

## Nickel (II) Complex Catalyzed Conjugate Addition Reaction of Functionalized Organozinc Reagents to $\alpha$ , $\beta$ -Unsaturated Esters

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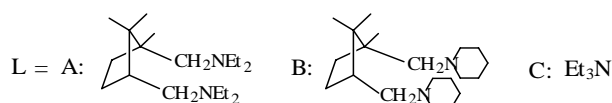
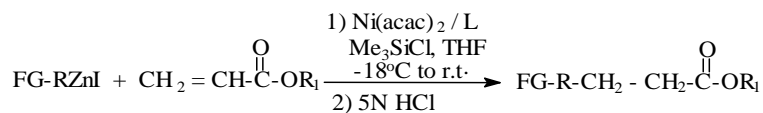
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**Abstract:** Functionalized organozinc reagents can easily under 1, 4-addition reaction with unsaturated esters in the presence of catalytic amount of Ni (acac)<sub>2</sub> and tertiary amines under very mild conditions to give the products in excellent yields.

**Keywords:** Conjugate addition reaction, organozinc reagents,  $\alpha$ ,  $\beta$ -unsaturated esters, nickel complex, catalysis.

Functionalized organozinc halides (FG-ZnX) have proved to be very useful in organic synthesis in recent years<sup>1</sup>. They can also be successfully used in conjugate addition reactions with carbonyl compounds<sup>2</sup>. However, stoichiometric copper salt CuCN·2LiCl must be used in most cases<sup>1, 2</sup> and unsaturated esters do not conduct the reaction with FG-ZnX under general conditions except the use of a polar solvent such as HMPA<sup>1, 3</sup>. We reported previously that functionalized organozinc halides could smoothly conduct 1, 4-addition reaction with unsaturated esters in the presence of Cu (OAc)<sub>2</sub><sup>4</sup>. Although the method avoided the use of toxic CN<sup>-</sup>, the amount of Cu (OAc)<sub>2</sub> used was still stoichiometric. In this paper, we first report that the conjugate addition reaction of functionalized organozinc halides with unsaturated esters can occur easily in the presence of catalytic amount of Ni (acac)<sub>2</sub> and tertiary amines under very mild conditions to give the products in excellent yields (**Scheme 1**, **Table 1**)

**Scheme 1**



### General procedure

Under nitrogen atmosphere, the mixture of zinc (0.013 mol), 1, 2-dibromoethane (0.04mL) and THF (2mL) was heated to 60-70°C for a minute and then cooled to room temperature. Chlorotrimethylsilane (0.05mL) was added, and the mixture was stirred at room temperature for 15 minutes. A solution of FG-R-I (0.012mol) in THF (10mL) was then added, the mixture was stirred 12h at 35-40°C, and the resulting solution of FG-RZnI in THF was ready for use.

Ni (acac)<sub>2</sub> (0.0012mol), L (0.0024 mol for A and B, 0.0048 mol for C) and THF (10 mL) were put into another three-neck flask and the mixture was stirred at 60°C for 10 minutes. The solution of R-ZnI in THF obtained as above was added at room temperature, and the resulting mixture was cooled to -18°C. A solution of unsaturated ester (0.01 mol) and Me<sub>3</sub>SiCl (0.022mol) in THF (5 mL) was added dropwise into the mixture and the temperature was allowed to rise to room temperature. After stirring for 10h, 5N HCl (10 mL) was added. The mixture was stirred for another 15 minutes and Et<sub>2</sub>O (15 mL) was added. The organic layer was separated, dried over anhydrous MgSO<sub>4</sub> and concentrated. The product was isolated from the crude reaction mixture by chromatography on silica gel (petroleum ether/diethyl ether).

**Table 1.** Conjugate addition reaction of functionalized organozinc reagents with unsaturated esters catalyzed by Ni (acac)<sub>2</sub>

L	FG-R-	R <sub>1</sub>	Product <sup>a</sup>	Yield (%) <sup>b</sup>
A	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	80
B	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	74
C	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	78
A	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	CH <sub>3</sub> -	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	76
A	Cl (CH <sub>2</sub> ) <sub>4</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	Cl (CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	72
C	Cl (CH <sub>2</sub> ) <sub>4</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	Cl (CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	73
C	Cl (CH <sub>2</sub> ) <sub>4</sub> -	CH <sub>3</sub> -	Cl (CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	68
C	CH <sub>3</sub> COO (CH <sub>2</sub> ) <sub>4</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	CH <sub>3</sub> COO (CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	62

a: The structures were determined by IR, <sup>1</sup>H NMR and MS.

b: Isolated yields

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