

# OMCOS18

Organometallic Chemistry  
Directed Towards Organic Synthesis  
IUPAC International Symposium

Sitges - Barcelona **2015**  
From June 28th to July 2nd



## Highlights from OMCOS 18

**Andrea Ambrosi**  
Denmark group meeting  
July 28, 2015



## OMCOS

- Conceived by **John Stille** and **Giorgio Modena** in **1979**
- The first symposium took place at **Colorado State University (Fort Collins)** in **1981** (key speakers: Posner, Kumada, Noyori, Heck, Tsuji, Larock, Negishi, Semmelhack, Trost)

FIRST  
IUPAC SYMPOSIUM  
ON  
ORGANOMETALLIC CHEMISTRY  
DIRECTED TOWARD  
ORGANIC SYNTHESIS

August 2-6, 1981  
Fort Collins, Colorado  
U.S.A.



Noyori, Tsuji, Stille, Meyers, Negishi, Murahashi

# OMCOS

19 - Seoul, summer 2017  
Chairs: Sukbok Chang, Chulbom Lee

18 - Sitges - Barcelona, Spain, June 28 – July 2, 2015  
Chair: Antonio Echavarren

17 - Ft. Collins, July 28 - August 1, 2013  
Chair: Tomislav Rovis

16 - Shanghai, July 24 - 28, 2011  
Chairs: Shengming Ma & Kuiling Ding

15 - Glasgow, July 26 - 30, 2009  
Chair: Pavel Kočovský

14 - Nara, August 2 - 6, 2007  
Chair: Koichiro Oshima

13 - Geneva, July 17 - 21, 2005  
Chairs: E. Peter Kündig & Alexandre Alexakis

12 - Toronto, July 6 - 10, 2003  
Chair: Mark Lautens

11 - Taipei, July 22 - 26, 2001  
Chair: Tien-Yau Luh

10 - Versailles, July 18 - 22, 1999  
Chair: Jean-Pierre Genet

9 - Goettingen, July 20 - 25, 1997  
Chair: Armin de Meijere

8 - Santa Barbara, California, August 6 - 10, 1995  
Chair: Bruce Lipshutz

7 - Kobe, September 19 - 23, 1993  
Chair: Shun-Ichi Murahashi

6 - Utrecht, August 25 - 29, 1991  
Chair: Gerard van Koten

5 - Florence, October 1 - 6, 1989  
Chair: Alfredo Ricci

4 - Vancouver, July 26 - 30, 1987  
Chairs: Michael Fryzuk & Gary Posner

3 - Kyoto, July 11 - 15, 1985  
Chair: Hitoschi Nozaki

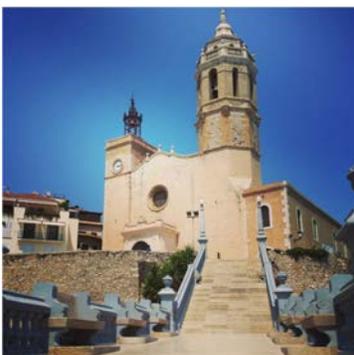
2 - Dijon, August 28 - September 1, 1983  
Chair: Manfred Schlosser

1 - Fort Collins, Colorado, August 2 - 6, 1981  
Chair: Louis Hegedus

## Sitges, Spain



## Sitges, Spain



## Format

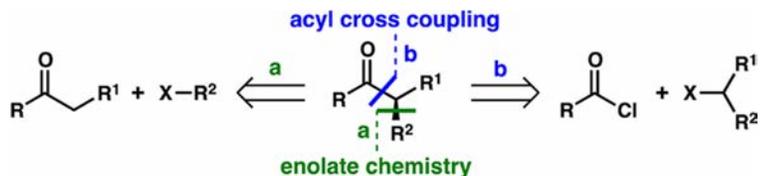
- Single venue
- ca. 900 attendees
- 23 invited lectures/plenary lectures (30-50 min)
- 28 oral communications (15 min)
- > 600 posters (2 sessions)



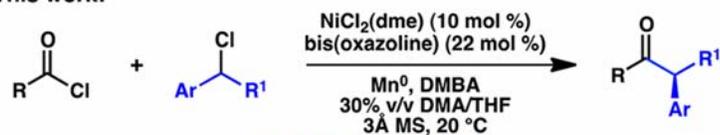


## Sarah Reisman

### Reductive Acyl-Benzyl Cross-Coupling



This work:

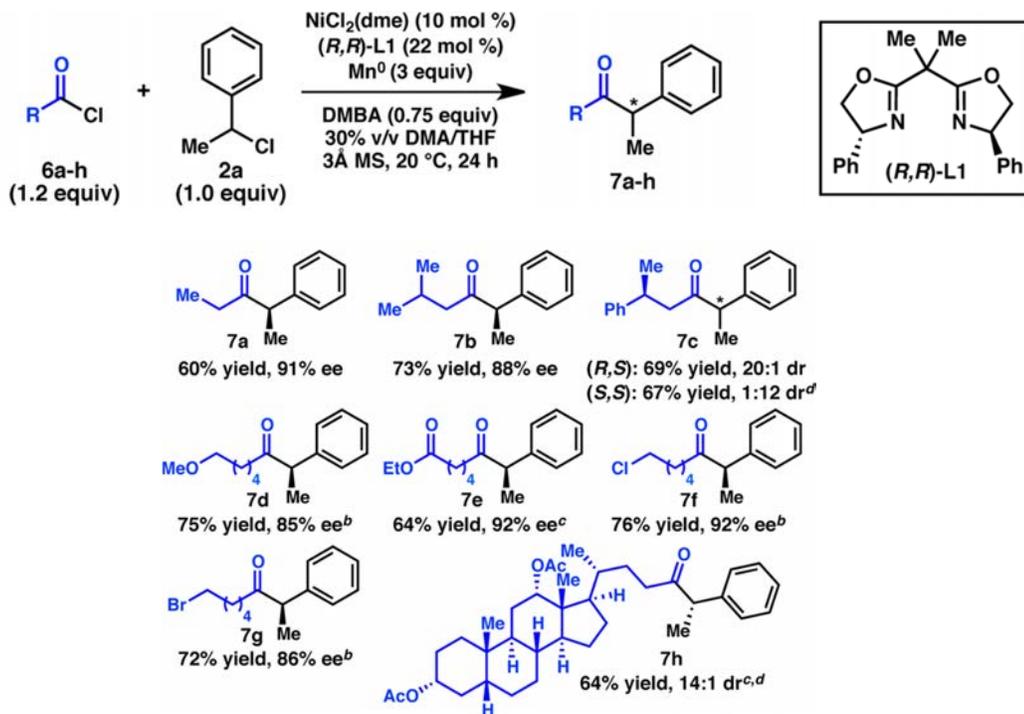


• **direct ketone formation**

- no pregeneration of organometallic reagents
- no stoichiometric chiral auxiliaries
- high functional group tolerance
- no epimerization of tertiary center

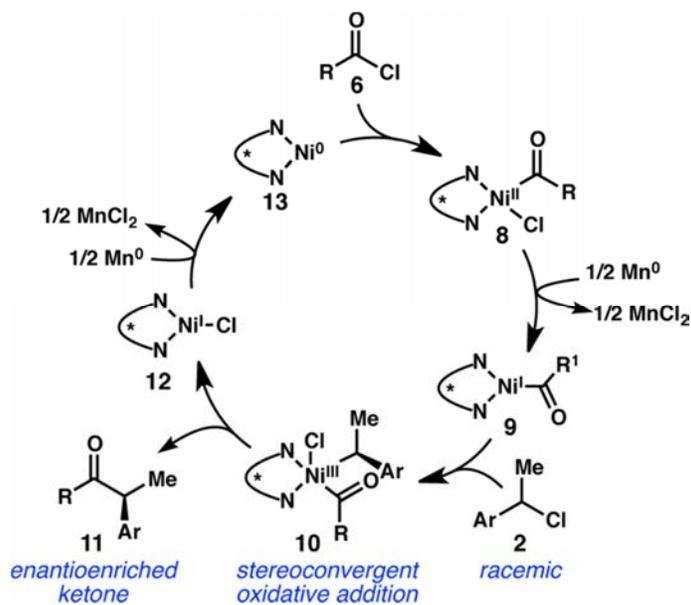
Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442.

## Sarah Reisman



Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442.

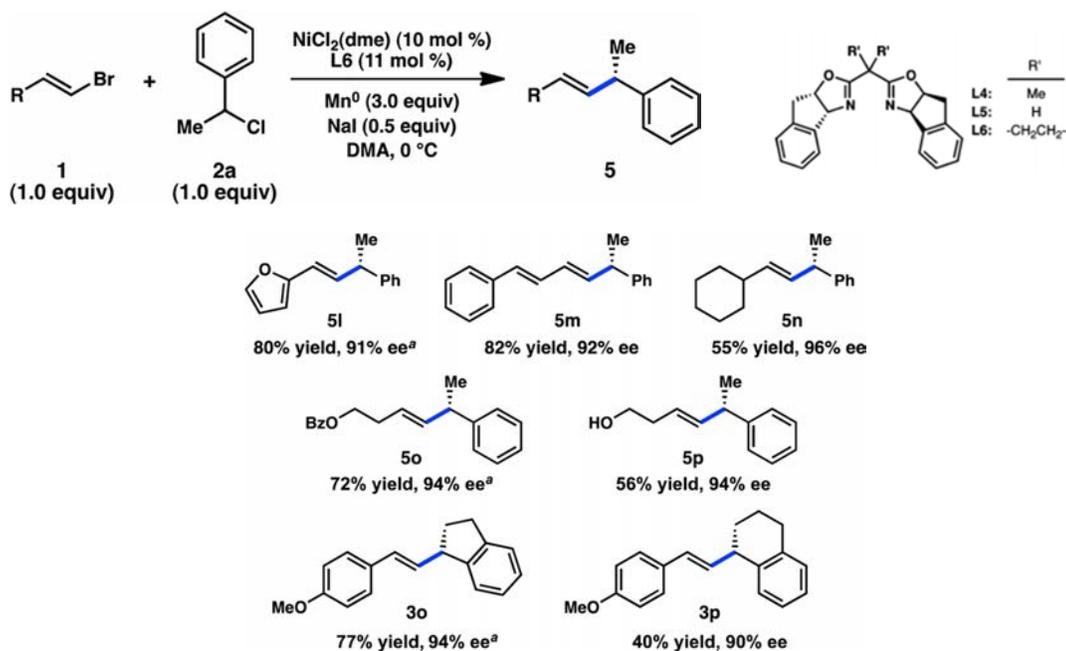
## Sarah Reisman



Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442.

## Sarah Reisman

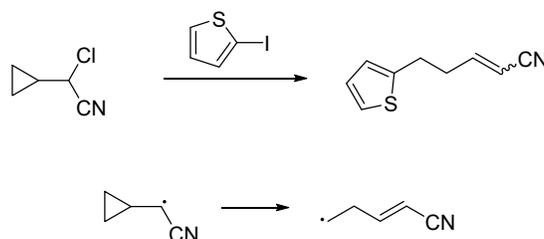
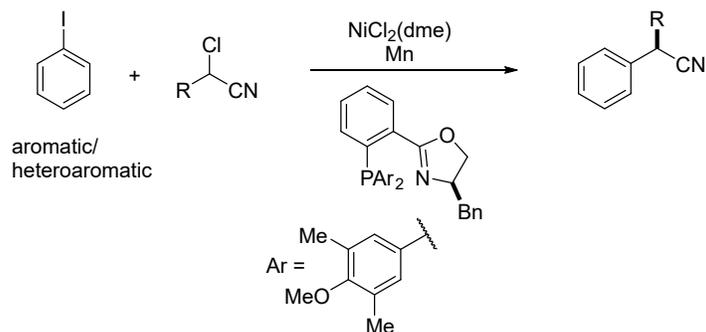
### Reductive Vinyl-Benzyl Cross-Coupling



Cherney, A. H.; Reisman, S. E. *J. Am. Chem. Soc.* **2014**, *136*, 14365.

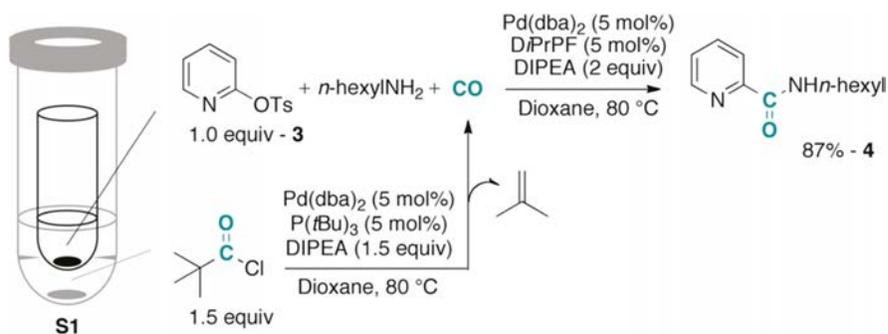
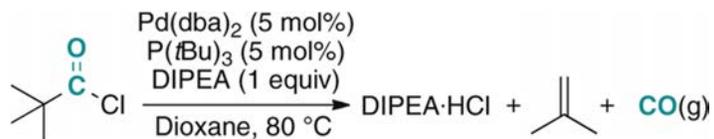
## Sarah Reisman

### Reductive Aryl-Nitrile Cross-Coupling

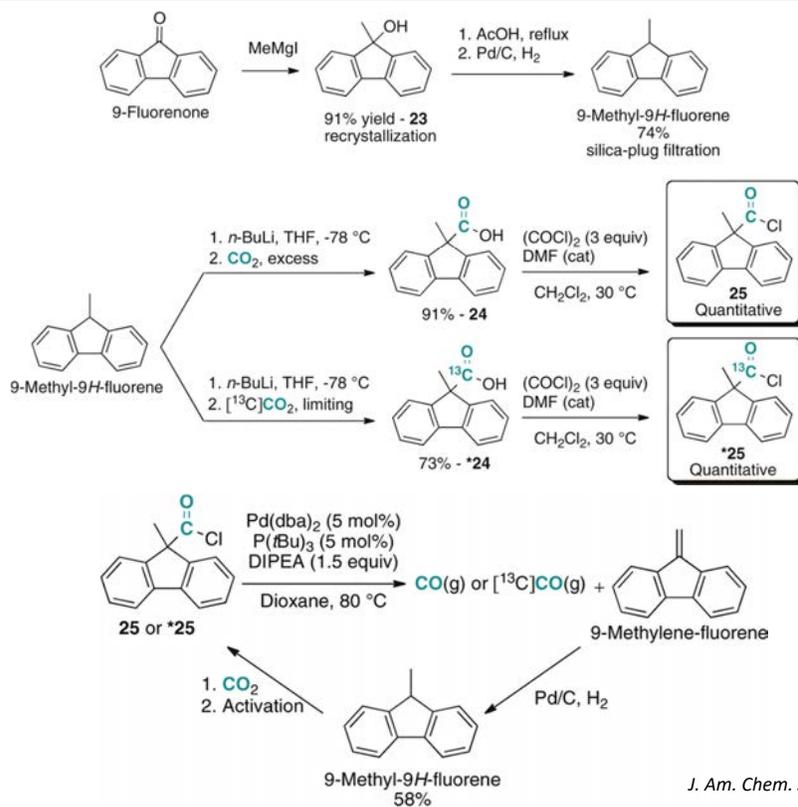


## Troels Skrydstrup

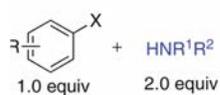
### Ex Situ Generation of Stoichiometric CO



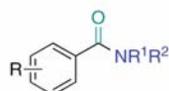
## Troels Skrydstrup



## Troels Skrydstrup

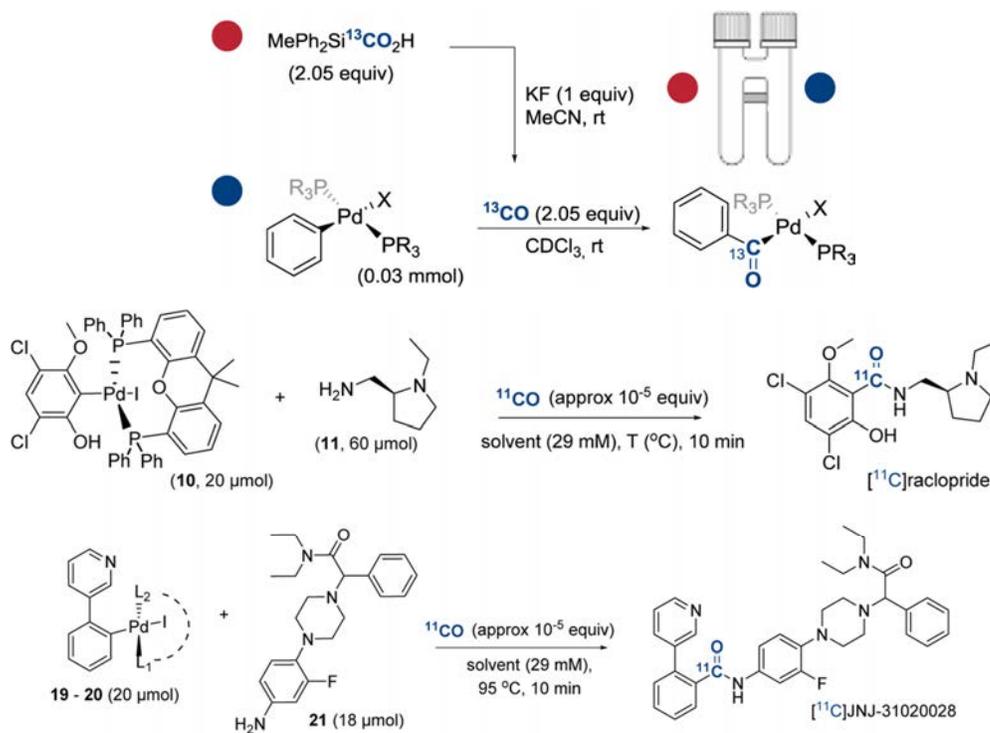


**Chamber 1:**  
 Pd-Catalyzed carbonylation  
**Chamber 2:**  
 25 or \*25 (1.0 equiv), Pd(dba)<sub>2</sub> (5 mol%),  
 P(tBu)<sub>3</sub> (5 mol%), DIPEA (1.5 equiv)



Entry	(Het)Ar-X	Product	25 <sup>b</sup>	*25 <sup>b</sup>
1			86%	87%
2			83%	90%
3			94%	89%
4			83%	95%
5			63%	62%
6			65%	66%
7			84%	75%
8			79%	80%
9			89%	91%

## Troels Skrydstrup



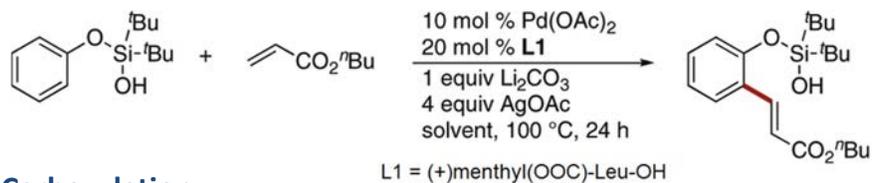
Andersen, T. L.; Friis, S. D.; Audrain, H.; Nordeman, P.; Antoni, G.; Skrydstrup, T. *J. Am. Chem. Soc.* **2015**, *137*, 1548.

## Vladimir Gevorgyan

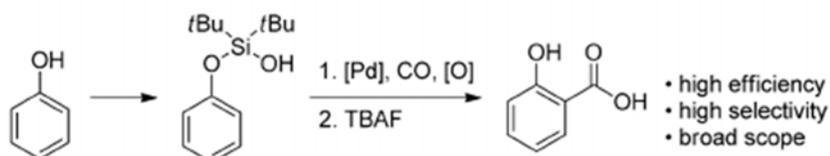


### Palladium-Catalyzed Silanol-Directed C-H activation

#### Alkenylation

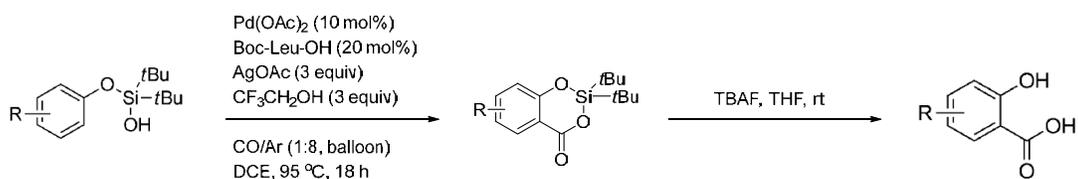


#### Carboxylation

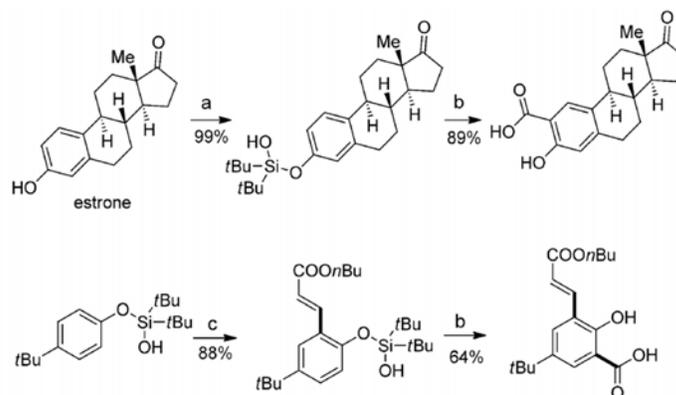


Huang, C.; Chattopadhyay, B.; Gevorgyan, V. *J. Am. Chem. Soc.* **2011**, *133*, 12406.  
Wang, Y.; Gevorgyan, V. *Angew. Chem. Int. Ed.* **2015**, *54*, 2255.

## Vladimir Gevorgyan



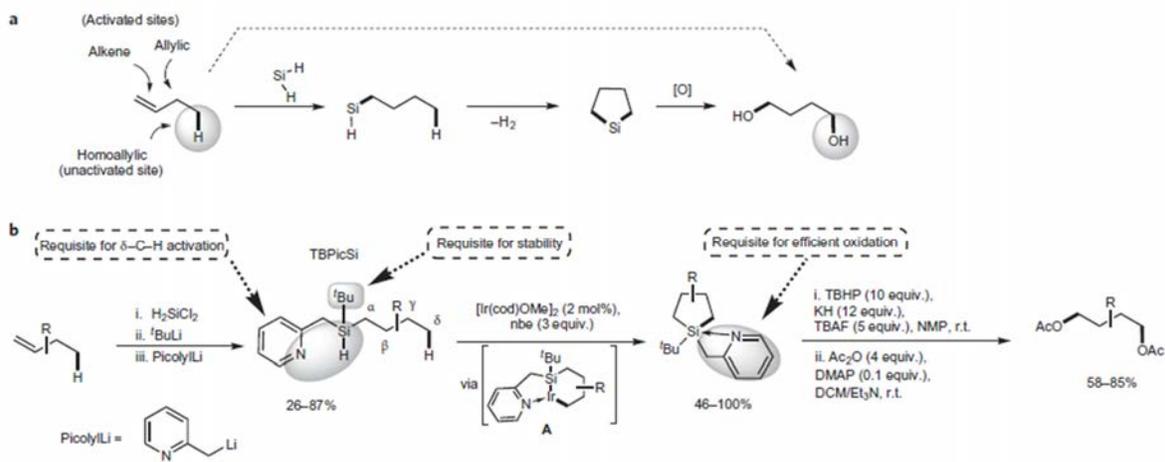
27 examples, 45-99%



Wang, Y.; Gevorgyan, V. *Angew. Chem. Int. Ed.* **2015**, *54*, 2255.

## Vladimir Gevorgyan

### Conversion of 1-alkenes into 1,4-diols

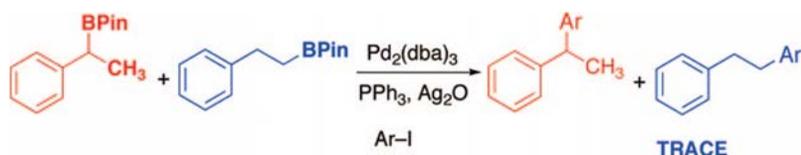
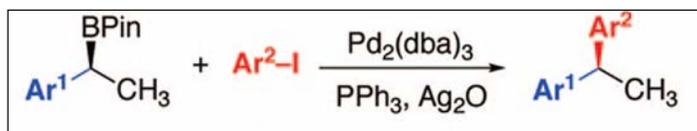
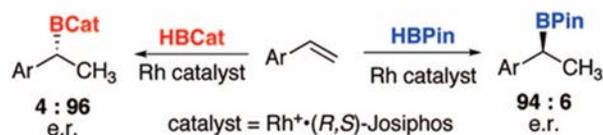


Ghvatdze, N.; Melkonyan, F. S.; Gulevich, A. V.; Huang, C.; Gevorgyan, V. *Nat. Chem.* **2014**, *6*, 122.



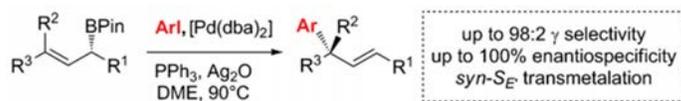
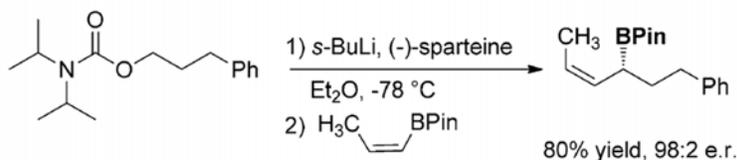
## Cathleen Crudden

### Cross Coupling Reactions of Chiral Secondary Organoboronic Esters



Imao, D.; Glasspoole, B. W.; Laberge, V. S.; Crudden, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 5024.

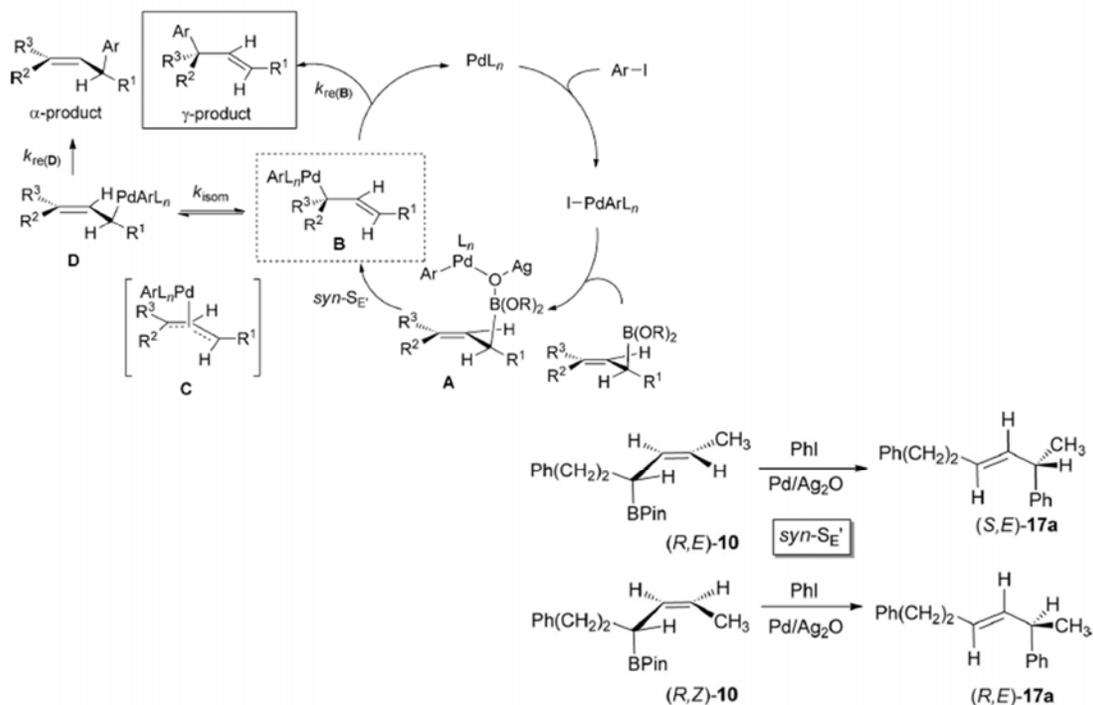
## Cathleen Crudden



Compound	$\gamma/\alpha^{[b]}$	<i>E/Z</i> <sup>[b]</sup>	Yield [%] <sup>[c]</sup>	e.r. (S.M.) <sup>[d]</sup>	e.s. [%] <sup>[e]</sup>	
	( <i>R,Z</i> )-10	83:17	94:6	75 <sup>[d]</sup>	98:2	96
	( <i>R,E</i> )-10	94:6	78:22	81	98:2	100
	( <i>R,Z</i> )-13	90:10	99:1	77 <sup>[d]</sup>	96:4	96
	( <i>R,E</i> )-14	92:8	99:1	71	96:4	100
	( <i>R,E</i> )-15	98:2	99:1	78	98:2	100

Chausset-Boissarie, L.; Ghozati, K.; LaBine, E.; Chen, J. L. Y.; Aggarwal, V. K.; Crudden, C. M. *Chem. Eur. J.* **2013**, *19*, 17698.

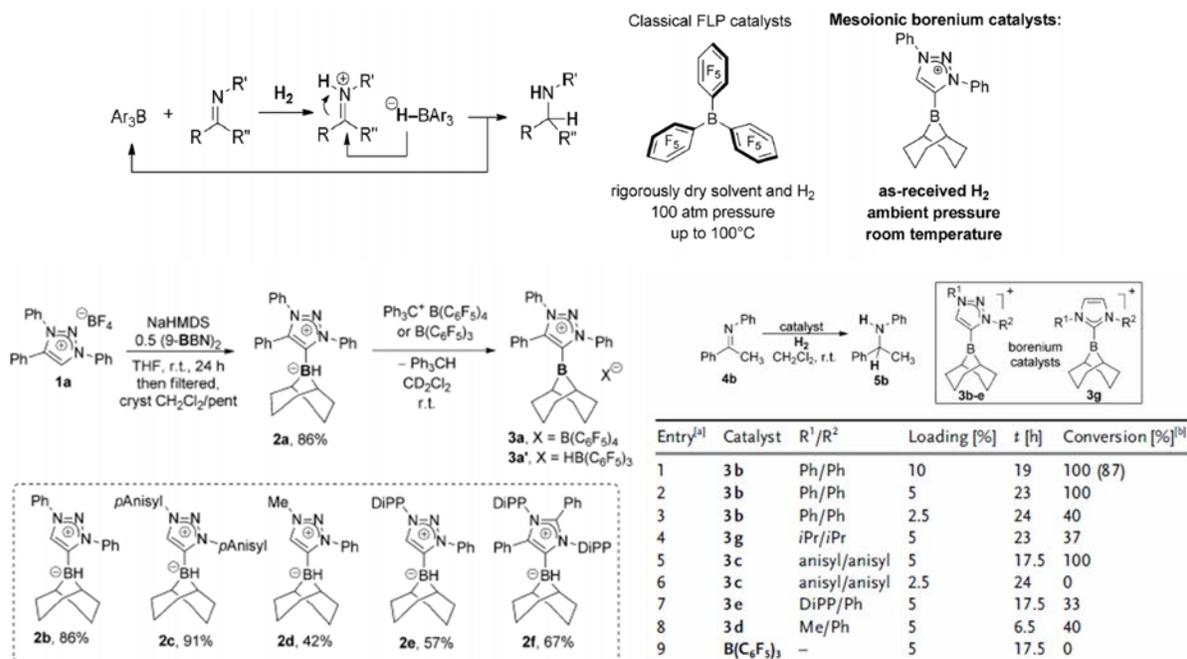
## Cathleen Crudden



Chausset-Boissarie, L.; Ghozati, K.; LaBine, E.; Chen, J. L. Y.; Aggarwal, V. K.; Crudden, C. M. *Chem. Eur. J.* **2013**, *19*, 17698.

## Cathleen Crudden

### Hydrogenations with Mesoionic Carbene-Stabilized Borenum Catalysts



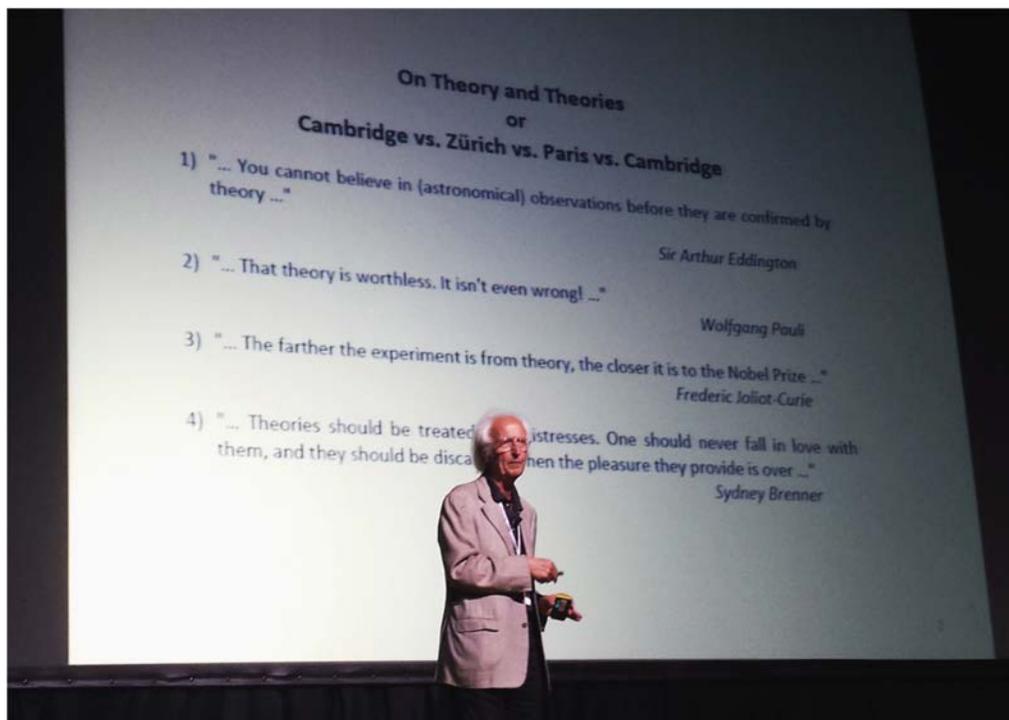
Eisenberger, P.; Bestvater, B. P.; Keske, E. C.; Crudden, C. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 2467.



## Helmut Schwarz

- Worked as a laboratory technician in chemical industry (Dynamit Nobel AG)
- Failed to pursue a professional career as a soccer player
- Completed his Ph.D. in 1972 at Technische Universität Berlin (TUB) under the supervision of the natural product chemist Ferdinand Bohlmann
- Spent some time abroad (ETH Zürich, Cambridge University, and MIT)
- In 1978 he returned to his alma mater to join the Institute of Chemistry
- Has occupied visiting and academic positions at 15 research institutions worldwide
- Published close to 1000 peer-reviewed articles
- Delivered more than 900 invited or name lectures
- Since January 2008 Dr. Schwarz has served as President of the Alexander von Humboldt-Stiftung

## Helmut Schwarz

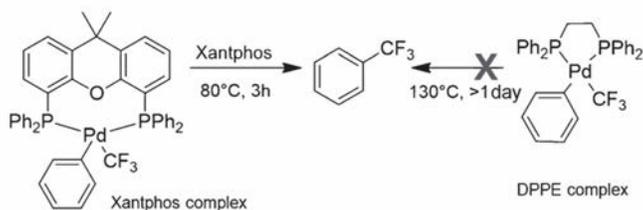




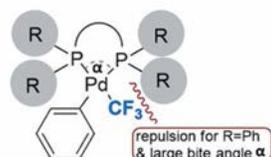
## Franziska Schoenebeck

### Reductive Elimination of $\text{ArCF}_3$ : the predictive power of computational analysis

Grushin et al.:



Our computational analysis:



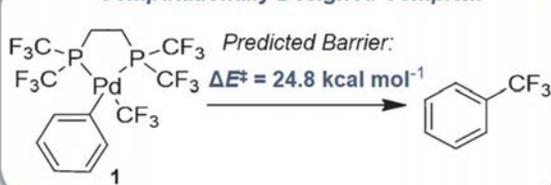
Calculated barrier ( $\Delta E^\ddagger$  in  $\text{kcal mol}^{-1}$ ) for elimination of  $\text{PhCF}_3$  from  $\text{Pd(II)}$  complex:

	Xantphos	dppe backbone
R = Ph	25.7	34.0
R = H	27.6	28.4

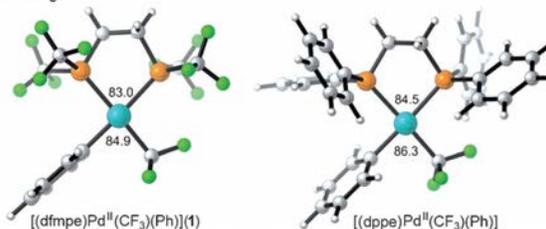
Nielsen, M. C.; Bonney, K. J.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2014**, *53*, 5903.

## Franziska Schoenebeck

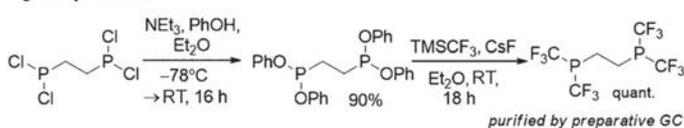
Computationally Designed Complex:



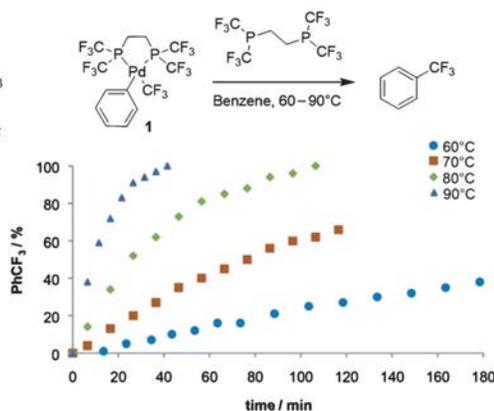
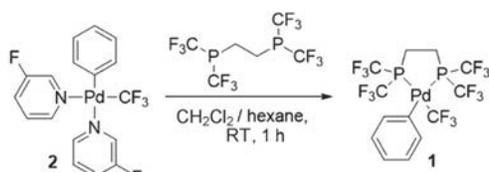
Calculated Angles:



Ligand synthesis:



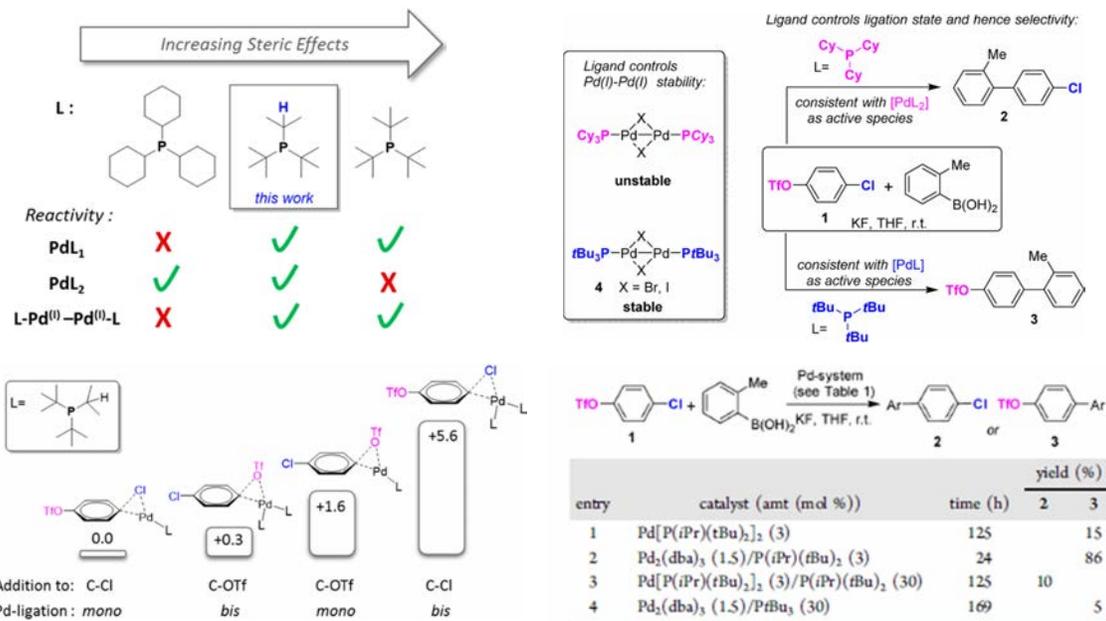
Synthesis of  $\text{Pd(II)}$  complex:



Nielsen, M. C.; Bonney, K. J.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2014**, *53*, 5903.

# Franziska Schoenebeck

## Combining the Reactivity Properties of $\text{PCy}_3$ and $\text{PtBu}_3$ into a Single Ligand, $\text{P}(i\text{Pr})(t\text{Bu})_2$

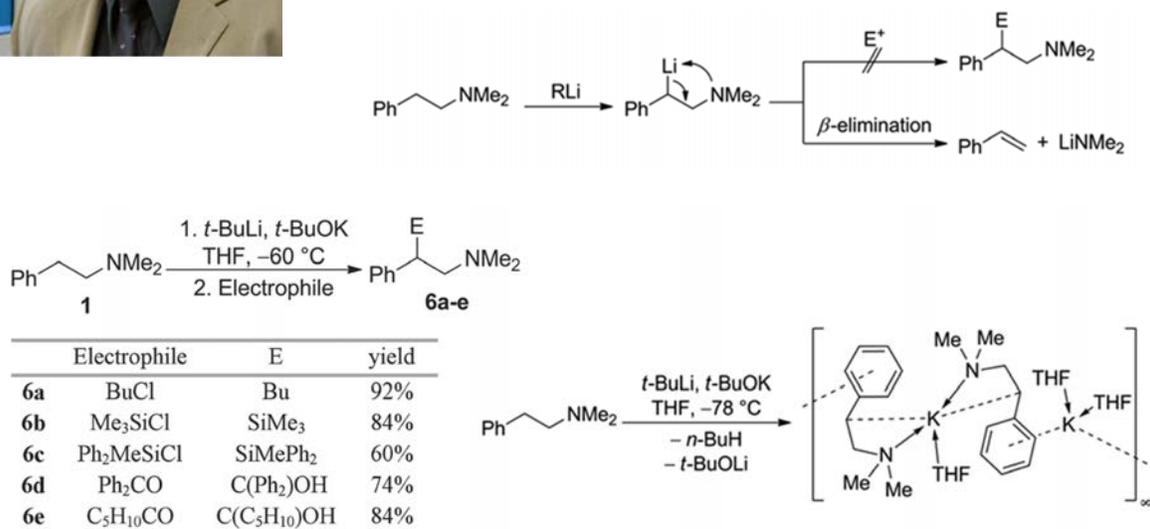


Proutiere, F.; Lyngvi, E.; Aufiero, M.; Sanhueza, I. A.; Schoenebeck, F. *Organometallics* **2014**, *33*, 6879.

# Carsten Strohmann



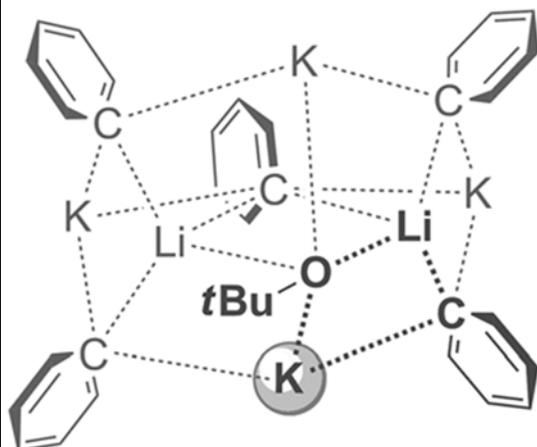
## Insights into the Metalation by Schlosser's Base



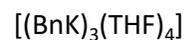
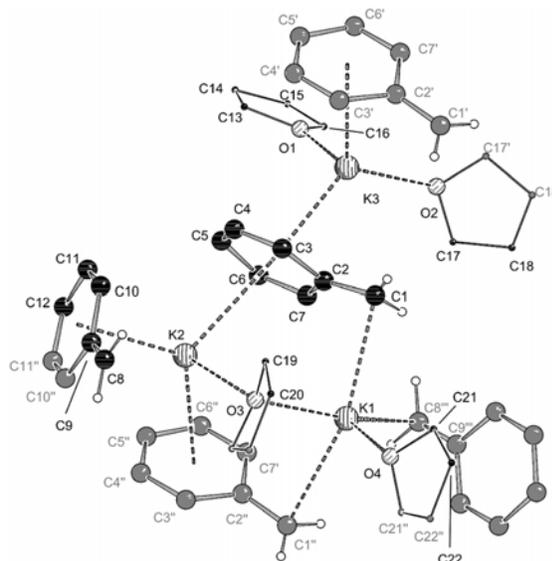
Unkelbach, C.; Rosenbaum, H. S.; Strohmann, C. *Chem. Commun.* **2012**, *48*, 10612.

# Carsten Strohmann

Deprotonation of benzene:



Deprotonation of toluene:

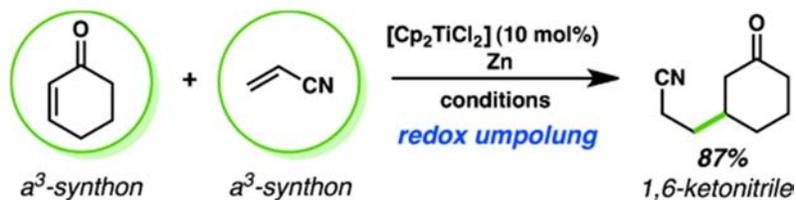
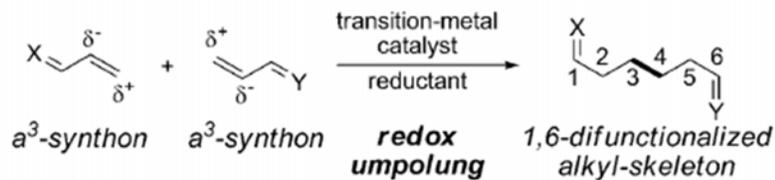


Unkelbach, C.; O'Shea, D. F.; Strohmann, C. *Angew. Chem. Int. Ed.* **2014**, *53*, 553.



## Jan Streuff

### Low-Valent Transition Metal Catalyzed Reductive Umpolung Reactions



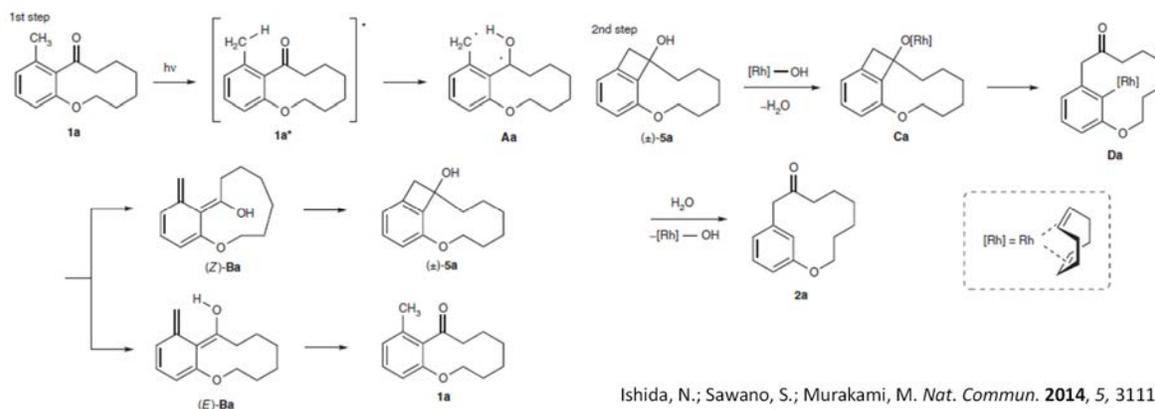
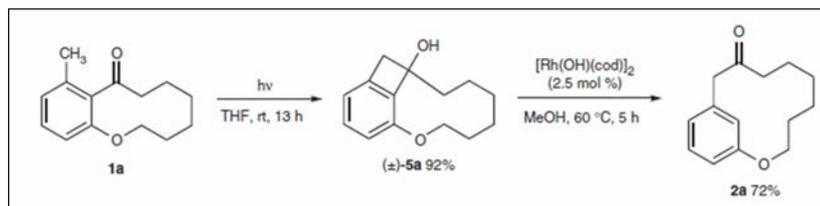
Streuff, J. *Chem. Eur. J.* **2011**, *17*, 5507.



# Naoki Ishida

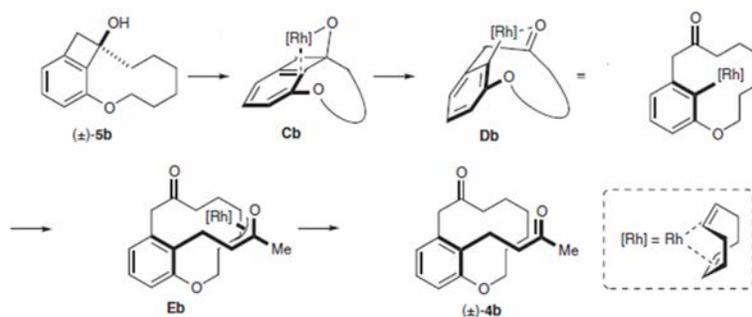
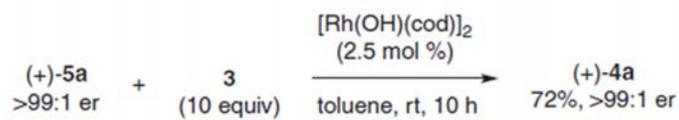
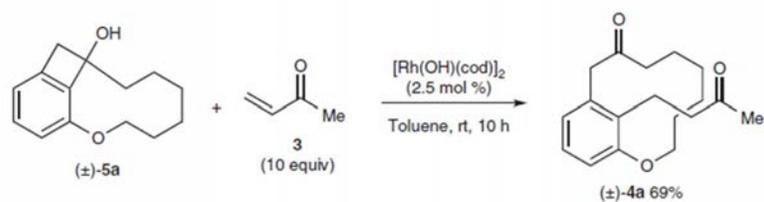


## Light and C-C activation: cyclophanes



Ishida, N.; Sawano, S.; Murakami, M. *Nat. Commun.* **2014**, *5*, 3111.

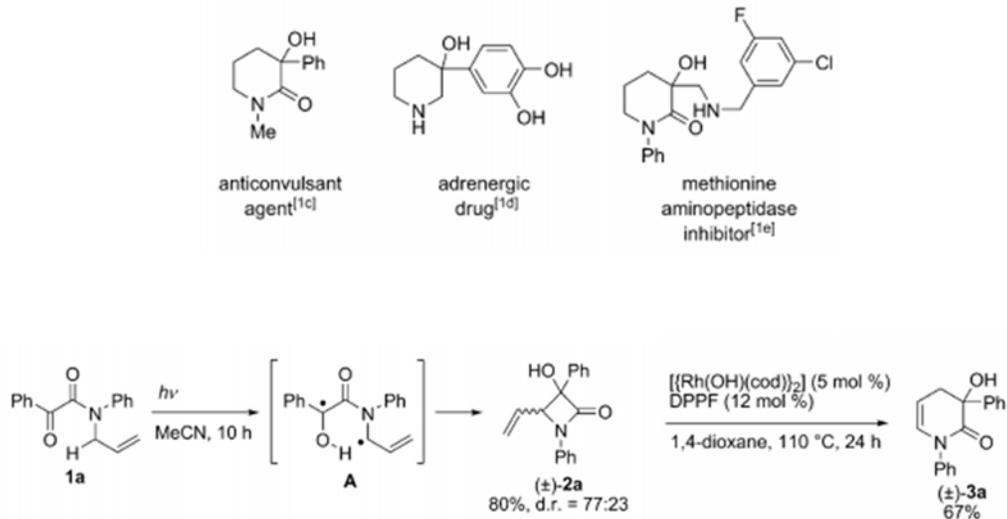
# Naoki Ishida



Ishida, N.; Sawano, S.; Murakami, M. *Nat. Commun.* **2014**, *5*, 3111.

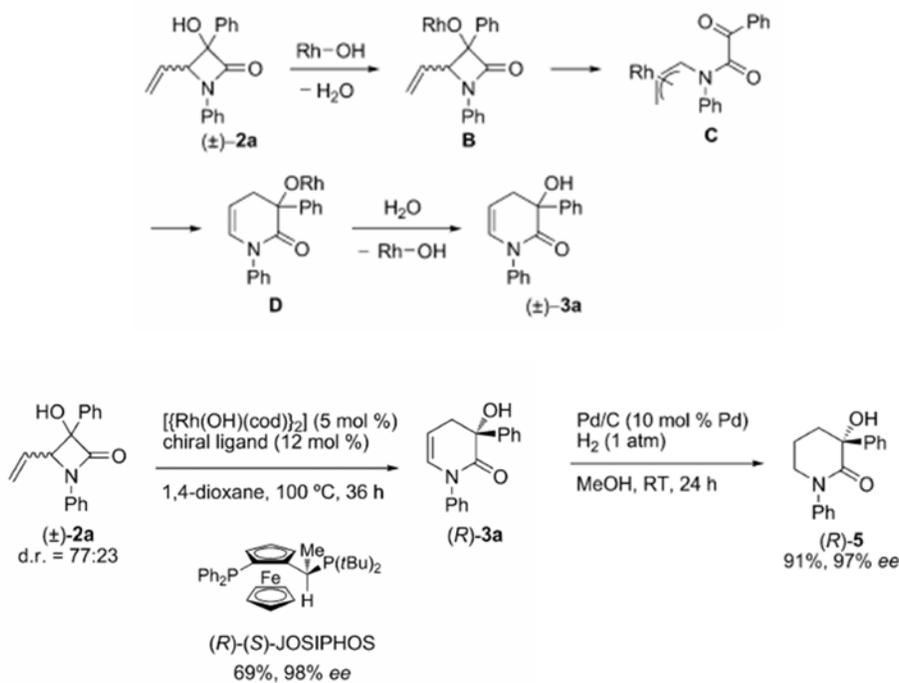
## Naoki Ishida

### Light and C-C activation: hydroxypyperidines



Ishida, N.; Nečas, D.; Masuda, Y.; Murakami, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 7418.

## Naoki Ishida



Ishida, N.; Nečas, D.; Masuda, Y.; Murakami, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 7418.



## Kálmán Szabó

### Synthesis and reactivity of allylboronic acids

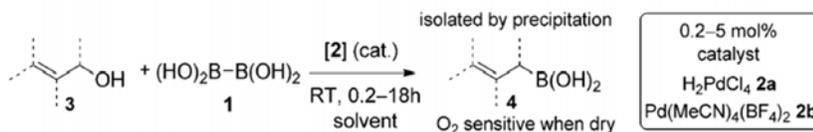


Table 1: Synthesis and isolation of allylboronic acids.<sup>[a]</sup>

Entry	Substrate	Cat. <sup>[a]</sup> (mol%)	Solvent <sup>[a]</sup> (molarity)	t [h]	Product	Yield <sup>[a]</sup> [%]
1		<b>2a</b> (0.5)	MeOH (1.0)	18		61 <sup>[a]</sup>
2		<b>2a</b> (0.5)	MeOH (1.0)	0.2		80
3		<b>2a</b> (0.2)	MeOH (1.0)	2		71
4		<b>2a</b> (0.2)	DMSO/H2O 3:2 (1.0)	14		55
5		<b>2a</b> (2.0)	DMSO/H2O 4:1 (1.0)	13		71

Table 2: Reaction of allylboronic acids with ketones.<sup>[a]</sup>

Entry	Boronic acid	Ketone	Solvent	t [h]	Product	Yield [%] <sup>[a]</sup>
1	<b>4a</b>		THF	1		86
2	<b>4a</b>		THF	24		89
3	<b>4a</b>		THF	14		91
4	<b>4a</b>		THF <sup>[a]</sup>	22		90

Raducan, M.; Alam, R.; Szabó, K. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 13050.

## Kálmán Szabó

Entry	Boronic acid	Imine	Time (h)	Product	Yield <sup>b</sup>
1			1		73
2	<b>2a</b>		3		84 <sup>d</sup>
9	<b>2a</b>		1		93
10	<b>2a</b>		24		65



Alam, R.; Das, A.; Huang, G.; Eriksson, L.; Himó, F.; Szabó, K. J. *Chem. Sci.* **2014**, *5*, 2732.

