Facile synthesis of novel styryl ligands containing a 15-crown-5 ether moiety

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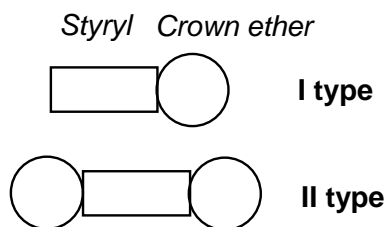E-mail: fedorova@photonics.ru*

Abstract

Novel ligands containing a 15-crown-5 ether moiety and six-membered heterocyclic residues with different combinations of N atoms were prepared by condensation of methyl-substituted six-membered heterocyclic bases with 4'-formylbenzo-15-crown-5 ether; the best results were obtained in the presence of *t*BuOK in DMF. For dimethyl-substituted heterocyclic bases as the initial heterocyclic components, the competition of mono- and bis-condensation reactions is analyzed. The role of complex formation in the syntheses is discussed.

Keywords: Methyl substituted pyridine, quinoline, bipyridine, phenanthroline, benzo-15-crown-5 ether, condensation

Introduction

Ligands containing two or more pyridine units can in principle be used as bridges to interconnect metal centers in a well-defined spatial arrangement.[1] The uses of such ligands as precursors for helical assembly,[2] chiral molecular recognition,[3] luminescent devices[4] and other applications in photonics and optoelectronics[5] and electrochemistry[6] have been reviewed elsewhere. The derivatives of pyridine, quinoline, and bipyridine containing styryl group in different positions have been prepared by condensation of heterocyclic methyl derivatives with substituted benzaldehydes under basic (Py,[7] piperidine,[8] NaOMe,[9] *t*BuOK,[10] lithium diisopropylamide[11]) or acidic conditions (ZnCl$_2$,[12] HCl,[13] acetic acid or acetic anhydride[14]). Wittig condensation was also used in the synthesis of ethylene-substituted bipyridines.[15]

We are interested in the design and synthesis of heterocyclic stilbene analogues containing an ionophoric fragment. In the design of the compounds, attention was paid to both stilbene and ionophoric parts. The simplified representation of the two types of prepared compounds is the following (Scheme 1):
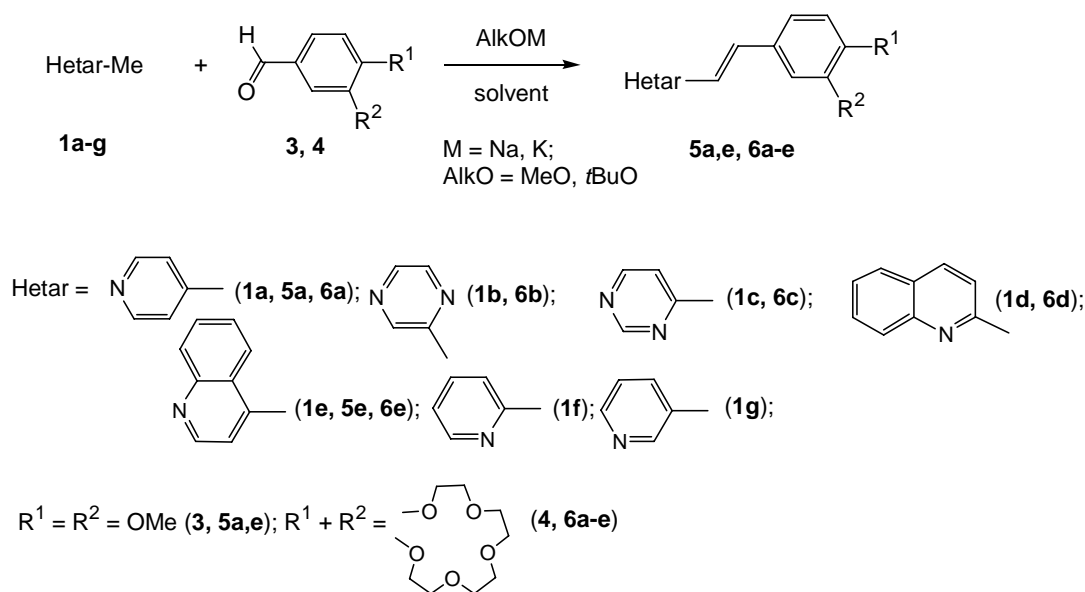
Styryl   Crown ether

I type

II type

Scheme 1. The simplified representation of crown-containing styryl derivatives.

These compounds may prove to be important for the development of novel chromo- and fluoroionophores, promising for ion analysis in chemistry, physics, and biology.[16a] The properties of the long-lived luminescent metal-to-ligand charge transfer state obtained for polypyridine transition metal complexes enable these compounds to sensitize photoinduced electron-transfer and energy-transfer porcesses.[16b-d] Only few stilbenes containing ionophoric groups and pyridine residues have been reported in the literature[17] up to now.

Results and Discussion

This paper deals with the study of condensation of 4'-formyl derivative of benzo-15-crown-5 ether with methyl-substituted six-membered heterocyclic bases (**1a-g, 2a-g**) containing one or two N atoms in the presence of alkali metal alkoxides (Schemes 2, 5) in DMSO or DMF at ambient temperature for 24 h to form **5a,e, 6a-e** and **7a, b, d-f**, **8c-f** in satisfactory to good yields, which are listed in Tables 1,2. In the method the commersial acceptable initial reagent are used, the condensation occurs in the mild reaction conditions what are the advantages of the described here method in comparison with widely used Wittig reaction and condensation in presence of lithium diisopropylamide.[11,15] Presented in the paper analysis of the influence of the heterocyclic component structure, nature of metal alkoxide and solvent allows the conclusion concerning the synthetic possibilities of method for the preparing of crown-containing stylbene ligands.

Scheme 2. Synthesis of the type I compounds.

The results of the experiments with variation of metal cations and solvents are shown in Table 1. The yields of **6d,e** are higher in the presence of *t*BuOK than with MeONa. The reaction does not occur in MeOH. The product yields are lower in the reactions carried out in DMSO than in DMF (Table 1). In our opinion, DMSO is not an inert solvent, it is able to condense with **4** in the presence of strong bases. It is known from the literature that condensation of heteroaromatic compounds with aromatic benzaldehyde proceeds without side reactions in DMF.[18]

The formation of **6e** is accompanied by the regioselective Michael reaction between **6e** and initial heterocyclic compound **1e** to yield bisheterocyclic product **9e** (Scheme 3).[19] To avoid the formation of **9e**, DMF should be used, instead of DMSO. The same result was acheived by the decrease of the amount of *t*BuOK in reaction mixture (Table 1).
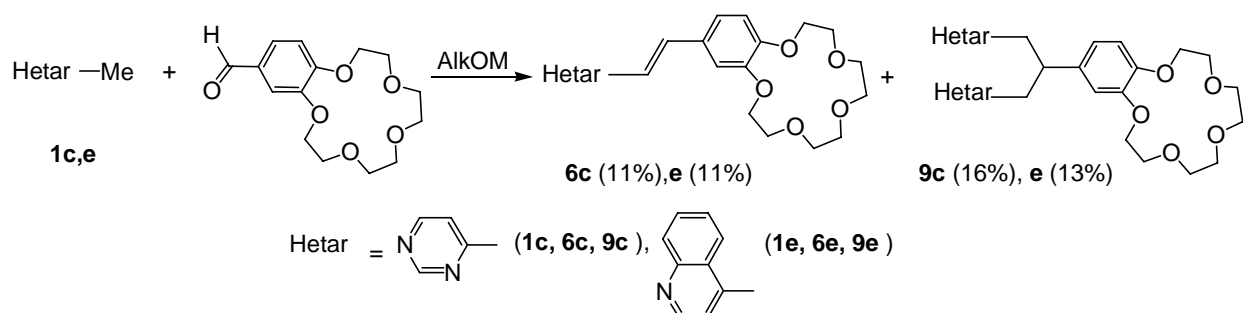
Condensation of compounds **1c** with **4** should be carried out with equimolar amounts of the reactants because an excess of the initial heterocyclic derivative **1c** induces the Michael reaction and affords a bisheterocyclic product **9c** (Scheme 3).

Analysis of the data obtained for the formation of compounds **5a,e** and **6a-e** from monomethyl-substituted heterocyclic bases **1a-e** permits one to conclude that the yields of **5a,e** and **6a-e** depend substantially on two main factors (Table 2). The first one is the acidity of the methyl group of the heterocyclic base (pK_a^{CH} is given in Table 2). Heterocyclic compounds possessing low acidity as 2- and 3-methylpyridine do not enter into the condensation. The yield of the product **6e** in the case of 4-methylquinoline derivative is the lowest compared to the yields of products **6a-d** listed in Table 2, while the acidity of the methyl group in this compound is the highest. This could be due to the steric factor, in particular, the *2*-position of the benzene ring relative to the methyl group may prevent the condensation involving the methyl substituent.

Table 1. Yields of **6a,c,d, 7a,d,e, 8c-e** in the presence of MeONa and *t*BuOK in MeOH, DMF, and DMSO

Hetar-Me	Product	Ratio Hetar-Me : **4** : AlkOM	Solvent	Yield, %
1a	**6a**	1 : 1 : 1 (MeONa)	DMSO	0
		1 : 1 : 1 (*t*BuOK)	DMSO	12
		5 : 1.5 : 1 (*t*BuOK)	DMSO	23
		5 : 1.5 : 1 (*t*BuOK)	DMF	78
1d	**6d**	1 : 1 : 1 (MeONa)	MeOH	0
		1 : 1 : 1 (MeONa)	DMSO	18
		1 : 1 : 1 (*t*BuOK)	DMSO	25
		1 : 1 : 1 (*t*BuOK)	DMF	47
		5 : 1.5 : 1 (*t*BuOK)	DMF	88
1e	**6e**	1 : 1 : 1 (MeONa)	MeOH	0
	6e + 9e	1 : 1 : 1 (*t*BuOK)	DMSO	11 + 16
	6e	1 : 1 : 0.1 (*t*BuOK)	DMSO	15
	6e	1 : 1 : 1 (*t*BuOK)	DMF	33
	6e	5 : 1.5 : 1 (*t*BuOK)	DMF	38
2a	**7a**	1 : 2.2 : 3 (*t*BuOK)	DMF	25
		2.5 : 1 : 1.5 (*t*BuOK)	DMF	24
2b	**7b**	1 : 2.2 : 3 (*t*BuOK)	DMF	20
		2.5 : 1 : 1.5 (*t*BuOK)	DMF	83
2c	**8c**	1 : 2 : 1 (*t*BuOK)	DMF	75
		5 : 1 : 0.5 (*t*BuOK)	DMF	55
2d	**7d + 8d**	1 : 2.2 : 3 (*t*BuOK)	DMF	56 + 5
	7d + 8d	1 : 2.2 : 5 (*t*BuOK)	DMF	5 + 5
	8d	5:1:1.5 (*t*BuOK)	DMF	4
2e	**7e + 8e**	1 : 2.2 : 3 (*t*BuOK)	DMF	9 + 10
	7e + 8e	2.5 : 1 : 1.5 (*t*BuOK)	DMF	54 + 10
2f	**7f + 8f**	1 : 2.2 : 3 (*t*BuOK)	DMF	33 + 69
	7f + 8f	2.5 : 1 : 1.5 (*t*BuOK)	DMF	37 + 18
2g	-	1 : 2.2 : 3 (*t*BuOK)	DMF	0
		2.5 : 1 : 1.5 (*t*BuOK)	DMF	0

According to ^{1}H NMR data, compound **9e** has a symmetrical structure; hence, the second heterocyclic molecule **1e** adds regioselectively to give only one isomer.
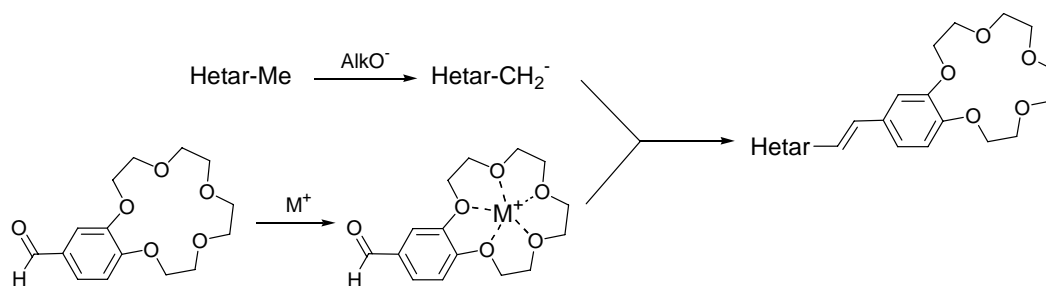
Scheme 3. Side reaction.

Comparison of the yields obtained for the crown-containing compound **6a** and analogous crown-free compound **5a** shows that the results for the crown-containing compound are much better. To interpret this phenomenon, we assumed that during the reaction, alkali metal alkoxides influence both the heterocyclic component by favouring proton abstraction and the formation of the reactive methylene derivative and the formyl component through the complexation with crown ether moieties (Scheme 4). The complexation of metal cations with the crown ether reactants brings about a situation when the ligand competes successfully with the anion for the cation, thus increasing the concentration of the anion not incorporated in ion pairs, which promotes efficient condensation. This phenomenon was found and analyzed in detail in our previous papers.[17]

Table 2. The yields of the compounds **5a,e, 6a-e** in the condensation of **1a-e** with **3** or **4** in DMF; reactant ratio Hetar-Me : **4(3)** : tBuOK = 5 : 1 : 1,5

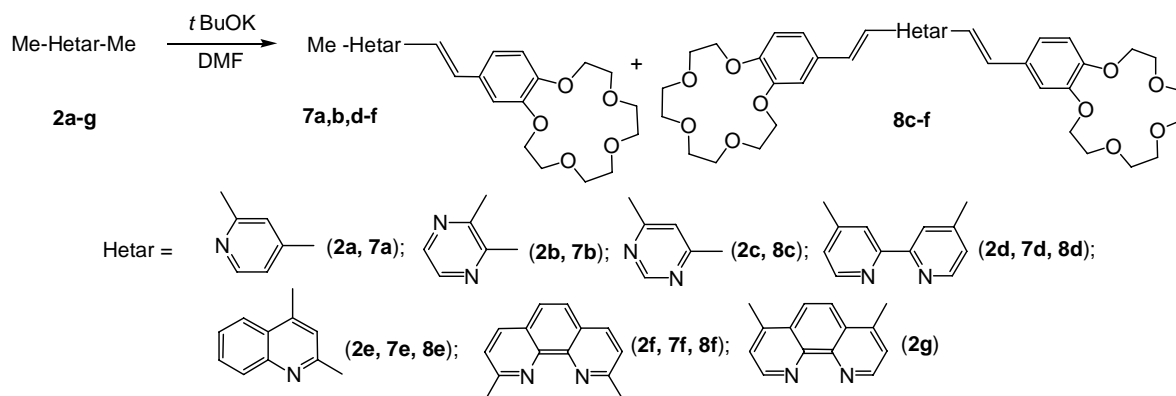| Hetar-Me	pK_a^{CH}	Product, yield in %	Hetar-Me	pK_a^{CH}	Products, yield, %
1a	25	**5a**, 28	**1c**	-	**6c,** 41*
1a	25	**6a,** 78	**1d**	23	0
1f	27	0	**1d**	23	**6d,** 88
1g	28	0	**1e**	22	**5e,** 38
1b	-	**6b,** 75	**1e**	22	**6e,** 38

* Equimolar amounts of reactants.

Scheme 4. Mechanism of the condensation reaction.

Condensation of dimethyl-substituted heterocyclic bases **2a-g** with **4** results in the formation of mono- (**7a,b,d-f**) and distyryl- (**8c-f**) derivatives (Scheme 5, Table 1). When a mixture of mono- and distyryl derivatives was formed, the individual components were separated by column chromatography on basic Al$_2$O$_3$ with a benzene/EtOH mixture as the eluent.

Based on the data for **2d-f** from Table 1, we can conclude that the content of the bisstyryl component can be increased by performing the condensation in the presence of an extra amount of formyl derivatives of benzocrown ether. Otherwise, an extra amount of the heterocyclic component in the reaction mixture leads to preferential formation of the monostyryl derivatives.
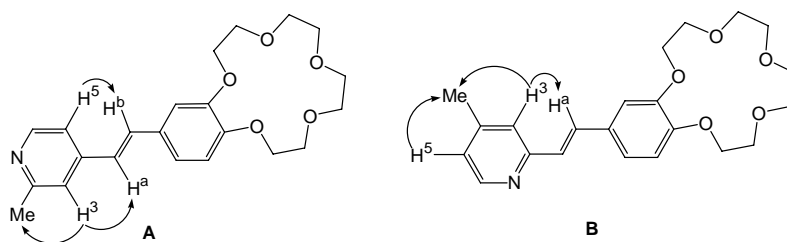

Scheme 5. Synthesis of the type II compounds.

As in the reaction of the monomethyl-substituted heterocyclic compounds **1a-g** with **4**, in the case of dimethyl-substituted heterocyclic compounds **2a-g**, the acidity of the methyl groups of **2a-g** and steric factor are significant. Thus, the closed arrangement of the Me groups in **2b** results in the formation of only monostyryl substituted product **7b**.

The reason for the formation of the monosubstituted product from **2a** is the large difference in acidity between the 2- and 4-methyl groups. As one can see from Table 2, the methyl group in 4-position is more acidic and it actively participates in the condensation. In compound **2c**, both methyl groups are in the 4-position to the N-heteroatom and are equally reactive in the condensation. In this case, it is impossible to control the formation of mono- or bis-products by
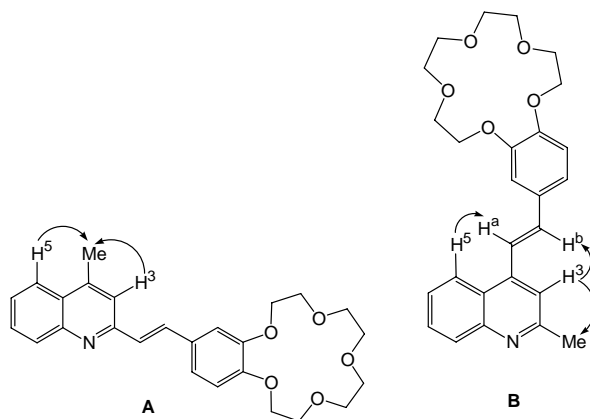
varying the ratio of the reactants. A deficiency of the heterocyclic component **2c** in the reaction between **2c** and **4** leads to a lower yield of bis-product **8c** instead of the formation of the mono-product (Table 1).

All compounds were formed as the *trans*-isomers, as indicated by the magnitudes of spin-spin coupling constants for the olefinic protons (15.9-16.2 Hz). The position of styryl substituents in **7a,e** was found from NOESY spectroscopy. Thus, the NOESY spectrum of compound **7a** exhibits cross-peaks corresponding to interaction between the protons H-5↔H-b and H-a↔H-3 (Scheme 6). The results indicate the formation of isomer **A**, which is the product of condensation with participation of the 4-Me group. In the case of the formation of isomer **B** containing the substituent in the 2-position, we find another combination of cross-peaks, as is pointed out on Scheme 6.

Scheme 6. The possible interaction between the protons of compound **7a**.

The NOESY spectrum of compound **7e** displays cross-peaks corresponding to the H-5↔Me↔H-3 interaction between protons (Scheme 7). The results indicate the formation of isomer **A**, which is the product of condensation involving the 2-Me group. In the case of isomer **B** containing the substituent in the 4-position, the interaction between protons H-5↔Me is impossible.

Scheme 7. The possible interaction between the protons of compound **7a**.

To summarize, we have found a simple and convenient route to hetarylphenylethenes containing a benzo-15-crown-5 ether fragment and six-membered heterocyclic bases with one or

two N atoms. The condensation of methyl-substituted six-membered heterocyclic bases with 4'-formylbenzo-15-crown-5 ether in the presence of *t*BuOK in DMF was carried out under mild conditions using a simple reaction procedure and gave the corresponding hetarylphenylethenes in good yields. In the case of dimethyl-substituted heterocyclic bases, it is possible to carry out selective mono-condensation using the difference in activity between the methyl substituents in 2-, 4- and 3-positions relative to the N-heteroatom. The condensation in the presence of *t*BuOK is accompanied by complex formation, which influences the efficiency of the reaction between crown ether aldehyde and the 2-methyl-substituted heterocyclic compound.

Experimental Section

General Procedures. Melting points [°C] were determined with a MEL-Temp II apparatus in a capillary and were not corrected. ^{1}H NMR spectra were recorded on a Bruker DRX500 instrument (500.13 MHz) for solutions in CDCl$_3$, [D$_6$]-DMSO or CD$_3$CN, the solvent being used as the internal reference (7.27, 2.50 and 1.96 ppm for ^{1}H, respectively); 2D homonuclear NOESY spectra were used to assign the proton and carbon signals. Electron impact mass spectra were measured at an ionizing voltage of 70 eV with a Finnigan MAT 8430 instrument. Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds in Moscow, Russia. The course of the reactions was monitored by TLC on Merck DC-Alufolien Aluminiumoxid 60 F$_{254}$ neutral (Typ E) and Kieselgel 60 F$_{254}$ plates. Column chromatography was performed with Merck Kieselgel 60 (0.063-0.100 mm) or Merck Aluminiumoxid 90 aktiv neutral (0.063-0.200 mm). Unless stated otherwise, the reagents and solvents were obtained from commercial sources and used as received. 4-Formylbenzo-15-crown-5 ethers (**4**)[20] were prepared according to published procedures.
Alkali metal alkoxides were prepared by dissolution of the alkali metal in anhydrous MeOH, evaporation of excess alcohol, and drying of the salt in vacuum.

Synthesis of the ligands 5a,e, 6a-e, 7a,b,d-f, 8c-f, 9c,e
A mixture of **1a-g** or **2a-g** (3 mmol), **3** or **4** (3-15 mmol) and alkali metal alkoxide (0.1-1.5 mmol) in 5 mL of anhydrous DMSO or DMF was kept at ambient temperature for 24 hours. After addition of distilled water (20 mL), the product was extracted with benzene or CH$_2$Cl$_2$ (4×30 mL). The products **5a,e, 6d,e, 7a, 8e,f, 9e** were purified by column chromatography on alumina (eluent: benzene/EtOH, 10:1) and the products **6a-c, 7b,d-f, 8c,d, 9c** were chromatographed on silica gel (eluent: benzene/EtOH, 5:1) followed by crystallization from MeOH. The reactant ratios, the solvents, and the product yields are listed in Tables 1,2.
Compound characterization. 2-Methoxy-4-[(*E*)-2-(4-pyridyl)-1-ethenyl]phenyl methyl ether (5a). M.p. 113-115 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.92 (m, 3 H, OMe), 3.97 (m, 3 H, OMe), 6.89 [d, $^3J_{H,H}$ = 15.9 Hz, 1 H, C(a)-H], 7.03 [dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$= 1.1 Hz, 1 H, C(6')-H], 7.10 (m, 2 H, C(2')-H, C(5')-H), 7.26 [d, 1 H, C(b)-H], 7.35 (m, 2 H, C(3)-H, C(5)-H),

8.56 (m, 2 H, C(2)-H, C(6)-H). MS (EI, 70 eV): m/z = 241 (100) [M$^+$], 226 (87), 198 (13), 167(14), 166 (24), 165 (21), 154 (20), 77 (15), 63 (13), 58 (45), 51 (27). $C_{15}H_{15}NO_2$. Calcd C 74.67, H 6.27, N 5.80; found C 74.64, H 6.24, N 5.81.

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]phenyl methyl quinoline (5e). M.p. 130-132 °C. ^{1}H NMR (500 MHz, [D$_6$] DMSO, 30 °C): δ = 3.81 (m, 3 H, OMe), 3.87 (m, 3 H, OMe), 7.01 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5')-H], 7.30 [dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(6')-H], 7.50 [d, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(2')-H], 7.54 [d, $^3J_{H,H}$ = 16.1 Hz, 1 H, C(a)-H], 7.66 (m, 1 H, C(6)-H), 7.78 (m, 1 H, C(7)-H), 7.81 [d, $^3J_{H,H}$ = 4.6 Hz, 1 H, C(3)-H], 7.96 [d, 1 H, C(b)-H], 8.03 [d, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(5)-H], 8.55[d, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(8)-H], 8.86 [d, $^3J_{H,H}$ = 4.6 Hz, 1 H, C(2)-H]. MS (EI, 70 eV): m/z =291 (100) [M$^+$], 290 (27), 276 (28), 261 (26), 260 (60), 233 (21), 217 (21), 216 (31), 205 (21), 204 (45), 102 (21). $C_{19}H_{17}NO_2$. Calcd C 78.33, H 5.88, N 4.81; found C 78.36, H 5.77, N 4.74.

4-[(*E*)-2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]pyridine (6a). M.p. 112-114 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.77 (m, 8 H, 4 CH_2O), 3.94 (m, 4 H, 2 CH_2O), 4.20 (m, 4 H, 2 CH_2OAr), 6.88 [d, $^3J_{H,H}$ = 16.3 Hz, 1 H, C(a)-H], 6.93 [dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(6')-H], 7.09 (m, 2 H, C(2')-H, C(5')-H), 7.34 [d, $^3J_{H,H}$ = 5.7 Hz, 2 H, C(3)-H, C(5)-H], 7.86 [d, 1 H, C(b)-H], 8.56 [d, $^3J_{H,H}$ = 5.7 Hz, 2 H, C(2)-H, C(6)-H]. MS (EI, 70 eV): m/z = 371 (31) [M$^+$], 240 (47), 239 (100), 224 (32), 183 (29), 182 (32), 167 (28), 154 (37), 153 (58), 129 (38), 83 (47). $C_{21}H_{25}NO_5$. Calcd C 67.91, H 6.78, N 3.77; found C 68.04, H 6.76, N 3.66.

2-[(*E*)-2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]pyrazine (6b). M.p. 101-103 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.78 (m, 8 H, 4 CH_2O), 3.94 (m, 4 H, 2 CH_2O), 4.18 (m, 2 H, CH_2OAr), 4.21 (m, 2 H, CH_2OAr), 6.88 [d, $^3J_{H,H}$ = 8.0 Hz, 1 H, C(5')-H], 7.07 [d, $^3J_{H,H}$ = 16.1 Hz, 1 H, C(a)-H], 7.18 [dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(6')-H], 7.27 [d, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(2')-H], 7.76 [d, 1 H, C(b)-H], 8.45 (m, 1 H, C(5)-H), 8.54 (m, 1 H, C(6)-H), 8.71 (s, 1 H, C(3)-H). MS (EI, 70 eV): m/z = 372 (14) [M$^+$], 371 (62), 370 (5), 282 (4), 239 (19), 238 (100), 212 (10), 185 (5), 154 (8), 45 (10). $C_{20}H_{24}N_2O_5$. Calcd C 64.50, H 6.50, N 7.52; found C 64.19, H 6.39, N 7.44.

4-[(*E*)-2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]pyrimidine (6c). M.p. 107-109 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.77 (m, 8 H, 4 CH_2O), 3.94 (m, 4 H, 2 CH_2O), 4.20 (m, 4 H, 2 CH_2OAr), 6.89 [d, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(5')-H], 6.97 [d, $^3J_{H,H}$ = 15.8 Hz, 1 H, C(a)-H], 7.17 [d, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(2')-H], 7.20 [dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(6')-H], 7.39 [d, $^3J_{H,H}$ = 5.0 Hz, 1 H, C(5)-H], 7.85 [d, 1 H, C(b)-H], 8.67 [d, $^3J_{H,H}$ = 5.0 Hz, 1 H, C(6)-H], 9.14 (s, 1 H, C(2)-H). MS (EI, 70 eV): m/z = 372 (58) [M$^+$], 371 (19), 283 (15), 240 (43), 239 (100), 213 (17), 45 (54), 44 (22), 43 (72), 40 (25). $C_{20}H_{24}N_2O_5$. Calcd C 64.50, H 6.50, N 7.52; found C 64.31, H 6.44, N 7.48.

2-[(*E*)-2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]quinoline (6d). M.p. 119-121 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.78 (m, 8 H, 4 CH_2O), 3.95 (m, 4 H, 2 CH_2O), 4.20 (m, 4 H, 2 CH_2OAr), 6.88 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(5')-H), 7.16 [dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, C(6')-H], 7.26 [d, $^3J_{H,H}$ = 16.2 Hz, 1 H, C(a)-H],

7.37 [d, $^4J_{H,H}$ = 1.1 Hz, 1 H, C(2')-H], 7.49 (m, 1 H, C(6)-H), 7.59 [d, 1 H, C(b)-H], 7.69 (m, 2 H, C(3)-H, C(7)-H), 7.78 [d, $^3J_{H,H}$ = 8.0 Hz, 1 H, C(4)-H], 8.06 [d, $^3J_{H,H}$ = 8.4 Hz, 1 H, C(5)-H], 8.12 [d, $^3J_{H,H}$ = 8.6 Hz, 1 H, C(8)-H]. MS (EI, 70 eV): m/z = 421 (100) [M$^+$], 420 (32), 332 (23), 290 (26), 289 (49), 288 (99), 263 (26), 262 (39), 204 (41), 178 (25), 108 (42). $C_{25}H_{27}NO_5$. Calcd C 71.24, H 6.46, N 3.32; found C 71.21, H 6.30, N 3.24.

4-[(*E*)-2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]quinoline (6e). M.p. 85-87 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.79 (m, 8 H, 4 C*H*$_2$O), 3.96 (m, 4 H, 2 C*H*$_2$O), 4.20 (m, 4 H, 2 C*H*$_2$OAr), 6.92 [d, $^3J_{H,H}$ = 8.0 Hz, 1 H, C(5')-H], 7.19 (m, 2 H, C(2')-H, C(6')-H), 7.28 [d, $^3J_{H,H}$ = 16.0 Hz, 1 H, C(a)-H], 7.59 (m, 1 H, C(6)-H), 7.60 [d, $^3J_{H,H}$ = 4.5 Hz, 1 H, C(3)-H], 7.67 [d, 1 H, C(b)-H], 7.74 (m, 1 H, C(7)-H), 8.14 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 8.23 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(8)-H], 8.89 [d, $^3J_{H,H}$ = 4.5 Hz, 1 H, C(2)-H]. MS (EI, 70 eV): m/z = 421 (100) [M$^+$], 323 (32), 290 (79), 289 (74), 288 (51), 263 (42), 217 (28), 216 (29), 204 (49), 109 (39), 108 (26). $C_{25}H_{27}NO_5$. Calcd C 71.24, H 6.46, N 3.32; found C 70.97, H 6.68, N 3.12.

2-Methyl-4-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]pyridine (7a). M.p. 82-84 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 2.57 (s, 3 H, Me), 3.78 (m, 8 H, 4 C*H*$_2$O), 3.94 (m, 4 H, 2 C*H*$_2$O), 4.17 (m, 2 H, C*H*$_2$OAr), 4.21 (m, 2 H, C*H*$_2$OAr), 6.82 [d, $^3J_{H,H}$ = 16.3 Hz, 1 H, C(a)-H], 6.87 [d, $^3J_{H,H}$ = 8.0 Hz, 1 H, C(5')-H], 7.08 (m, 2 H, C(2')-H, C(6')-H), 7.16 [d, $^3J_{H,H}$ = 4.9 Hz, 1 H, C(5)-H], 7.21 [d, 1 H, C(b)-H], 8.44 [d, $^3J_{H,H}$ = 5.1 Hz,1 H, C(6)-H], 7.21 (s, 1 H, C(3)-H). MS (EI, 70 eV): m/z = 485 (56) [M$^+$], 254 (35), 253 (79), 227 (22), 168 (21), 91 (20), 90 (23), 73 (19), 59 (34), 58 (100). $C_{22}H_{27}NO_5$. Calcd C 68.55, H 7.06, N 3.63; found C 68.41, H 6.99, N 3.63.

2-Methyl-3-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]pyrazine (7b). M.p. 133-135 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 2.69 (s, 3 H, Me), 3.78 (m, 8 H, 4 C*H*$_2$O), 3.94 (m, 4 H, 2 C*H*$_2$O), 4.17 (m, 2 H, C*H*$_2$OAr), 4.21 (m, 2 H, C*H*$_2$OAr), 6.87 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5')-H], 7.13 [d, $^3J_{H,H}$ = 15.8 Hz, 1 H, C(a)-H], 7.15 [d, $^4J_{H,H}$ = 1.1 Hz, 1 H, C(2')-H], 7.19 [dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, C(6')-H], 7.76 [d, 1 H, C(b)-H], 8.29 [d, $^3J_{H,H}$ = 2.4 Hz, 1 H, C(5)-H], 8.38 [d, $^3J_{H,H}$ = 2.4 Hz, 1 H, C(6)-H]. MS (EI, 70 eV): m/z = 386 (75) [M$^+$], 297 (8), 2543 (20), 257 (100), 227 (12), 198 (7), 71 (11), 59 (8), 58 (95), 57 (13). $C_{21}H_{26}N_2O_5$. Calcd C 65.27, H 6.78, N 7.25; found C 65.18, H 6.59, N 7.19.

4-Methyl-4'−(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylvinil)-2,2'−bipyridine (7d). M.p. 143-145 °C. Lit.[16d] 143-144 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 2.63 (s, 3 H, Me), 3.78 (m, 8 H, 4 C*H*$_2$O), 3.95 (m, 4 H, 2 C*H*$_2$O), 4.19 (m, 2 H, C*H*$_2$OAr), 4.23 (m, 2 H, C*H*$_2$OAr), 6.89 [d, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(5'')-H], 7.02 [d, $^3J_{H,H}$ = 16.1 Hz, 1 H, C(a)-H], 7.18 [d, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(2'')-H], 7.22 [dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(6'')-H], 7.45 (m, 1 H, C(5')-H, bpy), 8.82 (m, 1 H, C(6')-H, bpy), 7.60 (m, 1 H, C(5)-H, bpy), 7.72 [d, 1 H, C(b)-H], 9.01 (m, 1 H, C(6)-H, bpy), 8.72 (m, 2 H, C(3)-H, C(3')-H, bpy).

4-Methyl-2-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]quinoline (7e). M.p. 104-106 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 2.75

(s, 3 H, Me), 3.69 (m, 8 H, 4 CH_2O), 3.86 (m, 4 H, 2 CH_2O), 4.15 (m, 2 H, CH_2OAr), 4.22 (m, 2 H, CH_2OAr), 6.99 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5')-H], 7.25 [dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(6')-H], 7.37 [d, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(2')-H], 7.46 [d, $^3J_{H,H}$ = 16.1 Hz, 1 H, C(a)-H], 7.69 (s, 1 H, C(3)-H), 7.76 [d, 1 H, C(b)-H], 8.05 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 8.38 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(8)-H]. MS (EI, 70 eV): m/z = 485 (56) [M$^+$], 254 (35), 253 (79), 227 (22), 168 (21), 91 (20), 90 (23), 73 (19), 59 (34), 58 (100). $C_{26}H_{29}NO_5 \times H_2O$. Calcd C 68.87, H 6.84, N 3.09; found C 68.91, H 6.49, N 3.04.

2-Methyl-9-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl][1,10]phenanthroline (7f). M.p. 76-78 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 2.82 (s, 3 H, Me), 3.64 (m, 8 H, 4 CH_2O), 3.81 (m, 4 H, 2 CH_2O), 4.11 (m, 2 H, CH_2OAr), 4.21 (m, 2 H, CH_2OAr), 7.02 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5')-H], 7.26 [dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(6')-H], 7.45 [d, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(2')-H], 7.52 [d, $^3J_{H,H}$ = 16.3 Hz, 1 H, C(a)-H], 7.67 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(7)-H], 7.80 [d, 1 H, C(b)-H], 7.86 (s, 2 H, C(5)-H, C(6)-H), 8.06 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(4)-H], 8.35 [d, $^3J_{H,H}$ = 8.0 Hz, 1 H, C(8)-H], 8.41 [d, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(3)-H]. MS (EI, 70 eV): m/z = 486 (92) [M$^+$], 485 (5), 83 (2), 71 (2), 69 (1), 59 (7), 58 (100), 57 (8), 56 (2), 55 (4). $C_{29}H_{30}N_2O_5$. Calcd C 71.60, H 6.17, N 5.76; found C 71.72, H 6.29, N 5.79.

4,6-Bis[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]pyrimidine (8c). M.p. 169-171 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.78 (m, 16 H, 8 CH_2O), 3.94 (m, 8 H, 4 CH_2O), 4.19 (m, 8 H, 4 CH_2OAr), 6.88 [d, $^3J_{H,H}$ = 8.2 Hz, 2 H, C(5')-H, C(5'')-H], 7.08 [d, $^3J_{H,H}$ = 15.6 Hz, 2 H, C(a)-H, C(a')-H], 7.21 [d, $^4J_{H,H}$ = 1.0 Hz, 2 H, C(2')-H, C(2'')-H], 7.27 [dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.0 Hz, 2 H, C(6')-H, C(6'')-H], 7.43 (s, 1 H, C(3)-H), 8.20 [d, 2 H, C(b)-H, C(b')-H], 8.96 (s, 1 H, C(5)-H). $C_{36}H_{44}N_2O_{10}$. Calcd C 65.27, H 6.78, N 7.25; found C 65.17, H 6.67, N 7.29.

4,4'−Bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylvinyl)-2,2'−bipyridine (8d). M.p. 219-221 °C. Lit.[16d] 219-220 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30 °C): δ = 3.78 (m, 16 H, 8 CH_2O), 3.94 (m, 8 H, 4 CH_2O), 4.19 (m, 4 H, 2 CH_2OAr), 4.25 (m, 4 H, 2 CH_2OAr), 6.89 [d, $^3J_{H,H}$ = 8.4 Hz, 2 H, C(5'')-H, C(5''')-H], 7.00 [d, $^3J_{H,H}$ = 16.2 Hz, 2 H, C(a)-H, C(a')-H], 7.14 (m, 4 H, C(2'')-H, C(2''')-H, C(6'')-H, C(6''')-H), 7.40 [d, $^3J_{H,H}$ = 5.0 Hz, 2 H, C(5)-H, C(5')-H, bpy], 7.44 [d, 2 H, C(b)-H, C(b')-H], 8.66 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, C(6)-H, C(6')-H, bpy), 8.61 (s, 2 H, C(3)-H, C(3')-H, bpy).

2,4-Bis[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl]quinoline (8e). M.p. 169-171 °C. ^{1}H NMR (500 MHz, CD$_3$CN, 30 °C): δ = 3.67 (m, 8 H, 4 CH_2O), 3.69 (m, 8 H, 4 CH_2O), 3.85 (m, 4 H, 2 CH_2O), 3.90 (m, 4 H, 2 CH_2O), 4.15 (m, 4 H, 2 CH_2OAr), 4.22 (m, 4 H, 2 CH_2OAr), 6.99 (m, 2 H, C(5')-H, C(5'')-H), 7.26 (m, 2 H, C(2')-H, C(6')-H), 7.33 (m, 2 H, C(a')-H, C(6'')-H), 7.39 [d, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(2'')-H,], 7.51 [d, $^3J_{H,H}$ = 16.1 Hz, 1 H, C(a)-H], 7.59 (m, 1 H, C(6)-H), 7.75 (m, 1 H, C(7)-H), 7.80 [d, $^3J_{H,H}$ = 16.2 Hz, 1 H, H-b'], 7.83 [d, 1 H, C(b)-H], 7.99 (s, 1 H, C(3)-H), 8.01 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(5)-H], 8.61 [d, $^3J_{H,H}$ = 8.3 Hz, 1 H, C(8)-H]. $C_{41}H_{47}NO_{10}$. Calcd C 67.92, H 6.82, N 2.03; found C 67.83, H 6.63, N 1.98.

2,9-Bis[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-1-ethenyl][1,10]phenanthroline (8f). M.p. 93-95 °C. ^{1}H NMR (500 MHz, CD$_3$CN, 30 °C): δ = 3.67 (m, 8 H, 4 C*H*$_2$O), 3.69 (m, 8 H, 4 C*H*$_2$O), 3.86 (m, 8 H, 4 C*H*$_2$O), 4.16 (m, 4 H, 2 C*H*$_2$OAr), 4.23 (m, 4 H, 2 C*H*$_2$OAr), 6.99 [d, $^3J_{H,H}$ = 8.2 Hz, 2 H, C(5')-H, C(5'')-H], 7.33 [dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, C(6')-H, C(6'')-H], 7.42 [d, $^4J_{H,H}$ = 1.2 Hz, 2 H, C(2')-H, C(2'')-H], 7.53 [d, $^3J_{H,H}$ = 16.1 Hz, 2 H, C(a)-H, C(a')-H], 7.82 (s, 2 H, C(5)-H, C(6)-H), 7.89 [d, 2 H, C(b)-H, C(b')-H], 7.93 [d, $^3J_{H,H}$ = 8.3 Hz, 2 H, C(3)-H, C(8)-H], 8.32 [d, $^3J_{H,H}$ = 8.3 Hz, 2 H, C(4)-H, C(7)-H]. C$_{44}$H$_{48}$N$_2$O$_{10}$×H$_2$O. Calcd C 67.52, H 6.39, N 3.58; found C 67.20, H 6.33, N 4.00.

4-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-3-(4-pyrimidinyl)propyl]pyrimidine (9c). M.p. 58-60 °C. ^{1}H NMR (500 MHz, [D$_6$] DMSO, 30 °C): δ = 3.40 (m, 3 H, 2 C*H*$_2$), 3.74 (m, 8 H, 4 C*H*$_2$O), 3.87 (m, 4 H, 2 C*H*$_2$O), 4.04 (m, 2 H, C*H*$_2$OAr), 4.08 (m, 2 H, C*H*$_2$OAr), 4.16 (m, 1 H, C*H*), 6.55 [d, $^3J_{H,H}$ = 8.0 Hz, 1 H, C(5'')-H], 6.65 [dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(6'')-H], 6.69 [d, $^4J_{H,H}$ = 1.3 Hz, 1 H, C(2'')-H], 7.24 [d, $^3J_{H,H}$ = 4.7 Hz, 2 H, C(5)-H, C(5')-H], 8.68 [d, $^3J_{H,H}$ = 4.9 Hz, 2 H, C(6)-H, C(6')-H]. C$_{25}$H$_{30}$N$_4$O$_5$. Calcd C 64.36, H 6.48, N 12.00; found C 64.20, H 6.43, N 11.49.

4-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-3-(4-quinolyl)propyl]quinoline (9e). M.p. 62-64 °C. Lit. [19] 62-64 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 30°C): δ = 3.39 (m, 2 H, 2 CH$_2$), 3.78 (m, 8 H, 4 CH$_2$O), 3.91 (m, 4 H, 2 CH$_2$O), 4.10 (m, 4 H, 2 CH$_2$OAr), 4.15 (m, 1 H, CH), 6.30 [dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(6'')-H], 6.51 [d, $^4J_{H,H}$ = 1.2 Hz, 1 H, C(2')-H], 6.54 [d, $^3J_{H,H}$ = 8.2 Hz, 1 H, C(5'')-H], 6.99 [d, $^3J_{H,H}$ = 4.4 Hz, 2 H, C(3)-H, C(3')-H], 7.40 (m, 2 H, C(6)-H, C(6')-H), 7.64 [d, $^3J_{H,H}$ = 8.1 Hz, 2 H, C(5)-H, C(5')-H], 7.68 (m, 2 H, C(7)-H, C(7')-H), 8.12 [d, $^3J_{H,H}$ = 8.1 Hz, 2 H, C(8)-H, C(8')-H].

Acknowledgements

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