

# Electronic Supplementary Information

## Photostable trifluoromethyl-substituted platinum(II) emitters for continuous monitoring of molecular oxygen

Yang Xing, Chun Liu\*, Xinlong Song and Jiuyan Li

[\*] Dr. C. Liu, Corresponding-Author

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Linggong Road 2, Dalian 116024, China

Tel.: +86-411-84986182.

E-mail: cliu@dlut.edu.cn

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## Materials and Methods

Unless otherwise noted, all the cross-coupling reactions for preparing the ligands were carried out in air. All *N*-heteroaryl halides were purchased from Alfa Aesar. Phenylboronic acid was purchased from Trusyn Chem-Tech Co., Ltd, China. Other chemicals were purchased from commercial sources and used without further purification.

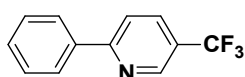
<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded with a MALDI micro MX spectrometer. The intensities of the crystal data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-K<sub>α</sub> (λ=0.71073 Å) using the SMART and SAINT programs.

UV/Vis absorption spectra were recorded on an HP8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded with a PTI-700 spectrofluorimeter. Luminescent quantum yields were measured with [Ir(ppy)<sub>3</sub>] (UP = 0.40, λ<sub>ex</sub> = 400 nm, in CH<sub>2</sub>Cl<sub>2</sub>, under degassed conditions). Phosphorescence lifetimes were measured on an Edinburgh FLS920 Spectrometer in a degassed dichloromethane solution with excitation wavelength at 410 nm. Cyclic voltammograms of the Pt(II) complexes were recorded on an electrochemical workstation (BAS100B/W, USA) at room temperature in a 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> solution under nitrogen gas protection.

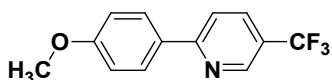
### Synthetic method and characterization of ligands

Ligands **L1** – **L3**: a mixture of 2-bromo-5-(trifluoromethyl)pyridine (0.25 mmol, 56.50 mg), 1.5 equiv of phenylboronic acid (0.375 mmol, 45.72 mg), 2 equiv of K<sub>2</sub>CO<sub>3</sub> (0.5 mmol, 69 mg), Pd(OAc)<sub>2</sub> (1.5 mol%, 0.00375 mmol, 0.84 mg), ethanol/water (3 mL/1 mL) was stirred at 80 °C in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted four times with ethyl acetate (4×15 mL). The solvent was concentrated and the product was isolated by short-column chromatography on silica gel (200-300 mesh).

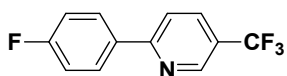
**L1 - L3** were conveniently synthesized according to the literature methods<sup>[1]</sup>



**L1**: yield: 80.1%; a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.95 (s, 1 H), 8.03-8.05 (d, *J* = 8.1 Hz, 2 H), 7.97-7.99 (d, *J* = 8.0 Hz, 1 H), 7.84(d, *J* = 7.8 Hz, 1 H), 7.48-7.53 (m, 3 H) ppm.



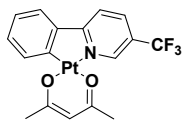
**L2**: yield: 82.7%; a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.89 (s, 1H), 7.99-8.02 (d, *J* = 8.0 Hz, 2 H), 7.91-7.94 (d, *J* = 7.9 Hz, 1 H), 7.76-7.78(d, *J* = 7.8 Hz, 1 H), 7.01-7.03 (d, *J* = 7.0 Hz, 2 H), 3.94(s, 3 H) ppm.



**L3**: yield: 79.2%; a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.93 (s, 1 H), 7.97-8.06 (m, 3 H), 7.79-7.82 (d, *J* = 7.8 Hz, 1 H), 7.17-7.19 (d, *J* = 7.2 Hz, 2 H) ppm.

## Synthetic method and characterization of platinum complexes

The targeted Pt(II) emitting materials were obtained as previously reported [2]. This involved heating the  $K_2PtCl_4$  salt with 1.2 equiv of cyclometalating ligand in a 3:1 mixture of 2-ethoxyethano and water to 80 °C for 16-24 h to provide the dimers, which were isolated in water and subsequently reacted with 5 equiv of the chelating diketone derivative and 10 equiv of  $Na_2CO_3$  in 2-ethoxyethanol at 100 °C for 18-24 h. The solvent was removed under reduced pressure, and the compound was purified by flash chromatography using dichloromethane/hexane.



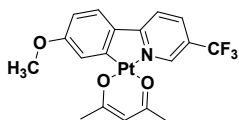
**LSTF1**

(Eluent:  $CH_2Cl_2$ /hexane 1:1, v/v). A yellow solid was obtained; Yield 70.4%.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.30 (t, 1 H), 7.99 -8.01 (d,  $J$  = 8.0 Hz, 1 H), 7.63 -7.70 (m, 2 H), 7.47-7.48 (d,  $J$  = 7.5 Hz, 1 H), 7.26 (t,  $J$  = 7.3 Hz, 1 H), 7.09-7.12 (t,  $J$  = 7.1 Hz, 1 H), 5.50 (s, 1 H), 2.04 (d,  $J$  = 2.0 Hz, 6 H) ppm.

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  186.23, 184.27, 171.77, 144.56, 144.51, 142.93, 140.85, 135.08, 135.05, 130.91, 130.86, 130.73, 124.34, 124.28, 124.00, 123.82, 118.06, 102.65, 28.28, 27.06 ppm.

HRMS (EI): calcd. for  $C_{17}H_{14}F_3NO_2Pt$   $[M+H]^+$  516.0624; found 517.0703.



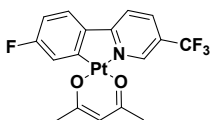
**LSTF2**

(Eluent:  $CH_2Cl_2$ /hexane 2:1, v/v). A yellow solid was obtained; Yield 41.2%.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.20 (t,  $J$  = 9.2 Hz, 1 H), 7.90-7.93 (d,  $J$  = 7.9 Hz, 1 H), 7.52-7.54 (d,  $J$  = 7.5 Hz, 1 H), 7.40-7.42 (d,  $J$  = 7.4 Hz, 1 H), 7.13 (s, 1 H), 6.68-6.70 (d,  $J$  = 6.7 Hz, 1 H), 5.49 (s, 1 H), 3.87 (s, 3 H), 2.01 (d,  $J$  = 2.0 Hz, 6 H) ppm.

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  186.23, 184.16, 171.29, 161.35, 144.35, 144.31, 143.54, 135.60, 134.80, 126.07, 121.47, 117.24, 114.16, 110.84, 102.67, 55.20, 28.25, 27.08 ppm.

HRMS (EI): calcd. for  $C_{18}H_{16}F_3NO_3Pt$   $[M+H]^+$  546.0730; found 547.0792.



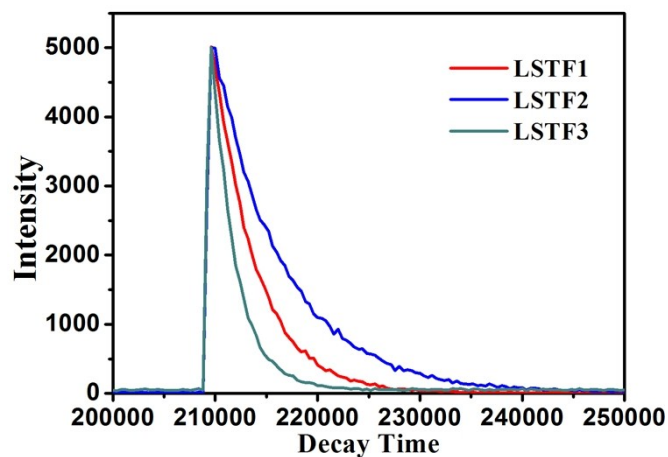
**LSTF3**

(Eluent:  $CH_2Cl_2$ /hexane 3:1, v/v). A yellow solid was obtained; Yield 39.4%.

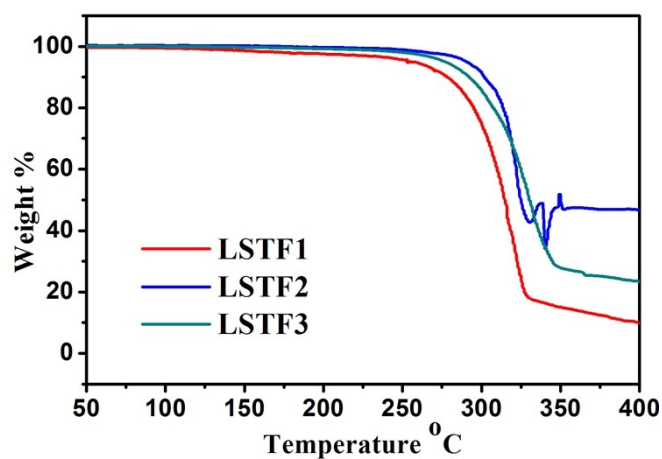
$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.27 (t,  $J$  = 9.3 Hz, 1 H), 8.00-8.01 (d,  $J$  = 8.0 Hz, 1 H), 7.61-7.63 (d,  $J$  = 7.6 Hz, 1 H), 7.49-7.50 (m, 1 H), 7.28 (m, 1 H), 6.82-6.86 (t, 1 H), 5.51 (s, 1 H), 2.06 (d,  $J$  = 2.1 Hz, 6 H) ppm.

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  186.35, 184.47, 170.64, 144.49, 139.06, 135.23, 126.27, 126.17, 123.91, 117.97, 117.05, 116.86, 111.21, 110.97, 102.79, 28.20, 27.02 ppm.

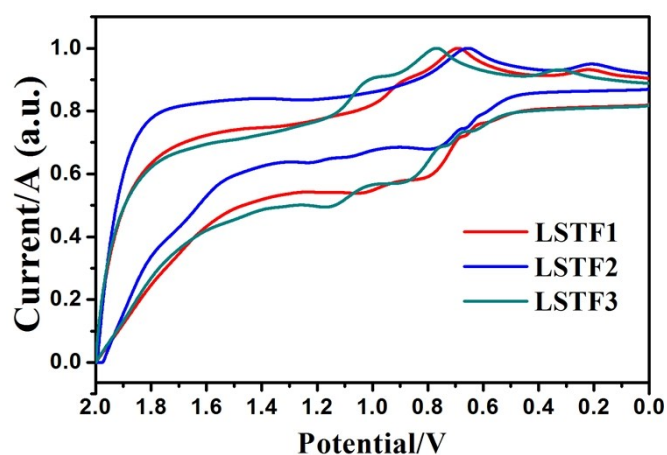
HRMS (EI): calcd. for  $C_{17}H_{13}F_4NO_2Pt$   $[M+H]^+$  534.0530; found 535.0568.



**Figure S1.** Phosphorescence emission decay curves of the Pt(II) complexes in  $\text{CH}_2\text{Cl}_2$  in neat  $\text{N}_2$ . Monoexponential decay regression gave lifetime.



**Figure S2.** Thermogravimetric analysis (TGA) curve of the Pt complexes under  $\text{N}_2$ .



**Figure S3.** Cyclic voltammogram of the Pt(II) complexes.

## X-ray Structural Analysis:

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of each of the respective solutions in CHCl<sub>3</sub>/hexane at room temperature. Geometric and intensity data were collected at 293 K using graphite-monochromated Mo-K<sub>α</sub> radiation ( $k = 0.71073 \text{ \AA}$ ) on a Bruker SMART APEX(II) CCD diffractometer. The collected frames were processed with the software SAINT and an absorption correction (SADABS) was applied to the collected reflections. The structure was solved by the Direct or Patterson methods (SHELXTL 97) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on  $F^2$ . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were assigned with anisotropic displacement parameters. Pertinent crystal data for the structures are collected in **Table S1**.

CCDC-966676 (for LSTF1), -966677 (for LSTF2), -966679 (for LSTF3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1** Summary of crystal data.

	LSTF1	LSTF2	LSTF3
CCDC number	966676	966677	966679
Moiety formula	C <sub>34</sub> H <sub>28</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> Pt <sub>2</sub>	C <sub>36</sub> H <sub>32</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> Pt <sub>2</sub>	C <sub>34</sub> H <sub>26</sub> F <sub>8</sub> N <sub>2</sub> O <sub>4</sub> Pt <sub>2</sub>
formula weight	1032.76	1092.82	1068.75
temperature, K	296(2)	296(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	Triclinic	Monoclinic	Triclinic
space group	P-1	P2(1)/c	P-1
unit cell dimensions			
a (Å)	11.618(3)	23.2937(10)	11.7020(6)
b (Å)	12.524(3)	11.9955(5)	12.4402(7)
c (Å)	12.655(3)	13.1606(5)	12.7534(7)
α (deg)	89.994(13)	90	89.883(3)
β (deg)	83.387(15)	100.226(2)	82.150(3)
γ (deg)	66.227(13)	90	65.050(3)
volume (Å <sup>3</sup> )	1671.7(7)	3618.9(3)	1664.35(16)
Z	2	4	2
density, calcd (g/cm <sup>3</sup> )	2.052	2.006	2.133
Absorption coefficient(mm <sup>-1</sup> )	8.433	7.801	8.482
F(000)	976	2080	1008
θ range for data collection(deg)	2.35-32.33	1.78-25.00	1.61-25.00
reflections collected	19264/11471 [R(int)=0.0456]	23169 / 6369 [R(int)=0.0359]	11633 / 5814 [R(int)=0.0323]
refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
data/restraints/parameters	11471/0/433	6369 / 0 / 469	5814 / 0 / 451
goodness-of-fit on F <sup>2</sup> <sup>a</sup>	0.925	1.043	1.059
final R indices [ $I > 2\sigma(I)$ ] <sup>b</sup>	0.0489	0.0299	0.0342
R indices (all data)	0.0985	0.0416	0.0410

<sup>a</sup> goodness-of-fit =  $\{[\sum(w(F_0^2 - F_C^2)^2)] / (N_{\text{obs}} - N_{\text{param}})\}^{1/2}$

<sup>b</sup>  $R_1 = \sum ||F_0| - |F_C|| / \sum |F_0|$ .  $wR2 = \{\sum[w(F_0^2 - F_C^2)^2] / \sum[w(F_0^2)^2]\}^{1/2}$

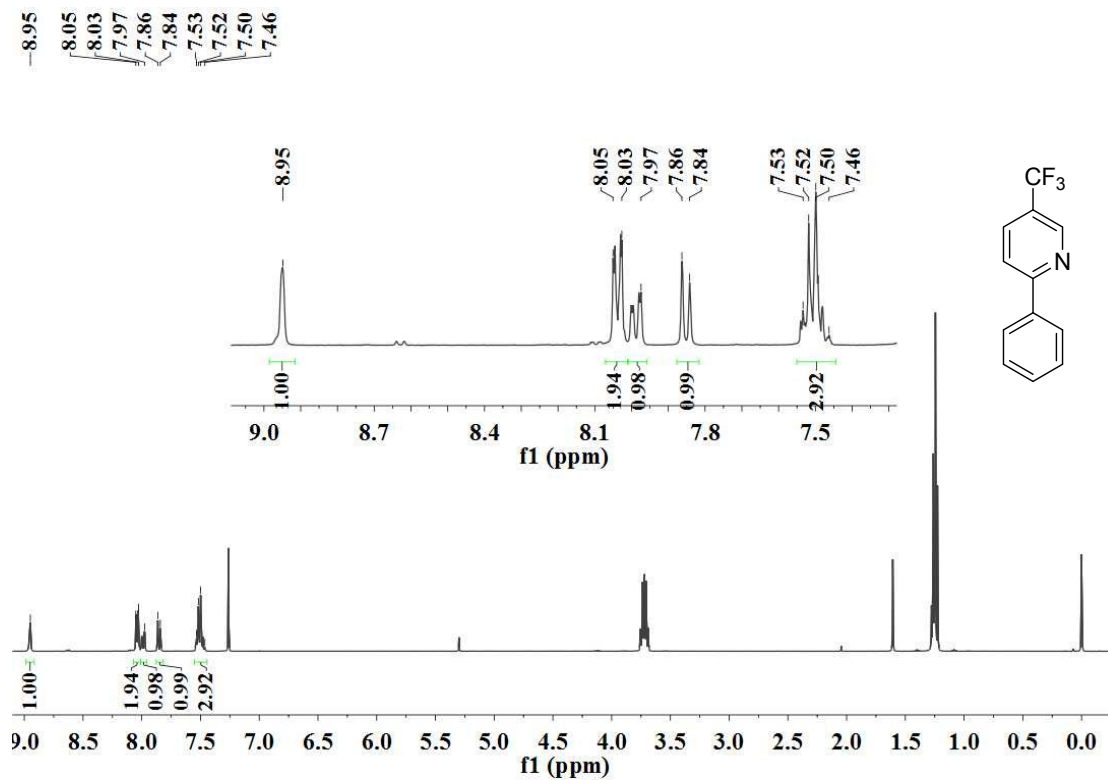


Figure S4. The  $^1\text{H}$  NMR spectrum of L1 in  $\text{CDCl}_3$ .

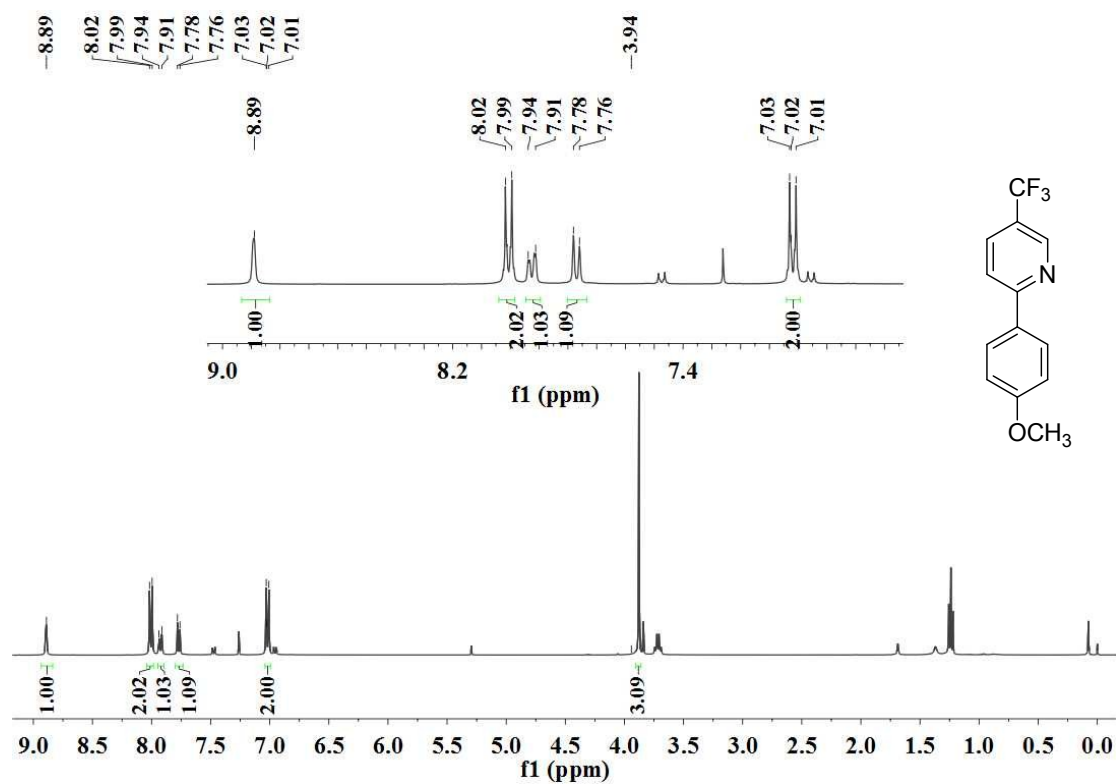


Figure S5. The  $^1\text{H}$  NMR spectrum of L2 in  $\text{CDCl}_3$ .

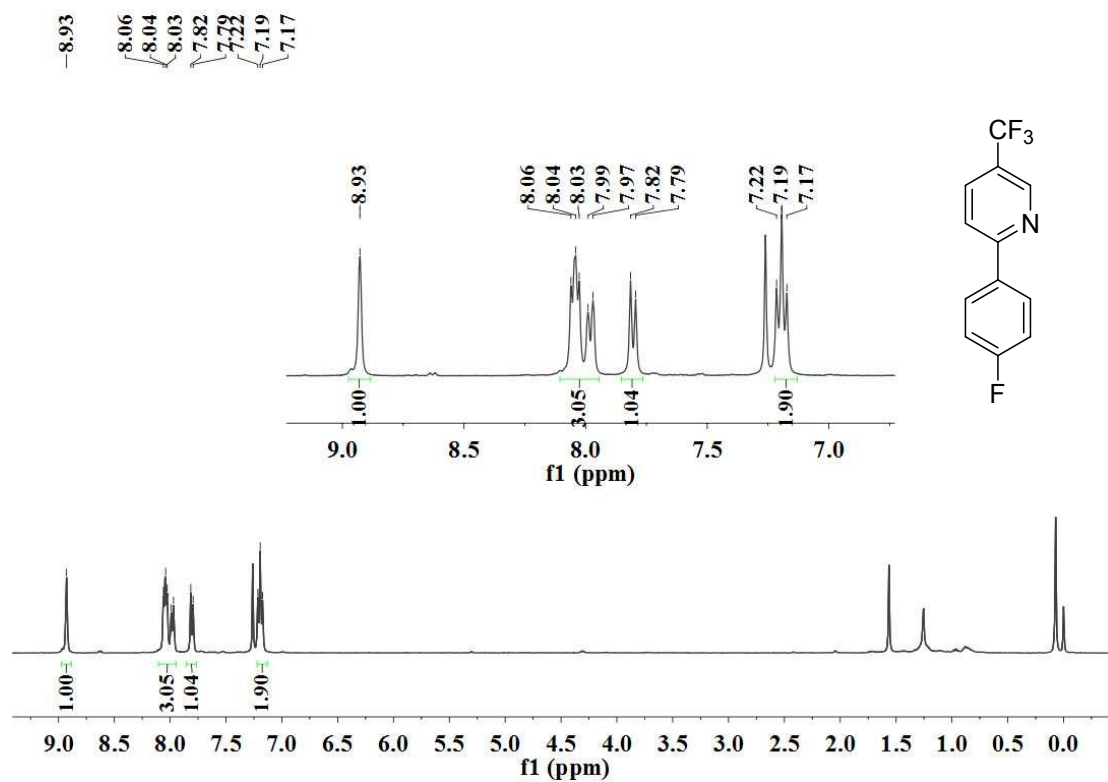


Figure S6. The  $^1\text{H}$  NMR spectrum of L3 in  $\text{CDCl}_3$ .

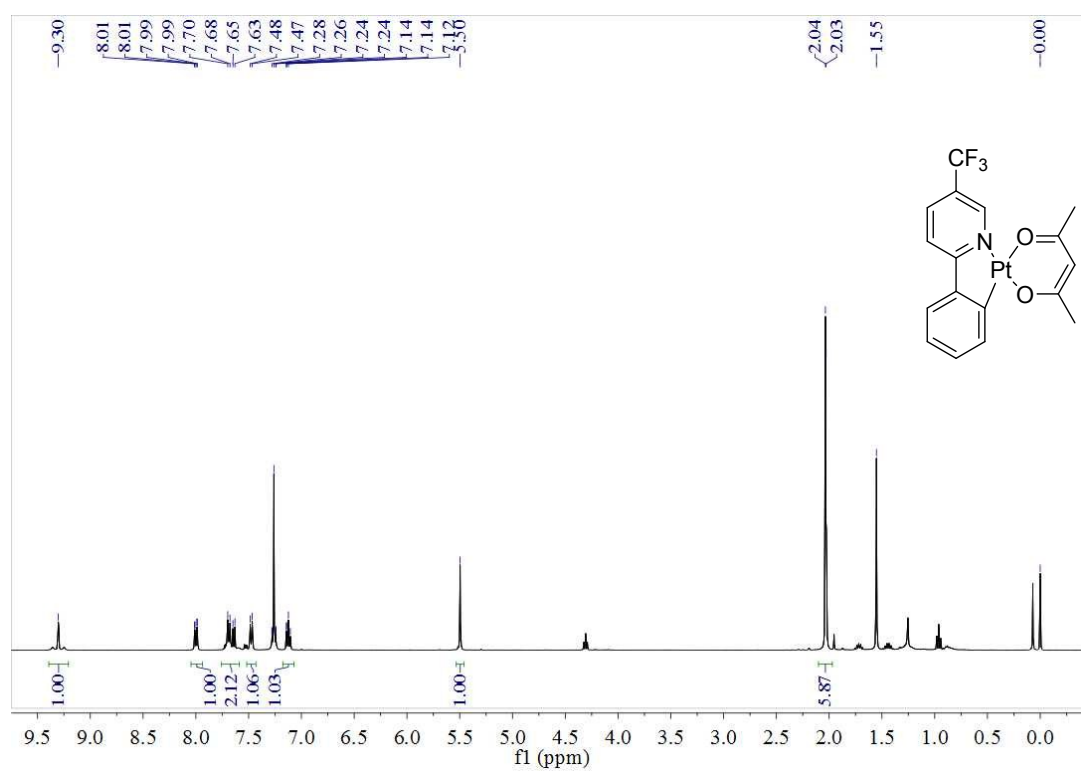
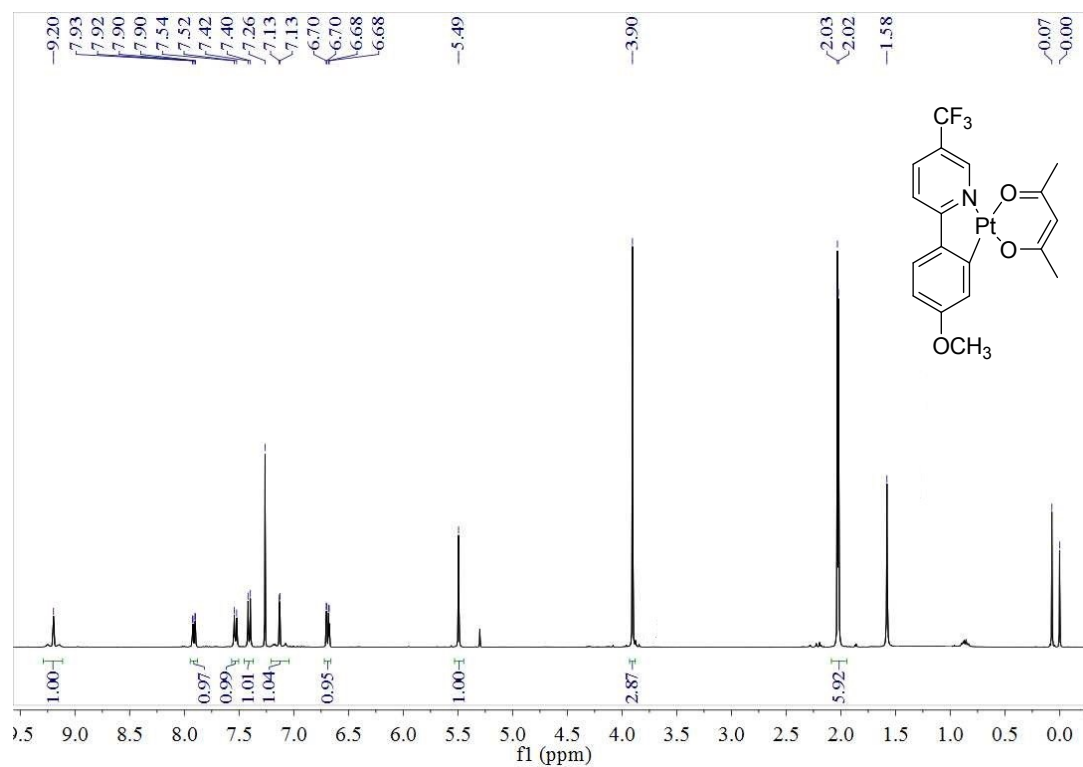
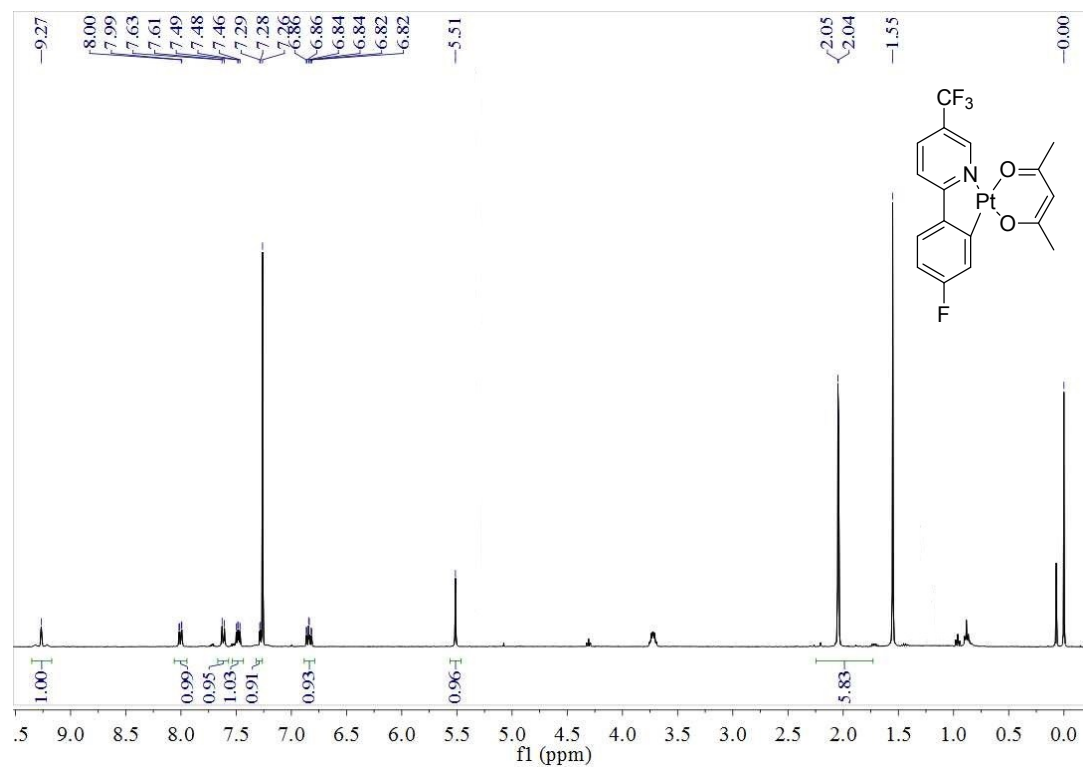


Figure S7. The  $^1\text{H}$  NMR spectrum of LSTF1 in  $\text{CDCl}_3$ .



**Figure S8.** The  $^1\text{H}$  NMR spectrum of LSTF2 in  $\text{CDCl}_3$ .



**Figure S9.** The  $^1\text{H}$  NMR spectrum of LSTF3 in  $\text{CDCl}_3$ .



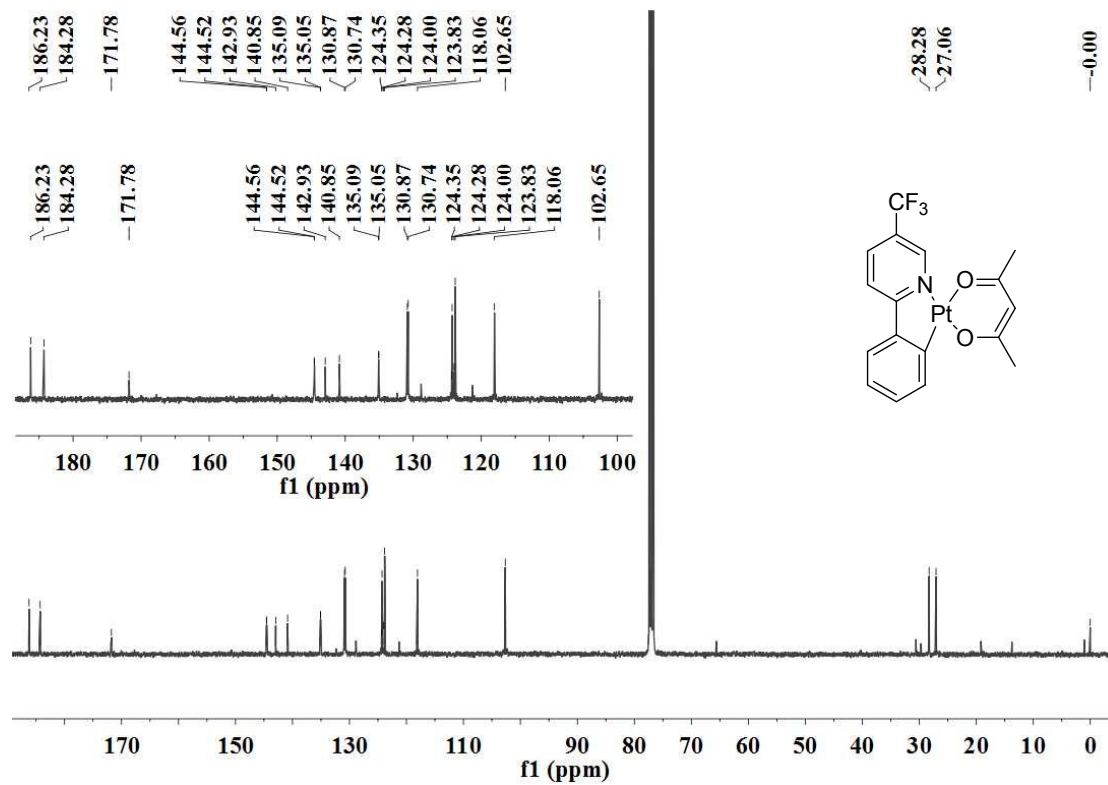


Figure S10. The  $^{13}\text{C}$  NMR spectrum of LSTF1 in  $\text{CDCl}_3$ .

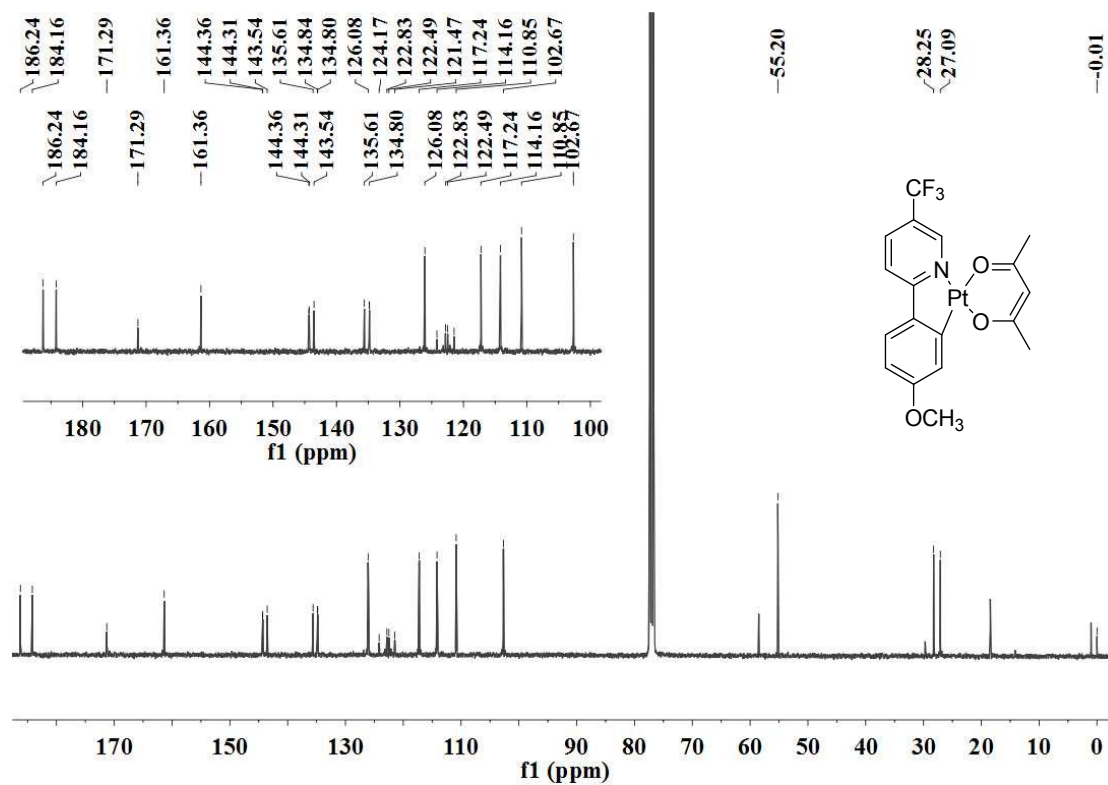
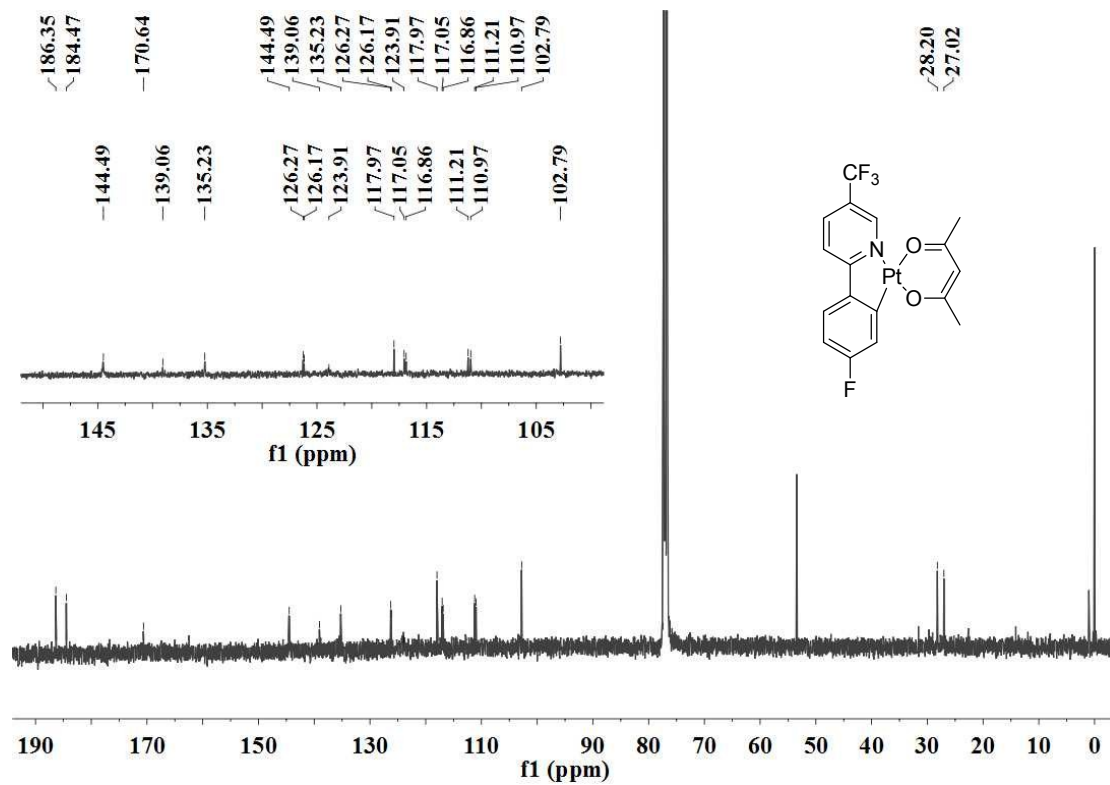
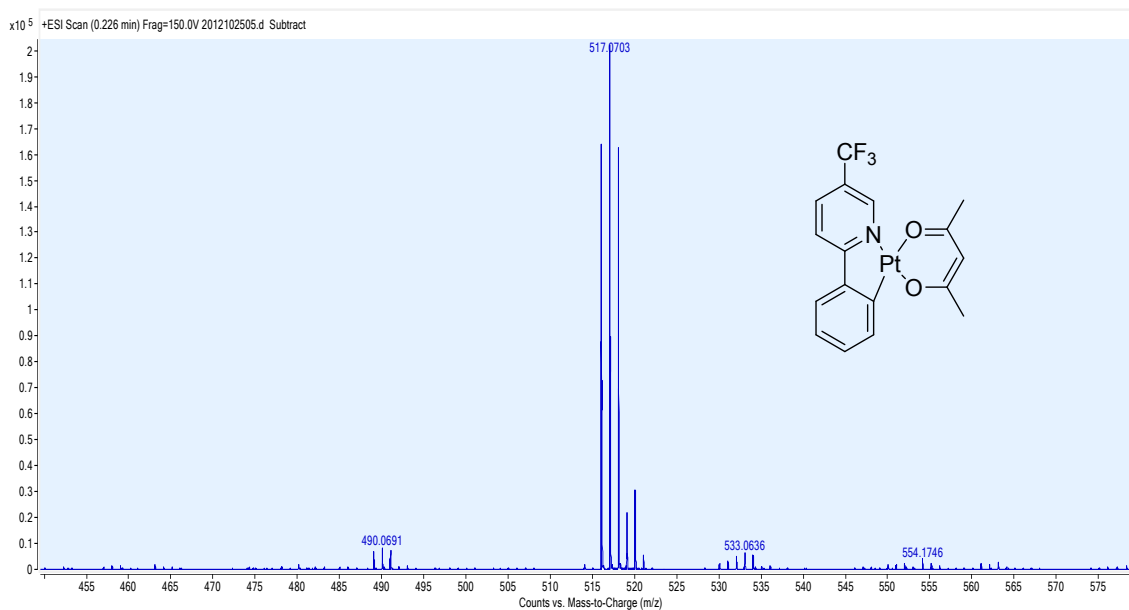


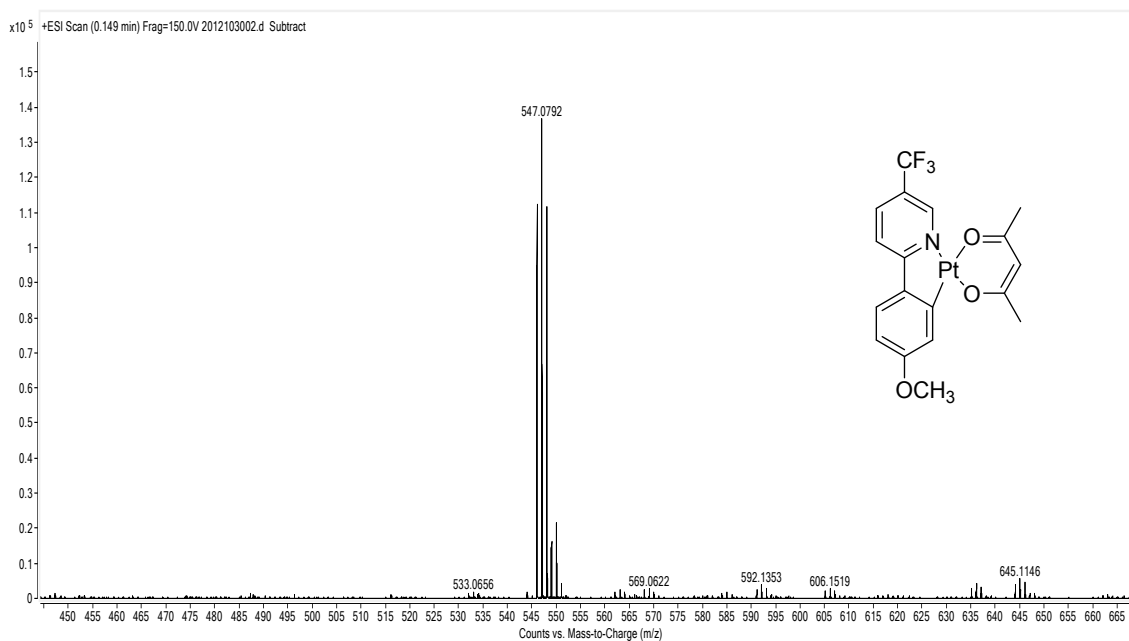
Figure S11. The  $^{13}\text{C}$  NMR spectrum of LSTF2 in  $\text{CDCl}_3$ .



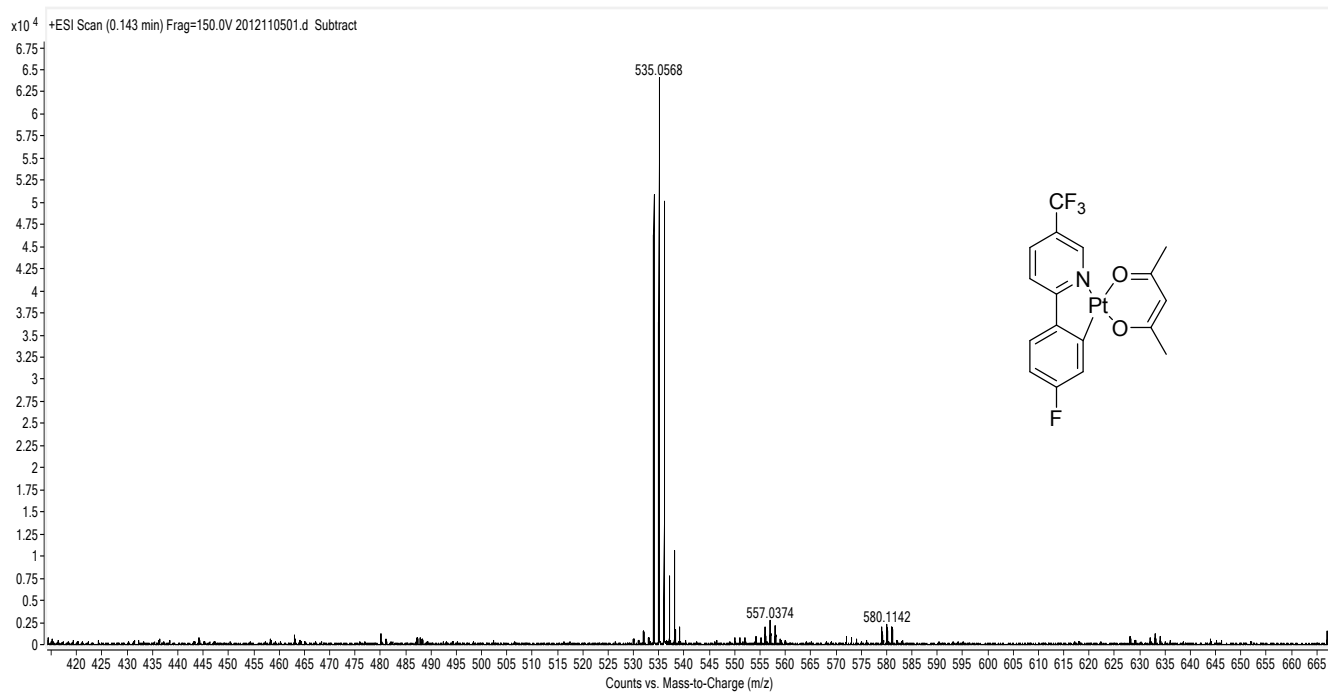
**Figure S12.** The <sup>13</sup>C NMR spectrum of LSTF3 in CDCl<sub>3</sub>.



**Figure S13.** The HRMS (EI) of LSTF1.



**Figure S14.** The HRMS (EI) of LSTF2.



**Figure S15.** The HRMS (EI) of LSTF3.

## Notes and references

[1] X. Rao, C. Liu, J. Qiu, Z. Jin. A highly efficient and aerobic protocol for the synthesis of N-heteroaryl substituted 9-arylcarbazolyl derivatives via a palladium-catalyzed ligand-free Suzuki reaction. *Org Biomol Chem.* 2012; 10: 7875

[2] Brooks J, Babayan Y, Lamansky S, Djurovich PI, Tsyba I, Bau R, et al. Synthesis and Characterization of Phosphorescent Cyclometalated Platinum Complexes. *Inorg Chem.* 2002; 41(12):3055