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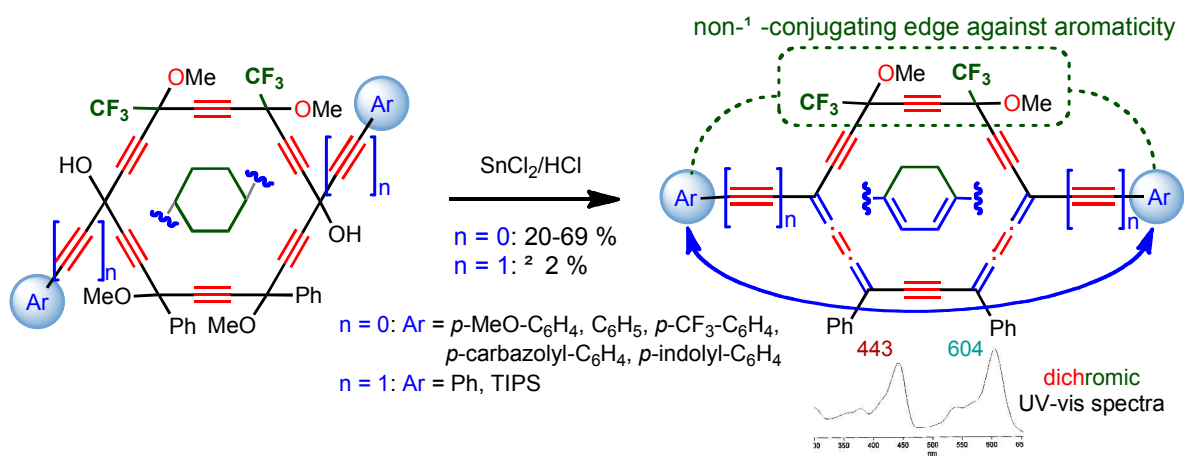
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## Graphical Abstract



## ***Carbo-cyclohexadienes vs carbo-benzenes:*** **structure and conjugative properties<sup>†‡</sup>**

Arnaud Rives,<sup>[a,b]</sup> Iaroslav Baglai,<sup>[a,b,c]</sup> Cécile Barthes,<sup>[a,b]</sup> Valérie Maraval,<sup>[a,b]\*</sup>  
Nathalie Saffon-Merceron,<sup>[d]</sup> Alix Saquet,<sup>[a,b]</sup> Zoia Voitenko,<sup>[c]</sup> Yulian Volovenko<sup>[c]</sup>  
and Remi Chauvin<sup>[a,b]\*</sup>

[a] CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4 (France)

[b] Université de Toulouse, UPS, Institut de Chimie de Toulouse, ICT-FR2599, 118 Route de Narbonne, F-31062 Toulouse, France.

[c] Kiev National Taras Shevchenko University, 60 Volodymyrska St, 01033 Kiev (Ukraine)

[d] Université de Toulouse, UPS, Institut de Chimie de Toulouse, ICT-FR 2599, 118 route de Narbonne, 31062 Toulouse (France)

Fax: (+33)5 61 55 30 03. E-mail: [ymaraval@lcc-toulouse.fr](mailto:ymaraval@lcc-toulouse.fr), [chauvin@lcc-toulouse.fr](mailto:chauvin@lcc-toulouse.fr).

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**Key-words.** Alkyne - Butatriene - Carbo-cyclohexadiene - Carbo-mer - Organic chromophore

**Abstract.** Ideally  $C_s$ -/ $C_{2v}$ -symmetric chromophores constituted by two electro-active groups conjugated through the *carbo*-mer of the cyclohexa-1,3-diene core are selectively prepared by  $\text{SnCl}_2$ -mediated reduction of tailored hexaoxy-[6]pericyclines: in the latter, one of the 1,4-dioxybut-2-yne edges is « chemically locked » by two  $\text{CF}_3$  substituents preventing complete reduction to the corresponding aromatic *carbo*-benzenic core expected to be more «  $\pi$ -insulating » between the electro-active ends. The bis-trifluoromethylated *carbo*-cyclohexadiene products are also shown to be significantly stabilized with respect to bis-phenyl analogues. Their structural (crystal X-ray diffraction analyses), spectroscopical (NMR and UV-vis spectra), physio-optical (dichromism in solution) and electrochemical (cyclic voltammograms) properties are compared on the basis of the electron-donating/electron-withdrawing nature of the substituents. These properties are also compared with those of aromatic *carbo*-benzene and flexible *carbo*-*n*-butadiene counterparts.

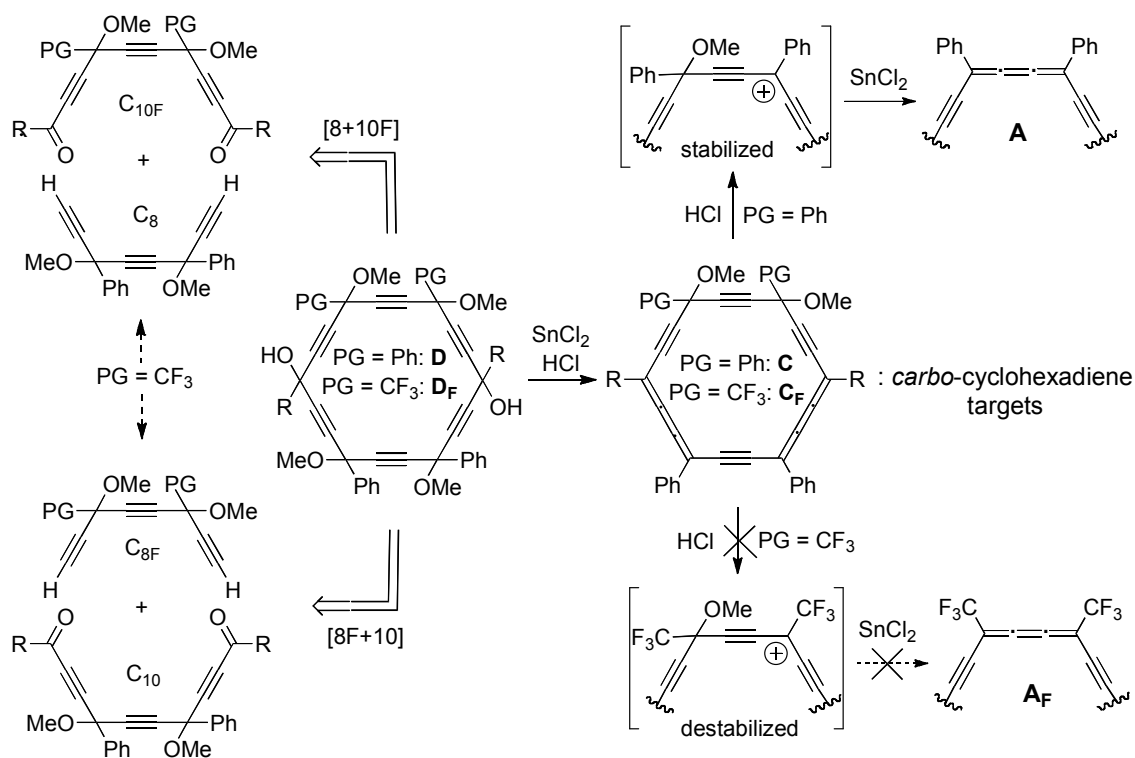
## Introduction

Until a recent past,<sup>1</sup> the chemistry of *carbo*-mers mainly focused on *carbo*-benzenes,<sup>2</sup> because of the stability, rigidity and  $\pi$ -electronic features anticipated to be associated with their unique aromatic structure,<sup>3</sup> as compared to those of acyclic fragments. Like the C<sub>6</sub> ring of benzene, the C<sub>18</sub> macrocycle of *carbo*-benzenes **A** (Fig. 1) can indeed be formally divided into two acyclic components relevant from both the viewpoints of experimental retro-synthesis<sup>4</sup> and theoretical aromaticity analysis.<sup>5</sup> While the ethylene and 1,3-butadiene components for benzene are stable molecules, the issue for their partial *carbo*-mers, dialkynylbutatriene (DAB) and di(alkynylbutatrienyl)-acetylene (DBA or *carbo*-butadiene) components, was less obvious (Fig. 1).<sup>6</sup> Recently, generic acyclic DBA derivatives **B** were shown to be actually quite stable and could be studied in a systematic manner.<sup>7</sup> In passing, they were found to be much more sensitive than the *carbo*-benzene counterparts **A** to the effects of electro-active substituents on the maximum UV-vis absorption wavelength (Fig. 1: R = 4-X-C<sub>6</sub>H<sub>4</sub>, X = NO<sub>2</sub>, CF<sub>3</sub>, H, OMe, NR'<sub>2</sub>...).<sup>7b</sup> Whereas the phenomenon was tentatively attributed to macrocyclic aromaticity (“macro-aromaticity”) making the C<sub>18</sub> ring of **A** quite  $\pi$ -independent from its substituents R, the same *carbo*-benzene ring, which is anyway three-time smaller and three-time less energetically aromatic than benzene,<sup>3f</sup> has at most a weak electrical insulating effect. Very recently, indeed, the single molecule conductance (SMC) of a functional *carbo*-benzene **A**(R = 4-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sup>4</sup> measured by STM techniques proved to be much higher than that of benzenoid or porphyrine parents of similar size (*ca* 2 nm), and almost two order of magnitude higher than the SMC of the acyclic DBA counterpart **B**(R = 4-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>) (106 nS vs 2.7 nS).<sup>8</sup> On the basis of NEGF-DFT-calculations, this SMC difference was correlated with the difference in conformational freedom between the rigid *carbo*-benzene **A** and the freely rotating DBA derivative **B** (Fig. 1). The stiffness of **A** is however also effective in the  $\sigma$ -cyclic and  $\pi$ -acyclic *carbo*-cyclohexadiene **C**, a rigid version of the non-macro-aromatic DBA **B**, thus locked in a *cisoid* conformation. Access to **C**(R = 4-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>) would thus allow appraisal of the role of macro-aromaticity of the equally rigid parent **A** on conduction. More fundamentally, the *carbo*-



## Results and discussion

The sole known *carbo*-cyclohexadiene **C** (R = 4-MeO-C<sub>6</sub>H<sub>4</sub>) was obtained by serendipity at low temperature, thus indicating that the formation of the two first butatrienic edges of the *carbo*-benzene target **A** (R = 4-MeO-C<sub>6</sub>H<sub>4</sub>) was slightly faster than the formation of the third one.<sup>10</sup> Assuming that the mechanism of action of the reducing system SnCl<sub>2</sub>/HCl starts by the formation of a bispropargylic carbenium from the corresponding carbinoxy vertex of the hexaoxy-[6]pericyclyne precursor **D** (Fig. 1),<sup>12</sup> the two anisyl-stabilized carbenium centers are likely to initially drive the formation of butatrienic edges conjugated with the anisyl substituents R, as found in **C**. The phenyl-substituted carbinol ether vertices, though less reactive, remain however prone to dissociate under the operating acidic conditions, thus leading to **A** and making partial reduction to **C** difficult to control.<sup>10a,12</sup> The selectivity in **C** should however be improved by increasing the difference in mesomeric donor stabilization (+M effect) of the two types of carbenium centers, and ultimately by deliberately changing two phenyl substituents by substituents exerting opposite mesomeric or inductive acceptor destabilization (−M or −I effect; the more or less protecting groups are denoted as PG in Scheme 1). Within this prospect, trifluoromethyl groups are ideal candidates:<sup>13</sup> it was indeed observed that the quite general method for the conversion of 1,4-dioxybut-2-yne derivatives to the corresponding butatrienes by treatment with SnCl<sub>2</sub>/HCl, is not compatible with CF<sub>3</sub> substituents.<sup>6c</sup> Two substituents PG = CF<sub>3</sub> at adjacent carbinoxy vertices of a hexaoxy-[6]pericyclyne **D<sub>F</sub>** are therefore anticipated to freeze the corresponding 1,4-dioxybut-2-yne edge towards reduction and thus optimize the selectivity in the partly reduced *carbo*-cyclohexadiene product **C<sub>F</sub>** vs the putative *carbo*-benzene **A<sub>F</sub>** (Scheme 1).



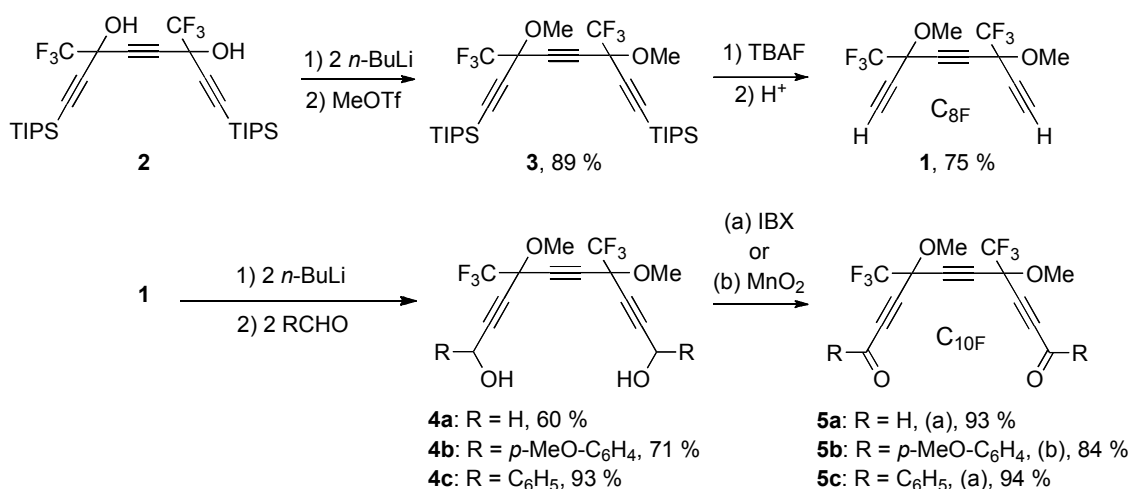
**Scheme 1.** [8+10F] and [8F+10] strategies to bis-trifluoromethylated hexaoxy-[6]pericyclines, envisaged as precursors for the selective synthesis of *carbo*-cyclohexadienes.

The envisaged [8F+10] and [8+10F] strategies to the bis-trifluoromethylated pericyclic precursors **D<sub>F</sub>** are inspired from a strategy previously used in the tetraphenylated series **D** and based on a [8+10] cyclization step between a C<sub>8</sub> dinucleophile and a C<sub>10</sub> dielectrophile, where the index F here refers to bis-trifluoromethylated synthons (Scheme 1). In spite of the recognized specificity of the chemistry of organofluorine compounds, both in terms of reactivity (due to extreme electronegativity and hardness) and purification (due to a high lipophilic character), the general strategic principles developed in the 1,4-diphenylbut-2-yne series<sup>10a</sup> are shown to be adaptable in the 1,4-bis(trifluoromethyl)but-2-yne series.



### 1. [8+10F] cyclization route to bis-trifluoromethylated hexaoxy-[6]pericyclynes.

The fluorinated dialdehyde or diynone synthon  $C_{10F}$  was targeted through the known triyne intermediate **1** (Scheme 2).<sup>6c</sup> The latter was prepared in two steps from the diol **2** via the silylated triyne **3**, in 75 % overall yield (in spite of its volatility) as a statistical mixture of *dl* and *meso* diastereoisomers, identified by two  $^{19}F$  NMR singlet signals at  $-79.52$  and  $-79.53$  ppm. The mixture was not resolved before use as either precursor of the  $C_{10F}$  synthon here, or  $C_{8F}$  synthon in the [8F+10] route (see section 2).

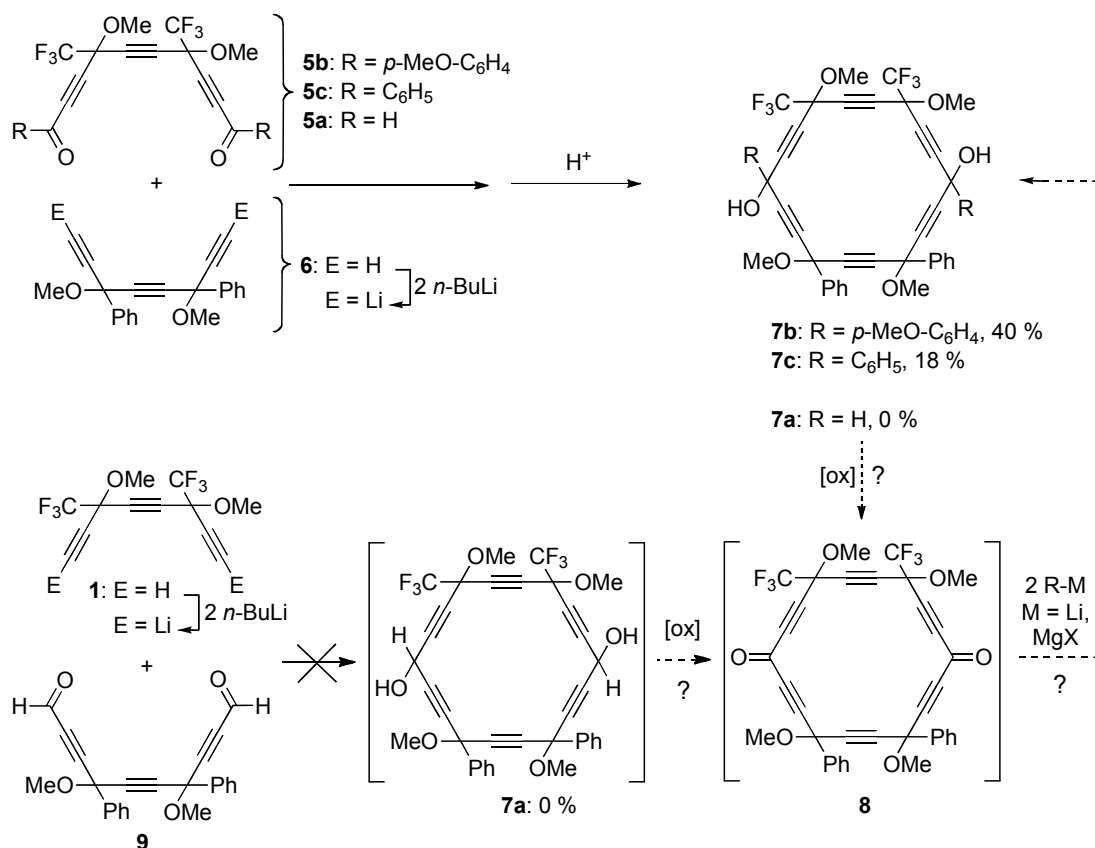


**Scheme 2.** Synthesis of the dicarbonyl synthons  $C_{10F}$ , **5a-c**, via the bis-trifluoromethylated triyne **1**.

Three  $C_{10F}$  synthons were prepared in two steps, starting by the addition of the dilithium salt of **1** to *p*-formaldehyde, *p*-anisaldehyde or benzaldehyde, giving the respective diols **4a**, **4b**, **4c** in 60–93 % yields. Subsequent oxidation gave the dialdehyde **5a** or diketones **5b**, **5c** using either  $MnO_2$  in dichloromethane (DCM) at room temperature, or IBX in refluxing 1,2-dichloroethane (Scheme 2).

The  $C_{10F}$  synthons **5a-c** were then treated with the known dilithiated  $C_8$  bis-terminal triyne **6** in THF at low temperature under quite diluted conditions (Scheme 3).<sup>14</sup> While the bis-tertiary [6]pericyclynediols **7b** and **7c** were obtained from the corresponding diketones in 40 and 18 % yield, respectively, the bis-secondary [6]pericyclynediol **7a** could not be from the dialdehyde **5a** (the final reaction mixture containing the starting triyne **6** and traces of linear oligomers). The  $CF_3$

substituents, replacing the original phenyl substituents,<sup>10a</sup> are therefore responsible for the uncontrolled reactivity of the carbaldehyde groups in  $\gamma$  position. The [6]pericyclynediol **7a** was also targeted as a possible precursor of the [6]pericyclynedione **8**, a putative pivotal reactant for the preparation of 1,10-disubstituted *carbo*-cyclohexadienes by addition of variable nucleophiles to its keto groups (Scheme 3). A similar approach indeed proved to be efficient in the tetraphenyl series for the synthesis of *carbo*-benzenes through the tetraphenyl-[6]pericyclynedione analogue of **8**.<sup>4,10a,14b</sup>

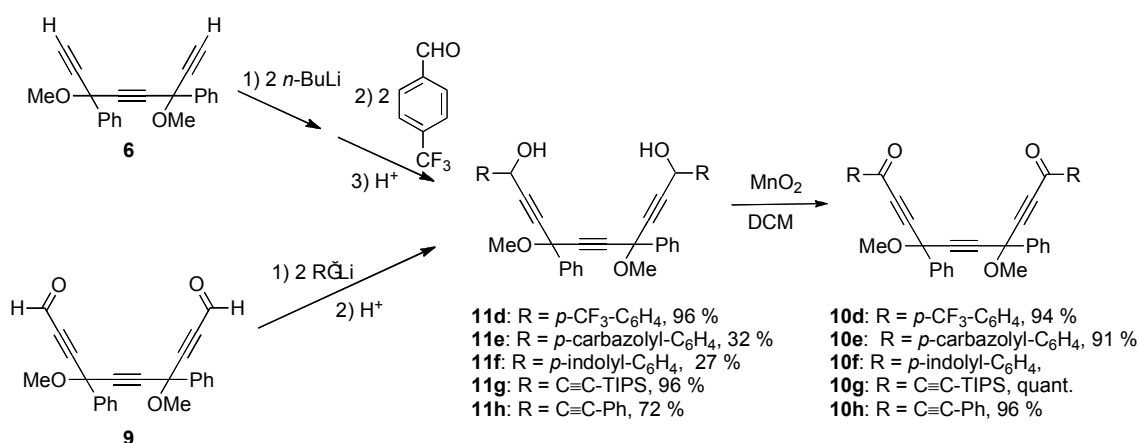


**Scheme 3.** The [8+10F] route to bis-trifluoromethylated bis-tertiary hexaalkoxy-[6]pericyclynediols **7b**, **7c**, and attempted [8+10F] and [8F+10] routes to the [6]pericyclynedione target **8** via the putative bis-secondary hexaalkoxy-[6]pericyclynediol **7a**.

The synthesis of **7a** was also attempted through the alternative [8F+10] strategy from the fluorinated triyne **1** as the C<sub>8F</sub> dinucleophile, and the known dialdehyde **9** as the C<sub>10</sub> dielectrophile,<sup>14b</sup> but without more success (Scheme 3).

## 2. [8F+10] cyclization route to bis-trifluoromethylated hexaoxy-[6]pericyclines.

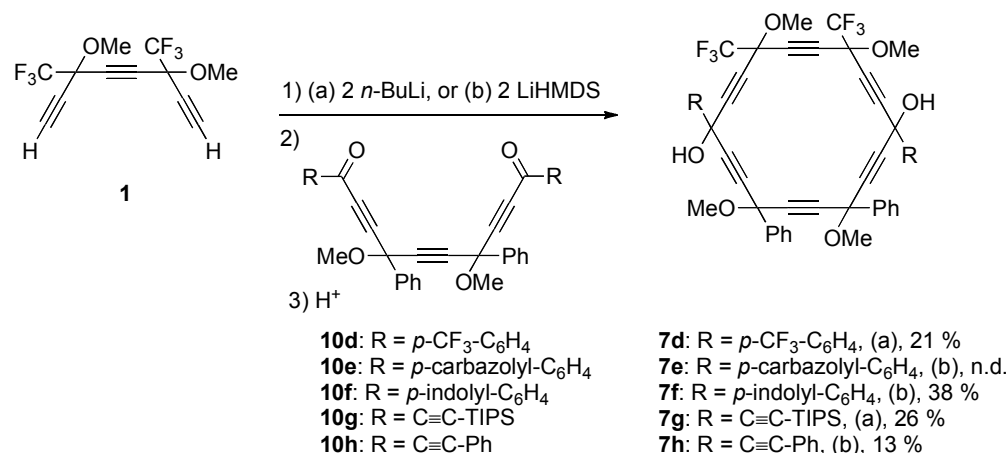
In spite of the intriguing failure of the [8F+10] strategy from the C<sub>10</sub> dialdehyde **9** (section 1, Scheme 3), the same strategy was envisaged from C<sub>10</sub> diketones. The triynediones **10d-h** were thus prepared using two alternative methods involving the bis-secondary diols **11d-h** as intermediates (Scheme 4). The first method, recently described and consisting in a double addition of the bis-terminal triyne **6** to two equivalents of 4-(trifluoromethyl)benzaldehyde, gave the diol **11d** in 96 % yield.<sup>7b</sup> The second method, involving the triynediol **9** as a dielectrophile towards various nucleophiles, led to the diols **11e-h**. The procedure previously described for the preparation of **11g** in 96 % yield from lithium triisopropylsilylacetylide,<sup>4</sup> was thus generalized to other nucleophiles, thus giving the diols **11e,f,h** in 27-72 % yield (Scheme 4). Isolation of the indolyl- and carbazolyl-substituted products **11e,f** required aqueous treatment of the reaction medium at low temperature. The diols **11d-h** were then oxidized to the corresponding diketones **10d-h** using MnO<sub>2</sub> in DCM (Scheme 4).



**Scheme 4.** Synthesis of C<sub>10</sub> diketone synthons to be involved in a [8F+10] cyclization route to bis-trifluoromethylated [6]pericyclines of type **D<sub>F</sub>** (see Schemes 1 and 5).

The five C<sub>10</sub> diketones **10d-h** were then involved in a [8F+10] cyclization process with the same bis-trifluoromethylated dinucleophile **1**, the dilithium salt of which was prepared from either base, *n*-butyllithium or lithium hexamethyldisilazane (LiHMDS) (Scheme 5). In comparison to the use of a stoichiometric amount of *n*-butyllithium, which turned out to be inefficient in a few cases,

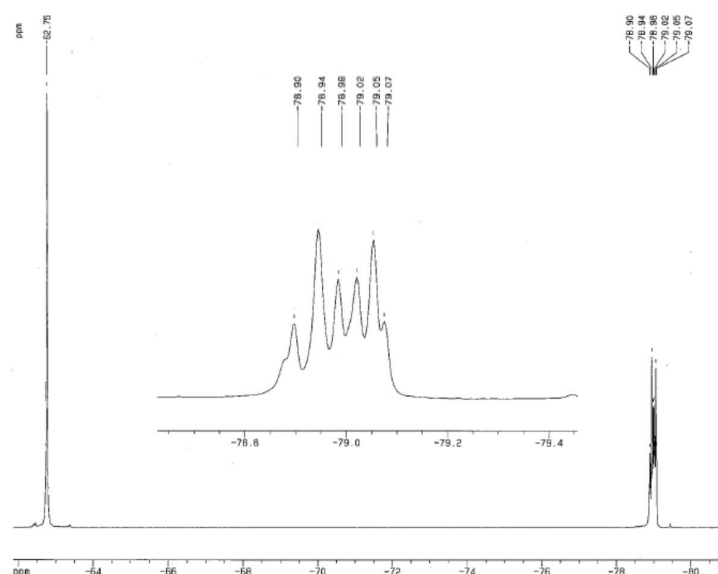
the alternative use of four equivalents of LiHMDS afforded **7e,f,h**. While **7e** proved to be elusive upon chromatography, the [6]pericyclinediols **7d,f-h** were finally obtained in 13 to 38 % yields, i.e. in the classical range of related [8+10] cyclization processes.<sup>14b,15</sup>



**Scheme 5.** [8F+10] cyclization strategy from triynediones **10** to bis-trifluoromethylated hexaoxy-[6]pericyclines **7** of type **D<sub>F</sub>** (Scheme 3).

The [6]pericyclinediols **7d-h** were obtained as mixtures of diastereoisomers (20 in theory): this was evidenced by the extended ranges of resolved <sup>1</sup>H NMR signals of C\*(R)OCH<sub>3</sub> vertices (R = Ph, CF<sub>3</sub>) and resolved <sup>19</sup>F NMR signals of C\*(OMe)CF<sub>3</sub> vertices (around -79 ppm), induced by the rigid (cyclic) close stereochemical environment (in contrast, the 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub> substituents of **7d**, remote from the stereogenic centers, resonate as a single broad <sup>19</sup>F singlet at -62.7 ppm: see Fig. 2).

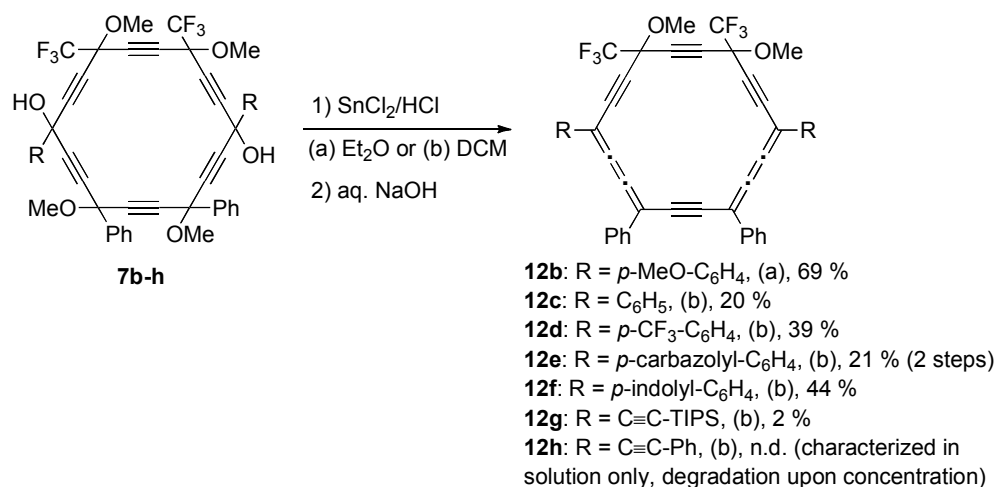
Although preparation of **7d-h** by the alternative [8+10F] route was not attempted, systematic comparison of the two routes will deserve special attention, in particular in view of elucidating the failure of both routes for the target **7a** and allow the design of a suitable procedure for this target.



**Figure 2.**  $^{19}\text{F}$  NMR spectrum of the [6]pericyclinediol **7d** evidencing the occurrence of a diastereoisomeric mixture, 20 diastereoisomers in theory ( $\text{CDCl}_3$ , 282 MHz).

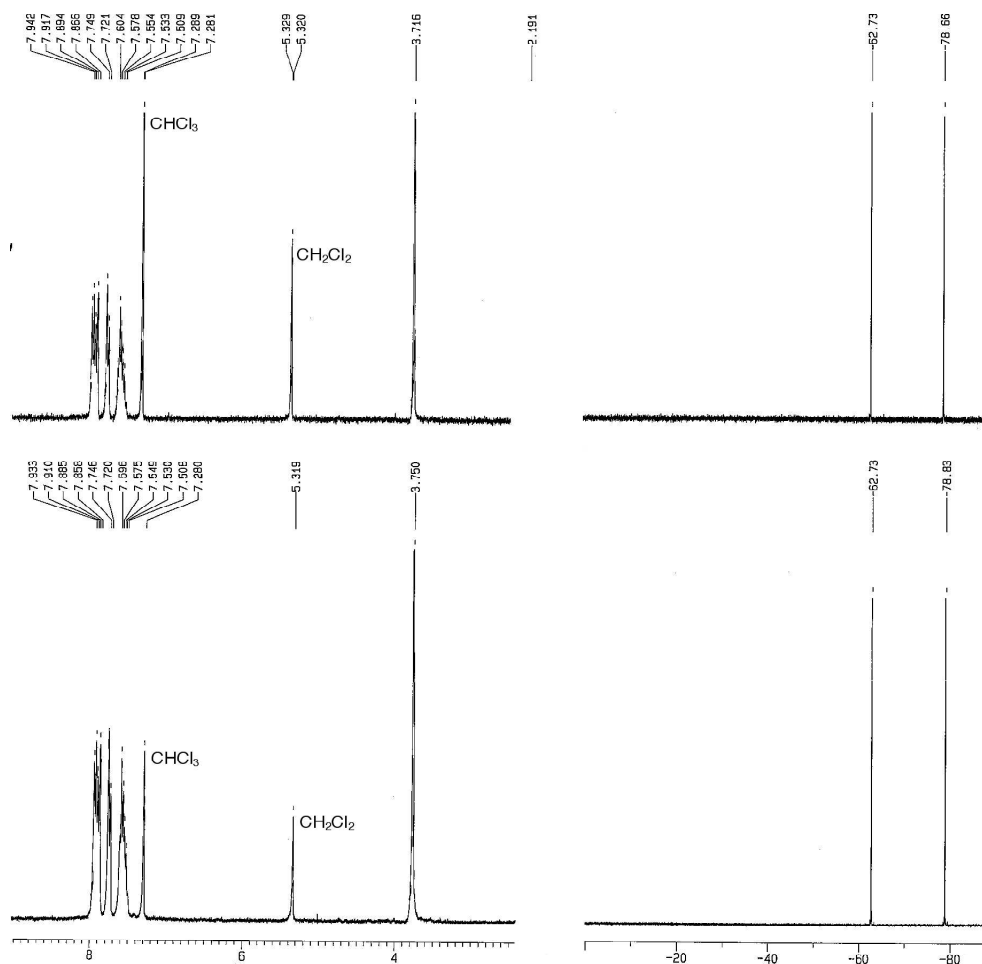
### 3. Reduction of bis-trifluoromethylated hexaoxy-[6]pericyclines to carbo-cyclohexadienes.

Reductive treatment of the [6]pericyclinediols **7b-h** with  $\text{SnCl}_2/\text{HCl}$  afforded the *carbo*-cyclohexadienes **12b-h** (Scheme 6). While the tetraaryl targets **12b-f** were readily obtained under classical conditions, the dialkynyl counterparts **12g,h** were more elusive. The reduction of **7g** was thus not selective, giving a mixture of undetermined products from which a minute quantity of **12g** could be obtained. The reduction of **7h** turned out to be selective (with one main spot observed on TLC plates), but the product **12h** proved to be unstable in the solid state, giving instantly a black insoluble material when concentrated to dryness. The *carbo*-cyclohexadienes **12h** could however be characterized in solution, using a procedure avoiding complete evaporation of the solvent.



**Scheme 6.** Selective four-electron reduction of bis-trifluoromethylated hexaoxy-[6]pericyclines to conjugated *carbo*-cyclohexadienes.

The diastereoselectivity of the partial reduction process could not be determined from <sup>1</sup>H or <sup>19</sup>F NMR spectra of the crude materials because of a low resolution, likely due to traces of SnCl<sub>2</sub>. After chromatography, however, the *carbo*-cyclohexadienes **12b**, **12d-h** were obtained as mixtures of *meso* (*cis*) and *d/l* (*trans*) isomers, identified by pairs of sharp <sup>1</sup>H NMR signals for the OCH<sub>3</sub> groups and pairs of sharp <sup>19</sup>F NMR signals for the CF<sub>3</sub> groups directly connected to the C<sub>18</sub> macrocycle. For the tetraphenylated *carbo*-cyclohexadiene **12c**, single slightly broadened OC<sup>1</sup>H<sub>3</sub> and C<sup>19</sup>F<sub>3</sub> NMR signals were observed. In all cases, except the case of **12h** (and, perhaps, **12c**), the mixture could be resolved by silicagel chromatography. <sup>1</sup>H and <sup>19</sup>F spectra of the two isomers of the representative example **12d** (without assignment) are shown in Fig. 3.



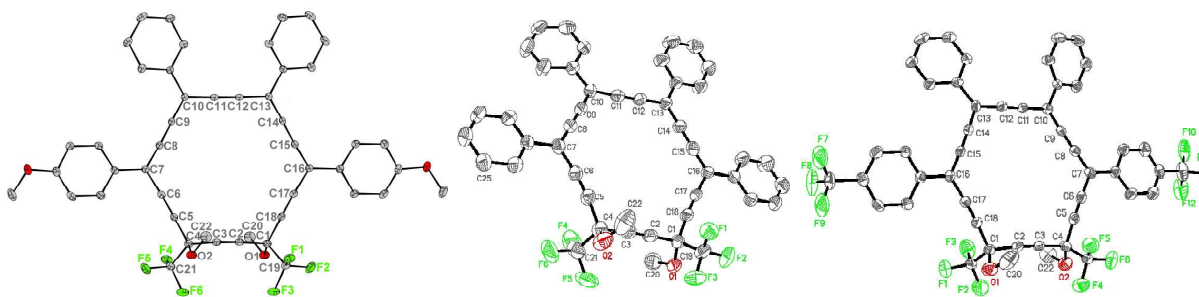
**Figure 3.**  $^1\text{H}$  NMR (300 MHz, *left*) and  $^{19}\text{F}$  (282 MHz, *right*) NMR spectra of the resolved *meso* (*cis*) and *dl* (*trans*) diastereoisomers of **12d**. *Top*: less polar (on TLC); *bottom*: more polar.

#### 4. X-ray crystallography of carbo-cyclohexadienes.

Three of the bis-trifluoromethylated *carbo*-cyclohexadienes were obtained as crystalline solids.<sup>16</sup> X-ray diffraction (XRD) analyses of selected crystals of **12b**, **12c** and **12d** thus confirmed the conjugated structure of the *carbo*-cyclohexadiene core. On the basis of experimental spectroscopic data only, it was indeed not possible *a priori* to decipher whether the structure of the previously isolated tetraphenylated *carbo*-cyclohexadiene product was indeed  $\text{C}(\text{R} = 4\text{-MeO-C}_6\text{H}_4)$ , i. e. the core *carbo*-mer of the 1,3-cyclohexadiene parent, instead of the core *carbo*-mer of the 1,4-cyclohexadiene isomer (Fig. 1).<sup>10a</sup> The assignment was proposed on the basis of a comparison of the experimental UV-vis spectrum with theoretical spectra of both the regioisomers calculated at semi-empirical ZINDO or TD-DFT levels (only the conjugated butatriene edges of **C** give rise to the

observed two-intense band spectrum: see section 5).<sup>10a</sup> Since **12b** exhibits the same two-band UV-vis pattern, the XRD data of **12b** confirms the original assignment to C(R = 4-MeO-C<sub>6</sub>H<sub>4</sub>).

XRD analysis also revealed that the three *carbo*-cyclohexadiene crystals correspond to the *meso* (*cis*) stereoisomers **12b-d**, with similar geometrical features (Fig. 4). The C<sub>18</sub> macrocycle is slightly distorted (maximum deviation from the mean plane: 0.43 Å for **12b**, 0.55 Å for **12c**, 0.23 Å for **12d**), with small torsion angles of the endocyclic DBA motif: 5.8°, 7.4° and 2.1° in **12b**, **12c** and **12d**, respectively. Nevertheless, in contrast to the quasi-planar *carbo*-benzenes of type **A** (Fig. 1), the butatriene and but-2-yne edges of the *carbo*-cyclohexadienes **12b-d** of type C<sub>F</sub>, are mesomerically non-equivalent and exhibit bond lengths close to those reported for the linear ( $\sigma$ -acyclic) DBA analogues of type **B**.<sup>7</sup> Indexing the DBA motif of **12b-d** as C7=C8=C9=C10(Ph)-C11 $\alpha$ C12-C13(Ph)=C14=C15=C16, the sequence of the bond lengths from C7 to C12 and C16 to C11, indeed reads (in Å): 1.355 ( $\pm$  0.010), 1.241 ( $\pm$ 0.010), 1.356 ( $\pm$ 0.010), 1.423 ( $\pm$ 0.005), 1.196 ( $\pm$ 0.005). The central and lateral *C*<sub>sp</sub>-*C*<sub>sp</sub> bonds exhibiting a significant difference in length ( $\Delta$  = 0.045 Å) are therefore assigned to fixed triple and double bonds, respectively.



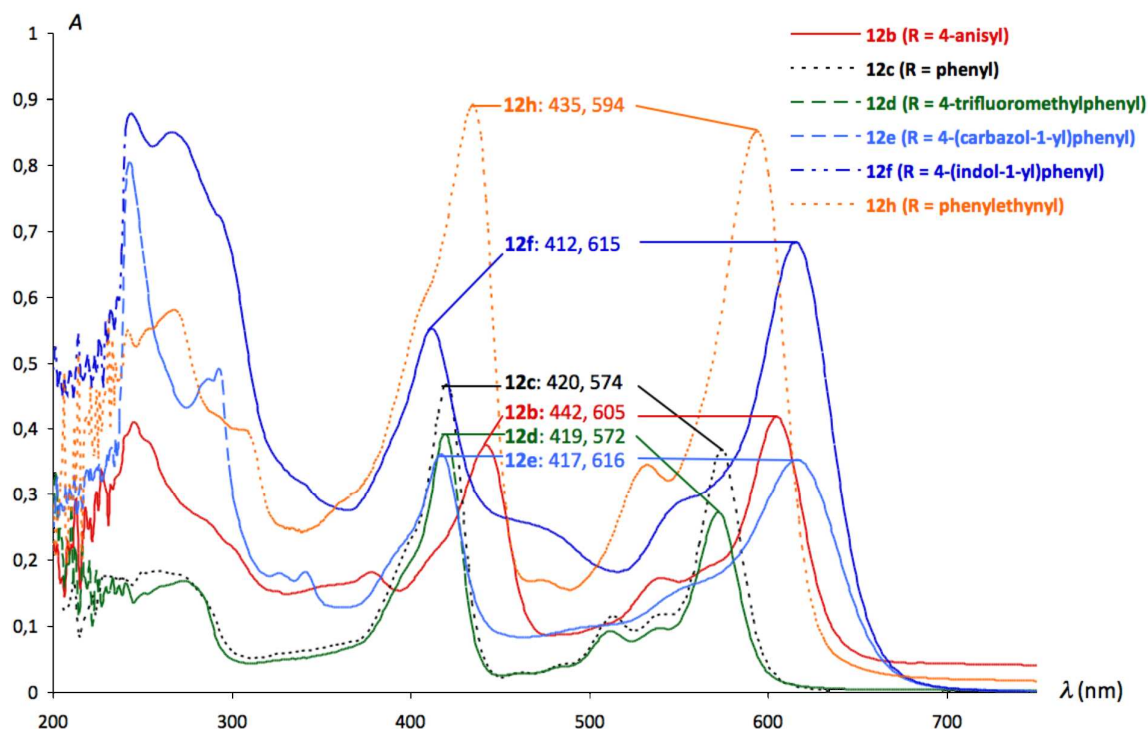
**Figure 4.** Molecular views of the X-ray crystal structures of the *carbo*-cyclohexadienes **12b** (*left*), **12c** (*middle*), and **12d** (*right*) (Scheme 6). 50 % probability level for the thermal ellipsoids. For clarity, all hydrogen atoms, disordered atoms and solvent molecules are omitted. DBA motifs : C7-C16.



### 5. Absorption spectroscopy of carbo-cyclohexadienes.

The *carbo*-cyclohexadienes **12** are highly chromophoric, possibly giving intense red (**12b,c**), blue (**12d-f,h**) or purple (**12g**) solutions in usual organic solvents. The electronic spectra of **12b-f,h** in diluted chloroform solutions are combined in Fig. 5 (the minute quantities and moderate stability of **12g** prevented full characterization). The spectra exhibit similar patterns, with two intense bands in the visible region (and a third intense band in the UV region due to carbazole and indole substituents for **12e** and **12f**, respectively). The same two-band pattern was previously observed for the tetraphenylated analogue **C**(R = 4-MeO-C<sub>6</sub>H<sub>4</sub>), theoretical spectra of which were also calculated at the TDDFT and ZINDO levels.<sup>10a</sup> These calculations were found to reproduce the observations, with high accuracy for the absolute transition energies (433 and 615 nm at the ZINDO level, vs 437 and 602 nm for the experimental values) and definite agreement for the relative oscillator strengths ( $f = 1.60$  at 433 nm, and  $f = 0.77$  at 615 nm at the ZINDO level). The transitions were shown to involve the four orbitals of the Gouterman model (HOMO-1, HOMO, LUMO, LUMO+1), and one-electron excitations from the ground state  $S_0$  to the first and third excited states  $S_1$  and  $S_3$ , both centered on the conjugated DBA core.<sup>10a</sup> As the Ph or CF<sub>3</sub> substituents at the  $sp^3$  carbon atoms of the *carbo*-cyclohexadiene ring are not  $\pi$ -conjugated with the DBA motif, the same interpretation can be inferred to apply in the **C<sub>F</sub>** series. The variation of the maximum absorption wavelength ( $\lambda_{\max}$ ) as a function of the substituents follows the same trend as the one previously observed for the  $\sigma$ -acyclic DBA derivatives of type **B**, with a slight general bathochromic shift for the present  $\sigma$ -cyclic series of type **C<sub>F</sub>** (Fig. 1).<sup>4,7</sup> In this series, and by reference to the tetraphenylated dye **12c**, the largest bathochromic shifts are thus observed for the most donating anilinyll-type substituents of **12e** and **12f**. The still  $\pi$ -donating anisyl substituents of **12b** and extended phenylethynyl substituents of **12h** also induce higher  $\lambda_{\max}$  values than the phenyl substituents of **12c**. In contrast, the electron-withdrawing *p*-trifluoromethylphenyl substituents of **12d** induce a small hypsochromic shift below the reference value of **12c** at 574 nm.

In the cyclic series  $C_F$ , the molar extinction coefficient was found to vary from 9900 to 112900  $L \cdot mol^{-1} \cdot cm^{-1}$ , the limit values being achieved for **12f** and **12d**, respectively. These values are in the same range as those previously reported in the acyclic series **B**.<sup>7b</sup> The fluorophore-substituted *carbo*-cyclohexadienes **12e** and **12f** were also found to be emissive at 427 ( $\lambda_{exc} = 243$  nm) and 485 nm ( $\lambda_{exc} = 348$  nm), respectively, namely at lower wavelengths than their  $\sigma$ -acyclic parents in the **B** series, emitting around 500 nm.<sup>4,7b</sup>



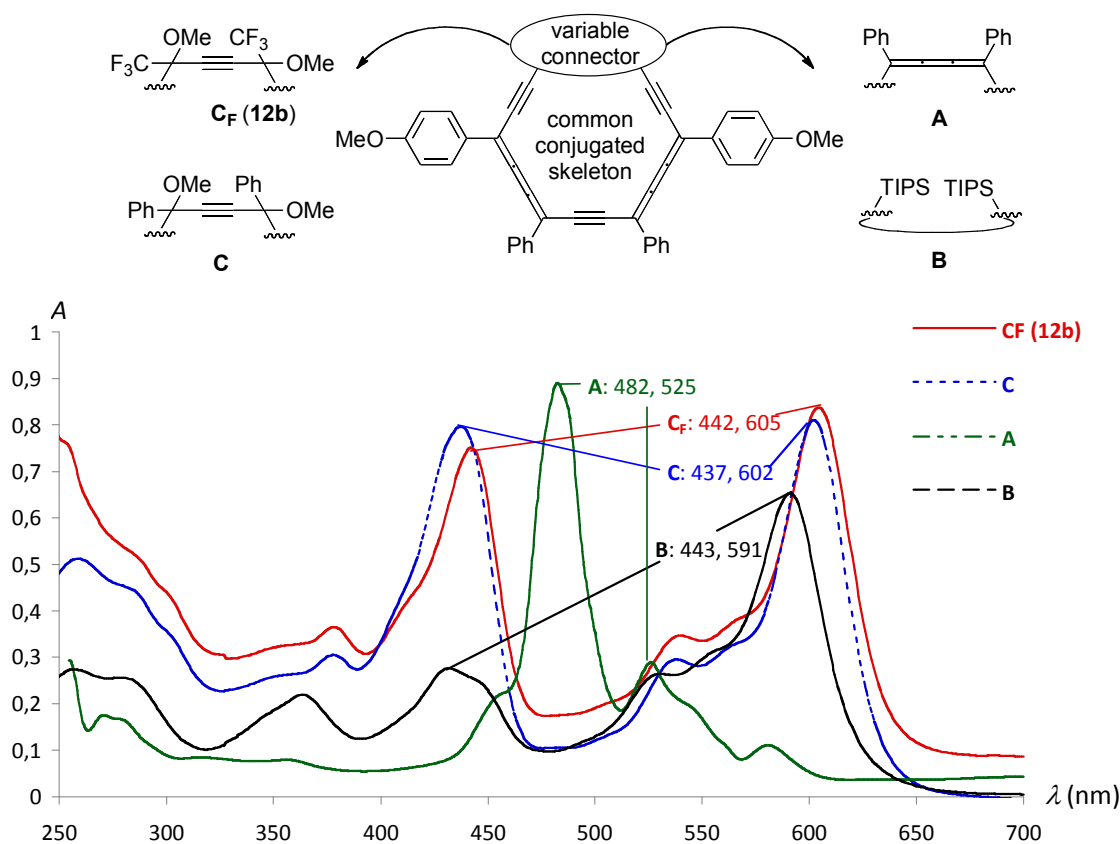
**Figure 5.** Absorption spectra of the *carbo*-cyclohexadienes of type  $C_F$ , **12b-f,h** (in  $CHCl_3$ ).

Possible solvato-chromism in the *carbo*-cyclohexadiene series  $C_F$  was finally investigated for the selected tetrakis(trifluoromethylated) representative **12d**, which, contrary to its congeners, is soluble in a typical range of aprotic solvents, including pentane (see S.I.). Starting from pentane, after a first step of *ca* 10 nm, a quasi-negligible bathochromic shift with dielectric constant ( $\epsilon_r$ ) is observed, followed by another step of 4 nm for toluene, an aromatic solvent prone to bind with **12b** through specific  $\pi$ - $\pi$ -stacking interactions: 416 and 568 nm in pentane ( $\epsilon_r = 1.8$ ), 423 and 578 nm in chloroform ( $\epsilon_r = 4.8$ ), 424 and 578 nm in THF ( $\epsilon_r = 7.5$ ), 427 and 582 nm in toluene ( $\epsilon_r = 2.4$ ).

In a related context, as previously reported for a tetraphenyl-*carbo*-cyclohexadiene of type **C**,<sup>10a</sup> the bis-trifluoromethylated dye of type **C<sub>F</sub>** appear more or less dichromic in diluted solution.<sup>11</sup> In particular, the dianisyl-*carbo*-cyclohexadienes of types **C** (R = 4-MeO-C<sub>6</sub>H<sub>4</sub>) and **C<sub>F</sub>** (**12b**) exhibit the same turquoise-blue/deep purple dichromism,<sup>11</sup> and almost superimposable UV-vis spectra, with two intense absorption bands at 437, 602 nm for the **C** version, and at 442, 605 nm for the **C<sub>F</sub>** version **12b** (Fig. 6).

The dianisyl series (Fig. 1, R = 4-MeO-C<sub>6</sub>H<sub>4</sub>) is completed by two additional representatives **A** and **B**, where the central core is a rigid aromatic *carbo*-benzene ring in **A** and a flexible  $\sigma$ -acyclic *carbo*-*n*-butadiene unit in **B**. The latter possesses formally the same  $\pi$ -conjugated system as in the  $\sigma$ -cyclic versions **C** or **C<sub>F</sub>** (**12b**) and exhibits also a two-band absorption spectrum, with similar absorption wavelengths at 443, 591 nm but with markedly different respective intensities (these intensities are similar in **C** and **C<sub>F</sub>**). This difference is attributed to the much greater flexibility of the DBA motif in **B** by comparison to **C** and **C<sub>F</sub>**. TDD-DFT or ZINDO calculations of absorption spectra in the free-rotating series **B** would thus be much more challenging than in the locked series **C**, **C<sub>F</sub>** or **A** (see above),<sup>10a</sup> as they would require full conformational analysis before relevant averaging. The effect of the *cisoid*-locked conformation of the DBA motif in **C** and **C<sub>F</sub>** (**12b**) is thus dramatic, resulting, in particular, in a much weaker dichromism of the freely rotating *carbo*-*n*-butadiene **B**.

In contrast to the **B**, **C** and **C<sub>F</sub>** representatives, the electronic spectrum of the quadrupolar dianisyl *carbo*-benzene **A** exhibits only one main absorption band (at 482 nm), as widely documented in the general *carbo*-benzene series.<sup>2c,4,10a</sup>



**Figure 6.** UV-vis absorption spectra in  $\text{CHCl}_3$  (bottom) of all the known dianisyl-substituted carbo-cyclohexadienic cores of the types **A**, **B**, **C** (Fig. 1, for  $\text{R} = 4\text{-MeO-C}_6\text{H}_4$ ) and  $\text{C}_F$  ( $= \mathbf{12b}$ ) (top).

### 6. Electrochemistry of carbo-cyclohexadienes.

The electrochemical properties of the carbo-cyclohexadienes of type  $\text{C}_F$  (excluding the poorly stable dialkynyl derivatives **12g** and **12h**) were investigated by square-wave (SW) and cyclic voltammetry (CV). The corresponding data are summarized in Table 1.

All the carbo-cyclohexadienes exhibit quasi-identical reduction behaviours, with three waves, the first one being reversible (except for **12e**) and occurring between  $-0.47$  and  $-0.67$  V (the latter limit values being achieved for **12d** and **12b**, respectively). As previously observed in the carbo-*n*-butadiene series **B**, and as expected,<sup>7b</sup> the acceptor-substituted derivative **12d** of the  $\text{C}_F$  series ( $\text{R} = 4\text{-CF}_3\text{-C}_6\text{H}_4$ ) is thus more prone to reduction. The first reduction potentials is however systematically higher (in algebraic value) in the carbo-cyclohexadiene series  $\text{C}_F$  than in the carbo-

*n*-butadiene series **B** (italicized values in Table 1), likely because of the greater average stabilization of the anion through the optimally conjugated quasi-planar DBA motif of the **C<sub>F</sub>** series. Another similarity between the series **C<sub>F</sub>** and **B** is the result of the less donating character of the indolylphenyl and carbazolylphenyl substituents with respect to the anisyl substituent, the latter giving the smallest half-wave potential of the *carbo*-cyclohexadiene series ( $E_{1/2} = -0.67$  V for **12b**).

In the oxidation process, the cations of the indolylphenyl- and carbazolylphenyl- substituted *carbo*-cyclohexadienes **12e** and **12f** were found to deposit on the electrode, giving electroactive films. In a complementary manner to what is observed in the reduction process, the *carbo*-cyclohexadienes **C<sub>F</sub>** are less prone to oxidation than the *carbo*-*n*-butadiene counterparts **B** (italicized values in Table 1). Only the first oxidation waves of the dianisyl- and diphenyl-substituted derivatives **12b** and **12c** are reversible, the most  $\pi$ -donating groups, R = 4-MeO-C<sub>6</sub>H<sub>4</sub>, giving the lowest potential of the series ( $E_{1/2} = +1.12$  V for **12b**). In contrast, the most electron-withdrawing groups, R = 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, induces the highest first oxidation potential at 1.54 V for **12d**. The quite high first oxidation potentials in the **C<sub>F</sub>** series make the results difficult to exploit (due to the close oxidation of the solvent), but can be correlated to the corresponding low first reduction potentials: following a general trend, molecules that are readily reduced are not easily oxidized.

compound	reductions				oxidations			
	First reduction C series		First reduction <i>B series</i> <sup>4,7b</sup>	Other reductions C series <sup>(d)</sup>	First oxidation C series		First oxidation <i>B series</i> <sup>4,7b</sup>	Other oxidations C series <sup>(d)</sup>
	$E_{1/2}$ <sup>(a)</sup> ( $\Delta E_p$ ) <sup>(b)</sup>	$RI_p$ <sup>(c)</sup>	$E_{1/2}$	$E_p^{\text{red(e)}}$	$E_{1/2}$ <sup>(a)</sup> ( $\Delta E_p$ ) <sup>(b)</sup>	$RI_p$ <sup>(c)</sup>	$E_{1/2}$ <sup>4,7b</sup>	$E_p^{\text{red(e)}}$
<b>12b</b>	-0.67 (0.06) <sup>(f)</sup>	1.00	-0.88	-0.95 -1.18 -1.44 <sup>(i)</sup> -1.52 <sup>(i)</sup> -1.61 <sup>(i)</sup>	1.12 (0.09) <sup>(g)</sup>	0.86	0.95	1.68 <sup>(h)</sup> 1.90
<b>12c</b>	-0.61 (0.06)	0.94	-0.80	-0.88 -1.07 -1.57 <sup>(i)</sup>	1.33 (0.06)	1.05	0.95	1.60 <sup>(g)</sup>
<b>12d</b>	-0.47 (0.06)	0.96	-0.65	-0.69 <sup>(k)</sup> -1.84	1.54 <sup>(h)</sup> irr.	-	1.31	1.86
<b>12e</b>	-0.59irr	-	-0.75	-0.80 <sup>(l)</sup> -1.00 -1.44 <sup>(i)</sup> -1.73 <sup>(i)</sup>	1.21 <sup>(h,1)</sup> irr.	-	1.06	1.42 1.68
<b>12f</b>	-0.60 (0.06)	1.17	-0.75	-0.85 -1.00 -1.43 <sup>(i)</sup> -1.74 <sup>(i)</sup>	1.17 <sup>(h,1)</sup> irr.	-	1.04	1.60

**Table 1.** CV and SWV data for *carbo*-cyclohexadienes of type **C<sub>F</sub>**, and comparison with the first reduction and oxidation potentials of the corresponding *carbo*-*n*-butadienes of type **B** (italicized values). Measurements performed at room temperature in DCM; supporting electrolyte: [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] (0.1 M); working electrode: Pt; reference electrode: saturated calomel electrode (SCE, 0.242 V vs the hydrogen electrode); scan rate: 0.2 V.s<sup>-1</sup> unless otherwise noted. (a) Half wave potential  $E_{1/2} = (E_p^{\text{red}} + E_p^{\text{ox}})/2$ , in V / SCE; (b) separation between the two peak potentials:  $\Delta E_p = |E_p^{\text{red}} - E_p^{\text{ox}}|$ , in V; (c) peak current ratio  $RI_p = |I_p^{\text{ox}}/I_p^{\text{red}}|$ ; (d) irreversible unless otherwise noted; (e)  $E_p$  values measured from CV in V / SCE; (f) scan rate: 0.1 mV.s<sup>-1</sup>; (g) scan rate: 0.5 mV.s<sup>-1</sup>; (h) after the first oxidation, a product deposited on the electrode; (i) formation of an electroactive deposit observed; (j) potentials obtained from SWV voltammograms; (k) reversible couple:  $E_{1/2} = -0.69$  V/SCE,  $\Delta E_p = 0.07$  V,  $RI_p = 0.92$ ; (l) shoulder of low intensity which can possibly correspond to an adsorbed product.

## Conclusion

Since the incidental isolation of the first example of *carbo*-cyclohexadiene resulting from a partial reduction of a [6]pericyclyne,<sup>10a</sup> the introduction of a trifluoromethyl group on two adjacent vertices of hexaoxy[6]pericyclynes allowed selective synthesis of conjugated *carbo*-cyclohexadienes, bearing various types of electroactive substituents at the 1,10 positions of the endo-macrocyclic DBA motif, with spectator phenyl substituents at the 4,7 positions. Whereas the tetraaryl bis-trifluoromethylated *carbo*-cyclohexadienes were found to be stable both in solution and in the solid state, two dialkynyldiphenyl counterparts appeared less stable. Moreover, the trifluoromethylated *carbo*-cyclohexadienes appear much more stable than their phenylated analogues, without modifying their chromophoric and spectroscopic properties, as evidenced in the anisyl-substituted series. The optical and electronic properties of this novel type of *carbo*-meric chromophores deserve systematic attention. In particular, as justified in the introduction, the dianilinyll derivative  $C_F(R = 4-NH_2-C_6H_4)$ , Fig. 1) is currently being targeted for measurement of its single molecule conductance (SMC) and comparison with the *carbo*-benzene  $A(R = 4-NH_2-C_6H_4)$ .<sup>8</sup> As neither the [8+10F] nor the [8F+10] strategy proved to be compatible with the  $NH_2$  substituents, further methodological improvements are required. In parallel, theoretical studies are being undertaken to bring out the specific, but subtle effects of the  $CF_3$  substituents in the  $C_F$  serie, with respect to the phenyl substituents in the  $C$  series.<sup>10a,17</sup>

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