A New Insight into the Catalytic Decomposition of Ethyl Diazoacetate in the Presence of *meso*-Tetraarylporphyrin (= 5,10,15,20-Tetraaryl-21*H*,23*H*-porphine) Complexes

by **Ana T. P. C. Gomes**[a]), **Raquel A. C. Leão**[a])[b]), **Cristina M. A. Alonso**[a]), **Maria G. P. M. S. Neves**[a]), **Maria A. F. Faustino**[a]), **Augusto C. Tomé**[a]), **Artur M. S. Silva**[a]), **Sergio Pinheiro**[a])[b]), **Maria Cecília B. V. de Souza**[b]), **Vítor F. Ferreira**[b]), and **José A. S. Cavaleiro***[a])

[a]) Department of Chemistry, University of Aveiro, P-3810-193 Aveiro (phone: +351234370717; fax: +351234370084; e-mail: jcavaleiro@ua.pt)

[b]) Departamento de Química Orgânica, Universidade Federal Fluminense, 24020-150, Niterói, RJ, Brazil

The decomposition of ethyl diazoacetate by several catalysts in the presence of *meso*-tetraarylporphyrin complexes with different electronic features was evaluated. The distribution of the obtained products (chlorins, bacteriochlorins, isobacteriochlorins, and porphyrin derivatives resulting from C–H insertion and *Büchner* ring expansion) is dependent on the catalyst and on the electronic features of the *meso*-aryl groups.

Introduction. – Porphyrins have important applications in several scientific areas, namely in medicine, catalysis, electronics, solar-cell production, *etc.* The functionalization of porphyrins at the β-pyrrolic positions (C(2), C(3), C(7), C(8), C(12), C(13), C(17), and C(18)) merits considerable attention due to the diversity of structural features that can be introduced into the macrocycle. Of special importance are those leading to reduced porphyrins, mainly chlorins (= 7,8-dihydro-21*H*,23*H*-porphines) and bacteriochlorins (= 7,8,17,18-tetrahydro-21*H*,23*H*-porphines), and π-extended porphyrin derivatives, which show strong light absorption near or above 600 nm, a requirement for a photosensitizer to be used in PDT (photodynamic therapy) [1]. Over the past years, we and others have been developing new methods for reaching those types of compounds, namely *Diels–Alder* reactions [2], 1,3-dipolar cycloadditions [3][4], and electrocyclization reactions [5].

In the early 1970s, *Callot* reported the functionalization of (*meso*-tetraphenylporphyrinato)zinc(II) (*meso* positions = C(5), C(10), C(15), and C(20)) by addition of carbenes generated from several diazoacetates catalyzed by CuCl [6]. These reactions afforded, after demetallation, a mixture of isomeric cyclopropa-fused chlorins, trace amounts of bacteriochlorins, and *N*-alkylated products. It is relevant to note that no isobacteriochlorins (= 12,13,17,18-tetrahydro-21*H*-22*H*-porphines) were isolated from those reactions. Having in mind that biologically significant compounds can be obtained along such procedures, and since *Callot* studied these reactions with only one *meso*-tetraarylporphyrin complex and one catalyst, we decided to revisit this subject using three *meso*-tetraarylporphyrin complexes with different electronic features and

several catalysts. Ethyl diazoacetate (EDA) was used as the precursor of the carbene.

In recent years, several catalysts based on Rh^{II}, Cu^{I}, Cu^{II}, and Pd^{II} complexes have been used to promote the decomposition of diazo compounds in the presence of alkenes [7][8]. Depending on the catalyst used, a different reactivity and selectivity of the short-lived transition-metal–carbene intermediates is observed. Furthermore, porphyrinatoiron, -rhodium, and -osmium complexes have also been reported as catalysts for the decomposition of diazo compounds [9]. For our studies, we selected the following catalysts: CuCl, $[Cu(OTf)(C_6H_6)]$, $[Cu(OTf)_2]$, $[Rh_2(OAc)_4]$, $[Pd(OAc)_2]$, and chloro[*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato]iron(III) ([FeCl(tdcpp)]). Three *meso*-tetraarylporphyrin complexes with different electronic features were used as substrates: (*meso*-tetraphenylporphyrinato)zinc(II) (**1a**), [*meso*-tetrakis(3-methoxyphenyl)porphyrinato]zinc(II) (**1b**) and [*meso*-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinato]zinc(II) (**1c**). While in **1a** the *meso*-phenyl groups have no substituents, in **1b** there are electron-releasing groups and in **1c** electron-withdrawing atoms.

Results and Discussion. – *Reactions of the Porphyrins with EDA*. Reactions of porphyrins **1a–c** with EDA (10 equiv. added dropwise) were performed in dry CH_2Cl_2 at 40° under N_2, in the presence of the selected catalyst. The slow addition of EDA allowed the formation of the isolated products in reliable yields and minimized the competitive formation of carbene dimers. Since copper and palladium catalysts are typically less active than Rh^{II} and Fe complexes [7][9], 2 mol-% (relative to EDA) of the catalysts based on copper and palladium were used instead of 1 mol-% in the case of $[Rh_2(OAc)_4,]$ and [FeCl(tdcpp)]. No improvement in the outcome of the reactions was observed when the catalysts were used in higher proportions. Depending on the catalyst, these reactions afforded monoadducts **2a–c** and **3a–c**, bis-adducts **6a–c** and **7c**, products **4a–c** resulting from the C–H insertion in one β-pyrrolic position, and products **5a**,**b** resulting from a *Büchner* expansion of one *meso*-aryl group (*Schemes 1* and *2*).

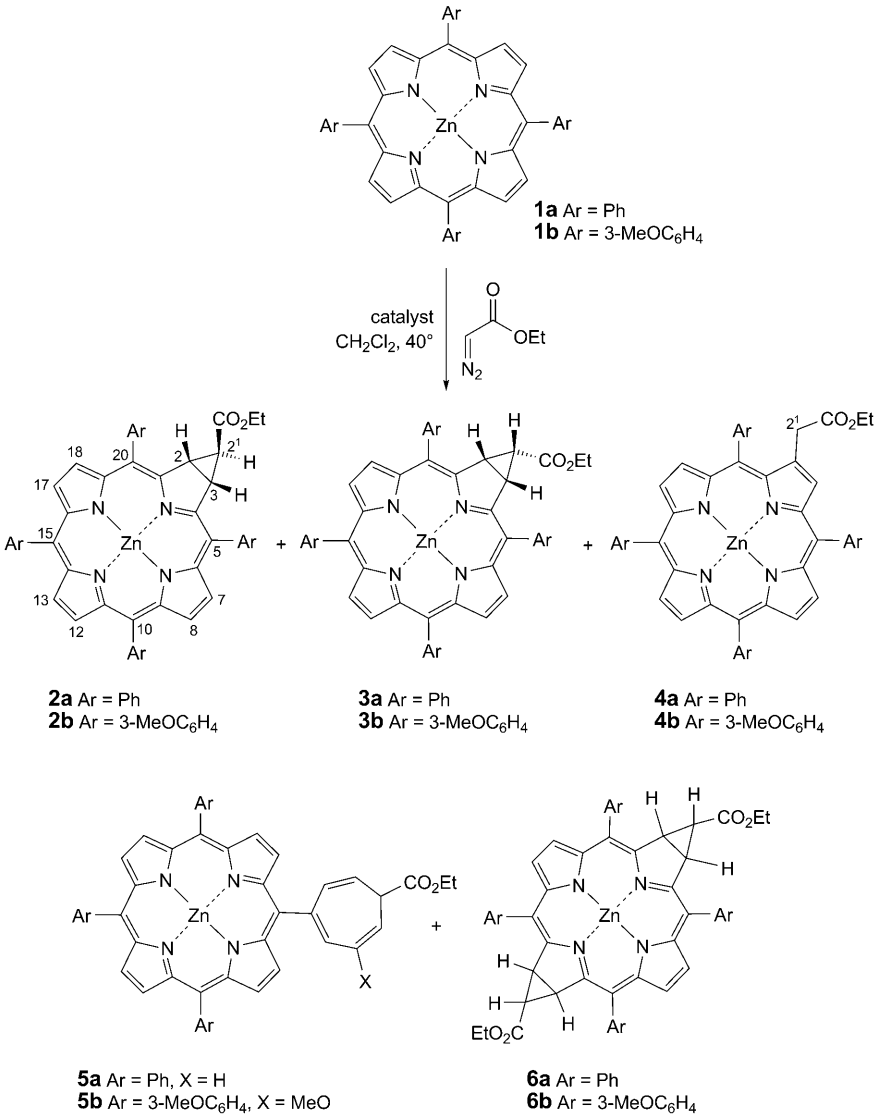
We started our experiments by repeating *Callot*'s work (porphyrin **1a**, EDA, and CuCl, but with CH_2Cl_2 as the solvent). Our results were similar to those reported, both in terms of products obtained and yields (*Table 1*, *Entry 3*). Taking these results into consideration, we decided to verify if porphyrin **1a** behaves similarly in the presence of other catalysts.

From *Table 1*, one can see that $[Rh_2(OAc)_4]$, $[Cu(OTf)_2]$, CuCl, and $[Cu(OTf)(C_6H_6)]$ are the catalysts that promote higher conversions of porphyrin **1a** (*Entries 1–4*). However, we can observe that Cu-based catalysts are more selective for the cyclopropanation reaction affording preferentially the *trans*-chlorin **2a**[1]). The same

---

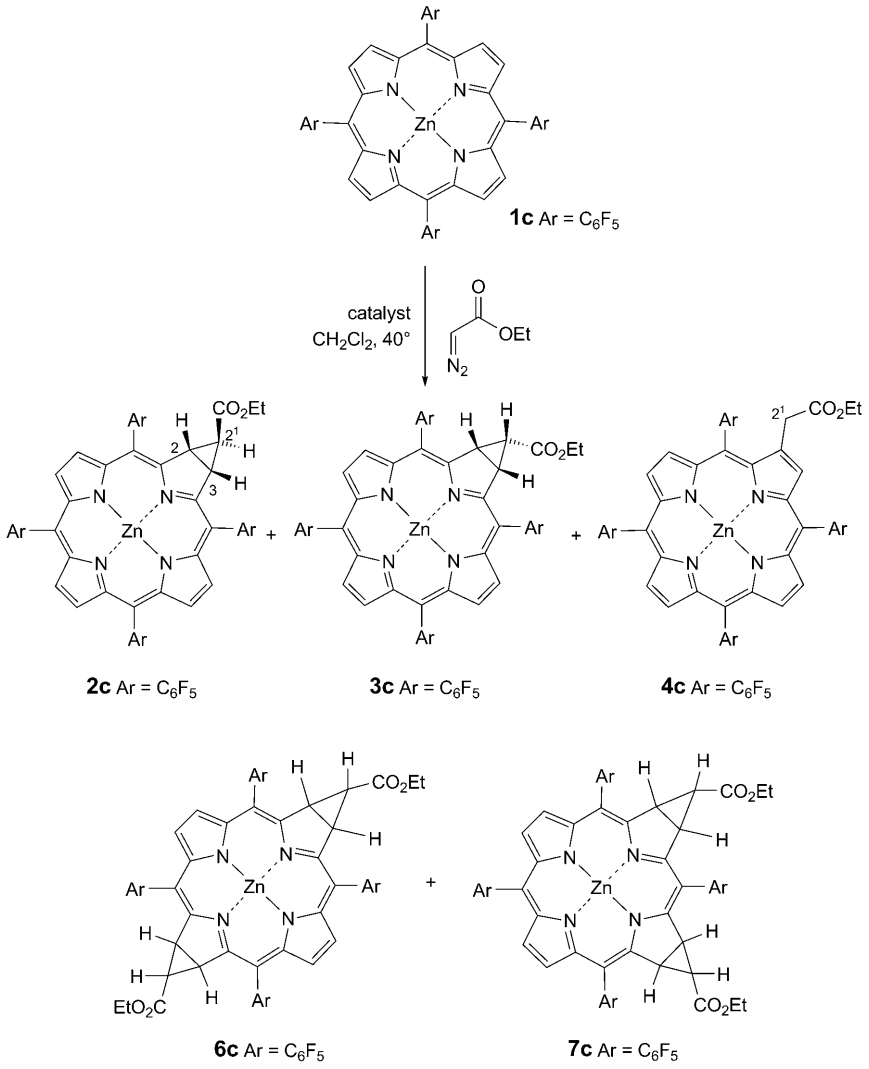
[1]) The *cis* and *trans* descriptors are used for simplicity. The *cis* isomer is the one with H–C(2), H–C(2^1), and H–C(3) in the same plane, while in the *trans* isomer H–C(2^1) is in a different plane than the other two H-atoms. In the *Exper. Part*, for the assignment of the configuration of the cyclopropane derivatives, we use the IUPAC Recommendations (1993 and 1999) concerning the configuration of cycloalkane compounds with more than two substituents, applied to the relationship of these H-atoms; systematic fusion names are also given in the *Exper. Part.*

Scheme 1



stereoselectivity is also observed in the reactions catalyzed by $[Pd(OAc)_2]$ and [FeCl(tdcpp)], but with lower yields (*Entries 5* and *6*). It is interesting to note that the Rh^{II} catalyst is the only one that promotes the formation of the C–H insertion product **4a** (*Entry 1*). The *Büchner* expansion product **5a** is obtained in the presence of $[Rh_2(OAc)_4]$ and, in minor amounts, when $[Cu(OTf)(C_6H_6)]$ and [FeCl(tdcpp)] are used (*Entries 4* and *6*). In the reaction catalyzed by CuCl, we also observe the

Scheme 2



formation, in small amounts, of the bacteriochlorin **6a**[2]) resulting from the cyclopropanation of two opposite pyrrole units (*Entry 3*).

The reactivity of porphyrin **1b** with EDA in the presence of the various catalysts has a similar profile to the one observed for porphyrin **1a**. In this case, the catalysts

---

[2]) The bacteriochlorins **6a**–**c** and the isobacteriochlorin **7c** give only one spot on TLC. The ^{1}H-NMR spectrum of **7c** shows that it is a mixture of *cis* and *trans* isomers (with respect to the porphyrin macrocycle). Probably compounds **6a**–**c** are also isomer mixtures, but due to the very low amounts isolated, it was not possible to confirm it by NMR.

Table 1. *Conversion and Selectivity of the Products Obtained from the Reaction of* **1a** *with EDA in the Presence of Several Catalysts*

Entry	Catalyst[a])	Conversion [%]	Selectivity [%]				
			2a	**3a**	**4a**	**5a**	**6a**[b])
1	1% $[Rh_2(OAc)_4]$	63.0	21.1	18.4	25.4	21.1	–
2	2% $[Cu(OTf)_2]$	63.2	28.2	2.7	–	–	–
3	2% CuCl	70.3	28.0	5.1	–	–	2.3
4	2% $[Cu(OTf)(C_6H_6)]$	66.0	20.2	1.2	–	1.2	–
5	2% $[Pd(OAc)_2]$	44.1	20.2	1.8	–	–	–
6	1% [FeCl(tdcpp)]	14.5	25.7	5.7	–	19.1	–

[a]) % Relative to EDA. [b]) Characterized only by UV/VIS and MS.

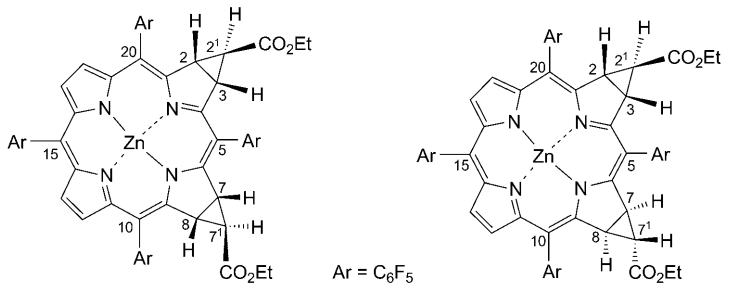
$[Rh_2(OAc)_4]$ and CuCl (*Table 2*, *Entries 1* and *3*) are the ones that promote the highest conversion of the porphyrin, but the Cu-based catalysts are the most selective for the cyclopropanation products, affording predominantly the *trans* isomer **2b** (*Entries 2–4*). This stereoselectivity is also observed when $[Pd(OAc)_2]$ is used (*Entry 5*).

Table 2. *Conversion and Selectivity of the Products Obtained from the Reaction of* **1b** *with EDA in the Presence of Several Catalysts*

Entry	Catalyst[a])	Conversion [%]	Selectivity [%]				
			2b	**3b**	**4b**	**5b**	**6b**[b])
1	1% $[Rh_2(OAc)_4]$	62.0	24.9	21.8	24.9	27.5	–
2	2% $[Cu(OTf)_2]$	33.8	26.5	2.7	–	–	–
3	2% CuCl	70.0	25.9	2.6	–	–	1.1
4	2% $[Cu(OTf)(C_6H_6)]$	51.7	26.2	1.7	–	5.2	–
5	2% $[Pd(OAc)_2]$	45.9	25.7	1.1	–	9.8	–
6	1% [FeCl(tdcpp)]	24.3	11.3	3.7	–	7.5	–

[a]) % Relative to EDA. [b]) Characterized only by UV/VIS and MS.

The outcome is different when the catalytic decomposition of EDA is performed in the presence of porphyrin **1c** (*Scheme 2* and *Table 3*). From *Table 3*, it is obvious that the highest conversions of porphyrin **1c** are obtained in the presence of the Cu-based catalysts CuCl and $[Cu(OTf)_2]$ (*Entries 2* and *3*). In the case of $[Cu(OTf)(C_6H_6)]$, a low conversion is observed, but the selectivity for chlorin **2c** is quite high (85%; *Entry 4*). The preference for the *trans*-chlorin **2c** is also observed with the two former catalysts (*Entries 2* and *3*). However, the CuCl is especially interesting because it also leads to the formation of isobacteriochlorin **7c** in remarkable yield (*Entry 3*). This isobacteriochlorin, which is a mixture of two diastereoisomers **7c1** and **7c2** (*Fig. 1*), results from the bis-cyclopropanation of two adjacent pyrrole units. Compound **7c** is also obtained when the reactions are carried out in the presence of $[Cu(OTf)_2]$, $[Cu(OTf)(C_6H_6)]$, and $[Pd(OAc)_2]$ (*Entries 2*, *4*, and *5*). The formation of isobacteriochlorins is not observed when porphyrins **1a** and **1b** are used. With CuCl, the bacteriochlorin **6c** is also detected but only in vestigial amounts (*Entry 3*). These results show that the site



7c1
(major isomer)

7c2
(minor isomer)

Fig. 1. *Structures of the isobacteriochlorins* **7c1** *and* **7c2**

Table 3. *Conversion and Selectivity of the Products Obtained from the Reaction of* **1c** *with EDA in the Presence of Several Catalysts*

Entry	Catalyst[a])	Conversion [%]	Selectivity [%]				
			2c	**3c**	**4c**	**6c**	**7c**
1	1% [$Rh_2(OAc)_4$]	31.9	11.0	1.8	8.7	–	–
2	2% $Cu(OTf)_2$	40.0	38.3	<1[b])	–	–	6.5
3	2% CuCl	65.8	41.0	2.7	–	<1[b])	39.5
4	2% [$Cu(OTf)(C_6H_6)$]	23.9	85.0	<1[b])	–	–	<1[b])
5	2% [$Pd(OAc)_2$]	20.1	19.1	<1[b])	–	–	9.5
6	1% [FeCl(tdcpp)]	13.9	39.6	<1[b])	–	–	–

[a]) % Relative to EDA. [b]) Characterized only by UV/VIS and MS.

selectivity of the bis-addition of carbenes to the porphyrin macrocycle is controlled by the electronic features of the *meso*-aryl groups.

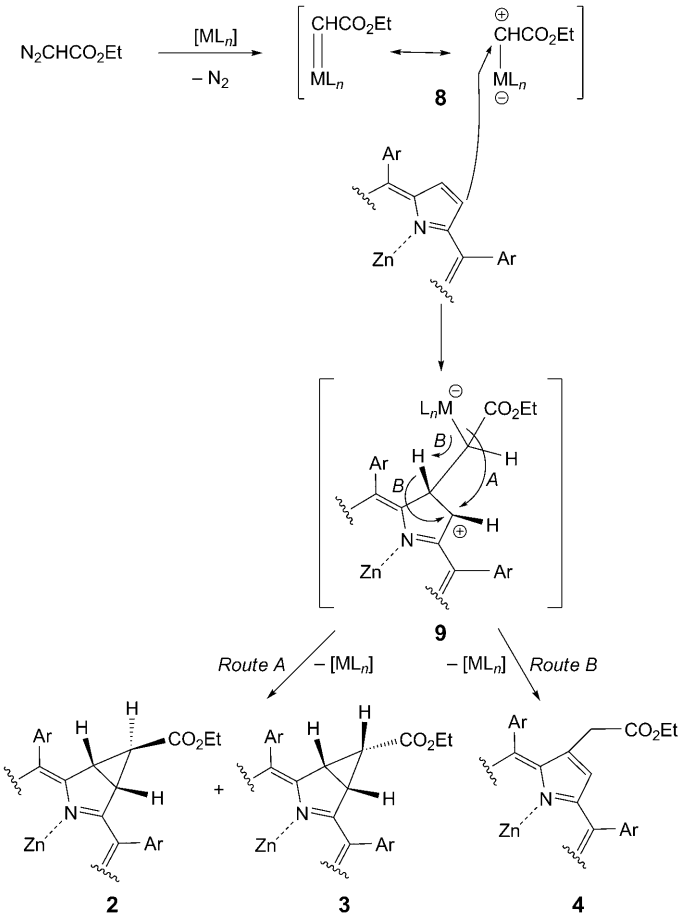
With porphyrin **1c**, the Rh^{II} catalyst (*Table 3*, *Entry 1*) is the least efficient catalyst. It leads to *trans*-chlorin **2c** and *cis*-chlorin **3c** and to the C–H insertion product **4c** with lower selectivity; a number of other minor unidentified products are also formed. As expected, the *Büchner* expansion product is not observed for this porphyrin.

Surprisingly, when the porphyrin complex [FeCl(tdcpp)] is used as the catalyst, the starting porphyrins **1a**–**c** are recovered for the most part and, as a consequence, the resulting products (chlorins and *Büchner* expansion derivatives) are isolated in very low yields. The low yields obtained are unexpected since this catalyst was successfully used in the decomposition of diazo compounds for the cyclopropanation of styrenes [9a]. The low efficiency of this catalyst in the functionalization of porphyrins **1a**–**c** is probably due to its reaction with the generated carbene or due to the conversion of the iron–carbene intermediate into an inactive species. To confirm this hypothesis, we performed the reaction of [FeCl(tdcpp)] with EDA under the same conditions as those used for the other reactions. The UV/VIS spectrum of the green reaction mixture did not show any absorption band typical of chlorins, but its MS showed a molecular ion corresponding to [FeCl(tdcpp)] plus a carbene unit ($[M+H]^+$ at m/z 1061). Probably,

the adduct results from the insertion of a carbene into the Fe–N bond, as already described [10].

Mechanistic Considerations and Spectroscopic Features of the Products. According to the literature, the decomposition of the diazo compounds involves the formation of the metal–carbene intermediate **8** (*Scheme 3*) [11–14]. The interaction of a C=C bond of the macrocycle with the electrophilic center of the metal–carbene intermediate leads to the transient intermediate **9** which can cyclize to chlorins **2** and **3** (*Route A*) or rearrange to the C–H insertion products **4** (*Route B*). The catalyst is regenerated in both cases.

Scheme 3

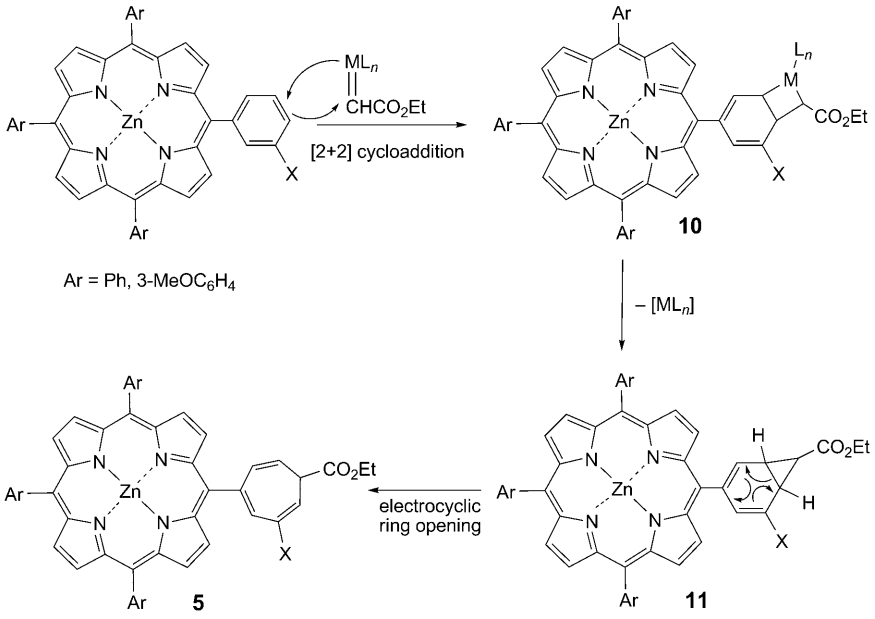


The formation of products **4** from chlorins **2** and **3**, by a cyclopropane-ring-opening reaction, was considered. However, heating solutions of the *trans*- and *cis*-chlorins **2a** and **3a** with $[Rh_2(OAc)_4]$ in refluxing CH_2Cl_2 for 24 h does not lead to the formation of

4a. This indicates that the reaction involved in the conversion of intermediate **9** into chlorins **2** and **3** is irreversible.

The formation of the *Büchner* expansion products occurs by a concerted [2 + 2] cycloaddition reaction between the metal–carbene intermediate and one of the *meso*-aryl groups. Elimination of the catalyst, and electrocyclic ring opening of the intermediate **11** leads to the products **5** (*Scheme 4*) [15]. The higher yield of the *Büchner* expansion product **5b**, relatively to the analogous **5a**, is due to the presence of a methoxy substituent in the *meso*-aryl groups. In opposition, the deactivation on the *meso*-aryl rings by the F-atoms in porphyrin **1c** prevents the formation of the *Büchner* expansion product.

Scheme 4



The structures of the new compounds were assigned on the basis of their ^{1}H- and ^{13}C-NMR and UV/VIS spectra; the molecular formulas of the new compounds were confirmed by HR-MS. All new porphyrinato-, chlorinato-, isobacteriochlorinato-, and bacteriochlorinatometal derivatives show the typical UV/VIS spectra of such systems.

All chlorin derivatives **2a–c** and **3a–c** have analogous NMR spectra, showing similar multiplicities and chemical shifts for the signals related to the resonance of the six β-pyrrolic H-atoms, typically two *d* and one *s*. The *trans*- and *cis*-cyclopropane isomers were distinguished by the coupling constant between the three H-atoms of the cyclopropane ring (H–C(2), H–C(3), and H–C(2^1)).

Due to the symmetry of **2a–c** and **3a–c**, the *s* that appears between δ(H) 8.28 and 8.50 is assigned to the resonance of H–C(12) and H–C(13). The *d* that occur between δ(H) 8.50 and 8.60 and between δ(H) 8.00 and 8.37 are assigned to the resonance of H–C(8) and H–C(17), and to H–C(7) and

H–C(18), resp. These attributions are established by the NOESY correlations between the signals of the H_o-atoms of Ar–C(10) and –C(15) and the signals of H–C(8) and H–C(17), and of H–C(12) and H–C(13). In the case of the *trans*-cyclopropanes **2a**–**c**, the cyclopropane H-atoms give rise to a ^3J of *ca.* 2.8 Hz, while in the *cis*-isomers **3a**–**c** ^3J is *ca.* 8.2 Hz.

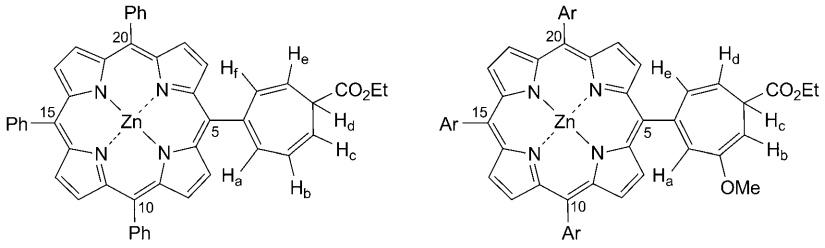
The ESI-MS of the isobacteriochlorin mixture **7c1**/**7c2** (*Fig. 1*) shows a peak at *m*/*z* 1209 ($[M+H]^+$), corresponding to the 'addition' of two carbene units to porphyrin **1c**. The ^{1}H-NMR spectrum of **7c1**/**7c2** is relatively complex and shows duplicated signals in a proportion of 2:1. From the ^{19}F-NMR spectrum it can be concluded that **7c1** is the major diastereoisomer.

In the ^{1}H-NMR spectrum of **7c1**/**7c2**, we can observe the presence of two *d* at δ(H) 7.62 and 7.69 due to the resonances of the β-pyrrolic H-atoms H–C(12) and H–C(18), and H–C(13) and H–C(17), resp., of the major diastereoisomer ($^3J = 4.4$ Hz). For the minor diastereoisomer, the resonances of the same β-pyrrolic H-atoms occur at δ(H) 7.60 and 7.97 as two *d* ($^3J = 4.3$ Hz). The resonances of the *Me*CH_2 protons appear as two *t* at δ(H) 1.29 ($^3J = 7.0$ Hz) for the major diastereoisomer and at δ(H) 1.30 ($^3J =$ 7.2 Hz) for the minor one; the resonances of the Me*C*H_2 protons appear as a *m* at δ(H) 4.22–4.28. The *d* at δ(H) 3.89 can be attributed to H–C(2), H–C(3), H–C(7), and H–C(8) of the major diastereoisomer. The corresponding coupling constant ($^3J = 2.6$ Hz) supports the *trans* configuration of both cyclopropane rings. The resonances of H–C(2) and H–C(8), and of H–C(3), and H–C(7) of the minor diastereoisomer appear as four *d* at δ(H) 3.86 ($^3J = 2.9$ Hz), 3.87 ($^3J = 2.6$ Hz), 3.94 ($^3J = 2.6$ Hz), and 3.95 ($^3J = 2.9$ Hz), with ^3J values confirming the *trans* configuration in both cyclopropane rings. The signals of H–C(2^1) and H–C(7^1) appear at δ(H) 1.44 (*t*, $^3J = 2.6$ Hz) for the major diastereoisomer and at δ(H) 1.32–1.40 (*m*) for the minor one.

The structures of products **4a**–**c** were deduced mainly from the analysis of their ^{1}H-NMR spectra. These spectra reveal the resonances of only seven β-pyrrolic H-atoms.

The signal of H–C(3) of **4a**–**c** appears as a *s* in the range δ(H) 8.79–8.89. The other signals appear as a *m* between δ(H) 8.90 and 8.99 and as two *d* between δ(H) 8.87 and 8.92 and between δ(H) 8.69 and 8.77 with the same coupling constant ($J = 4.6$ Hz). The aliphatic region shows one *s* between δ(H) 3.97 and 4.30 due to $CH_2(2^1)$. The *q* and the *t* ($J = 7.1$ Hz) of the Et group appear between δ(H) 4.12 and 4.16 and between δ(H) 1.22 and 1.26, resp.

The ^{1}H-NMR spectra of products **5a** and **5b** (*Fig. 2*) are consistent with structures resulting from *Büchner* expansion reactions.



5a **5b** Ar = 3-$MeOC_6H_4$

Fig. 2. *Structures of the* Büchner *expansion products* **5a** *and* **5b**

The eight β-pyrrolic H-atoms of **5a**,**b** appear between δ(H) 8.90 and 9.16 as two *d* and one *m*. The aryl groups at the *meso* positions 10, 15, and 20 give rise to a *m* between δ(H) 7.72 and 8.22. The H-atoms of the cycloheptatrienyl group are unequivocally assigned by means of 2D-COSY experiments. In the case of **5a**, these H-atoms appear at δ(H) 7.51 (*d*, $^3J = 6.0$ Hz, H_a), 6.77 (*dd*, $^3J = 6.0$, 9.1 Hz, H_b), 5.69 (*ddd*, $^4J = 1.3$, $^3J = 6.0$, 9.1 Hz, H_c), 3.37 (*t*, $^3J = 6.0$ Hz, H_d), and 5.33 (*ddd*, $^4J = 1.3$, $^3J = 6.0$, 9.1 Hz, H_e). The *m* between δ(H) 7.25 and 7.50 is attributed to H_f although this signal is overlapped with the signal of CH_2Cl_2. The *q* and the *t* at δ(H) 4.42 and 1.34 ($J = 7.1$ Hz), resp., are assigned to the Et group. The cycloheptatrienyl protons of **5b** appear at δ(H) 6.56 (*s*, H_a), 4.13 (*d*, $^3J = 7.5$, H_b), 7.19 (*dd*, $^3J = 7.5$, 9.7 Hz, H_c), 6.78 (*dd*, $^3J = 5.5$, 9.7 Hz, H_a), and 7.19 (*d*, $^3J = 5.5$ Hz, H_e), and the Et group gives rise to a *q* at δ(H) 4.46 and a *t* at δ(H) 1.42 ($J = 7.1$ Hz).

Conclusions. – The study of the efficiency of several catalysts in the decomposition of EDA in the presence of porphyrin complexes **1a**–**c** shows that the distribution of the products is dependent on the catalyst and on the electronic features of the *meso*-aryl substituents at the tetrapyrrole macrocycle. The CuCl is the most selective catalyst for the cyclopropanation reaction, affording predominantly the *trans* monoadduct of the three porphyrin complexes used. In the presence of this catalyst, **1c** is the most reactive one. Its reaction with EDA gives reasonable yields of the *trans*-chlorin **2c** and of the isobacteriochlorin **7c**. The cyclopropanation of tetrapyrrole macrocycles through the catalytic decomposition of diazo compounds allows the synthesis of reduced porphyrins that absorb at λ values higher than 600 nm, an important structural requirement for a good photosensitizer in PDT.

Amongst the studied catalysts, $[Rh_2(OAc)_4]$ is the only one that catalyzes the C–H insertion of carbene into the β-positions of the porphyrin macrocycle. This insertion reaction can be considered a new approach for the functionalization of *meso*-tetraarylporphyrins.

Thanks are due to the *Fundação para a Ciência e a Tecnologia* (*FCT*), *FEDER*, and the *GRICES-CAPES* collaborative programme for funding this work. *A. T. P. C. G.* and *C. M. A. A.* thank, respectively, the Aveiro Organic Chemistry Research Unit and *FCT* (SFRH/BPD/8375/2002) for their research grants. Also *R. A. C. L.* and *S. P.* thank *CAPES* for their travelling grants to Aveiro.

Experimental Part

General. meso-Tetraarylporphyrins (= [5,10,15,20-tetraaryl-21*H*,23*H*-porphinato(2–)-κN^{21},κN^{22},κN^{23},κN^{24}]zinc) **1a**–**1c** and chloro[5,10,15,20-tetrakis(2,6-dichlorophenyl)-21*H*,23*H*-porphinato(2–)-κN^{21},κN^{22},κN^{23},κN^{24}]iron were prepared according to [16][17]. EDA and the remaining catalysts were acquired from *Sigma–Aldrich* (Spain) and were used as received. The CH_2Cl_2 used as solvent of the reactions was distilled over CaH_2. Flash chromatography (FC): silica gel (SiO_2; 230–400 mesh). Prep. TLC: 20 × 20 cm glass plates coated with silica gel (1 mm thick). Anal. TLC: sheets precoated with silica gel (SiO_2; *Merck 60*, 0.2 mm thick). UV/VIS Spectra: *Shimadzu UV-2501-PC* spectrophotometer; in $CHCl_3$; λ_{max} (log ε) in nm. ^{1}H-, ^{13}C-, and ^{19}F-NMR Spectra: *Bruker Avance-300* spectrometers at 300.13, 75.47, and 282.38 MHz, resp., or *Bruker Avance-500* spectrometer at 500.13 and 125.77 MHz for ^{1}H and ^{13}C, resp.; $CDCl_3$ as solvent and $SiMe_4$ as internal reference; chemical shifts δ in ppm and coupling constants *J* in Hz; unequivocal ^{1}H assignments by 2D-COSY and NOESY experiments (mixing time 800 ms); ^{13}C assignments by 2D-HSQC and HMBC experiments (delay for long-range *J*(C,H) optimized for 7 Hz). MS and HR-MS: *VG AutoSpec-M* spectrometer; $CHCl_3$ as solvent and 3-nitrobenzyl alcohol (NBA) as matrix; in *m*/*z* (rel. %).

Reactions of Porphyrin Complexes **1a**–**c** *with EDA: General Procedure.* EDA (10 equiv.) was added dropwise by syringe during 7 h to a soln. of the porphyrin complex (50 mg) and the selected catalyst in

dry CH_2Cl_2 (6 ml) at 40° under N_2. The mixture was further stirred at 40° for 12 h. The solvent was then evaporated and the residue fractionated by FC (SiO_2), CH_2Cl_2/hexane in adequate proportions). The fractions obtained were purified by prep. TLC (AcOEt/1:4).

*[(2r,2^{1}t,3c)-2^1-(Ethoxycarbonyl)-5,10,15,20-tetraphenyl-2,3-dihydrocyclopropa[*b*]porphyrinato]zinc-(II)*[1]) (=*[Ethyl (1α,1aα,19aα)-1a,19a-Dihydro-3,8,13,18-tetraphenyl-1*H,*20*H,*22*H-*cyclopropa[*b*]porphine-1-carboxylato(2−)-*κN^{20},*κ*N^{21},*κ*N^{22},*κ*N^{23}]zinc*; **2a**). UV/VIS ($CHCl_3$): 420 (5.79), 524 (3.67), 518 (4.08), 585 (4.18), 617 (4.74). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 1.25–1.32 (*m*, *Me*CH_2, H−C(2^1)); 4.23 (*q*, *J* = 7.1, MeC*H*$_2$); 4.41 (*d*, *J* = 2.7, H−C(2), H−C(3)); 7.62–7.70 (*m*, 12 H, H$_m$ (Ph), H$_p$ (Ph)); 7.85–7.86 (*m*, 2 H$_o$ (Ph−C(5) and −C(20)); 8.03–8.05 (*m*, 2 H$_o$ (Ph−C(10) and −C(15)); 8.09–8.11 (*m*, 4 H$_o$ (Ph−C(5), −C(10), −C(15), and −C(20)); 8.32 (*d*, *J* = 4.6, H−C(7), H−C(18)); 8.45 (*s*, H−C(12), H−C(13)); 8.59 (*d*, *J* = 4.6, H−C(8), H−C(17)). ^{13}C-NMR (75.47 MHz, $CDCl_3$): 14.5 (*Me*CH_2); 22.0 (C(2^1)); 39.3 (C(2), C(3)); 61.1 (Me*C*H$_2$); 113.4, 124.9, 126.6, 127.37, 127.40, 127.5, 127.6 (C$_m$ (Ph), C$_p$ (Ph)); 128.0 (C(7), C(18)); 129.6 (C(12), C(13)); 132.6 (C$_o$ (Ph−C(5) and −C(20)); 133.5 (C(8), C(17)); 133.56 (C$_o$ (Ph−C(10) and −C(15)); 133.58 (C$_o$ (Ph−C(5), −C(10), −C(15), and −C(20)); 142.6, 146.8, 148.2, 153.7, 157.0 (C(α)); 173.7 (C=O). HR-ESI-MS: 762.1962 (*M*$^+$, $C_{48}H_{34}N_4O_2Zn^+$; calc. 762.1974).

*[(2r,2^{1}c,3c)-2^1-(Ethoxycarbonyl)-5,10,15,20-tetraphenyl-2,3-dihydrocyclopropa[*b*]porphyrinato]zinc-(II)*[1]) (=*[Ethyl (1α,1aβ,19aβ)-1a,19a-Dihydro-3,8,13,18-tetraphenyl-1*H,*20*H,*22*H-*cyclopropa[*b*]porphine-1-carboxylato(2−)-*κN^{20},*κ*N^{21},*κ*N^{22},*κ*N^{23}]zinc*; **3a**). UV/VIS ($CHCl_3$): 423 (5.32), 524 (3.67), 567 (3.67), 594 (3.87), 617 (4.31). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 0.88 (*t*, *J* = 7.1, *Me*CH_2); 2.62 (*t*, *J* = 8.2, H−C(2^1)); 3.52 (*q*, *J* = 7.1, MeC*H*$_2$); 4.47 (*d*, *J* = 8.2, H−C(2), H−C(3)); 7.63–7.67 (*m*, 12 H, H$_m$ (Ph), H$_p$ (Ph)); 7.90–7.93 (*m*, 2 H$_o$ (Ph−C(5) and −C(20)); 7.94–7.97 (*m*, 2 H$_o$ (Ph−C(5) and −C(20)); 8.06–8.12 (*m*, 4 H$_o$ (Ph−C(10) and −C(15)); 8.27 (*d*, *J* = 4.6, H−C(7), H−C(18)); 8.44 (*s*, H−C(12), H−C(13)); 8.55 (*d*, *J* = 4.6, H−C(8), H−C(17)). HR-ESI-MS: 762.1968 (*M*$^+$, $C_{48}H_{34}N_4O_2Zn^+$; calc. 762.1974).

{2-[(Ethoxycarbonyl)methyl]-5,10,15,20-tetraphenylporphyrinato}zinc(II) (=*[Ethyl 5,10,15,20-Tetraphenyl-21*H,*23*H-*porphine-2-acetato(2−)-*κN^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}]zinc*; **4a**). UV/VIS ($CHCl_3$): 419 (6.16), 511 (3.84), 548 (4.70), 583 (3.72). ^{1}H-NMR (300.13 MHz, $CDCl_3$): 1.25 (*t*, *J* = 7.1, *Me*CH_2); 3.97 (*s*, 2 H−C(2^1)); 4.12 (*q*, *J* = 7.1, MeC*H*$_2$); 7.67–7.78 (*m*, 12 H, H$_m$ (Ph), H$_p$ (Ph)); 8.05–8.08 (*m*, 2 H$_o$ (Ph−C(20)); 8.19–8.23 (*m*, 6 H$_o$ (Ph−C(5), −C(10), and −C(15)); 8.69 (*d*, *J* = 4.7, 1 H−C(β)); 8.79 (*s*, 1 H−C(3)); 8.87 (*d*, *J* = 4.7, 1 H−C(β)); 8.90–8.95 (*m*, 4 H−C(β)). ^{13}C-NMR (75.47 MHz, $CDCl_3$): 14.2 (*Me*CH_2); 29.7 (C(2^1)); 60.6 (Me*C*H$_2$); 121.1, 121.5, 126.5 (C$_m$ (Ph), C$_p$ (Ph)); 126.46, 126.53, 126.9 (C$_m$ (Ph), C$_p$ (Ph)); 128.1, 131.5, 131.9, 132.0, 132.5 (C(β)); 133.2 (C$_o$ (Ph−C(20)); 134.37, 134.40 (C$_o$ (Ph−C(5), −C(10), and −C(15)); 135.2 (C(3)); 138.0, 142.6, 142.7, 142.9, 148.2, 150.1, 150.2, 150.4, 151.0 (C(α); 172.3 (C=O). HR-ESI-MS: 762.1968 (M$^+$, $C_{48}H_{34}N_4O_2Zn^+$; calc. 762.1974).

{5-[5-(Ethoxycarbonyl)cyclohepta-1,3,6-trien-1-yl]-10,15,20-triphenylporphyrinato}zinc(II) (=*[Ethyl 4-(10,15,20-triphenyl-21*H,*23*H-*porphin-5-yl-*κN^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24})cyclohepta-2,4,6-triene-1-carboxylato(2−)]zinc*; **5a**). UV/VIS ($CHCl_3$): 420 (5.88), 483 (3.33), 510 (4.43), 547 (3.63), 584 (3.59). ^{1}H-NMR (500.13 MHz, $CDCl_3$; see *Fig. 2* for atom labels): 1.34 (*t*, *J* = 7.1, *Me*CH_2); 4.42 (*q*, *J* = 7.1, MeC*H*$_2$); 3.37 (*t*, *J* = 6.0, H$_d$); 5.53 (*ddd*, *J* = 9.1, 6.0, 1.5, H$_e$); 5.69 (*ddd*, *J* = 9.1, 6.0, 1.3, H$_c$); 6.77 (*dd*, *J* = 9.1, 6.0, H$_b$); 7.25–7.50 (*m*, H$_f$); 7.51 (*d*, *J* = 6.0, H$_a$); 7.72–7.77 (*m*, 9 H, H$_m$ (Ph), H$_p$ (Ph)); 8.20–8.22 (*m*, 6 H$_o$ (Ph)); 8.88–9.01 (*m*, 6 H−C(β)); 9.16 (*d*, *J* = 4.6, 1 H−C(β)); 9.39 (*d*, *J* = 4.6, 1 H−C(β)). HR-ESI-MS: 762.1968 (*M*$^+$, $C_{48}H_{34}N_4O_2Zn^+$; calc. 762.1974).

*[2^1,12^1-Bis(ethoxycarbonyl)-5,10,15,20-tetraphenyl-2,3,12,13-tetrahydrodicyclopropa[*b,l*]porphyrinato]zinc(II)* (=*[Diethyl 1a,9a,10a,18a-Tetrahydro-3,8,12,17-tetraphenyl-1*H,*10*H,*19*H,*21*H-*dicyclopropa[*b,l*]porphine-1,10-dicarboxylato(2−)-*κN^{19},*κ*N^{20},*κ*N^{21},*κ*N^{22}]zinc*; **6a**). UV/VIS ($CHCl_3$): 419 (100), 565 (9.0), 607 (13.7), 722 (20.1). HR-ESI-MS: 849.2414 ([*M* + H]$^+$, $C_{52}H_{41}N_4O_2Zn^+$; calc. 849.2419).

*[(2r,2^{1}t,3c)-2^1-(Ethoxycarbonyl)-5,10,15,20-tetrakis(3-methoxyphenyl)-2,3-dihydrocyclopropa[*b*]porphyrinato]zinc(II)*[1]) (=*[Ethyl (1α,1aα,19aα)-1a,19a-Dihydro-3,8,13,18-tetrakis(3-methoxyphenyl)-1*H,*20*H,*22*H-*cyclopropa[*b*]porphine-1-carboxylato(2−)-*κN^{20},*κ*N^{21},*κ*N^{22},*κ*N^{23}]zinc*; **2b**). UV/VIS ($CHCl_3$): 421 (5.46), 518 (3.85), 541 (3.75), 585 (3.93), 618 (4.48). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 1.24–1.30 (*m*, *Me*CH_2, H−C(2^1)); 3.91 (*s*, 3 MeO); 3.93 (*s*, 1 MeO); 4.15–4.26 (*m*, MeC*H*$_2$); 4.44 (*d*, *J* = 2.6, H−C(2), H−C(3)); 7.15–7.23 (*m*, 4 H$_p$ (Ar)); 7.38–7.71 (*m*, 12 H, H$_o$ (Ar), H$_m$ (Ar); 8.35–8.37 (*m*,

H–C(7), H–C(18)); 8.49 (*s*, H–C(12), H–C(13)); 8.63 (*d*, *J* = 4.6, H–C(8), H–C(17)). HR-ESI-MS: 882.2390 (M^+, $C_{52}H_{42}N_4O_6Zn^+$; calc. 882.2396).

*[(2*r*,2^1*c*,3*c*)-2^1-(Ethoxycarbonyl)-5,10,15,20-tetrakis(3-methoxyphenyl)-2,3-dihydrocyclopropa[*b*]porphyrinato]zinc(II)*[1]) (= *[Ethyl (1α,1aβ,19aβ)-1a,19a-Dihydro-3,8,13,18-tetrakis(3-methoxyphenyl)-1*H,*20*H,*22*H-*cyclopropa[*b*]porphine-1-carboxylato(2–)-κN^{20},κN^{21},κN^{22},κN^{23}]zinc*; **3b**). UV/VIS ($CHCl_3$): 423 (5.51), 521 (3.87), 567 (3.83), 593 (4.01), 617 (4.47). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 0.84–0.94 (*m*, *Me*CH_2); 2.64 (*t*, *J* = 8.2, H–C(2^1)); 3.90 (*s*, 4 MeO), 4.19 (*q*, *J* = 6.1, Me*C*H_2); 4.52 (*d*, *J* = 8.2, H–C(2), H–C(3)); 7.46–7.61 (*m*, 8 H, H_m (Ar), H_p (Ar)); 7.65–7.73 (*m*, 8 H_o (Ar)); 8.32 (*d*, *J* = 4.6, H–C(7), H–C(18)); 8.49 (*s*, H–C(12), H–C(13)); 8.60 (*d*, *J* = 4.6, H–C(8), H–C(17)). HR-ESI-MS: 882.2390 (M^+, $C_{52}H_{42}N_4O_6Zn^+$; calc. 882.2396).

{2-[(Ethoxycarbonyl)methyl]-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato}zinc(II) (= *[Ethyl 5,10,15,20-Tetrakis(3-methoxyphenyl)-21*H,*23*H-*porphine-2-acetato(2–)-κN^{21},κN^{22},κN^{23},κN^{24}]zinc*; **4b**). UV/VIS ($CHCl_3$): 420 (5.79), 484 (3.32), 510 (3.47), 547 (4.36), 583 (3.37). ^{1}H-NMR (300.13 MHz, $CDCl_3$): 1.26 (*t*, *J* = 7.1, *Me*CH_2); 3.92 (*s*, 1 MeO), 3.95–3.96 (*m*, 3 MeO), 4.06 (*s*, H–C(2^1)); 4.15 (*q*, *J* = 7.1, Me*C*H_2); 4.17 (*q*, *J* = 7.13, Me*C*H_2); 7.29–7.35 (*m*, 4 H, H_p (Ar)); 7.58–7.83 (*m*, 12 H, H_o (Ar), H_m (Ar)); 8.77 (*d*, *J* = 4.6, 1 H–C(*β*)); 8.86 (*s*, H–C(3)); 8.92 (*d*, *J* = 4.6, 1 H–C(*β*)); 8.95–8.99 (*m*, 4 H–C(*β*)). HR-ESI-MS: 882.2390 (M^+, $C_{52}H_{42}N_4O_6Zn^+$; calc. 882.2396).

{5-[5-(Ethoxycarbonyl)-3-methoxycyclohepta-1,3,6-trien-1-yl]-10,15,20-tris(3-methoxyphenyl)porphyrinato}zinc(II) (= *{Ethyl 3-Methoxy-5-[10,15,20-tris(3-methoxyphenyl)-21*H,*23*H-*porphin-5-yl-κN^{21},κN^{22},κN^{23},κN^{24}]cyclohepta-2,4,6-triene-1-carboxylato(2–)}zinc*; **5b**). UV/VIS ($CHCl_3$): 421 (5.69), 484 (3.29), 510 (4.48), 548 (4.32), 584 (3.45). ^{1}H-NMR (500.13 MHz, $CDCl_3$; see *Fig. 2* for atom labels): 1.42 (*t*, *J* = 7.1, *Me*CH_2); 3.88 (*s*, 1 MeO); 4.13 (*d*, *J* = 7.5, H_b); 4.46 (*q*, *J* = 7.1, Me*C*H_2); 6.04 (*dd*, *J* = 9.7, 7.5, H_c); 6.56 (*s*, H_a); 6.78 (*dd*, *J* = 9.7, 5.5, H_d); 7.19 (*d*, *J* = 5.5, H_e); 7.63 (*s*, 3 H_p (Ar)); 7.76–7.81 (*m*, 9 H, H_o (Ar), H_m (Ar)); 8.91–9.01 (*m*, 6 H–C(*β*)); 9.28 (*d*, *J* = 4.6, 1 H–C(*β*)); 9.43 (*d*, *J* = 4.6, 1 H–C(*β*)). HR-ESI-MS: 882.2390 (M^+, $C_{52}H_{42}N_4O_6Zn^+$; calc. 882.2396).

*[2^1,12^1-Bis(ethoxycarbonyl)-5,10,15,20-tetrakis(3-methoxyphenyl)-2,3,12,13-tetrahydrodicyclopropa[*b*,*l*]porphyrinato]zinc(II)* (= *{Diethyl 1a,9a,10a,18a-Tetrahydro-3,8,12,17-tetrakis(3-methoxyphenyl)-1*H,*10*H,*19*H,*21*H-*dicyclopropa[*b*,*l*]porphine-1,10-dicarboxylato(2–)-κN^{19},κN^{20},κN^{21},κN^{22}]zinc*; **6b**). UV/VIS ($CHCl_3$): 425 (100) 562 (7.4), 605 (10.9), 718 (12.9). HR-ESI-MS: 969.2836 ($[M+H]^+$, $C_{56}H_{49}N_4O_8Zn^+$; calc. 969.2764).

*[(2*r*,2^1*t*,3*c*)-2^1-(Ethoxycarbonyl)-5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydrocyclopropa[*b*]porphyrinato]zinc(II)*[1]) (= *[Ethyl (1α,1aα,19aα)-1a,19a-Dihydro-3,8,13,18-tetrakis(2,3,4,5,6-pentafluorophenyl)-1*H,*20*H,*22*H-*cyclopropa[*b*]porphine-1-carboxylato(2–)-κN^{20},κN^{21},κN^{22},κN^{23}]zinc*; **2c**). UV/VIS ($CHCl_3$): 415 (5.57), 453 (3.06), 516 (3.90), 575 (3.89), 621 (4.88). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 1.33 (*t*, *J* = 7.1, *Me*CH_2); 1.47 (*t*, *J* = 2.7, H–C(2^1)); 4.31 (*q*, *J* = 7.1, Me*C*H_2); 4.37 (*d*, *J* = 2.7, H–C(2), H–C(3)); 8.32 (*d*, *J* = 4.6, H–C(7), H–C(18)); 8.49 (*s*, H–C(12), H–C(13)); 8.61 (*d*, *J* = 4.6, H–C(8), H–C(17)). ^{19}F-NMR (282.38 MHz, $CDCl_3$): –160.79 to –160.88 (*m*, 4 F_o); –160.99 to –161.07 (*m*, 2 F_o); –162.05 to –162.17 (*m*, 2 F_o); –175.58 (*t*, *J* = 19.8, F_p); –175.82 (*t*, *J* = 19.8, 2 F_p); –184.43 to –185.37 (*m*, 2 F_m); –185.19 to –185.37 (*m*, 6 F_m). HR-ESI-MS: 1123.0162 ($[M+H]^+$, $C_{48}H_{15}F_{20}N_4O_2Zn^+$; calc. 1123.0167).

*[(2*r*,2^1*c*,3*c*)-2^1-(Ethoxycarbonyl)-5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydrocyclopropa[*b*]porphyrinato]zinc(II)*[1]) (= *[Ethyl (1α,1aβ,19aβ)-1a,19a-Dihydro-3,8,13,18-tetrakis(2,3,4,5,6-pentafluorophenyl)-1*H,*20*H,*22*H-*cyclopropa[*b*]porphine-1-carboxylato(2–)-κN^{20},κN^{21},κN^{22},κN^{23}]zinc*; **3c**). UV/VIS ($CHCl_3$): 410 (100), 513 (2.5), 566 (8.3), 616 (17.0). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 0.92 (*t*, *J* = 7.1, *Me*CH_2); 2.52 (*t*, *J* = 8.2, H–C(2^1)); 3.69 (*q*, *J* = 7.1, Me*C*H_2); 4.02 (*d*, *J* = 8.2, H–C(2), H–C(3)); 7.99 (*d*, *J* = 4.6, H–C(7), H–C(18)); 8.28 (*s*, H–C(12), H–C(13)); 8.51 (*d*, *J* = 4.6, H–C(8), H–C(17)). ^{19}F-NMR (282.38 MHz, $CDCl_3$): –160.46 to –161.12 (*m*, F_o); –162.65 to –162.98 (*m*, 2 F_o); –175.73 to –175.85 (*m*, 1 F_p); –176.20 to –176.45 (*m*, 2 F_p); –176.63 to –176.90 (*m*, 1 F_p); –184.543 to –185.15 (*m*, 5 F_m); –185.50 to –185.98 (*m*, 3 F_m). HR-ESI-MS: 1123.0160 ($[M+H]^+$, $C_{48}H_{15}F_{20}N_4O_2Zn^+$; calc. 1123.0167).

{2-[(Ethoxycarbonyl)methyl]-5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato}zinc(II) (= *[Ethyl 5,10,15,20-Tetrakis(2,3,4,5,6-pentafluorophenyl)-21*H,*23*H-*porphine-2-acetato(2–)-κN^{21},κN^{22},κN^{23},κN^{24}]zinc*; **4c**). UV/VIS ($CHCl_3$): 415 (5.73), 545 (4.39), 579 (3.87), 623 (3.14). ^{1}H-NMR

(300.13 MHz, $CDCl_3$): 1.22 (*t*, *J* = 7.1, *Me*CH_2); 4.16 (*q*, *J* = 7.1, MeCH_2); 4.30 (*s*, 2 H–C(2^1)); 8.77 (*d*, *J* = 4.6, 1 H–C(*β*)); 8.89 (*s*, H–C(3)); 8.92 (*d*, *J* = 4.6, 1 H–C(*β*)); 8.95–8.99 (*m*, 4 H–C(*β*)). ^{19}F-NMR (282.38 MHz, $CDCl_3$): –159.32 to –159.43 (*m*, 2 F_o (Ar–C(5) or –C(20)); –160.08 to –160.11 (*m*, 2 F_o (Ar–C(5) or –C(20)); –160.27 to –160.42 (*m*, 4 F_o (Ar–C(10) and –C(15)); –174.80 (*t*, *J* = 19.7, 1 F_p (Ar–C(20)); –175.39 to –175.64 (*m*, 3 F_p (Ar–C(5), –C(10), and –C(15)); –184.54 to –184.74 (*m*, 2 F_m (Ar–C(20)); –185.19 to –185.34 (*m*, 6 F_m (Ar–C(5), –C(10), and –C(15)). HR-ESI-MS: 1123.0162 ($[M+H]^+$, $C_{48}H_{15}F_{20}N_4O_2Zn^+$; calc. 1123.0167).

*[2^1,12^1-Bis(ethoxycarbonyl)-5,10,15,20-tetrakis(pentafluorophenyl)-2,3,12,13-tetrahydrodicyclopropa[*b,l*]porphyrinato]zinc(II)* (=*{Diethyl 1a,9a,10a,18a-Tetrahydro-3,8,12,17-tetrakis(2,3,4,5,6-pentafluorophenyl)-1*H,*10*H,*19*H,*21*H-*dicyclopropa[*b,l*]porphine-1,10-dicarboxylato(2–)-*κN^{19},*κN^{20},*κN^{21},*κN^{22}}zinc*; **6c**). UV/VIS ($CHCl_3$): 368 (57.9), 410 (100), 554 (10.4), 606 (3.4), 729 (59.2). HR-ESI-MS: 1209.0529 ($[M+H]^+$, $C_{52}H_{21}F_{20}N_4O_4Zn^+$; calc. 1209.0535).

*[2^1,7^1-Bis(ethoxycarbonyl)-5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8-tetrahydrodicyclopropa-[*b,g*]porphyrinato]zinc(II)* (=*{Diethyl 1a,4a,5a,18a-Tetrahydro-3,7,12,17-tetrakis(2,3,4,5,6-pentafluorophenyl)-1*H,*5*H,*19*H,*21*H-*dicyclopropa[*b,g*]porphine-1,5-dicarboxylato(2–)-*κN^{19},*κN^{20},*κN^{21},*κN^{22}}zinc*; **7c**). Compound **7c** is a 2:1 diastereoisomeric mixture of isobacteriochlorins **7c1** and **7c2**, resp. (see *Fig. 1*). UV/VIS ($CHCl_3$): 410 (5.25), 490 (3.55), 565 (4.30), 605 (4.80). ^{1}H-NMR (500.13 MHz, $CDCl_3$; see *Fig. 1*): 1.29 (*t*, *J* = 7.2, *Me*CH_2 (**7c1**); 1.30 (*t*, *J* = 7.0, *Me*CH_2 (**7c2**); 1.32–1.40 (*m*, H–C(2^1) and H–C(7^1) (**7c2**)); 1.44 (*d*, *J* = 2.6, H–C(2^1) and H–C(7^1) (**7c1**)); 3.87, 3.95 (2*d*, *J* = 2.9, H–C(2) and H–C(8) or H–C(3) and H–C(7) (**7c2**)); 3.89 (*d*, *J* = 2.6, H–C(2), H–C(3), H–C(7), and H–C(8) (**7c1**)); 3.86, 3.94 (2*d*, *J* = 2.6, H–C(3) and H–C(7) or H–C(2) and H–C(8) (**7c2**)); 4.22–4.28 (*m*, 4 MeCH_2 (**7c1**/**7c2**)); 7.60, 7.97 (2*d*, *J* = 4.3, 4 H–C(*β*) (**7c2**)); 7.62, 7.99 (2*d*, *J* = 4.4, 4 H–C(*β*) (**7c1**)). ^{13}C-NMR (75.47 MHz, $CDCl_3$): 14.1 (Me); 29.4, 29.7, 30.7, 35.6, 36.7, 37.1, 61.76, 61.82, 65.3, 106.7, 115.7, 123.5, 130.1, 139.0, 143.0, 151.2, 154.8, 166.7, 172.5, 172.6; 216.8 (C=O). ^{19}F-NMR (282.38 MHz, $CDCl_3$): –161.01 to –161.12 (*m*, 3 F, F_o); –161.24 to –161.53 (*m*, 2 F, F_o); –161.49 to –161.62 (*m*, 3 F, F_o); –162.44 to –162.64 (*m*, 4 F, F_o); –163.00 to –163.11 (*m*, 2 F, F_o); –174.98 (*t*, *J* = 19.8, 2 F, F_p); –176.03 (*t*, *J* = 22.5, 4 F, F_p); –176.38 (*t*, *J* = 19.8, 2 F, F_p); –182.85 to –183.04 (*m*, 2 F, F_m (A–C(5)); –184.45 to –184.82 (*m*, 6 F, F_m); –185.09 to –185.39 (*m*, 10 F, F_m). HR-ESI-MS: 1209.0529 ($[M+H]^+$, $C_{52}H_{21}F_{20}N_4O_4Zn^+$; calc. 1209.0457).

REFERENCES

[1] R. Bonnett, in 'Chemical Aspects of Photodynamic Therapy', Gordon and Breach Science Publishers, London, 2000, p. 177; R. K. Pandey, G. Zheng, K. M. Kadish, 'Porphyrins as Photosensitizers in Photodynamic Therapy', in 'The Porphyrin Handbook', Eds. K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, Vol. 6; J. G. Moser in 'Photodynamic Tumour Therapy – 2nd and 3rd Generation Photosensitizers', Harwood Academic Publishers, Amsterdam, 1998; R. Bonnett, *Chem. Soc. Rev.* **1995**, *24*, 19; E. D. Sternberg, D. Dolphin, C. Brückner, *Tetrahedron* **1998**, *54*, 4151.

[2] A. C. Tomé, P. S. S. Lacerda, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *Chem. Commun*. **1997**, 1199; A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *Tetrahedron Lett*. **2000**, *41*, 3065; S. Zhao, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, M. R. M. Domingues, A. J. Ferrer Correia, *Tetrahedron Lett*. **2005**, *46*, 2189; A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, J. A. S. Cavaleiro, C. O. Kappe, *Tetrahedron Lett*. **2005**, *46*, 4723.

[3] A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, A. M. S. Silva, J. A. S. Cavaleiro, *Chem. Commun*. **1999**, 1767; A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, A. M. S. Silva, J. A. S. Cavaleiro, D. Perrone, A. Dondoni, *Tetrahedron Lett*. **2002**, *43*, 603; A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *Synlett* **2002**, 1155; A. M. G. Silva, A. C. Tomé, M. G. P. M. S. Neves, A. M. S. Silva, J. A. S. Cavaleiro, *J. Org. Chem*. **2005**, *70*, 2306.

[4] J. Flemming, D. Dolphin, *Tetrahedron Lett.* **2002**, *43*, 7281; A. Desjardins, J. Flemming, E. D. Sternberg, D. Dolphin, *Chem. Commun.* **2002**, 2622; X. Li, J. Zhuang, Y. Li, H. Liu, S. Wang, D. Zhu, *Tetrahedron Lett*. **2005**, *46*, 1555.

[5] A. M. G. Silva, M. A. F. Faustino, A. C. Tomé, M. G. P. M. S. Neves, A. M. S. Silva, J. A. S. Cavaleiro, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2752; A. M. G. Silva, K. T. Oliveira, M. A. F. Faustino, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, P. Brandão, V. Félix, *Eur. J. Org. Chem*. **2008**, 704.
[6] H. J. Callot, *Tetrahedron Lett*. **1972**, *13*, 1011; H. J. Callot, *Bull. Soc. Chim. Fr.* **1972**, 4387.
[7] K. M. Lydon, M. A. McKervey, E. N. Jacobsen, in 'Comprehensive Asymmetric Catalysis', Eds. A. Pfaltz and H. Yamamoto, Springer, Berlin, 1999, Vol. II, p. 540; A. Pfaltz, E. N. Jacobsen, in 'Comprehensive Asymmetric Catalysis', Eds. A. Pfaltz and H. Yamamoto, Springer, Berlin, 1999, Vol. II, p. 513; A. B. Charette, H. Lebel, E. N. Jacobsen, in 'Comprehensive Asymmetric Catalysis', Eds. A. Pfaltz and H. Yamamoto, Springer, Berlin, 1999, Vol. II, p. 581.
[8] V. F. Ferreira, *Curr. Org. Chem.* **2007**, *11*, 177.
[9] a) P. Tagliatesta, A. Pastorini, *J. Mol. Catal. A* **2003**, *198*, 57; b) A. Penoni, R. Wanke, S. Tollari, E. Gallo, D. Musella, F. Ragaini, F. Demartin, S. Cenini, *Eur. J. Inorg. Chem.* **2003**, 1452; c) Y. Chen, L. Huang, M. A. Ranade, X. P. Zhang, *J. Org. Chem.* **2003**, *68*, 3714; d) L. Zhang, K. S. Chan, *Organometallics* **2007**, *26*, 679; e) G.-Y. Li, J. Zhang, P. W. H. Chan, Z.-J. Xu, N. Zhu, C.-M. Che, *Organometallics* **2006**, *25*, 1676; f) L. K. Baumann, H. M. Mbuvi, G. Du, L. K. Woo, *Organometallics* **2007**, *26*, 3995.
[10] L. Latos-Grazynski, R.-J. Cheng, G. N. La Mar, A. L. Balch, *J. Am. Chem. Soc.* **1981**, *103*, 4270.
[11] H. Zollinger, in 'Diazo Chemistry II – Aliphatic, Inorganic and Organometallic Compounds', VCH Publishers, New York, 1995.
[12] M. P. Doyle, *Chem. Rev.* **1986**, *86*, 919.
[13] V. F. Ferreira, L. O. R. Pereira, M. C. B. V. Souza, A. C. Cunha, *Quim. Nova* **2001**, *24*, 540.
[14] F. M. Wong, J. Wang, A. C. Hengge, W. Wu, *Org. Lett*. **2007**, *9*, 1663.
[15] J. J. Li, in 'Name Reactions – A Collection of Detailed Reaction Mechanisms', 3rd edn., Springer-Verlag, Berlin, 2006, p. 96.
[16] J.-H. Fuhrhop, in 'Porphyrins and Metalloporphyrins', Ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 798.
[17] A. D. Adler, F. R. Longo, V. Varadi, *Inorg. Synth*. **1976**, *16*, 213.

Received May 16, 2008