

## Recent Reviews:

Pu, L.; Yu, H.-B. *Chem. Rev.* **2001**, *101*, 757–824.

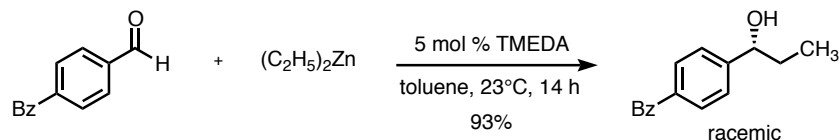
Lemire, A.; Cote, A.; Janes, M. K.; Charette, A. B. *Aldrichimica Acta* **2009**, *42*, 71–83.

Lumbroso, A.; Cooke, M. L.; Breit, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 1890–1932.

## Background:

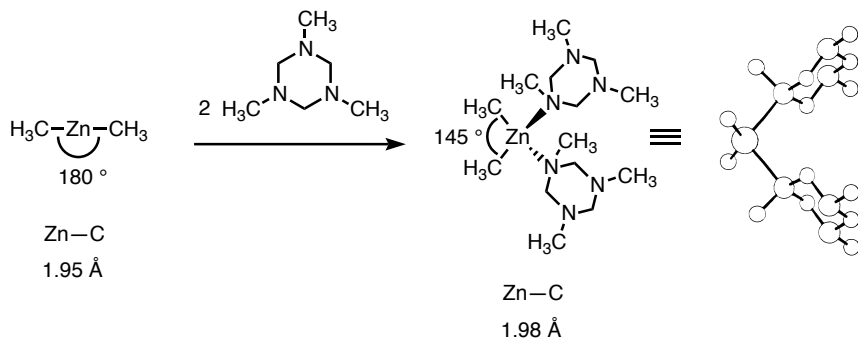
The reactivity of dialkylzinc reagents towards ketones and aldehydes is low; the rate of addition of  $\text{Et}_2\text{Zn}$  to benzaldehyde is negligible at room temperature.

The addition of a catalytic amount of TMEDA will promote the addition of diethylzinc at room temperature to 4-benzoylbenzaldehyde in 93% yield.



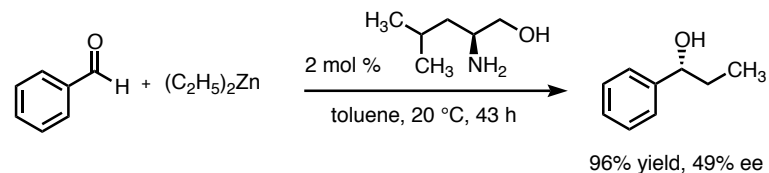
Soai, K.; Watanabe, M.; Koyano, M. *Bull. Chem. Soc. Jpn.* **1989**, *25*, 2124–2125.

X-Ray structures of dimethylzinc and its adduct with 1,3,5-trimethylhexahydro-1,3,5-triazine show that upon bis-complexation, dimethylzinc shifts from a linear geometry to a tetrahedral geometry and that the carbon-zinc bond length increases from 1.95 Å to 1.98 Å. This is proposed to increase the nucleophilicity of the methyl groups, accelerating addition to carbonyl compounds.



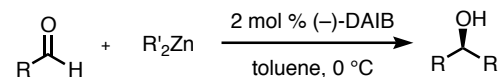
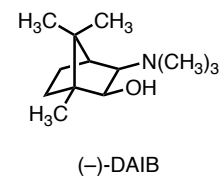
Hursthouse, M. B.; Motewaili, M.; O'Brien, P.; Walsh, J. R.; Jones, A. C. *J. Mater. Chem.* **1991**, *7*, 139–140.

In 1984, Oguni and Omi found that a small amount of (*S*)-leucinol catalyzed the enantioselective addition (49% ee) of diethylzinc to benzaldehyde.



Oguni, N.; Omi, T. *Tetrahedron Lett.* **1984**, *25*, 2823–2824.

In 1986, Noyori *et al.* published the first highly selective procedure for the asymmetric addition of diethyl- and dimethylzinc to aldehydes employing (–)-3-*exo*-(dimethylamino)isoborneol (DAIB) as a chiral catalyst.

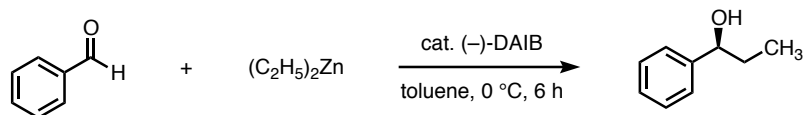


R	R'	% yield	% ee
Ph	Et	97	98
Ph	Me	59	91
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Et	86	93
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Et	96	93
( <i>E</i> )-PhC(H)=CH	Et	81	96
PhCH <sub>2</sub> CH <sub>2</sub>	Et	80	90
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Et	81	61

Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 6071–6072.

## Mechanism:

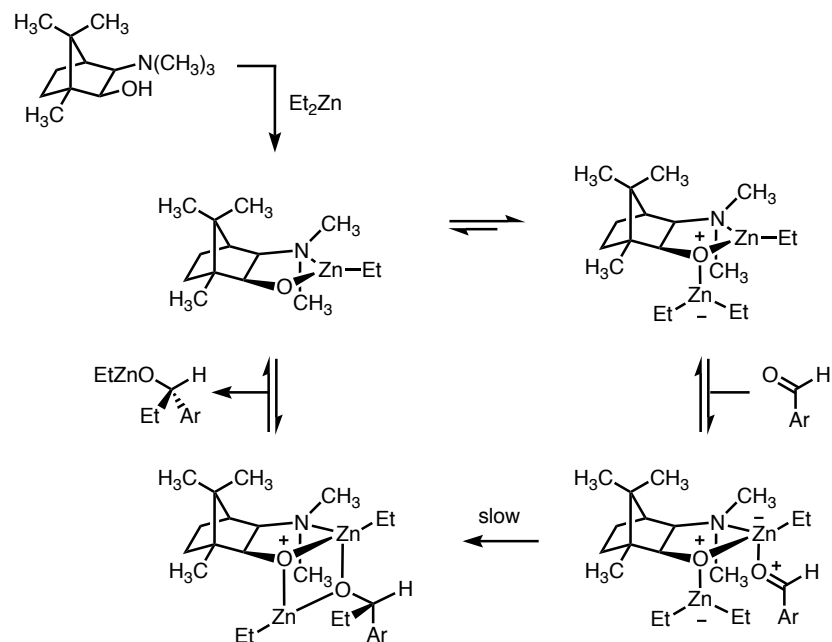
- The stoichiometry of aldehyde, diethylzinc, and DAIB ligand determines reactivity: alkylation occurs only when the ratio of  $\text{Et}_2\text{Zn}$  : DAIB is greater than 1:



aldehyde : $\text{Et}_2\text{Zn}$ : DAIB	% yield	% ee
1 : 1 : 0	0	—
1 : 1 : 1	1	0
50 : 50 : 1	97	98

Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028–4036.

- This observation is consistent with a mechanistic proposal involving two Zn atoms per aldehyde:

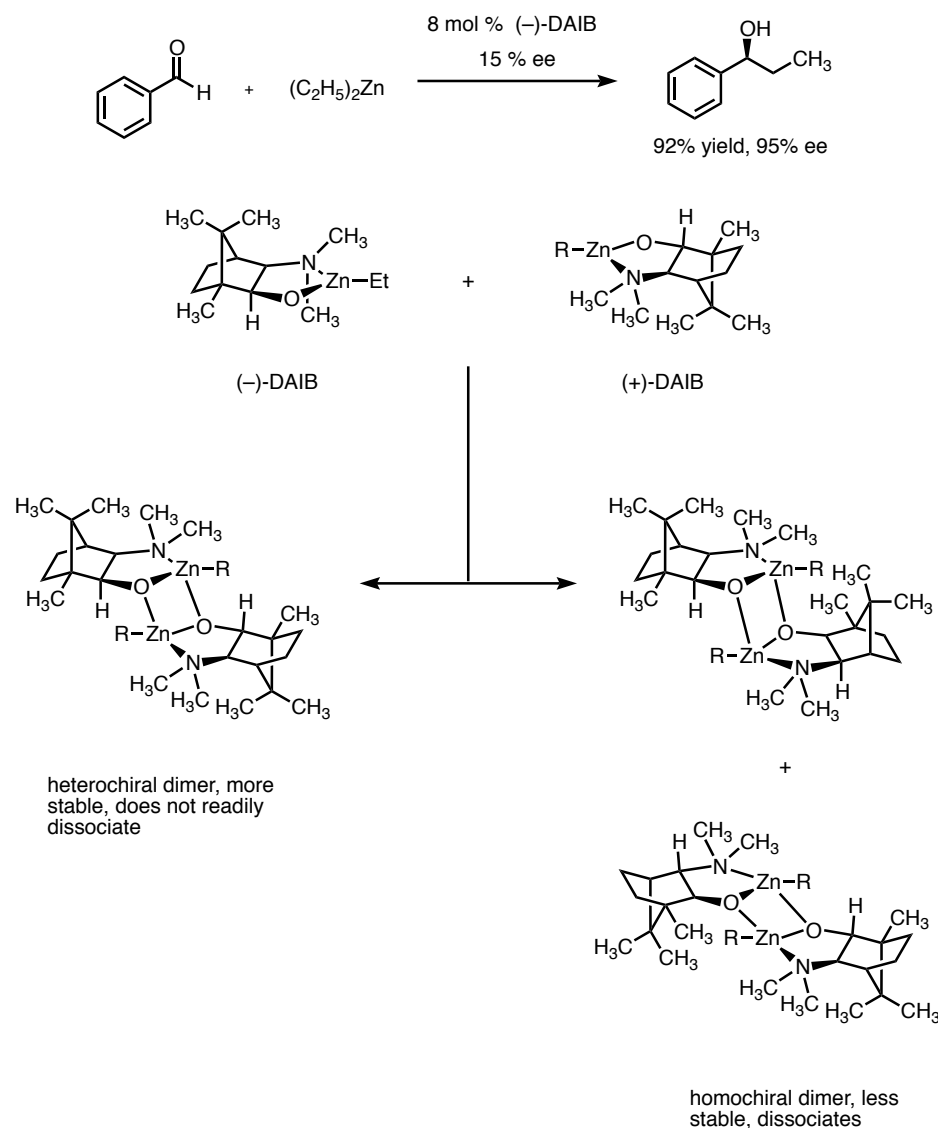


Itsuno, S.; Fréchet, J. M. J. *J. Org. Chem.* **1987**, *52*, 4142–4143.

Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1987**, *28*, 5237–5240.

Evans, D. A. *Science* **1988**, *240*, 420–426.

- A non-linear dependence of product ee on catalyst ee was observed. Heterochiral dimerization to form an unreactive species was invoked to account for *in situ* amplification of product ee:



Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028–4036.

Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877.

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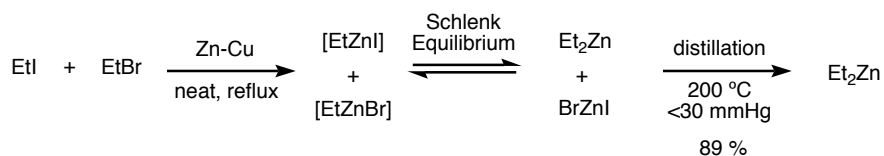
## Preparation of Organozinc Reagents:

Lemire, A.; Cote, A.; Janes, M. K.; Charette, A. B. *Aldrichimica Acta* **2009**, *42*, 71–83.

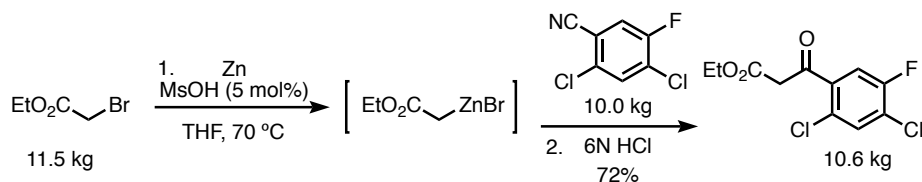
Knochel, P.; Perea, J. J. A.; Jones, P. *Tetrahedron* **1998**, *54*, 8275–8319.

## • Metallic Zinc Insertion:

- One of the early methods involves treatment of an alkyl iodide or bromide with zinc dust or an activated form of Zn, such as zinc-copper couple (Zn(Cu)). The method requires rather harsh conditions and is limited to low molecular weight dialkylzinc species due to the need to distill the products while avoiding competitive Wurtz coupling:



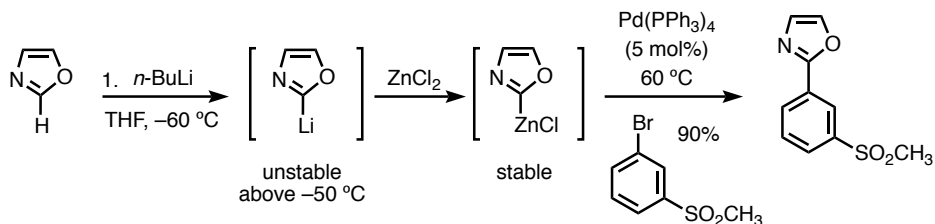
- methanesulfonic acid can be used to activate zinc metal:



Choi, B. S.; Chang, J. H.; Choi, H.-W.; Kim, Y. K.; Lee, K. K.; Lee, K. W.; Lee, J. H.; Heo, T.; Nam, D. H.; Shin, H. *Org. Process Res. Dev.* **2005**, *9*, 311–313.

## • Transmetalation with a Zinc Salt:

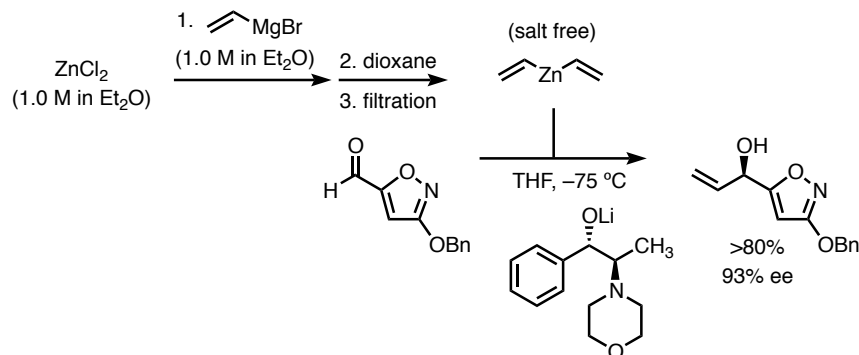
- Substrates that are less readily prepared by direct reduction can be prepared by treatment of a Zinc(II) halide with two equivalents of alkyllithium or alkylmagnesium halide:



Reeder, M. R.; Gleaves, H. E.; Hoover, S. A.; Imbordino, R. J.; Pangborn, J. J. *Org. Process Res. Dev.* **2003**, *7*, 696–699.

- In many cases, lithium or magnesium halide byproducts must be removed to avoid salt complexation with chiral additives in subsequent enantioselective processes.

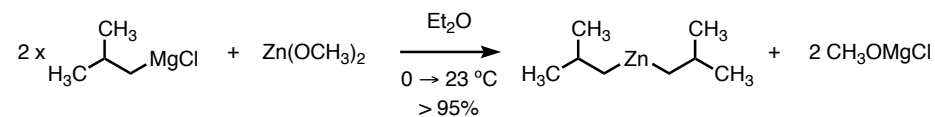
- 1,4-Dioxane forms insoluble complexes with magnesium halides and allows the synthesis of diorganozinc reagents that were not commercially available to subsequently be used in asymmetric additions to carbonyl compounds:



von dem bussche-Hünnefeld, J. L.; Seebach, D. *Tetrahedron* **1992**, *48*, 5719–5730.

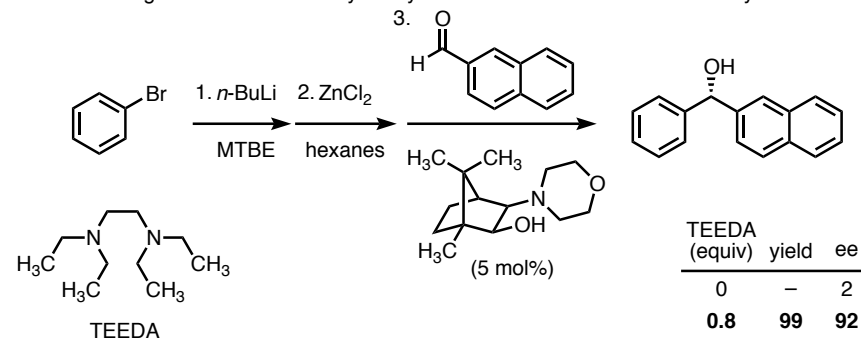
Brubaker, J. D.; Myers, A. G. *Org. Lett.* **2007**, *9*, 3523–3525.

- Zn(OCH<sub>3</sub>)<sub>2</sub> can also be used. The byproduct, CH<sub>3</sub>OMgCl, precipitates from the reaction mixture and salt-free ethereal solutions of diorganozinc can be obtained after filtration or centrifugation:



Cote, A.; Charette, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 2771–2773.

- N,N,N,N*-tetraethylethylenediamine (TEEDA) can be used to scavenge salts and the resulting *in situ* formed zinc reagents function in catalytic asymmetric addition reactions to aldehydes:



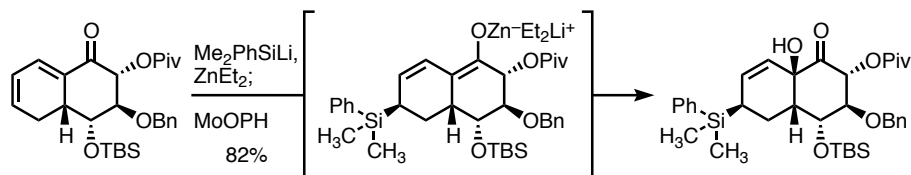
Kim, J. G.; Walsh, P. J. *Angew. Chem. Int. Ed.* **2006**, *45*, 4175–4178.

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• **Transmetalation with a Diorganozinc Reagent:**

• Functionalized diorganozinc reagents can be prepared via transmetalation of organolithium, organoboron, organonickel, and organozirconium with dimethyl-, diethyl-, or diisopropylzinc:

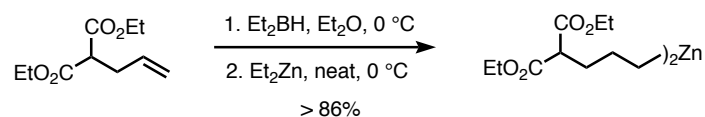
• organolithium:



Substrate decomposition occurred in the absence of  $\text{ZnEt}_2$ .

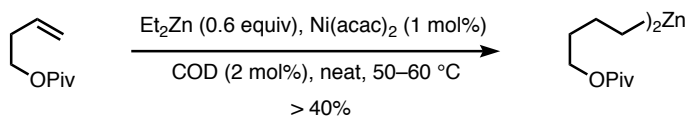
Milgram, B. C.; Liau, B. B.; Shair, M. D. *Org. Lett.* **2011**, *13*, 6436–6439.

• organoboron:



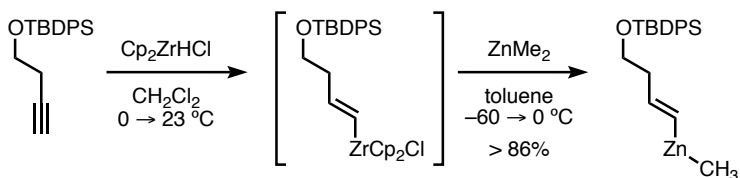
Langer, F.; Schwink, L.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. *J. Org. Chem.* **1996**, *61*, 8229–8243.

• organonickel:



Vettel, S.; Vaupel, A.; Knochel, P. *J. Org. Chem.* **1996**, *61*, 7473–7481.

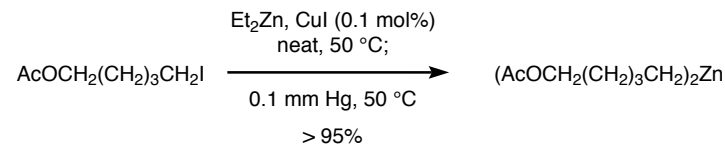
• organozirconium:



Wipf, P.; Xu, W. *Org. Synth.* **1997**, *74*, 205–211.

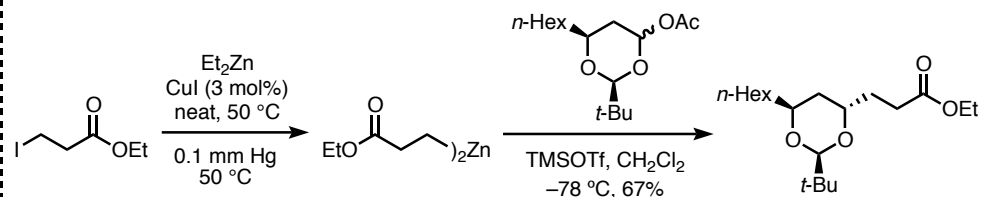
• **Halogen-Diorganozinc Exchange:**

• Iodine-zinc exchange reactions have been used to prepare dialkylzinc species containing esters, nitriles, chlorides, sulfonamides, and boronic acids.  $\text{CuI}$  or UV light were found to accelerate the reaction. Removal of excess  $\text{Et}_2\text{Zn}$  and  $\text{EtI}$  was necessary to drive the reaction:



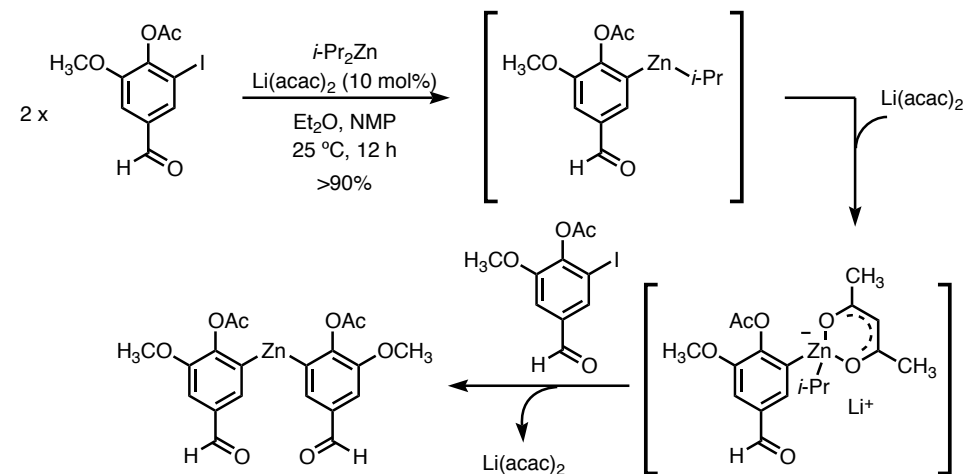
Rozema, M. J.; Eisenberg, C.; Lütjens, H.; Ostwald, R.; Belyk, K.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 3115–3118.

Rozema, M. J.; Sidduri, A.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956–1958.



Powell, N. A.; Rychnovsky, S. D. *J. Org. Chem.* **1999**, *64*, 2026–2037.

• Aryl and alkenyl iodides can undergo halogen-zinc exchange with  $i\text{-Pr}_2\text{Zn}$ .  $\text{Li}(\text{acac})_2$  activates the intermediate mixed diorganozinc as an ate complex and promotes the second exchange:

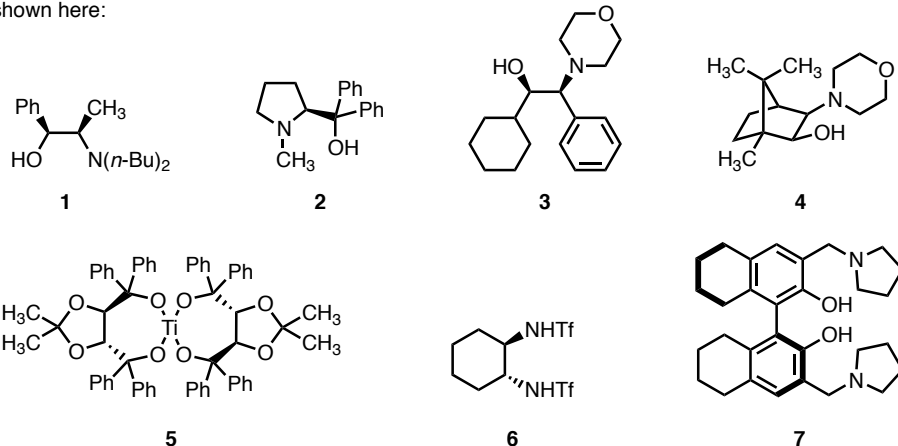


Kneisel, F. F.; Dochnahl, M.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 1017–1021.

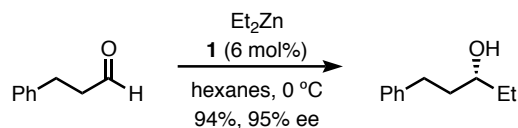
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## Alkylzinc Addition to Aldehydes:

- A variety of chiral catalysts and ligands have been developed that promote the addition of dialkylzinc reagents to give enantiomerically enriched secondary alcohols. Only a few representative ones are shown here:

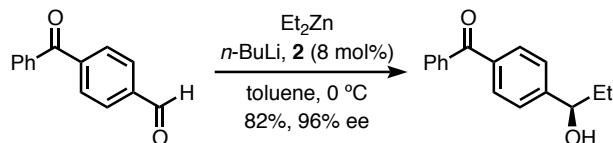


- Ligand **1** extends the scope of the initial DAIB reaction to include aliphatic aldehydes:

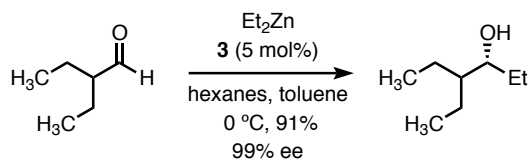


Hayasaka, T.; Yokoyama, S.; Soai, K. *J. Org. Chem.* **1991**, *56*, 4264–4268.

- Chemoselective addition to aldehydes can be achieved in the presence of ketones:

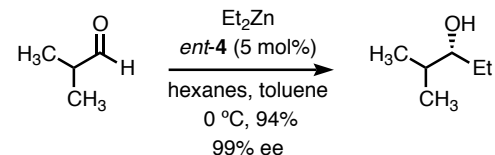


Watanabe, M.; Soai, K. *J. Chem. Soc., Perkin Trans. 1*, **1994**, 3125–3128.



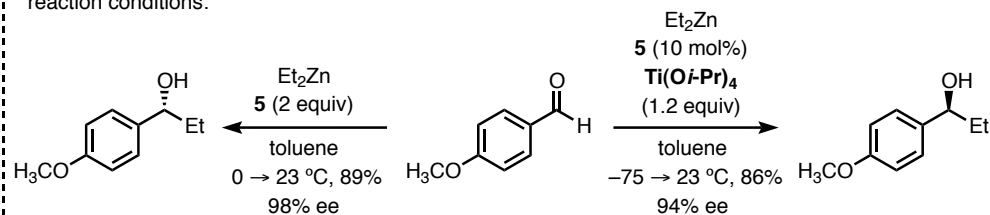
Nugent, W. A. *Org. Lett.* **2002**, *4*, 2133–2136.

- 3-*exo*-morpholinoisoborneol (MIB), **4**, more stable and easier to prepare than DAIB, catalyzes enantioselective additions to aldehydes with similar selectivity and efficiency. It also shows improved selectivity with  $\alpha$ -branched, aliphatic aldehydes:

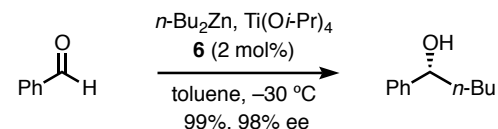


Nugent, W. A. *Chem. Commun.* **1999**, 1369–1370.

- Using **5** as a chiral additive, either enantiomer of the product can be obtained by changing the reaction conditions:



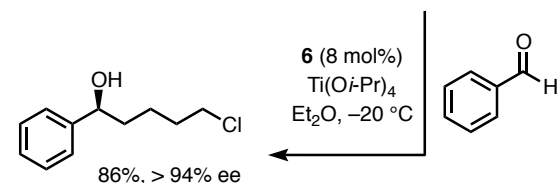
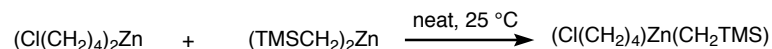
Schmidt, B.; Seebach, D. *Angew. Chem. Int. Ed.* **1991**, *30*, 99–101.



Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657–1660.

Takahashi, H.; Kawakita, T.; Yoshioka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 7095–7098.

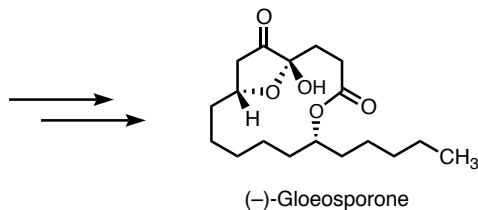
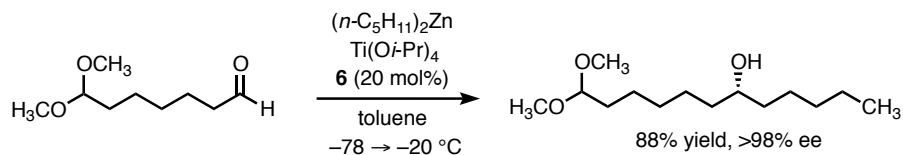
- Unsymmetrical dialkyl zinc containing a trimethylsilylmethyl group as a non-transferable group can be prepared to avoid losing one equivalent of valuable alkyl zinc precursor:



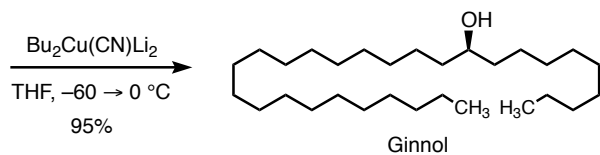
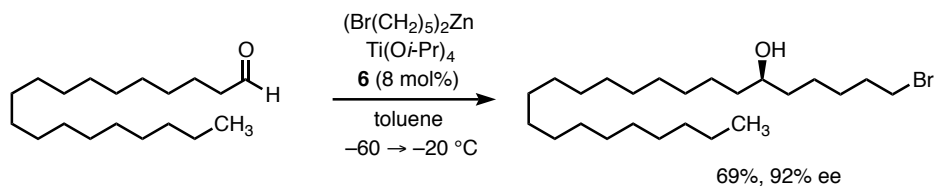
Berger, S.; Langer, F.; Lutz, C.; Knochel, P.; Mobley, T. A.; Reddy, C. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1496–1498.

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## Dialkylzinc Reagents in Synthesis:



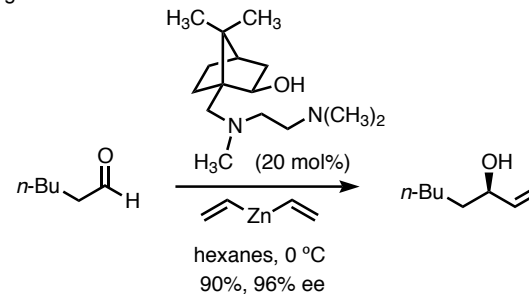
Fürstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130–9136.



Langer, F.; Schwink, L.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. *J. Org. Chem.* **1996**, *61*, 8229–8243.

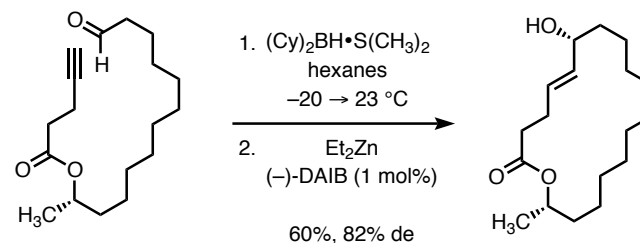
## Alkenylzinc Addition to Aldehydes:

- The first example of catalytic asymmetric vinylzinc additions to aldehydes was reported using a chiral diaminoalcohol ligand:



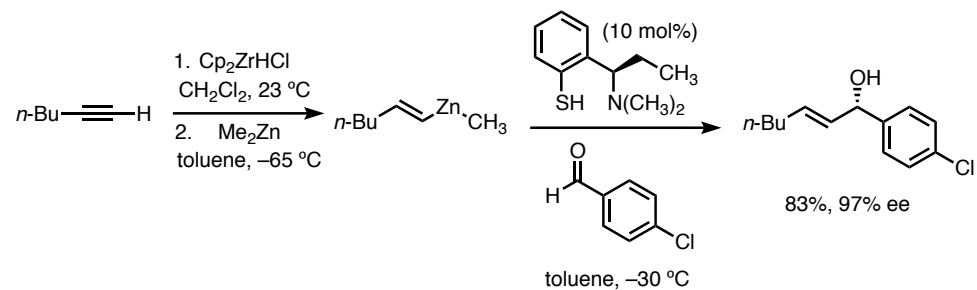
Oppolzer, W.; Radinov, R. N. *Tetrahedron Lett.* **1988**, *29*, 5645–5648.

- Mixed organozinc reagents, formed via transmetalation of organoboron or organozirconium with dialkylzinc, can be used to form enantiomerically enriched allylic alcohols in the presence of a chiral amino alcohol catalyst:



Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta.* **1992**, *75*, 170–173.

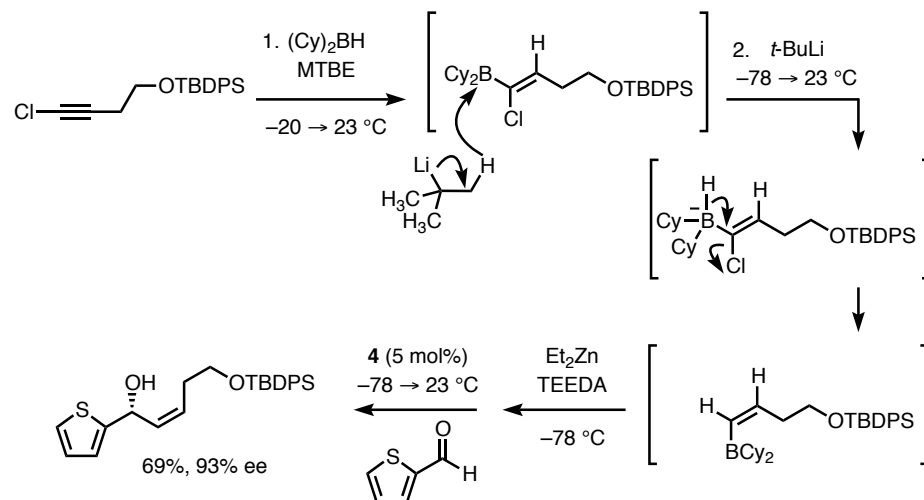
Oppolzer, W.; Radinov, R. N.; De Brabander, J. *Tetrahedron Lett.* **1995**, *36*, 2607–2610.



Wipf, P.; Ribe, S. *J. Org. Chem.* **1998**, *63*, 6454–6455.

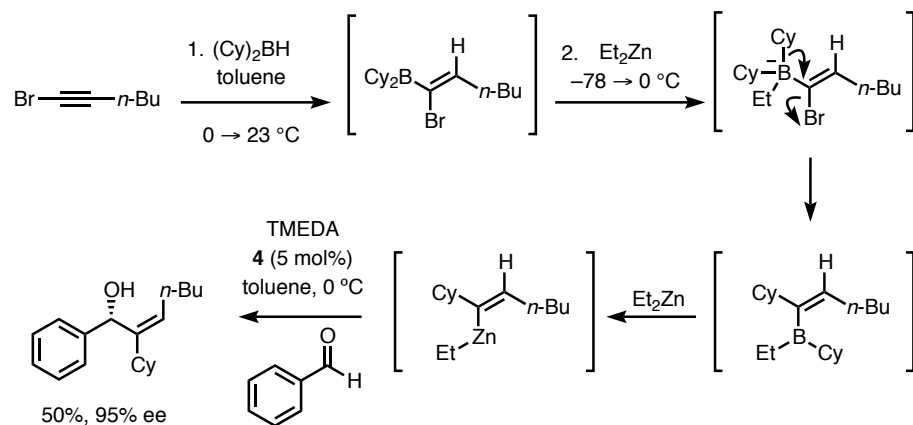
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- Hydride migration from a boron ate complex provides access to enantiomerically enriched Z-allylic alcohols:



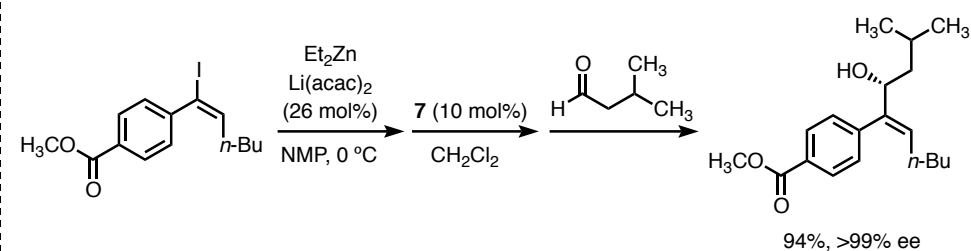
Salvi, L.; Jeon, S.-J.; Fisher, E. L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 16119–16125.

- Tri-substituted Z-allylic alcohol can also be prepared:



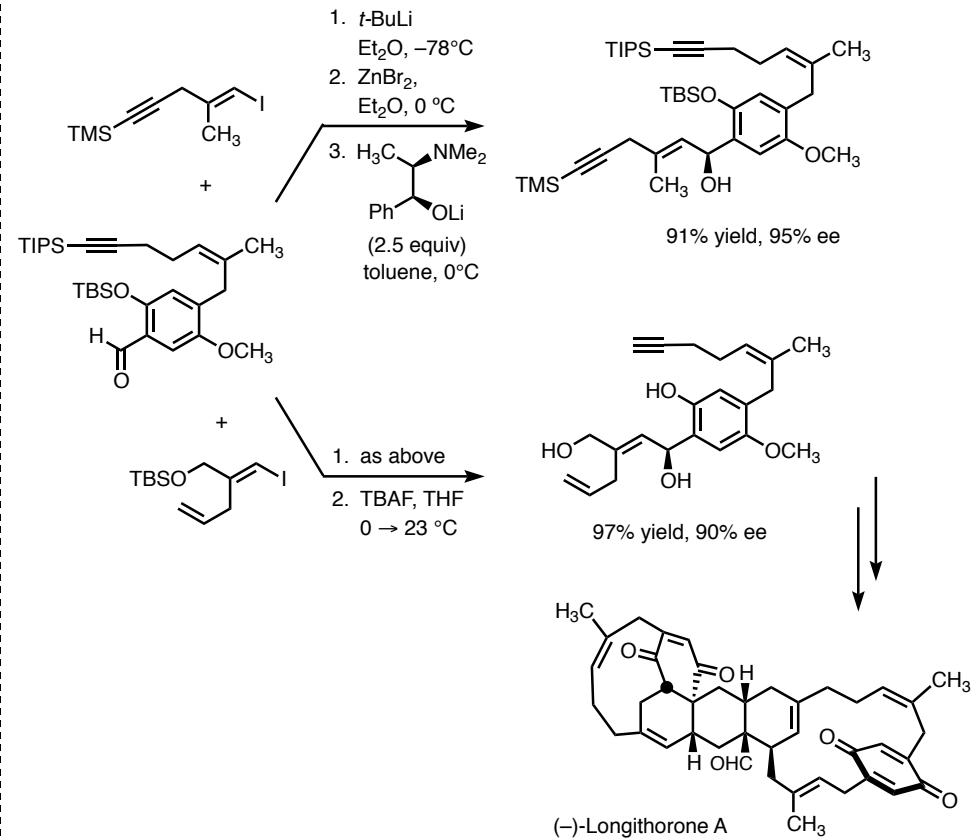
Kerrigan, M. H.; Jeon, S.-J.; Chen, Y. K.; Salvi, L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8434–8445.

- Direct transmetalations from vinyl iodides provide alkenylzinc reagents not accessible through hydroboration or hydrozirconation:



DeBerardinis, A. M.; Turlington, M.; Pu, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 2368–2370.

### Alkenylzinc Reagents in Synthesis:



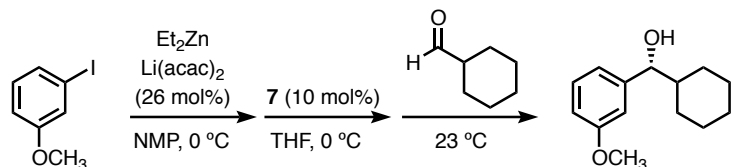
Layton, M. E.; Morales, C. A.; Shair, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 773–775.

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## Arylzinc Addition to Aldehydes:

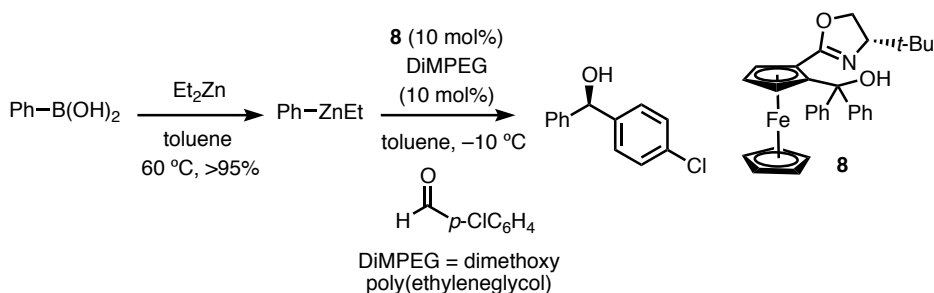
Schmidt, F.; Stemmler, R. T.; Rudolph, J.; Bolm, C. *Chem. Soc. Rev.* **2006**, *35*, 454–470.

- Unlike dialkylzinc additions, diphenylzinc additions to aldehydes take place smoothly even without a catalyst. This background reaction has made it more difficult to develop enantioselective variants.
- Ligand **7** (see page 5) has been found to promote highly enantioselective additions of diphenylzinc and functionalized diaryl zinc to aromatic and aliphatic aldehydes:

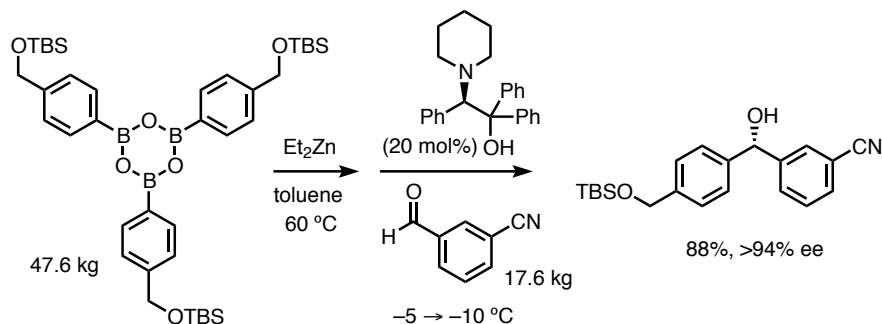


DeBerardinis, A. M.; Turlington, M.; Ko, J.; Sole, L.; Pu, L. *J. Org. Chem.* **2010**, *75*, 2836–2850.

- Widely available aryl boronic acids and boroxines can be directly transformed into arylzinc reagents and undergo enantioselective arylation of aldehydes with excellent selectivity:



Bolm, C.; Rudolph, J. *J. Am. Chem. Soc.* **2002**, *124*, 14850–14851.



Magnus, N. A.; Anzeveno, P. B.; Coffey, D. S.; Hay, D. A.; Laurila, M. E.; Schkeryantz, J. M.; Shaw, B. W.; Staszak, M. A. *Org. Process Res. Dev.* **2007**, *11*, 560–567.

## Alkynylzinc Additions to Aldehydes

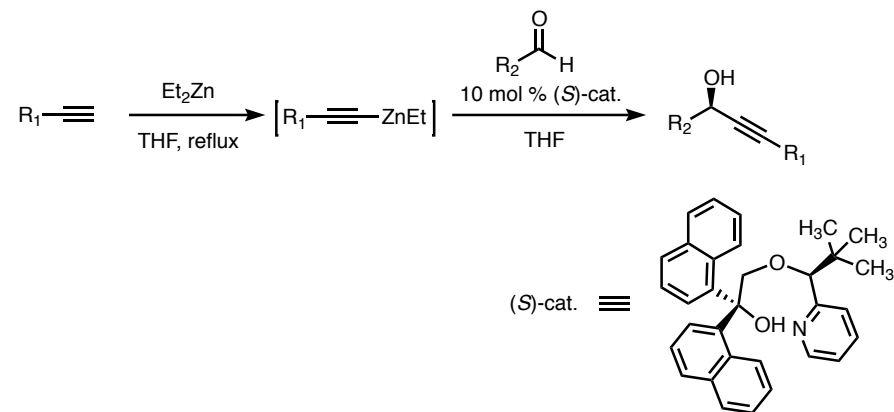
## Recent Reviews:

Wu, X.-F.; Neumann, H. *Adv. Synth. Catal.* **2012**, *354*, 3141–3160.

Trost, B. M.; Weiss, A. *Adv. Synth. Catal.* **2009**, *351*, 963–983.

Pu, L. *Tetrahedron* **2003**, *59*, 9873–9886.

- Mixed alkylalkynylzinc reagents can be prepared directly from terminal acetylenes and have been shown to undergo catalyzed 1,2-additions to aldehydes with good enantioselectivities.

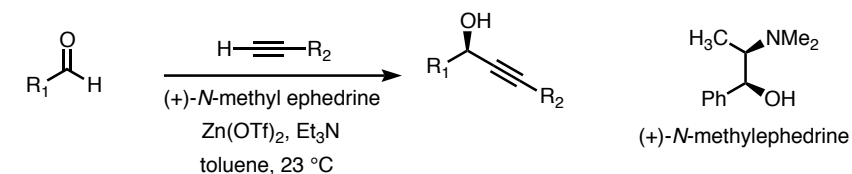


R <sub>1</sub>	R <sub>2</sub>	T (°C)	% yield	% ee
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0	64	90
C <sub>6</sub> H <sub>5</sub>	c-Hx	0	88	91
C <sub>6</sub> H <sub>5</sub>	t-Bu	0	61	95
Ph <sub>3</sub> Si	c-Hx	23	55	91
C <sub>6</sub> H <sub>13</sub>	t-Bu	23	67	87
C <sub>6</sub> H <sub>13</sub>	C <sub>6</sub> H <sub>5</sub>	23	41	78

- The low yields in these reactions was attributed in part to competitive addition of ethyl groups to the aldehydes.

Ishizaki, M.; Hoshino, O. *Tetrahedron: Asymmetry* **1994**, *5*, 1901.

- In 2000, Carreira *et al.* published an *in situ* preparation of alkynylzinc reagents and their addition to aldehydes with excellent enantioselectivities and yields.
- The reactions can be carried out without rigorous exclusion of oxygen or moisture using reagent-grade toluene (84–1000 ppm H<sub>2</sub>O).
- All reagents are stoichiometric or superstoichiometric.



R <sub>1</sub>	R <sub>2</sub>	yield (%)	ee (%)
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> Ph	94	97
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	Ph	90	97
<i>i</i> -Pr	Ph	96	92
Ph	Ph	82	93

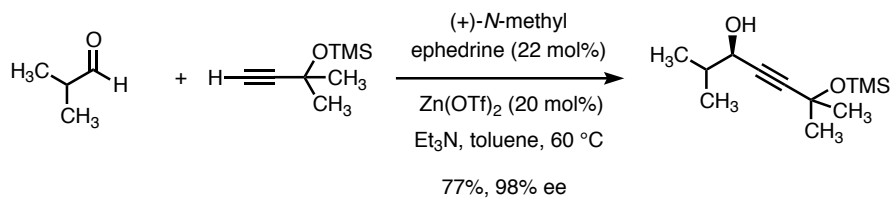
Frantz, D. E.; Fassler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806–1807.

Frantz, D. E.; Fassler, R.; Tomooka, C. S.; Carreira, E. M. *Acc. Chem. Res.* **2000**, *33*, 373–381.

Boyll, D.; Frantz, D.; Carreira, E. M. *Org. Lett.* **2002**, *4*, 2605–2606.

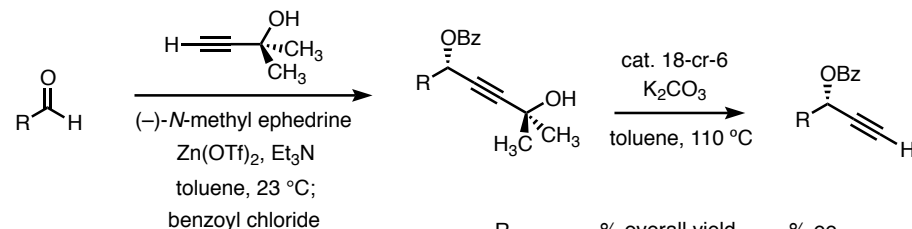
For an investigation on the reaction mechanism, see: Fässler, R.; Tomooka, C. S.; Frantz, D. E.; Carreira, E. M. *Proc. Natl. Acad. Sci.* **2004**, *101*, 5843–5845.

- It was shown that by raising the reaction temperature to 60 °C, the *in situ* zinc acetylide formation and addition reaction can be made catalytic in both zinc and chiral ligand.
- The system is less effective for aromatic aldehydes because of a competitive Cannizzaro reaction.



Anand, N. K.; Carreira, E. M. *J. Am. Chem. Soc.* **2001**, *123*, 9687–9688.

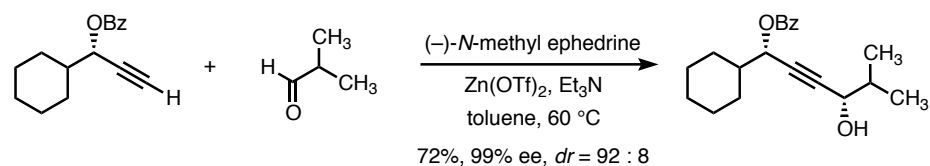
- Enantioselective additions of 2-methyl-3-butyn-2-ol to aldehydes provide access to optically active terminal acetylenes after cleavage of acetone from the products.
- Protection of the 2° propargylic alcohol prior to cleavage of acetone from the adducts leads to improved yields.



R	% overall yield	% ee
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	68	99
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	71	98
<i>t</i> -Bu	65	98
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	73	99
TIPSO(CH <sub>2</sub> ) <sub>2</sub>	71	97

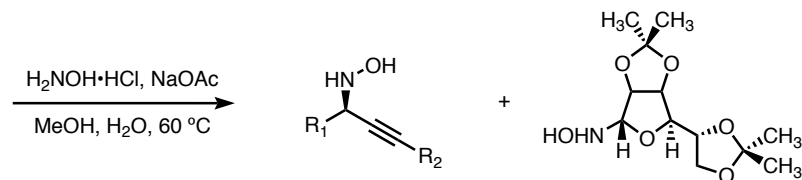
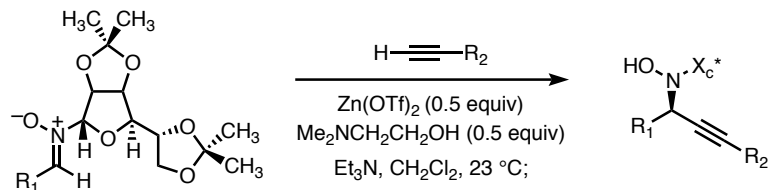
Boyll, D.; Lopez, F.; Sasaki, H.; Frantz, D.; Carreira, E. M. *Org. Lett.* **2000**, *2*, 4233–4236.

- The resulting terminal acetylene can be used to prepare enantiomerically enriched 1,4-diols:



Diez, S. R.; Adger, B.; Carreira, E. M. *Tetrahedron.* **2002**, *58*, 8341–8344.

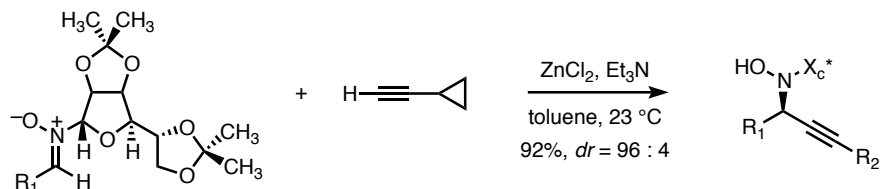
- A mannose-derived auxiliary was employed to promote diastereoselective alkynylzinc additions to nitrones. The nitron auxiliary was prepared from mannose, acetone and N-hydroxylamine.



$\text{R}_1$	$\text{R}_2$	overall yield (%)	<i>dr</i>
$\text{CH}_3$	Ph	88	95:5
<i>i</i> -Pr	$\text{C}(\text{OH})\text{Me}_2$	98	96:4
<i>t</i> -Bu	Ph	91	97:3
Ph	$\text{SiMe}_3$	88	95:5

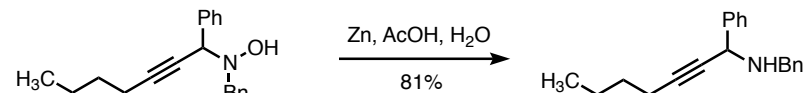
Fassler, R.; Frantz, D. E.; Oetiker, J.; Carreira, E. M. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 3054–3056.

- The use of  $\text{ZnCl}_2$  homogenizes the reaction mixture and obviates the need for *N,N*-dimethylethanolamine:



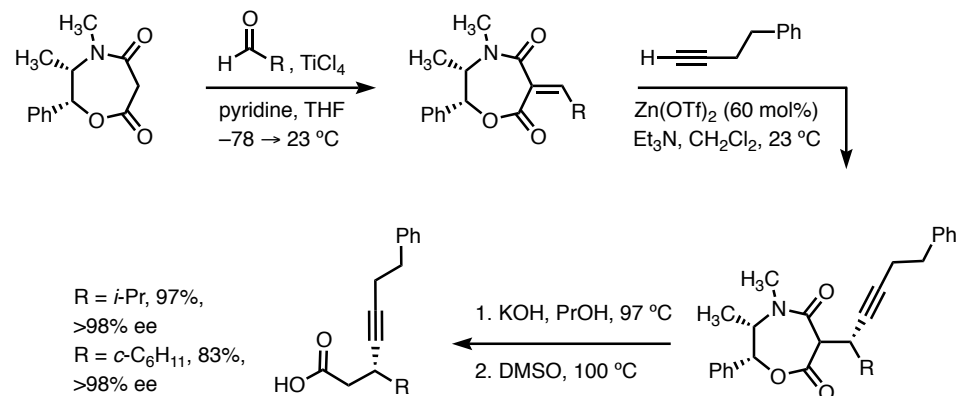
Topic, D.; Aschwanden, P.; Fässler, R.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 5329–5330.

- Hydroxylamines are readily reduced to free amines:



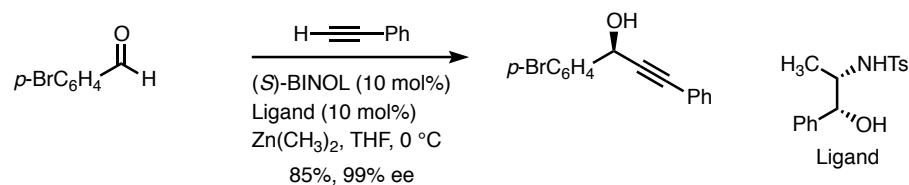
Pinet, S.; Pandya, S. U.; Chavant, P. Y.; Ayling, A.; Vallee, Y. *Org. Lett.* **2002**, *4*, 1463–1466.

- The oxazepanedione shown below, prepared in 3 steps from ephedrine and dimethyl malonate, undergoes condensation with aldehydes mediated by  $\text{TiCl}_4$ . Conjugate addition of zinc alkynylides followed by hydrolysis and decarboxylation give  $\beta$ -alkynyl acids in good yields and selectivities:



- Lowering the loading of  $\text{Zn}(\text{OTf})_2$  to 20 mol% resulted in lower selectivities and isolated yields.  
Knöpfel, T. F.; Boyall, D.; Carreira, E. M. *Org. Lett.* **2004**, *6*, 2281–2283.

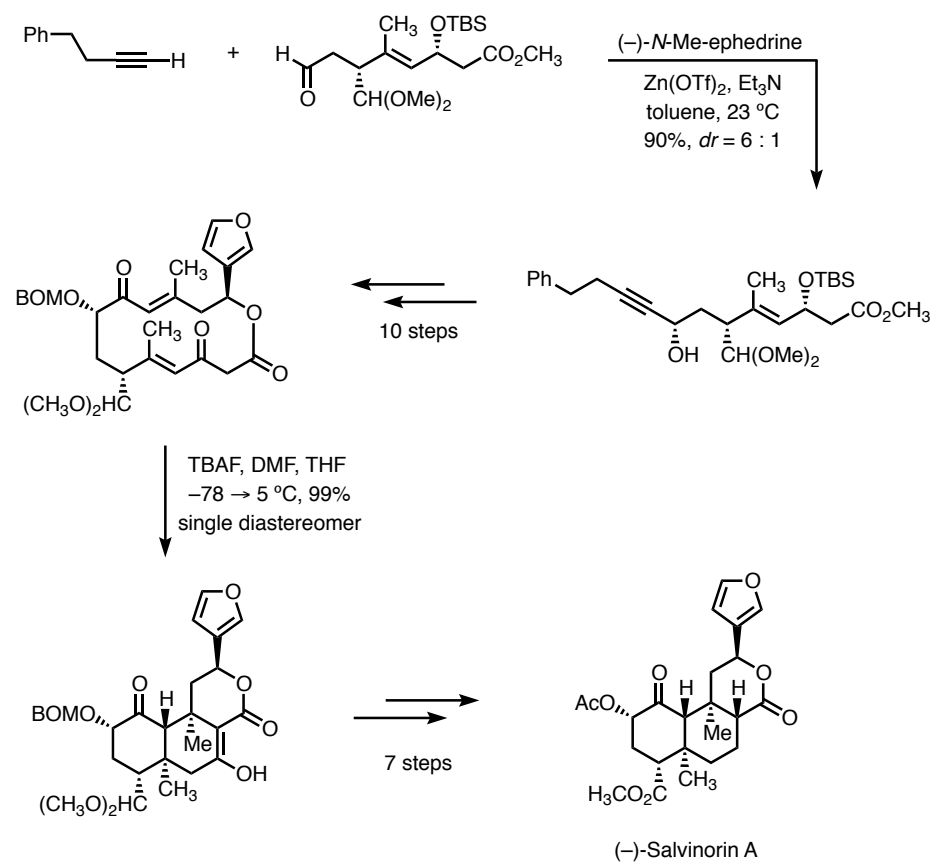
- A highly effective two-catalyst system was reported for the addition of zinc acetylide to aromatic aldehydes. The stereochemistry of BINOL determines the stereochemistry of the products, while the second ligand improves catalytic activity and enantioselectivity:



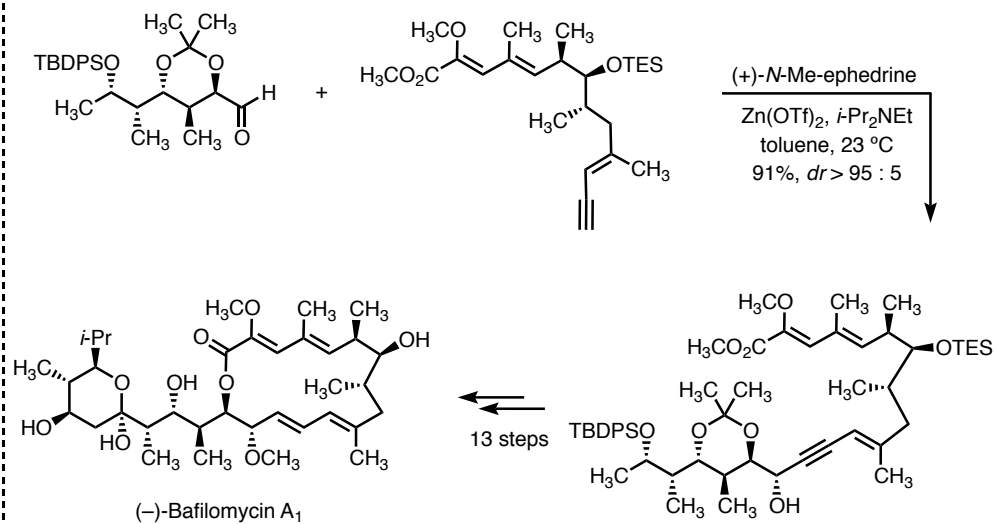
Li, X.; Lu, G.; Kwok, W. H.; Chan, A. S. C. *J. Am. Chem. Soc.* **2002**, *124*, 12636–12637.

Fan Liu, Michael Furrow

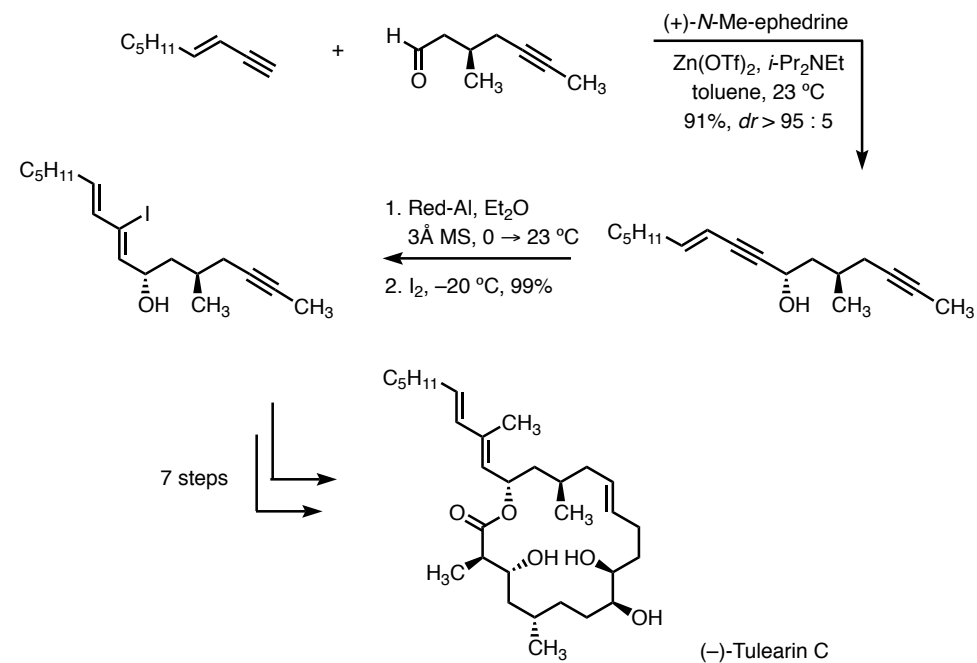
## Alkynylzinc Reagents in Synthesis:



Scheerer, J. R.; Lawrence, J. F.; Wang, G. C.; Evans, D. A. *J. Am. Chem. Soc.* **2007**, *129*, 8968–8969.



Kleinbeck, F.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 578–581.

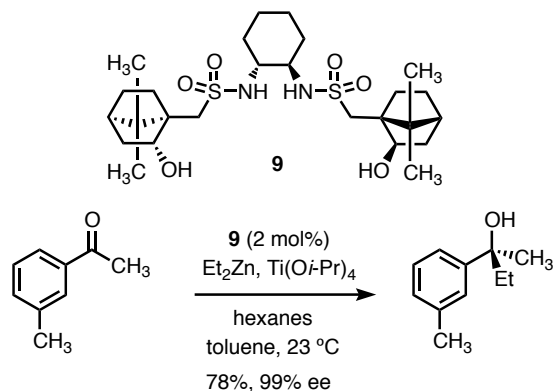


Lehr, K.; Mariz, R.; Leseurre, L.; Gabor, B. Fürstner, A. *Angew. Chem. Int. Ed.* **2011**, *123*, 11575–11579.

Fan Liu, Michael Furrow

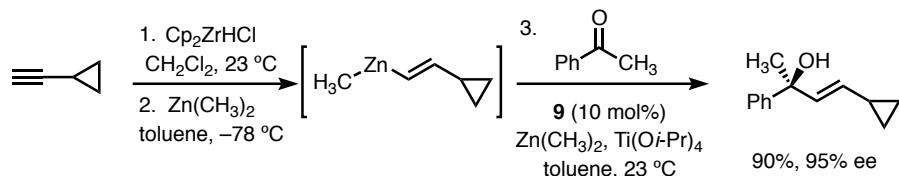
## Asymmetric Addition to Ketones:

- Ketones are less reactive than aldehydes and often give 1,2-addition products in lower yields because of competitive enolization or reduction of the carbonyl group.
- Using  $\text{Ti}(\text{O}i\text{-Pr})_4$  as a Lewis acid, ligand **9** catalyzes the formation of tertiary alcohols with high selectivity:

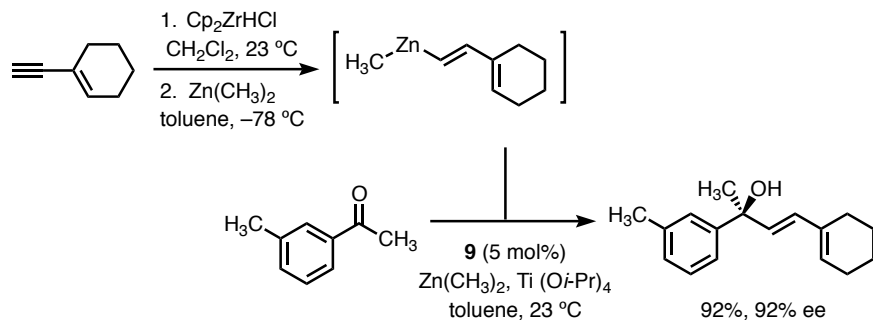


Garcia, C.; Larochelle, L. K.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 10970–10971.

Yus, M.; Ramon, D. J.; Prieto, O. *Tetrahedron: Asymmetry* **2002**, *13*, 2291–2293.

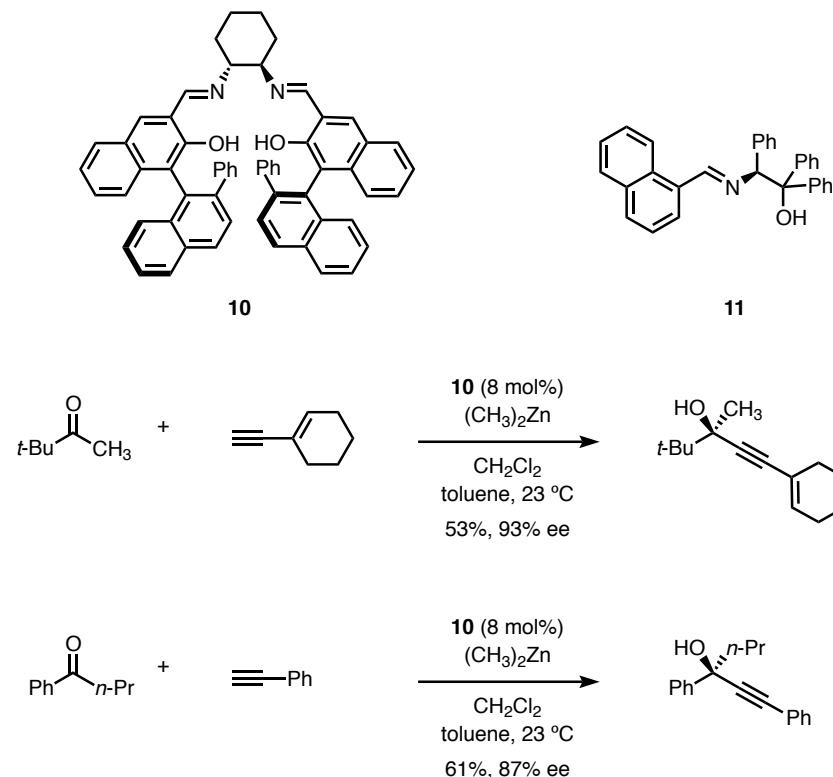


Li, H.; Walsh, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 6538–6539.

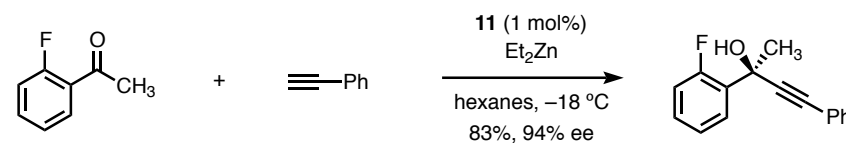


Li, H.; Walsh, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 8355–8361.

- Salen ligand **10** and Schiff base ligand **11** were found to promote efficient addition of zinc acetylides to ketones:



Saito, B.; Katsuki, T. *Synlett*. **2004**, 1557–1560.



- This method is only effective for aromatic ketones.

Chen, C.; Hong, L.; Xu, Z.-Q.; Liu, L.; Wang, R. *Org. Lett.* **2006**, *8*, 2277–2280.