Meso-substituted Corroles from Nitrosoalkenes and Dipyrromethanes

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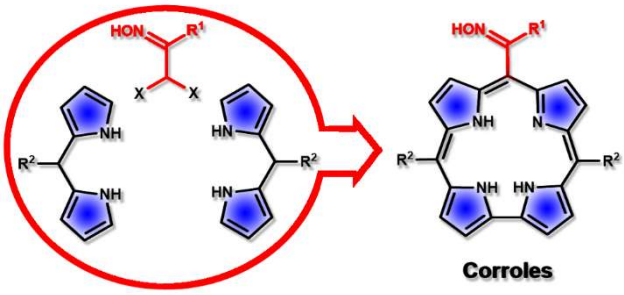


ABSTRACT

The synthesis of bilanes and hexapyrroles containing an oxime functionality, prepared by two and three consecutive hetero-Diels-Alder reactions (or conjugated additions) between nitrosoalkenes and dipyrromethanes, is described. Bilanes underwent oxidative macrocyclization to afford a new class of *trans*-A_2B-corroles. Porphyrins could also be obtained by reacting bilanes with aldehydes in presence of TFA followed by an oxidative step.

INTRODUCTION

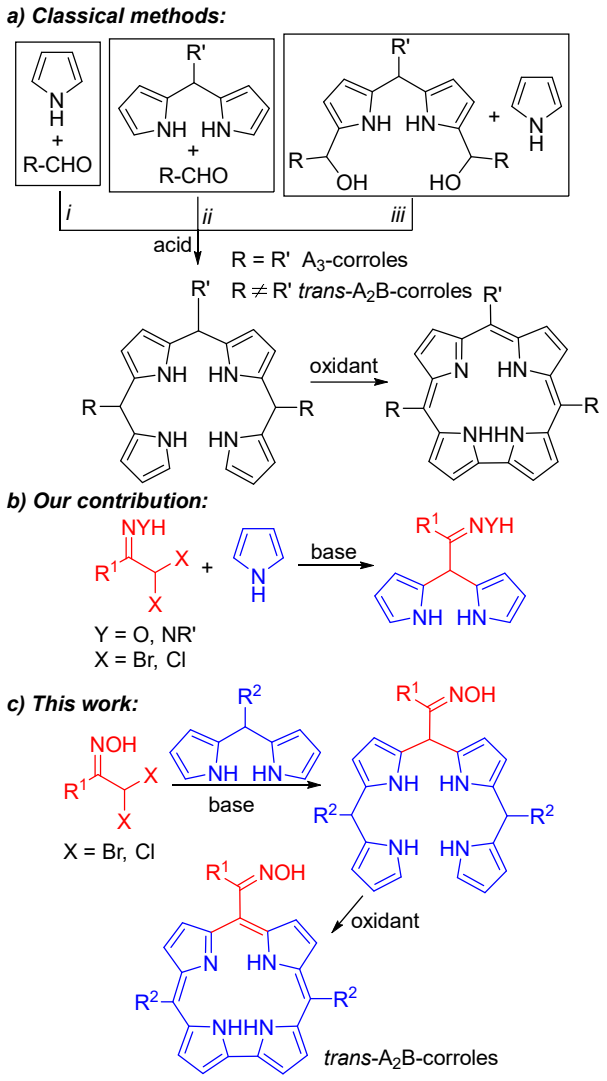
Corroles are a class of contracted porphyrinoids with a direct pyrrole-pyrrole link, trianionic character as ligand and high electron density.[1] The structural, spectroscopic and photophysical properties of free base corroles and their metal complexes[2] make them ideal compounds for numerous applications,[3] namely in catalysis,[4] as chemical sensors,[5] dye sensitized solar cells[6] and in photodynamic therapy.[7] The synthesis of *meso*-substituted corroles have been widely explored, however the most used synthetic strategy involves the formation of bilanes followed by oxidation (Scheme 1a). On the other hand, the most common methods to prepare tetrapyrrolic open-chain compounds are based on

the reaction of aldehydes with pyrrole (*i*) or with dipyrromethanes (*ii*) or the acid catalyzed reaction of dipyrromethane-diols with pyrrole (*iii*).[8]

In the last decade, our research group have been interested in the reactivity of nitrosoalkenes and azoalkenes which has been applied in the functionalization and synthesis of heterocycles.[9] The assembly of heterocyclic systems using the chemistry of these heterodienes included one-pot synthetic approaches to bis(heterocycle)methanes bearing an oxime or hydrazone functionality. Dehydrohalogenation of α,α-dihalo-oximes and α,α-dihalo-hydrazones in presence of pyrrole,[9d] indole[9e,f] and pyrazole[9g] afforded dipyrromethanes, bis(indolyl)methanes and bis(pyrazol-1-yl)methanes, respectively, via two consecutive hetero-Diels-Alder reactions or conjugated additions of the *in situ* generated nitrosoalkenes and azoalkenes.

Having developed a route to *meso*-substituted dipyrromethanes (Scheme 1b)[9d] we envisaged that the replacement of pyrrole by dipyrromethanes (DP) would lead to an approach to tetrapyrrolic compounds. In a preliminary study, we reported the bis(hetero-Diels–Alder) reaction of azoalkenes with 5,5-diethyldipyrromethane affording calix[4]pyrroles and bilanes.[9h]

Herein, a novel approach to *trans*-A_2B-corroles based on the reactivity of nitrosoalkenes towards dipyrromethanes is disclosed (Scheme 1c). The synthetic strategy comprises the synthesis of bilanes from α,α-dihalo-oximes and dipyrromethanes followed by oxidative macrocyclization to give the target tetrapyrrolic macrocycles.



Scheme 1. Synthetic approaches to dipyrromethanes, bilanes and corroles.

RESULTS AND DISCUSSION

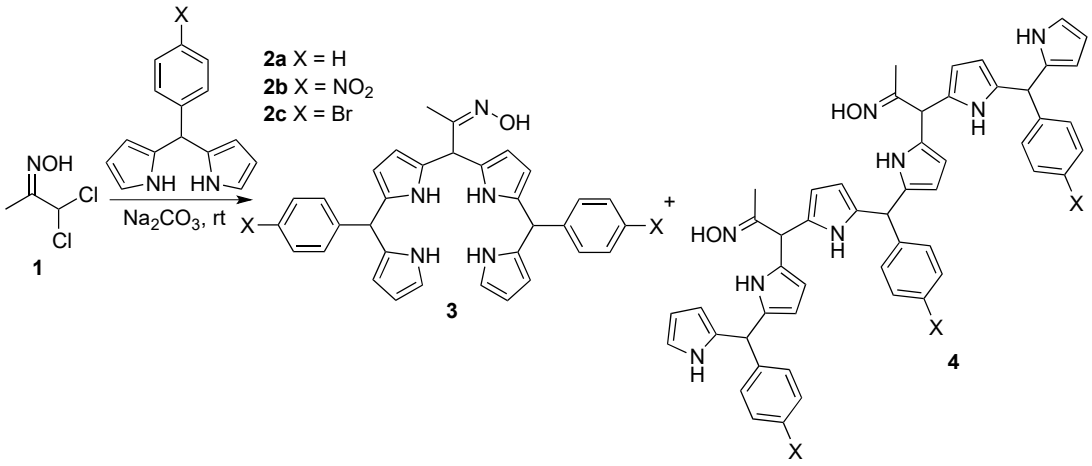
Initially, the reaction of a 1-methylnitrosoethylene, generated *in situ* from the 1,1-dichloropropan-2-one oxime (**1**) by the action of sodium carbonate, with dipyrromethane **2a** was explored (Table 1). The reaction carried out with 1:2 oxime/DP ratio in the solvent system H_2O/CH_2Cl_2 (85/15) for 20 min led to bilane **3a** in 11% yield, together with the formation of the hexapyrrole **4a** isolated in low yield (Entry 1). Usually, the use of an excess of dienophile/nucleophile leads to higher yields since it minimizes nitrosoalkene self-condensation reactions. In fact, the reaction using 1:2.5, 1:3 and 1:4 oxime/DP **2a** ratio gave bilane **3a** in 13%, 16% and 27% yield, respectively (Entries 2-4). However, in

the case of hexapyrrole **4a** only when 1:4 oxime/DP **2a** ratio was used an improvement of the yield to 13 % was observed (Entry 4).

On-water reactions are particularly interesting not only in the context of the development of more sustainable methodology but because they can also lead to different reactivities and selectivities.[10] In fact, we have previously demonstrated that reactions of nitrosoalkenes with pyrrole and indoles are faster and give higher or comparable yields using water as solvent than carrying out the reaction in dichloromethane although in some cases the use of a co-solvent was required.[9b, 9d-f] The effect of the reaction medium on the rate of the reaction was also observed in the reaction of α,α-dichloro-oxime **1** with dipyrromethane **2a**. Thus, the reaction carried out in dichloromethane was significantly slower than using H_2O/CH_2Cl_2 (17 h vs. 20 min), giving the target compounds **3a** and **4a** in 30% overall yield (Entries 4-5).

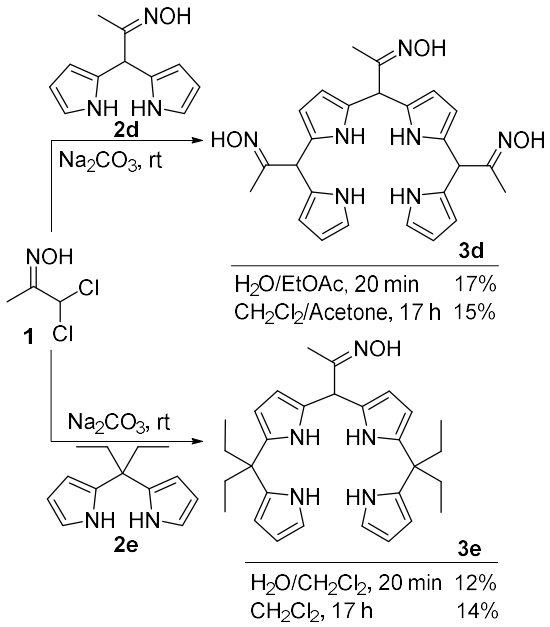
The optimized reaction conditions were applied to the reaction of α,α-dichloro-oxime **1** with other *meso*-aryl substituted dipyrromethanes (Table 1). Thus, bilane **3b** was obtained in 24% yield together with hexapyrrole **4b** (13%) using H_2O as solvent (Entry 6). In this case, ethyl acetate was used as co-solvent instead of dichloromethane due the low solubility of dipyrromethane **2b** in the latter. As expected, the reaction carried out in dichloromethane required longer reaction time leading to compounds **3b** and **4b** in 34% overall yield (Entry 7). α,α-Dichloro-oxime **1** reacted with dipyrromethane **2c** in water/dichloromethane to give, in only 20 minutes, the expected bilane **3c** and hexapyrrole **4c** in 25% overall yield (Entry 8). The same products were obtained in similar overall yield (24%) using dichloromethane as solvent, despite the long reaction time (Entry 9). Oximes **3** were obtained as single stereoisomers. The geometry of the oxime functionality, having the hydroxy and methyl groups *trans*, was assigned on the basis of two-dimensional NOESY spectra (400 MHz) where no connectivity was observed between protons of these groups.

Table 1. Reactivity of α,α-dichloro-oxime **1** toward *meso*-aryl-dipyrromethanes **2**.



entry	oxime/DP ratio	reaction conditions	3	4
1	**1/2a** (1:2)	H_2O/CH_2Cl_2, 20 min	**3a** 11%	**4a** 8%
2	**1/2a** (1:2.5)	H_2O/CH_2Cl_2, 20 min	**3a** 13%	**4a** 8%
3	**1/2a** (1:3)	H_2O/CH_2Cl_2, 20 min	**3a** 16%	**4a** 8%
4	**1/2a** (1:4)	H_2O/CH_2Cl_2, 20 min	**3a** 27%	**4a** 13%
5	**1/2a** (1:4)	CH_2Cl_2, 17 h	**3a** 22%	**4a** 8%
6	**1/2b** (1:4)	H_2O/EtOAc, 20 min	**3b** 24%	**4b** 13%
7	**1/2b** (1:4)	CH_2Cl_2, 17 h	**3b** 23%	**4b** 11%
8	**1/2c** (1:4)	H_2O/CH_2Cl_2, 20 min	**3c** 16%	**4c** 9%
9	**1/2c** (1:4)	CH_2Cl_2, 17 h	**3c** 16%	**4c** 8%

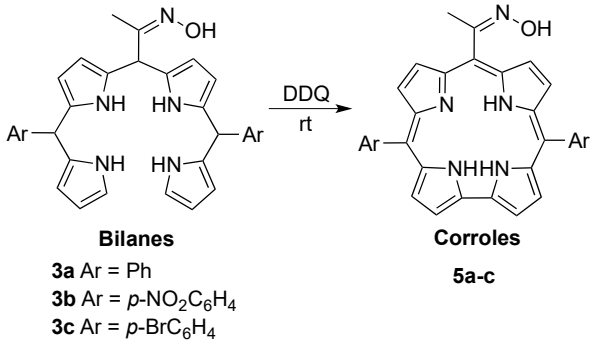
Bilanes were also prepared from the reaction of dipyrromethanes **2d** and **2e** with α,α-dichloro-oxime **1** (Scheme 2). We were pleased to observe that dipyrromethane **2d**,[9d] synthesized by our bis(hetero-Diels-Alder) reaction approach of nitrosoalkenes and pyrrole, afforded bilane **3d** bearing three oxime moieties. The reaction performed in aqueous media required the use of ethyl acetate as co-solvent, due to the low solubility of dipyrromethane **2d** in dichloromethane. Under these conditions, bilane **3d** was isolated in 17% yield, again with a very short reaction time (20 min). In order to carry out the reaction in organic media a mixture of dichloromethane/acetone (1:1) was needed to obtain a homogeneous solution yielding bilane **3d** (15%) after 17 h of reaction time. Bilane **3e** was also obtained from the reaction of oxime **1** with 5,5'-diethyldipyrromethane (**2e**), either using water/dichloromethane as solvent system (12%) or carrying out the reaction in dichloromethane (14%).



Scheme 2. Synthesis of bilanes from α,α-dichloro-oxime **1** and dipyrromethanes.

The oxidative macrocyclization of bilanes **3a-c** to the corresponding corroles was explored (Table 2). Thus, treatment of bilane **3a** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), in toluene at room temperature for 1 h, gave corrole **5a** in moderate yield (Entry 1). Increasing the reaction time to 2 and 3 h led to the isolation of corrole **5a** in 52% and 56% yield, respectively (Entries 2 and 3). Corrole **5a** was obtained in a similar yield when the reaction was left at room temperature overnight (Entry 4). However, the yield increased to 70% carrying the reaction in tetrahydrofuran (THF) for 3 h (Entry 5). Corrole **5a** was also formed using *p*-chloranil as oxidant, however all attempts to obtain the product in pure form were unsuccessful. The optimized reaction conditions, using DDQ, allowed the conversion of bilanes **3b** and **3c** into the corresponding tetrapyrrolic macrocycles **5b** and **5c** in 84% and 40% yield, respectively (Entries 6 and 7).

Table 2. Synthesis of corroles via oxidative macrocyclization of bilanes **3a-c**.

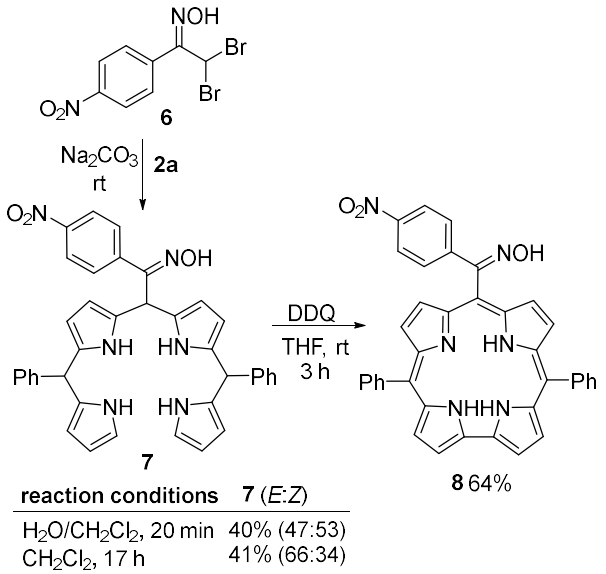


entry	bilane	reaction conditions[a]	corrole
1	**3a**	toluene, 1 h	**5a** 43%
2	**3a**	toluene, 2 h	**5a** 52%
3	**3a**	toluene, 3 h	**5a** 56%
4	**3a**	toluene, overnight	**5a** 55%
5	**3a**	THF, 3 h	**5a** 70%
6	**3b**	THF, 3 h	**5b** 84%
7	**3c**	THF, 3 h	**5c** 40%

[a]Concentration: 5 x 10^{-3} M.

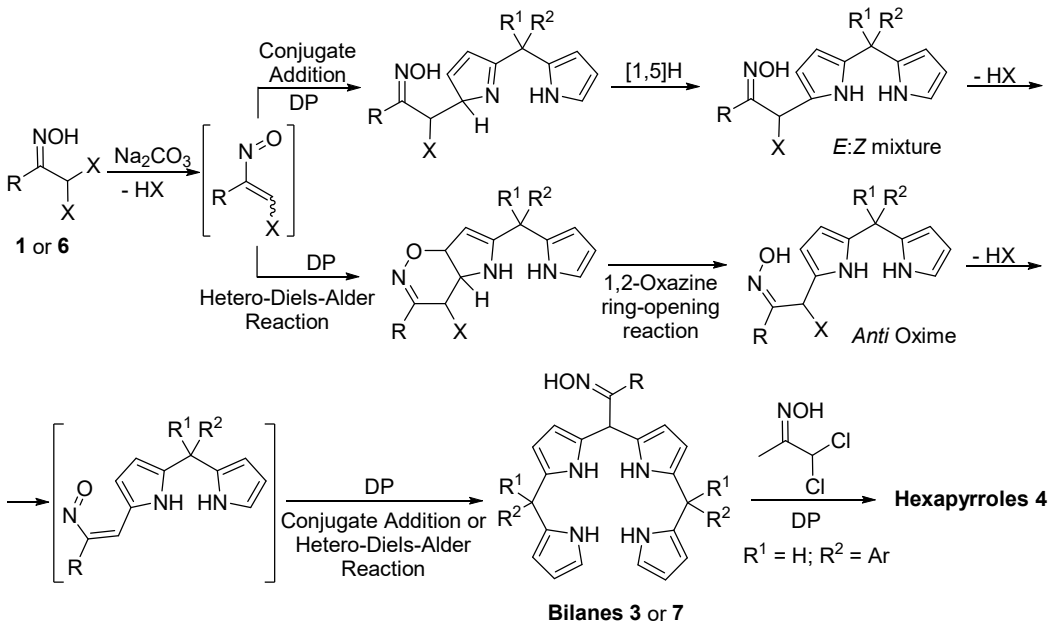
The reactivity of 2,2-dibromo-1-(4-nitrophenyl)ethanone oxime (**6**), precursor of a 1-(4-nitrophenyl)nitrosoethylene, toward dipyrromethane **2a** was also studied (Scheme 3). Dehydro-halogenation of α,α-dibromo-oxime **6** in the presence of dipyrromethane **2a** afforded bilanes **7** in 40% using H_2O/CH_2Cl_2 solvent system and 41% yield carrying out the reaction in dichloromethane. In both cases, the products were isolated as a mixture of *E* and *Z* isomeric oximes. Based on ^{1}H NMR data of other isomeric oximes,[11,12] including 1-(2'-hydroxyiminoethyl)-dipyrromethanes and *meso*-(hydroxyiminomethyl)-dipyrromethanes,[9d,12] the configuration of the oxime group could be assigned. In the ^{1}H NMR spectrum, the *meso* proton of bilane bearing a *Z-oxime* appears at lower chemical shift than the value observed for the derivative with the *E*-oxime. Bilanes **7** were efficiently converted into corrole **8** using DDQ as oxidant (64% yield).

It has been previously observed that the chemical behavior of nitrosoalkenes toward pyrrole and dipyrromethanes is strongly dependent on the nature of the 3- and/or 4-substituents.[9a,9d,12,13] In fact, conjugated nitrosoalkenes bearing a tetrazolyl, ester or phosphinyl group react with pyrrole via hetero-Diels−Alder reaction whereas 1-arylnitrosoethylenes react through conjugate addition affording two isomeric oximes. Interestingly, an easy and unambiguous way to determine the mechanism pathway is the outcome of the reaction regarding the selectivity of the oxime formation, single stereoisomer *vs E*/*Z* mixtures. We observed that in the synthesis of bilanes starting from α,α-dihalo-oxime **1**, precursor of 1-methylnitrosoethylenes, products were obtained as single oximes (Table 1 and Scheme 2) but the reaction of *meso*-phenyldipyrromethane with aryloxime **6** afforded a mixture of isomeric oximes (Scheme 3).



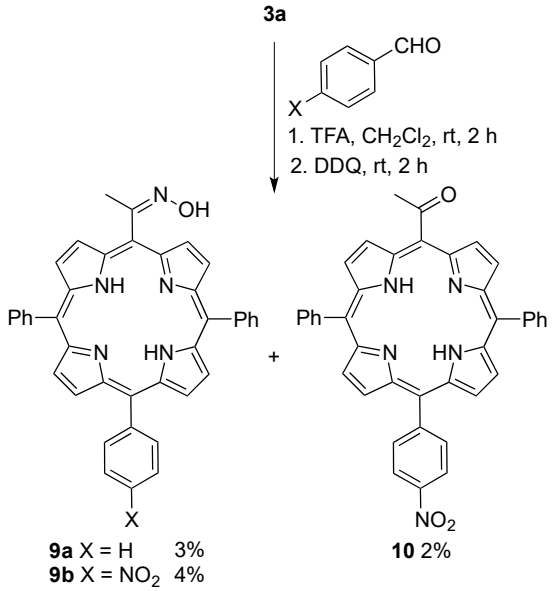
Scheme 3. Synthesis of 10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]corrole **8**.

In this context, the mechanism for the synthesis of bilanes and hexapyrroles from nitrosoalkenes and dipyrromethanes is as outlined in Scheme 4. Dehydro-halogenation of the starting oxime in presence of sodium carbonate generates the transient α-chloro-nitrosoalkene which reacts with the first molecule of the appropriate dipyrromethane either via hetero-Diels-Alder reaction or conjugated addition to give the corresponding alkylated dipyrromethane. The side-chain of this functionalized DP can undergo another dehydro-halogenation to afford a new nitrosoalkene which reacts with the second molecule of dipyrromethane to give the expected bilanes. From the outcome of this second alkylation reaction it is possible to conclude that 1-methylnitrosoethylene derivatives participated in the cycloaddition reaction to give bilanes **3** whereas 1-(*p*-nitrophenyl)nitrosoethylene underwent conjugated addition followed by [1,5]hydrogen shift to give bilanes **7**. The synthesis of hexapyrroles results from two consecutive hetero-Diels-Alder reactions, cycloaddition of bilanes **3a**-**3c** with the nitrosoalkene generated *in situ* from oxime **1**, generation of a second nitrosoalkene which was intercepted by a third molecule of dipyrromethane.



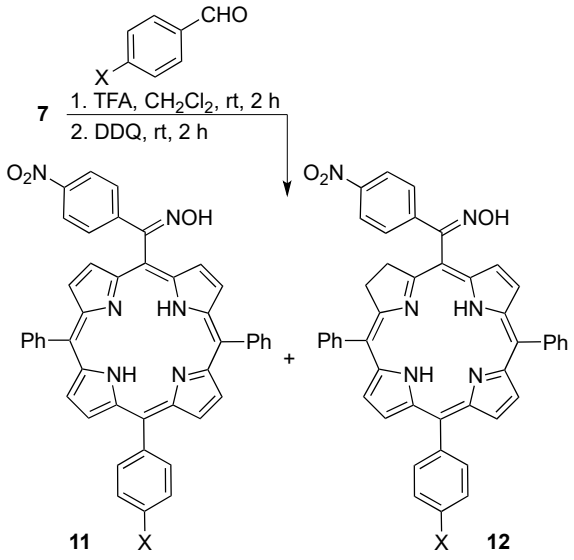
Scheme 4. Mechanism for the synthesis of bilanes and hexapyrroles from nitrosoalkenes and dipyrromethanes.

The promising results regarding the novel synthesis of bilanes led us to explore the synthesis of other tetrapyrrolic macrocycles from bilanes **3a** and **7**. Thus, trifluoroacetic acid catalyzed condensation of bilane **3a** with benzaldehyde and *p*-nitrobenzaldehyde, followed by oxidation with DDQ, gave the corresponding porphyrins **9a** and **9b** in 3% and 4% yield, respectively (Scheme 5). Porphyrin **10** was also isolated in 2% yield resulting from prophyrin **9b** by hydrolysis of the oxime group.



Scheme 5. Synthesis of porphyrins **9** and **10** from bilane **3a**.

The reaction of bilanes **7** with benzaldehyde in presence of TFA followed by oxidation with DDQ, afforded a mixture of porphyrin/chlorin **11a**/**12a** (57:43) in 9% yield. Porphyrin/chlorin **11b**/**12b** (76:24) was also isolated from the reaction of bilanes **7** with *p*-nitrobenzaldehyde, in this case with a higher percentage of porphyrin (Scheme 6). All the attempts to further oxidize the **11b**/**12b** mixture were unsuccessful. This result can be explained by the presence of the bulky hydroxyimino-1-(*p*-nitrophenyl)methyl group which makes the oxidation of the macrocyles to the corresponding porphyrin harder. In fact, reports on the controlled oxidation of *meso*-substituted-porphyrinogens to porphyrins/chlorins have demonstrated that steric effects play a crucial role in favoring the formation of chlorins.[14] Furthermore, chlorin formation was not observed starting for bilane **3a** bearing the less-bulkier hydroxyiminoethyl substituent (see Scheme 5).



Scheme 6. Synthesis of porphyrins **11** and chlorins **12** from bilanes.

CONCLUSIONS

In summary, consecutive hetero-Diels-Alder reactions or conjugated additions of nitrosoalkenes with dipyrromethanes led to a new class of bilanes and hexapyrroles *meso*-substituted with an oxime moiety. The oxidation of the tetrapyrrolic compounds or

treatment with aldehydes followed by oxidation gave *trans*-A_2B-corroles and porphyrins, respectively. Thus, the reported synthetic methodology provides a simple and versatile route to corroles and porphyrins containing the oxime functionality.

EXPERIMENTAL SECTION

General Information: NMR spectra were recorded at the following frequencies: proton (^{1}H, 400 MHz) and carbon (^{13}C, 100 MHz). The solvents were hexadeuterodimethyl sulfoxide (DMSO-d_6) and octadeuterotetrahydrofuran (THF-d_8) except where indicated otherwise. Chemical shifts are expressed in ppm relative to TMS, and coupling constants (*J*) are in Hz. Infrared spectra (IR) were recorded on a Fourier transform spectrometer with ATR. High-resolution mass spectra (HMRS) were performed by electrospray ionization (ESI) or electronic impact (EI) on a TOF analyzer. Melting points were determined in open capillaries and are uncorrected. Thin-layer chromatography (TLC) analyses were performed using precoated silica gel. Flash column chromatography was performed with silica gel 60 as the stationary phase. 1,1-Dichloro-2-propanone oxime (**1**),[9d] 2,2-dibromo-1-(4'-nitrophenyl)ethanone oxime (**6**),[11] 5-phenyldipyrromethane (**2a**),[15] 5-*p*-bromophenyldipyrromethane (**2b**),[16] 5-*p*-nitrophenyldipyrromethane (**2c**),[15] 5-(1-hydroxyiminoethyl)dipyrromethane (**2d**)[9d] and 5,5'-diethyldipyrromethane (**2e**),[17] were prepared as described in the literature.

General procedure for the synthesis of bilanes and hexapyrroles

Method A: In water/dichloromethane

The appropriate dipyrromethane (4 mmol) and a solution of oxime **1** or **6** (1 mmol) in dichloromethane (2.4 mL) were added to a solution of Na_2CO_3 (10 mmol) in water (14.6 mL). The reaction mixture was stirred at room temperature for 20 min. After this time, the mixture was extracted with ethyl acetate (3 × 20 mL) and dried over Na_2SO_4, and the solvent was evaporated. The products were purified by flash chromatography.

Method B: In dichloromethane

Sodium carbonate (10 mmol) was added to a solution of oxime **1** or **6** (1 mmol) and the appropriate dipyrromethane (4 mmol) in dichloromethane (30 mL). The reaction mixture was stirred at room temperature for the time indicated in each case. The reaction was monitored by TLC. Upon completion, the mixture was filtered through a Celite pad, which was washed with dichloromethane. The solvent was evaporated and the products were purified by flash chromatography.

(*Z*)-5,15-Diphenyl-10-(1-hydroxyiminoethyl)bilane (**3a**) and **5,15,25-triphenyl-10,20-di(1-hydroxyiminoethyl)hexapyrrole** (**4a**): Obtained from oxime **1** (1 mmol, 0.142 g) and dipyrromethane **2a** (4 mmol, 0.889 g). Purification of the crude product by flash chromathography [ethyl acetate/hexane (1:2) and (1:1)] gave, in order of elution, bilane **3a** (*Method A*: 0.137 g, 27%; *Method B*: 0.115 g, 22%) as a beige solid and hexapyrrole **4a** (*Method A*: 0.053 g, 13%; *Method B*: 0.033 g, 8%) as a beige solid.

Data for bilane **3a**: mp >118 °C with decomposition (from carbon tetrachloride); IR (KBr) ν 1028, 1450, 1493, 1581, 1682 and 3367 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 1.68 (s, 3H), 4.79 (s, 1H), 5.31 (s, 2H), 5.53-5.55 (m, 2H), 5.65-5.67 (m, 4H), 5.89 (br s, 2H), 6.59 (br s, 2H), 7.12-7.19 (m, 6H), 7.24-7.28 (m, 4H), 10.39 (br s, 3H), 10.51 (br s, 1H), 10.53 (br s, 1H); ^{13}C NMR δ (DMSO-d_6) 12.0, 43.3, 43.7, 105.6, 105.9, 106.0, 106.7, 116.7, 125.9, 127.9, 128.0, 129.2, 129.3, 132.4, 132.4, 133.2, 144.0, 155.9; HRMS (ESI-TOF) m/z: [M+H^+] Calcd. for $C_{33}H_{32}N_5O$ 514.2601; found 514.2603.

Data for hexapyrrole **4a**: mp >141 °C with decomposition (from carbon tetrachloride); IR (KBr) ν 1028, 1450, 1493, 1581, 1682 and 3352 cm^{-1}. ^{1}H NMR δ (DMSO-d_6) 1.73 (s, 6H), 4.83 (s, 2H), 5.33 (s, 1H), 5.36 (s, 2H), 5.59 (br s, 4H), 5.70 (br s, 6H), 5.94 (br s, 2H), 6.64 (br s, 2H), 7.15-7.24 (m, 9H), 7.28-7.33 (m, 6H), 10.44 (br s, 6H), 10.55 (br s, 1H), 10.58 (br s, 1H); ^{13}C NMR δ (DMSO-d_6) 12.0, 43.2, 43.3, 43.7, 105.5, 105.6, 105.7, 105.9, 106.0, 106.7, 116.7, 125.8, 125.9, 127.8, 127.9, 128.0, 129.3, 132.4, 132.5, 133.2, 143.9, 155.9; HRMS (ESI-TOF) m/z: [M+H^+] Calcd. for $C_{51}H_{49}N_8O_2$ 805.3973; found 805.3982.

(*Z*)-5,15-Di(*p*-nitrophenyl)-10-(1-hydroxyiminoethyl)bilane (**3b**) and **5,15,25-tri(*p*-nitrophenyl-10,20-di(1-hydroxyiminoethyl)hexapyrrole** (**4b**): Obtained from oxime **1** (1 mmol, 0.142 g) and dipyrromethane **2b** (4 mmol, 1.07 g), using ethyl acetate as co-solvent via *Method A*.. Purification of the crude product by flash chromathography [ethyl

acetate/hexane (1:1) and (2:1)] gave, in order of elution, bilane **3b** (*Method A*: 0.142 g, 24%; *Method B*: 0.139 g, 23%) as a beige solid and hexapyrrole **4b** (*Method A*: 0.061 g, 13%; *Method B*: 0.053 g, 11%) as a beige solid.

Data for bilane **3b**: mp >113 °C with decomposition (from carbon tetrachloride); IR (KBr) ν 1111, 1348, 1516, 1595 and 3404 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 1.69 (s, 3H), 4.80 (s, 1H), 5.50 (s, 2H), 5.59 (br s, 2H), 5.69-5.71 (m, 4H), 5.92 (d, *J* = 2.4 Hz, 2H), 6.65 (s, 2H), 7.38 (d, *J* = 8.4 Hz, 4H), 8.15 (d, *J* = 8.4 Hz, 4H), 10.43 (s, 1H), 10.54 (br s, 2H), 10.63 (br s, 1H), 10.65 (br s, 1H); ^{13}C NMR δ (DMSO-d_6) 12.0, 43.1, 43.8, 105.8, 105.9, 106.0, 106.3, 106.5, 107.0, 117.3, 123.3, 129.2, 129.6, 129.7, 129.7, 129.7, 131.1, 131.1, 131.2, 131.2, 131.8, 145.8, 151.8, 155.7; HRMS (ESI-TOF) m/z: [M+Na^+] Calcd. for $C_{33}H_{29}N_7NaO_5$ 626.2122; found 626.2121.

Data for hexapyrrole **4b**: mp >136 °C with decomposition (from carbon tetrachloride); IR (KBr) ν 1111, 1348, 1429, 1516, 1595 and 3408 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 1.68 (s, 6H), 4.79 (s, 2H), 5.46 (s, 1H), 5.50 (s, 2H), 5.58 (br s, 4H), 5.68 (br s, 6H), 5.92 (br d, *J* = 2.4 Hz, 2H), 6.64 (s, 2H), 7.35-7.39 (m, 6H), 8.13-8.17 (m, 6H), 10.42 (s, 2H), 10.54 (br s, 4H), 10.63 (br s, 1H), 10.65 (br s, 1H); ^{13}C NMR δ (DMSO-d_6) 11.9, 12.0, 43.1, 43.8, 105.8, 105.9, 106.4, 106.5, 107.0, 117.3, 123.2, 123.3, 129.2, 129.6, 129.7, 129.8, 129.8, 131.1, 131.2, 131.2, 131.3, 131.3, 131.8, 145.8, 145.8, 151.8, 152.0, 155.7; HRMS (ESI-TOF) m/z: [M+H^+] Calcd. for $C_{51}H_{46}N_{11}O_8$ 940.3525; found 940.3524.

(*Z*)-5,15-Di(*p*-bromophenyl)-10-(1-hydroxyiminoethyl)bilane (**3c**) and **5,15,25-tri(*p*-bromophenyl-10,20-di(1-hydroxyiminoethyl)hexapyrrole** (**4c**): Obtained from oxime **1** (1 mmol, 0.142 g) and dipyrromethane **2c** (4 mmol, 1.21 g). Purification of the crude product by flash chromathography [ethyl acetate/hexane (1:1) and (2:1)] gave, in order of elution, bilane **3c** (*Method A*: 0.106 g, 16%; *Method B*: 0.107 g, 16%) as a beige solid and hexapyrrole **4c** (*Method A*: 0.048 g, 9%; *Method B*: 0.044 g, 8%) as a beige solid.

Data for bilane **3c**: mp >92 °C with decomposition (from carbon tetrachloride). IR (KBr) ν 1011, 1072, 1404, 1427, 1487 and 3423 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 1.68 (s, 3H), 4.79 (s, 1H), 5.31 (s, 2H), 5.54 (br s, 2H), 5.65 (br d, *J* = 2.4 Hz, 4H), 5.90 (d, *J* = 2.4 Hz, 2H), 6.61 (d, *J* = 1.2 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.4 Hz, 4H), 10.44 (br s, 2H), 10.41 (s, 1H), 10.54 (s, 1H), 10.56 (s, 1H); ^{13}C NMR δ (DMSO-d_6) 12.0, 42.7, 43.8, 105.6, 105.7, 105.7, 106.0, 106.1, 106.8, 117.0, 119.0, 129.4, 129.5, 129.5, 130.3, 130.8,

131.9, 131.9, 132.0, 132.0, 132.7, 143.4, 155.8; HRMS (ESI-TOF) m/z: [M+Na^+] Calcd. for $C_{33}H_{29}Br_2N_5NaO$ 692.0631; found 692.0630.

Data for hexapyrrole **4c**: mp >115 °C with decomposition (from carbon tetrachloride); IR (KBr) ν 1011, 1072, 1404, 1427, 1487 and 3423 cm^{-1}; ^1H NMR δ (DMSO-d_6) 1.67 (s, 6H), 4.78 (s, 2H), 5.27 (s, 1H), 5.31 (s, 2H), 5.53 (br s, 4H), 5.65 (br s, 6H), 5.89 (br d, *J* = 2.8 Hz, 2H), 6.61 (s, 2H), 7.04-7.08 (m, 6H), 7.43-7.47 (m, 6H), 10.39 (br s, 1H), 10.40 (s, 2H), 10.43 (br s, 3H), 10.53 (s, 1H), 10.56 (s, 1H); ^{13}C NMR δ (DMSO-d_6) 12.0, 42.7, 43.8, 105.6, 105.7, 105.8, 106.0, 106.1, 106.1, 106.8, 117.0, 119.0, 129.4, 129.5, 129.5, 129.6, 130.3, 130.7, 130.8, 131.0, 132.1, 132.1, 132.7, 143.4, 143.5, 155.8. HRMS (ESI-TOF) m/z: [M+Na^+] Calcd. for $C_{51}H_{45}Br_3N_8NaO_2$ 1061.1108; found 1061.1071.

5,15-Di(1-hydroxyiminoethyl)-10-(1-hydroxyiminoethyl)bilane (**3d**): Obtained from oxime **1** (1 mmol, 0.142 g) and dipyrromethane **2d** (4 mmol, 0.813 g) via method *A* using ethyl acetate as co-solvent and via method *B* using acetone (30 mL) as solvent. Purification of the crude product by flash chromathography [ethyl acetate/hexane (2:1) and (3:1)] gave bilane **3d** (*Method A*: 0.079 g, 17%; *Method B*: 0.072 g, 15%) as a beige solid. mp >148 ºC with decomposition (from carbon tetrachloride); IR (KBr) ν 1026, 1367, 1431, 1674 and 3346 cm^{-1}; ^1H NMR δ (DMSO-d_6) 1.69 (s, 9H), 4.83 (s, 1H), 4.86 (s, 2H), 5.68-5.71 (m, 4H), 5.76 (br s, 2H), 5.90 (d, *J* = 2.8 Hz, 2H), 6.60 (d, *J* = 1.2 Hz, 2H), 10.38 (br s, 2H), 10.43 (s, 1H), 10.44 (s, 1H), 10.45 (s, 1H), 10.51 (br s, 2H); ^{13}C NMR δ (DMSO-d_6) 12.1, 12.2, 43.6, 43.7, 105.7, 105.7, 105.8, 105.9, 106.0, 107.0, 116.8, 129.1, 129.2, 129.2, 129.3,129.4, 129.5, 130.0, 130.1, 155.7, 155.8; HRMS (ESI-TOF) m/z: [M+H^+] Calcd. for $C_{25}H_{30}N_7O_3$ 476.2405; found 476.2399.

5,5',15,15'-Tetraethyl-10-(1-hydroxyiminoethyl)bilane (**3e**): Obtained from oxime **1** (1 mmol, 0.142 g) and dipyrromethane **2e** (4 mmol, 0.810 g). Purification of the crude product by flash chromathography [ethyl acetate/hexane (1:2)] gave bilane **3e** (*Method A*: 0.058 g, 12%; *Method B*: 0.065 g, 14%) as an orange solid. mp >120 ºC with decomposition (from carbon tetrachloride); IR (KBr) ν 1041, 1259, 1379, 1460, 1711, 2966 and 3346 cm^{-1}; ^1H NMR δ (DMSO-d_6) 0.62-0.65 (m, 12H), 1.69 (s, 3H), 1.92-2.02 (m, 8H), 4.87 (s, 1H), 5.64 (t, *J* = 2.8 Hz, 2H), 5.74 (t, *J* = 2.8 Hz, 2H), 5.82 (dd, *J* = 4.0 and 2.8 Hz, 2H), 5.91 (dd, *J* = 5.6 and 2.8 Hz, 2H), 6.60 (dd, *J* = 4.0 and 2.4 Hz, 2H), 9.76 (br s, 2H), 10.14 (s, 1H), 10.15 (s, 1H), 10.35 (s, 1H); ^{13}C NMR δ (DMSO-d_6) 8.4,

12.1, 28.2, 28.3, 42.6, 43.4, 104.7, 104.7, 106.1, 116.3, 129.3, 135.9, 136.8, 156.1; HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{29}H_{40}N_5O$ 474.3227; found 474.3214.

(*E*)- and **(*Z*)-5,15-Diphenyl-10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]bilanes** (**7**): Obtained from oxime **6** (1 mmol, 0.336 g) and dipyrromethane **2a** (4 mmol, 0.889 g). Purification of the crude product by flash chromathography [ethyl acetate/hexane (1:2)] gave bilanes **7** [*Method A*: 0.245 g, 40%, as a mixture of isomers *E*:*Z* (47:53); *Method B*: 0.252 g, 41%, as a mixture of isomers *E*:*Z* (66:34)] as a beige solid.

Data for **(*Z*)-7** isomer: ^{1}H NMR δ (DMSO-d_6) 5.20 (s, 1H), 5.30 (s, 2H), 5.50-5.52 (m, 4H), 5.64 (br s, 2H), 5.85-5.89 (m, 2H), 6.60 (s, 2H), 7.01-7.05 (m, 2H), 7.13-7.32 (m, 8H), 7.54-7.60 (m, 2H), 8.09-8.13 (m, 2H), 10.48-10.54 (m, 4H), 11.00 (s, 1H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{38}H_{33}N_6O_3$ 621.2609; found 621.2608.

Data for **(*E*)-7** isomer: ^{1}H NMR δ (DMSO-d_6) 5.26-5.27 (m, 2H), 5.50-5.52 (m, 4H), 5.57-5.60 (m, 2H), 5.81-5.84 (m, 2H), 6.12-6.13 (br d, J = 3.2 Hz, 1H), 6.58 (s, 2H), 7.01-7.05 (m, 2H), 7.13-7.32 (m, 10H), 8.03-8.07 (m, 2H), 10.50-10.54 (m, 4H), 11.84-11.85 (m, 1H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{38}H_{33}N_6O_3$ 621.2609; found 621.2607.

General procedure for the synthesis of corroles

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (3 equiv, 0.3 mmol) was added to a solution of the appropriate bilane (0.1 mmol) in dry tetrahydrofuran (20 mL). The reaction mixture was stirred at room temperature for 3 h. After that time, the reaction mixture was concentrated under reduced pressure until half volume. The product was purified by flash chromatography [ethyl acetate/hexane (1:3)] followed by recrystallization in methanol.

(*Z*)-5,15-Diphenyl-10-(1-hydroxyiminoethyl)corrole (**5a**): Obtained from bilane **3a** (0.051 g, 0.1 mmol) as dark green solid (0.036 g, 70%). ^{1}H NMR δ (THF-d_8) 3.03 (s, 3H), 7.67-7.71 (m, 2H), 7.79-7.83 (m, 4H), 8.35-8.36 (m, 6H), 8.85-8.88 (m, 6H), 10.77 (br s, 1H); ^{13}C NMR δ (THF-d_8) 21.6, 107.0, 115.9, 116.0, 116.1, 116.2, 125.2, 125.3, 125.3, 125.4, 128.1, 128.8, 135.9, 141.3, 157.5; HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{33}H_{26}N_5O$ 508.2132; found 508.2143; UV/Vis: λ_{abs} (THF, log ε) = 415 (5.04), 577 (4.24), 618 (4.11), 648 (3.91) nm.

(*Z*)-5,15-Di(*p*-nitrophenyl)-10-(1-hydroxyiminoethyl)corrole (**5b**): Obtained from bilane **3b** (0.060 g, 0.1 mmol) as dark green solid (0.050 g, 84%). ^{1}H NMR δ (THF-d_8) 3.04 (s, 3H), 8.54 (br s, 2H), 8.58-8.60 (m, 4H), 8.69-8.71 (m, 4H), 8.89-8.90 (m, 2H), 8.94-8.95 (m, 2H), 8.99-9.01 (m, 2H), 10.95 (br s, 1H); ^{13}C NMR δ (THF-d_8) 21.6, 109.2, 117.3, 117.4; 123.9, 124.2, 124.3, 126.3, 126.4; 126.4, 126.5, 136.5, 147.2, 148.2, 157.3; HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{33}H_{24}N_7O_5$ 598.1833; found 598.1838; UV/Vis: λ_{abs} (THF pH = 8, log ε) = 412 (4.58), 604 (3.98), 673 (3.91) nm.

(*Z*)-5,15-Di(*p*-bromophenyl)-10-(1-hydroxyiminoethyl)corrole (**5c**): Obtained from bilane **3c** (0.067 g, 0.1 mmol) as dark green solid (0.027 g, 40%). ^{1}H NMR δ (THF-d_8) 3.01 (s, 3H), 7.99 (d, J = 8.0 Hz, 4H), 8.25 (d, J = 8.0 Hz, 4H), 8.47 (br s, 2H), 8.83-8.87 (m, 4H), 8.92 (br d, J = 3.6 Hz, 2H), 10.88 (br s, 1H); ^{13}C NMR δ (THF-d_8) 21.6, 107.6, 116.3, 116.4, 122.9, 125.5, 125.6, 125.7, 125.8, 132.1, 132.2, 133.5, 133.6, 133.6, 133.7, 137.4, 140.3, 157.4; HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{33}H_{24}Br_2N_5O$ 664.0342; found 664.0343; UV/Vis: λ_{abs} (THF, log ε) = 418 (5.05), 578 (4.32), 614 (4.23), 644 (4.08) nm.

5,15-Diphenyl-10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]corrole (**8**): Obtained from bilanes **7** (0.062 g, 0.1 mmol) as dark green solid (0.039 g, 64%). ^{1}H NMR δ (THF-d_8) 7.66-7.70 (m, 2H), 7.77-7.81 (m, 4H), 7.92 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 8.31 (br d, J = 5.6 Hz, 4H), 8.44 (br s, 2H), 8.54 (d, J = 4.4 Hz, 2H), 8.76 (br s, 2H), 8.89 (br s, 2H), 11.19 (br s, 1H); ^{13}C NMR δ (THF-d_8) 99.8, 115.8, 115.8, 124.1, 128.2, 128.8, 135.9, 141.1, 147.5, 148.8, 156.6; HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{38}H_{27}N_6O_3$ 615.2139; found 615.2145; UV/Vis: λ_{abs} (THF, log ε) = 414 (5.00), 579 (4.27), 606 (4.13), 644 (3.82) nm.

General procedure for the synthesis of porphyrins

Trifluoroacetic acid (0.08 mmol) was added to a solution of bilane **3a** or **7** (0.10 mmol) and the appropriate aldehyde (0.10 mmol) in dichloromethane (19 mL). The reaction mixture was stirred at room temperature for 2 hours. After this time, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.105 mmol) was added the reaction was allowed to stir for another 2 hours. Upon completion, the solvent was evaporated off and the crude was

subject to a flash chromatography [ethyl acetate/hexane (1:2)] and the product was purified by preparative plates [ethyl acetate/hexane (1:3)].

(*Z*)-5,15,20-Triphenyl-10-(1-hydroxyiminoethyl)porphyrin (9a): Obtained from bilane **3a** (51 mg, 0.10 mmol) and benzaldehyde (10 μL, 0.10 mmol) as a violet solid (1.8 mg, 3%). ^{1}H NMR δ ($CDCl_3$) -2.85 (s, 2H), 3.16 (s, 3H), 7.74-7.80 (m, 9H), 8.20-8.21 (m, 6H), 8.83 (br s, 4H), 8.95 (d, *J* = 4.8 Hz, 2H), 9.21 (d, *J* = 4.8 Hz, 2H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{40}H_{29}N_5O$ 596.2423; found 596.2445; UV/Vis: λ_{abs} (CH_2Cl_2, log ε) = 416 (5.34), 512 (4.05), 547 (3.68), 587 (3.59), 644 (3.35) nm.

(*Z*)-5,15-Diphenyl-10-(1-hydroxyiminoethyl)-20-(*p*-nitrophenyl)porphyrin (**9b**) and **5,15-Diphenyl-10-acetyl-20-(*p*-nitrophenyl)porphyrin** (**10**): Obtained from bilane **3a** (51 mg, 0.10 mmol) and *p*-nitrobenzaldehyde (15 mg, 0.10 mmol). Purification of the crude product by flash chromatography [ethyl acetate/hexane (1:2)] gave, in order of elution, porphyrin **10** (1.3 mg, 2%) as a violet solid and porphyrin **9b** (2.6 mg, 4%) as a violet solid.

Porphyrin 10: ^{1}H NMR δ ($CDCl_3$) -2.87 (br s, 2H), 3.54 (s, 3H), 7.76-7.84 (m, 6H), 8.19-8.21 (m, 4H), 8.38 (d, *J* = 4.8 Hz, 2H), 8.64 (d, *J* = 8.8 Hz, 2H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.99 (d, *J* = 4.8 Hz, 2H), 9.22 (d, *J* = 4.8 Hz, 2H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{40}H_{27}N_5O_3$ 626.2171; found 626.2187; UV/Vis: λ_{abs} (CH_2Cl_2, log ε) = 417 (5.06), 513 (3.80), 549 (3.39), 589 (3.32), 645 (3.15) nm.

Porphyrin 9b: ^{1}H NMR δ ($CDCl_3$) -2.87 (br s, 2H), 3.17 (s, 3H), 7.74-7.83 (m, 6H), 8.19-8.21 (m, 4H), 8.38 (d, *J* = 8.4 Hz, 2H), 8.63 (d, *J* = 8.4 Hz, 2H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.96 (d, *J* = 4.8 Hz, 2H), 9.24 (d, *J* = 4.8 Hz, 2H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{40}H_{29}N_6O_3$ 641.2283; found 641.2269; UV/Vis: λ_{abs} (CH_2Cl_2, log ε) = 417 (5.17), 513 (3.99), 548 (3.62), 588 (3.54), 644 (3.34) nm.

5,15,20-Triphenyl-10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]porphyrin (**11a**) and **5,15,20-Triphenyl-10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]chlorin** (**12a**): Obtained from bilane **7** (62 mg, 0.10 mmol) and benzaldehyde (10 μL, 0.10 mmol). Purification of the crude product by flash chromatography [ethyl acetate/hexane (1:3)] gave the mixture porphyrin/chlorin **11a**/**12a** (57:43) (6.3 mg) as a violet solid.

Porphyrin 11a: ^{1}H NMR δ ($CDCl_3$) -2.72 (s, 2H), 7.66-7.70 (m, 3H), 7.73-7.79 (m, 6H), 8.06-8.12 (m, 6H), 8.18-8.20 (m, 4H), 8.84 (d, *J* = 4.8 Hz, 2H), 8.85 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.95 (d, *J* = 4.8 Hz, 2H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{45}H_{31}N_6O_3$ 703.2452; found 703.2436.

5,15-Diphenyl-10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]-20-(*p*-nitrophenyl)porphyrin (**11b**) and **5,15-Diphenyl-10-[1-hydroxyimino-1-(*p*-nitrophenyl)methyl]-20-(*p*-nitrophenyl)chlorin** (**12b**): Obtained from bilane **7** (62 mg, 0.10 mmol) and *p*-nitrobenzaldehyde (15 mg, 0.10 mmol). Purification of the crude product by flash chromatography [ethyl acetate/hexane (1:3)] gave the mixture porphyrin/chlorin **11b**/**12b** (76:24) (4.5 mg) as a violet solid.

Porphyrin 11b: ^{1}H NMR δ ($CDCl_3$) -2.76 (s, 2H), 7.71-7.80 (m, 8H), 8.07 (d, *J* = 9.2 Hz, 2H), 8.17-8.19 (m, 4H), 8.35-8.42 (m, 2H), 8.62-8.67 (m, 2H), 8.74 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.97 (d, *J* = 4.8 Hz, 2H); HRMS (ESI-TOF) m/z: [M+H$^+$] Calcd. for $C_{45}H_{30}N_7O_5$ 748.2303; found 748.2290.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}CNMR spectra for all new compounds and UV-Vis spectra for new corroles and porphyrins. This material is available free via the Internet at http://pubs.ac.org.

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Notes

The authors declare no competing financial interest.

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