# The application o monoterpene derived chiral ligands in Tsuji-Trost reaction

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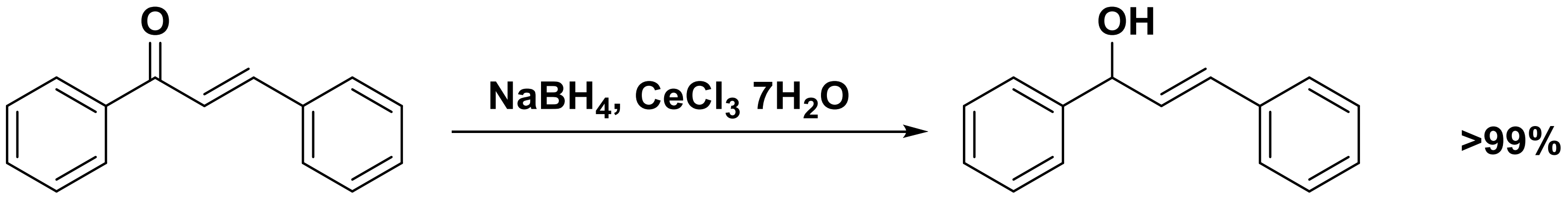
# Allylic substitution

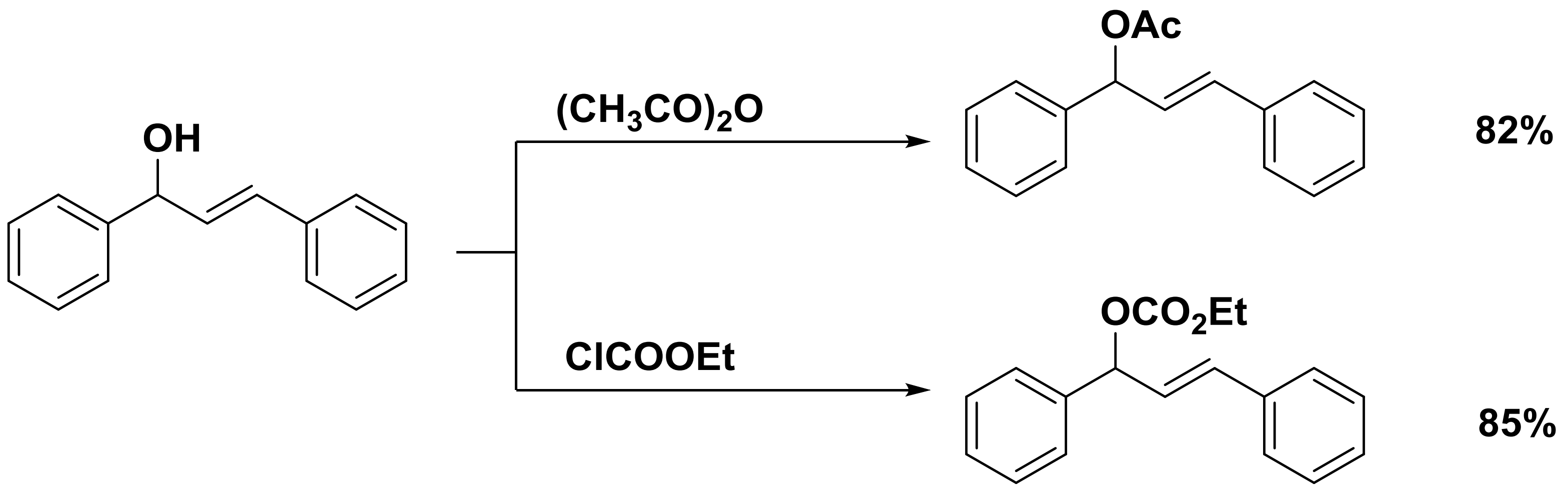
- Application: formation of carbon-carbon and carbon-heteroatom bonds
- Transitions metals: Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, Mo, W

Trost B.M., *Acc. Chem. Res.,* **1980***, 54,* 197*,*

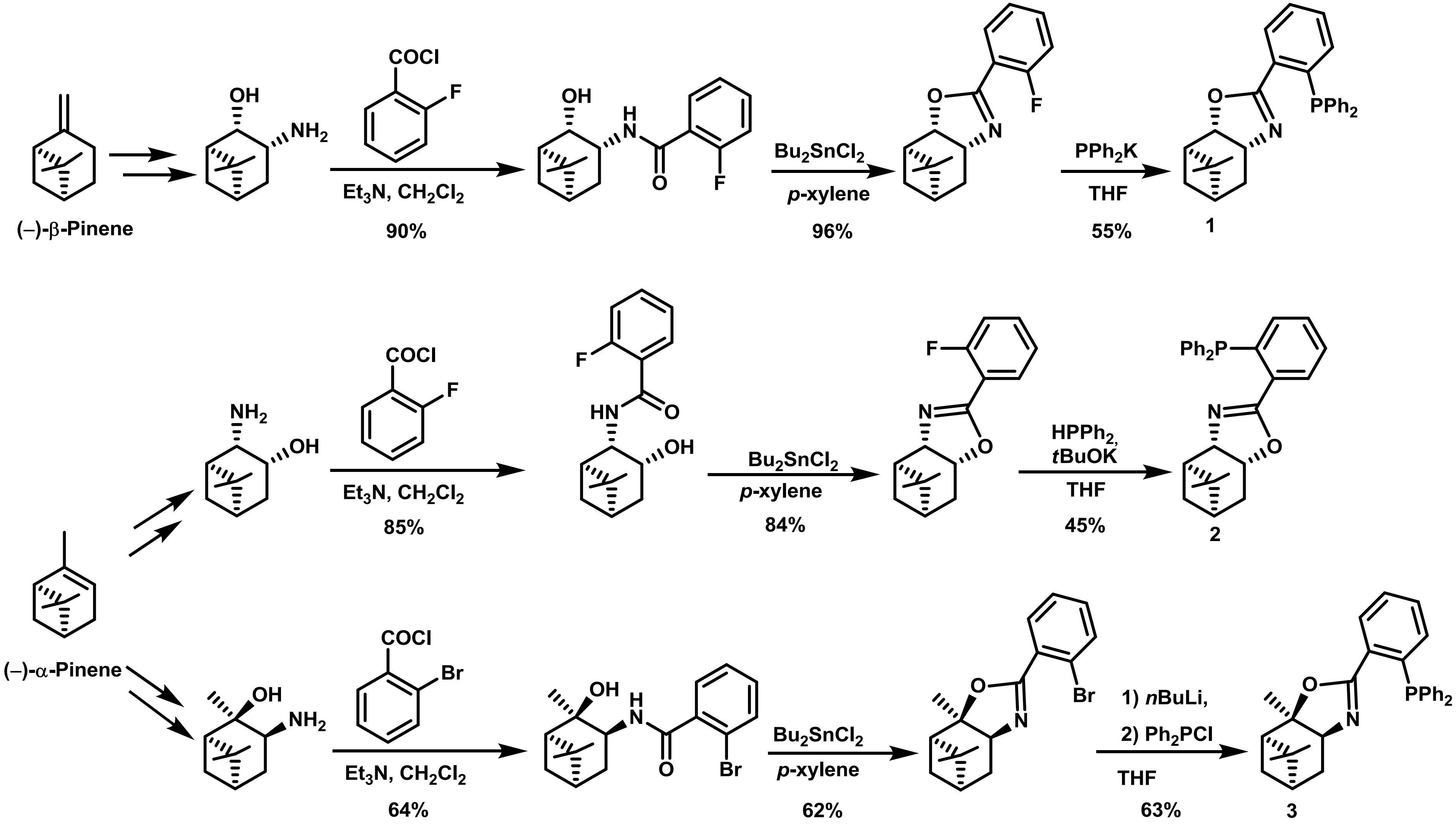
Tsuji J., *Tetrahedron*, **1986**, *42*, 4361.

# Substrate synthesis

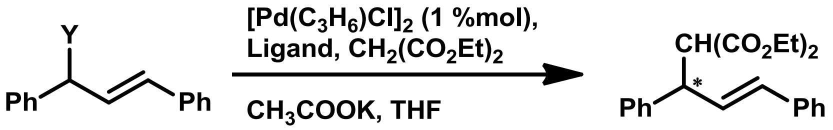




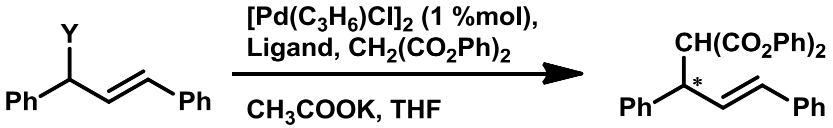
# Synthesis of PHOX ligands



# Allylic substitution

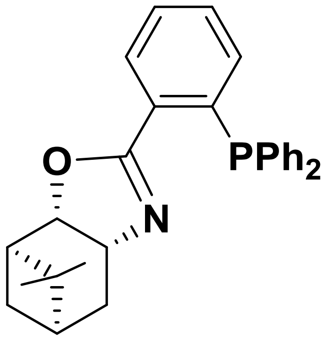


| Ligand | Y = OAc<br>+ BSA | | Y = $OCO_2Et$ | | Conf. |
|---|---|---|---|---|---|
| | W [%] | % ee | W [%] | % ee | |
| **1** | >99 | 95 | 78 | 96 | *R* |
| **2** | >99 | 93 | 71 | >99 | *S* |
| **3** | **>99** | **97** | **77** | **>99** | ***S*** |



| Ligand | Y = OAc<br>+ BSA | | Y = $OCO_2Et$ | | Conf. |
|---|---|---|---|---|---|
| | W [%] | % ee | W [%] | % ee | |
| **1** | 71 | 75 | 76 | 80 | *R* |
| **2** | **69** | **78** | 72 | 83 | *S* |
| **3** | 75 | 72 | **70** | **85** | ***S*** |

**1**



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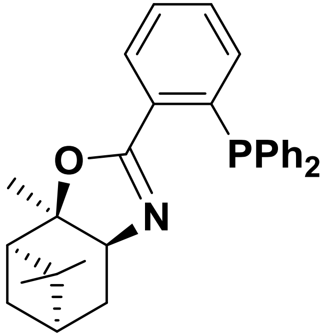

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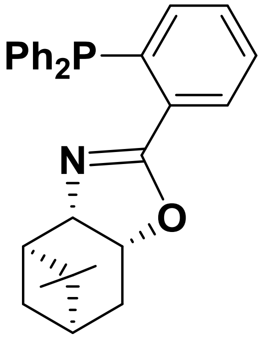
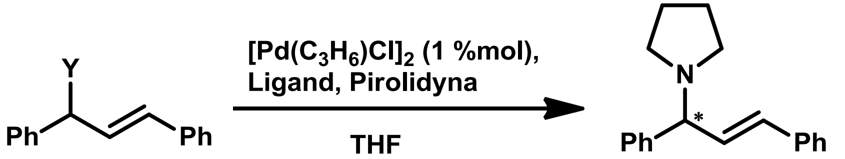
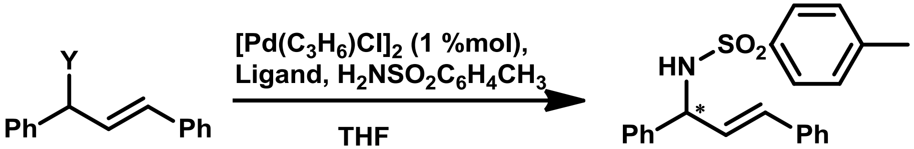


# Allylic substitution

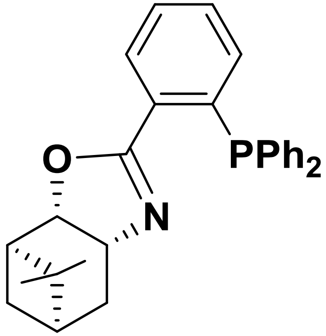


| Ligand | Y = OAc | | Y = $OCO_2Et$ | | Konfiguracja |
|---|---|---|---|---|---|
| | W [%] | % ee | W [%] | % ee | |
| **1** | 77 | 62 | 79 | 58 | *R* |
| **2** | **78** | **70** | 74 | 62 | *S* |
| **3** | 80 | 60 | **80** | **66** | ***S*** |



| Ligand | Y = OAc | | Y = $OCO_2Et$ | | Konfiguracja |
|---|---|---|---|---|---|
| | W [%] | % ee | W [%] | % ee | |
| **1** | 70 | 60 | **90** | **>99** | ***R*** |
| **2** | 72 | 58 | 89 | 92 | *S* |
| **3** | **74** | **66** | 91 | 98 | *S* |

**1**



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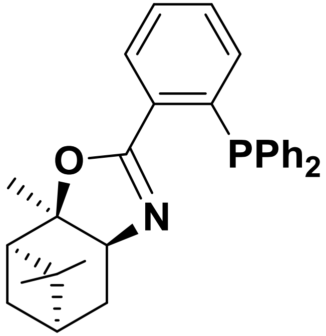

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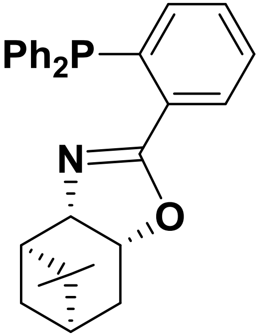
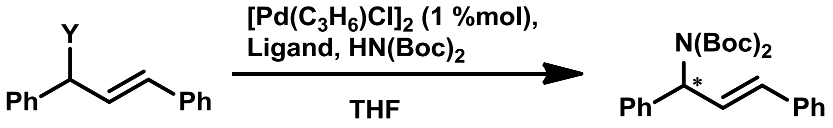


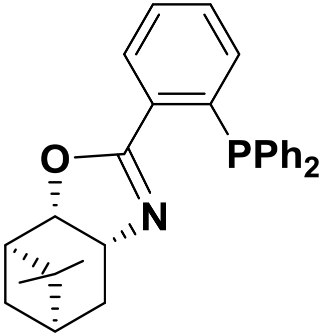
# Allylic substitution


$[Pd(C_3H_6)Cl]_2$ (1 %mol), Ligand, $HN(Boc)_2$

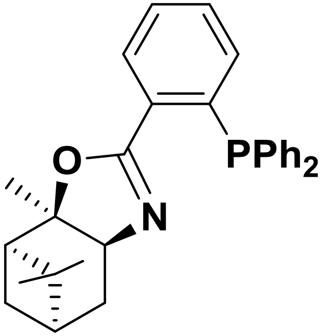
THF

| Ligand | Y = OAc | | Y = $OCO_2Et$ | | Konfiguracja |
|---|---|---|---|---|---|
| | W [%] | % ee | W [%] | % ee | |
| **1** | 70 | 60 | 69 | 48 | *R* |
| **2** | **68** | **65** | 64 | 52 | *S* |
| **3** | 65 | 63 | **70** | **56** | ***S*** |

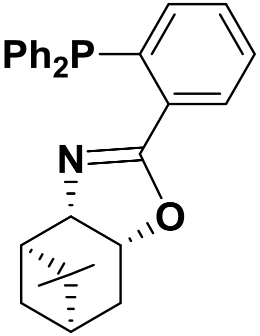
**1**



**2**



**3**



# Summary

- Palladium complexes with phosphinooxazoline ligands derived from monoterpenes catalyze asymmetric allylic substitution of 1,3-diphenyl-2-propenyl acetates and carbonates to give products with high enantiomeric excess and high yield.

- Enantioselectivity of the reaction is influenced by the leaving group (acetate or carbonate) and by the nucleophile (diethyl malonate, p-toluenesulfonamide and pyrrolidine)