Supporting Information of

Synthesis, Characterisation and Catalytic Use of Iron Porphyrin Amino Ester Conjugates.

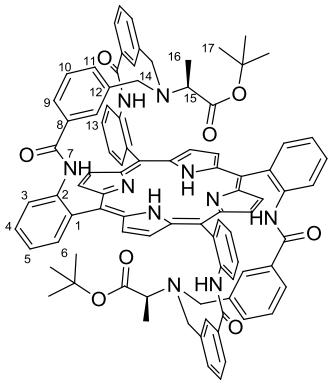
Daniela Maria Carminati,[a] Daniela Intrieri,[a] Stéphane Le Gac,[b] Bernard Boitrel,*[b] Lucio Toma,*[c] Laura Legnani[c] and Emma Gallo*[a]

[a] D. M. Carminati, D. Intrieri, E. Gallo, Department of Chemistry, University of Milan, Via C. Golgi 19, 20133 Milan (Italy), E-mail: emma.gallo@unimi.it. [b] S. Le Gac, B. Boitrel, Institut des Sciences Chimiques de Rennes, Université de Rennes 1, 263 avenue du Général Leclerc, 35042 Rennes Cedex (France). [c] L. Toma, L. Legnani, Department of Chemistry, University of Pavia, Via Taramelli 12, 27100 Pavia (Italy).

Table of Contents

1. NMR spectra

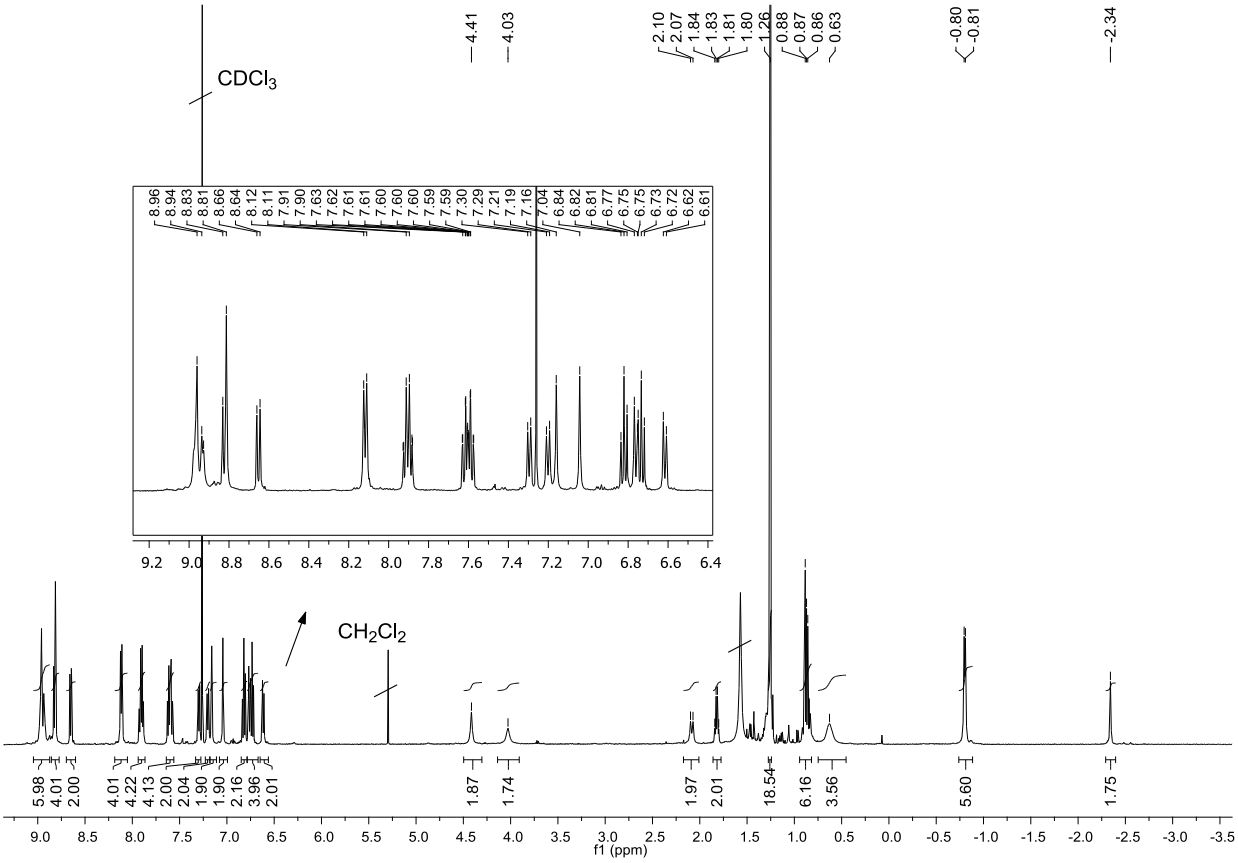
Compound **3**, NMR spectra



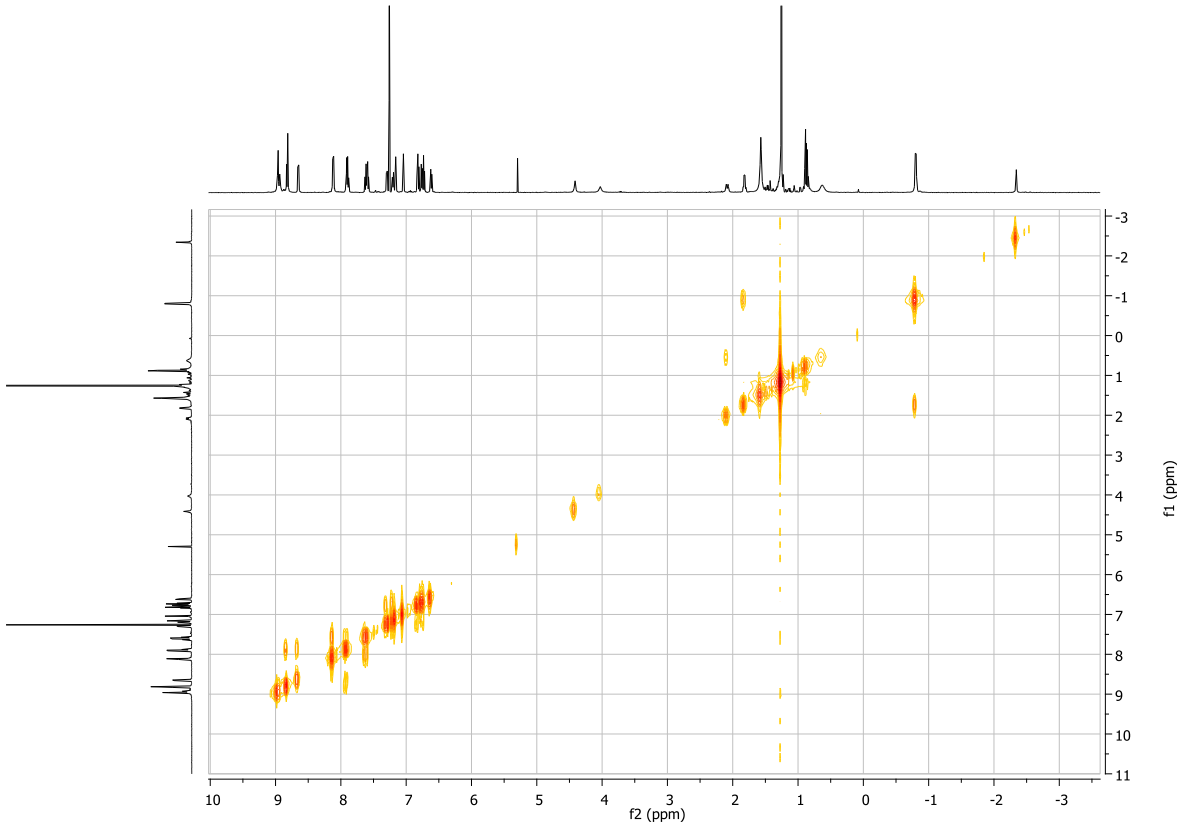
^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 8.96 (m, 4H, $H_{\beta pyr}$), 8.93 (d, 2H, *J*=4.4 Hz, $H_{\beta pyr}$), 8.82 (s, 2H, $H_{\beta pyr}$), 8.83 (d, 2H, *J*=7.6 Hz, H^3), 8.66 (d, 2H, *J*=7.6 Hz, $H^{3'}$), 8.12 (d, 4H, *J*=7.6 Hz, H^6 and $H^{6'}$), 7.91 (m, 4H, H^4 and $H^{4'}$), 7.60 (m, 4H, H^5 and $H^{5'}$), 7.30 (d, 2H, *J*=7.6 Hz, H^9), 7.20 (d, 2H, *J*=7.6 Hz, $H^{9'}$), 7.16 (s, 2H, *H*CONH), 7.04 (s, 2H, *H*CONH'), 6.81 (t, 2H, *J*=7.6 Hz, H^{10}), 6.77 (d, 2H, *J*=7.6 Hz, H^{11}), 6.74 (t, 2H, *J*=7.7 Hz, $H^{10'}$), 6.62 (d, 2H, *J*=7.6 Hz, $H^{11'}$), 4.41 (s, 2H, H^{13}), 4.03 (s, 2H, $H^{13'}$), 2.08 (d, 2H, J^2=13.1 Hz, H^{14A}), 1.82 (q, 2H, *J*=6.8 Hz, H^{15}), 1.26 (s, 18H, H^{17}), 0.87 (d, 2H, J^2=13.0 Hz, H^{14B}), 0.63 (bs, 4H, $H^{14'A}$ and $H^{14'B}$), -0.80 (d, 6H, *J*=6.8 Hz, H^{16}), -2.34 ppm (s, 2H, $-NH_2$).

^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 171.7, 165.0, 164.7, 139.0, 138.9, 138.8, 138.3, 134.2, 134.0, 133.6, 132.2, 131.7, 131.2, 130.6, 130.5, 128.6, 128.5, 126.9, 126.3, 124.2, 123.8, 123.7, 123.4, 121.9, 121.6, 115.5, 115.4, 80.8, 57.5, 52.4, 31.7, 28.1, 10.1 ppm.

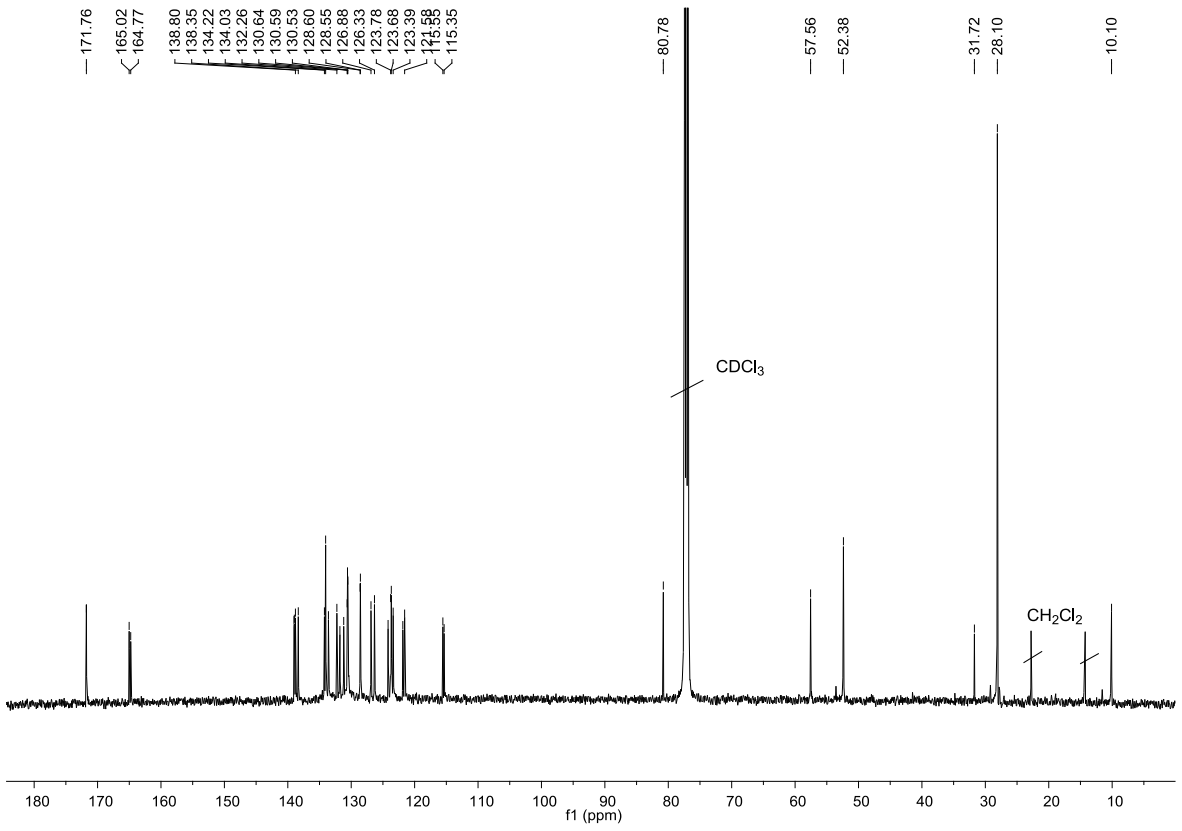
Compound **3**, ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K)



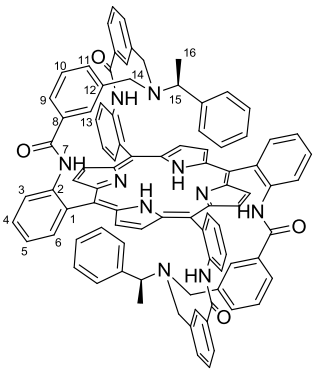
Compound **3,** COSY 2D NMR spectrum (500 MHz, $CDCl_3$, 298 K)



Compound **3**, ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K)



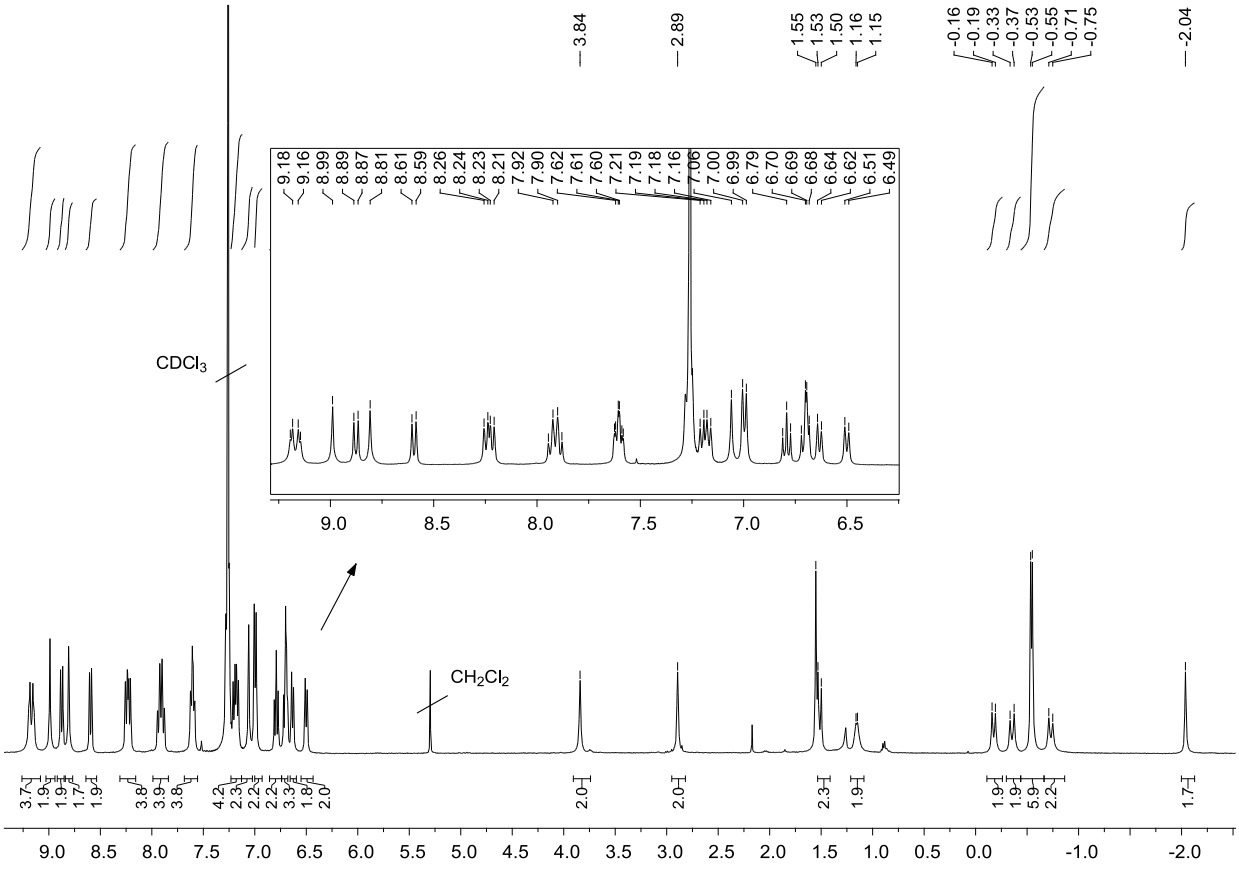
Compound **4**, NMR spectra



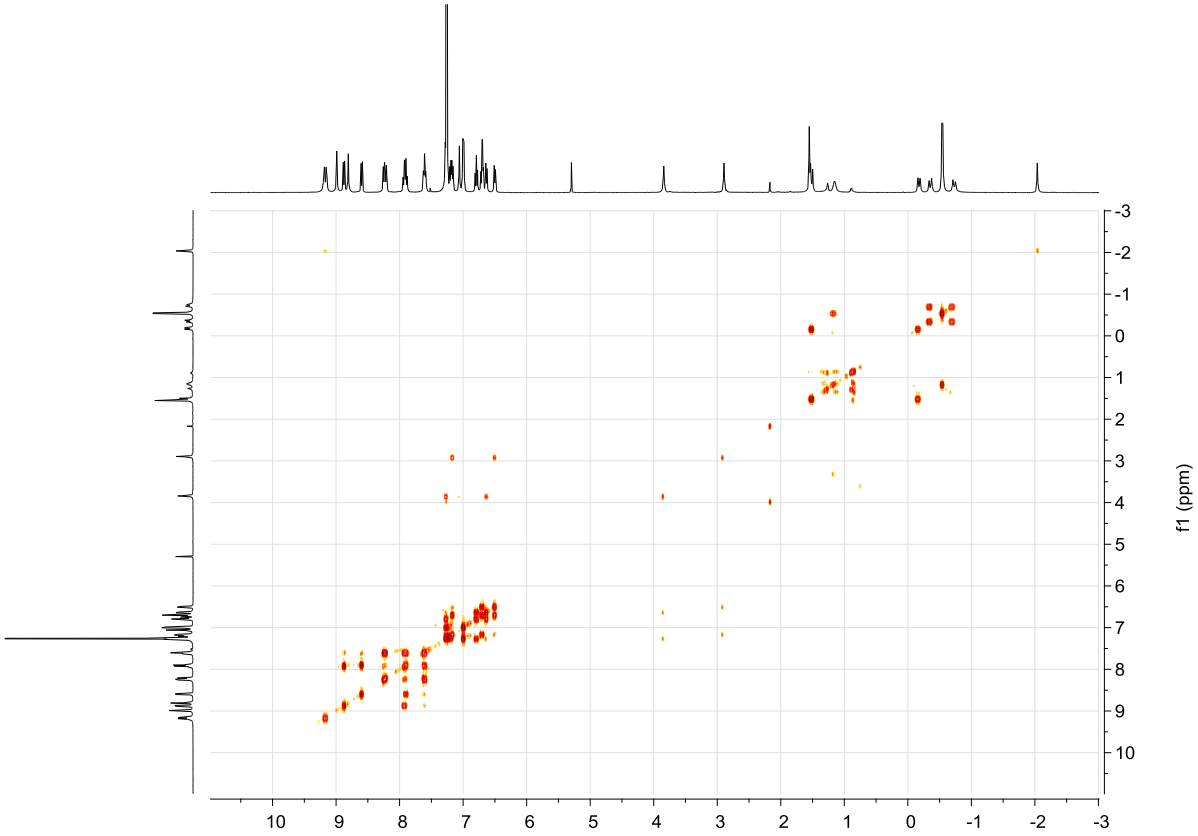
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.19 (d, 2H, *J*=4.9 Hz, $H_{\beta pyr}$), 9.15 (d, 2H, *J*=5.0 Hz, $H_{\beta pyr}$), 8.99 (s, 2H, $H_{\beta pyr}$), 8.88 (d, 2H, *J*=8.2 Hz, H^{3}), 8.81 (s, 2H, $H_{\beta pyr}$), 8.60 (d, 2H, *J*=8.1 Hz, $H^{3'}$), 8.23 (m, 4H, H^{6} and $H^{6'}$), 7.92 (m, 4H, H^{4} and $H^{4'}$), 7.60 (m, 4H, H^{5} and $H^{5'}$), 7.26 (m, 6H, $H^{9'}$ and H^{18}) 7.19 (t, 2H, *J*=6.5 Hz, H^{9}), 7.17 (d, 2H, *J*=7.6 Hz, H^{19}), 7.06 (s, 2H, *H*CONH), 7.0 (d, 4H, *J*=6.8 Hz, H^{17}), 6.79 (t, 2H, *J*=7.7 Hz, $H^{10'}$), 6.70 (t, 2H, *J*=7.7 Hz, H^{10}), 6.69 (s, 2H, *H*CONH'), 6.63 (d, 2H, *J*=7.7 Hz, $H^{11'}$), 6.50 (d, 2H, *J*=7.6 Hz, H^{11}), 3.84 (s, 2H, $H^{13'}$), 2.89 (s, 2H, H^{13}), 1.5 (d, 2H, J^{2}=13.0 Hz, H^{14A}), 1.16 (m, 2H, H^{15}), -0.18 (d, 2H, J^{2}=13.0 Hz, H^{14B}), -0.35 (d, 2H, J^{2}=15.7 Hz, $H^{14A'}$), -0.54 (d, 6H, *J*=6.7 Hz, H^{16}), -0.73 (d, 2H, J^{2}=15.3 Hz, $H^{14B'}$), -2.04 ppm (s, 2H, $-NH_2$).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ 207.05, 164.68, 164.61, 144.24, 140.46, 139.37, 138.46, 134.31, 133.95, 133.44, 132.59, 131.79, 131.32, 130.92, 130.79, 130.56, 130.04, 128.77, 128.60, 128.51, 127.33, 126.93, 125.94, 124.59, 123.97, 123.53, 122.05, 121.90, 120.70, 116.16, 115.76, 62.38, 55.65, 51.23, 31.73, 31.06, 29.21, 22.08, 18.08, 14.26, 11.57 ppm.

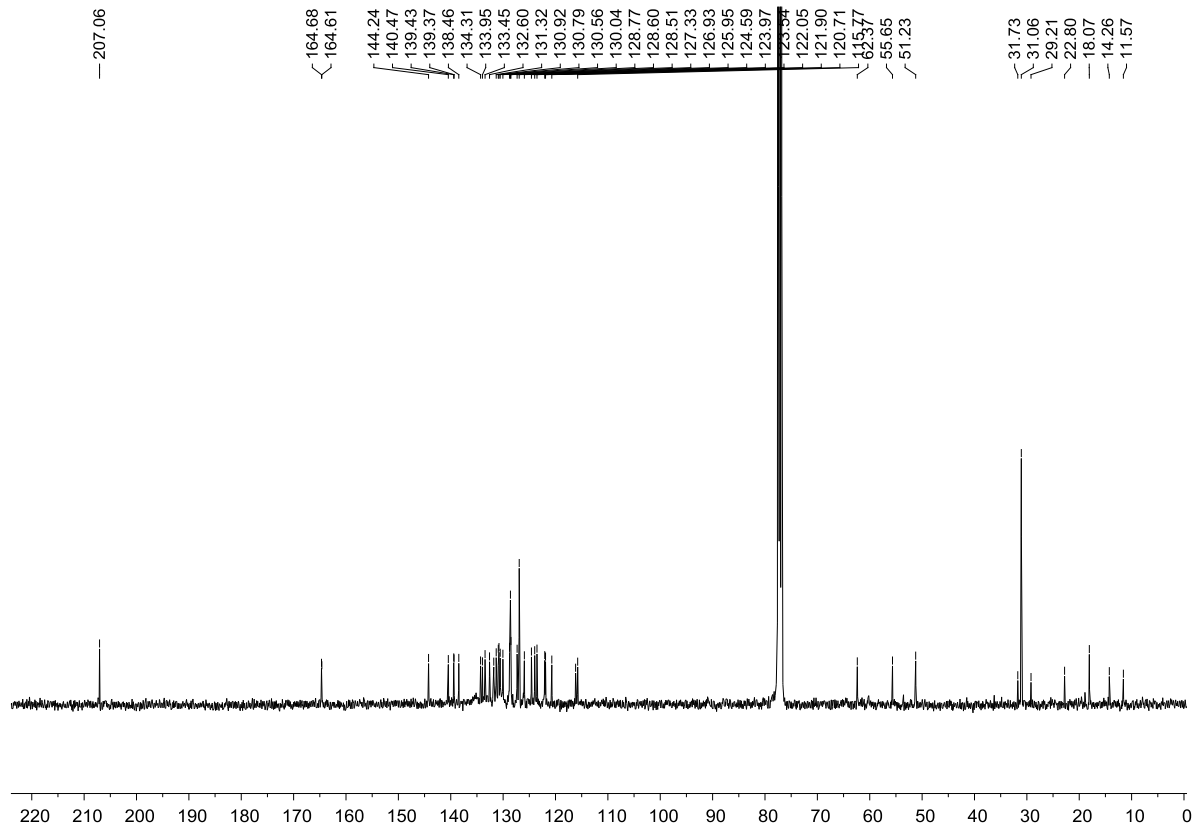
Compound **4**, ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K)



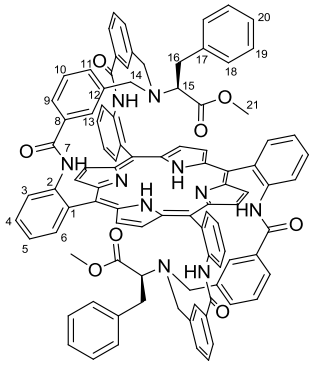
Compound **4,** COSY 2D NMR spectrum (400 MHz, $CDCl_3$, 298 K)



Compound **4**, ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K)



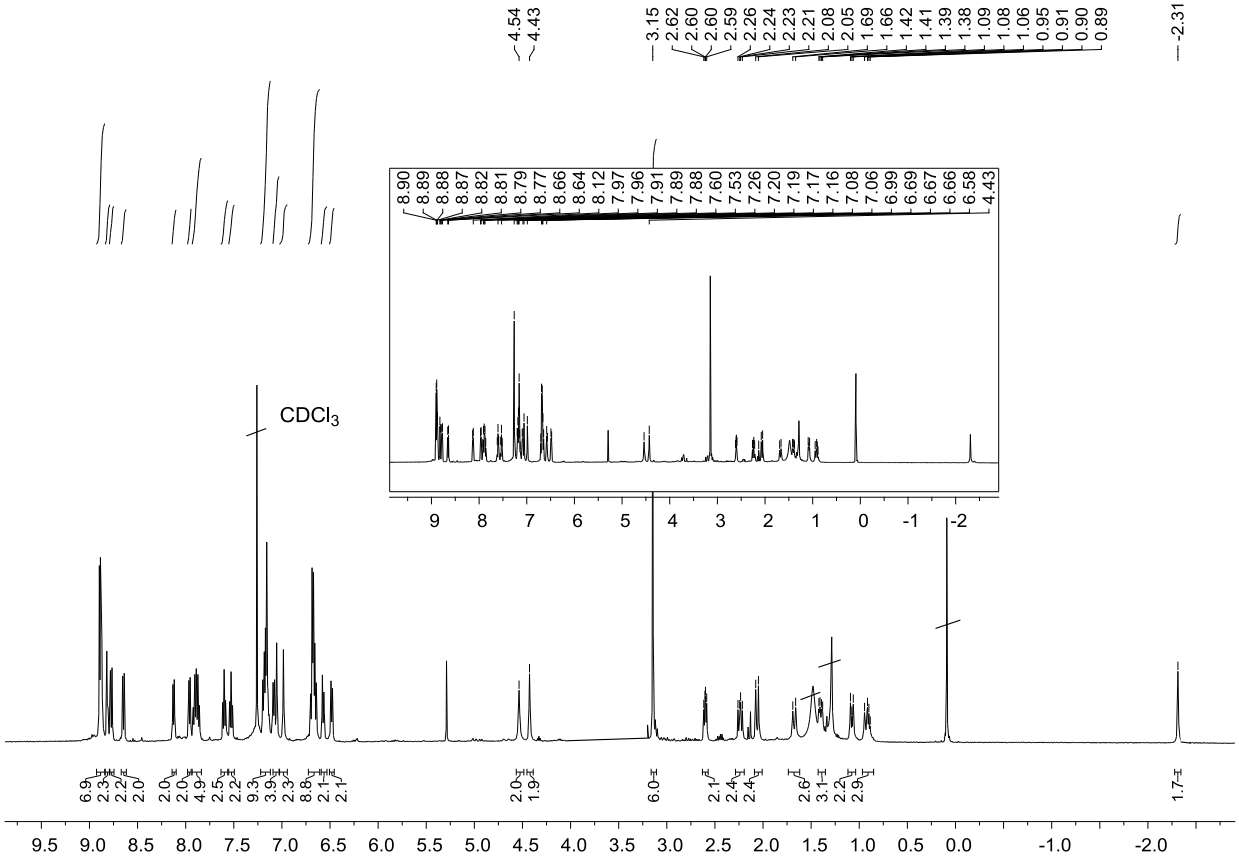
Compound **5**, NMR spectra



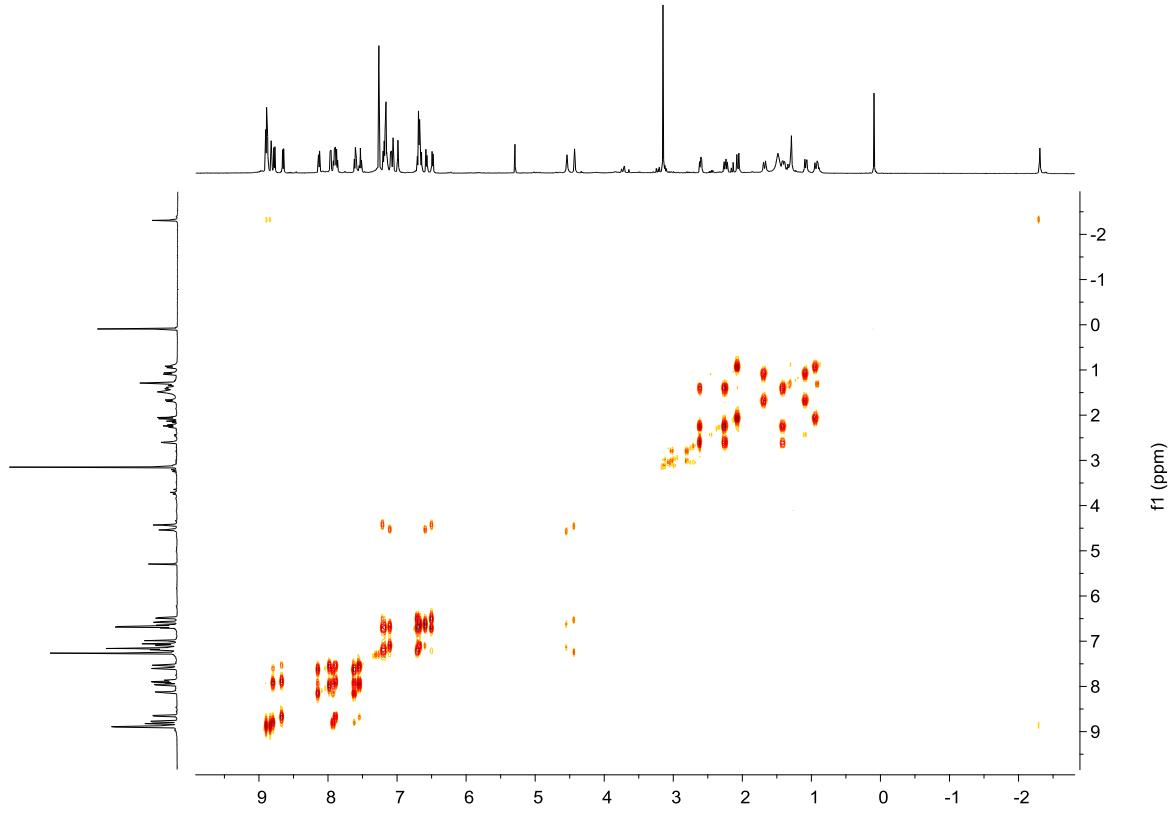
^{1}H NMR (500 MHz, $CDCl_3$, 330K): δ 8.90 (s, 2H, $H_{\beta pyr}$), 8.89 (s, 2H, $H_{\beta pyr}$), 8.88 (d, 2H, *J*=5.14 Hz, $H_{\beta pyr}$), 8.81 (d, 2H, *J*=4.8 Hz, $H_{\beta pyr}$), 8.77 (d, 2H, *J*=8.28 Hz, H^{3}), 8.65 (d, 2H, *J*=8.11 Hz, $H^{3'}$), 8.13 (d, 2H, *J*=6.6 Hz, H^{6}), 7.96 (d, 2H, *J*=7.4 Hz, $H^{6'}$), 7.91 (t, 2H, *J*=7.6 Hz, H^{4}), 7.87 (t, 2H, *J*=7.5 Hz, $H^{4'}$), 7.60 (t, 2H, *J*=7.5 Hz, H^{5}), 7.53 (t, 2H, *J*=7.5 Hz, $H^{5'}$), 7.21 (d, 2H, *J*=8.0 Hz, H^{9}), 7.18 (m, 6H, H^{19} and H^{20}), 7.11 (d, 2H, *J*=7.7 Hz, $H^{9'}$), 7.08 (s, 2H, *H*CONH), 7.01 (s, 2H, *H*CONH'), 6.69 (t, 4H, *J*=7.5 Hz, H^{10} and $H^{10'}$), 6.68 (d, 2H, *J*=7.7 Hz, H^{18}), 6.57 (d, 2H, *J*=7.7 Hz, $H^{11'}$), 6.48 (d, 2H, *J*=7.6 Hz, H^{11}), 4.54 (s, 2H, $H^{13'}$), 4.43 (s, 2H, H^{13}), 3.15 (s, 6H, H^{21}), 2.60 (dd, 2H, *J*=6.04, 8.95 Hz, H^{15}), 2.24 (dd, 2H, *J*=9.3 Hz, J^2=13.6 Hz, $H^{4'}$), 2.06 (d, 2H, *J*=14.2 Hz, H^{14A}), 1.68 (d, 2H, *J*=14.4 Hz, $H^{14A'}$), 1.40 (dd, 2H, *J*=5.7 Hz, J^2=13.5 Hz, $H^{16'}$), 1.08 (d, 2H, *J*=14.7 Hz, $H^{14'B}$), 0.93 (d, 2H, *J*=15.4 Hz, H^{14B}), -2.31 ppm (s, 2H, $-NH_2$).

^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 171.40, 165.09, 165.05, 138.91, 138.82, 138.19, 137.30, 134.27, 134.16, 134.06, 133.86, 131.89, 131.57, 131.39, 131.13, 130.50, 130.41, 129.07, 128.57, 128.49, 126.78, 126.61, 126.14, 124.28, 123.94, 123.78, 122.06, 121.85, 115.56, 115.28, 64.01, 53.12, 52.72, 51.22, 32.52, 29.84, 14.26 ppm.

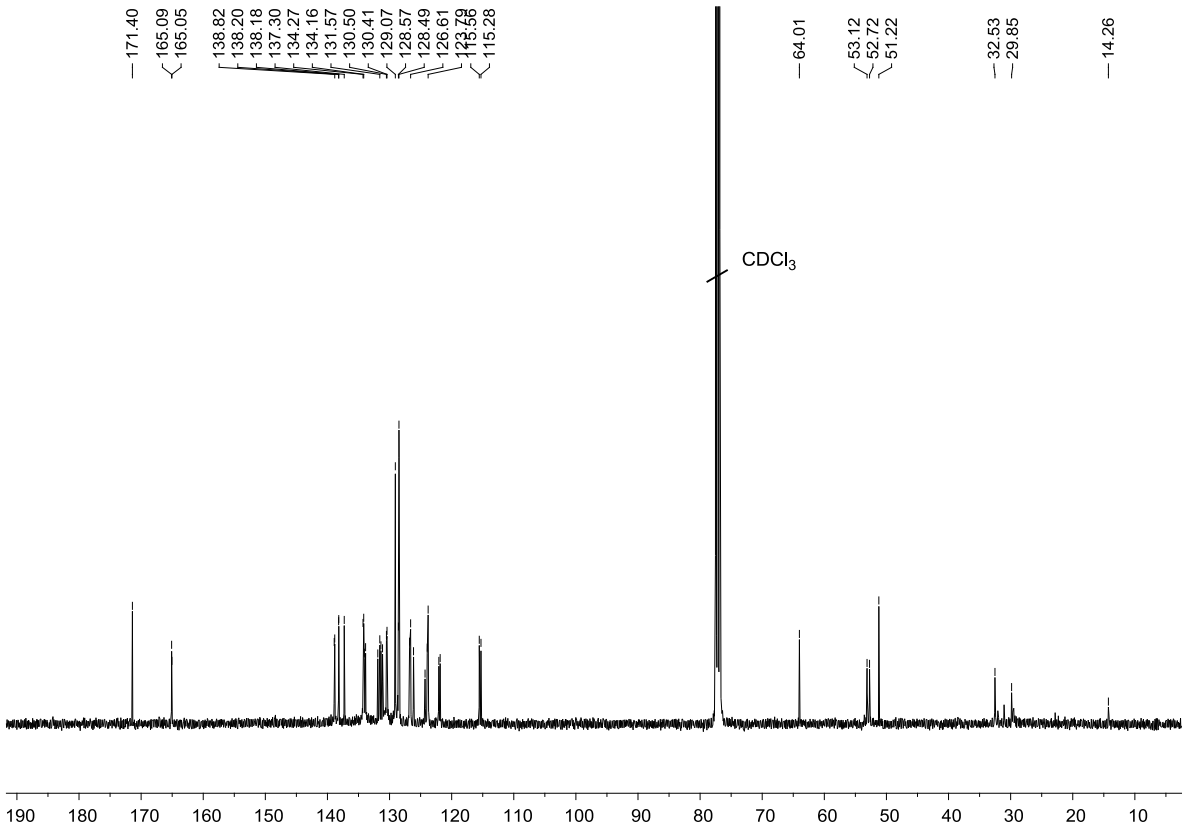
Compound **5**, ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K)



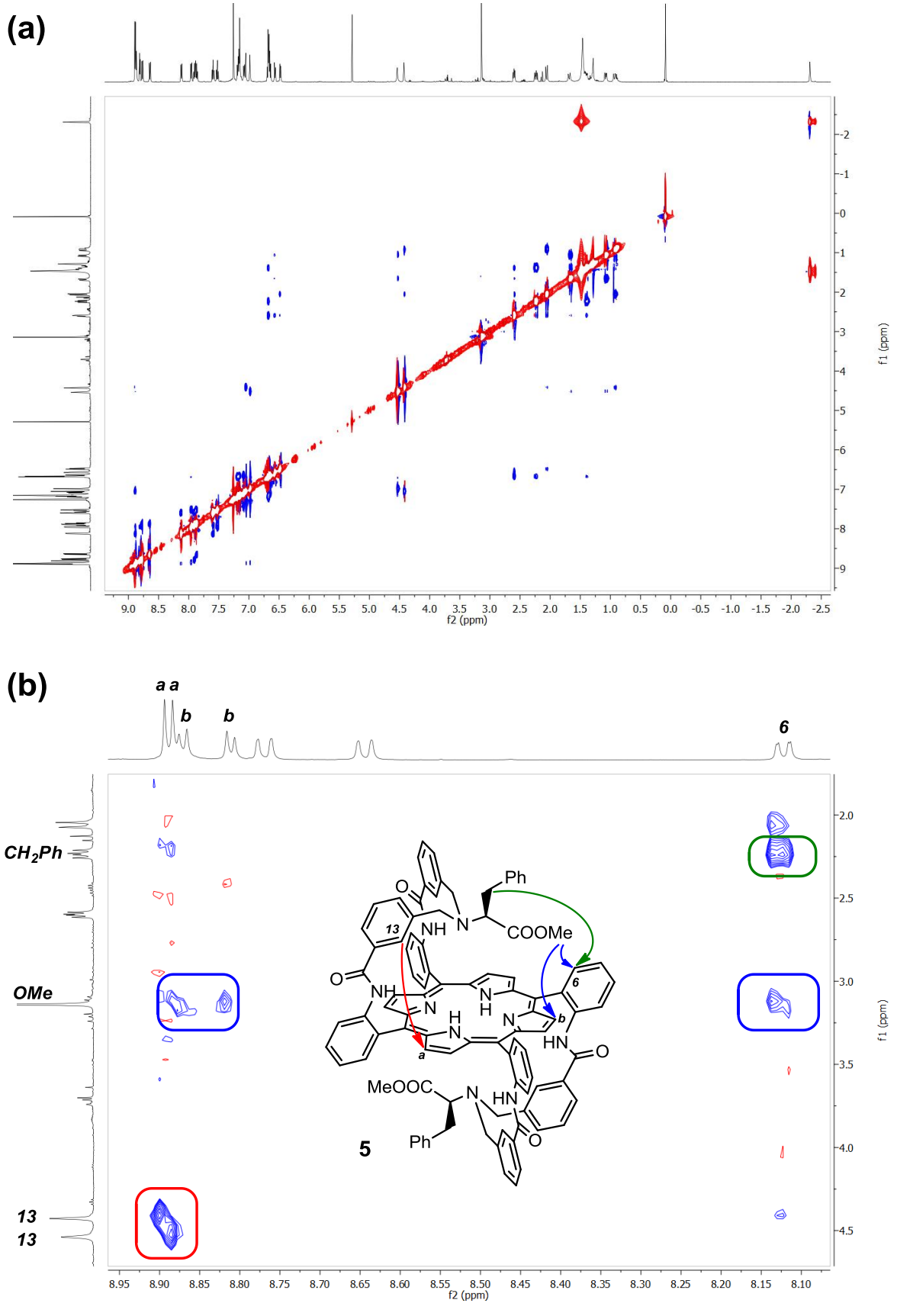
Compound **5,** COSY 2D NMR spectrum (500 MHz, $CDCl_3$, 298 K)



Compound **5**, ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K)



Compound **5**, 2D ROESY NMR spectrum (500 MHz, $CDCl_3$, 298 K)



Structural data of 5

Empirical formula	$C_{195}\ H_{155}\ Cl_9\ N_{20}\ O_{16}$
Extended formula	$2(C_{96}\ H_{76}\ N_{10}\ O_8)$, $3(C\ H\ Cl_3)$
Formula weight	3353.43
Temperature	150 *K*
Wavelength	0.71073 Å
Crystal system, space group	triclinic, *P* 1
Unit cell dimensions	*a* = 12.7372(10) Å, α = 82.596(3)°
	b = 13.5883(12) Å, β = 76.789(3)°
	c = 26.157(3) Å, γ = 82.552(3)°
Volume	4347.0(7) $Å^3$
Z, Calculated density	1, 1.281 ($g.cm^{-3}$)
Absorption coefficient	0.215 mm^{-1}
F(000)	1746
Crystal size	0.530 x 0.440 x 0.100 mm
Crystal color	blue
Theta range for data collection	2.096 to 27.495 °
h_min, h_max	-16, 15
k_min, k_max	-17, 17
l_min, l_max	-33, 33
Reflections collected / unique	93932 / 36039 [R(int)[a] = 0.0408]
Reflections [I>2σ]	29468
Completeness to theta_max	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.979, 0.856
Refinement method	Full-matrix least-square on F^2
Data / restraints / parameters	36039 / 3 / 2035
Flack parameter	0.07(6)
[b]Goodness-of-fit	1.077
Final *R* indices [I>2σ]	$R1^c$ = 0.0825, $wR2^d$ = 0.2298
R indices (all data)	$R1^c$ = 0.0962, $wR2^d$ = 0.2441
Largest diff. peak and hole	1.309 and -0.823 $e^-.Å^{-3}$

[a] $R_{int} = \sum |F_o^2 - < F_o^2 >| / \sum [F_o^2]$

[b] $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

[c] $R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

[d] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] /3$

Computational data

Table S1. Selected torsional angles (τ, °)[a] and distance (*d*, Å) of Cα from the centroid of the porphyrin of the two crystallographic independent molecules of compound **5** and of the corresponding B3LYP/6-31G(d) optimized structures.

	τ_1	τ_2	τ_3	$\tau_{1'}$	$\tau_{2'}$	$\tau_{3'}$	d
Conformation **A** upper side	-37	139	-75	24	-171	127	5.94
Conformation **A** lower side	-24	110	-75	14	160	150	5.76
Conformation **B** upper side	-31	-175	-156	31	-118	76	5.65
Conformation **B** lower side	-32	122	-76	21	178	136	5.90
5A upper side	-27	115	-67	16	167	142	6.25
5A lower side	-27	115	-67	16	167	142	6.25
5B upper side	-17	-160	-156	21	-107	74	6.31
5B lower side	-28	116	-67	17	170	138	6.27

[a] τ_1: N-CO-C8-C13; τ_2: C13-C12-C14-N; τ_3: C12-C14-N-C14'; $\tau_{1'}$: N-CO-C8'-C13'; $\tau_{2'}$: C13'-C12'-C14'-N; $\tau_{3'}$: C12'-C14'-N-C14.

Table S2. Relative energy (E_{rel}, kcal/mol), selected torsional angles (τ, °),[a] and distance (*d*, Å) of Cα from the centroid of the porphyrin, of the conformers the model compound **10** and of the TSs for the *trans* and *cis* attack of α-methylstyrene to the terminal carbene species deriving from Fe(TPP)(OMe).

	E_{rel}	τ_1	τ_2	τ_3	$\tau_{1'}$	$\tau_{2'}$	$\tau_{3'}$	d
10A	0.00	-25	109	-69	16	160	157	5.80
10B	0.00	-16	-160	-157	25	-109	69	5.80
10C	1.90	154	-142	84	-154	142	-84	10.92
10D	2.16	33	54	-178	-144	81	66	9.07
10E	2.16	144	-81	-66	-33	-54	178	9.07
trans-**10A-TS**	6.83	-28	137	-65	-7	-143	115	8.75
trans-**10B-TS**	7.25	14	147	-108	21	-126	60	8.56
trans-**10C-TS**	1.55	156	-138	81	-164	137	-83	11.98
trans-**10D-TS**	0.00	31	46	-173	-150	76	66	9.81
trans-**10E-TS**	0.41	147	-75	-65	-37	-47	174	9.76
cis-**10A-TS**	7.91	-26	136	-67	-5	-146	108	8.71
cis-**10B-TS**	7.86	16	141	-116	25	-125	58	8.62
cis-**10C-TS**	2.02	155	-136	79	-164	139	-84	11.97
cis-**10D-TS**	0.53	32	45	-173	-149	73	66	9.76
cis-**10E-TS**	1.18	147	-79	-66	-35	-46	173	9.77

[a] τ_1: N-CO-C8-C13; τ_2: C13-C12-C14-N; τ_3: C12-C14-N-C14'; $\tau_{1'}$: N-CO-C8'-C13'; $\tau_{2'}$: C13'-C12'-C14'-N; $\tau_{3'}$: C12'-C14'-N-C14.

Table S3. Relative energy (E_{rel}, kcal/mol), selected torsional angles (τ, °),[a] and distance (*d*, Å) of Cα from the centroid of the porphyrin, of the TSs for the *trans* and *cis* attack of α-methylstyrene to the terminal carbene species deriving from the model ligand **11**.

	E_{rel}	τ_1	τ_2	τ_3	$\tau_{1'}$	$\tau_{2'}$	$\tau_{3'}$	d
trans-(R,R)-**11D-TS**	0.82	31	39	-170	-150	76	71	9.71
trans-(R,R)-**11E-TS**	0.35	148	-71	-67	-36	-48	174	9.70
trans-(S,S)-**11D-TS**	1.19	38	37	-170	-148	77	71	9.59
trans-(S,S)-**11E-TS**	0.00	150	-74	-69	-30	-47	172	9.73
cis-(R,S)-**11D-TS**	1.28	31	38	-171	-151	73	71	9.68
cis-(R,S)-**11E-TS**	1.11	147	-77	-69	-35	-47	173	9.68
cis-(S,R)-**11D-TS**	1.82	36	36	-169	-148	81	73	9.60
cis-(S,R)-**11E-TS**	0.47	150	-71	-69	-31	-45	172	9.69

[a] τ_1: N-CO-C8-C13; τ_2: C13-C12-C14-N; τ_3: C12-C14-N-C14'; $\tau_{1'}$: N-CO-C8'-C13'; $\tau_{2'}$: C13'-C12'-C14'-N; $\tau_{3'}$: C12'-C14'-N-C14.

Table S4. Relative energy (E_{rel}, kcal/mol), selected torsional angles (τ, °),[a] and distance (*d*, Å) of Cα from the centroid of the porphyrin, of the TSs for the *trans* and *cis* attack of α-methylstyrene to the terminal carbene species deriving from the model ligand **12**.

	E_{rel}	τ_1	τ_2	τ_3	$\tau_{1'}$	$\tau_{2'}$	$\tau_{3'}$	d
trans-(R,R)-**12D-TS**	0.23	28	52	-175	-150	73	69	9.79
trans-(R,R)-**12E-TS**	0.43	148	-73	-68	-38	-43	171	9.77
trans-(S,S)-**12D-TS**	0.63	35	50	-175	-147	72	67	9.73
trans-(S,S)-**12E-TS**	0.00	151	-75	-69	-31	-42	170	9.81
cis-(R,S)-**12D-TS**	0.82	29	50	-175	-149	71	68	9.73
cis-(R,S)-**12E-TS**	1.14	147	-79	-70	-36	-42	170	9.75
cis-(S,R)-**12D-TS**	1.20	34	50	-175	-147	76	68	9.74
cis-(S,R)-**12E-TS**	0.49	150	-73	-69	-32	-41	170	9.75

[a] τ_1: N-CO-C8-C13; τ_2: C13-C12-C14-N; τ_3: C12-C14-N-C14'; $\tau_{1'}$: N-CO-C8'-C13'; $\tau_{2'}$: C13'-C12'-C14'-N; $\tau_{3'}$: C12'-C14'-N-C14.