Supporting information to the manuscript entitled 'Rational and new synthesis of corroles bearing up to three different meso substituents' (authors: Roger Guillard, Daniel T. Gryko, Gabriel Canard, Jean-Michel Barbe, Beata Koszarna, Stéphane Brandès and Mariusz Tasior).

Experimental Section

General. All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2 , hexanes) were distilled prior use. The acylations with acid chlorides were performed in freshly distilled toluene (CaH_2). In all acylation procedures involving EtMgBr , 1.0 M solution in THF has been used. All reported ^1H NMR spectra were collected on Bruker AM 500MHz. UV-Vis absorption spectra were recorded in toluene (Cary). Chromatography was performed on silica (Kieselgel 60, 200-400 mesh) or alumina (Fluka). Mass spectra were obtained via electron impact (EI) and electrospray (ESI-MS). The following compounds were prepared as described in the literature: ester **8**,¹ all dipyrromethanes,² diacyl derivatives **1a**,³ **1b**,⁴ **1c**,⁴ **1f**.⁵

1,9-Bis(4-methylbenzoyl)-5-(mesityl)dipyrromethane (1g). Following the general procedure⁴ starting from 5-mesityldipyrromethane (5.28 g, 20 mmol), 100 mL of ethylmagnesium bromide (1M in THF) and 6.66 mL (50 mmol) of 4-methylbenzoyl chloride. The crude product was purified on a silica gel column (eluent $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 99/1 and 95/5) and recrystallized from CH_2Cl_2 /heptane (49% yield, 4.93 g). ^1H NMR (CDCl_3 , 300K, 500MHz), δ (ppm) : 2.18 (s, 6H) ; 2.32 (s, 3H) ; 2.42 (s, 6H) ; 6.10 (m, 3H) ; 6.75 (m, 2H) ; 6.92 (s, 2H) ; 7.23 (d, $J = 8.0$ Hz, 4H) ; 7.72 (d, $J = 8.0$ Hz, 4H) ; 10.04 (br s, 2H). MS (MALDI/TOF) : $m/z = 501.05$ uma $[\text{M}+\text{H}^+]$. MS (EI) : $m/z = 500$ uma $[\text{M}^{++}]$; Anal. Calcd for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_2$: C, 81.57; H, 6.44; N, 5.60. Found: C, 81.18; H, 6.82; N, 5.38.

1,9-Bis(2,6-difluorobenzoyl)-5-(pentafluorophenyl)dipyrromethane (1d). Following the general procedure,⁴ a solution of EtMgBr (50.0 mL, 50.0 mmol) was added slowly to a stirred, tap-water cooled flask containing a solution of 5-pentafluorophenyldipyrromethane **1** (3.10 g, 10 mmol) in toluene (200 mL) under an Ar atmosphere. The resulting brown solution was stirred for 30 min at room temperature. Then a solution of 2,6-difluorobenzoyl chloride (3.14 mL, 25 mmol) in toluene (25 mL) was added over 10 min. The solution darkened and the mixture was stirred for an additional 10 min. The reaction was quenched by adding of satd aq NH_4Cl (150 mL). Ethyl acetate (200 mL) was then added. The organic phase was washed successively with water and brine and then dried (Na_2SO_4). The solvents were removed under vacuum to afford brown oil which was chromatographed (silica, hexanes/ EtOAc , 9:1 then 4:1). Fractions containing desired diacyldipyrromethane were evaporated and crystallized from EtOAc to afford 815 mg of **1d**. The supernatant was chromatographed (silica, toluene/hexanes, 9:1) to obtain additional 300 mg (total yield 19%): mp 280-281 °C; ^1H NMR (DMSO) δ 5.97 (br t, $J = 3.0$ Hz, 2H), 6.06 (s, 1H), 6.56 (s, 2H), 7.23 (t, $J = 8.0$ Hz, 4H), 7.55-7.65 (m, 2H), 12.51 (br s, 2H); ^{13}C NMR (DMSO) δ 32.6, 95.4, 110.5, 112.1, 116.7, 120.8, 131.7, 132.2, 138.8, 157.8, 159.8, 175.2; IR (KBr) $\nu = 3442, 3257, 1625, 1504, 1465, 1409, 1237$; EI-MS obsd 592.0838, calcd exact mass 592.0833 ($\text{C}_{29}\text{H}_{13}\text{F}_9\text{N}_2\text{O}_2$); Anal. Calcd for $\text{C}_{29}\text{H}_{13}\text{F}_9\text{N}_2\text{O}_2$: C, 58.80; H, 2.21; N, 4.73. Found: C, 58.39; H, 2.44; N, 4.47.

1,9-Bis(4-tert-butylbenzoyl)dipyrromethane (1e). Following the general procedure,⁴ a solution of EtMgBr (25.0 mL, 25.0 mmol) was added slowly to a stirred, tap-water cooled flask containing a solution of dipyrromethane (0.73 g, 5 mmol) in toluene (100 mL) under an Ar atmosphere. The resulting brown solution was stirred for 30 min at room temperature. Then a solution of 4-tert-butylbenzoyl chloride (2.44 mL, 12.5 mmol) in toluene (12.5 mL) was added over 10 min. The solution darkened and the mixture was stirred for an additional 10 min. The reaction was quenched by adding of satd aq NH_4Cl (75 mL). Ethyl acetate (100 mL) was then added. The organic phase was washed successively with water and brine and then dried (Na_2SO_4). The solvents were removed under vacuum to afford a brown oil which was chromatographed (silica, $\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 98:2 then 94:6 then 90:10). Fractions containing desired diacyldipyrromethane were evaporated and crystallized from THF/hexanes to afford 753 mg of **1e**. The supernatant was crystallized from THF/hexanes to obtain additional 101 mg (total yield 37%): mp 260-261 °C; ^1H NMR (DMSO) δ 1.30 (s, 18H), 4.01 (s, 2H), 6.05-6.10 (m, 2H), 6.65-6.70 (m, 2H), 7.51, 7.72 (AA'BB', 8H), 11.93 (br s, 2H); ^{13}C NMR (DMSO) δ 25.5, 30.9, 34.6, 109.3, 119.6, 125.1, 128.4, 131.1, 135.8, 137.9, 154.3, 182.8; IR (KBr) $\nu = 3294, 2961, 1630, 1544, 1481, 1408, 1301, 1232, 887$; EI-MS obsd 462.2618, calcd exact mass 462.2620 ($\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_2$); Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_2$: C, 79.79; H, 7.34; N, 6.00. Found: C, 79.40; H, 7.44; N, 5.81.

1-(4-Methylbenzoyl)-5-pentafluorophenyldipyrromethane (9). This compound was prepared as previously described¹ from 3.12 g (10 mmol) of 5-pentafluorophenyldipyrromethane, 25 mL of ethylmagnesium bromide (1M in THF), and 2.3 g (10 mmol) of *S*-2-pyridyl 4-methylbenzothioate. The 1-(4-methylbenzoyl)-5-pentafluorophenyldipyrromethane is obtained after column chromatography on silica gel (eluent: $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 95/5) (82% yield, 3.52 g). mp 169-170 °C; ^1H NMR (CDCl_3 , 300K, 300MHz), δ (ppm) : 2.43 (s, 3H) ; 5.93 (s, 1H) ; 6.07 (m, 1H) ; 6.13 (s, 1H) ; 6.18 (m, 1H) ; 6.75 (m, 1H) ;

6.79 (m, 1H); 7.27 (d, $J = 8.1$ Hz, 2H) ; 7.76 (d, $J = 8.1$ Hz, 2H) ; 8.32 (br s, 1H); 9.62 (br s, 1H). EI-MS obsd 430.11478 calcd exact mass 430.11045 ($C_{23}H_{15}F_5N_2O$); MS (MALDI/TOF) : $m/z = 431.08$ uma [$M+H^+$]. MS (EI) : $m/z = 430$ uma [M^+]. Anal. Calcd for $C_{23}H_{15}F_5N_2O$: C, 64.19; H, 3.51; N, 6.51. Found: C, 64.55; H, 3.52; N, 6.66.

1-(4-Methylbenzoyl)-5-pentafluorophenyl-9-(4-methoxybenzoyl)-dipyrrromethane (2a). This compound was prepared following the general procedure⁴ from 4.3 g (10 mmol) of 1-(4-methylbenzoyl)-5-pentafluorophenyldipyrrromethane **9**, 60 mL ethylmagnesium bromide (1M in THF), and 5.12 g (30 mmol) of 4-anisoyl chloride. The crude compound was chromatographed on silica gel (eluent CH_2Cl_2 /EtOAc 95/5) then recrystallized from ether/heptane (47% yield, 2.62 g). 1H NMR ($CDCl_3$, 300K, 300 MHz), δ (ppm) : 2.40 (s, 3H) ; 3.85 (s, 3H) ; 6.09 (s, 3H) ; 6.65 (m, 2 H) ; 6.92 (d, $J = 8.9$ Hz, 2H); 7.23 (d, $J = 8.1$ Hz, 2H) ; 7.72 (d, $J = 8.1$ Hz, 2H) ; 7.82 (d, $J = 8.9$ Hz, 2H); 10.72 (br s, 2H); MS (MALDI/TOF) : $m/z = 564.87$ [M^+]; Anal. Calc for $C_{31}H_{21}F_5N_2O_3$: C, 65.96 %; H, 3.75 %; N, 4.96 %. Found: C, 66.21 %; H, 4.00 %; N, 4.81 %.

1-(4-Methylbenzoyl)-5-pentafluorophenyl-9-(4-*tert*-butylbenzoyl)-dipyrrromethane (2b). Following the general procedure,⁴ to a stirred solution of monoacyl dipyrrromethane **9** (645 mg, 1.5 mmol) in dry toluene (6 mL) at room temperature was added a solution of EtMgBr (3.0 mL, 3.0 mmol) slowly under an Ar atmosphere. The resulting mixture was stirred for 5 min at room temperature. To the resulting mixture 4-*tert*-butylbenzoyl chloride (0.30 mL, 1.5 mmol) was added. After 10 min the same process was repeated once. After stirring for 10 min, the mixture was treated with additional EtMgBr (1.5 mL, 1.5 mmol) followed by 4-*tert*-butylbenzoyl chloride (0.15 mL, 0.75 mmol). After 20 min the reaction was quenched by adding of satd aq NH_4Cl (25 mL). Ethyl acetate (25 mL) was then added. The organic phase was washed successively with water and brine and then dried (Na_2SO_4). The solvents were removed under vacuum to afford a brown oil which was chromatographed (silica, toluene then toluene/EtOAc, 95:5). Fractions containing desired diacyldipyrrromethane were evaporated and washed with hot EtOAc to afford 378 mg of **2b**. The supernatant was evaporated, hot EtOAc was added and slurry was cooled down. Filtration afforded additional 447 mg (total yield 50%): mp 272-273 °C; 1H NMR ($CDCl_3$) δ 1.32 (s, 9H), 2.43 (s, 3H), 6.07 (m, 2H), 6.13 (s, 1H), 6.59 (m, 2H), 7.47-7.52 (m, 4H), 7.70-7.80 (4H), 11.05 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 25.5, 31.6, 35.1, 97.5, 99.4, 104.1, 110.7, 113.6, 120.4, 126.9, 127.9, 129.3, 130.9, 131.1, 131.6, 136.2, 136.5, 136.9, 137.1, 137.4, 138.9, 143.5, 146.2, 183.3; IR (KBr) $\nu = 3435, 3265, 1650, 1513, 1469, 1417, 1248$; EI-MS obsd 590.1987, calcd exact mass 590.1993 ($C_{34}H_{27}F_5N_2O_2$); Anal. Calcd for $C_{34}H_{27}F_5N_2O_2$: C, 69.15; H, 4.61; N, 4.74. Found: C, 68.82; H, 4.36; N, 4.66.

5,15-Bis-(4-methylbenzoyl)-10-mesityl bilane (3a). The experimental procedure for the synthesis of 5,15-bis-(4-methylbenzoyl)-10-mesityl bilane was adapted from literature.⁶ 1.88 g (3.75 mmol) of 1,9-bis-(4-methylbenzoyl)-5-mesityldipyrrromethane **1g** were dissolved in 165 mL of THF/MeOH (10/1). 11.41 g of solid $NaBH_4$ (300 mmol) were then slowly added and stirring was performed for one hour. The reaction mixture was poured in a flask containing 400 mL of CH_2Cl_2 and 400 mL of saturated NH_4Cl in water. The organic layer was washed with water, dried over $MgSO_4$ and then evaporated. After dissolution of the crude solid in 26 mL (375 mmol) of freshly distilled pyrrole, 70 μ L (0.56 mmol, 0.15 eq) of $BF_3 \cdot Et_2O$ were added. The reaction mixture was stirred at room temperature for 7 min. and 300 mL of CH_2Cl_2 were added. Neutralization was performed with 0.1 M NaOH in water. The organic layer was washed with water, dried over $MgSO_4$ and evaporated. The oil residue was chromatographed on silica gel (eluent: CH_2Cl_2). The resulting solid was taken with pentane, filtered and dried under vacuum (62% yield, 1.4 g); 1H NMR ($CDCl_3$, 300K, 300MHz), δ (ppm) : 2.01 (s, 6H) ; 2.23 (s, 3H) ; 2.31 (s, 6H) ; 5.30 (s, 2H) ; 5.72 (s, 5H) ; 5.81 (m, 2H) ; 6.11 (m, 2H) ; 6.64 (br s, 2H) ; 6.77 (s, 2H) ; 7.01-7.11 (m, 8H) ; 7.64 (br s, 2H) ; 7.85 (br s, 2H); EI-MS obsd 602.33812, calcd exact mass 602.34095 ($C_{42}H_{42}N_4$); Anal. Calcd for $C_{42}H_{42}N_4$: C, 83.68 %; H, 7.02 %; N, 9.29 %. Found: C, 83.36 %; H, 7.06 %; N, 9.30 %.

5-(4-Methylbenzoyl)-10-(pentafluorophenyl)-15-(4-methoxyphenyl) bilane (3b). 0.56 g (1 mmol) of 1-(4-methylbenzoyl)-5-pentafluorophenyl-9-(4-methoxybenzoyl)-dipyrrromethane **2a** were dissolved in 44 mL of THF/MeOH (10/1). 3.8g of solid $NaBH_4$ (100 mmol) were then slowly added and the reaction mixture was stirred at room temperature for one hour. The mixture is then poured in 100 mL of CH_2Cl_2 and 100 mL of a saturated NH_4Cl solution. The organic layer was washed with water, dried over $MgSO_4$ and evaporated. The crude solid was then dissolved in 10 mL (145 mmol) of freshly distilled pyrrole. 18.7 μ L (0.15 mmol, 0.15 eq) of $BF_3 \cdot Et_2O$ were added. The mixture was stirred at room temperature for 7 min., then diluted with 300 mL of CH_2Cl_2 , and neutralized by a 0.1 M NaOH solution. The organic layer was washed with water and dried over $MgSO_4$ and evaporated. The oil residue was chromatographed on two successive basic alumina columns (eluent: CH_2Cl_2 /heptane 1/1). The resulting solid was taken with pentane and filtered (65% yield, 0.36 g); 1H NMR (DMSO, 353K, 500 MHz), δ (ppm) : 2.27 (s, 3H) ; 3.73 (s, 3H) ; 5.27 (m, 2H) ; 5.56 (m, 2H) ; 5.65 (m, 4H) ; 5.72 (s, 1H) ; 5.90 (m, 2H) ; 6.59 (s, 2H) ; 6.83 (m, 2H) ; 7.05 (m, 6H) ; 10.23 (m, 4H); MS (MALDI/TOF) : $m/z = 666.42$ uma [M^+]; Anal. Calcd for $C_{39}H_{31}F_5N_4O$: C, 70.26%; H, 4.69%; N, 8.40%. Found: C, 69.77%; H, 5.27%; N, 8.13 %.

5,10,15-Triphenylcorrole (4). A solution of diacyldipyrrromethane **1a** (430 mg, 1.0 mmol) in THF/methanol (3:1, 80 mL) was reduced by adding portions of $NaBH_4$ (2.0 g, 50 mmol) during 2 hours. After the reduction was complete, the reaction mixture was poured into satd aq NH_4Cl (70 mL) and CH_2Cl_2 (80 mL). Organic layer was separated, washed twice with water

and dried (Na₂SO₄). Removal of the solvent under vacuum yielded the dicarbinol, which was immediately dissolved in pyrrole (3.5 mL, 50 mmol), and 0.2 mL of the pre-prepared solution of TFA (100 μ L) in CH₃CN (10 mL) has been added with vigorous stirring. After 10 min at RT the whole reaction mixture was transferred to bigger flask using CH₂Cl₂ (400 mL). Then DDQ (680 mg, 3 mmol) in THF (3 mL) was added and the reaction mixture was stirred for 1 h. Subsequently the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH₂Cl₂/hexanes, 1:1). Fluorescent fractions were chromatographed (silica, CH₂Cl₂/hexanes, 1:3) to afford 132 mg (25%) of pure corrole, which was subsequently crystallized from CH₂Cl₂/hexanes. *R*_f = 0.32 (silica, CH₂Cl₂/hexanes 2:3). All spectral and physical properties concur with published data.⁷

10-(Pentafluorophenyl)-5,15-bis-(4-methylphenyl)corrole (5a). A solution of diacyldipyrromethane **1b** (274 mg, 0.5 mmol) in THF/methanol (3:1, 40 mL) was reduced by adding portions of NaBH₄ (1.0 g, 25 mmol) during 2 hours. After the reduction was complete, the reaction mixture was poured into satd aq NH₄Cl (35 mL) and CH₂Cl₂ (40 mL). Organic layer was separated, washed twice with water and dried (Na₂SO₄). Removal of the solvent under vacuum yielded the dicarbinol, which was immediately dissolved in pyrrole (1.75 mL, 25 mmol), and 0.1 mL of the pre-prepared solution of TFA (100 μ L) in CH₃CN (10 mL) has been added with vigorous stirring. After 10 min at RT the whole reaction mixture was transferred to bigger flask using CH₂Cl₂ (200 mL). Then DDQ (340 mg, 1.5 mmol) in THF (2 mL) was added and the reaction mixture was stirred for 1 h. Subsequently the reaction mixture was evaporated to the dryness and chromatographed (silica, CH₂Cl₂/hexanes, 1:3) to afford corrole contaminated with another green compound. Hot cyclohexane has been added to this residue and after cooling down the slurry was filtered affording pink-violet crystals of corrole **5a** (86 mg). The supernatant was chromatographed (silica, CH₂Cl₂/cyclohexane, 5:95 then 1:9) to afford additional 10 mg of corrole **5a** (total yield 30%). *R*_f = 0.64 (silica, CH₂Cl₂/hexanes 1:1); ¹H NMR (C₆D₆) δ 2.68 (s, 6H), 7.51, 8.11 (br AA'BB', 4H), 8.28 (br s, 2H), 8.44 (br s, 2H), 8.80 (br s, 4H); ESI-MS obsd 645.2 [M+H⁺]; ESI-HR obsd 645.2065 [M+H⁺], calcd exact mass 646.2072 (C₃₉H₂₆F₅N₄); Anal. Calcd for C₃₉H₂₆F₅N₄: C, 72.66; H, 3.91; N, 8.69. Found: C, 72.47; H, 7.69; N, 8.36; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 416 (94), 582 (15), 600 (12), 6434 (4.9) nm.

10-(Mesityl)-5,15-bis-(4-*tert*-butylphenyl)corrole (5b). A solution of diacyldipyrromethane **1c** (584 mg, 1.0 mmol) in THF/methanol (3:1, 80 mL) was reduced by adding portions of NaBH₄ (2.0 g, 50 mmol) during 2 hours. After the reduction was complete, the reaction mixture was poured into satd aq NH₄Cl (70 mL) and CH₂Cl₂ (80 mL). Organic layer was separated, washed twice with water and dried (Na₂SO₄). Removal of the solvent under vacuum yielded the dicarbinol, which was immediately dissolved in pyrrole (3.5 mL, 50 mmol), and 0.2 mL of the pre-prepared solution of TFA (100 μ L) in CH₃CN (10 mL) has been added with vigorous stirring. After 10 min at RT the whole reaction mixture was transferred to bigger flask using CH₂Cl₂ (400 mL). Then DDQ (680 mg, 3 mmol) in THF (3 mL) was added and the reaction mixture was stirred for 1 h. Subsequently the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH₂Cl₂/hexanes, 1:1). Fluorescent fractions were chromatographed (silica, CH₂Cl₂/cyclohexanes, 5:95 then 10:90 then 15:95) to afford 114 mg (17%) of pure corrole, which was subsequently crystallized from CH₂Cl₂/hexanes. *R*_f = 0.46 (silica, CH₂Cl₂/hexanes 2:3); ¹H NMR (C₆D₆) δ 1.48 (s, 18H), 2.05 (s, 6H), 2.50 (s, 3H), 7.23 (s, 2H), 7.74, 8.38 (AA'BB', 8H), 8.48 (br s, 2H), 8.61 (br s, 2H), 8.75 (br s, 2H), 8.92 (br s, 2H); ESI-MS obsd 681.4 [M+H⁺]; ESI-HR obsd 681.3962 [M+H⁺], calcd exact mass 681.3952 (C₄₈H₄₉N₄); Anal. Calcd for C₄₈H₄₉N₄: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.48; H, 7.29; N, 8.08; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 418 (72), 580 (10), 617 (8.5), 648 (6.8) nm.

10-(Pentafluorophenyl)-5,15-bis-(2,6-difluorophenyl)corrole (5c). A solution of diacyldipyrromethane **1d** (296 mg, 0.5 mmol) in THF/methanol (3:1, 40 mL) was reduced by adding portions of NaBH₄ (1.0 g, 25 mmol) during 2 hours. After the reduction was complete, the reaction mixture was poured into satd aq NH₄Cl (35 mL) and CH₂Cl₂ (40 mL). Organic layer was separated, washed twice with water and dried (Na₂SO₄). Removal of the solvent under vacuum yielded the dicarbinol, which was immediately dissolved in pyrrole (1.75 mL, 25 mmol), and 0.1 mL of the pre-prepared solution of TFA (100 μ L) in CH₃CN (10 mL) has been added with vigorous stirring. After 10 min at RT the whole reaction mixture was transferred to bigger flask using CH₂Cl₂ (200 mL). Then DDQ (340 mg, 1.5 mmol) in THF (2 mL) was added and the reaction mixture was stirred for 1 h. Subsequently the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH₂Cl₂/hexanes, 1:1). Fluorescent fractions were chromatographed (silica, CH₂Cl₂/cyclohexanes, 5:95 then 20:80) to afford 192 mg (54%) of pure corrole, which was subsequently crystallized, from CH₂Cl₂/hexanes. *R*_f = 0.61 (silica, CH₂Cl₂/hexanes 1:1); ¹H NMR (C₆D₆) δ 7.02 (t, *J* = 8.0 Hz, 4H), 7.07-7.20 (m, 2H), 8.20-8.30 (m, 2H), 8.38 (br s, 2H), 8.64 (br s, 2H), 8.67-8.75 (m, 2H); ESI-MS obsd 689.1 [M+H⁺]; ESI-HR obsd 689.1396 [M+H⁺], calcd exact mass 689.1382 (C₃₇H₁₈F₉N₄); Anal. Calcd for C₃₇H₁₇F₉N₄: C, 64.54; H, 2.49; N, 8.14. Found: C, 64.48; H, 2.27; N, 7.91; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 412 (99), 423 (91), 566 (18), 604 (9.6), 635 (3.5) nm.

10-(Phenyl)-5,15-bis-(4-*tert*-butylphenyl)corrole (5e). A solution of diacyldipyrromethane **1f** (542 mg, 1.0 mmol) in THF/methanol (3:1, 80 mL) was reduced by adding portions of NaBH₄ (2.0 g, 50 mmol) during 2 hours. After the reduction was complete, the reaction mixture was poured into satd aq NH₄Cl (70 mL) and CH₂Cl₂ (80 mL). Organic layer was separated, washed twice with water and dried (Na₂SO₄). Removal of the solvent under vacuum yielded the dicarbinol, which

was immediately dissolved in pyrrole (3.5 mL, 50 mmol), and 0.2 mL of the pre-prepared solution of TFA (100 μ L) in CH₃CN (10 mL) has been added with vigorous stirring. After 10 min at RT the whole reaction mixture was transferred to bigger flask using CH₂Cl₂ (400 mL). Then DDQ (680 mg, 3 mmol) in THF (3 mL) was added and the reaction mixture was stirred for 1 h. Subsequently the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH₂Cl₂/hexanes, 1:1). Fluorescent fractions were chromatographed (silica, toluene/hexanes, 1:3) to afford 102 mg (16%) of pure corrole, which was subsequently crystallized from CH₂Cl₂/hexanes. *R*_f = 0.38 (silica, toluene/hexanes 1:1); ¹H NMR (THF-d₈/CD₃OD, 9:1) δ 1.58 (s, 18H), 7.65-7.80 (m, 3H), 7.88, 8.31 (AA'BB', 2 $\times$ 4H), 8.17 (d, *J* = 6.5 Hz, 2H), 8.45 (d, *J* = 4.5 Hz, 2H), 8.52 (br s, H), 8.8-8.9 (m, 2H), 8.92 (m, 2H); ESI-MS obsd 639.4 [M+H⁺]; ESI-HR obsd 639.3486 [M+H⁺], calcd exact mass 639.3482 (C₄₅H₄₃N₄); Anal. Calcd for C₄₅H₄₂N₄·½H₂O: C, 83.43; H, 6.69; N, 8.65. Found: C, 83.72; H, 6.60; N, 8.50; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 422 (83), 564 (11), 617 (9.0), 652 (9.4) nm.

10-(Mesityl)-5,15-bis-(4-methylphenyl)corrole (5f). The final cyclization was performed as described in the literature⁸. 1.2 g (2 mmol) of bilane **3a** and 1.07 g (20 mmol) of NH₄Cl were dissolved in 1L of propionitrile. 1.36 g (6 mmol) of DDQ were added and the mixture was stirred for one hour at room temperature, filtered and evaporated to dryness. The residue was chromatographed on basic alumina (eluent CH₂Cl₂) yielding the desired corrole (66% yield, 0.79 g); ¹H NMR (C₆D₆, 300K, 300MHz), δ (ppm) : -0.44 (br s, 3H) ; 2.06 (s, 6H) ; 2.41 (s, 6H) ; 2.52 (s, 3H) ; 7.25 (s, 2H) ; 7.41 (d, *J* = 7.27 Hz, 4H) ; 8.28 (d, *J* = 7.27 Hz, 4H) ; 8.45 (d, *J* = 4.39 Hz, 2H) ; 8.62 (d, *J* = 3.7 Hz, 2H) ; 8.77 (d, *J* = 3.7 Hz, 2H) ; 8.90 (d, *J* = 4.39 Hz, 2H); ¹H NMR (CDCl₃, 300K, 300MHz) δ (ppm) : -1.55 (br s, 3H) ; 1.84 (s, 6H) ; 2.59 (s, 3H) ; 2.65 (s, 6H) ; 7.25 (s, 2H) ; 7.60 (d, *J* = 7.5 Hz, 4H) ; 8.24 (d, *J* = 7.5 Hz, 4H) ; 8.33 (d, *J* = 4.5 Hz, 2H) ; 8.56 (d, *J* = 3.8 Hz, 2H) ; 8.84 (d, *J* = 4.5 Hz, 2H) ; 8.92 (d, *J* = 3.8 Hz, 2H); ESI-HR obsd 596.29613, calcd exact mass 596.29400 (C₄₂H₃₆N₄); λ_{abs} (CH₂Cl₂, $\epsilon \times 10^{-3}$) : 415 (108.1) ; 564 (12.4) ; 618 (10.8) ; 648 (10.2).

5-(4-Methylphenyl)-10-(pentafluorophenyl)-15-(4-methoxyphenyl)corrole (6a). 0.38 g (0.58 mmol) of bilane **3b** and 0.31 g (5.77 mmol) of NH₄Cl were dissolved in 290 mL of propionitrile. 0.39 g (1.73 mmol) of DDQ were added and the mixture was stirred at room temperature for one hour, filtered and evaporated. The resulting solid was purified on a basic alumina column (eluent CH₂Cl₂/heptane 1/1 then 2/1). The evaporation of the major fraction afforded the desired corrole (55% yield, 0.21 g). ¹H NMR (DMSO, 300K, 500 MHz), δ (ppm) : -2.49 (br s, 3H); 2.64 (s, 3H) ; 4.04 (s, 3H) ; 7.46 (br s, 2H) ; 7.68 (br s, 2H) ; 8.23-8.36 (m, 6H) ; 8.58 (br s, 2H) ; 8.81 (br s, 2H) ; 8.97 (br s, 2H). ESI-HR obsd 660.19528, calcd exact mass 660.19485 (C₃₉H₃₁F₅N₄O); λ_{abs} (CH₂Cl₂, $\epsilon \times 10^{-3}$) : 414 (113.4) ; 579 (20.4) ; 605 (17.2) ; 639 (8.5). Anal. Calcd for C₃₉H₃₁F₅N₄O: C, 70.90%; H, 3.81%; N, 8.48%. Found: C, 69.97%; H, 3.84%; N, 8.57%.

5-(4-Methylphenyl)-10-(pentafluorophenyl)-15-(4-*tert*-butylphenyl) corrole (6b). A solution of diacyldipyrromethane **2b** (177 mg, 0.3 mmol) in THF/methanol (3:1, 24 mL) was reduced by adding portions of NaBH₄ (0.6 g, 15 mmol) during 2 hours. After the reduction was complete, the reaction mixture was poured into satd aq NH₄Cl (20 mL) and CH₂Cl₂ (25 mL). Organic layer was separated, washed twice with water and dried (Na₂SO₄). Removal of the solvent under vacuum yielded the dicarbinol, which was immediately dissolved in pyrrole (1.05 mL, 15 mmol), and 60 μ L of the pre-prepared solution of TFA (100 μ L) in CH₃CN (10 mL) has been added with vigorous stirring. After 10 min at RT the whole reaction mixture was transferred to bigger flask using CH₂Cl₂ (120 mL). Then DDQ (204 mg, 0.9 mmol) in THF (1 mL) was added and the reaction mixture was stirred for 1 h. Subsequently the reaction mixture was concentrated to ¼ of initial volume and filtered through silica pad (CH₂Cl₂/hexanes, 1:1). Fluorescent fractions were chromatographed (silica, toluene/hexanes, 1:3) to afford 106 mg (51%) of pure corrole, which was subsequently crystallized from CH₂Cl₂/hexanes. *R*_f = 0.33 (silica, toluene/hexanes 1:3); ¹H NMR (C₆D₆) δ -2.51(-6.0) (br s, 3H), 1.51 (s, 9H), 2.45 (s, 3H), 7.47, 8.25 (AA'BB', 4H), 7.78, 8.36 (AA'BB', 4H), 8.23 (br s, 2H), 8.53 (br s, 2H), 8.60-8.80 (m, 2H), 8.93 (br s, 2H); ESI-MS obsd 687.3 [M+H⁺]; ESI-HR obsd 687.2534 [M+H⁺], calcd exact mass 687.2542 (C₄₂H₃₂F₅N₄); Anal. Calcd for C₄₂H₃₁F₅N₄: C, 73.46; H, 4.55; N, 8.16. Found: C, 73.27; H, 4.78; N, 7.81; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 417 (88), 582 (15), 602 (12), 639 (5.1) nm.

¹ Rao, P. D.; Littler, B. J.; Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 1084-1092.

² Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391-1396.

³ Gryko, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 2249-2252.

⁴ Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323-7344.

⁵ Clausen, C.; Gryko, D. T.; Yasseri, A. A.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7371-7378.

⁶ Lee, C. H.; Li, F. R.; Iwamoto, K.; Dadok, J.; Bothnerby, A. A.; Lindsey, J. S. *Tetrahedron* **1995**, *51*, 11645-11672

⁷ Paolesse, R.; Nardis, S.; Sagone, F.; Khoury, R. G. *J. Org. Chem.* **2001**, *66*, 550-556.

⁸ Ka, J. W.; Cho, W. S.; Lee, C. H. *Tetrahedron Lett.* **2000**, *41*, 8121-8125.