On Ring Carbomers of Cyclobutane, Cyclopentane, and Cyclodecane and Cyclization Reactions through Bis(alkynyl-propargyl) Coupling

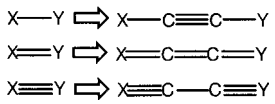
Luc Maurette, Cyril Godard, Silvana Frau, Christine Lepetit, Michèle Soleilhavoup, and Remi Chauvin*[a]

Abstract: A copper-mediated procedure for terminal alkynyl-propargyl coupling has been applied to "skipped" bisterminal undecatetrayne and 1,4-bis-(pseudo)halobut-2-ynes with the aim of preparing ring carbomers of representative strained and loose cycloalkanes, namely [*N*]pericyclynes. Two unprecedented, cyclic, "skipped" polyynes with CH_2 vertices have been isolated as mixtures of diastereoisomers: an isomer **1b** and a dimer **2a** of [5]pericyclyne **1a**. The isomer **1b** is a cyclotetrayne with an exocyclic allene function resulting from a unique formal S_N' process. Its structure has been established by $^1H/^{13}C$ HMQC and HMBC two-dimensional NMR analysis. According to density functional theory calculations, it is about 6 kcal mol^{-1} more stable than [5]pericyclyne (**1a**). Compound **1b** can also be regarded as a C13-relaxed [4]pericyclyne, a long sought "skipped" C12 tetrayne. The dimer **2a** is a C30 ring that results from a formal S_N process. It is a stable ring carbomer of cyclodecane, that is, a [10]pericyclyne, with four CH_2 vertices.

Keywords: alkynyl-propargyl coupling · carbomers · cyclization · density functional calculations · pericyclynes

Introduction

The fascination exerted by carbon-rich molecules stems from the peculiar status of the carbon element and from the combination of their extended size and high rigidity, which allows for simple pure geometrical representations.[1] This can be reconsidered and generalized through the formal definition of a "carbomer" structure,[2] in which the connectivity, π-resonance properties, symmetry, and shape of its antecedent are preserved, but in which the number of bonds, and thus the approximate size, is increased by a factor of three (Scheme 1).



Scheme 1. Basic process of definition of carbomers.[2]

Beyond the intellectual interest, that is, the comparison of any property of a molecule with that of its carbomer, this formalism has proved to be useful as a tool for suggesting novel synthetic targets. At the outset, however, it was anticipated that triple-bond-rich molecules would be highly reactive, and that strained cyclic polyynes would even be unstable or explosive.[3] Nevertheless, electron delocalization, aromaticity, and homoaromaticity resulting from acyclic or cyclic conjugation and homoconjugation are expected to contribute to their stabilization.

Through recent experimental and theoretical results, aromatic stabilization has proved to be a promising strategy. Although [C,C]$_6$carbobenzene itself is still unknown,[4] hexa- and tri-aryl derivatives have been described as new members of the family of dehydro[18]annulenes.[5, 6] On the other hand, a density functional theory (DFT) exploration has shown that the ring carbomers of aromatic (or antiaromatic) [*N*]annulene molecules and ions are aromatic (or antiaromatic) according to structural, magnetic, and energetic criteria.[7]

It is anticipated that homoaromaticity will produce more subtle effects.[8] However, owing to the well documented effects of transannular π-overlaps in cyclopolyynes,[9] in-plane homoaromaticity is a good candidate for stabilizing ring carbomers of cycloalkanes. These cyclic homoconjugated polyacetylenes, also called [*N*]pericyclynes or "exploded cycloalkanes", have been the concern of several groups in the recent past.[10] Functional hexaoxy[6]pericyclynes (which served as precursors of [C,C]$_6$carbobenzene derivatives)[6] and several decaalkyl [5]pericyclynes have been described,[10] but no [4]pericyclyne has been described.[11] By contrast, second-generation ring carbomers, namely cyclic homoconjugated

[a] Prof. R. Chauvin, L. Maurette, C. Godard, Dr. S. Frau, Dr. C. Lepetit, Dr. M. Soleilhavoup
Laboratoire de Chimie de Coordination, UPR 8241
205 Route de Narbonne, 31077 Toulouse cedex 4 (France)
Fax: (+33) 5-61-55-30-03
E-mail: chauvin@lcc-toulouse.fr

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polydiacetylenes, are known for $N \geqslant 4$ in the dioxy-substituted series.[12] The study of functional [5]pericyclynes, which might also be interesting as precursors to $[C,C]_5$-carbocyclopentadienyl cation,[2] and higher [*N*]pericyclynes is thus a natural challenge. It is tackled here by aiming at a cyclization by bis(alkynyl-propargyl) coupling.

Results and Discussion

It was thought that pericyclynes **1a** and **2a** would come from the tetrayne **4a** and the 1,4-bis[(pseudo)halo]but-2-ynes **3a–d**. The reactions correspond to [1+1] and [2+2] cyclizing bis(alkynyl-propargyl) S_N processes. However, it was also thought that the respective allenyne isomers **1b** and **2b** could come from a competitive S_N' processes (Scheme 2).

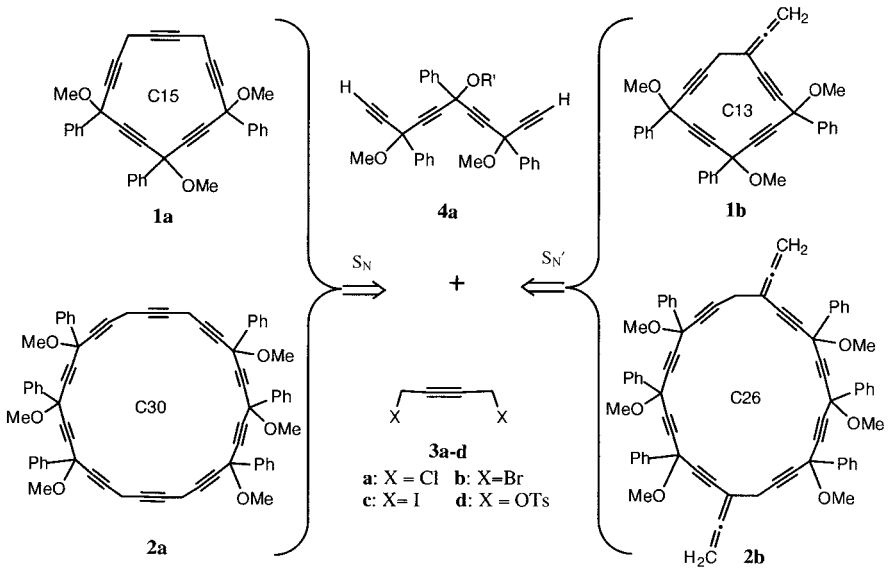
The synthesis of the dialkynyl reactant **4a** (a mixture of three diastereoisomers) from bis(trimethylsilyl)acetylene was achieved in six steps through the new compounds **7** and **8** in 60% overall yield (Scheme 3).

Alkynyl–propargyl coupling has to be mediated by cuprous salts, in either catalytic or stoichiometric quantities, whatever the acetylide metal is (MgX, Na, K).[13] The bispropargylic reactivity and the cyclic versus open-chain selectivity is a double challenge that has to be overcome. Moreover, the two CH_2 vertices in structure **1a** make this [5]pericyclyne target a priori fragile. Mild conditions were thus required. Indeed, the use of M = MgBr in the presence of catalytic CuCl and heating under reflux in THF for 16 hours mainly produced the monocoupled product **8a** (See Scheme 6, below). One procedure established for mono(alkynyl-propargyl) coupling could be suitable: it resorts to a three-component mixture of reagents in DMF at room temperature, that is, CuI, Na_2CO_3 and $[n\mathrm{Bu}_4\mathrm{N}]^+[\mathrm{Cl}]^-$.[14]

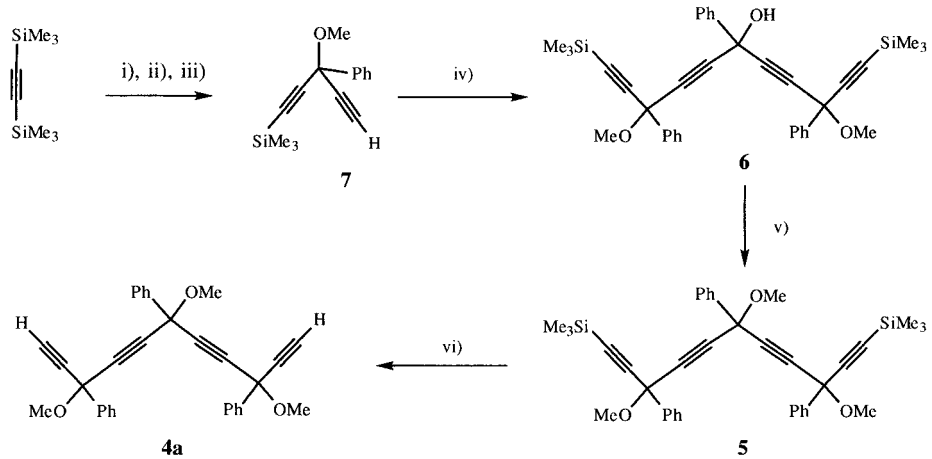
The reaction of **4a** with four 1,4-dihalo- or bispseudohalobut-2-yne **3a–d** (X = Cl, Br, I, OTs) in the presence of CuI and M_2CO_3 (M = Na, K, Cs) was thus investigated. As in classical mono(alkynyl-propargyl) couplings, the chloride **3a** alone did not react with **4a**, better leaving groups were required. In the presence of dissociated iodide ions of NaI (the CuI is not sufficient), the dichloride **3a** is converted in situ to **3c** and can be used in a bifunctional version of a modified procedure by using CuI and K_2CO_3 in DMF.[15] Nevertheless, in our case, the reaction was slow, even slower than the **3c** → **3e** isomerization (Scheme 4).[16]

Unexpectedly, **4a** also exhibited a very low reactivity toward the dibromide **3b**, even in high excess in the presence of Na_2CO_3 and $n\mathrm{Bu}_4\mathrm{NCl}$. This lack of reactivity of the *poly*-yne **4a** toward propargyl bromides was verified with the monofunctional reactant $CH_3C{\equiv}CCH_2Br$.

Finally, **4a** was successfully reacted, with about 50–60% conversion, with the ditosylate **3d** in the presence of Na_2CO_3 and $[n\mathrm{Bu}_4\mathrm{N}]^+[\mathrm{Cl}]^-$ (method A). Most of the products were isolated by sequential chromatography. The isolation of chlorinated products from the reaction mixture (e.g. **8b** and **10**, see Scheme 6, below) showed that the chloride ions act as cyclization inhibitors. We found that free chloride ions of $[n\mathrm{Bu}_4\mathrm{N}]^+[\mathrm{Cl}]^-$ can be replaced by free iodide ions of NaI (method B).[17]



Scheme 2. Putative cyclizing S_N and S_N' processes in bis(alkynl-propargl) coupling of **3** and **4a**.



Scheme 3. Synthesis of **4a** i) $PhCOCl/AlCl_3$, CH_2Cl_2, 91%; ii) $C_2H_2/EtMgBr$, THF, 91%; iii) *n*BuLi, THF, CH_3I/DMSO; 95%; iv) *n*BuLi, THF, −78 °C, then 0.5 equiv PhCOCl, and then NH_4Cl aq; 90%; v) *n*BuLi, THF, CH_3I/DMSO, 85%; vi) K_2CO_3, MeOH; quant.

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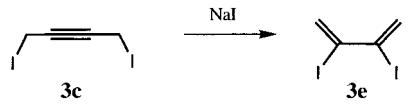
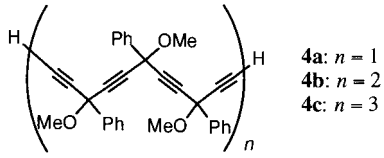


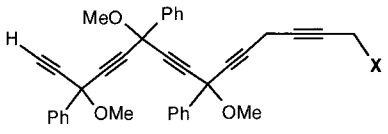
Scheme 4. Isomerisation of 1,4-diodobut-2-yne to 2,3-diodobutadiene.

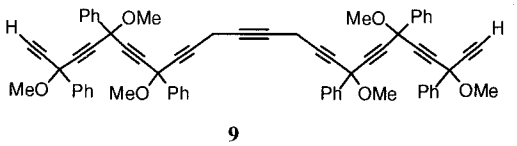
By using methods A or B, three types of products can be distinguished:

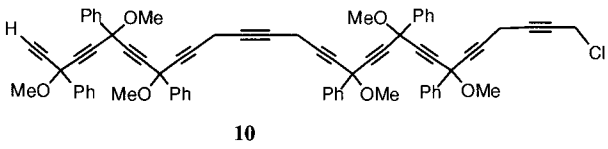
1) Recovered starting material **4a** and Eglinton C_{sp}–C_{sp} coupling byproducts (**4b**, **4c**, Scheme 5).[18]



Scheme 5. Starting material and Eglinton coupling products.





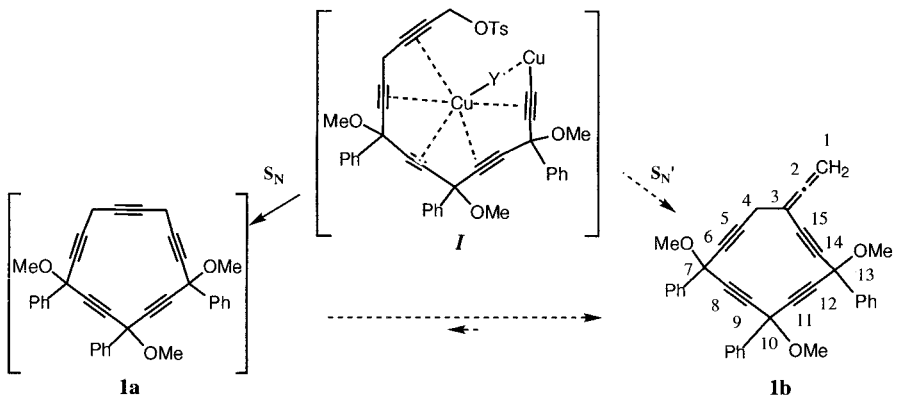


Scheme 6. Acyclic "skipped" polyynes isolated from the reaction of **4a** with **3d** (method A or B).

2) Acyclic "skipped" polyynes (Scheme 6). Compound **8b** (4% yield, mixture of four chiral diastereoisomers, method A) results from quenching the desired [1+1] cyclization with chloride ions. Compounds **9** (ca. 1% isolated yield, method A or B) and **10** (ca. 1% isolated yield, mixture of 32 chiral diastereoisomers, method A) come from quenching the [2+2] cyclization by chloride ions.
3) Cyclic "skipped" polyynes and allenyne. Although nothing is clearly established concerning the mechanism of the reaction, one may suppose that a binuclear intermediate ***I*** that involves two copper atoms bridged by an halide atom (Y = Cl or I) could lead to i) **1a** by a S_N process and to ii) **1b** by a S_N' process (Schemes 2 and 7). Compounds **1a** and **1b** are isomers, but only **1b** could be reproducibly isolated as a mixture of four chiral diastereoisomers.

The fascinating structure of **1b** was studied in $CDCl_3$ by two-dimensional $^1H/^{13}C$ HMQC and HMBC NMR experiments (Figure 1a and b). Since the stereocenters are quite far from each other, average signals could be assigned for the diastereomeric mixture. The corresponding short-range (^1J(C,H)) and long-range (^2J(C,H), ^3J(C,H)) correlations confirmed the topology and topography of the molecule. The sp^3 and sp^2 CH_2 units have been assigned by a ($\delta_{^1H}$, $\delta_{^{13}C}$) cross-peak spectrum as being at $\delta = 3.21$, 25.21 and $\delta = 5.03$, 78.55, respectively, in the HMQC (Figure 1a). The ^1H NMR signals of the sp^2 and sp^3 CH_2 unit gave two cross peaks with the sp allenic ^{13}C NMR signal at $\delta = 213.94$ in the HMBC spectrum (Figure 1b). Finally, from the HMBC spectrum, correlation peaks of the CH_2 protons indicate that the quaternary sp^2 C3 carbon atom occurs at $\delta = 83.79$. It is of note that all the characteristic signals of the exocyclic methyleneallenyl group are quite sharp and have a common ^1H and ^{13}C NMR behavior in all the diastereoisomers.

Since the mixture rules out the possibility of crystallizing **1b** to acquire an X-ray structure, this compound was modeled theoretically. DFT calculations at the B3PW91/6-31-G** level showed that, in their ground-state-optimized structures, a model for one diastereoisomer of **1b** (*cis-trans-cis*, where the phenyl and methyl groups are replaced by H atoms) is 5.7 kcal mol^{-1} more stable than the corresponding model for **1a** (Figure 2).[19] Thus, **1b**, which is the sole formal S_N' product, is also the thermodynamic product. If the S_N' process is also kinetically disfavored, a right-shifted **1a** ⇌ **1b** isomerization equilibrium could occur in a second step (Scheme 7). This cyclic C13 "skipped" tetrayne can be regarded as a one-carbon relaxation of a [4]pericyclyne, a long sought C12 "skipped" cyclotetrayne,[20] where a vertex is replaced by a single C_{sp^3}–C_{sp^2} bond. The calculated structure of the allenyl-[4]pericyclyne isomer of the models of **1a** and **1b** is less stable than these models (Figure 2). To the best of our knowledge, although many conjugated C12 cyclotetraynes are known,[21] **1b** is the smallest CH_2-"skipped" cyclotetrayne known



Scheme 7. Kinetic and thermodynamic relationships between isomers **1a** and **1b**. Atom numbering in **1b** is indicated for two-dimensional NMR analysis (Figure 1).

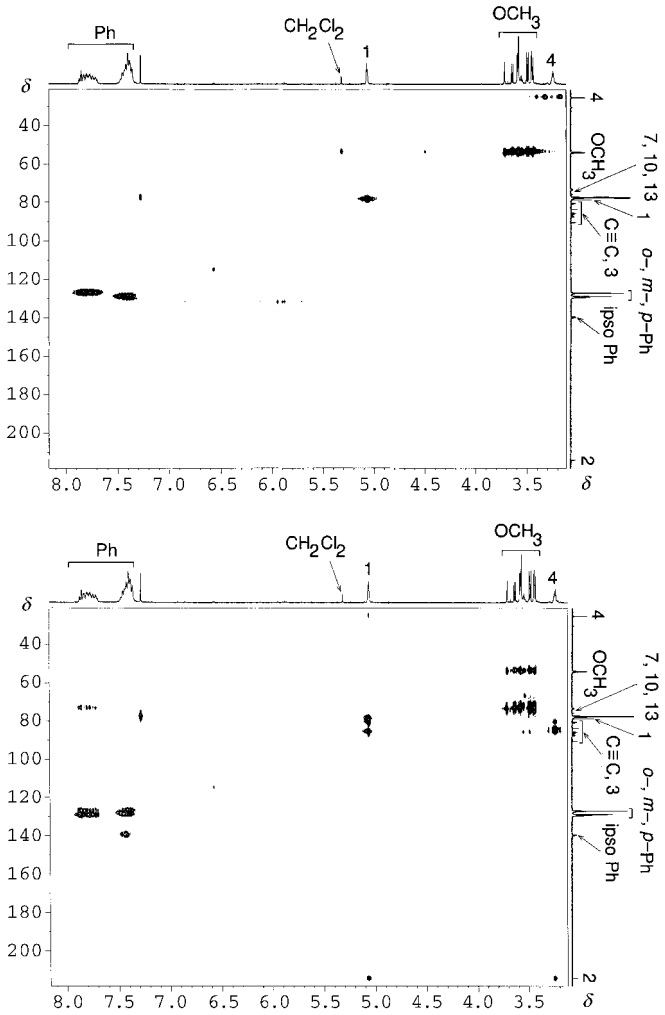


Figure 1. 400 MHz two-dimensional $^1H/^{13}C$ NMR spectra of molecule **1b** in $CDCl_3$ at RT (traces of CH_2Cl_2 occur at ^1H NMR $\delta = 5.35$). a) HMQC spectrum indicating the short-range ($^1J(C,H)$) correlations. b) HMBC spectrum indicating the long-range C-H correlations. The $\{^1H\}$ decoupling width of the ^{13}C spectrum is 150 ppm; a residual multiplet coupling pattern is thus observed for the sp^3-CH_2 (4) unit in the HMQC diagram.

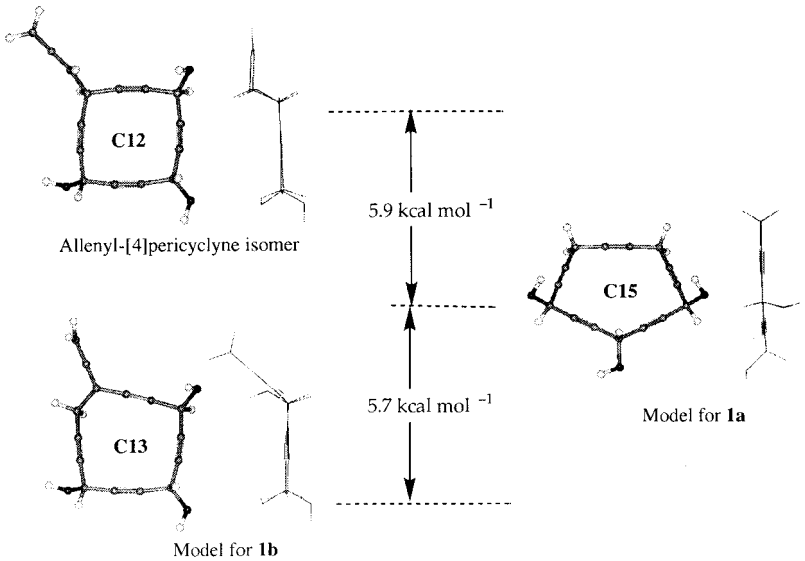


Figure 2. Calculated (B3PW91/6-31G**) structures of relevant models for [5]pericyclyne **1a**, its isomer **1b**, and a hypothetical allenyl-[4]pericyclyne isomer.

to date.[22] Compound **1b** would also be the first example of a molecule that displays a α-alkynyl-α-propargyl allene pattern. The triple bonds are closer to each other in **1b** than in **1a**: the stability of the strained quasi-planar structure **1b** may originate from transannular interactions between all four in-plane π orbitals.

The cyclic "skipped" decayne **2a** was also isolated (4% yield, method A) as a mixture of a priori 14 diastereoisomers (six of them being chiral: 20 stereoisomers). In accordance with the recognized kinetic S_N/S_N' selectivity of the alkynyl-propargyl coupling procedure,[13] isomeric S_N' products such as **2b** are not detected. To the best of our knowledge, compound **2a** is the first example of a [10]pericyclyne with CH_2 vertices. It is also a cyclic dimer of **1a** and **1b**. Despite the presence of two $\equiv C-CH_2-C\equiv C-CH_2-C\equiv$ sequences, the molecule is stable and does not isomerize to the conjugated diene form $\equiv C-CH=CH-CH=CH-C\equiv$. However, although orbital interactions and partial transannular overlaps between triple bonds can occur, the high flexibility of the structure rules out the possibility of a 20-electron in-plane homoaromaticity in a planar structure. This has been confirmed by a simple MM (CVFF) calculation of the geometry of **2a**.

In conclusion, the isolation of **2a** and **1b**, related as dimer and isomer of **1a**, respectively, is a step forward in the study of [*N*]pericyclynes. In particular, the stability of functional strained (**1b**) and loose (**2a**) "skipped" cyclopolyynes does not require all quaternary vertices. These molecules are potential precursors for rearrangement-aromatization to the hypothetical ring carbomers of charged [5]- and [10]annulenes.

Experimental Section

DMF was distilled over drierite, and THF and diethyl ether were distilled over Na/benzophenone before use. Commercial-synthesis grade pentane and dichloromethane were degassed by bubbling argon though them before use. Dry DMSO was purchased from SDS, and *n*BuLi was purchased from Aldrich as a 1.6 M solution in hexane. Compound **7** was prepared from bis-(trimethylsilyl)acetylene in three steps by following a previously described procedure.[6] Ditosylate **3d** was synthesized as previously reported.[23] IR spectra were recorded on a Perkin-Elmer GX FT-IR spectrometer with a CaF_2 cell. One-dimensional NMR spectra were recorded on a Brucker AC200 spectrometer at 200 MHz for ^1H and 50 MHz for ^{13}C. Two-dimensional NMR spectra were recorded on a Brucker AMX400 apparatus. Positive chemical shifts at low field are expressed in ppm by internal reference to TMS.

Bis(trimethylsilyl)-6-hydroxy-3,9-dimethoxy-3,6,9-triphenylundeca-1,4,7,10-tetrayne(6): *n*BuLi (35.6 mL, 57.5 mmol) was added dropwise to a solution of **7** (13.93 g, 57.5 mmol) in THF (100 mL) at $-78\,^\circ C$. After the mixture had been stirred for 10 min at $-78\,^\circ C$, benzoyl chloride (3.3 mL, 28.4 mmol) was added, and the mix-

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ture was then stirred for 3 h at RT. The mixture was diluted with diethyl ether (100 mL) and extracted twice with saturated aqueous NH_4Cl. The organic phase was dried over Na_2SO_4, concentrated under reduced pressure, and the crude oily residue chromatographed on silica gel (hexane/EtOAc 9:1). Product **6** was obtained as a deep orange oil. Yield: 13.04 g, 77%; $R_f = 0.40$ (heptane/EtOAc 9:1); ^{1}H NMR ($CDCl_3$): $\delta = 0.21$ (s, 18H; $Si(CH_3)_3$), 3.04 (s, 1H; OH), 3.46–3.56 (m, 6H; OCH_3), 7.27–7.34 (m, 9H; *m*- and *p*- C_6H_5), 7.71–7.73 (m, 6H; *o*-C_6H_5); ^{13}C NMR ($CDCl_3$): –0.22 (q, ^1J(C,H) = 120 Hz, $Si(CH_3)_3$), 53.30 (q, ^1J(C,H) = 143 Hz, OCH_3), 65.30 (s, ≡C*C*(OH)PhC≡), 72.22 (s, ≡C*C*(OCH_3)PhC≡), 83.36 and 86.30 (2s, C*C*≡CC), 92.61 (s, *C*≡CSi), 101.39 (s, ≡C-Si), 124.80–130.46 (m, *o*-, *m*-, *p*-C_6H_5), 139.72 (m, *ipso*-C_6H_5C-OMe), 141.15 (m, *ipso*-C_6H_5C-OH); IR ($CDCl_3$): 3573 (m, $\tilde{\nu}_{OH}$), 3065–2900 (m, $\tilde{\nu}_{Csp^3-H}$), 2827 (m, $\tilde{\nu}_{OCH_3}$), 2176 (w, $\tilde{\nu}_{C\equiv C}$), 1600(w) and 1450 (s) ($\tilde{\nu}_{C=C}$ Ph), 1252 (s, $\tilde{\nu}_{Si-C}$) cm^{-1}.

Bis(trimethylsilyl)-3,6,9-trimethoxy-3,6,9-triphenylundeca-1,4,7,10-tetrayne (5): A solution of *n*BuLi (24.3 mmol) in *n*-hexane (15.2 mL) was syringed into a solution of **6** (13.04 g, 22.2 mmol) in THF (200 mL) at –78 °C. After 10 min, CH_3I (11 mL, 177 mmol) was added dropwise. The temperature was allowed to rise to –25 °C, DMSO (3 mL, 42.3 mmol) was added, and the stirring was continued for 1 h at –25 °C and then for 1 h at RT. The mixture was diluted with diethyl ether (300 mL) and washed with saturated aqueous NH_4Cl (125 mL). The solvents were removed under reduced pressure, and the oily residue was chromatographed over silica gel (hexane/EtOAc 9:1). Compound **5** was obtained as a deep orange oil. Yield: 11.62 g, 87%; $R_f = 0.35$ (heptane/EtOAc 9:1); ^{1}H NMR ($CDCl_3$): $\delta = 0.21$ (s, 18H; $Si(CH_3)_3$), 3.48–3.57 (m, 9H; OCH_3), 7.34–7.35 (m, 9H; *m*-, *p*-C_6H_5), 7.71–7.73 (m, 6H; *o*-C_6H_5); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -0.22$ ($Si(CH_3)_3$), 53.30 (OCH_3), 72.30 (≡CC(OMe)PhC≡), 83.36 and 86.30 (C*C*≡CC), 92.61 (*C*≡CSi), 101.39 (≡CSi), 124.80–130.46 (m, *o*-, *m*-, *p*-C_6H_5), 139.72 (m, *ipso*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 620 [*M*+NH_4]$^+$.

3,6,9-Trimethoxy-3,6,9-triphenylundeca-1,4,7,10-tetrayne (4a): K_2CO_3 (4 g, 28.9 mmol) was added to a solution of **5** (3.81 g, 5.94 mmol) in methanol (25 mL). After this mixture had been stirred for 1 h at RT, diethyl ether (100 mL) was added, and the mixture was extracted with water (2 × 50 mL). The organic phase was dried over Na_2SO_4 and concentrated. The crude oil was chromatographed over silica gel (hexane/EtOAc 9:1). Compound **4a** was obtained as a yellow oil. Yield: 2.57 g, 95%; $R_f = 0.35$ (heptane/EtOAc 8:2); ^{1}H NMR ($CDCl_3$): $\delta = 2.76$, 3.77, 3.78 (3s for 3 diastereoisomers, 2H; ≡CH), 3.52–3.56 (m, 9H; OCH_3), 7.34–7.35 (m, 9H; *m*-, *p*-C_6H_5), 7.71–7.73 (m, 6H; *o*-C_6H_5); ^{13}C NMR ($CDCl_3$): $\delta = 53.45$ (q, ^1J(C,H) = 143 Hz, OCH_3), 71.90 (s, ≡C*C*(OMe)PhC≡), 75.55 (d, ^1J(C,H) = 245 Hz, ≡CH), 80.77 (d, ^2J(C,H) = 50 Hz, *C*≡CH), 83.40 and 86.30 (2s, C*C*≡CC), 124.80–130.46 (m, *o*-, *m*-, *p*-C_6H_5), 139.70 (m, *ipso*-C_6H_5); IR (CH_2Cl_2): $\tilde{\nu}$ = 3299 (s, Csp-H), 2900–3000 (m, Csp^3-H), 2827 (m, OCH_3), 2116 (w, C≡C), 1450(w), 1602(s) (C=C Ph) cm^{-1}; MS (DCI/NH_3): *m*/*z*: = 476 [*M*+NH_4]$^+$.

Reaction of 4a with 3d: method A (chloride ions): Na_2CO_3 (69 mg, 0.654 mmol), CuI (83 mg, 0.436 mmol), and [*n*Bu_4N]$^+$[Cl]$^-$ (121 mg, 0.436 mmol) were added to a solution of **4a** (100 mg, 0.218 mmol) in DMF (15 mL) at –20 °C. After 5 min, **3d** (86 mg, 0.218 mmol) was added. The temperature was allowed to rise to RT, and the mixture was then stirred for 48 h. Diethyl ether (100 mL) was added, and the organic phase was then washed with saturated aqueous NH_4Cl (150 mL), dried and concentrated. The residual oil was chromatographed over silica gel (hexane/acetone 8.5:1.5). Five pure oily products were isolated: **2a** (5 mg, 4%), **8b** (5 mg, 4%), **9** (1 mg, 1%), **10** (1 mg, 1%), and **1b** (3 mg , 3%).

Reaction of 4a with 3d: method B (iodide ions): K_2CO_3 (610 mg, 4.41 mmol), CuI (560 mg, 2.94 mmol), and NaI (485 mg, 3.24 mmol) were added to a solution of **4a** (674 mg, 1.47 mmol) in DMF (41 mL) at –20 °C. After 5 min, **3d** (580 mg, 1.47 mmol) was added. The temperature was allowed to rise to RT, and the mixture was then stirred for 21 h at 40 °C. Diethyl ether (250 mL) was added, and the organic phase was then washed with saturated aqueous NH_4Cl (400 mL), dried and concentrated. The residual oil was chromatographed over silica gel (heptane/acetone 9:1). Compounds **1b** (20 mg, 3%) and **2a** (60 mg, 4%) were isolated as orange oils.

12-Ethenylidene-3,6,9-trimethoxy-3,6,9-triphenylcyclotrideca-1,4,7,10-tetrayne (1b): $R_f = 0.45$ (heptane/acetone 8:2); ^{1}H NMR ($CDCl_3$): $\delta = 3.21$ (t, ^5J(H,H) = 2 Hz, 2H; ≡CCH_2C=), 3.37–3.60 (m, 9H; OCH_3), 5.03 (t, ^5J(H,H) = 2 Hz, 2H; CH_2C=C=), 7.25–7.46 (m, 9H; *p*-, *m*-C_6H_5), 7.68–7.83 (m, 12H; *o*-C_6H_5); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 25.21$ (≡C*C*H_2C=), 53.61–54.23 (OCH_3), 72.86–73.54 (≡C-*C*(OMe)Ph-C≡), 78.55 (=C=CH_2), 83.79 (CH_2-*C*=), 83.54–83.73 and 85.33–90.27 (C*C*≡CC), 127.02–127.16 (*o*-C_6H_5), 128.80–129.90 (*m*-, *p*-C_6H_5), 139.30–140.00 (*ipso*-C_6H_5), 213.94 (=C=); ^{13}C NMR ($CDCl_3$): $\delta = 25.21$ (t, ^1J(C,H) = 136 Hz, ≡C*C*H_2C=), 52.95–54.89 (m, OCH_3), 72.80–74.23 (m, ≡C-*C*(OMe)Ph-C≡), 78.55 (t, ^1J(C,H) = 170 Hz, =C=*C*H_2), 83.54–83.73 and 85.33–90.27 (C*C*≡CC), 126.28–130.27 (*o*-, *m*-, *p*-C_6H_5), 139.38–139.80 (*ipso*-C_6H_5), 213.94 (=C=); IR ($CDCl_3$): 2900–3000 (m, $\tilde{\nu}_{Csp^3-H}$), 2827 (m, $\tilde{\nu}_{O-CH_3}$), 2248 (w, C≡C), 1965(w) and 1942(m) ($\tilde{\nu}_{C=C=C}$), 1451(s) and 1601(m) ($\tilde{\nu}_{C=C}$ Ph) cm^{-1}; MS (DCI/NH_3): *m*/*z*: 526 [*M*+NH_4]$^+$.

3,6,9,18,21,24-Hexamethoxy-3,6,9,18,21,24-hexaphenylcyclotriaconta-1,4,7,10,13,16,19,22,25,28-decayne (2a): $R_f = 0.20$ (heptane/acetone 8:2); ^{1}H NMR ($CDCl_3$): $\delta = 3.23–3.25$ (m, 8H; ≡C-CH_2-C≡), 3.46–3.56 (m, 18H; OCH_3), 7.27–7.34 (m, 18H; *m*-, *p*-C_6H_5), 7.71–7.73 (m, 12H; *o*-C_6H_5); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 53.25$ (OCH_3), 71.77 (≡C-*C*(OMe)Ph-C≡C-CH_2), 74.00 (≡C-*C*(OMe)Ph-C≡), 75.26 (CH_2C≡C*C*H_2), 81.47 ((OMe)PhC-C≡*C*CH), 84.00 ((OMe)PhC-*C*≡CCH), 84.91 and 84.87 (C*C*≡CC), 126.44–128.98 (m, *o*-, *m*-, *p*-C_6H_5), 139.49 (m, *ipso*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 1034 [*M*+NH_4]$^+$.

15-Chloro-3,6,9-trimethoxy-3,6,9-triphenylpentadeca-1,4,7,10,13-pentayne (8b): $R_f = 0.15$ (hexane/acetone 8:2); ^{1}H NMR ($CDCl_3$): $\delta = 2.77$ (s, 1H; ≡CH), 3.34 (t, ^5J(H,H) = 2 Hz, 2H; ≡CCH_2C≡), 3.48–3.55 (m, 9H; OCH_3), 4.10 (t, ^5J(H,H) = 2 Hz, 2H; ≡CCH_2Cl), 7.34–7.37 (m, 9H; *m*-, *p*-C_6H_5), 7.72–7.75 (m, 6H; *o*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 562 [*M*+NH_4]$^+$.

3,6,9,18,21,24-Hexamethoxy-3,6,9,18,21,24-hexaphenylhexacosa-1,4,7,10,13,16,19,22,25-nonayne (9): $R_f = 0.20$ (hexane/acetone 7:3); ^{1}H NMR ($CDCl_3$): $\delta = 2.76$ (s, 2H; ≡CH), 3.25 (s, 4H; ≡CCH_2C≡), 3.47–3.53 (m, 18H; OCH_3), 7.31–7.34 (m, 18H; *m*-, *p*-C_6H_5), 7.72–7.74 (m, 12H; *o*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 984 [*M*+NH_4]$^+$.

30-Chloro-3,6,9,18,21,24-hexamethoxy-3,6,9,18,21,24-hexaphenyltriaconta-1,4,7,10,13,16,19,22,25,28-decayne (10): ^{1}H NMR ($CDCl_3$): $\delta = 2.77$ (s, 1H; ≡CH), 3.34 (t, ^5J(H,H) = 2 Hz, 6H; ≡CCH_2C≡), 3.48–3.55 (m, 18H; OCH_3), 4.10 (t, ^5J(H,H) = 2 Hz, 2H; ≡CCH_2Cl), 7.34–7.37 (m, 18H; *o*-, *m*-C_6H_5), 7.72–7.75 (m, 12H; *o*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 1070 [*M*+NH_4]$^+$.

3,6,9,14,17,20-Hexamethoxy-3,6,9,14,17,20-hexaphenyldocosa-1,4,7,10,12,15,18,21-octayne (4b): $R_f = 0.30$ (heptane/acetone 7:3); ^{1}H NMR ($CDCl_3$): $\delta = 2.75$ (s, 2H; ≡CH), 3.51–3.53 (m, 18H; OCH_3), 7.32–7.38 (m, 18H; *m*-, *p*-C_6H_5), 7.68–7.76 (m, 12H; *o*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 932 [*M*+NH_4]$^+$.

3,6,9,14,17,20,25,28,31-Nonamethoxy-3,6,9,14,17,20,25,28,31-nonaphenyltritriaconta-1,4,7,10,12,15,18,21,23,26,29,32-dodecayne (4c): $R_f = 0.20$ (heptane/acetone 7:3); ^{1}H NMR ($CDCl_3$): $\delta = 2.75$ (s, 2H; ≡C*H*), 3.51–3.53 (m, 27H; OCH_3), 7.32–7.38 (m, 27H; *m*-, *p*-C_6H_5), 7.68–7.76 (m, 18H; *o*-C_6H_5); MS (DCI/NH_3): *m*/*z*: 1389 [*M*+NH_4]$^+$.

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