

## PRACOWNICY AKADEMICY:

prof. dr hab. Tomasz Bauer  
dr hab. Anna Piątek, prof. ucz.  
dr Paweł Brzemiński  
dr Adrian Fabisiak  
dr Krzysztof Ziach  
dr Katarzyna Sęktas  
(obecnie grupa dr W. Danowskiego)

## DOKTORANCI:

mgr Paulina Rosiek  
mgr Yusuf Zaim Hakim

## MAGISTRANCI:

Jan Kulczycki (obrona 2025)

## LICENCJANCI:

Karol Illinicz-Zeydel (obrona 2025)  
Zuzanna Chońska (obrona 2025)

## STUDENCI ZWIĄZANI Z PRACOWNIĄ:

Aleksander Ułbin

Doktoraty w toku: 2  
Doktoraty zakończone: 0  
Magisteria zakończone: 1  
Licencjaty zakończone: 2

## Prace opublikowane w 2025 roku:

- Bauer T. "Recent Advances in the Enantioselective Organocatalytic [4+2] Cycloadditions" *Molecules* 2025, 30(9), 1978, IF = 4.6
- Bauer A., Rosiek P., Bauer T. "Microbial Transglutaminase—The Food Additive, a Potential Inducing Factor in Primary Biliary Cholangitis." *Molecules* 2025, 30(4), 762 IF = 4.6
- Bauer, T. Chapter 1.07 „Organozinc” in *Comprehensive Organic Synthesis*, 3rd edition; Molander, G., Knochel, P., Eds., Elsevier, 2025, vol. 1, pp. 295–364. ISBN: 9780323960250
- Ewendt F., Janjetovic Z., Kim T.-K., Mobley A.A., Brozyna A.A., Ravichandran S., Fabisiak A., Brzemiński P., Siciński R.R., Stangl G.I., Tuckey R.C., Slominski A.T. „The vitamin D3 hormone, 1,25(OH)2D3, regulates fibroblast growth factor 23 (FGF23) production in human skin cells” *Am. J. Physiol. Cell Physiol.* 2025, 328 (4), C1177, IF=4.8
- Jagleniec D., Sęktas K., Dobrzycki Ł., Ludwinek M., Nasulewicz-Goldeman A., Wietrzyk J., Romański J., "Multifunctional supramolecular receptors: aqueous ion recognition, HCl sensing and cytotoxic potential"; *Org. Biomol. Chem.*, 2025, 23, 6425, IF=2.8

## Źródła finansowania badań w 2025 roku:

- BST 501-D112-01-1120000 z.5011000301, prof. dr hab. Tomasz Bauer
- IDUB 501-D112-20-0004410 dec. BOB-IDUB-622-387/2025, Yusuf Hakim
- IDUB: dec. BOB-661-665/2025, dr Katarzyna Sęktas

## Zgłoszenia patentowe w 2025 roku:

- Piątek A., Żak D., Chapuis Ch. "Sposób syntezy estrów etylowych terminalnych alifatycznych pochodnych kwasów (2E)-pent-2-en-4-ynowych oraz jego zastosowanie w syntezie estrów etylowych terminalnych alifatycznych pochodnych kwasów (2E,4Z)-penta-2,4-dienowych", numer zgłoszenia: P.454344

## Palladium-Catalysed Asymmetric Allylic Substitution Using Allylindium Reagent

Yusuf Hakim, Tomasz Bauer

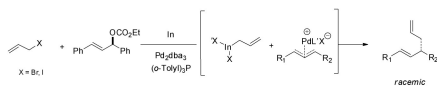
### Introduction

While palladium-catalysed asymmetric allylic substitution has been extensively reported using "hard" nucleophiles like organozinc, Grignard, or allylboronate reagents, the use of allylindium remains unexplored. Allylindium is exceptionally straightforward to prepare, offering a highly practical approach for asymmetric C–C bond formation. Herein, we report the first asymmetric allylic substitution of 1,3-diphenyl allylic substrates using an in situ generated allylindium reagent, prepared directly from indium metal and allyl bromide.

### State-of-The-Art

(Synlett 2002, 1, 146)

#### ALLYLINDIUM AS NUCLEOPHILES



#### "HARD" NUCLEOPHILES

\* relatively under explored



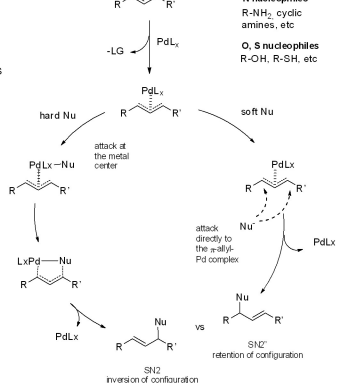
#### "SOFT" NUCLEOPHILES

\* common & well established

C nucleophiles  
β-keto esters, malonates, etc

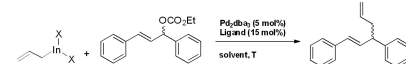
N nucleophiles  
R-NH2, cyclic amines, etc

O, S nucleophiles  
R-OH, R-SH, etc

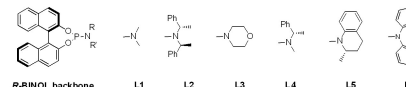


### Our Research

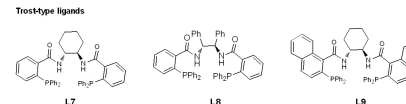
#### GENERAL REACTION SCHEME



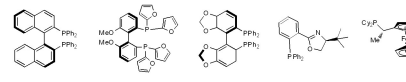
#### Phosphoramidite ligands



#### Trost-type ligands



#### "Other ligands"



### Key Findings

- Shift from Non-Polar to Polar Solvents:** Initial reactions in THF yielded poor results (<15% to 26%) likely due to incomplete indium dissolution. Moving to polar aprotic solvents (DMF, DMSO) significantly improved the solubility and solvation of the active allylindium species.
- Optimal Performance in DMSO:** DMSO emerged as the superior solvent for overall reaction efficiency, maximizing conversion to enable peak chemical yields of 86% (with ligand L3) and 82% (with ligand L1).
- Reactivity vs. Selectivity Trade-off & Divergent Pathways:** We observed a distinct divergence in ligand performance. Structurally accommodating monodentate phosphoramidites drove high conversions (>80% yield) but limited enantioselectivity (~20% ee). Conversely, the rigid, extended pockets of bidentate Trost-type ligands achieved the study's highest stereocontrol in DMSO (34% ee with L3) at the cost of lower catalytic turnover (42–46% yield). Furthermore, these two ligand classes favoured opposite enantiomeric configurations, suggesting they operate through fundamentally distinct transition state geometries.
- Crucial Role of Heteroatoms:** Successful asymmetric induction relied heavily on the heteroatom-rich environments (P, N, O atoms) provided by the phosphoramidite and Trost families. In stark contrast, traditional axially chiral diphosphines (like BINAP, or SEGHOS) completely failed to induce stereocontrol.

## Poszukiwanie nowych dróg syntetycznych kwasu 2-oktylocyklopropan-1-owego

Damian Żak, Anna Piątek

Kwas olibanowy (kwasu 2-oktylocyklopropan-1-owy) jest znanym związkiem zapachowym naturalnie występującym w drzewie kadzidłowca. Jest szeroko stosowany w przemyśle perfumeryjnym i kosmetycznym. Projekt zakłada opracowanie nowej drogi syntetycznej tego kwasu, która ma na celu rozwiązanie problemu przebiegu stereochemicznego dotychczasowych opracowań szkielet syntetycznych.

(Badania ujitajone z powodu potencjalnego charakteru aplikacyjnego)

### Ligand & Solvent Screening Table

Entry	Ligand	t (h)	Yield (%)	ee (%)
in THF				
1	L1	48	22	-32 (R)
2	L2	48	24	-14
3	L7	48	26	-16
4	L10	48	<15	-20
in DMF				
5	L1	3	70	-14
6	L7	24	34	14
7	L10	24	37	2
8	L11	44	18	-12
9	L13	22	33	-6
10	L14	48	11	-10
in DMSO				
11	L1	12	82	-20
12	L3	24	86	-20
13	L4	24	29	-6
14	L5	24	80	10
15	L6	24	35	8
16	L7	16	44	34
17	L8	24	42	30
18	L9	24	46	20
19	L10	48	32	-2
20	L12	48	28	-2
21	L13	16	38	-12
22	L14	22	17	-10

### General Procedure

An active palladium catalyst was pre-formed by stirring Pd(dba)<sub>3</sub> (5 mol%) and the appropriate ligand (15 mol%) in dry THF (or in DMF/DMSO) for 30 minutes under argon, followed by the addition of the allylic carbonate substrate (100 mg, 0.35 mmol). Concurrently, an allylindium suspension—prepared *in situ* by stirring indium powder (1.2 equiv) and allyl bromide (1.8 equiv) in THF (or DMF/DMSO) for 1 hour—was added dropwise over 1 hour using a syringe pump. The resulting mixture was stirred at room temperature for the designated time. Upon completion, the reaction was quenched with saturated aqueous NH<sub>4</sub>Cl, worked-up and purified by column chromatography. The enantioselectivity was determined by HPLC using a chiral OD-H column (Hexane: iPrOH 99:70, 3).