Bis[Pyrrolyl Ru(II)] Triads: a New Class of Photosensitizers for Metal-Organic Photodynamic Therapy

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Supporting Information

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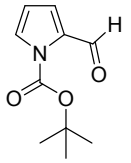
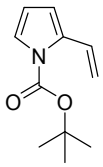
Additional Experimental Procedures

2-Formyl-*N*-Boc-pyrrole[1]



A solution of 2-formyl pyrrole (2.0 g, 21.03 mmol) in anhydrous THF (20 mL) was added drop-wise, over 20 minutes, to a stirred suspension of sodium hydride (60% dispersion in mineral oil, 1.01 g, 25.23 mmol) in anhydrous THF (120 mL) under argon, with continued stirring at room temperature for 1 hour. $(Boc)_2O$ (5.05 g, 23.13 mmol) was then added, as a solid in one portion, and the reaction was left to stir at room temperature overnight. After quenching with saturated aqueous ammonium chloride solution (20 mL), the reaction mixture was diluted with water (100 mL) and extracted with diethyl ether (3 x 100 mL). The combined organic extracts were washed with water (100 mL) and brine (100 mL), dried over anhydrous magnesium sulfate and concentrated to give the crude product, which was purified using column chromatography on silica, eluting with 20% ethyl acetate in hexanes, to give the title compound (3.63 g, 88% yield) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.31 (s, 1H, CHO), 7.42 (dd, 1H, J = 1.5, 3.0 Hz), 7.17 (dd, 1H, J = 1.5, 3.5 Hz), 6.27 (at, 1H, J = 3.0 Hz), 1.63 (s, 9H, ^{t}Bu) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 182.4, 148.5, 134.8, 127.4, 121.3, 111.8, 85.9, 28.0 ppm; LRMS: 218.1 $(M+Na)^+$; HRMS: 218.0788 Found, 218.0788 Calculated for $C_{10}H_{13}NO_3Na$.

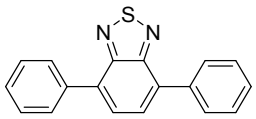
2-Vinyl-*N*-Boc-pyrrole (1a)[1]



n-BuLi (1.6 M in hexanes, 5.28 mL, 8.45 mmol) was added to a stirred suspension of methyl triphenylphosphonium bromide (3.29 g, 9.22 mmol) in anhydrous THF (70 mL), at 0 °C under argon. After 2 hours, the mixture was cooled to -78 °C and a solution of 2-formyl-*N*-Boc-pyrrole (1.5 g, 7.68 mmol) in THF (10 mL) was added drop-wise over 15 minutes, with stirring overnight warming to room temperature. The reaction mixture was then diluted with water (100 mL) and

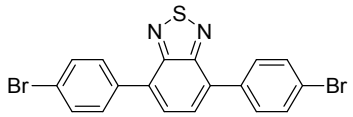
extracted with diethyl ether (3 x 100 mL). The combined organic extracts were washed with water (100 mL) and brine (100 mL), dried over anhydrous magnesium sulfate and concentrated to give the crude product, which was purified using column chromatography on silica, eluting with 10% ethyl acetate in hexanes, to give the product **1** (949 mg, 64% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26-7.20 (m, 2H), 6.42-6.43 (m, 1H), 6.14 (at, 1H, *J* = 3.5 Hz), 5.53 (dd, 1H, *J* = 1.5, 17.5 Hz), 5.12 (dd, 1H, *J* = 1.5, 11.0 Hz), 1.60 (s, 9H, ^{t}Bu) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.5, 134.6, 128.1, 122.0, 113.5, 110.9, 110.86, 83.9, 28.1 ppm; LRMS: 216.1 $(M+Na)^{+}$; HRMS: 216.0990 Found, 216.0995 Calculated for $C_{11}H_{15}NO_2Na$.

4,7-Diphenylbenzo[*c*][1,2,5]thiadiazole[2]



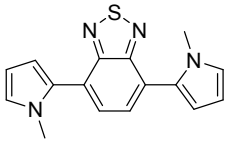
Potassium carbonate (564 mg, 4.08 mmol) and tetrakis(triphenylphosphine)palladium (118 mg, 0.102 mmol) were added to a stirred solution of 4,7-dibromobenzothiadiazole (300 mg, 1.02 mmol) and phenylboronic acid (275 mg, 2.14 mmol) in toluene (5 mL) and the resulting solution was bubbled with nitrogen for 10 minutes. Degassed (N_2) water (2 mL) was then added and the reaction mixture was heated to 90 °C, with stirring under nitrogen for 5 hours. After cooling to room temperature, the reaction mixture was separated between dichloromethane (50 mL) and water (50 mL). The aqueous phase was extracted with dichloromethane (3 x 50 mL) and the combined organic extracts were washed with water (100 mL) and brine (100 mL), dried over anhydrous sodium sulfate and concentrated to give the crude product, which was purified using column chromatography on silica, eluting with 20% diethyl ether in hexanes, to give the title compound (236 mg, 80% yield) as a pale yellow solid. M.p. 130−132 °C; 1H NMR (CDCl3, 500 MHz) δ 7.97 (d, 4H, *J* = 7.5, ArH), 7.80 (s, 2H, ArH), 7.57 (at, 4H, *J* = 7.5, ArH), 7.48 (t, 2H, *J* = 7.5 Hz, ArH) ppm; 13C NMR (CDCl3, 125 MHz) δ 154.2, 137.6, 133.5, 129.4, 128.8, 128.5, 128.3 ppm; NMR data matches that previously reported for this compound.[2]

4,7-Bis(4-bromophenyl)benzo[*c*][1,2,5]thiadiazole (i)[2]



A solution of bromine (0.83 mL, 16.23 mmol) in anhydrous chloroform (1 mL) was added drop wise, over 5 minutes, to a solution of 4,7-diphenylbenzo[*c*][1,2,5]thiadiazole (200 mg, 0.694 mmol) and iodine (10 mg, 0.04 mmol) in anhydrous chloroform (3 mL), with stirring at room temperature under nitrogen for 16 hours. The reaction was quenched by the addition of 1 M aq. KOH solution (4 mL), with stirring for 1 hour, before separating between chloroform (200 mL) and water (150 mL). The organic phase was washed with 5% aq. Na_2SO_3 (150 mL) and brine (150 mL), dried over anhydrous sodium sulfate and concentrated to give the crude product, which was purified by trituration with toluene, to give the title compound (**i**) (250 mg, 83% yield) as a yellow solid. M.p. 274−278 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, 4H, J = 8.3, ArH), 7.78 (s, 2H, ArH), 7.69 (d, 4H, J = 8.3, ArH) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.9, 136.2, 132.6, 132.0, 130.9, 128.1, 123.0 ppm; NMR data matches that previously reported for this compound.[2]

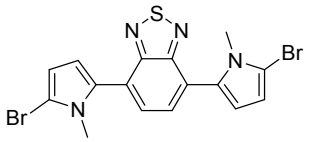
4,7-Bis(1-methyl-1H-pyrrol-2-yl)benzo[*c*][1,2,5]thiadiazole[3]



A solution of 4,7-dibromobenzothiadiazole (400 mg, 1.36 mmol), 1-methyl-2-pyrroleboronic acid pinacol ester (845 mg, 4.08 mmol) and sodium carbonate (577 mg, 5.44 mmol) in anhydrous DMF (12 mL) was bubbled with nitrogen for 10 minutes in a 5-20 mL capacity microwave vial. Tetrakis(triphenylphosphine)palladium (157 mg, 0.136 mmol) was then added with stirring and the vial was sealed and placed in a microwave reactor, with heating at 180 °C for 90 minutes. On completion of the reaction, the mixture was separated between dichloromethane (100 mL) and water (100 mL). The aqueous phase was extracted with dichloromethane (2 x 80 mL) and the combined organic extracts were washed with water (3 x 200 mL) and brine (200 mL), dried over anhydrous sodium sulfate and concentrated to give the crude product, which was purified by column chromatography on silica eluting with 15-20% diethyl ether in hexanes, to give the title compound (279 mg, 70% yield) as a deep red solid. M.p. 108−110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz)

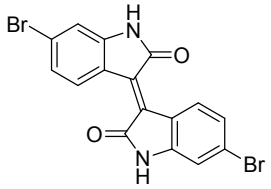
δ 7.58 (s, 2H, ArH), 6.88 (br s, 2H, PyH), 6.57 (br s, 2H, PyH), 6.33 (t, 2H, J = 3.0 Hz, PyH), 3.72 (s, 6H, 2 x CH_3) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.4, 130.2, 128.8, 125.5, 125.1, 112.0, 108.5, 35.9 ppm; LRMS: 317.1 $(M+Na)^+$; HRMS: 217.0845 Found, 217.0831 Calculated for $C_{16}H_{14}N_4SNa$

4,7-Bis(5-bromo-1-methyl-1H-pyrrol-2-yl)benzo[*c*][1,2,5]thiadiazole (j)[3]



N-Bromosuccinimide (411 mg, 2.31 mmol) was added in one portion to a stirred solution of 4,7-bis(1-methyl-1H-pyrrol-2-yl)benzo[*c*][1,2,5]thiadiazole (340 mg, 1.155) in anhydrous THF (10 mL), with stirring at −10 °C (ice-salt bath), under nitrogen, for 3 hours. The reaction mixture was then separated between 2:1 diethyl ether:THF (90 mL) and water (90 mL). The aqueous phase was extracted with 2:1 diethyl ether:THF (2 x 90 mL) and the combined organic extracts were washed with water (200 mL) and brine (200 mL), dried over anhydrous magnesium sulfate and filtered through a short pad of silica, washing with diethyl ether, to give the title compound **(j)** (523 mg, 100% yield) as an orange solid, without the need for further purification. M.p. 130−135 °C; ^{1}H NMR (THF-d_8, 500 MHz) δ 7.63 (s, 2H, ArH), 6.47 (d, 2H, J = 4.0 Hz, PyH), 6.28 (d, 2H, J = 4.0 Hz, PyH), 3.60 (s, 6H, 2 x NMe) ppm; ^{13}C NMR (THF-d_8, 125 MHz) δ 154.9, 132.6, 129.7, 126.6, 112.9, 111.6, 106.0, 34.9 ppm. **Note:** this compound was observed to be unstable in both dichloromethane and chloroform and will decompose very quickly in these solvents.

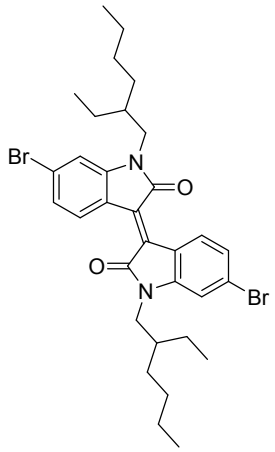
6,6'-Dibromoisoindigo[4]



Concentrated HCl (0.1 mL) was added drop wise to a suspension of 6-bromoisatin (533 mg, 2.36 mmol) and 6-bromooxindole (500 mg, 2.36 mmol) in glacial acetic acid (15 mL) and the reaction mixture was heated to reflux temperature with stirring under nitrogen for 24 hours. After cooling to room temperature, the reaction mixture was filtered and the solid material washed sequentially

with water, ethanol and ethyl acetate until the washings were colourless, before drying in a vacuum oven to give 6,6'-dibromoisoindigo (759 mg, 77% yield) as a dark brown solid. M.p./D.p. >250 °C; ^{1}H NMR (DMF-d_7, 500 MHz) δ 11.06 (br s, 2H, NH), 9.11 (d, 2H, J = 8.5 Hz, ArH), 7.21 (dd, 2H, J = 8.5, 1.5 Hz, ArH), 7.12 (d, 2H, J = 1.5 Hz, ArH) ppm; ^{13}C NMR (DMF-d_7, 125 MHz) δ 169.8, 146.6, 133.6, 131.8, 126.6, 124.8, 122.0, 113.3 ppm; LRMS: 420.9 $(M+H)^+$; HRMS: 420.9001 Found, 420.9025 Calculated for $C_{16}H_9N_2O_2Br_2$

***N*,*N*'-Bis(2-ethylhexyl)-6,6'-dibromoisoindigo (k)[4]**

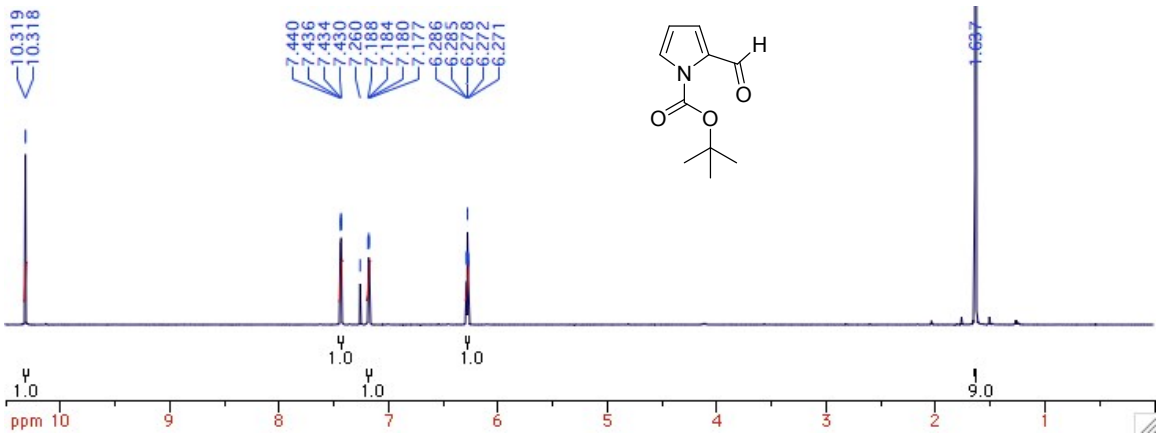


2-Ethylhexyl bromide (1.37 mL, 7.70 mmol) was added drop-wise, over 5 minutes, to a suspension of 6,6'-dibromoisoindigo (1.47 g, 3.50 mmol) and potassium carbonate (2.9 g, 20.99 mmol) in anhydrous DMF (40 mL), with stirring under nitrogen. The reaction mixture was then heated to 100 °C, with stirring for 18 hours, before cooling to room temperature, pouring into water (200 mL) and extracting with dichloromethane (3 x 150 mL). The combined organic extracts were washed with water (2 x 500 mL) and brine (500 mL), dried over anhydrous sodium sulfate and concentrated to give the crude product, which was purified using column chromatography over silica, eluting with 40% hexanes in dichloromethane, to give the title compound (**k**, 1.847 g, 82% yield) as a dark red solid. M.p. 94−96 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.04 (d, 2H, J = 8.5 Hz, ArH), 7.16 (dd, 2H, J = 8.5, 2.0 Hz, ArH), 6.89 (d, 2H, J = 2.0 Hz, ArH), 3.67-3.57 (m, 4H), 1.86-1.79 (m, 2H), 1.41-1.25 (m, 16H), 0.93 (t, 6H, J = 7.5 Hz, 2 x CH_3), 0.90 (t, 6H, J = 7.0 Hz, 2 x CH_3) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.3, 146.3, 132.7, 131.1, 126.8, 125.3, 120.5, 111.7, 44.5, 37.6, 30.7, 28.7, 24.1, 23.2, 14.2, 10.8 ppm.

NMR Spectra

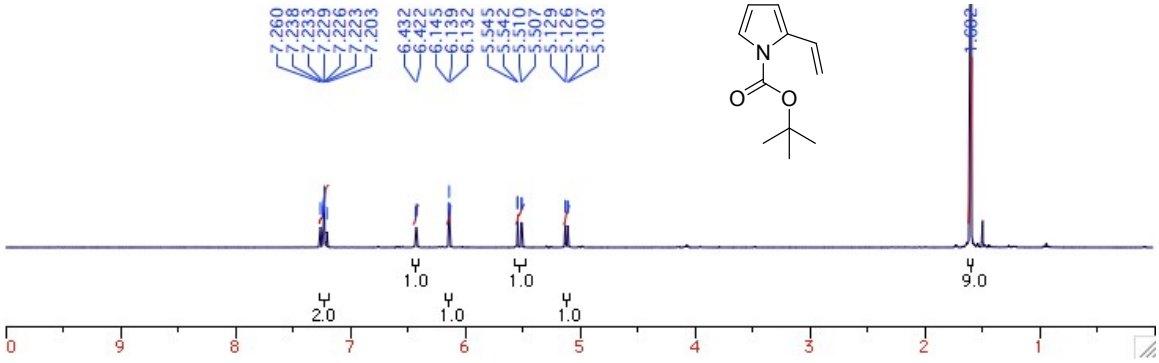
2-Formyl-*N*-Boc-pyrrole

^{1}H NMR ($CDCl_3$, 500 MHz):

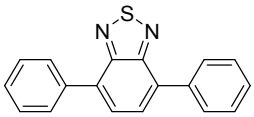


2-Vinyl-*N*-Boc-pyrrole (1a)

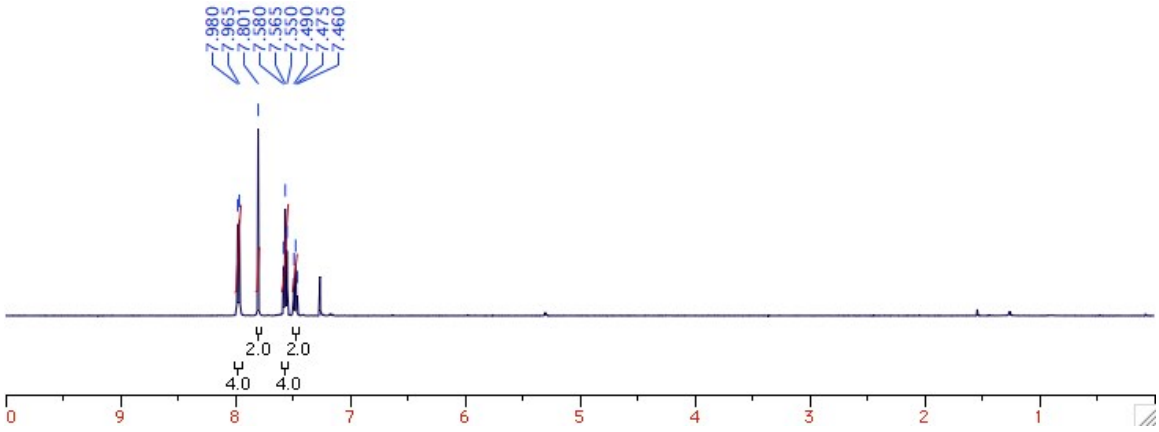
^{1}H NMR ($CDCl_3$, 500 MHz):



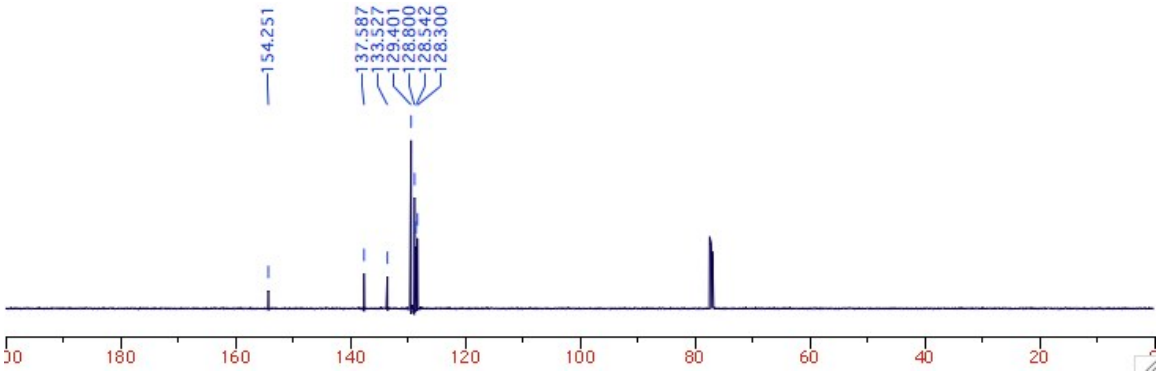
4,7-Diphenylbenzo[*c*][1,2,5]thiadiazole



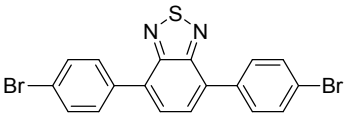
^{1}H NMR ($CDCl_3$, 500 MHz):



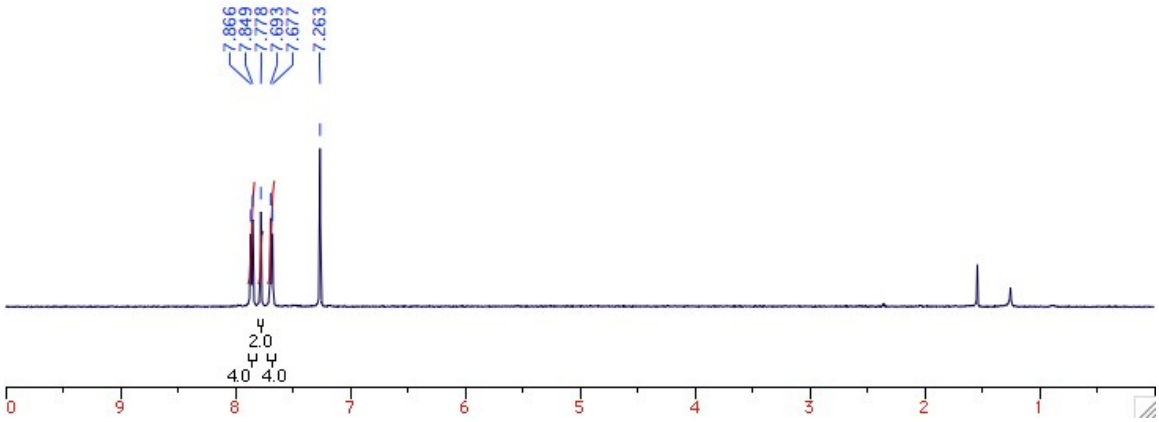
^{13}C udeft NMR ($CDCl_3$, 125 MHz):



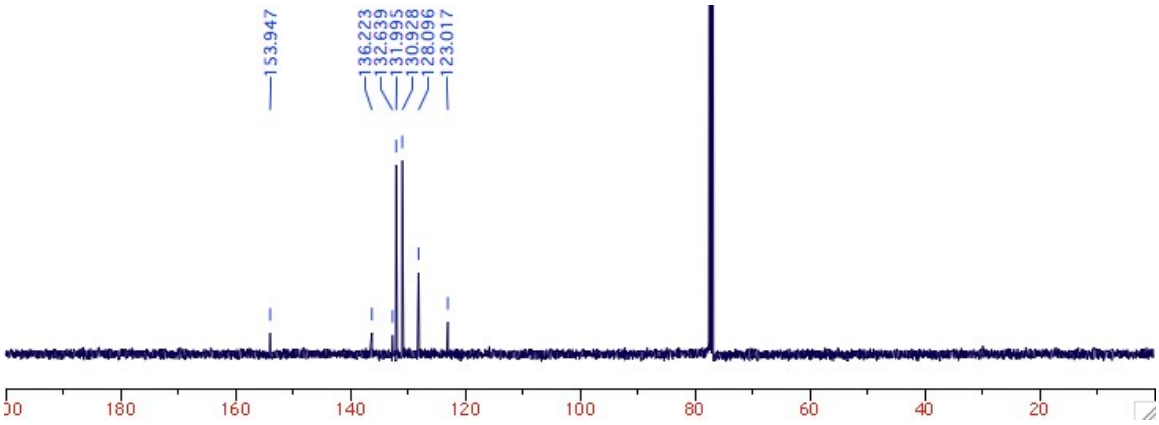
4,7-Bis(4-bromophenyl)benzo[*c*][1,2,5]thiadiazole (i)



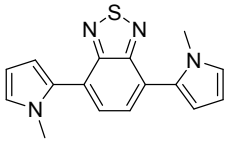
^{1}H NMR ($CDCl_3$, 500 MHz):



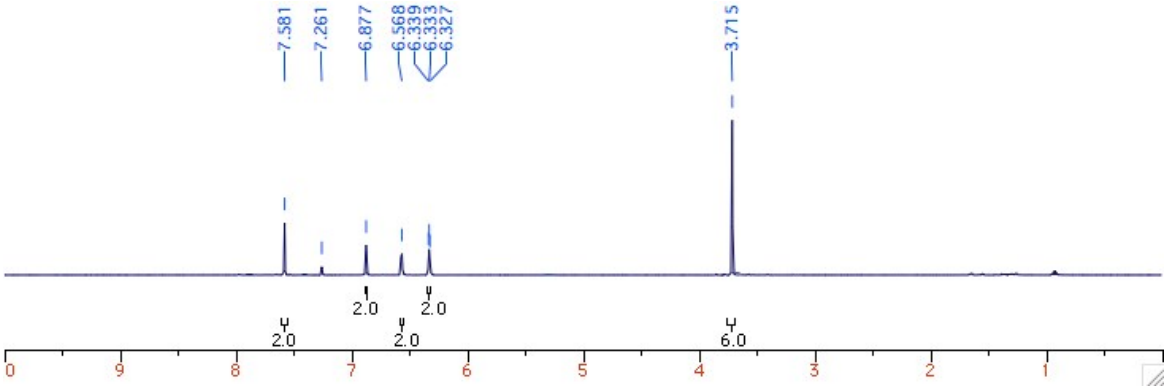
^{13}C udeft NMR ($CDCl_3$, 125 MHz):



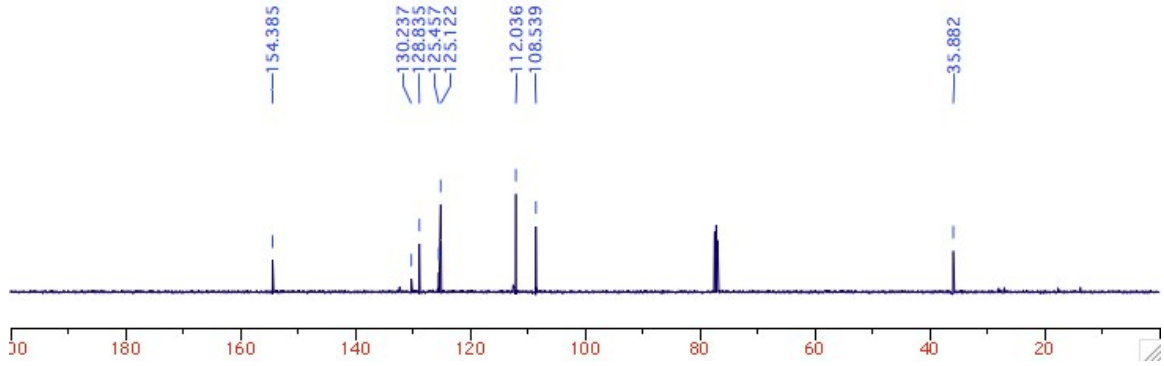
4,7-Bis(1-methyl-1H-pyrrol-2-yl)benzo[*c*][1,2,5]thiadiazole



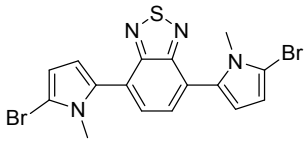
^{1}H NMR ($CDCl_3$, 500 MHz):



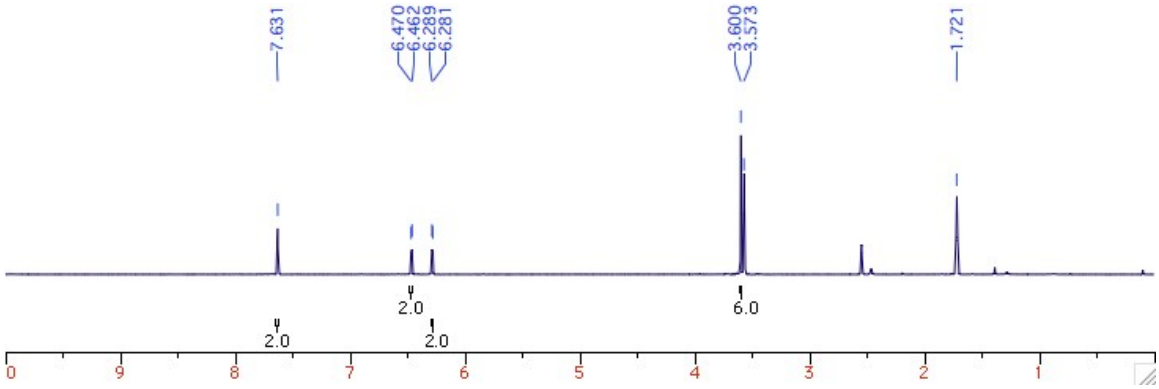
^{13}C udeft NMR ($CDCl_3$, 125 MHz):



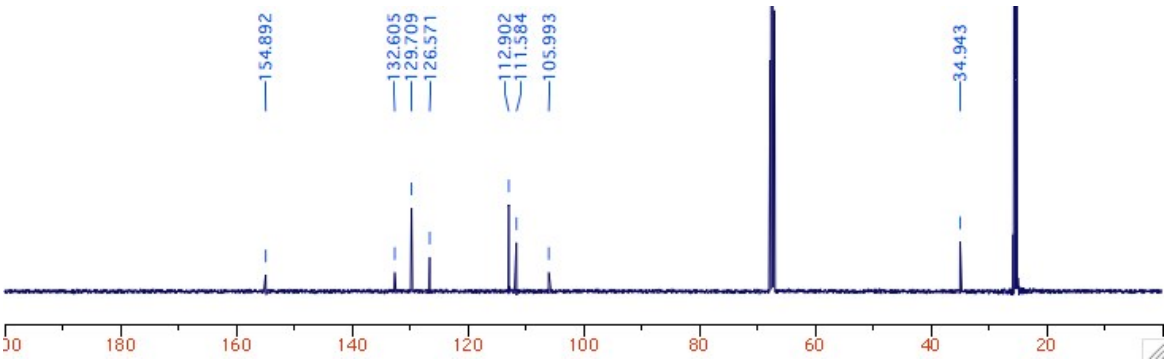
4,7-Bis(5-bromo-1-methyl-1H-pyrrol-2-yl)benzo[*c*][1,2,5]thiadiazole (j)



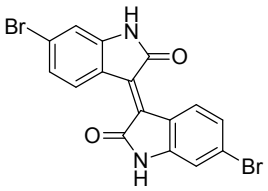
^{1}H NMR (THF-d_8, 500 MHz):



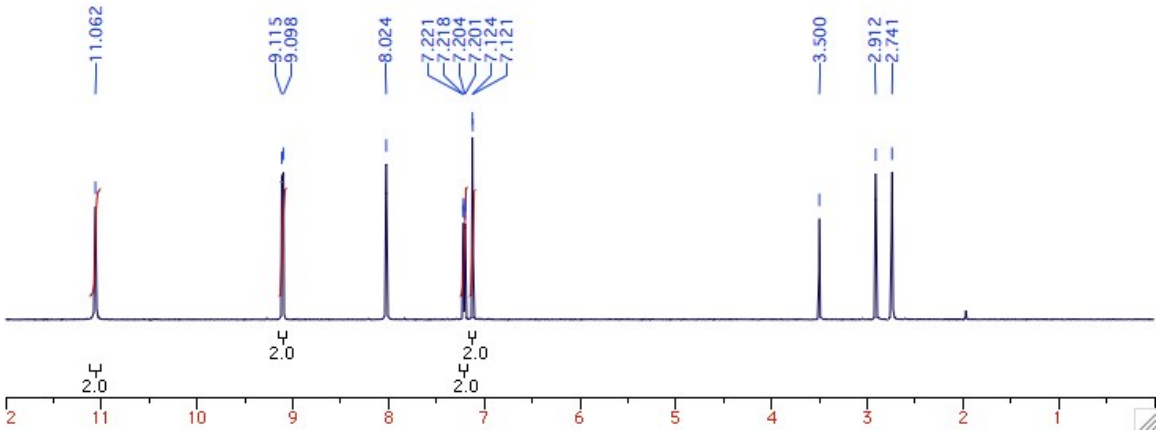
^{13}C udeft NMR (THF-d_8, 125 MHz):



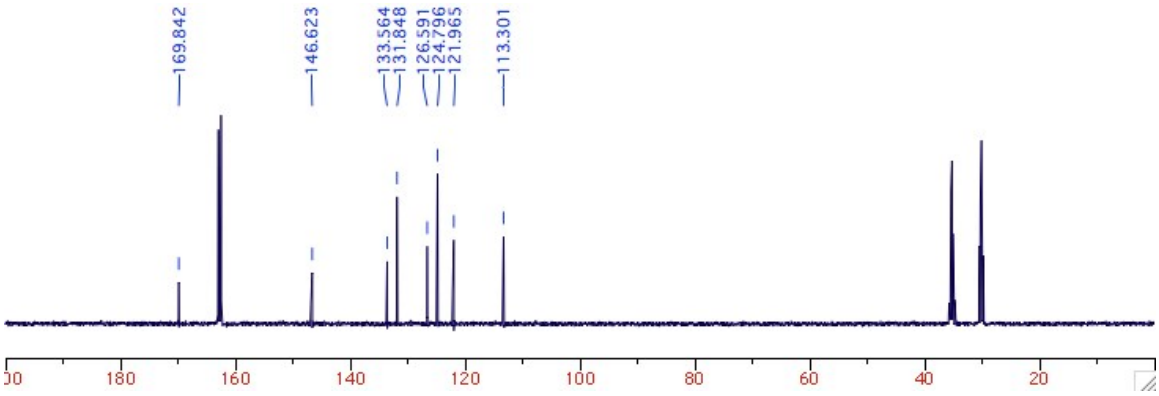
6,6'-Dibromoisoindigo



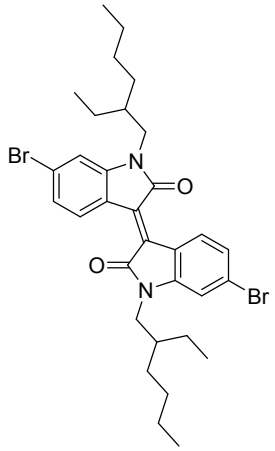
^{1}H NMR (DMF-d7, 500 MHz):



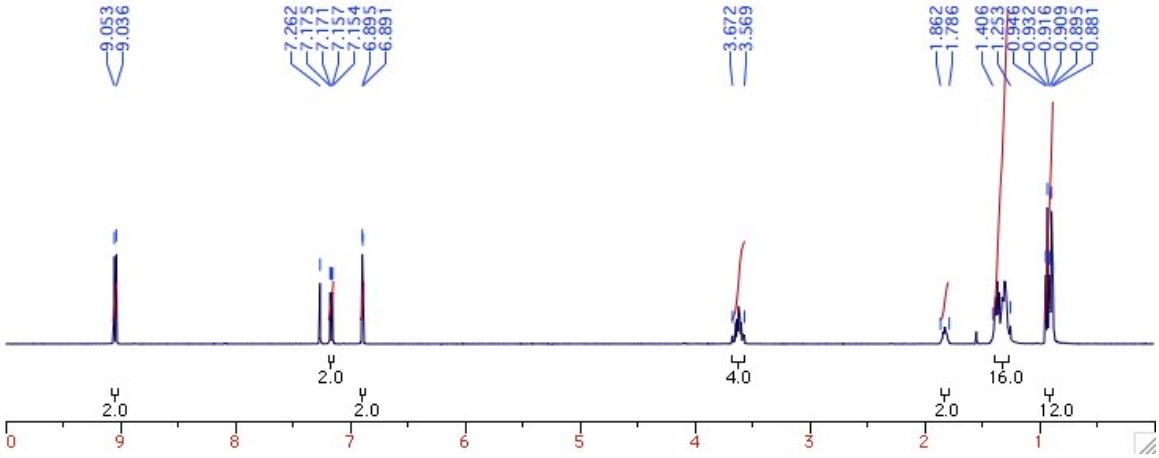
^{13}C udeft NMR (DMF-d_7, 125 MHz):



N,*N*'-Bis(2-ethylhexyl)-6,6'-dibromoisoindigo (k)



^{1}H NMR ($CDCl_3$, 500 MHz):



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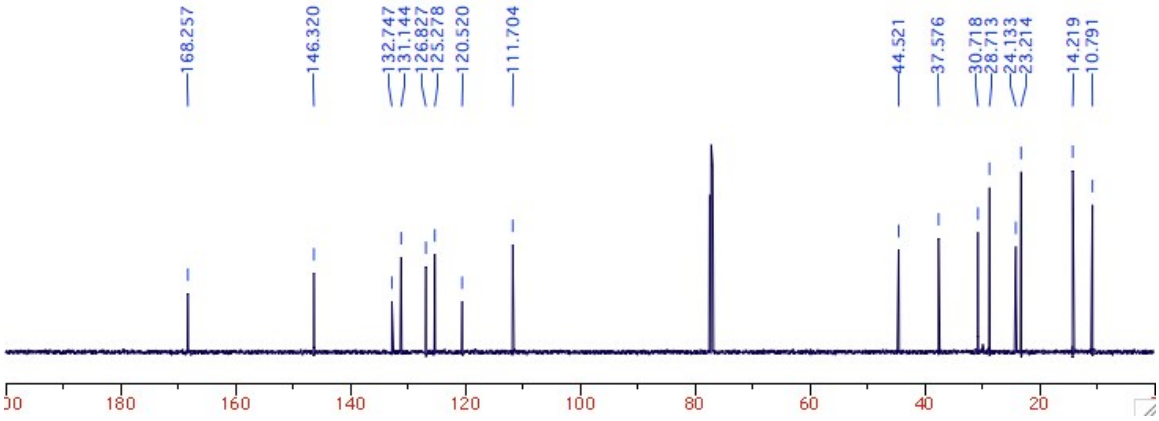
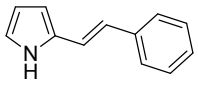
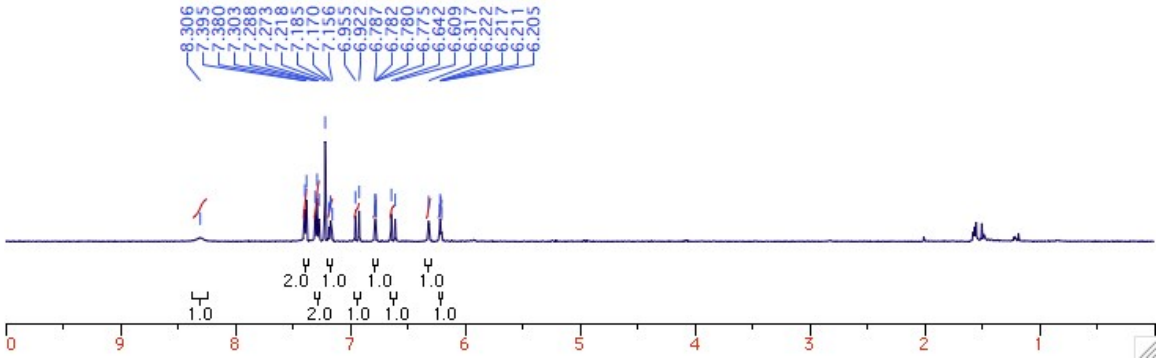


Bis(pyrroles)(2)

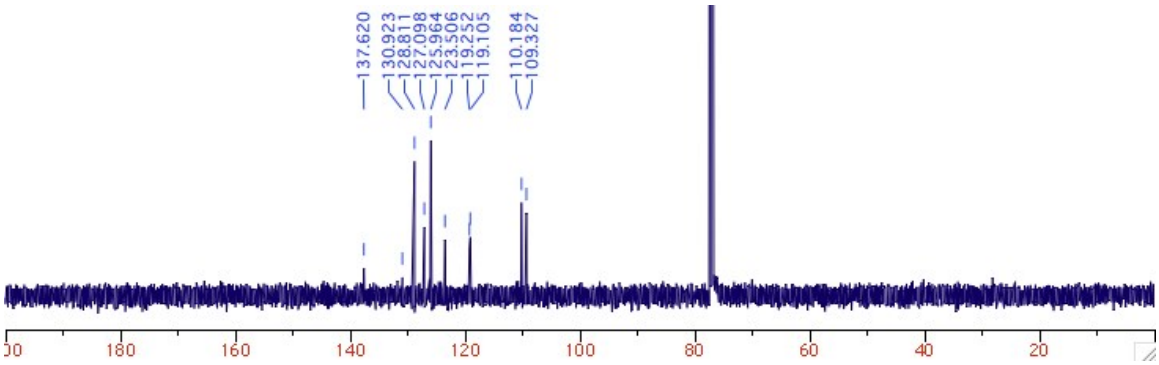
(*E*)-2-styryl-1H-pyrrole (2a).



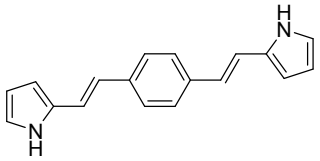
^{1}H NMR ($CDCl_3$, 500 MHz):



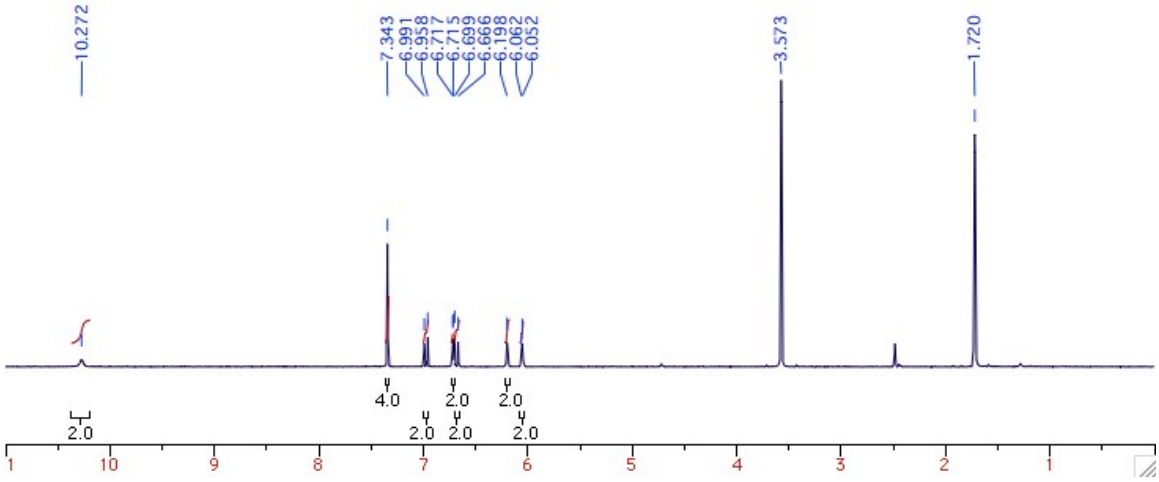
^{13}C udeft NMR ($THF\text{-}d_8$, 125 MHz):



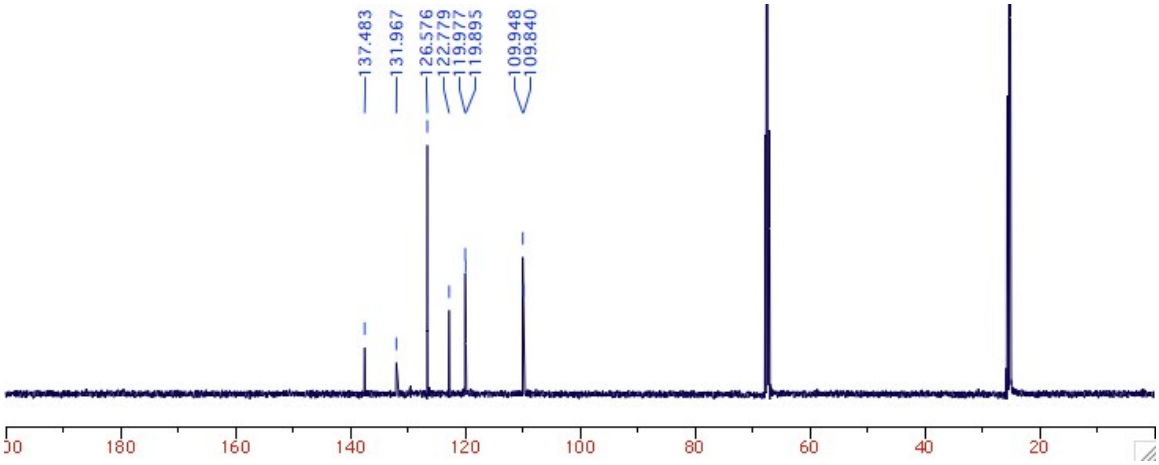
1,4-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)benzene (2b)



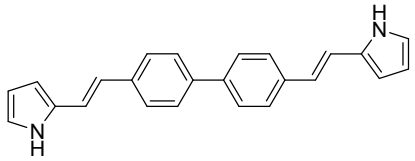
^{1}H NMR (THF-d_8, 500 MHz):



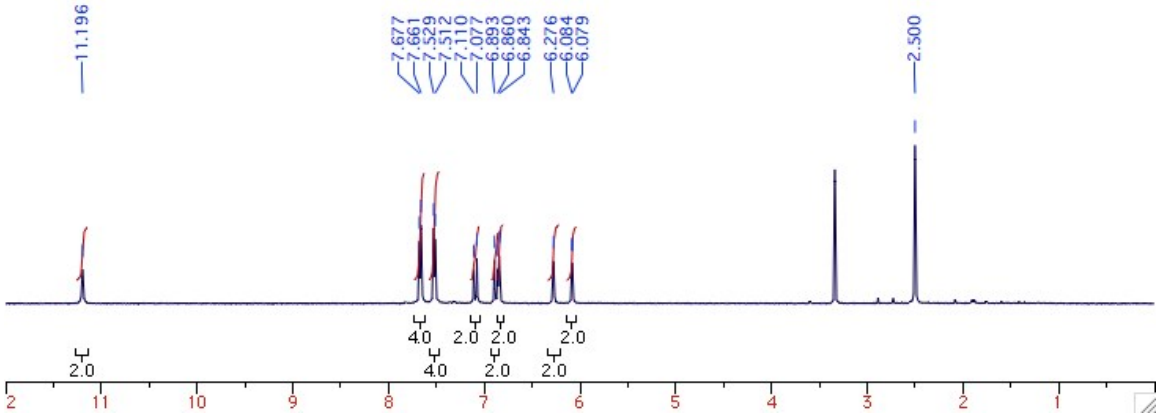
^{13}C udeft NMR (THF-d_8, 125 MHz):



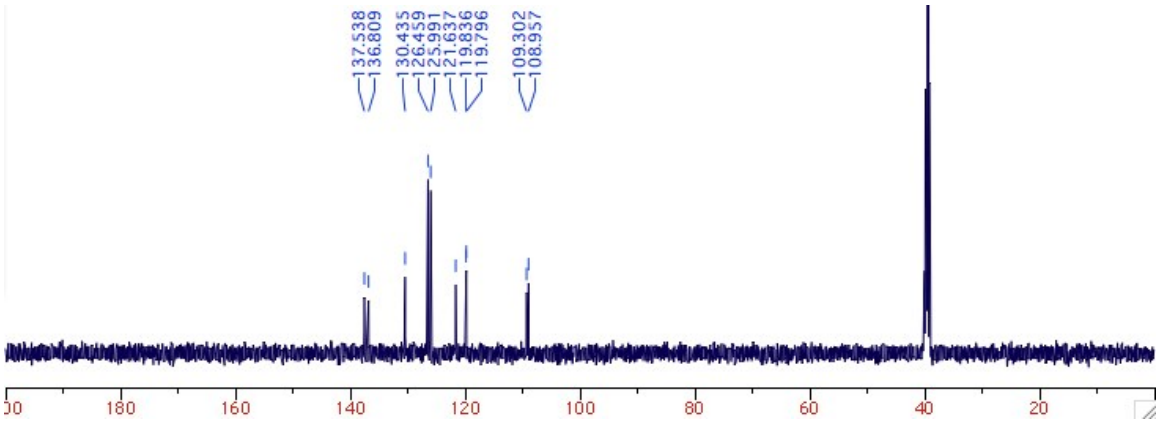
4,4'-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)-1,1'-biphenyl (2c)



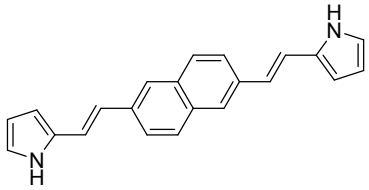
^{1}H NMR (DMSO-d_6, 500 MHz):



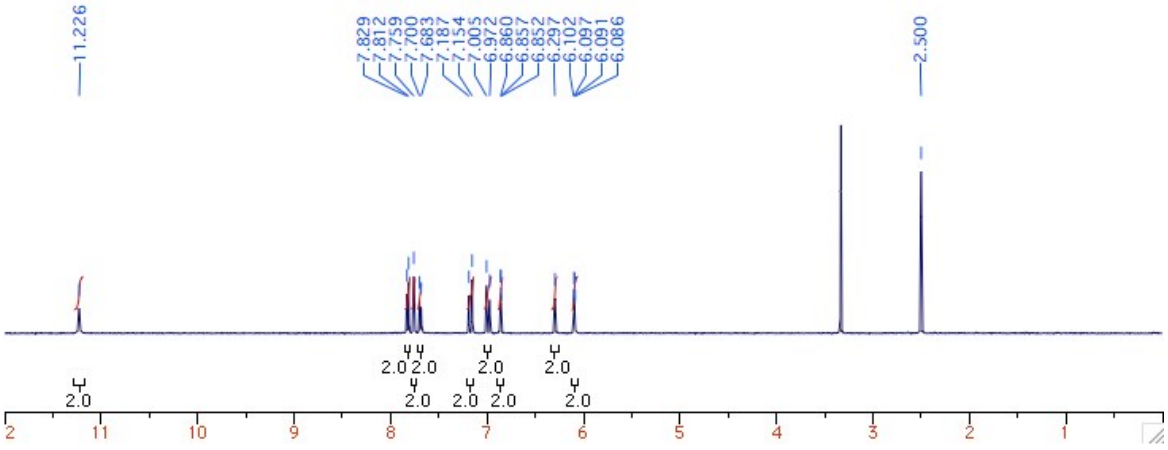
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



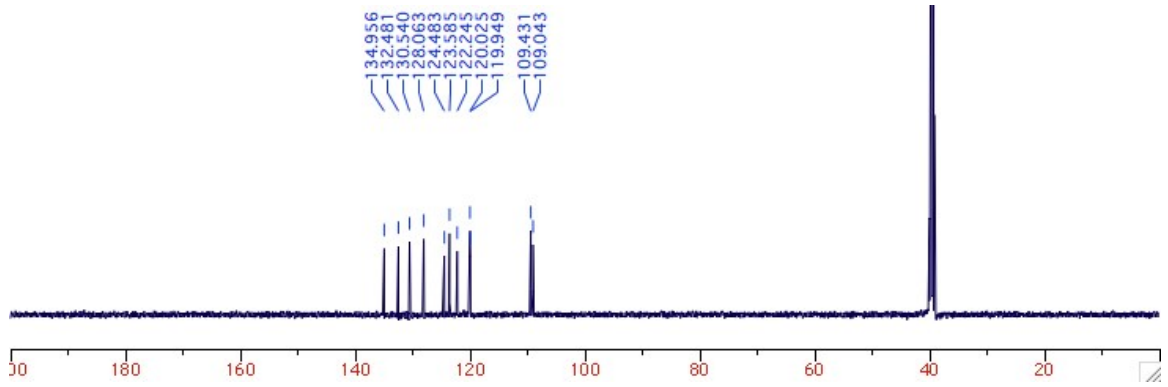
2,6-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)naphthalene (2d)



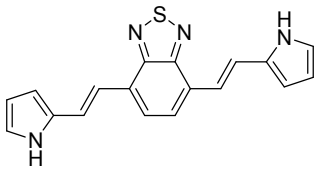
^{1}H NMR (DMSO-d_6, 500 MHz):



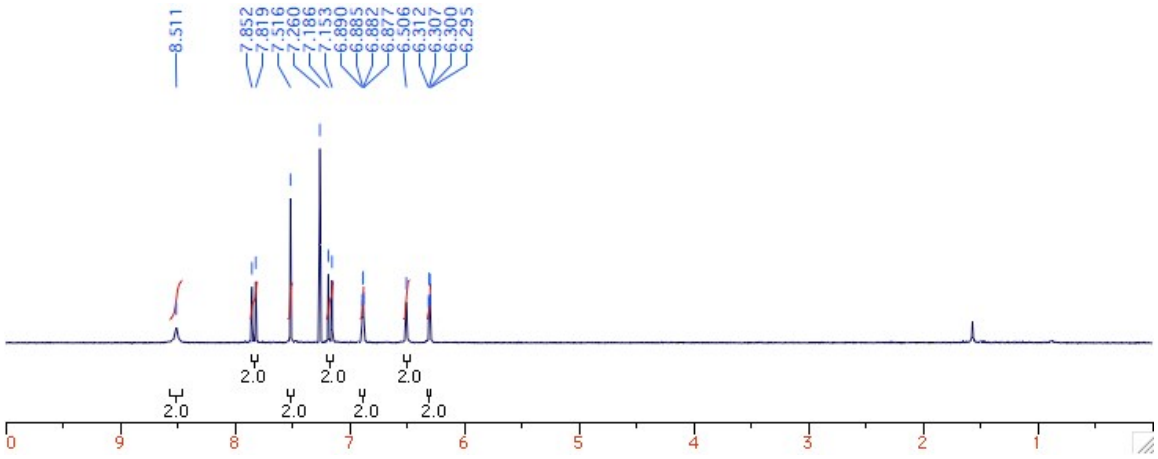
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



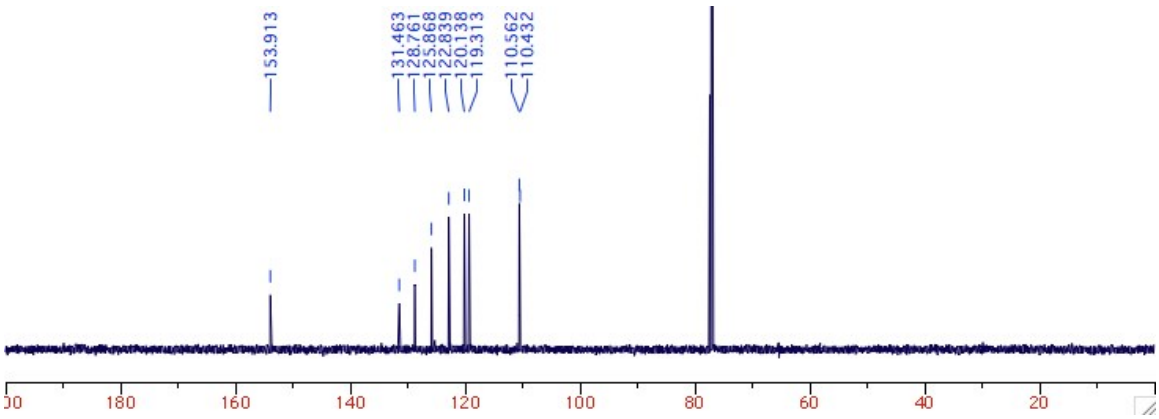
4,7-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)benzo[*c*][1,2,5]thiadiazole (2e)



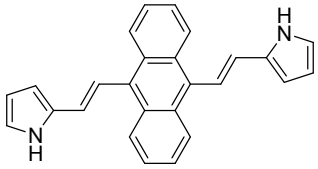
^{1}H NMR ($CDCl_3$, 500 MHz):



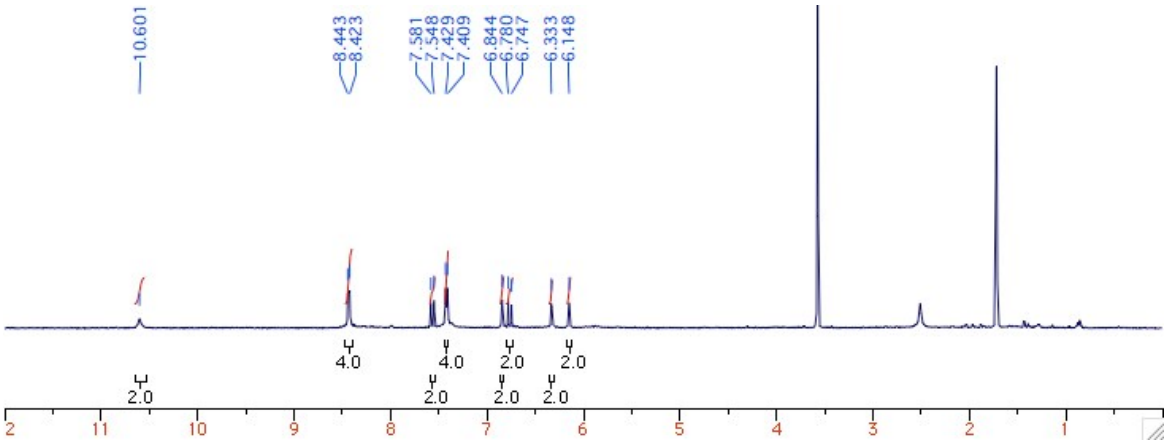
^{13}C udeft NMR ($CDCl_3$, 125 MHz):



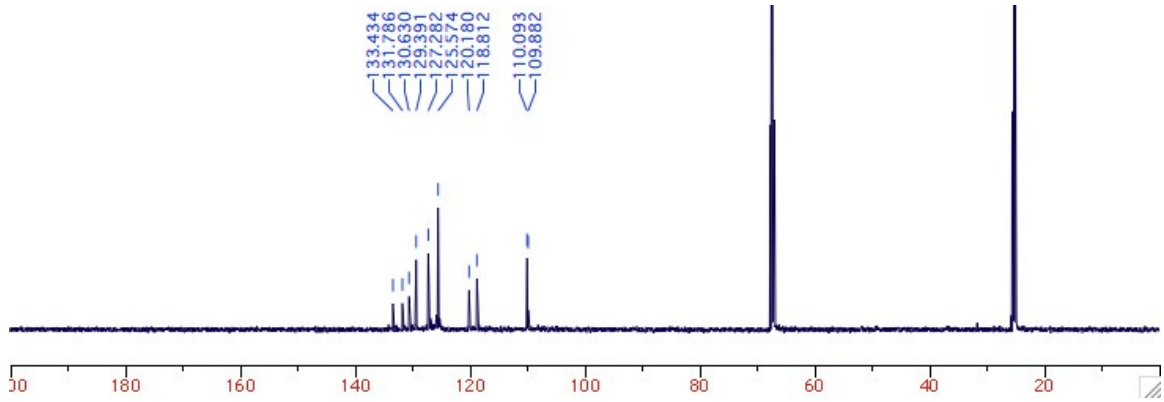
9,10-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)anthracene (2f)



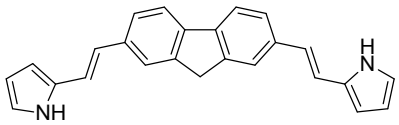
^{1}H NMR (THF-d_8, 500 MHz):



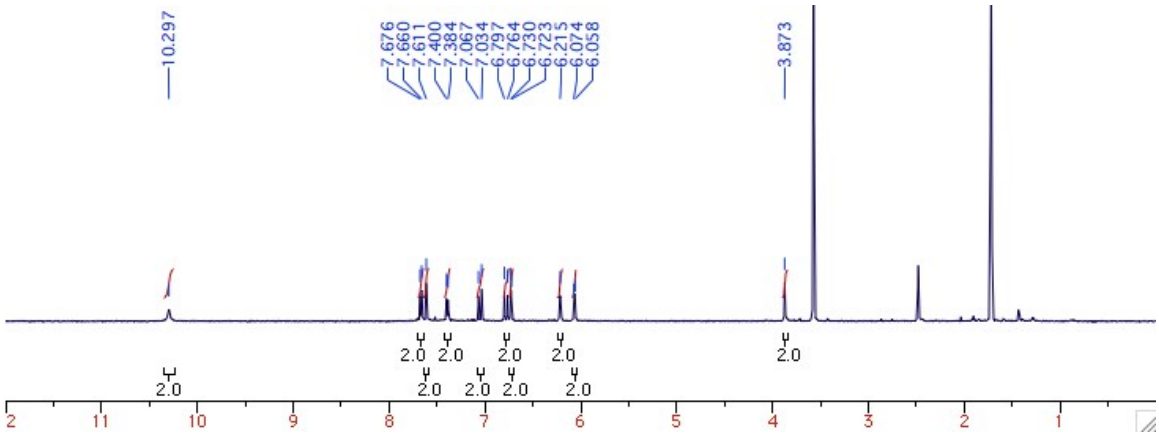
^{13}C udeft NMR (THF-d_8, 125 MHz):



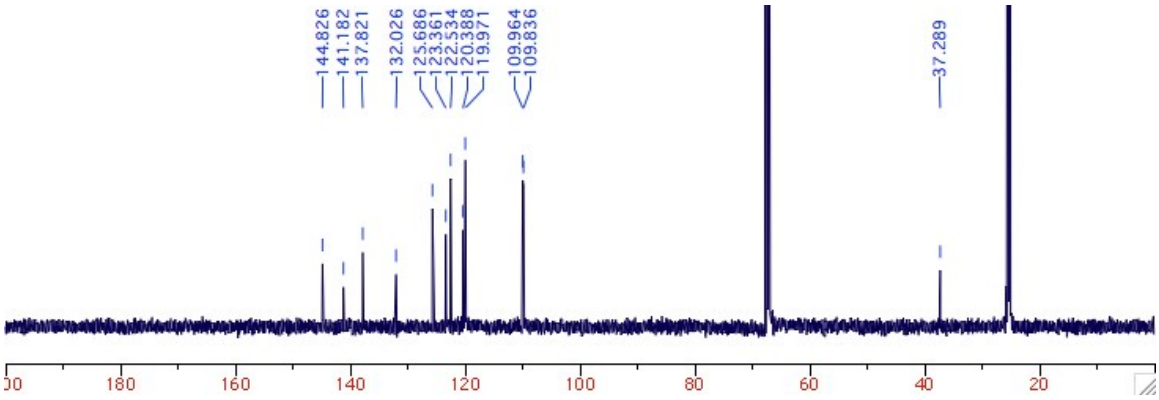
2,7-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)-9H-fluorene (2g)



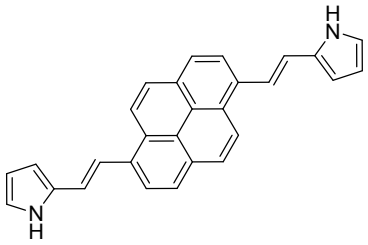
^{1}H NMR (THF-d_8, 500 MHz):



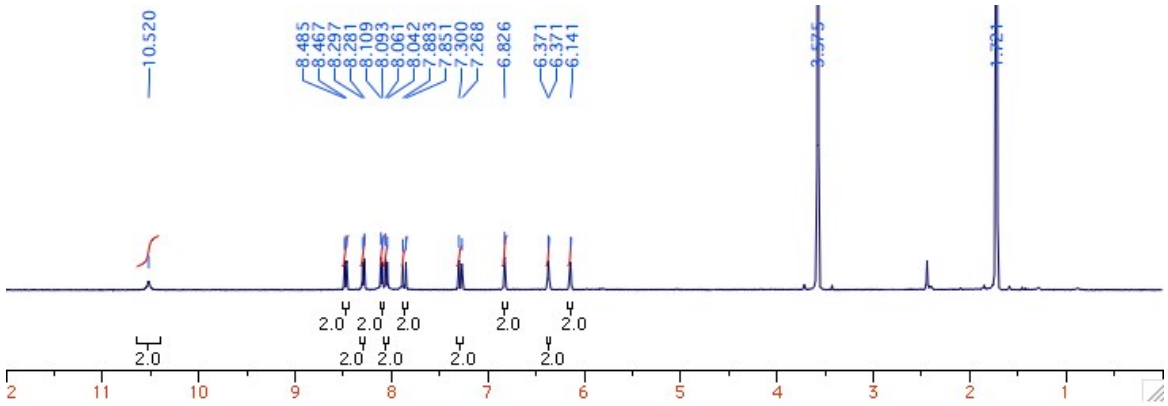
^{13}C udeft NMR (THF-d_8, 125 MHz):



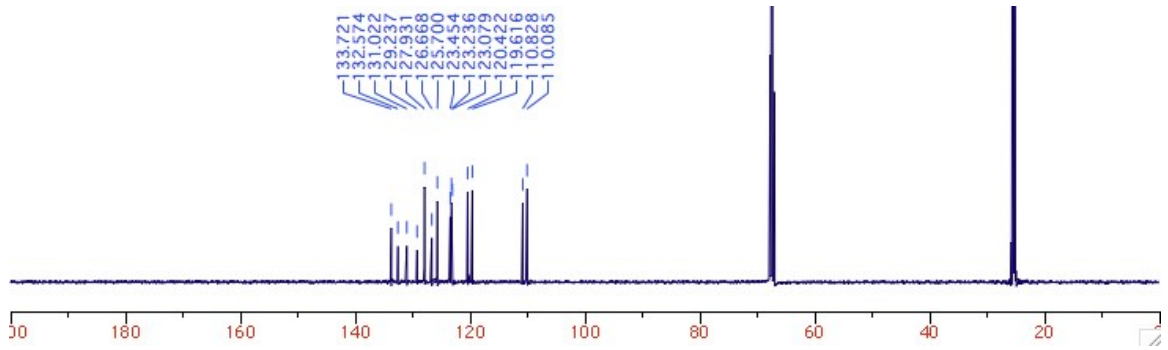
1,6-Bis((E)-2-(1H-pyrrol-2-yl)vinyl)pyrene (2h)



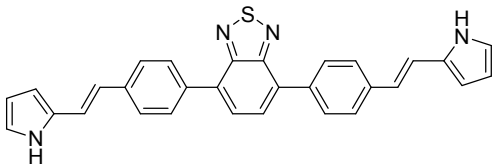
^{1}H NMR (THF-d_8, 500 MHz):



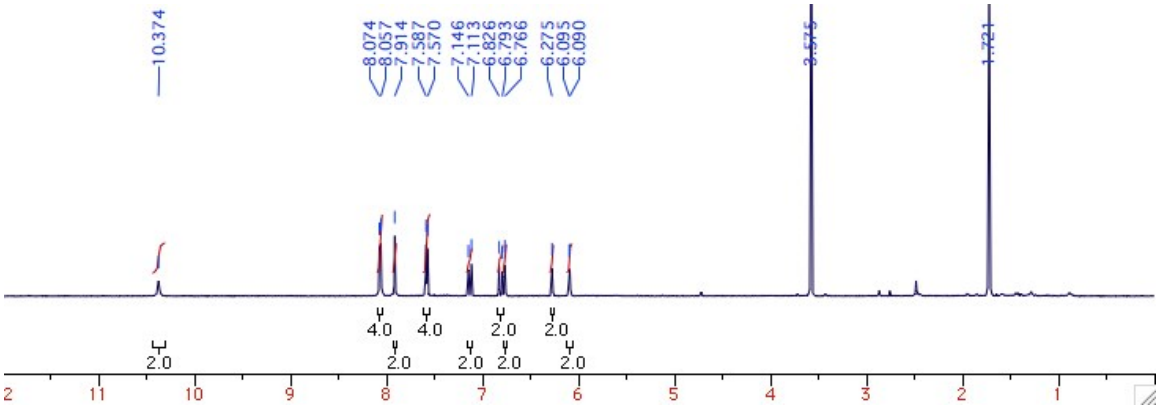
^{13}C udeft NMR (THF-d_8, 125 MHz):



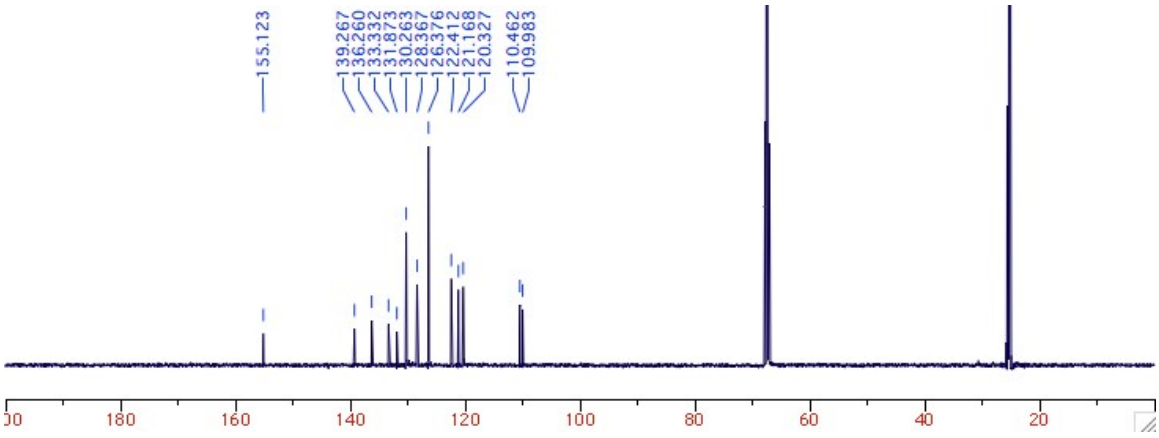
4,7-Bis(4-((E)-2-(1H-pyrrol-2-yl)vinyl)phenyl)benzo[*c*][1,2,5]thiadiazole (2i)



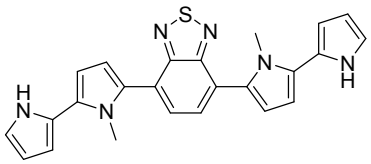
^{1}H NMR (THF-d_8, 500 MHz):



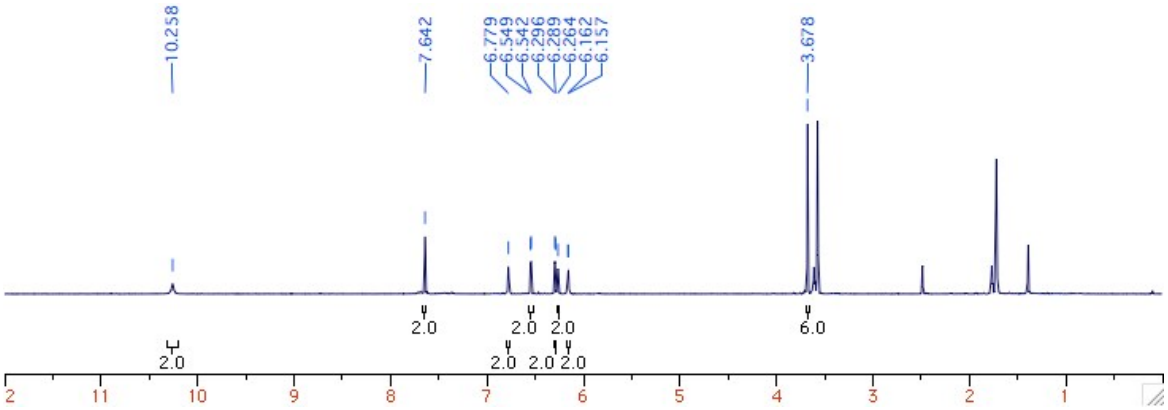
^{13}C udeft NMR (THF-d_8, 125 MHz):



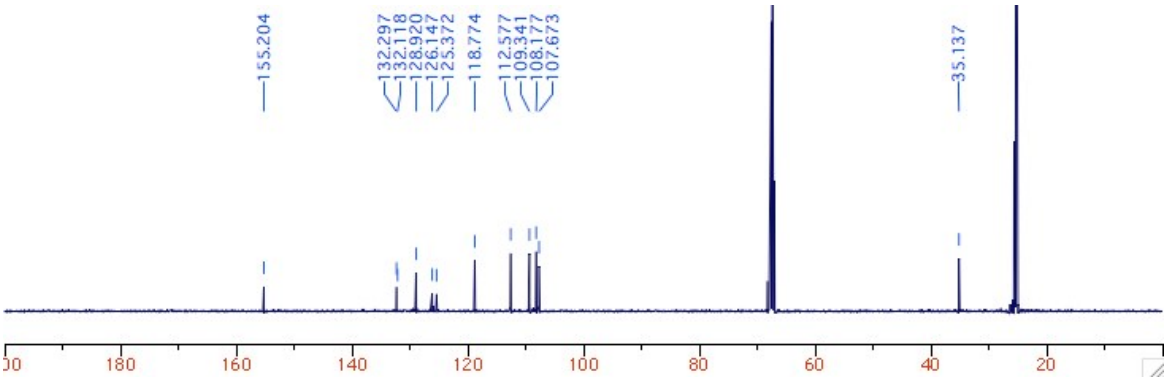
4,7-Bis(1-methyl-1H,1'H-[2,2'-bipyrrol]-5-yl)benzo[*c*][1,2,5]thiadiazole (2j)



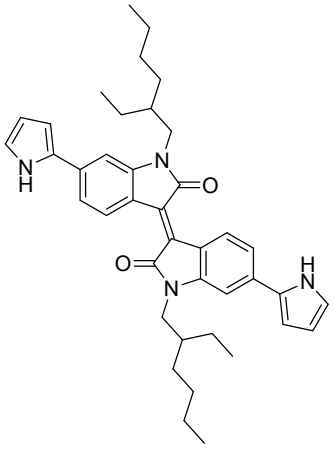
^{1}H NMR (THF-d_8, 500 MHz):



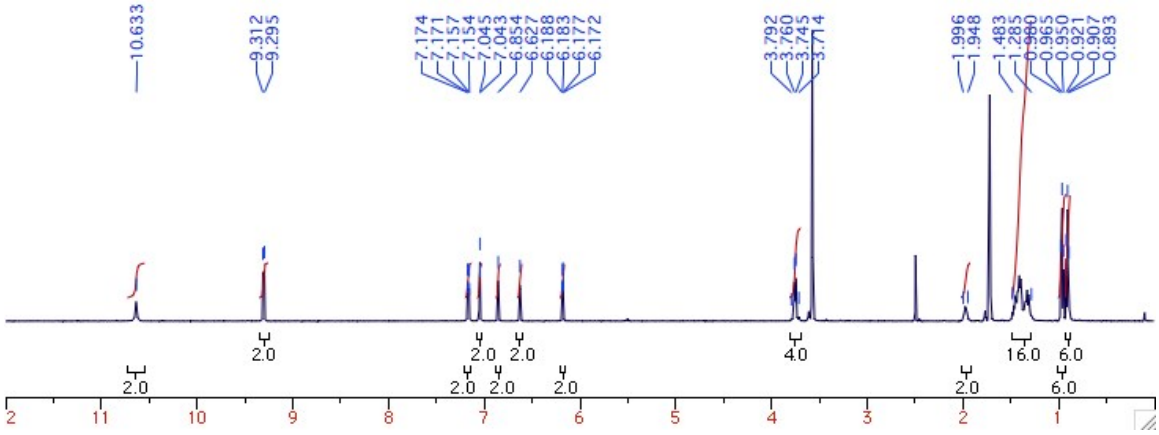
^{13}C udeft NMR (THF-d_8, 125 MHz):



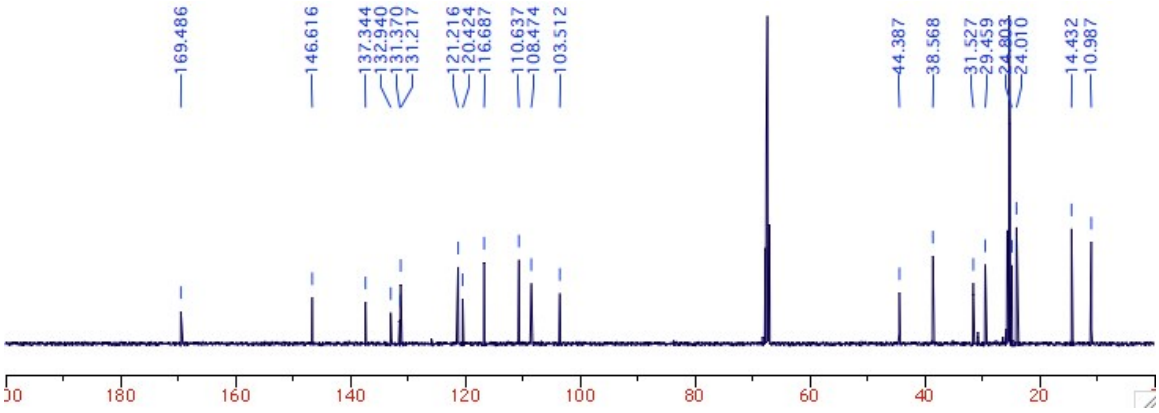
N,*N*'-Bis(2-ethylhexyl)-6,6'-Bis(1H-pyrrol-2-yl)isoindigo (2k)



^{1}H NMR (THF-d_8, 500 MHz):

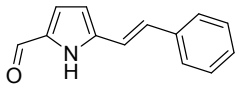


^{13}C udeft NMR (THF-d_8, 125 MHz):

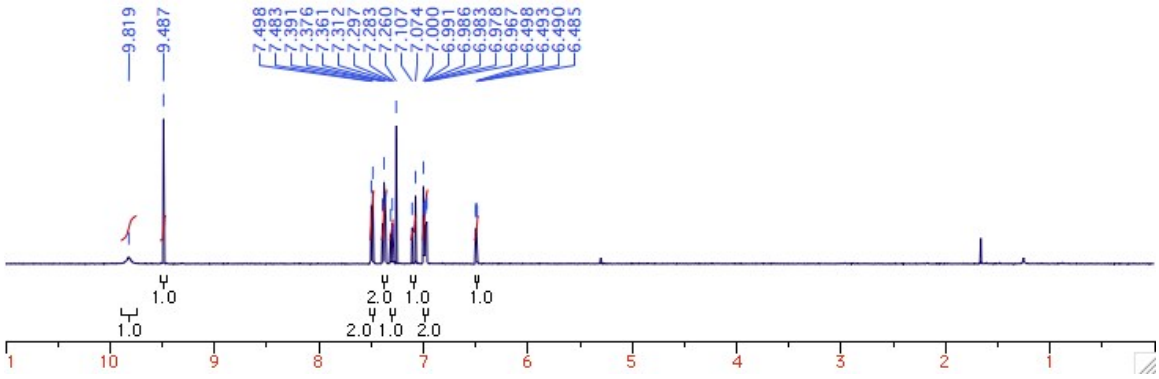


Bis(formylpyrroles) (3)

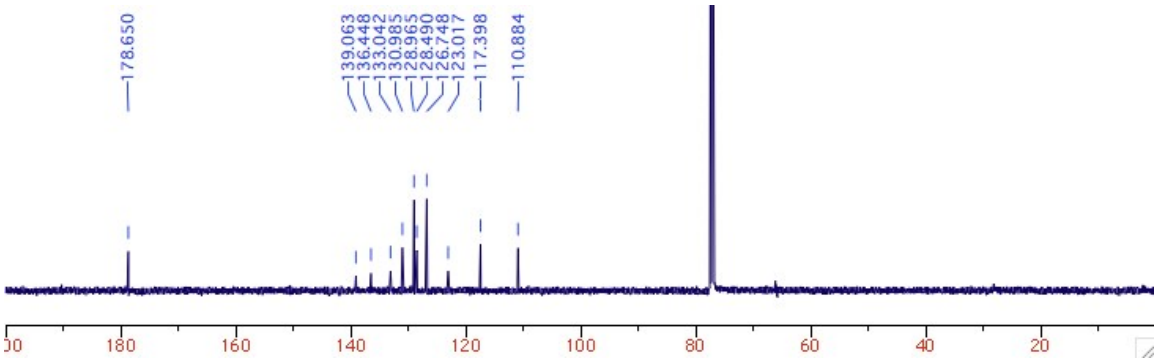
(*E*)-5-Styryl-1H-pyrrole-2-carbaldehyde (3a)



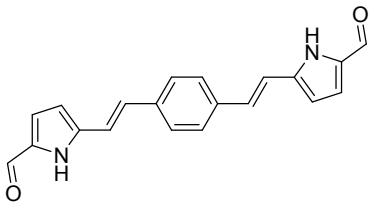
^{1}H NMR ($CDCl_3$, 500 MHz):



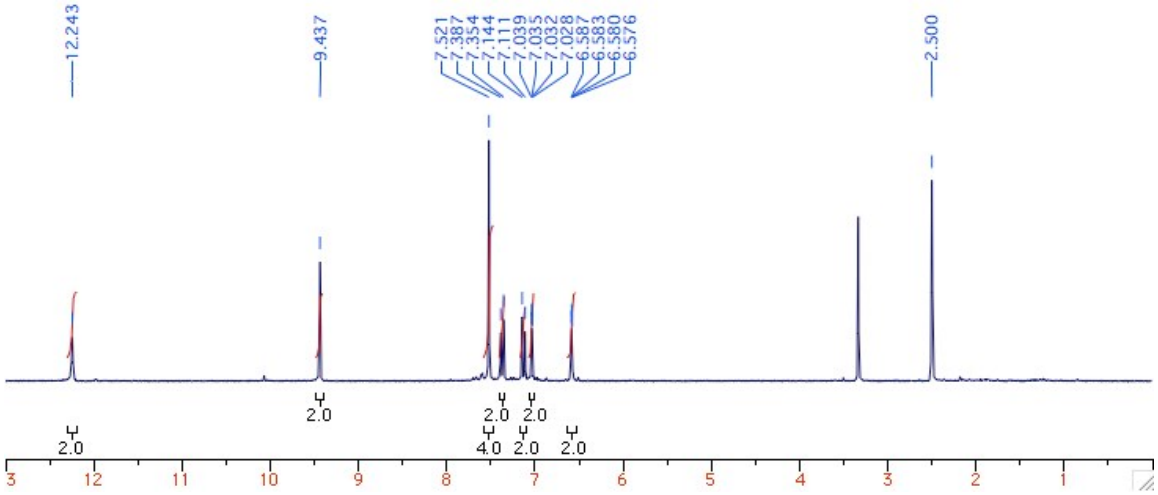
^{13}C udeft NMR ($CDCl_3$, 125 MHz):



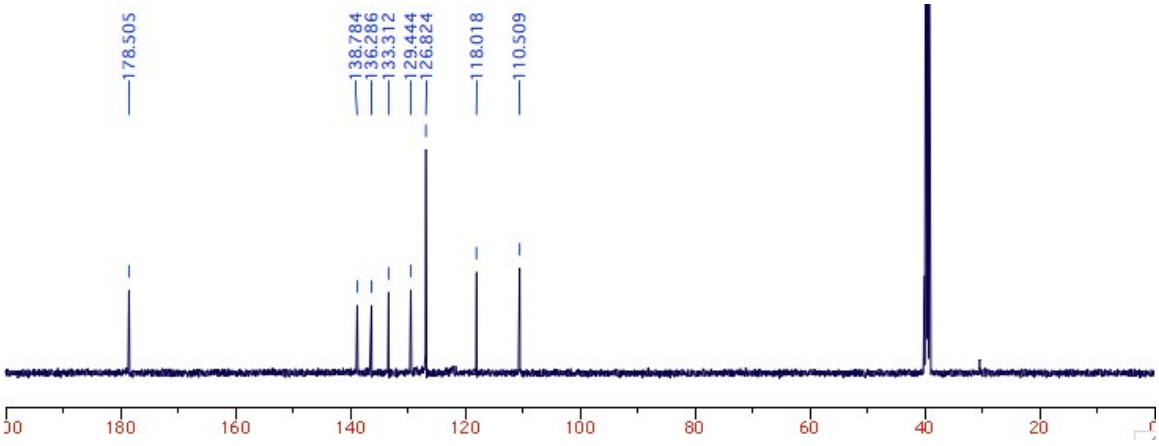
5,5'-((1E,1'E)-1,4-Phenylenebis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3b)



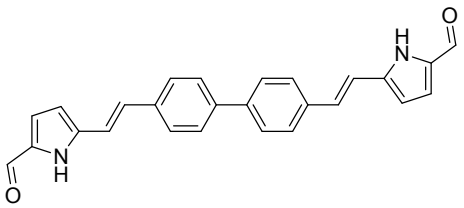
^{1}H NMR (DMSO-d_6, 500 MHz):



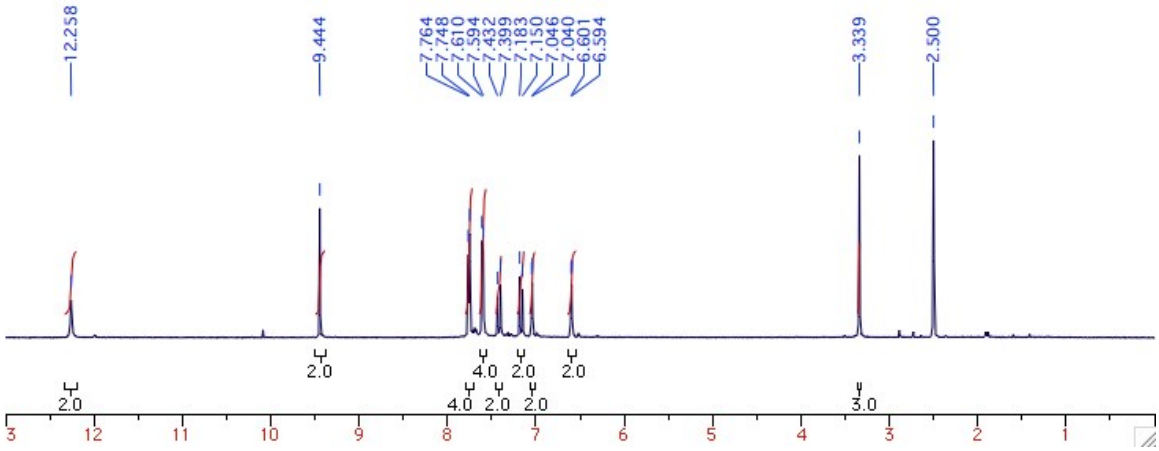
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



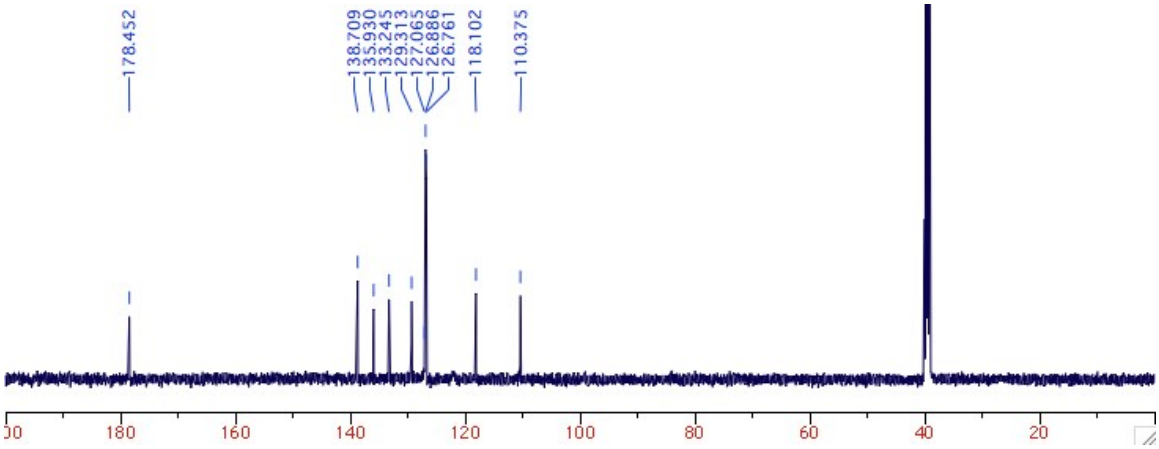
5,5'-((1E,1'E)-[1,1'-biphenyl]-4,4'-diylbis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3c)



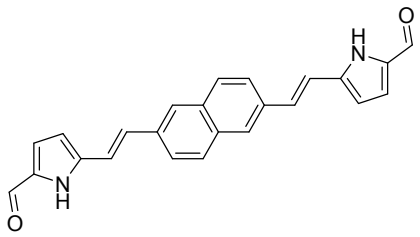
^{1}H NMR (DMSO-d_6, 500 MHz):



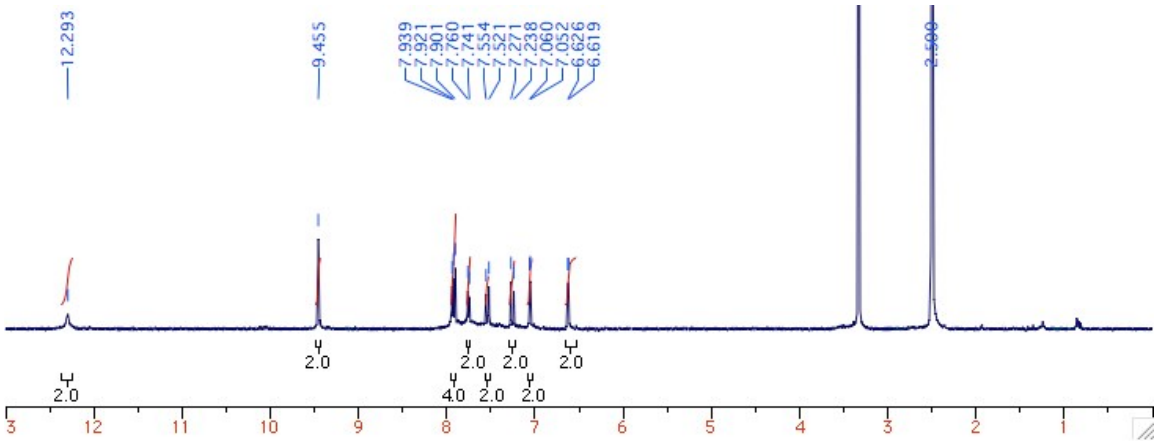
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



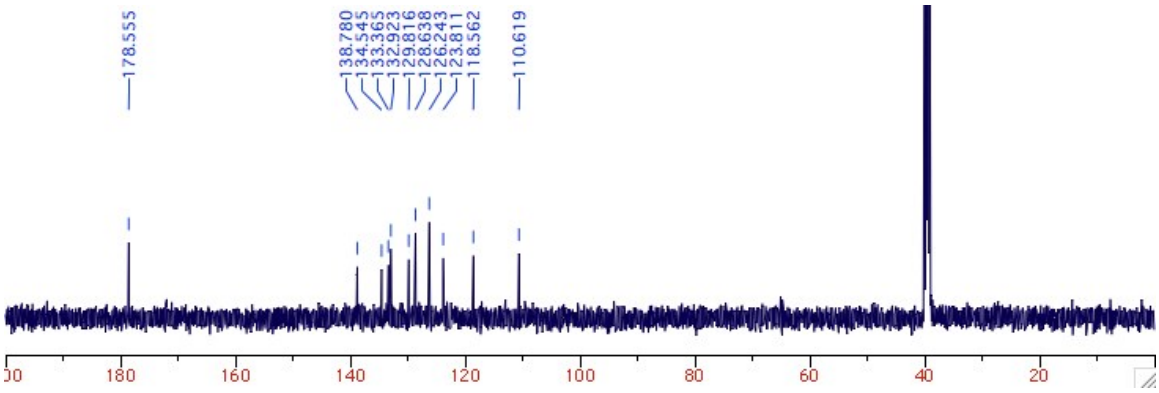
5,5'-((1E,1'E)-naphthalene-2,6-diylbis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3d)



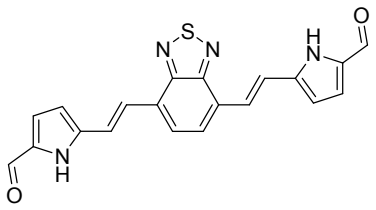
^{1}H NMR (DMSO-d_6, 500 MHz):



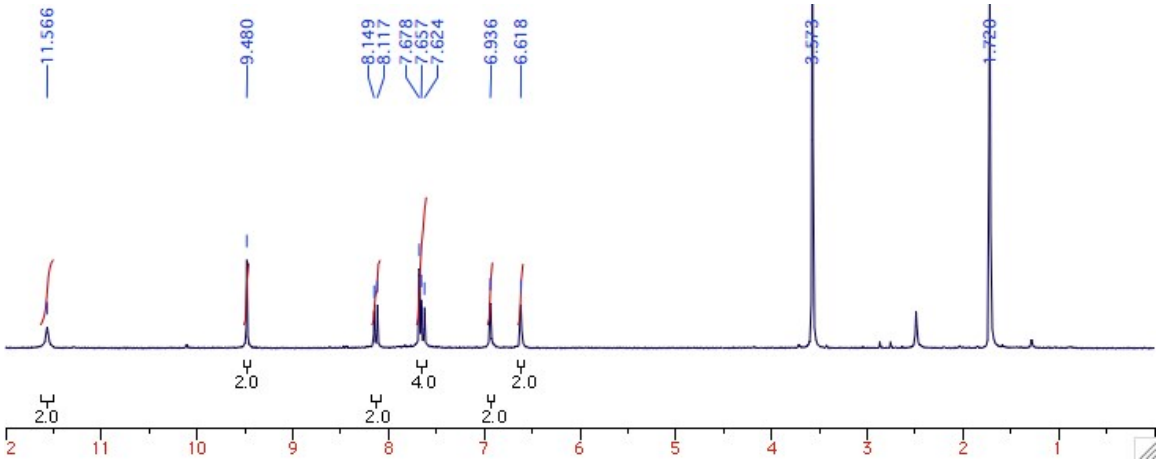
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



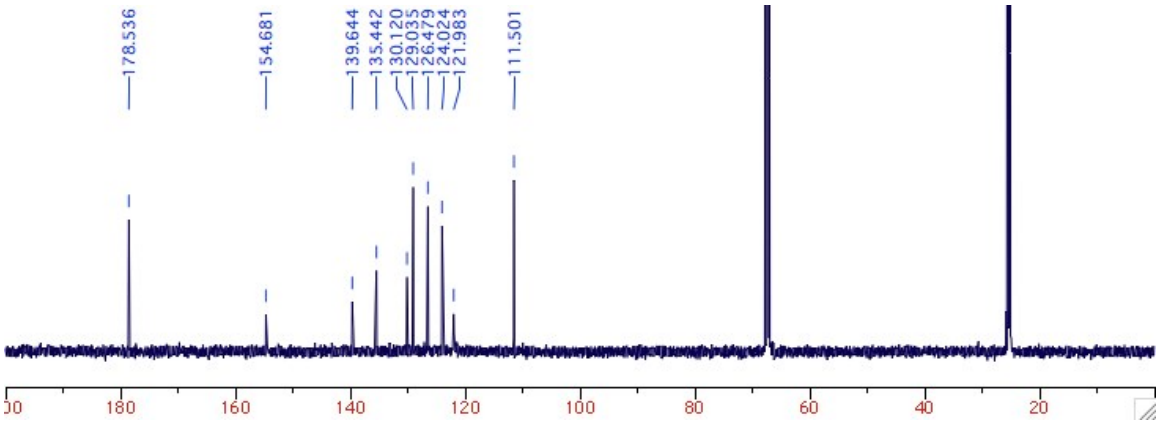
5,5'-((1E,1'E)-benzo[c][1,2,5]thiadiazole-4,7-diylbis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3e)



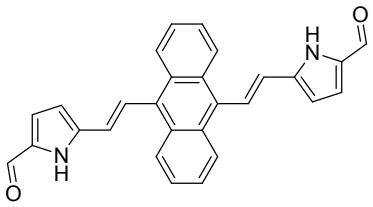
^{1}H NMR (THF-d_8, 500 MHz):



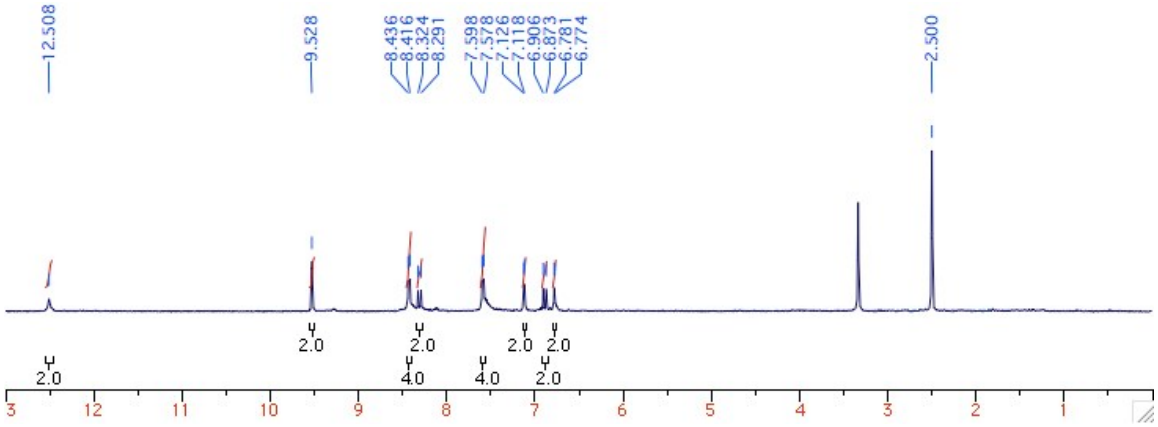
^{13}C udeft NMR (THF-d_8, 125 MHz):



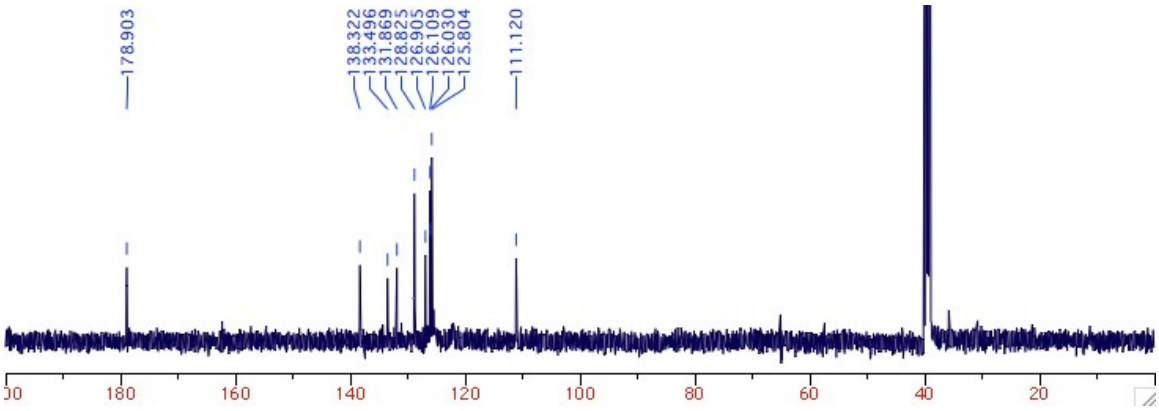
5,5'-((1E,1'E)-Anthracene-9,10-diylbis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3f)



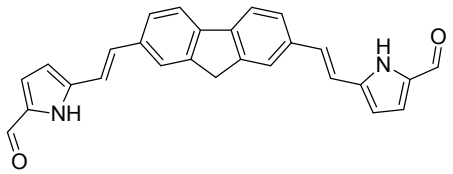
^{1}H NMR (DMSO-d_6, 500 MHz):



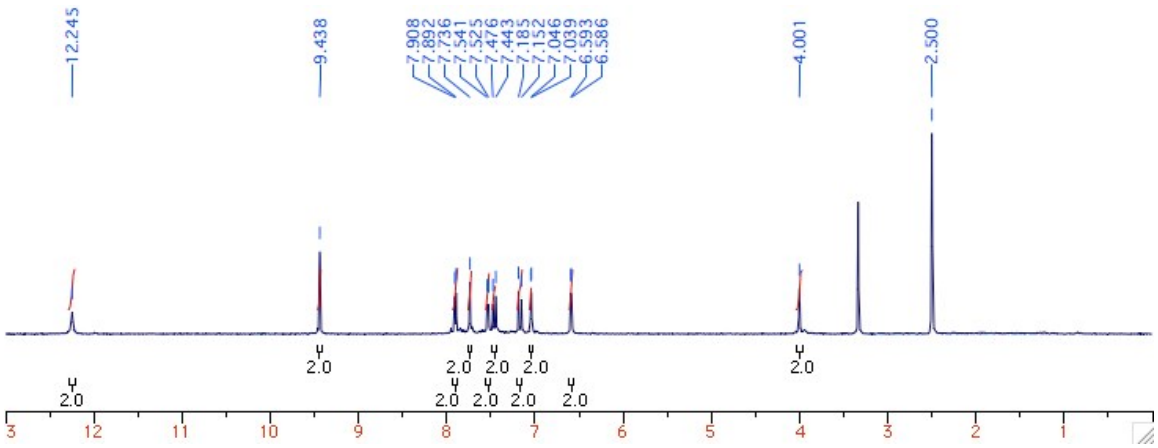
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



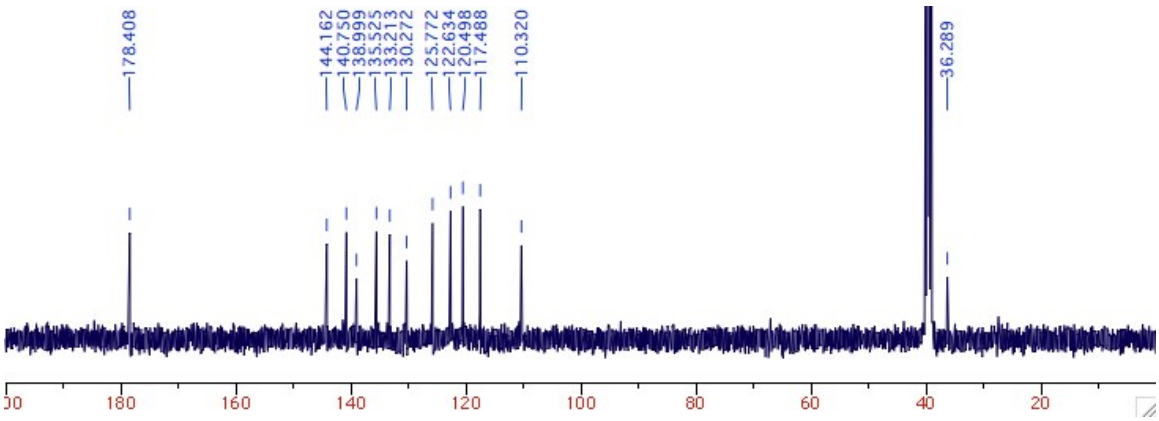
5,5'-((1E,1'E)-(9H-Fluorene-2,7-diyl)bis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3g)



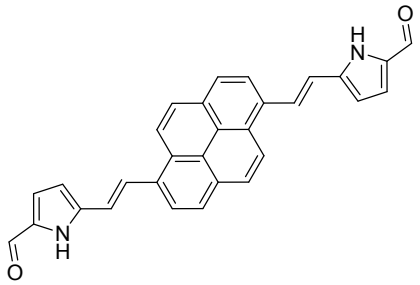
^{1}H NMR (DMSO-d_6, 500 MHz):



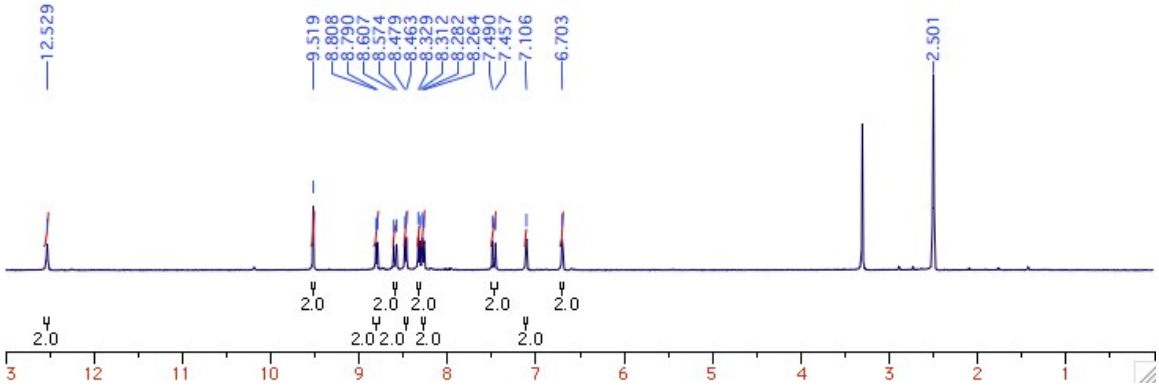
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



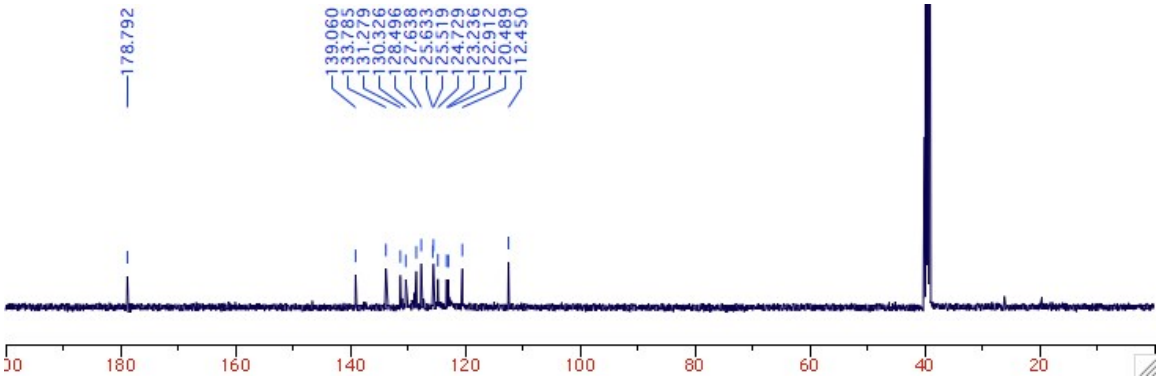
5,5'-((1E,1'E)-Pyrene-1,6-diylbis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3h)



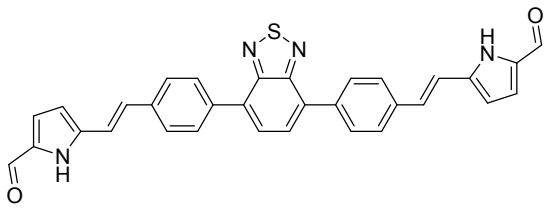
^{1}H NMR (DMSO-d_6, 500 MHz):



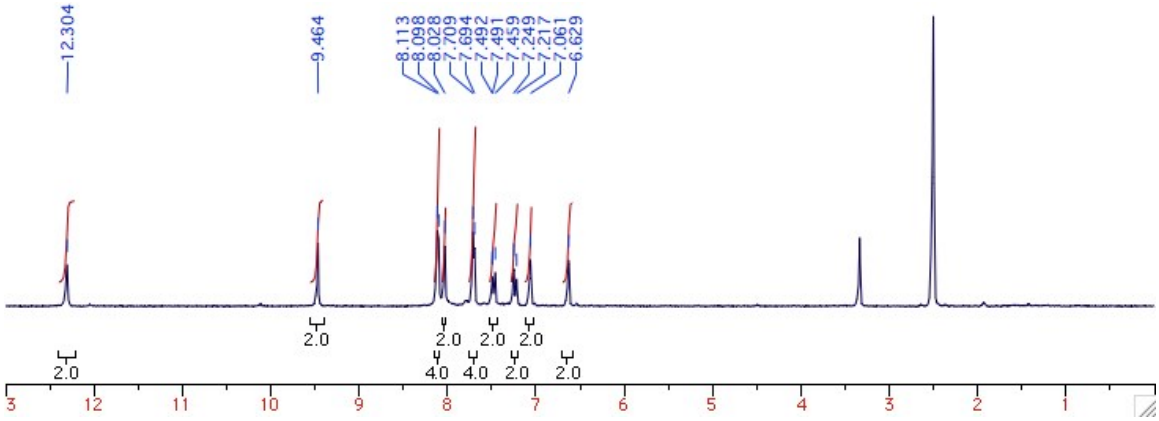
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



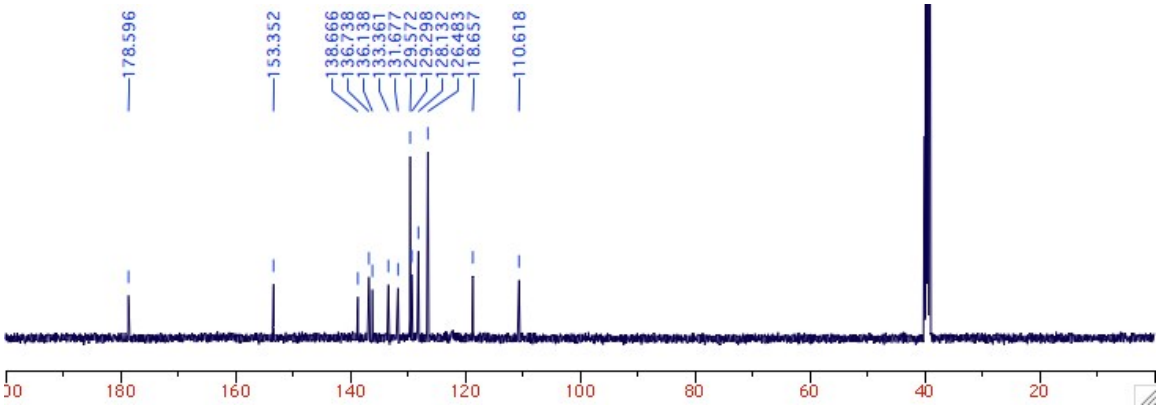
5,5'-((1E,1'E)-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(4,1-phenylene))bis(ethene-2,1-diyl))bis(1H-pyrrole-2-carbaldehyde) (3i)



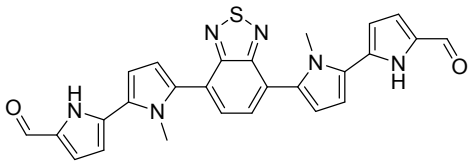
^{1}H NMR (DMSO-d_6, 500 MHz):



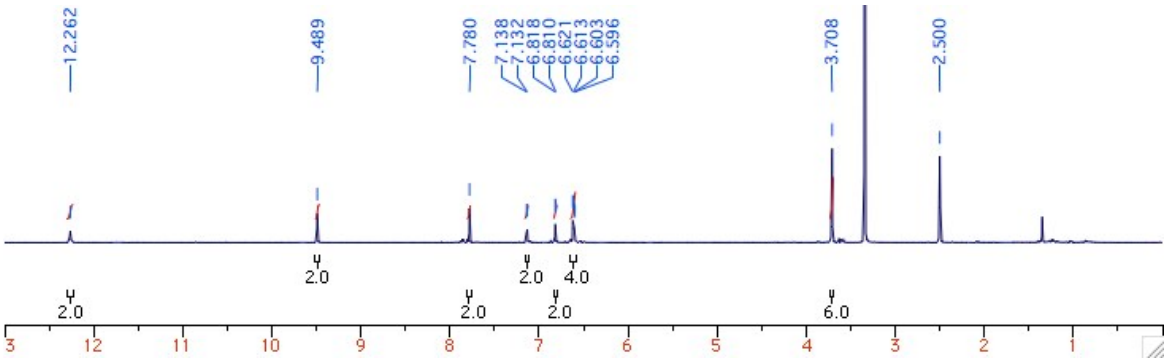
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



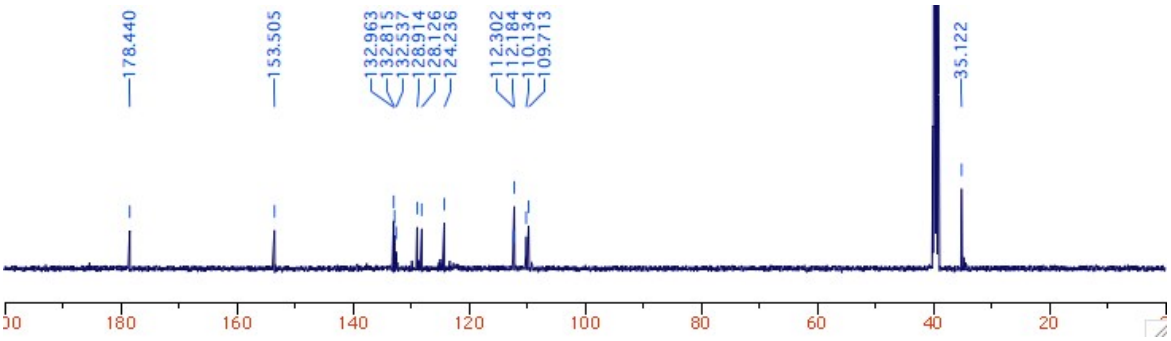
5',5'''-(Benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(1'-methyl-1H,1'H-[2,2'-bipyrrole]-5-carbaldehyde) (3j)



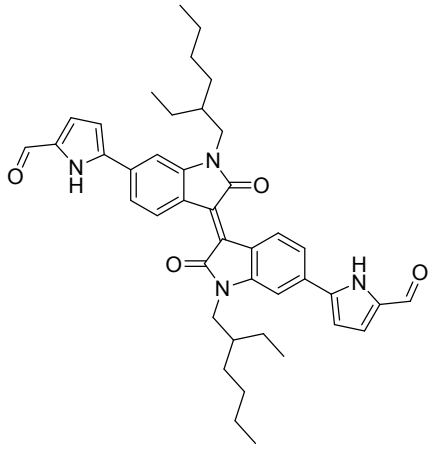
^{1}H NMR (DMSO-d_6, 500 MHz):



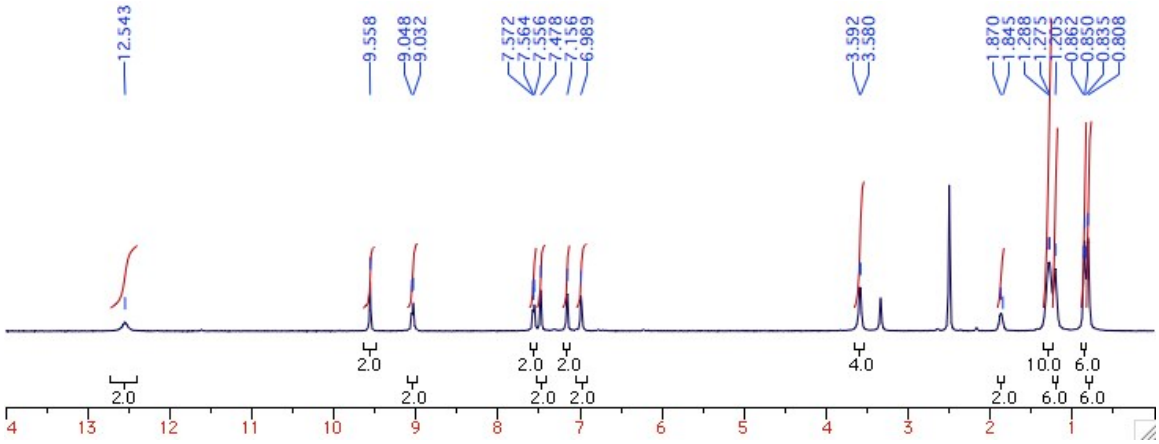
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



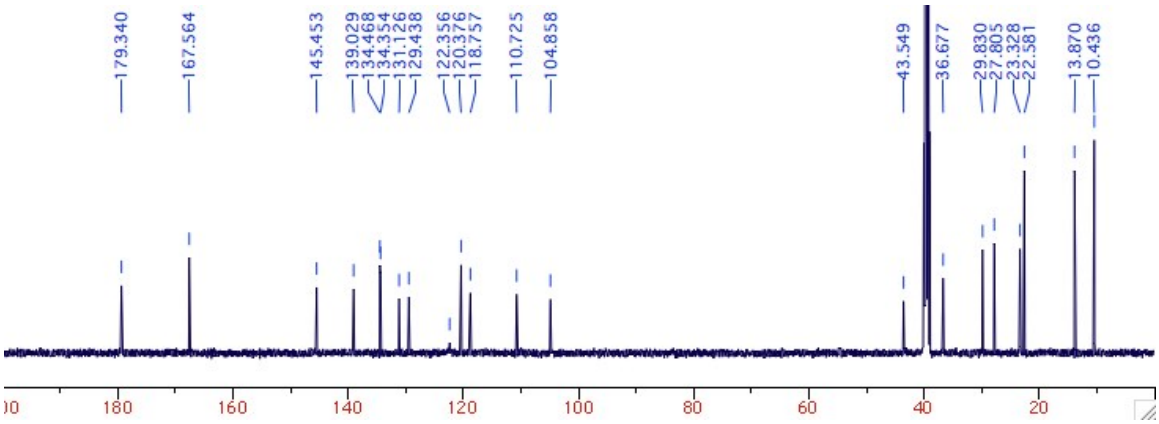
(*E*)-5,5'-(1,1'-Bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6,6'-diyl)bis(1H-pyrrole-2-carbaldehyde) (3k)



^{1}H NMR (DMSO-d_6, 500 MHz):



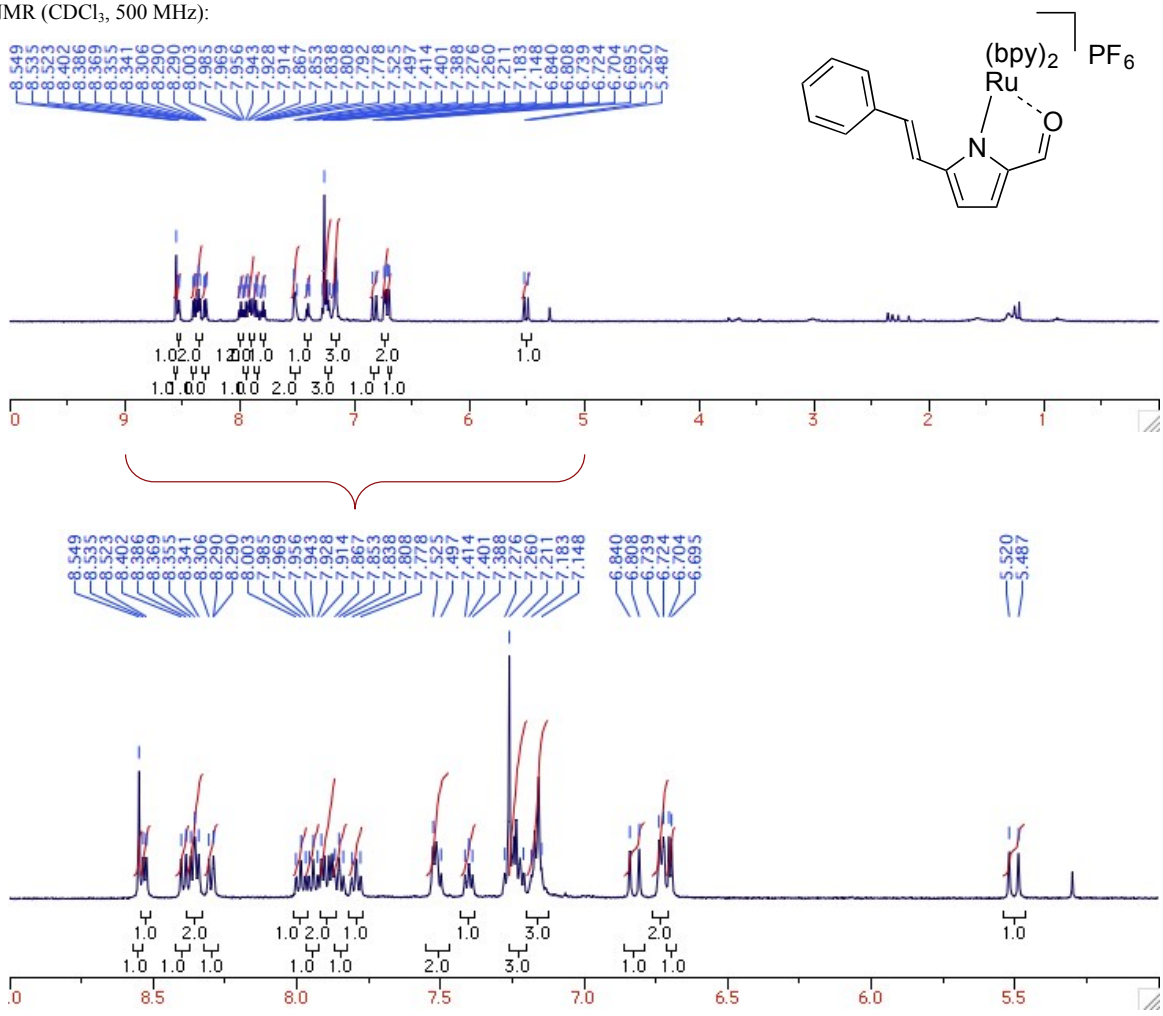
^{13}C udeft NMR (DMSO-d_6, 125 MHz):



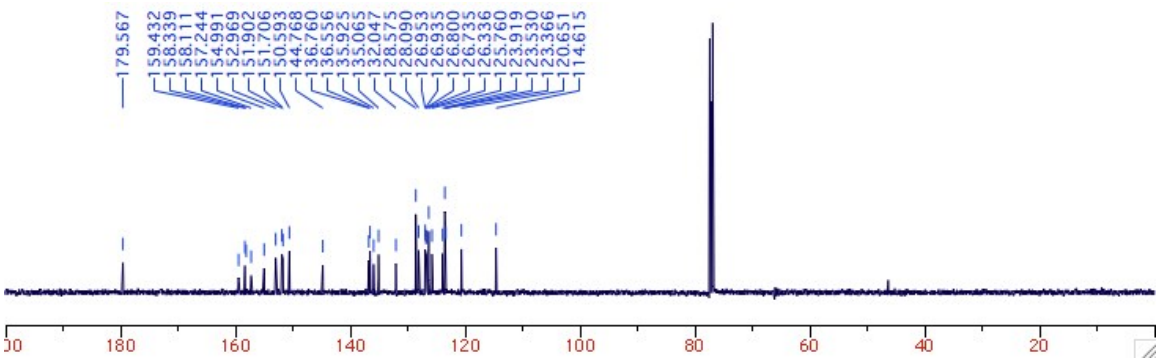
Bis(ruthenium) Complex Salts (4)

$[Ru(3a)(bpy)_2]PF_6$ complex salt (4a)

^1H NMR ($CDCl_3$, 500 MHz):

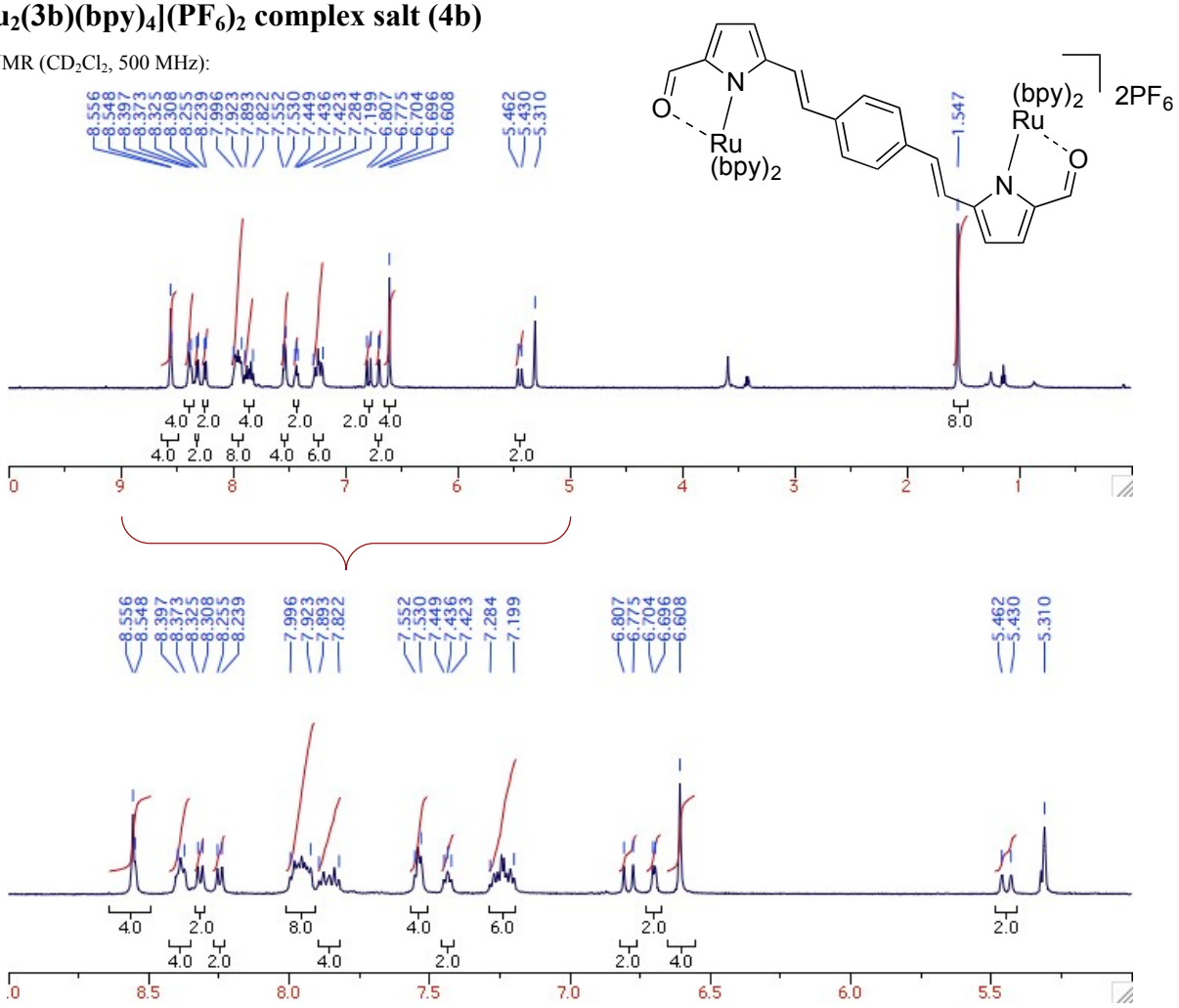


^{13}C udeft NMR ($CDCl_3$, 125 MHz):

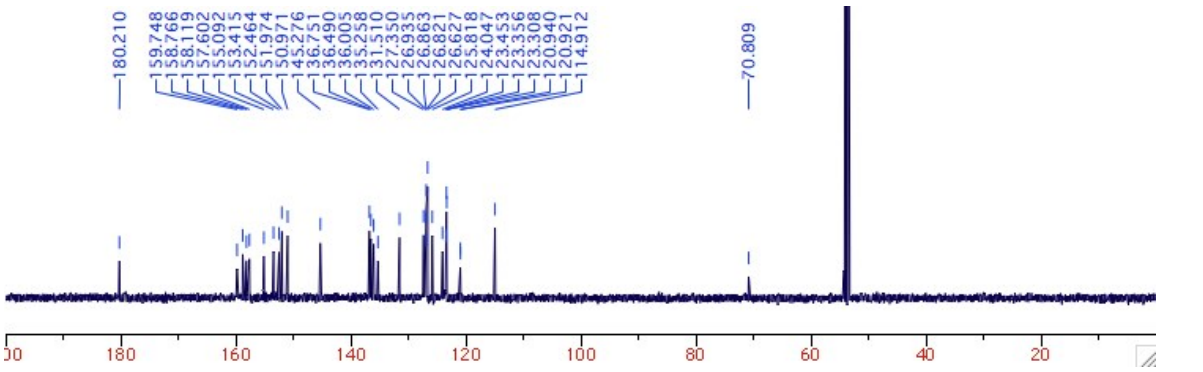


$[Ru_2(3b)(bpy)_4](PF_6)_2$ complex salt (4b)

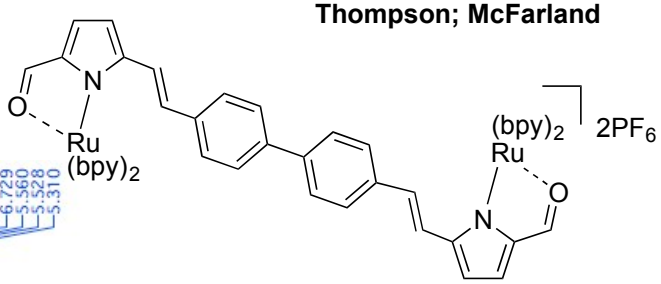
^{1}H NMR (CD_2Cl_2, 500 MHz):



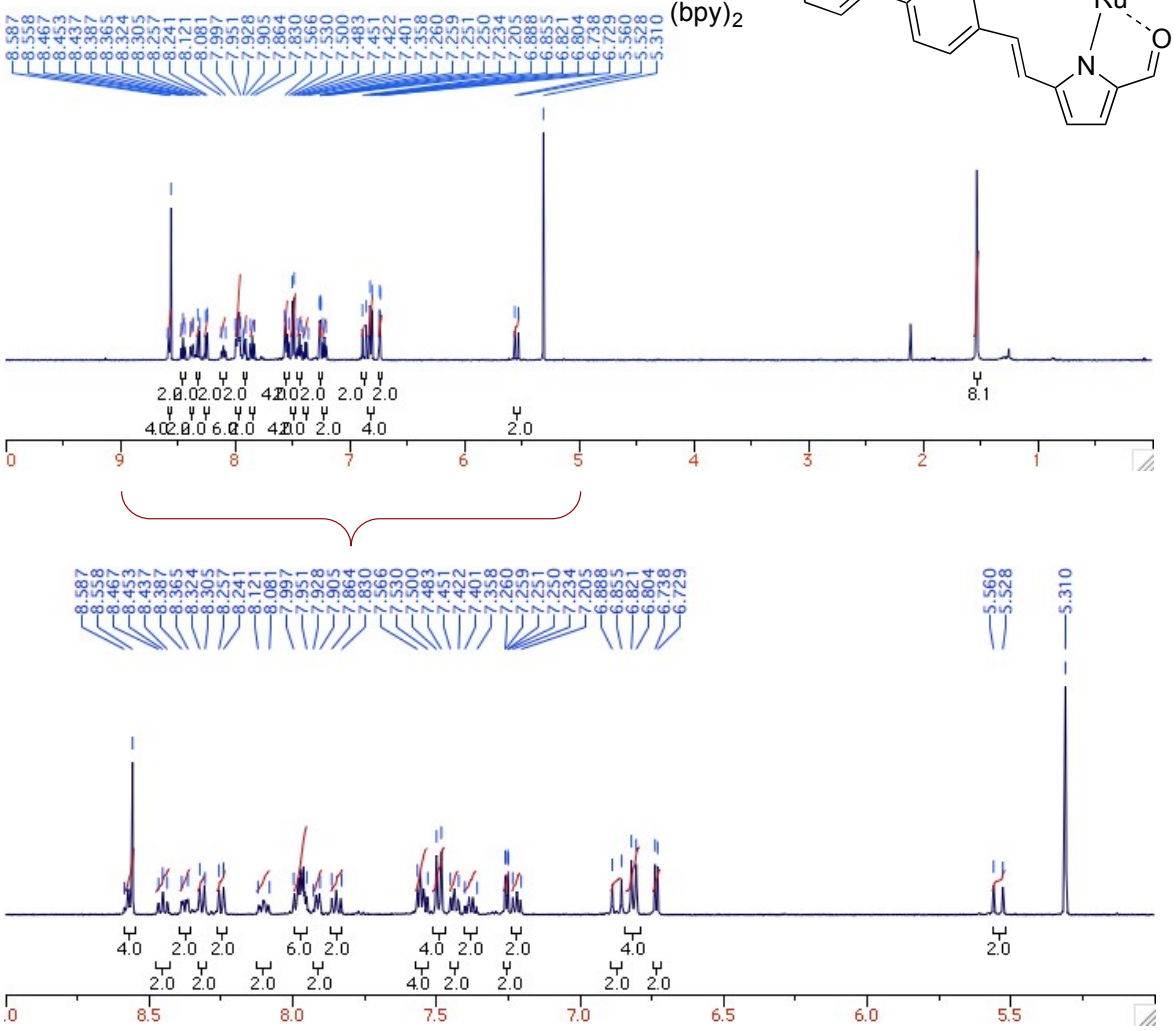
^{13}C udeft NMR (CD_2Cl_2, 125 MHz):



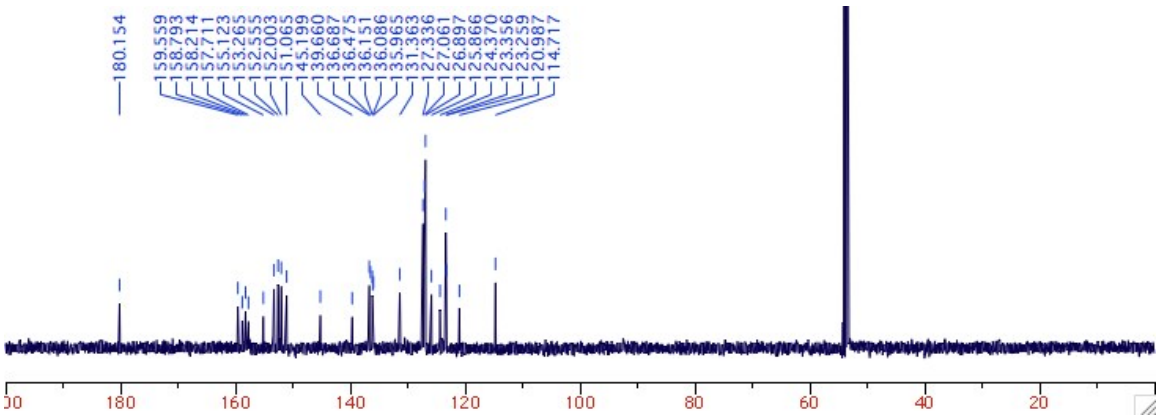
$[Ru_2(3c)(bpy)_4](PF_6)_2$ complex salt (4c)



^{1}H NMR (CD_2Cl_2, 500 MHz):

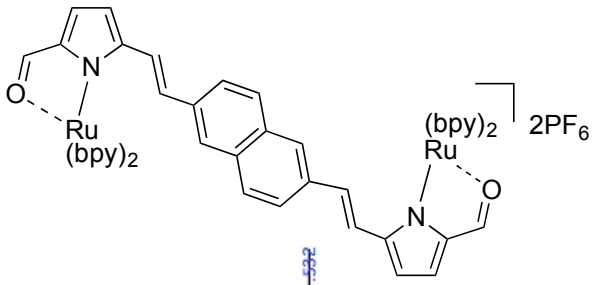


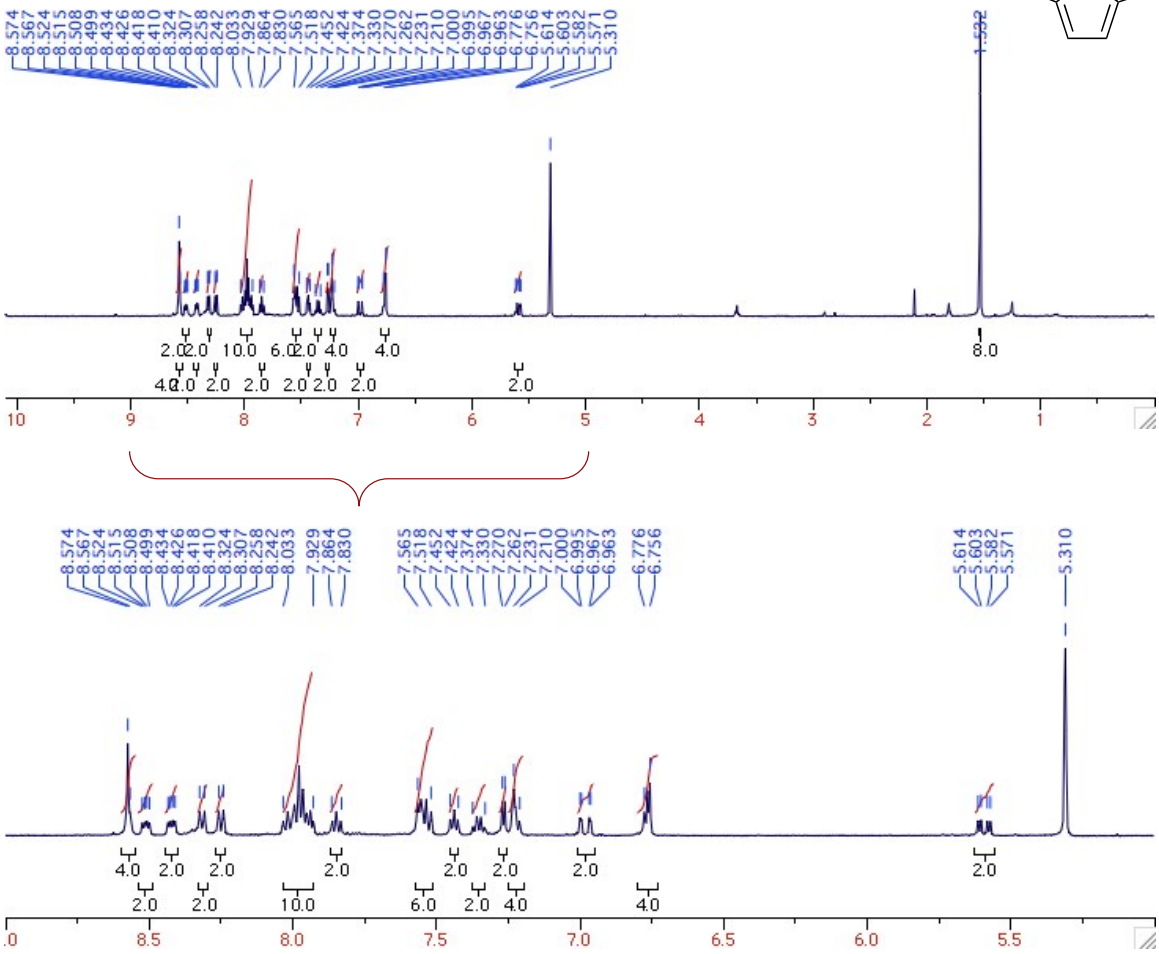
^{13}C udeft NMR (CD_2Cl_2, 125 MHz):



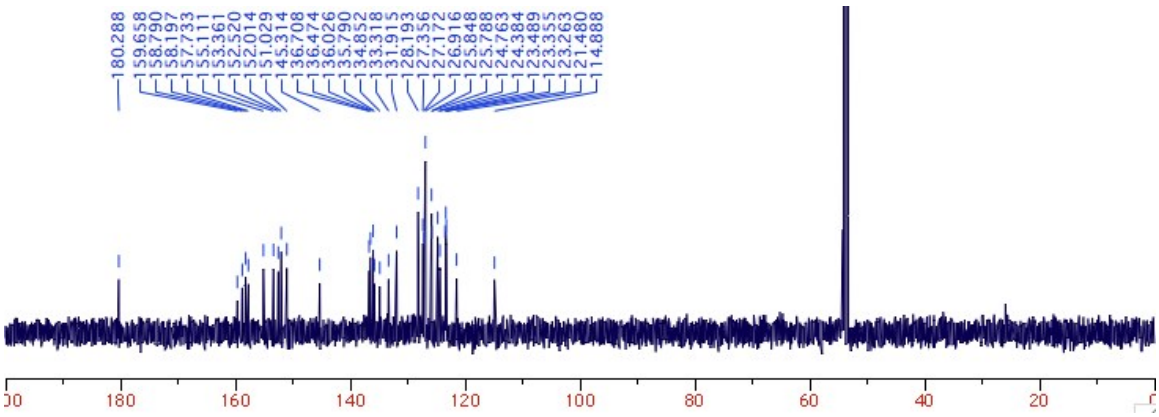
$[Ru_2(3d)(bpy)_4](PF_6)_2$ complex salt (4d)

^{1}H NMR (CD_2Cl_2, 500 MHz):



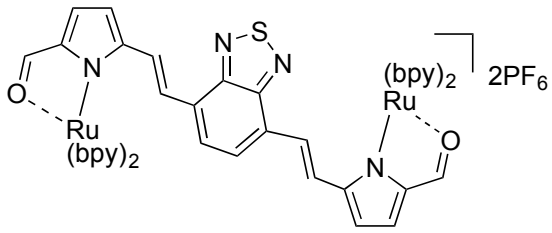


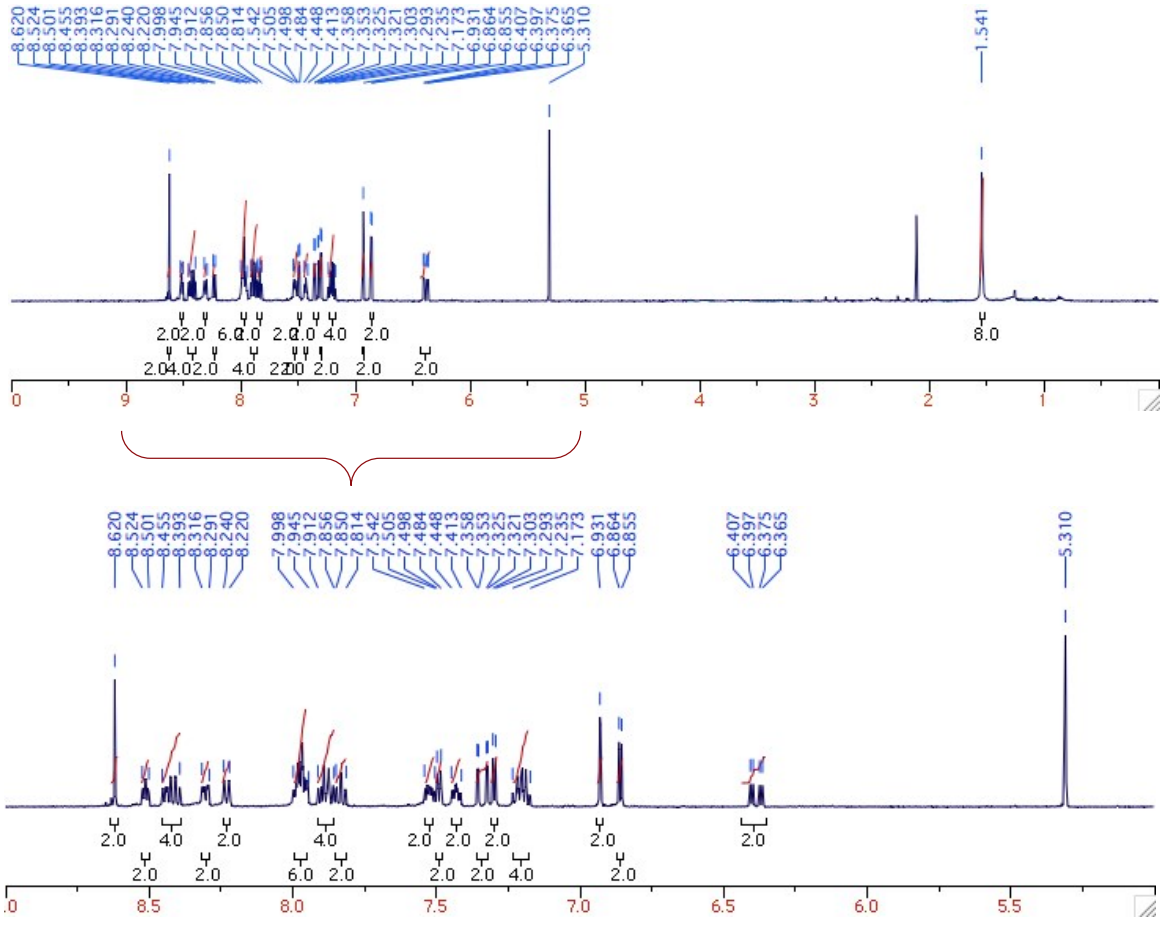
^{13}C udeft NMR (CD_2Cl_2, 125 MHz):



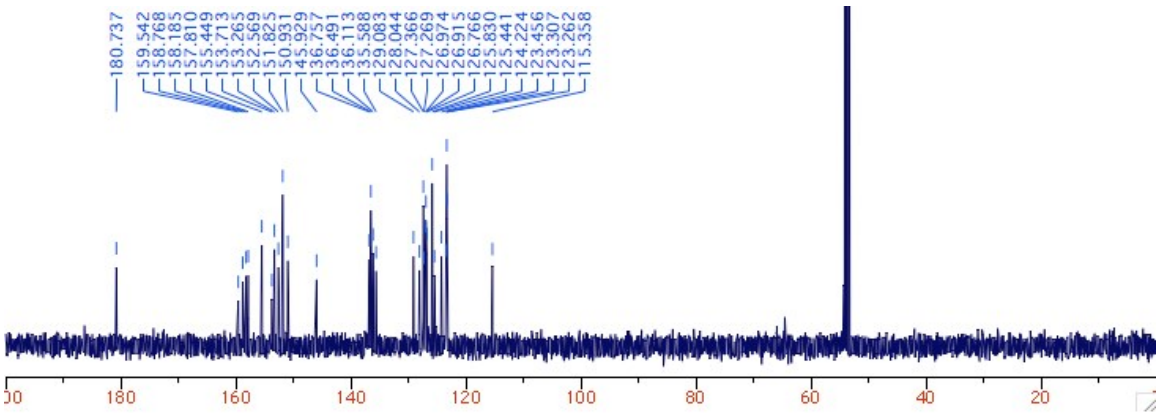
$[Ru_2(3e)(bpy)_4](PF_6)_2$ complex salt (4e)

^{1}H NMR (CD_2Cl_2, 500 MHz):



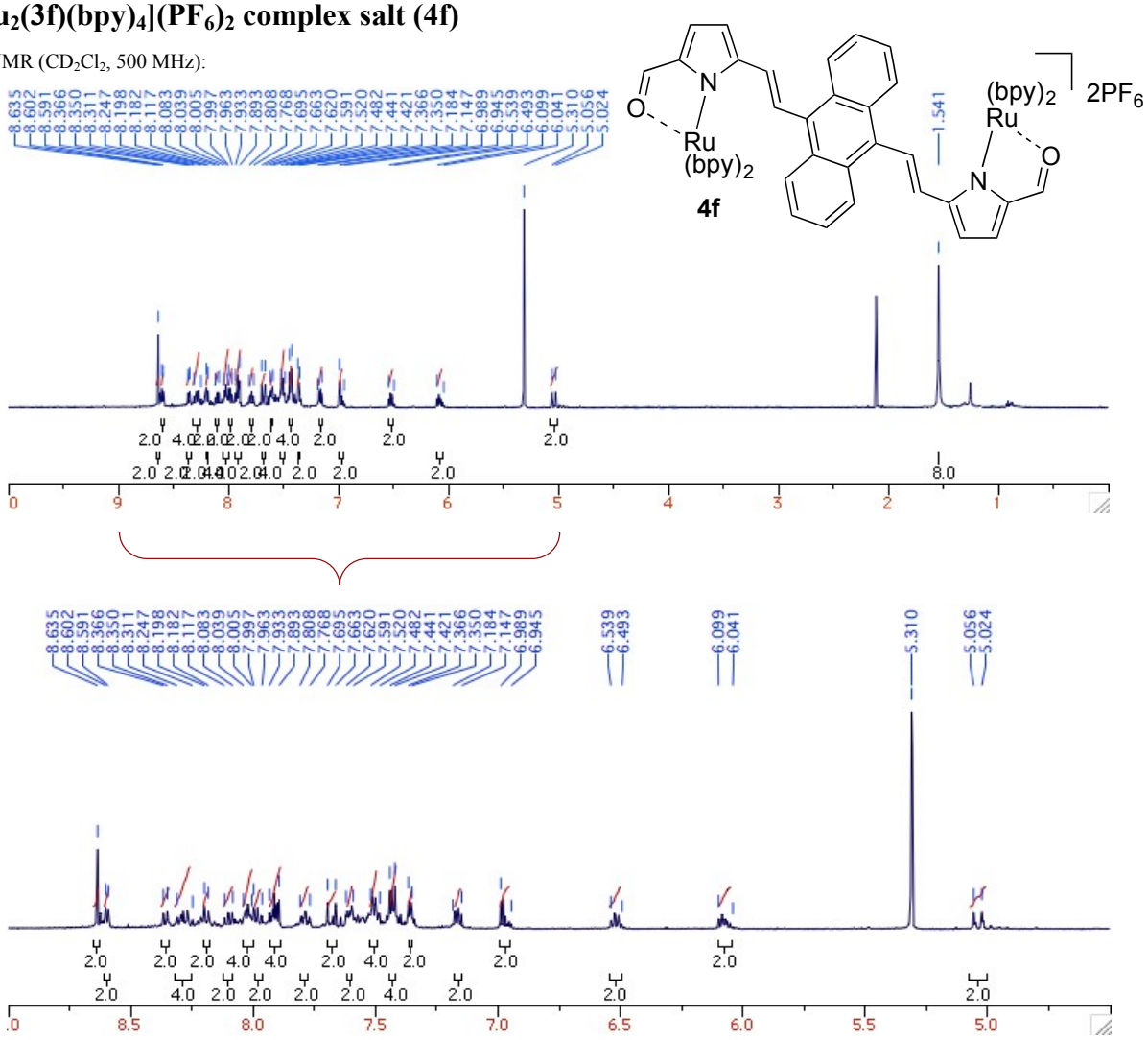


^{13}C udeft NMR (CD_2Cl_2, 125 MHz):

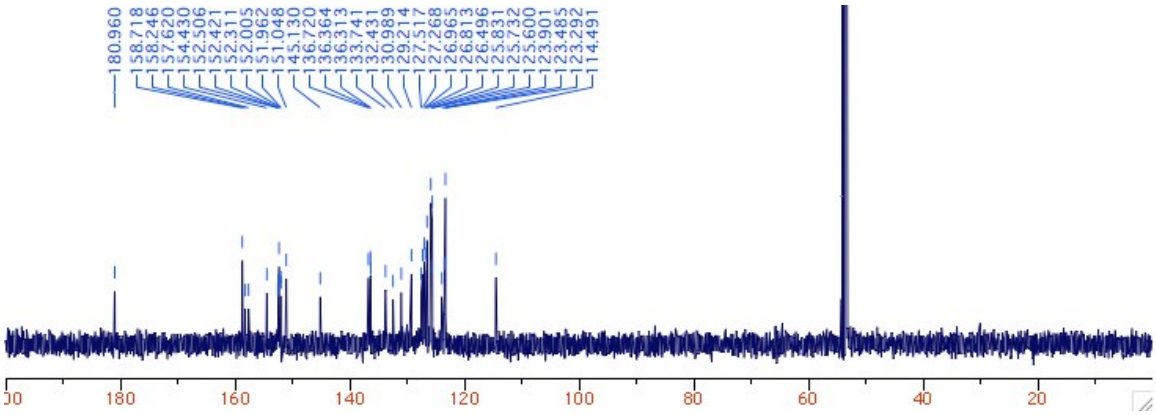


$[Ru_2(3f)(bpy)_4](PF_6)_2$ complex salt (4f)

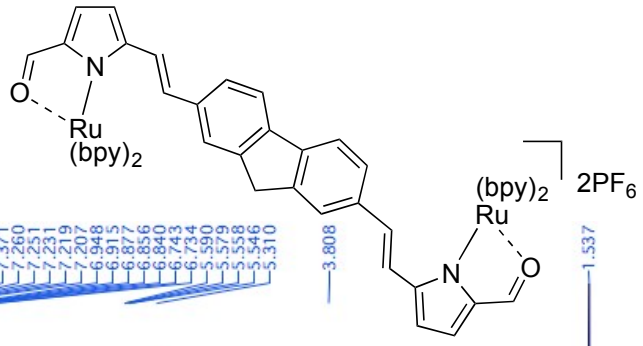
^{1}H NMR (CD_2Cl_2, 500 MHz):



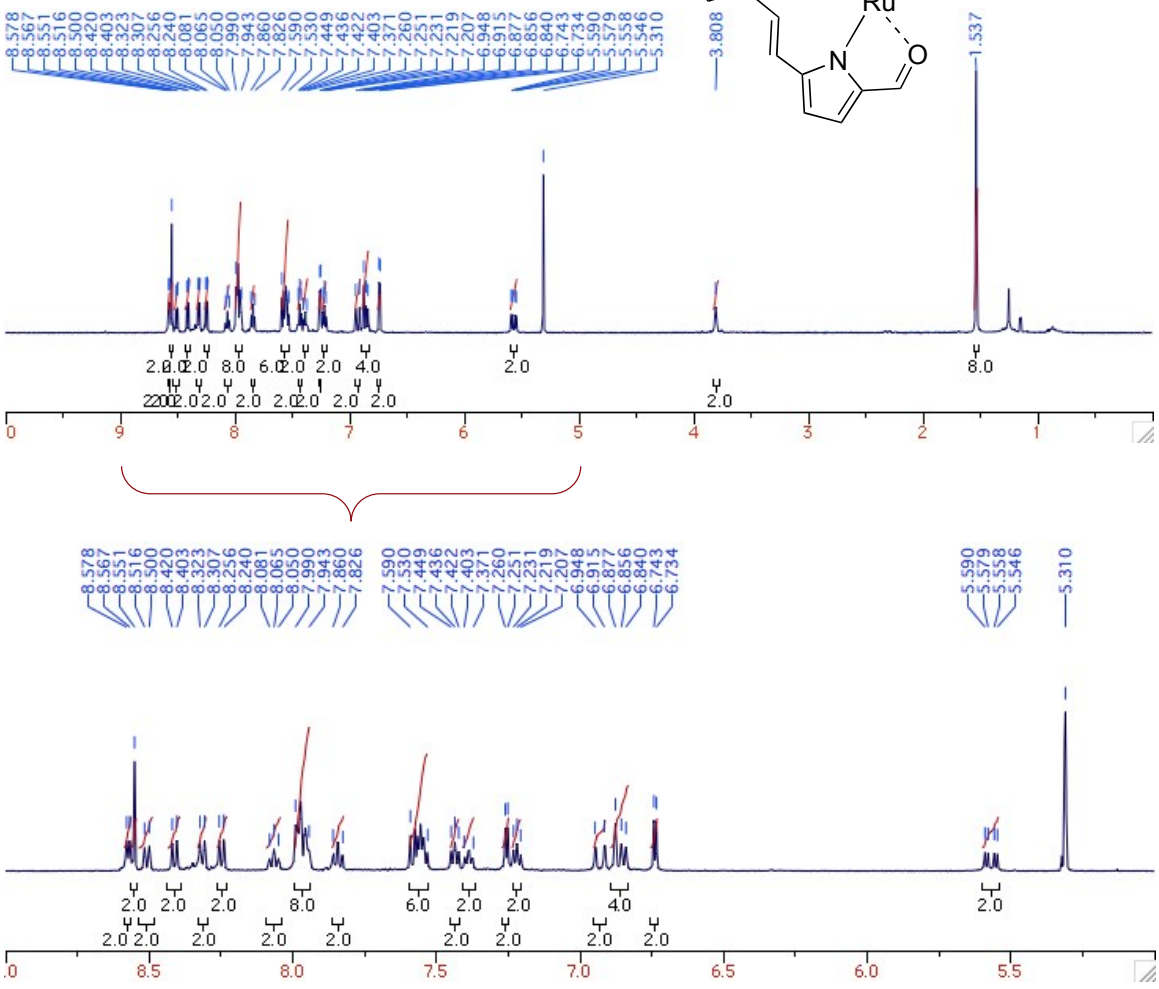
^{13}C udeft NMR (CD_2Cl_2, 125 MHz):



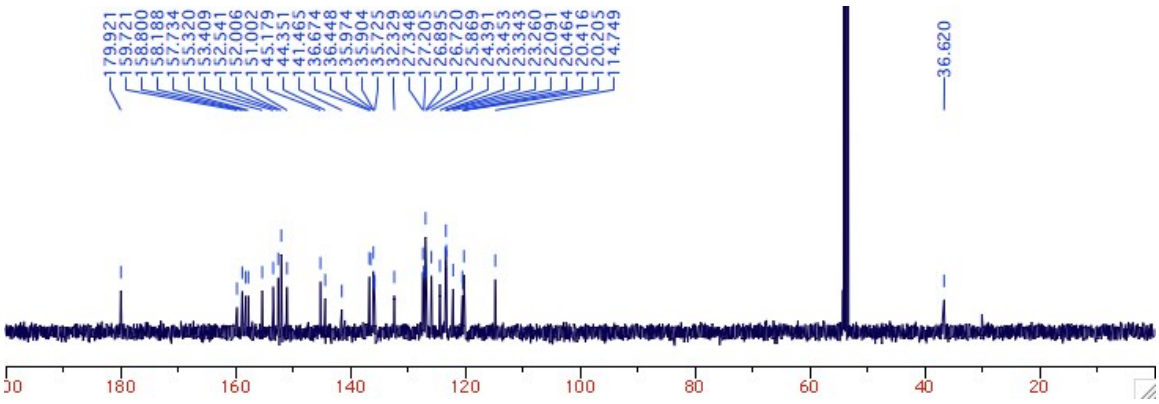
$[Ru_2(3g)(bpy)_4](PF_6)_2$ complex salt (4g)



^{1}H NMR (CD_2Cl_2, 500 MHz):

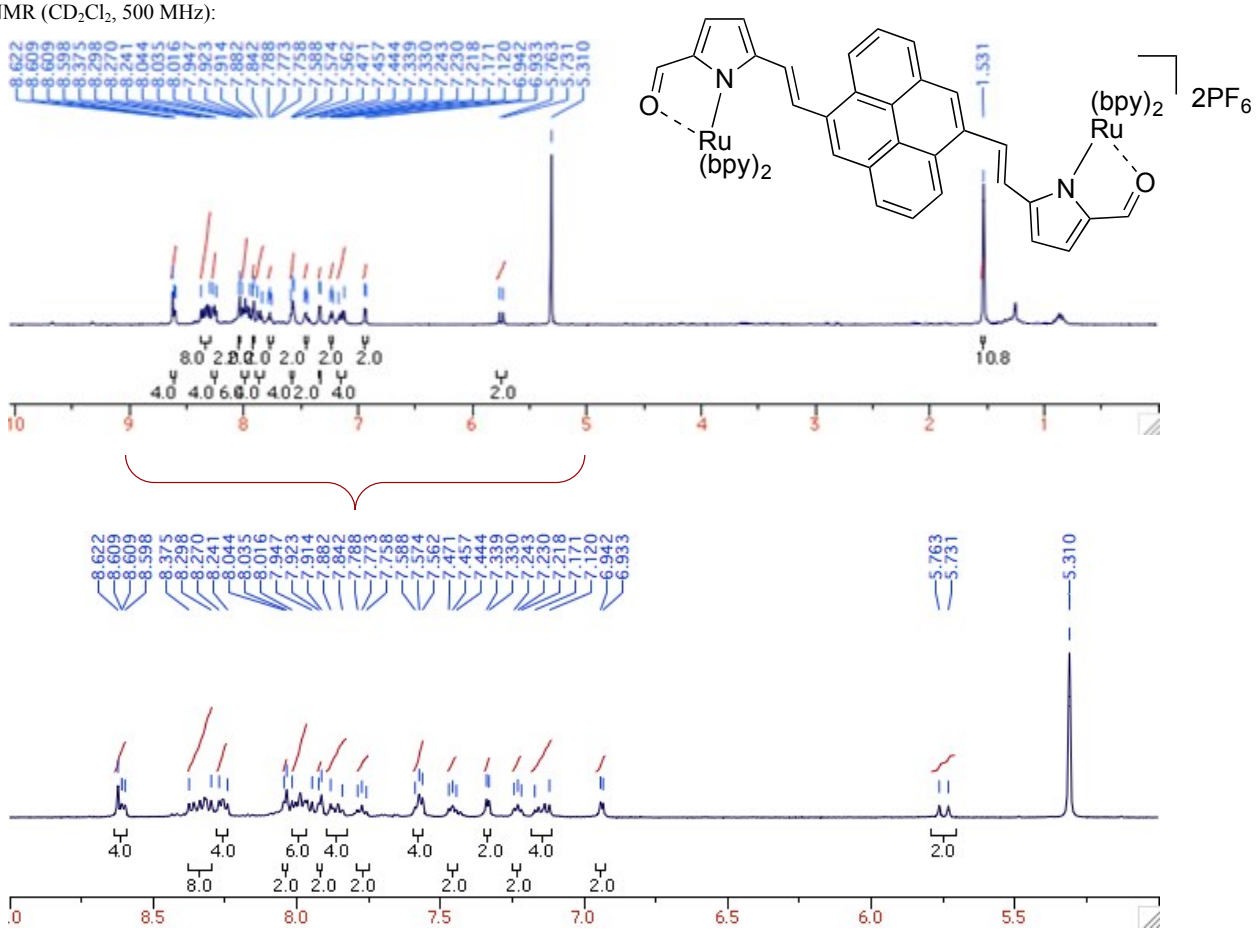


^{13}C udeft NMR (CD_2Cl_2, 125 MHz):

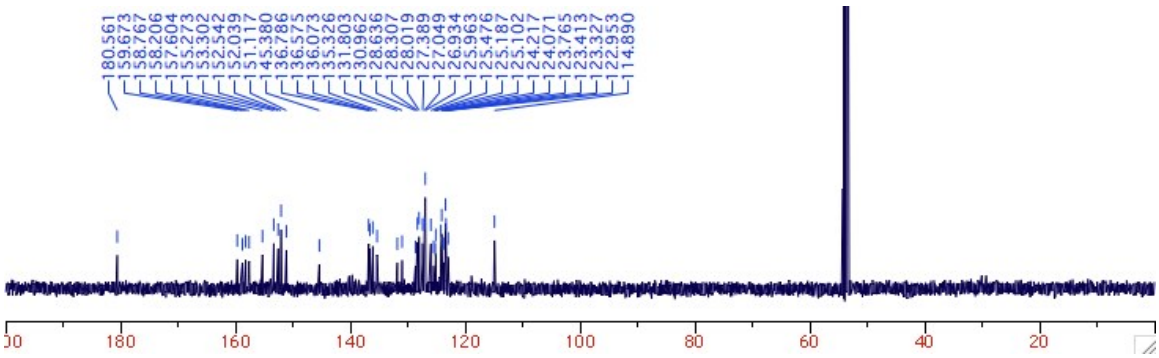


$[Ru_2(3h)(bpy)_4](PF_6)_2$ complex salt (4h)

^{1}H NMR (CD_2Cl_2, 500 MHz):

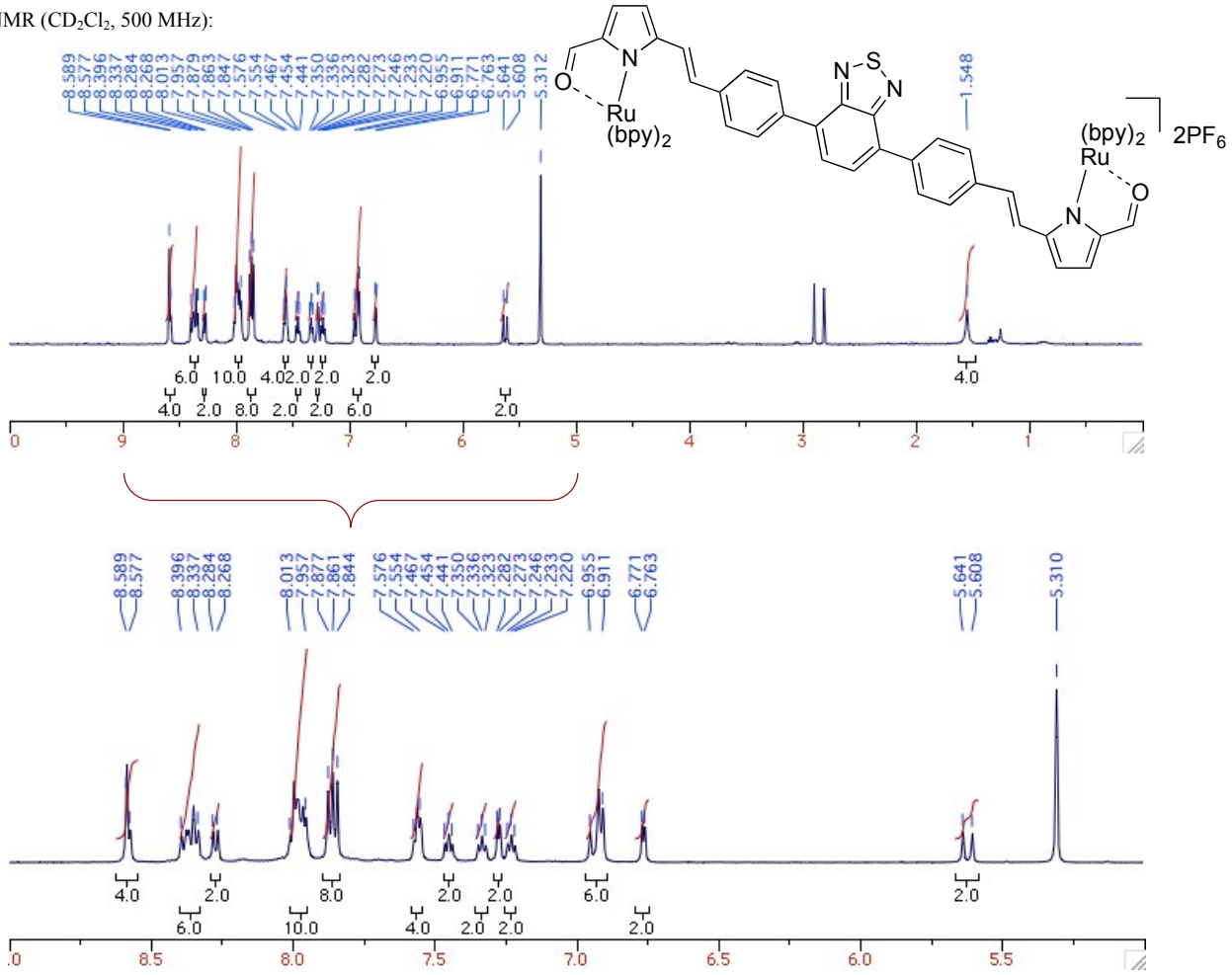


^{13}C udeft NMR (CD_2Cl_2, 125 MHz):

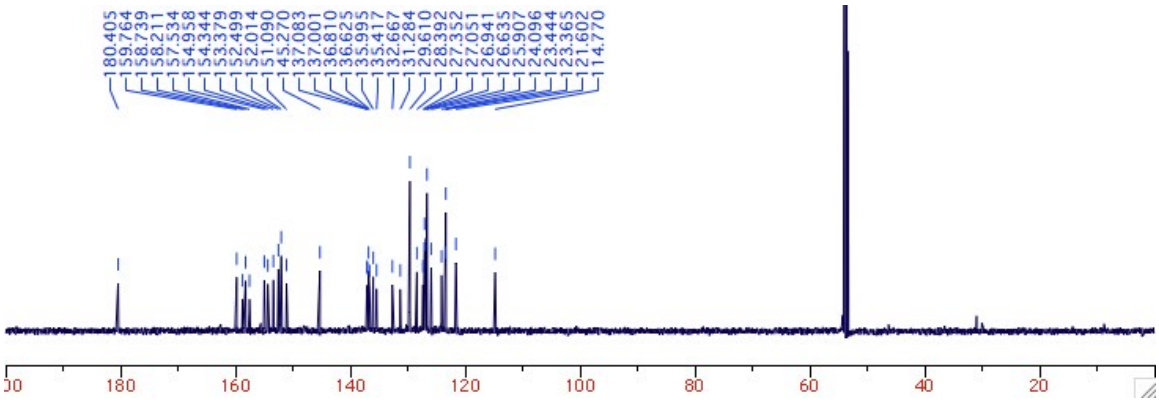


$[Ru_2(3i)(bpy)_4](PF_6)_2$ complex salt (4i)

^{1}H NMR (CD_2Cl_2, 500 MHz):

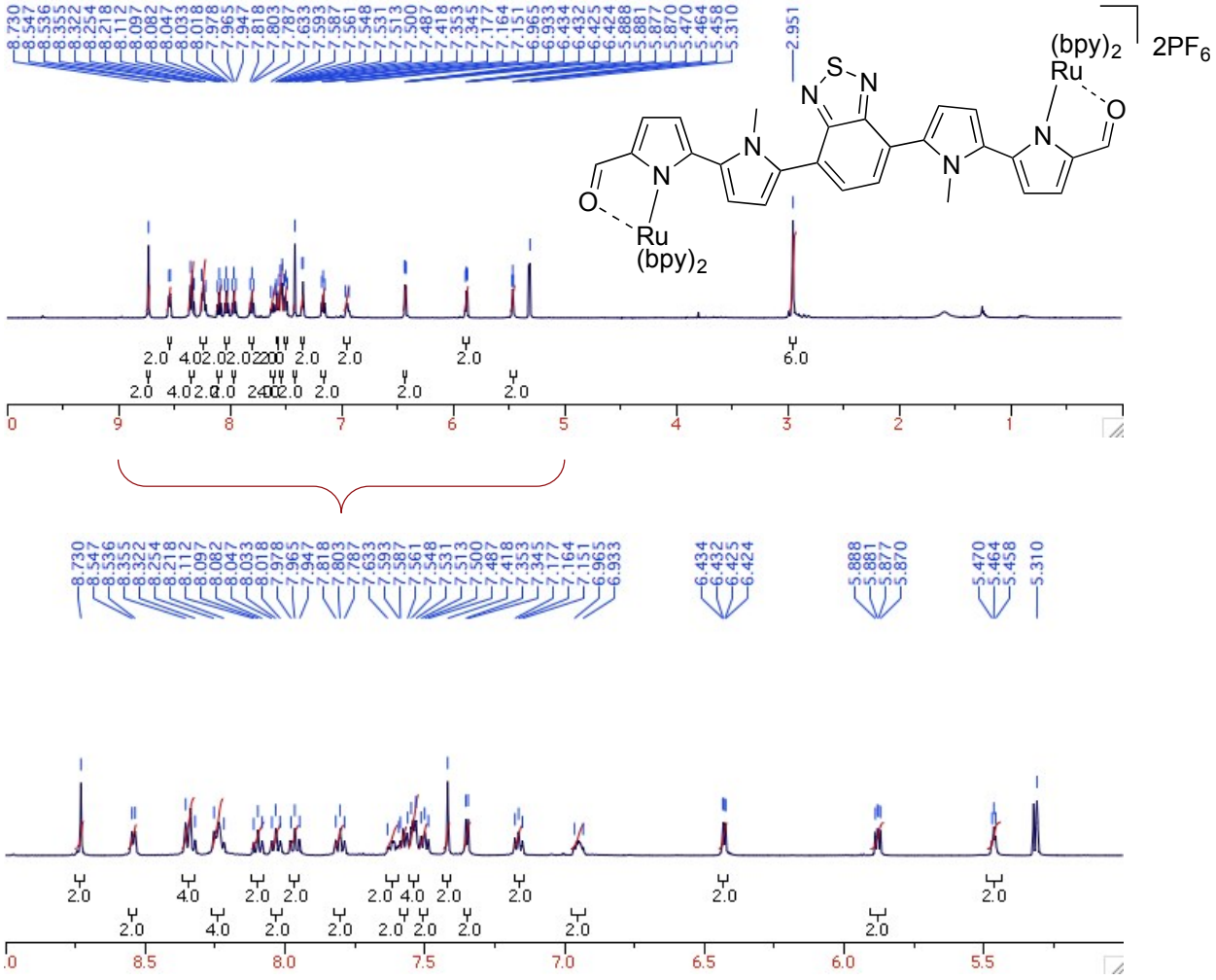


^{13}C udeft NMR (CD_2Cl_2, 125 MHz):

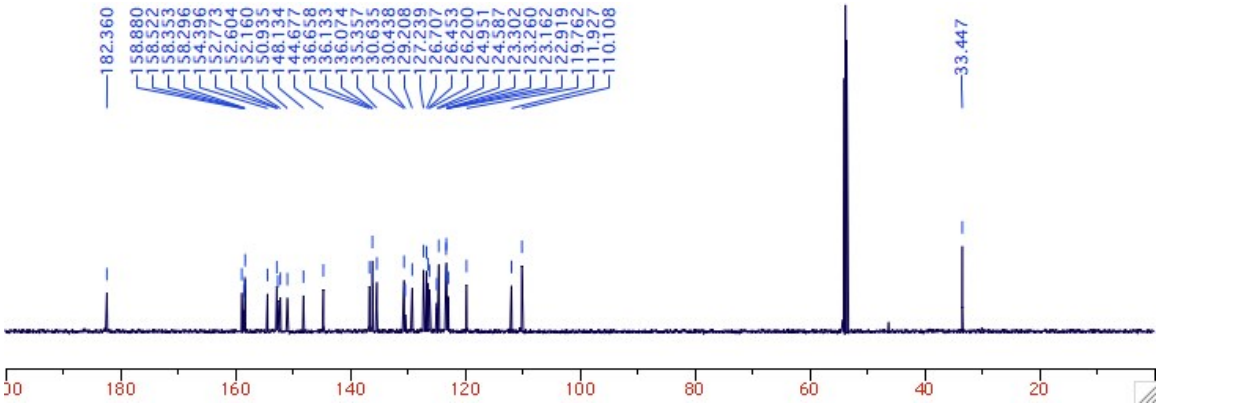


$[Ru_2(3j)(bpy)_4](PF_6)_2$ complex salt (4j)

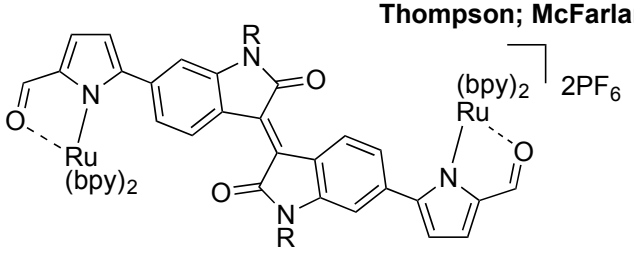
^{1}H NMR (CD_2Cl_2, 500 MHz):



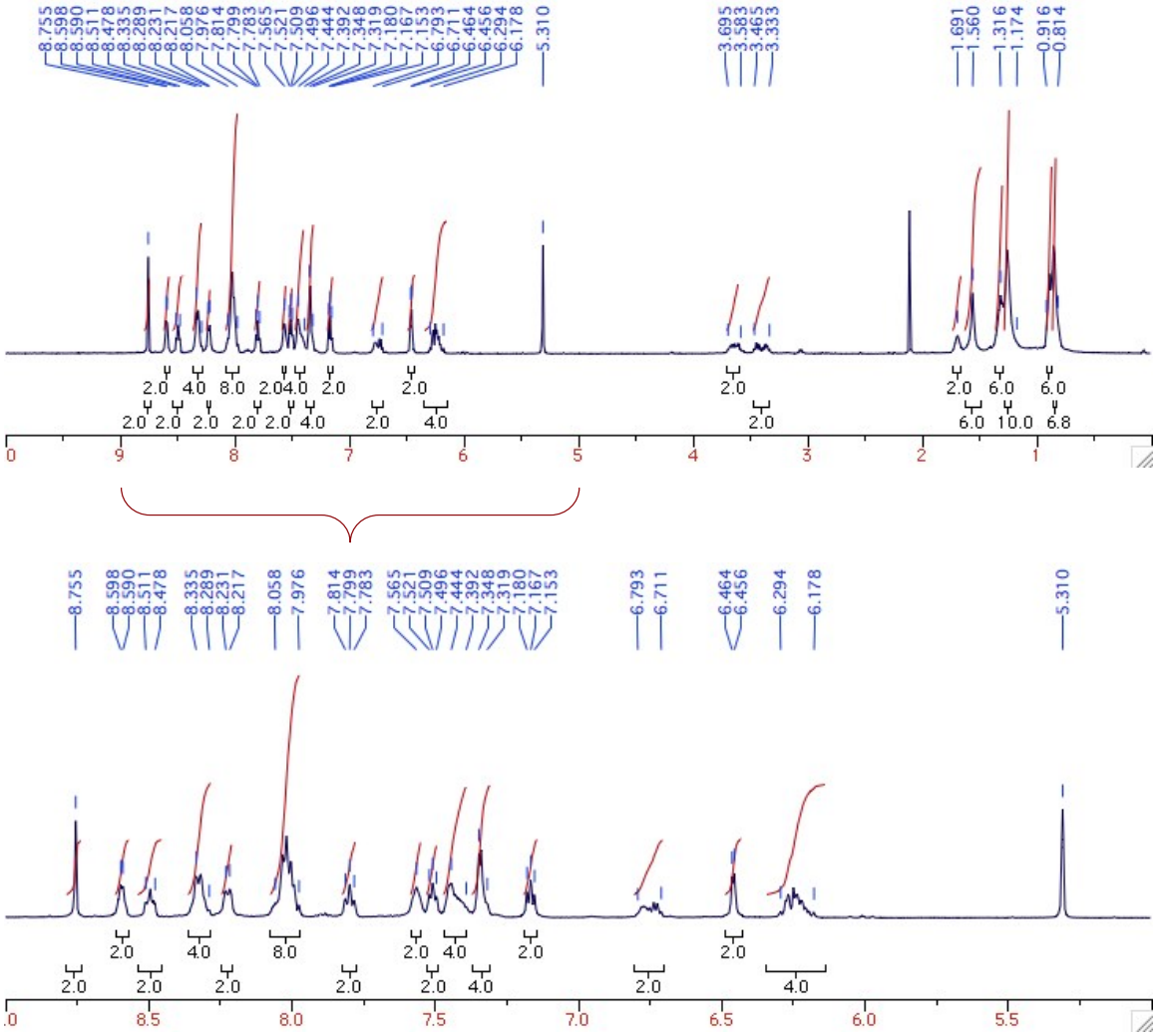
^{13}C udeft NMR (CD_2Cl_2, 125 MHz):



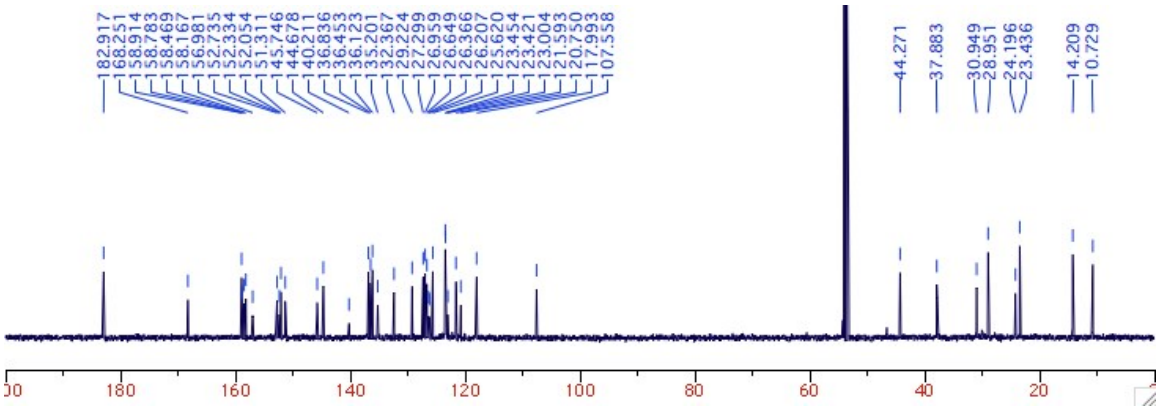
$[Ru_2(3k)(bpy)_4](PF_6)_2$ complex salt (4k)



^{1}H NMR (CD_2Cl_2, 500 MHz):

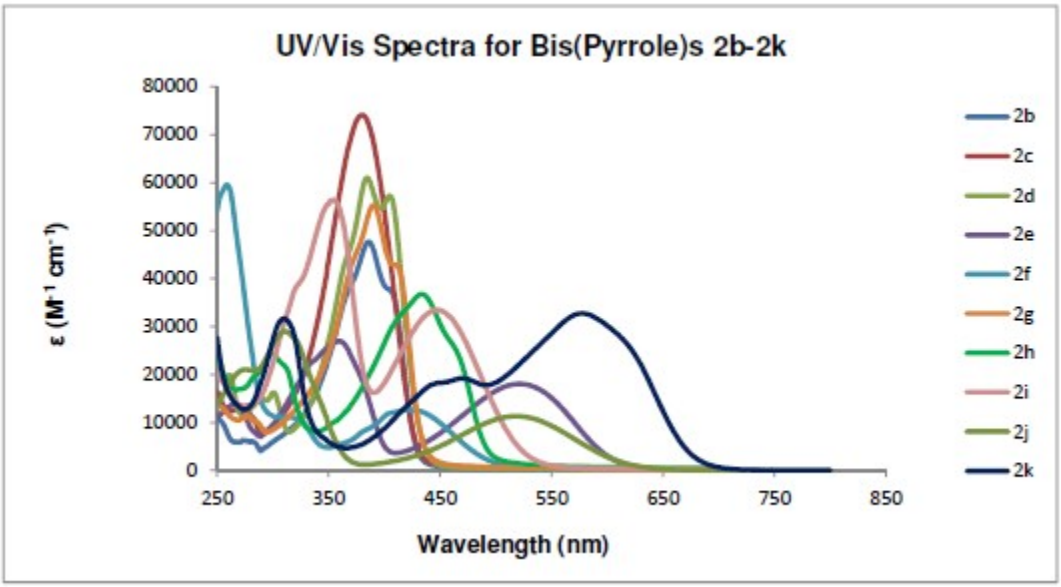


^{13}C udeft NMR (CD_2Cl_2, 125 MHz):



UV Spectra

Bis(pyrroles)



UV/Vis spectra recorded for bis(pyrroles) 2

Key:

Phenyl Linker = **2b**

Biphenyl Linker = **2c**

Naphthyl Linker = **2d**

Benzothiadiazole Linker = **2e**

Anthracene Linker = **2f**

Fluorene Linker = **2g**

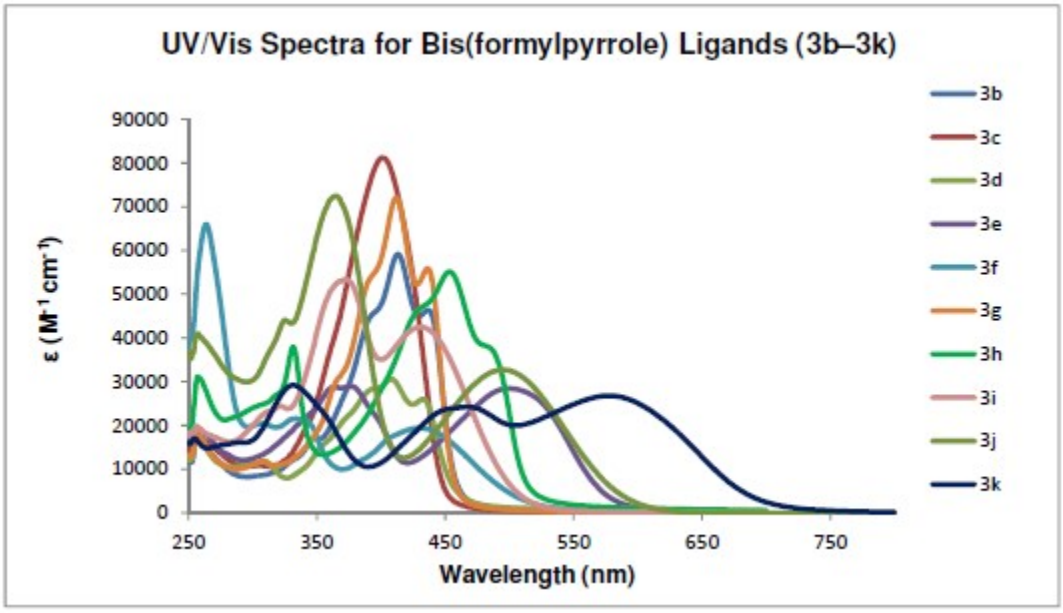
Pyrene Linker = **2h**

4,7-Diphenylbenzothiadiazole Linker = **2i**

4,7-Bis(1-methyl-1H-pyrrol-2-yl)benzothiadiazole Linker = **2j**

Isoindigo Linker = **2k**

Bis(formylpyrroles)



UV/Vis spectra recorded for ligands 3

Key:

Phenyl Linker = **3b**

Biphenyl Linker = **3c**

Naphthyl Linker = **3d**

Benzothiadiazole Linker = **3e**

Anthracene Linker = **3f**

Fluorene Linker = **3g**

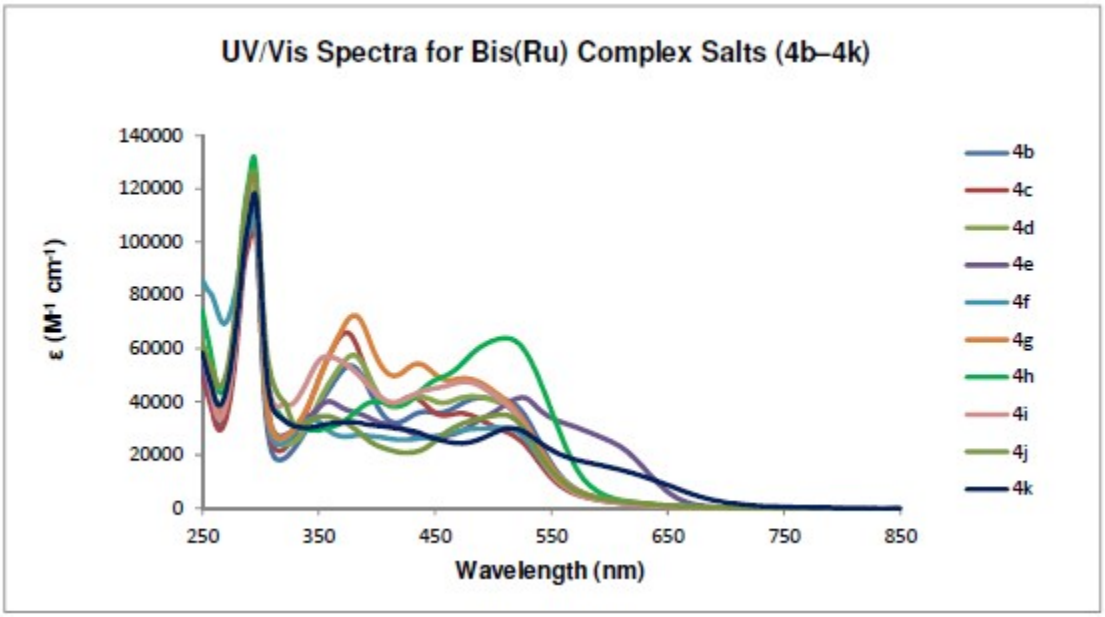
Pyrene Linker = **3h**

4,7-Diphenylbenzothiadiazole Linker = **3i**

4,7-Bis(1-methyl-1H-pyrrol-2-yl)benzothiadiazole Linker = **3j**

Isoindigo Linker = **3k**

Bis(ruthenium) Complex Salts



UV/Vis spectra recorded for bis(ruthenium) complexes 4

Key:

4a

Phenyl Linker = **4b**

Biphenyl Linker = **4c**

Naphthyl Linker = **4d**

Benzothiadiazole Linker = **4e**

Anthracene Linker = **4f**

Fluorene Linker = **4g**

Pyrene Linker = **4h**

4,7-Diphenylbenzothiadiazole Linker = **4i**

4,7-Bis(1-methyl-1H-pyrrol-2-yl)benzothiadiazole Linker = **4j**

Isoindigo Linker = **4k**

References

(1) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693.
(2) Liu, J.; Bu, L.; Dong, J.; Zhou, Q.; Geng, Y.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2007**, *17*, 2832.
(3) Sun, M.; Lan, L.; Wang, L.; Peng, J.; Cao, Y. *Macromol. Chem. Phys.* **2008**, *209*, 2504.
(4) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. *Org. Lett.* **2010**, *12*, 660.