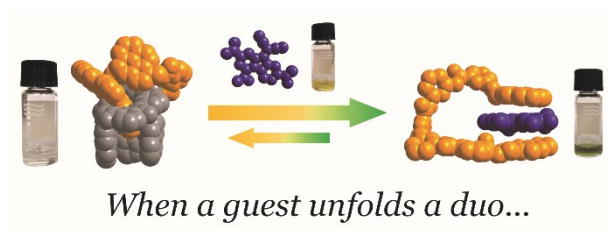


# Pyrene-functionalized Foldamer: Structural Impact and Recognition Properties supported by Donor-Acceptor Interactions

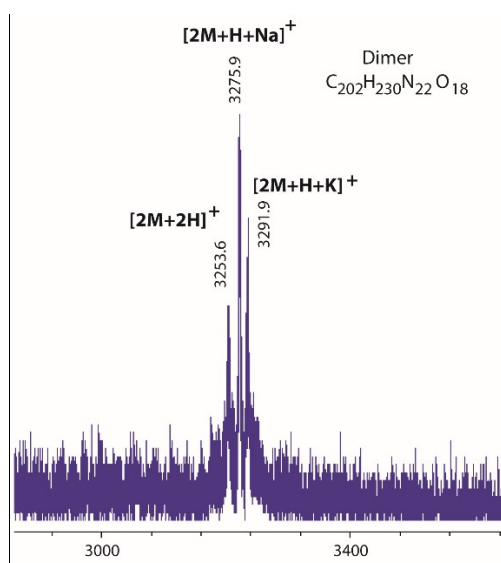
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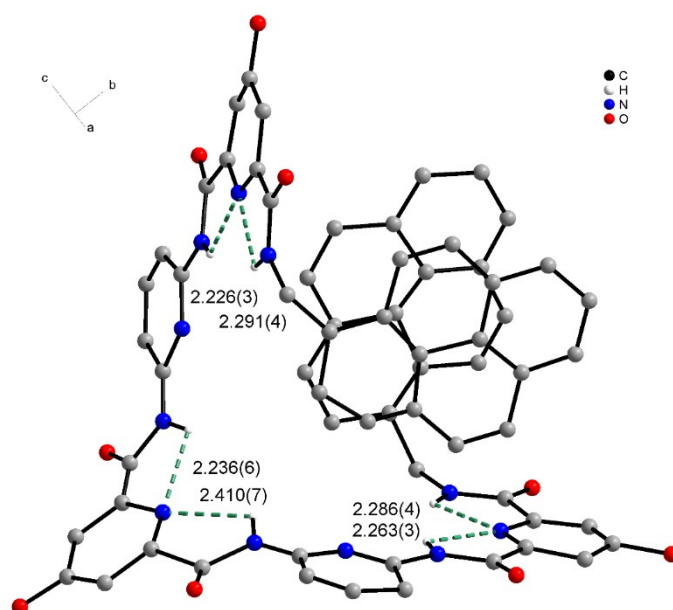
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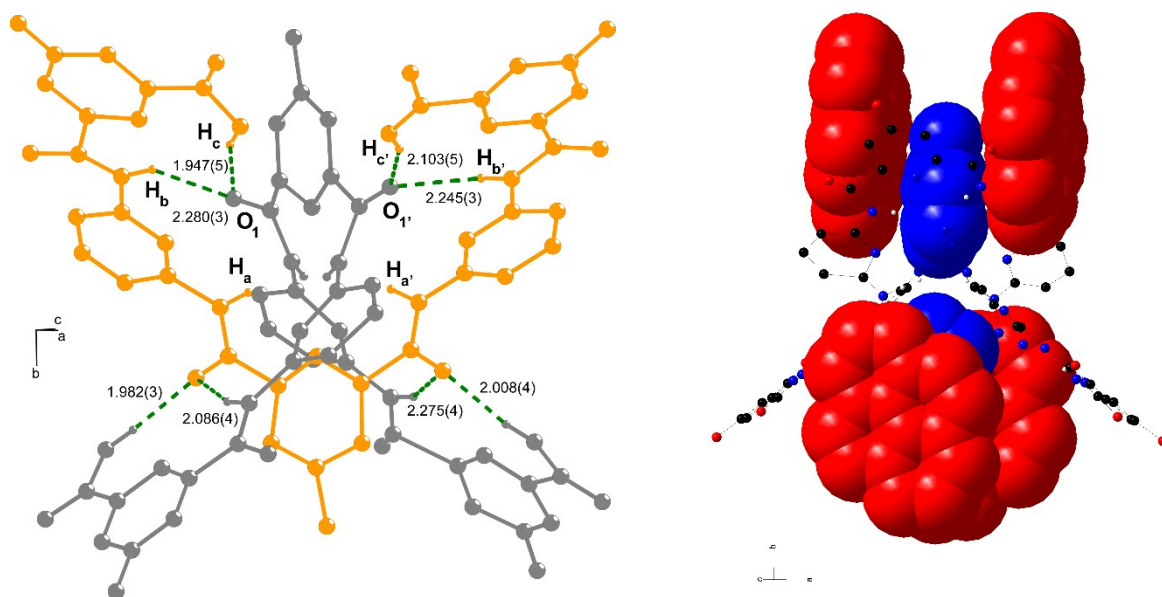
**Graphical abstract.** The structure of the dimer (left) corresponds to its X-ray crystal structure. Regarding the donor-acceptor charge-transfer complex (right), this illustration was prepared with the Hyperchem software. To do so, the pyrene-7-pyrene stack was first optimized with the Molecular Mechanics method and the geometry of the rest of the molecule was subsequently optimized with the same method.



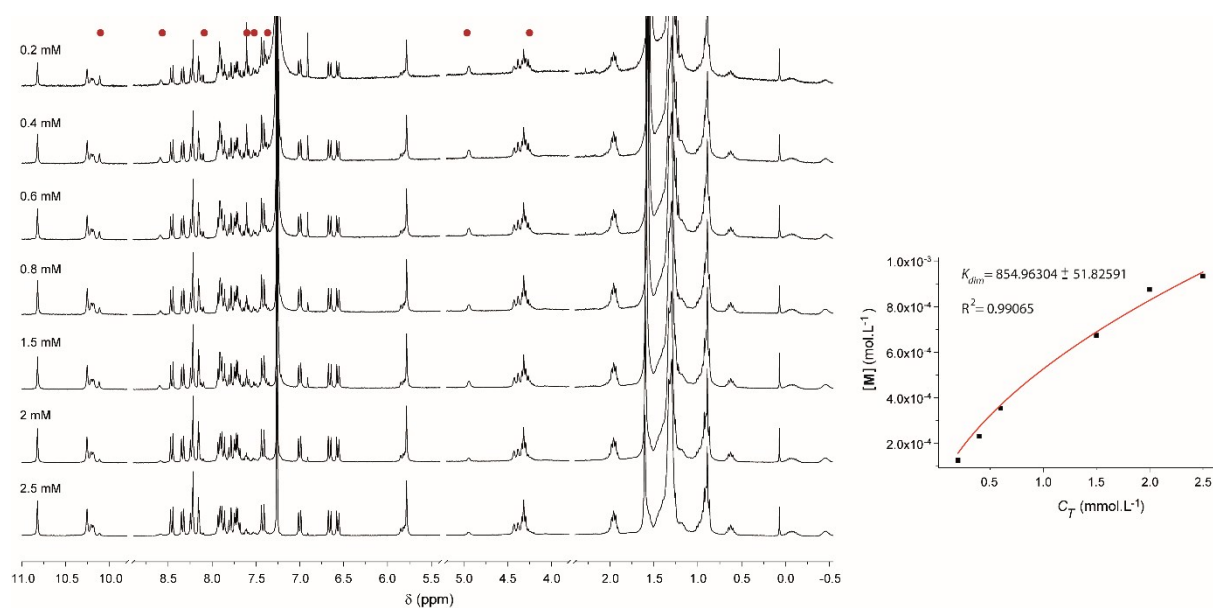
**Figure S1.** MALDI-TOF mass spectrum of dimer (**1**)<sub>2</sub>. Matrix: Dithranol



**Figure S2.** X-Ray crystal structure of foldamer **1** (a single strand is presented). Green dashed lines show intramolecular hydrogen bonds.



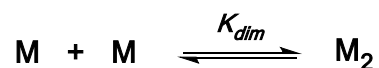
**Figure S3.** Intermolecular hydrogen bonds (left) and  $\pi$ - $\pi$  interactions between both strands of dimer ( $\mathbf{1}$ )<sub>2</sub>. Donor pyrene and acceptor pyridyl rings are represented in red and blue respectively.



**Figure S4.**  $^1\text{H}$  NMR spectra of compound  $\mathbf{1}$  at different concentrations (top) in  $\text{CDCl}_3$  and corresponding fit (bottom) for the dimerization process (300 MHz, 298 K). Monomer signals are indicated by red circles.

Concentration dependent  $^1\text{H}$  NMR experiments showed that the dimer and monomer forms were in slow equilibrium at the NMR time scale ( $\text{CDCl}_3$ , 298 K, 300 MHz).

To obtain the dimerization constant ( $K_{\text{dim}}$ ), the following model was used in which two molecules of monomer join to form a dimer:



When the equilibrium is reached,  $K_{dim}$  can be defined by the following equation:

$$K_{dim} = \frac{[M_2]}{[M]^2}$$

where  $[M]$  and  $[M_2]$  are the monomer and dimer concentration, respectively.

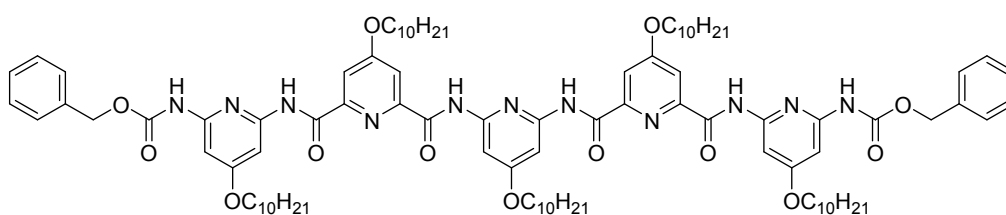
Taking into account the mass balance equation:

$$C_T = [M] + 2[M_2]$$

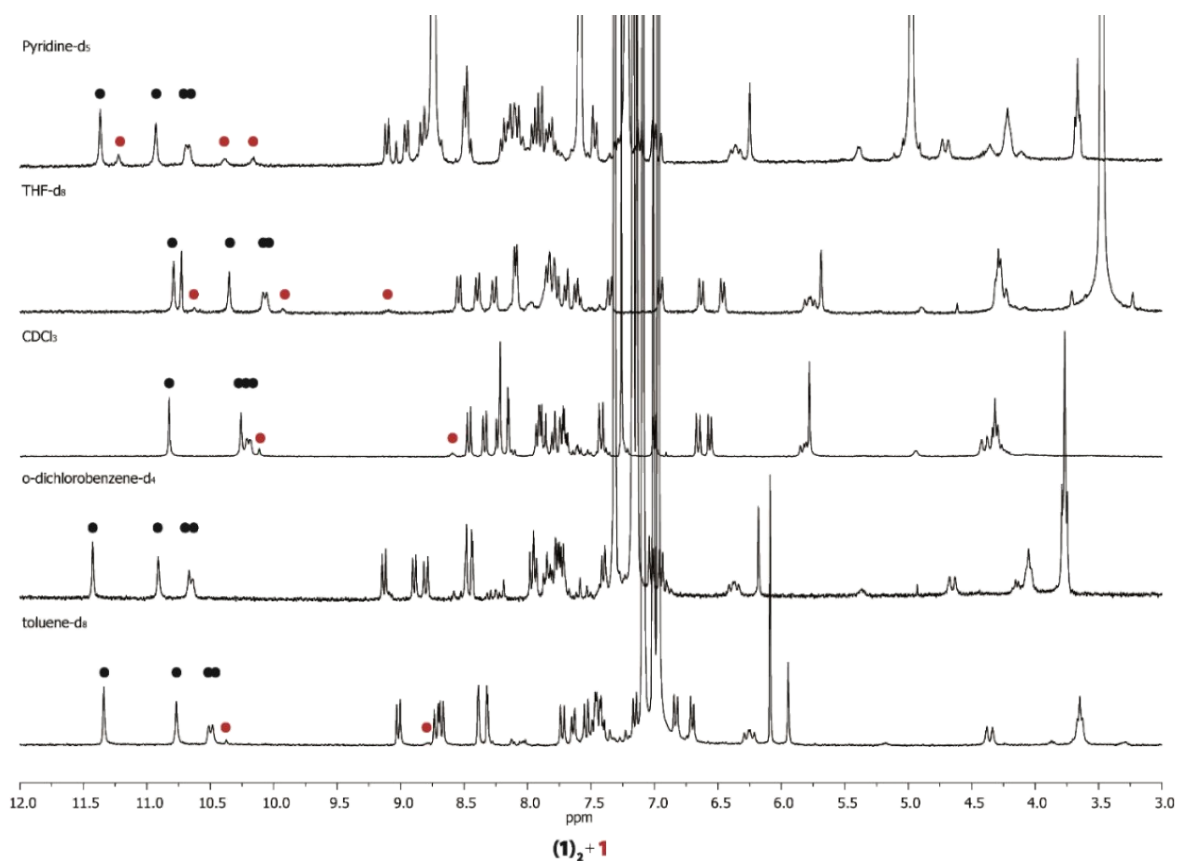
where  $C_T$  is the total concentration, the dimerization constant can be related to the total concentration by the following expression :

$$[M] + 2K_{dim}[M]^2 - C_T = 0$$

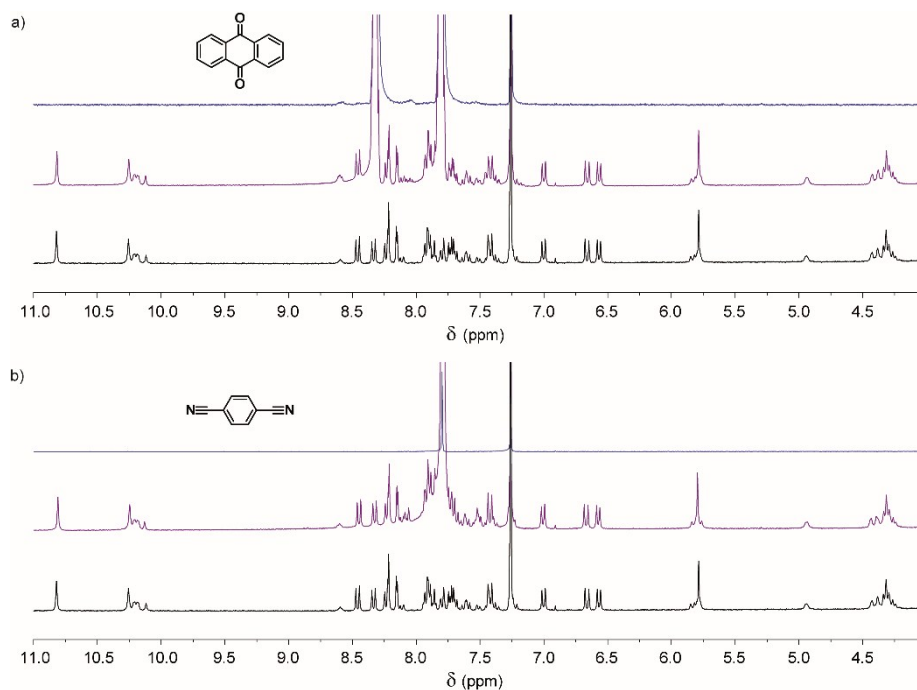
which allows to perform the corresponding non-linear fit by considering the monomer concentration in each experiment. To do so, the concentration of monomer was calculated by signal integration.



**Scheme S1.** Structure of previously reported compound **S1** (*Tetrahedron*, 2004, **60**, 10029)

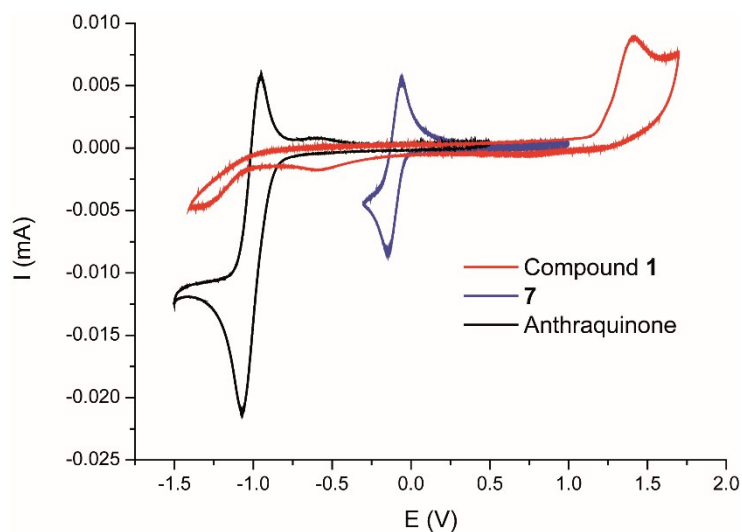


**Figure S5.** Partial  $^1\text{H}$  NMR spectra of compound **1** ( $2 \times 10^{-3}$  M) in different solvents (300 MHz, 298 K). Monomer NH signals are indicated by red circles and dimer NH signals by black circles.

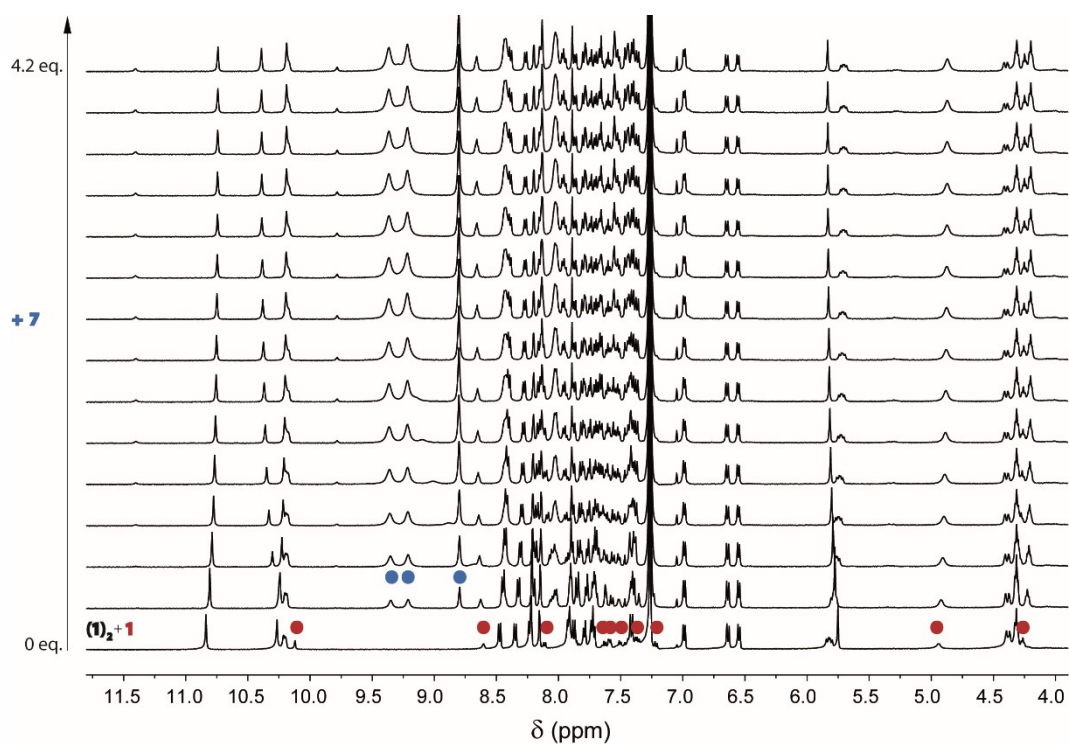


**Figure S6.** Partial  $^1\text{H}$  NMR spectra of compound **1** (black, 1.5 mM,  $\text{CDCl}_3$ ) in the presence of (a) anthraquinone (purple, 10 eq., solubility limit) and (b) 1,4-dicyanobenzene (purple, 40 eq.). For

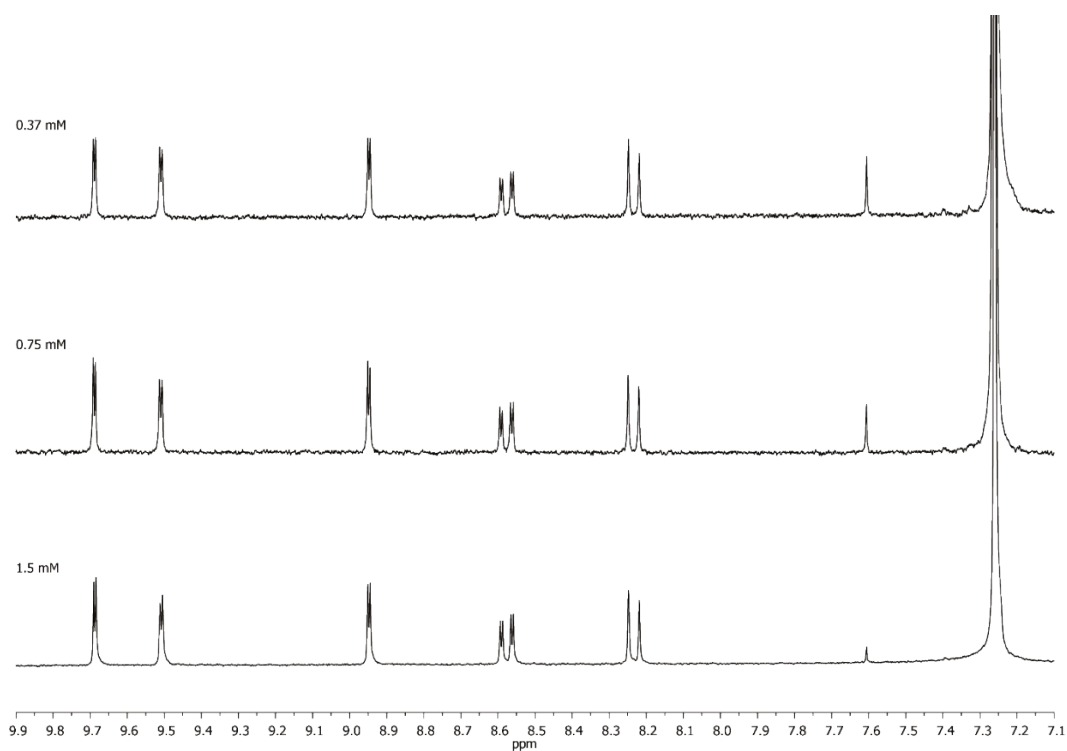
comparison purposes, the spectra of the electron poor derivatives are shown at the top of figures (a) and (b) respectively.



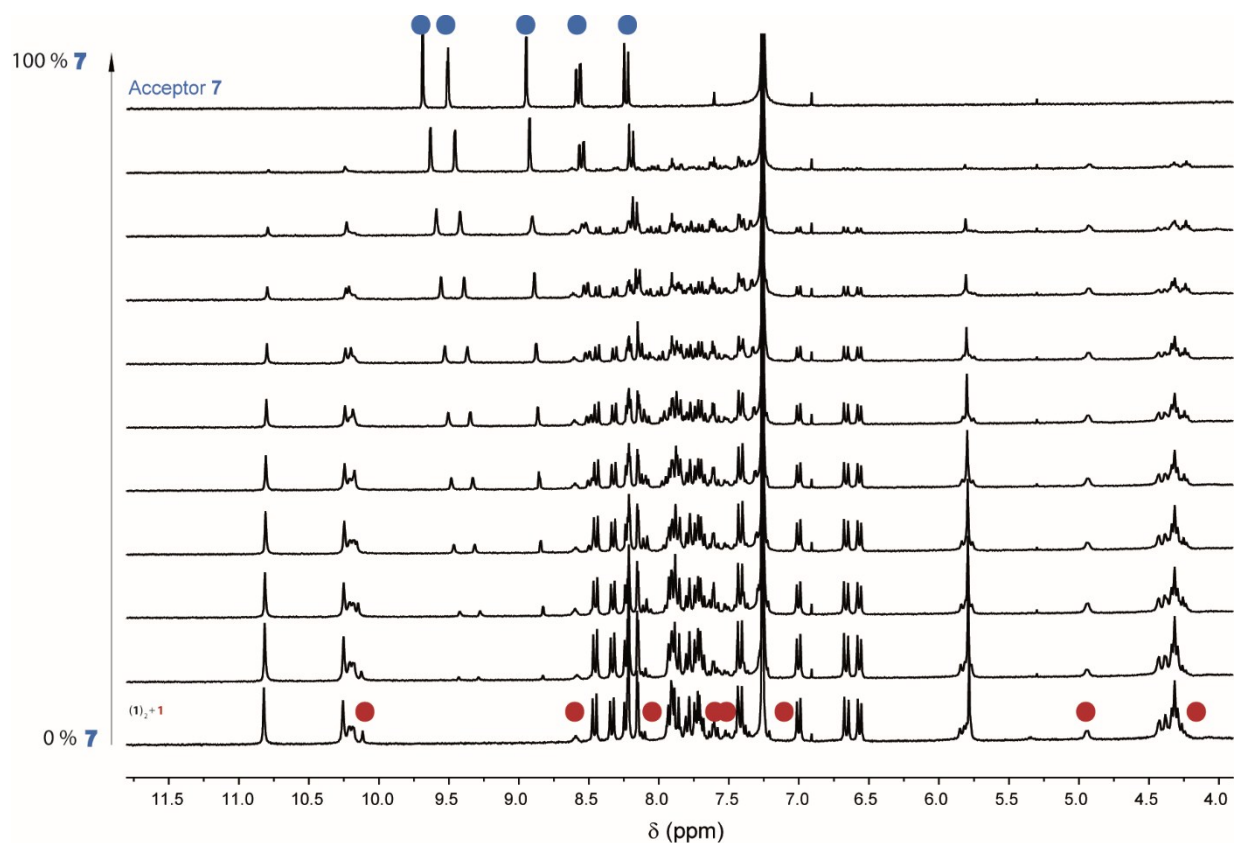
**Figure S7.** Cyclic voltammetry of foldamer **1**, anthraquinone and **7** ( $10^{-3}$  mM,  $\text{CH}_2\text{Cl}_2$ ,  $\text{NBu}_4\text{PF}_6$  (0.1 M), working electrode: Pt; reference electrode: Ag/Ag  $\text{NO}_3$ ; 100 mV/s).



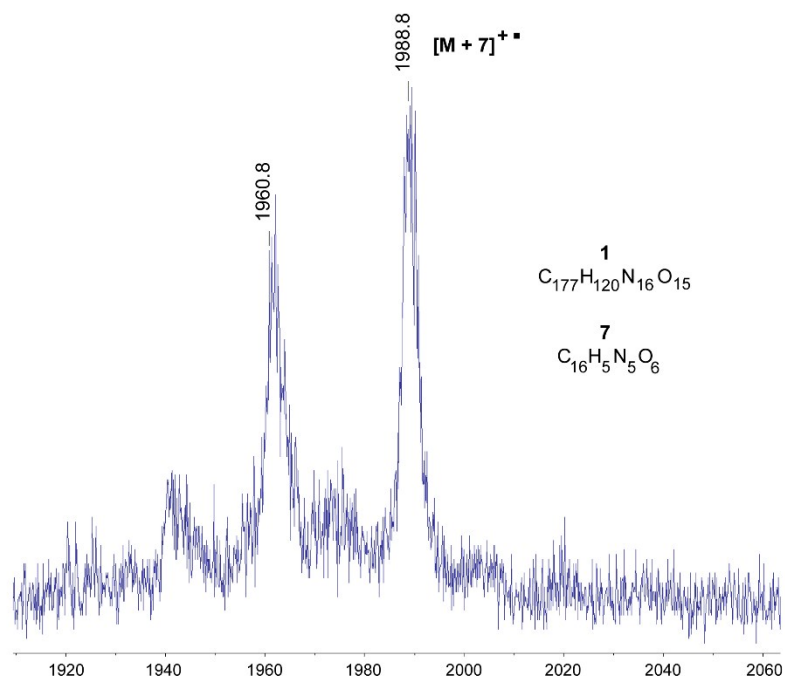
**Figure S8.**  $^1\text{H}$  NMR spectra of compound **1** upon addition of increasing amounts of **7** in  $\text{CDCl}_3$  ( $[\mathbf{1}] = 1.5$  mM, 500 MHz, 298 K). Red and blue circles indicate the signals of monomer **1** and acceptor **7**, respectively.



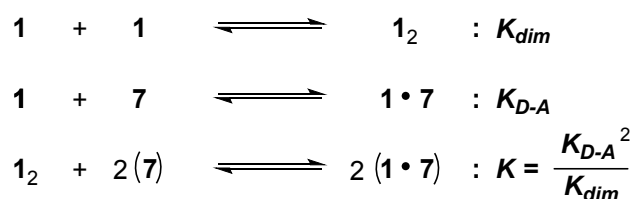
**Figure S9.**  $^1\text{H}$  NMR spectra of **7** at different concentrations in  $\text{CDCl}_3$  (300 MHz, 298 K).



**Figure S10.** Job plot experiment of compound **1** and **7** in  $\text{CDCl}_3$ . Total concentration = 1.5 mM, 300MHz, 298 K. The variation of the chemical shift at 10.1 ppm corresponding to the monomer unit was chosen for the Job plot analysis.



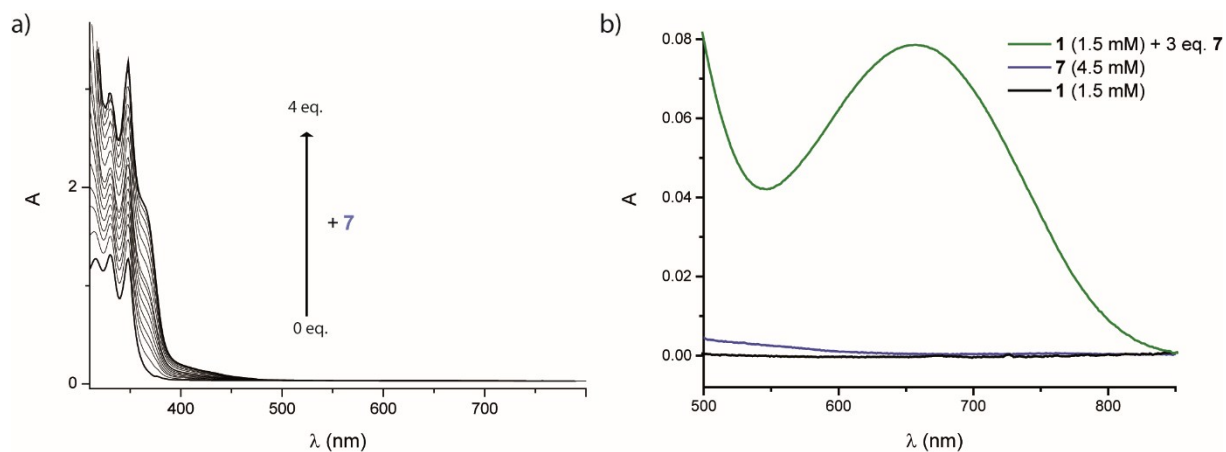
**Figure S11.** MALDI-TOF mass spectrum of ionized charge transfer complex  $1 \cdot 7^+$  (matrix: dithranol)



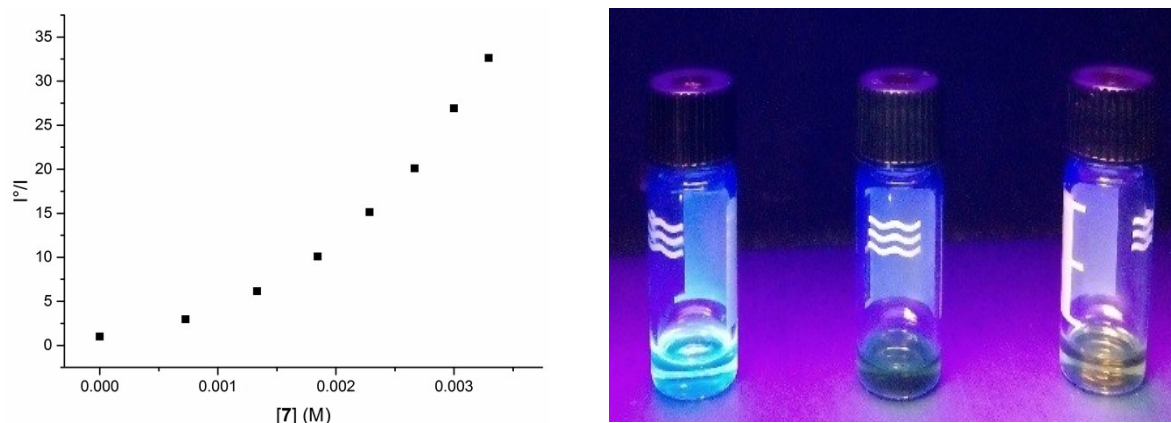
To determine the proportion between dimeric and monomeric species, signals located at 10.84 (dimer) and 10.11-10.39 ppm (monomer) were integrated ( $\text{CDCl}_3$ ,  $[\mathbf{1}] = 1.5 \text{ mM}$  - Figures 3 and S8). The concentrations of free monomer  $\mathbf{1}$  and charge transfer complex  $1 \cdot 7$  were subsequently calculated thanks to the variations of chemical shift, from 10.11 ppm (absence of  $\mathbf{7}$ ) to 10.39 ppm (4 equivalents of acceptor  $\mathbf{7}$ ). This allowed for determining  $K$ , and  $K_{D-A}$  was subsequently calculated as  $(K \cdot K_{dim})^{0.5}$ .

**Figure S12.** Calculation of  $K$  and  $K_{D-A}$  from the titration experiment showed in Figure 4 and s8.





**Figure S13.** (a) Evolution of the UV-vis absorption spectrum of foldamer **1** (0.25 mM) upon addition of **7** in  $\text{CHCl}_3$  ( $l = 0.1$  cm). (b) UV-vis absorption spectra of **1** (1.5 mM), **7** (4.5 mM) and a mixture of compound **1** (1.5 mM) and **7** (3 equivalents) in  $\text{CHCl}_3$  ( $l = 0.1$  cm).



**Figure S14.** *Left.* Stern-Volmer plot of the fluorescence intensity ( $\lambda_{\text{em}} = 451$  nm) of compound **1** (1.5 mM) with increasing amounts of **7** in  $\text{CHCl}_3$  ( $\lambda_{\text{exc}} = 316$  nm,  $l = 0.5$  cm). *Right.* Chloroform solutions of **1** (1.5 mM), **1** (1.5 mM) mixed with **7** (2.2 eq.), and **7** (from left to right) under a UV lamp.

## Experimental details

### General.

The starting materials were purchased and used without further purification. All solvents were dried according to standard procedures. All air-sensitive reactions were carried out under argon atmosphere. Thin-layer chromatography (TLC) was performed on aluminium plates coated with MerckSilica gel 60 F254. Developed plates were air-dried and scrutinized under a UV lamp. Silica gel 60 (35–70 mesh, SDS) was used for preparative silica gel chromatography.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using the deuterated solvent as an internal reference on a BRUKER Advance DRX 300 or 500 spectrometer. Coupling constants (J) are denoted in Hz and chemical shifts ( $\delta$ ) in parts per million (ppm). Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The mass spectra were recorded on a Jeol JMS 700 (high resolution mass spectra (HRMS)) or a Bruker Biflex III spectrometer (MALDI-TOF). The infrared absorption spectra were recorded on an FTIR BRUKER VERTEX 70. X-Ray single-crystal diffraction data were collected at 150 K on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). The structure was solved by direct methods, expanded and refined on  $F^2$  by full matrix least-squares techniques using SHELX97 programs (G.M. Sheldrick, 1998). All non-H atoms were refined anisotropically and the hydrogen atoms (added on the central core of the molecule, not on the alkyl chains) were included in the calculation without refinement. Multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.37.35g, 2014). The structure refinement showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE were used to remove the scattering contribution corresponding to chloroform molecules and missing atoms from the intensity data. The unit cell contains 2 voids of  $4723 \text{ \AA}^3$  containing 2256 electrons from which 1848 electrons can be attributed to the 208 carbon and 600 hydrogen missing atoms (alkyl chains) in the unit cell. The remaining 408 electrons can be attributed to approximately eight chloroform molecules. The assumed solvent composition (2 chloroform molecules per asymmetric unit) was used in the calculation of the empirical formula, formula weight, density, linear absorption coefficient and  $F(000)$ . UV-vis absorption spectra were recorded on a JASCO V-730 spectrophotometer. Fluorescence spectra were recorded on a Photon Technology International QuantaMaster 4. The cyclic voltammetry experiments were carried out on a potentiostat-galvanostat EG&G PAR model 273. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as supporting electrolyte. The cell was equipped with three electrodes: a platinum working electrode ( $\varnothing = 2 \text{ mm}$ ), a platinum wire as auxiliary electrode and a silver/silver nitrate reference electrode. The potentials are given with respect to the ferrocene/ferrocenium redox couple.

### Crystallographic data

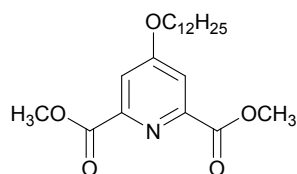
(1) $_2$  + 2 CHCl $_3$ : C $_{204}$ H $_{232}$ Cl $_6$ N $_{22}$ O $_{18}$ , M = 3492.82, colourless prism, 0.314 x 0.222 x 0.094 mm $^3$ , monoclinic, space group Cc, a = 19.7171(8)  $\text{\AA}$ , b = 48.1436(19)  $\text{\AA}$ , c = 22.2536(6)  $\text{\AA}$ ,  $\beta = 110.350(4)^\circ$ , V = 19805.8(12)  $\text{\AA}^3$ , Z = 4,  $\rho_{\text{calc}} = 1.171 \text{ g/cm}^3$ ,  $\mu(\text{CuK}\alpha) = 1.317 \text{ mm}^{-1}$ ,  $F(000) = 7424$ ,  $\theta_{\text{min}} = 2.56^\circ$ ,  $\theta_{\text{max}} = 72.96^\circ$ , 88348 reflections collected, 32932 unique ( $R_{\text{int}} = 0.034$ ), parameters / restraints = 1705 / 41,  $R_1 = 0.0792$  and  $wR_2 = 0.2173$  using 14597 reflections with  $I > 2\sigma(I)$ ,  $R_1 = 0.1154$  and  $wR_2$

= 0.2516 using all data, GOF = 0.864,  $-0.187 < \Delta\rho < 0.498 \text{ e.}\text{\AA}^{-3}$ . CCDC-1574008 contains the supplementary crystallographic data for this paper.

### Synthetic details and characterization

Diaminopyridine and 1-pyrenemethylamine hydrochloride were purchased from a commercial source. Dimethyl 4-hydroxypyridine-2,6-dicarboxylate was prepared by following the reported procedure (M. Di Antonio, K. I. E. McLuckie, S. J. Balasubramanian, *J. Am. Chem. Soc.* 2014, **136**, 5860) and showed identical spectroscopic properties to those reported therein.

### Dimethyl 4-(dodecyloxy)pyridine-2,6-dicarboxylate (2)

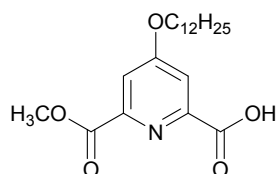


Chemical Formula:  $\text{C}_{21}\text{H}_{33}\text{NO}_5$   
Molecular Weight: 379.50

Dimethyl 4-hydroxypyridine-2,6-dicarboxylate (10.67 g, 50 mmol), 1-bromododecane (12.58 g, 50 mmol) and  $\text{K}_2\text{CO}_3$  (13.95 g, 101 mmol) were dissolved in dry DMF (25 mL) and the mixture was heated to  $50^\circ\text{C}$  under argon atmosphere for 17 h. Diethyl ether was added and the mixture was washed with water and ice. The organic phase was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated under reduced pressure. The residue was purified by precipitation in chloroform and methanol affording compound **2** as a white solid (17.65 g, 92%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (2H, s), 4.13 (2H, t,  $J = 6.54$  Hz), 4.01 (6H, s), 1.84 (2H, m), 1.47 (2H, br) 1.27 (16H, br), 0.88 (3H, t,  $J = 6.39$  Hz) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 165.4, 149.9, 114.7, 69.3, 53.4, 32.1, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 28.8, 26.0, 22.8, 14.3 ppm; FT-IR (neat):  $\nu = 2918, 2850, 1748, 1717, 1594, 1441, 1344, 1257, 1227, 11180, 1154, 1106, 1033, 991, 876, 797, 784, 734, 587, 454 \text{ cm}^{-1}$ . HRMS (ESI<sup>+</sup>) calcd. for  $\text{C}_{21}\text{H}_{34}\text{NO}_5$   $[\text{M}+\text{H}]^+$ , 380.2436; found, 380.2434.

### 4-(Dodecyloxy)-6-(methoxycarbonyl)picolinic acid (3)



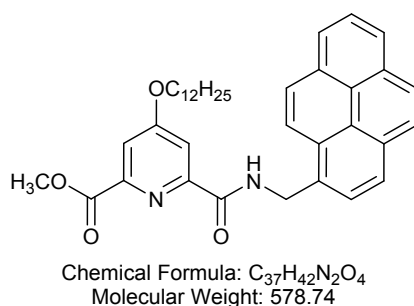
Chemical Formula:  $\text{C}_{20}\text{H}_{31}\text{NO}_5$   
Molecular Weight: 365.47

Sodium hydroxide (105 mg, 2.64 mmol) was dissolved in methanol (20 mL) and was added slowly to a solution of compound **2** (1 g, 2.64 mmol) in methanol (20mL). The mixture was stirred at room temperature overnight. Then, methanol was evaporated under reduced pressure and the crude was purified by silica gel chromatography (dichloromethane:methanol 95:5) to recover

the starting product and to isolate the corresponding carboxylate. The latter was dissolved in dichloromethane, protonated with hydrochloric acid 3M, washed with water, dried over magnesium sulfate and evaporated to afford **3** as a white solid (773 mg, 80%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 9.45 (1H, br), 7.79 (1H, d,  $J = 2.19$  Hz), 7.75 (1H, d,  $J = 2.19$  Hz), 4.11 (2H, t,  $J = 6.46$  Hz), 3.96 (3H, s), 1.80 (2H, m), 1.42 (2H, br), 1.35-1.17 (16H, br), 0.83 (3H, t,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 164.4, 164.1, 148.4, 148.1, 115.8, 112.4, 69.5, 53.1, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 25.8, 22.6 ppm; FT-IR (neat):  $\nu = 3224, 2954, 2915, 2851, 1719, 1590, 1445, 1366, 1304, 1226, 1109, 1031, 890, 787, 715, 695, 583$   $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd. for  $\text{C}_{20}\text{H}_{31}\text{NO}_5$   $[\text{M}+\text{H}]^+$ , 366.2280; found, 366.2278.

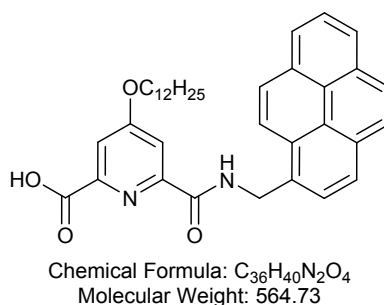
#### Methyl 4-(dodecyloxy)-6-((pyren-1-ylmethyl)carbamoyl)picolinate (**4**)



Compound **3** (1.07 g, 2.95 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.37 g, 8.85 mmol), 4-dimethylaminopyridine (1.08 g, 8.85 mmol) and 1-hydroxybenzotriazole hydrate (0.44 g, 3.24 mmol) were dissolved in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) and stirred for 15 minutes under argon atmosphere. 1-Pyrenemethylamine hydrochloride (0.71 g, 2.65 mmol) was subsequently added portionwise. The reaction mixture was stirred at room temperature for 16 hours. After evaporation of the solvent, the residue was purified by silica gel chromatography (eluent: chloroform/methanol 100/0.3) affording compound **4** as a white solid (0.91 g, 60%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.59 (1H, t,  $J = 5.90$  Hz), 8.32 (1H, d,  $J = 9.21$  Hz), 8.17 (1H, br), 8.15 (1H, br), 8.12 (1H, br), 8.09 (1H, br), 8.05-7.95 (4H, br), 7.92 (1H, d,  $J = 2.45$  Hz), 7.59 (1H, d,  $J = 2.45$  Hz), 5.37 (2H, d,  $J = 5.90$  Hz), 4.07 (2H, t,  $J = 6.52$  Hz), 3.82 (3H, s), 1.81 (2H, m), 1.45 (2H, br), 1.28 (16H, br), 0.90 (3H, t,  $J = 6.31$  Hz) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 165.1, 163.5, 152.0, 148.1, 131.3, 131.2, 131.0, 130.8, 129.1, 128.2, 127.5, 127.4, 127.1, 126.1, 125.4, 125.3, 125.0, 124.8, 124.8, 123.0, 114.7, 111.1, 69.1, 52.8, 41.9, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 25.9, 22.8, 14.2 ppm; FT-IR (neat):  $\nu = 3370, 2916, 2851, 1923, 1678, 1597, 1563, 1447, 1353, 1339, 1183, 1116, 1029, 889, 879, 850, 838, 784, 703, 560$   $\text{cm}^{-1}$ . HRMS (ESI $^+$ ) calcd. for  $\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_4$   $[\text{M}]^+$ , 578.3144; found, 578.3140.

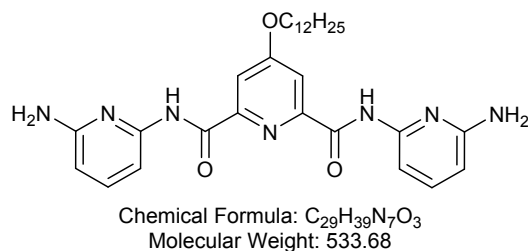
#### 4-(Dodecyloxy)-6-((pyren-1-ylmethyl)carbamoyl)picolinic acid (5)



NaOH (0.12 g, 3.16 mmol) was dissolved in water (4 mL) and was then added to a solution of compound 4 (0.91 g, 1.58 mmol) in dioxane (22 ml). The mixture was stirred at room temperature for 2 h. Then, an excess of acetic acid was added. The suspension was then filtered and washed with minimal amount of water and the residue obtained was dried to give pure 5 as a white solid (0.83 g, 93%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.84 (1H, t, J = 5.58 Hz), 8.51 (1H, d, J = 9.25 Hz), 8.34-8.25 (4H, br), 8.17 (2H, s), 8.12 (1H, d, J = 7.92 Hz), 8.09 (1H, t, J = 7.62 Hz), 7.76 (1H, d, J = 2.38 Hz), 7.65 (1H, d, J = 2.46 Hz), 5.32 (2H, d, J = 5.90 Hz), 4.21 (2H, t, J = 6.36 Hz), 1.75 (2H, m), 1.41 (2H, br), 1.23 (16H, br), 0.84 (3H, t, J = 6.96 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.4, 165.0, 163.0, 157.0, 132.3, 131.5, 130.1, 130.3, 130.2, 128.1, 127.8, 127.4, 127.2, 126.7, 126.3, 125.3, 125.2, 124.8, 124.1, 123.9, 123.1, 112.4, 111.0, 79.2, 68.8, 31.3, 29.0, 29.0, 28.9, 28.7, 28.6, 28.2, 25.2, 22.1, 14.0. ppm; FT-IR (neat): ν = 3265, 2922, 2851, 1757, 1644, 1598, 1534, 1448, 1359, 1339, 1280, 1175, 1108, 1045, 997, 842, 758, 581 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) calcd. for C<sub>36</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup>, 564.2988; found, 564.2976.

#### N<sup>2</sup>,N<sup>6</sup>-Bis(6-aminopyridin-2-yl)-4-(dodecyloxy)pyridine-2,6-dicarboxamide (6)

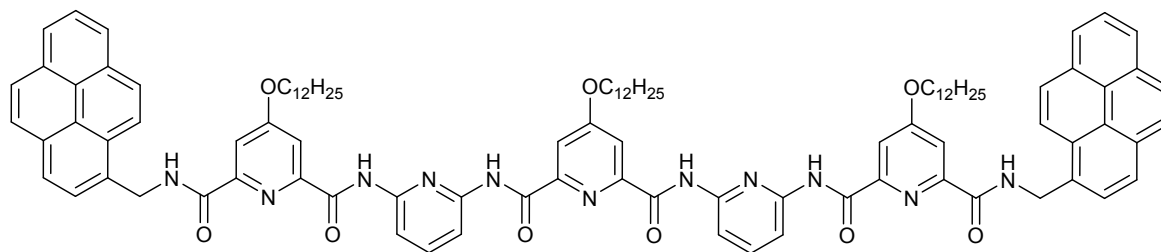


A 1.6 mM solution of *n*BuLi (40 mL, 64 mmol) in hexane was added dropwise to a solution of 2,6-diaminopyridine (7.33 g, 67.2 mmol) in dry THF (200 mL) at -78°C. After stirring for 20 min, a solution of compound 2 (3.62 g, 9.5 mmol) in dry THF (25 mL) was added dropwise. The reaction mixture was stirred at -78°C for 8 h, gradually warmed to r.t. and stirred overnight. Then, a solution of NaHCO<sub>3</sub> was added until pH 8-10 and the solution was extracted with chloroform. The combined organic extracts were evaporated to dryness and purified by column chromatography (silica gel, chloroform:methanol 100:2) affording 6 as a beige solid (1.58 g, 31%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 10.15 (2H, s), 7.94 (2H, s), 7.78 (2H, d, J = 8.01 Hz), 7.55 (2H, t, J = 8.01 Hz), 6.31 (2H, d, J = 8.01 Hz), 4.54 (4H, s), 4.18 (2H, t, J = 6.54 Hz), 1.86 (2H, m), 1.48 (2H, br), 1.27 (16H, br), 0.88 (3H, t, J = 6.39 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.4, 161.6, 157.5, 150.7, 149.5, 140.5, 112.0, 105.1, 104.0, 69.4, 32.1, 31.0, 29.8, 29.7, 29.5, 29.4, 28.9, 26.0, 22.8, 19.7, 14.3. ppm;

FT-IR (neat):  $\nu = 3476, 3363, 3341, 2946, 2850, 1691, 1622, 1600, 1532, 1458, 1343, 1296, 1249, 1206, 1128, 1065, 1035, 985, 971, 894, 868, 791, 716, 669, 638, 614, 579, 541, 467 \text{ cm}^{-1}$ . HRMS (ESI<sup>+</sup>) calcd. for C<sub>29</sub>H<sub>40</sub>N<sub>7</sub>O<sub>3</sub> [M+H]<sup>+</sup>, 534.3192; found, 534.3187.

***N*<sup>2</sup>,*N*'-(6,6'-((4-(Dodecyloxy)pyridine-2,6-dicarbonyl)bis(azanediyl))bis(pyridine-6,2-diyl))bis(4-(dodecyloxy)-*N*<sup>6</sup>-(pyren-1-ylmethyl)pyridine-2,6-dicarboxamide) (1)**

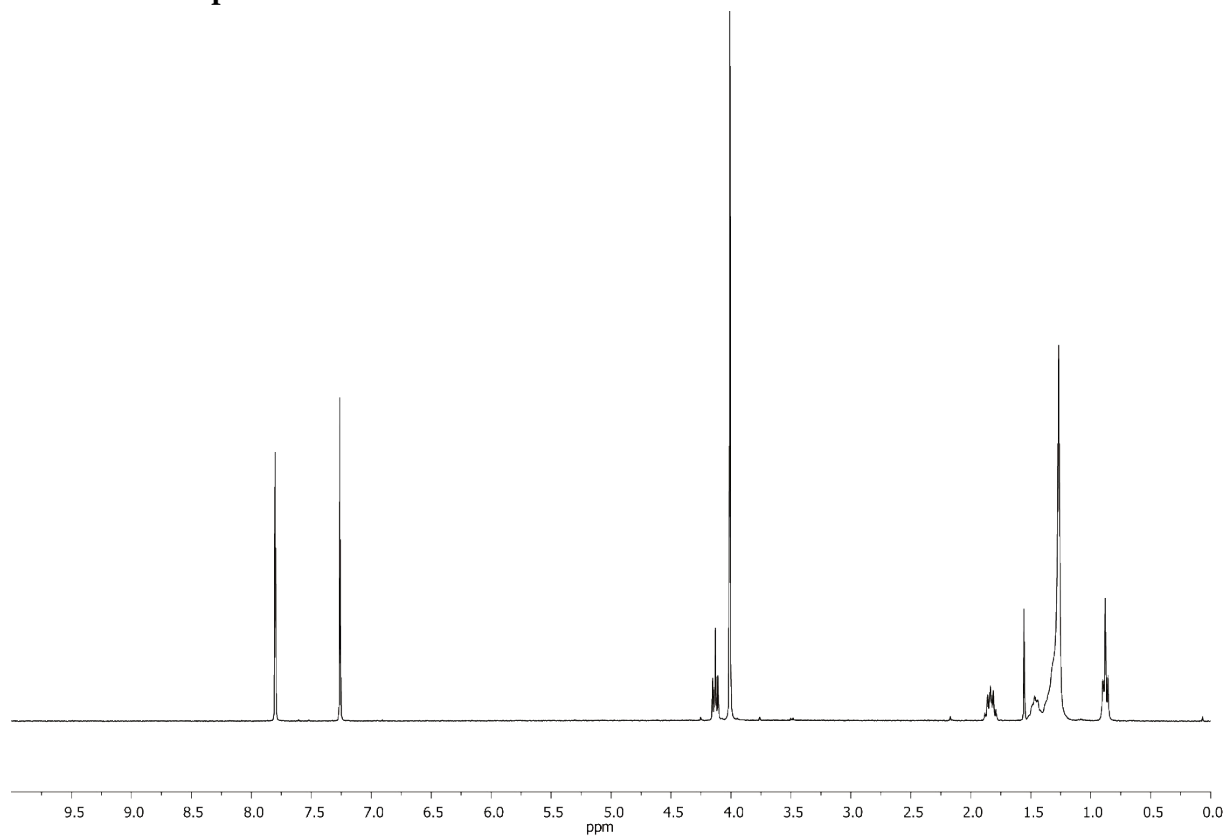


Chemical Formula: C<sub>101</sub>H<sub>115</sub>N<sub>11</sub>O<sub>9</sub>  
Molecular Weight: 1627.10

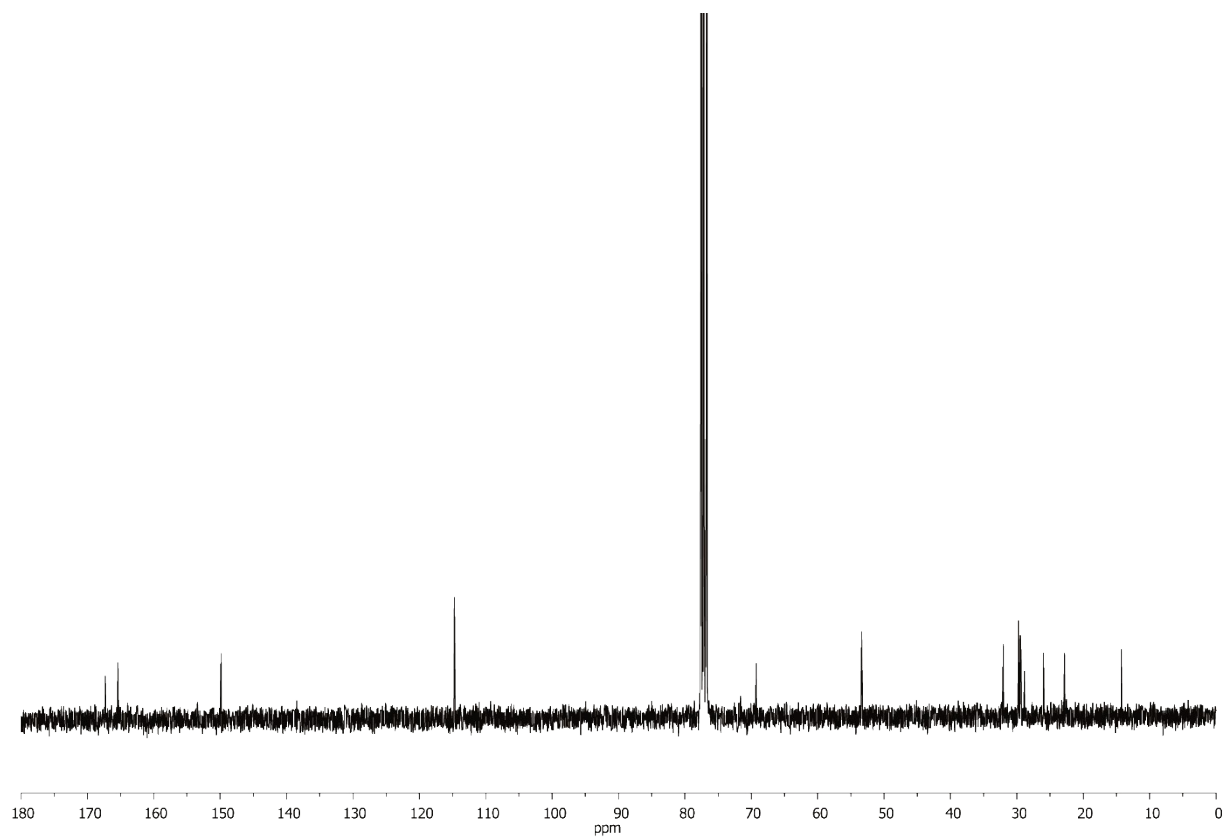
To a solution of compound **5** (0.83 g, 1.46 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL), *N,N*-diisopropylethylamine (0.52 mL, 2.96 mmol) was added under argon atmosphere, and the mixture was stirred for 5 min. After that, *o*-(benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HBTU) (1.12 g, 2.96 mmol) was added and the reaction mixture was stirred for 15 min. Compound **6** (0.20 g, 0.37 mmol) was subsequently added portionwise and the mixture was stirred at room temperature for 72 h. After evaporation of the solvent, the residue was purified by silica gel chromatography (eluent: chloroform/methanol 100/1) affording **1** as a white solid (0.16 g, 26%).

<sup>1</sup>H NMR (500 MHz, 373 K, DMSO-*d*<sub>6</sub>):  $\delta$  10.79 (2H, br), 10.63 (2H, br), 9.61 (2H, br), 8.26 (2H, d, *J* = 9.18 Hz), 8.19 (4H, br), 8.15 (2H, d, *J* = 9.18 Hz), 8.09 (2H, d, *J* = 7.73 Hz), 8.04-7.92 (12H, br), 7.87 (2H, d, *J* = 7.73 Hz), 7.77 (4H, br), 7.54 (2H, d, *J* = 1.94 Hz), 5.05 (4H, d, *J* = 5.70 Hz), 4.23 (2H, br), 4.19 (4H, t, *J* = 6.31 Hz), 1.78 (6H, m), 1.44 (6H, m), 1.25 (48H, br), 0.84 (9H, t, *J* = 7.09 Hz) ppm; <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  167.2, 166.7, 162.7, 161.6, 161.3, 150.8, 150.3, 149.8, 149.4, 149.1, 139.9, 131.7, 130.3, 129.8, 129.5, 127.2, 126.9, 126.6, 126.2, 125.4, 124.8, 124.5, 124.4, 123.9, 123.6, 123.5, 122.0, 111.2, 111.0, 110.4, 110.3, 78.5, 71.8, 68.6, 68.3, 60.0, 40.1, 40.0, 39.9, 39.8, 39.7, 39.6, 39.6, 39.5, 39.3, 39.2, 39.0, 30.6, 28.3, 28.3, 28.3, 28.2, 28.2, 28.0, 27.9, 27.7, 27.6, 24.7, 24.6, 21.3, 13.0 ppm; FT-IR (neat):  $\nu = 3338, 2921, 2851, 1673, 1580, 1523, 1498, 1439, 1337, 1291, 1238, 1157, 1117, 1037, 994, 884, 846, 802, 724, 681, 563 \text{ cm}^{-1}$ . HRMS (ESI<sup>+</sup>) calcd. for C<sub>101</sub>H<sub>115</sub>N<sub>11</sub>O<sub>9</sub> [M]<sup>+</sup>, 1625.8879; found, 1625.8835.

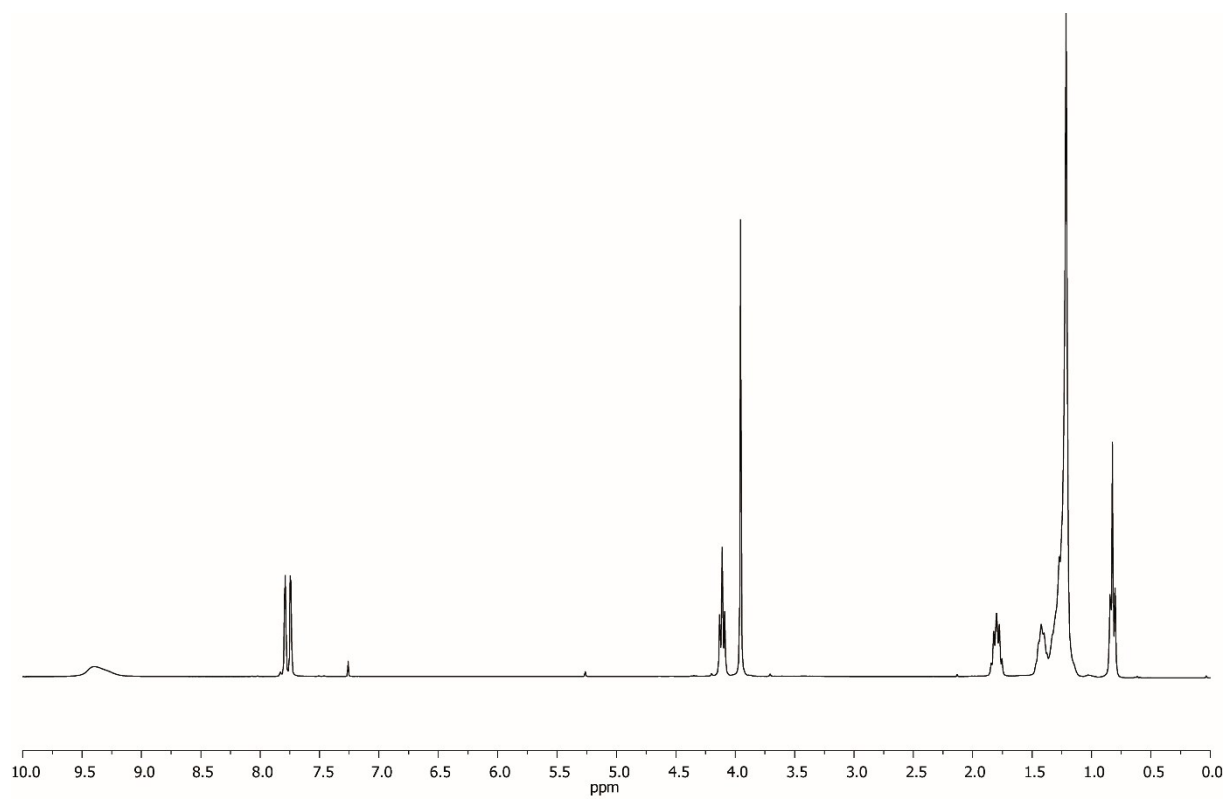
## Collection of spectra



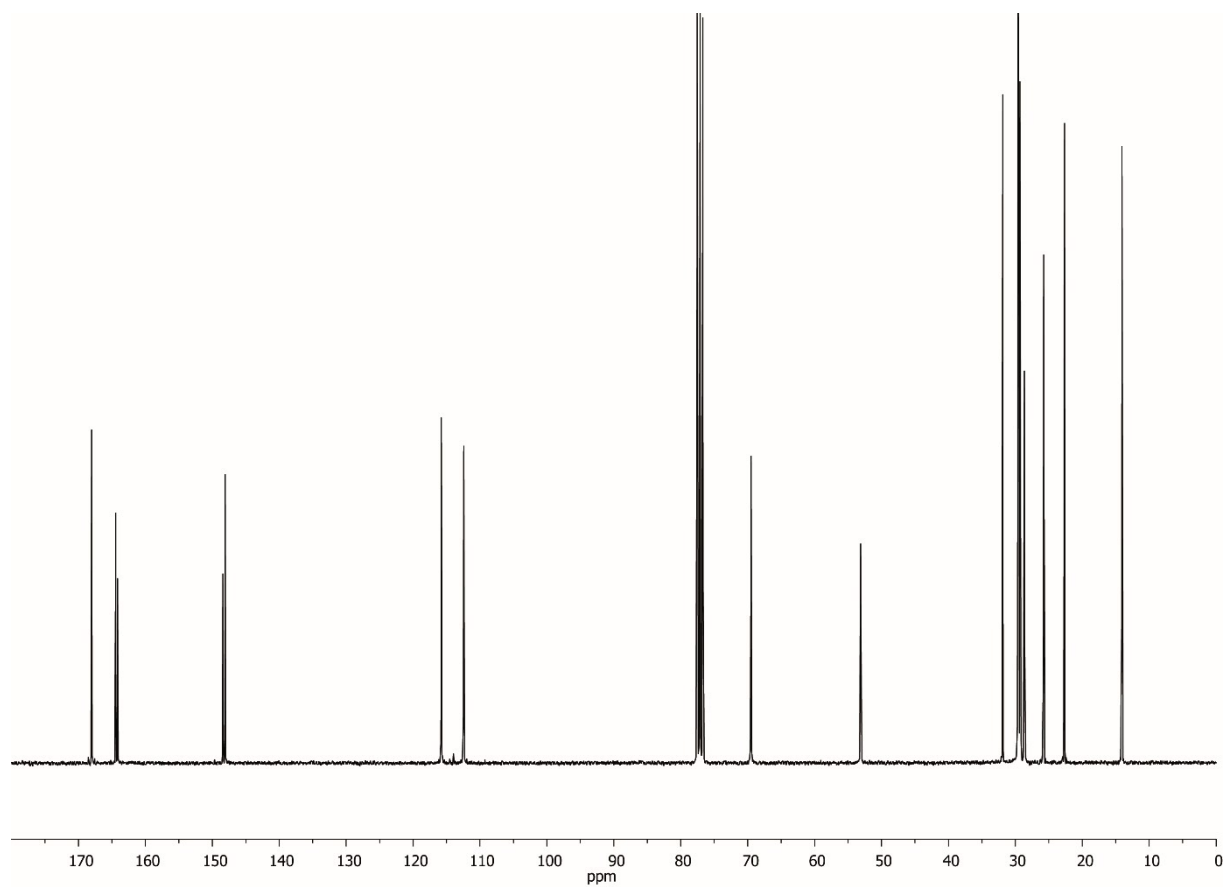
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K) of compound **2**.



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 298 K) of compound **2**.

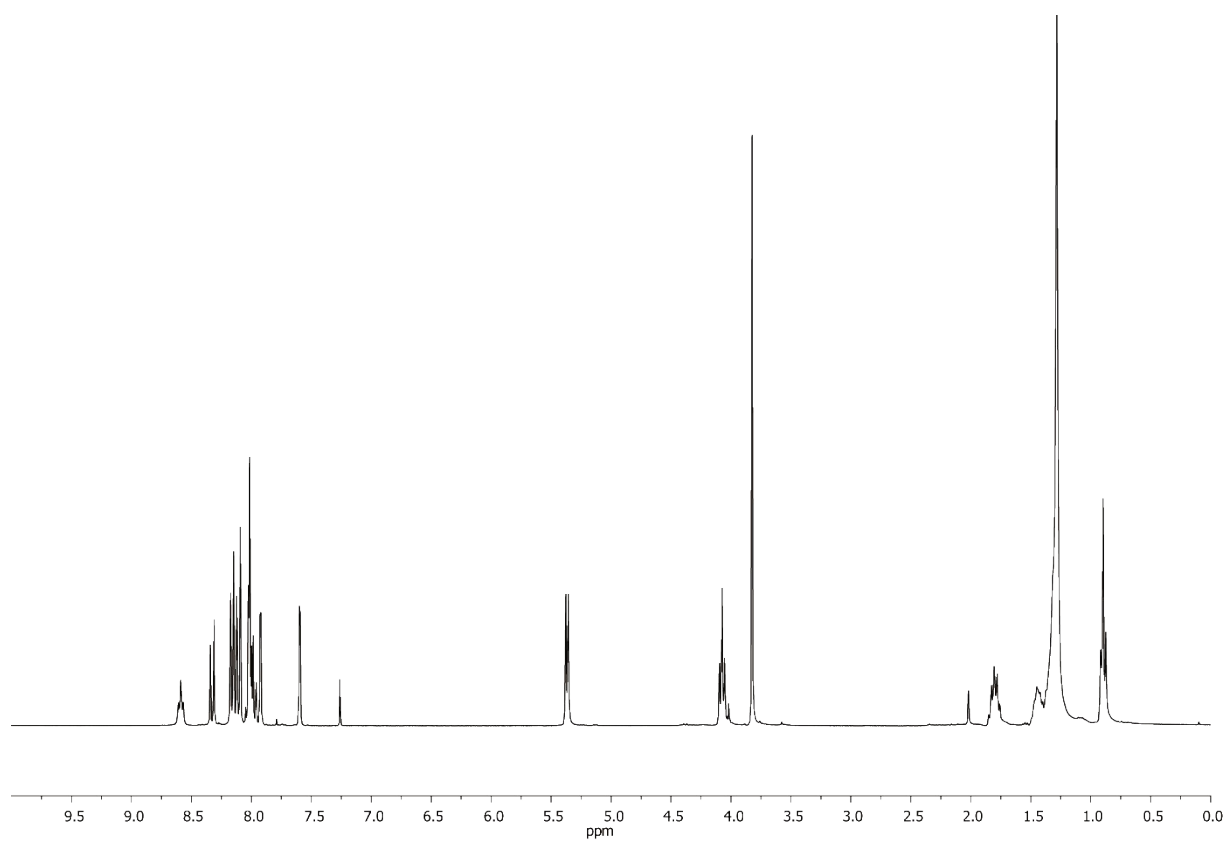


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K) of compound **3**.

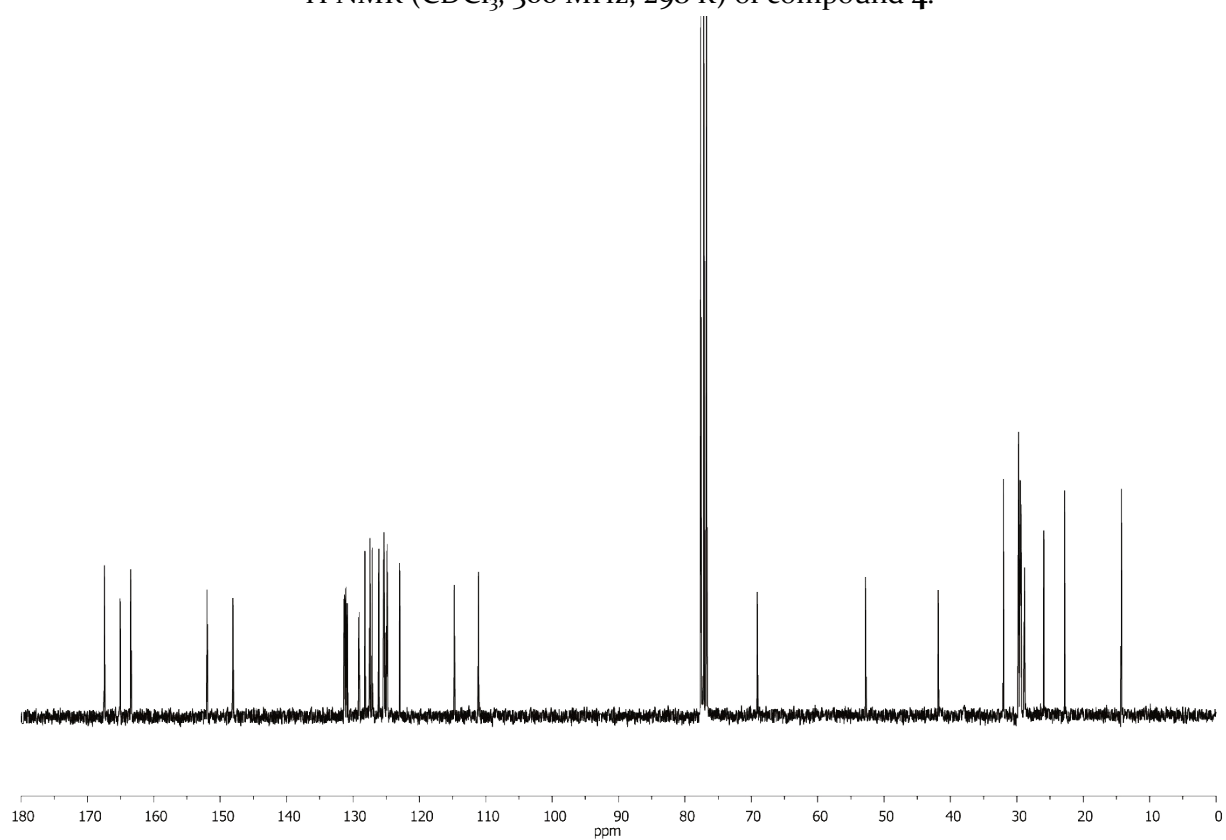


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 298 K) of compound **3**.

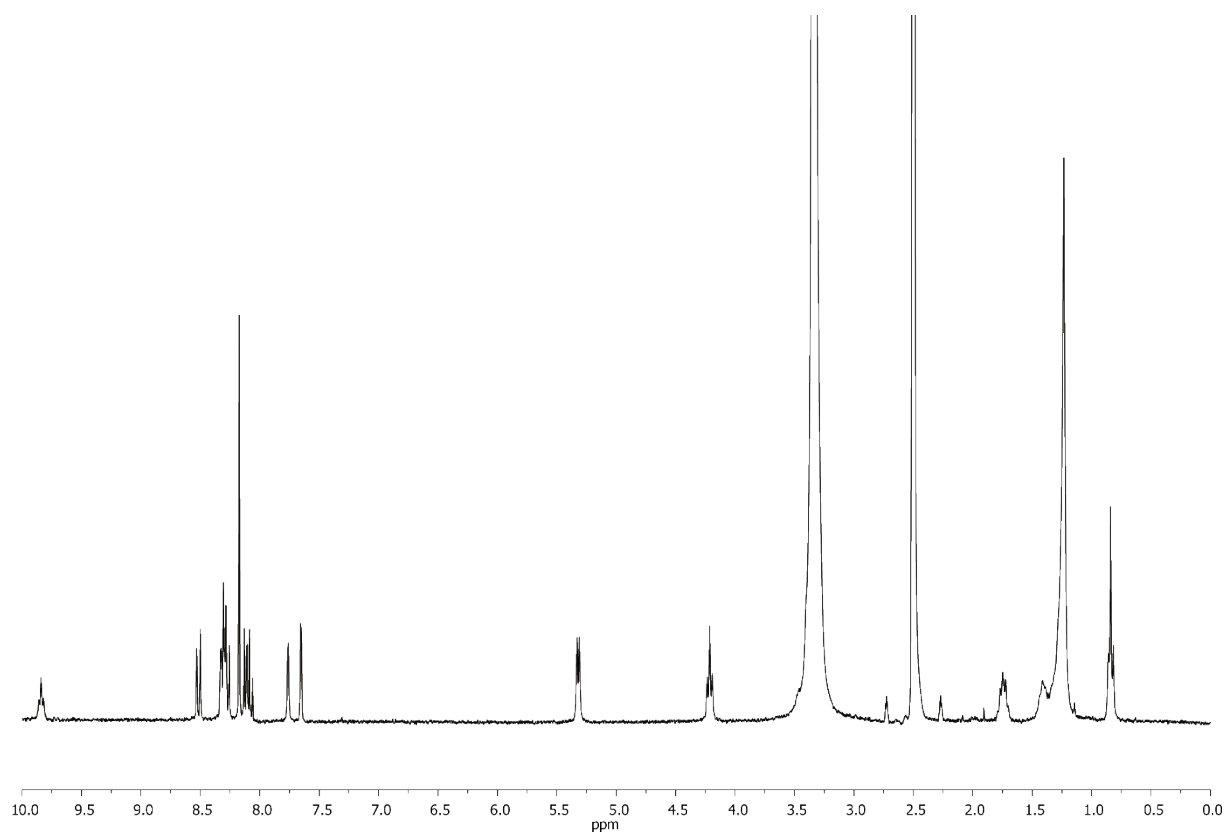




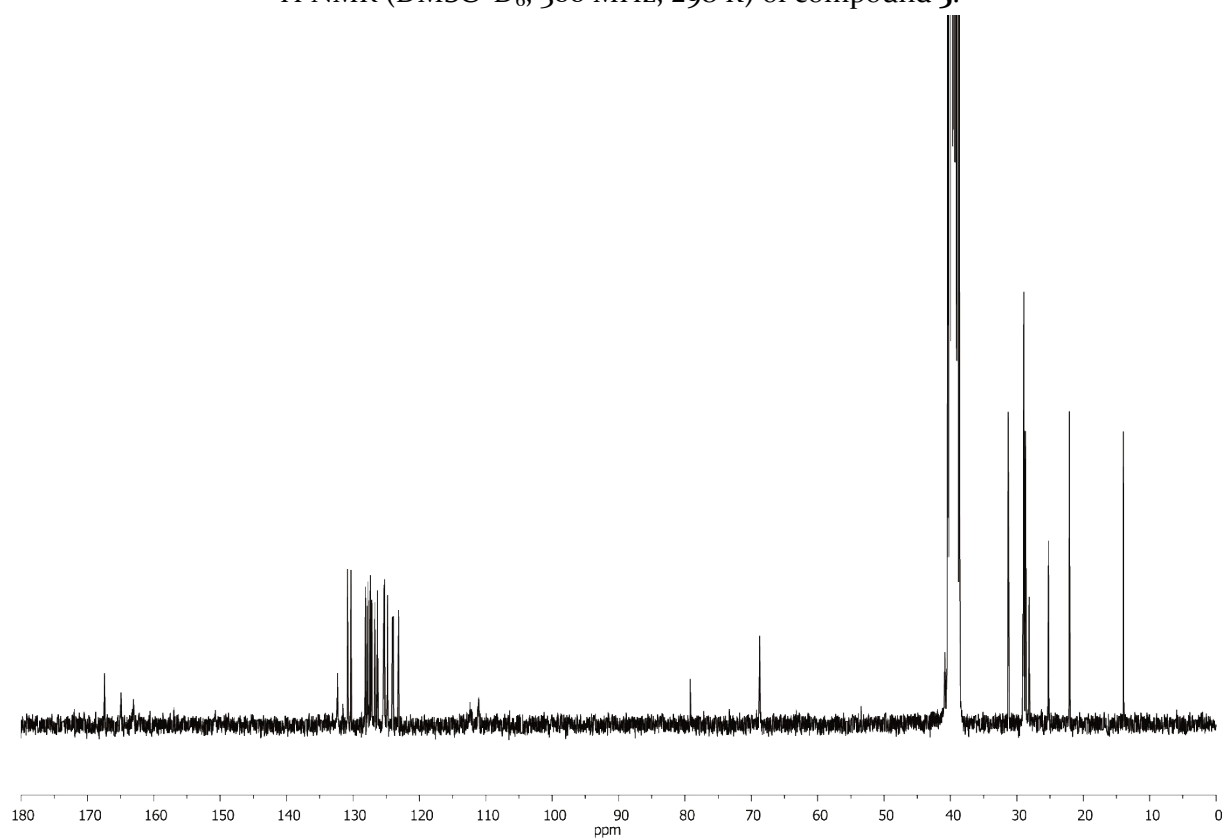
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K) of compound **4**.



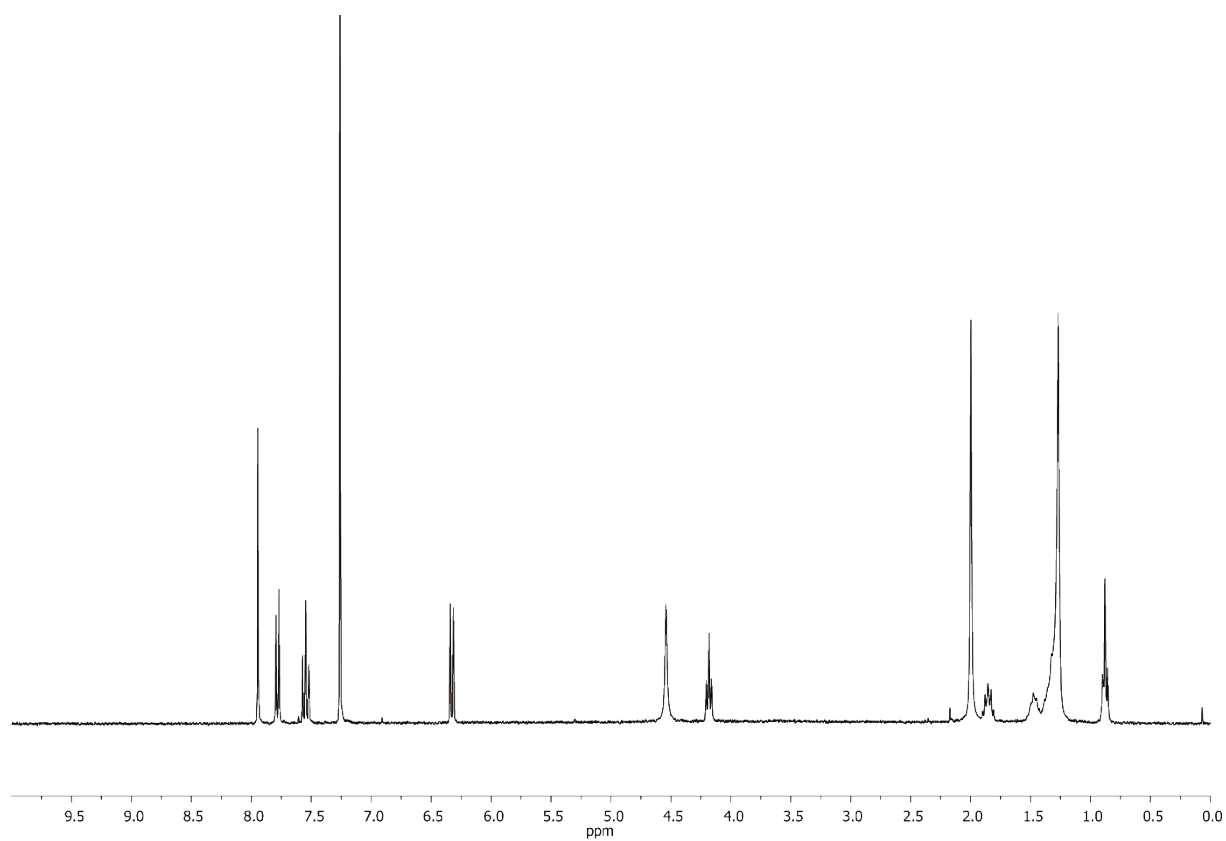
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 298 K) of compound **4**.



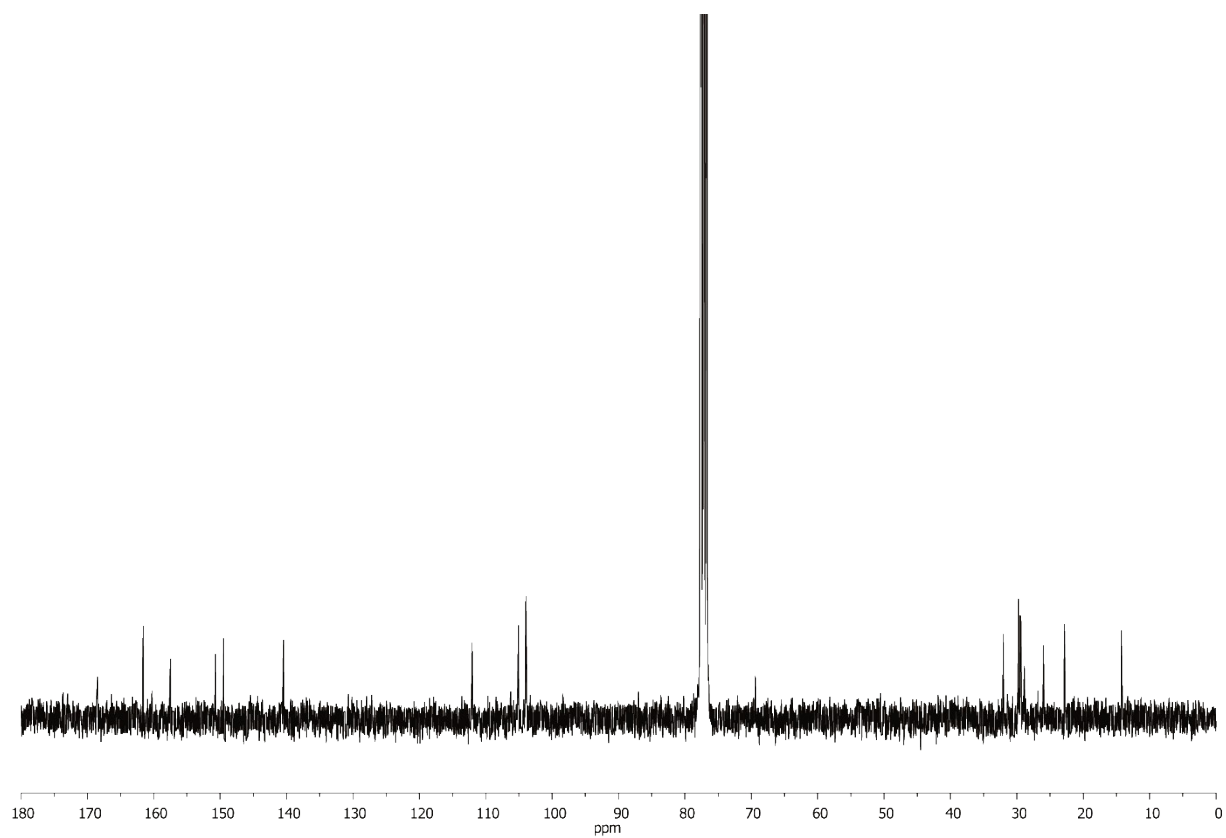
$^1\text{H}$  NMR (DMSO- $\text{D}_6$ , 300 MHz, 298 K) of compound **5**.



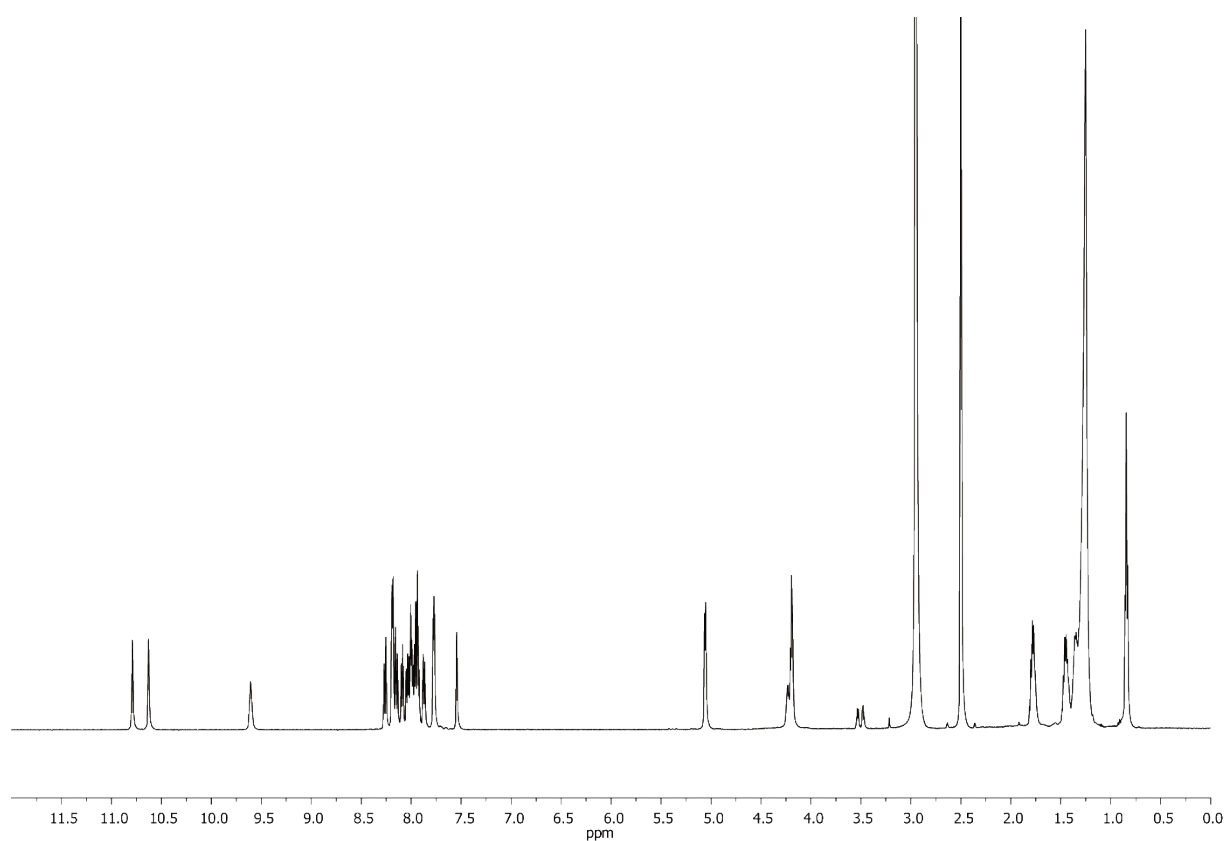
$^{13}\text{C}$  NMR (DMSO- $\text{D}_6$ , 75 MHz, 298 K) of compound **5**.



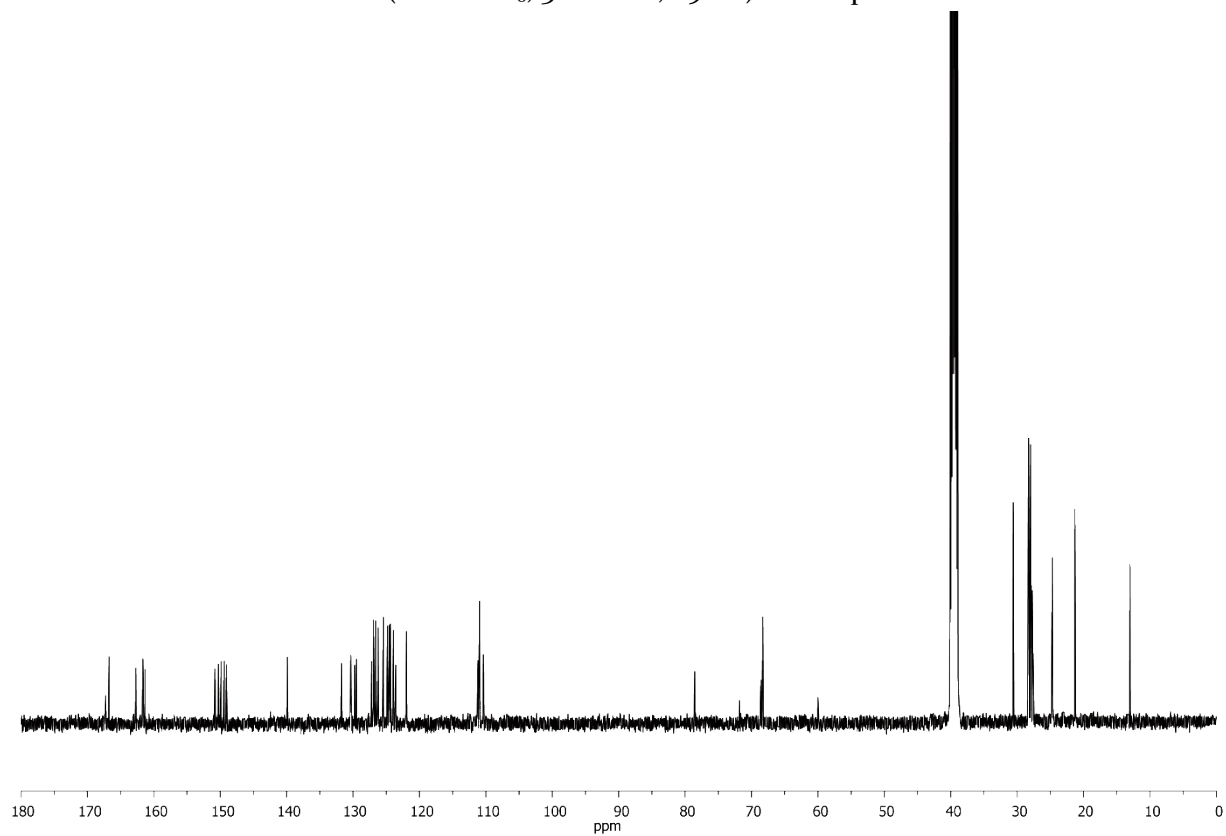
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K) of compound **6**.



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 298 K) of compound **6**.



$^1\text{H}$  NMR (DMSO- $\text{D}_6$ , 300 MHz, 298 K) of compound **1**.



$^{13}\text{C}$  NMR (DMSO- $\text{D}_6$ , 75 MHz, 298 K) of compound **1**.