A New Synthesis of Fused Oxa- and Thiacrown Ethers–Thiophene/Furan Oligomers

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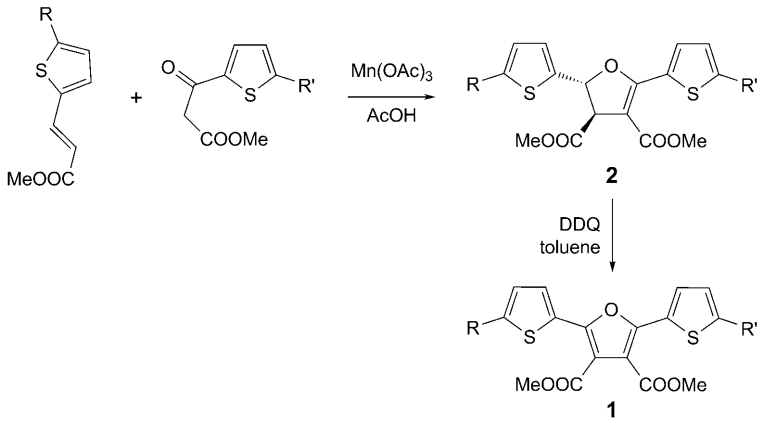
We have developed a two-step sequence for preparing a series of macrocyclic oxa- and thiacrown ethers affixed to a thiophene/furan oligomer. The sequence involves the intramolecular Mn^{III}-promoted cyclization of linear diester precursors into 2,3-dihydrofurans, whose dehydrogenation furnishes the title compounds. A preliminary NMR study has shown that one of them seems to specifically chelate Pb^{2+} cations.

Introduction. – We have previously reported a new approach toward the synthesis of functionalized alternate thiophene/furan oligomers **1** [1]. It is based on the intermolecular version of the $Mn(OAc)_3$-mediated radical addition of β-keto esters to alkenes in AcOH (*Scheme 1*), which allows the efficient one-pot synthesis of 2,3-dihydrofurans **2**. Their subsequent dehydrogenation with DDQ (=2,3-dichloro-5,6-dicyanobenzoquinone) furnishes the corresponding alternate thiophene/furan oligomers in an overall two-step sequence from readily available starting compounds.

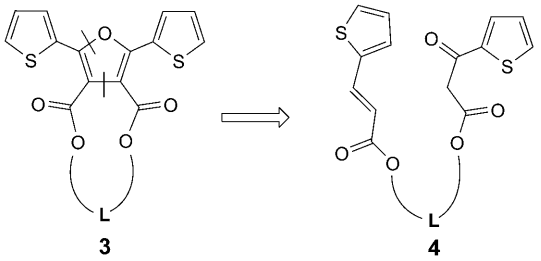
Scheme 1. *Formation of Oligomers* **1** *by Bimolecular Cyclization and Dehydrogenation*



Here, we describe for the first time the application of a related sequence to prepare fused crown ether–thiophene/furan oligomers **3** from open-chain precursors **4**, involving, as the key step, the intramolecular version of the $Mn(OAc)_3$-mediated

oxidative addition (*Scheme 2*)[1]). To this end, we had first to devise a practical access to the required **4** possessing both the β-keto ester and the alkenyl moieties linked by tethers of variable lengths and structures.

Scheme 2. *Formation of Oligomers* **3** *by Intramolecular Cyclization* (retrosynthetic analysis)



Results and Discussion. – The required starting compounds **4a** – **4i** were prepared as depicted in *Scheme 3*.

Starting from anhydrous α,ω-diols **5** (2 equiv.), the alkenyl moiety was first introduced by the slow addition of (*E*)-3-(thiophen-2-yl)prop-2-enoyl chloride (1 equiv.) in CH_2Cl_2 in the presence of Et_3N. This direct monoesterification of unprotected diols proved to be the most efficient method from the overall point of view of the yield, provided that the addition rate of the acid chloride is carefully controlled to avoid diesterification: mono-esters **6** were thus obtained with moderate-to-excellent yields (*Table*).

Table. *Synthesis of the Components* **4**, **6**, *and* **8** *for the Formation of* **3**

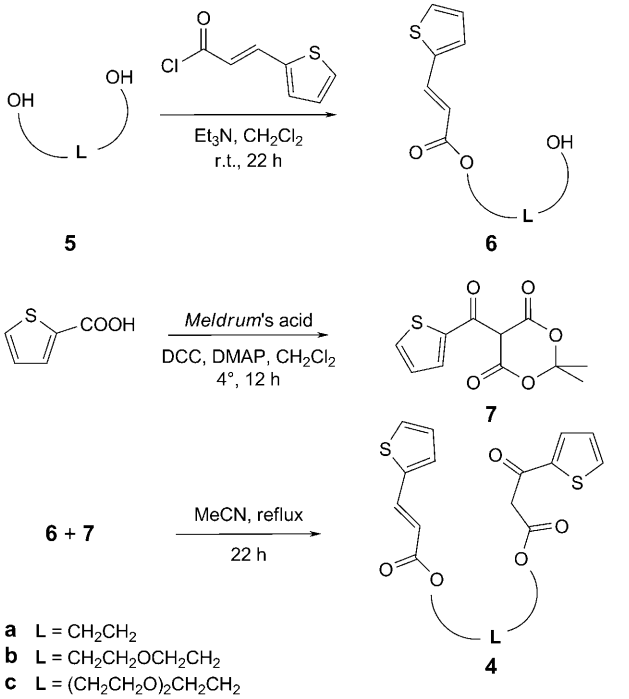
L[a])	Yield [%][b])			
	4	**6**	**8**	**3**
a	93	91	traces	–
b	89	85	78	83
c	89	60	67	71
d	95	52	67	68
e	88	63	53	90
f	79	66	72	78
g	90	70	69	traces
h	58	40	48	traces
i	91	45	50	61

[a]) The starting diols are either commercially available (**5a** – **5g**) or prepared according to a described procedure (**5h** and **5i**) [6]. [b]) Yield of the material based on its direct precursor.

The subsequent attachment of the β-keto acyl moiety onto **6** required the synthesis of thienoylated *Meldrum*'s acid compounds **7** according to a procedure already described in [3]. The latter compounds, **6** and crude **7**, were then refluxed in MeCN

[1]) For a review on intramolecular Mn^{III}-based radical cyclizations, see [2].

Scheme 3. *Preparation of Starting Compounds* **4a**–**4i**



a L = CH_2CH_2
b L = $CH_2CH_2OCH_2CH_2$
c L = $(CH_2CH_2O)_2CH_2CH_2$
d L = $(CH_2CH_2O)_3CH_2CH_2$
e L = $(CH_2CH_2O)_4CH_2CH_2$
f L = $(CH_2CH_2O)_5CH_2CH_2$
g L = $(CH_2CH_2S)_2CH_2CH_2$
h L = $(CH_2CH_2S)_3CH_2CH_2$
i L = $CH_2CH_2S(CH_2CH_2O)_2CH_2CH_2SCH_2CH_2$

DCC = *N*,*N*'-Dicyclohexylcarbodiimide; DMAP = 4-(dimethylamino)pyridine

(22 h) leading to ready-to-cyclize substrates **4** in excellent yield (*Table*). Though $Mn(OAc)_3$-based intramolecular cyclizations are well-known and have been extensively used in synthesis [2], $Mn(OAc)_3$-Mediated macrocyclizations were only recently reported [4][5]. However, the described procedure involves quite high dilutions ($C_{substrate} = 2 \cdot 10^{-3}$ M) to prevent the unwanted intermolecular cyclization.

In our study, experimental conditions were optimized to avoid the use of such a high dilution. The cyclization of substrates **4** ($C_{substrate} = 5 \cdot 10^{-2}$ M) was performed at 100° with 3.3 equiv. of $Mn(OAc)_3$ in degassed AcOH under an Ar atmosphere. ^{1}H-NMR Analysis of the crude product only showed the presence of 2,3-dihydro-2,5-di(thiophen-2-yl)furan **8**, while no intermolecular addition product was detected. Even experiments carried out at higher concentrations ($5 \cdot 10^{-2}$ M $< C_{substrate} < 10^{-1}$ M) furnished **8** as the sole product, in comparable yields. Although we do not have any concrete evidence, the enhanced rate of cyclization might be due to Mn complexation with the spacer. This fact would allow a pre-transition state of the polyether/thioether

backbone folding and, consequently, greatly promote the intramolecular trapping of the transient electrophilic radical (*Fig. 1*).

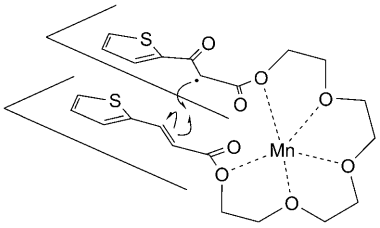
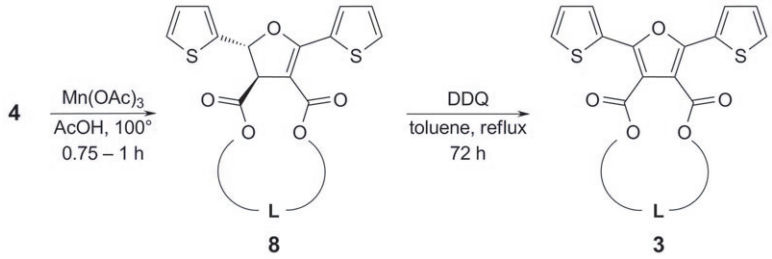


Fig. 1. *Proposed Model for the Intramolecular Trapping of the Intermediate Radical*

This could also account for the increase of yields in **8b**–**8i** (*ca.* +25%) compared to those of the intermolecular pathway [1]. Incidentally, it could also be noted that, as already observed in the intermolecular version, the macrocyclization is totally regio- and diastereoselective for such substrates, leading only to *trans*-2,3-dihydro-2,5-di(thiophen-2-yl)furans.

Having the dihydrofurans **8b**–**8i** in hand, targets **3b**–**3i** were obtained by treatment with DDQ as dehydrogenating agent in toluene under reflux (*Scheme 4*).

Scheme 4. *Synthesis of Thiophene/Furan Oligomers* **3**



The dehydrogenating conditions previously employed [1] showed their efficiency for all polyether compounds but failed with dihydrofurans containing a polythioether moiety (*i.e.*, for **3g** and **3h**; *Table*).

To evaluate the coordinating properties of such oligomers in the presence of mono- and divalent cations, we undertook a preliminary ^{1}H- and ^{13}C-NMR study of samples prepared by mixing equimolar amounts of **3b**–**3f** and various cations, introduced as perchlorate salts, in CD_3CN. Monovalent cations used in these tests (Li^+, Na^+, and Ag^+) entailed no significant changes in the ^{1}H-NMR spectrum of **3b**–**3f**. On the other hand, among the divalent cations used (Cd^{2+} and Pb^{2+}), only Pb^{2+} induced significant changes in the ^{1}H- and ^{13}C-NMR spectra of **3e** (*Fig. 2*). Coordination with Pb^{2+} resulted in a distinct downfield shift of the C=O signal in the ^{13}C-NMR spectrum possibly due to a rotation around the C–C=O bond leading to a perturbation in the sp^2 orbital overlap. Clear shifts were also observed for the aromatic thiophene signals in the ^{1}H-NMR spectrum.

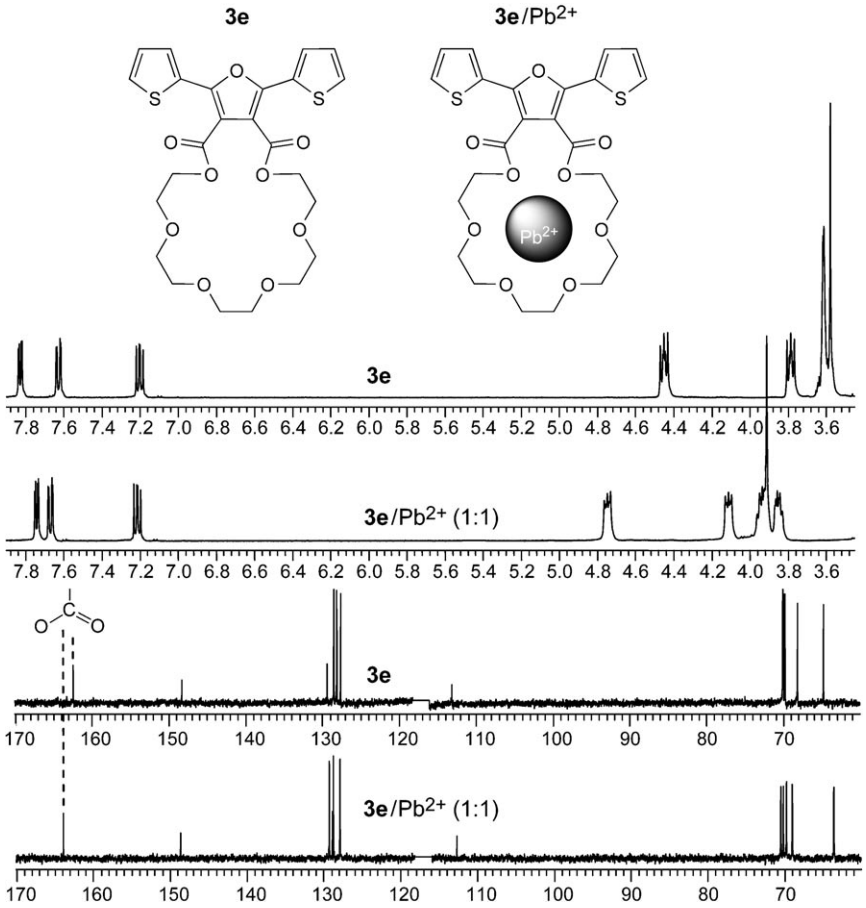


Fig. 2. *^{1}H- and ^{13}C-NMR spectra* (CD_3CN) *of* **3e** *with and without* Pb^{2+}

Conclusions. – We have shown that oxa- and thiacrown ether macrocycles (11- to 23-membered) appended to a thiophene/furan mixed oligomer can be prepared efficiently by a two-step sequence (intramolecular radical cyclization/dehydrogenation) on a series of readily accessible linear α,ω-diester precursors. In conjunction with the elaboration of larger rings (which we are currently investigating), the described procedure provides the basis of a general and versatile methodology for accessing diverse macrocycles with definite sizes and constitutions.

Experimental Part

General. All experiments were conducted under Ar unless otherwise stated, and the mixtures were stirred magnetically. $Mn(OAc)_3 \cdot 2\,H_2O$ (*Aldrich*) was used as purchased. CH_2Cl_2 and MeCN were distilled on P_2O_5 prior to use. Flash chromatography (FC): *Merck* silica gel *60 H*. TLC: *Merck* silica gel *60 F_{254}* Al-backed plates; visualization with a 254-nm UV lamp and staining with phosphomolybdic acid.

NMR Spectra: *Bruker AC 250* spectrometer (^{1}H: 250 MHz; ^{13}C: 62 MHz); chemical shifts δ in ppm, J in Hz.

General Procedure for the Preparation of Mono-esters **6**. Under Ar, a soln. of (2*E*)-3-(thiophen-2-yl)prop-2-enoyl chloride (413 mg, 2.4 mmol) in CH_2Cl_2 (60 ml) was added dropwise over 12 h to a stirred soln. of diol **5** (4.8 mmol) and Et_3N (0.67 ml, 4.8 mmol) in CH_2Cl_2 (20 ml) at r.t. The stirring was further continued for 10 h, followed by concentration under reduced pressure. The mixture was diluted with CH_2Cl_2 (20 ml), washed with H_2O (6 × 5 ml), and dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified on a silica-gel column (hexane/AcOEt from 1:1 to 0:1) to afford **6**.

*2-Hydroxyethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6a**). ^{1}H-NMR ($CDCl_3$): 7.80 (*d*, *J* = 15.7, 1 H); 7.36 (*d*, *J* = 5.0, 1 H); 7.24 (*d*, *J* = 3.6, 1 H); 7.03 (*dd*, *J* = 5.0, 3.6, 1 H); 6.25 (*d*, *J* = 15.7, 1 H); 4.33–4.29 (*m*, 2 H); 3.89–3.85 (*m*, 2 H); 2.47 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 167.11; 139.27; 137.80; 131.17; 128.67; 128.06; 116.11; 66.12; 61.17. Anal. calc. for $C_9H_{10}O_3S$ (198.24): C 54.53, H 5.08; found: C 54.30, H 4.98.

*2-(2-Hydroxyethoxy)ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6b**). ^{1}H-NMR ($CDCl_3$): 7.80 (*d*, *J* = 15.7, 1 H); 7.37 (*d*, *J* = 5.0, 1 H); 7.25 (*d*, *J* = 3.6, 1 H); 7.05 (*dd*, *J* = 5.0, 3.6, 1 H); 6.25 (*d*, *J* = 15.7, 1 H); 4.38–4.34 (*m*, 2 H); 3.80–3.72 (*m*, 4 H); 3.65–3.61 (*m*, 2 H); 2.21 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 166.82; 139.44; 137.71; 131.14; 128.64; 128.10; 116.39; 72.39; 69.25; 63.54; 61.75. Anal. calc. for $C_{11}H_{14}O_4S$ (242.30): C 54.53, H 5.82; found: C 54.69, H 5.96.

*2-[2-(2-Hydroxyethoxy)ethoxy]ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6c**). ^{1}H-NMR ($CDCl_3$): 7.78 (*d*, *J* = 15.7, 1 H); 7.35 (*d*, *J* = 5.0, 1 H); 7.24 (*d*, *J* = 3.6, 1 H); 7.02 (*dd*, *J* = 5.0, 3.6, 1 H); 6.25 (*d*, *J* = 15.7, 1 H); 4.38–4.33 (*m*, 2 H); 3.76–3.66 (*m*, 8 H); 3.62–3.57 (*m*, 2 H); 2.60 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 166.68; 139.39; 137.50; 130.97; 128.49; 128.01; 116.41; 72.43; 70.51; 70.27; 69.16; 63.41; 61.67. Anal. calc. for $C_{13}H_{18}O_5S$ (286.35): C 54.53, H 6.40; found: C 54.31, H 6.27.

*2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6d**). ^{1}H-NMR ($CDCl_3$): 7.77 (*d*, *J* = 15.7, 1 H); 7.35 (*d*, *J* = 3.6, 1 H); 7.23 (*d*, *J* = 5.0, 1 H); 7.02 (*dd*, *J* = 5.0, 3.6, 1 H); 6.24 (*d*, *J* = 15.7, 1 H); 4.34–4.30 (*m*, 2 H); 3.75–3.63 (*m*, 12 H); 3.60–3.56 (*m*, 2 H); 2.85 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 166.67; 139.35; 137.40; 130.95; 128.46; 127.99; 116.43; 72.40; 70.53; 70.45; 70.41; 70.20; 69.13; 63.51; 61.58. Anal. calc. for $C_{15}H_{22}O_6S$ (330.40): C 54.53, H 6.71; found: C 54.45, H 6.83.

*14-Hydroxy-3,6,9,12-tetraoxatetradec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6e**). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 15.7, 1 H); 7.34 (*d*, *J* = 5.0, 1 H); 7.22 (*d*, *J* = 3.6, 1 H); 7.01 (*dd*, *J* = 5.0, 3.6, 1 H); 6.23 (*d*, *J* = 15.7, 1 H); 4.34–4.29 (*m*, 2 H); 3.74–3.54 (*m*, 18 H); 2.81 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 166.77; 139.47; 137.48; 131.06; 128.56; 128.10; 116.56; 72.51; 70.57 (5 CH_2); 70.29; 69.22; 63.65; 61.67. Anal. calc. for $C_{17}H_{26}O_7S$ (374.46): C 54.53, H 7.00; found: C 54.45, H 7.19.

*17-Hydroxy-3,6,9,12,15-pentaoxaheptadec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6f**). ^{1}H-NMR ($CDCl_3$): 7.75 (*d*, *J* = 15.7, 1 H); 7.34 (*d*, *J* = 5.0, 1 H); 7.22 (*d*, *J* = 3.6, 1 H); 7.02 (*dd*, *J* = 5.0, 3.6, 1 H); 6.23 (*d*, *J* = 15.7, 1 H); 4.34–4.29 (*m*, 2 H); 3.75–3.56 (*m*, 22 H); 3.34 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 166.66; 139.36; 137.35; 130.92; 128.43; 127.97; 116.47; 77.48; 70.47 (3 CH_2); 70.43 (2 CH_2); 70.38 (2 CH_2); 70.11; 69.10; 63.55; 61.51. Anal. calc. for $C_{19}H_{30}O_8S$ (418.51): C 54.53, H 7.23; found: C 54.40, H 7.38.

*2-({2-[(2-Hydroxyethyl)sulfanyl]ethyl}sulfanyl)ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6g**). ^{1}H-NMR ($CDCl_3$): 7.77 (*d*, *J* = 15.7, 1 H); 7.37 (*d*, *J* = 5.0, 1 H); 7.25 (*d*, *J* = 3.6, 1 H); 7.04 (*dd*, *J* = 5.0, 3.6, 1 H); 6.21 (*d*, *J* = 15.7, 1 H); 4.33 (*AB*, *J* = 6.9, 2 H); 3.76–3.70 (*m*, 2 H); 2.85–2.72 (*m*, 8 H); 2.47 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 166.57; 139.25; 137.78; 131.21; 128.71; 128.07; 116.08; 63.44; 60.72; 35.13; 32.25; 31.71; 30.43. Anal. calc. for $C_{13}H_{18}O_3S_3$ (318.48): C 49.03, H 5.70; found: C 48.89, H 5.64.

*2-{[2-({2-[(2-Hydroxyethyl)sulfanyl]ethyl}sulfanyl)ethyl]sulfanyl}ethyl (2*E*)-3-(Thiophen-2-yl)-prop-2-enoate* (**6h**). ^{1}H-NMR ($CDCl_3$): 7.79 (*d*, *J* = 15.7, 1 H); 7.38 (*d*, *J* = 5.0, 1 H); 7.26 (*d*, *J* = 3.6, 1 H); 7.05 (*dd*, *J* = 5.0, 3.6, 1 H); 6.22 (*d*, *J* = 15.7, 1 H); 4.34 (*AB*, *J* = 6.9, 2 H); 3.74 (*AB*, *J* = 6.0, 2 H); 2.88–2.73 (*m*, 12 H); 2.26 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 167.02; 139.78; 138.25; 131.64; 129.16; 128.55; 116.63; 63.95; 61.18; 35.79; 32.81 (2 CH_2); 32.70; 32.37; 31.10. Anal. calc. for $C_{15}H_{22}O_3S_4$ (378.60): C 47.59, H 5.86; found: C 47.71, H 5.99.

*14-Hydroxy-6,9-dioxa-3,12-dithiatetradec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**6i**). ^{1}H-NMR ($CDCl_3$): 7.75 (*d*, *J* = 15.7, 1 H); 7.34 (*d*, *J* = 5.0, 1 H); 7.22 (*d*, *J* = 3.6, 1 H); 7.01 (*dd*, *J* = 5.0, 3.6, 1 H); 6.19 (*d*, *J* = 15.7, 1 H); 4.30 (*AB*, *J* = 6.9, 2 H); 3.71–3.58 (*m*, 10 H); 2.85–2.69 (*m*, 9 H). ^{13}C-NMR

($CDCl_3$): 166.56; 139.37; 137.65; 131.16; 128.70; 128.12; 116.34; 71.17; 71.09; 70.26 (2 CH_2); 63.64; 60.98; 35.82; 31.74; 31.41; 31.06. Anal. calc. for $C_{17}H_{26}O_5S_3$ (406.59): C 50.22, H 6.45; found: C 50.18, H 6.32.

General Procedure for the Preparation of Mixed Diesters **4**. A soln. of **6** (1 mmol) and crude 2,2-dimethyl-5-[(thiophen-2-yl)carbonyl]-1,3-dioxane-4,6-dione (**7**) (381 mg, 1.5 mmol) in MeCN (10 ml) was refluxed for 12 h under Ar. After cooling, the mixture was concentrated under reduced pressure, diluted with AcOEt (15 ml), and washed with sat. aq. $NaHCO_3$ (2 × 5 ml) and brine (2 × 5 ml). After drying ($MgSO_4$), the org. layer was concentrated on a rotary evaporator, and the crude product was purified by CC (SiO_2; hexane/AcOEt from 1:1 to 1:9) to give **4**.

*2-{[3-Oxo-3-(thiophen-2-yl)propanoyl]oxy}ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4a**). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 15.7, 1 H); 7.72 (*dd*, *J* = 3.6, 1.1, 1 H); 7.65 (*dd*, *J* = 5.0, 1.1, 1 H); 7.37 (*dd*, *J* = 5.0, 1.1, 1 H); 7.25 (*dd*, *J* = 3.9, 1.1, 1 H); 7.10 (*dd*, *J* = 5.0, 3.9, 1 H); 7.04 (*dd*, *J* = 5.0, 3.6, 1 H); 6.16 (*d*, *J* = 15.7, 1 H); 4.42–4.36 (*m*, 4 H); 3.96 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 184.46; 166.68; 166.31; 142.96; 139.25; 137.80; 134.98; 133.26; 131.23; 128.66; 128.27; 128.05; 115.90; 63.11; 61.82; 46.11. Anal. calc. for $C_{16}H_{14}O_5S_2$ (350.41): C 54.84, H 4.03; found: C 55.01, H 4.17.

*2-(2-{[3-Oxo-3-(thiophen-2-yl)propanoyl]oxy}ethoxy)ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4b**). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 15.6, 1 H); 7.69 (*d*, *J* = 3.6, 1 H); 7.66 (*d*, *J* = 4.9, 1 H); 7.34 (*d*, *J* = 4.9, 1 H); 7.22 (*d*, *J* = 3.6, 1 H); 7.10 (*dd*, *J* = 4.9, 3.6, 1 H); 7.01 (*dd*, *J* = 4.9, 3.6, 1 H); 6.23 (*d*, *J* = 15.6, 1 H); 4.33–4.26 (*m*, 4 H); 3.93 (*s*, 2 H); 3.74–3.64 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 184.58; 166.78; 166.54; 142.98; 139.28; 137.41; 134.89; 133.19; 130.98; 128.50; 128.23; 128.00; 116.33; 69.02; 68.67; 64.36; 63.36; 46.09. Anal. calc. for $C_{18}H_{18}O_6S_2$ (394.47): C 54.81, H 4.60; found: C 54.99, H 4.49.

*2-[2-(2-{[3-Oxo-3-(thiophen-2-yl)propanoyl]oxy}ethoxy)ethoxy]ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4c**). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 15.7, 1 H); 7.71 (*dd*, *J* = 3.9, 1.0, 1 H); 7.68 (*dd*, *J* = 5.0, 1.0, 1 H); 7.35 (*dd*, *J* = 5.0, 1.0, 1 H); 7.23 (*dd*, *J* = 3.6, 1.0, 1 H); 7.12 (*dd*, *J* = 5.0, 3.9, 1 H); 7.03 (*dd*, *J* = 5.0, 3.6, 1 H); 6.25 (*d*, *J* = 15.7, 1 H); 4.34–4.28 (*m*, 4 H); 3.95 (*s*, 2 H); 3.75–3.65 (*m*, 4 H); 3.64–3.61 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 184.66; 166.67; 166.86; 143.07; 139.37; 137.41; 134.90; 133.25; 130.98; 128.50; 128.28; 128.03; 116.46; 70.48; 70.47; 69.19; 68.82; 64.51; 63.55; 46.18. Anal. calc. for $C_{20}H_{22}O_7S_2$ (438.52): C 54.78, H 5.06; found: C 54.93, H 5.22.

*13,15-Dioxo-15-(thiophen-2-yl)-3,6,9,12-tetraoxapentadec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4d**). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 15.6, 1 H); 7.72 (*dd*, *J* = 3.8, 1.1, 1 H); 7.68 (*dd*, *J* = 4.9, 1.1, 1 H); 7.35 (*dd*, *J* = 5.0, 1.1, 1 H); 7.23 (*dd*, *J* = 3.6, 1.1, 1 H); 7.13 (*dd*, *J* = 4.9, 3.8, 1 H); 7.03 (*dd*, *J* = 5.0, 3.6, 1 H); 6.24 (*d*, *J* = 15.6, 1 H); 4.34–4.27 (*m*, 4 H); 3.94 (*s*, 2 H); 3.62–3.59 (*m*, 4 H); 3.69–3.63 (*m*, 6 H); 3.75–3.72 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 184.69; 166.87; 166.68; 143.06; 139.36; 137.40; 134.92; 133.28; 131.00; 128.50; 128.29; 128.03; 116.46; 70.49 (2 CH_2); 70.48 (2 CH_2); 69.13; 68.75; 64.51; 63.55; 46.17. Anal. calc. for $C_{22}H_{26}O_8S_2$ (482.58): C 54.76, H 5.43; found: C 54.50, H 5.71.

*16,18-Dioxo-18-(thiophen-2-yl)-3,6,9,12,15-pentaoxaoctadec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4e**). ^{1}H-NMR ($CDCl_3$): 7.77 (*d*, *J* = 15.7, 1 H); 7.72 (*dd*, *J* = 3.9, 1.1, 1 H); 7.68 (*dd*, *J* = 5.0, 1.1, 1 H); 7.36 (*dd*, *J* = 5.0, 1.1, 1 H); 7.24 (*dd*, *J* = 3.6, 1.1, 1 H); 7.13 (*dd*, *J* = 5.0, 3.9, 1 H); 7.03 (*dd*, *J* = 5.0, 3.6, 1 H); 6.25 (*d*, *J* = 15.7, 1 H); 4.35–4.28 (*m*, 4 H); 3.95 (*s*, 2 H); 3.76–3.72 (*m*, 2 H); 3.69–3.65 (*m*, 2 H); 3.67–3.60 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$): 184.69; 166.88; 166.70; 143.08; 139.39; 137.41; 134.92; 133.28; 130.99; 128.49; 128.29; 128.03; 116.49; 70.52 (2 CH_2); 70.48 (2 CH_2); 70.45 (2 CH_2); 69.15; 68.76; 64.54; 63.58; 46.20. Anal. calc. for $C_{24}H_{30}O_9S_2$ (526.63): C 54.74, H 5.74; found: C 54.60, H 5.59.

*19,21-Dioxo-21-(thiophen-2-yl)-3,6,9,12,15,18-hexaoxahenicos-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4f**). ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 15.7, 1 H); 7.71 (*dd*, *J* = 3.9, 1.0, 1 H); 7.67 (*dd*, *J* = 4.9, 1.0, 1 H); 7.35 (*dd*, *J* = 5.0, 1.0, 1 H); 7.22 (*dd*, *J* = 3.6, 1.0, 1 H); 7.12 (*dd*, *J* = 4.9, 3.9, 1 H); 7.02 (*dd*, *J* = 5.0, 3.6, 1 H); 6.23 (*d*, *J* = 15.7, 1 H); 4.33–4.26 (*m*, 4 H); 3.93 (*s*, 2 H); 3.75–3.71 (*s*, 2 H); 3.68–3.65 (*m*, 2 H); 3.64–3.57 (*m*, 16 H). ^{13}C-NMR ($CDCl_3$): 184.65; 166.83; 166.63; 143.05; 139.35; 137.35; 134.88; 133.24; 130.93; 128.45; 128.26; 127.99; 116.47; 70.49 (2 CH_2); 70.43 (4 CH_2); 70.39 (2 CH_2); 69.11; 68.71; 64.49; 63.54; 46.15. Anal. calc. for $C_{26}H_{34}O_{10}S_2$ (570.68): C 54.72, H 6.01; found: C 54.58, H 6.24.

*2-({2-[(2-{[3-Oxo-3-(thiophen-2-yl)propanoyl]oxy}ethyl)sulfanyl]ethyl}sulfanyl)ethyl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4g**). ^{1}H-NMR ($CDCl_3$): 7.75 (*d*, *J* = 15.7, 1 H); 7.70 (*dd*, *J* = 3.8, 1.1, 1 H); 7.66 (*dd*, *J* = 5.0, 1.1, 1 H); 7.34 (*dd*, *J* = 5.0, 1.1, 1 H); 7.22 (*dd*, *J* = 3.6, 1.1, 1 H); 7.10 (*dd*, *J* = 5.0, 3.8, 1 H); 7.00 (*dd*, *J* = 5.0, 3.6, 1 H); 6.18 (*d*, *J* = 15.7, 1 H); 4.28 (*AB*, *J* = 6.8, 4 H); 3.92 (*s*, 2 H); 2.82–2.72 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 184.50; 166.57; 166.30; 142.85; 139.14; 137.53; 135.00; 133.26; 131.08; 128.58;

128.24; 127.97; 116.04; 64.24; 63.33; 46.01; 32.03 (2 CH_2); 30.38; 30.08. Anal. calc. for $C_{20}H_{22}O_5S_4$ (470.65): C 51.04, H 4.71; found: C 50.88, H 4.82.

*13,15-Dioxo-15-(thiophen-2-yl)-12-oxa-3,6,9-trithiapentadec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4h**). ^{1}H-NMR ($CDCl_3$): 7.80 (*d*, *J* = 15.7, 1 H); 7.75 (*dd*, *J* = 3.9, 1.0, 1 H); 7.71 (*dd*, *J* = 4.9, 1.0, 1 H); 7.39 (*dd*, *J* = 5.0, 1.0, 1 H); 7.28 (*dd*, *J* = 3.6, 1.0, 1 H); 7.16 (*dd*, *J* = 4.9, 3.9, 1 H); 7.06 (*dd*, *J* = 5.0, 3.6, 1 H); 6.24 (*d*, *J* = 15.7, 1 H); 4.38–4.30 (*m*, 4 H); 3.96 (*s*, 2 H); 2.89–2.77 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$): 184.98; 167.13; 166.91; 143.50; 139.80; 138.14; 135.48; 133.74; 131.58; 129.11; 128.78; 128.53; 116.70; 64.84; 63.97; 46.68; 32.84; 32.76; 32.68; 32.66; 31.12; 30.76. Anal. calc. for $C_{22}H_{26}O_5S_5$ (530.77): C 49.79, H 4.94; found: C 50.03, H 5.02.

*16,18-Dioxo-18-(thiophen-2-yl)-6,9,15-trioxa-3,12-dithiaoctadec-1-yl (2*E*)-3-(Thiophen-2-yl)prop-2-enoate* (**4i**). ^{1}H-NMR ($CDCl_3$): 7.75 (*d*, *J* = 15.6, 1 H); 7.71 (*dd*, *J* = 3.8, 0.8, 1 H); 7.68 (*dd*, *J* = 5.0, 0.8, 1 H); 7.36 (*d*, *J* = 5.0, 1 H); 7.23 (*d*, *J* = 3.6, 1 H); 7.12 (*dd*, *J* = 5.0, 3.8, 1 H); 7.02 (*dd*, *J* = 5.0, 3.6, 1 H); 6.20 (*d*, *J* = 15.6, 1 H); 4.34–4.25 (*m*, 4 H); 3.92 (*s*, 2 H); 3.67–3.59 (*m*, 8 H); 2.86–2.67 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 184.55; 166.62; 166.39; 142.97; 139.26; 137.49; 134.96; 133.26; 131.03; 128.55; 128.26; 128.00; 116.24; 70.95; 70.93; 70.18 (2 CH_2); 64.42; 63.50; 46.12; 31.64; 31.59; 30.92; 30.53. Anal. calc. for $C_{24}H_{30}O_7S_4$ (558.76): C 51.59, H 5.41; found: C 51.70, H 5.18.

General Procedure for the Preparation of 2,3-Dihydrofurans **8**. A stirred soln. of **4** (1 mmol) and $Mn(OAc)_3 \cdot 2\ H_2O$ (884 mg, 3.3 mmol) in glacial AcOH (20 ml) was degassed by a stream of Ar. The brown soln. was then heated at 100° under Ar until complete discoloration. After cooling, H_2O was added, and the mixture was extracted with AcOEt (3 × 8 ml). The combined org. extracts were neutralized by washing with sat. aq. $NaHCO_3$ and dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by CC (SiO_2; hexane/AcOEt from 9:1 to 1:9) to afford **8**.

*(1*R**,12a*R**)-1,6,7,9,10,12a-Hexahydro-1,3-di(thiophen-2-yl)-4*H*,12*H*-furo[3,4-*i*][1,4,7]trioxacycloundecine-4,12-dione* (**8b**). ^{1}H-NMR ($CDCl_3$): 8.31 (*dd*, *J* = 3.9, 1.1, 1 H); 7.56 (*dd*, *J* = 5.0, 1.1, 1 H); 7.37 (*dd*, *J* = 5.0, 1.1, 1 H); 7.17 (*dd*, *J* = 3.5, 1.1, 1 H); 7.12 (*dd*, *J* = 5.0, 3.9, 1 H); 7.02 (*dd*, *J* = 5.0, 3.5, 1 H); 6.09 (*d*, *J* = 9.3, 1 H); 4.74–4.68 (*m*, 1 H); 4.55–4.50 (*m*, 1 H); 4.49 (*d*, *J* = 9.3, 1 H); 4.08–3.92 (*m*, 2 H); 3.90–3.85 (*m*, 2 H); 3.83–3.74 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 172.79; 163.56; 160.05; 141.20; 133.47; 131.48; 129.93; 127.31; 126.99; 126.68; 126.37; 100.81; 81.76; 72.41; 72.15; 65.00; 64.07; 58.75. Anal. calc. for $C_{18}H_{16}O_6S_2$ (392.45): C 55.09, H 4.11; found: C 55.19, H 4.00.

*(1*R**,15a*R**)-1,6,7,9,10,12,13,15a-Octahydro-1,3-di(thiophen-2-yl)-4*H*,15*H*-furo[3,4-*l*][1,4,7,10]tetraoxacyclotetradecine-4,15-dione* (**8c**). ^{1}H-NMR ($CDCl_3$): 8.30 (*dd*, *J* = 3.9, 1.2, 1 H); 7.55 (*dd*, *J* = 5.0, 1.2, 1 H); 7.31 (*dd*, *J* = 5.0, 1.2, 1 H); 7.14 (*dd*, *J* = 3.5, 1.2, 1 H); 7.11 (*dd*, *J* = 5.0, 3.9, 1 H); 6.99 (*dd*, *J* = 5.0, 3.5, 1 H); 5.99 (*d*, *J* = 5.9, 1 H); 4.64–4.55 (*m*, 1 H); 4.47 (*d*, *J* = 5.9, 1 H); 4.49–4.41 (*m*, 1 H); 4.18–4.06 (*m*, 2 H); 3.84–3.56 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 172.49; 164.08; 160.22; 142.19; 133.56; 131.47; 130.15; 127.22; 126.83; 126.10; 125.43; 99.51; 81.37; 69.88; 69.15; 68.98; 68.89; 64.49; 63.24; 57.52. Anal. calc. for $C_{20}H_{20}O_7S_2$ (436.51): C 55.03, H 4.62; found: C 55.00, H 4.82.

*(1*R**,18a*R**)-1,6,7,9,10,12,13,15,16,18a-Decahydro-1,3-di(thiophen-2-yl)-4*H*,18*H*-furo[3,4-*o*][1,4,7,10,13]pentaoxacycloheptadecine-4,18-dione* (**8d**). ^{1}H-NMR ($CDCl_3$): 8.30 (*dd*, *J* = 3.9, 1.2, 1 H); 7.56 (*dd*, *J* = 5.0, 1.2, 1 H); 7.31 (*dd*, *J* = 5.0, 1.2, 1 H); 7.13 (*dd*, *J* = 3.6, 1.2, 1 H); 7.12 (*dd*, *J* = 5.0, 3.9, 1 H); 7.00 (*dd*, *J* = 5.0, 3.6, 1 H); 6.00 (*d*, *J* = 5.5, 1 H); 4.51–4.36 (*m*, 2 H); 4.40 (*d*, *J* = 5.5, 1 H); 4.28–4.17 (*m*, 2 H); 3.81–3.75 (*m*, 4 H); 3.69–3.62 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 172.19; 164.01; 160.12; 142.22; 133.64; 131.48; 130.18; 127.31; 126.86; 126.06; 125.40; 99.40; 81.30; 71.24; 70.81; 70.60; 70.49; 69.24; 68.86; 65.08; 63.49; 57.42. Anal. calc. for $C_{22}H_{24}O_8S_2$ (480.56): C 54.99, H 5.03; found: C 54.72, H 5.19.

*(1*R**,21a*R**)-1,6,7,9,10,12,13,15,16,18,19,21a-Dodecahydro-1,3-di(thiophen-2-yl)-4*H*,21*H*-furo[3,4-r][1,4,7,10,13,16]hexaoxacycloicosine-4,21-dione* (**8e**). ^{1}H-NMR ($CDCl_3$): 8.30 (*dd*, *J* = 3.8, 1.1, 1 H); 7.55 (*dd*, *J* = 5.0, 1.1, 1 H); 7.31 (*dd*, *J* = 5.0, 1.1, 1 H); 7.15–7.10 (*m*, 2 H); 7.00 (*dd*, *J* = 5.0, 3.6, 1 H); 6.01 (*d*, *J* = 6.0, 1 H); 4.40 (*d*, *J* = 6.0, 1 H); 4.36–4.29 (*m*, 4 H); 3.80–3.71 (*m*, 4 H); 3.69–3.60 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$): 172.04; 163.96; 159.93; 142.13; 133.64; 131.43; 130.14; 127.30; 126.87; 126.11; 125.49; 99.55; 81.25; 70.83 (2 CH_2); 70.77 (2 CH_2); 70.71; 70.69; 69.12; 68.79; 65.16; 63.63; 57.67. Anal. calc. for $C_{24}H_{28}O_9S_2$ (524.61): C 54.95, H 5.38; found: C 55.10, H 5.10.

*(1*R**,24a*R**)-1,6,7,9,10,12,13,15,16,18,19,21,22,24a-Tetradecahydro-1,3-di(thiophen-2-yl)-4*H*,24*H*-furo[3,4-u][1,4,7,10,13,16,19]heptaoxacyclotricosine-4,24-dione* (**8f**). ^{1}H-NMR ($CDCl_3$): 8.29 (*dd*, *J* = 3.9, 1.2, 1 H); 7.55 (*dd*, *J* = 5.0, 1.2, 1 H); 7.31 (*dd*, *J* = 5.0, 1.2, 1 H); 7.15 (*dd*, *J* = 3.5, 1.2, 1 H); 7.11 (*dd*, *J* =

5.0, 3.9, 1 H); 6.99 (*dd*, *J* = 5.0, 3.5, 1 H); 6.01 (*d*, *J* = 6.4, 1 H); 4.39 (*d*, *J* = 6.4, 1 H); 4.38–4.33 (*m*, 4 H); 3.80–3.74 (*m*, 4 H); 3.65–3.61 (*m*, 16 H). ^{13}C-NMR ($CDCl_3$): 172.06; 163.99; 159.91; 142.14; 133.57; 131.40; 130.18; 127.28; 126.88; 126.11; 125.52; 99.67; 81.31; 70.86; 70.66 (2 CH_2); 70.62 (2 CH_2); 70.57 (2 CH_2); 70.46; 69.17; 68.96; 65.17; 63.65; 57.80. Anal. calc. for $C_{26}H_{32}O_{10}S_2$ (568.67): C 54.92, H 5.67; found: C 55.11, H 5.80.

*(1*R**,15a*R**-1,6,7,9,10,12,13,15a-Octahydro-1,3-di(thiophen-2-yl)-4*H,*15*H-*furo[3,4-*l*][1,4,7,10]dioxadithiacyclotetradecine-4,15-dione* (**8g**). ^{1}H-NMR ($CDCl_3$): 8.23 (*dd*, *J* = 3.9, 1.1, 1 H); 7.52 (*dd*, *J* = 5.0, 1.1, 1 H); 7.25 (*dd*, *J* = 5.0, 1.2, 1 H); 7.08 (*dd*, *J* = 3.6, 1.2, 1 H); 7.07 (*dd*, *J* = 5.0, 3.9, 1 H); 6.94 (*dd*, *J* = 5.0, 3.6, 1 H); 5.95 (*d*, *J* = 5.0, 1 H); 4.55–4.35 (*m*, 2 H); 4.32 (*d*, *J* = 5.0, 1 H); 4.30–4.15 (*m*, 2 H); 2.88–2.72 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 171.96; 163.97; 160.62; 142.09; 134.01; 131.87; 130.11; 127.35; 126.93; 126.13; 125.44; 98.74; 81.30; 66.51; 65.57; 57.43; 34.21; 33.25; 32.13; 31.53. Anal. calc. for $C_{20}H_{20}O_5S_4$ (468.64): C 51.26, H 4.30; found: C 51.40, H 4.49.

*(1*R**,18a*R**)-1,6,7,9,10,12,13,15,16,18a-Decahydro-1,3-di(thiophen-2-yl)-4*H,*18*H-*furo[3,4-*o*][1,4,7,10,13]dioxatrithiacycloheptadecine-4,18-dione* (**8h**). ^{1}H-NMR ($CDCl_3$): 8.25 (*dd*, *J* = 3.9, 1.1, 1 H); 7.58 (*dd*, *J* = 5.0, 1.1, 1 H); 7.34 (*dd*, *J* = 5.0, 1.2, 1 H); 7.16 (*dd*, *J* = 3.6, 1.2, 1 H); 7.13 (*dd*, *J* = 5.0, 3.9, 1 H); 7.02 (*dd*, *J* = 5.0, 3.6, 1 H); 6.01 (*d*, *J* = 6.7, 1 H); 4.46–4.36 (*m*, 2 H); 4.38 (*d*, *J* = 6.7, 1 H); 4.30–4.18 (*m*, 2 H); 2.87–2.75 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$): 171.86; 163.62; 160.22; 141.77; 133.73; 131.76; 130.00; 127.29; 126.96; 126.38; 125.74; 99.37; 81.28; 64.46; 62.95; 57.87; 32.67; 32.51; 31.51 (2 CH_2); 30.41; 30.14. Anal. calc. for $C_{22}H_{24}O_5S_5$ (528.75): C 49.98, H 4.58; found: C 50.00, H 4.71.

*(1*R**,21a*R**)-1,6,7,9,10,12,13,15,16,18,19,21a-Dodecahydro-1,3-di(thiophen-2-yl)-4*H,*21*H-*furo[3,4-*r*][1,4,7,10,13,16]tetraoxadithiacycloicosine-4,21-dione* (**8i**). ^{1}H-NMR ($CDCl_3$): 8.29 (*dd*, *J* = 4.0, 1.2, 1 H); 7.56 (*dd*, *J* = 5.0, 1.2, 1 H); 7.31 (*dd*, *J* = 5.0, 1.2, 1 H); 7.15–7.13 (*m*, 1 H); 7.12 (*dd*, *J* = 5.0, 4.0, 1 H); 7.00 (*dd*, *J* = 5.0, 3.6, 1 H); 6.00 (*d*, *J* = 6.0, 1 H); 4.47–4.36 (*m*, 2 H); 4.35 (*d*, *J* = 6.0, 1 H); 4.28–4.19 (*m*, 2 H); 3.72–3.61 (*m*, 8 H); 2.92–2.85 (*m*, 4 H); 2.77–2.72 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 171.74; 163.74; 160.11; 142.12; 133.63; 131.56; 130.12; 127.27; 126.91; 126.15; 125.47; 99.40; 81.31; 71.62; 71.46; 70.66; 70.62; 65.47; 63.60; 57.85; 32.40; 32.32; 31.23; 30.77. Anal. calc. for $C_{24}H_{28}O_7S_4$ (556.74): C 51.78, H 5.07; found: C 51.83, H 5.19.

General Procedure for the Preparation of Furans **3**. A stirred soln. of **8** (0.1 mmol) and DDQ (68 mg, 0.3 mmol) in toluene (10 ml) was refluxed for 72 h. After cooling, H_2O (20 ml) was added, and the mixture was extracted with AcOEt (2 × 10 ml). The org. extracts were washed with sat. aq. $NaHCO_3$, dried ($MgSO_4$), and evaporated. The crude product was purified by CC (silica gel; hexane/AcOEt from 9:1 to 1:9).

*6,7,9,10-Tetrahydro-1,3-di(thiophen-2-yl)-4*H,*12*H-*furo[3,4-*i*][1,4,7]trioxacycloundecine-4,12-dione* (**3b**). ^{1}H-NMR ($CDCl_3$): 7.93 (*dd*, *J* = 3.8, 1.1, 2 H); 7.46 (*dd*, *J* = 5.0, 1.1, 2 H); 7.13 (*dd*, *J* = 5.0, 3.8, 2 H); 4.46–4.42 (*m*, 4 H); 3.96–3.93 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 163.22; 149.97; 129.81; 128.85; 128.50; 127.71; 113.15; 72.11; 66.10. Anal. calc. for $C_{18}H_{14}O_6S_2$ (390.44): C 55.37, H 3.61; found: C 55.50, H 3.44.

*6,7,9,10,12,13-Hexahydro-1,3-di(thiophen-2-yl)-4*H,*15*H-*furo[3,4-*l*][1,4,7,10]tetraoxacyclotetradecine-4,15-dione* (**3c**). ^{1}H-NMR ($CDCl_3$): 7.77 (*dd*, *J* = 3.6, 1.1, 2 H); 7.43 (*dd*, *J* = 5.0, 1.1, 2 H); 7.11 (*dd*, *J* = 5.0, 3.6, 2 H); 4.51–4.48 (*m*, 4 H); 3.86–3.82 (*m*, 4 H); 3.67 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 163.04; 148.96; 130.09; 128.23; 128.08; 127.58; 113.58; 69.65; 68.80; 63.98. Anal. calc. for $C_{20}H_{18}O_7S_2$ (434.49): C 55.29, H 4.18; found: C 55.09, H 4.31.

*6,7,9,10,12,13,15,16-Octahydro-1,3-di(thiophen-2-yl)-4*H,*18*H-*furo[3,4-*o*][1,4,7,10,13]pentaoxacycloheptadecine-4,18-dione* (**3d**). ^{1}H-NMR ($CDCl_3$): 7.77 (*dd*, *J* = 3.8, 1.1, 2 H); 7.44 (*dd*, *J* = 5.0, 1.1, 2 H); 7.11 (*dd*, *J* = 5.0, 3.8, 2 H); 4.50 (*AB*, *J* = 5.1, 4 H); 3.87 (*AB*, *J* = 5.1, 4 H); 3.71–3.65 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 163.07; 149.13; 130.13; 128.40; 128.20; 127.64; 113.52; 71.12; 70.80; 69.08; 64.91. Anal. calc. for $C_{22}H_{22}O_8S_2$ (478.54): C 55.22, H 4.63; found: C 55.48, H 4.43.

*6,7,9,10,12,13,15,16,18,19-Decahydro-1,3-di(thiophen-2-yl)-4*H,*21*H-*furo[3,4-*r*][1,4,7,10,13,16]hexaoxacycloicosine-4,21-dione* (**3e**). ^{1}H-NMR ($CDCl_3$): 7.80 (*dd*, *J* = 3.7, 1.1, 2 H); 7.43 (*dd*, *J* = 5.0, 1.1, 2 H); 7.10 (*dd*, *J* = 5.0, 3.7, 2 H); 4.47 (*dd*, *J* = 5.0, 4.8, 4 H); 3.82 (*dd*, *J* = 5.0, 4.8, 4 H); 3.68 (*m*, 8 H); 3.65 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 163.06; 149.00; 130.01; 128.33; 128.13; 127.63; 113.41; 70.74 (2 CH_2); 70.62; 68.78; 64.75. Anal. calc. for $C_{24}H_{26}O_9S_2$ (522.60): C 55.16, H 5.01; found: C 54.98, H 5.26.

*6,7,9,10,12,13,15,16,18,19,21,22-Dodecahydro-1,3-di(thiophen-2-yl)-4*H,*24*H-*furo[3,4*-u*][1,4,7,10,13,16,19]heptaoxacyclotricosine-4,24-dione* (**3f**). ^{1}H-NMR ($CDCl_3$): 7.84 (*dd*, J = 3.8, 1.2, 2 H); 7.44 (*dd*, J = 5.0, 1.2, 2 H); 7.11 (*dd*, J = 5.0, 3.8, 2 H); 4.47 (*AB*, J = 4.7, 4 H); 3.85 (*AB*, J = 4.6, 4 H); 3.68–3.63 (*m*, 16 H). ^{13}C-NMR ($CDCl_3$): 163.28; 149.16; 130.09; 128.49; 128.19; 127.69; 113.58; 71.10; 70.68; 70.65; 70.30; 69.03; 65.15. Anal. calc. for $C_{26}H_{30}O_{10}S_2$ (566.65): C 55.11, H 5.34; found: C 55.00, H 5.44.

*6,7,9,10,12,13,15,16,18,19-Decahydro-1,3-di(thiophen-2-yl)-4*H,*21*H-*furo[3,4*-r*][1,4,7,10,13,16]tetraoxadithiacycloicosine-4,21-dione* (**3i**). ^{1}H-NMR ($CDCl_3$): 7.80 (*dd*, J = 3.8, 1.1, 2 H); 7.45 (*dd*, J = 5.0, 1.1, 2 H); 7.12 (*dd*, J = 5.0, 3.8, 2 H); 4.50 (*AB*, J = 7.2, 4 H); 3.76–3.64 (*m*, 8 H); 2.97 (*AB*, J = 7.2, 4 H); 2.78 (*AB*, J = 5.7, 4 H). ^{13}C-NMR ($CDCl_3$): 162.85; 149.11; 129.95; 128.43; 128.27; 127.67; 113.24; 71.63; 70.59; 65.15; 32.47; 30.83. Anal. calc. for $C_{24}H_{26}O_7S_4$ (554.73): C 51.97, H 4.72; found: C 52.15, H 4.92.

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Received April 9, 2010