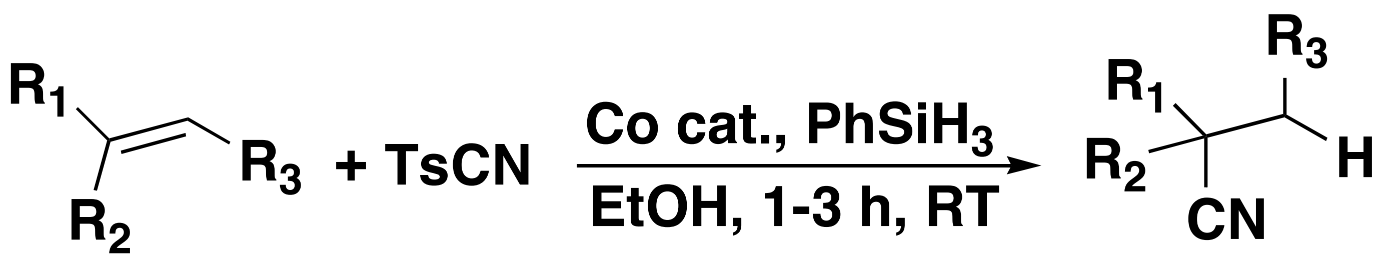
Mild Cobalt-Catalyzed Hydrocyanation of Olefins with Tosyl Cyanide



Gaspar, B.; Carreira, E. M. *Angew. Chem. Int. Ed.* ASAP

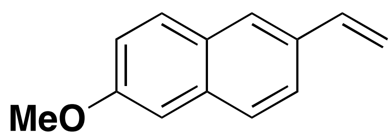
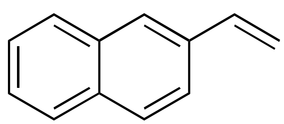
Current Literature
Kalyani Patil
12 May 2007

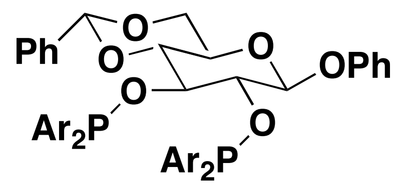
Outline

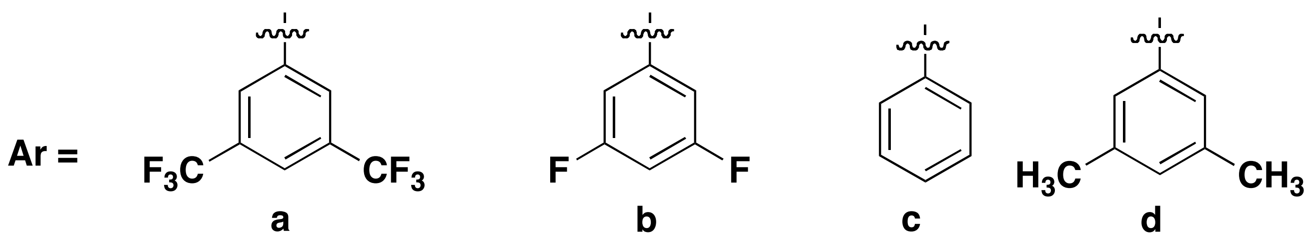
- Ni-Catalyzed Hydrocyanation
- Co-Catalyzed Hydrohydrazination/Hydroazidation
- Title Paper
- Summary

Ni-Catalyzed Asymmetric Hydrocyanation of Olefins

$$ArHC{=}CH_2 + HCN \xrightarrow{Ni(COD)_2/L} ArCH(CH_3)CN$$

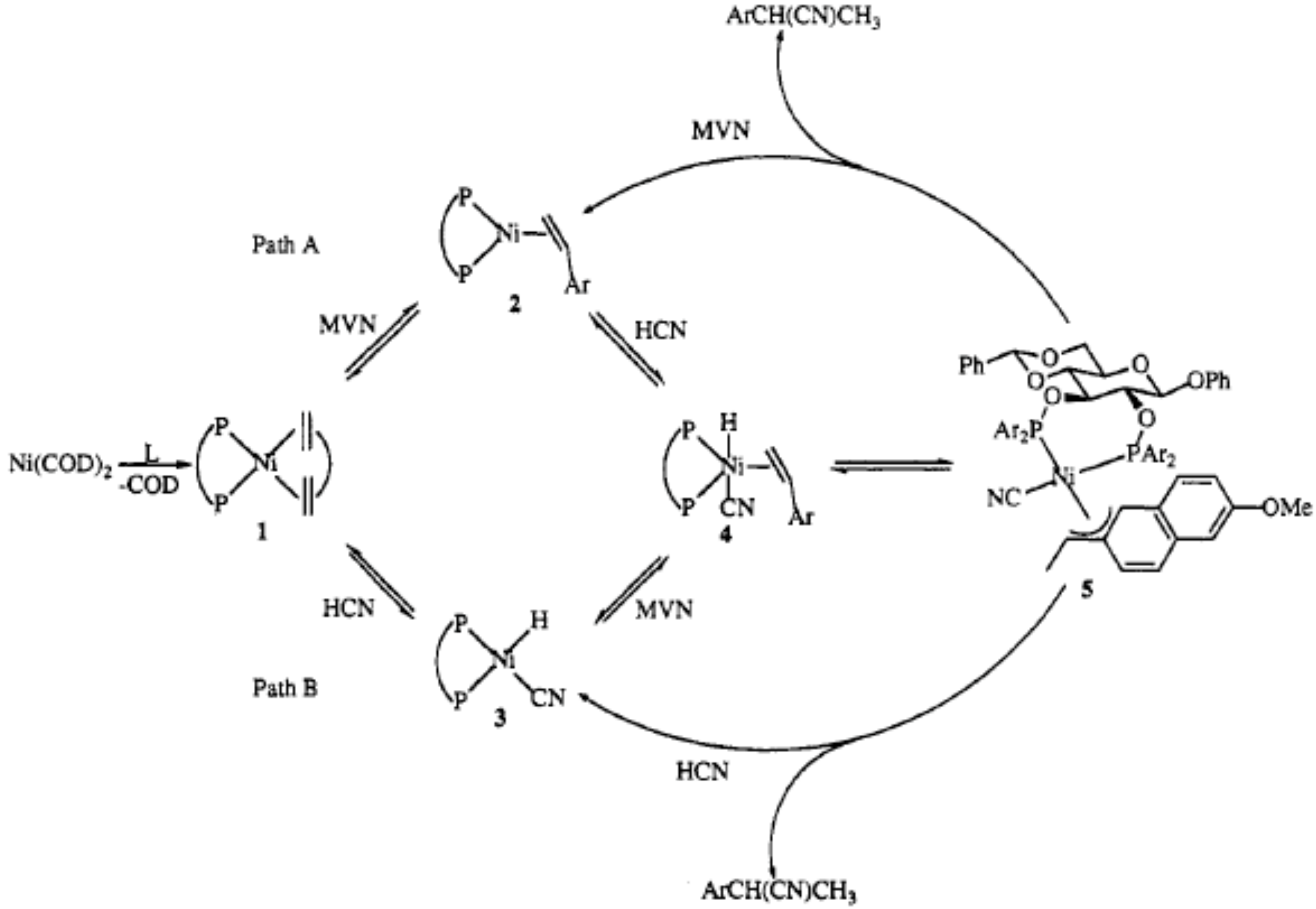
Substrate	ee(%) a	ee(%) b	ee(%) c	ee(%) d
	85-91	78	35	16
	77	75	46	25





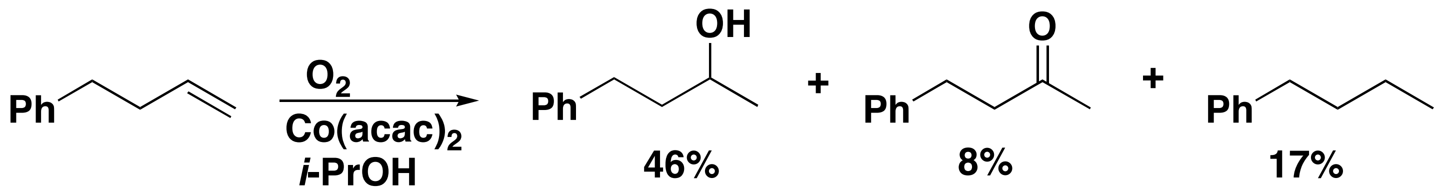
RajanBabu, T. V. et. al. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

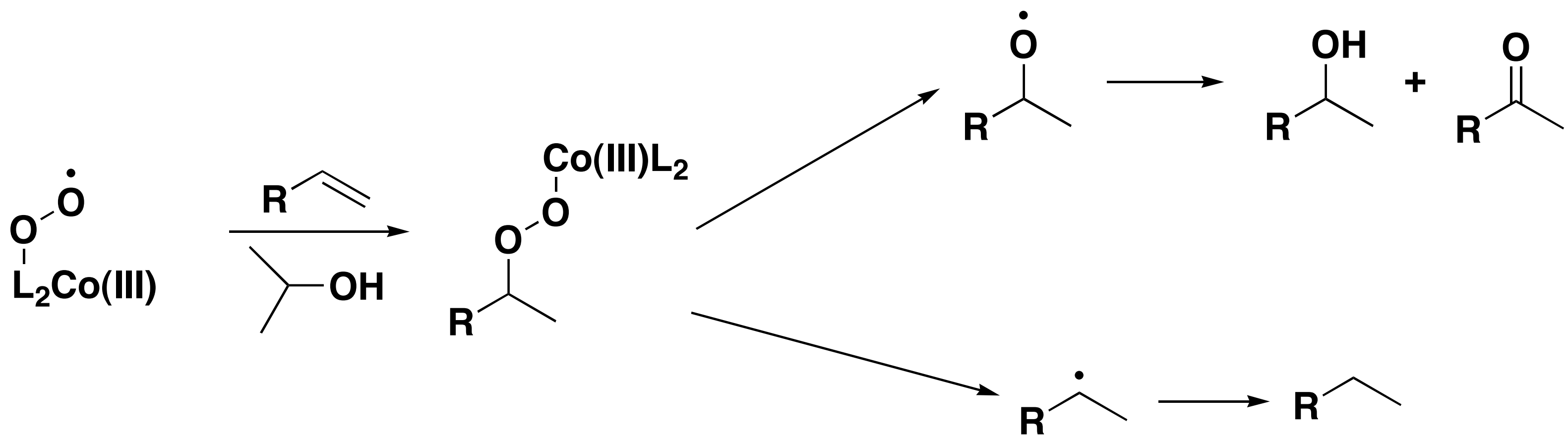
Ni-Catalyzed Hydrocyanation of Olefins



RajanBabu, T. V. et. al. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

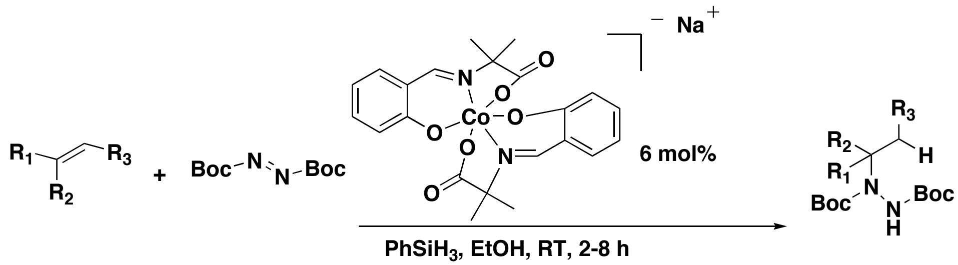
Co-Catalyzed Hydration of Olefins

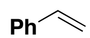
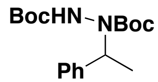
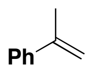
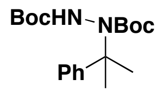
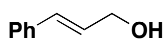
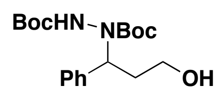
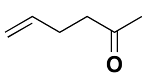
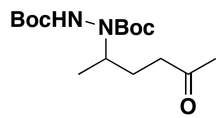
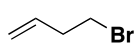
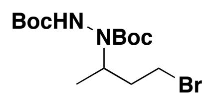
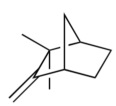
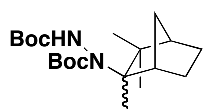
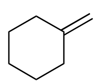
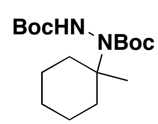
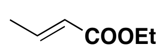
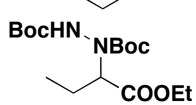




Yamada, T. et. al. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 179.

Co-Catalyzed Hydrohydrazination of Olefins



entry	Alkene	Products	Yield(%)
1			86
2			88
3			91
4			76
5			90
6			69 dr > 5:1
7			90
8			66

Compatibility:

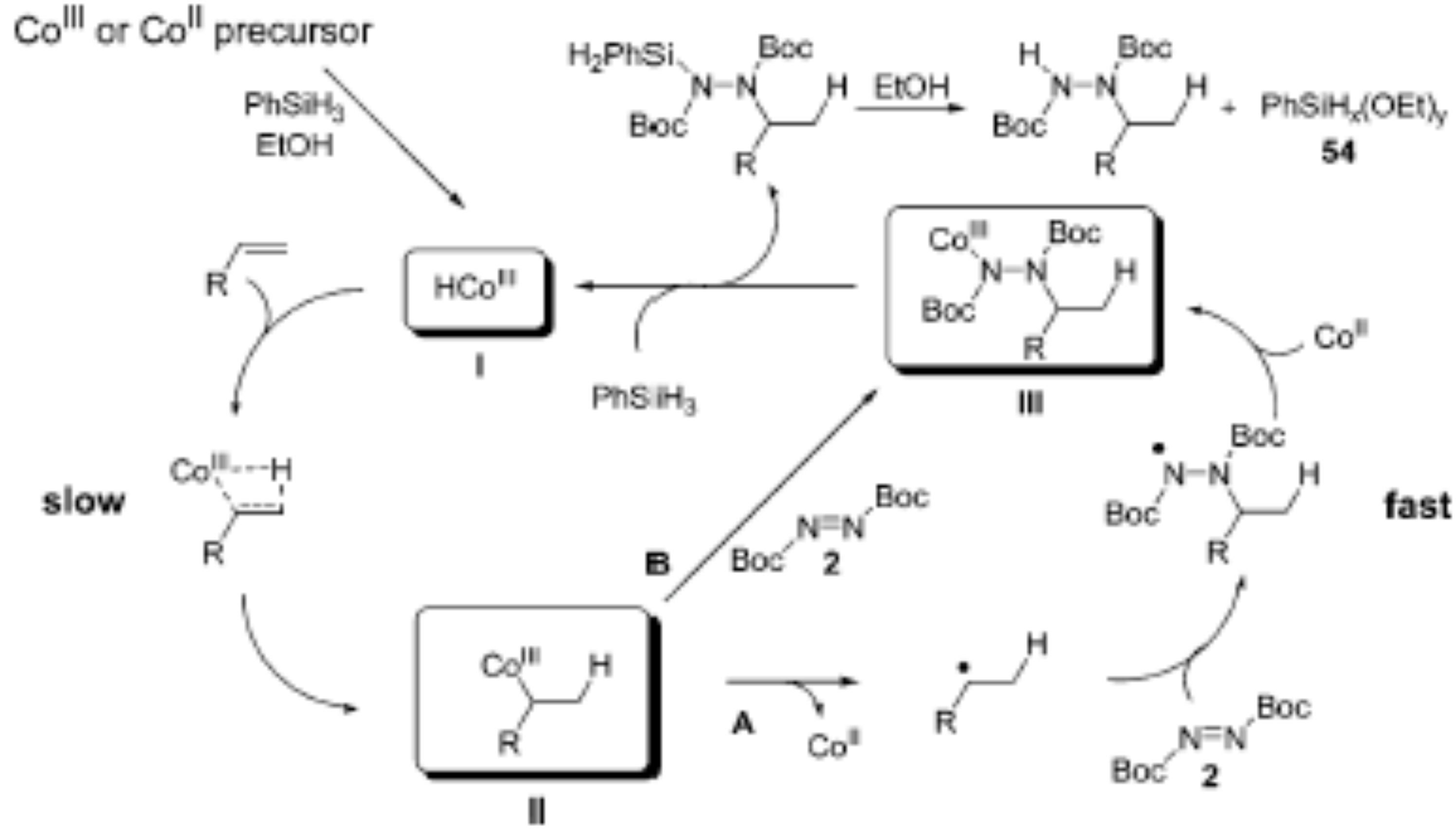
- monosubs, 1,1- and 1,2-disubs. trisubs. olefins
- primary Br and ketones
- styrene derivatives

Limitations:

- tetrasubs. olefins
- cyclohexene
- crotyl alcohol

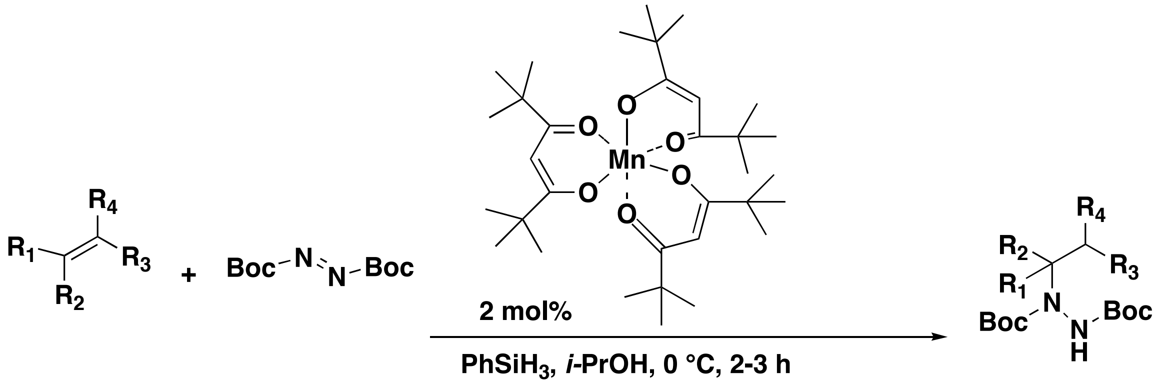
Waser, J.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, *126*, 5676.

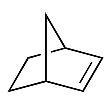
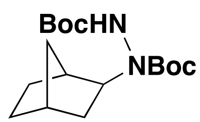
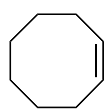
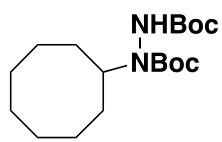
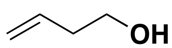
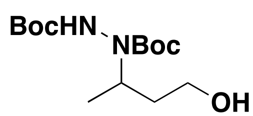
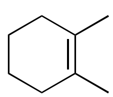
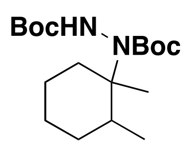
Mechanism for Co-Catalyzed Hydrohydrazination



Carreira, E. M. et. al. *J. Am. Chem. Soc.* **2006**, 128, 11693.

Mn-Catalyzed Hydrohydrazination of Olefins



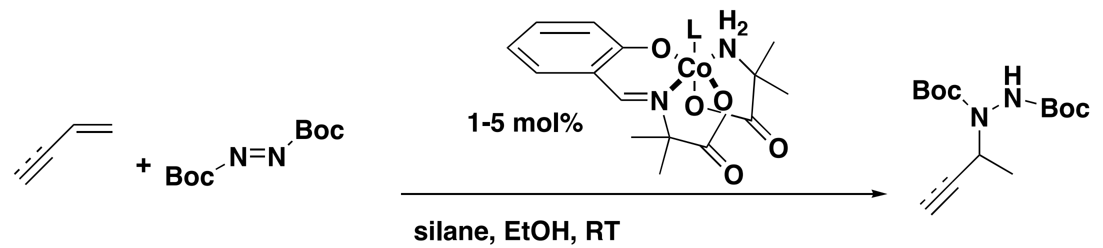
Entry	Alkene	Products	Yield(%)
1			98
2			95
3			72
4			79

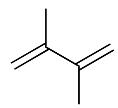
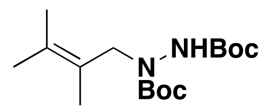
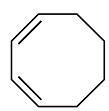
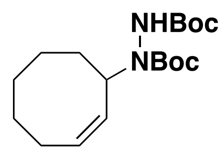
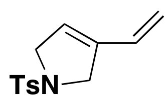
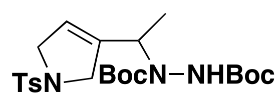
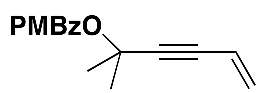
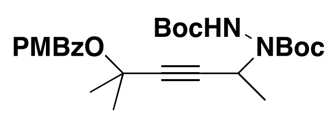
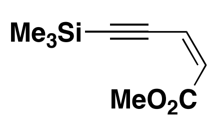
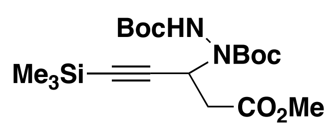
Advantages:

- broad range of substrates
- Faster reaction rates
- cheap PMHS reductant

Waser, J.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2004** *43*, 4099.

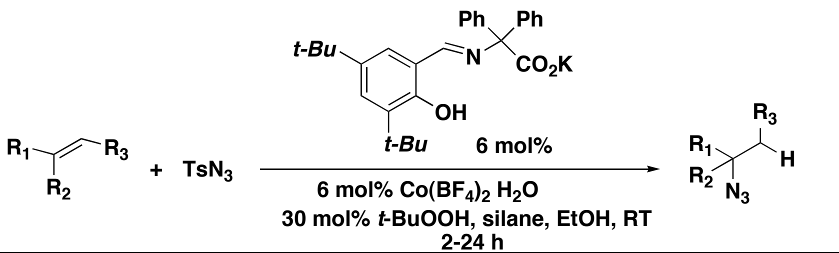
Co-Catalyzed Hydrohydrazination of Dienes and Enynes

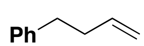
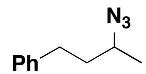
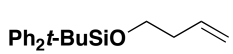
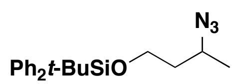
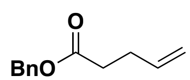
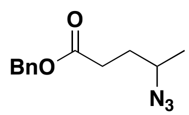
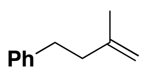
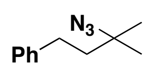
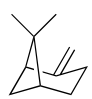
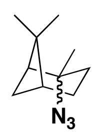
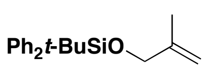
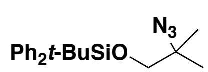
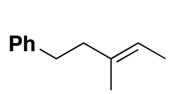
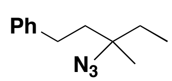


entry	diene	products	yield(%)
1			83
2			81
3			90
4			61
5			47

Carreira, E. M. et. al. *Org*. *Lett*. **2005**, *7*, 4249.

Co-Catalyzed Hydroazidation of Olefins



entry	Alkene	Products	Yield(%) with $PhSiH_3$	Yield(%) with TMDSO
1			90	86
2			73	85
3			75	77
4			86	90
5			89 dr = 4:1	76 dr = 4:1
6			73	58
7			66	48

Compatibility:

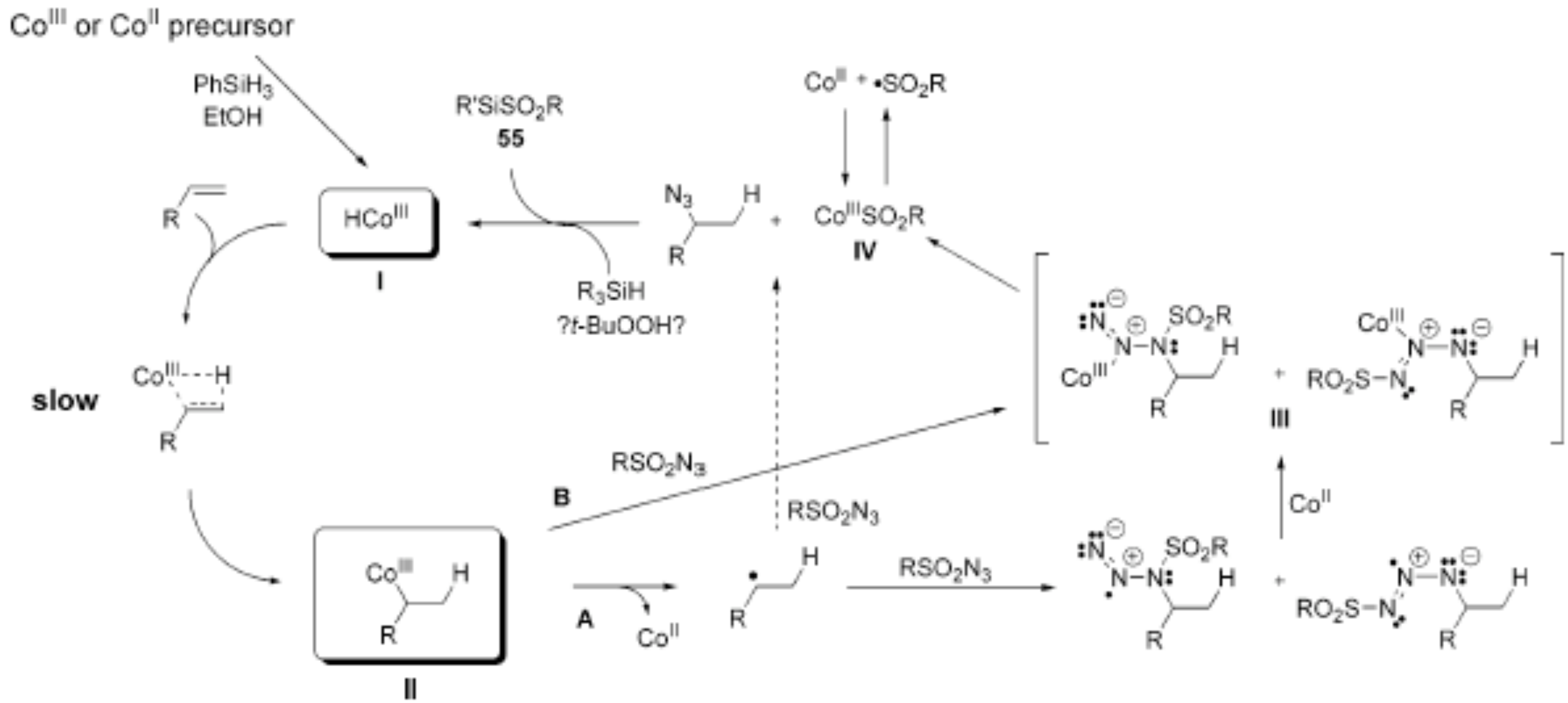
- Aromatic ring in allylic or homoallylic posn.
- Si protected allylic and homoallylic ethers
- Esters and ketones
- Geminally disubs. and trisubs. olefins with $PhSiH_3$

Limitations:

- Styrene derivatives
- Free alcohols

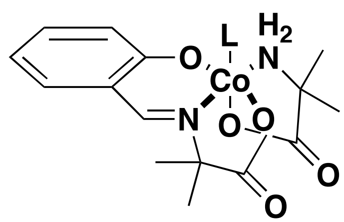
Carreira, E. M. et. al. *J. Am. Chem. Soc.* **2005**, 127, 8294.

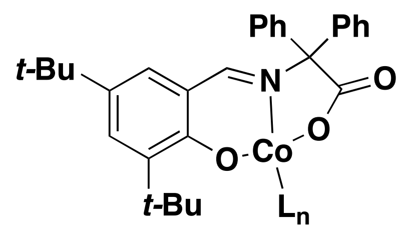
Catalytic Cycle for Co-Catalyzed Hydroazidation

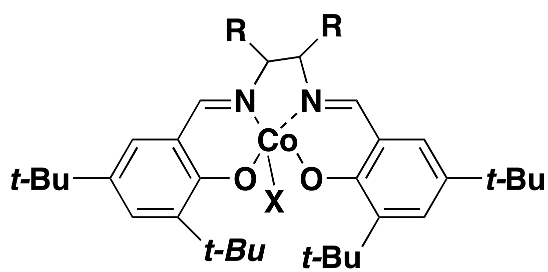


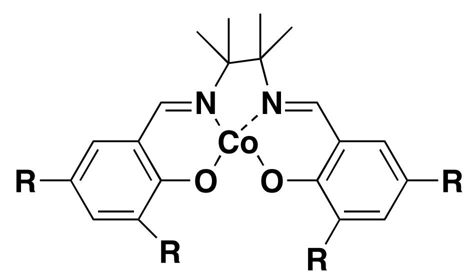
Carreira, E. M. et. al. *J. Am. Chem. Soc.* **2006**, 1*2*8, 11693.

Title Paper - Co-Catalyzed Hydrocyanation of Olefins









1 R = -$(CH_2)_4$-; X = OAc

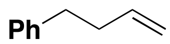
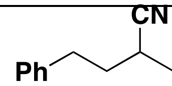
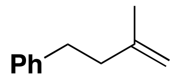
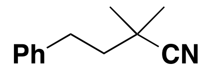
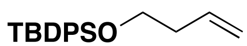
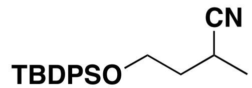
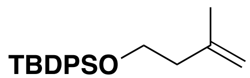
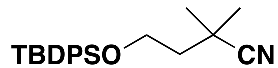
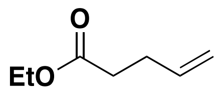
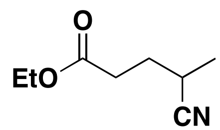
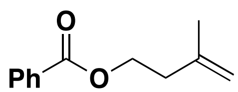
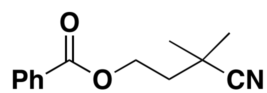
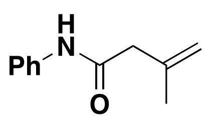
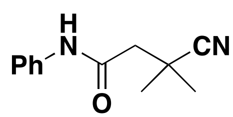
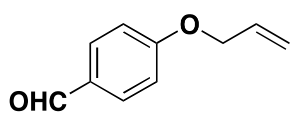
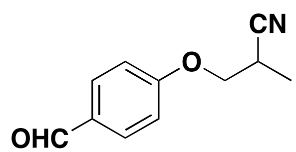
R = H; no X

2 R = *t*-Bu

R = H

Gaspar, B.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2007**, *46*, ASAP.

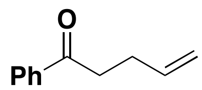
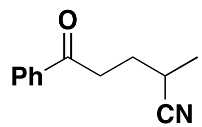
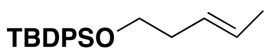
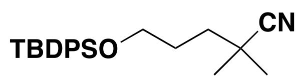
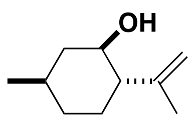
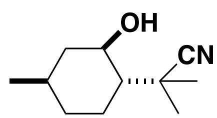
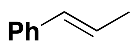
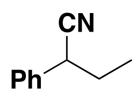
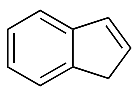
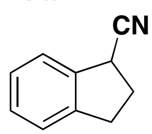
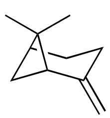
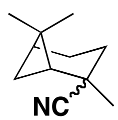
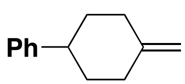
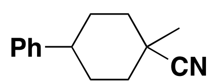
Title Paper - Co-Catalyzed Hydrocyanation of Olefins

Entry	Alkene	Products	Yield(%) 1	Yield(%) 2
1			99	99
2			95	99
3			84	95
4			88	99
5			82	89
6			99	96
7			86	87
8			64	81

Conditions: catalyst **1** (1 mol%), alkene (0.5 mmol), TsCN (0.75 mmol), *t*BuOOH (30 mol%), $PhSiH_3$ (0.5 mmol), EtOH (3 mL), argon, 23 °C

catalyst **2** (1 mol%), alkene (0.5 mmol), TsCN (0.6 mmol), $PhSiH_3$ (0.5 mmol), EtOH (2.5 mL), argon, 23 °C

Title Paper - Co-Catalyzed Hydrocyanation of Olefins

Entry	Alkene	Products	Yield(%) 1	Yield(%) 2
9			40	91
10			48	92
11			73	71
12			45	55
13			63	64
14			88[a]	60[a]
15			74[b]	81[c]

Conditions: catalyst **1** (1 mol%), alkene (0.5 mmol), TsCN (0.75 mmol), *t*BuOOH (30 mol%), $PhSiH_3$ (0.5 mmol), EtOH (3 mL), argon, 23 °C

catalyst **2** (1 mol%), alkene (0.5 mmol), TsCN (0.6 mmol), $PhSiH_3$ (0.5 mmol), EtOH (2.5 mL), argon, 23 °C

[a] dr could not be determined. [b] dr = 17:1 [c] dr = 3:1

Compatibility:

- Simple alkenes, protected alcohols, esters and amides
- **2** works better for aldehydes, ketones, and tri-subs. alkenes

Limitations:

- Styrene derivatives - moderate yield
- α,β-unsatd. Esters, cyclohexene

Gaspar, B.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2007**, *46*, ASAP.

Summary

- Synthesis of secondary and tertiary nitriles by Co catalyzed hydrocyanation of olefins
- Broad substrate scope
- Mild reaction conditions
- Readily available starting materials