Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

New Journal of Chemistry

Molecular Engineering of Fluorescent Bichromophore 1,3,5-Triaryl-Δ^2-Pyrazoline and 4-Amino-1,8-Naphthalimide Molecular Logic Gates

Darlene Sammut,[a] Nathalie Bugeja,[a] Konrad Szaciłowski[b] and David C. Magri[a]

[a] Department of Chemistry, Faculty of Science, University of Malta, Msida, MSD 2080, Malta. E-mail: david.magri@um.edu.mt

[b] AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Mickiewicza 30, 30-059 Kraków, Poland. Email: szacilow@agh.edu.pl

Table of Contents

Chemicals

4-Chloro-1,8-naphthalic anhydride (94%, Alfa Aesar, GPR), methylamine solution, 2M in THF (Argos Organics, GPR), 1,4-dioxane (Fischer Scientific, GPR), glacial acetic acid (Scharlau, ACS), 2-methoxyethanol (Carlo Erba, RPE), hydrazine monohydrate (64-65%, Sigma Aldrich, GPR), tetrahydrofuran (Carlo Erba, analytical grade), hydrochloric acid (37%, Carlo Erba, analysis grade), ethanol (96%, Carlo Erba, ACS), acetophenone (>99%, Fluka, analytical reagent grade), benzaldehyde, *N*,*N*-dimethylanilinebenzaldehyde (Carlo Erba, ACS), ferrocenecarboxyaldehyde (97%, BDH, GPR), chloroform-*d* with 0.03% tetramethylsilane (99.8%, Aldrich, NMR), ferric perchlorate hydrate (Sigma Aldrich, GPR), methanesulfonic acid (99%, Sigma Aldrich, GPR), sodium hydroxide (Fischer, analytical grade). All reagents and solvents were used as received. Thin-layer chromatography was performed on pre-coated silica gel plates on aluminium foils (Sigma-Aldrich, 0.2 mm, 20 × 20 cm, F_{25}) developed in a closed chamber and irradiated with 254 nm or 365 nm UV light.

Instrumentation

Syntheses were performed in round-bottom flasks immersed in a mineral oil bath heated with IKA C-MAG HS 7 hotplates fitted with an IKA ETS-D5 temperature probe. Melting points were recorded on a Stuart SMP11 (digital) melting point apparatus in open-end capillary tubes and were corrected by calibration with pure caffeine (m.p. = 235 ^{o}C). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III Ascend 500 HD NMR spectrometer equipped with a 11.75 Tesla superconducting magnet and a 5 mm multinuclear PABBO probe operating at 500.13 MHz (^{1}H NMR) and 125.76 MHz (^{13}C NMR). NMR samples were typically of 5 mg or greater dissolved in 0.8 mL of deuterated $CDCl_3$. was used as the internal reference standard. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) at 0.00 ppm. All spectra were carried out at 298 K.. The data was processed using Topspin Software version 3.2. Infrared spectra were recorded using Shimadzu IRAffinity-1 spectrophotometer with spectra recorded in wavenumbers (cm^{-1}). The Infrared spectrophotometer was calibrated against a blank measurement salt plate prior to adding the sample. Samples were prepared using KBr disc method. HRMS was performed by ES-ToF technique and performed by Medac Ltd (UK).

UV-vis absorption spectra were recorded at room temperature on a Jasco V-650 spectrophotometer using quartz Suprasil cells with a path length of 1.0 cm. The settings were set at 2.0 nm bandwidth with a medium response and scan speed of 400 nm min^{-1}. All spectra

were corrected by scanning the solvent as the blank solution prior to measurement of spectra. Samples were typically scanned over the range of 350-700 nm.

Fluorescence measurements were recorded at room temperature on Jasco FP-8300 spectrophotometer using Suprasil quartz cells with a path length of 1.0 cm. The parameters were set to emission mode using an excitation wavelength of 440 nm for all three molecules. The emission range was 450-700 nm region. The parameters were set at an excitation bandwidth of 1.0 nm, emission bandwidth of 2.5 nm, 50 m sec response, medium sensitivity, and a scan speed of 200 nm min^{-1}. The prepared solutions had absorbance values below 0.1 All spectra were corrected by scanning the solvent as the blank solution prior to measurement of spectra.

Titration Procedure

Standard stock solutions of **1-3** were prepared by adding 5 mg of each sample in a 100 mL volumetric flask (grade B) and made up to the mark with THF. The maximum wavelength and absorbance of each solution was determined using UV-vis spectra, and solutions diluted until the absorbance was approximately 0.1 with concentrations ca. 10 μM for **1** and **2**, and 20 μM for **3** in 50 mL grade B volumetric flasks. Molar equivalents of 1 M HCl and 0.01 M iron (III) solution were added separately into vials using Gibson 1-10 μL and 50-200 μL pipettes and eppendorf pipette tips, and transferred to a 1.0 cm Suprasil quartz cuvette. A blank measurement was run using THF and the fluorescence of each solution on addition of aliquots of acid and iron (III) solutions were measured. The excitation wavelength was 440 nm.

Fluorescence Quantum Yields

UV-vis absorption spectra of **1-3** were measured by dissolving 5 mg of sample in 100 mL of solvent and diluting to an absorbance of 0.1. Fluorescence quantum yield were calculated using the equation below:

$$\Phi_F = \frac{Area_{sample}}{Area_{standard}} \times \frac{Abs_{standard}}{Abs_{sample}} \times \frac{n^2_{sample}}{n^2_{standard}} \times \Phi_{standard}$$

where the $\Phi_{standard}$ is the fluorescence quantum yield of quinine sulfate in 0.1 M aerated aqueous sulfuric acid ($\Phi_F = 0.55$) or fluorescein in aerated aqueous water with 0.1 M NaOH ($\Phi_F = 0.95$). Calculations used the area under the emission curve of the sample and standard, the $\lambda_{max,}$ absorbance of the sample and standard, and the refractive indexes of the various solvents given in Table S1 and S2.

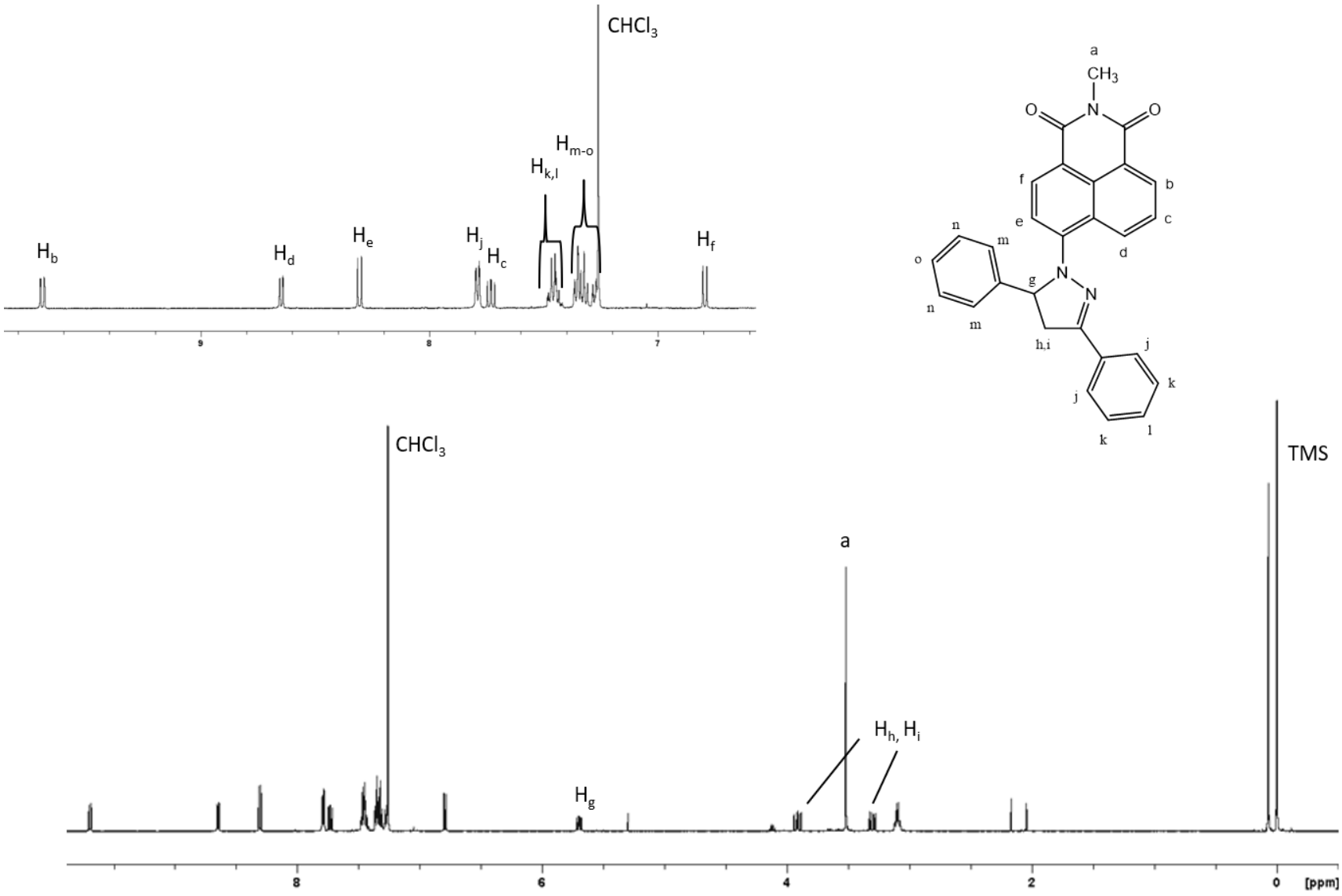

Fig. S1 ^{1}H NMR spectrum of **1** in $CDCl_3$ with 0.03% TMS.

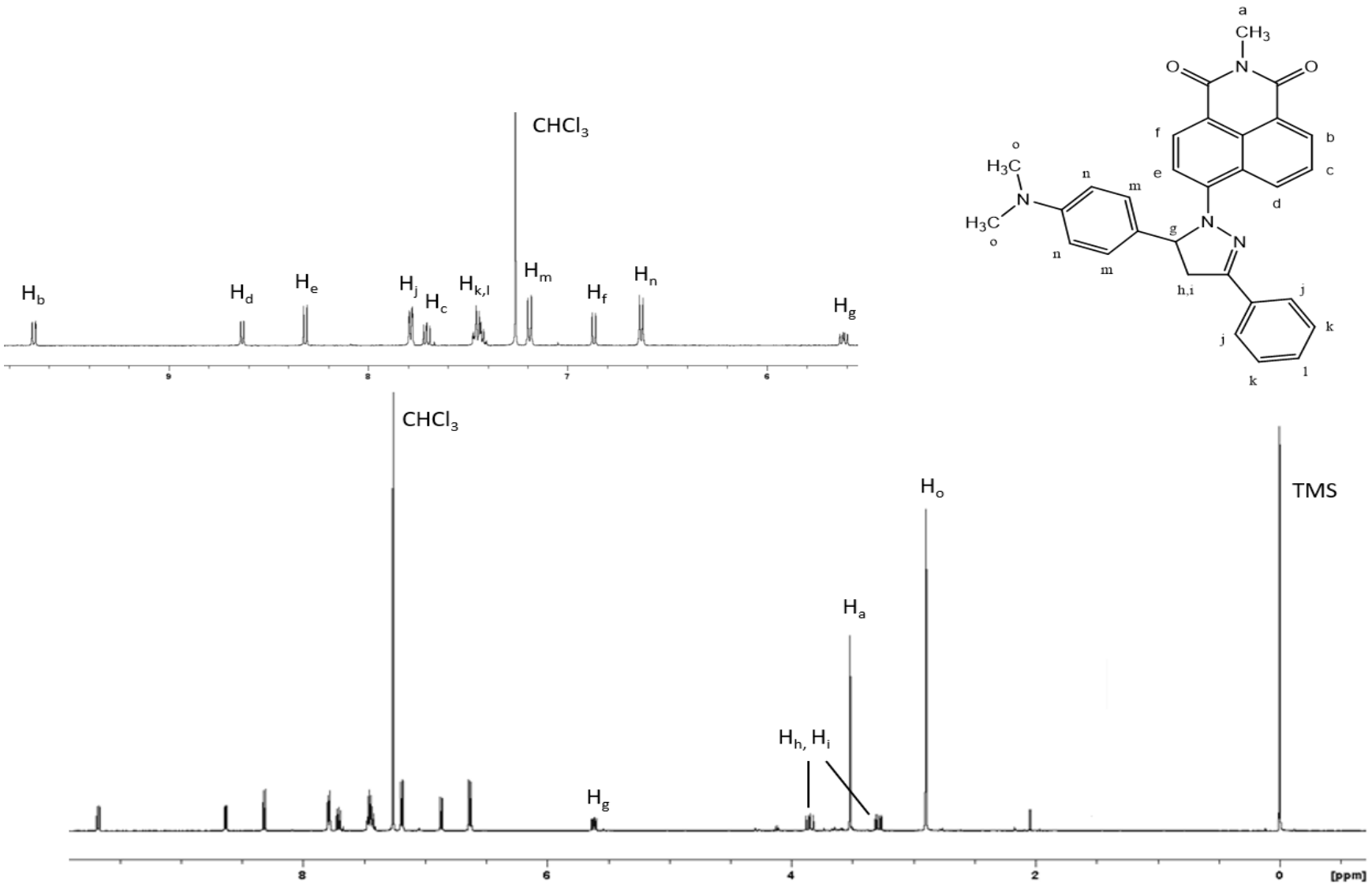

Fig. S2 ^{1}H NMR spectrum of **2** in $CDCl_3$ with 0.03% TMS.

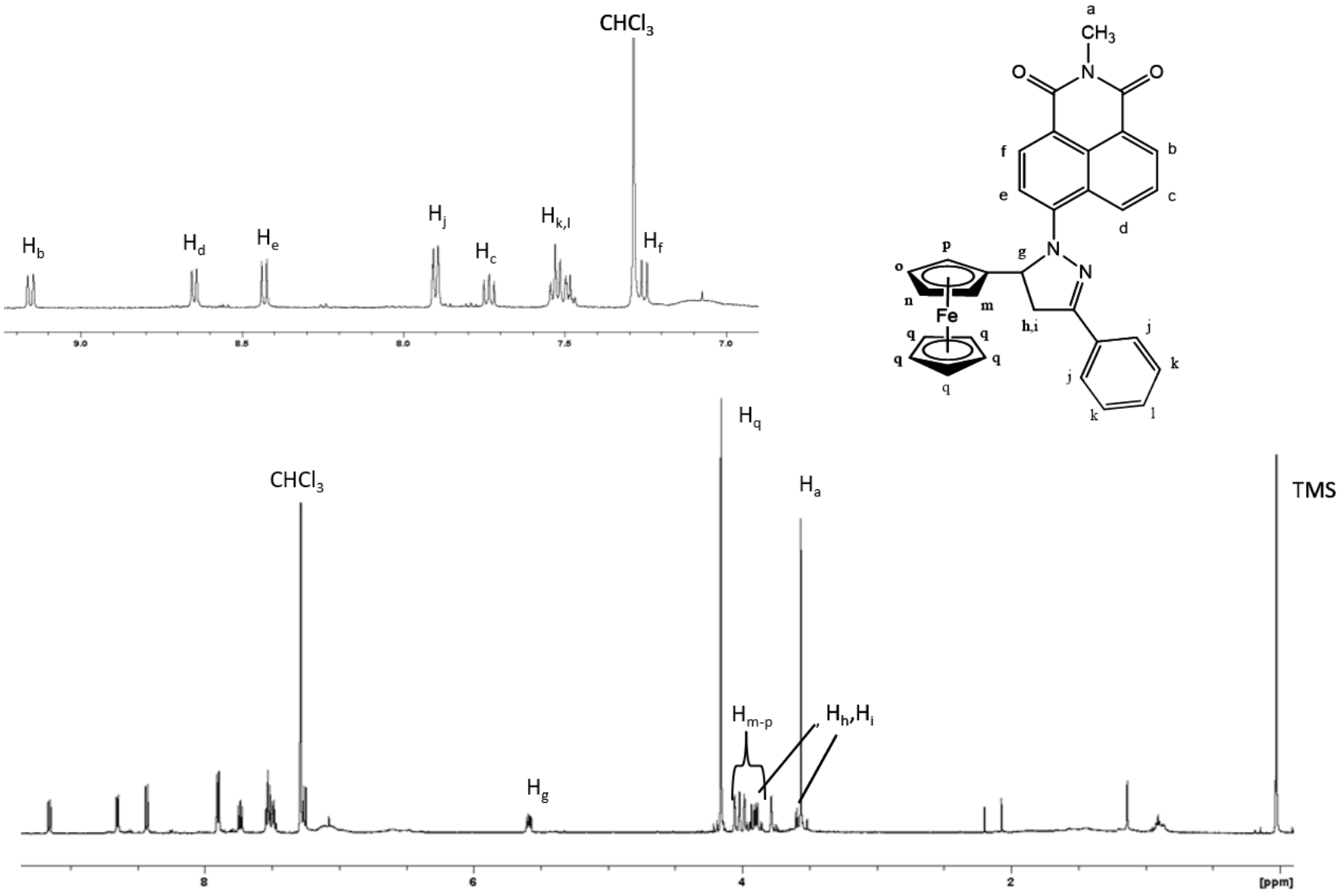

Fig. S3 ^{1}H NMR spectrum of **3** in $CDCl_3$ with 0.03% TMS.

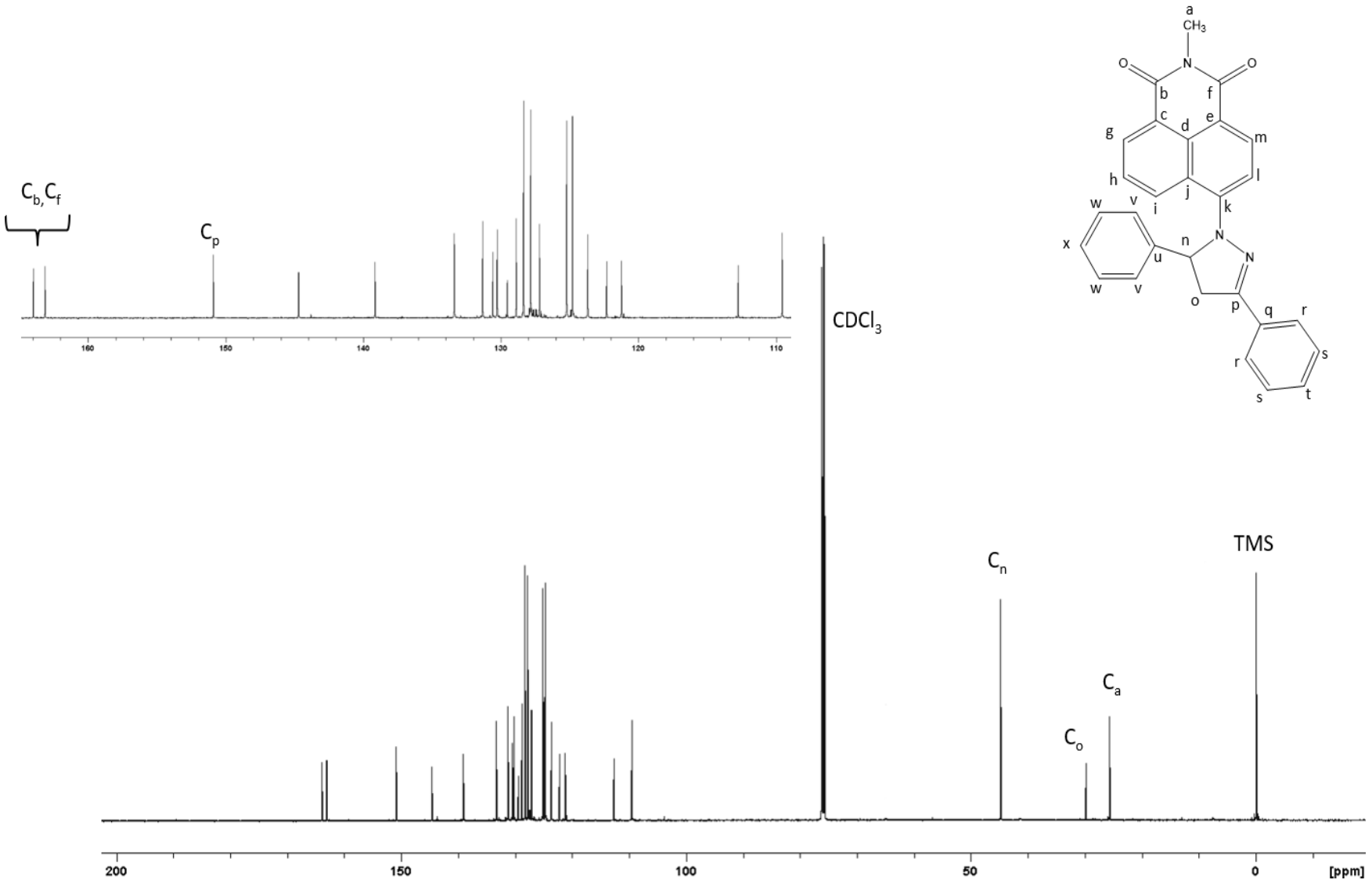

Fig. S4 ^{13}C NMR spectrum of **1** in $CDCl_3$ with 0.03% TMS.

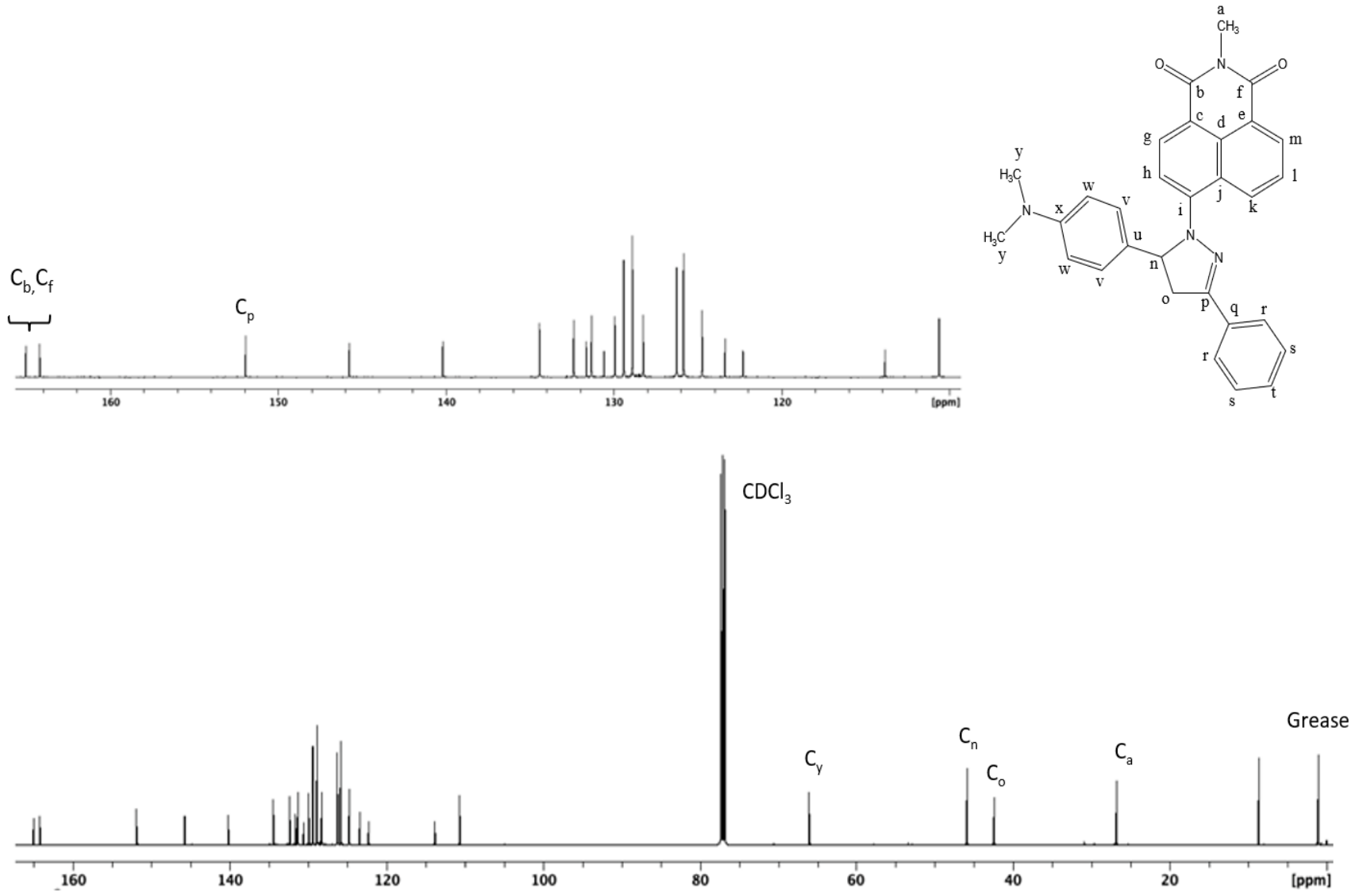

Fig. S5 ^{13}C NMR spectrum of **2** in $CDCl_3$ with 0.03% TMS.

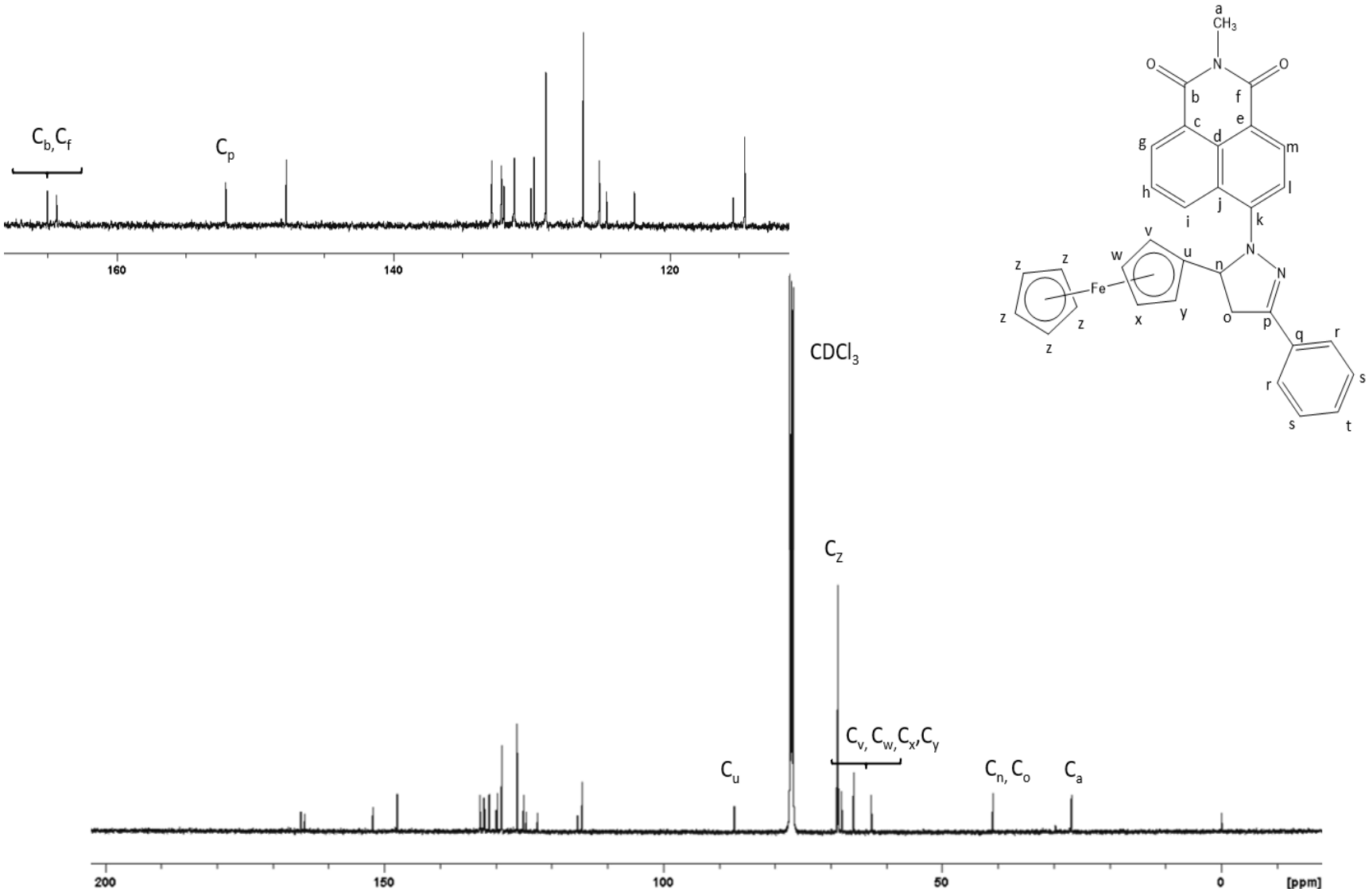

Fig. S6 ^{13}C NMR spectrum of **3** in $CDCl_3$ with 0.03% TMS.

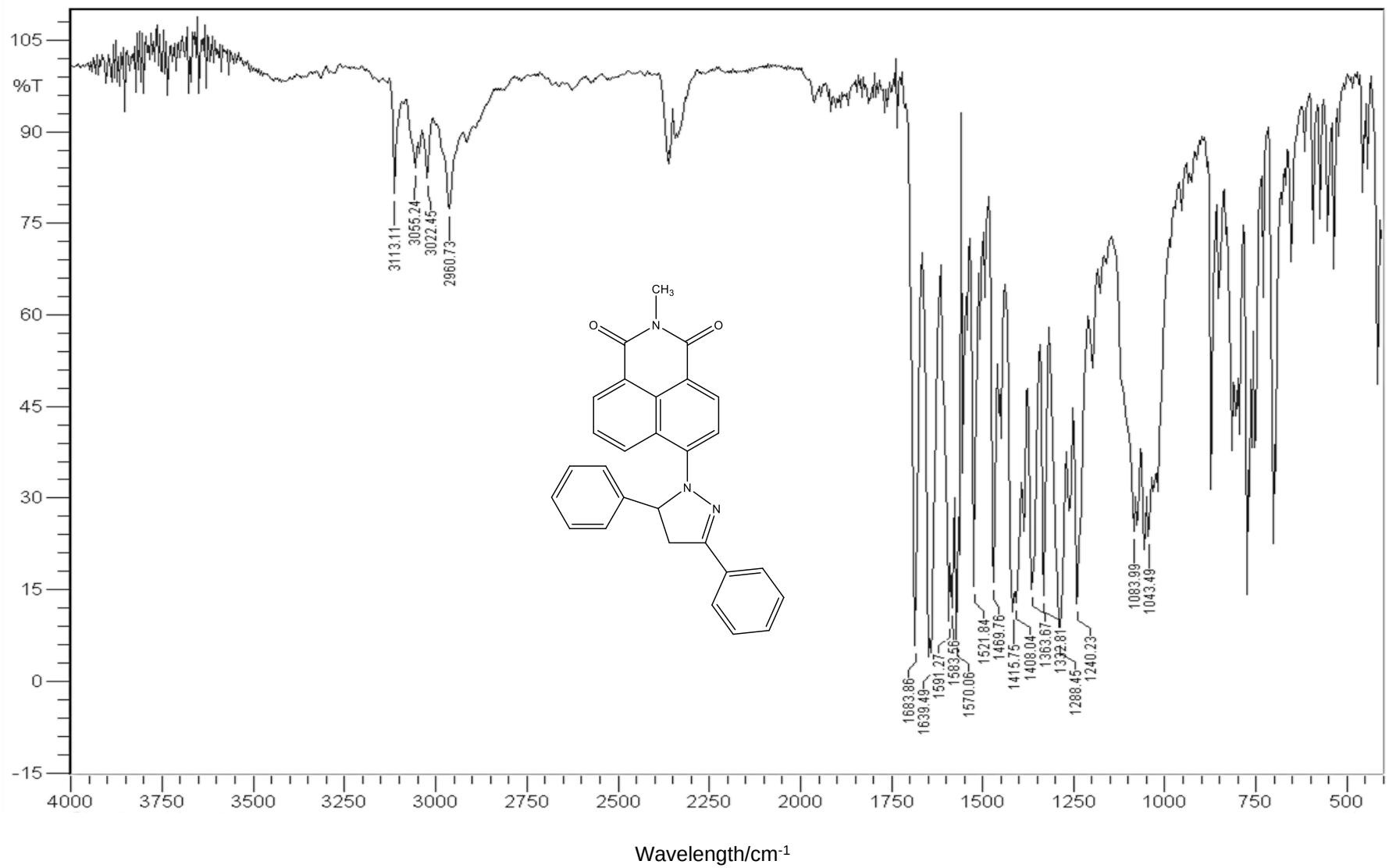

Fig S7 IR spectrum of **1** using KBr disc method.

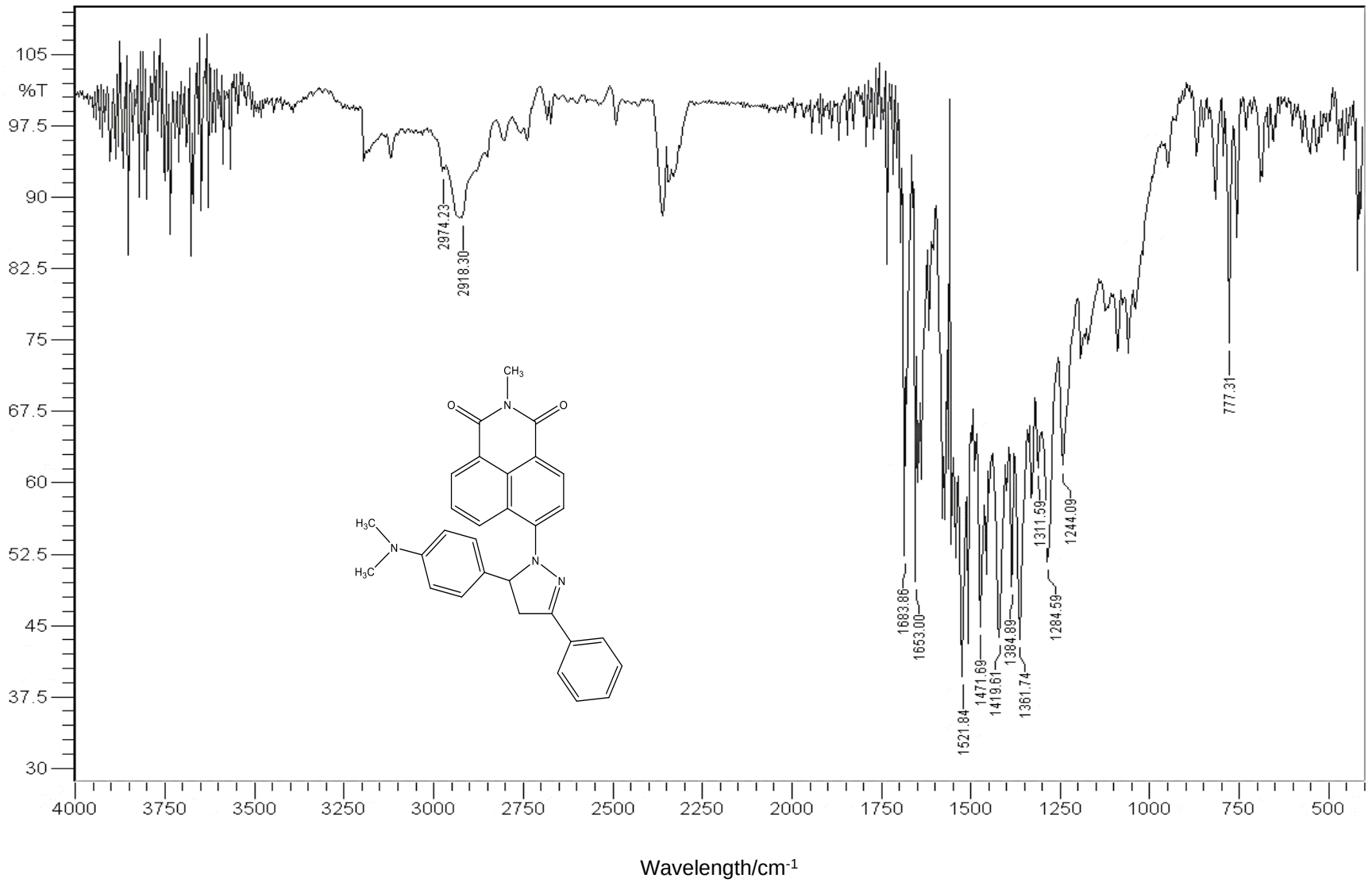

Fig. S8 IR spectrum of **2** using KBr disc method.

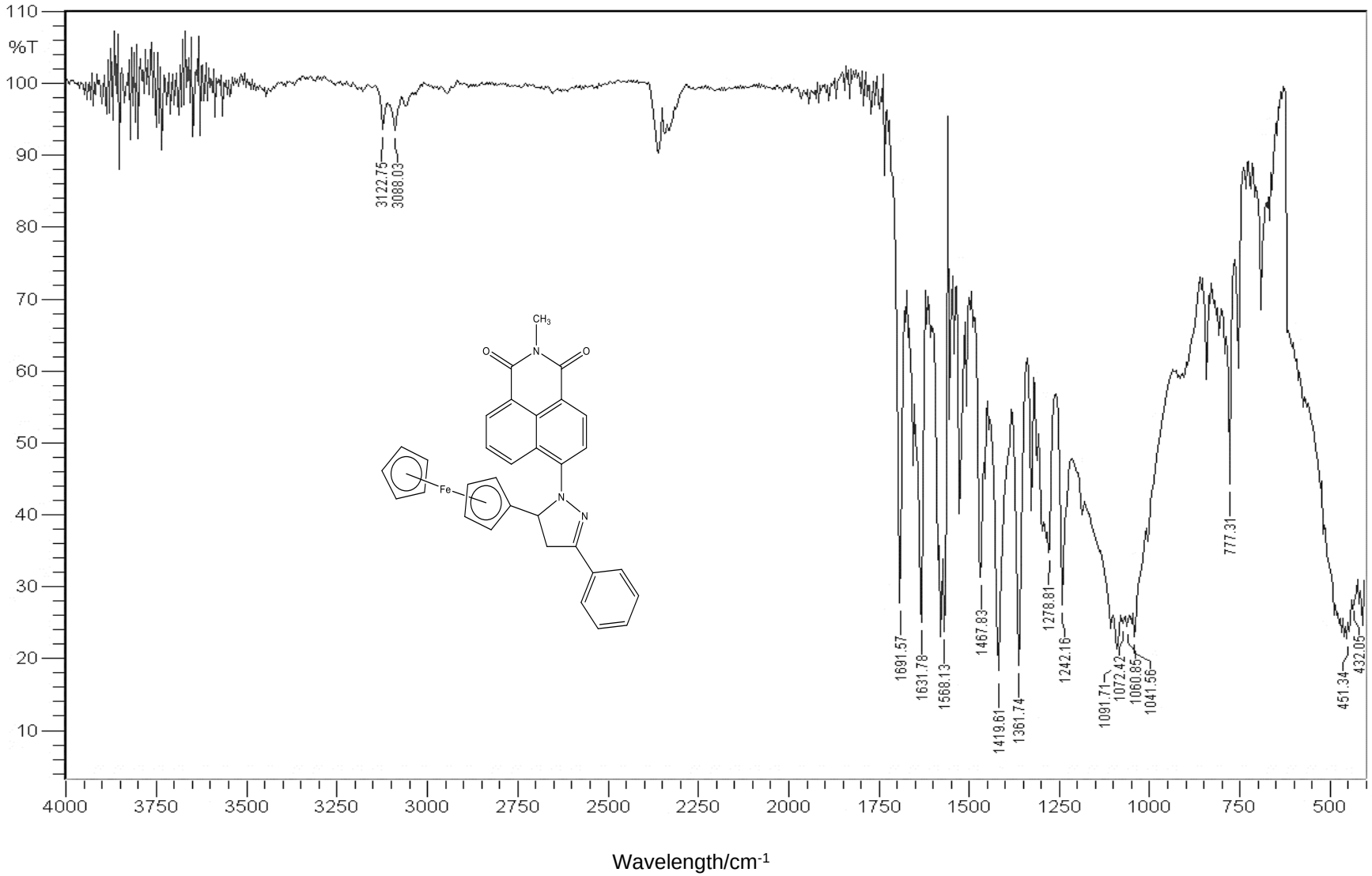

Fig. S9 IR spectrum of **3** using KBr disc method.

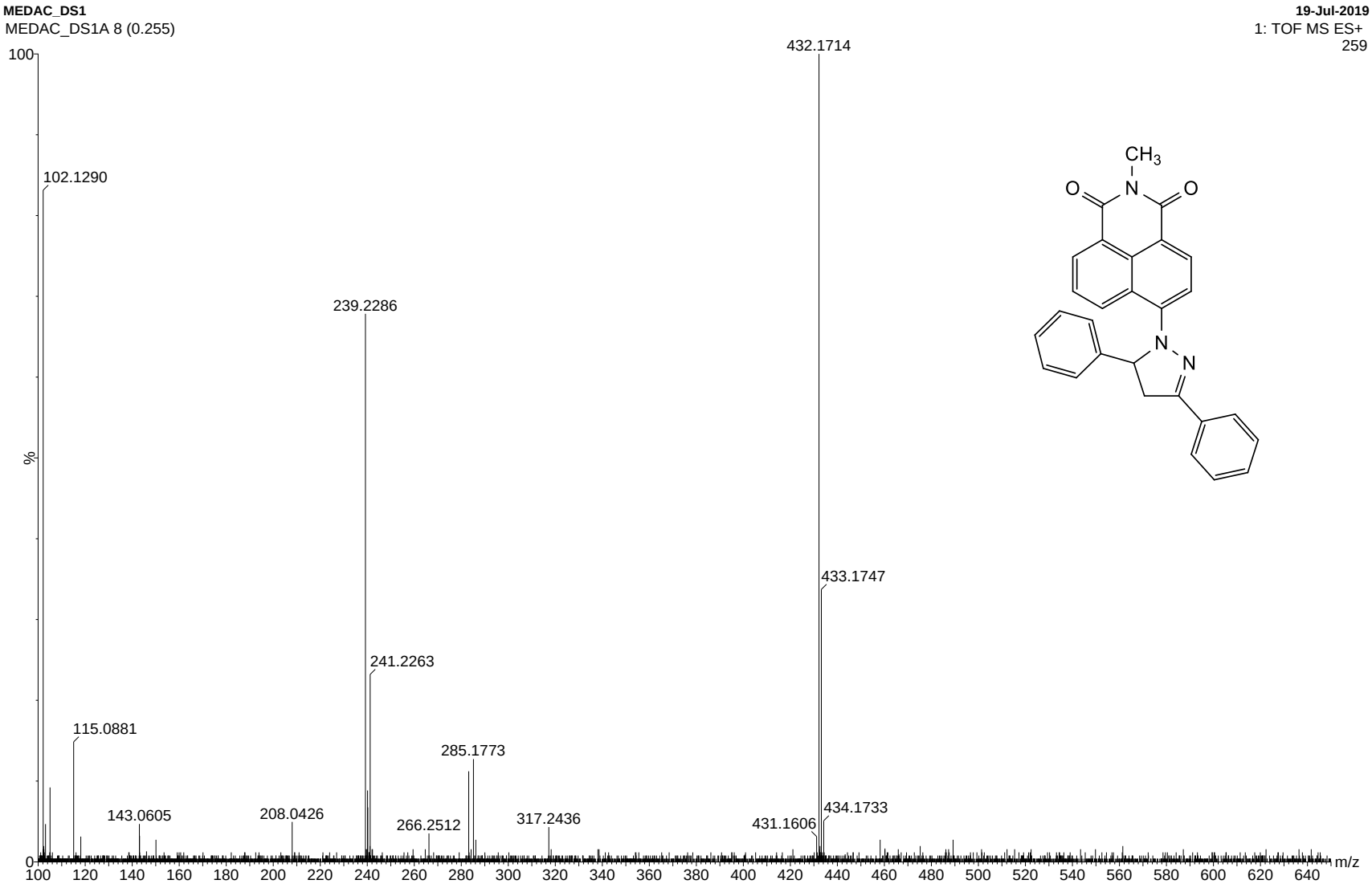

Fig. S10 HRMS of **1** by ESI-TOF.

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
432.1714	432.1712	0.2	0.5	19.5	48.9	C28H22N3O2

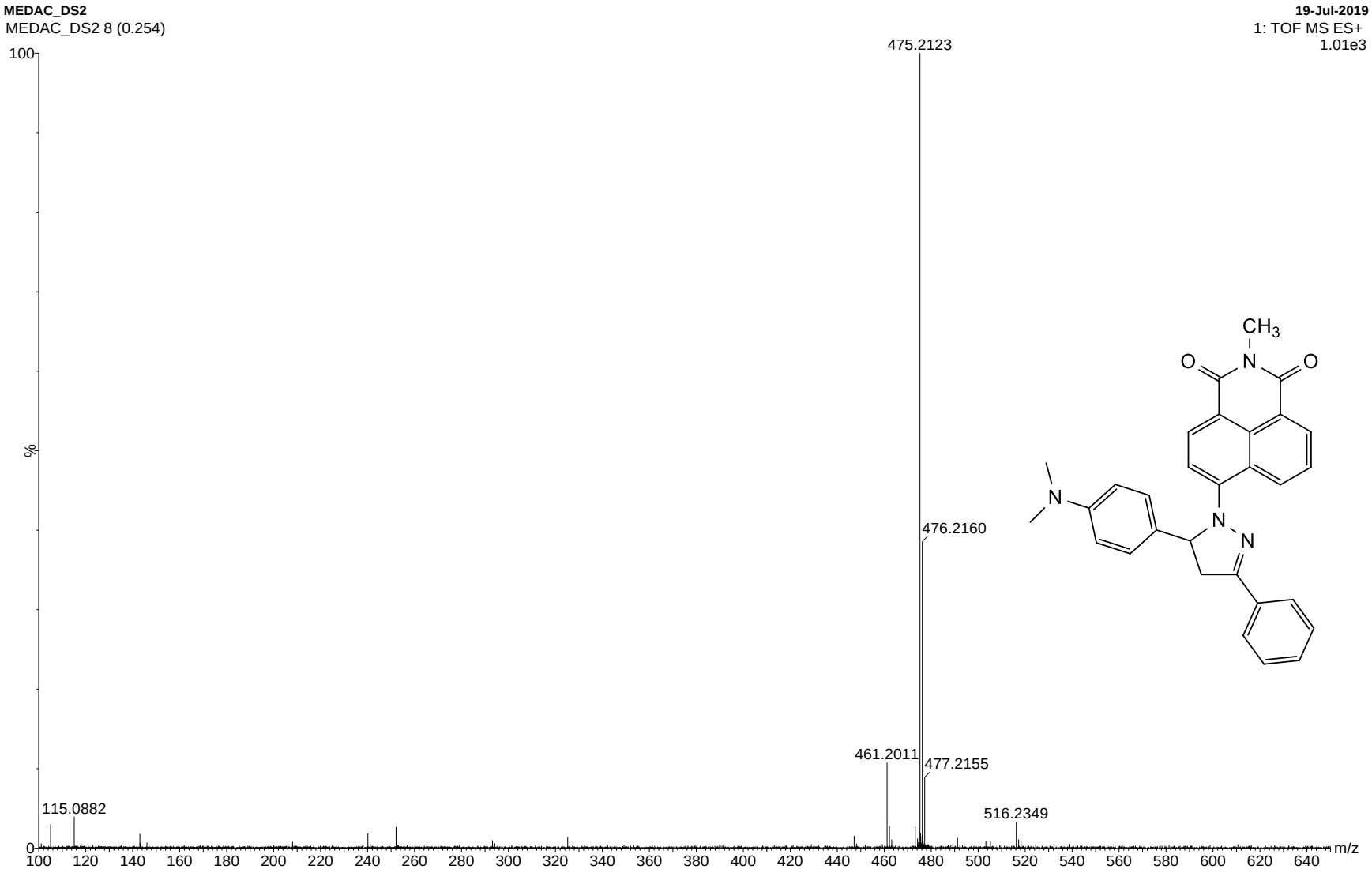

Fig. S11 HRMS of **2** by ESI-TOF.

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
475.2123	475.2134	-1.1	-2.3	19.5	96.6	C30H27N4O2

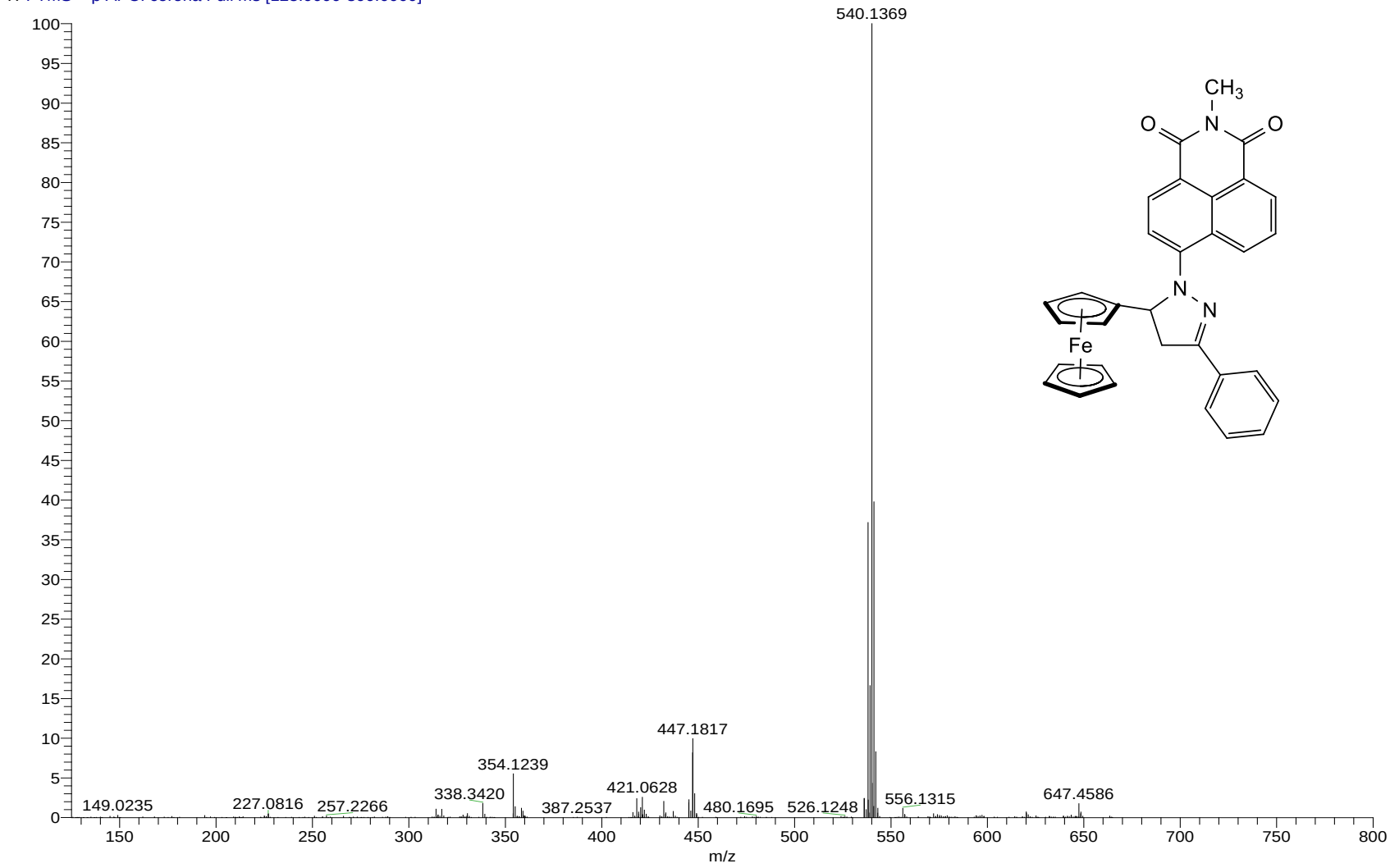

Fig. S12 HRMS of **3** by ESI-TOF.

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
540.1369	540.1374	-0.5	0.008	21.5	-	C32H26N3O2Fe

Fig. S13 Molecule **1** at 10^{-6} M in different solvents irradiated with a 365 nm UV-lamp. From left to right: hexane, carbon tetrachloride, benzene, chloroform, octan-1-ol and pyridine.

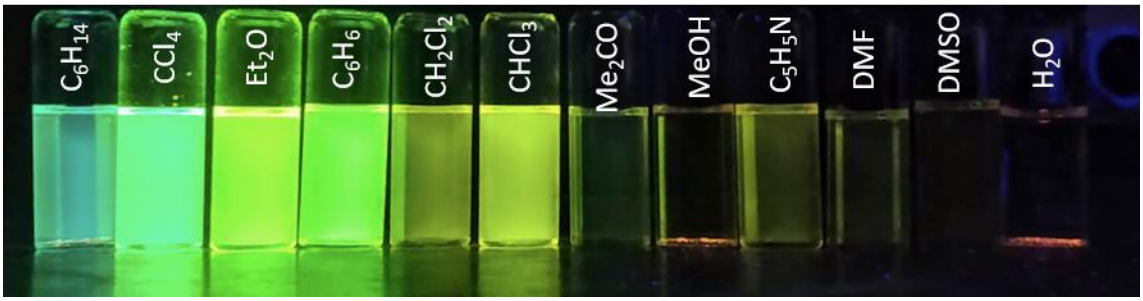

Fig. S14 Molecule **2** at 10^{-6} M in various solvents under a 365 nm UV-lamp. From left to right: hexane, carbon tetrachloride, diethyl ether, benzene, dichloromethane, chloroform, acetone, methanol, pyridine, *N*,*N*-dimethylformamide, dimethylsulfoxide and water. Note undissolved solid in methanol and water.

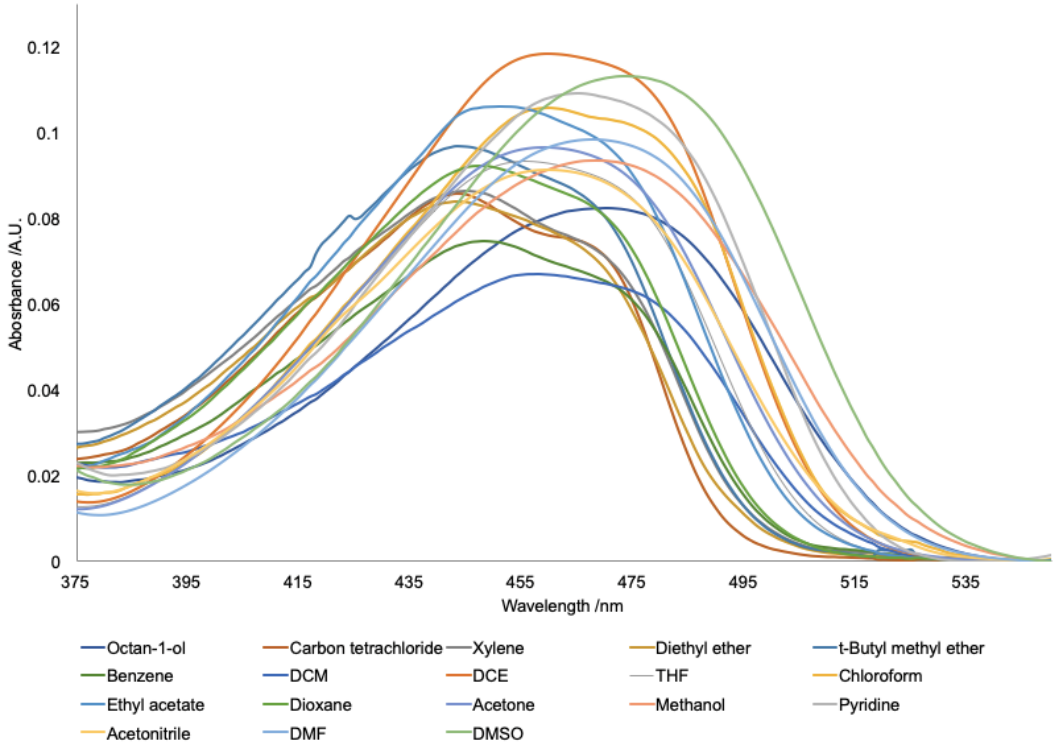

Fig. S15 UV-Vis absorption spectra of **1** at 10^{-6} M.

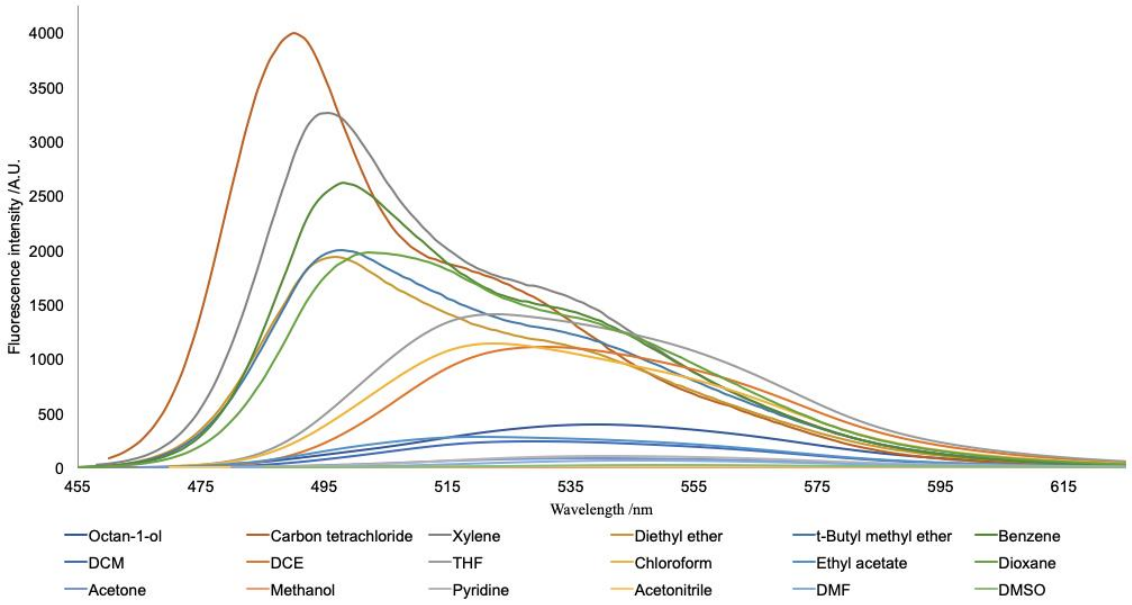

Fig. S16 Fluorescence emission spectra of **1** at 10^{-6} M excited at each respective λ_{max}.

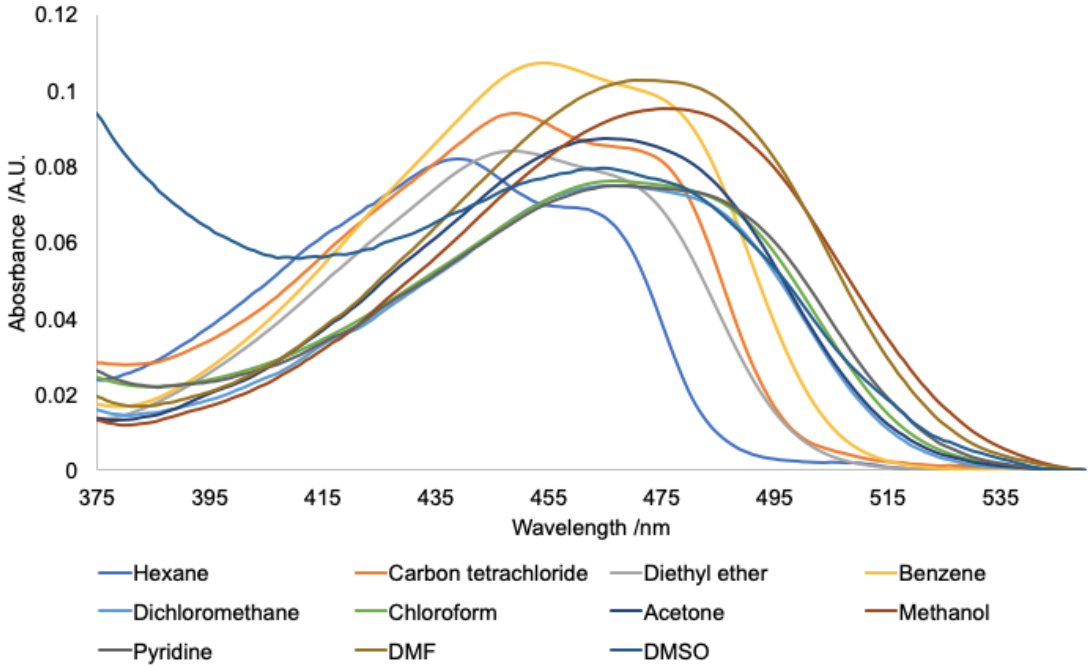

Fig. S17 UV-Vis absorption spectra of **2** at 10^{-6} M.

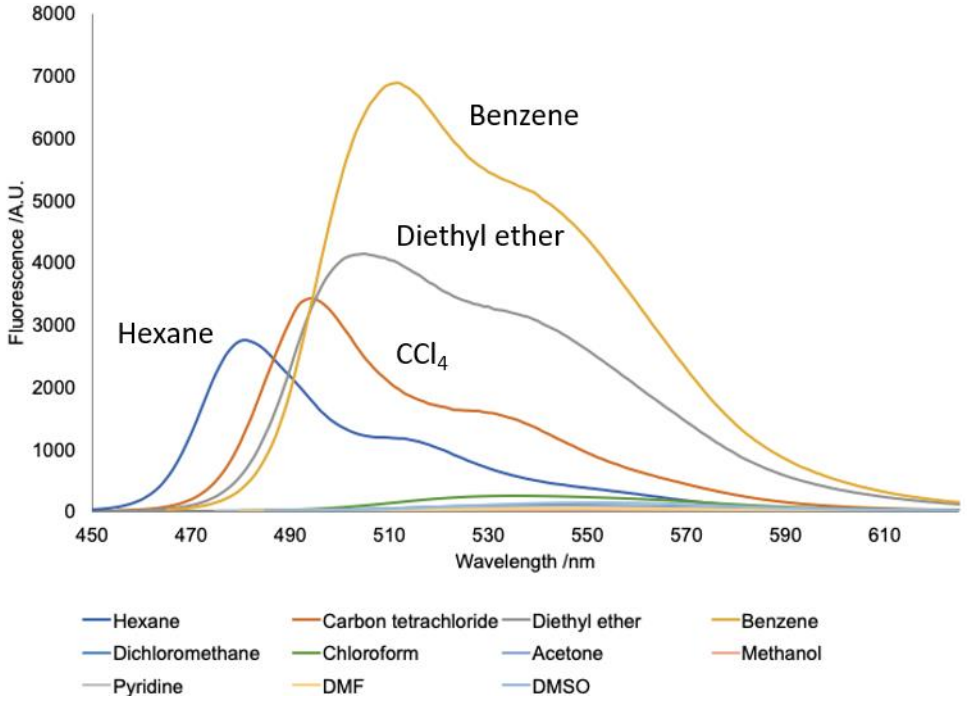

Fig. S18 Emission spectra of **2** at 10^{-6} M. Each solution was excited at its respective λ_{max}. Solutions of **2** in acetone, methanol, pyridine, DMF and DMSO are non-fluorescent. Solution concentrations varied.

Fig. S19 Solid samples of **1** (left) and **2** (right) irradiated with a 365 nm UV lamp.

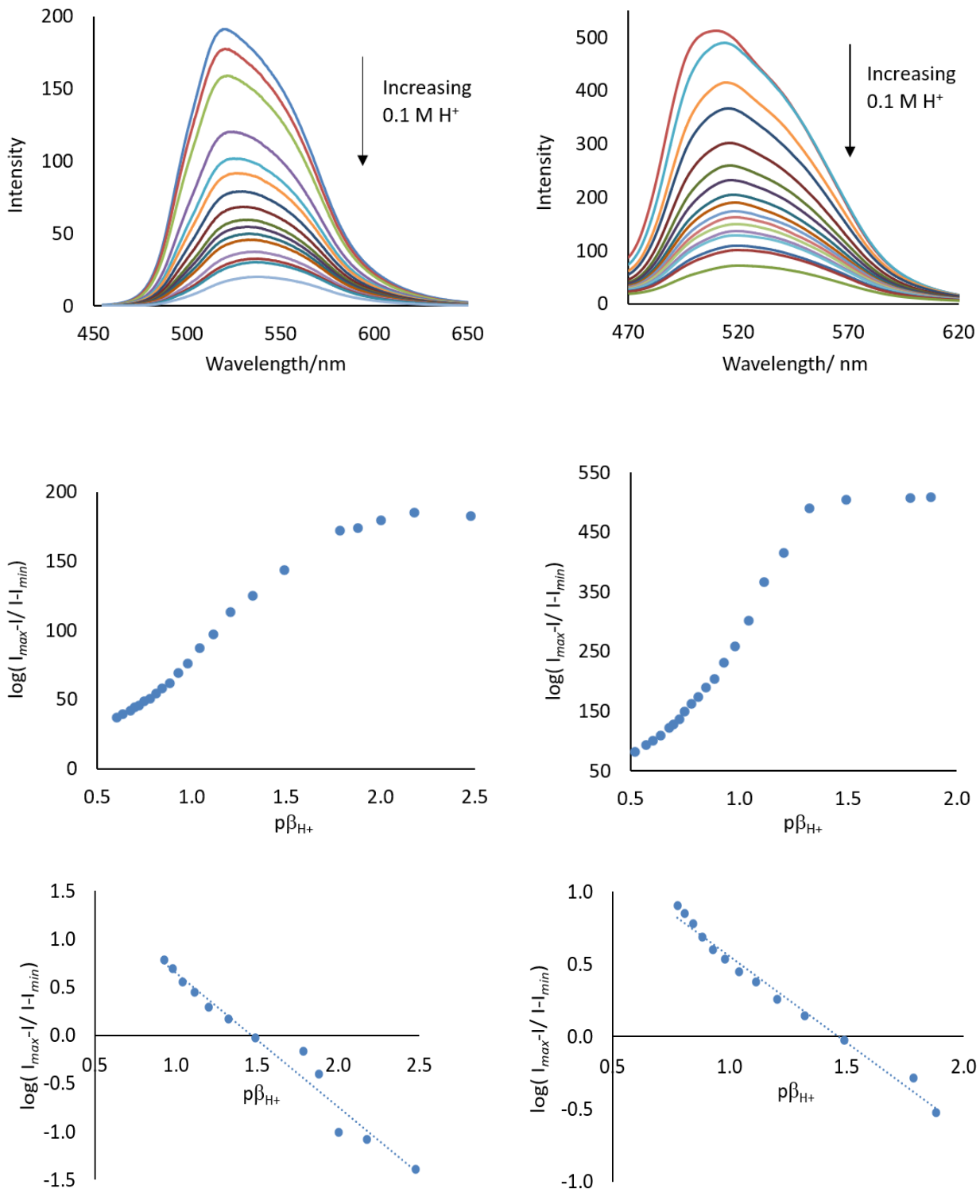

Fig.S20 Fluorescence spectra of 10 μM **1** in THF titrated with 1 mM HCl solution excited at 440 nm (top). Titration curves from the peak intensity (middle). Linearized Henderson-Hasselbalch plots (bottom).

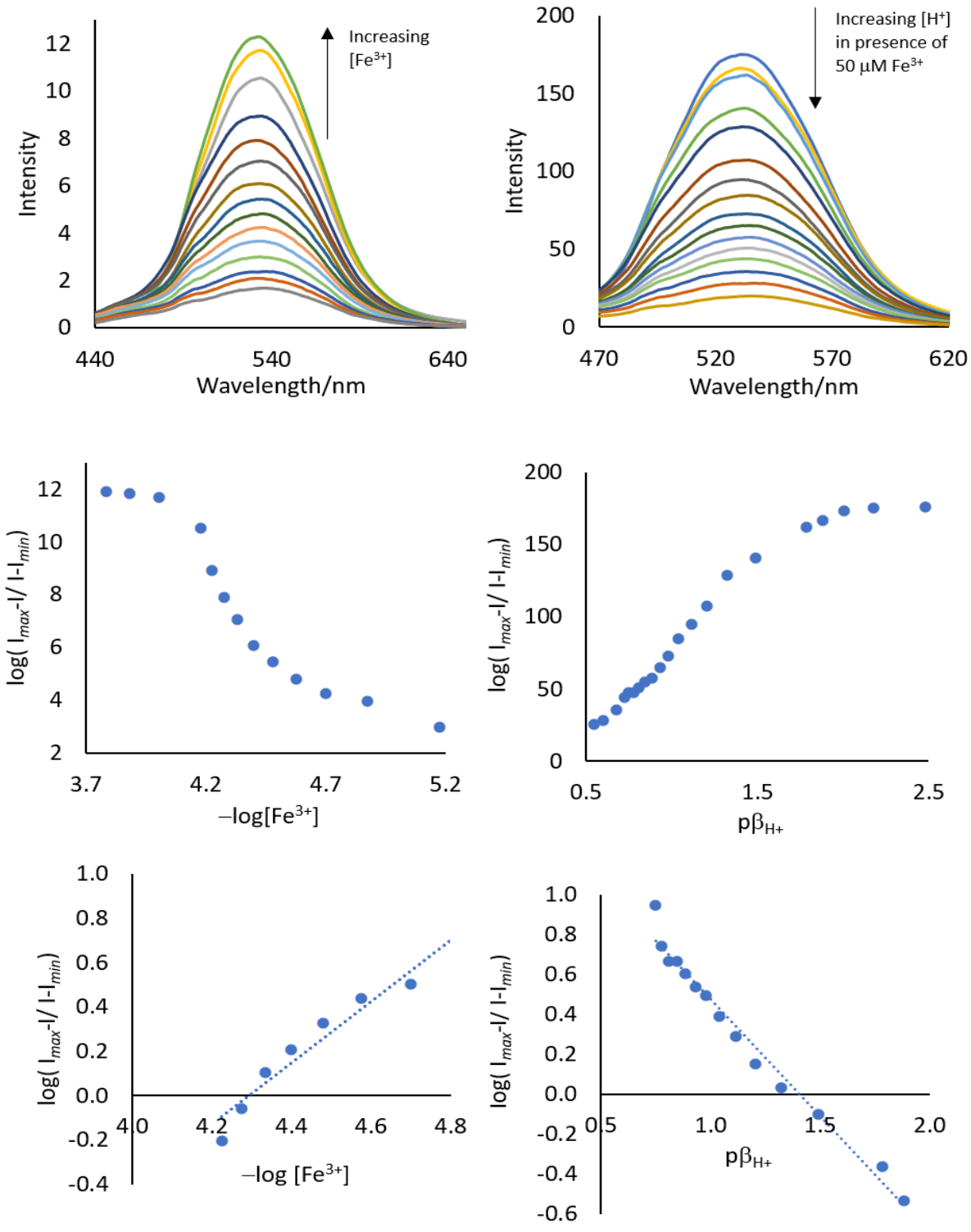

Fig.S21 Fluorescence spectra of 10 µM **3** in THF titrated with HCl solution and then with Fe^{3+} excited at 440 nm (top). Titration curves from the peak intensity (middle). Linearized Henderson-Hasselbalch plots (bottom).

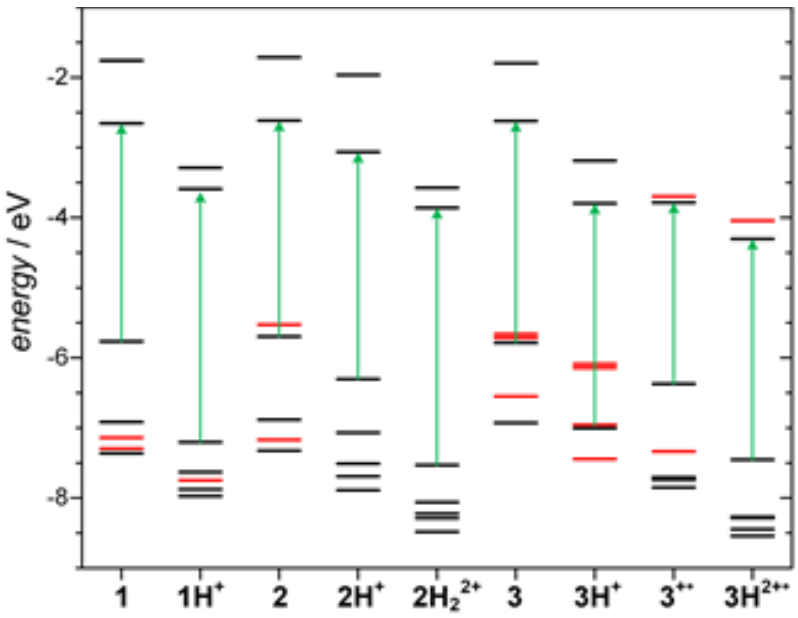

Fig. S22 Energy level HOMO-LUMO diagrams for **1**–**3** and their charged derivatives calculated at the B3LYP/6-31+g(d,p) level of theory with the IEFPCM solvent model for THF. Black lines indicate energy levels associated with the naphthalimide-pyrazoline framework, whereas the red lines with the 5-substituent (dimethylaniline or ferrocene). Green arrows indicate the lowest energy transition associated with the naphthalimide-pyrazoline chromophore. See Table S4 for energy level values.

Table S1. Summary of selected photophysical properties of **1** in various solvents.

Solvent	Δf	λ_{abs} /nm	ν_{abs} /cm^{-1}	λ_{flu} /nm	ν_{flu} /cm^{-1}	$\Delta\lambda$ /nm	$\Delta\nu$ /cm^{-1}	ε	η	Φ_F
Hexane	0.000	430	232558	474	210970	44	21588	1.88	1.3749	0.36
Benzene	0.003	449	222717	498	200803	49	21914	2.28	1.5011	0.60
Carbon tetrachloride	0.011	451	221729	490	204082	49	17648	2.24	1.4600	0.61
Chloroform	0.149	459	217865	523	191205	64	26660	4.81	1.4458	0.20
Diethyl ether	0.167	444	225225	497	201207	53	24018	4.33	1.3530	0.47
Ethyl acetate	0.200	454	220264	520	192308	66	27957	6.08	1.3720	0.13
Tetrahydrofuran	0.210	457	218818	522	191571	65	27247	7.60	1.4072	0.08
Pyridine	0.212	466	214592	541	184843	75	29749	12.4	1.5093	0.06
Dichloromethane	0.219	459	217865	529	189036	70	28829	9.08	1.4241	0.09
Octan-1-ol	0.226	469	213220	540	185185	71	28034	10.3	1.4290	0.26
Dimethylsulfoxide	0.265	475	210526	550	181818	75	28708	48.9	1.4790	0.01
Dimethylformamide	0.275	468	213675	546	183150	78	30525	37.6	1.4305	0.01
Acetone	0.284	458	218341	539	185529	81	32812	20.7	1.3588	0.01
Acetonitrile	0.306	459	217865	537	186220	78	31645	38.8	1.3441	0.01
Methanol	0.309	470	212766	548	182482	78	30284	33.6	1.3284	0.00

Notations: orientation polarizability, Δf; dielectric constant, ε; refractive index, n; absorption wavelength, λ_{abs} ; absorption wavenumber, $\nu_{abs} = 1/\lambda_{abs}$; emission wavelength, λ_{flu}; emission wavenumber, $\nu_{flu} = 1/\lambda_{flu;}$ Φ_F = fluorescence quantum yield.

Table S2. Summary of selected photophysical properties of **2** in various solvents.

Solvent	Δf	λ_{abs} /nm	ν_{abs} /cm^{-1}	λ_{flu} /nm	ν_{flu} /cm^{-1}	$\Delta\lambda$ /nm	$\Delta\nu$ /cm^{-1}	ε	η
Hexane	0.000	438	228311	482	207469	43	20842	1.88	1.3749
Carbon tetrachloride	0.011	440	227273	494	202429	54	24844	2.24	1.4600
Diethyl ether	0.167	450	222222	505	198020	55	24202	4.33	1.3530
Benzene	0.003	454	220264	511	195695	56	24570	2.28	1.5011
Dichloromethane	0.219	463	215983	540	185185	76	30798	9.08	1.4241
Tetrahydrofuran	0.210	454	220264	510	196078	56	24186	7.60	1.4072
Chloroform	0.149	470	212766	534	187266	64	25500	4.81	1.4458
Acetone	0.284	464	215517	541	184843	77	30674	20.7	1.3588
Methanol	0.309	474	210970	541	184843	67	26128	33.6	1.3284
Pyridine	0.212	464	215517	542	184502	78	31015	12.4	1.5093
Dimethylformamide	0.275	472	211864	547	182815	75	29049	37.6	1.4305
Dimethylsulfoxide	0.265	478	209205	554	180505	76	28700	48.9	1.4790

Notations: orientation polarizability, Δf; dielectric constant, ε; refractive index, n; absorption wavelength, λ_{abs}; absorption wavenumber, $\nu_{abs} = 1/\lambda_{abs}$; emission wavelength, λ_{flu}; emission wavenumber, $\nu_{flu} = 1/\lambda_{flu;}$

Table S3. Frontier orbitals calculated for molecules **1**–**3** and their corresponding protonated and oxidized forms at the B3LYP/6-31+g(d,p) level of theory.

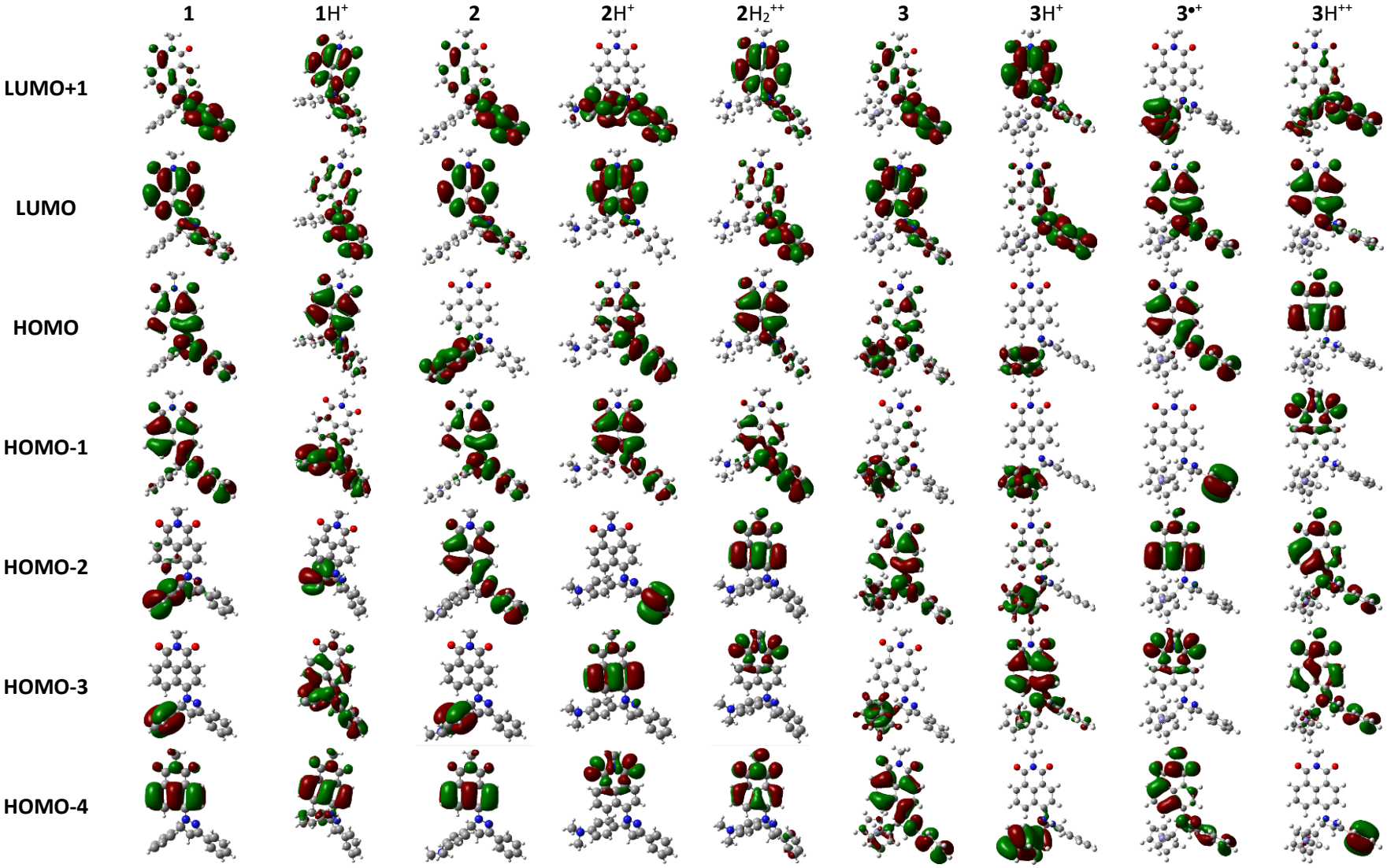

Table S4. Energies (in eV) of electronic levels of **1**–**3** and their charged derivatives as calculated at B3LYP/6-31+g level of theory with the IEFPCM solvent model for THF. The highest occupied and the lowest unoccupied orbitals for the naphthalimide-pyrazoline system (i.e. the levels engaged in the lowest energy electronic transition) are marked in blue, whereas orbitals associated with the substituent (quencher) are marked in red. $\Delta_{HOMO\text{-}LUMO}$ stands for the energy gap between the highest occupied and the lowest unoccupied orbitals of the chromophore.

	1	**1H$^+$**	**2**	**2H$^+$**	**2H$_2^{++}$**	**3**	**3H$^+$**	**3$^{+\bullet}$**	**3H$^{2+\bullet}$**
LUMO+1	-1.76	-3.29	-1.71	-1.96	-3.57	-1.80	-3.19	-3.70	-4.04
LUMO	-2.65	-3.59	-2.61	-3.06	-3.86	-2.62	-3.80	-3.78	-4.30
HOMO	-5.77	-7.21	-5.53	-6.30	-7.53	-5.67	-6.12	-6.37	-7.45
HOMO-1	-6.92	-7.63	-5.70	-7.07	-8.06	-5.72	-6.14	-7.33	-8.27
HOMO-2	-7.17	-7.75	-6.88	-7.51	-8.22	-5.76	-6.98	-7.70	-8.29
HOMO-3	-7.33	-7.88	-7.17	-7.69	-8.29	-6.55	-7.00	-7.74	-8.44
HOMO-4	-7.36	-7.97	-7.33	-7.89	-8.48	-6.93	-7.44	-7.85	-8.54
$\Delta_{HOMO\text{-}LUMO}$	3.11	3.61	3.08	3.24	3.67	3.14	3.21	2.59	3.15