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3-NO_2-5,10,15-triarylcorrolato-Cu as a versatile platform for synthesis of novel 3-functionalized corrole derivatives

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β–Nitrocorrole derivatives are potentially valuable platforms for the preparation of a wide range of more elaborated corrole derivatives possessing unique chemical functionalities and electronic properties. Here we report our results on the chemical manipulation of a copper 3-NO_2-triarylcorrolate using different organic reactions, all involving the reduction of $–NO_2$ to $–NH_2$ at an early stage, followed by further transformations. By way of a β-acylated copper corrolate, a novel corrole derivative bearing an alkyl azide group on the peripheral positions was obtained and exploited in the Huisgen 1,3-dipolar cycloaddition.

Introduction

Corroles are tetrapyrrolic macrocycles belonging to the class of contracted porphyrins, since they lack one methine bridge compared with the parent porphyrin macrocycle. The chemistry of this macrocycle has experienced impressive advancements in the last decade, since its structural features can be nowadays be easily modified by having in hand a rich set of synthetic approaches to address both the *meso*-aryl and *β*-pyrrolic positions[1-3]. The possible preparation of a wide range of *meso*-triarylcorroles with tunable properties has allowed a more exhaustive knowledge of the properties of these macrocycles, triggering their promising application in several different fields such as catalysis, medicine and material science[4]. Within this framework, the need to comply with the requirements of a specific application has prompted the development of synthetic procedures leading to corroles functionalized with peripheral substituents, which can be the entry point for subsequent modifications.

In this regard, the introduction of halogen[5] and boryl groups[6] in both the *β*-pyrrolic and *meso*-phenyl positions was demonstrated to be useful for the further elaboration of the corrole framework using metal-catalyzed coupling reactions; sulfonic and chlorosulfonic groups[7] also allowed for the preparation of water soluble corroles that can be conjugated with biomolecules[3]. Starting from formylcorroles[8], vinyl-[9] and carboxylic derivatives[10] were also obtained. The former can be used as efficient precursors in cycloaddition reactions, while the latter are potential dyes in solar cells applications[3]. In this field, we investigated modification of the corrole macrocycle by using the β-nitration reaction of corroles because the nitro group is particularly versatile for introduction of further modifications of the macrocycle[11]. In the last few years, we have focused our efforts on the definition of several synthetic protocols for the convenient preparation of β-nitrocorrole derivatives bearing from one to four nitro groups, both on corrole free base and metal complexes[3,12]. Beyond the development of synthetic protocols, these studies also highlighted additional aspects of these nitrated species, such as the electrochemical and spectroscopic features with relation to the number of nitro groups inserted. Furthermore, the per-nitration of the corrole macrocyle also illuminated the unusual reactivity of pyrrole subunit B, which became unexpectedly functionalized although the more reactive pyrroles A and D were still available for substitution[12g,12h].

The establishment of these synthetic protocols for the nitration of corroles led us to investigate the exploitation of the nitro group in the preparation of additional novel corrole derivatives. The feasible organic transformations dealing with the nitro functionality can take advantage of its activating effect in nucleophilic substitution reactions, or its easy modification into a different functional group, passing through the amino derivative as a key intermediate. We recently reported the introduction of amino groups onto the *β*-positions of the corrole framework, describing how copper and germanium 3-nitrocorrole[12a,12b] and copper 3,17-dinitrocorrole[12a] derivatives can be used as substrates for direct amination on the C2 and C18 *β*-carbons in a VNS (Vicarious Nucleophilic Substitution of hydrogen) reaction, where 4-amino-4*H*-1,2,4-triazole

constituted the $–NH_2$ source. To date, the resulting *β*-amino-nitrocorrole derivatives have represented the first examples of nucleophilic aromatic substitution carried out on a pyrrolic unit of a corrole ring, testifying to the ability of $–NO_2$ group to switch on the electrophilic character of the adjacent *β*–carbon even in the electron rich corrole ring.

In the present work, we report the transformation of the nitro group via early catalytic reduction to the amino group, followed by its further modification into other functionality.

The practical synthetic value of nitrocorroles has once again been concretely pointed out, since the preparation of the reactive aminated intermediate **(1)** provides access to several novel *β*-functionalized corroles with tunable structural as well as electronic properties.

Results and discussion

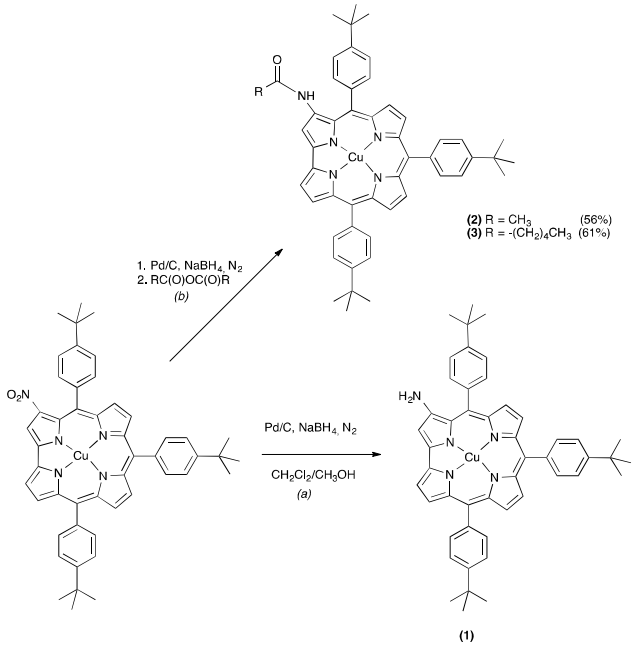
The straight manipulation of the $–NO_2$ group for further modifications of corrole ring, where the first step is its reduction to the amino group, is not unprecedented. Indeed aminocorroles substitued on the *orto* and *para meso*-phenyl positions were just reported in literature, being used as precursors for the preparation of a series of free base hemoprotein corrole analogs[13] in the former case and for the design of organic-inorganic hybrid materials and photoactive binuclear Ru-Cu species[14] in the latter. Herein, the exploitation of the nitro functionality on a *β*-pyrrolic unit firstly required the most appropriate synthetic procedure to obtain the key intermediate, copper 3-NH_2-corrolate. In tetrapyrrolic chemistry, the most applied reductive methods for the conversion of $–NO_2$ into $–NH_2$ make use of $SnCl_2$ in concentrated HCl[15] or catalytic hydrogenation systems[16]. In our studies, the former approach is *a priori* ruled out, since this method was reported by Maes and co-workers[17] to be an efficient method for the removal of the copper ion from Cu-corrolates. This type of reduction using 3-(NO_2)T*t*BuCorrCu would have given the corresponding *β*-aminocorrole free base, which we know to be an unstable species[18] and therefore not useful for further transformations.

Reduction:

For the reasons above, to reduce 3-(NO_2)T*t*BuCorrCu we used palladium, supported on carbon, as catalyst and a 50-fold molar excess of $NaBH_4$ in a dichloromethane/methanol solution at room temperature under N_2 atmosphere, with good results (Scheme 1, (a)).

In a few minutes, the formation of a new compound having a lower Rf value than the starting copper 3-nitrocorrole was apparent by TLC analysis, and concurrently a blue-shifted Soret band was shown by UV-Vis spectroscopy analysis, as expected for the formation of an electron releasing group on a β position. The chromatographic purification of the reaction mixture was performed on silica gel, eluting with dichloromethane/petroleum ether (2:1 v/v) and this permitted the isolation of the main reaction product in a 35% yield. FAB mass spectroscopy identified the product as the copper 3-aminocorrole **(1)** based on the molecular peak at 770 m/z. On the other hand, its further characterization by ^1H NMR spectroscopy was not decisive, giving both large and unresolved β-pyrrolic proton resonances and an uncertain assignment of the $–NH_2$ hydrogens in the spectrum. These unfavourable features could be ascribable to aggregation phenomena or to the formation of intramolecular complexes, due to coordination of the amino group by the copper ion, which can also induce paramagnetic character into the analysed sample. On the other hand, the experimental evidence for definitive identification of **(1)** was given by the occurrence of all the organic transformations involving the $–NH_2$ functionality described below, which unambiguously confirmed our assumption.

The moderate yield obtained for the reduced corrole was due to the progressive decomposition of this Cu complex observed during the chromatographic process. Ultimately, similar limited stability was recently reported for the analogous 2-aminoporphyrins which were shown to be photolabile and easily oxididized[19]. As for reactions involving β-aminoporphyrins, we decided to use immediately the crude reaction product containing the 3-aminocorrole **(1)**, without further purification for the following tranformations, or immediately consume it *in situ*, whenever it was compatible with the reaction conditions.



Scheme 1. Preparation of the copper corrole derivatives **(1)**, **(2)** and **(3)**

Acylation:

At first we focused our attention on the synthesis of Cu corrolates bearing an amide functionality on the β-pyrrolic position, starting from the corresponding 3-NO_2 derivative. Amide synthesis is a popular reaction for numerous reasons, *e.g.* the relative ease of formation of the amide linkage, its structural rigidity and its biomimetic character, which account

for the widespread use of such compounds both in technological and medical applications. Among the many reactants generally used for amide formation from the amino group, we decided to use a series of alkyl anhydrides, which allowed for the ready preparation of copper corroles **(2)**, **(3)** and **(4)** in satisfactory yields. The transformation of the -NO_2 group into the –NHC(O)R amide was performed in the case of corroles **(2)** and **(3)** by a "one pot" procedure outlined in Scheme 1*(b)*, first involving the Pd-catalyzed reduction of the substrate 3-(NO_2)T*t*BuCorrCu at room temperature followed by the *in situ* acylation of the amino derivative with the corresponding anhydride in a dichloromethane/methanol solvent mixture. After the rapid formation of the reduced corrole derivative **(1)**, a 12-fold molar excess of acetic or hexanoic anhydride was added, producing in a few minutes a small red-shift of the Soret band. Chromatographic purification on silica gel afforded the desired amides **(2)** and **(3)** as the main reaction products in 56 and 61 % yields, respectively.

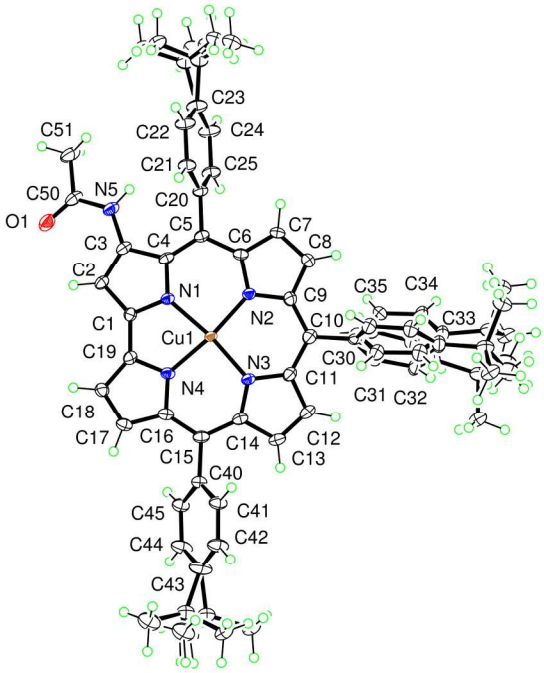


Figure 1. The molecular structure of compound 3-$CH_3C(O)NH$-TtBuCorrCu **(2)**

The FAB mass spectra showed the new compounds to have a molecular peak at m/z 813 and 869, respectively, while the proton NMR spectra showed the amide NH resonance as a sharp singlet at 6.59 and 6.68 ppm, respectively, thus allowing their definitive identification.

In addition, the copper 3-acetylamidocorrole **(2)** gave crystals suitable for an X-ray diffraction study from a $CDCl_3$/MeOH, solution, which afforded the structural characterization reported in Figure 1.

By least-squares (L.S.) plane analysis, the fitted plane (rms deviation = 0.141 Å) of 3-$CH_3C(O)NH$-TtBuCorrCu's 23 atom ($C_{19}N_4$) framework has a conformation best described as "saddled" with the β-pyrrole carbons for the 5-membered rings "A" and "C" residing above (deviations from L.S. plane: min = +0.138 (3) Å / max = +0.236 (4) Å) and "B" and "D" below (deviations from L.S. plane: min = -0.143 (3) Å / max = -0.229 (3) Å) its *intra*-pyrrole nitrogen counterpart (deviations from L.S. plane: N1, -0.141 (3) Å; N3, -0.183 (3) Å; N2, +0.169 (3) Å; N4, +0.206 (3) Å) – see Figure 2 for visual reference.

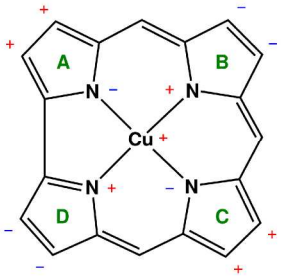


Figure 2. For visual reference, deviations of selected atomic sites from a least-squares fitted plane defined by the 23 atom ($C_{19}N_4$) corrole framework are indicated with "+" and "-" symbols (not indicating local atomic charges). This pattern of deviations most closely resembles a "saddled" corrole conformation

While the $C_{19}N_4$ core has nearly spherical anisotropic atomic displacement parameters, the *tert*-butylphenyl group (located at C10) and the *para* substituents (*tert*-butyl groups) on the *meso*-phenyl rings (located at C5 and C15) have positional disorder (not occupational) and were best modelled in 2 or 3 distinct orientations in the average structure. Relative to the corrole, the Cu atomic site is barely above (+0.017 (1) Å) the fitted 23 atom L.S. plane. The *meso*-phenyl rings form dihedral angles from this L.S. plane of 71.5 (1)° at C5, ~65° at C10 (average of 3 refined orientations with dihedral angles of 69.1 (3)°, 68.3 (3)°, and 57.3(4)° in occupancies of 36.2 (2) %, 33.4 (2) %, and 30.4 (2) %, respectively), and 57.3 (4)° at C15.

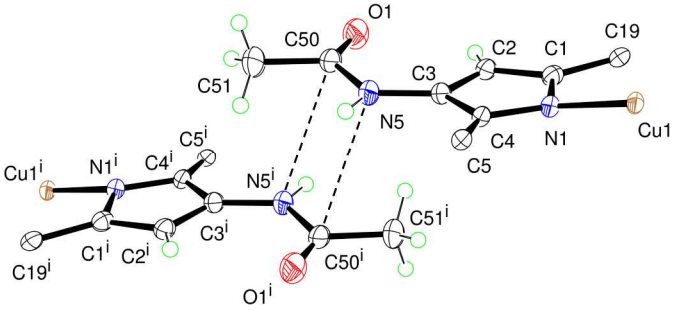


Figure 3. The packing relationship of two neighboring 3-acetylamido groups (with fragment of Cu corrole framework) is shown with a N5···$C50^i$ intermolecular distance of 3.498 (5) Å along the "interatomic" dashed lines (not indicating bonds). The angles are nearly orthogonal with values of 96.2 (2)° for N5—C50···$N5^i$ and 83.8 (2)° for C50—N5···$C50^i$. (Symmetry code: (i) $-x, -y+1, -z$.)

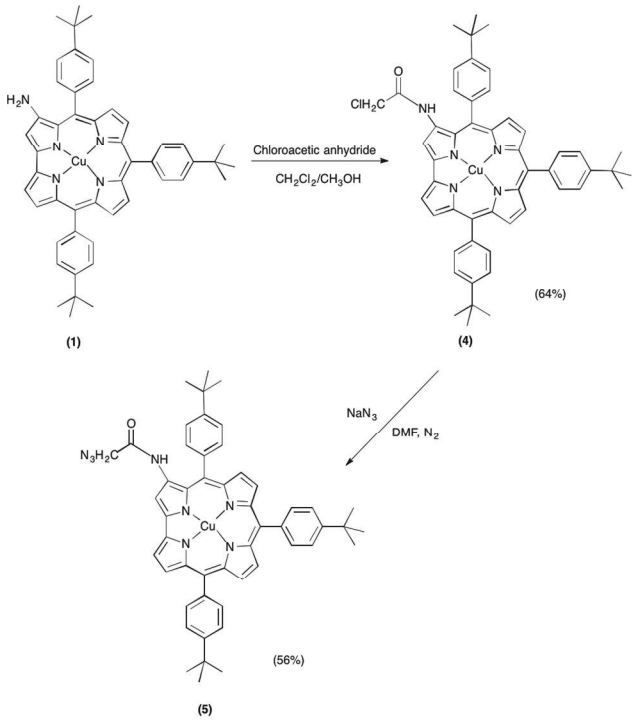
The occupancies of the 2-component positional disorder of the *tert*-butyl groups attached to the phenyl substituents is practically identical with ratios at C5 of 0.71 (1) : 0.29 (1) and

at C15 of 0.705 (5) : 0.295 (5). The 3-acetylamido group (located at C3) deviates significantly less from the 23 atom framework than the *meso*-substituents with a dihedral angle of 18.4 (2)° relative to the L.S. plane and forms a close contact (intermolecular) to a neighboring 3-acetylamido group as shown in Figure 3.

Considering the efficiency and the facile amide formation by this synthetic pathway, we believed these derivatives to be excellent precursors for the anchoring of further attractive functionalities to the corrole macrocycle. In this context, the possibility to introduce a halogen atom on the R chain of the acyl-amido substituent was particularly appealing, since it should enrich the options in hand to further modify the corrole periphery by nucleophilic substitution reactions.

For this purpose, the use of the chloroacetic anhydride in the above *"one pot"* procedure was prevented, since collateral dechlorination would occur in the presence of the Pd/C-$NaBH_4$ reducing system. Hence, for the preparation of copper corrolate **(4)**, the catalytic system was removed after the reduction of the nitrocorrole by filtration through a Celite plug and by washing the residue dissolved in CH_2Cl_2 extensively with water.

Then, the amino derivative formed was used as isolated for the acylation, which afforded the title amide in a 64% yield. The ^{1}H NMR spectrum allowed the identification of this derivative, showing two diagnostic singlets at 8.131 and 3.91 ppm corresponding to the –N*H*C(O) and –CH_2Cl hydrogens respectively.



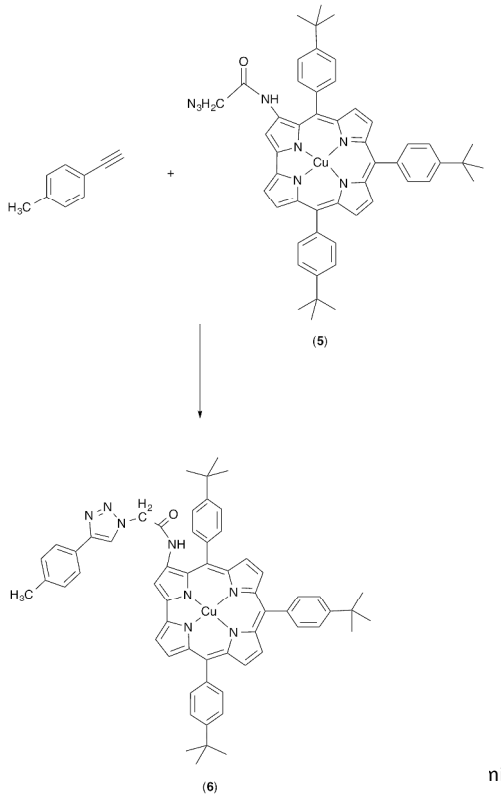
Scheme 2. Preparation of the copper corrole derivatives **(4)** and **(5)**.

Among all the feasible reactions for the chlorine displacement by a nucleophile, the introduction of an azide functionality was particularly attractive in visualizing additional structural enrichment of the corrole framework by applying the click chemistry concept. Therefore, we performed the conversion of the peripheral halogen of amide **(4)** into the $–N_3$ functionality by reaction with sodium azide in DMF at 60 °C. After five hours, the reaction was complete, as shown by TLC analysis; this pointed to total transformation of the starting material into a new, more polar, compound. Chromatographic purification on silica gel eluting with a CH_2Cl_2/petroleum ether solvent mixture (2:1 v/v) afforded the desired compound **(5)** as the main reaction product in a 56% yield. The molecular peak at 854 m/z obtained by FAB mass spectrometry combined with ^{1}H NMR spectrum signals at 7.85 and 3.79 ppm of the amide and the azidomethyl groups, respectively, enabled the characterization of this product. The presence of the azido group was further confirmed by IR spectroscopy which afforded an intense band at 2116 cm^{-1} corresponding to the N≡N asymmetric stretching absorption.

Cycloaddition reactions: click chemistry on β-substituted corroles

The preparation of the corrole (**5**), bearing a peripheral azido group, led us to explore its potential application in the copper-catalyzed Huisgen reaction. This reaction is one of the most popular "click" chemistry reactions, transformations characterized by mild conditions, high yields and simple purification procedures[20]. In the Huisgen cycloaddition, the azido group is reacted with terminal alkynes to give the corresponding triazole derivative and in the porphyin field this reaction has been successfully applied for the realization of elaborated structures involving different porphyrinoids[21].

On the other hand, to the best of our knowledge, in the corrole field there is only one recent report on the exploitation of the Huisgen reaction, for the elaboration of the *meso*-phenyl substituent in order to prepare a BODIPY-corrole dyad[22].

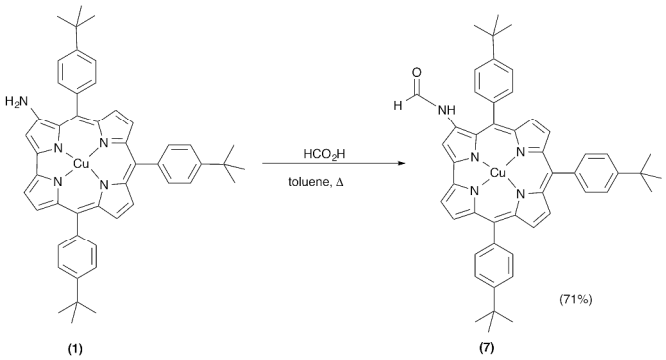


Scheme 3. Click chemistry on corrole (**5**) to give corrole (**6**)

For this reason we performed the reaction of the obtained β-azidomethylcorrole (**5**) with 4-ethynyltoluene in THF at 70 °C, using sodium ascorbate and $CuSO_4 \cdot H_2O$.
After 48 hours the solvent was evaporated and the residue purified on a silica gel column ($CHCl_3$ eluant) to afford the cycloaddition product **(6)** (Scheme 3). Altough the reaction time is longer than those usually observed for this reaction, the yields, although not optimized, were higher than 90%, so demonstrating the synthetic usefulness of this transformation.
The characterization of the product was straightforward, showing the molecular peak at m/z 971 in the FAB mass spectrum. Moreover, the success of the reaction was supported by the ^{1}H NMR spectrum, showing the two diagnostic resonances at 4.55 and 2.39 ppm, attributable to the proton on $-CH_2$ linked to the triazole moiety and the tolyl-CH_3 respectively.

***N*-Formylation:**

Another valuable organic transformation involving the amino group is *N*-formylation to give formamides, an important class of amine derivative involved in various synthetic procedures leading to drugs, fungicides, formamidines and isocyanides, among others. Although several formylation methods have been developed, in our case the employment of formic acid gave good results, affording the formamide **(7)** in a 71% yield. The condensation reaction of the aminocorrole **(1)** with a large excess of formic acid was carried out in refluxing toluene and was complete in about 20 minutes. The main product was purified on a silica gel column eluted with chloroform; it was structurally identified by the usual spectroscopic techniques. In particular, the
two proton resonances in the ^{1}H NMR spectrum at 7.86 and 6.56 ppm correspond to the formyl and amide hydrogens, respectively.



Scheme 4. Preparation of the copper corrole derivatives **(7)**.

Experimental

General. ^{1}H NMR spectra were recorded on a Bruker AV300 spectrometer (300 MHz). FAB mass spectra were recorded on a VGQuattro spectrometer in the positive-ion mode using $CHCl_3$ as solvent and *m*-nitrobenzyl alcohol (Aldrich) as matrix. UV-Vis spectra were measured on a Cary 50 spectrophotometer using CH_2Cl_2 as solvent. IR spectra were recorded in $CHCl_3$ solutions with a Perkin Elmer 100 FT-IR Spectrometer, using KBr cells.
Chromatographic purification on columns was performed using silica gel 60 (70-230 mesh, Sigma Aldrich). Reagents and solvents (Aldrich, Merck or Fluka) were of the highest grade available and were used without further purification. The compound 3-(NO_2)T*t*BuCorrCu used as substrate in all the described reactions was prepared using a literature procedure[12c].
A single crystal X-ray diffraction experiment was conducted at T = 90 K with compound **2** using a Bruker Kappa D8 APEX-II DUO diffractometer equipped with a CCD detector, Cu Kα (λ = 1.54178 Å) IμS microfocus tube, and Oxford Cryosystems cryostream cooler. After atomic assignments of fully occupied sites were completed and remaining electron-density deficient atomic sites were identified in the difference map, positionally disordered substituents (two *tert*-butyl groups and one *tert*-butylphenyl group) were refined as segregated components (using PART command) that were restrained / constrained to be structurally similar (using the SAME / EADP command) in SHELXL-2013. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were modelled in riding positions (with the exception on the amide hydrogen).

3-(NH_2)TtBuCorrCu (1):

3-(NO_2)T*t*BuCorrCu (50 mg, 0.06 mmol) was dissolved in 30 mL of a CH_2Cl_2/MeOH mixture (4:1 v/v) and the solution was purged with nitrogen for 5 min. Then, 10% palladium on carbon catalyst (60 mg) and $NaBH_4$ (118 mg, 3.12 mmol) were added and the solution was stirred under an inert N_2 atmosphere. The colour of the solution rapidly turned brilliant green and UV-Vis spectroscopy monitoring showed the formation in 10 min of a new compound having a blue-shifted Soret band and a single Q band centred at 419 nm and 640 nm, respectively. After 15 min, the reaction was complete and the solution was filtered through a Celite plug. After solvent evaporation under reduced pressure, the residue was taken up in CH_2Cl_2, washed with H_2O and dried over anhydrous Na_2SO_4. Chromatographic purification on silica gel using a CH_2Cl_2/petroleum ether (2:1 v/v) solvent mixture as eluant, afforded the aminocorrole **(1)** as a brownish fraction, which was collected and obtained in a 35 % yield (17 mg) after crystallization from CH_2Cl_2/MeOH.

Since corrole **(1)** was demonstrated to be unstable during the purification process, all the reactions described hereinafter using this substrate were carried out immediately using this crude product.

General procedure for the "one pot" reduction/acylation of 3-(NO_2)TtBuCorrCu

The reduction of 3-(NO_2)T*t*BuCorrCu (50 mg, 0.06 mmol) was carried out using the experimental conditions above described. When the substrate was all consumed, a 12-fold molar excess of anhydride was added, causing a rapid colour change of the solution from emerald green to brownish. Monitoring by UV-Vis spectroscopy evidenced a slight red-shifted of *ca.* 2 nm of the Soret band. After 10 min, the reaction was complete; the mixture was evaporated to dryness, taken up in CH_2Cl_2, filtered through a plug of Celite and evaporated under reduced pressure. After the chromatographic purification, the desired amide was obtained as a brown powder after crystallisation from CH_2Cl_2/MeOH.

3-NHC(O)CH_3-TtBuCorrCu (2): Chromatographic purification on silica gel eluting with $CHCl_3$ gave 28 mg (56% yield) of the title compound.
Mp> 300 °C. UV-Vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.06), 632 (3.91). ^{1}H NMR (300 MHz, $CDCl_3$): 8.66 (1H, br s, β-pyrrole), 8.07 (1H, br s, β-pyrrole), 7.77 (1H, br s, β-pyrrole), 7.68 (2H,d, *J* = 7.8 Hz phenyl), 7.51 (12H, m, β-pyrrole+phenyl), 7.33 (1H, d, *J* = 3.93 Hz β-pyrrole), 6.99 (1H, br s, β-pyrrole), 6.59 (1H, s, -N*H*C(O)CH_3), 1.70 (3H, s, -C*H*$_3$), 1.45 (9H, s, -*t*Bu), 1.44 (9H, s, -*t*Bu), 1.42 (9H, s, -*t*Bu). MS (FAB) : m/z 813(M+). Anal. Calcd for $C_{51}H_{51}CuN_5O$: C, 75.29; H, 6.32; N, 8.61%. Found: C, 75.34; H, 6.38; N, 8.63%.
$C_{51}H_{50}CuN_5O$, *M* = 812.50, Triclinic, *a* = 8.7172 (13) Å, *b* = 9.5695 (16) Å, *c* = 26.860 (5) Å, *α* = 88.821 (7)°, *β* = 89.825 (9)°, *γ* = 71.559 (6)°, *V* = 2125.1 (6) Å^3, *T* = 90(2) K, space group *P*-1 , *Z* = 2, *μ* (Cu Kα) = 1.06 mm^{-1}, 20501 reflections measured, 7465 independent reflections (R_{int} =0.029). The final R_1 values were 0.073 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.189 ($I > 2\sigma(I)$). The final R_1 values were 0.076 (all data). The final $wR(F^2)$ values were 0.187 (all data). The goodness of fit on F^2 was 1.06. CCDC number 997609.

3-[NHC(O)$(CH_2)_4CH_3$]-TtBuCorrCu (3): Chromatographic purification on a silica gel column using a CH_2Cl_2/petroleum ether solvent mixture (4:1 v/v) as eluant afforded 33 mg (61% yield) of the title compound**.**
Mp> 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.00), 632 (3.90). ^{1}H NMR (300 MHz, $CDCl_3$): 8.68 (1H, br s, β-pyrrole), 8.04 (1H, br s, β-pyrrole), 7.78 (1H, d, *J* = 3.33 Hz β-pyrrole), 7.67 (2H, d, *J* = 8.1 Hz phenyl), 7.51 (11H, m, β-pyrrole+phenyl), 7.33 (1H, d, *J* = 4.26 Hz β-pyrrole), 7.24 (1H, br s, β-pyrrole), 6.99 (1H, br s, β-pyrrole), 6.68 (1H, s, -N*H*C(O)), 1.81 (2H, t, -OC*H*$_2$-), 1.46 (9H, s, -*t*Bu), 1.44 (9H, s, -*t*Bu), 1.42 (9H, s, -*t*Bu), 1.24 (6H, m, -OCH$_2$(C*H*$_2$)CH$_3$), 0.89 (3H, t, -C*H*$_3$). MS (FAB) : m/z 869(M+). Anal. Calcd for $C_{55}H_{59}CuN_5O$: C, 75.96; H, 6.84; N, 8.05%. Found: C, 75.79; H, 6.81; N, 8.13%.

Preparation of the 3-functionalized corrole derivatives (4),(5) and (6)

3-NHC(O)CH_2Cl-TtBuCorrCu(4): 50 mg (0.06 mmol) of **1** was subjected to reduction as reported above. After work up, the crude product was dissolved in 30 mL of a CH_2Cl_2/MeOH mixture (4:1 v/v) and acetylated using 123 mg (0.72 mmol) of chloroacetic anhydride. The reaction was complete in 20 min. Chromatographic purification was performed on silica gel eluting with a CH_2Cl_2/petroleum ether solvent mixture (4:1 v/v). The amide was obtained as a brownish powder (33 mg, 64% yield) by crystallisation from CH_2Cl_2/MeOH.
Mp> 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 421 (5.03), 632 (3.94). ^{1}H NMR (300 MHz, $CDCl_3$): 8.75 (br s, 1H, β-pyrrole), 8.11 (s, 1H, -N*H*C(O)), 8.02 (br s, 1H, β-pyrrole), 7.74 (br s, 1H, β-pyrrole), 7.57 (m, 13H, β-pyrrole+phenyl), 7.32 (br s, 1H, β-pyrrole), 7.08 (br s, 1H, β-pyrrole), 7.05 (br s, 1H, β-pyrrole), 3.91 (s, 2H, -C*H*$_2$Cl), 1.44 (br s, 18H, -*t*Bu), 1.42(s, 9H,-*t*Bu). MS (FAB) : m/z 847 (M+). Anal. Calcd for $C_{51}H_{50}ClCuN_5O$: C, 72.24; H, 5.94; N, 8.26%. Found: C, 72.31; H, 5.89; N, 8.35%.

3-NHC(O)CH_2N_3-TtBuCorrCu (5):
Amide **(4)** (33 mg, 0.04 mmol) was dissolved in DMF (13 mL) and NaN_3 (51 mg, 0.78 mmol) was added. The solution rapidly turned brilliant green and it was stirred at 60 °C under N_2. After 5 h, distilled water (10 mL) was added and the precipitate formed was filtered. The residue was taken up in CH_2Cl_2 and applied to a silica gel column that was eluted with a CH_2Cl_2/petroleum ether solvent mixture (2:1 v/v). The main product corresponding to the desired compound was isolated as the first fraction and crystallised from CH_2Cl_2/MeOH to give 19 mg (56% yield). Mp> 300 °C. UV-Vis (CH_2Cl_2): λ_{max}, nm (log ε) 421 (5.03), 630 (3.90). ^{1}H NMR (300 MHz, $CDCl_3$): 8.64 (1H, br s, β-pyrrole), 7.93 (1H, br s, β-pyrrole), 7.85 (1H, s, 1H, -N*H*C(O)), 7.74 (1H, br s, β-pyrrole), 7.65 (4H, d, *J* = 7.86 Hz phenyl), 7.51 (8H, m, phenyl), 7.42 (1H, br s, β-pyrrole), 7.32 (1H, d, *J* =3.60 Hz, β-pyrrole), 7.09 (1H, br s, β-pyrrole), 7.02 (1H, br s, β-pyrrole), 3.79 (2H, s, -C*H*$_2$N$_3$), 1.46 (9H, s, -*t*Bu), 1.44 (9H, s, -*t*Bu), 1.42 (9H, s, -*t*Bu). IR: ($CHCl_3$): ν_{max}/cm^{-1} 2116. MS (FAB) : m/z 854(M+). Anal. Calcd for $C_{51}H_{50}CuN_8O$: C, 71.68; H, 5.90; N, 13.11%. Found: C, 71.59; H, 5.82; N, 13.23%.

3-NHC(O)CH_2(4-tolyl-triazole)TtBuCorrCu (6):
Amide **(5)** (27 mg, 0,03 mmol) was dissolved in THF (50 mL) and 4-ethynyltoluene (8.4 μl, 0.066 mmol) was added. Sodium ascorbate (1.2 mg, 0.0066 mmol) and $(CuSO_4)\cdot 5H_2O$ (0.9 mg, 0.033 mmol) in aqueous solution were added and the mixture heated at 70 °C, under inert atmosphere. After 20 e 40 h 4-ethynyltoluene (0.066 mmol), sodium ascorbate (0.0066 mmol) and $(CuSO_4)\cdot 5H_2O$ (0.033 mmol) were added. The course of the reaction was monitored by TLC (silica gel/$CHCl_3$). After 48 the starting material was all consumed and the presence of a new, more polar, compound was evident. The solvent was evaporated and the crude of the reaction was taken up with chloroform and purified on a silica plug using $CHCl_3$ as eluant. The main product was crystallised from CH_2Cl_2/MeOH giving 26,5 mg of the title compound (91% yield). UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 422 (5.10), 630 (3.92). ^{1}H NMR (300 MHz, $CDCl_3$): 8.46 (br s, 1H, β-pyrrole), 7.94 (s, 1H, -N*H*C(O)), 7.86

(br s, 1H, β-pyrrole), 7.74 (d, 4H, J = 7.7 Hz, phenyl), 7.69 (br s, 1H, β-pyrrole), 7.55 (m, 9H, phenyl and triazole), 7.44 (br s, 1H, β-pyrrole), 7.29 (br s, 1H, β-pyrrole), 7.23 (m, 4H, phenyl), 7.12 (br s, 1H, β-pyrrole), 6,96 (br s, 1H, β-pyrrole), 4.55 (s, 2H, -CH_2-triazole), 2.39 (s, 3H, -CH_3-tolyl), 1.49 (s,9H -tBu), 1.44 (s, 9H -tBu), 1.42 (s, 9H -tBu). MS (FAB) : m/z 970(M+). Anal. Calcd for $C_{60}H_{57}CuN_8O$: C, 74.32; H, 5.92; N, 11.56%. Found: C, 74.36; H, 5.89; N, 11.53%.

3-NHC(O)H-TtBuCorrCu (7):

The crude product from the reduction of 3-(NO_2)T*t*BuCorrCu (50 mg, 0.06 mmol) was dissolved in toluene (13 mL) and the solution was heated to reflux. Then, 1 mL of 85% formic acid was added and the reaction was monitored by UV-Vis spectroscopy. The red-shift of the Soret band was indicative of the effective formylation of the amino group. After 20 min, the solution was cooled and evaporated on a rotary evaporator. The crude material was applied to a silica gel column, using $CHCl_3$ as eluant. 35 mg of compound **5** were obtained as a brownish powder after crystallization from $CHCl_3$/MeOH (71% yield). Mp> 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 421 (4.99), 631 (3.92). ^{1}H NMR (300 MHz, $CDCl_3$): 8.56 (1H, br s, β-pyrrole), 7.91 (1H, br s, β-pyrrole), 7.86 (1H, s, -NHC*H*O), 7.72 (1H, br s, β-pyrrole), 7.63 (4H, m, phenyl), 7.53 (8H, m, phenyl), 7.43 (1H, br s, β-pyrrole), 7.31 (1H, d, J = 3.99 Hz, β-pyrrole), 7.14 (1H, br s, β-pyrrole), 7.09 (1H, br s, β-pyrrole), 6.56 (1H, s, -N*H*CHO), 1.45 (9H, s, -*t*Bu), 1.43 (9H, s, -*t*Bu), 1.42 (9H, s, -*t*Bu). MS (FAB) : m/z 799(M+). Anal. Calcd for $C_{50}H_{49}CuN_5O$: C, 75.11; H, 6.18; N, 8.76%. Found: C, 75.21; H, 6.13; N, 8.69%.

Conclusions

Herein we report the first examples of organic manipulation of the nitro group in a β-functionalized copper corrolate. The reduction performed on the Cu 3-NO_2-5,10,15-triarylcorrolato offers the corresponding amino-derivative which was exploited for the further derivatization of corrole macrocycle, via amide functions. This synthetic tool was demonstrated to be successful, affording easily a number of β-acylated products in good yields. Notably, it is to highlight that the achievement of corrole **(5)** bearing the azidomethyl group has been crucial for further corrole functionalization by Huisgen "click" reaction.

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Notes and references

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