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Palladium–Catalyzed Amination in the Synthesis of Macrocycles Comprising Two Naphthalene And Two Polyamine Moieties

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Two approaches were elaborated for the synthesis of macrocycles comprising two naphthalene and two polyamine moieties (cyclodimers). The first one includes the synthesis of N,N'-bis(7-bromonaphth-2-yl) substituted polyamines via Pd-catalyzed amination reaction of polyamine with excess of 2,7-dibromonaphthalene, followed by the Pd-catalyzed macrocyclization reaction with appropriate polyamine. The second route comprises the formation of 2,7-bis(polyamine) substituted naphthalenes which are used in situ for the macrocyclization with 2,7-dibromonaphthalene. The yields of cyclodimers are dependent on the nature of polyamines and catalytic systems employed. The two synthetic routes were compared and the one-pot method was found to be advantageous providing better yields of the target products.

Keywords: Palladium-catalized amination, naphthalene, polyamines, macrocycles, synthesis.

Палладий–катализируемое аминирование в синтезе макроциклов с двумя нафталиновыми и двумя полиаминными фрагментами

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Разработаны два подхода к синтезу макроциклов, содержащих по два фрагмента нафталина и полиамина (циклодимеров). Первый подход заключается в первоначальном получении N,N'-бис(7-бромнафт-2-ил) замещенных полиаминов Pd-катализируемым аминированием избытка 2,7-дибромнафталина полиаминами с последующей Pd-катализируемой макроциклизацией данных соединений с использованием соответствующих полиаминов. Второй подход заключается в синтезе 2,7-бис(полиамино)замещенных нафталинов, которые используются in situ на второй стадии макроциклизации. Найдено, что выходы макроциклов зависят от природы полиамина, в определенных случаях показано предпочтительное использование фосфиновых лигандов BINAP или Xantphos, произведено сравнение эффективности двух предложенных методов, установлено, что второй метод дает в целом более высокие выходы целевых циклодимеров. Выделены и охарактеризованы циклические и линейные побочные продукты в указанных реакциях.

Ключевые слова: Палладий-катализируемое аминирование, нафталин, полиамины, макроциклы, синтез.

Introduction

Worldwide applications of coordination chemistry in the development of chemotherapeutic or diagnostic agents, treatment of nuclear waste, chemosensoring have become of paramount importance and progress rapidly in comparison with the studies that elucidate the basic theory of this field. Therefore, the research is often carried out in a make-and-try manner and numerous ligands have been synthesized and their affinity to metal cations has been evaluated. Ideally, efficient ligands should match various criteria such as high binding constants and selectivity together with fast binding kinetics of the coordination pocket, water solubility, insensitivity to p*H* changes, non-toxicity, *etc*. Complex molecular architectures should be synthesized to adopt the system properties to a real-life application. Ligand properties could be tuned not only by varying the number and nature of donor groups but also by introducing different non-coordinated structural motifs. Aromatic moieties are of major interest in ligand design for chemosensoring and sequestration of toxic and radioactive metal ions. The first macrocyclic compounds comprising the naphthalene moiety were described in the literature over 70 years ago.[1] This rigid lipophilic fragment possessing interesting photophysical properties draws considerable interest and dozen of works appeared dealing with the synthesis and investigation of the macrocycles of different geometry based on naphthalene, as well with the azacrown ethers derivatives containing naphthalene as exocyclic substituents. In these polyazacycles nitrogen atoms are present in such fragments as Schiff bases,[2] diamides,[3] diimides,[4] lactames.[5] Naphthalene system can be condensed with tetraazamacrocycles,[6] macrocycles may contain phosphorus atoms[7] or only carbon atoms,[8] it can be incorporated into calixarene[9] and catenane[10] structures, combined in various manners with porphyrins.[11] Such compounds are valuable molecular precursors for supramolecular studies and could be used *e.g.* as organic anions receptors[12] or molecular rotors.[13]

Recently, we have synthesized a series of the nitrogen- and oxygen-containing macrocycles based on 2,7-diaminonaphthalene (Scheme 1).[14] Herein we report a detailed account on the synthesis of macrocyclic compounds composed by two aromatic groups and two linear chains (so-called cyclodimers).

Experimental

NMR spectra were registered using Bruker Avance 400 spectrometer, MALDI-TOF spectra were obtained with Bruker Ultraflex spectrometer using 1,8,9-trihydroxyanthracene as matrix and PEGs as internal standards. Dioxa- and trioxadiamines, tetraamine, BINAP and Xantphos ligands, sodium *tert*-butoxide were purchased from Aldrich and Acros and used without further purification, 2,7-dibromonaphthalene was obtained according to a reported procedure,[15] $Pd(dba)_2$ was synthesized according to the method described.[16] Dioxane was distilled over NaOH followed by the distillation over sodium under argon, acetonitrile, dichloromethane and methanol were used freshly distilled.

Typical procedure for the synthesis of *N,N'*-bis(7-bromonaphth-2-yl) substituted naphthalenes **4a-c**.

A two-neck flask equipped with a condenser and magnetic stirrer, flushed with dry argon, was charged with 2,7-dibromonaphthalene **2** (629 mg, 2.2 mmol), $Pd(dba)_2$ (11.5 mg, 0.02 mmol, 2 mol%) and Xantphos (15 mg, 0.025 mmol, 2.5 mol%) in the case of dioxa- and trioxadiamines **1a**,**b**, or $Pd(dba)_2$ (23 mg, 0.04 mmol, 4 mol%) and BINAP (28 mg, 0.045 mmol, 4.5 mol%) in the case of tetraamine **1c**, 20 ml (in the case of dioxa- and trioxadiamines **1a**,**b**) or 10 ml (in the case of tetraamine **1c**) dioxane were added, the mixture was stirred for 2–3 min, then corresponding polyamine **1a-c** (1 mmol) and ^{t}BuONa (288 mg, 3 mmol) were added, and the reaction mixture was refluxed for 5-8 h. After cooling it down to ambient temperature the reaction mixture was diluted with CH_2Cl_2, the residue was filtered off, the organic solvents were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2/MeOH (200:1–3:1), CH_2Cl_2/MeOH/NH_3aq (100:20:1–10:4:1).

N,N'-(2,2'-(Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl)) bis(7-bromonaphthalene-2-amine), ***4a***. Obtained from 148 mg of dioxadiamine **1a**. Eluent CH_2Cl_2/MeOH 500:1-200:1. Yield 150 mg (27 %), yellowish glassy compound. (MALDI-TOF) found: 557.0391. $C_{26}H_{27}Br_2N_2O_2$ requires 557.0439 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 3.38 (4H, t, ^3J = 5.1 Hz), 3.69 (4H, s), 3.77 (4H, t, ^3J = 5.1 Hz), 4.35 (2H, br.s), 6.66 (2H, d, ^4J = 2.0 Hz), 6.83 (2H, dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz), 7.23 (2H, dd, ^3J = 8.7 Hz, ^4J = 1.9 Hz), 7.47–7.57 (4H, m), 7.72 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 43.3 (2C), 69.4 (2C), 70.3 (2C), 103.4 (2C), 118.4 (2C), 120.5 (2C), 125.2 (2C), 126.0 (2C), 127.8 (2C), 128.9 (2C), 129.3 (2C), 136.4 (2C), 146.6 (2C).

N,N,N,'-Tris(7-bromonaphth-2-yl)substituted dioxadiamine ***8a*** was obtained as the second product in the synthesis of compound **4a**. Eluent CH_2Cl_2. Yield 50 mg (10 %), yellowish glassy compound. (MALDI-TOF) found: 761.0087. $C_{36}H_{32}Br_3N_2O_2$ requires 761.0014 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 3.30 (2H, t, ^3J = 5.2 Hz), 3.63 (4H, s), 3.70 (2H, t, ^3J = 5.2 Hz), 3.79 (2H, t, ^3J = 5.9 Hz), 4.15 (2H, t, ^3J = 5.8 Hz), 4.26 (1H, br.s), 6.61 (1H, d, ^4J = 1.6 Hz), 6.74 (1H, dd, ^3J = 8.7 Hz, ^4J = 2.3 Hz), 7.26 (1H, dd, ^3J = 9.0 Hz, ^4J = 1.9 Hz), 7.27 (2H, dd, ^3J = 9.0 Hz, ^4J = 2.1 Hz), 7.36 (2H, d, ^4J = 1.8 Hz), 7.39 (2H, dd, ^3J = 8.7 Hz, ^4J = 1.9 Hz), 7.48 (2H, d, ^3J = 8.9 Hz), 7.57 (2H, d, ^3J = 8.7 Hz), 7.64 (2H, d, ^3J = 9.0 Hz), 7.72 (1H, br.s), 7.82 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 43.2 (1C), 52.1 (1C), 68.2 (1C), 69.4 (1C), 70.4 (1C), 70.8 (1C), 103.3 (1C), 115.5 (2C), 118.4 (1C), 120.4 (1C), 120.6 (2C), 122.8 (2C), 125.1 (1C), 125.8 (1C), 127.4 (2C), 127.8 (1C), 128.4 (2C), 128.7 (2C), 128.8 (1C), 128.9 (2C), 129.1 (2C), 129.2 (1C), 135.7 (2C), 136.4 (1C), 145.8 (2C), 146.5 (1C).

Oligomer ***9a*** was obtained as the third product in the synthesis of compound **4a**. Eluent CH_2Cl_2/MeOH 100:1. Yield 55 mg (13 %), yellowish glassy compound. (MALDI-TOF) found: 829.1922. $C_{42}H_{47}Br_2N_4O_4$ requires 829.1964 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 3.37 (8H, t, ^3J = 5.0 Hz), 3.67 (8H, s), 3.75 (4H, t, ^3J = 4.6 Hz), 3.76 (4H, t, ^3J = 4.9 Hz), 4.11 (2H, br.s), 4.37 (2H, br.s), 6.60 (2H, d, ^3J = 8.0 Hz), 6.61 (2H, br.s), 6.65 (2H, d, ^4J = 1.9 Hz), 6.83 (2H, dd, ^3J = 8.6 Hz, ^4J = 2.0 Hz), 7.23 (2H, dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz), 7.40 (2H, d, ^3J = 9.1 Hz), 7.47 (2H, d, ^3J = 8.3 Hz), 7.50 (2H, d, ^3J = 8.7 Hz), 7.72 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 43.3 (2C), 43.5 (2C), 69.3 (2C), 69.6 (2C), 70.2 (2C), 70.3 (2C), 103.3 (2C), 103.6 (2C), 114.2 (2C), 118.5 (2C), 120.4 (2C), 125.1 (2C), 125.8 (2C), 127.8 (2C), 128.8 (2C), 128.9 (2C), 129.2 (2C), 136.4 (2C), 146.3 (2C), 146.6 (2C), two quaternary carbon atoms were not assigned.

N,N'-(3,3'-(2,2'-Oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl))bis(7-bromonaphthalene-2-amine), ***4b***. Obtained from 220 mg of trioxadiamine **1b**. Eluent CH_2Cl_2/MeOH 200:1. Yield 235 mg (37 %), yellowish glassy compound. (MALDI-TOF) found: 628.21. $C_{30}H_{34}Br_2N_2O_3$ requires 628.09 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.92 (4H, quintet, ^3J = 5.9 Hz), 3.29 (4H, t, ^3J = 6.2 Hz), 3.62 (4H, t, ^3J = 5.5 Hz), 3.61–3.65 (4H, m), 3.67–3.72 (4H, m), 4.37 (2H, br.s), 6.62 (2H, br.s), 6.81 (2H, d, ^3J = 8.8 Hz), 7.21 (2H, d, ^3J = 8.6 Hz), 7.47 (2H, d, ^3J = 8.6 Hz), 7.51 (2H, d, ^3J = 8.9 Hz), 7.72 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 28.8 (2C), 41.8 (2C), 69.9 (2C), 70.3 (2C), 70.7 (2C), 102.7 (2C), 118.5

(2C), 120.4 (2C), 124.8 (2C), 125.6 (2C), 127.7 (2C), 128.7 (2C), 129.3 (2C), 136.6 (2C), 147.0 (2C).

N,N,N,'-Tris(7-bromonaphth-2-yl)substituted trioxadiamine ***8b*** was obtained as the second product in the synthesis of compound **4b**. Eluent CH_2Cl_2/MeOH 200:1. Yield 67 mg (10 %), yellowish glassy compound. (MALDI-TOF) found: 832.13. $C_{40}H_{39}Br_3N_2O_3$ requires 832.05 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.91 (2H, quintet, ^3J = 6.0 Hz), 1.99 (2H, quintet, ^3J = 6.3 Hz), 3.28 (2H, t, ^3J = 6.3 Hz), 3.55 (2H, t, ^3J = 5.7 Hz), 3.63 (2H, t, ^3J = 5.6 Hz), 3.63–3.66 (4H, m), 3.71–3.75 (4H, m), 4.05 (2H, t, ^3J = 6.9 Hz), 4.39 (1H, br.s), 6.61 (1H, d, ^4J = 1.9 Hz), 6.81 (1H, dd, ^3J = 8.8 Hz, ^4J = 2.1 Hz), 7.21 (1H, dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz), 7.24 (2H, dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz), 7.31 (2H, d, ^4J = 1.9 Hz), 7.39 (2H, dd, ^3J = 8.7 Hz, ^4J = 1.8 Hz), 7.46 (1H, d, ^3J = 8.6 Hz), 7.50 (1H, d, ^3J = 8.8 Hz), 7.58 (2H, d, ^3J = 8.5 Hz), 7.64 (2H, d, ^3J = 9.0 Hz), 7.72 (1H, d, ^4J = 1.5 Hz), 7.83 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 27.5 (1C), 28.8 (1C), 41.7 (1C), 49.1 (1C), 68.2 (1C), 69.8 (1C), 70.3 (2C), 70.7 (2C), 102.6 (1C), 115.3 (2C), 118.4 (1C), 120.4 (3C), 122.8 (2C), 124.7 (1C), 125.5 (1C), 127.2 (2C), 127.6 (1C), 127.7 (2C), 128.6 (1C), 128.7 (2C), 128.8 (2C), 129.1 (2C), 129.2 (1C), 135.8 (2C), 136.5 (1C), 146.0 (2C), 146.9 (1C).

Oligomer ***9b*** was obtained as the third product in the synthesis of compound **4b**. Eluent CH_2Cl_2/MeOH 100:1. Yield 29 mg (6 %), yellowish glassy compound. (MALDI-TOF) found: 972.44. $C_{50}H_{62}Br_2N_4O_6$ requires 972.30 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.91 (4H, quintet, ^3J = 5.7 Hz), 1.92 (4H, quintet, ^3J = 5.8 Hz), 3.27 (4H, t, ^3J = 5.8 Hz), 3.28 (4H,t, ^3J = 6.2 Hz), 3.61 (8H, t, ^3J = 5.7), 3.61–3.65 (8H, m), 3.66–3.71 (8H, m), 4.33 (4H, br.s), 6.57 (2H, dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz), 6.58 (2H, br.s), 6.61 (2H, br.s), 6.81 (2H, dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz), 7.20 (2H, dd, ^3J = 8.4 Hz, ^4J = 1,8 Hz), 7.40 (2H, d, ^3J = 8.6 Hz), 7.46 (2H, d, ^3J = 8.6 Hz), 7.51 (2H, d, ^3J = 8.9 Hz), 7.72 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 28.8 (2C), 29.0 (2C), 41.7 (4C), 69.8 (4C), 70.2 (4C), 70.6 (4C), 102.6 (2C), 102.9 (2C), 113.8 (2C), 118.4 (2C), 120.3 (2C), 121.2 (1C), 124.7 (2C), 125.5 (2C), 127.6 (2C), 128.6 (2C), 128.7 (2C), 129.2 (2C), 136.6 (2C), 137.0 (1C), 146.7 (2C), 147.0 (2C).

N^1,$N^{1'}$-(Ethane-1,2-diyl)bis(N^3-(7-bromonaphthalene-2-yl) propane-1,3-diamine), ***4c***. Obtained from 174 mg of tetraamine **1c**. Eluent CH_2Cl_2/MeOH/NH_3aq 100:20:1. Yield 158 mg (27 %), yellowish glassy compound. (MALDI-TOF) found: 583.1025. $C_{28}H_{33}Br_2N_4$ requires 583.1072 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.79 (4H, quintet, ^3J = 6.5 Hz), 1.89 (2H, br.s), 2.72 (4H, s), 2.73 (4H, t, ^3J = 6.6 Hz), 3.21 (4H, t, ^3J = 6.5 Hz), 4.50 (2H, br.s), 6.60 (2H, d, ^4J = 1.5 Hz), 6.80 (2H, dd, ^3J = 8.7 Hz, ^4J = 2.2 Hz), 7.22 (2H, dd, ^3J = 8.6 Hz, ^4J = 1.8 Hz), 7.46 (2H, d, ^3J = 8.6 Hz), 7.51 (2H, d, ^3J = 8.8 Hz), 7.73 (2H, br.s). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.0 (2C), 42.4 (2C), 48.0 (2C), 49.3 (2C), 102.6 (2C), 118.2 (2C), 120.3 (2C), 124.7 (2C), 125.5 (2C), 127.6 (2C), 128.6 (2C), 129.2 (2C), 136.5 (2C), 146.8 (2C).

Oligomer ***9c*** was obtained as the second product in the synthesis of compound **4c**. Eluent CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yield 166 mg (37 %), yellowish glassy compound. (MALDI-TOF) found: 881.3156. $C_{46}H_{59}Br_2N_8$ requires 881.3229 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.76 (4H, quintet ^3J = 6.3 Hz), 1.77 (4H, quintet, ^3J = 6.0 Hz), 2.64-2.73 (16H, m), 3.15 (4H, t, ^3J = 6.5 Hz), 3.19 (4H, t, ^3J = 6.3 Hz), 4.48 (4H, br.s), 6.54-6.60 (6H, m), 6.76–6.81 (2H, m), 7.18-7.22 (2H, m), 7.37-7.50 (6H, m), 7.72 (2H, br.s), NH protons of dialkylamino groups were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 28.8 (2C), 28.9 (2C), 42.3 (2C), 42.4 (2C), 47.8 (2C), 47.9 (2C), 49.0 (4C), 102.5 (2C), 102.8 (2C), 113.7 (2C), 118.3 (2C), 120.2 (2C), 121.2 (1C), 124.6 (2C), 125.4 (2C), 127.5 (2C), 128.5 (2C), 128.6 (2C), 129.2 (2C), 136.5 (2C), 136.9 (1C), 146.6 (2C), 146.8 (2C).

Typical procedure for the synthesis of cyclodimers ***7*** *from compounds* ***4***.

A two-neck flask equipped with a condenser and magnetic stirrer, flushed with dry argon, was charged with compound **4a-c**, $Pd(dba)_2$ (8 mol%), BINAP (9 mol%) and dioxane to make 0.02 M solution, the mixture was stirred for 2-3 min, then equimolar amount of appropriate polyamine **1a-c** and ^{t}BuONa (3 equiv.) were added, and the reaction mixture was refluxed for 6-10 h. After cooling it down to ambient temperature the reaction mixture was diluted with CH_2Cl_2, the residue was filtered off, the organic solvents were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2/MeOH (200:1–3:1), CH_2Cl_2/MeOH/NH_3aq (100:20:1–10:4:1).

Cyclic dimer ***7a***. Obtained from compound **4a** (70 mg, 0.13 mmol), dioxadiamine **1a** (19 mg, 0.13 mmol), in the presence of $Pd(dba)_2$ (6 mg, 0.01 mmol), BINAP (7.3 mg, 0.012 mmol), ^{t}BuONa (37 mg, 0.39 mmol), in 6.5 ml dioxane. Eluent CH_2Cl_2/MeOH 75:1. Yield 8 mg (11 %), yellowish glassy compound. (MALDI-TOF) found: 544.3018. $C_{32}H_{40}N_4O_4$ requires 544.3050 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 3.28 (8H, t, ^3J = 5.2 Hz), 3.66 (8H, s), 3.70 (8H, t, ^3J = 5.1 Hz), 4.15 (4H, br.s), 6.44 (4H, d, ^4J = 2.1 Hz), 6.64 (4H, dd, ^3J = 8.8 Hz, ^4J = 2.1 Hz), 7.41 (4H, d, ^3J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 43.6 (4C), 69.5 (4C), 70.2 (4C), 104.5 (4C), 113.3 (4C), 121.7 (2C), 128.7 (4C), 136.8 (2C), 146.3 (4C).

Cyclic dimer ***7b***. Obtained from compound **4b** (148 mg, 0.24 mmol), trioxadiamine **1b** (52 mg, 0.24 mmol), in the presence of $Pd(dba)_2$ (11 mg, 0.019 mmol), BINAP (13 mg, 0.021 mmol), ^{t}BuONa (70 mg, 0.72 mmol), in 12 ml dioxane. Eluent CH_2Cl_2/MeOH 100:1-50:1. Yield 45 mg (28 %), yellowish glassy compound. (MALDI-TOF) found: 688.41. $C_{40}H_{56}N_4O_6$ requires 688.42 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.88 (8H, quintet, ^3J = 6.0 Hz), 3.27 (8H, t, ^3J = 6.4 Hz), 3.59 (8H, t, ^3J = 5.8 Hz), 3.59–3.62 (8H, m), 3.66–3.70 (8H, m), 4.12 (4H, br.s), 6.51 (4H, d, ^4J = 1.9 Hz), 6.57 (4H, dd, ^3J = 8.6 Hz, ^4J = 2.0 Hz), 7.39 (4H, d, ^3J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.1 (4C), 41.7 (4C), 69.6 (4C), 70.3 (4C), 70.7 (4C), 103.3 (4C), 113.6 (4C), 121.3 (2C), 128.5 (4C), 137.0 (2C), 146.7 (4C).

A mixture of cyclic tetramer and hexamer **10b** (n = 3, 5) was obtained as by-product in the synthesis of the cyclic dimer **7b**. Eluent CH_2Cl_2/MeOH 10:1. Yield 18 mg (11 %), yellowish glassy compound. (MALDI-TOF) found: 1376.75. $C_{80}H_{112}N_8O_{12}$ requires 1376.84 $[M]^+$ for 10b (n = 3). found: 2065.09. $C_{120}H_{168}N_{12}O_{18}$ requires 2065.26 $[M]^+$ for 10b (n = 5). ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.89 (4(n+1)H, br.s), 3.26 (4(n+1)H, t, ^3J = 5.7 Hz), 3.59 (8(n+1) H, br.s), 3.66 (4(n+1)H, br.s), 6.54 (2(n+1)H, d, ^3J = 9.3 Hz), 6.57 (2(n+1)H, br.s), 7.38 (2(n+1)H, d, ^3J = 9.3 Hz), NH protons were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.1 (2(n+1)C), 41.7 (2(n+1)C), 69.8 (2(n+1)C), 70.2 (2(n+1)C), 70.6 (2(n+1)C), 102.9 (2(n+1)C), 113.8 (2(n+1)C), 118.1 ((n+1)C), 128.5 (2(n+1) C), 137.0 ((n+1)C), 146.7 (2(n+1)C).

Cyclic dimer ***7c***. Obtained from compound **4c** (158 mg, 0.3 mmol), tetraamine **1c** (52 mg, 0.3 mmol), in the presence of $Pd(dba)_2$ (14 mg, 0.024 mmol), BINAP (17 mg, 0.027 mmol), ^{t}BuONa (86 mg, 0.9 mmol), in 15 ml dioxane. Eluent CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yield 37 mg (21 %), yellowish glassy compound. (MALDI-TOF) found: 596.4221. $C_{36}H_{52}N_8$ requires 596.4314 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.73 (8H, quintet, ^3J = 6.2 Hz), 2.69 (8H, t, ^3J = 6.4 Hz), 2.71 (8H, s), 3.19 (8H, t, ^3J = 6.4 Hz), 6.52–6.58 (8H, m), 7.38 (4H, d, ^3J = 9.0 Hz), NH protons were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.3 (4C), 42.7 (4C), 47.8 (4C), 48.9 (4C), 103.3 (4C), 113.5 (4C), 121.3 (2C), 128.6 (4C), 137.0 (2C), 146.7 (4C).

Cyclic tetramer **10c** (n = 3) was obtained as the second product in the synthesis of the cyclic dimer **7c**. Eluent CH_2Cl_2/MeOH/NH_3aq 10:4:1. Yield 19 mg (11 %), yellowish glassy compound. (MALDI-TOF) found: 1192.83. $C_{72}H_{104}N_{16}$ requires 1192.86 $[M]^+$. ^{1}H NMR (DMSO-d_6, 298 K) δ_H ppm: 1.74 (16H, br.s), 2.69 (32H, br.s), 3.08 (16H, br.s), 5.59 (8H, br.s), 6.41 (8H, br.s), 6.53 (8H, d, ^3J = 8.1 Hz), 7.26 (8H, d, ^3J = 8.1 Hz), NH protons of dialkylamino groups were not assigned. ^{13}C NMR (DMSO-d_6, 298 K) δ_c ppm: 28.0 (8C), 41.0 (8C), 46.7 (8C), 47.5 (8C), 101.1 (8C), 113.1 (8C), 119.7 (4C), 127.9 (8C), 137.1 (4C), 146.9 (8C).

*Cyclic dimer **7ab***. Obtained from compound **4b** (105 mg, 0.17 mmol), dioxadiamine **1a** (25 mg, 0.17 mmol), in the presence of $Pd(dba)_2$ (8 mg, 0.014 mmol), BINAP (9 mg, 0.014 mmol), ^{t}BuONa (49 mg, 0.51 mmol), in 8 ml dioxane. Eluent CH_2Cl_2/MeOH 50:1. Yield 14 mg (13 %), yellowish glassy compound. (MALDI-TOF) found: 616.50. $C_{36}H_{48}N_4O_5$ requires 616.36 $[M]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.91 (4H, quintet, ^3J = 6.0 Hz), 3.26-3.40 (8H, m), 3.57-3.75 (20H, m), 4.13 (4H, br.s), 6.59-6.65 (8H, m), 7.40 (2H, d, ^3J = 8.4 Hz), 7.42 (2H, d, ^3J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.0 (2C), 41.7 (2C), 43.7 (2C), 69.5 (2C), 69.8 (2C), 70.2 (4C), 70.6 (2C), 102.9 (2C), 103.5 (2C), 113.9 (2C), 114.0 (2C), 121.6 (2C), 128.5 (2C), 128.6 (2C), 136.9 (2C), 146.4 (2C), 146.7 (2C).

*Typical procedure for the synthesis of cyclic dimers **7** via bis(polyamine) derivatives **5***.

A two-neck flask equipped with a condenser and magnetic stirrer, flushed with argon, was charged with 2,7-dibromonaphthalene (143 mg, 0.5 mmol), $Pd(dba)_2$ (11.5 mg, 0.02 mmol, 4 mol%), diphosphine ligand (15 mg of Xantphos or 14 mg of BINAP, 0.023 mmol, 4.5 mol%), 5 ml of dioxane. The mixture was stirred for 2-3 min, then appropriate polyamine **1a-c** (2 mmol) and ^{t}BuONa (144 mg, 1.5 mmol) were added and the reaction mixture was refluxed for 4-6 h. After cooling it down to ambient temperature an aliquot (0.5 ml) was taken and analyzed using NMR and MALDI-TOF spectroscopy. Then 2,7-dibromonaphthalene (386 mg, 1.35 mmol), $Pd(dba)_2$ (62 mg, 0.11 mmol, 8 mol%), BINAP (76 mg, 0.12 mmol, 9 mol%), 20 ml abs. dioxane and ^{t}BuONa (390 mg, 4 mmol) were added, and the reaction mixture was refluxed for 6-15 h. After cooling it down to ambient temperature the reaction mixture was diluted with CH_2Cl_2, the residue was filtered off, the organic solvents were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2/MeOH (200:1–3:1), CH_2Cl_2/MeOH/NH_3aq (100:20:1–10:4:1).

*N^2,N^7-Bis(2-(2-(2-aminoethoxy)ethoxy)ethyl)naphthalene-2,7-diamine, **5a***. Obtained *in situ* using Xantphos ligand and 296 mg of dioxadiamine **1a**. (MALDI-TOF) found: 421.32. $C_{22}H_{37}N_4O_4$ requires 421.28 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 2.83 (4H, t, ^3J = 5.2 Hz), 3.35 (4H, t, ^3J = 4.9 Hz), 3.47 (4H, t, ^3J = 5.2 Hz), 3.59-3.63 (8H, m), 3.72 (4H, t, ^3J = 5.3 Hz), 4.23 (2H, br.s), 6.58-6.61 (4H, m), 7.41 (2H, d, ^3J = 9.3 Hz). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 41.7 (2C), 43.4 (2C), 69.5 (2C), 70.2 (4C), 73.3 (2C), 103.3 (2C), 114.1 (2C), 121.6 (1C), 128.6 (2C), 136.7 (1C), 146.3 (2C).

*Cyclic dimer **7a*** was synthesized from *in situ* obtained compound **5a**. Eluent CH_2Cl_2/MeOH 75:1. Yield 26 mg (10 %). Spectral data are given above. A mixture of cyclic trimer and tetramer **7a** (n = 2, 3) was obtained as the side product. Eluent CH_2Cl_2/MeOH 50:1-20:1. Yield 58 mg (21 %). (MALDI-TOF) found: 816.41. $C_{48}H_{60}N_6O_6$ requires 816.46 $[M]^+$ for **7a** (n = 2). found: 1088.67. $C_{64}H_{80}N_8O_8$ requires 1088.60 $[M]^+$ for **7a** (n = 3). ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 3.30-3.40 (4(n+1)H, m), 3.60-3.75 (8(n+1)H, m), 6.56-6.64 (4(n+1)H, m), 7.32-7.46 (2(n+1) H, m). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 43.4 (2(n+1)C), 69.4 + 69.5 (2(n+1)C), 70.1 (2(n+1)C), 103.4 (2(n+1)C), 114.0 (2(n+1)C), 128.7 (2(n+1)C), 146.3 (2(n+1)C), 2(n+1) quaternary carbon atoms were not assigned.

*N^2,N^7-Bis(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)-naphthalene-2,7-diamine, **5b***. Obtained *in situ* using Xantphos ligand and 440 mg of trioxadiamine **1b**. (MALDI-TOF) found: 565.44. $C_{30}H_{53}N_4O_6$ requires 565.40 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.63 (4H, quintet, ^3J = 6.5 Hz), 1.86 (4H, quintet, ^3J = 6.1 Hz), 2.68 (4H, t, ^3J = 6.8 Hz), 3.22 (4H, t, ^3J = 6.5 Hz), 3.46 (4H, t, ^3J = 6.2 Hz), 3.47-3.58 (20H, m), 6.48-6.52 (4H, m), 7.32 (2H, d, ^3J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 28.8 (2C), 33.1 (2C), 39.2 (2C), 41.5 (2C), 69.3 (2C), 69.6 (4C), 70.0 (2C), 70.1 (2C), 70.4 (2C), 102.7 (2C), 113.6 (2C), 121.0 (1C), 128.3 (2C), 136.8 (1C), 146.5 (2C).

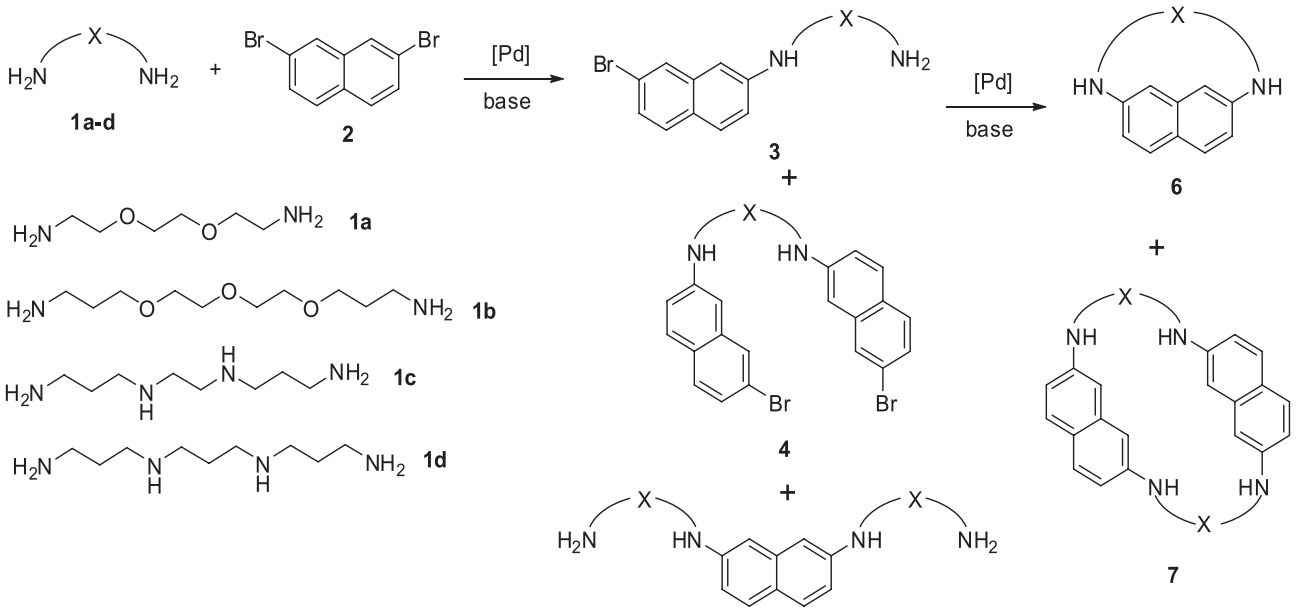
*Cyclic dimer **7b*** was synthesized from *in situ* obtained compound **5b**. Eluent CH_2Cl_2/MeOH 50:1. Yield 104 mg (30 %). Spectral data are given above. Macrocycle 6b was obtained as the side product. Eluent CH_2Cl_2/MeOH 200:1. Yield 100 mg (24 %). Spectral data are given in ref.[14] A mixture of cyclic trimer, tetramer and pentamer **10b** (n = 2-4) was obtained as the side product. Eluent CH_2Cl_2/MeOH 20:1. Yield 90 mg (25 %). (MALDI-TOF) found: 1032.55. $C_{60}H_{84}N_6O_9$ requires 1032.63 $[M]^+$ for **10b** (n = 2). found: 1376.95. $C_{80}H_{112}N_8O_{12}$ requires 1376.84 $[M]^+$ for **10b** (n = 3). found: 1721.12. $C_{100}H_{140}N_{10}O_{15}$ requires 1721.05 $[M]^+$ for **10b** (n = 4). ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.91 (4(n+1)H, quintet, ^3J = 6.1 Hz), 3.27 (t, ^3J = 5.9 Hz) + 3.28 (t, ^3J = 6.2 Hz) (4(n+1)H), 3.56-3.62 (8(n+1)H, m), 3.66-3.69 (4(n+1)H, m), 4.00 (2(n+1)H, br.s), 6.53-6.61 (4(n+1)H, m), 7.40 (d, ^3J = 8.0 Hz) + 7.41 (d, ^3J = 8.5 Hz) (2(n+1)H). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.0 (2(n+1)C), 41.6 (2(n+1)C), 69.7 (2(n+1)C), 70.1 (2(n+1)C), 70.5 (2(n+1)C), 102.8 (2(n+1)C), 113.7 (2(n+1)C), 121.2 ((n+1)C), 128.4 (2(n+1) C), 137.0 ((n+1)C), 146.6 (2(n+1)C).

*N^1,$N^{1'}$-(Naphthalene-2,7-diyl)bis(N^3-(3-(3-aminopropyl-amino)propyl)propane-1,3-diamine), **5d***. Obtained *in situ* using BINAP ligand and 376 mg of tetraamine **1d**. (MALDI-TOF) found: 501.41. $C_{28}H_{53}N_8$ requires 501.44 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.52-1.63 (8H, m), 1.77 (4H, quintet, ^3J = 6.6 Hz), 2.55-2.70 (20H, m), 3.19 (4H, t, ^3J = 6.4 Hz), 6.49-6.55 (4H, m), 7.35 (2H, d, ^3J = 8.6 Hz). ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.2 (2C), 30.2 (2C), 33.6 (2C), 40.2 (2C), 42.7 (2C), 47.7 (4C), 48.4 (4C), 102.8 (2C), 113.6 (2C), 121.1 (1C), 128.4 (2C), 136.9 (1C), 146.6 (2C).

*Cyclic dimer **7d*** was synthesized from *in situ* obtained compound **5d**. Eluent CH_2Cl_2/MeOH/NH_3aq 100:25:5, yellow glassy compound. Yield 75 mg (22 %). (MALDI-TOF) found: 625.4662. $C_{38}H_{57}N_8$ requires 625.4706 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.67 (4H, quintet, ^3J = 5.7 Hz), 1.74 (8H, quintet, ^3J = 6.3 Hz), 2.64-2.72 (16H, m), 3.15 (8H, t, ^3J = 6.3 Hz), 4.14 (4H, br.s), 6.52-6.56 (8H, m), 7.38 (4H, d, ^3J = 9.1 Hz), NH protons of dialkylamino groups were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.0 (6C), 42.7 (4C), 48.1 (4C), 48.9 (4C), 103.1 (4C), 113.6 (4C), 121.2 (2C), 128.5 (4C), 137.0 (2C), 146.7 (4C). Macrocycle 6d was obtained as the side product. Eluent CH_2Cl_2/MeOH/NH_3aq 100:25:5. Yield 65 mg (19 %). Spectral data are given in ref.[14] *Cyclic trimer* **10d** (n = 2) was obtained as the side product. Eluent CH_2Cl_2/MeOH/NH_3aq 10:4:1. Yield 80 mg (24 %), yellow glassy compound. (MALDI-TOF) found: 937.68. $C_{57}H_{85}N_{12}$ requires 937.70 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 1.55-1.82 (18H, m), 2.56-2.74 (24H, m), 3.18 (12H, t, ^3J = 6.1 Hz), 4.24 (6H, br.s), 6.52 (6H, d, ^3J = 8.5 Hz), 6.57 (6H, br.s), 7.38 (6H, d, ^3J = 8.5 Hz), NH protons of dialkylamino groups were not assigned. ^{13}C NMR ($CDCl_3$, 298 K) δ_c ppm: 29.2 (6C), 30.1 (2C), 42.7 (6C), 48.4 (12C), 102.9 (6C), 113.7 (6C), 128.5 (6C), 137.0 (3C), 146.7 (6C), three quaternary carbon atoms were not assigned.

Results and Discussion

Our synthetic aproach to the nitrogen- and oxygen-containing macrocycles based on 2,7-diaminonaphthalene is represented in Scheme 1. To synthesize the macrocycles **6** bearing the naphthalene fragment in the cycle, two successive Pd-catalyzed amination reactions of 2,7-dibromonaphtalene with a linear polyamine molecule should be carried out, which proceed in a one-pot manner when the synthesis of the macrocycles **6** is the synthetic goal (Scheme 1). The first amination reaction affords a linear intermediate compounds **3** whose intramolecular macrocyclization leads to the target compounds **6**. The cyclization competes with the formation of linear compounds: *N,N*'-bis(7-bromonaphth-2-yl) substituted polyamines **4** and 2,7-bis(polyamine)

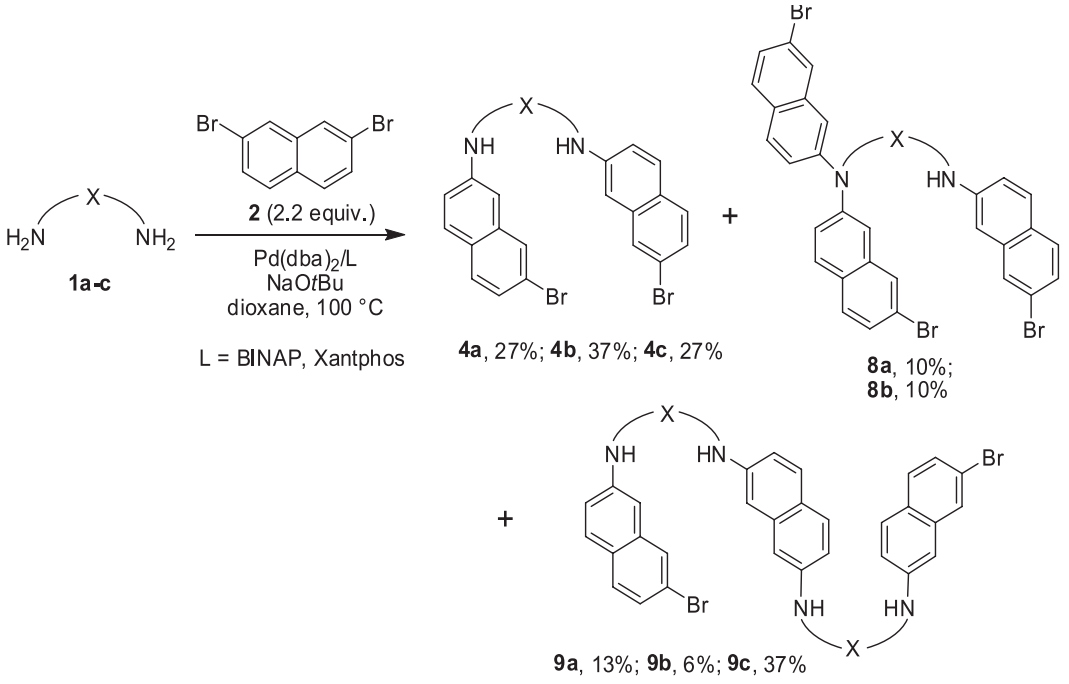


Scheme 1.

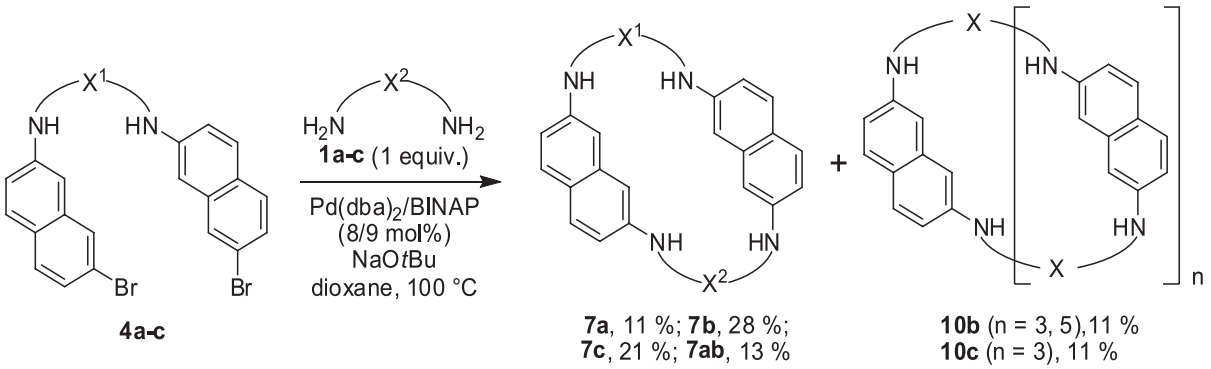
substituted naphthalenes **5**. By changing catalytic system and reaction conditions, we have shown how to manage this process and achieve good yields of the macrocycles **6**.[14] The best yields of the macrocycles were obtained when the starting compounds were reacted in the stoichiometric ratio. Interestingly, cyclodimers **7** were often isolated in notable yields under these conditions. These large macrocycles represent a new family of macrocyclic ligands and are of potential interest for supramolecular studies. Thus we focused on the development of the catalytic conditions for the synthesis of these large macrocycles. According to Scheme 1, target cyclodimers **7** can be formed from either intermediate **4** or intermediate **5**, and herein we compare these two synthetic approaches with the objective to find an optimal synthetic route to these ligands.

According to the first synthetic route, *N,N'*-bis(7-bromonaphth-2-yl) substituted polyamines **4a-c** were synthesized using the Pd-catalyzed reaction of 1 equiv. of di- and polyamines **1a-c** with 2.2 equiv. of 2,7-dibromonaphthalene (**2**) (Scheme 2).

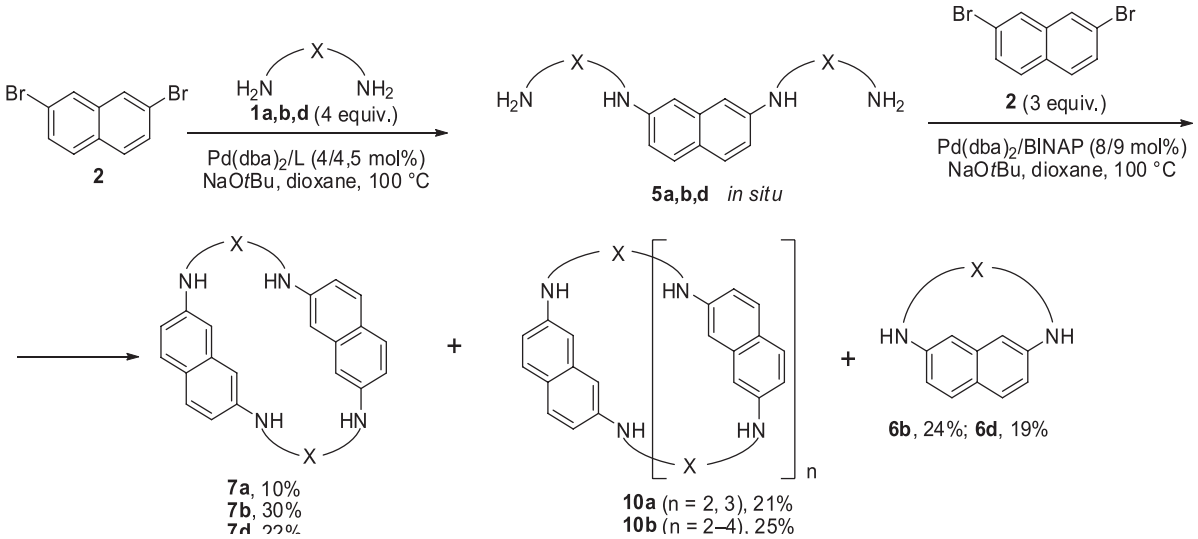
The reactivity of oxadiamines **1a**,**b** and polyamine **1c** was found to be significantly different. At first we carried out the cross-coupling reaction using a catalytic system $Pd(dba)_2$/BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene) which was found to be efficient in the synthesis of *N,N'*-bis(haloaryl) substituted di-



Scheme 2.



Scheme 3.



Scheme 4.

and polyamines.[17] However, in the case of dioxa- and trioxadiamines **1a**,**b**, side products like *N,N*-diarylated diamines **8a**,**b** and linear oligomers **9a**,**b** were predominant in the reaction mixtures, and the target compounds **4a**,**b** could not be isolated in pure form. We changed BINAP for a less efficient ligand Xantphos (9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene) and diluted the reaction mixtures (0.05 M solutions instead of usual 0.1-0.2 M were used). As a result, we managed to isolate target diarylated oxadiamines **4a**,**b** in moderate yields together with *N,N,N'*-triarylated amines **8a**,**b** and more complex oligomers **9a**,**b** resulting from the diamination reaction. The *N,N'*-diarylation of the tetraamine **1c** should be conducted using BINAP as ligand because Xantphos was not efficient for this reaction. Under these conditions, the target product **4c** and compound **9c** were obtained as major products and were isolated in pure form by column chromatorgphy.

The *N,N'*-bis(bromonaphthyl) derivatives **4a-c** were introduced in the Pd-catalyzed macrocyclization reaction with the same polyamines **1a-c** (Scheme 3). In this case we applied 8 mol% of the catalytic system $Pd(dba)_2$/BINAP, equimolar amounts of starting compounds and 0.02 M solutions of the reactants in dioxane. The best yield of the cyclodimers **7** was obtained for trioxadiamine derivative **7b** (28 %), tetraamine **1c** provided 21 % yield of the compound **7c**, while the short dioxadiamine **1a** gave a poor yield of the corresponding cyclodimer **7a** (11 %). The unsymmetric macrocycle **7a**,**b** was obtained upon reacting compound **4b** with dioxadiamine **1a**. Cyclic tetramers and hexamers **10b**,**c** were also isolated as by-products in these reactions.

An alternative method for the synthesis of cyclodimers included the formation of 2,7-bis(polyamine)substituted naphthalenes **5a**,**b**,**d** which cannot be separated by the column chromatography in pure form and were used *in situ* (Scheme 4). The reactions were conducted using 4 equiv. of di- and polyamines **1a**,**b**,**d** in dioxane (0.1 M solutions) in the presence of 4 mol% of the catalyst. As in the synthesis of *N,N'*-bis(bromonaphthyl) substituted polyamines **4**, Xantphos was applied in the reactions with dioxa- and trioxadiamines **1a**,**b** and BINAP was used for tetraamine **1d**. After NMR analysis proving that compounds **5a**,**b**,**d** were the major products in the reaction mixtures, 3 equiv. of 2,7-dibromonaphthalene (**2**), 8 mol% of $Pd(dba)_2$/BINAP catalytic system, additional amounts of ^{t}BuONa and dioxane were added and the reaction mixtures were refluxed for 24 h. The best yield of the cyclodimer was obtained in the case of trioxadiamine (**7b**, 30 %), compound **7d** was isolated in 22 % yield, while the product **7a** containing two dioxadiamine chains again was obtained in a low yield (10 %). Cyclic oligomers of higher masses **10a**,**b**,**d** were isolated in comparable yields 21-25 % in all cases, and also we observed the formation of the macrocycles comprising one naphthalene and one

polyamine unit **6b**,**d**. The latter compounds were formed at the second step of the process due to the presence of the excess of polyamines **1** in the reaction mixture which were not consumed at the first step.

Conclusions

To sum up, we investigated two alternative approaches for the synthesis of macrocycles comprising two naphthalene and two polyamine moieties (cyclodimers) based on the Pd-catalyzed amination reaction. The first one, including the synthesis of *N,N'*-bis(7-bromonaphth-2-yl) substituted polyamines, needs chromatographic isolation of these intermediate compounds due to the formation of by-products. The second route is a one-pot method with the formation of 2,7-bis(polyamine) substituted naphthalenes which are used *in situ* in the second macrocyclization step. Two synthetic routes were compared for different target cyclodimers. Optimization of experimental conditions are needed in both synthetic routes and the nature of the catalyst is a key factor influencing the product yields. The optimization of the one-pot reaction seems to be easier and better overall yields of the target cyclic dimers were obtained. Xantphos ligand was shown to be efficient for the synthesis of naphthalene linear derivatives with oxadiamines, while BINAP was found to be useful in the analogous reactions with tetraamine and in all macrocyclization reactions. Careful optimization of catalytic conditions allows to achieve the overall product yields up to 30 % without employing multistep methodologies.

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