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Cu$^{\mathrm{I}}$-mediated modification of polyamines with fluorophore groups

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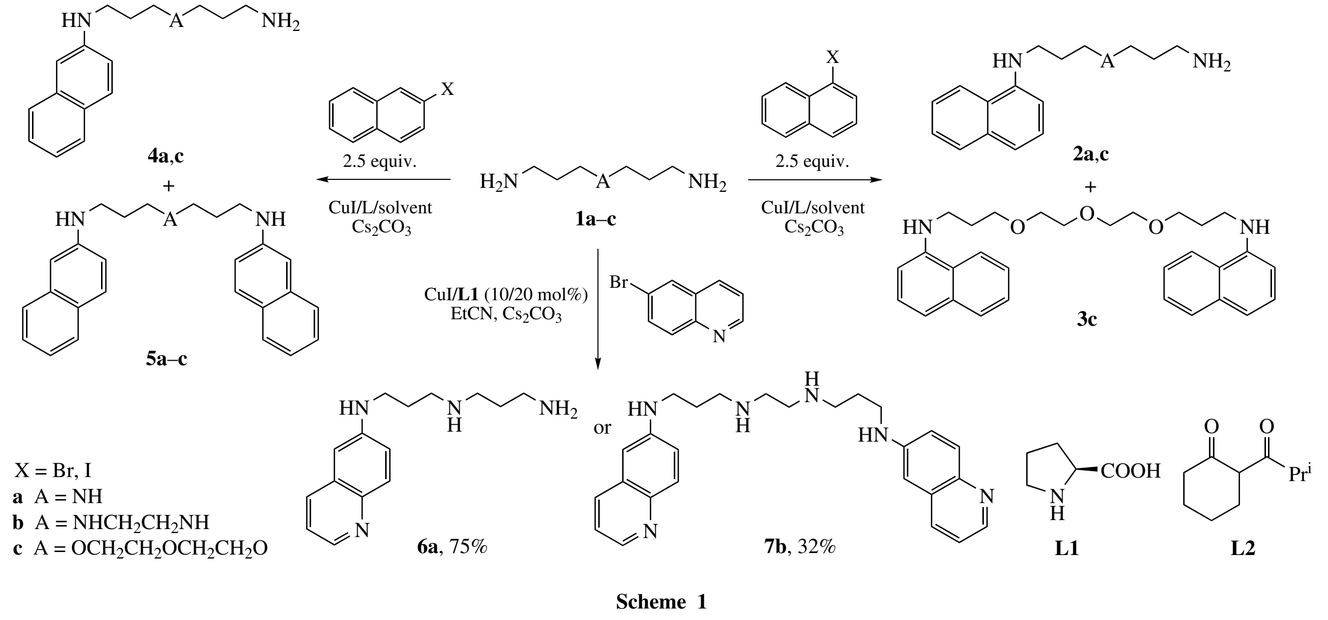
Copper(I)-catalyzed amination of halonaphthalenes and 6-bromoquinoline with α,ω-diamines $A[(CH_2)_3NH_2]_2$ [A = NH, $NH(NH_2)_2NH$, $O(CH_2CH_2O)_2$] affords α-mono- and/or α,ω-disubstitution products.

Decoration of linear and cyclic molecules, able to coordinate metal cations, with various fluorophore groups has been an important part of creating fluorescent chemosensors.[1] The majority of reported compounds were obtained from simple diamines and triamines, *e.g.*, their dansyl derivatives.[2–5] Anthracene-based chemosensors with polyamine receptor moieties were synthesized on the basis of triethylenetetraamine and contained one or two fluorophore groups,[6] as well as on the basis of two ethylenediamine groups attached to 9- and 10-positions of anthracene *via* methylene bridges.[7] Cyclene was also decorated with 9-anthrylmethyl group,[8,9] fluorosceine fluorophore,[10] and substituted 8-hydroxyquinoline.[11] Linear polyamines were modified with benzoxadiazole group for constructing diagnosis tools in the treatment of cancerous tumors;[12] it is interesting that mono-N^1-dansyl spermine was tested as a novel polyamine analogue and showed itself to be an antagonist of the stimulatory polyamine site on the NMDA receptor macrocomplex.[13] Tripodal heptaamine was substituted with three identical 1-naphthylmethyl groups for the studies of intramolecular excimer formation,[14] indole-containing ethylenediamine and diethylenetriamine were immobilized on a support.[15] *N*,*N*-Di(2-picolyl)ethylenediamine also became a widely used receptor which was decorated with fluorosceine,[16] tricarbocyanine,[17] and naphthalimide fluorophores.[18]

All the above-mentioned compounds do not contain direct link between nitrogen atom and fluorophore group. In many cases it would be preferable for the enhancement of fluorescent properties. Obviously, such *N*-aryl bond can be readily constructed using C–N cross-coupling methodology in view of our recent experience in Cu$^{\mathrm{I}}$-catalyzed arylation and heteroarylation of polyamines.[19–22] For this purpose we subjected linear triamine **1a**, tetraamine **1b**, and trioxadiamine **1c** to coupling with 1-bromo- and 1-iodonaphthalene, 2-bromo- and 2-iodonaphthalene, and 6-bromoquinoline (Scheme 1)[†] anticipating that aminonaphthyl and aminoquinolyl moieties in the products would possess fluorescent properties. Previously we demonstrated that these polyamines showed different reactivity towards substituted bromo- and iodobenzenes,[19] also their coordination of metal cations was different.



Scheme 1

[†] *Catalytic arylation of polyamines (general procedure).* A two-necked flask equipped with a magnetic stirrer was flushed with dry argon and charged with aryl halide (1.25 mmol), CuI (9.5 mg, 10 mol%), ligand **L1** (11.5 mg, 20 mol%) or **L2** (17 mg, 20 mol%), solvent (1 ml), appropriate amine (0.5 mmol) and Cs_2CO_3 (1.25 mmol, 420 mg). The reaction mixture was stirred under reflux (EtCN, MeCN) or at 140 °C (DMF) for 24–30 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (5 ml), the solid was filtered off, the filtrate was evaporated *in vacuo*, and the residue was analyzed by ^{1}H NMR spectroscopy. To obtain individual compounds, the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2–MeOH (50:1–3:1), CH_2Cl_2–MeOH–aq. NH_3 (100:20:1–10:4:1). Target compounds were obtained as yellow or brown viscous oils or solids.

We employed two catalytic systems which are most suitable for the polyamine and oxadiamine arylation, namely, CuI/L-proline (**L1**)/Cs_2CO_3/EtCN (for tri- and tetraamines) and CuI/2-(isobutyryl)cyclohexanone (**L2**)/Cs_2CO_3/DMF (for oxadiamines). The reactions with halonaphthalenes and 6-bromoquinoline were carried out using 2.5 equiv. of aryl halides to promote N,N′-diarylation, 0.5 M concentration of the polyamine component, 10 mol% CuI and 20% ligand, reaction time was 24–30 h (Table 1). No reaction was observed with 1-bromonaphthalene, thus we used more reactive 1-iodonaphthalene. In the reaction with triamine **1a** total conversion of the starting aryl iodide was moderate (entry 1), however, the reaction was enough selective and mononaphthyl derivative **2a** was isolated in 76% yield. The reaction between tetraamine **1b** and 1-iodonaphthalene was not selective presumably due to the competing arylation of the secondary amino groups, though we tried different combinations of ligands and solvents. In case of trioxadiamine **1c** the catalytic system CuI/**L2**/DMF provided enough high conversion of the starting aryl iodide (entry 2), and after chromatographic separation mono- (**2c**) and dinaphthyl (**3c**) derivatives were obtained.

Table 1 Synthesis of *N*-aryl derivatives of triamine **1a**, tetraamine **1b** and trioxadiamine **1c** *via* Cu^I-catalyzed amination reactions.

Entry	Aryl halide		Amine	Ligand	Solvent^a	Total conversion of aryl halide (%)	Product yield (%)^b
	Aryl	Hal					
1	1-naphthyl	I	**1a**	**L1**	EtCN	38	**2a** (76)
2	1-naphthyl	I	**1c**	**L2**	DMF	73	**2c** (30), **3c** (18)
3	2-naphthyl	Br	**1a**	**L1**	MeCN	69	**4a** (90)
4	2-naphthyl	Br	**1b**	**L1**	EtCN	48	**5b** (28)
5	2-naphthyl	I	**1a**	**L1**	EtCN	63	**5a** (18)
6	2-naphthyl	I	**1c**	**L2**	DMF	>95	**4c** (17), **5c** (46)
7	6-quinolyl	Br	**1a**	**L1**	EtCN	47	**6a** (75)
8	6-quinolyl	Br	**1b**	**L1**	EtCN	54	**7b** (32)

^{a} Reactions were run either in boiling EtCN and MeCN or in DMF at 140 °C. ^{b} Yields after chromatographic isolation.

2-Bromonaphthalene turned more reactive than its isomer and produced excellent yield of the triamine monoaryl derivative **4a** (90%, entry 3). Note that this reaction was conducted in MeCN. The conversion of 2-bromonaphthalene was almost the same in its reaction with tetraamine **2b**, however, the process was not enough selective and the target compound could not be isolated pure from the reaction mixture. When using standard EtCN as the solvent, N^1,N^4-dinaphthyl substituted tetraamine **5b** was obtained as a sole product (entry 4). However, the reactivity of this aryl bromide was insufficient to normally arylate trioxa-

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N^1*-(3-Aminopropyl)-*N^3*-(1-naphthyl)propane-1,3-diamine* **2a** was synthesized from 1-iodonaphthalene (318 mg) and triamine **1a** (66 mg). Eluent CH_2Cl_2/MeOH/aq. NH_3 (100:20:3). Yield 98 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.68 (quintet, 2H, *J* 6.9 Hz), 1.92 (quintet, 2H, *J* 6.2 Hz), 2.41 (br. s, 3H), 2.68 (t, 2H, *J* 7.0 Hz), 2.76 (t, 2H, *J* 6.8 Hz), 2.81 (t, 2H, *J* 6.3 Hz), 3.32 (t, 2H, *J* 6.3 Hz), 5.75 (br. s, 1H), 6.53 (d, 1H, *J* 7.6 Hz), 7.18 (d, 1H, *J* 8.2 Hz), 7.33 (t, 1H, *J* 7.9 Hz), 7.37–7.44 (m, 2H), 7.74–7.78 (m, 1H), 7.84–7.88 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 28.5, 33.0, 40.2, 43.7, 47.9, 49.0, 103.5, 116.6, 120.4, 123.4, 124.3, 125.5, 126.7, 128.4, 134.2, 144.1. MS (MALDI-TOF), *m/z*: 258.1914 $[M+H]^+$ (calc. for $C_{16}H_{24}N_3$, *m/z*: 258.1970).

N*-(1-Naphthyl)-4,7,10-trioxatridecane-1,13-diamine* **2c** was synthesized from 1-iodonaphthalene (318 mg) and trioxadiamine **1c** (110 mg). Eluent CH_2Cl_2/MeOH (20:1). Yield 52 mg (30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.63 (quintet, 2H, *J* 5.3 Hz), 2.12 (quintet, 2H, *J* 6.0 Hz), 2.87 (t, 2H, *J* 5.3 Hz), 3.41 (t, 2H, *J* 6.6 Hz), 3.44–3.48 (m, 4H), 3.53–3.57 (m, 2H), 3.63–3.71 (m, 4H), 3.81 (t, 2H, *J* 5.8 Hz), 6.67 (d, 1H, *J* 7.5 Hz), 7.24 (d, 1H, *J* 8.2 Hz), 7.32 (t, 1H, *J* 7.8 Hz), 7.40–7.47 (m, 2H), 7.74–7.78 (m, 1H), 7.96–8.00 (m, 1H) (3NH protons were not unambiguously assigned). MS (MALDI-TOF), *m/z*: 347.2279 $[M+H]^+$ (calc. for $C_{20}H_{31}N_2O_3$, *m/z*: 347.2335).

N,N′*-Di(1-naphthyl)-4,7,10-trioxatridecane-1,13-diamine* **3c** was obtained as the second product in the synthesis of compound **2c**. Eluent CH_2Cl_2/MeOH (100:1). Yield 42 mg (18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.06 (quintet, 4H, *J* 5.9 Hz), 3.41 (t, 4H, *J* 6.3 Hz), 3.61–3.65 (m, 4H), 3.68 (t, 4H, *J* 5.7 Hz), 3.72–3.76 (m, 4H), 5.10 (br. s, 2H), 6.63 (d, 2H, *J* 7.5 Hz), 7.26 (d, 2H, *J* 8.2 Hz), 7.39 (t, 2H, *J* 7.9 Hz), 7.42–7.50 (m, 4H), 7.80–7.83 (m, 2H), 7.85–7.88 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 28.7 (2C), 42.7 (2C), 70.3 (2C), 70.6 (4C), 103.8 (2C), 116.8 (2C), 120.1 (2C), 123.4 (2C), 124.4 (2C), 125.5 (2C), 126.6 (2C), 128.5 (2C), 134.3 (2C), 143.8 (2C). MS (MALDI-TOF), *m/z*: 473.2747 $[M+H]^+$ (calc. for $C_{30}H_{37}N_2O_3$, *m/z*: 473.2804).

N^1*-(3-Aminopropyl)-*N^3*-(2-naphthyl)propane-1,3-diamine* **4a** was synthesized from 2-bromonaphthalene (259 mg) and triamine **1a** (66 mg). Eluent CH_2Cl_2/MeOH/aq. NH_3 (100:25:5). Yield 116 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.65 (quintet, 2H, *J* 6.7 Hz), 1.86 (quintet, 2H, *J* 6.4 Hz), 2.10 (br. s, 3H), 2.69 (t, 2H, *J* 6.9 Hz), 2.78 (t, 2H, *J* 6.4 Hz), 3.28 (t, 2H, *J* 6.5 Hz), 4.56 (br. s, 1H), 6.77 (s, 1H), 6.86 (d, 1H, *J* 8.7 Hz), 7.16 (t, 1H, *J* 7.3 Hz), 7.33 (t, 1H, *J* 7.4 Hz), 7.59 (d, 2H, *J* 8.5 Hz), 7.64 (d, 1H, *J* 8.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 29.0, 33.1, 40.5, 42.9, 47.9, 48.4, 104.0, 118.1, 121.7, 125.8, 126.2, 127.3, 127.6, 128.8, 135.3, 146.2. MS (MALDI-TOF), *m/z*: 258.2030 $[M+H]^+$ (calc. for $C_{16}H_{24}N_3$, *m/z*: 258.1970).

N,N′*-Di(2-naphthyl)-4-azaheptane-1,7-diamine* **5a** was synthesized from 2-iodonaphthalene (318 mg) and triamine **1a** (66 mg). Eluent CH_2Cl_2/MeOH (3:1). Yield 34 mg (18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.12 (quintet, 4H, *J* 5.9 Hz), 3.02 (t, 4H, *J* 6.7 Hz), 3.24 (t, 4H, *J* 6.1 Hz), 6.67 (d, 2H, *J* 2.2 Hz), 6.79 (dd, 2H, *J* 8.7 and 2.2 Hz), 7.14–7.18 (m, 2H), 7.28–7.32 (m, 2H), 7.47 (d, 2H, *J* 8.7 Hz), 7.53 (d, 2H, *J* 8.2 Hz), 7.58 (d, 2H, *J* 8.0 Hz) (3NH protons were not unambiguously assigned). MS (MALDI-TOF), *m/z*: 384.2476 $[M+H]^+$ (calc. for $C_{26}H_{30}N_3$, *m/z*: 384.2440).

N,N′*-Di(2-naphthyl)-4,7-diazadecane-1,10-diamine* **5b** was synthesized from 2-bromonaphthalene (259 mg) and tetraamine **1b** (87 mg). Eluent CH_2Cl_2/MeOH/aq. NH_3 (100:20:2). Yield 59 mg (28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.83 (quintet, 4H, *J* 6.6 Hz), 2.75 (s, 4H), 2.77 (t, 4H, *J* 6.6 Hz), 3.27 (t, 4H, *J* 6.6 Hz), 4.24 (br. s, 2H), 6.78 (d, 2H, *J* 2.3 Hz), 6.84 (dd, 2H, *J* 8.8 and 2.3 Hz), 7.15–7.20 (m, 2H), 7.32–7.37 (m, 2H), 7.59 (d, 2H, *J* 8.8 Hz), 7.60 (d, 2H, *J* 8.1 Hz), 7.65 (d, 2H, *J* 8.1 Hz) (2NH protons were not unambiguously assigned). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 29.3 (2C), 42.7 (2C), 48.2 (2C), 49.3 (2C), 104.0 (2C), 118.0 (2C), 121.7 (2C), 125.8 (2C), 126.2 (2C), 127.3 (2C), 127.6 (2C), 128.8 (2C), 135.2 (2C), 146.1 (2C). MS (MALDI-TOF), *m/z*: 427.2819 $[M+H]^+$ (calc. for $C_{28}H_{35}N_4$, *m/z*: 427.2862).

N*-(2-Naphthyl)-4,7,10-trioxatridecane-1,13-diamine* **4c** was synthesized from 2-iodonaphthalene (318 mg) and trioxadiamine **1c** (110 mg). Eluent CH_2Cl_2/MeOH (20:1). Yield 29 mg (17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.73 (quintet, 2H, *J* 5.9 Hz), 1.94 (quintet, 2H, *J* 6.1 Hz), 3.32 (br. s, 2H), 3.38 (q, 2H, *J* 6.1 Hz), 3.55 (t, 2H, *J* 5.7 Hz), 3.58–3.69 (m, 10H), 4.32 (br. s, 1H), 6.78 (s, 1H), 6.88 (dd, 1H, *J* 8.7 and 2.2 Hz), 7.16 (t, 1H, *J* 7.5 Hz), 7.33 (t, 1H, *J* 7.5 Hz), 7.59 (d, 2H, *J* 8.5 Hz), 7.64 (d, 1H, *J* 8.1 Hz) (2NH protons were not unambiguously assigned). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 28.4, 28.9, 36.7, 41.7, 69.8, 70.0, 70.1, 70.2, 70.4, 70.5, 103.9, 118.1, 121.7, 125.8, 126.2, 127.3, 127.5, 128.7, 135.2, 146.2. MS (MALDI-TOF), *m/z*: 347.2389 $[M+H]^+$ (calc. for $C_{20}H_{31}N_2O_3$, *m/z*: 347.2335).

N,N′*-Di(2-naphthyl)-4,7,10-trioxatridecane-1,13-diamine* **5c** was obtained as the second produt in the synthesis of compound **4c**. Eluent CH_2Cl_2/MeOH (100:1). Yield 109 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.95 (quintet, 4H, *J* 6.1 Hz), 3.33 (t, 4H, *J* 6.5 Hz), 3.63 (t, 4H, *J* 5.8 Hz), 3.64–3.67 (m, 4H), 3.71–3.74 (m, 4H), 4.24 (br. s, 2H), 6.81 (d, 2H, *J* 2.3 Hz), 6.87 (dd, 2H, *J* 8.7 and 2.3 Hz), 7.19–7.24 (m, 2H), 7.36–7.41 (m, 2H), 7.62 (d, 2H, *J* 8.7 Hz), 7.63 (d, 2H, *J* 7.8 Hz), 7.68 (d, 2H, *J* 8.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 28.8 (2C), 41.8 (2C), 69.7 (2C), 70.1 (2C), 70.5 (2C), 103.9 (2C), 118.1 (2C), 121.8 (2C), 125.7 (2C), 126.1 (2C), 127.2 (2C), 127.5 (2C), 128.7 (2C), 135.2 (2C), 146.1 (2C). MS (MALDI-TOF), *m/z*: 473.2851 $[M+H]^+$ (calc. for $C_{30}H_{37}N_2O_3$, *m/z*: 473.2804).

diamine **2c**. More reactive 2-iodonaphthalene provided N^1,N^3-disubstituted triamine **5a** (entry 5), and again, the arylation of tetraamine **2b** was totally non-selective under various conditions. The reaction with a less reactive trioxadiamine **2c** provided its mono- and diaryl derivatives **4c** and **5c** in 17 and 46% yields, respectively (entry 6) in the presence of CuI/**L2**/DMF system. 6-Bromoqunoline was transformed into monoheteroarylated triamine **6a** in a high yield (75%, entry 7), and N^1,N^4-diquinolinyl derivative **7b** was obtained from tetraamine **2b** (entry 8).

In summary, iodo- and bromo-substituted naphthalene and quinoline produced mainly monosubstituted triamine derivatives. 2-Bromonaphthalene and 6-bromoquinoline were useful for the synthesis of N^1,N^4-disubstituted tetraamine, though in rather low yields, while iodonaphthalenes were too reactive to give only complex mixture with tetraamine **2b**. Both 1- and 2-iodonaphthalenes were good in the arylation of trioxadiamine. In view of the fact that polyamines and oxadiamines with one or two fluorophore groups are both valuable for the construction of fluorescent receptors as they possess amino groups useful for further transformations, the current results seem practically promising.

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N^1-*(3-Aminopropyl)*-N^3-*(quinolin-6-yl)propane-1,3-diamine* **6a** was synthesized from 6-bromoquinoline (260 mg) and triamine **1a** (66 mg). Eluent CH_2Cl_2/MeOH/aq. NH_3 (100:25:5). Yield 59 mg (28%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.51 (quintet, 2H, *J* 6.6 Hz), 1.74 (quintet, 2H, *J* 6.7 Hz), 2.52 (br.s, 2H), 2.60 (br.s, 4H), 3.13 (br.s, 2H), 6.24 (br.s, 1H), 6.64 (d, 1H, *J* 2.3 Hz), 7.20 (dd, 1H, *J* 9.1 and 2.3 Hz), 7.26 (dd, 1H, *J* 8.2 and 4.2 Hz), 7.69 (d, 1H, *J* 9.1 Hz), 7.95 (d, 1H, *J* 8.2 Hz), 8.45 (d, 1H, *J* 4.2 Hz) (3NH protons were not unambiguously assigned). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 28.7, 32.5, 41.3, 47.3, 47.4, 100.9, 121.3, 121.7, 129.3, 130.2, 133.1, 142.2, 144.8, 147.1 (one CH_2 carbon is overlapped by the CD_3 multiplet). MS (MALDI-TOF), *m/z*: 259.1870 [M+H]$^+$ (calc. for $C_{15}H_{23}N_4$, *m/z*: 259.1923).

N,N′-*Di(quinolin-6-yl)-4,7-diazadecane-1,10-diamine* **7b** was synthesized from 6-bromoquinoline (260 mg) and tetraamine **1b** (87 mg). Eluent CH_2Cl_2/MeOH/aq. NH_3 (100:20:2). Yield 60 mg (32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.79 (quintet, 4H, *J* 6.1 Hz), 2.72 (s, 4H), 2.74 (t, 4H, *J* 6.1 Hz), 3.20 (t, 4H, *J* 6.1 Hz), 4.67 (br.s, 2H), 6.58 (s, 2H), 7.02 (d, 2H, *J* 8.0 Hz), 7.15 (dd, 2H, *J* 8.1 and 4.0 Hz), 7.76–7.83 (m, 4H), 8.52 (d, 2H, *J* 4.0 Hz) (2NH protons were not unambiguously assigned). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 28.3 (2C), 42.2 (2C), 47.6 (2C), 48.3 (2C), 102.3 (2C), 121.2 (2C), 121.5 (2C), 129.8 (2C), 130.1 (2C), 133.6 (2C), 142.8 (2C), 145.6 (2C), 146.3 (2C). MS (MALDI-TOF), *m/z*: 429.2735 [M+H]$^+$ (calc. for $C_{26}H_{33}N_6$, *m/z*: 429.2767).

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