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Functional [6]Pericyclynes: Synthesis through [14+4] and [8+10] Cyclization Strategies**

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Abstract: Critical analysis of possible strategies for the synthesis of novel *carbo*-benzene derivatives suggests several [(18−*n*)+*n*] routes for the preparation of hexaoxy[6]pericyclyne precursors. Beyond the previously attempted [9+9] symmetrical scheme (*n*=9), the a priori most selective strategies are those for which *n*=1, 4, 7, 10, 13, and 16. They involve a cyclizing double-propargylation of a C_{18-n} ω-bis-terminal-skipped oligoyne containing (19−*n*)/3 triple bonds with a C_n ω-dicarbonyl-skipped oligoyne containing (*n*−1)/3 triple bonds. To complement the previously used [11+7] strategy, the [14+4] and [8+10] strategies were thus explored. They proved to be efficient, affording seven novel hexaoxy[6]pericyclynes corresponding to six different substitution patterns. These compounds were obtained in 7–15 steps as mixtures of stereoisomers. Thus, by using dibenzoylacetylene as the C_4 electrophile, a [14+4] strategy allowed the synthesis of two hexaphenyl representatives with two or four free carbinol vertices. This approach also afforded tetraphenyl representatives in which the two remaining carbinoxy vertices were substituted with either two alkynyl or one 4-anisyl and one 4-pyridyl groups. By using the hexacarbonyldicobalt complex of butynedial as the C_4 electrophile, a [14+4] strategy also allowed the isolation of a tetraphenylhexaoxy[6]pericyclyne with two adjacent unsubstituted carbinol vertices. A regioisomer with two opposite unsubstituted carbinol vertices was obtained through an [8+10] strategy and its oxidation afforded the corresponding pericyclynedione. Several attempts at synthesizing diphenylhexaoxy[6]pericyclynes with four unsubstituted carbinoxy vertices are described. Only an [8+10] strategy allowed the generation of a fragile diphenylhexaoxy[6]pericyclyne with four adjacent unsubstituted carbinoxy vertices, which could be partly characterized. These results show that the synthesis of the nonsubstituted hexahydroxy[6]pericyclyne, the ring *carbo*-mer of [6]cyclitol, is a difficult challenge.

Keywords: alkynes · butynedial · *carbo*-mers · cyclization · macrocycles · pericyclynes

Introduction

In the age of nanoscience, macroscopic processes and devices are transposed to the molecular level. Within this context, *carbo*-merization can be regarded as a "molecular inflation" through (di)carbon doping.[1] It involves the insertion of C_2 units into all symmetry-related bonds of the relevant Lewis–Cram model of any molecule. Since the *carbo*-mer model preserves the essential properties of the parent model (connectivity, shape, symmetry, π resonance), one may naturally wonder how related chemical properties would be modified.[2] Aromaticity is such a property underlying many others, for which benzene stands as a paradigm. Its ring *carbo*-mer $C_{18}H_6$ ("*carbo*-benzene") is thus the simplest molecule for the study of *carbo*-meric effects on aromaticity.[3] In 1995, the challenge of its synthesis and the first four examples of aryl-substituted derivatives **1a–d** were simultaneously reported by one of us[4] and by Kuwatani, Ueda, and co-worker,[5] respectively (Scheme 1a).

Both reports were based on the availability of functional *carbo*-cyclohexane key precursors, namely hexaoxy-[6]pericyclynes. These intriguing molecules were first exemplified by molecules with the type **2** structure (Scheme 1a),[5] and the goal here was to gain a systematic insight into the func-

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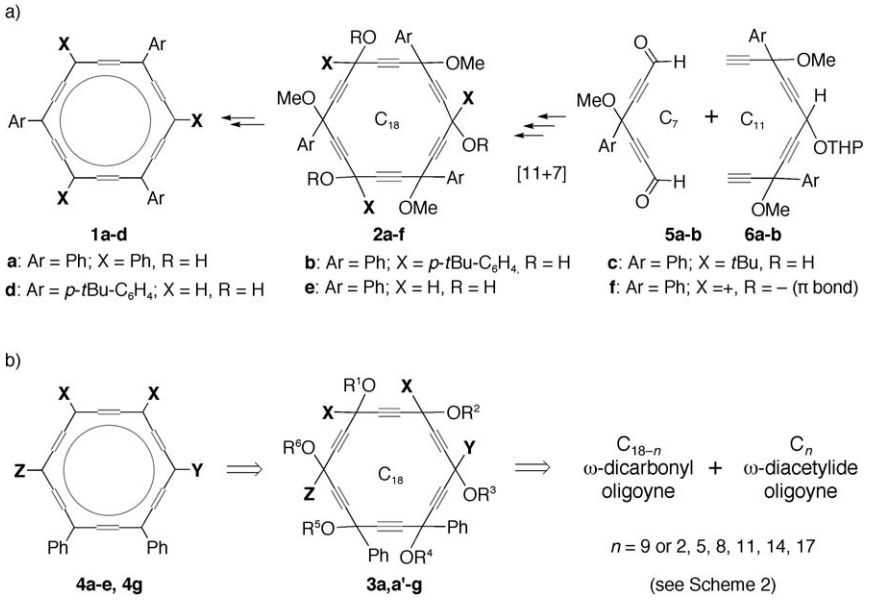
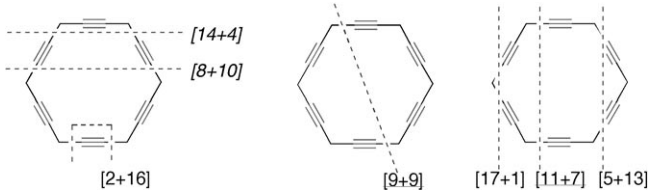


Scheme 1. a) Exemplified hexaoxy[6]pericyclynes with a star-shaped alternating substitution pattern. These molecules were devised as precursors of aryl-substituted *carbo*-benzene derivatives.[5] b) Targeted hexaoxy[6]-pericyclynes with various substitution patterns, regarded as potential precursors of novel *carbo*-benzene derivatives.

tional compatibility of hexaoxy-[6]pericyclynes in the alternative type **3** structure (Scheme 1b). The ultimate targets were the corresponding *carbo*-benzene derivatives **4**, which display reduced symmetry compared with the three-fold ideal symmetry of the known derivatives **1a–d** (Scheme 1b).[6] Since the ultimate aromatization step is devoted to the removal of all the stereochemical information contained in the highly stereogenic [6]pericyclyne precursors **3**, their stereochemical resolution was not required. In the following, the term "isolated molecule" is defined regardless of the stereochemistry.

In the pioneering work of Scott et al., the (nonfunctional) dodecamethyl[6]pericyclyne prototype was prepared through a ring-closing strategy in which the 18 carbon atoms of the ring were already present in the open-chain hexayne precursor.[7] In contrast, the first hexaoxy[6]pericyclynes were prepared through a cyclization strategy in which the 18 carbon atoms of the ring were brought together from either two C_9 ω-ynal moieties[4] or from a C_7 ω-dialdehyde **5a–b** and a C_{11} ω-diyne **6a–b** (Scheme 1).[5,8] The latter [11+7] strategy afforded the pivotal hexaoxy[6]pericyclynes **2d** and **2e** in 13 steps (**2a–c** were obtained from **2e** via the pericyclynetrione **2f**). Both the attempted [9+9] and successful [11+7] cyclization reactions relied on double alkynyl-oxopropargyl coupling (Scheme 1).[9] The same process also enabled the synthesis of homologous pentaoxy[5]pericyclynes through [(15−*n*)+*n*] cyclization strategies from C_{15-n} ω-diynes and C_n ω-dicarbonyl compounds (*n* = 4, 10).[10] A simple generalization led us to consider the homologous [(18−*n*)+*n*] strategy for the synthesis of hexaoxy[6]pericyclynes. Of the nine possibilities, the odd strategies, *n* = 7 and 9, have been attempted previously,[4,5,8] whereas the even strategies, *n* = 4 and 10, are addressed herein (Scheme 2).



Scheme 2. The seven [(18−*n*)+*n*] cyclization schemes for the preparation of [6]pericyclynes by cyclizing double alkynyl-propargyl coupling. The dissymmetrical [3+15] and [6+12] schemes involving different ambivalent nucleophilic/electrophilic reagents are nonselective and are not depicted. Underlined strategies have previously been investigated by double alkynyl-oxopropargyl coupling;[4,5,8] italicized strategies are investigated herein.

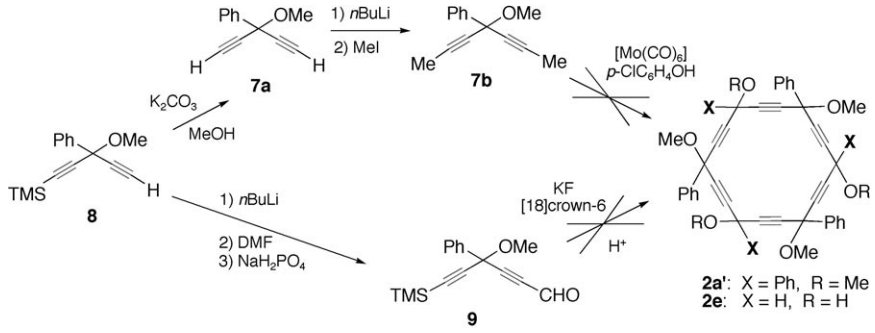
Results and Discussion

This section is divided into three subsections. Before tackling the study of the [14+4] and [8+10] cyclization strategies, the possibility of appealing alternative strategies is outlined. Their deceptive results are briefly reported in a preliminary subsection.

Attempted [6×3] and [3×6] sequential strategies to hexaoxy[6]pericyclynes of type 2: The most appealing route to highly symmetrical hexaoxy[6]pericyclynes would be a cyclizing sequential metathesis of six C_3 1,3-dicarbyne units. The 2,5-heptadiyne **7b** can be prepared either directly from methyl benzoate or from the known 1,4-diynes **8** and **7a** (Scheme 3).[10,11] However, attempts at metathesis of **7b** using the Mortreux instant catalyst under the original (135 °C) or modified (50/80 °C) conditions did not afford the yet unknown pericyclyne **2a′**.[12]

Alternatively, hexaoxy[6]pericyclynes could result from cyclizing sequential alkynyl-propargyl coupling of three C_6 heterodifunctional 1,4-diyne units. The 1,4-diynal brick **9** was thus generated by formylation of the 1,4-diyne **8**, but an attempt at in situ desilylation of **9** with KF in the presence of [18]crown-6[13] failed to produce the known pericyclyne **2a** by sequential condensation.[8]

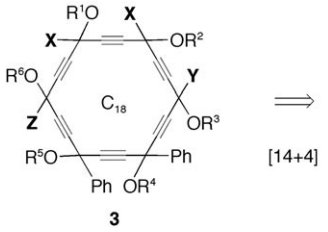
These disappointing results prompted us to resort to a step-by-step construction of the C_{18} [6]pericyclyne ring.

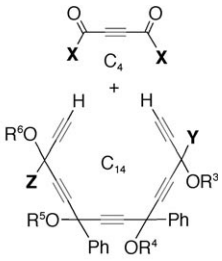


Scheme 3. Attempted sequential processes [6×3] metathesis or [3×6] alkynyl-oxopropargyl coupling) for the direct formation of symmetrical hexaoxy[6]pericyclynes.

[14+4] Cyclization strategy to hexaoxy[6]pericyclynes of type 3: The [14+4] strategy is envisaged for various C_4 dielectrophiles and C_{14} dinucleophiles (Scheme 4).

Hexaphenylhexaoxy[6]pericyclynes 3a and 3a′: Owing to a trade off between structural and synthetic simplicity, hexaphenyl-*carbo*-benzene **1a** acts as a reference molecule. Its hexaphenyl[6]pericyclyne precursor **2a** was first prepared in 15 steps via **2e** through an [11+7] strategy.[5,8] The alternative precursors **3a**,**a′** were targeted through a [14+4] strategy using dibenzoylacetylene (**10**) as the C_4 unit.[14] An obvious advantage of this route is its doubly convergent character, as **10** can also serve as a precursor to the C_{14} unit.

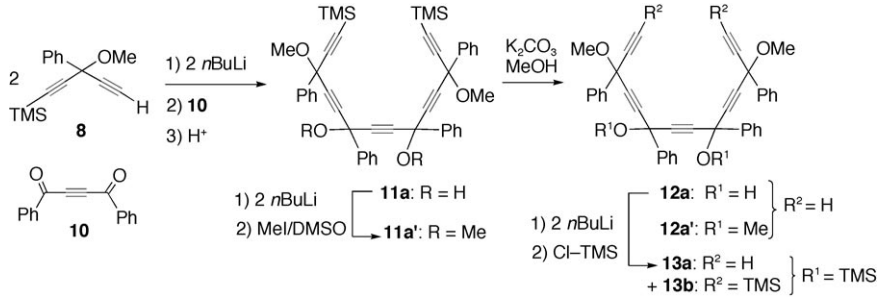




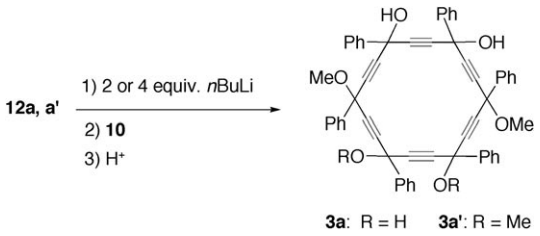
Scheme 4. General [14+4] strategy for the generation of hexaoxy[6]pericyclynes of type **3**.

The symmetric pentaynediol **11a** was obtained by double addition of 2 equiv of racemic monosilylated β-diyne **8** to dibenzoylacetylene (**10**), which were prepared as previously described in three[11] and two steps,[14] respectively. The hydroxy groups were methylated by treatment of the lithium dialkoxides with an excess of MeI/DMSO to give **11a′**. Desilylation of **11a** and **11a′** by treatment with K_2CO_3/MeOH afforded the symmetrical C_{14} bis-terminal pentaynes **12a** and **12a′**, respectively (Scheme 5). The pentaynes **12a,a′** were obtained as oily mixtures of diastereomers (six in theory) with almost superimposable TLC spots and NMR spectra. Their resolution was not attempted.

Formation of the hexaoxy[6]-pericyclynes **3a** and **3a′** resulted from the double 1,4-attack of dibenzoylacetylene (**10**) by the tetra- and dilithium salts of pentaynes **12a** and **12a′**, respectively (Scheme 6). Although



Scheme 5. Preparation of C_{14} tetraphenyltetraoxypentaynes.



Scheme 6. Formation of [6]pericyclynetetrol **3a** and [6]pericyclynediol **3a′** through a [14+4] strategy.

transient protection of the two hydroxy groups of **12a** was first envisioned through the bis(silyl ether) **13a** (which will be used for another purpose, see below), the poor solubility of the tetralithium salt of **12a** in THF was finally overcome by simple dilution, giving the [6]pericyclynetetrol **3a** in 39% yield after chromatography. The dilithium salt of the bis-(methyl ether) **12a′** was more soluble, but the [6]pericyclynediol **3a′** was isolated in a similar yield (40%).

The hexaoxy[6]pericyclyne **3a** was obtained as an oily mixture of at most 20 stereoisomers, corresponding to six chiral and eight achiral diastereomers. Likewise, the hexaoxy[6]pericyclyne **3a′** was obtained as an oily mixture of at most 36 stereoisomers, corresponding to 16 chiral and 4 achiral diastereomers. While the diastereomeric mixtures of the acyclic pentayne precursors **12a**,**a′** give almost degenerate ^{1}H NMR signals for topographically equivalent protons, the mixtures of the pericyclynes **3a** and **3a′** give much more complex NMR spectra. This is illustrated (Figure 1) for the

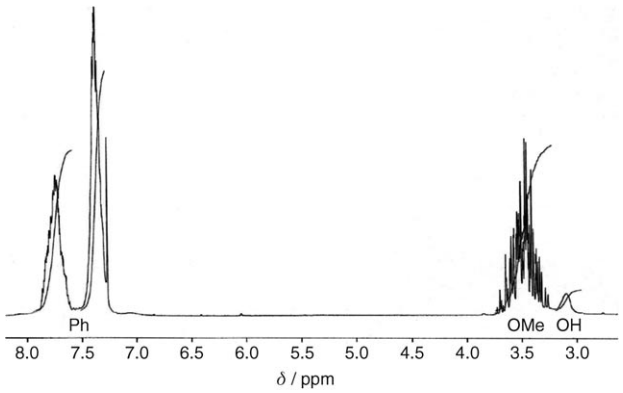


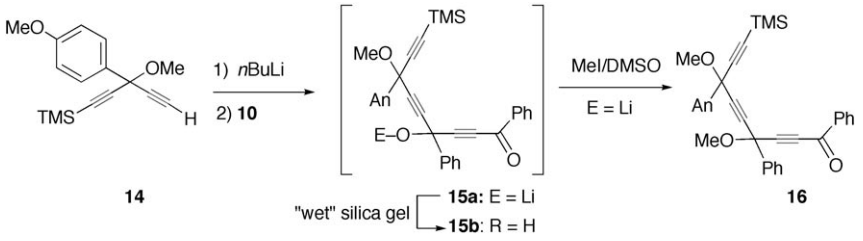
Figure 1. ^{1}H NMR spectrum of the stereoisomeric mixture of the pericyclynediol **3a′** ($CDCl_3$, 250 MHz, 293 K).

pericyclynediol **3a′**, which, in comparison with its precursor **12a′**, exhibits significant broadening of the characteristic ranges of the *o*-aromatic CH, *m*,*p*-aromatic CH, OCH_3, and OH NMR signals, integrating for 12, 18, 12, and 2 protons, respectively. As previously reported in the [5]pericyclyne series,[10] averaging of the magnetic environment over the NMR timescale is much less efficient in the locked cyclic series than in the free-rotating acyclic series.

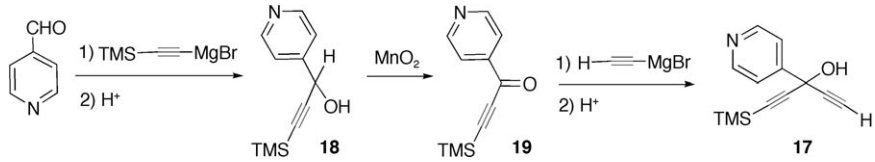
The [14+4] strategy thus afforded the novel hexaphenylhexaoxy[6]pericyclynes **3a** and **3a′** in eight and nine steps, and 12 and 11% overall yields, respectively. By comparison, the [11+7] strategy devised by Kuwatani, Ueda, and co-workers afforded the hexaphenylhexaoxy[6]pericyclyne **2a** in 14 steps and 2.5% overall yield from commercially available compounds.[8]

p-*Anisyl-4-pyridyl-tetraphenyl*-carbo-*benzene* ***3b*** *through a [14+4] cyclization strategy*: The success of the [14+4] strategy for the synthesis of the hexaphenyl representatives **3a,a′** prompted us to investigate the generalization of this approach to another hexaaryl derivative, the dissymmetric heteroaryl[6]pericyclyne **3b**. This target was indeed identified as a potential precursor of the donor–acceptor *carbo*-benzenic chromophore **4b**,[15] studied at the theoretical level for its nonlinear optical properties.[16] The first challenge was to obtain a totally dissymmetric tetraaryl C_{14} pentayne bearing both *p*-anisyl and 4-pyridyl substituents. The anisyl analogue **14** of the β-diyne **8** was prepared as previously described.[11] Reaction of dibenzoylacetylene (**10**) with 1 equiv of the lithium salt of **14** afforded the lithium triyne ketolate intermediate **15a**, which was converted in situ to the diether **16** in 46% yield (Scheme 7). The corresponding alcohol **15b** could also be isolated after treatment of the alkoxide **15a** with silica gel (simple hydrolysis resulted in decomposition).

Inspired by the sequence used for the synthesis of the phenyl and anisyl homologues **8** and **14**, the synthesis of pyridyl-β-diyne **17** was first envisaged from bis(trimethylsilyl)acetylene and isonicotinoyl chloride or its *N*-oxide in the presence of $AlCl_3$.[10] After several fruitless attempts, we finally resorted to an indirect route. Reaction of the Grignard salt of trimethylsilylacetylene with pyridine-4-carbaldehyde afforded the 4-pyridylcarbinol **18** in 95% yield. By using either the Dess–Martin periodinane reagent or activated MnO_2, the alcohol was oxidized to the 4-pyridyl alknyl ketone **19** in 85% yield.[17] Reaction of **19** with acetylenemagnesium bromide afforded racemic (pyridyl)dialkynylcarbinol **17** in 91% yield (Scheme 8). Monocrystals deposited from a chloroform solution were suitable for X-ray diffrac-



Scheme 7. Preparation of the anisyltriynone **16** via desymmetrization of the C_4 diketone **10**.



Scheme 8. Synthesis of (4-pyridyl)diethynylcarbinol **17**.

tion analysis. The crystal structure of **17** (Figure 2, Tables 1 and 2), which is locally similar to that of the previously reported anisyl homologue **14**,[10] reveals a network of O–H···N hydrogen bonds (H···*N* = 1.82 Å). This feature is consistent with the poor yields obtained in the attempted methylation of the hydroxy group of **17**, which competes with the methylation of the pyridyl nitrogen atom.

Nevertheless, double deprotonation of unprotected **17** and subsequent addition of triynone **16** directly afforded crude pentaynediol, which underwent desilylation to give pentaynediol **20a** as a brown powder in 77% yield over two steps (Scheme 9).

The spectroscopic simplicity of diastereomeric mixtures of open-chain carbinol-skipped pentaynes, already noticed for **12a,a′** (six diastereomers), is dramatically illustrated with the totally dissymmetric pentaynediol **20a** (eight diastereo-

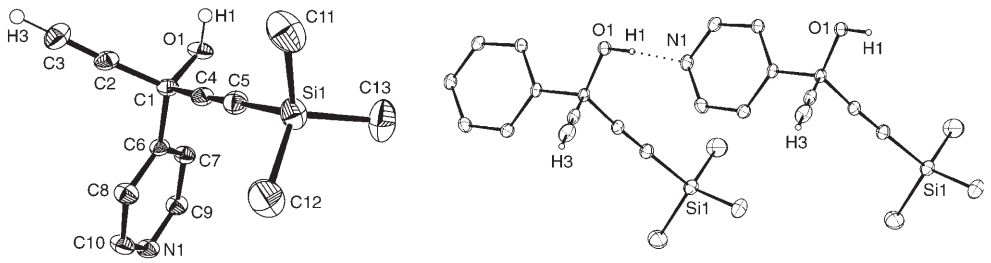


Figure 2. ORTEP view (left) and hydrogen-bond packing (right) of the X-ray crystal structure of (4-pyridyl)diethynylcarbinol (**17**). Bond lengths and angles are listed in Table 2.

Table 1. Crystallographic data for **17** (see Figure 2), **32** (see Figure 4, left), and **38** (see Figure 4, right).

	17	**32**	**38**
formula	$C_{13}H_{15}NOSi$	$C_{14}H_{17}OSi$	$C_{14}H_{22}O_2Si_2$
T [K]	160(2)	180	293(2)
crystal system	monoclinic	triclinic	monoclinic
space group	$P21/n$	$P\bar{1}$	$P21/n$
unit cell dimensions			
a [Å]	7.581(5)	5.8139(10)	9.649(2)
b [Å]	18.956(5)	10.1083(15)	7.9253(16)
c [Å]	9.237(5)	11.4864(17)	24.007(6)
α [°]	90	93.591(12)	89.82(3)
β [°]	97.927(5)	95.348(13)	92.81(3)
γ [°]	90	104.060(14)	89.85(3)
V [Å^3]	1314.7(12)	649.42(18)	1833.7(7)
Z	4	2	4
ρ_{calcd} [mg m^{-3}]	1.159	1.173	1.009
μ [mm^{-1}]	0.159	0.158	0.188
$F(000)$	488	246	600
crystal size [mm]	0.30×0.25×0.12	0.375×0.125×0.075	
θ range [°]	2.47–26.23	3.57–32.06	–
ω range	–	–	2.24–23.25°
index ranges	$-9\le h\ge 9$	$-8\le h\le 8$	$-10\le h\le 0$
	$-23\le k\ge 22$	$-11\le k\le 14$	$-8\le k\le 8$
	$-11\le l\ge 11$	$-17\le l\le 16$	$-26\le l\le 26$
reflections collected/unique	9029/2583	7051/4129	10364/2644
	[R(int) = 0.0436]	[R(int) = 0.0338]	[R(int) = 0.1101]
completeness [%]	97.3 (2θ = 26.23°)	90.3 (θ = 32.06°)	99.9 (θ = 23.25°)
absorption correction	empirical (DIFABS)	semi-empirical from equivalents	none
max/min transmission	0.979/0.953	0.995/0.9598	–
data/restraints/params	2583/0/156	4129/0/149	2644/25/174
GOF on F^2	1.047	0.785	1.017
final R indices [$I>2\sigma(I)$]	R_1 = 0.0356	R_1 = 0.0421	R_1 = 0.1189
	wR_2 = 0.0869	wR_2 = 0.0686	wR_2 = 0.3108
R indices (all data)	R_1 = 0.0461	R_1 = 0.1010	R_1 = 0.2525
	wR_2 = 0.0914	wR_2 = 0.0787	wR_2 = 0.3946
largest diff. peak/hole [e Å^{-3}]	0.221/−0.264	0.266/−0.225	0.410/−0.429

mers). Indeed, the Lewis structure of **20a** counts 34 topographically distinct carbons all chemically nonequivalent in the eight diastereomers. Therefore, 34×8 = 272 signals could be a priori expected in the ^{13}C NMR spectrum of **20a**. Instead, exactly 34 sharp signals are found just as if the sample contained a single diastereomer (Figure 3a).

An attempt at cyclization of the tetralithium salt of **20a** with dibenzoylacetylene (**10**) failed. The *O*-silylated substrate **20b** was thus prepared and isolated in 53% yield. However, double deprotonation of the pentayne **20b** with *n*BuLi and subsequent addition of dibenzoylacetylene (**10**) did not afford the targeted [6]pericyclyne. All attempts at tuning the conditions (concentration, temperature, and time) resulted in partial desilylation with retention of the terminal alkynyl units (^{1}H NMR signals at δ = 2.7–2.8 ppm). The use of a bulkier base, lithium diisopropylamide (LDA), afforded a lower ≡CH/OSi(CH$_3$)$_3$ ratio. Finally, deprotonation with 4 equiv LiHMDS at −78/−20 °C followed by addition of **10** led to the total disappearance of the ≡CH signals. Owing to the excess base, partial desilylation was, however, still observed. Total desilylation of the crude pericyclynediol was thus completed by treatment with tetrabutyl ammonium fluoride (TBAF) (Scheme 10). After chromatography, the [6]pericyclynetetrol **3b** was finally isolated as a brown powder in 14% yield over two steps.

As previously noticed for **3a,a′**, the diastereomeric mixture of the totally dissymmetric [6]pericyclynetetrol **3b** exhibits more complex or broader ^{13}C NMR signals than does the mixture of the open-chain precursors. Despite the existence of 32 diastereomers and 46 different topographical environments for the carbon atoms of each diastereomer (corresponding to 1472 ^{13}C NMR signals at infinite resolution), full functional assignment of the ^{13}C NMR spectrum was possible (Figure 3b).

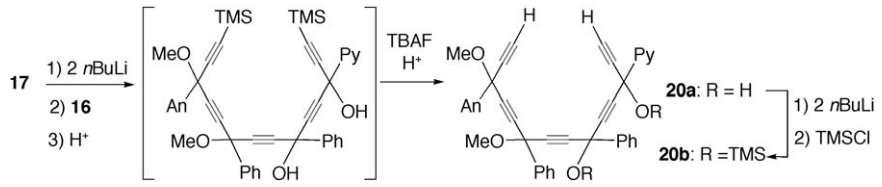
*Dialkynyltetraphenylhexaoxy[6]pericyclyne **3c** through a [14+4] cyclization strategy*: The dialknyl[6]pericyclyne **3c** was also synthesized through a [14+4] strategy. Whereas the tetraaryl C$_{14}$ synthons **12a, 12a′**, and **20b**, were prepared

Table 2. Bond lengths [Å], angles [°], and hydrogen bonds for **17** (see Figure 2).

C1−O1	1.4143(17)	C7−C9	1.387(2)	C11−H11B	0.9800
C1−C2	1.484(2)	C7−H7	0.9500	C11−H11C	0.9800
C1−C4	1.4855(19)	C8−C10	1.383(2)	C12−Si1	1.8543(19)
C1−C6	1.5353(19)	C8−H8	0.9500	C12−H12A	0.9800
C2−C3	1.186(2)	C9−N1	1.3311(19)	C12−H12B	0.9800
C3−H3	0.97(3)	C9−H9	0.9500	C12−H12C	0.9800
C4−C5	1.204(2)	C10−N1	1.3412(19)	C13−Si1	1.853(2)
C5−Si1	1.8463(16)	C10−H10	0.9500	C13−H13A	0.9800
C6−C7	1.3796(19)	C11−Si1	1.857(2)	C13−H13B	0.9800
C6−C8	1.385(2)	C11−H11A	0.9800	C13−H13C	0.9800
O1−H1	0.91(2)				
O1-C1-C2	110.49(11)	C6-C7-H7	120.9	Si1-C12-H12A	109.5
O1-C1-C4	110.03(11)	C9-C7-H7	120.9	Si1-C12-H12B	109.5
C2-C1-C4	109.42(11)	C10-C8-C6	118.97(13)	H12A-C12-H12B	109.5
O1-C1-C6	108.28(11)	C10-C8-H8	120.5	Si1-C12-H12C	109.5
C2-C1-C6	109.06(11)	C6-C8-H8	120.5	H12A-C12-H12C	109.5
C4-C1-C6	109.53(10)	N1-C9-C7	123.83(13)	H12B-C12-H12C	109.5
C3-C2-C1	177.44(16)	N1-C9-H9	118.1	Si1-C13-H13A	109.5
C2-C3-H3	179.2(16)	C7-C9-H9	118.1	Si1-C13-H13B	109.5
C5-C4-C1	176.54(15)	N1-C10-C8	122.81(14)	H13A-C13-H13B	109.5
C4-C5-Si1	178.86(13)	N1-C10-H10	118.6	Si1-C13-H13C	109.5
C7-C6-C8	118.82(12)	C8-C10-H10	118.6	H13A-C13-H13C	109.5
C7-C6-C1	120.61(12)	Si1-C11-H11A	109.5	H13B-C13-H13C	109.5
C8-C6-C1	120.56(12)	Si1-C11-H11B	109.5	C9-N1-C10	117.36(12)
C6-C7-C9	118.21(13)	H11A-C11-H11B	109.5	C1-O1-H1	106.5(13)
C6-C7-H7	120.9	Si1-C11-H11C	109.5	C5-Si1-C13	108.19(8)
C9-C7-H7	120.9	H11A-C11-H11C	109.5	C5-Si1-C12	107.38(8)
C10-C8-C6	118.97(13)	H11B-C11-H11C	109.5	C13-Si1-C12	111.20(10)
C5-Si1-C11	108.18(8)	C13-Si1-C11	110.58(10)	C12-Si1-C11	111.17(10)

hydrogen bonds (with H···A $< r$(A) + 2.000 Å and $\sphericalangle$D−H···A > 110°)

D−H	d(D−H)	d(H···A)	$\sphericalangle$DHA	d(D···A)	A
O1−H1	0.913	1.821	178.64	2.733	N1 [$x-1,y,z$]



Scheme 9. Preparation of totally dissymmetric C_{14} tetraarylpentaynes **20a**,**b**.

through a C_4+2C_5 process (see above), the dialkynyl C_{14} synthon **21** was synthesized through a stepwise $[C_4+2C_3]+2C_2$ process. The triynedicarbaldehyde **22** was first prepared according to a previously described method in five steps from commercial compounds.[10] In order to improve the yield of the production of the carbaldehyde functions (acetal hydrolysis, 32%), alternative synthetic routes were investigated (direct formylation and hydroxymethylation/oxidation). Rather disappointingly, all the methods gave similar yields (30–40%).[18]

Reaction of the C_{10} fragment **22** with 2 equiv of the Grignard reagent of either trimethylsilylacetylene or acetylene gave the pentaynediol **23a** or **23b**, respectively (**23a** could also be generated from the lithium salt of trimethylsilylacetylene). These unsubstituted diols were also characterized as their dimethyl and bis(tetrahydropyranyl) derivatives **23b′** and **23b″**, respectively (Scheme 11). Alternatively, oxidation with MnO_2 afforded the pentaynediones **24**. Addition of acetylenemagnesium bromide to dione **24a** (obtained in 68% yield from **22**) gave heptaynediol **25** in 71% yield. The latter was finally converted to tetraether **21** in 80% yield (Scheme 11).

Heptayne **21** was then deprotonated with 2 equiv of *n*BuLi and treated with dibenzoylacetylene (**10**) to give **3c** in a satisfactory yield for such a process (43%, Scheme 12). The hexaoxy[6]pericyclynediol **3c** is theoretically obtained as a mixture of 36 stereoisomers.

Indirect proof of the structure of **3c** will be illustrated by the X-ray crystal structure of its aromatization product (*carbo*-benzene **4c**).[6]

*Tetraphenylhexaoxy[6]pericyclyne **3d***: The unsubstituted analogue of dibenzoylacetylene (**10**) is acetylenedicarbaldehyde (butynedial). This unstable molecule has been extensively studied by Gorgues and coworkers, who showed that it can be stabilized by a hexacarbonyldicobalt moiety in complex **26** (Scheme 13).[19] Despite the introduction of six additional electrophilic carbonyl centers, it has been shown that the double-electrophilic reactivity of the carbaldehyde centers of **26** is preserved.[20] In particular, anionic carbon nucleophiles such as lithium trimethylsilylacetylide attack the CHO groups selectively over the carbonyl ligands.[21] In a cyclizing version, double attack of complex **26** by the dilithium salts of C_{11} triynes afforded pentaoxy[5]pericyclynes.[10] The analogous procedure was thus attempted with the dilithium salts of the C_{14} pentaynes. We found that after double deprotonation with *n*BuLi, the above-described pentayne **13a** (Scheme 5) reacts with **26** to give the hexaoxy[6]pericyclyne complex **27** in 18% yield (Scheme 13). Treatment of **27** with cerium ammonium nitrate (CAN) or TBAF resulted in simultaneous decomplexation and desilylation to give a stereoisomeric mixture of the free tetraphenylhexaoxy[6]pericyclynetetrol **3d** in 27 and 33% yields, respectively.[22] The presence of two adjacent secondary carbinol vertices does not induce marked instabil-

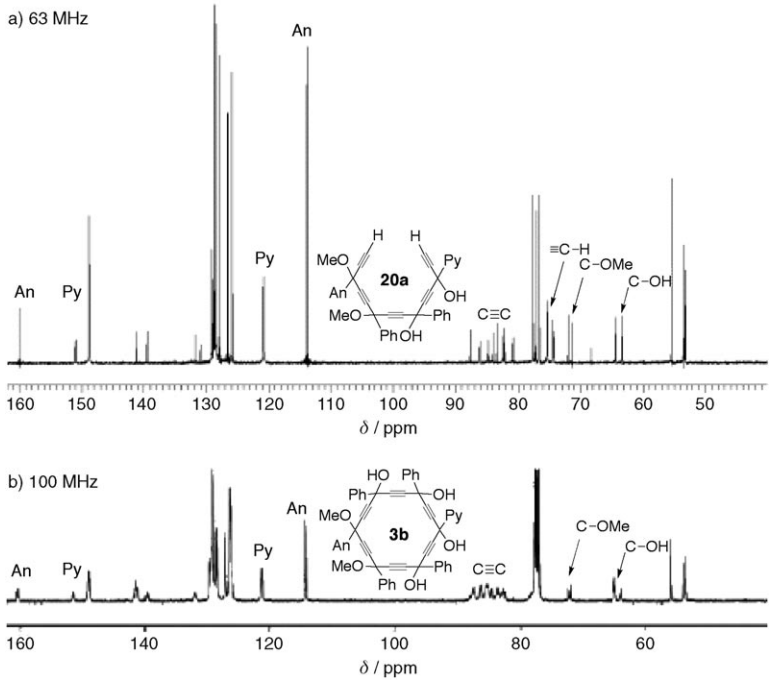
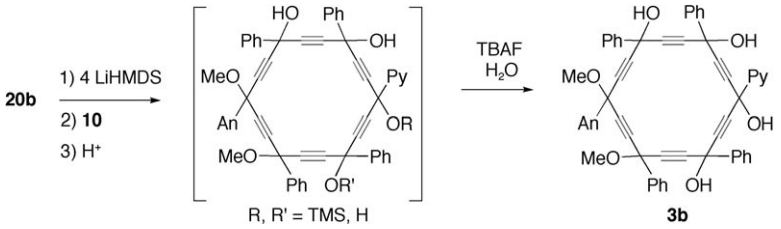


Figure 3. Topographical assignment and ring-closure broadening effect in the $^{13}C\{^1H\}$ NMR spectra of diastereomeric mixtures of acyclic pentayne **20a** and cyclic hexayne **3b** ($CDCl_3$, 293 K). a) Sharp low-frequency $^{13}C\{^1H\}$ NMR spectrum (63 MHz) of pentayne **20a**. Exactly 34 sharp signals (instead of 272) give the perception of a single diastereomer (instead of eight). b) Broadened high-frequency $^{13}C\{^1H\}$ NMR spectrum (100 MHz) of [6]pericyclyne **3b**. A functional assignment remains relevant.



Scheme 10. Formation of a totally dissymmetric heteroaryl-substituted hexaoxy[6]pericyclyne **3b**.

ity with respect to the hexaphenyl homologue **3a** containing tertiary carbinol vertices only. This feature was previously noticed in the pentaoxy[5]pericyclyne series.[10]

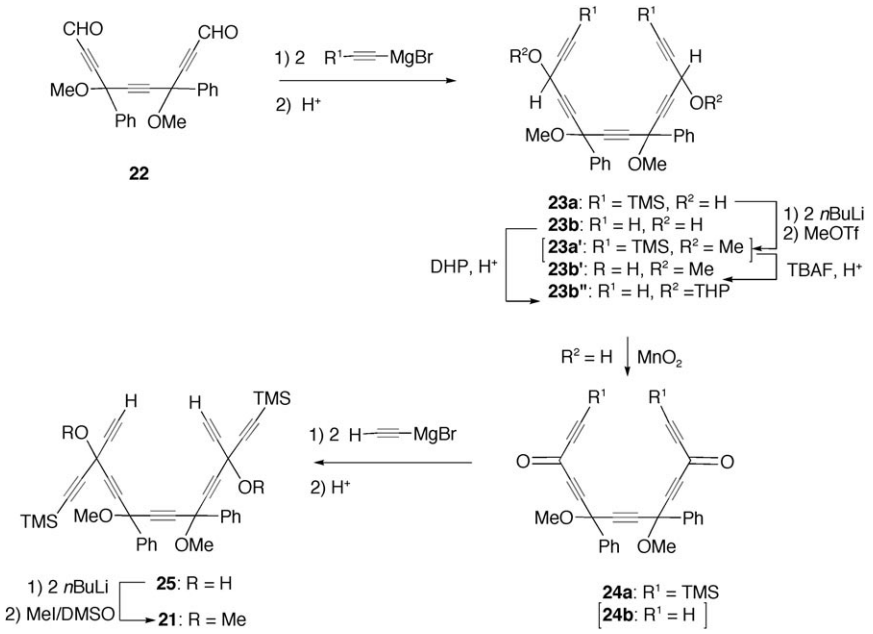
Similar to **3a′**, the hexaoxy[6]pericyclynetetrol **3d** is theoretically obtained as a mixture of 36 stereoisomers, 32 of them being chiral and thus partitioned into 16 pairs of enantiomers. In principle, 20 diastereomers could therefore be distinguished by classical spectroscopy. No attempt at resolving the diastereomeric mixture was undertaken. The chemical proof of the topographical structure of **3d** will be illustrated by the X-ray crystal structure of its aromatization product (**4d**).[6]

Diphenylhexaoxy[6]pericyclynes—Attempted [14+4] route: The challenge of the synthesis of a hexaoxy[6]pericyclyne with four secondary carbinol vertices was first tackled through a [14+4] cyclization strategy. Stimulated by the successful synthesis of **3d** (Scheme 13), the butynedial complex **26** was first envisioned as a possible C_4 synthon. The missing secondary carbinol vertices had then to be provided by a suitable C_{14} pentayne. The known pentayne cobalt complex **28a** was thus generated from **26** and 2 equiv of the lithium salt of **8**[21] and treated (without previous purification) with CAN to give pentayne **29a** (Scheme 14). An attempt at the *C*-desilylation of **29a** with TBAF failed, but protection of the hydroxy groups with two equivalents of 3,4-dihydro-2*H*-pyran (DHP) in the presence of *p*-toluenesulfonic acid (PTSA) afforded **30a** in 94% crude yield and with acceptable purity. As **30a** decomposes on silica gel, it was directly treated with TBAF to afford bis-terminal pentayne **30b** in 34% yield after chromatography. Nevertheless, reaction of the dilithium salt of **30b** with complex **26** did not afford any disubstituted hexaoxy[6]pericyclyne.

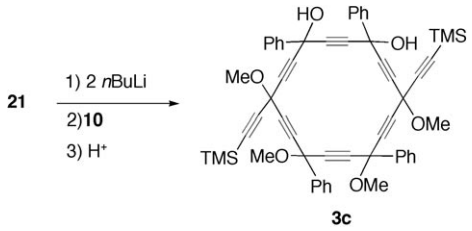
These results seem to indicate that the presence of at least two adjacent propargylic CH–O vertices in the nucleophilic pentayne precursor is precluded. Exploratory investigations into the nucleophilic reactivity of pentaynes **23b′** and **23b″** (Scheme 11) showed that nonadjacent propargylic CH–O vertices are problematic as well. The [14+4] strategy was thus given up, but the challenge will be resumed through the alternative [8+10] cyclization strategy (see below).

Hexaoxy[6]pericyclynes through a [8+10] cyclization strategy: Pursuing our efforts to synthesize hexaoxy[6]pericyclynes with secondary carbinol vertices (see above), the [8+10] strategy was envisaged (Scheme 15).

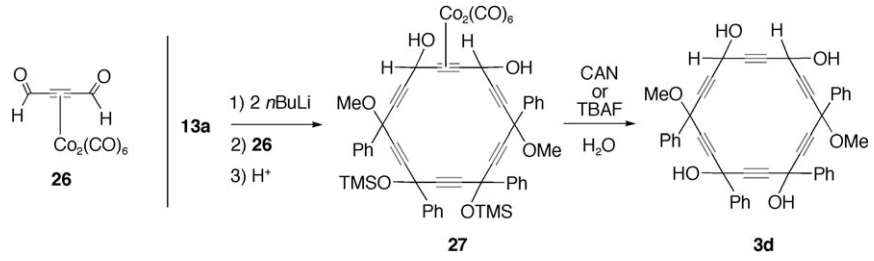
*Tetraphenylhexaoxy[6]pericyclyne **3e** through a [10+8] cyclization strategy*: The C_8 triynes **32** and **33** have previously been prepared from **8**[11] in two and three steps, respectively.[10] Triyne **32** can also be prepared more directly from trimethylsilylacetylene and dibenzoylacetylene (**10**) in 65% yield over two steps via the diol intermediate **31** (its isolation was however not required: Scheme 16). Single crystals



Scheme 11. Synthesis of bis-terminal carbinol-skipped heptaynes **25** and **21**.



Scheme 12. Cyclization of a stereoisomeric mixture of the bis-terminal heptayne tetraether **21** with dibenzoylacetylene (**10**) to the diethynyl[6]-pericyclynediol **3c**.

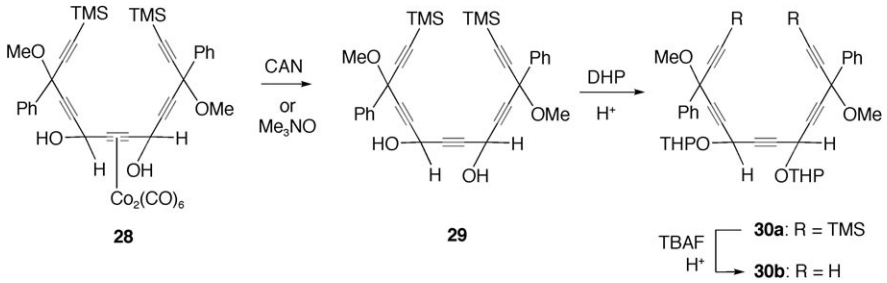


Scheme 13. Synthesis of a stable hexaoxy[6]pericyclyne **3d** with adjacent secondary carbinol vertices using Gorgues' acetylenedicarbaldehyde cobalt complex **26**.

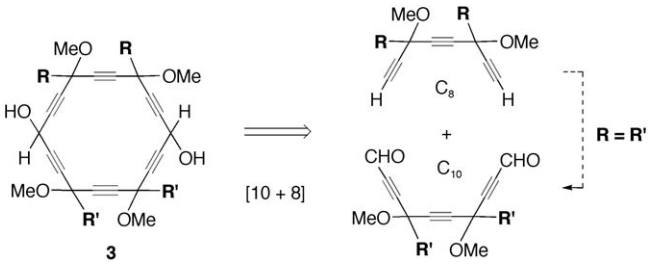
of **32** (prepared by the original method)[10] were obtained and submitted for X-ray diffraction analysis. It revealed a *meso* configuration (Figure 4 (left), Tables 1 and 3), as previously observed for the dianisyl derivative of **3**[10] and hereafter reported for the unsubstituted derivative **38** (Figure 4 (right), Tables 1 and 4). In this series, the *meso* isomers were thus selectively crystallized with respect to the corresponding (±) isomers. Both the *meso* and (±) isomers were, however, formed (see below) and the mixture was used in subsequent steps.

The C_{10} dialdehyde **22** was prepared as previously reported.[10] Alternatively, it could also be obtained from the C_8 synthon through double formylation or through hydroxymethylation with formaldehyde followed by MnO_2 oxidation.[18] The dilithium salt of the C_8 triyne **33** was treated with **22** (Scheme 17). After protonation, the integrated ^{1}H NMR spectrum of the crude material (*o*-CH/*m*,*p*-CH/OCH_3/C≡CH ≈2:3:3:0.13) revealed that the carbaldehyde functions had disappeared and that 87% of the terminal alkynes had been consumed. Three chromatographic runs were required to purify the hexaoxy[6]pericyclyne **3e** in 12% yield. A slightly more polar product was also isolated and assigned to the open nonaynediol structure **34a** on the basis of its ^{1}H NMR spectrum. The pericyclyne **3e** possesses two nonadjacent secondary carbinol vertices and is therefore compared with the less symmetrical pericyclyne **3d** in which the carbinol vertices are adjacent (see above). The ^{1}H NMR spectrum of **3e** exhibits at least 23 different OCH_3 signals showing that the compound is obtained as a mixture of stereoisomers. In theory, **3e**, just as **3a**, possesses 14 diastereomers (six of them being chiral) corresponding to 32 chemically distinguishable OCH_3 groups. Invoking possible overlaps in the ^{1}H NMR spectrum, the sample of **3e** was likely close to a statistical mixture of stereoisomers. This conclusion was confirmed after oxidation of the carbinol vertices.

Indeed, treatment of a mixture of **3e** and **34a** with MnO_2 led to [6]pericyclynedione **3f** (a "closed" version of the pentaynedione **24a**; Scheme 11) and nonaynedione **34b**. Oxidation of the carbonyl groups masks two potentially stereogenic centers, thus reducing both the number of stereoisomers from 14 in **3e** to five in **3f**, and the corresponding number of chemically nonequivalent OCH_3 groups decreases from 32 in **3e** to eight in **3f**. The number of OCH_3 signals distinguished in the ^{1}H NMR spectrum of **3f** is exactly eight (Figure 5, left). This shows that all the stereoisomers were present in the mixture and confirms a posteriori that indeed the (±) isomer was present in the starting material **32** along



Scheme 14. Preparation of skipped C_{14} pentaynes containing two adjacent secondary carbinoxy vertices, with a view to a putative [14+4] cyclization with the C_4 dicarbonylacetylenes **10** or **26**.



Scheme 15. General [8+10] cyclization strategy for the synthesis of targeted hexaoxy[6]pericyclynes of type **3** with secondary carbinol vertices. The total retrosynthetic scheme may become doubly convergent for symmetrical targets (R = R′).

with the crystallizable *meso* isomer (Figure 4, right, Tables 1 and 3).

Permethyl[4]- and -[5]pericyclynones and a [10]pericyclynedione have been reported by Scott and Cooney,[23] and the alternating [6]pericyclynetrione **2f** described by Kuwatani, Ueda, and co-workers.[8] The series is completed here with the [6]pericyclynedione **3f**, a ring *carbo*-mer of a 1,4-cyclohexanedione. This molecule might serve as a pivotal electrophile in the synthesis of other pericyclynes of type **3**, just as does the trione **2f** in the synthesis of pericyclynes of type **2** (Scheme 1).[8]

*En route to diphenylhexaoxy[6]pericyclyne **3g** through a [10+8] cyclization strategy*: The synthesis of a pericyclyne with four secondary carbinol vertices could not be achieved by the attempted [14+4] strategy (see above). Stimulated by the successful preparation of **3e**, the challenge was resumed through an [8+10] strategy in which two CHOH vertices are generated in the last cyclization step (Scheme 15). Using the C_{10} synthon **22**, the remaining CHOH vertices should be provided by the C_8 synthon **35** (Scheme 18). The parent octa-1,4,7-triyne-3,6-diol was indeed described in 1961 as a sublimable solid prepared from ethynylmagnesium bromide and propiolaldehyde[24a] and its ^{13}C NMR spectrum was later reported (without a reference to the preparative method used).[24b] The bis(methyl ether)

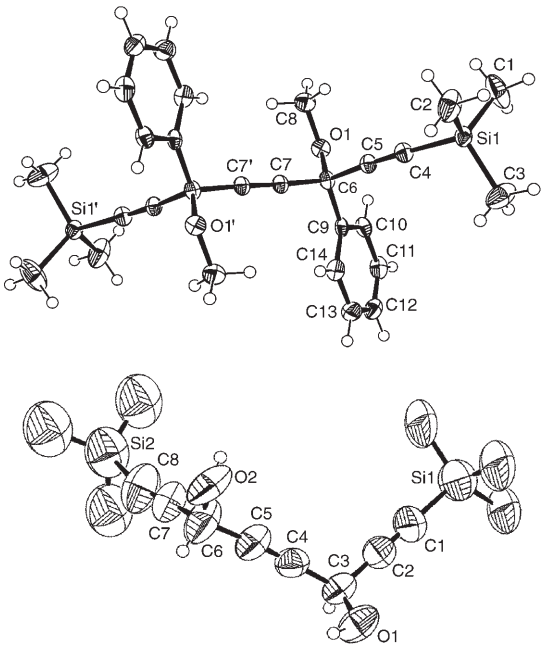
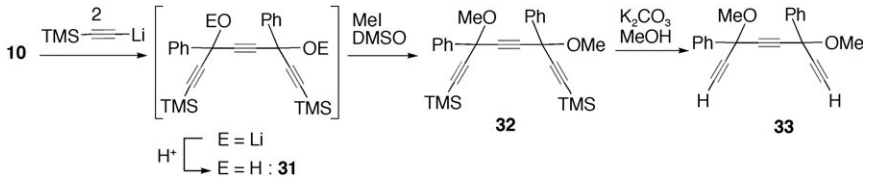


Figure 4. ORTEP views of the *meso* isomers of 1,8-bis(trimethylsilyl)octa-1,4,7-triyne-3,6-diol derivatives. Left: Diphenyltriyne diether **32** (Scheme 16; reliablity factor (R) = 0.042). Right: Unsubstituted triynediol **38** (Scheme 18; R = 0.119). Bond lengths and angles are listed in Tables 3 and 4.

35 was thus obtained from penta-1,4-diyn-3-ol **37**, itself prepared by the reaction of ethynylmagnesium bromide with trimethylsilylpropiolaldehyde **36**. Double deprotonation of **37** with EtMgBr and subsequent addition of **36** afforded triynediol **38** in 42% yield (Scheme 17; use of the dilithium salt of **37** was much less efficient).

X-ray diffraction analysis of the white crystals selectively deposited from a diastereomeric mixture of **38** indicated a *meso* configuration (Figure 4, right). This crystalline *meso* structure can be compared with those of diphenyl (**32**, Figure 4, left) and dianisyl derivatives.[10]



Scheme 16. Synthesis of C_8 triynes **32** and **33**.

Table 3. Bond lengths [Å] and angles [°] for **32** (see Figure 4, left).

C1−Si1	1.8454(18)	C6−O1	1.4253(16)	C10−C11	1.382(2)
C2−Si1	1.8489(16)	C6−C7	1.4885(19)	C11−C12	1.373(2)
C3−Si1	1.8418(16)	C6−C9	1.5294(19)	C12−C13	1.378(2)
C4−C5	1.1975(18)	C8−O1	1.4263(17)	C13−C14	1.384(2)
C4−Si1	1.8495(15)	C9−C14	1.3820(19)	C7−C7#1	1.185(3)
C5−C6	1.4977(18)	C9−C10	1.3906(19)		
C5-C4-Si1	176.44(13)	C14-C9-C10	119.00(14)	C6-O1-C8	115.02(10)
C4-C5-C6	176.46(16)	C14-C9-C6	120.67(13)	C3-Si1-C1	112.48(10)
O1-C6-C7	110.68(11)	C10-C9-C6	120.17(13)	C3-Si1-C2	109.29(9)
O1-C6-C5	110.84(11)	C11-C10-C9	119.89(14)	C1-Si1-C2	109.00(9)
C7-C6-C5	109.13(11)	C12-C11-C10	120.78(15)	C3-Si1-C4	107.86(7)
O1-C6-C9	106.44(10)	C11-C12-C13	119.62(15)	C1-Si1-C4	106.78(7)
C7-C6-C9	111.86(12)	C12-C13-C14	120.07(15)	C2-Si1-C4	111.44(7)
C5-C6-C9	107.84(11)	C9-C14-C13	120.64(14)	C7#1-C7-C6	177.5(2)

Table 4. Bond lengths [Å] and angles [°] for **38** (Figure 4, right).

Si1−C11B	1.71(3)	O2−C6	1.350(11)	Si2B−C8	1.855(15)
Si1−C1	1.827(10)	Si2A−C13A	1.763(18)	C5−C4	1.189(10)
Si1−C10A	1.846(16)	Si2A−C14A	1.762(18)	C5−C6	1.480(13)
Si1−C10B	1.853(18)	Si2A−C12A	1.782(19)	C4−C3	1.489(11)
Si1−C11A	1.862(18)	Si2A−C8	1.918(16)	C1−C2	1.180(11)
Si1−C9B	1.858(17)	Si2B−C12B	1.758(18)	C3−C2	1.488(12)
Si1−C9A	1.889(17)	Si2B−C13B	1.764(18)	C6−C7	1.481(14)
O1−C3	1.442(9)	Si2B−C14B	1.777(18)	C7−C8	1.174(12)
C11B-Si1-C1	120.0(9)	C1-Si1-C9A	102.4(8)	C14B-Si2B-C8	114.7(11)
C11B-Si1-C10A	119.5(15)	C10A-Si1-C9A	101.2(13)	C4-C5-C6	174.1(10)
C1-Si1-C10A	110.9(9)	C10B-Si1-C9A	137.2(12)	C5-C4-C3	179.0(9)
C11B-Si1-C10B	99(2)	C11A-Si1-C9A	102.2(17)	C2-C1-Si1	175.6(10)
C1-Si1-C10B	102.3(9)	C9B-Si1-C9A	20.3(11)	O1-C3-C4	107.0(6)
C10A-Si1-C10B	36.9(11)	C13A-Si2A-C14A	103.5(17)	O1-C3-C2	111.8(7)
C11B-Si1-C11A	16.9(10)	C13A-Si2A-C12A	119.4(18)	C4-C3-C2	112.2(6)
C1-Si1-C11A	103.1(7)	C14A-Si2A-C12A	127.7(18)	C1-C2-C3	178.5(10)
C10A-Si1-C11A	132.9(14)	C13A-Si2A-C8	110.9(12)	O2-C6-C5	113.3(9)
C10B-Si1-C11A	105.5(17)	C14A-Si2A-C8	113.3(11)	O2-C6-C7	112.9(8)
C11B-Si1-C9B	103(2)	C12A-Si2A-C8	79.2(12)	C5-C6-C7	111.9(9)
C1-Si1-C9B	114.7(11)	C12B-Si2B-C13B	125.2(17)	C8-C7-C6	174.9(11)
C10A-Si1-C9B	81.7(14)	C12B-Si2B-C14B	99.2(16)	C7-C8-Si2B	159.6(12)
C10B-Si1-C9B	117.0(13)	C13B-Si2B-C14B	90.0(17)	C7-C8-Si2A	164.7(12)
C11A-Si1-C9B	112.6(17)	C12B-Si2B-C8	114.0(13)	Si2B-C8-Si2A	35.3(4)
C11B-Si1-C9A	97.8(19)	C13B-Si2B-C8	110.2(13)		

Methylation of the secondary dialkynyl carbinol vertices of **38** proved to be difficult. The classical procedure used to methylate the tertiary counterparts did not work, but treatment of the dilithium salt of **38** with methyl triflate in diethyl ether below 0 °C afforded diether **39** in 95 % crude yield. This compound is quite unstable, but desilylation with TBAF at −80 °C gave the bis(methyl ether) **35**, which is slightly more stable than **39**, but still less stable than diol **38** and its desilylated derivative.[24] The peculiar reactivity of triynediol **38** prompted us to attempt the oxidation of its secondary carbinol vertices. Thus treatment of **38** with MnO_2 afforded the triynedione **40**. Owing to poor separation by column chromatography, this fragile compound was isolated in a very low yield (3 %), but it was still unknown despite its simplicity.

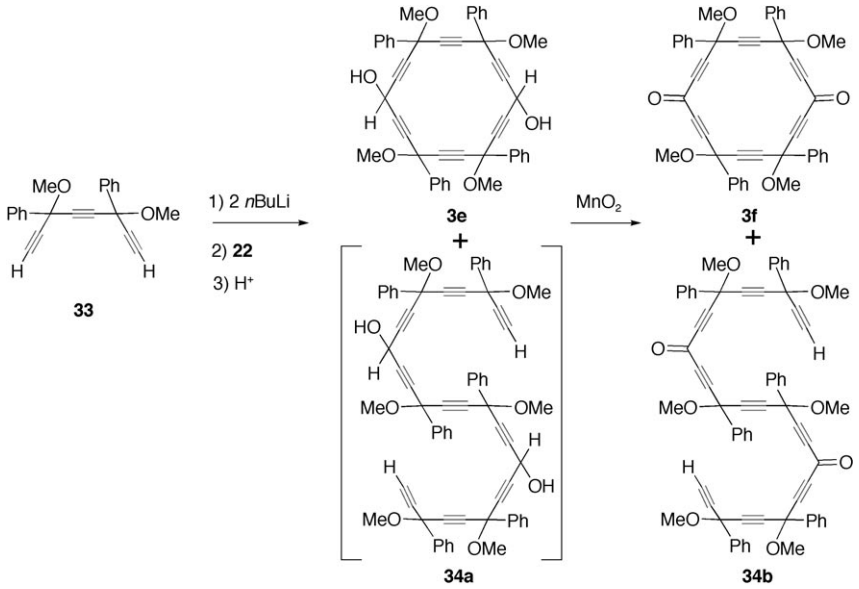
An attempt at [8+10] cyclization of **22** with doubly deprotonated triyne **35** (*n*BuLi) gave erratic results. Nonetheless, two successive chromatographic runs allowed the pericyclyne **3g** to be partly characterized (Scheme 19). As evidenced by ^{1}H NMR spectroscopy, the final samples contained a residual terminal alkyne, but the DCI/NH_3 mass spectrum (DCI: desorption chemical ionization) exhibits the $[M+NH_4]^+$ signal at *m*/*z* 550 as the main peak. Both the ^{1}H and ^{13}C NMR spectra indicate that the compound was obtained as a mixture of diastereomers (in theory 20, just as for **3a′**, **3c**, and **3d**).

Despite the limited number of steps (12) involved in the [8+10] strategy, the above synthesis is quite tedious, especially the preparation of the dialdehyde **22**. It did however provide evidence for the stability of a hexaoxy[6]pericyclyne with four adjacent secondary carbinol vertices. All-secondary hexaoxy[6]pericyclynes are the next natural targets, the ultimate goal being the nonethereal *carbo*[6]cyclitol, a symmetric isomer of the skeletal *carbo*mer of glucose $[C_3H_2O]_6$.

Conclusion

Regarding the synthetic methodology, the [14+4] and [8+10] cyclization strategies proved to compete with the [11+7] strategy of Kuwatani, Ueda, and co-workers.[5,8] Of course, the remaining [13+5], [16+2], and [17+1] strategies might be investigated as well. Nevertheless, the remarkably short synthesis of pericyclynedione **3f** (eight steps) and its potential pivotal role support the suitability of the [8+10] route for a scale-up study, which is in progress.[25]

Regarding chemical diversity, the eight hexaoxy[6]pericyclynes **3a, 3a′**, and **3b**–**3g** correspond to six different substitution patterns and enlarge the restricted family of known homoconjugated cyclic C_{18} molecules.[26] At the very outset, their intrinsic importance is limited by the fact that they were obtained as mixtures of stereoisomers. This limitation prompted us to tackle methodological studies for the stereo-



Scheme 17. Synthesis of the hexaoxy[6]pericyclyne **3e** with two "opposite" secondary carbinol vertices, nonaynediol **34a** (characterized by ^{1}H NMR spectroscopy only), pericyclynedione **3f**, and nonaynedione **34b**.

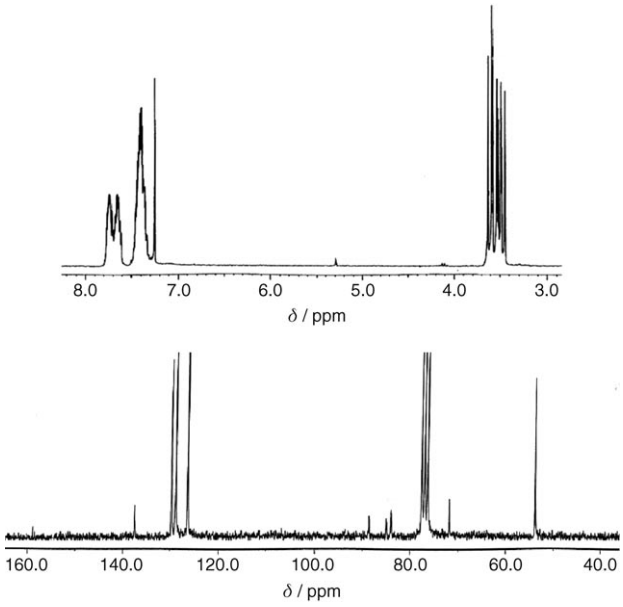
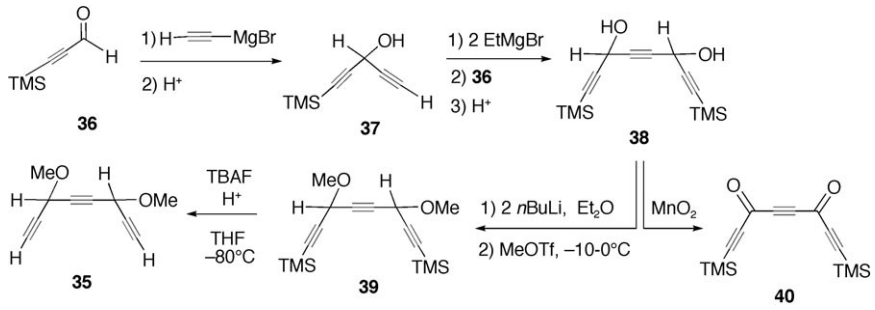


Figure 5. Resolved ^{1}H (left) and ^{13}C{^{1}H} (right) NMR spectra of the diastereomeric mixture of the tetramethoxypericyclynedione **3f**.



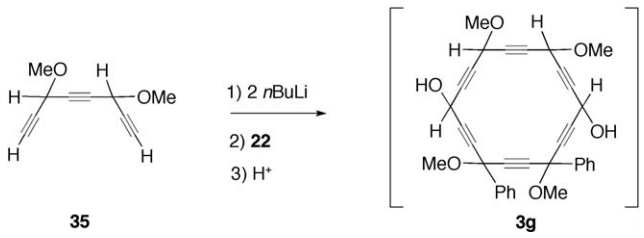
Scheme 18. Preparation of the unsubstituted skipped octatriynediol diether **35**.

selective addition of terminal alkynes to bis-oxopropargylic substrates such as the butynedial complex **26**.[27] As stated in the Introduction, however, the stereochemical disorder can be cancelled, either partly, through oxidation of secondary carbinol vertices (as in the pericyclynedione **3f**),[27] or completely, through reductive aromatization to *carbo*-benzene derivatives of type **4** (Scheme 1). This is the topic of the following paper.[6]

Experimental Section

General: THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane and dichloromethane over P_2O_5. Commercial solutions of EtMgBr were 3 M in diethyl ether, those of *n*BuLi were 1.6 or 2.5 M in hexane, and the effective concentrations of the latter were checked by titration with 2,2,2′-trimethylpropionanilide.[28] All other reagents were used as commercially available. In particular, activated MnO_2 was purchased from Fluka (no. 446286/1) and solutions of nBu$_4$NF (1 M in THF) were purchased from Aldrich. Previously described procedures were used for the preparation of **7a**,[10] **8**,[11] **10**,[15] **14**,[10] **22**,[10] **26**,[19,21] **28a**,**b**,[21] **32**,[10] **33**,[10] and **36**.[8] All reactions were carried out under nitrogen or argon using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, 70–200 μm). Silica gel thin-layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used. IR: Perkin-Elmer GX FT-IR spectrometer, 0.1 mm CaF_2 cell. ^{1}H and ^{13}C NMR: Bruker AC 200, WM 250, DPX 300, or AMX 400 spectrometer. X-ray diffraction: IPds STOE diffractometer. Mass spectrometry: Quadrupolar Nermag R10-10H spectrometer. Elemental analyses: Perkin-Elmer 2400 CHN (flash combustion and detection by catharometry). All IR and NMR spectra were recorded in $CDCl_3$ solutions. IR absorption frequencies $\tilde{\nu}$ are in cm^{-1}. NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants J are in Hz. As most compounds were isolated as oily mixtures of diastereomers, characteristic assignments are given to trace the analytical consistency within the homogeneous series of compounds studied.

X-ray crystallographic structure determinations (Table 1): Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems Cryostream Cooler Device using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The final unit cell parameters were obtained by means of a least-squares refinement of a set of well-measured reflections and crystal decay was monitored during data collection; no significant fluctuations in intensity were observed. Structures were solved by direct methods using the SIR92 program[29] and refined by least-squares procedures on F^2 with SHELXL-97.[30] All hydrogen atoms



Scheme 19. Formation of hexaoxy[6]pericyclyne **3g** with four adjacent secondary carbinol vertices by [8+10] cyclization.

were located on a difference Fourier map, but introduced and refined by using a riding model, except for OH hydrogen atoms, which were isotropically refined. All non-hydrogen atoms were anisotropically refined.

CCDC-638143 (**17**), CCDC-638145 (**32**), and CCDC-638144 (**38**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4-Methoxy-4-phenylhepta-2,5-diyne (7b): Compound **7a** (4.08 g, 24 mmol) was dissolved in THF (50 mL) at −80 °C and *n*BuLi (19.2 mL, 48 mmol) was added. After stirring for 1 h at −80 °C, iodomethane (23.9 mL, 384 mmol) and DMSO (6.8 mL) were added. The solution was allowed to warm up to RT, water was added, and the mixture extracted in diethyl ether. The organic layer was separated, dried with $MgSO_4$, and evaporated to dryness to give crude **7b** (3.62 g, 76 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95 (s, 3H; C-CH_3), 3.43 (s, 3H; OCH_3), 7.31–7.40 (m, 3H; *p*-, *m*-C*H*), 7.70–7.77 ppm (m, 2H; *o*-C*H*); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): δ = 3.61 (C-*C*H$_3$), 53.22 (O*C*H$_3$), 71.19 (*C*OMe), 77.35, 82.53 (*C*≡*C*), 126.31, 127.97, 128.18 (*o*-, *m*-, *p*-*C*H), 141.08 ppm (*ipso*-*C*); MS (EI): *m*/*z*: 198 $[M]^+$, 183 $[M-Me]^+$, 167 $[M-OMe]^+$.

6-Trimethylsilyl-4-phenyl-4-methoxyhexa-2,5-diynal (9): A solution of *n*-butyllithium (2.5 M in hexane, 8.26 mL, 20.6 mmol) was added through a syringe to a solution of 1-trimethylsilyl-3-phenyl-3-methoxypenta-1,4-diyne (**8**) (5 g, 20.6 mmol) in THF (50 mL) at −40 °C. After stirring for 10 min, DMF (3.19 mL, 41.20 mmol, 2 equiv) was added and stirring was continued at −40 °C for 15 min and then warmed to RT over 40 min. The reaction mixture was poured into a mixture of diethyl ether (89 mL) and aqueous 10 % NaH_2PO_4 and 20 % KCl (89 mL) at 0 °C. The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with water and brine, dried with $MgSO_4$, and concentrated under reduced pressure. The product was isolated as a brown oil and assigned to structure **9** on the basis of a NMR analysis (6.294 g, quantitative). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.24 (s, 9H; Si(CH_3)$_3$), 3.55 (s, 6H; OCH_3), 7.36–7.44 (m, 3H, *m*-, *p*-C*H*), 7.72–7.77 (m, 2H; *o*-C*H*), 9.28 ppm (s, 1H; C*H*(O)).

1,14-Bis(trimethylsilyl)-3,12-dimethoxy-3,6,9,12-tetraphenyltetradeca-1,4,7,10,13-pentayne-6,9-diol (11a): A solution of diyne **8** (8.82 g, 36 mmol) in THF (300 mL) was treated with *n*-butyllithium (16.60 mL, 36 mmol) for 15 min at −78 °C. A solution of dibenzoylacetylene (**10**) (4.26 g, 18 mmol) in THF (20 mL) was then added dropwise. After stirring for 30 min at −78 °C, the mixture was allowed to warm up to RT over 1.5 h and stirring was continued for another 30 min at this temperature. After treatment with saturated NH_4Cl and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and evaporated to dryness. The residue was then purified by chromatography through silica gel (heptane/acetone 8:2) to afford **11a** as a brown oil (10.60 g, 82 %). $R_f \approx 0.52$ (heptane/acetone 7.5:2.5); ^{1}H NMR ($CDCl_3$): δ = 0.25 (m, 18H; Si(CH_3)$_3$), 3.46–3.51 (m, 6H; OCH_3), 3.58 and 3.60 (2s, 2H; O*H*), 7.33–7.36 (m, 12H; *m*-, *p*-C*H*), 7.73–7.75 ppm (m, 8H; *o*-C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = −0.47 (Si(*C*H$_3$)$_3$), 52.4 (O*C*H$_3$), 63.4 (*C*(OH)Ph), 71.3 (*C*(OMe)Ph), 80.9 (HOC-*C*≡*C*-COH), 84.6 (HOC-*C*≡C-COMe), 87.7 (≡*C*-COMe), 91.8 (*C*≡C-Si), 101.6 (C≡*C*-Si), 125.4–128.9 (*o*-, *m*-, *p*-*C*H), 139.4 (*ipso*-*C*-C-OMe), 142.4 ppm (*ipso*-*C*-C-OH); IR ($CDCl_3$): $\tilde{\nu}$ = 3571 (O−H), 3065–2901 (C−H), 2825 (OC−H), 2069 (C≡C−Si), 1600, 1490, 1450 (aromatic), 1251 (C−Si), 1060 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 736 $[M+NH_4]^+$.

1,14-Bis(trimethylsilyl)-3,6,9,12-tetramethoxy-3,6,9,12-tetraphenyltetradeca-1,4,7,10,13-pentayne (11a′): A solution of pentayne **11a** (131 mg, 0.18 mmol) in THF (5 mL) was treated with *n*-butyllithium (160 μL, 0.36 mmol) for 10 min at −78 °C. Iodomethane (120 μL, 1.8 mmol) was added dropwise and the mixture was allowed to warm up to −25 °C. DMSO (50 μL, 0.36 mmol) was added and stirring was continued for 1 h at −25 °C, then for 3 h at RT. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give crude **11a′** as a brown oil displaying satisfactory analytical data for further use (127 mg, 95 %). $R_f \approx 0.54$ (heptane/acetone 7:3); ^{1}H NMR ($CDCl_3$): δ = 0.22 (m, 18H; Si(CH_3)$_3$), 3.47–3.58 (m, 12H; OCH_3), 7.28–7.35 (m, 12H; m-, *p*-C*H*), 7.73–7.76 ppm (m, 8H; *o*-C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = −0.44 (Si(*C*H$_3$)$_3$), 53.03 and 53.37 (O*C*H$_3$), 71.79 and 71.92 (*C*(OMe)Ph), 83.60–84.99 (≡C-*C*OMe), 92.33 (C≡*C*-Si), 101.15 (*C*≡C-Si), 126.24–128.83 (*o*-, *m*-, *p*-*C*H), 139.48 ppm (*ipso*-*C*-C-OMe); IR ($CDCl_3$): $\tilde{\nu}$ = 3571 (O−H), 3065–2900 (C−H), 2825 (OC−H), 2069 (C≡C−Si), 1601, 1490, 1450 (aromatic), 1251 (C−Si), 1058 cm^{-1} (C−O).

3,12-Dimethoxy-3,6,9,12-tetraphenyltetradeca-1,4,7,10,13-pentayne-6,9-diol (12a): A solution of pentayne **11a** (10.60 g, 15 mmol) in methanol (210 mL) was treated with potassium carbonate (1.02 g, 74 mmol) for 3 h at RT. The solution was then filtered, concentrated under reduced pressure, and diluted with Et_2O. After extraction with water, the organic layer was separated, dried with $MgSO_4$, and evaporated to dryness. Purification by column chromatography on silica gel (hexane/EtOAc 6:4) gave **12a** as a brown oil (5.60 g, 66 %). $R_f \approx 0.39$ (heptane/EtOAc 6:4); ^{1}H NMR ($CDCl_3$): δ = 2.74 (m, 2H; ≡C-*H*), 3.48 (m, 6H; OCH_3), 3.64 (m, 2H; O*H*), 7.34–7.37 (m, 12H; *m*-, *p*-C*H*), 7.71–7.80 ppm (m, 8H; *o*-C*H*); MS (DCI/NH_3): *m*/*z*: 592 $[M+NH_4]^+$, 574 $[M+NH_4-H_2O]^+$.

3,6,9,12-Tetramethoxy-3,6,9,12-tetraphenyltetradeca-1,4,7,10,13-pentayne (12a′): A solution of pentayne **11a′** (127 mg, 0.17 mmol) in methanol (5 mL) was treated with K_2CO_3 (117 mg, 0.85 mmol) for 3 h at RT. The solution was then filtered, concentrated under reduced pressure, and diluted with Et_2O. After treatment with water and extraction with Et_2O, the organic layers were combined, dried with $MgSO_4$, and evaporated to dryness. Purification by column chromatography on silica gel (hexane/acetone 7:3) gave **12a′** as an orange oil (72 mg, 70 %). $R_f \approx 0.25$ (heptane/acetone 8:2); ^{1}H NMR ($CDCl_3$): δ = 2.77 (s, 2H; ≡C-*H*), 3.51–3.58 (m, 12H; OCH_3), 7.34–7.39 (m, 12H; *m*-, *p*-C*H*), 7.74–7.79 ppm (m, 8H; *o*-C*H*); ^{13}C NMR ($CDCl_3$): δ = 53.52 (q, $^1J_{CH}$ = 142 Hz; O*C*H$_3$), 71.93 (s; *C*-(OMe)Ph), 75.66 (d, $^1J_{CH}$ = 240 Hz; ≡*C*-H), 80.81 (d, $^2J_{CH}$ = 50 Hz; *C*≡C-H) 84.25–84.56 (m; C≡C), 125.84–129.75 (m; *o*-, *m*-, *p*-*C*H), 139.58 ppm (s; *ipso*-*C*-C-OMe); IR ($CDCl_3$): $\tilde{\nu}$ = 3306 (C−H), 3066–2903 (C−H), 2827 (OC−H), 2117 (C≡CH), 1600, 1490, 1450 (aromatic), 1068 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 620 $[M+NH_4]^+$.

3,12-Dimethoxy-6,9-bis(trimethylsilyloxy)-3,6,9,12-tetraphenyltetradeca-1,4,7,10,13-pentayne (13a): A solution of pentayne **12a** (2.10 g, 3.65 mmol) in THF (50 mL) was treated with *n*-butyllithium (3.40 mL, 7.48 mmol) for 10 min at −78 °C. Chlorotrimethylsilane (0.925 mL, 7.29 mmol) was then added dropwise and the solution was stirred for 30 min at −78 °C, then for 2 h 30 min at RT. After cooling back to −78 °C, additional chlorotrimethylsilane (0.46 mL, 3.65 mmol) was added to complete the reaction (TLC monitoring). The mixture was allowed to warm up to RT and the stirring was continued for 1 h at this temperature. The solution was then concentrated to dryness and Et_2O (30 mL) was added, giving a white precipitate (LiCl). The solution was filtered, concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane/acetone 95:5) to afford **13a** as a brown oil (1.78 g, 68 %). $R_f \approx 0.66$ (heptane/EtOAc 7:3); ^{1}H NMR ($CDCl_3$): δ = 0.19–0.24 (m, 18H; Si(CH_3)$_3$), 2.79 (m, 2H; ≡C*H*), 3.53–3.56 (m, 6H; OCH_3), 7.36–7.40 (m, 12H; *m*-, *p*-C*H*), 7.74–7.79 ppm (m, 8H; *o*-C*H*); ^{13}C NMR ($CDCl_3$): δ = 0.4 (q, $^1J_{CH}$ = 139 Hz; Si(*C*H$_3$)$_3$), 53.4 (q, $^1J_{CH}$ = 143 Hz; O*C*H$_3$), 65.7 (s; *C*(OTMS)Ph), 72.1 (s; *C*(OMe)Ph), 75.4 (d, $^1J_{CH}$ = 253 Hz; ≡*C*-H), 80.6 (d, $^2J_{CH}$ = 49 Hz; *C*≡CH), 82.6, 85.7, 87.4 (m; *C*≡C), 125.7–128.9 (m; *o*-, *m*-, *p*-*C*H), 139.7 (s; *ipso*-*C*-C-OMe), 142.9–143.0 ppm (s; *ipso*-*C*-C-OSiMe$_3$); MS (DCI/NH_3): *m*/*z*: 736 $[M+NH_4]^+$, 629 $[M-SiMe_3O]^+$.

By-product: 1,14-bis(trimethylsilyl)-3,12-dimethoxy-6,9-bis(trimethylsilyloxy)-3,6,9,12-tetraphenyltetradeca-1,4,7,10,13-pentayne (13b): Yield: 3%; $R_f \approx 0.80$ (heptane/EtOAc 7:3); ^{1}H NMR ($CDCl_3$): $\delta = 0.20$–0.28 (m, 36H; Si(CH_3)$_3$), 3.48–3.52 (m, 6H; OCH_3), 7.31–7.36 (m, 12H; *m*-, *p*-C*H*), 7.70–7.73 ppm (m, 8H; *o*-C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -0.25$, 1.45 (Si(CH_3)$_3$), 53.2 (OCH_3), 65.7 (*C*(OTMS)Ph), 72.0 (*C*(OMe)Ph), 82.9, 85.6, 86.9, 92.31 (*C*≡*C*), 101.21 (C≡*C*-Si), 125.7–128.1 (*o*-, *m*-, *p*-*C*H), 139.9 (*ipso*-*C*-COMe), 143.1 ppm (*ipso*-*C*-COSiMe$_3$); IR ($CDCl_3$): $\tilde{\nu} =$ 2960–2901 (C–H), 2825 (OC–H), 2170 (C≡C–Si), 1599, 1489, 1449 (aromatic), 1252 (C–Si), 1066 cm^{-1} (C–O); MS (DCI/NH_3): *m*/*z*: 880 [*M*+NH_4]$^+$.

4,13-Dimethoxy-1,4,7,10,13,16-hexaphenylcyclooctadeca-2,5,8,11,14,17-hexayn-1,7,10,16-tetrol (3a): A solution of pentayne **12a** (82 mg, 0.14 mmol) in THF (8 mL) was treated with *n*-butyllithium (0.26 mL, 0.56 mmol) for 30 min at −78 °C. A solution of dibenzoylacetylene (**10**) (33 mg, 0.14 mmol) in THF (8 mL) was then added dropwise. The mixture was stirred for 30 min at −78 °C and the mixture was allowed to warm up to RT over a 2 h period. After treatment with saturated NH_4Cl and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated to dryness. Purification by column chromatography on silica gel (heptane/acetone 6:4) gave **3a** as a brown oil (49 mg, 39%). ^{1}H NMR ($CDCl_3$): $\delta = 3.35$–3.39 (m, 6H; OCH_3), 7.21–7.31 (m, 18H; *m*-, *p*-C_6H_5), 7.63–7.79 ppm (m, 12H; *o*-C_6H_5); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 53.42$ (OCH_3), 64.98 (≡C-*C*(OH)Ph-C≡), 71.93 (≡C-*C*-(OMe)Ph-C≡), 82.51, 85.03, 87.06 (C≡*C*), 125.92–128.86 (*o*-, *m*-, *p*-C_6H_5), 138.88 (*ipso*-C_6H_5-C-OMe), 140.59 ppm (*ipso*-C_6H_5-C-OH); IR ($CDCl_3$): $\tilde{\nu} = 3570$ (O–H), 3000–2901 (CC–H), 2825 (OCC–H), 1600, 1490 and 1449 (aromatic), 1067 cm^{-1} (C–O); MS (DCI/NH_3): *m*/*z*: 826 [*M*+NH_4]$^+$.

4,7,10,13-Tetramethoxy-1,4,7,10,13,16-hexaphenylcyclooctadeca-2,5,8,11,14,17-hexayn-1,16-diol (3a′): A solution of pentayne **12a′** (248 mg, 0.41 mmol) in THF (10 mL) was treated with *n*-butyllithium (0.37 mL, 0.82 mmol) for 30 min at −78 °C. A solution of dibenzoylacetylene (**10**) (96 mg, 0.41 mmol) in THF (8 mL) was then added dropwise. The mixture was stirred for another 30 min at −78 °C, and the mixture was allowed to warm up to RT over a 2 h period. After treatment with saturated NH_4Cl and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated to dryness. Purification of the residue by column chromatography on silica gel (heptane/acetone 7:3) gave **3a′** as a brown oil (133 mg, 40%). $R_f \approx 0.25$ (heptane/acetone 7:3); ^{1}H NMR ($CDCl_3$): $\delta = 3.07$–3.13 (m, 2H; O*H*), 3.34–3.63 (m, 12H; OCH_3), 7.30–7.36 (m, 18H; *m*-, *p*-C*H*), 7.65–7.83 ppm (m, 12H; *o*-C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 53.29$ (OCH_3), 64.86 (*C*(OH)Ph), 71.79 (*C*-(OMe)Ph), 82.65–86.46 (*C*≡C), 125.59–128.91 (*o*-, *m*-, *p*-*C*H), 139.18 (*ipso*-*C*-C-OMe), 140.51 ppm (*ipso*-*C*-C-OH); IR ($CDCl_3$): $\tilde{\nu} = 3571$ (O–H), 3065–2901 (C–H), 2826 (OC–H), 1599, 1490, 1450 (aromatic), 1070 cm^{-1} (C–O); MS (DCI/NH_3): *m*/*z*: 854 [*M*+NH_4]$^+$.

4-Hydroxy-7-methoxy-7-(4-methoxyphenyl)-9-(trimethylsilyl)-1,4-diphenylnona-2,5,8-triyn-1-one (15b): A solution of diyne **14** (150 mg, 0.55 mmol) in THF (2 mL) was treated with *n*-butyllithium (220 μL, 0.55 mmol) for 10 min at −78 °C. A solution of dibenzoylacetylene (**10**) (129 mg, 0.55 mmol) in THF (5 mL) was added dropwise and stirring was continued for 30 min at −78 °C. The mixture was then allowed to warm up to RT over a 1.5 h period. The reaction mixture was concentrated to 2 mL and directly deposited onto a preparative silica gel TLC plate for purification. After elution with a heptane/EtOAc mixture (8:2), subsequent extraction with Et_2O, filtration, and evaporation gave **15b** as an orange oil (129 mg, 45%). $R_f \approx 0.50$ (heptane/EtOAc 8:2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.24$ (s, 9H; Si(CH_3)$_3$), 3.49 (s, 3H; CH_3O-C-An), 3.79 (s, 3H; CH_3O-C_6H_4), 6.88 (d, $^3J_{HH} = 9.1$ Hz, 2H; *H*-2 of An), 8.08–8.54 (m, 10H; H_{ar}), 8.78 ppm (d, $^3J_{HH} = 8.5$ Hz, 2H; *o*-C*H* of Ph-C=O); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): $\delta = -0.24$ (Si(CH_3)$_3$), 53.10 (C(Ph)OCH_3), 55.33 ($C_6H_4O CH_3$), 65.84 (*C*(Ph)OH), 71.69 (*C*(An)OMe), 81.50, 84.50, 92.24, 92.50 (*C*≡*C*), 91.73 (≡*C*-C=O), 101.12 (≡*C*-Si), 113.73 (*C*-2 of 4-An), 124.11–135.73 (aromatic *C*), 160.00 (*C*-1 of 4-An), 177.51 ppm (*C*=O); MS (DCI/NH_3): *m*/*z*: 475 [*M*+H−MeOH]$^+$.

4,7-Dimethoxy-7-(4-methoxyphenyl)-9-(trimethylsilyl)-1,4-diphenylnona-2,5,8-triyn-1-one (16): A solution of diyne **14** (2.907 g, 10.67 mmol) in THF (25 mL) was treated with *n*-butyllithium (4.27 mL, 10.67 mmol) for 10 min at −78 °C. A solution of dibenzoylacetylene (**10**) (2.5 g, 10.67 mmol) in THF (30 mL) was added dropwise and the mixture allowed to warm up to −25 °C over a 3 h period. After cooling back to −78 °C, iodomethane (5.3 mL, 85.13 mmol) was added and the mixture allowed to warm up to −25 °C over 1 h. DMSO (0.76 mL, 10.67 mmol) was added and stirring was continued for 1 h at −25 °C, then overnight (17 h) at RT. After treatment with saturated NH_4Cl and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated to dryness. Purification of the residue by column chromatography on silica gel (heptane/EtOAc 9:1) afforded **16** as an orange oil (2.569 g, 46%). $R_f \approx 0.34$ (heptane/EtOAc 8:2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.24$ (s, 9H; Si(CH_3)$_3$), 3.53 (s, 3H; C(Ph)OCH_3), 3.66 (s, 3H; C(An)OCH_3), 3.80 (s, 3H; C_6H_4OCH_3), 6.89 (d, $^3J_{HH} = 8{,}46$ Hz, 2H; *H*-2 of 4-An), 7.41–7.85 (m, 10H; aromatic C*H*), 8.12 ppm (d, $^3J_{HH} =$ 6.98 Hz, 2H; *o*-*H* of Ph-C=O); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = -0.24$ (q, $^1J_{CH} = 120$ Hz; Si(CH_3)$_3$), 53.16, 53.88 (q, $^1J_{CH} = 144$ Hz; C(Ar)OCH_3), 55.32 (q, $^1J_{CH} = 144$ Hz; C_6H_4-OCH_3), 71.84, 73.41 (s; *C*(Ar)OMe), 101.21, 99.36, 89.91, 86.75, 83.24, 82.08 (s; C≡*C*), 113.73 (d, $^1J_{CH} = 160$ Hz; *C*-2 of 4-An), 124.11–135.73 (m; aromatic *C*), 160.01 (s; *C*-1 of 4-An), 177.15 ppm (s; *C*=O); IR ($CDCl_3$): $\tilde{\nu} = 3064$, 3002, 2960, 2931, 2900 (C–H), 1646 (C=O), 1607, 1509, 1492, 1450, 1311 (aromatic), 1252 (C–Si), 1063 cm^{-1} (C–O); MS (DCI/NH_3): *m*/*z*: 538 [*M*+NH_4]$^+$, 521 [*M*+H]$^+$, 489 [*M*+H−MeOH]$^+$; elemental analysis calcd (%) for $C_{33}H_{32}O_4Si$: C 76.12, H 6.20; found: C 76.08, H 6.06.

3-(Trimethylsilyl)-1-(pyridin-4-yl)prop-2-yn-1-ol (18): After the treatment of trimethylsilylacetylene (6.95 mL, 49.14 mmol) in THF (150 mL) with EtMgBr (16.4 mL, 49.14 mmol) at 0 °C for 1 h, a solution of pyridine-4-carbaldehyde (4.7 mL, 49.14 mmol) in THF (100 mL) was added dropwise. After 1 h at 0 °C, the mixture was warmed to RT and stirring was continued for 15 min at this temperature. Saturated aqueous NH_4Cl was added and the mixture extracted with Et_2O. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give **18** as a pink powder (9.609 g, 95%). $R_f \approx 0.14$ (heptane/EtOAc (6:4)+1% MeOH); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.15$ (s, 9H; Si(CH_3)$_3$), 5.46 (s, 1H; C*H*(OH)), 6.59 (s, 1H; O*H*), 7.49 (d, $^3J_{HH} =$ 6.15 Hz, 2H; *H*-3 of 4-Py), 8.46 ppm (d, $^3J_{HH} = 6.15$ Hz, 2H; *H*-2 of 4-Py); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = -0.28$ (q, $^1J_{CH} = 120$ Hz; Si(CH_3)$_3$), 62.77 (d, $^1J_{CH} = 146$ Hz; *C*H(OH)), 91.26 (s; *C*≡CSi), 104.57 (s; C≡*C*-Si), 121.49 (d, $^1J_{CH} = 164$ Hz; *C*-3 of 4-Py), 149.07 (d, $^1J_{CH} = 190$ Hz; *C*-2 of 4-Py), 153.04 ppm (s; *C*-4 of 4-Py); IR ($CDCl_3$): $\tilde{\nu} = 3595$ (O–H), 3081, 2960, 2900 (C–H), 2175 (C≡CSi), 1601, 1558, 1493, 1411, 1335 (aromatic), 1252 (C–Si), 1044 cm^{-1} (C–O); MS (DCI/NH_3): *m*/*z*: 206 [*M*+H]$^+$, 151 [*M*+NH_4−$SiMe_3$+H]$^+$, 134 [*M*+H−$SiMe_3$+H]$^+$.

3-(Trimethylsilyl)-1-(pyridin-4-yl)prop-2-yn-1-one (19)

Method 1: A solution of Dess–Martin periodinane (254 mg, 0.60 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of alcohol **18** (98 mg, 0.48 mmol) in CH_2Cl_2 (4 mL). After stirring for 30 min at RT, the reaction mixture was concentrated to 2 mL under reduce pressure, diluted with Et_2O (15 mL), and filtered before treatment with saturated $NaHCO_3$. The organic layer was then washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (heptane/EtOAc (6:4)+1% MeOH) gave **19** as a yellow oil (8 mg, 8%).

Method 2: Activated MnO_2 (34 g, 395 mmol) was added to a solution of alcohol **18** (5.409 g, 26.3 mmol) in CH_2Cl_2 (200 mL). After stirring for 2 h at RT, the reaction mixture was filtered through a small pad of Celite and evaporated to dryness to give **19** as a yellow oil (4.536 g, 85%).

Common analytical data: $R_f \approx 0.32$ (heptane/EtOAc (6:4)+1% MeOH); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.31$ (s, 9H; Si(CH_3)$_3$), 7.89 (d, $^3J_{HH} =$ 6.06 Hz, 2H; *H*-3 of 4-Py), 8.84 ppm (d, $^3J_{HH} = 6.06$ Hz, 2H; *H*-2 of 4-Py); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = -0.81$ (q, $^1J_{CH} = 122$ Hz; Si(CH_3)$_3$), 99.78 (s; *C*≡CSi), 103.20 (s; C≡*C*-Si), 122.03 (d, $^1J_{CH} = 164$ Hz; *C*-3 of 4-Py), 141.93 (s; *C*-4 of 4-Py), 150.89 (d, $^1J_{CH} = 182$ Hz; *C*-2 of 4-Py), 176.82 ppm (s; *C*=O); IR ($CDCl_3$): $\tilde{\nu} = 2963$, 2920, 2852 (C–H), 2155 (C≡CSi), 1651 (C=O), 1601, 1559, 1487, 1409, 1324 (aromatic), 1255 cm^{-1} (C–Si); MS (DCI/NH_3): *m*/*z*: 221 [*M*+NH_4]$^+$, 204 [*M*+H]$^+$.

1-(Trimethylsilyl)-3-(pyridin-4-yl)penta-1,4-diyn-3-ol (17): A saturated solution of acetylene in THF (200 mL) at 0 °C was treated with EtMgBr

(27 mL, 81 mmol) for 1 h at 0 °C and then pyridyl ketone **19** (8.15 g, 40 mmol) in THF (150 mL) was added dropwise. After stirring for 1 h at 0 °C, the reaction mixture was warmed to RT and stirring was continued overnight (17 h) at this temperature. A saturated aqueous NH_4Cl solution was added and the mixture extracted with Et_2O. The organic layer was separated, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give **17** as a brown solid (8.343 g, 91 %). M.p. 176.9 °C; $R_f \approx 0.13$ (heptane/EtOAc (6:4)+1 % MeOH); ^{1}H NMR (200 MHz, CD_3OD): $\delta = 0.28$ (s, 9H; Si(CH_3)$_3$), 3.36 (s, 1H; C≡C-*H*), 5.04 (s, 1H, O*H*), 7.85 (d, $^3J_{HH} = 6.18$ Hz, 2H; *H*-3 of 4-Py), 8.66 ppm (d, $^3J_{HH} = 6.27$ Hz, 2H; *H*-2 of 4-Py); ^{13}C NMR (63 MHz, CD_3OD): $\delta = -0.99$ (q, $^1J_{CH} = 120$ Hz; Si(CH_3)$_3$), 63.88 (s; *C*-OH), 74.47 (d, $^1J_{CH} = 254$ Hz; C≡*C*-H), 83.70 (d, $^2J_{CH} = 51$ Hz; *C*≡CH), 89.90 (s; *C*≡CSi), 104.86 (s; C≡*C*-Si), 121.65 (d, $^1J_{CH} = 166$ Hz; *C*-3 of 4-Py), 149.74 (d, $^1J_{CH} = 191$ Hz; *C*-2 of 4-Py), 153.48 ppm (s; *C*-4 of 4-Py); IR (CD_3OD): $\tilde{\nu} =$ 3600–3100 (O−H), 3309 (≡C−H), 2964 and 2903 (C−H), 1601, 1564, 1480, 1413, 1327 (aromatic), 1253 cm^{-1} (C−Si); MS (DCI/NH_3): *m*/*z*: 230 $[M+H]^+$.

Single crystals deposited from a chloroform solution were submitted to an X-ray diffraction study, which confirmed the molecular structure (Figure 2, Table 1).

9,12-Dimethoxy-12-(4-methoxyphenyl)-6,9-diphenyl-3-(pyridin-4-yl)tetradeca-1,4,7,10,13-pentayne-3,6-diol (20a)

Step 1: A solution of pyridyl diyne **17** (4.003 g, 17.5 mmol) in THF (50 mL) was treated with *n*-butyllithium (14 mL, 35 mmol) for 20 min at −20 °C. A solution of triynone **16** (9.089 g, 17.5 mmol) in THF (30 mL) was added dropwise and stirring was continued for 2 h at −20 °C, then for 2 h at RT. After treatment with a saturated NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give a brown oil (13.507 g, quantitative crude yield based on the expected 1,4-bis(trimethylsilyl) pentayne).

Step 2: A solution of the just obtained crude oil (13.507 g) in THF (150 mL) was treated with a *n*Bu_4NF solution (THF, 36 mL, 36 mmol) for 10 min at −78 °C. The mixture was allowed to warm up to RT over a 3 h period. The solution was then diluted with Et_2O (50 mL) before water was added. The organic layer was extracted with Et_2O, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (heptane/EtOAc (6:4)+1 % MeOH) to give **20a** as a brown solid (8.131 g, 77 % for the two steps). $R_f \approx 0.14$ (heptane/EtOAc (6:4)+1 % MeOH); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.69$ (s, 1H; An-C-C≡C-*H*), 2.76 (s, 1H; Py-C-C≡C-*H*), 3.44 (m, 6H; CH_3O-C-Ar), 3.74 (s, 3H, CH_3O-C$_6$H$_4$), 6.82 (d, $^3J_{HH} = 8.57$ Hz, 2H; *H*-2 of 4-An), 7.25–7.75 (m, 14H; aromatic C*H*), 8.27 ppm (d, $^3J_{HH} = 4.78$ Hz, 2H; *H*-2 of 4-Py); ^{13}C NMR (63 MHz, $CDCl_3$; see Figure 3a): $\delta = 53.34$, 53.58 (q, $^1J_{CH} = 143$ Hz; *C*H$_3$O-C-Ar), 55.51 (q, $^1J_{CH} = 144$ Hz; *C*H$_3$O-C$_6$H$_4$), 63.48, 64.53 (s; Ar-*C*-OH), 71.37, 72.03 (s; Ar-*C*-OMe), 74.50 (d, $^1J_{CH} = 255$ Hz; An-C-C≡*C*-H), 75.49 (d, $^1J_{CH} = 254$ Hz; Py-C-C≡*C*-H), 87.73, 86.22, 84.90, 84.07, 83.50, 82.27, 82.05, 80.91 (s; C-*C*≡C), 113.94 (d, $^1J_{CH} = 165$ Hz; *C*-2 of 4-An), 120.92 (d, $^1J_{CH} = 166$ Hz; *C*-3 of 4-Py), 124.63–130.61 (m; aromatic *C*H), 139.62, 141.22, 141.33 (s; *ipso-C* of Ar = Ph, An), 149.00 (d, $^1J_{CH} = 181$ Hz; *C*-2 of 4-Py), 151.09 (s; *C*-4 of 4-Py), 160.14 ppm (s; *C*-1 of 4-An); IR ($CDCl_3$): $\tilde{\nu} = 3571$ (O−H), 3304 (≡C−H), 3064, 2958, 2935 (C−H), 2825 (OC−H), 1602, 1510, 1490, 1450, 1311 (aromatic), 1253 (C−Si), 1175 (C−OMe), 1068 cm^{-1} (C−OH); MS (DCI/NH_3): *m*/*z*: 606 $[M+H]^+$, 574 $[M+H-MeOH]^+$.

4-[9,12-Dimethoxy-12-(4-methoxyphenyl)-6,9-diphenyl-3,6-bis(trimethylsilyloxy)tetradeca-1,4,7,10,13-pentayn-3-yl)pyridine (20b): A solution of pentayne **20a** (3.99 g, 6.59 mmol) in THF (30 mL) was treated with *n*-butyllithium (5.27 mL, 13.18 mmol) for 15 min at −78 °C and chlorotrimethylsilane (1.67 mL, 13.18 mmol) was then added dropwise. The mixture was allowed to warm up to RT over a 1 h 30 min period and the stirring was continued for 30 min at this temperature. The solution was then concentrated to dryness and diluted in Et_2O (30 mL). The white precipitate formed (LiCl) was filtered and the solution concentrated under reduced pressure. Purification by column chromatography on silica gel (heptane/EtOAc (7:3)+1 % MeOH) gave **20b** as an orange oil (2.621 g, 53 %). $R_f \approx 0.29$ (heptane/EtOAc (7:3)+1 % MeOH); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.20$ (s, 18H; OSi(CH_3)$_3$), 2.75, 2.78 (s, 2H; C≡C-*H*), 3.52 (m, 6H; CH_3O-C-Ar), 3.79 (s, 3H, CH_3O-C$_6$H$_4$), 6.85 (d, $^3J_{HH} = 7.37$ Hz, 2H; *H*-2 of 4-An), 7.31–7.74 (m, 14H; aromatic C*H*), 8.57 ppm (d, $^3J_{HH} = 4.68$ Hz, 2H; *H*-2 of Py); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 1.35$ (q, $^1J_{CH} = 119$ Hz; OSi(CH_3)$_3$), 53.25, 53.53 (q, $^1J_{CH} = 143$ Hz; *C*H$_3$O-C-Ar), 55.32 (q, $^1J_{CH} = 144$ Hz; O*C*H$_3$O-C$_6$H$_4$), 64.53, 65.65 (s; Ar-*C*-OSi), 71.31, 71.93 (s; Ar-*C*-OMe), 74.54, 75.15 (d, $^1J_{CH} = 253$ Hz; ≡*C*-H), 87.09, 86.41, 84.82, 84.06, 83.62, 82.95, 82.80, 80.83 (s; C-*C*≡C), 113.73 (d, $^1J_{CH} = 156$ Hz; *C*-2 of 4-An), 120.34 (d, $^1J_{CH} = 165$ Hz; *C*-3 of 4-Py), 125.59–131.82 (m; aromatic *C*H), 139.62, 142.47, 142.60 (s; *ipso-C* of Ar = Ph, An), 149.93 (d, $^1J_{CH} = 191$ Hz; *C*-2 of 4-Py), 151.69 (s; *C*-4 of 4-Py), 160.03 ppm (s; *C*-1 of 4-An); IR ($CDCl_3$): $\tilde{\nu} = 3305$ (≡C−H), 3062, 3026, 2958 (C−H), 2826 (OC−H), 1608, 1595, 1510, 1489, 1449, 1311 (aromatic), 1253 (C−Si), 1175 (C−OMe), 1067 cm^{-1} (C−OSi); MS (DCI/NH_3): *m*/*z*: 750 $[M+H]^+$, 718 $[M+H-MeOH]^+$, 678 $[M+H-SiMe_3+H]^+$, 646 $[M+H-SiMe_3+H-MeOH]^+$, 606 $[M+H+2H-2SiMe_3]^+$.

13,16-Dimethoxy-13-(4-methoxyphenyl)-1,7,10,16-tetraphenyl-4-(pyridin-4-yl)cyclooctadeca-2,5,8,11,14,17-hexayne-1,4,7,10-tetrol (3b)

Step 1: A solution of hexamethyldisilazane (0.354 mL, 1.68 mmol) in THF (5 mL) was treated with *n*-butyllithium (1.16 mL, 1.68 mmol) for 25 min at −78 °C. A solution of pentayne **20b** (300 mg, 0.4 mmol) in THF (150 mL) was then added dropwise and the mixture was allowed to warm up to −40 °C over a 45 min period. After warming up quickly to −20 °C, the stirring was continued for 1 h 30 min at −20 °C. After cooling back to −78 °C, a solution of dibenzoylacetylene (**10**) (94 mg, 0.4 mmol) in THF (15 mL) was added dropwise and the mixture was allowed to warm up to RT over a 1 h period. The stirring was continued overnight (17 h) at this temperature. After treatment with a saturated NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give a brown oil (439 mg, corresponding to a quantitative formal yield based on the expected bis-*O*-silylated hexaoxy[6]pericyclyne, but integrated ^{1}H NMR analysis suggested that partial desilylation occurred).

Step 2: A solution of the aforementioned brown oil (439 mg, 0.45 mmol) in THF (40 mL) was treated with a solution of *n*Bu_4NF (THF, 1.11 mL, 1.11 mmol) for 10 min at −78 °C and the mixture was allowed to warm up to RT over a 3 h period. The solution was then diluted with Et_2O (20 mL) before water was added. The organic layer was separated, dried with $MgSO_4$, concentrated under reduced pressure, and the residue purified by column chromatography on silica gel (heptane/EtOAc 4:6) to afford **3b** as a brown solid (47 mg, 14 % over the two steps). $R_f \approx 0.53$ (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.19$–3.43 (m, 6H; CH_3O-C-Ar), 3.60–3.76 (m, 3H, CH_3O-C$_6$H$_4$), 6.65–6.77 (m, 2H; *H*-2 of An), 7.00–7.35, 7.39–7.80 (m, 24H; aromatic C*H*), 7.90–8.15 ppm (m, 2H; *H*-2 of 4-Py); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; see Figure 3b): $\delta = 53.31$, 53.79 (*C*H$_3$O-C-Ar), 55.76 (*C*H$_3$O-C$_6$H$_4$), 63.70, 64.09, 64.47, 64.87 (Ar-*C*-OH), 71.96, 72.35 (Ar-*C*-OMe), 80.85–88.06 (C-*C*≡*C*-C), 114.18 (*C*-2 of 4-An), 121.23 (*C*-3 of 4-Py), 126.28–129.53 (m; aromatic *C*H), 139.65–141.51 (*ipso-C* of An and Ph), 149.07 (*C*-2 of 4-Py), 151.50 (*C*-4 of 4-Py), 160.28 ppm (s; *C*-4 of 4-An); IR ($CDCl_3$): $\tilde{\nu} = 3390$ (O−H), 3066, 2934 (C−H), 2825 (OC−H), 2048 (C≡C), 1602, 1509, 1490, 1450, 1312 (aromatic), 1175 (C−OMe), 1067 cm^{-1} (C−OH); MS (DCI/NH_3): *m*/*z*: 840 $[M+H]^+$, 808 $[M+H-MeOH]^+$.

1,14-Bis(trimethylsilyl)-6,9-dimethoxy-6,9-diphenyltetradeca-1,4,7,10,13-pentayne-3,12-diol (23a)

From trimethylsilylacetylenelithium: A solution of *n*-butyllithium (2.5 M in hexane 0.82 mL, 1.2 mmol) was added through a syringe to a solution of trimethylsilylacetylene (0.17 mL, 1.2 mmol) in THF (10 mL) at −80 °C. After stirring for 40 min at −80 °C, then for 30 min at RT, a solution of dialdehyde **22** (719 mg, 0.59 mmol) in THF (5 mL) was added. The mixture was then stirred for 1 h as it was warmed from −80 °C to RT. Diethyl ether was added. The organic layer was then washed with a saturated aqueous solution of NH_4Cl and extracted with diethyl ether. The organic layer was separated, washed with a saturated aqueous NH_4Cl solution, dried with $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (heptane/EtOAc 8:2). The product **23a** was isolated as an orange oil (144 mg, 43 %) and was characterized by NMR spectroscopy (see below).

From trimethylsilylacetylenemagnesium bromide: A solution of trimethylsilylacetylene (1.6 mL, 5.6 mmol) in THF (50 mL) was treated with EtMgBr (3.77 mL, 11.3 mmol) at 0 °C for 1 h and then dialdehyde **22** (2.094 g, 5.6 mmol) dissolved in THF (30 mL) was added dropwise. Stirring was continued for 1 h at 0 °C, then for 2 h at RT. After addition of a saturated aqueous NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give **23a** as an orange oil (2.51 g, 79 %). The crude product displayed satisfactory spectroscopic purity to be used as such in the next step. $R_f \approx 0.41$ (heptane/EtOAc 5:5); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.18$ (s, 18H; Si(CH_3)$_3$), 2.50 (s, 2H; O*H*), 3.52 (s, 6H; OCH_3), 5.20 (s, 2H; C*H*(OH)), 7.35–7.41 (m, 6H; *m*-, *p*-C*H*), 7.71–7.76 ppm (m, 4H; *o*-C*H*); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): $\delta = -0.54$ (Si-(CH_3)$_3$), 52.35 (OCH_3), 53.25 (*C*HOH), 71.64 (*C*PhOMe), 81.11, 84.14, 90.01 (C-*C*≡*C*-C), 90.92 (*C*≡C-Si), 101.01 (≡C-Si), 126.43, 128.31 (*o*-, *m*-CH), 128.88 (*p*-CH), 139.24 ppm (*ipso-Ci*); IR ($CDCl_3$): $\tilde{\nu} = 3585$ (O−H), 3066, 3032, 2998, 2961, 2935, 2901 (C−H), 2827 (OC−H), 2179 (C≡CSi), 1600, 1490, 1450, 1410 (aromatic), 1252 (C−Si), 1063 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 584 $[M+NH_4]^+$.

3,6,9,12-Tetramethoxy-6,9-diphenyltetradeca-1,4,7,10,13-pentayne (23b′)

*Prepared via 1,14-bis(trimethylsilyl)-3,6,9,12-tetramethoxy-6,9-diphenyltetradeca-1,4,7,10,13-pentayne (**23a′**)*: A solution of *n*-butyllithium (2.5 M in hexane, 0.64 mL, 1.60 mmol) was added through a syringe to a solution of pentynediol **23a** (454 mg, 0.80 mmol) and diethyl ether (6 mL) at −80 °C. After stirring for 1 min, methyl triflate (346 μL, 3.2 mmol) was added, the mixture was allowed to warm up to −10 °C, and then stirred between −10 and 0 °C over 15 h (CAUTION: above 0 °C, degradation occurs). The mixture was then poured into a saturated aqueous K_2CO_3 solution and diethyl ether was added. The organic layer was separated, washed again with saturated aqueous K_2CO_3, dried with $MgSO_4$, and concentrated to give a crude product, assigned to the fragile structure **23a′**, as a dark oil. In order to avoid degradation, the crude material was used in the next step.

The crude diether **23a′** was dissolved in THF (8 mL) at −80 °C and a solution of TBAF (1 M in THF, 1.60 mL, 1.60 mmol) was added. After stirring for 5 min at −80 °C, the mixture was poured into a mixture of water and diethyl ether. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated to give **23b′** as a dark oil. This sensitive product was analyzed without further purification (338 mg, 94 % crude yield). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.56$ (s br., 2H; ≡C*H*), 3.44 (m, 6H; CHOCH_3), 3.54 (m, 6H; CPhOCH_3), 5.09 (m, 2H; C*H*OMe), 7.36–7.41 (m, 6H; *m*-, *p*-C*H*), 7.72–7.76 ppm (m, 4H; *o*-C*H*); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): $\delta = 53.30$, 54.39 (CPhOCH_3 + CHOCH_3), 59.36 (*C*HOMe), 67.78 (*C*PhOMe), 71.64 (≡*C*−*H*), 77.71 (*C*≡CH), 81.44, 82.64, 84.18 (C-*C*≡*C*-C), 126.34, 128.30 (*o*-, *m*-*C*H), 128.85 (*p*-*C*H), 139.27 ppm (*ipso-C*); IR ($CDCl_3$): $\tilde{\nu} = 3306$ (spC−H), 3065 (sp^{2}C−H), 2934 (sp^{3}C−H), 2122 (C≡C), 1654, 1490, 1450 cm^{-1} (aromatic); MS (DCI/NH_3): *m*/*z*: 468 $[M+NH_4]^+$, 436 $[M+NH_4-MeOH]^+$, 419 $[M+H-MeOH]^+$, 404 $[M+NH_4-2MeOH]^+$.

6,9-Diphenyl-6,9-dimethoxytetradeca-1,4,7,10,13-pentayne-3,12-diol (23b): A solution of ethynylmagnesium bromide (0.5 M, 3.16 mL, 1.58 mmol) was added through a syringe to a solution of dialdehyde **22** (146 mg, 0.40 mmol) in diethyl ether (10 mL) at 0 °C. After stirring for 15 min at 0 °C, then for 1.5 h at RT, the mixture was poured into a mixture of aqueous saturated NH_4Cl and diethyl ether. The organic layer was separated, washed with a saturated aqueous NH_4Cl solution, dried with $MgSO_4$, filtered, and concentrated to give **23b** as an orange oil (161 mg, 97 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.55$ (s, 2H; ≡C*H*), 3.50 (s, 6H; OCH_3), 3.60 (s, 2H; O*H*), 5.18 (s, 2H; CH-OH), 7.34–7.40 (m, 6H; *p*-, *m*-C*H*), 7.70–7.74 ppm (m, 4H; *o*-C*H*); ^{13}C{^{1}H} NMR (60 MHz, $CDCl_3$): $\delta = 51.85$, 53.44 (OCH_3 + *C*HOH), 71.82 (*C*PhOMe), 73.35 (≡*C*−*H*), 80.18 (*C*≡CH), 81.46, 83.99–84.39 (C-*C*≡*C*-C), 126.57, 128.57 (*o*-, *m*-*C*H), 129.13 (*p*-*C*H), 139.17 ppm (*ipso-C*); IR ($CDCl_3$): $\tilde{\nu} = 3585$ (free O−H), 3408 (bound O−H), 3306 (spC−H), 3089–2903 (C−H), 2827 (OC−H), 2126 (C≡C), 1600, 1490, 1450 (aromatic), 1375, 1294, 1227, 1179, 1144, 1064 (C−O), 1029 cm^{-1}; MS (DCI/NH_3): *m*/*z*: 440 $[M+NH_4^+]$), 408 $[M-MeOH+NH_4]^+$, 391 $[M+H-MeOH]^+$, 376 $[M-2MeOH+NH_4]^+$.

3,12-Bis(tetrahydropyran-2-yloxy)-6,9-diphenyl-6,9-dimethoxytetradeca-1,4,7,10,13-pentayne (23b″): *p*-Toluenesulfonic acid (3 mg, 5.2×10^{-3} mmol) was added to a solution of pentaynediol **23b** (179 mg, 0.13 mmol) and dihydropyran (77 μL, 0.26 mmol) in toluene (15 mL). After stirring for 15 h at RT, the mixture was concentrated in vacuo and the reaction quenched with one drop of triethylamine. Diethyl ether (50 mL) and water (50 mL) were added. The organic layer was separated, again washed with water, dried with $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (heptane/EtOAc 8:2). The product **23b″** was isolated as an orange oil (47 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.49$–1.85 (m, 12H; CH_2), 2.52, 2.56 (2d, $^4J_{HH} = 2.3$ Hz, 2H; ≡C−H), 3.46–3.55 (s, 8H; OCH_3 + C*H*H-O THP), 3.80–3.89 (m, 2H; CH*H*-O THP), 4.95–5.00 (m, 2H; C*H*O$_2$ THP), 5.30, 5.32 (2d, $^4J_{HH} = 2.3$ Hz, 2H; C*H*-OTHP), 7.35–7.39 (m, 6H; *p*-, *m*-C*H*), 7.70–7.78 ppm (m, 4H; *m*-C*H*); ^{13}C{^{1}H} NMR (60 MHz, $CDCl_3$): $\delta = 15.09$, 25.22, 29.91 (C-*C*H_2-C THP), 53.47 (OCH_3), 54.39, 54.69 (*C*H-OTHP), 61.93, 62.05 (*C*H_2O THP), 71.82 (*C*PhOMe), 73.21, 73.62 (≡*C*−H), 78.52 (*C*≡CH), 81.45, 82.02, 82.24, 82.51, 84.25 (C-*C*≡*C*-C), 95.51, 95.89 (*C*HO$_2$ THP), 126.55, 126.63, 128.43, 128.93 (*o*-, *m*-*C*H), 128.93, 128.97 (*p*-*C*H), 139.54 ppm (*ipso-C*); IR ($CDCl_3$): $\tilde{\nu} = 3307$ (spC−H), 3066 (sp^{2}C−H), 2949(sp^{3}C−H), 2827 (OC−H), 2124 (C≡C), 1600, 1490, 1450 (aromatic), 1442, 1312, 1286, 1227, 1202, 1185, 1117, 1066 (C−O), 1016 cm^{-1}; MS (DCI/NH_3): *m*/*z*: 608 $[M+NH_4]^+$, 572 $[M-2H_2O+NH_4]^+$, 559 $[M+H-MeOH]^+$, 524 $[M-DHPOH+NH_4]^+$, 475 $[M-THPOH-MeOH+NH_4]^+$.

6,9-Dimethoxy-1,14-bis(trimethylsilyl)-6,9-diphenyltetradeca-1,4,7,10,13-pentayne-3,12-dione (24a): Manganese oxide (5.77 g, 66.4 mmol) was added to a solution of crude pentayne **23a** (2.51 g, 4.4 mmol) in CH_2Cl_2 (50 mL). After stirring at 0 °C for 1 h, the mixture was allowed to warm up to RT and stirring was continued for 1 h. The solution was then filtered and concentrated under reduced pressure to give **24a** as a yellow oil (2.13 g, 86 %).

$R_f \approx 0.56$ (heptane/EtOAc 8:2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.26$ (s, 18 H; Si(CH_3)$_3$), 3.57 (s, 6H; OCH_3), 7.39–7.43 (m, 6H; *m*-, *p*-C*H*), 7.70 ppm (m, 4H; *o*-C*H*); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = -0.99$ (q, $^1J_{CH} = 124$ Hz; Si(CH_3)$_3$), 53.91 (q, $^1J_{CH} = 144$ Hz; OCH_3), 71.91 (s; Ph-*C*-OMe), 84.06 (s; PhC-*C*≡*C*-CPh), 85.28 (s; O=C-C≡*C*-CPh), 87.39 (s; O=C-*C*≡C-CPh), 101.15 (s; O=C-*C*≡C-Si), 102.18 (s; C≡*C*-Si), 126.46 (d, $^1J_{CH} = 168$ Hz; *m*- or *o*-*C*H), 128.76 (d, $^1J_{CH} = 159$ Hz; *o*- or *m*-*C*H), 129.57 (d, $^1J_{CH} = 161$ Hz; *p*-*C*H), 137.99 (s; *ipso-C*), 159.55 ppm (s; *C*=O); IR ($CDCl_3$): $\tilde{\nu} = 3066$, 2961, 2935, 3903 (C−H), 2829 (OC−H), 2154 (C≡CC(O)), 1634 (C=O), 1490, 1451, 1422 (aromatic), 1254 (C−Si), 1070 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 580 $[M+NH_4]^+$, 531 $[M+H-MeOH]^+$, 508 $[M+H-SiMe_3+NH_4]^+$, 459 $[M+H-SiMe_3+H-MeOH]^+$, 436 $[M+H_2-2SiMe_3+NH_4]^+$, 387 $[M+H_2-2SiMe_3+H-MeOH]^+$.

3,12-Dioxo-6,9-dimethoxy-6,9-diphenyltetradeca-1,4,7,10,13-pentayne (24b): MnO_2 (330 mg, 3.8 mmol) was added to a solution of pentayne **23b** (107 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After stirring for 10 min at 0 °C and then for 2 h at RT, the mixture was filtered through a small pad of Celite, washed with ethyl acetate, and concentrated. The dark oily residue was purified by chromatography on silica gel (heptane/EtOAc 8:2, then 5:5) to afford a product assigned to structure **24b** according to NMR analysis (29 mg, 28 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.41$ (s, 2H; ≡C-*H*), 3.57 (s, 6H; OCH_3), 7.36–7.43 (m, 6H; *m*-, *p*-C*H*), 7.67–7.72 ppm (m, 4H; *o*-C*H*).

3,12-Diethynyl-6,9-dimethoxy-1,14-bis(trimethylsilyl)-6,9-diphenyltetradeca-1,4,7,10,13-pentayne-3,12-diol (25): A solution of ethynylmagnesium bromide (1.42 mL, 0.71 mmol) was added dropwise to a solution of crude dione **24a** (100 mg, 0.18 mmol) in THF (10 mL) at 0 °C. After stirring for 1 h at 0 °C and for 3 h at RT, the solution was treated with a saturated NH_4Cl solution. The organic layer was extracted with Et_2O, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (heptane/EtOAc 8:2) to give **25** as an orange oil (80 mg, 71 %). $R_f \approx 0.25$ (heptane/EtOAc 7:3); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.20$ (s, 18 H; Si(CH_3)$_3$), 2.68 (s, 2H; C≡C-*H*), 3.21 (s, 2H; O*H*), 3.54 (s, 6H; OCH_3), 7.35–7.39 (m, 6H; *m*-, *p*-C*H*), 7.71–7.77 ppm (m, 4H; *o*-C_6H_5); ^{13}C NMR (63 MHz,

$CDCl_3$): $\delta = -0.53$ (q, $^1J_{CH} = 121$ Hz; Si(CH_3)$_3$), 53.57 (q, $^1J_{CH} = 144$ Hz; OCH_3), 54.13 (s; *C*OH), 71.79 (s; *C*OMe), 71.87 (d, $^1J_{CH} = 256$ Hz; C≡*C*-H), 79.97, 80.02 (2s; C-*C*≡*C*-C), 80.50 (d, $^2J_{CH} = 57$ Hz; *C*≡CH), 84.34 (s; C-*C*≡*C*-C), 89.09 (s; *C*≡CSi), 100.37 (C≡*C*-Si), 126.66 (d, $^1J_{CH} = 167$ Hz; *m*- or *o*-*C*H), 128.50 (d, $^1J_{CH} = 165$ Hz; *o*- or *m*-*C*H), 129.10 (d, $^1J_{CH} = 161$ Hz; *p*-*C*H), 139.15 ppm (s; *ipso*-*C*); IR ($CDCl_3$): $\tilde{\nu} = 3569$ (O−H), 3306, 2961, 2931, 2900 (C−H), 2825 (OC−H), 2128 (C≡C), 1490, 1451, 1408 (aromatic), 1252 (C−Si), 1068 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 632 [*M*+NH_4]$^+$, 600 [*M*+NH_4−MeOH]$^+$.

3,12-Diethynyl-3,6,9,12-tetramethoxy-1,14-bis(trimethylsilyl)-6,9-diphenyltetradeca-1,4,7,10,13-pentayne (21): A solution of heptayne **25** (100 mg, 0.16 mmol) in THF (8 mL) was treated with *n*-butyllithium (117 μL, 0.29 mmol) for 20 min at −78 °C. Iodomethane (162 μL, 2.6 mmol) was added dropwise and the mixture was allowed to warm up to −40 °C over a 30 min period. DMSO (23 μL, 0.32 mmol) was added and stirring was continued for 1 h at −0 °C, then overnight (17 h) at RT. After treatment with a saturated NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography on silica gel (heptane/EtOAc 8:2) gave **21** as an orange oil (82 mg, 80 %). $R_f \approx 0.40$ (heptane/EtOAc 7:3). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 0.21 (s, 18 H; Si(CH_3)$_3$), 2.68 (s, 2 H; C≡C-*H*), 3.49, 3.56 (2s, 12 H; OCH_3), 7.36–7.39 (m, 6 H; *m*-, *p*-C*H*), 7.75 ppm (m, 4 H; *o*-C*H*); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = -0.49$ (q, $^1J_{CH} = 120$ Hz; Si(CH_3)$_3$), 52.75 (q, $^1J_{CH} =$ 144 Hz; SiC≡CC-OCH_3), 53.57 (q, $^1J_{CH} = 144$ Hz; PhC-OCH_3), 60.61 (s; HC≡C-*C*-OMe), 71.82 (s; Ph-*C*-OMe), 72.75 (d, $^1J_{CH} = 256$ Hz; C≡*C*-H), 78.57 (d, $^2J_{CH} = 49$ Hz; *C*≡CH), 81.32, 82.48, 84.28 (3s; *C*≡C), 90.07 (s; *C*≡CSi), 98.46 (s; C≡*C*-Si), 126.60 (d, $^1J_{CH} = 161$ Hz; *m*- or *o*-*C*H), 128.47 (d, $^1J_{CH} = 158$ Hz; *o*- or *m*-*C*H), 129.07 (d, $^1J_{CH} = 161$ Hz; *p*-*C*H), 139.31 ppm (s; *ipso*-*C*); IR ($CDCl_3$): $\tilde{\nu} = 3306$ (≡C−H), 3065, 3002, 2961, 2935, 2902 (C−H), 2827 (OC−H), 2124 (C≡C), 1490, 1450, 1408 (aromatic), 1252 (C−Si), 1061 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 660 [*M*+NH_4]$^+$, 628 [*M*+NH_4−MeOH]$^+$, 611 [*M*+H−MeOH]$^+$.

7,10,13,16-Tetramethoxy-7,16-bis[2-(trimethylsilyl)ethynyl]-1,4,10,13-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,4-diol (3c): A solution of heptayne **21** (212 mg, 0.33 mmol) in THF (12 mL) was treated with *n*-butyllithium (0.264 mL, 0.66 mmol) for 25 min at −78 °C. The mixture was allowed to warm up to −20 °C over a 15 min period. After cooling back to −78 °C, a solution of dibenzoylacetylene (**10**) (77 mg, 0.33 mmol) in THF (6 mL) was added dropwise and the mixture allowed to warm up to RT over a 1 h 30 min period. The stirring was continued for 2 h at this temperature. After treatment with a saturated NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (heptane/EtOAc 7:3) gave **3c** as an orange oil (126 mg, 43 %). $R_f \approx 0.25$ (heptane/EtOAc 7:3). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.21$ (s, 18 H; Si(CH_3)$_3$), 3.06 (m, 2 H; O*H*), 3.42–3.62 (m, 12 H; OCH_3), 7.33–7.40 (m, 12 H; *m*-, *p*-C*H*), 7.66–7.81 ppm (m, 8 H; *o*-C*H*); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): $\delta = -0.47$ (Si(CH_3)$_3$), 52.88 (SiC≡C-COCH_3), 53.57 (PhC-OCH_3), 60.90 (SiC≡C-*C*-OMe), 64.88 (Ph-*C*-OH), 71.83 (Ph-*C*-OMe), 80.45, 81.58, 82.23, 83.59, 84.51, 84.56 (*C*≡C), 90.59 (*C*≡CSi), 98.23 (C≡*C*-Si), 125.35–129.10 (*o*-, *m*-, *p*-C*H*), 139.25 (*ipso*-*C*-C-OMe), 140.47 ppm (*ipso*-*C*-C-OH); IR (dilute $CDCl_3$: C≡CSi masked): $\tilde{\nu} = 3570$ (O−H), 3064, 2960, 2934, 2900 (C−H), 2827 (OC−H), 1600, 1490, 1450, 1408 (aromatic), 1252 (C−Si), 1065 cm^{-1} (C−O); MS (DCI/NH_3): *m*/*z*: 894 [*M*+NH_4]$^+$, 845 [*M*+H−MeOH]$^+$.

Hexacarbonyl[7,10-bis(trimethylsilyloxy)-1,16-dihydroxy-4,13-dimethoxy-4,7,10,13-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne]dicobalt (27): A solution of pentayne **13a** (1.41 g, 1.97 mmol) in THF (120 mL) was treated with *n*-butyllithium (1.80 mL, 3.93 mmol) for 30 min at −78 °C. After addition of a solution of butynedial complex **26** (800 mg, 2.16 mmol) in THF (40 mL), the stirring was continued for 30 min at −78 °C and the mixture allowed to warm up to RT over a 1 h 30 min period. After treatment with a saturated NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography through a silica gel column (heptane/acetone 9:1) to give **27** as a red oil (377 mg, 18 %). $R_f \approx 0.35$ (heptane/EtOAc 8.5:1.5); ^{1}H NMR ($CDCl_3$): $\delta = -0.08$–0.31 (m, 18 H; Si(CH_3)$_3$), 3.36–3.55 (m, 6 H; OCH_3), 5.62–5.67 (m, 2 H; C*H*(OH)), 7.27–7.41 (m, 12 H; *m*-, *p*-C*H*), 7.63–7.79 ppm (m, 8 H; *o*-C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 1.3$ (Si(CH_3)$_3$), 53.3 (OCH_3), 63.6 (*C*H(OH)), 65.9 (*C*Ph(OSiMe$_3$)), 71.9 (*C*Ph(OMe)), 82.17, 83.64, 85.87, 88.06, 93.88 (*C*≡C), 125.7–128.9 (*o*-, *m*-, *p*-C*H*), 139.5 (*ipso*-*C*-C-OMe), 142.5 (*ipso*-*C*-C-OSiMe$_3$), 198.5 ppm (*C*≡O); IR ($CDCl_3$): $\tilde{\nu} = 2960$–2901 (C−H), 2820 (OC−H), 2100, 2065, 2037 (C≡O), 1559, 1489, 1449 (aromatic), 1253 (C−Si), 1070 cm^{-1} (C−O); MS (ES, negative mode): *m*/*z*: 1083 [*M*−3H]$^-$.

6,15-Dimethoxy-6,9,12,15-tetraphenylcyclooctadeca-1,4,7,10,13,16-hexayne-3,9,12,18-tetrol (3d): A solution of the pericyclyne complex **27** (0.52 g, 0.48 mmol) in acetone (35 mL) was treated with ceric ammonium nitrate (1.0 g, 1.91 mmol) at RT. After stirring for 3 h, IR monitoring indicated the complete disappearance of the vibrational bands associated with the carbonyl ligands of the [$Co_2(CO)_6$] unit. Water was added and the mixture extracted with Et_2O. The organic layer was separated, dried with Na_2SO_4, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (hexane/EtOAc 9:1) gave **3d** (98 mg, 33 %) as a vitreous yellow solid. $R_f \approx 0.20$ (heptane/EtOAc 7:3); ^{1}H NMR ($CDCl_3$): $\delta = 3.29$–3.61 (m, 10 H; OCH_3+O*H*), 5.05 (m, 2 H; C*H*(OH)), 7.30–7.41 (m, 12 H; *m*-, *p*-C*H*), 7.62–7.69 ppm (m, 8 H; *o*-C*H*); ^{13}C NMR ($CDCl_3$): $\delta = 52.5$ (q, $^1J_{CH} = 142$ Hz; OCH_3), 51.5 (d, $^1J_{CH} = 154$ Hz; *C*H(OH)), 64.7 (s; *C*Ph(OH)), 71.6 (s; *C*Ph-(OMe)), 81.3–86.8 (m; *C*≡*C*), 125.8–128.6 (m; *o*-, *m*-, *p*-C*H*), 138.6 (s; *ipso*-*C*-C-OMe), 140.5 ppm (s; *ipso*-*C*$_6$H$_5$-C-OH); IR ($CDCl_3$): $\nu = 3572$ (free O−H), 3376–3307 (H-bonded O−H), 3066, 2936 (C−H), 2827 (OC−H), 1600, 1490, 1450 (aromatic), 1070 cm^{-1} (C−O).

1,14-Bis(trimethylsilyl)-3,12-dimethoxy-3,12-diphenyltetradeca-1,4,7,10,13-pentayne-6,9-diol (29): Complex **28** (127 mg, 0.15 mmol)[21] was dissolved in acetone (6 mL) at 0 °C and cerium ammonium nitrate (CAN, 192 mg, 0.35 mmol) was added. The mixture was stirred for 15 min at 0 °C and then for 1.5 h at RT until complete disappearance of the CO stretching bands of **28** by IR monitoring. Water (15 mL) was added and the mixture was extracted with diethyl ether. The organic layer was separated, washed with water (2×10 mL), dried with $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by chromatography on silica gel (heptane/acetone 8:2) to afford **29** as a brown oil (79 mg, 90 %). $R_f = 0.17$ (heptane/acetone 7:3); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.22$ (s, 18 H; Si(CH_3)$_3$), 3.18 (s, 2 H; O*H*), 3.46 (s, 6 H; OCH_3), 5.23 (s, 2 H; C*H*OH), 7.34–7.36 (m, 6 H; *p*-, *m*-C*H*); 7.71–7.75 ppm (m, 4 H; *o*-C*H*); ^{13}C NMR (CDCl3, 50 MHz): $\delta = -0.40$ (q, $^1J_{CH} = 120$ Hz; Si(CH_3)$_3$), 51.90 (d, $^1J_{CH} = 153$ Hz; *C*H(OH)), 52.90 (q, $^1J_{C\text{-}H} = 143$ Hz; OCH_3), 71.71 (s; *C*(OMe)Ph), 81.11–82.66 (4s; ≡*C*-C), 92.49 (s; *C*≡C-Si), 100.76 (s, ≡*C*-Si), 126.46–128.74 (m; *o*-, *m*-, *p*-C*H*), 139.32 ppm (br; *ipso*-*C*); IR ($CDCl_3$): $\tilde{\nu} = 3674$ (free O−H), 3406 (bound O−H), 3064–2935 (C−H), 2826 (OC−H), 1490, 1449 (aromatic), 1251 cm^{-1} (C−Si); MS (DCI/NH_3): *m*/*z*: 584 [*M*+NH_4]$^+$, 552 [*M*+NH_4−MeOH]$^+$, 535 [*M*−MeO]$^+$, 520 [*M*+NH_4−2MeOH]$^+$, 503 [*M*−MeO−MeOH]$^+$.

1,14-Bis(trimethylsilyl)-6,9-bis(tetrahydropyran-2-yloxy)-3,12-diphenyl-3,12-dimethoxytetradeca-1,4,7,10,13-pentayne (30a): A mixture of **29** (211 mg, 0.37 mmol), DHP (68 μL, 0.74 mmol), and *p*-toluenesulfonic acid (3 mg, 1.49×10^{-3} mmol) in toluene (10 mL) was stirred for 5 h at RT. The reaction was quenched by addition of triethylamine (2 μL) and the solvent evaporated to dryness. Diethyl ether (75 mL) and water (75 mL) were added to the crude residue and the organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated to give **30a** as a red-brown oil (259 mg, 94 %). $R_f = 0.34$ (heptane/acetone 7:3); ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.22$ (s; Si(CH_3)$_3$), 1.54–1.90 (m, 12 H; C-CH_2-C THP), 3.45–3.52 (m, 8 H; OCH_3+CH*H*-O THP), 3.71–3.96 (m, 2 H; C*H*H-O THP), 4.94–4.97 (m, 2 H; C*H*O$_2$ THP), 5.39–5.40 (m, 2 H; C*H*OTHP), 7.32–7.35 (m, 6 H; *p*-, *m*-C*H*), 7.70–7.82 ppm (m, 4 H; *o*-C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): $\delta = -0.43$ (Si(CH_3)$_3$), 18.44, 23.26, 29.76 (C-*C*H$_2$-C THP), 52.92, 54.56 (OCH_3+*C*H$_2$O THP), 62.22 (*C*H-OTHP), 71.71 (*C*PhOMe), 79.44–82.66 (≡*C*-C), 91.94 (*C*≡*C*-Si), 94.49–95.80 (*C*HO$_2$ THP), 101.13 (C≡*C*-Si), 126.46, 126.52, 128.13, 128.59, 128.86 (aromatic *C*H), 139.60 ppm (*ipso*-C); IR ($CDCl_3$): $\tilde{\nu} = 2952$, 2902,

2874, 2854 (C–H), 2169 (C≡C), 1251 cm^{-1} (C–Si); MS (DCI/NH_3): *m/z* (%): 752 (100) $[M+NH_4]^+$.

6,9-Bis(tetrahydropyran-2-yloxy)-3,12-diphenyl-3,12-dimethoxytetradeca-1,4,7,10,13-pentayne (30b): A solution of TBAF (1 M in hexane, 0.78 mL, 0.78 mmol) was added through a syringe to a solution of the silylated pentayne **30a** (0.198 g, 0.27 mmol) in THF (10 mL) at −78 °C. After stirring for 1 h at −78 °C the solution was poured into a mixture of diethyl ether (70 mL) and saturated aqueous NH_4Cl (100 mL). The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated to give a brown oil displaying satisfactory analytical data for **30b** (137 mg, 85% crude yield). It can however be purified by chromatography on silica gel (CH_2Cl_2) to give **30b** as a brown-orange oil in a much lower yield (34%). R_f = 0.16 (heptane/acetone 7:3). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.62–1.87 (m, 12H; C-CH_2-C THP), 2.75 (m, 2H; ≡C*H*); 3.41–3.52 (m, 8H; OCH_3+C*H*H-O THP), 3.80–3.85 (m, 2H; CH*H*-O THP), 4.95–4.97 (m, 2H; C*H*O THP), 5.37–5.40 (m, 2H; C*H*OTHP), 7.34–7.37 (m, 6H; *p*-, *m*-C*H*), 7.71–7.78 ppm (m, 4H; *o*-C*H*); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ = 18.63, 25.24, 29.93 (C-*C*H_2-C THP), 53.22, 54.75 (OCH_3+*C*H_2O THP), 62.01 (*C*H-OTHP), 71.53 (*C*PhOMe), 75.17 (≡*C*-H), 80.73–83.65 (≡*C*-C), 95.59–95.90 (*C*HO_2 THP), 126.44–128.90 (aromatic *C*H), 139.54 ppm (*ipso*-C); IR ($CDCl_3$): $\tilde{\nu}$ = 3305 (spC–H), 3065–2948 (C–H), 2828 (OC–H), 2116 (C≡C), 1599, 1490, 1450 (aromatic), 1067 cm^{-1} (C–O); MS (DCI/NH_3): *m/z* (%): 608 (67) $[M+NH_4]^+$.

1,8-Bis(trimethylsilyl)-3,6-diphenylocta-1,4,7-triyne-3,6-diol (31): A solution of *n*-butyllithium (8.13 mL, 17.07 mmol) was added dropwise to a solution of trimethylsilylacetylene (2.53 mL, 17.9 mmol) in THF (20 mL) at −78 °C. After stirring for 20 min at −78 °C, then for 20 min at RT, the mixture was cooled back to −78 °C before addition of a solution of dibenzoylacetylene (**10**) (2.0 g, 8.35 mmol) in THF (20 mL). The reaction mixture was allowed to warm up to RT over 3 h and stirring was continued for 15 h. After addition of a saturated aqueous NH_4Cl solution and extraction with diethyl ether, the organic layer was separated, washed with brine, dried with $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (heptane: EtOAc 8:2) to afford **31** as a pale yellow solid (2.45 g, 67%). R_f ≈ 0.58 (heptane/EtOAc 5:5); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.21 (s, 18H; Si(CH_3)$_3$), 2.94 (s, 2H; O*H*), 7.36 (m, 6H; *m*-, *p*-C*H*), 7.78 ppm (m, 4H; *o*-C*H*); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): δ = −0.31 (Si(*C*H_3)$_3$), 65.33 (C-*C*PhOH), 84.89 (C-*C*≡*C*-C), 90.73 (*C*≡CSi), 103.76 (≡*C*-SiMe_3), 125.79–128.82 (*o*-, *m*-, *p*-*C*H), 141.06 ppm (*ipso*-*C*); IR ($CDCl_3$): $\tilde{\nu}$ = 3573 (O–H), 2962 (C–H), 2174 (C≡C), 1600, 1490, 1451 (aromatic), 1252 (C–Si), 1046 cm^{-1} (C–O); MS (DCI/NH_3): *m/z*: 430 $[M+NH_4-H_2O]^+$, 413 $[M+H-H_2O]^+$.

1,8-Bis(trimethylsilyl)-3,6-dimethoxy-3,6-diphenylocta-1,4,7-triyne (32): A solution de *n*-butyllithium (2.2 mL, 5.50 mmol) was added through a syringe to a solution of triynediol **31** (1.18 g, 2.75 mmol) in THF (20 mL) at −78 °C. After stirring for 10 min at −78 °C, iodomethane (2.74 mL, 44 mmol) was added and the temperature allowed to reach −25 °C before DMSO (0.4 mL, 5.5 mmol) was added. After 1 h at −25/−20 °C, stirring was continued for 15 h at RT. After addition of a saturated aqueous NH_4Cl solution and extraction with Et_2O, the organic layers were combined, washed with brine, dried with $MgSO_4$, filtered, and evaporated to dryness. Compound **32** was thus obtained as a spectroscopically pure orange oil (1.23 g, 97%). R_f ≈ 0.53 (heptane/acetone 8:2); MS (DCI/NH_3): *m/z*: 444 $[M+NH_4-MeOH]^+$, 427 $[M+H-MeOH]^+$; NMR analysis was consistent with previously reported data.[10] Crystals slowly separated from the oily product and were analyzed by means of X-ray crystallography (*meso* isomer, Figure 4, left).

4,7,13,16-Tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (3e): A solution of triyne **33** (500 mg, 1.59 mmol) in THF (200 mL) was treated with *n*BuLi (1.4 mL, 3.18 mmol) at −78 °C. The solution was allowed to warm up to −20 °C over a 30 min period and then stirring was continued for 15 min. After cooling back to −78 °C, a solution of dialdehyde **22** (590 mg, 1.59 mmol) in THF (200 mL) was added dropwise. Stirring was continued for 30 min at −78 °C and the temperature allowed to rise to −20 °C over a 30 min period. Stirring was then continued for 2 h at this temperature and finally for 30 min at RT. After treatment with a saturated aqueous NH_4Cl solution and extraction with Et_2O, the organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Chromatography on silica gel (heptane/EtOAc 7:3) gave **3e** as a yellow powder (130 mg, 12%). R_f ≈ 0.28 (heptane/EtOAc 5:5); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.57–2.75 (m, 2H; O*H*), 3.34–3.57 (m, 12H; OCH_3), 5.28–5.34 (m, 2H; C*H*-OH), 7.32–7.37 (m, 12H, *m*-, *p*-C*H*), 7.66–7.74 ppm (m, 8H; *o*-C*H*); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 52.10 (*C*HOH), 53.17 (PhC-OCH_3), 71.58 (Ph*C*-OCH_3), 81.67, 83.31, 83.48, 84.08 (*C*≡C), 126.26–128.95 (*o*-, *m*-, *p*-*C*H), 139.02 (*ipso*-*C*-C-OMe) ppm; IR ($CDCl_3$): $\tilde{\nu}$ = 3584 (O–H), 2956–2935 (C–H), 2826 (OC–H), 1600, 1490, 1450 (aromatic), 1064 cm^{-1} (C–O); MS (DCI/NH_3): *m/z*: 702 $[M+NH_4]^+$, 653 $[M+H-MeOH]^+$.

Byproducts, each corresponding to a single TLC spot, were isolated and assigned to the general formula H–C≡C–CPh(OMe)–[C≡C–CPh(OMe)–C≡C–CH(OH)–C≡C–CPh(OMe)]$_{2n}$–C≡C–CPh(OMe)–C≡C–H, according to their ^{1}H NMR spectrum and integration thereof. In particular for *n* = 0 (**33**), *n* = 1 (**34a**), and *n* = 3: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.5–3.5 (m, 2*n*H; O*H*), 3.40–3.50 (m, 6(2*n*+1)H; OCH_3), 5.15–5.25 (m, 2*n*H; C*H*-OH), 7.20–7.35 (m, 6(2*n*+1)H; *m*-, *p*-C*H*), 7.65–7.75 ppm (m, 4(2*n*+1)H; *o*-C*H*).

4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-dione (3f): A chromatographically purified sample of [6]pericyclynediol **3e** (70%, 85 mg, 0.076 mmol) and nonaynediol **34a** (30%, 0.033 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with MnO_2 (162 mg, 1.86 mmol) for 1 h at 0 °C. Stirring was continued for 1 h 30 min at RT and then the solution was filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/EtOAc 8:2) gave **3f** as a yellow oil (10 mg, 20%). R_f ≈ 0.44 (heptane/EtOAc 6:4). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.44–3.62 (m, 12H; OCH_3), 7.25–7.44 (m, 12H; *m*-, *p*-C*H*), 7.63–7.73 ppm (m, 8H: *o*-C*H*); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 53.73 (OCH_3), 71.78 (Ph*C*-OCH_3), 83.84, 83.96, 84.90, 88.51 (C≡*C*), 126.28–128.69 (*o*-, *m*-, *p*-CH), 137.42 (*ipso*-*C*-C-OMe), 158.92 ppm (*C*=O); IR ($CDCl_3$): $\tilde{\nu}$ = 2956–2931 (C–H), 2827 (OC–H), 1638 (C=O), 1451 (aromatic), 1068 cm^{-1} (C–O); MS (DCI/NH_3): *m/z*: 698 $[M+NH_4]^+$, 649 $[M+H-MeOH]^+$.

3,6,12,15,21,24-Hexamethoxy-3,6,12,15,21,24-hexaphenyl-1,4,7,10,13,16,19,22,25-nonayne-9,18-dione (34b): This compound was produced from **34a** in the above described procedure starting from a 70:30 **3e**/**34a** mixture. It was isolated as a pale yellow oil (23 mg, 70%). R_f ≈ 0.35 (heptane/EtOAc 6:4); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.79 (s, 2H; C≡C*H*), 3.52–3.54 (m, 18H; OCH_3), 7.34–7.40 (m, 18H; *m*-, *p*-C*H*), 7.65–7.76 ppm (m, 12H; *o*-C*H*); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): δ = 53.41, 53.86, 53.94 (OCH_3), 71.65, 71.88 (Ph*C*-OCH_3), 75.78 (C≡*C*H), 80.24, 81.94, 83.99, 84.68, 84.96, 86.38, 88.47, 89.25 (*C*≡C), 126.38–129.63 (*o*-, *m*, *p*-CH), 137.83, 138.09, 139.24 (*ipso*-*C*-C-OMe), 158.97 ppm (*C*=O); IR ($CDCl_3$): $\tilde{\nu}$ = 3305 (spC–H), 2958–2935 (C–H), 2828 (OC–H), 1640 (C=O), 1450 (aromatic), 1068 cm^{-1} (C–O); MS (DCI/NH_3): *m/z*: 1012 $[M+NH_4]^+$.

1-Trimethylsilylpenta-1,4-diyn-3-ol (37): A solution of acetylene in THF (200 mL), saturated by prolonged bubbling at 0 °C, was treated with a solution of EtMgBr (13 mL, 39 mmol). After stirring for 1 h at 4 °C, trimethylsilylpropynal (**36**) (5.00 g, 39 mmol) was added and stirring was continued for 17 h at RT. After addition of saturated aqueous NH_4Cl (30 mL) and Et_2O (50 mL), the organic layer was separated and washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (10 mL). The combined aqueous layers were again extracted with Et_2O (2 × 15 mL) and the combined organic layers dried with $MgSO_4$, filtered, and concentrated to dryness. Analytically pure product **37** was obtained (5.77 g, 98%). ^{1}H NMR ($CDCl_3$): δ = 0.16 (m, 9H; Si(CH_3)$_3$), 2.55 (2s, 1H; ≡C-H), 2.63 (s, 1H; O*H*), 5.09 ppm (s, 1H; C*H*(OH)); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −0.58 (Si(CH_3)$_3$), 52.09 (*C*H(OH)), 72.72 (≡*C*-H), 80.50 (*C*≡CH), 89.6 (*C*≡C-SiMe_3), 101.04 ppm (≡C-SiMe_3); IR ($CDCl_3$): $\tilde{\nu}$ = 3434 (O–H), 3307 (spC-H), 2249 (C≡C), 1254 cm^{-1} (C–Si); MS (DCI/NH_3): *m/z*: 187 $[M+N_2H_7]^+$, 174 $[M+NH_4]^+$.

1,8-Bis(trimethylsilyl)octa-1,4,7-triyne-3,6-diol (38): A solution of diynol **37** (3.29 g, 21.64 mmol) in THF (50 mL) at −78 °C was treated with a solution of EtMgBr (3 M, 15.15 mL, 45.45 mmol). After stirring for 20 min at −78 °C, then for 2 h at RT, the solution was cooled back to −78 °C and a solution of trimethylsilylpropynal (**36**) (4.91 g, 38.95 mmol) in THF

(60 mL) was added. Stirring was continued overnight and saturated aqueous NH_4Cl (100 mL) and Et_2O (50 mL) were added. The organic layer was separated and washed again with a saturated aqueous NH_4Cl solution (3×60 mL). The combined aqueous layers were extracted with Et_2O (2×30 mL) and the combined organic layers dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (heptane/EtOAc 9:1) to afford **38** as a brown oil (2.87 g, 47%). ^{1}H NMR ($CDCl_3$): $\delta=0.14$ (s, 9H; Si(CH_3)$_3$), 4.15 (br s, 2H; O*H*), 5.17 ppm (br s, 2H; C*H*OH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=-0.37$ (Si(*C*H$_3$)$_3$), 52.22 (*C*HOH), 81.31 (C-*C*≡*C*-C), 89.90 (*C*≡CSi), 101.18 ppm (C≡*C*-Si); IR ($CDCl_3$): $\tilde{\nu}=3585$ (free O–H), 3392 (bound O–H), 2962, 2900 (sp^{3}C–H), 2178 (C≡CSi), 1410, 1374, 1294, 1253 (Si–C), 1135, 1042 cm^{-1} (C–O); MS (DCI/NH_3): *m*/*z* (%): 296 (100) $[M+NH_4]^+$.

Crystals slowly separated from the oily product and were analyzed by means of X-ray crystallography (*meso* isomer, Figure 4, right).

1,8-Bis(trimethylsilyl)-3,6-dimethoxyocta-1,4,7-triyne (39): A solution of *n*-butyllithium (2.5 M in hexane, 0.29 mL, 0.719 mmol) was added through a syringe to a solution of triynediol **38** (100 mg, 0.36 mmol) in Et_2O (2 mL) at −80 °C. After stirring for 1 min, a solution of methyl triflate (0.155 mL, 0.144 mmol) was added and stirring was continued overnight at 0 °C. A saturated aqueous K_2CO_3 solution was added and the mixture extracted with Et_2O. The organic layer was washed with a saturated aqueous K_2CO_3 solution, then with water, dried with $MgSO_4$, and concentrated to leave crude **39** with acceptable purity (105 mg, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.16$ (s, +18H (slight excess); Si(CH_3)$_3$), 3.40 (s, 6H; OCH_3), 4.96 ppm (2m, 2H; C*H*OMe); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): $\delta=-0.35$ (Si(*C*H$_3$)$_3$), 54.66 (O*C*H$_3$), 60.16 (*C*HOMe), 80.24 (C-*C*≡*C*-C), 91.04 (*C*≡CSi), 98.79 ppm (≡*C*-Si); IR ($CDCl_3$): $\tilde{\nu}=$ 2961, 2902 (sp^{3}C–H), 2827 (OC–H), 2176 (C≡CSi), 1463, 1252 cm^{-1} (C–Si); MS (DCI/NH_3): *m*/*z*: 324 $[M+NH_4]^+$.

3,6-Dimethoxyocta-1,4,7-triyne (35): A solution of TBAF (1 M in THF, 4.06 mL, 4.06 mmol) was added through a syringe to a solution of triyne **39** (622 mg, 2.03 mmol) in THF (35 mL) at −80 °C. After stirring for 15 min, the mixture was quenched with water and extracted with diethyl ether. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure to give crude **35** as a black oil of acceptable purity (278 mg, 84%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=2.54$ (m, 2H; ≡C-*H*), 3.39 (s, 12H; OCH_3), 4.96 ppm (s, 2H; C*H*OMe); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): $\delta=54.63$ (OCH_3), 59.40 (*C*HOMe), 74.10 (≡*C*-H), 80.08 ppm (C-*C*≡) + masked peak under the $CDCl_3$ signal; IR ($CDCl_3$): $\tilde{\nu}=3306$ (C≡CH), 2935 (sp^{3}C–H), 2123 (C≡CH), 1463 cm^{-1}; MS (DCI/NH_3): *m*/*z*: 180 $[M+NH_4]^+$.

1,8-Bis(trimethylsilyl)octa-1,4,7-triyne-3,6-dione (40): MnO_2 (6.294 g, 72.34 mmol) was added to a solution of diol **38** (1.02 g, 3.6 mmol) in dichloromethane (150 mL) at 0 °C. After stirring for 30 min at 0 °C, then for 1.5 h at RT, the reaction mixture was filtered through a small pad of Celite. The filtrate was evaporated to dryness and the residue purified by chromatography on silica gel (heptane/EtOAc 97:3). The product decomposed on silica gel (dragging spot), but minute quantities of pure compound **40** were obtained as a brown oil (0.030 g, 3%). $R_f=0.58$ (heptane/EtOAc 7:3); ^{1}H NMR ($CDCl_3$): $\delta=0.27$ ppm (s; Si(CH_3)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=-1{,}00$ (Si(*C*H$_3$)$_3$), 83.80 (C-*C*≡*C*-C), 101.28 (*C*≡CSi), 104.19 (C≡*C*-Si), 158.53 ppm (*C*=O); IR ($CDCl_3$): $\tilde{\nu}=2963$ (sp^{3}C–H), 2156 (C≡C), 1639 (C=O), 1254 (Si–C), 1206 cm^{-1}; MS (DCI/NH_3): *m*/*z* (%): 292 (100) $[M+NH_4]^+$.

4,7-Diphenyl-4,7,13,16-tetramethoxycyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (3g): A solution of *n*-butyllithium (2.5 M in hexane, 0.45 mL, 1.25 mmol) was added through a syringe to a solution of triyne **35** (101 mg, 0.62 mmol) in THF (15 mL) at −80 °C. After stirring for 5 min, a solution of dialdehyde **22** (233 mg, 0.62 mmol) in THF (5 mL) was added. The mixture was stirred at −80 °C for 1.5 h, then at 0 °C for 2.5 h, and finally poured into a mixture of saturated aqueous NH_4Cl and diethyl ether. The organic layer was separated, washed with saturated aqueous NH_4Cl, dried with $MgSO_4$, and concentrated under reduced pressure to give a brown residue which was purified by chromatography twice on silica gel (first with heptane/EtOAc 6:4, secondly with heptane/EtOAc 7:3). A fraction containing the pericyclyne **3g** as the major product was obtained as a pale yellow solid (5 mg, <2%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=3.39$–3.60 (m, 12H; OCH_3), 5.04 (m, 2H; C*H*OMe), 5.25 (m, 2H; C*H*OH), 7.32–7.36 (m, 6H; *m*-, *p*-C*H*), 7.66–7.73 ppm (m, 4H; *o*-C*H*); ^{13}C NMR (50 MHz, $CDCl_3$, high dilution: quaternary carbon signals not unambiguously detected): $\delta=52.21$ (*C*HOH), 53.44, 54.88 (O*C*H$_3$), 59.63 (*C*HOMe), 126.48, 128.49, 129.07 ppm (*o*-, *m*-, *p*-*C*H); MS (DCI/NH_3): *m*/*z*: 550 $[M+NH_4]^+$.

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