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Supporting Information

Covalent versus non-covalent approaches for enantioselective sulfoxidation catalyzed by corrole metal complexes

Izana Nigel Etinger, Atif Mahammed, and Zeev Gross*

Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

Table S1. Sulfoxidation of thioanisole by PhIO in different solvents catalyzed by the metal complexes of corrole **2C**.

	2C- Mn		**2C- Fe**	
Solvents	Yield (%)[b]	ee (%)[c]	Yield (%)[b]	ee (%)[c]
THF	50	14	56	8
Benzene	50	13	60	7
Toluene	80	10	60	7
Dichloromethane	86	15	70	6
Acetonitrile	97	14	74	8
Methanol	24	8	16	5

[a] Reactions were carried out at room temperature for 3 h with 1 equiv of catalyst (0.7 Mm), 100 equiv of PhIO, and 2000 equiv of thioanisole. [b] Determined by GC and calculated relatively to iodobenzene. [c] ee of major enantiomer determined by chiral GC.

Table S2. Catalytic sulfoxidation of thioanisole in different solvents using H_2O_2 as an oxidant.

	2C- Mn, rt		**2C- Fe**, rt		**2C- Fe**, 5 ^{0}C	
Solvents	Yield (%)[b]	ee (%)[c]	Yield (%)[b]	ee (%)[c]	Yield (%)[b]	ee (%)[c]
THF	8	7	70	24	40	27
Benzene	2	4	20	10	10	13
Toluene	2	2	20	10	10	11
Dichloromethane	2	5	30	5	20	7
Acetonitrile	2	6	40	18	35	18
Methanol	2	2	10	1	4	3

[a] Reactions were carried out for 3 h with 1 equiv of catalyst (0.7 mM), 100 equiv of PhIO, and 2000 equiv of thioanisole. Hydrogen peroxide was used as a 0.5% solution. [b] Determined by GC and calculated relatively to sulfide. [c] ee of major enantiomer determined by chiral GC.

Table S3. Effect of catalyst and albumin source on asymmetric oxidation of thioanisole [a].

	% yield, major enantiomer, % ee				
Catalyst	HAS	BSA	PSA	RSA	SSA
5b-Mn	23, S, 11	20, S, 20	17, S, 10	13, S, 4	15, S, 10
6b-Mn	23, S, 7	15, S, 11	13, S, 11	14, S, 4	17, S, 2
7b'-Mn	10, S, 8	5, S, 5	20, S, 10	14, S, 2	20, S, 11
8b'-Mn	40, S, 5	20, S, 5	20, S, 8	25, S, 2	30, S, 3
9b'-Mn	23, 0, 0	10, S, 14	10, S, 4	25, 0, 0	20, S, 3

[a] Catalysts used without HPLC separation from minor isomer. * H_2O_2: thioanisole: albumin: catalyst (0.2 mM) = 75:50: 1.5: 1; pH 7.0; T= 24 ^{0}C; reaction time = 1.5 h. * % ee determined by HPLC using Merck Hitachi HPLC column, equipped with Daicel chiral column OD, and the enantiomers (R *vs.* S) were identified by reference to published works. * The enantiomeric sulfoxides were eluted with 80% hexane and 20% isopropyl alcohol with retention times of 16 and 19 min (S enantiomer and R enantiomer, respectively). [d] The eluent was eluted at a flow rate of 0.5 mL/min and monitored at 250 nm.

Table S4. Effect of catalyst and albumin source on asymmetric oxidation of the modafinil precursor, listed as % yield and % ee (R preference in all cases).

Catalyst	HSA	BSA	PSA	RSA	SSA
1b-Mn[a]	10, 40	14, 15	15, 34	16, 40	4, 23
2b'-Mn[a]	9, 2	7, 2	9, 20	20, 14	5, 10
5b-Mn[a]	4, 7	7, 5	4, 11	5, 14	3, 5
4b-Mn[a]	7, 25	9, 22	23, 44	24, 66	6, 28
4b-Mn[b]				58, 75	

Reaction conditions: H_2O_2: thioanisole: albumin: catalyst (0.2 mM) = 75:50: 1.5: 1; pH 7.0; T= 25 ^{0}C; reaction time = 18 h. % ee were determined by HPLC using chiral Pak AD-H column, and the enantiomers by reference to published works. [b]Gradual addition of H_2O_2, 15% CH_3CN, larger scale, isolated yield (see text).

Quantitative purification

Quantitative purification was performed by preparative HPLC chromatography, equipped with a Symmetry 300-5C18 HPLC column. The compounds were dissolved in methanol and the mobile phase was 95% water and 5% triethylamine (0.5%) in acetonitrile, turning to 10% water and 90% acetonitrile within 15 min, during which time the signals of the hydrolyzed corroles already appeared, and fractions containing the pure amphiphilic corrole were collected. The eluent was eluted at a flow rate of 10 mL/min and monitored at 420 nm.

Figure S1. **4b-Mn** before purification by preparative HPLC chromatography.

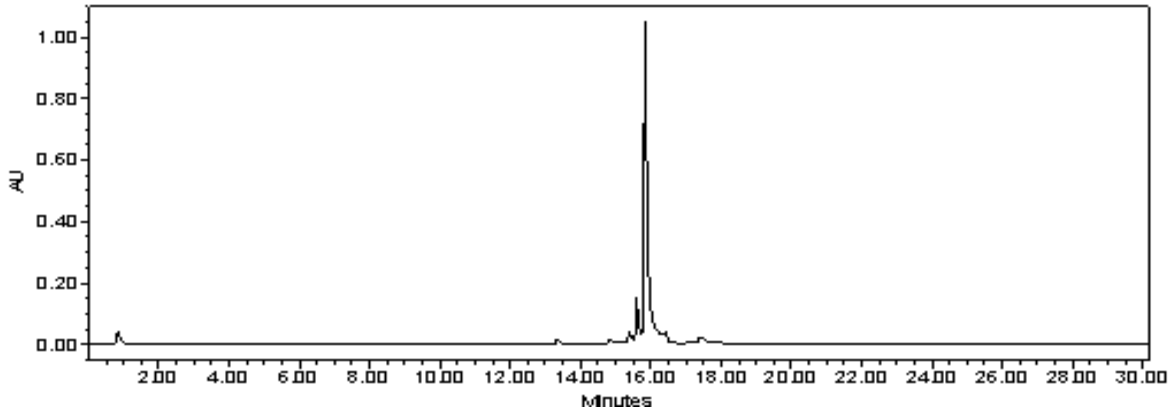


Figure S2. **4b-Mn** after purification by preparative HPLC chromatography.

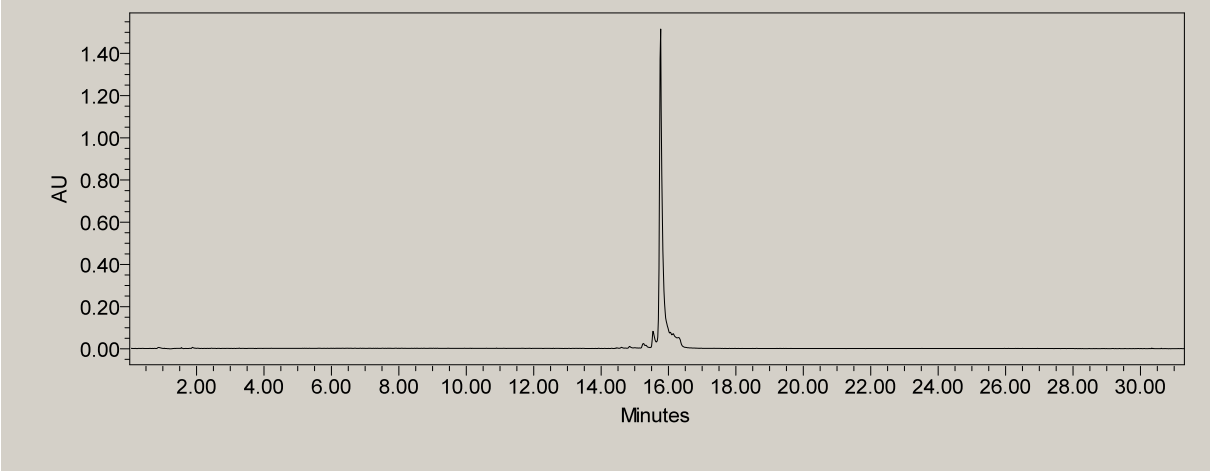


Figure S3. **1b-Mn** before purification by preparative HPLC chromatography

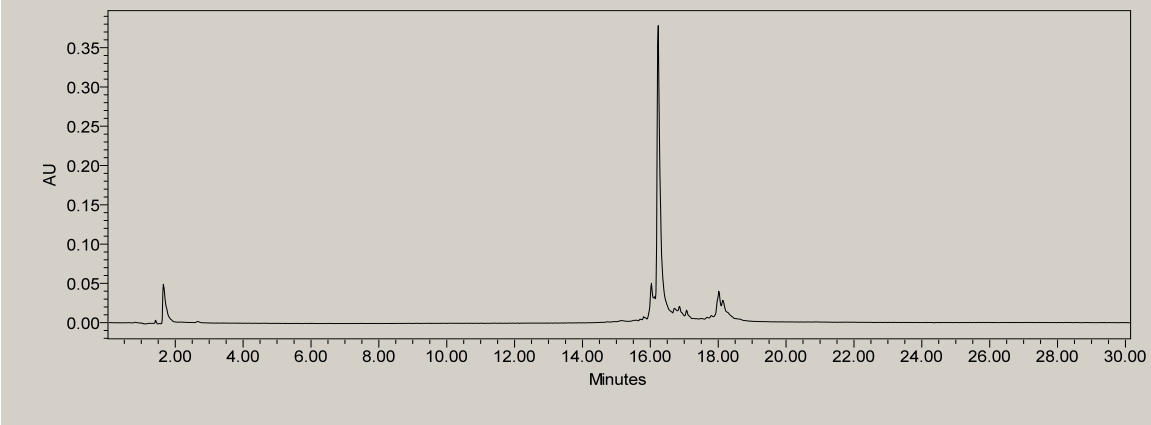


Figure S4. **1b-Mn** after purification by preparative HPLC chromatography

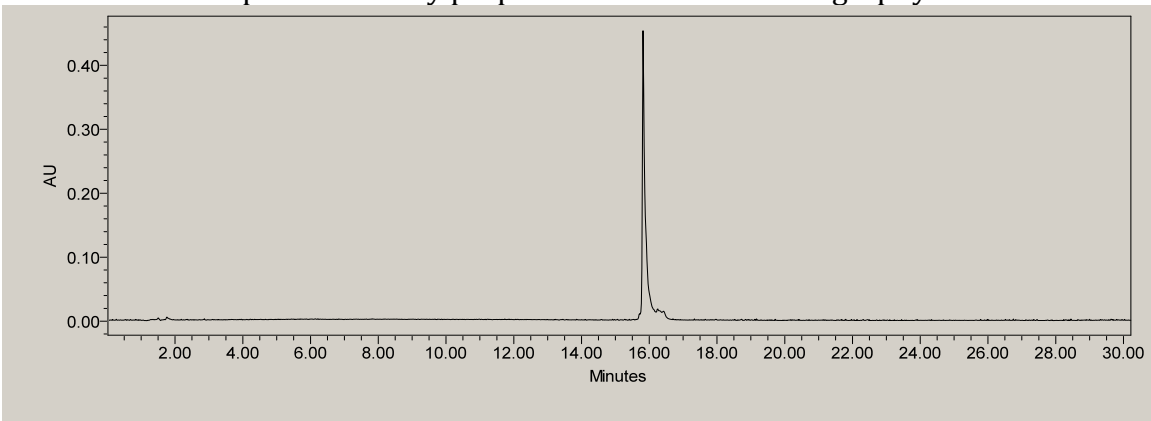
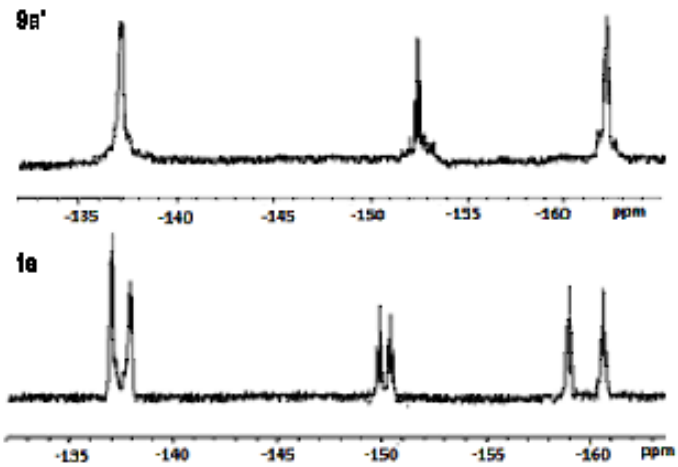


Figure S5. **^{19}F NMR spectra of 9a' and 1a.**



The structures of the chlorosulfonated corroles were identified by ^{19}F-NMR. This is exemplified in Figure S5 for **9a'** and **1a**, which display one and two sets of *ortho*-, *meta*- and *para*-F resonances, respectively. The conclusion is that the two C_6F_5 groups in **9a'** remain magnetically equivalent due to substitution on C3 and C17, while they are different in the lower symmetry C2,C17-bis-substituted corrole

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Experimental Section

Physical Methods

Nuclear Magnetic Resonance Spectroscopy. The ^{1}H NMR and ^{19}F NMR spectra were recorded on Brucker AM 200 and AM 300, operating at 200 and 300 MHz for ^{1}H and 188 and 282 MHz for ^{19}F, respectively. Chemical shifts are reported in ppm relative to residual hydrogen atoms in the deuterated solvents: 7.24 and 3.31 for chloroform and methanol.

HPLC analyses were performed on a Merck Hitachi HPLC, equipped with either Daicel chiral column OD (0.46 ϕ cm x 25 cm), or a Chiral Pak AD-H HPLC column (0.46 ϕ cm x 25 cm), or a Kromasil 100-5C18 HPLC column (0.46 ϕ cm x 46 cm).

Quantitative HPLC separation was performed with a Symmetry 300-5C18 HPLC column (0.46 ϕ cm x 46 cm).

Gas chromatographic. GC analysis was performed by HP-54890 GC with a $J\&W$ chiral cyclodex-B capillary column and FID detector. The yields were reproducible within $\pm 2\%$ for multiple experiments. An HP 8453 diode array **Spectrophotometer** was used to record the electronic spectra.

Circular dichroism spectroscopy. CD measurements were recorded on a J-810 JASCO spectropolarimeter.

Mass Spectrometry. MS measurements were performed on 700 Finnigan mat for CI method and on Micromass Maldi R for Maldi method.

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Materials

Solvents. The routine solvents that were used for synthesis and workup procedures were purchased from Aldrich, Merck, Fluka, BioLab and Frutarom. Solvents of spectroscopic grade, HPLC grade, and some solvents of analytical grade were used as received; acetonitrile, benzene, isopropyl alcohol, chloroform, dichloromethane, diethyl ether, ethyl acetate, n-hexane, methanol, pyridine, triethylamine, ethanol, toluene.

Some solvents were purified and dried; Diisopropylamine was distilled over CaH_2. N,N-dimethylformamide (DMF) was distilled over CaH_2 at reduced pressure. Tetrahydrofuran (THF) was distilled over potassium, and pyrrole was filtration trough a plug of basic alumina .

Deuterated solvents (Aldrich) with percent of deuteration minimum 99.5% , were used as received.

Serum Albumin. Serum albumins that were used for a chiral environment in the catalytic reactions were purchased from Sigma and used as supplied. The quality of the used albumins and their product number (P.N) are represented below.

Bovine Serum Albumin-Fatty Acid Free, lyophilized powder, ≥ 98% (P.N-B4287).

Pig Serum Albumin-lyophilized powder, (agarose gel electrophoresis) ≥96% (P.N-A1173).

Sheep Serum Albumin-lyophilized powder, (agarose gel electrophoresis)≥96% (P.N-A6289).

Rabbit Serum Albumin- lyophilized powder, Fatty Acid Free ≥ 96% (P.N-A0764).

Human Serum Albumin- lyophilized powder, fatty acid free ≥96% (P.N-1887).

Sulfides as substrates in the catalytic reactions

Thioanisole and 2-bromothioanisole, were purchased from Aldrich.

The covalent approach. Thioanisole was resolved by HP-54890 GC with J&W chiral cyclodex-B capillary column and FID detector. The GC retention times of the sulfoxides were 52 and 53 min under the following conditions: 130 ^{o}C at 7 psi. Reaction yields were calculated relatively to iodobenzene formed from iodosylbenzene, On the basis of the relative retention times of other sulfoxides with known absolute configuration on the same GC column, the R isomer was assumed to be the faster eluting.

The non-covalent approach. Reactions were performed at 24^0 C by subsequent feeding of the reaction vessel with sulfide, aqueous phosphate pH 7.00 buffer solution already containing albumin and catalyst, and hydrogen peroxide (3%). The ratio of oxidant: substrate: BSA: catalyst (0.2 mM) was 75: 50: 1.5: 1.

After 1.5 h, the solutions were extracted with CH_2Cl_2 and the extracts were concentrated under a stream of argon. The residue was taken up in the HPLC solvent and analyzed by HPLC using Merck Hitachi HPLC column, equipped with Daicel chiral column OD.

The enantiomeric sulfoxides were eluted with 80% hexane and 20% isopropyl alcohol with retention times of 16 and 19 min (S enantiomer and R enantiomer, respectively). The eluent was eluted at a flow rate of 0.5 mL/min and monitored at 250 nm. Reaction yields were measured by comparing the peak area ratios of the HPLC chromatograms of unreacted sulfide and produced sulfoxide. The response factors were calculated by a standard curve that was constructed from the peak area ratios of the HPLC chromatograms of sulfide/sulfoxide obtained after analogous workup by ^{1}H NMR. The response factor for thioanisole was found to be 3.

Quantitative purification The amphiphilic manganese(III) corrole complexes that provided the most interesting results in Table 1 and S3 were quantitatively purified by preparative HPLC chromatography equipped with Symmetry 300-5C18 HPLC column.

All the compounds were dissolved in methanol and the mobile phase was 95% water and 5% triethylamine (0.5%) in acetonitrile, turning to 10% water and 90% acetonitrile within 15 min, during which time the signals of the hydrolyzed corroles already

appeared, and fractions containing the pure amphiphilic corrole were collected. The eluent was eluted at a flow rate of 10 mL/min and monitored at 420 nm.

Synthesis of iodosylbenzene. 30 mL of NaOH (3M) were added during 5 minutes into an Erlenmeyer flask (100 mL) that contained 6.05 g (18.7 mmol) iodobenzene diacetate. The mixture was vigorously stirred for 15 min, until a white suspension was produced. The mixture was left at room temperature for 45 min with no stirring. 20 mL of distilled water were added, and the mixture was vigorously stirred for 20 min. After filtration, the product was stirred again with 40 mL of distilled water, filtered, washed with distilled water and dried. 15 mL of chloroform were added to the dry product, and the solid was filtered and dried for 24 h by vacuum pump. The product was obtained in 3.45 g (15.6mmol). The solid was kept at $-10\ ^{o}C$.

Preparation of LDA solution. In an oven-dried 500 ml three-neck round bottomed flask equipped with a thermometer and under Ar, diisopropylamine (32.8mmol) and distilled THF (100mL) were added. The solution was cooled to $-10\ ^{o}C$. BuLi (18.75 ml, 30mmol) was injected through a septum during 5 min. The solution was kept at cool condition until it was used.

Synthesis of 2,6-Dibromobenzaldehyde. LDA (15 mL, 30 mmol) was added dropwise to the solution of 1,3-dibromobenzene (6 g, 25 mmol) in THF (150 mL) at -70 °C. An orange precipitate was formed. The mixture was stirred 30 min at -75 °C, and then DMF (2.2 g, 30 mmol) was added dropwise while maintaining the temperature at -70 °C. The purple solution was stirred for 30 min at -70 °C and hydrolyzed with diluted aq H_2SO_4 at room temperature. The yellow organic phase was separated. The water phase was extracted with diethyl ether (25 mL), and the extract was added to the organic phase. Solvents were evaporated to leave the crude product as a yellow-brown solid residue. It was washed with water and petroleum ether. The final product was recrystallized from cyclohexane (25 mL), thus providing pale yellow needles. Yield: 4.6 g (70%).

^{1}H NMR ($CDCl_3$): δ 10.26 (s, 1H), 7.64 (d, *J*= 8.1 Hz, 2H), 7.23 (t, *J*= 8.1 Hz, 1H).

2,6-dibromophenyldipyrromethane. Pyrrole (10 mL, 0.14mol) and 2,6-dibromobenzaldehyde (1.5g, 5.7mmol) were added to a dry round-bottomed flask and degassed with a stream of Ar for 5 min. TFA (0.10 equiv) was then added, and the solution was stirred under Ar at room temperature for 5 min and then quenched with 0.1 M NaOH. Ethyl acetate was added and the organic phase was washed with water and dried (Na_2SO_4). The solvents were removed under vacuum to afford orange oil. Purification of the final product was performed on a chromatographic column with silica gel (20:3 n-hexane/CH_2Cl_2), yielding 0.7 g (30%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (br. s, 2H), 7.62 (d, J = 7.8 Hz, 2H), 6.94 (t, J = 7.8 Hz, 1H), 6.71 (m, 2H), 6.58 (s, 1H), 6.35 (m, 2H), 6.16 (m, 6.24).

Synthesis of 5-(pentafluorophenyl)dipyrromethane.

5-(Pentafluorophenyl)dipyrromethane was prepared in the same way, yielding 2.92 g, (65 % yield) as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (br. s, 2H), 6.72-6.75 (m, 2H), 5.90 (s, 1H), 6.02 (m, 2H), 6.16 (q, J = 2.9 Hz, 2 H).

Synthesis of free base corroles.

Synthesis of 5,15-bis(2,6-dibromophenyl)-10-(pentafluorophenyl)corrole, (2). 2,6-dibromophenyldipyrromethane (1 mmol, 0.34 g) and pentafluorobenzaldehyde (0.5 mmol, 63 μL) were dissolved in MeOH (100 ml). Subsequently, a solution of HCl aq (36%, 5 mL) in H_2O (50 mL) was added, and the reaction was stirred at room temperature for 2 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 250 mL with $CHCl_3$. *p*-Chloranil (369 mg, 1.5 mmol) was added, and the mixture was stirred overnight at room temperature. The pure compound was isolated by flash column chromatography [SiO_2; CH_2Cl_2/hexane: (1:8)] as purple solid. 70 mg (28% yield) were obtained.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta(J)$ 9.00 (d, J = 4.3 Hz, 2H), 8.59 (d, J = 4.5 Hz, 2H), 8.49 (d, J = 4.5 Hz, 2H), 8.41 (d, J = 4.3 Hz, 2H), 8.01 (d, J = 8.0 Hz 4H), 7.50 (t, J = 8.0 Hz 2H); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta(J)$ -136.94 (dd, ^1J = 24.0 Hz, ^2J = 8.1 Hz, 2F), -153.61 (t,

J = 21.2 Hz, 1F), -162.43 (m, 2F); UV-vis (CH_2Cl_2): λ_{max} $(\varepsilon(M^{-1}cm^{-1}))$ = 410nm (145000), 425 (109000), 566 (24000), 602 (12500); MS (MALDI-TOF LD$^-$): m/z (%): 932 ([M]$^-$, 100%); Anal. Calc. ($C_{37}H_{17}Br_4F_5N_4$): C, 47.33; H, 1.84; N, 6.01; Br, 34.29. Found: C, 47.76; H, 1.93; N, 5.74; Br, 33.82 %.

General procedure for the preparation of free base corroles corroles 1, and 4-9.

Pentafluorodipyrromethane (0.8mmol, 0.35g) and the corresponding aldehyde (0.4mmol) were dissolved in CH_2Cl_2 (24mL) and TFA (31 μL, 0.4mmol) was added to the mixture while stirring. The reaction mixture was left at room temperature. After 5h, triethylamine (56 μL, 0.4 mmol) was added and the reaction mixture was diluted with CH_2Cl_2 (600ml). Finally, DDQ (0.8mmol, 0.18 g) was added, and the reaction was stirred at room temperature for a further 10 min. The yield of the corroles was determined by chromatographic separation.

Spectral data for 5,15-bis(pentafluorophenyl)-10-(2,6 dibromophenyl)corrole, (1).

Purification of the final product was performed on a chromatographic column with silica gel (1:10 hexane/CH_2Cl_2) yielding 15mg (6 %).

^{1}H NMR (300 MHz, $CDCl_3$) $\delta(J)$ 9.07 (d, J = 4.2 Hz, 2H), 8.70 (d, J = 4.5 Hz, 2H), 8.50 (d, J = 4.2 Hz, 2H), 8.47 (d, J = 4.5 Hz, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta(J)$ -137.62 (dd, ^1J = 23.1 Hz, ^2J = 7.0 Hz, 4F), -153.65 (t, J = 21.56 Hz, 2F), -161.72 (m, 4F); UV-vis (CH_2Cl_2): λ_{max} $(\varepsilon(M^{-1}cm^{-1}))$ = 410nm (67000), 418 (54000), 565 (10800), 610 (6290); MS (MALDI-TOF LD$^-$): m/z (%): 862 ([M]$^-$, 100%). Anal. Calc. ($C_{37}H_{14}Br_2F_{10}N_4$): C, 51.42; H, 1.63; N, 6.48; Br , 18.49. Found: C, 51.20; H, 1.59; N, 6.35; Br, 18.23 %.

Palladium-catalyzed amidation of 5,15-bis(2,6-dibromophenyl)-10-(pentafluorophenyl) corrole, (2C).

In a N_2 filled glove box, 5,15-bis (2,6-dibromophenyl)-10-(pentafluorophenyl)corrole **(2)** (0.025mmol, 21.55mg), (S)-(+)-2,2-dimethylcyclopropanecarboxamide

(0.8mmol,91mg), $Pd(OAc)_2$(0.01mmol, 2mg), Xantphos(0.02mmol, 12mg), and Cs_2CO_3(0.4mmol, 130mg) were dissolved in THF (2mL) and placed in an oven-dried, resealable Schlenk tube . The tube was sealed, removed from the glove box and its contents were heated for 168 h. The resulting mixture was cooled to room temperature, taken up in ethyl acetate and concentrated *in vacuo.* The pure compound was isolated by flash column chromatography (silica gel, ethyl acetate : hexane (v/v)=1:7) and obtained as a purple solid in 28% yield (12 mg).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta(J)$ 9.05 (d, J = 4.5 Hz, 2H), 8.90 (d, J = 4.5 Hz, 2H), 8.72 (m, 4H), 8.50 (d, J = 8.1 Hz, 4H), 7.77 (t, J = 8.1 Hz, 2H), 6.74 (s, 4H, NH), 2.02 (s, 4H), 1.67 (s, 24H), 0.905 (s, 8H); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta(J)$ -134.54 (dd, $^1J = 24.5$ Hz, $^2J = 8.4$ Hz, 2F),

-151.61 (t, $J = 21.21$ Hz, 1F), -161.43 (m, 2F);; UV-vis (CH_2Cl_2): $\lambda_{max}\left(\varepsilon\left(M^{-1}cm^{-1}\right)\right)$ = 415nm (140200), 565 (19510), 603 (10300); MS (MALDI$^-$): m/z (%): 1060 ([M], 100%), 1061 ([M+1], 90%), 1056 ([M-1], 50%); Anal. Calc. ($C_{61}H_{57}O_4F_5N_8 \cdot 1.5H_2O$): C, 67.39; H, 5.47; N, 10.31. Found: C, 67.80; H, 5.50; N, 9.42 %.

Synthesis of the manganese(III) complex of corrole 2C.

A solution of corrole **2** (0.05 g, 0.047 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (0.115g, 0.47 mmol) in DMF (10mL) was heated to reflux for 10 minutes. Evaporation of solvent, followed by column chromatography on silica (eluent: hexane: ethyl acetate, 10:1) afforded **2C** in 91% yield (11 mg).

^{19}F NMR (188 MHz, $CDCl_3$): $\delta(J)$: -134.78 (br. s, 2F), -150.25 (br. s, 1F), -161.45 (br. s, 2F);

UV-vis (CH_2Cl_2): $\lambda_{max}\left(\varepsilon\left(M^{-1}cm^{-1}\right)\right)$ = 400 nm (33400), 418 (38100), 480 (25200), 540 (7710), 580 (9650), 620 (10300); MS (MALDI-TOF LD$^-$): m/z (%): 1112 ([M]$^-$, 60%), 1147 ([M+Cl]$^-$, 100%).

Synthesis of the iron(III) complex of corrole 2C.

2C-Fe was prepared by refluxing a DMF solution of corrole **2** with Iron(II) chloride tetrahydrate, followed by evaporation of the solvent. Washing the solid residue with diethyl ether, passing it through a short silica gel column (eluting with ether), and evaporation of the solvent, lead to a brownish solid that was obtained in 67% yield (8 mg).

MS (MALDI-TOF LD$^-$): m/z (%): 1112 ([M]$^-$, 100%), 1147 ([M+Cl]$^-$, 90%); UV-vis (CH_2Cl_2): λ_{max} $\left(\varepsilon\left(M^{-1}cm^{-1}\right)\right)$ 410nm (41500), 548 (12100).

General Procedure for Chlorosulfonation reaction of free base corroles, 1-9.

100 μmol of free base corrole and 2 mL of chlorosulfonic acid (30mmol) were stirred at room temperature for 1 h, after which the reaction mixture was cooled by an ice bath and treated with small ice chips (5-10 mg, caution!). The product was obtained *via* addition of 20 mL of distilled water and was extracted with dichloromethane, washed with H_2O, dried (Na_2SO_4), and filtered.

Spectral data for 1a:

^{1}H NMR (300 MHz, benzene): $\delta(J)$ 9.93 (s, 1H), 9.1 (s, 1H), 8.46 (m, 2H), 8.30 (m, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta(J)$ -136.97 (d, *J* = 15.5 Hz, 2F), -137.88 (d, *J* = 17.8 Hz, 2F), -149.60 (t, *J* = 21.05 Hz, 1F), -150.10 (t, *J* = 20.30 Hz, 1F), -159.80 (m, 2F) -161.40 (m, 2F); UV-vis (CH_2Cl_2): λ_{max} $\left(\varepsilon\left(M^{-1}cm^{-1}\right)\right)$ = 420nm (61400), 440 (48000), 580 (12900), 612 (16700), 650 (18000); MS (MALDI$^-$): m/z (%): 1062 (100%), 1060 ([M-2H], 90).

Spectral data for 2a:

Bis-chlorosulfonation of 5,15-bis(2,6-dibromophenyl)-10-(pentafluorophenyl) corrole (**2**) provided a mixture of both isomers, the lower-symmetry C_3, C_{17} and the higher symmetry C_3, C_{18} bis-sulfonated corrole, therefore ^{1}H NMR analysis was complicated and could not provide a clear information.

The ^{19}F NMR analysis provided more clear information of the isomeric mixture.

^{19}F NMR (symmetric product, 188 MHz, $CDCl_3$): $\delta(J)$ -136.97 (d, *J* = 19.4 Hz, 2F), -151.52 (t, *J* = 20.49 Hz, 1F), -162.02 (m, 2F); ^{19}F NMR (asymmetric product, 188 MHz,

$CDCl_3$): $\delta(J)$ - 135.76 (d, *J* = 19.5 Hz, 1F), -136.54 (d, *J* = 18.4 Hz, 1F), -150.42 (t, *J* = 20.7 Hz, 1F), -150.98 (t, *J* = 21.2 Hz, 1F), -160.36 (m, 1F) -161.39 (m, 1F); UV-vis (CH_2Cl_2): λ_{max} $(\varepsilon(M^{-1}cm^{-1}))$ = 423nm (72300), 446 (45600), 587 (13500), 614 (12300), 655 (15400); MS (MALDI$^-$): m/z (%): 1127 ([M+2H], 100%), 1125([M], 90%).

General Procedure for hydrolysis reaction of corroles, 1a-9a'.

A suspension of chlorosulfonated corrole in 20 mL water and excess of sodium carbonate was refluxed for 2h. The solution was filtered and evaporated to dryness to provide **1b-9b'**.

Spectral data for 1b. ^{1}H NMR (300 MHz, MeOH): $\delta(J)$ 9.72 (br. s, 1H), 9.23 (m, 2H), 9.10 (m, 2H), 8.90 (br. s, 1H) 8.12 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H); ^{19}F NMR (188 MHz, MeOH): $\delta(J)$ -137.10 (d, *J* = 17.3 Hz, 2F), -138.96 (d, *J* = 18.5 Hz, 2F), -150.62 (t, *J* = 21.1 Hz, 1F), -151.15 (t, *J* = 20.7 Hz, 1F), -160.50 (m, 2F) -161.98 (m, 2F); UV-vis (MeOH): λ_{max} $(\varepsilon(M^{-1}cm^{-1}))$ = 423nm (25400), 440 (19100), 580(4090), 600 (4850), 640 (7990); MS (MALDI$^-$): m/z (%): 1025 ([M+1], 100%), 1026 ([M+2], 60%);

Spectral data for 2b'. ^{1}H NMR (300 MHz, MeOH): 9.50 (br. s, 2H), 9.21 (d, *J* = 4.2 Hz, 2H), 9.00 (d, *J* = 4.5 Hz, 2H), 8.55 (d, *J* = 8.0 Hz, 4H), 7.85(t, *J* = 8.0 Hz, 2H); ^{19}F NMR $\delta(J)$ -137.21 (d, *J* = 19.7 Hz, 2F), -157.78 (t, *J* = 21.12 Hz, 1F), -164.17 (m, 2F); UV-vis (MeOH): λ_{max} $(\varepsilon(M^{-1}cm^{-1}))$ = 420 nm (34700), 480 (8800), 580 (7880), 610 (7610), 630 (7120); MS (MALDI$^-$): m/z (%): 1088 ([M]), 100%), 1007 ([M-Br], 60%); Anal. Calc. ($C_{37}H_{17}Br_4F_5N_4O_6S_2 \cdot 7H_2O$): C, 36.46; H, 2.57; N, 4.60. Found: C, 36.83; H, 3.03; N, 4.82 %.

Manganese(III) complexes of corroles 1b and 2b'.

The manganese(III) complexes were prepared at the same way as **2C**.

Spectral data for 1b-Mn. ^{19}F NMR (188 MHz, MeOH): $\delta(J)$ -121.21(br. s 2F), -126.37 (br. s, 2F), -157.40 (s, 1F), -160.02 (s, 1F), -162.26 (s, 2F), -165.54 (s, 2F); MS (MALDI$^-$):

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m/z (%): 1076 ([M], 100%), 1111 ([M+Cl], 60%);UV-vis (MeOH): $\lambda_{\max}\left(\varepsilon\left(M^{-1}cm^{-1}\right)\right)$ **:** 398 nm (10100), 420 (11100), 486 (9380), 585 (4670), 620 (4520), 650 (5280).

Spectral data for 2b'-Mn. ^{19}F NMR : $\delta(J)$ -133.43 (br. s, 2F), -157.31 (s, 1F), -163.98 (s, 2F). **MS** (MALDI^{-}): m/z (%): 1143 ([M-1], 100%), 1145 ([M+1], 70%); UV-vis (MeOH): $\lambda_{\max}\left(\varepsilon\left(M^{-1}cm^{-1}\right)\right)$ = 400nm (10600), 430(10900), 490(8200), 590(3540), 610(3550), 640(3630).