Supporting information

Cu-Ag/Hydrotalcite Catalysts for Dehydrogenative Cross-Coupling of Primary and Secondary Benzylic Alcohols

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S1 Effect of calcination temperature

As shown in Table S1, both the conversion of benzyl alcohol and yield of β -phenylpropiophenone were affected by the calcination and reduction temperature. At 300 °C the yield was 76% after 0.5 h and 98% after 1 h, but at 600 °C the yield after 0.5 h was only 29%. This decrease in yield may be ascribed to the increase in the size of Cu nanoparticles at the higher temperature.

S2 Effect of reaction conditions

S2.1 Reaction temperature

As shown in Fig. S1, increasing the reaction temperature caused both the conversion of benzyl alcohol and the yield of β phenylpropiophenone to increase. A 2% yield at 120 °C was increased to 24 and 76% at temperatures of 140 and 150 °C, respectively.

S2.2 Reaction time

Similar to the situation for temperature and as shown in Fig. S2, increasing the reaction time increased the yield of β -phenylpropiophenone, which reached nearly 99% after 1 h.

S2.3 Effect of solvents

The properties of solvents used affect the reaction rate of secondary and primary alcohols [8,11]. Toluene [8], *p*-xylene [11], and *o*-xylene [11] are common solvents for the cross-coupling of secondary and primary alcohols. The effect of the three solvents was investigated in the presence of Cu-Ag/HT with reactivity increasing in line with the order listed above, as shown in Table S2.

S2.4 Catalyst amount

As shown in Fig. S3, increasing the amount of catalyst increased both the conversion of benzyl alcohol and the yield of β phenylpropiophenone up to a point. With 0.04 g of catalyst the conversion and the yield were 73 and 45%, respectively. However, when the amount of catalyst was 0.1 g or more both values increased to the maximum observed value of nearly 99%.

Entry	Calcination and reduction temperature	Reaction time	Conversion of benzyl alcohol (%)	Yield to β- phenylpropiophenone (%)
1	300 °C	0.5 h	88	76
		1 h	99	98
2	600 °C	0.5 h	55	29
		1 h	84	80

Table S1 Effect of calcination and reduction temperature on catalytic activity ^a

^a Reaction conditions: benzyl alcohol (1.0 mmol), 1-phenylethanol (1.0 mmol), catalyst (0.1 g), oxylene (3 mL), 150 °C, 1 bar N₂

Entry	Solvents	T/°C ^b	t/h	Conversion of benzyl alcohol (%)	Yieldtoβ-phenylpropiophenone (%)
1	toluene	110	5	51	0
2	<i>p</i> -xylene	110	5	64	3
3	o-xylene	110	5	72	16
4	toluene	125	1	65	0
5	<i>p</i> -xylene	125	1	69	2
6	o-xylene	125	1	71	10
7	<i>p</i> -xylene	140	2	57	30
8	o-xylene	140	2	87	47
9	<i>p</i> -xylene	150	1	70	58
10	o-xylene	150	1	96	95

Table S2 The effect of reaction solvents on reactivity ^a

^a Reaction conditions: benzyl alcohol (1.0 mmol), 1-phenylethanol (1.0 mmol), solvent (3 mL), Cu-Ag/HT (0.1 g), 1 bar N₂.

^b Temperature of oil bath.



Fig. 1 Effect of reaction temperature on catalytic activity of Cu-Ag/HT in the dehydrogenation cross-coupling reaction. Reaction conditions: benzyl alcohol (1.0 mmol), 1-phenylethanol (1.0 mmol), Cu-Ag/HT (0.1 g), *o*-xylene (3 mL), 1 bar N_2 , reaction time (0.5 h).



Fig. 2 Effect of reaction time on yield of β -phenylpropiophenone. Reaction conditions: benzyl alcohol (1.0 mmol), 1-phenylethanol, (1.0 mmol), Cu-Ag/HT (0.1 g), 150 °C, *o*-xylene (3 mL), 1bar N₂.



Fig. 3 Effect of catalyst amount on catalytic activity of Cu-Ag/HT in the dehydrogenation cross-coupling reaction. Reaction conditions: benzyl alcohol (1.0 mmol), 1-phenylethanol (1.0 mmol), *o*-xylene (3 mL), 150 $^{\circ}$ C, 1 bar N₂, reaction time of 1 h.