Supporting Information

Pt(II) Phosphors with Dual 1,6-Naphthyridin-5-yl Pyrazolate Chelates and Non-doped Organic Light Emitting Diodes

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Experimental section

General information and materials. All reactions were performed under nitrogen atmosphere. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. Mass spectra were obtained on a JEOL Model:JMS-T200GC AccuTOF GCx instrument operating in FD (field desorption) mode. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker DMX-600, an AVANCE 500 instruments or Bruker AVIII HD 400MHz NMR instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

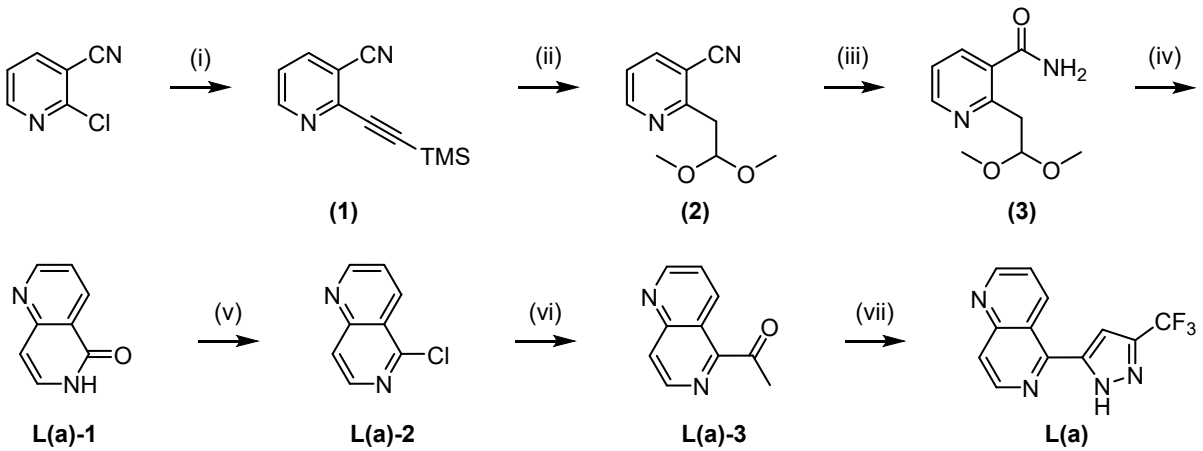
Steady-state spectra, lifetime and PLQY measurements. Thin films with a thickness of 100 nm for both UV-Vis and photoluminescence spectral measurement were deposited on alkali-free glass substrates with deposition rate of 0.5 Å s^{-1} and at < 5×10^{-6} torr, to which the thickness and deposition rate were measured by a quartz crystal monitor. Steady-state absorption and emission spectra were recorded by a Hitachi U-4100 spectrophotometer. Steady-state emission spectra were recorded by an Edinburgh FLS980 fluorescence

spectrometer using a Hamamatsu R928P photomultiplier as a visible-PMT detector with a spectral coverage from 200 nm to 870 nm and a near-infrared photomultiplier (NIR-PMT detector) with a spectral coverage from 500 nm to 1700 nm. The nanosecond time-resolved studies were performed by an Edinburgh FLS980 time-correlated single photon counting (TCSPC) system using a picosecond pulsed diode laser as the excitation light source. The absolute photoluminescence quantum yields (PLQYs) were obtained by the same Edinburgh FLS980 fluorescence spectrometer using an integrating sphere and calculated following the procedures outlined in the operational manual. All above photophysical measurements were carried out at room temperature (298 K).

NIR OLED fabrication and Characterization. All chemicals were purified by vacuum sublimation before the fabrications. The OLEDs were fabricated through vacuum deposition of the materials at 10^{-6} torr onto the ITO-coated glass substrates possessing a sheet resistance of 15 Ω sq^{-1}. The ITO surface was cleaned ultrasonically; i.e. with acetone, methanol, and deionized water in sequence and finally with N_2 plasma. The deposition rate of each organic material was ca. 1 - 2 Å·s^{-1}. The J–V–L characteristics of the devices were measured in a glove-box at the same time. The driving source of the device was originated from the programmable source measurement unit (2614B, Keithley) while the light intensity was measured by a calibrated silicon detector. Each EL spectrum was collected by an optical fiber connected to a spectrometer (CAS 125, Instrument Systems).

Angle-Dependent PL Spectra Measurement and Simulation. The angular dependent *p*-polarized fluorescence intensity was measured in an attempt to analyze the transition dipole moment of emitters. The experimental setup was composed of a motorized rotation stage, a fused silica-based half-cylindrical lens, a longpass filter to stop the excitation beam, a polarizer, and a fiber-guided spectrometer (Ocean Optics USB4000) to collect the polarized emission. A continuous-wave Nd:YAG laser (355 nm, 10 kHz) was used as the excitation source which was fixed at an incident angle of 45°. The sample was deposited on top of a quartz substrate and encapsulated under N_2 atmosphere. Measurements were performed automatically using the programmed rotation stage. Intensity of the *p*-polarized emission was recorded from 0° to 90° in steps of 5°. The data were analyzed using SETFOS 4.5 (Fluxim AG, Switzerland) to fit the ratio of horizontal dipoles (Θ).

Synthesis of L(a)



Scheme S1. Synthetic route for the preparation of chelate **L(a)**. (i) trimethylsilylacetylene, CuI, $Pd(PPh_3)_2Cl_2$, TEA. 100 °C, 12 h. (ii) NaOMe, MeOH, reflux, 4 h. (iii) NaOH, 30% $H_2O_{2(aq)}$, MeOH, 0 °C to RT, combined yield: 90%. (iv) PTSA, toluene, reflux, 12 h, yield: 72%. (v) $POCl_3$, toluene, reflux, 3 h, yield: 78%. (vi) (a.) tributyl(1-ethoxyvinyl)tin, $Pd(PPh_3)_2Cl_2$, DMF, 80°C, 12 h. (b.) 2N $HCl_{(aq)}$, acetone, RT, 2 h, overall yield: 83%. (vii) (a.) ethyl trifluoroacetate, NaH, THF, 0 °C to reflux, 12 h. (b.) hydrazine monohydrate, PTSA, EtOH, reflux, 24 h, overall yield: 63%.

2-((Trimethylsilyl)ethynyl)nicotinonitrile (1). A mixture of 2-chloronicotinonitrile (5.0 g, 36.1 mmol), CuI (275 mg, 1.4 mmol), and $Pd(PPh_3)_2Cl_2$ (500 mg, 0.72 mmol) in a pressure tube was added pre-degassed TEA (30 mL). Trimethylsilylacetylene (6.1 mL, 43.0 mmol) was then added rapidly. The tube was sealed and heated at 100 °C for 12 h. The reaction mixture was filtered and washed with ethyl acetate several times. The filtrate was extracted with ethyl acetate and washed with water in sequence. The combined organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 5) to afford a mixture of **(1)** and a trace amount of desilylation product as a brown solid. This mixture was used in the subsequent step.

2-(2,2-Dimethoxyethyl)nicotinonitrile (2). Compound **(1)** was dissolved in anhydrous MeOH (70 mL), to which NaOMe (4.2 g, 76.8 mmol) was added in several portions. The reaction mixture was then heated to reflux for 4 h. After the removal of solvents, the residue was extracted with ethyl acetate and washed with water in sequence. The combined organic

phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 2) to afford an amber oil (5.5 g, 73% in 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.74 (d, J = 4.8 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.27 (dd, J = 7.9, 4.8 Hz, 1H), 4.93 (t, J = 5.7 Hz, 1H), 3.37 (s, 6H), 3.36 (d, J = 5.7 Hz, 2H).

2-(2,2-Dimethoxyethyl)nicotinamide (3). A solution of NaOH (2.1 g, 52.2 mmol) in MeOH (30 mL) was slowly added to compound **(2)** (5.5 g, 26.1 mmol) in MeOH (30 mL) via an addition funnel at 0°C. After stirring for 5 min, 30% $H_2O_{2(aq)}$ (4.2 mL, 52.2 mmol) was slowly added, and then the mixture was warmed to RT for 12 h. After the removal of solvents, the residue was extracted with ethyl acetate and washed with water in sequence. The combined organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 1) to afford a yellow solid (5.4 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.63 (d, J = 4.3 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.87 (dd, J = 7.8, 4.3 Hz, 1H), 6.47 (s, 1H), 4.88 (t, J = 6.0 Hz, 1H), 4.12 (s, 1H), 3.41 (s, 6H), 3.34 (d, J = 6.0 Hz, 2H).

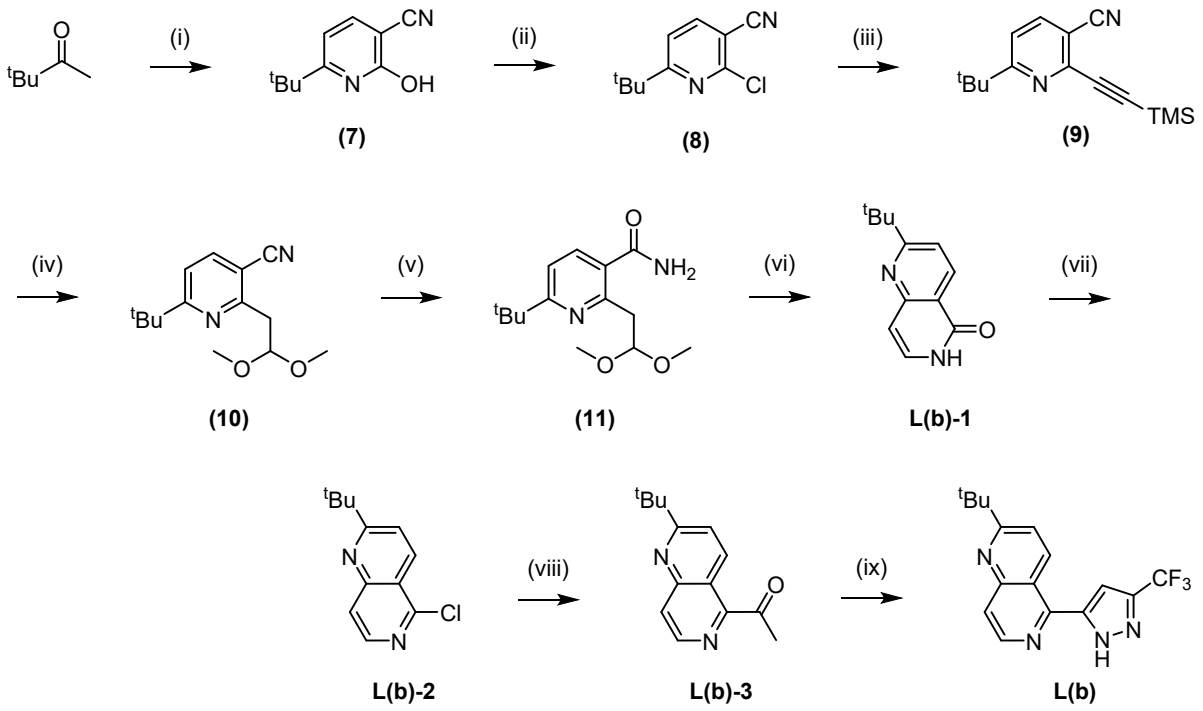
1,6-Naphthyridin-5(6*H*)-one, L(a)-1. A mixture of **(3)** (5.4 g, 23.6 mmol) and PTSA (450 mg, 2.36 mmol) in anhydrous toluene (50 mL) was heated to reflux for 12 h. The reaction mixture was then washed with water, and organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (CH_2Cl_2 / MeOH = 4: 1) to afford a white solid (2.5 g, 72%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 11.54 (s, 1H), 8.89 (d, J = 4.5 Hz, 1H), 8.47 (d, J = 8.1 Hz, 1H), 7.48 (dd, J = 8.1, 4.5 Hz, 1H), 7.42 (d, J = 7.3 Hz, 1H), 6.59 (d, J = 7.3 Hz, 1H).

5-Chloro-1,6-naphthyridine, L(a)-2. Compound **L(a)-1** (2.5 g, 17.1 mmol) in anhydrous toluene (35 mL) was slowly added $POCl_3$ (4.8 mL, 51.3 mmol) and 3 drops of DMF. After heated to reflux for 3 h, the mixture was cooled to RT and poured onto crushed ice. The mixture was then carefully adjusted to pH = 8 with $NaOH_{(aq)}$ and then extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 2) to afford a white solid (2.2 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.14 (d, J = 4.3 Hz, 1H), 8.66 (d, J = 8.6 Hz, 1H), 8.53 (d, J = 5.7 Hz, 1H), 7.90 (d, J = 5.7 Hz, 1H), 7.64 (dd, J = 8.6, 4.3 Hz, 1H).

1-(1,6-Naphthyridin-5-yl)ethanone, L(a)-3. A mixture of **L(a)-2** (2.2 g, 13.3 mmol) and $Pd(PPh_3)_2Cl_2$ (467 mg, 0.67 mmol) in DMF (30 mL) was degassed three times. Tributyl(1-ethoxyvinyl)tin (5.0 mL, 14.7 mmol) was then added, and the reaction mixture was heated at 80 °C for 12 h. The mixture was poured into iced water and extracted with ethyl acetate three times. The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo to afford a crude product as a yellow oil. The crude product in acetone (30 mL) was added 2N $HCl_{(aq)}$ (20 mL) and stirred at RT for 2 h. The reaction mixture was carefully neutralized with $NaHCO_{3(aq)}$ to pH = 7, then extracted with ethyl acetate and washed with water in sequence. The combined organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 2) to afford a white solid (1.9 g, 83% in 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.39 (*d*, *J* = 8.7 Hz, 1H), 9.10 (*d*, *J* = 5.5 Hz, 1H), 8.81 (d, *J* = 5.5 Hz, 1H), 8.10 (d, *J* = 4.8 Hz, 1H), 7.60 (dd, *J* = 8.7, 4.8 Hz, 1H), 2.88 (s, 3H).

5-(3-(Trifluoromethyl)-1H-pyrazol-5-yl)-1,6-naphthyridine L(a). NaH (60% in mineral oil) (485 mg, 14.3 mmol) was dissolved in anhydrous THF (25 mL) and cooled to 0 °C, then **L(a)-3** (1.9 g, 11.0 mmol) in anhydrous THF (25 mL) was slowly added and stirred at 0 °C for 1 h. Ethyl trifluoroacetate (1.8 mL, 14.3 mmol) was slowly added to the reaction mixture, which was then heated to reflux for 12 h. The reaction mixture was adjusted to pH = 5 with 2N $HCl_{(aq)}$, then extracted with ethyl acetate and washed with water in sequence. The combined organic phase was dried over $MgSO_4$, and concentrated. The crude 1.3-diketone was directly used in the next step. The crude 1,3-diketone and PTSA (210 mg, 1.1 mmol) in EtOH (30 mL) was added hydrazine monohydrate (2.7 mL, 55 mmol), then heated to reflux for 24 h. After the removal of solvents, the residue was extracted with ethyl acetate and washed with water in sequence. The combined organic phase was dried over $MgSO_4$ and concentrated, and the crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 3) to afford a brown solid (1.9 g, 63% in 2 steps). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 14.48 (s, 1H), 9.20 (d, *J* = 4.2 Hz, 1H), 8.86 (d, *J* = 5.8 Hz, 1H), 8.82 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 5.8 Hz, 1H), 7.77 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.50 (s, 1H). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K): δ –60.18 (s, 3F). MS (FD) Calcd. For $C_{12}H_7F_3N_4$ [M^+]: *m/z*: 264.0617, Found: 264.0611.

Synthesis of L(b)



Scheme S2. Synthetic route for the preparation of chelate **L(b)**. (i) (a.) NaH, ethyl formate, THF, 0 °C to reflux, 12 h. (b.) 2-cyanoacetamide, H_2O, AcOH, piperidine, reflux, 12 h, overall yield: 45%. (ii) $POCl_3$, toluene, reflux, 3 h, yield: 78%. (iii) trimethylsilylacetylene, CuI, $Pd(PPh_3)_2Cl_2$, TEA. 100 °C, 12 h. (iv) NaOMe, MeOH, reflux, 4 h, combined yield: 80%. (v) NaOH, 30% $H_2O_{2(aq)}$, MeOH, 0 °C to RT, yield: 79%. (vi) PTSA, toluene, reflux, 12 h, yield: 70%. (vii) $POCl_3$, toluene, reflux, 3 h, yield 79%. (viii) (a.) tributyl(1-ethoxyvinyl)tin, $Pd(PPh_3)_2Cl_2$, DMF, 80 °C, 12 h. (b.) 2N $HCl_{(aq)}$, acetone, RT, 2 h, overall yield: 83%. (ix) (a.) ethyl trifluoroacetate, NaH, THF, 0 °C to reflux, 12 h. (b.) hydrazine monohydrate, PTSA, EtOH, reflux, 24 h, overall yield: 41%.

6-(*tert*-Butyl)-2-hydroxynicotinonitrile (7). NaH (60% in mineral oil) (2.2 g, 55 mmol) was dissolved in anhydrous THF (100 mL) and cooled to 0 °C. Then, pinacolone (6.25 mL, 55 mmol) was slowly added and stirred at 0 °C for 30 min. Ethyl formate (9.0 mL, 100 mmol) was added slowly, and the reaction mixture was then heated to reflux for 12 h. After the removal of solvents, the crude sodium (*E*)-4,4-dimethyl-3-oxopent-1-en-1-olate was used directly in the next steps without further purification. The crude sodium (*E*)-4,4-dimethyl-3-oxopent-1-en-1-olate and 2-cyanoacetamide (4.2 g, 50 mmol) were dissolved in a mixture of water (45 mL), AcOH (20 mL), and piperidine (35 mL). The reaction mixture was then heated to reflux for 12 h. The mixture was cooled to RT, and a large amount of solid precipitated after a few drops

of AcOH were added. The solid was filtered and collected, washed with $NaHCO_{3(aq)}$, and extracted with ethyl acetate several times until TLC indicated no product left in the aqueous phase. The combined organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (ethyl acetate / hexane = 1 : 2) to afford a beige solid (4.0 g, 45% in 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 12.48 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 1.41 (s, 9H).

6-(*tert*-Butyl)-2-chloronicotinonitrile (8). A solution of compound **(7)** (4.0 g, 22.6 mmol) in anhydrous toluene (35 mL) was slowly added $POCl_3$ (7.0 mL, 67.8 mmol) and then heated to reflux for 3 h. The mixture was cooled to room temperature and poured onto crushed ice. The reaction mixture was carefully adjusted to pH = 8 with $NaOH_{(aq)}$ and then extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo* to afford a crude product, which was further purified by column chromatography (ethyl acetate / hexane = 1 : 2) to afford a white solid (3.4 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 1.39 (s, 9H).

6-(*tert*-Butyl)-2-(2,2-dimethoxyethyl)nicotinonitrile (10). This compound was prepared following the same method as for synthesis of compound **(1)** and **(2)** by using compound **(8)** and **(9)** as starting materials. White solid, 80% yield in 2 steps. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 3.5 Hz, 1H), 5.08 (t, *J* = 5.8 Hz, 1H), 3.40 (s, 6H), 3.36 (d, *J* = 5.8 Hz, 2H), 1.38 (s, 9H).

6-(*tert*-Butyl)-2-(2,2-dimethoxyethyl)nicotinamide (11). This compound was prepared following the same method as for synthesis of compound **(3)** by using compound **(10)** as starting material. Brown solid, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.51 (d, *J* = 8.9 Hz, 1H), 8.45 (d, *J* = 5.7 Hz, 1H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 9H).

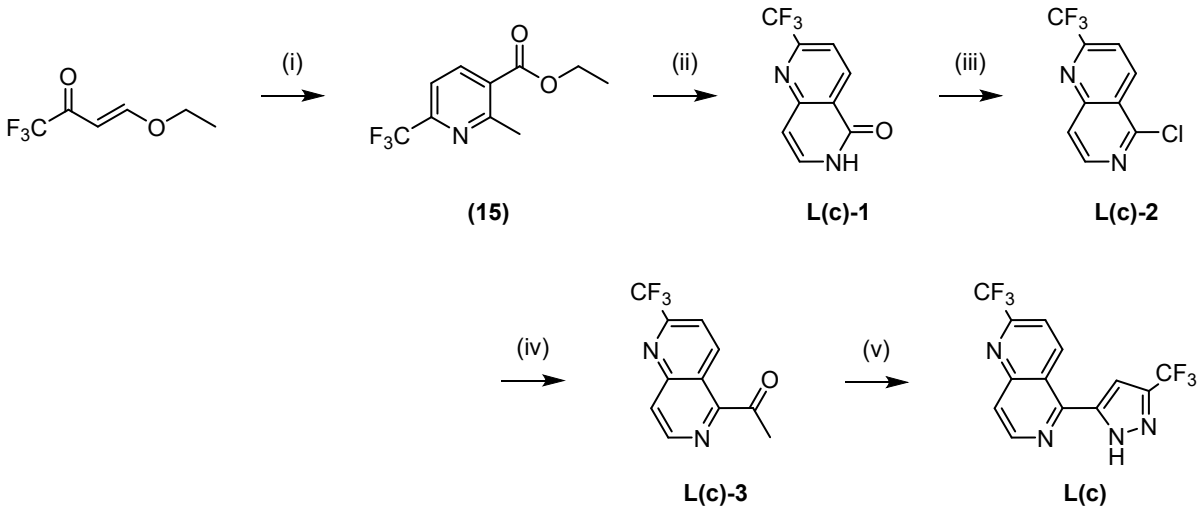
2-(*tert*-Butyl)-1,6-naphthyridin-5(6*H*)-one, L(b)-1. This compound was prepared following the same method as for synthesis of **L(a)-1** by using compound **(11)** as starting material. White solid in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 11.98 (s, 1H), 8.72 (d, *J* = 5.5 Hz, 1H), 7.93 (d, *J* = 5.5 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 1.49 (s, 9H).

2-(*tert*-Butyl)-5-chloro-1,6-naphthyridine, L(b)-2. This compound was prepared following the same method as for synthesis of **L(a)-2** by using **L(b)-1** as starting material, giving brown solid in 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.51 (d, J = 8.9 Hz, 1H), 8.45 (d, J = 5.7 Hz, 1H), 7.82 (d, J = 5.7 Hz, 1H), 7.71 (d, J = 8.9 Hz, 1H), 1.47 (s, 9H).

1-(2-(*tert*-Butyl)-1,6-naphthyridin-5-yl)ethenone L(b)-3. This compound was prepared following the same method as for synthesis of **L(a)-3** by using **L(b)-2** as starting material, giving beige solid in 83% yield in 2 steps. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.25 (d, J = 9.2 Hz, 1H), 8.75 (d, J = 5.6 Hz, 1H), 8.06 (d, J = 5.6 Hz, 1H), 7.71 (d, J = 9.2 Hz, 1H), 2.86 (s, 3H), 1.47 (s, 9H).

2-(*tert*-Butyl)-5-(3-(trifluoromethyl)-1H-pyrazol-5-yl)-1,6-naphthyridine, L(b). This sample was prepared following the same method as for synthesis of compound **L(a)** by using **L(b)-3** as starting material, giving brown solid in 41% yield in 2 steps. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 14.44 (s, 1H), 8.80 (d, J = 5.8 Hz, 1H), 8.71 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 5.8 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.45 (s, 1H). 1.44 (s, 9H). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K): δ -60.20 (s, 3F). MS (FD) Calcd. For $C_{16}H_{15}F_3N_4$ [M^+]: m/z: 320.1243, Found: 320.1245.

Synthesis of L(c)



Scheme S3. Synthetic route for the preparation of chelate **L(c)**. (i) ethyl acetoacetate, NH_4OAc, AcOH, reflux, 2 h, yield: 79%. (ii) (a.) DMFDMA, DMF, 120 °C, 4 h. (b.) 7N NH_3 MeOH solution, 80 °C, 12 h, overall yield: 50%. (iii) $POCl_3$, toluene, reflux, 3 h, yield: 79%. (iv) (a.) tributyl(1-ethoxyvinyl)tin, $Pd(PPh_3)_2Cl_2$, DMF, 80 °C, 12 h. (b.) 2N $HCl_{(aq)}$, acetone, RT, 2 h, overall yield:

83%. (v) (a.) ethyl trifluoroacetate, NaH, THF, 0 °C to reflux, 12 h. (b.) hydrazine monohydrate, PTSA, EtOH, reflux, 24 h, overall yield: 41%.

Ethyl 2-methyl-6-(trifluoromethyl)nicotinate (15). A mixture of (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (7.3 g, 43.4 mmol),[1] ethyl acetoacetate (5.0 mL, 40 mmol), and NH_4OAc (6.7 g , 86.8 mmol) in AcOH (10 mL) was heated to reflux for 2 h. The reaction mixture was quenched with water, and then extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo* to afford a crude product, which was further purified by column chromatography (ethyl acetate / hexane = 1 : 5) to afford a yellow oil (8.0 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.33 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 2.89 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): δ -68.46 (s, 3F).

2-(Trifluoromethyl)-1,6-naphthyridin-5(6*H*)-one, L(c)-1. A solution of **(15)** (8.0 g, 34.2 mmol) in DMF (10 mL) was added DMFDMA (4.6 mL, 34.2 mmol), then heated at 120 °C for 4 h. After the removal of solvents and volatiles in vacuo, yielding the crude as brown solid, which was used directly in the next step without further purification. The crude DMFDMA adduct in a pressure tube was added ammonia solution (7N solution in MeOH) (45 mL), the tube was sealed, and then heated at 80 °C for 12 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo to afford a crude product, which was further purified by recrystallization in CH_2Cl_2 / hexane to afford a beige solid (3.9 g, 50%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 11.80 (s, 1H), 8.76 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 7.4 Hz, 1H), 6.71 (d, J = 7.4 Hz, 1H). ^{19}F NMR (470 MHz, DMSO-d_6, 298 K): δ -66.86 (s, 3F).

5-Chloro-2-(trifluoromethyl)-1,6-naphthyridine, L(c)-2. This compound was prepared following the same method as for synthesis of **L9a)-2** by using **L(c)-1** as starting material. Yellow solid, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.86 (d, J = 8.8 Hz, 1H), 8.63 (d, J = 5.9 Hz, 1H), 8.00 (d, J = 5.9 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): δ -68.14 (s, 3F).

1-(2-(Trifluoromethyl)-1,6-naphthyridin-5-yl)ethenone, L(c)-3. This compound was prepared

following the same method as for synthesis of **L(a)-3** by using **L(c)-2** as starting material. Beige solid, 83% yield in 2 steps. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.64 (d, J = 8.9 Hz, 1H), 8.90 (d, J = 5.5 Hz, 1H), 8.19 (d, J = 5.5 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 2.88 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): δ -68.34 (s, 3F).

2-(Trifluoromethyl)-5-(3-(trifluoromethyl)-1H-pyrazol-5-yl)-1,6-naphthyridine, L(c). It was prepared following the same method as for synthesis of **L(a)** by using **L(c)-3** as starting material. Brown solid, 41% yield in 2 steps. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 14.60 (s, 1H), 9.15 (s, 1H), 9.00 (d, J = 5.8 Hz, 1H), 8.23-8.13 (m, 2H), 7.55 (s, 1H). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K): δ -60.24 (s, 3F), -66.84 (s, 3F). MS (FD) Calcd. For $C_{13}H_6F_6N_4$ [M^+]: m/z: 332.0491, Found: 332.0497.

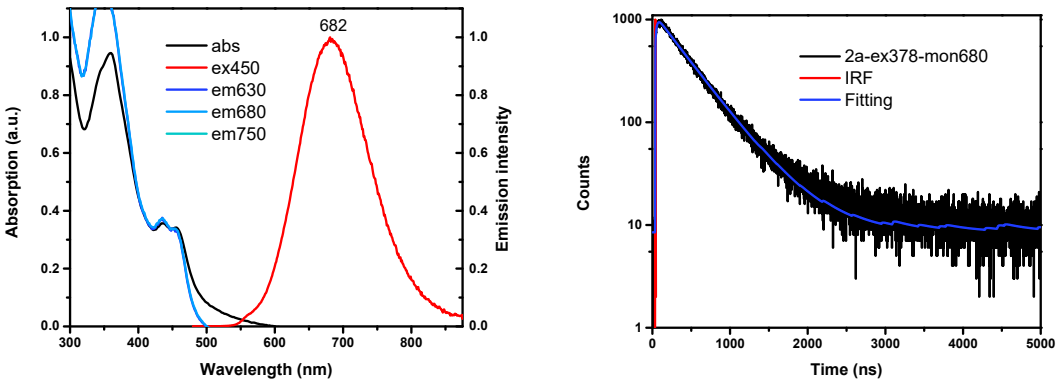


Figure S1. (a) Absorption, emission, and excitation spectra of vacuum deposited thin film of **Pt(a)**, and (b) associated transient emission decay monitored at 680 nm and with excitation at 378 nm.

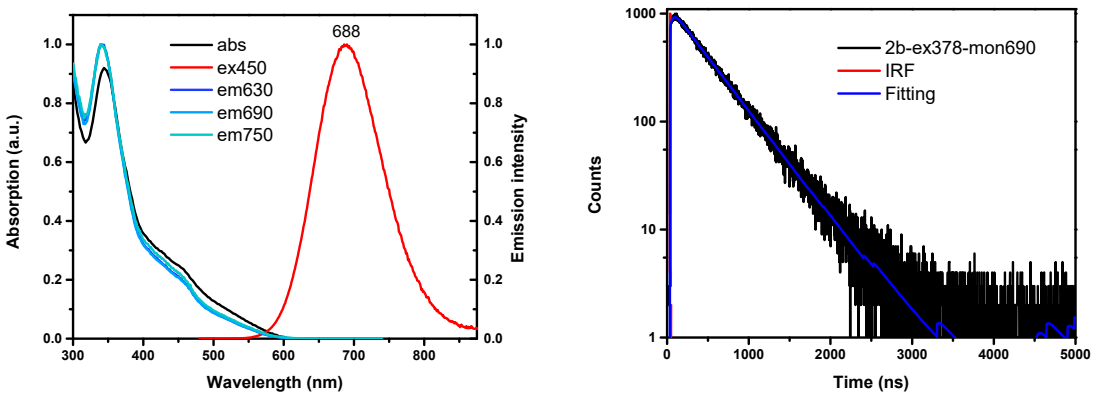


Figure S2. (a) Absorption, emission, and excitation spectra of vacuum deposited thin film of **Pt(b)**, and (b) associated transient emission decay monitored at 690 nm and with excitation at 378 nm.

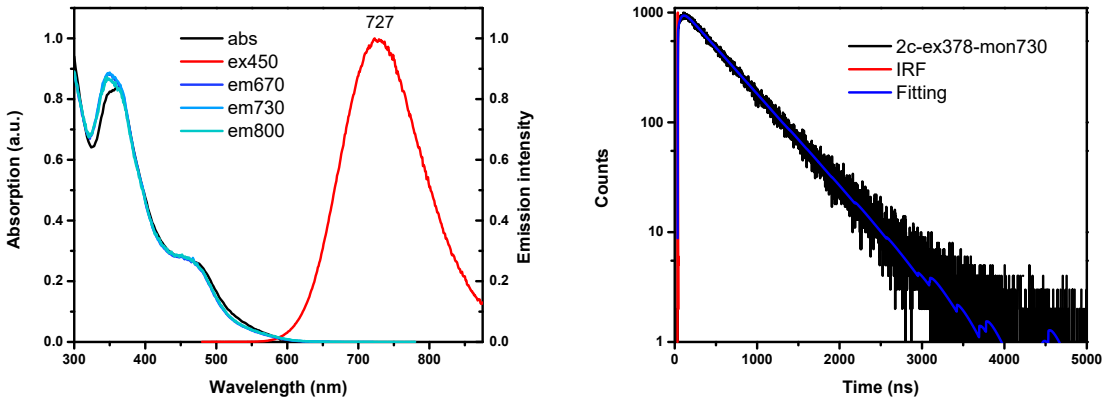


Figure S3. (a) Absorption, emission, and excitation spectra of vacuum deposited thin film of **Pt(c)**, and (b) associated transient emission decay monitored at 730 nm and with excitation at 378 nm.

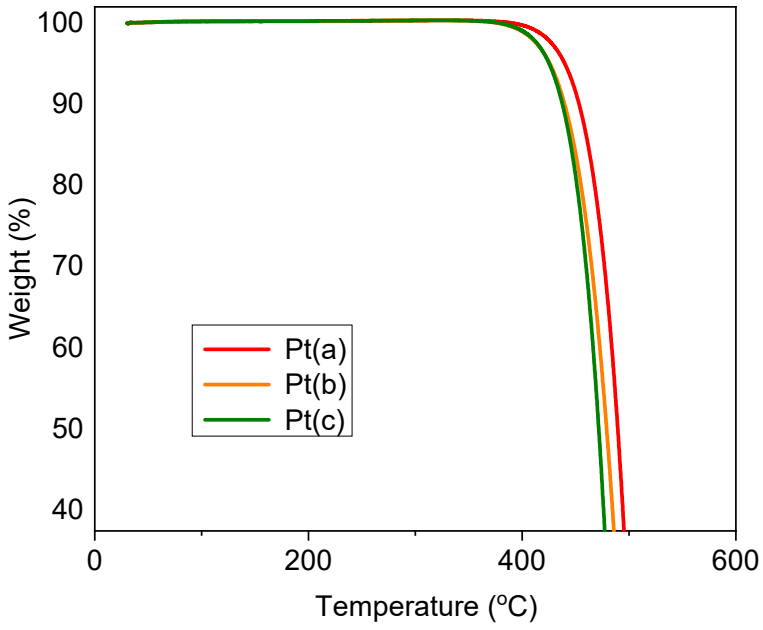
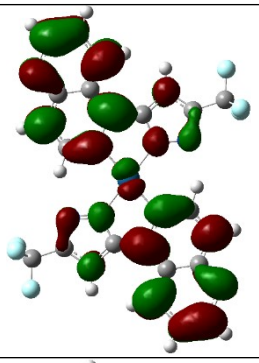
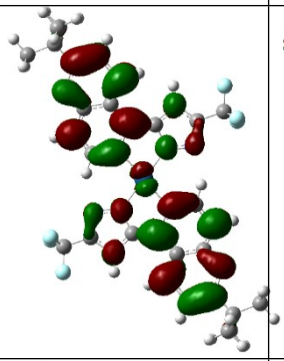
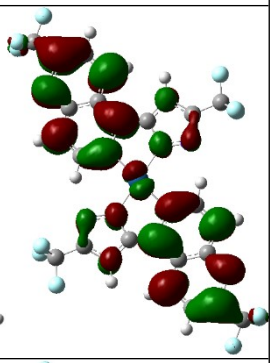
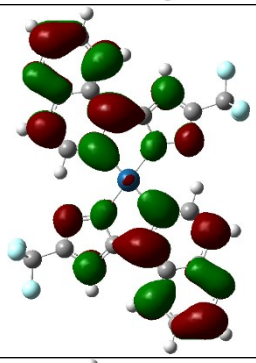
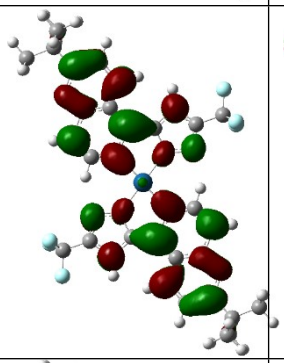
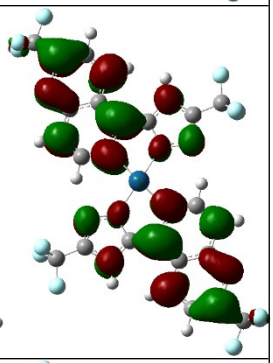
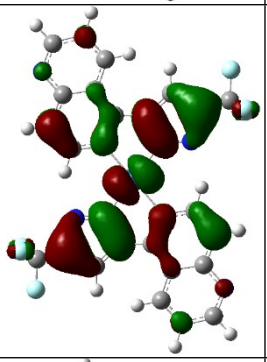
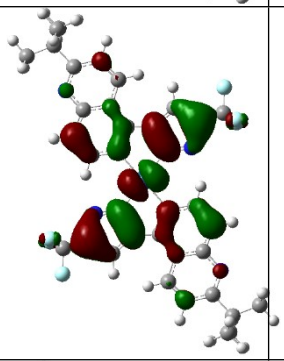
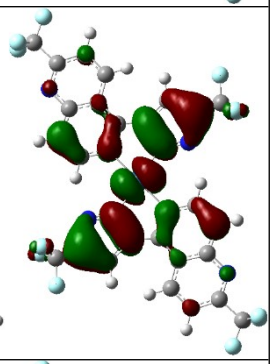
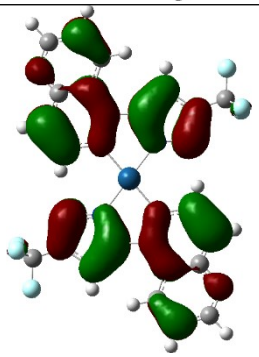
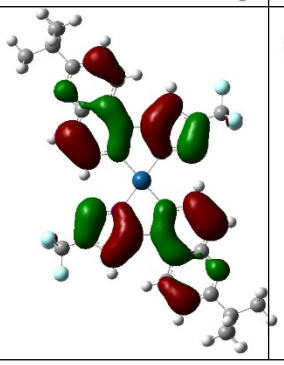
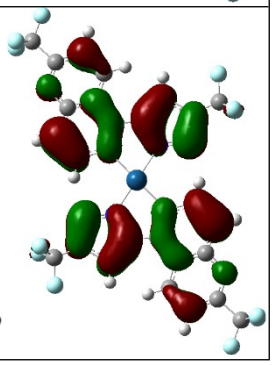


Figure S4. TGA diagram of the studied Pt(II) complexes, showing 5 wt.% loss of weight (T_d) for **Pt(a)**, **Pt(b)** and **Pt(c)** at 440 °C, 426 °C and 425 °C, respectively.

Monomeric forms

	Pt(a)	Pt(b)	Pt(c)
LUMO+1			
LUMO			
HOMO			
HOMO-1			

(a) Dimer forms

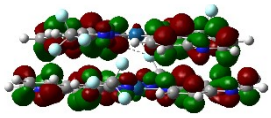
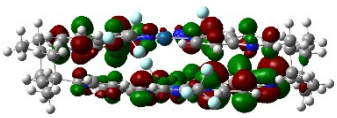
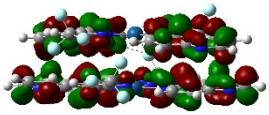
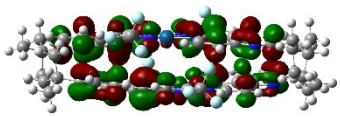
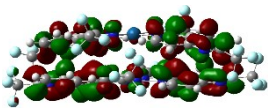
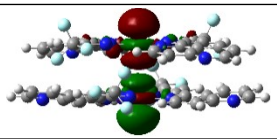
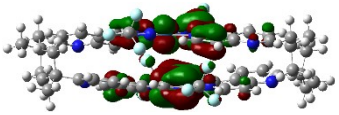
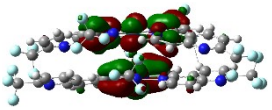
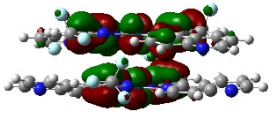
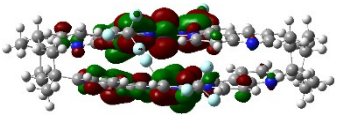
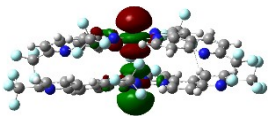
	Pt(a)	Pt(b)	Pt(c)
LUMO+1			
LUMO			
HOMO			
HOMO-1			

Figure S5. Frontier molecular orbitals associated with major optical transitions of (a) monomeric forms and (b) dimeric forms at S_0-optimized structure for all studied compounds.

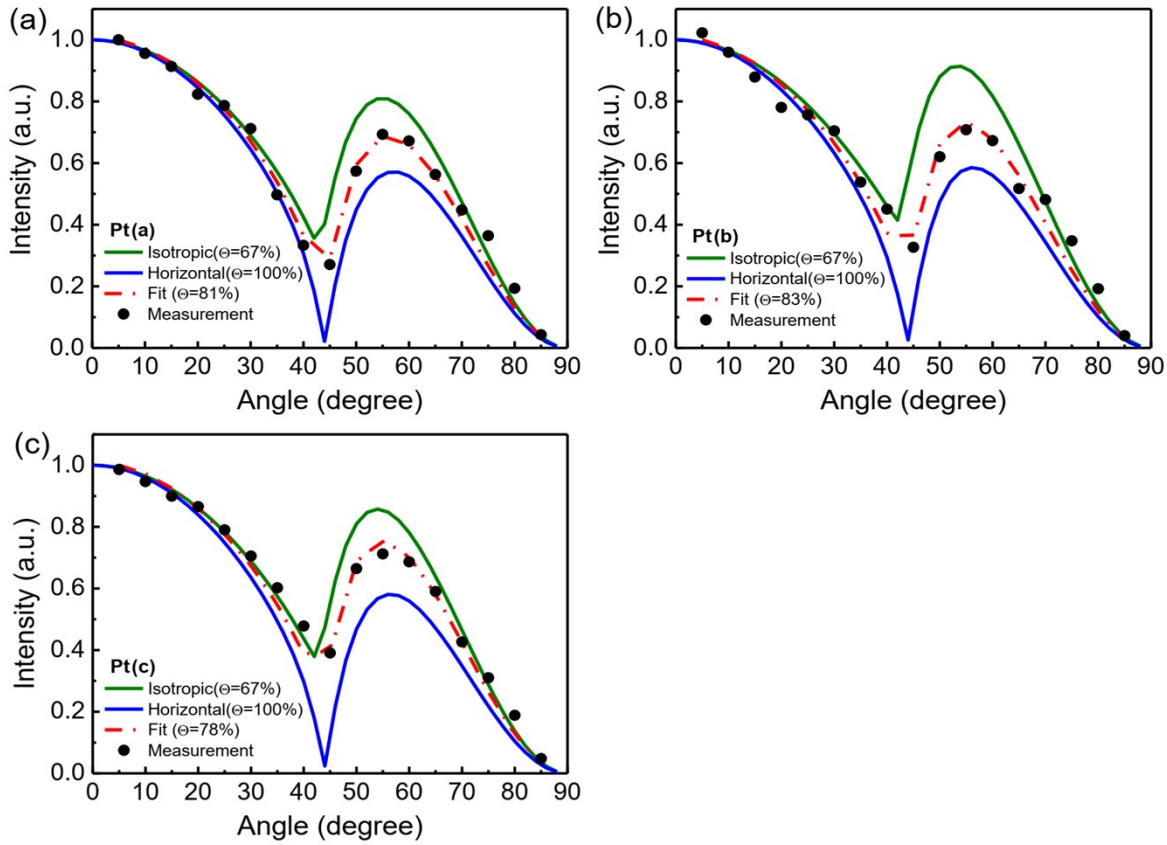


Figure S6. Angle-dependent PL intensity of *p*-polarized light at peak emission for a) **Pt(a)**, b) **Pt(b)**, and c) **Pt(c)**. The measured curves are compared to simulated curves with different horizontal dipole ratios (Θ) to extract the horizontal emitting dipole ratios of different emitting layers. [dashed line for fit, solid line for Θ = 1 (fully horizontal), and Θ = 0.67 (isotropic)]. The excitation wavelength is 355nm.

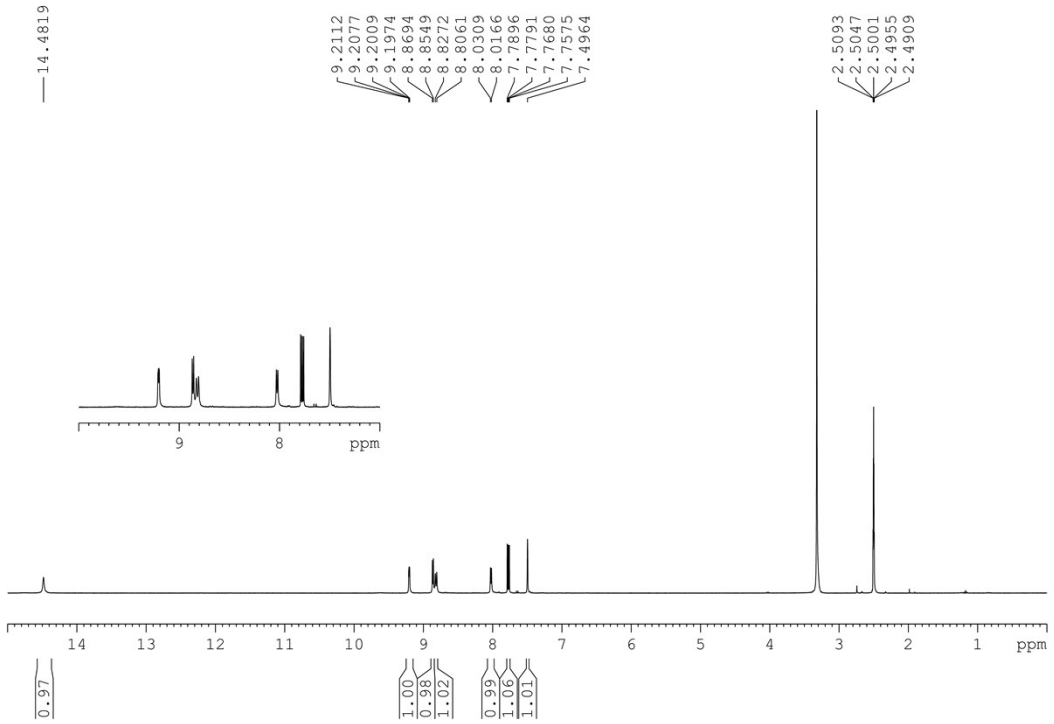


Figure S7. ^{1}H NMR spectrum of chelate **L(a)** recorded in DMSO-d_6 solution at RT.

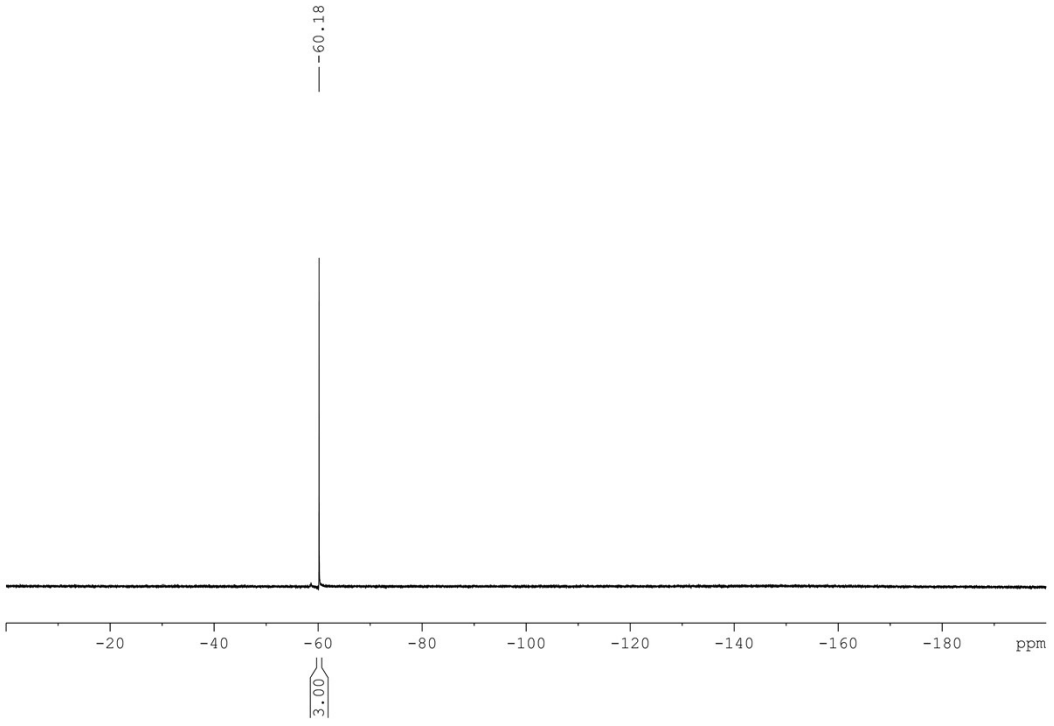


Figure S8. ^{19}F NMR spectrum of chelate **L(a)** recorded in DMSO-d_6 solution at RT.

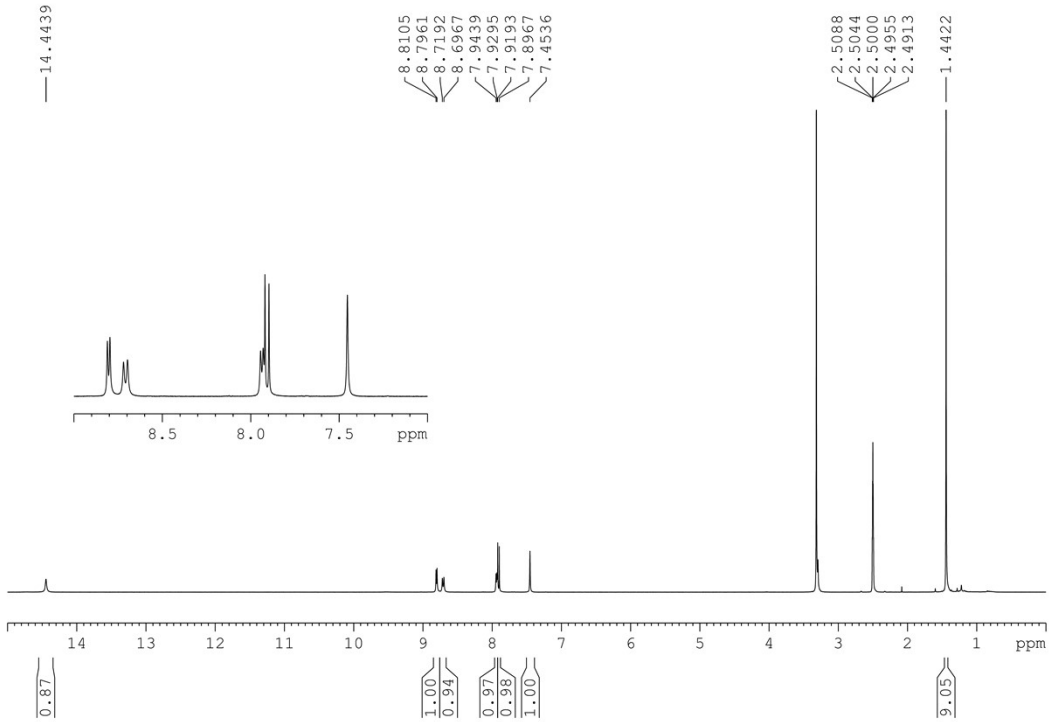


Figure S9. ^{1}H NMR spectrum of chelate **L(b)** recorded in DMSO-d_6 solution at RT.

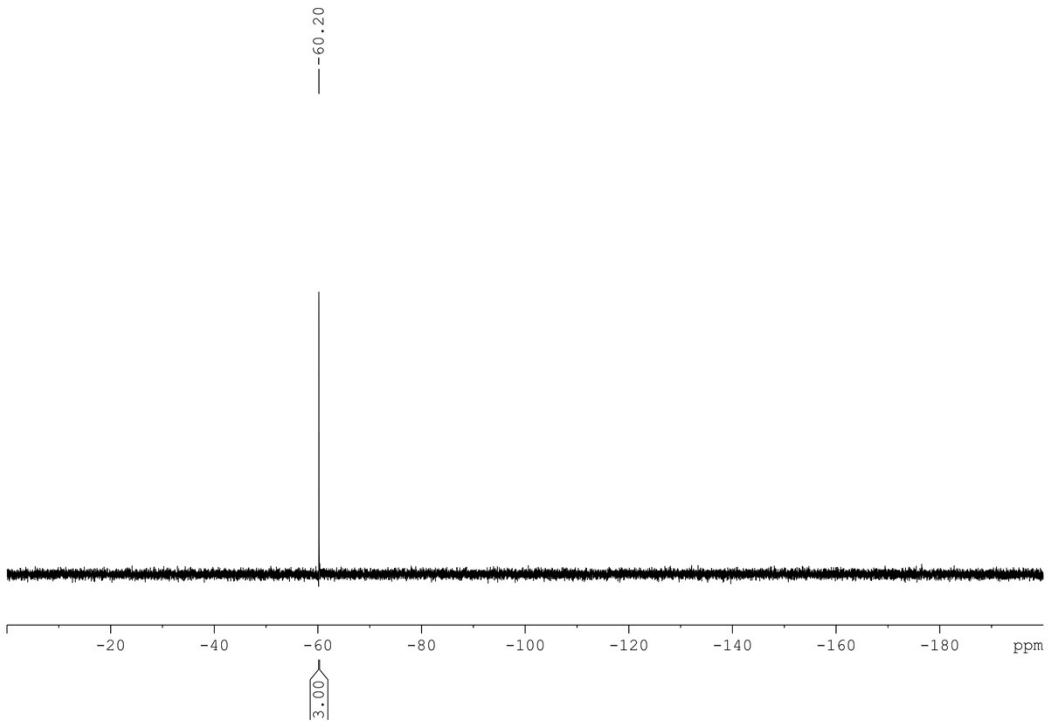


Figure S10. ^{19}F NMR spectrum of chelate **L(b)** recorded in DMSO-d_6 solution at RT.

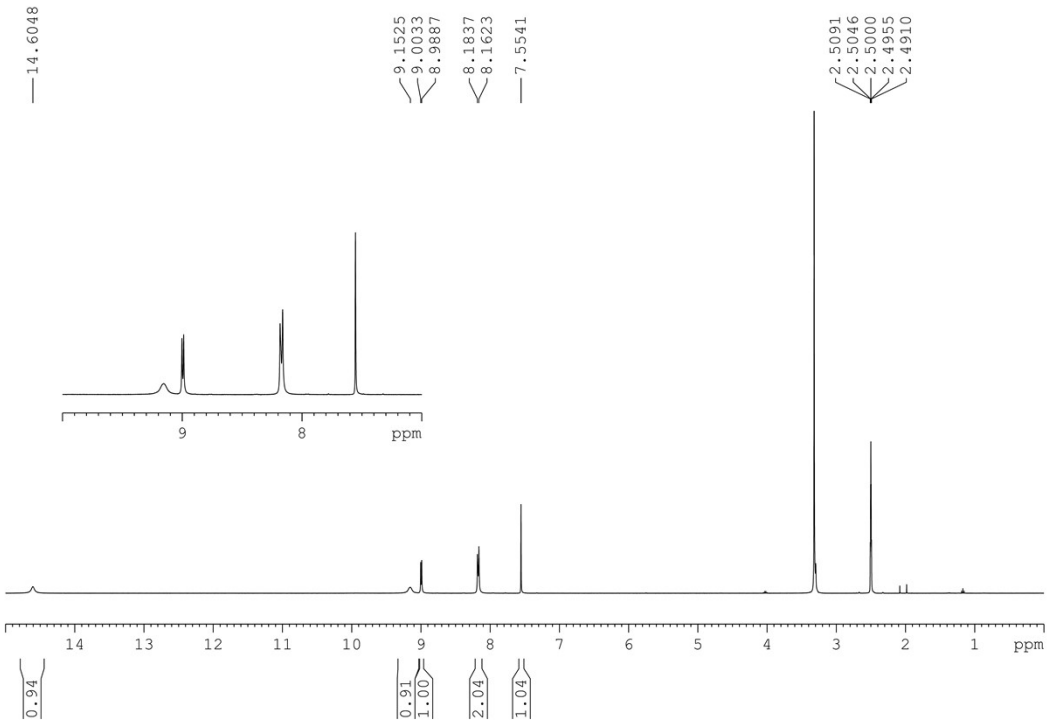


Figure S11. ^{1}H NMR spectrum of chelate **L(c)** recorded in DMSO-d_6 solution at RT.

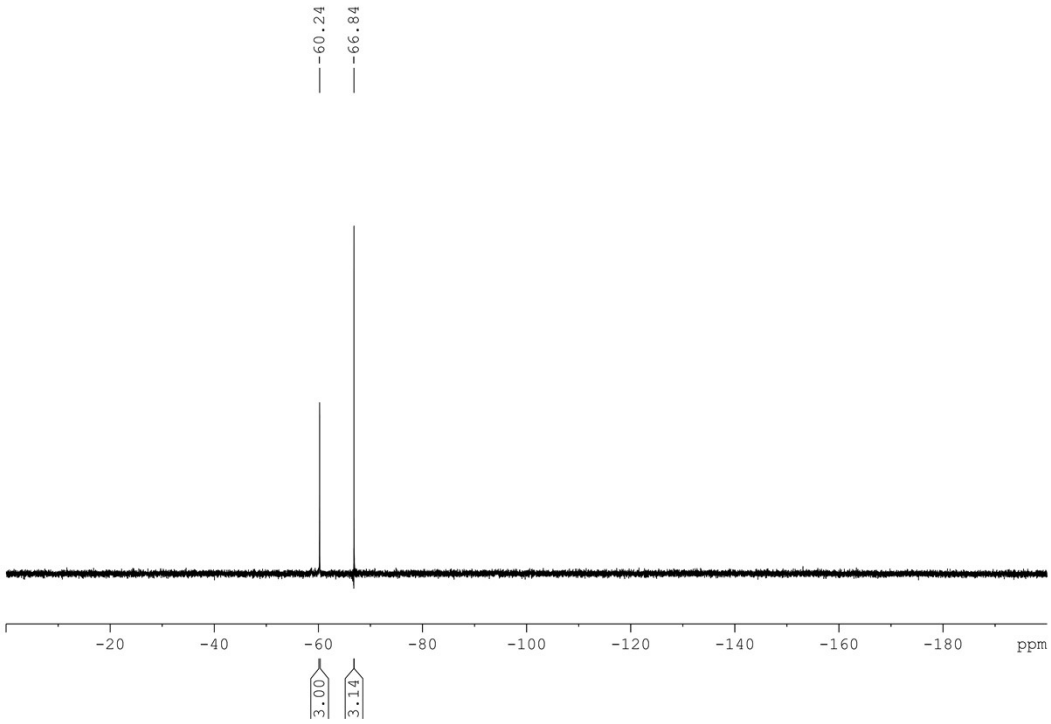
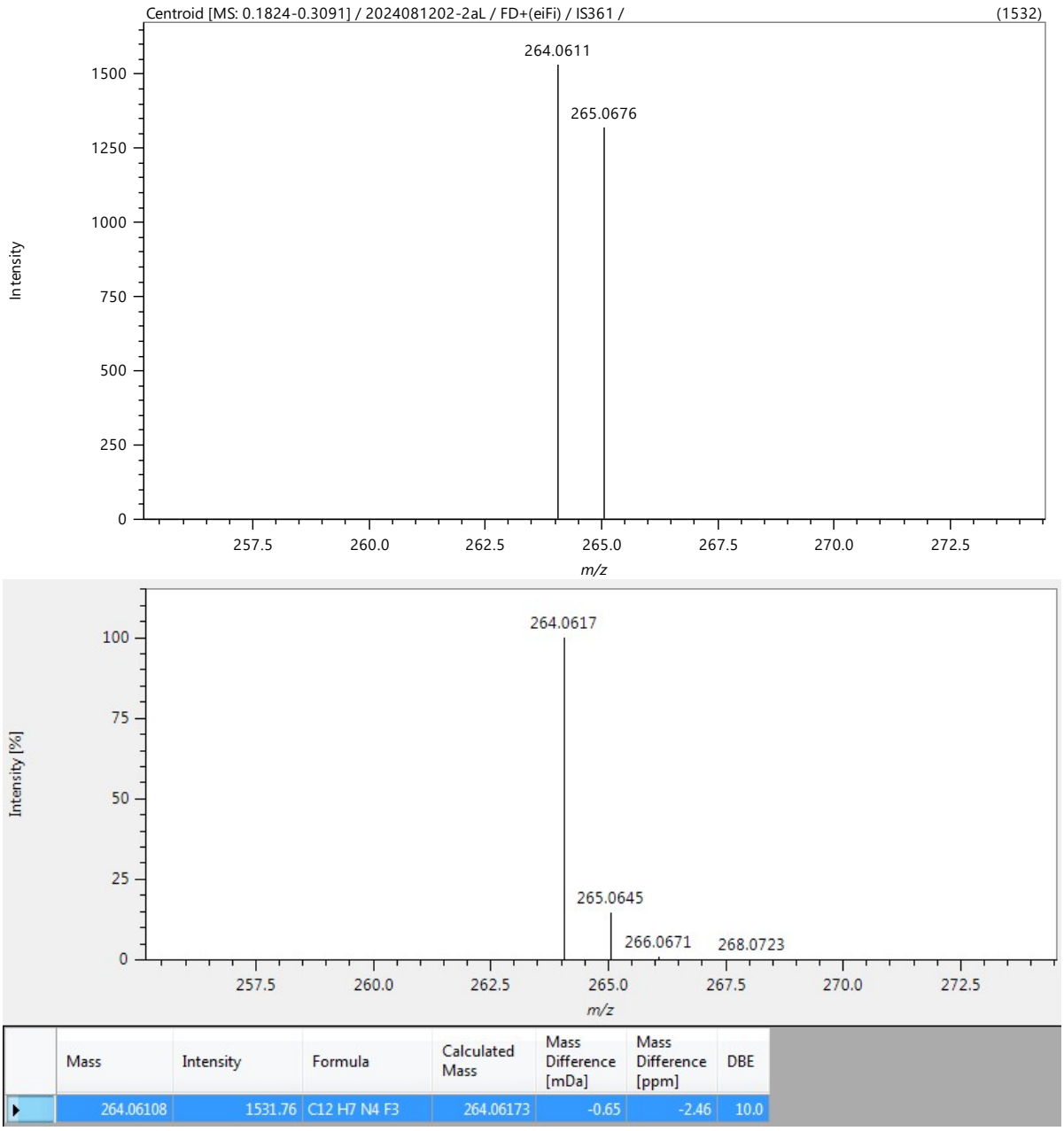
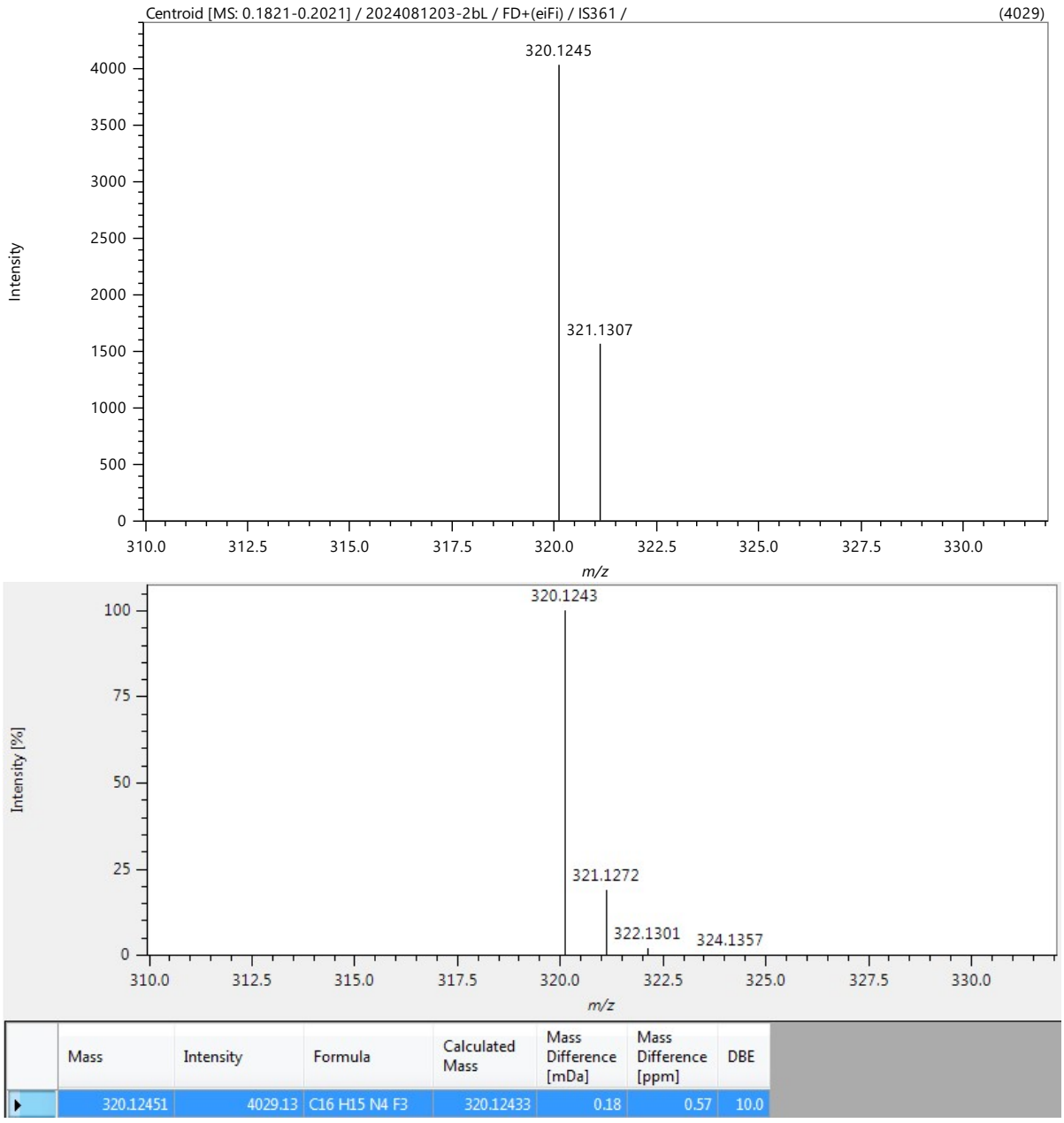


Figure S12. ^{19}F NMR spectrum of chelate **L(c)** recorded in DMSO-d_6 solution at RT.



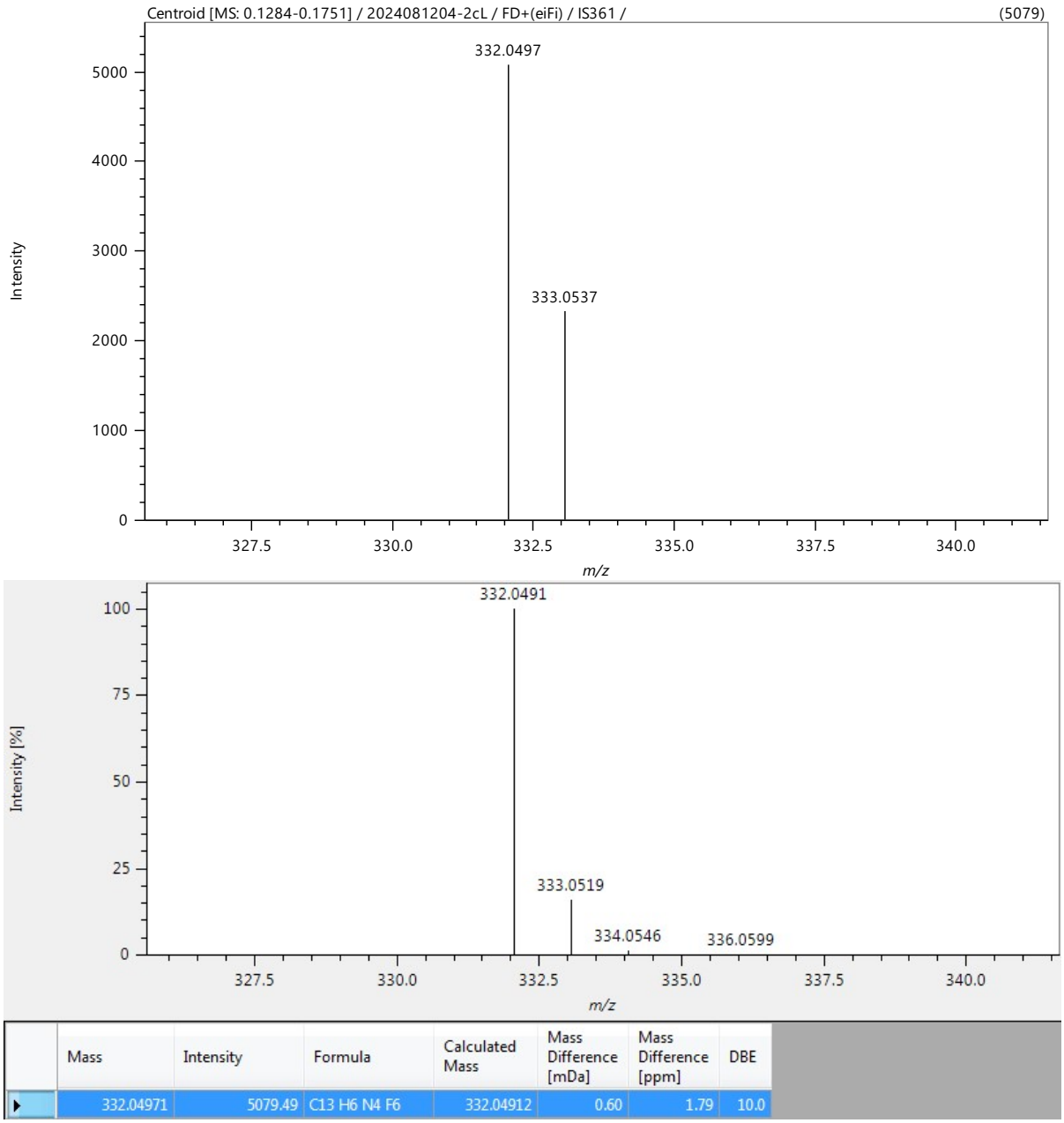
Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
264.06108	1531.76	C12 H7 N4 F3	264.06173	-0.65	-2.46	10.0

Figure S13. Experimental high resolution MS data and calculated isotope distribution pattern of **L(a)**.



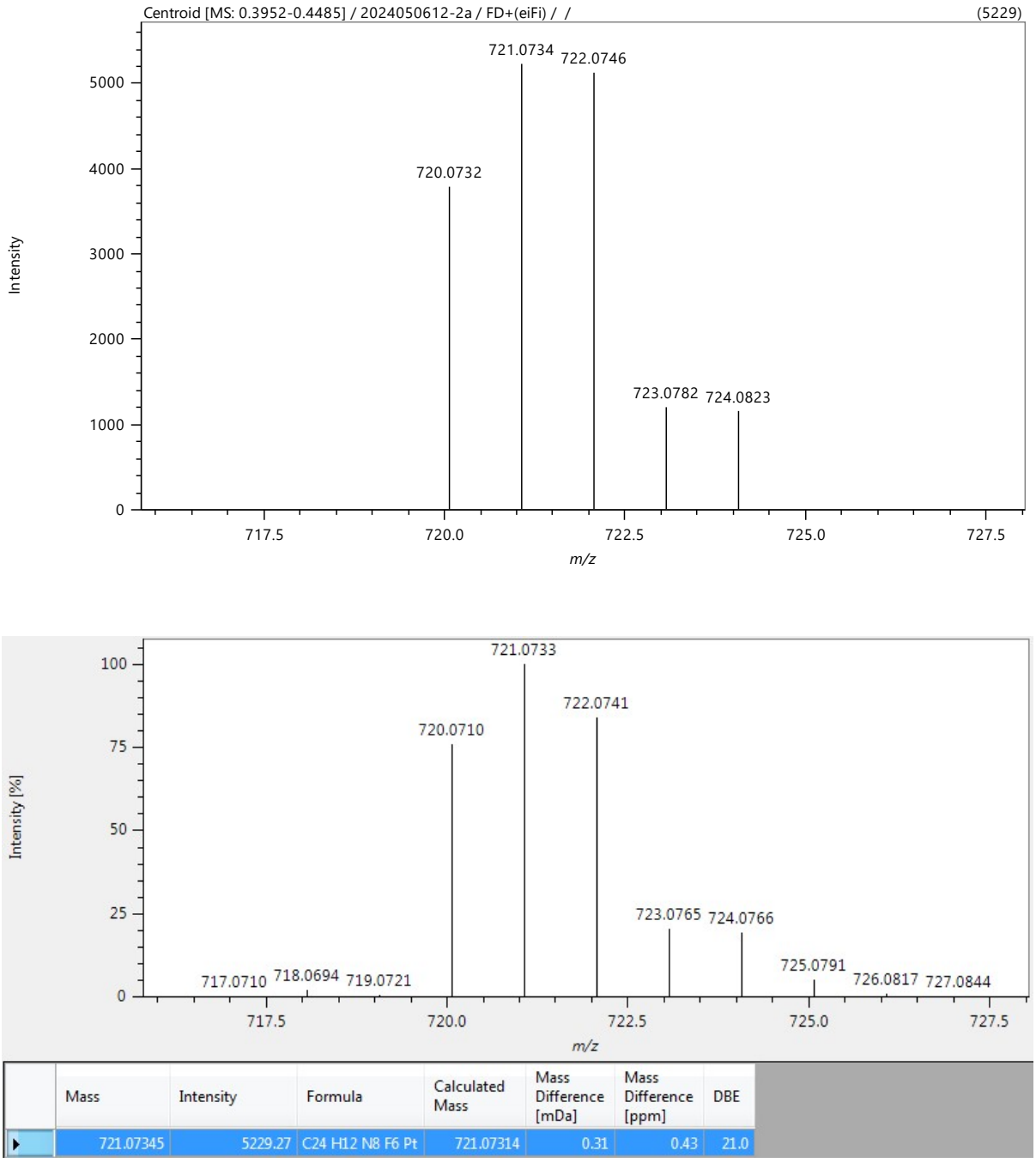
Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
320.12451	4029.13	C16 H15 N4 F3	320.12433	0.18	0.57	10.0

Figure S14. Experimental high resolution MS data and calculated isotope distribution pattern of **L(b)**.



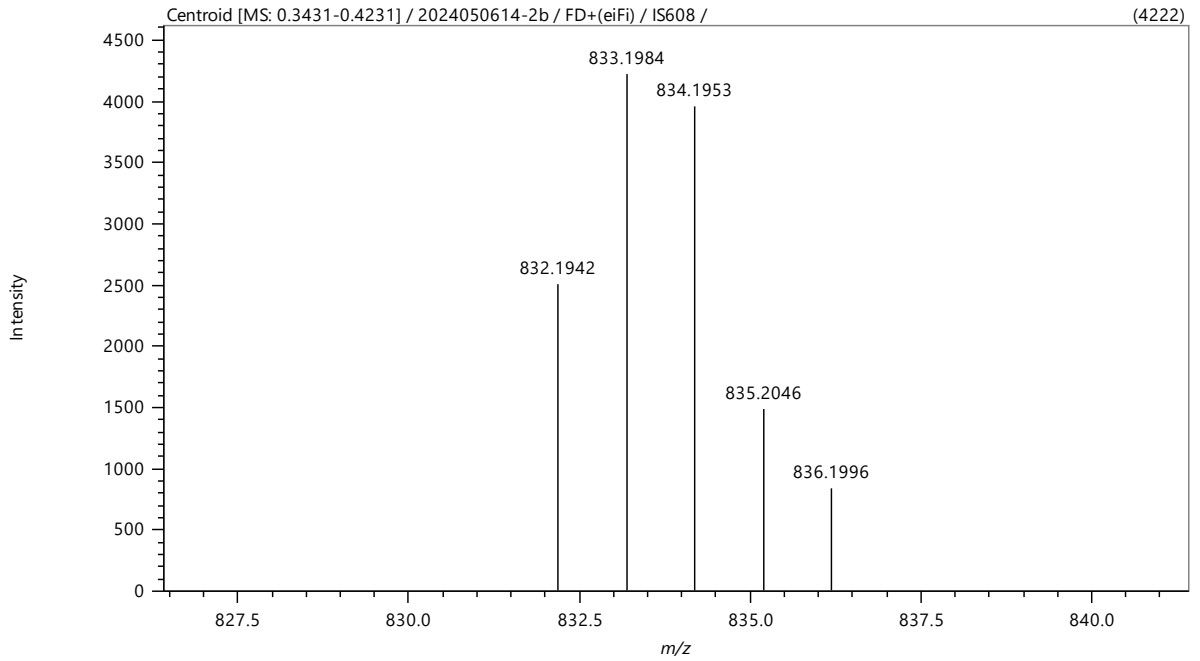
Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
332.04971	5079.49	C13 H6 N4 F6	332.04912	0.60	1.79	10.0

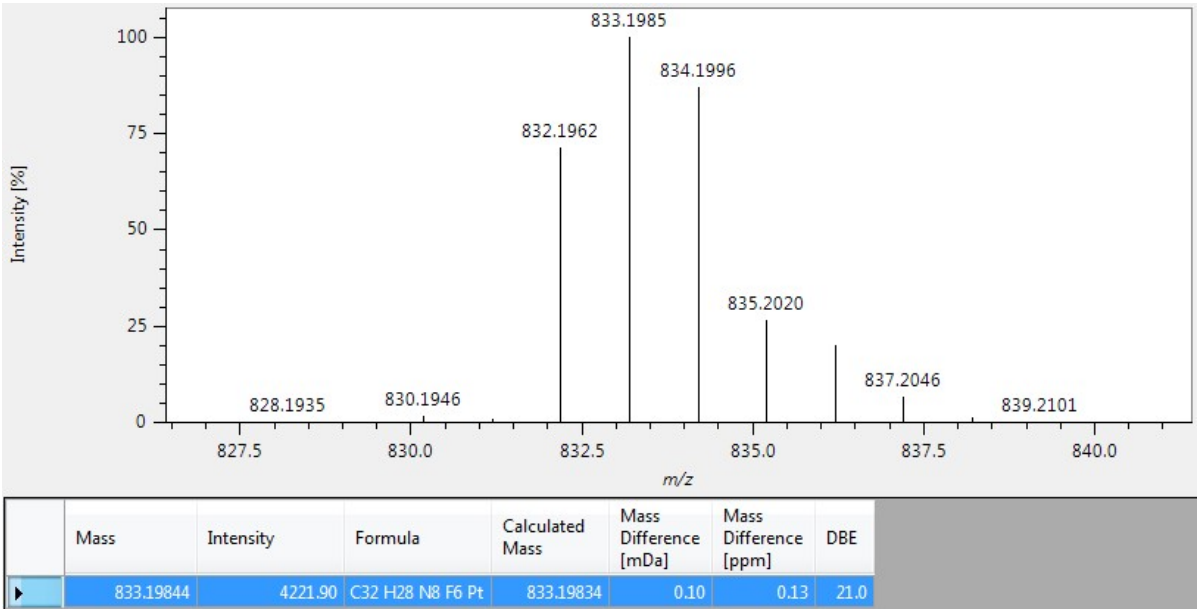
Figure S15. Experimental high resolution MS data and calculated isotope distribution pattern of **L(c)**.



Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
721.07345	5229.27	C24 H12 N8 F6 Pt	721.07314	0.31	0.43	21.0

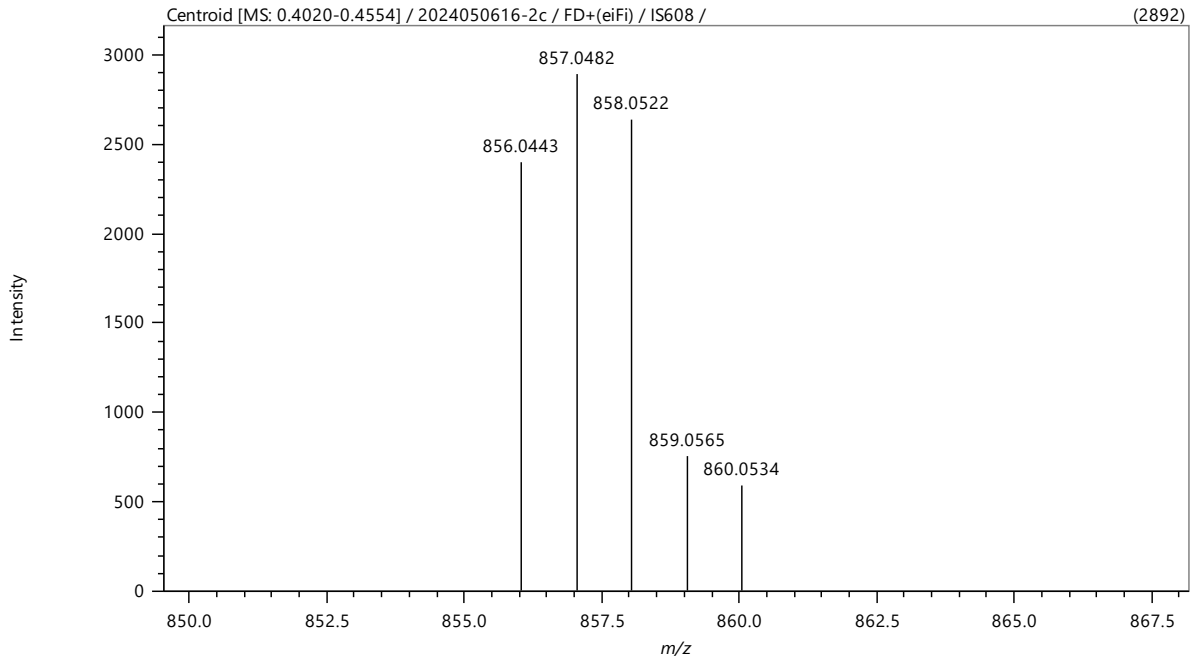
Figure S16. Experimental high resolution MS data and calculated isotope distribution pattern of **Pt(a)**.

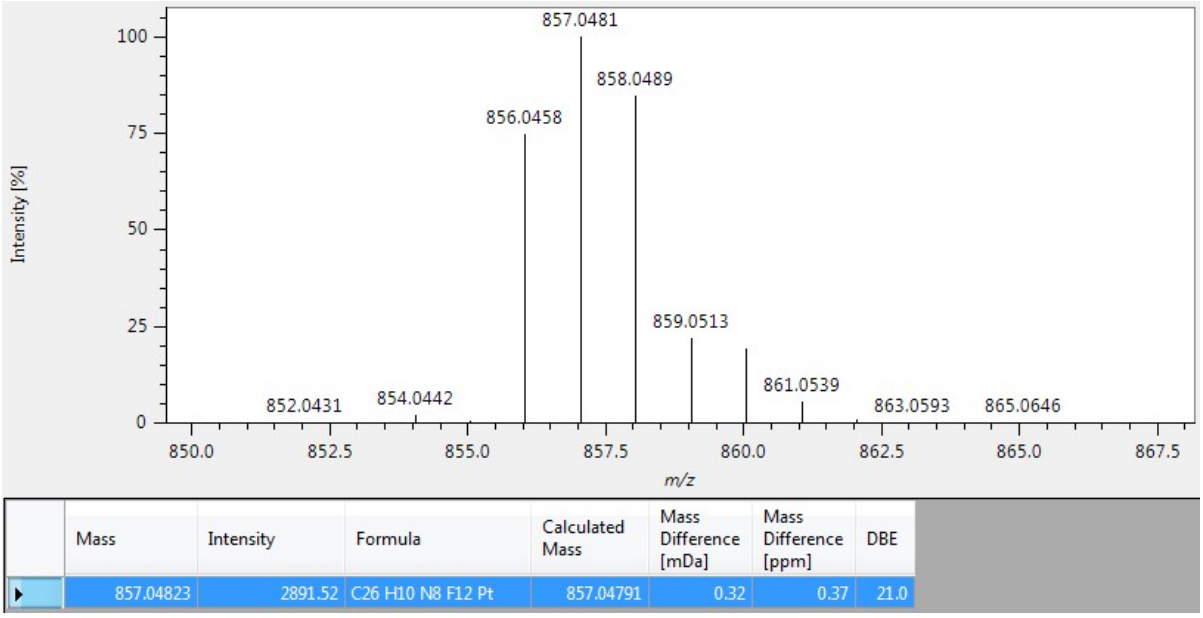




Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
833.19844	4221.90	C32 H28 N8 F6 Pt	833.19834	0.10	0.13	21.0

Figure S17. Experimental high resolution MS data and calculated isotope distribution pattern of **Pt(b)**.





	Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
▶	857.04823	2891.52	C26 H10 N8 F12 Pt	857.04791	0.32	0.37	21.0

Figure S18. Experimental high resolution MS data and calculated isotope distribution pattern of **Pt(c)**.

Table S1. The computed optical excitations and molecular orbital contributions for monomeric and dimeric forms of all studied Pt(II) complexes.

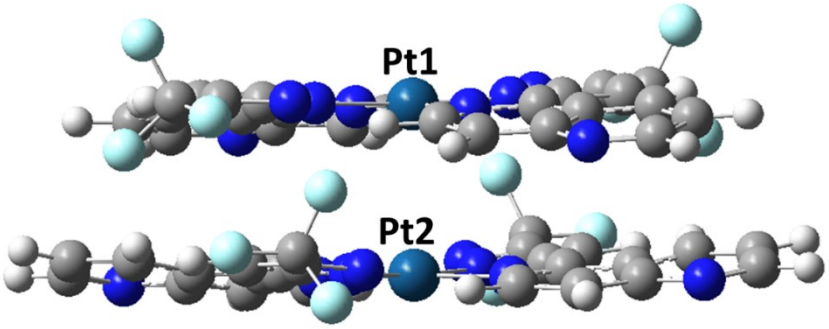
(a) Monomer of studied Pt(II) complexes.

	no.	E/eV	nm	f	contribution	weight
Pt(a) monomer @ optimized S_0	S_1	2.78	445.8	0.0724	HOMO→LUMO	97%
	S_2	3.17	391.3	0.0001	HOMO→LUMO+1	95%
	T_1	2.32	535.2	0	HOMO-2→LUMO	18%
	T_2	2.38	520.3	0	HOMO-2→LUMO+1	15%
Pt(b)-monomer @ optimized S_0	S_1	2.85	434.8	0.0799	HOMO→LUMO	97%
	S_2	3.25	381.7	0	HOMO→LUMO+1	94%
	T_1	2.38	520.6	0	HOMO-2→LUMO	18%
	T_2	2.45	506.6	0	HOMO-2→LUMO+1	14%
Pt(c)-monomer @ optimized S_0	S_1	2.61	474.6	0.0647	HOMO→LUMO	98%
	S_2	2.97	417.3	0.0001	HOMO→LUMO+1	97%
	T_1	2.20	563.8	0	HOMO-2→LUMO	19%
	T_2	2.27	545.6	0	HOMO-2→LUMO+1	15%

(b) Dimer of studied Pt(II) complexes.

	no.	E/eV	nm	f	contribution	weight
Pt(a) dimer @ optimized S_0	S_1	2.5	492.6	0.0285	HOMO→LUMO	99%
	T_1	2.27	546.2	0	HOMO-3→LUMO+2	12%
Pt(b) dimer @ optimized S_0	S_1	2.68	462.0	0.0114	HOMO→LUMO	91%
	T_1	2.30	538.6	0	HOMO-1→LUMO	36%
Pt(c) dimer @ optimized S_0	S_1	2.40	516.6	0.0223	HOMO-1→LUMO	97%
	T_1	2.16	574.7	0	HOMO-3→LUMO+2	10%

Table S2. Pt contribution of molecular orbitals in monomer and dimer forms



	MO	Monomer	Dimer(Pt1)	Dimer(Pt2)	Dimer(Pt1+Pt2)
Pt(a)	LUMO+1	2.92%	0.78%	0.72%	1.50%
	LUMO	3.38%	2.43%	2.56%	4.99%
	HOMO	29.52%	46.15%	44.97%	91.12%
	HOMO-1	0.02%	15.49%	17.06%	32.55%
	HOMO-2	19.74%	11.12%	13.23%	24.35%
	HOMO-3		0.23%	0.37%	0.60%
Pt(b)	LUMO+2		0.43%	0.43%	0.85%
	LUMO+1	2.84%	0.57%	1.29%	1.86%
	LUMO	3.56%	2.62%	2.19%	4.81%
	HOMO	29.35%	9.88%	20.77%	30.65%
	HOMO-1	0.02%	21.71%	12.79%	34.50%
	HOMO-2	0.02%	40.74%	36.94%	77.68%
	HOMO-3		2.91%	4.51%	7.41%
Pt(c)	LUMO+2		2.04%	0.77%	2.81%
	LUMO+1	3.01%	0.63%	0.71%	1.35%
	LUMO	2.87%	2.09%	2.22%	4.31%
	HOMO	30.72%	14.55%	18.79%	33.34%
	HOMO-1	0.02%	45.94%	44.27%	90.20%
	HOMO-2	18.85%	12.17%	14.69%	26.86%
	HOMO-3		0.36%	0.22%	0.58%

References

1. J. Šturala, S. Boháčová, J. Chudoba, R. Metelková and R. Cibulka, *J. Org. Chem.*, 2015, **80**, 2676-2699.