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Synthesis and characterization of a novel chiral chromogenic calix[4](azoxa)crown-7

Abdulkadir Sirit, Aysegul Karakucuk, Shahabuddin Memon, Erdal Kocabas and Mustafa Yilmaz*

Department of Chemistry, Selçuk University, 42031 Konya, Turkey

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Abstract—Two new chromogenic compounds, **5** and **6**, and a novel chiral chromogenic calix[4](azoxa)crown-7 **8** have been synthesized using a calix[4]arene platform. The starting reagents chiral diamine **e** and calix[4]arene diacid chloride derivative **7** were prepared conveniently according to recent approaches. The ^{1}H and ^{13}C NMR, data showed that these compounds exist in a cone conformation. Compounds **5** and **8** have shown broad absorption bands in UV–vis spectra suggesting their utility in different fields, for example, as sensors for ions as well as for chiral molecules.

1. Introduction

Chiral recognition is one of the most important and fascinating areas in host–guest chemistry or supramolecular chemistry.[1–3] The chiral nature of drug molecules is essentially required after the synthesis because the physiological effect of the enantiomers may significantly differ;[4] in this context, a tragic lesson is thalidomide,[5] where one enantiomer acts as a sedative, whereas the other leads to serious fetal abnormalities. Therefore, determination of the enantiometric purity has become one of the most important stages in the pharmaceutical industry. Several methods have already been developed for enantiometric purity determination by using the specific rotation,[6] circular dichroism,[7] capillary electrophoresis,[8] and separation techniques, including liquid and gas chromatography.[9] Other techniques such as polarimetry, absorbance spectrometry,[10] infrared transmission spectrometry,[11] X-ray anomalous scattering,[12] and NMR spectrometry[13] have also been used.

An alternative approach using the preparation and properties of chiral macrocyclic sensor molecules, having an ability for visual discrimination between the enantiomers of chiral guest species, have attracted considerable attention from a wide range of chemists especially in the fields of organic, biological, and medicinal chemistry. The design of such molecules constitutes as a timely and challenging research topic, and has lead to the synthesis of several chromogenic host molecules.[14] Among them, calixarenes with well-defined cavities, have been regarded as basic skeletons for the synthesis of host molecules similar to cyclodextrins.[15–20] The chiral calixarenes are of pivotal importance if enantioselective recognition or discrimination is to be exploited.[21] Chirality in calixarenes can be generated by either attaching chiral substituents at one of the rims (lower or upper) or synthesizing 'inherently' chiral derivatives, in which the nonplanarity of the molecule is exploited. The inherent chirality suffers severe limitations, due to the difficulties met in the resolution of racemates. Therefore, the former approach appears to be preferable when chiral derivatizing agents with high enantiometric excess are available.[22]

Herein we report the synthesis of a novel calix[4]arene derivative bearing a chiral (azoxa)crown-7 moiety at the lower rim and chromogenic nitro groups at the upper rim. This approach could provide an efficient methodology for developing improved optical sensors for biological and/or chemically important cations and amines.

* Corresponding author. E-mail: myilmaz@selcuk.edu.tr

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2. Results and discussion

2.1. Synthesis of intermediates b, d, and e

Calix[4]azacrowns containing a calix[4]arene element and an azacrown unit in their framework, have received much attention because of their special structures and good complexing properties toward metal cations.[23] Chiral calix(aza)crowns comprising of a calixarene and a chiral polyamine derived from an amino acid, could have chiral recognition abilities and could also serve as good anion receptors[24] by cooperation effects. However, adopting recent approaches made by different research groups,[21,25] we have developed a convergent synthetic pathway toward a novel chiral chromogenic macrocycle. A multistep route, as shown in Schemes 1–3, was chosen for the synthesis of this new type of chiral calix[4](azoxa)-crown-7 **8**.

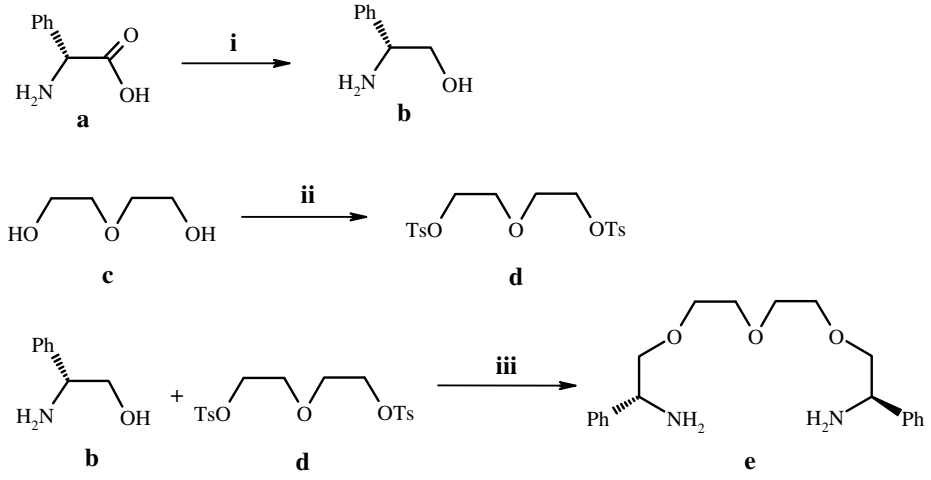
Thus, following the standard procedures,[25] one of the starting materials, chiral diamine **e**, can be prepared in a three-step synthesis (Scheme 1) starting from enantiomerically pure D-phenylglycine **a**, which has been firstly converted by reduction with $NaBH_4$–H_2SO_4 into the corresponding D-phenylglycinol **b**. Since the tosylate group behaves as a good leaving group in S_N reactions, therefore in the second step diethyleneglycol **c** was therefore treated with *p*-toluenesulfonylchloride to afford diethyleneglycol-*p*-ditosylate **d**. Finally, the condensation of **b** and **d** gives chiral diamine **e** in a quantitative yield.

2.2. Synthesis of 5–8

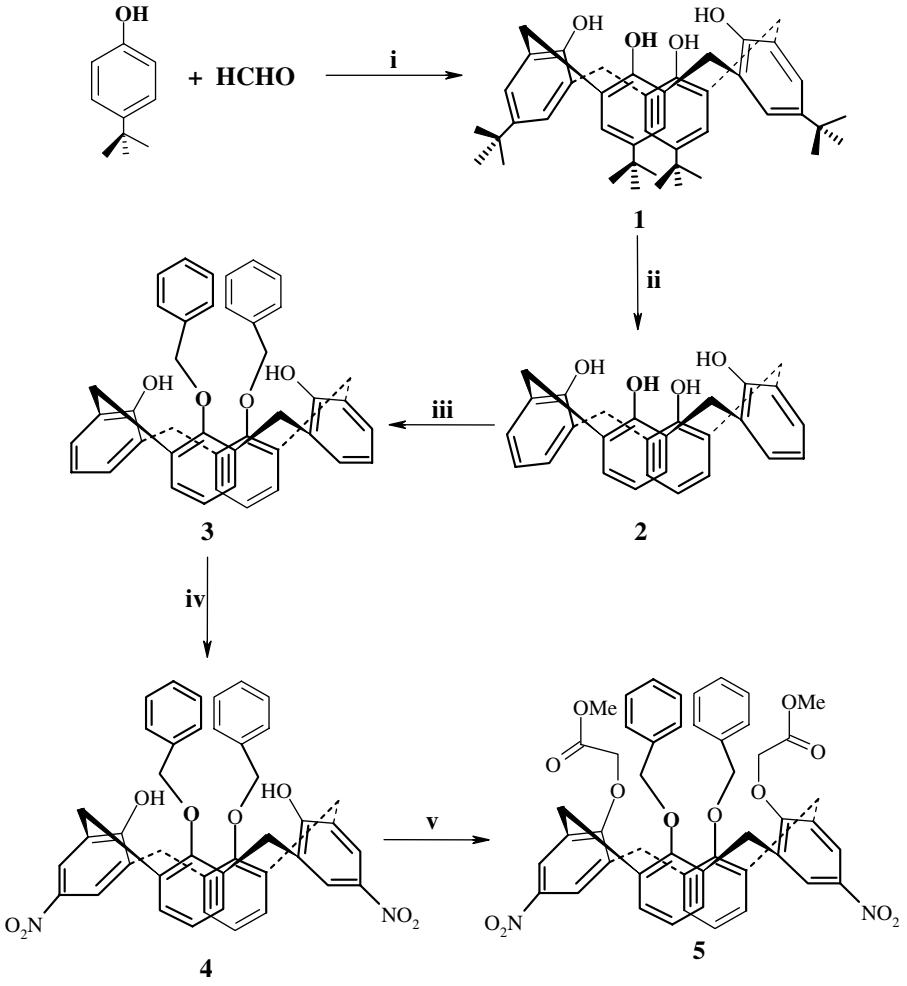
Chromogenic calix[4]arene **4** was obtained (Scheme 2) using previously described procedures.[26] *p-tert*-Butylcalix[4]arene **1**, easily accessible via base-induced condensation of *p-tert*-butylphenol and formaldehyde, provides a basic skeleton for the preparation of calixarene-based precursors caring a wide variety of groups on the upper and lower rims.[15–20]

Aluminum chloride catalyzed removal of the *p-tert*-butyl groups of **1** proceeded in excellent yield to give calix[4]arene **2**, which thereby disubstituted on the lower rim with benzyl bromide and K_2CO_3 followed by selective nitration of the upper rim to yield **4**.[26] Compound **4** was treated then with methyl bromoacetate in the presence of NaH in THF for the introduction of ester groups onto the lower rim at the 1,3-positions. After purification by column chromatography, compound **5** was obtained in 71% yield (Scheme 2). Employing the general protocol **5** was hydrolyzed with 15% aqueous NaOH in ethanol to produce diacid derivative **6** in 85% yield. The synthetic usefulness of the acid chloride is well known and it has been demonstrated that it can be bridged across the lower rim. Thus, the other reagent diacid chloride derivative **7** was prepared by the reaction of compound **6** with thionyl chloride, which is employed directly in the subsequent reaction without further purification. The desired product chiral chromogenic calix[4](azoxa)crown-7 **8**, as illustrated in Scheme 3 was synthesized under high dilution conditions from **7** and chiral diamine **e** in THF in the presence of pyridine to bind the hydrogen chloride formed in situ to inhibit the side reactions. This is a straightforward method and gives us a moderate yield (46%).

All new compounds were characterized by a combination of IR, ^1H NMR, ^{13}C NMR, FAB MS, and elemental analysis. The conformational characteristics of calixarenes were conveniently estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^1H and ^{13}C NMR spectroscopy.[15] ^1H and ^{13}C NMR data showed that these compounds **5**, **6**, and **8** have a cone conformation, the bridged methylene protons appeared in two sets of doublets covering a range of δ 3.40 and 4.28 ppm in the ^1H NMR (J 12.8–13.6 Hz), and two signals covering a range of δ 31.3 and 31.8 ppm in the ^{13}C NMR. Compound **8** is asymmetric due to the formation of a chiral sub-ring onto the lower rim of calix[4]arene. The splitting pattern for other protons (see Section 4) as well may reflect



Scheme 1. Synthesis of **b**, **d**, and **e**. Reagents and conditions: (i) $NaBH_4$, H_2SO_4, THF, rt, 12 h; (ii) *p*-TsCl, NaOH, THF, 0 °C, 2 h; (iii) NaH, THF, rt, 72 h.



Scheme 2. Synthesis of **1**–**5**. Reagents and conditions: (i) NaOH, diphenyl ether, reflux, 3 h; (ii) $AlCl_3$, phenol, toluene, rt, 1 h; (iii) benzylbromide, K_2CO_3, NaI; acetone, rt, 6 h; (iv) HNO_3 (70%), glacial AcOH, 0 °C, 2 h; (v) methyl bromoacetate, NaH, THF, reflux, 24 h.

the presence of a chiral moiety in the molecule because it is similar to what was observed in other chiral calix[4]arenes.[21] Moreover, compound **8** gave satisfactory elemental analysis and MS spectra which indicated that it was '1 + 1' cyclization product.

Figures 1 and 2 show UV–vis spectra of **5** and **8** in chloroform. Examination of the spectra showed broad absorption bands at 267 and 318 nm suggesting that compound **5** could be used in the recognition studies of cations, while compound **8** could be used as sensor for anions and chiral molecules.

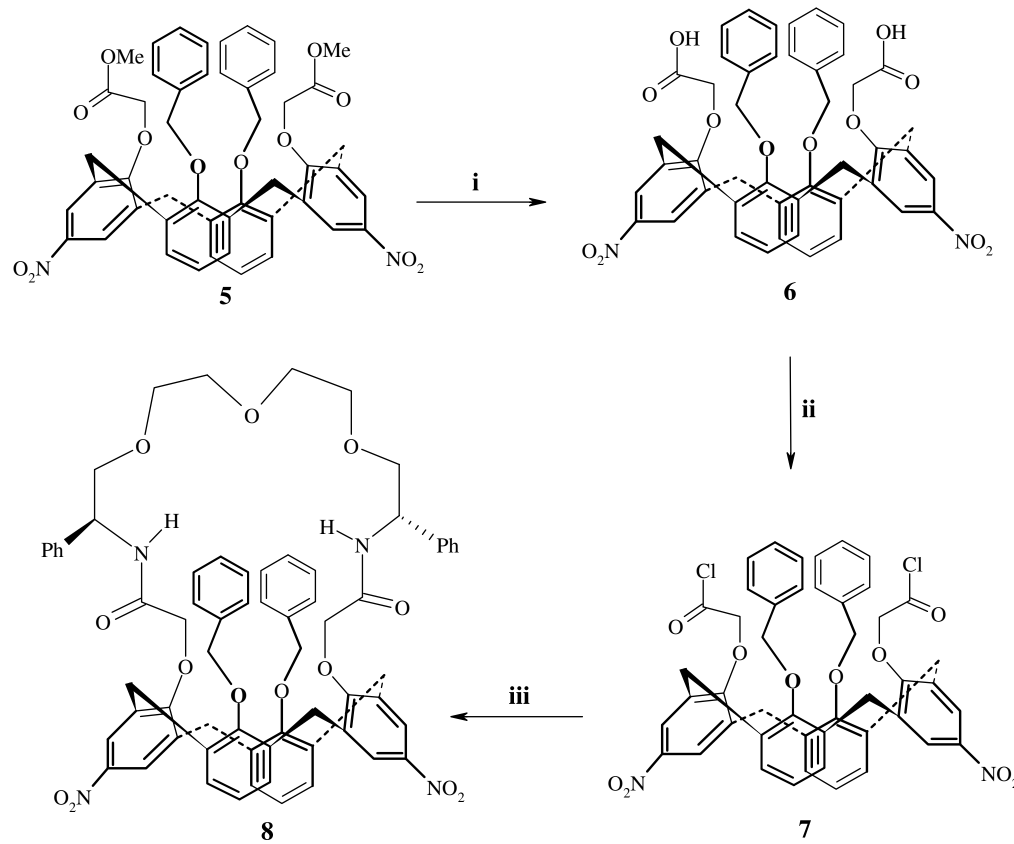
3. Conclusions

In conclusion, we have designed and synthesized two new chromogenic compounds **5** and **6** and a novel chiral chromogenic calix[4](azoxa)crown-7 **8** for applications in ionic as well as chiral recognition sensors. All compounds have been characterized by IR, ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis. The ^{1}H and ^{13}C NMR, data showed that these compounds exist in a cone conformation. Compounds **5** and **8** showed different absorption bands in the UV–vis spectra. Further investigations on their ionic and chiral recognition properties are currently in progress.

4. Experimental

Melting points were determined on a Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Varian 500 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were obtained on a Perkin–Elmer 1605 FTIR spectrometer as KBr pellets. Optical rotations were measured on A-Krüss Optronic polarimeter. UV–vis spectra were obtained on a Shimadzu 160 A UV–vis recording spectrophotometer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. Elemental analysis data were performed on a Leco CHNS-932 analyzer.

All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Aldrich, and used without further purification. Commercial grade solvents, such as chloroform, methanol, acetone,



Scheme 3. Synthesis of **6** and **8**. Reagents and conditions: (i) aqueous NaOH (15%), EtOH, reflux, 24h; (ii) $SOCl_2$, THF, reflux, 4h; (iii) chiral diamine **e**, pyridine, THF, rt, 2days.

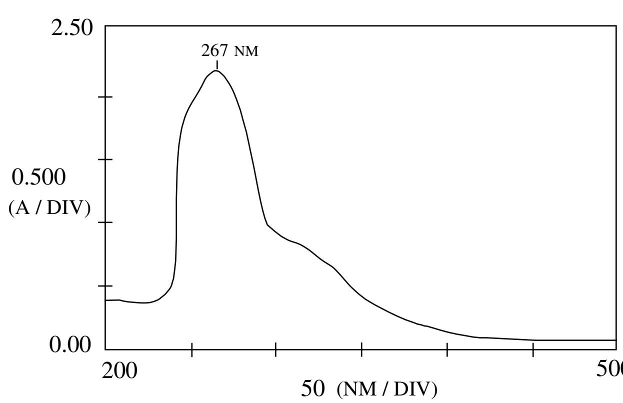


Figure 1. The UV–vis spectrum of compound **5**.

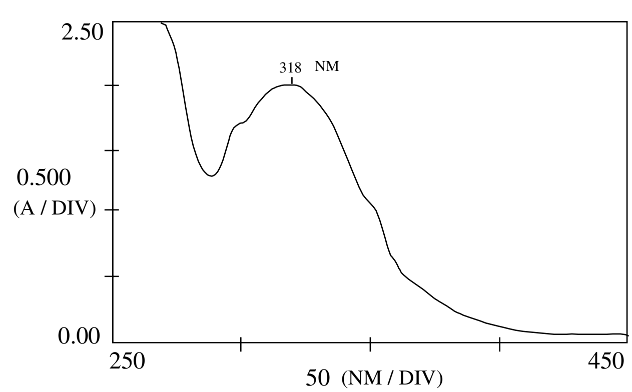


Figure 2. The UV–vis spectrum of compound **8**.

ethyl acetate and hexane, were distilled and then stored over 4Å molecular sieves. Toluene was dried with calcium hydride and stored over Na wire. THF was dried with sodium/benzophenone. The drying agent employed was anhydrous $MgSO_4$. Thin layer chromatography (TLC) was performed using aluminum sheet Merck 60 F_{254} silica gel plates. Column chromatography separations were performed on Merck Silica Gel 60 (230–400mesh).

Compounds **b**, **d**, **e**, and **1**–**4** were synthesized as described in the literature.[25,26] Compounds **5**–**8** were synthesized as follows.

4.1. Synthesis of 5,17-dinitro-25,27-bis(benzyloxy)-26,28-diacetonoyloxy calix[4]arene 5

To a suspension of NaH (90.24g, 6mmol) in dry THF was added compound **4** (1.4g, 2mmol) under a nitrogen atmosphere, and stirred for half an hour at rt. Methyl bromoacetate (0.73g, 4.8mmol) was added dropwise into the mixture by syringe and refluxed for 24h. The reaction was carried out by the addition of water (2mL). The solvent was evaporated under reduced pressure and the residue dried in vacuo. The crude product was purified by column chromatography (EtOAc/hexane) to give light yellow product **5** in 71% yield (1.2g).

Mp 108–109 °C. IR (KBr, cm^{-1}): 1758 (CO); ^1H NMR ($CDCl_3$): δ 8.01 (s, 4H, Ar*H*), 7.61–7.58 (m, 4H, Ar*H*), 7.42–7.36 (m, 6H, Ar*H*), 6.98 (d, 4H, Ar*H*), 6.84 (t, 2H, Ar*H*), 5.05 (s, 4H, CH_2CO_2Me), 4.75 (s, 4H, $ArCH_2O$), 4.27 (d, 4H, $ArCH_2Ar$), 3.88 (s, 6H, OCH_3), 3.46 (d, 4H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$): δ 169.4, 169.1 (*C*O), 151.9, 151.8, 149.8, 148.6, 147.7, 146.6, 145.6, 142.9, 141.3, 139.2, 133.7, 132.6, 131.9, 130.6, 129.7, 129.1, 128.9, 128.6, 127.7, 127.1, 126.5, 125.3 (Ar), 76.8, 75.1 (OCH_2), 65.4, 64.6 (OCH_2Ar), 31.7, 31.3 ($ArCH_2Ar$), 23.9, 23.8 (OCH_3); FAB-MS *m*/*z*: (861.8) $[M+Na]^+$ (calcd 861.8). Anal. Calcd for $C_{48}H_{42}N_2O_{12}$ (838.85): C, 68.72; H, 5.04; N, 3.34. Found: C, 68.84; H, 5.15; N, 3.42.

4.2. Synthesis of 5,17-dinitro-25,27-bis(benzyloxy)-26,28-dicarboxymethoxy calix[4]arene 6

A mixture of compound **5** (2 g, 2.45 mmol) and 15% aqueous NaOH (10 mL) in EtOH (150 mL) was stirred and heated under reflux for 24 h after which most of the ethanol was distilled off. The residue was taken in $CHCl_3$, acidified with 1 M HCl until pH = 1 and washed with water and then with brine. The organic phase was dried over anhydrous magnesium sulfate and concentrated to give the crude product. Recrystallization of the crude product from ethanol–acetone furnished **6**. Yield 1.93 g (85%). Mp 174–175 °C. IR (KBr, cm^{-1}): 1736 (CO), 3364 (OH); ^1H NMR ($CDCl_3$): δ 8.05 (s, 4H, Ar*H*), 7.93 (br, 2H, CO_2H), 7.60–7.56 (m, 4H, Ar*H*), 7.45–7.39 (m, 6H, Ar*H*), 6.95 (d, 4H, Ar*H*), 6.79 (t, 2H, Ar*H*), 5.04 (s, 4H, CH_2CO_2H), 4.72 (s, 4H, $ArCH_2O$), 4.26 (d, 4H, $ArCH_2Ar$), 3.48 (d, 4H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$): δ 169.6, 169.2 (*C*O), 154.3, 152.0, 151.6, 149.9, 148.3, 147.8, 146.4, 145.1, 144.8, 139.9, 135.1, 133.3, 132.0, 131.8, 131.2, 130.6, 129.4, 128.7, 127.2, 126.3, 126.4, 124.7 (Ar), 75.7, 77.8 (OCH_2), 68.3, 67.7 (OCH_2Ar), 31.8, 31.6 ($ArCH_2Ar$); FAB-MS *m*/*z*: (833.8) $[M+Na]^+$ (calcd 833.8). Anal. Calcd for $C_{46}H_{38}N_2O_{12}$ (810.80): C, 68.14; H, 4.72; N, 3.46. Found: C, 68.22; H, 4.85; N, 3.53.

4.3. Synthesis of 5,17-dinitro-25,27-bis(benzyloxy)-26,28-bis(chloroformylmethoxy) calix[4]arene 7

A mixture of compound **6** (2.11 g, 2.48 mmol) and thionyl chloride (1.25 mL) in dry THF was refluxed under a nitrogen atmosphere for 4 h. Removal of solvent and unreacted thionyl chloride gave acyl chloride **7** in quantitative yield, which was used in the subsequent reaction without purification.

4.4. Synthesis of the chiral calix[4](azoxa)crown-7 8

To the mixture of compound **7** obtained in the previous step in dry THF (500 mL) was added pyridine (4 mL) and stirred for 1 h at rt under a nitrogen atmosphere. A solution of chiral diamine **e** (2.22 g, 6.45 mmol) in dry THF (150 mL) was added dropwise in about 2 h with continuous stirring at rt. The reaction mixture was then stirred for further 2 days. The solvent was evaporated, the residue diluted with water (200 mL) and neutralized with 1 M HCl followed by filtration and washing with water. The yellow crude product was purified by column chromatography (SiO_2, hexane/$CHCl_3$ 2:1) and recrystallized from THF/EtOH to give pure compound **8** in 46% yield (3.32 g). Mp $\geqslant$190 °C (decomp.). $[\alpha]_D^{22} = -47.5$ (*c* 3.3, $CHCl_3$); IR (KBr, cm^{-1}): 3061 (NH), 1682 (CO); ^1H NMR ($CDCl_3$): δ 8.11 (s, 4H, Ar*H*), 7.95–7.85 (m, 2H, CON*H*), 7.62–7.57 (m, 4H, Ar*H*), 7.42–7.39 (m, 6H, Ar*H*), 7.38–7.20 (m, 10H, Ar*H*), 6.98 (d, 4H, Ar*H*), 6.82 (t, 2H, Ar*H*), 5.04 (s, 4H, CH_2CONH), 4.72 (s, 4H, $ArCH_2O$), 4.28 (d, 4H, $ArCH_2Ar$), 4.18 (m, 2H, NC*H*), 3.65–3.42 (m, 12H, OCH_2), 3.40 (d, 4H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$): δ 169.1, 169.4 (*C*O), 151.9, 151.7 (*C*HNH), 149.8, 148.6, 148.3, 147.7, 147.1, 146.6, 145.4, 143.3, 142.3, 141.7, 138.9, 137.9, 135.5, 133.4, 132.6, 132.2, 131.9, 130.6, 129.8, 129.6, 129.2, 128.9, 128.6, 127.8, 127.7, 127.3, 126.5, 125.6, 125.1, 123.9, 122.2, 120.6 (Ar); 77.0, 76.8, 75.1, 74.8, 64.6, 64.4, 53.8, 53.3 (OCH_2); 53.8, 53.4 (OCH_2Ar), 31.8, 31.7 ($ArCH_2Ar$); FAB-MS *m*/*z*: (1142.2) $[M+Na]^+$ (calcd 1142.2). Anal. Calcd for $C_{66}H_{62}N_4O_{13}$ (1119.22): C, 70.83; H, 5.58; N, 5.01. Found: C, 70.91; H, 5.64; N, 5.11.

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