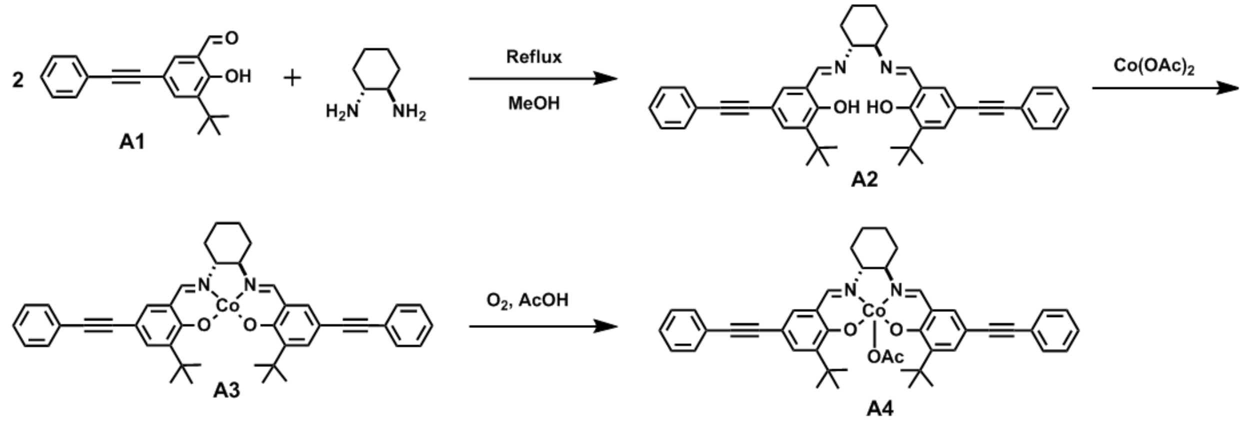
Electronic Supplementary Information for
Microporous Organic Networks Bearing Metal-Salen Species for Mild CO_2 Fixation to Cyclic Carbonates

Jiseul Chun,[a] Sung Ah Kang,[a] Narae Kang,[a] Sang Moon Lee,[b] Hae Jin Kim,[b] and Seung Uk Son*[a]
[a]*Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea*
and [b]*Korea Basic Science Institute, Daejeon 350-333, Korea*

Preparation of Co-salen model compound (A4, [*N,N'*-bis(5-phenylethynyl-3-*tert*-butyl-salicylidene)-1,2-cyclohexanediaminato]cobalt(III) acetate) in text.



5-Ethynyl-3-tert-butyl-2-hydroxybenzaldehyde was prepared by a known method (H. Sellner, J. K. Karjalainen and D. Seebach, *Chem. Eur. J.* 2001, **7**, 2873.). In a flame-dried 50 mL Schlenk flask, 5-ethynyl-3-tert-butyl-2-hydroxybenzaldehyde (1.0 g, 4.9 mmol), bis(triphenylphosphine)palladium(II) chloride (69 mg, 0.098 mmol) and copper iodide (37 mg, 0.19 mmol) were added. Iodobenzene (0.60 mL, 5.4 mmol), triethylamine (5 mL) and THF (9 mL) were added. The reaction mixture was refluxed overnight and cooled to room temperature. The product was extracted using methylene chloride and brine. After drying the solution using $MgSO_4$, the solvent was evaporated. The product was isolated by flash column chromatography using a mixture of hexane and ethylacetate (5:1) as an eluent. The isolated yield of **A1** was 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 11.9 (s, 1H), 9.9 (s, 1H), 7.7 (d, J = 1.5 Hz, 1H), 7.6 (d, J = 1.5 Hz, 1H), 7.5 – 7.6 (m, 2H), 7.3 - 7.4 (m, 3H), 1.44 (s, 9H) ppm, ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.8, 161.3, 138.9, 137.2, 135.3, 135.2, 131.6, 128.4, 123.2, 120.6, 114.4, 88.5, 88.4, 35.1, 29.1 ppm, HRMS (EI) calc. for $[M\text{-}H, C_{44}H_{46}N_2O_2]^+$; 278.1307, found; 278.1304.

For the preparation of **A2**, in a flame-dried 100 mL two-necked Schlenk flask, **A1** (1.3 g, 4.7 mmol) and trans-1,2-diaminocyclohexane (0.34 mL, 2.8 mmol) were dissolved in methanol (45 mL). The reaction mixture was refluxed for 2 hours and cooled to room temperature. After evaporating the solvent, the product was isolated by flash column chromatography. The isolated yield of **A2** was 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.3 (s, 2H), 7.5 (m, 4H), 7.4 (s, 2H), 7.3 (m, 6H), 7.2 (s, 2H), 3.3 (m, 2H), 2.0 (m, 2H), 1.9 (m, 2H), 1.8 (m, 2H), 1.5 (m, 2H), 1.4 (s, 18H) ppm, ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.1, 161.0, 137.9, 133.3, 132.9, 131.5, 128.4, 128.0, 123.7, 118.5, 112.5, 89.7, 87.4, 72.2, 35.0, 32.9, 29.3, 24.3 ppm, HRMS (FAB) calc. for $[M\text{-}H, C_{44}H_{47}N_2O_2]^+$; 635.3638, found; 635.3635

For the preparation of **A4**, in a flame-dried two-necked 50 mL Schlenk tube, **A2** (0.40 g, 0.63 mmol) was dissolved in methanol (5 mL). Cobalt acetate (0.17 g, 0.68 mmol) in methanol (10 mL) was added.[18] The reaction mixture was refluxed for 2 hours and cooled to room temperature. The product was extracted using methylene chloride and filtered through celite. The isolated red-colored product was dried under vacuum. The isolated yield of **A3** was 99%. NMR spectra could not be obtained because of the paramagnetic nature of **A3**. HRMS (FAB) calc. for [M+H, $C_{44}H_{45}N_2O_2Co]^+$; 692.2813, found; 692.2816. In a 250 mL two-necked Schlenk flask, **A3** (0.40 g, 0.61 mmol) was dissolved in methylene chloride (130 mL). Acetic acid (0.040 mL, 0.69 mmol) was added. The reaction mixture was stirred at room temperature for 3 hours under O_2 (balloon). After evaporating the solvent, the isolated brown solid was dried under vacuum. The isolated yield of **A4** was 94 %. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.6 (s, 1H), 7.5 (m, 4H), **7**.4 (s, 1H), 7.4 (s, 2H), 7.3 (m, 6H), 4.3 (m, 1H), 3.2 (m, 1H), 2.8 (m, 2H), 2.0 (m, 4H), 1.7 (s, 3H), 1.5 (s, 9H), 1.3 (s, 9H) ppm, ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 188.4, 166.7, 161.9, 143.4, 137.0, 134.7, 133.3, 131.4, 128.6, 127.9, 124.2, 90.4, 87.6, 75.1, 70.7, 35.9, 35.6, 31.0, 29.9, 24.7, 24.3, 22.9 ppm, HRMS (FAB) $[M\text{-}OAc]^+$ calc. for $[C_{44}H_{44}N_2O_2Co]^+$; 691.2735, found; 691.2738.

Figure S1. XPS spectra of **Co-MON** and the corresponding model compound (**A4**).