A novel green synthesis process about methyl-β-cyclodextrin has been investigated through the reaction between β-cyclodextrin and dimethyl carbonate by anhydrous potassium carbonate as catalyst in DMF. The influence of experimental factors including the molar ratio of dimethyl carbonate to β-cyclodextrin, reaction temperature, and reaction time on the average degree of substitution of methyl-β-cyclodextrin was studied. The results show that the average degree of substitution of methyl-β-cyclodextrin can be dependent on the reaction temperature and the molar ratio of raw material primarily. The structures of methyl-β-cyclodextrin were characterized by TLC, IR, MS, 1H NMR, and 13C NMR.