Diaminophosphine Oxide Ligand Enabled Asymmetric Nickel-Catalyzed Hydrocarbamoylations of Alkenes

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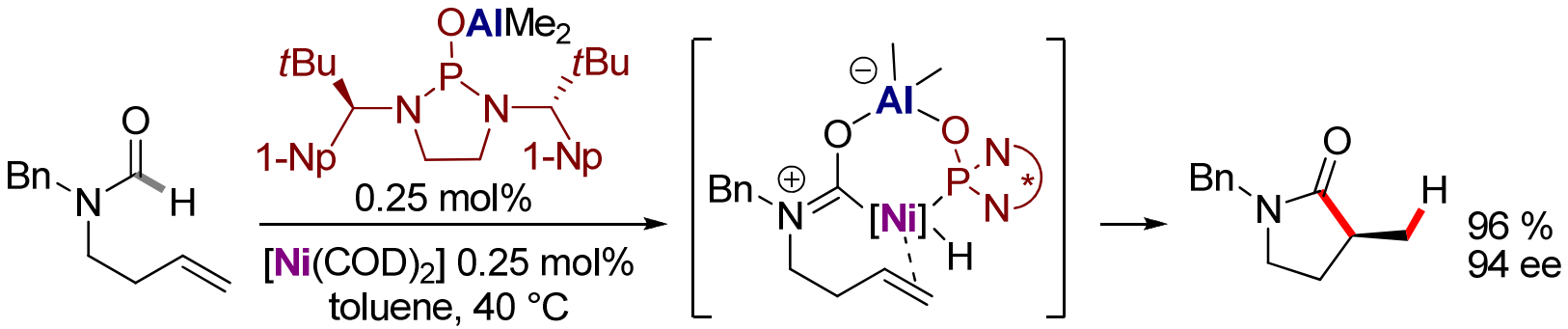
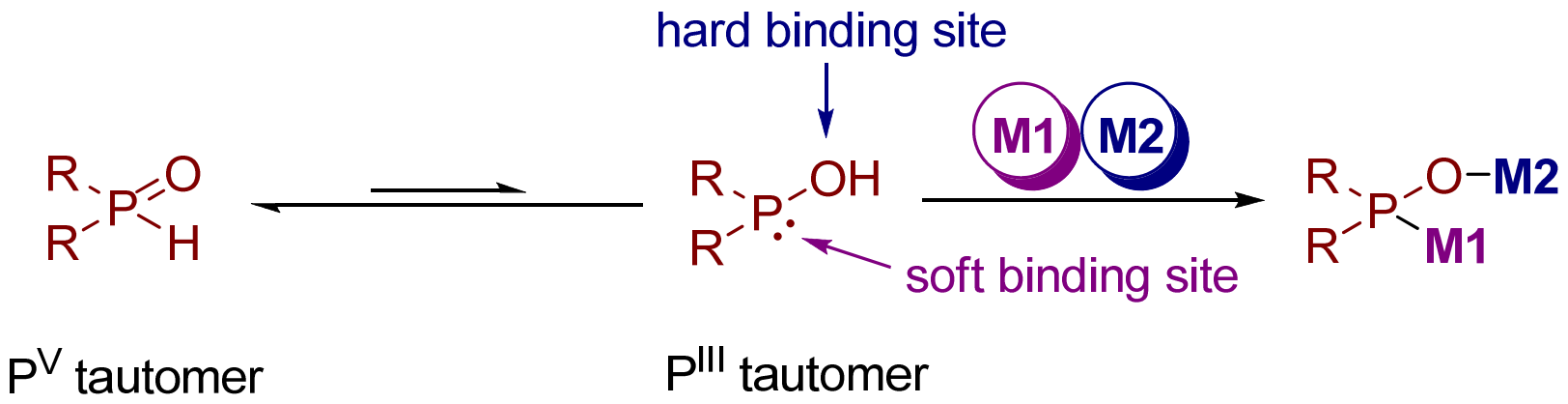


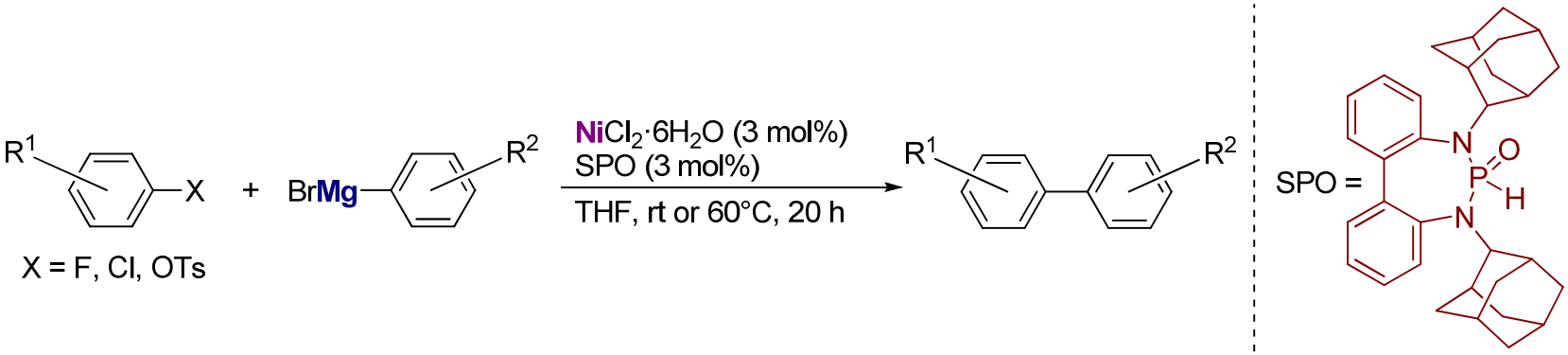
Vsevolod Peshkov
Wipf Group Current Literature
10/12/2013

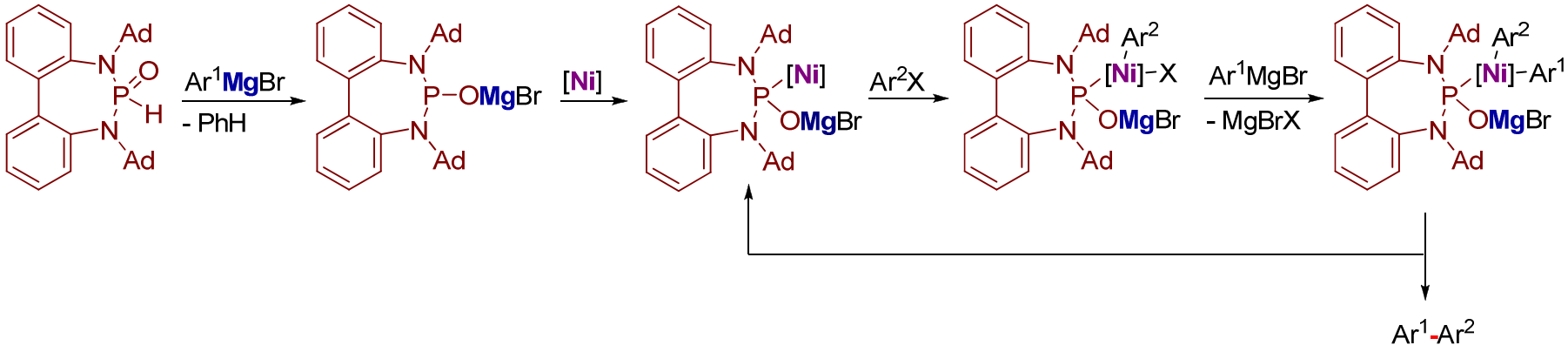
The secondary phosphine oxide (SPO) concept:



For review on SPO, see: Ackermann, L. *Synthesis* **2006**, 1557

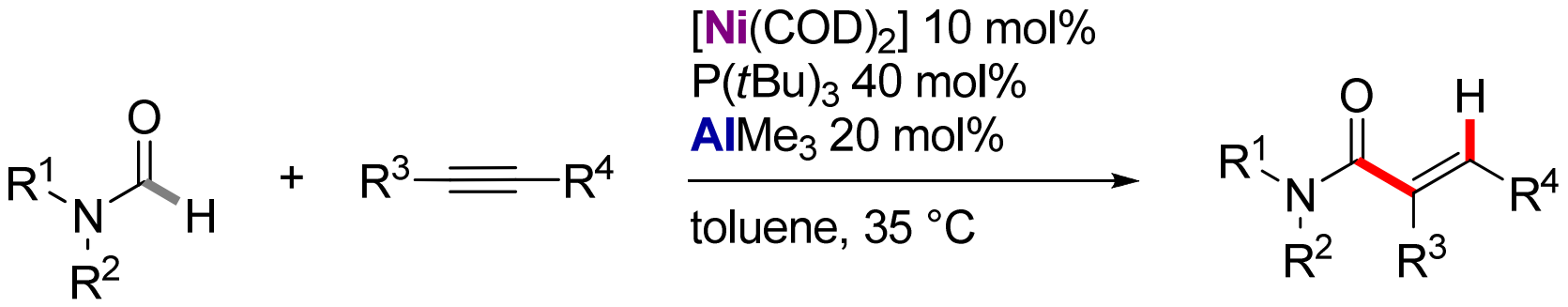
SPO early/late heterobimetallic intermediates in catalysis





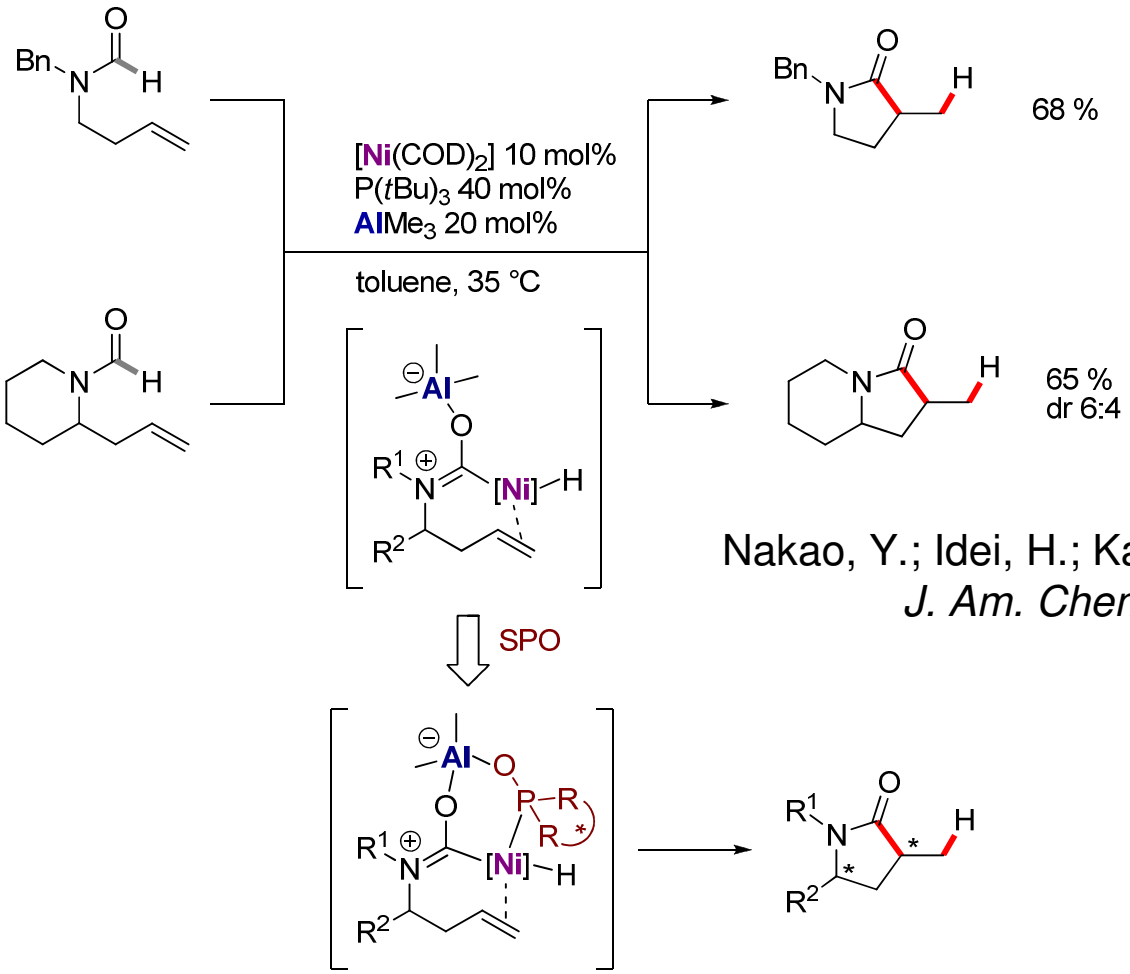
Ackermann, L.; Born, R.; Spatz, J. H.; Meyer, D. *Angew. Chem., Int. Ed.* **2005**, 44, 7216
Ackermann, L.; Althammer, A. *Chem. Unserer Zeit* **2009**, 43, 74
Jin, Z.; Li, Y.-J.; Ma, Y.-Q.; Qiu, L.-L.; Fang, J.-X. *Chem.—Eur. J.* **2012**, 18, 446

Hydrocarbamoylation of Unsaturated Bonds; a Background



Nakao, Y.; Idei, H.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2009**, 131, 5070

Hydrocarbamoylation of Unsaturated Bonds; a Background



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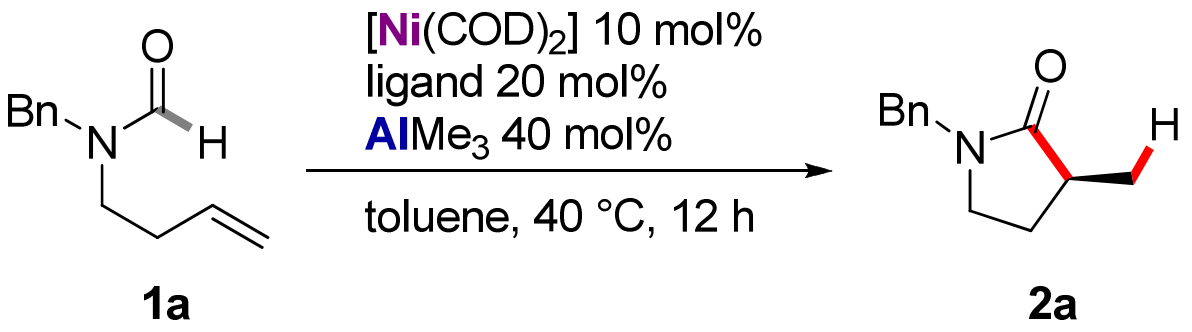
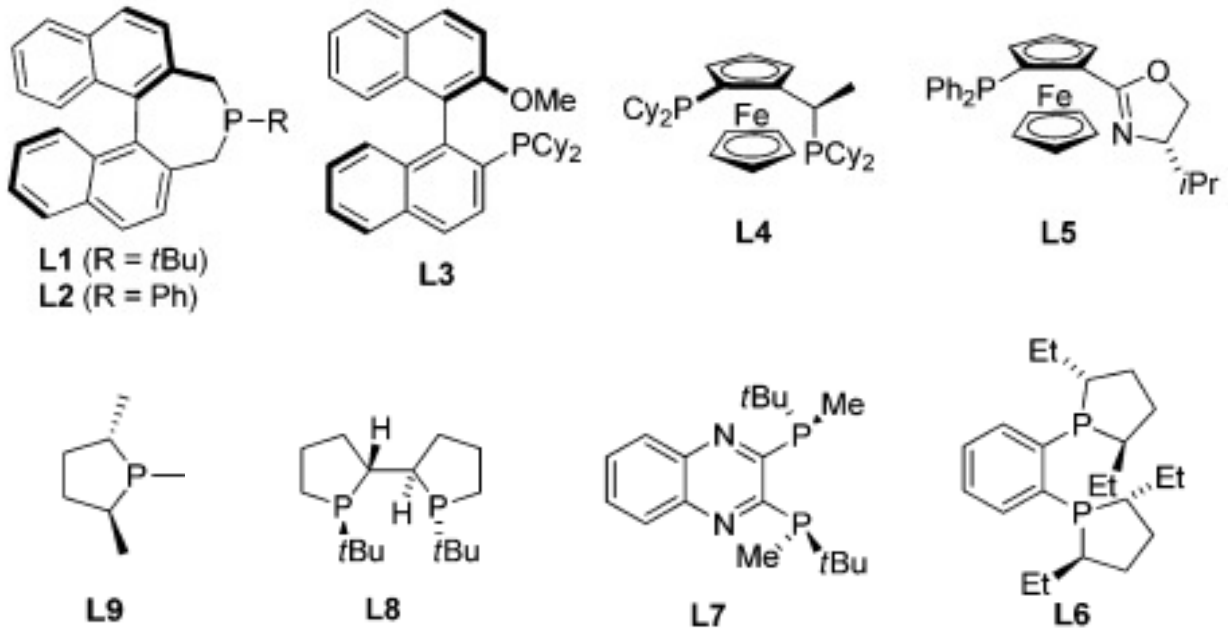
Optimization of Asymmetric Hydrocarbamoylation



1a **2a**

Ligand	Yield	ee
L1	50	57:43
L2	5	-
L3	2	-
L4	10	51:49
L5	3	-
L6	41	60:40
L7	26	72:28
L8	10	52:48
L9	14	68:32



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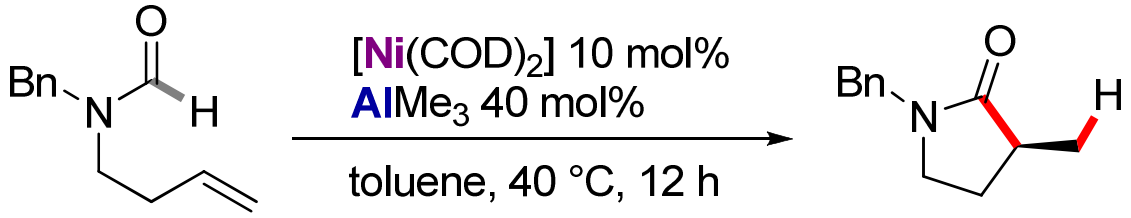
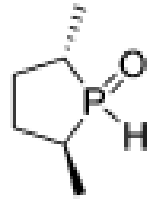
Optimization of Asymmetric Hydrocarbamoylation



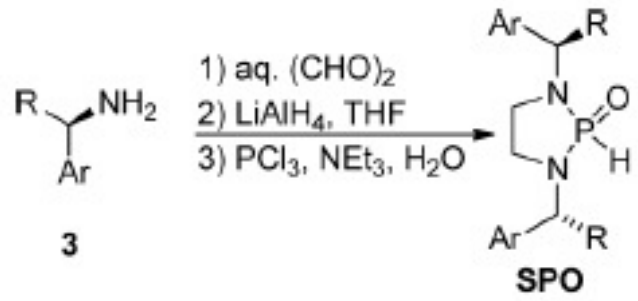
1a **2a**



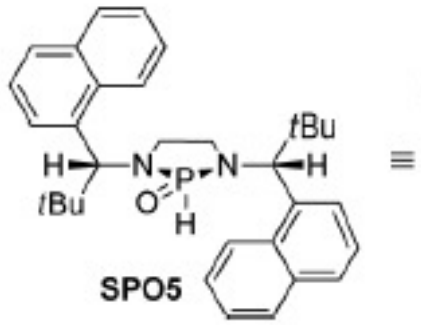
SPO1

SPO1	PPh_3	Yield	ee
10 mol%	-	18	61:39
10 mol%	10 mol%	87	14:86

SPO Preparation



SPO2 (Ar = Ph, R = Me), 46 %
SPO3(Ar = 1-Np, R = Me), 43 %
ent-**SPO4** (Ar = *o*-tolyl, R = *t*Bu), 24 %
SPO5 (Ar = 1-Np, R = *t*Bu), 42 %



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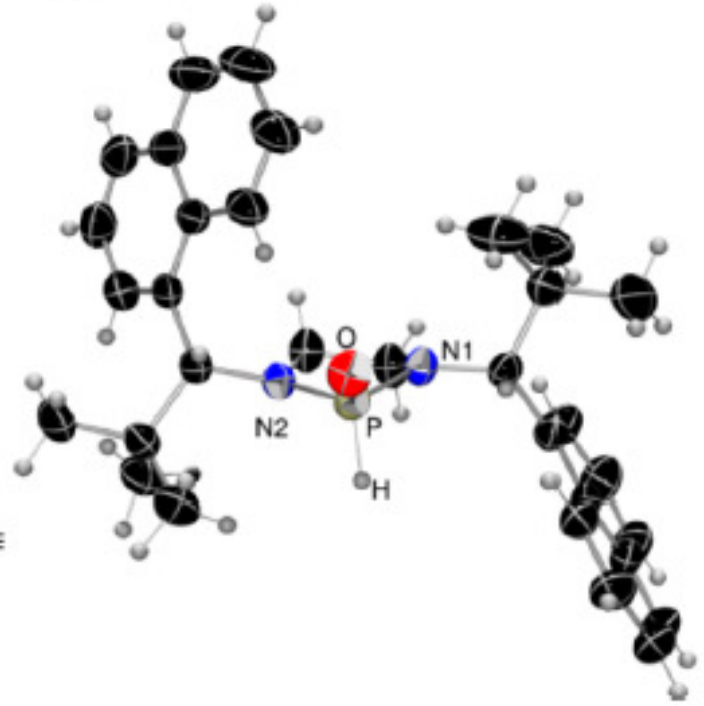

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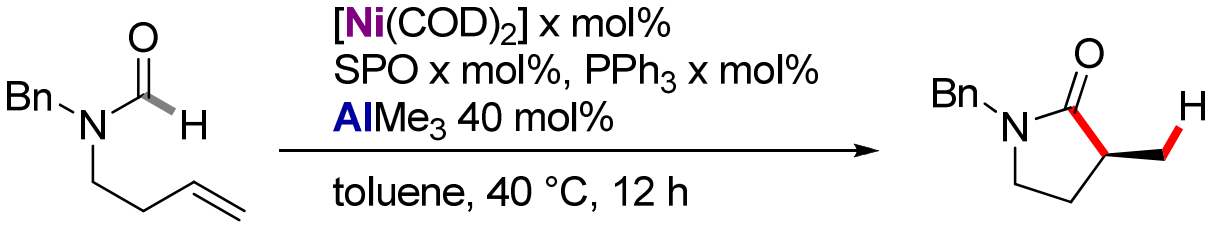
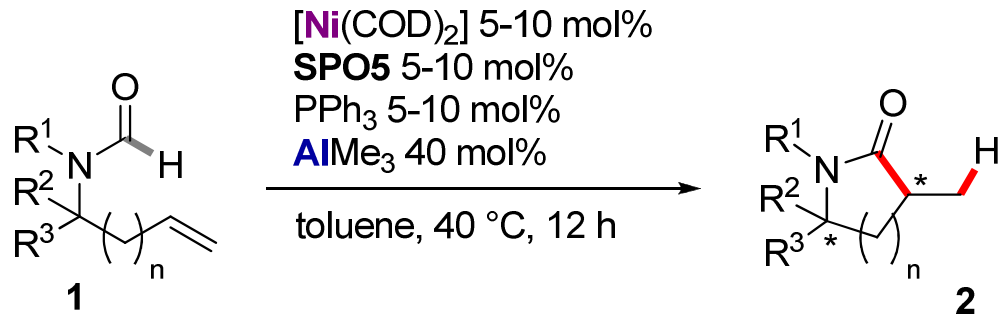
Optimization of Asymmetric Hydrocarbamoylation

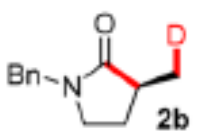


1a **2a**

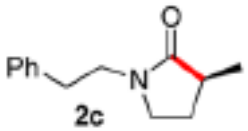
x	**SPO**	Yield	ee
10	**SPO2**	40	62:38
10	**SPO3**	83	84:16
10	**SPO4**	82	40:60
10	**SPO5**	88	96.5:3.5
0.5	**SPO5**	90	96.5:3.5
0.25	**SPO5**	61	96.5:3.5

Scope of Asymmetric Hydrocarbamoylation

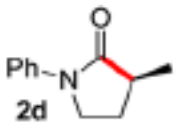




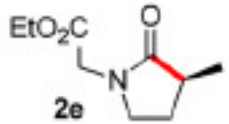
89 %
>95 % D
94:6



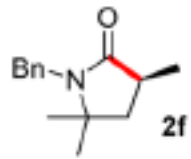
79 %
97:3



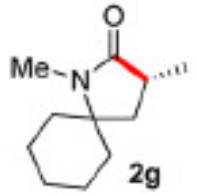
91 %
96.5:3.5



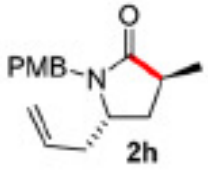
75 %
96:4



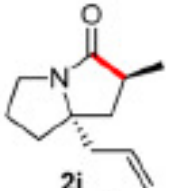
95 %
89.5:10.5



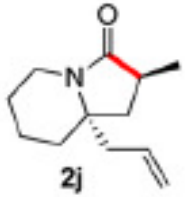
with SPO1
82 %
92:8



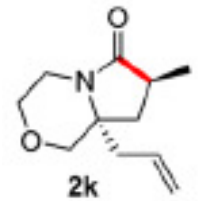
81 %
5:1 dr
97.5:2.5



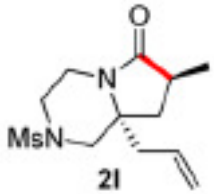
98 %
4:1 dr
94.5:5.5



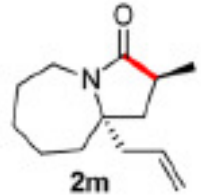
83 %
>20:1 dr
94:6



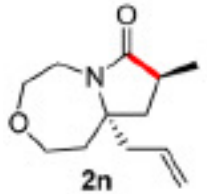
90 %
9:1 dr
96:4



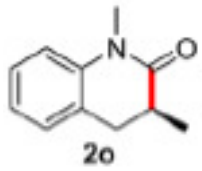
94 %
5:1 dr
96:4



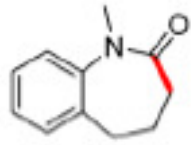
77 %
>20:1 dr
93:7



81 %
>20:1 dr
96:4



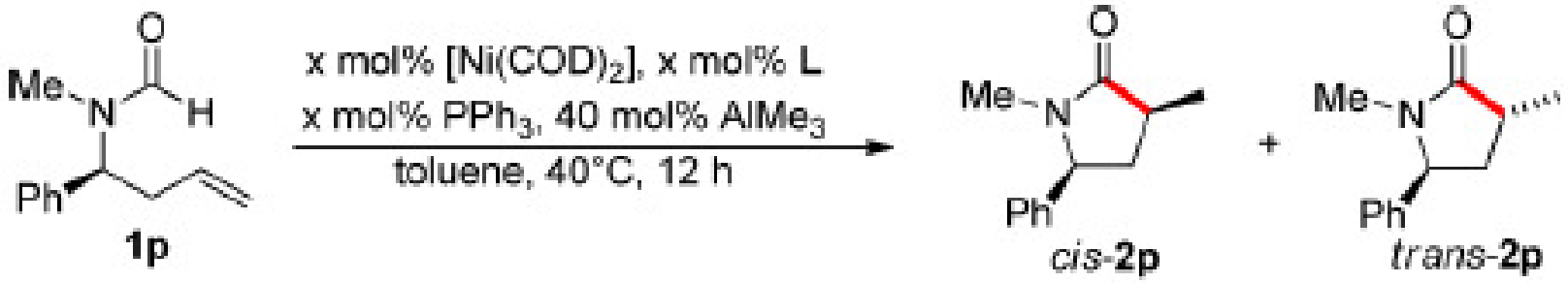
46 %
94:6



40 %

10

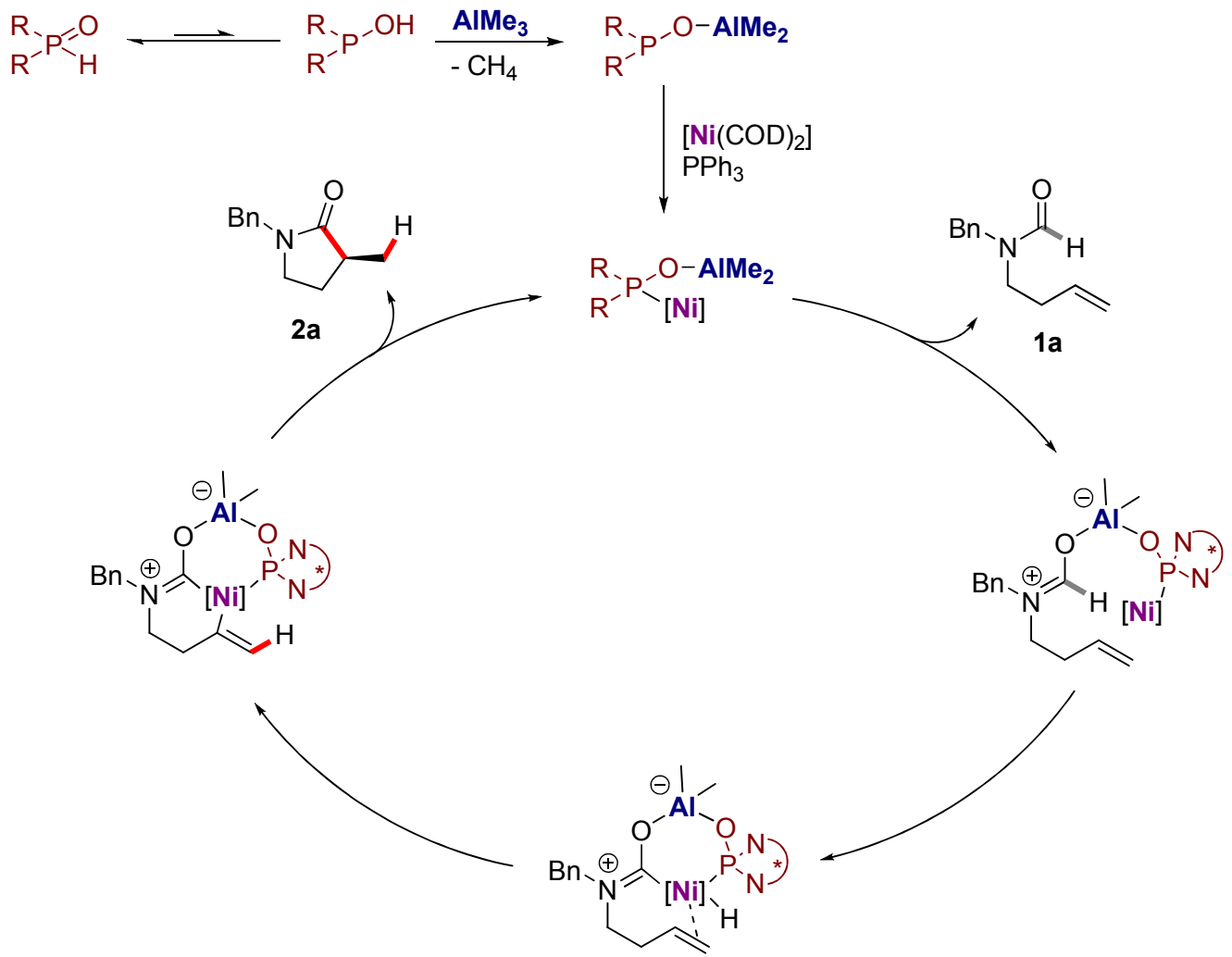
Matched/Mismatched Stereocontrol with Chiral Substrate **1p**



SPO5 (x = 5)	:	92 %, 16 : 1 dr (*cis/trans*)
ent-**SPO5** (x = 5)	:	99 %, 1 : 3 dr (*cis/trans*)
Cy_2POH (x = 10)	:	50 %, 4 : 1 dr (*cis/trans*)

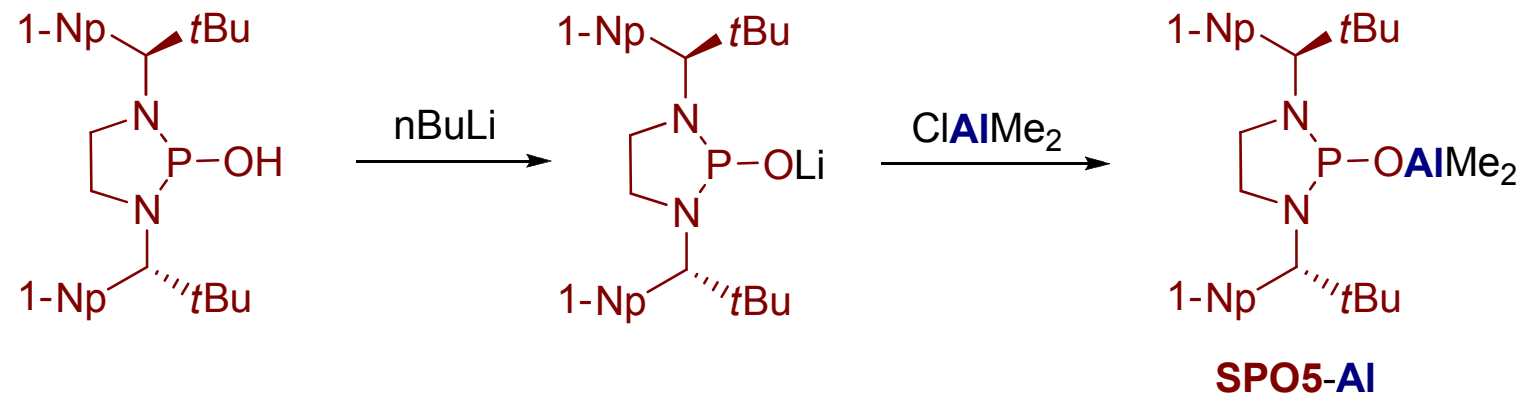
11

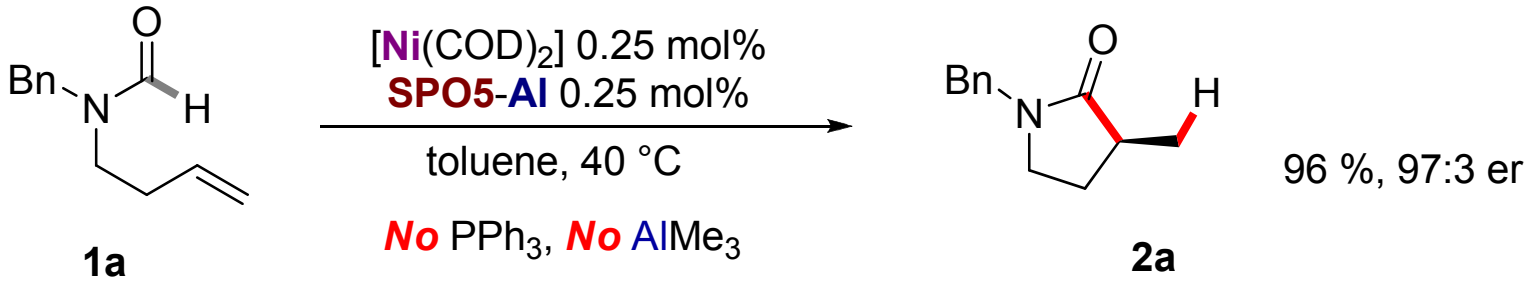
Mechanistic Proposal of the Bimetallic Activation with SPO Ligands



12

Catalytic Performance of the Preformed Lewis Acid/Ligand **SPO5-Al**





CONCLUSIONS

- Application of **SPO** in the process involving **C-H activation**
- New family of **chiral SPO's** prepared and utilized
- Possible further directions:
  - Better understanding of PPh_3 role
  - Expanding of substrate scope to the use of longer chains, internal double-bounds and different carbonyl functionalities