

# Synthesis of Jasmonic Acid Derivatives Using Intramolecular C-H Insertion Reaction

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**Keywords:** Jasmonic Acid Derivatives; C-H Insertion Reaction;  $\beta$ -Keto Phosphonate

Jasmonic acid derivatives such as methyl jasmonate which were recognized as aroma components, have been reported physiological activity of inducing the formation of potato-tuber. In this study, the synthesis of the title compounds using intramolecular C-H insertion reaction as key reaction, of  $\beta$ -keto phosphonate prepared from adipic acid as starting material was investigated.

Reaction of *tert*-butyl ethyl adipate **1** with dimethyl methylphosphonate in the presence of LDA gave the corresponding  $\beta$ -keto phosphonate **2** in 64% yield. The diazo transfer reaction of **2** with  $\text{TsN}_3$  gave **3** in 57% yield. Thermal decomposition of **3** in 1,2-dichloroethane containing Rh(II) catalysts were afforded the corresponding  $\alpha$ -phosphonocyclopentanone **4** in 4-21% yields (Table 1). The Horner-Wadsworth-Emmons (HWE) reaction of **4** with pentanal gave **5a** in 22% yield. Hydrogenation of **5a** and subsequent treatment of hydrochloric acid in methanol solution gave methyl dihydrojasmonate **6**. The similar reaction of **4** with 5-*tert*-butyldimethylsiloxy-2-pentynal gave the HWE product **5b**.

**Scheme 1.** Synthesis of Jasmonoide.

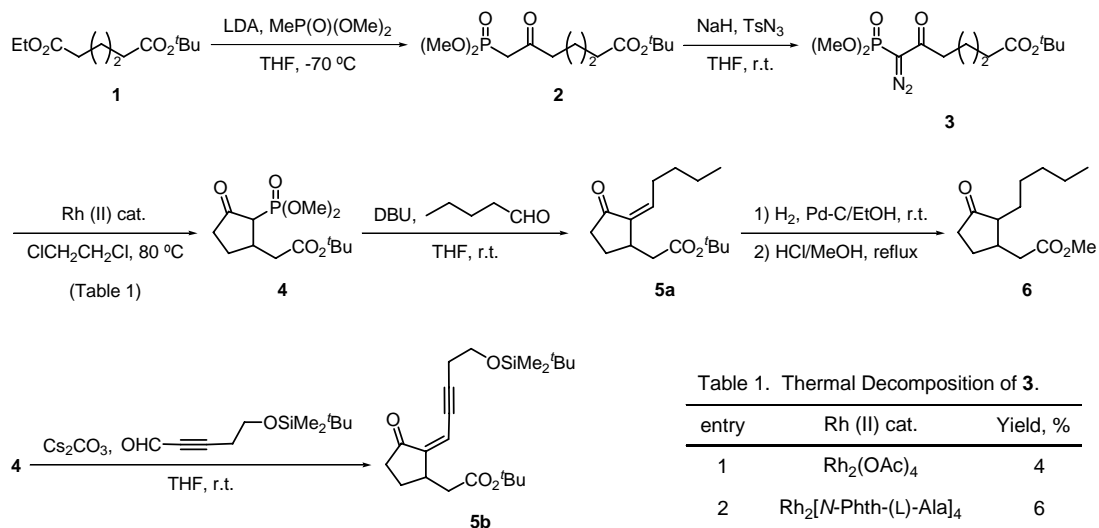


Table 1. Thermal Decomposition of **3**.

entry	Rh (II) cat.	Yield, %
1	Rh <sub>2</sub> (OAc) <sub>4</sub>	4
2	Rh <sub>2</sub> [ <i>N</i> -Phth-(L)-Ala] <sub>4</sub>	6
3	Rh <sub>2</sub> [ <i>N</i> -Phth-(L)-Phe] <sub>4</sub>	11
4	Rh <sub>2</sub> [ <i>N</i> -Phth-(L)-PhGly] <sub>4</sub>	13
5	Rh <sub>2</sub> [(S)-mandelate] <sub>4</sub>	21