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Supporting Information

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[Supporting Information]

**Titanium and Zirconium Complexes with
Non-Salicylaldimine-Type Imine–Phenoxy Chelate Ligands:
Syntheses, Structures, and Olefin Polymerization Behavior**

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S1. Preparation of 2,4-di-*tert*-butyl-6-nitrophenol

Concentrated nitric acid (6.0 g) was added dropwise to a well-stirred solution of 2,4-di-*tert*-butylphenol (10.0 g, 48.4 mmol) in acetic acid (200 mL) at 10 °C over a period of 5 min. The reaction mixture was then poured into water (300 mL). The mixture was extracted with toluene (100 mL x 3) and washed with brine (100 mL x 3). The organic phase was dried over Na₂SO₄, filtered and evaporated. The crude product was purified by column chromatography on silica gel using hexanes as eluent to give yellow crystals (10.2 g, 83.7%).

¹H NMR (CDCl₃, 27 °C) δ 11.45 (s, 1H, OH), 7.97 (d, 1H, ⁴J = 2.2 Hz, ArH), 7.28 (d, 1H, ⁴J = 2.2 Hz, ArH), 1.48 (s, 9H, CCH₃), 1.32 (s, 9H, CCH₃).

caution

Once in several trials of this preparation, a compound probably resulting from excessive nitration (2-*tert*-butyl-4,6-dinitrophenol) was obtained as a main product.

¹H NMR (CDCl₃, 27 °C) δ 11.67 (s, 1H, OH), 8.96 (d, 1H, ⁴J = 2.2 Hz, ArH), 8.46 (d, 1H, ⁴J = 2.2 Hz, ArH), 1.50 (s, 9H, CCH₃).

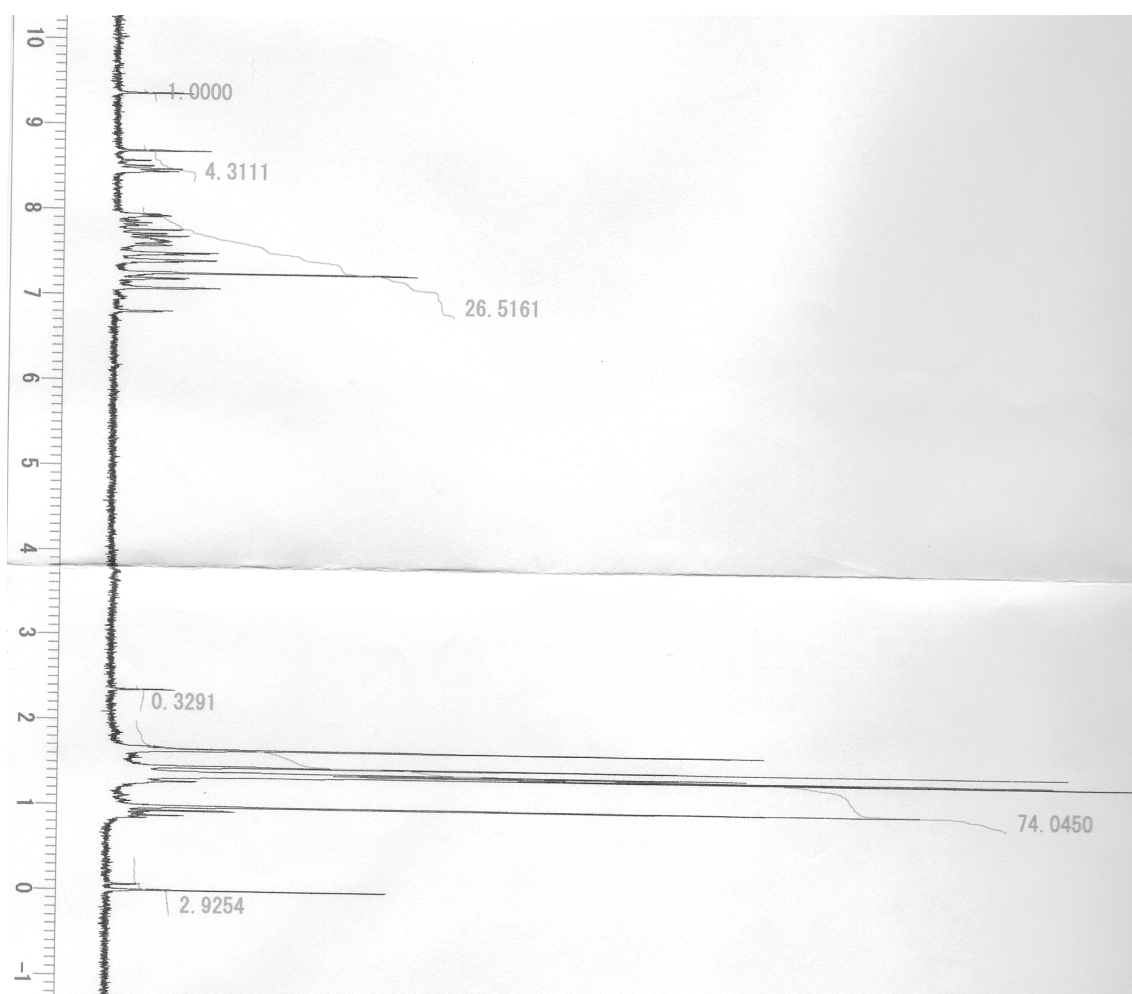
S2. Preparation of 2-amino-4,6-di-*tert*-butylphenol

Dried ethanol (200 mL) was added into a reaction vessel charged with 2,4-di-*tert*-butyl-6-nitrophenol (10.2 g, 40.6 mmol) and Pd/C (5%, 100 mg). The

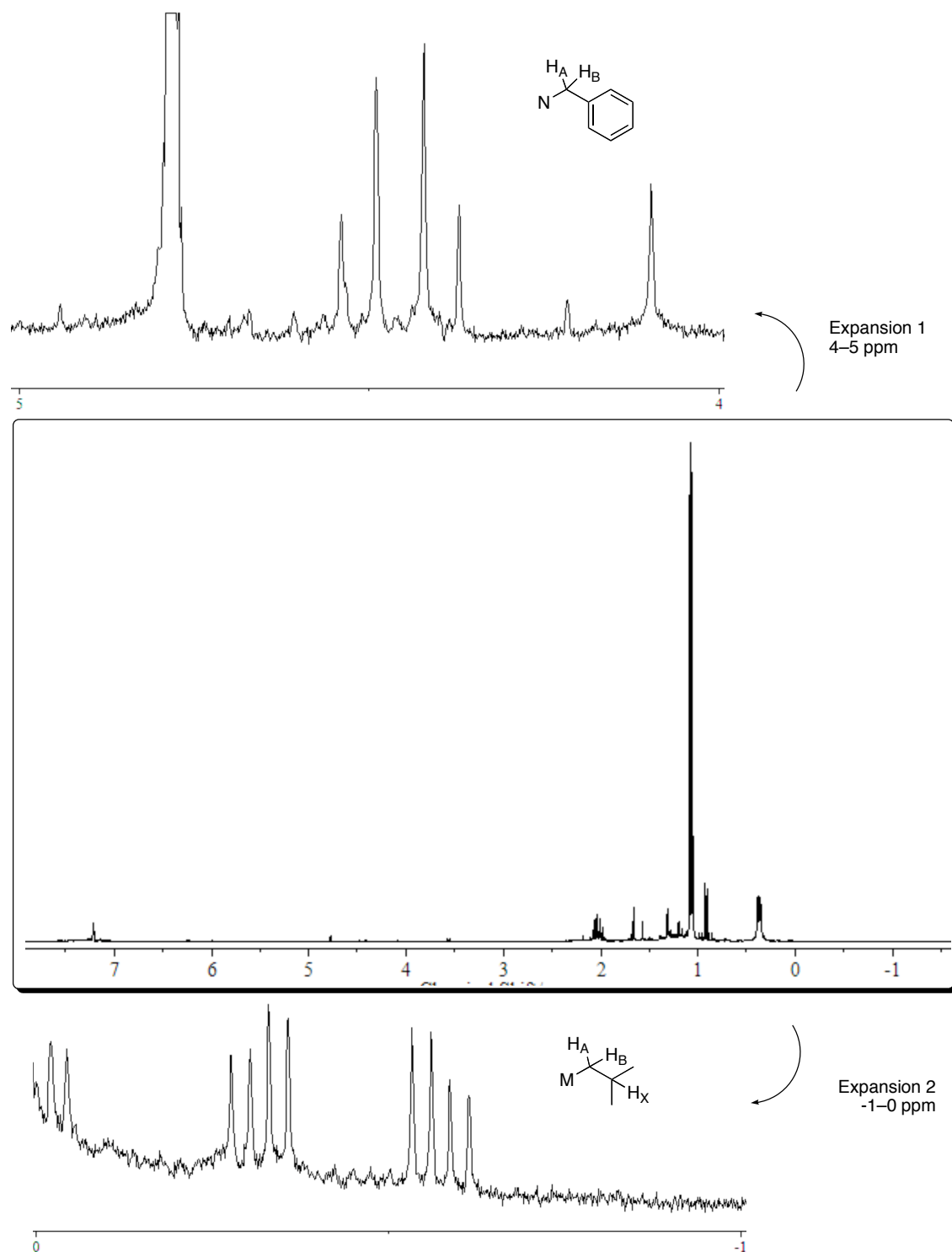
atmosphere in the vessel was replaced with hydrogen and the reaction mixture was stirred at room temperature for 2 days. The mixture was filtered thorough celite under an inert atmosphere and the filtrated was concentrated to ca. 20 mL. After cooling to 0°C, the white crystals were collected by filtration and dried under vacuum (8.2 g, 91.2%)

^1H NMR (CDCl_3 , 27 °C) δ 6.92 (d, 1H, $^4J = 2.2$ Hz, ArH), 6.82 (d, 1H, $^4J = 2.2$ Hz, ArH), 5.69 1H, OH), 3.17 (bs, 2H, NH_2), 1.41 (s, 9H, CCH_3), 1.27 (s, 9H, CCH_3).

S3. ^1H NMR chart of complex **3** (CDCl_3 , 25 °C)



S5. Reaction NMR Chart (complex **1**, $i\text{Bu}_3\text{Al}$, 75 °C in C_6D_6)



S6. Reaction of complex **1** with MAO

The procedure is similar to the reaction of complex **2** with MAO. Recovery of 2-benzilideneamino-4,6-di-*tert*-butylphenoxide was 85%.

S7. DFT Calculated Structure for Figure 4 (mol file)

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