New members of the family of highly luminescent 1,3-bis(4-phenylpyridin-2-yl)-4,6-difluorobenzene platinum(II) complexes: Exploring the effect of substituents on the 4-phenylpyridine unit

Giulia De Soricellis,[a,b] Bertrand Carboni,[c] Véronique Guerchais,[c] J. A. Gareth Williams,[d] Daniele Marinotto,[e] Alessia Colombo,[a] Claudia Dragonetti,[a] Francesco Fagnani,*[a] Simona Fantacci[f] and Dominique Roberto[a]

[a]Dipartimento di Chimica, Università degli Studi di Milano and UdR-INSTM di Milano, Via C. Golgi 19, I-20133 Milan, Italy

[b] Dipartimento di Chimica, Università di Pavia, Via Taramelli 12, I-27100 Pavia, Italy

[c]Université de Rennes 1, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France

[d]Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, United Kingdom.

[e]Istituto di Scienze e Tecnologie Chimiche (SCITEC) "Giulio Natta", Consiglio Nazionale delle Ricerche (CNR), via C. Golgi 19, I-20133 Milan, Italy

[f]Istituto di Scienze e Tecnologie Chimiche ‘‘Giulio Natta’’ SCITEC, Consiglio Nazionale delle Ricerche (CNR), Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), via Elce di Sotto 8, 06213, Perugia, Italy

General Information

All the reagents and the solvents (dioxane, 1,2-dimethoxyethane, acetonitrile) were used as received from the supplier. Anhydrous toluene was obtained via distillation under argon in the presence of benzophenone. The purifications were performed through column chromatography on silica gel (Merck Geduran 60, 0.063–0.200 mm). Grace Reveleris™ with Puriflash™ 40µm flash cartridges (Buchi) was used to perform flash chromatography.

The NMR characterizations were obtained recording on a Bruker AV III 300 MHz or AV III 400 MHz spectrometers. Chemical shifts of ^{1}H, ^{19}F and ^{13}C NMR spectra are reported in parts per million (ppm) and the coupling constants are measured in Hertz (Hz). The multiplicities of signals are listed as singlet (s), d (doublet), t (triplet), quartet (q), multiplet (m).

The molecules were analyzed through mass spectrometry at the Centre Régional de Mesures Physiques de l'Ouest, University of Rennes 1, on a LC-MS Agilent 6510, a Brucker MaXis 4G or a Thermo Fisher Q-Exactive using ESI and ASAP techniques. Elemental analyses were performed by the Department of Chemistry of the University of Milan.

Photophysical Characterizations

Solutions were sonicated for 20 minutes before photophysical characterizations.
UV-Visible spectra were collected by 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.*[2]
Φ was calculated through Equation:

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

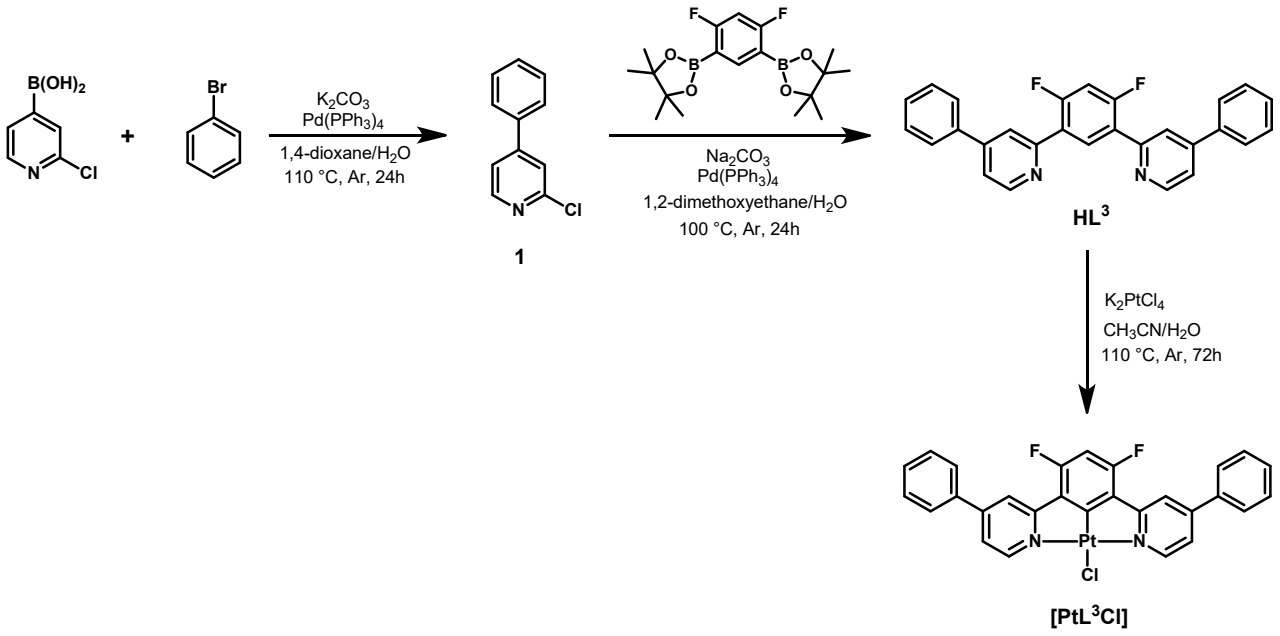
where PN(Em) is the number of emitted photons, PN(Abs) the number of absorbed photons, λ the wavelength, h the Planck's constant, c the speed of light, I_{em}^{sample} and $I_{em}^{reference}$ the photoluminescence intensities of the sample solution and reference in CH_2Cl_2, I_{exc}^{sample} and $I_{exc}^{reference}$ 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 for diluted solution, meanwhile quartz cuvettes of 1 mm optical path length were used for concerted solution. Time-resolved fluorescence measurements were performed through the time-correlated single photon counting technique with an Edinburgh Picosecond Pulsed Diode Laser (emitted wavelength 374 nm). 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.

Synthesis of PtL^3Cl



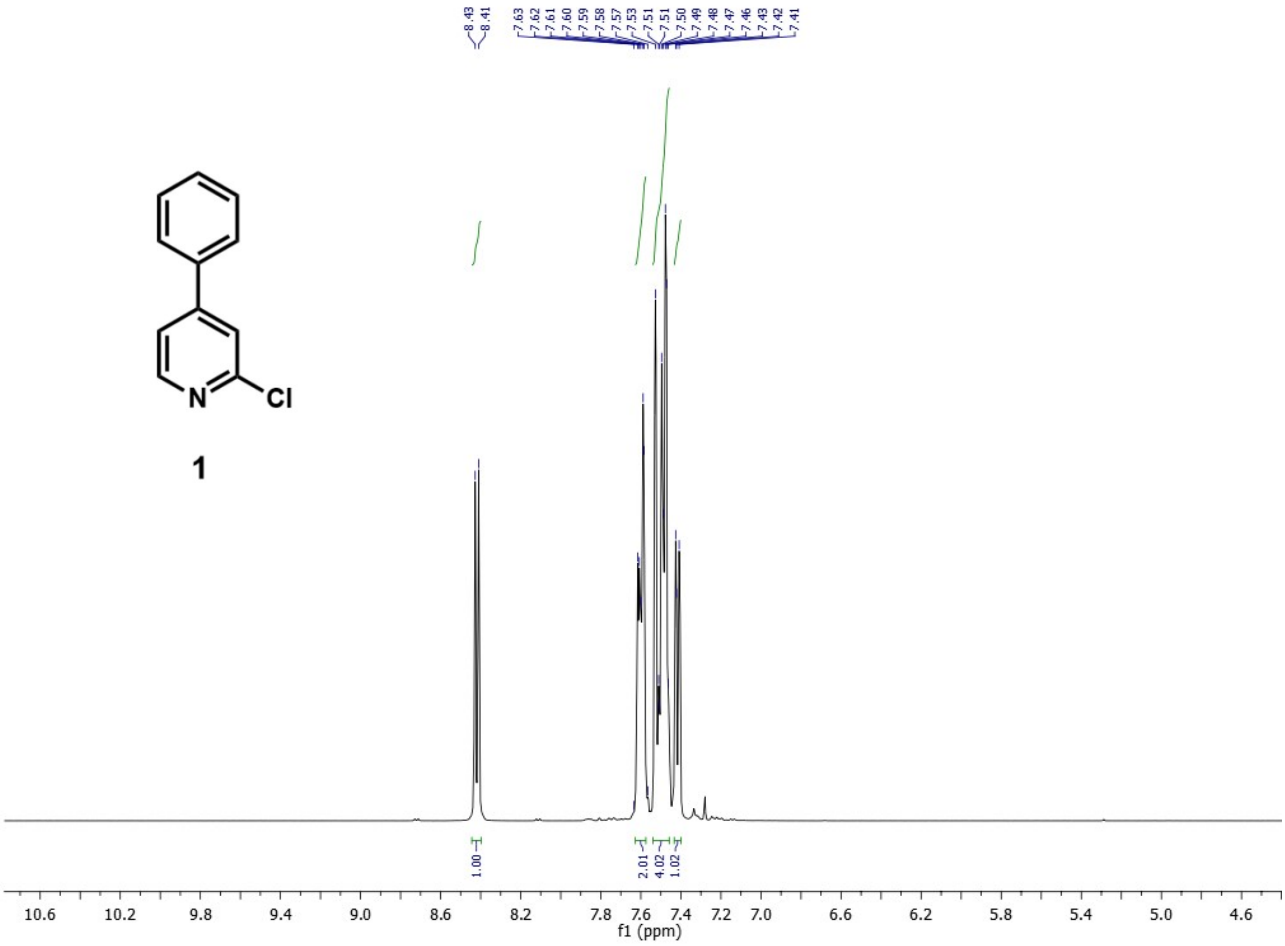
2-chloro-4-phenylpyridine (1): In a Schlenk flask, 2-chloro-pyridine-4-boronic acid (1.12 g, 7.1 mmol), bromobenzene (0.80 g, 5.1 mmol), $Pd(PPh_3)_4$ (0.29 g, 0.2 mmol) and Na_2CO_3 (1.62 g, 15.3 mmol) were solubilized in a mixture of distilled water (10 mL) and 1,4-dioxane (20 mL) under argon atmosphere. The obtained mixture was degassed by bubbling argon under stirring for 40 min. The vessel was then sealed and heated at 110 °C overnight. Then, the solution was allowed to cool to room temperature, was neutralized with aqueous 1M HCl, and extracted with ethyl acetate (3 x 20 mL). The organic layers were gathered, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The yellow oily residue was purified by silica gel chromatography (cyclohexane:AcOEt, 20:1, v/v) and a colorless oil was obtained (150 mg, 19% yield). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.42 (d, J = 5.2 Hz, 1H), 7.60 (m, 2H), 7.44-7.55 (m, 4H), 7.42 (dd, J = 5.1, 1.1 Hz, 1H). ^{13}C {1H} NMR (75.48 MHz, $CDCl_3$, δ): 152.19, 151.52, 149.98, 136.77, 129.68, 129.25, 127.01, 122.01, 120.47. HRMS (ESI+): $(M + H)^+$ calcd for $C_{11}H_8N^{35}Cl$, 190.0418; found: 190.0417.

2,2'-(4,6-difluoro-1,3-phenylene)bis(4-phenylpyridine) (HL^3): compound **1** (0.18 g, 0.98 mmol), 2,2'-(4,6-difluoro-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.16 g, 0.44 mmol), an aqueous Na_2CO_3 solution (1 M, 7 mL), $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol) and 1,2-dimethoxyethane (7 mL) were placed in a two neck round bottom flask under an argon atmosphere. Before sealing the

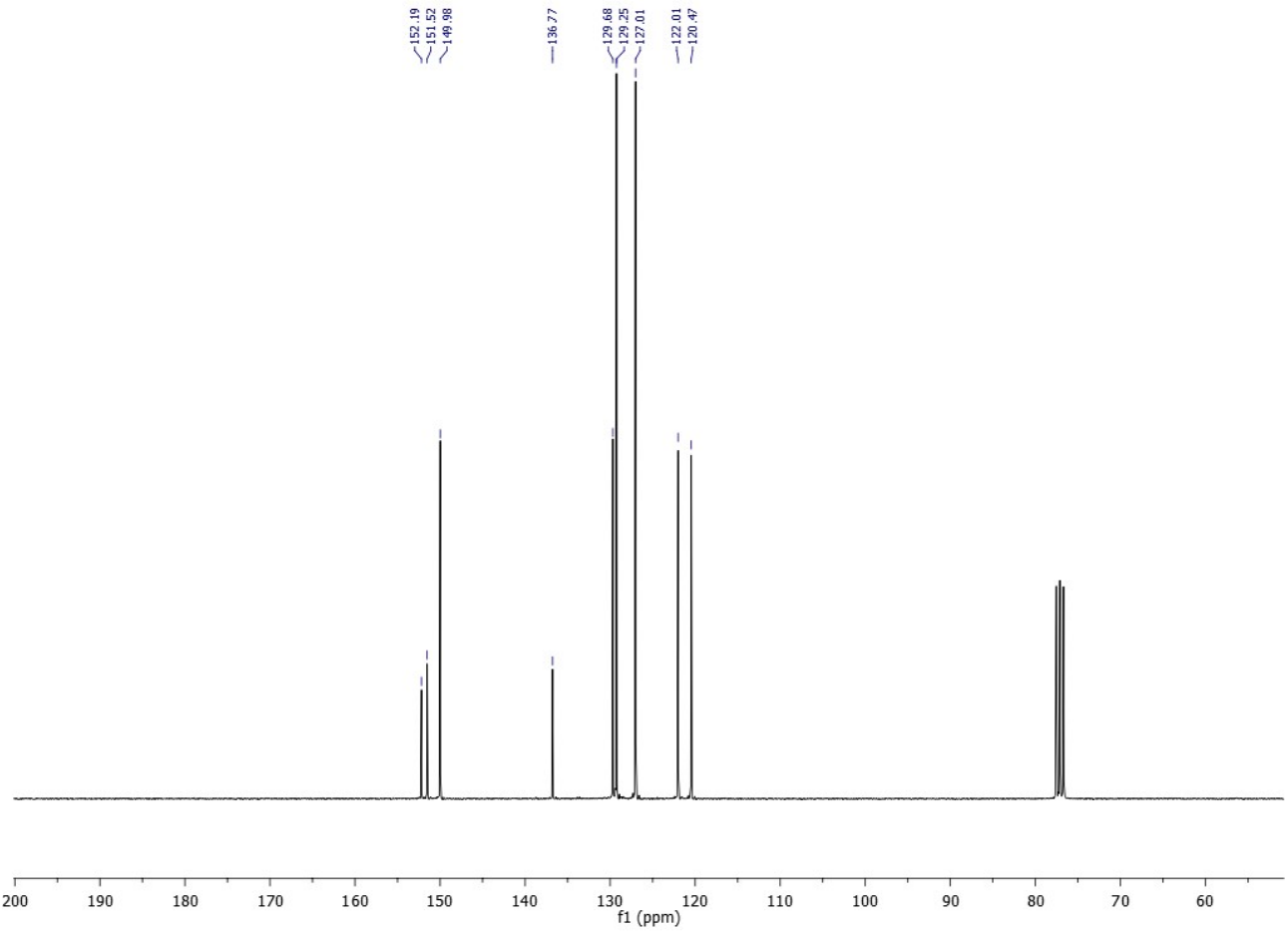
flask, the reaction mixture was degassed by bubbling argon for 30 min. The vessel was then heated to reflux at 100 °C overnight. Upon cooling to room temperature, the mixture was evaporated under reduced pressure. The oily residue was diluted in dichloromethane and washed with water (3 x 20 mL). The organic phase was collected, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by silica gel chromatography (cyclohexane:AcOEt, 16:1, v/v) to obtain a colorless oil (227 mg, 55% yield). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.80 (d, J = 5.2 Hz, 2H), 8.71 (t, J = 9.0 Hz, 1H), 8.02 (s, 2H), 7.72 (d, J = 6.8 Hz, 4H), 7.43-7.59 (m, 8H), 7.11 (t, J = 10.6 Hz, 1H). ^{19}F {1H} NMR (282.36 MHz, $CDCl_3$, δ): -112.43 (s, 2F). ^{13}C {1H} NMR (75.48 MHz, $CDCl_3$, δ): 162.4, 162.2, 158.9, 158.8, 153.1, 153.0, 150.1, 149.0, 138.2, 133.8 (t, J = 4.5 Hz), 129.1, 127.1, 124.7, 124.5, 122.3, 120.6, 105.1 (t, J = 27.0 Hz). HRMS (ESI+): $(M + H)^+$ calcd for $C_{28}H_{18}N_2F_2$, 421.15108; found: 421.1509.

PtL^{3}Cl: **HL^3** (0.10 g, 0.24 mmol) was dissolved in acetonitrile (9 mL) and then a solution of K_2PtCl_4 (0.16 g, 0.38 mmol) in water (1 mL) was added. Before sealing the flask, the reaction mixture was degassed by bubbling argon for 30 minutes. The reaction was heated at 110 °C for 72h. The obtained suspension was allowed to cool to room temperature and was filtered through a 0.45 μm Nylon membrane. The collected solid was then washed with water (5 mL), MeOH (3 mL) and diethyl ether (7 mL), and dried under vacuum to obtain the desired complex as a yellow powder (121 mg, 93% yield). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 9.32 (d, J = 6.1 Hz, ^{3}J(^{195}Pt) = 41 Hz, 2H), 8.11 (s, 2H), 7.69 – 7.78 (m, 4H), 7.58 (dd, J = 8.9, 5.0 Hz, 6H), 7.49 (dd, J = 6.0, 1.9 Hz, 2H), 6.77 (t, J = 11.3 Hz, 1H). ^{19}F{^{1}H} NMR (282.36 MHz, $CDCl_3$, δ): -108.30 (s, ^{3}J(^{195}Pt) = 43.2 Hz, 2F). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, δ): 151.8, 136.7, 130.3, 129.4, 127.2, 120.7, 120.4 (some peaks are not visible due to the poor solubility of the complex). Anal. calcd. for $C_{28}H_{17}F_2N_2{}^{195}Pt{}^{35}Cl$: C, 51.74; H, 2.64; N, 4.31; found: C, 51.83; H, 2.67; N, 4.33.

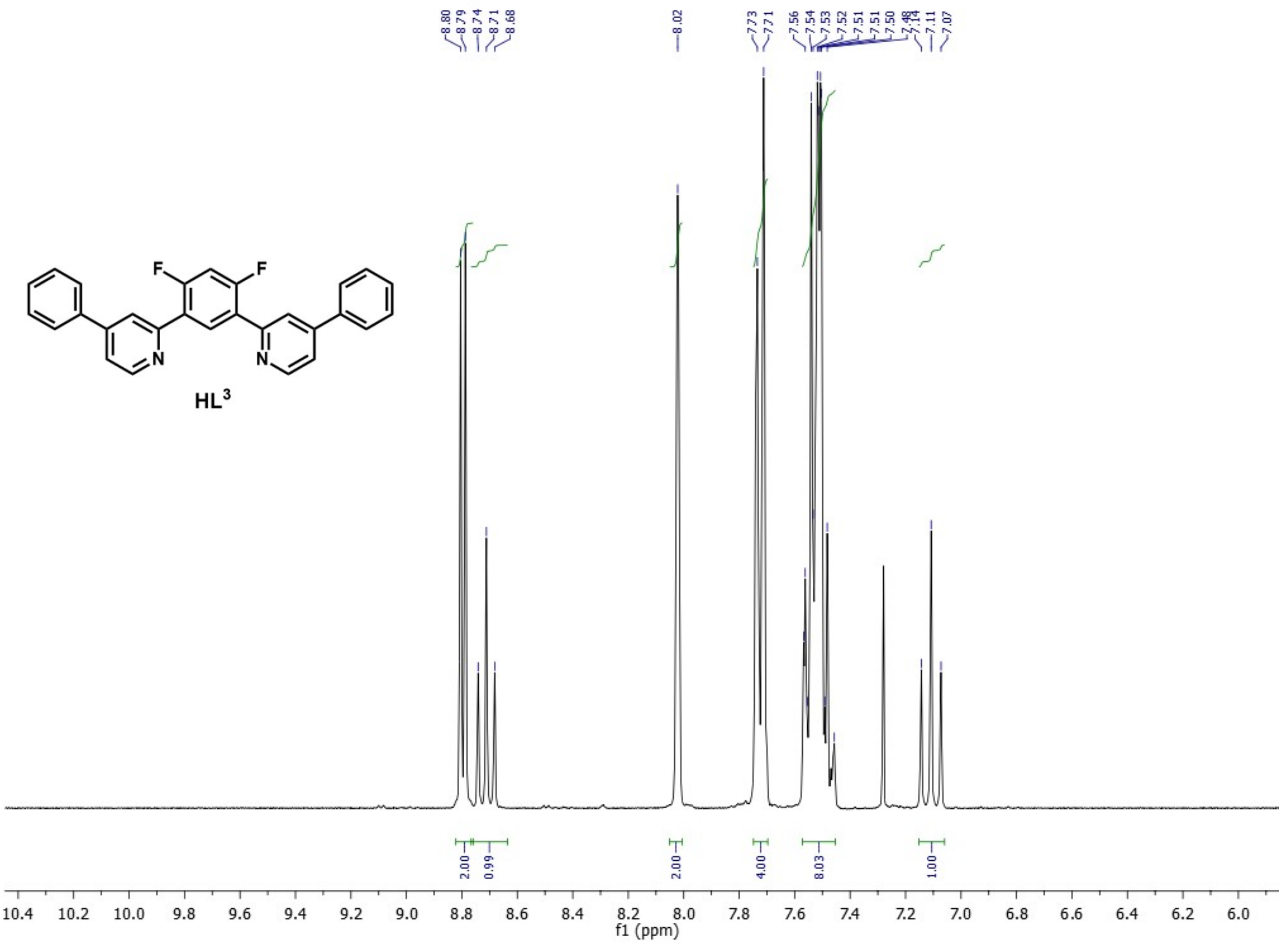
^{1}H, ^{13}C, and ^{19}F NMR Spectra



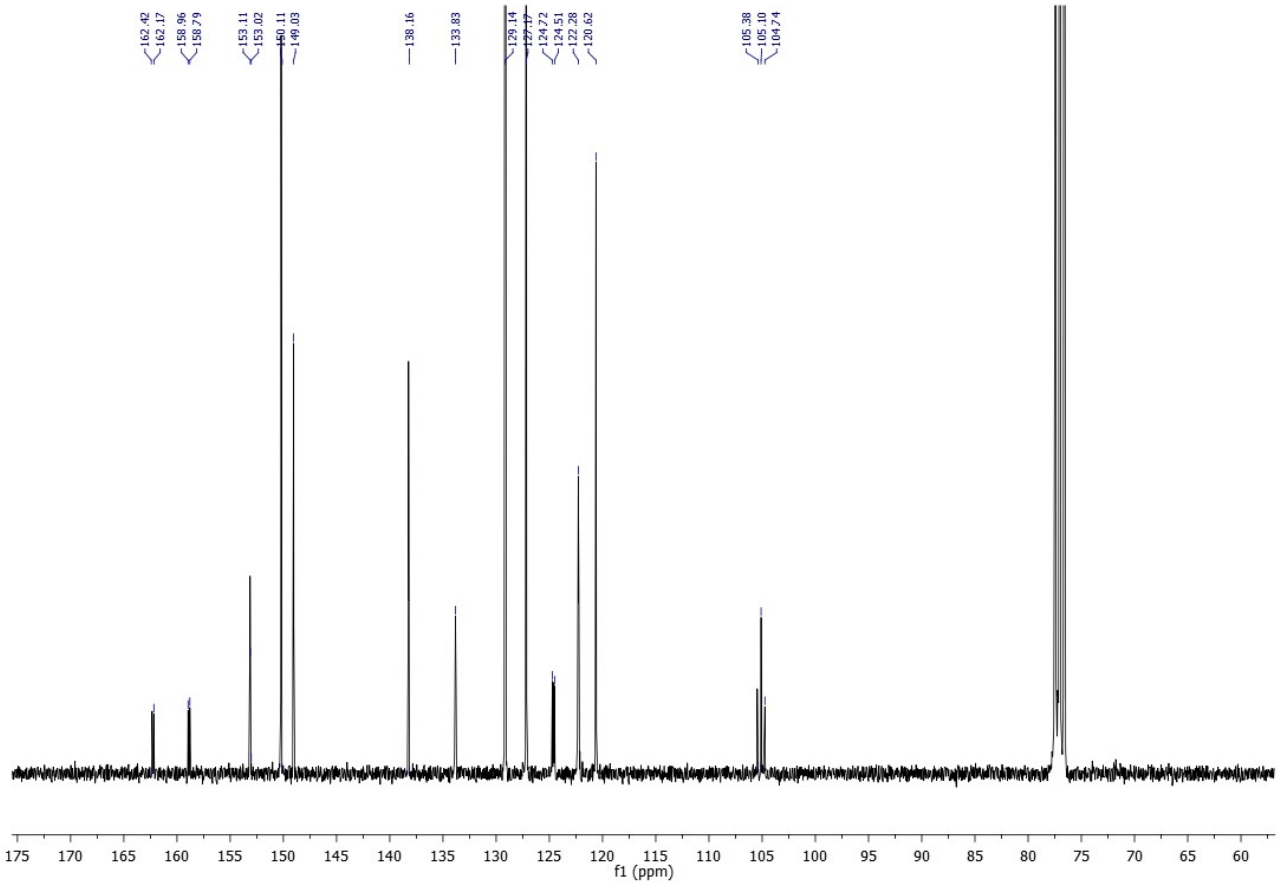
^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **1**.



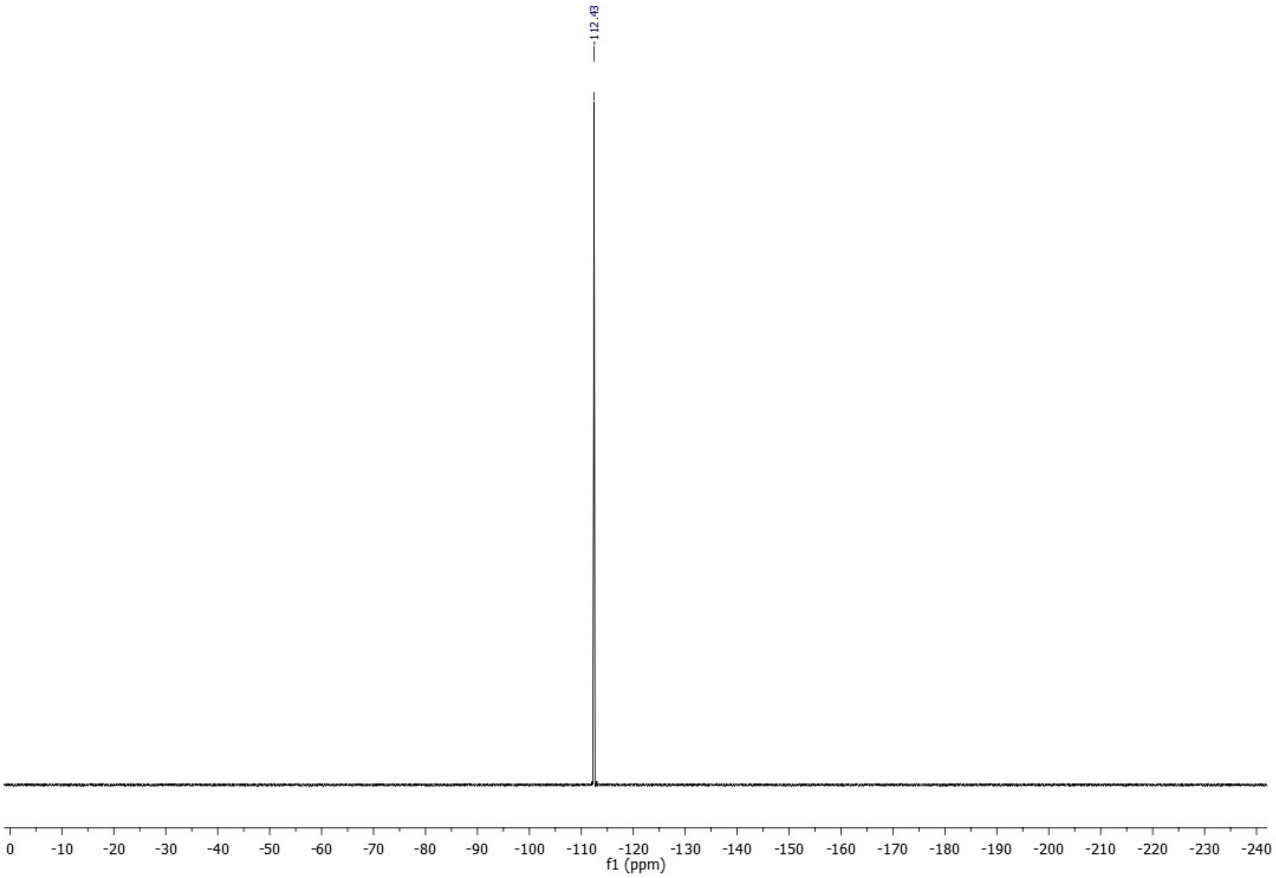
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75.48 MHz) of compound **1**.



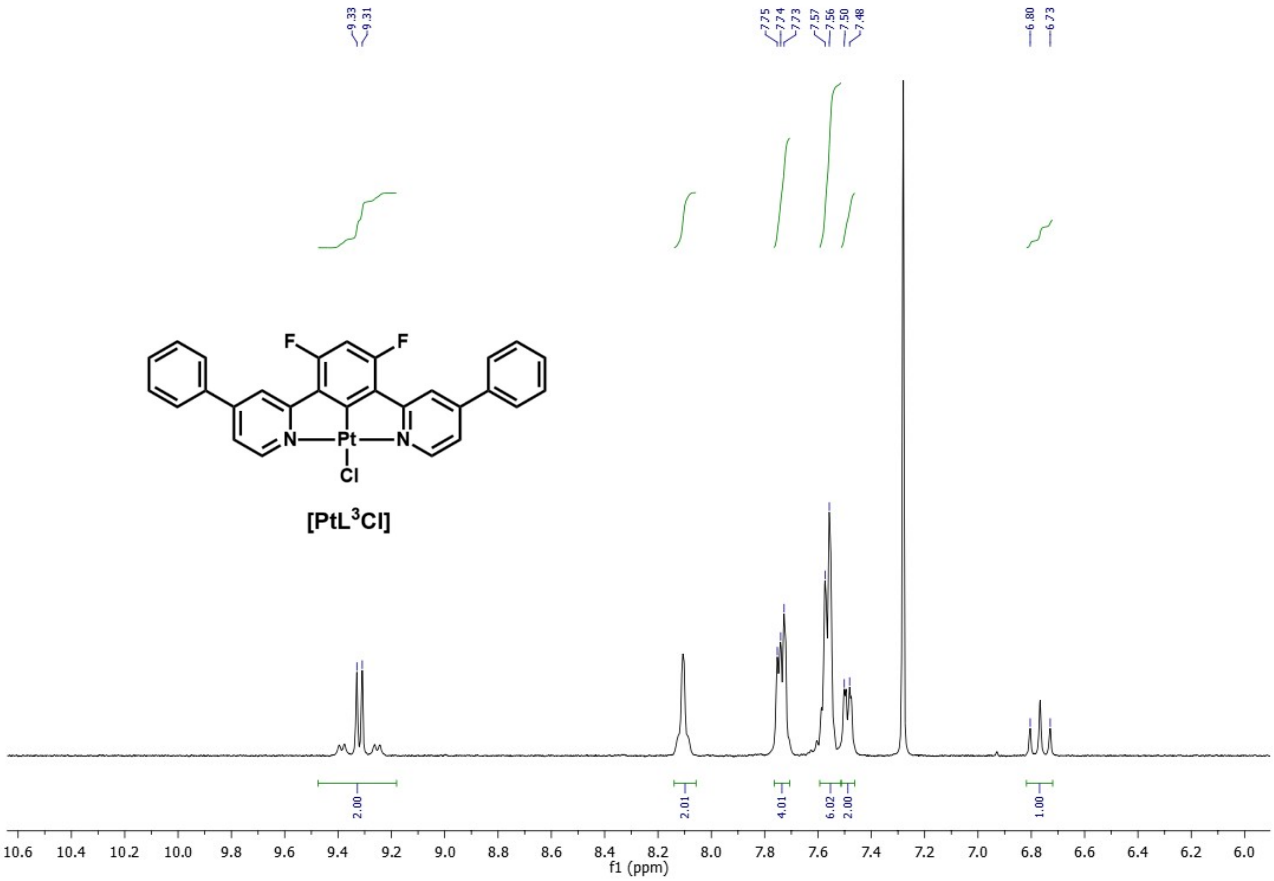
^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **HL^{3}**.



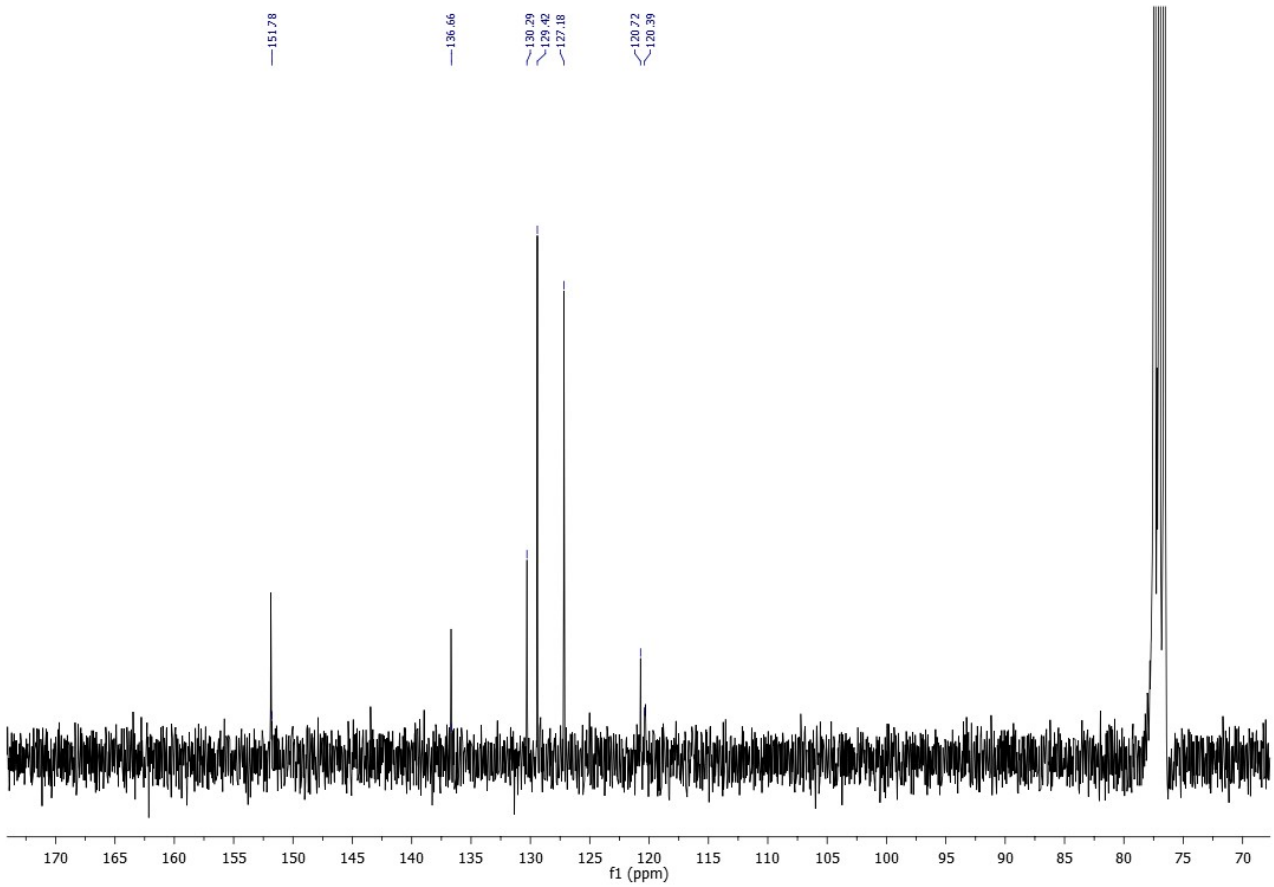
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75.48 MHz) of compound **HL^3**.



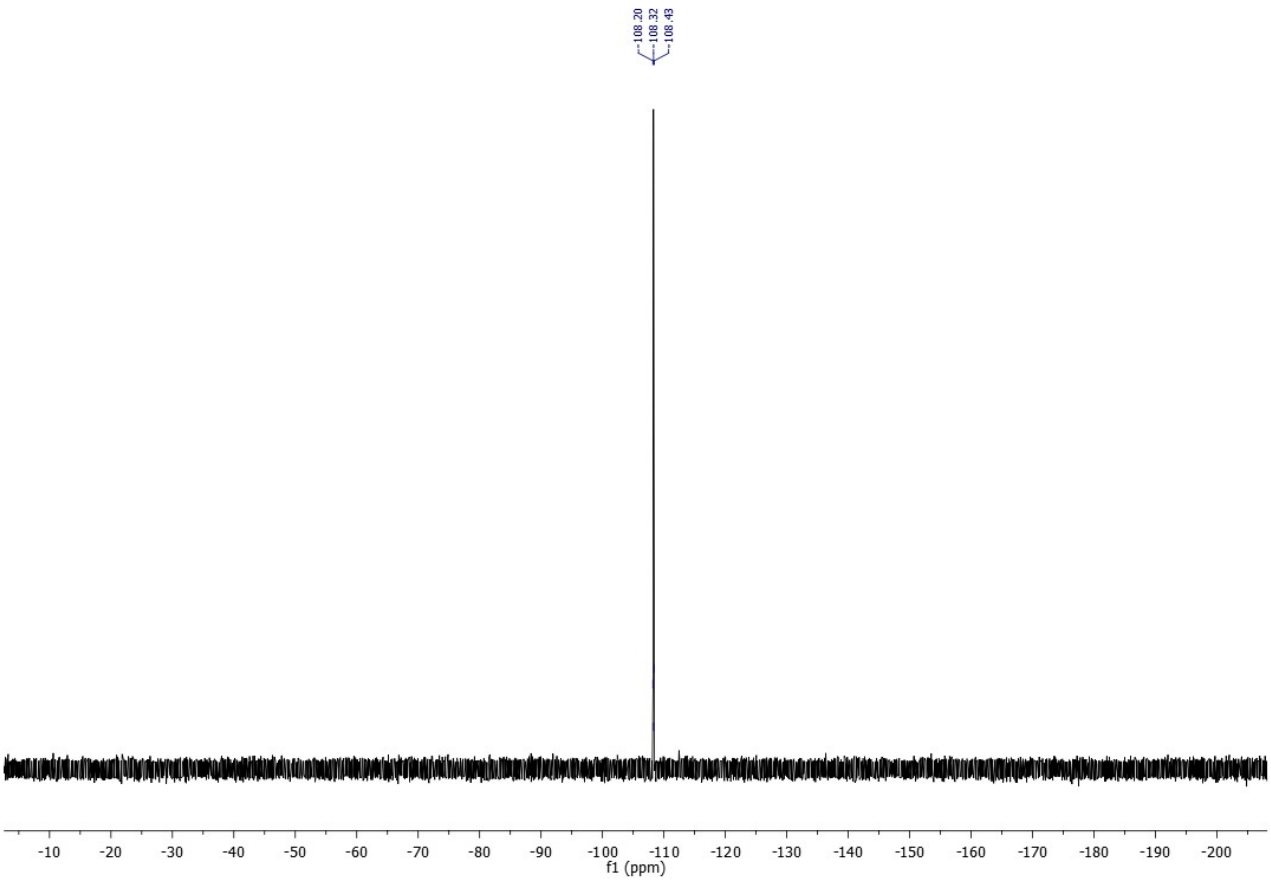
$^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 282.36 MHz) of compound **HL^3**.



^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **PtL^{3}Cl**.

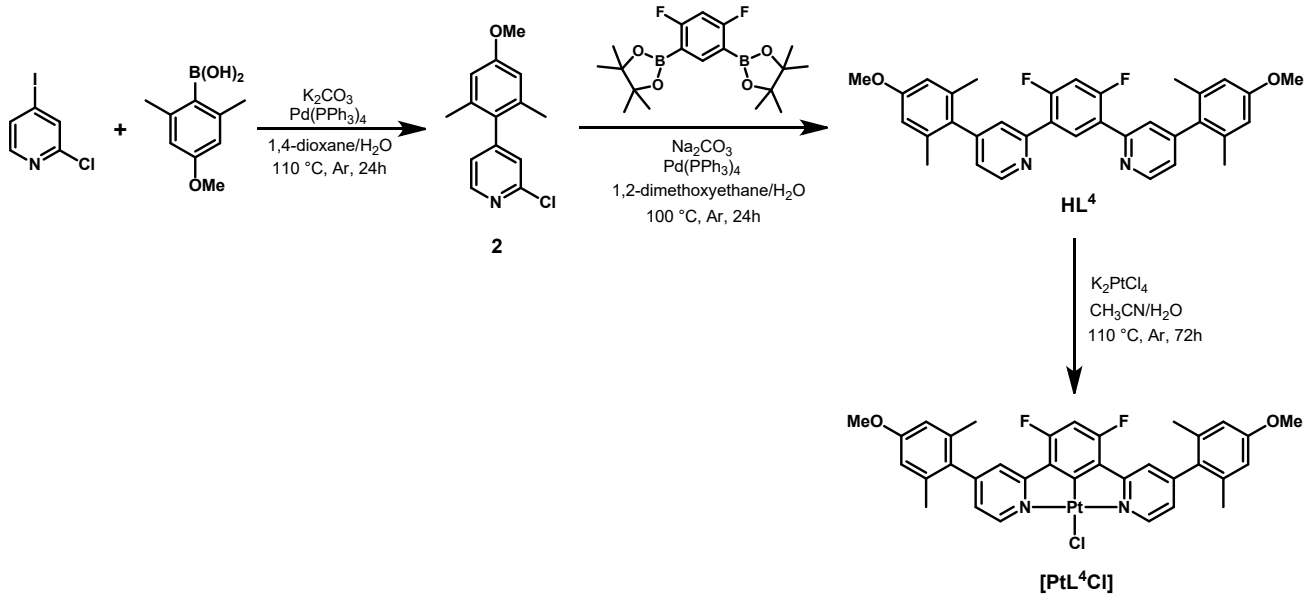


$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75.48 MHz) of compound **PtL^{3}Cl**.



$^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 282.36 MHz) of compound **PtL^{3}Cl**

Synthesis of PtL^4Cl



2-chloro-4-(4-methoxy-2,6-dimethylphenyl)pyridine (2): 2-chloro-4-iodopyridine (0.60 g, 2.5 mmol), 2,6-dimethyl-4-methoxybenzeneboronic acid (0.90 g, 5.0 mmol) and potassium carbonate (1.04 g, 7.5 mmol) were placed in a round-bottom flask under an argon atmosphere. The reagents were dissolved in a mixture of 1,4-dioxane (8 mL) and water (4 mL). To remove oxygen traces, a constant argon flow was maintained in the solution for 30 min using a needle. Following this, $Pd(PPh_3)_4$ (0.14 g, 0.1 mmol) was added, and the flask was sealed. The mixture was heated to reflux for 72 hours, then allowed to cool to room temperature. Upon completion, toluene was added, and the resulting organic phase was separated. The organic layer was washed with water (3 × 30 mL) and brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by silica gel chromatography (cyclohexane:ethyl acetate, 20:1, v/v) yielded the product as a colorless oil (602 mg, 59%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.42 (d, J = 5.0 Hz, 1H), 7.15 (s, 1H), 7.03 (d, J = 5.0 Hz, 1H), 6.67 (s, 2H), 3.81 (s, 3H), 2.02 (s, 6H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 159.2, 152.9, 151.8, 149.8, 136.5, 130.3, 125.6, 124.0, 113.1, 55.3, 20.9. HRMS (ESI+): $(M+Na)^+$ calcd for $C_{14}H_{14}NO^{35}Cl$ Na, 270.0656; found: 270.0659.

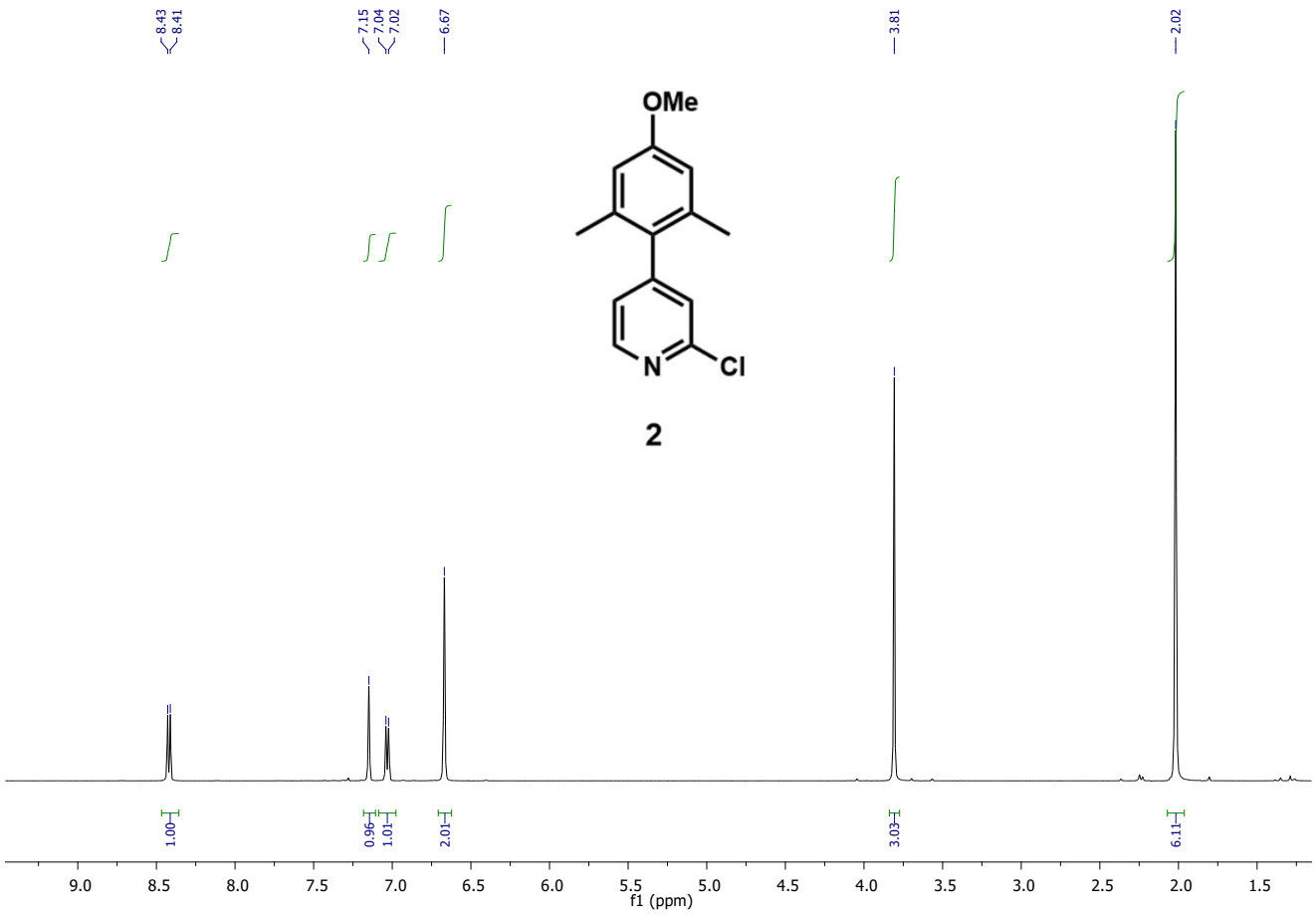
2,2'-(4,6-difluoro-1,3-phenylene)bis(4-(4-methoxy-2,6-dimethylphenyl)pyridine) (HL^4):
compound **2** (0.36 g, 1.5 mmol), the pinacol ester of benzene-1,3-difluoro-4,6-diboronic acid (0.24 g, 0.7 mmol), and an aqueous solution of sodium carbonate (1 M, 9 mL) were dissolved in dimethoxyethane (8 mL). $Pd(PPh_3)_4$ (0.13 g, 0.1 mmol) was added to the reaction in a Schlenk tube, and the solution was degassed for 10 minutes under an argon flow. The sealed tube was then heated

to 100 °C overnight. The solvent was removed *in vacuo* after cooling and the residue was dissolved in dichloromethane (30 mL) and water (20 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. Silica gel chromatography (cyclohexane:ethyl acetate, 16:1, v/v) yielded a colorless oil (413 mg, 79%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.79 (d, J = 4.9 Hz, 2H), 8.70 (t, J = 8.9 Hz, 1H), 7.61 (s, 2H), 7.12 (d, J = 5.0 Hz, 2H), 7.03 (t, J = 10.6 Hz, 1H), 6.74 (s, 4H), 3.86 (s, 6H), 2.09 (s, 12H). ^{13}C-NMR (75.48 MHz, $CDCl_3$, δ): 162.1, 158.9, 152.7, 150.1, 149.8, 136.9, 133.9, 131.6, 125.5, 124.6, 123.8, 112.8, 105.6, 105.1, 104.5, 55.2, 20.9. ^{19}F-NMR (282.36 MHz, $CDCl_3$, δ): -113.43 (s, 2F). HRMS (ESI+): $(M+H)^+$ calcd for $C_{34}H_{31}N_2O_2F_2$, 537.2348; found: 537.2346.

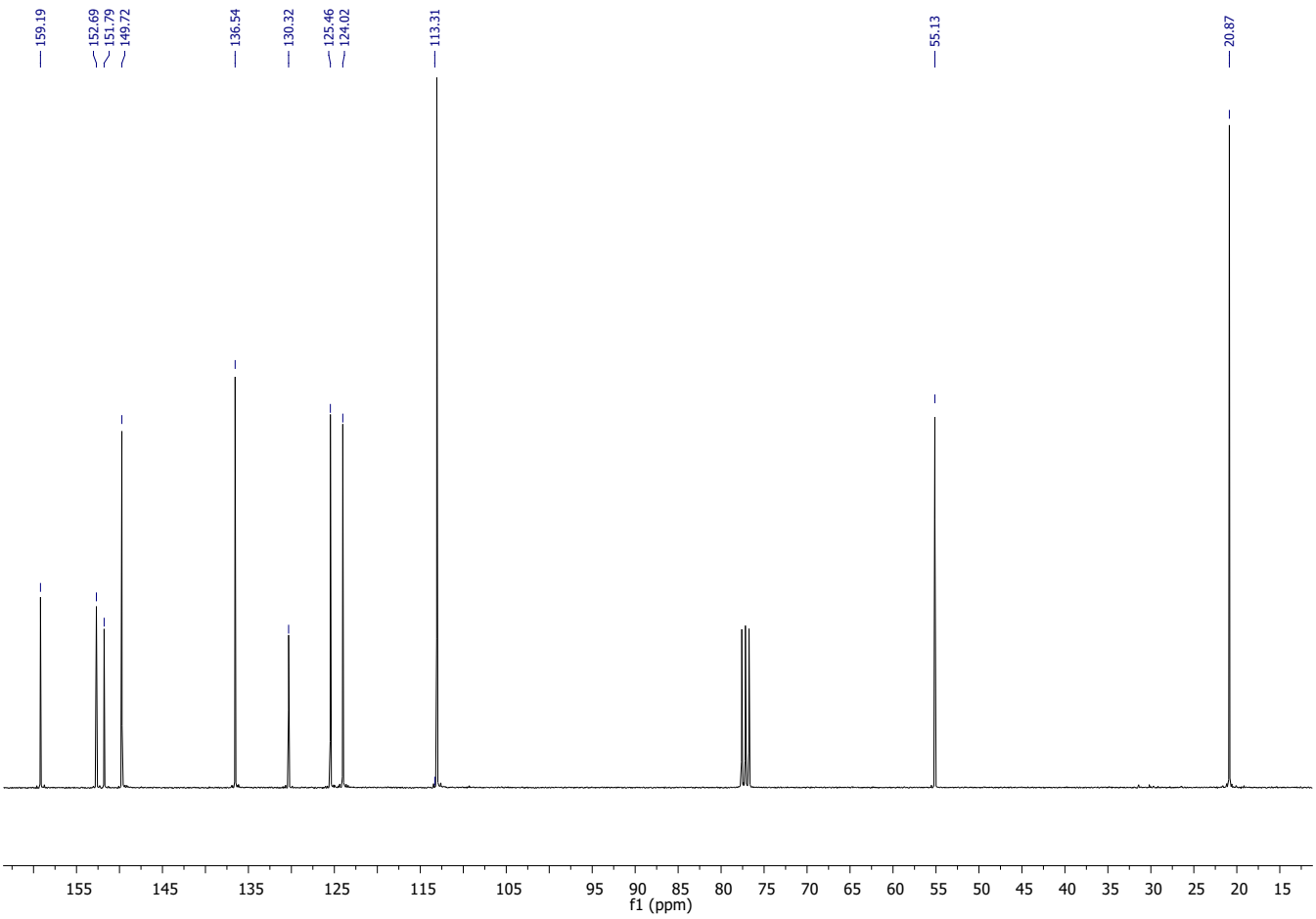
PtL^4Cl: **HL^4** (0.14 g, 0.27 mmol) was dissolved in acetonitrile (11.7 mL) in a Schlenk tube and a solution of K_2PtCl_4 (0.22 g, 0.53 mmol) in water (1.3 mL) was added via pipette. Argon was bubbled through the mixture for 40 minutes before sealing the reaction vessel. The reaction mixture was heated at 110 °C for three days, during which a yellow suspension was formed. After cooling to room temperature, the mixture was filtered through a nylon membrane. The resulting yellow solid was washed with water, methanol, and diethyl ether, then dried to yield the desired compound (124 mg, 81%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 9.40 (d, J = 5.9 Hz, $^{3}J(^{195}Pt)$ = 40.2 Hz, 2H), 7.76 (s, 2H), 7.17 (d, J = 5.8, 2H), 6.68–6.80 (m, 5H), 3.87 (s, 6H), 2.13 (s, 12H). $^{13}C\{^{1}H\}$-NMR (75.48 MHz, $CDCl_3$, δ): 164.2, 159.4, 153.8, 151.9, 136.3, 130.7, 124.9, 124.1, 113.3, 55.2, 21.2. $^{19}F\{^{1}H\}$-NMR (282 MHz, $CDCl_3$, δ): -108.10 (s, 2F). HRMS (ESI+): $(M+Na)^+$ calcd for $C_{34}H_{29}N_2O_2F_2{}^{35}Cl\,Na^{195}Pt$, 788.1426; found: 788.1436. Elemental analysis: calcd. for $C_{34}H_{29}ClF_2N_2O_2Pt$: C, 53.30; H, 3.82; N, 3.66; found: C, 53.55; H, 3.83; N, 3.64.

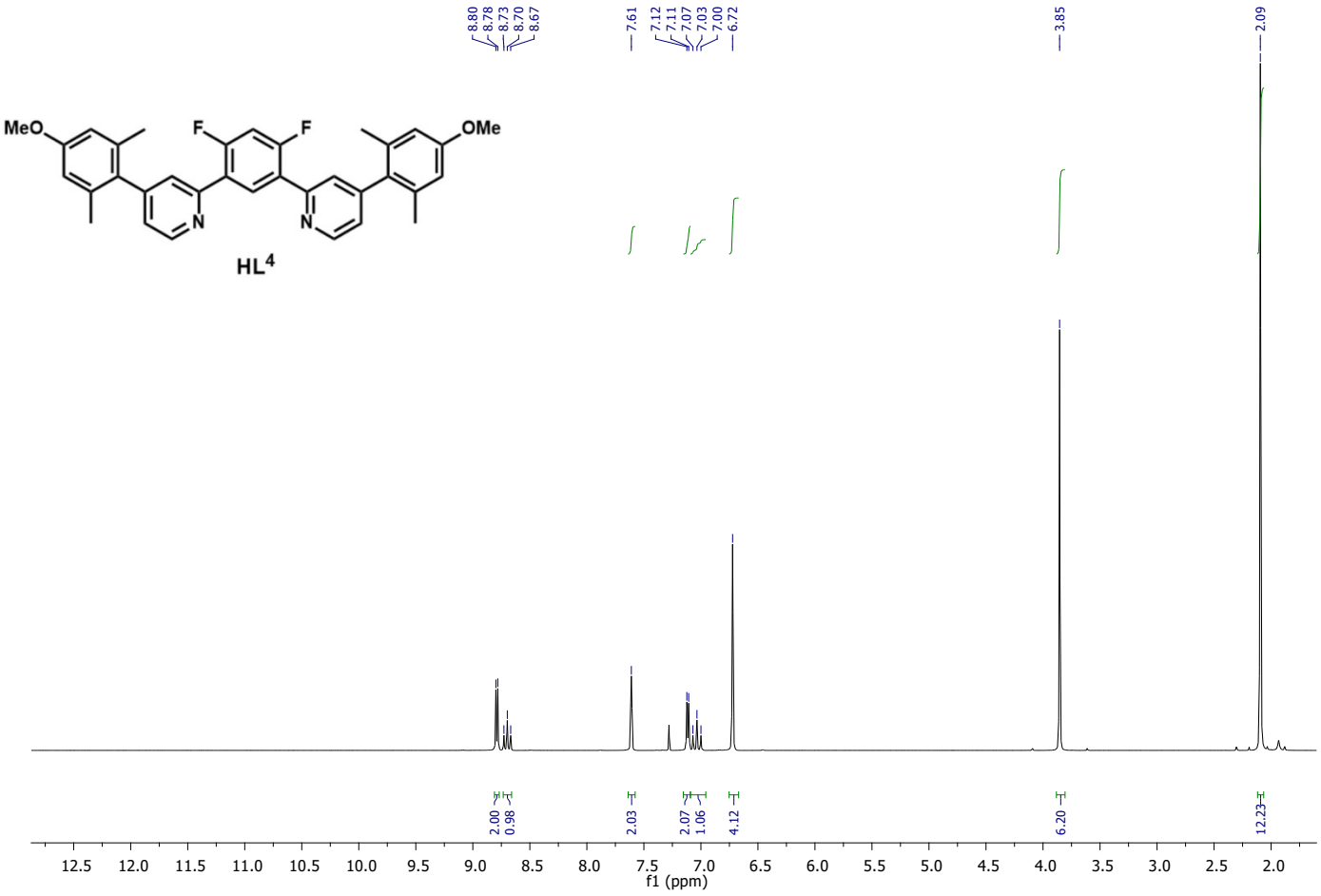
^{1}H, ^{13}C, and ^{19}F NMR Spectra



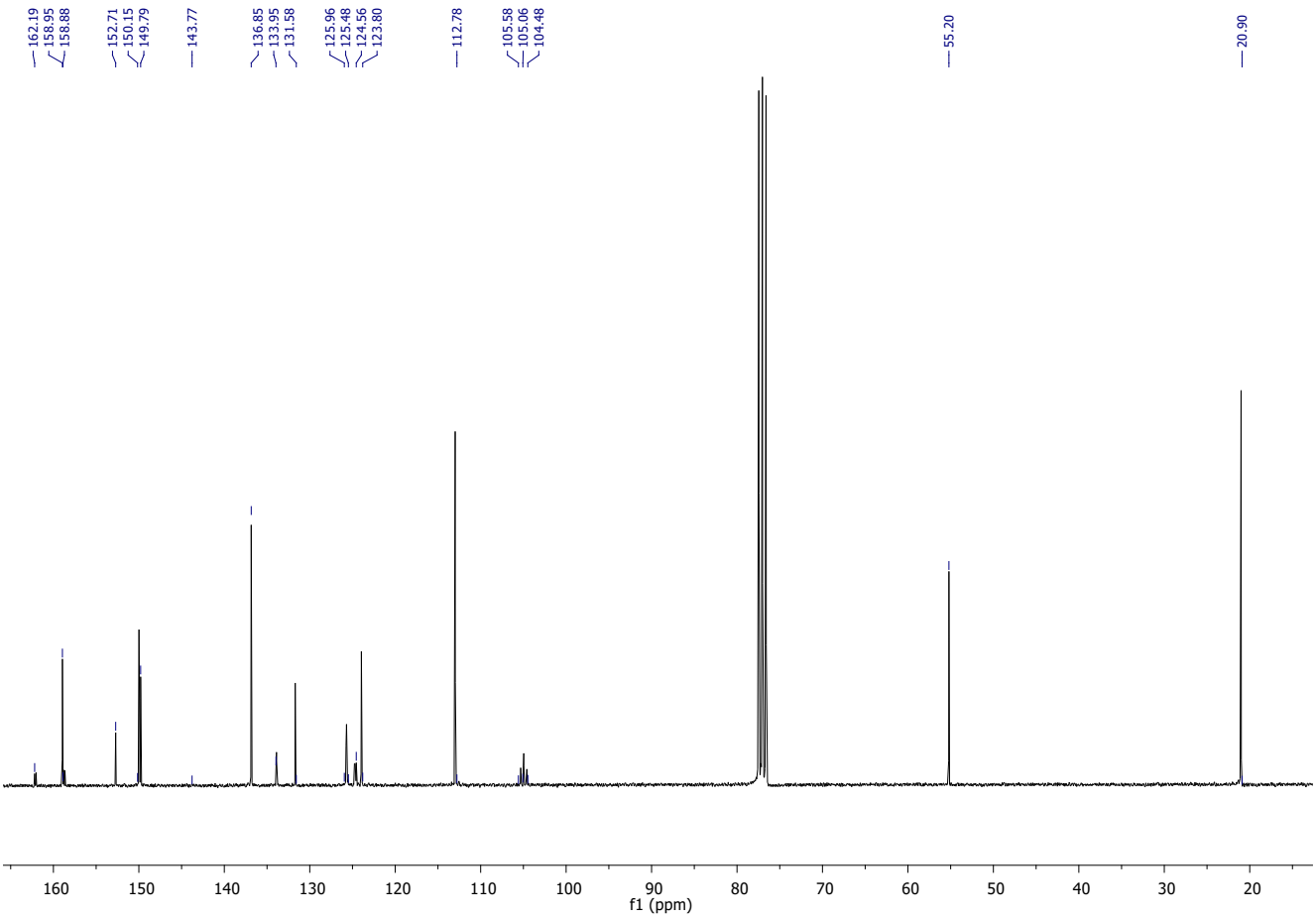
^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **2**.



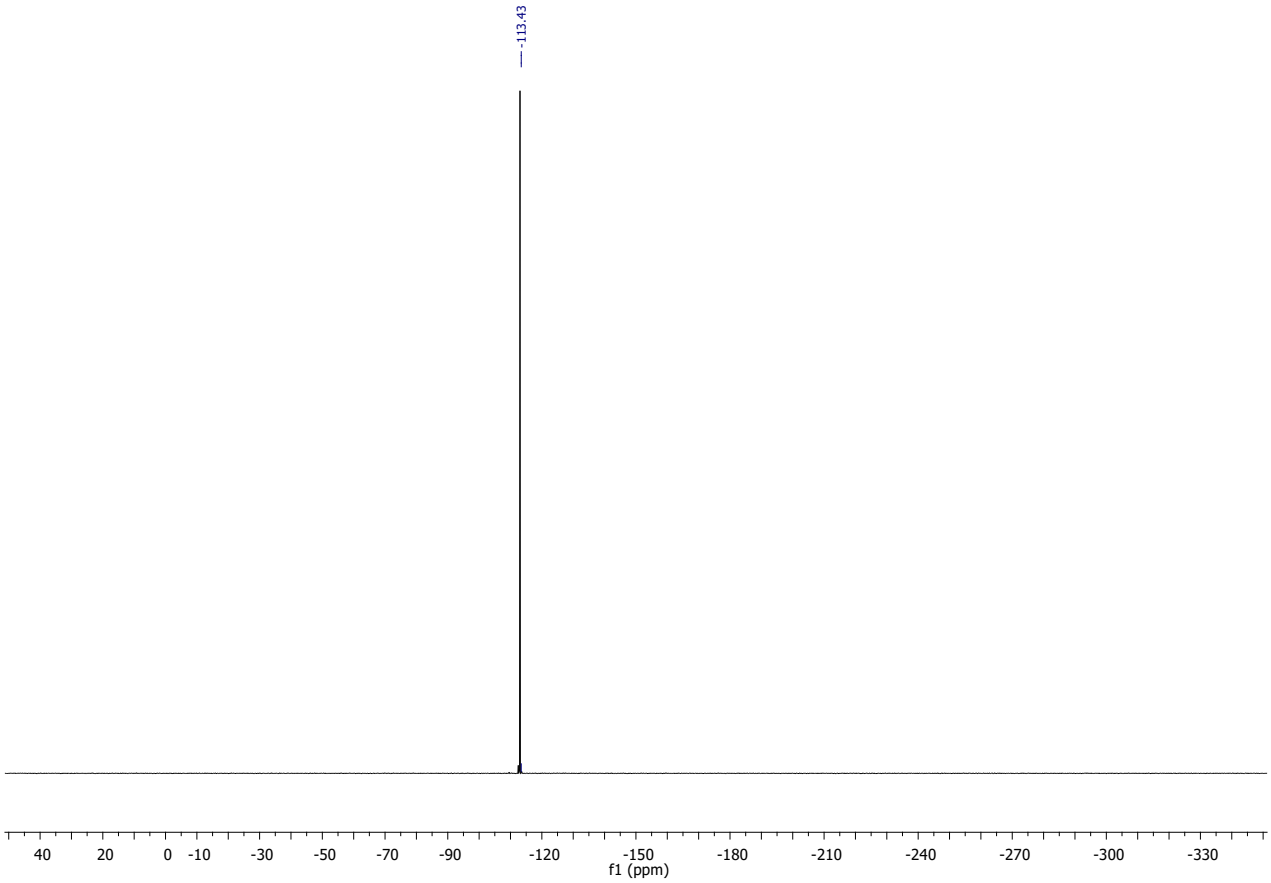
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75.48 MHz) of compound **2**.



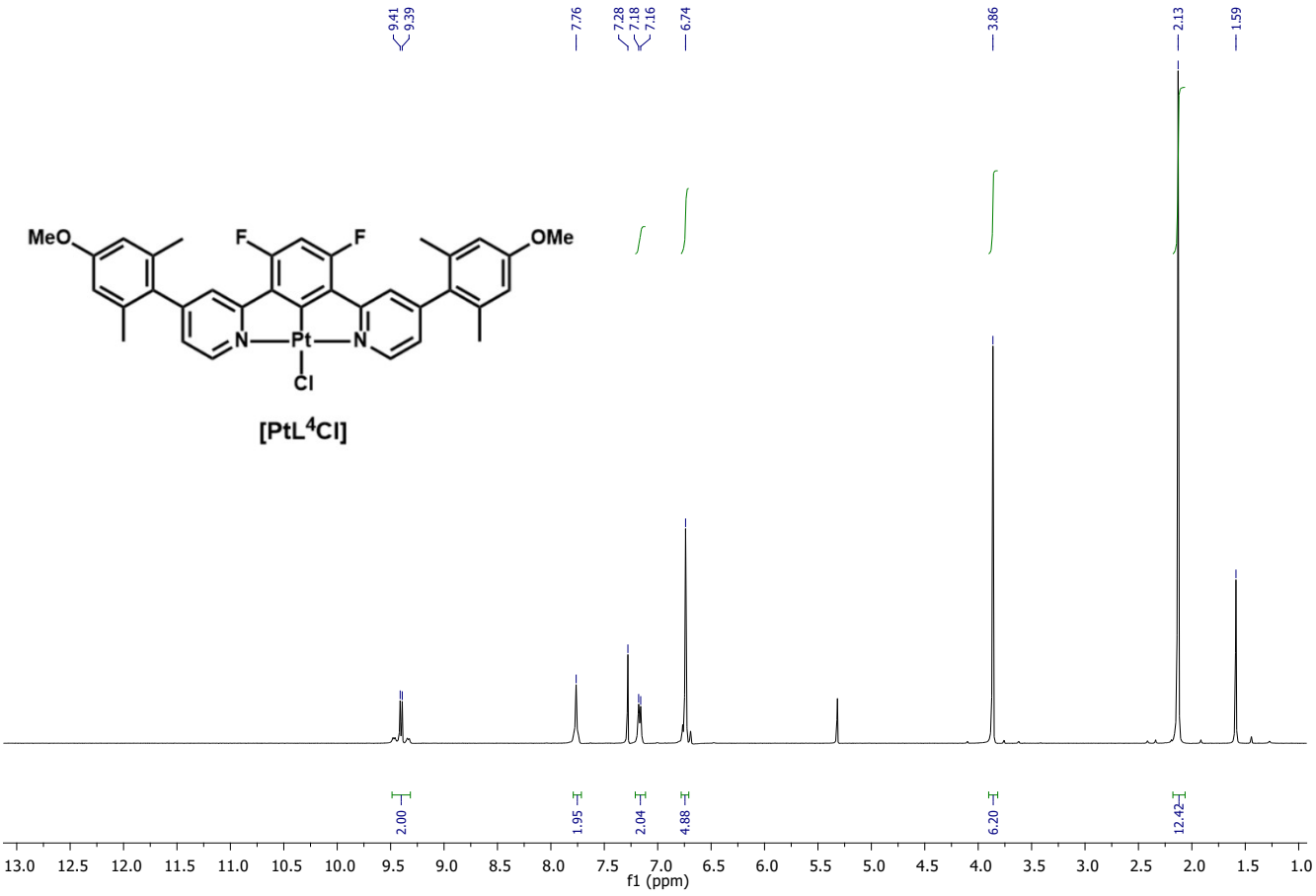
^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **HL^{4}**.



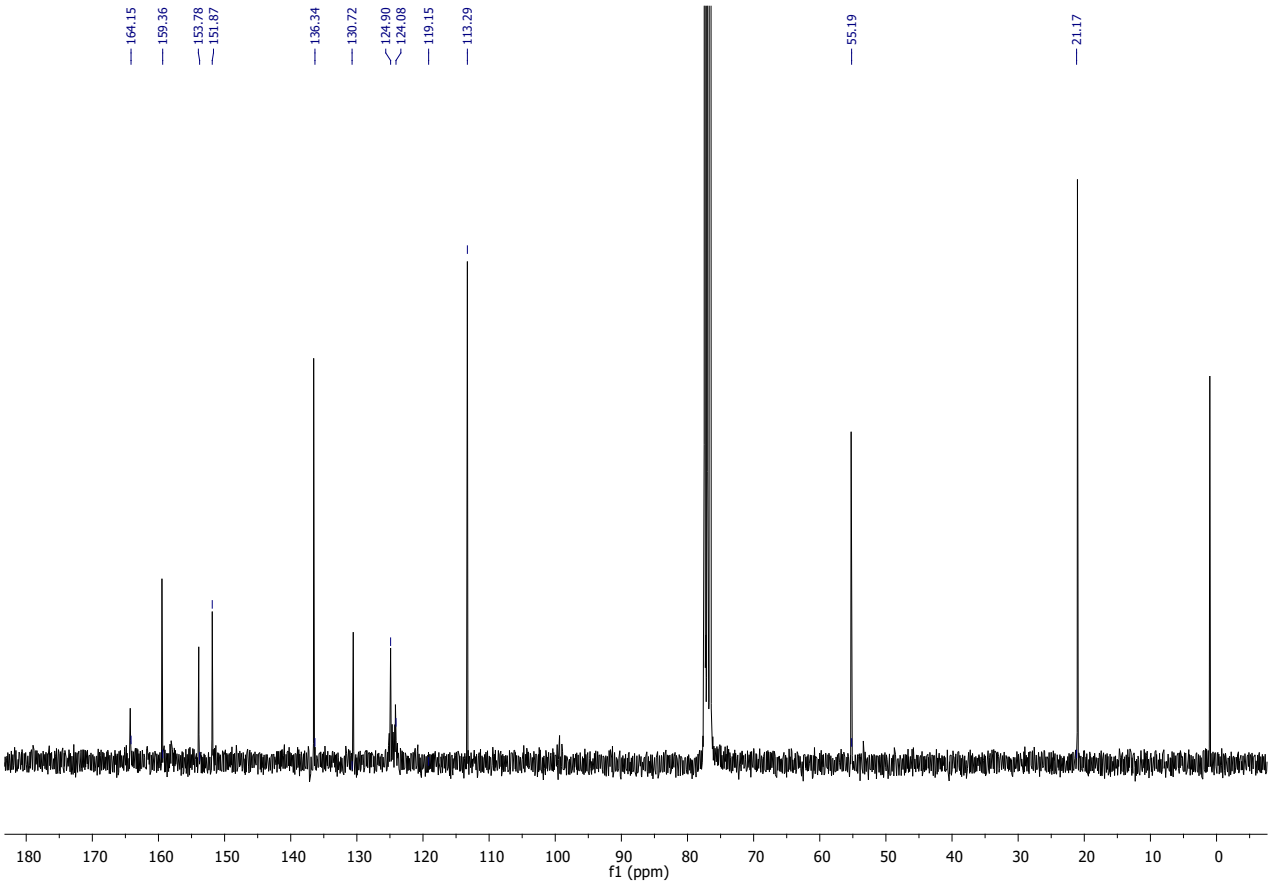
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75.48 MHz) of compound **HL^4**.



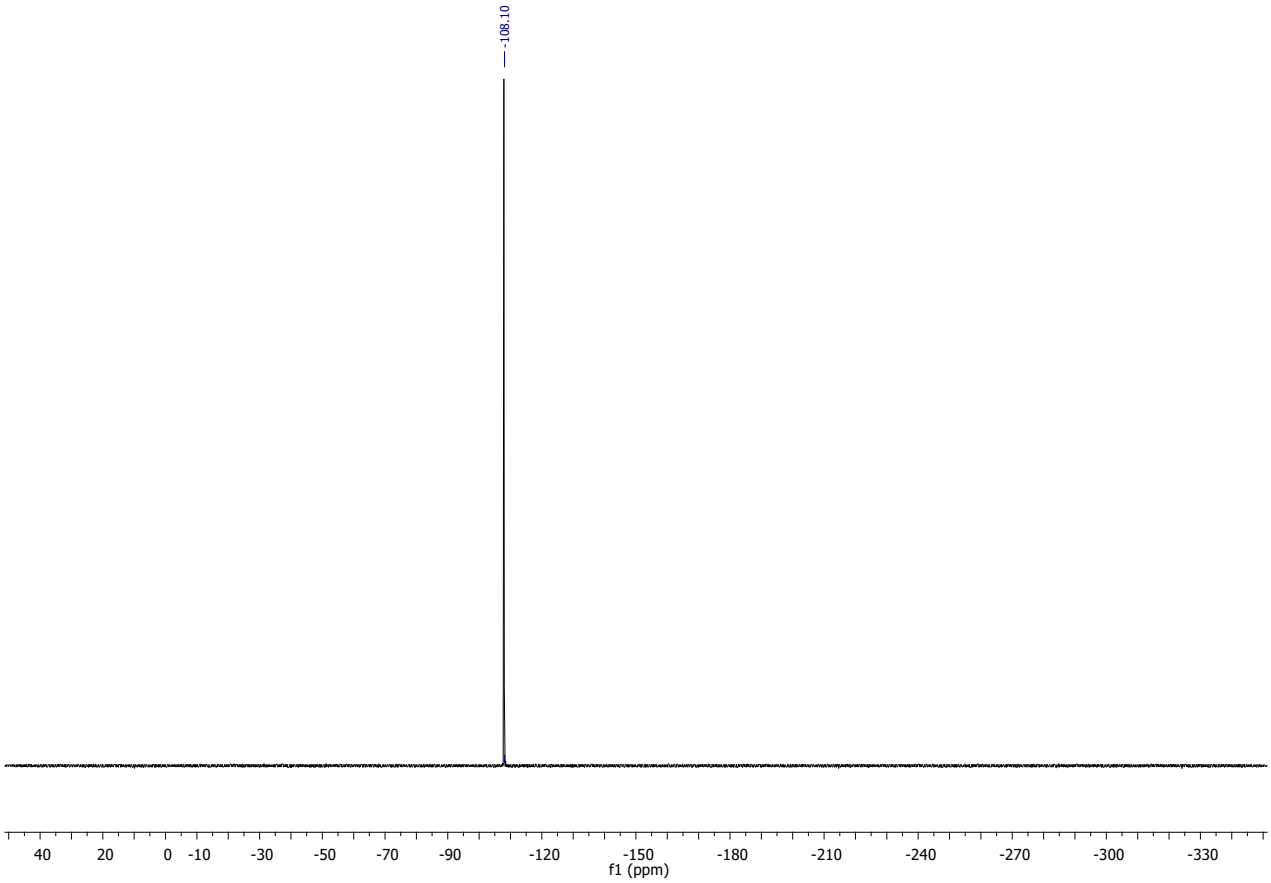
$^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 282.36 MHz) of compound **HL^4**.



^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **PtL^{4}Cl**.



$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75.48 MHz) of compound **PtL^{4}Cl**.



$^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 282.36 MHz) of compound **PtL^{4}Cl**.

Photophysical characterization of PtL^3Cl

UV-Vis absorption

Table S1. Molar extinction coefficients for **PtL^3Cl** at different wavelengths.

λ	277 nm	308 nm	340 nm	382 nm	471 nm
ε / M^{-1} cm^{-1}	$5.7 \cdot 10^3$	$3.4 \cdot 10^3$	$1.4 \cdot 10^3$	$2.1 \cdot 10^3$	262

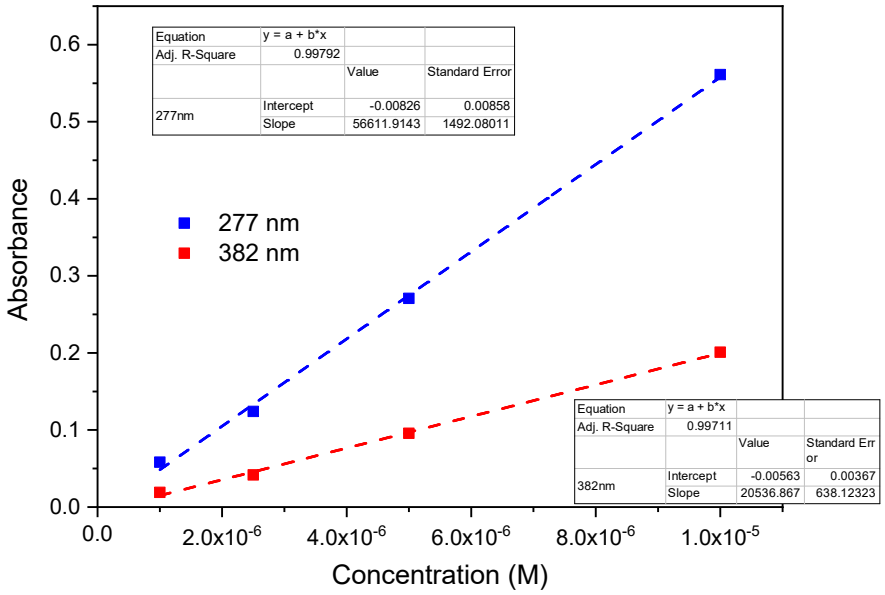


Figure S1. Absorbance vs Concentration for **PtL^3Cl** at 277 nm and 382 nm.

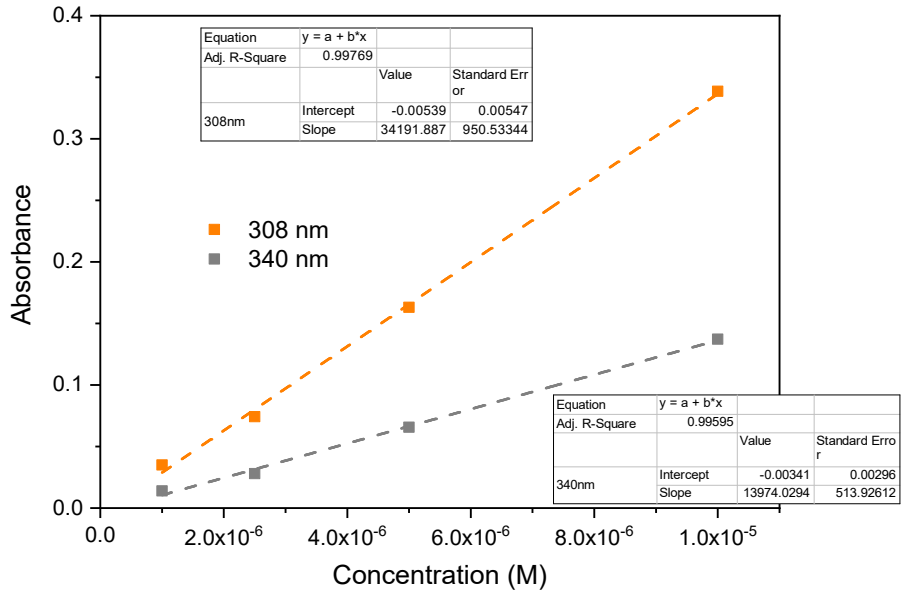


Figure S2. Absorbance vs Concentration for **PtL^3Cl** at 308 nm and 340 nm.

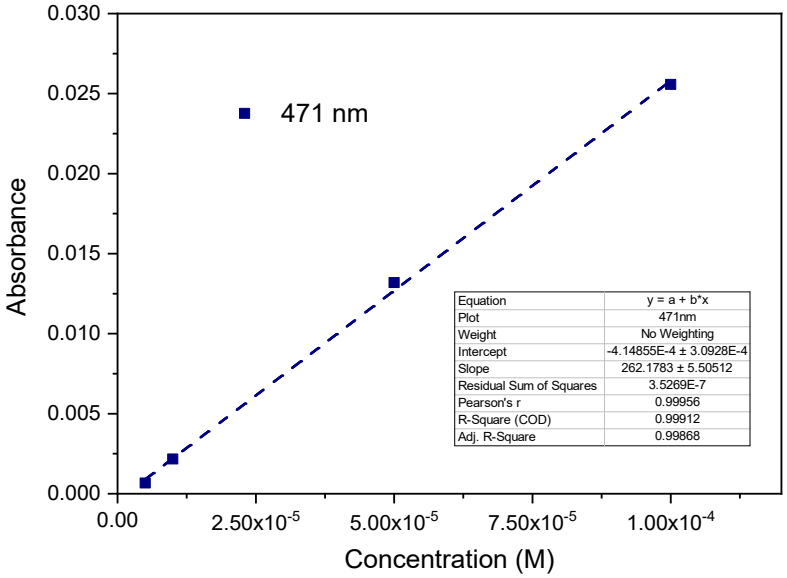


Figure S3. Absorbance vs Concentration for **PtL^{3}Cl** at 471 nm.

Excitation and emission spectra

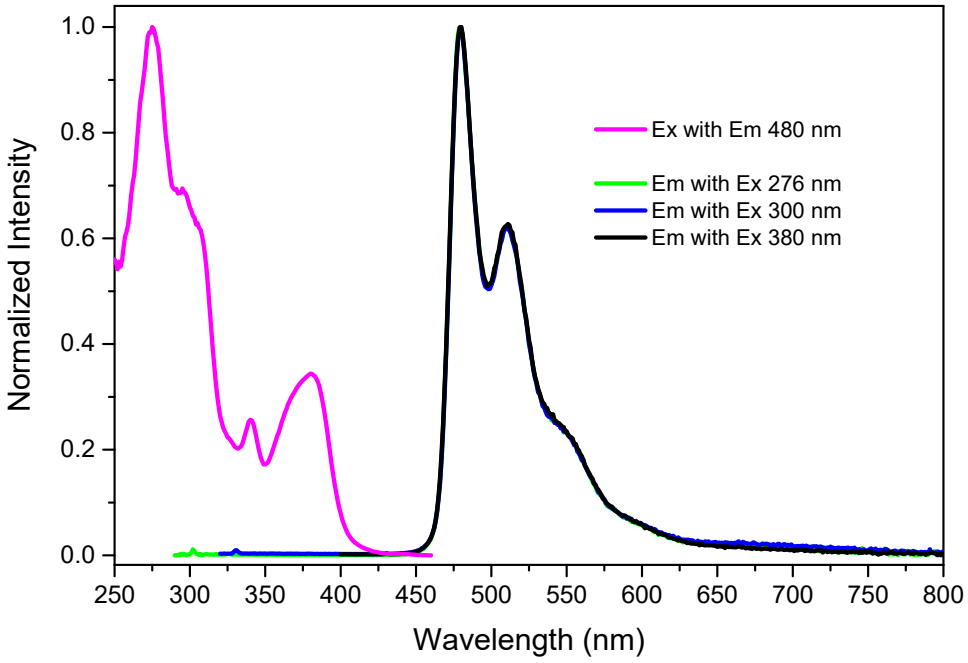


Figure S4. Normalized excitation (magenta) and emission spectra (green, blue and black) of a dichloromethane solution ($1.0 \cdot 10^{-6}$ M) of **PtL^{3}Cl** at room temperature.

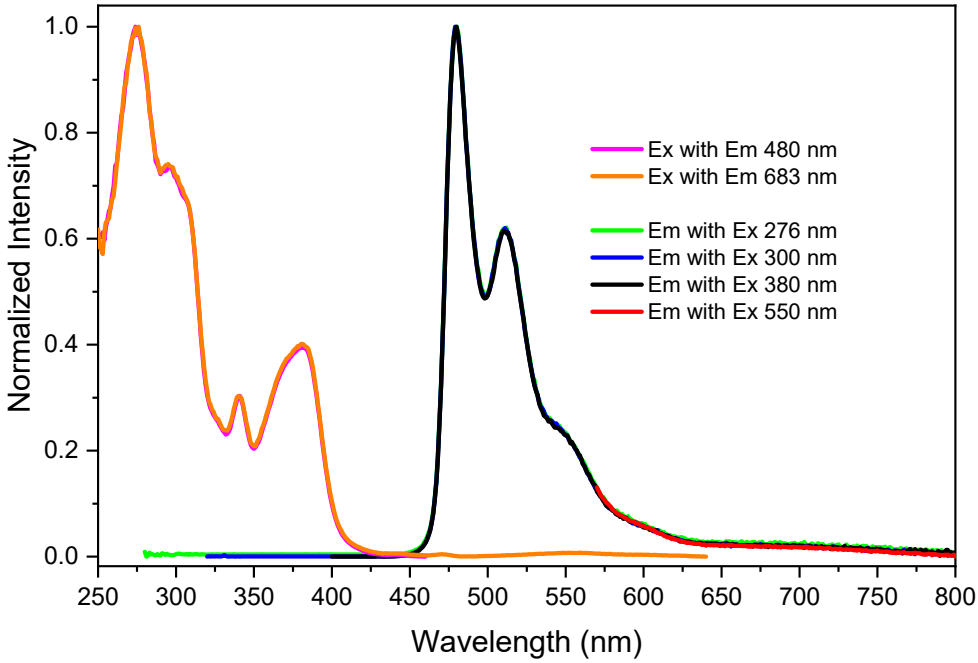


Figure S5. Normalized excitation (magenta and orange) and emission spectra (green, blue, black and red) of a dichloromethane solution ($5.0 \cdot 10^{-6}$ M) of **PtL^{3}Cl** at room temperature.

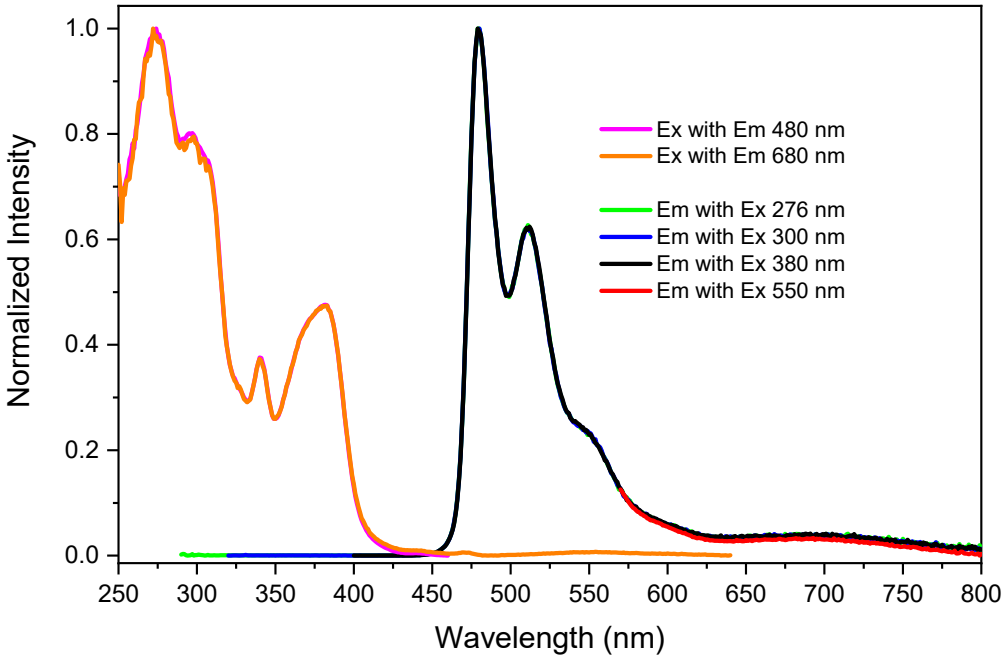


Figure S6. Normalized excitation (magenta and orange) and emission spectra (green, blue, black and red) of a dichloromethane solution ($1.0 \cdot 10^{-5}$ M) of **PtL^{3}Cl** at room temperature.

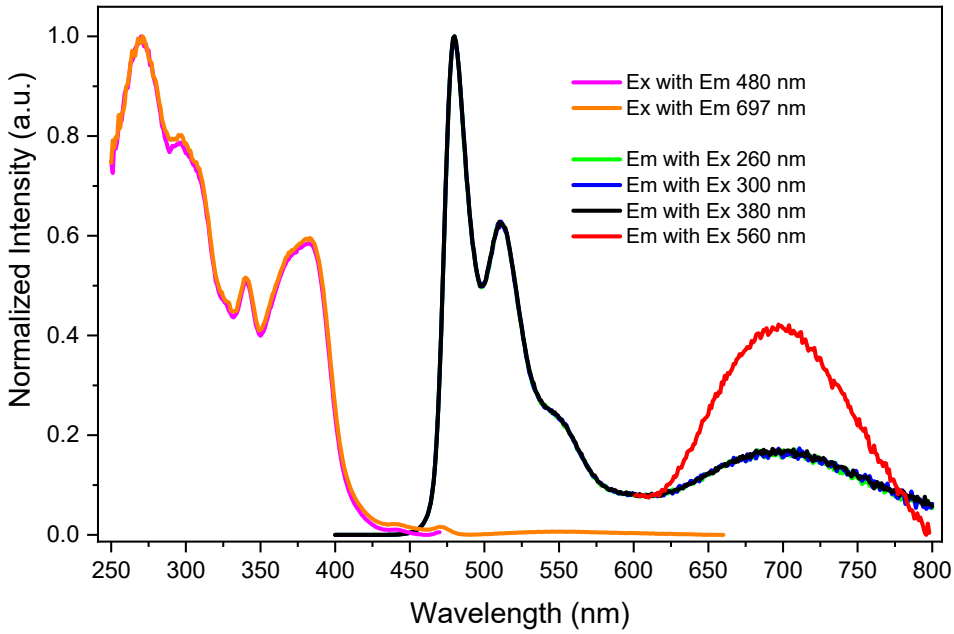


Figure S7. Normalized excitation (magenta and orange) and emission spectra (green, blue, black and red) of a dichloromethane solution ($5.0 \cdot 10^{-5}$ M) of **PtL^{3}Cl** at room temperature.

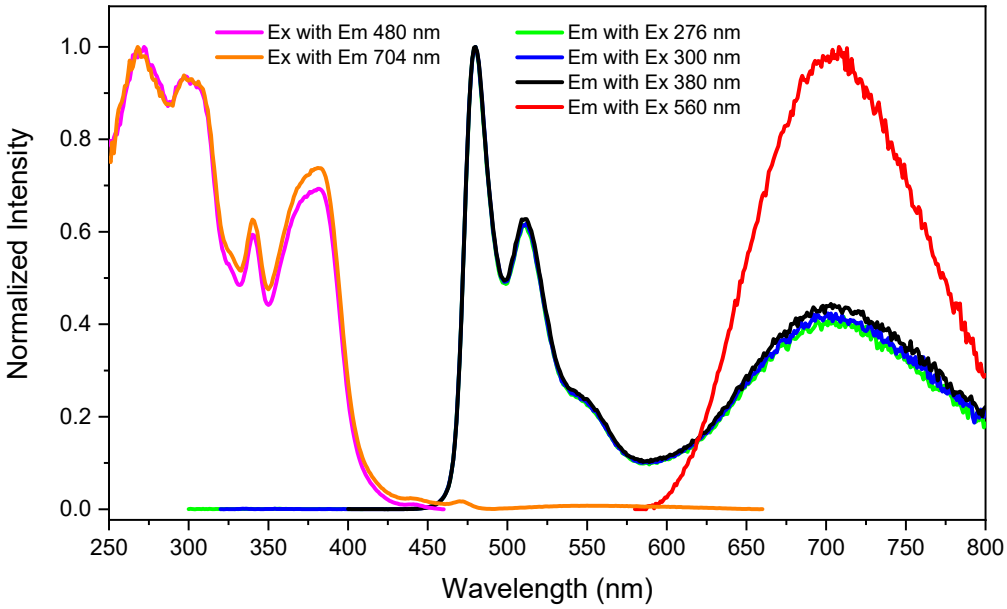


Figure S8. Normalized excitation (magenta and orange) and emission spectra (green, blue, black and red) of a dichloromethane solution ($1.9 \cdot 10^{-4}$ M) of **PtL^{3}Cl** at room temperature.

Lifetime measurements

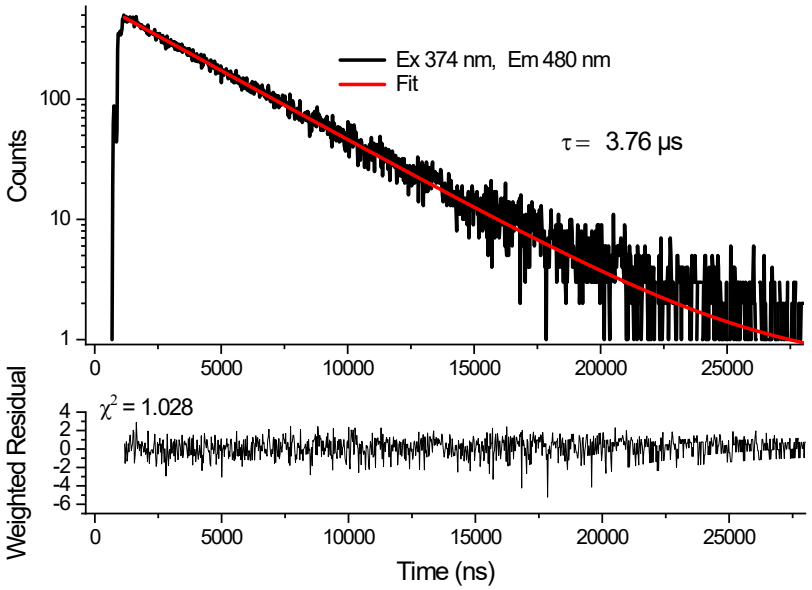


Figure S9. Lifetime measurement of **PtL^{3}Cl** at room temperature in dichloromethane solution ($1.0 \cdot 10^{-6}$ M), excitation 374 nm, emission 480 nm.

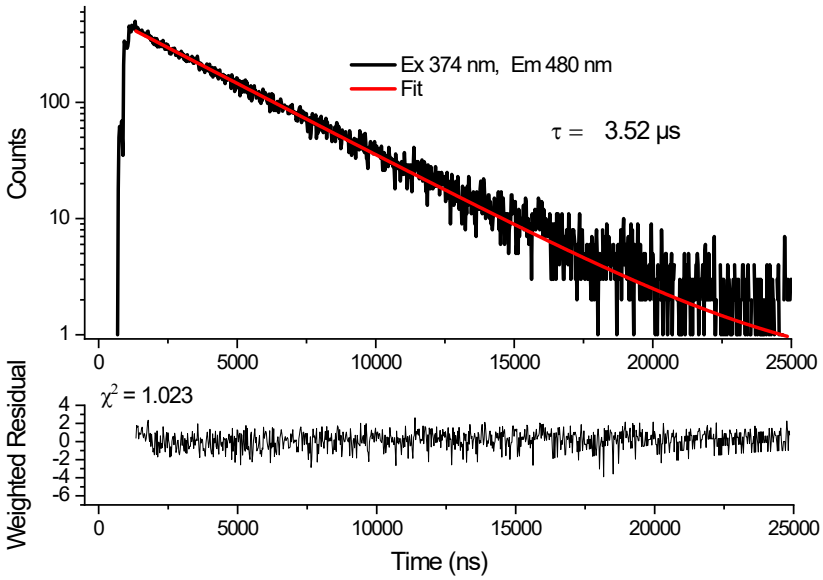


Figure S10. Lifetime measurement of **PtL^{3}Cl** at room temperature in dichloromethane solution ($5.0 \cdot 10^{-6}$ M), excitation 374 nm, emission 480 nm.

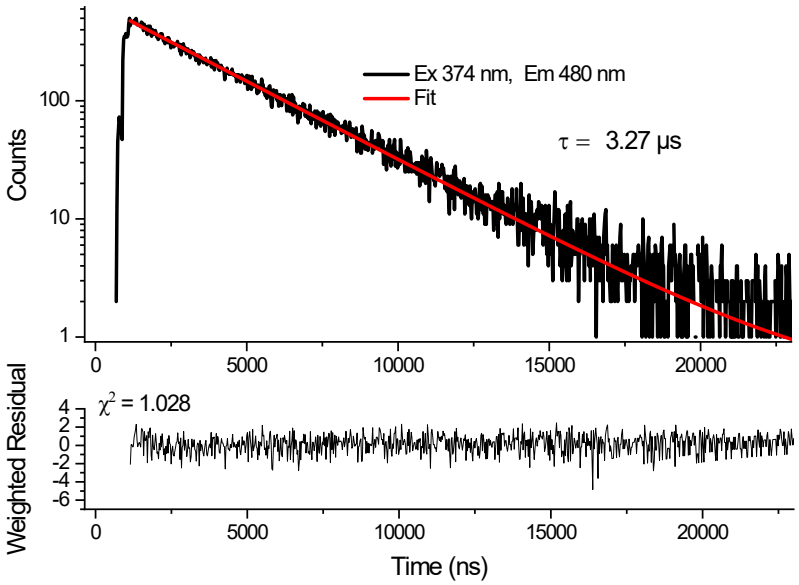


Figure S11. Lifetime measurement of **PtL^{3}Cl** at room temperature in dichloromethane solution ($1.0 \cdot 10^{-5}$ M), excitation 374 nm, emission 480 nm.

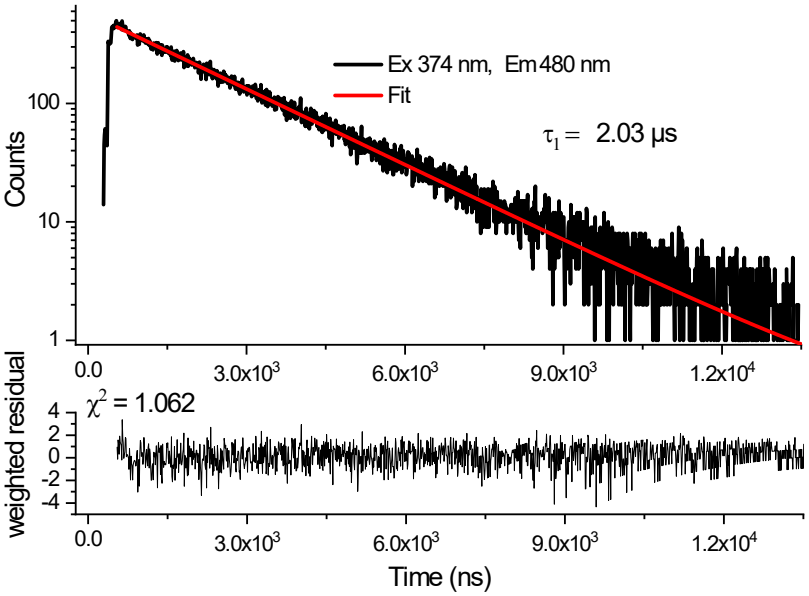


Figure S12. Lifetime measurement of **PtL^{3}Cl** at room temperature in dichloromethane solution ($5.0 \cdot 10^{-5}$ M), excitation 374 nm, emission 480 nm.

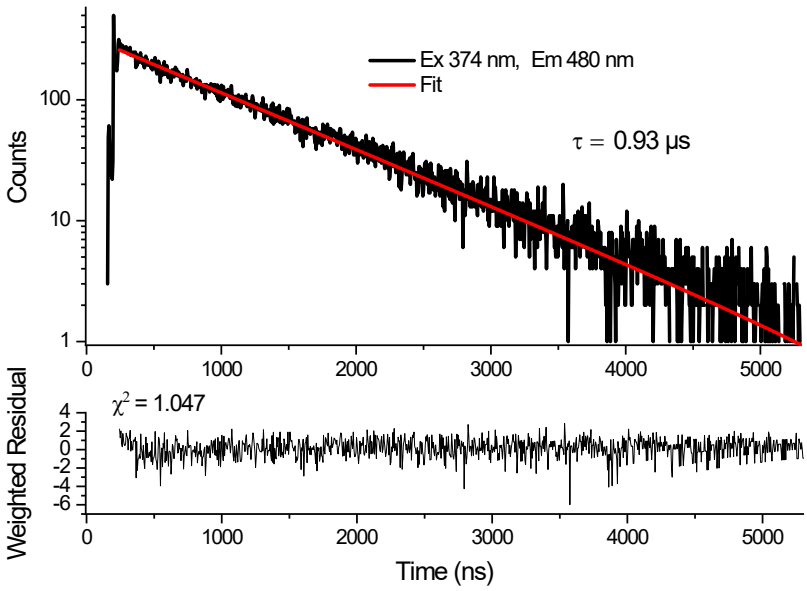


Figure S13. Lifetime measurement of **PtL^{3}Cl** at room temperature in dichloromethane solution ($1.9 \cdot 10^{-4}$ M), excitation 374 nm, emission 480 nm.

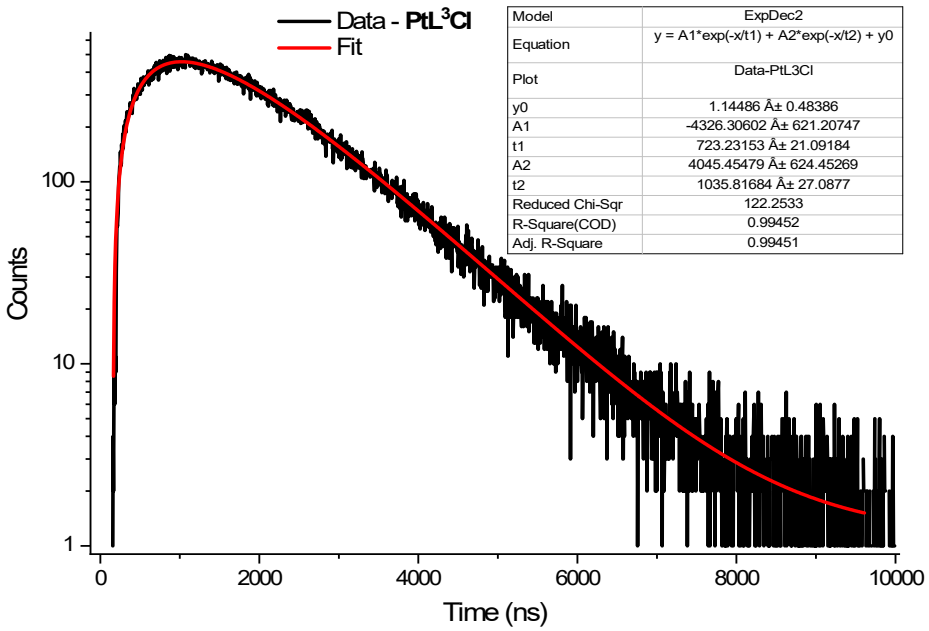


Figure S14. Lifetime measurement of **PtL^{3}Cl** at room temperature in dichloromethane solution ($1.9 \cdot 10^{-4}$ M), excitation 374 nm, emission 704 nm.

Table S2. Lifetimes of **PtL^{3}Cl** at different concentrations, λ_{ex} = 374 nm, λ_{em} = 480 nm.

c / M	$1.0 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-5}$	$5.0 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$
τ / μs	3.76	3.52	3.27	2.03	0.93

Photophysical characterization of PtL^{4}Cl

UV-Vis Absorption

Table S3. Molar extinction coefficients for **PtL^{4}Cl** at different wavelengths.

λ	238 nm	264 nm	335 nm	377 nm	467 nm
ε / M^{-1} cm^{-1}	3.9·10^4	3.8·10^4	1.6·10^4	1.4·10^4	214

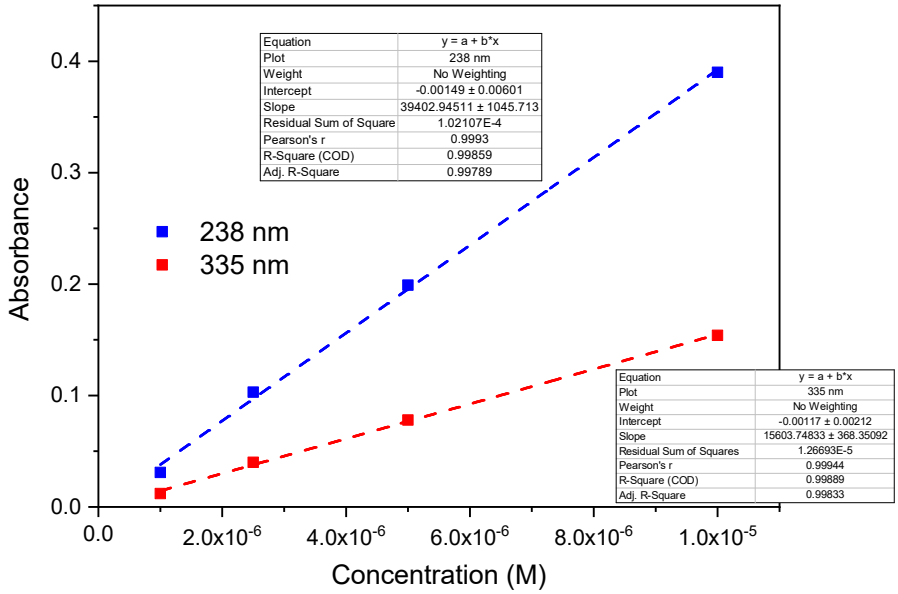


Figure S15. Absorbance vs Concentration for **PtL^{4}Cl** at 238 nm and 335 nm.

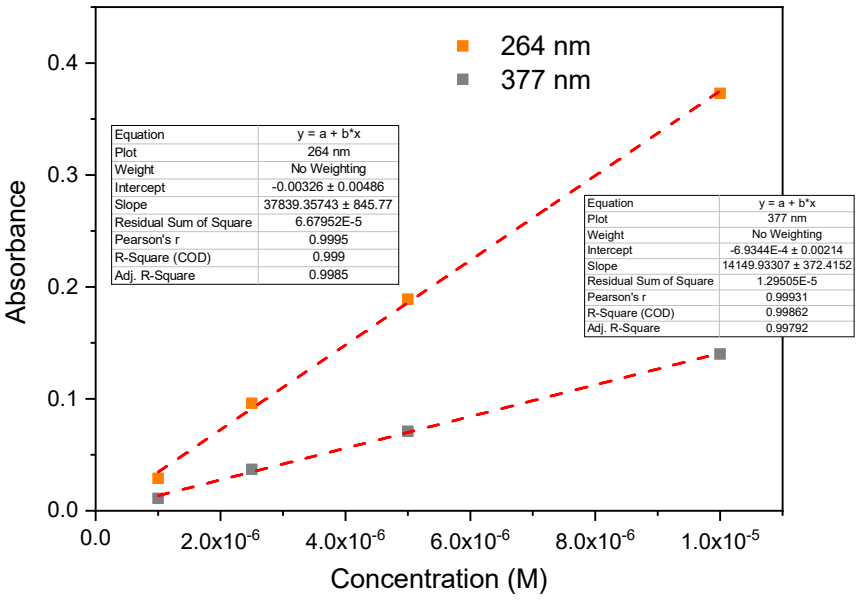


Figure S16. Absorbance vs Concentration for **PtL^{4}Cl** at 264 nm and 377 nm.

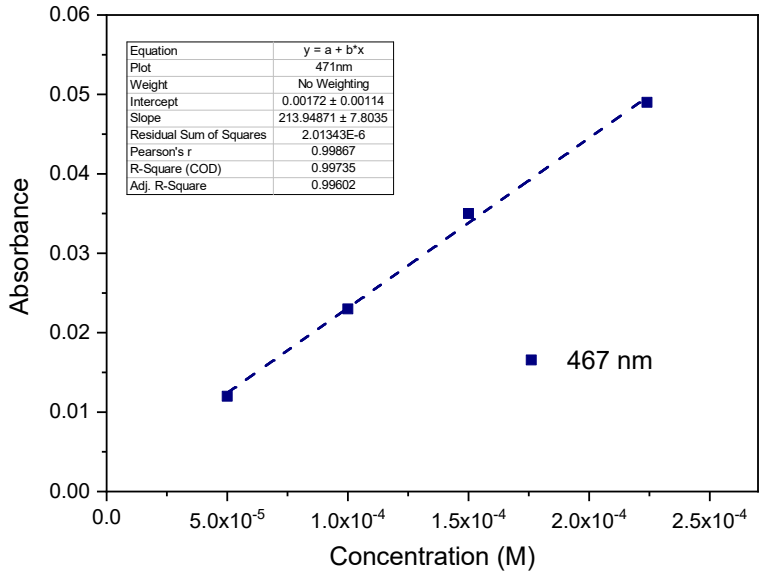


Figure S17. Absorbance vs Concentration for **PtL^{4}Cl** at 467 nm.

Excitation and emission spectra

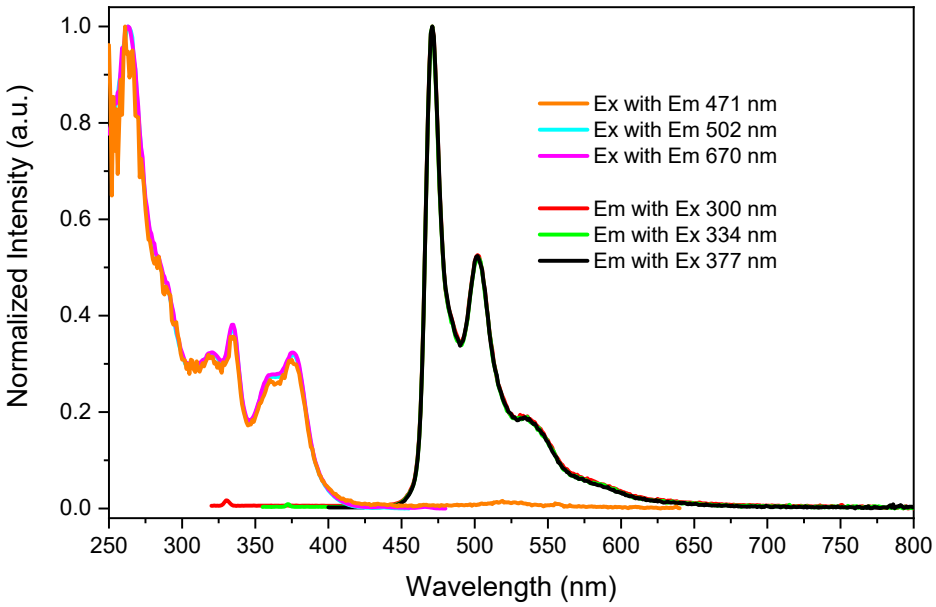


Figure S18. Normalized excitation (orange, cyan and magenta) and emission spectra (red, green and black) of a dichloromethane solution ($1.0 \cdot 10^{-6}$ M) of **PtL^{4}Cl** at room temperature.

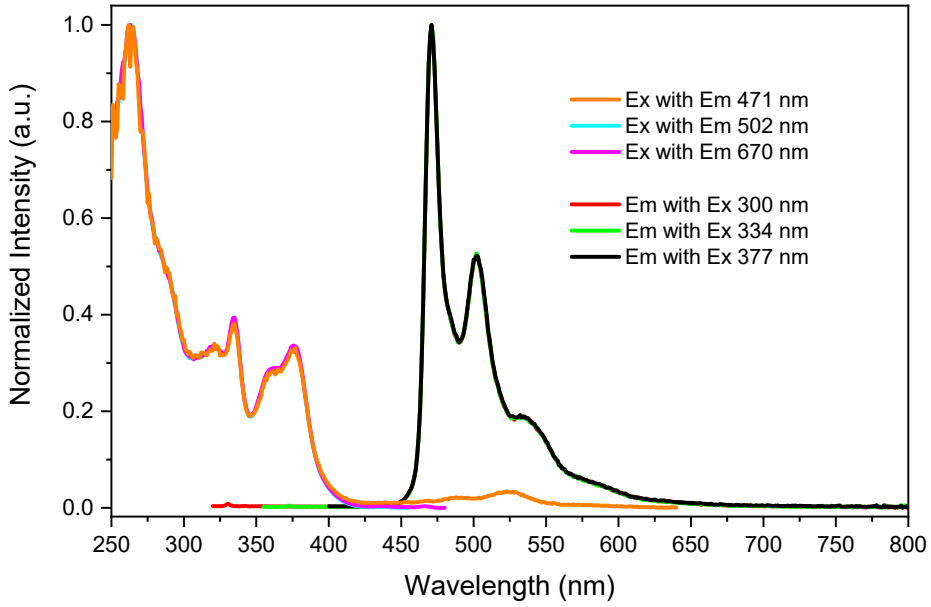


Figure S19. Normalized excitation (orange, cyan and magenta) and emission spectra (red, green and black) of a dichloromethane solution ($2.5 \cdot 10^{-6}$ M) of **PtL^{4}Cl** at room temperature.

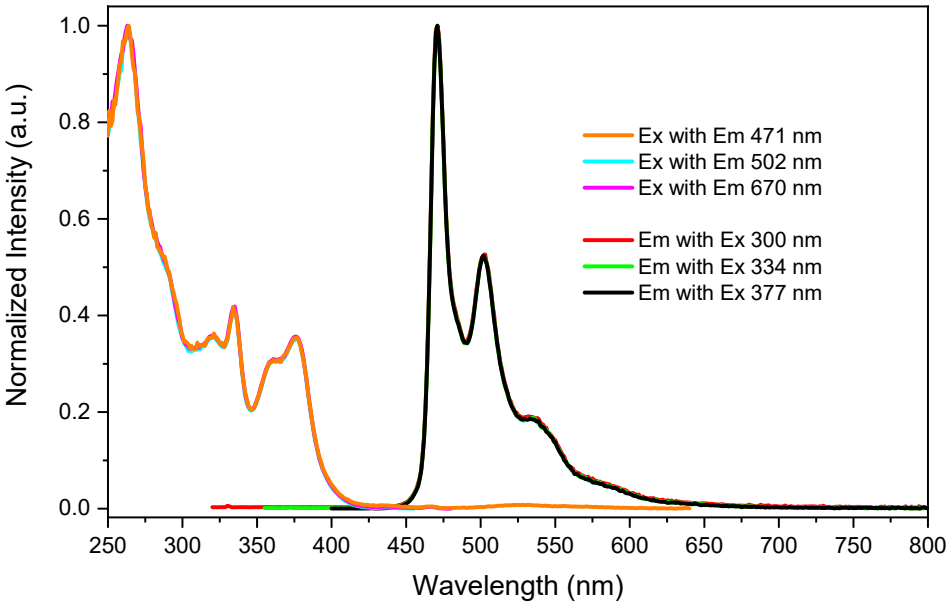


Figure S20. Normalized excitation (orange, cyan and magenta) and emission spectra (red, green and black) of a dichloromethane solution ($5.0 \cdot 10^{-6}$ M) of **PtL^{4}Cl** at room temperature.

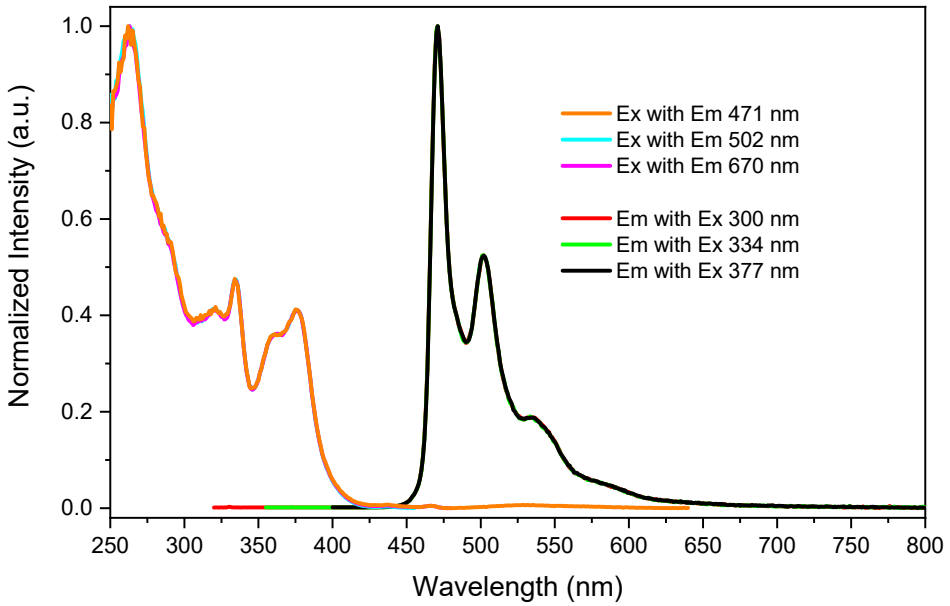


Figure S21. Normalized excitation (orange, cyan and magenta) and emission spectra (red, green and black) of a dichloromethane solution ($1.0 \cdot 10^{-5}$ M) of **PtL^{4}Cl** at room temperature.

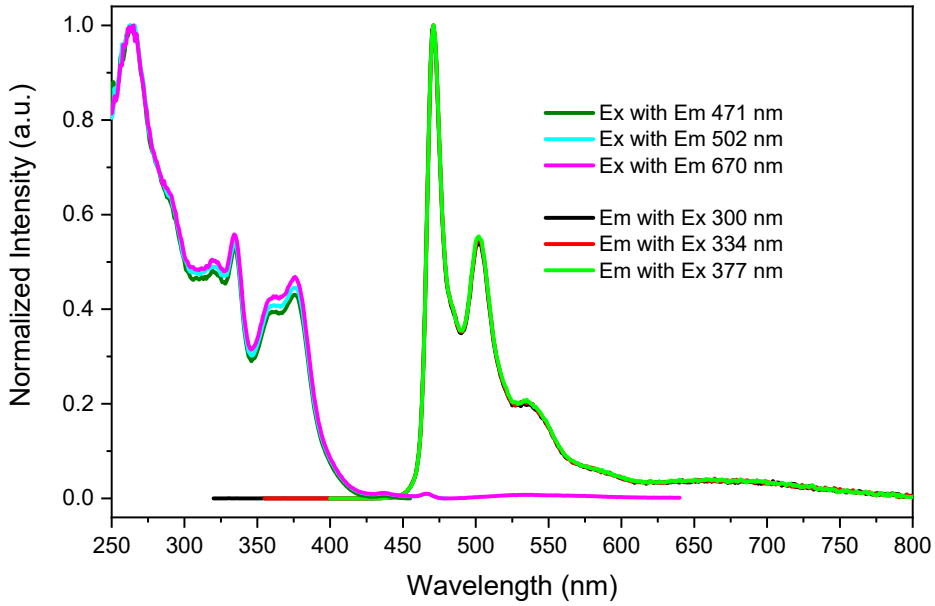


Figure S22. Normalized excitation (orange, cyan and magenta) and emission spectra (red, green and black) of a dichloromethane solution ($1.9 \cdot 10^{-4}$ M) of **PtL^{4}Cl** at room temperature.

Lifetime measurements

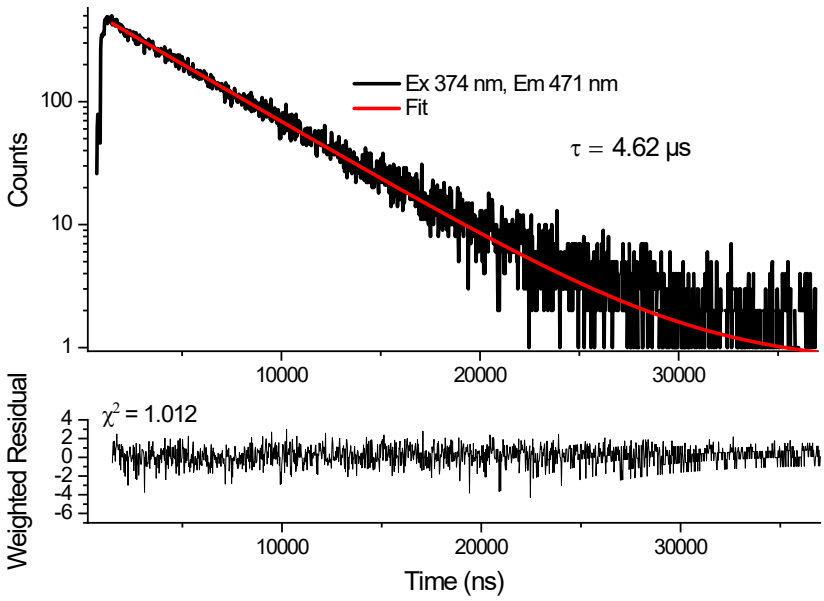


Figure S23. Lifetime measurement of **PtL^{4}Cl** at room temperature in dichloromethane solution ($1.0 \cdot 10^{-6}$ M), excitation 374 nm, emission 471 nm.

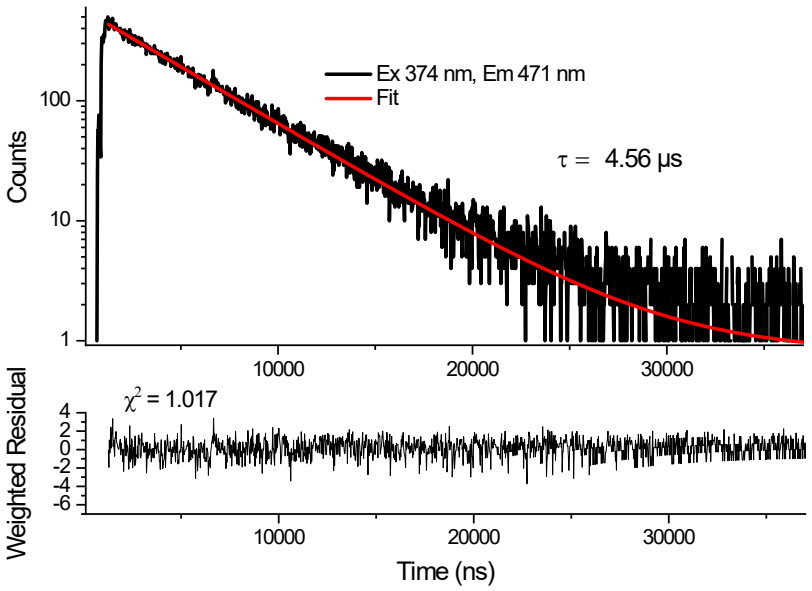


Figure S24. Lifetime measurement of **PtL^{4}Cl** at room temperature in dichloromethane solution ($2.5 \cdot 10^{-6}$ M), excitation 374 nm, emission 471 nm.

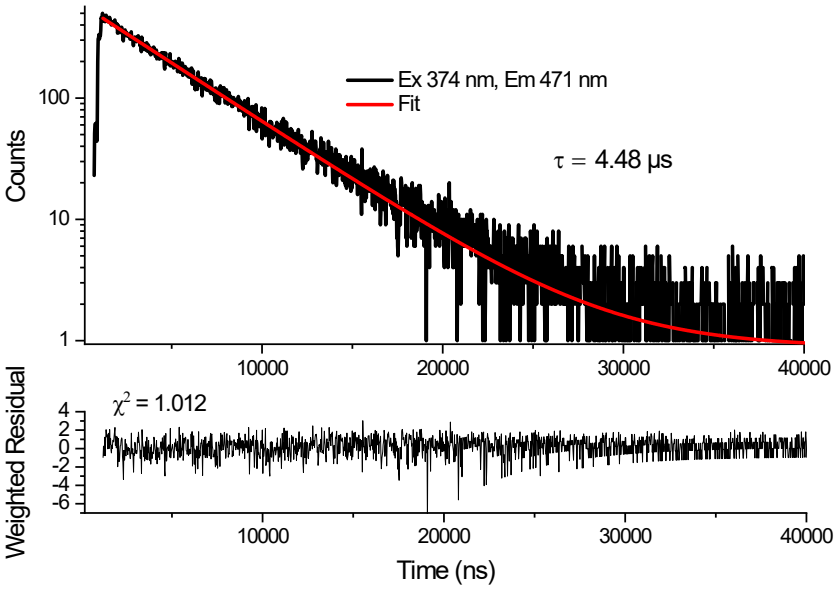


Figure S25. Lifetime measurement of **PtL^{4}Cl** at room temperature in dichloromethane solution ($5.0 \cdot 10^{-6}$ M), excitation 374 nm, emission 471 nm.

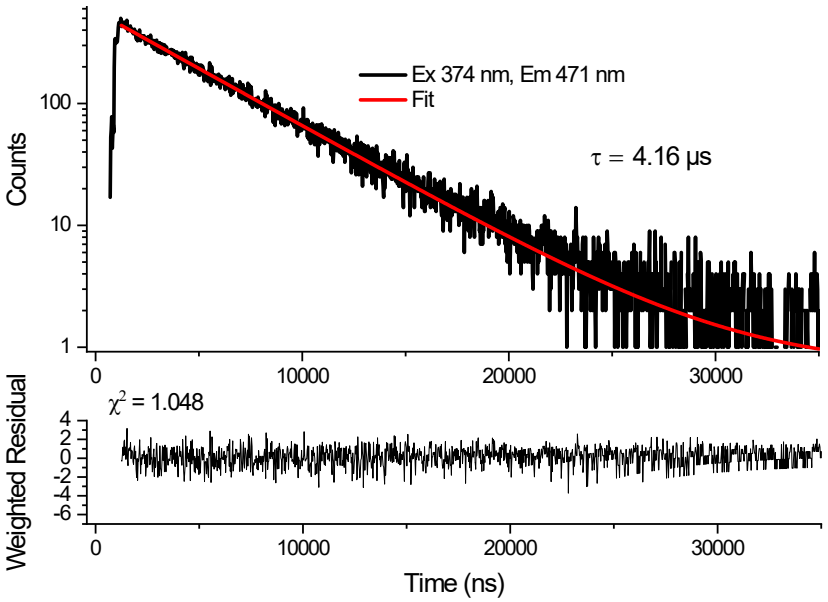


Figure S26. Lifetime measurement of **PtL^{4}Cl** at room temperature in dichloromethane solution ($1.0 \cdot 10^{-5}$ M), excitation 374 nm, emission 471 nm.

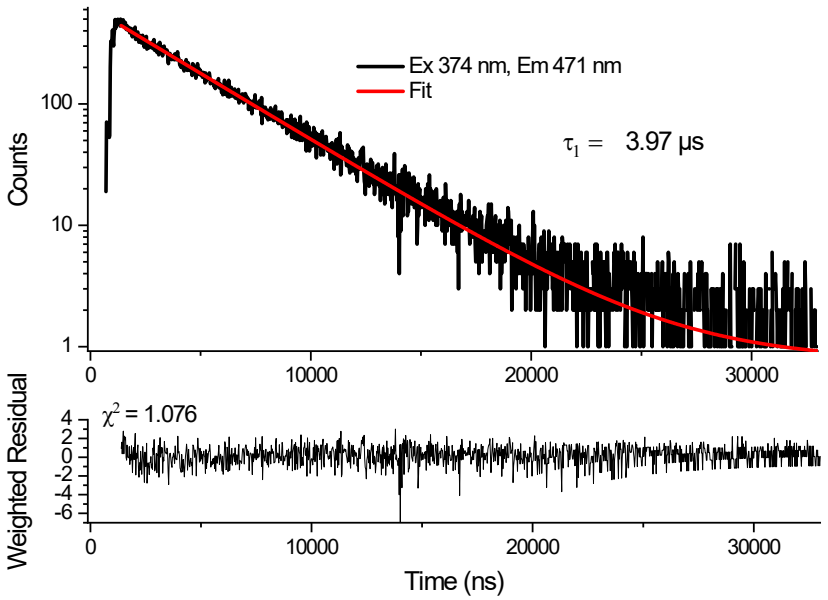


Figure S27. Lifetime measurement of **PtL^{4}Cl** at room temperature in dichloromethane solution ($1.9 \cdot 10^{-4}$ M), excitation 374 nm, emission 471 nm.

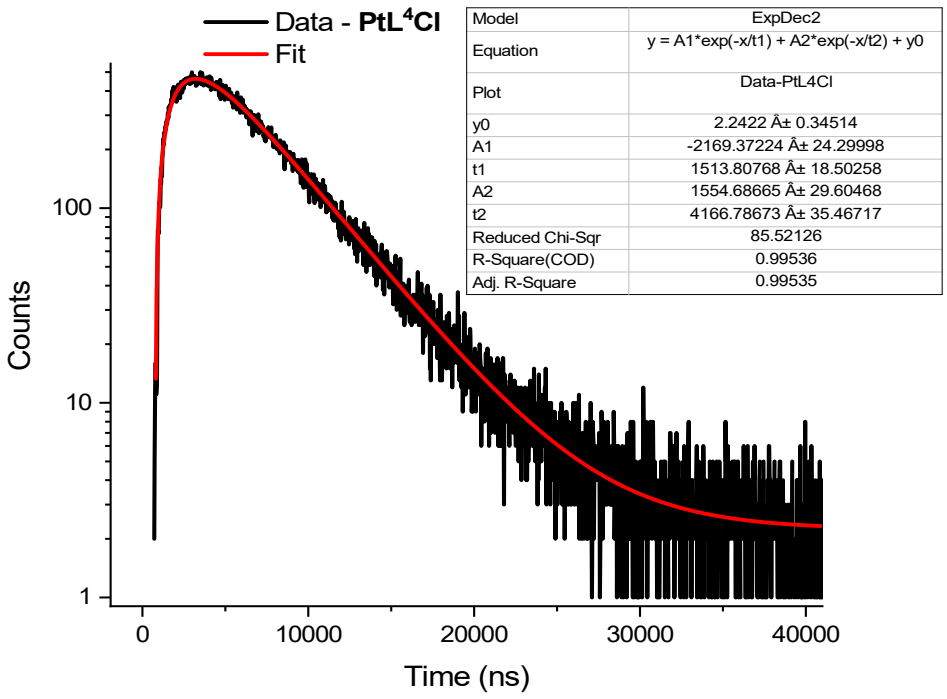


Figure S28. Lifetime measurement of **PtL^{4}Cl** at room temperature in dichloromethane solution ($1.9 \cdot 10^{-4}$ M), excitation 374 nm, emission 680 nm.

Table S4. Lifetime of **PtL^{4}Cl** at different concentrations, λ_{ex} = 374 nm, λ_{em} = 471 nm.

c / M	$1.0 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$
τ / µs	4.62	4.56	4.48	4.16	3.97

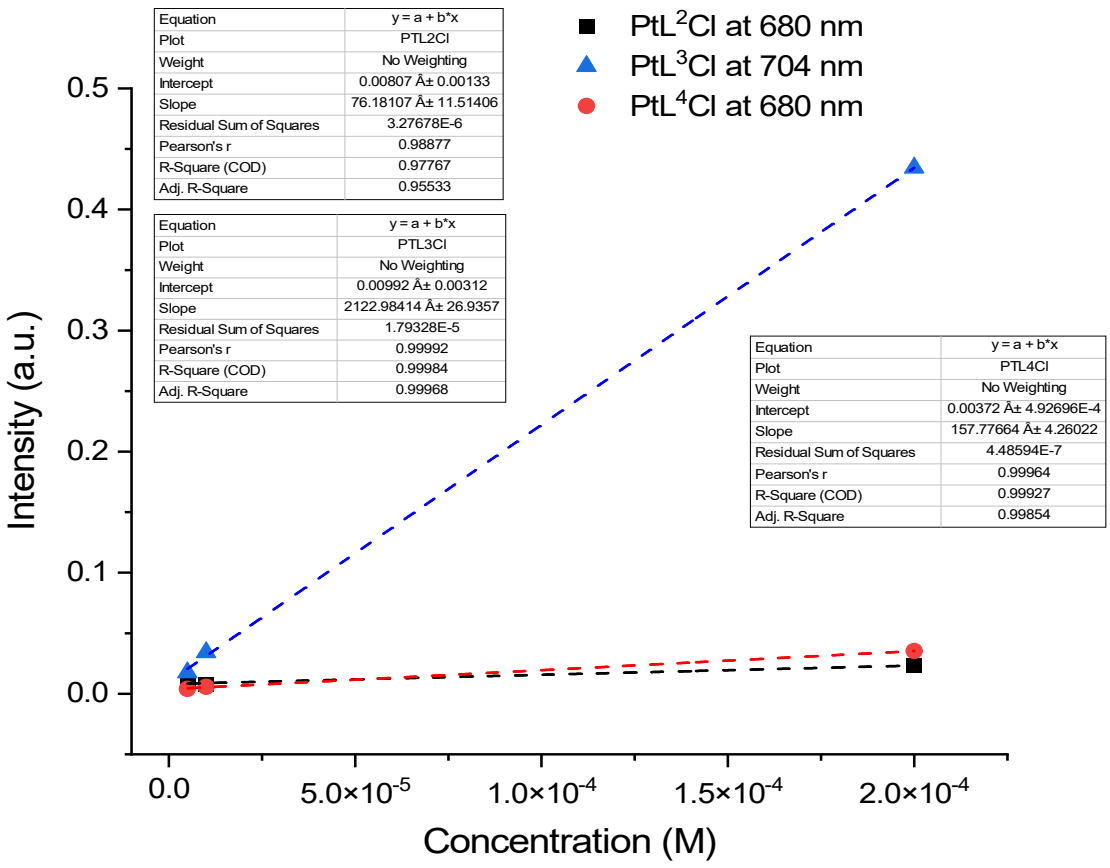


Figure S29. Excimer emission intensity dependence at various concentrations of **PtL^{2}Cl**, **PtL^{3}Cl** and **PtL^{4}Cl** at room temperature in dichloromethane solution.

Computational modelling

Optimized coordinates of **PtL^{3}Cl** computed at B3LYP/6-31G**/LANL2DZ/GD3-BJ/CPCM(CH_2Cl_2) level of calculation

C	1.949680	-0.736589	-3.308753
C	0.860683	-0.684569	-2.422775
C	0.119004	0.504803	-2.330692
C	0.460440	1.613776	-3.101983
C	1.542934	1.550126	-3.982351
C	2.284934	0.371235	-4.084318
C	0.500075	-1.860973	-1.604237
C	1.486840	-2.729482	-1.115271
C	1.141931	-3.838595	-0.349635
N	-0.181794	-4.096186	-0.063291
C	-1.134152	-3.268677	-0.522948
C	-0.836186	-2.151893	-1.288063
C	2.068487	-4.817391	0.227882
C	3.462092	-4.892717	0.144451
C	4.186222	-5.912830	0.757909
C	3.502522	-6.891561	1.476338
C	2.110106	-6.883644	1.602834
C	1.435546	-5.830320	0.965499
Pt	-0.487127	-5.791965	1.081233
Cl	-2.994264	-5.779379	1.168540
F	4.153658	-3.962579	-0.547054
F	4.233053	-7.867464	2.055634

C	1.222227	-7.818515	2.301397
C	1.612623	-8.945859	3.016678
C	0.660693	-9.763587	3.643349
C	-0.689508	-9.400338	3.517505
C	-1.033775	-8.272355	2.789202
N	-0.113879	-7.496317	2.193791
C	1.070281	-10.962881	4.403854
C	2.293625	-10.991331	5.094284
C	2.676658	-12.122846	5.811203
C	1.847109	-13.245989	5.846520
C	0.629861	-13.229663	5.161959
C	0.242813	-12.097429	4.448371
H	2.934128	-10.115522	5.093373
H	2.147253	-14.127854	6.403681
H	-0.693225	-12.104209	3.899629
H	-0.709433	0.570170	-1.632855
H	1.806290	2.413418	-4.585330
H	2.516980	-1.655907	-3.412118
H	5.264904	-5.945978	0.675514
H	-1.471291	-9.973282	4.000277
H	-1.645786	-1.533429	-1.655156
H	2.664018	-9.191402	3.061182
H	2.532827	-2.537620	-1.307615
H	-2.150616	-3.540011	-0.263314
H	-2.061891	-7.952704	2.666302

H	3.620391	-12.125127	6.347382
H	-0.016392	-14.101558	5.177942
H	-0.115349	2.529389	-3.011268
H	3.121742	0.311640	-4.773048

Optimized coordinates of **$(PtL^3Cl)_2$** computed at B3LYP/6-31G**/LANL2DZ/GD3-BJ/CPCM(CH_2Cl_2) level of calculation

C	19.606676	-0.522746	2.803426
C	18.887634	0.683708	2.774900
C	19.165270	1.607491	1.753075
C	20.116730	1.323906	0.778988
C	20.816070	0.115688	0.809865
C	20.563364	-0.802900	1.829660
C	17.832087	0.955966	3.772271
C	17.852827	0.365387	5.045426
C	16.816250	0.579882	5.948027
N	15.755358	1.391112	5.601551
C	15.744883	1.994095	4.403051
C	16.750444	1.799106	3.470595
C	16.706864	0.022494	7.298699
C	17.591040	-0.794706	8.007375
C	17.334035	-1.211441	9.310692
C	16.164564	-0.787748	9.935260

C	15.229621	0.028114	9.293343
C	15.544000	0.414749	7.980820
Pt	14.314536	1.577566	7.065835
N	13.335398	1.404277	8.875040
C	13.966861	0.584578	9.787269
C	13.392112	0.358023	11.034049
C	12.166867	0.949061	11.379822
C	11.578505	1.809834	10.439091
C	12.188379	2.013112	9.212217
F	18.759305	-1.177637	7.444960
F	15.967471	-1.163028	11.219113
C	11.503108	0.657437	12.667358
C	10.600570	1.572785	13.233910
C	9.936928	1.273931	14.419296
C	10.165577	0.057844	15.066078
C	11.070659	-0.854655	14.521492
C	11.732668	-0.559052	13.331803
H	10.445256	2.539182	12.768342
H	9.647838	-0.173437	15.991680
H	18.660067	2.566410	1.737969
H	21.559272	-0.103665	0.049768
H	12.404576	-1.293285	12.900526
H	19.392736	-1.262281	3.567459
Cl	12.667431	3.023231	5.842988
C	12.462276	2.405507	16.155186

C	11.762206	3.613288	16.123717
C	12.014970	4.531916	15.103965
C	12.972378	4.252222	14.130776
C	13.692021	3.046133	14.159803
C	13.414406	2.122338	15.181623
C	14.748145	2.774295	13.162944
C	15.830197	1.931915	13.465223
C	16.836142	1.737173	12.533119
N	16.825578	2.339573	11.334335
C	15.764492	3.150391	10.987439
C	14.727552	3.364613	11.889667
Pt	18.266429	2.152777	9.870070
N	19.245610	2.325726	8.060855
C	18.614101	3.145106	7.148362
C	19.188744	3.371101	5.901423
C	20.413942	2.779886	5.555835
C	21.002455	1.919599	6.496908
C	20.392649	1.716790	7.723889
C	15.874044	3.707676	9.636746
C	17.036965	3.315353	8.954762
C	17.351369	3.701751	7.642171
C	16.416491	4.517600	7.000111
C	15.247101	4.941551	7.624638
C	14.990005	4.524937	8.927980
H	13.186573	4.991918	13.366970

H	11.018383	3.832277	16.883312
H	13.920162	1.163714	15.197109
F	16.613556	4.892566	5.716155
F	13.821745	4.908020	9.490293
C	21.077546	3.070775	4.268059
C	21.979554	2.154830	3.701656
C	22.643221	2.453078	2.516130
C	22.415084	3.669121	1.869083
C	21.510456	4.582179	2.413496
C	20.848435	4.287193	3.603337
H	22.134475	1.188523	4.167563
H	22.932873	3.899938	0.943392
H	20.176901	5.021816	4.034538
Cl	19.913300	0.707219	11.093582
H	14.523327	5.538457	7.087132
H	18.057856	-1.808364	9.848118
H	17.696044	1.108083	12.729552
H	14.885334	2.623835	4.207166
H	15.918285	1.456091	14.433265
H	16.662437	2.275429	2.502794
H	13.896874	3.981210	11.579007
H	18.683326	-0.251642	5.355711
H	11.476710	5.474000	15.072140
H	20.327194	2.055729	0.006500
H	12.251980	1.673740	16.927772

H	20.821588	1.078328	8.486816
H	11.759459	2.651872	8.449531
H	21.952200	1.438684	6.301930
H	10.628759	2.290714	10.634142
H	18.662087	4.000913	5.199522
H	13.918556	-0.272386	11.735577
H	21.328725	5.531301	1.919124
H	9.255608	2.000361	14.849319
H	23.324235	1.726273	2.086257
H	11.252800	-1.803819	15.015627
H	21.101127	-1.745279	1.861120

Optimized coordinates of **PtL^{4}Cl** computed at B3LYP/6-31G**/LANL2DZ/GD3-BJ/CPCM(CH_2Cl_2) level of calculation

C	17.255463	0.662975	5.319231
C	16.120522	0.581608	6.146269
C	14.881306	1.099735	5.706187
C	14.802322	1.693680	4.449960
C	15.926628	1.772434	3.618943
C	17.148631	1.254761	4.054493
C	16.225669	-0.049001	7.489419
C	16.958535	0.564046	8.512356
C	17.064538	-0.032502	9.765999
N	16.437133	-1.235242	10.010860

C	15.728358	-1.829270	9.037661
C	15.602331	-1.271256	7.773346
Pt	16.722980	-1.961814	11.927956
Cl	15.358825	-4.065495	11.771585
C	17.803543	0.491424	10.918673
C	17.741684	-0.332090	12.053598
C	18.368559	-0.043200	13.275677
C	19.095585	1.149904	13.330229
C	19.194169	2.007138	12.236046
C	18.548982	1.667273	11.048559
C	18.151622	-1.062047	14.307089
N	17.375189	-2.119973	13.885058
C	17.101432	-3.126279	14.730572
C	17.574471	-3.140914	16.034938
C	18.359452	-2.077910	16.500635
C	18.641296	-1.035129	15.610136
F	19.731871	1.507118	14.465698
F	18.664651	2.517751	10.006957
C	18.877356	-2.050826	17.894547
C	20.265840	-2.170471	18.132695
C	20.732996	-2.152468	19.443536
C	19.850403	-2.004981	20.520638
C	18.480115	-1.878255	20.281916
C	17.984819	-1.905813	18.972326
C	21.246676	-2.340928	16.995688

O	20.421393	-1.995487	21.757651
C	19.565672	-1.855526	22.887760
C	16.497002	-1.756260	18.749640
C	13.651741	1.043214	6.582572
O	15.729575	2.369076	2.409937
C	16.844576	2.482386	1.530846
C	18.590898	0.106006	5.757277
H	19.764636	2.924161	12.307414
H	16.490018	-3.922909	14.323372
H	17.337788	-3.978561	16.679733
H	19.235750	-0.190690	15.929762
H	21.792875	-2.255968	19.652543
H	17.782133	-1.753419	21.100455
H	22.232098	-2.619842	17.375253
H	20.917261	-3.113816	16.294409
H	21.361600	-1.417105	16.418808
H	16.005919	-1.393878	19.655689
H	16.279646	-1.055531	17.938228
H	16.030920	-2.710255	18.480245
H	15.268701	-2.772963	9.307009
H	15.031739	-1.792046	7.013863
H	17.447643	1.512549	8.339263
H	18.027947	1.298981	3.424066
H	13.865030	2.109836	4.094972
H	19.059543	0.735158	6.521741

H	18.487263	-0.894130	6.188565
H	19.279868	0.044700	4.911749
H	13.269299	0.021441	6.677658
H	13.866304	1.396926	7.595839
H	12.852069	1.659807	6.166225
H	20.216344	-1.876929	23.762212
H	19.021670	-0.904188	22.862356
H	18.846171	-2.680266	22.948888
H	16.472988	2.983851	0.636984
H	17.646627	3.081526	1.977346
H	17.240267	1.497448	1.257274

Optimized coordinates of **$(PtL^4Cl)_2$** computed at B3LYP/6-31G**/LANL2DZ/GD3-BJ/CPCM(CH_2Cl_2) level of calculation

C	17.214096	0.783332	5.237837
C	16.144033	0.609578	6.142913
C	14.820856	0.908025	5.728680
C	14.597854	1.354562	4.431675
C	15.648900	1.486341	3.521734
C	16.954516	1.209008	3.930843
C	16.384518	0.038930	7.490975
C	17.290952	0.603490	8.400705
C	17.484645	0.036671	9.658445
N	16.773992	-1.086214	10.022968

C	15.909366	-1.639858	9.159516
C	15.698934	-1.116263	7.895377
C	18.368896	0.535481	10.718633
C	19.231691	1.633583	10.725278
C	19.972858	1.988376	11.850227
C	19.833829	1.238664	13.014471
C	18.988427	0.128582	13.091263
C	18.287269	-0.193877	11.916198
Pt	17.103148	-1.710171	11.964391
N	17.807261	-1.771118	13.900342
C	18.681658	-0.754988	14.221925
C	19.155094	-0.634660	15.527813
C	18.757893	-1.542966	16.517316
C	17.884685	-2.574593	16.142643
C	17.428123	-2.652847	14.837990
F	19.345113	2.412083	9.626618
F	20.531565	1.640138	14.102392
C	19.224237	-1.457220	17.924197
C	18.277858	-1.323981	18.958402
C	18.697015	-1.376842	20.290779
C	20.045314	-1.548341	20.599541
C	20.989063	-1.638604	19.570120
C	20.597285	-1.597899	18.234933
C	16.808950	-1.099113	18.680212
O	20.536098	-1.626448	21.870879

C	13.620185	0.772331	6.639949
O	15.297913	1.885565	2.269564
C	21.643186	-1.755754	17.154974
C	18.648501	0.486744	5.614902
Cl	15.586076	-3.705536	12.006924
N	17.278047	4.881434	10.100042
C	16.403694	3.878400	9.739578
C	15.974269	3.773714	8.415766
C	16.414564	4.688157	7.447690
C	17.277594	5.712227	7.867733
C	17.692186	5.772065	9.186209
C	16.058206	2.985434	10.853563
C	16.743658	3.276406	12.046386
C	16.629746	2.529201	13.230676
C	15.753607	1.442373	13.190238
C	15.023232	1.121077	12.048535
C	15.189574	1.892315	10.901957
C	17.494459	3.003221	14.318367
N	18.236038	4.114156	13.980046
C	19.091350	4.643498	14.867391
C	19.247512	4.115963	16.137217
C	18.513797	2.983954	16.524433
C	17.632714	2.432696	15.582944
Pt	17.947611	4.776663	12.045823
Cl	19.488730	6.754572	12.062878

C	18.677353	2.456325	17.902308
C	17.563334	2.385299	18.777395
C	17.771732	2.081788	20.119295
C	19.057849	1.839336	20.614105
C	20.144612	1.849752	19.743011
C	19.966774	2.158431	18.391353
C	16.155089	2.681621	18.314924
O	19.153871	1.603563	21.953179
C	21.197924	2.142735	17.511992
F	14.490618	1.531735	9.801328
F	15.613037	0.646046	14.272625
C	16.012004	4.630196	6.020127
C	17.014662	4.594233	5.020909
C	16.648098	4.699617	3.684065
C	15.306972	4.809800	3.309225
C	14.314197	4.797766	4.291289
C	14.655167	4.711736	5.645518
C	18.478028	4.393402	5.347215
O	15.070041	4.917742	1.972557
C	13.543821	4.741667	6.669567
H	14.365685	0.262483	12.041104
H	20.615373	2.857994	11.831575
H	19.637432	5.514892	14.525893
H	15.394302	-2.523251	9.517896
H	19.929742	4.593175	16.829306

H	15.007413	-1.611461	7.226008
H	17.058235	1.549056	15.817270
H	17.833093	1.502556	8.148353
H	16.936762	2.056094	20.811929
H	13.595623	1.607924	4.103549
H	21.139236	1.608060	20.095280
H	15.499706	2.845488	19.173251
H	12.840741	1.475856	6.336572
H	16.111897	3.568304	17.676327
H	13.184013	-0.231383	6.583245
H	15.735542	1.850391	17.738293
H	13.862415	0.956826	7.686209
H	21.849813	1.315594	17.805854
H	20.961525	2.035613	16.453540
H	21.779771	3.065134	17.621381
H	18.370665	6.533845	9.551469
H	16.744399	-3.424041	14.503484
H	17.624055	6.461498	7.167165
H	17.564623	-3.314960	16.865194
H	15.318513	2.961302	8.139819
H	19.818608	0.180682	15.772355
H	13.267678	4.865981	4.021383
H	17.959091	-1.257946	21.073395
H	17.404292	4.675163	2.906463
H	13.349984	3.746421	7.082387

H	16.654097	-0.522027	17.766430
H	13.782893	5.396210	7.512426
H	16.265306	-2.043481	18.565230
H	12.614122	5.093430	6.216420
H	16.350721	-0.551407	19.506667
H	19.006689	5.344488	5.474886
H	18.615821	3.819713	6.265827
H	18.968639	3.853355	4.533570
H	22.033911	-1.768368	19.833286
H	21.814269	-0.820325	16.613062
H	22.597317	-2.064761	17.587589
H	21.345544	-2.502997	16.413029
H	19.254205	0.335563	4.718215
H	19.097977	1.315088	6.173136
H	18.733675	-0.405883	6.239875
H	17.784252	1.316513	3.243551
C	20.459726	1.610307	22.533372
H	20.306904	1.547862	23.611144
H	21.047538	0.749441	22.202343
H	20.989599	2.538085	22.291414
C	19.593521	-1.658469	22.942297
H	20.181702	-1.748832	23.855697
H	19.001237	-0.738913	22.975839
H	18.923968	-2.521066	22.849858
C	13.729644	4.746958	1.521733

H	13.772891	4.779062	0.432575
H	13.335509	3.778168	1.845368
H	13.076894	5.551740	1.878951
C	16.326473	2.026048	1.295145
H	15.832348	2.362185	0.384233
H	17.063854	2.773240	1.602136
H	16.829058	1.069553	1.111235

References

1. Murphy, L.; Brulatti, P.; Fattori, V.; Cocchi, M.; Williams, J.A.G. *Chem. Commun*., 2012, 48, 5817.

2. 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.