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Bis-picket-fence corroles

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Dedicated to Christoph Elschenbroich on the occasion of his 70th anniversary.

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ABSTRACT

Superstructured corrole ligands related to the picket-fence porphyrins were obtained from (2,6-dichlorophenyl)dipyrromethane in two steps. Condensation with an aryl aldehyde followed by oxidative ring closure yields A_2B corroles with four peripheral bromine atoms. Palladium-catalyzed fourfold amidation at these positions results in the formation of the desired sterically encumbered species, accompanied mainly by disubstituted by-products. The insertion of iron ions into the blocked cavity of the new corrole ligands proves successful when directed towards the nitrosyl derivative. The X-ray crystallographic investigation of such an iron complex allows a detailed view of the steric restraints imposed by the bulky amido substituents.

1. Introduction

Over the last few years the chemistry of corroles, one-carbon short relatives of porphyrin (Fig. 1), and their metal complexes has been a fast growing field of research stimulated by their intriguing electronic structures and their numerous potential applications [1–14]. The basis for this development was provided by the introduction of new straightforward syntheses for *meso*-arylsubstituted corroles [15–21]. Besides the possibility of electronic fine-tuning of the macrocycle these methods allow the introduction of reactive groups in the periphery for further functionalization at the *meso*- and β-positions [20,22–25]. Despite the general interest in such species, in particular in sterically encumbered triarylcorroles, for bioinorganic model compounds or corrole based catalysts their synthesis has remained a great challenge [26–28]. Examples for corroles bearing groups larger than chlorine atoms or methyl groups in the 2- and 6-positions of the *meso*-substituents are rare. Collman and Decréau reported the syntheses of several single-sided hindered corroles [29]. To the best of our knowledge, the only example for a double-faced protected corrole so far was reported by Rose and Andrioletti [30]. Both groups used nitro-substituted triarylcorroles as starting material for their syntheses in analogy to the established methods developed for sterically demanding porphyrins [31].

Recently, Zhang et al. introduced the palladium-catalyzed amidation reaction as a new method for the preparation of sterically encumbered porphyrins starting from 5,15-bis(2,6-dibromophenyl)porphyrin [32]. Using a catalytic system developed by Buchwald et al. [33,34] the desired amidophenylporphyrins were obtained in high yields. Herein, we report the application of 5,15-bis(2,6-dibromophenyl)corroles as versatile synthons for the syntheses of both, single-sided and double-sided superstructured corroles.

2. Results and discussion

2.1. Preparation of bis-picket-fence corroles

A series of five new 5,15-bis(2,6-dibromophenyl)corroles **2a–e** with different meso-aryl substituents at the 10-position was prepared via a [2 + 1] approach developed by Gryko [19]. Starting from dipyrromethane **1** and the appropriate benzaldehydes, corroles **2a–e** were obtained in good yields (Scheme 1). All compounds were characterized by UV–Vis and ^{1}H NMR spectroscopy as well as HRMS.

The reaction of corrole **2a** with pivalamide **3a** was chosen for optimizing the coupling reaction. The initial attempt to use Zhang's conditions developed for the corresponding porphyrins (40 mol% $Pd(OAc)_2$ based on the amount of corrole **2a**) [32] yielded only trace amounts of the desired tetrasubstituted product **4a**. Furthermore, neither the starting material **2a** nor additional coupling

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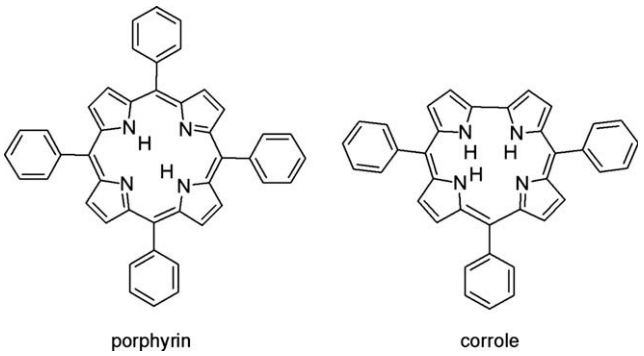
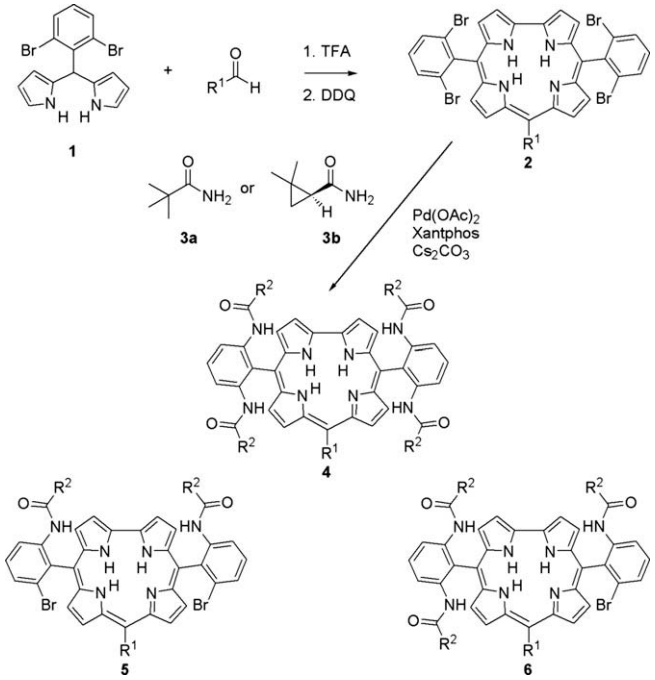


Fig. 1. Tetraphenylporphyrin and triphenylcorrole.



Scheme 1. Synthesis of sterically demanding bis-picket-fence corroles; for R^1 see Table 1.

products could be found. A palladium(II) induced oxidative degradation of the corrole macrocycle was suspected to account for this failure. Consequently, the amount of $Pd(OAc)_2$ was reduced to 10 mol%, which resulted in an increase of the yield for **4a** to 6%. In addition, two previously unobserved species were isolated in 72% and 18% yield, and could be identified as the disubstituted (**5a**) and trisubstituted (**6a**) triarylcorrole, respectively. A further increase of the yield of **4a** to 30% was obtained by increasing the reaction temperature to 125 °C. The disubstituted corrole **5a** was unambiguously characterized as the α,α-atropisomer by ^{1}H NMR spectroscopy. The surprising selectivity of the formation of this isomer suggests a strong cooperativity of more than one palladium atom during the coupling step. However, the nature of this cooperativity has not been discovered, yet.

Corroles **2a**–**e** were coupled with pivalamide **3a** using the optimized procedure from above (Table 1). In all the cases, the formation of di-, tri- and the desired tetra-substituted products **4a**–**e**, **5a**–**e** and **6a**–**e** was observed in comparable relative amounts except for the cyano derivative **2d** (entry 4 in Table 1) which reacts sluggishly and thus produces larger amounts of the di- and trisubstituted byproducts **5d** and **6d**. In addition, the chiral corroles **4f** and **5f** have been prepared from the cyclopropylamide **3b** in 41% and 21% yield, respectively. The increase in yield compared to corrole **4a** is most likely due to the reduced steric bulk of **3b**. These tetrapyrroles are rare examples for chiral corroles, and in particular the tetrasubstituted **4f** is of interest as ligand for enantioselective catalysis using metallocorroles [27,35–38].

2.2. Nitrosyl iron chelate 7

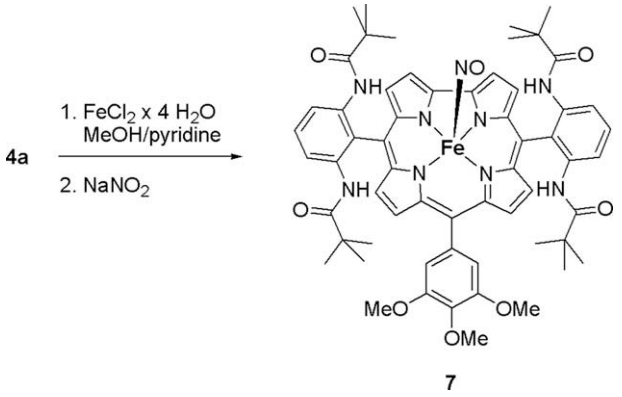
Despite the steric encumbrance imposed by two bulky pivalamido substituents on each side of the corrole plane the insertion of iron into the N_4 cavity of the macrocycle **4a** was performed easily by a standard protocol [39]. Furthermore, *in situ* treatment of the primarily formed iron complex with sodium nitrite resulted in the immediate formation of the stable nitrosyliron complex **7** which was isolated in an excellent yield of 75% (Scheme 2). The compound was unambiguously characterized as a typical nitrosyliron corrole [39–42] containing a linear $\{FeNO\}^6$ unit [43]. In addition, a characteristic high field shift of the *tert*-butyl proton signals in the ^{1}H NMR spectrum of **7** to 0.78 and 0.50 ppm revealed that the bulky groups are oriented towards the central iron ion and thus form protected binding pockets on both sides of the tetrapyrrole plane. This feature of the new functional ligands is very similar to the scenario found for the parent picket fence porphyrins [44,45]. A single crystal X-ray crystallographic analysis was undertaken in order to visualize and further characterize the binding pocket of **7**. Fig. 2 presents the result of this study.

The orientation of the pivalamido substituents in **7** directly above and below the tetrapyrrole π system was confirmed for the crystalline state. The *tert*-butyl groups on either side of the macrocyclic plane are situated about 2.5 Å apart from each other. As shown in Fig. 1 this scenario results in the formation of two groove-like pockets, one of which being occupied by the axial NO ligand. With minimum distances N5–$H_{t\text{-Bu}}$ and O1–$H_{t\text{-Bu}}$ of 2.805 and 2.663 Å, respectively, the slim and almost linearly coordinated NO ligand (Fe–N5–O1 170.63°; Fe–N5 1.646 Å; N5–O1 1.156 Å) does not fill the empty space above the iron atom entirely. Therefore, it can be expected that sufficient space remains within the

Table 1
Syntheses of sterically demanding corroles[a]

Entry	R1	2	3	5: yield (%)[b]	6: yield (%)[b]	4: yield (%)[b]
1	3,4,5-$(OMe)_3C_6H_2$	**2a**	**3a**	**5a**: 41	**6a**: 13	**4a**: 30
2	4-MeC_6H_4	**2b**	**3a**	**5b**: 40	**6b**: 19	**4b**: 24
3	Ph	**2c**	**3a**	**5c**: 36	**6c**: 18	**4c**: 23
4	4-NCC_6H_4	**2d**	**3a**	**5d**: 63	**6d**: 15	**4d**: 6
5	4-$NO_2C_6H_4$	**2e**	**3a**	**5e**: 49	**6e**: 16	**4e**: 24
6	3,4,5-$(OMe)_3C_6H_2$	**2a**	**3b**	**5f**: 21	**6f**: n. i.	**4f**: 41

[a] Reactions were carried out in THF under Argon with 1.0 equiv. of **2**, 4.0 equiv. of **3**, 10 mol% $Pd(OAc)_2$ and 20 mol% Xantphos in the presence of 2 equiv. of Cs_2CO_3 at 125 °C.
[b] Isolated yields.



Scheme 2. One-pot preparation of nitroso iron corrole **7**.

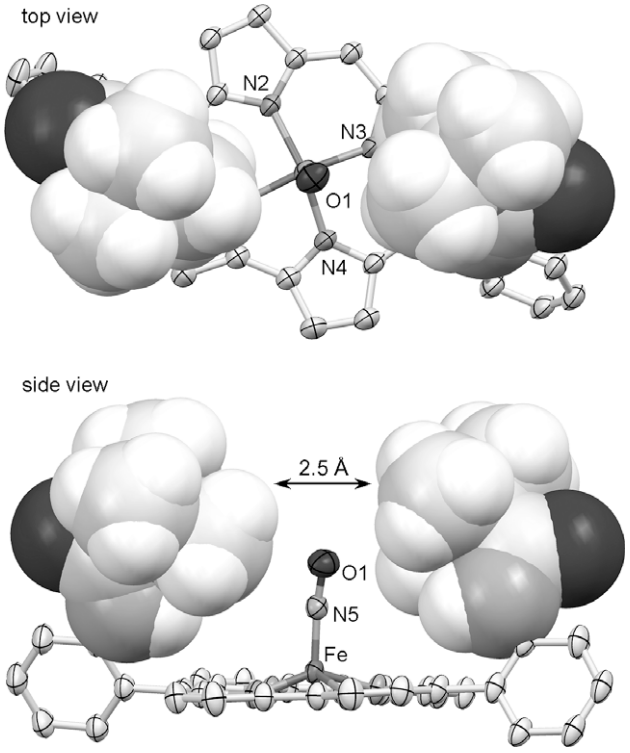


Fig. 2. Truncated views of the molecular structure of **7** illustrating the seating of the NO ligand within the binding pocket of the bis-picket-fence corrole (ellipsoids set to 50% probability; space-fill model used for pivalamido groups; 10-(3,4,5-trimethoxyphenyl) substituent as well as opposite pivalamido groups removed for clarity). Selected bond lengths/Å and angles/°: Fe–N1 1.906(2), Fe–N2 1.888(2), Fe–N3 1.930(2), Fe–N4 1.979(2), Fe–N5 1.647(4), N5–O1 1.155(5); N1–Fe–N2 88.17(9), N1–Fe–N3 148.35(10), N1–Fe–N4 91.32(8), N1–Fe–N5 104.75(15), N2–Fe–N3 78.37(9), N2–Fe–N4 147.17(10), N2–Fe–N5 101.51(14), N3–Fe–N4 85.22(8), N3–Fe–N5 105.94(15), N4–Fe–N5 110.31(14), Fe–N5–O1 170.7(4).

groove to bind, activate and transfer atoms or small molecules as required for bioinorganic models as well as stereoselective catalysts. Preliminary experiments have shown that the cyclopropanation of styrene with ethyl diazoacetate occurs in a diastereoselective fashion (*E*/*Z* 6:1) when catalyzed by **7**. In-depth catalytic studies are currently being undertaken in our laboratories and will be published elsewhere in due course.

In summary, we have developed a new method for the synthesis of sterically demanding A_2B-corroles starting from readily accessible 5,15-bis(2,6-dibromophenyl)corroles and shown the favourable sterics of these species. Further investigations towards the coordination chemistry and application of these fascinating new non-natural porphyrinoids in catalysis and as protein analogues are currently under way.

3. Experimental

3.1. General remarks

NMR spectra (^{1}H, ^{13}C for **7**) were obtained at ambient temperature on an instrument *Bruker ARX 300*. Chemical shifts are given in ppm relative to the residual proton resonance of the solvent. High resolution mass spectra were recorded using the ESI method on a *Finnigan TSQ 700*. UV–Vis spectra were measured on a *Shimadzu UV-1601 PC* spectrometer in concentrations of about 10^{-5} mol/L. IR spectra were recorded in nujol film on a *Bruker Vector 22* instrument. All reactions were performed in an inert atmosphere of argon by using standard Schlenk techniques and vacuum-line methods. Solvents were dried and distilled under nitrogen prior to use. Column chromatography was carried out under nitrogen using silica (particle size 0.063–0.200 nm). Free base corroles were purified using the DCVC method [46] on silica PF 60 (Merck) as the stationary phase. Chemicals were obtained from commercial sources and used as received.

3.2. Crystal structure determination

Data of **7** were collected at 173 K on a STOE IPDS2 diffractometer with Mo Kα radiation, $\lambda = 0.71073$ Å. The structure was solved by direct methods using SHELXS [47] and refined by full-matrix least-squares procedures (SHELXL [48]). Disorder models were applied for two of the *t*-Bu groups as well as for the FeNO subunit. A heavily disordered solvent molecule was treated with the SQUEEZE function as implemented in PLATON [49]. Crystal data for **7**: triclinic, space group $P\bar{1}$, $a = 14.0095(10)$, $b = 14.5716(11)$, $c = 17.6620(14)$ Å, $\alpha = 75.646(6)°$, $\beta = 86.984(6)°$, $\gamma = 63.670(5)°$, $V = 3123.8(4)$ Å^3, $Z = 2$, $\rho = 1.165$ g cm^{-3}, $R_1 = 0.0703$, $wR_2 = 0.2106$ (for 16,727 reflections, $I_o > 2\sigma(I_o)$).

3.3. Syntheses of the compounds

3.3.1. Preparation and analyses for *1*

A solution of 2,6-dibromobenzaldehyde [50] (6.5 g, 24.6 mmol) in pyrrole (170 mL, 2.5 mol) was purged with argon for 30 min and treated under stirring with magnesiumbromide-etherate (2.26 g, 12.5 mmol) for 2 h at ambient temperature. Finely ground NaOH (4.33 g, 0.1 mol) is then added and stirring continued for 45 min. The solution is kept unstirred for 2 h and carefully filtered through a plug of silica in order to remove all solids. The filter cake is washed with additional pyrrole, and the filtrates concentrated *in vacuo* at 65 °C until all pyrrole is completely removed. The dark residue is first chromatographed on silica with *n*-hexane/ethyl acetate (7/3) and the product fraction finally recrystallized from ethanol/water (4/1) to yield the title compound (4.2 g, 45%) as a slightly yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.31$ (*br s*, 2H, N*H*), 7.68 (*d*, *J* = Hz, 2H, *meta-H*), 6.97 (*t*, *J* = Hz, 1H, *para-H*), 6.76–6.73 (*m*, 2H, α-*H*), 6.55 (*s*, 1H, *meso-H*), 6.23–6.19 (*m*, 2H, β-*H*), 6.13–6.08 (*m*, 2H, β-*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.4$, 133.9, 129.3, 129.1, 125.9, 116.8, 108.7, 107.7, 44.6; HRMS-EI (M^+): *m*/*z*: 379.9346 (calcd for $C_{15}H_{12}Br_2N_2$: 379.9347).

3.3.2. General procedure for the synthesis of 10-aryl-5,15-bis(2,6-dibromophenyl)corroles ***2a–e***

2,6-Dibromophenyldipyrromethane **1** (250 mg, 0.66 mmol) was dissolved in 5 mL of a previously prepared solution of TFA (30 μL,

0.39 mmol) in CH_2Cl_2 (100 mL). Substituted benzaldehyde (0.33 mmol) was added and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted to 10 mL with CH_2Cl_2 and slowly added to vigorously stirred CH_2Cl_2 (150 mL) simultaneously with a solution of DDQ (195 mg, 0.86 mmol) in THF (10 mL). The mixture was stirred for further 15 min and evaporated to dryness. The crude product was passed over a chromatography column (silica, CH_2Cl_2/hexane, 4:1). The first, violet band contained the corrole **2a** contaminated with unreacted aldehyde. Dry column vacuum chromatography (DCVC) (silica, CH_2Cl_2/hexane, 3:1) of this mixture afforded the pure corrole.

2a (67.5 mg, 22%). UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 411 (1.00), 427 (0.79), 569 (0.16), 610 (0.10), 638 (0.05) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.04 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.70 (d, *J* = 4.7 Hz, 2H, β-*H*), 8.52 (d, *J* = 4.7 Hz, 2H, β-*H*), 8.41 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.03 (d, *J* = 8.1 Hz, 4H, *meta*-*H*), 7.54 (t, *J* = 8.1 Hz, 2H, *para*-*H*), 7.44 (s, 2H, *ortho*-*H*), 4.06 (s, 3H, *para*-OCH_3), 3.94 (s, 6H, *meta*-OCH_3); HRMS-ESI ([M+H]$^+$): *m*/*z*: 932.8944 (calcd for $C_{40}H_{29}Br_4N_4O_3$: 932.8927).

2b (50.7 mg, 18%). UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 411 (1.00), 426 (0.77), 570 (0.14), 611 (0.09), 639 (0.05) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.04 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.62 (d, *J* = 4.7 Hz, 2H, β-*H*), 8.52 (d, *J* = 4.7 Hz, 2H, β-*H*), 8.41 (d, *J* =4.2 Hz, 2H, β-*H*), 8.07 (d, *J* = 7.9 Hz, 2H, *Ph*-*H*), 8.02 (d, *J* = 8.1 Hz, 4H, *meta*-*H*), 7.58–7.50 (m, 4H, *Ph*-*H* and *para*-*H*), 2.67 (s, 3H, C*H* $_3$); HRMS-ESI ([M+H]$^+$): *m*/*z*: 856.8761 (calcd for $C_{38}H_{25}Br_4N_4$: 856.8766).

2c (55.4 mg, 20%). UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 410 (1.00), 425 (0.77), 570 (0.14), 610 (0.09), 639 (0.04) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.04 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.59 (d, *J* = 4.7 Hz, 2H, β-*H*), 8.53 (d, *J* = 4.7 Hz, 2H, β- *H*), 8.41 (d, *J* =4.2 Hz, 2H, β-*H*), 8.21–8.17 (m, 2H, *Ph*-*H*), 8.03 (d, *J* = 8.1 Hz, 4H, *meta*-*H*), 7.77–7.72 (m, 3H, *Ph*-*H*), 7.53 (t, *J* = 8.1 Hz, 2H, *para*-*H*); HRMS-ESI ([M+H]$^+$): *m*/*z*: 842.8597 (calcd for $C_{37}H_{23}Br_4N_4$: 842.8610).

2d (59.9 mg, 21%). UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 412 (1.00), 428 (0.81), 570 (0.15), 608 (0.09), 638 (0.03) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.04 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.59 (d, *J* = 4.8 Hz, 2H, β-*H*), 8.55 (d, *J* = 4.8 Hz, 2H, β-*H*), 8.44 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.35 (d, *J* = 8.2 Hz, 2H, *Ph*-*H*), 8.05 (d, *J* = 8.2 Hz, 2H, *Ph*-*H*), 8.00 (d, *J* = 8.1 Hz, 4H, *meta*-*H*), 7.49 (t, *J* = 8.1 Hz, 2H, *para*-*H*); HRMS-ESI ([M+H]$^+$): *m*/*z*: 867.8583 (calcd for $C_{38}H_{22}Br_4N_5$: 867.8562).

2e (73.0 mg, 25%). UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 411 (1.00), 423sh (0.89), 570 (0.22), 608 (0.12), 639 (0.04) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.06 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.62–8.55 (m, 6H, β-*H* and *Ph*-*H*), 8.44 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.40 (d, *J* =8.8 Hz, 2H, *Ph*-*H*), 8.04 (d, *J* = 8.1 Hz, 4H, *meta*-*H*), 7.55 (t, *J* = 8.1 Hz, 2H, *para*-*H*); HRMS-ESI ([M+H]$^+$): *m*/*z*: 887.8450 (calcd for $C_{37}H_{22}Br_4N_5O_2$: 887.8466).

3.3.3. General procedure for the palladium-catalyzed amidation of bromo-arylcorroles described for **4a**/**5a**/**6a**

Corrole **2a** (50 mg, 53.6 μmol), pivalinamide **3a** (202 mg, 2 mmol), $Pd(OAc)_2$ (1.25 mg, 5.5 μmol), Xantphos (7.5 mg, 12 mmol), and Cs_2CO_3 (325 mg, 1 mmol) were placed in an oven-dried resealable Schlenk tube under an argon atmosphere. The tube was sealed with a Teflon screwcap, evacuated and backfilled with argon. THF (5 mL) was added via syringe. The tube was sealed again with the Teflon screwcap and its contents were heated with stirring. After 65 h at 125 °C, the mixture was cooled to room temperature, taken up in ethyl acetate and concentrated in vacuo. The crude product was purified by column chromatography (silica, EtOAc/CH_2Cl_2, 1:9, then 1:4, then 2:5). Careful chromatography yielded pure corroles **6aa** (21.5 mg, 41%) and **5aa** (6.9 mg, 13%) from the first and second violet band, respectively. The third violet fraction contained corrole **4aa** contaminated with unidentified products. Pure corrole **4aa** was obtained by subsequent DCVC (silica, EtOAc/CH_2Cl_2, 5:2) as a purple solid (16.3 mg, 30%).

(toluene)/nm 414 ($\epsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1} 100), 430 (91), 569 (16), 609 (9.5), 638 (3.6); 409 (97), 567.7 (15), 605.7 (9.7), 638 (5.2), 673 (1.5).

4a: UV–Vis (CH_2Cl_2): λ_{max} (lg ε) = 416 (4.99), 568 (3.20), 615 (2.95), 643sh (2.78) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.14 (d, *J* = 4.3 Hz, 2 H, β-*H*), 8.79 (d, *J* = 4.8 Hz, 2H, β-*H*), 8.71 (d, *J* = 4.8 Hz, 2H, β-*H*), 8.59 (d, *J* = 4.3 Hz, 2H, β-*H*), 8.41 (d, *J* = 8.3 Hz, 4H, *meta*-*H*), 7.80 (t, *J* = 8.3 Hz, 2H, *para*-*H*), 7.34 (*s*, 2H, *ortho*-*H*), 7.22 (s, 4H, N*H*), 4.06 (s, 3 H, *para*-OCH_3), 3.93 (s, 6 H, *meta*-OCH_3), 0.18 (s, 36H, *t*-Bu-*H*); HRMS-ESI ([M+H]$^+$): *m*/*z*: 1013.5282 (calcd for $C_{60}H_{69}N_8O_7$: 1013.5284).

5a: UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 415 (1.00), 566 (0.16), 612 (0.10), 636sh (0.07) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.13–9.10 (m, 2H, β-*H*), 8.79–8.75 (m, 2H, β-*H*), 8.75–8.72 (m, 1H, *meta*-*H*), 8.70–8.63 (m, 2H, β-*H*), 8.56–8.54 (m, 2H, β-*H*), 8.46–8.41 (m, 2H, *meta*-*H*), 7.83–7.77 (m, 2H, *meta*-*H* + *para*-*H*), 7.69 (t, *J* = 8.2 Hz, 1H, *para*-*H*), 7.42–7.33 (m, 2H, *meta*-*H* + N*H*), 7.31 (s, 1H, N*H*), 7.24 (s, 1H, N*H*), 4.06 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 0.21 (s, 9H, *t*-Bu-*H*), 0.19 (s, 9 H, *t*-Bu-*H*), 0.14 (s, 9H, *t*-Bu-*H*); HRMS-ESI ([M+H]$^+$): *m*/*z*: 992.3704 (calcd for $C_{55}H_{59}BrN_7O_6$: 992.3705).

6a: UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 412 (1.00), 564 (0.15), 611 (0.09), 636 (0.06) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.10 (d, *J* = 4.3 Hz, 2H, β-*H*), 8.78-8.73 (m, 4H, β-*H* + *meta*-*H*), 8.63 (d, *J* = 4.8 Hz, 2H, β-*H*), 8.50 (d, *J* = 4.3 Hz, 2H, β-*H*), 7.79 (dd, *J* = 8.1 Hz, *J* = 1.2 Hz, 2H, *meta*-*H*), 7.68 (t, *J* = 8.2 Hz, 2H, *para*-*H*), 7.54 (d, *J* = 1.8 Hz, 1H, *ortho*-*H*), 7.49 (br s, 4H, N*H*), 7.30 (d, *J* = 1.8 Hz, 1H, *ortho*-*H*), 4.06 (s, 3H, –OCH_3), 3.98 (s, 3H, –OCH_3), 3.91 (s, 3H, –OCH_3), 0.17 (s, 18H, *t*-Bu-*H*); HRMS-ESI ([M+H]$^+$): *m*/*z*: 973.2106 (calcd for $C_{50}H_{49}Br_2N_6O_5$: 973.2105).

3.3.4. Preparation and analyses for **7**

Under a blanket of Argon, corrole **4a** (20 mg, 20 μmol) and $FeCl_2 \times 4H_2O$ (12 mg, 60 μmol) are dissolved in 2 mL of methanol/pyridine (2:1) and heated to reflux for 90 min. Saturated aqueous sodium nitrite (20 μL) is then added and the mixture is heated for another 30 min. All volatiles are removed in vacuo and the residue is subjected to column chromatography (neutral alumina II, methyl-*t*-butylether). The product elutes in the first red band and yields a dark red solid after removal of the solvent. Yield: 16 mg (15 μmol, 75%).

7: UV–Vis (CH_2Cl_2): λ_{max} (ε_{rel}) = 373 (1.00), 413 (0.85), 540 (0.24) nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.24 (dd, ^4J = 0.9 Hz, ^3J = 8.1 Hz, 2H, *meta*-H), 8.13 (d, ^3J = 4.8 Hz, 2H, β-H), 8.12 (dd, ^4J = 0.9 Hz, ^3J = 8.1 Hz, 2H, *meta*-H), 7.73 (d, ^3J = 4.5 Hz, 2H, β-H), 7.66 (d, ^3J = 4.8 Hz, 2H, β-H), 7.64 (t, ^3J = 8.4 Hz, 2H, *para*-H), 7.58 (d, ^3J = 4.8 Hz, 2H, β-H), 7.38 (bs, 2H, NH), 7.15 (bs, 2H, NH^{NO}), 6.99 (d, ^3J = 1.8 Hz, 1H, *ortho*-H), 6.86 (d, ^3J = 1.8 Hz, 1H, *ortho*-H), 3.93 (s, 3H, *para*-OCH$_3$), 3.90 (s, 3H, *meta*-OCH$_3$), 3.81 (s, 3H, *meta*-OCH$_3$), 0.78 (s, 18 H, *t*-BuH), 0.50 (s, 18H, *t*-BuH^{NO}); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 176.1, 175.9, 153.3 (2C), 148.5, 147.2, 146.9, 138.5, 137.3 (4C), 134.0, 133.7, 130.1, 127.4 (2C), 125.9 (2C),125.5 (2C), 121.0, 120.2 (2C), 118.9 (2C), 118.0 (2C), 117.7 (2C), 107.7 (2C), 60.7, 56.3, 56.2, 39.4 (2C), 39.2 (2C), 26.9 (6C), 26.4 (6 C); IR (nujol): ν (cm^{-1}) = 3429, 1776 (ν_{NO}), 1690 (amide), 1582, 1500 (amide), 1348, 1296, 1261, 1127, 1055, 1017, 798; HRMS-ESI ([M−NO+H]$^+$): *m*/*z*: 1066.4398 (calcd for $C_{60}H_{66}N_8O_7Fe$: 1066.4417); Anal. calc. ($C_{60}H_{65}N_9O_8Fe$): C, 65.75; H, 5.98; N, 11.50. Found: C, 65.52; H, 5.88; N, 11.35%.

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Appendix A. Supplementary data

CCDC 650380 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.039.

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