Supplementary information

# Photokinetic study on remarkable excimer phosphorescence from cyclometalated platinum(II) complexes bearing a benzoylated 2-phenylpyridinate ligand

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**Table S1** Crystallographic data for **Pt-1a−c**

| | **Pt-1a** | **Pt-1b** | **Pt-1c** |
|---|---|---|---|
| Empirical Formula | $C_{23}H_{19}NO_3Pt$ | $C_{23}H_{18}FNO_3Pt$ | $C_{23}H_{17}F_2NO_3Pt$ |
| Formula Weight | 552.50 | 570.49 | 588.48 |
| $T$ / K | 298 | 293 | 293 |
| Color, habit | yellow, prism | yellow, prism | yellow, block |
| Size, mm | 0.50 x 0.40 x 0.20 | 0.50 x 0.30 x 0.30 | 0.40 x 0.40 x 0.30 |
| Crystal system | monoclinic | triclinic | monoclinic |
| Lattice Type | Primitive | Primitive | Primitive |
| Space group | $P2_1/c$ (#14) | $P$-1 (#2) | $P2_1/c$ (#14) |
| $a$ / Å | 14.133(2) | 6.9367(11) | 11.922(3) |
| $b$ / Å | 8.6154(13) | 11.512(2) | 12.312(2) |
| $c$ / Å | 16.031(2) | 13.017(3) | 14.055(3) |
| $\alpha$ / ° | 90 | 81.915(9) | 90 |
| $\beta$ / ° | 94.639(2) | 76.395(9) | 103.866(3) |
| $\gamma$ / ° | 90 | 72.742(9) | 90 |
| $V$/ Å$^3$ | 1945.5(5) | 962.0(3) | 2002.9(7) |
| $Z$ | 4 | 2 | 4 |
| $D_{calc}$ / g cm$^{-3}$ | 1.886 | 1.969 | 1.951 |
| $F_{000}$ | 1064.00 | 548.00 | 1128.00 |
| $\mu$ (MoKα) / cm$^{-1}$ | 72.072 | 72.983 | 70.207 |
| $2\theta_{max}$ / ° | 61.5 | 61.2 | 61.3 |
| Total reflections | 16271 | 8152 | 17067 |
| Unique reflections | 5269 | 4902 | 5540 |
| Reflection/Parameter Ratio | 16.10 | 16.41 | 15.00 |
| $R$ ($I > 3.00\sigma(I)$)[a] | 0.0339 | 0.0274 | 0.0353 |
| $R$w ($I > 3.00\sigma(I)$)[b] | 0.0369 | 0.0306 | 0.0431 |
| Goodness of Fit Indicator | 1.073 | 1.061 | 1.069 |
| Max. and min. peak in Final Diff. Map / e Å$^{-3}$ | 2.43 and –1.84 | 1.72 and –1.39 | 1.36 and –1.83 |

[a] $R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo|$, [b] $R_W = [\, \Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2]^{1/2}$

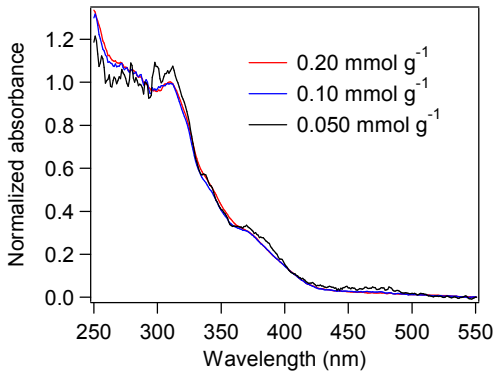


**Fig. S1** Normalized UV-vis absorption spectra of **Pt-1a** in PMMA.

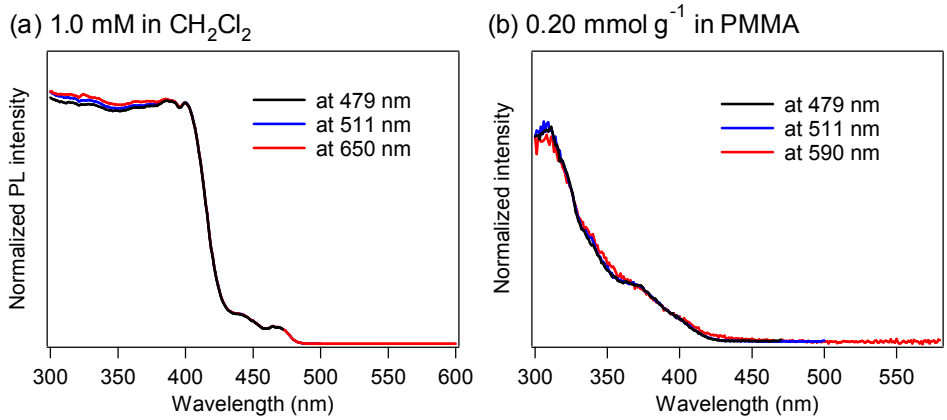


**Fig. S2** Excitation spectra of **Pt-1a** in (a) dichloromethane detected at 479, 511 (monomer emission) and 650 nm (excimer emission), and in (b) PMMA detected at 479, 511 (monomer emission) and 590 nm (excimer emission) under deaerated conditions.

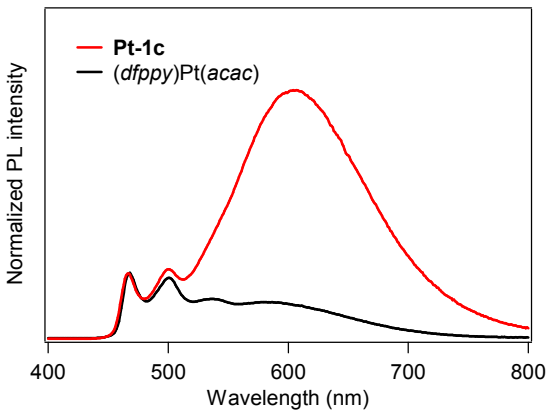


**Fig. S3** PL spectra of **Pt-1c** and (*dfppy*)Pt(*acac*) in PVCz film (0.50 mmol $g^{-1}$) under a nitrogen atmosphere.

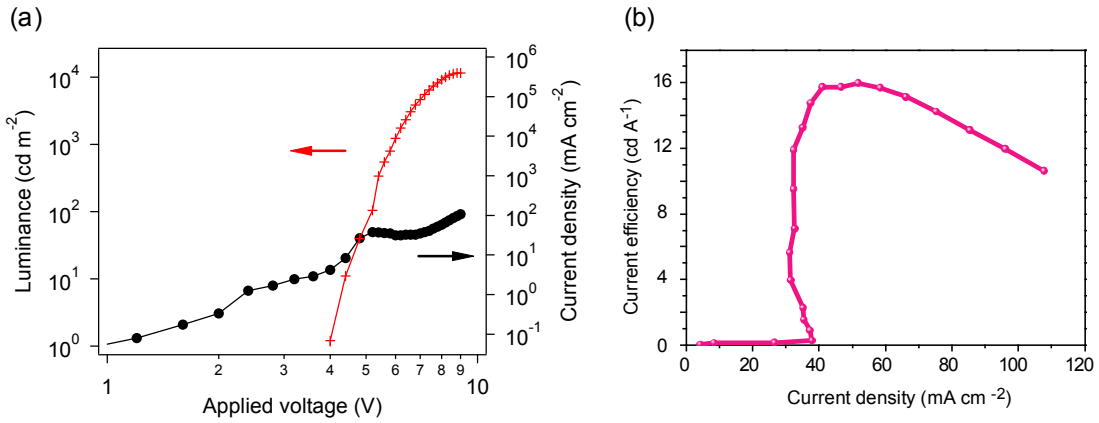


**Fig. S4** (a) The current density-voltage-luminance and (b) current density-current efficiency curves of the device whose structure is ITO (150 nm, anode)/F4TCNQ (3 nm)/NPB (50 nm)/TAPC (15 nm)/mCP:**Pt-1c** (15%, 30 nm)/TPBi (15 nm)/$Alq_3$ (20 nm)/LiF (1.5 nm)/Al (100 nm, cathode).

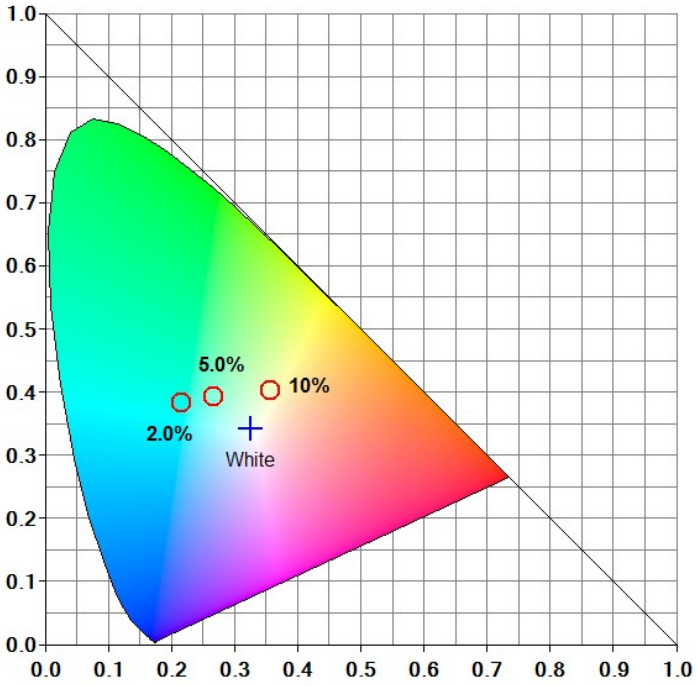


**Fig. S5** CIE chromaticity coordinates of devices doped with 2.0, 5.0 and 10% of **Pt-1c**, where the device structure was ITO (150 nm, anode)/m-MTDATA (60 nm)/F4TCNQ (3 nm)/NPB (50 nm)/TAPC (15 nm)/mCP:**Pt-1c** (30 nm)/TPBi (15 nm)/$Alq_3$ (20 nm)/LiF (1.5 nm)/Al (100 nm). The CIE chromaticity coordinates were (0.21, 0.39), (0.26, 0.40) and (0.35, 0.41) for the 2.0%-, 5.0%- and 10%-doped devices, respectively.

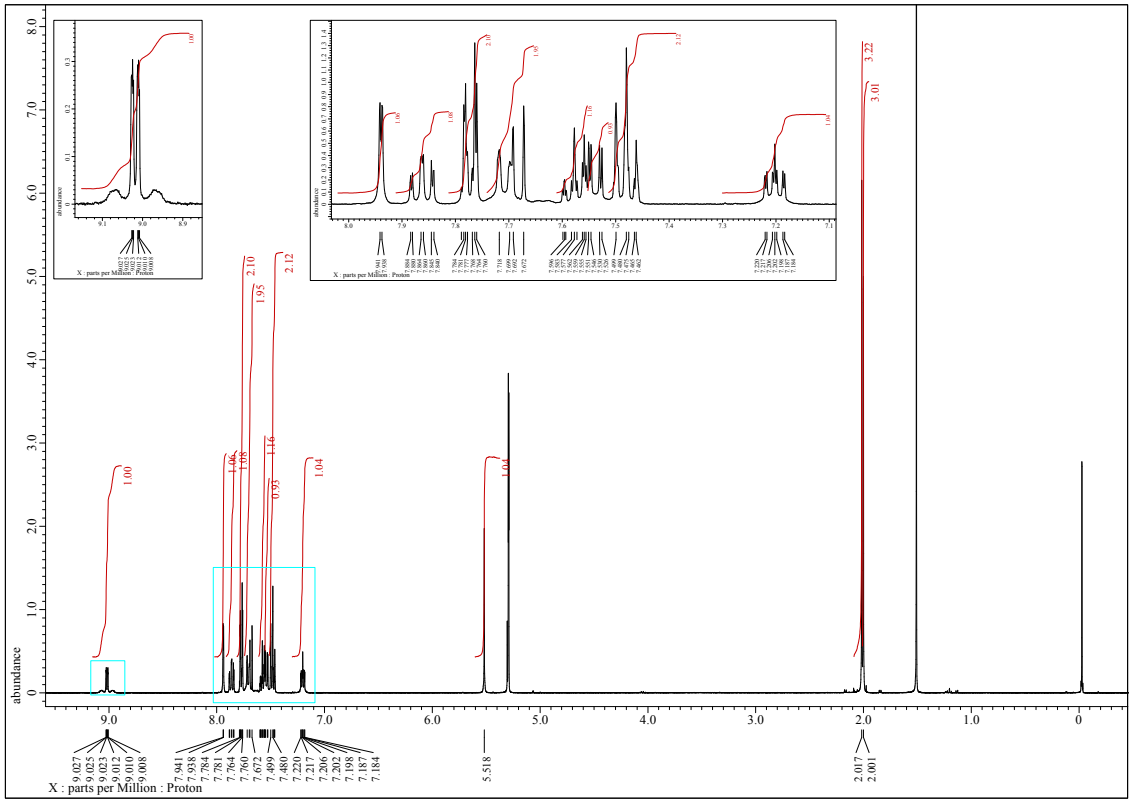


**Fig. S6** $^{1}$H NMR spectrum of **Pt-1a** in $CD_2Cl_2$.

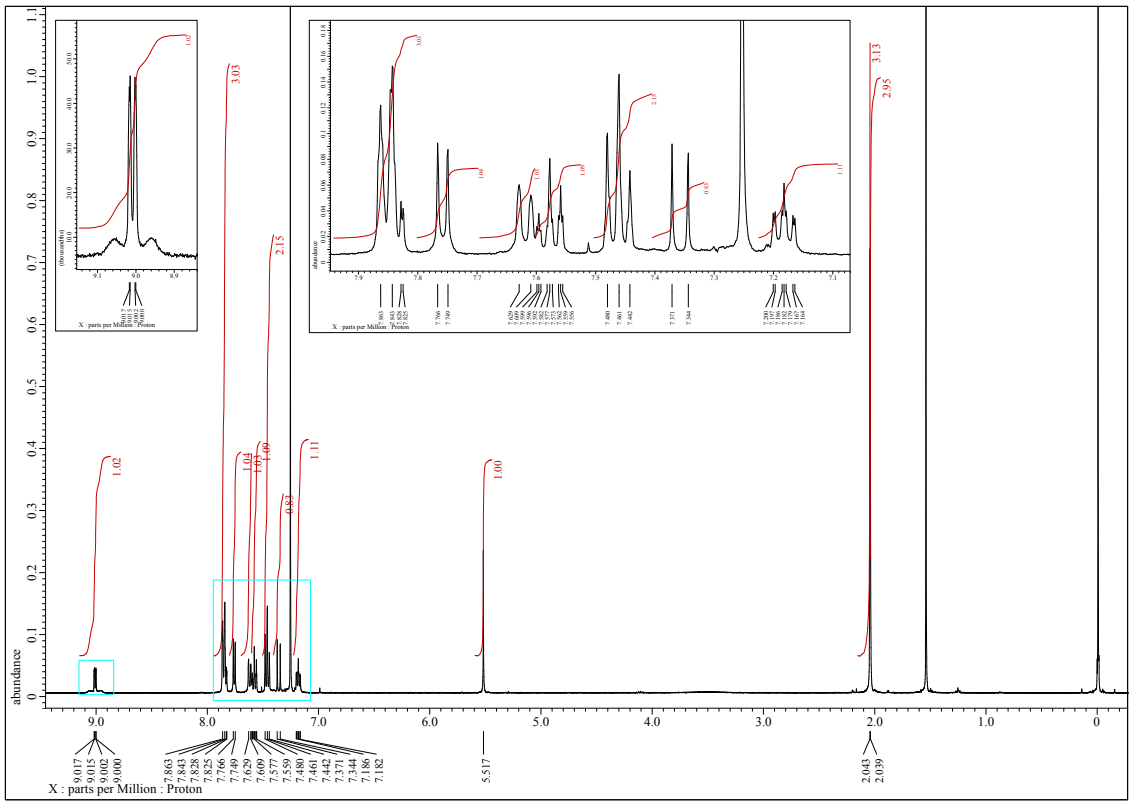


**Fig. S7** $^{1}$H NMR spectrum of **Pt-1b** in $CDCl_3$.

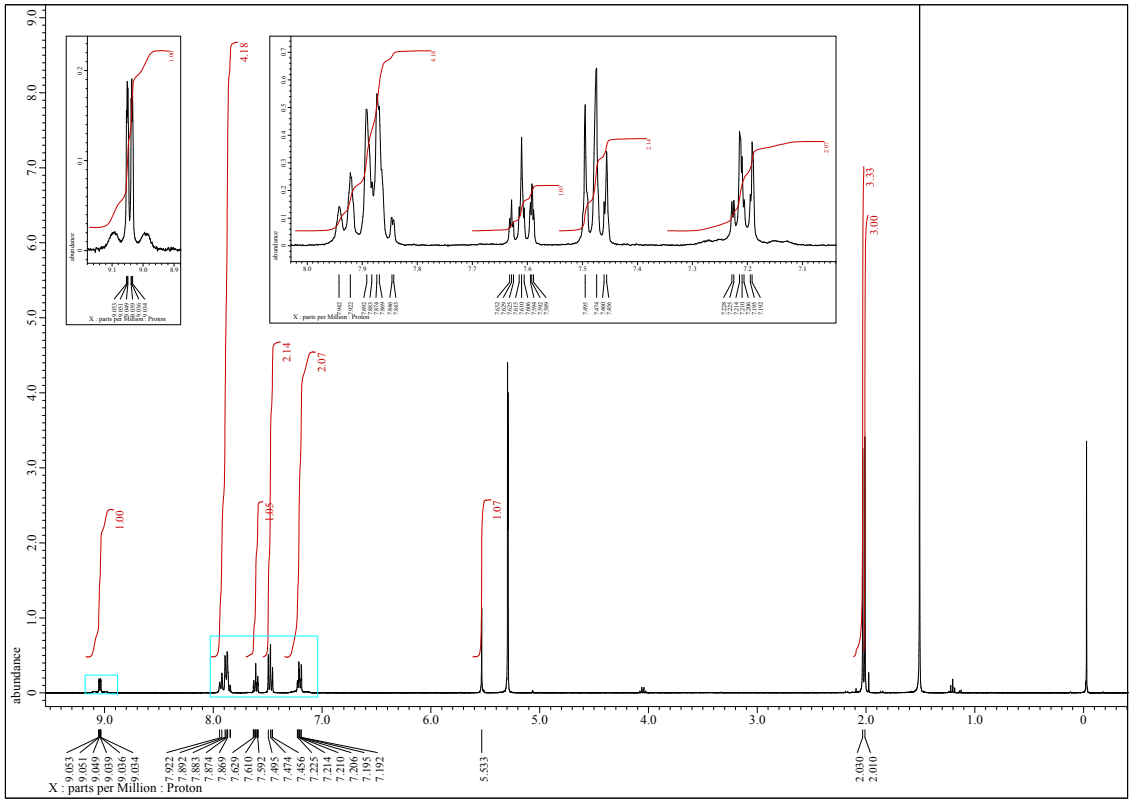


**Fig. S8** $^{1}H$ NMR spectrum of **Pt-1c** in $CD_2Cl_2$.

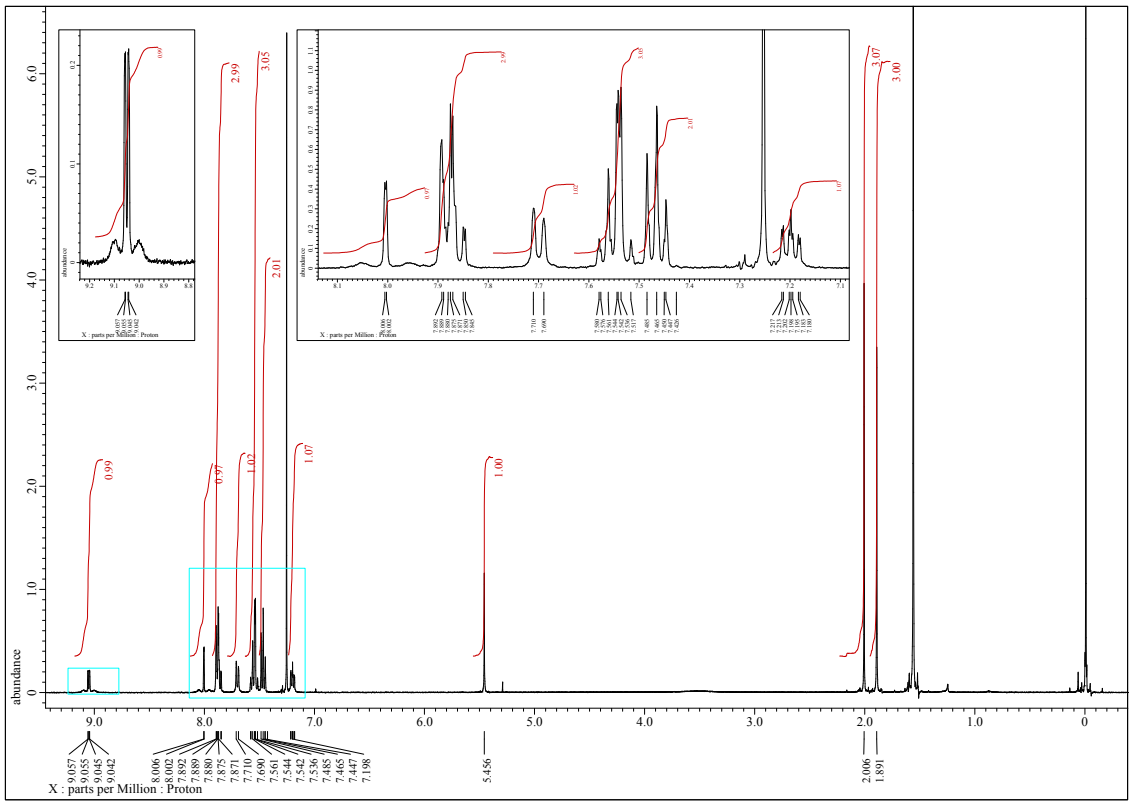


**Fig. S9** $^{1}H$ NMR spectrum of **Pt-2b** in $CDCl_3$.

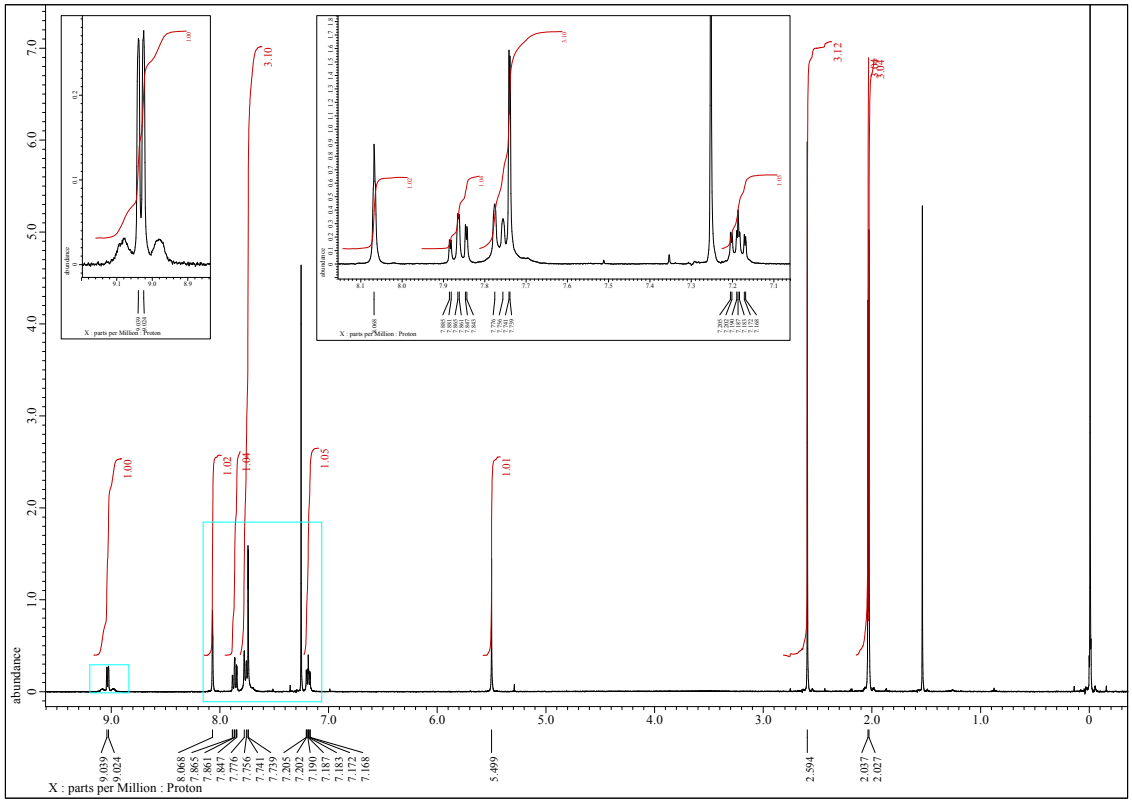


**Fig. S10** $^{1}$H NMR spectrum of **Pt-2c** in $CDCl_3$.

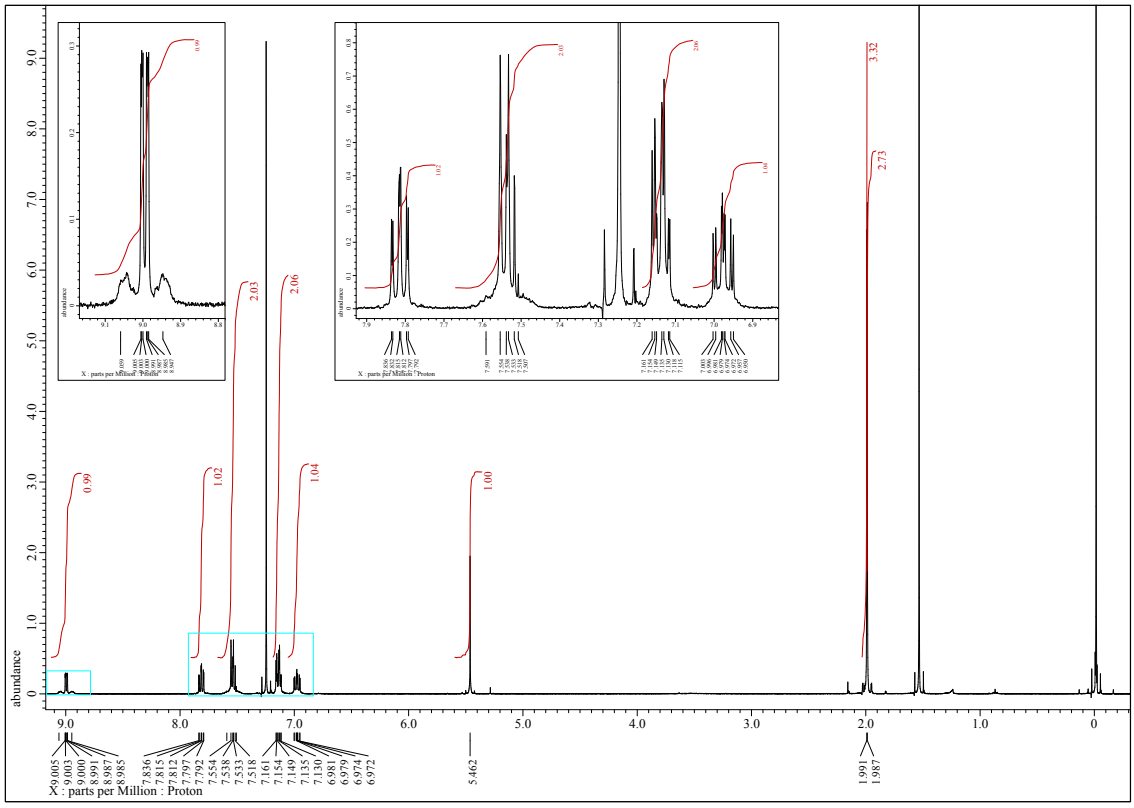


**Fig. S11** $^{1}$H NMR spectrum of **Pt-2d** in $CDCl_3$.