

ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis of Sterically Hindered Xanthene-Modified Iron Corroles with Catalase-Like Activity

Björn Zyska and Matthias Schwalbe*

Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin (Germany). Fax: (+49) 30 2093-6966; E-mail: matthias.schwalbe@hu-berlin.de

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General Methods. Silica gel 60 (60-200 μm mesh, ACROS) was used for column chromatography. Solvents for synthesis were of reagent grade or better and were dried according to standard methods.¹ Compounds 10-(4-(5-Bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl) corrole (**3a**)² and 10-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl) corrole (**3b**)³ were prepared according to literature procedures. ¹H NMR spectra were recorded at ambient temperature on a Bruker DPX 300, AM 300, AV 400 or AV 500 MHz spectrometer. All spectra were referenced to deuterated chloroform (CDCl_3) as an internal standard (measured values for δ are given in parts per million (ppm) and for J in Hertz (Hz)). Electrospray ionization (ESI) mass spectra were obtained using a Thermo Finnigan LCQ XP or LTQ FT instrument in either positive or negative scan mode. MALDI-FT mass spectra were recorded on a MALDI LTQ Orbitrap XL from Thermo Fisher Scientific. Microwave reactions were carried out in a CEM monomode microwave (model: Discover®).

¹ D. Bradley G. Williams, Michelle Lawton, *J. Org. Chem.* **2010**, *75*, 8351–8354.

² M. Schwalbe, D. K. Dogutan, S. A. Stoian, T. S. Teets, D. G. Nocera, *Inorg. Chem.*, **2011**, *50*, 1368–1377.

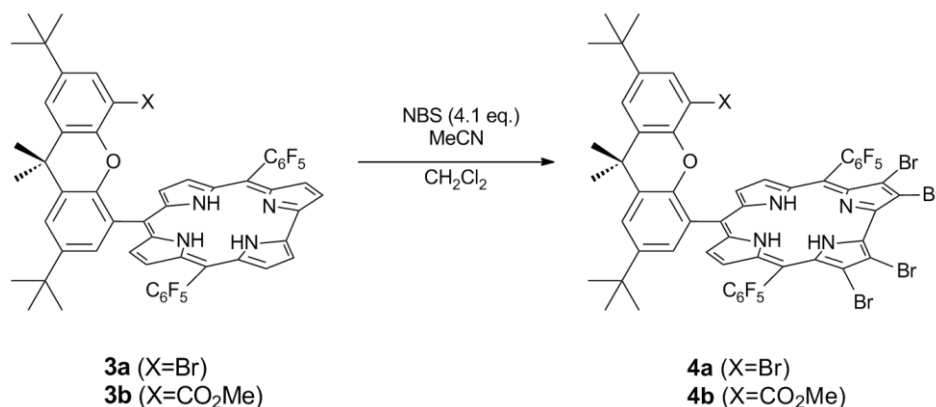
³ D. K. Dogutan, S. A. Stoian, R. McGuire, M. Schwalbe, T. S. Teets, D. G. Nocera, *J. Am. Chem. Soc.* **2011**, *133*, 131–140.

Table S1. Optimization of reaction conditions for bromination of **3a** to yield **4a**.

entry	rxn n [μmol]	rxn time [min]	yield [%]
1	54	1020	52
2	54	900	37
3	54	720	38
4	54	540	41
5	54	360	43
6	54	15+360 ^[a]	58
7	54	720+360 ^[a]	0
8	84	900	39
9	107	1020	32

[a] Two step reaction (x+y min): 1st 80% of reagent (NBS) over x min, 2nd 20% of reagent over y min.

Synthesis.



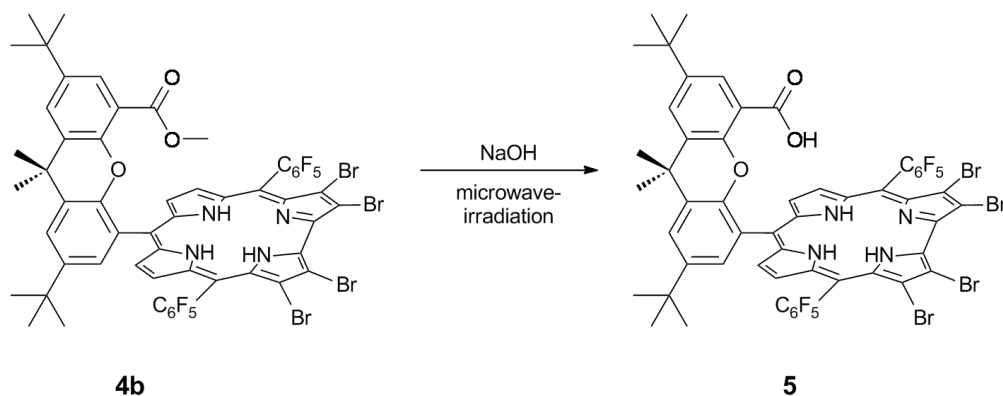
General Protocol for the Synthesis of 2,3,17,18-Tetrabrominated Corroles (4). Method 1.

An optimized procedure following a published one by Chen et al. was used for partial bromination.⁴ A sample of **3** (50 μmol , 1eq.) in CH_2Cl_2 (10 mL) was placed in a round-bottom flask. 4.1 eq. NBS (205 μmol , 36.5 mg) in 11 mL MeCN was added drop wise in two steps by a syringe pump (1st: 80% over 15 min; 2nd: 20 % over 7 h). After the addition the mixture was stirred for further 15 min. Then, the mixture was subsequently washed with H_2O , saturated NaHCO_3 and brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure to yield the crude product, which was purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2 (4:1) as eluent).

⁴ R.-B. Du, C. Liu, D.-M. Shen, Q.-Y. Chen, *Synlett* **2009**, 2009, 2701–2705.

2,3,17,18-Tetrabromo-10-(4-(5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl) corrole (4a). Method 1 was followed. Yield: 39 mg (μmol , 58%). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ =8.54 ppm (m, 4H; β -H), 7.95 ppm (d, $^4J(\text{H,H})=2.0$ Hz, 1H; Xan-H), 7.86 ppm (d, $^4J(\text{H,H})=2.0$ Hz, 1H; Xan-H), 7.40 ppm (d, $^4J(\text{H,H})=2.0$ Hz, 1H; Xan-H), 7.10 ppm (d, $^4J(\text{H,H})=2.0$ Hz, 1H; Xan-H), 1.88 ppm (s, 6H; CH_3), 1.53 ppm (bs, 9H; *t*Bu), 1.25 (bs, 9H, *t*Bu), pyrrolic protons (3H) were not observed at room temperature; HRMS (ESI+) m/z calcd for $\text{C}_{54}\text{H}_{36}\text{Br}_5\text{F}_{10}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 1340.8641, found 1340.8631. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)=418 nm (98), 433 nm (83), 575 nm (18), 648 nm (21).

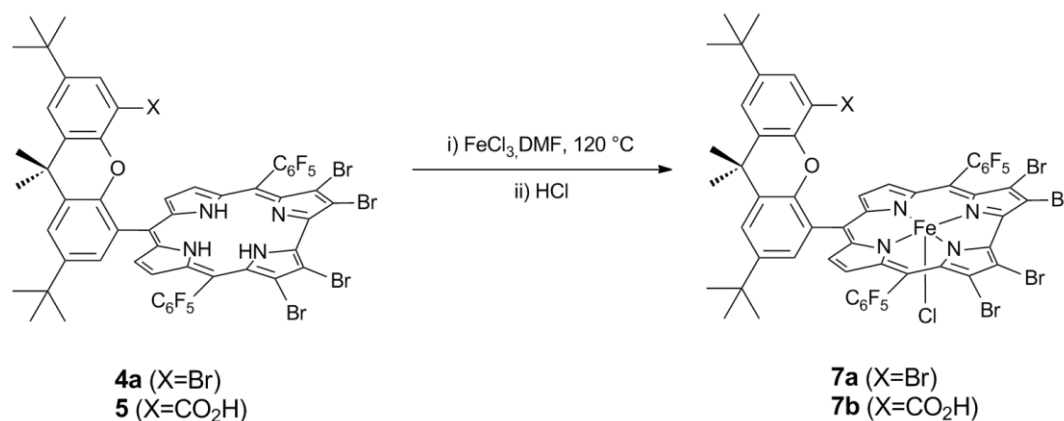
2,3,17,18-Tetrabromo-10-(4-(5-methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl) corrole (4b). Method 1 was followed. Yield: 39 mg (μmol , 59%). ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ =8.53 ppm (m, 4H; β -H), 7.93 ppm (d, $^4J(\text{H,H})=2.5$ Hz, 1H; Xan-H), 7.88 ppm (d, $^4J(\text{H,H})=2.5$ Hz, 1H; Xan-H), 7.67 ppm (d, $^4J(\text{H,H})=2.5$ Hz, 1H; Xan-H), 7.33 ppm (d, $^4J(\text{H,H})=2.5$ Hz, 1H; Xan-H), 1.91 ppm (s, 6H; CH_3), 1.70 ppm (s, 3H; OCH_3), 1.53 ppm (s, 9H; *t*Bu), 1.28 ppm (s, 9H; *t*Bu), pyrrolic protons (3H) were not observed at room temperature; HRMS (ESI+) m/z calcd for $\text{C}_{56}\text{H}_{39}\text{Br}_4\text{F}_{10}\text{N}_4\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 1320.9591, found 1320.9587; UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)=417 nm (106), 433 nm (92), 576 nm (20), 597 nm (18), 646 nm (22).



2,3,17,18-Tetrabromo-10-(4-(5-hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl) corrole (5).

A procedure described by Dogutan et al. was used for basic hydrolysis of **4b**.⁵ A solution of **4b** (78 mg, 59 μmol) in THF (4 mL) was combined with 6 N NaOH (10 mL). The resulting mixture was stirred vigorously to obtain a homogeneous solution and subjected to microwave irradiation (50 W) for 8 h at 75 °C. The reaction mixture was extracted with 100 mL of CH_2Cl_2 . The organic phase was separated, washed with water, brine and subsequently treated with 20% HCl(aq) (50 mL) and stirred overnight at room temperature. The organic phase was separated, washed with water until the solution changed from sheer green to opaque green, and then the solution was washed with brine, dried over Na_2SO_4 , and concentrated to dryness. The resulting crude product was chromatographed (silica, hexanes/ CH_2Cl_2 (1:1) \rightarrow hexanes/ CH_2Cl_2 (2:3) to afford a purple solid (50 mg, 38 μmol , 65%). ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ =8.56 ppm (d, $^3J(\text{H,H})=4.8$ Hz, 2H; β -H), 8.49 ppm (d, $^3J(\text{H,H})=4.8$ Hz, 2H; β -H), 7.94 ppm (m, 2H; Xan-H), 7.75 ppm (d, $^4J(\text{H,H})=2.4$ Hz, 1H; Xan-H), 7.66 ppm (d, $^4J(\text{H,H})=2.4$ Hz, 1H; Xan-H), 1.97 ppm (s, 6H; CH_3), 1.53 ppm (s, 9H; *t*Bu), 1.28 ppm (s, 9H; *t*Bu), pyrrolic (3H) and carboxylic acid protons were not observed at room temperature; HRMS (ESI) m/z calcd for $\text{C}_{55}\text{H}_{35}\text{Br}_4\text{F}_{10}\text{N}_4\text{O}_3^-$ [$\text{M}-\text{H}$] $^-$: 1304.9288, found 1304.9309, for $\text{C}_{55}\text{H}_{36}\text{Br}_3\text{F}_{10}\text{N}_4\text{O}_3^-$ [$\text{M}-\text{Br}$] $^-$: 1227.0183, found 1227.0202; UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)=417 nm (103), 433 nm (91), 573 nm (19), 599 nm (15), 647 nm (19).

⁵ D. K. Dogutan, S. A. Stoian, R. McGuire, M. Schwalbe, T. S. Teets, D. G. Nocera, *J. Am. Chem. Soc.* **2011**, *133*, 131–140.



General Synthesis of FeCl Corroles (7). Method 2. A solution of **4a** or **5** (0.10 mmol) and anhydrous FeCl₃ (162 mg, 1.00 mmol) in 20 mL of dimethylformamide (DMF) was degassed with argon for 20 min. Subsequent heating to reflux (115 °C) for 4 h resulted in a color change from dark green to dark red. DMF was removed under vacuum, and the resulting product was dissolved in 100 mL of CH₂Cl₂. This solution was washed with water and brine to remove residual DMF, dried over Na₂SO₄, and concentrated to dryness. The resulting crude product was chromatographed (silica, diethylether) to afford the corresponding iron- μ -oxo dimer as a major brown band. The collected fraction was concentrated to dryness, and CH₂Cl₂ (30 mL) and 7% HCl(aq) (10 mL) were added. The mixture was stirred vigorously for several hours. The organic phase was washed with water and brine, and dried over Na₂SO₄. The solution was concentrated to dryness, and the resulting crude product was purified by flash column chromatography (silica gel, CH₂Cl₂/EtOH (49:1) as eluent). Treatment with hexane and vacuum drying yielded a dark brown solid.

2,3,17,18-Tetrabromo-10-(4-(5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl)corrolato Iron Chloride (7a). Method 2 was followed. The iron- μ -oxo dimer was treated with HCl for 2 h. Yield: 99 mg (69 μ mol, 69%). HRFTMS (MALDI+) *m/z*. calcd for C₅₄H₃₂Br₅F₁₀FeN₄O⁺ [M-Cl]⁺: 1392.7684, found 1392.7683; EA: Found: C, 46.68; H, 2.61; N, 3.79%. Calc. for C₅₄H₃₂N₄OBr₅ClFeF₁₀*0.5C₆H₁₄: C, 46.36; H, 2.66; N, 3.79%; UV/Vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)=375 nm (56), 508 nm (14), 629 nm (5.9).

2,3,17,18-Tetrabromo-10-(4-(5-hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl)corrolato Iron Chloride (7b). Method 2 was followed. The iron- μ -oxo dimer was treated with HCl overnight. Yield: 85 mg (61 μ mol, 61%). HRMS (ESI⁺): *m/z*. calcd for C₅₅H₃₃Br₄F₁₀FeN₄O₃⁺ [MCl]⁺ 1358.8477, found 1358.8473; UV/Vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)=377 nm (48), 433 nm (47), 518 nm (13), 636 (5.6).

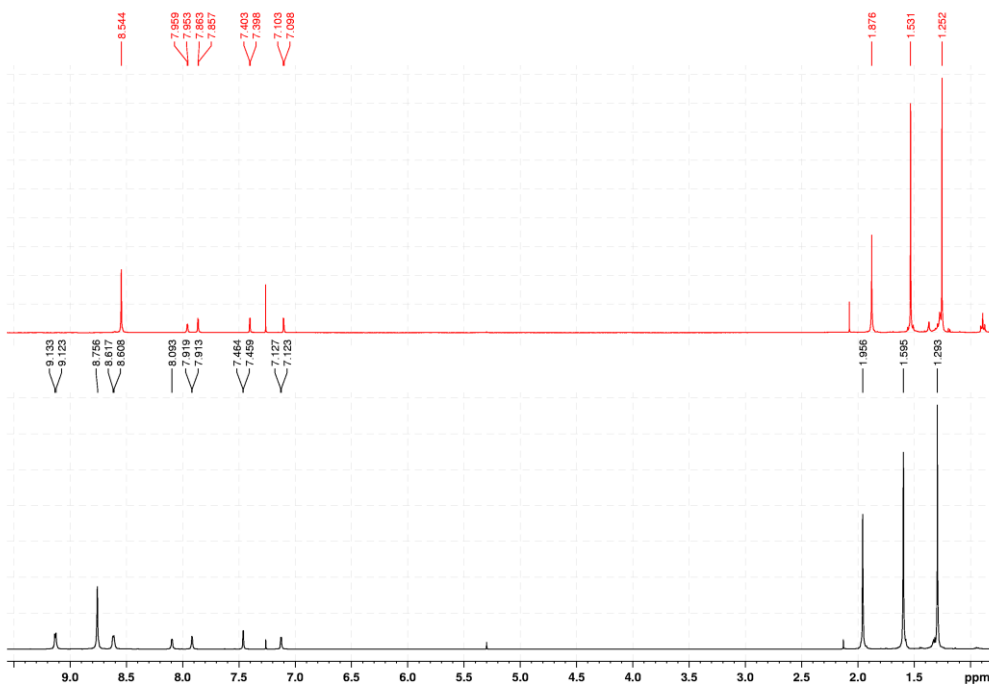


Figure S1a. Full ¹H NMR spectra (400 MHz, CDCl₃) of **3a** (black) and **4a** (red). Two signals in the aromatic region from 8 till 9.5 ppm are missing in the red spectrum indicating the bromination of four β-pyrrolic positions.

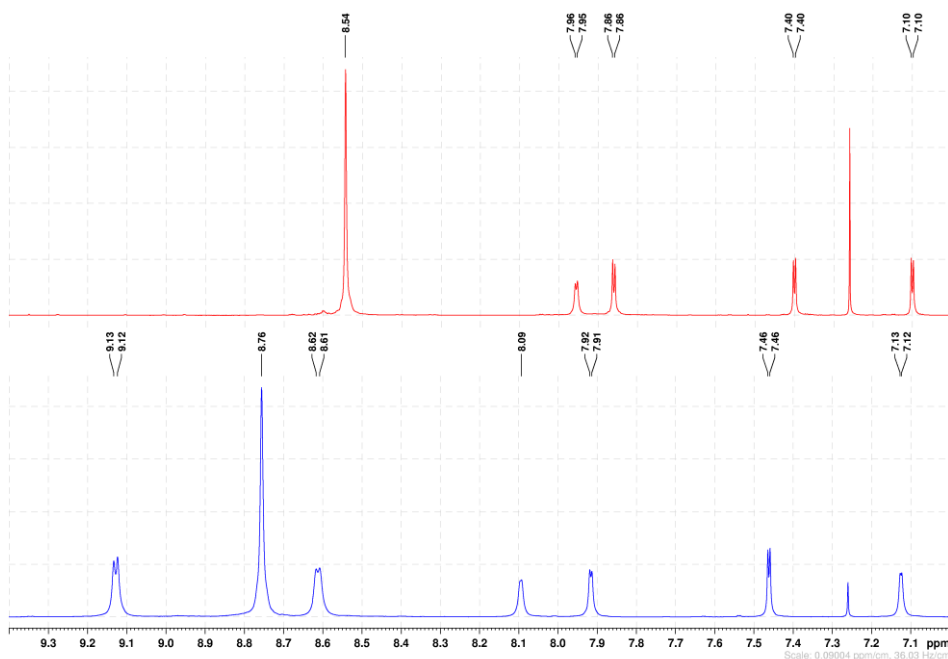


Figure S1b. Aromatic region of the ¹H NMR spectra (400 MHz, CDCl₃) of **3a** (blue) and **4a** (red).

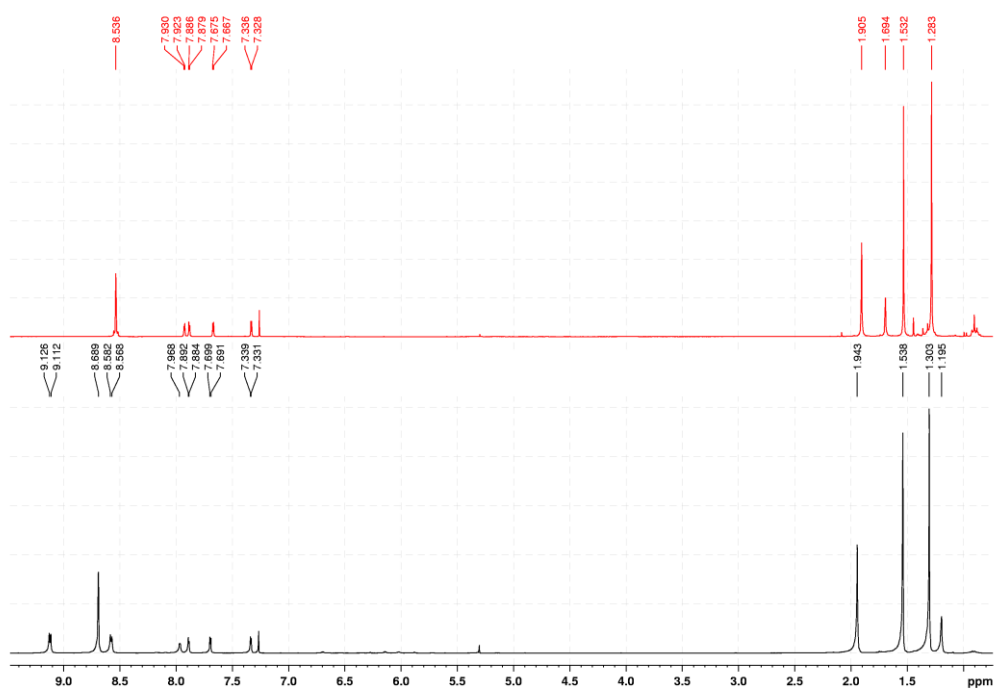


Figure S2a. Full ¹H NMR spectra (300 MHz, CDCl₃) of **3b** (black) and **4b** (red).

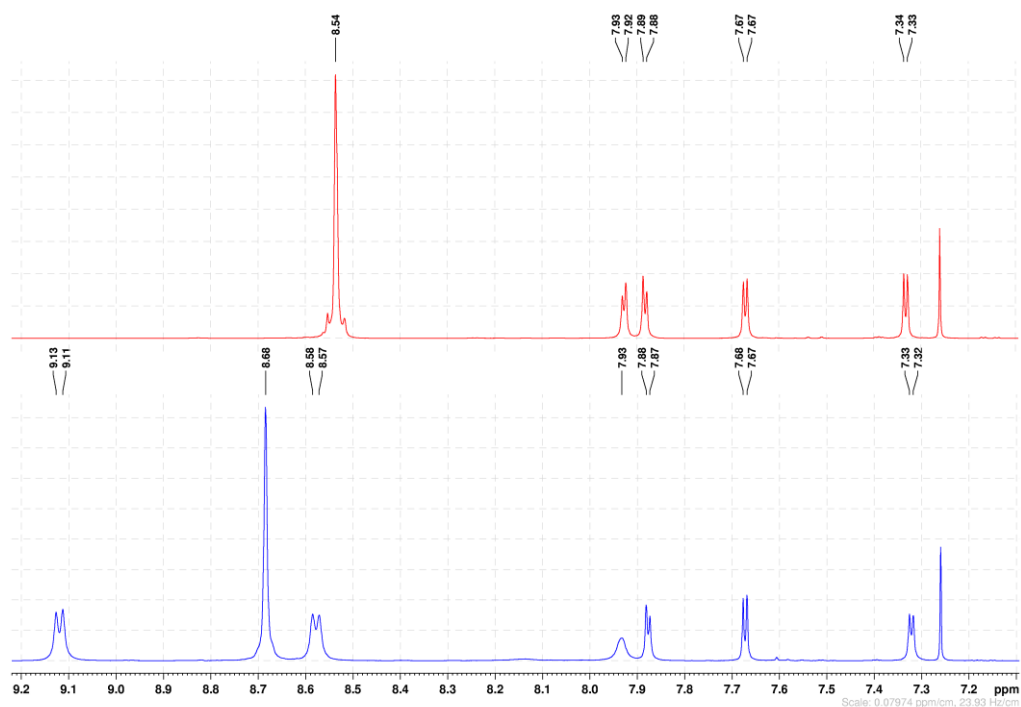


Figure S2b. Aromatic region of the ¹H NMR spectra (500 MHz, CDCl₃) of **3b** (blue) and **4b** (red).

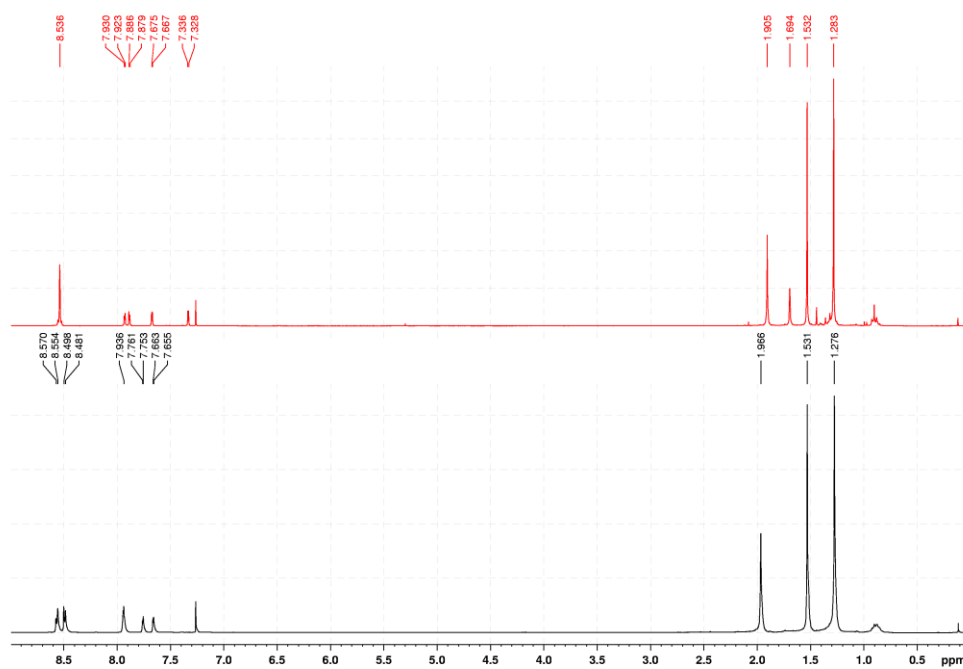


Figure S3a. Full ¹H NMR spectra (300 MHz, CDCl₃) of **4b** (red) and **5** (black). The signal at 1.69 ppm corresponds to the methoxy protecting group in the spectrum of **4b** and disappears in the spectrum of **5**.

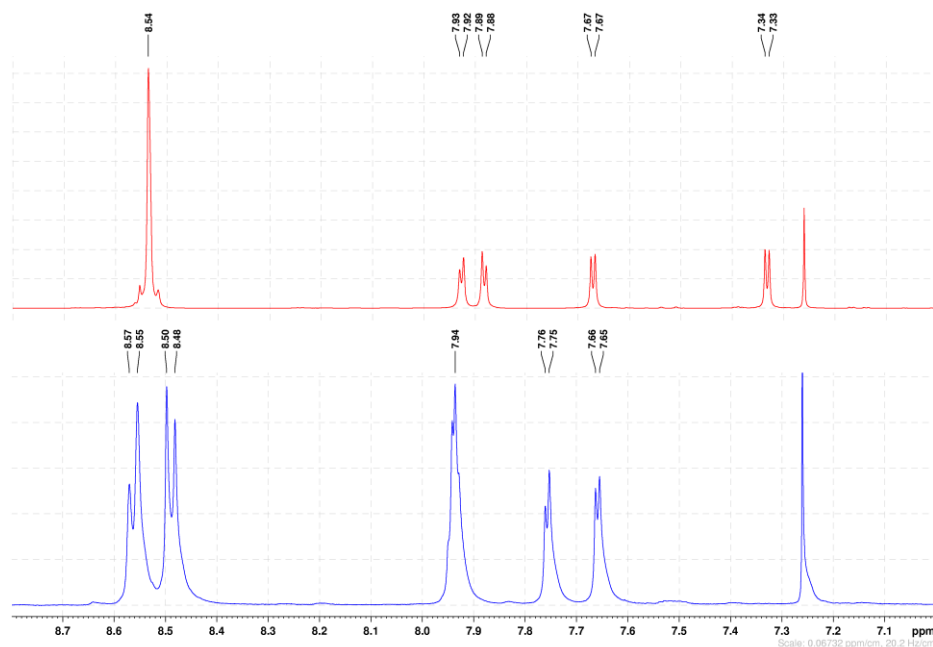


Figure S3b. Aromatic region of the ¹H NMR spectra (300 MHz, CDCl₃) of **4b** (red) and **5** (blue).

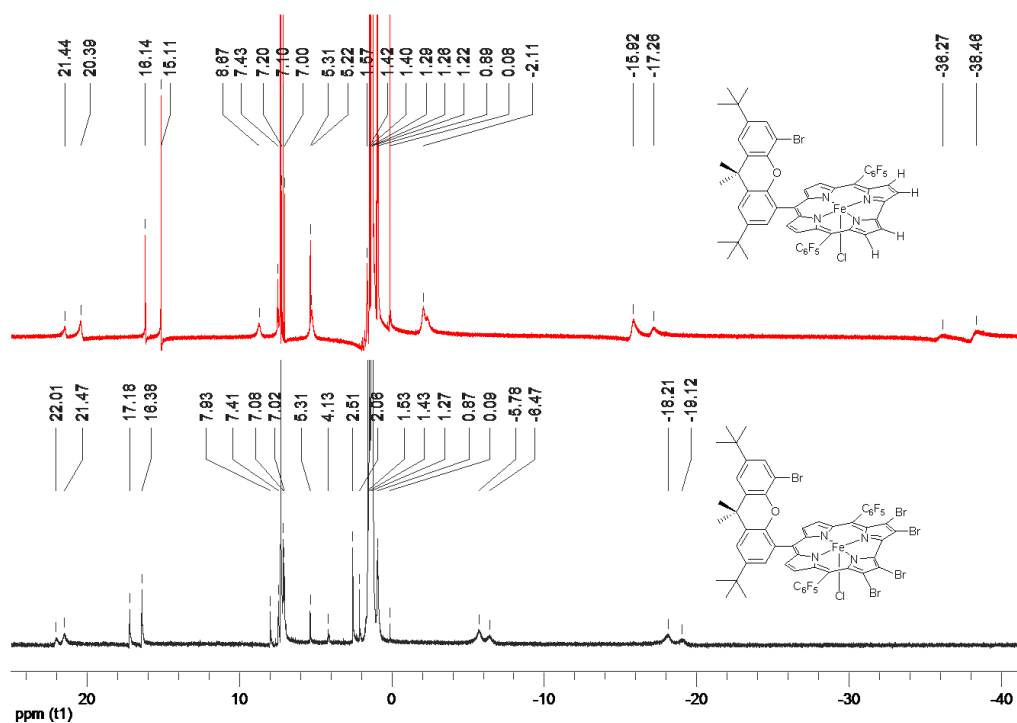


Figure S4a. Full ^1H NMR spectra (300 MHz, CDCl_3) of **2a** (red) and **7a** (black).

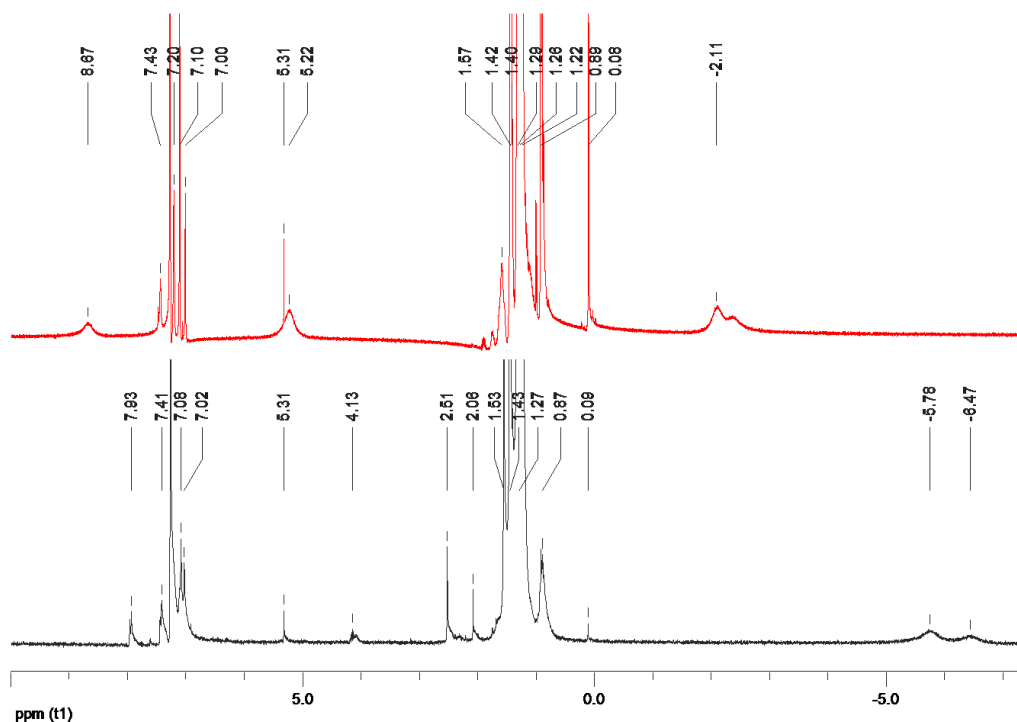


Figure S4b. Cutout from -7.5 to 10 ppm of the ^1H NMR spectra (300 MHz, CDCl_3) of **2a** (red) and **7a** (black). (Signals at 5.31 ppm and around 1.3 ppm correspond to solvent residues, CH_2Cl_2 and hexane.)

Discussion of ^1H NMR spectra of **7**:

The NMR spectra of iron chloride corroles always show big paramagnetic shifts. Tri-(pentafluorophenyl) corrolate iron chloride, $\text{Cor}(\text{C}_6\text{F}_5)_3\text{FeCl}$, was synthesized and investigated before by Walker and coworkers.⁶ It basically shows the expected four signals, which we could also reproduce with a self-made sample. The authors also mention that there are always some impurities in the NMR spectra – most of them solvents – that are hard to remove; as we had to experience too.

Surprisingly, all Hangman corroles show a doubling of the signals which we assign to two isomers in solution. The intensity ratio of the signals for the two isomers depends on the substituents in the compounds. Although, a crystal structure could be obtained for **2a** showing the chloride apical ligand in a “down” formation,² i.e. away from the xanthene backbone, we can imagine that this is not always the case in solution and a minor “up” form is also likely resulting in a second set of signals.

In the ^1H NMR spectrum of **2a** the signals around -37 ppm and 5 ppm correspond presumably to the two β -pyrrolic positions that become brominated and which disappear in the spectrum of **7a**. By comparison with $\text{Cor}(\text{C}_6\text{F}_5)_3\text{FeCl}$ signals at $15 - 22$ ppm can be assigned to the xanthene backbone. Further assignment is not possible because the paramagnetic nature prohibits the recording of 2D spectra.

⁶ a) S. Cai, S. Licoccia, C. D'Ottavi, R. Paolesse, S. Nardis, V. Bulach, B. Zimmer, T. K. Shokhireva, F. A. Walker, *Inorg. Chim. Acta* **2002**, 339, 171-178; b) S. Nardis, R. Paolesse, S. Licoccia, F. R. Fronczek, M. G. H. Vicente, T. K. Shokhireva, S. Cai, F. A. Walker, *Inorg. Chem.* **2005**, 44, 7030-7046.

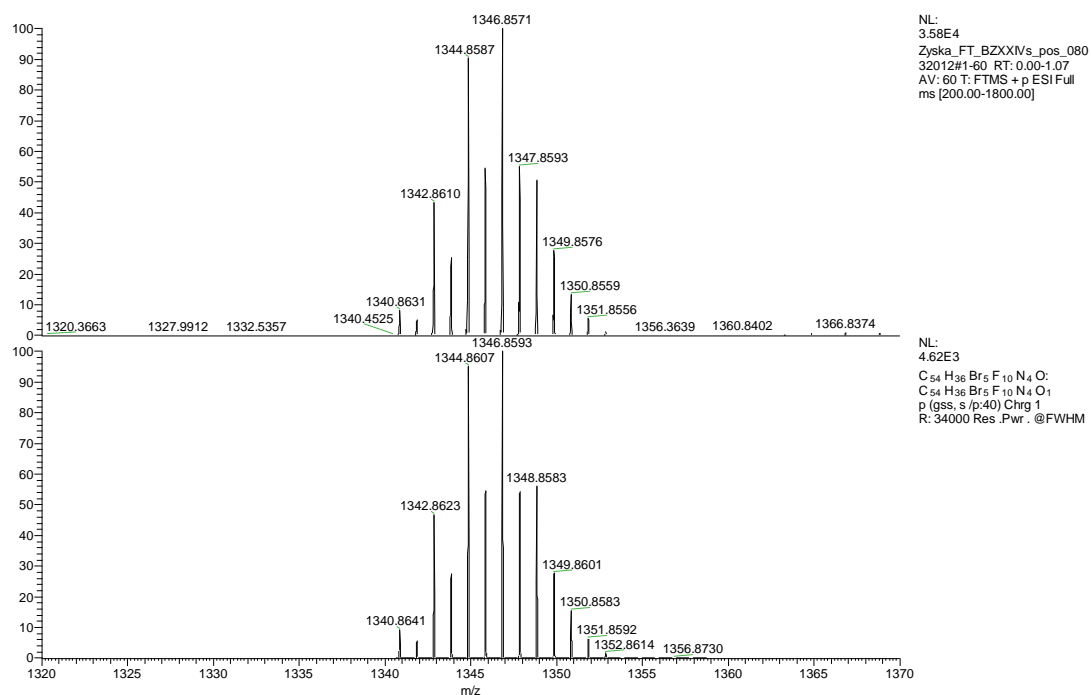


Figure S5a. Calculated (bottom) and measured (top) HRMS (ESI+) isotopic pattern of 4a.

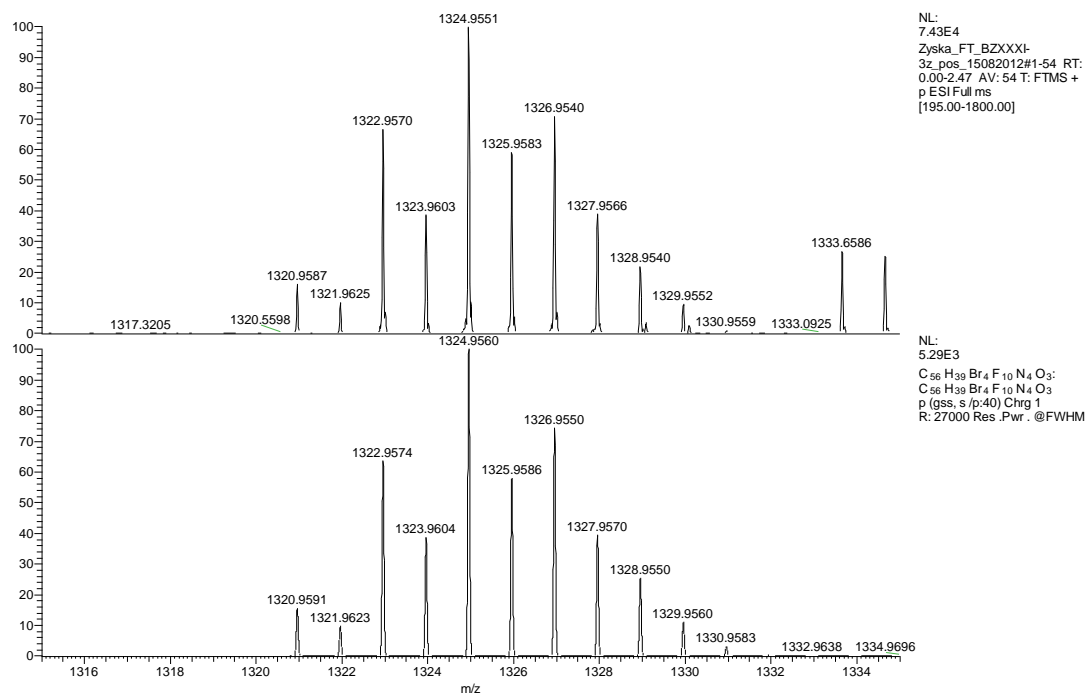


Figure S5b. Calculated (bottom) and measured (top) HRMS (ESI+) isotopic pattern of 4b.

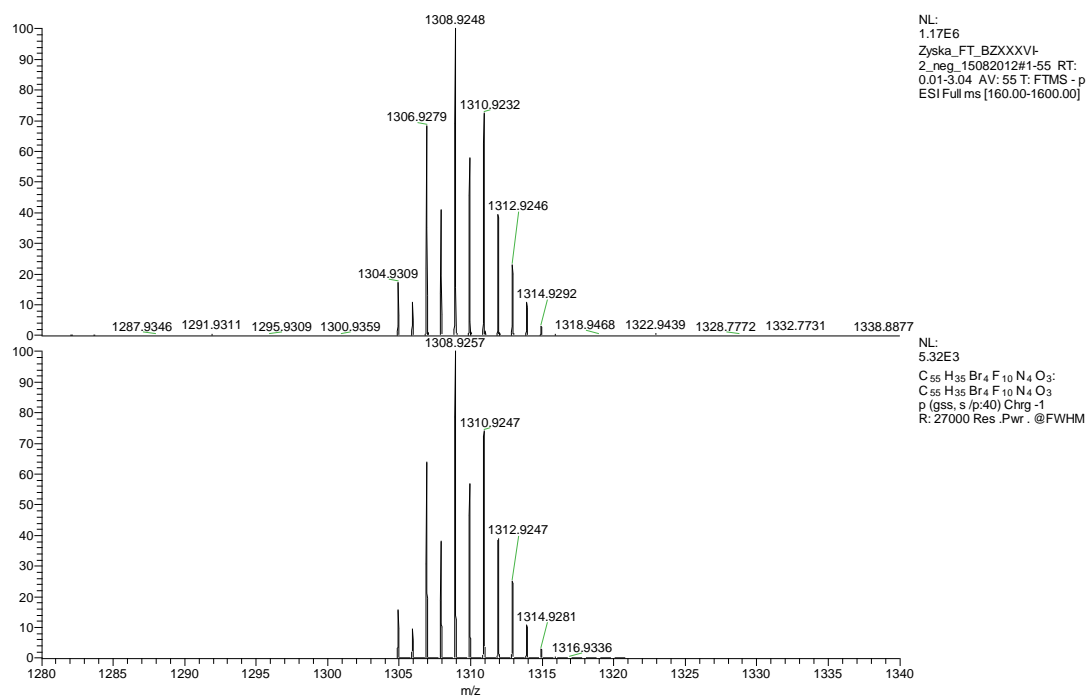


Figure S6. Calculated (bottom) and measured (top) HRMS (ESI+) isotopic pattern of **5**.

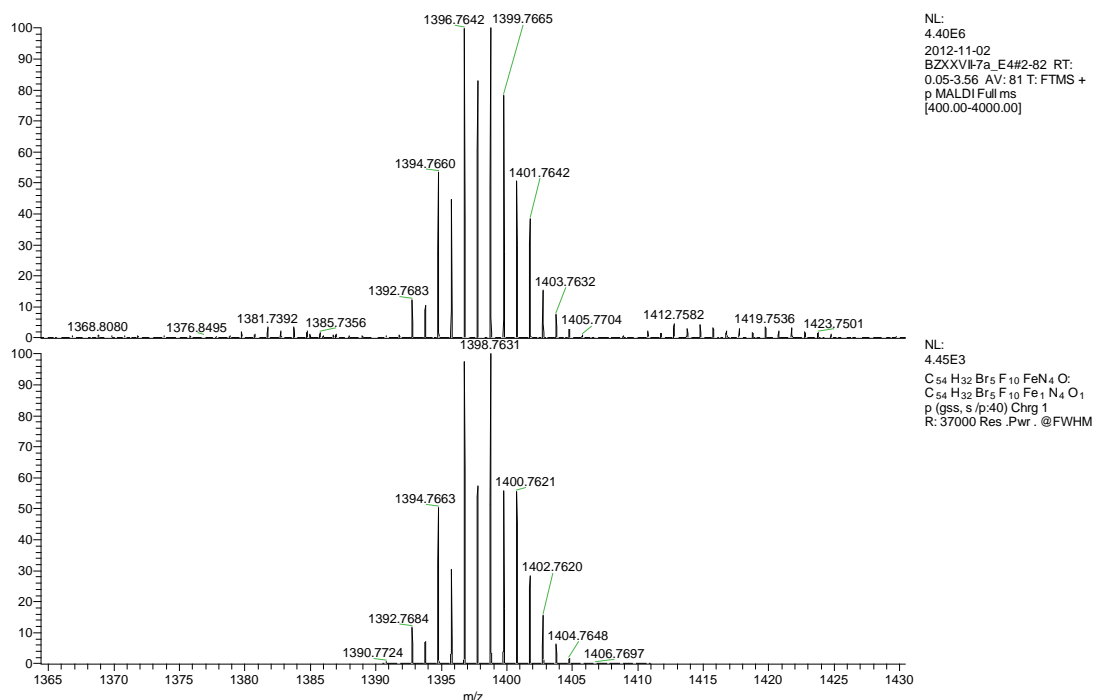


Figure S7a. Calculated (bottom) and measured (top) HRMS (MALDI+) isotopic pattern of **7a**.

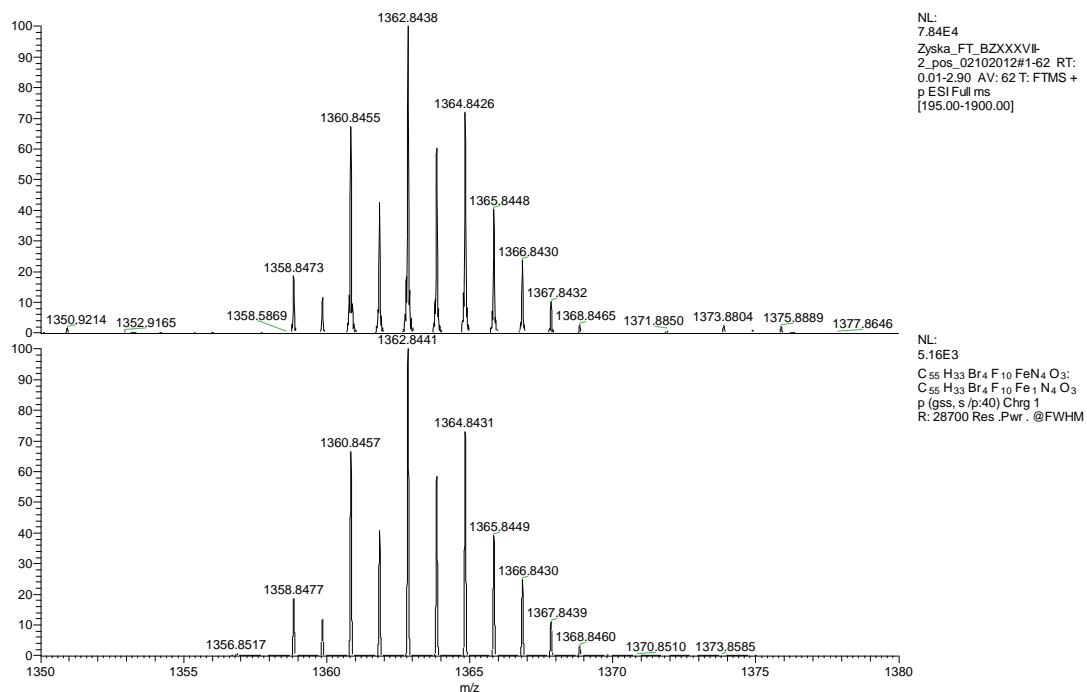


Figure S7b. Calculated (bottom) and measured (top) HRMS (ESI+) isotopic pattern of **7b**.

Catalytic Assay. Hydrogen peroxide dismutation reactions were performed at room temperature in a sealed (PTFE septum) 15 mL reaction vial equipped with a magnetic stirbar and a capillary gas delivery tube linked to a graduated buret filled with water. The reaction vial was charged with 3 μmol of the iron corrole catalyst, 75 μmol of 1,5-dicyclohexylimidazole, 4.5 mL of CH_2Cl_2 and 1.5 mL of CH_3OH so that a 0.5 mM solution was received. The dicyclohexylimidazole is used as a ligand to axially coordinate iron opposite the hangman cleft. The solution was stirred for 5-10 min to ensure gas pressure equilibration. An aliquot of 10.4 M (30%) aqueous H_2O_2 (0.33 mL) was added to the reaction mixture via syringe, and the reaction mixture was stirred vigorously. The time was set to zero immediately after addition of H_2O_2 . The O_2 evolution reaction was monitored volumetrically, and the TON for produced O_2 was calculated using the ideal gas equation.

The concentration dependant experiments were performed under similar conditions as described above. A fixed ratio (1:25) of iron corrole catalyst to dicyclohexylimidazole as axial ligand was used and the reaction volume was kept constant at 6 mL CH_2Cl_2 : CH_3OH (3:1). Concentrations of 0.167 mM, 0.250 mM, 0.333 mM, 0.417 mM and 0.5 mM were investigated.

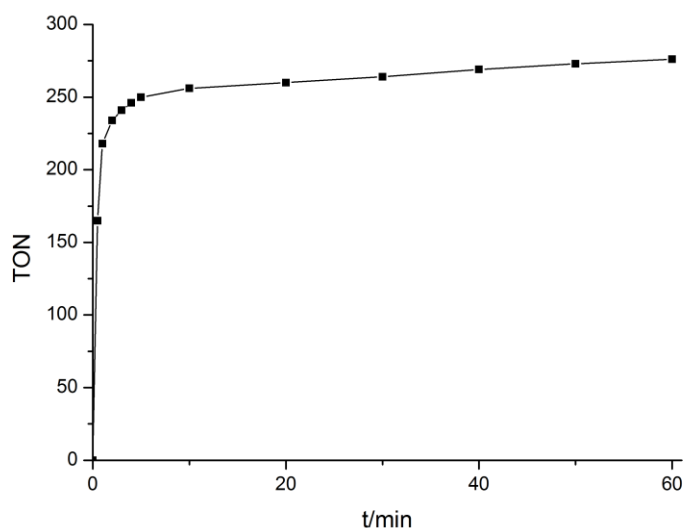


Figure S8. O_2 evolution over 60 min at 0.33 mM catalyst (**7a**) concentration.

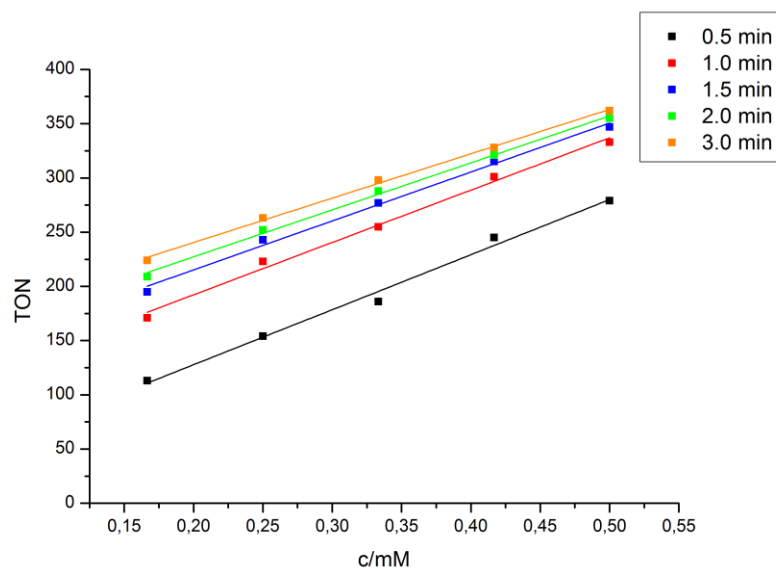


Figure S9. Dependency of TON vs. catalyst concentration for **7a** at different times of the reaction. Data of the fitting graphs are given in Table S2.

Table S2. Mathematical Data of the fitting graphs for the concentration dependency of the catalytic activity of **7a**.

entry	rxn time	slope	constant term	R ²
1	0.5 min	508 ± 27	26 ± 9	0.989
2	1.0 min	482 ± 23	96 ± 8	0.991
3	1.5 min	451 ± 19	125 ± 7	0.993
4	2.0 min	433 ± 13	141 ± 5	0.996
5	3.0 min	409 ± 11	159 ± 4	0.997

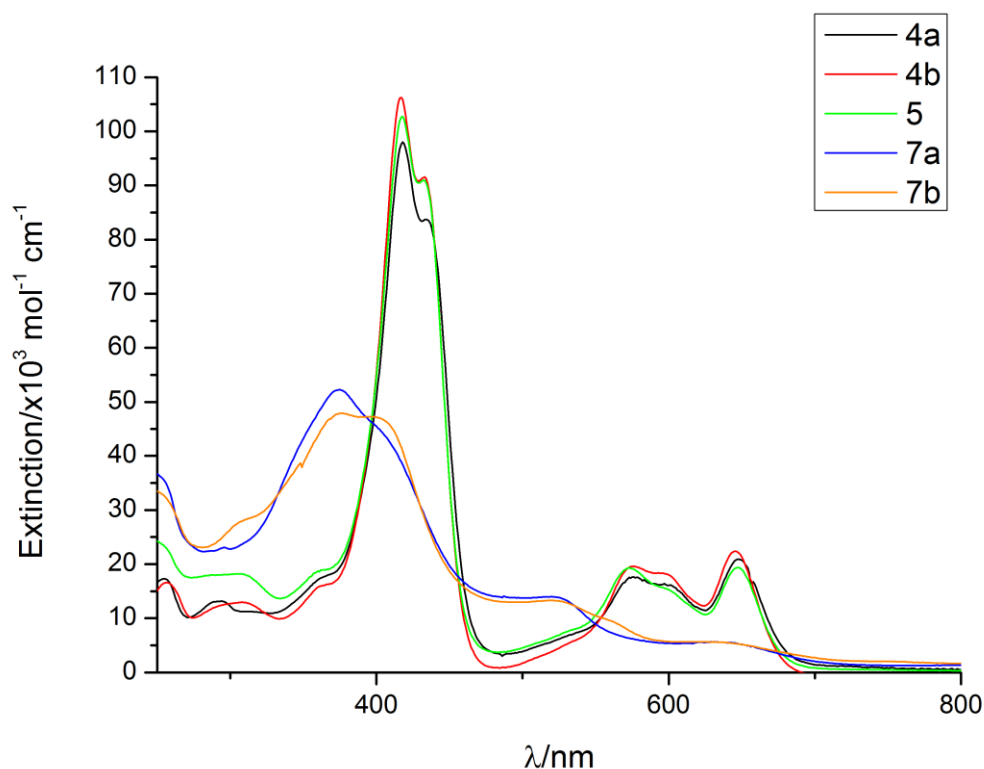


Figure S10. Overview of UV/vis spectra of **4**, **5** and **7**.

Table S3. Comparison of absorption maxima in CH₂Cl₂ of xanthene modified corroles (sh = shoulder).

Compound	$\lambda_{\text{abs, max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)				
3a	414 (134)		560 (21)	612 (12)	630 (sh, 8.6)
3b	411 (139)		558 (22)	612 (13)	630 (sh, 8.6)
4a	418 (98)	433 (83)	575 (18)	598 (16)	648 (21)
4b	417 (106)	433 (92)	576 (20)	597 (18)	646 (22)
5	417 (103)	433 (91)	573 (19)	599 (15)	647 (19)
2a	367 (sh, 48)	395 (53)	510 (sh, 10)		623 (4.8)
2c	365 (sh, 40)	396 (47)	512 (sh, 8.7)		622 (3.7)
7a	375 (52)	398 (sh, 46)	521 (14)		637 (5.6)
7b	377 (48)	396 (47)	518 (13)		636 (5.6)

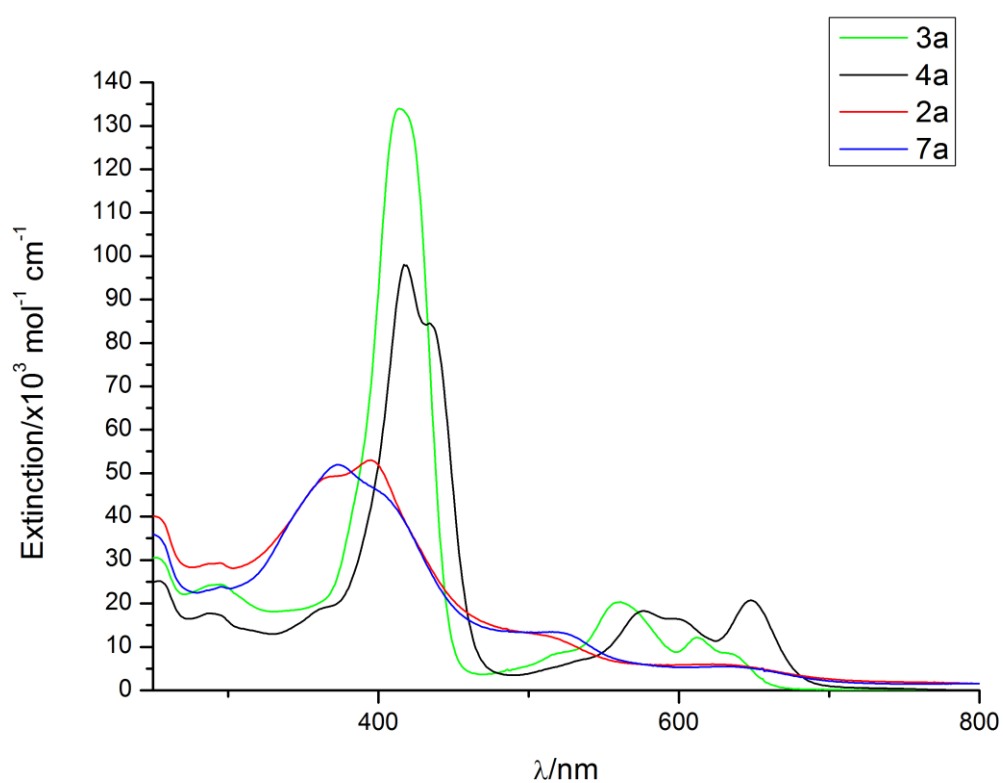


Figure S11. Comparison of UV/vis spectra of **3a** and **4a** as well as **2a** and **7a**.