Supporting information for

Red-light activated photoCORMs of Mn(I) species bearing electron deficient 2,2'-azopyridines.

E. Kottelat,[a] A. Ruggi*[a] and F. Zobi*[a]

Département de Chimie, Université de Fribourg, Chemin du Musée 9, CH-1700 Fribourg.
Email: albert.ruggi@unifr.ch, fabio.zobi@unifr.ch.

S1. NMR spectra of ligands and complexes

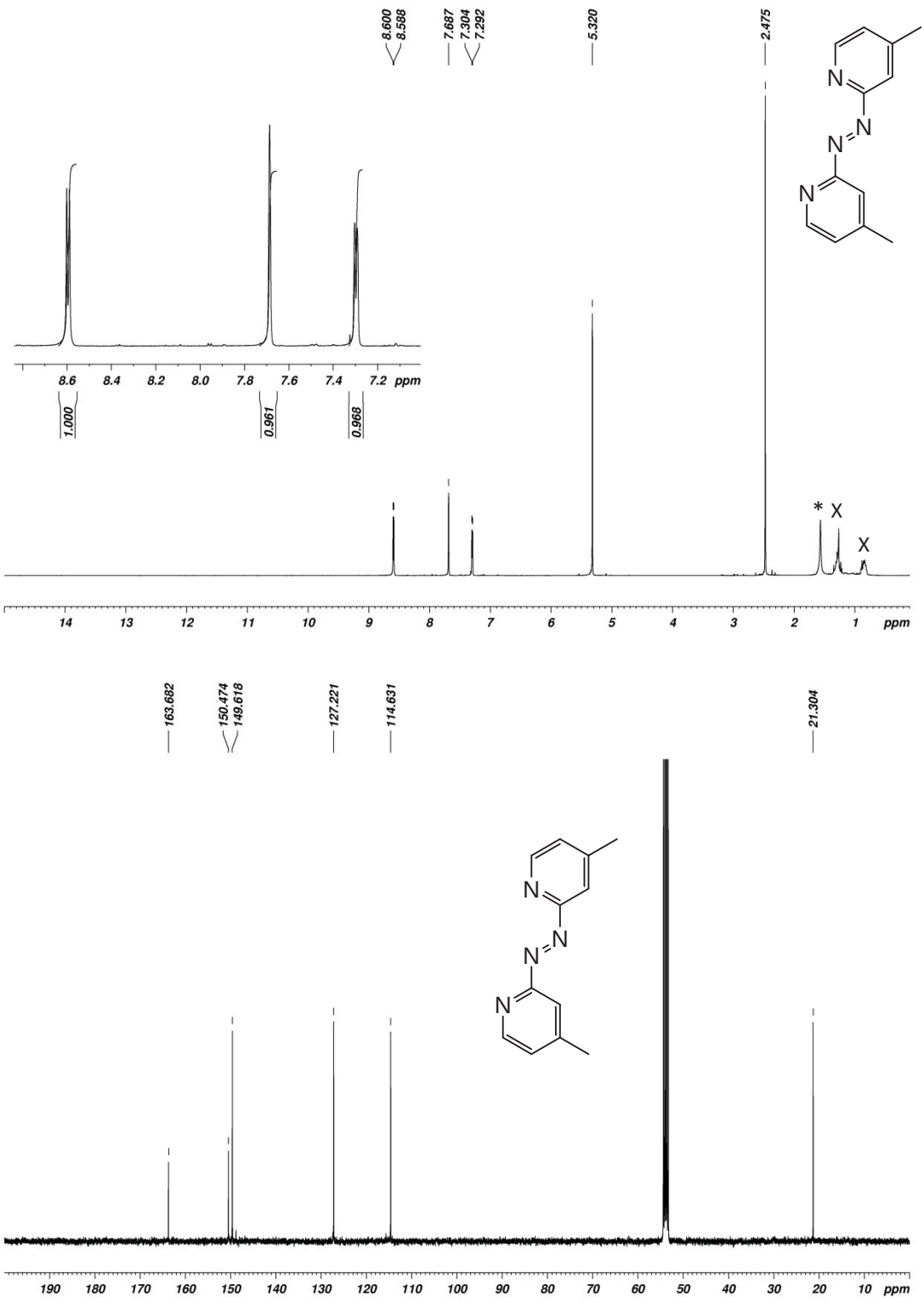

Figure S1. ^{1}H- (top) and ^{13}C-NMR spectra of 1,2-bis(4-methylpyridin-2-yl)diazene (**Azpy_Me**) in CD_2Cl_2. Asterisk (*) indicates traces of water and (x) grease.

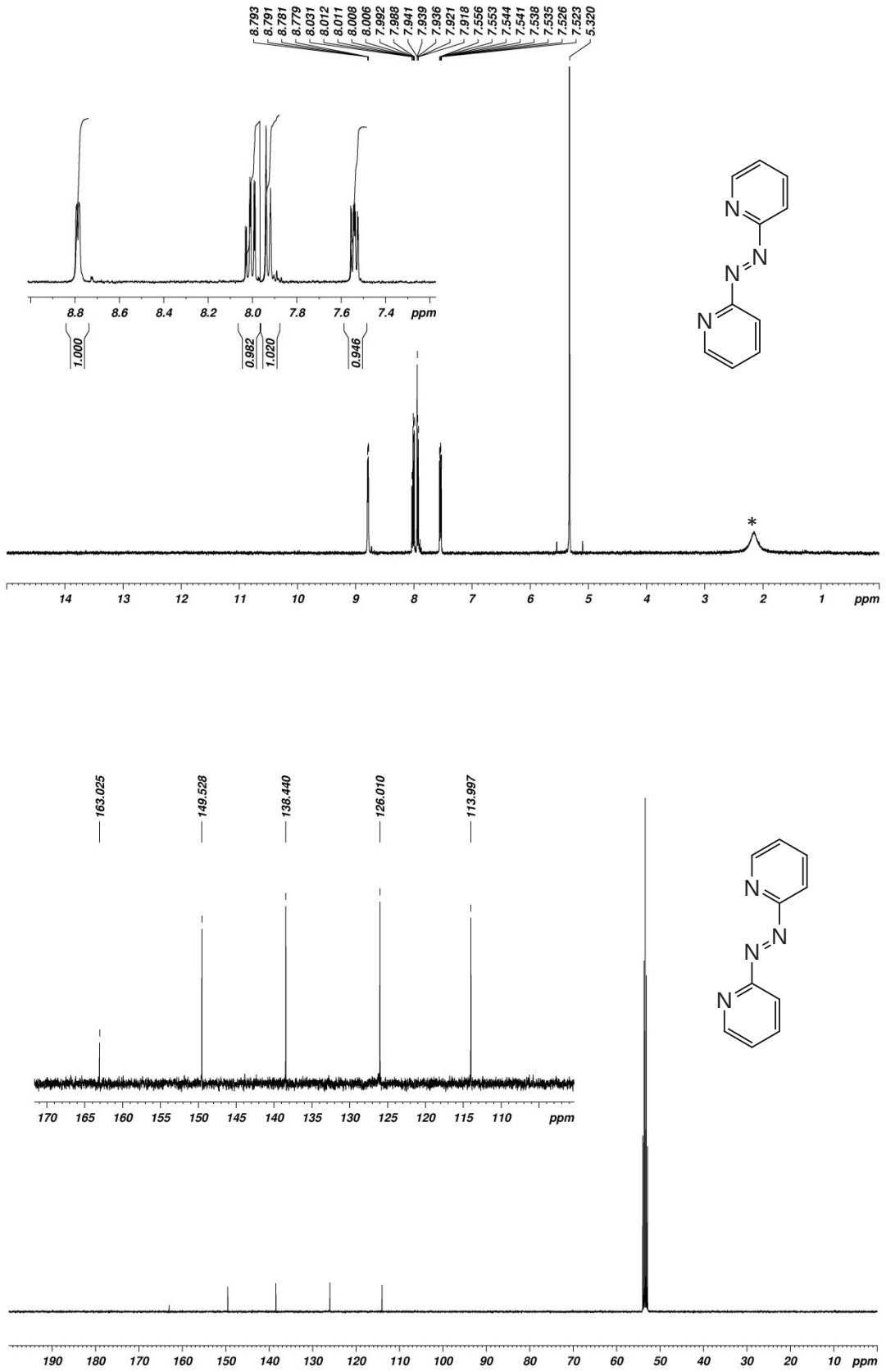

Figure S2. ^{1}H- (top) and ^{13}C-NMR spectra of 1,2-di(pyridin-2-yl)diazene (**Azpy_H**) in CD_2Cl_2. Asterisk (*) indicates traces of water.

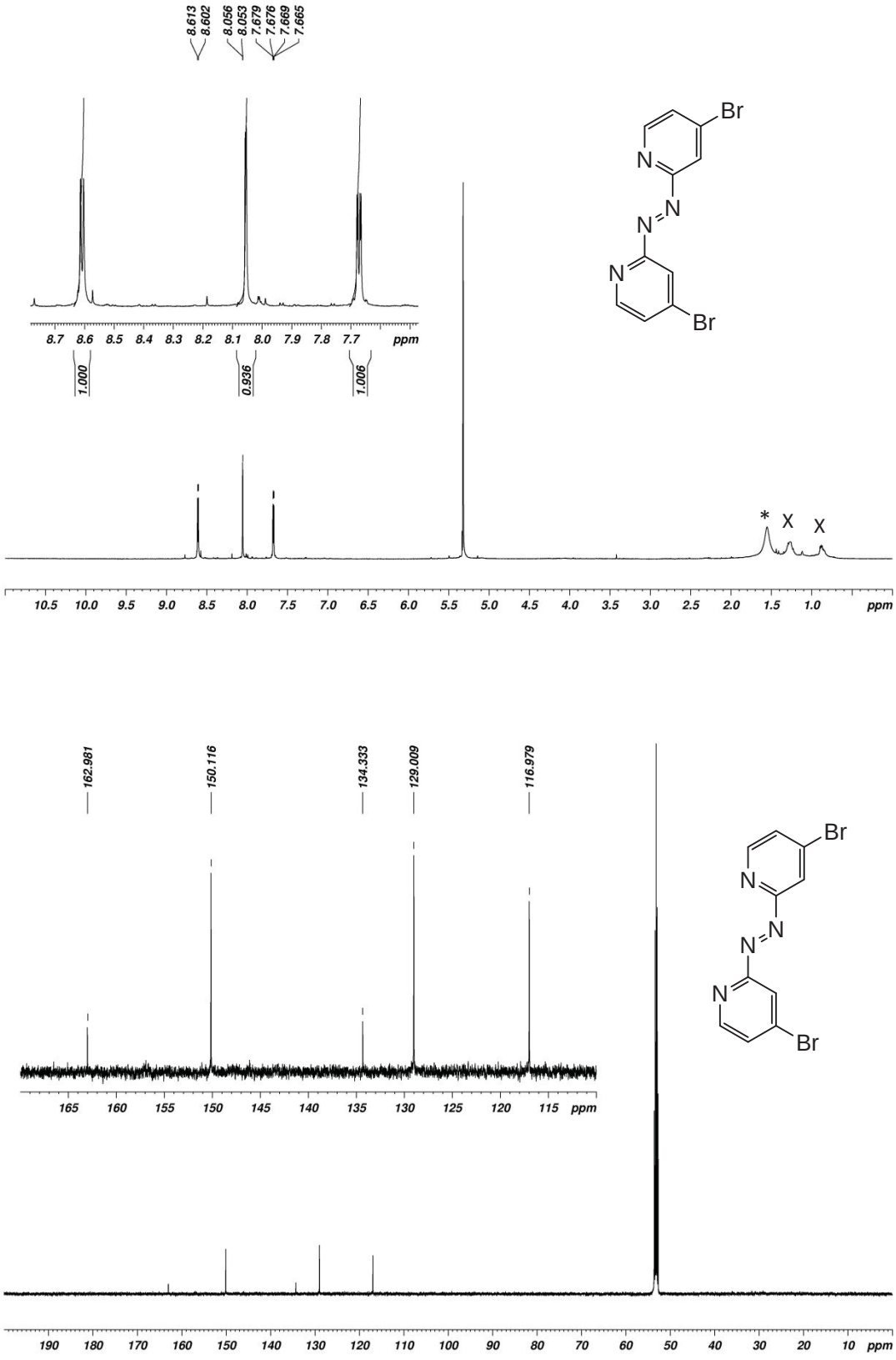

Figure S3. ^{1}H- (top) and ^{13}C-NMR spectra of 1,2-bis(4-bromopyridin-2-yl)diazene (**Azpy_Br**) in CD_2Cl_2. Asterisk (*) indicates traces of water and (x) grease.

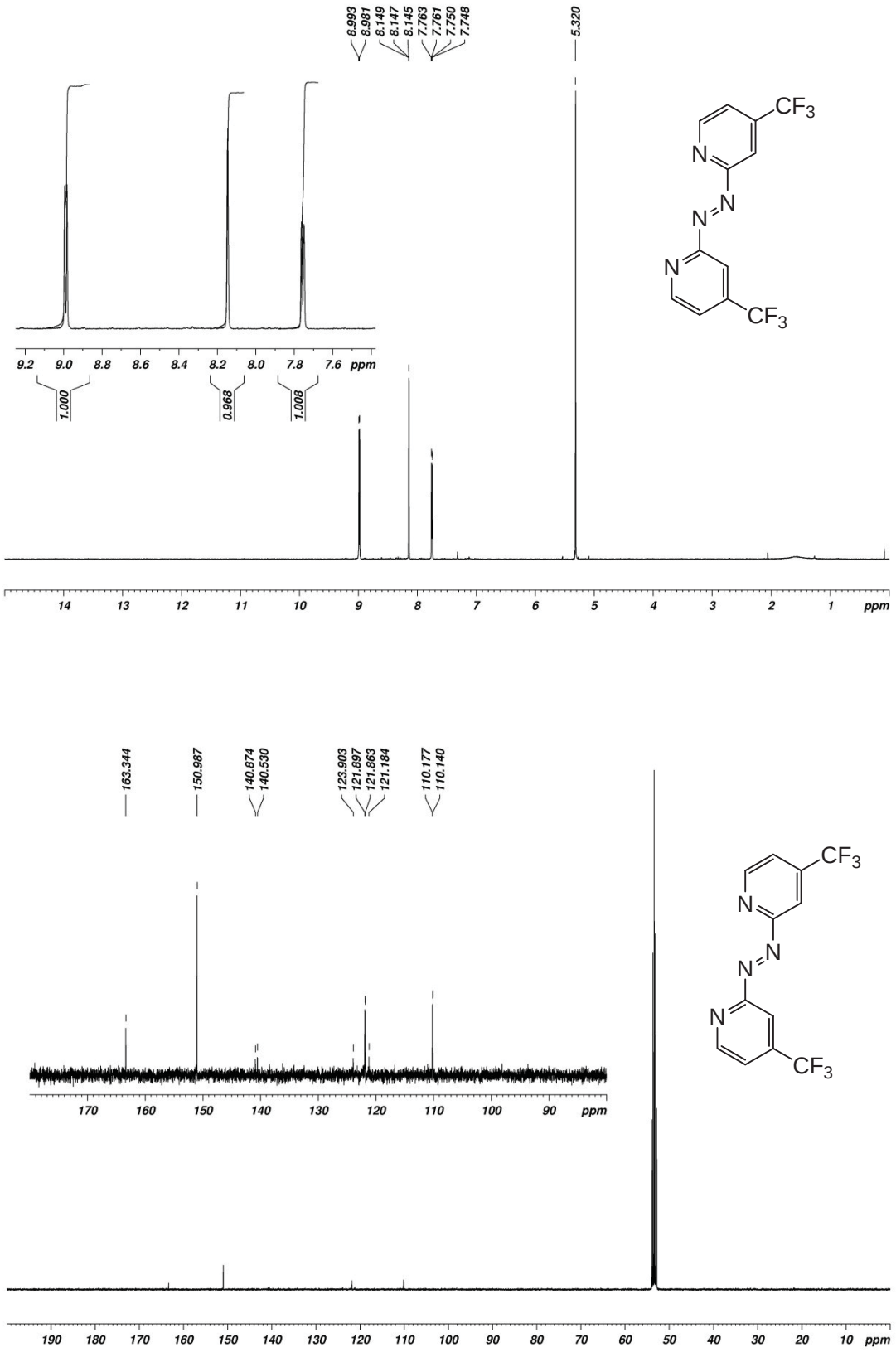

Figure S4. ^{1}H- (top) and ^{13}C-NMR spectra of 1,2-bis(4-(trifluoromethyl)pyridin-2-yl)diazene (**Azpy_CF$_3$**) in CD_2Cl_2.

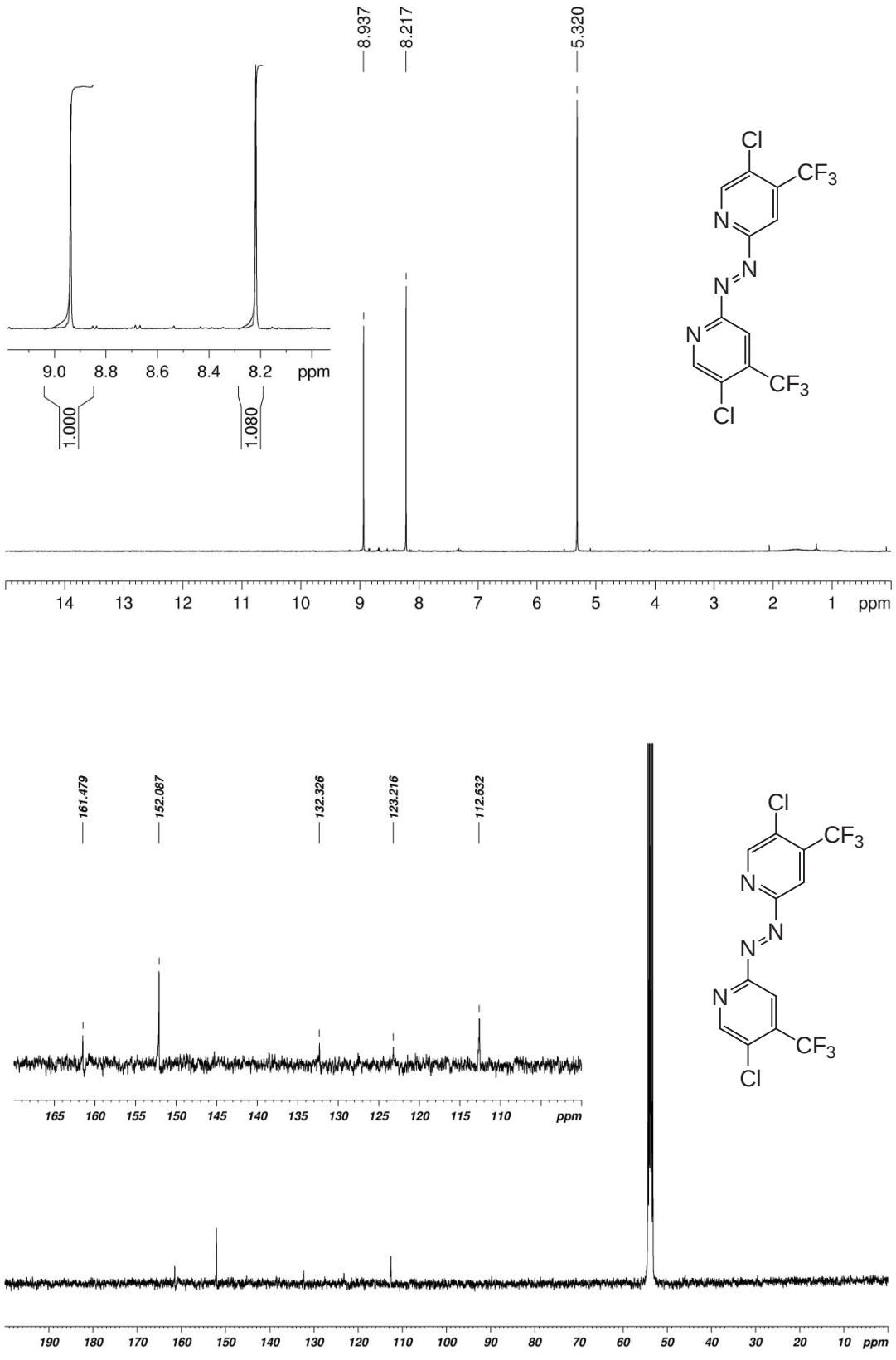

Figure S5. ^{1}H- (top) and ^{13}C-NMR spectra of 1,2-bis(5-chloro-4-(trifluoromethyl)pyridin-2-yl)diazene (**Azpy_CF_3Cl**) in CD_2Cl_2.

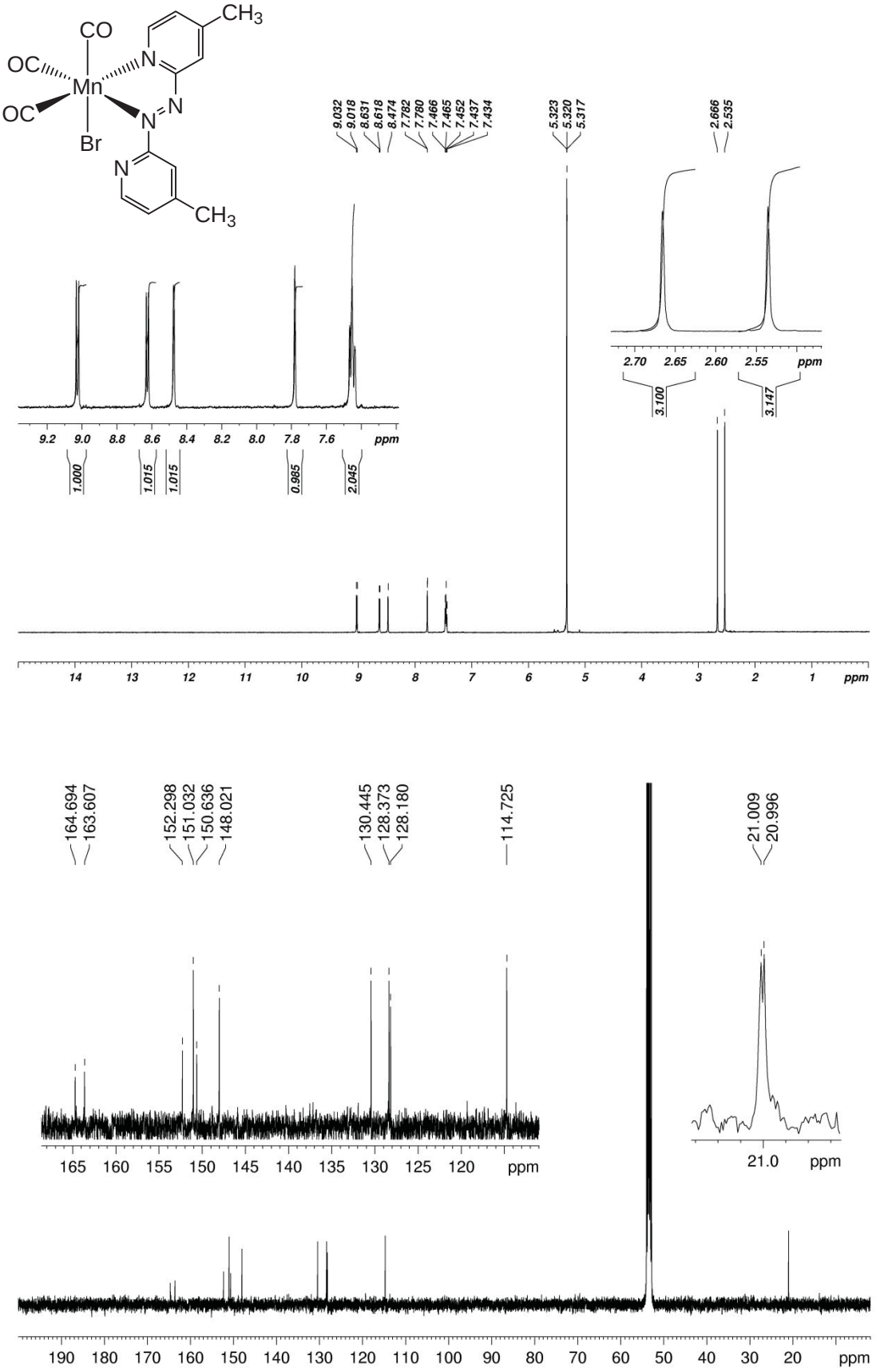

Figure S6. ^{1}H- (top) and ^{13}C-NMR spectra of complex **1** in CD_2Cl_2.

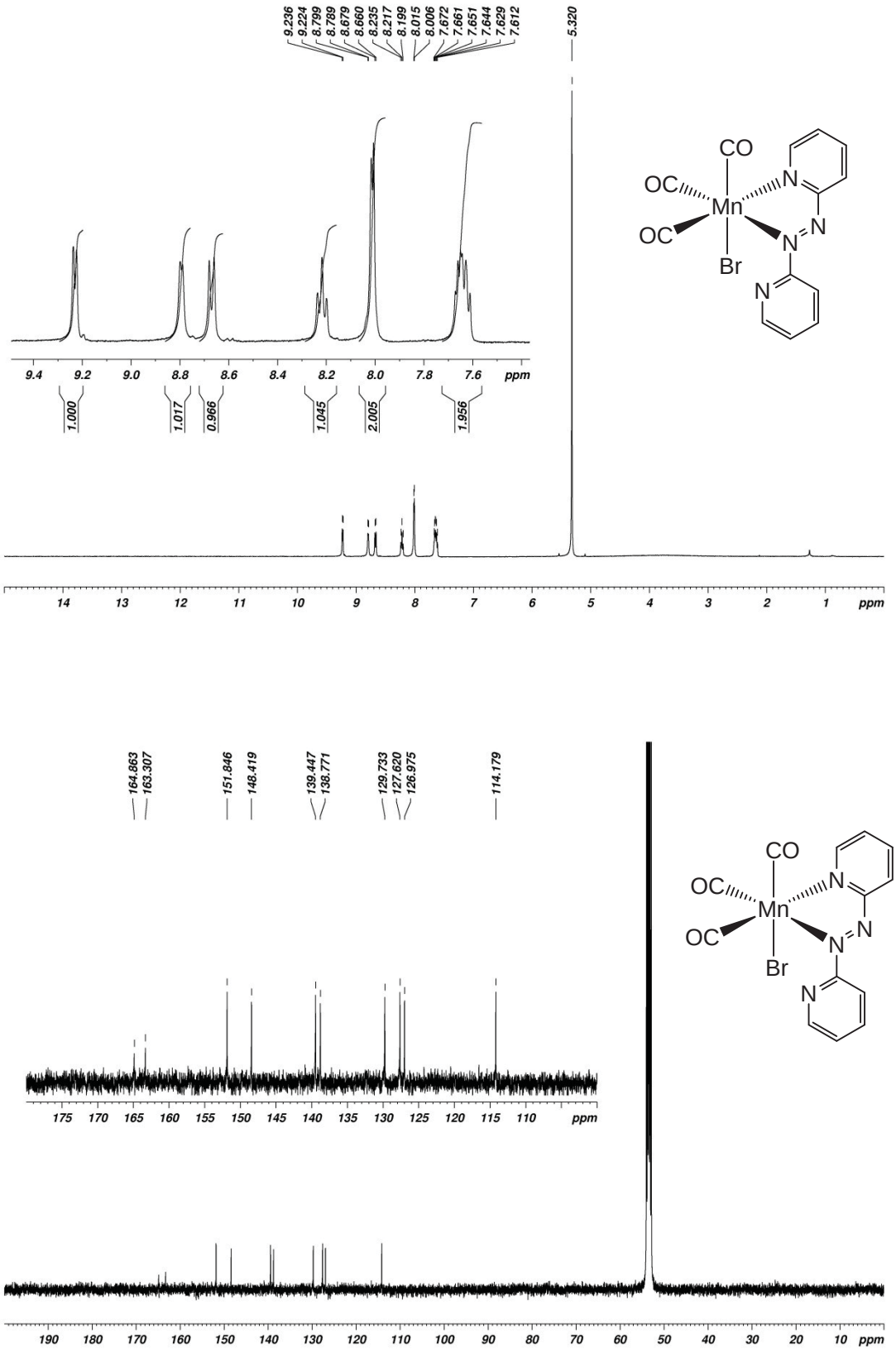

Figure S7. ^{1}H- (top) and ^{13}C-NMR spectra of complex **2** in CD_2Cl_2.

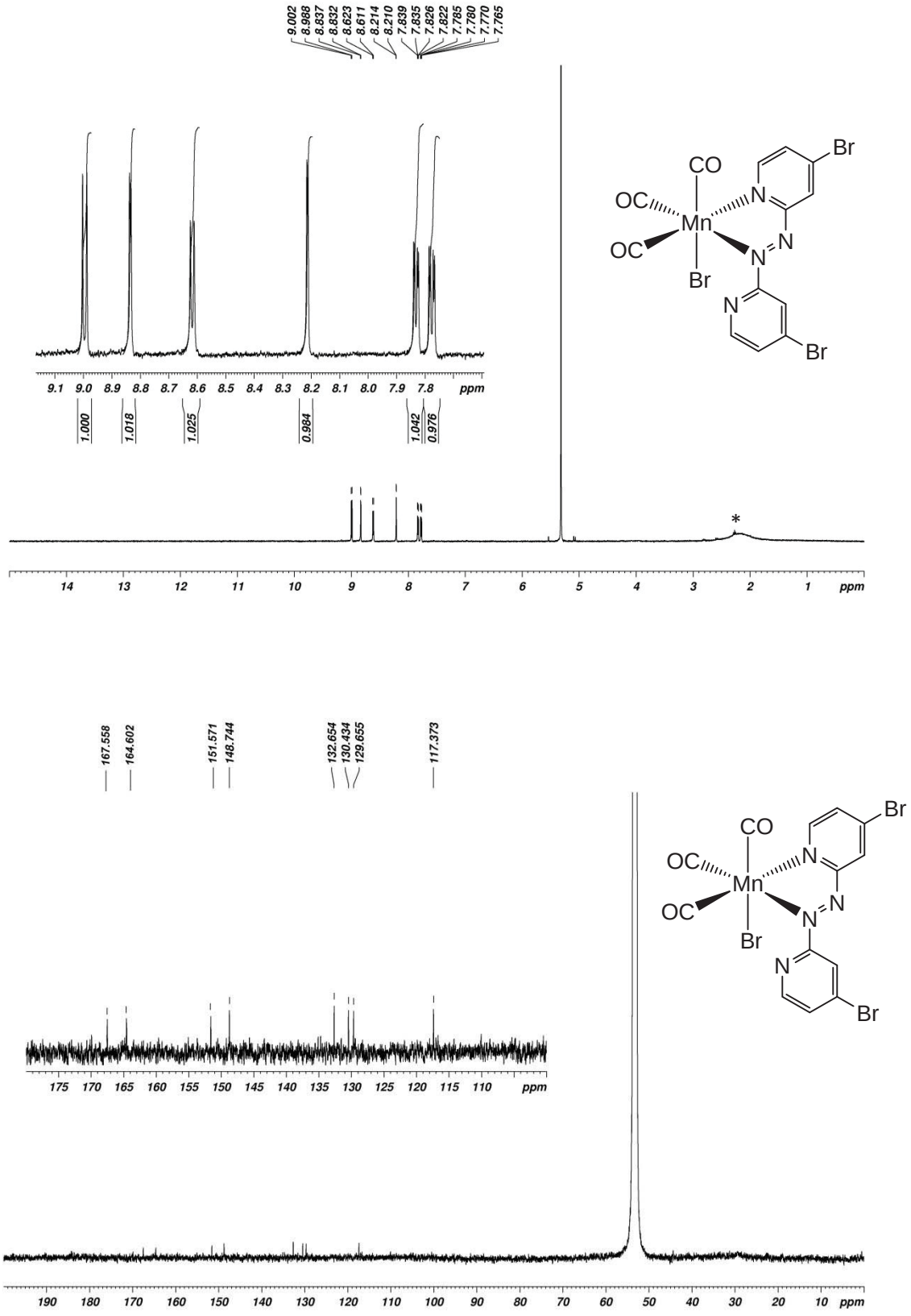

Figure S8. ^{1}H- (top) and ^{13}C-NMR spectra of complex **3** in CD_2Cl_2. Asterisk (*) indicates traces of water.

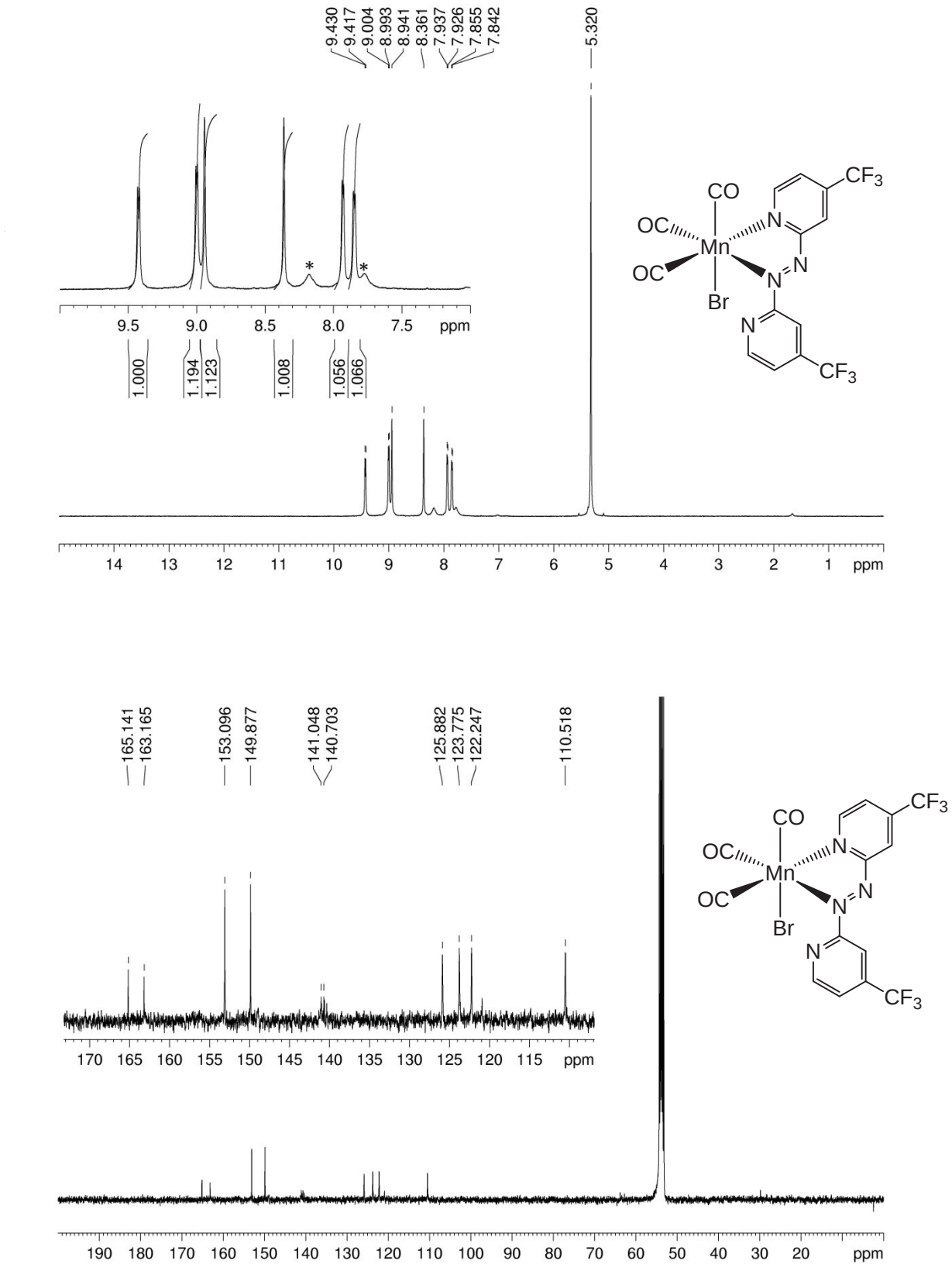

Figure S9. ^{1}H- (top) and ^{13}C-NMR spectra of complex **4** in CD_2Cl_2. Asterisks (*) indicate paramagnetic decomposition product.

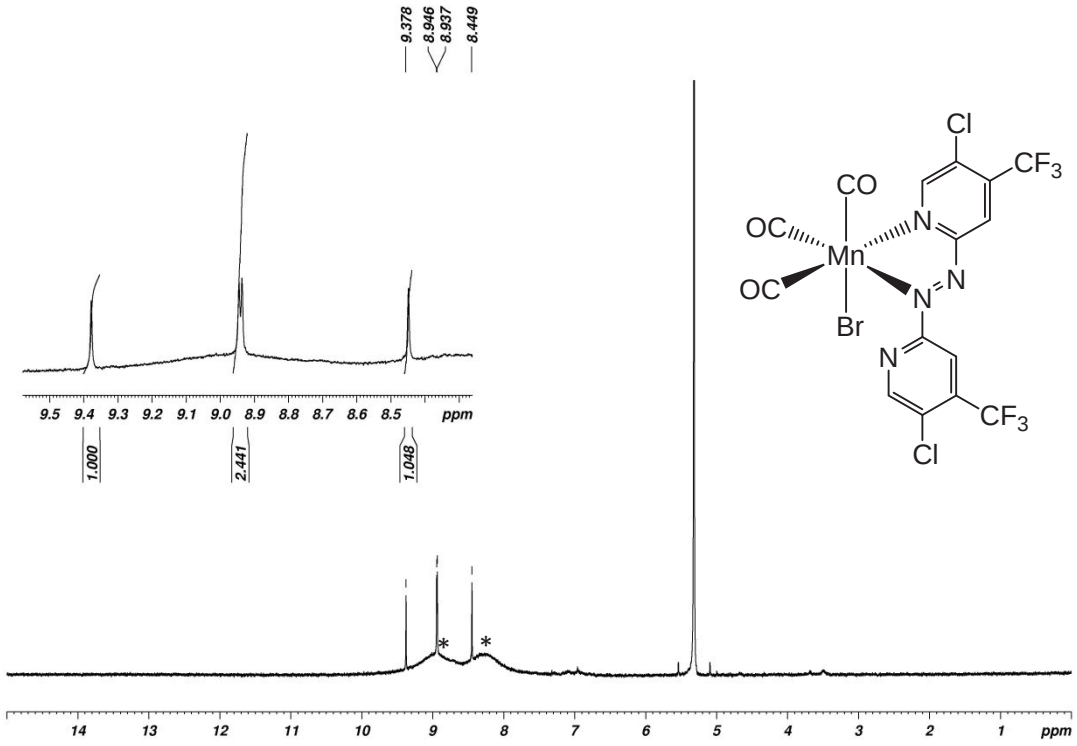

Figure S10. ^{1}H-NMR spectrum of complex **5** in CD_2Cl_2. Asterisks (*) indicate paramagnetic decomposition product.

S2. Crystallographic details

Table S1. Crystal data and structure refinement for 1,2-bis(4-(trifluoromethyl)pyridin-2-yl)diazene (Azpy_CF_3).

Identification code	shelx	
Empirical formula	C12 H6 F6 N4	
Formula weight	320.21	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 4.6634(4) Å	α= 113.797(8)°.
	b = 11.6504(12) Å	β= 93.861(8)°.
	c = 13.1188(14) Å	γ = 100.985(8)°.
Volume	631.90(12) $Å^3$	
Z	2	
Density (calculated)	1.683 Mg/m^3	
Absorption coefficient	0.167 mm^{-1}	
F(000)	320	
Crystal size	0.200 x 0.100 x 0.020 mm^3	
Theta range for data collection	1.719 to 24.989°.	
Index ranges	-5<=h<=5, -13<=k<=13, -15<=l<=15	
Reflections collected	8137	
Independent reflections	2095 [R(int) = 0.0982]	
Completeness to theta = 24.989°	94.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2095 / 0 / 199	
Goodness-of-fit on F^2	0.779	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0864	
R indices (all data)	R1 = 0.1351, wR2 = 0.1029	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.186 and -0.170 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for 1,2-bis(5-chloro-4-(trifluoromethyl)pyridin-2-yl)diazene (Azpy_CF_3Cl).

Identification code	shelx	
Empirical formula	C12 H4 Cl2 F6 N4	
Formula weight	389.09	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 4.7813(5) Å	α= 75.795(8)°.
	b = 6.6169(7) Å	β= 86.893(8)°.
	c = 11.6910(12) Å	γ = 88.052(8)°.
Volume	357.95(7) $Å^3$	
Z	1	
Density (calculated)	1.805 Mg/m^3	
Absorption coefficient	0.526 mm^{-1}	
F(000)	192	
Crystal size	0.670 x 0.050 x 0.050 mm^3	
Theta range for data collection	1.799 to 24.993°.	
Index ranges	-5<=h<=5, -7<=k<=7, -13<=l<=13	
Reflections collected	4600	
Independent reflections	1265 [R(int) = 0.1694]	
Completeness to theta = 24.993°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1265 / 0 / 109	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0782	
R indices (all data)	R1 = 0.0397, wR2 = 0.0810	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.271 and -0.403 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement for 1,2-bis(4-bromopyridin-2-yl)diazene (Azpy_Br).

Identification code	EK210	
Empirical formula	C10 H6 Br2 N4	
Formula weight	342.01	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 3.9747(3) Å	α= 90°.
	b = 9.2426(11) Å	β= 95.821(7)°.
	c = 14.9310(14) Å	γ = 90°.
Volume	545.69(9) Å3	
Z	2	
Density (calculated)	2.081 Mg/m3	
Absorption coefficient	7.402 mm-1	
F(000)	328	
Crystal size	0.420 x 0.120 x 0.080 mm3	
Theta range for data collection	2.595 to 24.985°.	
Index ranges	-4<=h<=4, -10<=k<=10, -17<=l<=17	
Reflections collected	6662	
Independent reflections	952 [R(int) = 0.1061]	
Completeness to theta = 24.985°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.8404 and 0.1446	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	952 / 0 / 73	
Goodness-of-fit on F2	1.118	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0708	
R indices (all data)	R1 = 0.0401, wR2 = 0.0732	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.445 and -0.401 e.Å-3	

Table S4. Crystal data and structure refinement for **2**.

Identification code	ek186	
Empirical formula	C13 H8 Br Mn N4 O3	
Formula weight	403.08	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 7.0251(4) Å	α= 87.090(5)°.
	b = 8.8782(5) Å	β= 80.778(5)°.
	c = 12.4114(7) Å	γ = 69.965(4)°.
Volume	717.85(7) $Å^3$	
Z	2	
Density (calculated)	1.865 Mg/m^3	
Absorption coefficient	3.720 mm^{-1}	
F(000)	396	
Crystal size	0.220 x 0.170 x 0.150 mm^3	
Theta range for data collection	1.662 to 24.987°.	
Index ranges	-8<=h<=8, -10<=k<=10, -14<=l<=14	
Reflections collected	9293	
Independent reflections	2529 [R(int) = 0.0491]	
Completeness to theta = 24.987°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2529 / 0 / 199	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0701	
R indices (all data)	R1 = 0.0307, wR2 = 0.0716	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.763 and -0.522 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for **2a**.

Identification code	shelx	
Empirical formula	C30 H24 Br4 Mn2 N12	
Formula weight	982.13	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.0263(9) Å	α= 90°.
	b = 7.7630(4) Å	β= 105.517(6)°.
	c = 19.2201(15) Å	γ = 90°.
Volume	1729.0(2) $Å^3$	
Z	2	
Density (calculated)	1.886 Mg/m^3	
Absorption coefficient	5.395 mm^{-1}	
F(000)	956	
Crystal size	0.060 x 0.050 x 0.040 mm^3	
Theta range for data collection	1.757 to 24.999°.	
Index ranges	-14<=h<=14, -9<=k<=9, -10<=l<=22	
Reflections collected	2987	
Independent reflections	2987 [R(int) = ?]	
Completeness to theta = 24.999°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2987 / 0 / 217	
Goodness-of-fit on F^2	0.876	
Final R indices [I>2sigma(I)]	R1 = 0.0743, wR2 = 0.1732	
R indices (all data)	R1 = 0.1380, wR2 = 0.1982	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.728 and -1.189 $e.Å^{-3}$	

S3. MLCT- σ Hammet parameter correlation of complexes 1-5

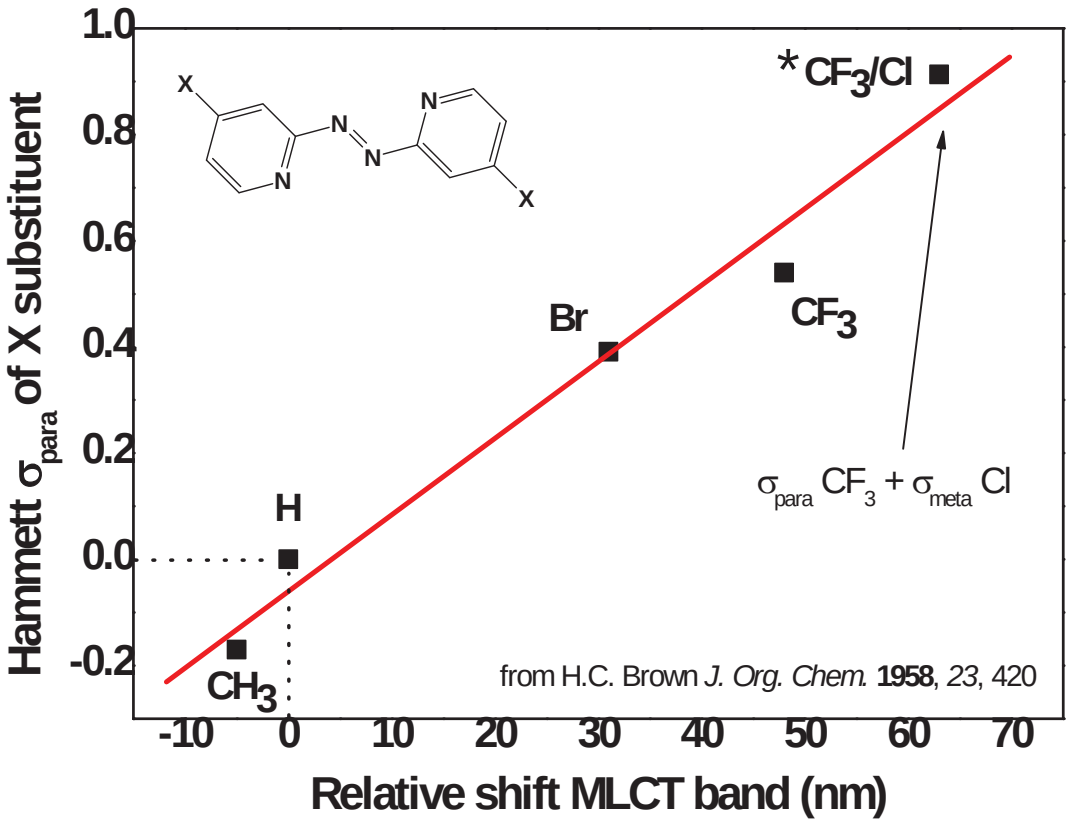

Figure S11. Correlation between the relative MLCT shift of complexes **1**-**5** and Hammet parameters σ of corresponding 2,2'-azopyridines ligands. $R^2 = 0.98$.

S4. Results of DFT calculations

Table S6. Selected bond distances and angles of complex **1** compared with DFT calculated values.

	X-Rays length (Å)	DFT length (Å)
C(1)-Mn(1)	1.805(3)	1.826
C(2)-Mn(1)	1.806(3)	1.802
C(3)-Mn(1)	1.829(3)	1.834
Br(1)-Mn(1)	2.5206(5)	2.570
Mn(1)-N(3)	2.007(2)	1.995
Mn(1)-N(1)	2.014(2)	2.041
	X-Rays angles (°)	**DFT angles (°)**
C(1)-Mn(1)-C(2)	88.82(13)	92.79
C(1)-Mn(1)-C(3)	87.68(12)	91.60
C(2)-Mn(1)-C(3)	90.55(12)	92.24
C(1)-Mn(1)-N(3)	172.48(11)	168.44
C(2)-Mn(1)-N(3)	93.15(11)	94.32
C(3)-Mn(1)-N(3)	99.55(11)	97.21
C(1)-Mn(1)-N(1)	96.01(11)	93.50
C(2)-Mn(1)-N(1)	93.90(10)	95.24
C(3)-Mn(1)-N(1)	174.27(11)	170.73
N(3)-Mn(1)-N(1)	76.62(8)	76.80
C(1)-Mn(1)-Br(1)	89.78(10)	85.53
C(2)-Mn(1)-Br(1)	177.96(8)	177.53
C(3)-Mn(1)-Br(1)	87.92(9)	86.01
N(3)-Mn(1)-Br(1)	88.43(6)	87.62
N(1)-Mn(1)-Br(1)	87.72(6)	86.67

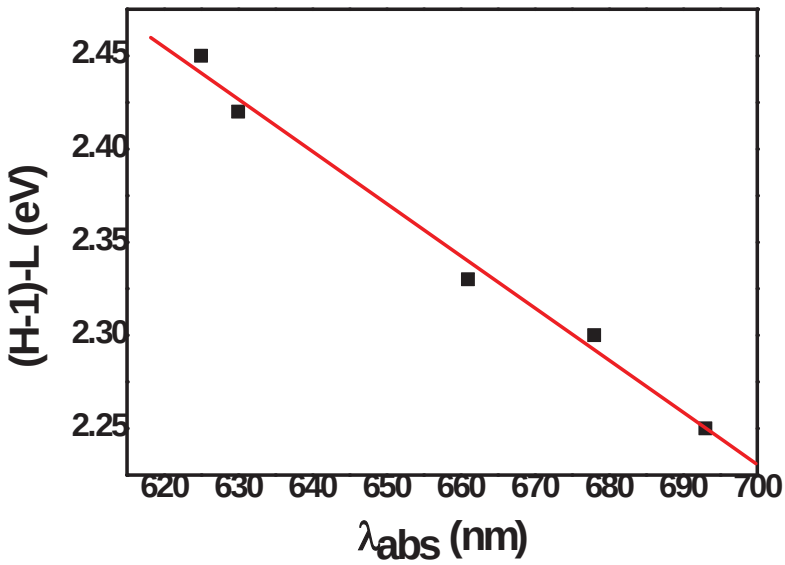

Figure S12. Correlation between the calculated HOMO-1/LUMO gap and the relative MLCT absorption of complexes **1**-**5**. $R^2 = 0.99$.

S5. Electronic absorption spectra

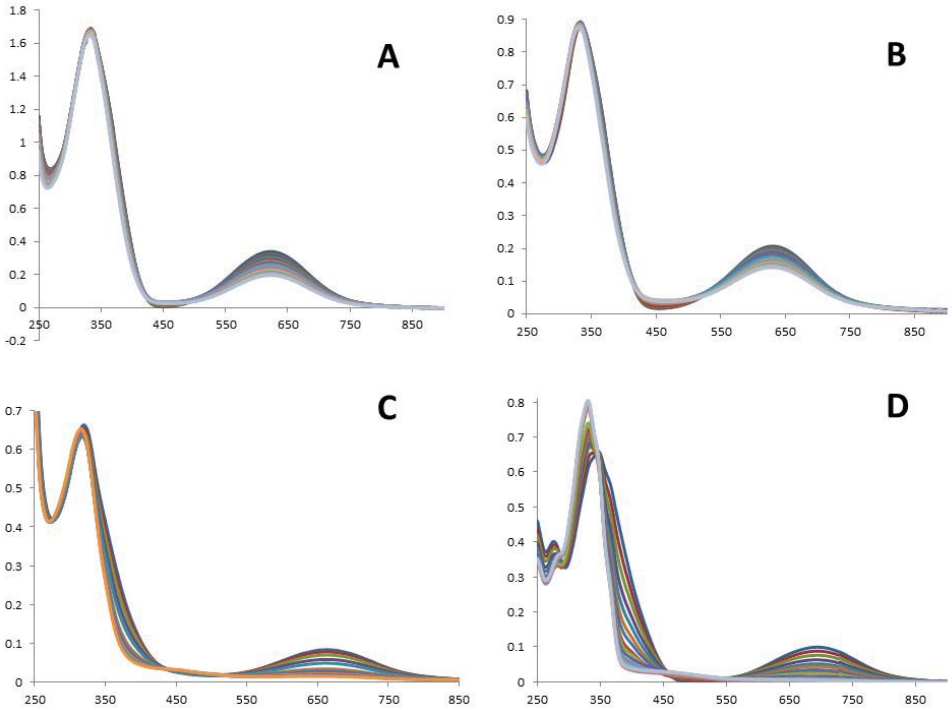

Figure S13. Changes observed in the electronic absorption spectra of **1** (A), **2** (B), **3** (C) and **5** (D) upon photoirradiation at λ_{max} (vis.).

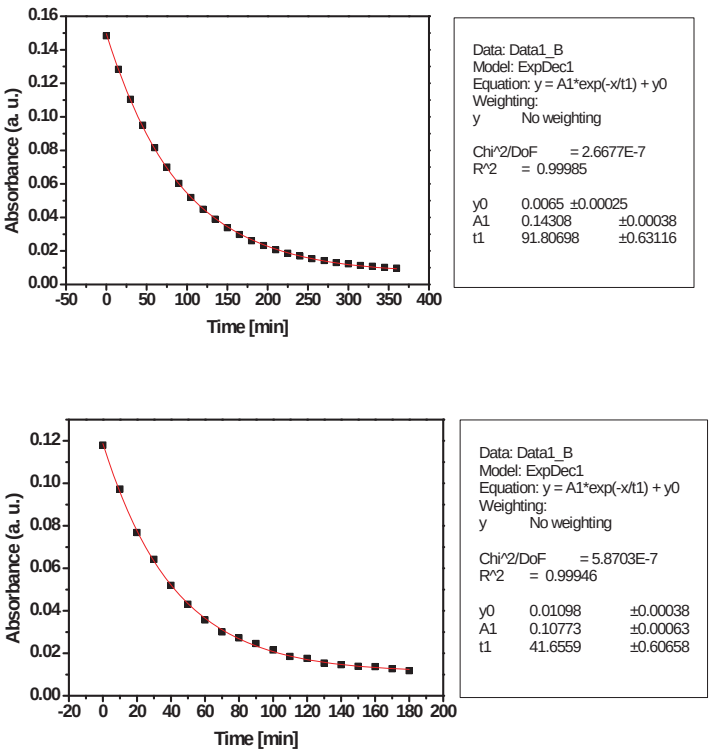

Figure S14. Fitting of the monoexponential decay of thermal (top) and photodecomposition kinetics of **4**. Graphs are given as typical examples of the procedure used to calculate t½.

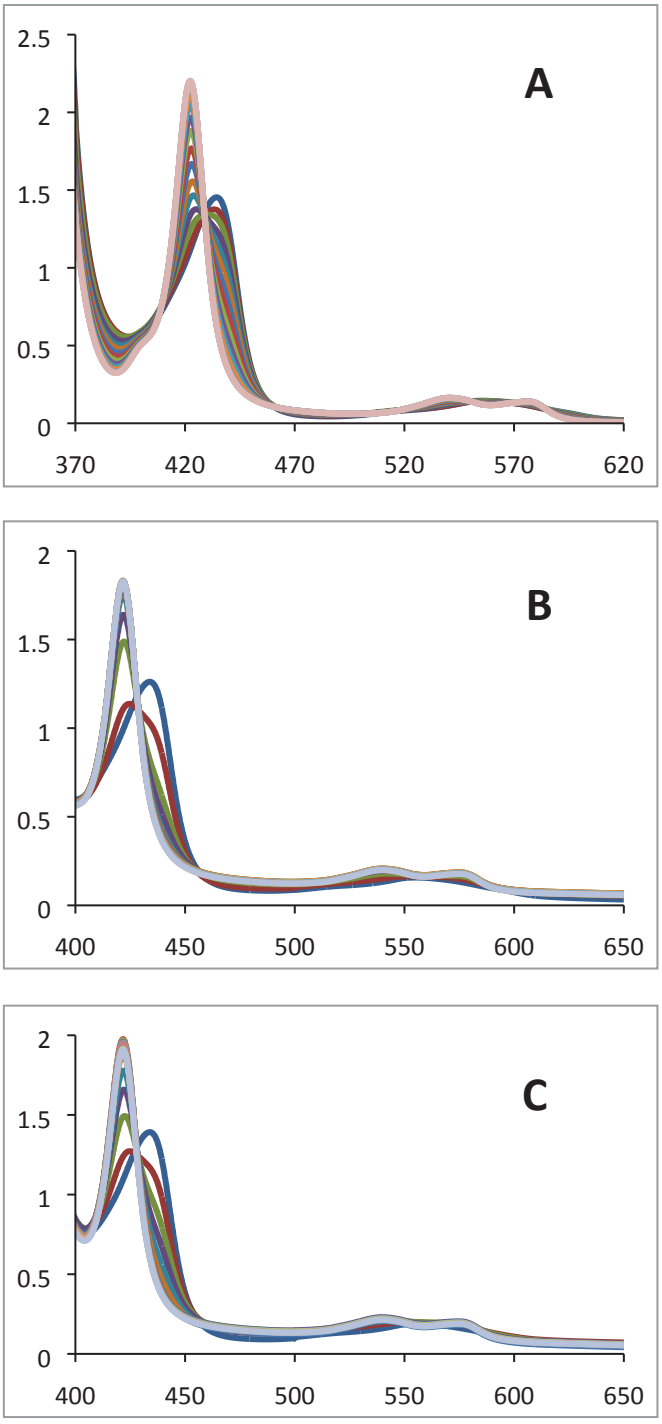

Figure S15. Changes observed in the electronic absorption spectra of a Mb solution upon photoirradiation at λ_{max} (vis.) in the presence of **3** (A), **4** (B) and **5** (C).