

Supporting Information

Structure-properties relationship of blue solid state emissive phenanthroimidazole derivatives

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EXPERIMENTAL SECTION

Material Characterization. ^1H and ^{13}C NMR spectra were recorded using a Varian Unity Inova 300 apparatus. The samples were prepared by dissolving 20-30 mg of the material in ~ 1 ml of deuterated chloroform (CDCl_3) or dimethyl sulfoxide ($\text{DMSO-}d_6$) with an inner standard, tetramethylsilane (TMS). Hydrogen nuclei (^1H) were excited using the frequency of 300 MHz, and carbon nuclei (^{13}C) were excited with the 75 MHz frequency. Spectrum scale is divided into parts per million (ppm). The presented chemical shifts (δ) are relative to TMS, the δ of which is attributed to zero ($\delta_{\text{TMS}} = 0$). IR spectra in the range of $400\text{-}4000\text{ cm}^{-1}$ were recorded using a Perkin-Elmer Spectrum GX II FT-IR System spectrometer. The samples were semi-transparent pellets of potassium bromide (KBr) containing $\sim 1\%$ of the analyzed material. Mass spectra were recorded either on a Waters ZQ 2000 analytical system. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. Melting points were recorded on Electrothermal MEL-TEMP melting point apparatus. Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q100 calorimeter (TA Instruments) under nitrogen environment. Heating and cooling rates were of $10\text{ }^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was performed using a Mettler TGA/SDTA851e/LF/1100 apparatus under nitrogen gas with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. Optical properties of the PI derivatives were assessed in the form of dilute 10^{-5} M dimethylformamide (DMF) solutions, polystyrene (PS) films and neat films prepared from 10^{-3} M DMF solutions by drop casting. Low concentration PS films (0.5 wt%) were prepared by dissolving compounds and PS at an appropriate ratio in chlorobenzene and then casting the solutions on pre-cleaned glass substrates. Absorption spectra were recorded on a UV-vis-NIR spectrophotometer Lambda 950 (Perkin Elmer). Fluorescence of the investigated compounds was excited by a 340 nm wavelength by using a Xenon lamp coupled to monochromator and measured using a back-thinned CCD spectrophotometer PMA-11 (Hamamatsu). Fluorescence transients were recorded using a time-correlated single photon counting system PicoHarp 300 (PicoQuant) utilizing light-emitting diode as an excitation source (repetition rate 2.5 MHz, pulse duration 700 ps, emission wavelength 330 nm). For the phosphorescence measurements the studied compounds were dispersed in poly(methyl methacrylate) (PMMA) matrix at

the concentration of 2 wt% along with 25 wt% of triplet sensitizer, benzophenone. The films were prepared by drop casting the mixture of chlorobenzene on pre-cleaned glass substrates. Phosphorescence spectra were recorded using a time-gated intensified CCD camera New iStar DH340T (Andor) coupled with spectrograph SR-303i (Shamrock) and pulsed light-emitting diode as an excitation source (excitation wavelength – 330 nm, pulse duration – 700 ps, repetition rate – 10 kHz). Fluorescence quantum yields (Φ_F) of the solutions were estimated by comparing wavelength-integrated fluorescence intensity with that of the reference. Quinine sulphate in 0.1 M H₂SO₄ with $\Phi_F = 53\% \pm 2.3\%$ was used as a reference.¹ Optical densities of the reference and sample solutions were kept below 0.05 to avoid reabsorption effects. Estimated quantum yields of the solutions were verified using the integrated sphere method. An integrating sphere (Sphere Optics) coupled to the CCD spectrometer via optical fiber was also employed to measure Φ_F of the films. Cyclic voltammetry measurements were performed on a μ -Autolab Type III potentiostat (EcoChemie, Netherlands). The data were collected using General Purpose Electrochemical System (GPES) software. Electrochemical experiments were carried out at room temperature using a three-electrode cell consisting of a platinum coil as counter electrode, a glassy carbon working electrode, and a silver wire as reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) was used as supporting electrolyte. For the measurements, silver reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal standard.² To obtain the solid state ionization potentials of the studied compounds, photoelectron emission spectrometry was used.³ The samples for the measurements were fabricated by thermal vacuum evaporation of the layers of the compounds onto fluorine doped tin oxide (FTO) coated glass slides. Charge-transporting properties of the layers of the compounds were investigated by the time-of-flight (TOF) technique. To deposit organic layer on pre-cleaned ITO coated glass substrates with thickness higher than 1 μ m, the studied compound were thermally sublimated in a vacuum chamber with a base pressure below $3 \cdot 10^{-6}$ mbar. The charge extraction by linearly increasing voltage (CELIV) technique was exploited to measure the thickness (*d*) of the organic layers taking 3 as permittivity of investigated compounds.⁴ To get 6 mm² of active area of TOF samples, Al electrode was deposited on the top of organic layer through a shadow mask. Hole/electron transport of compounds was detected applying positive/negative voltage (U) to the ITO

electrode by a Keithley 6517B electrometer. Hole/electron charges in organic layer were photogenerated by light pulse of third-harmonic Nd:YAG laser EKSPLA NL300 through the ITO. To detect the onset of the laser pulse by the DET10A/M Si based detector for synchronization with a digital storage oscilloscope Tektronix TDS 3032C, the light pulse was previously split into two beams. The TOF photocurrent transients for the studied compounds at different surface potentials at the moment of photogeneration were recorded by the oscilloscope. To calculate the drift mobility (μ) using the formula $\mu = d^2/U \cdot t_{tr}$, the transit time (t_{tr}) was determined at a kink of photocurrent transients in the log-log scale (Figure S6, Supporting Information).

Materials. 9,10-Phenanthrenequinone, benzaldehyde, aniline, 3,4,5-trimethoxybenzaldehyde, *p*-anisidine, 4-(trifluoromethyl)benzaldehyde, 4-(trifluoromethyl)aniline, 3,5-bis(trifluoromethyl)benzaldehyde were purchased from Aldrich and used as received. 2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazole (**1**),⁵ 1,2-diphenyl-1*H*-phenanthro[9,10-*d*]imidazole (**3**),⁶ 2-[4-(diphenylamino)phenyl]-1-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (**9**)⁷ were synthesized according to the reported procedures.

Synthesis of 2-(4-tert-Butylphenyl)-1H-phenanthro[9,10-d]imidazole (2) was synthesized by refluxing 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 2,6-diisopropylaniline (1.02 g, 5.76 mmol) and ammonium acetate (3.70 g, 48.00 mmol) in glacial acetic acid (50 ml) for 4 h under nitrogen atmosphere. The reaction mixture was cooled down to room temperature and poured into water (500 ml). The resulting precipitate was filtered and dried. The residue was purified by silica gel column chromatography using toluene/acetone (20:1, v/v) as an eluent. The pure product was obtained as white powder with 20% yield (0.40 g). It was recrystallized from the eluent mixture of solvents. FW = 350.50 g/mol; m.p. 295-296 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 13.39 (s, 1H, NH), 8.84 (d, *J* = 8.2 Hz, 2H), 8.58 (d, *J* = 8.2 Hz, 2H), 8.27 (d, *J* = 8.2 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 4H), 1.45-1.27 (s, 9H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ (ppm) 152.42, 149.76, 128.23, 128.09, 127.56, 126.42, 126.25, 125.67, 124.44, 122.43, 49.11, 35.16, 31.55; IR, KBr, (cm⁻¹): 3653, ν (NH); 3072, 2953, 2866, ν (CH_{ar}); 1615, 1527, 1485, 1456, 1428, ν (C=C); 1363, 1268, 1237, 1135, ν (C-N, C=N); 1028, 965, 841, 749, 722, 615, γ (CH_{ar}); MS (APCI⁺), *m/z*: 351 ([M+H]⁺); Elemental analysis Calc. (%) for C₂₅H₂₂N₂: C, 85.68; H, 6.33; N, 7.99. Found: C, 84.98; H, 6.97; N, 8.05.

Synthesis of 2-(4-Methoxyphenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (4) was obtained using 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 4-methoxybenzaldehyde (0.65 g, 4.80 mmol), aniline (0.54 g, 5.76 mmol) and ammonium acetate (3.70 g, 48.00 mmol) by the procedure employed for the synthesis of compound **2**. The residue was purified by vacuum sublimation at 201-202 °C. White powder was obtained with the yield of 68% (1.30 g). It was recrystallized from the eluent mixture of solvents. FW = 400.50 g/mol; m.p. 217-218 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.85 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.1 Hz, 1H), 8.74 (dd, *J*₁ = 8.3 Hz, *J*₂ = 0.5 Hz, 1H), 8.68 (dd, *J*₁ = 8.3 Hz, *J*₂ = 0.5 Hz, 1H), 7.75-7.68 (m, 1H), 7.66-7.44 (m, 9H), 7.27-7.12 (m, 2H), 6.82-6.76 (m, 2H), 3.77 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 160.26, 151.22, 139.17, 137.54, 131.03, 130.36, 129.98, 129.42, 127.44, 125.77, 124.93, 124.32, 123.38, 122.92, 121.04, 113.96, 55.58, 31.11; IR, KBr, (cm⁻¹): 3055, 2835, ν (CH_{ar}); 1677, 1609, 1496, 1472, 1452, ν (C=C); 1382, 1286, 1254, 1179, ν (C-N, C=N); 1027, 833, 785, 756, 723, 700, γ (CH_{ar}); MS (APCI⁺, 20 V), m/z: 401 ([M+H]⁺); Elemental analysis Calc. (%) for C₂₈H₂₀N₂O: C, 83.98; H, 5.03; N, 7.00; O, 4.00. Found: C, 83.28; H, 5.70; N, 7.16.

Synthesis of 2-(3,4,5-Trimethoxyphenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (5) was prepared from 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 3,4,5-trimethoxybenzaldehyde (0.94 g, 4.80 mmol), aniline (0.54 g, 5.76 mmol) and ammonium acetate (3.70 g, 48 mmol) using the same procedure as for the synthesis of compound **2**. The reaction mixture was cooled down to room temperature and poured into methanol (500 ml). The resulting precipitate was filtered off and dried. The crude product was purified by silica gel column chromatography using chloroform/acetone (40:1, v/v) as an eluent. After evaporation of the solvents white powder was obtained with 47% yield (1.04 g). It was recrystallized from the eluent mixture of solvents. FW = 460.50 g/mol; m.p. 211-212 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.88 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.2 Hz, 1H), 8.77 (d, *J* = 8.3 Hz, 1H), 8.71 (d, *J* = 8.3 Hz, 1H), 7.78-7.70 (m, 1H), 7.69-7.61 (m, 3H), 7.59-7.54 (m, 2H), 7.54-7.47 (m, 1H), 7.30-7.17 (m, 3H), 6.83 (s, 2H), 3.8 (s, 3H), 3.69 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 153.15, 150.6, 139.38, 137.52, 130.04, 129.57, 129.43, 128.52, 127.51, 126.57, 125.94, 125.21, 124.37, 123.39, 122.93, 121.05, 106.92, 61.16, 56.17, 31.21; IR, KBr, (cm⁻¹): 2935, ν (CH_{ar}); 1586, 1482, 1449, 1415, ν (C=C); 1379, 1329, 1232, 1122, ν (C-N,

C=N); 1007, 851, 756, 709, γ (CH_{ar}); MS (APCI⁺, 20 V), m/z: 461 ($[\text{M}+\text{H}]^+$); Elemental analysis Calc. (%) for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_3$: C, 78.24; H, 5.25; N, 6.08; O, 10.42. Found: C, 78.88; H, 4.92; N, 6.43.

Synthesis of 2-(3,4,5-Trimethoxyphenyl)-1-(4-methoxyphenyl)-1H-phenanthro[9,10-d]imidazole (6) was synthesized from 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 3,4,5-trimethoxybenzaldehyde (0.94 g, 4.80 mmol), *p*-anisidine (0.71 g, 5.76 mmol) and ammonium acetate (3.70 g, 48 mmol) using the same procedure as for the synthesis of compound **2**. The reaction mixture was stirred for 6 h. The crude product was purified by silica gel column chromatography using toluene/acetone (10:1, v/v) as an eluent. After drying, white powder was obtained with the yield of 21% (0.50 g). It was recrystallized from the eluent mixture of solvents. FW = 490.60 g/mol; m.p. 200-201 °C. ¹H NMR (300 MHz, CDCl_3): δ (ppm) 8.87 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.4$ Hz, 1H), 8.77 (d, $J = 8.3$ Hz, 1H), 8.70 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.4$ Hz, 1H), 7.77-7.70 (m, 1H), 7.68-7.61 (m, 1H), 7.55-7.41 (m, 3H), 7.32-7.24 (m, 2H), 7.14-7.08 (m, 2H), 6.87 (s, 2H), 3.93 (s, 3H), 3.85 (s, 3H), 3.73 (s, 6H); ¹³C NMR (75 MHz, CDCl_3): δ (ppm) 160.26, 153.05, 137.38, 130.42, 128.42, 127.57, 126.6, 125.85, 125.11, 124.32, 123.36, 122.98, 121.04, 115.57, 106.92, 61.16, 56.25, 31.17; IR, KBr, (cm^{-1}): 3005, 2936, 2827, ν (CH_{ar}); 1656, 1585, 1514, 1483, 1454, 1416, ν (C=C); 1347, 1297, 1254, 1125, ν (C-N, C=N); 1004, 836, 754, 729, γ (CH_{ar}); MS (APCI⁺, 20 V), m/z: 491 ($[\text{M}+\text{H}]^+$); Elemental analysis Calc. (%) for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{O}_4$: C, 75.90; H, 5.34; N, 5.71; O, 13.05. Found: C, 75.91; H, 5.67; N, 5.94.

Synthesis of 1,2-Bis(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazole (7) was prepared from 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 4-(trifluoromethyl)benzaldehyde (0.84 g, 4.80 mmol), 4-(trifluoromethyl)aniline (0.93 g, 5.76 mmol) and ammonium acetate (3.70 g, 48.00 mmol) using the same procedure as for the synthesis of compound **2**. The reaction mixture was stirred for 6 h. It was cooled down to room temperature and poured into water (500 ml). The resulting precipitate was filtered, washed with water and dried. The crude product was washed with methanol and recrystallized from methanol/THF mixture. White crystals were obtained with the yield of 21% (0.51 g). FW = 506 g/mol; m.p. 229-230 °C. ¹H NMR (300 MHz, CDCl_3): δ (ppm) 8.85 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.3$ Hz, 1H), 8.82-8.76 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.0$ Hz, 1H), 8.74-8.68 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.0$ Hz, 1H), 7.95-7.88 (m, 2H), 7.80-7.73 (m, 1H), 7.73-7.52 (m, 8H), 7.35-7.28 (m, 1H), 7.14-7.08 (m, 1H); ¹³C NMR (75 MHz, CDCl_3): δ

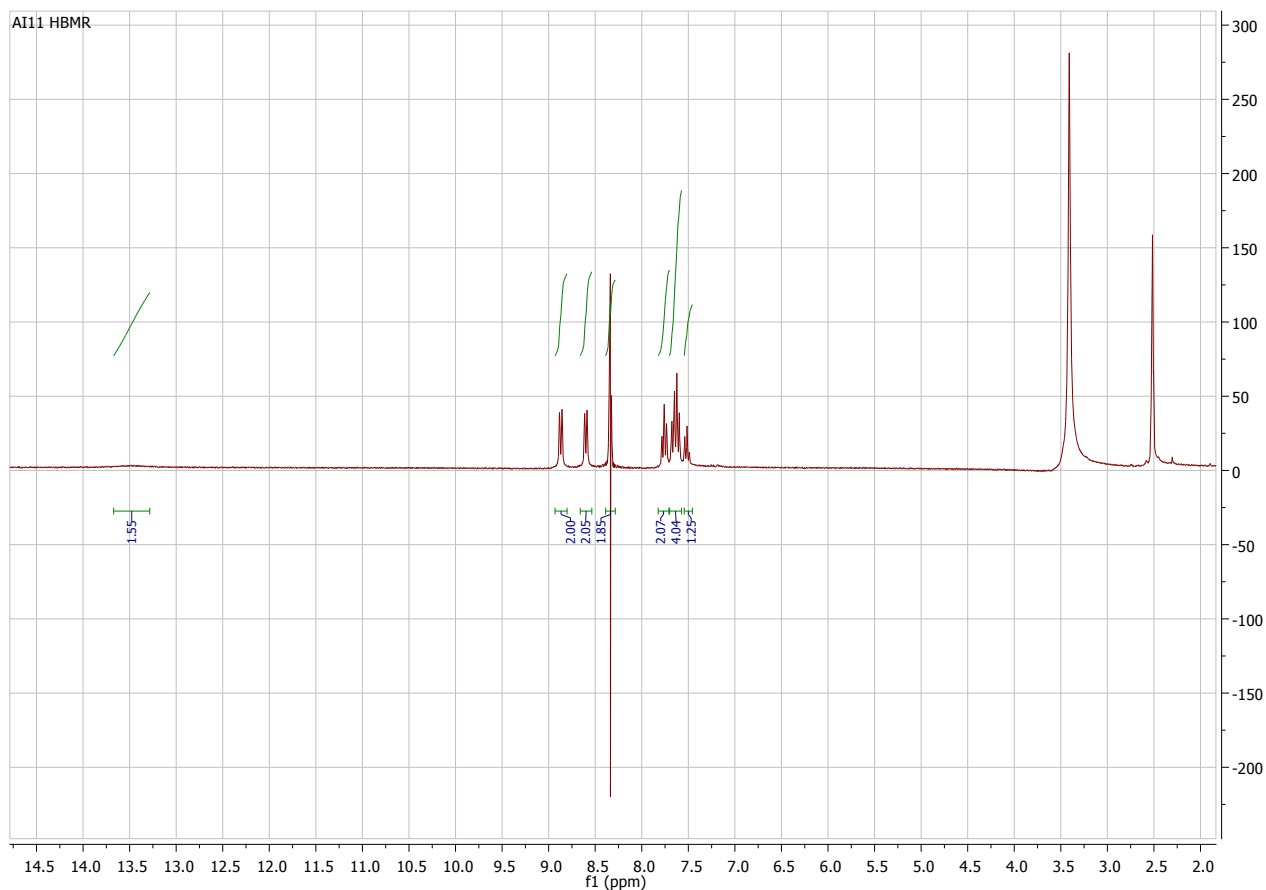
(ppm) 141.65, 137.8, 133.68, 133.52, 132.47, 129.69, 129.51, 128.43, 128.22, 127.57, 127.48, 126.82, 126.56, 126.13, 125.46, 125.32, 124.31, 123.18, 122.74, 122.47, 121.92, 120.68, 120.52; IR, KBr, (cm⁻¹): 3051, ν (CH_{ar}); 1614, 1516, 1452, 1414, ν (C=C); 1384, 1324, 1108, 1068, ν (C-N, C=N); 845, 755, 724, γ (CH_{ar}); MS (APCI⁺, 20 V), m/z: 507 ([M+H]⁺); Elemental analysis Calc. (%) for C₂₉H₁₆F₆N₂: C, 68.78; H, 3.18; N, 5.53; F, 22.51. Found: C, 69.69; H, 3.33; N, 5.83.

Synthesis of 2-(3,5-Bis(trifluoromethyl)phenyl)-1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazole (8) was synthesized from 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 3,5-bis(trifluoromethyl)benzaldehyde (1.16 g, 4.80 mmol), 4-(trifluoromethyl)aniline (0.93 g, 5.76 mmol) and ammonium acetate (3.70 g, 48.00 mmol) using the same procedure as for the synthesis of compound **2**. The crude product was purified by silica gel column chromatography using acetone/hexane (1:10, v/v) as an eluent. After drying white powder was obtained with the yield of 33% (0.90 g). It was recrystallized from the eluent mixture of solvents. FW = 574.00 g/mol; m.p. 239-240 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.85 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.5$ Hz, 1H), 8.83-8.77 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.5$ Hz, 1H), 8.75-8.69 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.5$ Hz, 1H), 8.00-7.92 (m, 4H), 7.85-7.66 (m, 5H), 7.63-7.54 (m, 1H), 7.39-7.30 (m, 1H), 7.23-7.21 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 147.05, 141.21, 137.89, 131.95, 131.87, 131.53, 129.76, 129.47, 128.92, 128.82, 128.46, 128.38, 127.82, 127.71, 127.61, 127.67, 126.62, 126.26, 125.78, 124.53, 124.37, 123.11, 122.67, 122.12, 120.52; IR, KBr, (cm⁻¹): 3085, ν (CH_{ar}); 1615, 1520, 1428, ν (C=C); 1365, 1329, 1279, 1178, 1124, ν (C-N, C=N); 994, 899, 863, 753, γ (CH_{ar}). MS (APCI⁺, 20 V), m/z: 575 ([M+H]⁺); Elemental analysis Calc. (%) for C₃₀H₁₅F₉N₂: C, 62.73; H, 2.63; N, 4.88; F, 29.77. Found: C, 61.68; H, 2.70; N, 4.83.

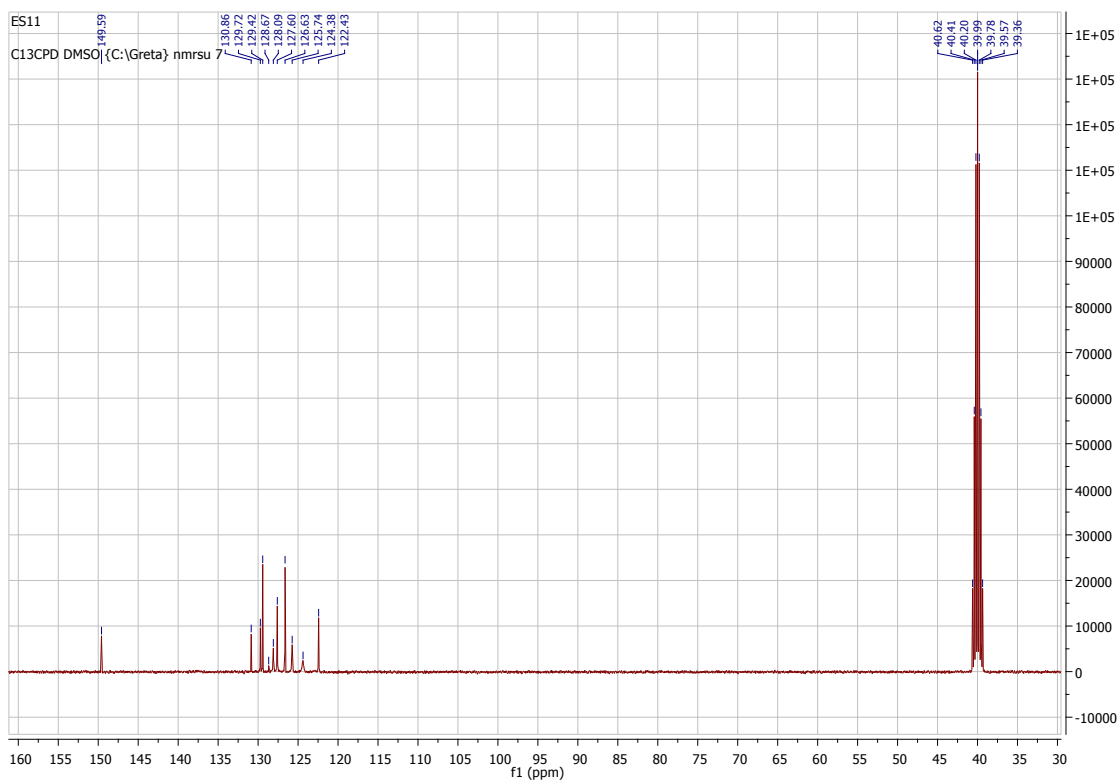
Synthesis of 2-(9-Ethyl-9H-carbazol-3-yl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (10) was prepared from 9,10-phenanthrenequinone (1.00 g, 4.80 mmol), 9-ethyl-9H-carbazole-3-carbaldehyde (1.07 g, 4.80 mmol), aniline (0.54 g, 5.76 mmol) and ammonium acetate (3.70 g, 48.00 mmol) using the same procedure as for the synthesis of compound **2**. The crude product was purified by silica gel column chromatography using acetone/toluene (1:8, v/v) as an eluent. White crystals were obtained with the yield of 30% (0.70 g). It was recrystallized from the eluent mixture of solvents. FW = 487.60 g/mol; m.p. 289-290 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.94 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.7$ Hz, 1H), 8.79 (d, $J = 8.2$

Hz, 1H), 8.73 (dd, $J_1 = 8.2$ Hz, $J_2 = 0.7$ Hz, 1H), 8.25 (d, $J_1 = 1.7$ Hz, $J_2 = 0.7$ Hz, 1H), 7.93 (dd, $J_1 = 7.7$ Hz, $J_2 = 0.7$ Hz, 1H), 7.80-7.73 (m, 2H), 7.69-7.57 (m, 6H), 7.54-7.43 (m, 2H), 7.39 (d, $J = 8.1$ Hz, 1H), 7.33-7.18 (m, 4H), 4.34 (q, $J = 7.2$ Hz, 2H), 1.41 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 1521.86, 140.42, 140.21, 138.69, 130.23, 129.48, 127.49, 126.32, 126.02, 124.17, 123.19, 122.92, 121.94, 120.85, 120.59, 119.31, 108.66, 108.25, 37.63, 13.81; IR, KBr, (cm^{-1}): 3054, ν (CH_{ar}); 2969, 2932, ν (CH_{al}); 1598, ν (C=C); 1495, 1456, 1417, γ (CH_{al}); 1380, 1350, 1234, 1154, 1125, ν (C-N, C=N); 888, 811, 755, 747, 723, 701, γ (CH_{ar}); MS (APCI $^+$), m/z : 488 ($[\text{M}+\text{H}]^+$); Elemental analysis Calc. (%) for $\text{C}_{35}\text{H}_{25}\text{N}_3$: C, 86.21; H, 5.17; N, 8.62. Found: C, 86.36; H, 5.32; N, 8.62.

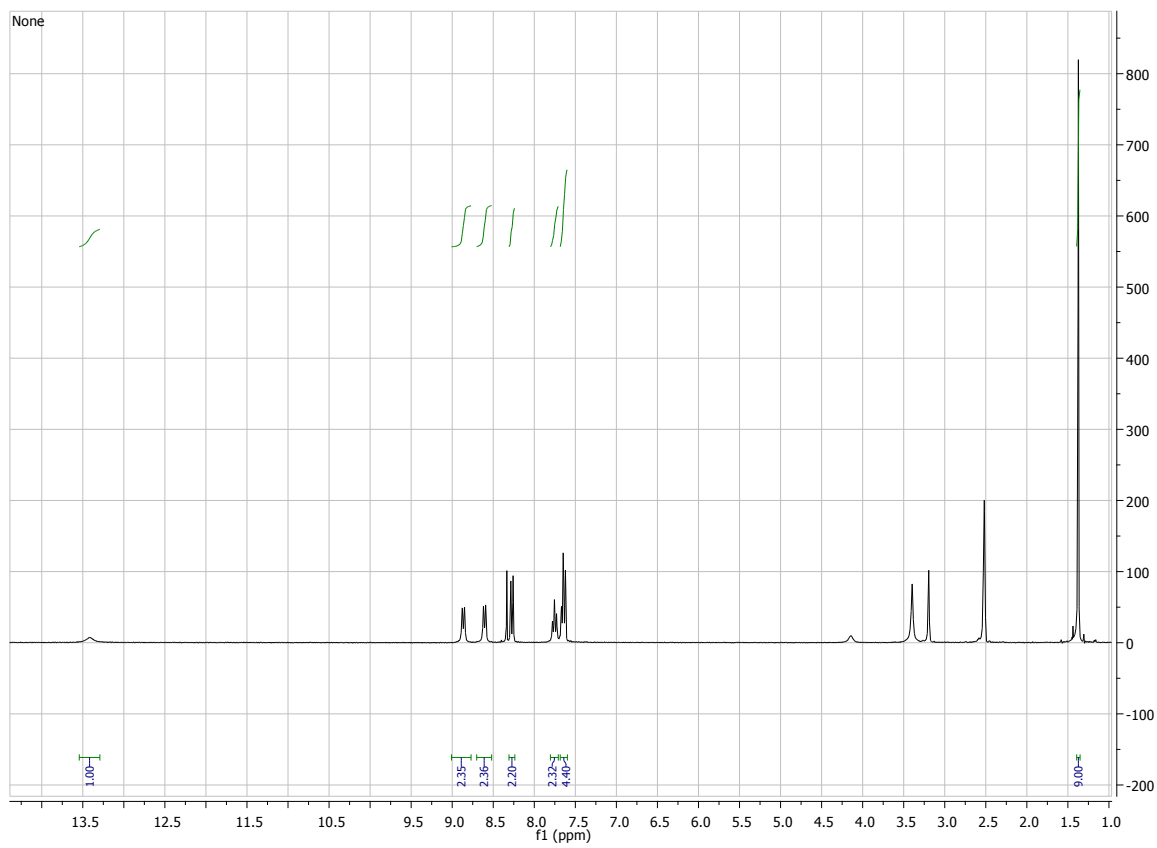
NMR, IR spectra



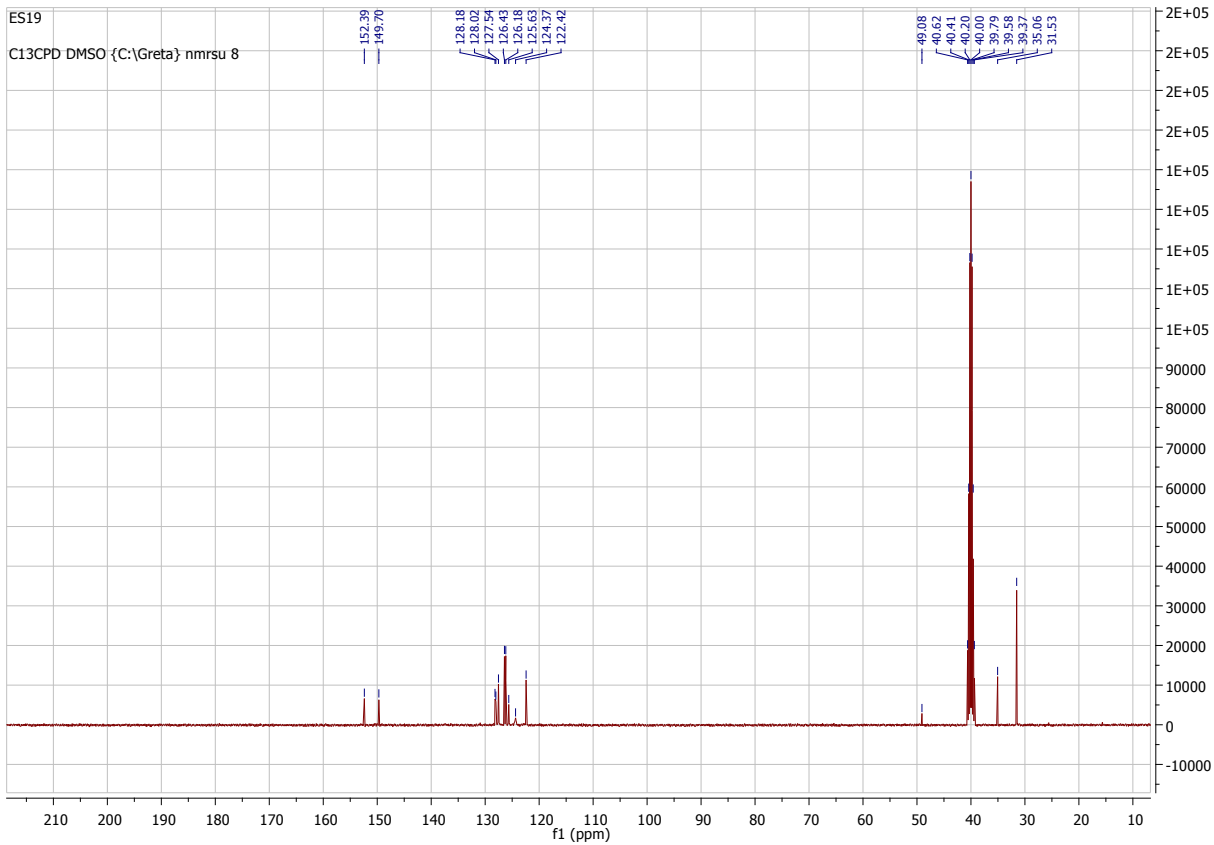
^1H NMR spectra in DMSO for compound **1**.



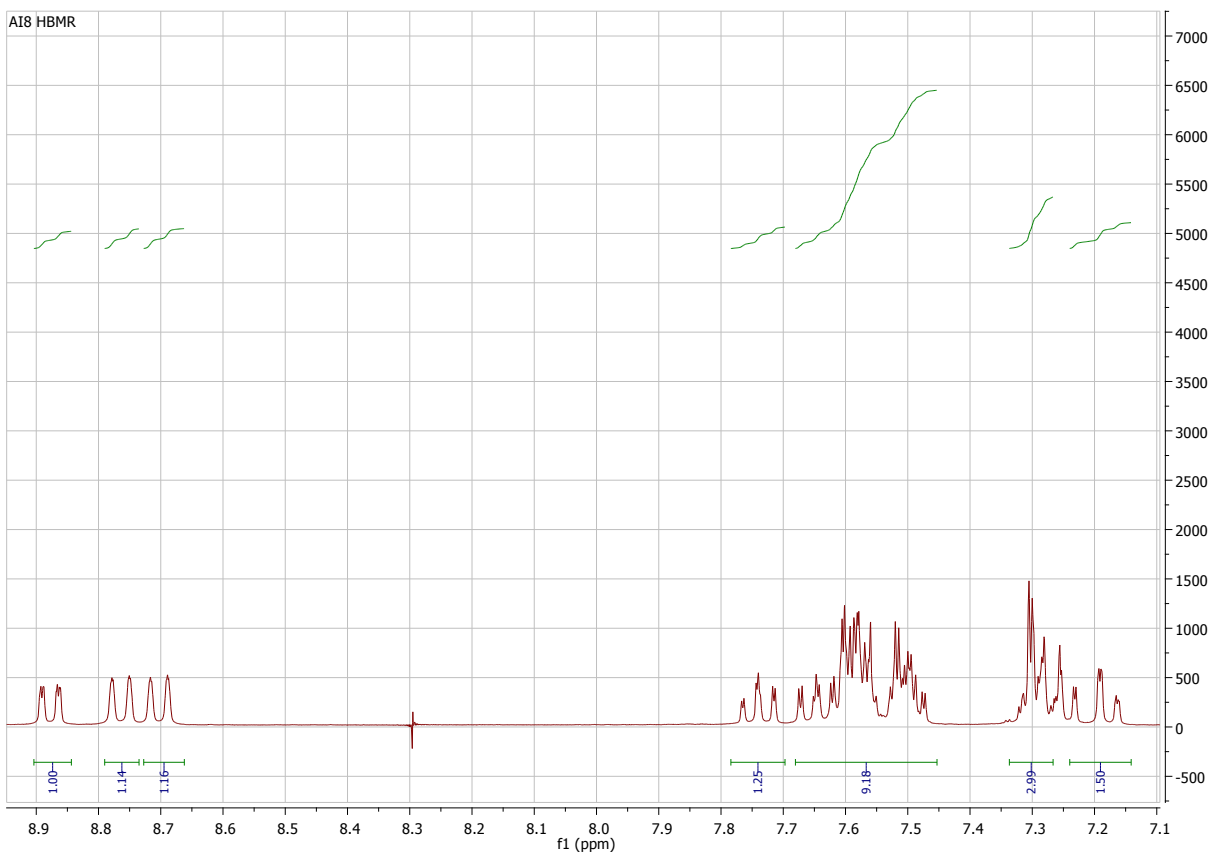
^{13}C NMR spectra in DMSO for compound **1**.



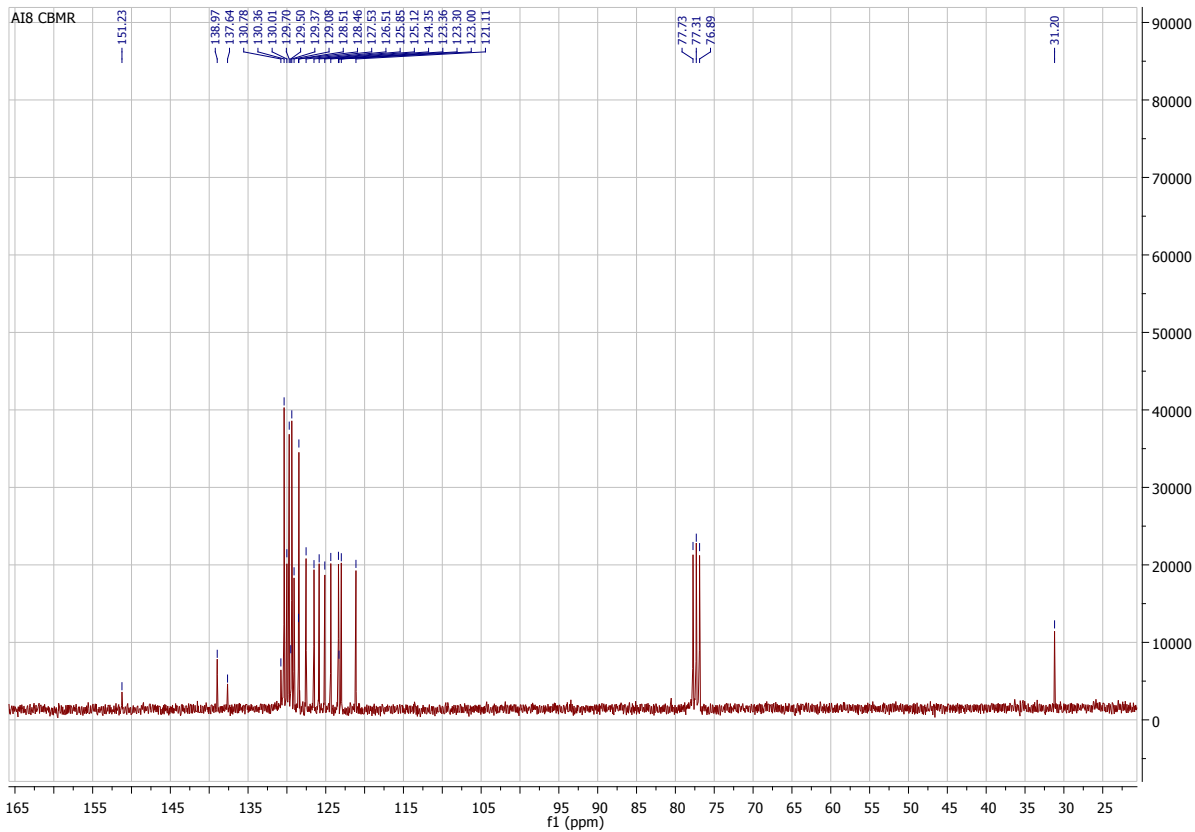
^1H NMR spectra in DMSO for compound **2**.



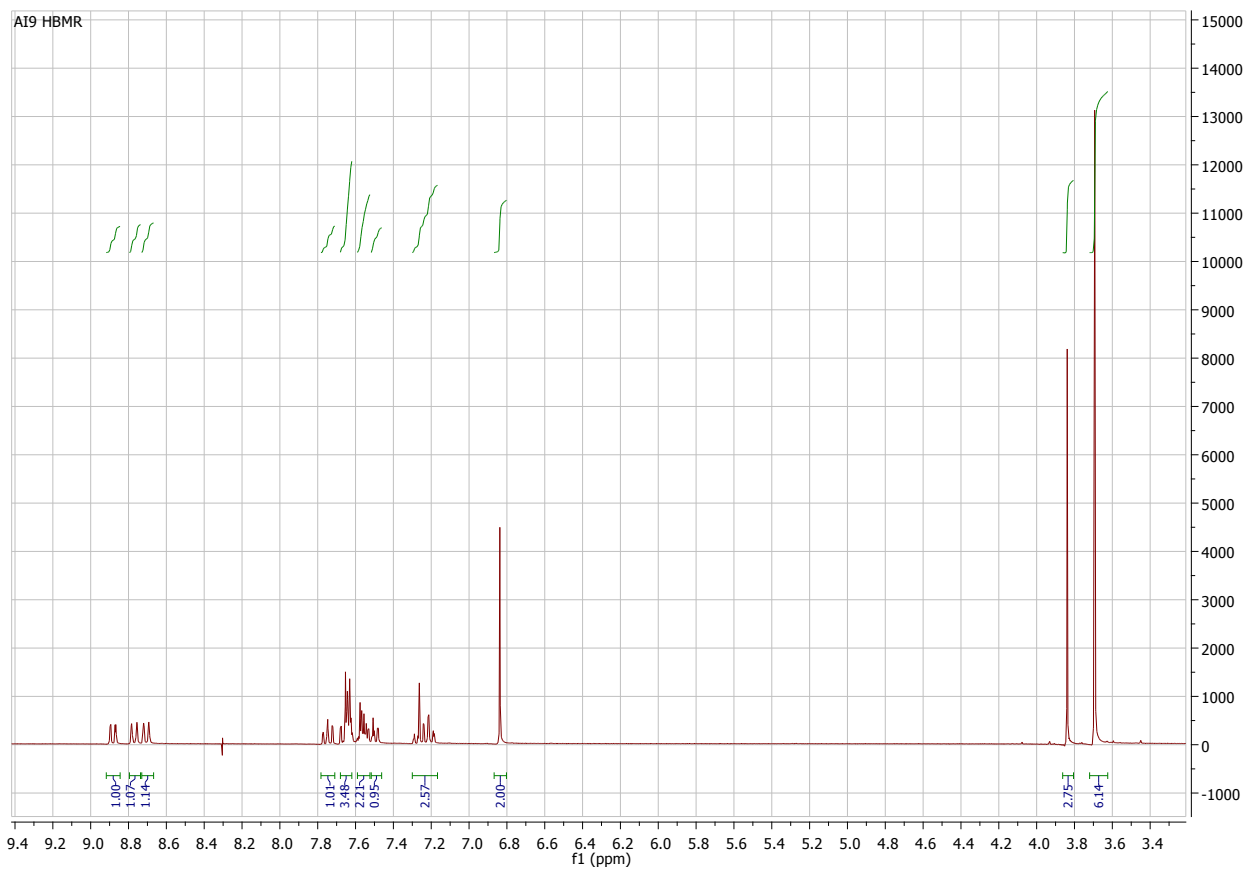
^{13}C NMR spectra in DMSO for compound **2**.



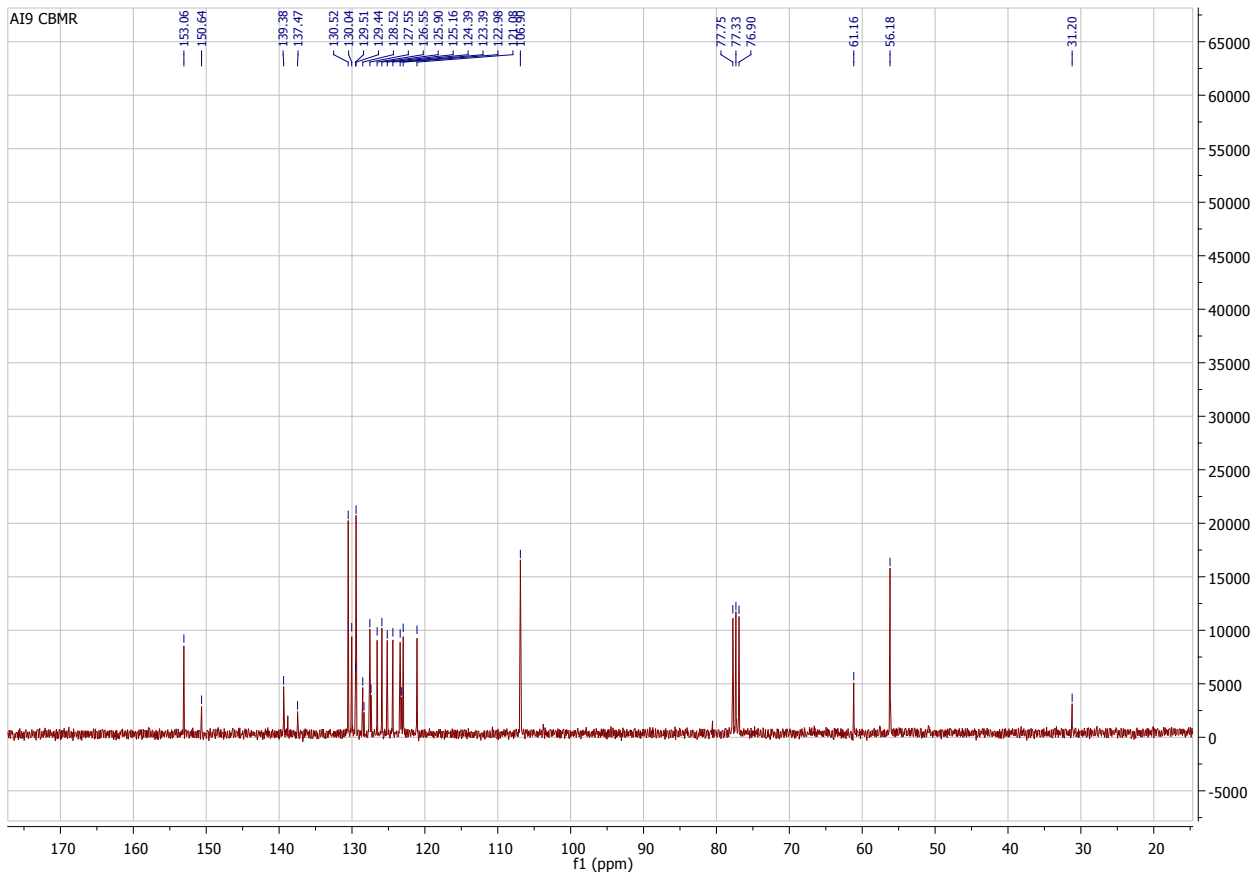
^1H NMR spectra in CDCl_3 for compound **3**.



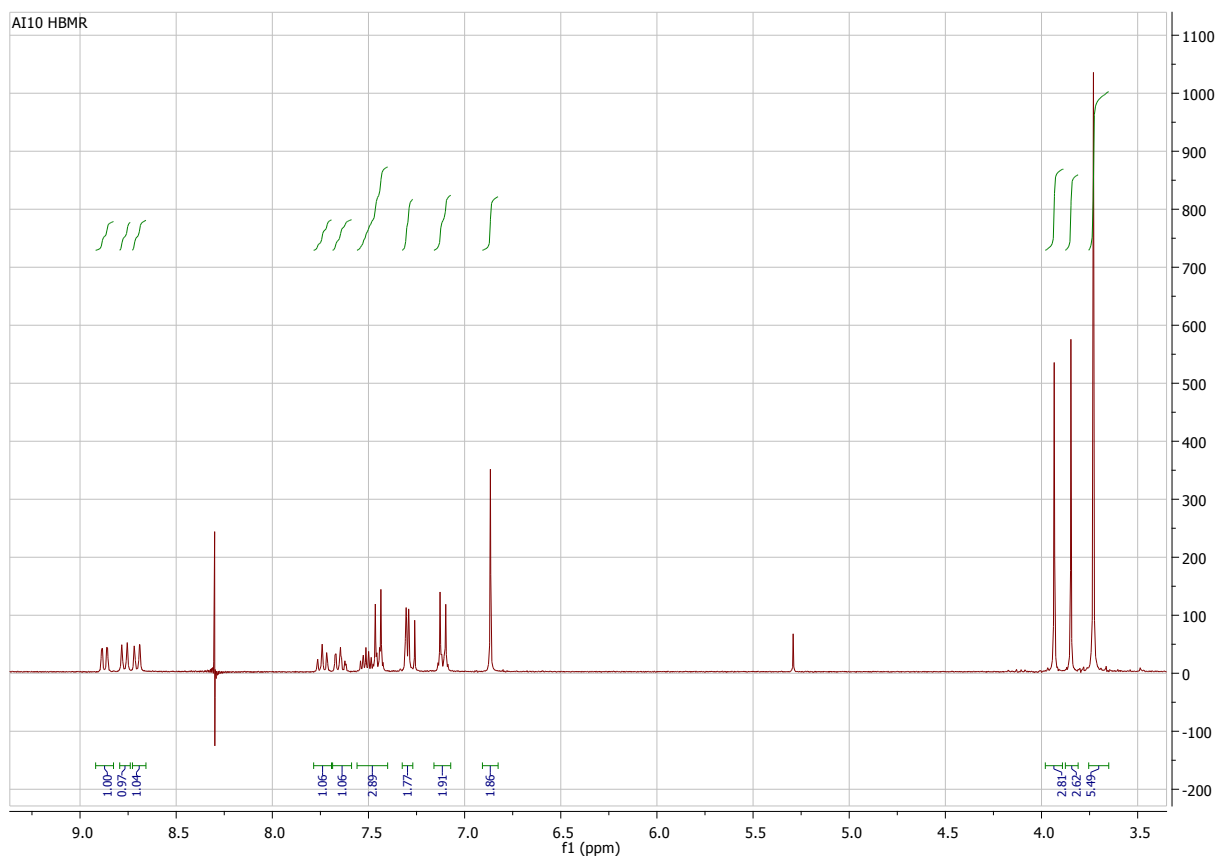
^{13}C NMR spectra in CDCl_3 for compound **3**.



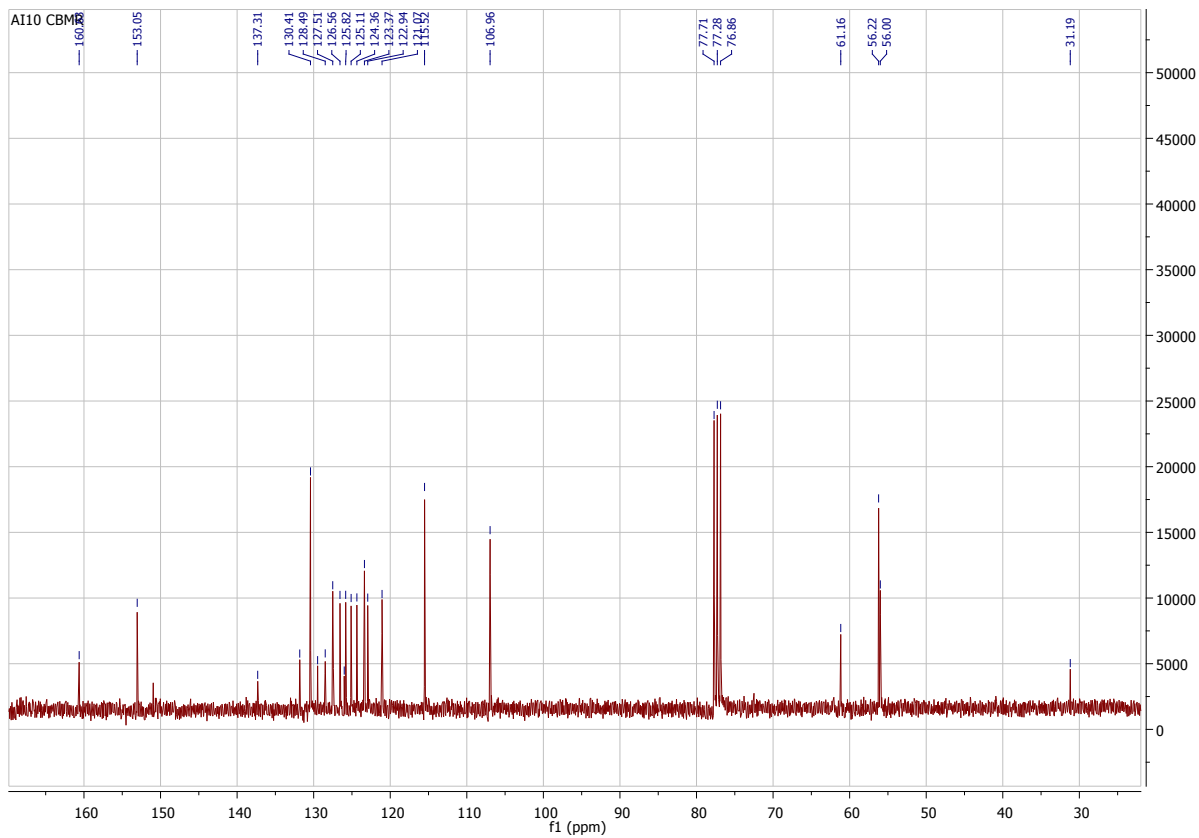
^1H NMR spectra in CDCl_3 for compound **4**.



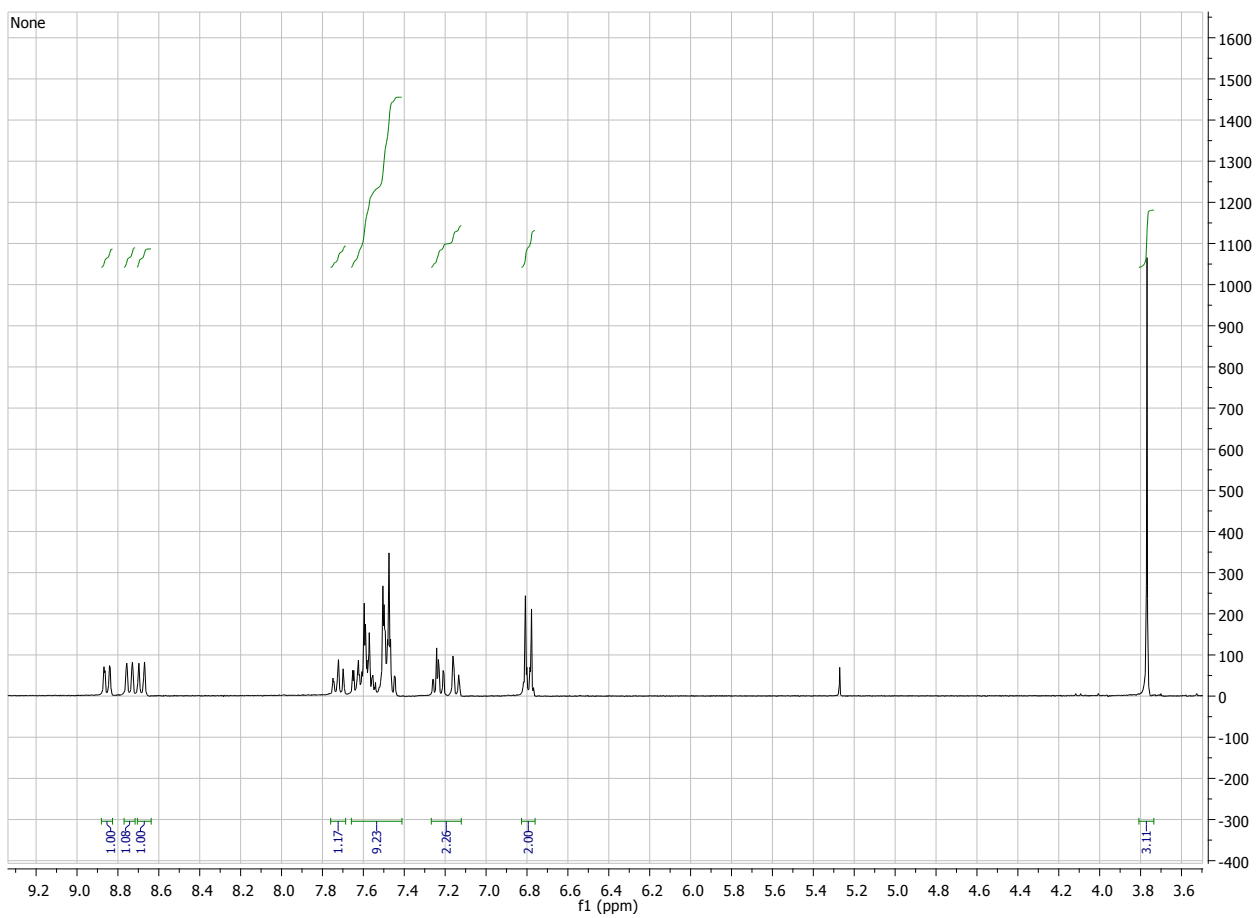
^{13}C NMR spectra in CDCl_3 for compound **4**.



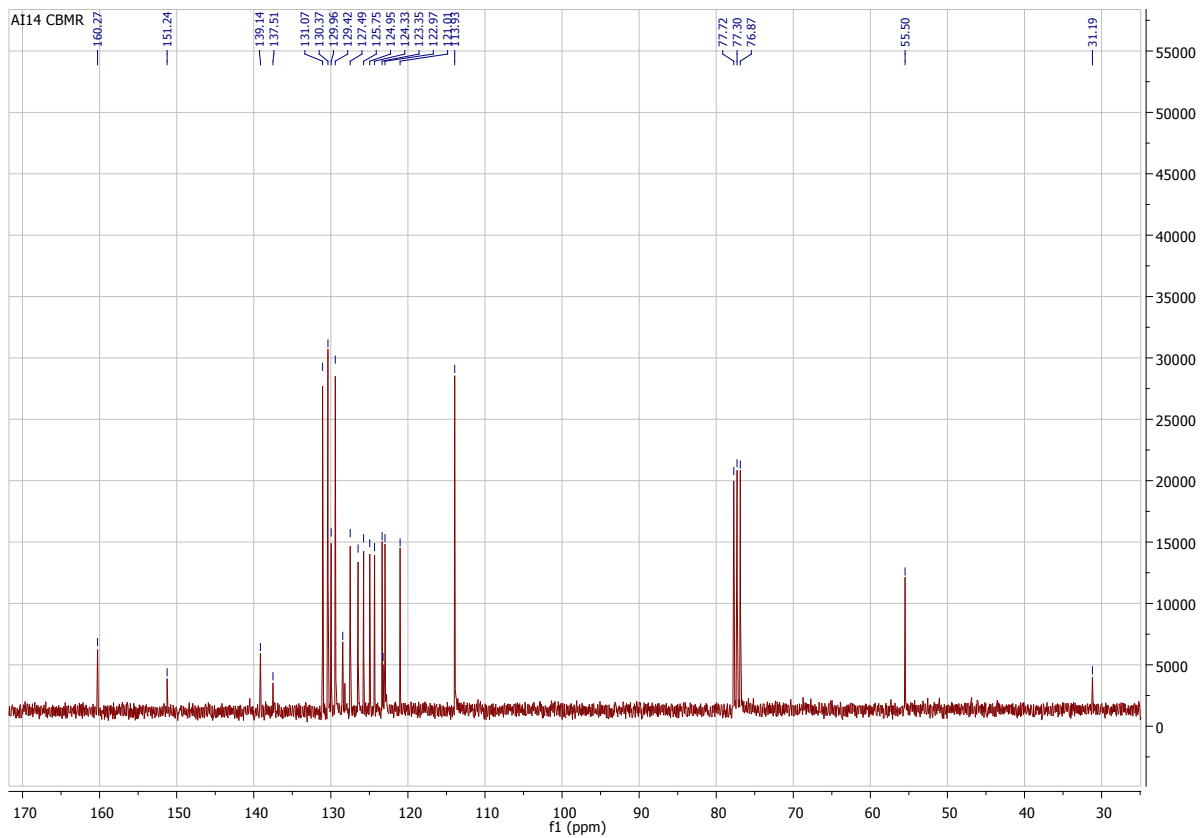
^1H NMR spectra in CDCl_3 for compound **5**.



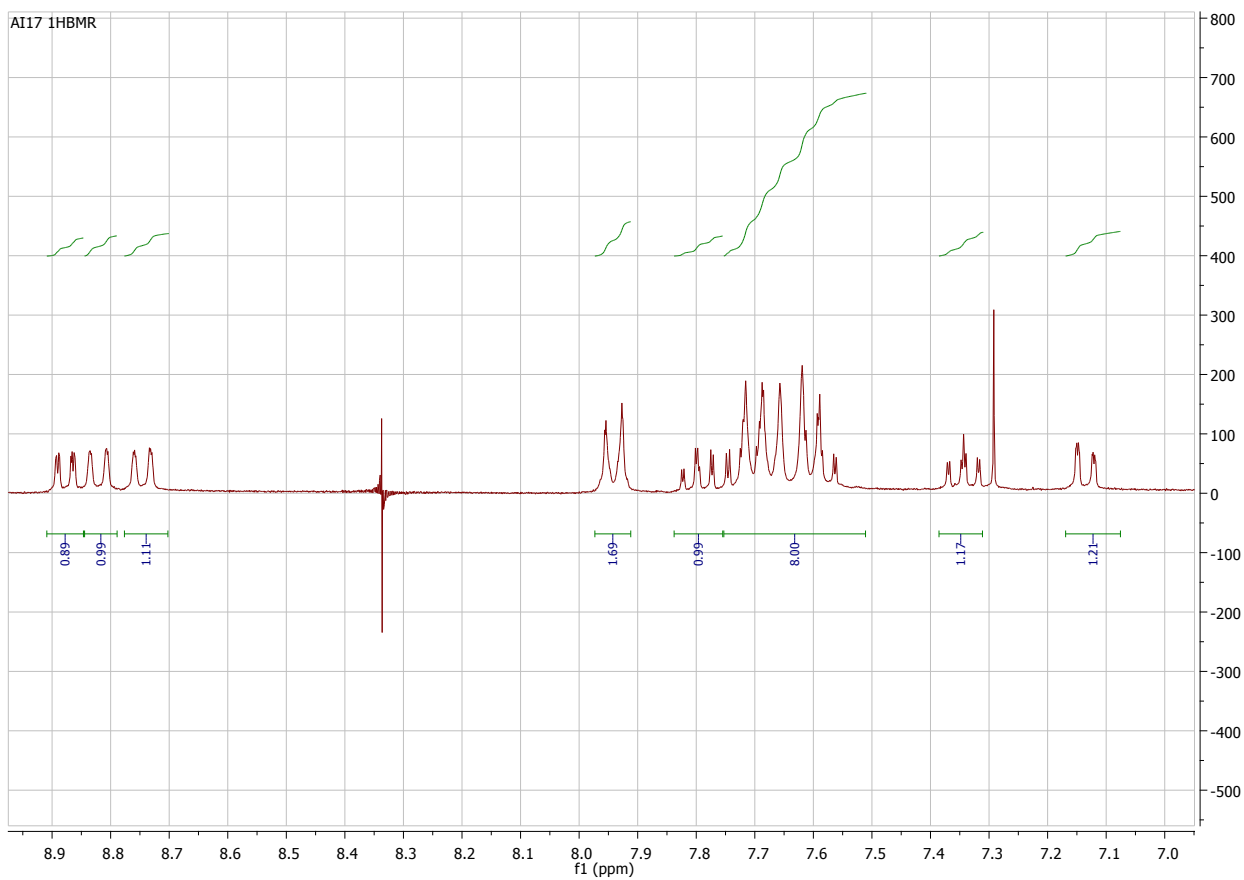
^{13}C NMR spectra in CDCl_3 for compound **5**.



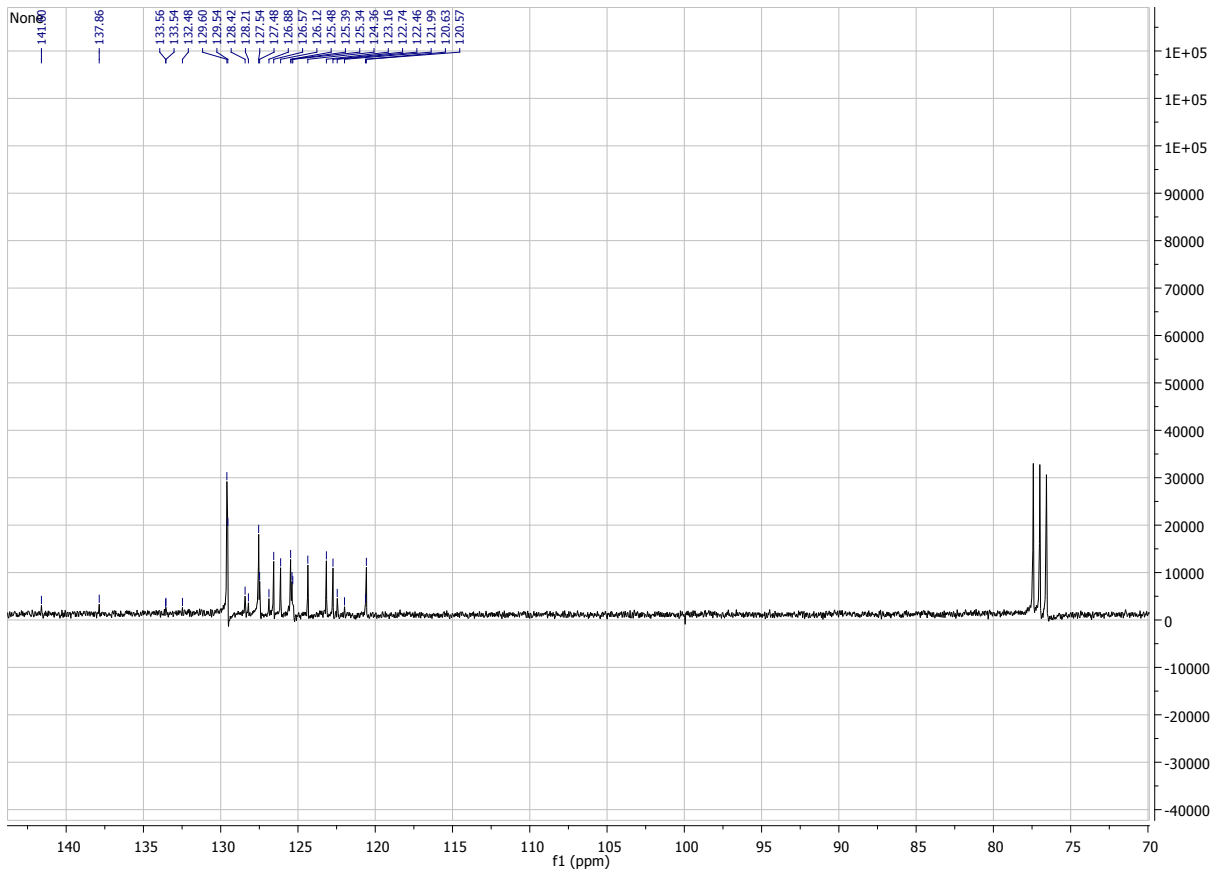
^1H NMR spectra in CDCl_3 for compound **6**.



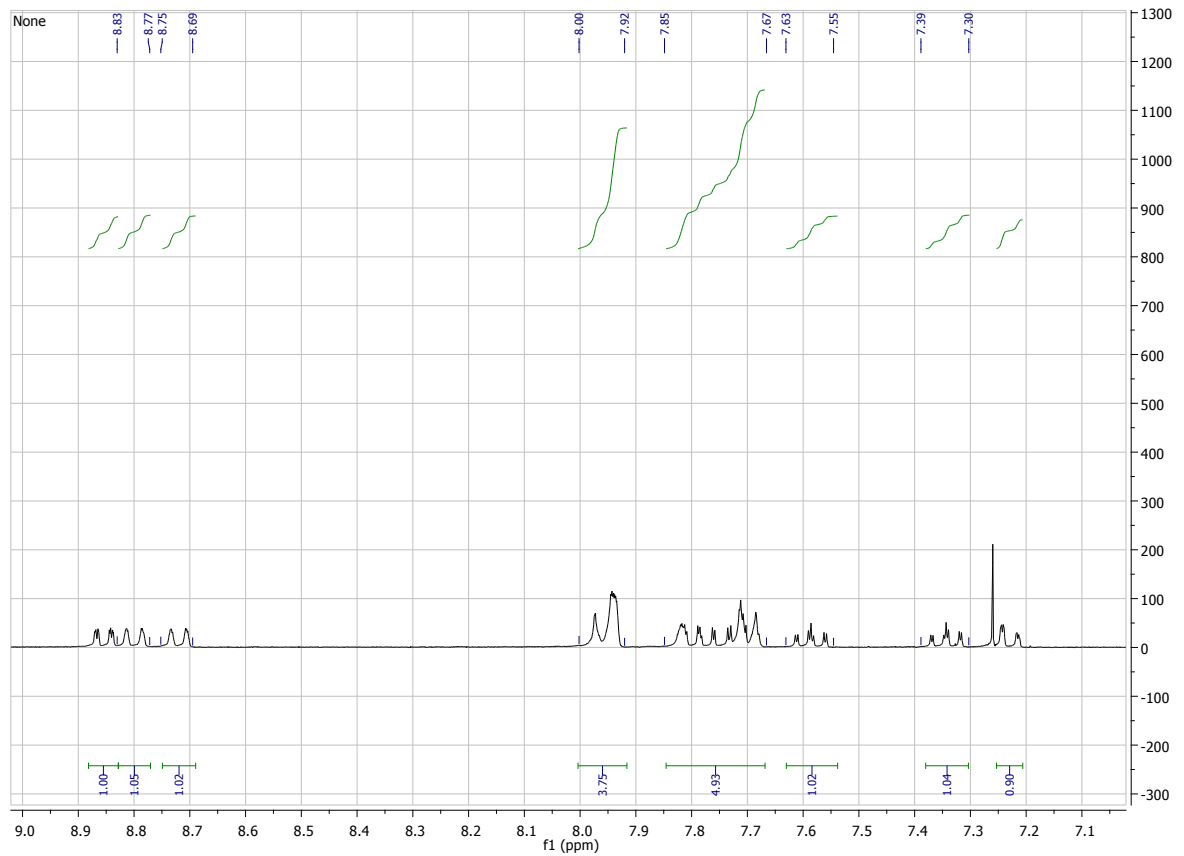
^{13}C NMR spectra in CDCl_3 for compound 6.



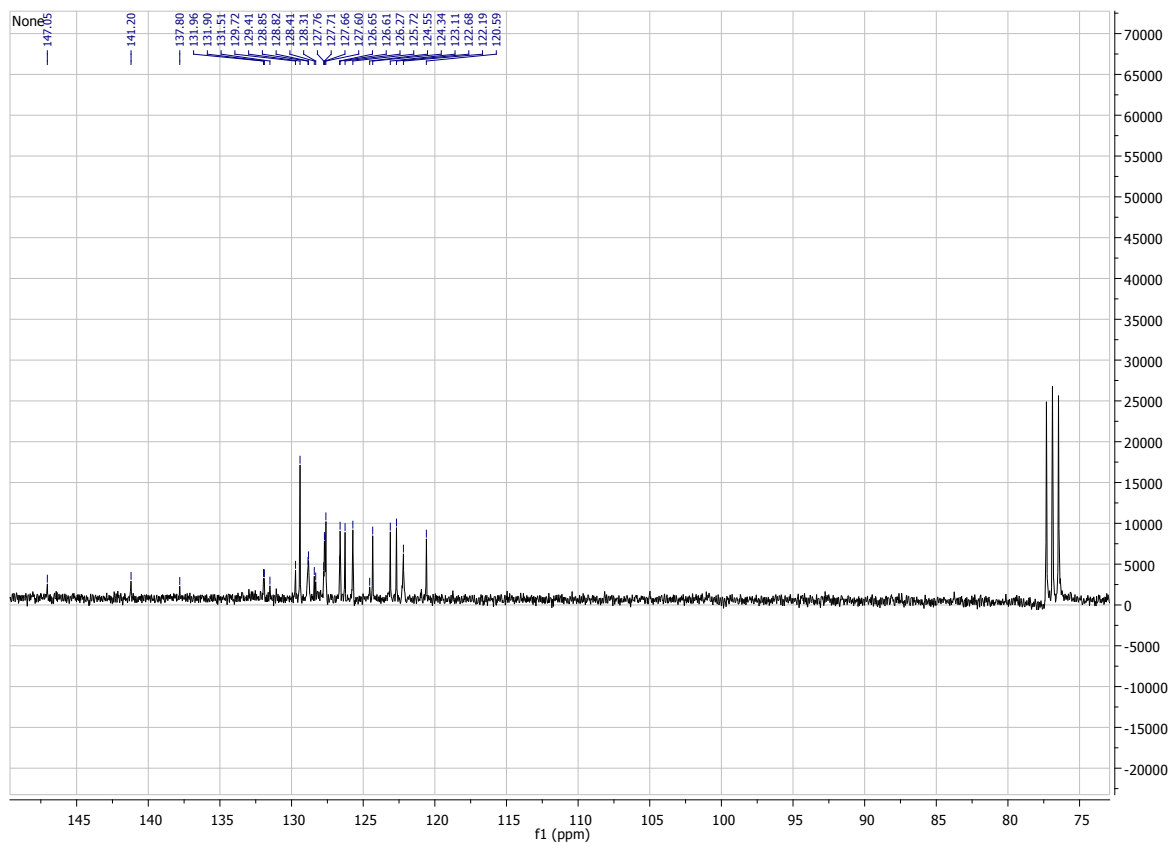
^1H NMR spectra in CDCl_3 for compound 7.



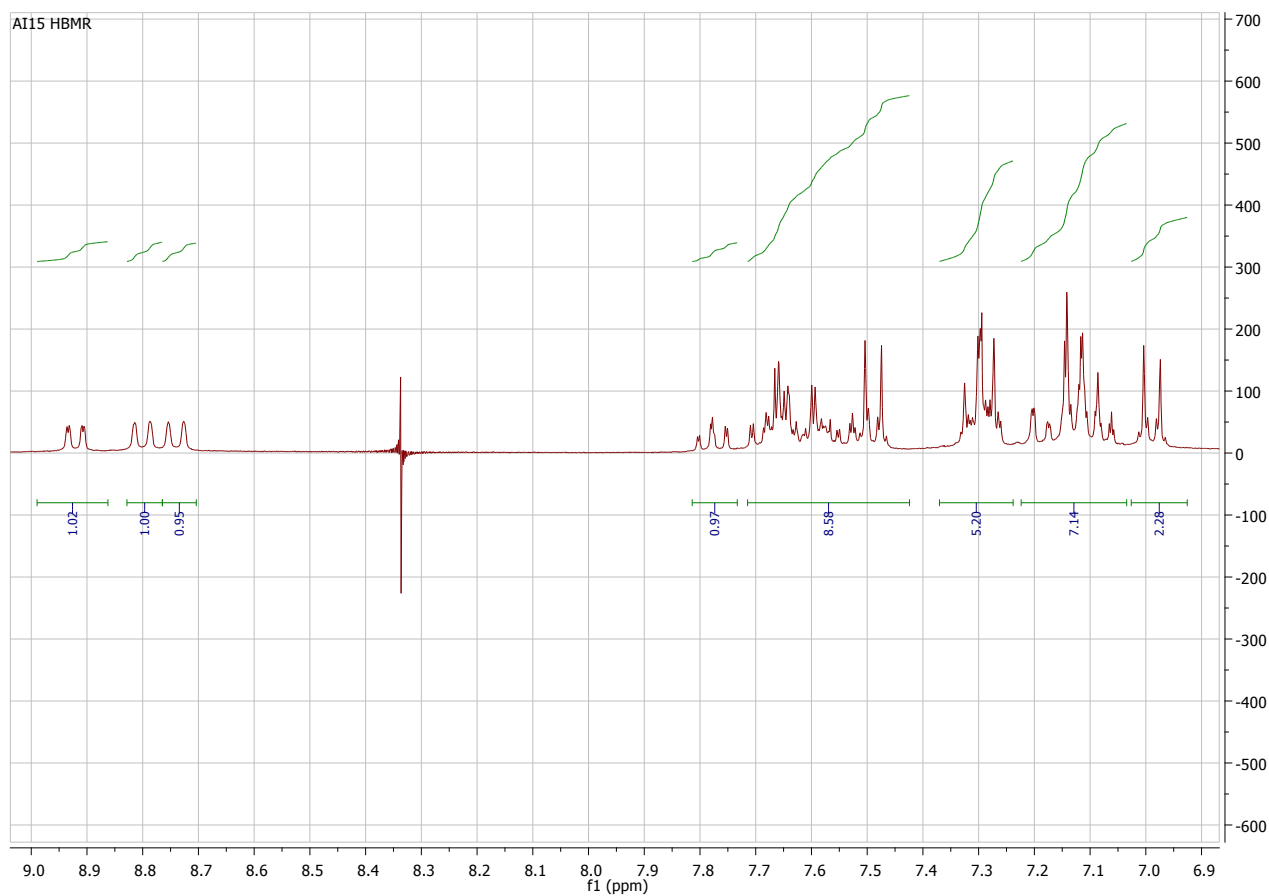
^{13}C NMR spectra in CDCl_3 for compound 7.



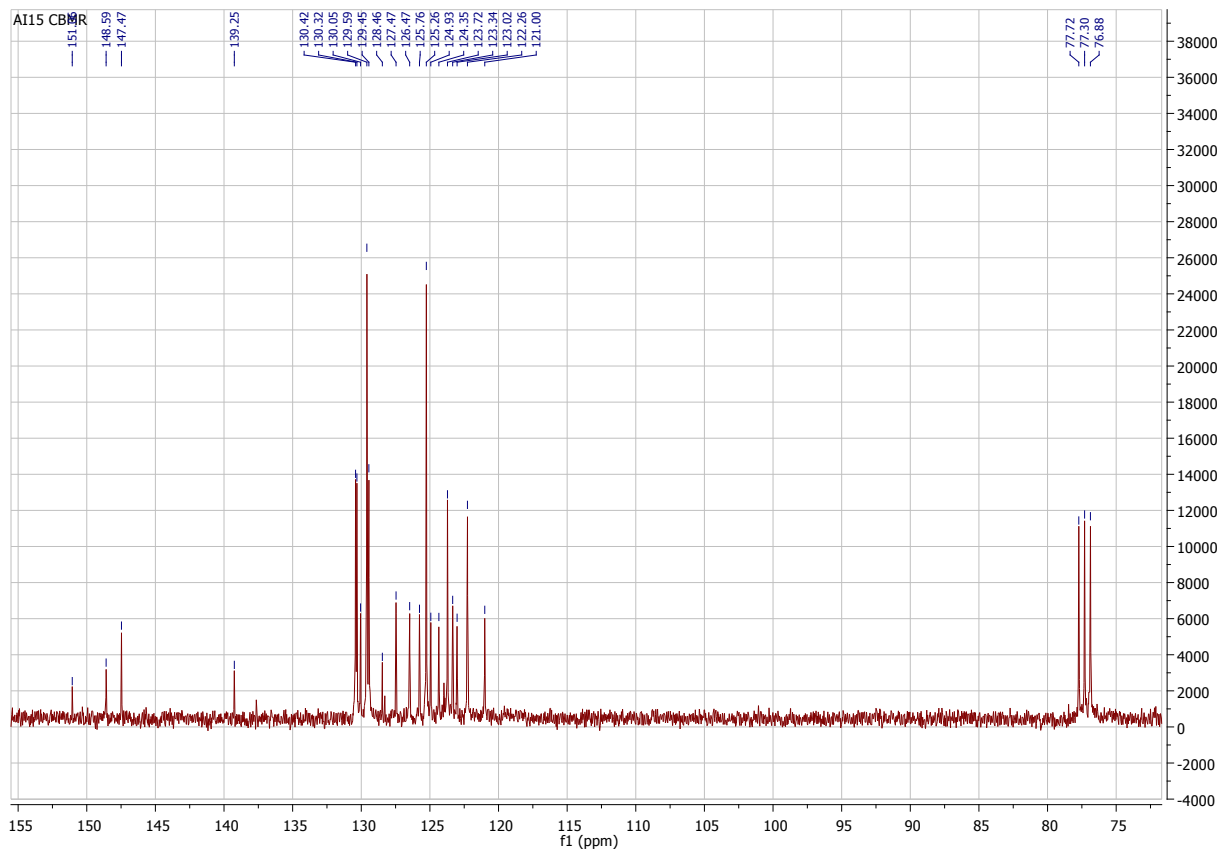
^1H NMR spectra in CDCl_3 for compound 8.



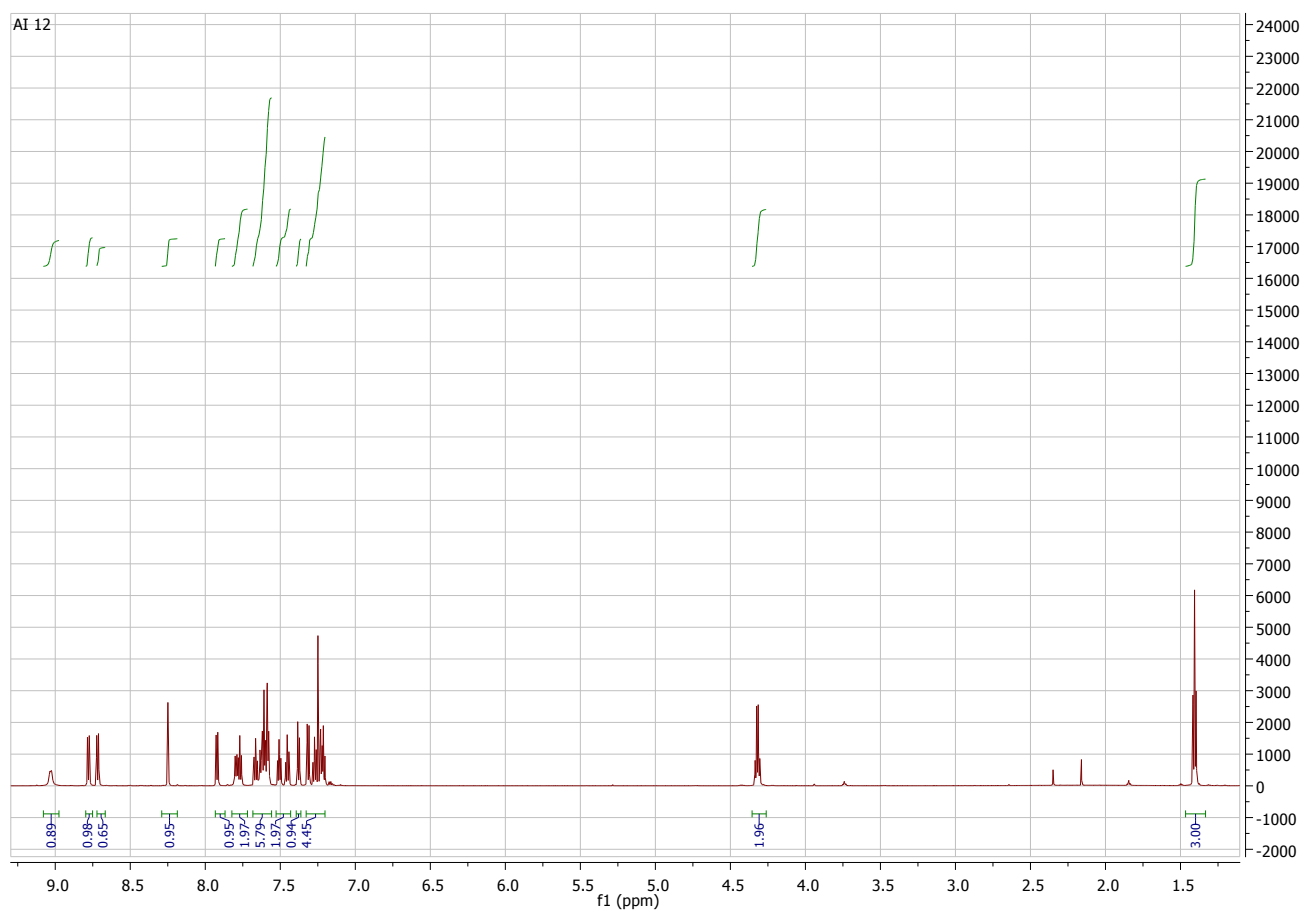
^{13}C NMR spectra in CDCl_3 for compound **8**.



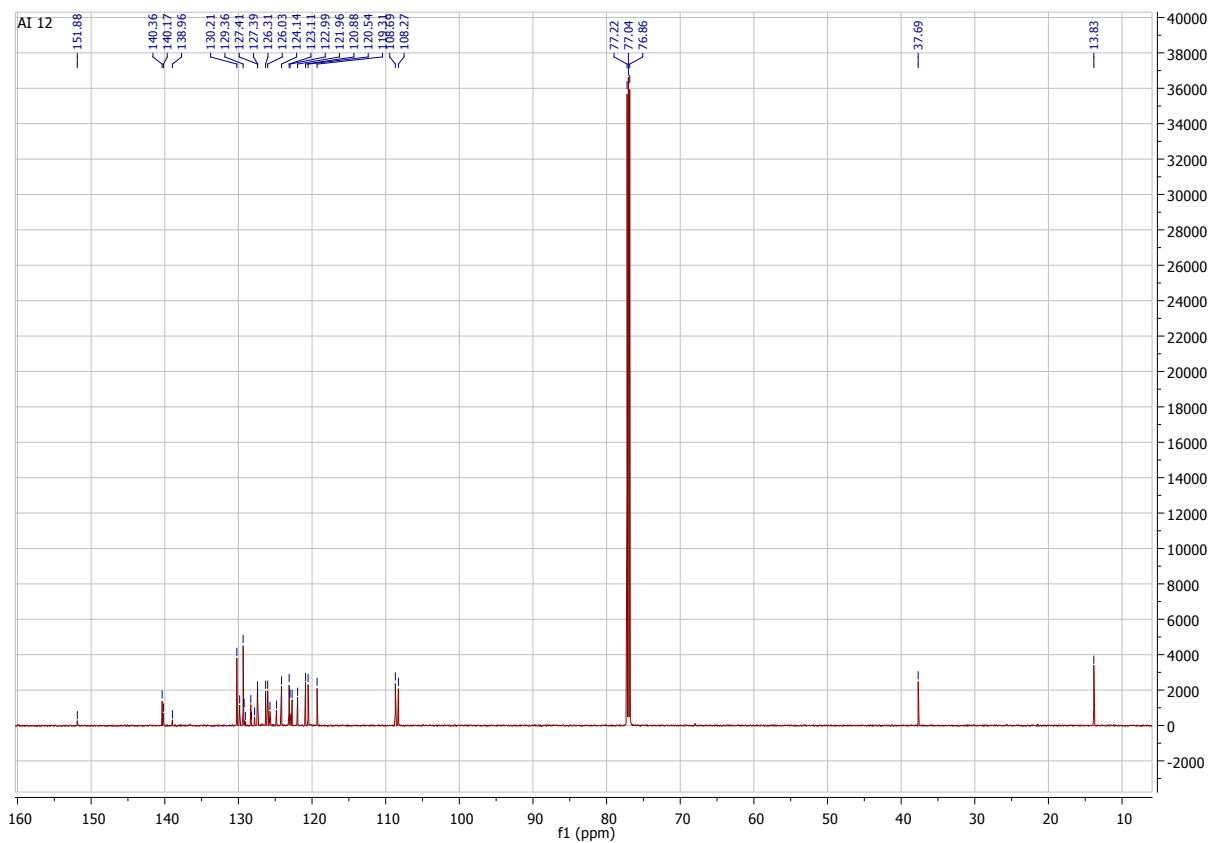
^1H NMR spectra in CDCl_3 for compound **9**.



^{13}C NMR spectra in CDCl_3 for compound **9**.



^1H NMR spectra in CDCl_3 for compound **10**.



^{13}C NMR spectra in CDCl_3 for compound **10**.

TGA and DSC curves

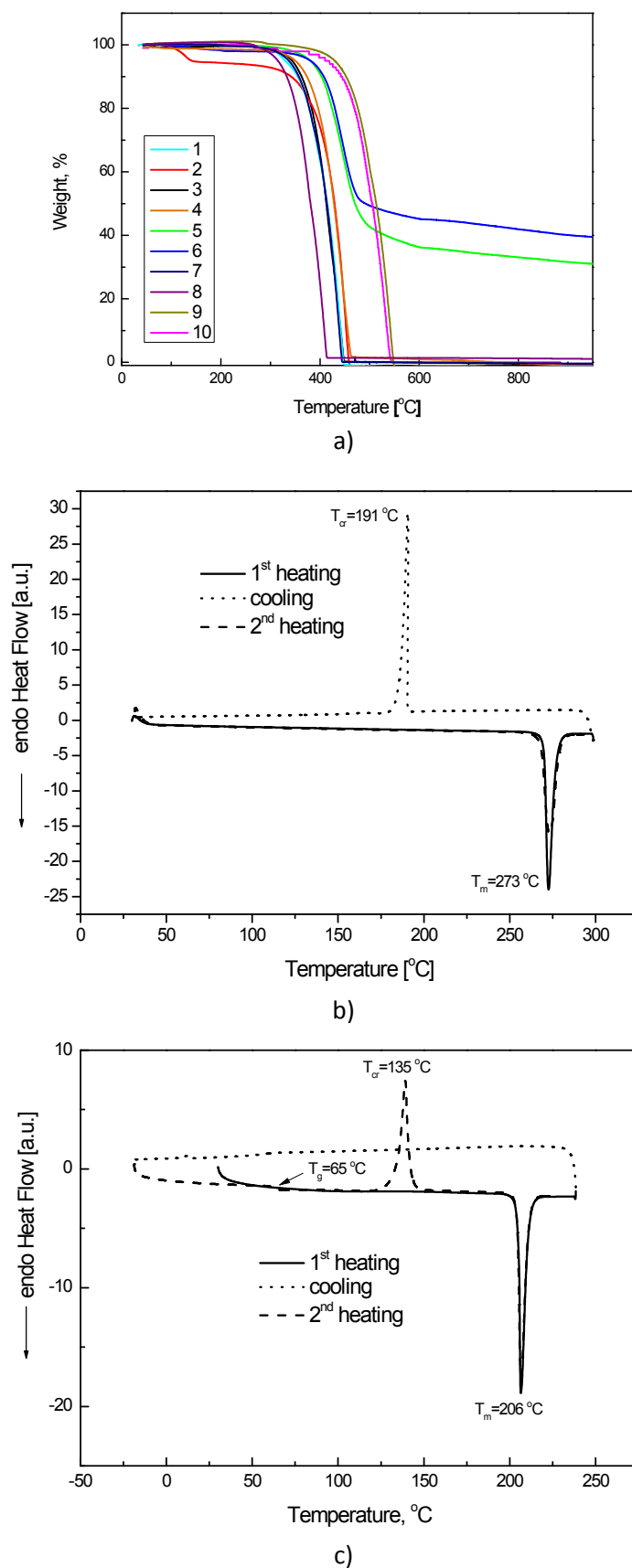


Figure S1. (a) TGA curves of **1-9** and **10** recorded at the heating rate of 20 °C/min in N₂. (b, c) DSC curves of compound **8**, **3** at a recorded heating rate of 10 °C/min in nitrogen atmosphere.

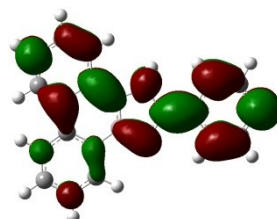
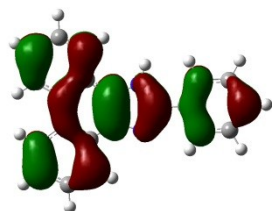
Spatial distribution of frontier orbitals

Compound

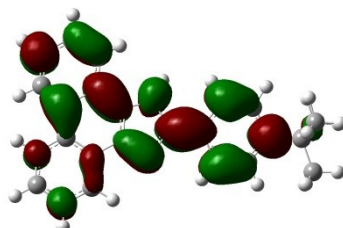
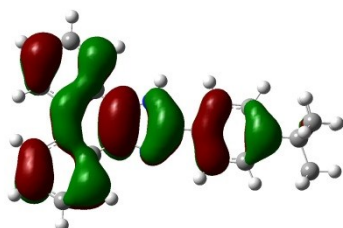
HOMO

LUMO

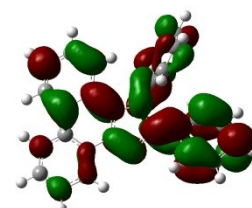
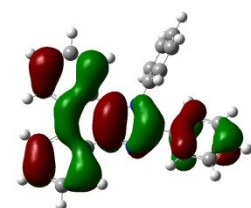
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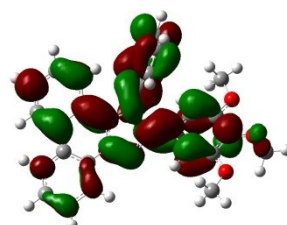
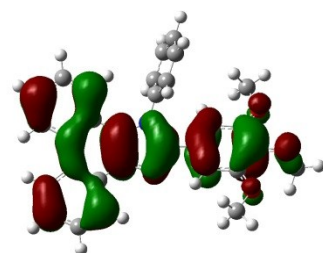
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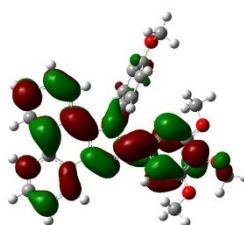
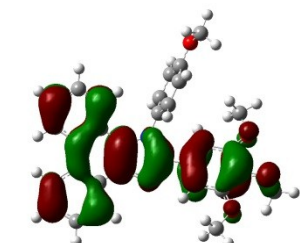
3



4



5



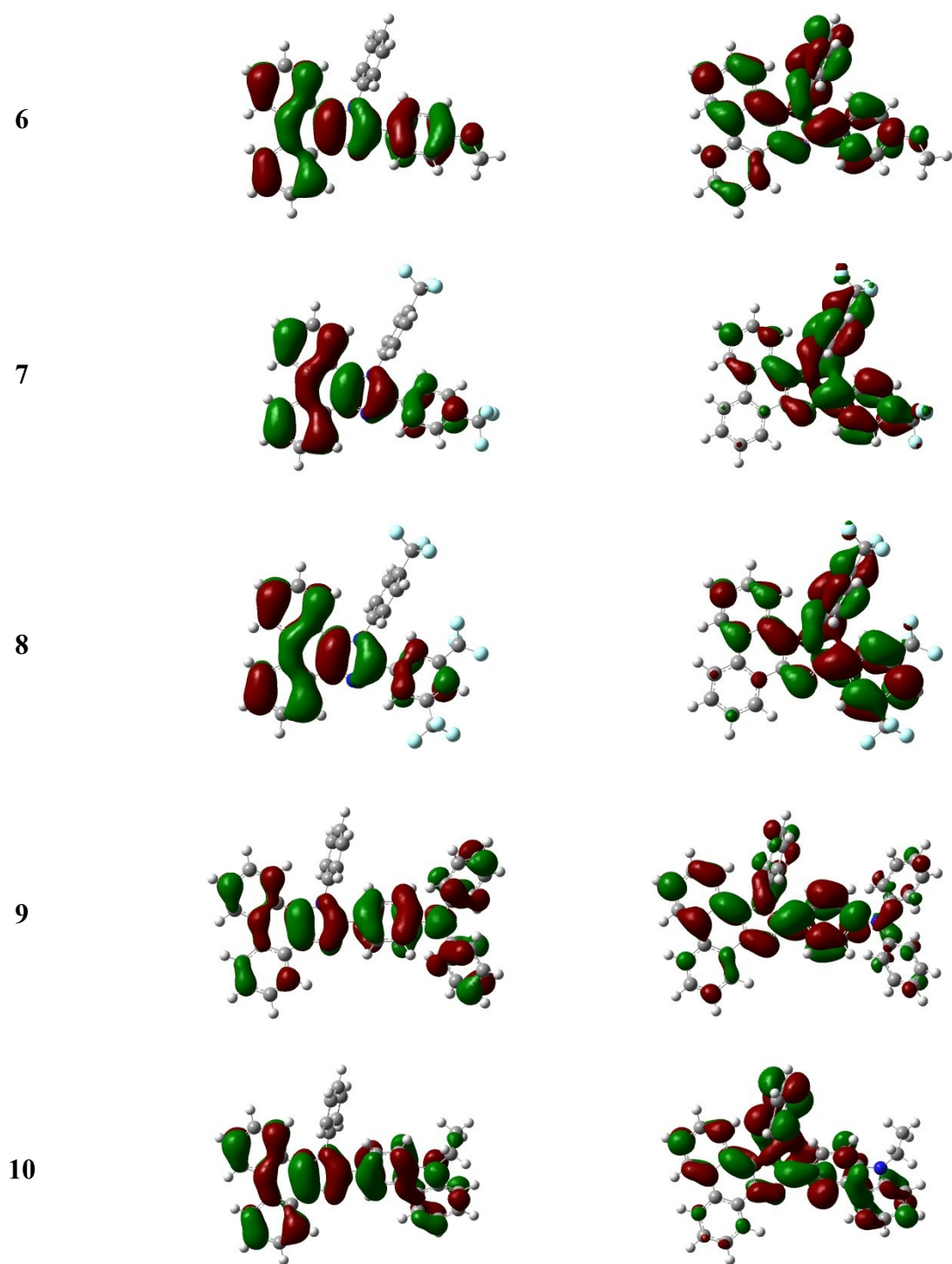


Figure S2. HOMO and LUMO of phenanthroimidazole compounds **1-10** as obtained by DFT using B3LYP/6-31G* basis set.

Absorption and fluorescence spectra

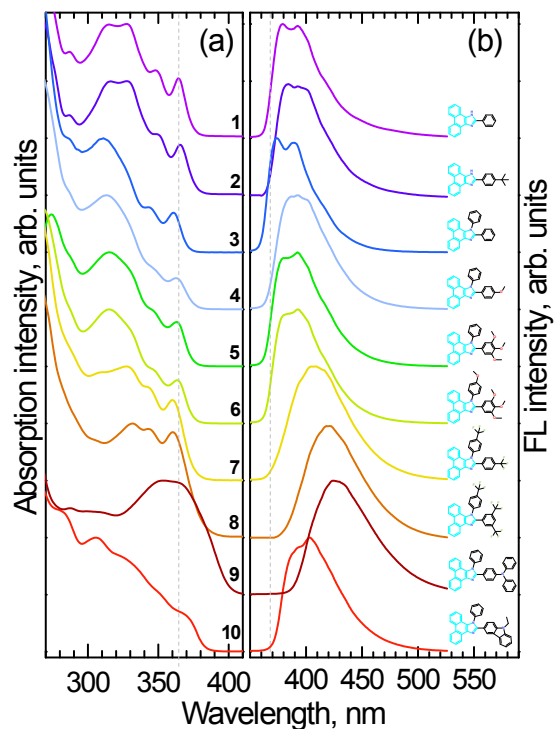


Figure S3. Absorption (a) and fluorescence spectra (b) of 10⁻⁵ M DMF solutions of PI derivatives. The intensity of each spectrum was scaled and arbitrarily shifted for clarity.

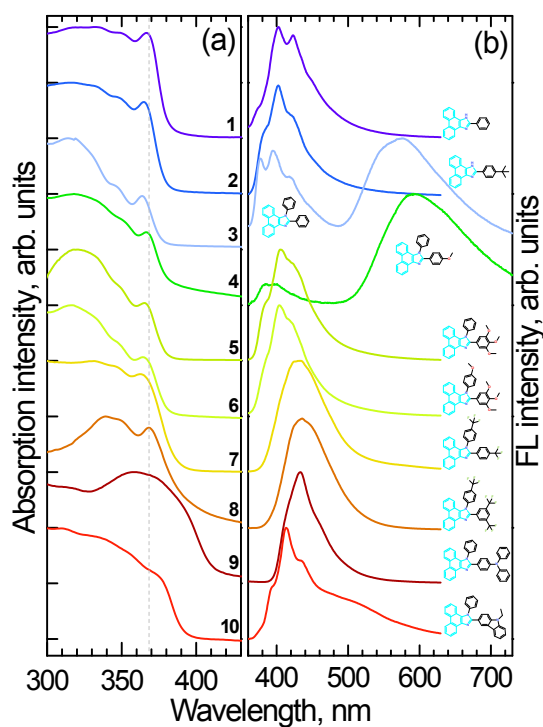


Figure S4. Absorption (a) and fluorescence spectra (b) of the neat films of PI derivatives. The intensity of each spectrum was scaled and arbitrarily shifted for clarity.

Cyclic voltammograms

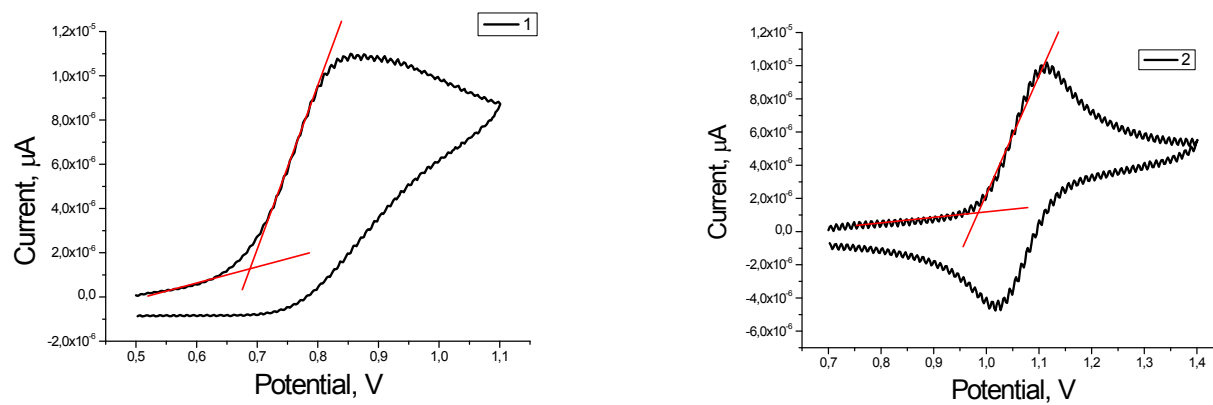
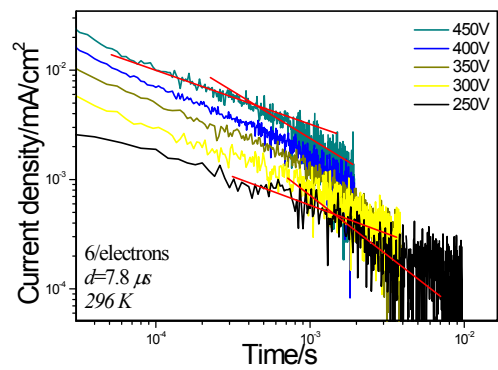
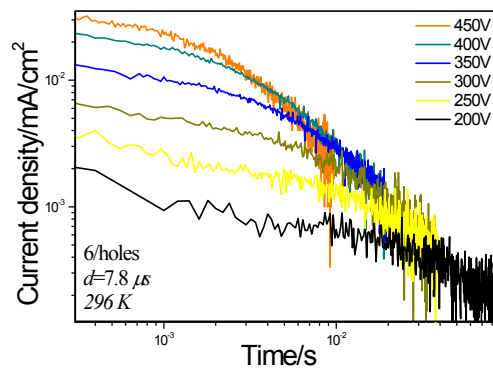
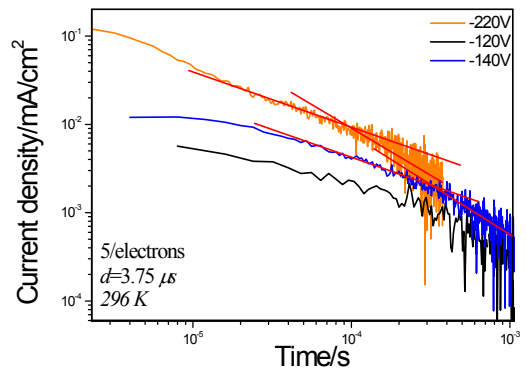
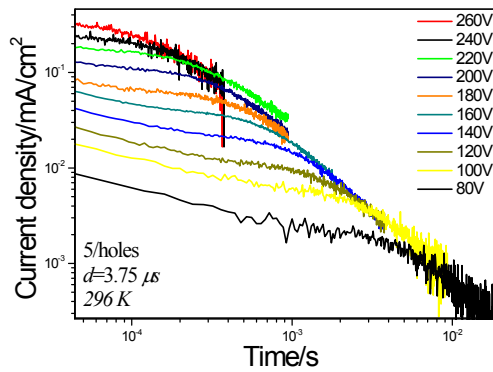
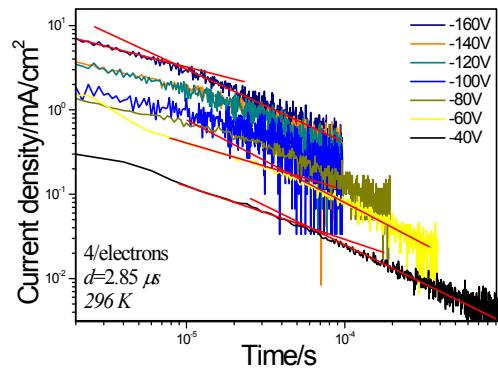
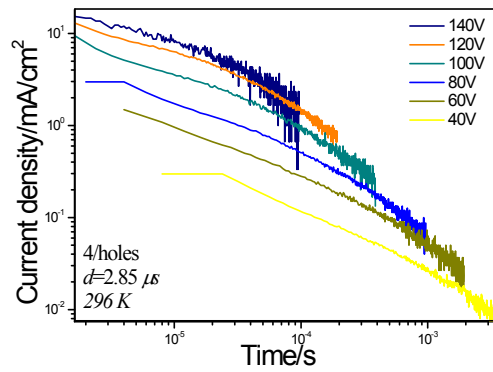


Figure S5. Cyclic voltammograms of compounds **1** and **2** in a 0.1 M $\text{Bu}_4\text{NPF}_6/\text{DCM}$ electrolyte.

TOF transients for hole and electron transport



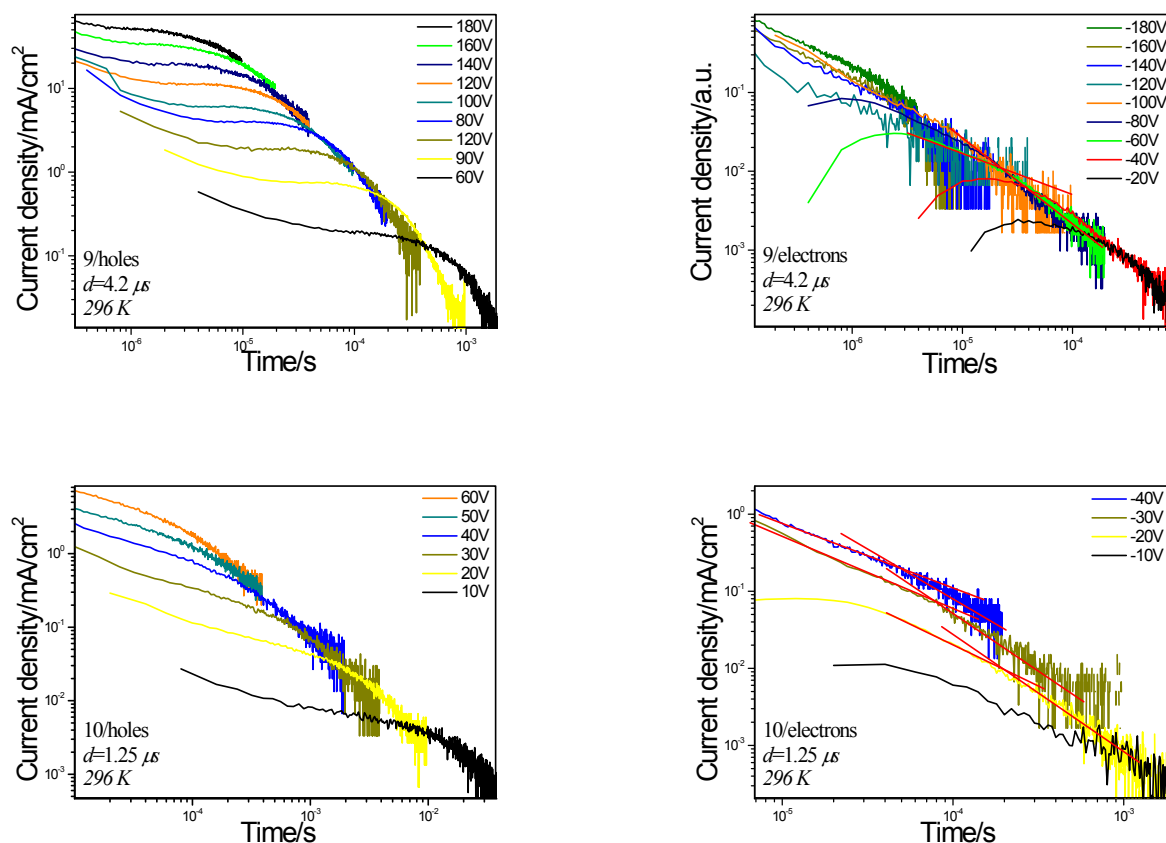


Figure S6. TOF transients for hole and electron transport of the vacuum-deposited layers of compounds **4-6, 9 and 10.**

References

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