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Synthesis of naphthalenophane-type macrocyclic compounds using Mn(III)-based dihydrofuran-clipping reaction

Chiaki Matsumoto [a], Ken-ji Yasutake [a], Hiroshi Nishino [b,*]

[a] Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Chûou-Ku, Kumamoto 860-8555, Japan
[b] Department of Chemistry, Kumamoto University, Kurokami 2-39-1, Chûou-Ku, Kumamoto 860-8555, Japan

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Dedicated to Dr. Kazu Kurosawa, Professor Emeritus of Kumamoto University, who was awarded the 2015 Order of the Sacred Treasure, Gold Rays with Neck Ribbon.

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ABSTRACT

The Mn(III)-based oxidation of 2,7-, 1,8-, and 1,5-disubstituted naphthalenes bearing both the 1,4-dioxa-7,7-diphenylhep-6-enyl and 1,4-dioxa-5,7-dioxooctyl groups gave new [12]naphthalenophanes along with the corresponding diploids via assembly of the dihydrofuran ring. A similar reaction of the 2,6-disubstituted naphthalene having the same substituents did not produce the naphthalenophane, but the diploid, [12,12](2,6)naphthalenophane, was obtained in a small amount. The 2,6-disubstituted naphthalene tethered to the 1,4,7-trioxa-10,10-diphenyldec-9-enyl and 1,4,7-trioxa-8,10-dioxoundecyl groups also underwent the dihydrofuran-clipping reaction to afford a trace amount of the desired [18](2,6)naphthalenophane. The reaction details and the structure determination of the products are described.

1. Introduction

The synthesis of cyclic compounds from acyclic linear compounds as the starting materials is one of the goals of organic synthesis. There are many cyclic products in nature from small to large rings including heterocycles. In 1926, Ruzicka found that the structure of the most famous perfume, muscone, was a fifteen-membered cyclic ketone.[1] Ever since then, macrocyclic compounds are attractive for investigation from the standpoint of not only flavor chemistry, but also pharmaceutical and supramolecular chemistries such as antibiotics, molecular recognition, anion binding, metal ion transport, enzymatic catalysis, chemical switching, etc.[2,3] Macrocyclic cyclophanes consisting of an aromatic unit and aliphatic chain are also interesting compounds because the aromatic π-electrons of the cyclophanes undergo many interactions with metal cations and guest polycyclic aromatics depending on the ring size.[4,5] Although macrolides have been prepared by Yamaguchi,[6] Corey-Nicolaou,[7] Shiina macrolactonization,[8] and ring-closing metathesis (RCM),[9] the synthesis of cyclophanes containing a flat and rigid aromatic ring is more challenging in organic chemistry.[10] We recently reported the synthesis of cyclophane-type macrocycles consisting of benzene and biphenyl from a 21 to 100 ring size using Mn(III)-mediated oxidative radical cyclization.[3,11] The characteristic of the reaction is assembly of the dihydrofuran by intramolecular addition resulting in forming macrocycles, the so-called 'dihydrofuran-clipping reaction.' In this case, we could achieve the macrocyclization using the relatively flexible chain binding with a disubstituted benzene and biphenyl. In connection with our study, we were very interested in the synthesis of cyclophanes consisting of a more flat and rigid aromatic unit such as naphthalene from the standpoint of the potential of the reaction and the distorted structure. In this paper, we describe the synthesis of naphthalenophanes using the Mn(III)-mediated dihydrofuran-clipping reaction and the characteristics of the products.

* Corresponding author. Fax: +81 96 342 3374; e-mail address: nishino@sci.kumamoto-u.ac.jp (H. Nishino).

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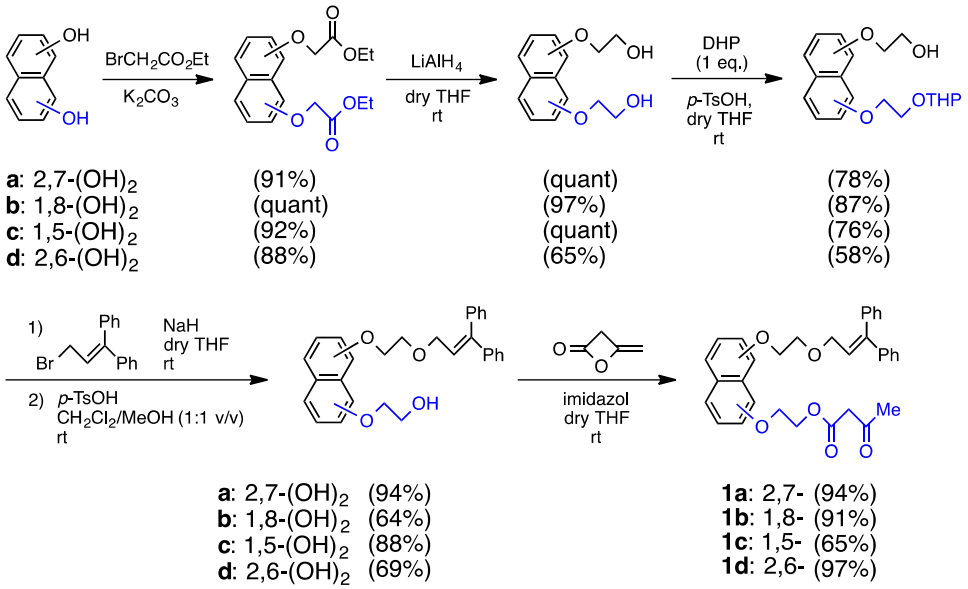
2. Results and discussion

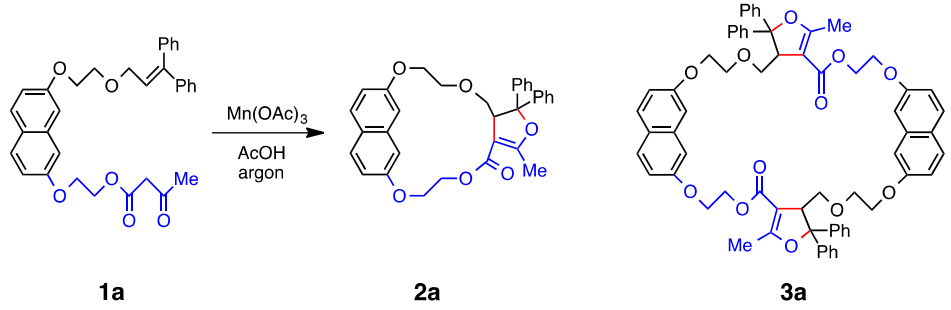
Initially, we prepared disubstituted naphthalenes **1a**–**d** bearing the 1,4-dioxa-7,7-diphenylhep-6-enyl and 1,4-dioxa-5,7-dioxooctyl groups (Scheme 1). Naphthalenediols were allowed to react with ethyl bromoacetate to give the corresponding bis(ethoxycarbonylmethyloxy)-substituted naphthalenes. The carboxylates were reduced by lithium aluminum hydride (LAH) to give the diols, one of which was protected by a tetrahydropyranyl group (THP). The THP-protected alcohols were then allowed to react with 3-bromo-1,1-diphenyl-1-prorene, followed by deprotection and esterification with diketene to finally give the desired disubstituted naphthalenes **1a**–**d**.



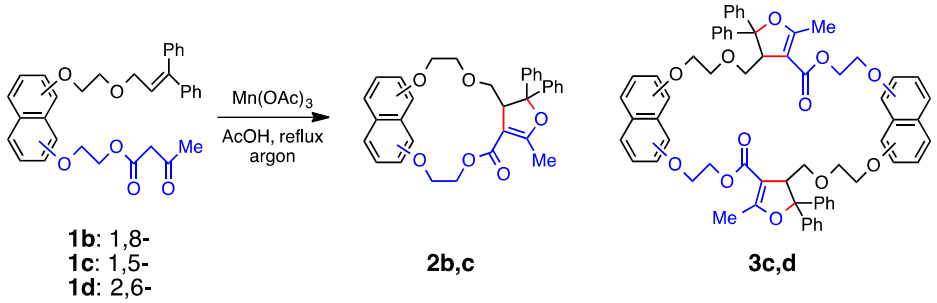
Scheme 1. Preparation of disubstituted naphthalenes **1a-d**.

With the substrate naphthalenes **1a**–**d** in hand, the macrocyclization using manganese(III) acetate was investigated. First of all, we chose the 2,7-disubstituted naphthalene **1a**, and the preliminary reaction was carried out at the molar ratio of **1a**:$Mn(OAc)_3$=1:3 in boiling acetic acid (10 mL) (Scheme 2 and Table 1, entry 1).[12] Although the reaction gave an intractable mixture, we were please to isolate the desired naphthalenophane **2a** in 7% yield. We were then sure of the usefulness of the dihydrofuran-clipping reaction and scrutinized the reaction under various conditions (Table 1). When the reaction was carried out at 100 °C (entry 6) or under concentrated conditions (entries 7–9, 11), a more polar mixture was produced, and after separation, the corresponding diploid **3a** was barely isolated together with **2a**. The factor, which complicated the reaction, would be the following reasons: the benzylic and allylic oxidation of **1a** with manganese(III) acetate to break the side-chain of **1a**, and the intermolecular addition of **1a** to produce the oligomer. In order to overcome this difficulty, we considered the conditions whose contact of the oxidant and the substrate **1a** as well as each **1a** should decrease as much as possible. Therefore, we chose more diluted conditions and successively added two or three portions of the oxidant to the reaction mixture (entries 3, 10, 12).[13] A solution of **1a** in acetic acid (5 mL) was poured into a boiling mixture of three equivalents of manganese(III) acetate and acetic acid (50 mL) using a syringe (0.2 mL/min) and the rest of the oxidant (3 equiv) was added after 10 min since the brown color of the reaction mixture turned transparent, which meant the consumption of the brownish Mn(III) oxidant, and continued to heat under reflux. As a result, the reaction finished after 31 min and the maximum yield of the product **2a** was realized (35% as shown in entry 10).

With this technique in mind, we examined the dihydrofuran-clipping reaction of other substituted naphthalenes **1b**–**d** under various conditions (Scheme 3 and Table 2). Although the reaction



Scheme 2. Oxidation of **1a** with $Mn(OAc)_3$.



Scheme 3. Oxidation of **1b**–**d** with $Mn(OAc)_3$.

Table 1
Oxidation of 2,7-disubstituted naphthalene **1a** with $Mn(OAc)_3$[a]

Entry	**1a**:$Mn(OAc)_3$[b]	AcOH/mL	Temp/°C	Time/min	Product Yield/%[c]	
					2a	**3a**
1	1:3	10	Reflux	5	7	
2	1:3[d]	50	Reflux	11	20	
3	1:3[e,f]	50	Reflux	17	26	
4	1:3	100	100	5	12	
5	1:3	100	Reflux	10	8	
6	1:3	200	100	30	14	22
7	1:4	50	Reflux	8	16	16
8	1:6	50	Reflux	14	17	21
9	1:6	100	Reflux	18	13	10
10	1:6[e,f]	50	Reflux	41	35	
11	1:8	50	Reflux	11	13	17
12	1:8[e,f]	50	Reflux	40	32	

[a] The reaction of **1a** (0.2 mmol) was carried out in acetic acid under an argon atmosphere.
[b] Molar ratio.
[c] Isolated yield based on the amount of **1a** used.
[d] The naphthalene **1a** (15%) was recovered.
[e] Two- or three-portions of $Mn(OAc)_3$ were successively added.
[f] The naphthalene **1a** was dropwise added during the reaction.

was plagued by low yields, the modified technique mentioned above was effective for the 1,8-disubstituted naphthalene **1b** (entry 6). In addition, the distance between the α-carbonyl carbon and alkenic double bond in **1b** would be close to each other, so that the intramolecular addition would be superior to the intermolecular reaction, such as the diploid and oligomer formation (entries 1–7),[3] and thus the synthesis of naphthalenophane **2b** was realized in a yield similar to that of **2a** (entry 5). The reaction of the 1,5-disubstituted naphthalene **1c** of which the reaction site was farther than that of **1a** and **1b** was more difficult and we were again afflicted by the indecent side reactions (entries 8–16). However, the naphthalenophane **2c** could be barely isolated in 15% yield together with a small amount of the diploid **3c** (entry 15). Isolation of a monoploid naphthalenophane, except for the diploid **3d**, failed for the reaction of the 2,6-disubstituted naphthalene **1d** of which the distance between the reaction sites was the farthest (entries 17 and 18).[14–19]

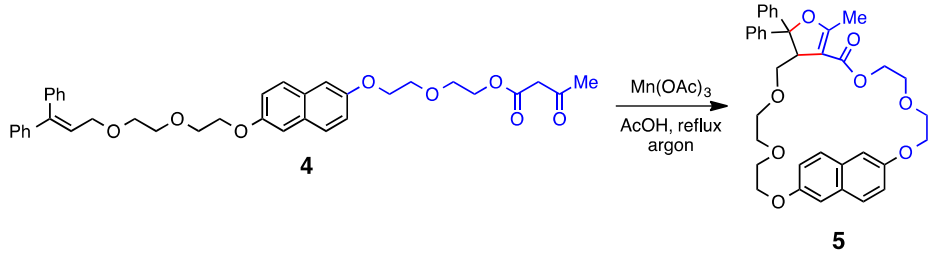
Table 2
Oxidation of disubstituted naphthalenes **1b**–**d** with $Mn(OAc)_3$[a]

Entry	**1**	**1**:Mn $(OAc)_3$[b]	AcOH/mL	Temp/°C	Time/min	Product (Yield/%)[c]		**1**/rec/%
1	**1b**: 1,8-	1:3	100	Reflux	5	**2b** (8)		
2	**1b**: 1,8-	1:4	100	100	6	**2b** (8)		
3	**1b**: 1,8-	1:4	50	Reflux	5	**2b** (15)		
4	**1b**: 1,8-	1:4	100	Reflux	4	**2b** (20)		
5	**1b**: 1,8-	1:4[d]	100	Reflux	26	**2b** (30)		10
6	**1b**: 1,8-	1:4[d,e]	50	Reflux	21	**2b** (28)		16
7	**1b**: 1,8-	1:6[d,e]	50	Reflux	29	**2b** (15)		
8	**1c**: 1,5-	1:4	50	70	100	Complex mixture		
9	**1c**: 1,5-	1:4	50	100	9	**2c** (4)	**3c** (6)	
10	**1c**: 1,5-	1:4	50	Reflux	4	**2c** (7)	**3c** (7)	
11	**1c**: 1,5-	1:3	100	Reflux	8	**2c** (7)	**3c** (12)	3
12	**1c**: 1,5-	1:4	100	Reflux	12	**2c** (8)	**3c** (8)	
13	**1c**: 1,5-	1:4	150	Reflux	5	**2c** (5)	**3c** (8)	
14[f]	**1c**: 1,5-	1:4	100	Reflux	5	**2c** (2)		8
15	**1c**: 1,5-	1:4[d]	100	Reflux	11	**2c** (15)	**3c** (2)	
16	**1c**: 1,5-	1:8[d,e]	50	Reflux	32	**2c** (12)	**3c** (2)	
17	**1d**: 2,6-	1:4	100	Reflux	5		**3d** (4)	
18	**1d**: 2,6-	1:4	50	Reflux	11		**3d** (2)	

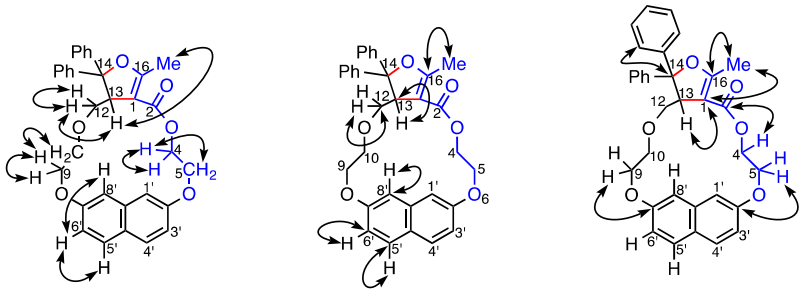
[a] The reaction of **1** (0.2 mmol) was carried out in acetic acid under an argon atmosphere.
[b] Molar ratio.
[c] Isolated yield based on the amount of **1** used.
[d] The naphthalene **1** was dropwise added during the reaction.
[e] Three-portions of $Mn(OAc)_3$ were successively added.
[f] NaOAc (2 equiv) was added.

In order to further explore the possibility of the dihydrofuran-clipping reaction for the 2,6-disubstituted naphthalene, we prepared a naphthalene **4** bearing longer tethers, i.e., the 1,4,7-trioxa-10,10-diphenyldec-9-enyl and 1,4,7-trioxa-8,10-dioxoundecyl groups, which underwent the reaction under modified conditions.[3] As a result, although each reaction site in **4** might be still apart and the benzylic and allylic oxidation and oligomerization predominantly proceeded, the corresponding naphthalenophane **5** could be isolated in a very low yield (3%) (see Scheme 4).

The structure of the product **2a** was deduced by a spectroscopic analysis. A triplet at δ 6.27 ppm (1H, J=7.0 Hz) assigned to the



Scheme 4. Oxidation of **4** with $Mn(OAc)_3$.



Scheme 5. Result of 2D NMR spectrum of [12](2,7)naphthalenophane **2a**.

olefinic sp^2 proton and a singlet at δ 3.49 ppm (2H) due to the methylene proton adjacent to the carbonyl group of **1a** in the ^1H NMR spectrum disappeared and a broad singlet assigned to an sp^3 methine proton newly appeared at δ 3.92 ppm (1H, H-13) in that of **2a**. In the ^{13}C NMR spectrum of **2a**, the carbonyl group of **1a** appeared at δ 200.2 and 167.0 ppm then converted into the enol ester group shown at δ 167.2 (C-16) and 163.9 ppm (C-2). The sp^2 vinyl carbons at δ 125.2 and 124.5 ppm in **1a** transformed into an alkoxyl sp^3 quaternary carbon (C-14) at δ 93.2 ppm and a methine sp^3 carbon (C-13) at δ 49.4 ppm in **2a**. These data showed the presence of the 4,5-dihydrofuran ring in the product **2a**. In addition, several methylene protons corresponding to the allylic (δ 4.18 (2H, d, *J*=6.8 Hz)) and *O*-methylene protons (δ 4.54, 4.26, 4.20, and 3.82 ppm (t, *J*=4.5 Hz)) of **1a** shifted from downfield to upfield in the range from δ 4.78 to 2.50 ppm in the ^1H NMR spectrum of **2a** (see Experimental section). Furthermore, a singlet appeared at δ 2.24 ppm due to the methyl protons of **1a** that also shifted upfield (δ 2.09 ppm) in **2a**.[20] These results clearly supported the fact that both the paramagnetic and diamagnetic shift must be caused by the construction of the naphthalenophane. In order to clarify the correlation of the protons and carbons of **2a**, the 2D NMR spectrum, such as HH COSY, HMQC, and HMBC, was taken in $CDCl_3$. The results are shown in Scheme 5. All of the data supported the structure of the naphthalenophane **2a**.[21] Finally, a single crystal of **2a** was successfully grown from $CHCl_3$/hexane and subjected to an X-ray crystallographic measurement. As a result, we obtained the exact structure of the product **2a** as a [12](2,7)naphthalenophane and illustrated in Fig. 1.[15] In addition, the product **2c** from the 1,5-disubstituted naphthalene **1c** was also obtained as a single crystal from CH_2Cl_2 and the exact [12](1,5)naphthalenophane structure was proved by the X-ray analysis (see Experimental section, Fig. 2).[22]

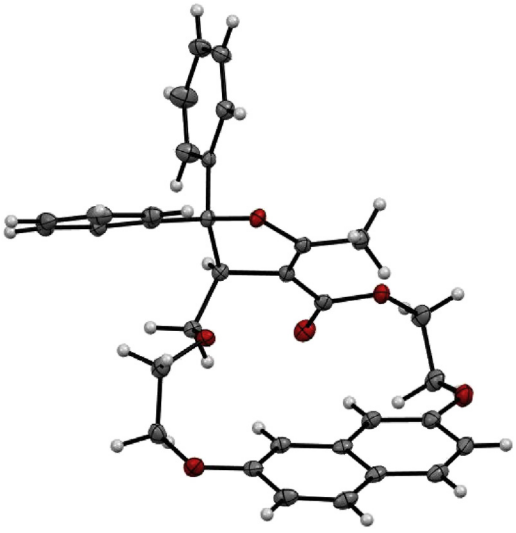


Fig. 1. ORTEP drawing of **2a**.

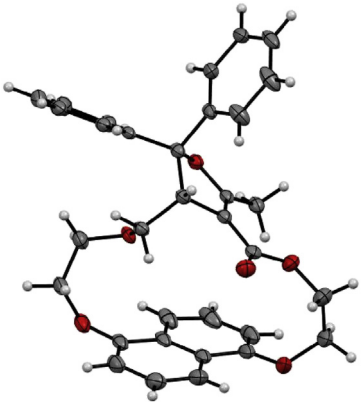


Fig. 2. ORTEP drawing of **2c**.

3. Conclusion

We have accomplished the unique synthesis of naphthalenophane macrocycles using the Mn(III)-mediated dihydrofuran-clipping reaction and the characterization of the dihydrofuran-fused naphthalenophanes obtained from the reaction. It was surprising that the strained [12]naphthalenophanes **2a**–**c** could be obtained from the reaction of the 2,7-, 1,8-, and 1,5-disubstituted naphthalenes bearing both the 1,4-dioxa-7,7-diphenylhept-6-enyl and 1,4-dioxa-5,7-dioxooctyl groups.[3] In this study, it was proved that the reaction could be used for the synthesis of macrocyclic compounds including aromatics as a single technique. However, it was difficult to optimize the reaction depending on the position of the substituent and probably tethered chain length.

4. Experimental section

4.1. Measurements

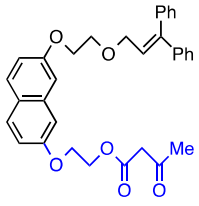
Melting points were taken using a Yanagimoto micromelting point apparatus and are uncorrected. The NMR spectra were recorded using a JNM ECX 500 or AL300 FT-NMR spectrometer at 500 or 300 MHz for the ^1H and at 125 or 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants in Hz. The following abbreviations are

used for the multiplicities; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet for the ^{1}H NMR spectrum. The IR spectra were measured in $CHCl_3$ or KBr using a Shimadzu 8400 FTIR spectrometer and expressed in cm^{-1}. The EIMS spectra were obtained by a Shimadzu QP-5050A gas chromatograph-mass spectrometer at the ionizing voltage of 70 eV. The high-resolution mass spectra and the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan. The X-ray analysis was performed by a SuperNova A diffractometer with a Cu micro-focus source and the final structures obtained were very high quality and automatically solved by the AutoChem module.

4.2. Materials

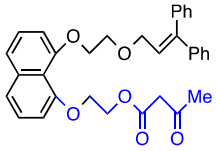
Manganese(II) acetate tetrahydrate, $Mn(OAc)_2{\cdot}4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3{\cdot}2H_2O$, was prepared according to our modified method.[23] 3-Bromo-1,1-diphenylprop-1-ene was prepared by the Grignard reaction of propiophenone with phenylmagnesium bromide followed by dehydration and bromination. 1,8-Naphthosultone, 1,5-naphthalenediol, ethyl bromoacetate, lithium aluminum hydride, diketene, propiophenone, and 2-(2-chloroethoxy)ethanol were purchased from Tokyo Kasei Co., Ltd., and 2,7-naphthalenediol, 2,6-naphthalenediol, *N*-bromosuccinimide (NBS), sodium hydride, bromobenzene, and dihydropyran (DHP) were from Wako Pure Chemical Ind., Ltd., and *p*-toluenesulfonic acid (*p*-TsOH), imidazole, and magnesium were from Kishida Chemical Co., Inc., and used as received. Flash column chromatography was performed on silica gel 60N (40–50 μm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 (45 μm) from Wako Pure Chemical Ind., Ltd. The solvents were commercially available first grade and used as received.

The disubstituted naphthalene **1a** was prepared by the reaction of 2,7-dihydroxynaphthalene with ethyl bromoacetate, reduction with lithium aluminum hydride (LAH), protection of one of the hydroxyl groups with dihydropyran (DHP), reaction with 3-bromo-1,1-diphenylpropene, deprotection, and then esterification with diketene. The other disubstituted naphthalenes **1b**–**d** and **4** were also prepared by a similar procedure (see Supplementary data).



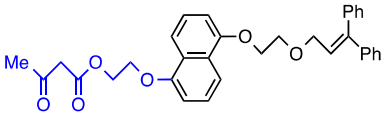
1a

*4.2.1. 2-((7-(2-((3,3-Diphenylallyl)oxy)ethoxy)naphthalen-2-yl)oxy) ethyl 3-oxobutanoate (**1a**).* Yellow liquid. R_f=0.35 (Et_2O-hexane, 5:5 v/v). IR ($CHCl_3$) ν 1746, 1719 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (1H, d, J=8.7 Hz, arom H), 7.64 (1H, d, J=9.6 Hz, arom H), 7.37–7.34 (3H, m, arom H), 7.26–7.23 (5H, m, arom H), 7.18 (2H, d, J=1.6, 8.1 Hz, arom H), 7.03–6.98 (4H, m, arom H), 6.27 (1H, t, J=6.8 Hz, C=CH), 4.54 (2H, t, J=4.5 Hz, CH_2), 4.26 (2H, t, J=4.5 Hz, CH_2), 4.20 (2H, t, J=4.5 Hz, CH_2), 4.18 (2H, d, J=6.8 Hz, CH_2), 3.82 (2H, t, J=4.5, CH_2), 3.49 (2H, s, CH_2C=O), 2.24 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2 (CH_3C=O), 167.0 (OC=O), 157.4, 156.8, 144.9, 141.7, 139.1, 135.6 (arom C), 125.2 (C=*C*H), 124.5 (>*C*=CH), 129.7 (2C), 129.2 (2C), 129.0 (2C), 128.1 (2C), 127.5 (2C), 127.4 (2C), 116.6, 116.0, 106.3, 106.2 (arom CH), 68.9, 68.5, 67.3, 65.5, 63.5 (CH_2), 49.8 (CH_2C=O), 30.0 (CH_3). FAB HRMS (acetone/NBA/NaI): calcd for $C_{33}H_{32}O_6$ 547.2097 (M+Na); found 547.2105.



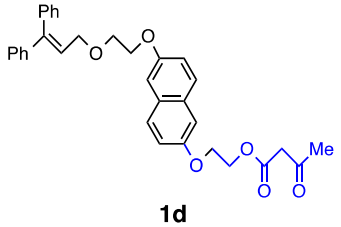
1b

*4.2.2. 2-((8-(2-((3,3-Diphenylallyl)oxy)ethoxy)naphthalen-1-yl)oxy) ethyl 3-oxobutanoate (**1b**).* Yellow liquid. R_f=0.31 (Et_2O-hexane, 5:5 v/v). IR ($CHCl_3$) ν 1744, 1717 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.06 (14H, m, arom H), 6.68 (2H, d, J=7.7 Hz, arom H), 6.17 (1H, t, J=6.7 Hz, C=CH), 4.42 (2H, t, J=4.7 Hz, CH_2), 4.11 (2H, t, J=4.7 Hz, CH_2), 4.06 (2H, d, J=6.7 Hz, CH_2), 4.05 (2H, t, J=4.7 Hz, CH_2), 3.74 (2H, t, J=4.7 Hz, CH_2), 3.28 (2H, s, CH_2C=O), 2.03 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6 (CH_3C=O), 167.3 (>C=O), 156.0, 155.9, 144.9, 141.9, 139.3, 137.6, 118.6 (arom C), 129.9 (2C), 128.37 (2C), 128.34 (2C), 127.8 (2C), 127.74, 127.70, 126.6, 126.4, 125.6, 122.0, 121.3 (C=CH), 109.6, 108.2 (arom CH), 69.0, 68.9, 68.7, 68.1, 64.2 (CH_2), 50.0 (CH_2C=O), 30.2 (CH_3). FAB HRMS (acetone/NBA): calcd for $C_{33}H_{32}O_6$ 524.2199 (M); found 524.2224.



1c

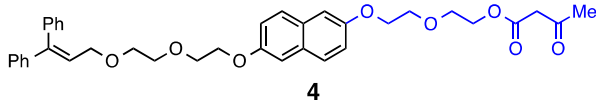
*4.2.3. 2-((5-(2-((3,3-Diphenylallyl)oxy)ethoxy)naphthalen-1-yl)oxy) ethyl 3-oxobutanoate (**1c**).* Yellow microcrystals (from $CHCl_3$), mp 87–90 °C. R_f=0.44 (Et_2O-hexane, 7:3 v/v). IR (KBr) ν 1751, 1717 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (1H, d, J=8.5 Hz, arom H), 7.71 (1H, d, J=8.5 Hz, arom H), 7.24–7.17 (5H, m, arom H), 7.15–7.10 (5H, m, arom H), 7.08 (2H, dd, J=8.0, 1.7 Hz, arom H), 6.68 (1H, d, J=7.6 Hz, arom H), 6.66 (1H, d, J=7.7 Hz, arom H), 6.16 (1H, t, J=6.7 Hz, C=CH), 4.48 (2H, t, J=4.5 Hz, CH_2), 4.12 (2H, t, J=4.5 Hz, CH_2), 4.11 (2H, t, J=4.7 Hz, CH_2), 4.08 (2H, d, J=6.7 Hz, CH_2), 3.76 (2H, t, J=4.5 Hz, CH_2), 3.35 (2H, s, CH_2C=O), 2.03 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5 (CH_3C=O), 167.3 (>C=O), 154.5, 154.0, 145.3, 141.9, 139.3, 126.9, 126.7 (arom C), 129.9 (2C), 128.34 (2C), 128.30 (2C), 127.8 (2C), 127.7, 127.6, 125.5, 125.4, 125.2 (C=CH), 115.3, 114.5, 105.9, 105.8 (arom CH), 69.2, 68.8, 67.9, 66.2, 63.7 (CH_2), 50.0 (CH_2C=O), 30.3 (CH_3). FAB HRMS (acetone/NBA): calcd for $C_{33}H_{32}O_6$ 524.2199 (M); found 524.2213.



1d

*4.2.4. 2-((6-(2-((3,3-Diphenylallyl)oxy)ethoxy)naphthalen-2-yl)oxy) ethyl 3-oxobutanoate (**1d**).* Yellow liquid. R_f=0.31 (Et_2O-hexane, 5:5 v/v). IR ($CHCl_3$) ν 1745, 1717 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (1H, d, J=8.9 Hz, arom H), 7.60 (1H, d, J=8.9 Hz, arom H), 7.36–7.31 (3H, m, arom H), 7.26–7.24 (5H, m, arom H), 7.18 (2H, dd, J=1.7, 8.1 Hz, arom H), 7.16–7.11 (2H, m, arom H), 7.07 (2H, d, J=1.7 Hz, arom H), 6.27 (1H, t, J=6.7 Hz, C=CH), 4.52 (2H, t, J=4.7 Hz, CH_2),

4.24 (2H, t, J=4.7 Hz, CH_2), 4.17 (2H, d, J=6.7 Hz, CH_2), 4.16 (2H, J=4.7 Hz, CH_2), 3.80 (2H, t, J=4.7 Hz, CH_2), 3.49 (2H, s, CH_2C=O), 2.23 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5 (CH_3C=O), 167.0 (>C=O), 155.5, 155.0, 145.1, 139.0130.1, 129.8 (arom C), 141.9 (*C*=CH), 129.8 (2C), 128.5, 128.33 (2C), 128.3, 128.2 (2C), 127.7 (2C), 127.7, 127.6, 119.6, 119.0, 107.4, 107.2 (arom CH), 69.1, 68.7, 67.5, 65.9, 63.4 (CH_2), 50.0 (CH_2C=O), 30.2 (CH_3). FAB HRMS (acetone/NBA): calcd for $C_{33}H_{32}O_6$ 524.2199 (MH); found 524.2223.

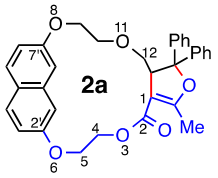


4

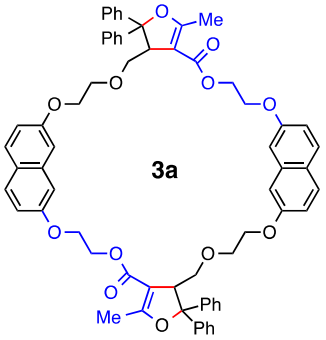
*4.2.5. 2-(2-((6-(2-(2-((3,3-Diphenylallyl)oxy)ethoxy)ethoxy)naphthalen-2-yl)oxy)ethoxy)ethyl 3-oxobutanoate (**4**).* Yellow liquid. R_f=0.63 (Et_2O). IR ($CHCl_3$) ν 1745, 1717 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (2H, d, J=8.8 Hz, arom H), 7.32–7.12 (12H, m, arom H), 7.06 (2H, m, arom H), 6.24 (1H, t, J=6.6 Hz, C=CH), 4.29 (2H, t, J=4.5 Hz, CH_2), 4.14 (4H, m, CH_2), 4.08 (2H, d, J=6.6 Hz, C=CHCH_2), 3.85–3.81 (4H, m, CH_2), 3.73 (2H, t, J=4.5 Hz, CH_2), 3.68 (2H, t, J=4.5 Hz, CH_2), 3.57 (2H, t, J=4.5 Hz, CH_2), 3.39 (2H, s, CH_2C=O), 2.16 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1 (CH_3C=O), 166.7 (OC=O), 155.0, 154.8, 144.1, 138.8, 127.16, 127.14, (arom C), 141.4 (>*C*=CH), 129.3 (2C), 127.84 (2C), 127.82 (3C), 127.79 (3C), 127.19 (3C), 119.0, 118.8, 106.7 (arom CH), 125.3 (C=*C*H), 70.4, 69.3, 69.23, 69.19, 68.6, 68.5, 67.1, 67.0, 63.4 (CH_2), 49.5 (CH_2C=O), 29.7 (CH_3). FAB HRMS (acetone/NBA): calcd for $C_{37}H_{40}O_8$ 612.2723 (M); found 612.2726.

4.3. Oxidation of 2-((7-(2-((3,3-diphenylallyl)oxy)ethoxy) naphthalen-2-yl)oxy)ethyl 3-oxobutanoate (1a) with manganese(III) acetate

To a 100 mL three-necked flask, manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$ (161 mg, 0.6 mmol) and glacial acetic acid (50 mL) were added and degassed under reduced pressure for 30 min using an ultrasonicator for exchange with an argon atmosphere. The mixture was heated under an argon atmosphere using an oil bath at 140 °C, and after boiling, a solution of the allyloxynaphthalenyl oxobutanoate **1a** (105 mg, 0.2 mmol) in glacial acetic acid (5 mL) was dropwise added (0.1 mL/min) using a syringe. When the solution of **1a** (0.2 mL) was poured into the reaction mixture, the dark-brown color of the reaction mixture turned transparent, so that additional $Mn(OAc)_3 \cdot 2H_2O$ (161 mg, 0.6 mmol) was added to the mixture. Normally, three portions of $Mn(OAc)_3 \cdot 2H_2O$ (107 mg, 0.2 mmol) were successively added after decoloration of the dark-brownish reaction mixture. Dropwise adding of the rest of the solution of **1a** resumed and the reaction mixture was continued to be heated under reflux until the dark-brown color of the solution turned transparent again (total for 41 min). The solvent was removed under reduced pressure and the residue was triturated with 2 M hydrochloric acid (30 mL). The aqueous solution was extracted three times with chloroform (25 mL) and the combined extracts were washed with a saturated aqueous solution of sodium hydrogencarbonate, brine, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated on silica gel TLC developed with chloroform, giving the desired naphthalenophane **2a** (37 mg, 35%) (Table 1, entry 10). The TLC separation of the more polar products afforded the diploid **3a** (45 mg) in 22% maximum yield (Table 1, entry 6). The physical data of **2a** and **3a** are given below.



*4.3.1. [12](2,7)Naphthalenophane (**2a**): 1^5-Methyl-1^2,1^2-diphenyl-1^2,1^3-dihydro-3,6,8,11-tetraoxa-1(3,4)-furana-7(2,7)-naphthalenacyclododecaphan-2-one.* Pale pink prisms (from $CHCl_3$/hexane), mp 260–261 °C. R_f=0.49 (EtOAc-hexane, 2:8 v/v). IR (KBr) ν 1676 (C=O), 1636 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (1H, d, J=9.0 Hz, naph CH-4′or 5′), 7.52 (1H, d, J=9.0 Hz, naph CH-5′or 4′), 7.53 (1H, d, J=2.5 Hz, naph CH-1′or 8′), 7.52 (1H, d, J=2.5 Hz, naph CH-8′or 1′), 7.30–7.14 (10H, m, ph×2), 6.88 (1H, dd, J=2.5, 9.0 Hz, CH-3′or 6′), 6.83 (1H, dd, J=2.5, 9.0 Hz, CH-6′or 3′), 4.78 (1H, ddd, J=14.0, 3.5, 2.0 Hz, *H*–CH– at C-4), 4.67 (1H, ddd, J=14.0, 8.0, 2.0 Hz, *H*–CH– at C-5), 4.35 (1H, dt, J=14.0, 3.5 Hz, *H*–CH– at C-5), 4.13 (1H, ddd, J=13.8, 7.3, 1.5 Hz, *H*–CH– at C-9), 4.05 (1H, ddd, J=14.0, 8.0, 2.0 Hz, *H*–CH– at C-4), 3.97 (1H, dq, J=13.8, 2.0 Hz, *H*–CH– at C-9), 3.92 (1H, br s, *H*–C< at C-13), 3.62 (1H, dd, J=10.0, 3.0 Hz, *H*–CH– at C-12), 2.98 (1H, d, J=10.0 Hz, *H*–CH– at C-12), 2.76 (1H, dd, J=11.5, 2.0 Hz, *H*–CH– at C-10), 2.50 (1H, ddd, J=11.5, 7.3, 2.0 Hz, *H*–CH– at C-10), 2.09 (3H, s, CH_3 at C-16). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2 (C=CCH_3 at C-16), 163.9 (>*C*=O at C-2), 155.1, 154.9 (naph-*C*-O at C-2′ and C-7′), 1434.9, 139.5 (Ph-C), 134.7, 123.2 (naph-*C* at 4′a and C-8′a), 127.9, 127.4 (naph-CH at C-4′ and C-5′), 127.2 (2C), 126.9, 126.3 (2C), 1256.9, 125.7 (2C), 125.0 (2C, Ph-CH), 116.3, 116.0 (naph-CH at C-3′ and C-6′), 1078.8, 107.0 (naph-CH at C-1′ and C-8′), 102.3 (*C*=CCH$_3$ at C-1), 93.2 (*C*–O at C-14), 69.6 (CH_2 at C-10), 67.4 (CH_2 at C-9), 66.9 (CH_2 at C-12), 66.3 (CH_2 at C-5), 63.2 (CH_2 at C-4), 49.4 (C=C*C*H at C-13), 14.1 (CH_3). FAB HRMS (acetone/NBA/NaI): calcd for $C_{33}H_{30}O_6Na$ 545.1940 (M+Na); found 545.1899. X-ray crystallographic data: empirical formula $C_{33}H_{30}O_6$; formula weight 522.57; colorless prisms; space group $P2_1/n$; cell lengths a=10.3788(7), b=13.70209(8), c=18.70260(12) Å; cell angles α=90.00, β=104.8307(7), γ=90.00°; cell volume 2571.14 Å^3; formula units per cell Z=4, Z'=0; density ρ=1.350 g/cm^3; absorption coefficient μ=0.748; radiation (CuK_α) λ=1.54184; total data collected 5352; R=0.0479; R_w=0.1264; GOF=1.039.

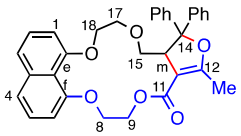


*4.3.2. [12,12](2,7)Naphthalenophane (**3a**): 1^5,13^5-Dimethyl-1^2,1^2,13^2,13^2-tetraphenyl-1^2,1^3,13^2,13^3-tetrahydro-3,6,8,11,15,18,20,23-octaoxa-1(3,4),13(4,3)-difurana-7,19(2,7)-dinaphthalenacyclotetracosaphane-2,14-dione.* Brown liquid. IR ($CHCl_3$) ν 1728 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–6.90 (32H, m, arom H), 4.72–3.47 (16H, m, CH_2 and CH), 2.39–2.02 (12H, m,

CH_2 and CH_3). FAB HRMS (acetone/NBA/NaI): calcd for $C_{66}H_{60}O_{12}Na$ 1067.3982 (M+Na); found 1067.4015.

4.4. Oxidation of 2-((8-(2-((3,3-diphenylallyl)oxy)ethoxy) naphthalen-1-yl)oxy)ethyl 3-oxobutanoate (1b) with manganese(III) acetate

To a 200 mL three-necked flask, manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$ (210 mg, 0.8 mmol) and glacial acetic acid (50 mL) were added and degassed under reduced pressure for 30 min using an ultrasonicator for exchange with an argon atmosphere. The mixture was heated under an argon atmosphere using an oil bath at 140 °C, and after boiling, a solution of the allyloxynaphthalenyl oxobutanoate **1b** (105 mg, 0.2 mmol) in glacial acetic acid (50 mL) was dropwise added using a 100 mL dropping funnel. The reaction mixture was continued to be heated under reflux until the dark-brown color of the solution turned transparent (total for 26 min). The solvent was removed under reduced pressure and the residue was triturated with 2 M hydrochloric acid (30 mL). The aqueous solution was extracted three times with chloroform (25 mL) and the combined extracts were washed with a saturated aqueous solution of sodium hydrogencarbonate, brine, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated on silica gel TLC developed with EtOAc/hexane (3:7 v/v), giving the desired naphthalenophane **2b** (31 mg, 30%) (Table 2, entry 5). The physical data of **2b** are given below.

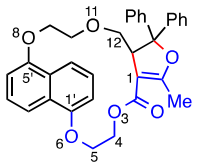


2b

*4.4.1. [12](1,8)Naphthalenophane (**2b**): 12-Methyl-14,14-diphenyl-8,9,14a,15,17,18-hexahydro-11H,14H-furo[3,4-m]naphtho[1,8-ef][1,4,8,11]tetraoxacyclopentadecin-11-one.* Yellow amorphous. R_f=0.56 (EtOAc-hexane, 3:7 v/v). IR ($CHCl_3$) ν 1697 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (2H, d, J=7.0 Hz, H-3 and H-4), 7.36–7.17 (12H, m, arom H), 6.75 (1H, d, J=7.0 Hz, H-1 or H-6), 6.67 (1H, d, J=7.5 Hz, H-6 or H-1), 4.81–4.77 (1H, m, H-9), 4.39–4.37 (2H, m, H-8 and H-9), 4.29–4.27 (1H, m, H-8), 4.22–4.21 (2H, m, H-18), 4.10 (1H, br s, H-14a), 3.80–3.77 (1H, m, H-17), 3.75–3.72 (1H, m, H-15), 3.59–3.56 (1H, m, H-17), 3.52–3.49 (1H, m, H-15), 2.36 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4 (C-12), 165.6 (C-11), 156.1, 155.7 (C-6a and C-19a), 145.1, 140.5, 137.5, 117.4 (arom C), 128.1 (2C), 127.7, 127.5 (2C), 127.1 (2C), 126.8 (2C), 126.2 (2C), 120.7 (2C), 120.4, 105.9, 105.7 (arom CH), 103.8 (C-11a), 94.8 (C-14), 70.1 (C-15), 69.4 (C-18), 67.5 (C-17), 66.3 (C-8), 62.0 (C-9), 51.3 (C-14a), 14.3 (CH_3). FAB HRMS (acetone/NBA/NaI): calcd for $C_{33}H_{30}O_6Na$ 545.1940 (M+Na); found 545.1919.

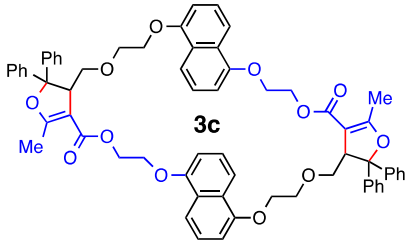
4.5. Oxidation of 2-((5-(2-((3,3-diphenylallyl)oxy)ethoxy) naphthalen-1-yl)oxy)ethyl 3-oxobutanoate (1c) with manganese(III) acetate

Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$ (210 mg, 0.8 mmol) in glacial acetic acid (90 mL) was degassed under reduced pressure for 30 min using an ultrasonicator for exchange with an argon atmosphere and heated using an oil bath at 140 °C. After boiling, a solution of the allyloxynaphthalenyl oxobutanoate **1c** (105 mg, 0.2 mmol) in glacial acetic acid (10 mL) was dropwise added and the mixture was continued to be heated under reflux until the dark-brown color of the solution turned transparent (total for 11 min). After the same work-up described above, the desired naphthalenophane **2c** (16 mg) was obtained in 15% yield (Table 2, entry 15). The physical data of **2c** are given below.



2c

*4.5.1. [12](1,5)Naphthalenophane (**2c**): 1^5-Methyl-1^2,1^2-diphenyl-1^2,1^3-dihydro-3,6,8,11-tetraoxa-1(3,4)-furana-7(1,5)-naphthalenacyclododecaphan-2-one.* Colorless prisms (from CH_2Cl_2), mp 226–227 °C. R_f=0.43 (EtOAc-hexane, 2:8 v/v). IR (KBr) ν 1690 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (1H, d, J=8.5 Hz, arom H), 7.88 (1H, d, J=8.5 Hz, arom H), 7.44 (1H, t, J=7.5 Hz, arom H), 7.35 (1H, t, J=7.5 Hz, arom H), 7.31–7.14 (10H, m, arom H), 7.11 (1H, d, J=7.5 Hz, arom H), 7.07 (1H, d, J=7.5 Hz, arom H), 4.88–4.84 (1H, m), 4.67–4.57 (2H, m), 4.12–4.06 (3H, m), 3.16 (1H, m), 2.93–2.88 (1H, m), 2.37 (1H, dd, J=9.6 and 6.7 Hz), 2.06–2.03 (1H, m), 1.87 (1H, dd, J=9.6 and 2.1 Hz), 1.94 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1 (C=*C*CH_3 at C-16), 164.1 (>*C*=O at C-2), 156.4, 155.7, 144.7, 140.5, 130.3, 129.3 (arom C), 128.2 (2C), 128.1, 128.0, 127.6, 127.1 (2C), 126.9, 126.7, 126.0, 125.4, 124.8, 117.5, 117.1, 114.9, 113.8 (arom CH), 102.9 (*C*=CCH_3 at C-1), 93.9 (C–O at C-14), 73.6, 72.2, 70.8, 67.2, 64.2 (CH_2), 49.7 (C=*C*CH at C-13), 14.7 (CH_3). FAB HRMS (acetone/NBA): calcd for $C_{33}H_{31}O_6$ 523.2121 (M+H); found 523.2119. X-ray crystallographic data: empirical formula $C_{33}H_{30}O_6$; formula weight 522.57; colorless prisms; space group $P2_1/n$; cell lengths a=12.49783(14), b=9.48078(11), c=22.6036(2) Å; cell angles α=90.00, β=104.2923(11), γ=90.00°; cell volume 2595.39(5) Å^3; formula units per cell Z=4; density ρ=1.337 g/cm^3; absorption coefficient μ=0.741; radiation (CuK_α) λ=1.54184; total data collected 5352; R=0.0500; R_w=0.1355; GOF=1.041.



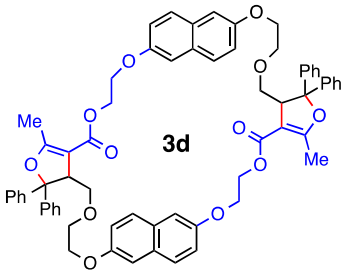
3c

*4.5.2. [12,12](1,5)Naphthalenophane (**3c**): 1^5,13^5-dimethyl-1^2,1^2,13^2,13^2-tetraphenyl-1^2,1^3,13^2,13^3-tetrahydro-3,6,8,11,15,18,20,23-octaoxa-1(3,4),13(4,3)-difurana-7,19(1,5)-dinaphthalenacyclotetracosaphane-2,14-dione.* Yellow amorphous. R_f=0.44 (EtOAc-hexane, 3:7 v/v). IR ($CHCl_3$) ν 1697 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (2H, t, J=8.5 Hz, arom H), 7.63–7.59 (4H, m, arom H), 7.53 (2H, t, J=8.6 Hz, arom H), 7.39–7.14 (20H, m, arom H), 6.74 (2H, d, J=7.6 Hz, arom H), 6.08 (1H, d, J=7.5 Hz, arom H), 6.04 (1H, d, J=7.5 Hz, arom H), 4.79–4.75 (2H, m), 4.44–4.27 (6H, m), 4.09 (2H, dd, J=17.1 and 7.8 Hz), 3.58 (2H, ddd, J=18.2, 9.8, 2.3 Hz), 3.19–3.04 (6H, m), 2.88–2.77 (2H, m), 2.71–2.64 (2H, m), 2.39 (6H, s, CH_3). FAB HRMS (acetone/NBA): calcd for $C_{66}H_{60}O_{12}$ 1044.4085 (M); found 1044.4095.

4.6. Oxidation of 2-((6-(2-((3,3-diphenylallyl)oxy)ethoxy) naphthalen-2-yl)oxy)ethyl 3-oxobutanoate (1d) with Manganese(III) acetate

To glacial acetic acid (100 mL), manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$ (220 mg, 0.8 mmol) and the allyloxynaphthalenyl

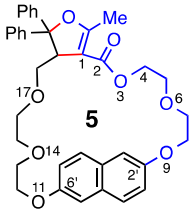
oxobutanoate **1d** (104.5 mg, 0.2 mmol) were added and degassed according to the same procedure described above and then heated at 140 °C. It was confirmed by the color change from dark brown to transparent of the reaction mixture that the Mn(III) was completely consumed after 5 min. After the same work-up described above, the corresponding diploid **3d** (8.1 mg) was obtained in 4% yield along with an intractable mixture (Table 2, entry 17). The physical data of **3d** are given below.



*4.6.1. [12,12](2,6)Naphthalenophane (**3d**): $1^5,13^5$-dimethyl-$1^2,1^2,13^2,13^2$-tetraphenyl-$1^2,1^3,13^2,13^3$-tetrahydro-3,6,8,11,15,18,20,23-octaoxa-1(3,4),13(4,3)-difurana-7,19(2,6)-dinaphthalenacyclotetracosaphane-2,14-dione.* Brown liquid. R_f=0.35 (EtOAc-hexane, 3:7 v/v). IR ($CHCl_3$) ν 1701 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61–7.00 (28H, m, arom H), 6.85 (2H, dt, J=8.5, 2.4 Hz, arom H), 6.52 (2H, dd, J=10.0, 2.4 Hz, arom H), 4.6–3.2 (22H, m, CH_2, CH), 2.36 (6H, s, $CH_3\times2$). FAB HRMS (acetone/NBA): calcd for $C_{66}H_{60}O_{12}$ 1044.4085 (M); found 1044.4106.

4.7. Oxidation of 2-(2-((6-(2-(2-((3,3-Diphenylallyl)oxy)ethoxy)ethoxy)naphthalen-2-yl)oxy)ethoxy)ethyl 3-oxobutanoate (4) with Manganese(III) acetate

To glacial acetic acid (45 mL), manganese(III) acetate dihydrate, $Mn(OAc)_3\cdot2H_2O$ (110 mg, 0.4 mmol) was added and degassed according to the same procedure described above. The solution was heated under reflux and the allyloxynaphthalenyl oxobutanoate **4** (122.3 mg, 0.2 mmol) dissolved in acetic acid (5 mL) was slowly added (0.5 mL/min) using a syringe. When the solution of **4** in acetic acid (1.6 mL) was added, the color of the solution changed from dark brown to transparent. Additional $Mn(OAc)_3\cdot2H_2O$ (107.8 mg, 0.4 mmol) was then put into the boiling solution and the rest of **4** in acetic acid was slowly added. The Mn(III) was completely consumed within 17 min. After the same work-up mentioned above, the residue was separated by silica gel TLC developed with EtOAc/hexane (5:5 v/v), isolating the desired [18](2,6)naphthalenophane **5** (3.5 mg, 3%). The physical data of **5** are given below.



*4.7.1. [18](2,6)Naphthalenophane (**5**): 1^5-methyl-$1^2,1^2$-diphenyl-$1^2,1^3$-dihydro-3,6,9,11,14,17-hexaoxa-1(3,4)-furana-10(2,6)-naphthalenacyclooctadecaphan-2-one.* Yellow liquid. R_f=0.66 (EtOAc-hexane, 5:5 v/v). IR ($CHCl_3$) ν 1728 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (2H, t, J=9.0 Hz, arom H), 7.42–7.18 (12H, m, arom H), 7.02 (2H, d, J=7.1 Hz, arom H), 4.41–4.31 (6H, m), 4.04–3.99 (1H, m), 3.82 (2H, t, J=4.3 Hz), 3.66 (2H, t, J=4.3 Hz), 3.54–3.51 (4H, m), 3.12 (1H, dd, J=9.6, 2.3 Hz), 3.05 (1H, ddd, J=2.8, 5.8, 12.0 Hz), 2.84–2.79 (1H, m), 2.71–2.67 (1H, m), 1.92 (3H, s, CH_3). FAB HRMS (acetone/NBA): calcd for $C_{37}H_{38}O_8$ 610.2567 (M); found 610.2652.

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Supplementary data

Supplementary data (Preparation details of the disubstituted naphthalenes **1a**–**d** and **4**, copies of ^{1}H NMR, ^{13}C NMR, DEPT, IR, and MS spectral charts of disubstituted naphthalenes **1a**–**d** and **4**, naphthalenophanes **2a**–**c**, **3a**, **3c**, **3d**, **5**, and 2D NMR spectral charts of **2a**, **2c** are available in Supplementary data.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2016.09.025.

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14. One of the reviewers suggested that the yield of naphthalenophanes which would be obtained using 1,1-bis(4-halophenyl)ethenyl substrate might increase compared to that using the 1,1-diphenylethenyl-naphthalenes **1a**–**d**. However, the effect of the substituent group such as a halo group has already been proved, that is, the yield of dihydrofurans produced by the Mn(III)-based oxidation of 1,1-bis(4-halophenyl)ethenes in the presence of acetoacetate esters[16] and acetylacetone[17] was quite similar or low compared to that using 1,1-diphenylethene. Furthermore, it was reported that the Mn(III)-based macrocyclization using 4-chlorophenyl-substituted diene led to decrease the yield of the corresponding macrodiolide compared to that using the diene bearing phenyl group.[18]
15. One of the reviewers also suggested that the reaction of naphthyl 1,1,1-trifluoroacetoacetate ester instead of acetoacetate esters such as **1a**–**d** should be carried out. However, it could be considered that the use of the trifluoroacetoacetate ester might be unsuitable in the dihydrofuranation due to the strong electron-withdrawing character of the trifluoromethyl group. Actually, the oxidation of a mixture of 1,1-diphenylethene and ethyl 1,1,1-trifluoroacetoacetate with $Mn(OAc)_3$ (molar ratio=1:1:2) afforded ethyl 5,5-diphenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate[19] in 41% yield, while the same reaction using the acetoacetate gave the corresponding dihydrofuran in 77% yield.[16b]
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21. One of the reviewers suggested that conformational ring flipping of **2a** would not be permitted at room temperature because the peaks of H-12 methylene and H-13 methine protons distinguishably appeared. However, when the naphthalene ring of **2a** would rotate, dihedral one of the H-12 methylene proton and H-13 methine proton angle was almost similar both in the most stable rotamers based on our molecular modeling study.
22. X-ray coordinates were deposited with the Cambridge Crystallographic Data Centre:(a) **2a**: CCDC 1483190 and (b) **2c**: CCDC 1483191.
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