

## ***Supplementary Information***

### **Recyclable Indium Catalysts for Additions of 1,3-Dicarbonyl Compounds to Unactivated Alkynes Affected by Structure and Acid Strength of Solid Supports**

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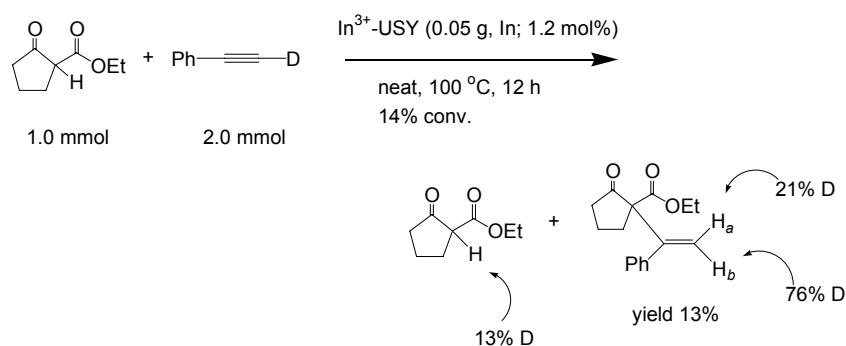
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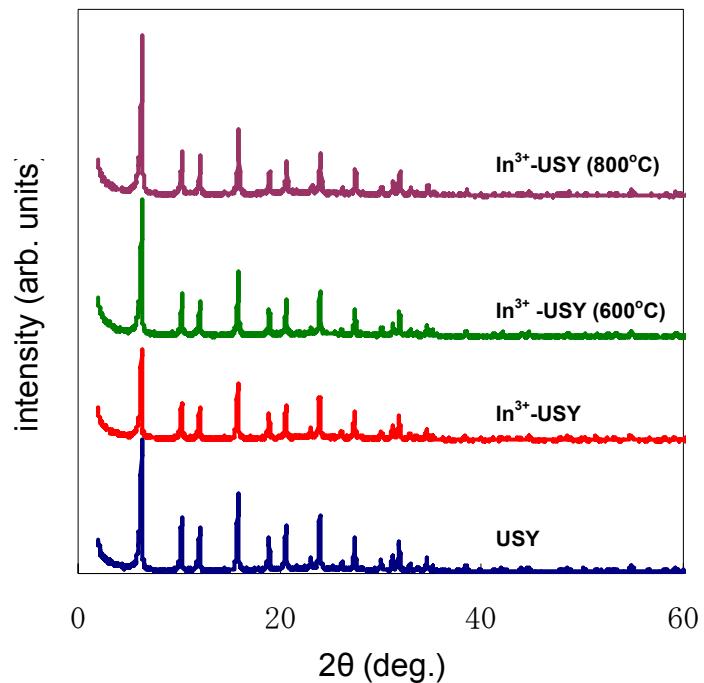
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**Reaction with Deuterated Phenylacetylene:** Into a pyrex pressure tube (15 mL) were placed the  $\text{In}^{3+}$ -USY (5.0 $\times$ 10<sup>-2</sup> g, In: 1.2 $\times$ 10<sup>-2</sup> mmol), ethyl cyclopentanone-2-carboxylate (1.0 mmol), and 1-deutero-2-phenylethyne (2.0 mmol). The resulting mixture was vigorously stirred at 100 °C under Ar. After 12 h, the catalyst was separated by filtration and <sup>1</sup>H NMR analysis revealed 14% yield of the addition product. The ratios of deuterium at *cis/trans*-position of product and deuterium incorporation to the dicarbonyl substrate were also determined by <sup>1</sup>H NMR.

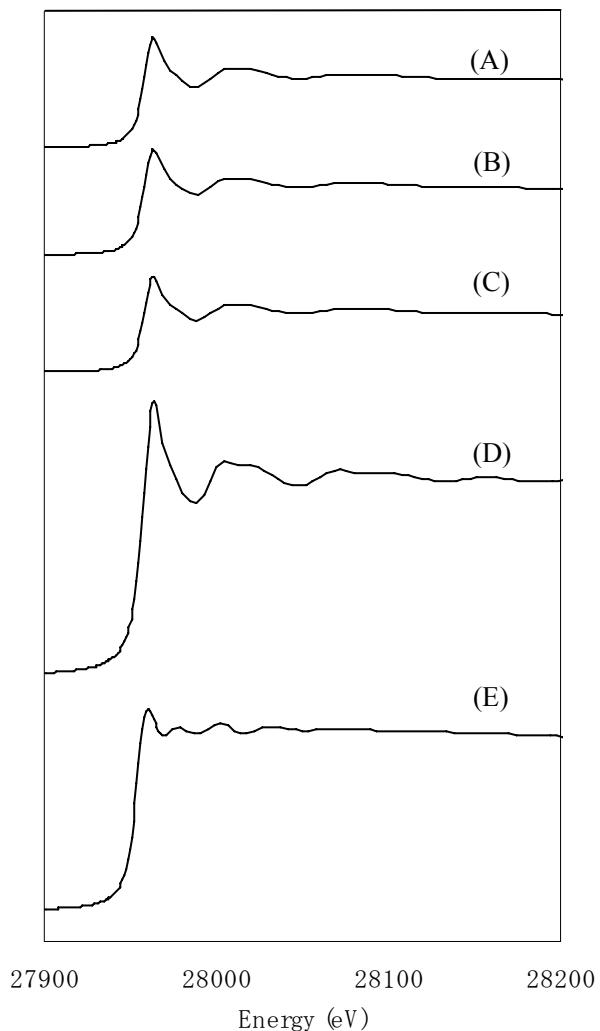


## XRD

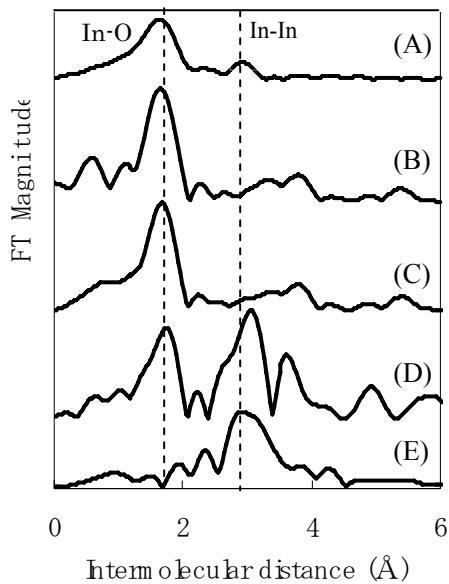


**Figure 1S.** XRD patterns of  $\text{In}^{3+}\text{-USY}$  samples and USY.

## XAFS

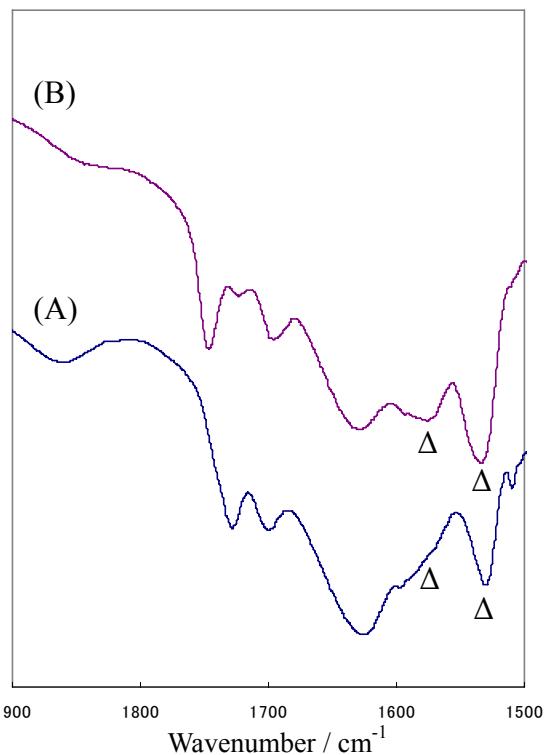


**Figure 2S.** In K-edge XANES spectra for (A) used  $\text{In}^{3+}$ -USY calcined at 800  $^{\circ}\text{C}$ , (B) used  $\text{In}^{3+}$ -USY, (C) fresh  $\text{In}^{3+}$ -USY, (D)  $\text{In}_2\text{O}_3$ , and (E) In foil.

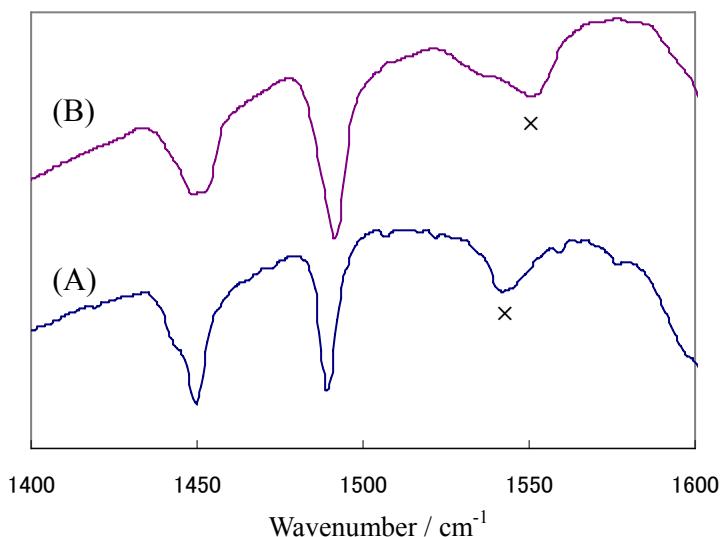


**Figure 3S.** In K-edge FT-EXAFS spectra for (A) used  $\text{In}^{3+}$ -USY calcined at 800  $^{\circ}\text{C}$ , (B) used  $\text{In}^{3+}$ -USY, (C) fresh  $\text{In}^{3+}$ -USY, (D)  $\text{In}_2\text{O}_3$ , and (E) In foil.

## FT-IR



**Figure 4S.** FT-IR spectra for (A) In<sup>3+</sup>-USY treated with acetyl acetone and (B) In<sup>3+</sup>-mont treated with acetyl acetone. Δ: enolate species.



**Figure 5S.** FT-IR spectra for (A) In<sup>3+</sup>-USY treated with pyridine and (B) In<sup>3+</sup>-mont treated with pyridine. ×: Lewis acid site. After the adsorption of pyridine, the excess and weakly adsorbed pyridine was removed by evacuating the samples at 150 °C for 12 h. The IR spectra of the strongly adsorbed pyridine were obtained with self-supporting wafers.