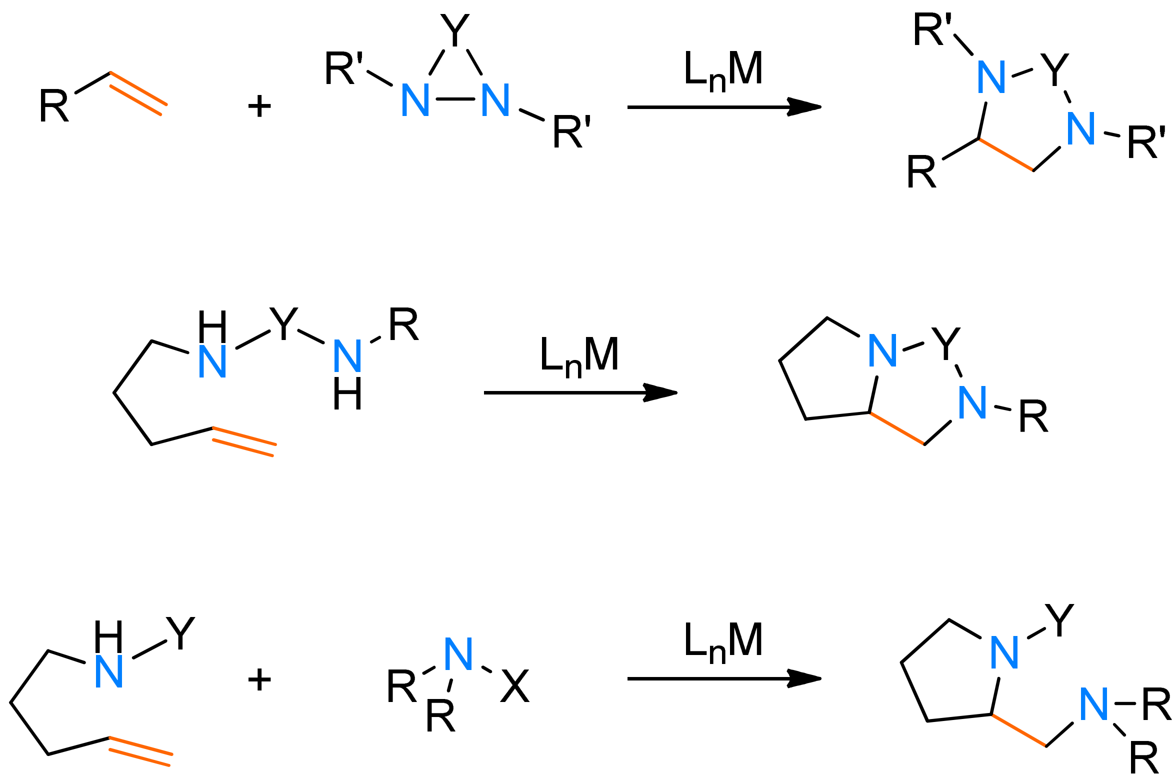
Transition Metal-Catalyzed 1,2-Diamination of Alkenes

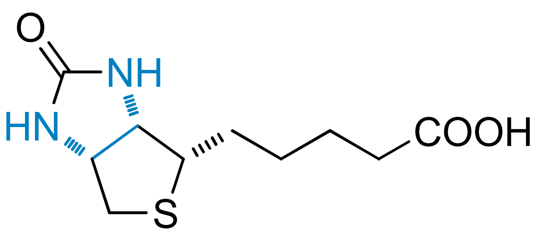


Group Meeting

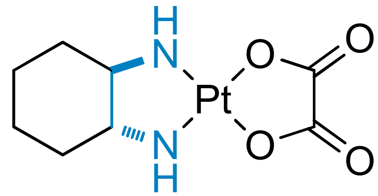
Timothy Chang

04-27-10

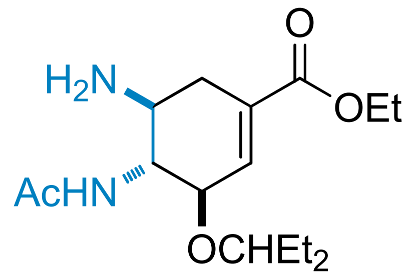
Valuable 1,2-Diamine Motif



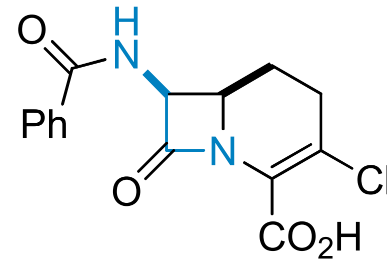
Biotin



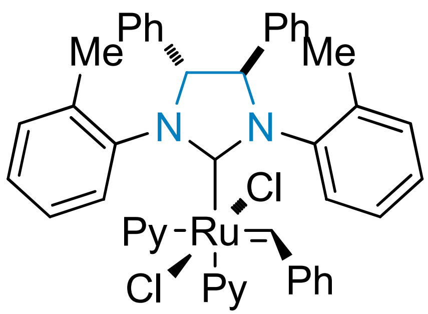
Eloxatin
(Anticaner)



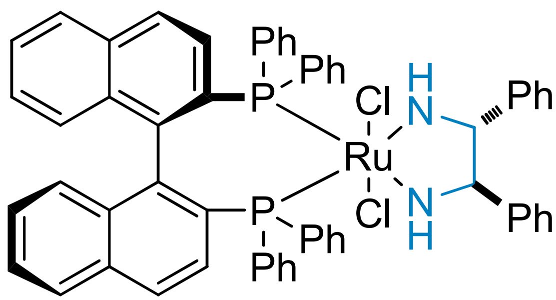
Tamiflu
(Antiviral)



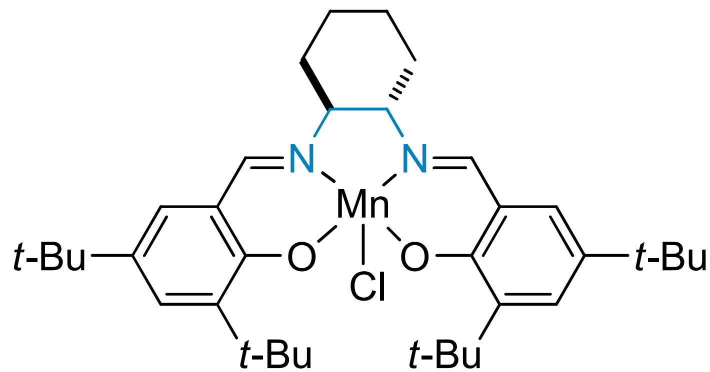
Lorabid
(Antibacterial)



Metathesis Catalyst
(Grubbs)



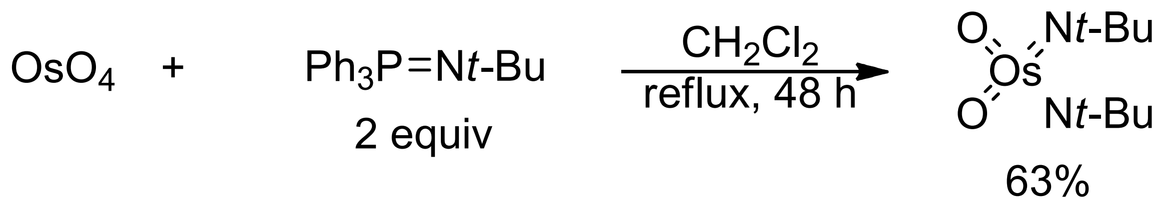
Hydrogenation Catalyst
(Noyori)

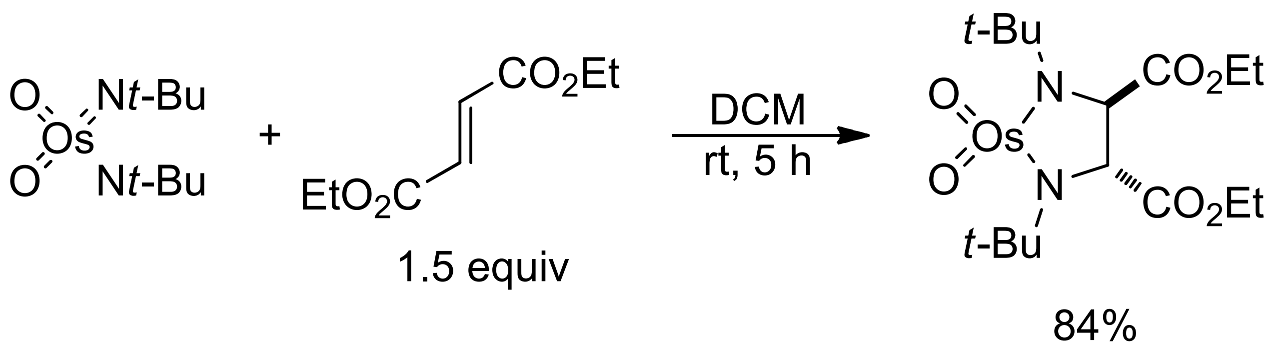


Epoxidation Catalyst
(Jacobsen)

For a review on various synthetic methods of vicinal diamines, see
Lucet, D.; Gall, T. L.; Mioskowski, C. *Angew. Chem. Int. Ed.* **1998**, *37,* 2580.
For a review on the transition-metal catalyzed diamination, see
Cardona, F.; Goti A. *Nature Chemistry* **2009**, *1,* 269.

Osmium Mediated Diamination



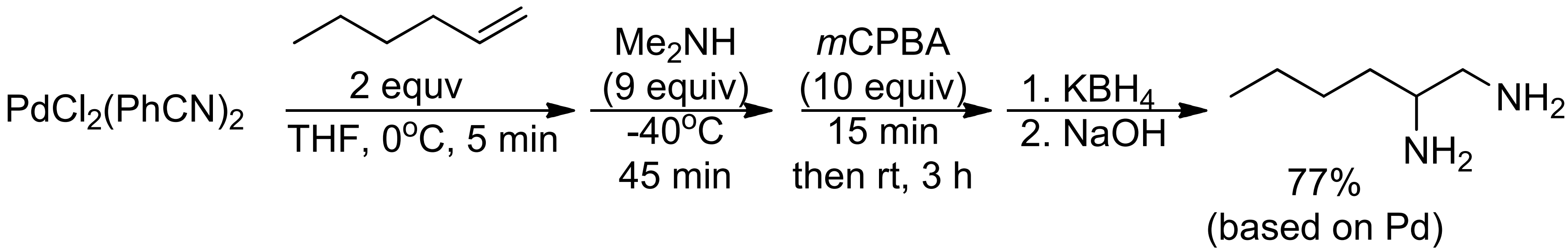


recovered unchanged from preparative GLC at 250 ^{o}C

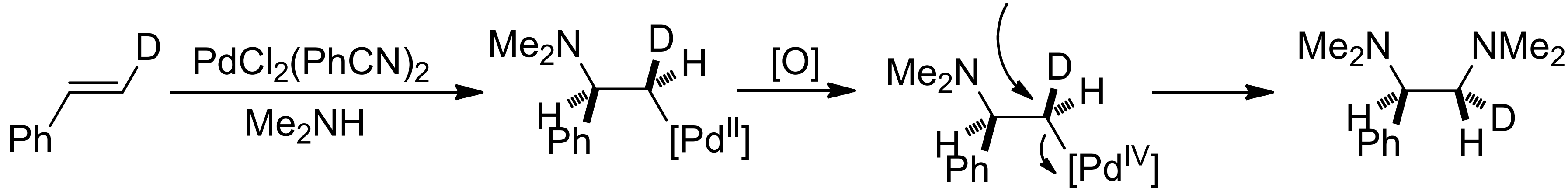
- Cis-disubstituted olefins react sluggishly.
- Different amounts of hydroxyaminated products were observed for other olefins such as styrene and 1-decene.

Chong, A. O.; Oshima, K. Sharpless, K. B. **1977** *J. Am. Chem. Soc. 99, 3420.*
For a review on osmium mediated diamination, see Muñiz, K. *New J. Chem.* **2005**, *29*, 1371.

Palladium Mediated Diamination

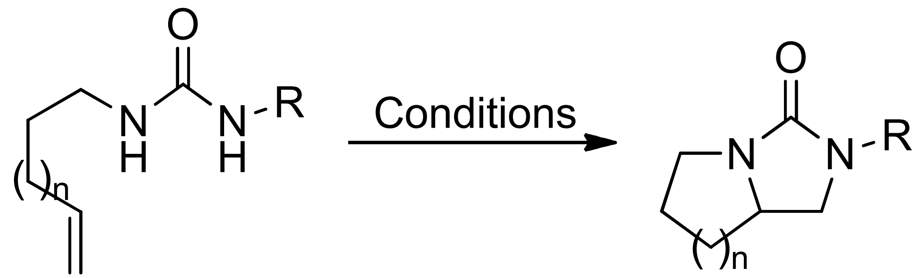


Proposed Mechanism:

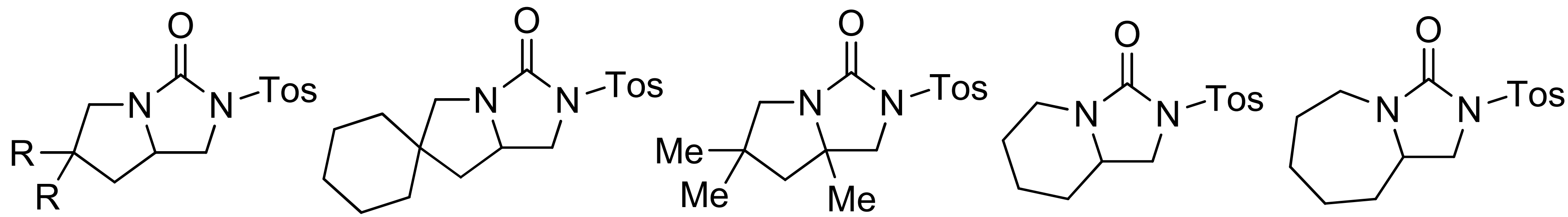


Bäckvall, J.-E. C. *Tet. Lett.* **1978**, *19,* 163.

Palladium Catalyzed Oxidative Intramolecular Diamination



Conditions:
A: $Pd(OAc)_2$ (5 mol %), $PhI(OAc)_2$ (2.2 equiv), NMe_4Cl/NaOAc (1 equiv), CH_2Cl_2, RT, 12 h.
B: $Pd(OAc)_2$ (25 mol%), $PhI(OAc)_2$ (2.2 equiv), CH_2Cl_2, RT, 48 h.
C: $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (2.2 equiv), CH_2Cl_2, RT, 12 h.



R = Me, 92% (A)
R = Ph, 95% (A)

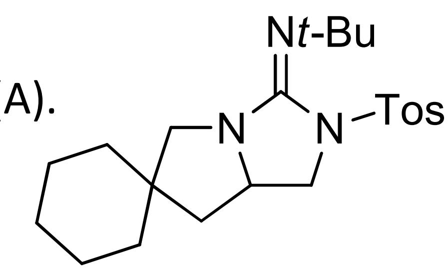
91% (A)

94% (A)

86% (B)

89% (C)

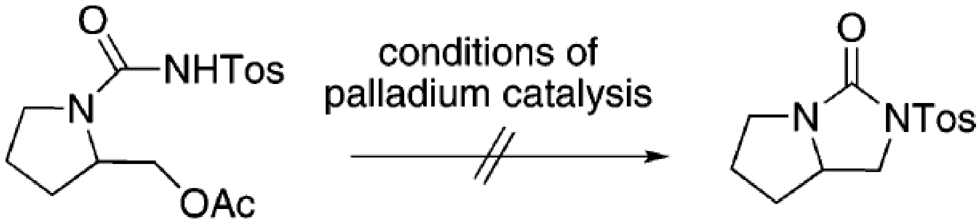
- Base is required (generated in situ from NMe_4Cl/NaOAc) for reactivity (A).
- No reactivity difference by using Me_4NOAc.
- Chlorinated intermediate may not be involved.
- Sulfamide substrates gave aminoacetoxylated product.



95% (A)
$PhI(OAc)_2$ (2 equiv)

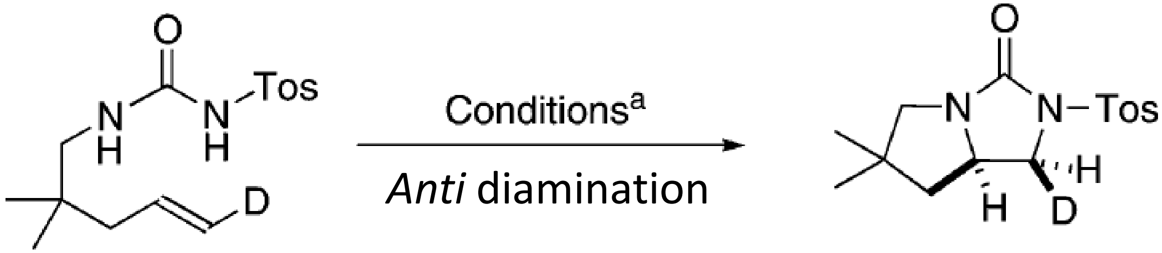
Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2005**, 127, 14586.

The Overall Stereochemistry of Diamination



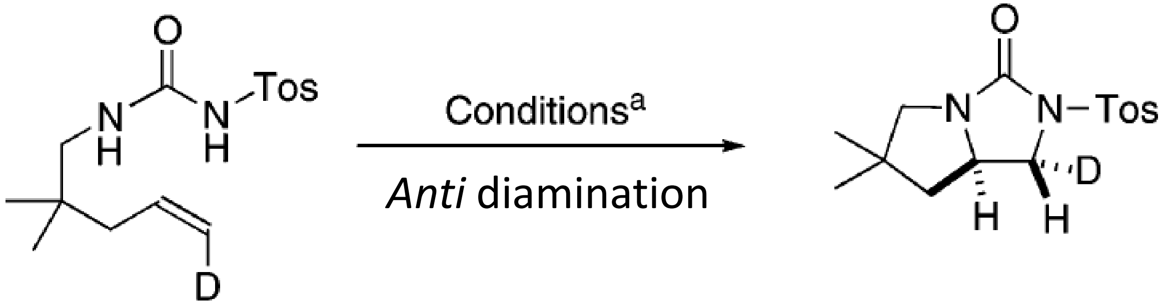
The acetoxy intermediate is not involved.

Conditions:
$Pd(OAc)_2$ (5 mol%)
$PhI(OAc)_2$ (2 equiv)
NMe_4Cl/NaOAc (1 equiv)
CH_2Cl_2, RT, 12 h



(*E*)-1b-d$_1$

***syn*-2b-d$_1$** (J_{syn} = 8.8 Hz)



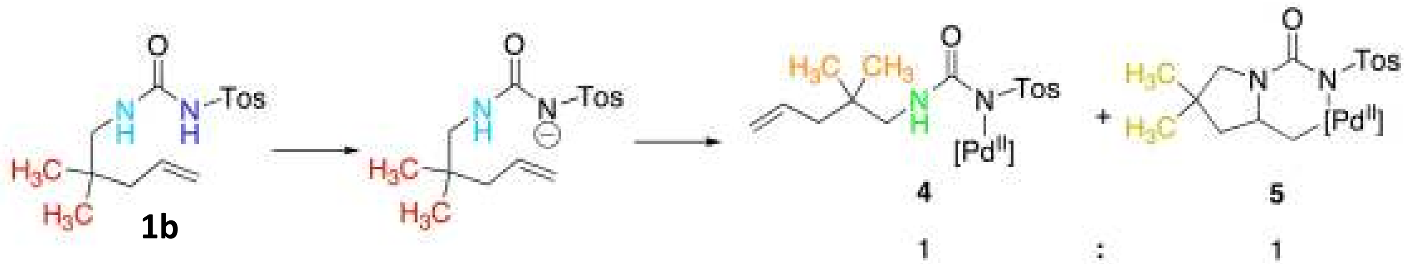
(*Z*)-1b-d$_1$

***anti*-2b-d$_1$** (J_{trans} = 4.4 Hz)

Which step involves the inversion of the configuration?

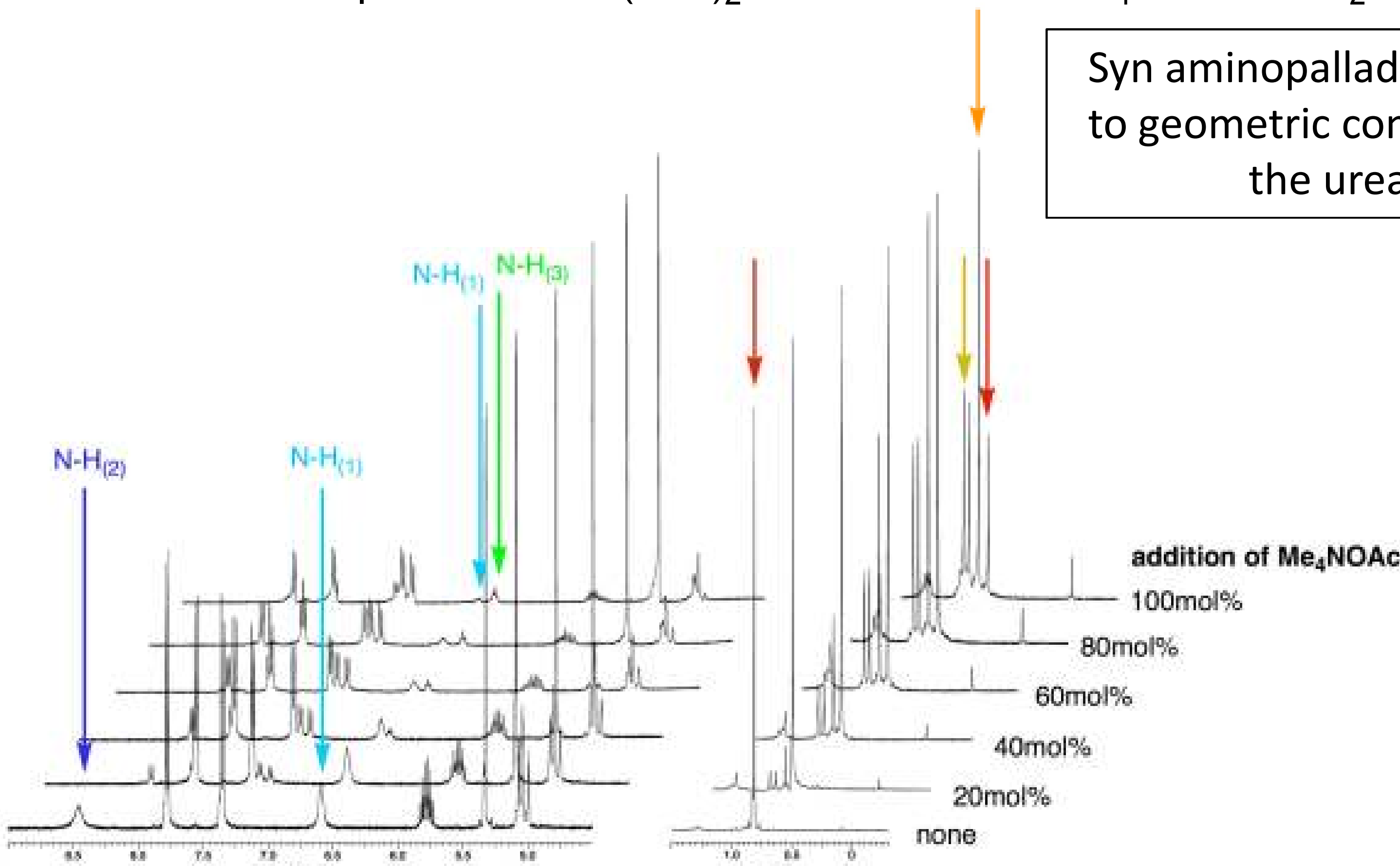
Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130*,* 763.

Stereochemistry of Aminopalladation and Titration Experiment



Not isolable

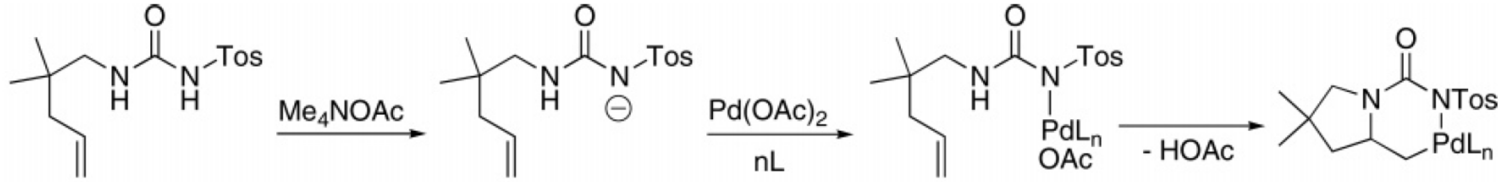
NMR titration experiment of $Pd(OAc)_2$ / **1b** mixture with Me_4NOAc in CD_2Cl_2.



Syn aminopalladation due to geometric constraint of the urea.

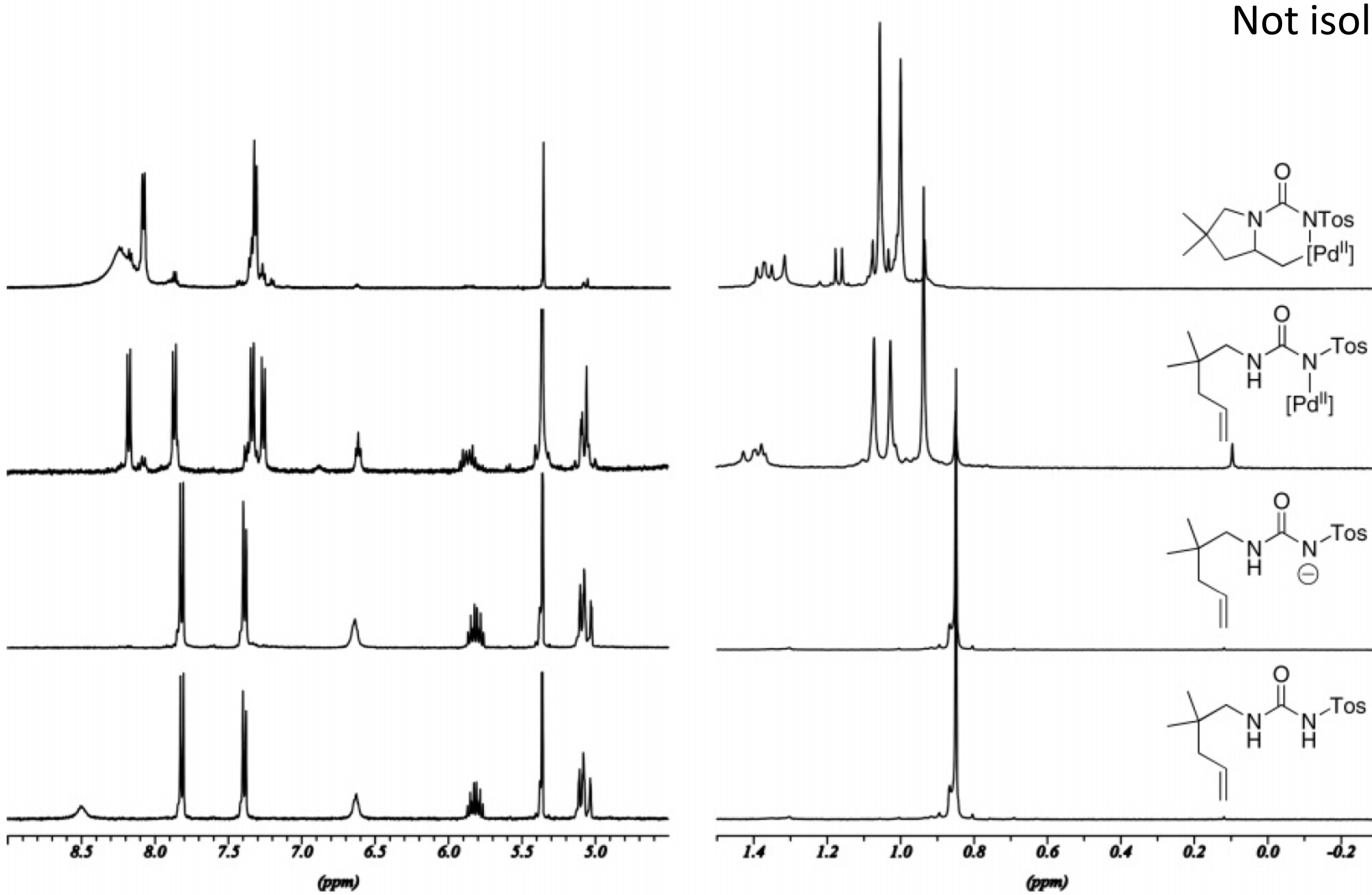
Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130, 763.

Stereochemistry of Aminopalladation and Titration Experiment



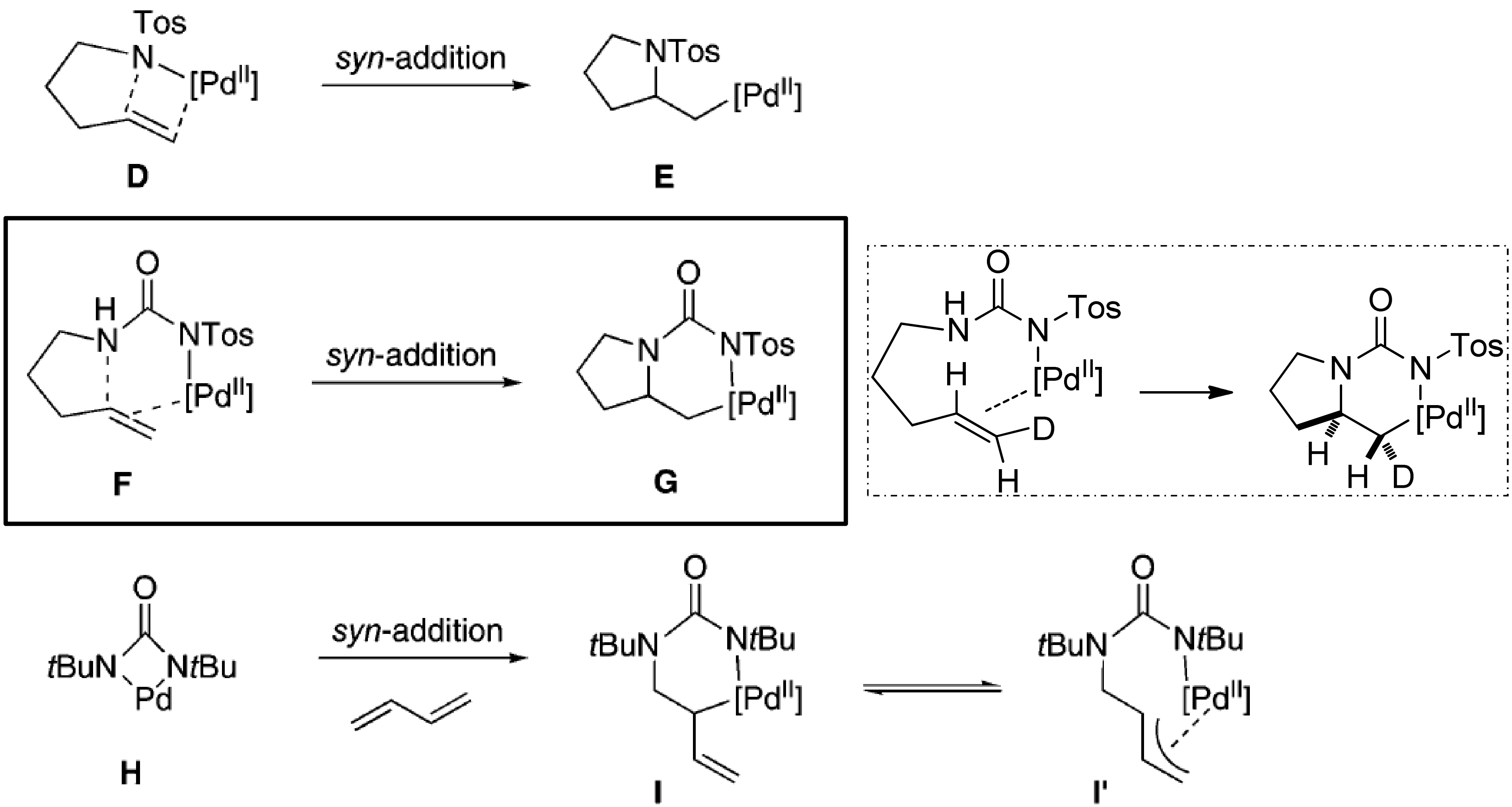
1b **1b-H+** **4** **5**

Not isolable



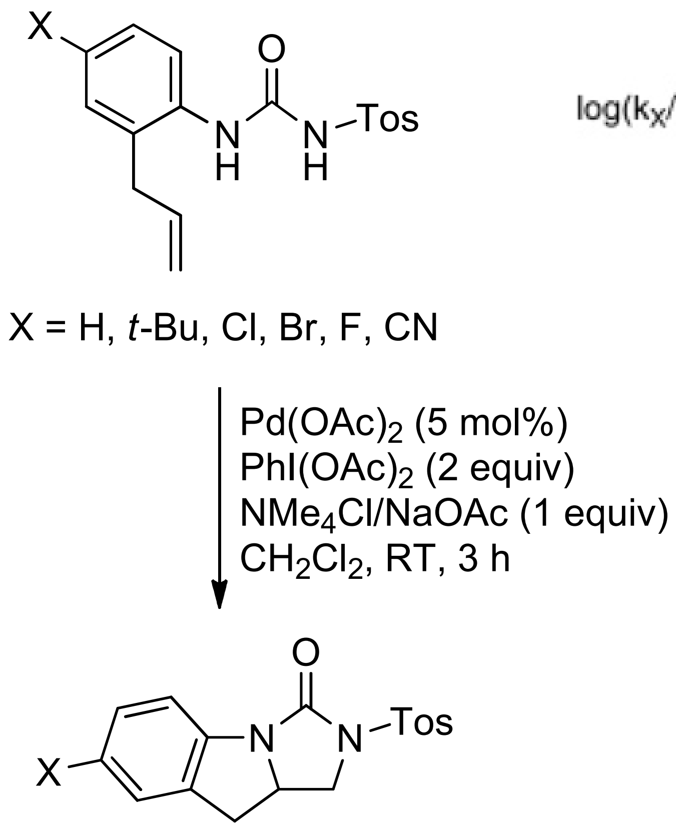
Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130*,* 763.

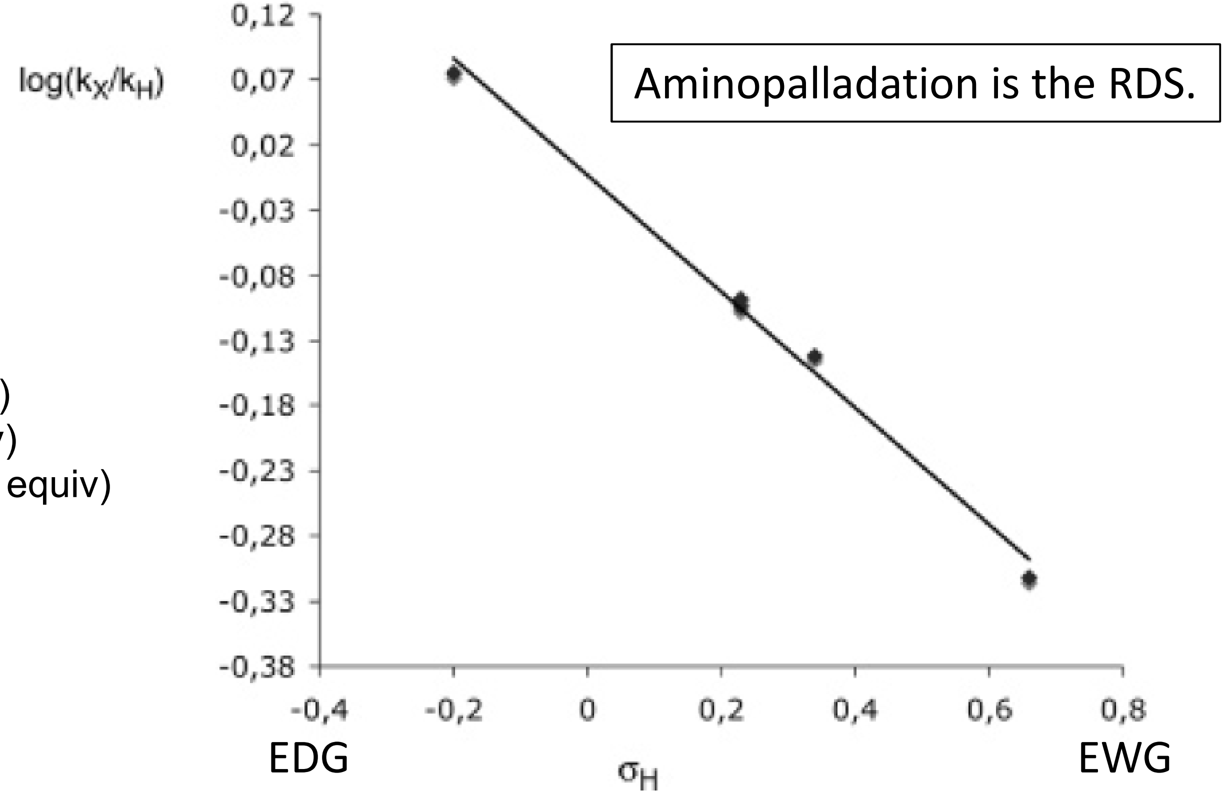
Modes of Syn Aminopalladation



Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130*,* 763.

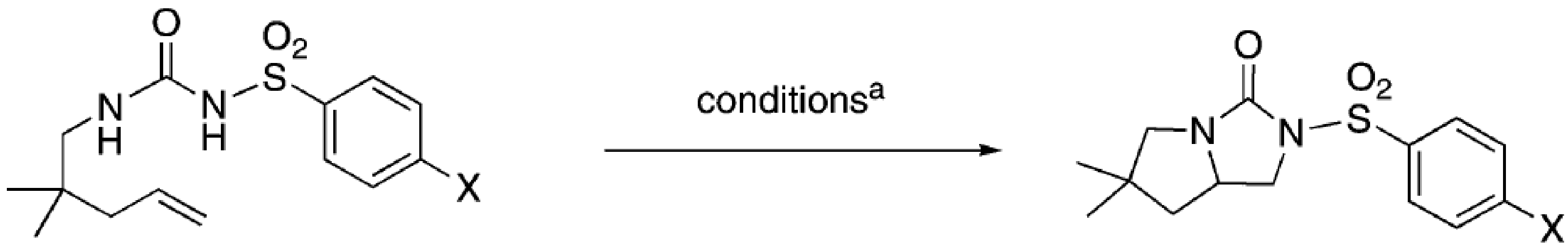
Rate Determining Step





Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130, 763.

Proposed Mechanism for the Second C-N Bond Formation



1s: X = H,
1b: X = Me,
1t: X = Cl,
1u: X = F

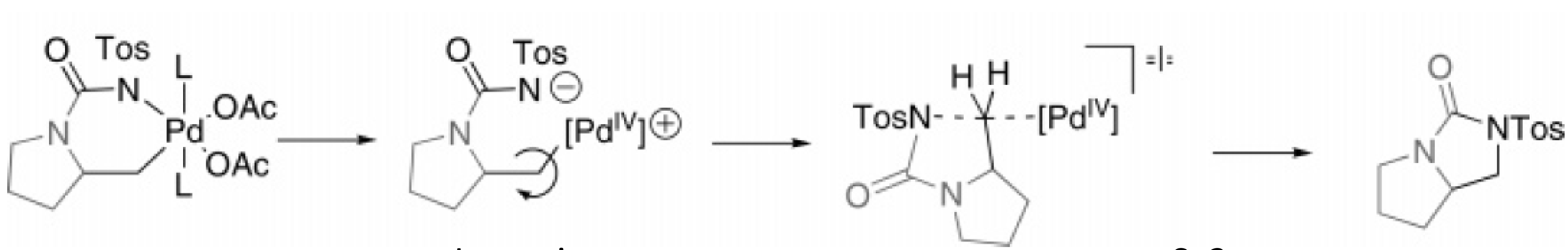
competition experiments:

$\frac{k_H}{k_{Me}} = 1.04$ $\frac{k_H}{k_{Cl}} = 0.95$ $\frac{k_H}{k_F} = 1.06$

2s: 93%
2b: 92%
2t: 92%
2u: 86%

Conditions: $Pd(OAc)_2$ (5 mol%), $PhI(OAc)_2$ (2 equiv), $NMe_4Cl/NaOAc$ (1 equiv), CH_2Cl_2, RT, 2 h

The second C-N bond formation is not the RDS.

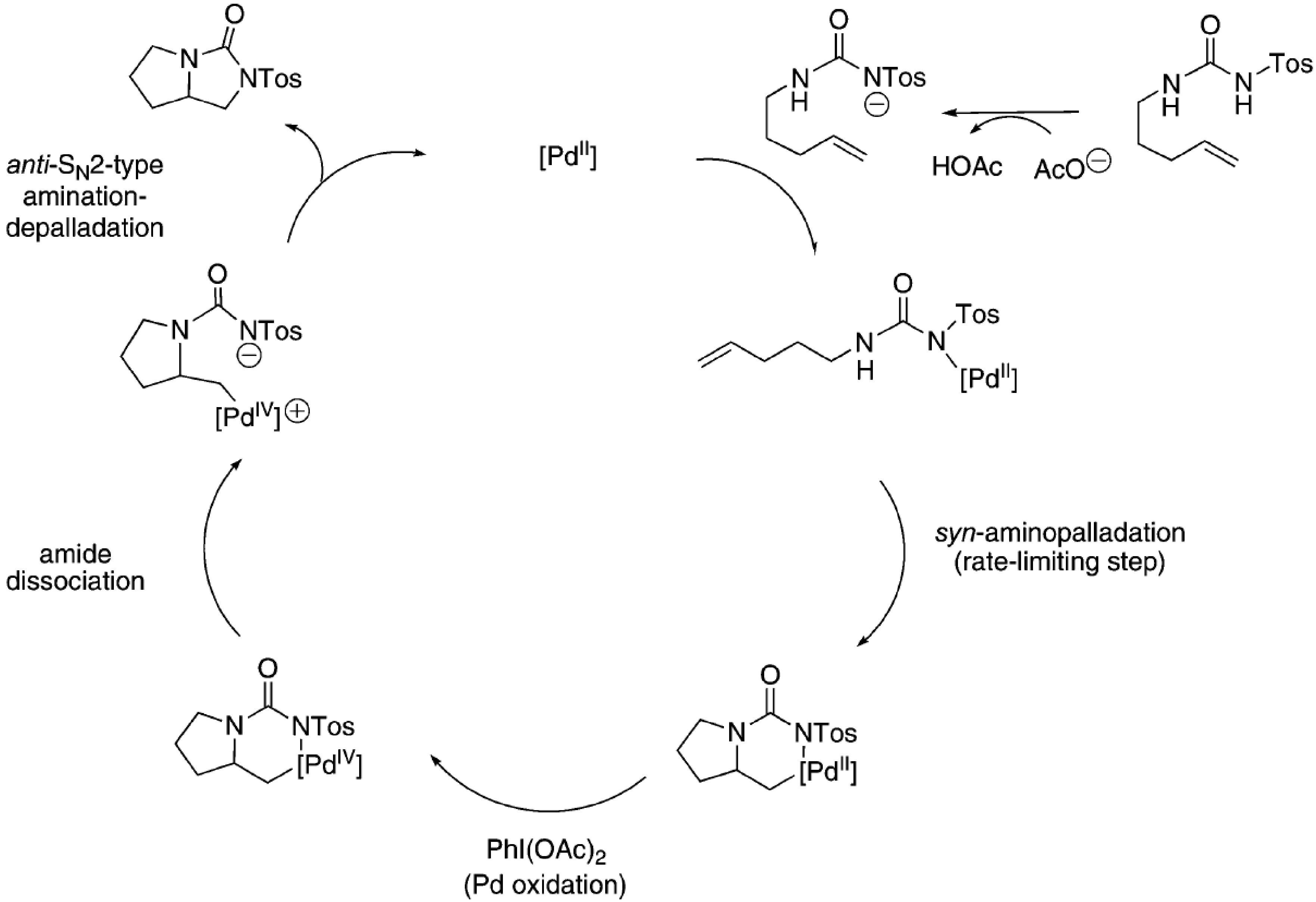


Ion pair
Electrophilicity of -$\underline{C}H_2$-$[Pd^{IV}]^+$ is enhanced

S_N2 type
reductive elimination

Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130, 763.

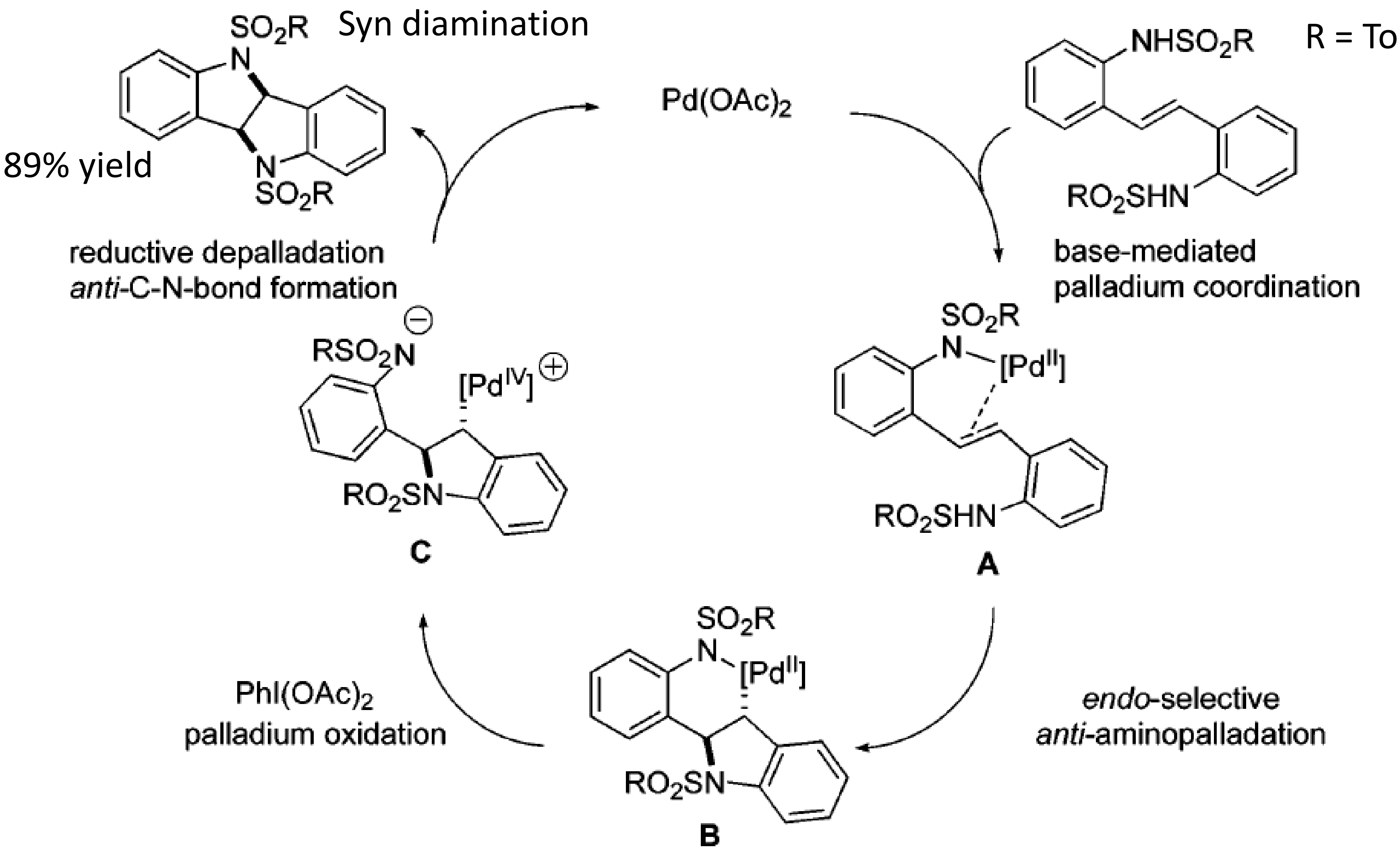
Proposed Catalytic Cycle



Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2008**, 130*,* 763.

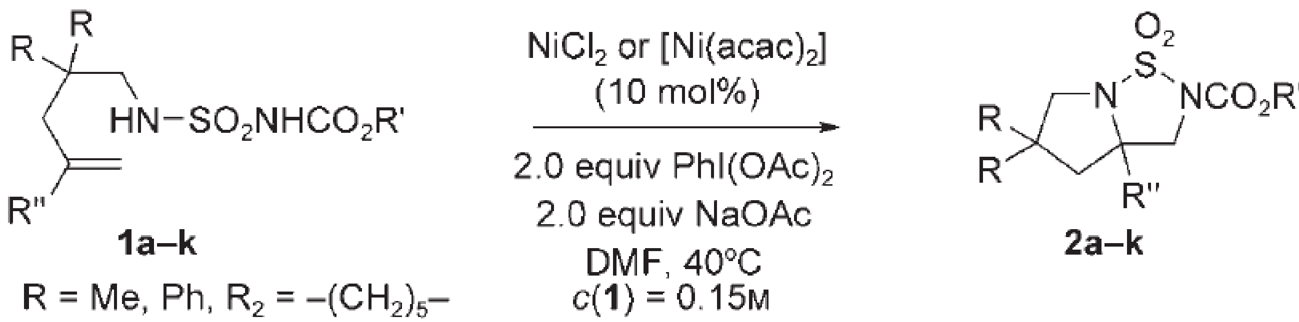
An Example of Syn Diamination

Conditions: $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (1.4 equiv), $NMe_4Cl/NaOAc$ (1.1 equiv), DMF, RT, 14 h

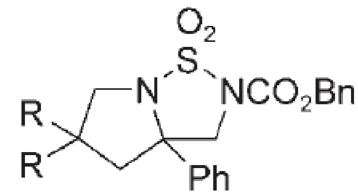


Muñiz, K. *J. Am. Chem. Soc.* **2007**, 129*,* 14542.

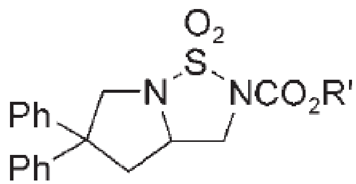
Nickel-Catalyzed Diamination Using Sulfamide



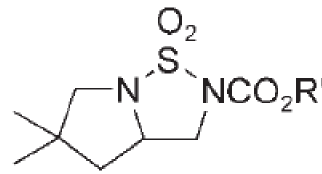
R = Me, Ph, R_2 = –$(CH_2)_5$–
R' = Me, Bn, *t*Bu
R'' = H, Me, Ph



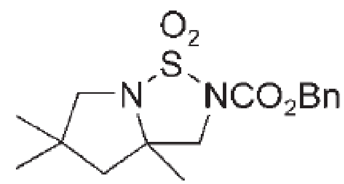
2j: R = Ph: 72% ($NiCl_2$)
2k: R_2 = –$(CH_2)_5$–: 80% ($NiCl_2$)



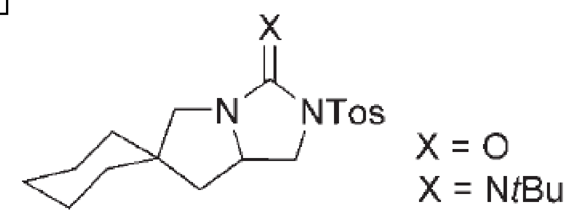
2a: R' = Me: 92% ($NiCl_2$)
92% ([Ni(acac)$_2$])



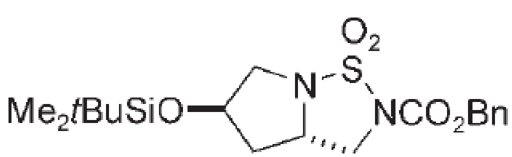
2d: R' = Me: 78% ($NiCl_2$)
2e: R' = Bn: 93% ($NiCl_2$)



2g: 94% ($NiCl_2$)

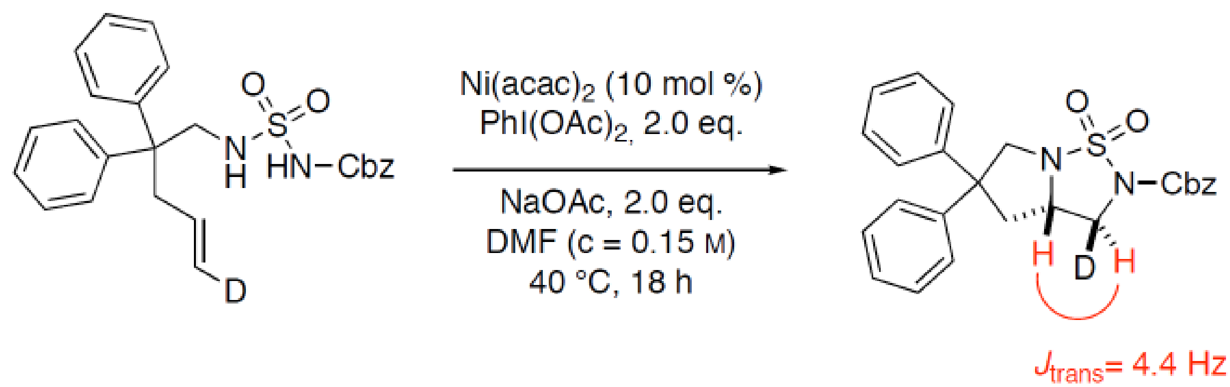


7a: 68% ($NiCl_2$), **81% ([Ni(acac)$_2$])**
7b: 61% ($NiCl_2$), **70% ([Ni(acac)$_2$])**



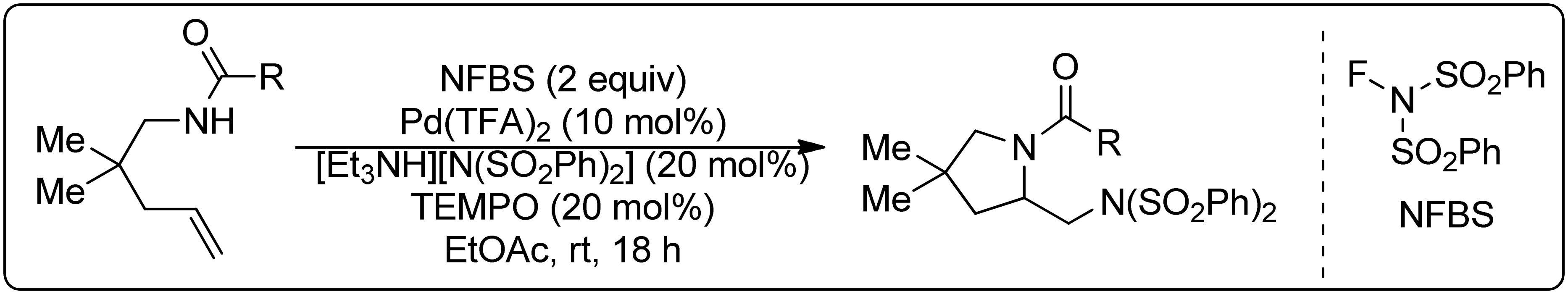
2p: 74%, d.r. >20:1

Terminal alkenes are good substrates.



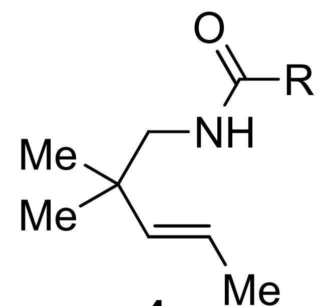
Muñiz, K.; Streuff, J.; Hövelmann, C. H.; Núñez, A. *Angew. Chem. Int. Ed.* **2007**, 46, 7125.

Pd-Catalyzed Diamination of Terminal Alkenes Using NFBS

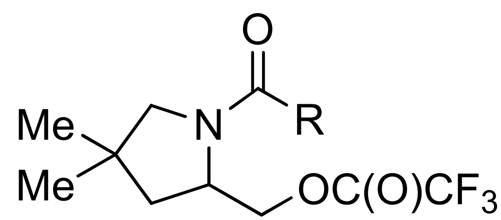


entry	R	alkene	product	% yield
1	*p*-Tol	**1a**	**3a**	77
2	Ph	**1b**	**3b**	74
3	*p*-$MeOC_6H_4$	**1c**	**3c**	82
4	*p*-BrC_6H_4	**1d**	**3d**	73
5	OBn	**1e**	**3e**	59
6	O*t*-Bu	**1f**	**3f**	30
7	NHBn	**1g**	**3g**	57
8	NHPh	**1h**	**3h**	49

Byproducts



4a

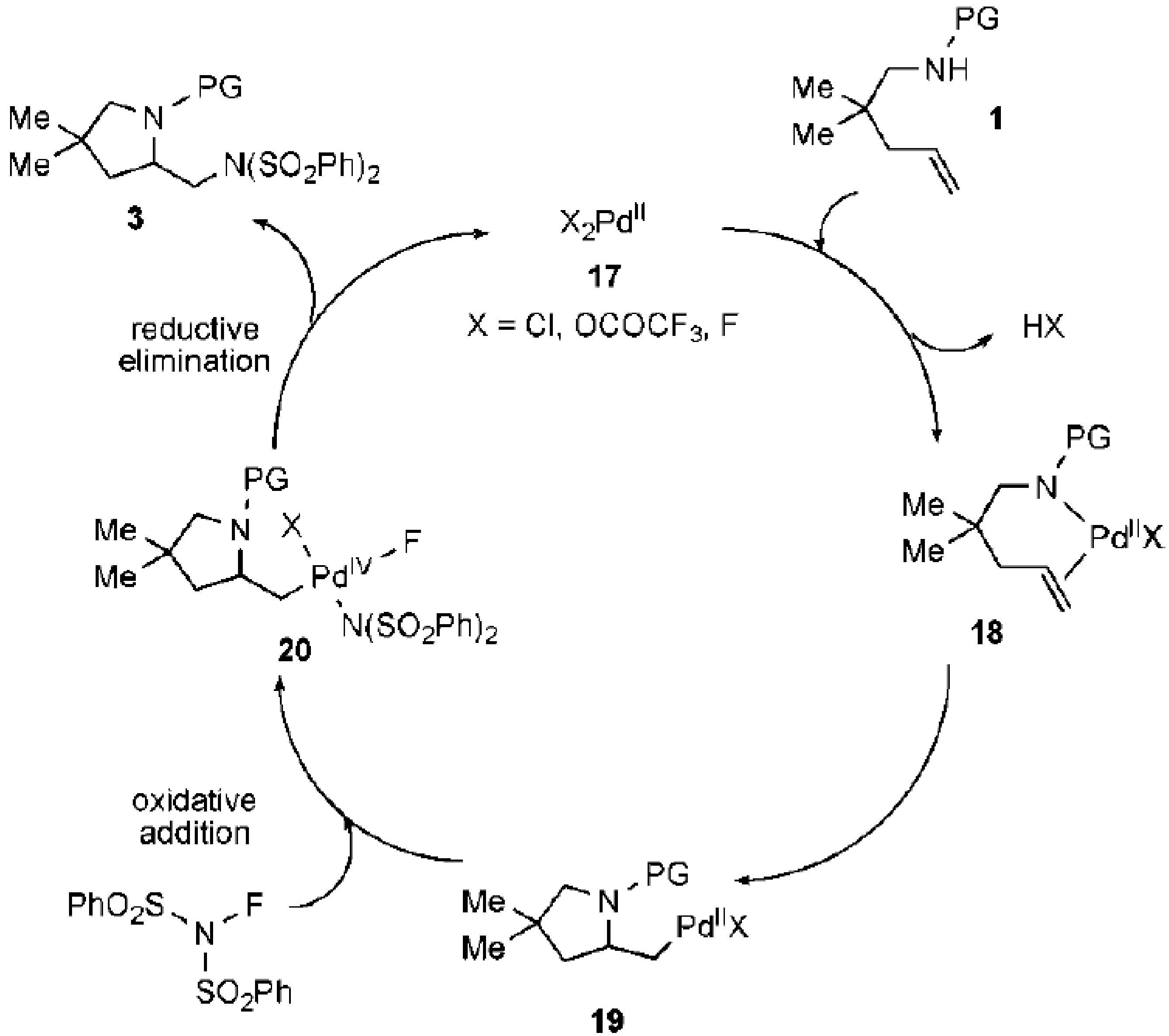


5a

Purposes of additives:
TEMPO reduces isomerization product **4a**.
$[Et_3NH][N(SO_2Ph)_2]$ reduces amount of **5a**.

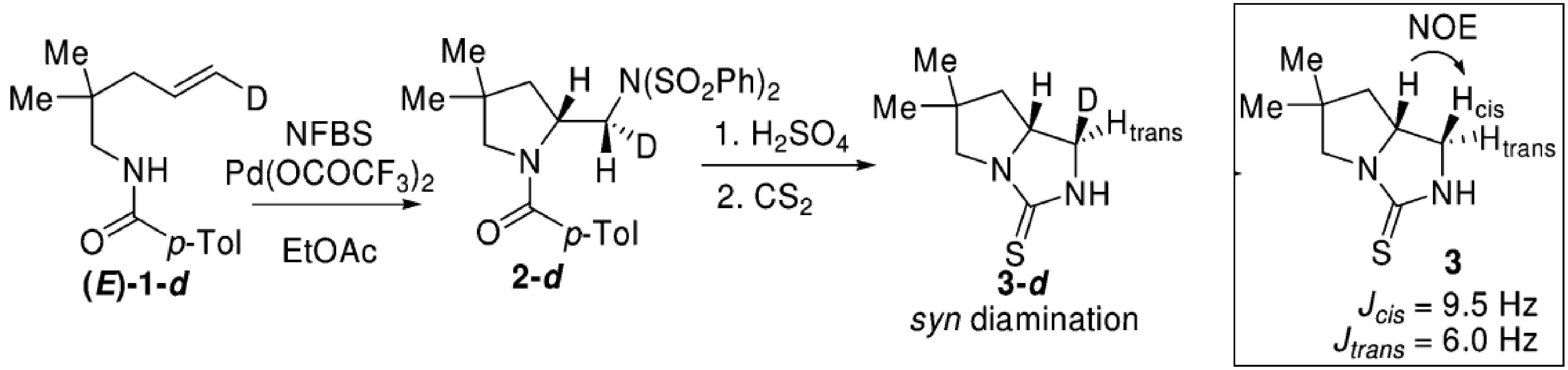
Sibbald, P. A.; Michael, F. E. *Org. Lett.* **2009**, 11*,* 1147.

Proposed Catalytic Cycle



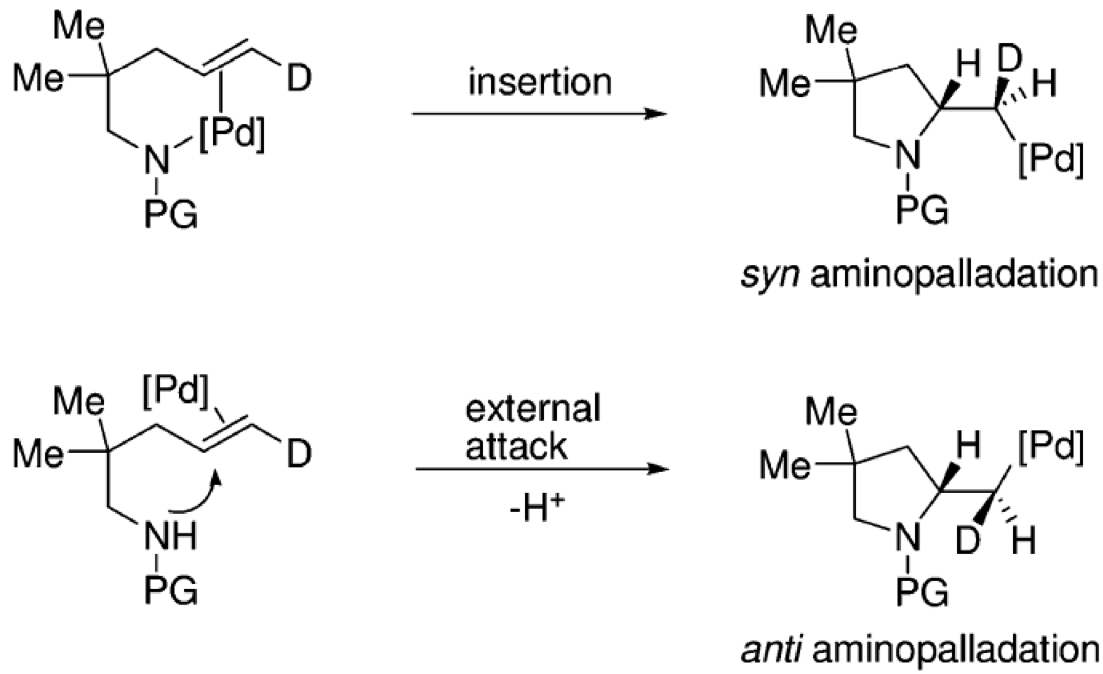
Sibbald, P. A.; Michael, F. E. *Org. Lett.* **2009**, 11*,* 1147.

The Overall Stereochemistry of Diamination



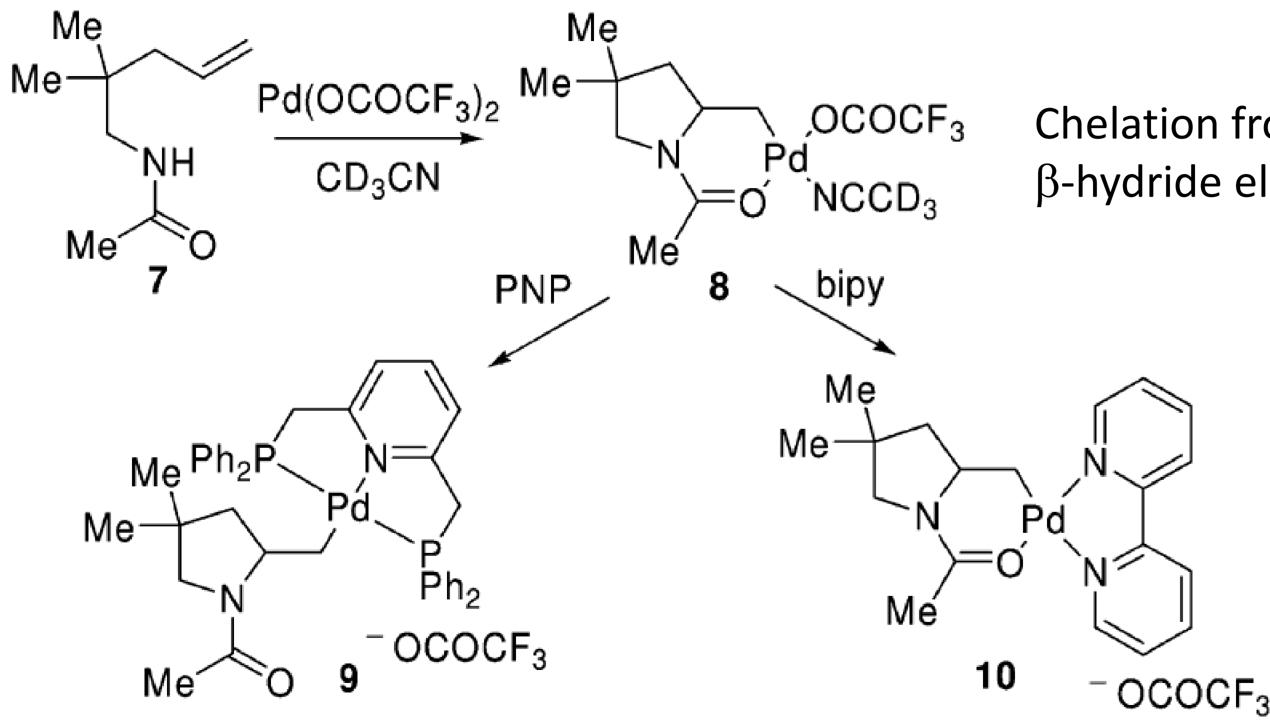
Mechanistic implications of the two C-N bond formations from the overall *syn* diamination:

1. *Anti* aminopalladation followed by S_N2 displacement of the C-Pd bond.
2. *Syn* aminopalladation followed by C-N reductive elimination (retentive).

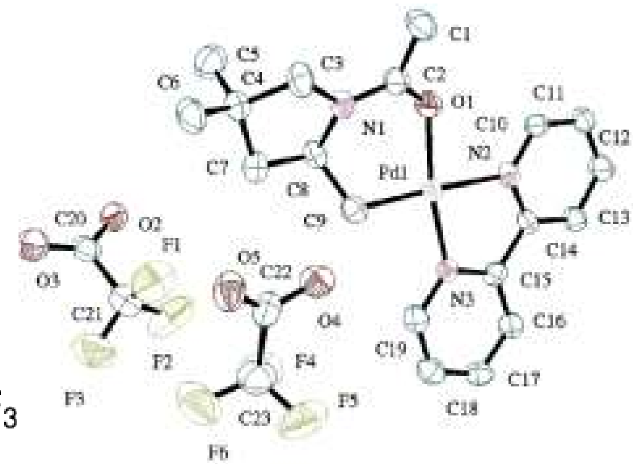


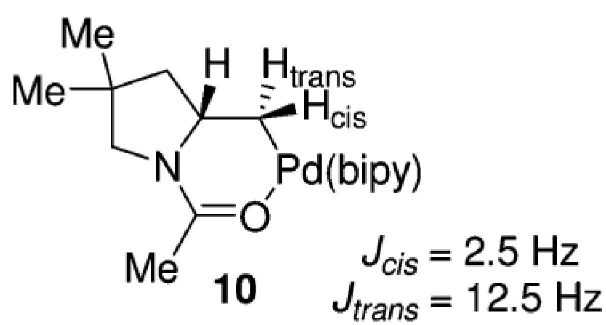
Sibbald, P. A.; Rosewall C. F.; Swartz, R. D.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, 131*, 15945*.

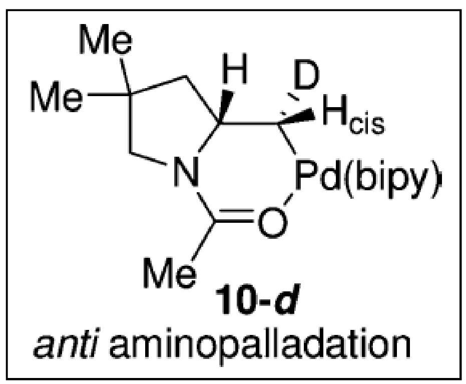
Stereochemistry of the Aminopalladation (1st C-N Bond Formation)



Chelation from the acetamide minimizes β-hydride elimination.



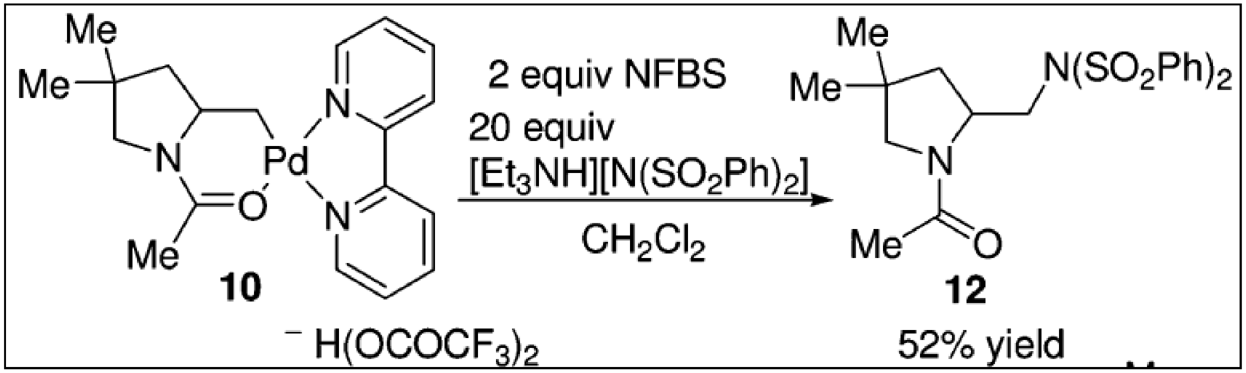


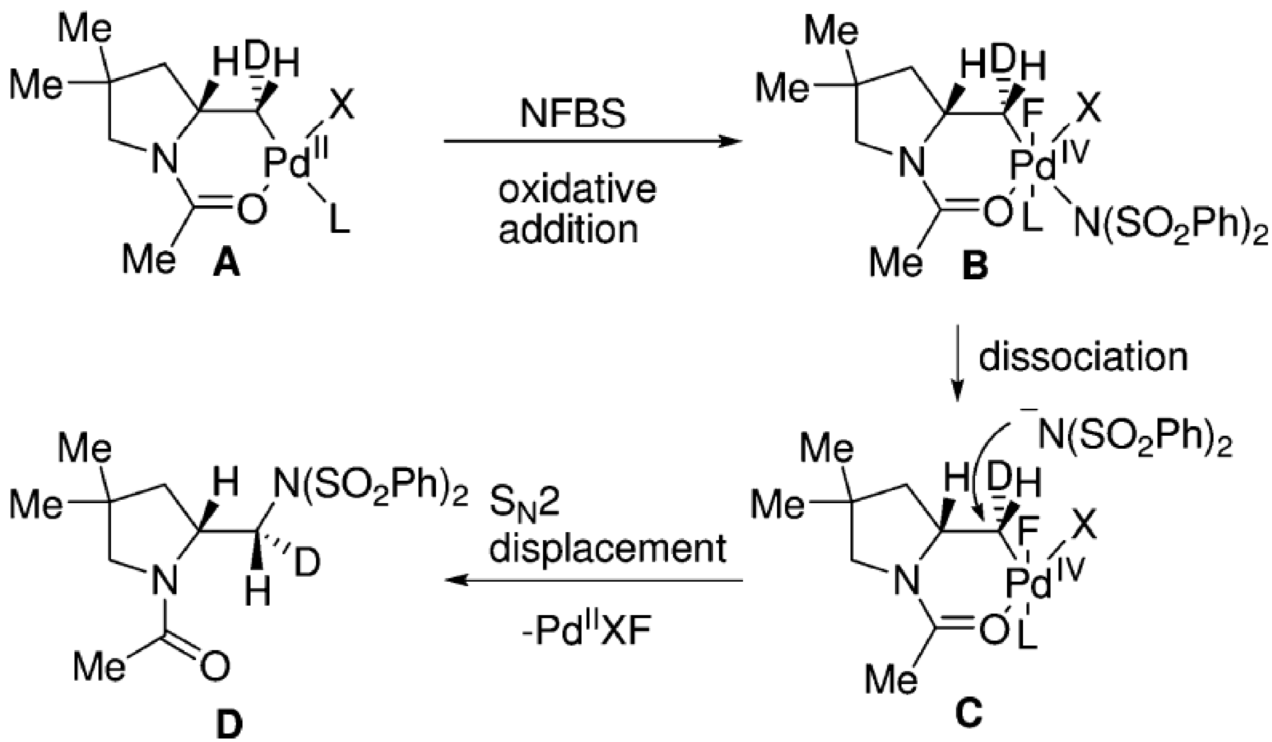


Inversion is required for the 2nd C-N bond formation for the overall syn diamination.

Sibbald, P. A.; Rosewall C. F.; Swartz, R. D.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, 131*, 15945*.

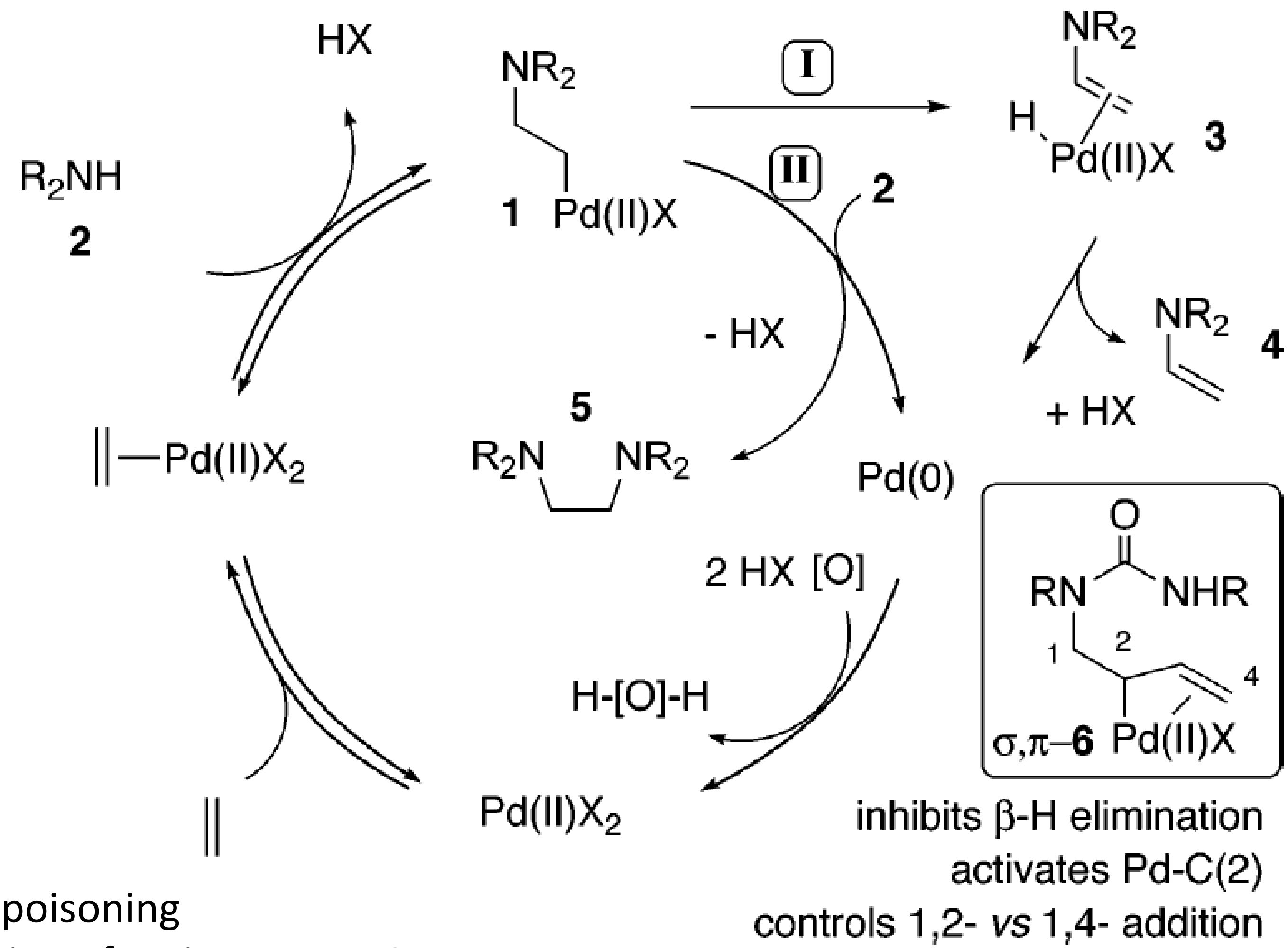
Proposed Mechanism for the 2nd C-N Bond Formation





Sibbald, P. A.; Rosewall C. F.; Swartz, R. D.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, 131*, 15945*.

Challenges in the Palladium Catalyzed Alkene Diamination

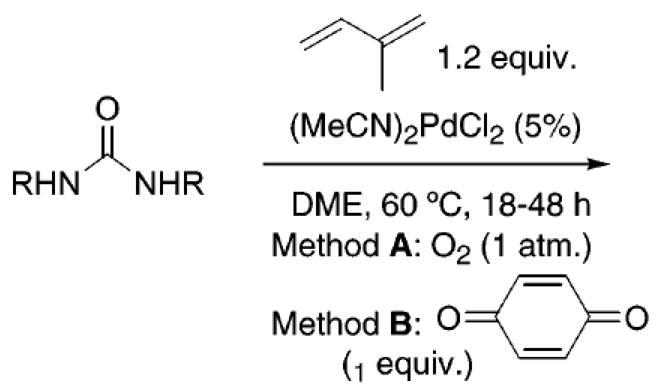


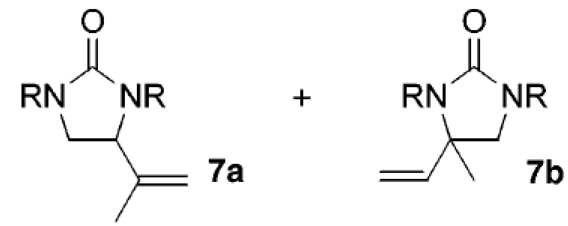
Challenges:

1. Catalyst poisoning
2. Protonation of amine source **2**
3. Oxidation of amine source **2**
4. β-hydride elimination (route I)
5. Activation of Pd-C bond for a second attack by amine **2**

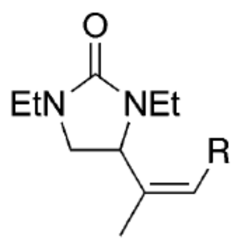
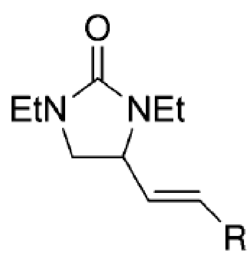
Bar, G. L. J.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *J. Am. Chem. Soc.* **2005**, 127*,* 7308.

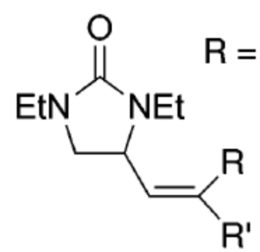
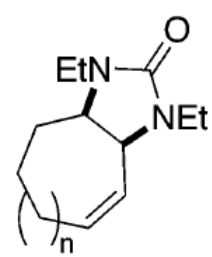
Pd-Catalyzed Intermolecular 1,2-Diamination of Conjugated Dienes





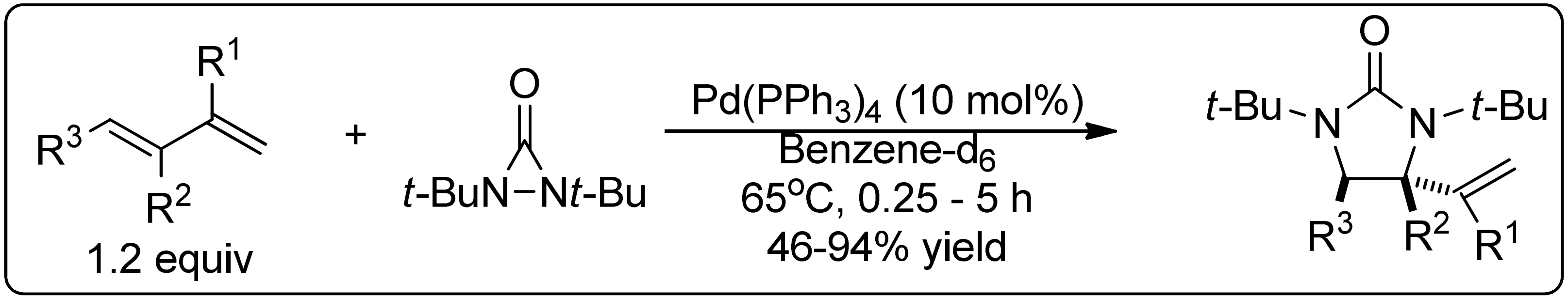
Method	R=	yield (**7ab**)	**7a** / **7b**
A	Me	45%	78 / 22
A	Et	15%	64 / 36
A / B	H	0 %	--
B	Me	29 %	67 / 33
B	Et	81%	77 / 23
B	Bu	82%	90 / 10

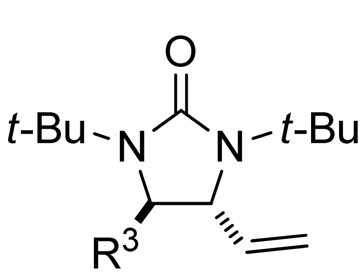
product		method[a]	yield(%)
	R = H (**7b**)	A	15
		B	**81** [b]
	R = Me	A	0 [c]
		B	**43** [d,e]
	R = Et	A	17
		B	**60** [f]
	R = Ph	A	78
		B	**99**[f]

	R = Me, R' = Ph	A	**0** [c]
		B	**30** [d]
	R, R' = Ph	A	20
		B	**6** [f,g]
	n = 0	A	0 [c]
		B	**36** [h]
	n = 1	A	0 [c]
		B	**68** [d]

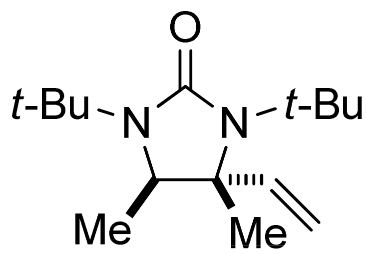
Bar, G. L. J.; Lloyd-Jones, G. C.; Booker-Milburn, K. l.
J. Am. Chem. Soc. **2005**, 127, 7308.

Pd-Catalyzed Diamination of Conjugated Alkenes



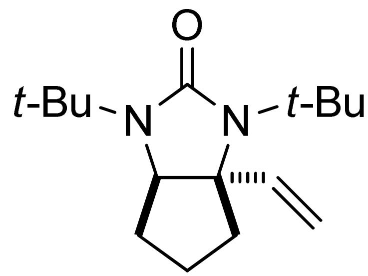


R^3	Yield (%)	Time (min)
Me	94	30
C_5H_{11}	91	40
OMe	94	15
CO_2Me	62	120
Ph	90	30
2-furyl	78	30

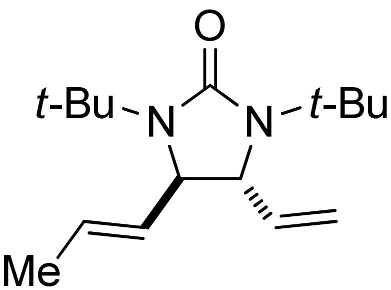


88%, 5 h

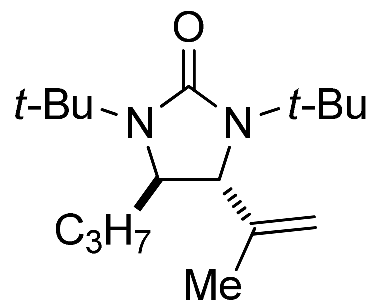
E/Z$_{(SM)}$ = 1/1.2



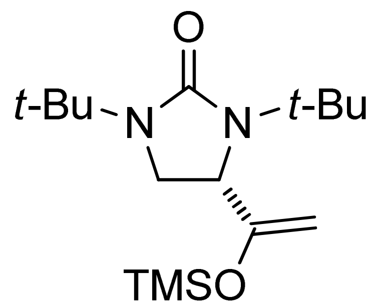
72%, 30 min



86%, 30 min



46%, 2.5 h

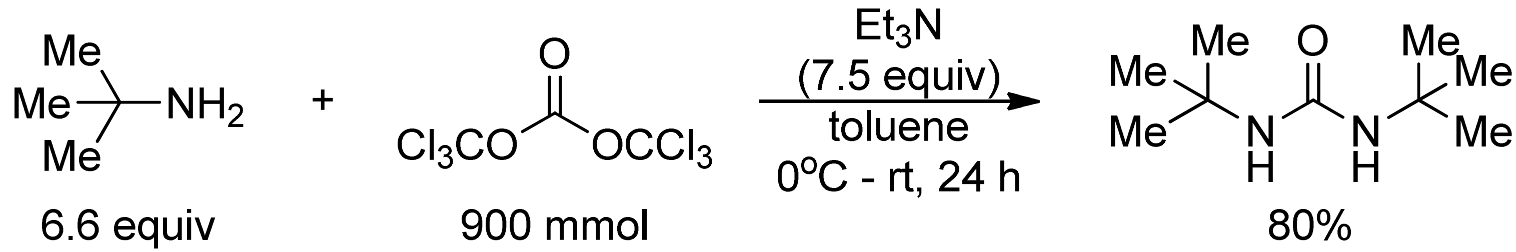


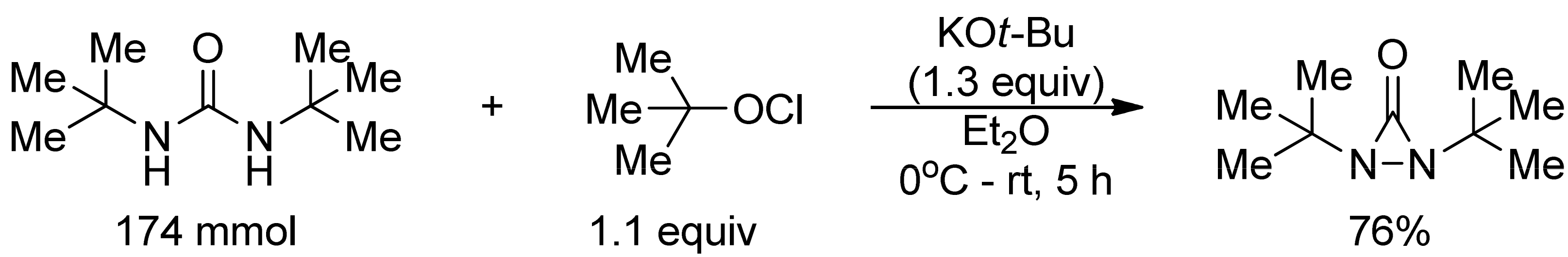
90%, 1 h

- Conjugated dienes are effective substrates.
- Highly stereoselective and regioselective at the internal double bond.
- Z isomers do not react.

Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 762.

Synthesis of Di-*tert*-butyldiaziridinone

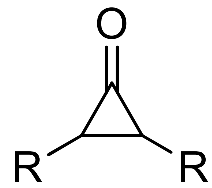
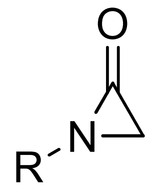
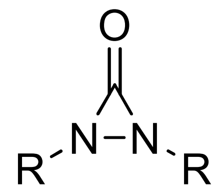




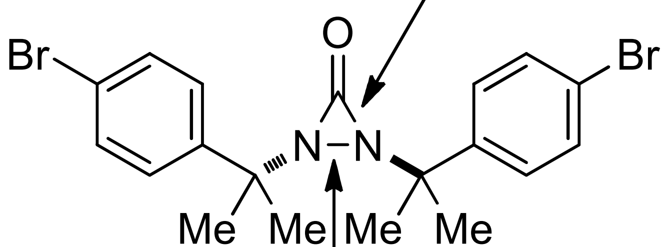
Possible reasons for choosing diaziridinone as the nitrogen source:
1. Electrophilic relative to Pd(0) for oxidative addition.
2. Strained.
3. Weak N-N bond.
4. C=O withdraws electron density from the nitrogen atoms to minimize catalyst poisoning due to strong ligand coordination.

Greene, F. D.; Stowell, J. C.; Bergmark, W. R. *J. Org. Chem.* **1969**, *34*, 2254.
Du, H.; Zhao, B.; Shi, Y. *Org. Synth.* **2009**, *86*, 315.

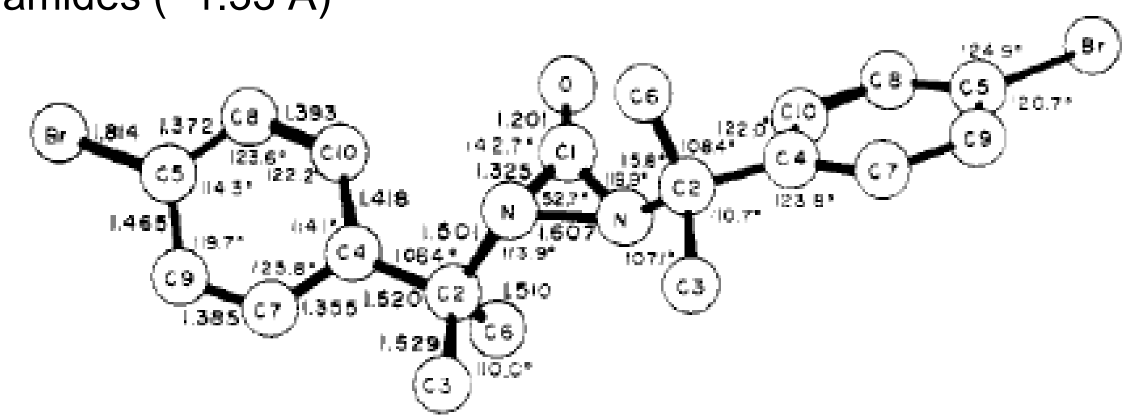
Properties of Diaziridinones

				
	cyclopropanones	aziridinones	diaziridinones	
$\upsilon_{C=O}$	1813-1840	1837-1850	1855-1880	cm^{-1}
	ketones (saturated, aliphatic)	amides	ureas	
$\upsilon_{C=O}$	~1710	1650-1690	1660-1695	cm^{-1}

1.325 Å, typical amides (~1.33 Å)



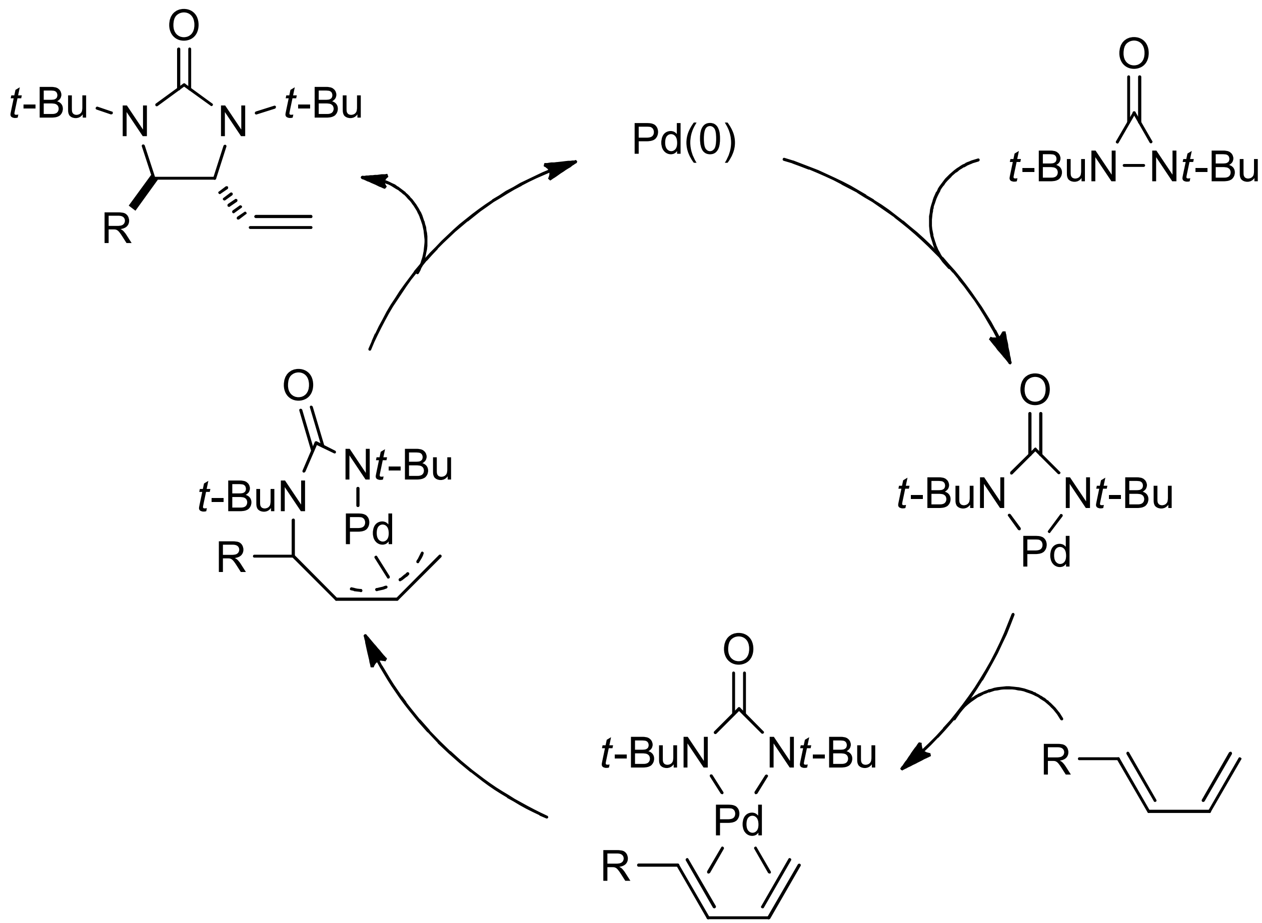
1.601 Å
$F_2N\text{-}NF_2$ (1.47 Å)
$H_2N\text{-}NH_2$ (1.45 Å)



The angle between the N-substituent and the diaziridinone plane is 56°.

Greene et. al. *JOC* **1969**, *34*, 2254.; *JOC* **1978**, *43*, 922.; *JOC* **1976** *41* 2813.
Heine, H. W. The Chemistry of Heterocyclic Compounds; Hassner, A., Ed; John Wiley & Sons, Inc: New York, 1983; pp 547.

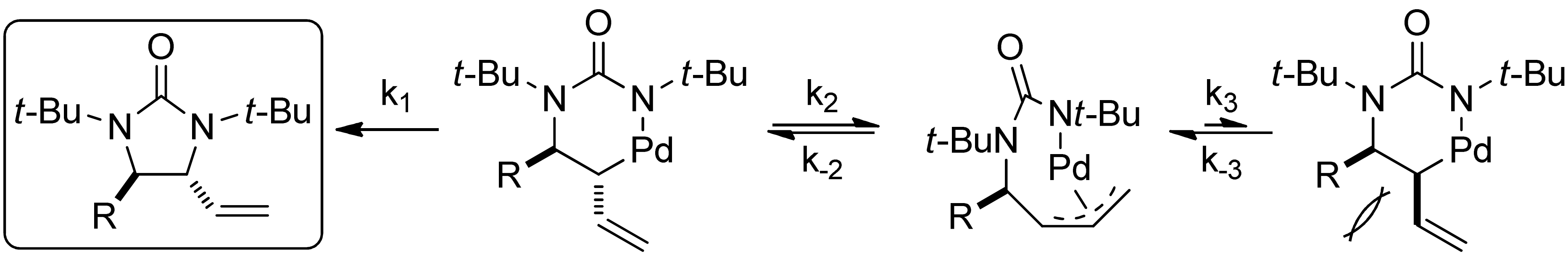
Proposed Catalytic Cycle



Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 762.

Possible Reasons for High Stereoselectivity and Reactivity of *E*-Isomer

Hypothesis for high stereoselectivity:

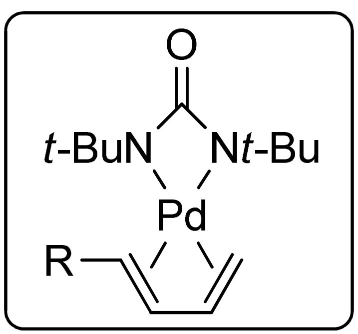


Scenarios for high stereoselectivity:

1. $k_1 >> k_2$
2. $k_2 > k_1$, $k_{-3} >> k_3$

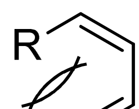
Hypothesis for the selective reactivity with *E*-isomer:

- Is s-cis conformation required for the coordination of diene to Pd(II) prior to insertion?
- Only conjugated dienes are the viable substrates.

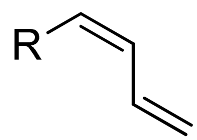


Proposed by Shi et. al.

Conformations of diene with cis-internal C=C:

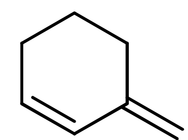


s-cis



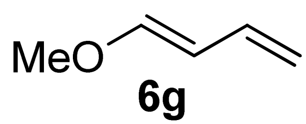
s-trans

(incorrect geometry for bidentate coordination)



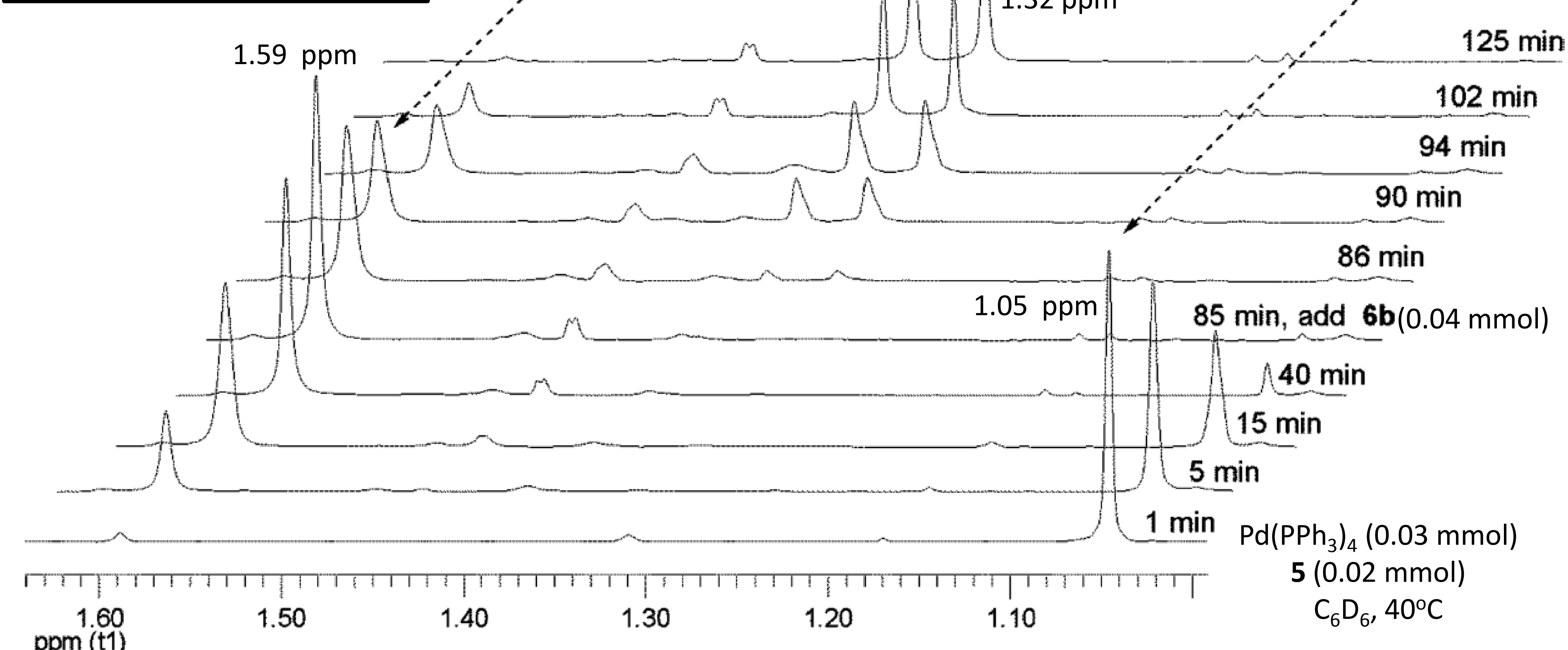
test substrate (locked in s-trans)

NMR Study of the Stoichiometric Reaction



6g

A is consumed in 1 min when (*E*)-1-methoxybutadiene (**6g**) was added at 85 min.

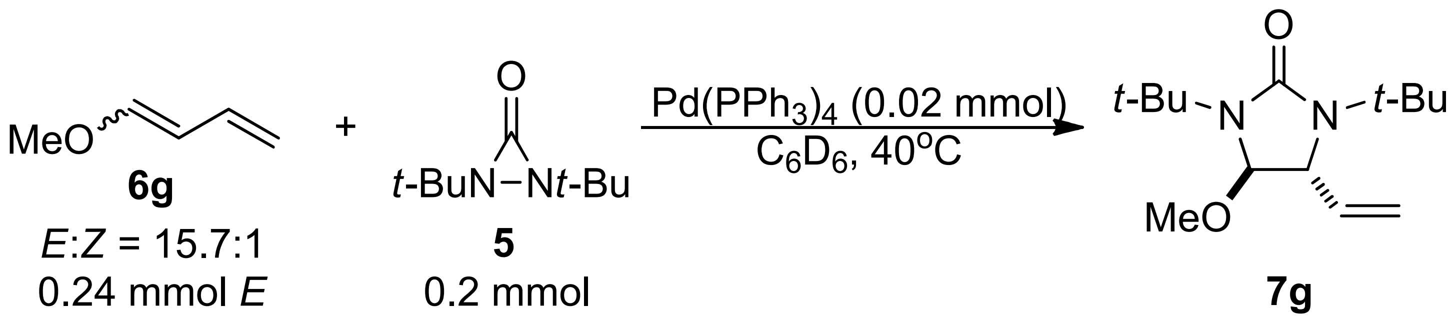


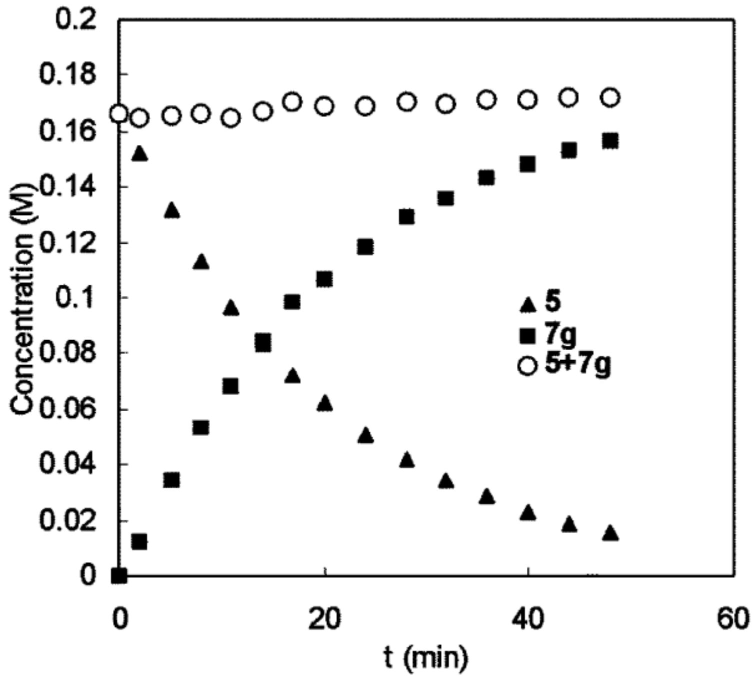
Stoichiometric Reaction monitored by ^{1}H NMR

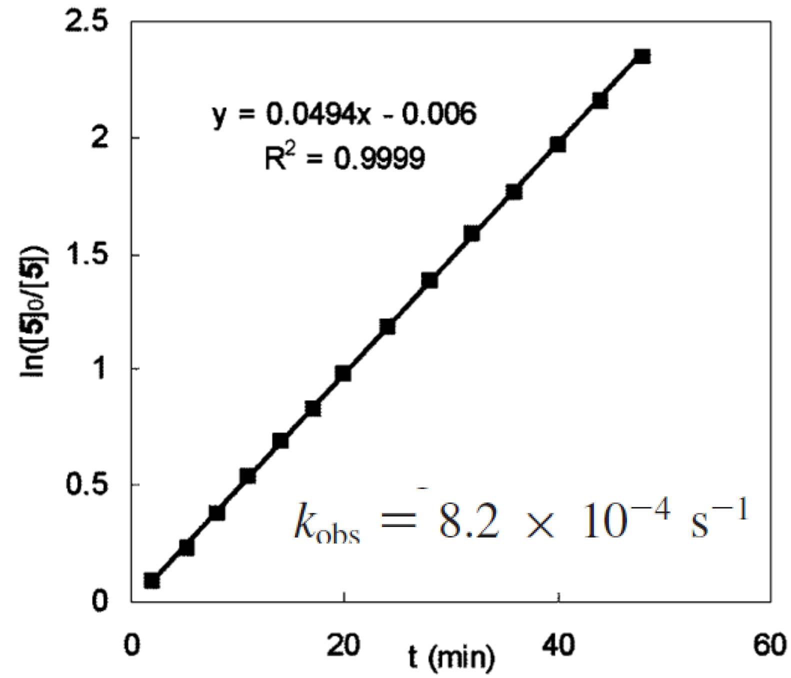
A is a possible intermediate.
Oxidative Addition is likely the RDS.

Zhao, B.; Du, H.; Cui, S.; Shi, Y. *J. Am. Chem. Soc.* **2010**, *132,* 3523.

Kinetic Studies







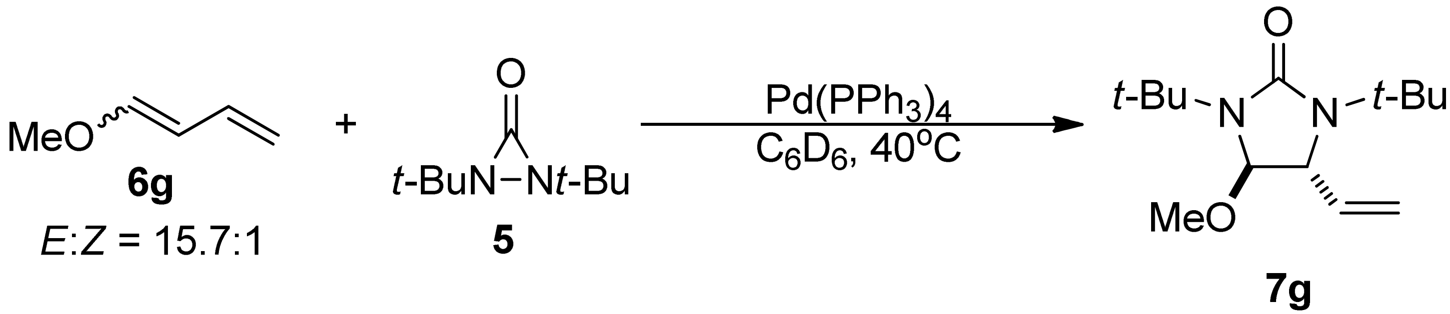
No induction period.
PPh_3 dissociates rapidly.
Quantitative conversion . No side reaction.

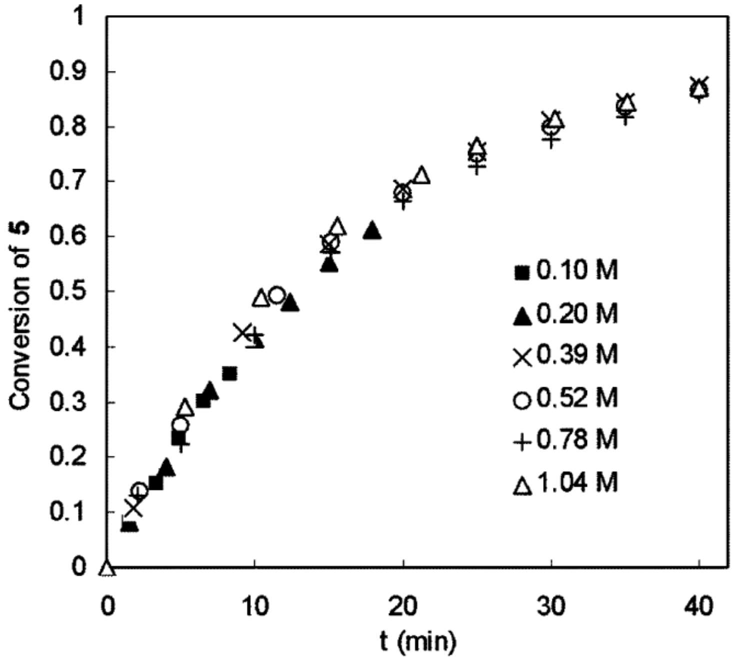
1st order in diaziridinone **5**.

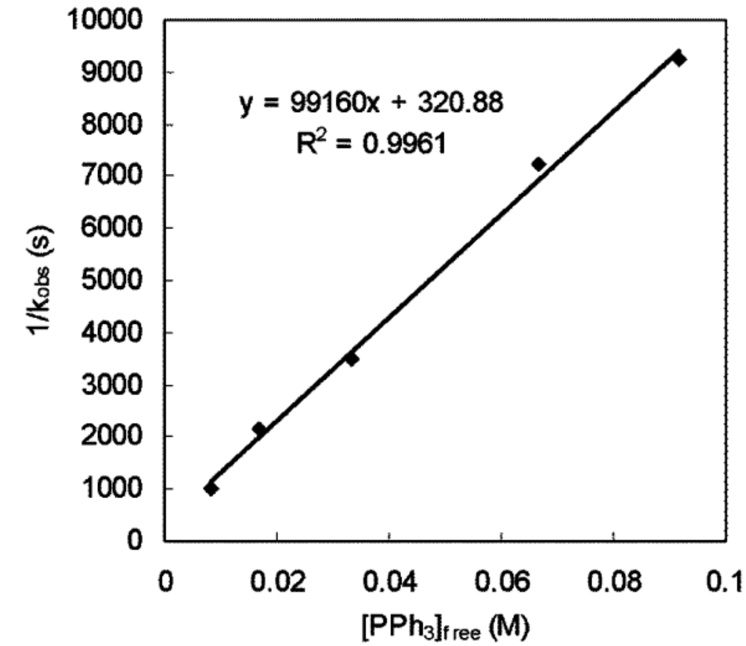
1st order in $Pd(PPh_3)_4$ (not shown).

Zhao, B.; Du, H.; Cui, S.; Shi, Y. *J. Am. Chem. Soc.* **2010**, *132,* 3523.

Kinetic Studies







6g (0.12 mmol *E* isomer),
5 (0.1 mmol), $Pd(PPh_3)_4$ (0.01 mmol)

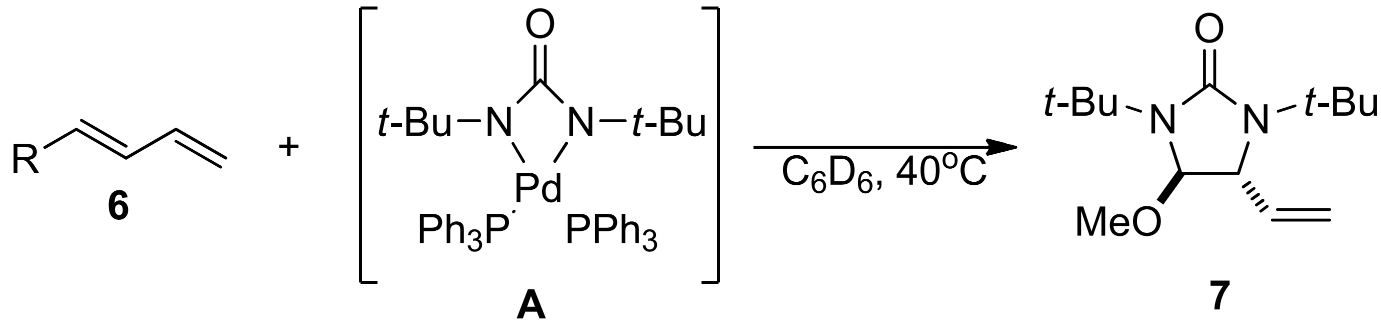
6g (0.12 mmol *E* isomer),
5 (0.1 mmol), $Pd(PPh_3)_4$ (0.01 mmol)

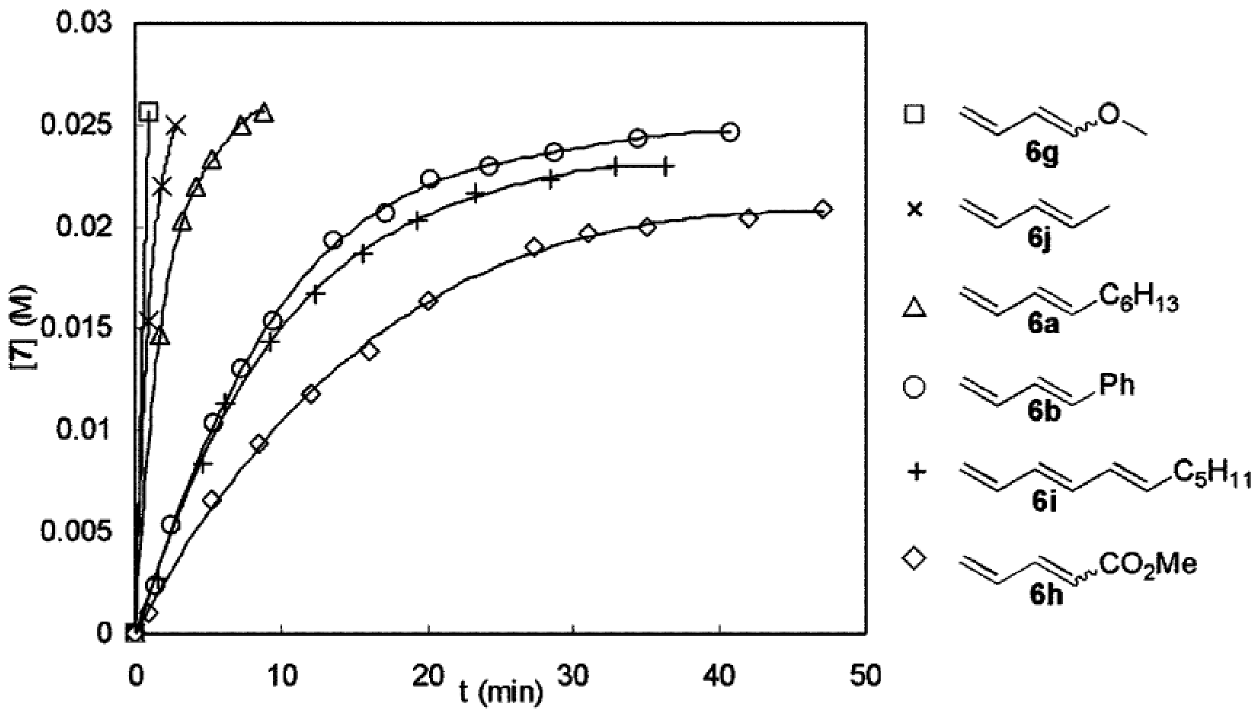
Zero-order in diene **6g**.

Inverse 1st-order in PPh_3.

Zhao, B.; Du, H.; Cui, S.; Shi, Y. *J. Am. Chem. Soc.* **2010**, *132,* 3523.

Kinetic Studies





C-N bond formation is slower for e-deficient dienes.

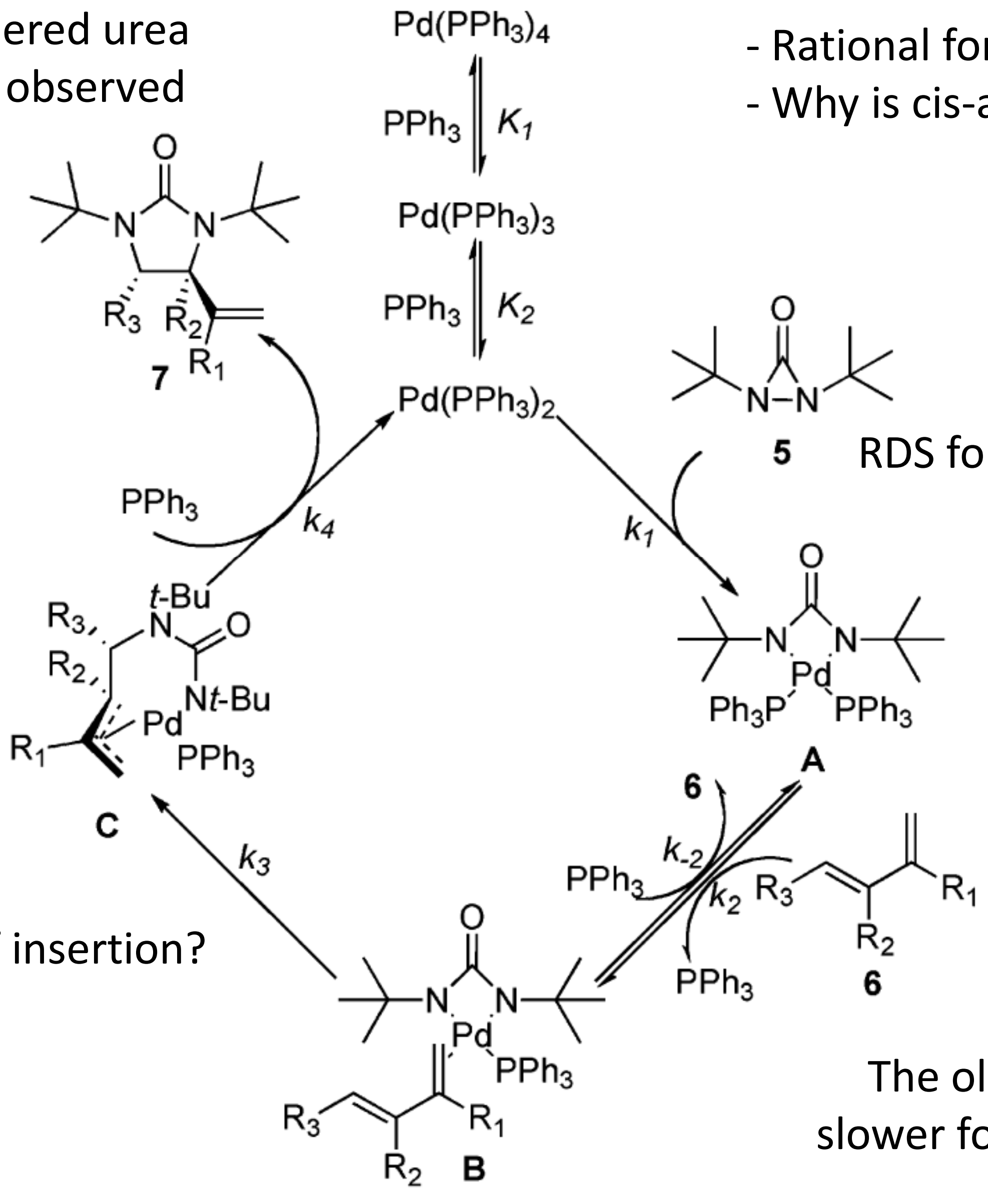
- **A** can be observed using **6i** under catalytic reaction conditions ([**A**] is independent of PPh_3).

Zhao, B.; Du, H.; Cui, S.; Shi, Y. *J. Am. Chem. Soc.* **2010**, *132,* 3523.

Refining the Catalytic Cycle

7-membered urea was not observed

- Rational for high regioselectivity?
- Why is cis-alkene unreactive?



$$\text{rate} = \frac{K_2 k_1 [\mathrm{Pd(PPh_3)_4}]_0[\mathbf{5}]}{[\mathrm{PPh_3}]}$$

RDS for e-rich dienes.

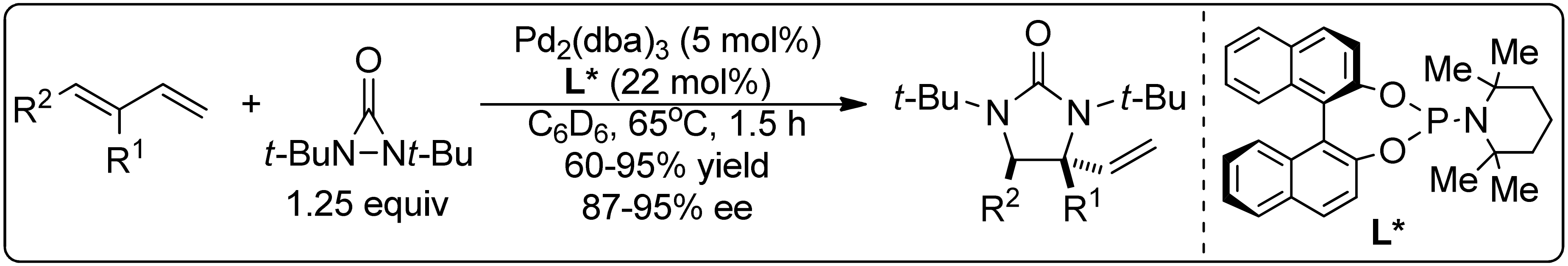
Associative displacement?

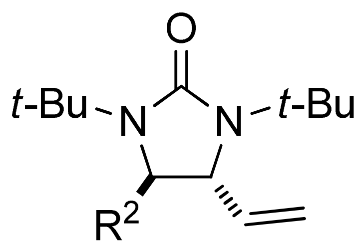
Details of insertion?

The olefin insertion into Pd-N is slower for electron-deficient dienes.

Zhao, B.; Du, H.; Cui, S.; Shi, Y. *J. Am. Chem. Soc.* **2010**, *132,* 3523.

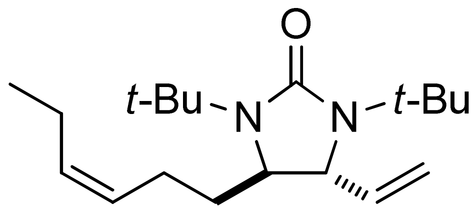
Catalytic Asymmetric Diamination of Conjugated Alkenes



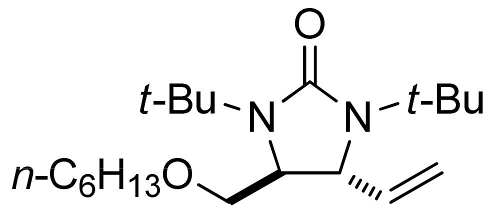


R^2	Yield (%)	ee (%)
Me	94	91
n-C_5H_{11}	91	92
CH_2Ph	94[a]	92
c-C_6H_{11}	72[b]	95
Ph	*62*[c]	93
p-$MeOC_6H_4$	*82*[c]	92
2-thienyl	72[b]	93

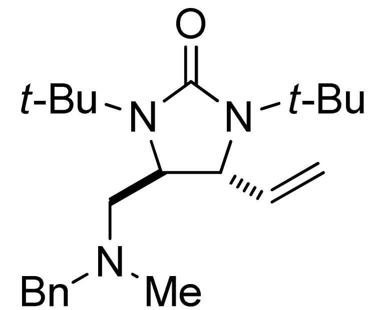
[a] $E/Z_{(SM)}$ = 1/1.5 [b] $E/Z_{(SM)}$ = 1.67/1
[c] 2 h



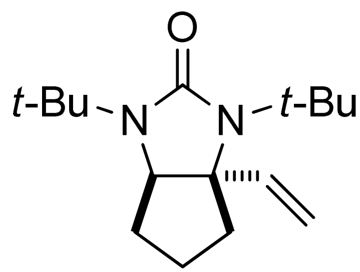
90% (93% ee)



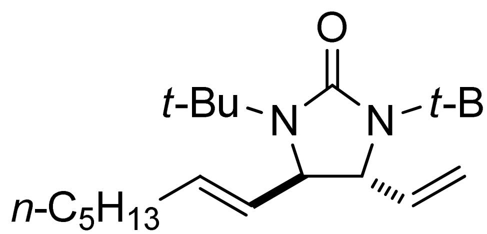
86% (92% ee)



86% (92% ee)



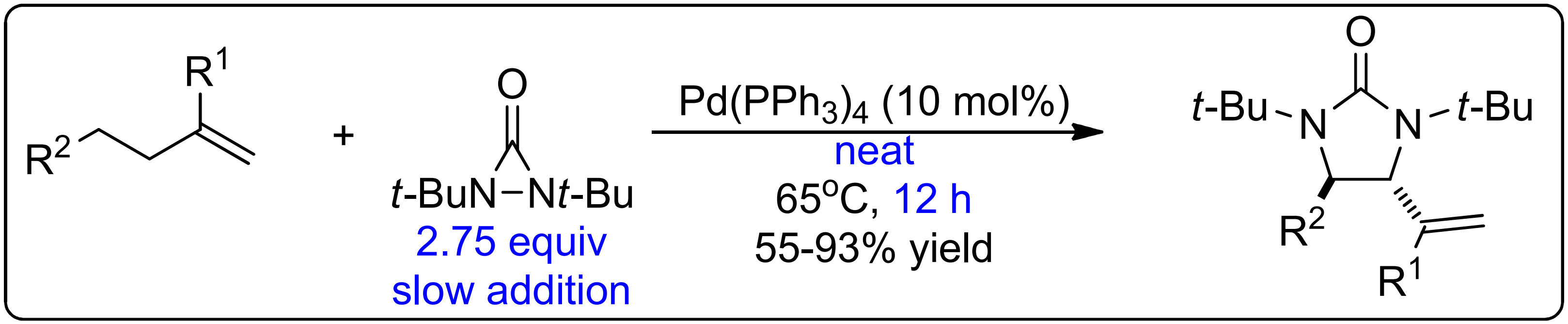
83% (87% ee)

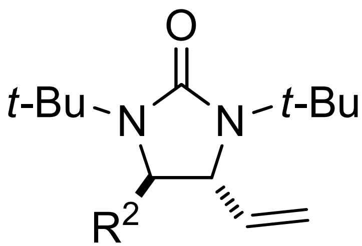


60% (92% ee)

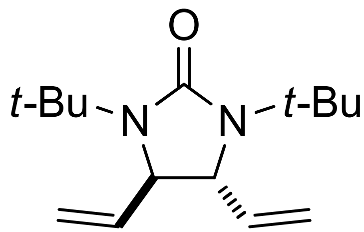
Du, H.; Yuan, W.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 11688.

Diamination at Allylic and Homoallylic Carbons

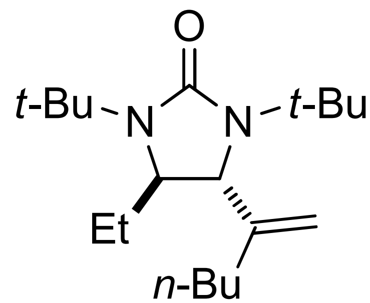




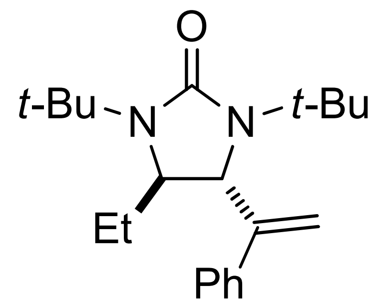
R^2	Yield (%)
Ph	90 (7 h)
Et	68
n-C_6H_{13}	74
CH_2OBn	90
CH_2On-C_6H_{13}	78



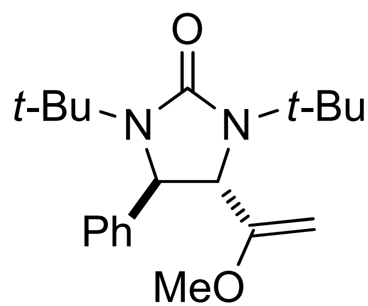
76%



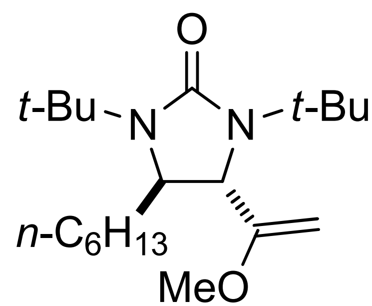
55%



92%



93%

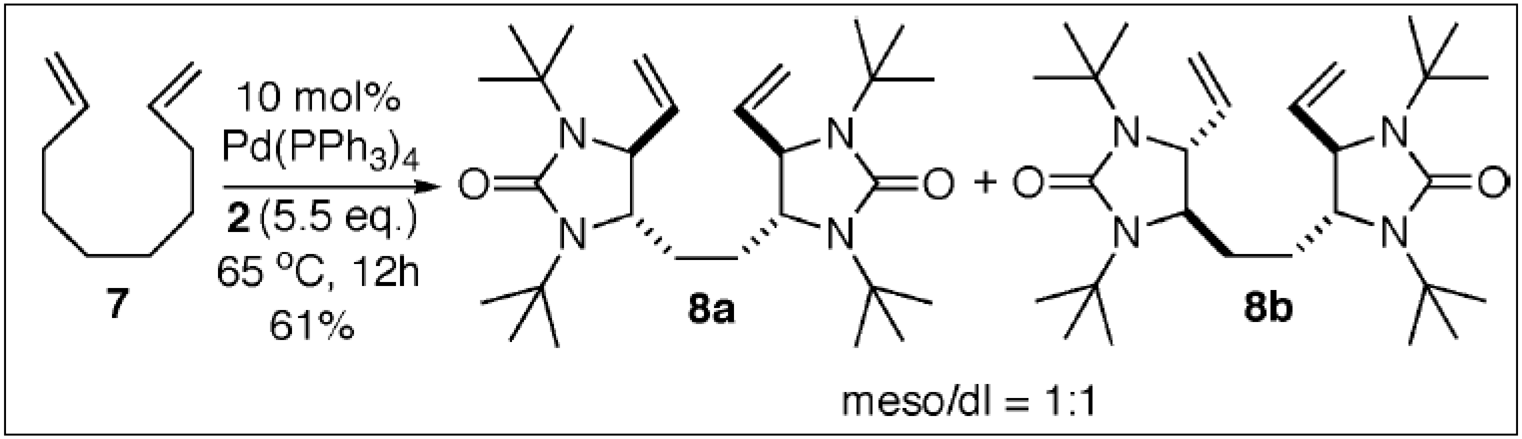


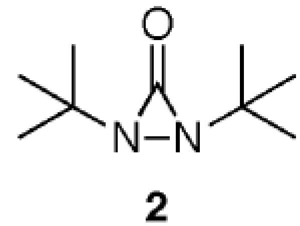
64%

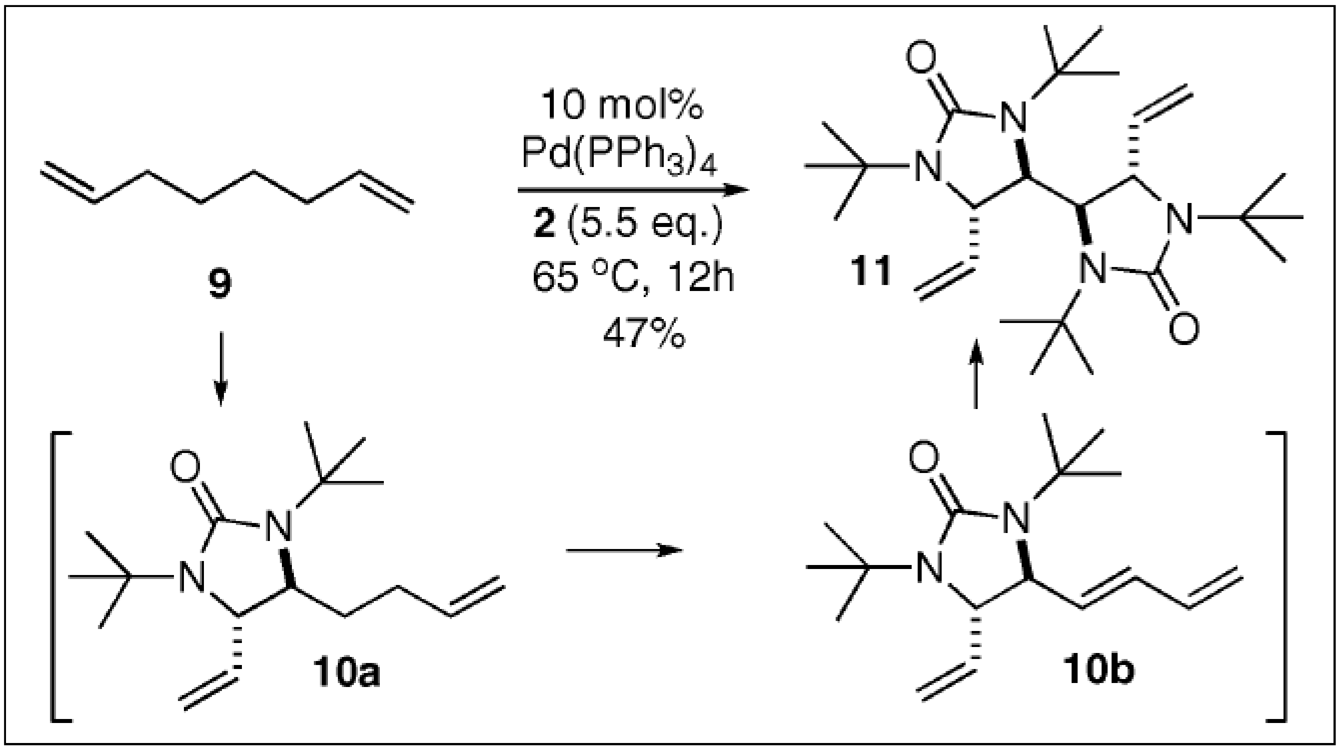
- Highly stereoselective.
- No reactions for olefins with internal double bonds (e.g. trans-5-decane and cis-cyclooctene).

Du, H.; Yuan, W.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 7496.

Bisdiamination







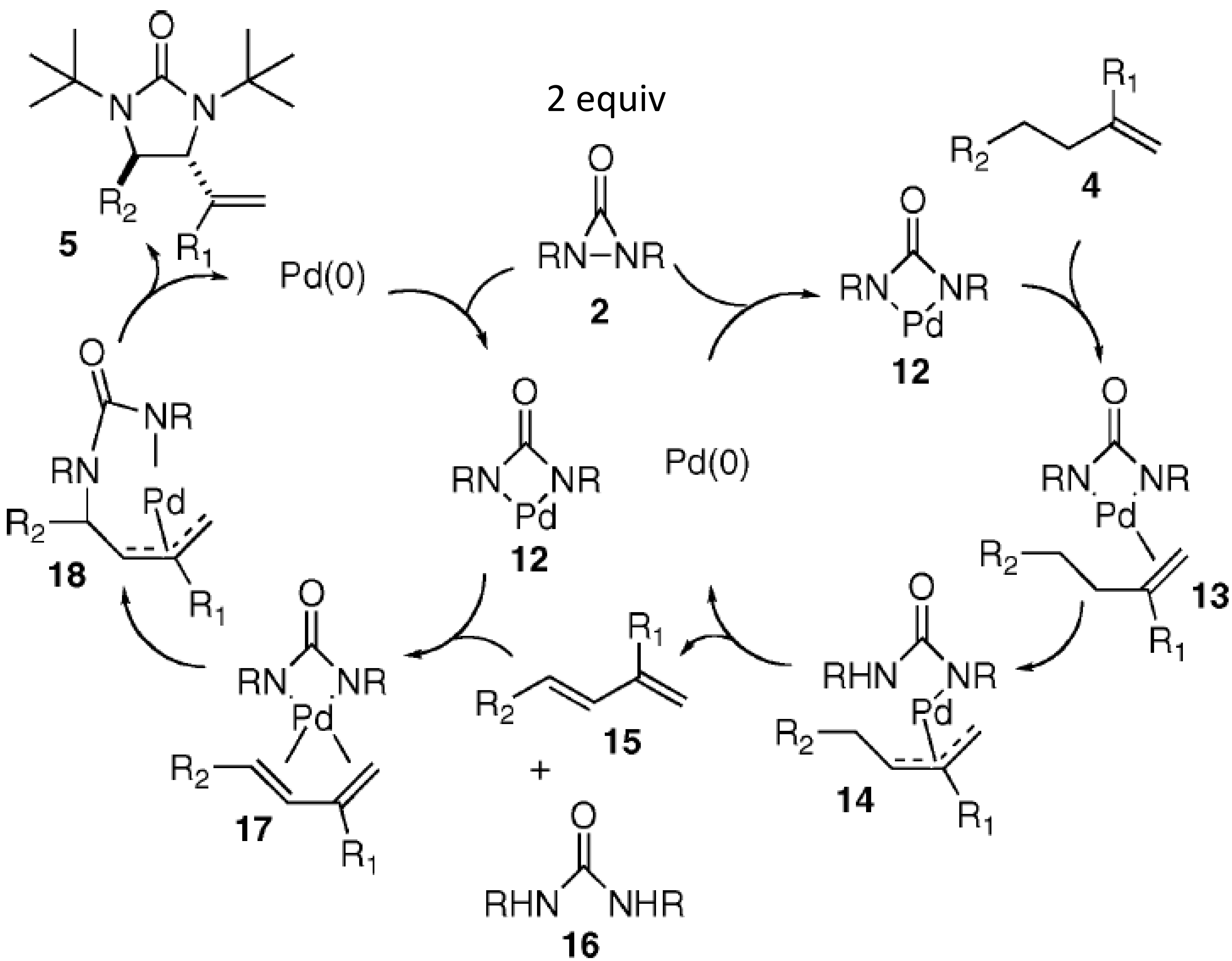
A single diastereomer

Using 5 mol% $Pd(PPh_3)_4$:
10a (14%) and
10b (20%) were isolated
after 12 h.

10a and 10b gave 11
under the diamination
reaction condition.

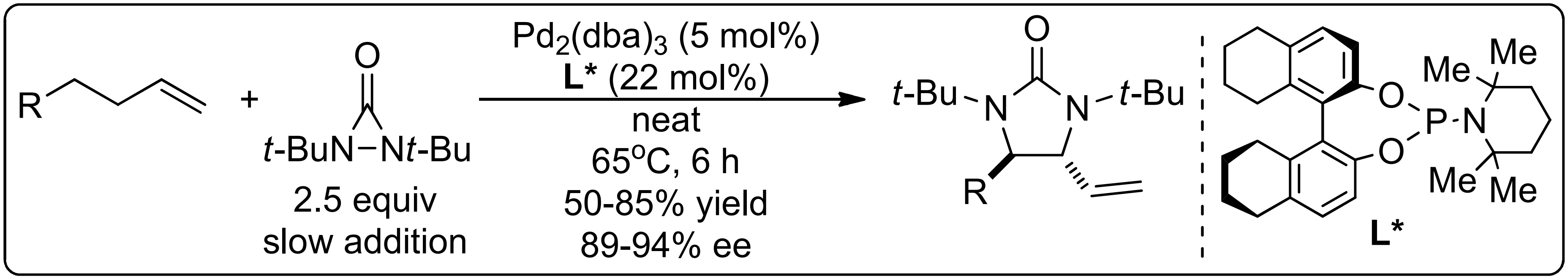
Du, H.; Yuan, W.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 7496.

Proposed Catalytic Cycles

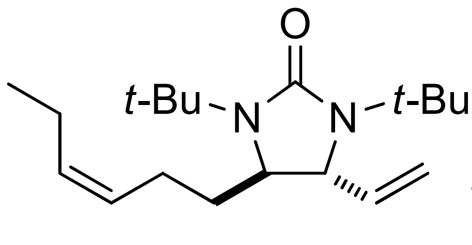


Du, H.; Yuan, W.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 7496.

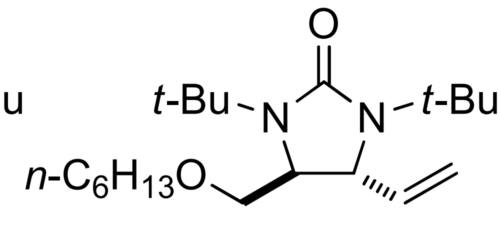
Asymmetric Diamination at Allylic and Homoallylic Carbons



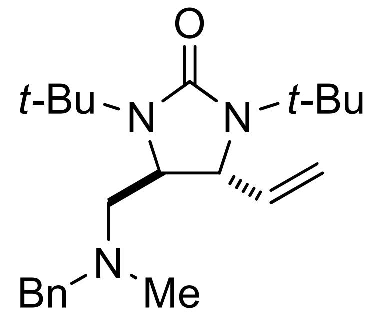
R	Yield (%)	ee (%)
Et	50	90
n-C_5H_{11}	71	91
CH_2Ph	67	93
i-Pr	51	94
Ph	80	90



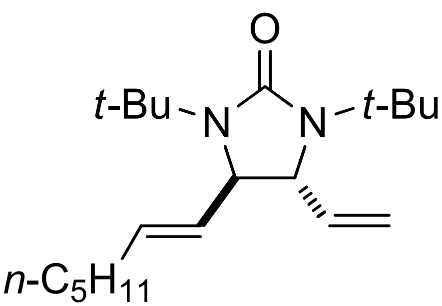
80% (92% ee)



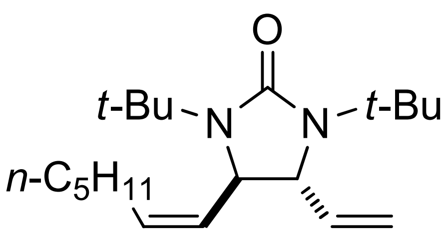
85% (91% ee)



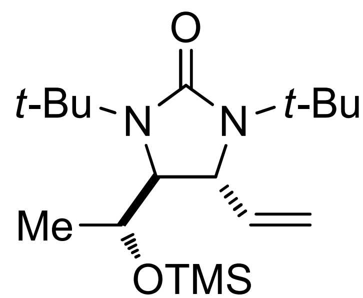
67% (92% ee)



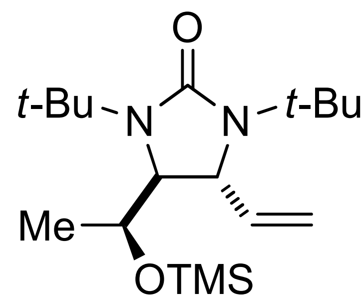
81% (90% ee)



69% (89% ee)



70% (97:3 dr)

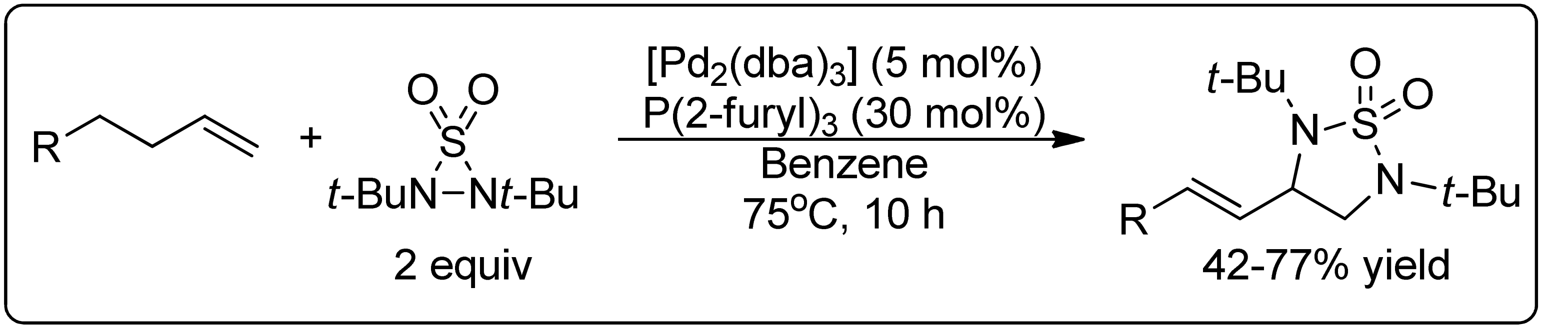


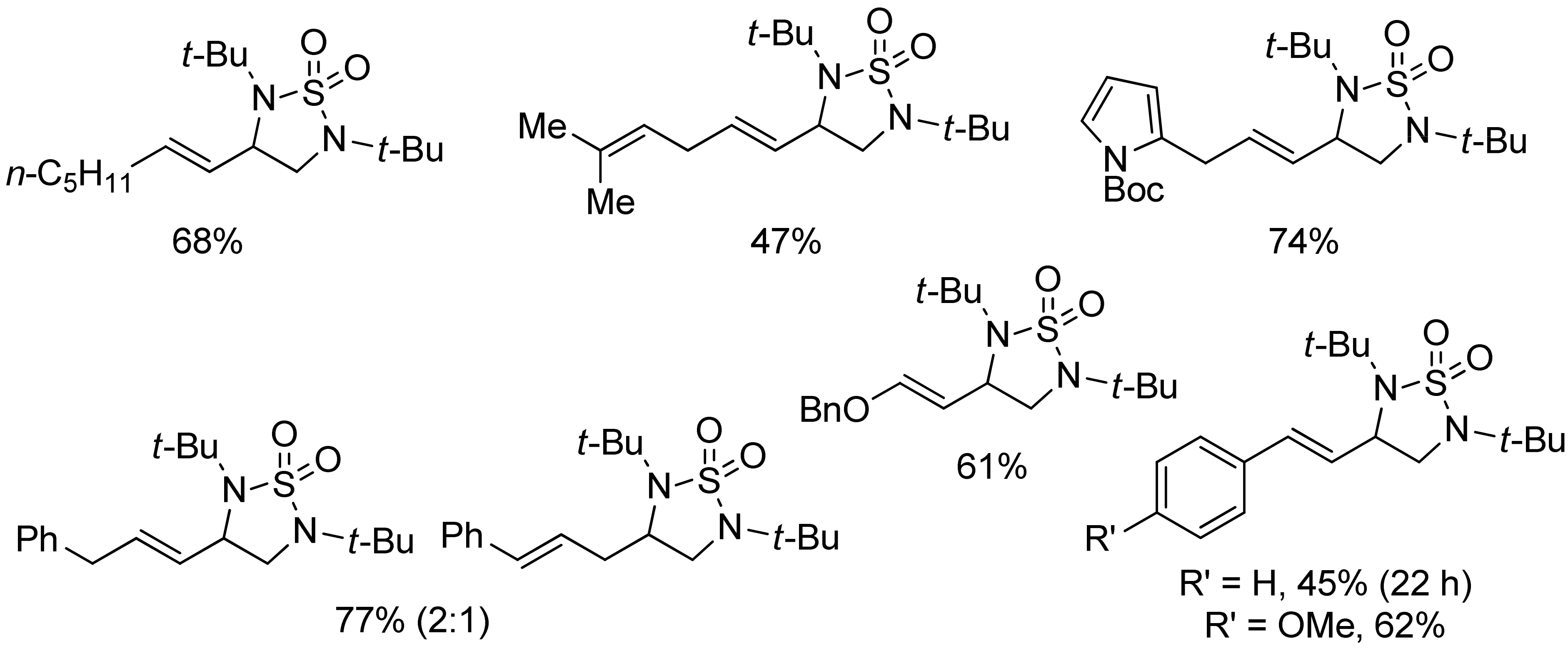
66% (94:6 dr)

Ligand control overrides substrate control

Du, H.; Yuan, W.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129,* 8590.

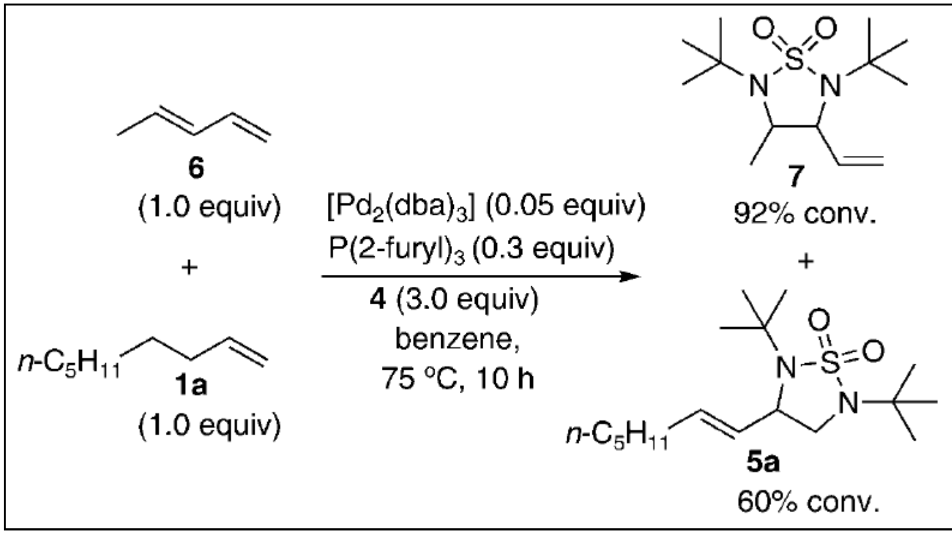
Diamination using Thiadiaziridine



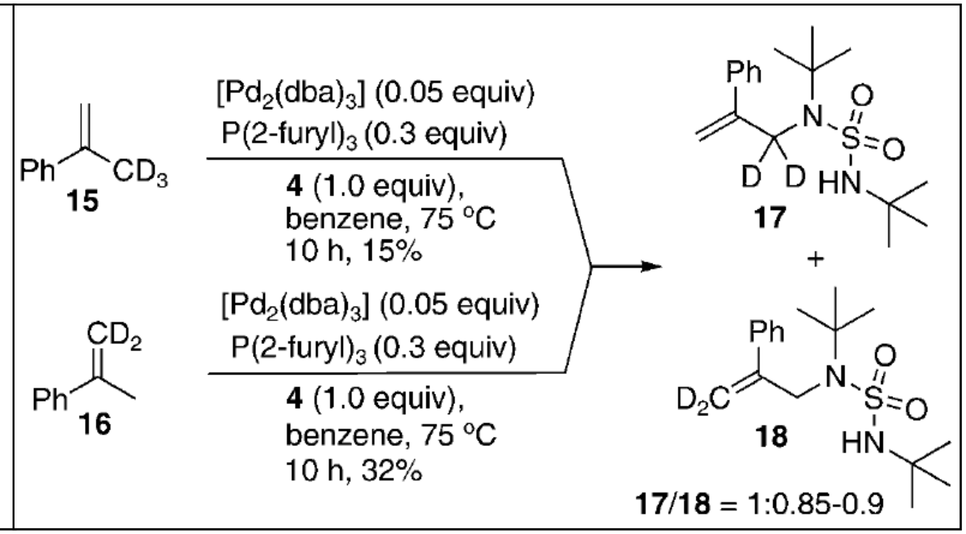


Wang, B.; Du, .; Shi, Y. *Angew. Chem. Int. Ed.* **2008**, *47,* 8224.

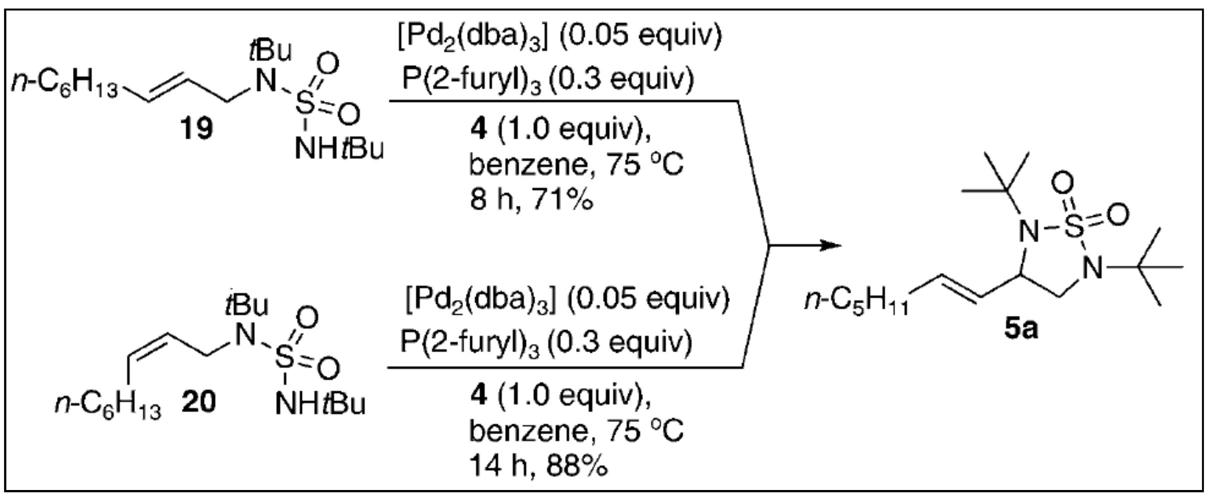
Preliminary Studies on Mechanism



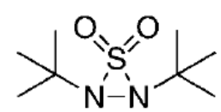
Diamination may not proceed via a diene species



Initial allylic amination is possible.



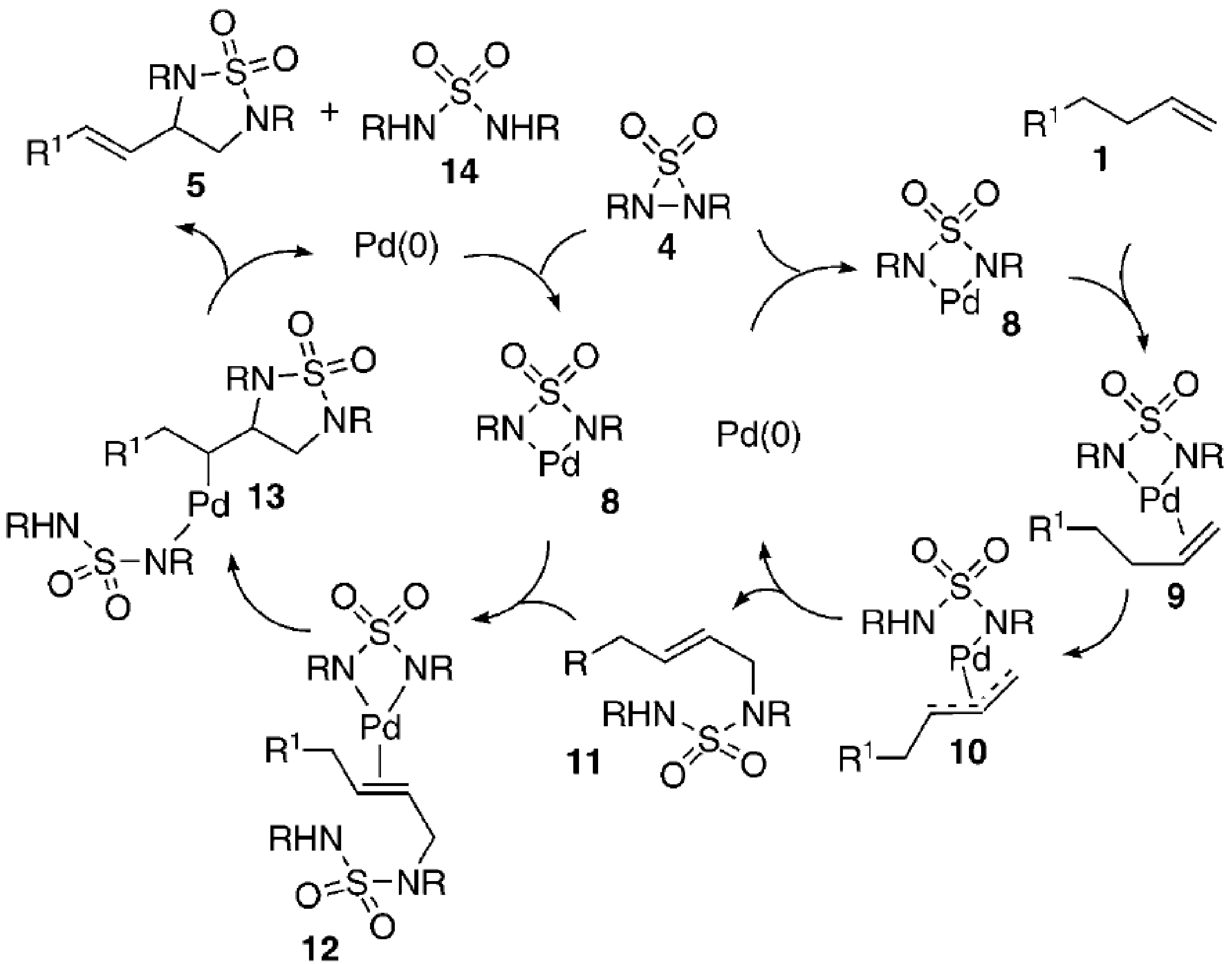
No cyclization was observed without **4**.



4

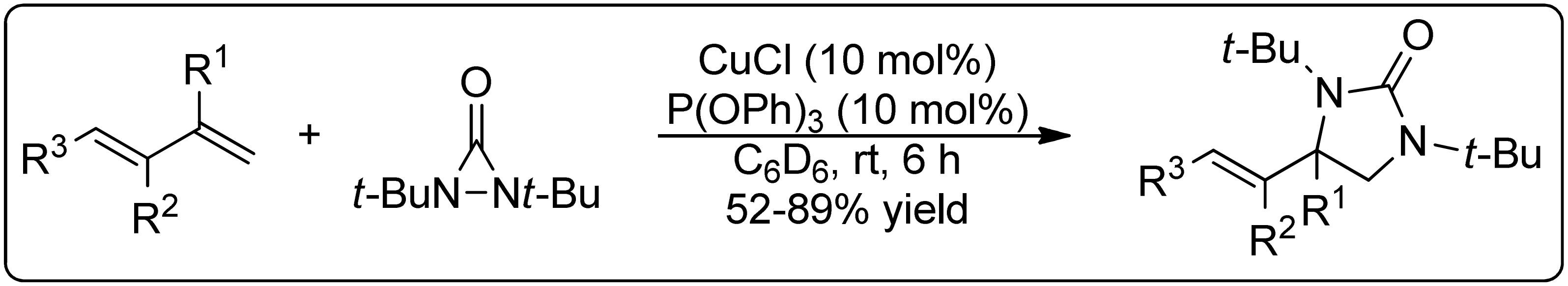
Wang, B.; Du, .; Shi, Y. *Angew. Chem. Int. Ed.* **2008**, *47,* 8224.

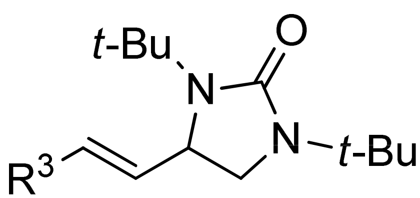
Proposed Catalytic Cycle



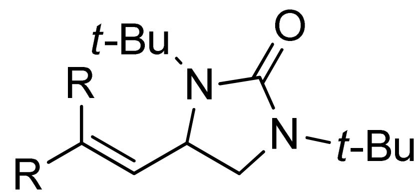
Wang, B.; Du, .; Shi, Y. *Angew. Chem. Int. Ed.* **2008**, *47,* 8224.

Cu(I)-Catalyzed Diamination of Conjugated Dienes (1)

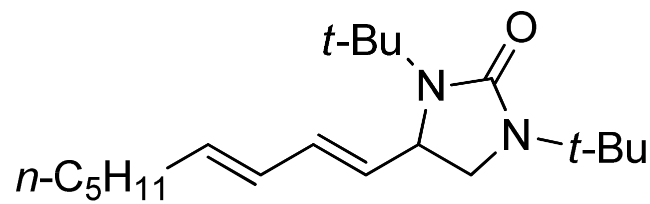




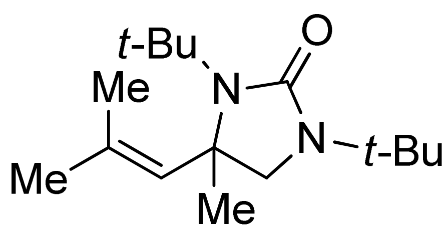
R^3	Yield (%)
Ph	75
p-$MeOC_6H_4$	82
4-$NO_2C_6H_4$	73
2-furyl	73
CO_2Me	50



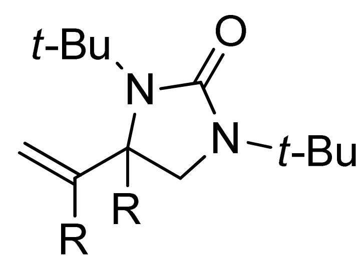
R = Me, 62%
Ph, 83%



68%



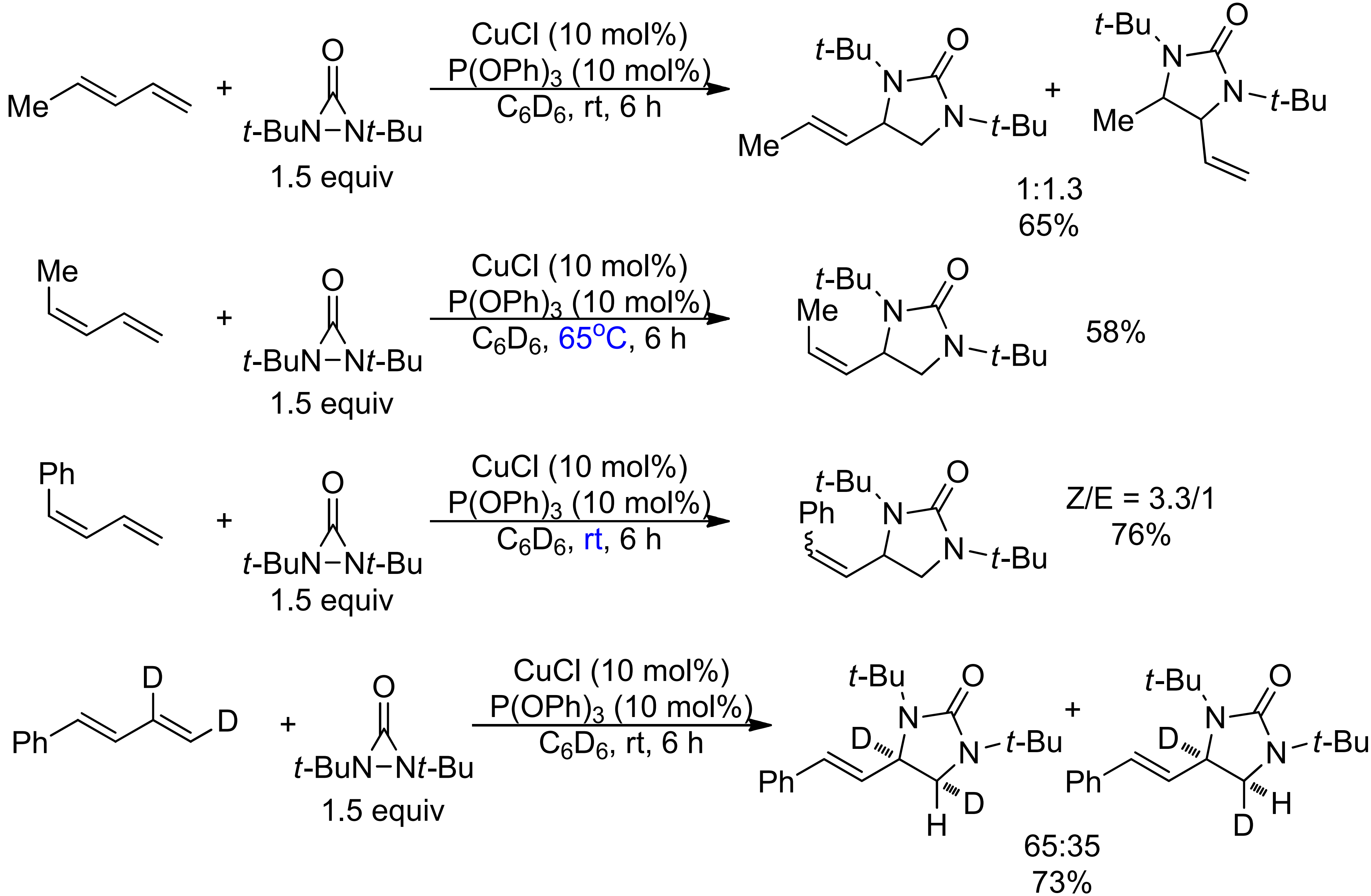
79%



R = Me, 89%
Ph, 76%
OMe, 52%

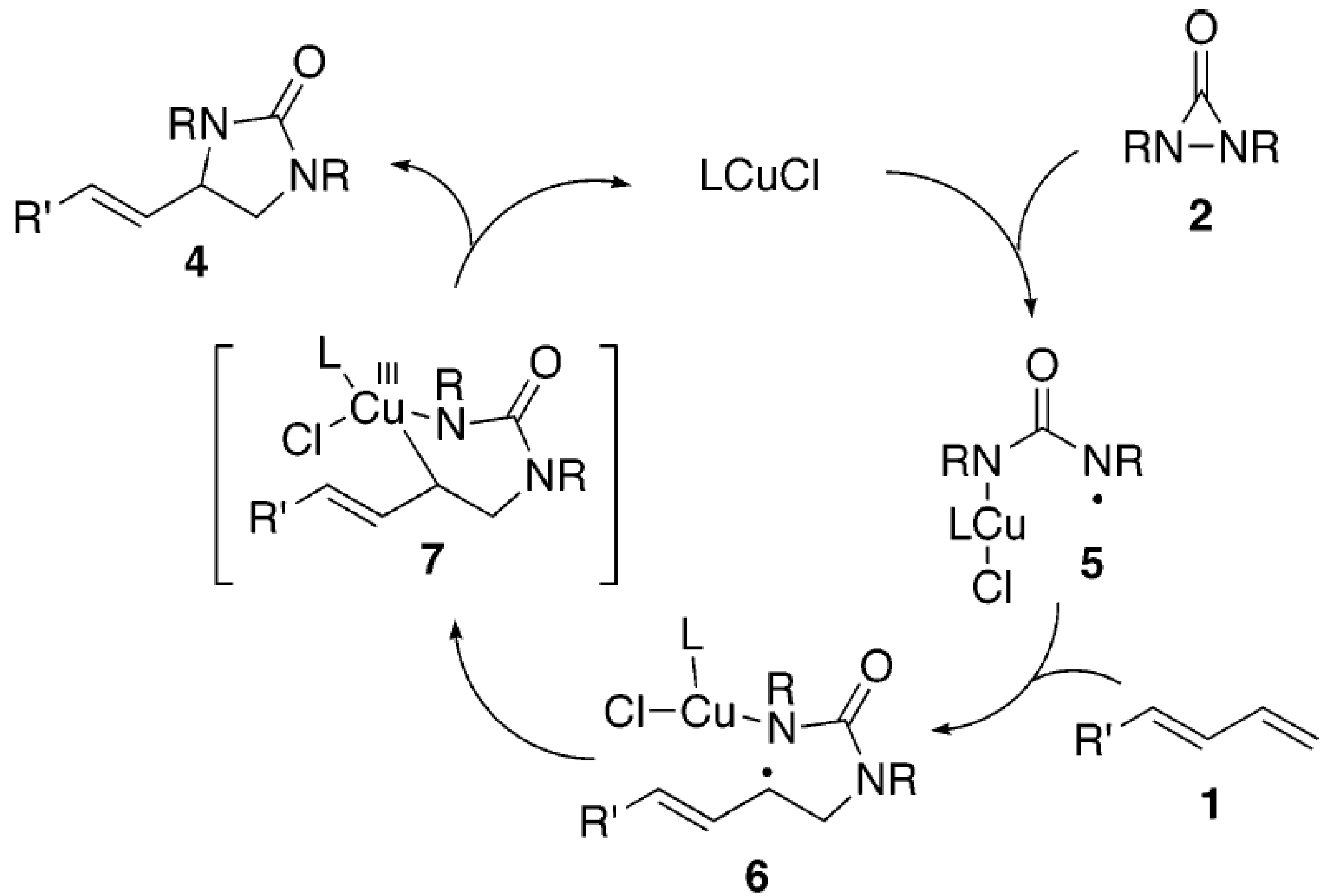
Yuan, W.; Du, H.; Zhao, B.; Shi, Y. *Org. Lett.* **2007**, *9,* 2589.

Cu(I)-Catalyzed Diamination of Conjugated Dienes (2)



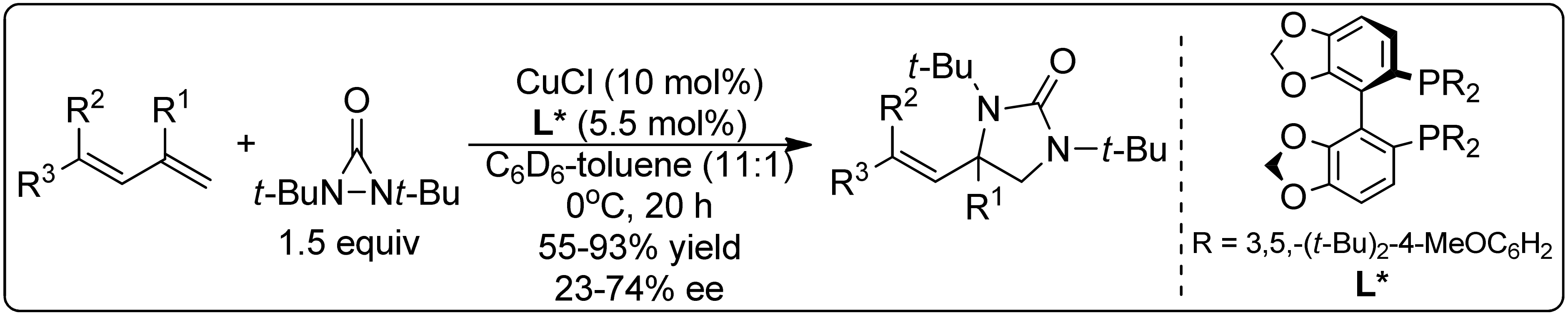
Yuan, W.; Du, H.; Zhao, B.; Shi, Y. *Org. Lett.* **2007**, *9,* 2589.

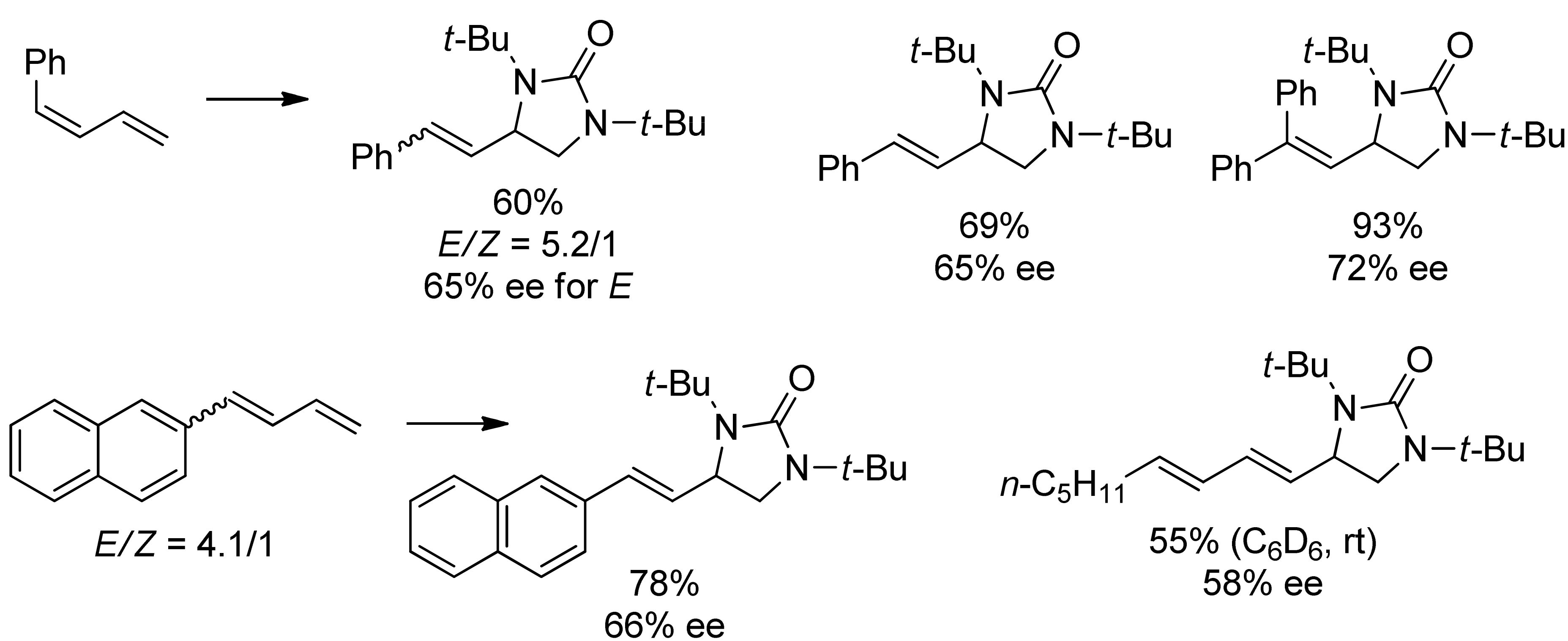
Proposed Catalytic Cycle



Yuan, W.; Du, H.; Zhao, B.; Shi, Y. *Org. Lett.* **2007**, *9,* 2589.

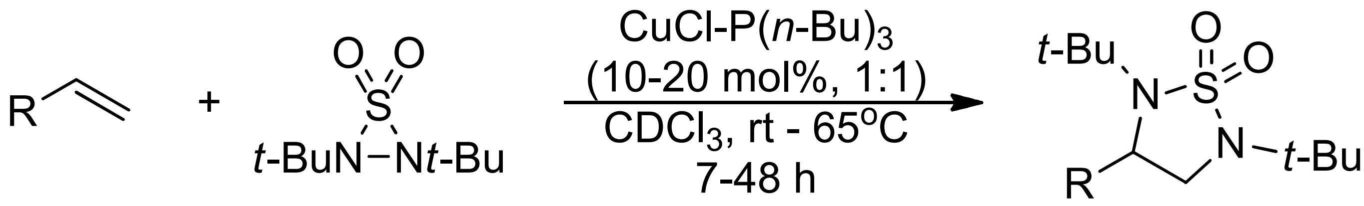
Cu(I)-Catalyzed Asymmetric Diamination of Conjugated Dienes





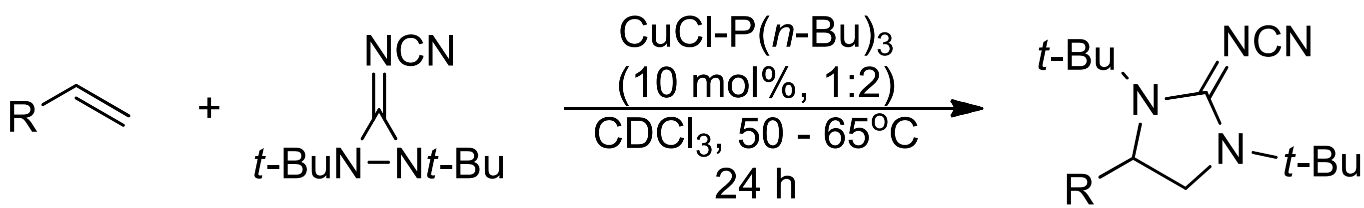
Du, H.; Zhao, B.; Yuan, W.; Shi, Y. *Org. Lett.* **2008**, *10,* 4231.

Cu(I)-Catalyzed Diamination with Other Nitrogen Sources



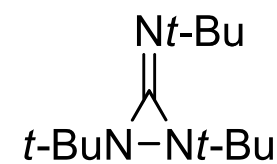
R = aryl 1.2 equiv 45-91% yield
heteroaryl
alkyne
alkylether

- Electron-deficient olefin (ethyl acrylate) and aliphatic substituted olefin (1-octene) are not reactive.

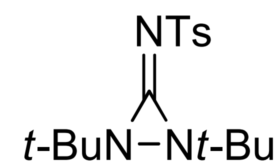


R = aryl 1.2 equiv 48-86% yield
heteroaryl
alkyne
alkene
diene

- No multiple diaminations with dienes or trienes.
- Selective at the terminal olefin.
- Electron-deficient olefin (ethyl acrylate) and aliphatic substituted olefin (1-octene) are not reactive.



No reaction



Decomposed rapidly

Zhao, B.; Yuan, W.; Du, H.; Shi, Y. *Org. Lett.* **2007**, *9,* 4943.
Du, H.; Zhao, B.; Shi, Y. *Org. Lett.* **2008**, *10,* 1087.

Conclusions

- Transition-metal catalyzed 1,2-diamination allows rapid access to protected diamines from alkenes. However, deprotection conditions are quite harsh (e.g. LAH, reflux con. HCl).

- High catalyst loadings are often required.

- Limited enantioselective approach available.

- The dinitrogen source has a strong influence on the reaction at the terminal or the internal alkene.

- Some mechanistic details are elucidated. More studies are required (e.g. nickel catalyzed and copper catalyzed diaminations).

- Much work remained to be done to make this methodology general and practical.