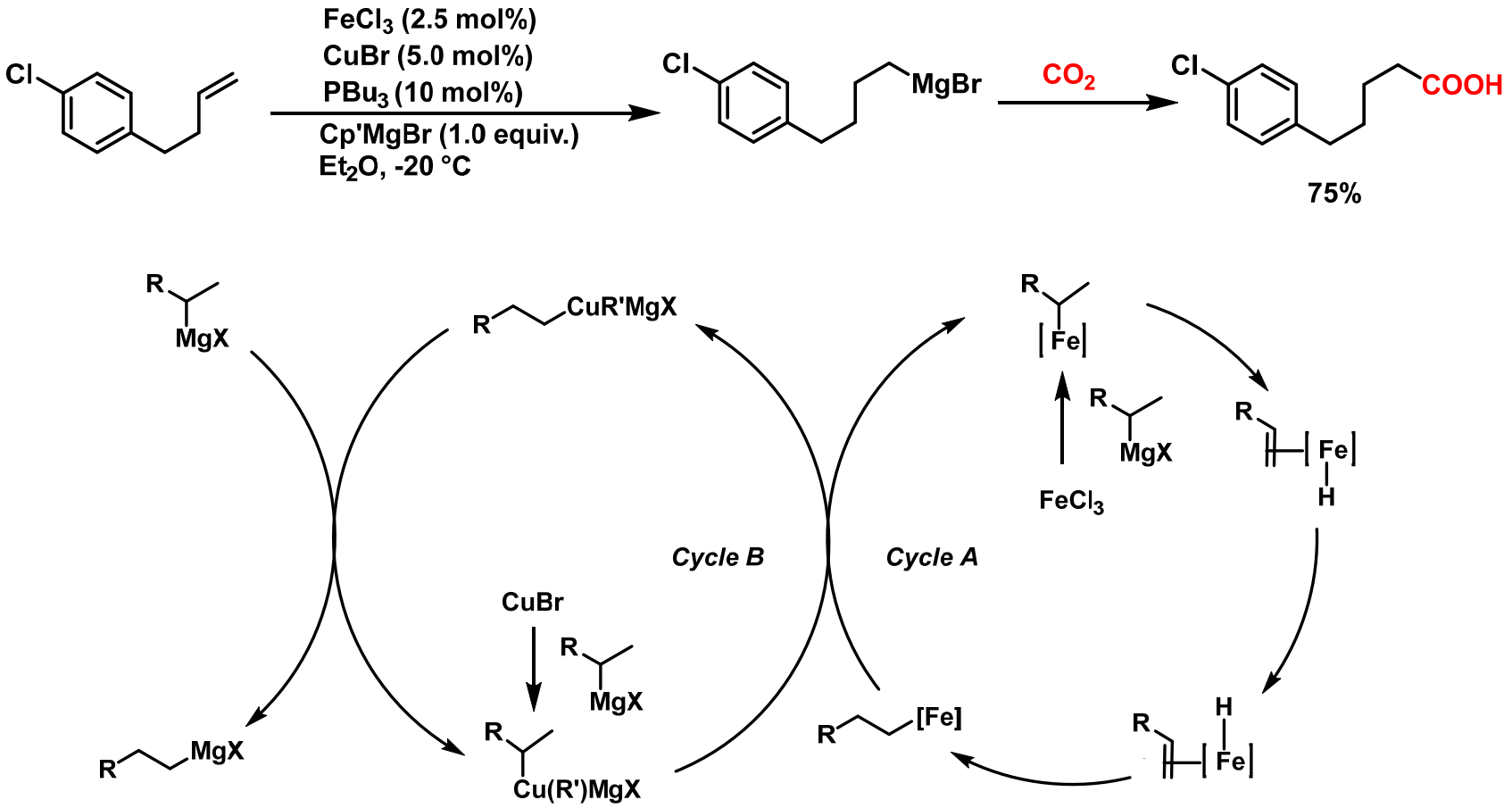
Ni-catalyzed alkylative carboxylation of disubstituted alkynes



R = ^{t}Bu, 81%; R = Ph, 94%; R = 4-MeOC$_6$H$_4$, 100%

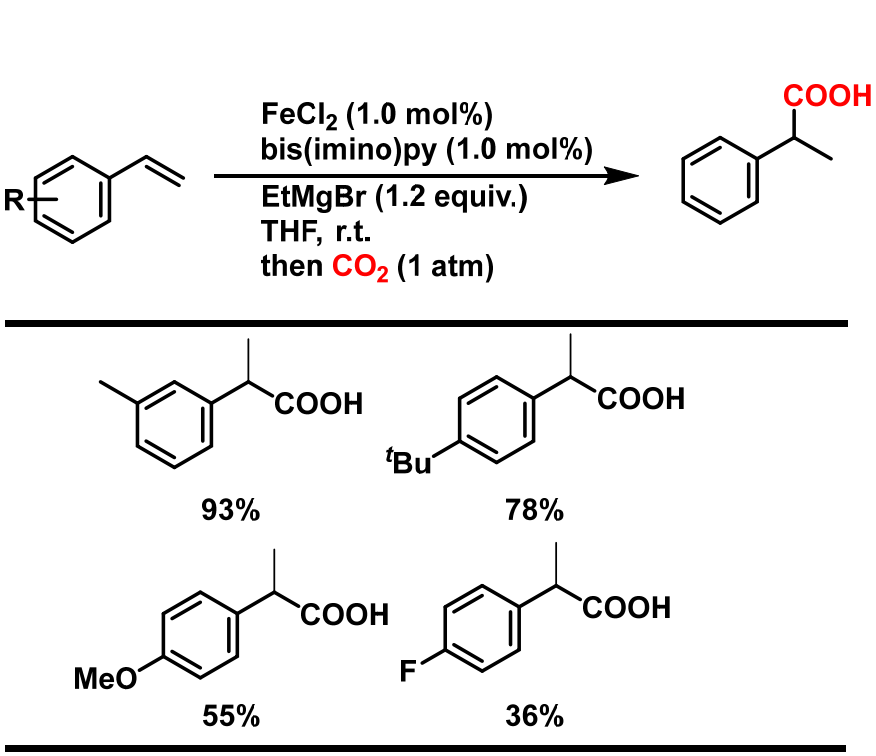
Mori, M. et al. *Org. Lett.* **2005**, *7*, 195.

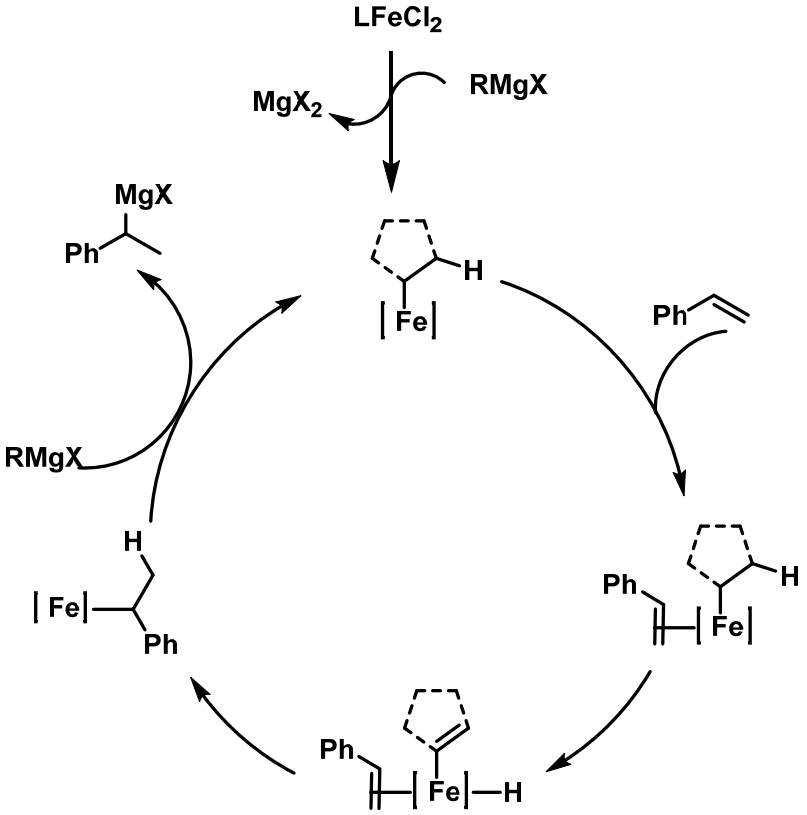
Fe/Cu-catalyzed Carboxylation of Alkenes



Hayashi, T. et al. *J. Am. Chem. Soc.* **2012**, *134*, 272.

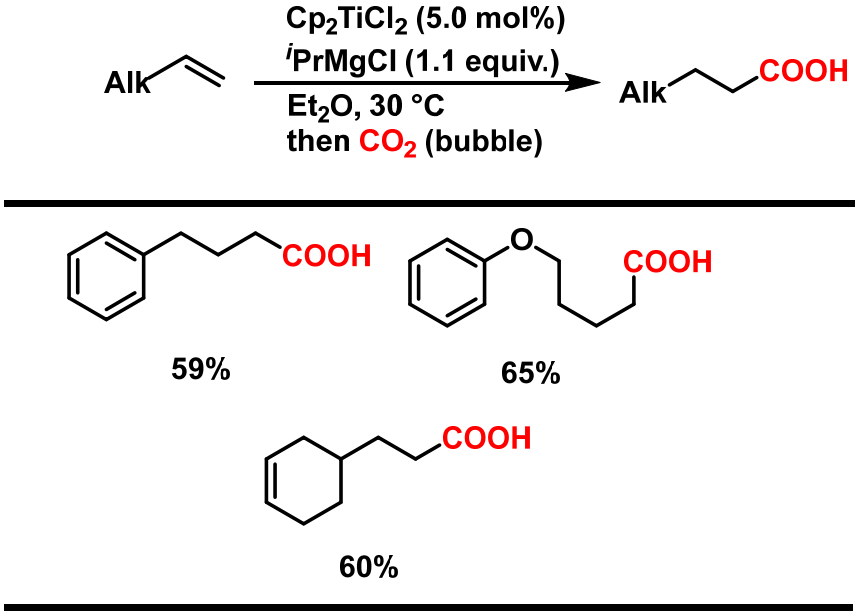
Fe-catalyzed Carboxylation of Styrenes

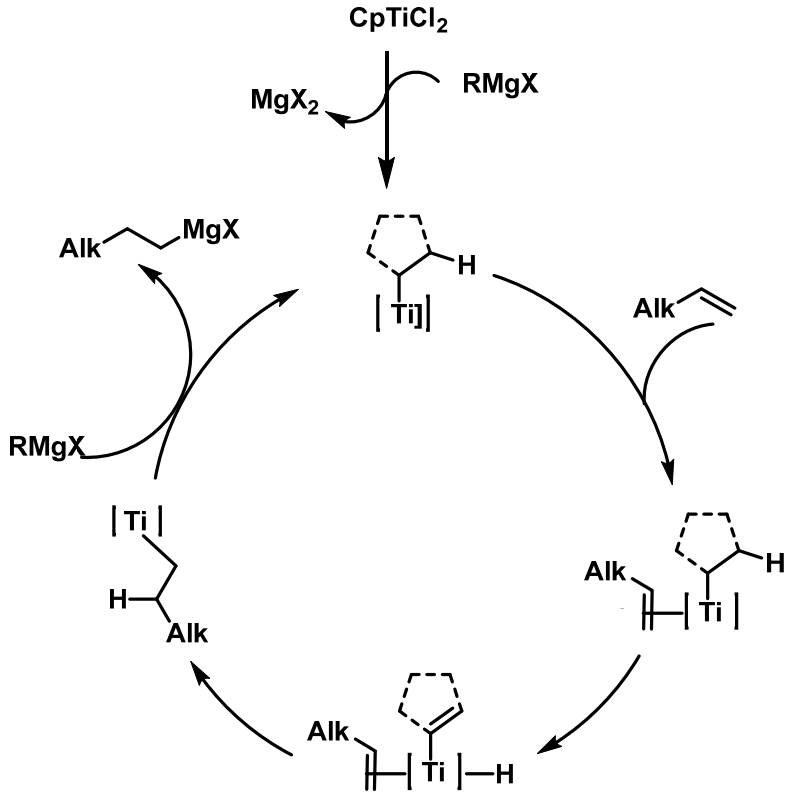




Thomas, S. P. et al. *J. Am. Chem. Soc.* **2012**, *134*, 11900.

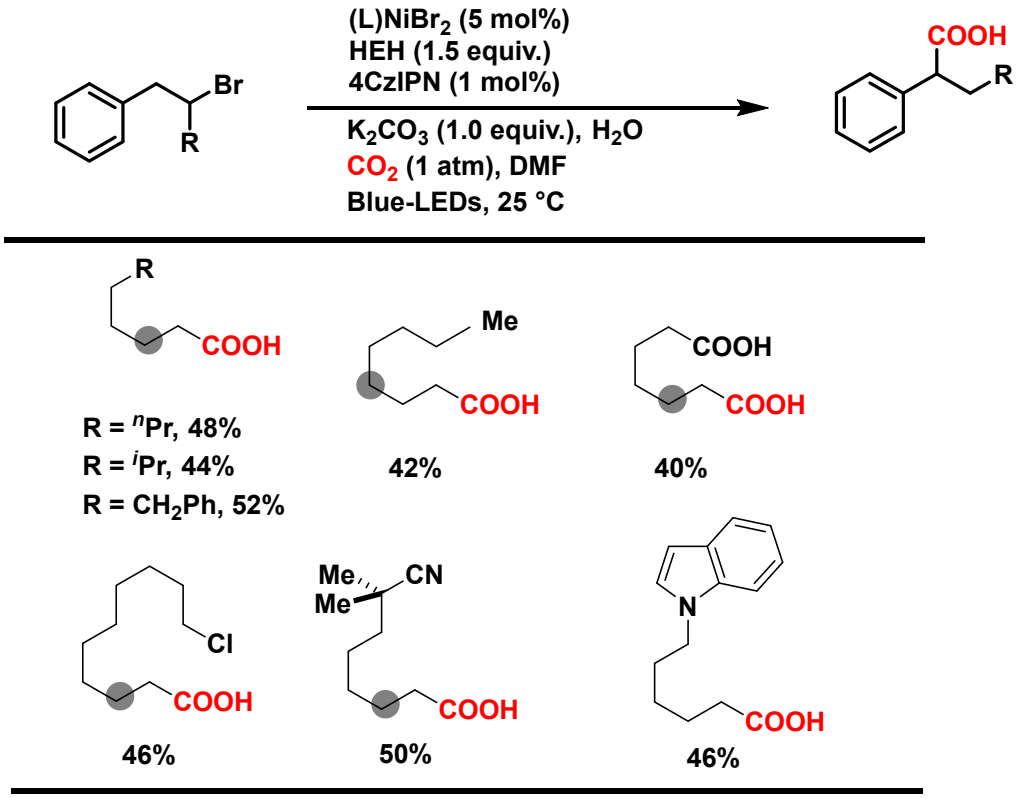
Ti-catalyzed Carboxylation of Olefins

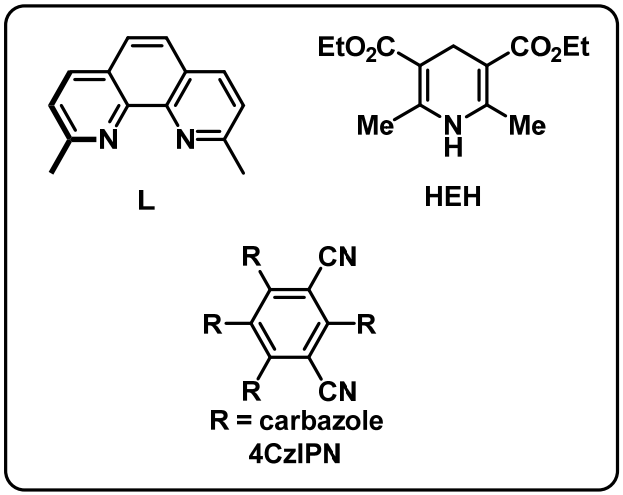




Xi, C. et al. *Org. Lett.* **2016**, *18*, 2050.

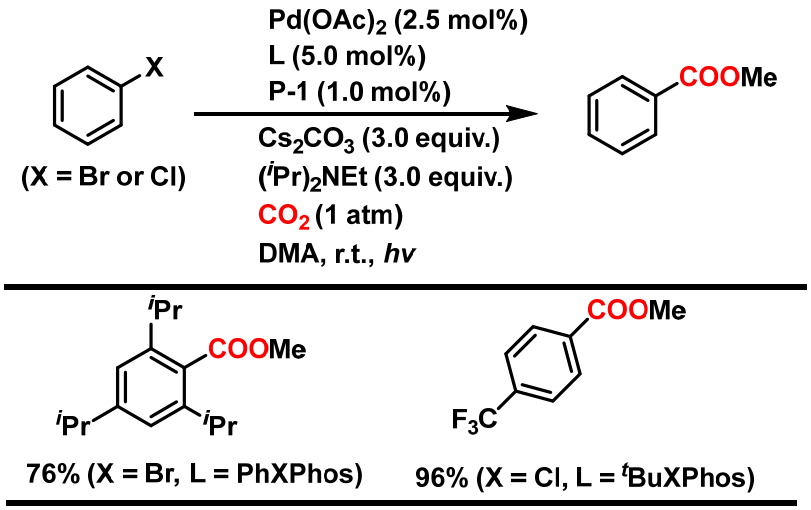
Nickel-catalyzed Carboxylation of Benzylic sp^3 C-H Bonds by Photoredox Catalysis

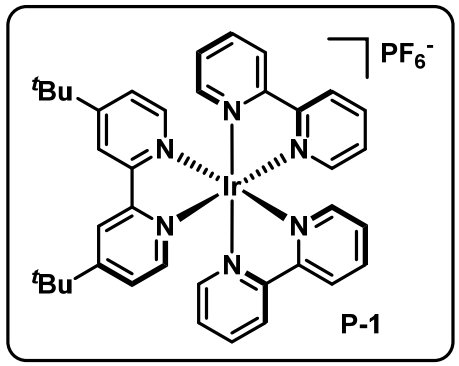




Martin, R. et al. *Chem. Eur. J.* DOI : 10.1002/chem.201902095.

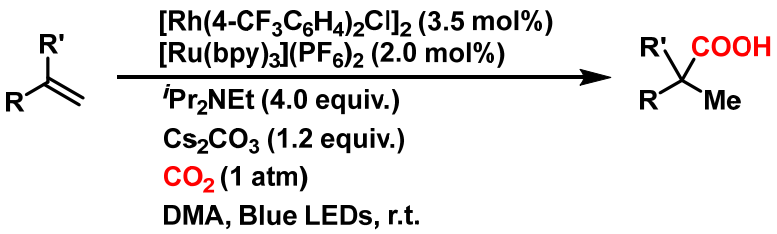
Pd/photoredox-catalyzed carboxylation of aryl halides

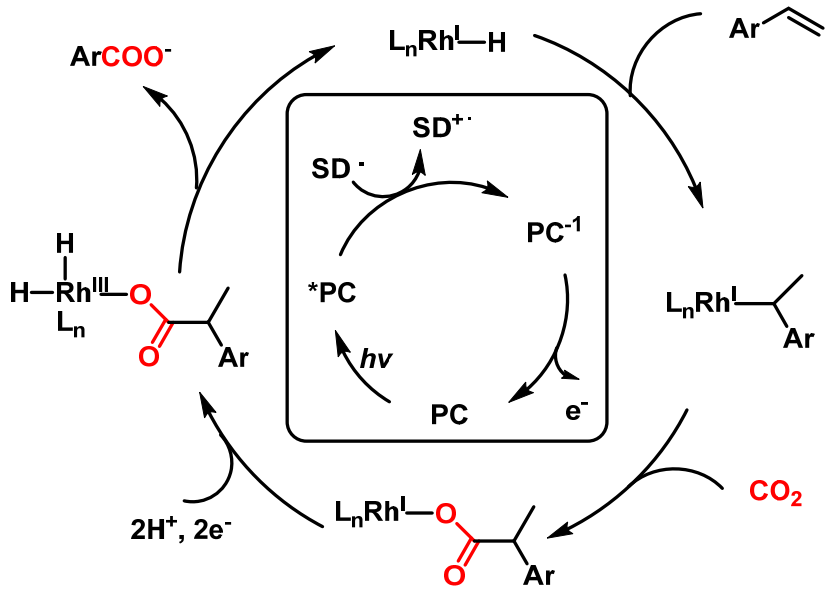




Iwasawa, N. et al. *J. Am. Chem. Soc.* **2017**, *139*, 9467.

Rh-catalyzed Photocarboxylation of Electrondeficient Alkenes





PC: Photoredox catalyst
SD: Sacrificial electron donor

Iwasawa, N. et al. *Chem. Commun.* **2017**, *53*, 3098.