Supplementary Materials: New Members of the 1,3-Di(2-pyridyl)benzene Pro-Ligand Family Bearing Tri- or Tetra-Phenylethylene and Related Platinum(II) Complexes †

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† In memoriam of Bertrand Carboni, a great chemist full of humanity.

1. **Synthesis of the pro-ligands and related platinum(II) complexes…….S2**
2. **NMR characterization of intermediates, pro-ligands and platinum(II) complexes……S5**
3. **Photophysical characterization of 1 and 2……...S20**

1. Synthesis of the pro-ligands and related platinum(II) complexes

General comments

All reagents and solvents were purchased from Sigma-Aldrich, whereas deuterated solvents for NMR measurements were bought from Eurisotop; all of them were used as such, without further purification.

1.1. Synthesis of the pro-ligands

1.1.1 Synthesis of 2,2'-(4,6-difluoro-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**I1** in Scheme 1 of the manuscript)

1,3-dibromo-4,6-difluorobenzene (0.50 g, 1.8 mmol), bis(pinacolato)diboron (1.02 g, 4.0 mmol), KOAc (0.92 g, 9.4 mmol) and Pd(dppf)Cl_2 (0.08 g, 0.1 mmol) were placed in a two neck round bottom flask under an argon atmosphere and dissolved in 8.4 mL of anhydrous toluene. The mixture was heated at 115 °C overnight and subsequently cooled to room temperature. Then, the reaction mixture was diluted with 25 mL of ethyl acetate and washed with 25 mL of water. The collected organic phase was further washed twice with a mixture of 30 mL of water and 50 mL of brine, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*.
The crude product was thus filtered on a pad of silica gel using a mixture of cyclohexane:ethyl acetate 8:2 as the eluent, in order to remove the insoluble species and most of the impurities. The solvent was then removed under reduced pressure and the residue dissolved in pentane. The flask was finally placed in the freezer to crystallize the product.
The colorless crystalline solid was filtered on a Büchner funnel and dried under vacuum (1.74 g). Yield: 65%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.15 (t, J = 7.5 Hz, 1H), 6.75 (t, J = 9.7 Hz, 1H), 1.37 (s, 24H). ^{19}F-NMR (282.36 MHz, $CDCl_3$, δ): -94.28 (s, 2F*).*

1.1.2 Preparation of 1,3-bis(4-triphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L1**)

*1.1.2.1. Synthesis of 2-chloro-4-triphenylethylene-pyridine (**I2** in Scheme 1)*

2-chloro-pyridine-4-boronic acid (0.22 g, 1.4 mmol), 1-bromo-1,2,2-triphenylethylene (0.30 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) and Na_2CO_3 (0.28 g, 2.7 mmol) were placed in a Schlenk tube and solubilized in a mixture of 2.5 mL of distilled water and 7.5 mL of 1,4-dioxane. Air was removed from the reaction vessel by vigorously bubbling argon for 10 minutes. The reaction mixture was then stirred and heated at 115 °C overnight. The vessel was thus cooled to room temperature. The mixture was acidified with HCl and extracted three times with 50 mL of ethyl acetate. The organic layer was separated and washed three times with 50 mL of water and 20 mL of brine. The solution was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified using silica gel chromatography (cyclohexane:ethyl acetate, 20:1) to obtain a colorless oil (83.8 mg). Yield: 25%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.11 (d, J = 5.2 Hz, 1H), 6.95-7.25 (m, 16H), 6.86 (d, J = 5.2 Hz, 1H). ^{13}C-NMR (75.48 MHz, CDCl3, δ): 155.0, 151.3, 149.0, 144.7, 142.1, 141.7, 137.0, 131.2, 131.0, 128.2, 127.8, 127.7, 127.3, 126.3, 124.8. HRMS (ESI+): (M+H)+ calcd for $C_{25}H_{19}N^{35}Cl$, 368.1200; found: 368.1200.

*1.1.2.2. Synthesis of 1,3-bis(4-triphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L1**)*

I1 (0.05 g, 0.15 mmol; see 3.2.1), **I2** (0.12 g, 0.3 mmol; see 3.2.2.1) and $Pd(PPh_3)_4$ (0.03 g, 0.02 mmol) were added to a two neck round bottom flask together with an aqueous solution of Na_2CO_3 (1 M, 3 mL) and 3 mL of 1,2-dimethoxyethane (DME) under an argon atmosphere. Air was removed by bubbling argon for 20 minutes. The vessel was then sealed and heated at 115 °C overnight. After cooling to room temperature, the solvents were evaporated under reduced pressure and the residue was dissolved in a mixture of dichloromethane (30 mL) and water (20 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified using silica gel chromatography (cyclohexane:ethyl acetate, 16:1) to obtain a colorless oil (75 mg). Yield: 65%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.45 (d, J = 5.1 Hz, 2H), 8.19 (t, J = 8.9

Hz, 1H), 7.03-7.17 (m, 32H), 6.92 (d, J = 5.1 Hz, 2H), 6.81 (t, J = 10.5 Hz, 1H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 163.4, 152.3, 152.1, 149.2, 143.7, 142.7, 142.5, 142.2, 138.2, 131.2, 131.1, 128.1, 128.0, 127.7, 127.3, 126.9, 124.8, 124.3, 123.9, 123.4, 119.1, 104.6. ^{19}F-NMR (282.36 MHz, $CDCl_3$, δ): -112.81 (s, 2F). HRMS (ASAP): (M)+ calcd for $C_{56}H_{38}N_2F_2$, 776.2998; found: 776.3006.

1.1.3. Preparation of 1,3-bis(4-tetraphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L2**)

*1.1.3.1. Synthesis of 2-chloro-4-tetraphenylethylene-pyridine (**I3** in Scheme 1)*

2-chloro-pyridine-4-boronic acid (0.23 g, 1.5 mmol), 1-(4-bromophenyl)-1,2,2-triphenylethylene (0.50 g, 1.2 mmol), $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol) and Na_2CO_3 (0.39 g, 3.6 mmol) were placed in a Schlenk tube and solubilized in a mixture of 5 mL of distilled water and 15 mL of 1,4-dioxane. Air was removed from the reaction vessel by vigorously bubbling argon for 10 minutes. The reaction mixture was stirred and heated at 115 °C overnight. The vessel was thus cooled to room temperature. The mixture was then acidified with HCl_{aq} and extracted three times with 50 mL of ethyl acetate. The organic layer was separated and washed three times with 50 mL of water and 20 mL of brine. The solution was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure.

The crude product was purified using silica gel chromatography (cyclohexane:ethyl acetate, 20:1) to obtain a colorless oil (253 mg). Yield: 47%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.40 (d, J = 5.2 Hz, 1H), 7.51 (d, J = 1.1 Hz, 1H), 7.39 (dd, J = 6.1, 2.1 Hz, 3H), 7,03-7,20 (m, 17H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 152.2, 151.0, 149,.9, 145.6, 143.4, 143.3, 142.1, 139.8, 134.4, 132.2, 131.3, 131.2, 127.9, 127.8, 127.7, 126.8, 126.7, 126.2, 121.7, 120.1. HRMS (ESI+): (M+Na)+ calcd for $C_{31}H_{22}N^{35}ClNa$, 466.1333; found: 466.1335.

*1.1.3.2. Synthesis of 1,3-bis(4-tetraphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L2**)*

I1 (0.05 g, 0.15 mmol; see 3.2.1), **I3** (0.15 g, 0.3 mmol; see 3.2.3.1) and $Pd(PPh_3)_4$ (0.03 g, 0.03 mmol) were added to a two neck round bottom flask together with an aqueous solution of Na_2CO_3 (1 M, 3 mL) and 3 mL of 1,2-dimethoxyethane (DME) under an argon atmosphere. Air was removed by bubbling argon for 20 minutes. The vessel was then sealed and heated at 115 °C overnight. After cooling to room temperature, the solvents were evaporated under reduced pressure and the residue was dissolved in a mixture of dichloromethane (30 mL) and water (20 mL). The organic phase was collected, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified using silica gel chromatography (cyclohexane:ethyl acetate, 16:1, v/v) to obtain a colorless oil (80 mg). Yield: 56%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.74 (d, J = 5.2 Hz, 2H), 8.64 (t, J = 8.9 Hz, 1H), 7.96 (s, 2H), 7.43-7.52 (m, 6H), 7.02-7.22 (m, /35H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 145.0, 143.4, 143.2, 141.8, 140.0, 132.1, 131.4, 131.3, 131.2, 127.8, 127.7, 126.7, 126.6, 126.3, 120.3. ^{19}F-NMR (282.36 MHz, $CDCl_3$, δ): -112.92 (s, 2F). HRMS (ESI+): (M+Na)+ calcd for $C_{68}H_{46}N_2F_2Na$, 951.3521; found: 951.3521.

1.2. Synthesis of the platinum(II) complexes

1.2.1. Synthesis of **1**

A Schlenk tube was charged with **L1** (0.20 g, 0.26 mmol), K_2PtCl_4 (0.21 mg, 0.5 mmol) and a mixture of 9.0 mL of acetonitrile and 1.0 mL of water. The reaction vessel was filled with argon and a needle was inserted in the solvent in order to directly bubble argon in the reaction mixture. After 40 minutes, the vessel was sealed and heated at 110 °C for 72h. The reaction mixture was then cooled and the precipitate was isolated after filtration through a nylon membrane filter and washed with water, methanol and diethyl ether. The orange solid was collected and dried (70 mg). Yield: 27%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.99 (d, J = 6.0 Hz, ^{3}J(195Pt) = 37.2 Hz, 2H), 7.47, (s, 2H), 7.04-7.20 (m, 30H), 6.87 (d, J = 6.0 Hz, 2H), 6.50 (t, J = 11.1 Hz, 1H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 155.82, 150.97, 145.77, 142.21, 141.95, 141.28, 137.32, 131.23, 131.04, 130.98, 128.39, 128.29, 127.81, 125.40. ^{19}F-NMR (282.36 MHz, $CDCl_3$, δ): -108.94 (s, 2F). HRMS (ESI+): (M+Na)+ calcd for $C_{56}H_{37}N_2F_2{}^{35}ClNa^{195}Pt$, 1028.2153; found: 1028.2160.

Elem. Anal. calcd. for $C_{56}H_{37}ClF_2N_2Pt$: C, 66.83; H, 3.71; N, 2.78; found: C, 66.86; H,3.73; N, 2.76.

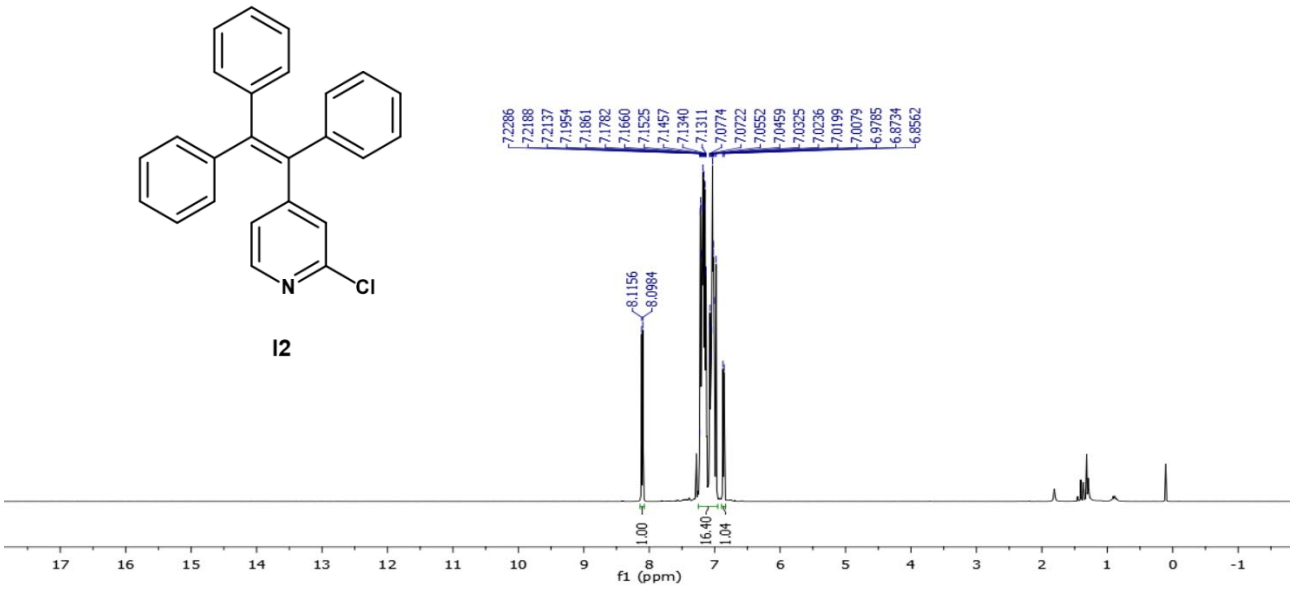
1.2.2. Synthesis of **2**

A Schlenk tube was charged with **L2** (0.09 g, 0.1 mmol), K_2PtCl_4 (0.21 g, 0.2 mmol) and a mixture of 9.0 mL of acetonitrile and 1.0 mL of water. The reaction vessel was filled with argon and a needle was inserted in the solvent in order to directly bubble argon in the reaction mixture. After 40 minutes, the vessel was sealed and heated at 110 °C for 72h. The reaction mixture was then cooled and the precipitate was isolated after filtration through a nylon membrane filter and washed with water, methanol and diethyl ether. The orange solid was then collected and dried (50 mg). Yield: 43%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 9.23 (d, J = 6.1 Hz, ^{3}J(195Pt) = 36.0 Hz, 2H), 8.02 (s, 2H), 7.48 (d, J = 8.4 Hz, 4H), 7.39 (dd, J = 6.1, 2.0 Hz, 2H), 7.03-7.23 (m, 34H), 6.69 (t, J = 11.3 Hz, 1H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 151.1, 146.3, 143.3, 143.2, 142.3, 139.8, 134.1, 132.3, 131.3, 131.3, 127.9, 127.8, 127.7, 126.9, 126.8, 126.4. ^{19}F-NMR (282.36 MHz, $CDCl_3$, δ): -108.41 (s, 2F). HRMS (ESI+): (M+Na)+ calcd for $C_{68}H_{45}N_2F_2{}^{35}ClNa^{195}Pt$, 1180.2780; found: 1180.2784. Elem. Anal. calcd. for $C_{68}H_{45}ClF_2N_2Pt$: C, 70.49; H, 3.91; N, 2.42; found: C, 70.85; H,3.93; N, 2.44.

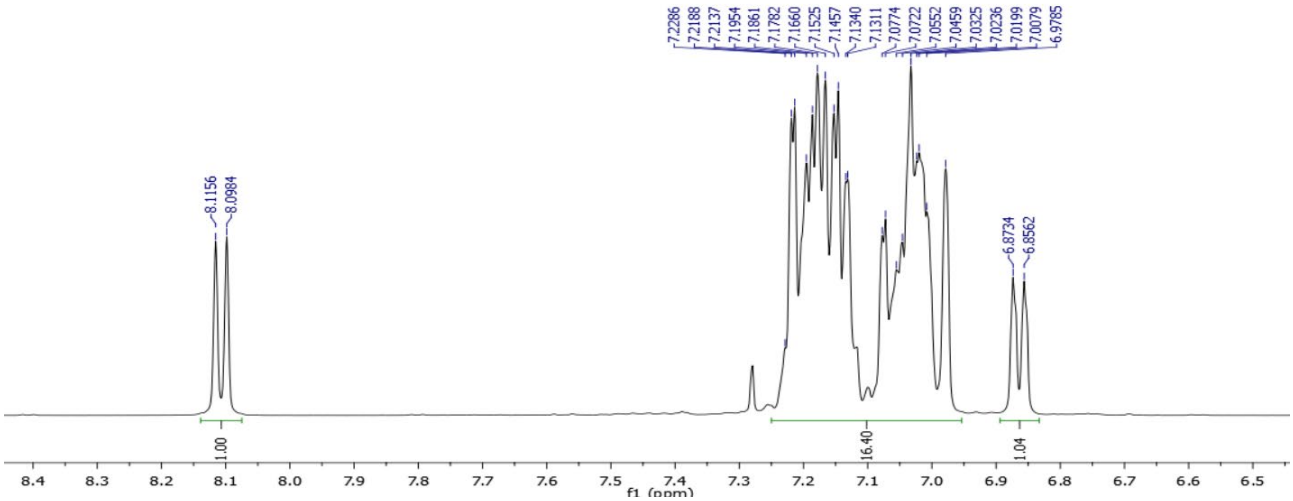
2. NMR characterization of intermediates, pro-ligands and platinum(II) complexes

Intermediate I2

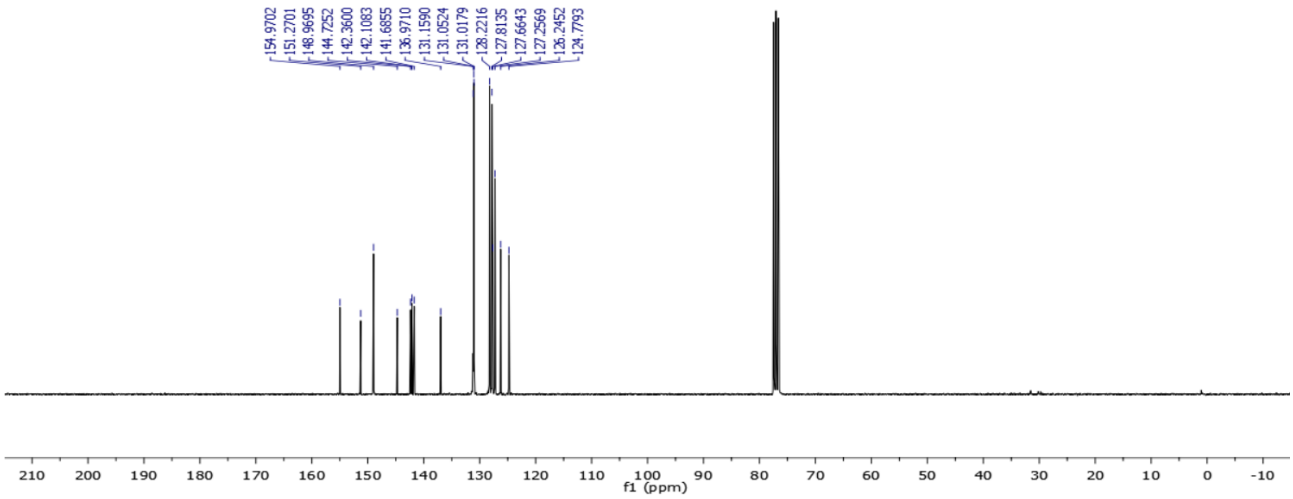
^{1}H-NMR spectra

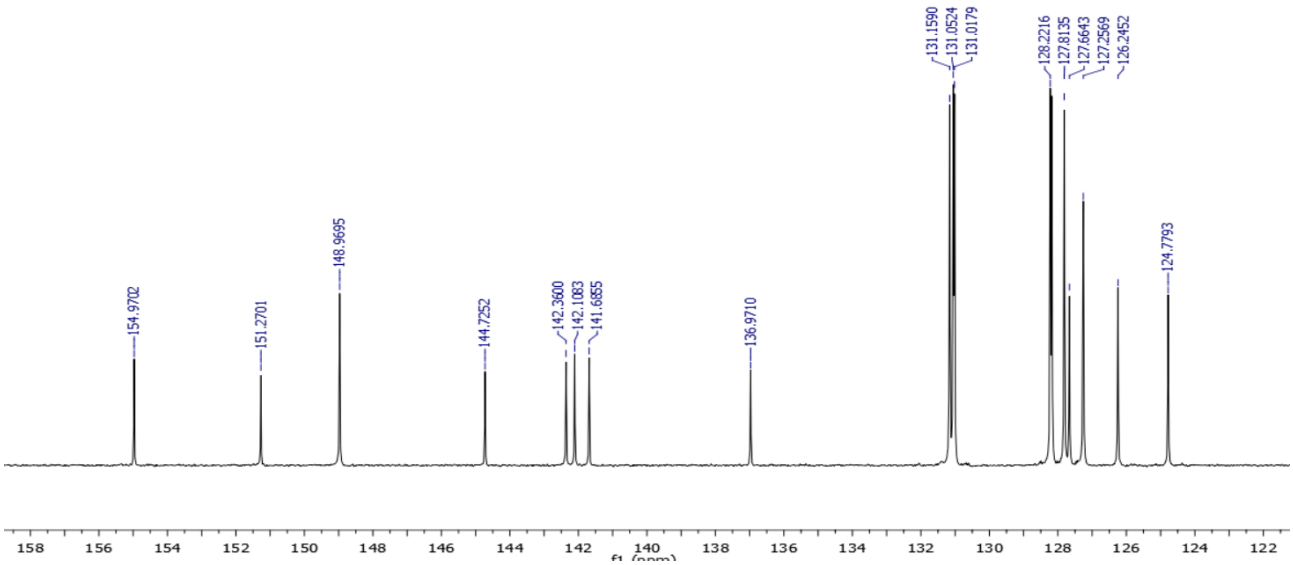


I2



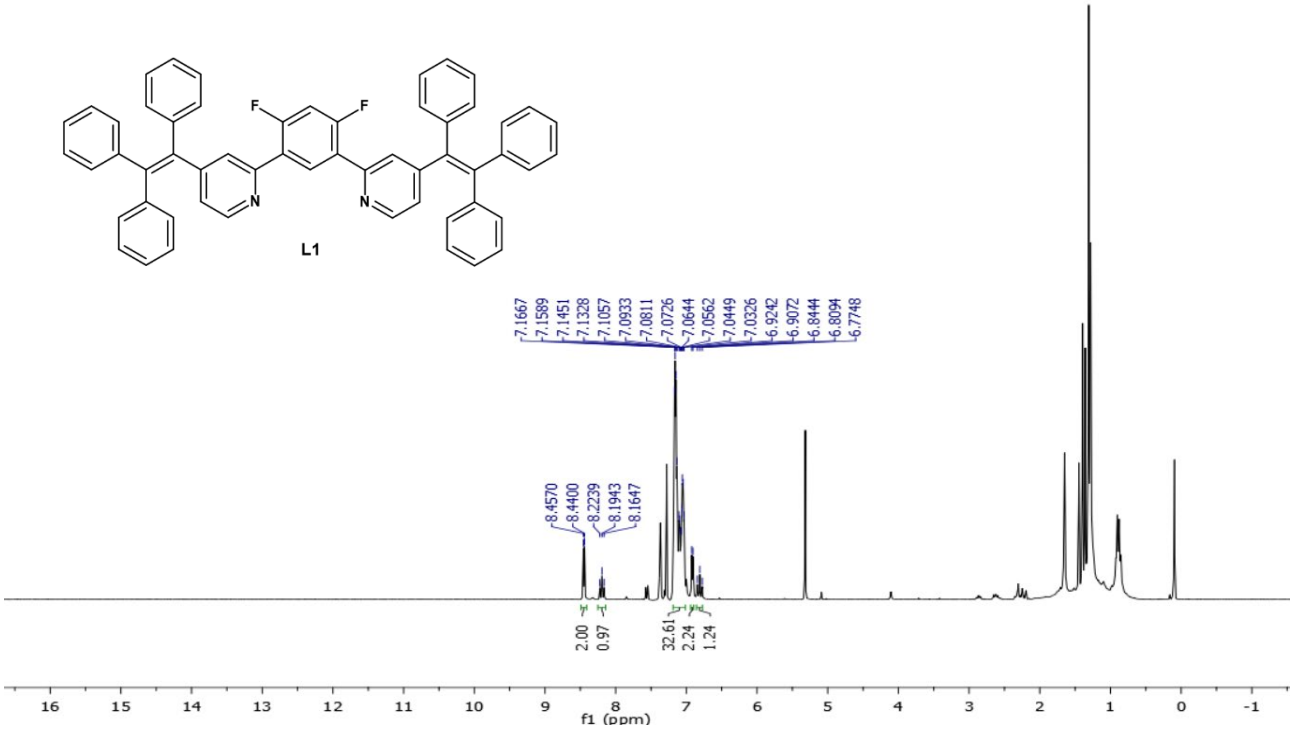
^{13}C-NMR spectra

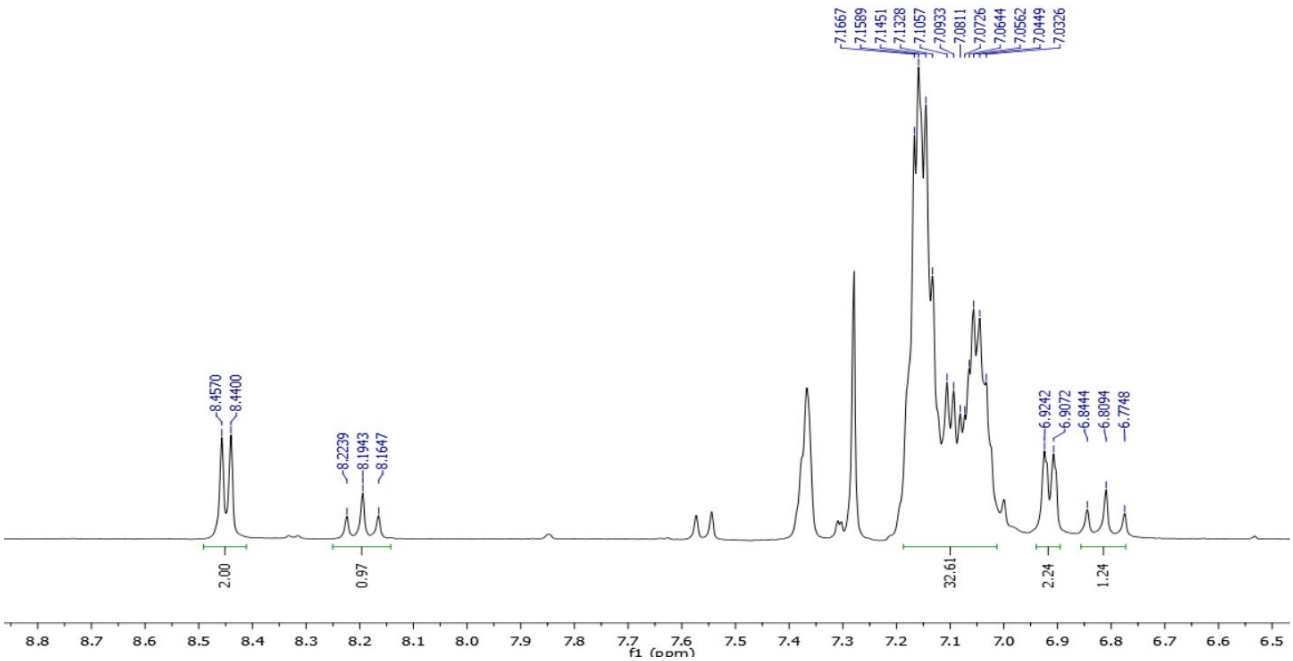




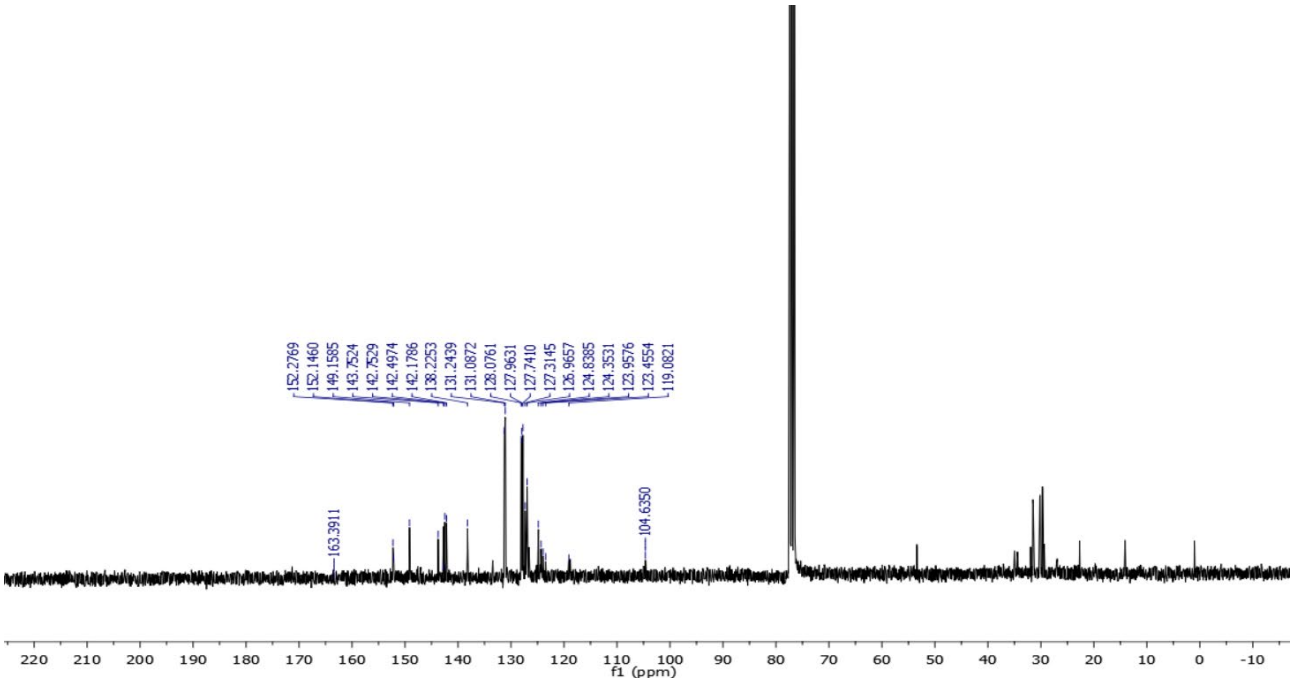
Ligand L1

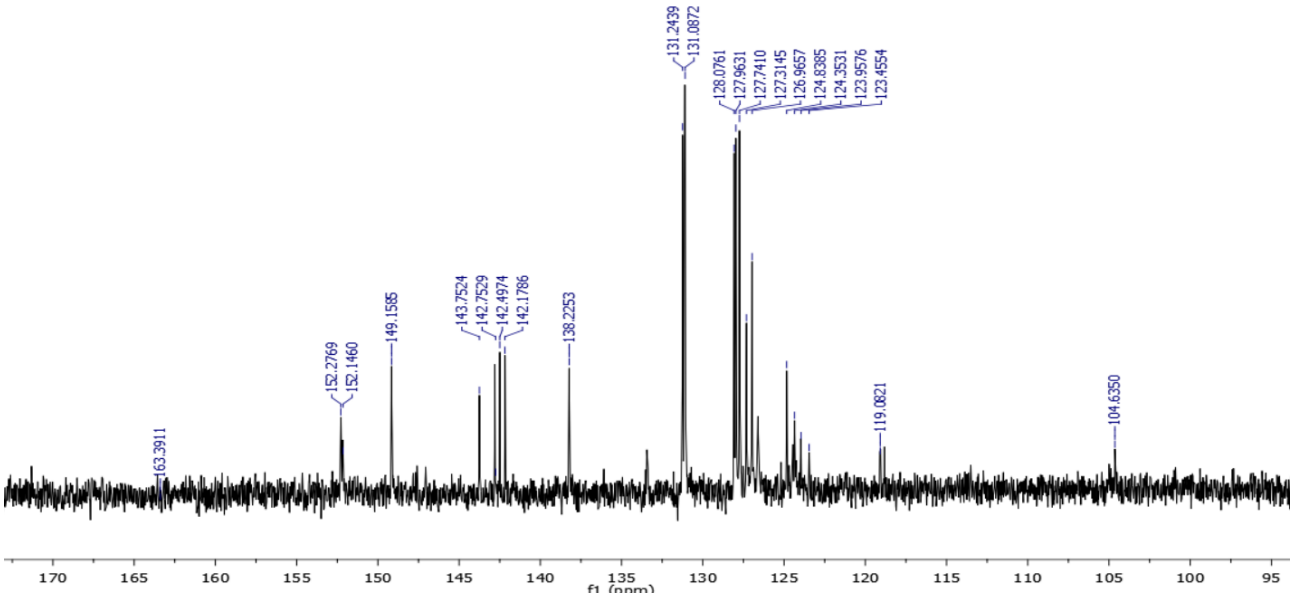
^{1}H-NMR spectra



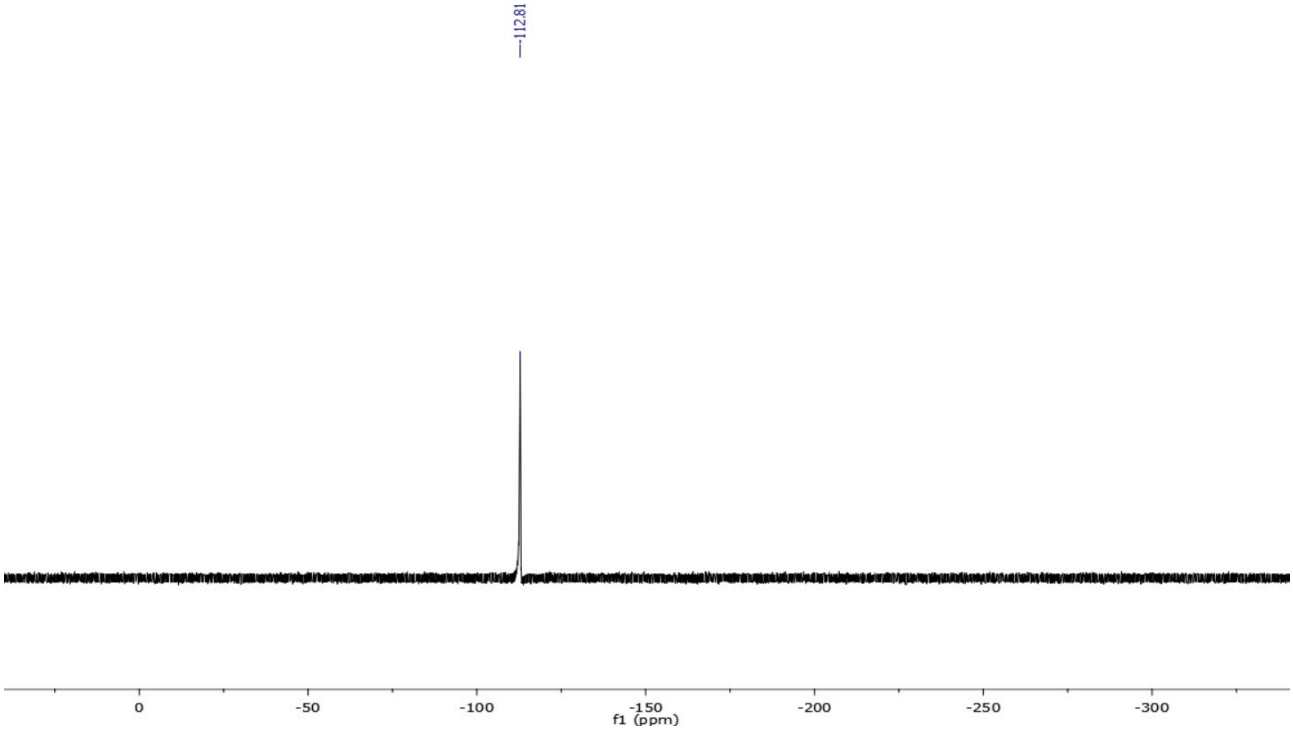


^{13}C-NMR spectra



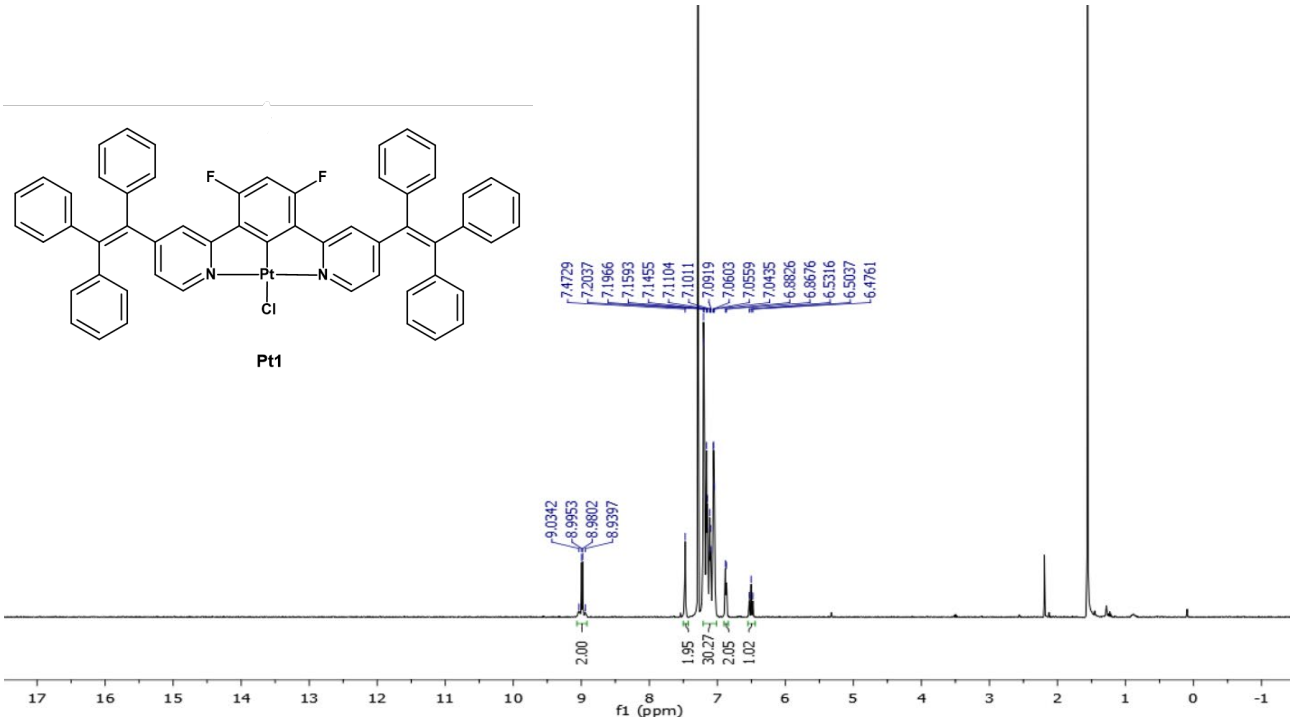


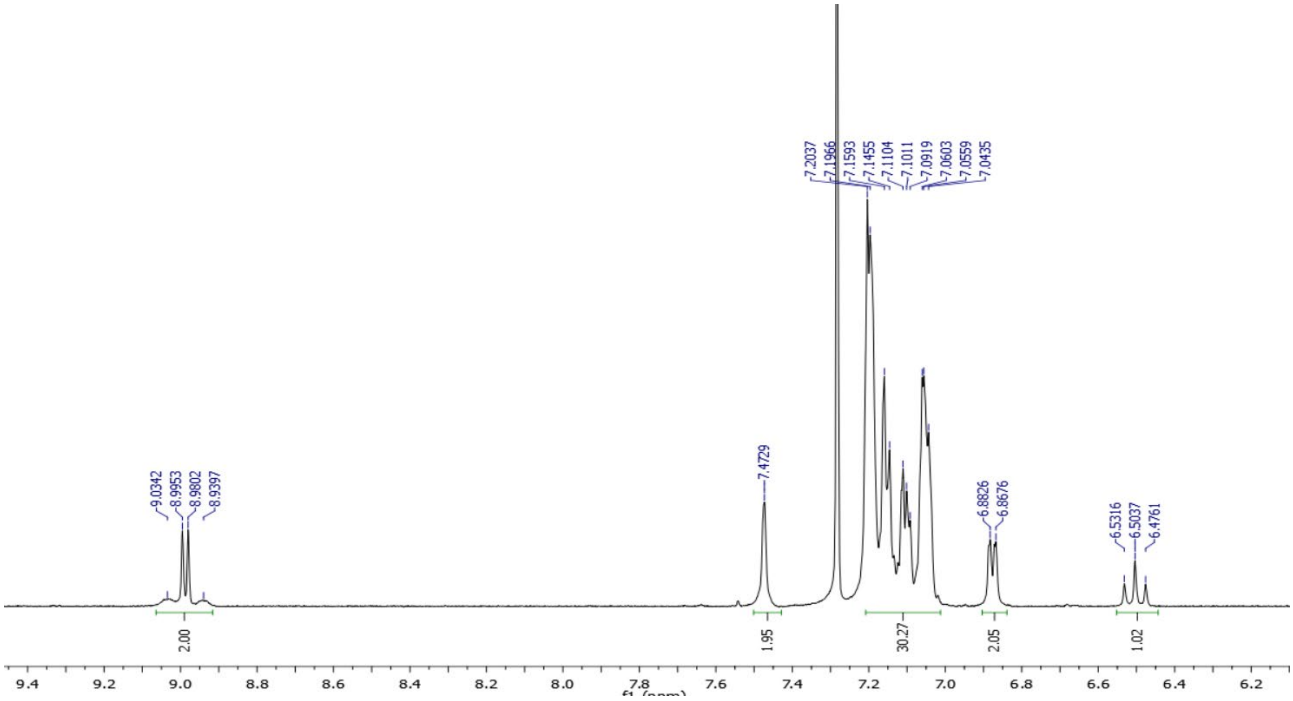
^{19}F-NMR spectra



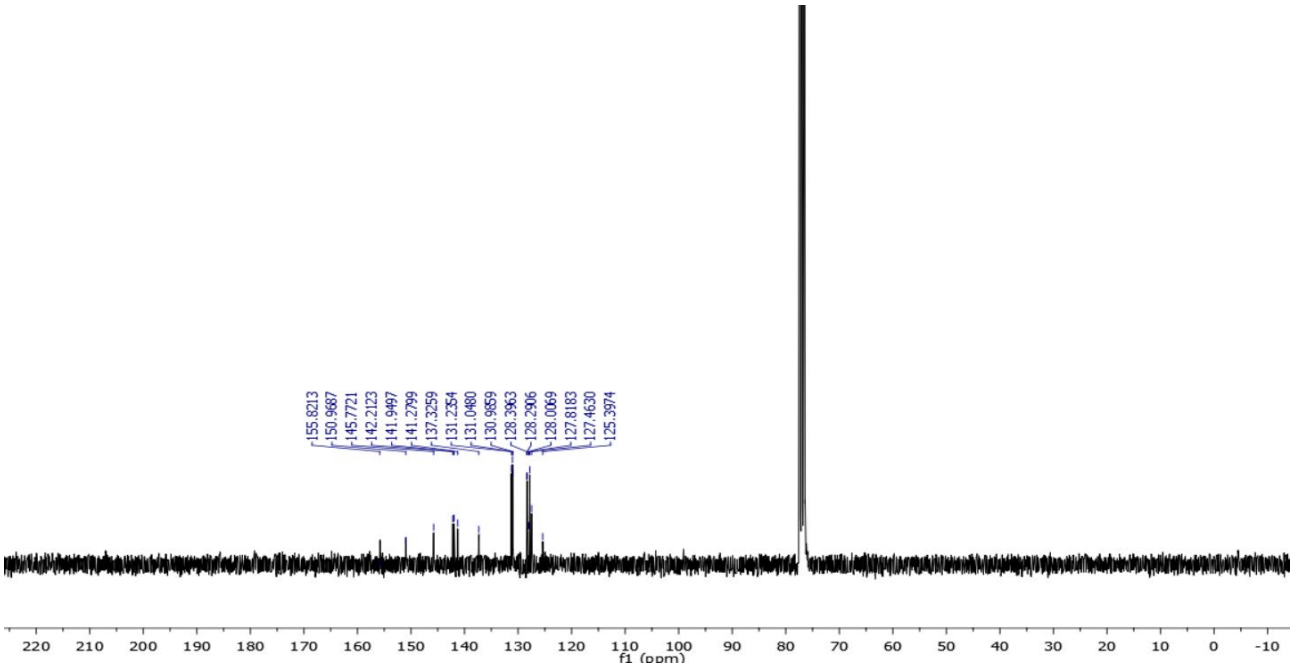
Complex 1

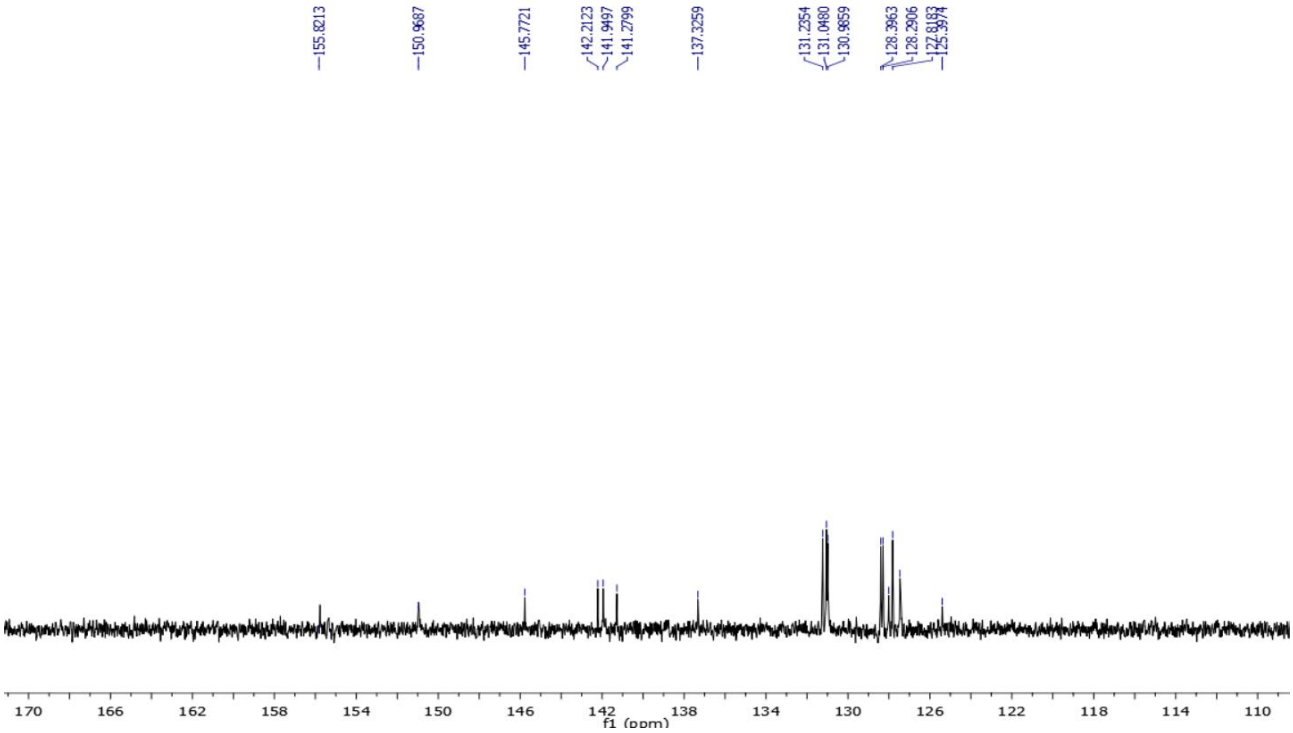
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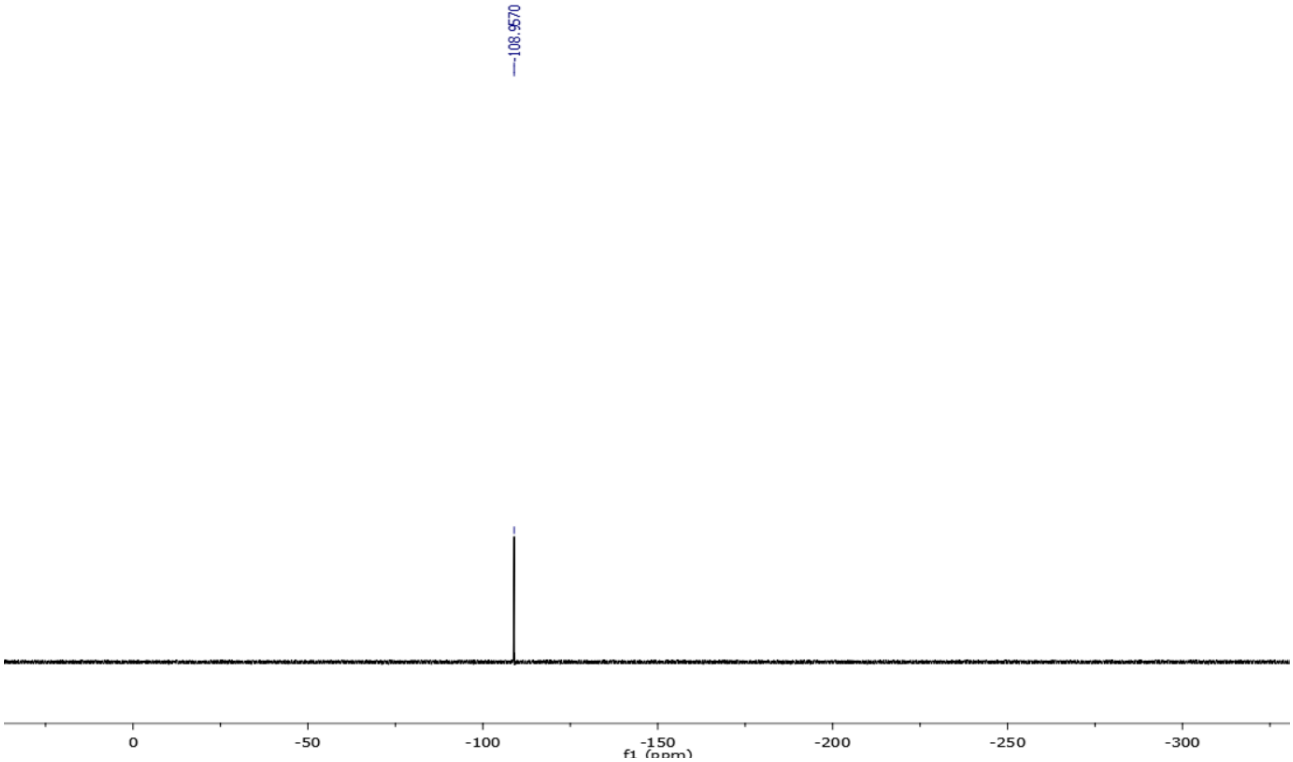


^{13}C-NMR spectra



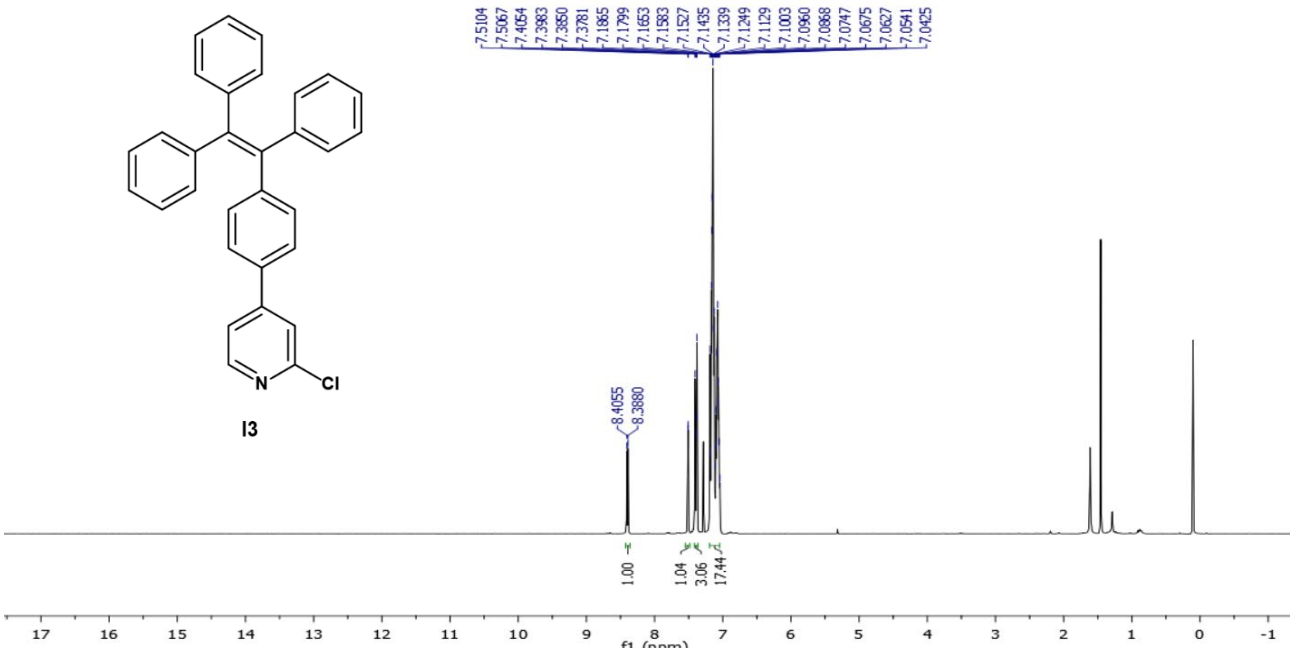


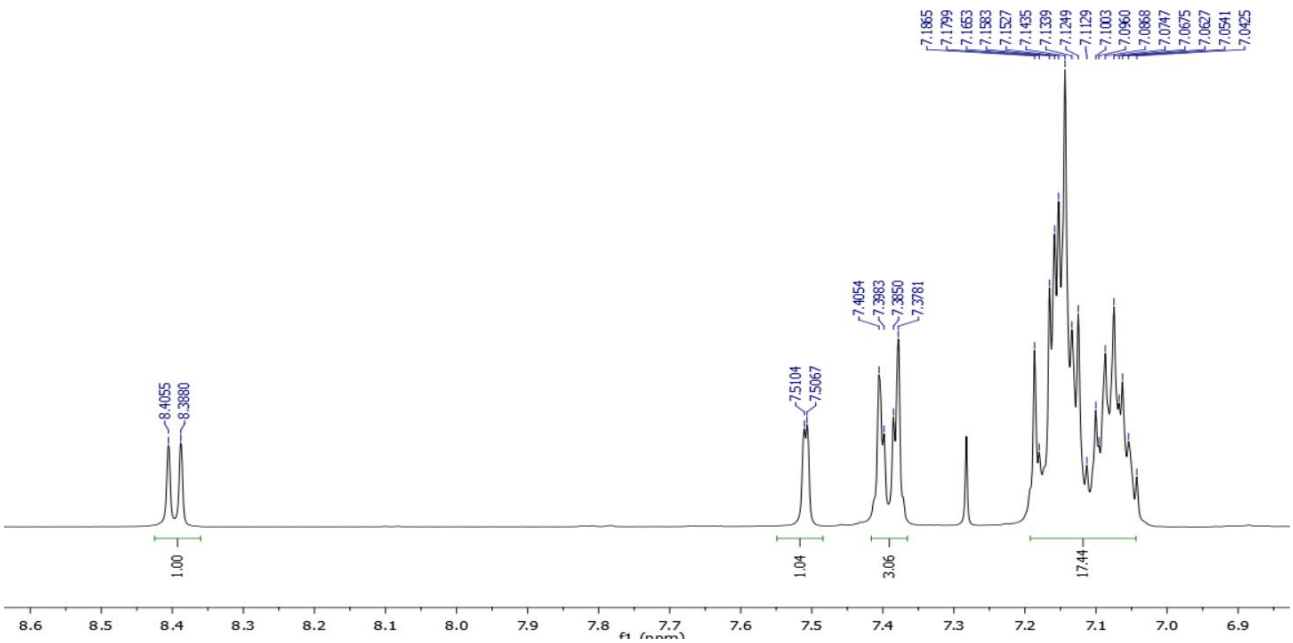
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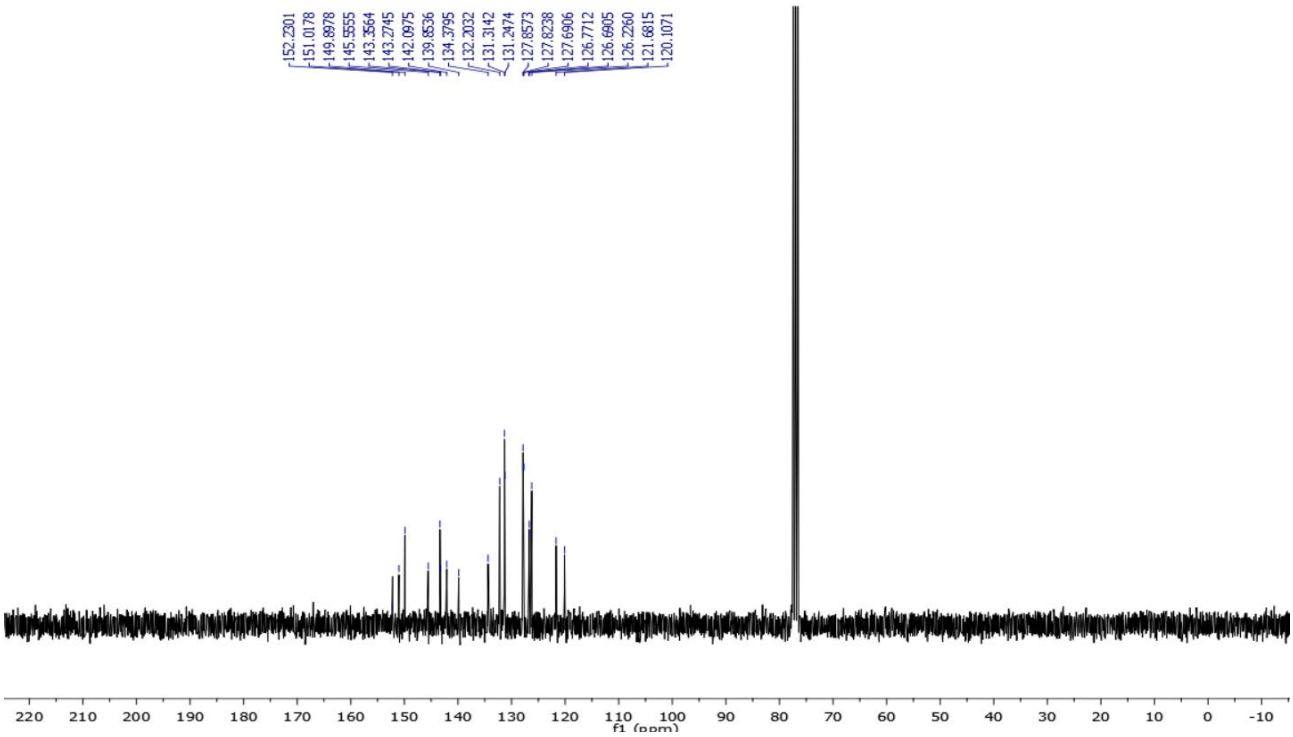
Intermediate I3

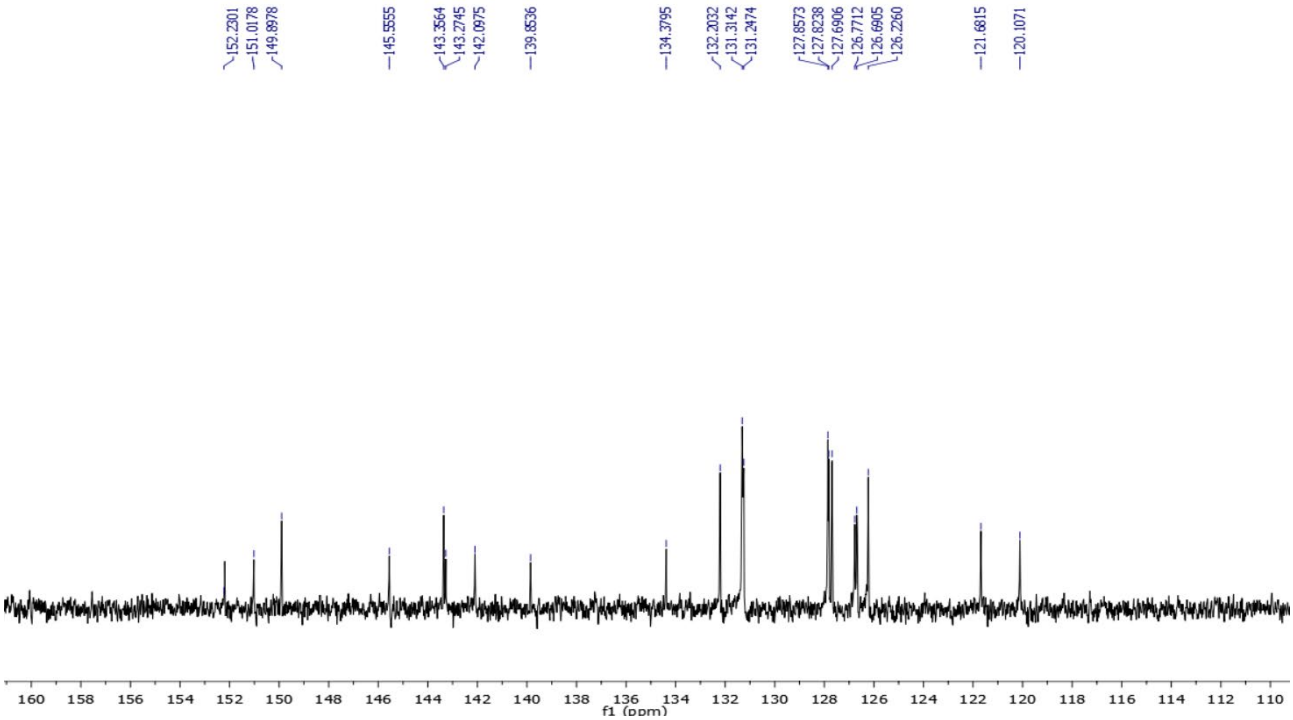
^{1}H-NMR spectra





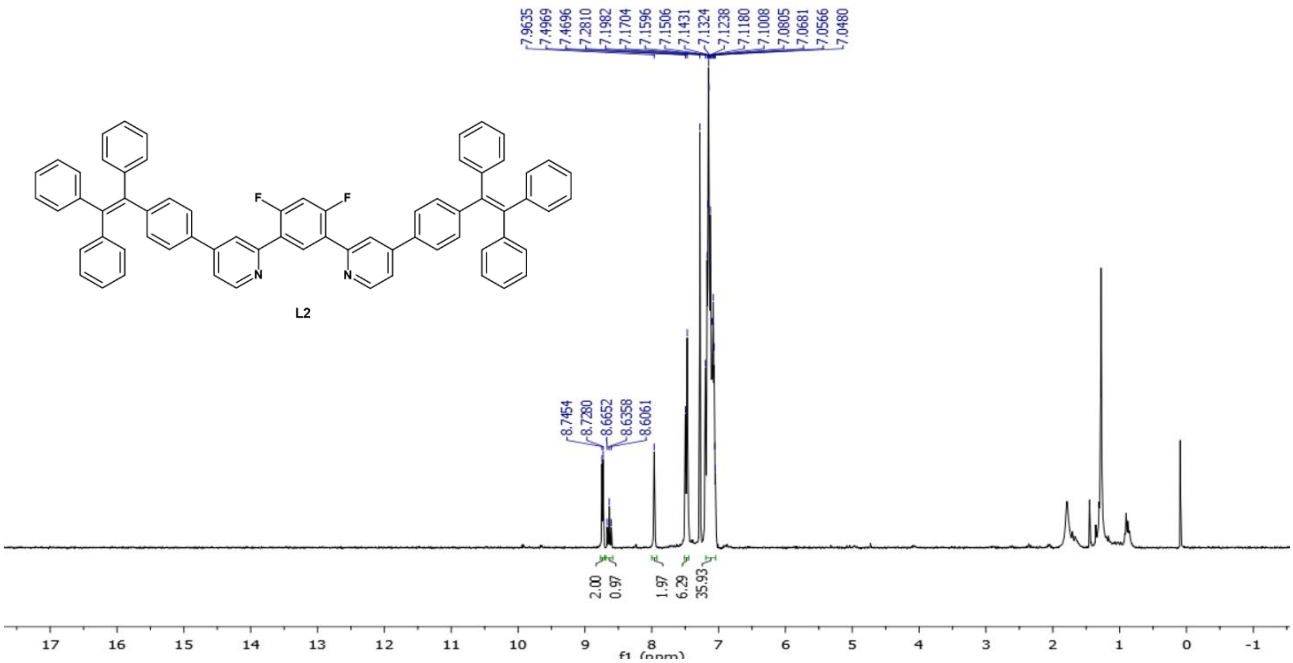
^{13}C-NMR spectra

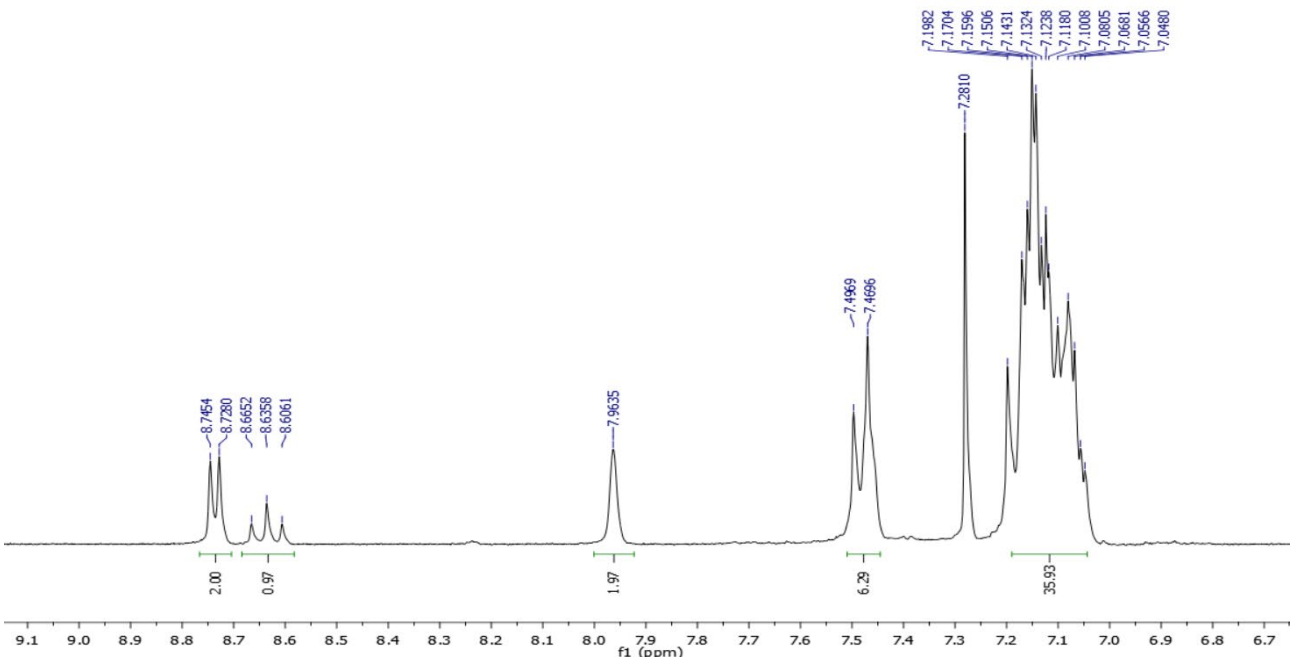




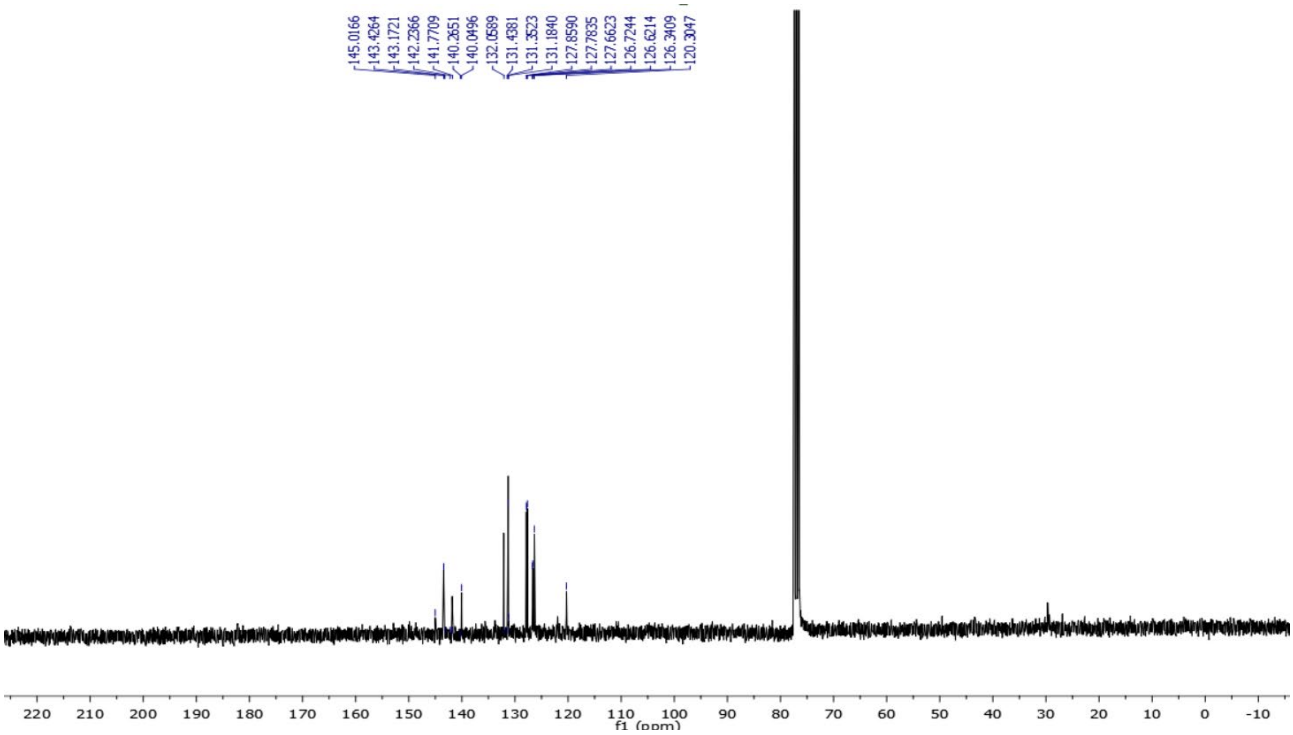
Ligand L2

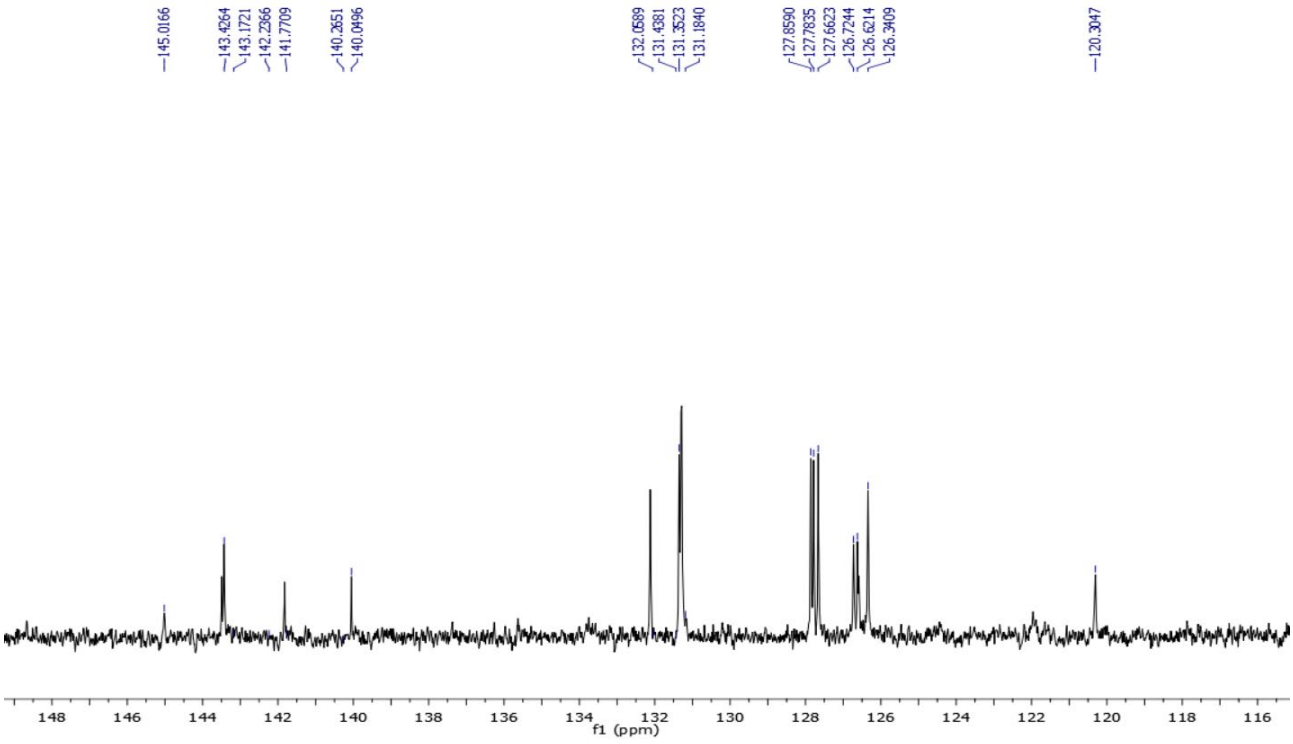
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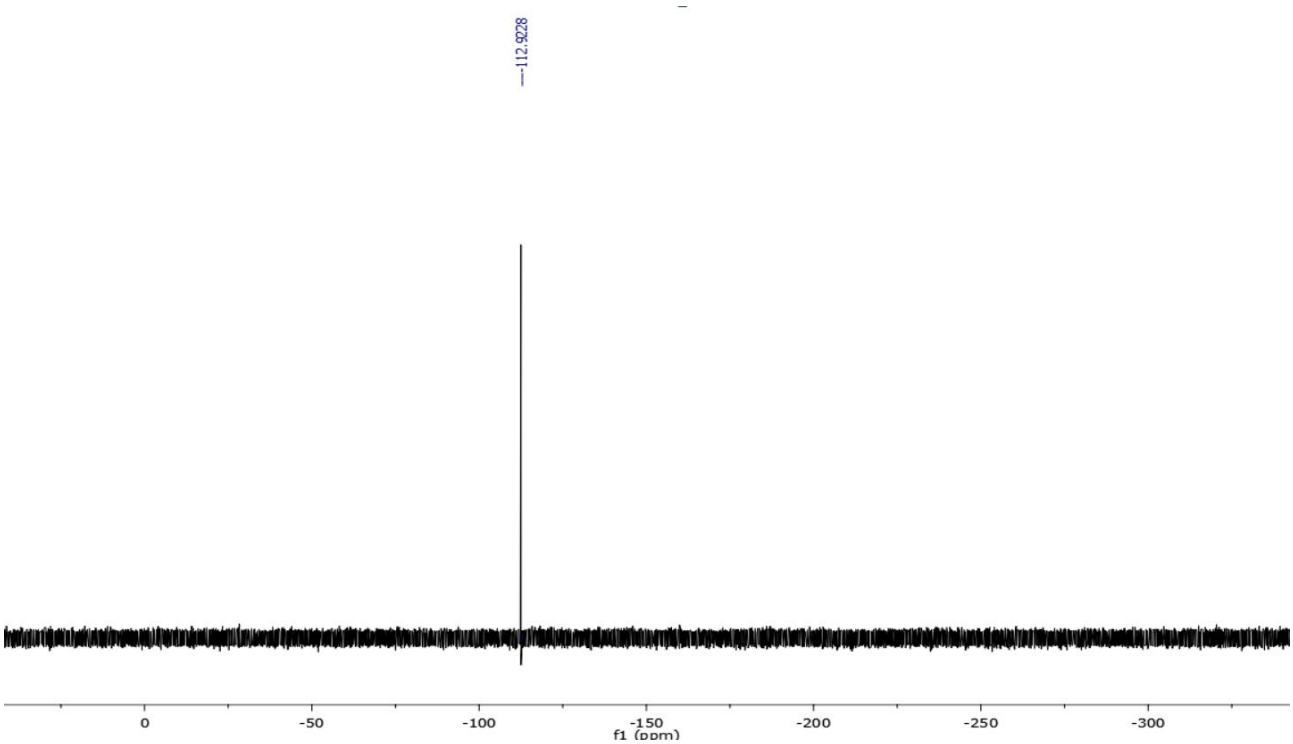


^{13}C-NMR spectra



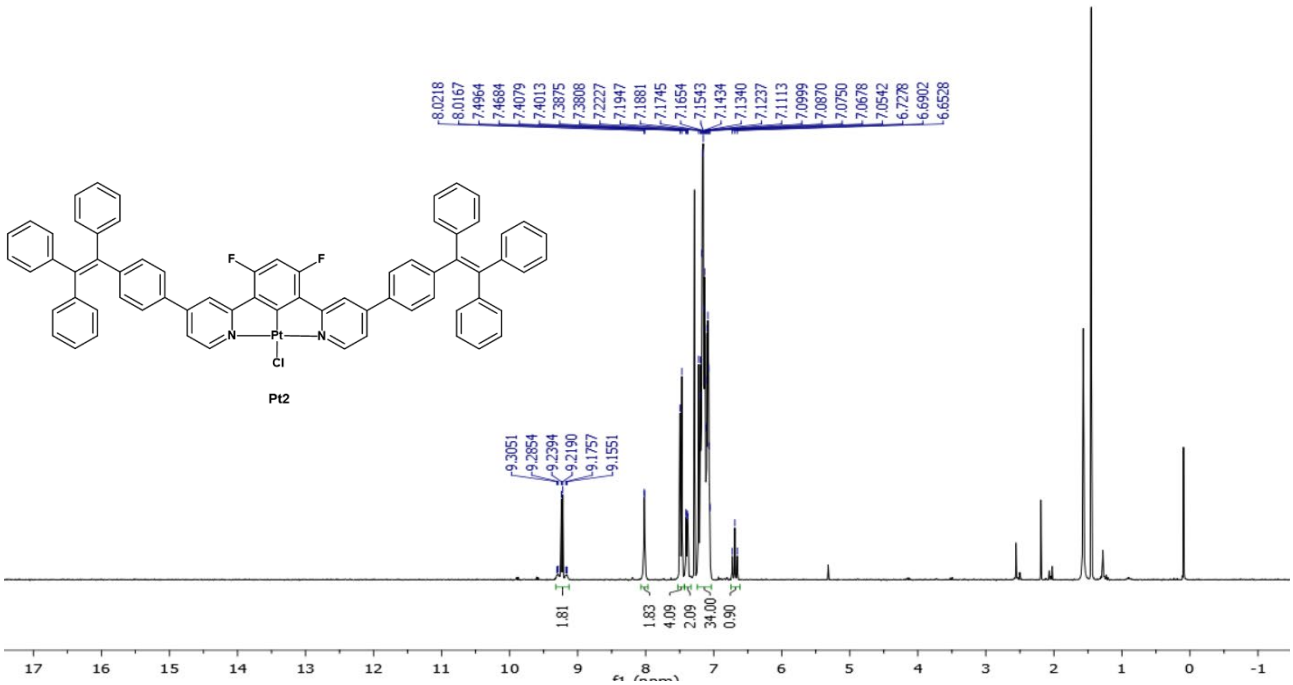


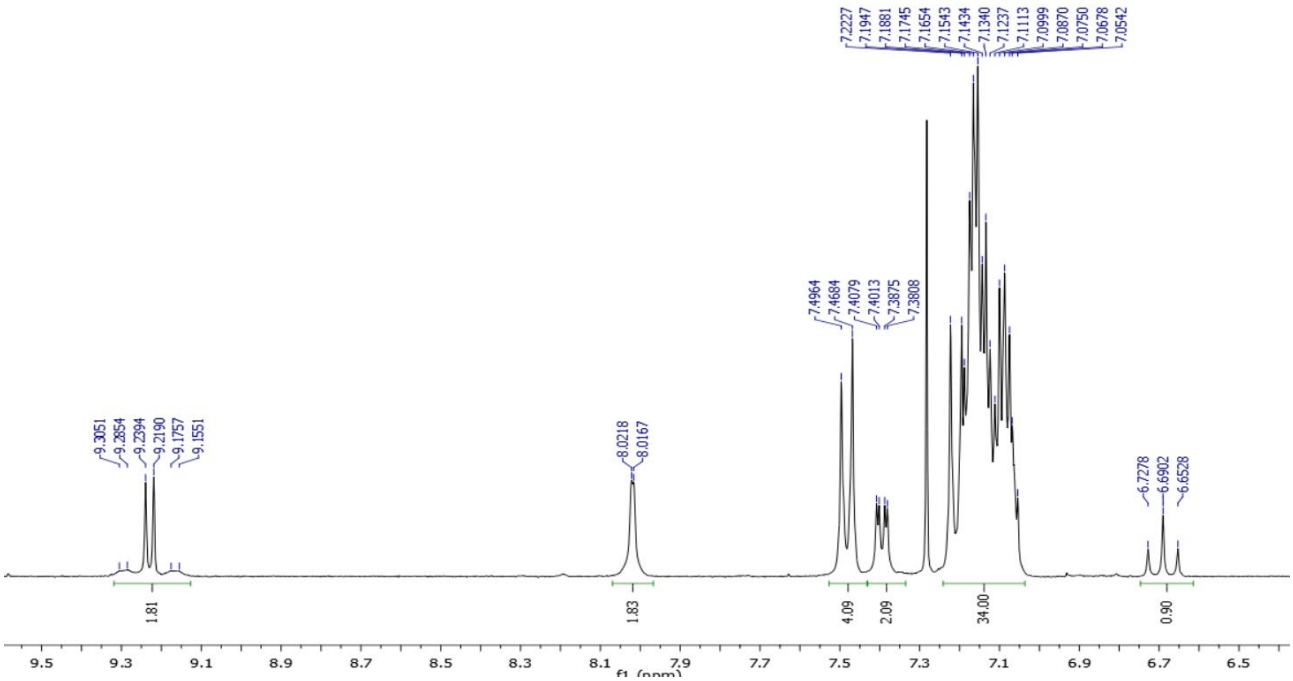
^{19}F-NMR spectra



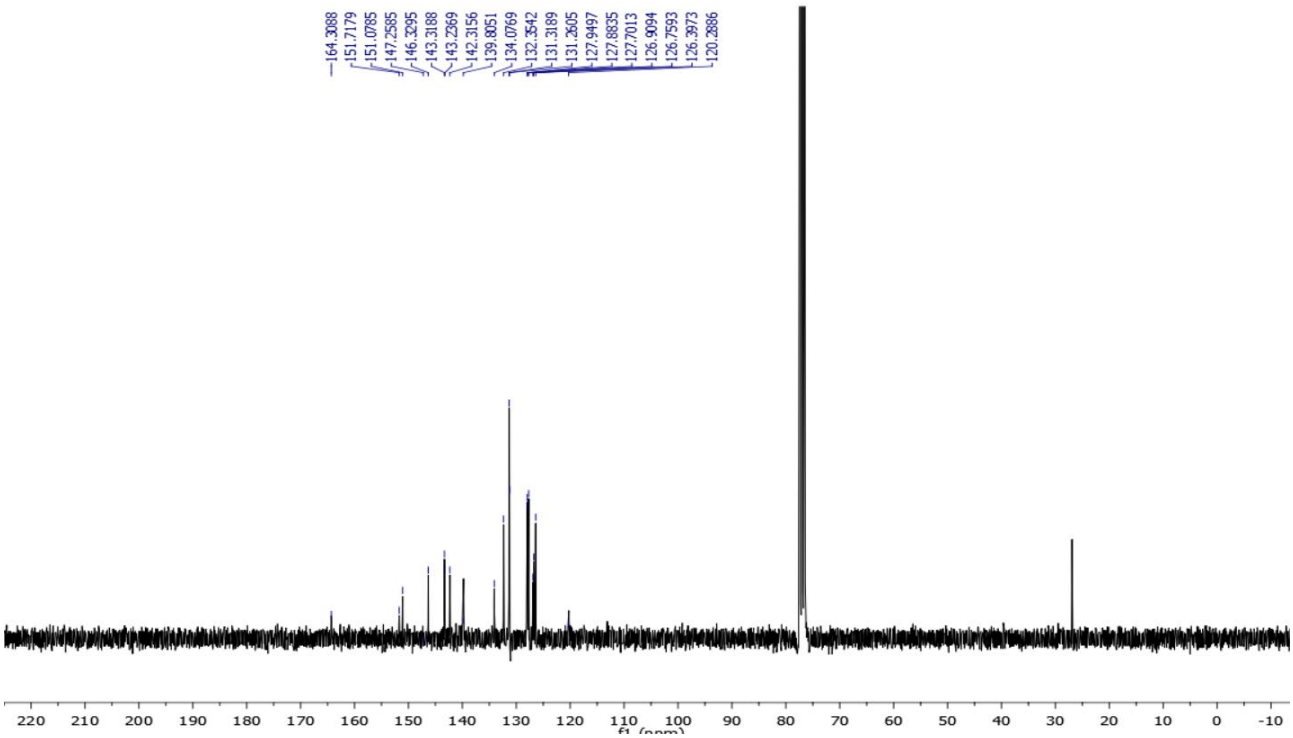
Complex 2

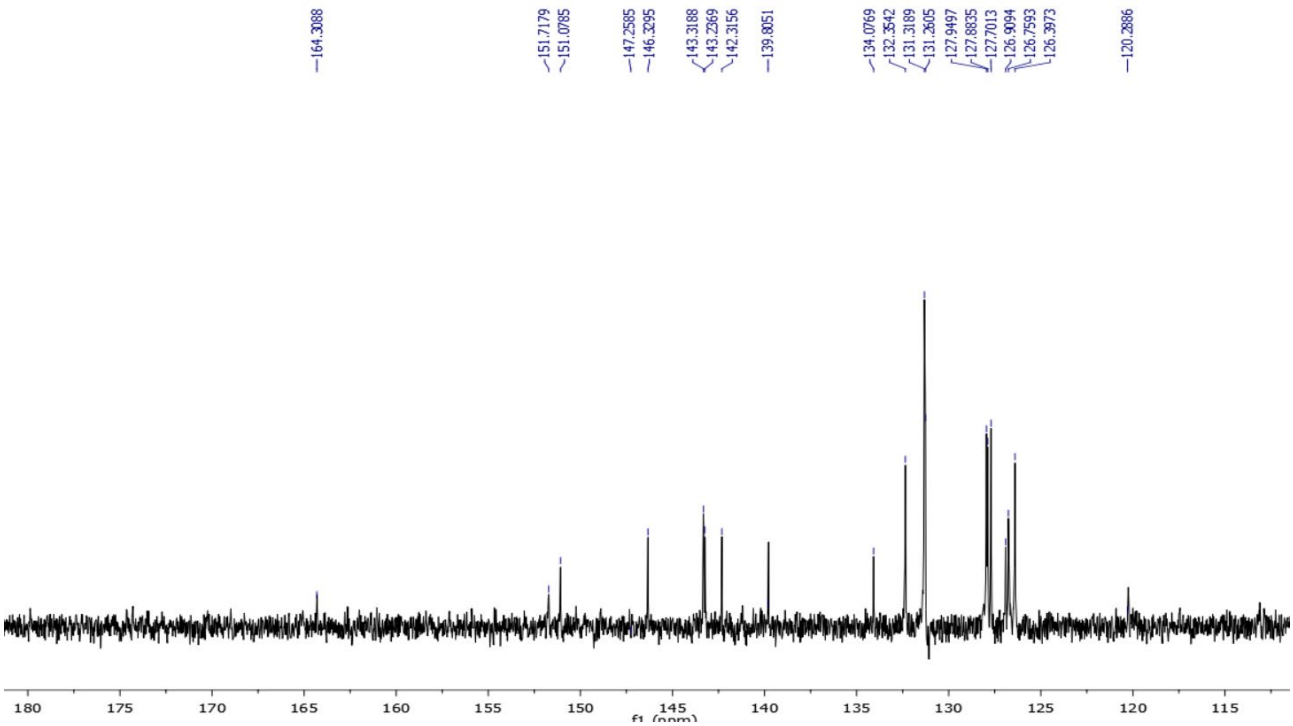
^{1}H-NMR spectra



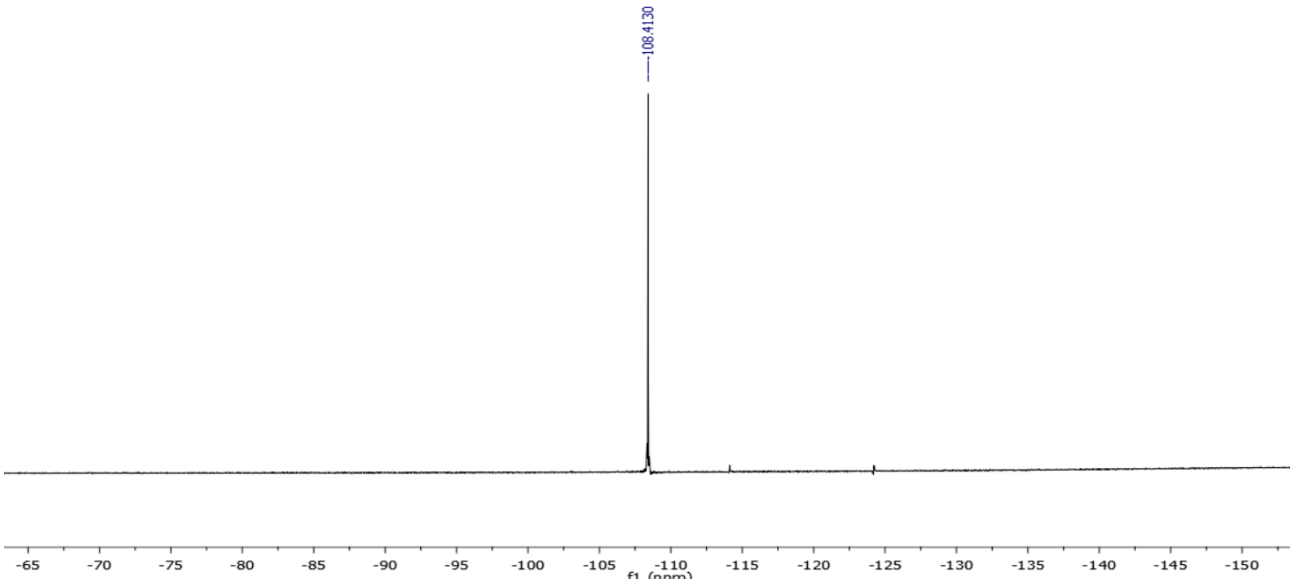


^{13}C-NMR spectra





^{19}F-NMR spectra



3. Photophysical characterization of 1 and 2

General comments

UV-Visible spectra were collected with a Shimadzu UV3600 spectrophotometer.

Luminescence measurements were carried out in CH_2Cl_2 solution after the Freeze-Pump-Thaw (FPT) procedure, necessary to remove dissolved oxygen.

Absolute photoluminescence quantum yield (Φ) was measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer. A description of the experimental setup and measurement method can be found in the article of K. Suzuki *et al.*[1]

Φ was calculated through Equation:

$$\Phi = \frac{PN\ (Em)}{PN\ (Abs)} = \frac{\int \frac{\lambda}{hc}\left[I_{em}^{sample}(\lambda) - I_{em}^{reference}(\lambda)\right]d\lambda}{\int \frac{\lambda}{hc}\left[I_{exc}^{sample}(\lambda) - I_{exc}^{reference}(\lambda)\right]d\lambda}$$

where PN(Em) is the number of emitted photons, PN(Abs) the number of absorbed photons, λ the wavelength, h the Planck's constant, c the speed of light, I_{em}^{sample} and $I_{em}^{reference}$ the photoluminescence intensities of the sample solution and reference in CH_2Cl_2, I_{exc}^{sample} and $I_{exc}^{reference}$ the excitation light intensities of the sample solution and reference in CH_2Cl_2. PN(Em) is calculated in the wavelength interval [λ_i, λ_f], where λ_i is taken 10 nm below the excitation wavelength, while λ_f is the upper end wavelength in the emission spectrum.

Steady state and time-resolved fluorescence data were obtained using a FLS980 spectrofluorimeter (Edinburg Instrument Ltd). Emission spectra were corrected for background intensity and quantum efficiency of the photomultiplier tube. Excitation spectra were corrected for the intensity fluctuation of a 450 W Xenon arc lamp. Quartz cuvettes with 1 cm optical path length were used.

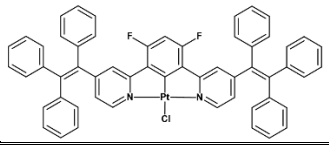
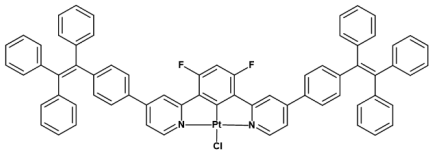
Photoluminescence lifetime measurements were performed using a microsecond flash Xe-lamp (60 W, 0.1÷100 Hz) and multi-channel scaling (MCS) data acquisition methods. Moreover, time-resolved fluorescence curves were fitted using an exponential function:

$$I(\lambda, t) = \alpha(\lambda) \exp\left(\frac{-t}{\tau}\right)$$

where α (λ) is the amplitude at wavelength λ and τ is the lifetime. The quality of the fit was evaluated through the reduced χ^2 values.

Absorption maxima and molar extinction coefficients

Table S1. Absorption maxima and corresponding molar extinction coefficients for complexes **Pt1** and **Pt2** in CH_2Cl_2 solution.

Complex		$\lambda_{max,\,abs}$ / nm	ε / (104 cm^{-1} M^{-1})
	**1**	244 391	5.6 3.1
	**2**	243 282 393	6.4 6.1 4.6

Excitation and Emission spectra

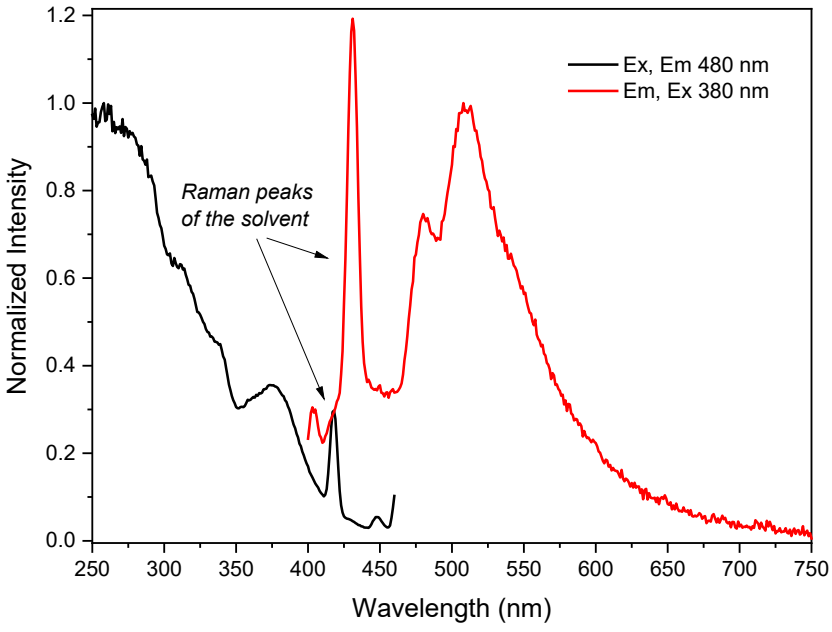


Figure S1. Excitation and Emission spectra of complex **Pt1** in CH_2Cl_2.

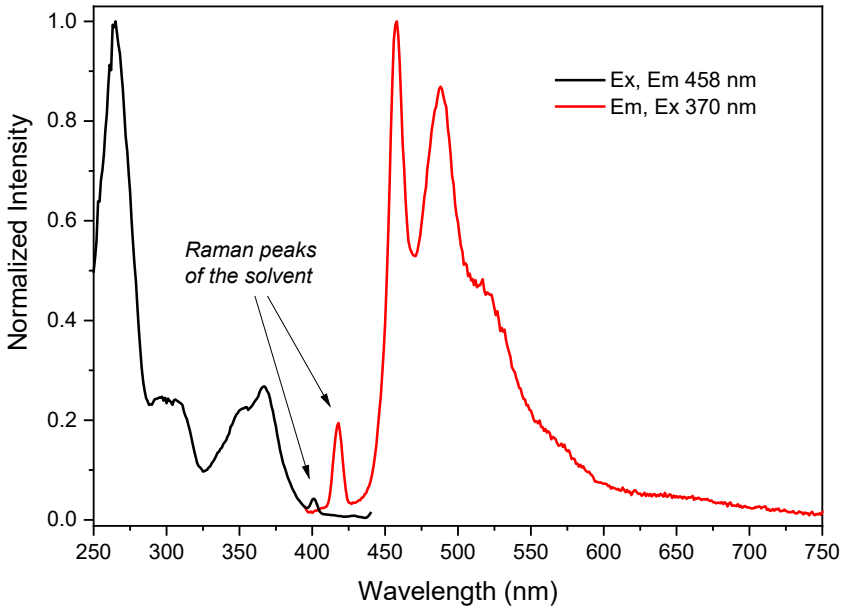


Figure S2. Excitation and Emission spectra of complex **2** in CH_2Cl_2.

Lifetimes measurements

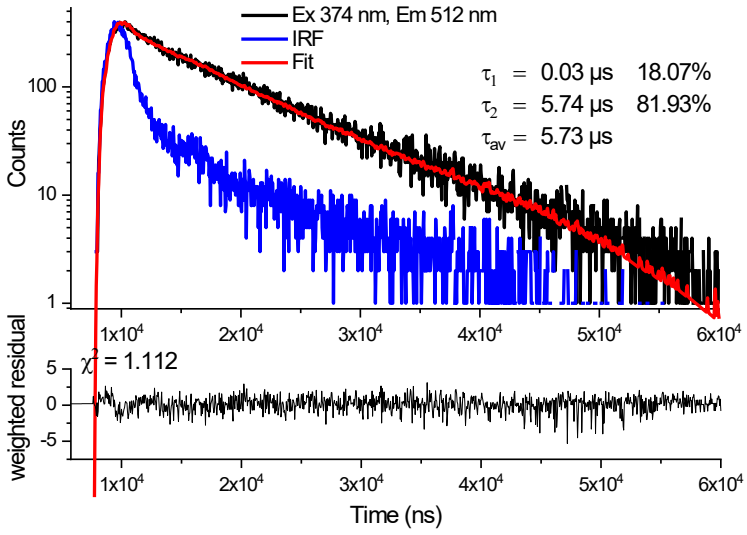


Figure S3. Excited state decay of complex **1** in CH_2Cl_2 solution.

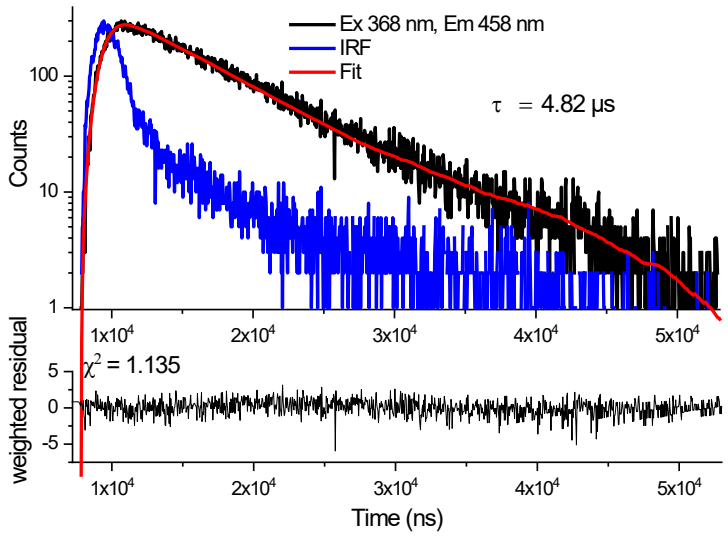


Figure S4. Excited state decay of complex **2** in CH_2Cl_2 solution.

References

1. Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishic, S.; Tobita, S. *Phys. Chem. Chem. Phys.*, 2009, 11, 9850–9860.