

# Highly Efficient Microwave-Assisted Substitution of $\beta$ -Dicarbonyl Compounds with Secondary Alcohols Using Fluoroboric Acid as the Catalyst

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The microwave-assisted substitution of  $\beta$ -dicarbonyl compounds with secondary alcohols has been achieved efficiently, using very cheap fluoroboric acid (HBF<sub>4</sub>) as the catalyst. For various  $\beta$ -dicarbonyl compounds and a series of secondary alcohols, the direct substitution gives high yields after only 5 min of microwave irradiation.

**Keywords** substitution, alcohols, acid catalysis, dicarbonyl compounds, microwave chemistry

## Introduction

The carbon-carbon bond linkage is one of the most fundamental strategies for the construction of molecular framework in organic chemistry.<sup>1</sup> The direct substitution of  $\beta$ -dicarbonyl compounds with alcohols has attracted much attention in recent years because of the feature of green chemistry. In this reaction, only H<sub>2</sub>O is generated as a side product, and the preparation of the active intermediates in the traditional protocol, such as organometallic compounds and halides or a related species, are not required.<sup>2</sup> Since the pioneering work of Baba *et al.* in 2006,<sup>3</sup> the Lewis acidic metal catalysts, such as InCl<sub>3</sub>,<sup>3</sup> InBr<sub>3</sub>,<sup>4</sup> FeCl<sub>3</sub>,<sup>5</sup> Bi(OTf)<sub>3</sub>,<sup>6</sup> and Ln(OTf)<sub>3</sub> (Ln=La, Yb, Sc, Hf),<sup>7</sup> have been reported as effective catalysts for the direct substitution of  $\beta$ -dicarbonyl compounds with allylic and benzylic alcohols. Recently, we have successfully applied a perchloric ruthenium complex to the substitution of  $\beta$ -diketones with secondary alcohols.<sup>8</sup> Further mechanistic investigations of this Lewis acid catalyzing substitution reveal that the ruthenium complex reacts first with the  $\beta$ -diketone to form a stable  $\beta$ -diketone chelate ruthenium complex and concomitantly yields an equivalent of perchloric acid, which has been proved to be the true catalyst for the substitution reaction.

Recently, molecular iodine<sup>9</sup> and various Brønsted acids, such as dodecylbenzenesulfonic acid,<sup>10</sup> *p*-toluenesulfonic acid,<sup>11</sup> phosphotungstic acid,<sup>12</sup> H-montmorillonite<sup>13</sup> and triflic acid (TfOH)<sup>14</sup> have been disclosed to be the effective catalysts for the substitution of  $\beta$ -diketones with benzylic alcohols. As a very recent progress, we have demonstrated that HClO<sub>4</sub> is an effec-

tive catalyst for the substitution of  $\beta$ -diketones with secondary alcohols, and illustrated unambiguously that the mechanism of the Brønsted acid catalyzed substitution is an S<sub>N</sub>1 mechanism.<sup>15</sup> Moreover, we have successfully applied the silica gel supported TfOH as the efficient catalyst to the heterogeneous substitution of  $\beta$ -diketones with secondary alcohols.<sup>16</sup>

Although remarkable progress has been achieved, the substitution of  $\beta$ -dicarbonyl compounds with secondary alcohols catalyzed by various catalysts usually consumes rather long reaction time (several hours to dozens of hours) to achieve high yields in the traditional thermal heating methods. In recent years, microwave irradiation (MW) has emerged as a powerful technique to promote a variety of chemical reactions.<sup>17</sup> Compared with the conventional thermal heating method, controlled microwave heating approach often dramatically reduces reaction time, increases product yields and enhances product purity by reducing unwanted side reactions. The microwave-assisted substitution of  $\beta$ -dicarbonyl compounds with secondary alcohols is still very rare.<sup>18</sup> Herein, we report the microwave-assisted substitution of  $\beta$ -dicarbonyl compounds with secondary alcohols in the presence of fluoroboric acid (HBF<sub>4</sub>) as the catalyst.

## Experimental

1-Phenyl-3-*p*-tolylpropane-1,3-dione (**1c**) was prepared according to the literature.<sup>19</sup> 1-(4-Fluorophenyl)ethanol (**2b**), 1-(4-chlorophenyl)ethanol (**2c**), 1-(4-methylphenyl)ethanol (**2d**), 1-(naphthalene-3-yl)ethanolhydrate (**2e**), benzhydrol (**2f**) and 1,3-diphenyl-2-

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propenol (**2g**) were prepared by reductions of the corresponding ketone precursors with NaBH<sub>4</sub> in methanol. The other reagents were obtained from Aldrich and used without further purification. The microwave irradiation reactions were performed with Microprocessor-Controlled Microwave Chemical Reactor (2450 MHz, 650 W) manufactured by Nanjing Lingjiang Scientific Company. <sup>1</sup>H NMR spectra were obtained from a Bruker DPX-400 spectrometer. Chemical shifts ( $\delta$ ) were reported using TMS as the internal standard. <sup>13</sup>C NMR spectra were recorded with a Bruker DPX-400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to CDCl<sub>3</sub> ( $\delta=77.0$ ). HRMS was carried out with Waters Micromass Q-ToF-2. Melting points were determined on a Barnstead Electrothermal 9100 apparatus and were uncorrected.

#### Typical procedure for the microwave-assisted substitution of $\beta$ -dicarbonyl compounds with alcohols catalyzed by HBF<sub>4</sub>

A mixture of  $\beta$ -dicarbonyl compound (1.5 mmol) and alcohol (1.0 mmol) in nitromethane (2 mL) was added HBF<sub>4</sub> (7.8  $\mu$ L, 40% aqueous solution, 0.05 mmol), and the resulting mixture was stirred under the irradiation of microwave (650 W, 70% with 30% interval) for 5 min. Then the solvent of the reaction mixture was removed under reduced pressure and the residue was passed through the flash column chromatography on silica gel to afford the product.

**3a** (CAS No. 116140-58-0), **3b** (CAS No. 960391-72-4), **3c** (CAS No. 727401-27-6), **3d** (CAS No. 945548-16-3), **3e** (CAS No. 1129424-70-9), **3f** (CAS No. 60999-93-1), **3g** (CAS No. 258881-76-4), **3h** (CAS No. 5870-49-5), **3i** (CAS No. 727401-25-4), **3k** (CAS No. 33925-42-7), **3n** (CAS No. 171927-27-8), **3o** (CAS No. 19289-28-2) and **3p** (CAS No. 60999-96-4) are known compounds and the spectral data of the new compounds **3j**, **3l**, **3m** are listed below.

**2-(1-(Naphthalen-6-yl)ethyl)-1-phenylbutane-1,3-dione (3j)** Characterized as a 1 : 0.5 diastereomeric mixture and the spectral data reported here are arisen from the unisolable two compounds. White solid, m.p. 132–135 °C (petroleum ether); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 1.29 (d,  $J=7.2$  Hz, 3H), 1.38 (d,  $J=7.2$  Hz, 1.5H), 1.92 (s, 3H), 2.28 (s, 1.4H), 4.01–4.10 (m, 1.5H), 4.94 (d,  $J=11.2$  Hz, 0.5H), 5.03 (d,  $J=11.2$  Hz, 1H), 7.29–7.40 (m, 2H), 7.42–7.54 (m, 6H), 7.60–7.71 (m, 4H), 7.77–7.84 (m, 4H), 8.11–8.14 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 20.4, 21.7, 27.5, 27.9, 40.4, 41.0, 70.8, 71.5, 125.5, 125.6, 125.8, 125.9, 126.2, 127.5, 127.7, 128.2, 128.5, 128.6, 128.7, 128.9, 132.3, 132.5, 133.4, 133.5, 133.6, 133.9, 136.9, 137.2, 140.7, 141.0, 195.1, 195.2, 203.1, 203.7; HRMS-ESI calcd for C<sub>22</sub>H<sub>19</sub>O<sub>2</sub> [M–H<sup>+</sup>]: 315.1391, found 315.1382.

**1-Phenyl-2-(1-phenylethyl)-3-*p*-tolylpropane-1,3-dione (3l)** Characterized as a 1 : 1 diastereomeric mixture and the spectral data reported here are arisen

from the unisolable two compounds. White solid, m.p. 92–95 °C (petroleum ether); <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz)  $\delta$ : 1.32 (t,  $J=6.8$  Hz, 3H), 2.29 (s, 1.5H), 2.38 (s, 1.5H), 3.93–4.01 (m, 1H), 6.12 (d,  $J=10.0$  Hz, 1H), 7.03–7.07 (m, 1H), 7.14–7.18 (m, 3H), 7.31–7.42 (m, 4H), 7.46–7.53 (m, 1.5H), 7.61–7.64 (m, 0.5H), 7.79 (d,  $J=8.0$  Hz, 1H), 7.88 (d,  $J=8.0$  Hz, 1H), 8.08 (d,  $J=8.0$  Hz, 1H), 8.16 (d,  $J=8.0$  Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 20.3, 21.6, 21.7, 41.1, 64.8, 126.6, 127.7, 128.4, 128.5, 128.7, 128.8, 129.0, 129.2, 129.6, 133.0, 133.5, 134.4, 134.7, 137.0, 137.2, 143.9, 144.0, 144.6, 194.1, 194.5, 194.7, 195.1. HRMS-ESI calcd for C<sub>24</sub>H<sub>22</sub>NaO<sub>2</sub><sup>+</sup> [M + Na<sup>+</sup>]: 365.1512, found 365.1520.

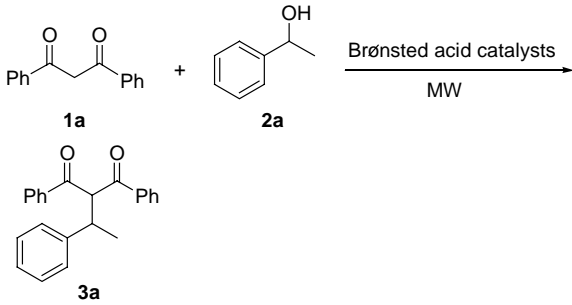
**2-Benzhydryl-1-phenyl-3-*p*-tolylpropane-1,3-dione (3m)** White solid, m.p. 174–176 °C (petroleum ether); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 2.34 (s, 3H), 5.32 (d,  $J=11.6$  Hz, 1H), 6.32 (d,  $J=11.6$  Hz, 1H), 7.03–7.07 (m, 2H), 7.12–7.16 (m, 6H), 7.24–7.26 (m, 4H), 7.30–7.34 (m, 2H), 7.44–7.48 (m, 1H), 7.75 (d,  $J=7.2$  Hz, 2H), 7.82 (d,  $J=7.2$  Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 21.6, 52.4, 62.3, 126.6, 128.3, 128.5, 128.6, 128.8, 129.3, 133.2, 134.5, 137.1, 141.8, 144.2, 193.5, 194.2. HRMS-ESI calcd for C<sub>29</sub>H<sub>24</sub>NaO<sub>2</sub><sup>+</sup> [M + Na<sup>+</sup>]: 427.1669, found 427.1678.

## Results and discussion

As the first stage to screen the effective Brønsted acid catalysts and the reaction conditions under MW (650 W, 70% with 30% interval), we chose 3-diphenylpropane-1,3-dione (**1a**) and 1-phenylethanol (**2a**) as the substrates for the model reaction. It can be seen from Table 1 that **1a** and **2a** did not react under MW without the catalyst (Table 1, Entry 1). When various Brønsted acids such as CH<sub>3</sub>COOH, CF<sub>3</sub>COOH, 12-phosphomolybdic acid (PMA), HNO<sub>3</sub>, HCl and CH<sub>3</sub>SO<sub>3</sub>H were used as the catalysts, the yields of the reactions of **1a** and **2a** varied remarkably in 13%–88% after 10 min of MW (Table 1, Entries 2–7). Surprisingly, when TfOH<sup>14</sup> and HClO<sub>4</sub><sup>15</sup> which are effective catalysts under thermal heating conditions, were used as the catalysts for the reaction of **1a** and **2a** under MW, only 22% and 38% yields were obtained, respectively (Table 1, Entries 8, 9). As HBF<sub>4</sub> was applied as the catalyst for the reaction of **1a** and **2a**, we were gratified to obtain 99% isolated yield after 10 min of MW (Table 1, Entry 10). Then the influence of solvent for the HBF<sub>4</sub>-catalyzed reaction of **1a** and **2a** was investigated under MW, and CH<sub>3</sub>NO<sub>2</sub> stands out as the solvent of choice. The reactions in other solvents tested only afforded negligible product except that the reaction in CH<sub>2</sub>Cl<sub>2</sub> gave moderate 52% yield (Table 1, Entries 11–16). If the catalyst loading of HBF<sub>4</sub> was decreased to 1 mol%, the yield of the reaction decreased to 53% after 10 min of MW (Table 1, Entry 17). At last, the molar ratio of **1a** to **2a** was reduced from 3 : 1 to 1.5 :

1 and the reaction time was reduced to 5 min, and similar 95% yield was still obtained under MW (Table 1, Entries 18, 19). Note that the reaction of **1a** with **2a** did not proceed in the absence of microwave heating even after 1 h.

**Table 1** Microwave-assisted reactions of **1a** and **2a** using Brønsted acids as catalysts under various conditions<sup>a</sup>



Entry	Catalyst	Solvent	<i>n</i> ( <b>1a</b> ) : <i>n</i> ( <b>2a</b> )	Yield <sup>b</sup> /%
1	None	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	<5
2	CH <sub>3</sub> COOH	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	13
3	CF <sub>3</sub> COOH	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	16
4	PMA	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	25
5	HNO <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	65
6	HCl	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	74
7	CH <sub>3</sub> SO <sub>3</sub> H	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	88
8	TfOH	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	22
9	HClO <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	38
10	HBF <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	99
11	HBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	3 : 1	52
12	HBF <sub>4</sub>	DCE	3 : 1	16
13	HBF <sub>4</sub>	Toluene	3 : 1	<5
14	HBF <sub>4</sub>	Dioxane	3 : 1	<5
15	HBF <sub>4</sub>	Methanol	3 : 1	<5
16	HBF <sub>4</sub>	THF	3 : 1	<5
17 <sup>c</sup>	HBF <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	3 : 1	53
18	HBF <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	1 : 1	92
19 <sup>d</sup>	HBF <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	1.5 : 1	95

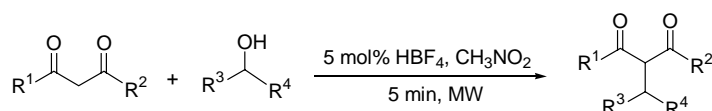
<sup>a</sup> Reaction conditions: catalyst (0.05 mmol), **2a** (1.0 mmol), solvent (2 mL), 10 min of MW at 650 W (70% with 30% interval), unless noted. <sup>b</sup> Isolated yields based on **2a**. <sup>c</sup> HBF<sub>4</sub> (0.01 mmol) was used. <sup>d</sup> MW time: 5 min.

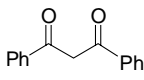
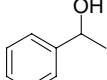
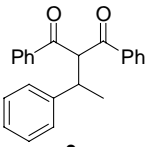
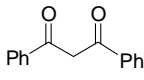
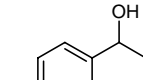
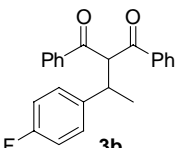
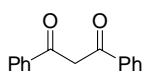
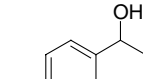
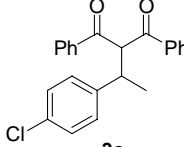
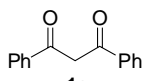
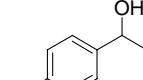
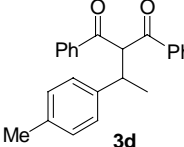
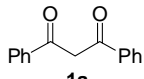
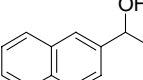
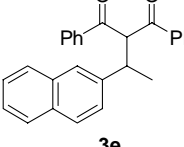
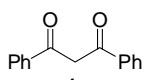
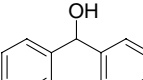
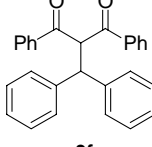
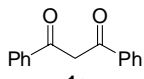
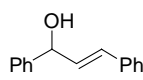
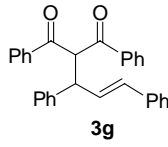
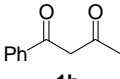
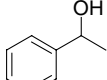
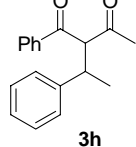
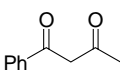
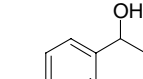
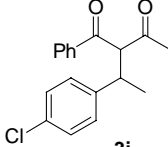
Subsequently, the microwave-assisted direct substitution of various  $\beta$ -dicarbonyl compounds with a series of alcohols was examined in CH<sub>3</sub>NO<sub>2</sub> using 5 mol% HBF<sub>4</sub> as the catalyst. The results after 5 min of MW (650 W, 30% interval) are summarized in Table 2. When  $\beta$ -diketone **1a** reacted with the benzylic alcohol **2b** and **2c** bearing a fluoride or a chloride group, excellent

98% and 95% yields were obtained (Table 2, Entries 2, 3). But the reaction of **1a** with 1-(4-nitrophenyl)ethanol with a much stronger electron-withdrawing substituent did not proceed, possibly because the strong electron-withdrawing substituent on the aromatic ring reduced the stability of the corresponding carbon cation, the intermediate.<sup>15</sup> The reaction of **1a** with the benzylic alcohol **2d** bearing an electron-donating methyl group gave only 70% yield (Table 2, Entry 4). When 1-(4-methoxyphenyl)ethanol was used as the substrate, its reaction with **1a** gave very low yield, probably because the methoxyl substitution on aromatic systems is unstable under strong Brønsted acid conditions.<sup>20</sup> The reactions of **1a** with 1-(2-naphthyl)ethanol (**2e**) and benzhydrol **2f** proceeded smoothly to generate the products **3e** and **3f** in excellent yields (Table 2, Entries 5, 6). When the allylic alcohol **2g** was applied to the reaction with **1a**, the allylation product **3g** was generated in 70% yield (Table 2, Entry 7). Moreover, when the  $\beta$ -diketone benzoylacetone **1b** was employed in the reactions with secondary alcohols **2a**, **2c**, **2e** and **2f**, high yields (84–94%) of the corresponding products were obtained (Table 2, Entries 8–11). When the unsymmetrical  $\beta$ -diketone **1c** bearing an electron-donating methyl group on one aromatic ring was used as the nucleophile to react with **2a** and **2f**, the substitution products **3l**, **3m** were obtained in excellent yields (Table 2, Entries 12, 13). Furthermore, the reaction of acetylacetone **1d** with allylic alcohol **2g** could also proceed smoothly to provide the product **3n** in 88% yield (Table 2, Entry 14). At last, with the hope to expand the substrate scope,  $\beta$ -keto esters **1e** and **1f** were used as the nucleophiles to react with benzhydrol **2f**, and the products **3o** and **3p** were obtained successfully both in excellent 98% yields (Table 2, Entries 15 and 16). It is noteworthy that under the present conditions, the reaction of **1a** with the primary alcohol such as benzylic alcohol did not proceed and the reaction of **1a** with the propargylic alcohol such as 1,3-diphenylprop-2-yn-1-ol only afforded rather low 52% yield.

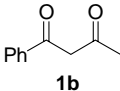
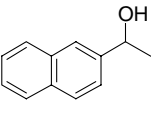
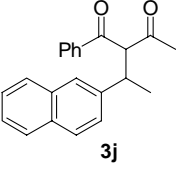
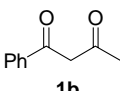
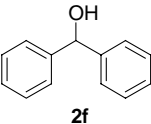
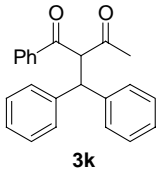
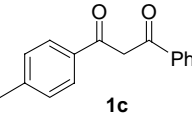
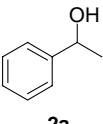
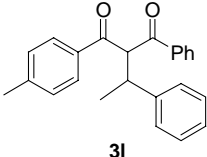
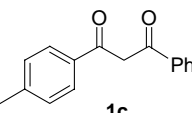
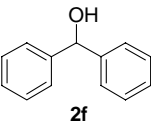
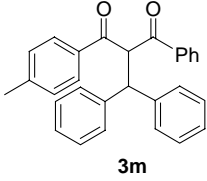
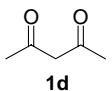
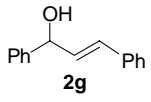
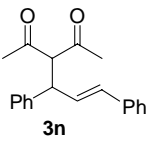
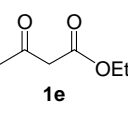
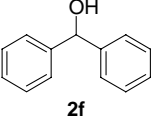
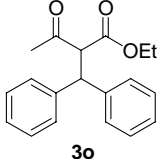
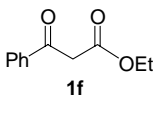
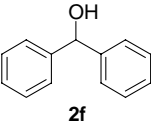
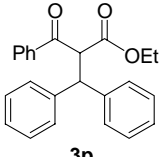
## Conclusions

In summary, we have successfully developed a highly efficient protocol for the direct substitution of  $\beta$ -dicarbonyl compounds with secondary alcohols using very cheap HBF<sub>4</sub> as the catalyst under microwave heating conditions. For various  $\beta$ -dicarbonyl compounds and a series of secondary alcohols, the reactions afford high yields in most cases after only 5 min. Moreover, it is the first time that HBF<sub>4</sub> was discovered to be the effective catalyst in the substitution of  $\beta$ -dicarbonyl compounds with alcohols.

**Table 2** Microwave-assisted reactions of  $\beta$ -dicarbonyl compounds and various alcohols catalyzed by  $\text{HBF}_4^a$ 

Entry	$\beta$ -Dicarbonyl compound	Alcohol	Product	Yield <sup>b</sup> /%
1	 <b>1a</b>	 <b>2a</b>	 <b>3a</b>	95
2	 <b>1a</b>	 <b>2b</b>	 <b>3b</b>	98
3	 <b>1a</b>	 <b>2c</b>	 <b>3c</b>	95
4	 <b>1a</b>	 <b>2d</b>	 <b>3d</b>	70
5	 <b>1a</b>	 <b>2e</b>	 <b>3e</b>	92
6	 <b>1a</b>	 <b>2f</b>	 <b>3f</b>	95
7	 <b>1a</b>	 <b>2g</b>	 <b>3g</b>	70
8	 <b>1b</b>	 <b>2a</b>	 <b>3h</b>	84 (1 : 0.8) <sup>c</sup>
9	 <b>1b</b>	 <b>2c</b>	 <b>3i</b>	90 (1 : 0.8) <sup>c</sup>

Continued

Entry	$\beta$ -Dicarbonyl compound	Alcohol	Product	Yield <sup>b</sup> /%
10	 <b>1b</b>	 <b>2e</b>	 <b>3j</b>	92 (1 : 0.7) <sup>c</sup>
11	 <b>1b</b>	 <b>2f</b>	 <b>3k</b>	94
12	 <b>1c</b>	 <b>2a</b>	 <b>3l</b>	93 (1 : 1) <sup>c</sup>
13	 <b>1c</b>	 <b>2f</b>	 <b>3m</b>	93
14	 <b>1d</b>	 <b>2g</b>	 <b>3n</b>	88
15	 <b>1e</b>	 <b>2f</b>	 <b>3o</b>	98
16	 <b>1f</b>	 <b>2f</b>	 <b>3p</b>	98

<sup>a</sup> Reaction conditions:  $\text{HBF}_4$  (0.05 mmol),  $\beta$ -diketone (1.5 mmol), alcohol (1.0 mmol),  $\text{MeNO}_2$  (2 mL), 5 min of MW at 650 W (70% with 30% interval). <sup>b</sup> Isolated yield based on the alcohols used. <sup>c</sup> The ratio of the diastereomers was determined by  $^1\text{H}$  NMR.

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