Supplementary Material (ESI) for Chemical Communications

Functionalization of the corrole ring: the role of isocorrole intermediates

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Electronic Supplementary Information

Reagents and solvents (Sigma-Aldrich and Carlo Erba Reagenti) were of synthetic grade and used without further purification. Analytical TLC's were performed on Merck Silica Gel 60 F_{254} aluminum support. Chromatographic separations were performed on silica gel 60 (70-230 mesh) or neutral alumina (Brockmann Grade III) columns (Carlo Erba Reagenti).

UV-Visible spectra were recorded on a Varian Cary 50 Spectrophotometer. ^{1}H NMR experiments were conducted on a Bruker Avance 300 spectrometer. Mass spectra were recorded on a VG Quattro spectrometer in the positive-ion mode, using m-nitrobenzyl alcohol (NBA, Aldrich) as a matrix (FAB) or on a Voyager DE STR Biospectrometry workstation in the positive mode, using α-cyano-4-hydroxycinnamic acid as a matrix (MALDI).

3-NO_2-ttcorrH_3. The parent ttcorrH_3 was prepared according to literature methods (R. Paolesse, A. Marini, S. Nardis, A. Froiio, F. Mandoj, D. J. Nurco, L. Prodi, M. Montalti, K. M. Smith, *J. Porphyrins Phthalocyanines* **2003**, *7*, 25). The corrole was nitrated with $AgNO_2$ (100 equiv.) and demetallated with DBU (20 equiv.) following the method previously published (M. Stefanelli, J. Shen, W. Zhu, M. Mastroianni, F. Mandoj, S. Nardis, Z. Ou, K. M. Kadish, F. R. Fronczek, K. M. Smith, R. Paolesse, *Inorg. Chem.* **2009**, *48*, 6879).

Anal. found for $C_{40}H_{31}N_5O_2$: C, 78.2; H, 5.1; N, 11.3. Calcd: C, 78.3; H, 5.0; N, 11.4%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 397 (4.75), 438 (4.68) 465 (4.69), 587 (4.20) 664 (4.29) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.96 (s, 1H, *β* –pyrr.), 8.60 (d, ^{1}J= 4.6 Hz, 2H, *β* –pyrr.), 8.52 (d, ^{1}J= 3.98 Hz, 1H, *β* –pyrr.), 8.38 (d, ^{1}J= 4.11 Hz, 1H, *β* –pyrr.), 8.34 (d, ^{1}J= 4.87 Hz, 1H, *β* –pyrr.), 8.23 (d, ^{1}J= 4.58 Hz, 1H, *β* –pyrr.), 8.12 (d, ^{1}J=

7.74 Hz, 2H, phenyl), 7.97 (m, 4H, phenyl), 7.62 (d, ^{1}J= 7.79 Hz, 2H, phenyl), 7.55 (m, 4H, phenyl), 2.68 (s, 3H, *p*-CH_3), 2.67 (s, 3H, *p*-CH_3), 2.63 (s, 3H, *p*-CH_3). MS (FAB): *m/z* 613 (M^+).

General procedures for bromination of 3-NO_2-ttcorrH_3

Method A

3-NO_2-ttcorrH_3 (50 mg, 81 μmol) and N-bromosuccinimide (29 mg, 162 μmol) were dissolved in 50 mL of $CHCl_3$ and heated under reflux. After 30 min. the reaction was quenched with pyridine and the crude mixture was chromatographed on silica gel, eluting with CH_2Cl_2/hexane (1:1). Two fractions were collected, but TLC analysis showed the incomplete separation of the two products; the first green-brownish fraction was then reacted with Co(II) acetate and PPh_3 in refluxing methanol and the crude reaction mixture was chromatographed on preparative TLC, eluting with CH_2Cl_2/hexane (1:1). The first red fraction was isolated, affording 8 mg (9% yield) of (2,3-Br_2-17-NO_2-ttcorr)Co(PPh_3).

(2,3-Br_2-17-NO_2-ttcorr)Co(PPh_3): Anal. found for $C_{58}H_{41}Br_2CoN_5O_2P$: C, 63.8; H, 3.6; N, 6.5. Calcd: C, 63.9; H, 3.7; N, 6.4%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 395 (4.76), 594 (3.86) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 9.11 (s, 1H, *β* –pyrr.), 8.35 (d, 2H, ^{1}J= 4.86 Hz, *β* –pyrr.), 8.16 (d, 1H, ^{1}J= 4.83 Hz, *β* –pyrr.), 8.10 (d, 1H, ^{1}J= 5.05 Hz, *β* –pyrr.), 7.91 (d, 2H, ^{1}J= 7.93 Hz, phenyl), 7.41 (m, 8H, phenyl), 7.17 (m, 5H, phenyl+*p*-PPh_3), 6.80 (m, 6H, *m*-PPh_3), 4.87 (m, 6H, *o*-PPh_3), 2.62 (s, 3H, *p*-CH_3), 2.59 (s, 3H, *p*-CH_3), 2.57 (s, 3H, *p*-CH_3). MS (FAB): *m/z* 1089 (M^+).

The second green band of the original column was chromatographed on preparative TLC, eluting with CH_2Cl_2/hexane (1:1); the second green spot was crystallized from CH_2Cl_2/hexane, to give 30 mg (52% yield) of 2-Br-15-OH-17-NO_2-ttisocorrH_2.

2-Br-15-OH-17-NO_2-ttisocorrH_2: Anal. found for $C_{40}H_{30}BrN_5O_3$: C, 67.7; H, 4.1; N, 9.8. Calcd: C, 67.8; H, 4.2; N, 9.8%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 400 (4.77), 631 (4.10), 685 (4.09) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 16.25 (s, 1H, NH), 14.70 (s, 1H, NH), 7.47 (m, 4H, phenyl), 7.33 (m, 3H, phenyl), 7.23 (m,

3H, phenyl), 7.10 (m, 3H, phenyl + β –pyrr.), 6.90 (d, ^{1}J= 4.76 Hz, 1H, β –pyrr.), 6.70 (d, ^{1}J= 4.76 Hz, 1H, β –pyrr.), 6.54 (m, 1H, β –pyrrolic), 6.27 (m, 2H, β –pyrrolic), 2.49 (s, 3H, *p*-CH_3), 2.45 (s, 3H, *p*-CH_3), 2.29 (s, 3H, *p*-CH_3). MS (MALDI): *m/z* 708.518 (M^+).

Method B

A solution of NBS (29 mg, 162 μmol) in $CHCl_3$ (15 mL) was added dropwise to 3-NO_2-ttcorrH_3 (50 mg, 81 μmol) dissolved in $CHCl_3$ (20 mL), for 1 h at room temperature. After the addition was completed, the mixture was stirred for further 30 min. The reaction was quenched with pyridine, the mixture was concentrated under reduced pressure to yield the crude product, which was then purified by silica gel chromatography, eluting with CH_2Cl_2/hexane (1:1). The green fraction was crystallized from CH_2Cl_2/hexane, obtaining green crystals of 2-Br-15-OH-17-NO_2-ttisocorrH_2 (46 mg, yield: 80%).

Bromination of 3-NO_2-5-OH-ttisocorH_2

3-NO_2-5-OH-ttisocorH_2. ttcorH_3 (1g, 1.7 mmol) and $NaNO_2$ (2.14 g, 0.17 mol) were dissolved in DMF (30 mL) and stirred at room temperature for 15 min. Chloranil (418 mg, 1.7 mmol) was added and stirring was continued for additional 15 min, checking the reaction progress by TLC (CH_2Cl_2/hexane 1:1) and UV-vis spectroscopy. Hydrazine was then added to quench the excess chloranil, the crude mixture was precipitated with water and filtered under vacuum. The precipitate was dissolved with $CHCl_3$, washed with water and dried over sodium sulfate. The product was evaporated under reduced pressure and purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (1/1) as eluant (858 mg, yield: 80%). Anal. found for $C_{40}H_{31}N_5O_3$: C, 76.4; H, 4.8; N, 11.1. Calcd: C, 76.4; H, 4.9; N, 11.2%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 397 (4.75), 616 (4.06), 672 (4.01) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 16.38 (s, 1H, NH), 14.96 (s, 1H, NH), 7.49 (m, 4H, phenyl), 7.32 (m, 3H, phenyl), 7.22 (m, 3H, phenyl), 7.15 (d, ^{1}J= 2.70, 1H, β –pyrr.), 7.11 (m, 3H, phenyl + β –pyrr.), 6.93 (d, ^{1}J= 4.50 Hz, 1H, β –pyrr.), 6.88 (d, ^{1}J= 4.70 Hz, 1H, β –pyrr.), 6.69 (d,

^{1}J= 4.70 Hz, 1H, β –pyrr.), 6.54 (m, 1H, β –pyrr.), 6.27 (m, 1H, β –pyrr.), 2.49 (s, 3H, *p*-CH_3), 2.45 (s, 3H, *p*-CH_3), 2.29 ppm (s, 3H, *p*-CH_3). MS(MALDI): *m/z* 630.701 (M^+).

2-Br-15-OH-17-NO_2-ttisocorrH_2. A solution of NBS (28 mg, 158 μmol) in $CHCl_3$ (15 mL) was added dropwise to 3-NO_2-5-OH-ttisocorH_2 (50 mg, 79 μmol) dissolved in $CHCl_3$ (20 mL), for 1 h at room temperature. After the addition was completed, the mixture was stirred for further 30 min. The reaction was quenched with pyridine, the mixture was concentrated under reduced pressure to yield the crude product, which was purified by silica gel chromatography, eluting with CH_2Cl_2/hexane (1:1), to give the title isocorrole (48 mg, 85% yield)

2-Br-17-NO_2-ttcorrH_3. $NaBH_4$ (50 mg, 1.31 mmol) was added to a solution of 2-Br-15-OH-17-NO_2-ttisocorrH_2 (24 mg, 34 μmol) in dichloromethane (20 mL) and methanol (4 mL) under a N_2 atmosphere. The progress of the reaction was monitored by TLC (petroleum ether/CH_2Cl_2 1/1) and UV-vis spectroscopy. The crude mixture was washed several times with water, extracted with dichloromethane, the organic phase dried over sodium sulfate and the solvent evaporated under reduced pressure. Pure corrole was obtained after two chromatographic separations: a silica gel short plug column using a solution of petroleum ether/CH_2Cl_2 (2/3) was first carried out to remove baseline material and then a column chromatography on basic alumina (petroleum ether/ CH_2Cl_2 1/1 as eluant) afforded the 2-Br-17-NO_2-ttcorrH_3, crystallized from CH_2Cl_2/hexane as green crystals (15 mg, 65% yield).

Anal. found for $C_{40}H_{30}BrN_5O_2$: C, 69.4; H, 4.3; N, 10.0. Calcd: C, 69.3; H, 4.3; N, 10.1%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 398 (4.68), 436 (4.69) 465 (4.76), 664 (4.28) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 9.21 (s, 1H, β –pyrr.), 8.55 (d, ^{1}J= 5.01 Hz, 1H, β –pyrr.), 8.50 (d, ^{1}J= 4.70 Hz, 1H, β –pyrr.), 8.45 (s, 1H, β –pyrr.), 8.28 (d, ^{1}J= 5.01 Hz, 1H, β –pyrr.), 8.17 (d, ^{1}J= 4.78 Hz, 1H, β –pyrr.), 8.03 (m, 4H, phenyl), 7.93 (d, ^{1}J= 7.91 Hz, 2H, phenyl), 7.56 (m, 6H, phenyl), 2.49 (s, 3H, *p*-CH_3), 2.45 (s, 3H, *p*-CH_3), 2.29 (s, 3H, *p*-CH_3). MS (MALDI): *m/z* 692.702 (M^+).

(3-Br-17-NO_2ttcor)Ag. The bromination reaction was carried out with the same procedure shown in method B, but using 1:3 equivalent of NBS. Yield: 75%. Anal. found for $C_{40}H_{27}AgBrN_5O_2$: C, 60.3; H, 3.5; N, 8.8. Calcd: C, 60.2; H, 3.4; N, 8.7%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 428 (4.72), 449 (sh. 4.68), 588 (4.45), 617 (4.44) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 9.39 (s, 1H, β –pyrr.), 8.96 (s, 1H, β –pyrr.), 8.60 (d, ^{1}J= 4.76 Hz, 1H, β –pyrr.), 8.44 (m, 3H, β –pyrr.), 8.00 (m, 4H, phenyl), 7.88 (d, ^{1}J= 7.78 Hz, 2H, phenyl), 7.57 (m, 6H, phenyl), 2.69 (s, 3H, *p*-CH_3), 2.67 (s, 3H, *p*-CH_3), 2.65 ppm (s, 3H, *p*-CH_3). MS (MALDI): *m/z* 797.397 (M^+).

3-Br-17-NO_2-ttcorrH_3. (3-Br-17-NO_2ttcor)Ag (III) was demetallated with DBU, according to the previously published procedure (M. Stefanelli, J. Shen, W. Zhu, M. Mastroianni, F. Mandoj, S. Nardis, Z. Ou, K. M. Kadish, F. R. Fronczek, K. M. Smith, R. Paolesse, *Inorg. Chem.* **2009**, *48*, 6879) Yield: 70%. Anal. found for $C_{40}H_{30}BrN_5O_2$: C, 69.3; H, 4.2; N, 10.2. Calcd: C, 69.3; H, 4.3; N, 10.1%. UV-vis: λ_{max} (CH_2Cl_2, log ε)= 398 (4.75), 436 (4.68) 465 (4.67), 664 (4.28) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.93 (s, 1H, β –pyrr.), 8.65 (s, 1H, β –pyrr.), 8.56 (d, ^{1}J= 4.71 Hz, 1H, β –pyrr.), 8.37 (d, ^{1}J= 4.39 Hz, 1H, β –pyrr.), 8.28 (d, ^{1}J= 4.83 Hz, 1H, β –pyrr.), 8.17 (d, ^{1}J= 4.32 Hz, 1H, β –pyrr.), 8.02 (d, ^{1}J= 7.72 Hz, 2H, phenyl), 7.91 (m, 4H, phenyl), 7.54 (d, ^{1}J= 7.47 Hz, 6H, phenyl), 2.69 (s, 6H, *p*-CH_3), 2.67 (s, 6H, *p*-CH_3), 2.63 ppm (s, 3H, *p*-CH_3). MS (MALDI): *m/z* 692.648 (M^+).

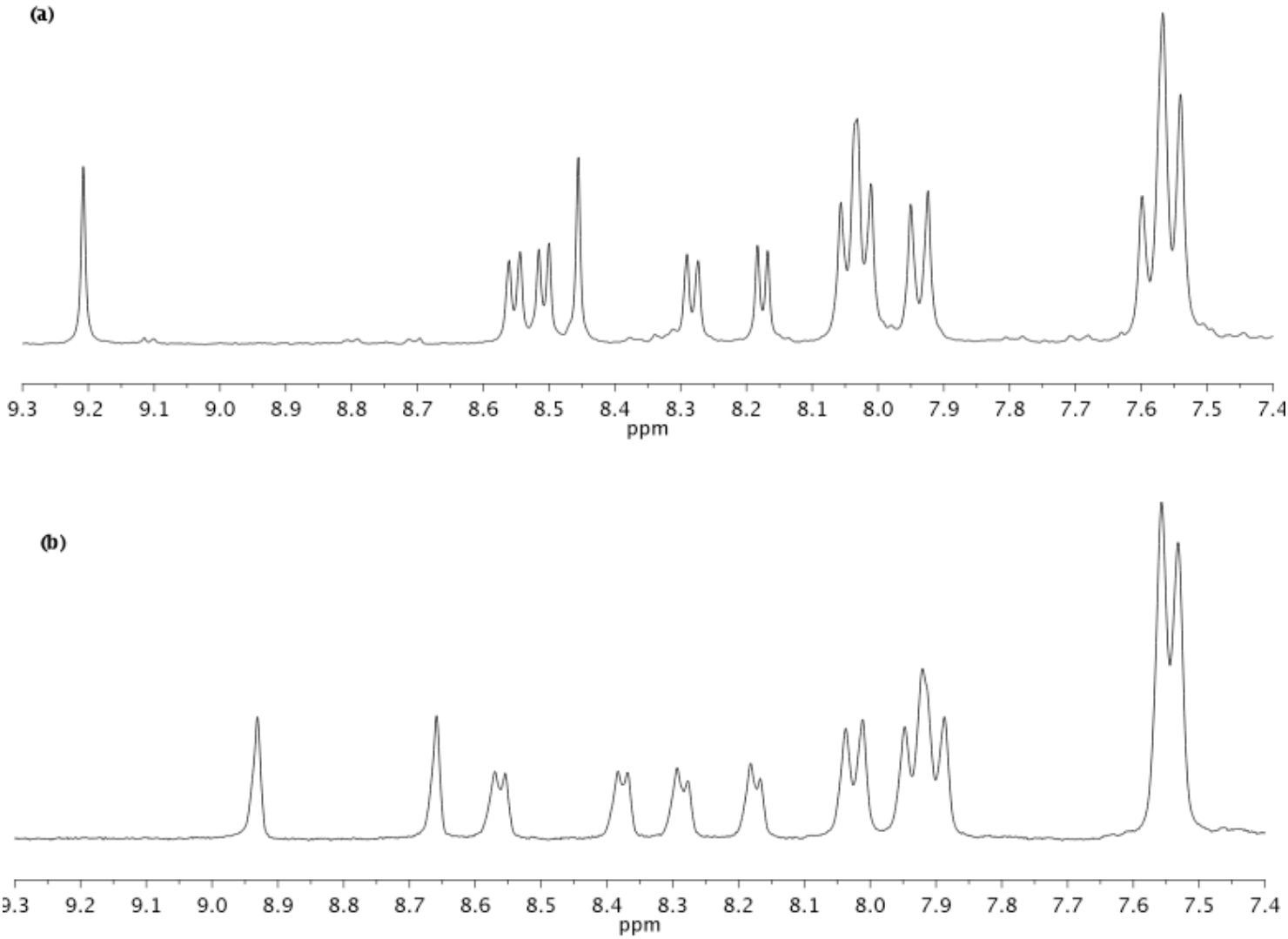

Figure S1. ^{1}H NMR spectra of (a) 2-Br-17-NO_2-ttcorrH_3 and (b) 3-Br-17-NO_2-ttcorrH_3 (aromatic region)