Electronic Supplementary Material (ESI) for Dalton Transactions.

# Supporting Information

## A new ruthenium black dye design with improved optical properties for transparent dye sensitized solar devices

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**Contents:**

## Materials and Equipment for Synthesis and Purification

All reagents and solvents were purchased from Sigma-Aldrich, except for 2-bromo-4-iodopyridine and 2,6-dibromo-4-iodopyridine which were purchased from Combi Blocks, and were used without any further purification. GuNCS (Guanidinium thiocyanate), PMII (1-Methyl-3-propylimidazolium iodide), BzIm ( benzimidazole) were from Sigma-Aldrich and used as received.

Microwave (MW) reactions were performed in single-mode Biotage Initiator 2.5 and MARS MD 9668

Flash-chromatography purifications of the ligand and of its precursors were performed on a Biotage Isolera flash purification system. NBD was purified by column chromatography on Sephadex LH 20.

## Analytical Measurement

GC-MS spectra were recorded on a Thermo Finnigan Trace GC with a cross-linked methyl silicone capillary column, coupled to a Thermo Finnigan Trace MS mass spectrometer equipped with an electronic impact source (EI).

UV–Vis absorption spectra were recorded in transmission mode with a PerkinElmer λ40 spectrophotometer.

Emission spectra were recorded on an Edinburgh Instruments FS920 steady state spectrofluorimeter configured with a TMS300-X single excitation monochromator (300mm focal length, f/4.1 aperture), a double emission monochromator consisting of two coupled 300mm focal length, f/4.1 monochromators to reduce stray light and increase spectral resolution. A NIR detector assembly including a two stage TE cooled InGaAs photodiode (Hamamatsu G8605-23) with 3mm diameter active area, chopper, lock-in, VF converter, and lens focussing optics, was mounted on one of the two exit ports of the first emission monochromator, while a red sensitive photomultiplier (Hamamatsu R928P) in a standard uncooled housing was placed at the end of the second emission monochromator. The instrument was PC controlled through of a proprietary Edinburgh Instruments F900 software providing emission and excitation spectra factory corrected for instrumental response by means of a calibrated source. Absolute luminescence quantum yield measurements were carried out by using a 120 mm diameter integrating sphere from Edinburgh Instruments, following the detailed procedure described in the manual.

MS-ESI spectra were recorded with a LCQ Deca XP plus spectrometer from Thermo with ESI interface and Ion Trap analyzer.

$^{1}$H NMR (200 MHz) and $^{13}$C NMR (50 MHz) spectra were recorded on a Bruker Avance 200 NMR. and Varian (400MHz)

## Computational Details.

Ground state optimization of both BD and NBD was carried out at the DFT-B3LYP-LANL2DZ level in the presence of ethanol described within the Polarizable Continuum Model (PCM). Vertical optical transitions in ethanol (PCM) were obtained on the ground state optimized structures via time dependent B3LYP-LANL2DZ. All calculations were performed with Gaussian 09 A02. Electron Density Difference Maps were generated with Gausssum 2.2 and visualized with Gauss View 5.0.

### Electrochemical and Photo-electrochemical Measurements

For cyclic voltammetry a PGSTAT 30 potentiostat, a three electrode, one compartment electrochemical cell was used. The reference electrode was SCE, the auxiliary electrode was Pt and the working electrode was glassy carbon; the supporting electrolyte was 0.1 M solution of Lithium perchlorate (Fluka, electrochemical grade, 99.0%) in anhydrous DMF (Aldrich).

Current–voltage measurements were performed with an Auto-lab PGSTAT 302/N potentiostat. Cell performances were evaluated under AM 1.5 G illumination (ABET sun simulator).

IPCE spectra were collected with a custom-built apparatus comprising an Applied Photophysics Monochromator, a 175 W Xe source (Luxtel) and various optical elements. Short circuit photocurrents were measured with an Agilent 34401 A multimeter while incident irradiance was provided by a calibrated silicon photodiode (Centronic OSD 100 7Q) having an active area of 1 cm$^2$

### Solar Cell Fabrication.

Mesoporous titania films (ca. 6 μm thick) were prepared by blading a commercial colloidal $TiO_2$ paste (Dyesol DSC 18NR-T for transparent device and Dyesol DSC 18NR-AO for opaque device) on FTO electrodes, sintered using heating ramp until 500°C. The resulting films were immersed in a 0.4 M $TiCl_4$ solution for 12 h, rinsed with water and fired at 450 °C for 30 min. Finally, the photoanodes were dipped for 18 h in a saturated solution of the BD dye in EtOH and in a mixture of ethanol and DMSO (60:40) for the NBD dye. This solvent mixture was chosen to avoid dye aggregation via stacking interactions which was evident in pure ethanol. Bynell sealed (60 micron thickness) solar cells were equipped with transparent screen printed platinum counter electrodes and filled with the electrolyte via vacuum back-filling. The electrolyte injection hole was closed with epoxy resin. The active cell area was 0.25 cm$^2$. Different iodide based electrolyte compositions (see Table 2 in the main text) were evaluated to optimize performance.

# S1

***Synthesis of isobutyl-4-ethynylbenzoate (1).***

1,06 g of methyl-4-ethynyl benzoate (6.64 mmol), 100 ml of 2-methyl-1-propanol and 1.82 g of p-toluensulfonic acid (10.57 mmol) were placed in a round bottom flask, heated and stirred overnight at reflux, monitoring the reaction on TLC (PE/$Et_2O$ 9:1) until the starting material disappeared. Saturated $Na_2CO_3$ aqueous solution was added to quench the reaction. The mixture was diluted in petroleum ether and washed with saturated $Na_2CO_3$ aqueous solution. Organic phase was treated with anhydrous $Na_2SO_4$, filtered and evaporated under vacuum. The obtained oil was purified by flash-chromatography silica gel (PE/$Et_2O$ 9:1). 1.140 g of intermediate **1** as colorless needle crystals were obtained (yield: 85%)[1]. $^1$H NMR (200 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 4.11 (d, J = 6.6 Hz, 2H), 3.22 (s, 1H), 2.29 – 1.88 (m, 1H), 1.02 (d, J = 6.7 Hz, 6H). $^{13}$C NMR (50 MHz, $CDCl_3$) δ 166.10, 132.21, 130.65, 129.56, 126.77, 82.99, 80.10, 71.38, 28.02, 19.33. GC/MS-EI (m/z) calcd. for [M+] 202.10, found 202.17.

***Synthesis of isobutyl 4-((2-bromopyridin-4-yl)ethynyl)benzoate (2).***

To a mixture of 2-bromo-4-iodopyridine (1.61 g, 5.67 mmol), $Pd(PPh_3)_2Cl_2$ (400 mg, 0.56 mmol), CuI (108 mg, 0.56 mmol) in a flame-dried round bottom flask was added dry TEA (40 mL). The yellow heterogeneous mixture was deoxygenated with argon for 20 min. The solution was cooled to 0 °C and isobutyl-4-ethynylbenzoate (5.67 mmol) dissolved in 40 mL of dry toluene was added dropwise in 2 hours. The mixture changes color from yellow to amber during the additions. The cooling bath was then removed and the reaction mixture was stirred at RT overnight. The mixture was filtered through silica gel/celite and the filter cake washed with $Et_2O$ (500 mL). The organic solution and $Et_2O$ was combined and washed with saturated $NH_4Cl$ (2 x 250 mL). The organic phase was dried by anhydrous $MgSO_4$, and concentrated in vacuum to give the crude mixture, that was purified by flash-chromatography using a Biotage Isolera instrument (cartridge: silica gel; eluent: PE/DCM, 80:20) to afford 1.5 g of a white-yellow solid (yield 75%). $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.38 (d, J = 5.1 Hz, 1H), 8.06 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 0.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.35 (dd, J = 5.1, 1.0 Hz, 1H), 4.13 (d, J = 6.6 Hz, 2H), 2.23 – 1.96 (m, 1H), 1.03 (d, J = 6.7 Hz, 6H). $^{13}$C NMR (50 MHz, MeOD) δ: 165.93, 150.14, 142.42, 133.63, 132.04, 131.29, 129.90, 129.77, 126.12, 124.65, 94.55, 87.76, 71.51, 28.03, 19.33. MS-ESI (m/z) calcd for $[M+H]^+$ 358.04, found 358.19.

***Synthesis of isobutyl 4-((2,6-dibromopyridin-4-yl)ethynyl)benzoate (3).***

To a mixture of 2,6-bromo-4-iodopyridine (2.01g, 5.54 mmol), $Pd(PPh_3)_2Cl_2$ (400 mg, 0.56 mmol), and CuI (108 mg, 0.56 mmol) in a flame-dried round bottom flask 40 mL of dry TEA was added. The yellow heterogeneous mixture was deoxygenated with argon for 20 min, cooled to 0°C and isobutyl-4-ethynyl benzoate (5.33 mmol), dissolved in 40ml of dry toluene, was added dropwise in 2 hours. The mixture changed color from yellow to amber during the additions. The cooling bath was then removed and the reaction mixture was stirred at RT overnight. The mixture was filtered through silica gel/celite and the filter cake was washed with $Et_2O$ (500 mL). The organic solution and $Et_2O$ was combined and washed with saturated $NH_4Cl$ (2 x 250 mL). The organic phase was dried by anhydrous $MgSO_4$ and concentrated in vacuum to give a crude mixture that was purified by flash-chromatography using a Biotage Isolera instrument (cartridge: silica gel; eluent PE/DCM, 80:20) to afford 1.41 g of a white – yellow solid (yield 57%). $^1H$ NMR (200 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.56 (s, 1H), 4.12 (d, J = 6.6 Hz, 2H), 2.27 – 1.93 (m, 1H), 1.03 (d, J = 6.7 Hz, 6H). $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 165.83, 140.97, 135.33, 132.12, 131.58, 129.81, 128.67, 125.64, 95.79, 86.48, 71.54, 28.02, 19.32. MS-ESI (m/z) calcd for $[M+H]^+$ 437.94, found 437.96.

***Synthesis of triisobutyl-4,4',4''-([2,2':6',2''-terpyridine]-4,4',4''-triyltris(ethyne-2,1-diyl))tribenzoate (4).***

A 10 ml microwave vial was charged with the intermediate **2** (278 mg, 0.776 mmol), tetrakis(triphenylphosphine)palladium (0) (48 mg, 0.0682 mmol) and hexamethyldistannane (288 mg, 0.879 mmol). The vial was closed and filled with Argon. Degassed anhydrous toluene (5 ml) was added by a syringe and the resulting reaction mixture was further degassed with argon for 15 min. The mixture was heated by microwave irradiation at 150°C for 30 min. A small aliquot of the solution was dried under vacuum in order to characterize the stannyl intermediate: $^1H$ NMR (200 MHz, $CDCl_3$) δ 8.75 (d, J = 5.1 Hz, 1H), 8.04 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.55 (s, 1H), 7.24 (d, J = 5.1 Hz, 1H), 4.11 (d, J = 6.6 Hz, 2H), 2.25 – 1.94 (m, 1H), 1.02 (d, J = 6.7 Hz, 6H), 0.37 (s, 9H). $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 173.84, 166.00, 155.77, 150.29, 132.11, 131.87, 130.73, 129.66, 128.62, 126.91, 92.67, 89.93, 71.39, 28.01, 19.32, -9.28. MS-ESI (m/z) calcd for $[M+H]^+$ 444.09, found 443.97.

The crude solution of stannyl intermediate was poured in a 20 ml MW vial, charged with 140 mg of compound **3** (0.32 mmol) and 90 mg of tetrakis(triphenylphosphine)palladium (0) (0.136 mmol).

The vial was closed, filled with argon and degassed, anhydrous toluene (15 ml) was added by a syringe. The mixture was heated at 180°C for 30 min in a MW reactor. Once cooled to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The crude product was purified by crystallization in chloroform and flash-chromatography using a Biotage Isolera instrument (cartridge: silica gel; eluent: DCM/ethyl acetate 90/10) to afford 173 mg of a white solid (yield 65%). $^{1}$H NMR (200 MHz, $CDCl_3$) δ 8.71 (d, J = 5.3 Hz, 2H), 8.69 (d, J = 1.1 Hz, 2H), 8.58 (s, 2H), 8.05 (d, J = 8.3 Hz, 6H), 7.66 (d, J = 8.2 Hz, 4H), 7.62 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 5.0, 1.4 Hz, 2H), 4.12 (d, J = 6.6 Hz, 6H), 2.26 – 1.93 (m, 3H), 1.04 (d, J = 6.7 Hz, 6H), 1.03 (d, J = 6.7 Hz, 12H). $^{13}$C NMR (50 MHz, $CDCl_3$) δ 165.92, 155.81, 155.34, 149.36, 133.11, 132.09, 131.99, 130.96, 130.81, 129.70, 126.91, 126.69, 126.09, 123.66, 123.25, 93.22, 89.90, 89.74, 71.41, 28.01, 19.33. MS-ESI (m/z) calcd for $[M+Na]^+$ 856.34, found 856.56.

***Synthesis of 4,4',4''-([2,2':6',2''-terpyridine]-4,4',4''-triyltris(ethyne-2,1-diyl))tribenzoic acid (5).***
A 20 ml microwave vial was charged with compound **4** (127 mg, 0.152 mmol), dissolved in 10 ml of THF. Then 85 mg of LiOH (3.54 mmol) dissolved in 5 ml of water were added to the vial in order to have two phase in the vial. The vial was shacked vigorously right before heating the solution to 150°C in the MW reactor for 20 min. After cooling to RT the two phases were separated and the aqueous phase was centrifuged in order to remove completely a white solid. The basic water solution were then acidified with HCl conc. to pH 3. The obtained white precipitate was centrifuged and washed with ACN, and $Et_2O$ and placed under vacuum overnight to obtain 100 mg of a brownish solid soluble in hot DMSO (yield quantitative). $^{1}$H NMR (200 MHz, DMSO) δ 13.17 (b, 3H), 8.78 (d, J = 5.0 Hz, 2H), 8.72 (d, J = 0.9 Hz, 2H), 8.48 (s, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 4H), 7.77 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 8.4 Hz, 4H), 7.66 (dd, J = 5.0, 1.5 Hz, 2H). Low solubility of compound in deuterated solvents prevents to obtain $^{13}$C spectra. MS-ESI (m/z) calcd for $[M-H]^-$ 664.16, found 664.63.

Elemental Analysis for C42H23N3O6*8$H_2O$: Found: C 62.2 (DEVST 0.921) H 4.22 (DEVST 0.286) N 5.06 (DEVST 0.061)
Calculated: C, 62.30; H, 4.85; N, 5.19;

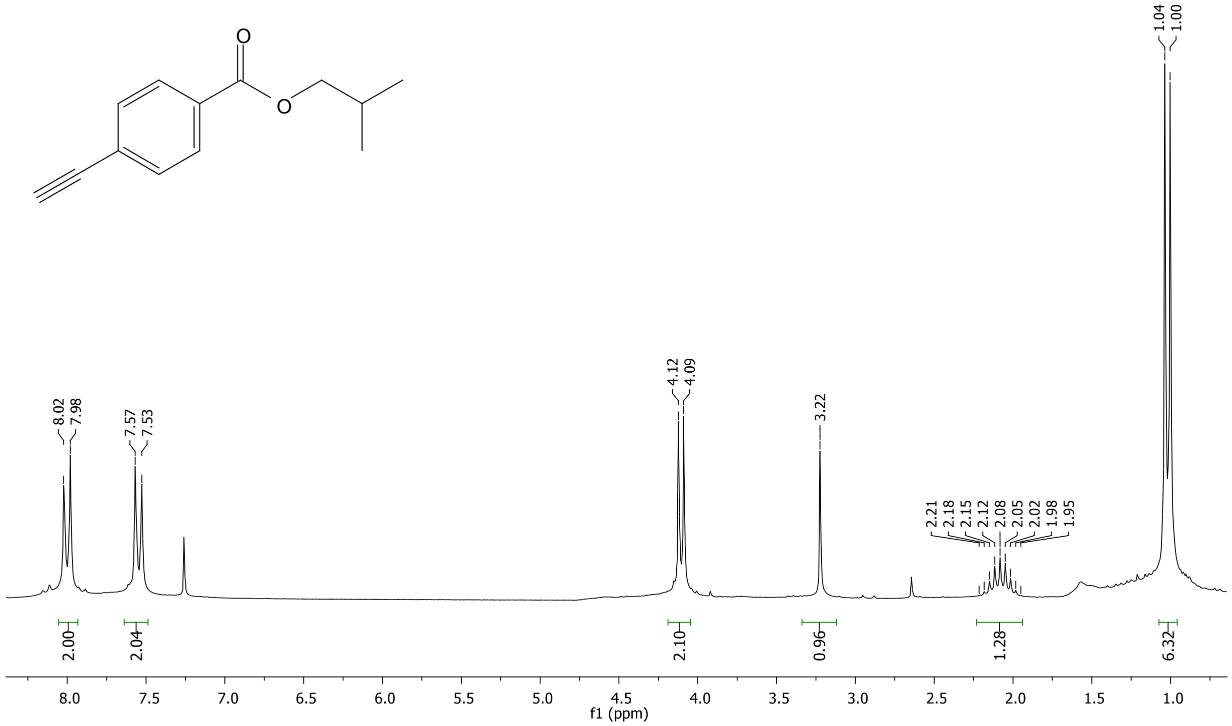
# *S2*

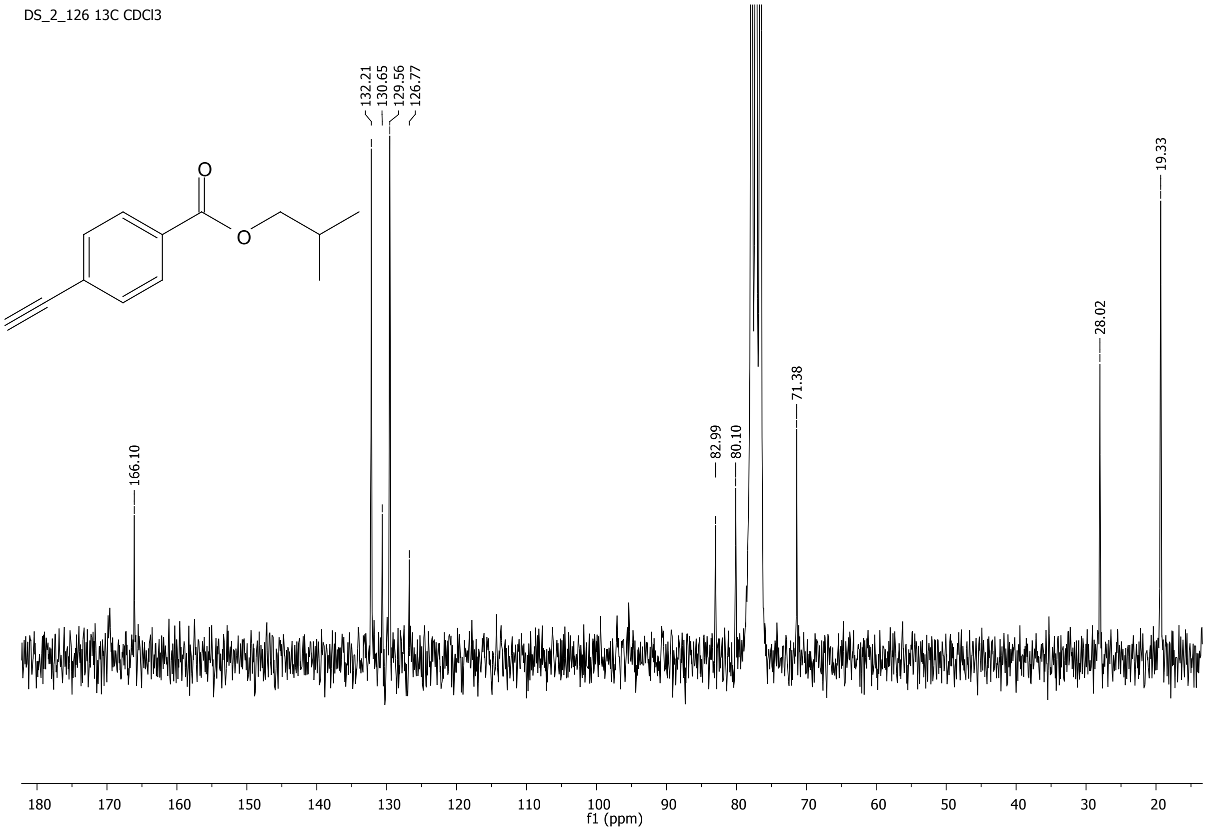
### ***Synthesis of NBD (6)***

A suspension of 4,4',4''-([2,2':6',2''-terpyridine]-4,4',4''-triyltris(ethyne-2,1-diyl))tribenzoic acid (**5**) (50mg) and dichloro(p-cymene)ruthenium (II) dimer (23 mg) in 20ml of DMF were refluxed under MW heating under argon at 160°C for 20min. Then 342 mg of $NH_4NCS$ was added and the solution was refluxed by MW at 160°C for 15 min. The solvent was evaporated by rotary evaporation. 20 ml of water and 96 mg of TBANCS were added to the solid and the pH was increased to 9.0 by addition of tetrabutylammonium hydroxide (40 wt% solution in water). The pH of the solution was then lowered to 5.0 by addition of 0.1 M $HClO_4$ . The resulting precipitate was centrifuged and washed with distilled water. The crude product was purified several times by LH20 chromatography using DMF and then MeOH as eluent.

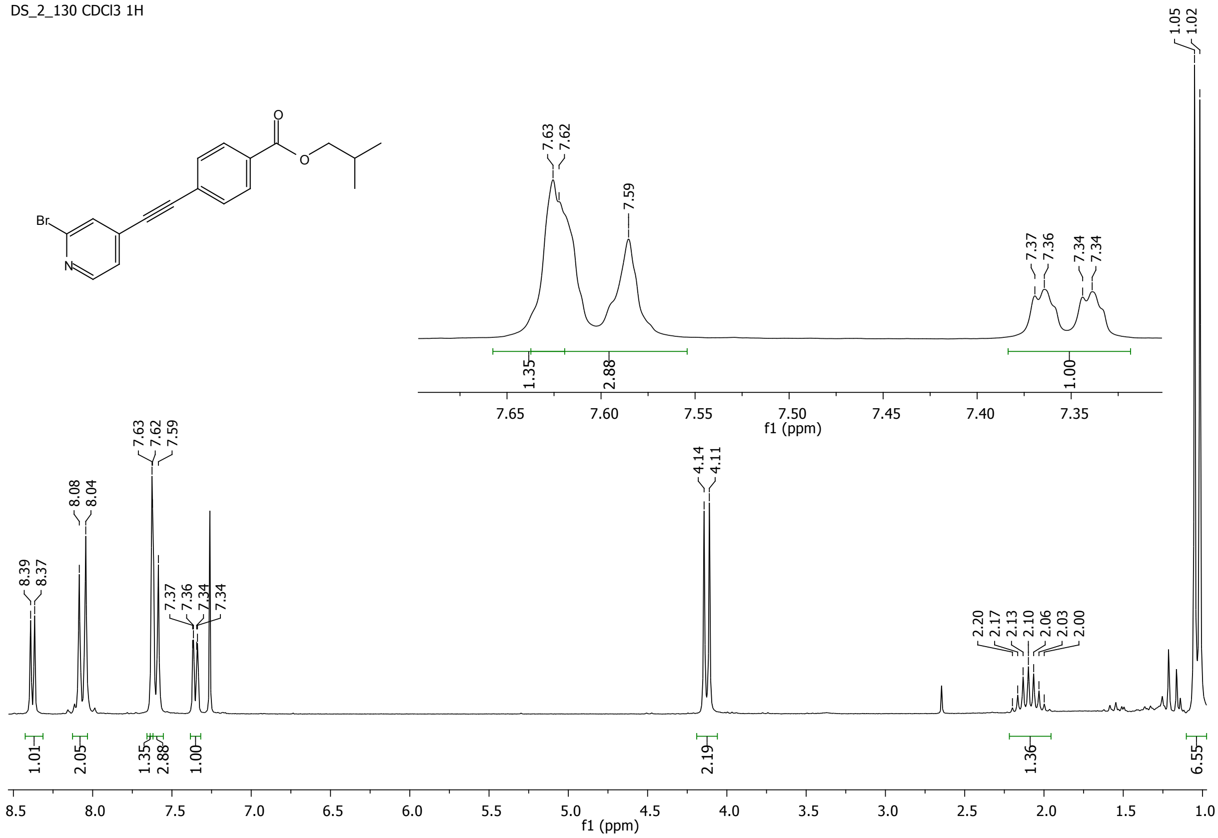
# $^1$H and $^{13}$C NMR ($CDCl_3$) spectra of compound 1

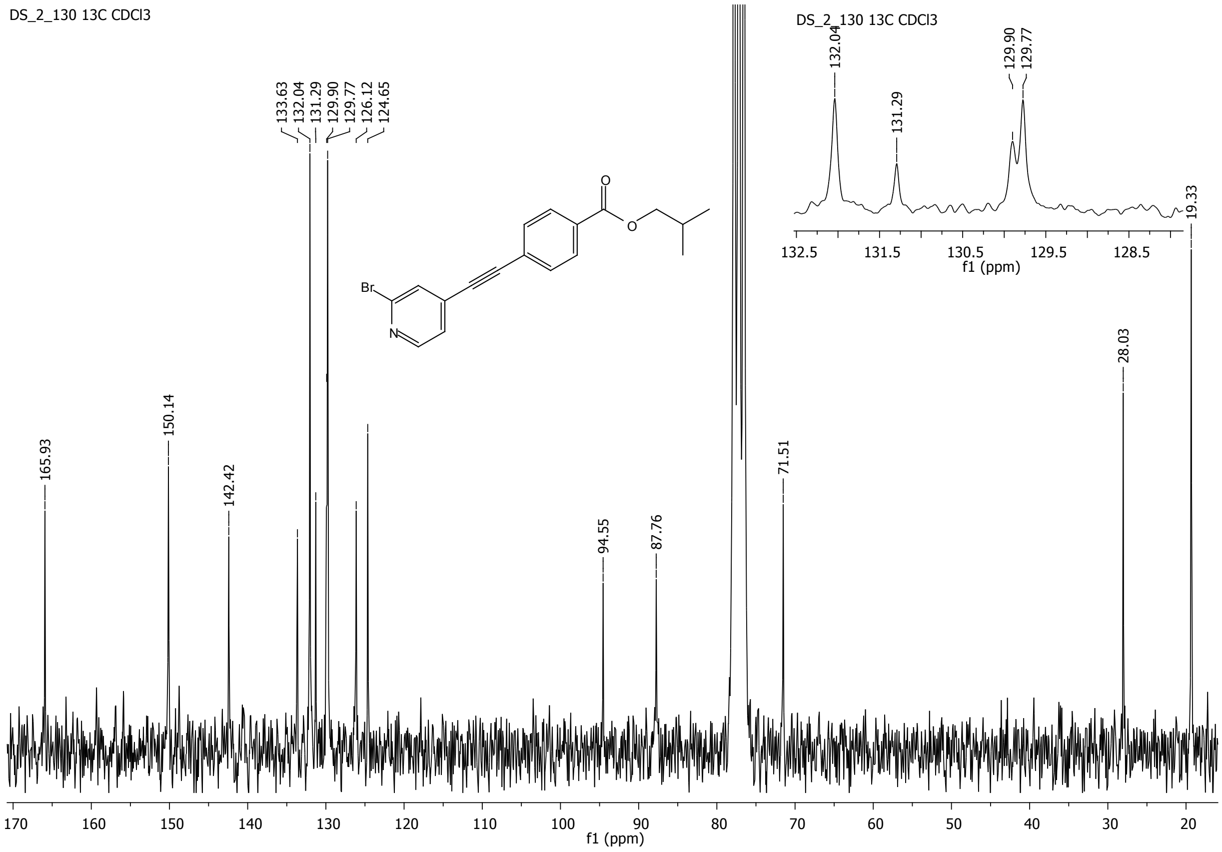
DS_2_126 col 1H CDCl3



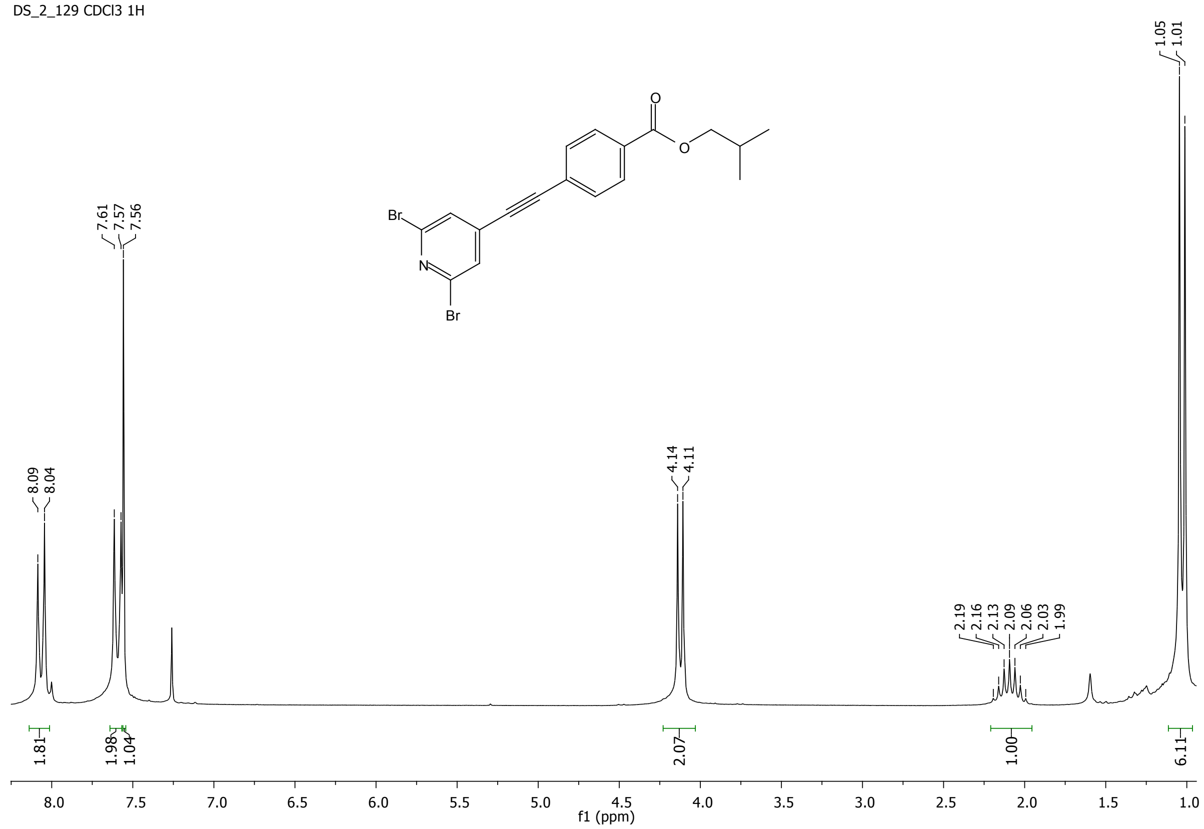

DS_2_126 13C CDCl3
O
O
132.21
130.65
129.56
126.77
166.10
82.99
80.10
71.38
28.02
19.33
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

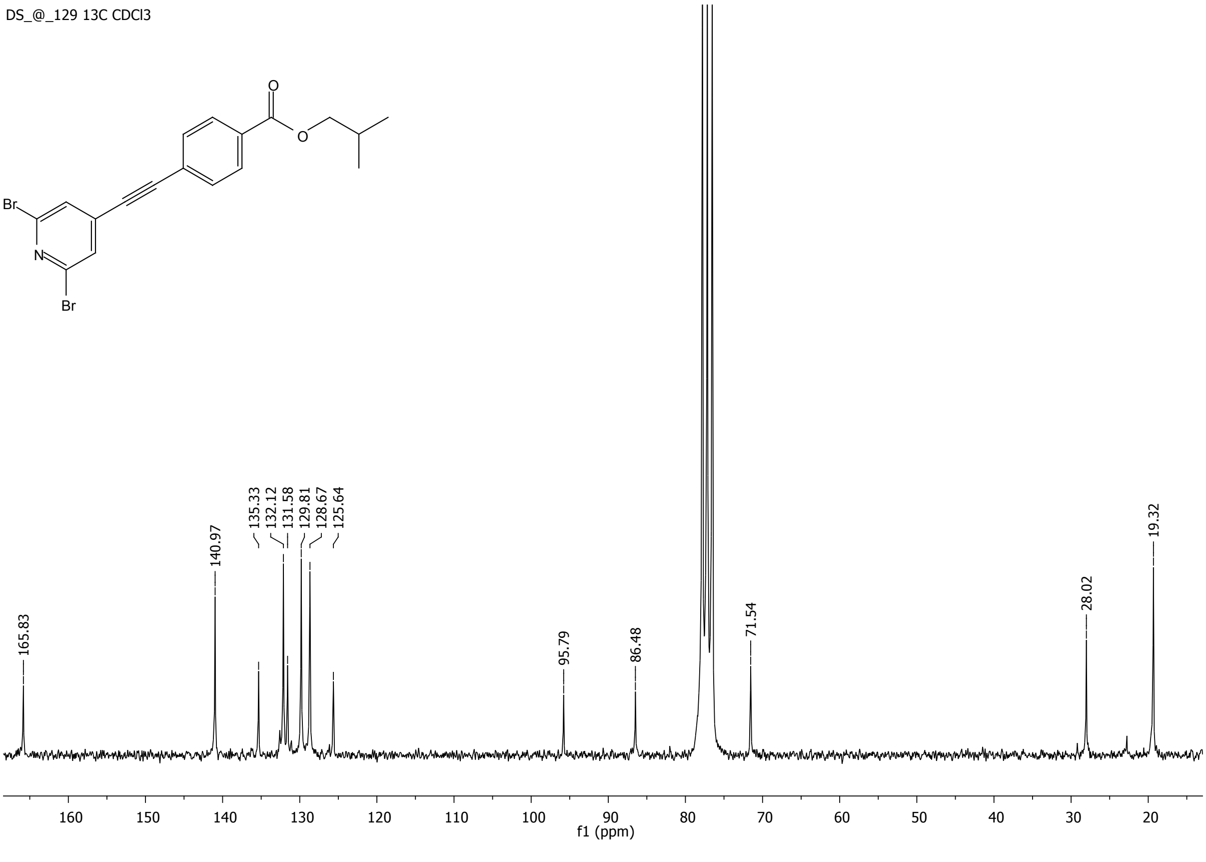
# $^1$H and $^{13}$C NMR (CDCl$_3$) spectra of compound 2



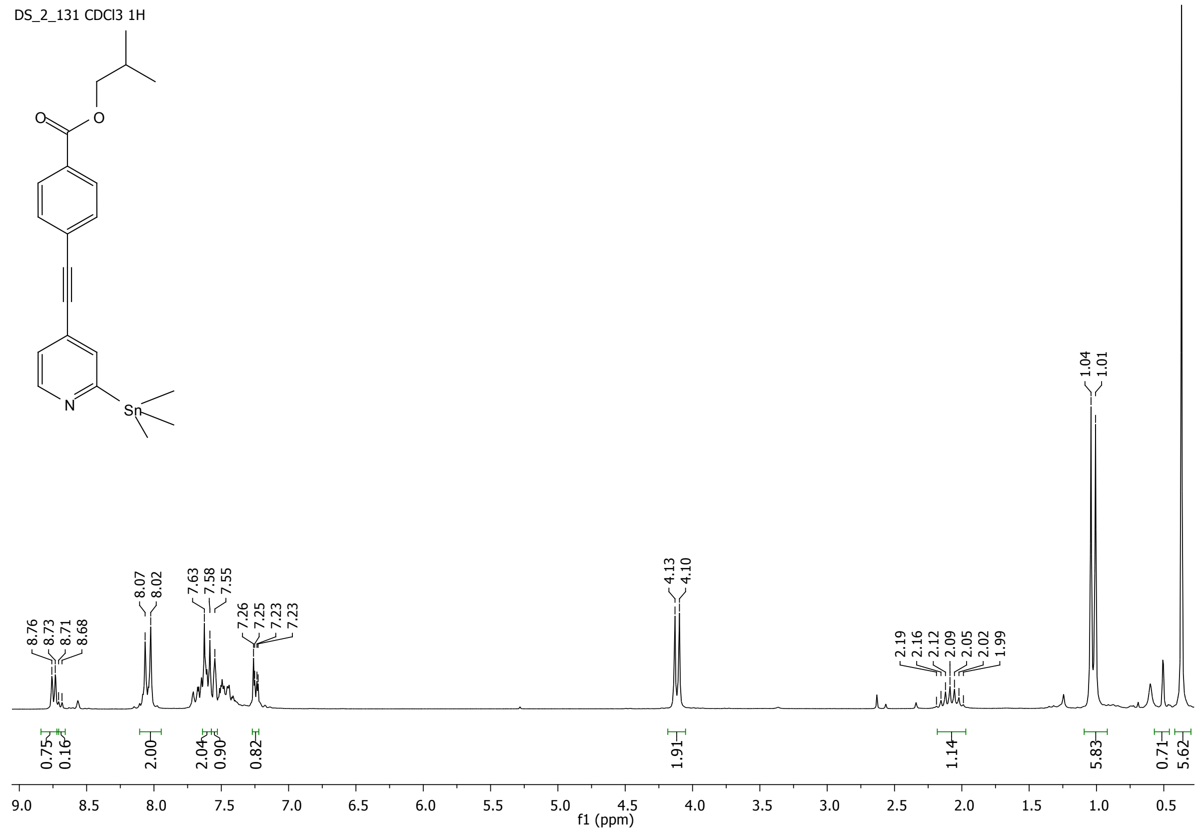


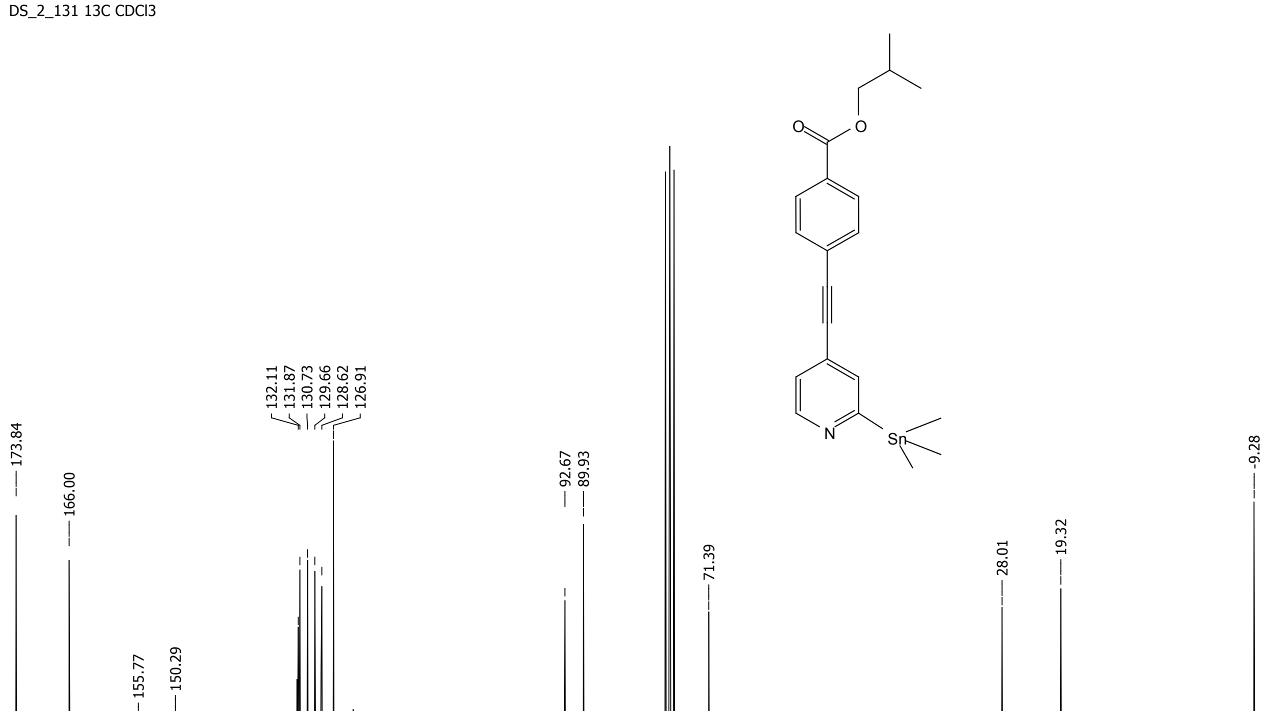
# $^{1}H$ and $^{13}C$ NMR ($CDCl_3$) spectra of compound 3



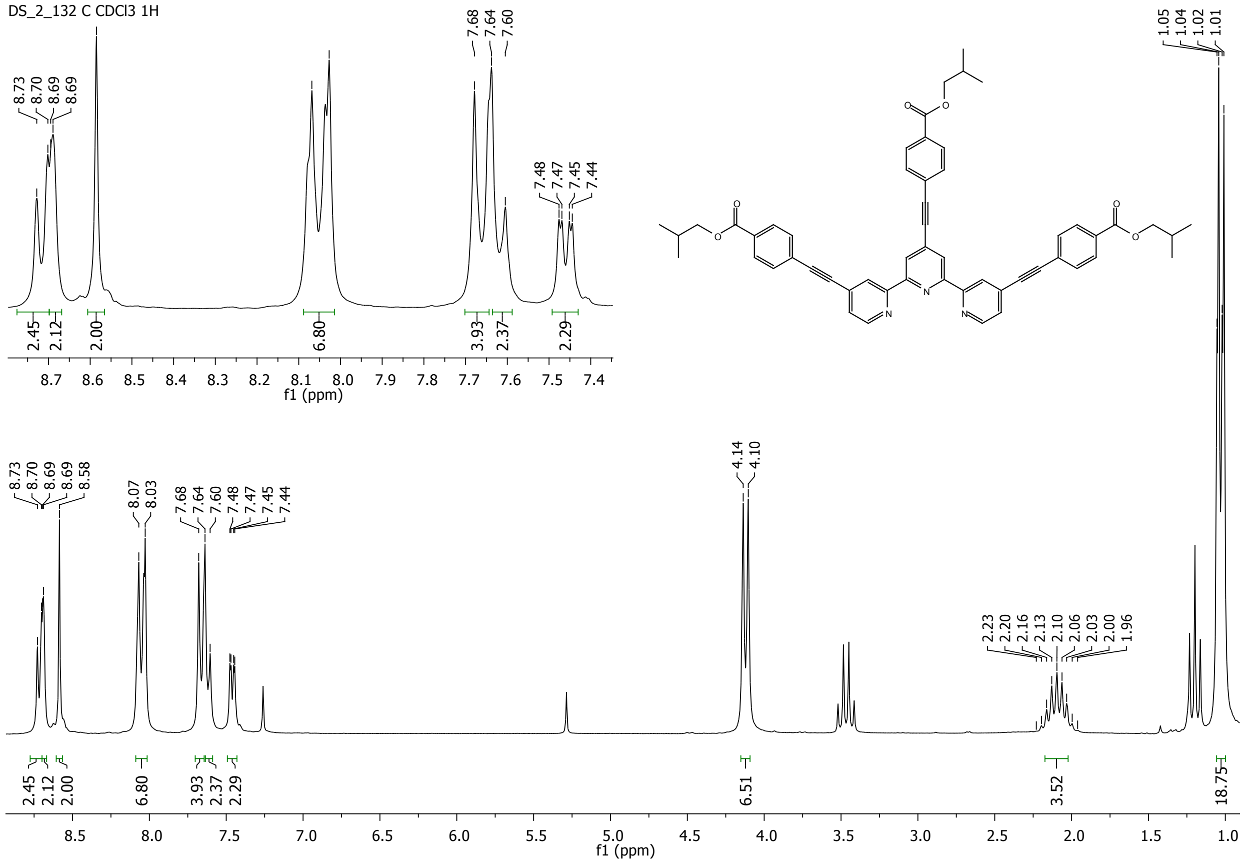


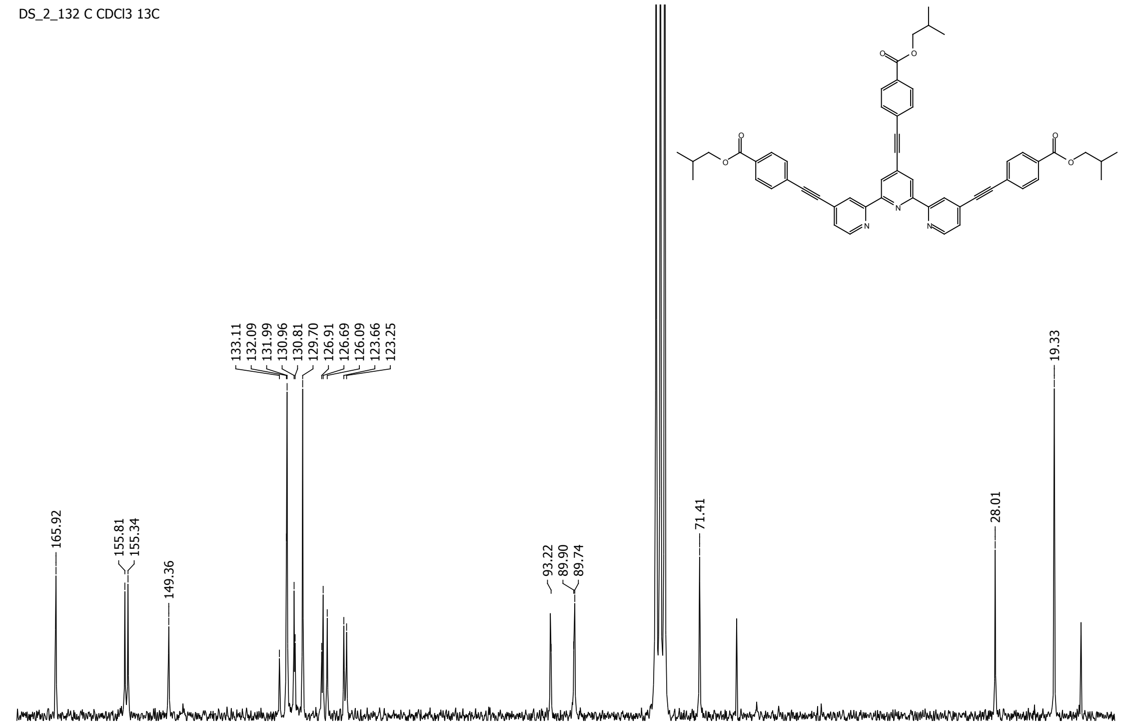
# $^1$H NMR (CDCl$_3$) of stannyl intermediate of product 4



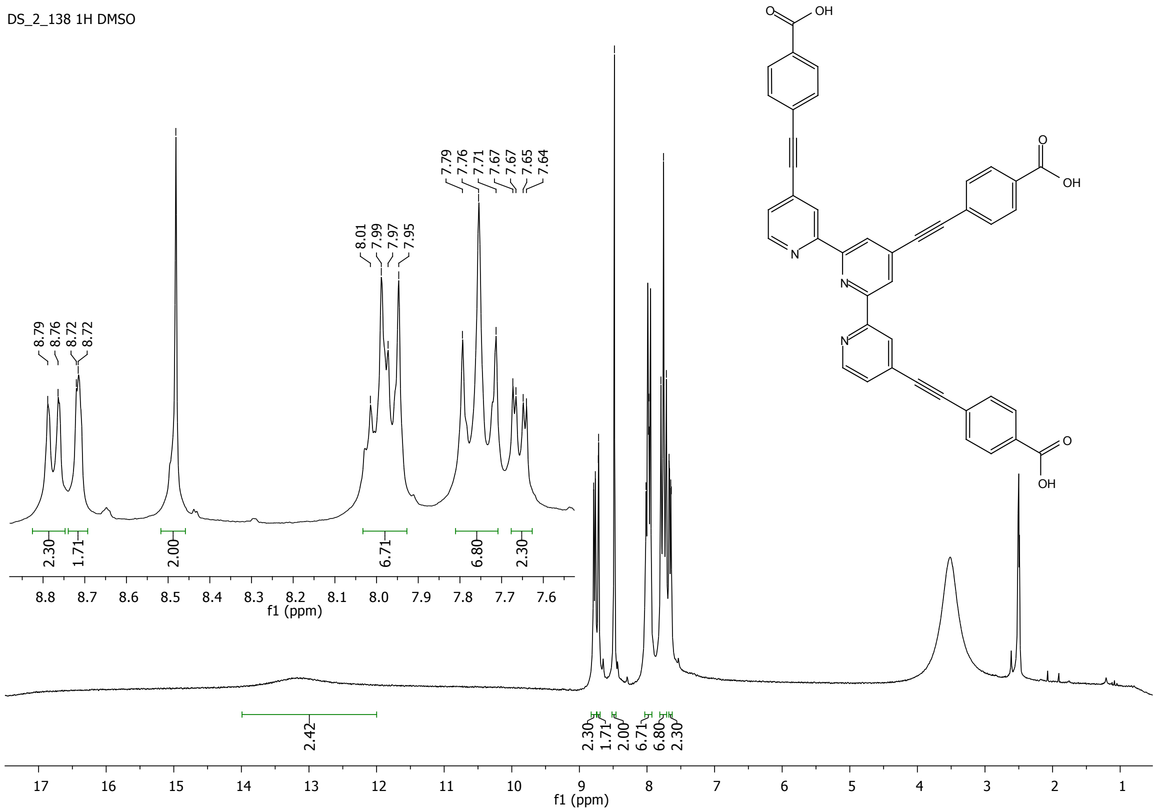


# $^1$H and $^{13}$C NMR (CDCl$_3$) of product 4

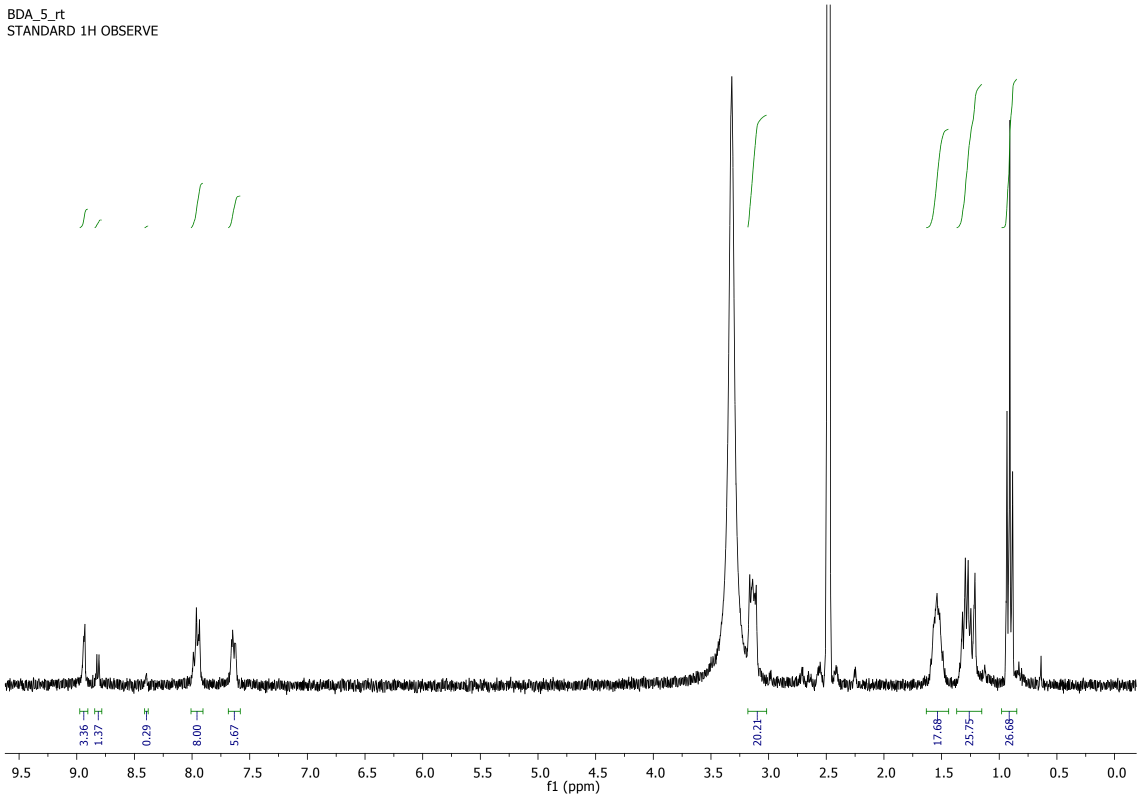


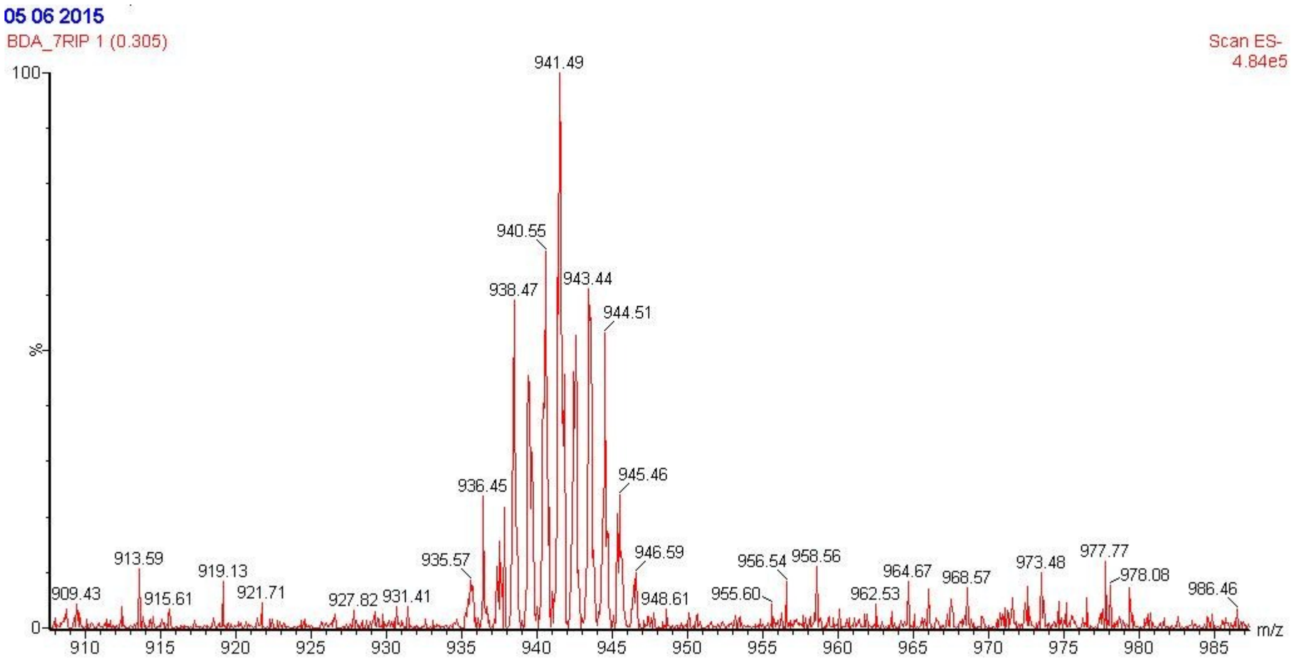


# $^1$H NMR (DMSO) of product 5

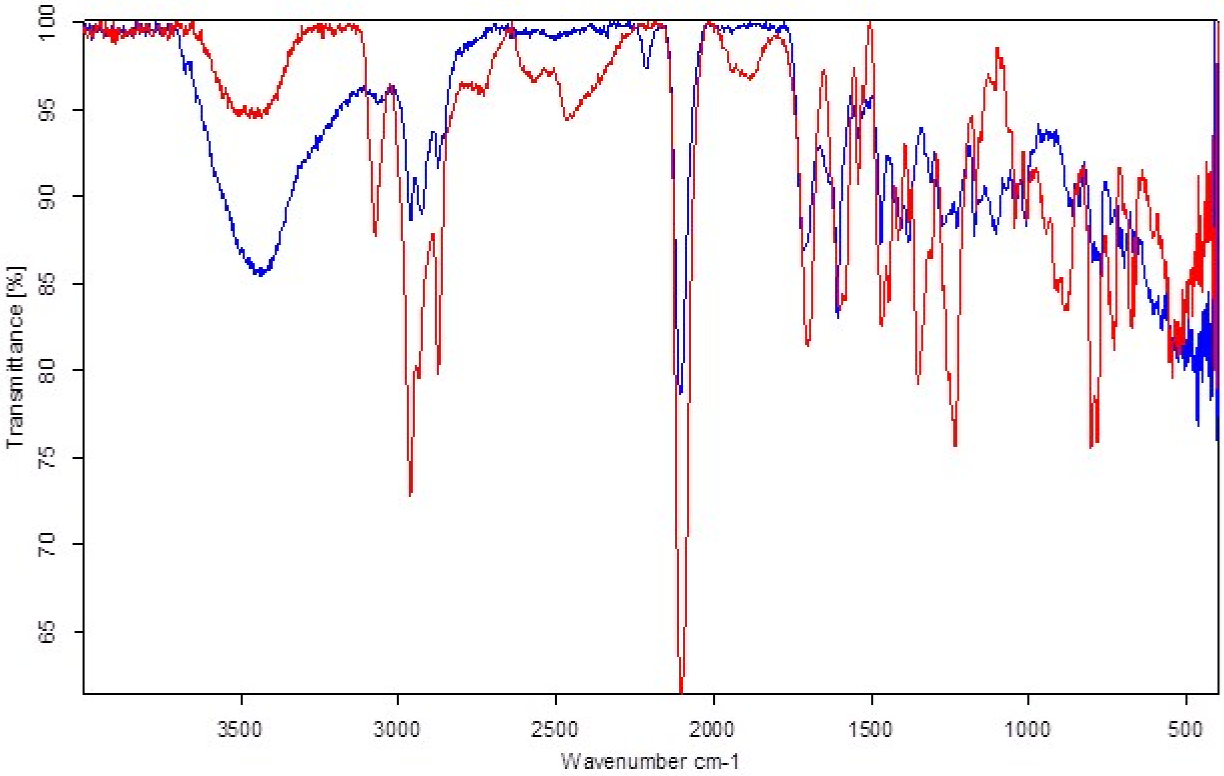


# $^1$H NMR (DMSO) of NBD





ESI MS negative for NBD m/z= 940.99 calcd. For $C_{45}H_{23}N_6O_6RuS_3$, found 941.49



Infrared spectra of NBD complex (6) (blue) and BD complex (Solaronix) (red)

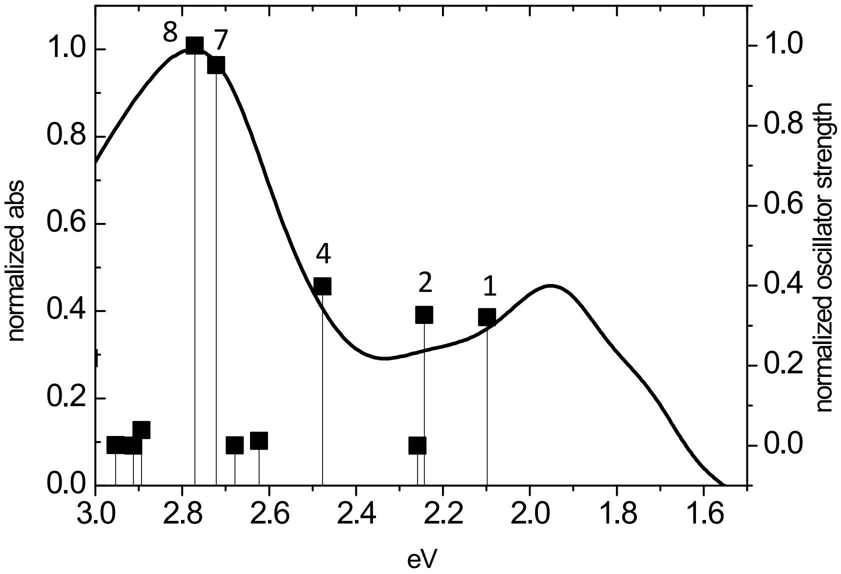


Fig. S1A. TDDFT calculations for NBD carried out at the B3LYP/LANL2DZ level in Ethanol (PCM). Numbers 1,2,4,7,8 identify the most intense transitions whose EDDMS are given in Figure S2

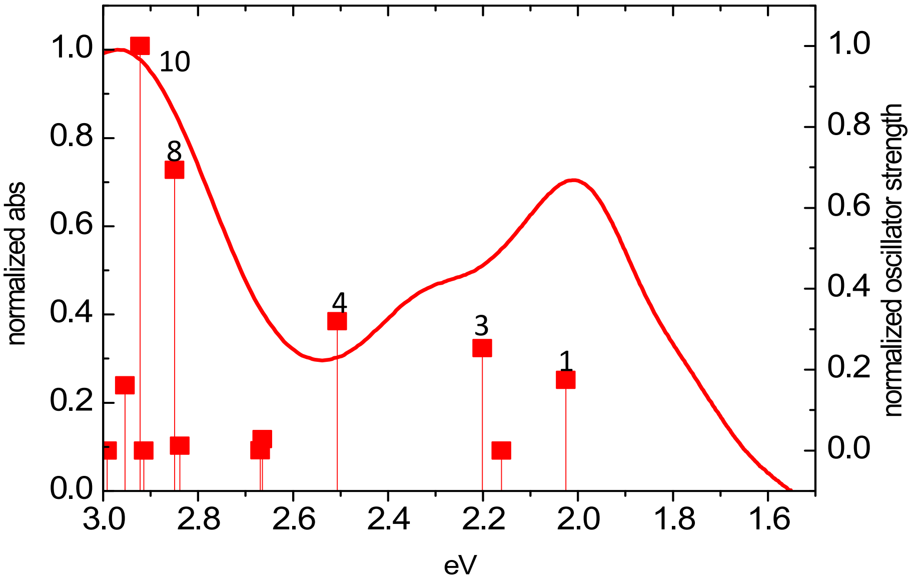
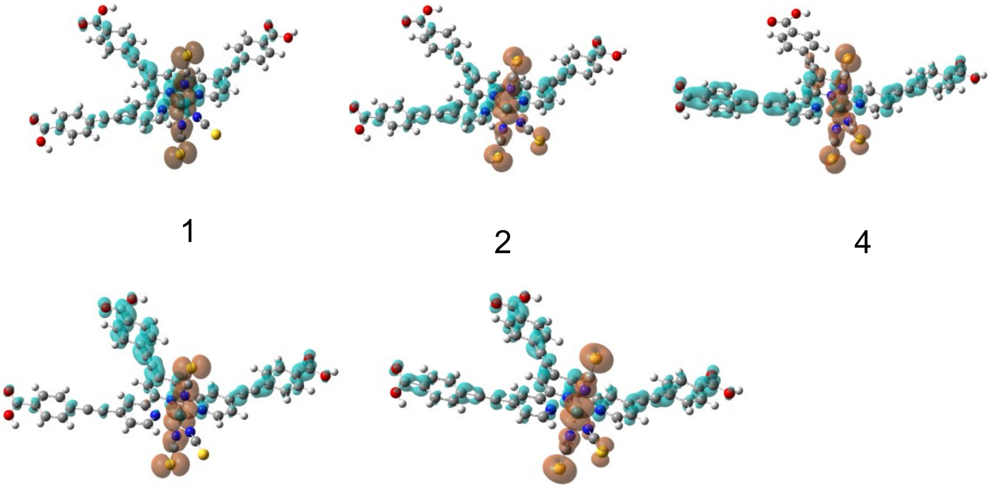


Fig. S1B. TDDFT calculations for BD carried out at the B3LYP/LANL2DZ level in Ethanol (PCM). Numbers 1,3,4,8,10 identify the most intense transitions



1 2 4

7 8

Fig.S2. Electron Density Difference Maps (EDDMs) associated to the most intense visible transitions in NBD. EDDMs clearly show their mixed MLCT LLCT nature. The increased oscillator strength of the transitions is motivated by larger dipole moment arising from excited state delocalization on the conjugated terpy ligand arms. Depleted electron density is indicated by orange lobes, increased density by cyan ones.

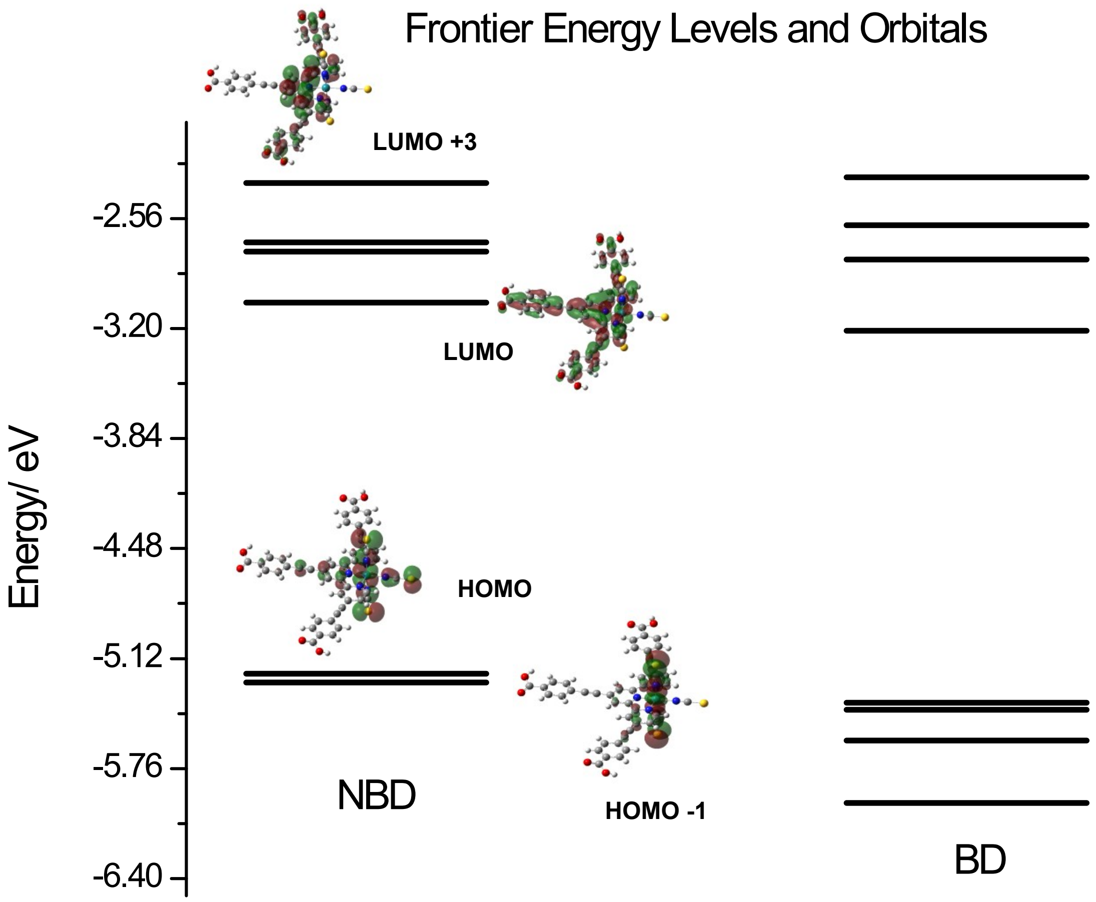


Fig.S3. Energy (vs. Vacuum) of the frontier orbitals od NBD and BD. Isodensity surfaces of the occupied and virtual orbitals involved in the main transitions (1-2-4-7-8) of NBD are reported.

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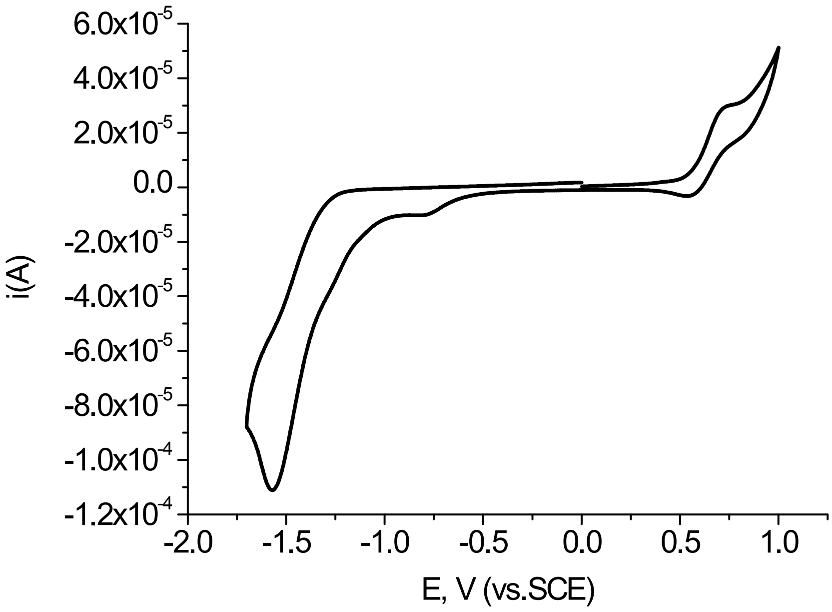

Fig.S4. Cyclic voltammetry of NBD solution in dimetylformamide containing 0.1 M $LiClO_4$ as supporting electrolyte

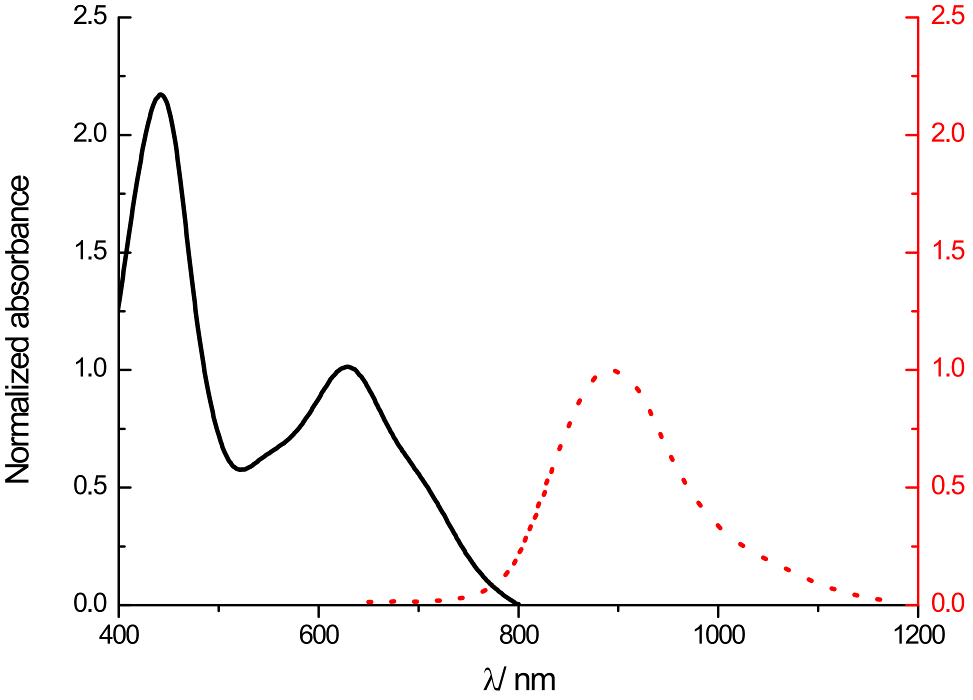

Fig.S5. Normalized Absorption Spectrum ( normalization was to the lowest MLCT band, solid line) and Normalized Emission (dotted red line) spectra of NBD in EtOH. Excitation at 640 nm