Synthesis and chemical properties of polyacetylenic derivatives of benzo- and dibenzo- crown ethers

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Dedicated to Professor Boris A. Trofimov, for his 65th birthday
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Abstract
4’,5’-Diethynylbenzo-15-crown-5- (6), 4’,5’(5’’)-diethnyldibenzo-18-crown-6 (10, 11) and 4’,5’,4’’,5’’-tetraethynyl-dibenzo-18-crown-6 (12) ethers were synthesized by cross-coupling of the corresponding di- and tetra- iodides (1–4) with trimethylsilylacetylene (5a) or 2-methylbut-3-yn-2-ol (5c) followed by treatment of the resulting products with alkali. The Mannich reaction with the di- and tetraethynyl derivatives was also carried out.

Keywords: Benzocrown ethers, alkynes, cross-coupling reaction, polyethynylbenzocrown ethers, aminoalkylation, the retro-Favorsky reaction, the Mannich reaction, homogeneous catalysis

Introduction

The crown ethers are very attractive compounds for analytical and coordination chemistry as well as for pharmaceutical applications because of their ability to bind cations selectively. However, the chemistry of acetylenic derivatives of the crown ethers remains poorly studied owing to the limited synthetic approaches to these compounds. Only a few publications are devoted to the synthesis of acetylenylbenzocrown ethers by cross-coupling of iodoarenes with terminal acetylenes, whereas the preparation of polyethynyl-benzo-crown ethers is not described at all.

Moreover, we have found some important details, both when we tried to obtain even simple monoethynylbenzocrown ethers and when we carried out the Mannich reaction with them. For the above reasons, and the fact that the introduction of several acetylenic groups—especially terminal ones—into the crown ether molecules increases their synthetic and application potential through increasing their reactivity, we undertook investigations to develop methods of synthesis
of poly(ethynyl)benzocrown ethers and to study their behavior in the cross-coupling and Mannich reactions.

**Results and Discussion**

The cross-coupling of aryl halides with terminal acetylenes (the Sonogashira reaction) has become a general method for the preparation of arylalkynes, and we therefore used this approach to obtain the target polyacetylenic compounds.

Since 1975, when Sonogashira et al. discovered the catalytic system (PdCl₂(PPh₃)₂-CuI-Et₂NH) for the cross-coupling of 1-alkynes with sp²-halides, this method is considered the best one for the preparation of various aryl- and hetarylacetylene derivatives. However, the Pd/Cu-catalyzed cross-coupling of 1-alkynes with iodoarenes having electron-donor substituents (NR₂, OR) is accompanied by homocoupling of the alkynes and the reductive de-iodination of iodoarenes. Sometimes such side-reactions become the only ones. The replacement of iodine atoms by acetylenic groups in the weakly reactive polyhalobenzocrown ethers (owing to the deactivating influence of several alkoxy groups possessing +M effects) has not been attempted.

We have investigated the possibility of using the cross-coupling of poly-iodocrown ethers to introduce several acetylenic groups into a crown ether molecule. The starting diiodobenzocrown ethers 1–3 were synthesized by direct oxidative iodination of the corresponding ethers in an I₂–HIO₃–H₂SO₄ system at 50–55 °C (yield 50–80%) (Scheme 1). Under the above conditions, for dibenzo-18-crown-6 (2 mol of iodination mixture / mol of starting compound) a mixture of cis-(2) and trans- (3) isomers was obtained in a total yield of 83%. Tetraiododibenzocrown ether 4 (60%) was obtained from dibenzo-18-crown-6 and I₂, NaIO₄, and H₂SO₄ in dioxane under reflux.
Scheme 1. i. I₂-HIO₃-H₂SO₄, acetic acid; ii. I₂-HIO₃-H₂SO₄, dioxane.

The synthesis of individual cis- (2) and trans- (3) isomers was realized from the corresponding dinitrodibenzo-18-crown ethers (2a, 3a) (Scheme 2). Nitration of dibenzo-18-crown ether by nitric acid mixed with acetic acid in chloroform resulted in a mixture of cis- and trans- dinitrodibenzo-18-crown ethers, which were separated by recrystallization from DMF. Reduction of the nitro derivatives by hydrazine hydrate in the presence of 4% Pd/C in boiling ethanol led to the cis-amino- (2b, 63%), and trans-amino- crown ether (3b, 87%). Denitration of the isomers (2b) and (3b) was carried out in diluted H₂SO₄ followed by KI addition in the presence of freshly prepared Cu(0), as described for p-iodo-phenols. The cis-iodocrown ether (2) and trans- isomer (3) were formed in 32% and 42% yields, respectively.

We used trimethylsilylacetylene (5a), p-ethynylbenzaldehyde (5b) and 2-methylbut-3-yn-2-ol (5c) as acetylenic components in the cross-coupling of polyiodocrown ethers (1–4). A special interest in acetylenylbenzocrown ethers bearing formyl groups was caused by the possibility of their forming stable nitronyl-nitroxide radicals, since they are precursors of 2-imidazoline. We have previously shown that acetylenic derivatives of heterarylnitronyl-nitroxides possess very interesting optical and magnetic properties. 2-Methylbut-3-yn-2-ol (5c) and trimethylsilylacetylene (5a) allowed the synthesis of terminal acetylenes, which are very promising key compounds, owing to their unusually high CH-acidity that could possibly be used both for functionalizing and building C–C bonds.

Usually, condensation of aryl iodides with 1-alkynes has been carried out in the presence of PdCl₂(PPh₃)₂, CuI, and Et₂NH at 70–75 °C under argon. These reaction conditions proved to be inefficient in cross-coupling of iodides with p-ethynylbenzaldehyde (5b). In our reaction, a finely dispersed black precipitate, apparently of metallic palladium, was obtained, formed as a result of complex decomposition. Previously, the attempt to conduct the cross-coupling of isomeric...
bromobenzaldehydes with trimethylsilylacetylene in the presence of catalytic amounts of Pd(OAc)$_2$ and PPh$_3$ was reported: however, iodide 1 did not react with alkyne 5b under these conditions. It is known$^3$ that activation of the alkynyl component with the addition of Cul (for aryl halides with terminal acetylenes) leads to a considerable increase in cross-coupling. We have found that the reaction of 1 with 5b in the system involving Pd(OAc)$_2$, PPh$_3$, and NEt$_3$ in the presence of Cul afforded the ether 6b in 75% yield. The diethynyl derivative 6 was prepared from compound 6a by removing the trimethylsilyl group.

Scheme 3. i. PdCl$_2$(PPh$_3$)$_2$, Cul, NEt$_3$. ii. Pd(OAc)$_2$, Cul, NEt$_3$, 65–70 °C. iii. KOH (K$_2$CO$_3$), methanol, 20 °C. iv. KOH, benzene, 80 °C, or KOH, toluene, 110 °C.

For the synthesis of poly(formylacetylenyl) crown ethers 6b, (7+8)b, 9b we proposed a scheme involving cross-coupling of the corresponding diodo derivatives (1, 2+3, 4) with p-ethynyl-benzaldehyde (5b) (route A) or cross-coupling of ethynylbenzocrown ethers (6, 10+11) with p-bromobenzaldehyde 13 (route B) in the presence of Pd(OAc)$_2$, PPh$_3$, Cul and NEt$_3$ in
C₆H₆ at 40–80 °C. The yields of the target compounds (7+8)b, 6b, were 50–70%. One should note that the reaction duration and the yields of the products were almost identical in both routes.

Scheme 4. i. Pd(OAc)₂, CuI, NEt₃, 65-70 °C.

The interaction of dihalobenzocrown ethers (1, 2+3) with 2-methylbut-3-yne-2-ol (5c) in the presence of PdCl₂(PPh₃)₂ (or Pd(OAc)₂ + PPh₃), CuI and NEt₃ led to acetylenic alcohols (6c) and (7+8)c in 60–90% yields. Since cross-coupling of the tetra-iodide 4 with butynol (5c) under these conditions was accompanied by their resification we used trimethylsilylacetylene (5a) as acetylenic component for introduction of four ethynyl groups into benzo-crown ring. The yield of tetrakis-acetylenic derivative 9a was 30%.

The replacement of the iodine atom in (1, 2+3) by the acetylenic moiety of the tertiary acetylenic alcohol 5c proceeded smoothly at 75–80 °C in the catalytic system PdCl₂(PPh₃)₂-CuI-Et₃N; the yield of (6c) and (7+8)c was 60–90%. A mixture of diiodocrown ether, terminal acetylene, PdCl₂(PPh₃)₂, CuI, in triethylamine was heated for 2–5 h at 75–80 °C under argon.

A usual way for ethynyl-arene preparations involved the cleavage of the tertiary acetylenic alcohols or the trimethylsilylacetylene derivatives by treatment with a catalytic amount of alkali. But earlier⁴ we discovered a specific cleavage “crown-effect” for mono-acetylenic alcohols of benzo-15-crown-5 ether and benzo-18-crown-6 ether that required an extra equimolar amount of KOH, over that used with the corresponding benzo-12-crown-4-ether derivative. Our investigation confirmed the reverse-Favorsky reaction for diacetylenic alcohols (6c) and (7+8)c that could be realized only in the presence of the extra equimolar amount of KOH. Ethynyl crown ethers (6, 10+11) were obtained by Retro-Favorsky reaction. A mixture of tertiary acetylenic alcohols (6c) and (7+8)c and powdered KOH was heated at reflux in dry toluene during 2–4 h, the yields of ethynyl crown ethers (6, 10+11) were 25–30%. Ethynylbenzocrown ethers could also be obtained in another way. For example, the reaction of iodobenzocrown ethers 1–4 with trimethylsilylacetylene 5a led to disubstituted acetylenes (6–9)a in 70–90% yields. Treatment of (6–9)a with KOH or K₂CO₃ in methanol at room temperature resulted in 6, 10–12 in 50–60% yields.

The ethynylbenzocrown ethers did not undergo a Mannich reaction that was carried in the presence¹⁵ of copper(I) salts. It is known¹ that the crown ethers are able to form complexes not only with appropriately sized cations (K⁺-crown-6), but also with the large ones in a “sandwich” type complex. We found⁴ unusual behavior of ethynylcrown ethers in these conditions.¹⁵
Taking into account the high biological activity of compounds having a propargylamino fragment (N-CH₂-C≡C), we carried out the aminoalkylation reaction on the obtained alkynes (6, 10+11).

![Scheme 5](image)

**Scheme 5.** i. (CH₂O)x, amine (14a-c), Cu(OAc)₂, 30% H₂SO₄, dioxane, 80 °C.

The typical procedure for aminoalkylation of ethynylarenes involved interaction of secondary amines with paraformaldehyde under reflux in dioxane in the presence of CuCl. To avoid the problems we found earlier for mono-ethynylcrown ethers for the Mannich condensation, the aminoalkylation was carried out in the presence of Cu(OAc)₂ and 30% sulfuric acid.

Aminopropargylcrown ethers 15a–c, (16+17)a–c were obtained by the condensation of alkynes (6, 10+11) with paraformaldehyde and secondary amines 14a–c in the presence of catalytic amounts of Cu(OAc)₂ under reflux in dioxane (1.5–2 h). Yields of the Mannich bases were 70–80% and depended on the reaction conditions and the nature of the starting amines.

The IR and NMR spectra of 2 and 3; 7a and 8a; 10 and 11 had barely perceptible differences. From reference data for nitro-₈,¹⁰,₁⁶,₁₇ and amino derivatives¹⁰,¹⁸ [2a, 203–205°C (200–201°C), ¹⁰ 3a, 243–247°C (247–252°C), ₁⁶ 2b, 179–181°C (180–182°C), 3b, 194–197°C (199–203°C) ¹⁸] we supposed the compounds with lower melting points to be the *trans*-isomers (iodo- and ethynyl derivatives), and *vice versa* for the trimethylsilyl derivatives (Table).

**Conclusions**

In summary, we have established that Pd–Cu- catalyzed cross-coupling of polyiodobenzo- and dibenzo- crown ethers with terminal acetylenes is a convenient method for the introduction of several acetylenic groups into one molecule of the crown ether. The ease of both the introduction and elimination of the protective silyl and alcohol groups makes this procedure attractive for
preparing polyfunctional synthons, such as polyethynylbenzocrown ethers. A series of the Mannich bases has been synthesized by aminoalkylation of ethynyl derivatives.

**Experimental Section**

**General Procedures.** Melting points were determined with a hot-stage microscope. Column chromatography was performed on silica gel (Merck 60, 70–230 mesh). The RF values were measured on aluminum-backed TLC plates of silica gel Silufol UV-254, with the indicated eluent. NMR spectra were recorded on a “Bruker Avance 300” spectrometer at 25 °C. 1H NMR chemical shifts (δ in ppm) were given from internal CHCl3 (7.26) or DMSO-d6 (2.5) standards. Coupling constants (J in Hz) were accurate to ± 0.2 Hz for 1H. Mass spectra (HRMS) at 70 eV using the electron impact mode were recorded on a Finnigan SSQ−710. The IR spectra were recorded in KBr pellets on a “Bruker IFS 66” instrument.

- p-Bromobenzaldehyde, 19 and p-ethynylbenzaldehyde 20 were synthesized according to known procedures. Pd(PPh3)2Cl2, Pd(OAc)2, NaNO2, NaIO4, KI, I2, CuI, PPh3, 2-methylbut-3-yn-2-ol, and ethynyltrimethylsilane (“Aldrich”) were commercially available reactants. All the organic solvents were of analytical quality. See Table on page 231.

**3,4-Diiodobenzo-15-crown-5 (1).** A mixture of iodine (2.0 g, 8.2 mmol) and HIO3 (1.5 g, 8.5 mmol) was slowly added by portions to a stirred solution of benzo-15-crown-5 (2.7 g, 10.1 mmol) in a mixture of 80% acetic acid (40 mL) and 30% sulfuric acid (5 mL). The reaction mixture was stirred to its discoloration during 2 h at 50–55 °C, and then cold water (300 mL) was added. The solution was washed with 30% Na2SO3 aq. and extracted with CHCl3 (3x100 mL), the organic layer was dried over Na2SO4, filtered through a SiO2 bed (height/diameter of the column: 2.5x2 cm). The solvent was removed in vacuo and the residue recrystallized from a mixture of benzene-hexane. The yield of 1 was 3.9 g (75%), mp 97–99 °C. 1H NMR data: δ (CDCl3) 3.67–3.75 (8 Н, m, 2 СН2ОCH2), 3.76–3.85 (4 Н, m, 2 Ar OCH2CH2), 4.10–4.20 (4 Н, m, 2 ArOCH2CH2), 6.91 (2H, s, 2-H, 5-Н). Anal. Calcd. for C14H18I2O5 (520.10): С, 32.33; H, 3.49; I, 48.80. Found: С, 32.52; H, 3.27%.

**3,3′(4′)-Diiododibenzo-18-crown-6 (2+3).** A mixture of iodine (2.1 g, 8.4 mmol) and HIO3 (1.5 g, 8.5 mmol) was slowly added in portions to a stirred solution of dibenzo-18-crown-6 (4.2 g, 10 mmol) in a mixture of 80% acetic acid (40 mL) and 30% sulfuric acid (5 mL). The reaction mixture was stirred to its discoloration during 2 h at 50–55 °C, and then cold water (300 mL) was added. The solution was washed with 30% Na2SO3 aq. and extracted with CHCl3 (3x100 mL), and the organic layer dried on Na2SO4, filtered through a SiO2 bed (2.5x2 cm). The solvent was removed in vacuo and the residue was recrystallized from toluene. The yield of mixture of cis- and trans- isomers (2+3) was 5.6 g (83%), mp 176–180 °C; 1H NMR: δ (CDCl3) 3.94–4.07 (8H, m, 2 CH2OCH2), 4.09–4.22 (8H, m, 4 ArOCH2), 6.62 (2H, d, 4-H, 12(15)-H), 2J =
8.1 Hz), 7.13 (2H, c, 1-H, 15(12)-H), 7.21 (2H, d, 3-H, 13(14)-H, J = 8.1 Hz). Anal. Calcd. for C\textsubscript{20}H\textsubscript{22}I\textsubscript{4}O\textsubscript{6} (612.19): C, 39.24; H, 3.62; I, 41.46. Found: C, 39.72; H, 3.39%.

3,4,3',4'-Tetraiododibenzo-18-crown-6 (4). A mixture of iodine (4.3 g, 16.9 mmol) and H\textsubscript{2}O\textsubscript{2} (2.1 g, 11.9 mmol) was slowly added by portions to stirred solution of dibenzo-18-crown-6 (4.2 g, 10 mmol) in a mixture of dioxane (40 mL) and 30% sulfuric acid (10 mL). The reaction mixture was stirred to its discoloration during 2 h at 50–55 °C, and then cold water (300 mL) was added. The resulting brown precipitate was filtered, washed with water (20 mL), dried in air, and recrystallized from DMF. The yield of the compound 4 was 2.9 g (63%); mp 237–239 °C. 1H NMR data: δ (CD\textsubscript{3})\textsubscript{2}SO 3.78–3.85 (8H, m, 2 CH\textsubscript{2}OCH\textsubscript{2}); 3.98–4.05 (8H, m, 4 ArOCH\textsubscript{2}); 7.31 (4H, s, 2-H, 5-H, 2'-H, 15-H). Anal. Calcd. for C\textsubscript{20}H\textsubscript{20}I\textsubscript{4}O\textsubscript{6} (863.9): C, 27.80; H, 2.33; I, 58.75. Found: C, 27.62; H, 2.29%.

3,3'-Diiododibenzo-18-crown-6 (2). Amine 2b (1.6 g, 4.1 mmol) in a mixture of water (10 mL), ice (10 g) and H\textsubscript{2}SO\textsubscript{4} (2 mL) was denitrated by a cold solution of NaNO\textsubscript{2} (0.7 g, 10.1 mmol in 5 mL H\textsubscript{2}O) at 0 +5 °C. Sulfuric acid (5mL) was added after 20 min and the solution obtained was slowly added to a cold solution of aqueous KI (2.0 g, 12 mmol in 5 mL) containing Cu\textsuperscript{6} (0.5 g, 7.8 mmol), and the reaction mass carefully heated on a hot-water bath (65–70 °C) until nitrogen gas liberation stopped. The solution was extracted with CHCl\textsubscript{3} (3x100 mL), washed with water, and then 30% Na\textsubscript{2}SO\textsubscript{3} aq., and the organic layer dried over Na\textsubscript{2}SO\textsubscript{4}, and filtered through a SiO\textsubscript{2}-bed (2.5x2 cm). The solvent was removed in vacuo and the residue was recrystallized from benzene. The yield of compound 2 was 0.8 g (32%), mp 231–232 °C. Anal. Calcd. for C\textsubscript{20}H\textsubscript{22}I\textsubscript{4}O\textsubscript{6} (612.19): C, 39.24; H, 3.62; I, 41.46. Found: C, 39.37; H, 3.69%. The NMR \textsuperscript{1}H and IR spectra are given in the Table.

3,4'-Diiododibenzo-18-crown-6 (3). According to the procedure above, the denitration of amine 3b (1.2 g, 3.9 mmol) was carried out by using NaNO\textsubscript{2} (0.6 g, 8.7 mmol), KI (1.6 g, 9.6 mmol) and Cu\textsuperscript{6} (0.5 g, 7.8 mmol); the purification by column chromatography resulted in 0.8 g (42%) of compound 3, mp 189–191 °C (from benzene–hexane). Anal. Calcd. for C\textsubscript{20}H\textsubscript{22}I\textsubscript{4}O\textsubscript{6} (612.19): C, 39.24; H, 3.62; I, 41.46. Found: C, 39.37; H, 3.69; I, 41.73%. The \textsuperscript{1}H- NMR and IR spectra are given in the Table.

3,4'-bis-(Trimethylsilanylenethylenyl)benzo-15-crown-5 (6a). A mixture of iodide (1) (0.5, 1 mmol) and the acetylene 5a (0.4 mL, 2.8 mmol) in the presence of PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (15 mg, 0.021 mmol) and CuI (7.5 mg, 0.075 mmol) in Et\textsubscript{3}N (1 mL) and benzene (10 mL) was stirred at 75–80 °C for 0.5 h. Finally, the mixture was filtered through a SiO\textsubscript{2} column (2.5x2 cm) and evaporated in vacuo, and the residue was recrystallized from a mixture of benzene–hexane. The yield of compound 6a was 0.36 g (87.7%), mp 97–99 °C. IR (KBr): ν [cm\textsuperscript{-1}] 2152 (C≡C). 1H NMR data: δ (CDCl\textsubscript{3}) 0.26 (18 H, s, 2 Si(CH\textsubscript{3})\textsubscript{3}); 3.83 (8 H, s, 4 OCH\textsubscript{2}); 3.86–3.93 (4 H, m, 2 ArOCH\textsubscript{2}CH\textsubscript{2}); 4.08–4.17 (4 H, s, 2 ArOCH\textsubscript{2}CH\textsubscript{2}); 6.91 (2 H, s, 2-H, 5-H). MS, m/z, %: 460.0 [M]+ (100), 372.0 (9), 328.0 (18), 312.9 (38), 73.0 (54). Calcd. for C\textsubscript{24}H\textsubscript{36}O\textsubscript{5}Si\textsubscript{2} M = 460.2161. Found: m/z 460.2100 [M]+.

3,3'-bis-(Trimethylsilylethylenyl)dibenzo-18-crown-6 (7+8)a. From the mixture of iodides (2+3) (2.5 g, 4.2 mmol) and the acetylene 5a (1.3 mL, 9.3 mmol) in the presence of PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}
(90 mg, 0.129 mmol), Cul (45 mg, 0.45 mmol), a mixture of the compounds (7+8)a, 1.6 g (69.6%), m.p. 181–184.5 °C was synthesized as above. IR (KBr): ν [cm⁻¹] 2143 (C≡C). 1H NMR: δ (CDCl₃) 0.28 (18 H, s, 2 Si(CH₃)₃), 4.03–4.05 (8 H, m, 2 CH₂OCH₂); 4.17–4.19 (8 H, m, 4 ArOCH₂); 6.78 (2 H, d, 5-H, 5’(2’)-H, J = 8.2), 6.98 (2 H, d, 2-H, 2’(5’)-H, J = 2.5), 7.08 (2 H, dd, 4-H, 4’(3’)-H, 1°J = 8.2, 2°J = 2.5). Anal. Calcd. for C₃₀H₄₀O₆Si₂ (552.81): C, 65.18; H, 7.29. Found: C, 65.21; H, 7.09%.

3,3’-bis-(Trimethylsilylethynyl)dibeno-18-crown-6 (7a). A mixture of iodide (2) (0.63 g, 1 mmol), acetylene 5a (0.4 mL, 3.1 mmol) in the presence of PdCl₂(PPh₃)₂ (30 mg, 0.043 mmol) and Cul (15 mg, 0.15 mmol) in Et₃N (2 mL) and benzene (10 mL) was stirred at 75–80 °C for 0.25 h. Finally, the mixture was filtered through a SiO₂ column (2.5x2 cm) and evaporated in vacuo, and the residue was recrystallized from a mixture of benzene–hexane. The yield of compound 7a was 0.2 g (40%), mp 176–178 °C. Anal. Calcd. for C₃₀H₄₀O₆Si₂ (552.81): C, 65.18; H, 7.29. Found: C, 65.31; H, 7.63%. The ¹H-NMR and IR spectra are given in the Table.

3,4’-bis-(Trimethylsilylethynyl)dibeno-18-crown-6 (8a). A mixture of iodide (3) (0.65 g, 1 mmol) and the acetylene 5a (0.4 mL, 3.1 mmol) in the presence of PdCl₂(PPh₃)₂ (30 mg, 0.043 mmol) and Cul (15 mg, 0.15 mmol) in Et₃N (2 mL) and benzene (10 mL) was stirred at 75–80 °C for 0.25 h. Finally, the mixture was filtered through a SiO₂ column (2.5x2 cm) and evaporated in vacuo, and the residue was recrystallized from a mixture of benzene–hexane. The yield of compound 8a was 0.24 g (41%), mp 191–193 °C. Anal. Calcd. for C₃₀H₄₀O₆Si₂ (552.81): C, 65.18; H, 7.29. Found: C, 64.91; H, 7.55%. The ¹H-NMR and IR spectra are given in the Table.

3,4,3’,4’-tetrakis-(Trimethylsilylethynyl)dibeno-18-crown-6 (9a). A mixture of the iodide (4) (0.5 g, 0.5 mmol) and the acetylene 5a (0.4 mL, 3.1 mmol) in the presence of PdCl₂(PPh₃)₂ (30 mg, 0.043 mmol) and Cul (15 mg, 0.15 mmol) in Et₃N (2 mL) and benzene (10 mL) was stirred at 75–80 °C for 0.25 h. Finally, the mixture was filtered through a SiO₂ column (2.5x2 cm) and evaporated under reduced pressure. The residue was recrystallized from benzene–hexane mixture. The yield of compound 9a was 0.13 g (40.2%), mp 98–100 °C. IR (KBr): ν [cm⁻¹] 2154 (C≡C). 1H NMR data: δ (CDCl₃) 0.31 (36 H, s, 4 Si(CH₃)₃), 4.01–4.03 (8 H, m, 2 CH₂OCH₂); 4.17–4.18 (8 H, m, 4 ArOCH₂); 6.91 (4-H, s, 2-H, 5-H, 5’-H, 2’-H). Anal. Calcd. for C₄₀H₅₆O₆Si₄ (745.21): C, 64.47; H, 7.57. Found: C, 64.11; H, 7.29%.

3,4-bis-(p-Ethynylbenzaldehyde)benzo-15-crown-5 (6b). Route A (Scheme 3). A mixture of iodide (1) (0.9 g, 1.7 mmol), acetylene 5b (0.4 g, 3.1 mmol) in the presence of Pd(OAc)₂ (20 mg, 0.089 mmol) and Cul (15 mg, 0.15 mmol), PPh₃ (60 mg, 0.228 mmol) in Et₃N (7 mL) and benzene (15 mL) was stirred at 75–80 °C for 0.25 h. Finally, the mixture was filtered through a SiO₂ column (2.5x2 cm) and evaporated in vacuo, and the residue was purified by column chromatography and then recrystallized from benzene–hexane mixture. The yield of compound 6b was 0.69 g (76.7%).

Route B (Scheme 4). A mixture of the acetylene (6) (0.1 g, 0.3 mmol), 4-bromobenzaldehyde 13 (0.14 g, 0.7 mmol) in presence of Pd(OAc)₂ (10 mg, 0.044 mmol) and Cul (5 mg, 0.026 mmol), PPh₃ (30 mg, 0.114 mmol) in Et₃N (2 mL) and benzene (10 mL) was stirred at 75–80 °C for 0.25
h. Finally, the mixture was filtered through a SiO$_2$ column (2.5x2 cm) and evaporated in vacuo, and the residue was purified by column chromatography and then recrystallized from benzene. The yield of compound 6b was 0.08 g (62.5%); mp 156–157 °C. IR (KBr): ν [cm$^{-1}$] 1697 (C=O), 2204 (C≡N). 1H- NMR data: δ (CDCl$_3$) 3.69 (8 H, s, 4 OCH$_2$); 3.86–3.95 (4 H, m, 2 ArOCH$_2$CH$_2$); 4.15–4.22 (4 H, m, 2 ArOCH$_2$CH$_2$); 7.08 (2 H, s, 2-H, 5-H), 7.69 (4 H, d, 2,2’-H, 2,6’-H, J = 8.2), 7.89 (4 H, d, 2,3’-H, 2,5’-H, J = 8.2), 10.05 (2 H, s, CHO). Anal. Calcd. for C$_{32}$H$_{28}$O$_2$ (524.56): C, 73.27; H, 5.38. Found: C, 73.14; H, 5.45%.

3,3’(4’)-bis-(p-Ethynylbenzaldehyde)dibenzo-18-crown-6 (7+8)b. Route A (Scheme 3). The compounds mixture (7+8)b, 0.79 g (52.3%) was prepared from a mixture of the compounds (2+3) (1.5 g, 2.4 mmol), p-ethynylbenzaldehyde 5b (0.78 g, 5.9 mmol) in the presence of Pd(OAc)$_2$ (20 mg, 0.089 mmol), CuI (10 mg, 0.0520 mmol), PPh$_3$ (60 mg, 0.228 mmol) in NEt$_3$ (10 mL) and benzene (15 mL).

Route B (Scheme 4). The mixture of (7+8)b 0.9 g (52.9%), mp 147–154 (toluene) was prepared from a mixture of the compounds (10+11) (1.1 g, 2.7 mmol), p-bromobenzaldehyde 13 (1.2 g, 6.7 mmol) in the presence of Pd(OAc)$_2$ (20 mg, 0.089 mmol), CuI (10 mg, 0.052 mmol), PPh$_3$ (60 mg, 0.228 mmol) in NEt$_3$ (10 mL) and benzene (15 mL). IR (KBr): ν [cm$^{-1}$] 1653 (C=O), 2201 (C≡N). 1H NMR data: δ (CDCl$_3$) 3.91–3.94 (8 H, s, 4 OCH$_2$); 4.16–4.19 (8 H, s, 2 ArOCH$_2$); 7.02 (2 H, d, 5-H, 5(2’)-H, J = 8.4); 7.23 (2 H, s, 2-H, 2’(5’)-H; 7.27 (2 H, d, 4-H, 4’(3’)-H, J = 8.4); 7.65 (4 H, d, 2’(2’)-H, 2,6’-H, J = 8.2); 7.87 (4 H, d, 2,3’-H, 2,5’-H, J = 8.2); 10.04 (2 H, s, CHO). Anal. Calcd. for C$_{38}$H$_{32}$O$_8$ (616.66): C, 74.01; H, 5.23. Found: C, 74.21; H, 5.28%.

3,4,3’,4’-tetraakis(p-Ethynylbenzaldehyde)-18-crown-6 (9b). Route A (Scheme 3). The compound (9b) (0.9 g, 89.1%), mp 223–225 (toluene) was prepared from the compound (4) (1 g, 1.3 mmol), p-ethynylbenzaldehyde 5b (0.9 g, 0.7 mmol) in the presence of Pd(OAc)$_2$ (20 mg, 0.089 mmol), CuI (10 mg, 0.0520 mmol), PPh$_3$ (60 mg, 0.228 mmol) in NEt$_3$ (10 mL) and benzene (15 mL). IR (KBr): ν [cm$^{-1}$] 1698 (C=O), 2203 (C≡N). 1H NMR data: δ (CDCl$_3$) 3.86–3.95 (4 H, s, 4 OCH$_2$); 3.89–4.20 (4 H, m, 2 ArOCH$_2$); 4.15–4.18 (8 H, m, 4 ArOCH$_2$); 7.68 (8 H, d, 4,2’-H, 6’-H, J = 8.2); 7.88 (8 H, d, 4,3’-H, 5’-H, J = 8.2); 10.04 (4 H, s, 4 CHO). Anal. Calcd. for C$_{52}$H$_{40}$O$_{10}$ (872.91): C, 77.05; H, 4.62. Found: C, 77.21; H, 5.28%.

3,4-bis-(3-Hydroxy-3-methylbut-1-ynyl)benzo-15-crown-5 (6c). A mixture of iodide 1 (0.5, 1 mmol), and the acetylene 5c (0.23 mL, 2.5 mmol) in the presence of PdCl$_2$(PPh$_3$)$_2$ (15 mg, 0.021 mmol) and CuI (7.5 mg, 0.075 mmol) in Et$_3$N (1 mL) and benzene (15 mL) was stirred at 75–80 °C for 2.5–3 h. Finally, the mixture was filtered through a SiO$_2$ bed in a column (2.5x2 cm) and evaporated in vacuo, and the residue was recrystallized from benzene. The yield of compound 6c was 0.2 g (48.8%), mp 103–105 °C. IR (KBr): ν [cm$^{-1}$] 2200 (C≡C); 3222 (br., OH). 1H NMR data: δ (CD$_2$)$_2$SO) 1.18 (12 H, s, 2 C(CH$_3$)$_2$); 3.76–3.81 (8 H, m, 4 OCH$_2$); 3.89–3.95 (4 H, m, 2 ArOCH$_2$CH$_2$); 4.10–4.20 (4 H, m, 2 ArOCH$_2$CH$_2$); 6.89 (2 H, s, 1-H, 4-H). Anal. Calcd. for C$_{24}$H$_{32}$O$_7$ (432,51):C, 66.65; H, 7.46. Found: C, 66.52; H, 7.39%.

3,3’(4’)-bis-(3-Hydroxy-3-methylbut-1-ynyl)dibenzo-18-crown-6 (7+8)c. A mixture of iodides (2+3) (1g, 1.5 mmol), and carbinol 5c (0.3 mL, 3.3 mmol) in the presence of
PdCl₂(PPh₃)₂ (30 mg, 0.043 mmol) and Cul (15 mg, 0.15 mmol) in Et₃N (2 mL) and benzene (10 mL) was stirred at 75–80 °C for 2.5–3 h. Finally, the mixture was filtered through a SiO₂ column (2.5x2 cm) and evaporated in vacuo, and the residue was recrystallized from mixture of benzene-hexane. The yield of the mixed compounds (7+8)c was 0.75 g (86.2%), mp 87–91 °C. IR (KBr): ν [cm⁻¹] 2223 (C≡C); 3374 (br., OH). 1H NMR data: δ (CDCl₃) 1.57 (2 H, s, 2 C(CH₂)₂); 3.98–4.05 (8 H, m, 4 OCH₂); 4.17–4.18 (4 H, m, 2 ArOCH₂CH₂); 6.79 (2 H, d, 5-H, 5’(2’)-H, J = 8.2); 6.93 (2 H, s, 2-H, 2′(5’)-H); 7.02 (2 H, d, 4-H, 4′(3’)-H, J = 8.2). Anal. Calcd. for C₃₀H₃₆O₈ (524.60): C, 68.68; H, 6.92. Found: C, 68.6166.52; H, 7.09%.

3,4-Diethynylbenzo-15-crown-5 (6). Procedure iii (Scheme 3). The compound 6a (0.24 g, 0.5 mmol) was treated with a 10% solution of KOH in methanol (15 mL). The yield of the compound 6 was 0.1 g (60%), mp 109–110 °C. Procedure iv (Scheme 3). A mixture of 6c (0.2 g, 0.48 mmol) and powdered KOH (0.1 g, 1.7 mmol) (20 mL) was boiled in dry benzene for 2.5–3 h. Finally, the mixture was filtered through a SiO₂ column (2.5x2 cm) and evaporated in vacuo. The residue was recrystallized from benzene–hexane mixture. The yield of compound 6 was 0.03 g (20%).

IR (KBr): ν [cm⁻¹] 2120 (C≡C); 3219, 3277 (C≡CH). 1H NMR: δ (CDCl₃) 3.26 (2 H, s, 2 C≡CH); 3.69–3.82 (8 H, m, 4 OCH₂); 6.97 (2 H, s, 2-H, 5-H). MS, m/z, %: 316.20 [M⁺] (21), 228.2 (11), 184.1 (90), 128.1 (12), 45.1 (10). Calcd. for C₁₈H₂₀O₅: M = 316.13292. Found: m/z 316.0234 [M⁺].

3,3′(4’)-Diethynyldibenzo-18-crown-6 (10+11) Procedure iii (Scheme 3). The compounds (7+8)a (0.3 g, 5.4 mmol) were treated with a 10% solution of KOH in methanol (15 mL) at room temperature during 1–1.5 h. The yield of the compounds 10+11 was 0.06 g (27.3%); mp 141–145 °C. Procedure iv (Scheme 3). A mixture of (7+8)c (1.6 g, 3 mmol) and powdered KOH (0.4 g, 8 mmole) was boiled in dry toluene (45mL) for 2.5–33 h. Finally, the mixture was filtered through an SiO₂ column (2.5x2 cm) and evaporated in vacuo. The residue was purified by column chromatography and recrystallized from benzene–hexane mixture. The yield of compounds (10+11) was 0.2 g (16.7%).

IR (KBr): ν [cm⁻¹] 2101 (C≡C); 3288 (C≡CH). 1H NMR: δ (CDCl₃) 3.02 (2 H, s, 2 C≡CH), 4.06–4.17 (8 H, m, 2 CH₂OCH₂); 4.18–4.21 (8 H, m, 4 ArOCH₂CH₂); 6.81 (2 H, d, 5-H, 5′(2’)-H, J = 8.5); 7.01 (2 H, d, 2-H, 2′(5′)-H, J = 2.3); 7.11 (2 H, dd, 4-H, 4′(3’)-H, ¹J = 8.5, ²J = 2.3). Anal. Calcd. for C₂₄H₂₄O₆ (408.44):C, 70.57, 5.93. Found: C, 70.81.11; H, 5.87%.

3,3′-Di-ethynyldibenzo-18-crown-6 (10). Procedure iii (Scheme 3). The compound 7a (0.2 g, 0.36 mmol) was treated with K₂CO₃ (0.15 g, 1 mmol) solution in methanol (7 mL) at room temperature for 1–1.5 h. The yield of the compound 10 was 0.1 g (68%); mp 192–194 °C. Anal. Calcd. for C₂₄H₂₄O₆ (408.44):C, 70.57, 5.93. Found: C, 70.24; H, 5.86%. The ¹H NMR and IR spectra are given in the Table.

3,4′-Diethynyldibenzo-18-crown-6 (11). Procedure ii (Scheme 3). The compound 8a (0.2 g, 0.36 mmol) was treated with K₂CO₃ (0.15 g, 1 mmol) solution in methanol (7 mL) at room temperature for 1–1.5 h. The yield of compound 10 was 0.1 g (68%); mp 171–173 °C. Anal.
Calcd. for C_{24}H_{24}O_{6} (408.44): C, 70.57, 5.93. Found: C, 70.33; H, 5.69%. The $^1$H- NMR and IR spectra are given in the Table.

**3,4,3',4'-Tetakis(ethynyl)dibenzo-18-crown-6 (12).** Procedure iii (Scheme 3). The compound 9a (0.15 g, 0.2 mmol) was treated with K_{2}CO_{3} (0.15 g, 1 mmol) solution in methanol (7 mL) at room temperature for 1–1.5 h. The yield of compound 12 was 0.05 g (55%); mp 115–117 °C. IR (KBr): ν [cm$^{-1}$] 2141 (C=C); 3278 (C=CH). 1H NMR data: δ (CDCl$_3$) 3.2 (4 H, s, 4 C≡CH), 4.01–4.03 (8 H, m, 2 CH$_2$OCH$_2$); 4.17–4.18 (8 H, m, 4 ArOCH$_2$); 6.95 (4 H, s, 2-H, 5-H, 5’-H, 2’-H). Anal. Calcd. for C$_{28}$H$_{26}$O$_{5}$ (456.49): C, 73.67, H, 5.30. Found: C, 73.80; H, 5.47%.

**3,4-bis-(3-Diethylaminoprop-1-ynyl)benzo-15-crown-5 (15a).** A mixture of the acetylene (6) (0.08 g, 0.25 mmol), (CHO)$_3$ (0.02 g, 0.5 mmol) and diethylamine 14a (0.06 mL, 0.5 mmol) in the presence of Cu(OAc)$_2$ (50 mg), and 30% H$_2$SO$_4$ (0.1 mL) was stirred in an atmosphere of argon under refluxing in dioxane (10 mL) at 75–80 °C for 0.25 h. Finally, the mixture was diluted with water (40 mL) and extracted with CHCl$_3$ (3x15 mL). The organic layer was washed with a 15% solution of NH$_4$OH, dried under MgSO$_4$, and filtered through a SiO$_2$ column (2.5x2 cm) and evaporated in vacuo. The residue was purified by column chromatography then recrystallized from benzene–hexane mixture. The yield of the compound 15a was 0.08 g (80%); mp 56–58 °C. IR (KBr): ν [cm$^{-1}$] 2237 (C≡C). 1H NMR data: δ (CDCl$_3$) 1.25 (12 H, t, 4 CH$_2$CH$_3$, J = 6.9); 2.17 (8 H, q, 4 CH$_2$CH$_3$, J = 6.9); 3.75 (4 H, s, 2 C≡CCH$_2$N); 3.94 – 3.89 (8 H, m, 4 OCH$_2$); 4.01 – 4.06 (4 H, m, 2 ArOCH$_2$CH$_2$); 4.14 (4 H, s, 2 ArOCH$_2$CH$_2$); 6.59 (2 H, s, 1-H, 4-H). Anal. Calcd. for C$_{28}$H$_{42}$N$_2$O$_5$ (486.64): C, 69.10; H, 7.46; N, 5.76. Found: C, 69.58; H, 7.37; N, 5.62%.

**3,4-bis-(3-Morpholinoprop-1-ynyl)benzo-15-crown-5 (15b).** The compound 15b 0.07 g (58.3%), mp 93–95 °C (from hexane) was prepared from compound 6 (0.08 g, 0.25 mmol), paraformaldehyde (0.02 g, 0.5 mmol), the morpholine 14b (0.05 mL, 0.5 mmol), Cu(OAc)$_2$ (50 mg), 30% H$_2$SO$_4$ (0.1 mL) in boiling dioxane (10 mL), as above. IR (KBr): ν [cm$^{-1}$] 2226 (C≡C). 1H NMR data: δ (CDCl$_3$) 2.53–2.55 (4 H, m, N(CH$_2$CH$_2$)$_2$O); 3.16 (4 H, s, 2 C≡CCH$_2$N); 3.59–3.62 (16 H, m, 4 OCH$_2$, 2 N(CH$_2$CH$_2$)$_2$O); 3.65–3.77 (4 H, m, 2 ArOCH$_2$CH$_2$); 4.04 (4 H, s, 2 ArOCH$_2$CH$_2$); 6.83 (2 H, s, 2-H, 5-H). Anal. Calcd. for C$_{28}$H$_{38}$N$_2$O$_7$ (514.61): C, 65.35; H, 7.44; N, 5.44. Found: C, 65.78; H, 7.37; N, 5.42%.

**3,4-bis-(3-Piperidinoprop-1-ynyl)benzo-15-crown-5 (15c).** The compound 15c, 0.06 g (50%), mp 103–105 °C (from hexane) was prepared from compound 6 (0.08 g, 0.25 mmol), paraformaldehyde (0.02 g, 0.5 mmol), piperidine 14c (0.05 mL, 0.5 mmol), Cu(OAc)$_2$ (50 mg), 30% H$_2$SO$_4$ (0.1 mL) in boiling dioxane (10 mL). IR (KBr): ν [cm$^{-1}$] 2220 (C≡C). 1H NMR data: δ (CDCl$_3$) 1.41–1.46 (2 H, m, (CH$_2$)$_2$CH$_2$(CH$_2$)$_2$); 1.64 (4 H, p, 2 NCH$_2$CH$_2$CH$_2$, J = 6.9); 2.55 (4 H, t, 2 NCH$_2$, J = 6.9); 3.44 (2 H, s, C≡CCH$_2$N); 3.69–3.82 (8 H, m, 4 OCH$_2$); 3.85–3.97 (4 H, m, 2 ArOCH$_2$CH$_2$); 4.14 (4 H, s, 2 ArOCH$_2$CH$_2$); 6.97 (2 H, 2-H, 5-H). Anal. Calcd. for C$_{30}$H$_{32}$N$_2$O$_7$ (510.66): C, 70.56; H, 8.29; N, 5.49. Found: 70.72; H, 8.09; N, 5.61%.

**3,4-bis-(3-Diethylaminoprop-1-ynyl)dibenzo-18-crown-6 (16+17)a.** A mixture of the compounds (16+17)a, 0.08 g (61.5%), mp 145–149 °C (from benzene–hexane) was obtained from mixture of the compounds 10+11 (0.1 g, 0.2 mmol), paraformaldehyde (0.02 g, 0.5 mmol),
diethylamine 14a (0.05 mL, 0.5 mmol), Cu(OAc)\textsubscript{2} (50 mg), 30% H\textsubscript{2}SO\textsubscript{4} (0.1 mL) in boiling dioxane (10 mL). IR (KBr): ν [cm\textsuperscript{-1}] 2143 (C≡C). 1H NMR data: δ (CDCl\textsubscript{3}) 1.15 (12 H, t, 4 CH\textsubscript{2}CH\textsubscript{2}, J = 6.8); 2.65 (8 H, q, 4 CH\textsubscript{2}CH\textsubscript{3}, J = 6.8); 3.65 (4 H, s, 2 C≡CCH\textsubscript{2}N); 4.05–4.06 (8 H, m, 2 CH\textsubscript{2}OCH\textsubscript{2}); 4.17–4.19 (8 H, m, 4 ArOCH\textsubscript{2}); 6.80 (2 H, d, 5-H, 2'(5')-H, J = 8.4). 6.95 (2 H, d, 2-H, 5'(2')-H, J = 2.6), 7.08 (2 H, dd, 4-H, 4'(3')-H, \textsuperscript{1}J = 8.4, \textsuperscript{2}J = 2.6). Anal. Calcd. for C\textsubscript{34}H\textsubscript{46}N\textsubscript{2}O\textsubscript{6} (578.74): C, 70.56; H, 8.01; N, 4.84. Found: C, 70.21; H, 8.09; N, 4.53%.

3,3'(4')-bis-(3-Morpholinoprop-1-ynyl)dibenzo-18-crown-6 (16+17)b. The compounds (16+17)b, 0.06 g (42.9%), mp 128–132 °C (from benzene) were prepared from the mixture of compound 10+11 (0.1 g, 0.2 mmol), paraformaldehyde (0.02 g, 0.5 mmol), morpholine 14b (0.05 mL, 0.5 mmol), Cu(OAc)\textsubscript{2} (50 mg), 30% H\textsubscript{2}SO\textsubscript{4} (0.1 mL) in boiling dioxane (10 mL). IR (KBr): ν [cm\textsuperscript{-1}] 2155 (C≡C). 1H NMR data: δ (CDCl\textsubscript{3}) 2.68–2.59 (4 H, m, N(CH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}O); 3.05 (4 H, s, 2 C≡CCH\textsubscript{2}N); 4.05–4.06 (16 H, m, 2 CH\textsubscript{2}OCH\textsubscript{2}, 2 O(CH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}N); 4.17–4.19 (8 H, m, 4 ArOCH\textsubscript{2}); 6.88 (2 H, d, 5-H, 5'(2')-H, J = 8.4), 7.10 (2 H, d, 2-H, 2'(5')-H, J = 2.6), 7.08 (2 H, dd, 4-H, 4'(3')-H, J = 8.4, 2.6). Anal. Calcd. for C\textsubscript{34}H\textsubscript{42}N\textsubscript{2}O\textsubscript{8} (606.71): C, 66.42; H, 6.98; N, 4.62. Found: C, 66.21; H, 6.09; N, 4.53%.

3,3'(4')-bis-(3-Piperidinoprop-1-ynyl)dibenzo-18-crown-6 (16+17)c. A mixture of the compounds (16+17)c, 0.07 g (50%), mp 126–130 °C (from benzene–hexane) was prepared from a mixture of the compounds 10+11 (0.1 g, 0.2 mmol), paraformaldehyde (0.02 g, 0.5 mmol), piperidine 14c (0.05 mL, 0.5 mmol), Cu(OAc)\textsubscript{2} (50 mg), 30% H\textsubscript{2}SO\textsubscript{4} (0.1 mL) in boiling dioxane (10 mL). IR (KBr): ν [cm\textsuperscript{-1}] 2210 (C≡C). 1H NMR data: δ (CDCl\textsubscript{3}) 1.42–1.56 (2 H, m, (CH\textsubscript{2})\textsubscript{2}CH\textsubscript{2}(CH\textsubscript{2})); 1.68 (4 H, p, 2 CH\textsubscript{2}CH\textsubscript{2}(CH\textsubscript{2})); 2.59 (4 H, t, 2 NCH\textsubscript{2}, J = 6.9); 3.49 (4 H, s, 2 C≡CCH\textsubscript{2}N); 4.05–4.06 (8 H, m, 2 CH\textsubscript{2}OCH\textsubscript{2}); 4.17–4.18 (8 H, m, 4 ArOCH\textsubscript{2}); 6.79 (2 H, d, 5-H, 5'(2')-H, J = 8.4), 6.96 (2 H, d, 2-H, 2'(5')-H, J = 2.6), 7.05 (2 H, dd, 4-H, 4'(3')-H, \textsuperscript{1}J = 8.4, \textsuperscript{2}J = 2.6). Anal. Calcd. for C\textsubscript{36}H\textsubscript{46}N\textsubscript{2}O\textsubscript{8} (602.76): C, 71.73; H, 7.69; N, 4.65. Found: C, 71.42; H, 7.87; N, 4.43%.

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