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Synthesis and stereochemical resolution of functional [5]pericyclynes

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Abstract—Three different kinds of ring *carbo*-mers of [5]cyclitol ethers were targeted as challenging examples of functional [5]pericyclynes. Three *tertiary* pentaaryl-*carbo*-[5]cyclitol methyl ethers were synthesized through a [11+4] ring-closing double addition of triphenyl- and tri-*p*-anisyl-undecatetrayn-diides to dibenzoylacetylene. These compounds, obtained as oily mixtures of stereoisomers, are stable and can behave as acetylenic ligands of one or two $Co_2(CO)_6$ units. NMR analysis reveals that the broad diasteroisomeric dispersity of a triether, is consistently reduced in the symmetrized pentaether. Three bis-*secondary* triaryl-*carbo*-[5]cyclitol methyl ethers with adjacent CH(OR) vertices were synthesized through a similar [11+4] ring-closing process, where the same tetrayn-diides add to both the carbaldehyde ends of the (η^2–OCH–C≡C–CHO)$Co_2(CO)_6$ complex. Despite the possibility of tautomeric isomerization, the occurrence of two adjacent bis-propargylic carbinol vertices does not diminish the stability of the [5]pericyclyne framework. Finally, two bis-*secondary carbo*-[5]cyclitol methyl ethers with non-adjacent CH(OH) vertices were synthesized through an alternative [10+5] ring-closing process. The bis-*secondary carbo*-[5]cyclitols are regarded as isohypsic equivalents of the challenging $[C,C]_5$*carbo*-cyclopentadienyl cation. A diphenyl-hexaoxy-[5]pericyclyne with two non-adjacent secondary carbinol vertices was also prepared through a [10+5] ring-closing strategy: this molecule is an isohypsic equivalent of the previously calculated zwitterionic *carbo*-cyclopentadienone, which could be observed as a DCI/NH_3-MS fragment after treatment with $SnCl_2$/HCl. Analytical HPLC showed that the C_{11} triphenyl-undecatetrayne precursor of the [11+4] strategy was obtained as a statistical 1:2:1 mixture of the three possible diastereoisomers. Semi-preparative HPLC allowed for the resolution of this mixture. The pure major diastereoisomer was employed to prepare a partly resolved sample of pentamethoxy-pentaphenyl-[5]pericyclyne. Analytical HPLC showed that the latter corresponds to the statistical distribution of the expected three residual diastereoisomers. Semi-preparative HPLC finally afforded samples of diastereoisomerically pure pentamethoxy-[5]pericyclyne as crystalline solids.

1. Introduction

In the general field of carbon-rich molecules,[1] we have been interested for some time in a carbon 'enrichment' process which could preserve some memory of its poorer parent molecule. Meeting the field of polyacetylenic chemistry,[2] it consists in the linear insertion of two sp carbon atoms into each bond of the parent Lewis skeleton. It is readily checked from basic VSEPR and mesomerism that the resulting '*carbo*-mer' structure preserves essential features of the parent model (connectivity, shape, symmetry, π-resonance, CIP configurations of stereogenic centers), while it has experienced a three-fold size expansion.[3] Focusing on cyclic hydrocarbons, *carbo*-mers of unsaturated rings such as annulenes[4] and radialenes,[5] were theoretically compared in terms of aromaticity. In a more subtle manner, ring *carbo*-mers of saturated cycloalkanes were theoretically compared in terms of *homo*-aromaticity.[6] These '*carbo*-cycloalkanes' are actually [N]pericyclynes, a generic term coined by Scott et al. in 1983 as they reported the synthesis of the first representative, decamethyl[5]pericyclyne (Scheme 1).[7] An octamethyl analogue was later reported.[8] The fascinating structure and stability of these rigid π-electron-rich 15-membered rings then attracted a considerable theoretical interest.[9,2,4,6] Nevertheless, an open question is whether the stability of [5]pericyclynes is compatible with functionalities at the sp^3 vertices. Hexaoxy-[6]pericyclynes,[10a] and expanded peroxy-pericyclynes (made with butadiyne edges and ketal vertices) have been described.[10b] To the best of our knowledge however, beside mentions of few peralkyl-monohydroxy-[5]periclynes,[11] no functional simple [5]pericyclyne was hitherto described in the literature. We focus here on the synthesis of pentaoxy-[5]pericyclynes, which can be alternatively regarded as '*carbo*-[5]cyclitol' derivatives (Scheme 1). Beyond the

Keywords: *Carbo*-mers; Pericyclynes; Cyclization reactions; Acetylenedicarbaldehyde; Diastereoisomeric resolution.

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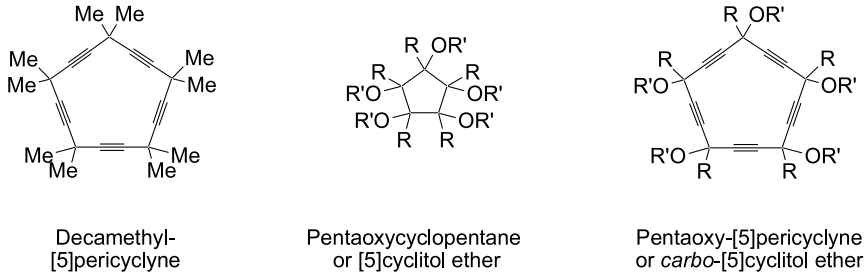
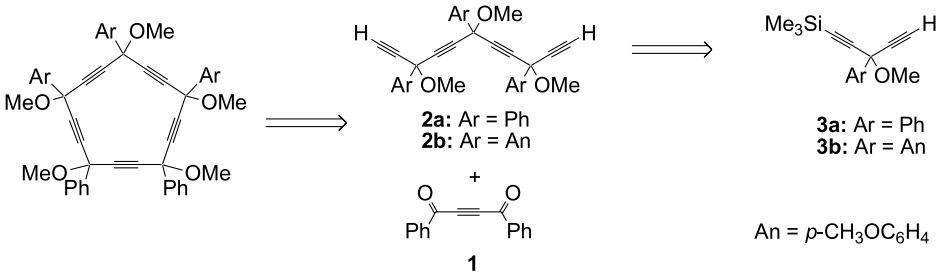


Scheme 1. Scott's [5]pericyclyne,[7] [5]cyclitol ethers and ring *carbo*-mer thereof.



Scheme 2. Targeted functional [5]pericyclynes (R≠H).

academic aestetical concern, one may figure out applications such as, for example, rigid crown ether-like properties or possible aromatization to the challenging ring *carbo*-mers of cyclopentadienyl cations.[4]

The envisioned pathways to *tertiary* and bis-*secondary* *carbo*-[5]cyclitol ethers (Scheme 2) are based on sequential alkynyl-propargyl coupling reactions.[12] The results are described in Sections 1 and 2. Since the stereogenic carbons of the *carbo*-[5]cyclitols stand in remote (γ) positions, their relative configuration is likely poorly controlled. A third section is therefore devoted to the diastereomeric resolution of *carbo*-[5]cyclitol ethers using HPLC techniques.

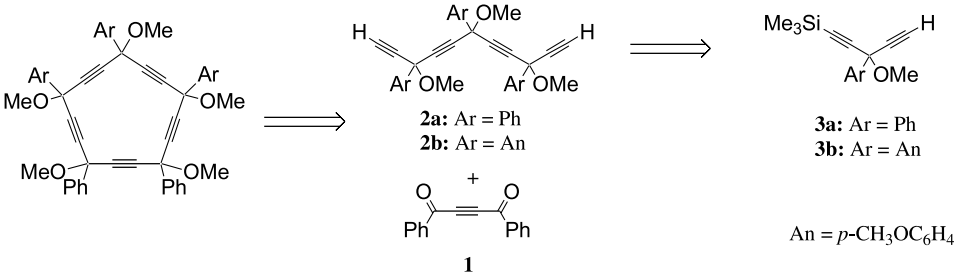
2. Results and discussion

2.1. *Tertiary carbo*-[5]cyclitol ethers

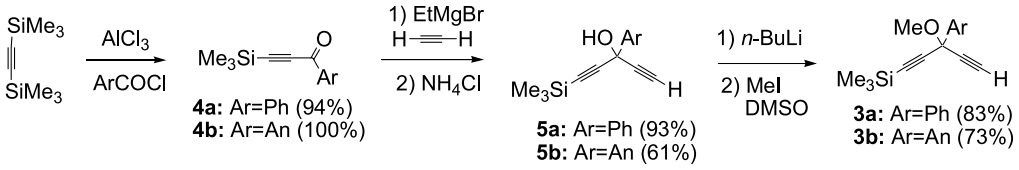
The selected strategy is straightforwardly inspired from the previously attempted [11+4] ring-closing double substitution of 1,4-ditosyloxy-but-2-yne ($TsOCH_2C{\equiv}CCH_2$-OTs). This strategy actually afforded a cyclic isomer and a cyclic dimer of the desired [5]pericyclyne through [11+4] and [11+4+11+4] processes, respectively.[13] Just changing the C_4 dielectrophile, the present strategy is based on a ring-closing double addition to the dibenzoylacetylene **1** (Scheme 3).

Some procedures will be inspired from those utilized by Ueda, Kuwatani et al. for the synthesis of homologous '*carbo*-[6]cyclitol' derivatives.[10a] The synthesis of the known triphenylundecatetrayne **2a** was extended to the trianisyl analogue **2b**.[13] In analogy with **3a**, the starting diyne **3b** was thus prepared through the three-step sequence depicted in Scheme 4. Acylation of bistrimethylsilylacetylene with *p*-anisoyl chloride afforded the anisylethynylketone **4b**. Reaction of **4b** with magnesium acetylide lead to the diethynyl-anisyl carbinol **5b**, the X-ray crystal structure of which was determined (see Section 2.2.2 and Fig. 3). The ether **3b** was finally obtained by methylation of the monolithium salt of **5b**.

Two equivalents of the lithium salt of **3b** reacted with anisoyl chloride to give **6b** in 52% yield (instead of 77% in the phenyl series **6a** from **3a**).[13] Methylation of the lithium alkoxide of **6b** with MeI/DMSO,[10a] followed by desilylation with K_2CO_3/MeOH,[14] afforded the undecatetrayne **2b**. The



Scheme 3. Retrosynthetic analysis to tertiary *carbo*-[5]cyclitol ethers.



Scheme 4. Synthesis of the 1,4-pentadiynes precursors of the C_{11} tetraynes **2a** and **2b**.

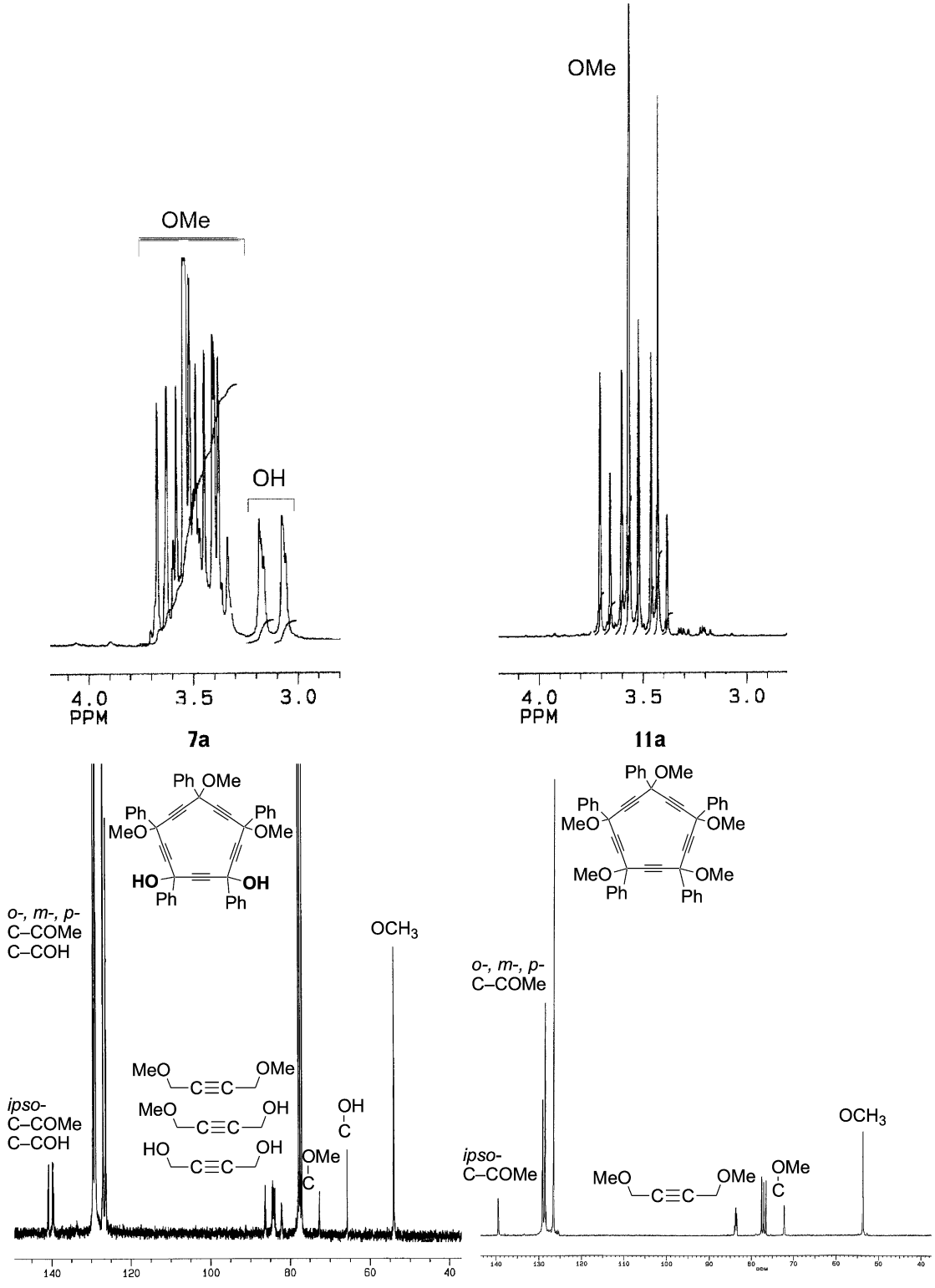
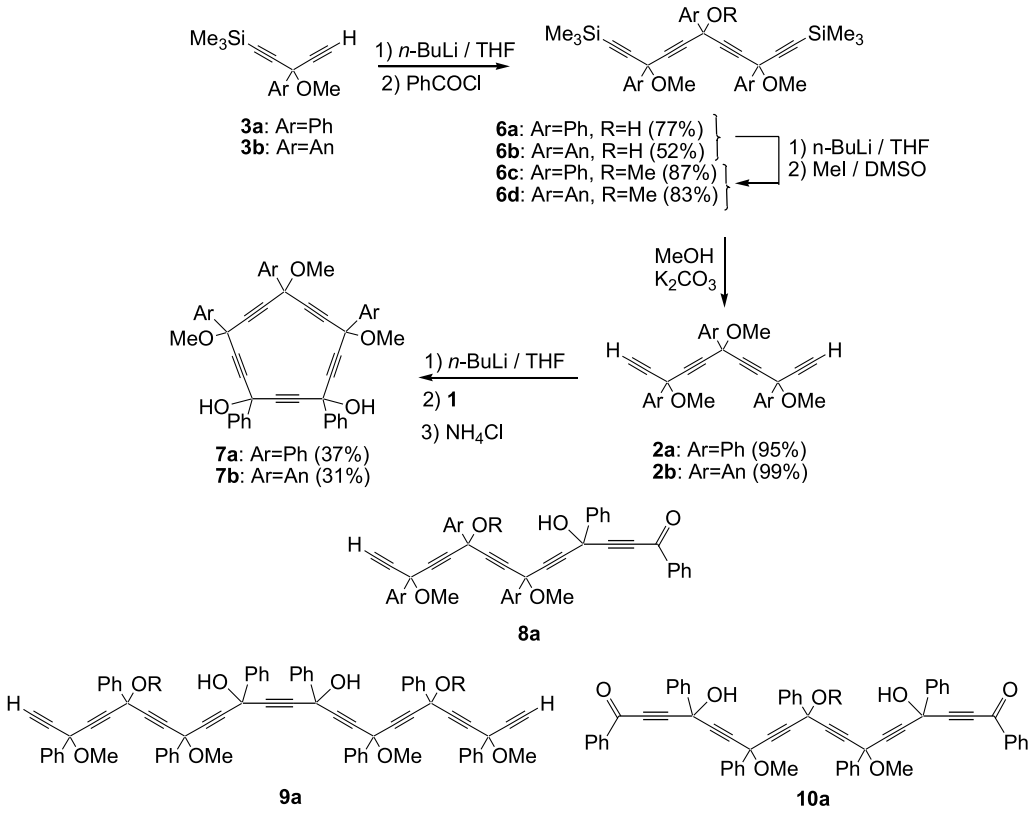


Figure 1. ^{1}H (250 MHz) and ^{13}C NMR (100 MHz, 62 MHz) spectra in $CDCl_3$ of the less symmetric triether **7a** as compared with those of the more symmetric pentaether **11a**.



Scheme 5. Synthesis of tertiary *carbo*-[5]cyclitol derivatives (**7**) and isolated side-products (**8**–**10**).

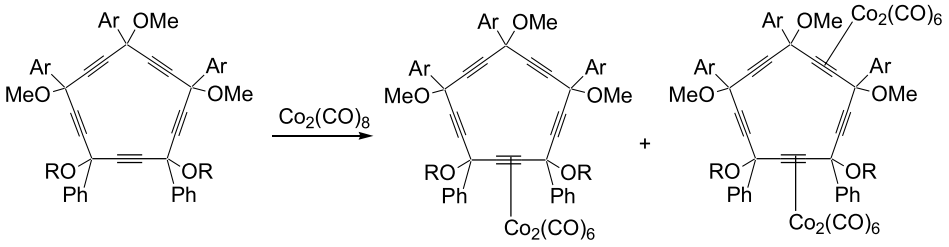
tetraynes **2a** and **2b** were obtained as statistical mixtures of stereoisomers (see Section 2.3 for the HPLC analysis of **2a**). The stereoisomers of these open-chain polyynes are nearly degenerate in their ^{1}H and ^{13}C NMR spectra (see Section 2.3, Fig. 6). This is due partly to the remote γ positions of the stereogenic centers, but mainly to an averaging free rotation process. Indeed the NMR degeneracy clears up in the next locked cyclic derivatives **7** (see discussion below, and Fig. 1). The latters were indeed obtained upon double-attack of the dilithium salts of **2a** and **2b** to dibenzoyl-acetylene **1**, prepared from the *trans*-1,2-dibenzoylethylene according to the Schuster's procedure.[15] Beside some unreacted tetraynes **2** and several acyclic products **8**, **9**, **10** (isolated in the phenyl series **a**), pentaphenyl[5]pericyclyne **7a** and diphenyl-trianisyl-[5]pericyclyne **7b** were formed rather selectively, in 37 and 31% yield, respectively. These novel functional pentaoxy-[5]perictyclynes are stable and could be characterized by MS, IR, ^{1}H and ^{13}C NMR spectroscopy (Scheme 5).

Starting from a mixture of the three stereoisomers of undecatetraynes **2a**–**2b**, the obtained [5]pericyclynes with two adjacent CPh(OH) vertices and three CAr(OMe) vertices are theoretically obtained as mixtures of 10 diastereoisomers (six of them being chiral). Considering the possible symmetry-equivalence of pairs of MeO groups, 26 different OCH_3 signals are a priori expected in the NMR spectrum of **7a** (resp. **7b**). Consistently, a large number of signals (ca. 16) are indeed observed in the range 3.3–3.7 ppm. The possibility of overlap precludes an exact count of the stereoisomers of **7a** (Fig. 1). Nevertheless, two well-separated broad D_2O-exchangeable OH signals of equal intensities occur at 3.05 and 3.15 ppm. Assuming that the primary factor determining the chemical shifts of these hydroxyls is their relative *cis* or *trans* orientation with respect to the mean ring plane, this observation suggests that the ring closing process is definitely non-stereoselective.[16] It must be stressed that the ^{13}C chemical shifts are much less sensitive to diastereotopicity than are the ^{1}H chemical shifts: the formers solely undergo the influence of the proximate (topological) chemical environement (Fig. 1).

For the pentaphenyl derivative **7a**, methylation of the two hydroxyl groups results in an increased symmetry (all the five vertices become identical in nature: CPh(OMe), and would allow to reduce the theoretical number of diastereoisomers from ten to four (Scheme 6).

Scheme 6. Symmetrization of a *carbo*-[5]cyclitol triether to the corresponding pentaether.

The NMR spectra of the pentamethoxy-pentaphenyl-[5]pericyclyne **11a** are indeed significantly simplified (Fig. 1). Only eight well-resolved ^{1}H NMR signals are now observed in the OCH_3 region, out of 10 expected in the



Scheme 7. Cobalt complexes of pentaoxy[5]pericyclynes. The depicted regiochemistry of the complexation may not be unique, but it corresponds to experimental data on decamethyl-[5]pericyclyne.[8] For **12** and **12′**, the preferred complexation on the 'butyndiol edge' is suggested by DFT calculations on a model butyndiol complex revealing chelating hydrogen bonds involving the carbonyl ligands of the $Co_2(CO)_6$ moiety.[17]

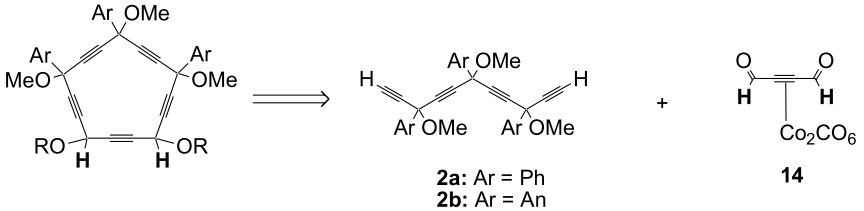
statistical distribution. All the possible diastereoisomers are thus significantly present in the product (two signals are likely degenerate with other(s) under the most intense signal(s): Fig. 1). As stressed above, the ^{13}C chemical shifts are much less sensitive to diastereotopicity and all carbons of given chemical type resonate as single frequencies in all the stereoisomers (only sp-carbon atoms, at the midpoint between two stereogenic vertices, remain very slightly non-degenerate: Fig. 1). No stereochemical correlation was thus possible. A first attempt at separation of the diastereoisomers by HPLC remained unsuccessful, thus requiring a stepwise resolution method (see Section 2.3).

Scott et al. showed that peralkylpericyclynes act as ligands for one or two $Co_2(CO)_6$ units, and that use of a large excess $Co_2(CO)_8$ does not lead to further complexation.[8] This behaviour was tested for functional versions. Reaction of the *carbo*-[5]cyclitol ethers **7a**, **7b** or **11a** with a single equivalent of $Co_2(CO)_8$ lead to two red complexes which could be separated by chromatography (Scheme 7). According IR, MS (APCI>0/CH_3CN, MALDI) and elemental analyses, the less polar products **12a**, **12b**, **13a** (isolated in 50–60% yield) contain a single $Co_2(CO)_6$ unit. The most polar products **12a′**, **13a′** (20–30% yield) contain two $Co_2(CO)_6$ units. The proposed structures in Scheme 7 are based on Scott's results on decamethyl-[5]pericyclyne, showing that the two $Co_2(CO)_6$ units of the bis-complex are bound to non-adjacent triple bonds. For **12a**, **12a′** and **12b**, the proposed hapticity of the triple bonds lying between the CPh(OH) vertices is supported by standard steric arguments, and by DFT calculations (B3PW91/6-31G**/LANL2DZ(Co)) on a model $Co_2(CO)_6$ complex of 2*R*,5*R*-diphenyl-hexa-3-yn-2,5-diol displaying two stabilizing O–H···(CO) hydrogen bond-like distances (2.34 Å).[17]

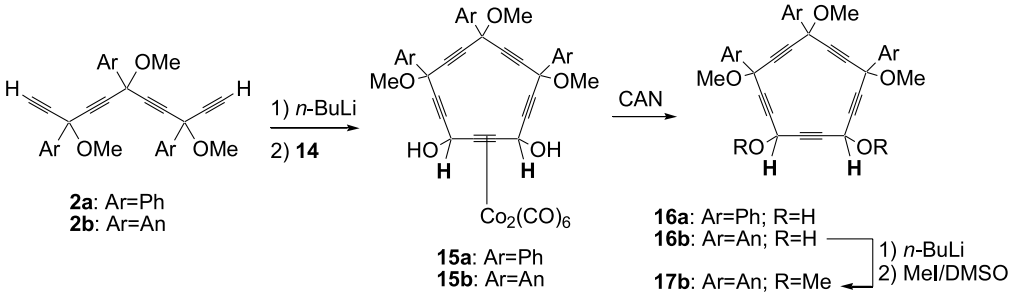
2.2. Bis-*secondary carbo*-[5]cyclitol ethers

[5]Pericyclynes with several secondary carbinol vertices are specifically interesting for several reasons: (i) they are not exemplified in the literature,[18] and possibly tautomerically instable;[19] (ii) if stable, they are more versatile than their all-tertiary counterparts for further functionalization (by full reduction to CH_2 or full oxidation to C=O); and (iii) they are redox (isohypsic) equivalents of the challenging *carbo*-cyclopentadienyl ring cation.[4a,b,6] The synthesis of [5]pericyclynes with two secondary carbinol vertices at either adjacent or non-adjacent positions (Scheme 2) has been envisioned through two cyclization strategies, [11+4] and [10+5].

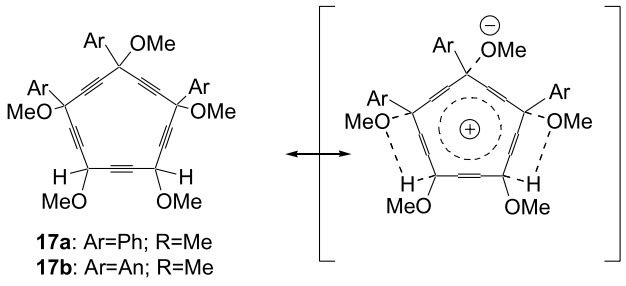
2.2.1. Bis-*secondary carbo*-[5]cyclitol ethers with adjacent CH(OH) vertices: a [11+4] strategy. The preceeding route to pentaaryl-*carbo*-[5]cyclitol ethers (Section 2.1) suggests the replacement of dibenzoylacethylene **1** for acetylenedicarbaldehyde (CHO–C≡C–CHO). Extensive studies by Gorgues et al. have shown that this highly functional C_4 molecule is however quite instable,[20] and cannot be used as such for synthetic purpose. Nonetheless, it can be stabilized as a ligand in the cobalt(0) complex **14**. X-ray diffraction analyses of single crystals of **14** showed that the propargylic aldehyde functions do not interact with the cobalt centers.[21] This structural feature is consistent with our recent studies showing that the dialdehyde ligand preserves its theoretical 1,4-electrophilicity, not only towards neutral nucleophiles (silylenol ethers and trimethoxybenzene in Nicholas-type reactions),[22] but also towards anionic nucleophiles.[23] Despite the presence of six 'electrophilic' carbonyl ligands, alkyl, aryl, ethynyl lithium and Grignard reactants add to both aldehydic functions in a



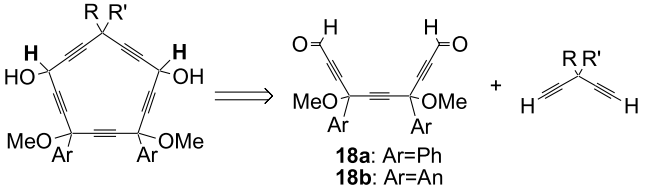
Scheme 8. [11+4] retrosynthesis of bis-secondary pentaoxy[5]pericyclynes based on the use of Gorgue's complex **14**.



Scheme 9. Synthesis of bis-*secondary* pentaoxy[5]pericyclynes *via* cobaltcarbonyl complexes.



Scheme 10. Formal isohypsic equivalence of bis-secondary pentaoxy[5]-pericyclynes with *carbo*-cyclopentadienyl cations.

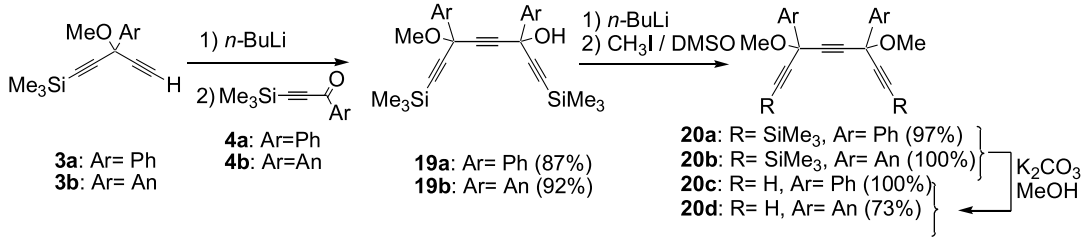


Scheme 11. [10+5] retrosynthesis of bis-*secondary* pentaoxy-[5]pericyclynes.

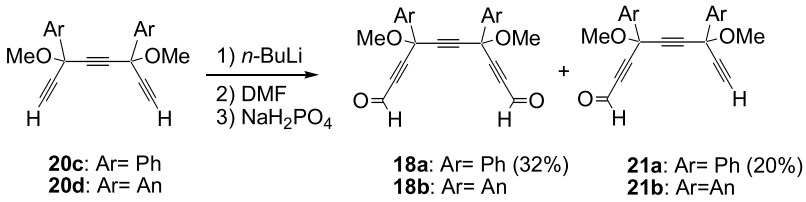
chemo- and regio-selective manner. Moreover, the double additions take place with some stereoselectivity (*meso*:*dl* ratio up to 80:20). We therefore envisioned to apply the reaction in a ring-closing version from tetraynes **2a** and **2b** (Scheme 8).

Double deprotonation of the triphenyl-tetrayne **2a** with *n*-BuLi in THF followed by addition of the acetylene-dicarbaldehyde complex **14** and protonation, afforded a mixture of compounds. Chromatography allowed to isolate a single-spot red complex, whose ^{1}H, ^{13}C NMR and IR analyses are consistent with the expected structure **15a** (25% yield, Scheme 9). The same sequence from the trianisyl-tetrayne **2b** afforded the analogous complex **15b** (6% yield. Scheme 9). Rather surprisingly, whereas 2 equiv. of various monoacetylides (RC≡C–Li) were shown to afford the corresponding acyclic triyndiol complexes in rather low yields (9–16%) as compared with alkyl and aryl nucleophiles,[23] the yield in the cyclic product **15a** is here relatively high. The tandem cyclic feature of the process is therefore highly beneficial. Nevertheless, none of the classical MS methods, including atmospheric pressure chemical ionization (APCI), gave relevant fragmentation peaks. Their structure was confirmed in the next step. Indeed, oxidative decomplexation of the corresponding samples of **15a–b** afforded the bis-*secondary carbo*-[5]cyclitols **16a** ($[MNH_4]^+=558$) and **16b** ($[M]^+=630$; $[MH-MeOH]^+=599$: stabilized α-*p*-anisyl carbocationic fragment). The procedure previously employed for O-methylation of *tertiary* diethynyl-aryl carbinols (deprotonation with *n*-BuLi, then MeI/DMSO) turned out to be unsuccessful for *secondary* diethynyl carbinols (from diol **16a**) in the phenyl series. In one attempt in the anisyl series (from diol **16b**), however, it afforded a crude compound whose NMR and MS spectra were consistent with the bis-*secondary* pentamethoxy-[5]pericyclyne structure **17b** ($[MH-MeOH]^+=627$).

These stable molecules constitute the first examples of redox (isohypsic) equivalents of *carbo*-cyclopentadienyl cations (Scheme 10).[4a,b,6] The corresponding fragments could however not be detected in their mass spectrum. In an attempt at triggering aromatization through double 1,4-elimination of methanol, a yellow solution of **17b** ($CDCl_3$, −60 °C) treated with triflic acid turned immediately to violet with concomitant formation of a black precipitate. No signal could be detected by ^{1}H NMR analysis of the highly diluted supernatent, but the water-sensitive violet color remained persistent over 12 h at room-temperature. Despite the expected stabilizing effect of three anisyl substituents,



Scheme 12. Preparation of the octatriyne precursors of the C_{10} dialdehydes envisioned in the [10+5] strategy (Scheme 11).



Scheme 13. Double formylations of triynes **20**,[25] affording the key C_{10} dialdehydes for the envisioned [10+5] strategy (Scheme 11).

compound **17b** is definitely more prone to polymerization than to dissociative aromatization. Speculatively, 1,4-elimination from **17** is indeed not regio-directed: if it first took place on the bis-secondary edge, the resulting trisubstituted butatriene edge (≡C–(H)C=C=C=C(OMe)–C≡) in a not-yet-aromatic pentagonal ring would be likely quite instable. The design of an optimized precursor structure was therefore suggested as a prerequisite for any further attempt at quantitative formation of the *carbo*-cyclopentadienyl ring cation.

2.2.2. Bis-*secondary carbo*-[5]cyclitol ethers with non-adjacent CH(OH) vertices: a [10+5] strategy. The second kind of bis-*secondary carbo*-[5]cyclitols (Scheme 2) was targeted through the alternative [10+5] strategy disclosed in Scheme 11.

The C_{10} trisacetylenic dialdehyde precursors **18a**, **18b** were prepared in three steps from the 1,4-diynes **3a**, **3b** (Schemes 12 and 13). Addition of the corresponding lithium acetylides to trimethylsilylpropynal afforded the corresponding triynes **19a** and **19b** as mixtures of *meso* and *dl* isomers in an undetermined ratio (the ^{1}H NMR signals are not split significantly). After methylation of the hydroxyl group, both the terminal alkynes were readily deprotected with K_2CO_3/MeOH, affording **20c** and **20d** in 84 and 67% yield, respectively.

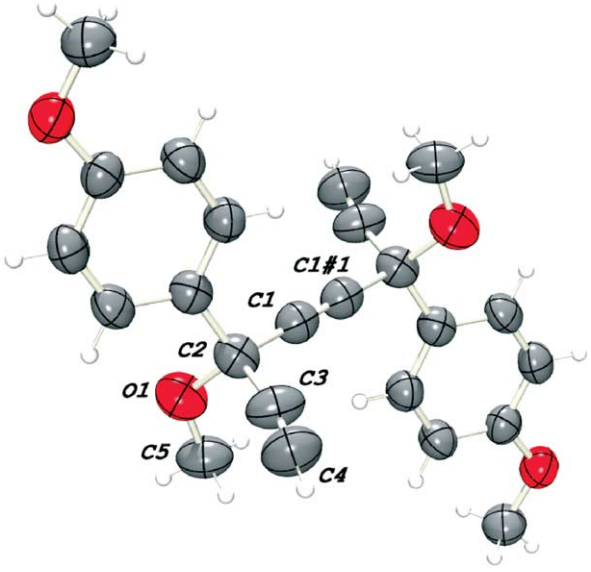


Figure 2. ORTEP view of **20d** with 50% probability displacement ellipsoids for non-hydrogen atoms. Bond distances (Å): C(2)–C(3)=1.473(6); C(3)–C(4)=1.139(6); C(1)–C(2)=1.494(6); C(2)–O(1)=1.450(5); C(1)–C(1)#1=1.187(8). Bond angles (°): C(1)#1–C(1)–C(2)=177.6(5); C(3)–C(2)–C(1)=107.6(4); C(4)–C(3)–C(2)=166.5(6).

While **20c** was isolated as an orange oil, its anisyl couterpart **20d** is an orange powder. A single crystal of **20d** was obtained as an orange powder, revealing a *meso* configuration in a perfect C_2 conformation (Fig. 2). The crystal structure can be compared with the structure of the 1,4-diyne precursor **5b**. In *meso*-**20d**, the measured bond angle at the C3 sp carbon atom and the corresponding triple bond distance are C2–C3–C4(H)=166.5(6)° and C3–C4=1,139(6) Å, respectively. These values appear as rather 'abnormal' with respect to the classical structural features of alkynes and to the 'normal' values measured from the X-ray crystal structure of the dialkynylcarbinol **5b** (true racemate, Fig. 3: C1–C2–C3(H)=177.66(14)°; C2–C3=1,184(2) Å). Beyond possible experimental error, the apparent bond shortening can be due to an artifact of the X-ray measurement, as previously discussed for tetraethynylmethane on the basis of a 'π electron compression' effect.[24]

The carbaldehyde groups were then introduced by double formylation according to the Journet and Cai's procedure.[25] The hydrolysis step is crucial for a successful production of

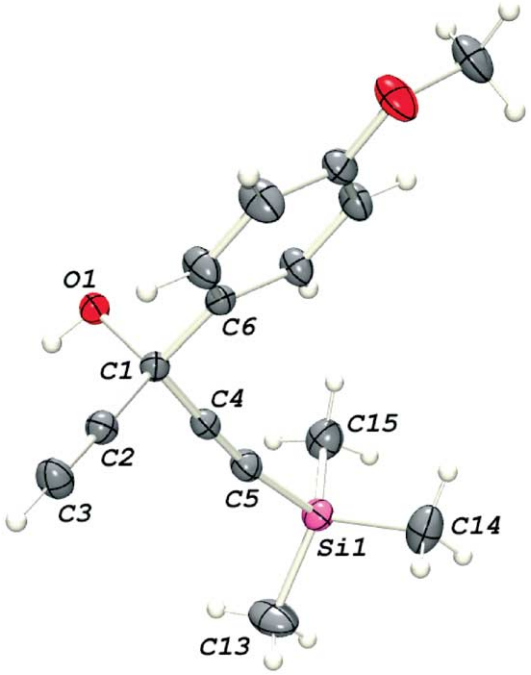
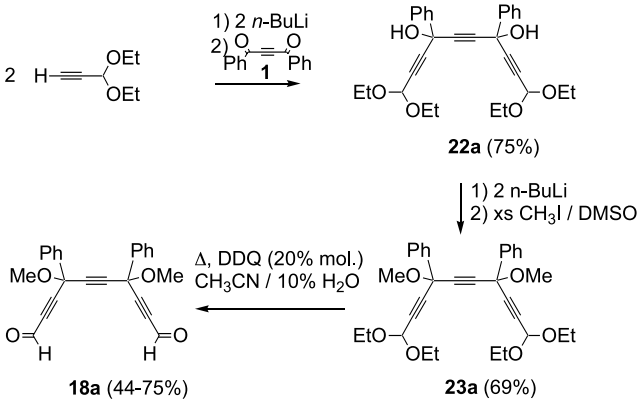


Figure 3. ORTEP view of **5b** with 50% probability displacement ellipsoids for non-hydrogen atoms. Bond distances (Å): C(1)–C(2)=1.475(2); C(1)–C(4)=1.4832(19); O(1)–C(1)=1.4437(15); C(2)–C(3)=1.184(2); Si(1)–C(5)=1.8499(17). Bond angles (°): C(3)–C(2)–C(1)=177.66(14); C(5)–C(4)–C(1)=177.02(15); C(2)–C(1)–C(4)=108.78(11); C(4)–C(5)–Si(1)=172.16(12).



Scheme 14. Alternative synthesis of the key C_{10} dialdehyde **18a** for the envisioned [10+5] strategy (Scheme 11).

18a–18b: it consists in the addition of the alkaline solution into a 1:1 mixture of diethylether and KH_2PO_4 aqueous buffer (alternatively, $NaHPO_4$+KCl, can be used. The use of other acids triggered back reaction and untransformed triyne **20** was recovered). Monoaldehydes **21a**, **21b** were formed as side-products in ca. 20% yield according to NMR analysis of the crude materials.

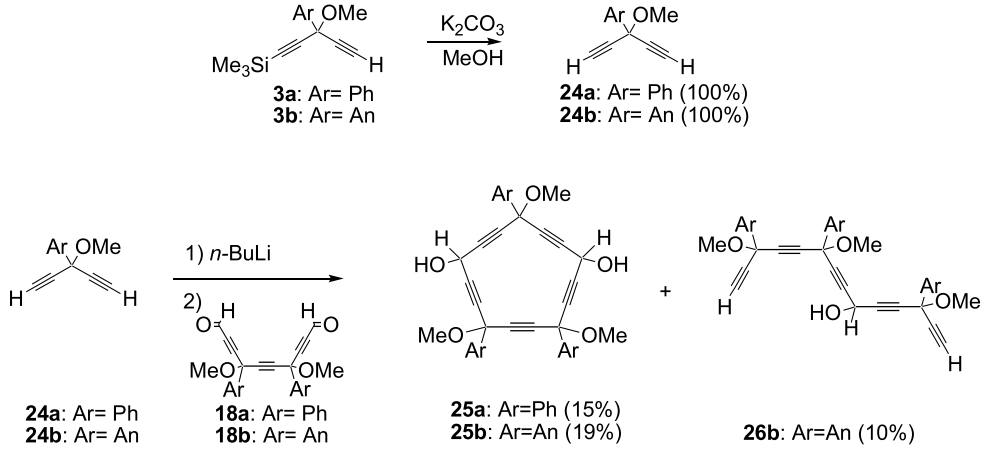
Attempts at purification by chromatography resulted in partial decomposition, affording pure **18a** in 32% yield only. The anisyl derivative **18b** could not be successfully purified. To make up this problem, an alternative route was addressed from commercially available propiolaldehyde diethylacetal and dibenzoylacetylene **1** (Scheme 14).

Addition of two equivalents of lithium 3,3-diethoxypropynide to diketone **1** in THF and subsequent hydrolysis afforded diol **22a**. After methylation of the hydroxyl groups, hydrolysis of the acetal functions by conventional acidic treatments (formic acid or PTSA) remained unsuccessful. Compound **23a** could, however, be deprotected in an 'oxidizing' neutral medium using DDQ in the dark.[26] Dialdehyde **18a** was finally obtained in three steps and 61% yield. At this stage, the lack of a rapid procedure for the preparation of the dianisyl analogue of diketone **1**, prevented the use of this strategy (Scheme 14) to obtain the anisyl analogue **18b**. The crude dialdehyde **18b** obtained by the first method (Scheme 13) was thus used as such in the cyclization step (see below).

The C_5 1,4-diyne moieties **24a**, **24b** were obtained by quantitative desilylation of the diynes **3a**, **3b** in basic medium (Scheme 15). The [10+5] ring closing step is based on a double nucleophilic attack of the dilithium salts of **24a**, **24b** to the C_{10} dialdehyde moieties **18a**, **18b**. In the phenyl series, the *carbo*-[5]cyclitol ether **25a** was isolated in 15% yield. Attempt at templating the triyne electrophiles with $AgBF_4$ did not increase the yield. In the anisyl series, two major products were obtained from the crude mixture **18b**+**21b** (Scheme 13). The *carbo*-[5]cyclitol ether **25b** and the acyclic product **26b** could finally be separated in 19 and 10% yield, respectively.

The DCI/NH_3 mass spectrum of the *carbo*-[5]cyclitol ether **25a** exhibits a base peak at $m/e=558$ ($[MNH_4]^+$) and a major peak at $m/e=509$ ($[MH–MeOH]^+$) (Fig. 4). Two secondary peaks at $m/e=526$ and 494 correspond to the '*carbo*-cyclopentene' ($[M+NH_4–MeOH]^+$) and '*carbo*-cyclopentadiene' ($[M-2MeOH+NH_4]^+$) parent ions respectively. The corresponding *carbo*-cyclopentadienyl fragments (($[MH-3MeOH]^+$or ($[M+NH_4-3MeOH]^+$) were not observed. The DCI/NH_3 mass spectrum of the anisyl *carbo*-[5]cyclitol ether **25b** exhibits similar features, with a main base peak at $m/e=599$, corresponding to $[MH-MeOH]^+$(stabilized α-*p*-anisyl carbocation, as in the case of **7b** discussed in Section 2.1).

As an alternative C_5 1,4-diyne fragment, the pentadiyn-3-one ketal **27** possesses a non-asymmetric bis-propargylic carbon center. It was used by Bunz et al. for the synthesis of functional expanded pericyclynes.[10b] Within the framework of the present [10+5] strategy, the resulting [5]pericyclyne should be topologically more symmetrical, with a reduced number of diastereoisomers (five instead of eight in the previous case). The known C_5 precursor **27** was prepared by addition of 2 equiv. of trimethylsilylacetylide to ethyl formate, followed by oxidation of alcohol **28**, and ketalization of ketone **29** with 2,2-dimethyl-1,3-propandiol under specific conditions of dilution in toluene (instead of benzene in the previously described procedure).[10b] Quantitative



Scheme 15. Ultimate steps of the [10+5] strategy, affording pentaoxy-[5]pericyclynes with non adajacent CH(OH) vertices.

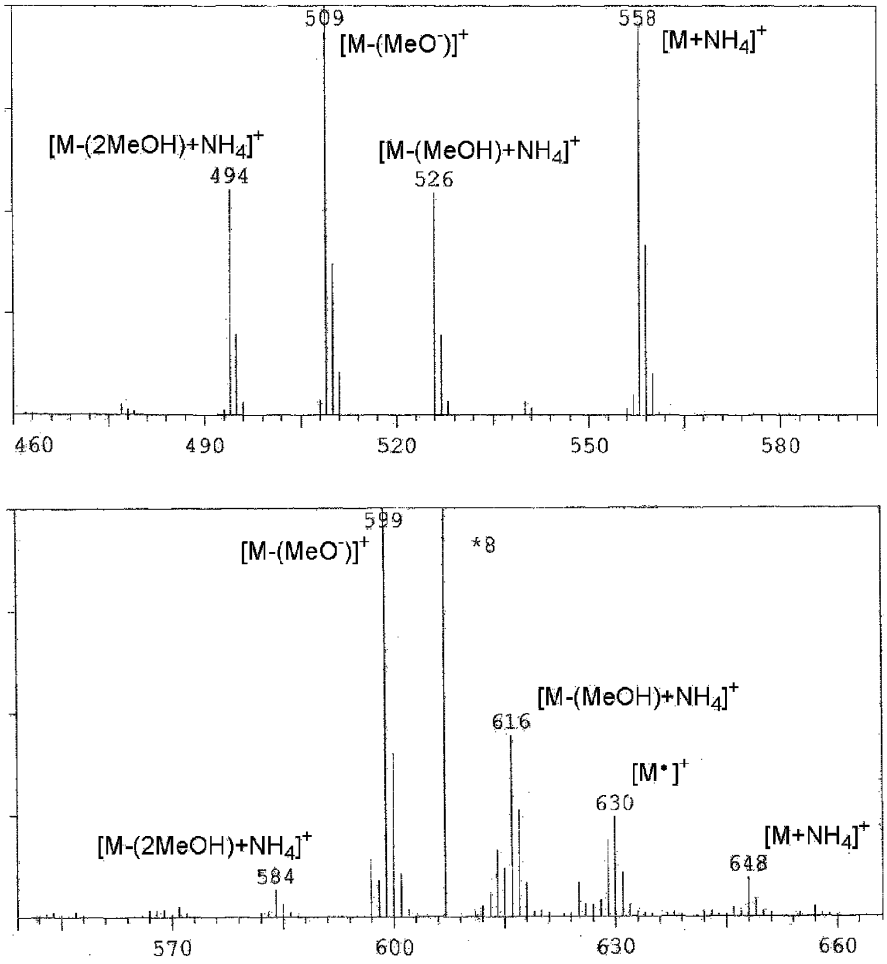
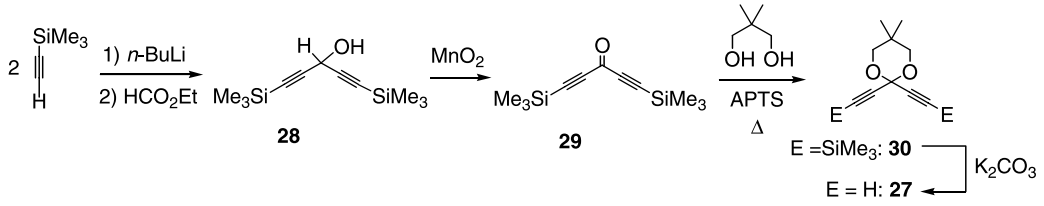
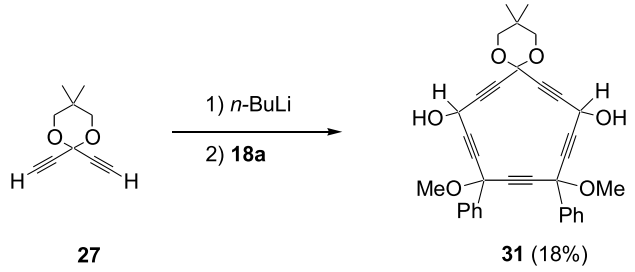


Figure 4. MS (DCI/NH_3) spectra of bis-*secondary* pentaoxy-[5]pericyclynes **25a** and **25b** showing the preferred fragmentations through one or two methanol eliminations from the protonated or ammoniated species. The third methanol elimination which could produce the corresponding dihydroxy-triphenyl-*carbo*-cyclopentadienyl cations was not observed.



Scheme 16. Four-step synthesis of the 2,2-dimethyl-1,3-propanediol ketal of diethynyl ketone,[10b] an alternative C_5 moiety for the [10+5] strategy.

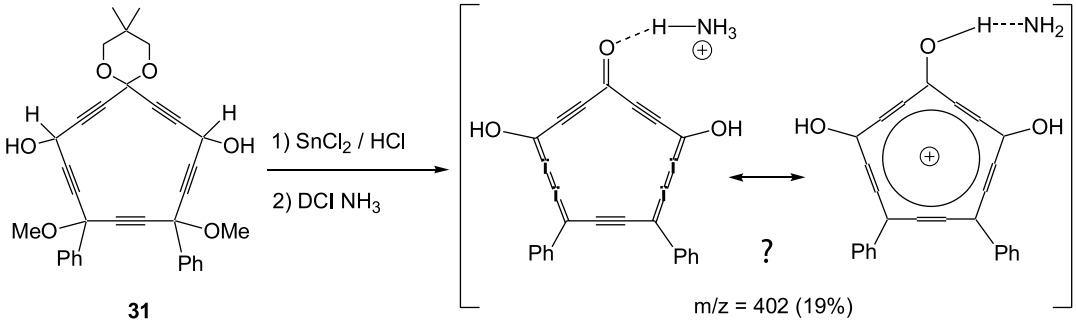


27 **31** (18%)

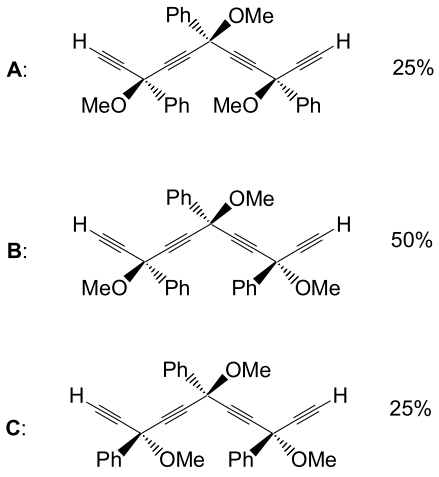
Scheme 17. [10+5] ring closing process affording a bis-*secondary* hexaoxy[5]pericyclyne.

desilylation of **30** afforded **27** in 27% overall yield (Scheme 16).

The dilithium salt of **27** was then allowed to react with dialdehyde **18a**, affording the novel [5]pericyclyne **31** as a pale yellow powder in 18% yield (Scheme 17). All attempts at deprotection of the ketal vertex of **31** remained unsuccessful. Inspection of the literature reveals that no effective deprotection of such hindered ketals of dialkynyl-ketones has been hitherto reported. In particular, deprotection of Bunz decaoxy-expanded [5]pericyclyne was not reported.[10b] Moreover, it seems that **30** is the sole known ketal derivative of the ketone **29**, and consistently, our



Scheme 18. Possible aromaticity-stabilized structure of the observed fragment at $m/z=402$ in the DCI/NH_3 mass spectrum of the hexaoxy-[5]pericyclyne after acidic treatment.



Scheme 19. Stereoisomers **A**, **B**, **C** of the tetrayne **2a** and their statistical ratio.

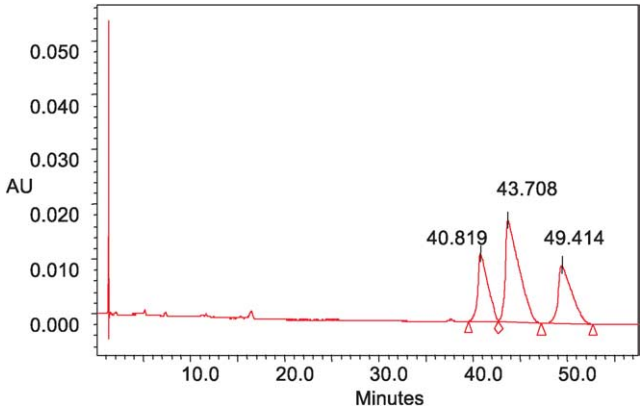


Figure 5. HPLC separation of the stereoisomers **A**, **B**, **C** (Scheme 19).

personal attempts at preparing the less hindered 1,3-propylene ketal or the acyclic diethylketal of **29** failed.

Aromatisation of the *carbo*-[5]cyclitol derivative **31** with the classical reactant $SnCl_2/HCl$[10a] afforded a complex mixture of products. However, DCI-MS analysis of the mixture exhibited a secondary peak at $m/z=402$ (19%). This value is consistent with the parent *carbo*-cyclopentadienone-ammonium structure or with its zwitterionic oxyl-*carbo*-cyclopentadienyl resonance form (Scheme 18). The geometry of the *carbo*-cyclopentadienone model molecule ($C_{15}H_4O$) was optimized at the B3PW91:6-31G** level,[27] and it was shown that this model is aromatic in both the structural sense (planarity, C···O distance of 1.44 Å corresponding to $a^{+}C–O^{-}$ single bond description) and the magnetic sense (NICS = −8.1 ppm,).[28] This aromaticity might account for the observed MS fragmentation of ketal **31**.

2.3. Diastereoisomeric resolution of *carbo*-[5]cyclitol pentaether 11a

As previously stressed (Section 2.1), all the compounds containing more than two dialkynylcarbinol units were obtained as mixtures of diastereoisomers. All attempts at separating them by TLC and column chromatography failed. Focusing on the most symmetric pentaoxy-[5]pericyclyne target **11a** (with four diastereoisomers only: Scheme 6), we therefore turned to HPLC techniques. Since **11a** is obtained from tetrayne **2a** and dibenzoylacetylene **1**, and since the three stereogenic sp^3 carbon atoms of **2a** are retained in **11a**, a preliminary diastereoselective separation of **2a** was attempted. In theory, **2a** possesses three diastereisomers **A**, **B** and **C**, anticipated to form in the statistical distribution **A**:**B**:**C** = 1:2:1 (Scheme 19).

Their separation was achieved by HPLC, with a direct phase column of Prontosil type. After several trials, a 70:30 pentane:dichloromethane mixture was determined as an optimal eluting system. The analytical HPLC chromatogram displays three peaks with baseline separation for retention times of 40.8, 43.7 and 49.4 min, integrating for 25, 50 and 25%, respectively (Fig. 5). The three peaks correspond to identical UV spectra, as expected for closely related diastereoisomers **A**, **B**, **C**. This confirmed the statistical ratio, and allowed for the assignment of the major intermediate signal (at $R_t=43.7$ min) to the structure **B** (Scheme 19).

The three diastereoisomers were then sequentially separated twice by semi-preparative HPLC. The three stereochemically pure products are oils, the NMR spectra of which were recorded separately (Fig. 6). It is predicted that the isomer **B** should exhibit three non-equivalent methoxy NMR signals, while both **A** and **C** should exhibit two different signals only. These features were confirmed, in accordance with the

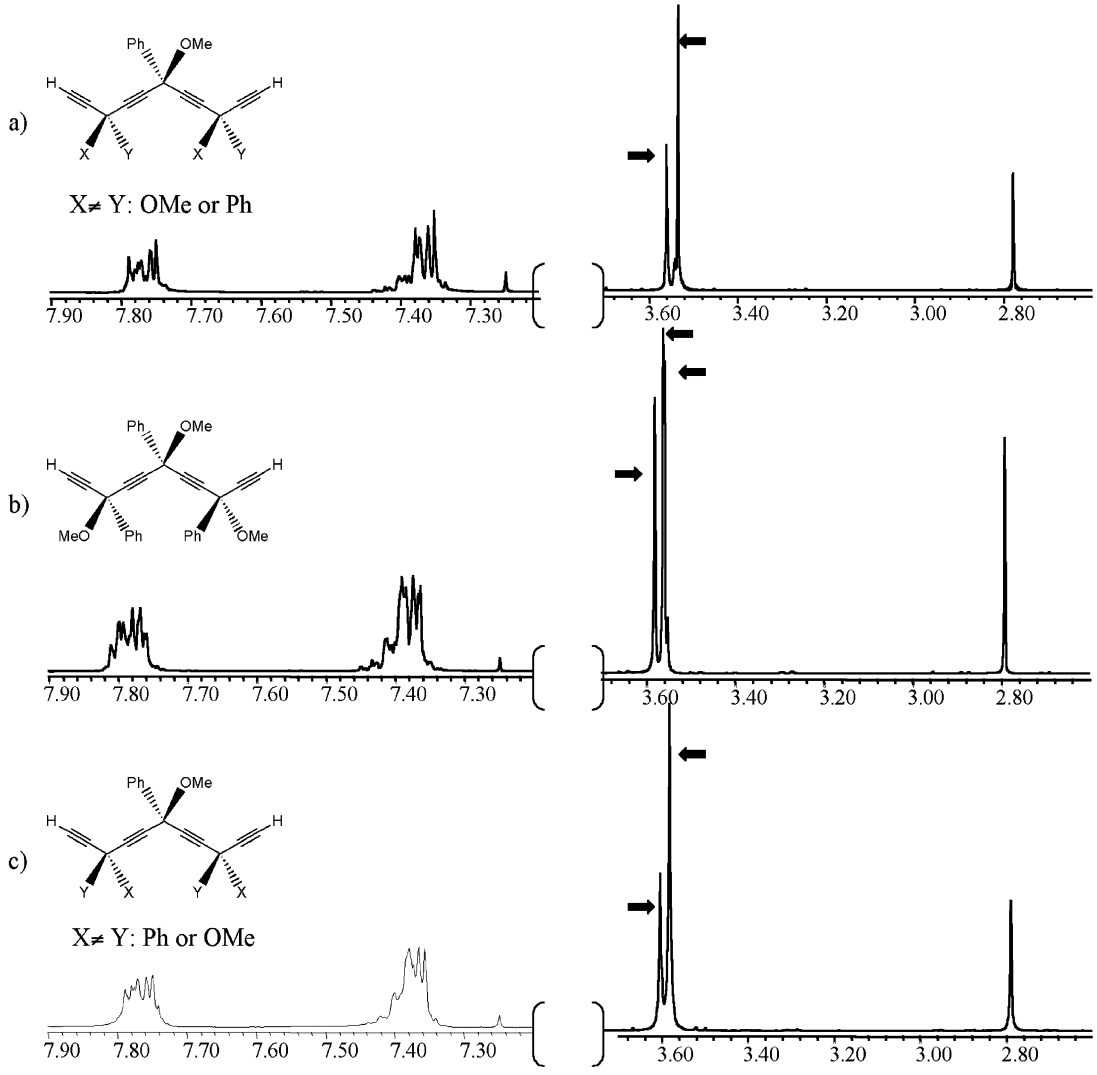
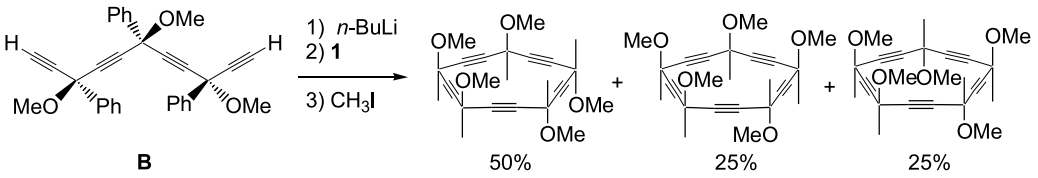


Figure 6. NMR spectra ($CDCl_3$, 250 MHz) of separated diastereoisomers of tetrayne **2a**. a) Stereoisomer **A** or **C**. b) Stereoisomer **B**. c) Stereoisomer **C** or **A**, different from the stereoisomer corresponding to spectrum a).



Scheme 20. Statistical stereoisomeric distribution of the pentamethoxy-[5]pericyclyne **11a** resulting from a [11+4] ring closing process involving the pure isomer **B** of tetrayne **2a**. For clarity, the phenyl substituents are not depicted.

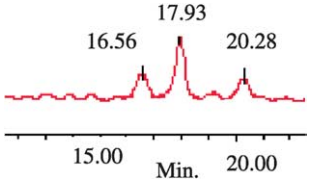


Figure 7. HPLC separation of the three isomers of pericyclyne **11a** in statistical distribution (Scheme 19).

HPLC assignment. In particular, only the compound of the major HPLC peak displays three OCH_3 NMR signals of equal intensities, thus confirming structure **B** (Fig. 6(b)). Nonetheless, neither the HPLC integration nor the multiplicities of the NMR signals allow for an assignment of structures **A** and **B** to their respective HPLC retention time and ^{1}H NMR spectrum.

Having pure diastereoisomers of **2a** in hand, the double addition to dibenzoylacetylene **1** was carried out from the

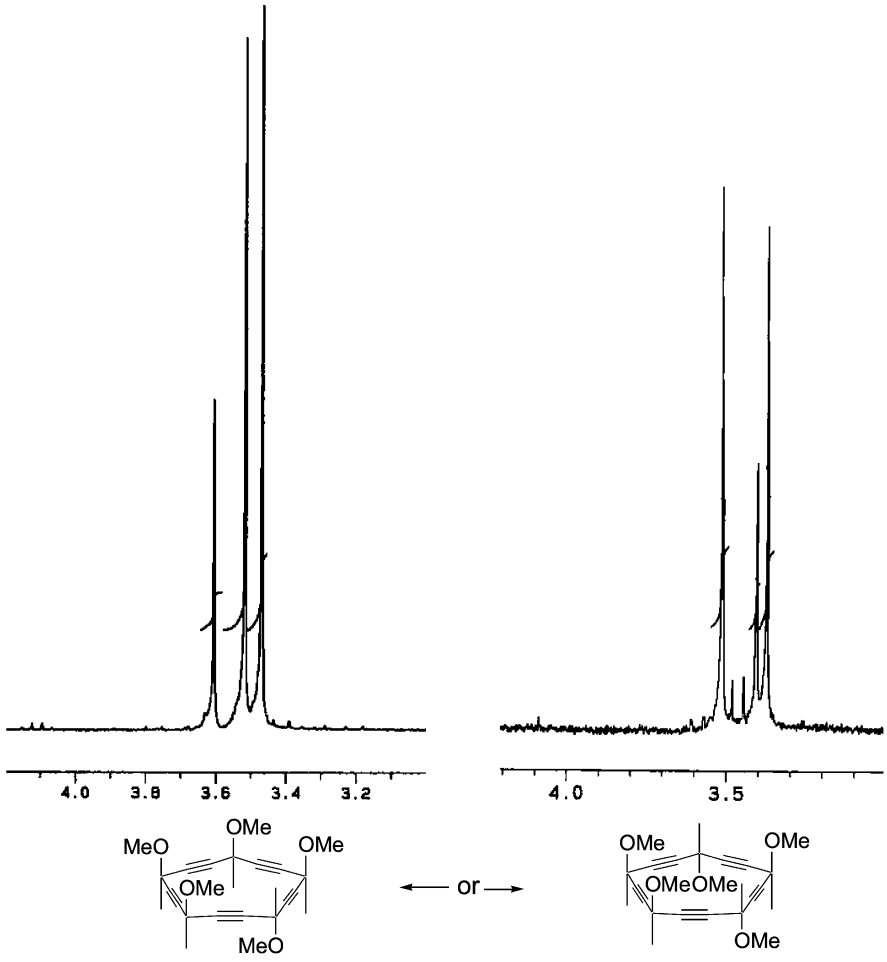


Figure 8. ^{1}H NMR spectra ($CDCl_3$, 250 MHz) of two minor isomers of pentamethoxy-pentaphenyl -[5]pericyclynes (R_t=16.56 and 20.26 min in Fig. 7). R=Me. The exact assignment.

dilithium salt of the major diastereoisomer **B** (Scheme 20); the cyclization process creates two additional stereogenic carbon atoms. After methylation in situ of the intermediate OLi groups of the partly resolved salt of **7a**, the expected number of stereoisomers of the product **11a** is reduced to three. Their corresponding statistical ratio would be 1:2:1 (Scheme 20).

Analytical HPLC resolution was successfully attempted: three peaks were obtained with baseline separation, and their relative UV-integration confirmed the statistical distribution (Fig. 7).

Semi-preparative HPLC separation of the mixture was carried out under optimized conditions (see Section 4). Two out of three diastereoisomers were finally isolated as pure white crystalline compounds. Their respective NMR spectra confirmed their stereochemical purity, and were consistent

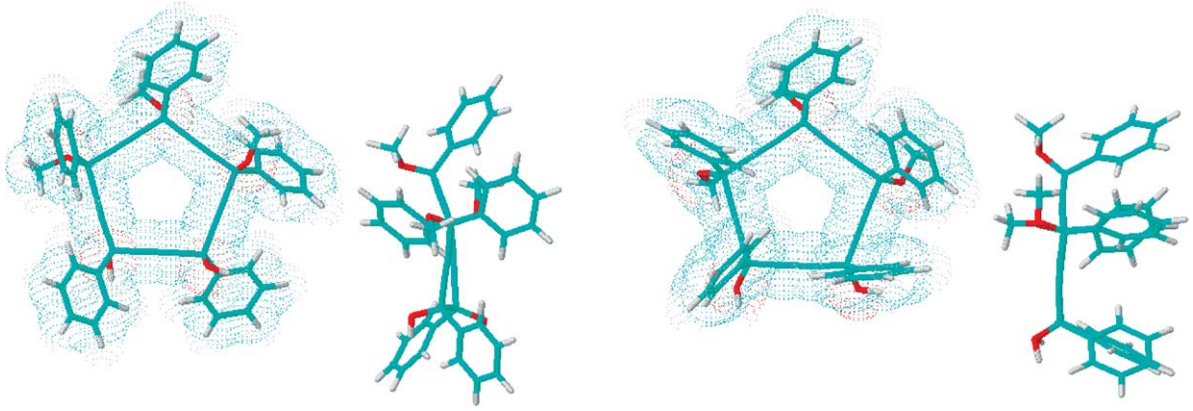


Figure 9. MM2-optimized geometries of two stereoisomer of **11a**.[4].

with the theoretical number (3) and relative intensities (1:2:2) of non-equivalent OCH_3 signals for the proposed structures (Fig. 8). These compounds are the first examples of disymmetrically and stereoselectively substituted functional [5]pericyclynes.

3. Conclusion

Functional [5]pericyclynes with either tertiary or secondary carbinol vertices are definitely stable compounds. The stereochemical complexity arising from the stereogenicity of the sp^3 vertices (with respect to the symmetrical decamethyl- and pentacyclopropylidene-derivatives)[29] has been studied by NMR and resolved by HPLC techniques. Monocrystals of stereochemically pure samples were not suitable for an X-ray structure determination, but insights may be gained on the basis of MM modeling (Fig. 9). The phenyl and methoxy substituents do not alter the features calculated at higher (DFT) level for unsubstituted models (slight ring distortion from planarity, absence of homo-aromaticity as revealed by the lengths of 'fixed' single and triple bonds).[6] Although effective dissociation of isohypsic equivalents of the *carbo*-cyclopentadienyl cation remains to be achieved, preliminary MS data on **31** are encouraging. Much work however has still to be done, especially in terms of scale-up of the stereoisomeric resolution. Alternatively, direct stereoselective synthesis under the influence of chiral auxiliaries or catalysts deserves to be envisioned.

4. Experimental

4.1. General

All reagents were used as commercially available from Acros Organics, Avocado, Aldrich, Lancaster, Strem. THF and diethylether were dried and distilled on sodium/benzophenone, pentane and dichloromethane on P_2O_5. Commercial solutions of EtMgBr are 3 M in diethylether. Commercial solutions of *n*-BuLi are 1.6 or 2.5 M in hexane, and their effective concentration were checked by titration with 2,2,2′-trimethylpropionanilide.[30] Previously described procedures were used for the preparation of **1**,[15] **4a**, **5a** and **3a**,[10a] **6a**, **6c** and **2a**,[13] **14**,[21,23], **28**, **29**, **30** and **27**.[10b] All reactions were carried out under nitrogen or argon atmosphere, using Schlenk and vacuum line techniques. Column chromatographies were carried out with SDS silicagel (60 Å C.C 70–200 μm). Thin Layer Chromatography plates were purchased from SDS (60F254, 0.25 mm) and revealed by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used. IR: 0.1 mm CaF_2 cell, Perkin-Elmer GX FT-IR. ^1H and ^{13}C NMR: Brucker AC 200, WM 250, DPX 300 or AMX 400. X-Ray diffraction: IPds STOE. Mass spectrometry: Quadrupolar Nermag R10-10H. Elemental analyses: Perkin-Elmer 2400 CHN (flash combustion and detection by catharometry). Analytical and semi-preparative HPLC chains: Waters quaternary chains (600 Controller), coupled with UV detectors and driven with a Millenium software (version 4.00). HPLC columns: analytical Prontosil 120-3-SI column 150 mm×4.0 mm i.d., particle size: 3 μm, Bischoff); semi-preparative Prontosil 120-5-SI column (250 mm×8 mm i.d., particle size: 5 μm, Bischoff). All IR and NMR spectra were recorded in $CDCl_3$ solutions. IR absorption frequencies ν 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. Since most compounds are isolated as oily mixtures of diastereoisomers, characteristic assignments are given to trace the analytical consistency within the quite homogeneous series of compounds studied (diethynyl carbinol series and phenyl- and *p*-anisyl-derivatives thereof).

4.1.1. 3-Trimethylsilyl-1-(4-methoxyphenyl) prop-2-yn-1-one (4b). Aluminum chloride (9.00 g, 67 mmol) was added to a solution of bistrimethylsilylacetylene (13.1 mL, 67 mmol) and anisoyl chloride (11.50 g, 67 mmol) in DCM (160 mL) at 0 °C. After stirring for 3 h at r.t., the mixture was cooled to 0 °C, hydrolyzed with ice (50 g) and extracted in dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ and water, then dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude ketone **4b** as an orange oil (15.66 g, 100%), displaying satisfactory analytical data. $R_f \approx 0.45$ (heptane/EtOAc 9:1). ^1H NMR: $\delta=0.24$ (s, 9H; $Si(CH_3)_3$), 3.79 (s, 3H; OCH_3), 6.87 (d, 2H; *m*-C*H*), 8.03 (d, 2H; *o*-C*H*). ^{13}C NMR: $\delta=-0.69$ (q, $^1J_{CH}=120$ Hz; $Si(CH_3)_3$), 55.51 (q, $^1J_{CH}=145$ Hz; OCH_3), 99.38 (s; *C*≡CSi), 100.96 (s; ≡*C*–Si), 113.79 (d, $^1J_{CH}=158$ Hz; *m*-*C*H), 129.66 (s; *ipso*-*C*–C═O), 131.92 (d, $^1J_{CH}=159$ Hz; *o*-*C*H), 164.48 (s; *p*-*C*–OMe), 176.22 (s; *C*═O). IR: $\nu=2978$, 2875 (C–H), 2155 (C≡CSi), 1634 (C═O), 1598, 1509 (aromatic C–C), 1257 (C–Si), 1166, 1110, 1040–1026 (C–O).

4.1.2. 1-Trimethylsilyl-3-(4-methoxyphenyl)penta-1,4-diyn-3-ol (5b). A saturated solution of acetylene in THF (350 mL) at 0 °C was treated with EtMgBr (81.0 mL, 243 mmol) for 1 h at 0 °C. Anisylketone **4b** (15.66 g, 67 mmol) was added, and the stirring was continued overnight (17 h) at r.t. The reaction mixture was hydrolyzed with a saturated aqueous NH_4Cl, and extracted with diethylether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification through column chromatography on silicagel (heptane/EtOAc 8:2) afforded diyne **5b** as a brown oil (10.72 g, 61%). $R_f \approx 0.20$ (heptane/EtOAc 85:15). MS (DCI/NH_3): $m/z=258$ ($[M]^+$), 241 ($[M-OH]^+$), 161 ($[M-C{\equiv}CSiMe_3)]^+$). ^1H NMR: $\delta=0.20$ (s, 9H; $Si(CH_3)_3$), 2.74 (s, 1H; ≡C–*H*), 3.24 (s, 1H; O*H*), 3.78 (s, 3H; OCH_3), 6.91 (d, 2H; *m*-C*H*), 8.09 (d, 2H; *o*-C*H*). ^{13}C NMR: $\delta=-0.48$ (q, $^1J_{CH}=121$ Hz; $Si(CH_3)_3$), 55.26 (q, $^1J_{CH}=144$ Hz; OCH_3), 64.51 (s, >*C*(OH)An), 73.03 (d, $^1J_{CH}=154$ Hz; ≡*C*–H), 83.75 (d, $^2J_{CH}=49$ Hz; *C*≡CH), 89.92 (s; *C*≡CSiMe$_3$), 104.01 (s; ≡*C*–SiMe$_3$), 113.61 (d, $^1J_{CH}=170$ Hz; *m*-*C*H), 127.62 (d, $^1J_{CH}=153$ Hz; *o*-*C*H), 133.32 (s; *ipso*-*C*–C), 159.66 (s; *p*-*C*–OMe). IR: $\nu=3576$ (O–H), 3305 (≡CH), 2963 (C–H), 2840 (OC–H), 2176 (C≡CSi), 2101 (≡CH), 1608, 1510 (aromatic C–C), 1252 (C–Si), 1173, 1091, 1035 (C–O).

4.1.3. 1-Trimethylsilyl-3-(4-methoxyphenyl)-3-methoxypenta-1,4-diyne (3b). A solution of alcohol **5b** (10.72 g, 42 mmol) in THF (180 mL) was treated with *n*-butyllithium (18.80 mL, 42 mmol) at −78 °C. After stirring for 0.5 h,

methyl iodide (20.4 mL, 328 mmol) was added dropwise. The temperature was allowed to warm up to −25 °C, and DMSO (2.9 mL, 42 mmol) was added. After stirring for 1 h at −25 °C, then 2 h at r.t., the reaction mixture was treated with saturated aqueous NH_4Cl and extracted with diethylether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give ether **3b** as an orange powder (8.16 g, 73%). $R_f \approx 0.34$ (heptane/EtOAc 85:15). MS (DCI/NH_3): $m/z = 272$ ($[M]^+$) = 241 ($[M-OCH_3]^+$). ^1H NMR: $\delta = 0.22$ (s, 9H; $Si(CH_3)_3$), 2.73 (s, 1H; ≡C–*H*), 3.46 (s, 3H; Csp^3–OCH_3), 3.81 (s, 3H; CH_3O–C_6H_4), 6.87 (d, 2H; *m*-C*H*), 7.68 (d, 2H; *o*-C*H*). ^{13}C NMR: $\delta = -0.43$ (q, $^1J_{CH} = 121$ Hz; $Si(CH_3)_3$), 55.15 (q, $^1J_{CH} = 144$ Hz; OCH_3), 55.66 (q, $^1J_{CH} = 143$ Hz; OCH_3), 71.81 (s, >*C*(OMe)An), 73.03 (d, $^1J_{CH} = 254$ Hz; ≡*C*–H), 81.27 (d, $^2J_{CH} = 49$ Hz; *C*≡CH), 91.71 (s; –*C*≡$CSiMe_3$), 101.37 (s; ≡*C*–$SiMe_3$), 113.41 (d, $^1J_{CH} = 154$ Hz; *m*-*C*H), 127.81 (d, $^1J_{CH} = 160$ Hz; *o*-*C*H), 131.79 (s; *ipso*-*C*–C–OMe), 159.75 (s; *p*-*C*–OMe). IR: $\nu = 3305$ (≡CH), 2961 (C–H), 2839 (OC–H), 2170 (C≡CSi), 2117 (≡CH), 1609, 1509 (aromatic C–C), 1252 (C–Si), 1174, 1089, 1060 (C–O).

4.1.4. 1,11-Bis(trimethylsilyl)-3,9-dimethoxy-3,6,9-tris(4-methoxyphenyl)undeca-1,4,7,10-tetrayn-6-ol (6b). A solution of diyne **3b** (12.64 g, 46 mmol) in THF (100 mL) was treated with *n*-butyllithium (19.73 mL, 46 mmol) at −78 °C. After stirring for 10 min, anisoyl chloride (3.96 g, 23 mmol) was added and the reaction mixture was stirred for 3 h at r.t. The mixture was hydrolyzed with saturated NH_4Cl and extracted with diethylether. The organic layer was washed with saturated aqueous NH_4Cl and brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification through column chromatography (heptane/EtOAc 9:1) afforded tetrayne **6b** as a brown oil (8.18 g, 52%). $R_f \approx 0.21$ (heptane/EtOAc 85:15). MS (DCI/NH_3): $m/z = 679$ ($[MH]^+$), 661 ($[M-OH]^+$), 647 ($[M-OCH_3]^+$). ^1H NMR: $\delta = 0.19$–0.21 (m, 18H; $Si(CH_3)_3$), 3.12 (s, 1H; O*H*), 3.41–3.46 (m, 6H; Csp^3OCH_3), 3.71–3.81 (m, 9H; $C_6H_4OCH_3$), 6.83–6.91 (m, 6H; *m*-C*H*), 7.62–7.73 (m, 6H; *o*-C*H*). ^{13}C NMR: $\delta = -0.02$ (q, $^1J_{CH} = 120$ Hz; $Si(CH_3)_3$), 52.92 (q, $^1J_{CH} = 144$ Hz; Csp^3–OCH_3), 55.29 (q, $^1J_{CH} = 144$ Hz; C_6H_4–OCH_3), 67.94 (s; >*C*(OH)An), 74.48 (s; >*C*(OMe)An), 83.02 and 86.18 (s; *C*≡C), 92.08 (s; *C*≡$CSiMe_3$), 101.50 (s; ≡*C*–$SiMe_3$), 113.65 (d, $^1J_{CH} = 155$ Hz, *m*-*C*H), 127.20 (d, $^1J_{CH} = 154$ Hz, *o*-*C*H), 132.00 (broad s; *ipso*-*C*–O), 159.96 (s; *p*-*C*–OMe). IR: $\nu = 3570$ (O–H), 2961 (C–H), 2840 (OC–H), 2171 (C≡CSi), 1609, 1510 (aromatic C–C), 1252 (C–Si), 1174, 1061, 1035 (C–O).

4.1.5. 1,11-Bis(trimethylsilyl)-3,6,9-dimethoxy-3,6,9-tris(4-methoxyphenyl)undeca-1,4,7,10-tetrayne (6d). A solution of alcohol **6b** (8.18 g, 12 mmol) in THF (200 mL) was treated with *n*-butyllithium (7.6 mL, 12 mmol) at −78 °C for 10 min. Iodomethane (6.0 mL, 96 mmol) was added and the temperature was allowed to warm up to −25 °C. DMSO (0.86 mL, 12 mmol) was added, and stirring was continued for 1 h at −20 °C, then for 3 h at r.t. After treatment with saturated aqueous NH_4Cl and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give ether **6d** as a brown oil (7.22 g, 83%). The crude product displays satisfactory analyses and was used as such in the next step. $R_f \approx 0.23$ (heptane/EtOAc 9:1). MS (DCI/NH_3): $m/z = 693$ ($[MH]^+$), 661 ($[M-OCH_3]^+$). ^1H NMR: $\delta = 0.21$–0.22 (s, 18H; $Si(CH_3)_3$), 3.45–3.54 (s, 9H; Csp^3OCH_3), 3.79–3.80 (m, 9H; $C_6H_4OCH_3$), 6.83–6.88 (m; 6H; *m*-C*H*), 7.63–7.69 (m, 6H; *o*-C*H*). $^{13}C\{^1H\}$NMR: $\delta = -0.43$ ($Si(CH_3)_3$), 53.06 (Csp^3–OCH_3), 55.13 (C_6H_4–OCH_3), 71.47 (>*C*(OMe)An), 83.82 and 84.53 (*C*≡C), 91.86 (*C*≡$CSiMe_3$), 101.45 (≡*C*–$SiMe_3$), 113.08 (*m*-*C*H), 127.70 (*o*-*C*H), 131.81 (*ipso*-*C*–C), 159.83 (*p*-*C*–OMe). IR: $\nu = 2960$, 2935 (C–H), 2840 (OC–H), 2170 (C≡CSi), 1609, 1509 (aromatic C–C), 1252 (C–Si), 1174, 1061 (C–O).

4.1.6. 3,6,9-Trimethoxy-3,6,9-tris(4-methoxyphenyl)-undeca-1,4,7,10-tetrayne (2b). Tetrayne **6d** (7.22 g, 10 mmol) and K_2CO_3 (7.20 g, 52 mmol) were dissolved in methanol (25 mL) at 0 °C. After stirring for 1 h at r.t., the reaction mixture was filtered, concentrated and diluted with diethylether (100 mL). The organic layer was washed with water (2×50 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated to dryness under reduced pressure to give crude tetrayne **2b** as a brown oil (5.45 g, 99%). $R_f \approx 0.18$ (heptane/EtOAc 8:2). MS (DCI/NH_3): $m/z = 566$ ($[M+NH_4]^+$), 548 ($[MH]^+$), 517 ($[M-OCH_3)]^+$). ^1H NMR: $\delta = 2.76$ (s, 2H; ≡C–*H*), 3.49–3.53 (m, 9H; Csp^3–OCH_3), 3.79–3.81 (m, 9H; $C_6H_4OCH_3$), 6.84–6.92 (m, 6H; *m*-C*H*), 7.65–7.70 (m, 6H; *o*-C*H*). ^{13}C NMR: $\delta = 53.75$ (q, $^1J_{CH} = 152$ Hz; Csp^3–OCH_3), 54.53 (q, $^1J_{CH} = 144$ Hz; C_6H_4–OCH_3), 71.65 (s; ≡*C*–H), 72.41 (s; >*C*(OMe)An), 74.95 (s, *C*≡CH), 84.01 and 84.33 (s; *C*≡C), 113.57 (d, $^1J_{CH} = 155$ Hz; *m*-*C*H), 127.82 (d, $^1J_{CH} = 154$ Hz; *o*-*C*H), 131.62 (s; *ipso*-*C*–C), 159.93 (s; *p*-*C*–OMe). IR: $\nu = 3305$ (≡CH), 3003, 2957, 2936 (C–H), 2839, 2826 (OC–H), 2117 (≡CH), 1609, 1508 (aromatic C–C), 1258, 1177, 1060 (C–O).

4.1.7. 1,4,13-Trimethoxy-1,4,7,10,13-pentaphenylcyclopentadeca-2,5,8,11,14-pentayn-7,10-diol (7a) and side-products. A solution of tetrayne **2a** (300 mg, 0.65 mmol) in THF (10 mL) was treated with *n*-butyllithium (0.59 mL, 1.31 mmol) for 10 min between −78 °C and −15 °C while the color turned to deep green. After cooling back to −78 °C, a solution of dibenzoylacetylene **1** (153 mg, 65 mmol) in THF (12 mL) was added dropwise. The temperature was allowed to warm up to r.t. over a 45 min period, and stirring was continued for a further 1.5 h. The mixture was diluted with diethylether (50 mL), treated with saturated aqueous NH_4Cl (30 mL). The organic layer was separated, washed with aqueous NH_4Cl (30 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The dark brown crude oil (370 mg) was chromatographed over silicagel (heptane/acetone 8:2) to afford [5]pericyclyne **7a** as an orange oil (166 mg, 37%). $R_f = 0.20$ (heptane/acetone 8:2). MS (DCI/NH_3): $m/z = 710$ ($[M+NH_4]^+$), 661 ($[M-CH_3O]^+$). ^1H NMR: $\delta = 3.09$ and 3.18 (2s, 2H; O*H*), 3.40–3.69 (m, 9H; OCH_3), 7.32–7.47 (m, 15H; *m*-, *p*-C*H*), 7.68–7.90 (m, 10H; *o*-C*H*). $^{13}C\{^1H\}$ NMR: $\delta = 53.96$–54.10 (OCH_3), 65.68 (>*C*(OH)Ph), 72.58 (>*C*(OMe)Ph), 81.80–82.30 and 83.77–84.48 and 86.05–86.31 (*C*≡C), 126.26–127.00 (*m*-, *p*-C*H*), 128.87–129.67 (*o*-C*H*), 139.50–139.78 (*ipso*-*C*–C–OMe), 140.82–140.95 (*ipso*-*C*–C–OH). IR: $\nu = 3683$, 3558, 3291 (O–H), 3062–2896

(C–H), 2822 (OC–H), 1604, 1490 (aromatic C–C), 1451 (C–H), 1224, 1178, 1069 (C–O). The main characteristics of three side-products (**8a**–**10a**, 10–25%) are listed below.

4.1.8. 4-Hydroxy-7,10,17-trimethoxy-1,4,7,10,13-pentaphenylpentadeca-2,5,8,11,14-pentayn-1-one (8a). $R_f \approx 0.26$ (heptane/acetone 8:2). MS (DCI/NH_3): $m/z = 710$ ($[M+NH_4]^+$). ^{1}H NMR: $\delta = 2.76$ (s, 1H; ≡C–*H*), 3.50–3.55 (m, 9H; OCH_3), 7.32–7.46 (m, 12H; Csp^3-phenyl *m*-, *p*-C*H*), 7.52–7.58 (m, 3H; benzoyl *m*-, *p*-C*H*), 7.72–7.82 (m, 8H; Csp^3-phenyl *o*-C*H*), 8.05–8.10 (m, 2H; benzoyl *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.62$ (O*C*H$_3$), 65.56 (>*C*(OH)Ph), 71.97 (>*C*(OMe)Ph), 75.52 (≡*C*–H), 80.64 (*C*≡CH), 81.21–91.87 (*C*≡C), 125.78–136.33 (aromatic *C*H), 139.36 (*ipso-C*–C–OCH$_3$), 139.89 (*ipso-C*–C–OH), 177.37 (*C*=O). IR: $\nu = 3571$ (O–H), 3305 (≡C–H), 1649 (C=O).

4.1.9. 3,6,9,18,21,24-Hexamethoxy-3,6,9,12,15,18,21,24-octaphenylhexacosa-1,4,7,10,13,16,19,22,25, 28-nonayn-12,15-diol (9a). $R_f \approx 0.15$ (heptane/acetone 8:3). MS (DCI/NH_3): $m/z = 1168$ ($[M+NH_4]^+$). ^{1}H NMR: $\delta = 2.75$ (s, 2H; ≡C–*H*), 3.09 (m, 2H; O*H*) 3.46–3.51 (m, 18H; OCH_3), 7.31–7.34 (m, 18H; *m*-, *p*-C*H*), 7.71–7.73 (m, 12H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.33$ and 53.48 (O*C*H$_3$), 65.17 (>*C*(OH)Ph), 71.92 (>*C*(OMe)Ph), 75.45 (≡*C*–H), 80.52 (*C*≡CH), 82.55–86.34 (*C*≡*C*), 125.84–129.01 (aromatic *C*H), 139.44 (*ipso-C*–C–OMe), 140.76 (*ipso-C*–C–OH). IR: $\nu = 3571$ (O–H), 3305 (≡C–H).

4.1.10. 4,16-Dihydroxy-7,10,13-trimethoxy-1,4,7,10,13,16,19-heptaphenylnonadeca-2,5,8,11,14,17-hexayn-1,19-dione (10a). $R_f \approx 0.15$ (heptane/acetone 8:2). MS (DCI/NH_3): $m/z = 944$ ($[M+NH_4]^+$). ^{1}H NMR: $\delta = 3.49$–3.52 (m, 9H; OCH_3), 3.90 (m, 2H; O*H*), 7.25–7.44 (m, 15H; Csp^3-phenyl *m*-, *p*-C*H*), 7.54–7.60 (m, 6H; benzoyl *m*-, *p*-C*H*), 7.70–7.80 (m, 10H; Csp^3–phenyl *o*-C$_6H_5$), 8.04–8.10 (m, 4H; benzoyl *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.62$ (O*C*H$_3$), 64.94 (>*C*(OH)Ph), 72.02 (>*C*(OMe)Ph), 81.64–85.79 and 92.02 (*C*≡C), 125.89–136.33 (aromatic *C*H), 139.12 (*ipso-C*–C–OMe), 139.78 (*ipso-C*–C–OH), 177.52 (*C*=O).

4.1.11. 1,4,13-Trimethoxy-1,4,13-tris(4-methoxyphenyl)-7,10-diphenyl-cyclopentadeca-2,5,8,11, 14-pentayn-7,10-diol (7b). The above Section 4.1.9 for the preparation of **7a** was applied to tetrayne **2b** (412 mg, 0.75 mmol) and dibenzoylacetylene **1** (176 mg, 0.75 mmol) to afford trianisyl-[5]pericyclyne **7b** as an orange oil (180 mg, 31%). $R_f \approx 0.20$ (heptane/EtOAc 7:3). MS (DCI/NH_3): $m/z = 800$ ($[M+NH_4]^+$), 768 ($[M-MeOH+NH_4]^+$), 751 ($[M-MeO]^+$). ^{1}H NMR: $\delta = 3.30$–3.62 (m, 9H; OCH_3), 3.69–3.86 (m, 9H; C$_6$H$_4$OCH_3), 6.78–6.92 (m, 6H; *p*-anisyl *m*-C*H*), 7.30–7.40 (m, 6H; phenyl *m*-, *p*-C*H*), 7.51–7.84 (m, 10H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.44$ (Csp^3–O*C*H$_3$), 55.45 (C$_6$H$_4$O*C*H$_3$), 65.22 (>*C*(OH)Ph), 71.76 (>*C*(OMe)An), 81.63–85.85 (*C*≡C), 113.87 (*p*-anisyl *m*-*C*H), 125.94–129.07 (phenyl *C*H), 128.63 (*p*-anisyl *o*-*C*H), 131.45 (anisyl *ipso-C*–C–OMe), 140.67 (phenyl *ipso-C*–C–OH), 160.15 (*p*-anisyl *p*-*C*–OMe).

4.1.12. 1,4,7,10,13-Pentamethoxy-1,4,7,10,13-pentaphenylcyclopentadeca-2,5,8,11,14-pentayne (11a). *n*-Butyllithium (105 μL, 0.23 mmol) was syringed into a solution of [5]pericyclyndiol **7a** (80 mg, 0.12 mmol) in THF (3 mL) at −78 °C. After stirring for 15 min, methyl iodide was added (115 μL, 1.85 mmol), and the temperature was allowed to warm up to −25 °C. DMSO (20 μL; 0.23 mmol) was added and stirring was continued at −25 °C for 1 h, then at r.t. for a further 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution, and extracted with diethylether. The organic layer was washed with aqueous NH_4Cl and brine, dried with magnesium sulfate and the solvent was removed under reduced pressure. Purification by column chromatography (heptane/acetone 7:3) gave **11a** as a yellow oil (80 mg, 92%). $R_f \approx 0.26$ (heptane/acetone 7:3). MS (DCI/NH_3): $m/z = 738$ ($[M+NH_4]^+$), 689 ($[M-CH_3O]^+$). MS (APCI/CH_3CN): $m/z = 730$ ($[M-CH_3O+CH_3CN]^+$). ^{1}H NMR: $\delta = 3.37$–3.69 (8s, 15H; OCH_3), 7.33–7.45 (m, 15H; *m*-, *p*-C*H*), 7.74–7.90 (m, 10H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.73$ (O*C*H$_3$), 72.35 (>*C*(OMe)Ph), 83.42–83.86 (*C*≡C), 126.57 (*m*-, *p*-*C*H), 128.32–129.16 (*o*-*C*H), 139.53 (*ipso-C*–C–OMe). IR: $\nu =$ 3067–2902 (C–H), 2827 (OC–H), 1601, 1490, 1451 (aromatic C–C), 1230, 1178, 1154, 1071 (C–O). Notice: the cylization step (4.8) and methylation steps can also be performed subsequently in one pot.

4.1.13. Dicobalthexacarbonyl-1,4,13-trimethoxy-1,4,7,10,13-pentaphenylcyclopentadeca-2,5,8, 11,14-pentayn-7,10-diol (12a), and side-product. Dicobaltoctacarbonyle (126 mg, 0.37 mmol) was added into a solution of [5]pericyclyndiol **7a** (256 mg, 0.37 mmol) in diethylether (25 mL) at 0 °C. The color turned red, and the reaction was monitored by TLC. After stirring for 30 min, the solution was concentrated and the oily residue was chromatographed over silicagel (heptane/acetone 8:2). The dinuclear complex **12a** was obtained as a red-orange oil (231 mg, 64%). $R_f \approx 0.33$ (heptane/acetone 7:3). MS (APCI>0/CH_3CN): $m/z = 716$ ($[M-Co_2(CO)_6-OH+CH_3CN]^+$), 702 ($[M-Co_2(CO)_6-CH_3O+CH_3CN]^+$). MS (MALDI/dithranol–NaI): $m/z = 1001$ ($[M+Na]^+$), 715 ($[M+Na-Co_2(CO)_6]^+$). Elemental analysis % (calcd): C = 65.96 (66.27), H = 4.22 (3.71), Co = 10.07 (12.04). ^{1}H NMR: $\delta = 3.27$–3.72 (m, 9H; OCH_3), 7.19–7.42 (m, 15H; *m*-, *p*-C*H*), 7.52–7.80 (m, 10H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta =$ 52.11–52.92 (O*C*H$_3$), 72.02 (>*C*(OMe)Ph), 85.26–86.03 (*C*≡*C*), 100.72–101.55 ((*C*≡*C*)(Co$_2$(CO)$_6$)), 125.56–129.16 (aromatic *C*H), 139.54 (*ipso-C*–C–OMe), 141.78 (*ipso-C*–C–OH), 198.75 (Co$_2$(*C*≡O)$_6$). IR: $\nu = 3689$, 3536 (O–H), 2097, 2063 and 2037 (CoC≡O).

The less polar tetranuclear complex **12a′** was also isolated as a red oil from the chromatography column (79 mg, 17%): bis(dicobalthexacarbonyl)-1,4,13-trimethoxy-1,4,7,10,13-penta-phenylcyclo-pentadeca-2,5,8,11,14-pentayn-7,10-diol (**12a′**) $R_f \approx 0.48$ (heptane/acetone 7:3). MS (MALDI/dithranol–NaI): $m/z = 715$ ($[M+Na-2Co_2(CO)_6]^+$). Elemental analysis % (calcd): C = 57.79 (56.98), H = 3.00 (2.87). ^{1}H NMR: $\delta = 3.29$–3.57 (m, 9H; OCH_3), 7.21–7.44 (m, 15H; *m*-, *p*-C*H*), 7.59–7.80 (m, 10H; *o*-C*H*). IR: $\nu =$ 3689, 3409 (O–H), 2095, 2064, 2035 (Co$_2$(C≡O)$_6$).

4.1.14. Dicobalthexacarbonyl-1,4,13-trimethoxy-1,4,13-tris(4-methoxyphenyl)-7,10-diphenyl-cyclopentadeca-2,5,8,11,14-pentayn-7,10-diol (12b). The above Section 4.1.13 for the preparation of **12a** was applied to

pericyclyndiol **7b** (180 mg, 0.23 mmol) and dicobalt–octacarbonyle (80 mg, 0.23 mmol) to afford the dinuclear complex **12b** as a red oil (180 mg, 57%). $R_f \approx 0.24$ (heptane/EtOAc 7:3). ^{1}H NMR: $\delta = 3.21$–3.57 (m, 9H; OCH_3), 3.61–3.86 (m, 9H; C_6H_4–OCH_3), 6.64–6.97 (m, 6H; *m*-C*H*), 7.31–7.50 (m, 6H; phenyl *m*-, *p*-C*H*), 7.53–7.81 (m, 10H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.43$ (Csp^3–OCH_3), 55.44 (C_6H_4–OCH_3), 64.55 (>*C*(OH)Ph), 71.83 (>*C*(OMe)An), 84.32–89.35 (*C*≡*C*), 103.06 (*C*≡C(Co_2 $(CO)_6$)), 113.87 (*p*-anisyl *m*-*C*H), 125.53–129.45 (aromatic *C*H), 128.17 (*p*-anisyl *o*-*C*H), 133.67 (i*pso*-*C*–C–OMe), 143.83 (*ipso*-*C*–C–OH), 160.12 (*p*-*C*–OMe), 198.29 (*C*≡O). IR: $\nu =$ 3536 (O–H), 2097, 2062, 2036 (Co_2(C≡O)$_6$).

4.1.15. Dicobalthexacarbonyle-1,4,7,10,13-pentamethoxy-1,4,7,10,13-pentaphenylcyclopenta-deca-2,5,8,11,14-pentayne (13a). The above Section 4.1.13 for the preparation of **12a** was applied to pericyclyne **11a** (80 mg; 0.11 mmol) and dicobaltoctacarbonyle (38 mg; 0.11 mmol) to afford the dinuclear complex **13a** as a reddish oil (56 mg, 54%). $R_f \approx 0.38$ (heptane/acetone 7:3). MS (APCI/CH_3CN): $m/z = 730$ ([M−$Co_2(CO)_6$–CH_3O+CH_3CN]$^+$), 689 ([M−$Co_2(CO)_6$–CH_3O]$^+$). ^{1}H NMR: $\delta = 3.11$–3.81 (m, 15H; OCH_3), 6.89–7.20, 7.35–7.45 and 7.54–7.94 (m, 25H; aromatic C*H*). ^{13}C{^{1}H} NMR: $\delta = 52.51$–53.94 (OCH_3), 85.23–87.05 (*C*≡*C*), 100.77–101.57 (*C*≡C($Co_2CO)_6$)), 125.63–129.15 (aromatic *C*H), 139.57 (*ipso*-*C*–C–OMe), 141.75 (*ipso*-*C*–C–OMe in β position from Co), 198.73–199.33 (*C*≡O). IR: $\nu = 3065$–2900 (C–H), 2827 (OC–H), 2094, 2060, 2034 (Co_2(C≡O)$_6$). 1600, 1490 (aromatic C–C), 1450 (C–H), 1230, 1177, 1151, 1068 (C–O).

The less polar tetranuclear complex **13a′** was also isolated as a red oil from the chromatography column (38 mg, 27%): bis(dicobalthexacarbonyl)-1,4,7,10,13-pentamethoxy-1,4,7,10,13-penta-phenylcyclopentadeca-2,5,8,11,14-pentayne (**13a′**) $R_f \approx 0.50$ (heptane/acetone 7:3). ^{1}H NMR: $\delta = 3.29$–3.57 (m, 9H; OCH_3), 7.21–7.44 (m, 15H; *m*-, *p*-C*H*), 7.59–7.80 (m, 10H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 52.52$–53.95 (OCH_3), 85.26–87.04 (*C*≡C), 100.72–101.55 (*C*≡*C*($Co_2(CO)_6$)), 125.64–129.14 (aromatic *C*H), 139.54 (*ipso*-*C*–C–OMe), 141.73 (*ipso*-*C*–C–OMe in β position from Co), 198.75–199.32 (*C*≡O). IR: $\nu = 2095$, 2064, 2035 (Co_2(C≡O)$_6$).

4.1.16. Dicobalthexacarbonyle-1,4,13-trimethoxy-1,4,13-triphenylcyclopentadeca-2,5,8,11,14-pentayn-7,10-diol (15a). *n*-Butyllithium (1.00 mL, 2.18 mmol) was added dropwise into a solution of tetrayne **2a** (500 mg, 1.09 mmol) in THF (30 mL) at −78 °C. The temperature was allowed to warm up to −15 °C while the color turned to green. After cooling back to −78 °C, a solution of complex **14** (401 mg, 1.09 mmol) in THF (25 mL) was added dropwise. The temperature was allowed to warm up to −30 °C and then quenched with saturated aqueous NH_4Cl (30 mL), and diluted with diethylether (50 mL). The organic layer was separated, then washed with saturated aqueous NH_4Cl (2× 20 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The deep red residue (580 mg) was purified by column chromatography over silicagel (heptane/acetone 7:3). Complex **15a** was isolated as a deep red oil (226 mg, 25%). $R_f \approx 0.36$ (heptane/acetone 7:3). ^{1}H NMR: $\delta = 3.21$–3.27 (m, 2H; O*H*), 3.32–3.69 (m, 9H; OCH_3), 5.76–5.79 (m, 2H; >C*H*(OH)), 7.36–7,44 (m, 9H; *m*-, *p*-C*H*), 7.69–7.77 (m, 6H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.35$–53.51 (OCH_3), 63.50 and 63.94 (>*C*H(OH)), (>*C*(OMe)Ph), 83.34–85.68 (*C*≡*C*), 92.21–93.13 ((*C*≡*C*)($Co_2(CO)_6$)), 126.50–129.09 (aromatic *C*H), 138.93 (*ipso*-*C*–C–OMe), 198.39–198.63 (*C*≡O). IR: $\nu =$ 3583 (O–H), 3066–2900 (C–H), 2827 (OC–H), 2100, 2066, 2038 (Co_2(C≡O)$_6$), 1600–1577, 1490 (aromatic C–C), 1450 (C–H), 1228, 1178, 1069 (C–O).

4.1.17. Dicobalthexacarbonyle-1,4,13-trimethoxy-1,4,13-tris(4′-methoxyphenyl)cyclopentadeca- 2,5,8,11,14-pentayn-7,10-diol (15b). The above Section 4.1.16 for the preparation of **15a** was applied to tetrayne **2b** (197 mg, 0,36 mmol), *n*-butyllithium (0.29 mL, 0.72 mmol) and complex **14** (130 mg, 0.36 mmol) to afford complex **15b** as a red-orange oil (22 mg, 6%). $R_f \approx 0.25$ (heptane/EtOAc 7:3). ^{1}H NMR: $\delta = 3.29$–3.50 (m, 9H; OCH_3), 3.80–3.81 (m, 9H; C_6H_4–OCH_3), 5.74 and 5.78 (2s, 2H; C*H*(OH)), 6.80–6.92 (m, 6H; anisyl *m*-C*H*), 7.57–7.70 (m, 6H; anisyl *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.32$ (Csp^3–OCH_3), 55.34 (C_6H_4–OCH_3), 63.96 (*C*H(OH)), 71.67 (>*C*(OMe)An), 84.02 and 84.34 (*C*≡*C*), 92.65 ((*C*≡*C*)$Co_2(CO)_6$), 113.63 (anisyl *m*-*C*H), 127.85 (anisyl *o*-*C*H), 131.66 (*ipso*-*C*–C–OMe), 160.13 (anisyl *p*-*C*–OMe), 198.52 (Co_2(*C*≡O)$_6$). IR: $\nu =$ 3689, 3587, 3537 (O–H), 2097, 2062, 2036 (Co_2(C≡O)$_6$).

4.1.18. 1,4,13-Trimethoxy-1,4,13-triphenylcyclopentadeca-2,5,8,11,14-pentayn-7,10-diol (16a). Cerium ammonium nitrate (146 mg, 0.27 mmol) was added to a solution of complex **15a** (110 mg, 0.14 mmol) in acetone (6 mL) at 0 °C. After 15 min, the reaction mixture was warmed to r.t. and stirring was continued for 1.5 h. The IR spectrum reveals the complete disappearance of carbonyl stretching vibrations. The reaction mixture was treated with water and diluted with diethylether. The organic layer was separated, washed with water (2×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over silicagel (heptane/acetone 8:2) to give free [5]pericyclyndiol **16a** as a brown oil (50 mg, 70%). $R_f \approx 0.22$ (heptane/acetone 7:3). MS (DCI/NH_3): $m/z = 558$ ([M+NH_4]$^+$), 526 ([M−MeOH+NH_4]$^+$), 509 ([MH−MeOH]$^+$), 494 ([M−2MeOH+NH_4]$^+$). ^{1}H NMR: $\delta = 3.35$–3.62 (m, 9H; OCH_3), 5.14–5.21 (m, 2H; >C*H*(OH)), 7.21–7.39 (m, 9H; *m*-, *p*-C*H*), 7.60–7.79 (m, 6H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 52.89$ and 53.04 (OCH_3), 63.22 and 63.36 (>*C*H(OH)), 71.97 (>*C*(OMe)Ph), 83.32–85.75 (*C*≡*C*), 126.53–129.15 (aromatic *C*H), 138.97 (*ipso*-*C*–C–OMe).

4.1.19. 1,4,13-Trimethoxy-1,4,13-tri(4-methoxyphenyl)-cyclopentadeca-2,5,8,11,14-pentayn-7,10-diol (16b). The above Section 4.1.18 for the preparation of **16a** was applied to complex **15b** (22 mg; 0,03 mmol), ceric ammonium nitrate (33 mg, 0,06 mmol) to afford free [5]pericyclyndiol **16b** as an orange oil (16 mg, 100%). $R_f \approx 0.31$ (heptane/EtOAc 5:5). MS (DCI/NH_3): $m/z = 630$ ([M]$^+$), 599 ([M−CH_3O]$^+$). ^{1}H NMR: $\delta = 2.82$ (m, 2H; O*H*), 3.37–3.60 (s, 9H; OCH_3), 3.80–3.82 (s, 9H, C_6H_4–CH_3O), 5.15–5.21 (m, 2H; C*H*(OH)), 6.87–6.90 (m, 6H; *m*-C*H*), 7.59–7.68 (m, 6H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.32$ (OCH_3), 55.44 (C_6H_4–OCH_3), 65.76 (*C*H(OH)), 71.55 (>*C*(OMe)An), 83.03 and 83.56 (*C*≡*C*), 113.82 (*m*-*C*H), 128.45 (*o*-*C*H), 131.12

(*ipso-C*–C–OMe), 160.15 (*p-C*–OMe). IR: $\nu = 3686$ (O–H), 2923 (C–H), 2843 (OC–H), 1605, 1509 (aromatic C–C), 1457 (C–H), 1250, 1170, 1060, 1034 (C–O).

4.1.20. 1,4,7,10,13-Pentamethoxy-1,4,13-tri(4-methoxyphenyl)cyclopentadeca-2,5,8,11,14-pentayne (17b). *n*-Butyllithium (20 μL, 0.05 mmol) was syringed dropwise into a solution of [5]pericyclyndiol **16b** (16 mg, 0.03 mmol) in THF (3 mL) at −78 °C. After stirring for 10 min, methyl iodide (27 μL; 0.40 mmol) was added, and the temperature was allowed to warm up to −25 °C. DMSO (4 μL; 0.05 mmol) was introduced and the reaction mixture was stirred for 1 h at −25 °C, and then for a further 2 h at r.t. The reaction mixture was diluted with diethylether (20 mL) and treated with saturated aqueous NH_4Cl (20 mL). The organic layer was separated, washed with saturated aqueous NH_4Cl (2×10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Crude pentamethoxy[5]pericyclyne **17b** (13 mg, 67%) exhibited consistent spectroscopic data. $R_f \approx 0.40$ (heptane/EtOAc 5:5). MS (DCI/NH_3): $m/z = 627$ ($[M-CH_3O]^+$). ^{1}H NMR: $\delta =$ 3.32–3.66 (s, 9H; Csp^3–OCH_3), 3.81–3.83 (s, 9H; C_6H_4–OCH_3), 5.19 (m, 2H; C*H*(OMe)), 6.83–6.98 (m, 6H; *m*-C*H*), 7.51–7.73 (m, 6H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = 53.3$–55.4 (O*C*H_3), 71.7 (>*C*–OMe), 113.8 (*m-C*H), 128.5 (*o-C*H), 131.1 (*ipso-C*–C–OMe), 160.2 (*p-C*−OMe).

4.1.21. 1,8-Bis(trimethylsilyl)-6-methoxy-3,6-diphenylocta-1,4,7-triyn-3-ol (19a). EtMgBr (0.33 mL, 0.99 mmol) was added dropwise into a solution of diyne **3a** (239 mg, 0.99 mmol) in THF (4 mL) at 0 °C. After stirring for 1 h at 0 °C, benzoylethynylketone **4a** (200 mg, 0.99 mmol) was introduced and the reaction mixture was stirred for 2 h at r.t. The reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and diluted with dietehylether (20 mL). The organic layer was separated, washed with saturated aqueous NH_4Cl (2×5 mL) and brine (10 mL), dried over magnesium sulfate, and concentrated under reduced pressure. Purification by column chromatography (heptane/acetone 8:2) gave **19a** as a brown oil (415 mg, 87%). $R_f \approx 0.30$ (heptane/acetone 8:2). ^{1}H NMR: $\delta = 0.22$ and 0.24 (2s, 18H; Si(CH_3)$_3$), 3.02 (s, 1H; O*H*), 3.50–3.51 (m, 3H; OCH_3), 7.36–7.40 (m, 6H; *m*-, *p*-C*H*), 7.77–7.83 (m, 4H; *o*-C*H*). ^{13}C NMR: $\delta = -0.21$ (q, $^1J_{CH} =$ 120 Hz; Si(*C*H_3)$_3$), 53.14 (q, $^1J_{CH} = 143$ Hz; O*C*H_3), 65.33 (s; >*C*(OH)Ph), 72.07 (s, >*C*(OMe)Ph), 82.7 and 86.77 (2 s; C–*C*≡*C*–C), 90.54 (s, (HO)C–*C*≡C–SiMe$_3$), 92.32 (s, (MeO)C–*C*≡C–SiMe$_3$), 101.39 (s; (MeO)C–C≡*C*–SiMe$_3$), 104.05 (s; (HO)C–C≡*C*–SiMe$_3$), 126.03–129.67 (m; aromatic *C*H), 139.75 (s; *ipso*-*C*–C–OMe), 141.18 (s; *ipso*-*C*–C–OH).

4.1.22. 1,8-Bis(trimethylsilyl)-6-methoxy-3,6-di(4-methoxyphenyl)octa-1,4,7-triyn-3-ol (19b). The above Section 4.1.21 for the preparation of **19a** was applied to diyne **3b** (5.00 g, 183 mmol), EtMgBr (6.70 mL, 183 mmol) and anisoylethynylketone **4b** (4.28 g; 183 mmol) to afford triyne **19b** as an orange oil (8.8 mg, 92%). ^{1}H NMR: $\delta = 0.20$ (s, 18H; Si(CH_3)$_3$), 3.56 (m, 2H; O*H*), 3.78 (s, 6H; C_6H_4–OCH_3), 6.89 (d, $^3J_{HH} = 9$ Hz, 4H; *m*-C*H*), 7.70 (d, $^3J_{HH} =$ 9 Hz, 4H; *o*-C*H*). ^{13}C NMR: $\delta = -0.37$ (q, $^1J_{CH} = 12$ Hz; Si(*C*H_3)$_3$), 55.19 (q, $^1J_{CH} = 144$ Hz; C_6H_4–O*C*H_3), 64.66 (s; *C*–OH), 84.74 (s, *C*≡*C*), 89.73 (s; *C*≡CSiMe$_3$), 104.35 (s; C≡*C*–SiMe$_3$), 113.55 (dd, $^1J_{CH} = 160$ Hz, $^2J_{CH} = 5$ Hz; *m-C*H), 127.39 (dd, $^1J_{CH} = 160$ Hz, $^2J_{CH} = 5$ Hz; *o-C*H), 133.66 (s; *ipso-C*–C–OH), 159.39 (s; *p-C*–OMe).

4.1.23. 1,8-Bis(trimethylsilyl)-3,6-dimethoxy-3,6-diphenylocta-1,4,7-triyne (20a). *n*-Butyllithium (2.20 mL, 5.50 mmol) was added dropwise into a solution of alcohol **19a** (1.18 g, 2.75 mmol) in THF (20 mL) at −78 °C. After stirring for 10 min, methyl iodide was added (2.74 mL, 44 mmol), and the temperature was allowed to warm up to −25 °C before addition of DMSO (0.40 mL, 5.50 mmol). Stirring was continued for 1 h at −25 °C, for a further 1 h at r.t. Diethylether (25 mL) was added and the organic layer was washed with saturated aqueous NH_4Cl (2×20 mL) and brine (20 mL), then dried over $MgSO_4$, and concentrated under reduced pressure. Crude diether **20a** was obtained as an orange oil (1.23 g, 97%) displaying satisfactory analytical data. ^{1}H NMR: $\delta = 0.20$–0.24 (s, 18H; Si(CH_3)$_3$), 3.50 and 3.51 (2s, 6H; OCH_3), 7.34–7.38 (m, 6H; *m*-, *p*-C*H*), 7.74–7.78 (m, 4H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta = -0.25$ (Si(*C*H_3)$_3$), 53.25 (O*C*H_3), 72.17 (>*C*(OMe)Ph), 84.55 (C–*C*≡*C*–C), 92.28 (–*C*≡CSiMe$_3$), 101.53 (≡*C*–SiMe$_3$), 126.62–128.89 (m; aromatic *C*H), 139.84 (*ipso*-*C*–C–OMe). IR: $\nu = 3065$–2901 (C–H), 2826 (OC–H), 2171 (C≡CSi), 1600, 1490 (aromatic C–C), 1450 (C–H), 1251 (C–Si), 1062 (C–O).

4.1.24. 1,8-Bis(trimethylsilyl)-3,6-dimethoxy-3,6-di(4-methoxyphenyl)octa-1,4,7-triyne (20b). The above Section 4.1.23 for the preparation of **19a** was applied to alcohol **19b** (0.83 g, 1.68 mmol), *n*-butyllithium (1.69 mL, 3.69 mmol), methyl iodide (1.67 mL, 27 mmol) and DMSO (0.26 mL, 3.69 mmol). Crude diether **20b** was obtained as an orange oil with a single TLC spot and a consistent ^{1}H NMR spectrum (0.87 g, quant.). $R_f \approx 0.25$ (heptane/EtOAc 7:3). ^{1}H NMR: $\delta = 0.21$ (s, 18H; Si(CH_3)$_3$), 3.51 and 3.53 (2s, 6H; OCH_3), 3.76 (s, 6H; C_6H_4–OCH_3), 6.84–6.92 (m, 4H; *m*-C*H*), 7.65–7.70 (m, 4H; *o*-C*H*).

4.1.25. 3,6-Dimethoxy-3,6-diphenylocta-1,4,7-triyne (20c). K_2CO_3 (1.86 g, 13.45 mmol) was added into a solution of **20a** (1.23 g, 2.70 mmol) in methanol (60 mL). TLC monitoring indicates that the reaction was completed after 1.5 h. The reaction mixture was filtered, concentrated to few milliters under reduced pressure, and diethylether (60 mL) was added. The organic layer was washed with saturated aqueous NH_4Cl (2×40 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated to give crude **20c** as a red-orange oil (0.85 g, quant.). MS (DCI/NH_3): $m/z = 332$ ($[M+NH_4]^+$), 315 ($[MH]^+$), 283 ($[M-OCH_3]^+$). ^{1}H NMR: $\delta = 2.77$ (s, 2H; ≡C–*H*), 3.54 (s, 6H; OCH_3), 7.35–7.43 (m, 6H; *m*-, *p*-C*H*), 7.74–7.78 (m, 4H; *o*-C*H*). ^{13}C NMR: $\delta = 53.74$ (q, $^1J_{CH} = 152$ Hz; O*C*H_3), 71.42 (s; >*C*(OMe)Ph), 75.26 (d, $^1J_{CH} = 254$ Hz; ≡*C*–H), 80.52 (d, $^2J_{CH} = 50$ Hz; –*C*≡CH), 84.05 (s; C–*C*≡*C*–C), 126.32–128.96 (m; aromatic *C*H), 139.43 (s; *ipso*-*C*–C–OMe). IR: $\nu = 3306$ (≡C–H), 3065–2901 (C–H), 2827 (OC–H), 2116 (C≡CH), 1600, 1490 (aromatic C–C), 1450 (C–H), 1068 (C–O).

4.1.26. 3,6-Dimethoxy-3,6-di(4-methoxyphenyl)octa-1,4,7-triyne (20d). The above Section 4.1.25 for the preparation of **20c** was applied to triyne **20b** (0.87 g,

1.68 mmol) and K_2CO_3 (2.32 g; 16.80 mmol) to give **20d** as an orange powder. $R_f \approx 0.26$ (heptane/EtOAc). Mp = 103 °C. MS (DCI/NH_3): $m/z = 374$ ($[M]^+$), 343 ($[M-OCH_3]^+$). ^1H NMR: $\delta = 2.79$ (s, 2H; ≡C–*H*), 3.52 (s, 6H; OCH_3), 3.78 (s, 6H; C_6H_4–OCH_3), 6.91 (d, $^3J_{HH} = 9$ Hz, 4H; *m*-C*H*), 7.69 (d, $^3J_{HH} = 9$ Hz, 4H; *o*-C*H*). $^{13}C\{^1H\}$ NMR: $\delta = 53.23$ (OCH_3), 55.34 (C_6H_4–OCH_3), 71.33 (>*C*(OMe)An), 75.18 (≡*C*–H), 80.93 (–*C*≡CH), 84.25 (C–*C*≡*C*–C), 113.75 (*m*-*C*H), 127.95 (*o*-*C*H), 131.90 (*ipso*-*C*–C–OMe), 160.11 (*ipso*-*C*–OMe).

4.1.27. 1,10-Bis(diethoxy)-4,7-diphenyldeca-2,5,8-triyn-4,7-diol (22a). *n*-Butyllithium (15.4 mL, 38.5 mmol) was added into a solution of 3,3-diethoxy-1-propyne (4.94 g, 38.5 mmol) in THF (50 mL) at −78 °C. After 15 min, a solution of diketone **1** (5.67 mL; 19.3 mmol) in THF (50 mL) was added dropwise, and the solution was stirred for a further 30 min at −78 °C. The temperature was allowed to warm up slowly to r.t. After stirrring for another 30 min, the reaction was quenched by saturated aqueous NH_4Cl (30 mL) and diluted with diethylether (50 mL). The organic layer was washed with saturated aqueous NH_4Cl (2×20 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Diol **22a** was obtained as a brown oil (10.97 g, 97%) which was used without further purification in the next step. ^1H NMR: $\delta = 1.19$ (t, $^3J_{HH} = 7$ Hz, 12H; C–C*H*$_3$), 3.62 and 3.63 (2m, 2^d order pattern, 8H; C*H*$_2$Me), 3.83 (s, 2H; O*H*), 5.32 (s; 2H; C*H*(OEt)$_2$), 7.29–7.40 (m, 6H; *m*-, *p*-C*H*), 7.71–7.77 (m, 4H; *o*-C*H*). $^{13}C\{^1H\}$ NMR: $\delta = 15.06$ (q, $^1J_{CH} = 126$ Hz; C–*C*H$_3$), 61.11 (tt-like, $^1J_{CH} = 143$ Hz, $^2J_{CH} \approx 4$ Hz; O–*C*H$_2$Me), 64.68 (s; >*C*(OH)Ph), 80.49, 84.92 and 85.13 (3 s; C–*C*≡*C*–C), 91.23 (d, $^1J_{CH} = 168$ Hz; C*H*(OEt)$_2$), 125.82 (broad d, $^1J_{CH} = 167$ Hz; *m*-or *o*-*C*H), 128.45 (broad d, $^1J_{CH} = 159$ Hz; *o*-or *m*-*C*H), 129.76 (d, $^1J_{CH} = 160$ Hz; *p*-*C*H), 141.18 (t, $^2J_{CH} = 7$ Hz; *ipso*-*C*–C–OH). IR: ν = 3572, 3380 (O–H), 2980, 2932, 2889 (C–H), 1599, 1490 (aromatic C–C), 1450 (C–H), 1328, 1144, 1116, 1051 (C–O).

4.1.28. 1,10-Bis(diethoxy)-4,7-dimethoxy-4,7-diphenyldeca-2,5,8-triyne (23a). *n*-Butyllithium (4.8 mL, 12.05 mmol) was added into a solution of diol **22a** (2.95 g, 6.0 mmol) in THF (15 mL) at −78 °C. After 30 min, methyl iodide (6.0 mL, 96 mmol) was added dropwise, and the temperature was allowed to warm up to −25 °C. DMSO (0.87 mL, 12 mmol) was then added, and the reaction mixture was stirred for 1 h at −25 °C, and then for 10 h at r.t. (TLC monitoring). The reaction mixture was diluted with diethylether (50 mL) and saturated aqueous NH_4Cl (80 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (heptane/acetone 8:2) afforded diether **23a** (2.14 g, 69%) as a brown oil. MS (DCI/NH_3): $m/z = 536$ (100%, $[M+NH_4]^+$) 487 (38%, $[M-CH_3O]^+$). ^1H NMR: $\delta = 1.20$ (t, $^3J_{HH} = 7$ Hz, 12H; C–C*H*$_3$), 3.53 (s, 6H; OCH_3), 3.66 and 3.67 (2qd-like 2^d order pattern $^3J_{HH} \approx 7$ Hz, $^2J_{HH} \approx 18$ Hz, 8H; C*H*$_2$Me), 5.35 (s, 2H; C*H*(OEt)$_2$), 7.29–7.40 (m, 6H; *m*-, *p*-C*H*), 7.71–7.77 (m, 4H; *o*-C*H*). ^{13}C NMR: $\delta = 15.09$ (q, $^1J_{CH} = 128$ Hz; C–*C*H$_3$), 53.44 (q, $^1J_{CH} = 143$ Hz; O*C*H$_3$), 61.05 (tq-like, $^1J_{CH} = 144$ Hz, $^2J_{CH} \approx 4$ Hz; O–*C*H$_2$Me), 71.86 (s; >*C*(OMe)Ph), 82.08, 82.68 et 84.39 (3s; C–*C*≡*C*–C), 91.31 (broad d, $^1J_{CH} = 171$ Hz; C*H*(OEt)$_2$), 126.53 (td-like, $^1J_{CH} = 160$ Hz; *m* or *o*-*C*H), 128.32 (td-like, $^1J_{CH} = 165$ Hz; *o*-or *m*-*C*H), 128.96 (dt-like, $^1J_{CH} = 160$ Hz; *p*-*C*H), 139.67 (broad s; *ipso*-*C*–C–OMe).

4.1.29. 3,6-Dimethoxy-3,6-diphenylocta-1,4,7-triyn-1,8-dial (18a) by formylation of bisterminal triyne (20c). *n*-Butyllithium (1.00 mL, 2.48 mmol) was added dropwise into a solution of triyne **20c** (391 mg, 1.24 mmol) in THF (20 mL) at −78 °C. After warming up to −40 °C, the solution was stirred for 10 min before addition of DMF (1.00 mL, 25 mmol). The reaction mixture was then placed at r.t. and stirring was continued for a further 30 min. The solution was poured into a biphasic mixture of diethylether (7 mL) and 10% aqueous NaH_2PO_4 (7 mL, ca8 equivalents of $H_2PO_4^-$) at 0 °C. The organic layer was separated, washed with water (2x20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue over silicagel (heptane/acetone 8:2) afforded dialdehyde **18a** as an orange oil (146 mg, 32%). $R_f \approx 0.16$ (heptane/acetone 8:2). MS (DCI/NH_3): $m/z = 388$ ($[M+NH_4]^+$), 356 ($[M-MeOH+NH_4]^+$), 339 ($[M-MeO]^+$), 324 ($[M-2MeOH+NH_4]^+$). ^1H NMR: $\delta = 3.56$ (s, 6H; OCH_3), 7.38–7.45 (m, 6H; *m*-, *p*-C*H*), 7.67–7.72 (m, 4H; *o*-C*H*), 9.31 (s, 2H; ≡C–C*H*O). ^{13}C NMR: $\delta = 53.92$ (q, $^1J_{CH} = 144$ Hz; O*C*H$_3$), 71.84 (s; >*C*(OMe)Ph), 83.88, 84.32 and 90.59 (3s; C–*C*≡*C*–C), 126.18–129.52 (m; aromatic *C*H), 137.77 (s; *ipso*-*C*–C–OMe), 175.90 (d, $^1J_{CH} = 190$ Hz; –*C*HO). IR: $\nu = 3088$, 2887 (C–H), 2829 (OC–H), 2740 (aldehydic C–H), 1679 (CH=O), 1599, 1490 (aromatic C–C), 1451 (C–H), 1178–1072 (C–O).

The monoaldehyde 3,6-dimethoxy-3,6-diphenylocta-1,4,7-triynal (**21a**) was also isolated as side-product from the chromatography (85 mg, 20%). $R_f \approx 0.18$ (heptane/acetone 8:2). MS (DCI/NH_3): $m/z = 360$ ($[M+NH_4]^+$), 343 ($[MH]^+$), 328 ($[M-MeOH+NH_4]^+$), 311 ($[M-MeO]^+$), 296 ($[M-2MeOH+NH_4]^+$). ^1H NMR: $\nu = 2.85$ (s, 1H; ≡C–*H*), 3.57–3.60 (m, 6H; O*C*H$_3$), 7.39–7.45 (m, 6H; *m*-, *p*-C*H*), 7.72–7.81 (m, 4H; *o*-C*H*), 9.29 (s, 1H; ≡C–C*H*O). $^{13}C\{^1H\}$ NMR: $\delta = 53.31$ and 53.70 (OCH_3), 71.51 and 71.71 (>*C*(OMe)Ph), 75.76 (≡*C*–H), 80.07 (*C*≡CH), 81.91, 84.07, 86.11 and 90.59 (C–*C*≡*C*–C), 126.27–129.53 (m; aromatic *C*H), 138.05 and 139.11 (*ipso*-*C*–C–OMe), 175.90 (–*C*HO).

4.1.30. 3,6-Dimethoxy-3,6-diphenylocta-1,4,7-triyn-1,8-dial (18a) by deprotection of bisketal (23a). Bisketal **23a** (4.859 g, 9.4 mmol)) and DDQ (2.127 g, 9.4 mmol) were dissolved in a mixture of acetonitrile (243 mL) and water (27 mL). The mixture was refluxed in the dark for 2 h. After cooling to r.t., the mixture was diluted with diethylether and water. The organic layer was separated washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The brown residue was flash-chromatographed over silicagel (heptane/EtOAc 8:2). Dialdehyde **18a** was obtained a light orange oil (2.118 g, 61%). The spectroscopic data are identical to those of samples of **18a** prepared by the formylation method (see Section 4.1.29). Notice: some decomposition occurs on silicagel, and the yield is actually quite erratic (between 40 and 75%).

4.1.31. 3,6-Dimethoxy-3,6-di(4-methoxyphenyl)octa-1,4,7-triyn-1,8-dial (18b). The formylation Section 4.1.29 for the preparation of **18a** was applied to bisketal **20d** (400 mg, 1.07 mmol), *n*-butyllithium (0.94 mL, 2.35 mmol) and DMF (0.50 mL, 6.42 mmol) to give crude dialdehyde **18b** in an orange oil containing 17% of side product assigned to the monoaldehyde structure **21b** (spectroscopic yield of **18b** ≈83%). Attempts at purification by chromatography failed, but the main spectrospcopic characteristics of **18b** could be attributed. $R_f \approx 0.20$ (heptane/EtOAc 8:2).

MS (DCI/NH_3): $m/z=448$ ($[M+NH_4]^+$), 416 ($[M-MeOH+NH_4]^+$), 399 ($[M-MeO]^+$), 384 ($[M-2MeOH+NH_4]^+$). ^{1}H NMR: $\delta=3.53$ (s, 6H; OCH_3), 3.81 (s, 6H; C_6H_4–OCH_3), 6.92 (d, $^3J_{HH}=9$ Hz, 4H; *m*-C*H*), 7.64 (d, $^3J_{HH}=9$ Hz, 4H; *o*-C*H*), 9.31 (s, 2H; ≡C–C*H*O). ^{13}C NMR: $\delta=53.70$ (q, $^1J_{CH}=144$ Hz; OCH_3), 55.39 (q, $^1J_{CH}=139$ Hz; C_6H_4–OCH_3), 71.53 (s; >*C*(OMe)An), 84.00, 84.33 and 91.11 (3s; C–*C*≡*C*–C), 114.01 (d, $^1J_{CH}=161$ Hz; *m*-*C*H), 127.85 (d, $^1J_{CH}=158$ Hz; *o*-*C*H), 129.99 (s; *ipso*-*C*–C–OMe), 160.53 (s; *p*-*C*–OMe), 176.08 (d, $^1J_{CH}=197$ Hz; –*C*HO). IR: $\nu=3006$–2862 (C–H), 2840, 2741 (aldehydic C–H), 2828 (OC–H), 1674 (C=O), 1608, 1463 (aromatic C–C), 1063 (C–O).

4.1.32. 3-Phenyl-3-methoxypenta-1,4-diyne (24a). A solution of diyne **3a** (4.19 g, 16 mmol) in methanol (60 mL) and water (few drops) was treated at 0 °C with K_2CO_3 (11.29 g, 82 mmol). After stirring for 1 h at r.t., the reaction mixture was filtered, concentrated to few milliters under reduced pressure, and diluted with diethylether (100 mL). The organic phase was washed with saturated aqueous NH_4Cl (2×50 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure to give diyne **24a** as a spectroscopically pure brown oil (2.78 g, quant.). $R_f \approx 0.29$ (heptane/acetone 8:2). ^{1}H NMR: $\delta=2.78$ (s, 2H; ≡C–*H*), 3.54 (s, 3H; OCH_3), 7.37–7.40 (m, 3H; *m*-, *p*-C*H*), 7.75–7.80 (m, 2H; *o*-C*H*).

4.1.33. 3-(4-Methoxyphenyl)-3-methoxypenta-1,4-diyne (24b). The above Section 4.1.32 for the preparation of **24a** was applied to diyne **3b** (3.61 g, 5.22 mmol) and K_2CO_3 (3.60 g, 26 mmol) to give 1,4-pentadiyne **24a** as a spectroscopically pure brown oil (1.05 g, quant.). $R_f \approx 0.29$ (heptane/acetone 8:2). ^{1}H NMR: $\delta=2.77$ (s, 2H; ≡C–*H*), 3.50 (s, 3H; OCH_3), 3.81 (s, 3H; C_6H_4–OCH_3), 6.89 (d, 2H; *m*-C*H*), 7.68 (d, 2H; *o*-C*H*). ^{13}C NMR: $\delta=52.87$ (q, $^1J_{CH}=143$ Hz; C_6H_4–OCH_3), 55.17 (q, $^1J_{CH}=144$ Hz; Csp^3–OCH_3), 71.81 (s; >*C*(OMe)An), 74.89 (d, $^1J_{CH}=263$ Hz, ≡*C*–H), 80.80 (d, $^2J_{CH}=49$ Hz; *C*≡CH), 113.46 (dd, $^1J_{CH}=160$ Hz, $^2J_{CH}=5$ Hz; *m*-*C*H), 127.61 (dd, $^1J_{CH}=160$ Hz, $^2J_{CH}=5$ Hz; *o*-*C*H), 131.89 (s; *ipso*-*C*–C(OMe)–), 159.53 (broad s; *p*-*C*–OMe).

4.1.34. 4,7,13-Trimethoxy-4,7,13-triphenylcyclopentadeca-2,5,8,11,14-pentayn-1,10-diol (25a). *n*-Butyllithium (0.32 mL, 0.80 mmol) was added into a solution of diyne **24a** (150 mg, 0.40 mmol) in THF (8 mL) at −78 °C. After stirring for 10 min, a solution of dialdehyde **18a** (68 mg; 0.40 mmol) in THF (8 mL) was added dropwise. The temperature was allowed to warm up to r.t. and stirring was continued for a further 40 min. The reaction mixture was diluted with diethylether (20 mL) and hydrolyzed with saturated aqueous NH_4Cl (10 mL). The organic layer was separated, washed with and saturated aqueous NH_4Cl (10 mL) and brine (20 mL), dried over magnesium sulfate, and concentrated to dryness under reduced pressure. The brown residue (190 mg) was chromatographed over silicagel (heptane/acetone 8:2) to give [5]pericyclyndiol **25a** as an orange oil (35 mg, 15%). MS (DCI/NH_3): $m/z=558$ ($[M+NH_4]^+$), 526 ($[M-MeOH+NH_4]^+$), 509 ($[M-MeO]^+$), 494 ($[M-2MeOH+NH_4]^+$). MS (APCI/CH_3CN): $m/z=568$ ($[M-MeO+MeCN]^+$), 559 ($[MH]^+$). ^{1}H NMR: $\delta=2.41$ (m, 2H; O*H*), 3.40–3.58 (m, 9H; OCH_3), 5.24–5.34 (m, 2H; >C*H*(OH)), 7.36–7.39 (m, 9H; *m*-, *p*-C*H*), 7.69–7.90 (m, 6H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta=52.23$ and 53.30 (OCH_3), 62.19 (>*C*H(OH)), 71.72 (>*C*(OMe)Ph), 80.79–82.63 (*C*≡*C*), 126.43–128.99 (aromatic *C*H), 138.77 (*ipso*-*C*–C–OMe).

4.1.35. 4,7,13-Trimethoxy-4,7,13-tri(4-methoxyphenyl)-cyclopentadeca-2,5,8,11,14-pentayn-1,10-diol (25b). The above Section 4.1.34 for the preparation of **25a** was applied to pentadiyne **24b** (168 mg, 0.84 mmol), *n*-butyllithium (0.70 mL, 1.68 mmol) and crude dialdehyde **18b** of 83% spectroscopic purity (361 mg, ca0.84 mmol). The pericyclyne **25b** was isolated as an orange oil (100 mg, 19%). $R_f \approx 0.12$ (heptane/acetone 7:3). MS (DCI/NH_3): $m/z=648$ ($[M+NH_4]^+$), 630 ($[M]^+$), 616 ($[M-MeOH+NH_4]^+$), 599 ($[M-MeO]^+$), 584 ($[M-2MeOH+NH_4]^+$). ^{1}H NMR: $\delta=3.35$–3.53 (m, 9H; OCH_3), 3.78–3.87 (s, 9H; C_6H_4–OCH_3), 5.31 (m, 2H; C*H*(OH)), 6.83–6.93 (m, 6H; *m*-C*H*), 7.57–7.72 (m, 6H; *o*-C*H*). ^{13}C{^{1}H} NMR: $\delta=$ 53.15, 52.97 and 52.20 (3s; OCH_3), 55.21 (C_6H_4–OCH_3), 64.85 (*C*H–OH), 71.67 (>*C*(OMe)An), 83.05–84.57 (*C*≡*C*), 113.70 (*m*-*C*H), 128.17 (*o*-*C*H), 138.53 (*ipso*-*C*–C–OMe), 160.07 (*p*-*C*–OMe).

The side-product resulting from the attack of the monoaldehyde impurity (**21b**) was also isolated and partly characterized: 3,9,12-trimethoxy-3,6,9,12-tetra(4-methoxyphenyl)tetradeca-1,4,7, 10,13-pentayn-6-ol (**26b**) $R_f \approx 0.25$ (heptane/acetone 7:3). ^{1}H NMR: $\nu=2.76$ (s, 2H; ≡C–*H*), 3.46–3.48 (m, 9H; –OCH_3), 3.78–3.79 (s, 9H, CH_3O–An–), 5.32 (d, 1H; C*H*(OH)), 6.83–6.90 (m, 6H; *m*-C*H*), 7.62–7.68 (m, 6H; *o*-C*H*).

4.1.36. 12,15-Dimethoxy-12,15-diphenyl-3,3-dimethyl-1,5-dioxaspiro[5.14]icosa-7,10,13,16,19-pentayn-9,18-diol (31). *n*-Butyllithium (2.26 mL, 5.66 mmol) was added to a solution of diyne **27**[10b] (465 mg, 2.83 mmol) in THF (100 mL) at −78 °C. After stirring for 40 min at −50 °C, the solution was cooled back to −78 °C and a solution of dialdehyde **18a** (1.049 g, 2.83 mmol) in THF (100 mL) was added. The reaction mixture was allowed to warm up to r.t. over a 3 h period, and stirring was continued for 1 h at r.t. The reaction was quenched with saturated aqueous NH_4Cl and diluted with diethylether. The organic layer was separated, washed with aqueous NH_4Cl and brine, dried over magnesium sulfate, and the solvents were removed under reduced pressure. Purification through column chromatography (heptane/acetone 8:2) gave [5]pericyclyne **31** as a pale yellow solid (271, mg, 18%). MS (DCI/NH_3) $m/z=552$ (60%; $[MNH_4]^+$), 503 (31%; $[MH-MeOH]^+$), 520 (21%; $[MNH_4-MeOH]^+$), 488 (7%; $[MNH_4-2MeOH]^+$). ^{1}H NMR (250 MHz): $\delta=0.98$ (s, 6H;

C(CH_3)$_2$), 2.44−2.71 (m, 2H; O*H*), 3.33−3.71 (m, 10H; OCH_3+CH_2O−), 5.23−5.33 (m, 2H; C*H*OH); 7.33−7.78 (m, 10H; aromatic C*H*). ^{13}C NMR (62.9 MHz): δ=22.29 (C(CH_3)$_2$), 29.96 (*C*(CH_3)$_2$), 52.15 (>*C*H(OH)), 53.51 (O*C*H$_3$), 71.94 (>*C*(OMe)Ph), 72.88 (CH_2O), 78.67 (≡*C*–CO_2), 80.42, 81.11, 82.15 and 83.26 (other –*C*≡), 87.22 (>CO_2), 126.53 and 128.52 (*o*- and *m*-*C*H), 129.15 (*p*-*C*H), 139.89 (*ipso*-*C*–C–OMe). In another assay, the spectrum exhibited higher resolution, and most signals were split in two or three lines by ca. 0.05 ppm. IR: ν=3585 (O–H), 2961, 2934 and 2872 (C–H), 2827 (OC–H), 1601, 1490, 1450 (aromatic C–C), 1254, 1203, 1178, 1229, 1145, 1116, 1072, 1009 (C–O).

4.2. Semi-preparative HPLC resolution of tetrayne 2a

A diastereoisomeric mixture of tetrayne **2a** (152 mg) was dissolved in dichloromethane (1 mL). Samples (20 μL) were sequentially injected and divided by HPLC (Prontosil column, pentane/dichloromethane 65:35, 4.8 mL/min) in three pools, respectively, enriched in diastereoisomer **A**, **B** and **C**. Each pool was purified further under the same conditions, affording separated diastereoisomers **A** (30 mg), **B** (35 mg) and **C** (21 mg).

4.3. Semi-peparative HPLC resolution of the [5]pericylyne 11a prepared from the isomer B of tetrayne 2a

A diastereoisomeric mixture of the title sample (11 mg) was dissolved in dichloromethane (0.5 mL). Samples (20 μL) were sequentially injected and divided by HPLC (Prontosil column, pentane:EtOAc 97:3, 4.8 mL/min) in three pools, respectively enriched in one of the three diastereoisomers (Scheme 20). Each pool was purified further under the same conditions, affording separated diastereoisomers (ca. 1 mg, 1 mg, 2 mg).

4.4. X-ray crystallographic structure determinations

Data were collected on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device, and using graphite-monochromated Mo K 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. The structures were solved by Direct Methods using the program SIR92,[31] and refined by least-squares procedures on *F*2 with SHELXL-97.[32] All hydrogen atoms were located on a difference Fourier maps, but introduced and refined by using a riding model, except for OH hydrogen atoms, which were isotropically refined. All non-hydrogens atoms were anisotropically refined.

4.5. Crystallographic and structural parameters for 5b (Fig. 3)

Empirical formula	$C_{15}H_{18}O_2Si$; MW=258.38
Temperature	180(2) K
Crystal system, space group	Monoclinic, *P*21/*n*
Unit cell dimensions	*a*=6.449(5) Å *b*=24.646(5) Å *c*=9.420(5) Å β=99.650(5)°
Volume	1476.0(14) Å^3
Z, Calculated density	4, 1.163 mg/cm^3
Absorption coefficient	0.151 mm^{-1}
F(000)	552
Theta range for data collection	2.34–26.08°
Index ranges	$7\le h\le 7$, $-30\le k\le 30$, $-11\le l\le 11$
Reflections collected/unique	11012/2831 [*R*(int)=0.0328]
Completeness to 2theta=26.08	97.0%
Refinement method	Full-matrix least-squares on *F*2
Data/restraints/parameters	2831/0/171
Goodness-of-fit on *F*2	1.023
Final *R* indices [*I*>2sigma(*I*)]	*R*1=0.0337, *wR*2=0.0867
R indices (all data)	*R*1=0.0427, *wR*2=0.0913
Largest diff. peak and hole	(0.225 and −0.206) e A^{-3}

Bond lengths [A] and angles [deg] for **5b**

Si(1)–C(5)	1.8499(17)	Si(1)–C(15)	1.857(2)	O(2)–C(9)	1.3641(17)
Si(1)–C(13)	1.8513(18)	O(1)–C(1)	1.4437(15)	O(2)–C(12)	1.427(2)
Si(1)–C(14)	1.8521(18)	O(1)–H(1O)	0.86(2)	C(1)–C(2)	1.475(2)
C(1)–C(4)	1.4832(19)	C(2)–C(3)	1.184(2)	C(6)–C(11)	1.380(2)
C(1)–C(6)	1.5321(17)	C(4)–C(5)	1.203(2)	C(6)–C(7)	1.390(2)
C(7)–C(8)	1.380(2)	C(8)–C(9)	1.388(2)	C(9)–C(10)	1.382(2)
C(10)–C(11)	1.3928(19)				
C(5)–Si(1)–C(13)	109.57(8)	O(1)–C(1)–C(2)	109.93(11)	C(4)–C(5)–Si(1)	172.16(12)
C(5)–Si(1)–C(14)	105.93(8)	O(1)–C(1)–C(4)	109.42(11)	C(11)–C(6)–C(7)	118.53(13)
C(13)–Si(1)–C(14)	111.40(10)	C(2)–C(1)–C(4)	108.78(11)	C(11)–C(6)–C(1)	120.86(12)
C(5)–Si(1)–C(15)	107.35(8)	O(1)–C(1)–C(6)	106.00(10)	C(7)–C(6)–C(1)	120.56(12)
C(13)–Si(1)–C(15)	111.53(9)	C(2)–C(1)–C(6)	112.36(11)	C(8)–C(7)–C(6)	120.53(14)
C(14)–Si(1)–C(15)	110.82(9)	C(4)–C(1)–C(6)	110.30(11)	C(7)–C(8)–C(9)	120.45(14)
C(1)–O(1)–H(1O)	107.2(13)	C(3)–C(2)–C(1)	177.66(14)	O(2)–C(9)–C(10)	124.67(13)
C(9)–O(2)–C(12)	117.81(12)	C(5)–C(4)–C(1)	177.02(15)	O(2)–C(9)–C(8)	115.63(13)
C(10)–C(9)–C(8)	119.70(13)	C(9)–C(10)–C(11)	119.31(13)	C(6)–C(11)–C(10)	121.47(13)

4.6. Crystallographic and structural parameters for 20d (Fig. 2)

Empirical formula	$C_{12}H_{11}O_2$; MW = 187.21
Temperature	293(2) K
Crystal system, space group	Triclinic, $P-1$
Unit cell dimensions	a = 6.5680(10) Å, b = 8.382(2) Å, c = 9.674(2) Å α = 105.68(3)°, β = 103.88(3)°, γ = 93.24(3)°
Volume	493.58(17) Å^3
Z, Calculated density	2, 1.260 mg/cm^3
Absorption coefficient	0.085 mm^{-1}
F(000)	198
Crystal size	0.1×0.1×0.1 mm^3
Theta range for data collection	2.27–23.25°
Index ranges	$-7\leq h\leq 7$, $-9\leq k\leq 9$, $-10\leq l\leq 10$
Reflections collected/unique	3643/1347 [R(int) = 0.0469]
Completeness to 2theta = 23.25°	94.4%
Refinement method	Full-matrix least-squares on $F2$
Data/restraints/parameters	1347/0/129
Goodness-of-fit on $F2$	1.080
Final R indices [$I>2$sigma(I)]	$R1$ = 0.0769, $wR2$ = 0.2114
R indices (all data)	$R1$ = 0.1063, $wR2$ = 0.2465
Largest diff. peak and hole	(0.317 and −0.247) e Å^{-3}

Bond lengths [A] and angles [deg] for **20d**

C(1)–C(1)#1	1.187(8)	C(3)–C(4)	1.139(6)	C(8)–C(9)	1.398(6)
C(1)–C(2)	1.494(6)	C(5)–O(1)	1.364(5)	C(9)–O(2)	1.371(5)
C(2)–O(1)	1.450(5)	C(6)–C(7)	1.384(6)	C(9)–C(10)	1.373(6)
C(2)–C(3)	1.473(6)	C(6)–C(11)	1.400(6)	C(10)–C(11)	1.370(6)
C(2)–C(6)	1.521(6)	C(7)–C(8)	1.380(6)	C(12)–O(2)	1.423(5)
C(1)#1–C(1)–C(2)	177.6(5)	C(4)–C(3)–C(2)	166.5(6)	O(2)–C(9)–C(8)	124.3(4)
O(1)–C(2)–C(3)	112.9(3)	C(7)–C(6)–C(11)	118.1(4)	C(10)–C(9)–C(8)	119.6(4)
O(1)–C(2)–C(1)	111.2(3)	C(7)–C(6)–C(2)	122.0(4)	C(11)–C(10)–C(9)	120.7(4)
C(3)–C(2)–C(1)	107.6(4)	C(11)–C(6)–C(2)	119.8(4)	C(10)–C(11)–C(6)	120.7(4)
O(1)–C(2)–C(6)	105.3(3)	C(8)–C(7)–C(6)	121.5(4)	C(5)–O(1)–C(2)	118.5(4)
C(3)–C(2)–C(6)	108.4(3)	C(7)–C(8)–C(9)	119.3(4)	C(9)–O(2)–C(12)	117.3(3)
C(1)–C(2)–C(6)	111.5(3)	O(2)–C(9)–C(10)	116.1(3)		

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