Supporting Information

An Efficient Direct α -Alkylation of Ketones with Primary Alcohols Catalyzed by $[\text{Ir}(\text{cod})\text{Cl}]_2/\text{PPh}_3/\text{KOH}$ System without Solvent

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General Procedures. All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). ^1H - and ^{13}C -NMR were measured at 270 MHz and 67.5 MHz, respectively, in CDCl_3 with Me_4Si as the internal standard. Infrared (IR) spectra were measured using NaCl plates.

A typical reaction procedure is as follows: To a mixture of $[\text{IrCl}(\text{cod})]_2$ (0.02 mmol), KOH (0.2 mmol), and PPh_3 (0.08 mmol) were added ketone (2 mmol) and alcohol (4 mmol) under Ar. The reaction mixture was stirred at 100 °C for 4 h. The product was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane : ethyl acetate = 20:1). The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GC. The isolated yields of **3fa** and **3gb** were given in Table 3. The products **3aa**,¹ **3ca**,² **3ea**,³ **3fa**,⁴ **3ab**,⁵ **3ac**,⁶ **3ad**,⁷ **3ae**,⁸ and **3gb**⁹ were reported previously. **3ba** (Aldrich), **3da** (Lancaster Synthesis), and **3bb** (Lancaster Synthesis) were commercially available.

The reaction of 1a with 2a. As shown in Table 1 Run 15, the reaction under equimolar amounts of starting substrates, **1a** and **2a**, for 4 h produced **3aa** (68%), **4aa** (1%) and **5a** (5%). For a longer time (8 h), almost the same yield (70%) of **3aa** was obtained at 85% conversion of **1a**. In these reactions, several side-products having high-boiling temperature were detected in 1~3% yields, respectively, by GC-MS analysis. These by-products were identified as 5-butyldodecan-6-one, (*E*)- and (*Z*)-5-butyl-4-dodecen-6-one *etc.* derived from **3aa** and butyl aldehyde. In the case of the reaction of **1a** with two equimolar amount of **2a** (Table 1 Run 1), almost the same side-products were produced in 1~3% yields, respectively, and most of **2a** was recovered unchanged.

References

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