DOI: 10.1002/ejoc.201000505

27- to 39-Membered Pyridine Macrocycles

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Keywords: Combinatorial chemistry / Macrocycles / Metathesis / Nitrogen heterocycles

A set of 27- to 39-membered pyridine macrocycles **2** and **3** has been synthesized by Williamson ether synthesis or ring-closing metathesis. The pyridines are 2,6-disubstituted to allow *endo* interactions. In addition to the length, also the nature of the aliphatic chain was varied: saturated (**2**) and unsaturated (**3**).

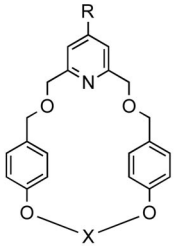
Introduction

Supramolecules and molecules differ in their mode of binding, but besides the covalent bonds in "ordinary" molecules and the supramolecular ion–dipole, π–π binding, or hydrogen-bonding interactions in "ordinary" supramolecules, a subclass of supramolecules exists, in which the fragments are held together only mechanically: the rotaxanes and catenanes. First only perceived as an exotic class of molecules,[1] the interest in molecular machines[2] has drawn attention to catenanes and rotaxanes.[3] While catenanes are mechanically interlocked, a stable rotaxane is only obtained if the stoppers at either end of the axis are large enough to prohibit a dethreading of the axis. If such a process takes place, the supramolecules are called pseudorotaxanes. Therefore, the size of the ring must be adjusted to the size of the stopper.

For interaction with the axis, the macrocyclic ring must possess respective groups in an *endo* orientation. By incorporating a pyridine with a 2,6-disubstitution pattern into the ring, the pyridine nitrogen atom is forced to adopt an *endo* orientation where it can act as a base, as a hydrogen-bond acceptor, or as a ligand for transition metal ions. The latter (i.e., **1**) have already been employed in rotaxane synthesis with click chemistry.[4]

Rotaxanes can be synthesized by several approaches, that is, by threading, clipping, or slipping. While the threading and clipping construct one part of the rotaxane (ring or axis) in the presence of the other (axis or ring), slipping starts from preformed axes and rings and assembles the rotaxane by administering heat, which provides the activation energy for the slipping of the ring onto the axis.

In this work, we have developed a series of macrocyclic pyridines ready to be studied in slipping experiments for the construction of rotaxanes. As stated above, the ring size of the macrocycle must be adjusted to the size of the stopper groups of the rotaxane. Studying polymethylene macrocycles of ring sizes from 14 to 42, it was shown[5] that macrocycles larger than 29 may slip on and off the axis. Macrocycles with a ring size of 24 or smaller do not form a rotaxane. Only if the macrocycle of matching size (29-membered) is used, high temperature allows slipping, the thermal energy deforming the macrocycle, and stopper as well. At low temperature, the activation energy for these deformations is lacking, and thus the rotaxane is stable.



1 R = H, X = $(CH_2)_n$

2 R = OMe, X = $(CH_2)_n$

3 R = OMe, X = $(CH_2)_p$-CH=CH-$(CH_2)_q$

The ring size 29 cannot directly be transcribed into the world of the pyridine macrocycles such as **1**–**3**, because these possess stiff aromatic units, as well as oxygen atoms, which result in different bond lengths, angles, and dihedral angles. Furthermore, it is advisable to allow modified axes with stoppers other than trityl. Therefore, pyridine macrocycles of this family are needed in varying ring sizes. As Harrison's work has shown,[5] the window for slipping is narrow. Therefore, fine-tuning of the ring size is advisable. The finer the differences within the family of macrocycles, the higher the chance to find the matching pair of macrocycle and axis (to be more precise: the stopper). However, the search for rotaxanes formed by slipping in the presence of unreacted material, that is, axis and ring alone, is not easy. Therefore careful attention has also to be given to analytics.

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As a result of these considerations, we have chosen to synthesize macrocyclic pyridines **2** and **3** with the following properties: (i) The pyridine ring is substituted in the 4-position to increase the electron density at the pyridine nitrogen atom for future *endo* interactions. In addition, NMR spectra for 2,4,6-trisubstituted pyridines are simplified allowing easier analysis. (ii) For the construction of macrocycles **3**, ring-closing metathesis was used, resulting in macrocycles that still contain a double bond. Such a double bond can easily be hydrogenated, but the *E*/*Z* mixture can also be used in rotaxane formation with the advantage to use two very similar yet not identical macrocycles whose diameters should slightly differ due to the differing configuration of the double bond.

Results and Discussion

A retrosynthetic analysis of envisioned pyridine macrocycles **2** and **3** allows several synthetic approaches. In the past, Williamson ether syntheses under high dilution conditions have been used to synthesize pyridine macrocycles such as a 29-membered ring **1**.[6] We have adopted this route to 4-methoxypyridine derivatives **2**.

In the past decade, ring-closing metathesis has proven to be a very powerful tool for the synthesis of macrocycles. Due to the very encouraging results with other macro- and oligomacrocycles,[6–10] we have chosen a metathesis route to methoxy-substituted rings **3**.

Figures 1 and 2 summarize the two synthetic alternatives, and Tables 1 and 2 list macrocycles **2** and **3** obtained by the respective strategy. In principle, it should be easy to hydrogenate unsaturated macrocycles **3** to rings **2**, as has been shown[7–10] for several other classes of (oligo)macrocycles.

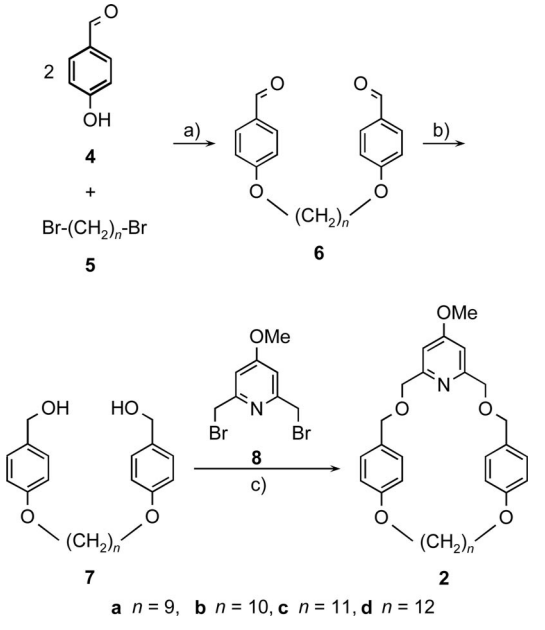

Figure 1. Synthesis of pyridine macrocycles **2** by a double Williamson ether synthesis. (a) K_2CO_3 (general method A), (b) $NaBH_4$ (general method B), (c) NaH, two-component, high-dilution cyclization (general method C).

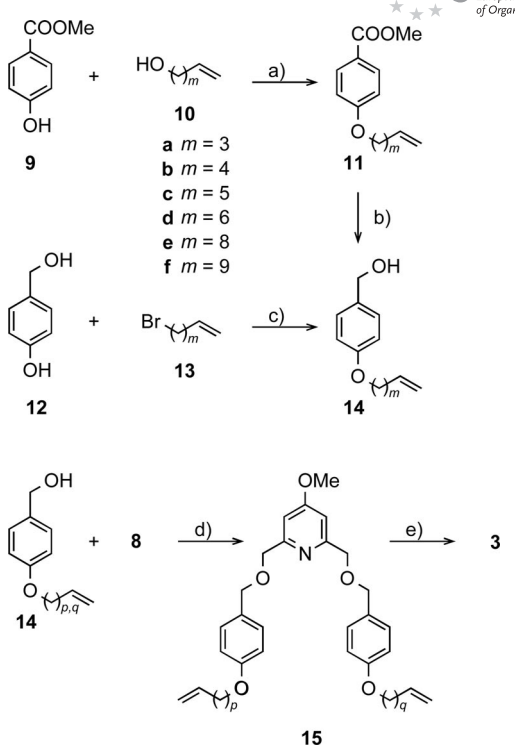

Figure 2. Synthesis of pyridine macrocycles **3** by ring-closing metathesis. For ring sizes, see Table 2. (a) Mitsunobu reaction, DIAD, PPh_3, THF (general method D), (b) $LiAlH_4$, THF (general method E), (c) Williamson ether formation, K_2CO_3, NaI, butanone, (d) Williamson ether formation, NaH, THF (general method F; for library formation, see method G), (e) ring-closing metathesis, Grubbs' catalyst (general method H; for library formation, see method I).

Table 1. 4-Methoxypyridine macrocycles **2** of varying ring size.

	Ring size	Number of C atoms in **5**	Isolated yield [%]
2a	28	9	8
2b	29	10	14
2c	30	11	28
2d	31	12	46

Table 2. 4-Methoxypyridine macrocycles **3** of varying ring size, yield if isolated, and library compositions.

	Ring size	Number of C atoms in alkenyl residues p + 2, q + 2	Isolated yield [%]	In library with **3**
3a	27	5, 5	45	**b/c**, **d/g**
3b	28	5, 6		**a**, **c**
3c	29	6, 6	50	**a/b**, **h/m**
3d	30	5, 8		**a**, **g**
3e	31	7, 7		**f**, **g**
3f	32	7, 8		**f**, **h**
3g	33	8, 8		**a/d**, **e/f**, **j/m**
3h	34	6, 11		**c/m**
3i	35	7, 11		**e/m**
3j	36	8, 11		**g/m**
3k	37	10, 10		**l/m**
3l	38	10, 11		**k/m**
3m	39	11, 11	41	**c/h**, **e/i**, **g/j**, **k/l**

However, in this work, we chose to leave unsaturated macrocycles **3** as *E*/*Z* mixtures for their slight differences in ring size (see above).

As stated above, it is important to have access to a full set of macrocycles **1**, **2**, or **3**. With ring-closing metathesis, macrocycles with an odd number of carbon atoms in the chain formed by the metathesis can only be obtained when the two precursor alkenyl groups differ in length ($p \neq q$), more precisely, if one chain contains an odd number, and the other an even number of carbon atoms (for instance $p = q + 1$). Due to the fact that the synthesis of an unsymmetrically substituted precursor is tedious, we decided to generate mixtures, because a slipping process in the construction of rotaxanes will select the matching macrocycle anyway. By carrying out the connection between the alkenyloxy containing residues and the pyridine part with a mixture of two alkenyl benzyl alcohols **14**, also mixtures of products **15** are formed. Statistically, two homo- and one hetero-substituted products will be formed in a ratio of 1:1:2. Thus, the otherwise inaccessible macrocycles **3** with an odd number of carbon atoms between the phenolic oxygen atoms can be synthesized accompanied by two others.

For the synthesis of precursors **15** for the metathesis, bis(bromomethyl)pyridine **8** on one hand and alkenyloxybenzyl alcohols **14** on the other hand have to be provided. Whereas pyridine **8** is known in the literature,[11] benzyl alcohols **14** have to be synthesized from 4-hydroxybenzoic ester (**9**) or 4-hydroxybenzyl alcohol (**12**) and suitable alkenyl derivatives **10** or **13**. In principle, the alkylation can be carried out by using Williamson ether formation or by the Mitsunobu reaction. The choice depends on the availability of starting materials ω-bromoalkenes **13** or ω-hydroxyalkenes **10**. Neither non-8-enol nor non-8-enyl bromide are easily accessible, but macrocycle **3** of identical ring size can be generated by the same approach as discussed above for the chains with an odd number of carbon atoms: Here the combination of hept-6-enyl and undec-10-enyl substituents leads to the same chain lengths as if two non-8-enyl residues had been used (although with a different position of the double bond in **3i**).

Tables 1 and 2 summarize macrocycles **2** and **3** synthesized so far and by which method the products were generated and whether they were obtained as a mixture or in isolated form. Table 3 compiles the MS data of the combinatorial mixtures of macrocycles **3** with even and odd numbers of carbon atoms in the alkenylene chain. Macrocycles **2** were obtained in a kinetically controlled macrocyclization under high-dilution conditions. In the synthesis of macrocycles **3**, reversible ring-closing metathesis was used, and therefore, ethyl vinyl ether was added before workup to stop the metathesis. For details, see general procedures C and H in the Experimental Section.

Table 3. Compilation of combinatorial syntheses of macrocycles **3** from benzyl alcohols **14** with different chain lengths *p* and *q*. Analyses by MALDI-MS or CI-MS.

Benzyl alcohol **14**		Macrocycles **3**		
p + 2	*q* + 2	*m*/*z*	*m*/*z*	*m*/*z*
5 (**14a**)	6 (**14b**)	490[a]	504[a], 526[b]	518[a], 540[b]
5 (**14a**)	8 (**14d**)	490[a]	532[a]	574[a]
7 (**14c**)	8 (**14d**)	546[a], 568[b]	560[a], 582[b]	574[a], 596[b]
6 (**14b**)	11 (**14f**)	n.d.[c]	588[a,d], 610[b]	658[a,d]
7 (**14c**)	11(**14f**)	546[a]	602[a], 624[b]	658[a]
8 (**14d**)	11 (**14f**)	574[a]	616[a]	658[a]
10 (**14e**)	11 (**14f**)	630[a]	644[a], 666[b]	658, 680[b]

[a] $[M + H]^+$, MALDI-TOF, Cl-CCA. [b] $[M + Na]^+$, MALDI-TOF, Cl-CCA. [c] Not detected. [d] $[M + H]^+$, CI, isobutane.

Conclusions

Using Williamson ether syntheses or ring-closing metathesis for macrocyclization, 27- to 39-membered pyridines have been synthesized in saturated (i.e., **2**) and unsaturated form (i.e., **3**). Four saturated 4-methoxy-substituted pyridine macrocycles **2a**–**d** and three unsaturated ones (**3a**,**c**,**m**) were isolated and characterized. The rest of the set of 27- to 39-membered rings (**3a**–**m**) was made available as mixtures for combinatorial experiments. All macrocycles possess a methoxy group in the 4-position of the pyridine ring, allowing (i) easier NMR spectroscopic analysis (especially important in mixtures, for instance after the slipping process), and (ii) stronger interactions, due to increased electron density at the pyridine nitrogen atom, with partners such as binding sites on an axis of a rotaxane (e.g., hydrogen-bond donors) or with transition-metal ions (see click chemistry, ref.[4]). Slipping experiments with these libraries of rings and axes carrying stoppers of different sizes are currently being carried out in our laboratory.

Experimental Section

Remarks: NMR spectra were recorded with Bruker AC 200, DRX 500, or AV 600 instruments. Assignments are supported by COSY, HSQC, and HMBC. Even when obtained by DEPT, the type of ^{13}C signal is always listed as singlet, doublet, etc. All chemical shifts are referenced to TMS or to the residual proton or carbon signal of the solvent. If not stated otherwise, coupling constants are ^3J. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. MALDI mass spectra were recorded with a Bruker-Daltonics Biflex III by using CCA (α-cyano-4-hydroxycinnamic acid) and Cl-CCA (α-cyano-4-chlorocinnamic acid) as matrix. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. IR spectra were recorded with a Perkin–Elmer Paragon 1000, Perkin–Elmer Spectrum 100 equipped with an MKII Golden Gate™ Single Reflection ATR unit. Elemental analyses were carried out with a Euro EA 3000 Elemental Analyzer from Euro Vector. 2,6-Bis(bromomethyl)-4-methoxypyridine (**8**) was synthesized according to a literature procedure.[11]

General Procedure A for the Williamson Ether Synthesis of 6: To a solution of 4-hydroxybenzaldehyde (**4**, 2 equiv.) and 1,ω-dibromoalkane (**5**, 1 equiv.) dissolved in ethyl methyl ketone were added potassium carbonate (10 equiv.) and sodium iodide (15 mg). The suspension was heated to reflux under an atmosphere of nitrogen for 18–20 h. After cooling, the mixture was filtered, and the filtrate was concentrated in vacuo. The remaining oil was dissolved in dichloromethane (75 mL), then washed twice with water (25 mL) and brine (25 mL). The combined aqueous layer was extracted once with dichloromethane (20 mL). The combined organic layer was

dried with magnesium sulfate, and the solvent was evaporated in vacuo. The residue was recrystallized. See also: **6a**,[12] **6b**,[6] **6c**,[13] **6d**.[14]

General Procedure B for Reduction of 6 to 7: To a solution of 1,ω-bis(4-formylphenoxy)alkane (**6**, 1 equiv.) in a mixture of chloroform and methanol (5:1) was added sodium borohydride (10 equiv.) in portions. After heating at reflux for 4 h, the mixture was cooled to 0 °C and 1 M hydrochloric acid (20 mL) was added. The mixture was extracted with dichloromethane (6 × 80 mL). The combined organic layer was dried with magnesium sulfate, and the solvent was evaporated in vacuo. The residue was recrystallized.

General Procedure C for the Williamson Ether Synthesis of 2: 1,ω-Bis(4-hydroxymethylphenoxy)alkane (**6**, 1 equiv.) and 2,6-bis(bromomethyl)-4-methoxypyridine (**8**, 1 equiv.) were dissolved separately in dry THF (60 mL each). Synchronously and slowly, both solutions were dropped into a warm mixture (60 °C) of sodium hydride in dry THF. After addition was completed, the mixture was heated to reflux for 15–20 h. Next, the solvent was removed in vacuo, the residue was dissolved in dichloromethane (20 mL), washed three times with aqueous sodium chloride solution, dried with magnesium sulfate, and the solvent was evaporated in vacuo. The residue was purified by chromatography with silica gel.

General Procedure D for the Mitsunobu Reaction of Methyl 4-Hydroxybenzoate (9) with ω-Hydroxyalkenes 10 To Give Alkenylated Esters 11: Methyl 4-hydroxybenzoate (**9**, 1 equiv.), an ω-hydroxyalkene (1.25 equiv.), and triphenylphosphane (1.2 equiv.) were dissolved in dry THF. At 0 °C under an atmosphere of nitrogen, diisopropyl azodicarboxylate (DIAD, 1.5 equiv.) was added dropwise. After stirring at 0 °C for 15 min and 16–18 h at room temperature, deionized water (20 mL) was added. The aqueous mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed with 2 N sodium hydroxide solution (3 × 20 mL) and brine (20 mL). After drying with magnesium sulfate, the solvent was evaporated, and the residue was purified by chromatography (silica gel).

General Procedure E for the Reduction of Esters 11 to Benzyl Alcohols 14: Lithium aluminum hydride was suspended in dry THF and cooled to 0 °C. Under an atmosphere of nitrogen, ester **11**, dissolved in dry THF, was added slowly. After stirring for 1 h at room temperature and 4 h at 65 °C, deionized water was added until hydrogen production ceased. The residue was isolated by filtration and washed several times with ethyl acetate. The filtrate was evaporated, and the crude product was purified by chromatography (silica gel).

General Procedure F for the Williamson Ether Synthesis of 15: Sodium hydride (2.1 equiv.) was added to dry THF and cooled to 0 °C. Under an atmosphere of nitrogen, benzyl alcohol **14** (2 equiv.) in dry THF was added, and after 30 min of stirring, 2,6-bis(bromomethyl)-4-methoxypyridine (**8**, 1 equiv.) in dry THF was added dropwise. After heating at reflux for 18 h to 2 d, the mixture was allowed to cool to room temperature and filtered. The solvent was evaporated, and the residue was dissolved in dichloromethane (25 mL) and washed twice with water (25 mL) and once with brine (25 mL). The combined water layer was extracted with dichloromethane (25 mL), the combined organic layer was dried with magnesium sulfate, and the solvent was evaporated. The residue was purified by chromatography with silica gel.

General Procedure G of the Combinatorial Syntheses of the Mixtures of 15: Sodium hydride (2.1 equiv.) was mixed with dry THF. At 0 °C under an atmosphere of nitrogen, two different benzyl alcohols **14** (1 equiv. each) in dry THF were added, followed by stirring (30 min) and the addition of 2,6-bis(bromomethyl)-4-methoxypyridine (**8**, 1 equiv.). The mixture was heated to reflux for 18 h to 2 d, cooled to room temperature, filtered, and the filtrate was concentrated. The residue was dissolved in dichloromethane, washed with deionized water (2 × 25 mL) and brine (25 mL). The combined aqueous layer was extracted with dichloromethane (25 mL). The combined organic layer was dried with magnesium sulfate, and the solvent was evaporated. The crude product was purified by chromatography (silica gel), yielding a mixture of three bis(alkenyloxy)-substituted pyridines **14** (see Table 3).

General Procedure H for the Ring-Closing Metathesis of 15 To Give 3: Precursor **15** was dissolved in dry dichloromethane. Under an atmosphere of nitrogen, benzylidenebis(tricyclohexylphosphane)-ruthenium dichloride (Grubbs' catalyst 1st generation, 12 mol-%) was added, and the mixture was stirred at room temperature for 2–5 d. The conversion was controlled by MALDI-TOF-MS. Finally, to deactivate the catalyst, ethyl vinyl ether (ca. 0.5 mL) was added, and the mixture was stirred for 1 h at room temperature. After evaporation of the solvent, the product was purified by chromatography with silica gel.

General Procedure I for the Combinatorial Syntheses of the Mixtures of 3: According to general procedure H, a mixture of three bis(alkenyl)-substituted pyridines **14**, synthesized as described by method G, was cyclized to give a library of pyridine macrocycles **3** (three different ring sizes, each as a mixture of *E*/*E*-, *E*/*Z*- and *Z*/*Z*-isomers).

4^5-Methoxy-3,7,10,20-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinaeicosaphan (2a): According to general procedure C, 2,6-bis(bromomethyl)-4-methoxypyridine (**8**,[11] 123 mg, 416 μmol) in THF (60 mL), 1,9-bis[(4-hydroxymethyl)phenoxy]nonane (**7a**,[15] 155 mg, 416 μmol) in THF (60 mL), and sodium hydride (400 mg, 10.0 mmol) in THF (380 mL). Time of addition: 52 h. Purification: silica gel; CH_2Cl_2/ethyl acetate, 15:1; R_f = 0.07. Yield: 16.4 mg (8%). M.p. 101 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.6 Hz, 4 H, Bn-$H^{2,6}$), 6.89 (s, 2 H, Py-$H^{3,5}$), 6.81 (d, J = 8.6 Hz, 4 H, Bn-$H^{3,5}$), 4.58 (s, 4 H, Py-CH_2), 4.36 (s, 4 H, Bn-CH_2), 3.97 (t, J = 6.2 Hz, 4 H, C$H_2^{1,9}$), 3.88 (s, 3 H, OCH_3), 1.73 (m_c, 4 H, C$H_2^{2,8}$), 1.42 (m_c, 4 H, C$H_2^{3,7}$), 1.4–1.3 (m, 6 H, C$H_2^{4,5,6}$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.1 (s, Py-C^4), 159.6 (s, Py-$C^{2,6}$), 158.9 (s, Bn-C^4), 130.1 (d, Bn-$C^{2,6}$), 129.3 (s, Bn-C^1), 114.7 (d, Bn-$C^{3,5}$), 106.0 (d, Py-$C^{3,5}$), 72.1 (t, Bn-CH$_2$), 71.0 (t, Py-CH$_2$), 67.4 (t, CH$_2^{1,9}$), 55.2 (s, OCH$_3$), 29.4 (t, CH$_2^5$), 28.7, 28.6 (2 t, CH$_2^{2,4,6,8}$), 25.6 (t, CH$_2^{3,7}$) ppm. MS (MALDI-TOF, CCA): *m*/*z* = 545 [M + K]$^+$, 529 [M + Na]$^+$, 506 [M + H]$^+$. MS (EI, 70 eV): *m*/*z* (%) = 505 (3) [M]$^+$ 152 (100) [$C_8H_{10}NO_2$]$^+$, 137 (33) [$C_8H_{11}NO$]$^+$, 121 (20) [C_7H_7NO]$^+$, 107 (83) [C_6H_5NO]$^+$. MS (CI, isobutane): *m*/*z* (%) = 506 (100) [M + H]$^+$, 152 (8) [$C_8H_{10}NO_2$]$^+$. IR (ATR): $\tilde{\nu}$ = 2921, 2850 (aliph. C-H), 1598, 1574, 1509 (arom. C=C), 1242 (C-O-C), 829 (isol. arom. H), 800 (1,4-disub. arom.) cm^{-1}. HRMS (ESI, $CHCl_3$): calcd. for $C_{31}H_{39}NO_5$ + H 506.2901; found 506.2882 (Δ = –3.8 ppm). HRMS (ESI, $CHCl_3$): calcd. for $C_{30}{}^{13}CH_{39}NO_5$ + H 507.2934; found 507.2966 (Δ = 6.3 ppm).

4^5-Methoxy-3,7,10,21-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinaheneicosaphan (2b): According to general procedure C, 2,6-bis(bromomethyl)-4-methoxypyridine (**8**,[11] 177 mg, 600 μmol) in THF (60 mL), 1,10-bis[(4-hydroxymethyl)phenoxy]decane (**7b**,[6,15] 232 mg, 600 μmol) in THF (60 mL), and sodium hydride (400 mg, 10.0 mmol) in THF (400 mL). Time of addition: 6 h. Purification: silica gel; CH_2Cl_2/ethyl acetate, 19:1; R_f = 0.14. Yield: 42.5 mg (14%). M.p. 104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.7 Hz, 4 H, Bn-$H^{2,6}$), 6.89 (s, 2 H, Py-$H^{3,5}$), 6.80 (d, J = 8.7 Hz, 4 H, Bn-$H^{3,5}$), 4.59 (s, 4 H, Py-CH_2), 4.35 (s, 4 H, Bn-CH_2), 3.96

(t, J = 6.4 Hz, 4 H, C$H_2^{1,10}$), 3.88 (s, 3 H, OCH_3), 1.72 (m_c, 4 H, C$H_2^{2,9}$), 1.41 (m_c, 4 H, C$H_2^{3,8}$), 1.3–1.2 (m, 8 H, C$H_2^{4,5,6,7}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.2 (s, Py-C^4), 159.6 (s, Py-$C^{2,6}$), 158.8 (s, Bn-C^4), 130.1 (d, Bn-$C^{2,6}$), 129.3 (s, Bn-C^1), 114.6 (d, Bn-$C^{3,5}$), 105.8 (d, Py-$C^{3,5}$), 72.3 (t, Bn-CH$_2$), 70.9 (t, Py-CH$_2$), 67.4 (t, CH$_2^{1,10}$), 55.2 (s, OCH$_3$), 29.4, 28.7, 28.6 (3t, CH$_2^{2,4,5,6,7,9}$), 25.6 (t, CH$_2^{3,8}$) ppm. MS (MALDI-TOF, CCA): m/z = 558 [M + K]$^+$, 542 [M + Na]$^+$, 520 [M + H]$^+$. MS (EI, 70 eV): m/z (%) = 519 (4) [M]$^+$, 152 (100) [$C_8H_{10}NO_2$]$^+$, 137 (37) [$C_8H_{11}NO$]$^+$, 121 (22) [C_7H_7NO]$^+$, 107 (95) [C_6H_5NO]$^+$. MS (CI, isobutane): m/z (%) = 520 (56) [M + H]$^+$, 97 (100) [C_7H_{13}]$^+$. IR (ATR): $\tilde{\nu}$ = 2925, 2852 (aliph. C-H), 1597, 1580, 1509 (arom. C=C), 1238 (C-O-C), 835 (isol. arom. H), 795 (1,4-disub. arom.) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{32}H_{41}NO_5$ 519.29846; found 519.29596 (Δ = –4.8 ppm). HRMS (EI, 70 eV): calcd. for $C_{31}{}^{13}CH_{41}NO_5$ 520.30182; found 520.30177 (Δ = –0.1 ppm).

4^5-Methoxy-3,7,10,22-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinadocosaphan (2c): According to general procedure C, 2,6-bis(bromomethyl)-4-methoxypyridine (**8**,[11] 177 mg, 600 μmol) in THF (60 mL), 1,11-bis[(4-hydroxymethyl)phenoxy]undecane (**7c**,[15] 240 mg, 600 μmol) in THF (60 mL), and sodium hydride (400 mg, 10.0 mmol) in THF (400 mL). Time of addition: 6 h. Purification: silica gel; CH_2Cl_2/methanol, 19:1; R_f = 0.57. Yield: 89.9 mg (28%). M.p. 72 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.6 Hz, 4 H, Bn-$H^{2,6}$), 6.89 (s, 2 H, Py-$H^{3,5}$), 6.81 (d, J = 8.6 Hz, 4 H, Bn-$H^{3,5}$), 4.59 (s, 4 H, Py-CH_2), 4.35 (s, 4 H, Bn-CH_2), 3.95 (t, J = 6.2 Hz, 4 H, C$H_2^{1,11}$), 3.88 (s, 3 H, OCH_3), 1.73 (m_c, 4 H, C$H_2^{2,10}$), 1.43 (m_c, 4 H, C$H_2^{3,9}$), 1.4–1.3 (m, 10 H, C$H_2^{4,5,6,7,8}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1 (s, Py-C^4), 159.7 (s, Py-$C^{2,6}$), 158.9 (s, Bn-C^4), 130.0 (d, Bn-$C^{2,6}$), 129.3 (s, Bn-C^1), 114.6 (d, Bn-$C^{3,5}$), 105.7 (d, Py-$C^{3,5}$), 72.3 (t, Bn-CH$_2$), 71.0 (t, Py-CH$_2$), 67.6 (t, CH$_2^{1,11}$), 55.2 (s, OCH$_3$), 29.4, 29.0, 28.7, 28.6 (2 t, CH$_2^{2,4,5,6,7,8,10}$), 25.6 (t, CH$_2^{3,9}$) ppm. MS (EI, 70 eV): m/z (%) = 533 (4) [M]$^+$ 152 (100) [$C_8H_{10}NO_2$]$^+$, 137 (35) [$C_8H_{11}NO$]$^+$, 121 (18) [C_7H_7NO]$^+$, 107 (91) [C_6H_5NO]$^+$. MS (CI, isobutane): m/z (%) = 534 (100) [M + H]$^+$, 152 (12) [$C_8H_{10}NO_2$]$^+$. IR (ATR): $\tilde{\nu}$ = 2928, 2850 (aliph. C-H), 1598, 1509 (arom. C=C), 1241 (C-O-C), 829 (isol. arom. H), 780 (1,4-disub. arom.) cm^{-1}. $C_{33}H_{43}NO_5$ (533.31): calcd. C 74.27, H 8.12, N 2.62; found C 74.41, H 8.42, N 2.29.

4^5-Methoxy-3,7,10,23-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinatricosaphan (2d): According to general procedure C, 2,6-bis(bromomethyl)-4-methoxypyridine (**8**,[11] 177 mg, 600 μmol) in THF (60 mL), 1,12-bis[(4-hydroxymethyl)phenoxy]dodecane (**7d**,[15] 328 mg, 600 μmol) in THF (60 mL), and sodium hydride (400 mg, 10.0 mmol) in THF (400 mL). Time of addition: 6 h. Purification: silica gel; CH_2Cl_2/methanol, 19:1; R_f = 0.71. Yield: 151 mg (46%). M.p. 62 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, J = 8.7 Hz, 4 H, Bn-$H^{2,6}$), 6.89 (s, 2 H, Py-$H^{3,5}$), 6.82 (d, J = 8.7 Hz, 4 H, Bn-$H^{3,5}$), 4.59 (s, 4 H, Py-CH_2), 4.39 (s, 4 H, Bn-CH_2), 3.96 (t, J = 6.4 Hz, 4 H, C$H_2^{1,12}$), 3.88 (s, 3 H, OCH_3), 1.74 (m_c, 4 H, C$H_2^{2,11}$), 1.43 (m_c, 4 H, C$H_2^{3,10}$), 1.4–1.3 (m, 12 H, C$H_2^{4,5,6,7,8,9}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.6 (s, Py-$C^{2,6}$), 158.8 (s, Bn-C^4), 129.9 (d, Bn-$C^{2,6}$), 129.4 (s, Bn-C^1), 114.6 (d, Bn-$C^{3,5}$), 105.9 (d, Py-$C^{3,5}$), 72.3 (t, Bn-CH$_2$), 71.0 (t, Py-CH$_2$), 67.6 (t, CH$_2^{1,12}$), 55.3 (s, OCH$_3$), 29.6, 29.4, 29.3, 29.1, 29.0, 28.7, 28.7 (2 t, CH$_2^{2,4,5,6,7,8,9,11}$), 25.6 (t, CH$_2^{3,10}$) ppm. The signal for Py-C^4 could not be detected. MS (EI, 70 eV): m/z (%) = 547 (5) [M]$^+$ 152 (100) [$C_8H_{10}NO_2$]$^+$, 137 (38) [$C_8H_{11}NO$]$^+$, 121 (15) [C_7H_7NO]$^+$, 107 (97) [C_6H_5NO]$^+$. MS (CI, isobutane): m/z (%) = 534 (24) [M + H]$^+$, 152 (60) [$C_8H_{10}NO_2$]$^+$. IR (ATR): $\tilde{\nu}$ = 2919, 2850 (aliph. C–H), 1598, 1510 (arom. C=C), 1242 (C-O-C), 834 (isol. arom. H), 807 (1,4-disub. arom.) cm^{-1}.

4^5-Methoxy-3,7,10,19-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinacyclononadecaphan-14-ene (3a): According to general procedure H, 2,6-bis[4-(pent-4-enyloxy)phenyloxymethyl]-4-methoxypyridine (**15a**, 104 mg, 200 μmol) and benzylidenebis(tricyclohexylphosphane)-ruthenium dichloride (20.0 mg, 24.0 μmol) were allowed to react in dichloromethane (200 mL) for 7 d. Chromatography (dichloromethane/ethyl acetate, 9:1; R_f = 0.26) yielded 44.0 mg (90.0 μmol, 45%) of **3a**. M.p. 108 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.23 (d, J = 8.5 Hz, 4 H, Ar-$H^{2,6}$), 6.88 (s, 2 H, Py-$H^{3,5}$), 6.78 (d, J = 8.0 Hz, 4 H, Ar-$H^{3,5}$), 5.42 (m_c, 2 H, CH=CH), 4.55 (s, 4 H, PyCH$_2$OCH_2), 4.50 (s, 4 H, PyCH_2), 3.92 (t, J = 6.7 Hz, 4 H, OCH_2), 3.69 (s, 3 H, OCH_3), 2.16 (m_c, 4 H, OCH$_2$CH_2), 1.81 [m_c, 4 H, O(CH$_2$)$_2$CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.64 (s, Ar-C^1)*, 158.60 (s, Py-$C^{2,6}$)*, 130.30 (d, Ar-$C^{3,5}$), 130.20 (d, CH=CH), 129.40 (s, Ar-C^4), 114.55 (d, Ar-$C^{2,6}$), 107.06 (d, Py-$C^{3,5}$), 71.76 (t, PyCH$_2$OCH$_2$), 66.71 (t, PyCH$_2$), 55.47 (q, OCH$_3$), 28.44, 28.35 (2 t, OCH$_2$$CH_2$$CH_2$) ppm. *Assignments can be reversed. The signal for Py-C^4 could not be detected. MS (EI, 70 eV): m/z (%) = 489 (4) [M]$^+$, 152 (100) [M – $C_{22}H_{25}O_3$]$^+$, 107 (61) [M – $C_{24}H_{30}O_4$]$^+$. MS (MALDI-TOF, CCA): m/z = 512 [M + Na]$^+$, 490 [M + H]$^+$. IR (ATR): $\tilde{\nu}$ = 2926, 2848 (aliph. C–H), 1602, 1576, 1508 (arom. C=C), 1244 (C–O–C), 849 (1,4-disub. arom.) cm^{-1}. $C_{30}H_{35}NO_5$ (491.27): calcd. C 73.59, H 7.21, N 2.86; found C 73.83, H 7.82, N 2.82.

4^5-Methoxy-3,7,10,21-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinacycloheneicosaphan-15-ene (3c): According to general procedure H, 2,6-bis[4-(hex-5-enyloxy)phenyloxymethyl]-4-methoxypyridine (**15c**, 55.0 mg, 100 μmol) and benzylidenebis(tricyclohexylphosphane)-ruthenium dichloride (10.0 mg, 12.0 μmol) in dichloromethane (200 mL) were allowed to react for 5 d. Chromatography (dichloromethane/ethyl acetate, 95:5; R_f = 0.14) yielded 26.0 mg (50.0 μmol, 50%) of **3c**. M.p. 88 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.21 (d, J = 8.4 Hz, 4 H, Ar-$H^{2,6}$), 6.87 (s, 2 H, Py-$H^{3,5}$), 6.79 (d, J = 8.5 Hz, 4 H, Ar-$H^{3,5}$), 5.41 (m_c, 1 H, CH=CH_{cis}), 5.38 (m_c, 1 H, CH=CH_{trans}), 4.58 (s, 4 H, PyCH$_2$OCH_2), 4.44 (s, 4 H, PyCH_2), 3.95 (m_c, 2 H, OCH_2), 3.88 (s, 3 H, OCH_3), 2.04 [m_c, 4 H, O(CH$_2$)$_2$CH_2], 1.73 (m_c, 4 H, OCH$_2$CH_2), 1.57 [m_c, 4 H, O(CH$_2$)$_3$-CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 167.00 (s, Py-C^4), 158.88 (s, Ar-C^1)*, 158.65 (s, Py-$C^{2,6}$)*, 130.41, 130.11 (d, CH=CH), 129.94 (d, Ar-$C^{2,6}$), 129.34 (s, Ar-C^4), 114.54 (d, Ar-$C^{3,5}$), 106.19 (d, Py-$C^{3,5}$), 72.27 (t, PyCH$_2$OCH$_2$), 71.99 (t, PyCH$_2$), 67.67 (t, OCH$_2$), 55.33 (q, OCH$_3$), 31.39 [t, O(CH$_2$)$_2$$CH_2$], 28.38 (t, OCH$_2$$CH_2$), 25.90 [t, (OCH$_2$)$_3$$CH_2$] ppm. *Assignments can be reversed. MS (EI, 70 eV): m/z (%) = 517 (5) [M]$^+$, 152 (100) [M – $C_{24}H_{29}O_3$]$^+$, 107 (72) [$C_{26}H_{34}O_4$]$^+$. MS (CI, isobutane): m/z (%) = 518 (100) [M + H]$^+$, 152 (11) [M – $C_{24}H_{29}O_3$]$^+$, 107 (5) [M – $C_{26}H_{34}O_4$]$^+$. MS (MALDI-TOF, CCA): m/z = 556 [M + K]$^+$, 540 [M + Na]$^+$, 518 [M + H]$^+$. IR (ATR): $\tilde{\nu}$ = 3008 (arom. C–H), 2934, 2847 (aliph. C–H), 1601, 1580, 1509 (arom. C=C), 1241 (C–O–C), 832 (1,4-disub. arom.) cm^{-1}. $C_{32}H_{39}NO_5$ (517.28): calcd. C 74.25, H 7.59, N 2.71; found C 73.83, H 7.64, N 2.81.

4^5-Methoxy-3,7,10,31-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinacyclohentriacontaphan-20-ene (3m): According to general procedure H, 2,6-bis[4-(undec-10-enyloxy)phenyloxymethyl]-4-methoxypyridine (**15m**, 274 mg, 400 μmol), benzylidenebis(tricyclohexylphosphane)ruthenium dichloride (40.0 mg, 48.0 μmol) in dichloromethane (300 mL) were allowed to react for 6 d. Chromatography (dichloromethane/ethyl acetate, 9:1; R_f = 0.34) yielded 67.0 mg (102 μmol, 26%) of **3m**. M.p. 80 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.25 (d, J = 8.5 Hz, 4 H, Ar-$H^{2,6}$), 6.92 (s, 2 H, Py-$H^{3,5}$), 6.83 (d, J = 8.4 Hz, 4 H, Ar-$H^{3,5}$), 5.37 (m_c, 2 H, CH=CH), 4.59 (s, 4 H, PyCH$_2$OCH_2), 4.57 (s, 4 H, PyCH_2), 3.92 (m_c, 2 H, OCH_2), 3.88 (s, 3 H, OCH_3), 2.04–1.96 [m, 4 H,

$OCH_2CH_2(CH_2)_7$], 1.78–1.70 [m, 4 H, $OCH_2CH_2CH_2(CH_2)_6$], 1.44–1.26 [m, 24 H, $O(CH_2)_2(CH_2)_6$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 167.00 (s, Py-C^4), 158.94 (s, Ar-C^4)*, 158.90 (s, Py-$C^{2,6}$)*, 130.42, 129.93 (d, $CH=CH$), 129.90 (d, Ar-$C^{2,6}$), 129.38 (s, Ar-C^1), 114.50 (d, Ar-$C^{3,5}$), 106.57 (d, Py-$C^{3,5}$), 72.60 (t, $PyCH_2O\underline{C}H_2$), 70.69 (t, $Py\underline{C}H_2$), 67.98 (t, $O\underline{C}H_2$), 55.57 (q, $O\underline{C}H_3$), 32.43, 29.53, 29.40, 29.28, 29.14, 28.88, 27.21, 25.93 [8t, $OCH_2(\underline{C}H_2)_8$] ppm. *Assignments can be reversed. MS (EI, 70 eV): *m/z* (%) = 657 (13) $[M]^+$, 152 (74) $[M - C_{34}H_{49}O_3]^+$, 107 (100) $[M - C_{36}H_{54}O_4]^+$. MS (MALDI-TOF, Cl-CCA): *m/z* = 696 $[M + K]^+$, 680 $[M + Na]^+$, 658 $[M + H]^+$. IR (ATR): $\tilde{\nu}$ = 3081 (arom. C–H), 2920, 2851 (aliph. C–H), 1604, 1583, 1511 (arom C=C), 1246 (C–O–C), 826 (1,4-disub. arom.) cm^{-1}. $C_{42}H_{59}NO_5$ (657.44): calcd. C 76.67, H 9.04, N 2.13; found C 77.15, H 9.35, N 2.24.

Methyl 4-(Pent-4-enyloxy)benzoate (11a): According to general procedure D, methyl *p*-hydroxybenzoate (**9**, 3.04 g, 20.0 mmol), pent-4-en-1-ol (**10a**, 2.60 mL, 25.0 mmol), triphenylphosphane (6.30 g, 24.0 mmol), diisopropyl azodicarboxylate (6.00 mL, 30.0 mmol) in THF (60 mL) were allowed to react for 18 h. Chromatography (cyclohexane/ethyl acetate, 3:1; R_f = 0.71) yielded 3.88 g (17.6 mmol, 88%) of **11a**.[16] ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.96 (d, J = 9.0 Hz, 2 H, Ar-$H^{2,6}$), 6.90 (d, J = 9.0 Hz, 2 H, Ar-$H^{3,5}$), 5.90 (ddt, J_d = 16.8 Hz, J_d = 10.1 Hz, J_t = 6.6 Hz, 1 H, $CH=CH_2$), 5.04 (m_c, 2 H, $CH=CH_2$), 4.02 (t, J = 6.4 Hz, 2 H, OCH_2), 3.86 (s, 3 H, OCH_3), 2.26 (m_c, 2 H, OCH_2CH_2), 1.91 [m_c, 2 H, $O(CH_2)_2CH_2$] ppm. MS (EI, 70 eV): *m/z* (%) = 220 (57) $[M]^+$, 189 (11) $[M - OCH_3]^+$, 152 (41) $[M - C_5H_8]^+$, 121 (100) $[M - C_6H_{11}O]^+$. MS (CI, isobutane): *m/z* (%) = 221 (100) $[M + H]^+$, 121 (1) $[M - C_6H_{11}O]^+$.

Methyl 4-(Hex-5-enyloxy)benzoate (11b): According to general procedure D, methyl *p*-hydroxybenzoate (**9**, 1.52 g, 10.0 mmol), 5-hexen-1-ol (**10b**, 1.50 mL, 12.5 mmol), triphenylphosphane (3.15 g, 12.0 mmol), diisopropyl azodicarboxylate (3.00 mL, 15.0 mmol) in THF (30 mL) were allowed to react for 18 h. Chromatography (cyclohexane/ethyl acetate, 2:1; R_f = 0.75) yielded 2.02 g (8.64 mmol, 86%) of **11b**.[17] ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.98 (d, J = 8.5 Hz, 2 H, Ar-$H^{2,6}$), 6.90 (d, J = 8.6 Hz, 2 H, Ar-$H^{3,5}$), 5.82 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 1 H, $CH=CH_2$), 5.02 (ddt, J_d = 17.1 Hz, ^2J_d = 3.0 Hz, ^4J_t = 1.5 Hz, 1 H, $CH=CH_{trans}$), 4.98 (m_c, 1 H, $CH=CH_{cis}$), 4.01 (t, J = 6.4 Hz, 2 H, OCH_2), 3.88 (s, 3 H, OCH_3), 2.13 [m_c, 2 H, $O(CH_2)_3CH_2$], 1.82 (m_c, 2 H, OCH_2CH_2), 1.57 [m_c, 2 H, $O(CH_2)_2CH_2$] ppm. MS (EI, 70 eV): *m/z* (%) = 234 (25) $[M]^+$, 152 (63) $[M - C_6H_{10}]^+$, 121 (100) $[M - C_7H_{13}O]^+$. MS (CI, isobutane): *m/z* (%) = 235 (100) $[M + H]^+$.

Methyl 4-(Oct-7-enyloxy)benzoate (11d): According to general procedure D, methyl *p*-hydroxybenzoate (**9**, 1.97 g, 13.0 mmol), 7-octen-1-ol (**10d**, 1.50 mL, 12.5 mmol), triphenylphosphane (5.03 g, 19.2 mmol), and diisopropyl azodicarboxylate (4.80 mL, 24.0 mmol) in THF (50 mL) were allowed to react for 16 h. Chromatography (cyclohexane/ethyl acetate, 3:1; R_f = 0.76) yielded 1.50 g (5.70 mmol, 44%) of **11d**.[17] ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.97 (d, J = 9.0 Hz, 2 H, Ar-$H^{2,6}$), 6.89 (d, J = 9.0 Hz, 2 H, Ar-$H^{3,5}$), 5.81 (ddt, J_d = 16.9 Hz, J_d = 10.1 Hz, J_t = 6.6 Hz, 1 H, $CH=CH_2$), 5.03 (ddt, J_d = 17.1 Hz, ^2J_d = 2.1 Hz, J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 4.94 (ddt, J_d = 10.1 Hz, ^2J_d = 2.2 Hz, J_t = 1.6 Hz, 1 H, $CH=CH_{cis}$), 4.00 (t, J = 6.5 Hz, 2 H, OCH_2), 3.88 (s, 3 H, OCH_3), 2.08–1.26 [m_c, 10 H, $OCH_2(CH_2)_5$] ppm. MS (EI, 70 eV): *m/z* (%) = 262 (32) $[M]^+$, 231 (9) $[M - OCH_3]^+$, 152 (100) $[M - C_8H_{14}]^+$, 121 (94) $[M - C_{19}H_{17}O]^+$. MS (CI, isobutane): *m/z* (%) = 263 (100) $[M + H]^+$.

Methyl 4-(Dec-9-enyloxy)benzoate (11e): According to general procedure D, methyl *p*-hydroxybenzoate (**9**, 2.28 g, 15.0 mmol), 9-decen-1-ol (**10e**, 3.35 mL, 18.8 mmol), triphenylphosphane (4.72 g, 18.0 mmol), diisopropyl azodicarboxylate (4.43 mL, 22.5 mmol) in THF (40 mL) were allowed to react for 3 d. Chromatography (cyclohexane/ethyl acetate, 3:1; R_f = 0.74) yielded 3.74 g (12.9 mmol, 86%) of **11e**. M.p. 35 °C (ref.[18] 36 °C). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.98 (d, J = 9.0 Hz, 2 H, Ar-$H^{2,6}$), 6.90 (d, J = 9.0 Hz, 2 H, Ar-$H^{3,5}$), 5.81 (ddt, J_d = 16.8 Hz, J_d = 10.1 Hz, J_t = 6.6 Hz, 1 H, $CH=CH_2$), 5.04 (ddt, J_d = 16.8 Hz, ^2J_d = 2.2 Hz, ^4J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 4.93 (ddt, J_d = 10.1 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.2 Hz, 1 H, $CH=CH_{cis}$), 4.00 (t, J = 6.5 Hz, 2 H, OCH_2), 2.10–1.21 [m_c, 14 H, $OCH_2(CH_2)_7$] ppm. MS (EI, 70 eV): *m/z* (%) = 290 (33) $[M]^+$, 259 (6) $[M - OCH_3]^+$, 152 (100) $[M - C_{10}H_{18}]^+$, 121 (71) $[M - C_{11}H_{21}O]^+$. MS (CI, isobutane): *m/z* (%) = 291 (100) $[M + H]^+$, 259 (1) $[M - OCH_3]^+$, 152 (3) $[M - C_{10}H_{18}]^+$, 121(2) $[M - C_{11}H_{21}O]^+$.

Methyl 4-(Undec-10-enyloxy)benzoate (11f): According to general procedure D, methyl *p*-hydroxybenzoate (**9**, 3.04 g, 20.0 mmol), 10-undecen-1-ol (**10f**, 5.00 mL, 25.0 mmol), triphenylphosphane (6.30 g, 24.0 mmol), diisopropyl azodicarboxylate (6.00 mL, 30.0 mmol) in THF (60 mL) were allowed to react for 3 d. Chromatography (cyclohexane/ethyl acetate, 3:1; R_f = 0.70) yielded 4.56 g (15.0 mmol, 75%) of **11f**. M.p. 57 °C (ref.[19] 57–59 °C). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.61 (d, J = 9.0 Hz, 2 H, Ar-$H^{2,6}$), 6.90 (d, J = 9.0 Hz, 2 H, Ar-$H^{3,5}$), 5.81 (ddt, J_d = 16.8 Hz, J_d = 10.1 Hz, J_t = 6.6 Hz, 1 H, $CH=CH_2$), 5.02 (ddt, J_d = 17.0 Hz, ^2J_d = 2.2 Hz, ^4J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 4.92 (ddt, J_d = 10.1 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.2 Hz, 1 H, $CH=CH_{cis}$), 3.95 (t, J = 6.5 Hz, 2 H, OCH_2), 3.88 (s, 3 H, OCH_3), 2.09–1.23 [m_c, 16 H, $OCH_2(CH_2)_8$] ppm. MS (EI, 70 eV): *m/z* (%) = 304 (31) $[M]^+$, 273 (6) $[M - OCH_3]^+$, 152 (100) $[M - C_{11}H_2O]^+$, 121 (75) $[M - C_{12}H_{23}O]^+$. MS (CI, isobutane): *m/z* (%) = 305 (100) $[M + H]^+$, 273 (2) $[M - OCH_3]^+$, 153 (4) $[M - C_{11}H_{19}]^+$, 121 (2) $[M - C_{12}H_{23}O_9]^+$.

4-(Pent-4-enyloxy)phenylmethanol (14a): According to general procedure E, methyl 4-(pent-4-enyloxy)benzoate (**11a**, 3.88 g, 17.6 mmol), lithium aluminum hydride (1.40 g, 37.0 mmol), THF (90 mL). Chromatography (cyclohexane/ethyl acetate, 2:1; R_f = 0.39) yielded 2.69 g (13.8 mmol, 80%) of **14a**. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.26 (d, J = 8.6 Hz, 2 H, Ar-$H^{2,6}$), 6.87 (d, J = 8.6 Hz, 2 H, Ar-$H^{3,5}$), 5.85 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 1 H, $CH=CH_2$), 5.02 (m_c, 2 H, $CH=CH_2$), 4.78 (s, 1 H, CH_2OH), 4.58 (s, 2 H, CH_2OH), 3.96 (t, J = 6.5 Hz, 2 H, OCH_2), 2.23 (m_c, 2 H, OCH_2CH_2), 1.88 [m_c, 2 H, $O(CH_2)_2CH_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 158.68 (s, Ar-C^4), 137.82 (d, $CH=CH_2$), 133.05 (s, Ar-C^1), 129.44 (d, Ar-$C^{2,6}$), 115.22 (t, $CH=CH_2$), 114.60 (d, Ar-$C^{3,5}$), 67.26 (t, OCH_2), 65.05 (t, CH_2OH), 30.12 [t, $O(CH_2)_2CH_2$], 28.43 (t, OCH_2CH_2) ppm. MS (EI, 70 eV): *m/z* (%) = 192 (100) $[M]^+$, 124 (99) $[M - C_5H_8]^+$, 106 (53) $[M - C_5H_8O]^+$. MS (CI, isobutane): *m/z* (%) = 193 (6) $[M + H]^+$, 175 (100) $[M - OH]^+$, 107 (8) $[M - C_5H_8O]^+$. IR (ATR): $\tilde{\nu}$ = 3364 (OH), 3075 (arom. C–H), 2939, 2870 (aliph. C–H), 1640 (aliph. C=C), 1611, 1585, 1511 (arom. C=C), 1241 (C–O–C), 824 (1,4-disub. arom.) cm^{-1}. $C_{12}H_{16}O_2 \cdot 0.25C_6H_{12}$ (213.29): calcd. C 76.01, H 8.98; found C 76.05, H 8.65.

4-(Hex-5-enyloxy)phenylmethanol (14b): According to general procedure E: methyl 4-(hex-5-enyloxy)benzoate (**11b**, 2.02 g, 8.64 mmol), lithium aluminum hydride (683 mg, 18.0 mmol), THF (50 mL). Chromatography (cyclohexane/ethyl acetate, 3:1; R_f = 0.23) yielded 1.37 g (13.8 mmol, 77%) of **14b**.[6] ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.25 (d, J = 8.4 Hz, 2 H, Ar-$H^{3,5}$), 6.84 (d, J = 8.6 Hz, 2 H, Ar-$H^{2,6}$), 5.81 (ddt, J_d = 16.9 Hz, J_d =

10.1 Hz, J_t = 6.6 Hz, 1 H, C*H*=CH$_2$), 5.00 (m_c, 2 H, CH=CH_2), 4.60 (s, 2 H, CH_2OH), 3.96 (t, J = 6.4 Hz, 2 H, OCH_2), 2.14 [m_c, 2 H, O(CH$_2$)$_3$CH_2], 1.81 (m_c, 2 H, OCH$_2$CH_2), 1.57 [m_c, 2 H, O(CH$_2$)$_2$CH_2] ppm. MS (EI, 70 eV): *m*/*z* (%) = 206 (7) [M]$^+$, 124 (100) [M – C$_6$H$_{10}$]$^+$, 106 (51) [M – C$_6$H$_{12}$O]$^+$. MS (CI, isobutane): *m*/*z* (%) = 207 (6) [M + H]$^+$, 206 (11), [M]$^+$ 189 (100) [M – OH]$^+$.

4-(Hept-6-enyloxy)phenylmethanol (14c): 4-Hydroxybenzyl alcohol (**12**, 1.24 g, 10.0 mmol) and 7-bromo-1-heptene (**13c**, 1.52 mL, 10.0 mmol) were dissolved in butanone (70 mL), and potassium carbonate (6.91 g, 50.0 mmol) and sodium iodide (ca. 3 mg, ca. 20 μmol) were added. Under an atmosphere of nitrogen, the mixture was heated to reflux for 18 h, cooled to room temperature, and filtered. The filtrate was concentrated, and the remaining oil was dissolved in dichloromethane (50 mL). The organic layer was washed with deionized water (2 × 25 mL) and brine (25 mL). The combined aqueous layer was extracted with dichloromethane (25 mL), and the combined organic layer was dried with magnesium sulfate and concentrated in vacuo. Chromatography (silica gel; cyclohexane/ethyl acetate, 2:1; R_f = 0.15) yielded 780 mg (4.75 mmol, 48%) of a colorless solid. M.p. 28 °C. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ = 7.27 (d, J = 8.6 Hz, 2 H, Ar-$H^{2,6}$), 6.87 (d, J = 8.6 Hz, 2 H, Ar-$H^{3,5}$), 5.81 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 1 H, C*H*=CH$_2$), 5.01 (ddt, J_d = 17.1 Hz, ^2J_d = 2.6 Hz, ^4J_t = 1.7 Hz, 1 H, CH=CHH_{trans}), 4.95 (ddt, J_d = 10.2 Hz, ^2J_d = 2.4 Hz, J_t = 1.2 Hz, 1 H, CH=CHH_{cis}), 4.60 (s, 2 H, CH_2OH), 3.95 (t, J = 6.5 Hz, 2 H, OCH_2), 2.08 [m_c, 2 H, O(CH$_2$)$_2$CH_2], 1.79 (m_c, 2 H, OCH$_2$CH_2), 1.47 [m_c, 4 H, O(CH$_2$)$_3$(CH_2)$_2$] ppm. ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ = 158.78 (s, Ar-C^4), 138.84 (d, *C*H=CH$_2$), 132.97 (s, Ar-C^1), 128.65 (d, Ar-$C^{2,6}$), 114.59 (d, Ar-$C^{3,5}$), 114.47 (t, CH=*C*H$_2$), 67.98 (t, O*C*H$_2$), 65.09 (t, *C*H$_2$OH), 33.69 [t, O(CH$_2$)$_2$*C*H$_2$], 29.13 (t, OCH$_2$*C*H$_2$), 28.66, 25.56 [2 t, O(CH$_2$)$_2$(*C*H$_2$)$_2$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 220 (46) [M]$^+$, 124 (100) [M – C$_7$H$_{12}$]$^+$, 106 (43) [M – C$_7$H$_{14}$O]$^+$. MS (CI, isobutane): *m*/*z* (%) = 221 (4) [M + H]$^+$, 220 (9) [M]$^+$, 203 (100) [M – OH]$^+$. IR (ATR): $\tilde{\nu}$ = 3327 (OH), 3081 (arom. C–H), 2936, 2860 (aliph. C–H), 1642 (aliph. C=C), 1610, 1582, 1509 (arom. C=C), 1520 (C–O–C), 817 (1,4-disub. arom.) cm^{-1}. C$_{14}$H$_{20}$O$_2$ (220.31): calcd. C 76.33, H 9.15; found C 76.80, H 9.36.

4-(Oct-7-enyloxy)phenylmethanol (14d): According to general procedure E: methyl 4-(oct-7-enyloxy)benzoate (**11d**, 1.50 g, 15.7 mmol), lithium aluminum hydride (456 mg, 12.0 mmol), THF (40 mL). Chromatography (cyclohexane/ethyl acetate, 3:1; R_f = 0.26) yielded 1.19 g (5.08 mmol, 89%) of **14d**. M.p. 33 °C. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ = 7.27 (d, J = 8.7 Hz, 2 H, Ar-$H^{2,6}$), 6.88 (d, J = 8.6 Hz, 2 H, Ar-$H^{3,5}$), 5.81 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 1 H, C*H*=CH$_2$), 5.00 (ddt, J_d = 17.1 Hz, ^2J_d = 2.2 Hz, ^4J_t = 1.9 Hz, 1 H, CH=CHH_{trans}), 4.94 (ddt, J_d = 10.2 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.1 Hz, 1 H, CH=CHH_{cis}), 4.71 (s, 1 H, CH$_2$O*H*), 4.60 (s, 2 H, CH_2OH), 3.95 (t, J = 6.6 Hz, 2 H, OCH_2), 2.06 [m_c, 2 H, O(CH$_2$)$_2$CH_2], 1.78 (m_c, 2 H, OCH$_2$CH_2), 1.45 [m_c, 6 H, O(CH$_2$)$_3$(CH_2)$_3$] ppm. ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ = 158.80 (s, Ar-C^4), 139.03 (d, *C*H=CH$_2$), 132.95 (s, Ar-C^1), 128.65 (d, Ar-$C^{2,6}$), 114.59 (d, Ar-$C^{3,5}$), 114.31 (t, CH=*C*H$_2$), 68.03 (t, O*C*H$_2$), 65.10 (t, *C*H$_2$OH), 33.71 [t, O(CH$_2$)$_2$*C*H$_2$], 29.22 (t, OCH$_2$*C*H$_2$), 28.86, 28.84, 22.67 [3t, O(CH$_2$)$_3$(*C*H$_2$)$_3$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 234 (38) [M]$^+$, 180 (6) [M – C$_8$H$_{14}$O]$^+$, 137 (2) [M – C$_7$H$_{13}$]$^+$, 124 (100) [M – C$_8$H$_{14}$]$^+$. MS (CI, isobutane): *m*/*z* (%) = 235 (5) [M + H]$^+$, 217 (100) [M – OH]$^+$, 107 (12) [M – C$_8$H$_{15}$O]$^+$. IR (ATR): $\tilde{\nu}$ = 3329 (OH), 3063 (arom. C–H), 2933, 2856 (aliph. C–H), 1642 (aliph. C=C), 1582, 1510 (arom. C=C), 1251 (C–O–C), 818 (1,4-disub. arom.) cm^{-1}. HRMS (EI, 70 eV): calcd. for C$_{15}$H$_{22}$O$_2$ 234.16199; found 234.16396 (Δ = –8.4 ppm). HRMS (EI, 70 eV): calcd. for C$_{14}$^{13}CH$_{22}$O$_2$ 235.16533; found 235.16433 (Δ = –0.0 ppm).

4-(Dec-9-enyloxy)phenylmethanol (14e): According to general procedure E: methyl 4-(dec-9-enyloxy)benzoate (**11e**, 2.40 g, 8.30 mmol), lithium aluminum hydride (660 mg, 17.4 mmol), THF (76 mL). Chromatography (cyclohexane/ethyl acetate, 2:1; R_f = 0.49) yielded 2.11 g (8.04 mmol, 97%) of **14e**.[20] ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ = 7.26 (d, J = 8.8 Hz, 2 H, Ar-$H^{2,6}$), 6.88 (d, J = 8.7 Hz, 2 H, Ar-$H^{3,5}$), 5.81 (ddt, J_d = 16.8 Hz, J_d = 10.1 Hz, J_t = 6.6 Hz, 1 H, C*H*=CH$_2$), 5.04 (m_c, 1 H, CH=CHH_{trans}), 4.93 (m_c, 1 H, CH=CHH_{cis}), 4.61 (s, 2 H, CH_2OH), 3.95 (t, J = 6.5 Hz, 2 H, OCH_2), 2.07–1.25 [m_c, 14 H, OCH$_2$(CH_2)$_7$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 262 (17) [M]$^+$, 124 (100) [M – C$_{10}$H$_{18}$]$^+$, 106 (48) [M – C$_{10}$H$_{20}$]$^+$. MS (CI, isobutane): *m*/*z* (%) = 263 (3) [M + H]$^+$, 245 (100) [M – OH]$^+$.

4-(Undec-10-enyloxy)phenylmethanol (14f): According to general procedure E, methyl 4-(undec-10-enyloxy)benzoate (**11f**, 4.41 g, 17.4 mmol), lithium aluminum hydride (1.14 g, 30.0 mmol), THF (95 mL). Chromatography (cyclohexane/ethyl acetate, 2:1; R_f = 0.43) yielded 3.62 g (13.1 mmol, 90%) of **14f**. M.p. 52 °C (ref.[19] 49.5–50.5 °C). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ = 7.27 (d, J = 8.8 Hz, 2 H, Ar-$H^{2,6}$), 6.88 (d, J = 8.7 Hz, 2 H, Ar-$H^{3,5}$), 5.80 (ddt, J_d = 16.8 Hz, J_d = 10.1 Hz, J_t = 6.6 Hz, 1 H, C*H*=CH$_2$), 5.04 (ddt, J_d = 17.7 Hz, J_d = 2.2 Hz, ^4J_t = 1.6 Hz, 1 H, CH=CHH_{trans}), 4.94 (ddt, J_d = 10.1 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.2 Hz, 1 H CH=CHH_{cis}), 4.60 (s, 2 H, CH_2OH), 3.95 (t, J = 6.5 Hz, 2 H, OCH_2), 2.09–1.31 [m, 16 H, OCH$_2$(CH_2)$_8$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 276 (30) [M]$^+$, 163 (3) [M – C$_7$H$_{13}$O]$^+$, 124 (100) [M – C$_{11}$H$_2$O]$^+$, 106 (3) [C$_{11}$H$_{22}$O]$^+$. MS (CI, isobutane): *m*/*z* (%) = 277 (3) [M + H]$^+$, 276 (9) [M]$^+$, 259 (100) [M – OH]$^+$, 124 (2) [M – C$_{11}$H$_2$O]$^+$, 107 (3) [M – C$_{11}$H$_{21}$O]$^+$.

4-Methoxy-2,6-bis[4-(pent-4-enyloxy)phenylmethyloxymethyl]-pyridine (15a): According to general procedure G, sodium hydride (170 mg, 7.00 mmol) in THF (35 mL), 4-(pent-4-enyloxy)phenylmethanol (**14a**, 769 mg, 4.00 mmol) in THF (35 mL), and 2,6-bis-(bromomethyl)-4-methoxypyridine (**8**,[11] 590 mg, 2.00 mmol) in THF (35 mL) were allowed to react for 2 d. Chromatography (dichloromethane/ethyl acetate, 95:5; R_f = 0.23) yielded 460 mg (890 μmol, 44%) of **15a**. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ = 7.30 (d, J = 8.5 Hz, 4 H, Ar-$H^{2,6}$), 6.92 (s, 2 H, Py-$H^{3,5}$), 6.87 (d, J = 8.6 Hz, 4 H, Ar-$H^{3,5}$), 5.85 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 2 H, C*H*=CH$_2$), 5.06 (ddt, J_d = 17.1 Hz, ^2J_d = 2.4 Hz, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.00 (ddt, J_d = 10.2 Hz, ^2J_d = 2.4 Hz, ^4J_t = 1.3 Hz, 2 H, CH=CHH_{Hcis}), 4.59 (s, 4 H, PyCH$_2$-OCH_2), 4.56 (s, 4 H, PyCH_2), 3.97 (t, J = 6.5 Hz, 4 H, OCH_2), 3.85 (s, 3 H, OCH_3), 2.23 [m_c, 4 H, O(CH$_2$)$_2$CH_2], 1.88 (m_c, 4 H, OCH$_2$-CH_2) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ = 167.33 (s, Py-C^4), 159.83 (s, Py-$C^{2,6}$), 158.82 (s, Ar-C^1), 137.83 (d, *C*H=CH$_2$), 129.92 (s, Ar-C^4), 129.54 (d, Ar-$C^{2,6}$), 115.22 (t, CH=*C*H$_2$), 114.48 (d, Ar-$C^{3,5}$), 105.87 (d, Py-$C^{3,5}$), 72.69 (t, PyCH$_2$-O*C*H$_2$)*, 72.53 (t, Py-*C*H$_2$)*, 67.21 (t, O*C*H$_2$), 55.28 (q, O*C*H$_3$), 30.12 [t, O(CH$_2$)$_2$*C*H$_2$], 28.43 (t, OCH$_2$*C*H$_2$) ppm. *Assignments can be reversed. MS (EI, 70 eV): *m*/*z* (%) = 327 (62) [M – C$_{12}$H$_{14}$O$_2$]$^+$, 258 (4) [M – C$_{17}$H$_{23}$O$_2$]$^+$, 175 (100) [M – C$_{20}$H$_{24}$NO$_4$]$^+$, 107 (75) [M – C$_{26}$H$_{34}$O$_4$]$^+$. MS (CI, isobutane): *m*/*z* (%) = 518 (100) [M + H]$^+$, 327 (14) [M – C$_{12}$H$_{14}$O$_2$]$^+$, 191 (31) [M – C$_{20}$H$_{24}$NO$_3$]$^+$, 175 (27) [M – C$_{20}$H$_{24}$NO$_4$]$^+$, 107 (6) [M – C$_{26}$H$_{34}$O$_4$]$^+$. MS (MALDI-TOF, Cl-CCA): *m*/*z* (%) = 540 [M + Na]$^+$, 518 [M + H]$^+$. IR (ATR): $\tilde{\nu}$ = 3075 (arom. C–H), 2938, 2856 (aliph. C–H), 1640 (aliph. C=C), 1599, 1577, 1511 (arom.

C=C), 1242 (C–O–C), 824 (1,4-disub. arom.) cm^{-1}. $C_{32}H_{39}NO_5$ (517.28): calcd. C 74.25, H 7.59, N 2.71; found C 74.06, H 7.71, N 2.81.

2,6-Bis[4-(hex-5-enyloxy)phenylmethyloxymethyl]-4-methoxypyridine (15c): According to general procedure G, sodium hydride (205 mg, 8.54 mmol) in THF (12 mL), 4-(hex-5-enyloxy)phenylmethanol (**14b**,[6] 1.31 g, 6.35 mmol) in THF (12 mL), and 2,6-bis(bromomethyl)-4-methoxypyridine (**8**,[11] 938 mg, 3.18 mmol) in THF (17 mL) were allowed to react for 18 h. Chromatography (dichloromethane/ethyl acetate, 95:5; R_f = 0.18) yielded 580 mg (1.06 mmol, 33%) of **15c**. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.29 (d, J = 8.6 Hz, 4 H, Ar-$H^{2,6}$), 6.92 (s, 2 H, Py-$H^{3,5}$), 6.87 (d, J = 8.6 Hz, 4 H, Ar-$H^{3,5}$), 5.82 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_d = 6.7 Hz, 2 H, CH=CH$_2$), 5.03 (ddt, J_d = 17.1 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 4.97 (ddt, J_d = 10.2 Hz, ^2J_d = 2.2 Hz, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 4.58 (s, 4 H, PyCH$_2$-OCH_2), 4.56 (s, 4 H, PyCH_2), 3.96 (t, J = 6.5 Hz, 4 H, OCH_2), 3.85 (s, 3 H, OCH_3), 2.12 [m$_c$, 4 H, O(CH$_2$)$_2$CH_2], 1.80 (m$_c$, 4 H, OCH$_2$CH_2), 1.57 [m$_c$, 4 H, O(CH$_2$)$_3$CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 167.27 (s, Py-C^4), 159.89 (s, Py-$C^{2,6}$), 158.85 (s, Ar-C^1), 138.56 (d, CH=CH$_2$), 129.88 (s, Ar-C^4), 129.53 (d, Ar-$C^{2,6}$), 114.76 (t, CH=CH$_2$), 114.45 (d, Ar-$C^{3,5}$), 105.84 (d, Py-$C^{3,5}$), 72.68 (t, PyCH$_2$-OCH$_2$)*, 72.61 (t, Py-CH$_2$)*, 67.81 (t, OCH$_2$), 55.26 (q, OCH$_3$), 33.45 [t, O(CH$_2$)$_2$$CH_2$], 28.72 (t, OCH$_2$$CH_2$), 25.34 [t, O(CH$_2$)$_3$$CH_2$] ppm. *Assignments can be reversed. MS (EI, 70 eV): m/z (%) = 341 (53) [M – $C_{13}H_{16}O_2$]$^+$, 189 (55) [M – $C_{21}H_{26}NO_4$]$^+$, 152 (9) [M – $C_{26}H_{33}O_3$]$^+$, 107 (100) [M – $C_{28}H_{38}O_4$]$^+$. MS (CI, isobutane): m/z (%) = 546(100) [M + H]$^+$, 342 (31) [M – $C_{13}H_{15}O_2$]$^+$, 205 (85) [M – $C_{21}H_{26}NO_3$]$^+$, 107 (29) [M – $C_{28}H_{37}O_4$]$^+$. MS (MALDI-TOF, Cl-CCA): m/z (%) = 569 [M + Na]$^+$, 546 [M + H]$^+$. IR (ATR): $\tilde{\nu}$ = 3074 (arom. C–H), 2937, 2858 (aliph. C–H), 1640 (aliph. C=C), 1599, 1577, 1511 (arom. C=C), 1241 (C–O–C), 821 (1,4-disub. arom.) cm^{-1}. $C_{34}H_{43}NO_5$ (545.31): calcd. C 74.83, H 7.94, N 2.57; found C 74.84, H 8.20, N 2.77.

4-Methoxy-2,6-bis[4-(undec-10-enyloxy)phenylmethyloxymethyl]-pyridine (15m): According to general procedure G, sodium hydride (170 mg, 7.00 mmol) in THF (35 mL), 4-(undec-10-enyloxy)phenylmethanol (**14f**,[19] 1.11 g, 4.00 mmol) in THF (35 mL), and 2,6-bis(bromomethyl)-4-methoxypyridine (**8**,[11] 590 mg, 2.00 mmol) in THF (35 mL) were allowed to react for 4 d. Chromatography (dichloromethane/ethyl acetate, 95:5; R_f = 0.15) yielded 556 mg (800 µmol, 41%) of **15m**. M.p. 39 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.29 (d, J = 8.7 Hz, 4 H, Ar-$H^{3,5}$), 6.93 (s, 2 H, Py-$H^{3,5}$), 6.87 (d, J = 8.7 Hz, 4 H, Ar-$H^{2,6}$), 5.81 (ddt, J_d = 16.9 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 2 H, CH=CH$_2$), 4.99 (ddt, J_d = 17.1 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 4.93 (ddt, J_d = 10.2 Hz, ^2J_d = 2.3 Hz, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 4.60 (s, 4 H, PyCH_2), 4.56 (s, 4 H, PyCH$_2$OCH_2), 3.94 (t, J = 6.6 Hz, 4 H, OCH_2), 3.85 (s, 3 H, OCH_3), 2.04 [m, 4 H, O(CH$_2$)$_7$CH_2], 1.77 (m$_c$, 4 H, OCH$_2$CH_2), 1.47–1.29 [m$_c$, 24 H, OCH$_2$CH$_2$(CH_2)$_6$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 167.45 (s, Py-C^4), 159.77 (d, Py-$C^{2,6}$), 158.91 (s, Ar-C^1), 139.24 (d, CH=CH$_2$), 129.78 (s, Ar-C^4), 129.53 (Ar-$C^{2,6}$), 114.46 (t, CH=CH$_2$), 114.19 (d, Ar-$C^{3,5}$), 105.90 (d, Py-$C^{3,5}$), 72.72 (t, PyCH$_2$OCH$_2$), 72.42 (t, PyCH$_2$), 68.08 (t, OCH$_2$), 55.31 (q, OCH$_3$), 33.82 [t, O(CH$_2$)$_7$$CH_2$], 29.53, 29.44, 29.39, 29.28, 29.13, 28.94 [6t, OCH$_2$CH$_2$(CH$_2$)$_6$] ppm. MS (EI, 70 eV): m/z (%) = 411 (98) [M – $C_{18}H_{26}O_2$]$^+$, 259 (31) [M – $C_{29}H_{46}O_2$]$^+$, 151 (29) [M – $C_{36}H_{54}O_3$]$^+$, 107 (100) [M – $C_{38}H_{58}O_4$]$^+$. MS (CI, isobutane): m/z (%) = 686 (24) [M + H]$^+$, 412 (14) [M – $C_{18}H_{25}O_2$]$^+$, 275 (100) [M – $C_{26}H_{36}NO_3$]$^+$, 107 (3) [M – $C_{38}H_{58}O_4$]$^+$. MS (MALDI-TOF, Cl-CCA): m/z = 724 [M + K]$^+$, 708 [M + Na]$^+$, 686 [M + H]$^+$. IR (ATR): $\tilde{\nu}$ = 3080 (arom. C–H), 2920, 2851 (aliph. C–H), 1602, 1574, 1513 (arom. C=C), 1240 (C–O–C), 828 (1,4-disub. arom.) cm^{-1}. $C_{44}H_{63}NO_5$ (685.47): calcd. C 77.04, H 9.26, N 2.04; found C 77.42, H 9.59, N 2.17.

Acknowledgments

We are grateful for the support of the Deutsche Forschungsgemeinschaft through its Sonderforschungsbereich 677 “Funktion durch Schalten”.

[1] G. Schill, H. Zollenkopf, *Nachr. Chem. Techn.* **1967**, *15*, 149.
[2] a) R. P. Feynman, *Eng. Sci.* **1960**, *23*, 22–36; b) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines: A Journey into the Nano World*, Wiley-VCH, Weinheim, **2003**; c) T. R. Kelly (Ed.), *Topics in Current Chemistry Vol. 262: Molecular Machines*, **2005**, pp. 1–227; d) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, *Nature* **1999**, *401*, 152–155; e) M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem.* **2000**, *122*, 3422–3425; *Angew. Chem. Int. Ed.* **2000**, *39*, 3284–3287; f) A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Wurpel, *Science* **2001**, *291*, 2124–2128; g) D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* **2003**, *424*, 174–179; h) J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845–1849.
[3] A few examples of recent reviews on rotaxanes and molecular machines: a) J. D. Crowley, S. M. Goldup, A.-L. Lee, D. A. Leigh, R. T. McBurney, *Chem. Soc. Rev.* **2009**, *38*, 1530–1541; b) P. Bodis, M. R. Panman, B. H. Bakker, A. Mateo-Alonso, M. Prato, W. J. Buma, A. M. Brouwer, E. R. Kay, D. A. Leigh, S. Woutersen, *Acc. Chem. Res.* **2009**, *42*, 1462–1469; c) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77–92; d) V. Balzani, A. Credi, S. Silvi, M. Venturi, *Chem. Soc. Rev.* **2006**, *35*, 1135–1149; e) V. Balzani, A. Credi, B. Ferrer, S. Silvi, M. Venturi, *Top. Curr. Chem.* **2005**, *262*, 1–27; f) H. Tian, Q.-C. Wang, *Chem. Soc. Rev.* **2006**, *35*, 361–374; g) J.-P. Collin, J.-P. Sauvage, *Chem. Lett.* **2005**, *34*, 742–747.
[4] V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby, D. B. Walker, *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187.
[5] I. T. Harrison, *J. Chem. Soc., Chem. Commun.* **1972**, 231–232.
[6] 4-Unsubstituted pyridine macrocycles by ring-closing metathesis: A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin, D. B. Walker, *J. Am. Chem. Soc.* **2005**, *127*, 12612–12619.
[7] U. Lüning, F. Fahrenkrug, M. Hagen, *Eur. J. Org. Chem.* **2001**, 2161–2163.
[8] S. Lüthje, C. Bornholt, U. Lüning, *Eur. J. Org. Chem.* **2006**, 909–915.
[9] T. Liebig, M. Abbass, U. Lüning, *Eur. J. Org. Chem.* **2007**, 972–980.
[10] O. Winkelmann, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2007**, 981–987.
[11] F. Vögtle, G. Brodesser, M. Nieger, K. Rissanen, *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 325–329.
[12] N. S. Nesunts, S. A. Avetisyan, I. A. Dzhagatspanyan, N. E. Akopyan, O. L. Mndzhoyan, *Pharm. Chem. J.* **1983**, *17*, 480–484.
[13] A. C. Griffin, T. R. Britt, R. S. L. Hung, M. Steele, *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 305–314.
[14] R. W. Wagner, T. E. Johnson, J. S. Lindsey, *Tetrahedron* **1997**, *53*, 6755–6790.
[15] C. A. Schalley, G. Silva, C. F. Nising, P. Linnartz, *Helv. Chim. Acta* **2002**, *85*, 1578–1596.
[16] C. F. Chow, S. Fujii, J.-M. Lehn, *Chem. Asian J.* **2008**, *3*, 1324–1335.
[17] D. R. Medeiros, M. A. Hale, R. J. P. Hung, J. K. Leitko, C. G. Willson, *J. Mater. Chem.* **1999**, *9*, 1453–1460.

[18] D. M. Walba, H. Yang, R. K. Shoemaker, P. Keller, R. Shao, D. A. Coleman, C. D. Jones, M. Nakata, N. A. Clark, *Chem. Mater.* **2006**, *18*, 4576–4584.
[19] U. Beginn, G. Zipp, M. Möller, *Chem. Eur. J.* **2000**, *6*, 2016–2023.
[20] a) Y. Haramoto, *PCT Int. Appl.* WO 2004085359 A1 20041007, **2004**; b) Y. Haramoto, *PCT Int. Appl.* WO 2004085380 A1 20041007, **2004**; c) Y. Haramoto, *PCT Int. Appl.* WO 2004085398 A1 20041007, **2004**.

Received: April 13, 2010
Published Online: July 14, 2010

