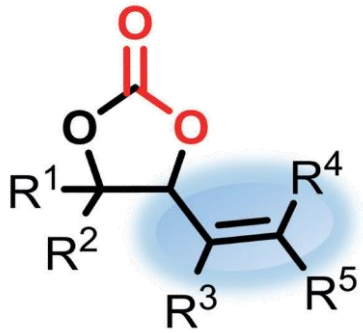
GDCh Homogeneous Catalysis Angewa International Edition

Catalytic Transformations of Functionalized Cyclic Organic Carbonates

Wusheng Guo,* Jos8 Enrique Glmez, hlex Cristmfol, Jianing Xie, and **Arjan W. Kleij**



Supervisor: Prof. Huang

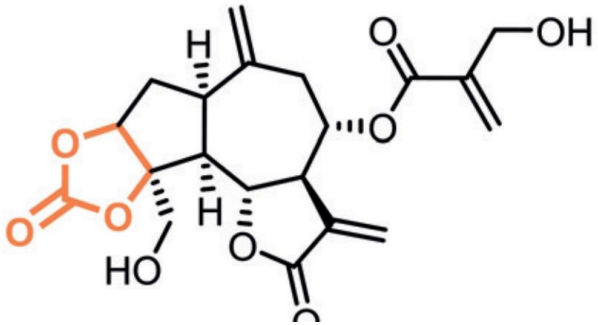
Reporter: Fangfang Guo

2018/10/15

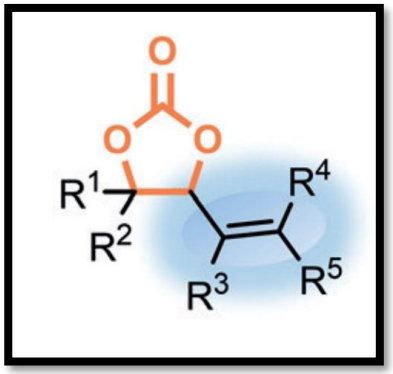
Contents

1. Introduction

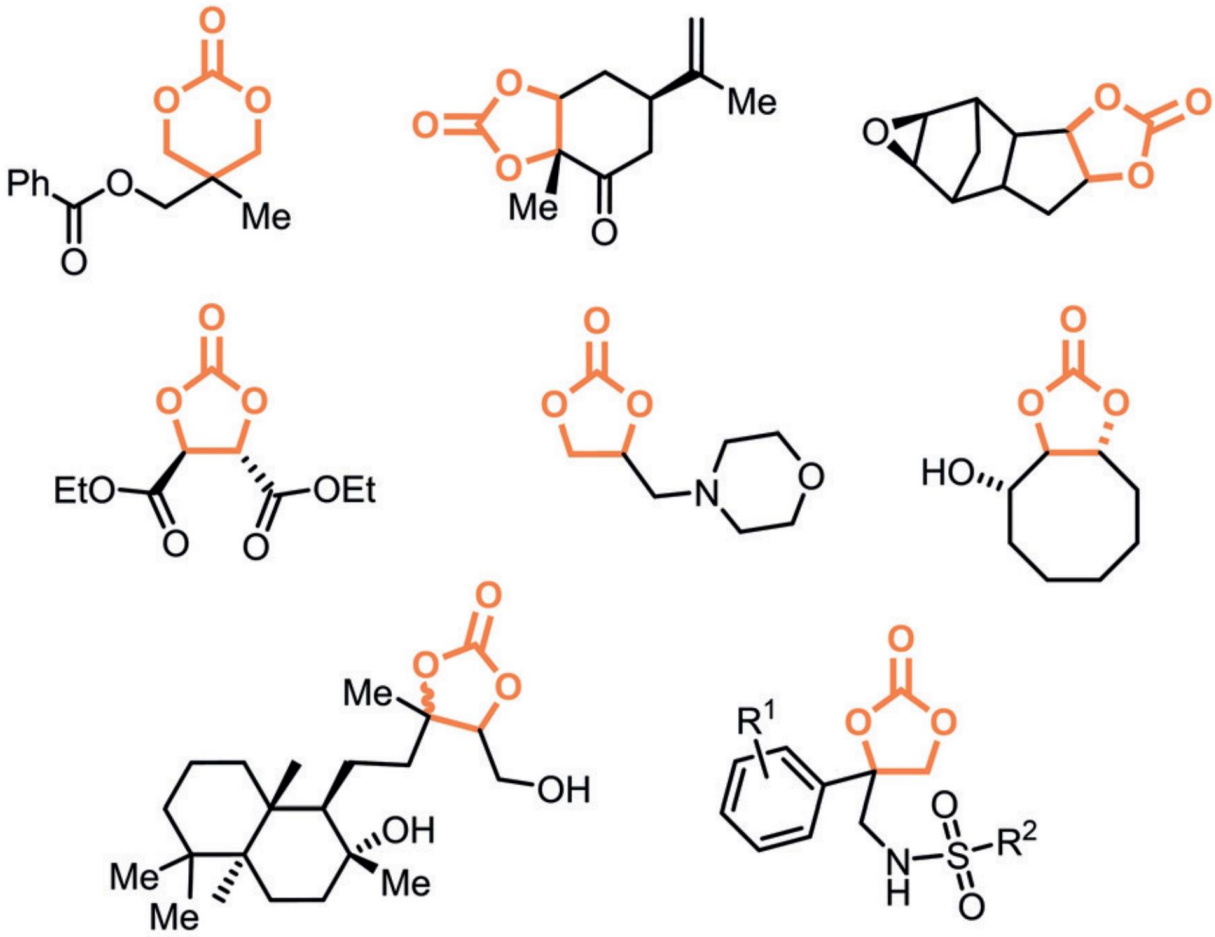
Hololeucin



naturally occurring cyclic carbonates



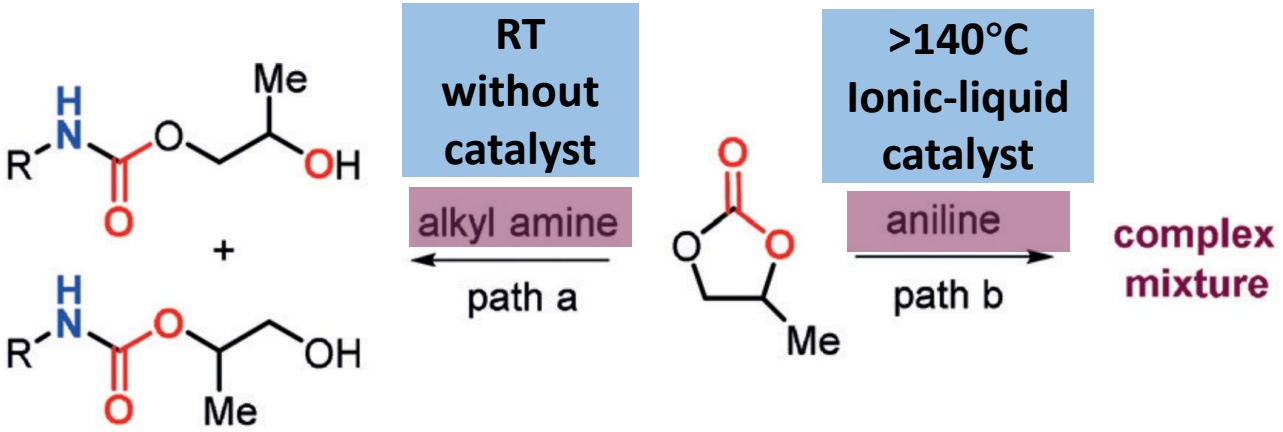
vinyl substituted cyclic carbonates (VCCs)



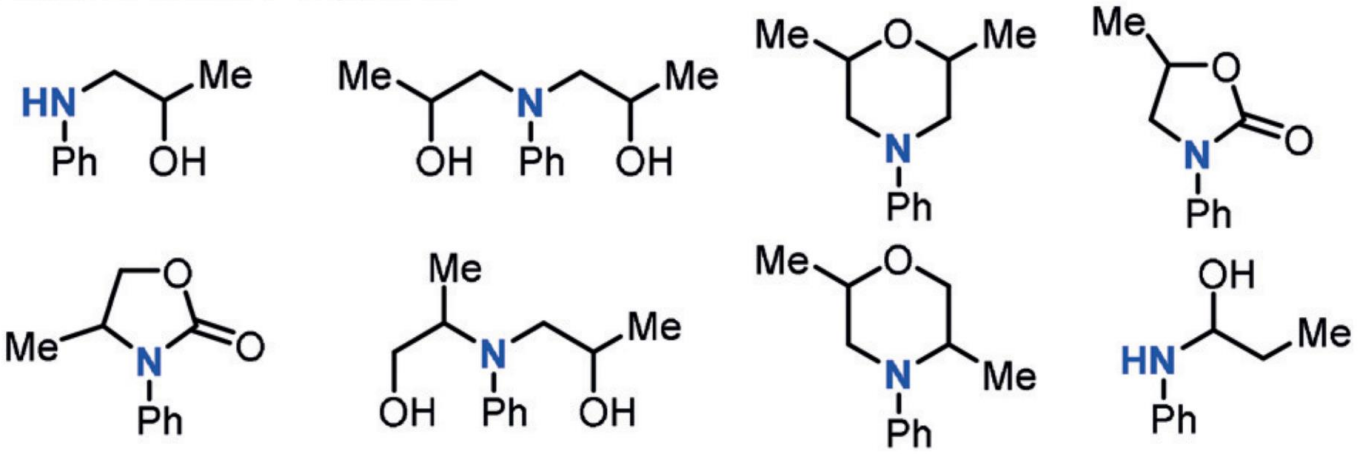
synthetic cyclic carbonates

H. Zhang, H.-B. Liu, J.-M. Yue, Chem. Rev. 2014, 114, 883.

2. Carbamates via Ring-Opening Chemistry

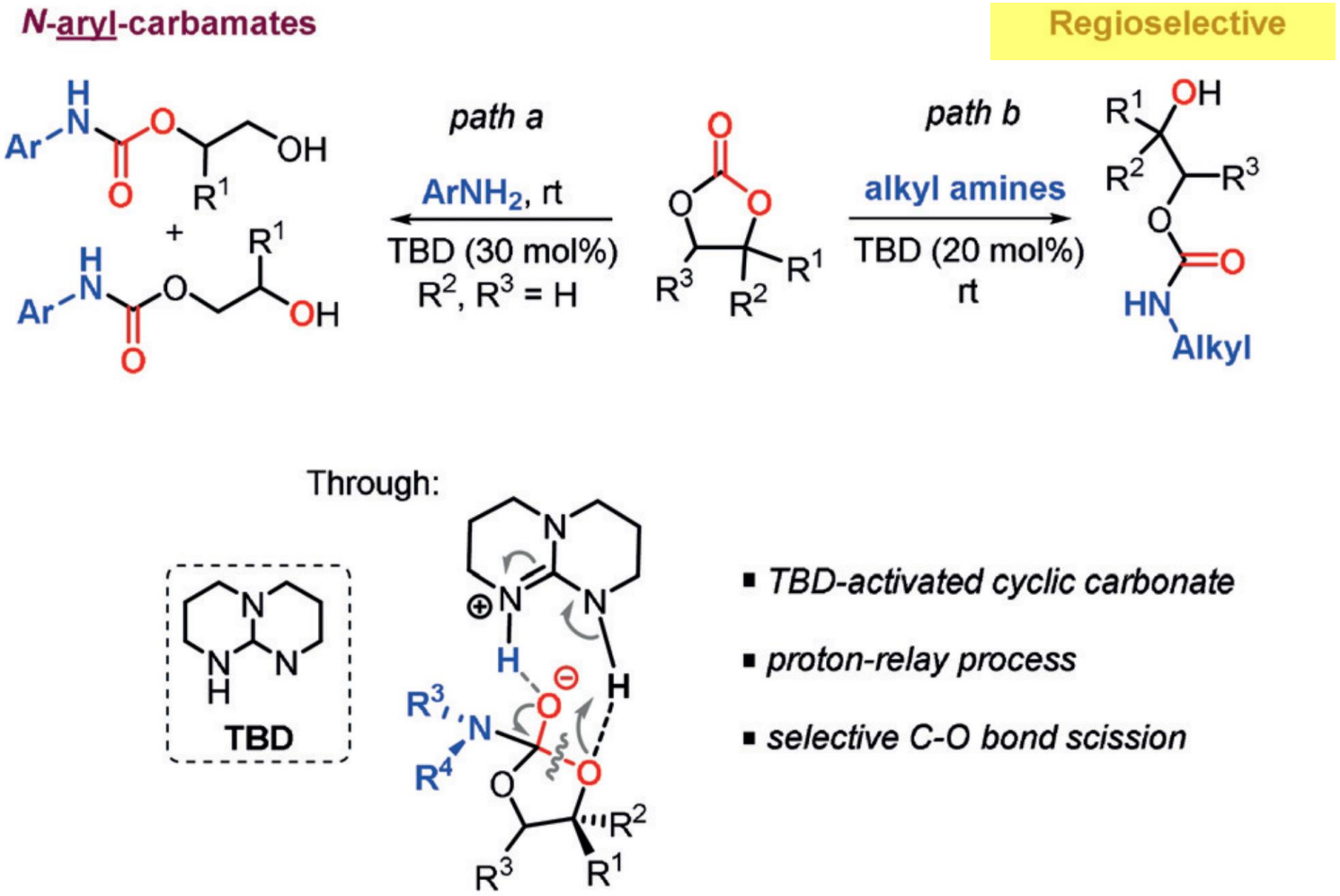


reaction mixture of path b: **without any linear carbamate product**



M. Blain, L. Jean-G8rard, R. Auvergne, D. Benazet, S. Caillol, B. Andrioletti, *Green Chem.* **2014**, *16*, 4286.
A. Cornille, M. Blain, R. Auvergne, B. Andrioletti, B. Boutevin, S. Caillol, *Polym. Chem*. **2017,** *8,* 592.
M. Selva, M. Fabris, V. Lucchini, A. Perosa, *Org. Biomol. Chem*. **2010**, *8*, 5187.

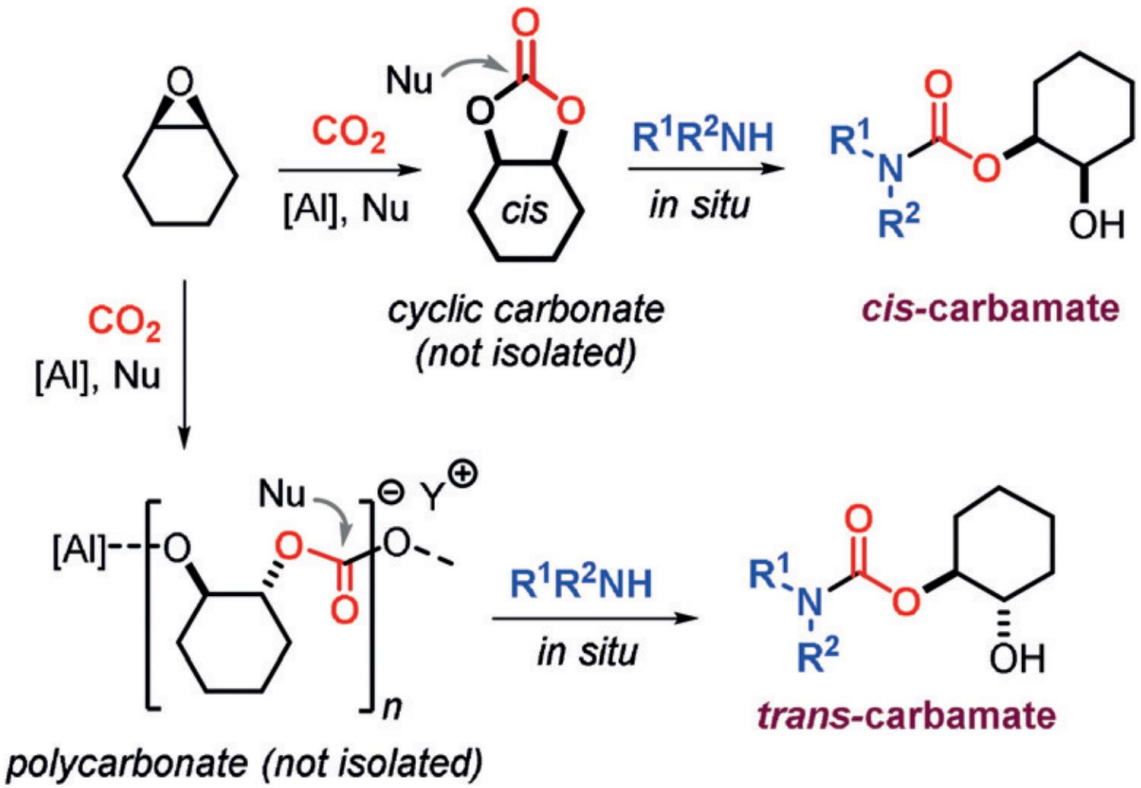
2015, The Kleij group



W. Guo, J. Glnzalez-Fabra, N. A. G. Bandeira, C. Bo, A. W. Kleij, *Angew. Chem. Int. Ed*. **2015**, *54*, 11686.

2016, Kleij group's work

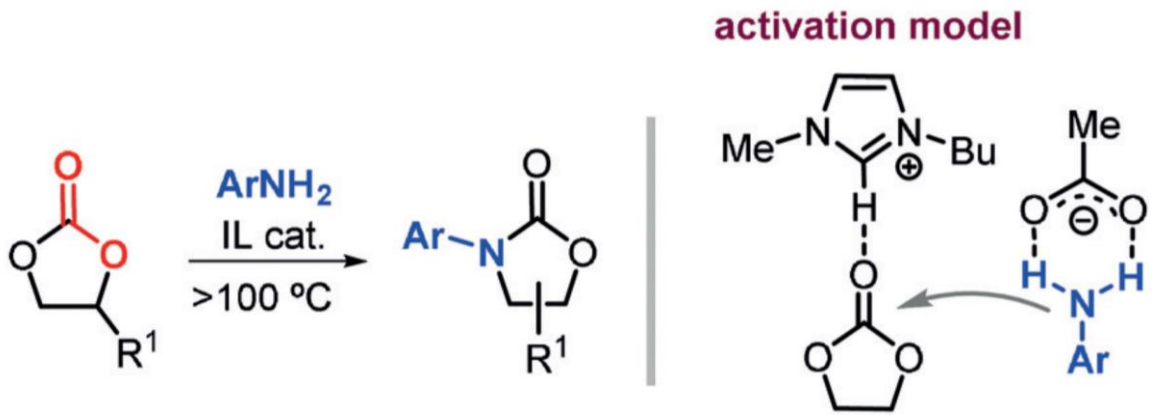
in situ prepared cyclic or polycarbonate reagent



W. Guo, V. Laserna, E. Martin, E. C. Escudero-Adan, A. W. Kleij, *Chem. Eur. J.* **2016**, *22*, 1722.

2011, Gao group's work

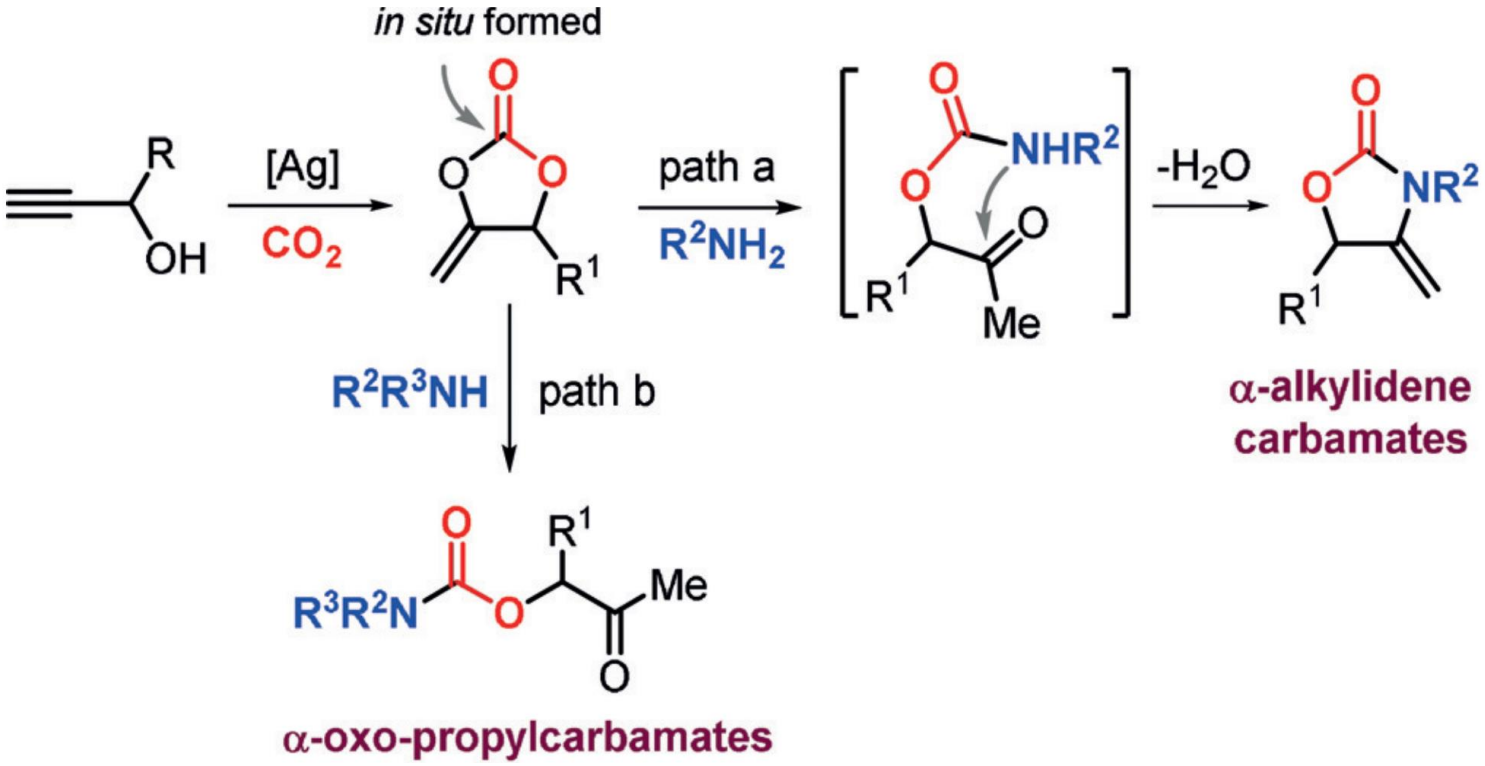
Acylation of amines with cyclic carbonates



L. Zhang, X. Fu, G. Gao, *ChemCatChem*, **2011**, *3*, 1359.
Y. Song, C. Cheng, H. Jing, *Chem. Eur. J*. **2014,** *20*, 12894.
B. Wang, E. H. Elageed, D. Zhang, S. Yang, S. Wu, G. Zhang, G. Gao, *ChemCatChem* **2014**, *6*, 278.
R. Gupta, M. Yadav, R. Gaur, G. Arora, R. K. Sharma, *Green Chem*. **2017**, *19*, 3801.
U. R. Seo, Y. K. Chung, *Green Chem*. **2017**, *19*, 803.

He group's work

Acylation of amines with cyclic carbonates

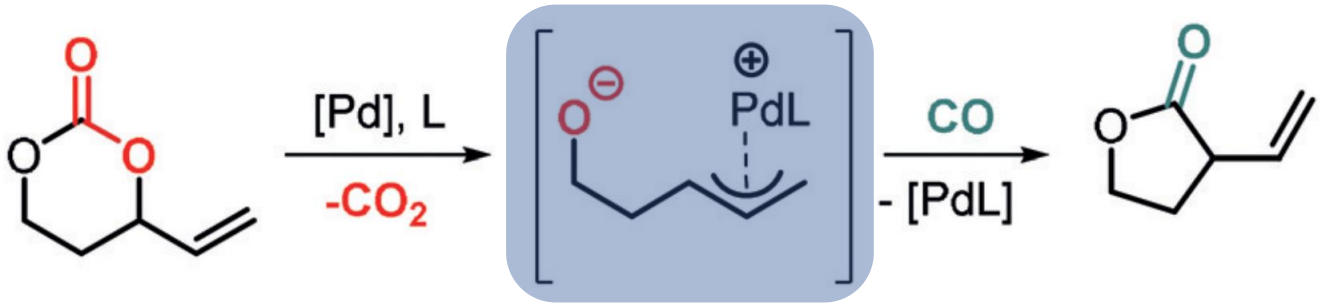


Q.-W. Song, B. Yu, X.-D. Li, R. Ma, Z.-F. Diao, R.-G. Li, W. Li, L.-N. He, *Green Chem*. **2014**, *16*, 1633.
Q.-W. Song, W.-Q. Chen, R. Ma, A. Yu, Q.-Y. Li, Y. Chang, L.-N. He, *ChemSusChem* **2015**, *8*, 821.

3. Transition-Metal-Catalyzed Decarboxylation

Yoshida group's work

Pd-catalyzed decarboxylative carbonylation of a VCC

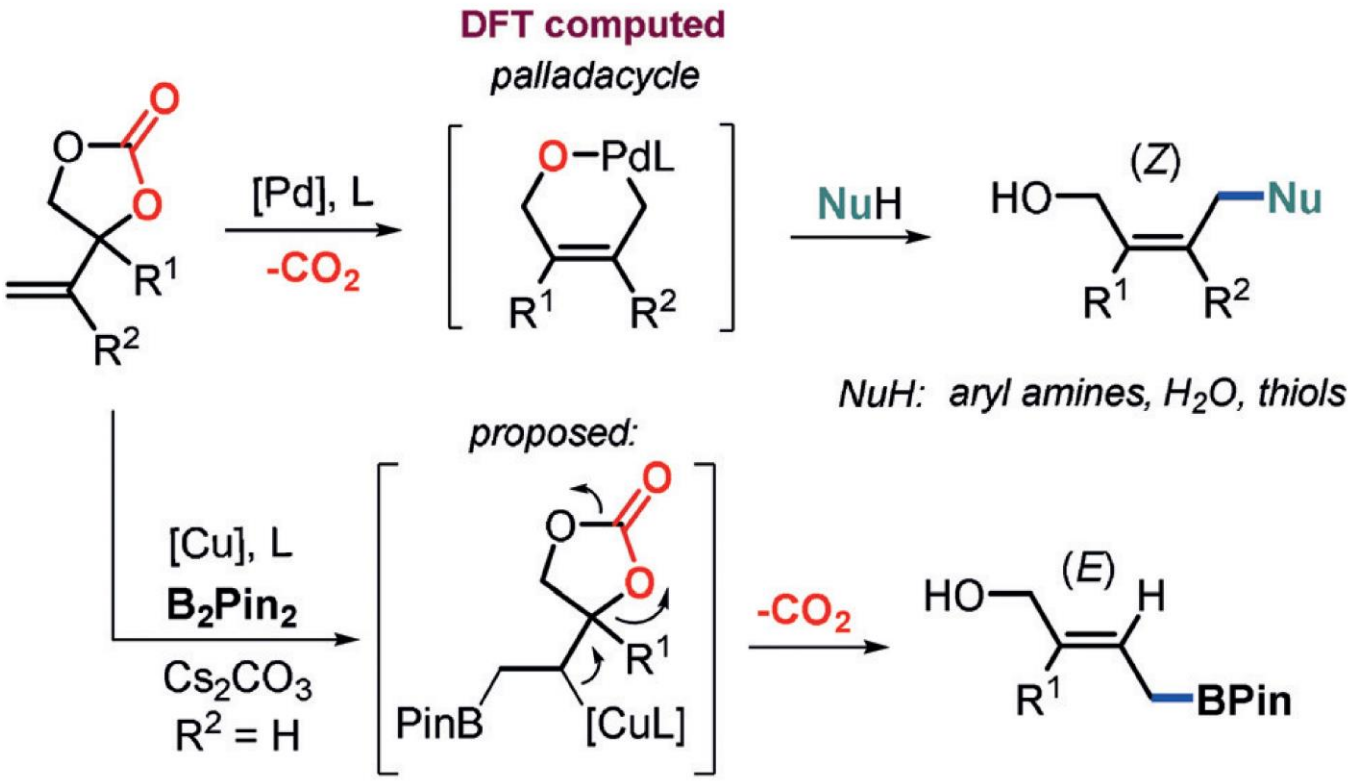


R. A. Braun, *J. Org. Chem*. **1963**, *28*, 1383.
Y. Tamaru, T. Bando, M. Hojo, Z. Yoshida, *Tetrahedron Lett*. **1987**, *28*, 3497.

3.1. Reactions of VCCs with Nucleophiles

2016, Kleij group's work

Stereoselective C-N, C-O, C-S, C-C and C-B bond formation reactions

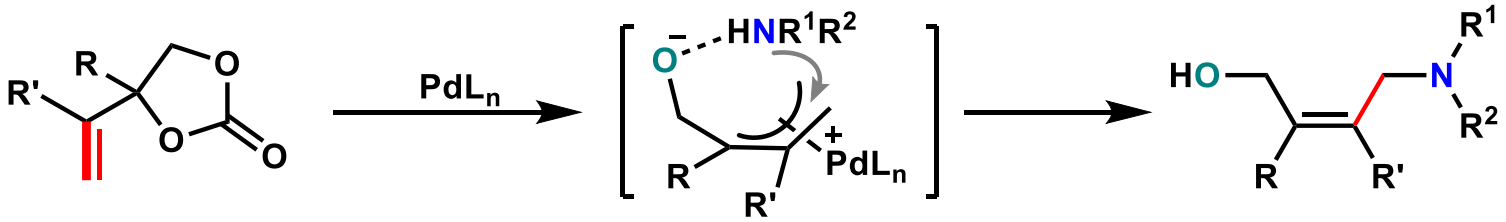


W. Guo, L. Mart&nez-Rodr&guez, R. Kuniyil, E. Martin, A. W. Kleij, *J. Am. Chem. Soc*. **2016**, *138*, 11970.
W. Guo, L. Mart&nez-Rodr&guez, E. Martin, A. W. Kleij, *Angew. Chem. Int. Ed*. **2016**, *55*, 11037.
J. E. Glmez, W. Guo, A. W. Kleij, *Org. Lett*. **2016**, *18*, 6042.
N. Miralles, J. E. Glmez, A. W. Kleij, E. Fernandez, *Org. Lett*. **2017**, *19,* 6096.
W. Guo, A. Cai, J. Xie, A. W. Kleij, *Angew. Chem. Int. Ed*. **2017**, *56*, 11797.

3.1. Reactions of VCCs with Nucleophiles

2016, Kleij group's work

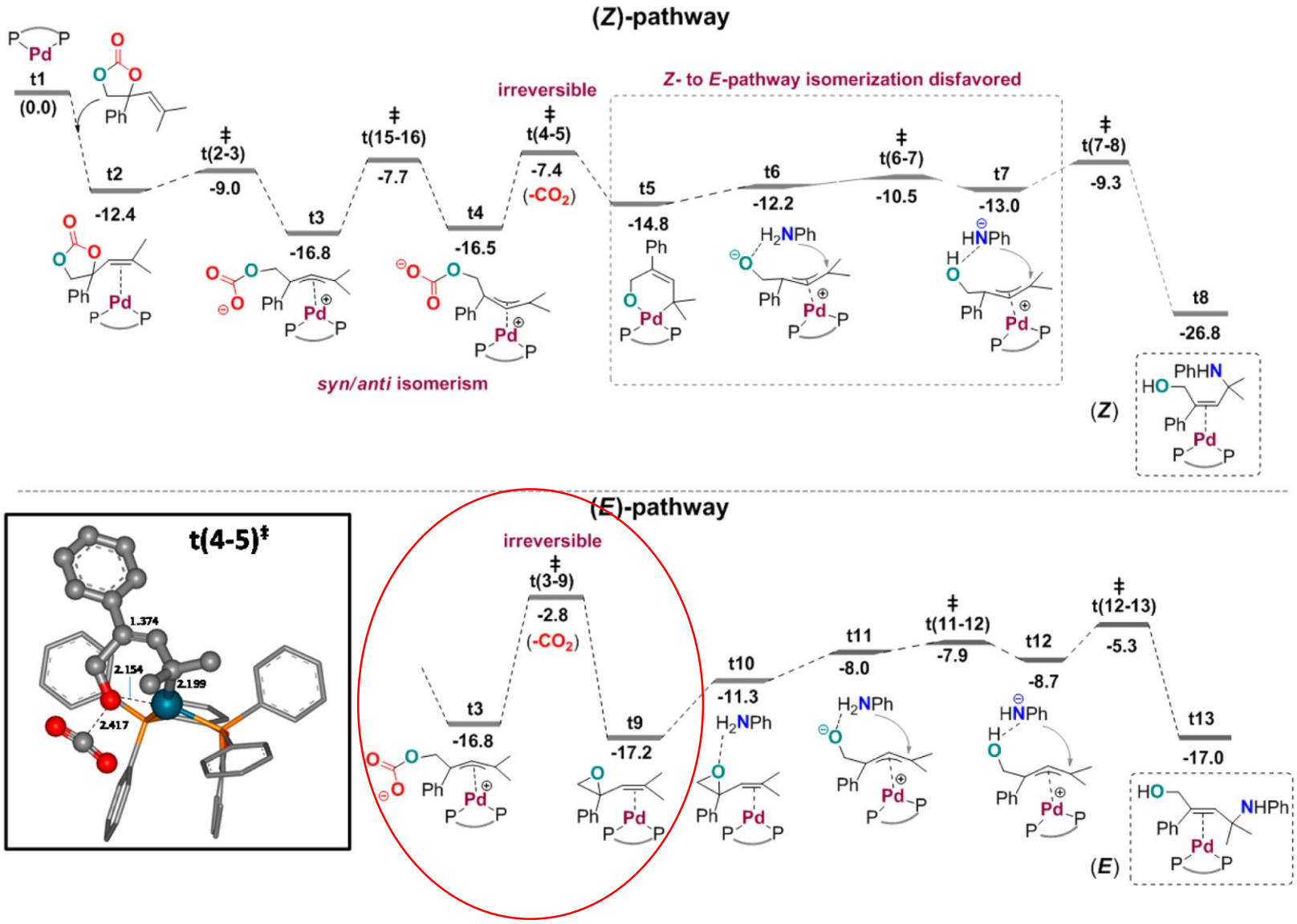
Pd-catalyzed decarboxylative formation of highly substituted (Z)-configured allylic scaffolds from VCCs



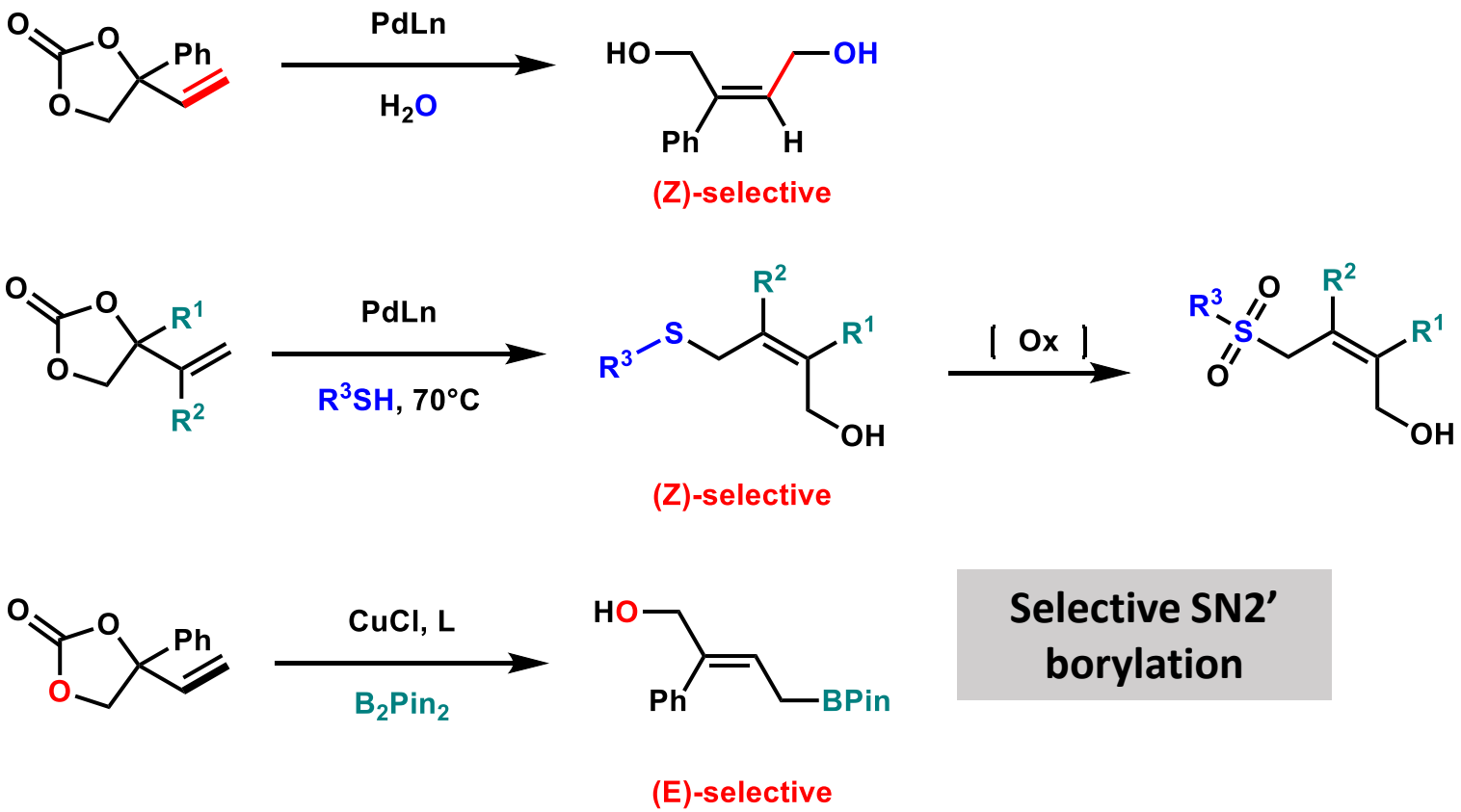
Six-membered palladacycle

(Z)-selective

W. Guo, L. Mart&nez-Rodr&guez, R. Kuniyil, E. Martin, A. W. Kleij, *J. Am. Chem. Soc*. **2016**, *138*, 11970.


(Z)-pathway
t1
(0.0)
t2
-12.4
‡ t(2-3)
-9.0
t3
-16.8
‡ t(15-16)
-7.7
t4
-16.5
irreversible
‡ t(4-5)
-7.4
(-CO2)
syn/anti isomerism
Z- to E-pathway isomerization disfavored
t5
-14.8
t6
-12.2
‡ t(6-7)
-10.5
t7
-13.0
‡ t(7-8)
-9.3
t8
-26.8
(Z)
t(4-5)‡
1.374
2.154
2.199
2.417
(E)-pathway
irreversible
‡ t(3-9)
-2.8
(-CO2)
t3
-16.8
t9
-17.2
t10
-11.3
t11
-8.0
‡ t(11-12)
-7.9
t12
-8.7
‡ t(12-13)
-5.3
t13
-17.0
(E)

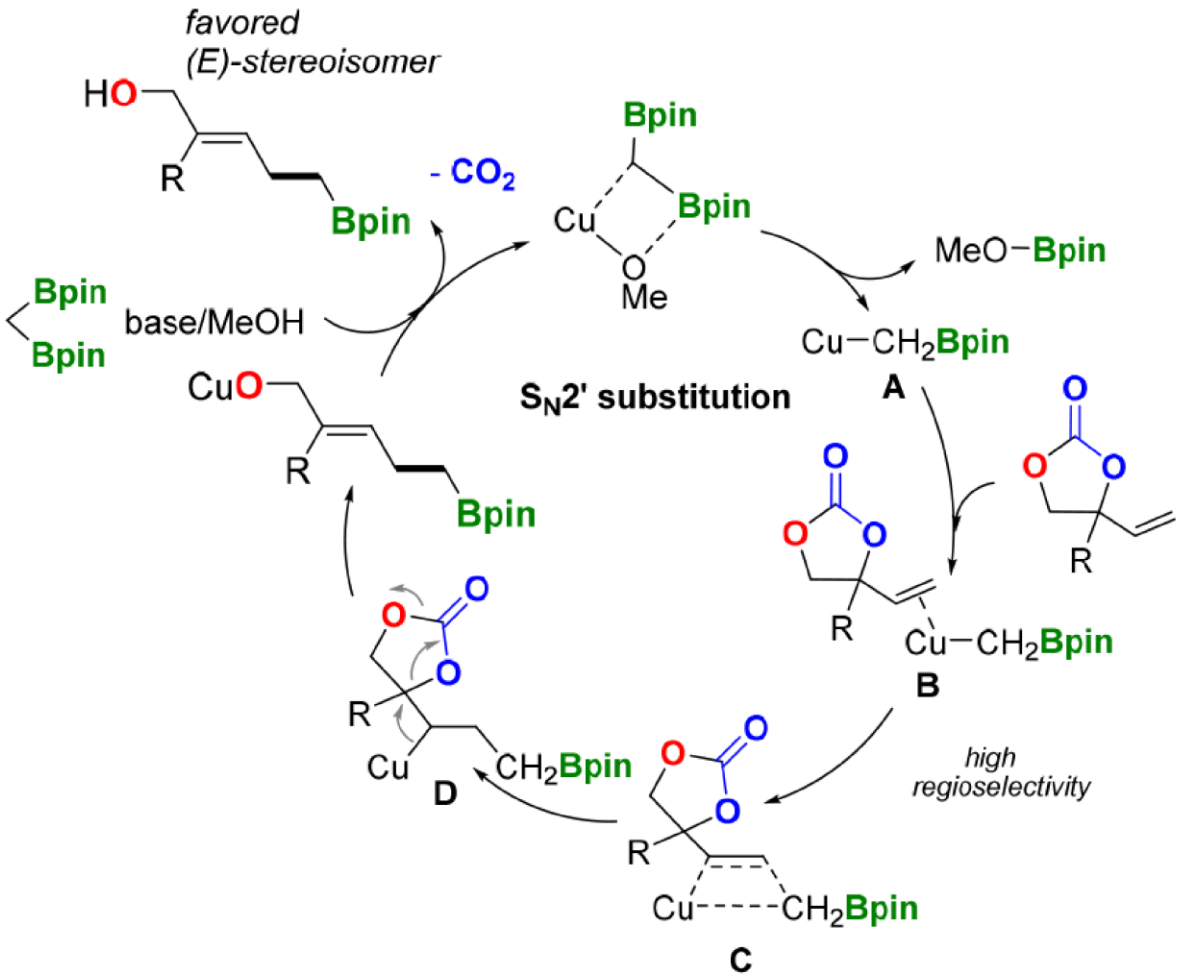
2016, Kleij group's work



Selective SN2' borylation

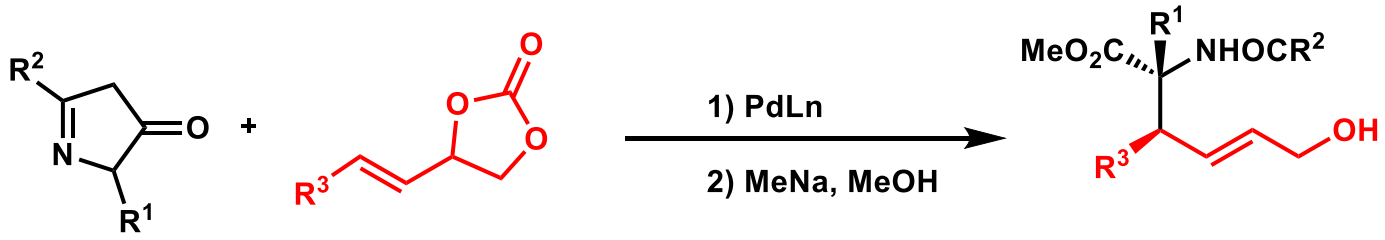
W. Guo, L. Mart&nez-Rodr&guez, E. Martin, A. W. Kleij, *Angew. Chem. Int. Ed*. **2016**, *55*, 11037.
J. E. Glmez, W. Guo, A. W. Kleij, *Org. Lett*. **2016**, *18*, 6042.
N. Miralles, J. E. Glmez, A. W. Kleij, E. Fernandez, *Org. Lett*. **2017**, *19*, 6096.
W. Guo, A. Cai, J. Xie, A. W. Kleij, *Angew. Chem. Int. Ed*. **2017**, *56*, 11797.

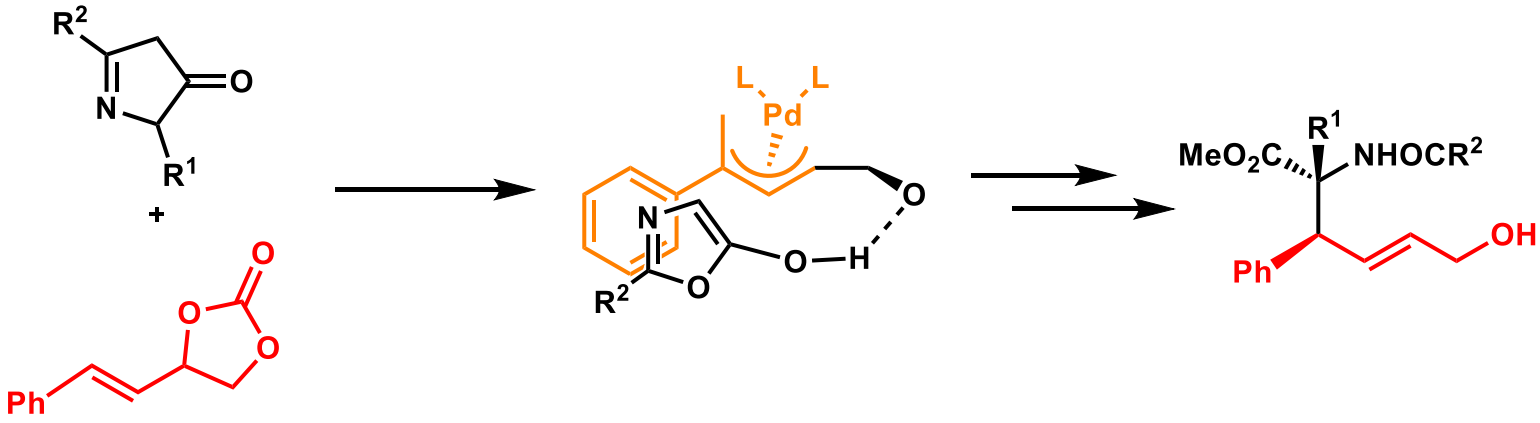
Mechanism of Cu-catakyzed decarboxylation to form C-B bond



2015, Zhang group's work

asymmetric decarboxylative alkylation of VCCs with azlactone nucleophiles

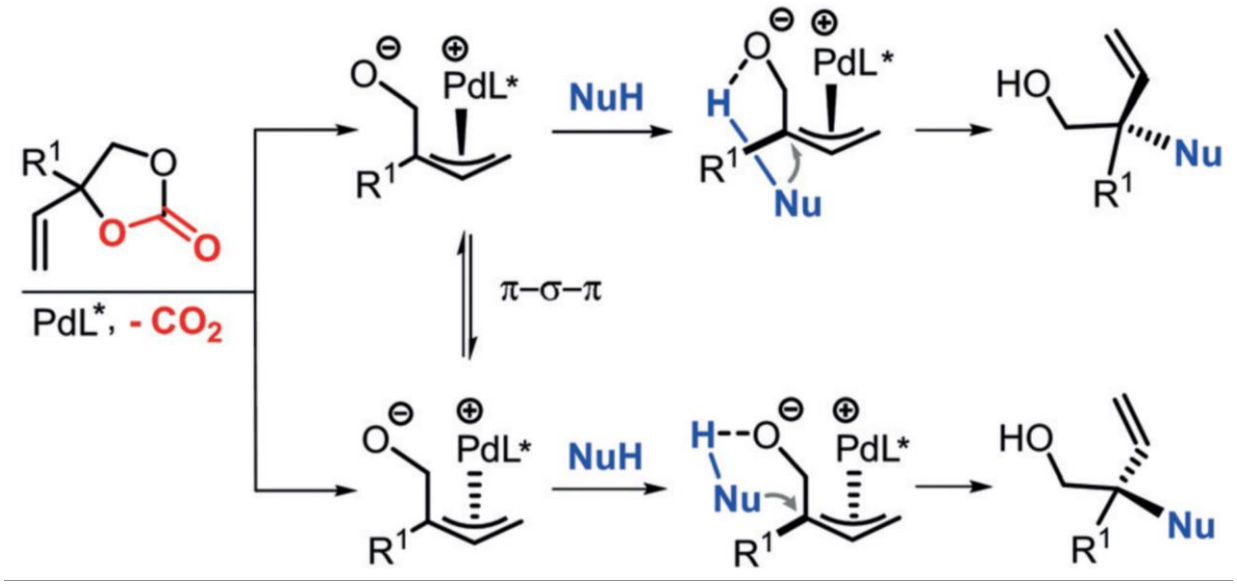


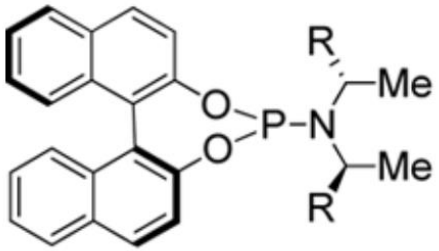


X. Wei, D. Liu, Q. An, W. Zhang, *Org. Lett*. **2015**, *17*, 5768.

Kleij group's work

the first general method toward the synthesis of otherwise challenging sterically demanding chiral a,a-disubstituted allylic aryl amines using VCCs

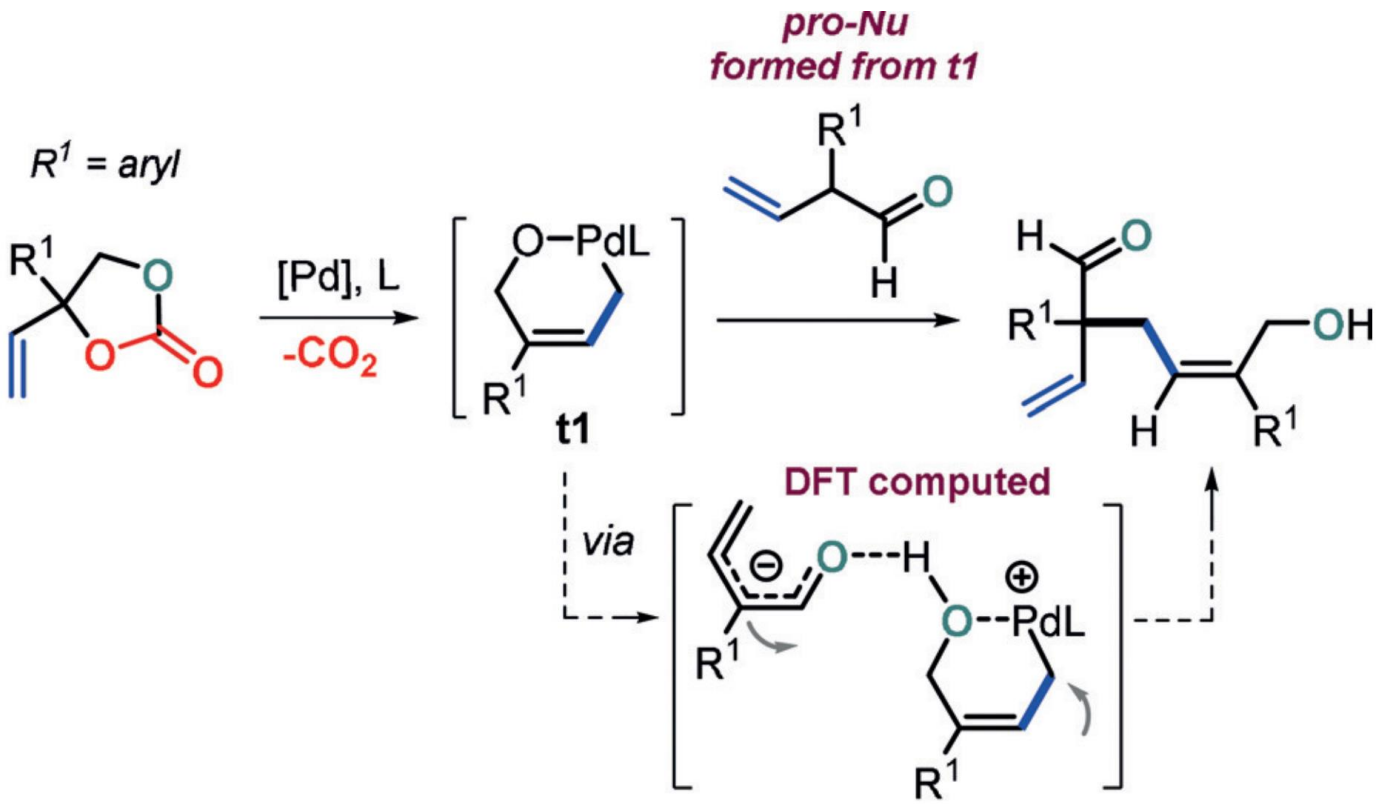




L1: R = Ph

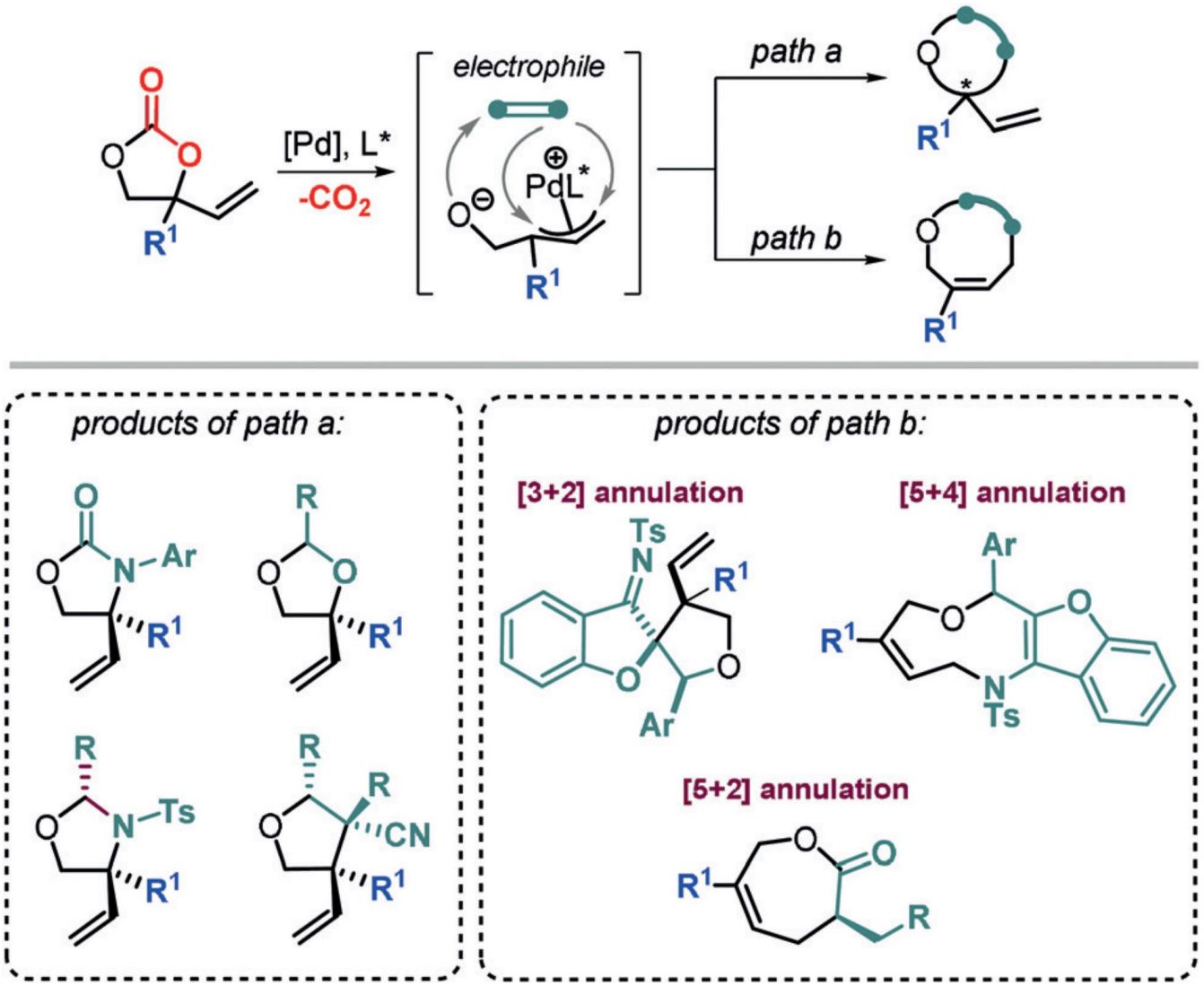
Cai, W. Guo, L. Mart&nez-Rodr&guez, A. W. Kleij, *J. Am. Chem. Soc*. **2016**, *138*, 14194.
J. Xie, W. Guo, A. Cai, E. C.Escudero-Adan, A. W. Kleij, *Org. Lett*. **2017**, *19*, 6388.

VCC itself can produce a nucleophilic species in situ



W. Guo, R. Kuniyil, J. E. Glmez, F. Maseras, A. W. Kleij, *J. Am. Chem. Soc*. **2018**, *140*, 3981.

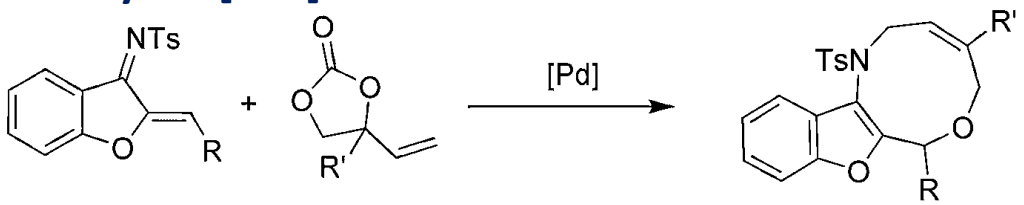
3.2. Reactions of VCCs with Electrophiles



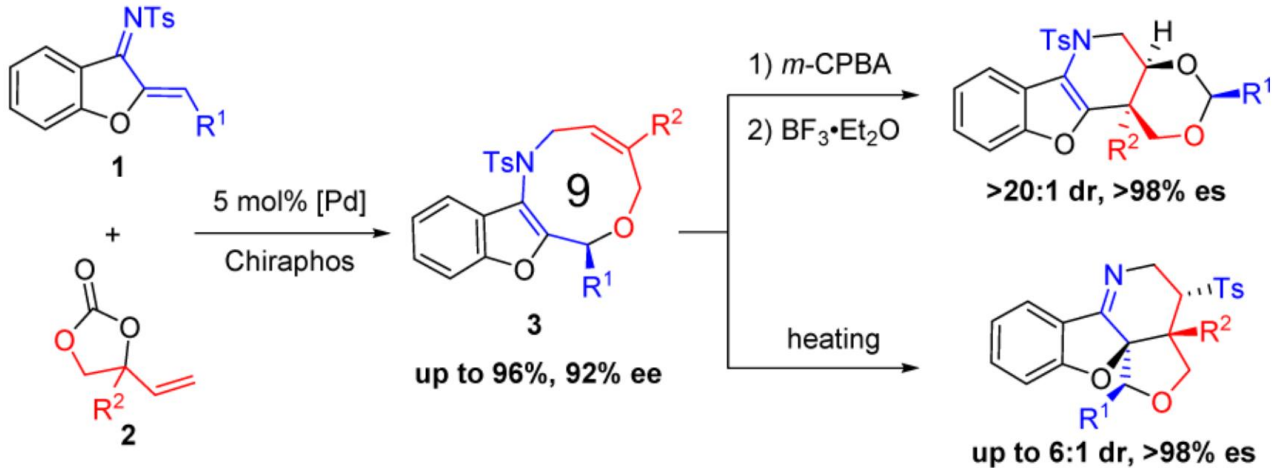
Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang, *Angew. Chem. Int. Ed*. **2014**, *53*, 6439.
A. Khan, L. Yang, J. Xu, L. Y. Jin, Y. J. Zhang, *Angew. Chem. Int. Ed*. **2014**, *53*, 11257.
A. Bayer, U. Kazmaier, *J. Org. Chem*. **2014,** *79*, 8498.
B. I. Khan, C. Zhao, Y. J. Zhang, *Chem. Commun*. **2018,** *54*, 4708.

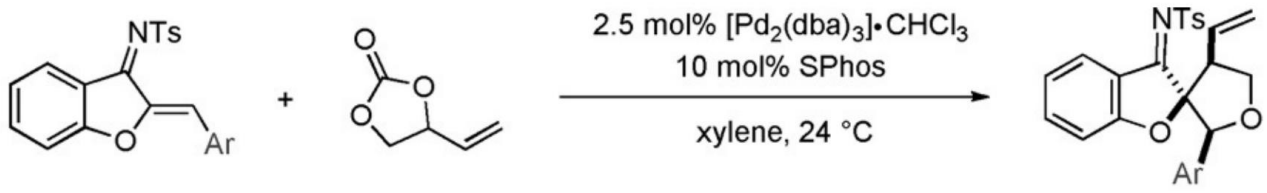
2017, Zhao's group's work

decarboxylative formation of nine-membered heterocycles through Pd-catalyzed [5+4] annulation



R^1: aryl group
[5+4]



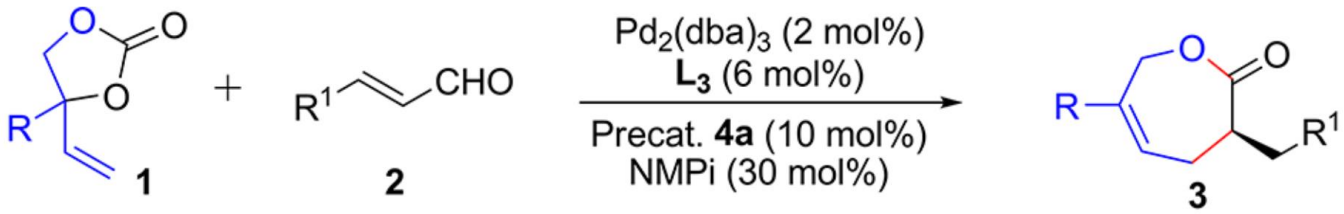


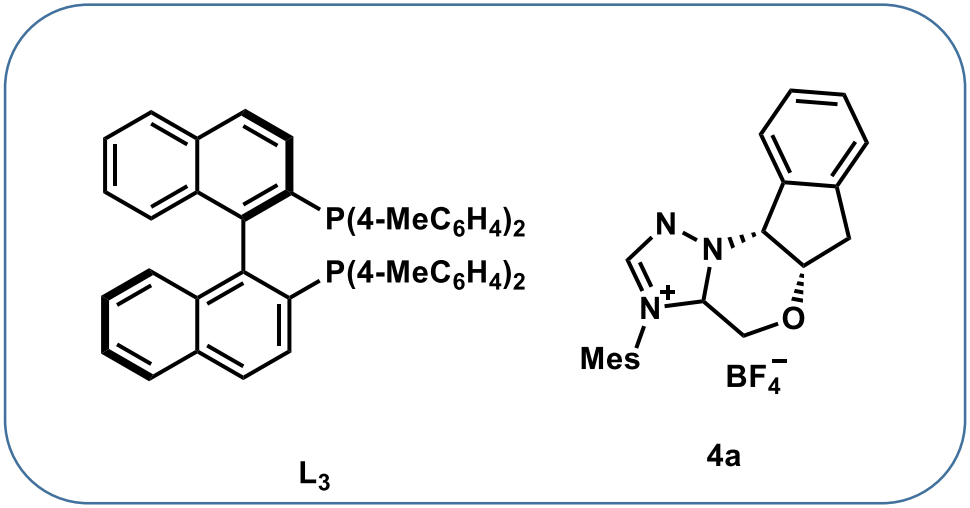
Non-substituted VCCs
[3+2]

L.-C. Yang, Z.-Q. Rong, Y.-N. Wang, Z. Y. Tan, M. Wang, Y. Zhao, *Angew. Chem. Int. Ed*. **2017**, *56*, 2927.
Z.-Q. Rong, L.-C. Yang, S. Liu, Z. Yu, Y.-N. Wang, Z. Y. Tan, R.-Z. Huang, Y. Lan, Y. Zhao, *J. Am. Chem. Soc*. **2017**, *139*, 15304.

2018, Glorius group's work

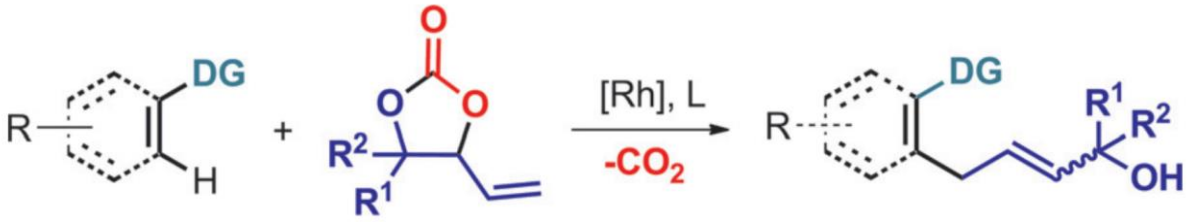
the first VCC-based enantioselective [5+2] cycloaddition using a dual catalyst derived from a chiral NHC and a Pd–allyl species

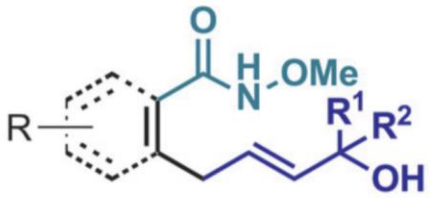




S. Singha, T. Patra, C. G. Daniliuc, F. Glorius, *J. Am. Chem. Soc*. **2018**, *140*, 3551.

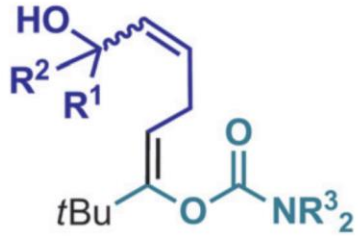
3.3. Allylation through C-H Activation with VCCs



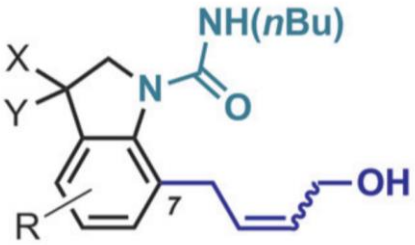


2014, Wang's work

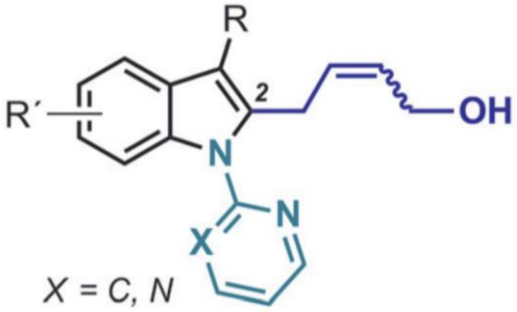
1: *E/Z typically >20:1*
for $R^1 = R^2 = H$



2: *(Z,Z)/(Z,E) up to 8:1*
for $R^1 = R^2 = H$; $R^3 = Me$



3: *Z/E up to 5:1*

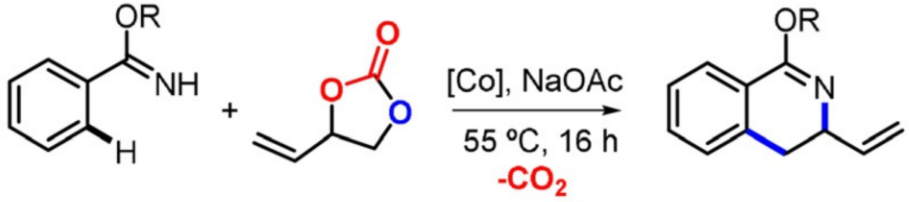


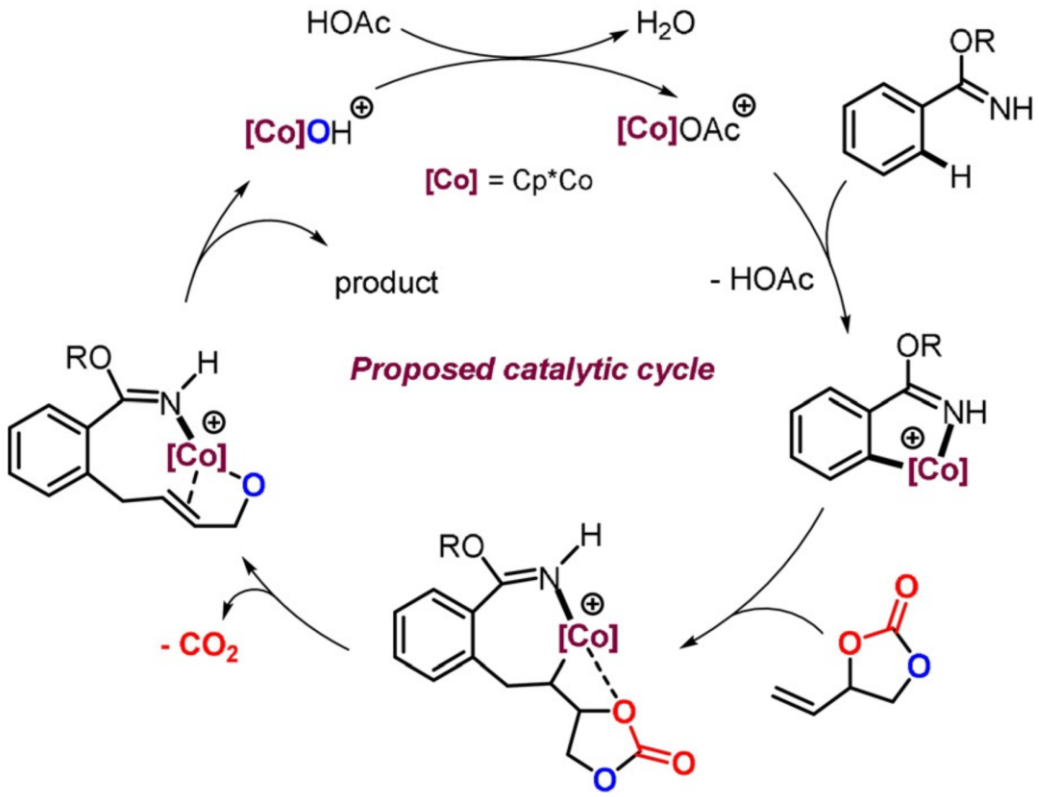
4: *E/Z > 20:1*

S.-S. Zhang, J.-Q. Wu, Y.-X. Lao, X.-G. Liu, Y. Liu, W.-X. Lv, D.-H. Tan, Y.-F. Zeng, H. Wang, *Org. Lett*. **2014**, *16*, 6412.
S.-S.Zhang, J.-Q. Wu, X. Liu, H. Wang, ACS Catal. **2015**, 5, 210.
S. Sharma, S. H. Han, Y. Oh, N. K. Mishra, S. Han, J. H. Kwak, S.-Y. Lee, Y. H. Jung, I. S. Kim, *J. Org. Chem*. **2016**, *81*, 2243.
S. Sharma, Y. Shin, N. K. Mishra, J. Park, S. Han, T. Jeong, Y. Oh, Y. Lee, M. Choi, I. S. Kim, *Tetrahedron* **2015**, *71*, 2435.
H. Wang, M. M. Lorion, L. Ackermann, *Angew. Chem. Int. Ed*. **2017**, *56*, 6339.
Q. Lu, F. J. R. Klauck, F. Glorius, *Chem. Sci*. **2017**, *8*, 3379.

2017, Ackermann group's work

domino C-H/N-H allylation of aryl imidates by a versatile cobalt(III) catalyst



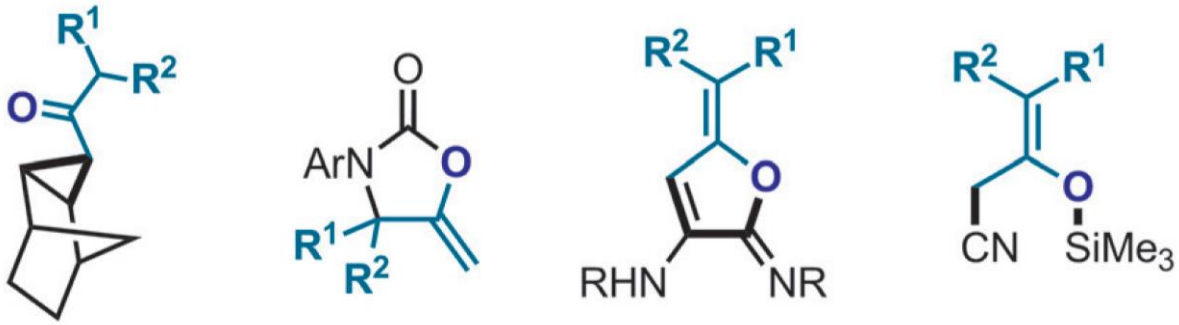


H. Wang, M. M. Lorion, L. Ackermann, *ACS Catal*. **2017**, *7*, 3430.

3.4. Transformations of Cyclic Alkenyl Carbonates

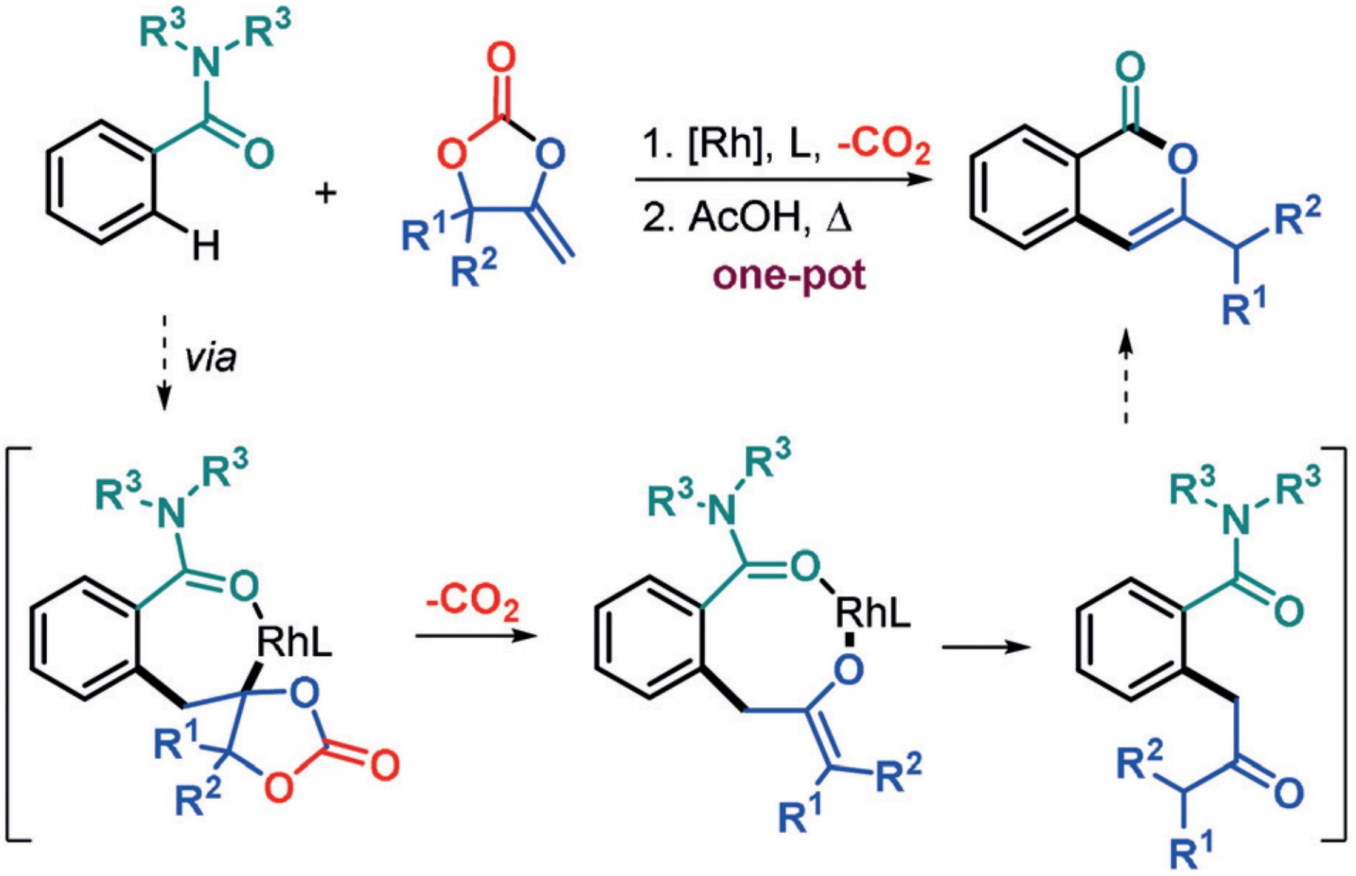
η³-ally-Pd species

η²-Pallada cyclobutanone



K. Ohe, H. Matsuda, T. Ishihara, S. Ogoshi, N. Chatani, S. Murai, *J. Org. Chem*. **1993**, *58*, 1173.
R. Shintani, K. Moriya, T. Hayashi, *Chem. Commun*. **2011**, *47*, 3057.

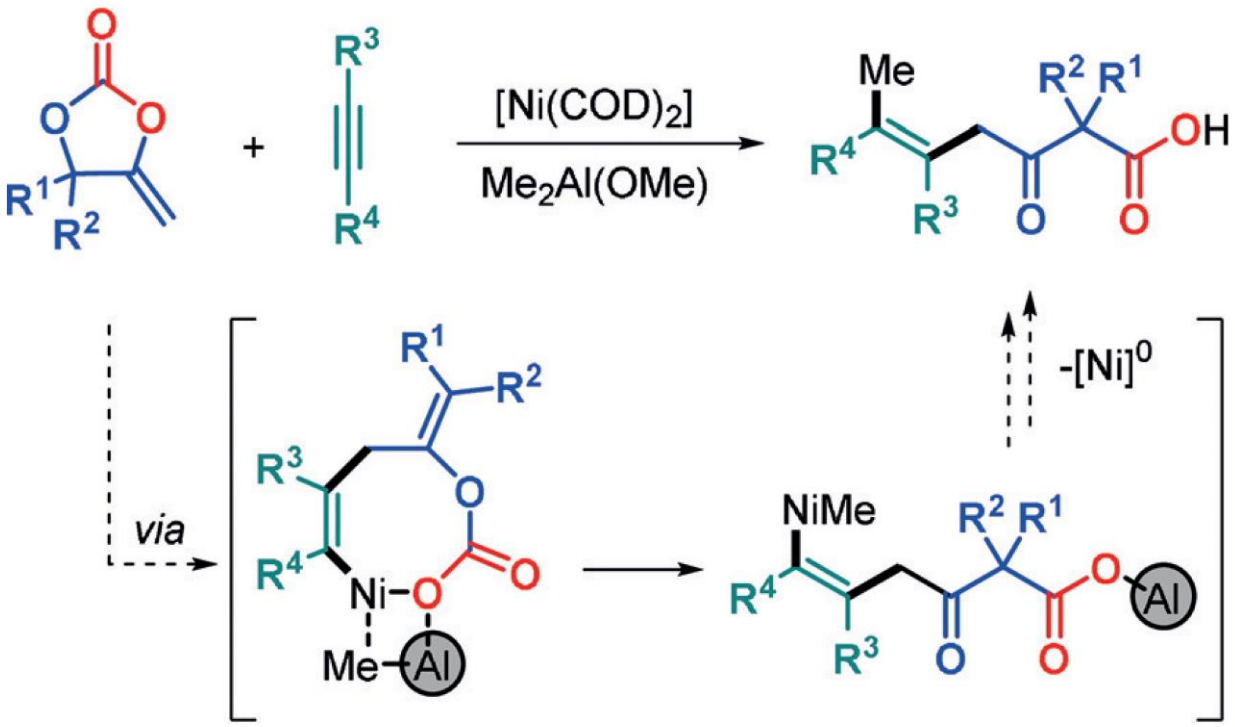
2015, Kakiuchi group's work



Y. Hara, S. Onodera, T. Kochi, F. Kakiuchi, *Org. Lett*. **2015**, *17*, 4850.

2017, Kimura group's work

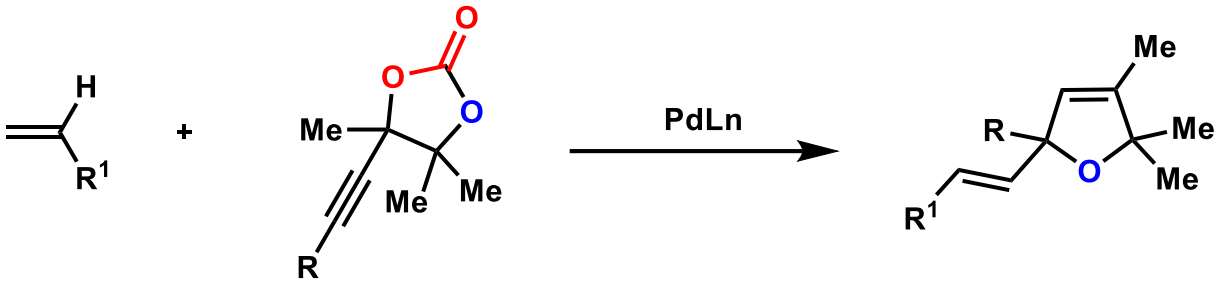
reported Ni-catalyzed coupling reactions between cyclic alkenyl carbonates and internal alkynes

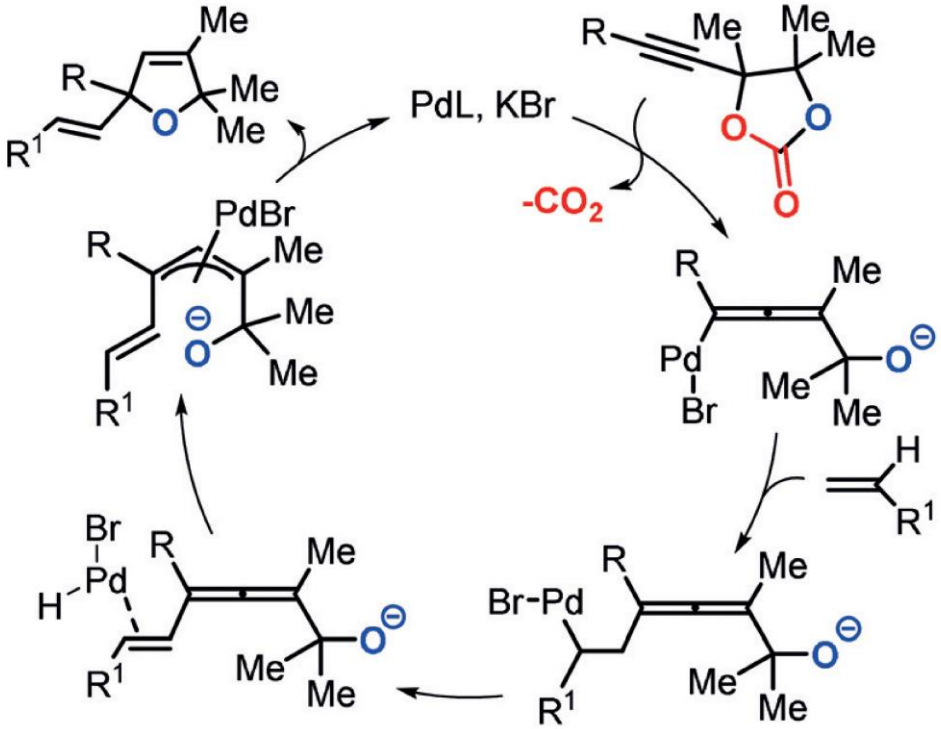


R. Ninokata, T. Yamahira, G. Onodera, M. Kimura, *Angew. Chem. Int. Ed*. **2017**, *56*, 208.

3.5. Conversion of Alkynyl-Substituted Cyclic Carbonates

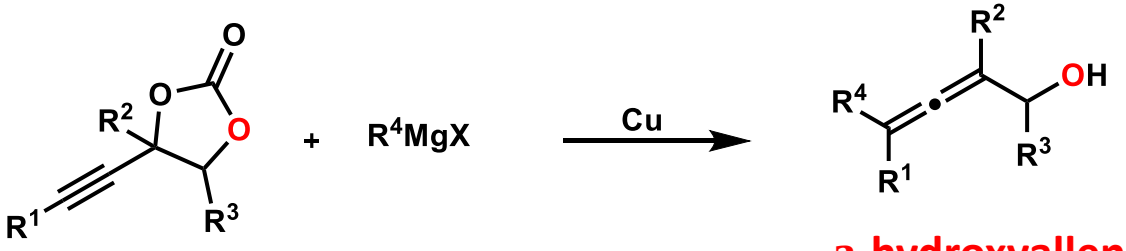
1996, Dixneuf group's work





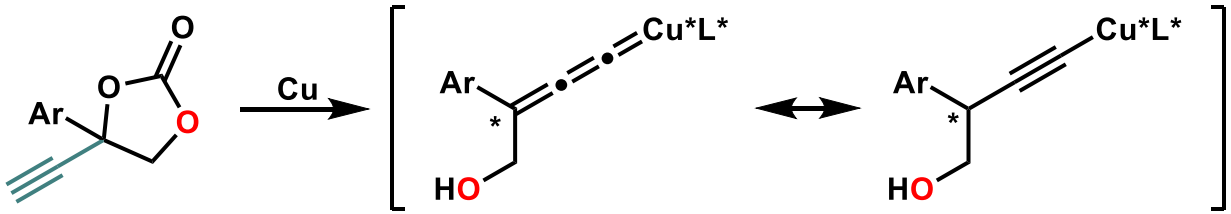
C. Darcel, C. Bruneau, M. Albert, P. H. Dixneuf, *Chem. Commun*. **1996**, *919.*

2009, Krause group's work

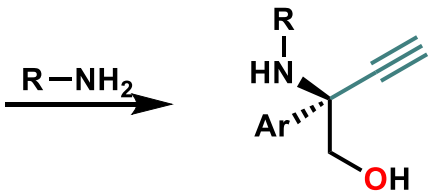


a-hydroxyallens

2018, Zhang group's work



Cu-allenylidene intermediate



β-aminoalcohols

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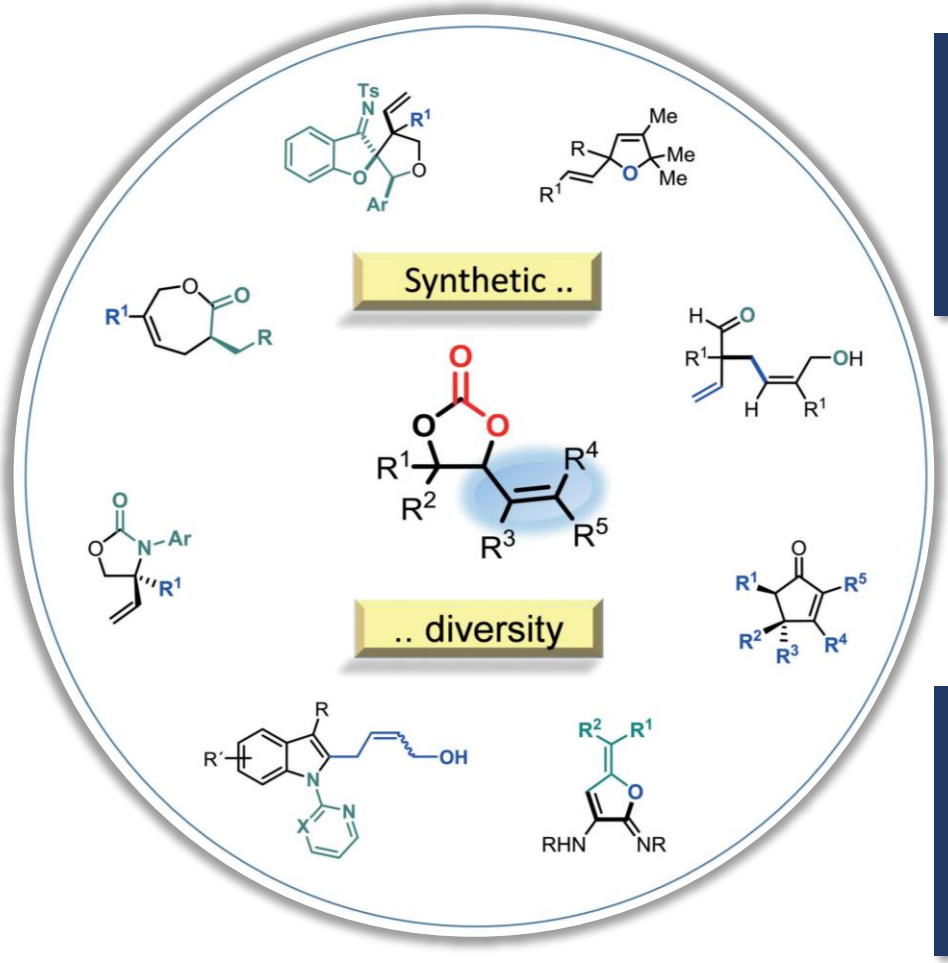
Conclusion



Ease of synthesis and their modular character

Carbamates via Ring-Opening Chemistry

Transition-Metal-Catalyzed decarboxylation

Outlook

the development of cheaper catalysts

Domino or cooperative catalytic systems

Acknowledgement

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