## **Electronic Supplementary Information**

## The cascade synthesis of α,β-unsaturated ketones via oxidative C–C coupling of ketones and primary alcohols over ceria catalyst

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	Ph + R $OH$ cataly	$rac{Ph}{3}$ $R + Ph$	$\frac{\text{Of}}{\text{R} + \text{Ph}}$	+ 0 + R + 6	Ph O R	
Entry	Primary alcohol (2)	Conv. (%) <sup>b</sup>	Sel. (%)			
			3	4	6	7
1	benzyl alcohol	64	86	5	7	2
2	<i>p</i> -nitrobenzyl alcohol	57	19	-	81	-

Table S1 The coupling reaction of acetophenone with benzyl alcohol or *p*-nitrobenzyl alcohol catalyzed by CeO<sub>2</sub> <sup>a</sup>

<sup>a</sup> Reaction conditions: 1 (0.5 mmol), 2 (0.75 mmol), CeO<sub>2</sub>, *p*-xylene (2 mL), 150 °C, for 12 h, 1 atm air. <sup>b</sup> The conversions and selectivity based on primary alcohol consumption were determined by GC-MS.



Fig. S1 TPO-MS of the recovered CeO<sub>2</sub>.



Fig. S2 XRD patterns of (a)  $CeO_2$  nanorods, (b)  $CeO_2$  nanocubes, and (c)  $CeO_2$  nanooctahedrons



**Fig. S3** TEM image (a) and HRTEM (e) images of  $CeO_2$  nanorods, TEM image (b) and HRTEM (f) images of  $CeO_2$  nanooctahedrons, TEM image (c) and HRTEM (g) images of  $CeO_2$  nanocubes



Fig. S4 Raman spectra (532 nm) of the CeO<sub>2</sub> with different morphologies



























Fig. S5 MS of different corresponding coupling products