p-(1H-Phenanthro[9,10-*d*] imidazol-2-yl)-Substituted Calix[4]arene, a Deep Cavity for Guest Inclusion

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Supporting Information

Experimental Section

General. All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. Thin layer chromatography (TLC) was performed on Alugram Sil G/UV254-coated aluminum sheets (Macherey-Nagel) with detection by UV at 254/365 nm and / or with bromocresol green (1.4 mM in EtOH, 4% 0.1M NaOH). Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on Bruker AC-200 (^{1}H: 200 MHz; ^{13}C: 50 MHz), Bruker AC-300 and Bruker AMX-500 (^{1}H: 500 MHz; ^{13}C: 125 MHz) spectrometers at 298 K or indicated otherwise using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, br = broad. Mass spectra by electrospray ionization (ESI) were recorded on a HP1100MSD spectrometer and by MALDI-TOF method on a

REFLEX spectrometer using ditranol as matrix and fast atom bombardment ionization (FAB) on a VG-autospec spectometer using *m*-nitrobenzyl alcohol as matrix. Elemental analyses were performed on a LECO CHNS 932 micro-analyser. 5,11,17,23-tetraformyl-25,26,27,28-tetrapropoxycalix[4]arene (**4)** was synthesized as described in the literature. For reasons of clarity and in order to reduce space, the name calix[4]arene was used instead of the original IUPAC name: pentacyclo[19.3.1.13,7.19,13. 115,19]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecane.

5,11,17,23-Tetrakis(1H-phenanthro[9,10-*d*]imidazol-2-yl)-25,26,27,28-tetrapropoxycalix[4] arene (2). A mixture of **4** (300 mg, 0.425 mmol), **3** (709 mg, 3.404 mmol) and ammonium acetate (5.24 g, 68.00 mmol) in glacial AcOH (39 mL) was refluxed for 7 h. The reaction was cooled to room temperature and the yellow precipitate was collected by filtration, subsequently washed with AcOH, 10% aq Na_2CO_3 and water and dried under vacuum at 130ºC, affording **1** (400 mg, 65%) as a pale yellow solid, m. p. > 315ºC. ^{1}H NMR (ROESY) (500 MHz, [D_6]-DMSO): δ 13.18 (s, 4 H, NH), 8.68 (d, *J* = 8.5 Hz, 4 H, Hd), 8.65 (d, *J* = 8.5 Hz, 4 H, He), 8.47 (d, *J* = 7.5 Hz, 4 H, Ha), 8.36 (d, *J* = 8.1 Hz, 4 H, Hh), 8.05 (s, 8 H, Hi), 7.53 (t, *J* = 7 Hz, 4 H, Hg), 7.47 (m, 12 H, Hb, Hc, Hf), 4.71 (d, *J* = 12 Hz, 4 H, CH_{ax}), 4.10 (t, *J* = 7.2 Hz, 8 H, OCH_2), 3.69 (d, *J* = 12 Hz, 4 H, CH_{eq}), 2.13 (h, *J* = 7.2 Hz, 8 H, CH_2), 1.10 (t, *J* = 7.2 Hz, 12 H, CH_3); ^{13}C NMR (DEPT) (75 MHz, [D_6]-DMSO): δ 157.5 (C), 149.3 (Cimid.), 136.8, 135.1, 127.5 (C), 127.2, 126.8 (CH), 125.1 (C), 124.9, 123.9, 123.7 (CH), 122.4 (C), 121.9 (CH), 77.04 (CH_2O), 31.1 (CH_2), 23.0 (CH_2), 10.4 (CH_3); ESI-MS (180v, MeOH+ 0.1%TFA): *m/z* = 729.6 [$(M+2H)^{2+}$], 1458.7 [$(M+H)^+$]; MALDI-TOF MS (ditranol): *m/z* = 1458.7 [$(M+H)^+$]; elemental analysis calcd (%) for $C_{100}H_{80}N_8O_4 \cdot 5(H_2O)$: C 77.60, H 5.86, N 7.24; found: C 77.48, H 5.62, N 7.19.

2-(4-Methoxyphenyl)-1H-phenanthro[9,10-*d*]imidazole (5). A mixture of 4-methoxybenzaldehyde (175 μL, 1.44 mmol), **3** (300 mg, 1.44 mmol) and ammonium acetate (2.22 g, 28.08 mmol) in glacial AcOH (20 mL) was refluxed for 2 h. The solution was cooled to room temperature and poured into

ice/water (150 mL) and the white precipitate was collected by filtration and washed with water. The solid was purified by precipitation in MeOH/water and dried under vacuum, yielding **5** (253 mg, 54%) as a white solid, m. p. 126°C (dec.) ^{1}H NMR (200 MHz, [D_6]-DMSO): 8.83 (d, *J* = 7.8 Hz, 2 H, Hd), 8.56 (d, *J* = 7.8 Hz, 2 H, Ha), 8.26 (d, *J* = 8.6 Hz, 2 H, Hi), 7.73 (t, *J* = 7 Hz, 2 H, Hb), 7.61 (t, *J* = 7 Hz, 2 H, Hc), 7.17 (d, *J* = 8.6 Hz, 2 H, Hj), 3.86 (s, 3 H, OCH_3); ^{13}C NMR (50 MHz, [D_6]-DMSO): δ 160.4, 149.4, 136.4, 127.9, 127.6, 127.2, 125.2, 124.0, 123.0, 122.0, 115.2, 114.5, 55.5.

2-(4-Methoxyphenyl)-1-methylphenanthro[9,10-d]imidazole (6). A mixture of **5** (100 mg, 0.308 mmol) and NaH (60% on a dispersion oil, 25 mg, 0.616 mmol) in dry THF (12 mL) was heated for 30 min at 80ºC in a sealed tube. The mixture was cooled to room temperature and methyl iodide (38 μL, 0.616 mmol) was added. The reaction was stirred at room temperature for 24 h, 30% aq NH_3 (1 mL) was added and the mixture was stirred for 1 h and concentrated at reduced pressure. The residue was dissolved in $CHCl_3$/EtOH 6% (50 mL), washed with water (3×) and brine, dried (Na_2SO_4) and concentrated to dryness. The solid was triturated with Et_2O, filtered off and dried, giving **6** (68 mg, 65%) as a pale yellow solid, m. p. 176-177°C; ^{1}H NMR (COSY) (500 MHz, $CDCl_3$): δ 8.80 (m, 1 H, He), 8.78 (m, 1 H, Hd), 8.67 (d, *J* = 8 Hz, 1 H, Hh), 8.38 (m , 1 H, Ha), 7.72 (AA´BB´, *J* = 8.5 Hz, 2 H, Hi), 7.70 (m, 1H, Hf), 7.63-7.55 (m, 3 H, Hb, Hc, Hg), 7.06 (AA´BB´, *J* = 8.5 Hz, 2 H, Hj), 4.20 (s, 3 H, NMe), 3.88 (s, 3H, OMe); ^{13}C NMR (DEPT) (125 MHz, $CDCl_3$): δ160.6 (C), 152.6 (Cimid.), 137.3 (C), 131.3(CH), 129.0, 128.0, 127.5, 127.3 (C), 127.2, 126.6, 125.3, 124.7, 124.4 (CH), 123.4 (C), 123.1, 122.6, 120.6, 114.2 (CH), 55.4 (OMe), 36.1 (NMe); FAB^{+} MS (m-NBA): *m/z* = 339.2 [$(M+H)^{+}$]

The crystallographic data were recorded on a Nonius Kappa CCD diffractometer. The structure was solved using direct methods (SHELXS-97) and the refinement was made by full matrix least-squares techniques (SHELXL-97). No absorption correction was performed.

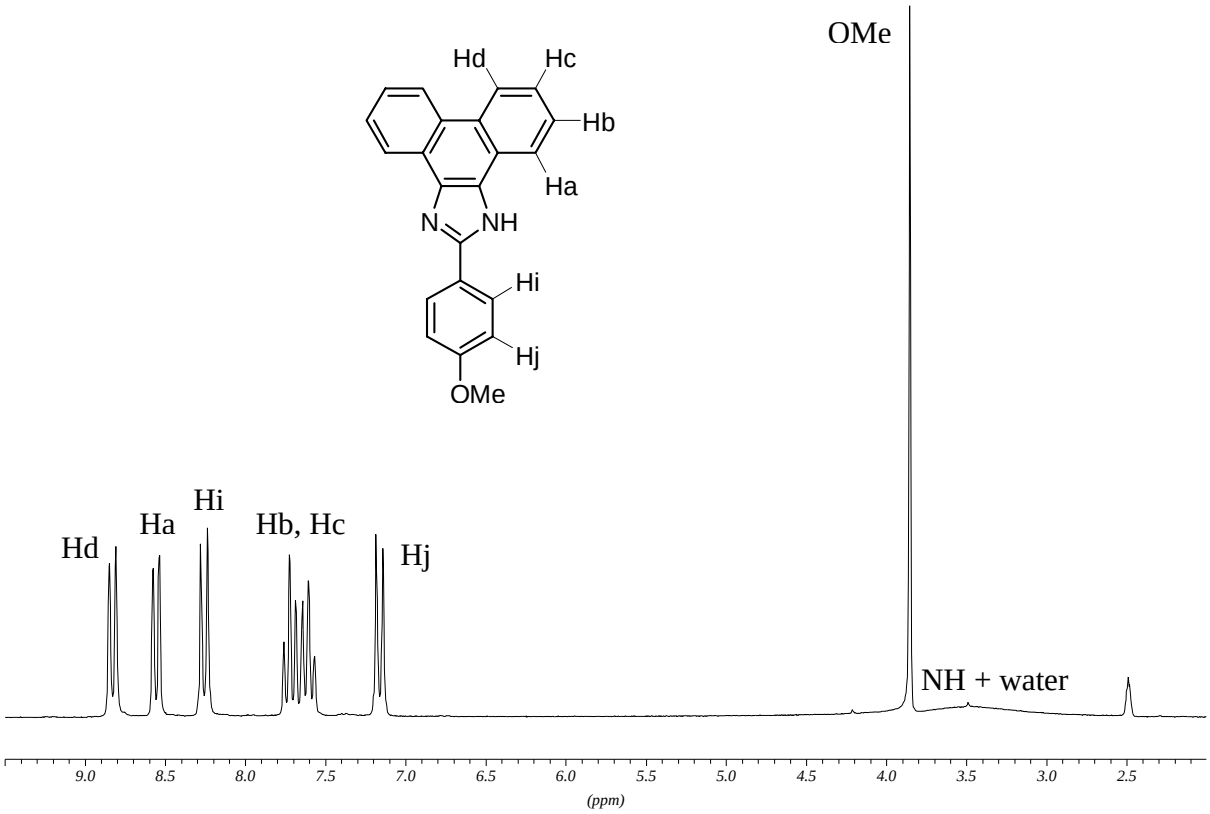
Crystal data and structure refinement for **7**.

Empirical formula	C111 H83 Cl4 F9 N8 O13
Formula weight	2049.65
Temperature	123(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	P-1 No.2
Unit cell dimensions	a = 14.7972(2) Å alpha = 97.406(1) deg.
	b = 16.9446(3) Å beta = 106.599(1) deg.
	c = 22.5701(3) Å gamma = 109.447(1) deg.
Volume	4954.22(13) $Å^3$
Z	2
Density (calculated)	1.374 Mg/m^3
Absorption coefficient	0.205 mm^{-1}
F(000)	2116
Crystal size	0.40 x 0.30 x 0.15 mm
Theta range for data collection	2.92 to 24.71 º
Index ranges	-17<=h<=17, -19<=k<=19, -26<=l<=26
Reflections collected	32705
Independent reflections	16844 [R(int) = 0.0409]

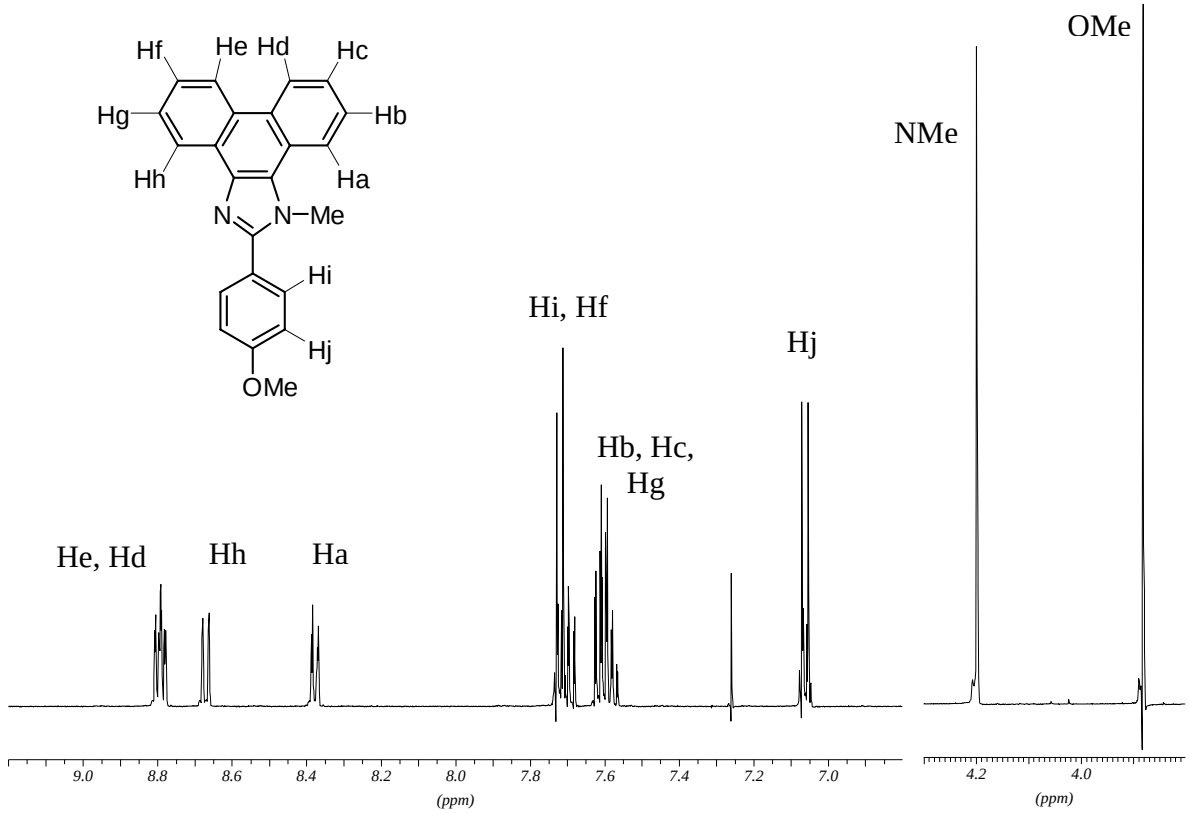
Completeness to theta = 25.70 º	99.8 %
Max. and min. transmission	0.9224 and 0.9699
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	16844 / 37 / 1298
Goodness-of-fit on F2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.1021, wR2 = 0.2687
R indices (all data)	R1 = 0.1468, wR2 = 0.3044
Largest diff. peak and hole	1.332 and -1.628 e.Å^{-3} [a]

[a] The large remaining electron density is due to rotational disorder of the trifluoromethyl end of the TFA molecule

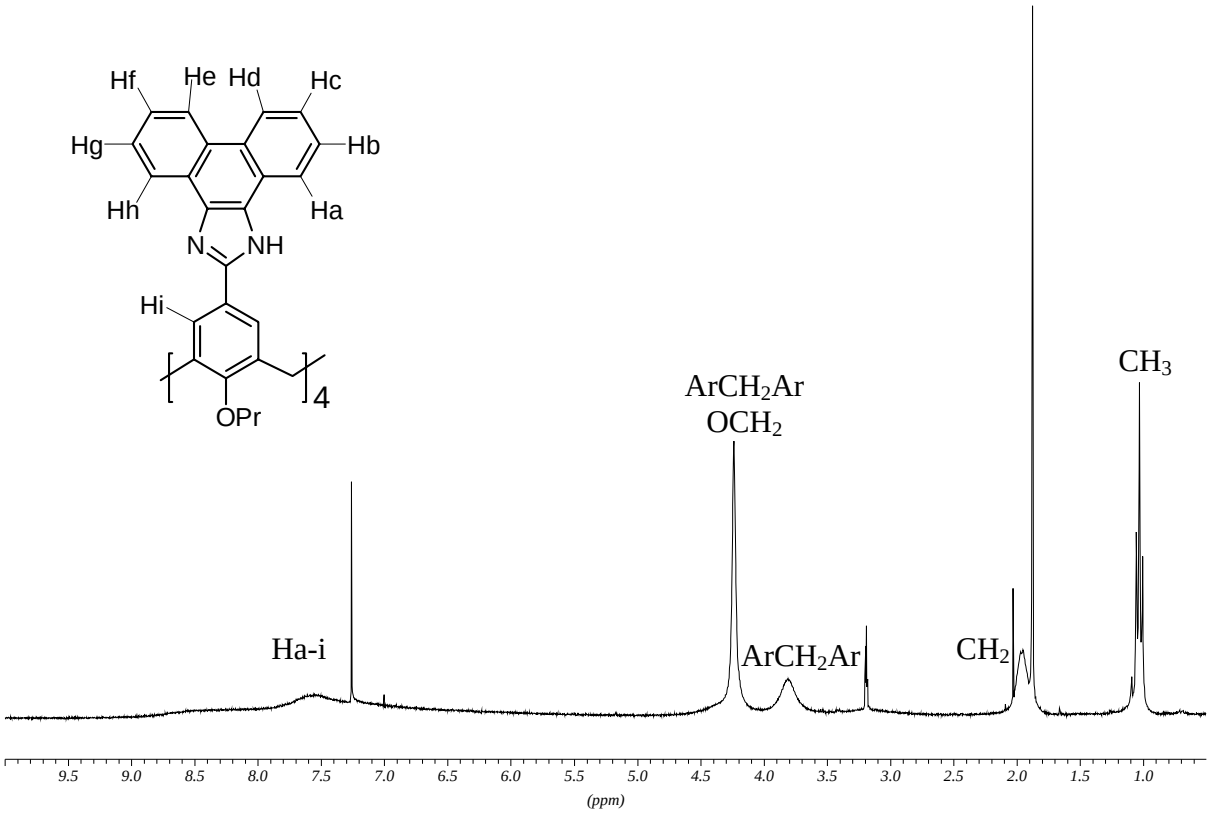
^{1}H NMR spectrum (DMSO-d_6, 200 MHz, 298K) of compound **5** (2.00-9.50 ppm)



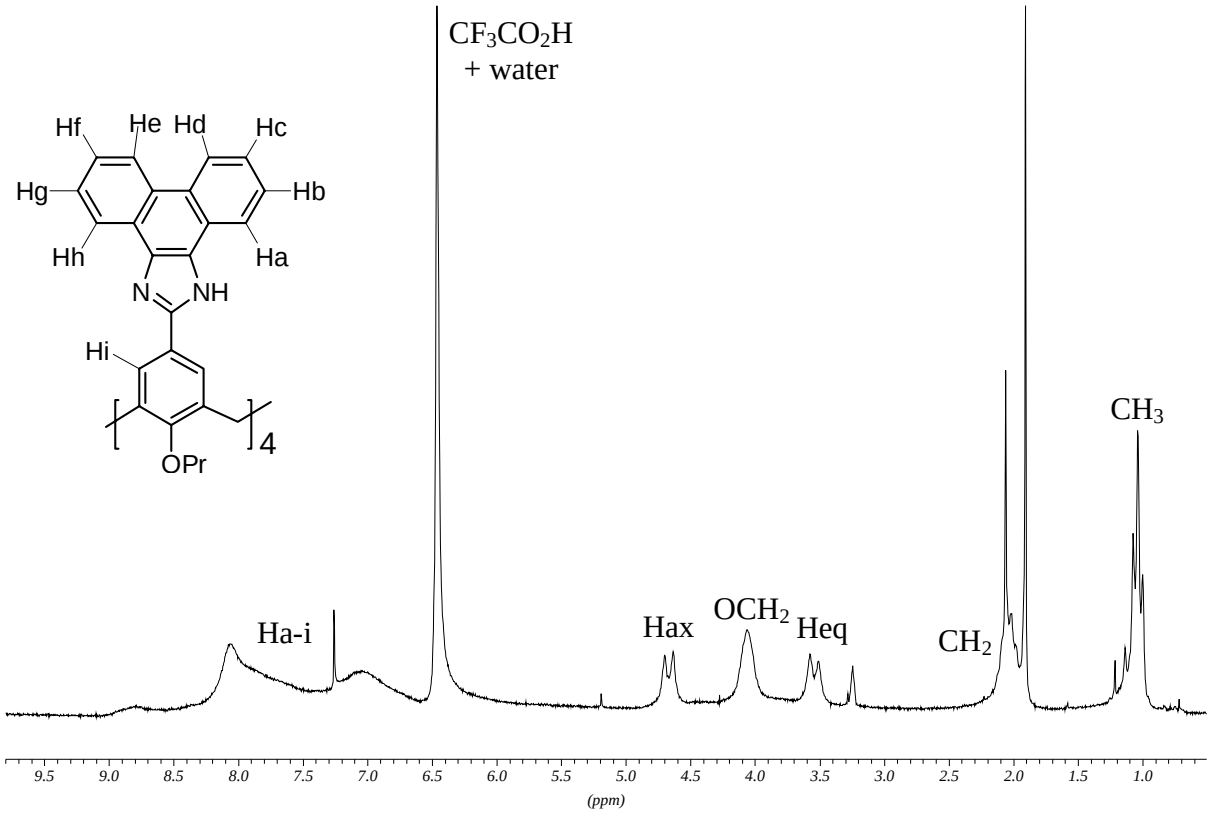
^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298K) of compound **6** (6.80-9.20 ppm) (3.80-4.30 ppm)



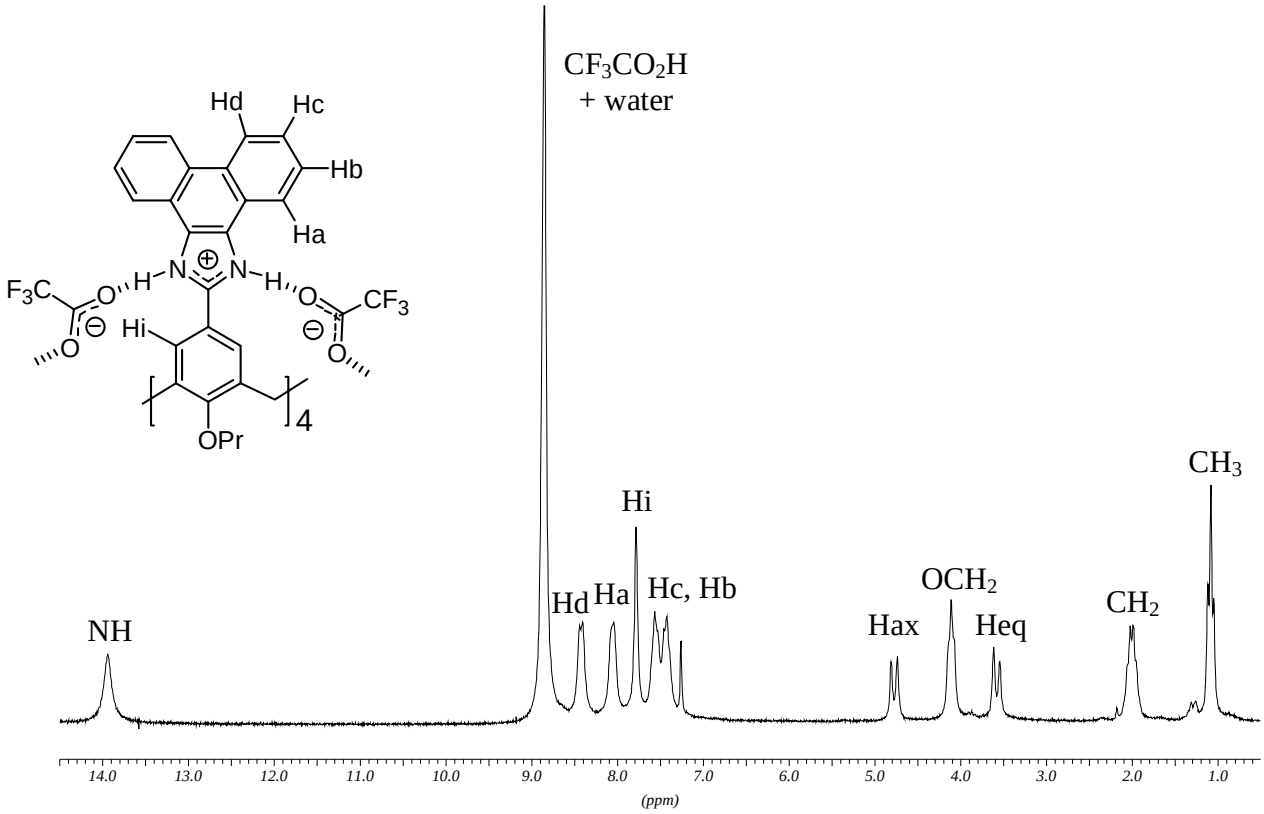
^{1}H NMR spectrum ($CDCl_3$/MeOD, 300 MHz, 298K) of compound **2** (0.50-10.00 ppm)



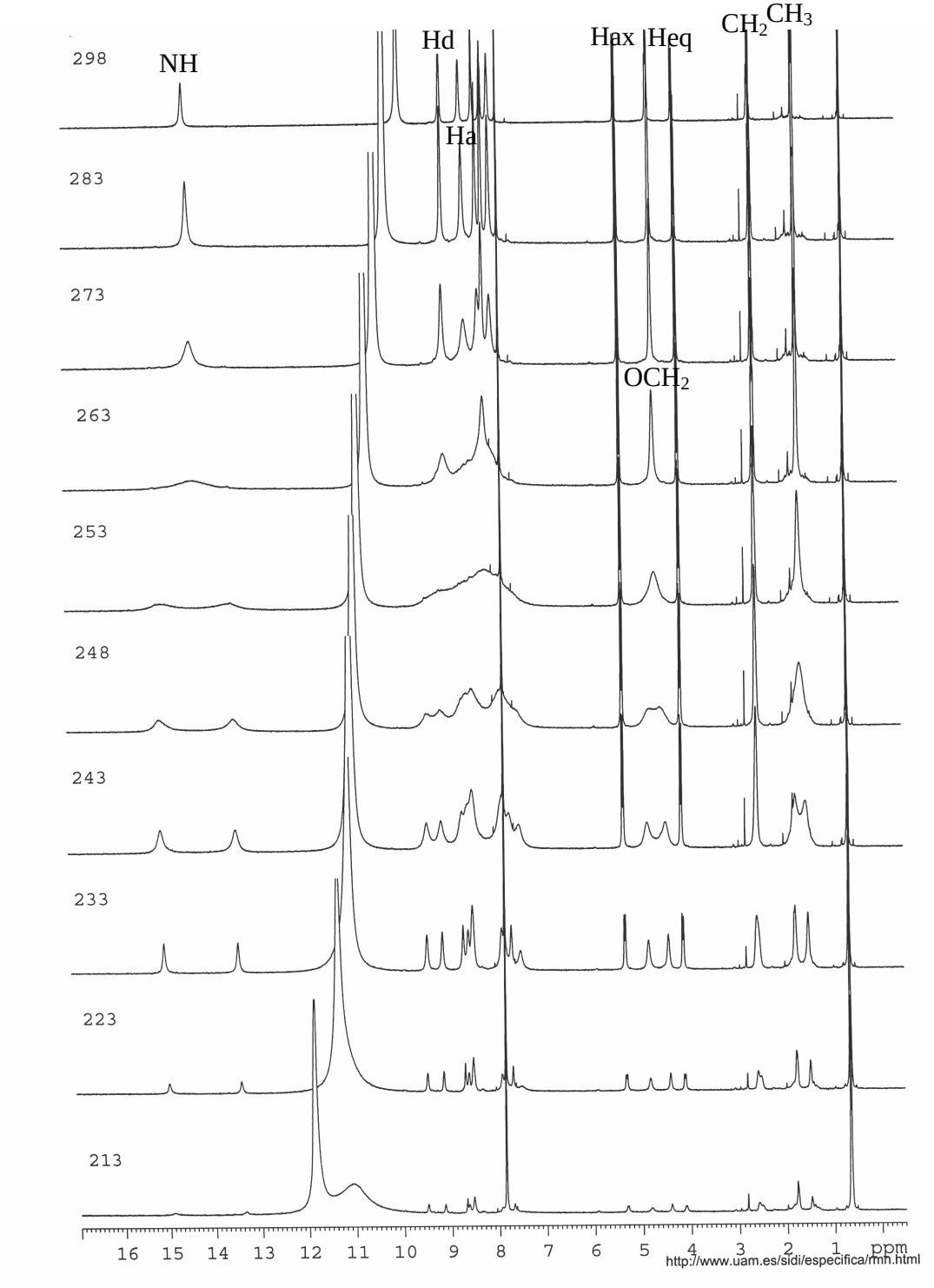
^{1}H NMR spectrum ($CDCl_3$/MeOD/TFA-*d*, 200 MHz, 298K) of compound **2** (0.50-10.00 ppm)



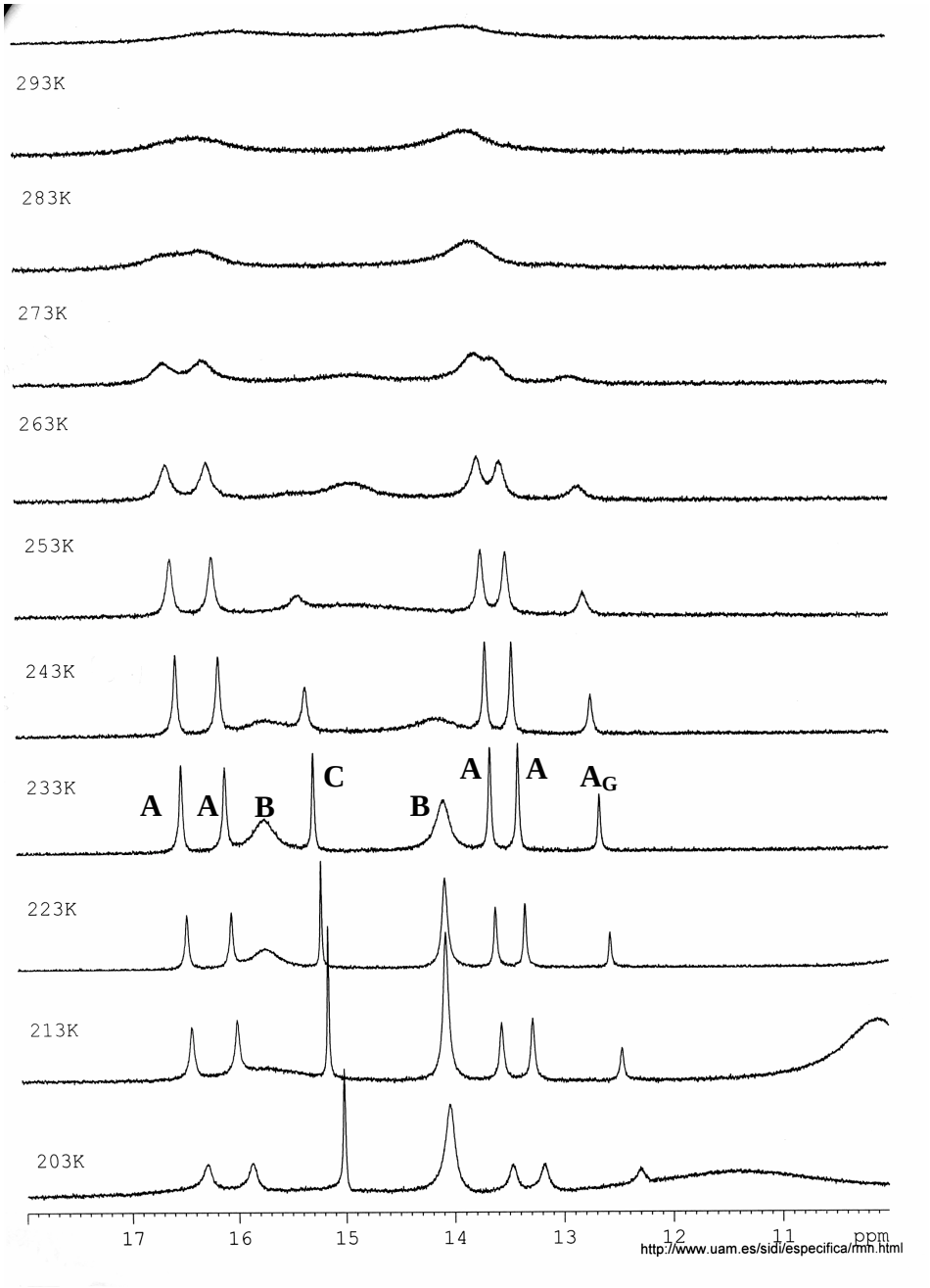
^{1}H NMR spectrum ($CDCl_3$ + TFA, 200 MHz, 298K) of compound **2** (0.50-14.50 ppm)



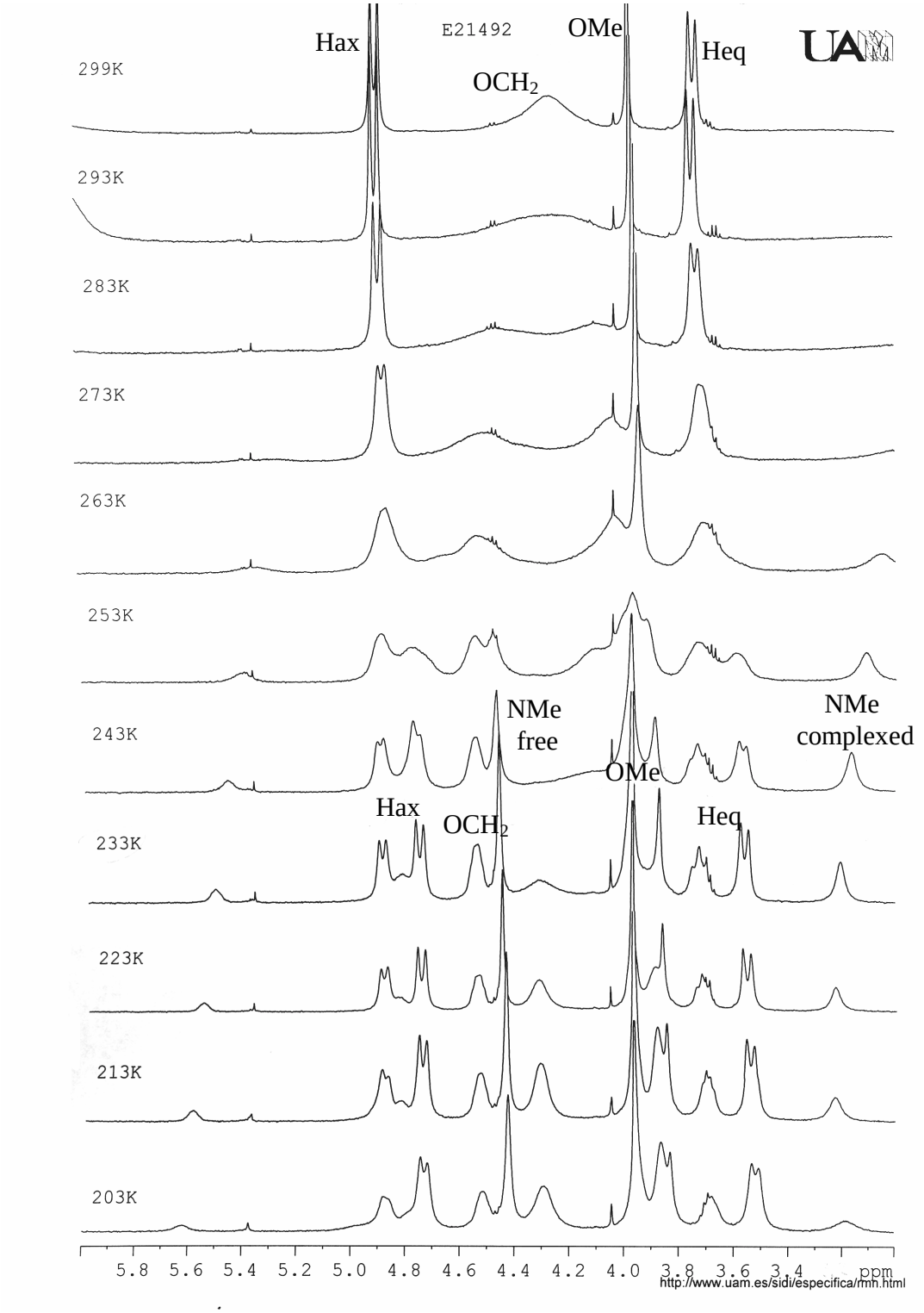
VT-^{1}H NMR spectra ($CDCl_3$ + TFA, 500 MHz) of compound **2** (0-16 ppm).



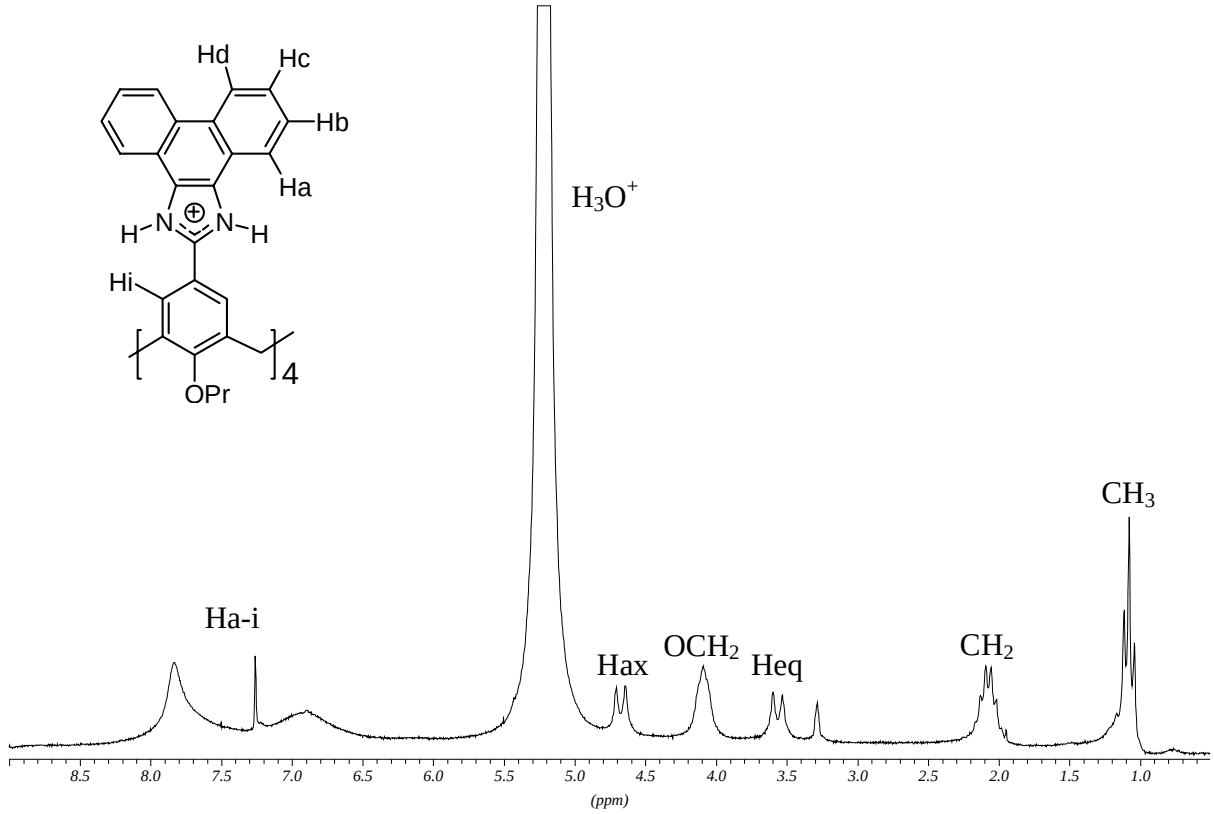
VT-^{1}H NMR spectra ($CDCl_3$ + TFA, 500 MHz) of a 1:1 mixture of compounds **2** and **6** (10-18 ppm). **A**: NHs signals of complexed **2** (*pinched cone*); $\mathbf{A_G}$: NH signal of complexed **6**; **B**: NH signal of free **2** (*pinched cone*); **C**: NH signal of free **6**.



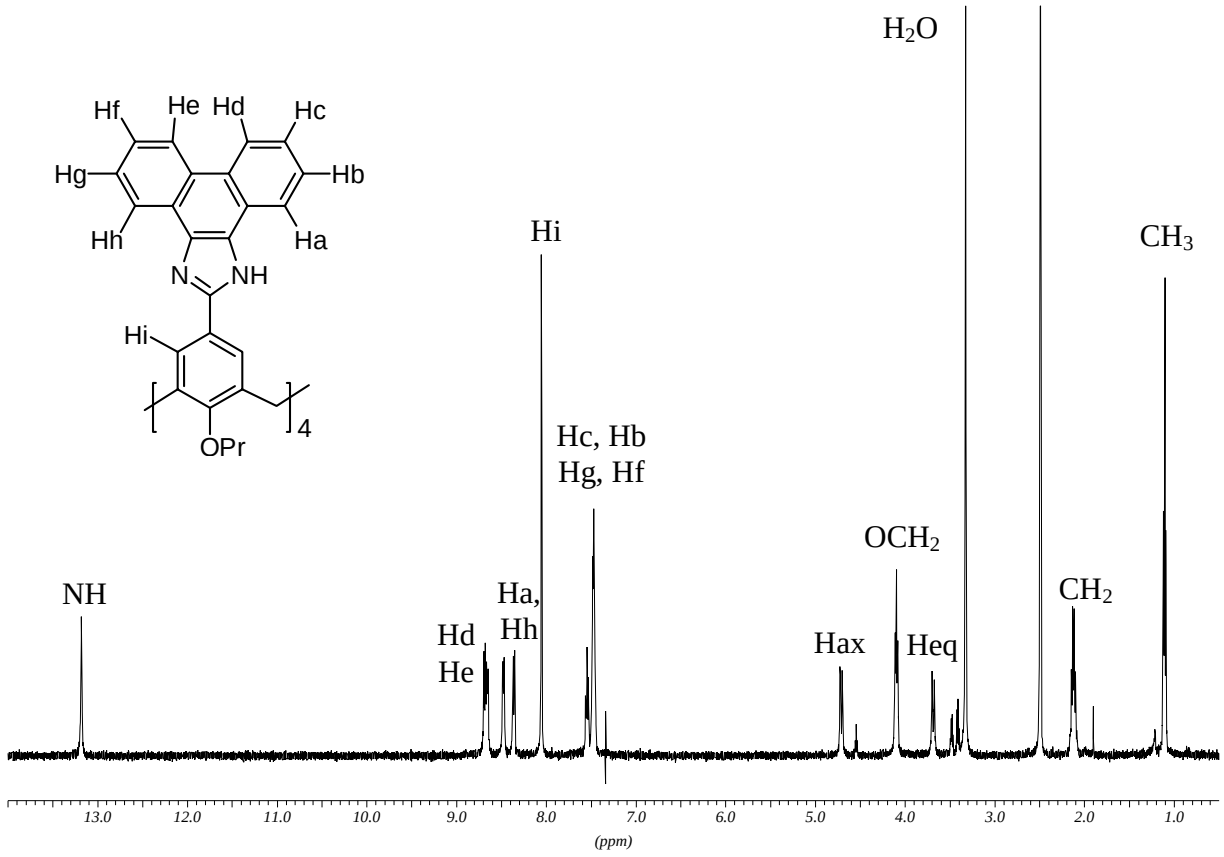
VT-^{1}H NMR spectra ($CDCl_3$ + TFA, 500 MHz) of a 1:1 mixture of compounds **2** and **6** (3-6 ppm).



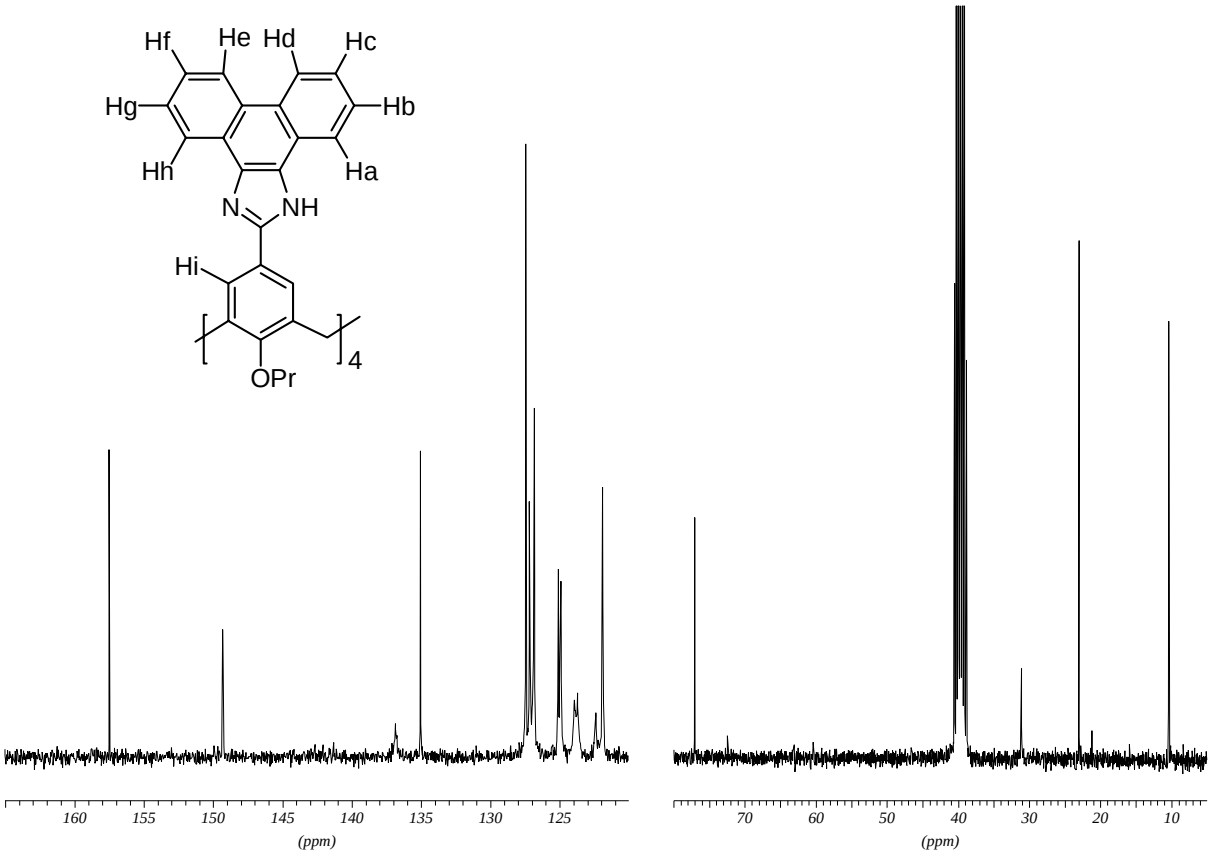
^{1}H NMR spectrum ($CDCl_3$/MeOD + 60% HNO_3, 200 MHz, 298K) of compound **2** (0.50-9.00 ppm)



^{1}H NMR spectrum (DMSO-d_6, 500 MHz, 298K) of compound **2** (0.50-14.00 ppm)



^{13}C NMR spectrum (DMSO-d_6, 75 MHz, 298K) of compound **2** (165-120 ppm) (80-5 ppm)



T-ROESY spectrum (DMSO-d_6, 500 MHz, 298K, mixing time 300 ms) of compound **2**