

Synthesis of a New Potential Tridentate Anthracene Ligand Bearing Deprotectable Methoxymethoxy (OMOM) Group at 1,8-Positions: Attempt To Synthesize Anionic Hypervalent Carbon Compounds

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Abstract: A novel potential tridentate ligand bearing deprotectable coordinating atoms, 1,8-bis(methoxymethoxy)-9-bromoanthracene (**15**), was synthesized. The key steps are as follows: 1) stepwise mono-oxygenation from 1,8-dibromo-9-methoxyanthracene by use of electrophilic oxaziridine and gaseous dioxygen, and 2) selective reduction of the methoxy group by LDBB (lithium di-*tert*-butylbiphenylide) followed by treatment with BrCF₂CF₂Br. The corresponding 1,8-bis(methoxymethoxy)-9-

lithioanthracene (**14**), which should be a useful versatile trianion equivalent, could be generated by treatment of the bromide with one equivalent of *n*BuLi. The lithioanthracene reacted with hexafluoroacetone to give the deprotected ether **17** together with the adduct alcohol **16**. The ether could easily be depro-

ected to give 1,2-dihydro-1,1-bis(trifluoromethyl)-2-oxa-9-hydroxyanthrylene (**8**), which was deprotonated with KH in the presence of [18]crown-6 to give the corresponding anion (**9-K** ([18]crown-6)). The X-ray structure and NMR spectra of **9-K** ([18]crown-6) showed that it has an unsymmetrical structure probably due to the interaction between the oxygen atom of the phenoxide and the potassium cation surrounded by the crown ether.

Keywords: anthracene • carbon • hypervalent compounds • trianionic tridentate ligands

Introduction

Although various trianionic OCO pincer ligands (Figure 1)^[1–13] have been utilized for synthesis of hypervalent phosphorus, sulfur and iodine compounds, application of these ligands for synthesis of hypervalent second period

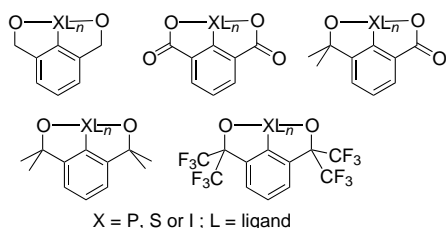


Figure 1. Hypervalent compounds with OCO pincer ligands.

element compounds have never been reported except unsuccessful attempts which were described in a PhD thesis.^[14]

Recently, we reported synthesis of hypervalent pentacoordinated carbon compounds bearing rigid 1,8-dimethoxy-9-anthryl substituent (**1**)^[15] from 1,8-dimethoxy-9-trifluoromethanesulfonyloxyanthracene (**2**) (Figure 2). Although we tried

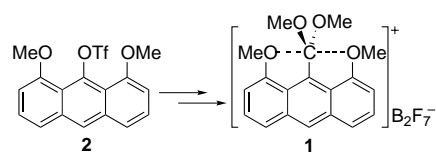


Figure 2. Reported hypervalent pentacoordinated carbon compound **1**.

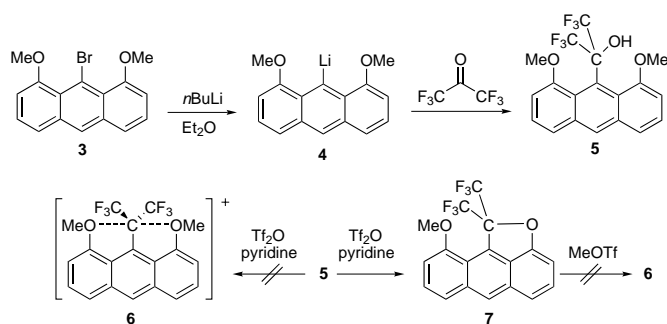
to synthesize hypervalent carbon compounds with stronger apical bonds, no other hypervalent carbon compound could be synthesized from **2**. Therefore, recently reported 1,8-dimethoxy-9-lithioanthracene (**4**)^[16] was used for introduction of strongly electron-withdrawing group in order to strengthen the interaction between the two methoxy groups and the central carbon. The lithium derivative **4**, generated by the reaction of **3** with 1.1 equivalents of *n*BuLi in diethyl ether, reacted with gaseous hexafluoroacetone at $-78\text{ }^\circ\text{C} \rightarrow \text{RT}$ to give alcohol derivative **5** (Scheme 1). However, when **5** was treated with triflic anhydride (Tf₂O) in the presence of pyridine in CH₂Cl₂, unexpected cyclic ether **7** was obtained.

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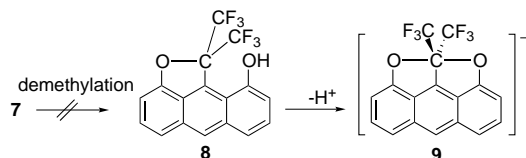
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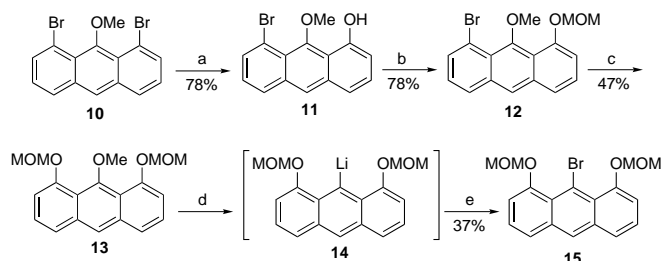


Scheme 1. Attempt to synthesize hypervalent pentacoordinate carbocation **6** bearing two CF₃ groups.

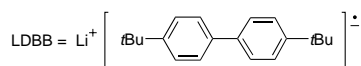
Regeneration of cationic hypervalent carbon compound **6** by the reaction of **7** with Me⁺ (MeOTf, Me₃O⁺BF₄⁻) was unsuccessful (**7** was recovered). Although we tried demethylation of **7** in order to generate anionic hypervalent carbon compound **9**, demethylation was not successful under various reagents and conditions (Scheme 2). Therefore, we designed a novel tridentate anion equivalent **15** bearing two methoxymethyl (MOM) protected oxygen atoms (Scheme 3).



Scheme 2. Attempt to synthesize anionic hypervalent pentacoordinate carbon species from **7**.



- a : 1) *n*BuLi, THF
2)
- b : MOMCl, NaH, THF
c : 1) *n*BuLi, THF
2) O₂
3) MOMCl, pyridine, CH₂Cl₂
- d : LDBB, THF
e : BrCF₂CF₂Br

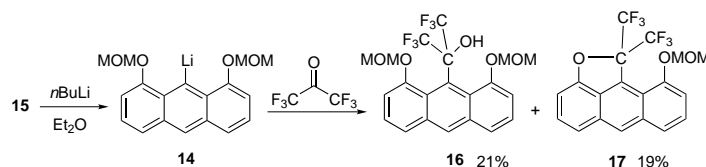


Scheme 3. Synthesis of a new potential tridentate ligand **15**.

Synthesis of **15** is illustrated in Scheme 3. Since bis-oxygenation of dilithiated **10**^[17] by various oxygenation reagent [oxaziridine, O₂, (RO)₃B then H₂O₂] afforded only a complex mixture without detectable amount of expected bis-hydroxylated product, we were forced to carry out stepwise oxygenation. Monolithiated **10**^[17] was treated with oxaziridine reagent (shown in Scheme 3)^[18] to give corresponding phenol derivative **11** in high yield, and the hydroxyl group of **11** was protected by a methoxymethyl (MOM) group to give **12**.

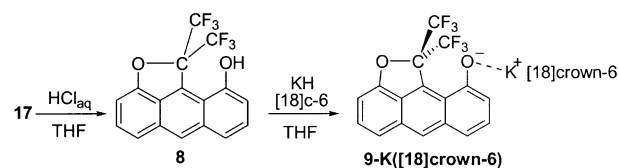
Then, **12** was lithiated with *n*BuLi and treated with gaseous O₂^[19] followed by one-pot reaction with methoxymethyl chloride to give **13**. LDBB (lithium di-*tert*-butylbiphenylide) could reduce the methoxy group from 9-position of **13** selectively, and trapping of the generated lithium derivative **14** with BrCF₂CF₂Br gave a new potential anthracene ligand **15** bearing two deprotectable methoxymethoxy groups in 37% yield. Although **15** was not quite stable to chromatographic treatment (silica gel) or prolonged standing at RT, it could be purified by recycle HPLC (Japan Analytical Industry Co., LC908, 1,2-dichloromethane as an eluent).

After quantitative regeneration of lithium derivative **14** by the reaction of **15** with *n*BuLi in diethyl ether, **14** was treated with gaseous hexafluoroacetone to give alcohol derivative **16** together with cyclized product **17** (Scheme 4).



Scheme 4. Formation of cyclic ether **17** together with adduct **16**.

Cyclic ether **17** was easily deprotected with HCl/THF at RT to give **8** (Scheme 5), which was deprotonated with KH in the presence of [18]crown-6 to generate the desired anion species (**9-K**([18]crown-6)).



Scheme 5. Generation of **9-K**([18]crown-6).

Although ¹H NMR spectrum of **8** showed a symmetrical anthracene pattern (four kinds of peaks: two doublets, a triplet and a singlet) at room temperature in undistilled [D₈]THF solution, it showed an unsymmetrical anthracene pattern (seven kinds of peaks) in distilled (vacuum distilled from potassium) [D₈]THF solution. These results indicate that water-mediated proton transfer reaction is rapid in **8**. ¹H NMR spectrum of **9-K**([18]crown-6) showed a similar unsymmetrical anthracene pattern in distilled [D₈]THF solution although the peaks are shifted to higher fields in comparison with those in **8**. On the other hand, in ¹⁹F and ¹³C NMR spectra of **9-K**([18]crown-6), chemical shifts were shifted to lower fields from **8** [¹⁹F: from δ = -69.6 to -67.7; ¹³C (central carbon): from δ = 95.8 to 96.6], respectively.

Single crystals of **9-K**([18]crown-6), which decomposed slowly under air, suitable for X-ray analysis were obtained from a THF/hexane solution under nitrogen atmosphere at RT. The ORTEP drawing of **9-K**([18]crown-6) is shown in Figure 3. The shorter C–O (O1–C15) bond length is 1.470(5) Å and the longer C–O (O2–C15) length is 2.991(5) Å. Although the former is nearly equal to the sum

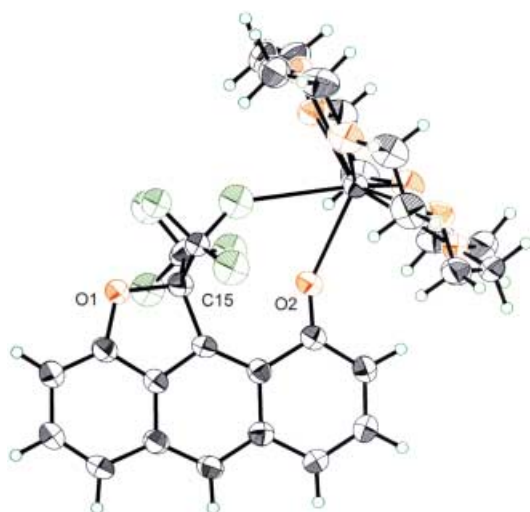


Figure 3. X-ray structure of **9-K**([18]crown-6) (30% thermal ellipsoid). Two of four disordered trifluoromethyl groups were omitted to clarify. Selected bond lengths [Å]: O1–C15 1.470(5), O2–C15 2.991(5), O2–K1 2.570(3).

(1.44 Å)^[20] of covalent radius of carbon and oxygen atom, the latter is shorter than that of the van der Waals radius (3.25 Å).^[20] Apparently, the potassium cation surrounded by crown ether interacted with the phenoxide oxygen atom [O2–K1, 2.570(3) Å] in the solid state. In order to evaluate the TBP character of the central carbon atom, %TBP_c^[21] was calculated to be 27%, showing that **9-K**([18]crown-6) had low TBP character. But the value was similar to pentacoordinated germanium in **18** (Figure 4, 30%)^[22] bearing a weak coordi-

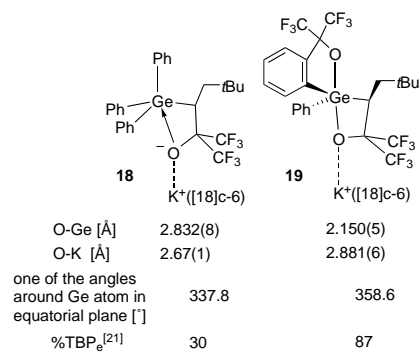


Figure 4. Interaction between an oxygen atom and a potassium cation in hypervalent germanium ate complexes.

nation between the oxygen anion with the central germanium. Therefore, the structure of the carbon atom in **9** should be regarded as normal tetracoordinate carbon or pentacoordinate carbon with very weak coordination. Although bidentate ligands such as Martin ligands with electron-withdrawing groups (Figure 4) could lead to pentacoordinated germanium with high TBP character (% TBP_c^[21] 30% in **18**, 87% in **19**) and could weaken the interaction between the oxygen atom and the potassium cation [2.62(1) in **18**, 2.881(6) Å in **19**],^[22–24] tridentate anthracene ligand and the two electron withdrawing trifluoromethyl groups did not affect the structure of tetracoordinated carbon compounds in **9-K**([18]crown-6).

The difference between the germanium and the carbon is probably due to higher electronegativity of carbon atom, which could not sufficiently delocalize the electron density on the central carbon atom to stabilize the pentacoordinated state. Experimental effort of countercation exchange is under way in order to clarify the fundamental nature of the anionic part of **9**.

Conclusion

Thus, the new potential tridentate ligand, 1,8-dimethoxy-2-methoxy-9-bromoanthracene (**15**), was synthesized by stepwise oxygenation by the use of oxaziridine reagent and gaseous dioxygen. Compound **15** was successfully used as a trianion equivalent (**20** in Figure 5) for the synthesis of **9-K**([18]crown-6), which showed unsymmetrical structure in solution and in the solid state.

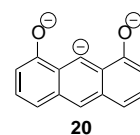


Figure 5. Trianion equivalent.

Experimental Section

General: Diethyl ether and tetrahydrofuran were freshly distilled from sodium/benzophenone and other solvents were distilled from calcium hydride under argon atmosphere. Merck silica gel 9385 was used for column chromatography. LC908-C60 (Japan Analytical Industry) with 40 ϕ column was used for HPLC purification. Melting points were taken on a Yanagimoto micro melting point apparatus. ¹H NMR (400 MHz), ¹³C NMR (99 MHz) and ¹⁹F NMR (372 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Chemical shifts (δ) are reported as parts per million from internal CHCl₃ for ¹H (δ = 7.26) and ¹³C (δ = 77.0) or from external CFCl₃ for ¹⁹F (δ = 0.00). Mass spectrometry was recorded on a JEOL SX-102A spectrometer. Elemental analysis was performed on Perkin–Elmer 2400CHN elemental analyzer.

Materials: Compound **3**,^[16] **10**,^[17] 3-phenyl-1,2-benzisothiazole 1,1-dioxide,^[18] 4,4'-di-*tert*-butylbiphenyl,^[25] were prepared according to literature.

Synthesis of 5: A solution of *n*BuLi in *n*-hexane (3.45 mL, 5.5 mmol) was added dropwise to a solution of **3**^[16] (1.59 g, 5 mmol) in diethyl ether (150 mL) in a three necked flask equipped a three-way cock, rubber septum, and a cooling gas trap at –100 °C. After the solution was stirred for 2 h at –100 °C and allowed to warm to RT, gaseous hexafluoroacetone, which was generated by dehydration of the trihydrate (5 mL, excess) with fuming H₂SO₄ and drying through H₂SO₄, was bubbled through a needle to the solution at RT for 1 h. The reaction mixture was stirred at RT for 2 h. Water (50 mL) was added to the mixture and the mixture was stirred for more 2 h at RT. The mixture was extracted with CH₂Cl₂ and the collected organic layer was dried over Na₂SO₄ to give **5** (ca. 1.3 g, 80%). ¹H NMR (400 MHz, CDCl₃, 25 °C, CHCl₃): δ = 3.97 (s, 6H; OMe), 6.70–6.90 (br m, 2H; CH), 6.80 (s, 1H; OH, disappeared with D₂O treatment), 7.35 (d, ³J(H,H) = 8 Hz, 2H; CH), 7.45–7.60 (br m, 2H; CH), 8.31 (s, 1H; CH); ¹⁹F NMR (372 MHz, CDCl₃, 25 °C, CFCl₃): δ = –72.9 (s, 3F; CF₃), –62.3 (s, 3F; CF₃); elemental analysis calcd (%) for C₁₉H₁₄F₆O₅: C 56.44, H 3.49; found: C 56.34, H 3.58.

Synthesis of 7 directly from 3: A solution of *n*BuLi in *n*-hexane (2.1 mL, 3.3 mmol) was added dropwise to a solution of **3**^[16] (951 mg, 3 mmol) in diethyl ether (250 mL) in a three necked flask equipped with a three-way

cock, rubber septum, and a cooling gas trap at -100°C . After the solution was stirred for 2 h at -100°C and allowed to warm to RT, gaseous hexafluoroacetone, which was generated by dehydration of the trihydrate (5 mL, excess) with fuming H_2SO_4 and drying through H_2SO_4 , was bubbled through a needle to the solution at RT for 1 h. The reaction mixture was stirred at RT for 2 h. Water (50 mL) was added to the mixture and the mixture was stirred for more 2 h at RT. The mixture was extracted with CH_2Cl_2 and the collected organic layer was dried over MgSO_4 to give a crude product. The crude product was purified by column chromatography with two times [CH_2Cl_2 /hexane 1:1 (1st), 3:5 (2nd)] to give **7** as pale yellow-green solid (771 mg, 69%). M.p. $176.1\text{--}177.3^{\circ}\text{C}$ (decomp); ^1H NMR (400 MHz, CDCl_3 , 25°C , CHCl_3): $\delta = 4.01$ (s, 3H; OMe), 6.90 (d, $^3J(\text{H,H}) = 7$ Hz, 1H; CH), 6.92 (d, $^3J(\text{H,H}) = 7$ Hz, 1H; CH), 7.46 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.48 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.53 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.72 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 8.47 (s, 1H; CH); ^{19}F NMR (372 MHz, CDCl_3 , 25°C , CFCl_3): $\delta = -71.2$ (s; CF_3); elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{10}\text{F}_6\text{O}_2$: C 58.08, H 2.71; found: C 57.78, H 2.73.

Dehydroxylation of 5: (CF_3SO_2) $_2\text{O}$ (0.1 mL, 0.6 mmol) was added dropwise at RT under Ar atmosphere to a mixture of **5** (20 mg, 0.05 mmol), CH_2Cl_2 (0.5 mL), and pyridine (0.1 mL, excess). After the mixture was stirred for 5 min, the mixture was poured into water and was extracted with CH_2Cl_2 . Collected organic layer was dried over MgSO_4 to give a crude product. ^1H NMR of the crude product showed 90% conversion from **5** to **7**.

Synthesis of 1-bromo-8-hydroxy-9-methoxyanthracene (11): *n*BuLi (20.5 mL, 32 mmol) was added at -78°C under Ar atmosphere to a solution of (10.98 g, 30 mmol) of 1,8-dibromoanthracene (**10**)^[17] in THF (300 mL). The reaction mixture was stirred for 2.5 h at -78°C and was transferred to the solution of 3-phenyl-1,2-benzisothiazole 1,1-dioxide^[20] (9.08 g, 35 mmol) in THF (100 mL) at -78°C . The reaction mixture was stirred for 10 min and was allowed to warm to RT. The reaction mixture was stirred for 30 min at RT. HCl_{aq} (1N, 200 mL) was poured into the reaction mixture, and the reaction mixture was extracted with CH_2Cl_2 (400 mL, 100 mL, 100 mL). The collected organic layer was dried over MgSO_4 and MgSO_4 was removed by filtration. After addition of silica gel to the filtrate, solvents were removed under reduced pressure to give crude product absorbed on silica gel. The crude product was purified with column chromatography (CH_2Cl_2 /hexane 1:3) to give **11** as yellow solid (7.89 g, 87%). M.p. $157\text{--}159^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 25°C , CHCl_3): $\delta = 3.99$ (s, 3H; OMe), 6.93 (dd, $^3J(\text{H,H}) = 7$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H; CH), 7.22 (dd, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 7$ Hz, 1H; CH), 7.41 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.50 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.80 (dd, 1H, $^3J(\text{H,H}) = 8$, $^4J(\text{H,H}) = 7$ Hz, 7.91 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 8.24 (s, 1H; CH), 9.89 (s, 1H; OH); ^{13}C NMR (99 MHz, CDCl_3 , 25°C , CDCl_3): $\delta = 65.7, 109.1, 114.9, 117.0, 119.0, 120.9, 124.3, 125.4, 127.6, 128.7, 132.9, 133.89, 133.91, 151.1, 153.5$; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{11}\text{BrO}_2$: C 59.43, H 3.66; found: C 59.54, H 3.34.

Synthesis of 1-bromo-8-methoxymethoxy-9-methoxyanthracene (12): THF (150 mL) was added to a mixture of 7.89 g (26 mmol) of **11** and 3.23 g (80 mmol) of NaH (oil dispersion) at 0°C . Chloromethyl methyl ether (4.6 mL, 60 mmol) was added to the reaction mixture at RT, and the reaction mixture was stirred for 1 h at 85°C . After cooling of the reaction mixture to RT, the reaction mixture was filtered through Celite 545, Katayama Chemical Co. Ltd.) pad to the flask including sat NaHCO_3 aq. After washing the Celite with CH_2Cl_2 , the filtrate was extracted with CH_2Cl_2 and collected organic layer was dried over K_2CO_3 . After filtration to remove K_2CO_3 , silica gel was added to the filtrate. Solvents were removed under reduced pressure to give crude product absorbed on silica gel. The crude product was purified with column chromatography (CH_2Cl_2 /hexane 1:1) to give **12** as yellow oil (6.59 g, 73%). ^1H NMR (400 MHz, CDCl_3 , 25°C , CHCl_3): $\delta = 3.65$ (s, 3H; OCH_2OCH_3), 3.95 (s, 3H; OCH_3), 5.42 (s, 2H; OCH_2OCH_3), 7.14 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.16 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.35 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.56 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.79 (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 8.09 (s, 1H; CH); ^{13}C NMR (99 MHz, CDCl_3 , 25°C , CDCl_3): $\delta = 56.7, 64.5, 96.3, 110.5, 116.3, 119.3, 122.5, 122.9, 123.3, 125.5, 126.1, 128.4, 128.7, 132.9, 134.0, 134.6, 153.5$; elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{15}\text{BrO}_3$: C 58.81, H 4.35; found: C 59.21, H 4.41.

Synthesis of 1,8-bis(methoxymethoxy)-9-methoxyanthracene (13):^[19] *n*BuLi (6.9 mL, 17 mmol) was added at -78°C under Ar atmosphere to a solution of **12** (5.39 g, 15.5 mmol) in THF (150 mL). The reaction mixture

was stirred for 1 h at -78°C . O_2 gas was bubbled through Pasteur pipette with thermometer holder for 30 min at -78°C . The reaction mixture was allowed to warm to RT and was stirred for 30 min at RT. Chloromethyl methyl ether (4.6 mL, 60 mmol) and pyridine (6.0 mL, 80 mmol) were added to the reaction mixture at RT, and the reaction mixture was stirred for 1 h at 85°C . The reaction mixture was poured into HCl_{aq} and was extracted with CH_2Cl_2 . Collected organic layer was washed with sat NaHCO_3 (aq) and was dried over MgSO_4 . After filtration to remove MgSO_4 , solvents were removed under reduced pressure to give crude product as brown oil. The crude product was purified with HPLC ($\text{CICH}_2\text{CH}_2\text{Cl}$ eluent, $t_{\text{R}} = 66$ min) to give **13** as yellow oil (2.41 g, 47%). ^1H NMR (400 MHz, CDCl_3 , 25°C , CHCl_3): $\delta = 3.66$ (s, 6H, OCH_2OCH_3), 4.02 (s, 3H; OCH_3), 5.42 (s, 4H; OCH_2OCH_3), 7.09 (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 7.33 (t, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 7.60 (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH) 8.13 (s, 1H; CH); ^{13}C NMR (99 MHz, CDCl_3 , 25°C , CDCl_3): $\delta = 56.7, 63.9, 96.6, 110.3, 119.5, 122.6, 122.7, 125.9, 134.9, 154.0$; HRMS: m/z : calcd for $\text{C}_{19}\text{H}_{20}\text{O}_5$: 328.1310; found: 328.1306.

Synthesis of 1,8-bis(methoxymethoxy)-9-bromoanthracene (15): THF (20 mL) was added to a mixture of Li (68.7 mg, 10 mmol) and 4,4'-di-*tert*-butylbiphenyl^[24] (DTBB, 2.9298 g, 11 mmol) at 0°C under Ar atmosphere. After Li was dissolved, the generated solution of lithium 4,4'-di-*tert*-butyl biphenylide (LDBB) (5.3 mL, 2.7 mmol) was added via syringe to a solution of **13** (220 mg, 0.67 mmol) in THF (10 mL) at -78°C . After the reaction mixture was stirred for 45 min at -78°C , $\text{BrCF}_2\text{CF}_2\text{Br}$ (0.24 mL, 2 mmol) was added to the reaction mixture at -78°C . The reaction mixture was stirred for 1 h at -78°C and for more 30 min at RT. The reaction mixture was diluted with CH_2Cl_2 , and silica gel was added to the mixture. After removing solvents under reduced pressure to give crude product absorbed on silica gel, this crude product charged on the top of column chromatography. First of all, hexane eluted to separate DTBB. Next, the solvents were replaced to a mixture of CH_2Cl_2 and hexane (1:3 \rightarrow 1:1 \rightarrow 1:0) to separate the desired product **15**. Removing the solvents of third yellow fraction gave the yellow solid of **15** (93.3 mg, 37%). ^1H NMR (400 MHz, CDCl_3 , 25°C , CHCl_3): $\delta = 3.55$ (s, 6H; OCH_2OCH_3), 5.30 (s, 4H; OCH_2CH_3), 7.11 (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 7.24 (t, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 7.49 (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH) 8.17 (s, 1H; CH); ^{13}C NMR (99 MHz, CDCl_3 , 25°C , CDCl_3): $\delta = 56.9, 95.9, 111.1, 111.9, 122.5, 126.0, 126.3, 127.3, 134.2, 154.0$; HRMS: m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{BrO}_4$: 376.0310, 378.0290; found: 376.0310, 378.0282.

Synthesis of 1,2-dihydro-1,1-bis(trifluoromethyl)-2-oxa-9-hydroxyanthrylene (8): *n*BuLi (0.32 mL, 0.5 mmol) was added at -100°C under Ar to a solution of **15** in diethyl ether (20 mL). The reaction mixture was stirred for 1 h at -100°C . Gaseous hexafluoroacetone was bubbled via needle for 5 min at -100°C . The reaction mixture was stirred for 14 h at -100°C to RT and quenched with HCl_{aq} . After extraction, drying (MgSO_4) and evaporation, the crude product was purified by preparative TLC (silica gel, Merck 7730; CH_2Cl_2 /hexane 1:1). Compound **18** was obtained as the second fraction (yellow solid, 25.2 mg, 19%, ca. 98% purity). THF (2 mL) and conc. HCl_{aq} (0.5 mL) were continuously added to **18** (25.2 mg, 0.06 mmol) at RT under Ar atmosphere. The reaction mixture was stirred for 19 h at RT and was diluted with HCl_{aq} (1N). After extraction, drying (MgSO_4) and evaporation, the crude product was purified by preparative TLC (made from Merck silica gel 7730; CH_2Cl_2). Compound **8** was obtained as yellow fraction (quant.). M.p. $207\text{--}224^{\circ}\text{C}$ (decomp); ^1H NMR (400 MHz, $[\text{D}_8]\text{THF}$, 25°C , $\text{C}_4\text{HD}_7\text{O}$): $\delta = 6.84$ (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 6.85 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.34 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.39 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.50 (d, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 7.64 (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 8.51 (s, 1H; CH), 9.67 (s, 1H; OH); (400 MHz, undistilled $[\text{D}_8]\text{THF}$, 25°C , $\text{C}_4\text{HD}_7\text{O}$): $\delta = 6.91$ (d, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 7.37 (t, $^3J(\text{H,H}) = 8$ Hz, 2H; CH), 7.60 (t, $^3J(\text{H,H}) = 8$ Hz, 1H; CH), 8.56 (s, 1H; CH); ^{13}C NMR (99 MHz, $[\text{D}_8]\text{THF}$, 25°C , $[\text{D}_8]\text{THF}$): $\delta = 95.8$ (sep; $\text{C}(\text{CF}_3)_2$); ^{19}F NMR (372 MHz, $[\text{D}_8]\text{THF}$, 25°C , CFCl_3): $\delta = -69.6$ (s; CF_3); elemental analysis calcd (%) for $\text{C}_{17}\text{H}_8\text{F}_6\text{O}_2$: C 57.00, H 2.25; found: C 56.88, H 2.11.

Deprotonation of 8 to give 9-K([18]crown-6): All the manipulation of this reaction was carried out in grove box. To THF-washed KH (in oil, 247 mg, 2 mmol), THF (3 mL) solution of **8** (100 mg, 0.28 mmol) and [18]crown-6 (99.3 mg, 0.35 mmol) was slowly added dropwise at RT. The reaction mixture was filtered and solvents were removed under reduced pressure. $[\text{D}_8]\text{THF}$ added to the crude product in order to measure NMR spectra. Single crystals suitable for X-ray analysis were obtained from hexane-

diluted [D₈]THF solution of product. Data for **9-K**([18]crown-6): ¹H NMR (400 MHz, [D₈]THF, 25 °C, C₄HD₇O): δ = 6.29 (d, ³J(H,H) = 8 Hz, 1H; CH), 6.46 (d, ³J(H,H) = 8 Hz, 1H; CH), 6.59 (d, ³J(H,H) = 8 Hz, 1H; CH), 7.11 (t, ³J(H,H) = 8 Hz, 1H; CH), 7.12 (t, ³J(H,H) = 8 Hz, 1H; CH), 7.22 (d, ³J(H,H) = 8 Hz, 1H; CH), 8.02 (s, 1H; CH), (400MHz, undistilled [D₈]THF, 25 °C, C₄HD₇O): δ = 6.34 (d, ³J(H,H) = 8 Hz, 2H; CH), 6.98 (d, ³J(H,H) = 8 Hz, 2H; CH), 7.13 (t, ³J(H,H) = 8 Hz, 2H; CH), 8.11 (s, 1H; CH); ¹³C NMR (99 MHz, [D₈]THF, 25 °C, [D₈]THF): δ = 96.6 (sep, C(CF₃)₂); ¹⁹F NMR (372 MHz, [D₈]THF, 25 °C, CFCl₃): δ = -67.7 (s, CF₃).

X-ray structural analysis of 9-K([18]crown-6): CCDC-183680 [9-K([18]crown-6)] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Data were collected at 150 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about φ. Data were processed by using SCALEPACK. The structure was solved by a direct method (SIR-97^[26]) and refined by full-matrix least-squares (SHELXL-97^[27]). Two trifluoromethyl groups were disordered and their occupancies were refined (0.5:0.5). All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. Crystal data for **9-K**([18]crown-6): orthorhombic system, space group *Pbca* (no. 14), *a* = 13.9100(3), *b* = 19.2280(5), *c* = 23.5150(7) Å, *V* = 6289.4(3) Å³, *Z* = 8, ρ_{calcd} = 1.395 g cm⁻³. *R* = 0.1050 (*Rw* = 0.2823) for 7374 observed reflections (390 parameters) with *I* > 2σ(*I*). Goodness of fit = 1.939. Structure was drawn by Oak Ridge Thermal Ellipsoid Plot program (ORTEP-III^[28]).

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research (Nos. 11166248, 11304044, 12304044) provided by the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government and JSPS Research Fellowships (No. 08982) for Young Scientists.

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Received: August 16, 2002
 Revised: February 22, 2003 [F4354]