

## Electronic Supplementary Information

### Synthesis and structure of bismuth compounds bearing a sulfur-bridged bis(phenolato) ligand and their catalytic application to solvent-free synthesis of propylene carbonate from CO<sub>2</sub> and propylene oxide

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**General.** All weighing manipulations of air-sensitive materials were carried out in a glovebox filled with nitrogen. 2,2'-thiobis(6-tert-butyl-4-methylphenol) was prepared according to the literature procedure.<sup>S1</sup> Anhydrous MeOH, THF and toluene were purchased from Kanto Chemical and used as received. Propylene oxide (Kanto Chemical) and CDCl<sub>3</sub> (CIL) were distilled from CaH<sub>2</sub>. C<sub>6</sub>D<sub>6</sub> (CIL) was distilled from Na/benzophenone ketyl. CO<sub>2</sub> was dried by passing through 4A molecular sieves in a glass tube. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on Jeol LA500 spectrometer. Chemical Shifts are given in ppm using an external reference (tetramethylsilane (0 ppm) for <sup>1</sup>H and <sup>13</sup>C), and coupling constants were reported in hertz. GC-MS analysis was conducted on Shimadzu QP-5000 spectrometer.

#### **General procedure for the coupling reaction of propylene oxide (PO) with CO<sub>2</sub>.**

The coupling reaction of PO with CO<sub>2</sub> was conducted in a 400 ml glass flask equipped with a vacuum-tight valve. Compound **2a** or **2b** (0.024 mmol) and an iodide co-catalyst (0.112 mmol) were added to the flask, followed by evacuation to remove nitrogen in the flask. Then the flask was charged by 1 atm CO<sub>2</sub>, and propylene oxide (1.60 mL, 23 mmol) was introduced into the flask by a syringe. After the reaction mixture was vigorously stirred at room temperature for 12 h, 1 atm CO<sub>2</sub> was again introduced to balance the CO<sub>2</sub> pressure. The mixture was further stirred for 12 h (total 24 h) and then analyzed by <sup>1</sup>H NMR and GC-MS spectroscopies. The PO conversion and the PC yield were estimated by <sup>1</sup>H NMR spectroscopy.

#### References:

- S1 T. K. Prakasha, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1993, **115**, 2690-2695.