Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Synthesis of flexible tetrapyridylethanes from pyridylpyrylium dications

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1- *General experimental details*

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line Techniques. Infrared-spectra were recorded on a Perkin-Elmer spectrum1000 FTIR using KBr plates.

All NMR data are reported in ppm (δ) relative to tetramethylsilane as external reference. Coupling constants are reported in Hz. ^{1}H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^{1}H-^{1}H cosy, ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC. Spectra were recorded at room temperature in $CDCl_3$ on a Bruker DRX 500 spectrometer and a Bruker Advance 300 spectrometer at the "Institut Universitaire de Technologie de Lannion". Mass spectra or elemental analyses were performed at the "Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes). Microanalytical data were obtained with a Thermo-Finnigan Flasch EA 1112 CHNS/0 analyzer. Mass spectra were obtained with a high resolution MS/MS Zab specra Tof micromass. ESR spectra of toluenic solution were recorded at 293K in a glass capillary using a Brücker Elexsys E 500 spectrometer with 100 KHz modulation. UV-vis absorption spectra were recorded on a UV-vis Perkin Elmer spectrophotometer lambda 25. Emission measurements were performed using a JYB fluoromax-4 spectrofluorimeter at 25°C. Quantum yield was determined using the corrected emission quantum yield of a coumarin 317 standard. The electrochemical studies of the compounds were performed in a glovebox (Jacomex) (O_2 < 1 ppm, H_2O < 1 ppm) with a home-designed 3-electrodes cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene was added at the end of each experiment to determine redox potential values. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Ecochemie) potentiostat monitored by a computer. Anhydrous "extra-dry" dichloromethane (H_2O < 30 ppm, Acros) was used as received and kept under N_2 in the glovebox. The supporting salt NBu_4PF_6 was synthesized from NBu_4OH (Fluka) and HPF_6 (Aldrich). It was then purified, dried under vacuum for 48 hours at 100° C, then kept under N_2 in the glovebox. Single crystal of **4c** was mounted on a glass fiber with oil and measured on a Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated MoK_α radiation source (λ = 0.71073 Å), from the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data were collected at 293 K. Structures were solved by the direct method using SIR97 and refined by a full matrix least-squares procedure based on F^2 with SHELXL2013. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors *H*iso (H).

2- *General procedure*

2-1 *synthesis of compounds 1*

2-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl]-pyridine 1a

Small excess of *n*-butyllithium 2.5 M in hexanes (0.70 mL, 1.75 mmol, 1.1 equiv.) was added dropwise at -78 °C, under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl tributylphosphonium tetrafluoroborate salt (1g, 1.67 mmol, 1 equiv.) in dry THF

(15 mL). After 15 min, the 4-(2-pyridylbenzaldehyde) (295 mg, 1.60 mmol, 0.95 equiv.) was added. The solution was stirred at -78°C for 30 min, and allowed to warm to room temperature for 2h. THF was evaporated and the residue dissolved in a mixture of CH_2Cl_2/water 1:1 (30 mL) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated. The crude product was obtained by crystallization in a diethylether/dichloromethane (80/20) solution (515 mg, 77%) as a yellow solid. mp : 188-190°C ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 6.01 (s, 1H), 6.44 (d, 1H, *J* = 2.0 Hz), 7.08 (d, 1H, *J* = 2.0 Hz),7.24 (dd, 1H, J = 4.5 Hz, *J* = 4.4 Hz) 7.42-7.48 (m, 6H), 7.52 (d, 2H, *J* = 8.2 Hz), 7.78-7.81 (m, 6H, 4H(ph) +2H (pyridine)), 8.03 (d, 2H, *J* = 8.2 Hz), 8.72 (d, 1H, *J* = 2.5 Hz) ; ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 157.1(C), 152.8(C), 151.0(C), 149.7(CH), 139.4(C), 136.8 (CH), 135.0(C), 133.4(C), 133.3(C), 130.9(CH), 130.1(C), 129.3(CH), 129.1(CH), 128.6(CH), 128.1(CH), 127.0(CH), 124.9 (CH), 124.6(CH), 121.8(CH), 120.2(CH) 113.7 (CH), 108.6 (CH), 102.2 (CH). HRMS (ESI) m/z calculated for $C_{29}H_{22}NO$ $[M+H]^+$ 400.17014, found 400.1699. IR ν(cm^{-1}) = 3049 ; 2958 ; 1722 ; 1655 ; 760.

3-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl]-pyridine 1b

Small excess of *n*-butyllithium 2.5 M in hexanes (0.8 mL, 1.92 mmol, 1 equiv.) was added dropwise at -78 °C, under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl tributylphosphonium tetrafluoroborate salt (1.2 g, 2 mmol, 1 equiv.) in dry THF (15 mL). After 15 min, the 4-(3-pyridylbenzaldehyde) (350 mg, 1.9 mmol, 0.95 equiv.) was added. The solution was stirred at -78°C for 30 min, and allowed to warm to room temperature for 2h. THF was evaporated and the residue dissolved in a mixture of CH_2Cl_2/water 1:1 (30 mL) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated. The crude product was obtained after silicagel chromatography (diethylether/ethyl acetate : 80/20) and crystallization in a diethylether/dichloromethane (80/20) solution (600 mg, 71%) as a yellow solid. mp : 188-190°C ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 6.08 (s, 1H), 6.73 (d, 1H, *J* = 2.0 Hz), 7.17 (d, 1H, *J* = 2.0 Hz), 7.40-7.52 (m, 7H, 6H(ph)+ 1H(pyridine)), 7.60 (d, 2H, *J* = 8.0 Hz), 7.72 (d, 2H, , *J* = 8.0 Hz), 7.89-7.92 (m, 4H), 8.05 (d, 1H, *J* = 10.0 Hz), 8.55 (d, 1H, *J* = 6 Hz), 8.91 (d, 1H, *J* = 2.5 Hz) ; ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 153.1(C), 151.2(C), 146.9(CH), 144.3(CH), 139.0(C), 135.1(CH), 133.4(C), 130.3(CH), 129.5(CH), 128.8(CH), 127.1(CH), 124.9(CH), 124.5(CH), 123.9(CH), 113.2(CH), 108.5(CH), 102.0(CH). HRMS (ESI) m/z calculated for $C_{29}H_{22}NO$ $[M+H]^+$ 400.1696, found 400.16959.) m/z calculated for $C_{29}H_{21}NO$ M^{+}. 399.16176, found 399.1616. Elemental analysis for $C_{29}H_{21}NO$ Calc.C 87.19 H 5.30 N 3.51, found C 87.07 H 5.28 N 3.61. IR ν (cm^{-1}) = 3051 ; 2972 ; 1654 ; 1588 ; 860.

4-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl]-pyridine 1c

Small excess of *n*-butyllithium 2.5 M in hexanes (0.66 mL, 1.65 mmol, 1.1 equiv.) was added dropwise at -78 °C, under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl tributylphosphonium tetrafluoroborate salt (975mg, 1.63 mmol, 1 equiv.) in dry THF (15 mL). After 15 min, the 4-(4-pyridylbenzaldehyde) (300 mg, 1.6 mmol, 1 equiv.) was added. The solution was stirred at -78°C for 30 min, and allowed to warm to room temperature for 2h. THF was evaporated and the residue dissolved in a mixture of CH_2Cl_2/water 1:1 (30 mL) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated. The crude product was obtained by crystallization in a diethylether/dichloromethane (80/20) solution (620 mg, 96%) as a yellow solid. mp : 191-193°C ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 5.97 (s, 1H), 6.45 (d, 1H, *J* = 2.0 Hz), 7.04 (d, 1H, *J* = 2.0 Hz), 7.41-7.47 (m, 6H), 7.51 (d, 2H, *J* = 8.0 Hz), 7.54 (d, 2H, *J* = 5.5 Hz), 7.66 (d, 2H, *J* = 8.0 Hz), 7.78 (m, 4H), 8.66 (d, 2H, *J* = 5.5 Hz) ; ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 153.2(C), 151.2(C), 150.32(CH), 150.35(CH), 147.9(C), 139.7(C), 134.7(C), 133.4(C), 133.2(C), 130.4(C), 129.5(CH), 129.2(CH), 128.7(CH), 128.4(CH), 127.1(CH), 125.0(CH), 124.6(CH), 121.1(CH), 113.2(CH), 108.6(CH), 102.0(CH). HRMS (ESI) m/z calculated for $C_{29}H_{22}NO$ $[M+H]^+$ 400.17014, found 400.1700. Elemental analysis for $C_{29}H_{21}NO$ Calc.C 87.19 H 5.30 N 3.51, found C 86.2 H 5.21 N 3.53. IR ν(cm^{-1}) = 3053 ; 2880 ; 1655 ; 1591 ; 1579 ; 1448 ; 1277 ; 1070 ; 944 ; 914 ; 868.

2-2 synthesis of compound 2a

4,4'-(1,2-bis(4-(pyridin-2-yl)phenyl)ethane-1,2-diyl)bis(2,6-diphenylpyrylium) 2a

$AgBF_4$ (78 mg, 0.4 mmol) was added to a solution of compound **1a** (160 mg, 0.4 mmol) in 10mL of methylene chloride. The green mixture obtained was stirred 2h at room temperature.

After this time, the formation of a green precipitate and a metallic residue of Ag was observed. After addition of 50 mL of methylene chloride, the mixture was filtered to eliminate Ag residue. The solution obtained was concentrated to 10 mL by solvent evaporation and 30 mL of diethylether were added. After 24h at -18°C the crude product **2a** was obtained by filtration as a green powder. 180 mg (46% yield) of compound **2a** were obtained as a mixture of two diastereoisomers (60% Maj / 40% min) after recrystallization of the product in diethylether /CH_2Cl_2 (20/80). Due to the low solubility of this compound in acetone d_6 or CD_2Cl_2, 2D (HMQC) investigation were performed to determine ^{13}CH chemical shifts instead of usual 13C or Jmod analysis. ^{1}H NMR (500 MHz, acetone d_6) δ(ppm) 6.51 (s, 2H, Maj), 6.55 (s, 2H,min), 7.26-7.60 (m, 16H, min), 7.70-7.87 (m, 16H, Maj), 7.98 (m, 6H, min), 8.08 (m, 6H, Maj), 8.12 (d, 4H, J = 8 Hz, min), 8.18 (d, 4H, J = 10 Hz, Maj), 8.31 (d, 4H, J = 10 Hz, min), 8.51 (m, 10H, min + Maj), 8.65 (d, 2H, J = 4 Hz, min), 8.74 (d, 2H, J = 4 Hz, Maj), 9.17 (s, 4H, min), 9.32 (s, 4H, Maj). 2D HMQC (500 MHz/125MHz, acetone d_6) δ(ppm, major isomer) 147.0, 136.9, 131.1, 130.5, 130.0, 129.8, 129.6, 129.5, 119.0, 54.1. δ(ppm, minor isomer) 147.5, 130.5, 130.2, 129.0, 125.5, 122.1, 118.9, 54.1. HRMS (ESI) m/z calculated for $C_{29}H_{21}NO$ $[A]^+$ 399.16176, found 399.1619, m/z calculated for $C_{58}H_{40}N_2O_2$ $M^{4+\cdot}$ 796.30843, found 796.3079. IR ν(cm^{-1}) = 3065 ; 1619 ; 1508 ; 1466 ; 1438 ; 1059 ; 1021, 779 ; 680.

2-3 synthesis of compounds 3

Compound **1a**, **1b** or **1c** and $AgBF_4$ were stirred in degassed solution of methylene chloride (10mL) at room temperature for 6h. The initial yellow solution became green and we observed apparition of a green precipitate. A pH=9 (glycine buffer) was then added to the solution and the heterogeneous mixture was stirred half an hour. Ag residue was then eliminated by filtration and the organic layer was extracted 3 times with diethylether and washed 3 times with water. The extract was dried over $MgSO_4$. After evaporation of the solvent, the crude product was obtained without other purification as red powder.

1,2-bis(2,6-diphenyl-4H-pyran-4-ylidene)-1,2-bis(4-(pyridin-2-yl)phenyl)ethane 3a

Compound **1a** (380mg, 0.95mmol) react with $AgBF_4$ (185mg, 1 eq). Compound **3a** was obtained as red powder (280 mg, 73%yield). mp : 275-277°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 6.66 (s, 2H), 7.06 (s, 2H), 7.17 (m, 2H), 7.29-7.44 (m, 12H), 7.55 (d, 4H, J = 10.0 Hz), 7.68 (m, 8H), 7.74 (d, 4H, J = 10.0 Hz), 7.91 (d, 4H, J = 8 Hz), 8.66 (d, 2H, J = 4 Hz);

^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 157.3(C), 152.3(C), 151.4(C), 149.6(CH), 142.0(C), 137.0(C), 136.6(CH), 133.7(C), 133.6(C), 130.4(C), 129.9(CH), 129.0(CH), 128.6(CH), 128.0(C), 126.8(CH), 124.7(CH), 124.6(C),121.8(CH), 120.3(CH), 106.4(CH), 104.7(CH). HRMS (ESI) m/z calculated for $C_{58}H_{41}N_2O_2$ $[M+H]^+$ 797.31625, found 797.3169. Elemental analysis for $C_{58}H_{40}N_2O_2$ Calc.C 87.41 H 5.06 N 3.51, found C 86.28 H 5.75 N 3.14. IR ν(cm^{-1}) = 2923 ; 1649 ; 1598 ; 1584 ; 1463 ; 1273 ; 1068 ; 916 ; 762 ; 690.

1,2-bis(2,6-diphenyl-4H-pyran-4-ylidene)-1,2-bis(4-(pyridin-3-yl)phenyl)ethane 3b

Compound **1b** (200 mg, 0.5mmol) react with $AgBF_4$ (100mg, 1 eq). Compound **3b** was obtained as red powder (160 mg, 80%yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 6.66 (s, 2H, *J* = 1.9 Hz), 7.06 (s, 2H, *J* = 2.0 Hz), 7.33-7.50(m, 14H), 7.57 (d, 8H, *J* = 2.2 Hz), 7.70 (dd, 4H, *J* = 7.8 Hz, *J* = 1.8 Hz), 7.77 (dd, 4H, *J* = 8.2 Hz, *J* = 1.6 Hz), 7.93 (dt, 2H, *J* = 8.2 Hz, *J* = 1.9 Hz), 8.57 (dd, 2H, *J* = 4.9 Hz, *J* = 1.5 Hz), 8.88 (d, 2H, *J* = 2.0 Hz); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 152.5(C), 151.6(C), 147.6(CH), 141.2(C), 136.5(C), 135.1(C) 134.4(CH), 133.6(C), 133.5(C), 130.2(CH), 129.1(CH), 129.0(CH), 128.6(CH), 128.5(CH), 128.55(C), 126.9(CH), 124.8(CH), 124.7(CH), 123.9(C), 123.7(CH), 120.3(CH), 106.2(CH), 104.4(CH). HRMS (ESI) m/z calculated for $C_{58}H_{40}N_2O_2$ $M^{+\cdot}$ 796.30843, found 796.3092. IR ν(cm^{-1}) = 2922 ; 1647 ; 1593 ; 1484; 1446 ; 1278 ; 1066 ; 912 ; 690.

1,2-bis(2,6-diphenyl-4H-pyran-4-ylidene)-1,2-bis(4-(pyridin-4-yl)phenyl)ethane 3c

Compound **1c** (200 mg, 0.5mmol) react with $AgBF_4$ (100mg, 1 eq). Compound **3c** was obtained as red powder (120 mg, 60%yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 6.65 (d, 2H, *J* = 1.9 Hz), 7.05 (d, 2H, *J* = 1.9 Hz), 7.35-7.41 (m, 6H), 7.42-7.53 (m, 8H), 7.56 (d, 4H, *J* = 6.0 Hz), 7.60 (d, 4H, *J* = 6.0 Hz), 7.65 (m,2H), 7.69 (m, 4H), 7.77 (d, 4H, *J* = 7.5 Hz), 8.63 (d, 4H, *J* = 6.0 Hz); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 152.5 (C), 151.8(C), 149.3(CH), 148.6 (C), 142.5(C), 135.1(C), 133.5(C), 133.4(C), 132.2(CH), 132.0(CH), 131.9(CH), 131.8(CH), 130.2 (CH), 129.2(CH), 129.0(C), 128.6(CH), 128.5(CH), 128.4(CH), 126.9(CH), 124.7(CH), 124.6(CH), 123.6(C), 121.3(CH), 106.2(CH), 104.2(CH). HRMS (ESI) m/z calculated for $C_{58}H_{40}N_2O_2$ C^{++} 398.15394, found 398.1546. IR ν(cm^{-1}) = 3055 ; 1649 ; 1585 ; 1465 ; 1278 ; 1070 ; 916 ; 782 ; 680.

2-4 synthesis of compounds 4 and 5

1,2-bis(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridin-2-yl)phenyl)ethane 4a and spiro compound 5

20mL (excess) of an ammonia solution 25% was added to a suspension of salt **2a** (two diastereoisomers) (500mg, 0.62 mmol) in diethylether at room temperature. The mixture was stirred until we observed the lack of the solid (2h). The yellow solution was extract three times with diethylether and the combined organic extracts were washed with water and dried over $MgSO_4$. TLC analysis of the residue shows the existence of two major products (UV detection). These compounds were separated by silica gel chromatography (ethyl acetate/ petroleumether : 30/70). The crudes products **4a** (133mg, 27%) and **5** (102mg, 21%) were isolated as white crystalline powders. **4a** was obtained as un sole diastereoisomer **:** ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 8.64 (d, 2H, *J* = 4.5 Hz), 7.97 (d, 8H, *J* =6.7 Hz), 7.91 (d, 4H, *J* = 8.5Hz), 7.71 (t, 2H, *J* = 7.7 Hz), 7.61 (d, 2H, *J* = 7.7 Hz), 7.57 (s, 4H), 7.49 (d, 4H, *J* = 8.1 Hz), 7.38-7.47 (m, 12H), 7.20 (t, 2H, *J* = 6.0 Hz), 5.1 (s, 2H). ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 157.1 (C), 155.1 (C), 149.5 (CH), 142.1 (C), 139.4 (C), 137.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 127.5 (CH), 127.1 (CH), 122.2 (CH), 120.5 (CH), 119.0 (CH),55.6 (CH). HRMS (ASAP) m/z calculated for $C_{58}H_{43}N_4$ $[M+H]^+$ 795.34822, found 795.3487. IR ν(cm^{-1}) = 3034 ; 1591 ; 1554 ; 1466 ; 1435 ; 1415 ; 1014 ; 774 ; 748 ; 734 ; 690.

5 : ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 8.68 (d, 1H, *J* = 4.3 Hz), 8.61 (d, 1H, *J* = 4.3 Hz), 8.02 (d, 2H, *J* = 4.5 Hz, 7.3 Hz), 7.94 (d, 2H, *J* = 7.9 Hz), 7.83 (d, 2H, *J* = 8.1 Hz), 7.59-7.79 (m, 6H), 7.55 (d, 2H, 6.7 Hz), 7.38-7.50 (m, 8H), 7.35 (d, 2H, *J* = 7.6 Hz), 7.14-7.25 (m, 6H), 7.07 (t, 1H, *J* = 7.0 Hz), 5.64 (s, 1H), 5.17 (d,1H, *J* = 12.4 Hz), 5.00 (s,1H), 3.64 (d, 1H, *J* = 12.1 Hz). ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 157.6 (C), 156.4 (C), 155.1 (C), 149.8 (C), 149.7 (CH), 148.3 (C), 141.7 (C), 140.5 (C), 139.9 (C), 139.4 (C), 137.05 (CH), 134.5 (C), 134.15 (C), 130.0 (CH), 129.5 (CH), 129.3 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 126.4 (CH), 124.8 (CH), 122.1 (CH), 122.0 (CH), 120.6 (CH), 115.9 (CH), 102.0 (CH), 101.2 (CH), 70.7 (CH), 51.8 (C), 51.3 (CH). HRMS (ESI) m/z calculated for $C_{58}H_{43}N_3O$ $[M+H]^+$ 796.33224, found 796.3331. IR ν(cm^{-1}) = 3055 ; 1686 ; 1587 ; 1560 ; 1495 ; 1467 ; 1435 ; 1283 ; 1060 ; 1027 ; 913 ; 777 ; 741 ; 762 ; 694.

1,2-bis(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridin-3-yl)phenyl)ethane 4b

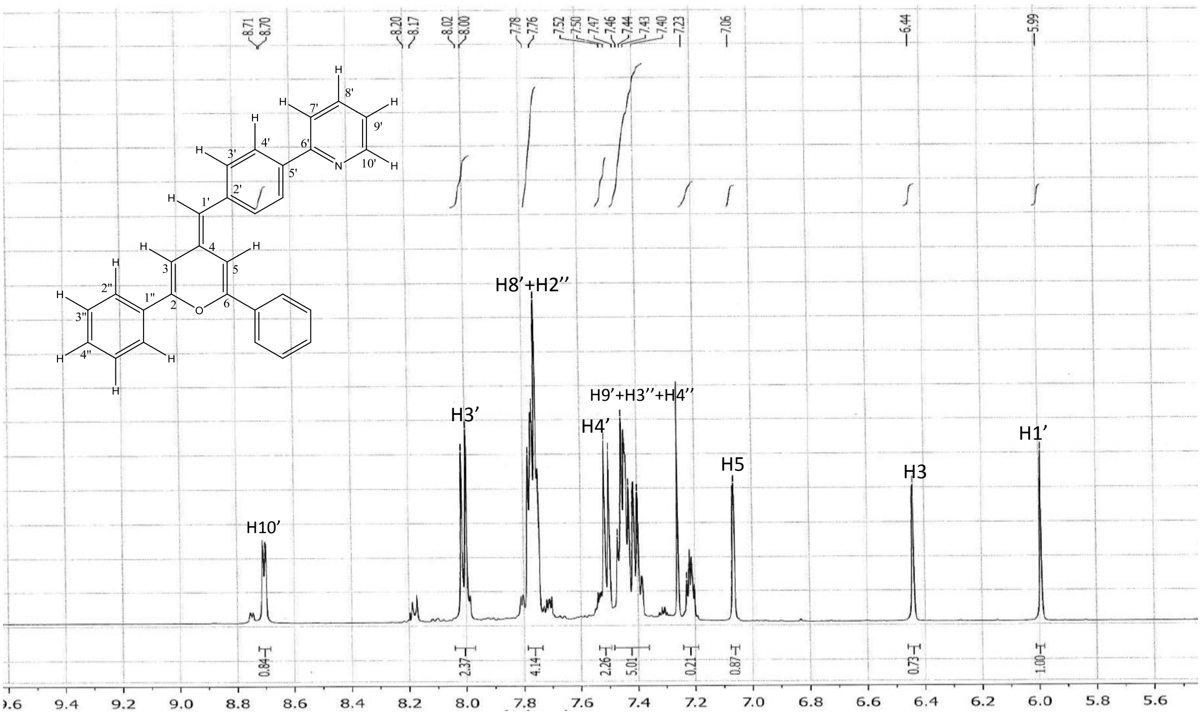
$AgBF_4$ (49 mg, 0.25 mmol) was added to a solution of compound **1b** (100 mg, 0.25 mmol) in 10mL of methylene chloride. The green mixture obtained was stirred 2h at room temperature. After this time, the formation of a green precipitate and a metallic residue of Ag were observed. After addition of 50 mL of methylene chloride, the mixture was filtered to eliminate Ag residue. Methylene chloride was then evaporated and 30 mL of diethylether and 20 mL of ammoniac solution (25%) were added to the obtained residue. The degassed mixture was stirred at room temperature 10 hours. We observed the formation of a yellow precipitate. After filtration, the solid was dissolved in acetone and recrystallized by addition of diethylether at low temperature (-18°C). Compound **4b** was obtained as a white crystalline powder (m = 40 mg, 40%). ^{1}H NMR (300 MHz, acetone d_6) δ(ppm) 8.71 (d, 2H, J = 2.1 Hz), 8.46 (d, 2H, J = 4.8 Hz), 8.18 (s, 4H), 8.16 (s, 2H), 7.99 (d, 4H, J = 8.3 Hz), 7.86 (dt, 4H, J = 8.2 Hz, J = 2.0 Hz), 7.60 (d, 4H, J = 8.2 Hz), 7.40-7.54 (m, 14H), 7.33 (dd, 2H, J = 8.0 Hz, J = 4.8 Hz), 5.94 (s, 2H). ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 156.7 (C), 154.4 (C), 148.4 (CH), 147.8 (CH), 142.4 (C), 139.4 (C), 136.2 (C), 135.5 (C), 133.7 (CH), 129.4 (CH), 128.9 (CH), 128.6 (CH), 127.3 (CH), 126.8 (CH), 123.4 (CH), 118.9 (CH), 54.0 (CH). HRMS (ESI) m/z calculated for $C_{58}H_{43}N_4$ $[M+H]^+$ 795.34822, found 795.3479. IR ν(cm^{-1}) = 3034 ; 2923; 1593 ; 1555 ; 1474 ; 1415 ; 1028 ; 776 ; 735 ; 692.

1,2-bis(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridin-4-yl)phenyl)ethane 4c

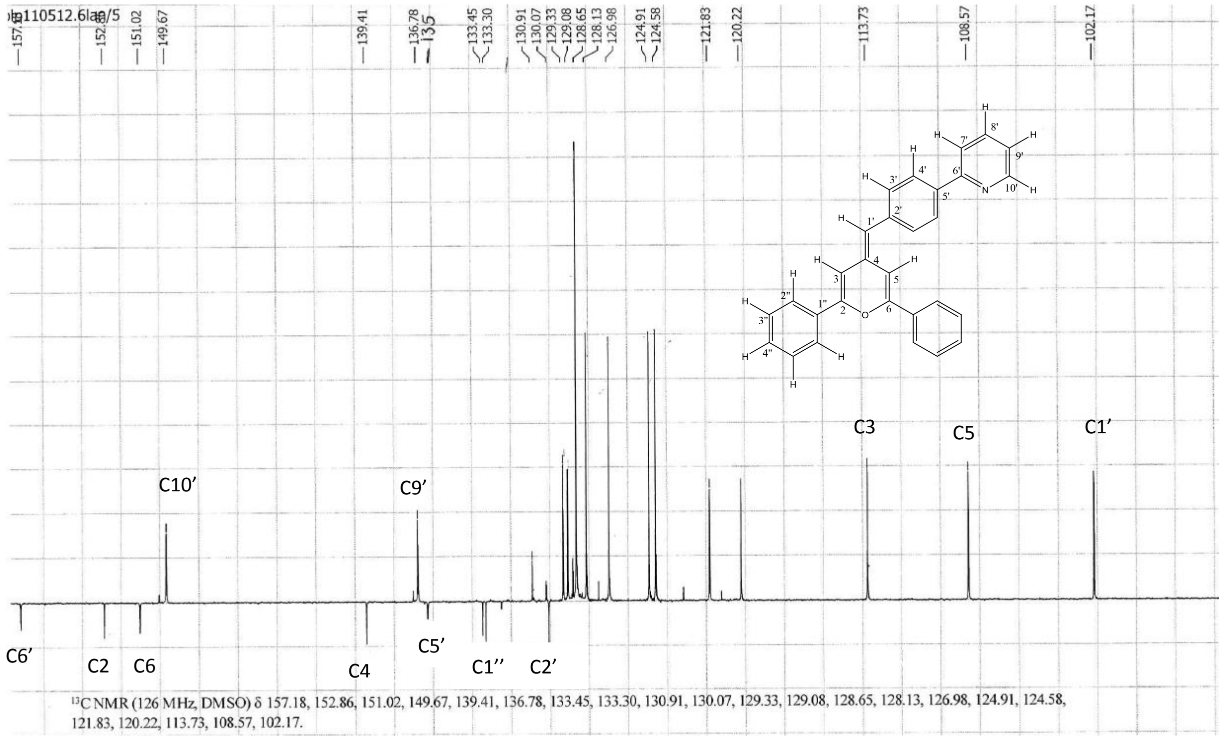
We used the exact same procedure as it followed for the synthesis of **4b**. $AgBF_4$ (100 mg, 0.50 mmol) was added to a solution of compound **1c** (200 mg, 0.50 mmol) in 10mL of methylene chloride. Compound **4c** was obtained as a white crystalline powder (m = 100 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 8.51 (d, 4H, J = 6.1 Hz), 8.18 (s, 8H), 8.16 (s, 4H), 8.01 (d, 4H, J = 8.4 Hz), 7.67 (d, 4H, J = 8.3 Hz), 7.43-7.53 (m, 16H), 5.97 (s, 2H). ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ (ppm) 156.7 (C), 154.2 (C), 150.2 (CH), 146.9 (C), 139.4 (C), 137.7 (C), 136.4 (C), 129.5 (CH), 129.0 (CH), 128.6 (CH), 127.2 (CH), 126.8 (CH), 123.7 (CH), 121.0 (CH), 118.9 (CH), 54.0 (CH). HRMS (ESI) m/z calculated for $C_{58}H_{43}N_4$ $[M+H]^+$ 795.34822, found 795.3480. IR ν(cm^{-1}) = 3033 ; 1595 ; 1554 ; 1490 ; 1416 ; 1083 ; 805; 776 ; 735 ; 693.

3- ^{1}H, ^{13}C, 2D NMR spectra

3-1 monopyrans 1

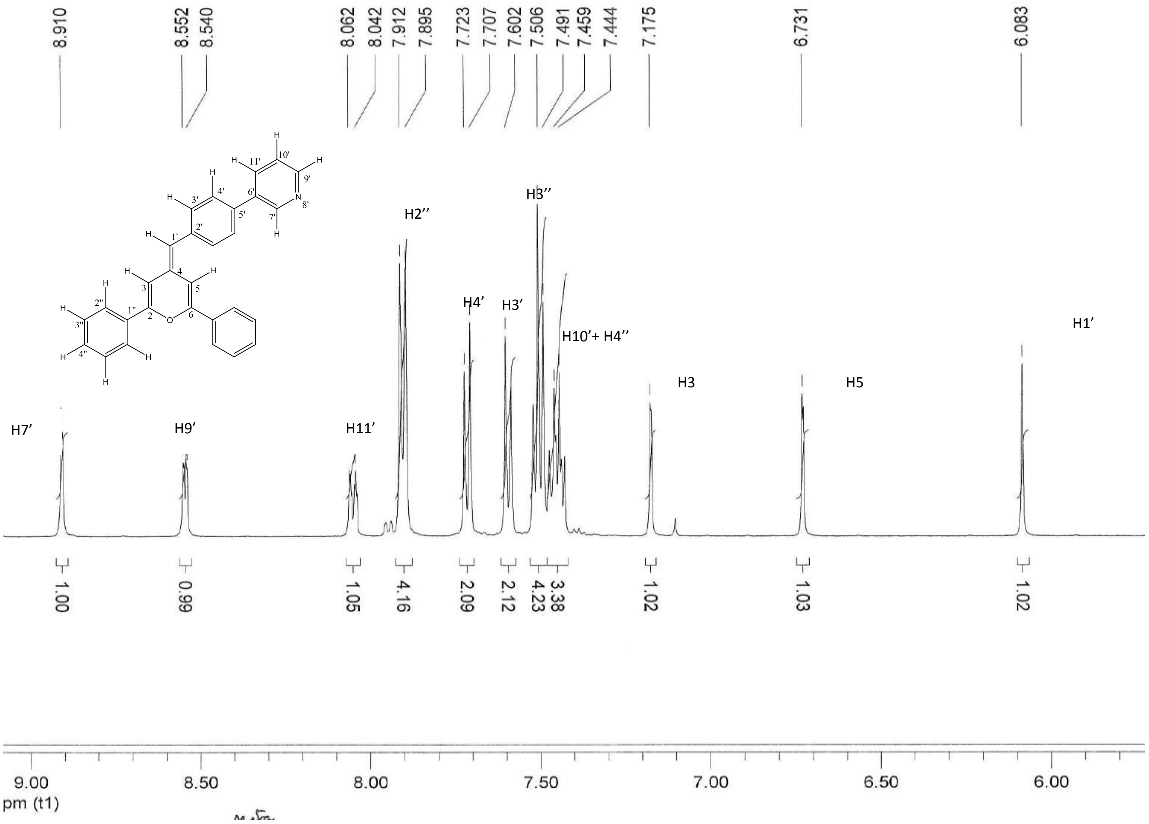


^{1}H NMR spectrum of compound 1a in $CDCl_3$ at 293K

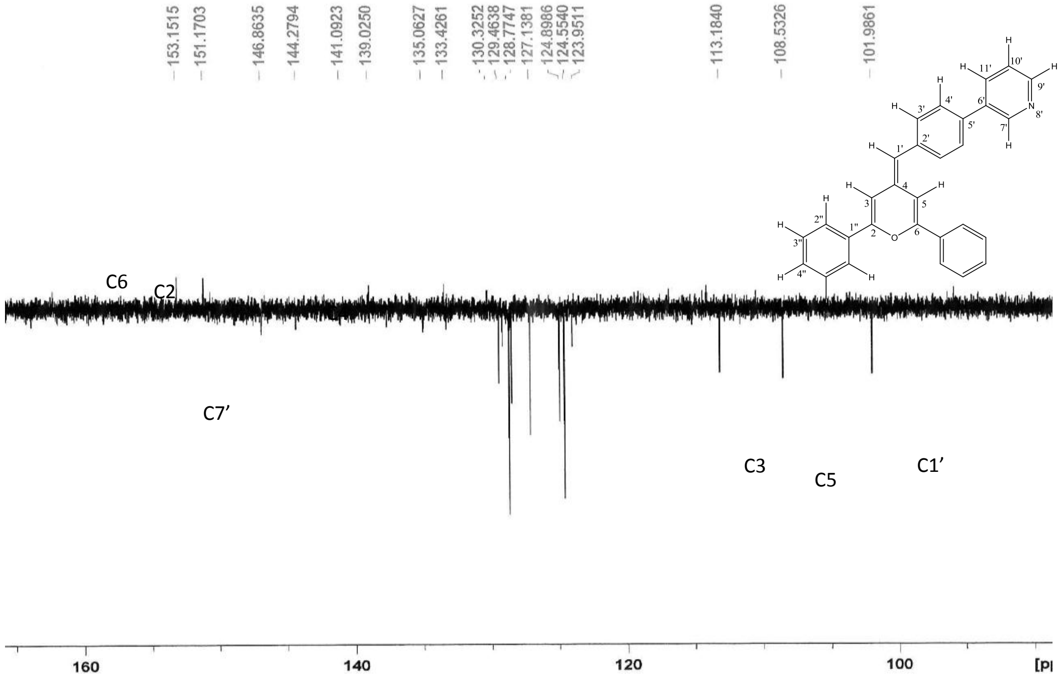


^{13}C NMR (126 MHz, DMSO) δ 157.18, 152.86, 151.02, 149.67, 139.41, 136.78, 133.45, 133.30, 130.91, 130.07, 129.33, 129.08, 128.65, 128.13, 126.98, 124.91, 124.58, 121.83, 120.22, 113.73, 108.57, 102.17.

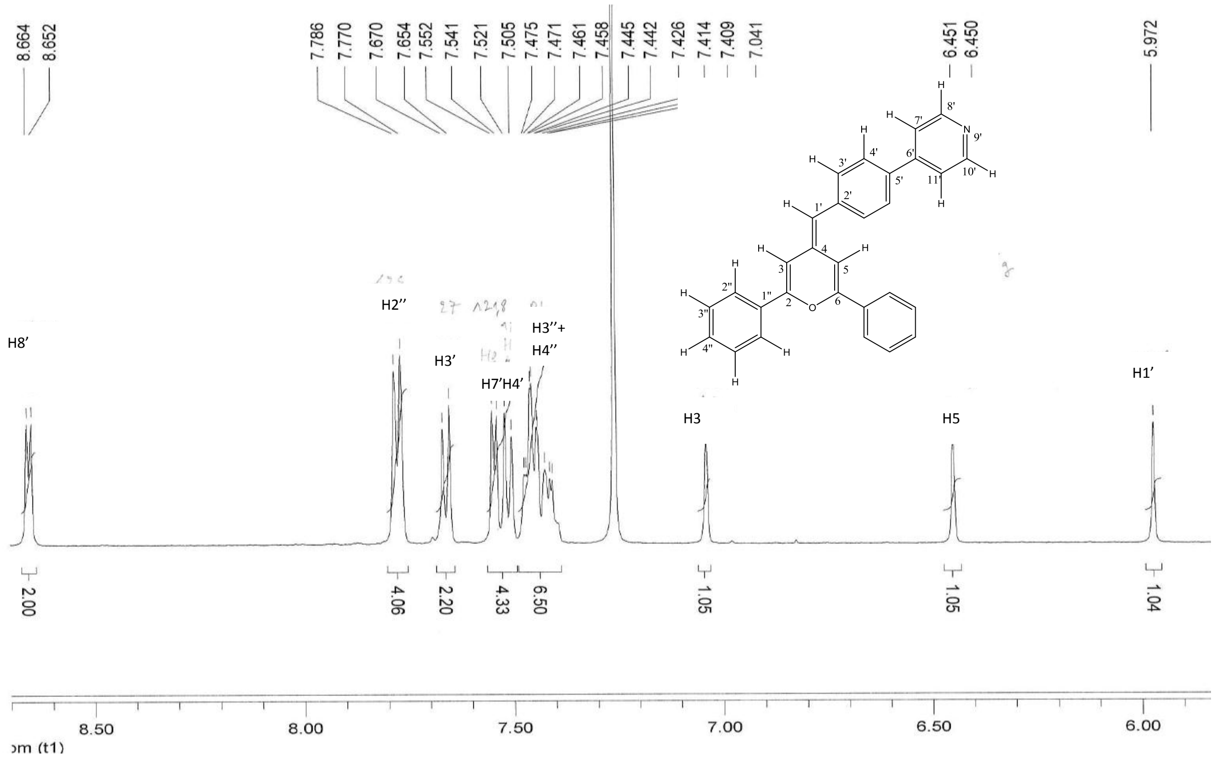
^{13}C (Jmod) NMR spectrum of compound 1a in $CDCl_3$ at 293K



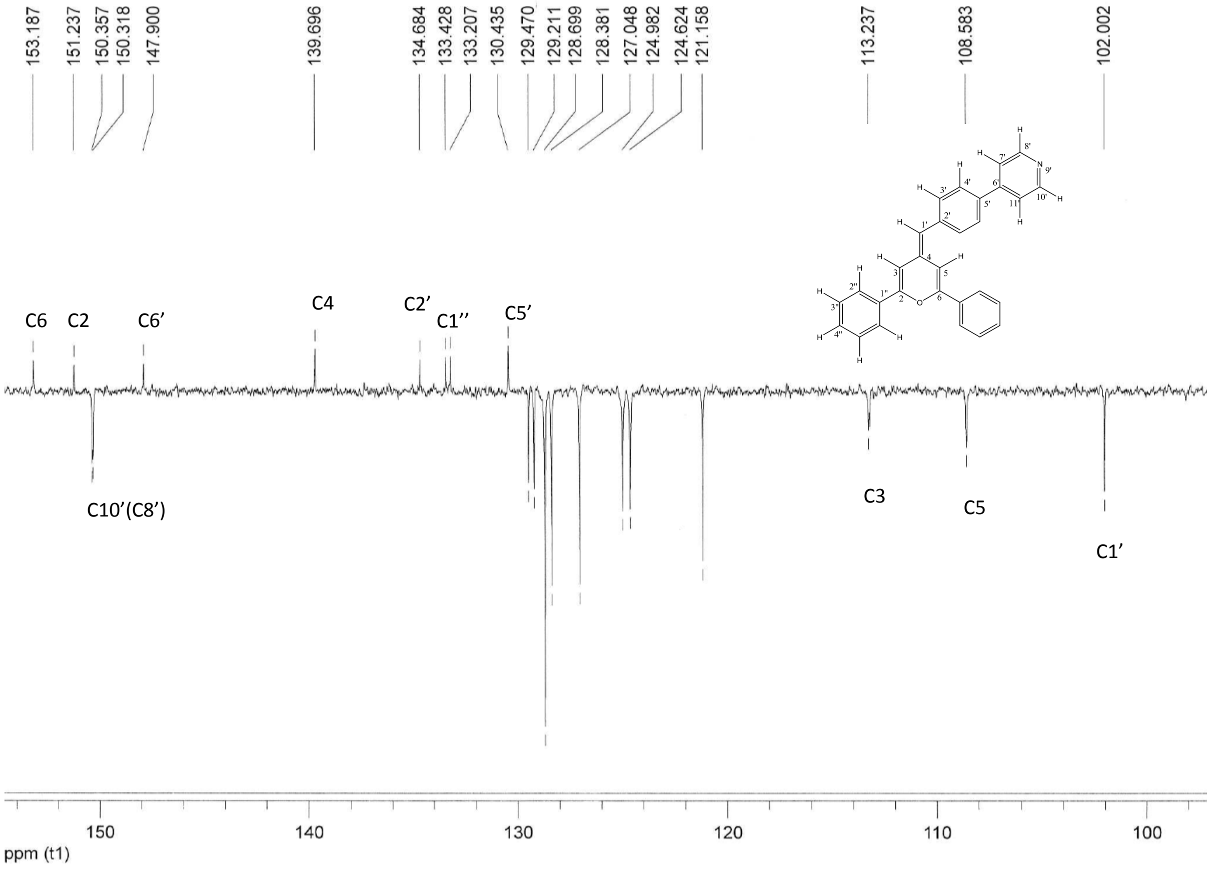
^{1}H NMR spectrum of compound 1b in acetone-*d6* at 293K



^{13}C (Jmod) NMR spectrum of compound 1b in acetone-*d6* at 293K

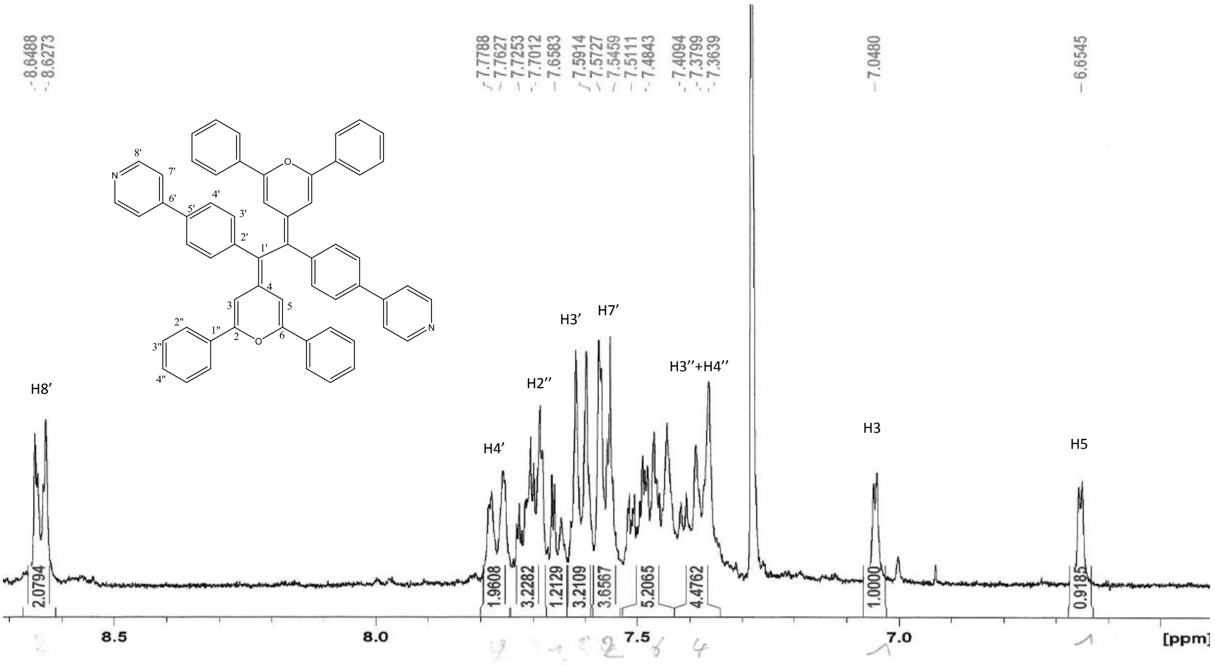


^{1}H NMR spectrum of compound 1c in $CDCl_3$ at 293K

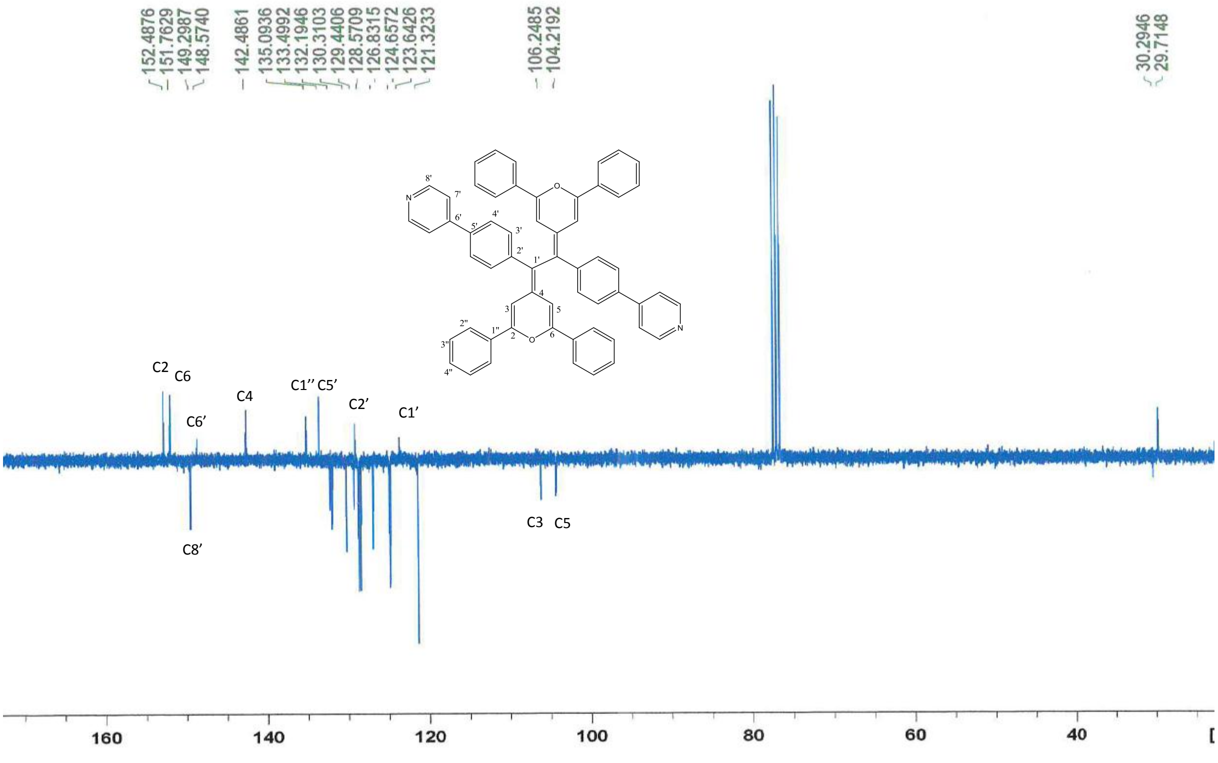


^{13}C (Jmod) NMR spectrum of compound 1c in $CDCl_3$ at 293K

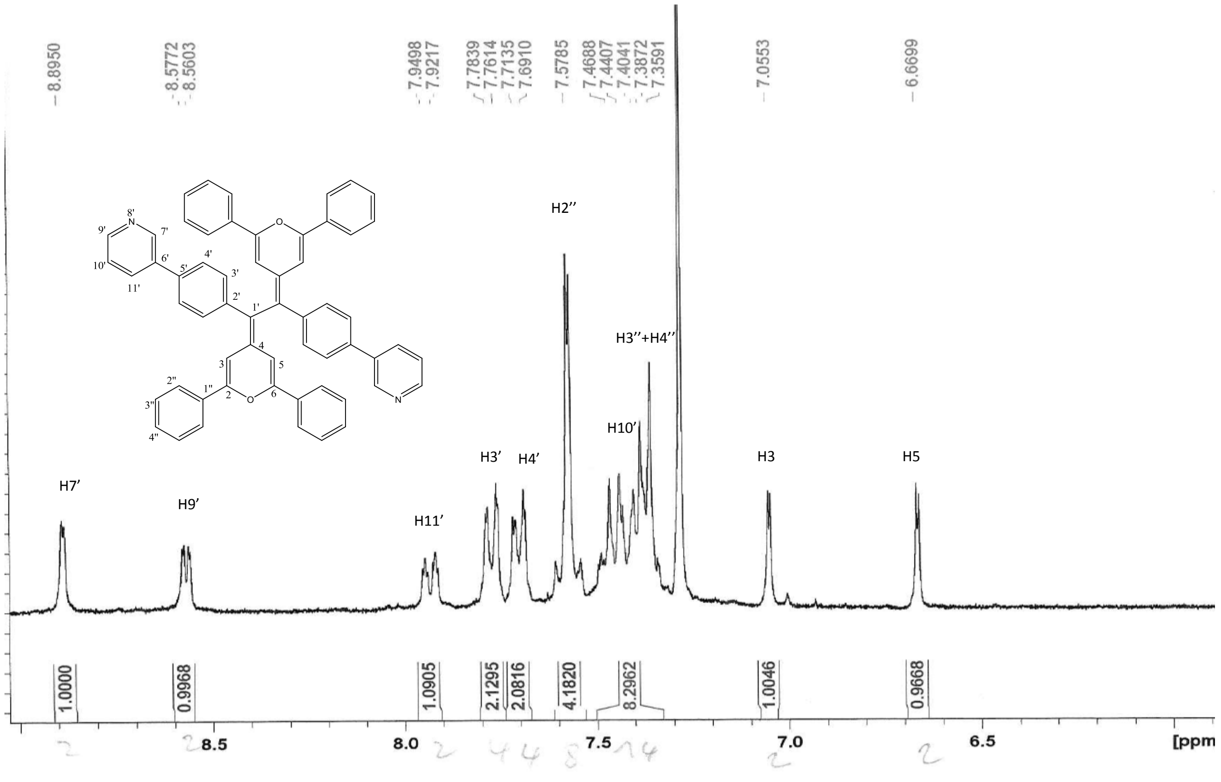
3-2 bispyrans 3



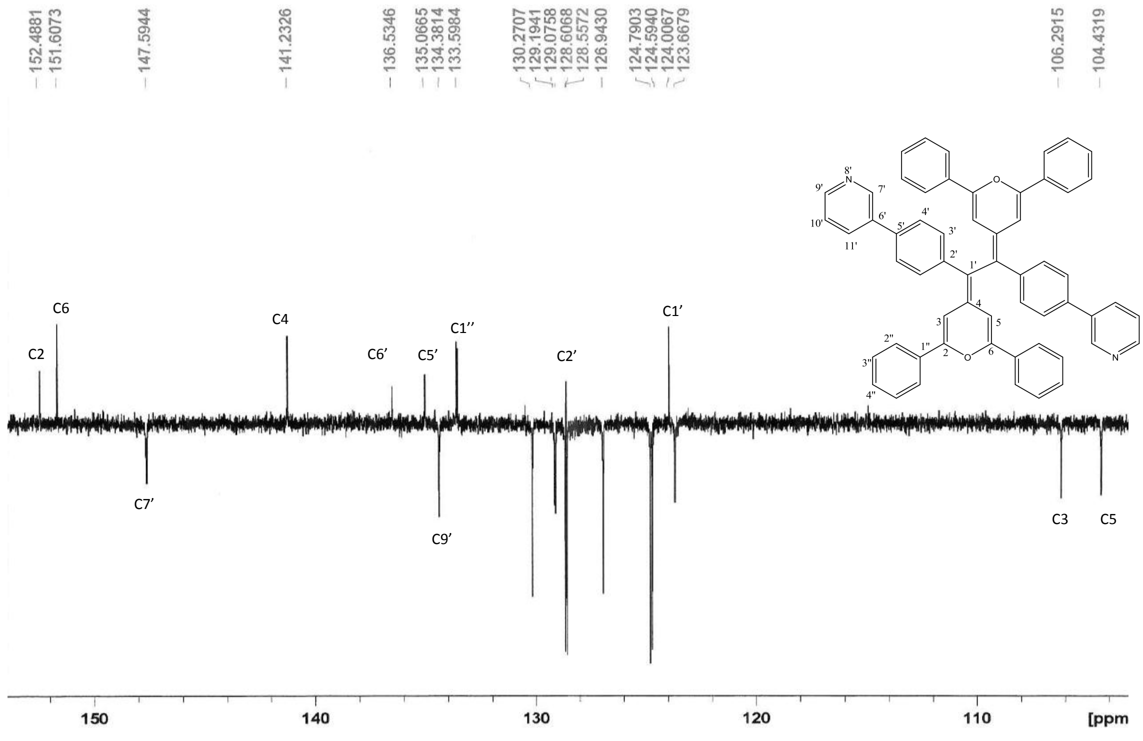
^{1}H NMR spectrum of compound 3c in CDCl3 at 293K



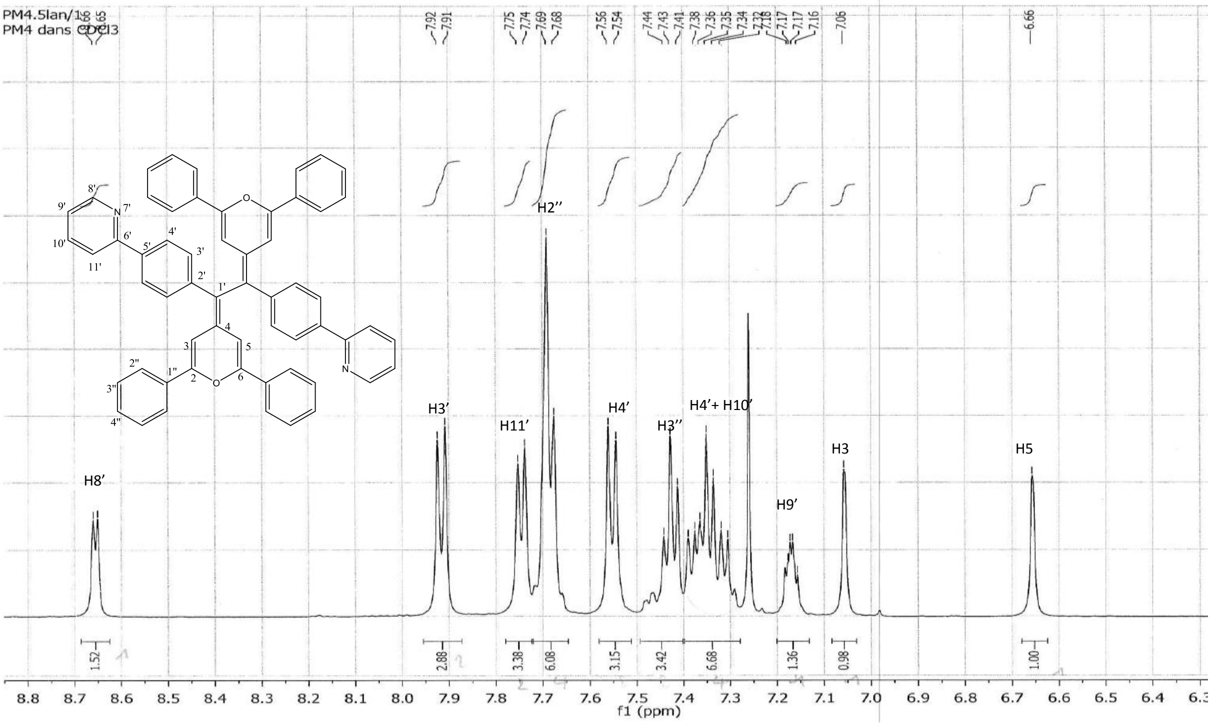
^{13}C (Jmod) NMR spectrum of compound 3c in $CDCl_3$ at 293K



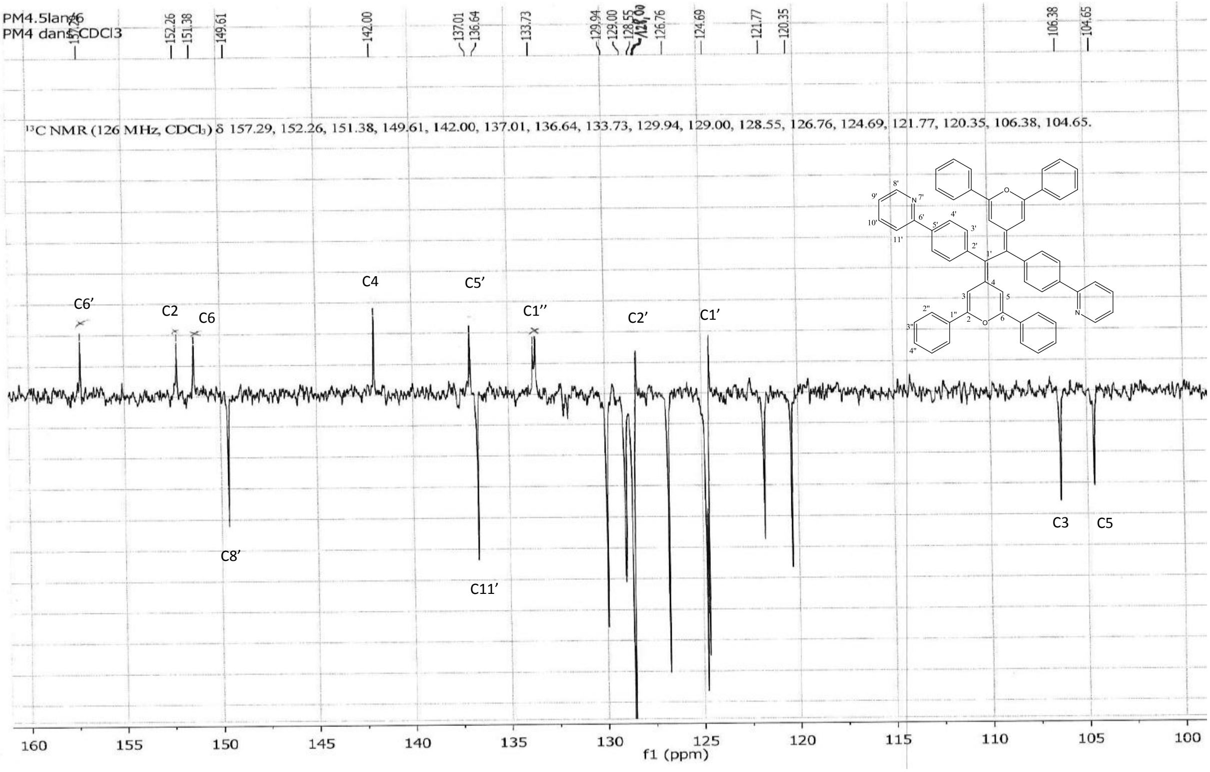
^{1}H NMR spectrum of compound 3b in $CDCl_3$ at 293K



^{13}C (Jmod) NMR spectrum of compound 3b in $CDCl_3$ at 293K



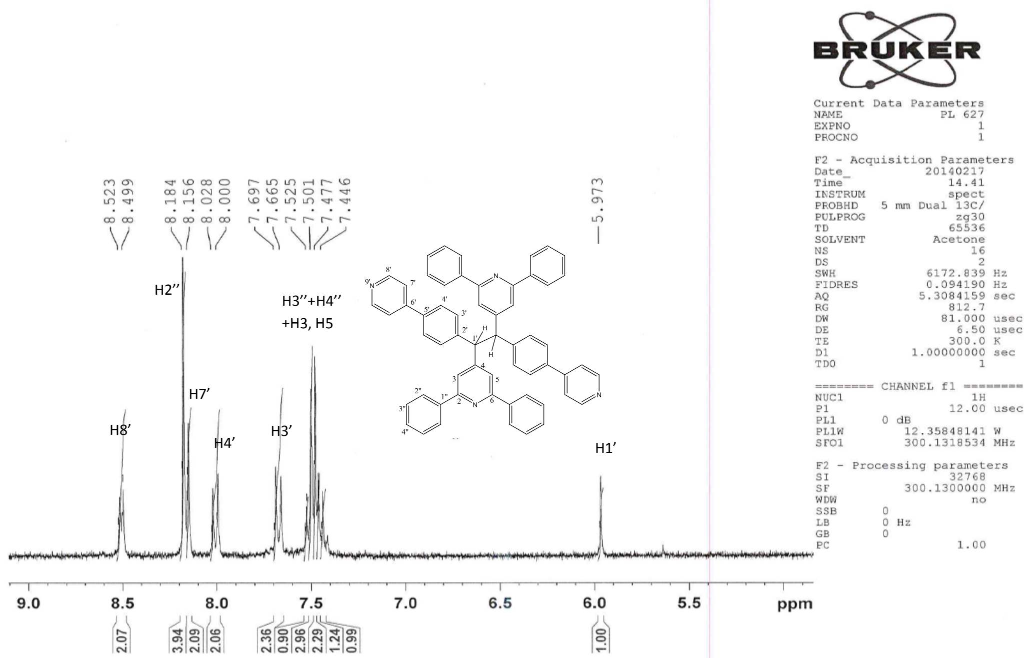
^{1}H NMR spectrum of compound 3a in CDCl$_3$ at 293K



^{13}C NMR (126 MHz, CDCl$_3$) δ 157.29, 152.26, 151.38, 149.61, 142.00, 137.01, 136.64, 133.73, 129.94, 129.00, 128.55, 126.76, 124.69, 121.77, 120.35, 106.38, 104.65.

^{13}C (Jmod) NMR spectrum of compound 3a in CDCl$_3$ at 293K

3-3 tetrapyridines 4



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Current Data Parameters
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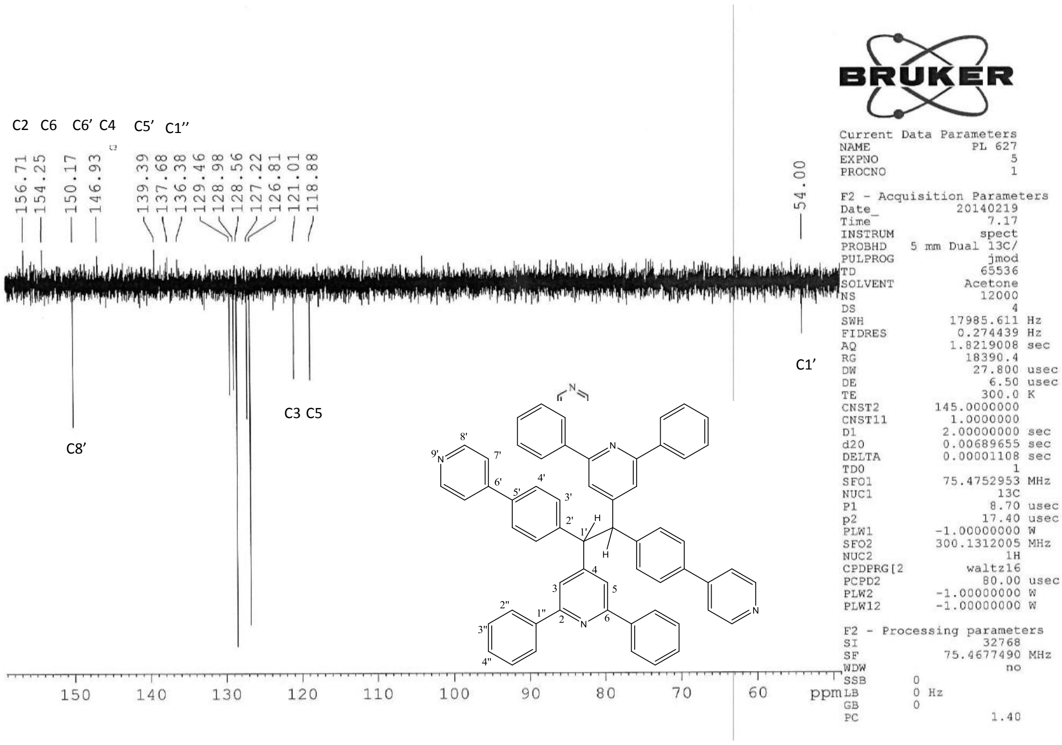
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140217
Time                 14.41
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG               zg30
TD                   65536
SOLVENT            Acetone
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084159 sec
RG                   812.7
DW                  81.000 usec
DE                    6.50 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1        0 dB
PL1W           12.35848141 W
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF             300.1300000 MHz
WDW                     no
SSB        0
LB         0 Hz
GB         0
PC                    1.00
```

^{1}H NMR spectrum of compound 4c in acetone-*d6* at 293K



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Current Data Parameters
NAME                PL 627
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140219
Time                  7.17
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG               jmod
TD                   65536
SOLVENT            Acetone
NS                   12000
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219008 sec
RG                 18390.4
DW                  27.800 usec
DE                    6.50 usec
TE                   300.0 K
CNST2          145.0000000
CNST11           1.0000000
D1              2.00000000 sec
d20             0.00689655 sec
DELTA           0.00001108 sec
TD0                      1
SFO1            75.4752953 MHz
NUC1                   13C
P1                    8.70 usec
p2                   17.40 usec
PLW1           -1.00000000 W
SFO2           300.1312005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     no
SSB        0
LB         0 Hz
GB         0
PC                    1.40
```
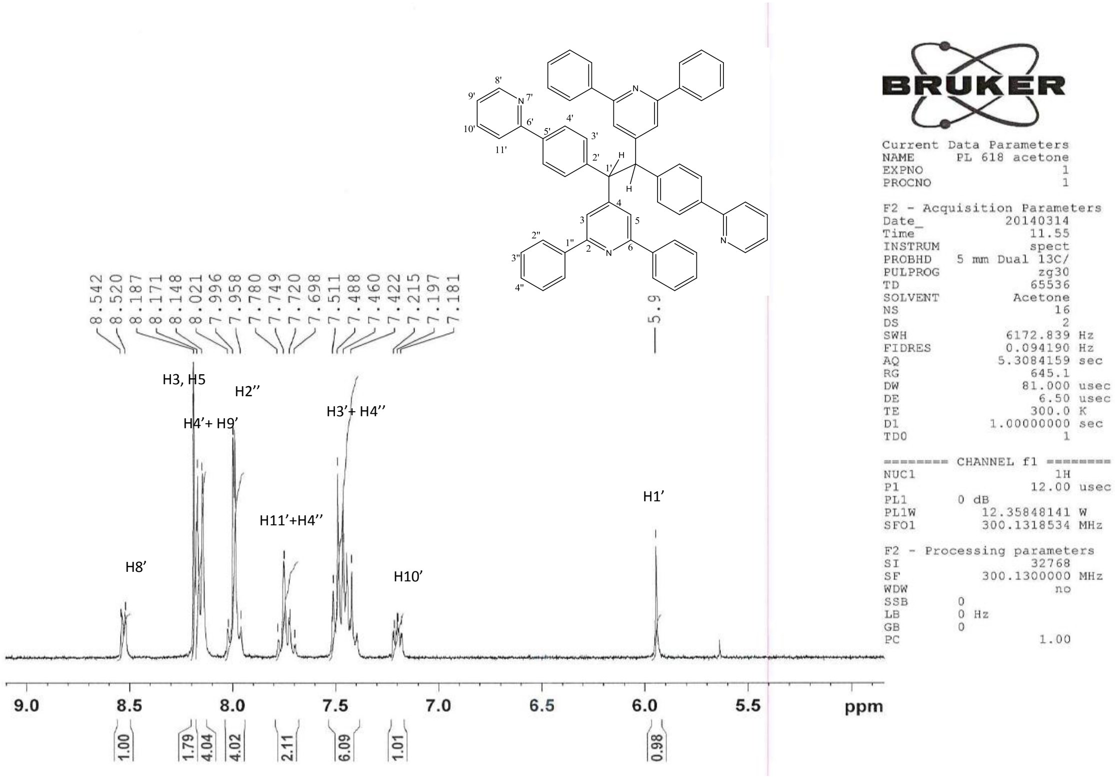
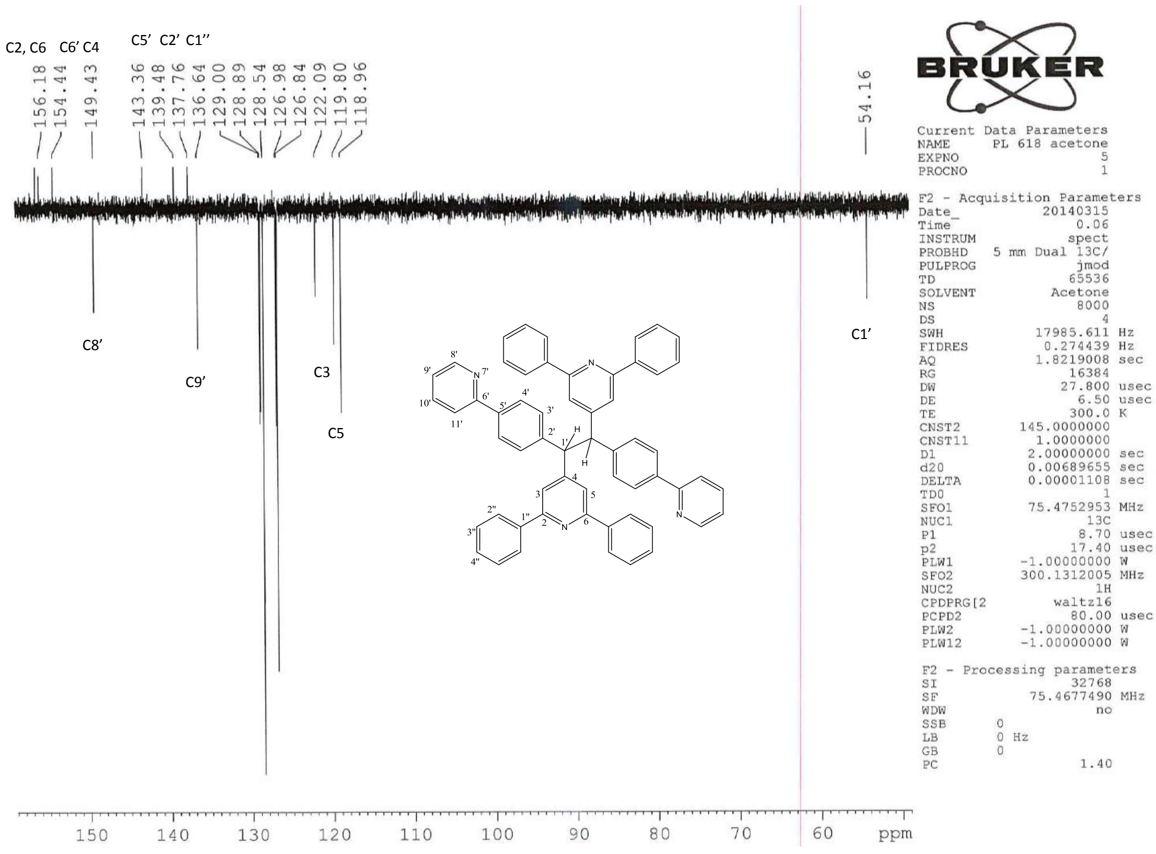

^{13}C (Jmod) NMR spectrum of compound 4c in acetone-*d6* at 293K



```
Current Data Parameters
NAME      PL 618 acetone
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140314
Time               11.55
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084159 sec
RG                 645.1
DW                81.000 usec
DE                  6.50 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1          0 dB
PL1W         12.35848141 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   no
SSB          0
LB           0 Hz
GB           0
PC                  1.00
```

^{1}H NMR spectrum of compound 4a in acetone-*d6* at 293K



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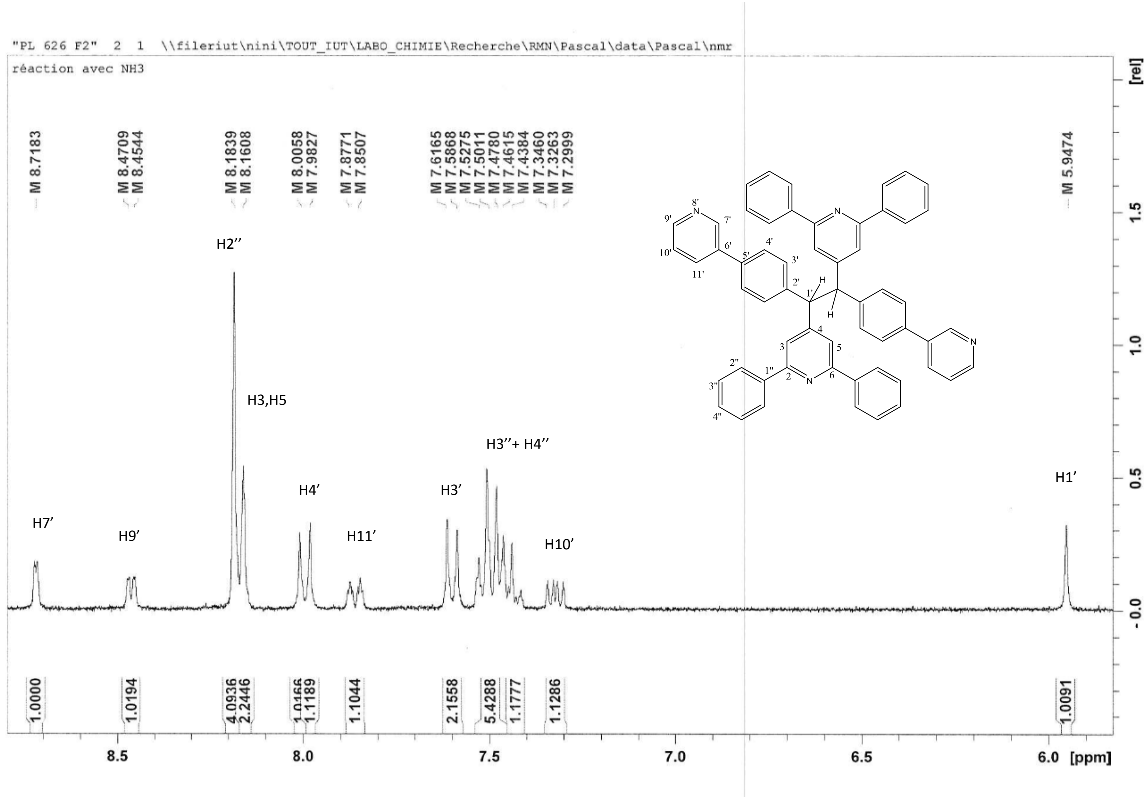
Current Data Parameters
NAME      PL 618 acetone
EXPNO                  5
PROCNO                 1

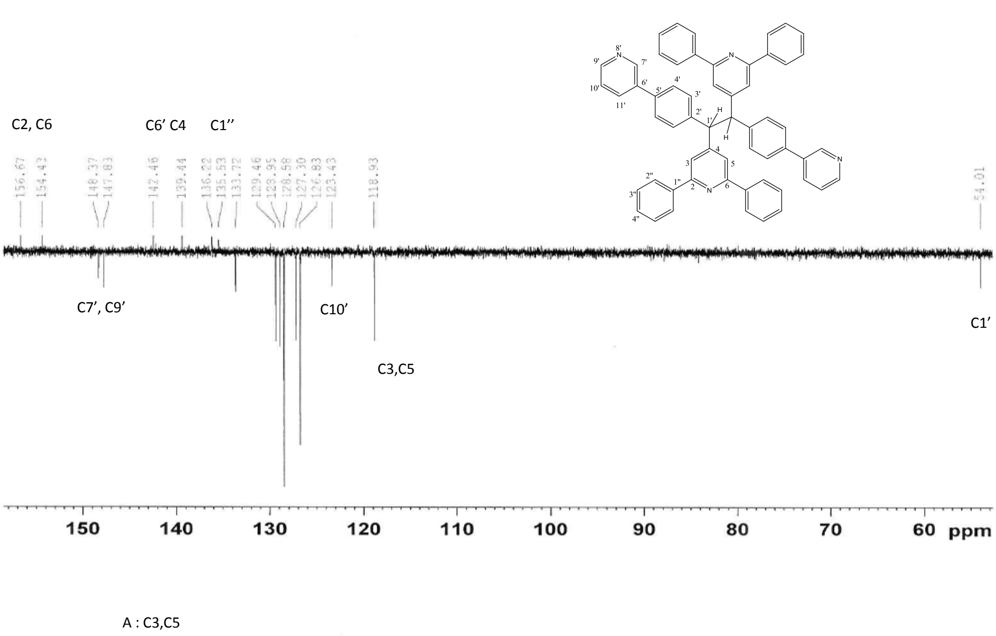
F2 - Acquisition Parameters
Date_           20140315
Time                0.06
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG             jmod
TD                 65536
SOLVENT          Acetone
NS                  8000
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219008 sec
RG                 16384
DW                27.800 usec
DE                  6.50 usec
TE                 300.0 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001108 sec
TD0                    1
SFO1          75.4752953 MHz
NUC1                 13C
P1                  8.70 usec
p2                 17.40 usec
PLW1         -1.00000000 W
SFO2         300.1312005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   no
SSB          0
LB           0 Hz
GB           0
PC                  1.40
```

^{13}C (Jmod) NMR spectrum of compound 4a in acetone-*d6* at 293K



^{1}H NMR spectrum of compound 4b in acetone-*d6* at 293K



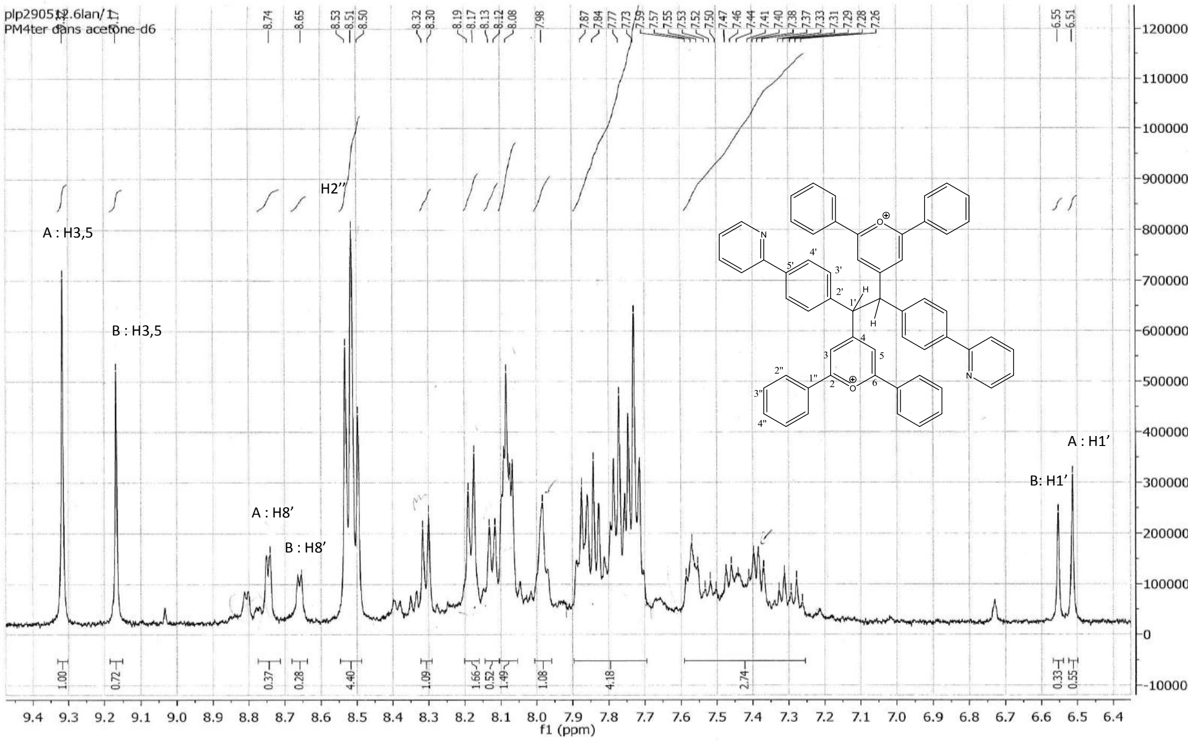
```
Current Data Parameters
NAME                 PL 626
EXPNO                     7
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140314
Time                  10.48
INSTRUM               spect
PROBHD     5 mm Dual 13C/
PULPROG                jmod
TD                    65536
SOLVENT             Acetone
NS                    15299
DS                        4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                1.8219008 sec
RG                  20642.5
DW                   27.800 usec
DE                     6.50 usec
TE                    300.0 K
CNST2           145.0000000
CNST11            1.0000000
D1               2.00000000 sec
d20              0.00689655 sec
DELTA            0.00001108 sec
TD0                       1
SFO1             75.4752953 MHz
NUC1                    13C
P1                     8.70 usec
p2                    17.40 usec
PLW1            -1.00000000 W
SFO2            300.1312005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            -1.00000000 W
PLW12           -1.00000000 W

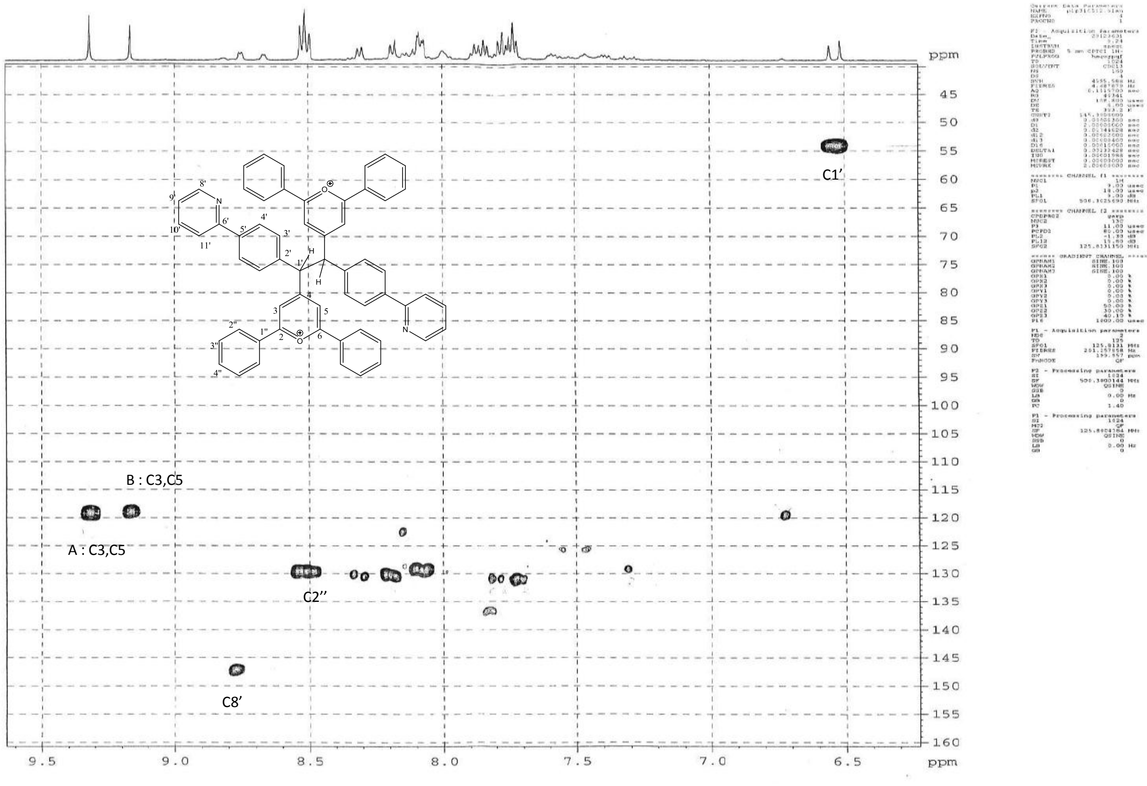
F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                     1.40
```

^{13}C (Jmod) NMR spectrum of compound 4b in acetone-*d6* at 293K

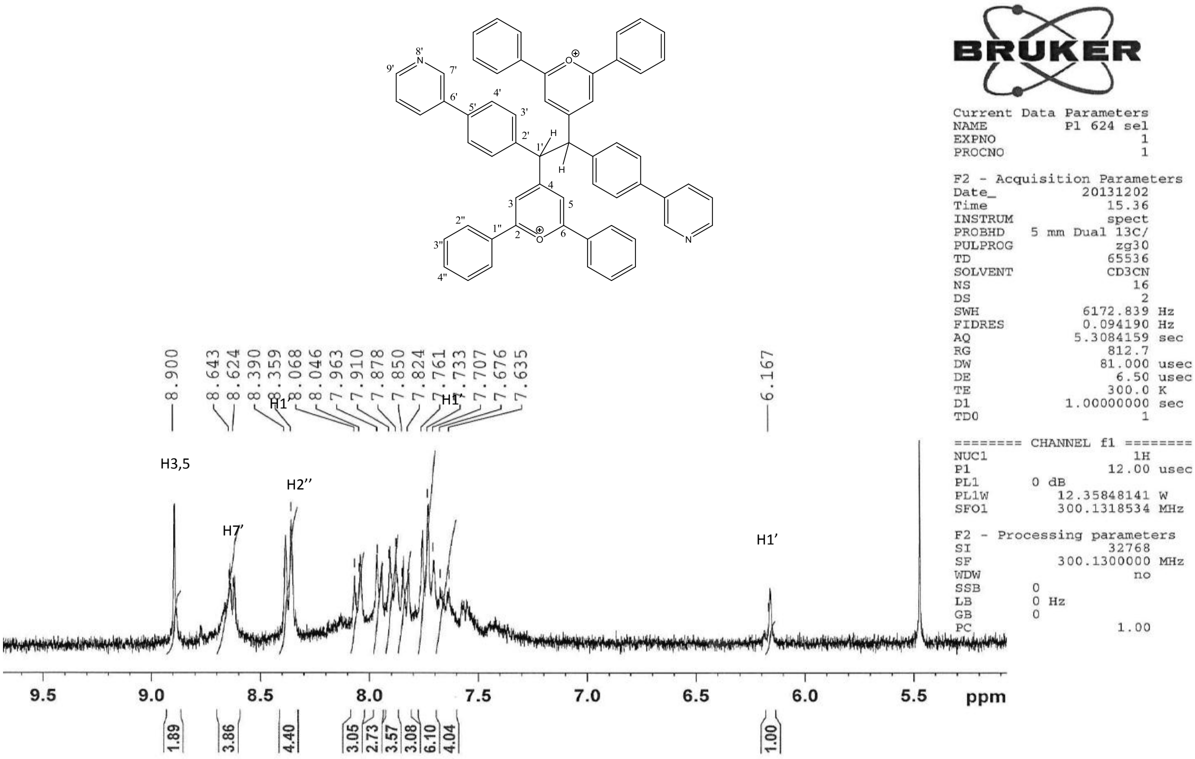
3-4 pyrylium dications 2



^{1}H NMR spectrum of compound 2a in acetone-*d6* at 293K



2D (^{1}H/^{13}C) HSQC spectrum of compound 2a in acetone-*d6* at 293K



```
Current Data Parameters
NAME             P1 624 sel
EXPNO                     1
PROCNO                    1

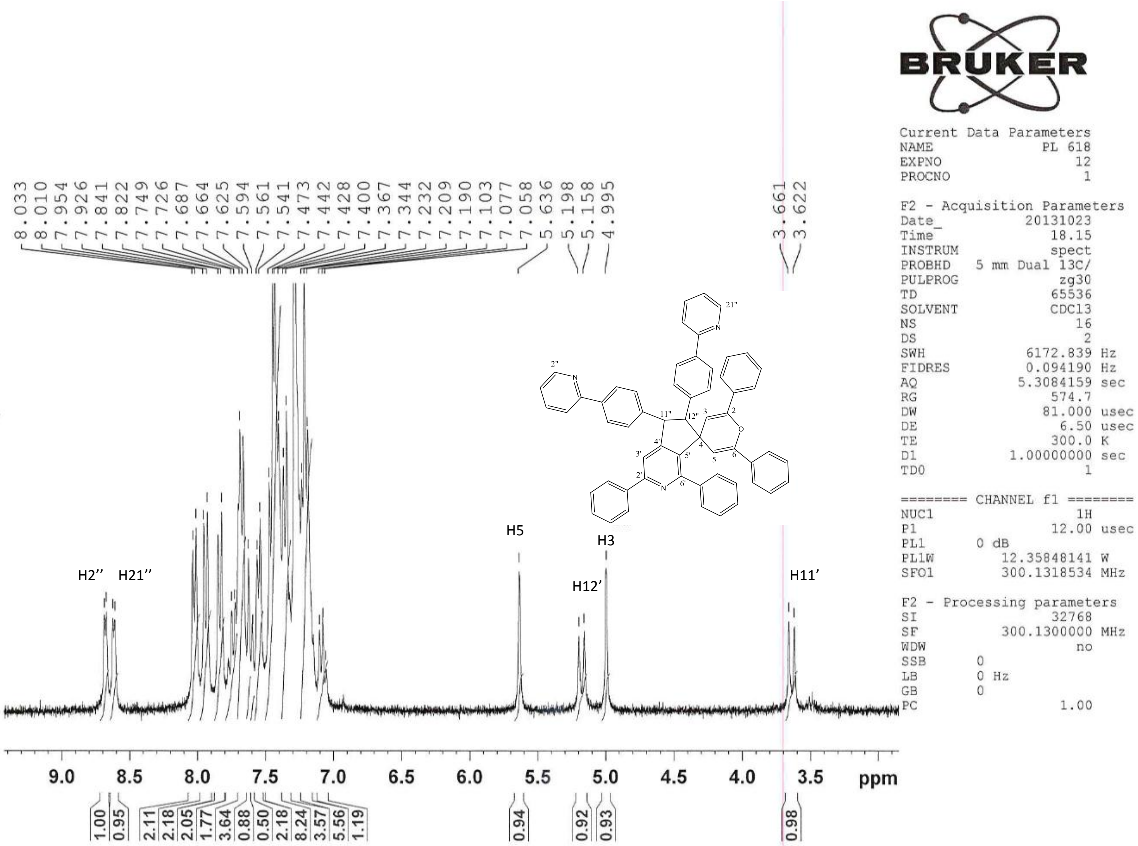
F2 - Acquisition Parameters
Date_              20131202
Time                  15.36
INSTRUM               spect
PROBHD   5 mm Dual 13C/
PULPROG                zg30
TD                    65536
SOLVENT                CD3CN
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                5.3084159 sec
RG                    812.7
DW                   81.000 usec
DE                     6.50 usec
TE                    300.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.00 usec
PL1       0 dB
PL1W            12.35848141 W
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300000 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                     1.00
```

^{1}H NMR spectrum of compound 2b in acetone-*d6* at 293K

3-5 spiropyran 5



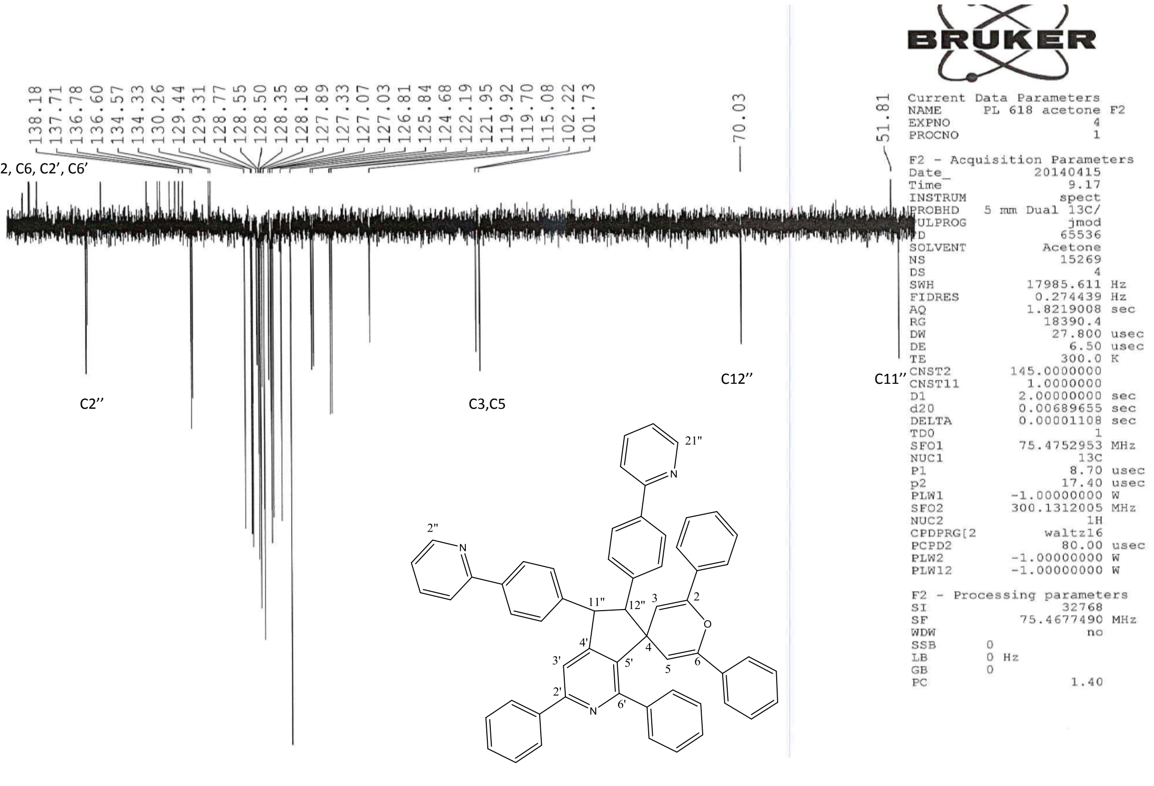
```
Current Data Parameters
NAME                 PL 618
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20131023
Time                  18.15
INSTRUM               spect
PROBHD   5 mm Dual 13C/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ            5.3084159 sec
RG                    574.7
DW              81.000 usec
DE                6.50 usec
TE                  300.0 K
D1           1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1               12.00 usec
PL1        0 dB
PL1W        12.35848141 W
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF          300.1300000 MHz
WDW                      no
SSB        0
LB         0 Hz
GB         0
PC                     1.00
```

^{1}H NMR spectrum of compound 5 in acetone-*d6* at 293K



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Current Data Parameters
NAME      PL 618 acetone F2
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140415
Time                   9.17
INSTRUM               spect
PROBHD   5 mm Dual 13C/
PULPROG                jmod
TD                    65536
SOLVENT             Acetone
NS                    15269
DS                        4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219008 sec
RG                  18390.4
DW              27.800 usec
DE                6.50 usec
TE                  300.0 K
CNST2       145.0000000
CNST11        1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001108 sec
TD0                       1
SFO1         75.4752953 MHz
NUC1                    13C
P1                8.70 usec
p2               17.40 usec
PLW1        -1.00000000 W
SFO2        300.1312005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2            80.00 usec
PLW2        -1.00000000 W
PLW12       -1.00000000 W

F2 - Processing parameters
SI                    32768
SF           75.4677490 MHz
WDW                      no
SSB        0
LB         0 Hz
GB         0
PC                     1.40
```
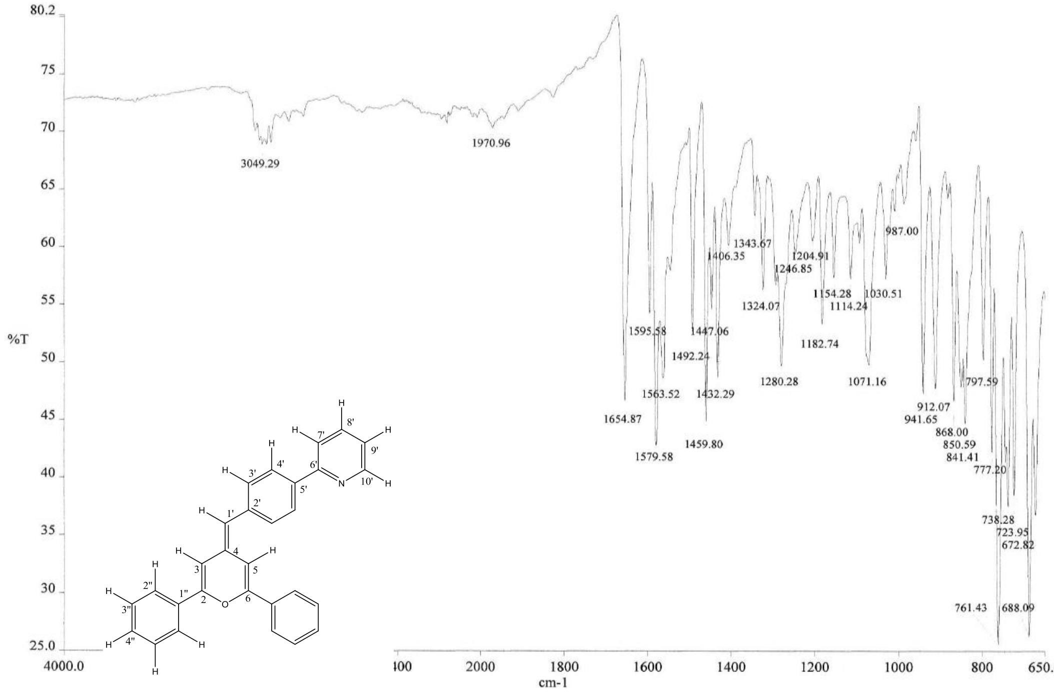
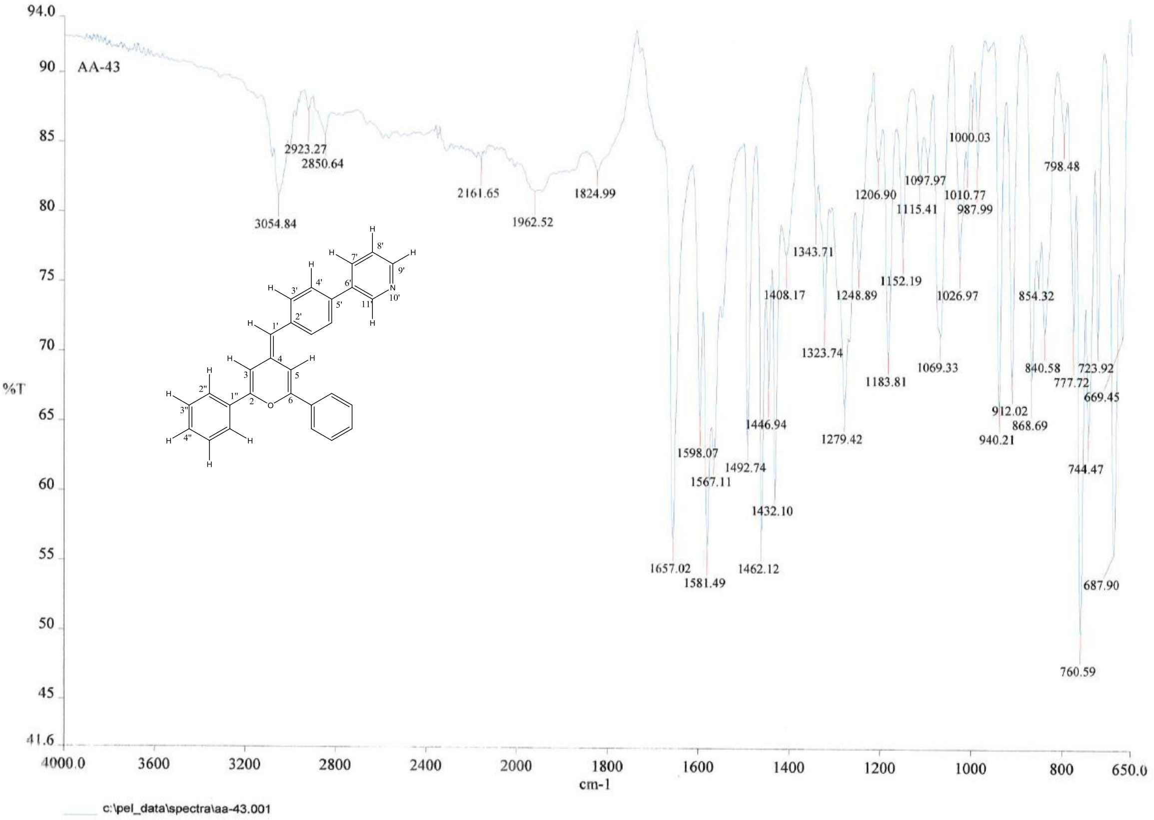

^{13}C (Jmod) NMR spectrum of compound 5 in acetone-*d6* at 293K

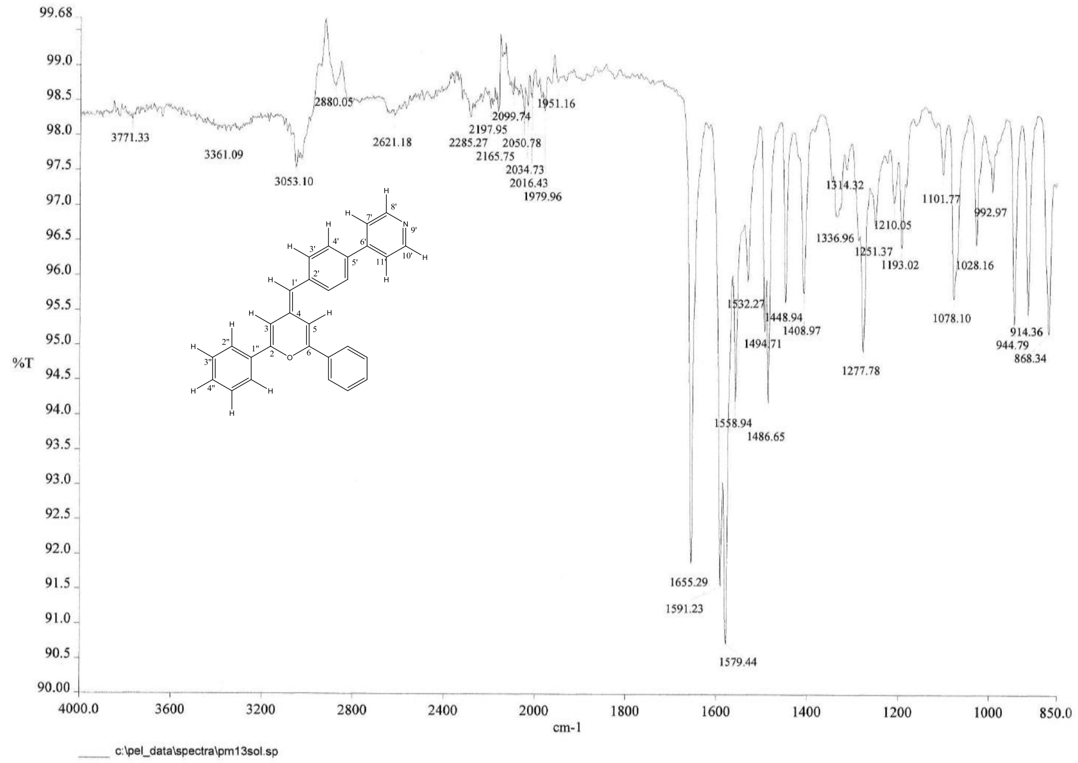
4- IR spectra of compounds 1-5



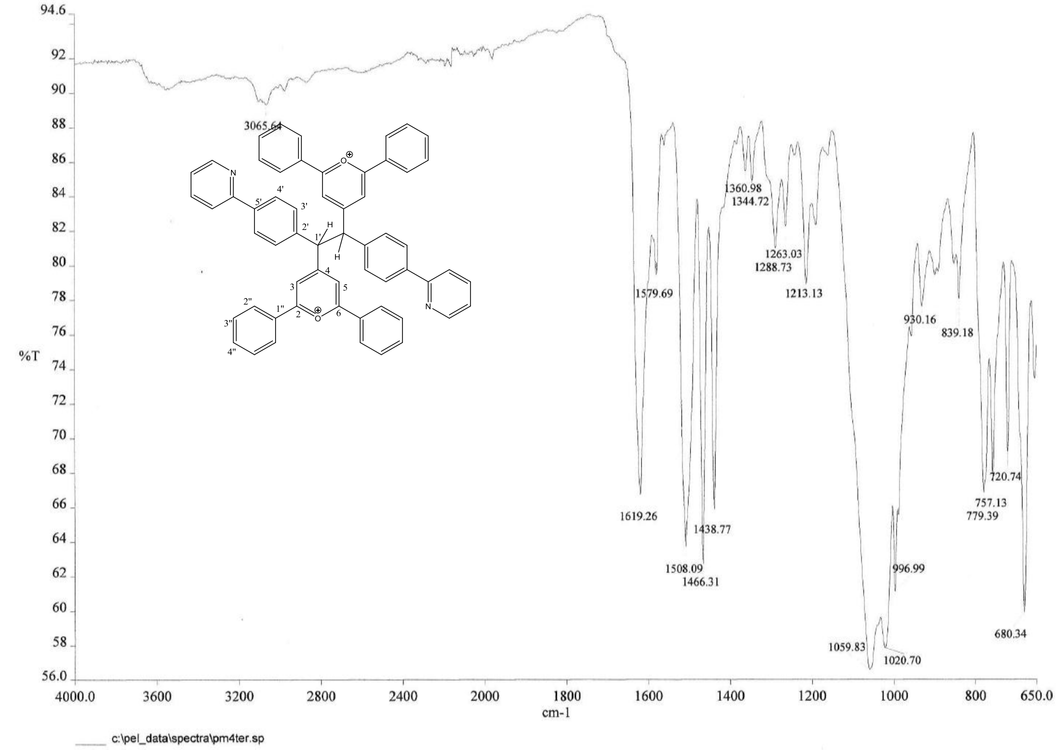
IRTF/ATR spectrum of compound 1a



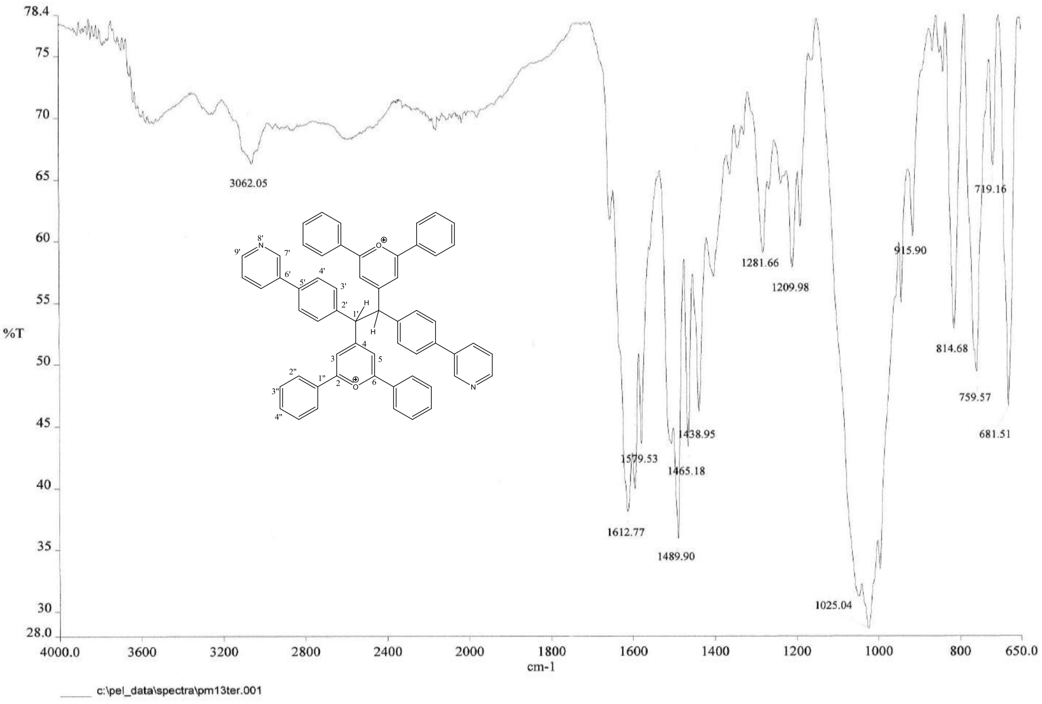
IRTF/ATR spectrum of compound 1b



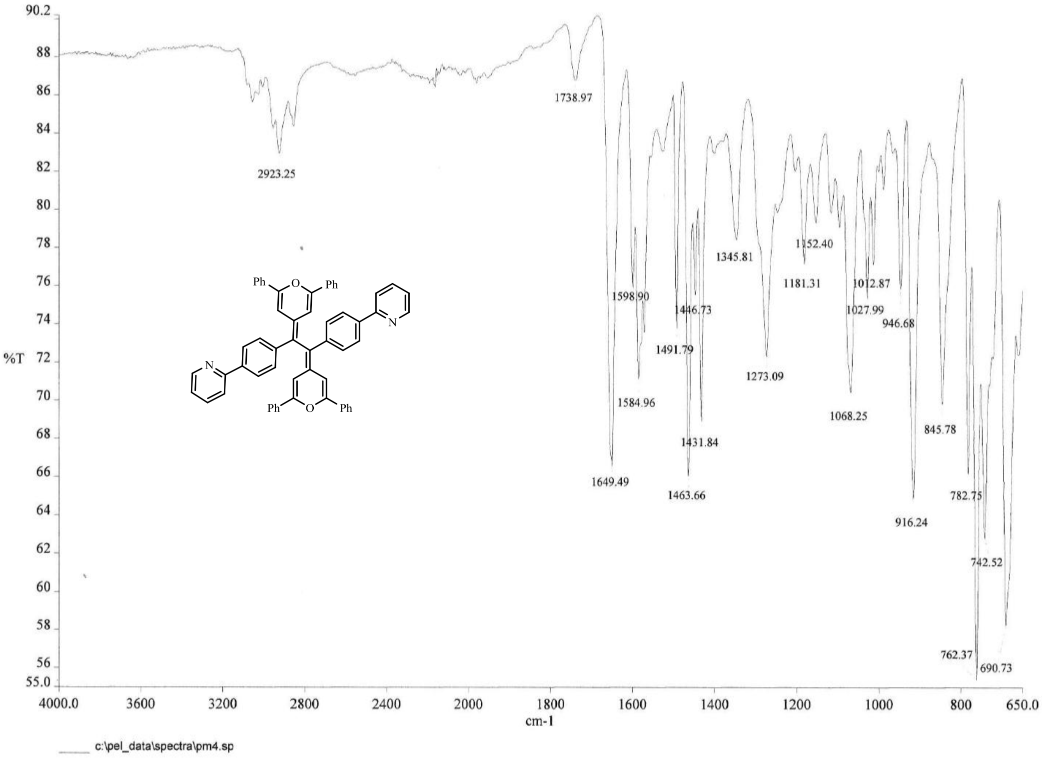
IRTF/ATR spectrum of compound 1c



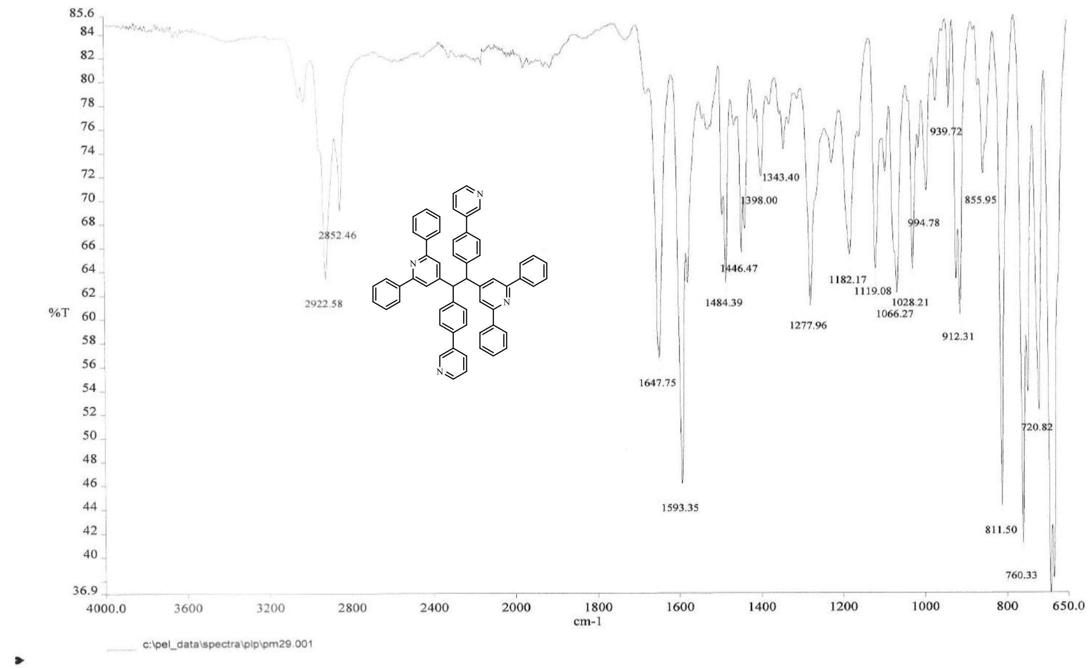
IRTF/ATR spectrum of compound 2a



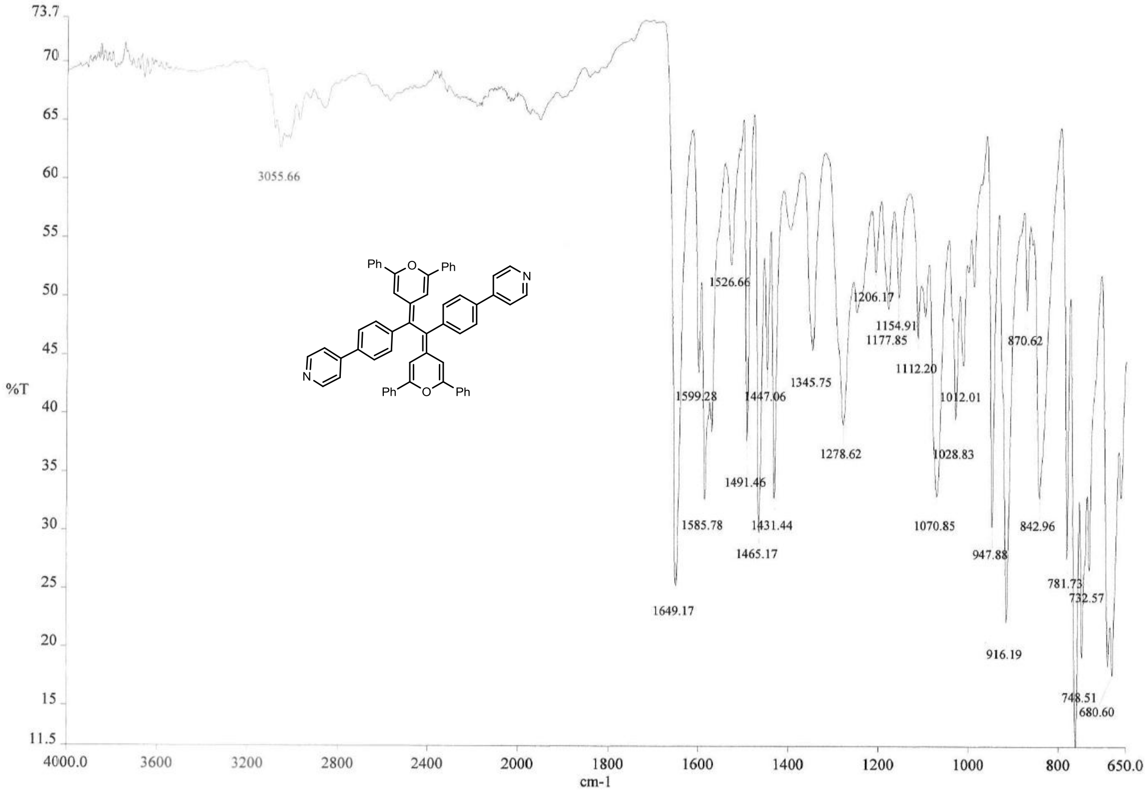
IRTF/ATR spectrum of compound 2b



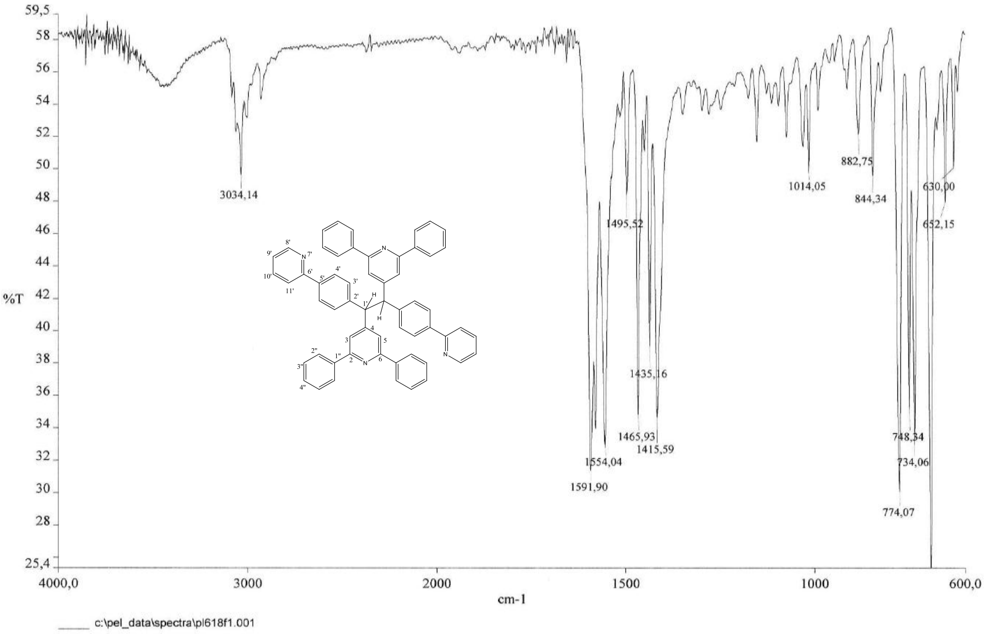
IRTF/ATR spectrum of compound 3a



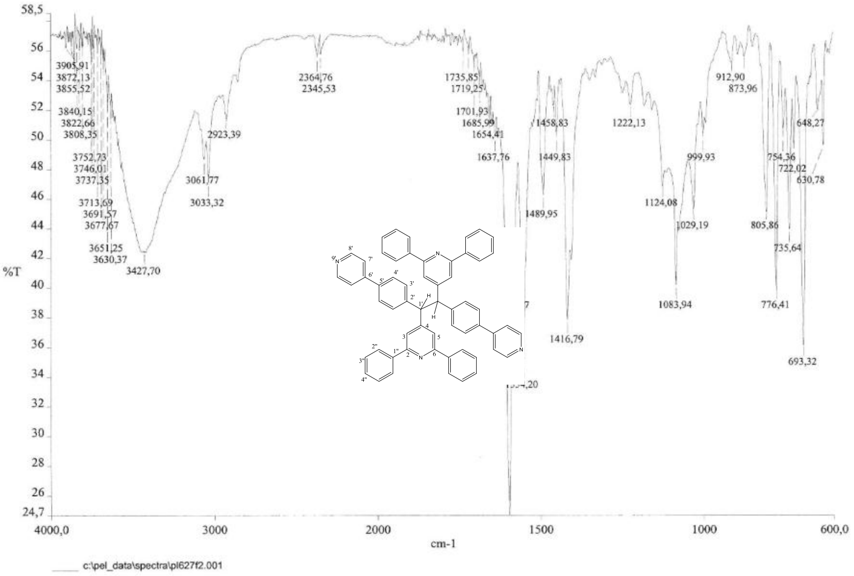
IRTF/ATR spectrum of compound 3b



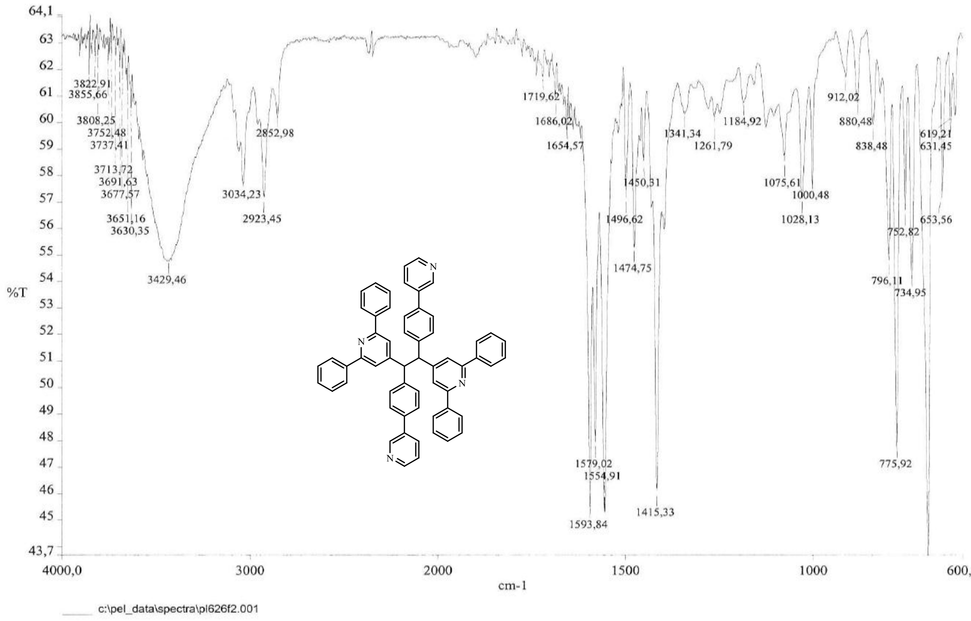
IRTF/ATR spectrum of compound 3c



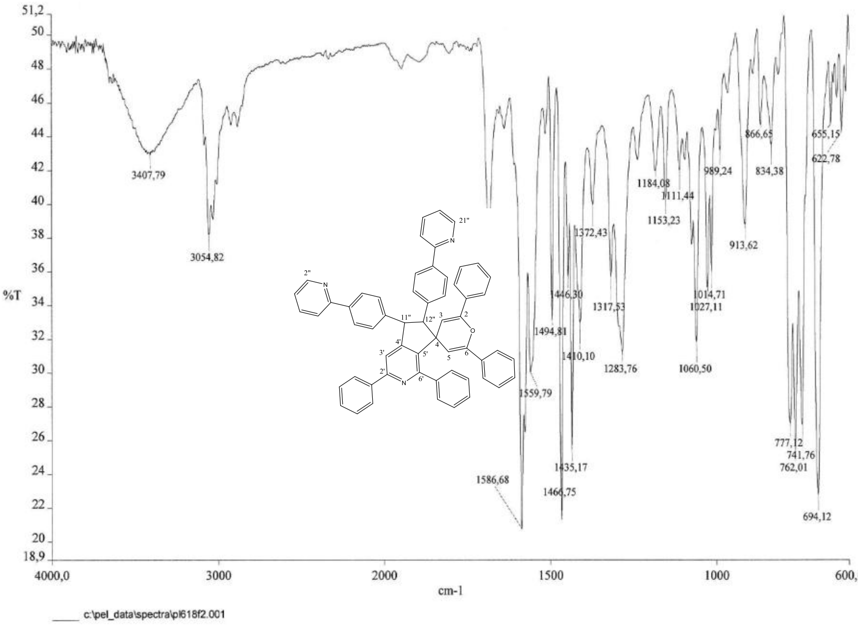
IRTF/ATR spectrum of compound 4a



IRTF/ATR spectrum of compound 4c

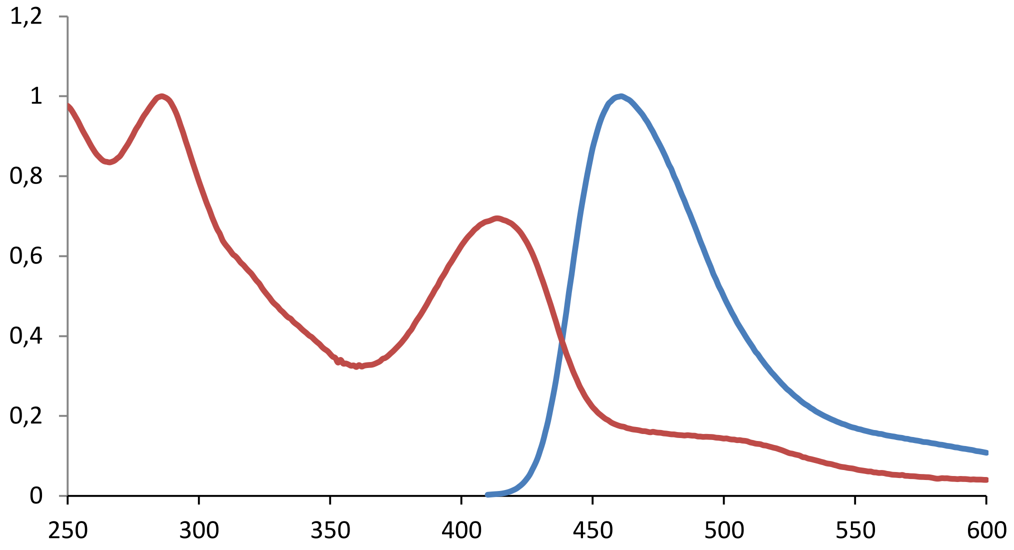


IRTF/ATR spectrum of compound 4b



IRTF/ATR spectrum of compound 5

5- *Absorption and emission spectra of compound 2a*



UV-vis (red curve) and emission (blue curve) spectra of compound **2a** in CH_2Cl_2 at 25°C. Excitation at 400 nm. [2a]= 8.10^{-6}M. Emission intensity was normalized with the absorbance at 286 nm.

6- *Crystallographic data of compound 4c*

6-1 Crystal data

Empirical formula	C_{58} H_{42} N_4
Formula weight	794.95
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, P 2_1/n
Unit cell dimensions	a = 10.9142(17) Å
	b = 13.574(2) Å
	c = 14.539(2) Å
	β= 76.691(8)°.
Volume	2096.1(5) $Å^3$
Z	2
Density (calculated)	1.260 Mg/m^3
Absorption coefficient	0.074 mm^{-1}
F(000)	836
Crystal size	0.018 x 0.015 x 0.012 mm^3
Theta range for data collection	5.194 to 25.258°.
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected	7210

Independent reflections	3743 [R(int) = 0.1898]
Completeness to theta = 25.242°	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3743 / 0 / 280
Goodness-of-fit on F^2	0.935
Final R indices [$I>2\sigma(I)$]	R1 = 0.0919, wR2 = 0.2180
R indices (all data)	R1 = 0.2867, wR2 = 0.3083
Largest diff. peak and hole	0.293 and -0.175 e.Å^{-3}

6-2 selected bond distances

Bond	C1-C1^{i}	C1-C2	C1-C19	C2-C6	C2-C3	C6-C5	C3-C4	C4-N1	C5-N1
d(Å)	1.479(13)	1.522(8)	1.532(9)	1.364(9)	1.414(9)	1.379(8)	1.443(8)	1.334(7)	1.331(7)

Symmetry transformations used to generate equivalent atoms: i: -x,-y+1,-z

Bond	C25-C26	C25-C29	C26-C27	C29-C28	C28-N2	C27-N2
d(Å)	1.382(8)	1.406(8)	1.375(9)	1.388(9)	1.340(9)	1.351(8)

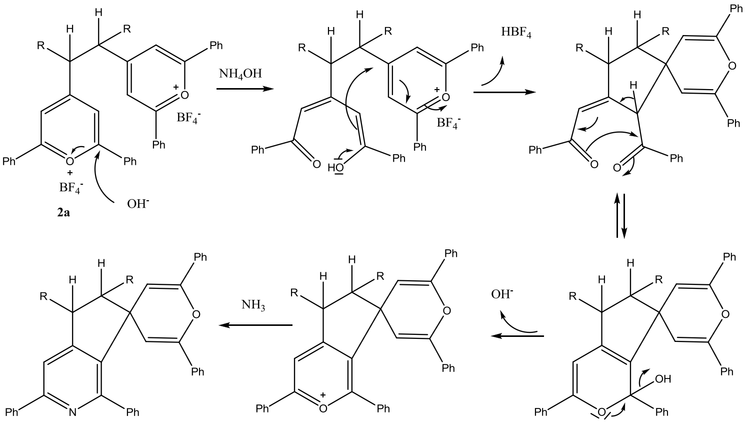
7- Electrochemical data

Redox potential of compounds 2

Electrochemical data for monopyrans 2 in CH2Cl2 with Bu_4NPF_6 as supporting electrolyte at 0.1 V/s. E vs $FeCp_2^+/FeCp_2$. (a) irreversible peak.(b) on the reverse cathodic scan.

compound	Epa (V)(a)	Epc (V) (b)
1a	0.27	-0.79
1c	0.31	-0.79
1b	0.30	-0.78

8- Formation of spiropyran 5



Proposed mechanism for the formation of spiropyran 5