**SUPPORTING INFORMATION**

# Bimetallic Platinum(II) Complexes with Bridging Di-NHC and N^C^C Ligands: Synthesis and Photophysical Properties

*Mariano Paredes, Dionisio Poveda, Pablo González-Herrero and Ángela Vivancos*[*]

Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia, Spain.

*E-mail: angela.vivancos@um.es

**Contents:**

# 1. NMR spectra of new compounds

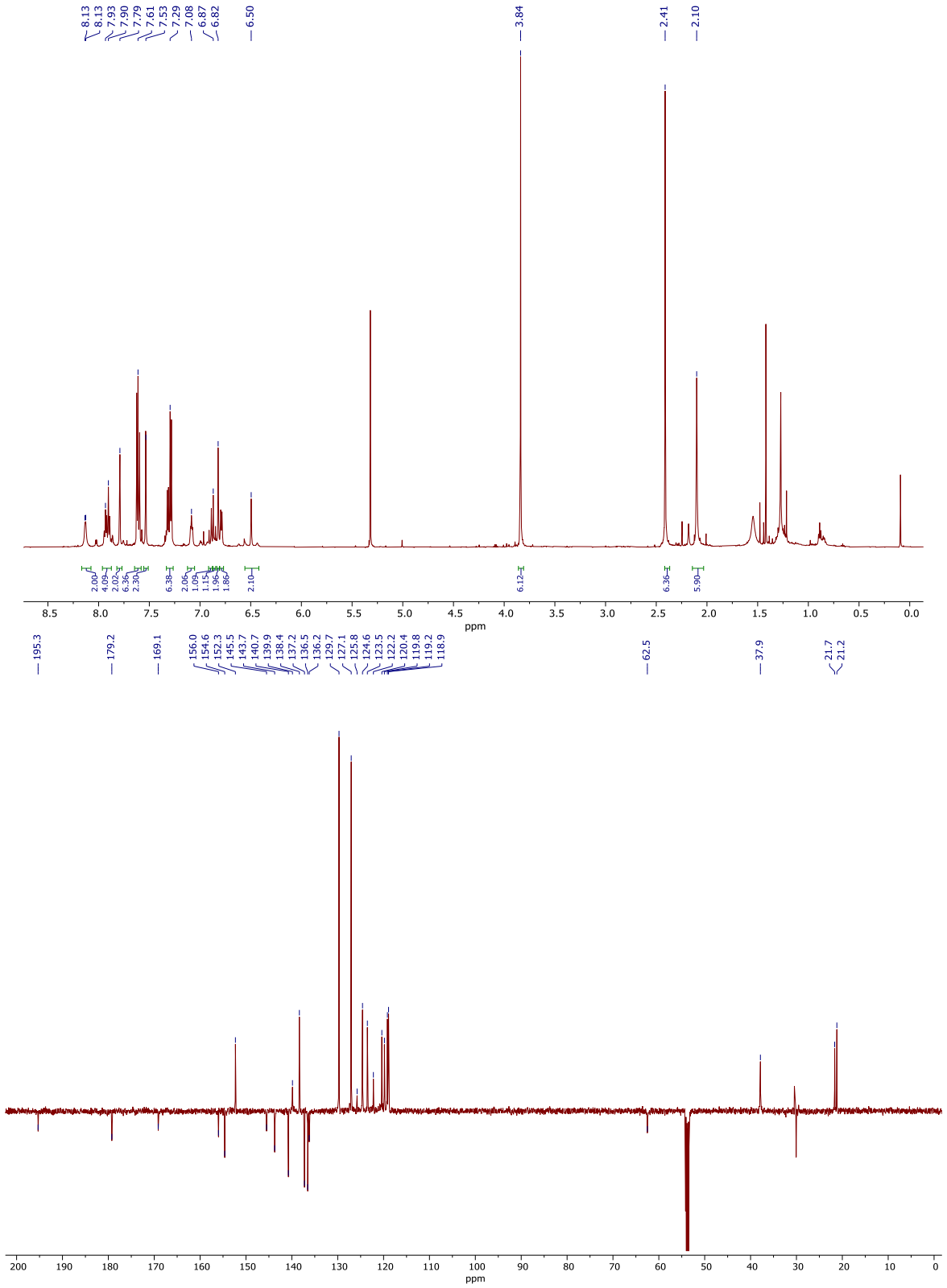


**Figure S1.** $^{1}H$ (top) and $^{13}C\{^{1}H\}$ APT (bottom) NMR spectra of conformer [{Pt(N^C^C)}$_2${μ-($Im_{Me}$)$_2$($CH_2$)$_1$}] (**1a**) ($CD_2Cl_2$, 600 and 151 MHz, respectively).

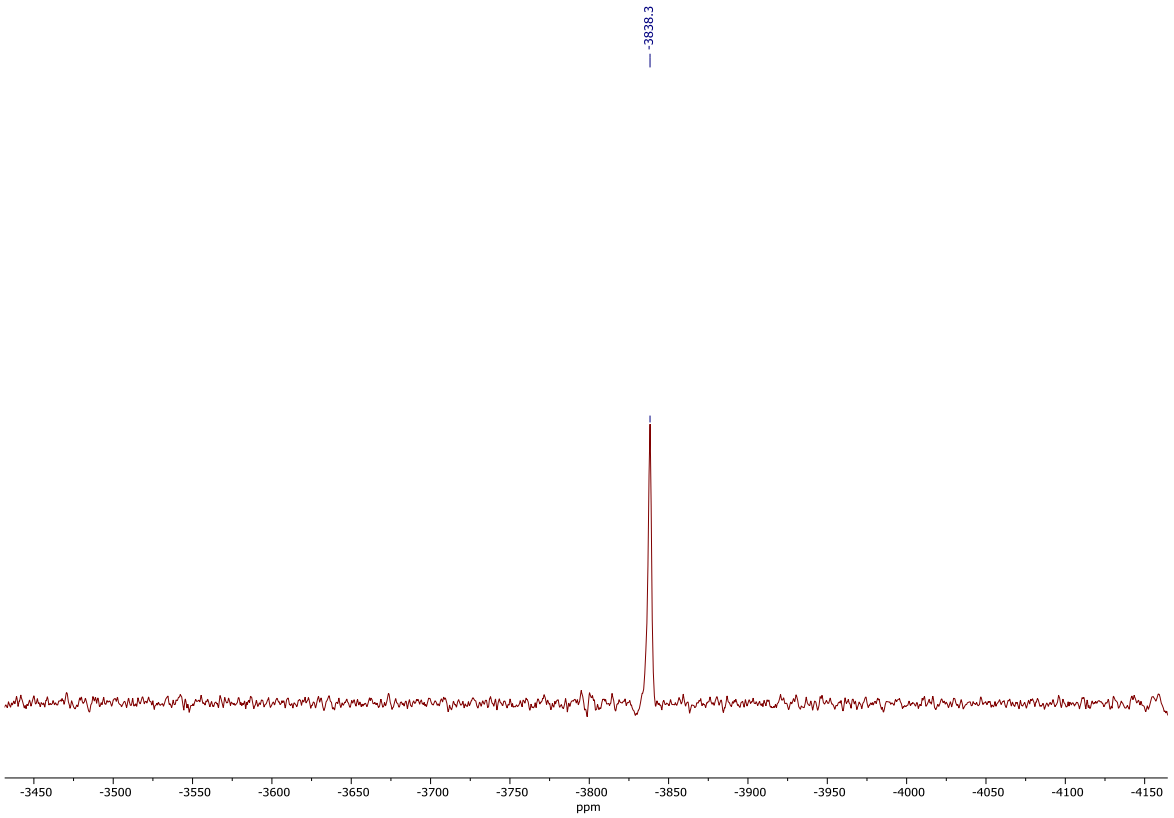


**Figure S2.** $^{195}Pt\{^{1}H\}$ NMR spectrum of conformer [{Pt(N^C^C)}$_2${μ-($Im_{Me}$)$_2$($CH_2$)$_1$}] (**1a**) ($CD_2Cl_2$, 129 MHz).

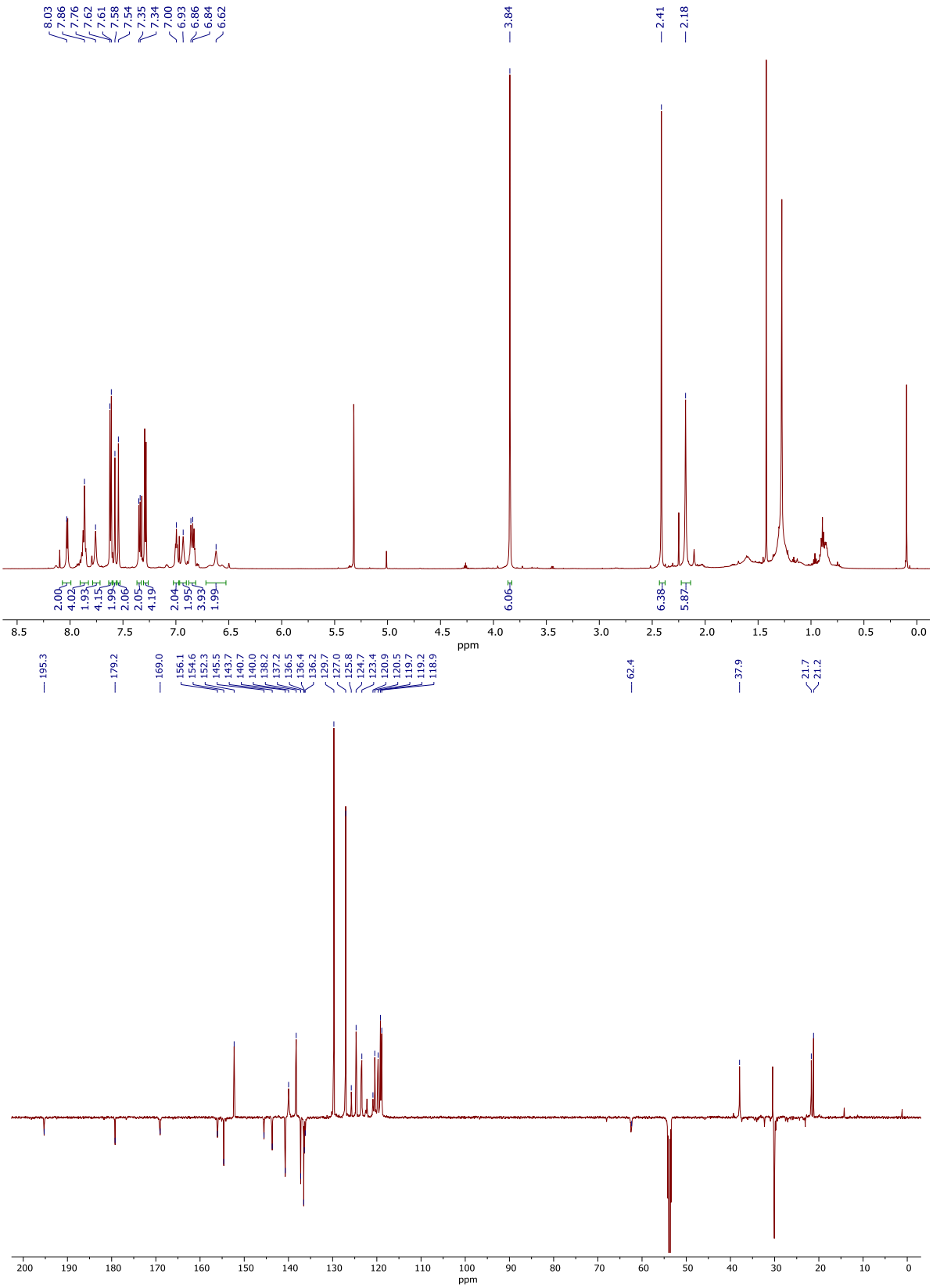


**Figure S3.** $^{1}H$ (top) and $^{13}C\{^{1}H\}$ APT (bottom) NMR spectra of conformer [{Pt(N^C^C)}$_2${μ-($Im_{Me}$)$_2$($CH_2$)$_1$}] (**1b**) ($CD_2Cl_2$, 600 and 151 MHz, respectively).

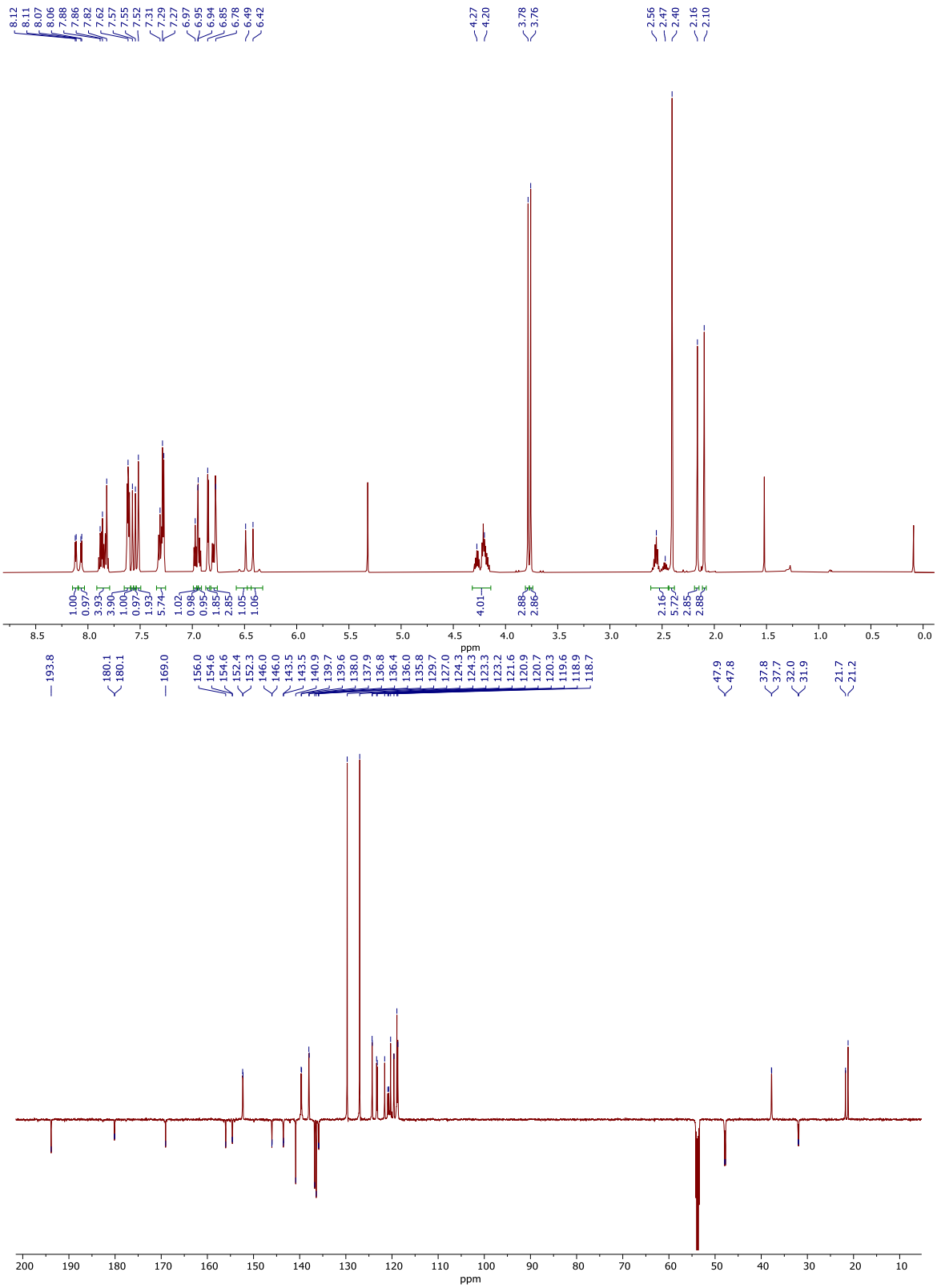

**Figure S4.** $^{1}H$ (top) and $^{13}C\{^{1}H\}$ APT (bottom) NMR spectra of complex [{Pt(N^C^C)}$_2${μ-(Im$_{Me}$)$_2$(CH$_2$)$_3$}] (**2**) ($CD_2Cl_2$, 600 and 151 MHz, respectively).

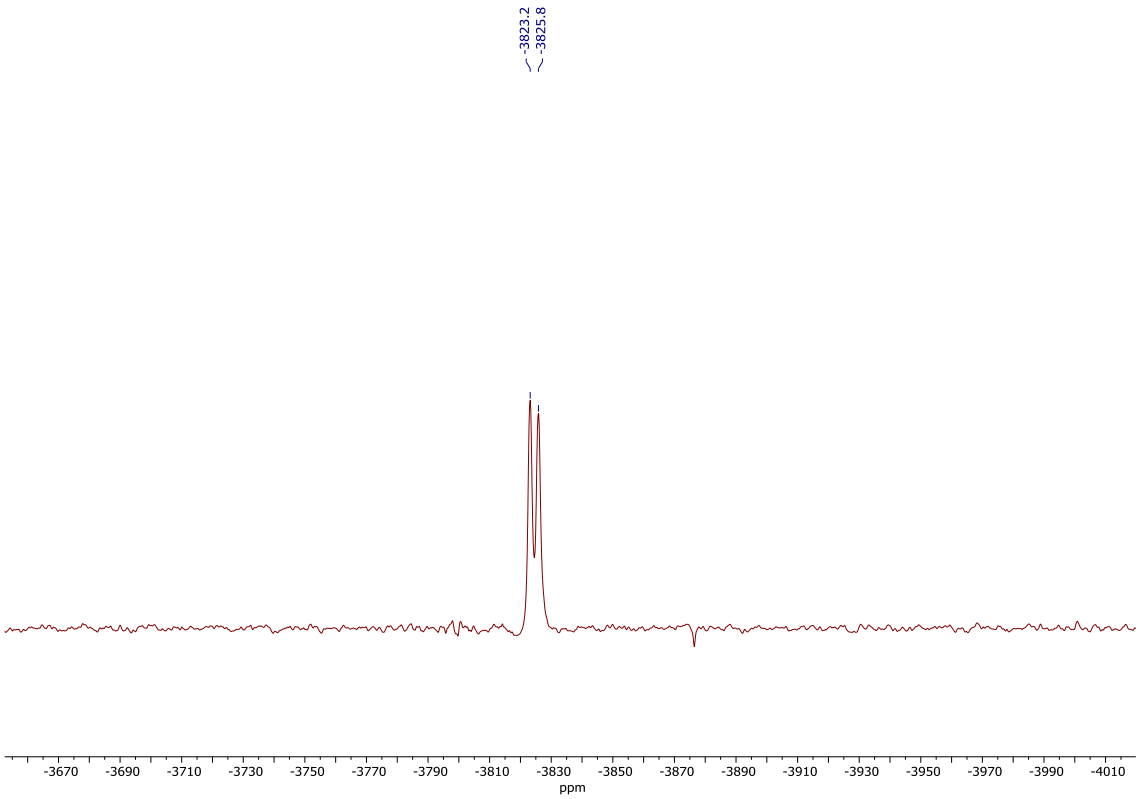


**Figure S5.** $^{195}Pt\{^{1}H\}$ NMR spectrum of complex [{Pt(N^C^C)}$_2${μ-($Im_{Me}$)$_2$($CH_2$)$_3$}] (**2**) ($CD_2Cl_2$, 129 MHz).

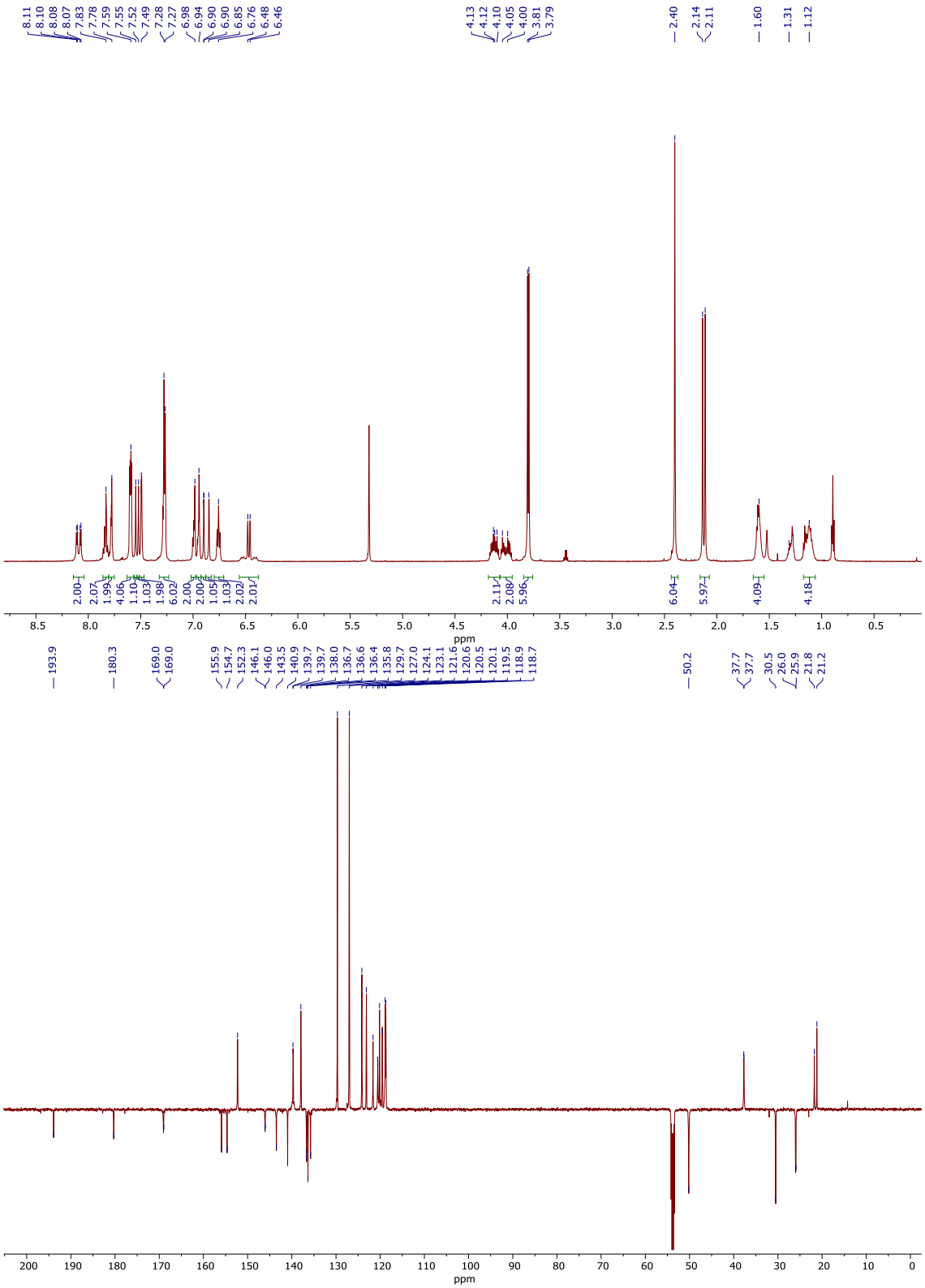

**Figure S6.** $^{1}H$ (top) and $^{13}C\{^{1}H\}$ APT (bottom) NMR spectra of complex [{Pt(N^C^C)}$_2${μ-(Im$_{Me}$)$_2$(CH$_2$)$_6$}] (**3**) ($CD_2Cl_2$, 600 and 151 MHz, respectively).

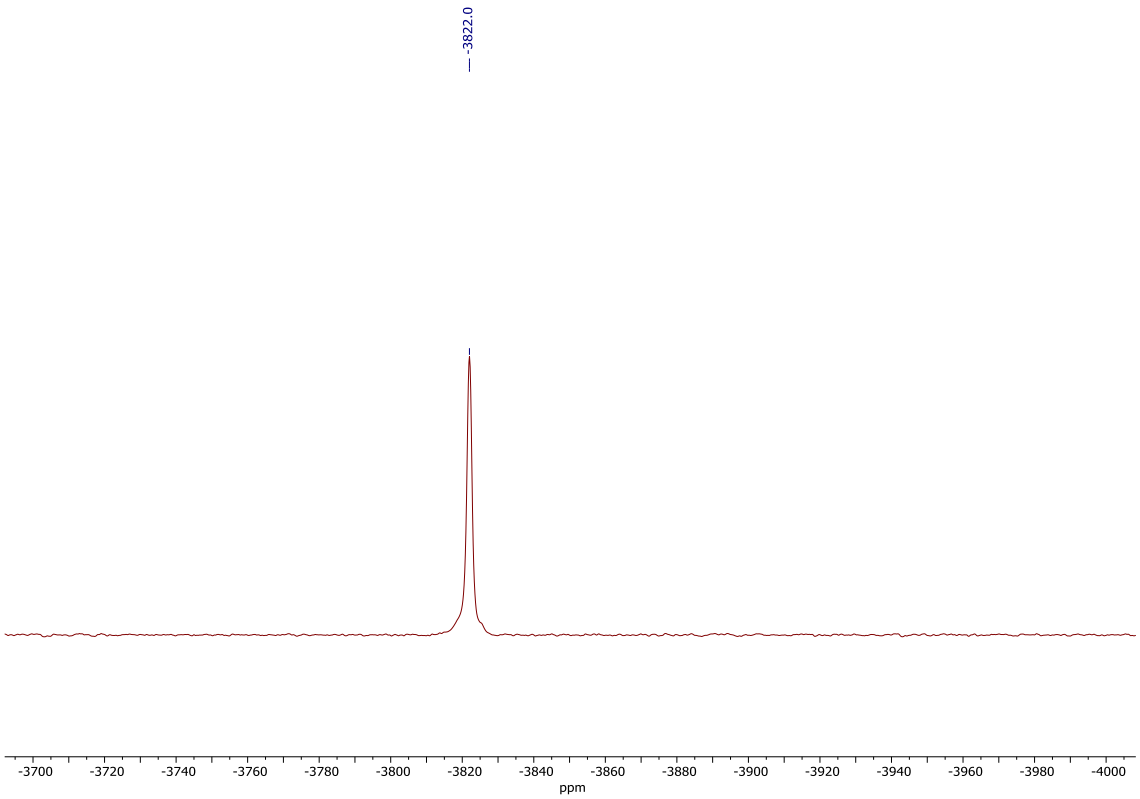


**Figure S7.** $^{195}Pt\{^{1}H\}$ NMR spectrum of complex [{Pt(N^C^C)}$_2${μ-($Im_{Me}$)$_2$($CH_2$)$_6$}] (**3**) ($CD_2Cl_2$, 129 MHz).

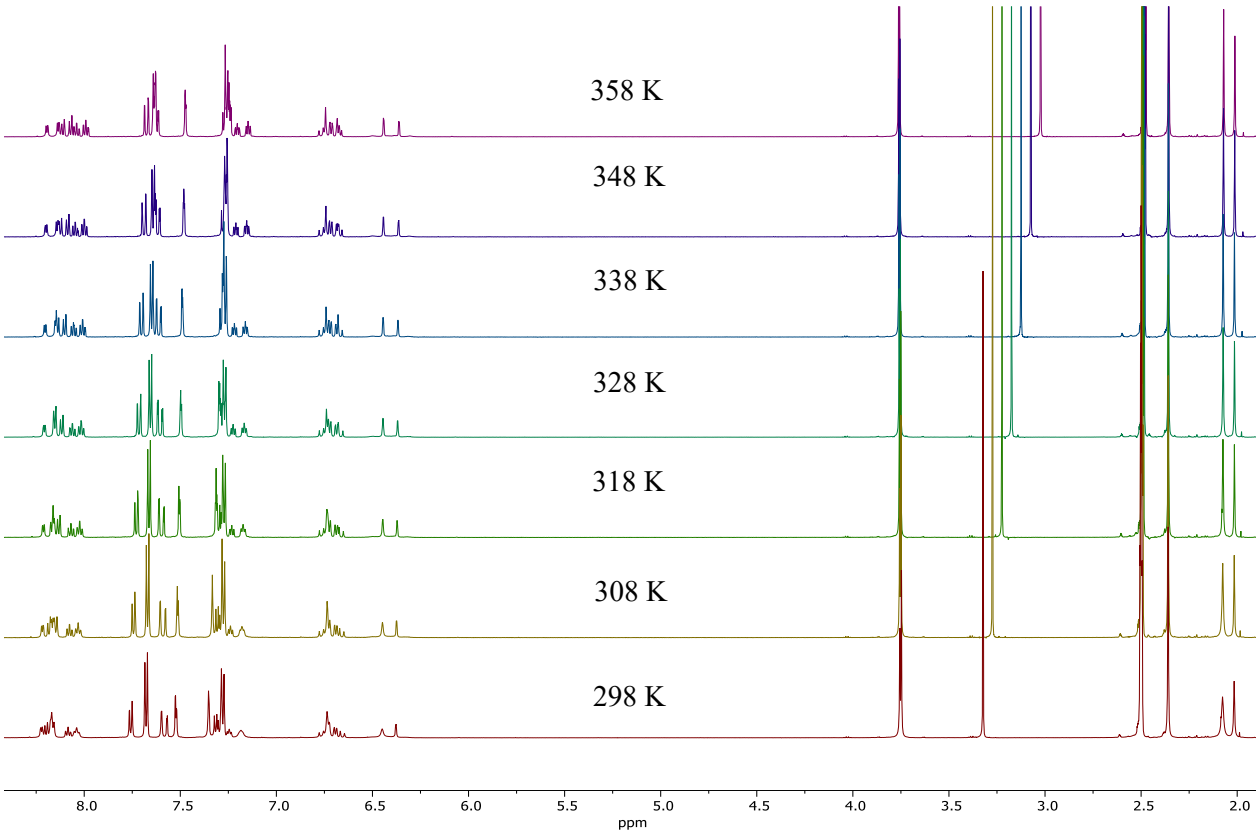


**Figure S8.** $^{1}$H NMR spectra of complex **1** at different temperatures (DMSO-$d_6$, 600 MHz, 298 to 358 K).

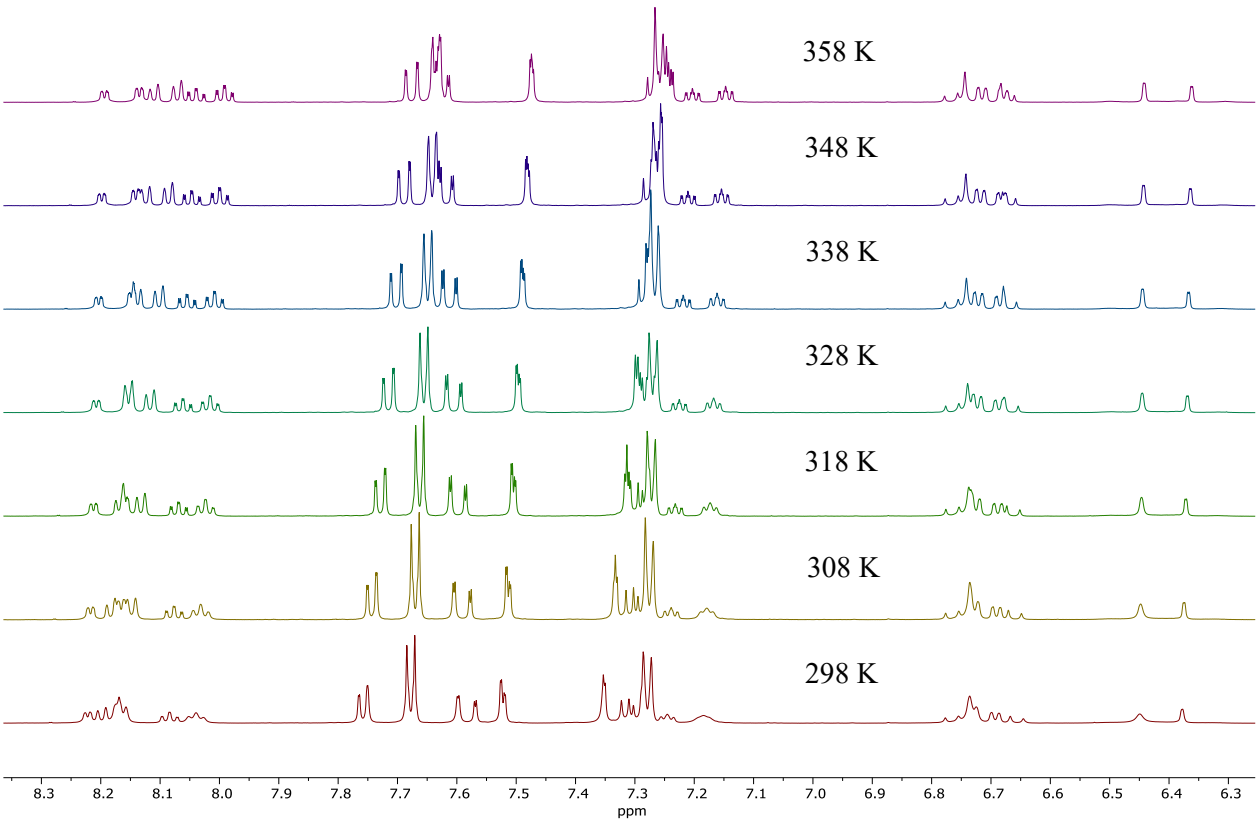


**Figure S9.** Aromatic region of the $^{1}$H NMR spectra of complex **1** (DMSO-$d_6$, 600 MHz, 298 to 358 K).

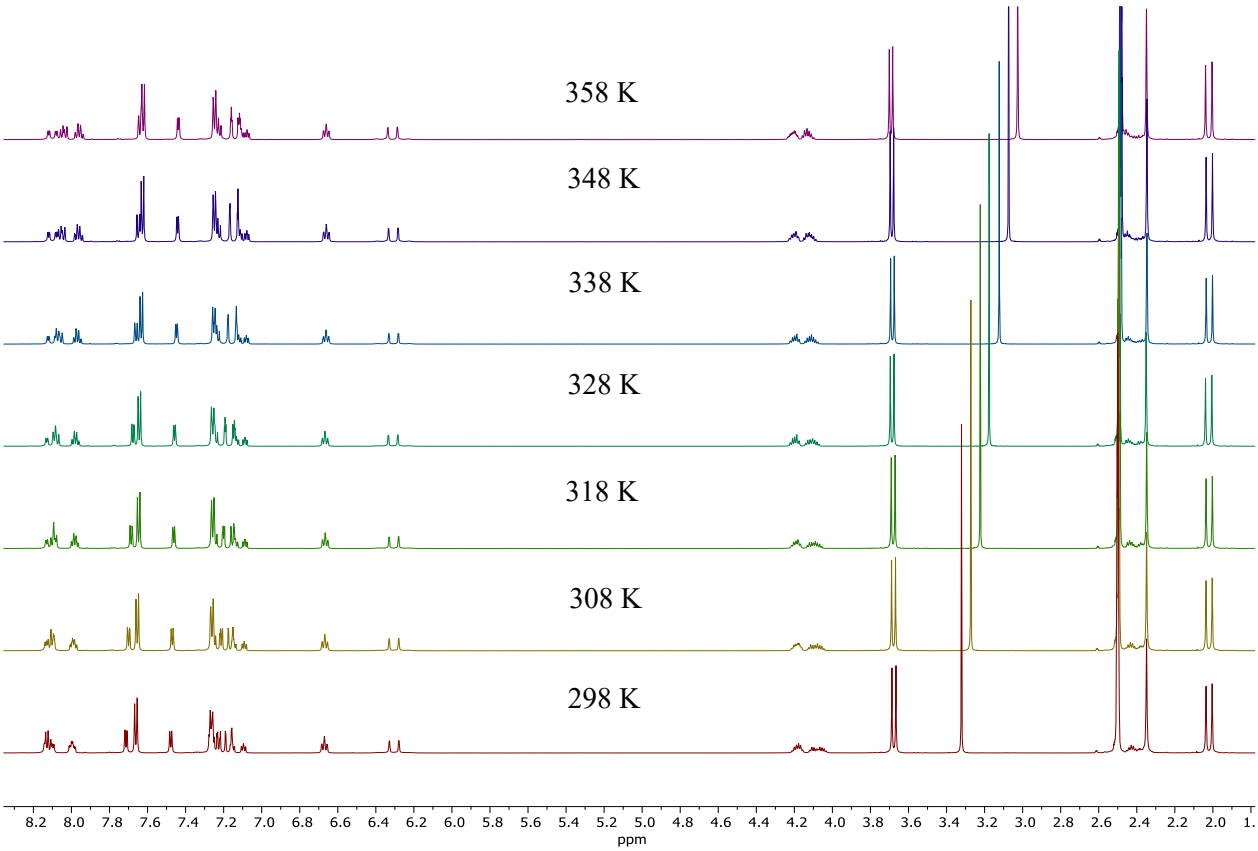


**Figure S10.** $^{1}$H NMR spectra of complex **2** at different temperatures (DMSO-$d_6$, 600 MHz, 298 to 358 K).

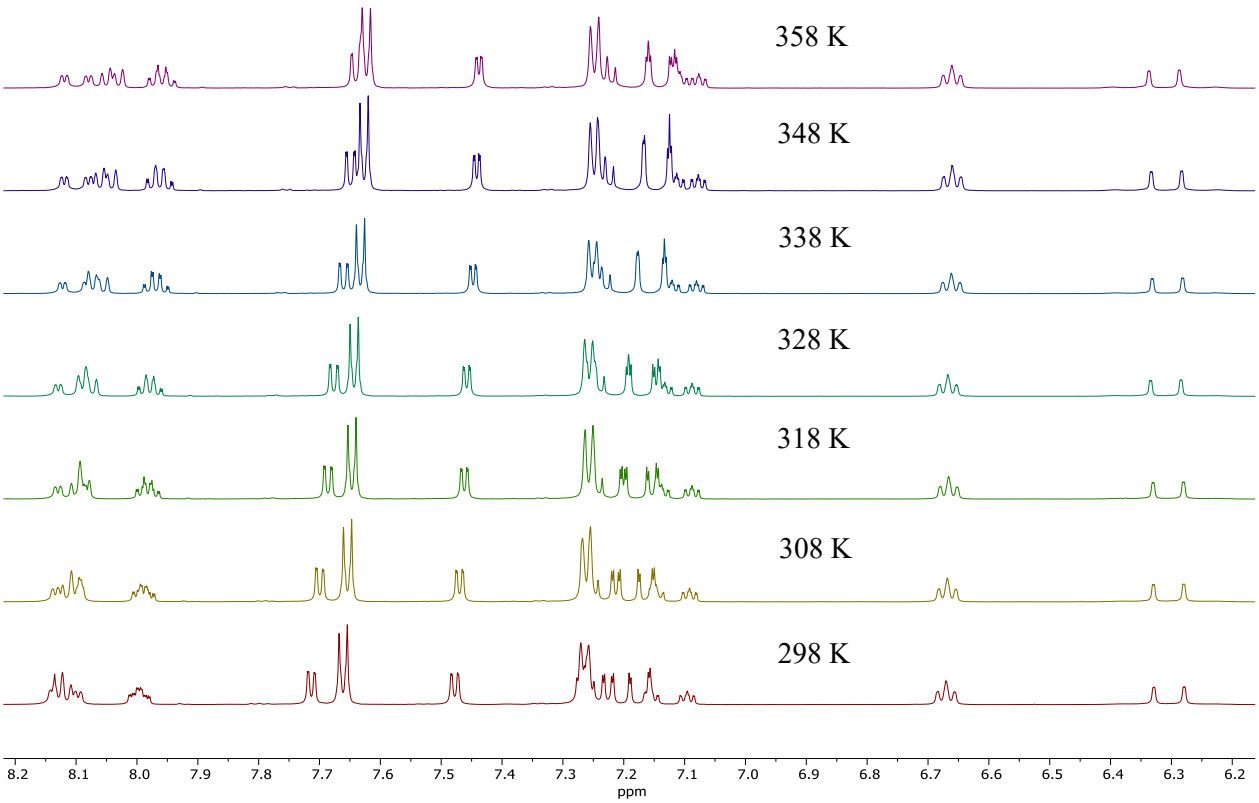


**Figure S11.** Aromatic region of the $^{1}$H NMR spectra of complex **2** (DMSO-$d_6$, 600 MHz, 298 to 358 K).

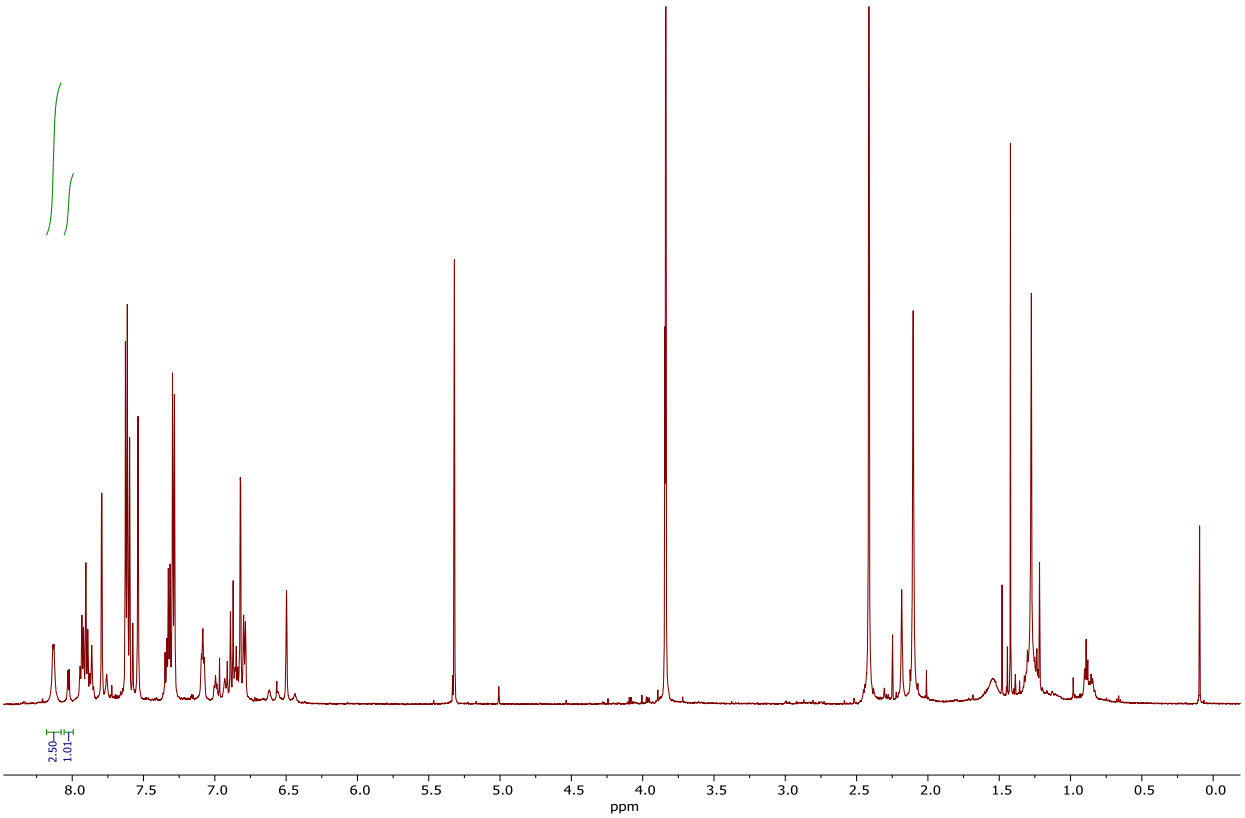


**Figure S12.** $^{1}$H NMR spectrum of mixture **1a**:**1b** (2.5:1 ratio) after 72 h of atropisomer **1a** in $CD_2Cl_2$ solution ($CD_2Cl_2$, 600 MHz, 298 K).

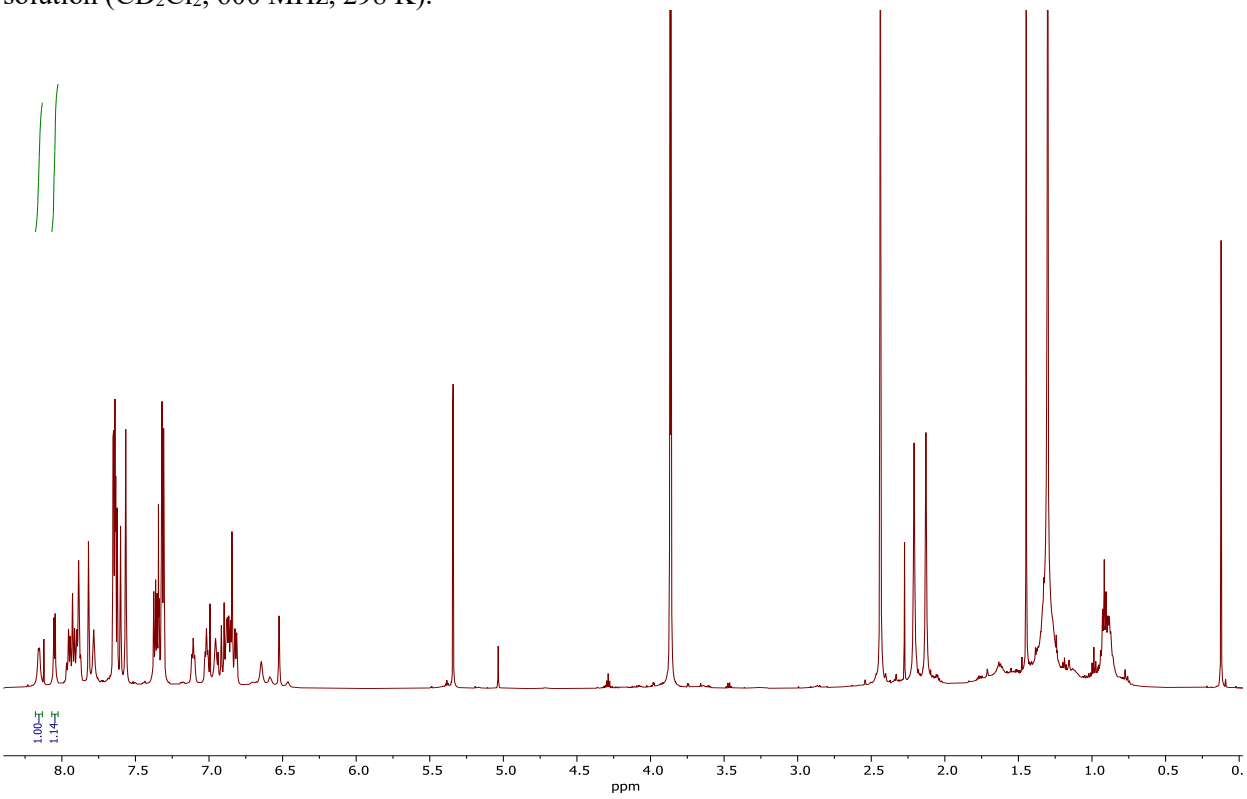


**Figure S13.** $^{1}$H NMR spectrum of mixture **1a**:**1b** (1:1.1 ratio) after 24 h of atropisomer **1b** in $CD_2Cl_2$ solution ($CD_2Cl_2$, 600 MHz, 298 K).

## 2. Additional photophysical data

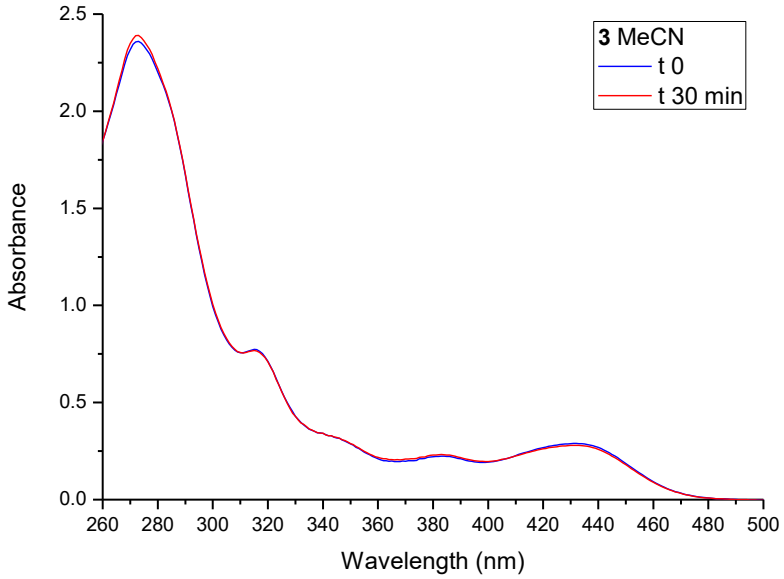


**Figure S14.** Absorption spectra of complex **3** in MeCN solution (ca. 2.5 x $10^{-5}$ M) before and after 30 min of continuous irradiation at 430 nm, using the 450 W xenon lamp of the spectrofluorometer (15 nm bandpass).

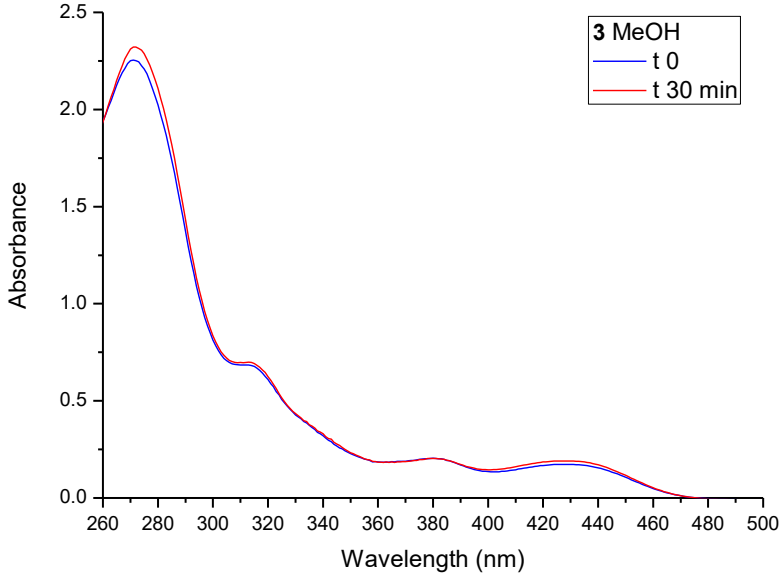


**Figure S15.** Absorption spectra of complex **3** in MeOH solution (ca. 2.5 × $10^{-5}$ M) before and after 30 min of continuous irradiation at 430 nm, using the 450 W xenon lamp of the spectrofluorometer (15 nm bandpass).

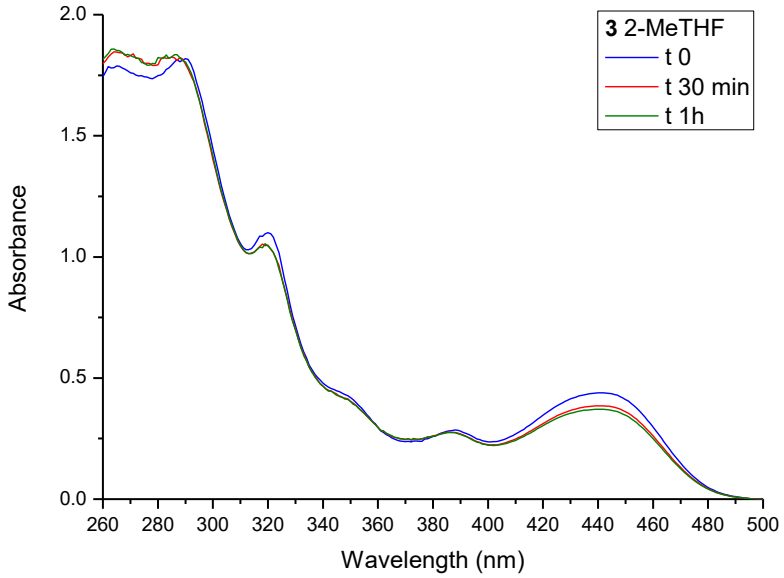


**Figure S16.** Absorption spectra of complex **3** in 2-MeTHF solution (ca. $2.5 \times 10^{-5}$ M) before and after 30 or 60 min of continuous irradiation at 430 nm, using the 450 W xenon lamp of the spectrofluorometer (15 nm bandpass).

**Figure S17.** Photographs of MeCN solutions of complexes **1**, **2** and **3** (from left to right) at $2.5 \times 10^{-5}$ M concentration under UV irradiation at 298 K.

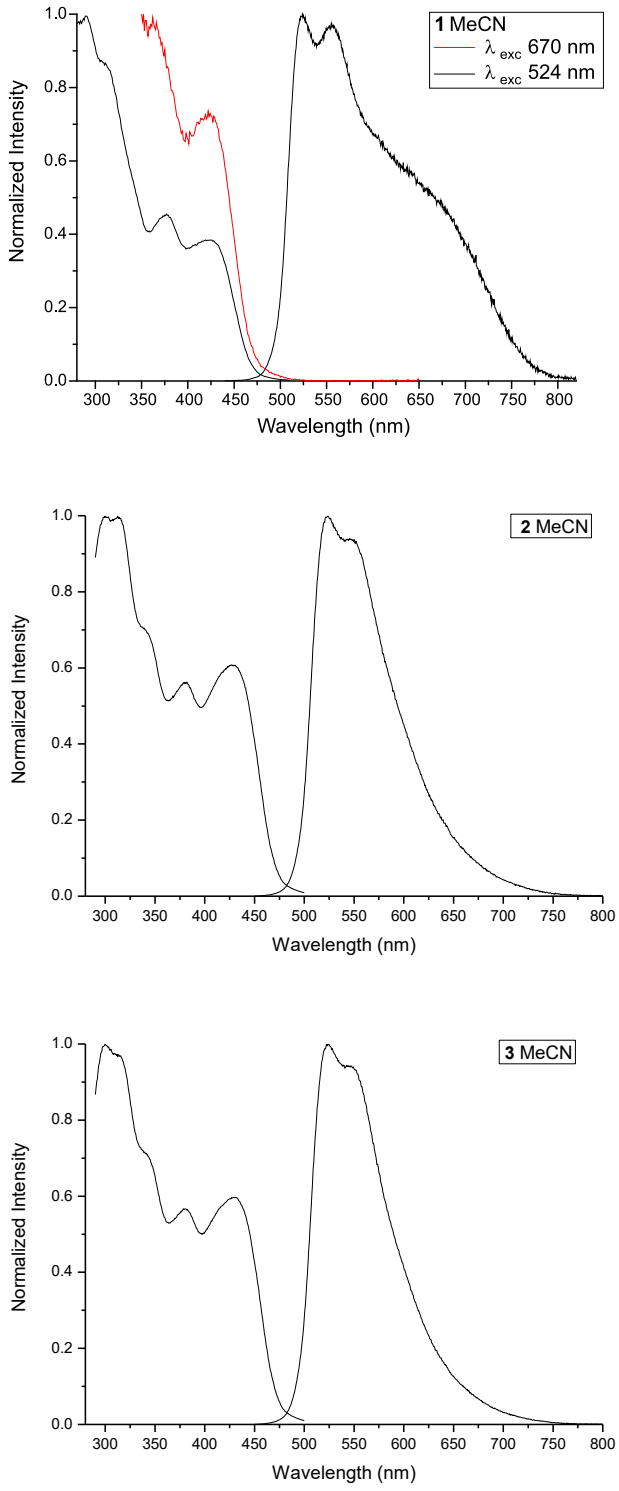


**Figure S18.** Excitation and emission spectra of complexes **1-3** in MeCN solution (*ca.* $2.5 \times 10^{-5}$ M) at 298 K. The collected $\lambda_{em}$ for excitation spectra corresponds in all cases to the highest-energy emission peak, with the exception of **1**, for which two emission wavelengths have been monitored.

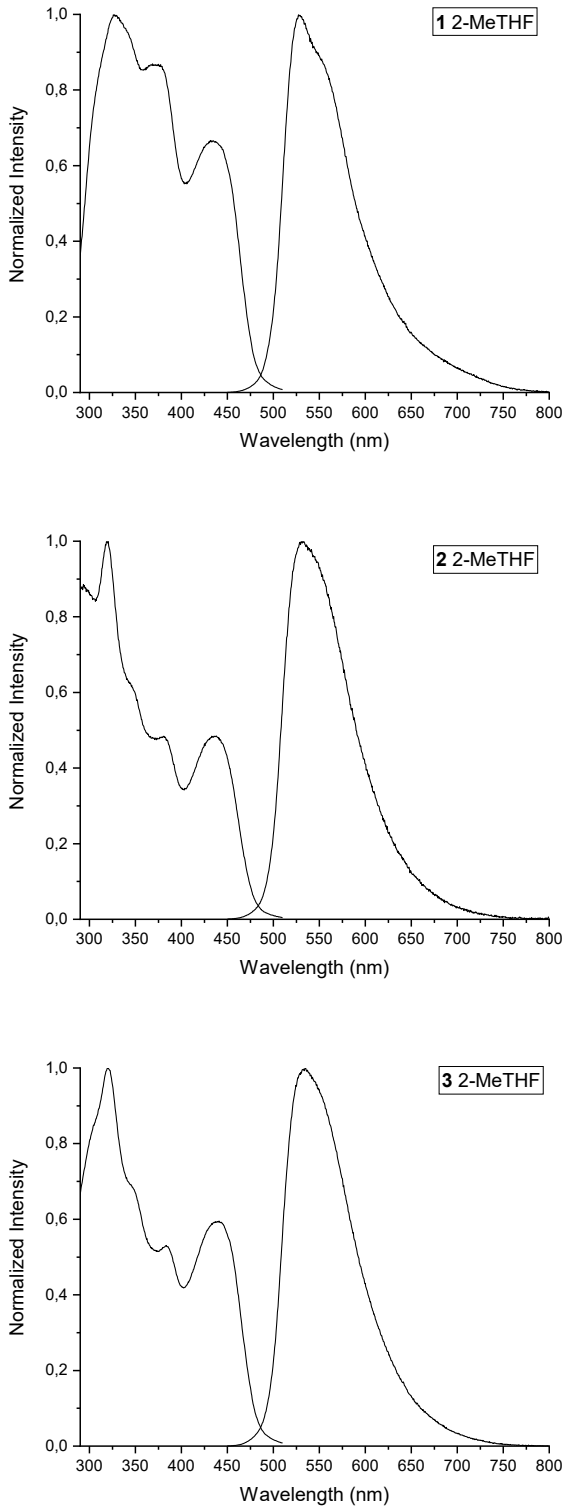


**Figure S19.** Excitation and emission spectra of complexes **1**-**3** in 2-MeTHF solution (*ca.* $2.5 \times 10^{-5}$ M) at 298 K. The collected $\lambda_{em}$ for excitation spectra corresponds in all cases to the highest-energy emission peak.

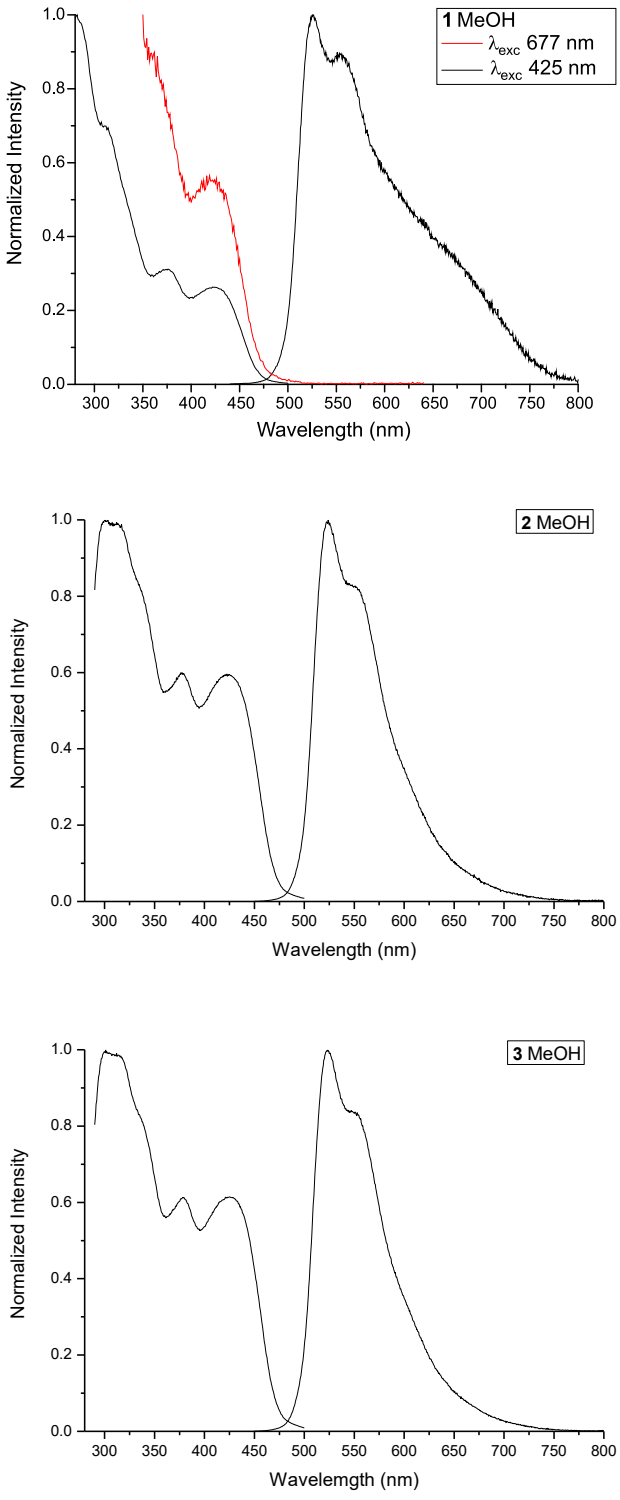


**Figure S20.** Excitation and emission spectra of complexes **1**-**3** in MeOH solution (*ca.* $2.5 \times 10^{-5}$ M) at 298 K. The collected $\lambda_{em}$ for excitation spectra corresponds in all cases to the highest-energy emission peak.

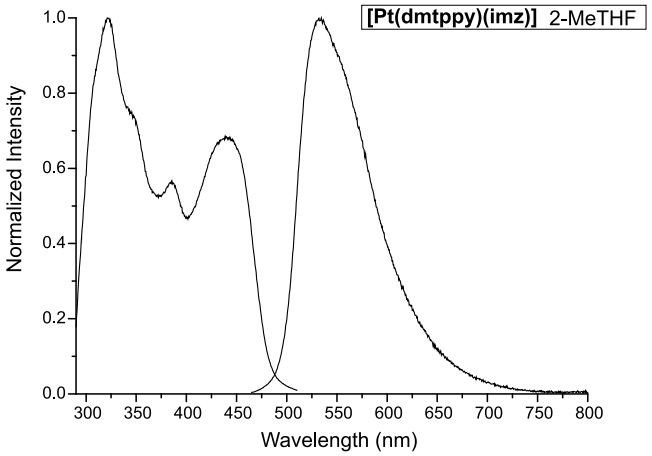


**Figure S21.** Excitation and emission spectra of complex **[Pt(dmtppy)(imz)]** in 2-MeTHF solution (*ca.* $5 \times 10^{-5}$ M) at 298 K. The collected $\lambda_{em}$ for excitation spectra corresponds to the highest-energy emission peak.

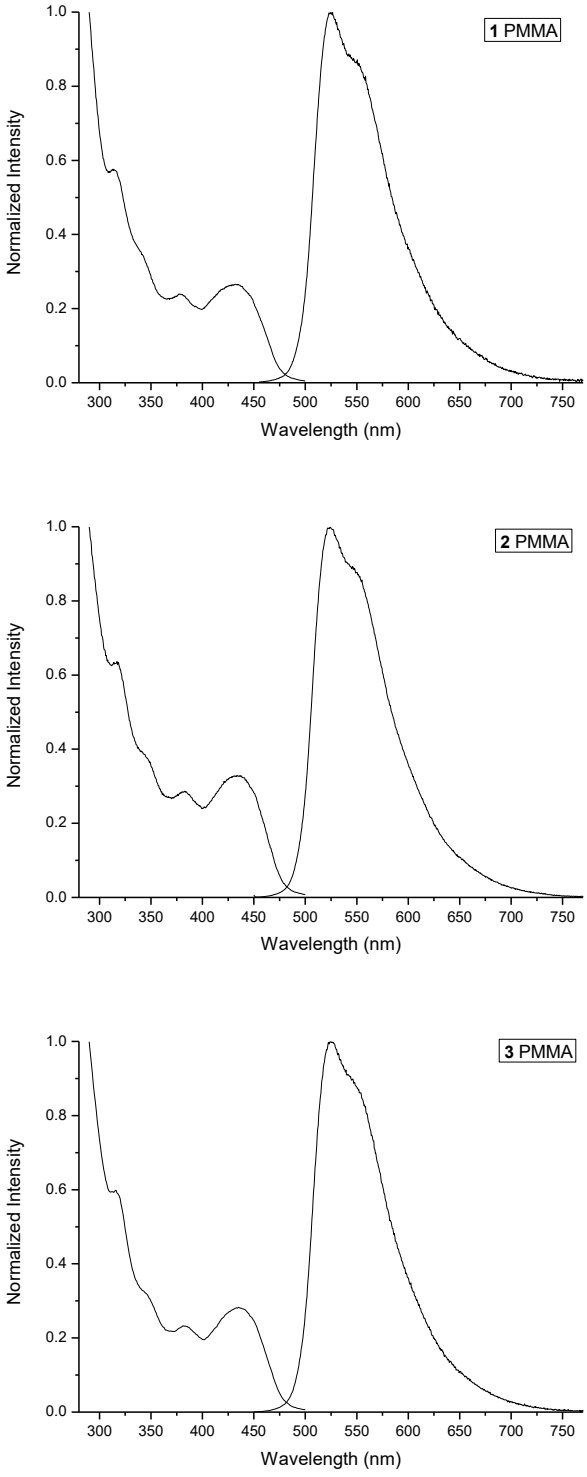


**Figure S22.** Excitation and emission spectra of complexes **1**-**3** in PMMA matrices (2 wt%) at 298 K. The collected $\lambda_{em}$ of the excitation spectra corresponds to the highest-energy peak of the emission.

## 3. Computational methods and data

DFT calculations were carried out with Gaussian 16,[1] using the B3LYP functional[2,3] together with the 6-31G**[4,5] basis set for the C, H, N, and O atoms and the LANL2DZ[6] basis set and effective core potential for the Pt atom. Geometry optimizations were performed with no restrictions on symmetry. The solvent effect (dichloromethane) was accounted by using the SMD variation of the Polarizable Continuum Model, as implemented in Gaussian.[7] The optimized structures were confirmed as minima on the potential energy surface by performing frequency calculations (no imaginary frequencies).

**Table S1.** Energies, free energies, enthalpies and entropies of the optimized structures.[a]

| Stereoisomers | $E_0$ [b] | ZPE [c] | G [d] | H [e] | S [f] |
|---|---|---|---|---|---|
| *cisoid* | -2845.491766 | -2844.551455 | -2844.659086 | -2844.489771 | 356.353 |
| *transoid* | -2845.491906 | -2844.551050 | -2844.658061 | -2844.489483 | 354.801 |

[a] Thermal corrections from vibrational calculations at 298.15 K. [b] Electronic energy (Hartrees). [c] Sum of electronic and zero-point energies (Hartrees). [d] Free Energy (Hartrees). [e] Enthalpy (Hartrees). [f] Entropy (cal $mol^{-1}$ $K^{-1}$).

**Table S2.** Cartesian coordinates (Å) of the optimized structures.

**1**

| | | | |
|---|---|---|---|
| C | -3.818563026 | 7.368097483 | 6.829944912 |
| C | -3.789044699 | 8.757182893 | 6.638027881 |
| C | -4.793178596 | 9.443205051 | 5.743408391 |
| H | -4.557416140 | 6.771379013 | 6.299578813 |
| H | -4.403508847 | 10.389337300 | 5.355082092 |
| H | -5.718876475 | 9.671782846 | 6.287898336 |
| H | -5.068550307 | 8.811817851 | 4.892372458 |
| C | 4.698299919 | 6.419750786 | 11.504560731 |
| C | 5.392568955 | 7.450074394 | 10.879572448 |
| C | 4.703588051 | 8.253590041 | 9.969909243 |
| C | 3.358016278 | 8.001207631 | 9.723240994 |
| C | 2.706985521 | 6.950203246 | 10.382935790 |
| C | 1.285950908 | 6.594392031 | 10.205786139 |
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| N | 3.399960920 | 6.166966677 | 11.271900968 |
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| N | 4.083338064 | 2.350800834 | 13.288207207 |
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| C | 4.570627203 | 2.467554576 | 10.034066904 |
| C | 5.621557762 | 2.267916278 | 9.202252604 |
| H | 3.741530954 | 3.158117164 | 9.993220136 |
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| H | 8.342961728 | 1.490966027 | 9.035894888 |
| H | 7.967686475 | -0.103579563 | 9.746829441 |
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| C | 5.203048029 | -2.199087130 | 11.843461928 |

| | | | |
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| H | 10.744084816 | -0.752348816 | 15.254759883 |
| C | 8.804845941 | -5.204464658 | 15.990827391 |
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| H | 3.050712116 | 5.861634315 | 14.589058608 |
| H | 3.420219513 | 5.211792122 | 16.205394266 |

**1'**

| | | | |
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| C | -5.503738141 | 8.747685114 | 5.805980426 |
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