Supplementary Information for the communication entitled "Preparation and Structures of Novel Silamacrocyclic Compounds: Silacalix[4]quinone and Silacalix[4]hydroquinone Octamethyl Ether"

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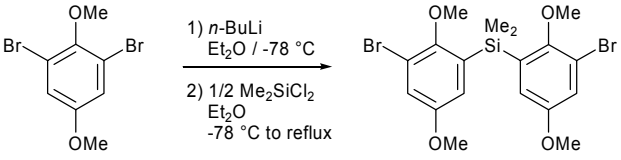
Experimental

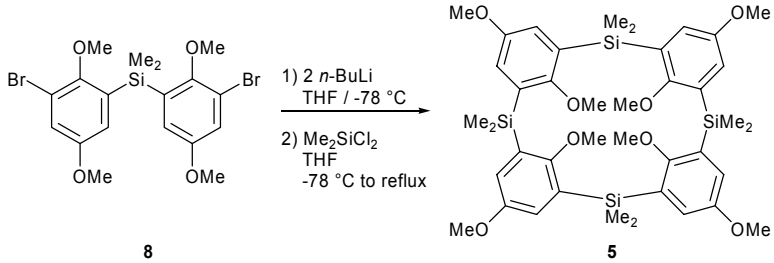
Preparation of 8



7 **8**

To a Et_2O (500 ml) solution of **7** (21.6 g, 73.0 mmol) was added a hexane (48.0 ml) solution of *n*-BuLi (1.55 N, 74.4 mmol) at –78 °C. The mixture was stirred at –78 °C for 2 h. Then a Et_2O (10 ml) solution of Me_2SiCl_2 (4.71 g, 36.5 mmol) was added to the solution at –78 °C. After stirring at room temperature for 1 night and under reflux for 1 h, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over Mg_2SO_4, and filtered. The filtrate was concentrated and distillation gave **8** (11.4 g, 23.3 mmol, 64%). **8**: colorless crystals; mp 84-84.5 °C; bp 180-220 °C / 0.8 mmHg; ^{1}H NMR ($CDCl_3$, δ) 0.58 (s, 6H), 3.47 (s, 6H), 3.74 (s, 6H), 6.92 (d, J = 2.7 Hz, 2H), 7.08 (d, J = 2.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, δ) -1.47, 55.66, 61.13, 116.48, 119.61, 120.52, 134.16, 155.26, 155.82; ^{29}Si NMR ($CDCl_3$, δ) -8.56; MS (70 eV) m/z 488 (M^+). Anal. Calcd for $C_{18}H_{22}Br_2O_4Si$: C, 44.10; H, 4.52%, Found: C, 44.10; H, 4.71%.

Preparation of 5

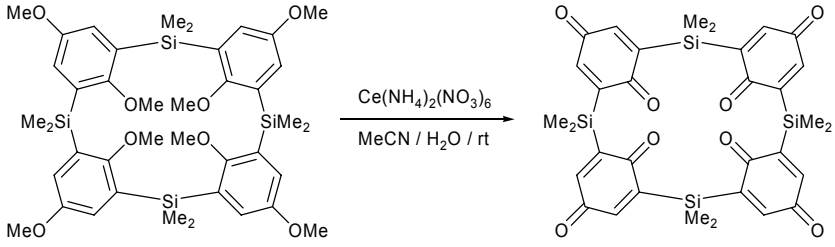


8 **5**

To a THF (200 ml) solution of **8** (1.12 g, 2.29 mmol) was added a hexane (3.1 ml) solution of

n-BuLi (1.55 N, 4.81 mmol) at –78 °C. The mixture was stirred at –78 °C for 2 h. Then Me_2SiCl_2 (0.28 ml, 2.31 mmol) was added to the solution at –78 °C. After stirring at –78 °C for 1 h, at room temperature for 1 night, and under reflux for 1 h, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over Mg_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and separated by using recycle GPC with $CHCl_3$ solution to give **5** (81.0 mg, 0.104 mmol, 9.1%). **5**: colorless crystals; mp 294-294.5 °C; ^{1}H NMR ($CDCl_3$, δ) 0.51 (s, 24H), 2.68 (s, 12H), 3.78 (s, 12H), 7.04 (s, 8H); ^{13}C NMR ($CDCl_3$, δ) -0.57, 55.56, 61.61, 121.82, 132.52, 154.51, 164.05; ^{29}Si NMR ($CDCl_3$, δ) -11.16; MS (70 eV) m/z 777 (M^+). Anal. Calcd for $C_{40}H_{56}O_8Si_4$: C, 61.81; H, 7.26%, Found: C, 61.71; H, 7.14%.

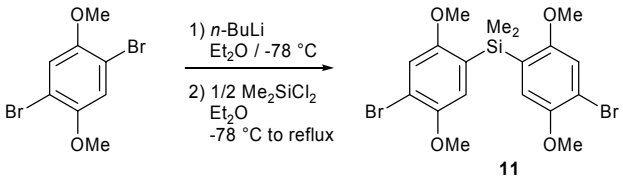
Preparation of 4



5 **4**

A mixture of **5** (81.0 mg, 0.104 mmol), $Ce(NH_4)_2(NO_3)_6$ (3.68 g, 6.72 mmol), CH_3CN (50 ml), and H_2O (35 ml) was stirred at room temperature for 2 days. The mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined, washed with water and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure, and separated by using recycle GPC with $CHCl_3$ solution to give **4** (10.7 mg, 1.62 x 10^{-5} mol, 16%). **4**: orange crystals; mp 163-165 °C (decomp.); ^{1}H NMR ($CDCl_3$, δ) 0.29 (s, 24H), 6.95 (s, 8H); ^{13}C NMR ($CDCl_3$, δ) -4.26, 144.18, 150.12, 185.15, 192.44; ^{29}Si NMR ($CDCl_3$, δ) -11.92; MS (70 eV) m/z 656 (M^+); FAB-HRMS m/z found 657.1269 [M+H$^+$], calcd for $C_{32}H_{33}O_8Si_4$, 657.1253; IR $\nu_{C=O}$ 1648, 1653 cm^{-1}; UV (CH_2Cl_2) $\lambda_{max/nm}$ (ε) 249 (32300).

Preparation of 11

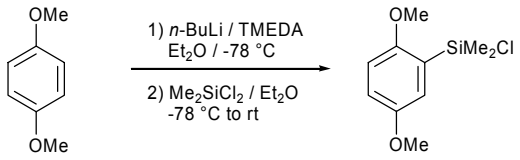


11

To a Et_2O (700 ml) solution of 1,4-dibromo-2,5-dimethoxybenzene (48.0 g, 162 mmol) was added a hexane (108 ml) solution of *n*-BuLi (1.55 N, 167 mmol) at –78 °C. The mixture was stirred at –78 °C for 1.5 h. Then a Et_2O (20 ml) solution of Me_2SiCl_2 (10.4 g, 80.4 mmol) was

added to the solution at –78 °C. After stirring at room temperature for 1 night and under reflux for 1.5 h, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over Mg_2SO_4, and filtered. The filtrate was concentrated and distillation gave **11** (18.3 g, 37.3 mmol, 46%). **11**: colorless crystals; mp 67.6-67.8 °C; ^{1}H NMR ($CDCl_3$, δ) 0.52 (s, 6H), 3.67 (s, 6H), 3.76 (s, 6H), 6.84 (s, 2H), 7.02 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) –2.23, 55.88, 56.94, 113.67, 115.30, 119.62, 126.07, 149.99, 158.59; ^{29}Si NMR ($CDCl_3$, δ) –7.77; MS (70 eV) m/z 488 (M^+). Anal. Calcd for $C_{18}H_{22}Br_2O_4Si$: C, 44.10; H, 4.52%, Found: C, 43.99; H, 4.66%.

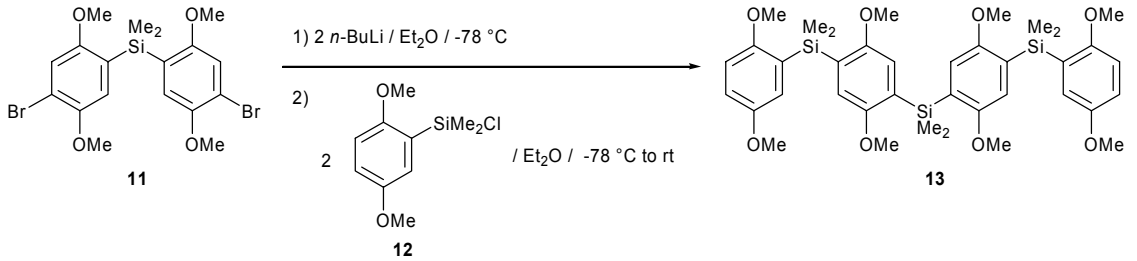
Preparation of 12



12

To a mixture of 1,4-dimethoxybenzene (15.2 g, 110 mmol), TMEDA (18.0 ml, 119 mmol), and Et_2O (450 m) was added a hexane (72.0 ml) solution of *n*-BuLi (1.55 N, 112 mmol) at room temperature. After the mixture was stirred for 17 h at room temperature, the mixture was added to a Et_2O (500 ml) solution of Me_2SiCl_2 (18.0 ml, 131 mmol) at 0 °C. After it was stirred at 0 °C for 5 h and at room temperature for 3 h, distillation gave **12** (20.0 g, 86.5 mmol, 79%) as a pale yellow oil. **12**: bp 110-175 °C / 1 mmHg; ^{1}H NMR ($CDCl_3$, δ) 0.64 (s, 6H), 3.776 (s, 3H), 3.782 (s, 3H), 6.7-6.9 (m, 2H), 7.19 (d, J = 3 Hz, 1H); ^{13}C NMR ($CDCl_3$, δ) 3.08, 56.06, 56.09, 111.12, 117.15, 121.06, 125.20, 153.96, 158.17; ^{29}Si NMR ($CDCl_3$, δ) 20.56; MS (70 eV) m/z 230 (M^+). Anal. Calcd for $C_{11}H_{15}ClO_2Si$: C, 52.05; H, 6.55%, Found: C, 52.35; H, 6.71%.

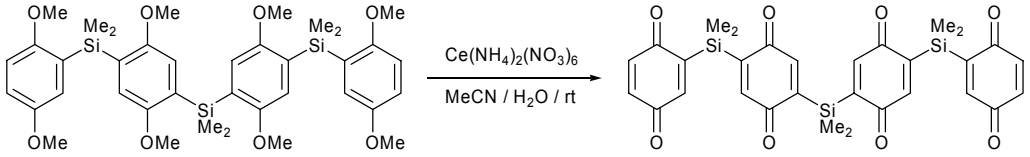
Preparation of 13



To a mixture of **11** (3.49 g, 7.11 mmol) and Et_2O (300ml) was added a hexane (10.0 ml) solution of *n*-BuLi (1.55 N, 15.5 mmol) at –78 °C. After it was stirred for 2 h, a Et_2O (20 ml) solution of **12** (3.50 g, 15.2 mmol) was added to the mixture at –78 °C. After it was stirred for 1.5 h at –78 °C and at room temperature for 16 h, a workup similar to that for **5** gave **13** (3.16 g, 1.35 mmol, 62%). **13**: colorless crystals; mp 38-39 °C; ^{1}H NMR ($CDCl_3$, δ) 0.53 (s, 12H), 0.54 (s, 6H), 3.59 (s, 6H), 3.60 (s, 6H), 3.67 (s, 6H), 3.71 (s, 6H), 6.7-6.9 (m, 10H); ^{13}C NMR ($CDCl_3$, δ) -1.91

(4C), -1.85 (2C), 55.64 (2C), 55.69 (2C), 55.78 (2C), 55.80 (2C), 110.50 (2C), 114.63 (2C), 117.43 (2C), 117.73 (2C), 122.21 (2C), 127.94 (2C), 128.49 (2C), 128.74 (2C), 153.35 (2C), 158.39 (4C), 158.57 (2C); ^{29}Si NMR ($CDCl_3$, δ) -8.46; MS (70 eV) m/z 721 (M^+). Anal. Calcd for $C_{38}H_{52}O_8Si_3$: C, 63.30; H, 7.27%, Found: C, 63.06; H, 7.54%. UV (CH_2Cl_2) $\lambda_{max/nm}$ (ε) 307 (28300).

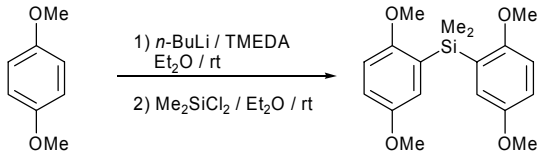
Preparation of 9



13 **9**

A mixture of **13** (502 mg, 0.696 mmol), $Ce(NH_4)_2(NO_3)_6$ (10.1 g, 18.4 mmol), CH_3CN (400 ml), and H_2O (250 ml) was stirred at room temperature for 16 h. A workup similar to that for **4** gave **9** (191 mg, 0.319 mmol, 46%). **9**: orange crystals; mp 214 °C (decomp.); ^{1}H NMR ($CDCl_3$, δ) 0.436 (s, 6H), 0.441 (s, 12H), 6.7-6.75 (m, 4H), 6.869 (s, 2H), 6.871 (s, 2H), 6.9-6.95 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) -3.64 (2C), -3.62 (4C), 136.60 (2C), 137.62 (2C), 144.48 (2C), 145.64 (4C), 148.79 (4C), 148.87 (2C), 186.16 (2C), 189.00 (4C), 190.30 (2C); ^{29}Si NMR ($CDCl_3$, δ) -10.60; HRMS m/z found 600.1068, calcd for $C_{30}H_{28}O_8Si_3$, 600.1090; IR $\nu_{C=O}$ 1639 cm^{-1}; UV (CH_2Cl_2) $\lambda_{max/nm}$ (ε) 250 (52000), 434 (sh, 1810). Anal. Calcd for $C_{30}H_{28}O_8Si_3$: C, 59.97; H, 4.70%, Found: C, 59.52; H, 5.07%.

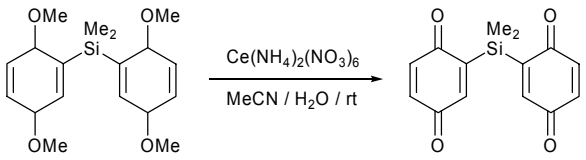
Preparation of 14



14

To a mixture of 1,4-dimethoxybenzene (40.4 g, 292 mmol), TMEDA (35.4 g, 305 mmol), and Et_2O (500 ml) was added a hexane (195 ml) solution of *n*-BuLi (1.51 N, 292 mmol) at room temperature. After it was stirred for 14 h at room temperature, a Et_2O (20 ml) solution of Me_2SiCl_2 (19.1 g, 148 mmol) was added to the mixture at room temperature. After it was stirred for 5.5 h at room temperature, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. Recrystallization from the solution of $CHCl_3$/EtOH gave **14** (36.7 g, 110 mmol, 76%). **14**: colorless crystals; mp 77-80 °C; ^{1}H NMR ($CDCl_3$, δ) 0.52 (s, 6H), 3.67 (s, 6H), 3.71 (s, 6H), 6.7-6.9 (m, 6H); ^{13}C NMR ($CDCl_3$, δ) -1.96, 55.68, 55.76, 110.69, 114.82, 122.02, 127.74, 153.37, 158.62; ^{29}Si NMR ($CDCl_3$, δ) -8.48; MS (70 eV) m/z 332 (M^+). Anal. Calcd for $C_{18}H_{24}O_4Si$: C, 65.03; H, 7.28%, Found: C, 64.80; H, 7.22%. UV (CH_2Cl_2) $\lambda_{max/nm}$ (ε) 301 (7730).

Preparation of 10



14 **10**

A mixture of **14** (1.40 g, 4.20 mmol), $Ce(NH_4)_2(NO_3)_6$ (11.1 g, 20.3 mmol), CH_3CN (65 ml), and H_2O (50 ml) was stirred at room temperature for 6 h. A workup similar to that for **4** gave **10** (702 mg, 2.58 mmol, 61%). **10**: orange crystals; mp 106-107.5 °C; ^{1}H NMR ($CDCl_3$, δ) 0.45 (s, 6H), 6.7-6.75 (m, 4H), 6.9-6.95 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) -3.61, 136.61, 137.59, 144.44, 148.89, 186.11, 190.25; ^{29}Si NMR ($CDCl_3$, δ) -9.52; MS (70 eV) m/z 272 (M^+); Anal. Calcd for $C_{14}H_{12}O_4Si$: C, 61.75; H, 4.44%, Found: C, 61.58; H, 4.54%. IR $\nu_{C=O}$ 1648, 1656 cm^{-1}; UV (CH_2Cl_2) $\lambda_{max/nm}$ (ε) 249 (27100), 368 (sh, 120).