

# Expanding the registry of aromatic amide foldamers: folding and assembly using diaza- anthracene units.

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**General Procedures and Materials.** THF was distilled over sodium/benzophenone while  $\text{CH}_2\text{Cl}_2$  and N,N-diisopropylethylamine (DIEA) were distilled from  $\text{CaH}_2$  prior to use. 2,6-diaminopyridine (98%) was purified by recrystallization from boiling chloroform after filtration with charcoal. Silica gel chromatography was performed using Merck Kieselgel Si 60. 400 MHz  $^1\text{H}$  and 100 MHz  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm and are calibrated against residual  $^1\text{H}$  and  $^{13}\text{C}$  solvent signals of  $\text{CDCl}_3$  ( $\delta$  7.26, 77.2),  $\text{DMSO-d}_6$  ( $\delta$  2.50, 39.4), or  $\text{CD}_3\text{OD}$  ( $\delta$  3.31, 49.1). All coupling constants are reported in Hz. The following notation is used for the  $^1\text{H}$  NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m).

Electrospray ionization (ESI) and high resolution electrospray ionization time of flight (HR-ESI) mass spectra were obtained in the positive ion mode and matrix assisted laser desorption ionization time of flight (MALDI) mass spectra were obtained in positive ion mode using  $\alpha$ -cyanohydroxycinnamic acid as a matrix.

The solid state structures of monomers **2**, **3a** and **4a**, dimer **11**, pentamer **6**, macrocycle **7**, and octamer **10** were all characterized by single crystal X-ray diffraction analysis. The crystallographic data are summarized in Table 2.

Spectrofluorimetric measurements. Fluorescence emission spectra were recorded on dilute (abs <0.2 at 370 nm) samples that were degassed by repeated freeze-pump-thaw cycles and sealed. The fluorescence decay measurements were measured using a single-photon counting apparatus equipped with a hydrogen flash lamp and the data were deconvoluted using the Decan 1.0 program.<sup>1</sup> Photoreaction quantum yields were determined upon excitation at 360 nm using Aberchrome 540 as a chemical actinometer on an optical bench equipped with a 2000 W Hg-Xe lamp and a monochromator. Samples ( $2.5 \times 10^{-5}$  M) were stirred during the irradiation, and the amount of converted material was monitored at 10 min intervals by UV-vis spectroscopy by measuring the disappearance of the 1La band of anthracene at 370 nm until 90% of the starting material was converted. Solutions were allowed to stand for 2 min before measurement of the UVvis spectrum. The preparative photocyclization reactions were tried by irradiating degassed solutions of the pentamer **6** ( $2.5 \times 10^{-5}$  M) in benzene using a Hg lamp (400 W) and a  $\text{Pb}(\text{NO}_3)_2/\text{KBr}$  ( $7.0 \text{ g L}^{-1}/540 \text{ g L}^{-1}$ ) solution filter with stirring over a period of 12 h.

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(1) de Roek, T.; Boens, N.; Dockx, J. DECAN 1.0; Leuven, Belgium, 1991.

**Table S1.** Crystallographic parameters for compounds **2**, **3a**, **4a**, **6**, **7**, **10** and **11**.

Compound	<b>2</b>	<b>3a</b>	<b>4a</b>	<b>11</b>	<b>6</b>	<b>7</b>	<b>10</b>
Solvent/precipitant	nitrobenzene/CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub> /Heptane	nitrobenzene/CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub> /Heptane	CH <sub>2</sub> Cl <sub>2</sub> /Hexane	CH <sub>2</sub> Cl <sub>2</sub> /Hexane	Toluene/Hexane
Formula	C <sub>21</sub> H <sub>21</sub> N <sub>3</sub> O <sub>9</sub>	C <sub>35</sub> H <sub>50</sub> N <sub>2</sub> O <sub>6</sub>	C <sub>27</sub> H <sub>33</sub> N <sub>3</sub> O <sub>6</sub>	C <sub>35</sub> H <sub>50</sub> N <sub>2</sub> O <sub>6</sub>	C <sub>88</sub> H <sub>115</sub> N <sub>11</sub> O <sub>13</sub>	C <sub>76</sub> H <sub>98</sub> N <sub>10</sub> O <sub>8</sub>	C <sub>97.5</sub> H <sub>74</sub> N <sub>18</sub> O <sub>24.5</sub> Cl <sub>2.6</sub>
Aspect	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P21/n	P-1	P-1	P21/n	P-1	P21/n	C2/c
Z	4	1	2	4	2	4	8
Unit cell parameters							
a, Å	7.0804(10)	10.236(2)	7.10530(10)	12.722(4)	11.8350(10)	6.937(3)	31.540(6)
b, Å	10.7575(2)	11.502(3)	13.1643(2)	17.796(3)	14.8280(10)	24.3618(10)	24.658(5)
c, Å	25.6538(4)	16.042(4)	15.1583(3)	15.650(2)	24.2940(10)	43.7079(10)	30.770(6)
α, °	90	105.70(2)	71.8697(7)	90	82.560(10)	90	90
β, °	97.0277(7)	102.39(2)	81.2798(7)	107.430(10)	86.990(10)	94.102(10)	115.59(3)
γ, °	90	96.23(2)	86.5898(11)	90	78.870(10)	90	90
Temperature, K	423(2)	296(2)	296(2)	296(2)	180(2)	293(2)	173(2)
Volume, Å <sup>3</sup>	1939.3(3)	1747.7(7)	1331.77(4)	3380.5(13)	4146.3(5)	7368(3)	21582(7)
FW, g·mol <sup>-1</sup>	459.41	1189.54	495.56	594.77	1534.91	1279.64	2184.33
ρ, g·cm <sup>-3</sup>	1.573	1.130	1.236	1.169	1.229	1.154	1.345
λ, E	0.71073	1.54180	0.71073	1.54180	0.71073	1.54180	1.54180
θ measured	3.06≤θ≤26.37	4.06≤θ≤59.96	3.05≤θ≤26.37	3.86≤θ≤65.10	3.07≤θ≤26.37	6.36≤θ≤71.05	2.37≤θ≤50.43
Radiation	MoKα	CuKα	MoKα	CuKα	MoKα	CuKα	CuKα
Reflections measured	13417	5179	10640	5737	30355	58549	100264
Reflections unique	3932	5179	5423	5737	16672	11959	100264
GOF	1.060	1.045	1.036	1.040	1.039	1.088	2.141
R1 (I > 2σ(I))	0.0396	0.0854	0.0574	0.0601	0.0858	0.1031	0.3295
wR2 (all data)	0.1162	0.2793	0.2116	0.1799	0.2825	0.3651	0.6937

Chemical structure: COC(=O)c1nc2c(nc(=O)OC)c3cc(OC)c(OC)cc3n2c1

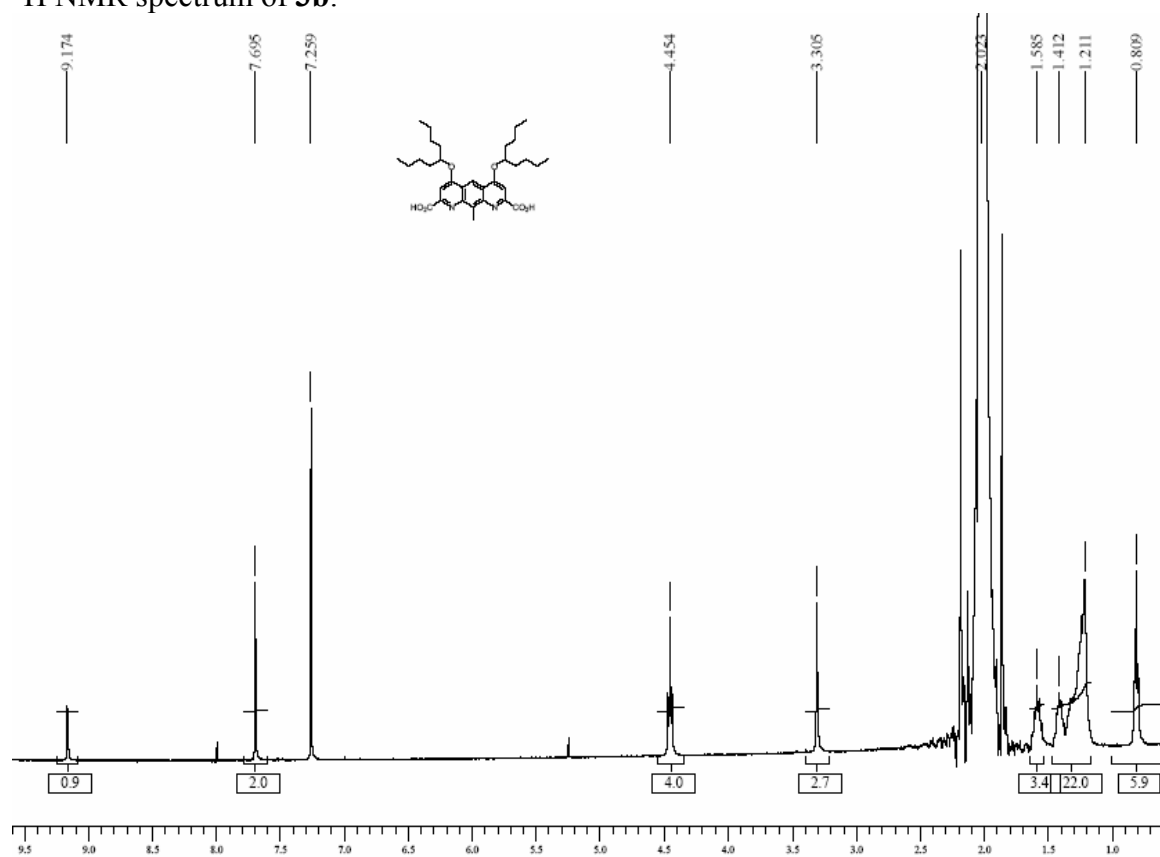
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) data:

Chemical Shift (ppm)	Integration
9.000	0.7
7.507	1.9
7.260	
4.191	6.5
4.098	3.2
3.489	3.0
1.624	
1.248	
-0.067	

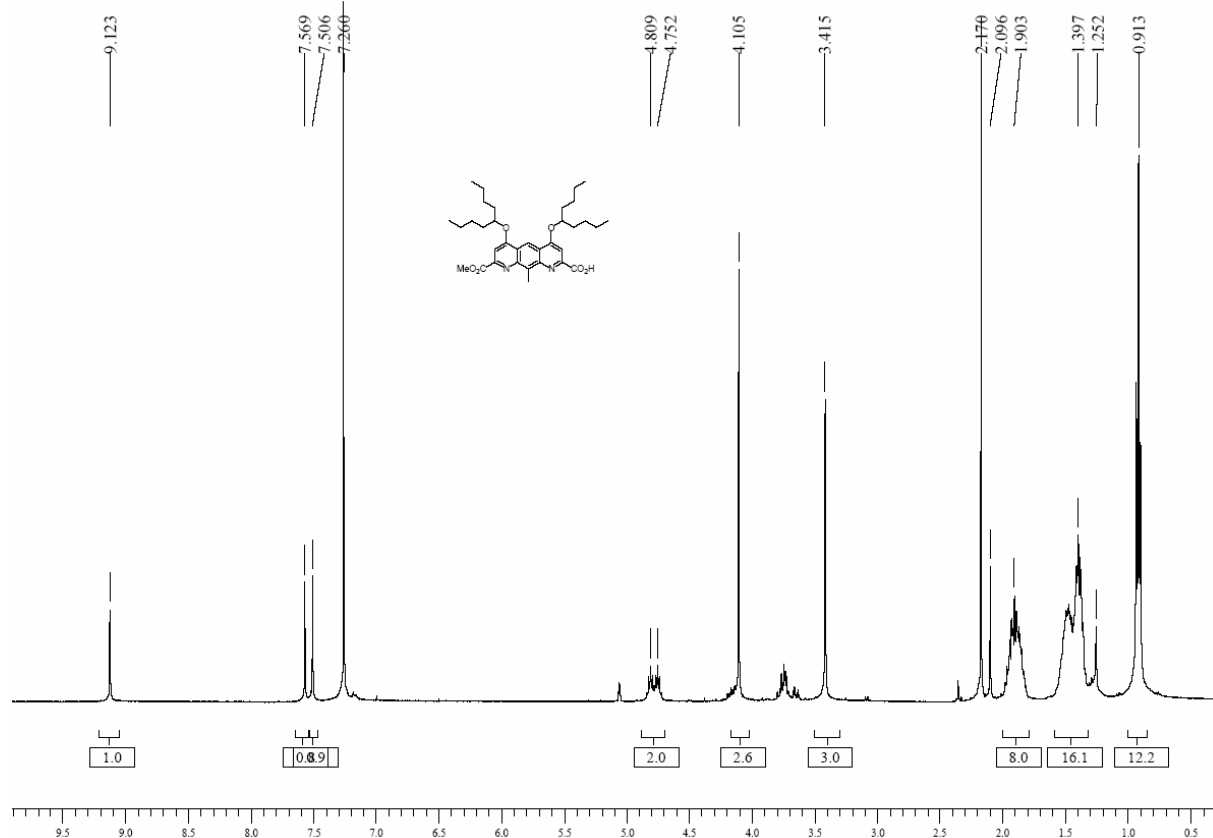
Chemical structure of **5a** is shown above the spectrum. The structure is a naphthalene derivative with two 4-oxopentyl groups at positions 1 and 8, and two methoxycarbonyl groups at positions 2 and 7.

<sup>1</sup>H NMR spectrum of **5a** in CDCl<sub>3</sub>. The spectrum shows peaks at 9.077, 7.483, 7.260, 4.740, 4.095, 3.493, 2.355, 1.897, 1.544, 1.489, 1.394, and 0.915 ppm. Integration values are 0.9, 1.8, 2.0, 5.9, 2.9, 8.0, 16.9, and 12.6.

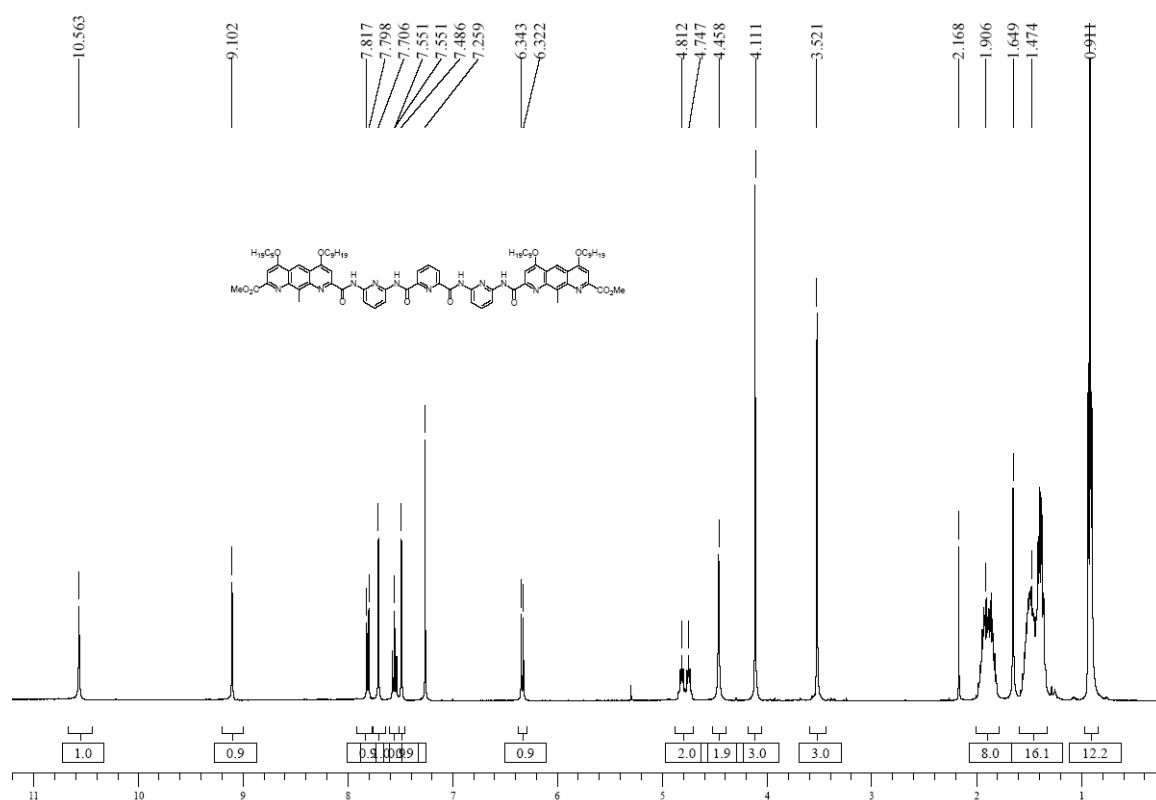
$^1\text{H}$  NMR spectrum of **3b**:



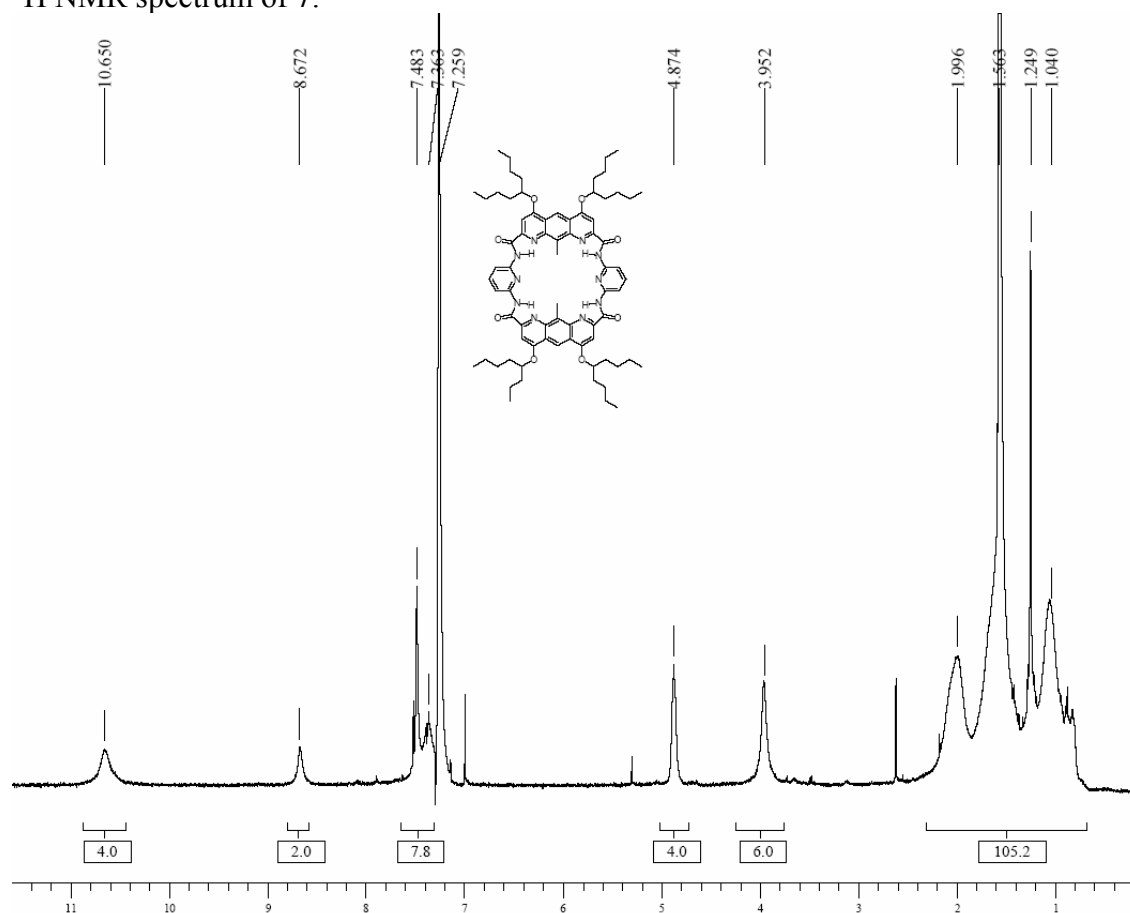
$^1\text{H}$  NMR spectrum of **3d**:



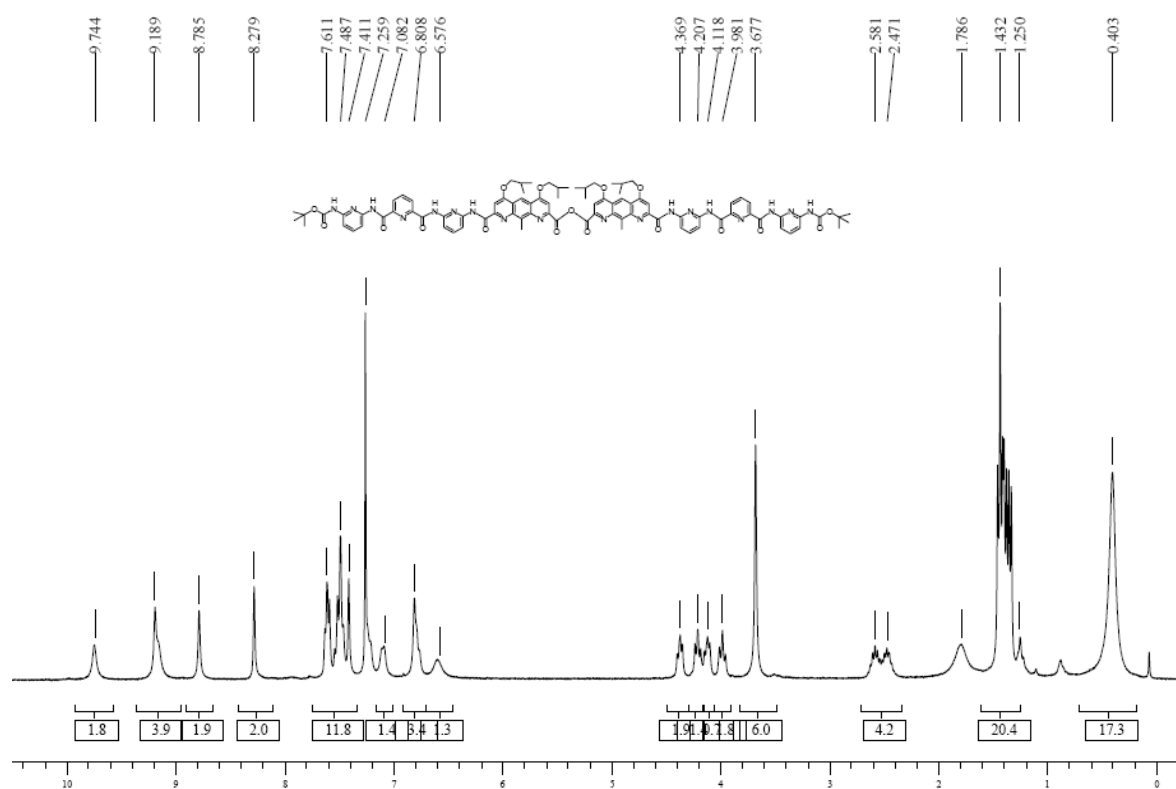
$^1\text{H}$  NMR spectrum of **6**:



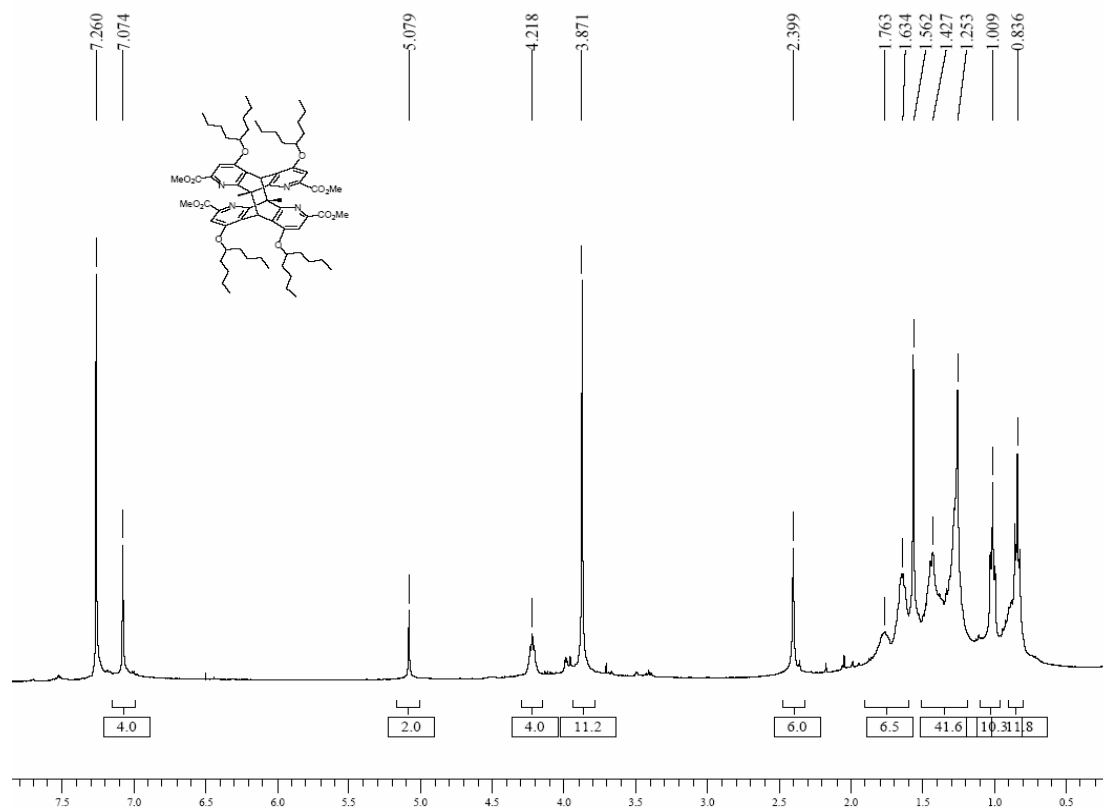
$^1\text{H}$  NMR spectrum of **7**:



$^1\text{H}$  NMR spectrum of **10**:



$^1\text{H}$  NMR spectrum of **11**:



$^1\text{H}$  NMR spectrum of **12**:

