

tion of 0.93 g (3.90 mmol) of compound **9** and 0.23 g of Pd(OH)₂/C (20 wt %) in 20 mL of EtOH and 10 mL of cyclohexene was heated at reflux for 1 hr. The resulting solution was filtered through a pad of Celite, and the solvent was removed under reduced pressure to yield 0.58 g (99% yield) of alcohol **10**: $[\alpha]_D^{28} = -37.00$ (C=1.00, CHCl₃); ¹H NMR (CDCl₃) δ 3.6-3.2 (m, 3H), 3.39, 3.36 (2s, 6H), 2.29 (br. s, 1H), 1.20 (d, *J*=6.0 Hz, 3H), 1.17 (d, *J*=6.3 Hz, 3H); ¹³C NMR (CDCl₃) δ 77.4, 77.2, 76.3, 56.9, 56.6, 15.6, 14.8.

(2R,4R)-2,4-Dimethoxy-3-Pentanone (11). Alcohol **11** (0.58 g, 3.89 mmol) was dissolved in CH₂Cl₂ containing both 4 Å molecular sieves (2 g) and trimethyl *N*-oxide (0.44 g, 1.5eq). After stirring the mixture for 10 min, tetrapropylammonium perruthenate (TPAP, 70 mg, 5 mol %) was added and stirred for 1 hr. The reaction mixture was filtered through a pad of silica gel, eluting with ethyl acetate. The filtrate was evaporated and chromatographed on silica gel (Pentane : Ether=3 : 1) to give 0.37 g (65% yield) of C₂ symmetric ketone **11**: $[\alpha]_D^{28} = +16.7$ (C=1.00, CHCl₃); ¹H NMR (CDCl₃) δ 4.09 (q, *J*=6.8 Hz, 2H), 3.38 (s, 6H), 1.35 (d, *J*=6.9 Hz, 6H); ¹³C NMR (CDCl₃) δ 212.0, 80.3, 57.7, 17.3; MS (*M*⁺): 145; IR (film) ν 1730 cm⁻¹.

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Orthocyclophanes. 5.¹ Functionalization of [1₆] Starand on the Aromatic Ring

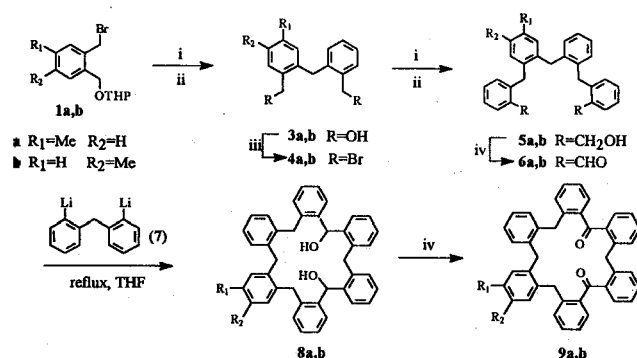
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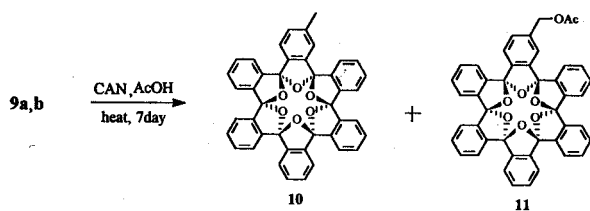
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Since the first starand, [1₆]orthocyclophano-12-crown-6 ([1₆]starand)² has the up-down-up arrangement of the six oxygen atoms which forms a preorganized spherical cavity, it is expected to have an unusual cation binding properties.² In order to improve the binding ability of [1₆]starand towards cations, we planned to attach side arm donor functional groups on the benzene ring which could provide internal solvation to the starand-bound cation.³ Herein, we report the first synthesis of the functionalized [1₆]starands-methyl[1₆]orthocyclophano-12-crown-6 (**10**) and acetoxymethyl[1₆]orthocyclophano-12-crown-6 (**11**).

Reaction of the isomeric mixture of **1a** and **1b**⁴ with Grignard reagent **2** in the presence of catalytic amounts of CuI, followed by removal of the THP protecting group gave benzylic diols **3a** and **3b**, which upon treatment with dry HBr gas in CH₂Cl₂ furnished the corresponding dibromides **4a** and **4b** in 82% overall yield. Benzylic diols **5a** and **5b** were obtained in 55% yield by the same method as the synthesis of **3a** and **3b**. Oxidation of **5a** and **5b** with PCC to give the aromatic dialdehydes **6a** and **6b** followed by condensation with 1 molar equivalent of dilithio reagent **7**⁵ gave the cyclic diols **8a** and **8b**. Oxidation of **8a** and **8b** with PCC gave



Scheme 1. Reagents and conditions: i) CuI, **2**, THF; ii) TsOH, MeOH; iii) HBr, CH₂Cl₂; iv) PCC, CH₂Cl₂.



Scheme 2.

the corresponding cyclic diones, methyl[1₆]orthocyclophano-1,3-diones (**9a** and **9b**, 17% overall yield from **5a** and **5b**).⁶ It is known that oxidation of the methyl group on the aromatic ring with ceric ammonium nitrate (CAN) in AcOH usually gives rise to hydroxymethyl and acetoxy-methyl group on the aromatic ring. However, no hydroxymethyl group was observed on oxidation with CAN. Further oxidation of **9a** and **9b** by heating with CAN in AcOH for 1 week afforded methyl[1₆]orthocyclophano-12-crown-6 (**10**, 8.2% yield) and acetoxy-methyl[1₆]orthocyclophano-12-crown-6 (**11**, 2.5% yield). The structure was unambiguously proved by mass spectra, ¹H NMR, and IR spectroscopy; details are in the experimental section.

In summary, synthetic sequences leading to two functionalized [1₆]starands have been developed. **11** is expected to display better binding affinity towards cations than [1₆]starand. Since acetyl group can be converted to the other functional groups, **11** can be used as a starting material for the synthesis of various functionalized starands as host molecules.

Experimental

Benzylic diol (3a, 3b). The Grignard reagent **2** prepared from 2-bromobenzyl tetrahydropyran-2-yl (THP) ether (10.3 g, 38.2 mmol) was added to a solution of **1** (7.63 g, 25.5 mmol) containing a catalytic amount of CuI (0.5 g) in THF (40 mL) at 0 °C, by cannulation under nitrogen. After being stirred overnight at 50 °C, the resulting mixture was treated with aq. NH₄Cl solution, extracted with CH₂Cl₂, dried (MgSO₄), and concentrated to give the coupling product, a di-THP ether. The THP protecting groups were removed from the crude product by heating with TsOH in methanol. Usual workup and purification by chromatography (SiO₂, CH₂Cl₂) afforded 5.41 g (87.6%) of an aromatic diol **3a** and **3b** as a white powdery solid: mp 137-138 °C; IR (KBr) 3232, 3008, 2896, 1596, 1475, 1436, 1091, 739 cm⁻¹; ¹H NMR (CDCl₃, 80 MHz) δ 7.46-6.84 (m, 8H, ArH), 5.08 (m, 2H, OH), 4.48 (d, 4H, ArCH₂O), 3.99 (s, 2H, ArCH₂Ar).

Benzylic dibromide (4a, 4b). Dry HBr gas was passed into a suspension of benzylic diol **3a** and **3b** (4.00 g, 16.5 mmol) in CH₂Cl₂ (80 mL) at rt until the solution was saturated, whereupon the solid dissolves immediately into the solvent to give a clear, orange solution. After repeated saturation with drying HBr gas, the reaction flask was stoppered, and the mixture was stirred for more than 5 h. The resulting solution was washed successively with aqueous NaHCO₃ and water, dried (MgSO₄), and concentrated. The crude product was chromatographed (SiO₂, CH₂Cl₂) to give 5.68 g (93%) of the crystalline dibromide **4a** and **4b**: mp 85-86 °C; IR (KBr)

3024, 2912, 1600, 1484, 1196, 1072, 819, 758, 720 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 7.39-6.81 (m, 7H, ArH), 4.48 (s, 2H, CH₂O) 4.44 (s, 2H, CH₂O), 4.23 (s, 2H, ArCH₂), 2.31 (s, 3H, ArCH₃); ¹³C NMR (CDCl₃, 20.15 MHz) δ 138.90, 136.73, 135.92, 135.71, 135.51, 131.28, 130.55, 130.23, 130.20, 129.92, 129.17, 127.02, 34.21, 32.04, 31.86, 20.86, 20.82.

Diol (5a, 5b). The Grignard reagent **2** prepared from 2-bromobenzyl (THP) ether (7.78 g, 28.5 mmol) was added dropwise to a cooled (0 °C), stirred solution of **4a** and **4b** (3.77 g, 10.2 mmol) in THF (50 mL) containing CuI (0.4 g) under nitrogen. After being stirred overnight at rt, the reaction mixture was quenched with aqueous NH₄Cl (50 mL) and the solvent was removed under reduced pressure. The aqueous layer was extracted with CH₂Cl₂. The extract was washed successively with aqueous NaHCO₃ and water, and concentrated to give an oily product. A solution of the crude THP ether in MeOH (60 mL) was refluxed with *p*-TsOH (1 g) for more than 5 h. The reaction mixture was cooled to rt, quenched with aqueous NH₄Cl (20 mL), and concentrated under reduced pressure. The crude product was filtered off and washed successively with distilled water and diethyl ether to give 2.39 g (55%) of the benzylic diol **5a** and **5b** as powdery solid: mp 119-121 °C; IR (KBr) 3344, 3024, 2896, 1593, 1481, 1043, 995, 780, 758 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 7.36-6.76 (m, 15H, ArH), 4.42 (s, 4H, CH₂O), 3.87 (s, 2H, ArCH₂Ar), 3.84 (s, 2H, MeArCH₂Ar), 3.80 (s, 2H, ArCH₂Ar), 2.24 (s, 3H, ArCH₃).

Dialdehyde (6a, 6b). A mixture of diol **5a** and **5b** (2.39 g, 5.67 mmol), PCC (5 g), and Celite (5 g) in CH₂Cl₂ (100 mL) was stirred at rt for 6 h. The reaction mixture was filtered and solvent was removed from the filtrate at reduced pressure. The crude product was chromatographed on silica gel (*n*-hexane/EtOAc, 8:1) to give 2.10 g (86%) of **6a** and **6b** as a crystalline white solid: mp 92-93 °C; IR (KBr) 3024, 2848, 2753, 1689, 1593, 1484, 1443, 1395, 1040, 953, 870, 809, 752 cm⁻¹; ¹H NMR (CDCl₃, 80 MHz) δ 10.07 (s, 2H, C(=O)H), 7.87-6.71 (m, 15H, ArH), 4.29 (s, 2H, ArCH₂), 4.27 (s, 2H, MeArCH₂), 3.85 (s, 2H, ArCH₂ArMe), 2.23 (s, 3H, ArCH₃).

Diketone (9a, 9b). A solution of **6a** and **6b** (1.19 g, 2.7 mmol) in THF (100 mL) was added to the dilithio reagent **7**.⁵ The reaction mixture was stirred at rt for 2 h, and then heated under reflux for 20 h, cooled and treated with aqueous NH₄Cl. After evaporation of the solvent, the reaction mixture was taken up with CH₂Cl₂. The organic layer was washed with water, dried (MgSO₄), and concentrated to give **8a** and **8b** as a biscondensation product. The diol **8a** and **8b** was so difficult to purify by chromatography that it was oxidized directly without purification. A mixture of the crude **8a**, **8b**, PCC (6 g) and Celite (7 g) in CH₂Cl₂ (80 mL) was stirred for 4 h and filtered off. The solvent was removed *in vacuo* to give an oxidation product. The crude product was chromatographed (SiO₂, CH₂Cl₂) and then recrystallized from *n*-hexane/CH₂Cl₂ to give 0.33 g (20%) of the diketone **9a** and **9b** as a crystalline white solid: ¹H NMR (CDCl₃, 80 MHz) δ 7.6-6.6 (m, 26H, ArH), 4.38 (s, 2H, ArCH₂), 4.07 (s, 4H, ArCH₂), and 3.71 (s, 2H, ArCH₂), 2.20 (s, 3H, ArCH₃).

Methyl[1₆]Orthocyclophano-12-crown-6 (10).

Acetoxy-methyl[1₆]Orthocyclophano-12-crown-6 (11). A suspension of the diketone **9a** and **9b** (332 mg, 0.57 mmol) and CAN (5 g) in AcOH (70 mL) was heated

at 80 °C for more than one week, adding more CAN during the reaction. Water (300 mL) was added, and the reaction mixture was extracted several times with CH₂Cl₂. The combined organic layer was washed successively with aqueous NaHCO₃ and water, dried (MgSO₄), and evaporated under reduced pressure. The crude product was chromatographed (SiO₂, benzene : Et₂O, 20 : 1) to give 30 mg (8.2%) of **10** and 10 mg (2.5%) of **11** : **10**; ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.15 (m, 23H, ArH), 2.37 (s, 3H, ArCH₃); EIMS m/z (relative intensity) 638 (22.3, M⁺), 578 (28.3), 386 (33.7), 282 (49.3), 236 (48.1), 148 (100); HRMS calcd for C₄₃H₂₆O₆ 638.1729, found 638.1077. **11**; IR (KBr) 3040, 2944, 1776, 1644, 1456, 1065, 1036, 1004, 988, 912, 748; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.25 (m, 23H, ArH), 5.11 (s, 2H, CH₂O), 2.05 (s, 3H, C=(O)CH₃); EIMS m/z 696 (M⁺).

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- Reduction of 4-methylphthalic anhydride with LAH followed by monobromination of the resulting 1,2-bis(hydroxymethyl)-4-methylbenzene with HBr in benzene gave rise to two isomeric benzyl alcohols, 2-(bromomethyl)-4-methylbenzyl alcohol and 2-(bromomethyl)-5-methylbenzyl alcohol, which were protected with dihydropyran in the presence of catalytic amounts of *p*-TsOH to give **1a** and **1b** (69% overall yield from 1,2-bis(hydroxymethyl)-4-methylbenzene).
- The precursor of the dilithio reagent **7**, bis(2-bromophenyl)methane was prepared by modification of the literature procedures: Lee, W. Y.; Park, C. H.; Kim, Y. D. *J. Org. Chem.* **1992**, *57*, 4074 and references therein.
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Photopolymerization of Methacrylic Acid with Disilanes

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Today photopolymerization technology applicable conveniently is extensively used on a commercial basis in the areas of surface coatings, photoresists, adhesives, and holography. A wide variety of unsaturated vinyl derivatives can be polymerized *via* a free-radical chain process, only a few unsaturated compounds will undergo chain photopolymerization with 250-500 nm wavelength light which is the most convenient wavelength range for experimental work.¹ Although the detailed mechanism forming the propagating radicals is not completely apprehended, it apparently involves the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.² The capability performing a thermodynamically feasible polymerization depends upon its kinetic feasibility on whether the process proceeds at a reasonable rate under a given set of reaction conditions. Hence, an initiator (or promotor) is often needed to attain the kinetic feasibility. In addition, a chain transfer agent is often used in controlling the molecular weights.

Hydrosilanes have participated in versatile catalytic reactions such as free radical reduction of organic halides,³ nucleophilic reduction of carbonyl compounds,⁴ dehydropolymerization,⁵ cross-dehydrocoupling with alcohols and amines,⁶ and hydrosilation of olefins.⁷ The hydrosilation has been also applied for the preparation of many interesting types of silicon containing dendrimers⁸ and copolymers.⁹ We reported the bulk photopolymerization of methyl methacrylate (MMA) with various silanes to produce poly(methyl methacrylates), poly(MMA)s containing the corresponding silyl moiety probably as an end group.¹⁰ We recently described the bulk photopolymerization of methacrylic acid (MA) with primary and secondary silanes.¹¹ In this paper we wish to report the bulk photopolymerization of MA with disilanes such as 2-phenyl-1,3-disilapropane (PhCH(SiH₃)₂) **1** and 1,2-diphenyldisilane (PhSiH₂SiH₂Ph) **2** giving poly(methacrylic acids), poly(MA)s containing the disilyl moiety presumably as an end group.

Experimental Section

Materials and Instrumentation. All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were used throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recor-