

Supplementary Material (ESI) for Chemical Communications  
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## **Electronrich heteroaromatic conjugated bipyridine based ruthenium sensitizer for efficient dye-sensitized solar cells**

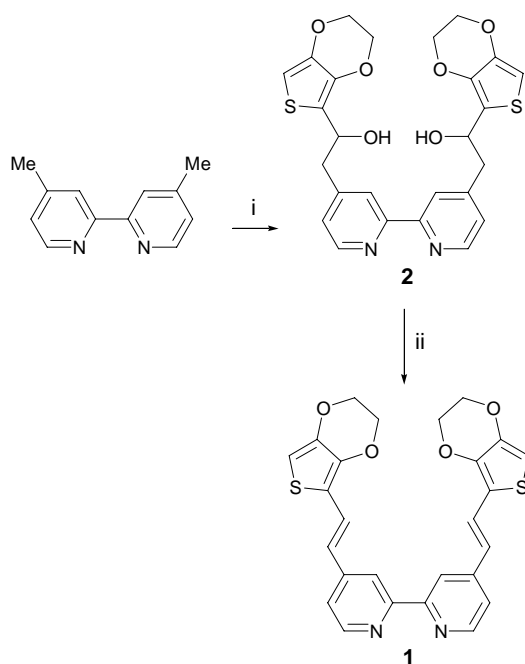
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### **Electronic Supplementary Information**

## Experimental Procedures.

All chemicals and solvents were purchased at the highest purity grade and used without further purification unless otherwise stated. Reactions were performed under nitrogen in dry solvents.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 27 °C using a Bruker AMX-500 (ligand) or a Bruker AC-400 spectrometer (Ru-EDOT complex). Coupling constants  $J$  are given in Hertz. Ligand low resolution mass spectra were recorded on a Applied Biosystems API 2000 QTrap LC/MS/MS system, while high resolution mass spectrometry was provided by the Washington University Mass Spectrometry Resource (NIH National Center for Research Resources P41RR0954). Ru\_EDOT mass spectra were recorded on a Thermo Finnigan Advantage Max Ion Trap Spectrometer in negative ion acquiring mode; sheath gas flow rate was set at 25 (arbitrary unit), auxiliary gas flow rate at 5 (arbitrary unit), spray voltage at 3,25 (KV), capillary temperature at 270 °C, capillary voltage at -7 (V), and tube lens offset at -60,00 (V). Nitrogen was used as sheath and auxiliary gas.

## Synthesis of ligand 1.



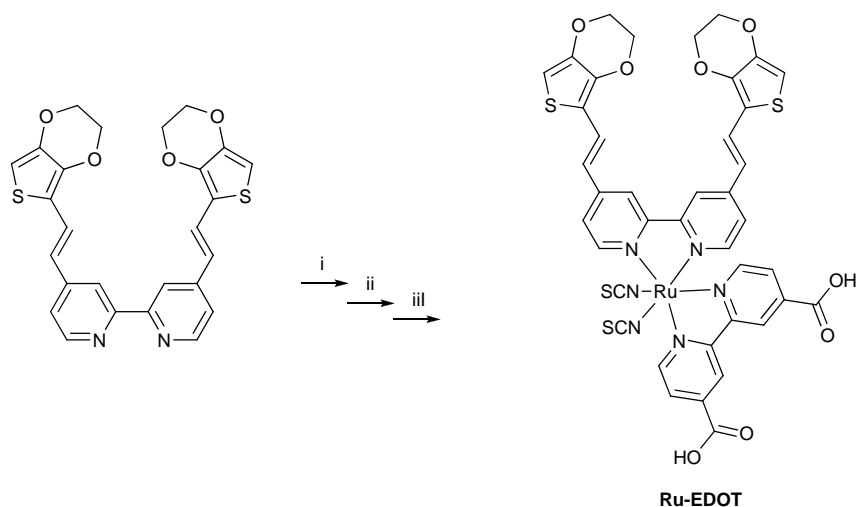
**Scheme 1** Synthesis of ligand 1. i. 3,4-ethylenedioxythiophene-2-carbaldehyde, LDA, THF, 0°C; ii. POCl<sub>3</sub>, pyridine, rt  
→ -78 °C, 15 s.

**4,4'-Bis[2-hydroxy-2-(3,4-ethylenedioxythien-2-yl)ethyl]-2,2'-bipyridine (2).** LDA (1.8 mL, 1.8 M in hexane, 3.24 mmol) was added dropwise to a stirred solution of 4,4'-dimethyl-2,2'-bipyridine (270 mg, 1.47 mmol) in THF (15 mL) at 0 °C. After 10 minutes a solution of 3,4-ethylenedioxythiophene-2-carbaldehyde<sup>1</sup> (500 mg, 2.94 mmol) in THF (15 mL) was added dropwise and the resulting mixture was allowed to warm up to room temperature and stirred for 1.5 h. AcOEt and brine were added to the reaction mixture. The organic layer was separated, washed to neutrality, dried, and evaporated to dryness to give **2** as a pale yellow solid (440 mg, 0.84 mmol, 57%) which was used without any further purification in the subsequent step;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.56 (2 H, d, *J* 4.8, 2 H, H<sub>6</sub> pyridine), 8.32 (2 H, s, H<sub>3</sub> pyridine), 7.20 (2 H, d, *J* 5.0, H<sub>5</sub> pyridine), 6.28 (2 H, s, H<sub>5</sub> EDOT), 5.29 (2 H, t, *J* 6.7, CHOH), 4.20-4.10 (8 H, m, CH<sub>2</sub> EDOT), 3.22 (4 H, d, *J* 6.8, 4 H, CH<sub>2</sub>CHOH).

**4,4'-Bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2'-bipyridine (1).** Diol **2** (2.80 g, 5.34 mmol) was dissolved in pyridine (80 mL). Freshly distilled POCl<sub>3</sub> (5 mL, 8.3 g, 54.1 mmol) was added at room temperature in 15 s and the resulting mixture was quickly cooled to -78 °C. H<sub>2</sub>O (50 mL) and AcOEt (10 mL) were added to the reaction mixture to give a dark brown precipitate which was collected by filtration and suspended in CHCl<sub>3</sub> (100 mL). The suspension was filtered and the solvent partially removed under reduced pressure to leave a yellow/brown solid, which was collected by filtration and taken up with EtOH (150 mL). A solution of HBF<sub>4</sub> (1 mL, 8 M in H<sub>2</sub>O) was added and the mixture stirred overnight. The resulting red solid was collected and treated with a saturated solution of NaHCO<sub>3</sub> (50 mL) for 12 h to afford the product as a dark yellow solid (1.20 g, 2.52 mmol, 47%): mp > 250 °C;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.64 (2 H, d, *J* 5.1, H<sub>6</sub> pyridine), 8.48 (2 H, s, H<sub>3</sub> pyridine), 7.50 (2 H, d, *J* 16.2, olefin proton  $\beta$  to pyridine), 7.36 (2 H, dd, *J* 5.1 and 1.5 Hz, H<sub>5</sub> pyridine), 6.93 (2 H, d, *J* 16.2, olefin proton  $\alpha$  to pyridine), 6.35 (2 H, s, H<sub>5</sub> EDOT), 4.36-4.32 (4 H, m, CH<sub>2</sub> EDOT), 4.29-4.24 (4 H, m, CH<sub>2</sub> EDOT);  $\delta_{\text{C}}$  (125.77 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si)

156.17 (2C, C), 149.28 (2C, CH), 146.11 (2C, C), 142.07 (2C, C), 140.74 (2C, C), 123.41 (2C, CH), 122.99 (2C, CH), 120.50 (2C, CH), 118.03 (2C, CH), 116.16 (2C, C), 99.86 (2C, CH), 64.93 (2C, CH<sub>2</sub>), 64.67 (2C, CH<sub>2</sub>); LRMS-ESI  $m/z$  489 ( $[M+H]^+$ , 100%); HRMS-ESI  $m/z$  found 489.0936, calc. for  $M+H$  489.0943.

### Synthesis of complex Ru-EDOT.



**Scheme 2** Synthesis of complex **1**. i.  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  dimer, DMF, 80°C, 4h, dark; ii. 4,4'-dicarboxylic acid-2,2'-bipyridine, DMF, 100→130°C, 9h, dark; iii.  $\text{NH}_4\text{NCS}$ , DMF, 90°C, overnight, dark.

### Ru-EDOT complex

4,4'-Bis[(E)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2'-bipyridine ligand (0.050 g, 0.102 mmol) and dichloro(*p*-cymene)ruthenium(II) dimer (0.031 g, 0.052 mmol) in DMF were heated at 80 °C for 4 h under argon in the dark. After this period, 4,4'-dicarboxylic acid-2,2'-bipyridine (25 mg, 0.102 mmol) was added and the reaction mixture was heated to 100 °C for another 4 h and then to 130 °C for 5 h. To the resulting dark green solution was added solid  $\text{NH}_4\text{NCS}$  (0.15 g, 2 mmol) and then the reaction mixture was further heated overnight at 90 °C. DMF was removed on a rotary evaporator under vacuum and water (20 ml) was added to get the precipitate. The purple solid was filtered off, washed with water and  $\text{Et}_2\text{O}$ , and dried under vacuum. To the crude compound was then added basic methanol (20 ml + 0.1 mmol TBAOH) to get a new precipitate (Yield: 95%) which was filtered off, washed with water, DCM, and  $\text{Et}_2\text{O}$ , and dried under vacuum.

$\delta_{\text{H}}$  (400 MHz,  $\text{DMSO-d}_6$ ): 9.32 (1H, d,  $J$  5.2, H pyridine), 9.06 (1H, d,  $J$  = 5.2, H pyridine), 8.92 (2H, d, H pyridine), 8.76 (2H, d, H pyridine), 8.21 (1H, d,  $J$  5.2, H pyridine), 8.04 (1H, d,  $J$  5.2, H

pyridine), 7.88 (1H, d,  $J$  12, olefin proton  $\beta$  to pyridine), 7.71 (1H, d,  $J$  5.2, H pyridine), 7.62 (1H, d,  $J$  12, olefin proton  $\beta$  to pyridine), 7.57 (1H, d,  $J$  5.2, H pyridine), 7.29 (2H, m, H pyridine), 7.10 (1H, d,  $J$  12, olefin proton  $\alpha$  to pyridine), 6.82 (1H, d,  $J$  12, olefin proton  $\alpha$  to pyridine), 6.79 (1H, s, H thiophene), 6.72 (1H, s, H thiophene), 4.41-4.22 (8H, m, CH<sub>2</sub> EDOT). MS (ESI, anion mode): found 949 (molecular anion, 100%), 951 (72%), 948 (68%).

This compound was further purified on the Sephadex LH-20 with methanol as eluent. The main band was collected, concentrated, and precipitated with acidic methanol (pH=5.3) in order to obtain pure **RuEDOT** (yield: 35%), with approximately one equivalent of TBA.

See Figure SI4 for NMR spectra.  $\delta_{\text{H}}$  (400 MHz, DMSO-d<sub>6</sub>): 9.25 (1H, d,  $J$  5.2, H pyridine), 9.09 (1H, d,  $J$  = 5.2, H pyridine), 8.94 (1H, s, H pyridine), 8.84 (1H, s, H pyridine), 8.79 (1H, s, H pyridine), 8.69 (1H, s, H pyridine), 8.26 (1H, d,  $J$  5.2, H pyridine), 8.05 (1H, d,  $J$  5.2, H pyridine), 7.90 (1H, d,  $J$  12, olefin proton  $\beta$  to pyridine), 7.62 (2H, d + d,  $J$  12,  $J$  5.2, olefin proton  $\beta$  to pyridine + H pyridine), 7.53 (1H, d,  $J$  5.2, H pyridine), 7.30 (2H, m, H pyridine), 7.10 (1H, d,  $J$  12, olefin proton  $\alpha$  to pyridine), 6.82 (1H, d,  $J$  12, olefin proton  $\alpha$  to pyridine), 6.80 (1H, s, H thiophene), 6.73 (1H, s, H thiophene), 4.42-4.24 (8H, m, CH<sub>2</sub> EDOT), 3.16 (10H, t, NCH<sub>2</sub>CH<sub>2</sub> TBA), 1.56 (10H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> TBA), 1.30 (10H, q, CH<sub>2</sub>CH<sub>3</sub> TBA), 0.93 (15H, t, CH<sub>3</sub> TBA). MS (ESI, anion mode): 949 (molecular anion), 1190 (molecular anion + TBA)

## Electrochemistry

Electrochemical data were obtained by cyclic-voltammetry using a three-electrode cell and an Auto lab System (PGSTAT 30, GPES 4.8 software). The working electrode was a 0.03 cm<sup>2</sup> glassy carbon disk, the auxiliary electrode was a platinum foil, and a platinum wire was used as quasi-reference electrode. The sensitizers were dissolved in dimethylformamide (DMF) containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. After the measurement, ferrocene was added as the internal reference for calibration.

## DSC preparation

The FTO glass substrates were immersed in 40 mM TiCl<sub>4</sub> *aq.* at 70 °C for 30 min and washed with water and ethanol. The 7 or 9  $\mu\text{m}$  thick mesoporous nano-TiO<sub>2</sub> films composed of 20 nm anatase TiO<sub>2</sub> particles were coated on the FTO glass plates by repetitive screen printing. After

drying the nanocrystalline TiO<sub>2</sub> layer at 125 °C, a 5 μm thick second layer of 400 nm sized light scattering anatase particles (CCIC, HPW-400) was deposited by screen printing onto the transparent layer. The TiO<sub>2</sub> electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and 500 °C for 15 min. The TiO<sub>2</sub> electrodes were treated again by TiCl<sub>4</sub> and sintered at 500 °C for 30 min. The dye-adsorbed TiO<sub>2</sub> electrode and thermally platinised counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film (Surlyn 1702, 25 μm thickness, Du-Pont).

### **Photochemical measurements**

The measurement of incident photon-to-current conversion efficiency (IPCE) was plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.). In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO<sub>2</sub> layer, a light shading mask was used onto the DSCs, so active area of DSCs was fixed to 0.2 cm<sup>2</sup>. The irradiation source was a 450 W xenon light source (Osram XBO 450, USA), whose power of an AM 1.5 solar simulator was calibrated by using a reference Si photodiode equipped with an IR cut-off filter (KG-3, Schott) in order to reduce the mismatch in the region of 350-750 nm between the simulated light and AM 1.5 to less than 2%. The measurement delay time of photo I-V characteristics of DSCs was fixed to 40 ms. The active area of DSCs was 0.2 cm<sup>2</sup> same like IPCE measurement.

### **Computational Details.**

All calculations were performed using the B3LYP exchange-correlation functional together with 3-21G\* and DZVP basis sets for geometry optimizations and excited states calculations, respectively. Solvation effects were included by means of the C-PCM solvation model, as implemented in the Gaussian03 program package.<sup>2</sup>

We considered in both cases the protonated dyes and optimized the corresponding geometrical structures in water solution, followed by TDDFT calculation of vertical excitation energies.

The calculated absorption spectrum has been obtained from vertical excitation energies and oscillator strengths by a Gaussian convolution with  $\sigma=0.15$  eV, corresponding to a FWHM of ca. 0.37 eV. The two spectra have been rescaled so that the intensity of the low-energy absorption bands match.

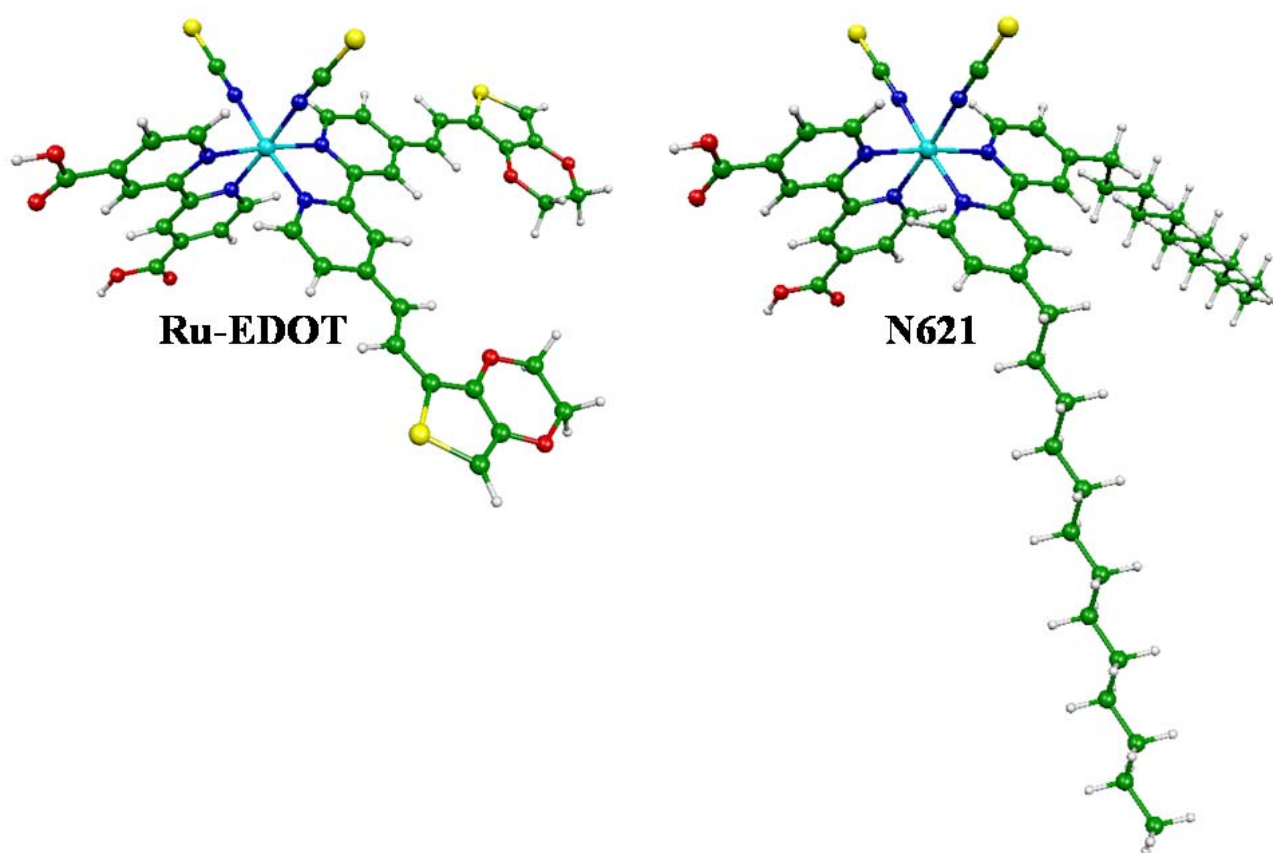


Figure S1. Optimized molecular structures of Ru-EDOT and of the N621 sensitizers.

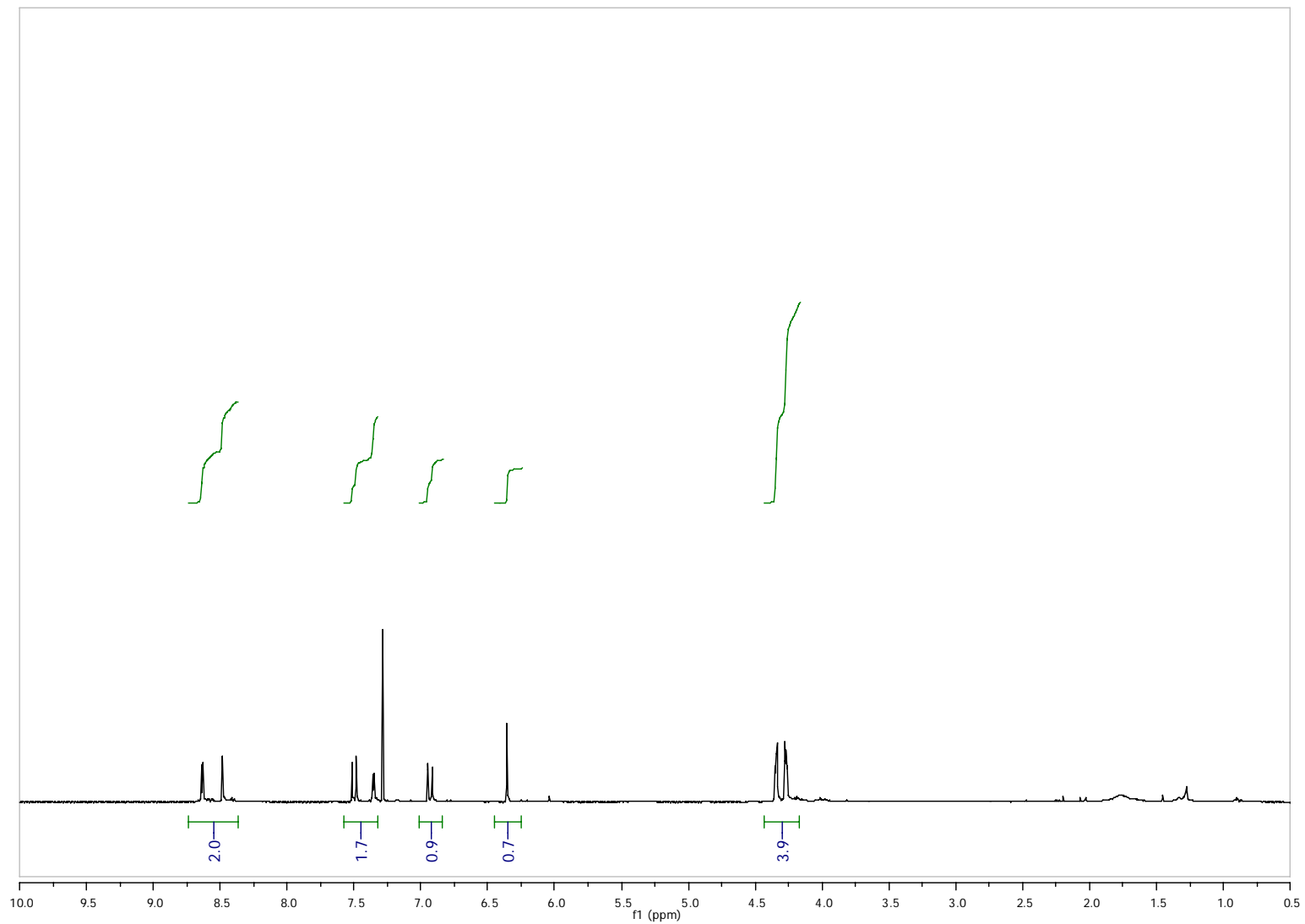


Figure S2a.  $^1\text{H}$  NMR spectrum of 4,4'-Bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2'-bipyridine (**1**) ( $\text{CDCl}_3$ )



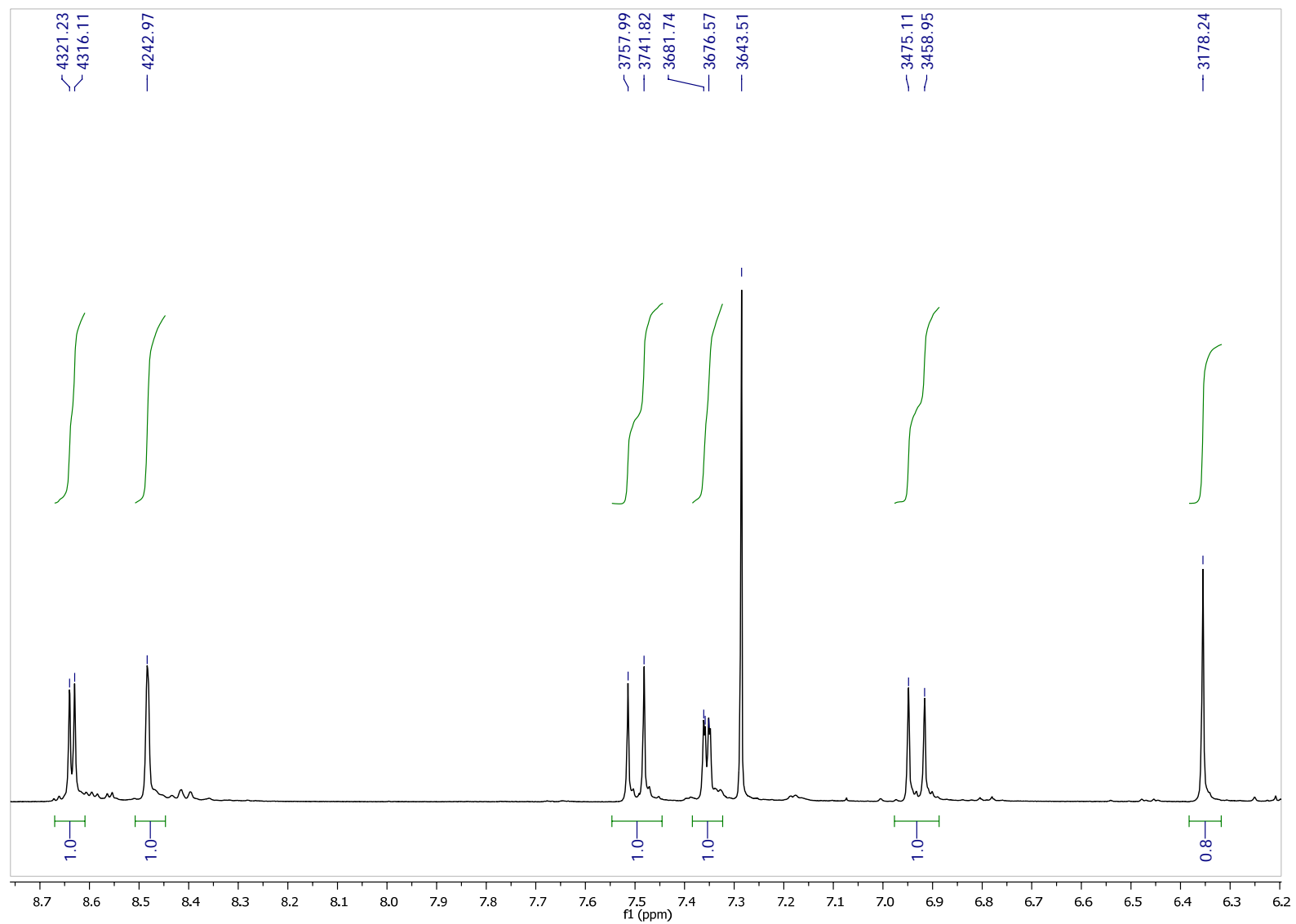


Figure S2b. <sup>1</sup>H NMR spectrum of 4,4'-Bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2'-bipyridine (**1**) (CDCl<sub>3</sub>, aromatic region).

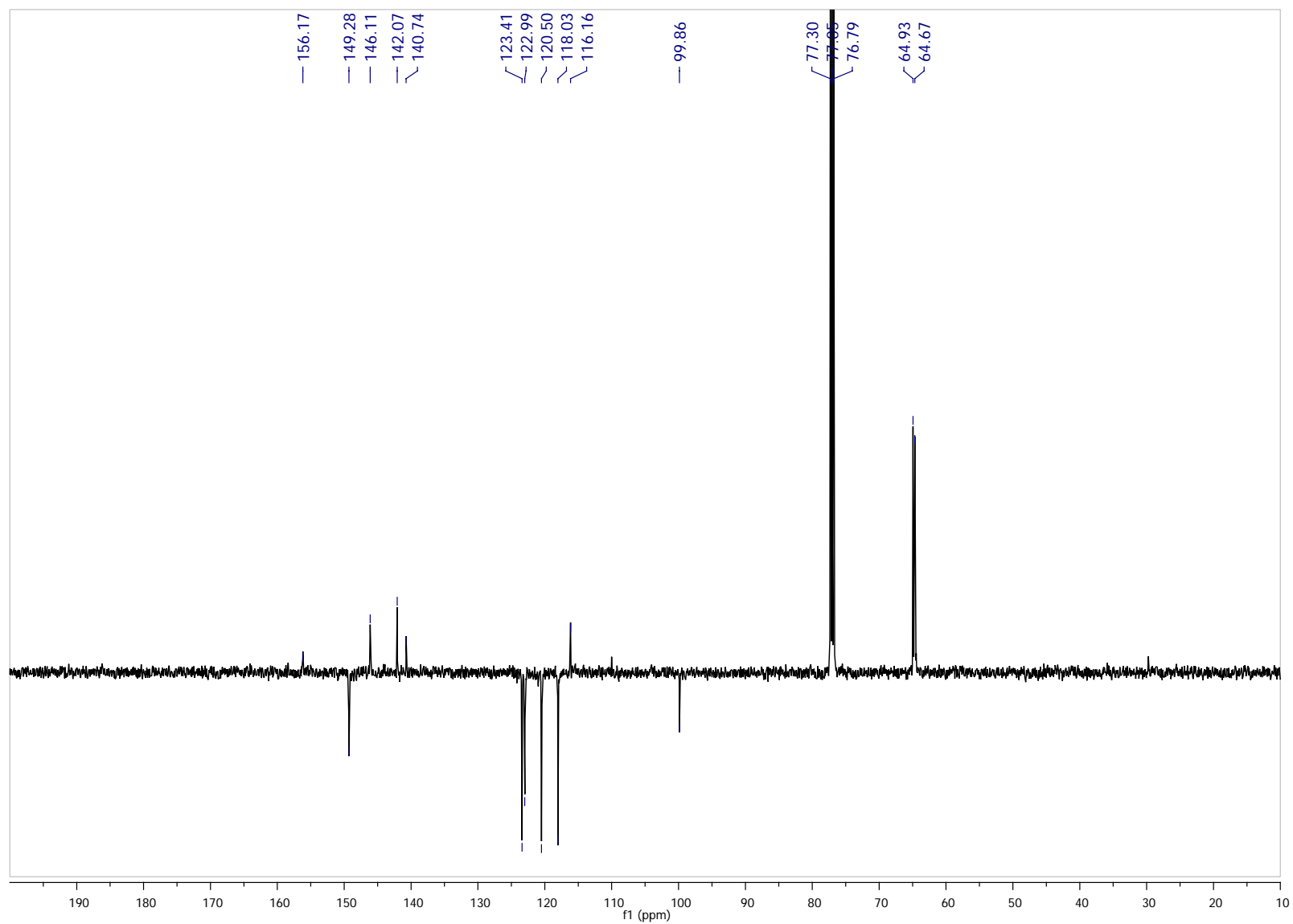


Figure S3a.  $^{13}\text{C}$  NMR spectrum of 4,4'-Bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2'-bipyridine (**1**) ( $\text{CDCl}_3$ ).

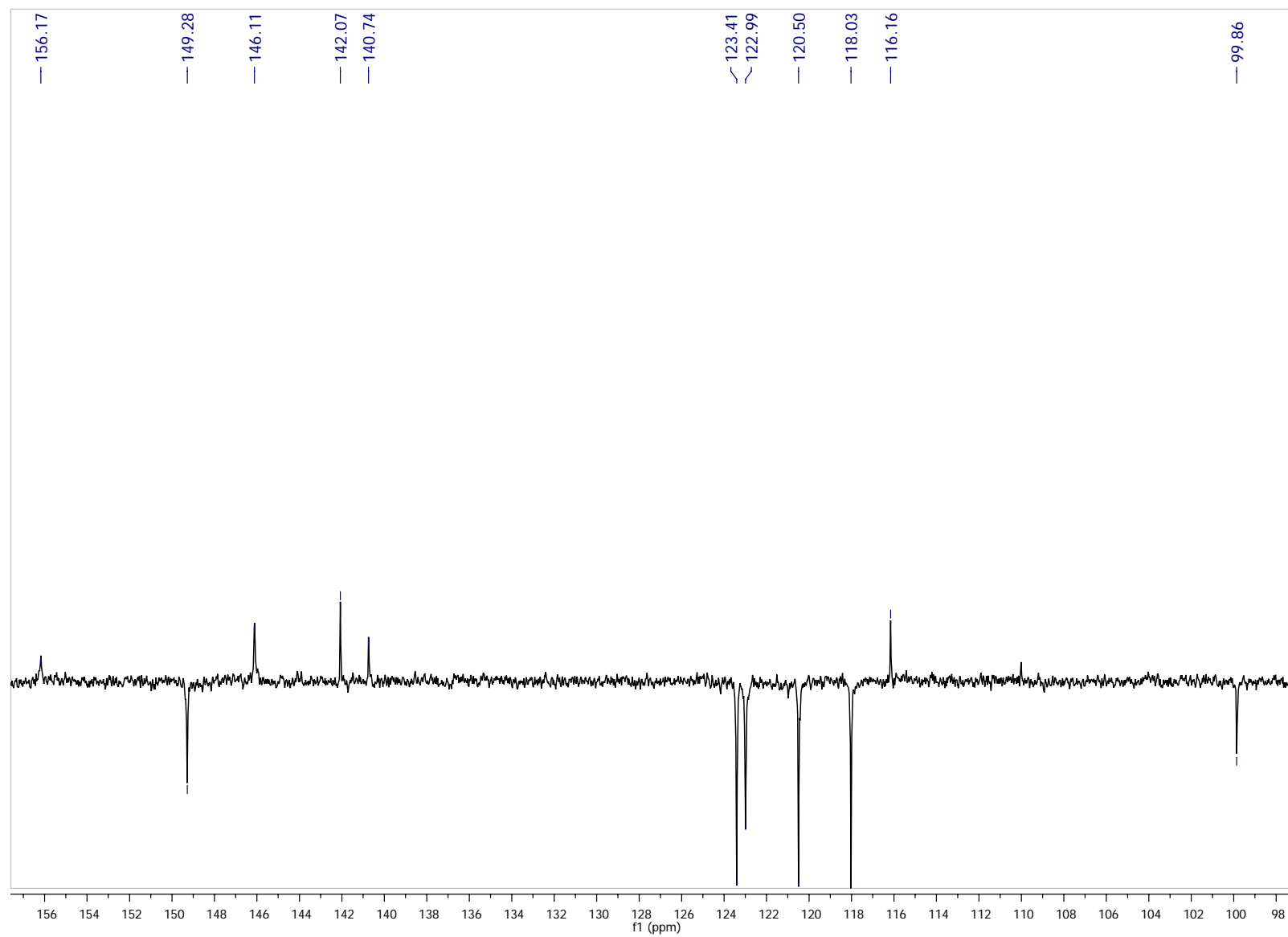


Figure S3b. <sup>13</sup>C NMR spectrum of 4,4'-Bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2'-bipyridine (**1**) (CDCl<sub>3</sub>, aromatic region).

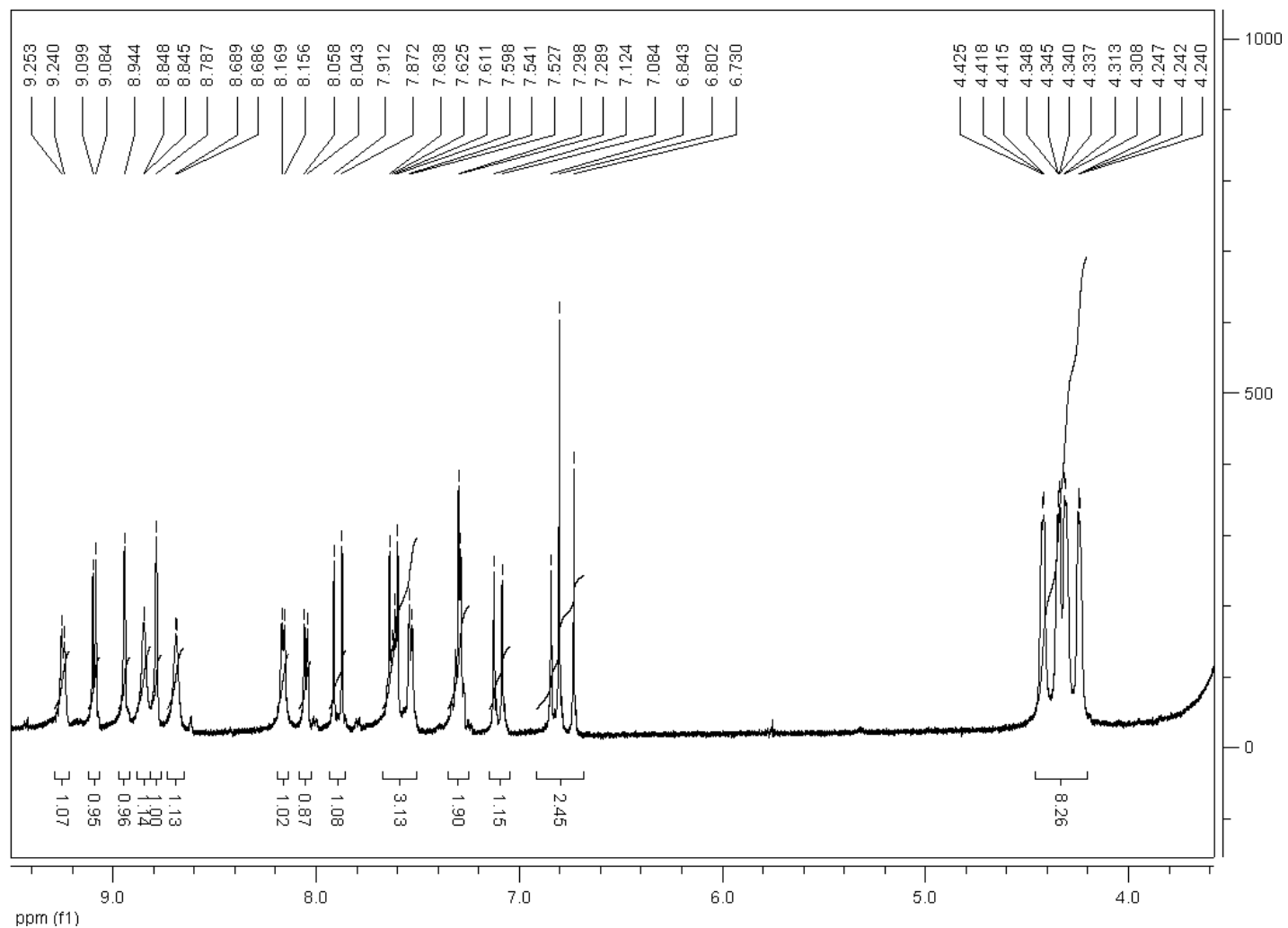


Figure S4a. <sup>1</sup>H NMR spectrum of Ru-EDOT complex (aliphatic region) (DMSO-d<sub>6</sub>).

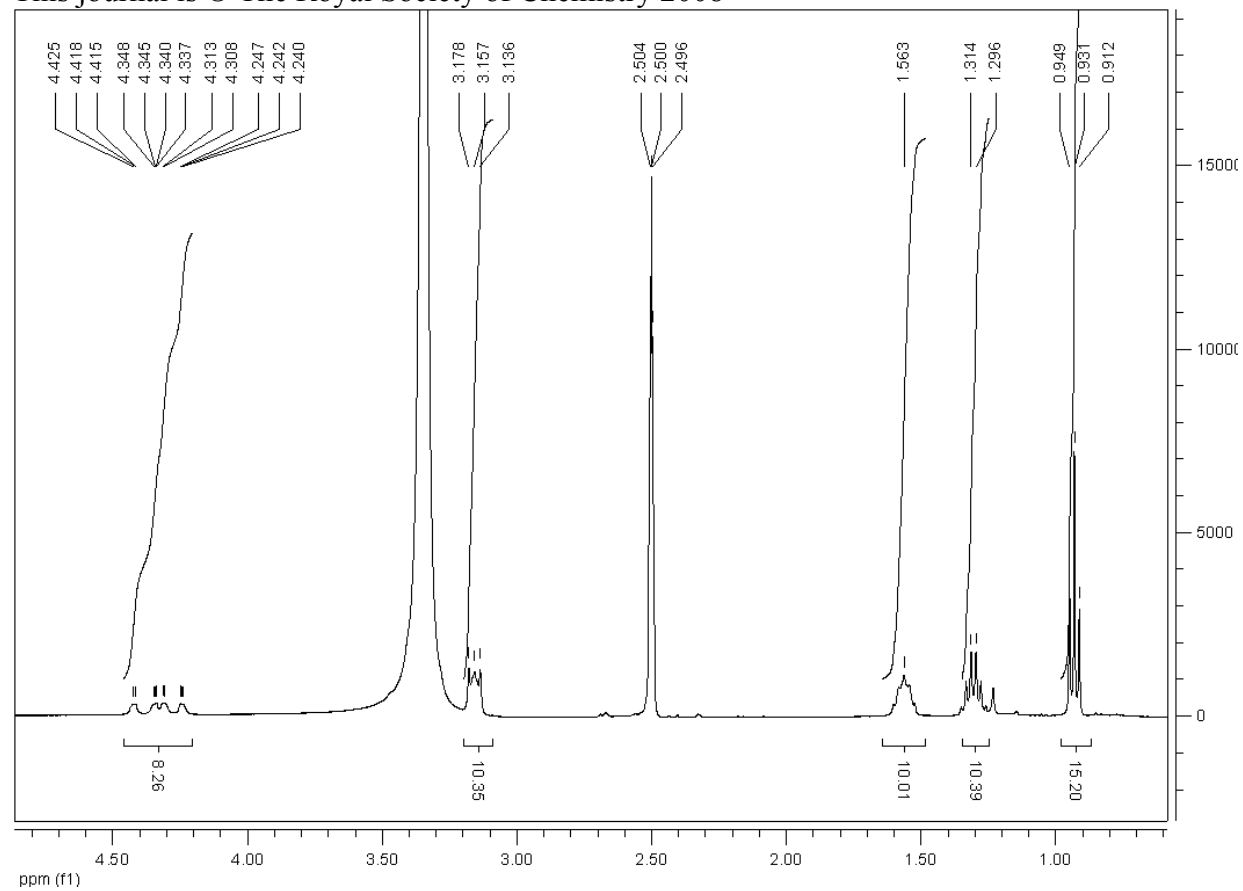


Figure S4b.  $^1\text{H}$  NMR spectrum of Ru-EDOT complex (aromatic plus EDOT region) ( $\text{DMSO-d}_6$ )

**Notes and references.**

1. J.-M. Raimundo, P. Blanchard, N. Gallego-Planas, N. Mercier, I. Ledoux-Rak, R. Hierle and J. Roncali, *J. Org. Chem.*, 2002, **67**, 205.
2. Gaussian 03, Revision B.05, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, Jr., J.A.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M. C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M. W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Pittsburgh PA, 2003.