Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

Photophysical and electrochemical properties of two trans-A_2B-corroles: Differences between phenyl or pyrenyl groups *meso*-10 position

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Synthetic methodology

Synthesis of 5,15-bis(pentafluorophenyl)-10-(phenyl)corrole ***1a*** *and 5,15-bis(pentafluorophenyl)-10-(1-pyrenyl)corrole* ***1b***

The same synthetic methodology was used for the synthesis of the two mono-substituted corroles[1,2]. C_6F_5-DPM (0.094 g; 0.30 mmol) and the respective aldehyde (16 μL; 0.15 mmol for PhCHO and 0.034 g; 0.15 mmol for PyrCHO) were dissolved in 50 mL MeOH. Subsequently, a solution of HCl_{aq} (37%; 2.0 mL) in H_2O (50 mL) was added and the reaction was stirred at room temperature for 1.0 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with water, dried (Na_2SO_4), filtered, and diluted to 250 mL with CH_2Cl_2. A solution of *p*-chloranil (0.111 g; 0.45 mmol) in dichloromethane was added, and the mixture was stirred for 24 h. The reaction mixture was concentrated to half of this volume and it was purified first on a silica-gel chromatography column (CH_2Cl_2/hexane, 1:2, v/v). Then, the resulting residue was purified again by preparative silica-gel TLC plates using the same mixture, to obtain pure dark purple corroles **1a** and **1b**, respectively.

Spectroscopic data for corrole 1a: Yield 0.019 g; 0.027 mmol (18%). M.p. > 300ºC (decomp.). ^{1}H NMR (600.13 MHz, $CDCl_3$): δ = 7.77 (m, 3H; H_a), 8.19 (m, 2H;H_b), 8.57 (bs, 2H; $H_{3,17}$), 8.70 (s, 4H; $H_β$), 9.13 (d, 2H, J = 6.0 Hz; $H_{2,18}$). ^{19}F RMN (564.68 MHz, $CDCl_3$): −161.78 (m, 4F; F_{meta}), −152.85 (bs, 2F; F_{para}), −137.84 (m, 4F; F_{orto}). FT-IR (KBr pellets, cm^{-1}): 3358 ($ν_{N—H}$), 2923 ($ν_{C=C}$), 1519 ($ν_{C=N}$), 987 ($ν_{C—N}$), 759 ($δ_{C—H}$). Anal. Calcd for $C_{37}H_{16}N_4F_{10}$ (%): C, 62.90; H, 2.28; N, 7.93. Found (%): C, 62.98; H, 2.29; N, 7.97. HRMS-APCI-(+) $[M+H]^+$: m/z = 707.1284 (calcd for $C_{37}H_{17}N_4F_{10}$: 707.1288).

Spectroscopic data for corrole 1b: Yield 0.015 g; 0.018 mmol (12%). M.p.> 300ºC (decomp.). ^{1}H NMR (600.13 MHz, $CDCl_3$): δ = 7.48 (d, 1H, J = 12.0 Hz; H_d), 7.73 (d, 1H, J = 12.0 Hz; H_e), 8.08 (m, 1H; H_c), 8.13 (d, 1H, J = 12.0 Hz; H_f), 8.35 (dd, 4H, J^1 = 12.0 Hz e J^2 = 6.0 Hz; H_i, H_b and $H_{3,17}$), 8.40 (d, 1H, J = 6.0 Hz; H_g), 8.53 (d, 1H, J = 6.0 Hz; H_a), 8.59 (s, 4H; $H_β$), 8.73 (d, 1H, J = 12.0 Hz; H_j), 9.15 (d, 2H, J = 6.0 Hz; $H_{2,18}$). ^{19}F RMN (564.68 MHz, $CDCl_3$): −165.78 (m, 4F; F_{meta}), −156.86 (bs, 2F; F_{para}), −141.85 (m, 4F; F_{orto}). FT-IR (KBr pellets, cm^{-1}): 3250 ($ν_{N—H}$), 2924 ($ν_{C=C}$), 2853 ($ν_{C=C}$), 1522 ($ν_{C=N}$), 988 ($ν_{C—N}$), 801 ($δ_{C—H}$). Anal. Calcd for $C_{47}H_{20}N_4F_{10}$ (%): C, 67.96; H, 2.43; N, 6.74. Found (%): C, 68.03; H, 2.46; N, 6.88. HRMS-APCI-(+) $[M+H]^+$: m/z = 831.1601 (calcd for $C_{47}H_{21}N_4F_{10}$: 831.1601).

Tables

Table S1. Elemental analysis (CHN%) of corroles **1a** and **1b**.

	Corrole 1a	**Corrole 1b**
$\%C_{exp}$; $\%C_{calcd}$	62.98; 62.90	68.03; 67.96
$\%H_{exp}$; $\%H_{calcd}$	2.29; 2.28	2.46; 2.43
$\%N_{exp}$; $\%N_{calcd}$	7.97; 7.93	6.88; 6.74
Molecular formula	$C_{37}H_{16}F_{10}N_4$	$C_{47}H_{20}F_{10}N_4$

Table S2. Main geometric parameters of corroles **1a** and **1b**. Bond lengths are given in angstroms (Å).

Bond lengths	**Corrole 1a**		**Corrole 1b**	
	Singlet ($^1S_0$)	Triplet ($^3S_0$)	Singlet ($^1S_0$)	Triplet ($^3S_0$)
H35–H36	2.130	2.153	2.111	2.164
H35–H37	2.067	2.250	2.077	2.206
N9–N16	2.636	2.648	2.697	2.644
N9–N24	3.903	3.935	3.896	3.929
N9–N31	2.639	2.679	2.640	2.678
N9–H35	1.029	1.025	1.028	1.025
N9–C8	1.367	1.372	1.367	1.372
N9–C4	1.369	1.364	1.369	1.364
N9–C15	2.838	2.862	2.839	2.861
N16–C15	1.383	1.365	1.382	1.363
N16–C11	1.369	1.386	1.368	1.387
N16–C23	3.053	3.059	3.053	3.067
N24–C23	1.384	1.384	1.384	1.384
N24–C32	1.391	1.384	1.392	1.384
N24–C28	2.996	3.014	2.992	3.008
N31–C28	1.379	1.384	1.380	1.384
N31–C30	1.383	1.379	1.383	1.380
N31–N24	2.765	2.835	2.760	2.825
C8–C15	2.485	2.508	2.485	2.508
C11–C23	2.521	2.543	2.520	2.542
C32–C28	2.484	2.510	2.484	2.513
C4–C30	1.419	1.456	1.420	1.456

Table S3. Bader's atomic point charge. Last column presents the percentual difference between the absolute values.

Corrole 1b			
Atom / State	S	T	Percentual Diff.
N9	-1.1485	-1.1466	0.16
N16	-1.0428	-1.0066	3.47
N24	-1.1038	-1.0887	1.37
N31	-1.0913	-1.1048	1.22
H35	+0.4901	+0.4878	0.47
H36	+0.4361	+0.4384	0.52
H37	+0.4452	+0.4466	0.31
C4	+0.3872	+0.3926	1.37
C11	+0.3789	+0.3408	10.0
C17	-0.0102	+0.0172	40.7
C23	+0.3623	+0.3423	5.52
C30	+0.3537	+0.3556	0.53
$C_{Pyr/Ph}$	-0.0098	-0.0150	34.7

Figures

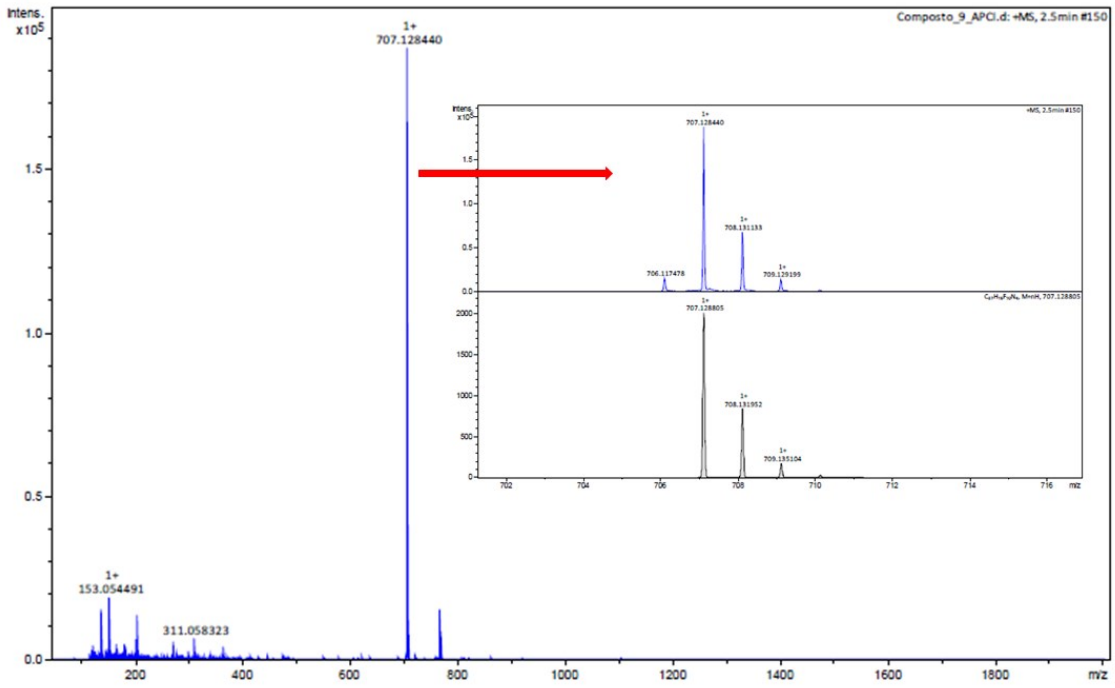

Figure S1. HRMS-APCI mass spectra analysis of corrole **1a**, in the positive mode.

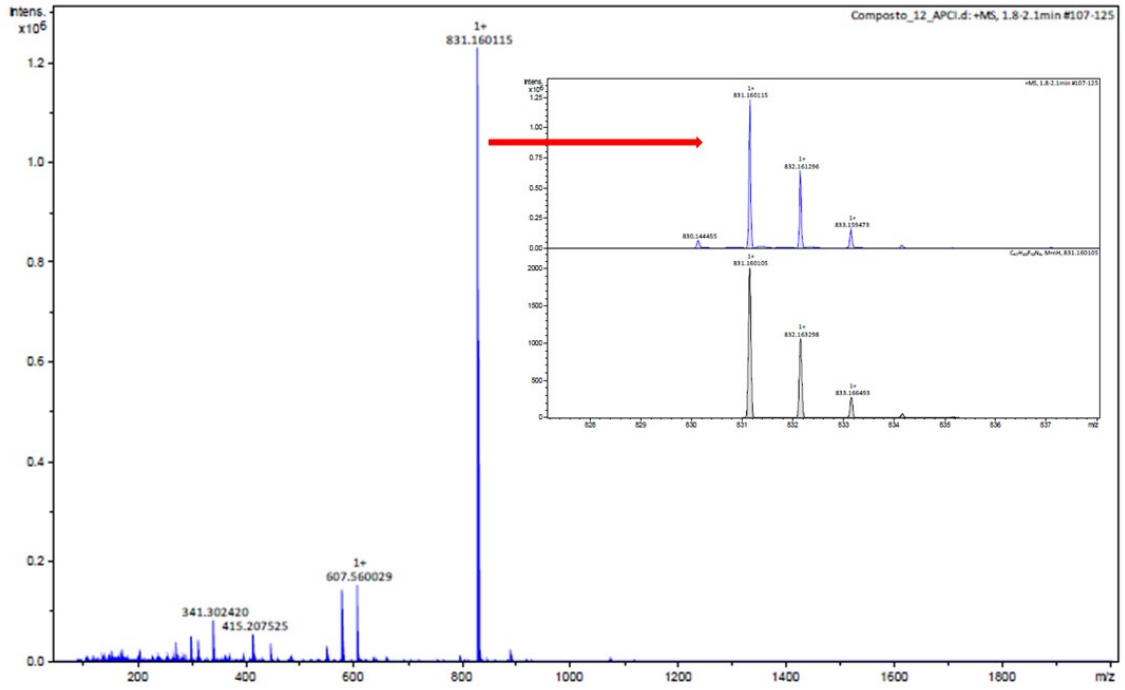

Figure S2. HRMS-APCI mass spectra analysis of corrole **1b**, in the positive mode.

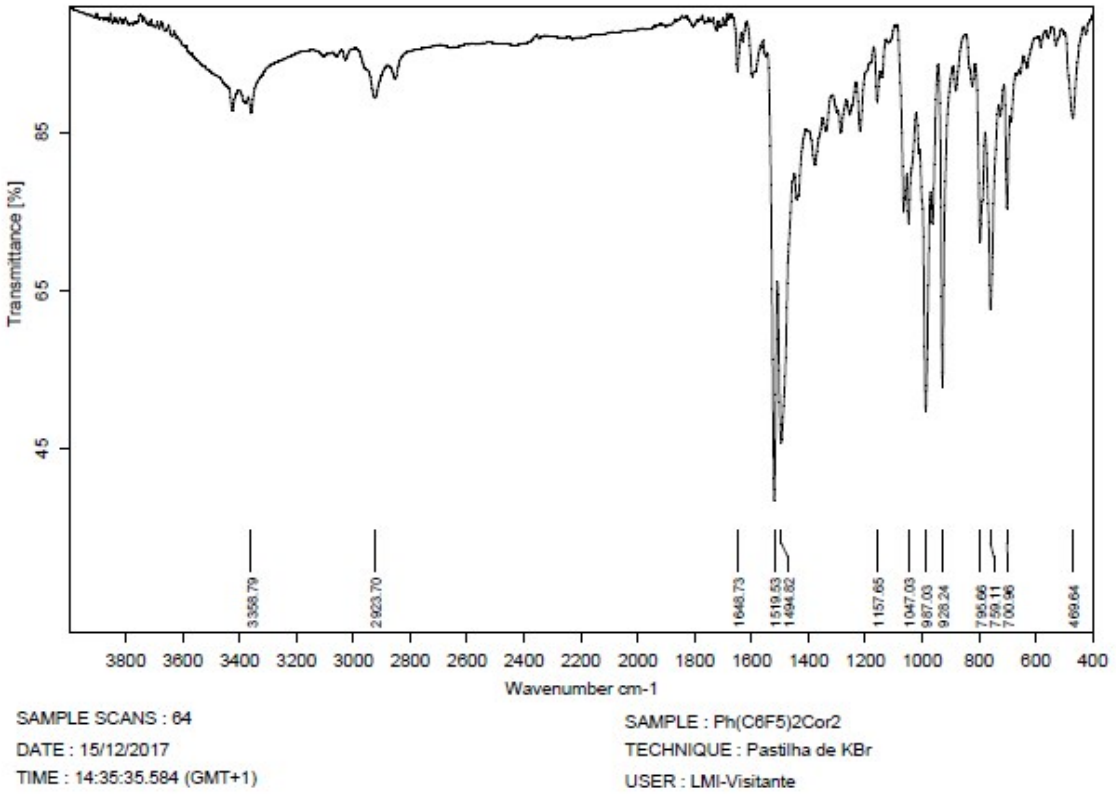

Figure S3. FTIR vibrational spectra analysis of corrole **1a**, in KBr pellets, at 4000 to 400 cm^{-1}.

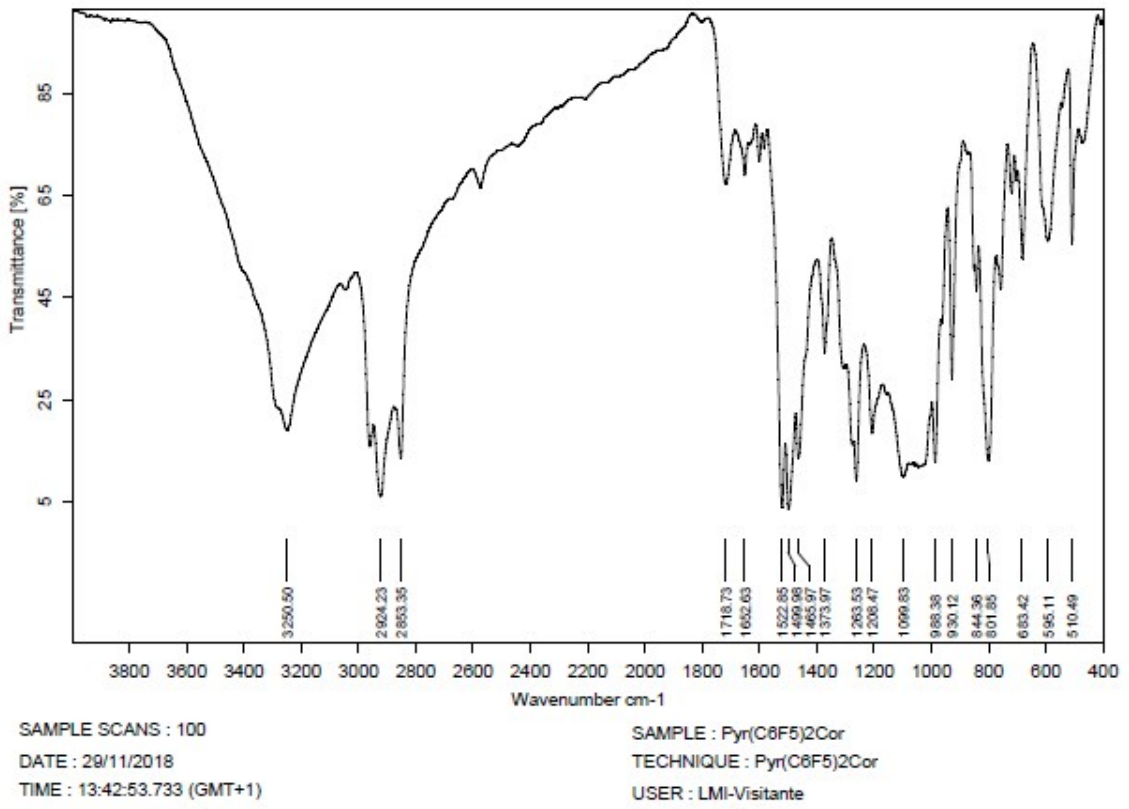

Figure S4. FTIR vibrational spectra analysis of corrole **1b**, in KBr pellets, at 4000 to 400 cm^{-1}.

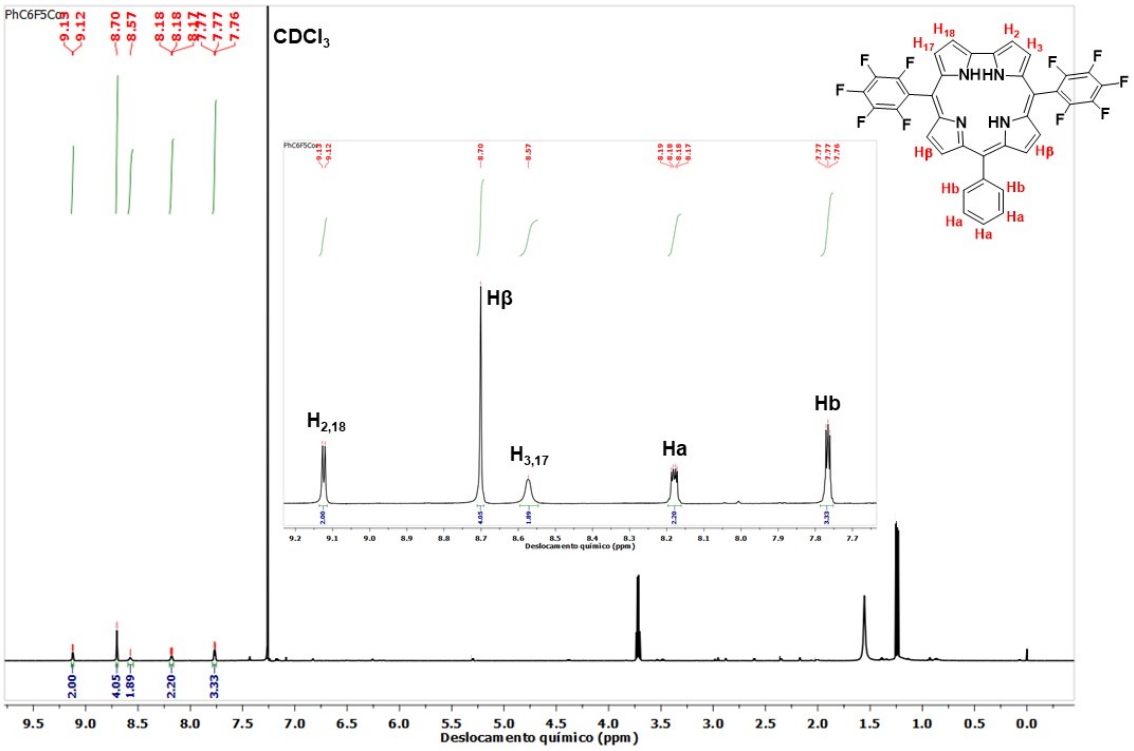

Figure S5. ^{1}H-NMR spectra of corrole **1a**, in $CDCl_3$.

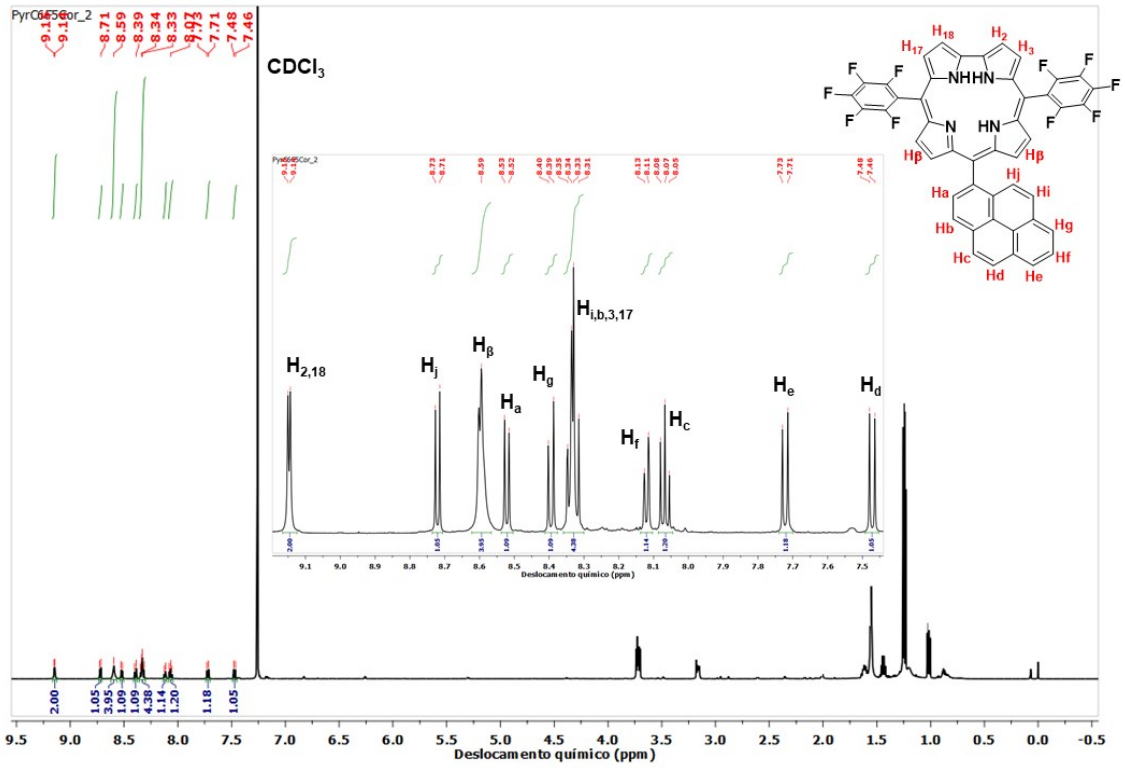

Figure S6. ^{1}H-NMR spectra of corrole **1b**, in $CDCl_3$.

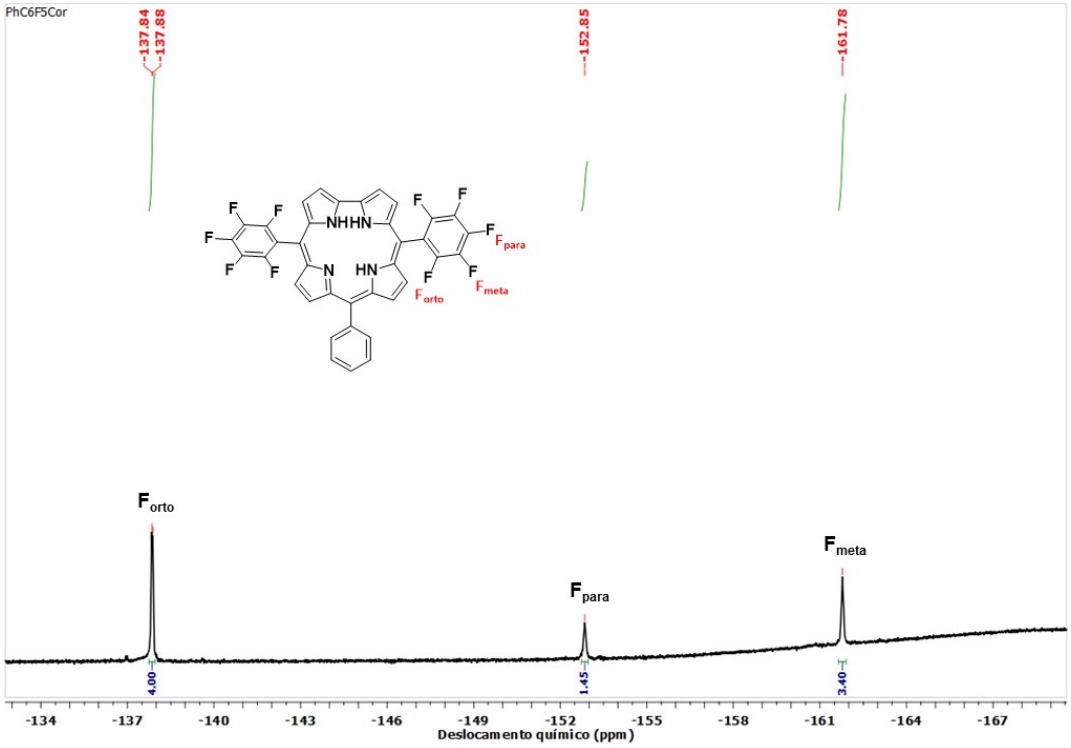

Figure S7. ^{19}F-NMR spectra of corrole **1a**, in $CDCl_3$.

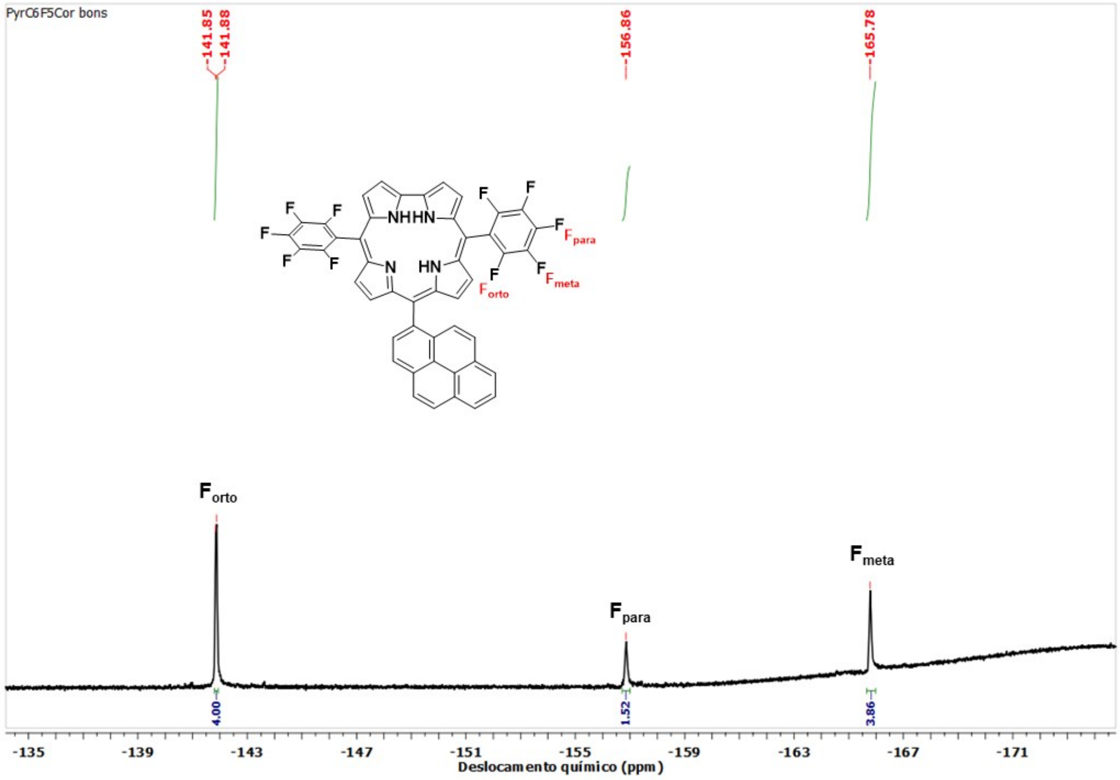

Figure S8. ^{19}F-NMR spectra of corrole **1b**, in $CDCl_3$.

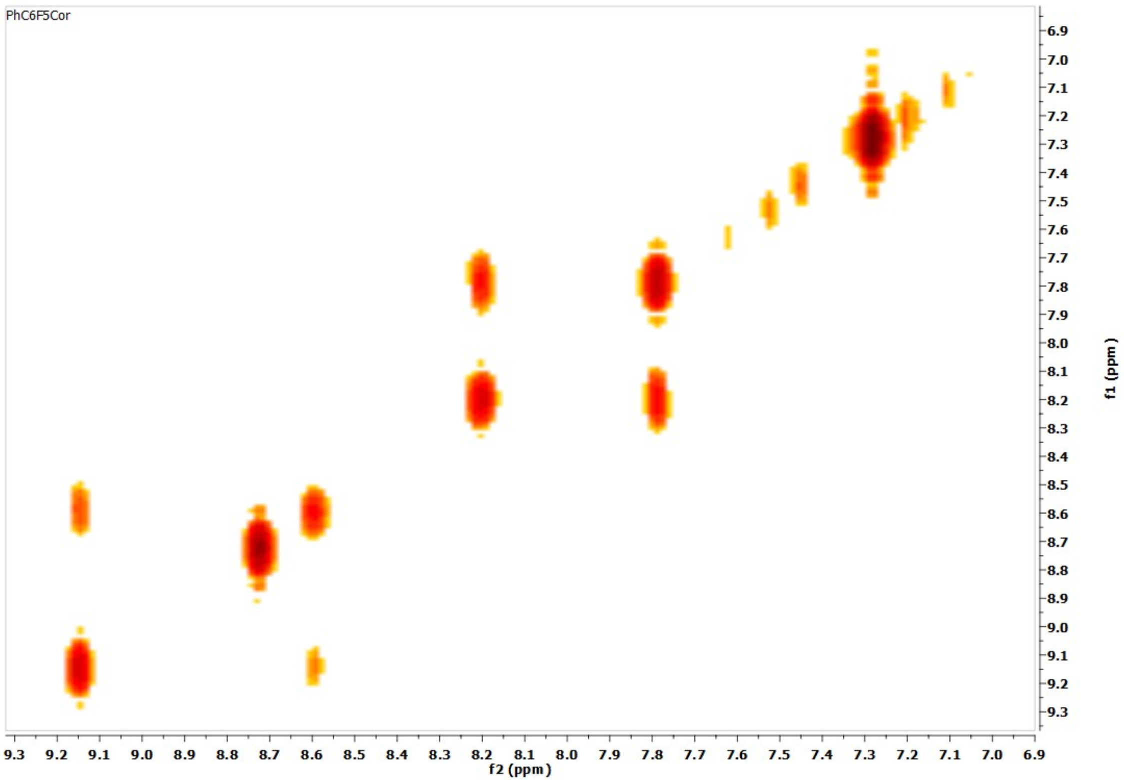

Figure S9. COSY 2D-NMR spectra of corrole **1a**, in $CDCl_3$.

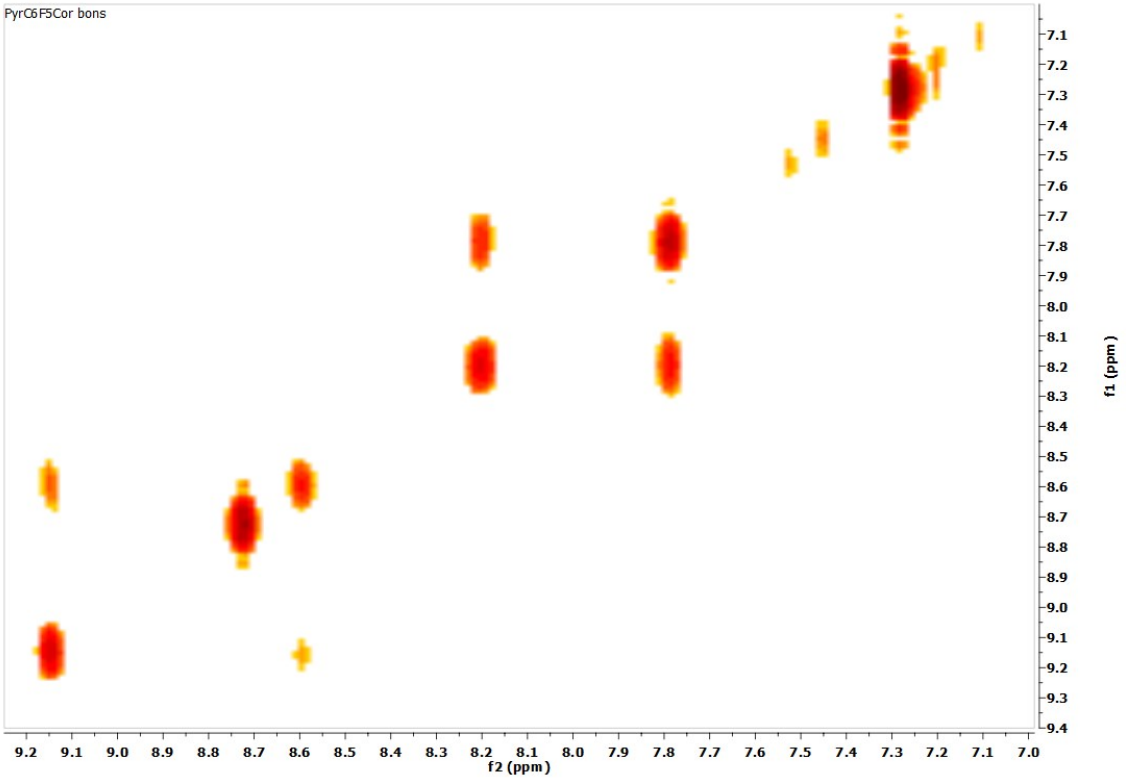

Figure S10. COSY 2D-NMR spectra of corrole **1a**, in $CDCl_3$.

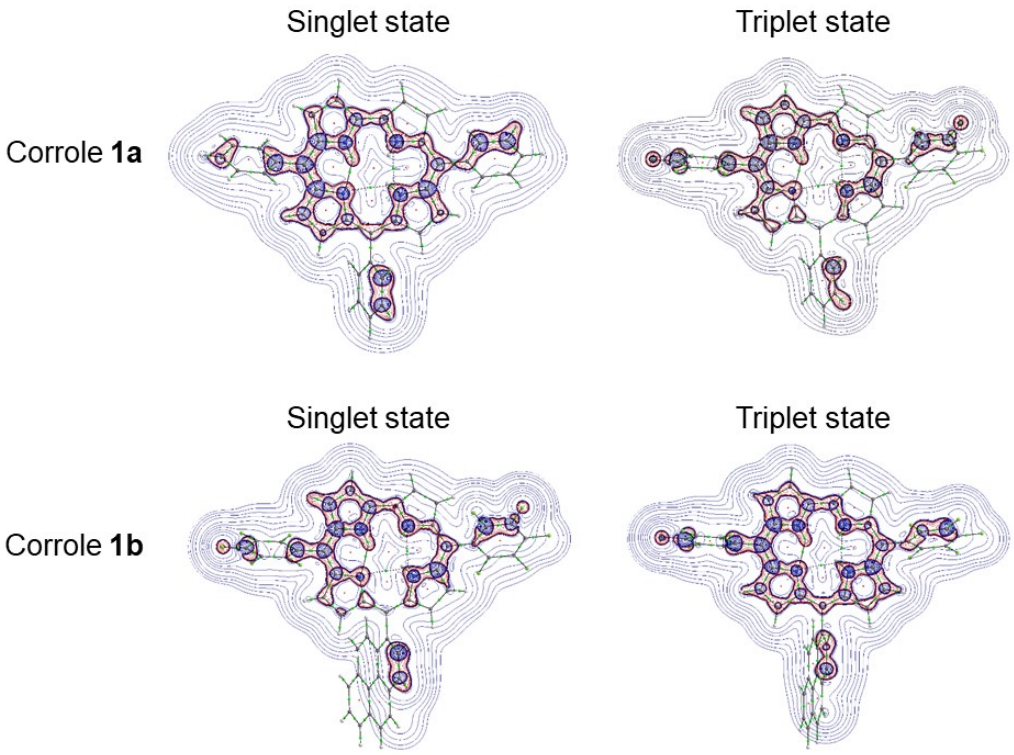

Figure S11. Laplacian of rho, $\nabla^2(\rho)$, of corroles **1a** and **1b**. On left top corner, the Triplet ($^3S_0$) state followed by the Singlet ($^1S_0$) of corrole **1a**, at right top corner; below, the same for corrole **1b**. The blue and red curves are quite similar.

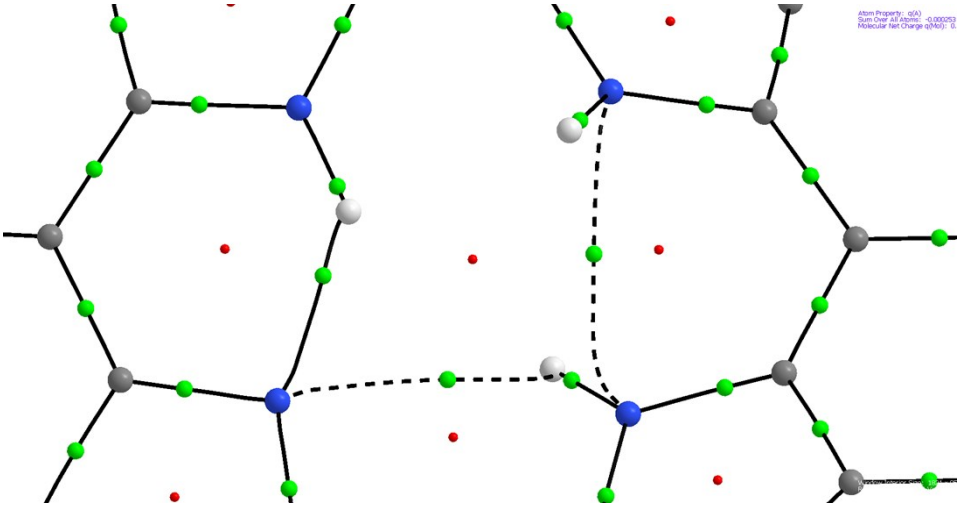

Figure S12. BCP map around the corrole center. It is possible to see that N16 interacts with both hydrogens, H35 and H37.

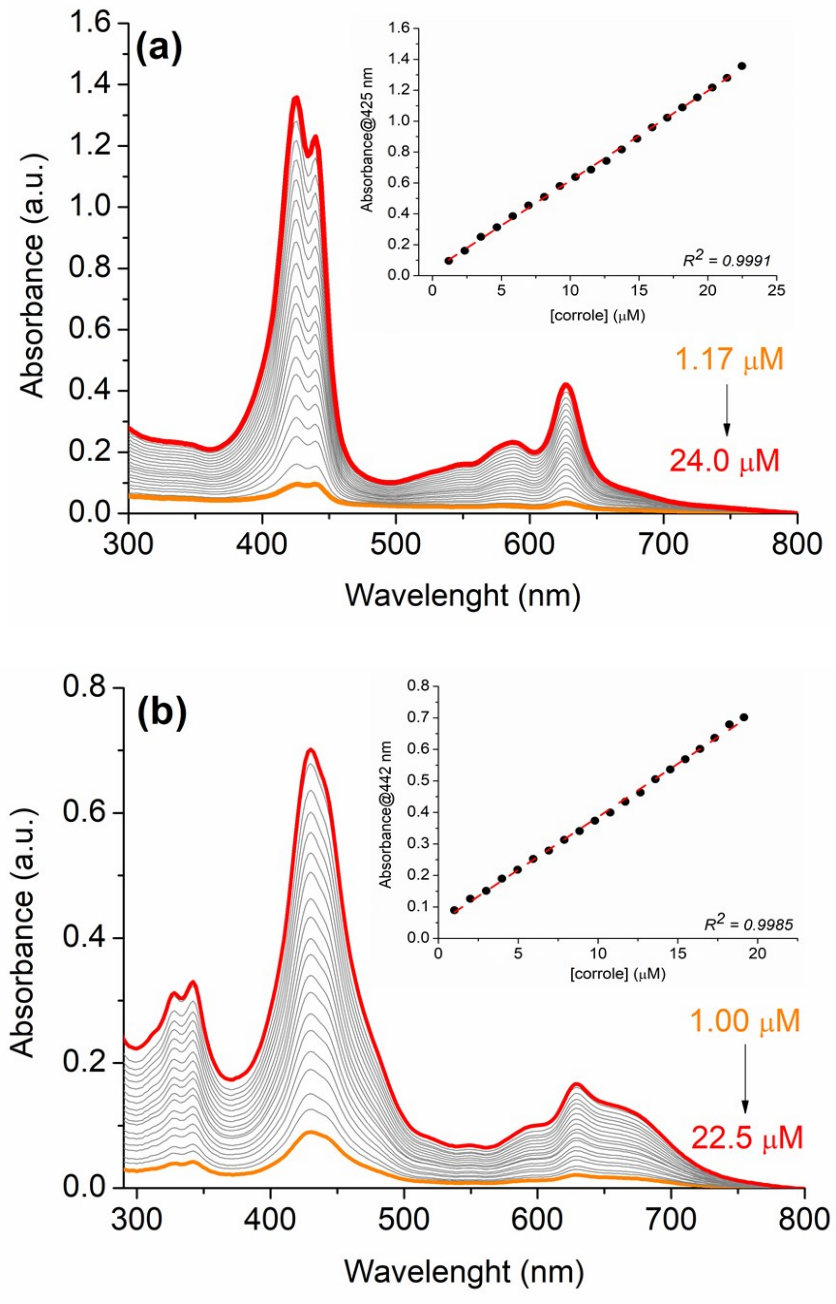

Figure S13. Aggregation study for **(a)** corrole **1a** and **(b)** corrole **1b**, using dimethyl sulfoxide (DMSO) as solvent. The *inset* shows the linear behavior of the absorbance at Soret band as a function of the concentration.

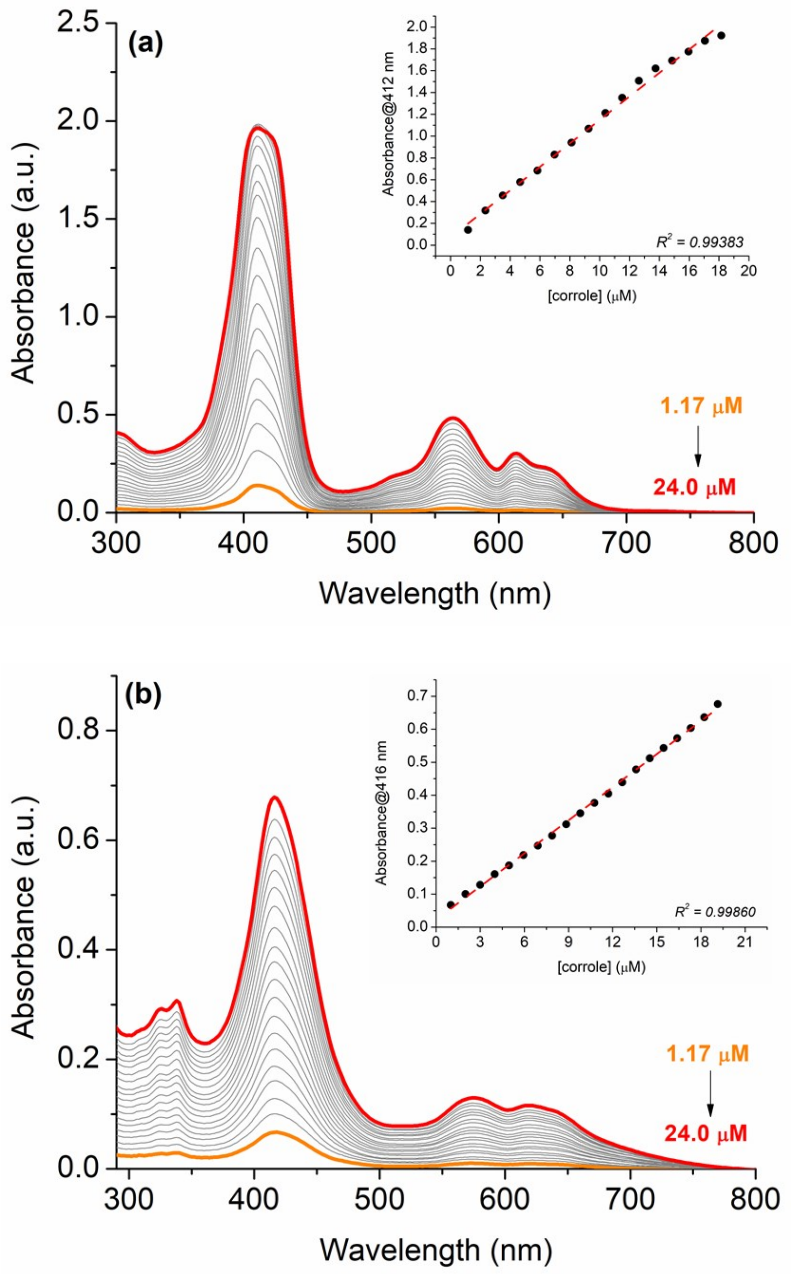

Figure S14. Aggregation study for **(a)** corrole **1a** and **(b)** corrole **1b**, using dimethyl sulfoxide (DCM) as solvent. The *inset* shows the linear behavior of the absorbance at Soret band as a function of the concentration.

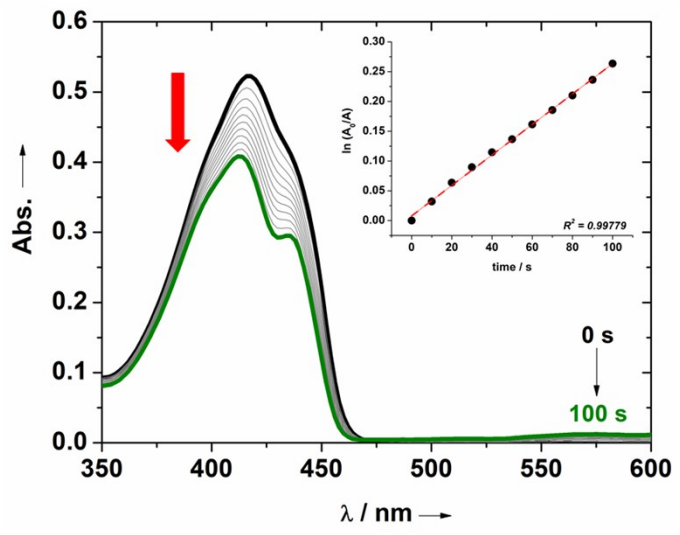

Figure S15. Photo-oxidation of DPBF by irradiation with diode laser (660 nm) in the presence of standard corrole **TPhCor**. The inset shows the kinetic profile.

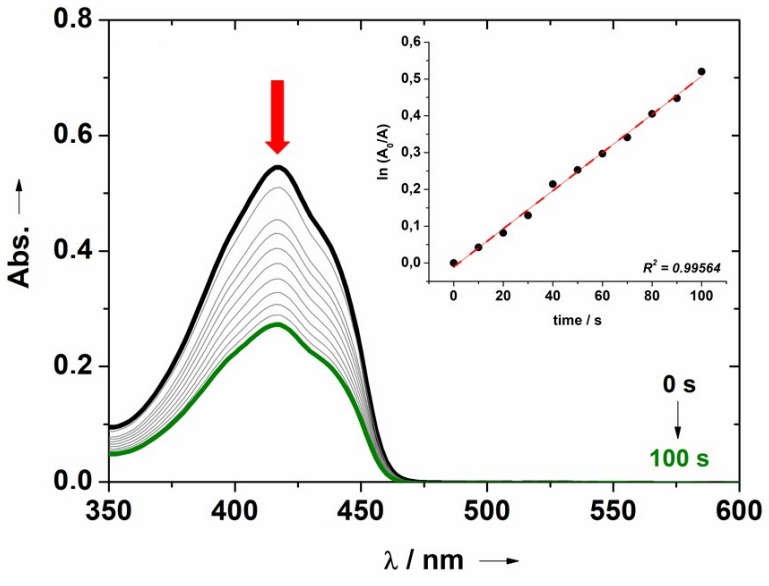

Figure S16. Photo-oxidation of DPBF by irradiation with diode laser (660 nm) in the presence of corrole **1a**. The inset shows the kinetic profile.

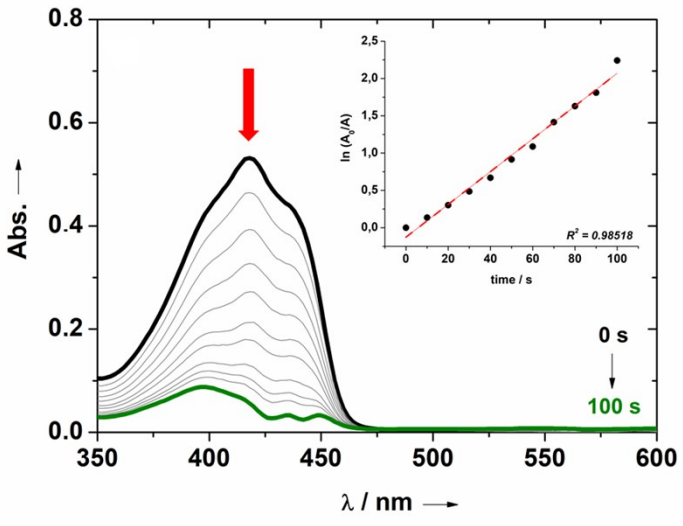

Figure S17. Photo-oxidation of DPBF by irradiation with diode laser (660 nm) in the presence of corrole **1b**. The inset shows the kinetic profile.

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[1] D.T. Gryko, K. Jadach, A Simple and Versatile One-Pot Synthesis of meso-Substituted trans-A_2B-Corroles, J. Org. Chem. 66 (2001) 4267-4275.

[2] P. Yadav, T. Anand, S.S.B. Moram, S. Bhattacharya, M. Sankar, S.V. Rao, Synthesis and femtosecond third order nonlinear optical properties of push-pull trans-A_2B-corroles, Dyes Pig. 143 (2017) 324-330.