

## Supporting information

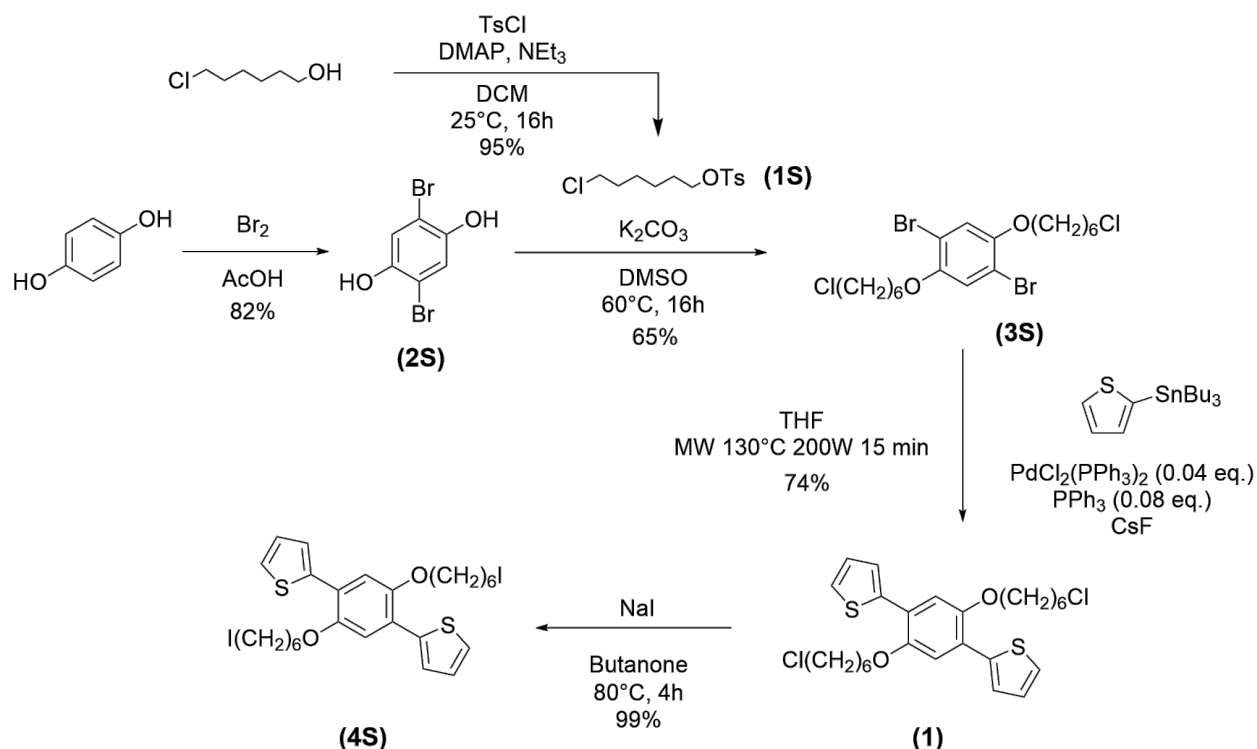
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### Synthesis, solubility and optical properties of $\pi$ -conjugated oligoelectrolytes derived from bis-thiophene-dialkoxyphenylene derivatives

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#### Synthetic procedure

An improved and general procedure has been developed to reach two families of molecular  $\pi$ -conjugated polyelectrolytes : starting from hydroquinone, dibromination was carried out to give **(2S)** in 82% yield after recrystallization. 6-Chlorohexanol which was quantitatively tosylated in the presence of DMAP and triethylamine was reacted in DMSO on the 2,5-dibromohydroquinone **(2S)** in a Williamson etherification, in the presence of potassium carbonate, to give the **(3S)** in 65% isolated yield. Compound **(4S)** resulted from a 74% yield Stille cross-coupling reaction between 2-tributylstannyl thiophene and half equimolar amount of dibrominated moiety **(3S)**, in the presence of bis(triphenylphosphine) dichloropalladium as the catalyst (Scheme 1S).



**Scheme 1S.** Synthesis of oligoelectrolytes precursors.

#### 2,5-dibromohydroquinone (**(2S)**)

50 g (454 mmol, 1.0 eq.) of hydroquinone were dissolved in 300 mL of previously degassed glacial acetic acid in a 3 L three-necked round bottom flask. Then 50 mL of bromine diluted in 100 mL of glacial acetic acid were added dropwise. The mixture was stirred for 24 hours and then carefully poured into 3 L of iced water before filtration. The residue was

recrystallized in 1.3 L of degassed water under nitrogen. After cooling to room temperature, ivory-white crystals were dried in a desiccator before being isolated in 82 % yield. The spectral data agree with those reported in the literature.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.14 (s, 2H), 5.2 (s, 2H).

#### 1,4-dibromo-2,5-bis((6-chlorohexyl)oxy)benzene (3S)

In a 1 L three-necked round bottom flask, 20 g (75 mmol, 1.0 eq.) of 2,5-dibromohydroquinone (**2S**) were dissolved in 200 mL of DMSO and the mixture was degassed by 3 cycles Vacuum/Nitrogen. 30.95 g (224 mmol, 3.0 eq.) of potassium carbonate were then introduced and the mixture was heated at 60°C for an hour. 25.50 g (187 mmol, 2.5 eq.) of 6-chlorohexyl-1-oxy-4-methylbenzenesulfonate (**1S**) were then added dropwise to the medium and the reaction was stirred over-night. After neutralization with HCl (1 M), the organic compound was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The organic layers were washed with a brine solution, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to obtain (**3S**) as a white powder (73% yield) after recrystallization in EtOH. The spectral data agree with those reported in the literature.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.08 (s, 2H, H<sub>Ph</sub>), 3.96 (t, *J* = 6.3 Hz, 4H, OCH<sub>2</sub>), 3.56 (t, *J* = 6.7 Hz, 4H, CH<sub>2</sub>Cl), 1.87-1.78 (m, 8H, 2 CH<sub>2</sub>), 1.57-1.48 (m, 8H, 2 CH<sub>2</sub>). IR (cm<sup>-1</sup>): 3417, 3107, 2940, 2855, 1689, 1638, 1617, 1494, 1465, 1396, 1361, 1307, 1257, 1210, 1057, 1026, 996, 856. MS (FAB) *m/z* (%): 502 (3, M<sup>+</sup>), 460 (4), 391 (3), 307 (35), 154 (100).

#### 1,4-bis(thiophen-2-yl)-2,5-bis(6-chlorohexyloxy)benzene (1)

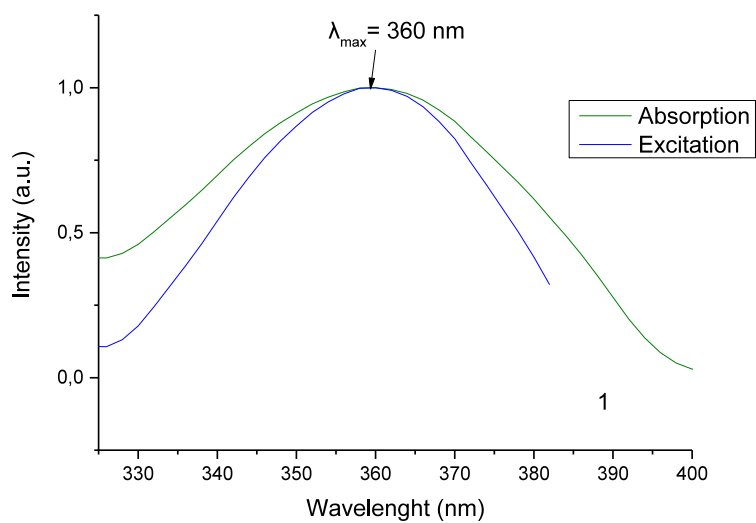
In a 80 microwave vessel, 6.00 g (11.9 mmol, 1.0 eq.) of (**3S**), 9.43 mL (29.7 mmol, 2.5 eq.) of 2-tributylstannyl thiophene, 330 mg (0.48 mmol, 0.04 eq.) of bis(triphenylphosphine)dichloropalladium and 4.51 g (29.7 mmol, 2.5 eq.) of CsF were introduced under nitrogen and dissolved into 10 mL of dry THF. The mixture was stirred at 120 °C at 200 W power for 15 minutes and then cooled to room temperature. The solution was filtered over a plug of silica gel/K<sub>2</sub>CO<sub>3</sub> (10% w/w) and eluted with dichloromethane. The filtrate was concentrated *in vacuo* and the residue was recrystallized in EtOH to obtain (**4S**) as yellowish crystals in 81% yield. The spectral data agree with those reported in the literature.<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ = 7.52 (dd, *J* = 1.0, 3.7 Hz, 2H, H<sub>Th</sub>), 7.34 (dd, *J* = 0.9, 5.1 Hz, 2H, H<sub>Th</sub>), 7.25 (s, 2H, H<sub>Ph</sub>), 7.10 (dd, *J* = 3.7, 5.1 Hz, 2H, H<sub>Th</sub>), 4.09 (t, *J* = 6.4 Hz, 4H, OCH<sub>2</sub>), 3.55 (t, *J* = 6.5 Hz, 4H, CH<sub>2</sub>Cl), 1.97 - 1.86 (m, 4H, CH<sub>2</sub>), 1.87 - 1.78 (m, 8H, 2 CH<sub>2</sub>), 1.58 - 1.42 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 149.31 (C<sub>Ph-O</sub>), 139.29 (C<sub>Th</sub>), 126.87 (CH<sub>Th</sub>), 125.92 (CH<sub>Th</sub>), 125.32 (CH<sub>Th</sub>), 123.13 (C<sub>Ph</sub>), 112.96 (CH<sub>Ph</sub>), 69.57 (OCH<sub>2</sub>), 45.17 (CH<sub>2</sub>Cl), 32.62 (CH<sub>2</sub>), 29.40 (CH<sub>2</sub>), 27.39 (CH<sub>2</sub>), 26.77 (CH<sub>2</sub>). HRMS (CI): Calculated for MH<sup>+</sup>: 511.1299; Found: 511.1293. Chem. Anal. Calculated for C<sub>26</sub>H<sub>32</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 61.04; H, 6.30; S, 12.54; Found: C, 59.16; H, 6.22; S, 12.30.

#### 1,4-bis(thiophen-2-yl)-2,5-bis(6-iodohexyloxy)benzene (4S)

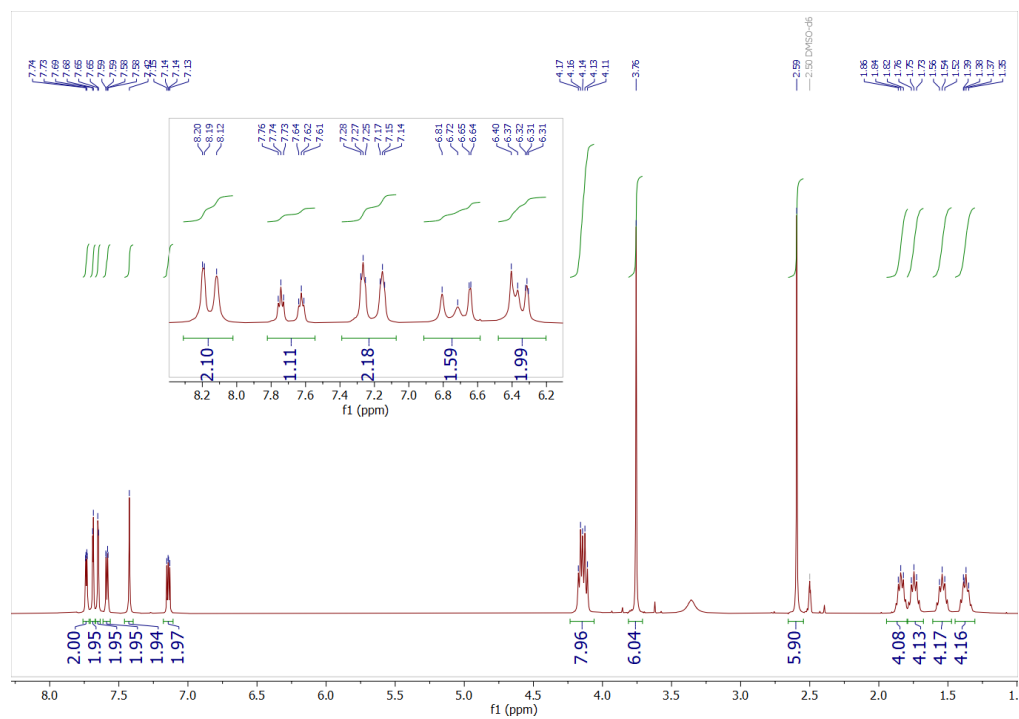
Compound (**4S**) is obtained by reacting (**1**) (5.0 g, 9.77 mmol, 1.0 eq.) with 8 eq. of NaI (11.72 g, 78.19 mmol) in Butanone (50 mL) under nitrogen for 16 hours. After completion, the crude was evaporated and then extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give compound (**4S**) as a yellowish solid with 81% yield.

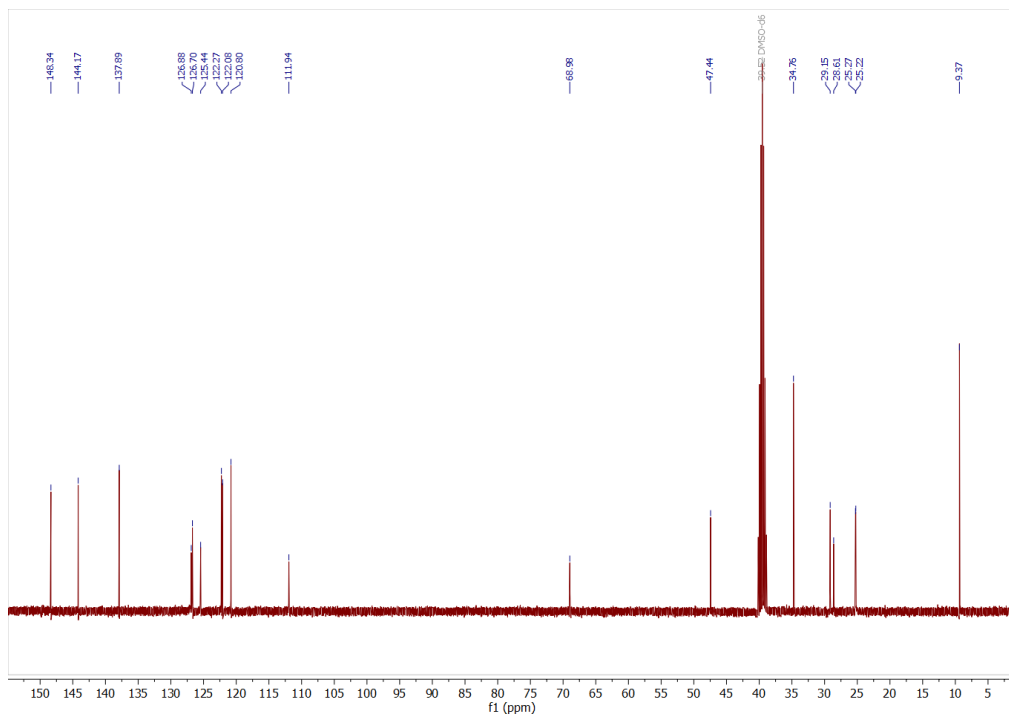
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ = 7.52 (dd, *J* = 3.7, 1.2 Hz, 2H, H<sub>Th</sub>), 7.24 (s, 2H, H<sub>Ph</sub>), 7.10 (dd, *J* = 5.2, 3.7 Hz, 2H, H<sub>Th</sub>), 4.09 (t, *J* = 6.7 Hz, 4H, OCH<sub>2</sub>), 3.20 (t, *J* = 6.8 Hz, 4H, CH<sub>2</sub>I), 1.93 - 1.86 (m, 8H, 2 CH<sub>2</sub>), 1.61 - 1.46 (m, 8H, 2 CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 149.2 (C<sub>Ph-O</sub>), 139.1 (C<sub>Th</sub>), 126.8 (CH<sub>Th</sub>), 125.9 (CH<sub>Th</sub>), 125.3 (CH<sub>Th</sub>), 123.1 (C<sub>Ph</sub>), 113.0 (CH<sub>Ph</sub>), 77.4 (CH<sub>2</sub>O), 29.2 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 17.1 (CH<sub>2</sub>), 7.0 (CH<sub>2</sub>I). IR (cm<sup>-1</sup>): 2935, 2865, 1469, 1395, 1287, 1213, 1039, 1014, 798, 697. HRMS (ESI): Calculated for MH<sup>+</sup>: 695.0011; Found: 694.9999.

**Figure S1. Excitation and absorption spectrum of (1) in CHCl<sub>3</sub> (10<sup>-6</sup> M)**



**Figure S2. <sup>1</sup>H and <sup>13</sup>C NMR spectra of (2.Cl) in DMSO-d<sub>6</sub>**





**Figure S3. Excitation and absorption spectrum of (2.Cl) in CHCl<sub>3</sub> (10<sup>-6</sup> M)**

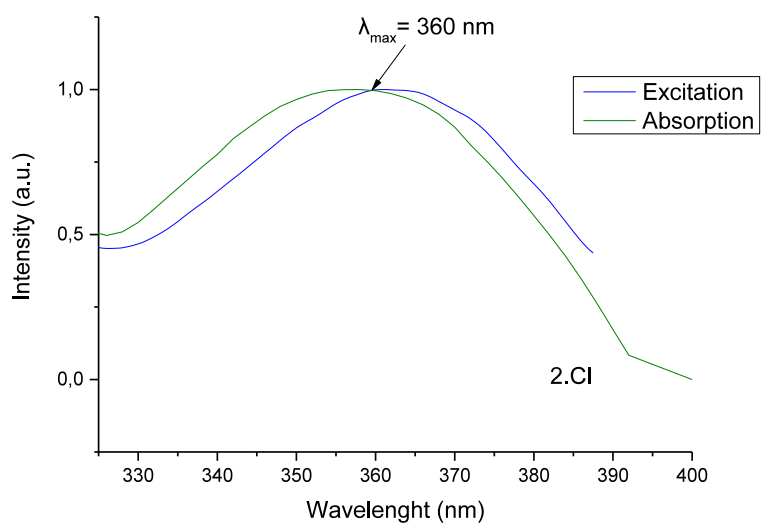
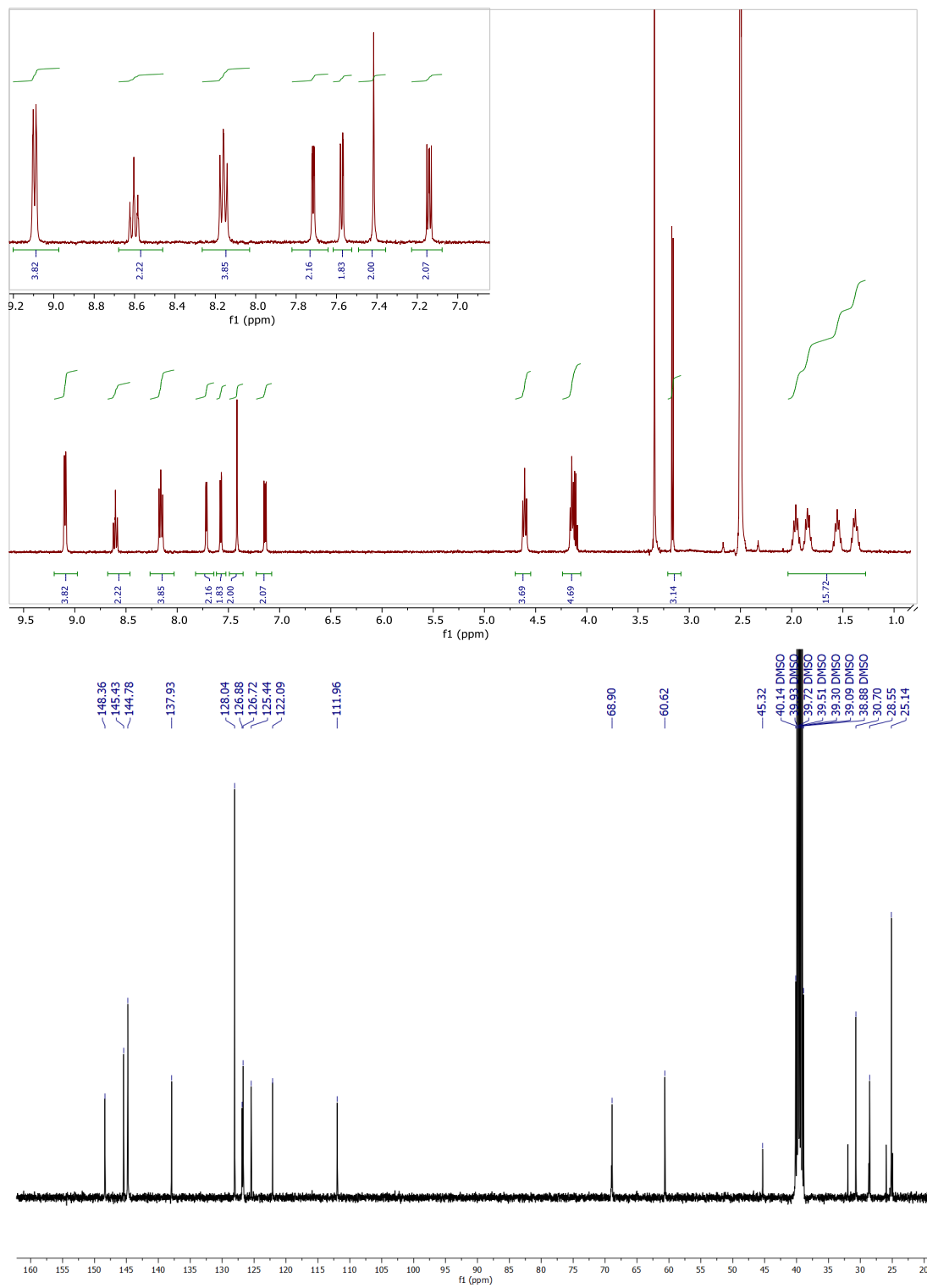
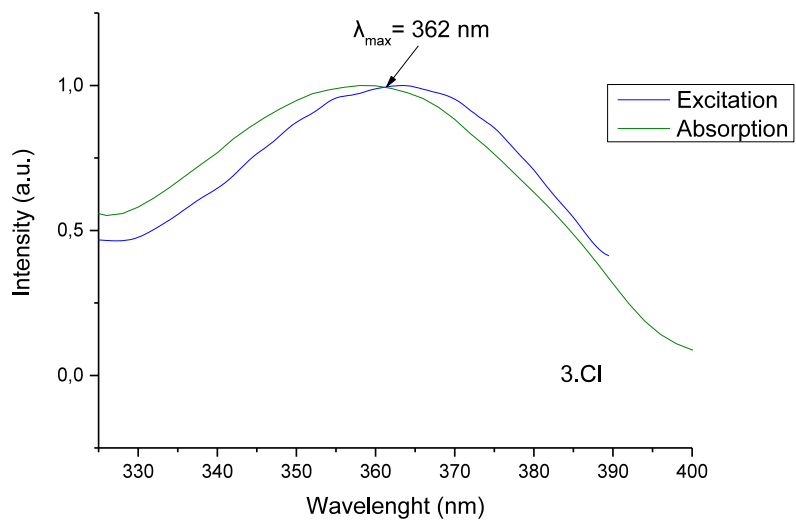


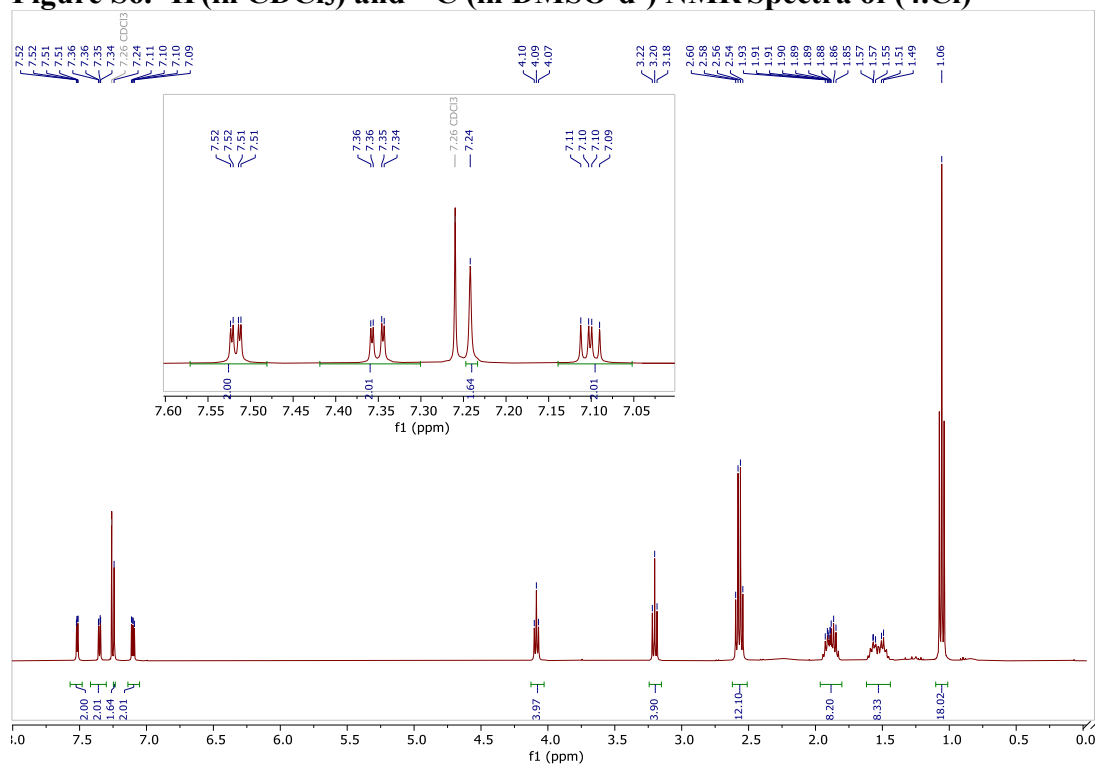
Figure S4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (3.Cl) in  $\text{DMSO-d}_6$

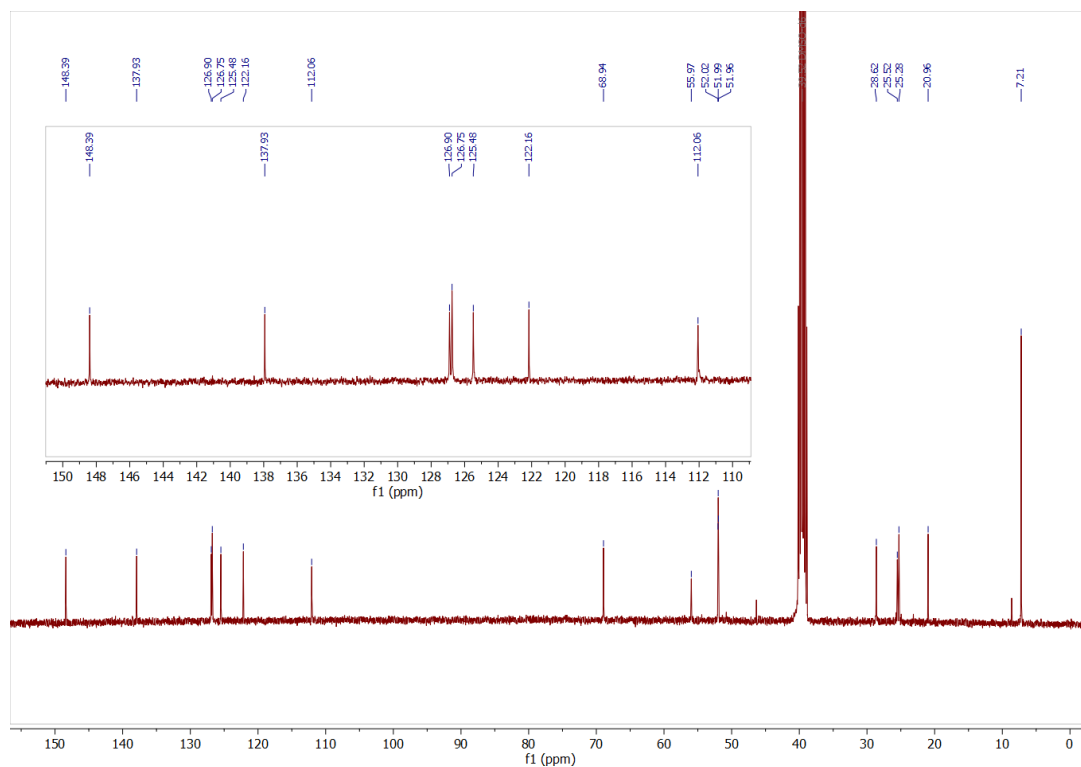


**Figure S5. Excitation and absorption spectrum of (3.Cl) in CHCl<sub>3</sub> (10<sup>-6</sup> M)**

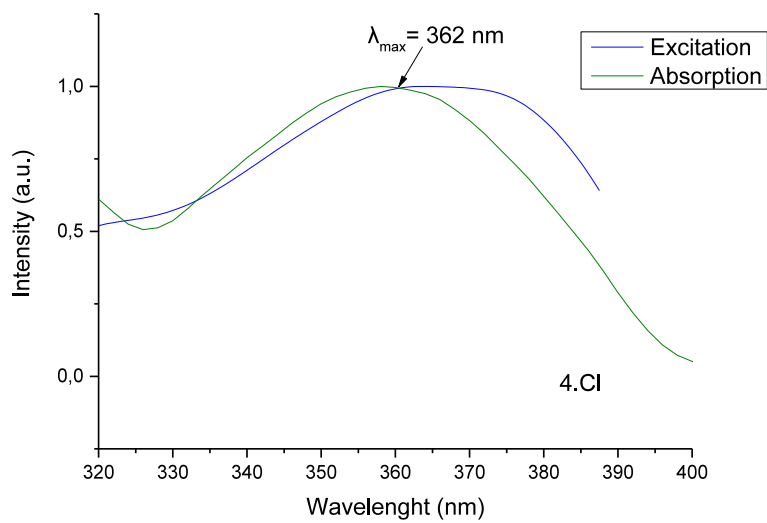


**Figure S6. <sup>1</sup>H (in CDCl<sub>3</sub>) and <sup>13</sup>C (in DMSO-d<sub>6</sub>) NMR Spectra of (4.Cl)**



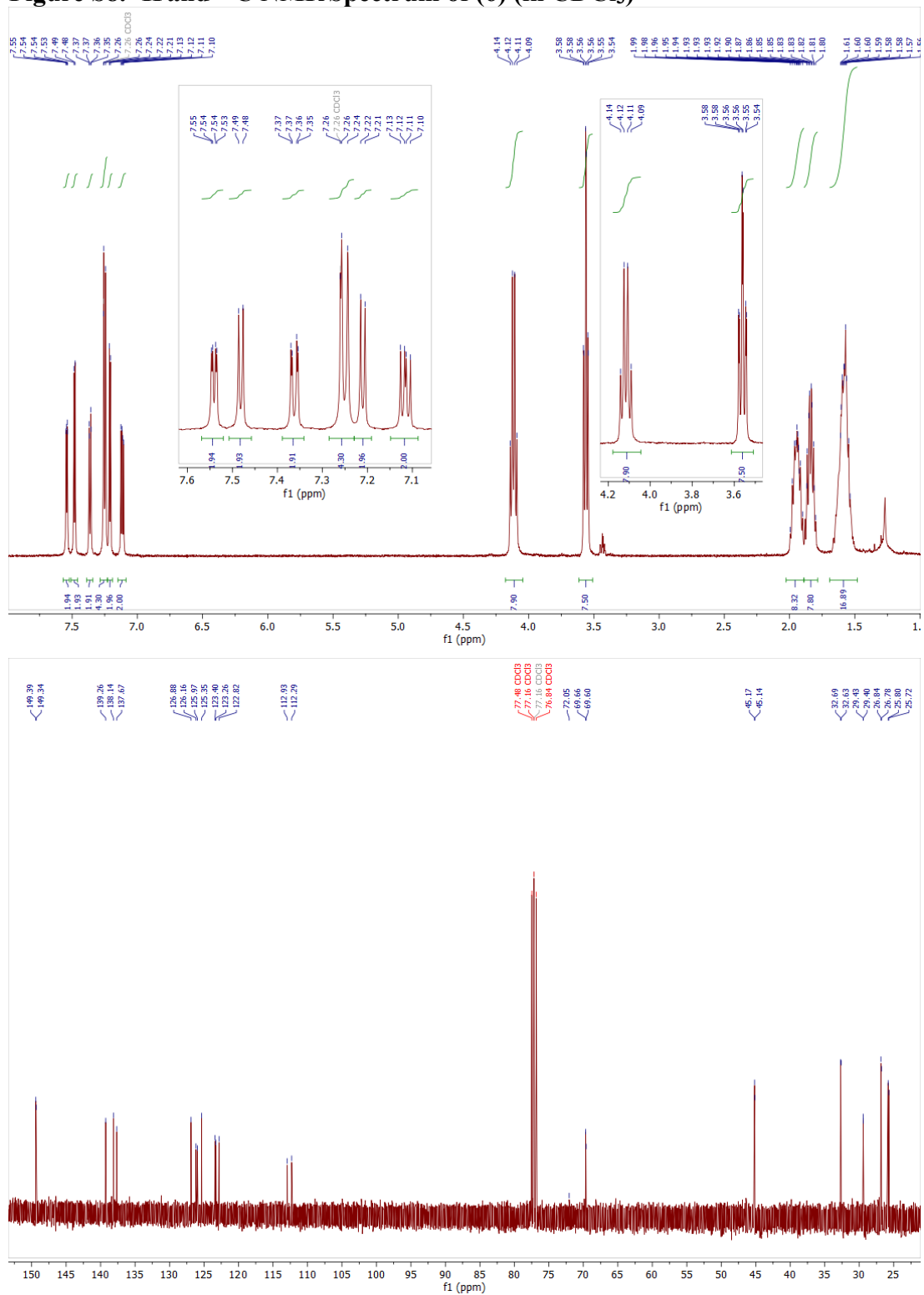


**Figure S7. Excitation and absorption spectrum of (4.Cl) in CHCl<sub>3</sub> (10<sup>-6</sup> M)**



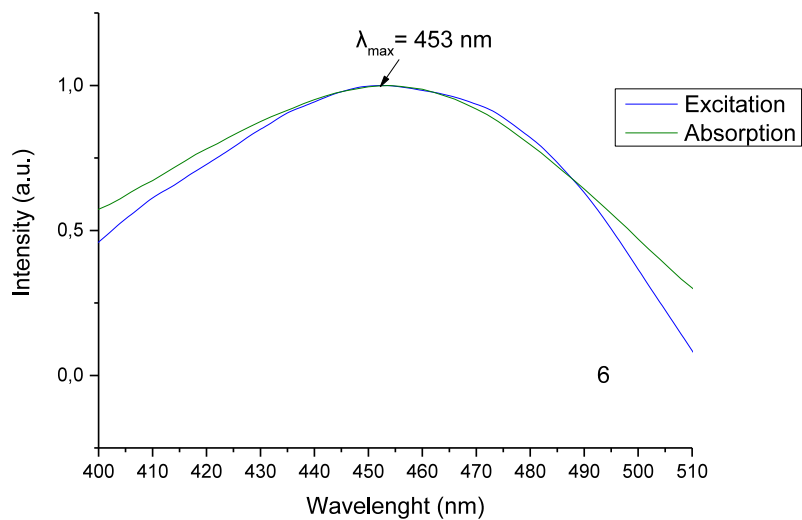
Excitation spectrum from (4.Cl) and (4.F) are identical.

**Figure S8.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectrum of (6) (in  $\text{CDCl}_3$ )**

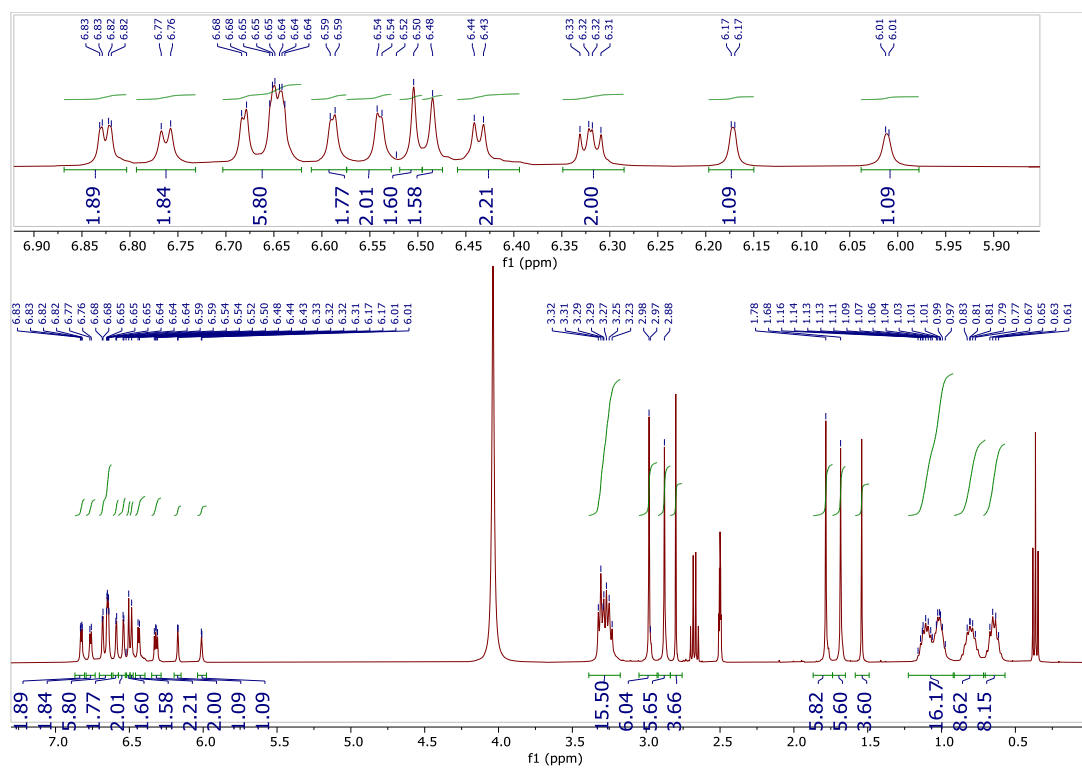


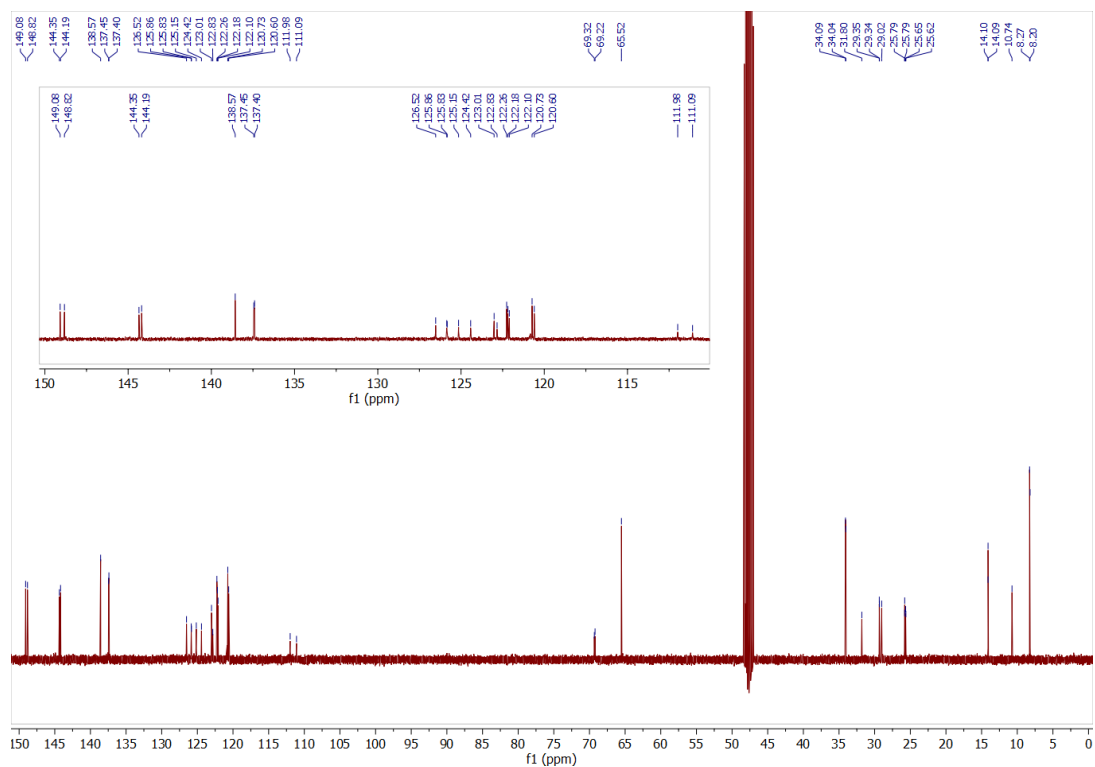


**Figure S9. Excitation and absorption spectrum of (6) in CHCl<sub>3</sub> (10<sup>-6</sup> M)**



**Figure S10. <sup>1</sup>H and <sup>13</sup>C NMR spectra of (7.Cl) in DMSO-d<sub>6</sub>**





**Figure S11. Excitation and absorption spectrum of (7.Cl) in CHCl<sub>3</sub> (10<sup>-6</sup> M)**

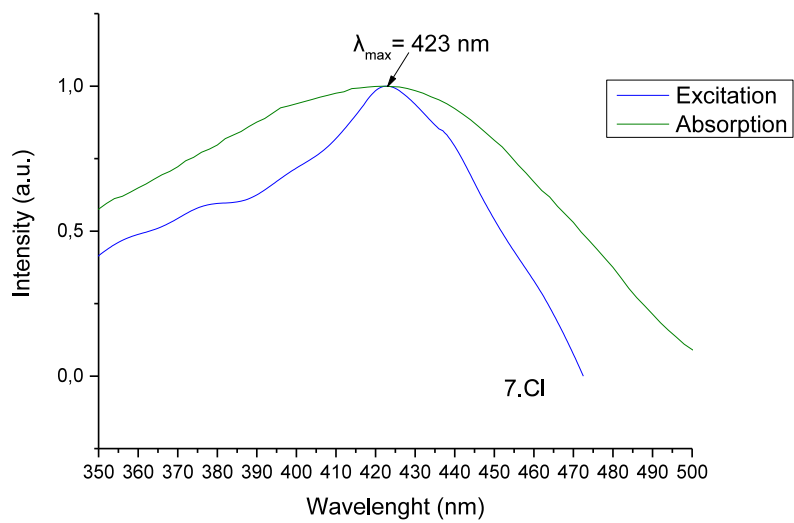
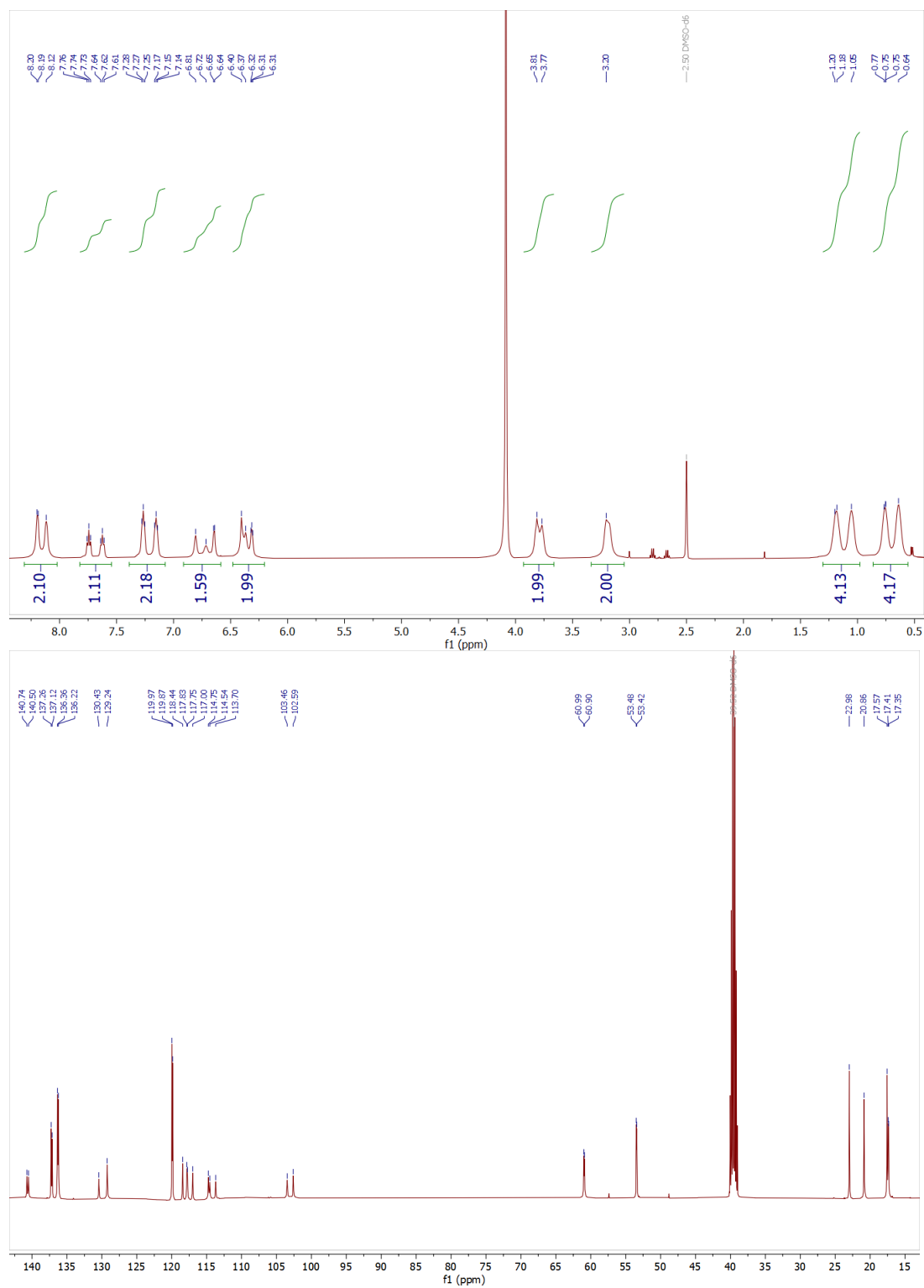


Figure S12. <sup>1</sup>H and <sup>13</sup>C NMR spectra of (8.Cl) in DMSO-d<sub>6</sub>



## **Bibliography:**

1. L. Bian, J. Hai, E. Zhu, J. Yu, Y. Liu, J. Zhou, G. Ge and W. Tang, *J. Mat. Chem. A*, 2015, **3**, 1920-1924.
2. N. Cheminet, T. Jarrosson, J.-P. Lère-Porte, F. Serein-Spirau, L. Cury, J. Moreau, L. Viau and A. Vioux, *J. Mat.Chem.*, 2011, **21**, 13588-13593.
3. S. L. Nogueira, S. K. Sahoo, T. Jarrosson, F. Serein-Spirau, J. P. Lère-Porte, E. A. Moujaes, A. Marletta, A. P. Santos, C. Fantini, C. A. Furtado and R. A. Silva, *J. Colloid Interf. Sci.*, 2016, **464**, 117-125.