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Dipyrrolonaphthyridinediones – structurally unique cross-conjugated dyes

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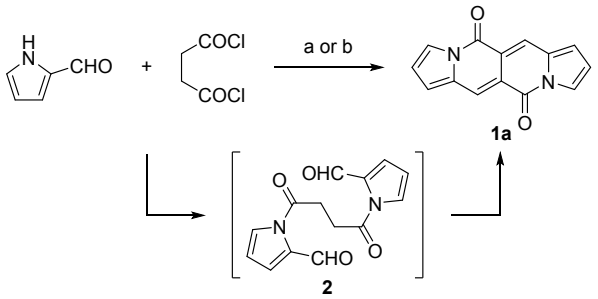
1. Reaction of 2-formylpyrrole with succinyl chloride

We expected, that in the first step of the reaction of 2-formylpyrrole and succinyl chloride an *N*-acylation of pyrrole would occur leading to the dialdehyde **2**, which in the second step would undergo an intramolecular aldol-type condensation providing the desired DPND **1a** (Scheme S1). The reaction of 2-formylpyrrole and succinyl chloride was performed in dichloromethane using 4-dimethylaminopyridine (DMAP) as a catalyst and triethylamine as a base. Two compounds were separated from the reaction mixture: unreacted 2-formylpyrrole (65% of the initial mass), and small amount of a brown-coloured dye showing yellow fluorescence in solution, which was found to be a designed product **1a** (3.4% yield). In addition, a large amount of black precipitate was formed, which presumably was a product of base-promoted polymerization of succinyl chloride (its formation was also observed in the absence of aldehyde). Interestingly, dialdehyde **2** was not detected in the reaction mixture. Numerous reactions were conducted under various conditions in order to improve the yield of compound **1a**, however, we could not achieve the yield higher than 6.4%, which was obtained using K_2CO_3 as a base in DMF (Scheme S1). Under these conditions the amount of insoluble, black by-product was noticeably smaller, than in the reactions employing organic bases.



Scheme S1. Synthesis of compound **1a**. Reaction conditions: a) DMAP (20 mol%), Et_3N, CH_2Cl_2, RT, 2 h. Yield: 3.4%; b) K_2CO_3, DMF, 0 °C, 2 h. Yield: 6.4%.

2. Experimental procedures

(I) General

All chemicals were used as received unless otherwise noted. All reported ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 500 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS or the residual signal of the solvent as the internal reference. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh).

Diffractions experiments were performed using Bruker APEX-II CCD apparatus and the crystal structure was solved using SHELXL-97 software.

Absorption spectra at room temperature were recorded with a Perkin Elmer UV/VIS spectrometer, model Lambda 35. Fluorescence spectra were measured with a Hitachi spectrophotometer, model: F-7000 FL. Spectroscopic grade solvents: *n*-heptane (Merck) and dichloromethane (Merck) were used as received.

For the spectroscopic studies at 5 K, solution of **1a** in *n*-nonane (concentration $<10^{-4}$ M) was poured into a fused silica cylindrical cuvette, immersed in a liquid N_2, and next inserted into a pre-cooled liquid-helium optical cryostat. As the excitation source we used cw diode laser emitting 445 nm wavelength light (~10 mW). Fluorescence spectra were dispersed with a McPherson 207 monochromator (1200 G/mm), detected by an EMI 9659 photomultiplier and collected in a PC computer.

Fluorescence kinetics studies were performed with the aid of the "time correlated" single photon counting technique (in the inverted time mode). Excitation pulses (time-width ~30 ps, wavelength 430 nm) were provided by the second harmonic of a mode-locked Coherent Mira-HP femtosecond laser pumped by a Verdi 18 laser. Original repetition rate of a Mira laser was reduced with the aid of APE Pulse selector to 2 MHz. Fluorescence photons were dispersed with a McPherson 207 monochromator, detected with a HMP-100-50 hybrid detector and collected with a SPC-150 module (inserted into a PC), both from Becker&Hickl GmbH. Fluorescence decays (see ESI) were fitted to single exponential dependencies without using a deconvolution procedure. Estimated precision of determination of the decay time was 10 ps.

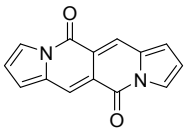
All calculations were performed with aid of Gaussian 09 package.[1] Optimization of the molecular geometry (C_{2h} symmetry) in the electronic ground (S_0) and lowest excited (S_1) states were obtained with B3LYP and TD B3LYP methods, in cc-PVDZ basis. Transition energies for **1a** in solutions were calculated with the use of a simple polarizable-continuum model (PCM) included in the Gaussian package. Vibrational structures of the electronic spectra was calculated with a

procedure included in Gaussian 09, which used the Franck-Condon factors and the Duchinsky matrix.[2,3] All frequencies of the vibrations, calculated for the structures optimized in the both states, S_0 and S_1, were positive.

Cyclic voltammetry measurements were performed in dichloromethane using tetrabutylammonium hexafluorophosphate (0.1M) as an electrolyte and platinum as a working electrode. Saturated calomel electrode (SCE) was used as the reference. The experiment's scan rate was 100 mV s^{-1}.

(II) Synthesis

Synthesis of dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1a) by the condensation of 2-fromylpyrrole and succinyl chloride



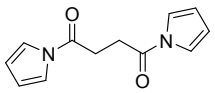
Procedure 1. 2-Formylpyrrole (1.14 g, 12.0 mmol) and 4-dimethylaminopyridine (DMAP, 98 mg, 0.80 mmol) were dissolved in 25 ml of dry dichloromethane. The mixture was stirred under an argon atmosphere and triethylamine (2.2 ml, 15.8 mmol) was added. Then succinyl chloride (0.44 ml, 4.0 mmol) was added dropwise. The stirring was continued for 2 h at room temperature. Reaction mixture contained a large amount of a black tar, which was removed by filtration through Celite. Celite was then washed with dichloromethane. The combined filtrates were washed twice with water and dried over Na_2SO_4. The drying agent was filtered off and the solvents were evaporated. The product was purified by column chromatography (silica, dichloromethane : acetone 19:1) and recrystallized by slow addition of pentane to the solution of product in small amount of hot chloroform. Compound **1a** (32 mg, 3.4% yield) was obtained as brown powder. Mp. >280 °C (decomposition). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H, CH (6-membered ring)), 7.81 (dd, J = 3.1, 0.7 Hz, 1H, pyrrole: 5-H), 6.80 (dd, J = 3.6, 1.2 Hz, 1H, pyrrole: 3-H), 6.54 (t, J = 3.4 Hz, 1H, pyrrole: 4-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 131.7, 125.2, 123.6, 120.3, 118.4, 116.2. HRMS (EI) calcd for $C_{14}H_8N_2O_2$ (M^+): 236.0586; found: 236.0580. Elemental analysis calcd (%) for $C_{14}H_8N_2O_2$: C 71.18, H 3.41, N 11.86; found: C 71.19, H 3.60, N 11.65.

I addition to the dye **1a**, unreacted 2-formylpyrrole (0.74 g, 65% of the initial amount) was also separated from the reaction mixture.

Procedure 2. A mixture consisting of 2-formylpyrrole (238 mg, 2.5 mmol), powdered potassium carbonate (1.38 g, 10.0 mmol) and 10 ml of dry DMF was stirred under an argon

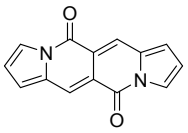
atmosphere at 0 °C. The solution of succinyl chloride (110 μl, 1.0 mmol) in 1.0 ml of dry dichloromethane was added dropwise. The stirring was continued for 2 h at 0 °C. The reaction mixture was then diluted with water and passed through Celite, which was washed twice with water. Then two portions of ethanol and three portions of chloroform were passed through Celite in order to recover the product. These filtrates were combined and washed twice with water and dried over Na_2SO_4. The drying agent was filtered off and the solvents were evaporated. The product was recrystallized by slow addition of pentane to its solution in small amount of hot chloroform. Compound **1a** (15 mg, 6.4% yield) was obtained as a brown powder. The product was identified by the comparison with previously synthesized sample.

1,4-Di(pyrrol-1-yl)butane-1,4-dione (3)



A mixture of succinamide (1.16 g, 10 mmol), 2,5-dimethoxytetrahydrofuran (3.9 ml, 30 mmol), *para*-toluenesulfonic acid monohydrate (190 mg, 1.0 mmol) and 25 ml of toluene was refluxed for 2 h under the Dean-Stark apparatus. The reaction mixture was cooled and the black precipitate, which was formed in the reaction, was filtered off and washed with chloroform. The filtrates were washed with water three times and dried over Na_2SO_4. Solvents were evaporated and the product was purified by the column chromatography (silica, hexanes : dichloromethane 1:2). The product was recrystallized from ethanol. Compound **3** (632 mg, 29% yield) was obtained as a white powder. Mp. 162–164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (br s, 4H, pyrrole: 2-H and 5-H), 6.36 – 6.27 (m, 4H, pyrrole: 3-H and 4-H), 3.34 (s, 4H, CH_2CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 119.0, 113.5, 28.9. HRMS (EI) calcd for $C_{12}H_{12}N_2O_2$ (M^+): 216.0899; found: 216.0910. Elemental analysis calcd (%) for $C_{12}H_{12}N_2O_2$: C 66.65, H 5.59, N 12.96; found: C 66.86, H 5.73, N 12.92.

Synthesis of dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1a) by the Vilsmeier-Haack formylation of compound 3

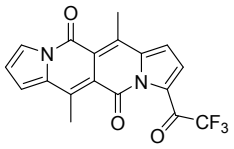


Under an argon atmosphere, to the solution of compound **3** (432 mg, 2.0 mmol) in 10 ml of dry 1,2-dichloroethane DMF (390 μl, 5.0 mmol) was added. Then phosphorus(V) oxychloride (480 μl, 5.2 mmol) was added dropwise and the mixture was refluxed for 2 h. The reaction was quenched by

the addition of saturated aqueous solution of sodium bicarbonate (10 ml). The resulting mixture was stirred for 5 min and diluted with dichloromethane and water. Layers were separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with water and dried over Na_2SO_4. The products were separated by column chromatography (silica, dichloromethane : acetone 19:1). Dye **1a** was recrystallized by slow addition of pentane to its solution in small amount of hot chloroform. The product was obtained as a brown powder (39 mg, 8.3% yield) and identified by the comparison with previously synthesized sample. In addition to compound **1a**, 2-formylpyrrole (127 mg, 33% yield) was also obtained.

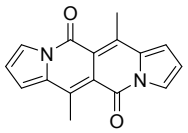
Acylation of compound 3 with acetic acid

The reaction was conducted following modified literature procedure for the selective 2-acylation of *N*-tosylpyrroles.[4] Compound **3** (216 mg, 1.0 mmol) was dissolved in 4.5 ml of dry dichloromethane under an argon atmosphere, and the solution was cooled to 0 °C. Trifluoroacetic anhydride (3.0 ml, 22 mmol) and acetic acid (460 µl, 8.0 mmol) were added and the resulting mixture was stirred at 0 °C for 10 min and then at room temperature for 4 h. The reaction mixture was then poured into a beaker containing 50 ml of saturated aqueous $NaHCO_3$ and mixed (CO_2 gas evolved). When the evolution of carbon dioxide was no longer observed, layers were separated. Aqueous layer was extracted three times with chloroform, and the combined organic layers were washed with water and dried over Na_2SO_4. Obtained mixture was separated using column chromatography (silica, hexanes : dichloromethane 1:2 → pure dichloromethane) to give two crude products, compounds **4** and **1b**, which were recrystallized by slow addition of methanol to hot solutions of the dyes in small amount of chloroform.



6,12-Dimethyl-3-trifluoroacetyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (4). Compound **4** (34 mg, 9.4% yield) was obtained as a dark brown powder. Mp. > 180 °C (decomposition). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 1.9 Hz, 1H, DPND: 9-H), 7.19 (d, J = 3.9 Hz, 1H, DPND: 1-H), 6.97 (d, J = 3.1 Hz, 1H, DPND: 7-H), 6.89 (d, J = 4.0 Hz, 1H, DPND: 2-H), 6.56 (t, J = 3.4 Hz, 1H, DPND: 8-H), 2.86 (s, 3H, CH_3), 2.81 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1 – 173.5 (m), 158.4, 143.3, 139.4, 137.8, 133.4, 128.4, 124.3, 124.3, 123.9, 119.1, 118.9, 116.0, 116.1 (q, J = 290 Hz), 114.80, 114.54, 18.27, 17.81. HRMS (ESI) calcd for

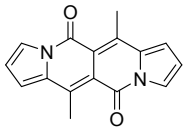
$C_{18}H_{11}F_3N_2O_3Na$ (M+Na^+): 383.0619; found: 383.0606. Elemental analysis calcd (%) for $C_{18}H_{11}F_3N_2O_3$: C 60.01, H 3.08, N 7.78; found: C 59.92, H 3.02, N 7.68.



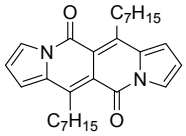
6,12-Dimethyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1b). Compound **1b** (33 mg, 12% yield) was obtained as a dark brown powder. Mp. > 280 °C (decomposition). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 1.7 Hz, 2H, pyrrole: 5-H), 6.95 – 6.85 (m, 2H, pyrrole: 3-H), 6.54 (t, J = 3.3 Hz, 2H, pyrrole: 4-H), 2.85 (s, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 140.5, 133.7, 122.7, 117.1, 115.6, 115.0, 18.3. HRMS (ESI) calcd for $C_{16}H_{12}N_2O_2Na$ (M+Na^+): 287.0796; found: 287.0786. Elemental analysis calcd (%) for $C_{16}H_{12}N_2O_2$: C 72.72, H 4.58, N 10.60; found: C 72.79, H 4.50, N 10.62.

General procedure for the preparation of 6,12-disubstituted DPND derivatives (1b-1e)

Compound **3** (108 mg, 0.50 mmol) was dissolved in 3.0 ml of dry dichloromethane under an argon atmosphere, and the solution was cooled to 0 °C. Subsequently, to the reaction flask were slowly added: carboxylic acid (3.0 mmol), trifluoroacetic anhydride (830 µl, 6.0 mmol) and trifluoroacetic acid (230 µl, 3.0 mmol). The resulting mixture was stirred at room temperature for given time. The reaction mixture was then slowly poured into a beaker containing 20 ml of vigorously stirred saturated aqueous $NaHCO_3$ (CO_2 evolved). When the evolution of carbon dioxide was no longer observed, the mixture was diluted with chloroform and layers were separated. Aqueous layer was extracted four times with chloroform, and the combined organic layers were washed with water and dried over Na_2SO_4. The product was purified by column chromatography and recrystallized (see below for details).

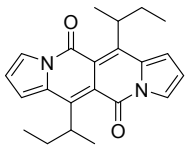


6,12-Dimethyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1b). Carboxylic acid used: acetic acid (172 µl, 3.0 mmol). Reaction time: 5 h. Product was purified using column chromatography (silica, dichloromethane) and recrystallized by slow addition of methanol to a hot solution of the dye in small amount of chloroform. Compound **1b** (23 mg, 17% yield) was obtained as a dark brown powder and identified by the comparison with previously synthesized sample.



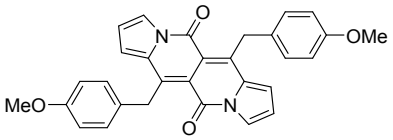
6,12-Diheptyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1c). Carboxylic acid used: caprylic acid (475 µl, 3.0 mmol). Reaction time: 3 h. Product was purified using column chromatography (silica, hexanes : dichloromethane 2:1 → 1:1) and recrystallized by slow addition of methanol to a solution of the dye in small amount of dichloromethane. Compound **1c** (63 mg, 29% yield) was obtained as a red solid. Mp. 107–109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 3.0, 1.3 Hz, 2H, pyrrole: 5-H), 6.87 (dd, J = 3.7, 1.3 Hz, 2H, pyrrole: 3-H), 6.54 (t, J = 3.4 Hz, 2H, pyrrole: 4-H), 3.35 – 3.22 (m, 4H, CH_2(CH$_2$)$_5$CH$_3$), 1.76 – 1.62 (m, 4H, CH$_2$(CH_2)$_5$CH$_3$), 1.58 – 1.47 (m, 4H, CH$_2$(CH_2)$_5$CH$_3$), 1.44 – 1.35 (m, 4H, CH$_2$(CH_2)$_5$CH$_3$), 1.35 – 1.23 (m, 8H, CH$_2$(CH_2)$_5$CH$_3$), 0.89 (t, J = 6.9 Hz, 6H, CH$_2$(CH$_2$)$_5$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 145.6, 133.4, 122.6, 116.7, 115.6, 114.6, 32.1, 31.2, 30.6, 30.5, 29.4, 22.8, 14.3. HRMS (ESI) calcd for $C_{28}H_{37}N_2O_2$ (M+H$^+$): 433.2855; found: 433.2848. Elemental analysis calcd (%) for $C_{28}H_{36}N_2O_2$: C 77.74, H 8.39, N 6.48; found: C 77.48, H 8.48, N 6.33.

The synthesis of compound **1c** was repeated in 10-times larger scale, using the same procedure and following amounts of reagents: compound **3** (1.08 g, 5.00 mmol), caprylic acid (4.75 ml, 30 mmol), trifluoroacetic anhydride (8.3 ml, 60 mmol), trifluoroacetic acid (2.30 ml, 30 mmol) and dichloromethane (30 ml) as a solvent. After 3.5 h of the reaction at room temperature 525 mg of product **1c** was obtained (23% yield).



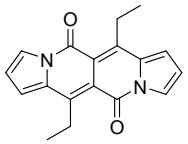
6,12-Di-*sec*-butyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1d). Carboxylic acid used: 2-methylbutyric acid (330 µl, 3.0 mmol). Reaction time: 6 h. Product was purified using column chromatography (silica, hexanes : dichloromethane 1:1) and recrystallized by slow addition of methanol to a solution of the dye in small amount of dichloromethane. Compound **1d** (36 mg, 21% yield) was obtained as red crystals. Mp. 176–178 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 2.9, 1.0 Hz, 2H, pyrrole: 5-H), 7.01 (d, J = 3.0 Hz, 2H, pyrrole: 3-H), 6.50 (t, J = 3.4 Hz, 2H, pyrrole: 4-H), 4.74 (br s, 2H, CH(CH$_3$)CH$_2$CH$_3$), 2.00 – 1.90 (m, 2H, CH(CH$_3$)CH_2CH$_3$), 1.90 – 1.79 (m, 2H, CH(CH$_3$)CH_2CH$_3$), 1.46 (dd, J = 7.1, 1.7 Hz, 6H, CH(CH_3)CH$_2$CH$_3$), 0.96 (t, J = 7.4 Hz, 6H, CH(CH$_3$)CH$_2$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 150.7, 130.3, 121.6, 118.7, 116.8, 115.2, 35.9, 30.6, 20.5, 13.1. HRMS (ESI) calcd for $C_{22}H_{24}N_2O_2Na$ (M+Na$^+$): 371.1735;

found: 371.1724. Elemental analysis calcd (%) for $C_{22}H_{24}N_2O_2$: C 75.83, H 6.94, N 8.04; found: C 75.63, H 6.89, N 7.94.



6,12-Bis(4-methoxybenzyl)dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1e). Carboxylic acid used: 4-methoxyphenylacetic acid (499 mg, 3.0 mmol). Reaction time: 6 h. Product was purified using column chromatography (silica, dichloromethane → dichloromethane : ethyl acetate 19:1) and recrystallized by slow addition of methanol to a solution of the dye in small amount of chloroform. Compound **1e** (25 mg, 10.5% yield) was obtained as red crystals. Mp. > 270 °C (decomposition). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 3.0, 1.2 Hz, 2H, pyrrole: 5-H), 7.24 – 7.18 (AA'BB', 4H, benzene: 2-H and 6-H), 6.91 (dd, J = 3.7, 1.2 Hz, 2H, pyrrole: 3-H), 6.83 – 6.78 (AA'BB', 4H, benzene: 3-H and 5-H), 6.52 (t, J = 3.4 Hz, 2H, pyrrole: 4-H), 4.69 (s, 4H, CH_2Ar), 3.75 (s, 6H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 158.0, 142.4, 133.6, 130.8, 129.3, 123.1, 118.2, 115.8, 115.3, 113.9, 55.2, 34.7. HRMS (ESI) calcd for $C_{30}H_{24}N_2O_4Na$ ($M+Na^+$): 499.1634; found: 499.1624. Elemental analysis calcd (%) for $C_{30}H_{24}N_2O_4$: C 75.62, H 5.08, N 5.88; found: C 75.65, H 5.10, N 5.92.

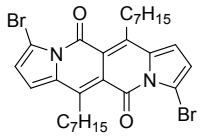
6,12-Diethyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (1f)



Compound **3** (216 mg, 1.0 mmol) was dissolved in 6.0 ml of dry dichloromethane under an argon atmosphere, and the solution was cooled to 0 °C. Subsequently, to the reaction flask were slowly added: propionic anhydride (380 µl, 3.0 mmol), trifluoroacetic anhydride (1.10 ml, 7.9 mmol) and trifluoroacetic acid (920 µl, 12.0 mmol). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was then slowly poured into a beaker containing 20 ml of vigorously stirred saturated aqueous $NaHCO_3$ (CO_2 evolved). When the evolution of carbon dioxide was no longer observed, the mixture was diluted with chloroform and layers were separated. Aqueous layer was extracted four times with chloroform, and the combined organic layers were washed with water and dried over Na_2SO_4. The product was purified by column chromatography (silica, toluene) and recrystallized by slow addition of methanol to the solution of product in small amount of dichloromethane. Compound **1f** (67 mg, 23%) was obtained as dark red crystals.

Mp. 226–229 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 3.0, 1.3 Hz, 2H, pyrrole: 5-H), 6.89 (dd, J = 3.6, 1.3 Hz, 2H, pyrrole: 3-H), 6.55 (t, J = 3.4 Hz, 2H, pyrrole: 4-H), 3.33 (q, J = 7.4 Hz, 4H, CH_2CH$_3$), 1.35 (t, J = 7.4 Hz, 6H, CH$_2$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 146.8, 133.0, 122.7, 116.7, 115.7, 114.5, 24.4, 14.5. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_4Na$ ($M+Na^+$): 315.1109; found: 315.1097.

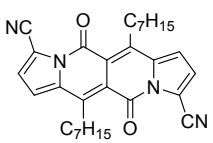
3,9-Dibromo-6,12-diheptyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (5)



A solution of compound **1c** (108 mg, 0.25 mmol) in 5 ml of chloroform was stirred at 0 °C (water-ice bath). Freshly recrystallized *N*-bromosuccinimide (93 mg, 0.52 mmol) was added and the obtained mixture was stirred in the darkness (protection with aluminium foil) for 16 h. During this time ice in the ice bath melted and the reaction mixture warmed to the room temperature. The reaction mixture was diluted with chloroform, washed with water three times, and dried over Na_2SO_4. The product was purified using column chromatography (silica, hexanes : dichloromethane 3:1 → 2:1) and recrystallized by slow addition of methanol to a solution of the dye in small amount of dichloromethane. Compound **5** (107 mg, 72% yield) was obtained as a red solid. Mp. 133–135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, J = 4.0 Hz, 2H, pyrrole: 3-H), 6.59 (d, J = 4.0 Hz, 2H, pyrrole: 4-H), 3.24 – 3.05 (m, 4H, CH_2(CH$_2$)$_5$CH$_3$), 1.71 – 1.59 (m, 4H, CH$_2$(CH_2)$_5$CH$_3$), 1.55 – 1.46 (m, 4H, CH$_2$(CH_2)$_5$CH$_3$), 1.41 – 1.23 (m, 12H, CH$_2$(CH_2)$_5$CH$_3$), 0.89 (t, J = 6.8 Hz, 6H, CH$_2$(CH$_2$)$_5$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 143.3, 135.0, 120.5, 115.8, 115.4, 106.6, 31.9, 30.3, 30.2 (2 signals), 29.2, 22.7, 14.1. HRMS (ESI) calcd for $C_{28}H_{34}Br_2N_2O_2$ (M^+): 588.0987; found: 588.0985. Elemental analysis calcd (%) for $C_{28}H_{34}Br_2N_2O_2$: C 56.96, H 5.80, N 4.74; found: C 56.98, H 5.77, N 4.76.

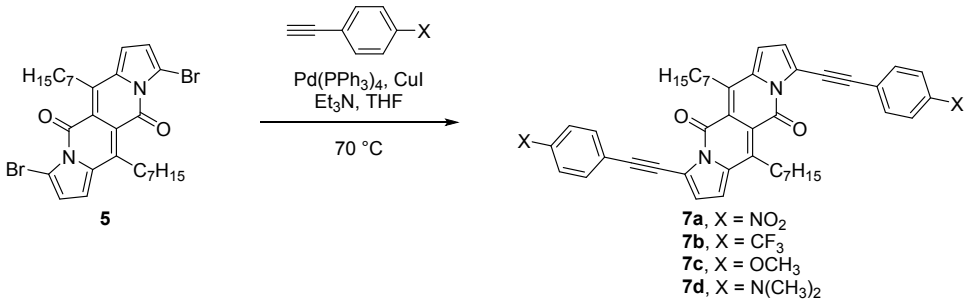
The synthesis of compound **5** was repeated in 4-times larger scale, using the same procedure and following amounts of reagents: compound **1c** (433 mg, 1.00 mmol), *N*-bromosuccinimide (374 mg, 2.10 mmol) and chloroform (15 ml) as a solvent. 379 mg of the product **5** was obtained (64% yield).

3,9-Dicyano-6,12-diheptyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (6)

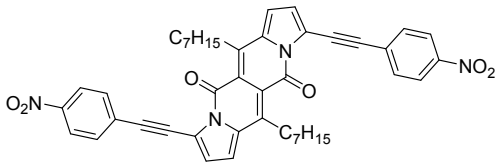


A mixture of compound **5** (59 mg, 0.10 mmol), copper(I) cyanide (20 mg, 0.22 mmol) and 2 ml of dry NMP was stirred under argon at 140 °C for 16 h and at 160 °C for 5 h. The mixture was diluted with water and passed through Celite, which was washed with water. Then the product was extracted from Celite with one portion of ethanol and three portions of chloroform. The organic filtrates were combined, washed with water twice and dried over Na_2SO_4. Product was purified by column chromatography (silica, hexanes : dichloromethane 2:3). After evaporation of eluent 16 mg of product was obtained (33% yield), which was recrystallized by slow addition of methanol to the warm solution of the dye in small amount of chloroform. Compound **6** (11 mg, 23% yield) was obtained as red crystals. Mp. 222-225 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 4.0 Hz, 2H, pyrrole: 3-H), 6.92 (d, J = 4.0 Hz, 2H, pyrrole: 4-H), 3.43 – 3.15 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.76 – 1.62 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.59 – 1.47 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.42 – 1.25 (m, 12H, $CH_2(CH_2)_5CH_3$), 0.90 (t, J = 6.8 Hz, 6H, $CH_2(CH_2)_5CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 146.6, 136.2, 127.0, 116.9, 116.0, 112.5, 106.4, 31.8, 31.1, 30.2, 30.1, 29.1, 22.7, 14.1. HRMS (ESI) calcd for $C_{30}H_{34}N_4O_2Na$ ($M+Na^+$): 505.2579; found: 505.2574.

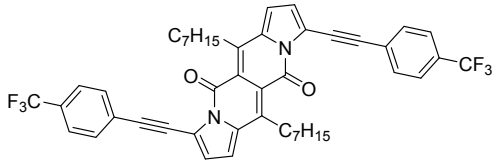
General procedure for the Sonogashira coupling of compound 5 with *para*-substituted phenylacetylenes – synthesis of compounds 7a-d



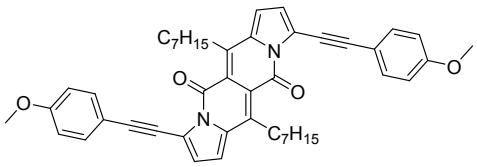
In a Schlenck flask containing a magnetic stirring bar were placed: bromoderivative **5** (0.10 mmol, 59 mg), copper(I) iodide (1.9 mg, 0.010 mmol), tetrakis(triphenylphosphine)-palladium(0) (5.8 mg, 0.005 mmol), and *para*-substituted phenylacetylene (0.30 mmol). The vessel was evacuated and backfilled with argon (3 times) and anhydrous, degassed THF was added (3 ml) followed by dry triethylamine (56 µl, 0.40 mmol). The vessel was tightly closed and again carefully evacuated (until the mixture start to boil) and backfilled with argon (3 times). The content of the flask was stirred for 20 h at 70 °C (above the boiling point). Solvents were evaporated and the product was purified as described below.



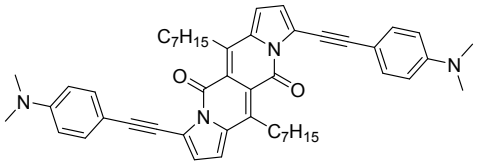
6,12-Diheptyl-3,9-bis((4-nitrophenyl)ethynyl)dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (7a). Prepared from 4-nitrophenylacetylene (44 mg, 0.30 mmol). Product was purified using column chromatography (silica, hexanes : dichloromethane 1:1 → 1:2) and recrystallized from toluene. Compound **7a** (56 mg, 78% yield) was obtained as a dark violet powder. Mp. > 400 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 8.26 – 8.18 (AA'BB', 4H, benzene: 3-H and 5-H), 7.77 – 7.67 (AA'BB', 4H, benzene: 2-H and 6-H), 6.89 (s, 4H, pyrrole: 3-H and 4-H), 3.34 – 3.27 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.80 – 1.69 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.61 – 1.54 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.44 – 1.23 (m, 12H, $CH_2(CH_2)_5CH_3$), 0.90 (t, J = 6.9 Hz, 6H, $CH_2(CH_2)_5CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 50 °C) δ 158.4, 147.5, 144.3, 135.5, 132.2, 130.3, 123.8, 118.6, 116.9, 116.3, 96.2, 88.1, 32.1, 31.0, 30.5 (2 signals), 29.2, 22.8, 14.2. Elemental analysis calcd (%) for $C_{44}H_{42}N_4O_6$: C 73.11, H 5.86, N 7.75; found: C 73.20, H 5.93, N 7.71.



6,12-Diheptyl-3,9-bis((4-(trifluoromethyl)phenyl)ethynyl)dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (7b). Prepared from 4-(trifluoromethyl)phenylacetylene (51 mg, 0.30 mmol). Product was purified using column chromatography (silica, hexanes : dichloromethane 4:1 → 3:7) and recrystallized by slow addition of methanol to hot solution of the dye in small amount of chloroform. Compound **7b** (44 mg, 57% yield) was obtained as a dark green powder. Mp. 200–203 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.67 (AA'BB', 4H, benzene: 3-H and 5-H), 7.67 – 7.58 (AA'BB', 4H, benzene: 2-H and 6-H), 6.89 (d, J = 4.0 Hz, 2H, pyrrole: 3-H), 6.87 (d, J = 4.0 Hz, 2H, pyrrole: 4-H), 3.34 – 3.23 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.77 – 1.68 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.59 – 1.52 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.48 – 1.40 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.38 – 1.29 (m, 8H, $CH_2(CH_2)_5CH_3$), 0.89 (t, J = 7.0 Hz, 6H, $CH_2(CH_2)_5CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 144.0, 135.1, 131.8, 125.5, 125.4, 123.4, 118.8, 116.6, 116.1, 96.5, 85.2, 32.1, 30.9, 30.5, 29.9, 29.2, 22.8, 14.3 (signals of CF_3 group and adjacent carbon atom were not identified due to low intensities caused by ^{13}C-^{19}F coupling). HRMS (ESI) calcd for $C_{46}H_{42}F_6N_2O_2$ (M^+): 768.3150; found: 768.3153.



6,12-Diheptyl-3,9-bis((4-methoxyphenyl)ethynyl)dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (7c). Prepared from 4-methoxyphenylacetylene (40 mg, 0.30 mmol). Product was purified using column chromatography (silica, hexanes : dichloromethane 3:2 → 5:4) and recrystallized by slow addition of methanol to solution of the dye in small amount of dichloromethane. Compound **7c** (33 mg, 48% yield) was obtained as a dark violet powder. Mp. 185–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.48 (AA'BB', 4H, benzene: 2-H and 6-H), 6.95 – 6.87 (AA'BB', 4H, benzene: 3-H and 5-H), 6.84 (d, J = 4.0 Hz, 2H, pyrrole: 3-H), 6.77 (d, J = 3.9 Hz, 2H, pyrrole: 4-H), 3.85 (s, 6H, OCH_3), 3.34 – 3.21 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.78 – 1.66 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.60 – 1.51 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.48 – 1.39 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.39 – 1.27 (m, 8H, $CH_2(CH_2)_5CH_3$), 0.90 (t, J = 6.5 Hz, 6H, $CH_2(CH_2)_5CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 158.6, 143.3, 134.3, 133.2, 122.1, 119.7, 116.0, 115.8, 115.5, 114.1, 98.3, 81.9, 55.3, 32.0, 30.7, 30.3, 29.0, 22.7, 14.2. HRMS (ESI) calcd for $C_{46}H_{48}N_2O_4Na$ ($M+Na^+$): 715.3512; found: 715.3506.



3,9-Bis((4-(dimethylamino)phenyl)ethynyl)-6,12-diheptyldipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (7d). Prepared from 4-(dimethylamino)phenylacetylene (44 mg, 0.30 mmol). Product was purified using column chromatography (silica, hexanes : dichloromethane 1:1 → 1:3) and recrystallized by slow addition of methanol to solution of the dye in small amount of dichloromethane. Compound **7d** (40 mg, 56% yield) was obtained as a black powder. Mp. 235–239 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.46 (AA'BB', 4H, benzene: 2-H and 6-H), 6.83 (d, J = 4.0 Hz, 2H, pyrrole: 3-H), 6.74 (d, J = 4.0 Hz, 2H, pyrrole: 4-H), 6.73 – 6.59 (m, 4H, benzene: 3-H and 5-H), 3.32 – 3.23 (m, 4H, $CH_2(CH_2)_5CH_3$), 3.02 (s, 12H, NCH_3), 1.77 – 1.68 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.59 – 1.52 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.47 – 1.40 (m, 4H, $CH_2(CH_2)_5CH_3$), 1.37 – 1.30 (m, 8H, $CH_2(CH_2)_5CH_3$), 0.90 (t, J = 6.8 Hz, 6H, $CH_2(CH_2)_5CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 150.2, 142.8, 134.0, 132.9, 121.5, 120.2, 115.8, 111.9, 99.9, 81.8, 40.3, 32.1, 30.7, 30.4, 29.1, 22.7, 14.2. HRMS (ESI) calcd for $C_{48}H_{55}N_4O_2$ ($M+H^+$): 719.4325; found: 719.4325.

Elemental analysis calcd (%) for $C_{48}H_{54}N_4O_2$: C 80.19, H 7.57, N 7.79; found: C 80.08, H 7.50, N 7.72.

3. X-ray structure of compound 1f

Description

Single crystals of compound **1f** were obtained by slow diffusion of methanol vapours into the solution of **1f** in 1,2-dichloroethane. Crystal selected for X-ray experiment was small needle with dimensions 0.084 mm × 0.101 mm × 0.337 mm.

Crystal data for compound **1f**: $C_{18}H_{16}N_2O_2$; M_r = 292.33, tetragonal, a = 24.3920(10) Å, b = 24.3920(10) Å, c = 4.8236(3) Å, $\alpha = \beta = \gamma = 90°$, V = 2869.9(3) Å^3, T = 296(2) K, λ = 1.54178 Å (CuK\α), space group $I4_1/a$ (no. 88), Z = 8, μ = 0.720 mm^{-1}, d = 1.353 g cm^{-3}, F(000) = 1232, 7619 reflections collected, 1156 independent (R_{int} = 0.0582) which were used in all calculations, 2θ range 3.624–68.298°, Goodnes of Fit = 1.045. The final R_1 and $wR_2(F^2)$ were 0.0538 and 0.1108 (all data), 0.0401 and 0.1033 ($I > 2\sigma(I)$). Largest diff. peak and hole: 0.098 and -0.108 eÅ^{-3}.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 1433015. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

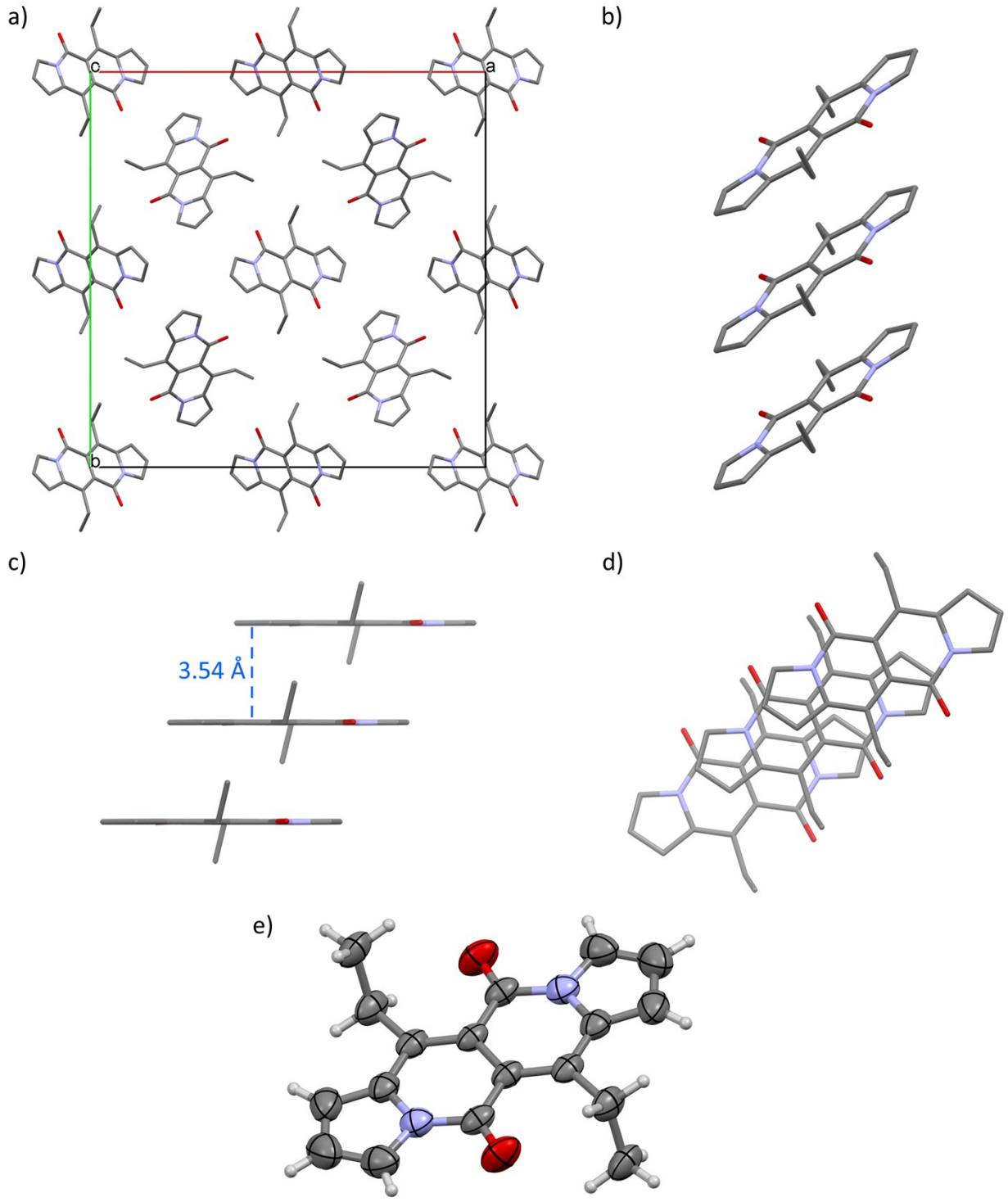


Figure S1. X-ray structure of compound **1f**. a) Crystal unit cell, view along c axis. b) Columnar stack, view along b axis; c) view along the chromophore plane; d) view perpendicular to the chromophore. e) Thermal ellipsoid plots drawn at 50 % probability level. On a)–d) hydrogen atoms were omitted for clarity.

4. Photophysical properties and DFT calculations of dye 1a

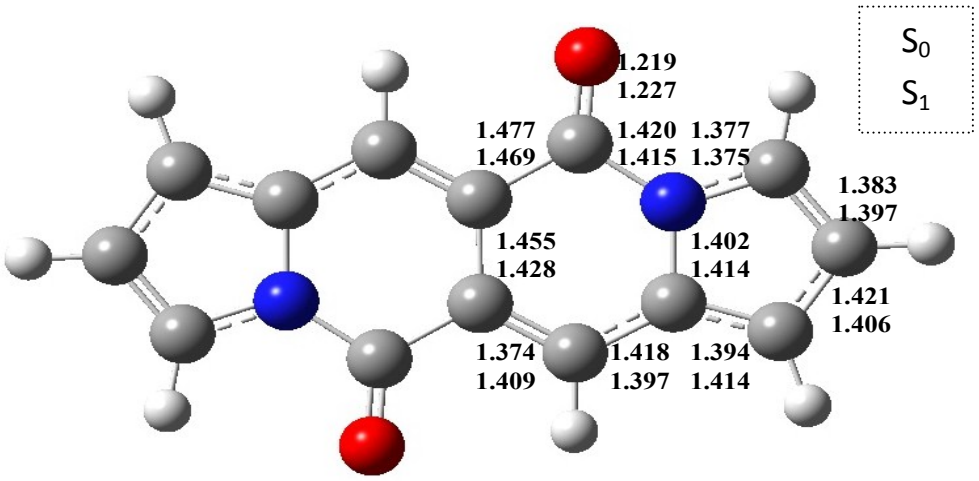


Figure S2. Calculated bond lengths for the structure of **1a**, optimized in the ground S_0 state (upper values) and in the lowest excited S_1 state (lower values).

Description

Molecule of the dye **1a** has interesting and unusual distribution of electronic charge, as shown in Figure S3. Characteristic feature is localization of charges on the C=O and N–C bonds (in both, the S_0 and S_1 states), which can be illustrated as the system of two pairs of close lying dipoles. These dipoles are indicated on Figure S3 in form of the blue arrows. The molecule, as the whole, has no dipole moment, but the strong local charges may considerably influence the shape of surrounding this molecule solvent cage, especially in polar solvents.

On Figure S5 the diagram of the electronic states of **1a** is shown. Molecular skeletons presented on the right side of the figure remind that the geometry of the molecule in the S_0 and S_1 states is different. Spectacular result is creation of a "chain" of delocalized π bonds connecting both sides of the molecule in the excited S_1 state (such the connection is absent in the S_0). Different geometry of the molecule in both states is reflected in vibrational structure of the absorption and fluorescence spectra, pointing for vibrations which play the role of accepting modes in the non-radiative relaxation by internal conversion channel.

We should notice a very good agreement between the experimental and calculated values of the rate constants k_{fl}, describing radiative relaxation of the S_1 state (Table S2). The remaining non-radiative relaxation, described by the rate constant k_{nr}, may proceed either by intersystem crossing or internal conversion channels. According to calculations, the triplet state T_2 is located slightly

below the S_1 (Figure S5), and from the energetic point of view efficient intersystem crossing between both states should be possible, and even expected.[5] However, in the group symmetry C_{2h} (to which **1a** belongs) the spin-orbit coupling (responsible for mixing of singlet and triplet states) cannot contribute to the transition between purely electronic $S_1(B_u)$ and $T_2(A_g)$ states. Symmetry prohibition can be broken if to take into account possibility of additional vibronic coupling (which should lead however to less efficient intersystem crossing than purely electronic one). We are not able to discuss further this point because of lack of data. The T_1 state is located far to the red (out of the detection range of our set-up), and expected phosphorescence extremely weak.

Table S1. Energies (ν) and oscillator strengths (f) for the $S_0 \rightarrow S_i$ transitions calculated for isolated **1a** molecule and for this molecule in *n*-heptane and dichloromethane solvents. The nπ* transition are presented in italic.

isolated molecule				heptane (ε=1.91, n=1.387)				dichloromethane (ε=8.93, n=1.424)			
ν [cm^{-1}]	λ [nm]	f	sym	ν [cm^{-1}]	λ [nm]	f	sym	ν [cm^{-1}]	λ [nm]	f	sym
21049	475.09	0.4573	B_U	20073	498.19	0.5874	B_U	18739	533.65	0.7667	B_U
24337	410.89	0.0000	A_G	24089	415.13	0.0000	A_G	23739	421.24	0.0000	A_G
28008	*357.04*	*0.0000*	*A_U*	*28259*	*353.86*	*0.0000*	*A_U*	*28643*	*349.12*	*0.0000*	*A_U*
29282	341.50	0.0000	A_G	29086	343.81	0.0000	A_G	28809	347.12	0.0000	A_G
31764	*314.82*	*0.0000*	*B_G*	31816	314.31	0.1737	B_U	31450	317.96	0.2381	B_U
32070	311.81	0.1336	B_U	*32000*	*312.50*	*0.0000*	*B_G*	*32366*	*308.97*	*0.0000*	*B_G*
33225	300.97	0.0000	A_G	32896	303.99	0.0000	A_G	32438	308.28	0.0000	A_G
38133	262.24	0.0165	B_U	37918	263.73	0.0771	B_U	37168	269.05	0.8192	B_U
39008	256.35	0.6820	B_U	38210	261.71	0.7154	B_U	37689	265.33	0.0646	B_U
40669	*245.89*	*0.0000*	*B_G*	*40835*	*244.89*	*0.0000*	*B_G*	40725	245.55	0.0000	A_G
41227	242.56	0.0000	A_G	41020	243.78	0.0000	A_G	*41094*	*243.34*	*0.0000*	*B_G*
44066	*226.93*	*0.0002*	*A_U*	*44221*	*226.14*	*0.0003*	*A_U*	43951	227.53	0.1170	B_U
44531	224.56	0.1108	B_U	44276	225.86	0.1131	B_U	*44466*	*224.89*	*0.0004*	*A_U*
45617	219.21	0.0000	A_G	45310	220.70	0.0000	A_G	44854	222.95	0.0000	A_G
46286	216.05	0.1230	B_U	46010	217.34	0.1683	B_U	45569	219.45	0.2669	B_U
47072	212.44	0.0000	A_G	46961	212.94	0.0000	A_G	46827	213.55	0.0000	A_G
50052	199.79	0.1464	B_U	49706	201.18	0.1908	B_U	49198	203.26	0.2581	B_U

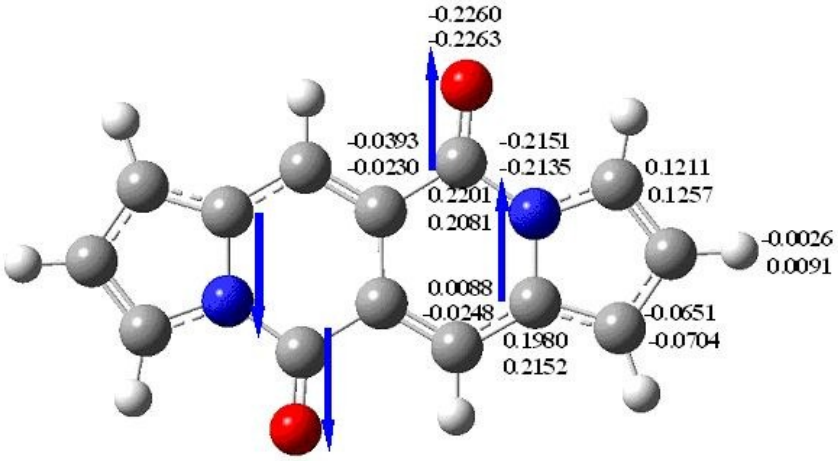


Figure S3. Distribution of charges in the electronic ground S_0 state (upper values) and in the excited S_1 state (lower values).

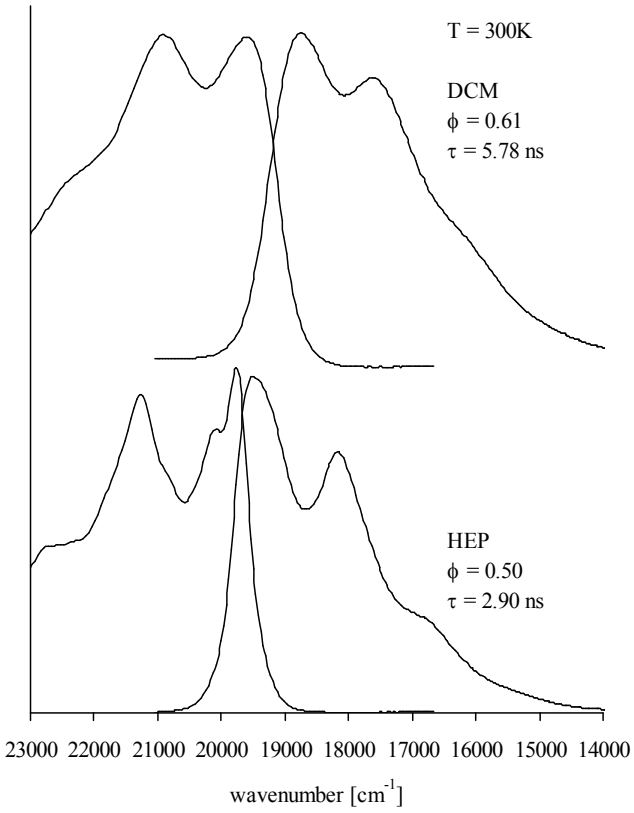


Figure S4. Experimentally monitored absorption and fluorescence spectra of **1a** in *n*-heptane and dichloromethane at room temperature.

Table S2. Collection of spectroscopic data for **1a** in *n*-heptane (HEP at room temperature, RT, and at 5 K) and in dichloromethane (DCM at RT). Calculated data were obtained by using the TD B3LYP.ccPVDZ method. ϕ_{fl} - fluorescence quantum yield, τ_{fl} - fluorescence decay time, k_f and k_{nr} are respectively the radiative (fluorescence) and non-radiative rate constants, calculated according to the formulas: $k_f=\phi/\tau$, $k_{nr}=(1-\phi)/\tau$.

	experiment			calculations		
	HEP - 4K	HEP - RT	DCM - RT	ISOL	HEP	DCM
ν_{abs} [cm^{-1}]	19278	19801	19644	21049	20073	18739
ν_{flu} [cm^{-1}]	19193	19417	18691	19378	18276	16732
$\delta\nu$ [cm^{-1}]	285	384	953	1670	1797	2007
$\nu(0,0)$ [cm^{-1}]	19227	19685	19193	20201	19175	17735
f –oscillator strength				0.4573	0.5874	0.7667
τ_{fl} [sec]		$4.43\ 10^{-9}$	$5.93\ 10^{-9}$			
ϕ_{fl}		0.50	0.61			
k_f [sec^{-1}]		$1.13\ 10^8$	$1.03\ 10^8$	$1.14\ 10^8$	$1.32\ 10^8$	$1.43\ 10^8$
k_{nr} [sec^{-1}]		$1.13\ 10^8$	$0.66\ 10^8$			

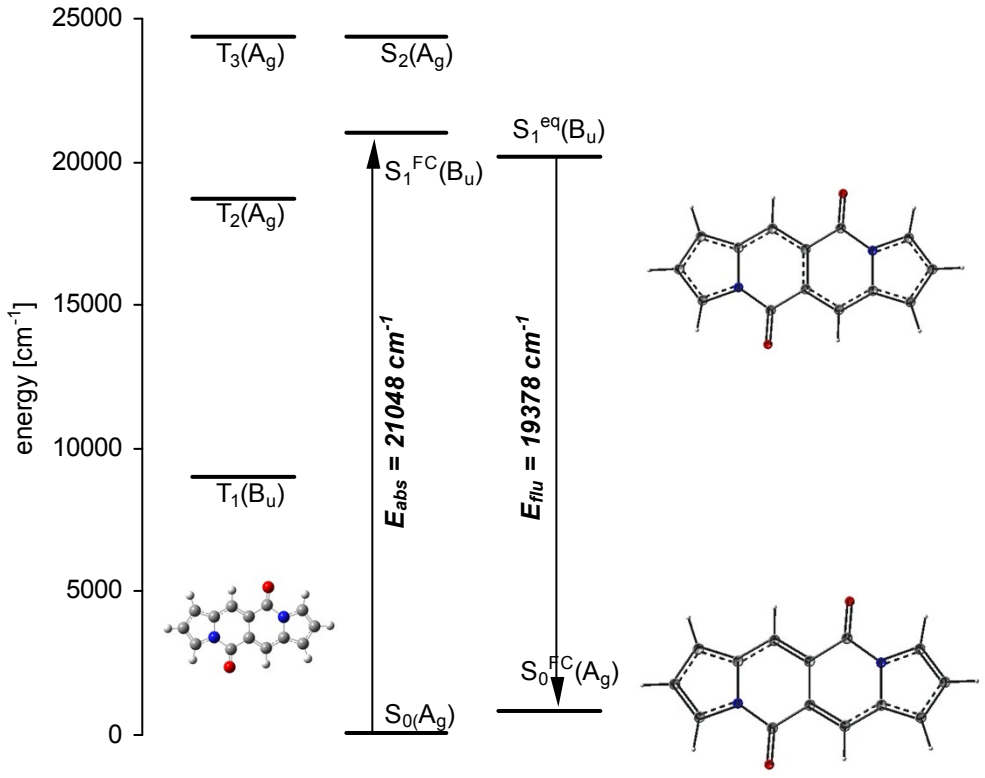
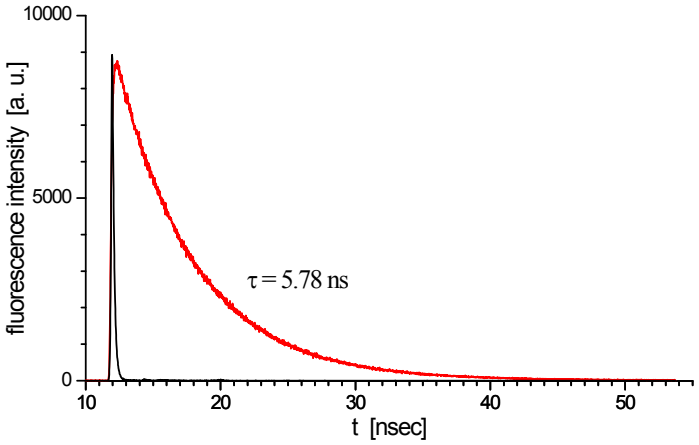
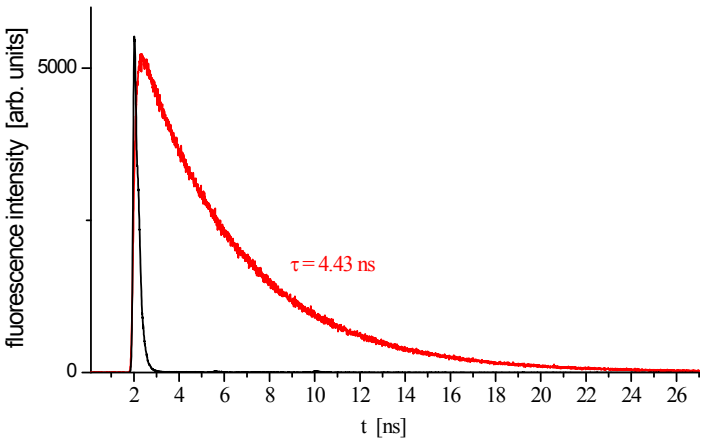


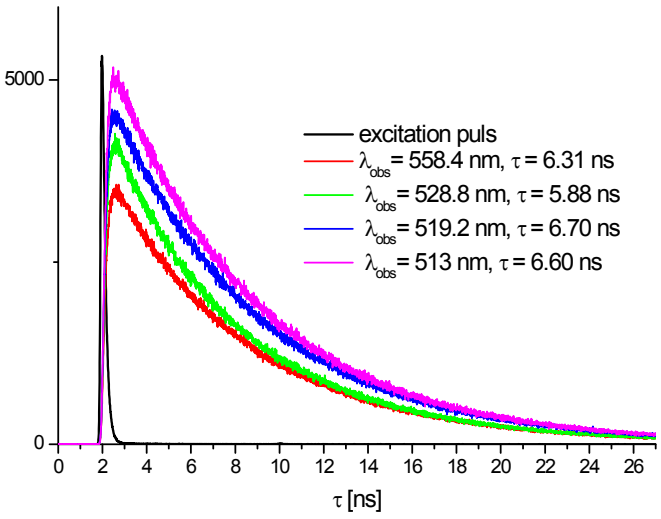
Figure S5. Diagram of the electronic states of **1a**. On right side - the structures of the molecule optimized in the S_0 and S_1 states.



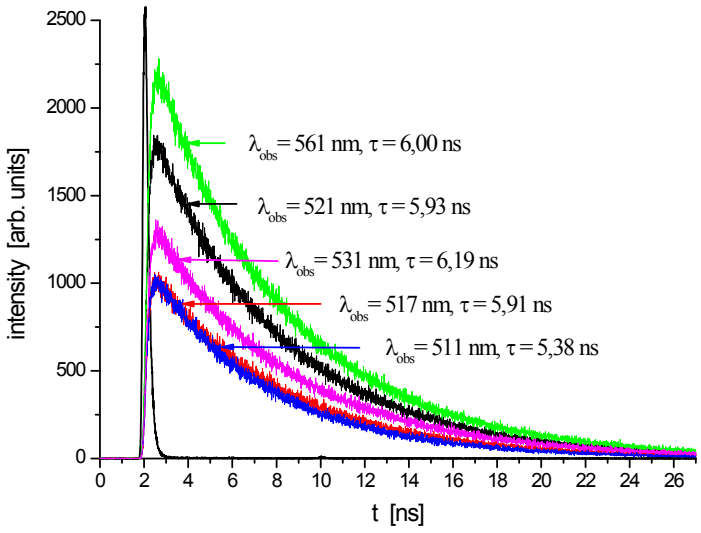
1a in dichloromethane at 300 K, λ_{exc}= 430 nm, λ_{obs}= 535 nm.



1a in *n*-nonane at 300 K, λ_{exc}= 430 nm, λ_{obs}= 511 nm.

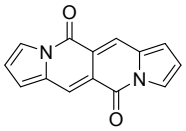
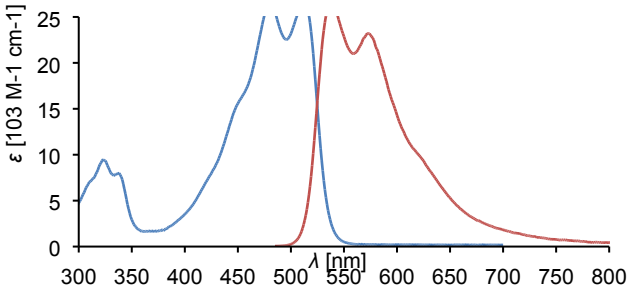
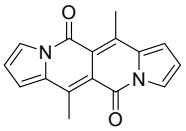
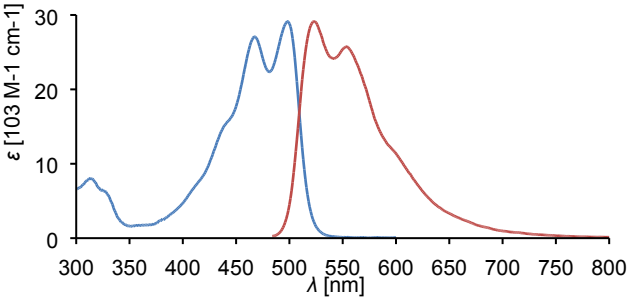
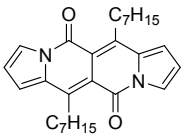
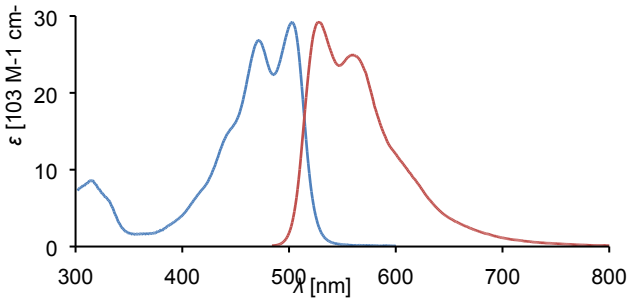
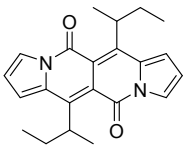
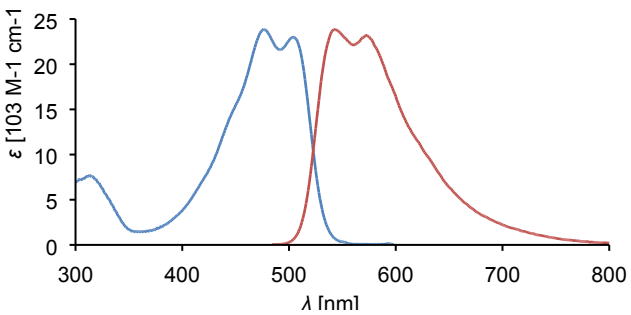


1a in *n*-nonane at 5 K, λ_{exc}= 430 nm.

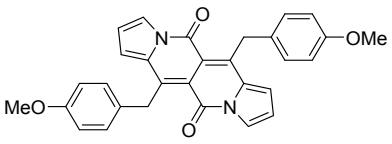


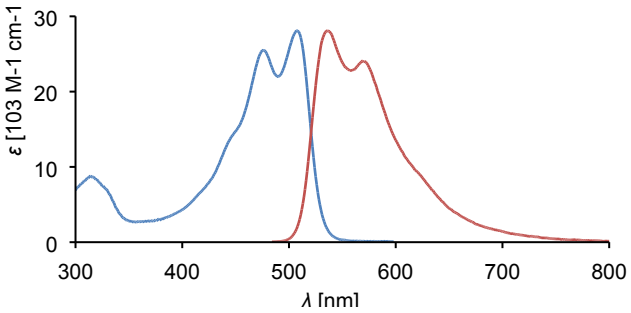
1a in *n*-hepane at 5 K, λ_{exc}= 430 nm.

5. UV-Vis absorption and emission spectra of obtained dyes in CH_2Cl_2

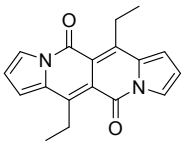
Dye	Structure	UV-Vis absorption and emission spectra
1a		
1b		
1c		
1d		

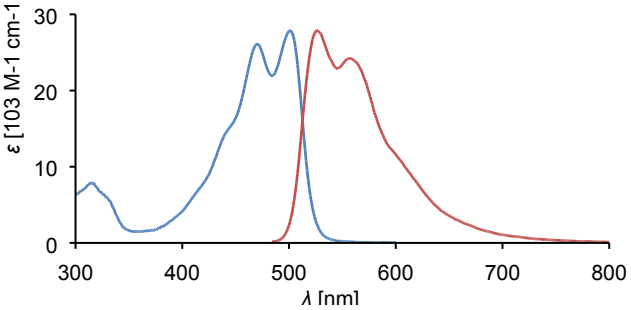
1e


MeO
OMe
O
N
O
N

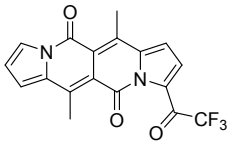

ε [103 M-1 cm-1
30
20
10
0
300
400
500
600
700
800
λ [nm]

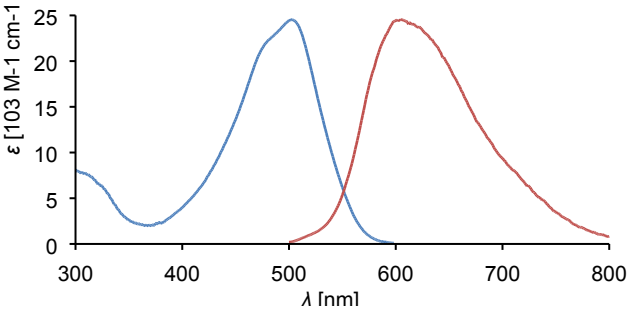
1f


O
N
O
N
O

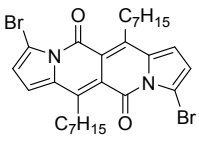

ε [103 M-1 cm-1
30
20
10
0
300
400
500
600
700
800
λ [nm]

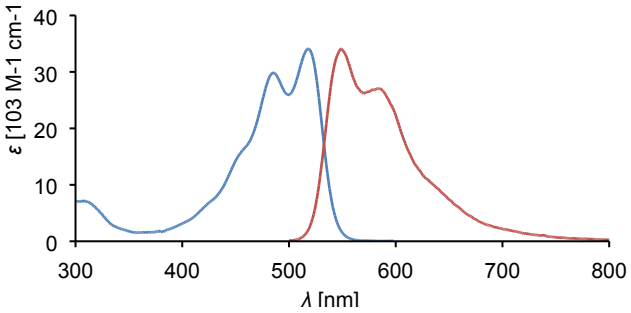
4


O
N
O
N
O
O
CF3

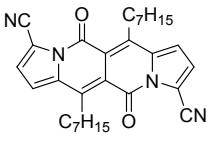

ε [103 M-1 cm-1
25
20
15
10
5
0
300
400
500
600
700
800
λ [nm]

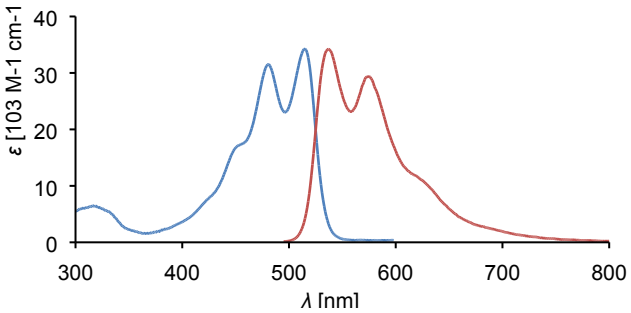
5


Br
O
C7H15
N
N
C7H15
O
Br

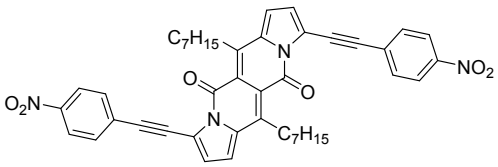

ε [103 M-1 cm-1
40
30
20
10
0
300
400
500
600
700
800
λ [nm]

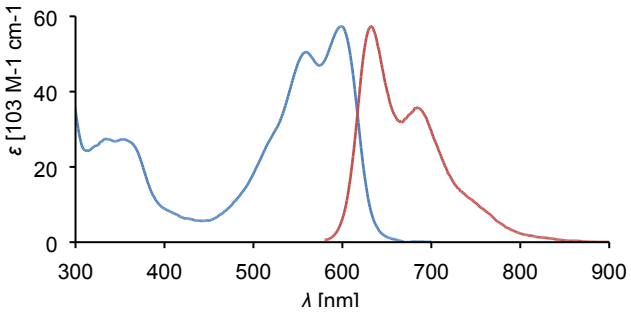
6


NC
O
C7H15
N
N
C7H15
O
CN

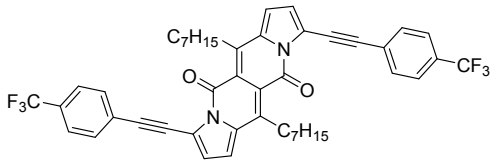

ε [103 M-1 cm-1
40
30
20
10
0
300
400
500
600
700
800
λ [nm]

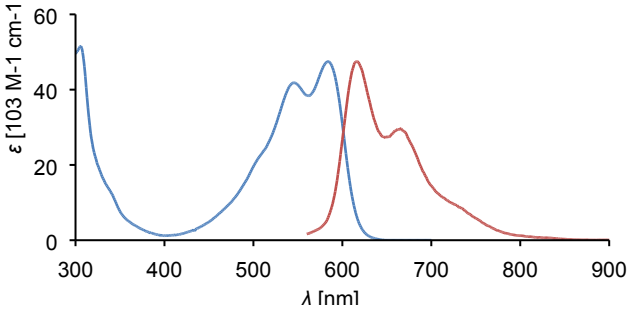
7a


C7H15
N
O
O
N
C7H15
O2N
NO2

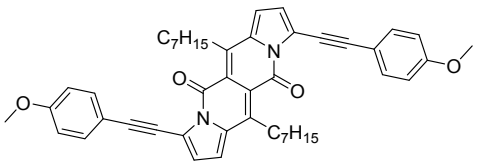

ε [103 M-1 cm-1
60
40
20
0
300
400
500
600
700
800
900
λ [nm]

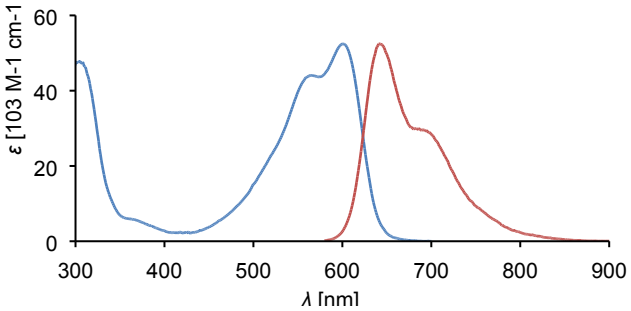
7b


C7H15
N
O
O
N
C7H15
F3C
CF3

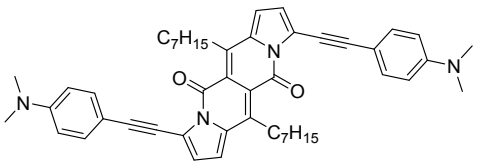

ε [103 M-1 cm-1
60
40
20
0
300
400
500
600
700
800
900
λ [nm]

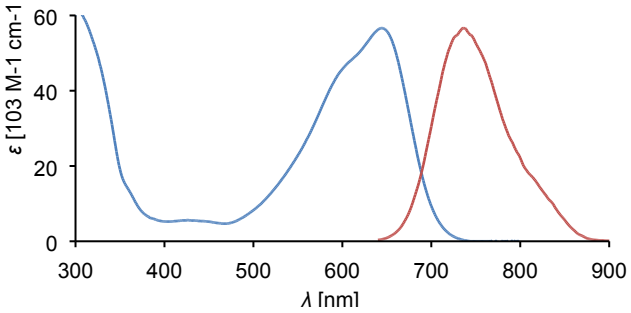
7c


C7H15
N
O
O
N
C7H15
O
O


ε [103 M-1 cm-1
60
40
20
0
300
400
500
600
700
800
900
λ [nm]

7d


C7H15
N
O
O
N
C7H15
N
N


ε [103 M-1 cm-1
60
40
20
0
300
400
500
600
700
800
900
λ [nm]

6. Cyclic voltammetry

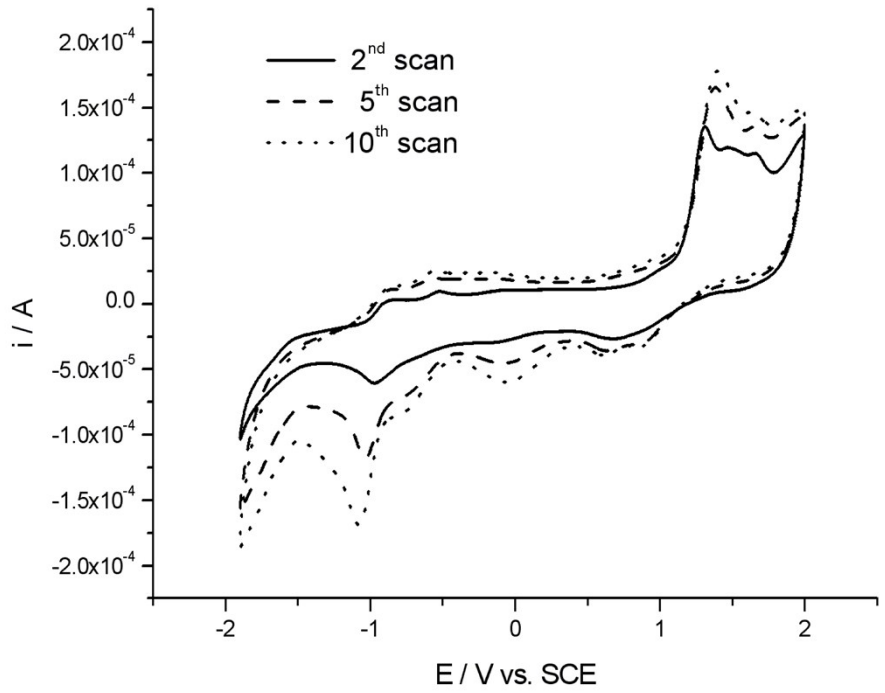


Figure S6. Cyclovoltammetric curve registered for **1a** in dichloromethane in the entire range of examined potentials: -1800 ÷ 2100 mV, v = 100 mV s^{-1}.

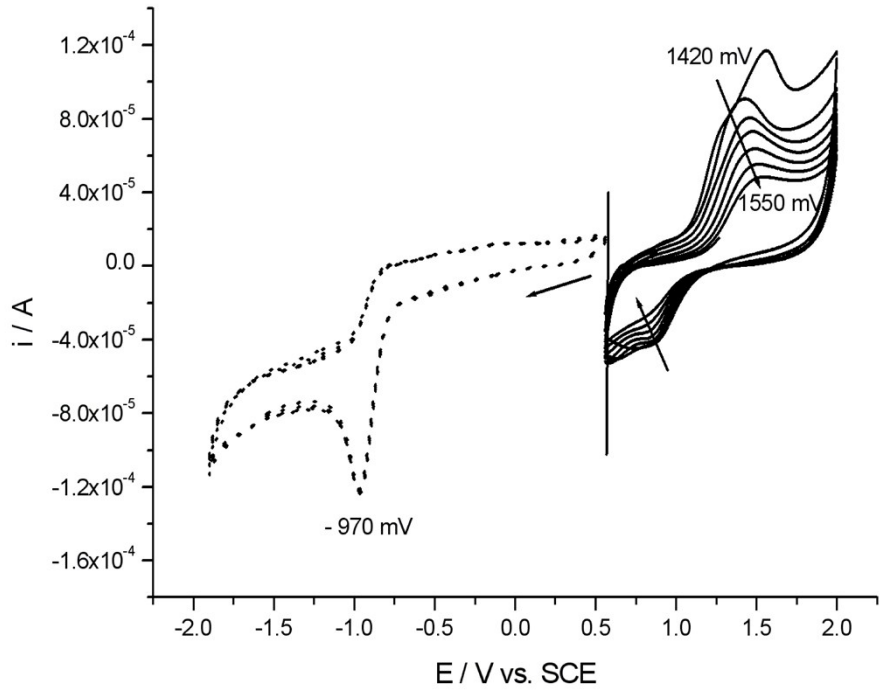


Figure S7. Cyclovoltammetric curve registered for **1a** in dichloromethane in the selected ranges of potentials: -1800 ÷ 560 mV (dotted line), and 560 ÷ 2100 mV, v = 100 mV s^{-1}.

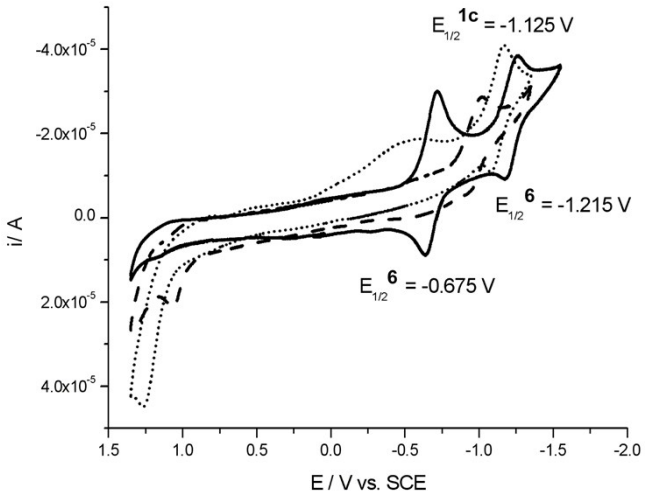


Figure S8. Cyclovoltammogramms of the dyes **1c** (dotted line), **6** (solid line) and **7b** (dashed line) in dichloromethane measured using the saturated calomel electrode (SCE) as the reference.

Cyclic voltammetry was carried out with a CH Instrument 440A potentiostat. A homemade three-electrode electrochemical cell was used which consisted of a platinum button, a platinum wire as a working and counter electrode, respectively. A saturated calomel electrode (SCE) separated from the bulk of the solution by a low porosity fritted-glass bridge was used as a reference electrode. Concentration of solutions during measurements was 10^{-4} mol/dm^3.

Table S3. Redox potentials (vs. SCE) of the selected DPNDs measured in dichloromethane.

Dye	$E1/2_{red1}$ [V]	$E1/2_{red2}$[V]	$E1/2_{ox}$ [V]	E_{red1}^{onset} [V]	E_{ox}^{onset} [V]	electron affinity [eV]	ionic potential[eV]
1c	–1.125	-	-	–1.036		–3.3	-
6	–0.675	–1.215	-	–0.55		–3.8	-
7b	–1.020		1.065	–0.804	0.93	–3.5	–5.3

The ionic potential (HOMO) and electron affinity (LUMO) values were estimated from the onset potentials of the first oxidation and reduction events, respectively. The ionic potential and electron affinity were calculated according to the following equations:
ionic potential (eV) = – [E_{ox}^{onset} – 0.46 + 4.8]
electron affinity (eV) = – [E_{red}^{onset} – 0.46 + 4.8]
where '– 0.46' is difference between electrochemical potentials measured vs. Fc/Fc^+ and vs. SEC.

7. Literature

[1] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts,

R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] V. Barone, J. Bloino, M. Biczysko and F. Santoro, *J. Chem. Theor. Comput*. 2009, **5**, 540–554.

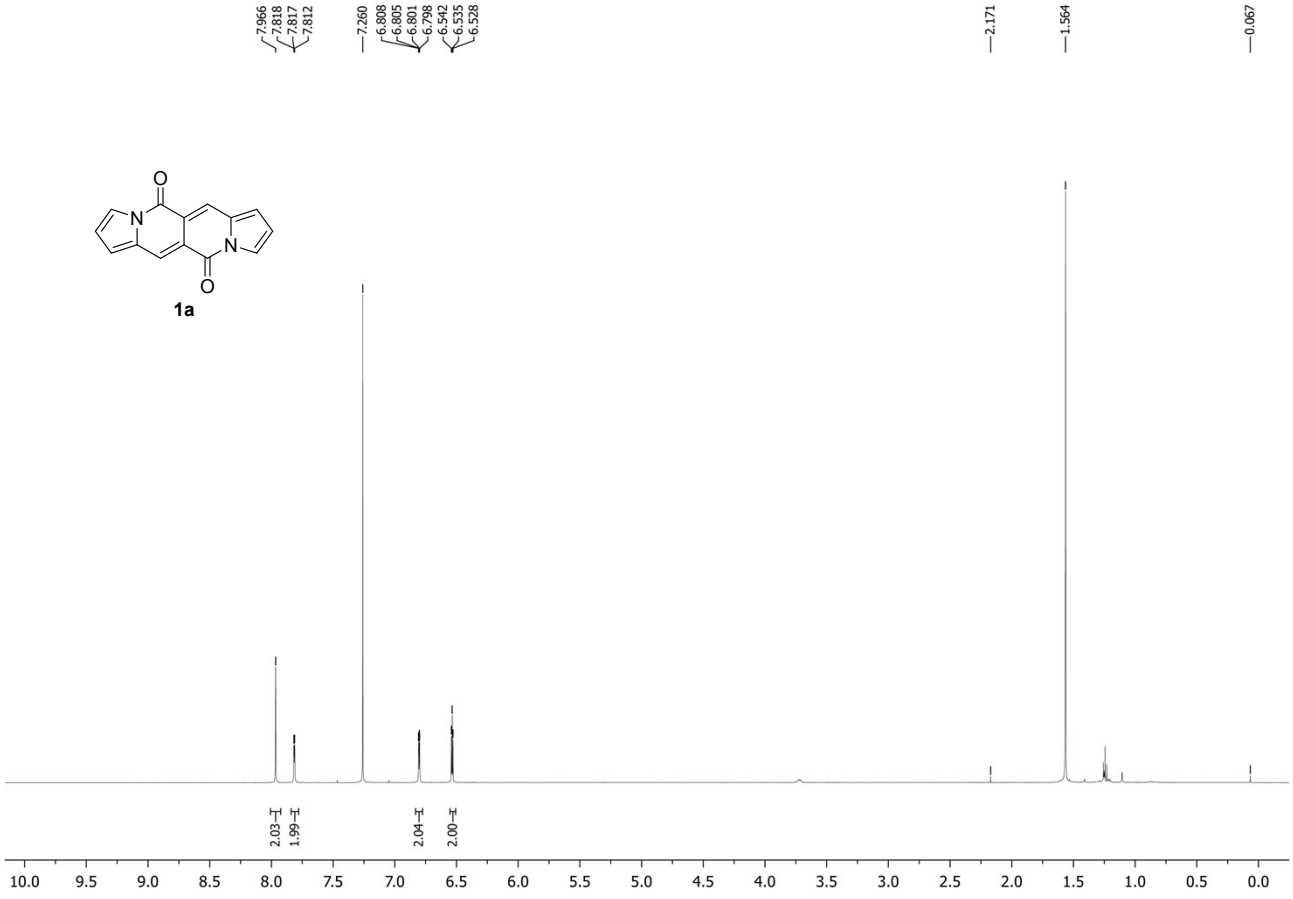
[3] J. Bloino, M. Biczysko, F. Santoro and V. Barone, *J. Chem. Theor. Comput*. 2010, **6**, 1256–1274.

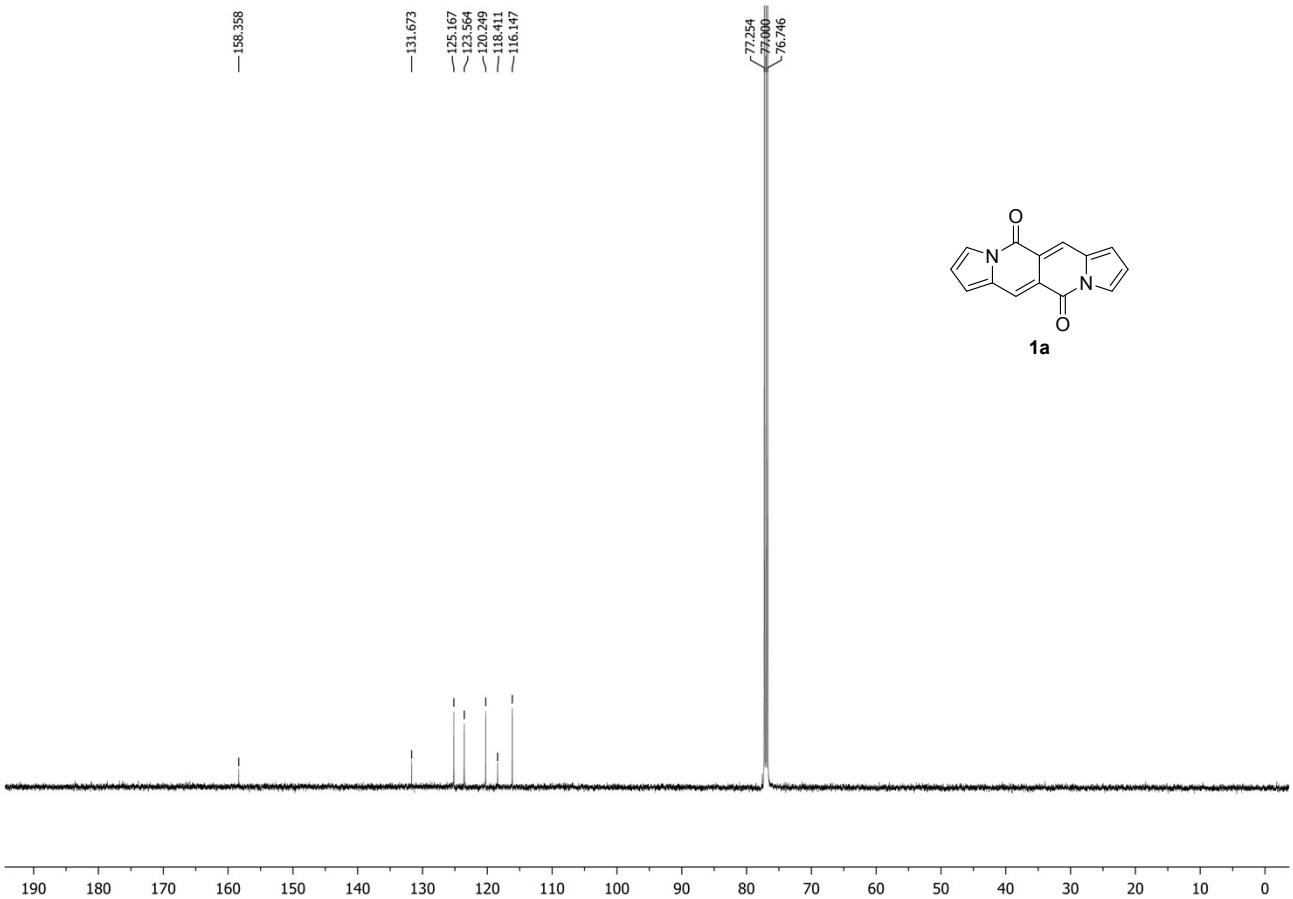
[4] C. Song, D. W. Knight and M. A. Whatton, *Tetrahedron Lett.* 2004, **45**, 9573–9576.

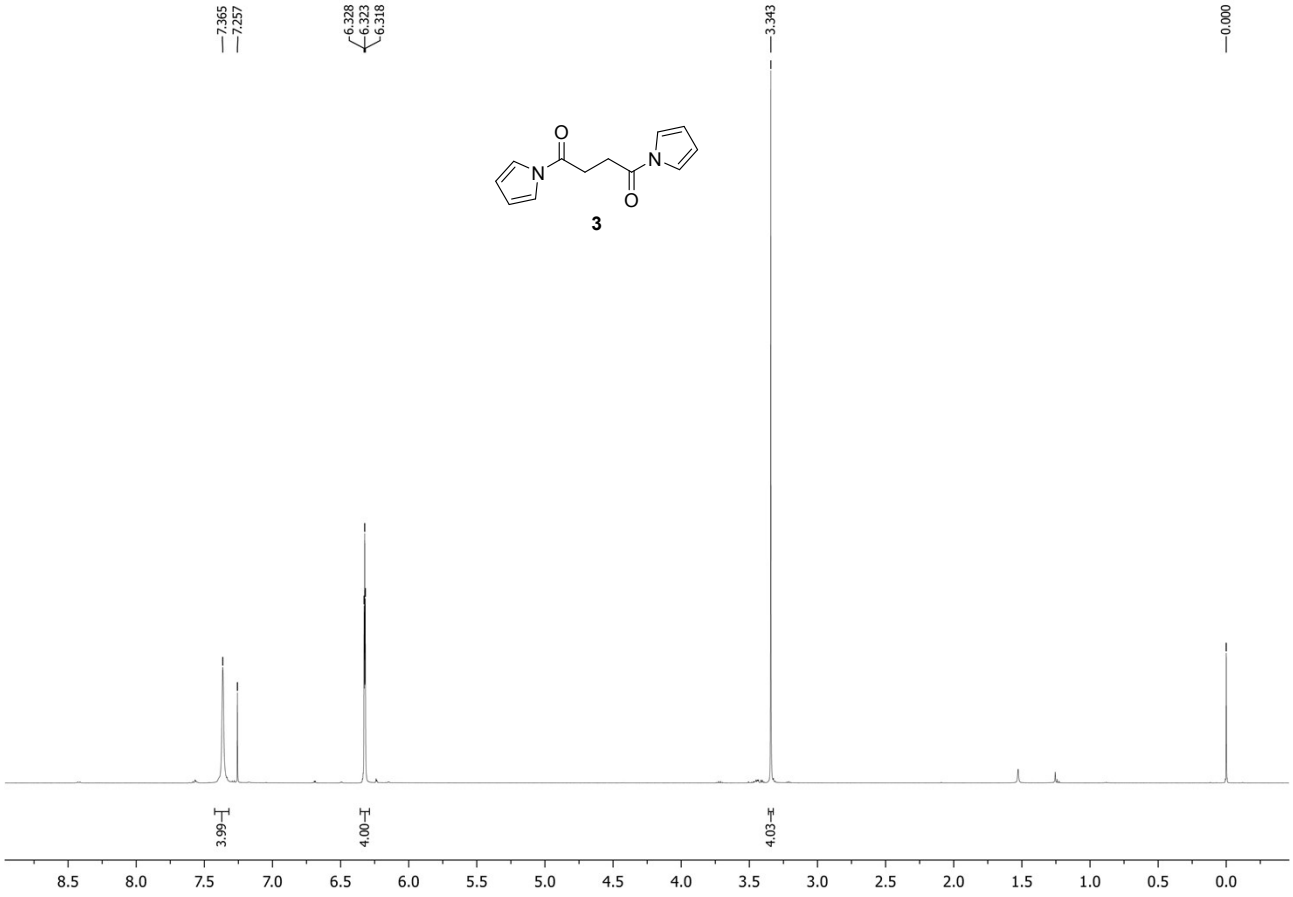
[5] M. Banasiewicz, I. Deperesińska, A. Makarewicz, D. Firmansyah, D. T. Gryko and B. Kozankiewicz, *Phys. Chem. Chem. Phys.* 2015, **17**, 8948–8950.

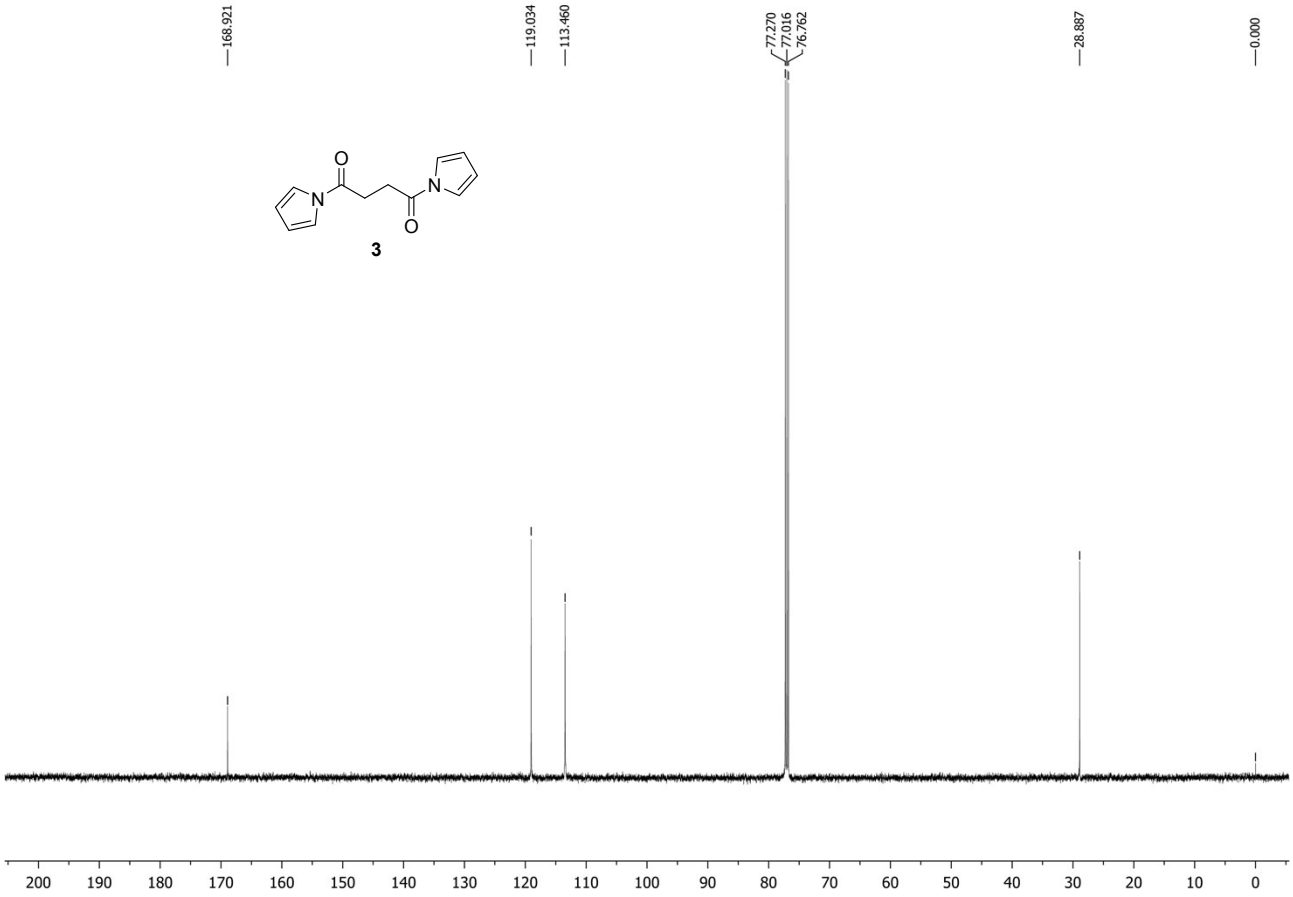
8. NMR spectra

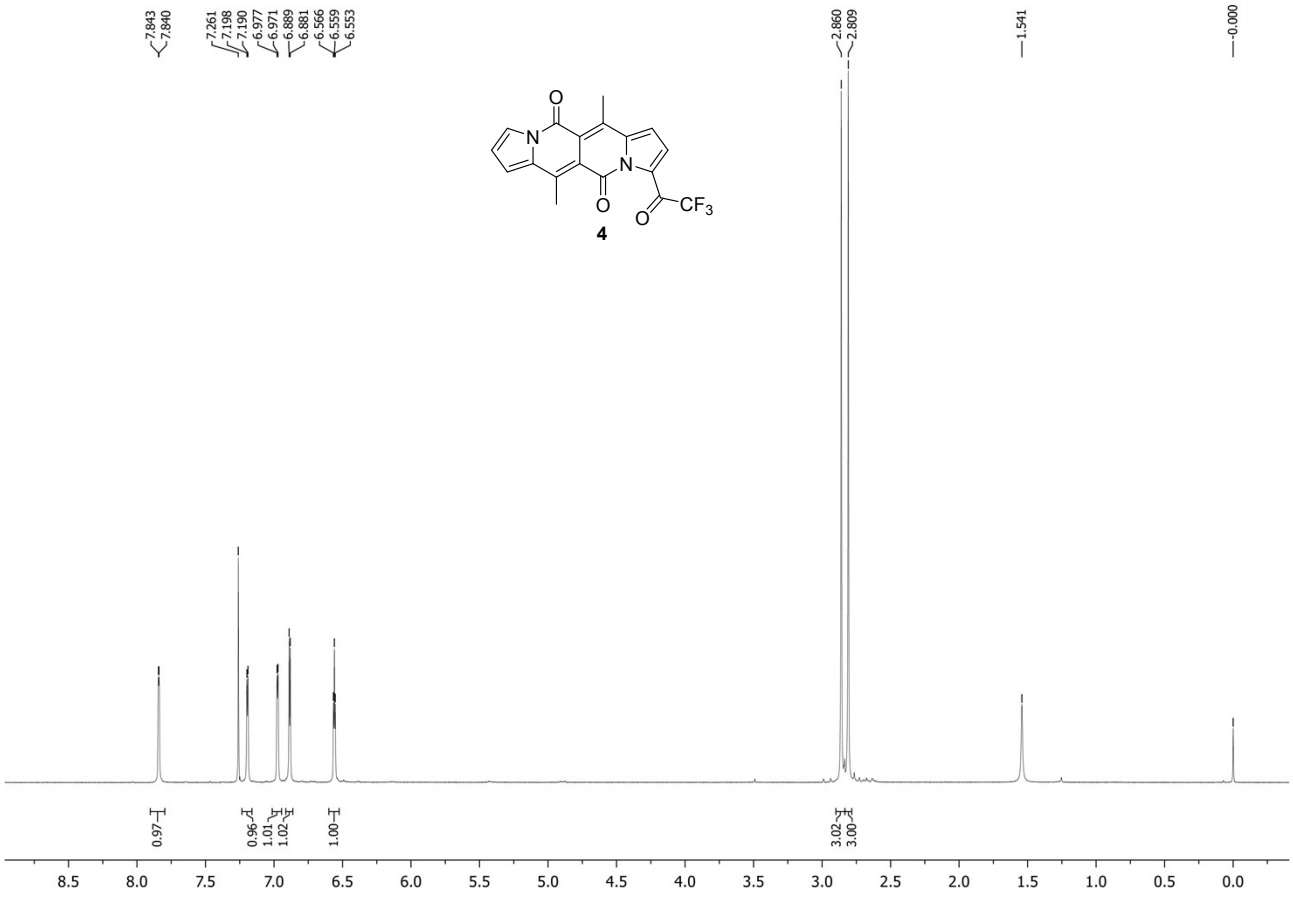
NMR spectra of the obtained compounds are shown on the following pages.


7.966
7.818
7.817
7.812
7.260
6.808
6.805
6.801
6.798
6.542
6.535
6.528
2.171
1.564
0.067
1a
2.03
1.99
2.04
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


158.358
131.673
125.167
123.564
120.249
118.411
116.147
77.254
77.000
76.746
1a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.365
7.257
6.328
6.323
6.318
3.343
0.000
3
3.99
4.00
4.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


168.921
119.034
113.460
77.270
77.016
76.762
28.887
0.000
3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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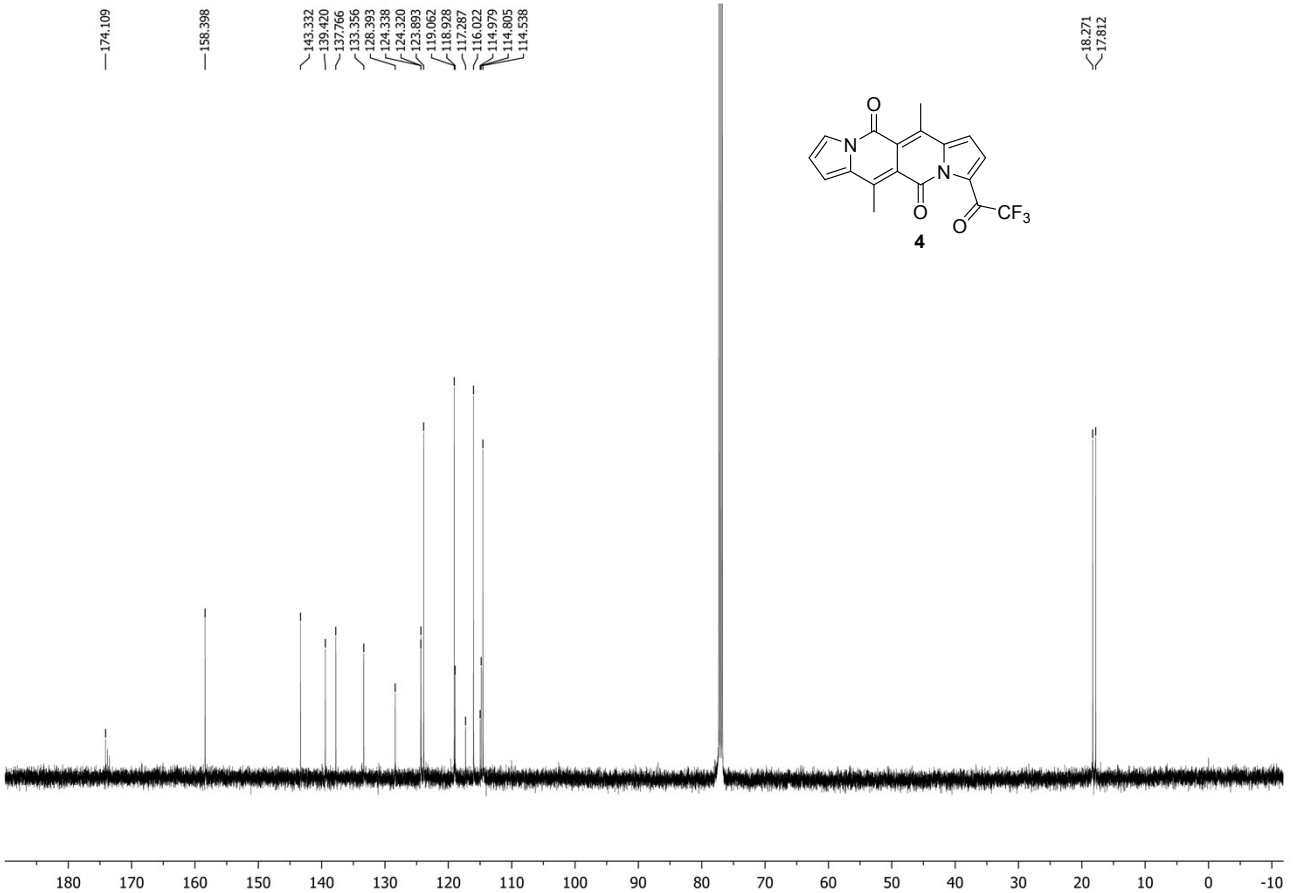
7.840
7.261
7.198
7.190
6.977
6.971
6.889
6.881
6.566
6.559
6.553
2.860
2.809
1.541
0.000
0.97
0.96
1.01
1.02
1.00
3.02
3.00
4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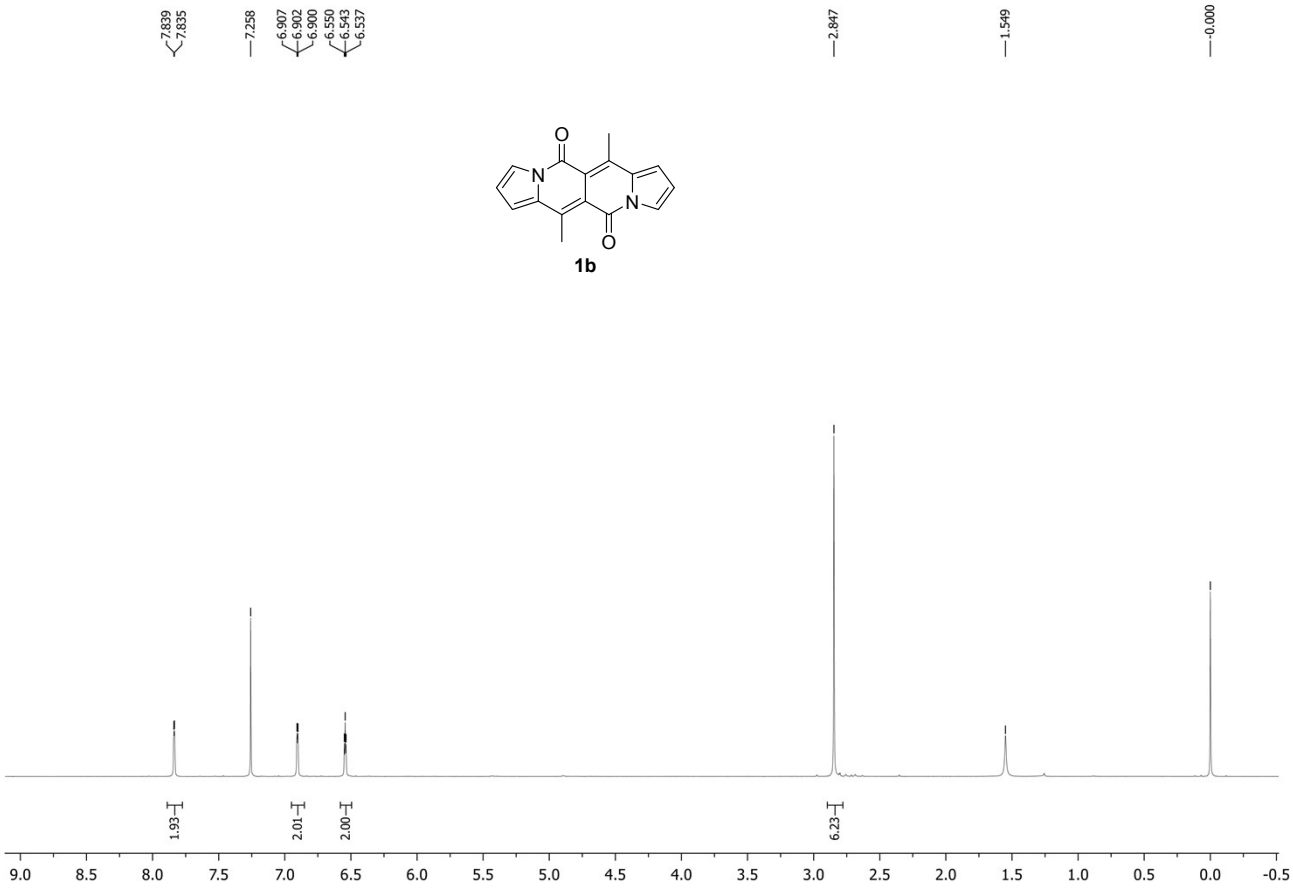
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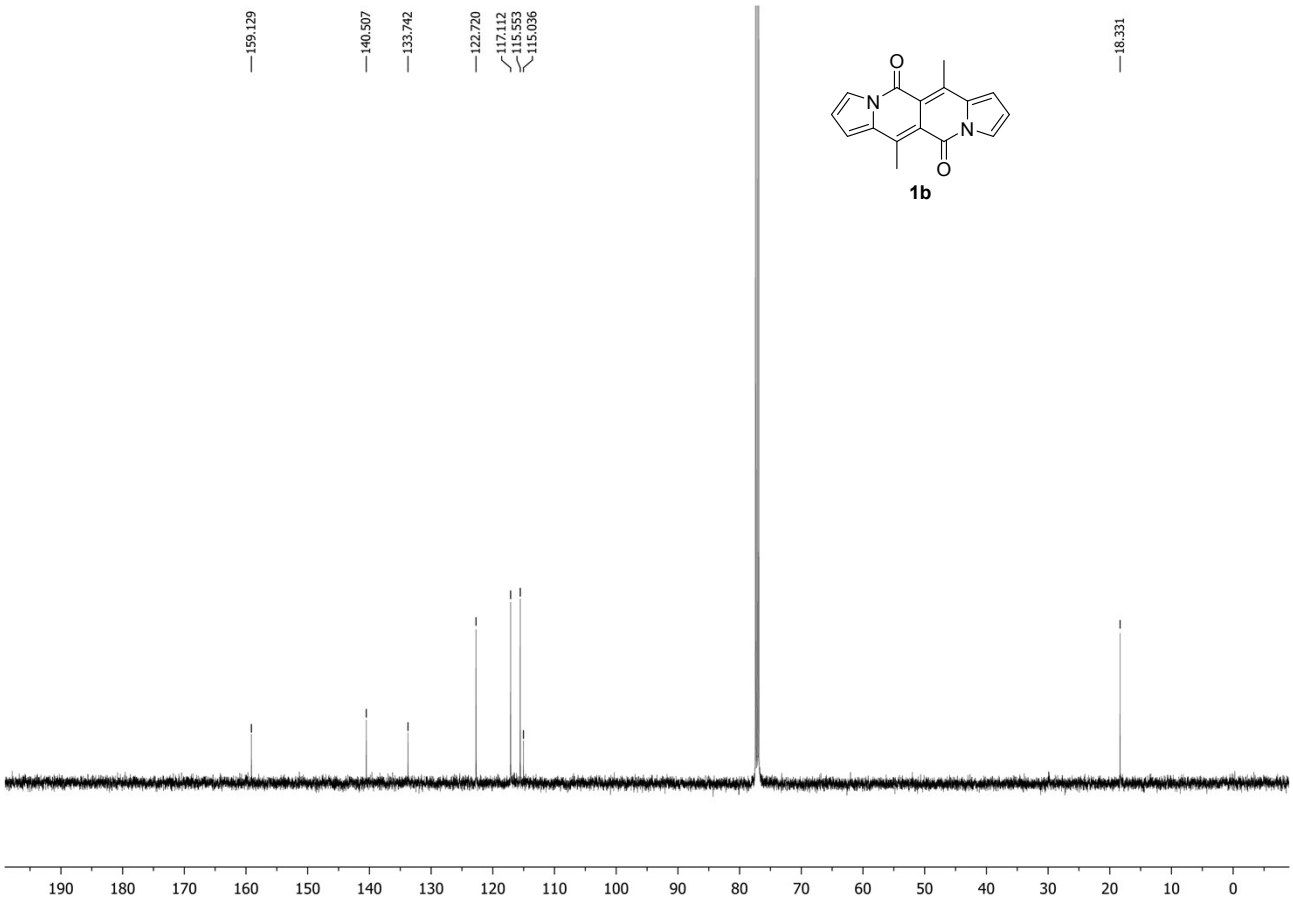
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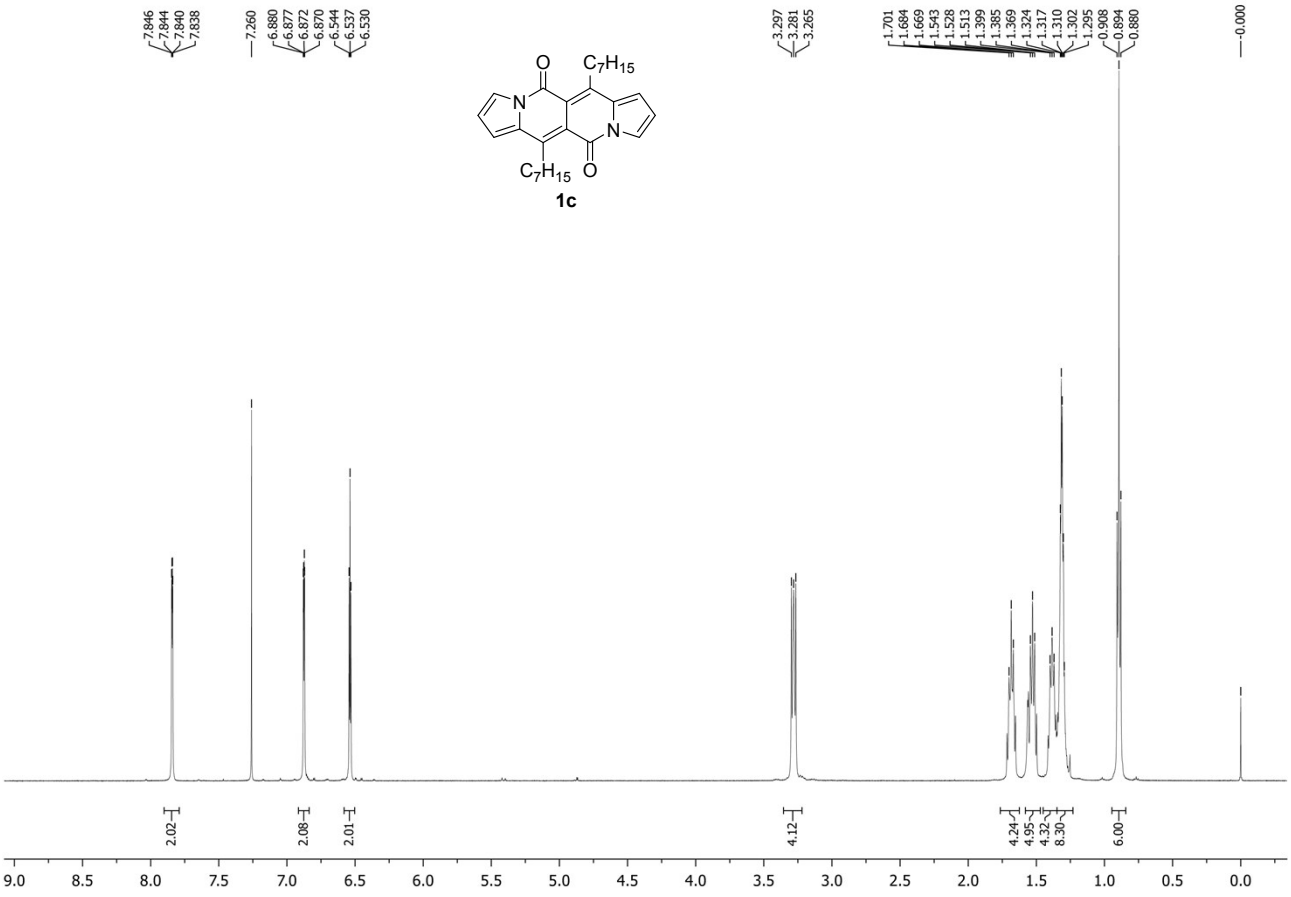
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1.369
1.324
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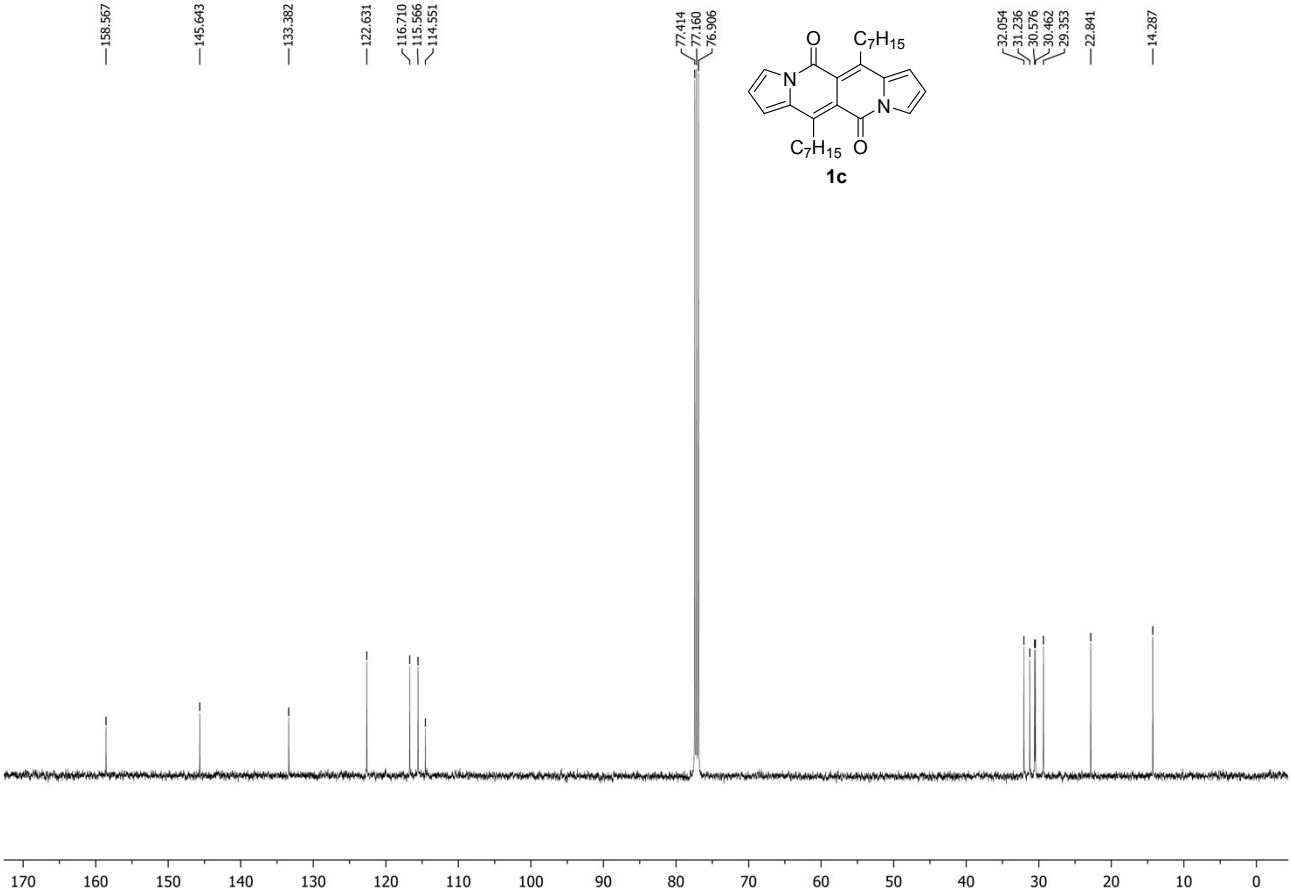
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C7H15
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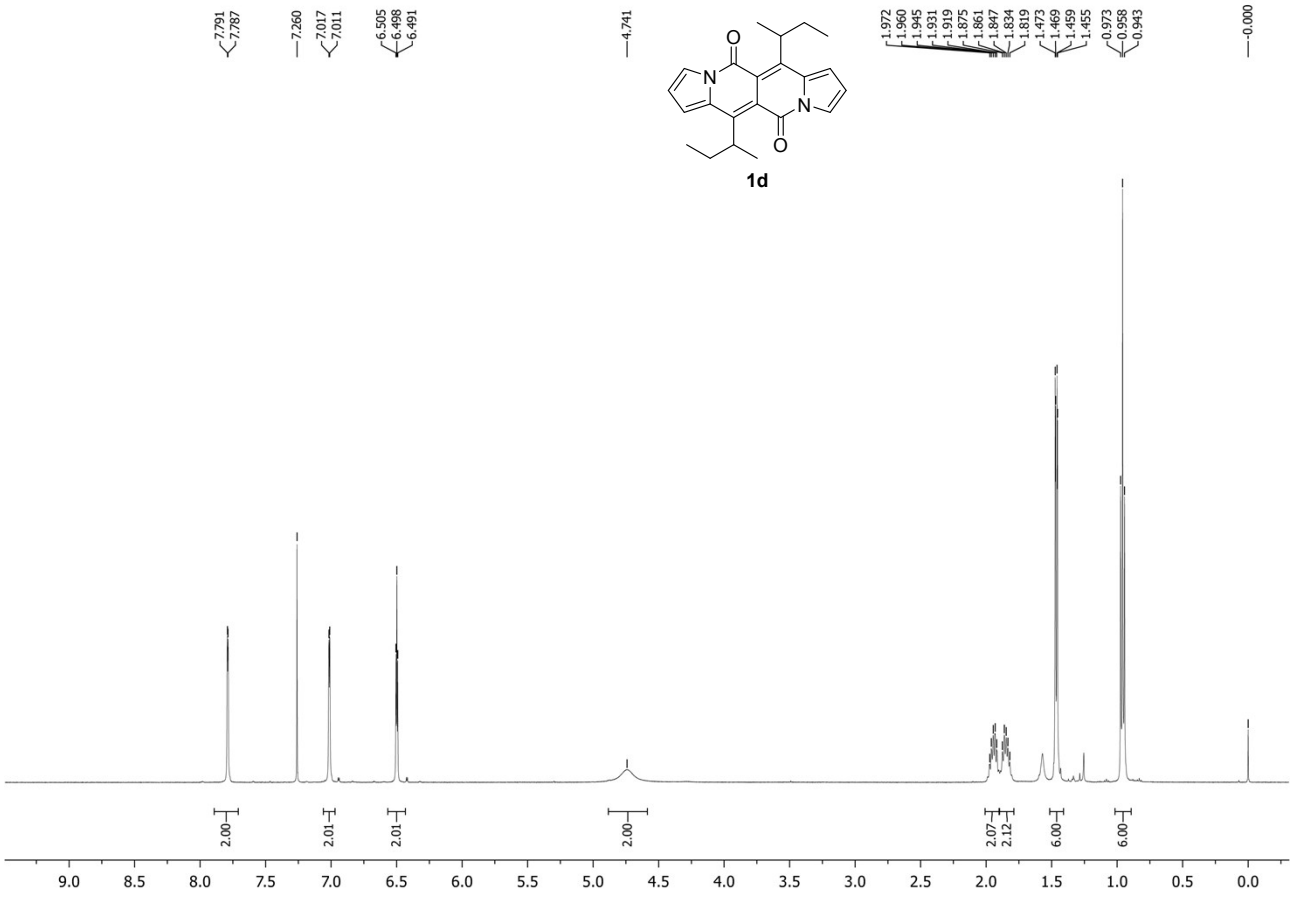
1c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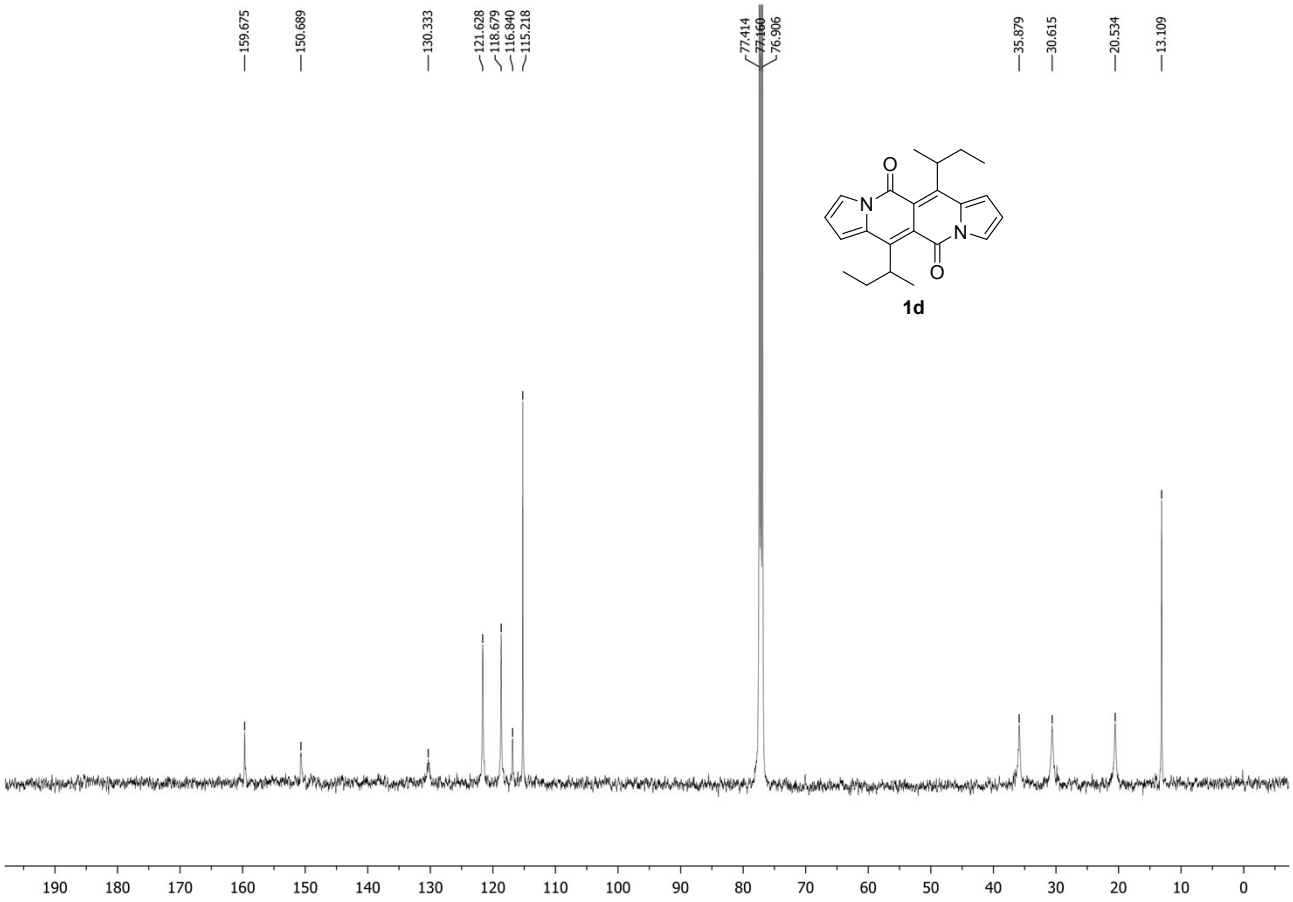
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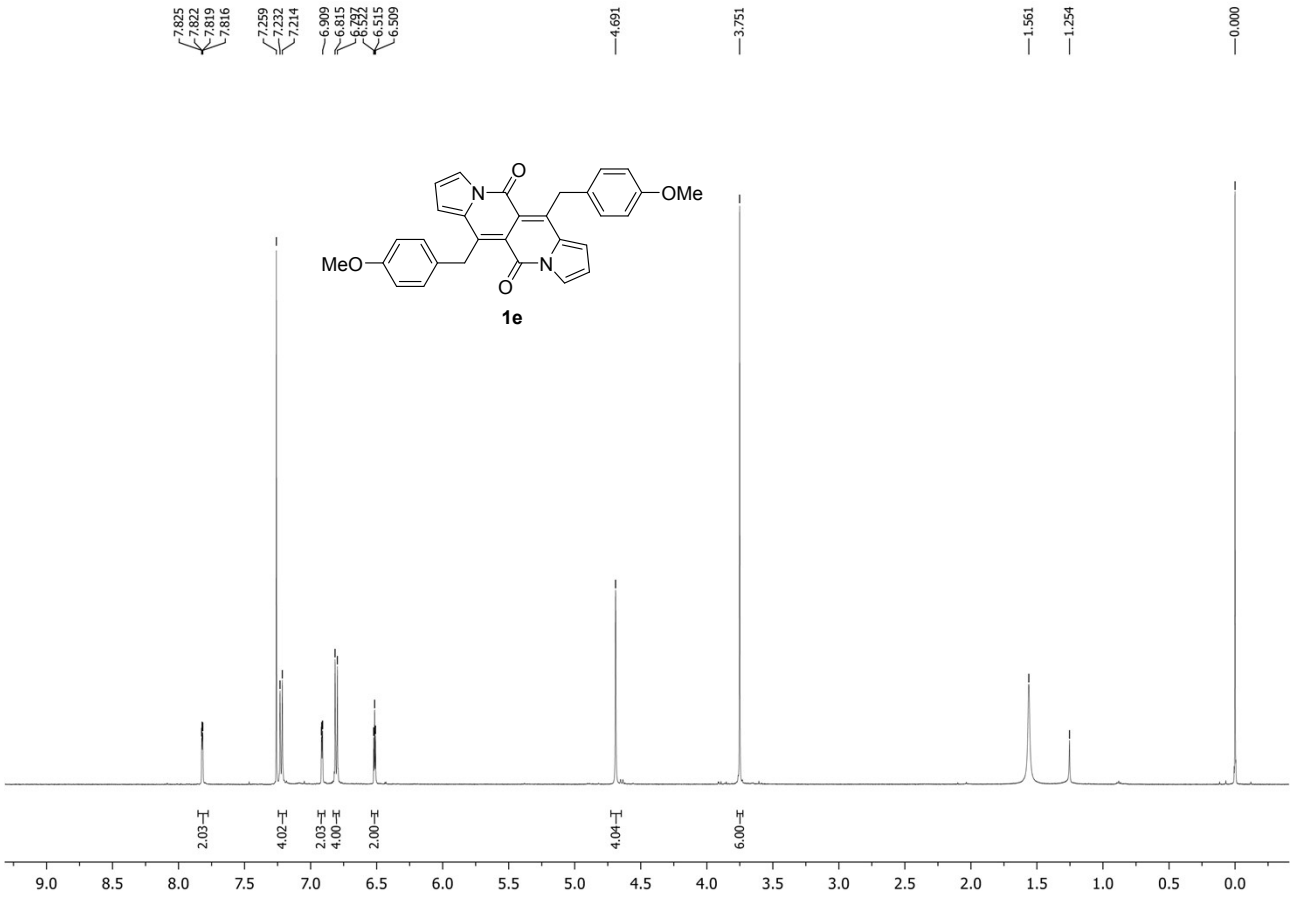
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N
1e
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4.02
2.03
4.00
2.00
4.04
6.00
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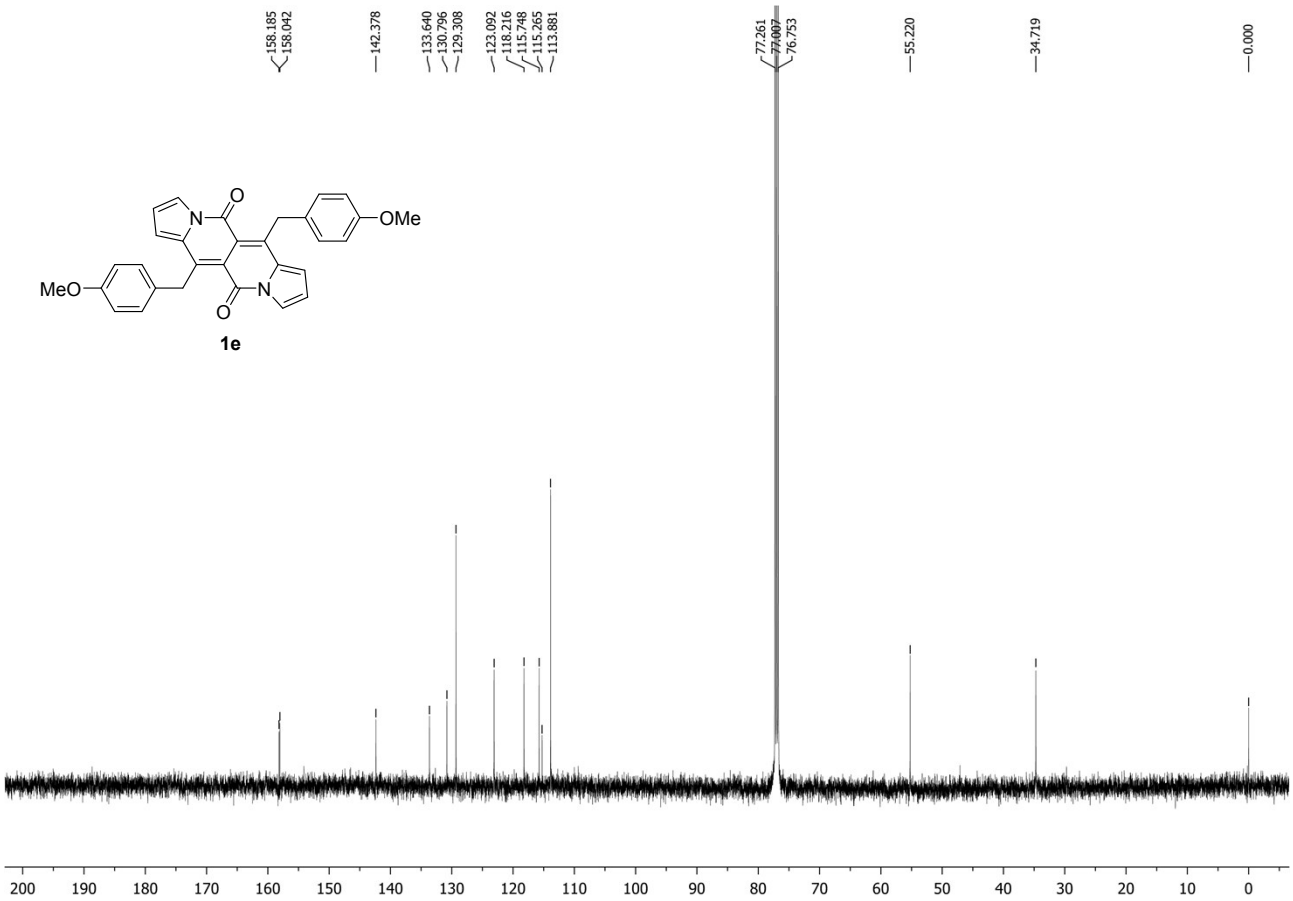
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OMe
MeO
O
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1e
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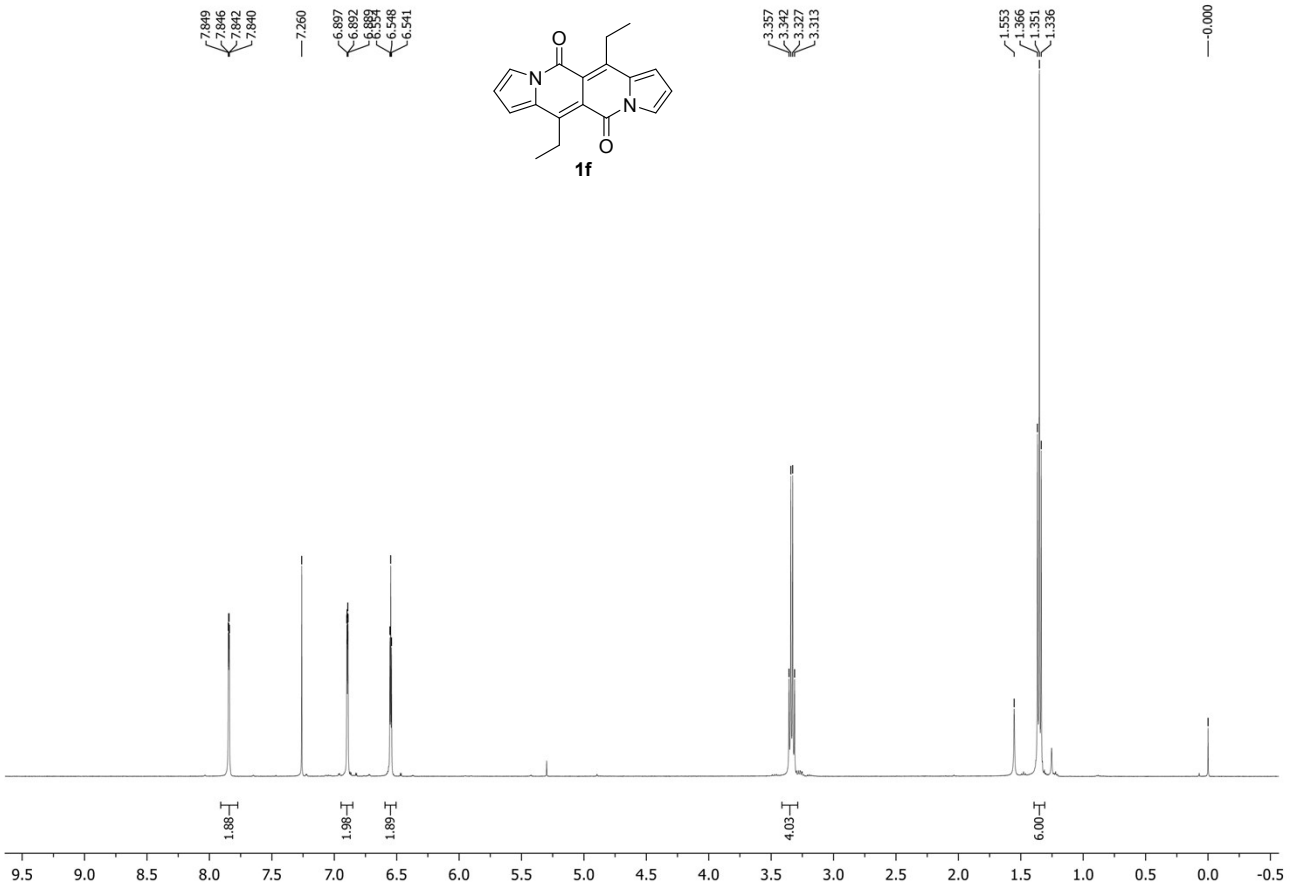
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1.98
1.89
4.03
6.00
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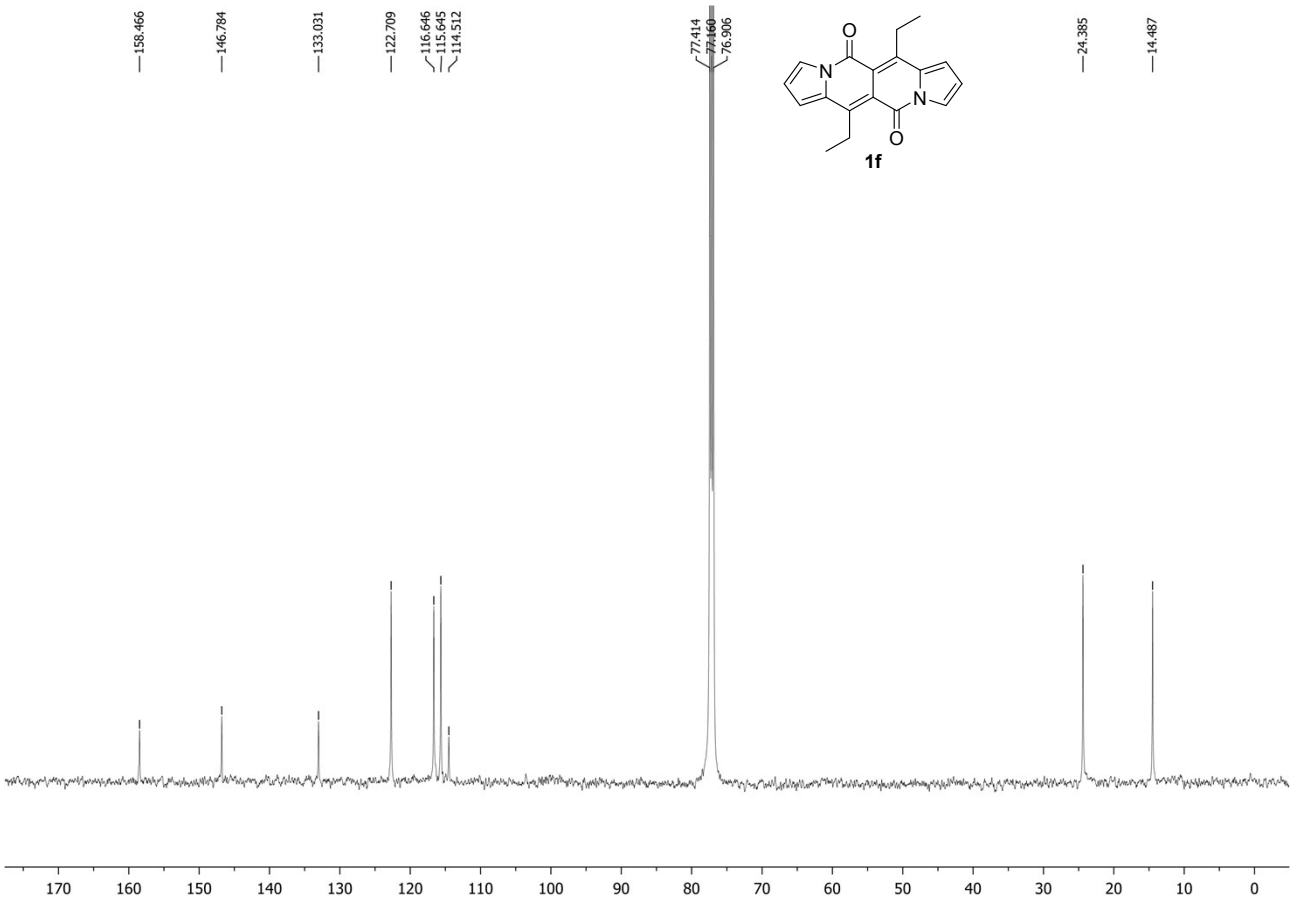
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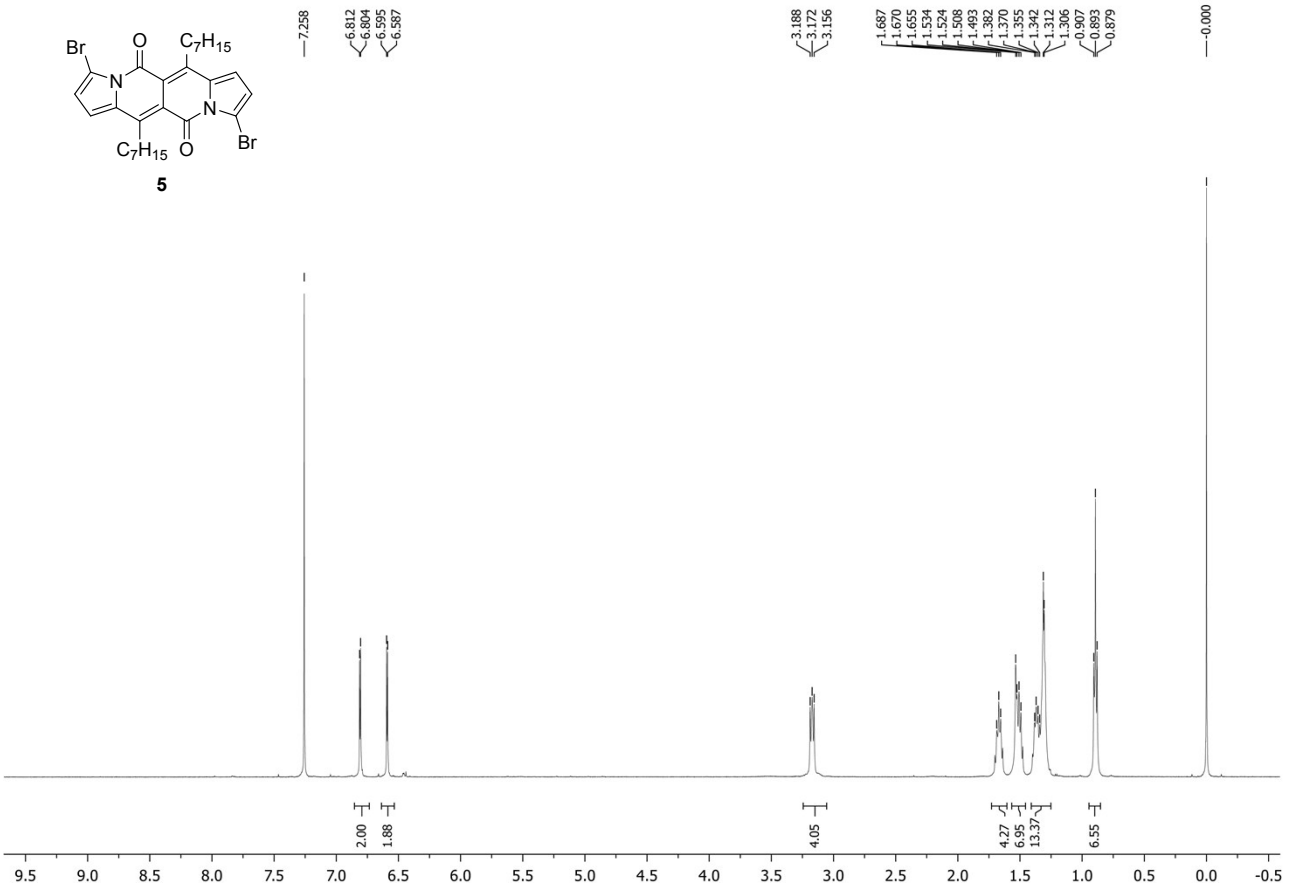
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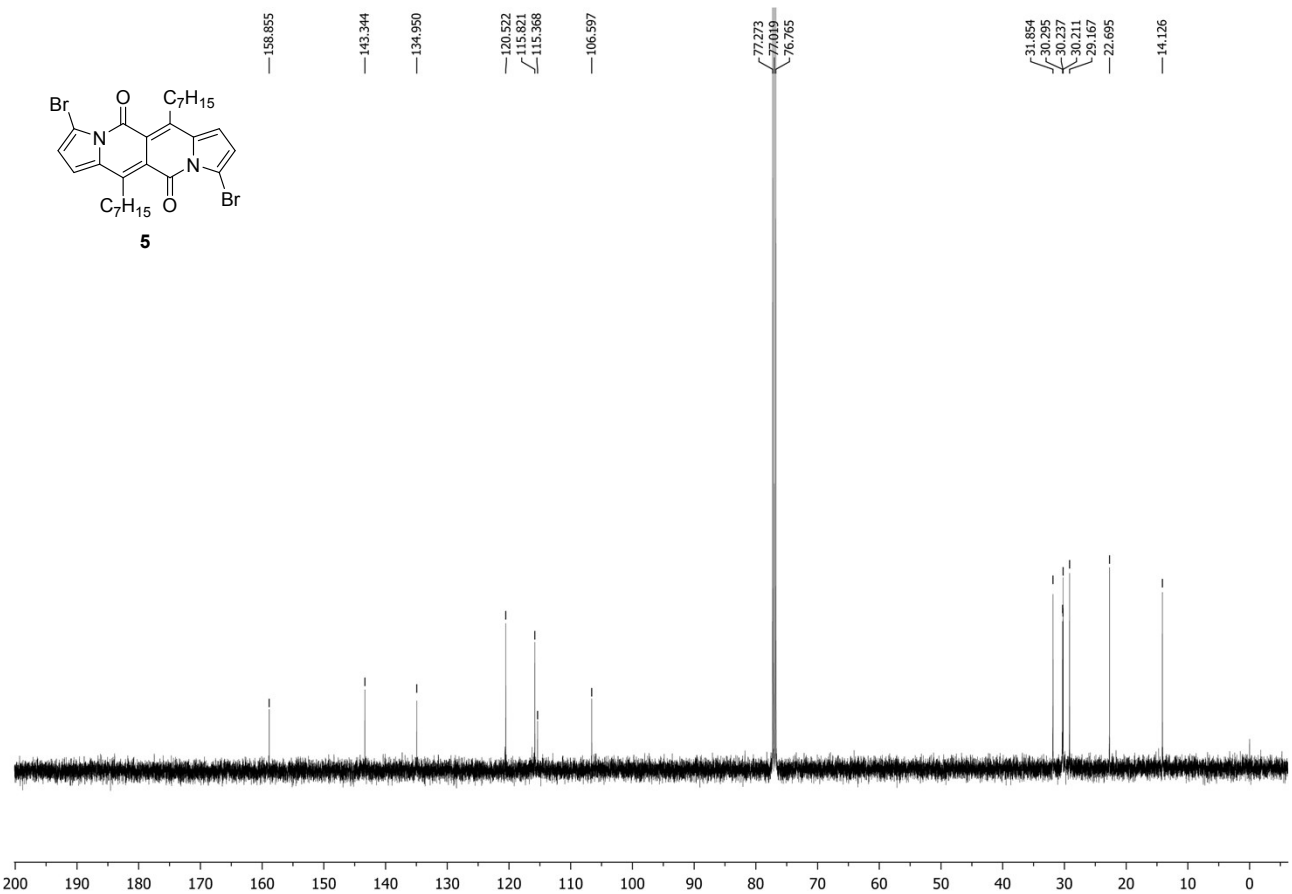
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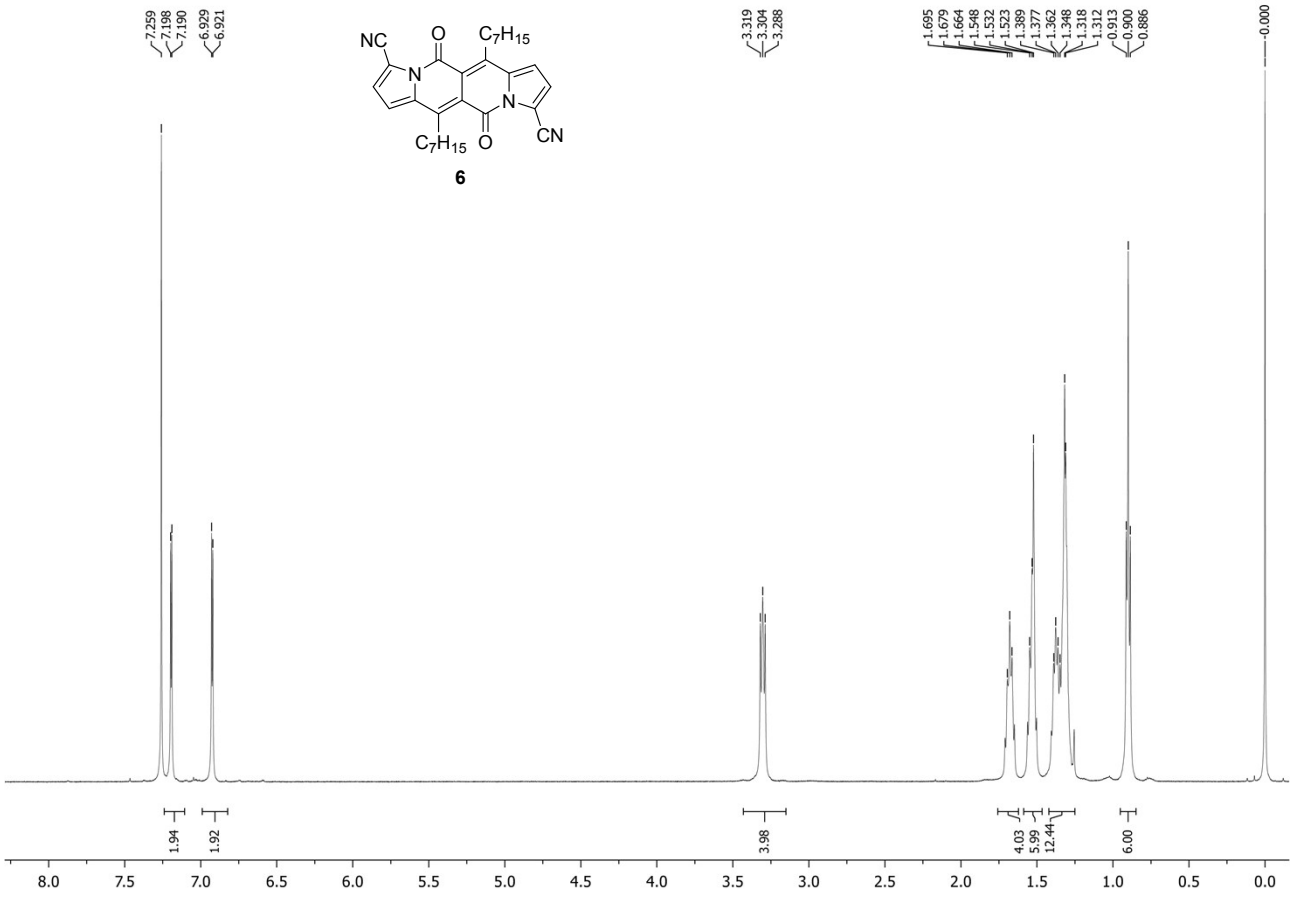
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1.312
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0.900
0.886
0.000
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N
CN
C_7H_{15}
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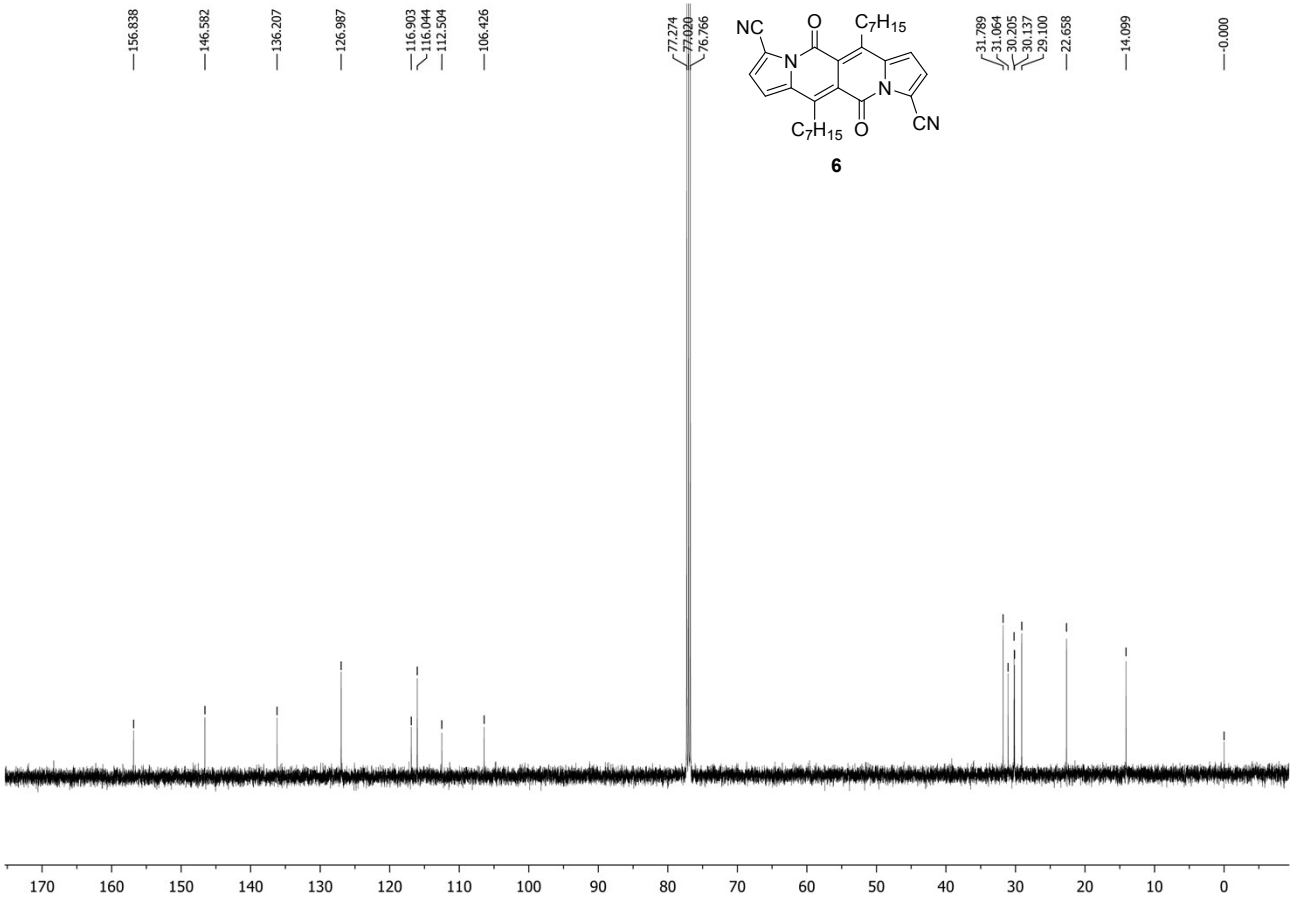
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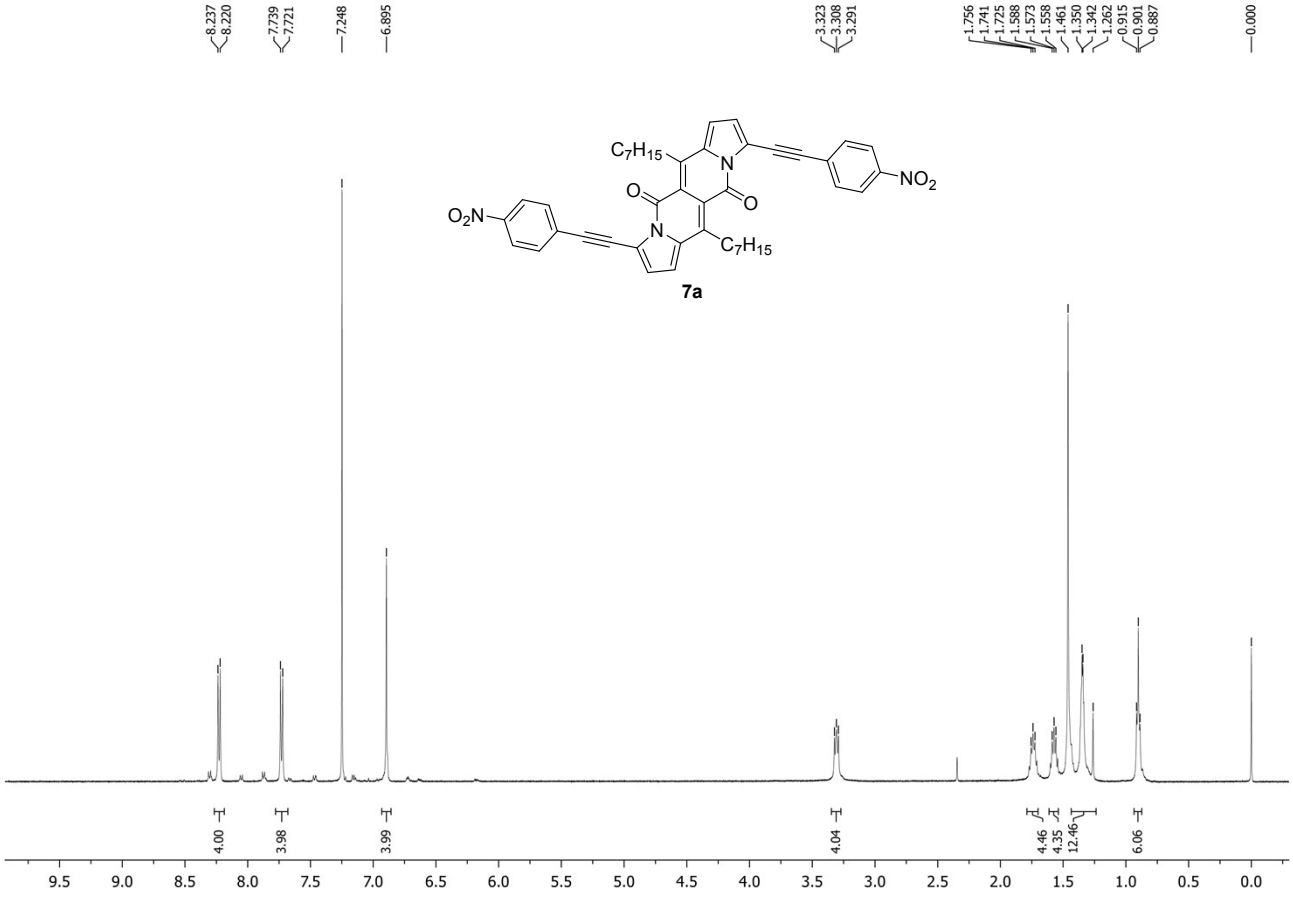
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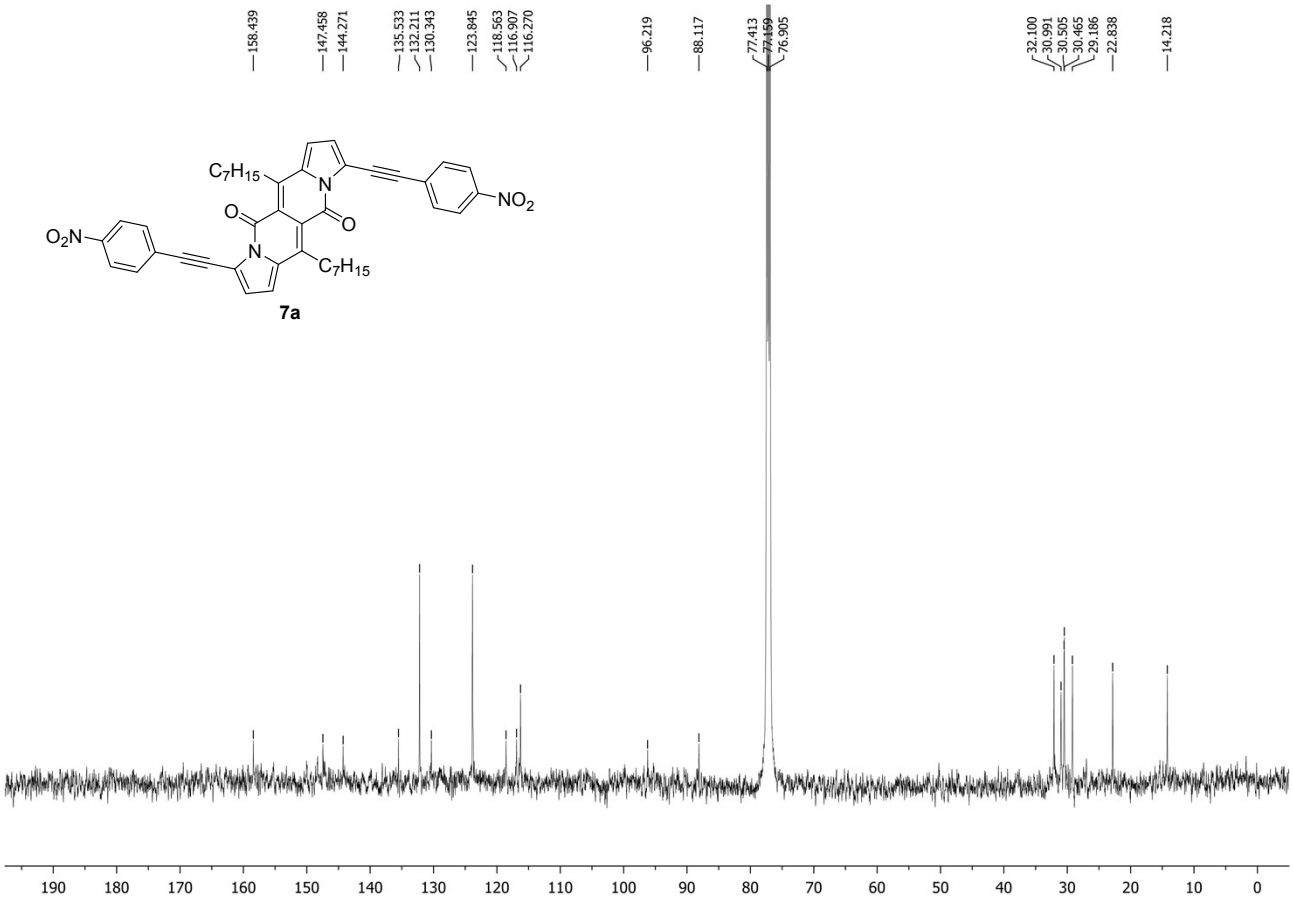
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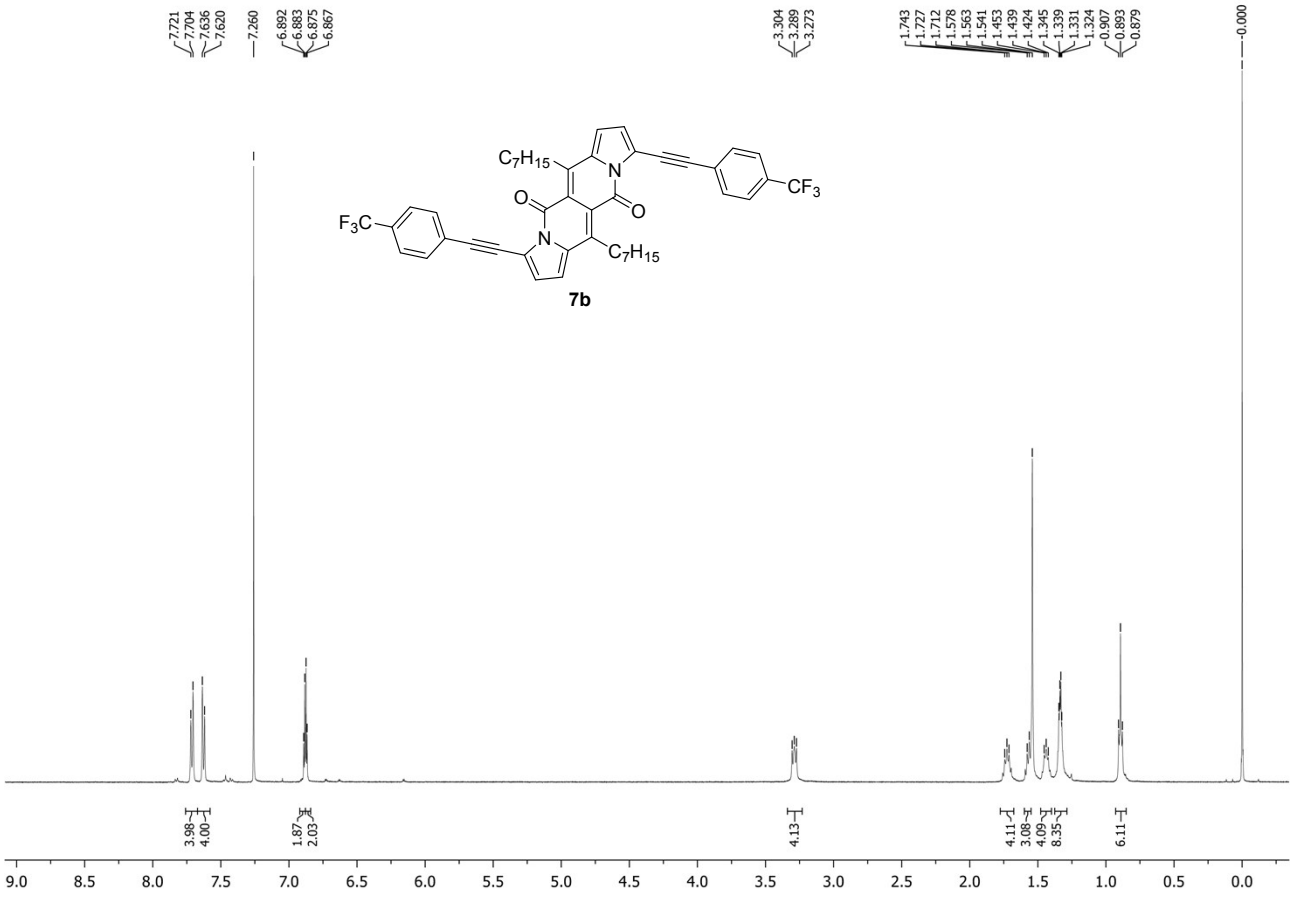
7a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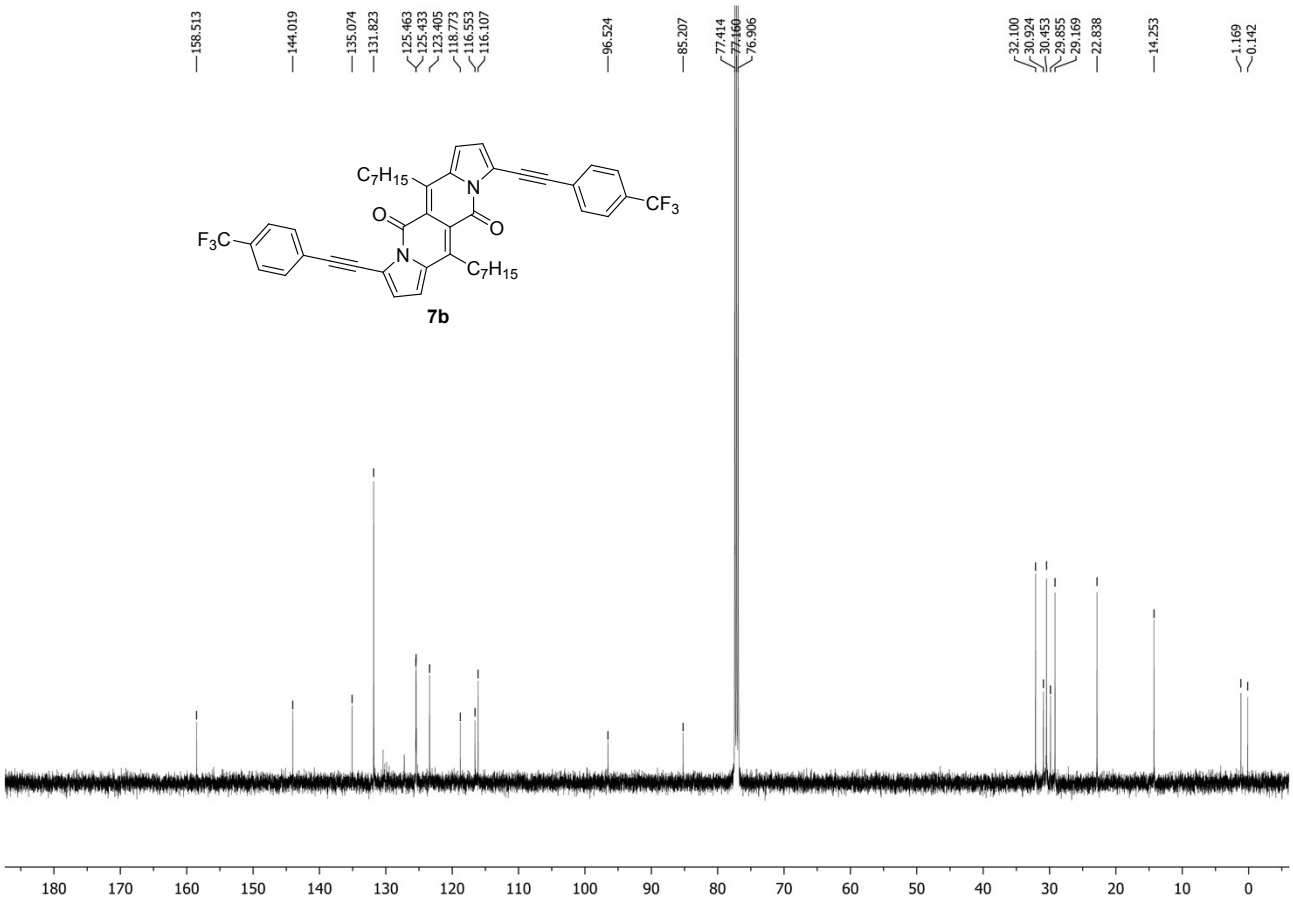
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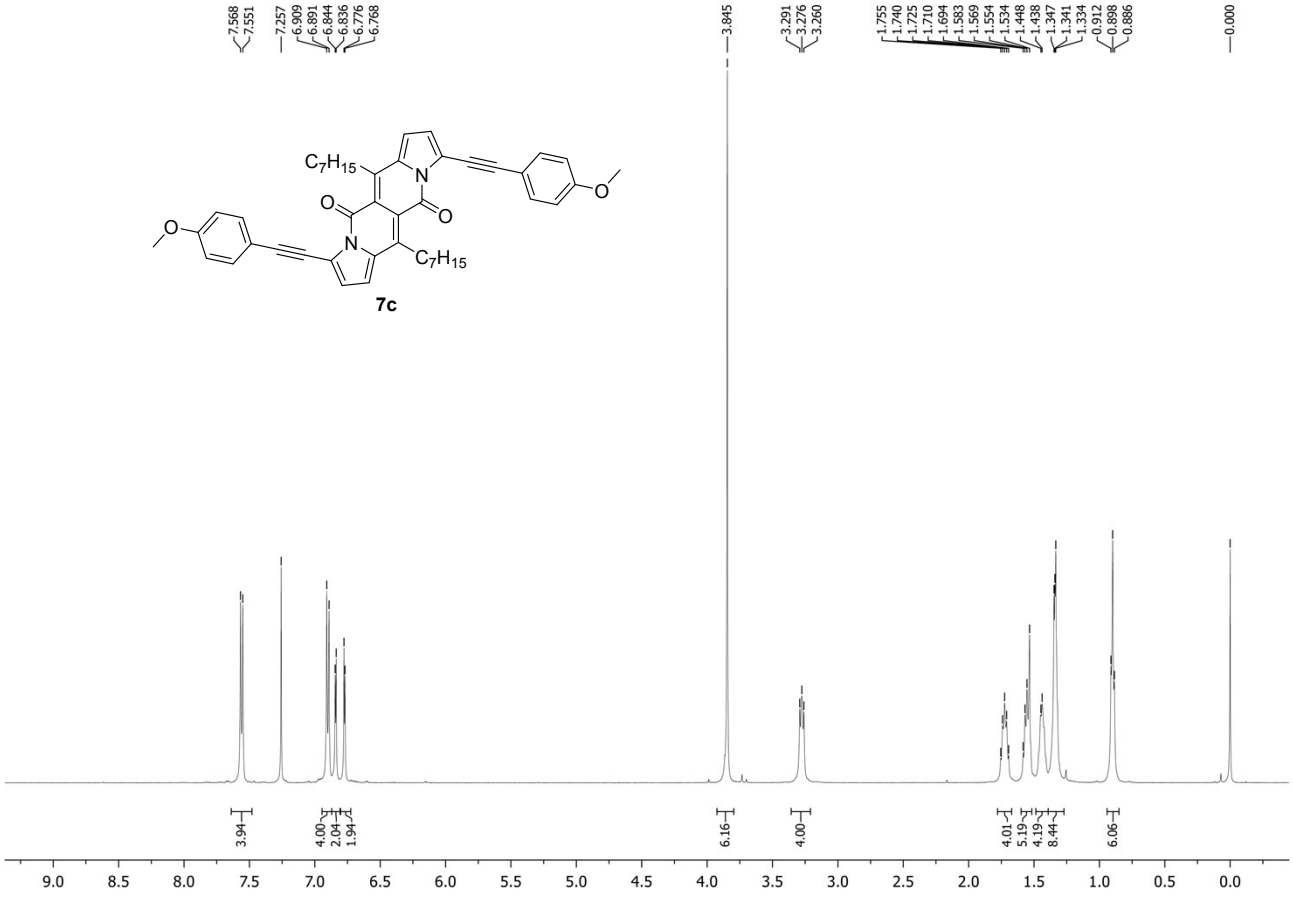
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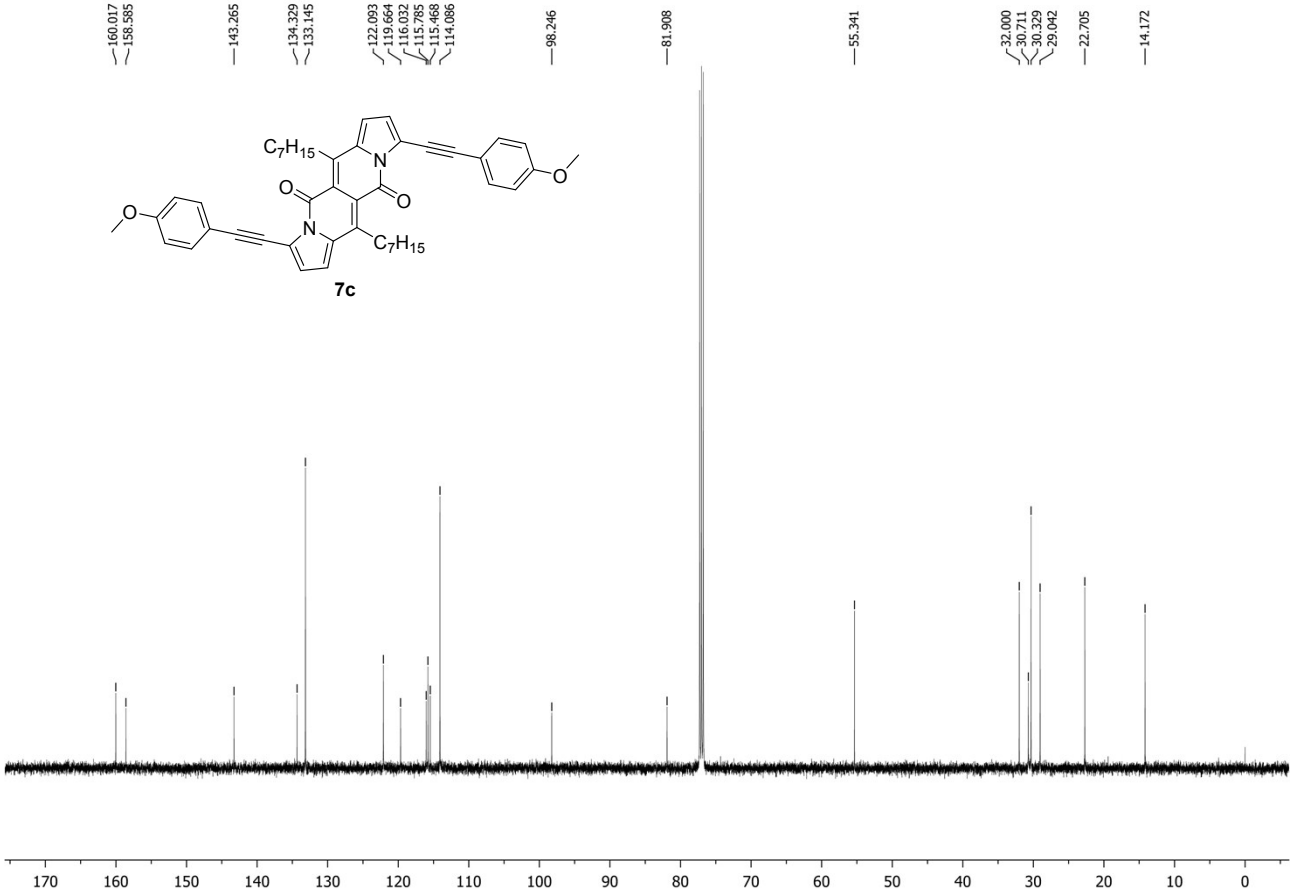
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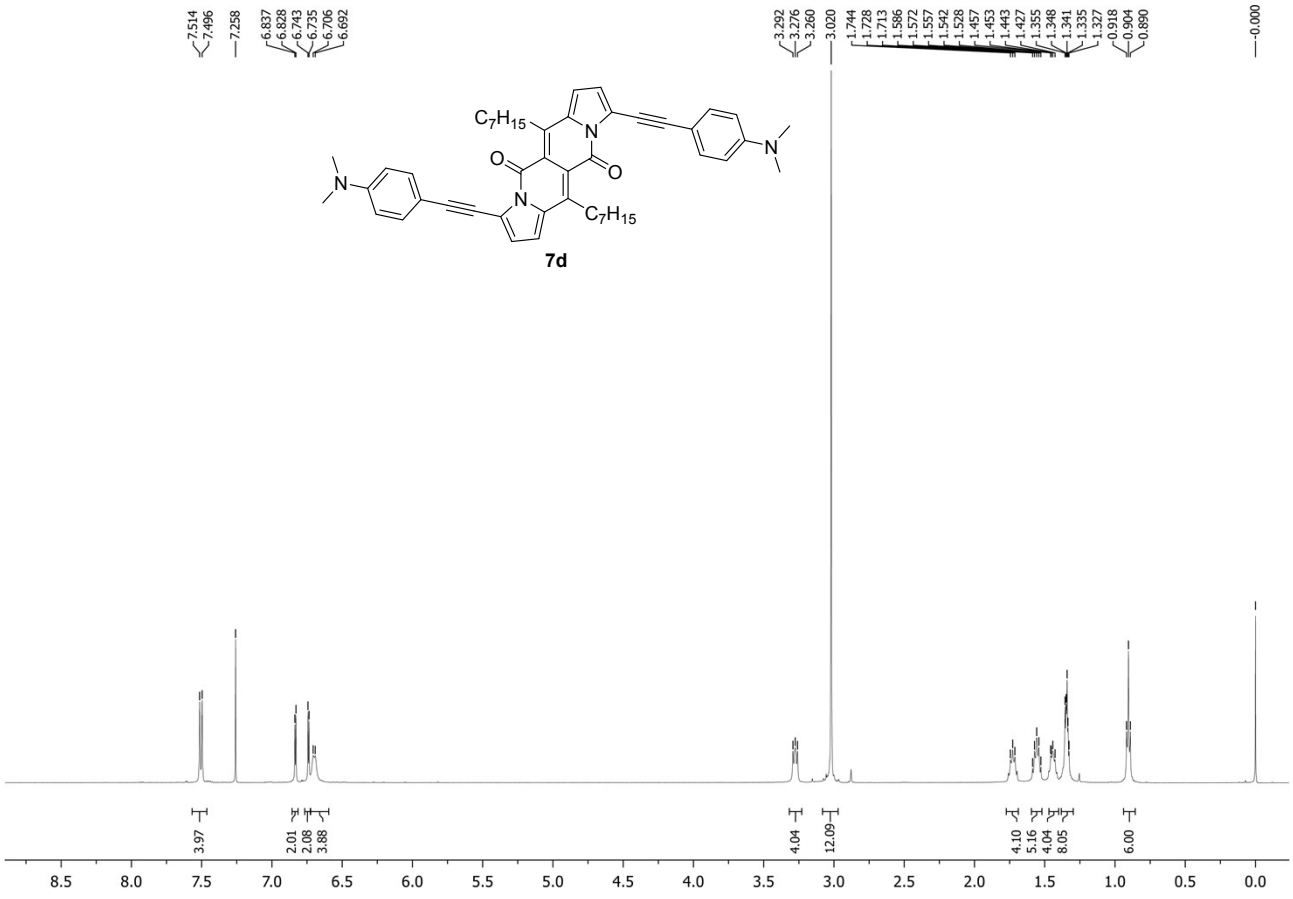
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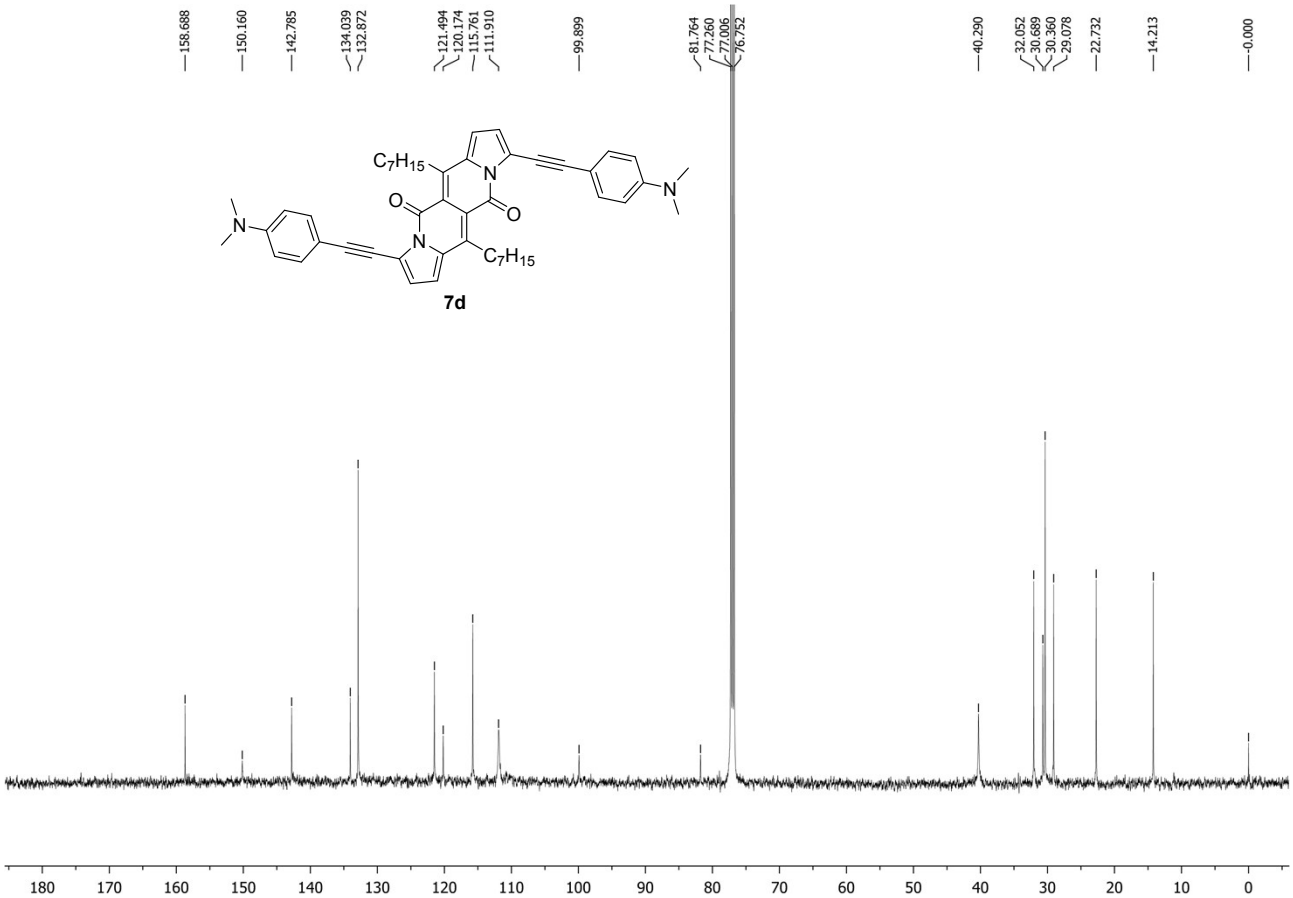
7d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C7H15
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C7H15
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7d