

Electronic Supplementary Information (ESI)

Tuning the ease of formation of on-surface metal-adatom coordination polymers featuring diketones

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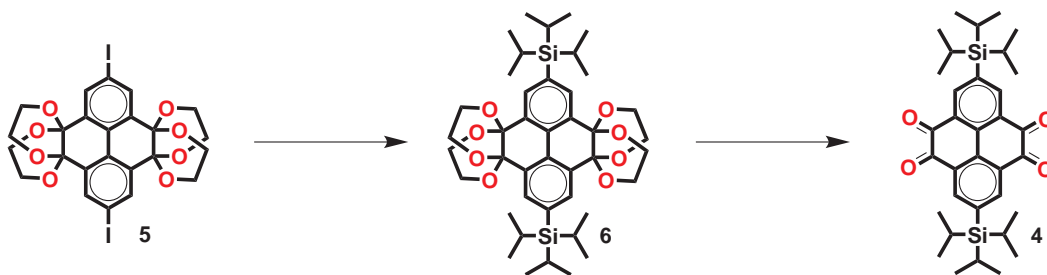
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General information

Commercial chemicals and solvents were used as received. Tetrahydrofuran was dried using an Innovative Pure Solve solvent purification system. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20 × 20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck. Column chromatography was carried out using Silica gel 60 (40-60 μm) from Scharlab. NMR spectra in solution were recorded on a Bruker Avance 400 MHz spectrometer at 298 K using partially deuterated solvents as internal standards. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on Bruker REFLEX spectrometer in POLY-MAT by Dr. Antonio Veloso. Compound 5 was synthesised according to the literature.¹

Synthesis



Synthesis of compound 6

To a dispersion of compound 5¹ (1 g, 1.45 mmol) in dry THF at -70°C under nitrogen, *n*-BuLi (3.2 mL, 5.1 mmol, 1.6 in hexanes) was slowly added and the mixture was stirred for 1.5 h. Triisopropylsilyl chloride (1.25 mL, 5.8 mmol) was added at -70°C and the mixture was stirred overnight at room temperature. The reaction was quenched by adding a saturated solution of NH_4Cl (aq.) and then the mixture was extracted with dichloromethane. The organic phase was washed with water, dried over sodium sulphate and evaporated. The resulting mixture was loaded onto a chromatographic column (eluent mixture hexane:ethyl acetate) to yield compound 6 as a white solid. The white solid was precipitated from methanol (144 mg, 13%).

¹H-NMR (CDCl_3): 7.89 (s, 4H), 4.21 (4H, *br s*), 3.69 (4H, *br s*), 1.60-1.46 (m, 6H) and 1.13 (d, 36H, $J = 4\text{Hz}$). ¹³C-NMR (CDCl_3): 136.40, 133.65, 131.27, 129.42, 92.93, 61.25, 18.56, and 10.77. MS (MALDI, pos.) (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{42}\text{H}_{62}\text{NaO}_8\text{Si}_2$: 773.388; found: 773.329.

Synthesis of compound 4

To a solution of compound 6 (27 mg, 39.1 μmol) in dichloromethane (2 mL), water (0.5 mL) and trifluoroacetic acid (2.5 mL) were subsequently added and the mixture was stirred at 40°C for 8 hours. The reaction mixture was poured into ice (*ca.* 100 ml) and the mixture was extracted with dichloromethane. The organic layer was washed with water, dried over sodium sulphate and evaporated to obtain compound 4 as an orange solid (10.8 mg, 48%).

¹H-NMR (CDCl_3): 8.56 (s, 4H), 1.58-1.47 (m, 6H) and 1.12 (d, 36H, $J = 4\text{Hz}$). ¹³C-NMR (CDCl_3): 178.73, 143.16, 141.46, 134.70, 129.88, 18.55, and 10.76. MS (MALDI, pos.) (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{34}\text{H}_{46}\text{NaO}_4\text{Si}_2$: 597.283; found: 597.262.

¹S. More, R. Bhosale, S. Choudhary and A. Mateo-Alonso, *Org. Lett.*, 2012, 14, 4170–4173.