

Supporting Information
to the paper

**Synthesis and characterization of novel titanium complexes bearing
[ONX]-type β -enaminoketonato ligands and their application to
ethylene (co)polymerization**

Ping Tao, Xiao-Yan Tang, Bai-Xiang Li, Jing-Yu Liu, Yue-Sheng Li

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China

Correspondence e-mail: l jy@ciac.jl.cn

Additional experimental details

Synthesis of titanium complex 3a [(2-OMeC₆H₄)NC(CF₃)C(H)C(Ph)O]TiCl₂(thf): To a stirred solution of ligand **1a** (0.65 g, 2.0 mmol) in dried THF (20.0 mL) at -78 °C was added a 2.20 M *n*-butyllithium hexane solution (0.90 mL, 2.0 mmol) dropwise over a 5 min period. The mixture was allowed to warm to room temperature and stirred for 2.5 h. The resulting mixture was added dropwise to TiCl₄ (2.0 mL, 2.0 mmol) in THF (20.0 mL) at -78 °C with stirring over 30 min. The mixture was allowed to warm to room temperature and stirred for 16 h. The evaporation of the solvent in a vacuum yielded a crude product. To the crude product was added dried CH₂Cl₂ (20.0 mL), and the mixture was stirred for 10 min and then filtered. The filtrate was concentrated and recrystallized in CH₂Cl₂/*n*-hexane at room temperature and yielded the pure complex **3a** as an yellow solid (35%). ¹H NMR (300 MHz, CDCl₃): δ 7.66-7.57 (m, 2H, Ph-H), 7.50 (m, 2H, Ph-H), 7.34 (dd, 1H, Ph-H), 7.00 (m, 2H, Ph-H), 6.79 (s, 1H, N=CH), 6.53(d, 1H, Ph-H) 4.60 (s, 4H, OCH₂), 3.68 (s, 3H, OCH₃), 2.03 (s, 4H, OCH₂CH₂). And then, cooling the filtrate in the freezer (-20 °C) gave complex **4a** as a black solid.

