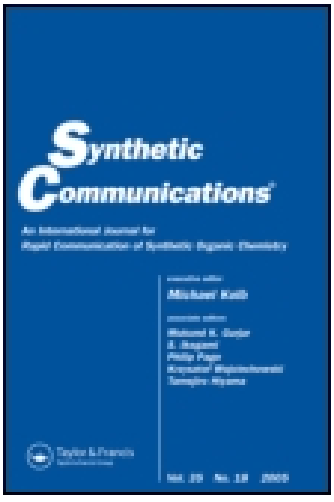


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# Novel Synthesis and Characterization of N-Substituted-calix[4]azacrown Derivatives

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# Novel Synthesis and Characterization of *N*-Substituted-calix[4]azacrown Derivatives

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**Abstract:** Novel calix[4]azacrown derivatives from the reaction between calix[4]amidocrown and the different *N*-(4-bromoacetamidephthalimido)alkanes derivatives, which may be useful intemediate compounds of pseudorotaxane, have been synthesized and structurally characterized by IR, $^{1}$H NMR, $^{13}$C NMR, MS, and elemental analyses. From their analysis data, it was found that compounds **6a–d** adopted a cone conformation.

**Keywords:** calix[4]azacrown, characterization, conformation, *n*-(4-bromoacetamidephthalimido)alkanes, synthesis

## INTRODUCTION

Interlocked supermolecules such as pseudorotaxanes, catenanes, and [2]rotaxanes have attracted a great deal of attention in view of the design of molecular machines, devices, and recognition systems.[1] Calix[4]azacrown ether is particularly well suited as a pseudorotaxane building block because of its application as a bulky stopper and its good complexation ability with metal ions,[2] ammonium ions,[3] and anions.[4] Its incorporation into the pseudorotaxane could give rise to the complexation ability of pseudorotaxane. *N*-(4-Aminophthalimido)alkane derivatives (APn), which have the potential to probe subtle changes in their microenvironment resulting from inter- or intramolecular interactions,[5] could be bound to $\beta$-cyclodextrin ($\beta$-CD).[6]

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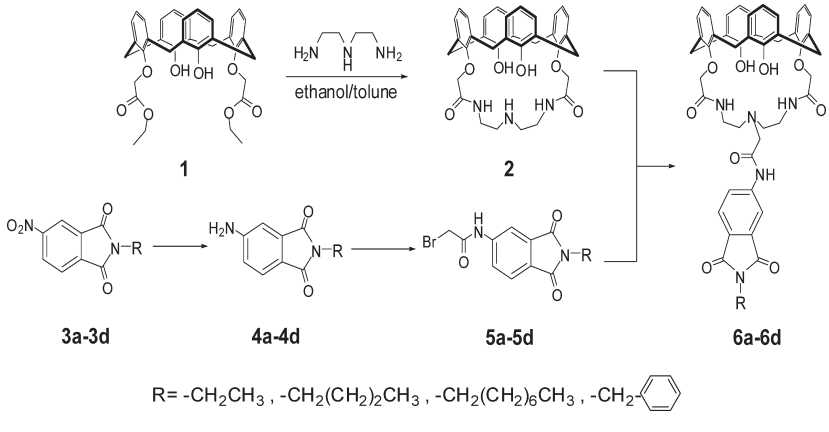
Consequently, calix[4]azacrown derivatives with an APn group may form pseudorotaxane with $\beta$-CD. However, as we know, the pseudorotaxanes containing calix[4]azacrown derivatives and APn unit have not been found before. In this communication, we report four novel calix[4]azacrown derivatives that may be useful intemediate compounds of pseudorotaxane, and the further valuation of their self-assembly activities with $\beta$-CD is in progress.

## RESULTS AND DISCUSSION

The synthetic pathway of the target compounds (**6a**–**d**) is depicted as shown in Scheme 1. Compounds **1**, **2**, **3a**–**d**, **4a**, and **4b** were synthesized according to the literature procedure.[7]

According to the reported literature by Kim,[8] reaction of calix[4]amidocrown **2** with *N*-(1-pyrenylmethyl)chloroacetamide using $K_2CO_3$ as a base in acetonitrile with a catalytic amount of sodium iodide provide bis-O-substituted product in medium yield. However, under similiar conditions, (potassium iodide instead of sodium iodide), absolutely different products (*N*-substituted-calix[4](aza)monocrown **6a**–**d** were obtained. Research into the cause is now in progress.

The structures of compounds **6a**–**d** were established by infrared radiation (IR), $^1$H NMR, $^{13}$C NMR, mass spectroscopy (MS), and elemental analyses. The results showed that compounds **6a**–**d** were in a cone conformation. Take compound **6b** as an example. In the $^1$H NMR spectra in $CDCl_3$, two doublets at $\delta$ 4.16 and 3.54 ppm for the protons of the methylene bridge of the calix[4]arene skeleton indicated that compound **6b** is in a cone conformation in solution. Moreover, in the $^{13}$C NMR data, the signal peak of the methylene carbons of $ArCH_2Ar$ appeared at about 31 ppm according to the




*Scheme 1.*

Mendoza rule.[9] It is also consistent with the cone conformation. Furthermore, a singlet at $\delta$ 3.39 corresponding to NC**H**$_2$CO was found. From doublets at $\delta$ 8.21 and $\delta$ 7.76 both with $J = 8$ Hz and a singlet at $\delta$ 8.26, the structure of the phthalimide unit was confirmed. MS and elemental analysis data further confirmed their structures.

## EXPERIMENTAL

Melting points were measured on a Yanagimoto MP-500 apparatus (uncorrected). The fourier transform infrared radiation (FT-IR) spectra (KBr pellets) were measured on a Bio-Rad FTS3000 infrared spectrometer. The $^1$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on Varian Inova 500-MHz and 75-MHz instruments at 298 K. MS analyses were carried out on an LCQ Advantage MAX spectrometer. Elemental analyses were performed on a Vario EL III elemental analyzer. All reagents are commercially available and purified by standard methods prior to use.

### General Procedure for the Synthesis Compounds 4c–d

A mixture of *N*-substituted-4-nitrophthalimide **3c–d** (20 mmol) and $SnCl_2 \cdot 2H_2O$ (14.89 g, 66 mmol) in 110 mL of 18% aqueous HCl solution was heated to 40°C–90°C until no strating material was detected by thin-layer chromatographys (TLC) (about 0.5–4 h). After cooling to room temperature, the product, *N*-substituted-4-aminophthalimide, was collected by filtration, washed with water, and recrystallized from ethanol. All the products were characterized by the spectra.

### Data

***N*-Octyl-4-aminophthalimide 4c:** yellow solid, yield 46%, mp 52–54°C; IR (KBr, cm$^{-1}$): 3470, 3362, 1691; $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.59 (d, 1H, $J = 8$ Hz, ArH), 7.03 (s, 1H, ArH), 6.81 (d, 1H, $J = 8$ Hz, ArH), 4.36 (w, 2H, $NH_2$), 3.61 (t, 2H, $J = 7$ Hz, $NCH_2$), 1.64 (m, 2H, $CH_2$), 1.31–1.25 (m, 10H, $CH_2$), 0.86 (t, 3H, $J = 7$ Hz, $CH_3$). ESI-MS $m/z$ 275.3 $(M + H)^+$ (calcd. for $C_{16}H_{22}N_2O_2$ 274.2). Anal. calcd. for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08. Found: C, 70.08; H, 8.06.

***N*-Benzyl-4-aminophthalimide 4d:** yellow solid, yield 81%, mp 126–127°C; IR (KBr, cm$^{-1}$): 3468, 3373, 1693; $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.58 (d, 1H, $J = 8$ Hz, ArH), 7.40 (d, 2H, $J = 8$ Hz, ArH), 7.31 (t, 2H, $J = 8$ Hz, ArH), 7.23 (t, 1H, $J = 8$ Hz, ArH), 7.02 (s, 1H, ArH), 6.79 (d, 1H, $J = 8$ Hz,

ArH), 4.79 (s, 2H, $NCH_2$), 4.42 (w, 2H, $NH_2$). ESI-MS $m/z$ 253.2 $(M + H)^+$ (calcd. for $C_{15}H_{12}N_2O_2$ 252.1). Anal. calcd. for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79. Found: C, 71.36; H, 4.81.

## General Procedure for the Synthesis Compounds 5a–d

To a stirred mixture of N-substituted-4-aminophthalimide **4a–d** (3 mmol) and $NEt_3$ (1 mL, 7 mmol) in 50 mL of $CH_2Cl_2$, a solution of bromoacetyl bromide (0.72 mL, 7 mmol) in 20 mL of $CH_2Cl_2$ was added during 3 h. The reaction mixture was stirred at room temperature for 6 h and poured into 50 mL of $H_2O$. The $CH_2Cl_2$ layer was removed; the aqueous phase was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and distilled to afford a solid, which was purified by column chromatography. After purification, all the products were characterized by their spectra.

## Data

**2-Bromo-N-(2-ethyl-phthalimide-4-yl) acetamide 5a:** pale yellow solid, yield 83%, mp 156–158°C; IR (KBr, $cm^{-1}$): 3350, 1687; $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 8.61 (s, 1H, NH), 8.06 (s, 1H, ArH), 7.94 (d, 2H, $J = 8$ Hz, ArH), 7.82 (d, 2H, $J = 8$ Hz, ArH), 4.07 (s, 2H, $BrCH_2CO$), 3.73 (t, 2H, $J = 7$ Hz, $NCH_2$), 1.27 (t, 3H, $J = 7$ Hz, $CH_3$). ESI-MS $m/z$ 333.3 $(M + Na)^+$ (calcd. for $C_{12}H_{11}BrN_2O_3$ 310.0). Anal. calcd. for $C_{12}H_{11}BrN_2O_3$: C, 46.32; H, 3.56. Found: C, 46.34; H, 3.54.

**2-Bromo-N-(2-butyl-phthalimide-4-yl) acetamide 5b:** pale yellow solid, yield 90%, mp 152–154°C; IR (KBr, $cm^{-1}$): 3346, 1690; $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 8.53 (s, 1H, NH), 8.05 (s, 1H, ArH), 7.93 (d, 2H, $J = 8$ Hz, ArH), 7.82 (d, 2H, $J = 8$ Hz, ArH), 4.07 (s, 2H, $BrCH_2CO$), 3.68 (t, 2H, $J = 7$ Hz, $NCH_2$), 1.65 (m, 2H, $CH_2$), 1.36 (m, 2H, $CH_2$), 0.95 (t, 3H, $J = 7$ Hz, $CH_3$). ESI-MS $m/z$ 339.1 $(M + H)^+$ (calcd. for $C_{14}H_{15}BrN_2O_3$ 338.0). Anal. calcd. for $C_{14}H_{15}BrN_2O_3$: C, 49.57; H, 4.46. Found: C, 49.60; H, 4.44.

**2-Bromo-N-(2-octyl-phthalimide-4-yl) acetamide 5c:** pale yellow solid, yield 94%, mp 136–138°C; IR (KBr, $cm^{-1}$): 3353, 1686; $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 8.54 (s, 1H, NH), 8.06 (s, 1H, ArH), 7.93 (d, 2H, $J = 8$ Hz, ArH), 7.82 (d, 2H, $J = 8$ Hz, ArH), 4.08 (s, 2H, $BrCH_2CO$), 3.66 (t, 2H, $J = 7$ Hz, $NCH_2$), 1.65 (m, 2H, $NCH_2CH_2$), 1.32–1.23 (m, 10H, $CH_2$), 0.87 (t, 3H, $J = 7$ Hz, $CH_3$). ESI-MS $m/z$ 417.4 $(M + Na)^+$ (calcd. for $C_{18}H_{23}BrN_2O_3$ 394.1). Anal. calcd. for $C_{18}H_{23}BrN_2O_3$: C, 54.69; H, 5.86. Found: C, 54.73; H, 5.83.

**2-Bromo-N-(2-benzyl-phthalimide-4-yl) acetamide 5d:** yellow solid, yield 88%, mp 190–192°C; IR (KBr, $cm^{-1}$): 3305, 1697; $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 8.47 (s, 1H, NH), 8.06 (s, 1H, ArH), 7.90 (d, 2H, $J = 8$ Hz, ArH), 7.82 (d, 2H, $J = 8$ Hz, ArH), 7.42 (d, 2H, $J = 7.5$ Hz, ArH), 7.31 (t, 2H, $J = 7.5$ Hz, ArH), 7.26 (t, 1H, $J = 7.5$ Hz, ArH), 4.84 (s, 2H, $NCH_2$), 4.05 (s, 2H, $BrCH_2CO$). ESI-MS $m/z$ 373.3 $(M + H)^+$ (calcd. for $C_{17}H_{13}BrN_2O_3$ 372.0). Anal. calcd. for $C_{17}H_{13}BrN_2O_3$: C, 54.71; H, 3.51. Found: C, 54.65; H, 3.55.

## General Procedure for the Preparation of Compounds 6a–d

Under nitrogen, calix[4]amidocrown (**2**) (0.24 g, 0.4 mmol), $K_2CO_3$(0.14 g, 1 mmol), the appropriate N-(4-bromoacetamidephthalimido)alkanes derivatives **5a–d** (0.88 mmol), and a catalytic amount of potassium iodide in 30 mL of acetontrile were heated to reflux temperature. After refluxed for 12 h, acetontrile was removed in vacuo. To the resulting yellow solid, water (30 mL) and $CH_2Cl_2$ (20 mL) were added, and the organic phase was separated and washed twice with 20 mL of distilled water. The $CH_2Cl_2$ layer was dried over $MgSO_4$ and distilled off to afford a yellowish solid. Column chromatography on silica gel using $CH_2Cl_2/CH_3CO_2Et = 5/1$ as an eluent gave the products. All the products were characterized by the spectra.

## Data

***N*-[*N*-(2-Ethyl-phthalimide-4-yl)aminocarbonylmethoxy]-calix[4](aza)*mono*-crown6a:** white solid, yield 61%, mp (>250°C decomposed); IR (KBr, $cm^{-1}$): 3410, 3324, 1736, 1708, 1665; $^1H$ NMR ($CDCl_3$, $\delta$ ppm): 10.05 (s, 1H, CONH), 9.12 (t, 2H, $J = 5.5$ Hz), 8.26 (s, 1H, ArH), 8.21 (d, 1H, $J = 8$ Hz, ArH), 8.04 (s, 2H, OH), 7.77 (d, 1H, $J = 8$ Hz, ArH), 7.13 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.99 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.87 (t, 2H, $J = 8$ Hz, ArHp), 6.78 (t, 2H, $J = 8$ Hz, ArHp), 4.66 (s, 4H, $OCH_2CO$), 4.16 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.72 (q, 2H, $J = 7$ Hz, $NCH_2CH_3$), 3.62 (m, 4H, $CONHCH_2$), 3.54 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.39 (s, 2H, $NCH_2CO$), 3.02 (m, 4H, $NCH_2$), 1.27 (t, 3H, $J = 7$ Hz, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 14.22 (1**C**$H_3$), 31.90 (4Ar**C**$H_2$Ar), 33.08 (1 N**C**$H_2CH_3$), 40.63 (2CONH**C**$H_2$), 54.80 (2 N**C**$H_2$), 61.96 (1 N**C**$H_2CO$), 75.27 (2**C**$H_2O$), [114.22 (1**C**), 121.33 (2**C**), 123.73 (1**C**), 124.41 (1**C**), 126.63 (1**C**), 127.19 (2**C**), 127.75 (4**C**), 129.44 (4**C**), 130.05 (4**C**), 132.80 (4**C**), 133.93 (1**C**), 144.67 (1**C**), 150.96 (2**C**), 151.96 (2**C**)] (aromatic 30**C**), 168.28 (hetero 2**C**), 168.35 (1 N$CH_2$**C**O), 169.37 (2**C**O$CH_2$). ESI-MS $m/z$ 838.3 $(M + H)^+$ (calcd. for $C_{48}H_{47}N_5O_9$ 837.3). Anal. calcd. for $C_{48}H_{47}N_5O_9$: C, 68.80; H, 5.65. Found: C, 68.88; H, 5.61.

***N*-[*N*-(2-Butyl-phthalimide-4-yl)aminocarbonylmethoxy]-calix[4](aza)*mono*-crown 6b:** white solid, yield 55%, mp (>250°C decomposed); IR (KBr, $cm^{-1}$): 3395, 3317, 1735, 1713, 1662; $^1$H NMR ($CDCl_3$, $\delta$ ppm): 10.05 (s, 1H, CONH), 9.12 (t, 2H, $J = 5.5$ Hz), 8.26 (s, 1H, ArH), 8.21 (d, 1H, $J = 8$ Hz, ArH), 8.04 (s, 2H, OH), 7.76 (d, 1H, $J = 8$ Hz, ArH), 7.13 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.99 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.86 (t, 2H, $J = 8$ Hz, $ArH_p$), 6.78 (t, 2H, $J = 8$ Hz, $ArH_p$), 4.66 (s, 4H, $OCH_2CO$), 4.16 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.64 (m, 2H, $NCH_2CH_2$), 3.62 (m, 4H, $CONHCH_2$), 3.54 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.39 (s, 2H, $NCH_2CO$), 3.02 (m, 4H, $NCH_2$), 1.64 (m, 2H, $NCH_2CH_2$), 1.34 (m, 2H, $CH_2CH_3$), 0.93 (t, 3H, $J = 7$ Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 13.89 (1**C**$H_3$), 20.31 (1**C**$H_2$), 30.91 (1**C**$H_2$), 31.91 (4Ar**C**$H_2$Ar), 37.99 (1 N**C**$H_2CH_2CH_2CH_3$), 40.64 (2CONH**C**$H_2$), 54.80 (2 N**C**$H_2$), 61.96 (1**NC**$H_2$CO), 75.27 (2**C**$H_2$O), [114.22 (1**C**), 121.33 (2**C**), 123.72 (1**C**), 124.41 (1**C**), 126.55 (1**C**), 127.19 (2**C**), 127.75 (4**C**), 129.44 (4**C**), 130.05 (4**C**), 132.79 (4**C**), 133.85 (1**C**), 144.67 (1**C**), 150.96 (2**C**), 151.96 (2**C**)] (aromatic 30**C**), 168.50 (hetero 2**C**), 168.56 (1 N**C**$H_2$**C**O), 169.37 (2**C**O**C**$H_2$). ESI-MS $m/z$ 866.4 $(M + H)^+$ (calcd. for $C_{50}H_{51}N_5O_9$ 865.4). Anal. calcd. for $C_{50}H_{51}N_5O_9$: C, 69.35; H, 5.94. Found: C, 69.41; H, 5.91.

***N*-[*N*-(2-Octyl-phthalimide-4-yl)aminocarbonylmethoxy]-calix[4](aza)*mono*-crown 6c:** white solid, yield 64%, mp (>250°C decomposed); IR (KBr, $cm^{-1}$): 3361, 3325, 1767, 1708, 1657; $^1$H NMR ($CDCl_3$, $\delta$ ppm): 10.05 (s, 1H, CONH), 9.12 (t, 2H, $J = 5.5$ Hz), 8.26 (s, 1H, ArH), 8.21 (d, 1H, $J = 8$ Hz, ArH), 8.04 (s, 2H, OH), 7.77 (d, 1H, $J = 8$ Hz, ArH), 7.13 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.99 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.85 (t, 2H, $J = 8$ Hz, $ArH_p$), 6.78 (t, 2H, $J = 8$ Hz, $ArH_p$), 4.66 (s, 4H, $OCH_2CO$), 4.13 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.64 (m, 2H, $NCH_2CH_2$), 3.63 (m, 4H, $CONHCH_2$), 3.54 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.39 (s, 2H, $NCH_2CO$), 3.02 (m, 4H, $NCH_2$), 1.65 (m, 2H, $NCH_2CH_2$), 1.34–1.21 [m, 10H, $(CH_2)_5CH_3$], 0.86 (t, 3H, $J = 7$ Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 14.31 (1**C**$H_3$), 22.85 (1**C**$H_2$), 27.11 (1**C**$H_2$), 28.92 (1**C**$H_2$), 29.39 (1**C**$H_2$), 29.40 (1**C**$H_2$), 31.90 (4Ar**C**$H_2$Ar), 32.01 (1**C**$H_2$), 38.28 (1 N**C**$H_2CH_2CH_2$), 40.63 (2CONH**C**$H_2$), 54.81 (2 N**C**$H_2$), 61.96 (1**NC**$H_2$CO), 75.27 (2**C**$H_2$O), [114.23 (1**C**), 121.33 (2**C**), 123.74 (1**C**), 124.41 (1**C**), 126.55 (1**C**), 127.19 (2**C**), 127.75 (4**C**), 129.44 (4**C**), 130.05 (4**C**), 132.79 (4**C**), 133.86 (1**C**), 144.64 (1**C**), 150.96 (2**C**), 151.96 (2**C**)] (aromatic 30**C**), 168.50 (hetero 2**C**), 168.54 (1 N**C**$H_2$**C**O), 169.38 (2**C**O**C**$H_2$). ESI-MS $m/z$ 922.4$(M + H)^+$ (calcd. for $C_{54}H_{59}N_5O_9$ 921.4). Anal. calcd. for $C_{54}H_{59}N_5O_9$: C, 70.34; H, 6.45. Found: C, 70.38; H, 6.43.

***N*-[*N*-(2-Benzyl-phthalimide-4-yl)aminocarbonylmethoxy]-calix[4](aza)*mono*-crown 6d:** white solid, yield 51%, mp (>250°C decomposed); IR (KBr, $cm^{-1}$): 3352, 3310, 1766, 1712, 1670; $^1$H NMR ($CDCl_3$, $\delta$ ppm): 10.06 (s, 1H, CONH), 9.11 (t, 2H, $J = 5.5$ Hz), 8.27 (s, 1H, ArH), 8.22 (d, 1H,

$J = 8$ Hz, ArH), 8.03 (s, 2H, OH), 7.77 (d, 1H, $J = 8$ Hz, ArH), 7.12 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 7.40 (d, 2H, $J = 8$ Hz, ArH), 7.29 (t, 2H, $J = 8$ Hz, $ArH_{meta}$), 7.25 (t, 1H, $J = 8$ Hz, $ArH_p$), 6.98 (d, 4H, $J = 8$ Hz, $ArH_{meta}$), 6.85 (t, 2H, $J = 8$ Hz, $ArH_p$), 6.78 (t, 2H, $J = 8$ Hz, $ArH_p$), 4.82 (s, 2H, $NCH_2Ar$), 4.65 (s, 4H, $OCH_2CO$), 4.14 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.61 (m, 4H, $CONHCH_2$), 3.53 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.38 (s, 2H, $NCH_2CO$), 3.02 (m, 4H, $NCH_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 31.91 (4Ar**C**$H_2$Ar), 40.63 (2CONH**C**$H_2$), 41.78 (1 N**C**$H_2$Ar), 54.78 (2 N**C**$H_2$), 61.98 (1**NC**$H_2$CO), 75.27 (2**C**$H_2$O), [114.39 (1**C**), 121.32 (2**C**), 123.84 (1**C**), 124.64 (1**C**), 126.44 (1**C**), 127.19 (2**C**), 127.75 (4**C**), 127.93 (1**C**), 128.72 (2**C**), 128.85 (2**C**), 129.44 (4**C**), 130.05 (4**C**), 132.79 (4**C**), 133.81 (1**C**), 136.81 (1**C**), 144.84 (1**C**), 150.96 (2**C**), 151.96 (2**C**)] (aromatic 36**C**), 168.09 (hetero 2**C**), 168.11 (1 N**C**$H_2$**C**O), 169.37 (2**C**O$CH_2$). ESI-MS $m/z$ 900.4 $(M + H)^+$ (calcd. for $C_{53}H_{49}N_5O_9$ 899.4). Anal. calcd. for $C_{53}H_{49}N_5O_9$: C, 70.73; H, 5.49. Found: C, 70.80; H, 5.42.

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