^{3}MMLCT excited states of luminescent binuclear Pd^{II} complexes: excited state inner-sphere electron-transfer reactions and application

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General Information

Chemicals and instrumentations

All chemicals were purchased from commercial sources and used without further purification. Unless otherwise noted, solvents of analytical grade were used for the synthesis. Dry DMF (99.8%, water: ≤30 ppm, with molecular sieves) was purchased from J&K Scientific and used as received. Solvents for photophysical measurements are of HPLC grade.

NMR spectra were performed on Bruker Advance 400, 500 and 600 FT-NMR spectrometers at 298 K. Chemical shifts are reported relevant to the solvent residual peak(s) or tetramethylsilane (TMS) as internal reference. High-resolution electrospray ionization (ESI) mass spectra were recorded on a Bruker Q-Tof Maxis II mass spectrometer. Elemental analyses were conducted at the Institute of Chemistry of the Chinese Academy of Sciences, Beijing. X-Ray diffraction data of single crystals were collected on SuperNova (Cu) X-ray Source diffractometer and Bruker D8 VENTURE Duo FIXED-CHI X-ray diffractometer. The X-ray crystallographic coordinates for structures reported in this work have been deposited at Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2353065 (**1**), CCDC 2053114 (**2**)**,** CCDC 1976305 (**3**), CCDC 2353099 (**4**), CCDC 2018758 (**5**) and CCDC 2353067 (**Ref-Pt1**). Cyclic voltammetry was conducted on CH Instruments Electrochemical Analyzer CHI620E with a three-electrode cell system (working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: saturated calomel electrode) and with samples in 0.1 M NBu_4PF_6 as supporting electrolyte in CH_2Cl_2 for anodic sweeps and DMF in cathodic sweeps. EPR (electron paramagnetic resonance) spectra were recorded by Bruker EMXplus-10/12 instrument at Southern University of Science and Technology. UV-Vis absorption spectra were recorded on a Hewlett-Packard 8453 A diode array spectrophotometer. Steady-state emission spectra were recorded on a Horiba Fluorolog-3 spectrophotometer. Emission spectrum of **Ref-Pt1** in deoxygenated CH_2Cl_2 was measured in Edinburgh FLS1000 photoluminescence spectrometer equipped with a NIR-PMT 1700 detector. Solutions for photophysical studies were degassed by five freeze-pump-thaw cycles using a high vacuum line prior to measurement. The thin films were prepared by drop-cast from a chlorobenzene solution containing different weight percent of the complex and PMMA. These thin films were then placed in an oven at 60 ˚C for 30 minutes at the time they became translucent. Emission quantum yields of samples in thin films were measured with Hamamatsu

C11347 Quantaurus-QY Absolute PL quantum yields measurement system. The emission quantum yield in solution was measured with $[Ru(2,2'\text{-bipyridine})_3](PF_6)_2$ (in degassed MeCN, $\Phi_{em} = 0.062$)[1] or Pt(tptbp) (in toluene, Φ_{em}: 0.51)[2] as reference standard and calculated by: $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, in which the subscripts s and r refer to sample and reference standard solution, respectively; n is the refractive index of the solvents; D is the integrated emission intensity and Φ is the luminescence quantum yield; B is calculated by: $B = 1–10^{-AL}$; A is the absorbance at the excitation wavelength and L is the optical path length (λ = 1 cm in all cases). The emission lifetime measurements were performed on a Quanta Ray GCR 150-10 pulsed Nd:YAG laser system.

Time-resolved spectroscopy

Femtosecond time-resolved transient absorption (fs-TA) measurements were performed based on a commercial Ti:Sapphire regenerative amplifier laser system (800 nm, 120 fs, 1 kHz, and 3.5 mJ/pulse). A 400 nm excitation wavelength was used for all measurements. The 400 nm excitation pulse was produced from the second harmonic of the 800 nm fundamental laser pulse. In the fs-TA, the samples were probed by a white light continuum pulse created from sapphire pumped by the 800 nm laser. The temporal delay of probe to pump pulse was varied by a computer controlled optical delay line. The fs-TA signals were collected by a monochromator and detected with an air-cooled CCD detector. The instrument response function (IRF) for the fs-TA is ~200–400 fs varying slightly with the spectral wavelength. Femtosecond time-resolved fluorescence (fs-TRF) measurements were performed on the same setup as fs-TA. The output 800 nm laser pulse (200 mW) is used as gate pulse while the 400 nm laser pulse (10 mW) (second harmonic) is used as the pump laser. After excitation by the pump laser, the sample fluorescence is focused into the nonlinear crystal (BBO) mixing with the gate pulse to generate the sum frequency signal. Broad band fluorescence spectra are obtained by changing the crystal angles and the spectra are detected by the air-cooled CCD. For the present experiments, the compound in solution were excited by a 400 nm pump beam (the second harmonic of the fundamental 800 nm from the regenerative amplifier). The 1 mL solutions were studied in a 2 mm path-length cuvette with an absorbance of 2 at 400 nm throughout the data acquisition. Nanosecond time-resolved emission (ns-TRE) measurements were performed on a LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd., Livingston, UK). The excitation source was the 355 nm output (third harmonic) of a Nd:YAG laser (Spectra-Physics Quanta-Ray Lab-130 Pulsed Nd:YAG Laser). The signals were processed by a PC plug-in controller with L900 software. The preparation of samples for the ns-TRE measurements was the same as those for steady-state emission measurements.

Computational details

All calculations were performed with the Gaussian 09 program package and the Amsterdam Density Functional (ADF) package.[3] DFT-D3 methods developed by Grimme[4] have been utilized in this work. The DFT-D3 method has been proved that it could provide quite reliable calculated energies compared to SCS-MP2 method for large dimeric complexes.[5] For the geometry optimization, hybrid functional PBE0[6] with dispersion corrections in revision three (D3)[7] in the Gaussian program has been employed.[8] The effective core potentials LAN2DZ (ECPs) proposed by Hay and Wadt[9,10] were employed on platinum atom. The 6-31G* basis set[11,12] was used for other atoms. Solvent effects were taken into account by the polarizable continuum model (PCM) with CH_2Cl_2 as solvent.[13] The optimization of the triplet excited states was performed using unrestricted DFT method. The single point energy calculation was performed at a higher calculation level of PBE0-D3/def2-TZVP/PCM(CH_2Cl_2) level.

To calculate the radiative decay rate, spin–orbit coupling approach (SOC)[14] implemented in the Amsterdam density functional program package (ADF2014) has been used. B3LYP[15,16] functional with COSMO model[17-19] was used for its accuracy in predicting the radiative decay rate.[20] As for the basis set, relativistic effects were taken into account by a scalar zero order regular approximation (ZORA) approach.[21-24] Slater basis sets orbitals were employed for Pt atoms and double-ζpolarized (DZP)[25] Slater basis sets orbitals were used for other atoms.

The radiative rate constant from the three spin sublevels i (i = 1,2,3) of T_1 state can be expressed as equation (1):[26]

$$k_i = \frac{4}{3t_0}\alpha_0^3(\Delta E_i)^3\sum_{j\in x,y,z}\left|M_j^i\right|^2 \qquad (1)$$

where ΔE_i is the transition energy, α_0 is the fine structure constant, $t_0 = (4\pi\varepsilon_0)^2\hbar^3/m_e e^4$ and M_j^i is the j projection of the electric dipole transition moment between the ground state and the ith substate of the emissive triplet state, T_1. The average radiative decay rate over three substates can be given with respect to the temperature T:

$$k_{r,avg} = \frac{k_1 + k_2 e^{-\left(\frac{\Delta E_{1,2}}{k_B T}\right)} + k_3 e^{-\left(\frac{\Delta E_{1,3}}{k_B T}\right)}}{1 + e^{-\left(\frac{\Delta E_{1,2}}{k_B T}\right)} + e^{-\left(\frac{\Delta E_{1,3}}{k_B T}\right)}} \quad (2)$$

$k_{1,2,3}$ are the radiative decay rates of three substates respectively. The ZFS was calculated as the energy separations between the individual substates (i.e., $\Delta E_{1,2}$ and$\Delta E_{1,3}$). Generally, the ZFSs for d^8 organometallic compounds are less than 100 cm^{-1};[27] therefore, at room temperature (RT), the average phosphorescence rates of d^8 transition metal complexes can be simplified as:

$$k_{r,avg} = \frac{k_1 + k_2 + k_3}{3} \quad (3)$$

OLED fabrication

Figure S1 shows the chemical structures of the materials used in OLED fabrication. HAT-CN, TAPC, CCP, PPF, and TmPyPb were obtained commercially and used as received without further purification. Indium-tin-oxide (ITO) coated glass with a sheet resistance of 10 Ω/sq was used as the anode substrate. Before film deposition, patterned ITO substrates were cleaned with detergent, rinsed in de-ionized water, acetone, and isopropanol, and then dried in an oven for 1 hr in a cleanroom. The slides were then treated in an ultraviolet-ozone chamber for 5 mins. The OLEDs were fabricated in a Kurt J. Lesker SPECTROS vacuum deposition system with a base pressure of 10^{-7} mbar. In the vacuum chamber, organic materials were thermally deposited in sequence at a rate of 0.5 Å s^{-1}. The doping process in the EMLs or ETLs was realized using co-deposition technology. Afterward, LiF (1.2 nm) and Al (100 nm) were thermally deposited at rates of 0.02 and 0.2 nm s^{-1}, respectively. The film thicknesses were determined in situ with calibrated oscillating quartz-crystal sensors. Current density-brightness-voltage characteristics, EL spectra, and EQE of EL device were obtained by using a Keithley 2400 source-meter and an absolute external quantum efficiency measurement system (C9920-12, Hamamatsu Photonics). All devices were encapsulated in a 200-nm-thick Al_2O_3 thin film deposited by atomic layer deposition (ALD) in a Kurt J. Lesker SPECTROS ALD system.

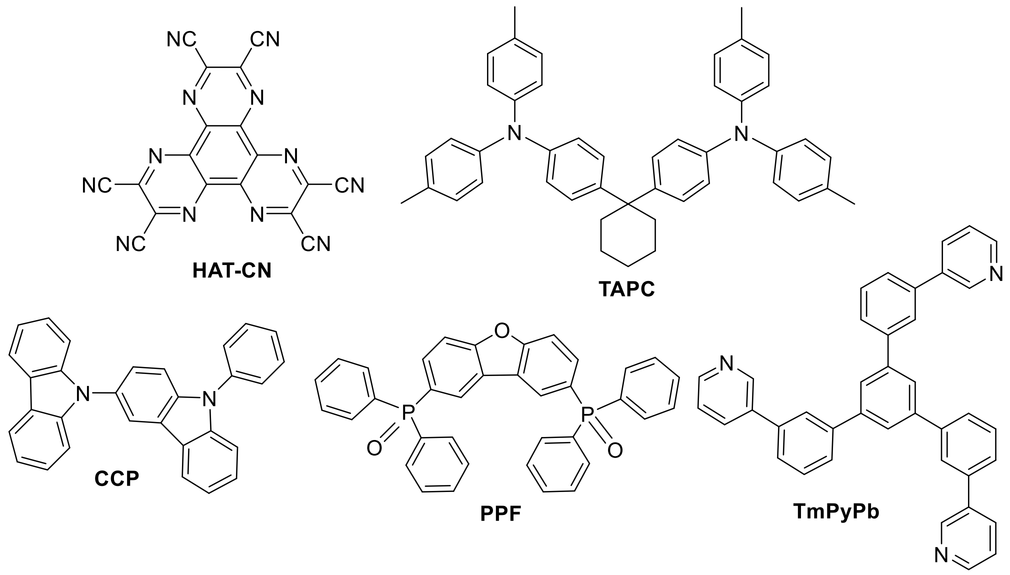


Figure S1. Chemical structures of materials used in OLED fabrication.

EPR experiment

*1. Chemical oxidation of complex **1** with (TBPA)SbCl$_6$*

A pre-chilled CH_2Cl_2 solution of (TBPA)SbCl$_6$ (0.00049 mmol, 0.4 mg, 150 µL) was added to a pre-chilled CH_2Cl_2 solution of complex **1** (0.00098 mmol, 1.16 mg, 150 µL). The resulting reaction mixture was quickly transferred to a pre-chilled EPR tube and frozen in liquid nitrogen, then analyzed by EPR at 100 K.

*2. Chemical oxidation of complex **5** with (TBPA)SbCl$_6$*

A pre-chilled CH_2Cl_2 solution of (TBPA)SbCl$_6$ (0.00049 mmol, 0.4 mg, 150 µL) was added to a pre-chilled CH_2Cl_2 solution of complex **5** (0.00098 mmol, 1.17 mg, 150 µL). The resulting solution was transferred to the pre-chilled EPR tube and frozen in liquid nitrogen, then analyzed by EPR at 100 K.

*3. Photoreaction of complex **5** with benzyl bromide*

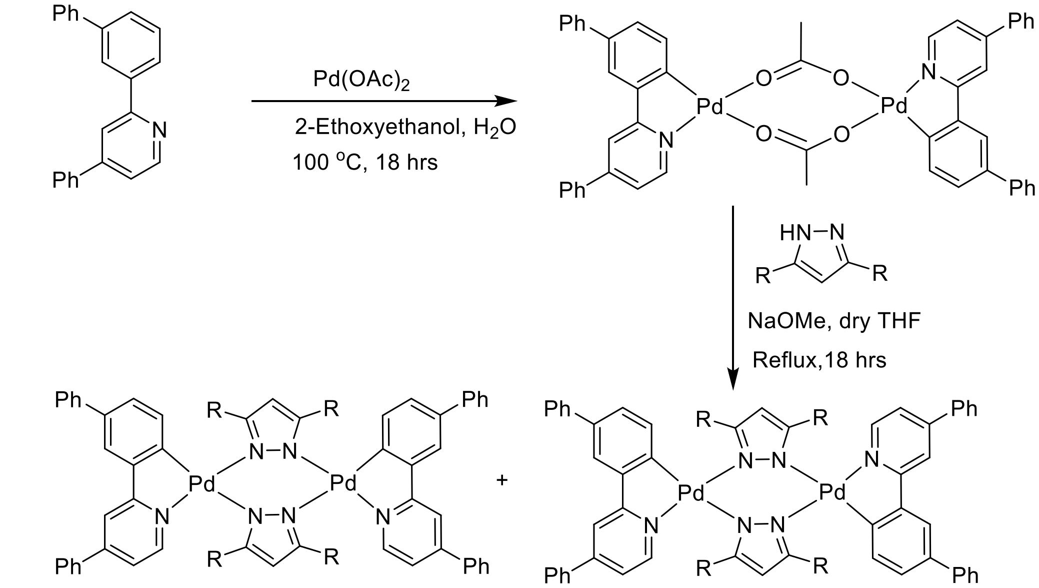
A 0.3 mL benzene solution of benzyl bromide (0.049 mmol, 8.38 mg) and complex **5** (0.00098 mmol, 2 mg) was added to the EPR tube. The reaction was frozen in liquid nitrogen and irradiated by light (($\lambda > 380$ nm). The reaction mixture was subjected to EPR analysis at 100 K at different irradiation time intervals until sufficient radicals were generated to give optimal EPR resolution.

Procedures for photocatalysis

***Photo-induced intramolecular cyclization of indoles/pyrroles*:** A J-Young tube containing indoles/pyrroles (0.05 mmol), DIPEA (0.10 mmol), complex **5** (2.5 mol%) and 0.56 mL benzene-d_6 was degassed by five freeze-pump-thaw cycles using a high vacuum line. The tube was then placed in a photoreactor equipped with LED lamps (λ_{max} = 400 nm, 24 W) for 2 hrs. The internal standard, 1,3,5-trimethoxybenzene, was added to the reaction mixture, which was subsequently subjected to ^{1}H NMR analysis to calculate the substrate conversion and product yield. The identification of product is based on the previously reported literature.[28]

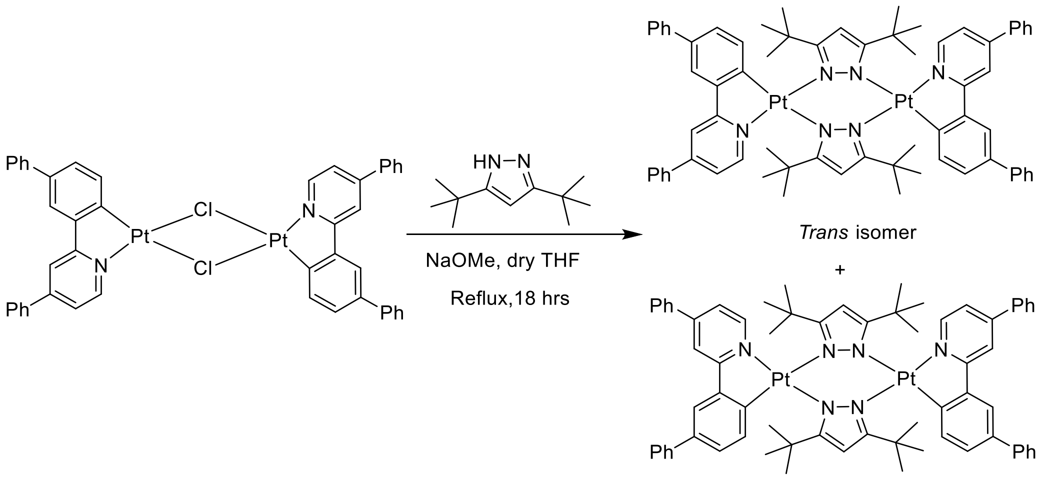
Photo-induced aerobic C-C coupling reaction of N-phenyl-1,2,3,4-tetrahydroisoquinoline with acetone: *N*-Phenyl-1,2,3,4-tetrahydroisoquinoline (0.128 mmol), acetone (0.4 mL), L-proline (0.128 mmol), **PC** (1 mol%), MeCN (0.4 mL) and MeOH (0.8 mL) were added to a 10 mL reaction tube. The reaction tube was sealed, and the reaction mixture was bubbled with oxygen for 15 mins. The tube was then placed in a photoreactor equipped with LED lamps (λ_{max} = 455 nm, 24 W) for 6 hrs. After reaction, solvents were removed under vacuum, and the internal standard, 1,3,5-trimethoxybenzene, was added to the reaction mixture, which was subsequently subjected to ^{1}H NMR analysis to calculate the substrate conversion and product yield. The identification of product is based on the previously reported literature.[29]

Syntheses and Characterization of Metal Complexes



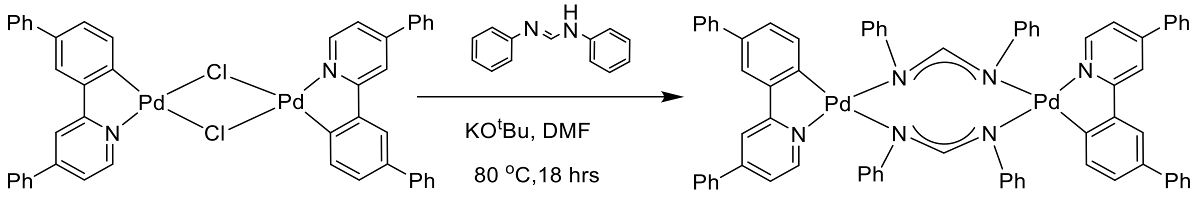
cis isomer + *trans* isomer

$[Pd(C^{\wedge}N)(Pz)]_2$: R = ^{t}Bu **1** R = H **2**



Cis isomer

Ref-Pt1



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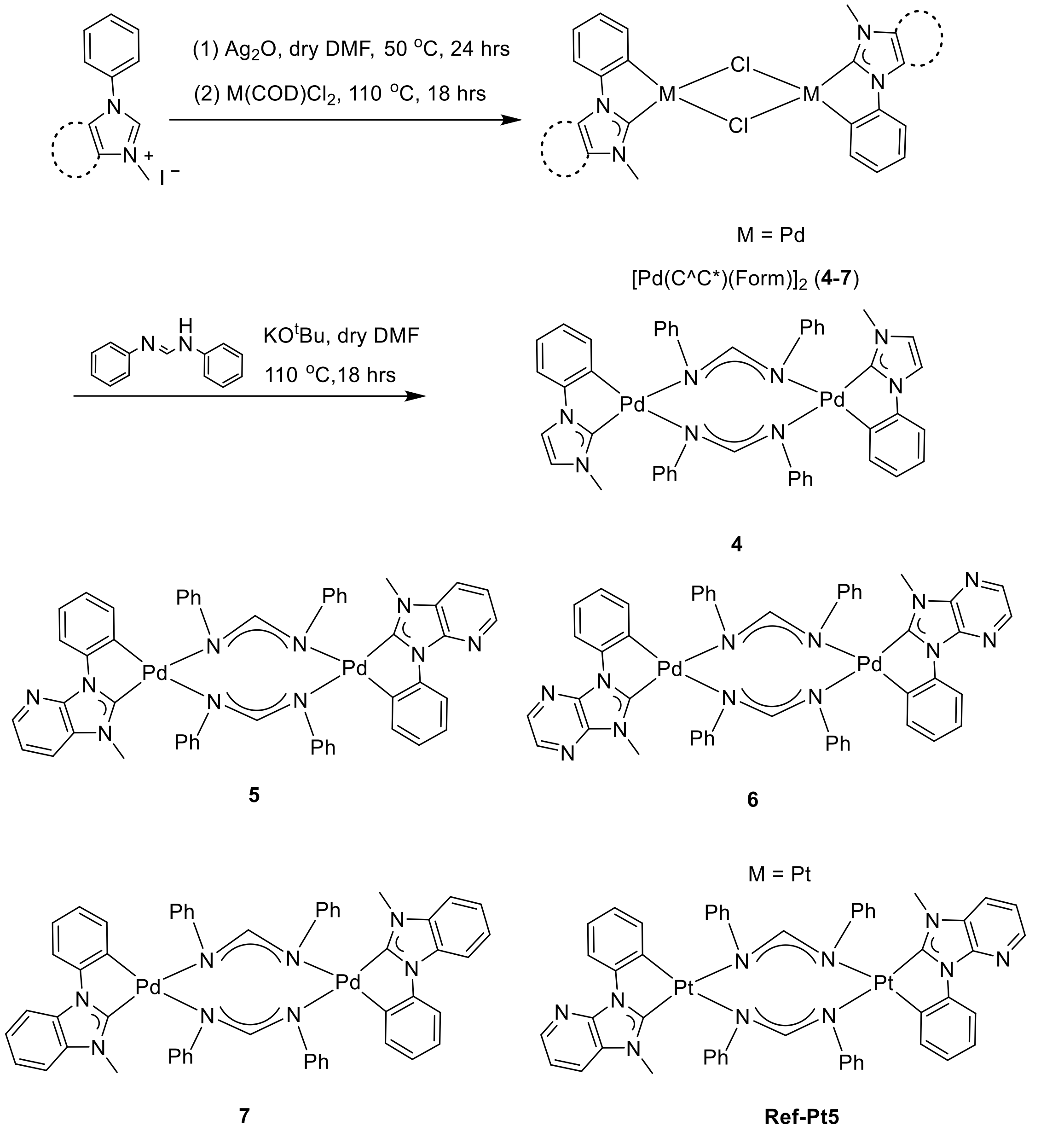


Scheme S1. Synthetic scheme and chemical structures of complexes **1**–**7**, **Ref-Pt1** and **Ref-Pt5**.

1: A mixture of $[Pd(C\text{^}N)(OAc)]_2$ (C^N = 2-[1,1'-biphenyl]-3-yl-4-phenylpyridine) (94.3 mg, 0.10 mmol), 3,5-di-*tert*-butyl-1h-pyrazole (36.0 mg, 0.20 mmol) and sodium methoxide (10.8 mg, 0.20 mmol) in dry THF (30 mL) was refluxed under argon for 18 hrs. Afterwards, the reaction was cooled down to room temperature and quenched with H_2O and the product was extracted with CH_2Cl_2. The organic layers were combined and dried with $MgSO_4$. Solvent was removed under vacuum and the resulting orange solids were washed with MeOH three times to obtain the analytical pure product. Yield: 69%. This complex was isolated as a mixture of *cis* and *trans* isomers (with mutual orientation of the two cyclometalated ligands) with the *cis*/*trans* ratio of 1:1.4. ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.05 *trans* and 8.03 *cis* (d, 2H total), 7.63 *cis* (s, 1H), 7.48–7.22 (m, 23H), 7.04–6.97 (m, 3 H), 6.87 *cis* (d, *J* = 8.0, 1H), 6.81 *trans* (dd, *J* = 5.9, 1.7, 1H), 6.68 *trans* (d, *J* = 8.0, 1 H), 6.11 *cis* and 6.09 *trans* and 6.07 *cis* (m, 2H total), 1.57–1.55 (m, 36H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 166.49, 165.44, 160.02, 159.83, 159.20, 158.86, 158.34, 157.05, 152.02, 151.25, 150.39, 150.20, 145.90, 145.26, 141.87, 141.64, 138.61, 137.77, 137.57, 136.54, 136.45, 129.98, 129.74, 129.47, 129.33, 128.93, 128.89, 128.78, 127.36, 127.29, 127.27, 127.12, 126.97, 126.93, 120.61, 119.54, 119.30, 116.01, 115.43, 100.79, 100.11, 99.49, 32.74, 32.67, 32.63, 32.42, 32.34, 32.22. Anal. Calcd. for $C_{68}H_{70}N_6Pd_2$: C 68.97, H 5.96, N 7.10; found: C 69.02, H 5.90, N 7.09. HRMS(ESI-QTOF) m/z: calcd: 1185.3808; found:1185.3825 [$(M+H)^+$].

2: The synthetic procedure of **2** is similar to that of **1**, except that pyrazole was used instead of 3,5-di-*tert*-butyl-1h-pyrazole. Pale yellow solid, yield: 30%. This complex was isolated as a mixture of *cis* and *trans* isomers (with mutual orientation of the two cyclometalated ligands) with the *cis*/*trans* ratio of 1:2.0. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.42 *cis* (d, *J* = 6.0 Hz, 1H), 8.31 *trans* (d, *J* = 6.0 Hz, 2H), 8.05 *cis* (s, 1H), 8.03 *trans* (s, 2H), 7.83 (t, *J* = 2.2 Hz, 3H), 7.76–7.70 (m, 9H), 7.67 *trans* (d, *J* = 1.9 Hz, 2H), 7.66 *cis* (d, *J* = 2.1 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 6H), 7.55–7.47 (m, 9H), 7.45–7.40 (m, 6H), 7.36–7.29 (m, 9H), 7.20 *trans* (d, *J* = 8.0 Hz, 2H), 7.10 *cis* (d, *J* = 8.0 Hz, 1H), 6.46 *cis* and 6.44 *trans* and 6.42 *cis* (m, 3H total). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 166.72, 166.45, 156.57, 156.18, 151.42, 151.40, 150.68, 150.55, 146.93, 146.73, 141.67, 141.62, 139.73, 138.20, 138.09, 137.85, 137.83, 137.56, 136.33, 130.31, 130.27, 129.63, 129.61, 129.12, 129.10, 128.39, 128.16, 127.50, 127.37, 127.33, 127.21, 127.19, 122.04, 120.79, 120.52, 116.96, 105.69, 105.50, 105.29. Anal. Calcd. for $C_{52}H_{38}N_6Pd_2 \cdot CH_3OH$: C 64.18, H 4.27, N 8.47; found: C 64.23, H 4.20, N 8.30. HRMS(ESI-QTOF) m/z: calcd: 983.1145; found 983.1085 [$(Monna)^+$].

3: A mixture of $[Pd(C^\wedge N)Cl]_2$ (C^N = 2-[1,1'-biphenyl]-3-yl-4-phenylpyridine) (100 mg, 0.33 mmol), *N*,*N*-diphenylformamidine (134 mg, 0.68 mmol) and potassium *tert*-butoxide (76.3 mg, 0.68 mmol) was heated at 80 ˚C in DMF (10 mL) under argon atmosphere for 12 hrs. After cooling to room temperature, the reaction mixture was filtered through a short pad of celite and the solvent was removed under vacuum. The product was purified by column chromatography on SiO_2 with CH_2Cl_2/hexane (1:1 v/v) as eluent and recrystallized in methanol. Yellow solid, yield: 35%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.15 (s, 2H), 7.63 (d, *J* = 7.8 Hz, 4H), 7.53 (d, *J* = 7.8 Hz, 4H), 7.44–7.22 (m, 32H), 7.19 (s, 2H), 7.12 (t, *J* = 7.8 Hz, 4H), 7.02 (t, *J* = 7.3 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (126 MHz,

CD_2Cl_2) δ 165.18, 162.10, 157.64, 152.27, 151.92, 151.15, 149.40, 146.28, 141.60, 138.24, 137.58, 136.66, 135.91, 129.89, 129.55, 129.19, 129.04, 128.94, 127.81, 127.28, 127.16, 126.97, 124.22, 123.09, 122.48, 122.28, 121.52, 119.38, 115.39. Anal. Calcd. for $C_{72}H_{54}N_6Pd_2\cdot 0.5CH_3OH$: C 70.67, H 4.58, N 6.82; found: C 70.78, H 4.74, N 6.72. HRMS(ESI-QTOF) m/z: calcd:1217.2585; found 1217.2555 [$(M+H)^+$].

4: To a solution of 1-methyl-3-phenylimidazolium iodide (100 mg, 0.35 mmol) in dry DMF (10 mL) was added Ag_2O (40 mg, 0.17 mmol). The mixture was stirred at 50 ^oC for 24 hrs in dark. $Pd(COD)Cl_2$ (99.8 mg, 0.35 mmol) was added subsequently to the mixture and the resulting mixture was heated at 110 ^oC for 18 hrs. Afterwards, the reaction was cooled down to room temperature and the reaction mixture was added *N,N*-diphenylformamidine (137 mg, 0.7 mmol), potassium *tert*-butoxide (79 mg, 0.7 mmol) and heated at 110 ˚C for 18 hrs. The reaction mixture was then cooled to room temperature and filtered through a short pad of celite. Solvent was removed under vacuum. The analytical products were obtained by column chromatography on SiO_2 with CH_2Cl_2/hexane (1:2 v/v) as eluent. Pale yellow solid, yield: 15%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.10 (s, 2H), 7.45 (dd, *J* = 8.4, 1.0 Hz, 4H), 7.38 (dd, *J* = 8.5, 0.9 Hz, 4H), 7.34 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.22–7.16 (m, 4H), 7.07–7.01 (m, 4H), 6.98–6.89 (m, 4H), 6.88 (d, *J* = 2.0 Hz, 2H), 6.83–6.74 (m, 6H), 6.17 (d, *J* = 2.0 Hz, 2H), 2.42 (s, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm) 173.13, 162.13, 153.97, 152.50, 147.23, 145.48, 137.80, 128.79, 128.55, 124.39, 123.74, 123.69, 122.58, 122.26, 121.53, 120.64, 113.21, 110.31, 35.29. Anal. Calcd. for $C_{46}H_{42}N_8Pd_2$: C 60.07, H 4.60, N 12.18; found: C 60.11, H 4.30, N 11.85. HRMS(ESI-QTOF) m/z: calcd:919.1528; found: 919.1510 [$(M+H)^+$].

5: The synthetic procedure of **5** is similar to that of **4** using 1-methyl-3-phenyl-3H-imidazo[4,5-b]pyridin-1-ium iodide. The product was purified by column chromatography on SiO_2 with CH_2Cl_2/hexane (2:1 v/v) as eluent. Greenish yellow solid, yield: 30%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.21 (s, 2H), 8.10 (d, *J* = 4.6 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.46 (dd, *J* = 7.9, 3.3 Hz, 8H), 7.26 (d, *J* = 7.8 Hz, 4H), 7.22–7.14 (m, 6H), 7.10 (t, *J* = 7.8 Hz, 4H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 2H), 2.88 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm) 184.79, 162.33, 153.60, 151.96, 147.24, 145.03, 144.48, 143.76, 137.00, 128.85, 128.82, 126.75, 124.22, 123.70, 123.67, 122.81, 122.49, 122.05, 118.41, 114.31, 31.99. Anal. Calcd. for $C_{52}H_{42}N_{10}Pd_2$: C 61.24, H 4.15, N 13.73; found: C 60.98, H 4.11, N 13.62. HRMS(ESI-QTOF) m/z: calcd: 1360.4951; found: 1360.4888 [$(M)^+$].

6: The synthetic procedure of **6** is similar to that of **4** using 1-methyl-3-phenyl-1H-imidazo[4,5-b]pyrazin-3-ium iodide. The product was purified by column chromatography on SiO_2 with CH_2Cl_2/ hexane (1:1 v/v) as eluent and recrystallized from CH_2Cl_2/MeOH solution. Yellow solid, yield: 20%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) 8.29 (d, *J* = 2.8 Hz, 2H), 8.26 (d, *J* = 2.8 Hz, 2H), 8.21 (s, 2H), 7.54 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.48 (dd, *J* = 8.5, 1.0 Hz, 4H), 7.38 (dd, *J* = 8.5, 1.0 Hz, 4H), 7.25–7.19 (m, 4H), 7.14–7.06 (m, 4H), 6.98–6.92 (m, 2H), 6.92–6.86 (m, 2H), 6.82 (dd, *J* = 7.5, 1.2 Hz, 2H), 6.36 (td, *J* = 7.6, 1.3 Hz, 2H), 6.16 (td, *J* = 7.4, 1.3 Hz, 2H), 3.69 (s, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm) 188.30, 162.40, 153.17, 151.79, 146.35, 144.56, 140.06, 138.68, 138.11, 137.22, 136.04, 129.16, 128.65, 124.04, 123.51, 123.30, 122.71, 122.59, 122.52, 113.80, 31.27. Anal. Calcd. for $C_{50}H_{40}N_{12}Pd_2$: C 58.77, H 3.95, N 16.45; found: C 59.01, H 3.88, N 16.33. HRMS(ESI-QTOF) m/z: calcd: 1022.1567; found: 1022.1634 [$(M)^+$].

7: The synthetic procedure of **7** is similar to that of **4** using 1-phenyl-3-methylbenzimidazolium iodide. The product was purified by column chromatography on SiO_2 with CH_2Cl_2/hexane (1:20 v/v) as eluent and recrystallized from CH_2Cl_2/MeCN solution. Greenish solid, yield: 25%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) 8.22 (s, 2H), 7.46 (dd, *J* = 13.4, 7.8 Hz, 10H), 7.20 (dd, *J* = 16.0, 8.1 Hz, 6H), 7.04 (dt, *J* = 12.1, 7.5 Hz, 6H), 6.91 (ddd, *J* = 11.1, 8.1, 5.7 Hz, 10H), 6.79 (ddd, *J* = 9.9, 8.6, 4.5 Hz, 4H), 2.69 (s, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm) 183.04, 162.20, 153.70, 152.08, 148.23, 145.89, 137.73, 134.11, 130.12, 128.87, 128.66, 124.17, 123.91, 123.87, 123.73, 122.83, 122.64, 122.40, 121.78, 111.76, 111.11, 110.90, 31.63. Anal. Calcd. for $C_{54}H_{44}N_8Pd_2 \cdot 0.2CH_2Cl_2$: C 62.91, H 4.32, N 10.83; found: C 62.83, H 4.48, N 11.26. HRMS(ESI-QTOF) m/z: calcd: 1018.1757; found: 1018.1796 [$(M)^+$].

Ref-Pt1: The Pt(II) μ-dichloro-bridged dimer (50 mg, 0.047 mmol), 3,5-di-*tert*-butyl-1H-pyrazole (18.5 mg, 0.10 mmol) and NaOMe (5.3 mg, 0.10 mmol) were suspended in dry THF (15.0 mL) and refluxed for 18 hrs under argon atmosphere. After cooling to room temperature, the reaction mixture was added H_2O and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The product was purified by flash column chromatography on SiO_2 using CH_2Cl_2/hexane (9:1 v/v) as eluent. Red solid, yield: 17%. This complex was isolated as a mixture of *cis* and *trans* isomers (with mutual orientation of the two cyclometalated ligands) with a *cis*/*trans* ratio of 1:0.16. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.30 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.77 *cis* (d, *J* = 1.9 Hz, 2H), 7.65–7.58 (m, 5H), 7.57–7.51 (m, 4H), 7.51–7.41 (m, 6H), 7.41–

7.30 (m, 5H), 7.25 (t, *J* = 7.4, 2H), 7.18 *cis* (dd, *J* = 8.0, 1.9 Hz, 2H), 7.14–6.95 (m, 4H), 6.34 *cis* and 6.30 *trans* and 6.07 *cis* (m, 2H total), 1.56–1.49 (m, 36H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 168.37, 159.55, 158.02, 150.90, 150.10, 147.01, 145.45, 142.16, 137.77, 137.44, 135.64, 130.00, 129.86, 129.51, 129.42, 128.95, 127.95, 127.30, 127.26, 126.95, 126.82, 126.77, 121.20, 119.40, 116.53, 102.39, 101.80, 32.97, 32.95, 32.91, 32.85, 32.41, 32.35, 32.23, 31.97. Anal. Calcd. for $C_{68}H_{70}N_6Pt_2$: C 59.99, H 5.18, N 6.17; found: C 59.92, H 5.20, N 6.09. HRMS(ESI-QTOF) m/z: calcd: 1360.4951; found: 1360.4888 [M].

Ref-Pt5: This complex was previously reported by Strassner and co-workers and was synthesized according to the literature.[30]

<u>NMR analysis of complexes **1**, **2** and **Ref-Pt1**</u>

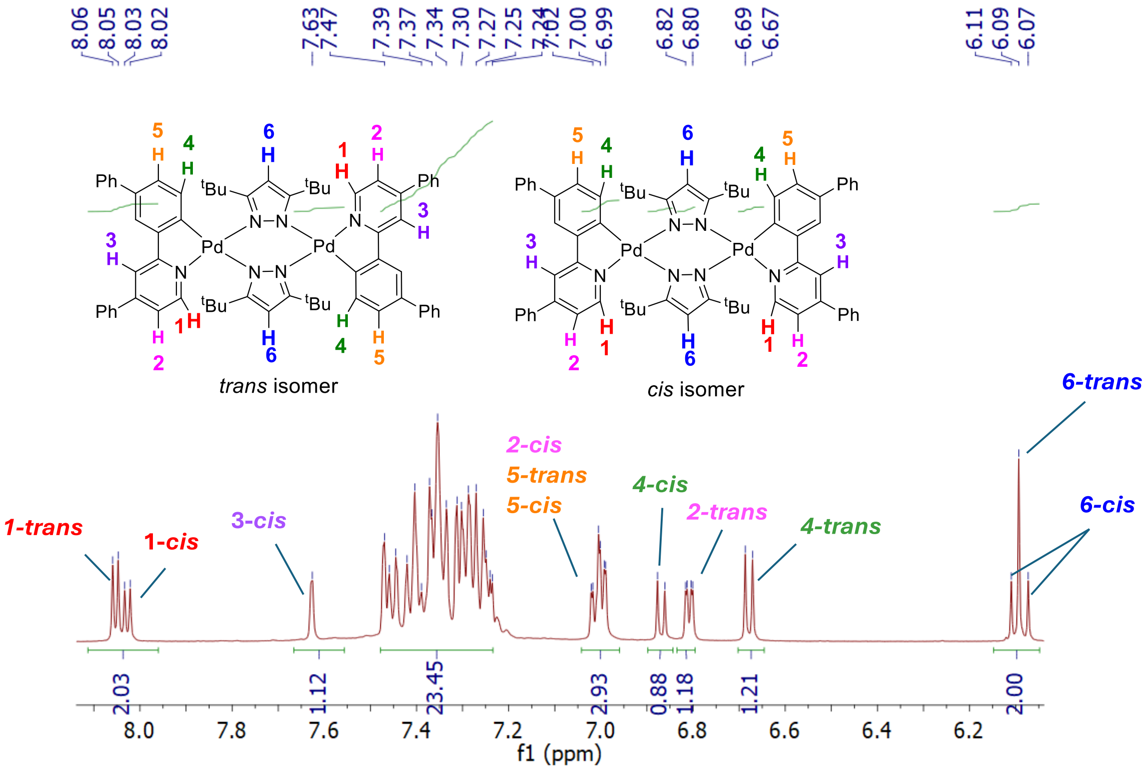


Figure S2. ^{1}H NMR spectrum of complex **1** in CD_2Cl_2, focusing on aromatic region and assignment of characteristic protons.

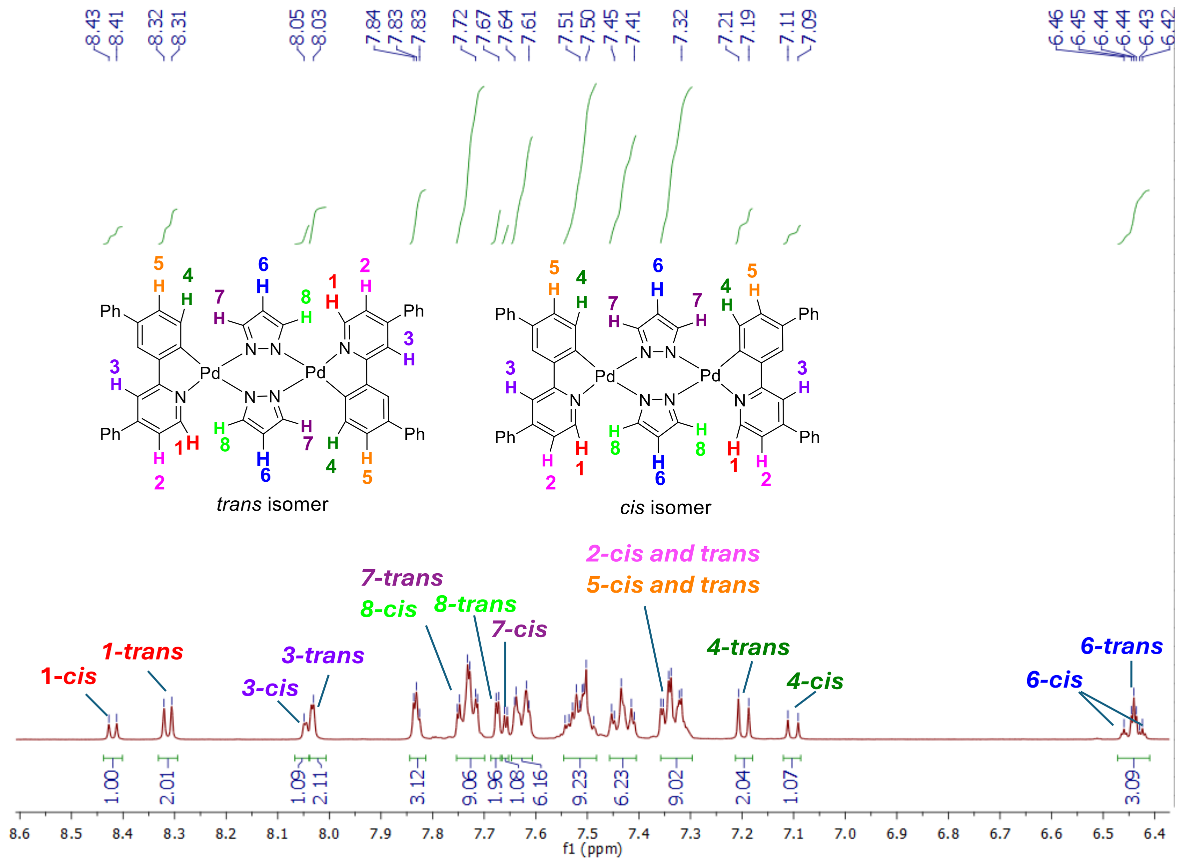


Figure S3. ^{1}H NMR spectrum of complex **2** in CD_2Cl_2, focusing on aromatic region and assignment of characteristic protons.

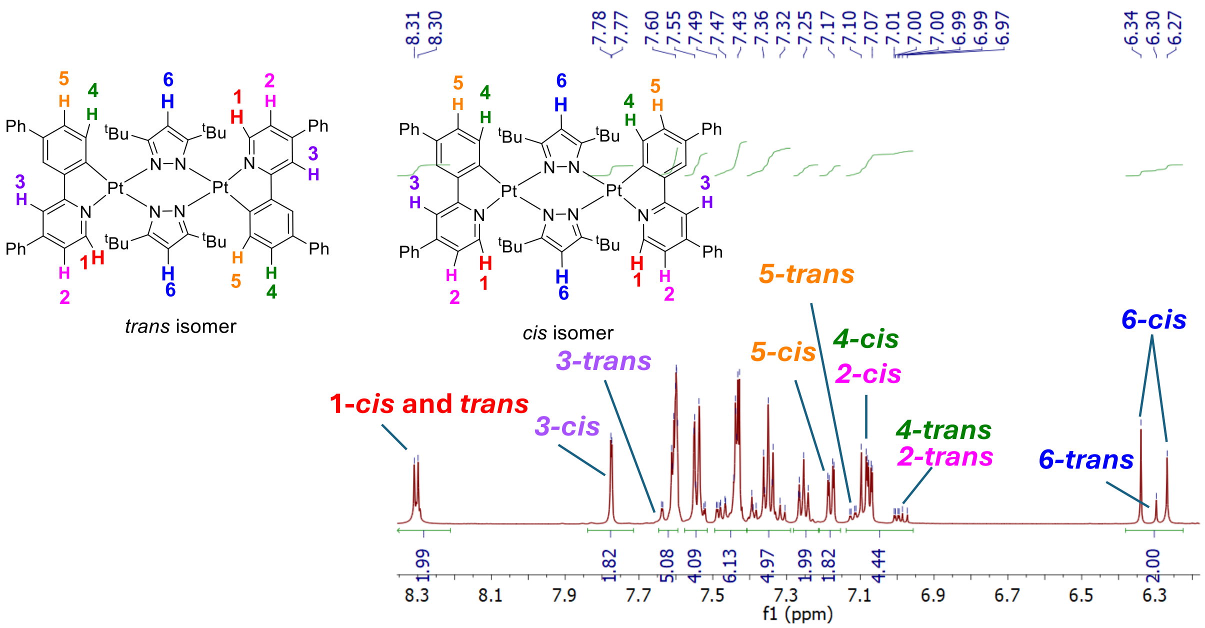
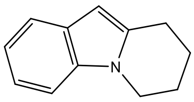


Figure S4. ^{1}H NMR spectrum of complex **Ref-Pt1** in CD_2Cl_2, focusing on aromatic region and assignment of characteristic protons.

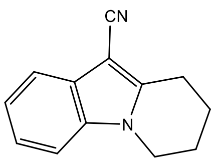
The ^{1}H NMR spectrum of **complex 1** is shown in Figure S2 and served as a representative example of the *cis* and *trans* ^{1}H NMR assignment for this class of complexes. Due to the presence of a C2 symmetry axis in the *trans* isomer, the paired proton signals are magnetically equivalent and have the same chemical shifts. This symmetry axis is replaced by a symmetry plane (Cs symmetry) passing through the two pyrazolate ligands in the *cis* isomer, making the two cyclometalated ligands magnetically equivalent (but with different chemical shifts with respect to the *trans* isomers) and the two pyrazolate ligands chemically distinguishable. This *cis*/*trans* difference is evident in the signals corresponding to the pyridyl proton 1 and pyrazolate proton 6 in the ^{1}H NMR spectrum of complex **1** (Figure S2). The pairs of the pyridyl proton 1 signals for the *trans* and *cis* isomers appear as a doublet with chemical shifts at 8.05 and 8.03 ppm, respectively. For the pyrazolate proton 6 signals, only one singlet at 6.09 ppm was observed for the *trans* isomer, whereas two singlet signals at 6.11 and 6.07 ppm were found for the *cis* isomer. Integrations of the pyrazolate proton 6 signals were used to estimate the ratio of the *cis* and *trans* isomer, which are 1:1.4 for complex **1**, 1: 2.0 for complex **2** and 1:0.16 for **Ref-Pt1**.

Characterization of Photo-Catalytic Reaction Products



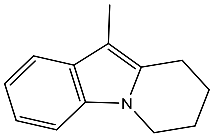
8a[31]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.46 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.1 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.03 (t, *J* = 6.2 Hz, 2H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.13–1.99 (m, 2H), 1.93–1.82 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.83, 136.75, 128.72, 120.25, 119.73, 119.68, 108.88, 97.62, 42.76, 24.62, 23.84, 21.67. HRMS(ESI-QTOF) m/z: calcd: 172.1121; found: 172.1120 $[M+H]^{+}$.



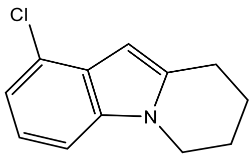
8b[31]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.62 (m, 1H), 7.34–7.28 (m, 1H), 7.28–7.21 (m, 2H), 4.07 (t, *J* = 6.2 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.18–2.09 (m, 2H), 2.00–1.90 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.35, 135.52, 127.41, 122.70, 122.30, 118.98, 116.57, 109.69, 82.63, 42.65, 23.36, 22.69, 19.89. HRMS(ESI-QTOF) m/z: calcd:197.1073; found: 197.1071$[M+H]^{+}$.



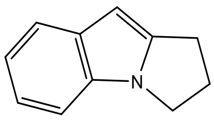
8c[31]

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 8.5 Hz, 1H), 7.12–7.07 (m, 1H), 7.06–7.01 (m, 1H), 4.04–3.93 (m, 2H), 2.92–2.82 (m, 2H), 2.21 (s, 3H), 2.09–2.01 (m, 2H), 1.97–1.83 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 136.40, 133.48, 129.07, 120.21, 119.02, 117.83, 108.61, 104.83, 42.76, 23.94, 22.78, 21.68, 8.21. HRMS(ESI-QTOF) m/z: calcd:186.1277; found: 186.1276 $[M+H]^+$.



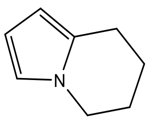
8d[32]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.19 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.06–6.99 (m, 2H), 6.25 (s, 1H), 4.04 (t, *J* = 6.2 Hz, 2H), 2.99 (t, *J* = 6.3 Hz, 2H), 2.08 (ddd, *J* = 8.6, 7.6, 4.4 Hz, 2H), 1.90 (ddd, *J* = 15.7, 7.7, 4.4 Hz, 2H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 138.88, 137.50, 127.22, 124.80, 120.87, 119.45, 107.73, 96.24, 43.12, 24.57, 23.61, 21.38. HRMS(ESI-QTOF) m/z: calcd: 206.0731; found:206.0731$[M+H]^+$.



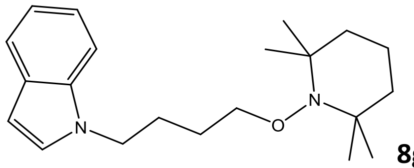
8e[31]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 6.6 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.22 (s, 1H), 4.11 (t, *J* = 7.0 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.71–2.59 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.70, 133.39, 132.79, 120.43, 120.24, 119.23, 109.50, 92.41, 43.73, 27.98, 24.42. HRMS(ESI-QTOF) m/z: calcd:158.0964; found: 158.0965 $[M+H]^+$.



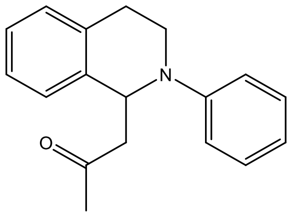
8f[33]

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.51 (s, 1H), 6.12 (t, *J* = 3.0 Hz, 1H), 5.82 (s, 1H), 3.93 (t, J = 6.1 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 1.94 (m, 2H), 1.88–1.76 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.34, 118.69, 107.62, 104.02, 45.48, 24.05, 23.46, 21.70. HRMS(ESI-QTOF) m/z: calcd: 122.0964; found: 122.0962 $[M+H]^+$.



8g

[1]H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 13.1, 5.3 Hz, 2H), 6.49 (d, *J* = 2.9 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.81–3.69 (m, 2H), 2.02–1.90 (m, 2H), 1.67–1.38 (m, 8H), 1.14 (s , 6H). 1.09 (s, 6H). [13]C NMR (101 MHz, $CDCl_3$) δ 136.08, 128.69, 127.94, 121.45, 121.06, 119.30, 109.53, 101.03, 76.23, 59.85, 46.62, 39.72, 33.23, 29.85, 27.69, 26.39, 20.33, 17.25. HRMS(ESI-QTOF) m/z: calcd: 329.2587; found: 329.2627 $[M+H]^+$.



9[34]

[1]H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.9 Hz, 2H), 7.20–7.10 (m, 4H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 5.39 (t, *J* = 6.3 Hz, 1H), 3.70–3.59 (m, 1H), 3.58–3.48 (m, 1H), 3.10–2.95 (m, 2H), 2.85–2.82 (m, 1H), 2.82–2.76 (m, 1H), 2.07 (s, 3H). [13]C NMR (126 MHz, $CDCl_3$) δ 207.40, 149.00, 138.40, 134.56, 129.48, 128.80, 126.99, 126.94, 126.41, 118.40, 114.91, 54.92, 50.33, 42.19, 31.22, 27.33. HRMS(ESI-QTOF) m/z: calcd: 266.1539; found: 266.1541$[M+H]^+$.

X-Ray Crystallographic Data

Table S1. Crystallographic data of **1**, **2** and **Ref-Pt1**.

	1·CH_2Cl_2	**2·CH_2Cl_2·hexane**	**Ref-Pt1**
Formula	$C_{68}H_{70}N_6Pd_2 \cdot CH_2Cl_2$	$C_{52}H_{38}N_6Pd_2 \cdot CH_2Cl_2 \cdot C_6H_{14}$	$C_{68}H_{70}N_6Pt_2$
Formula weight	1269.02	1130.78	1533.82
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*1	$P2_1/c$
a [Å]	28.7870(19)	12.4062 (18)	17.465 (14)
b [Å]	14.0679(9)	12.6181 (18)	19.390 (13)
c [Å]	18.2253(14)	19.276 (3)	20.394 (17)
α [˚]	90	102.182 (4)	90
β [˚]	125.365(2)	95.522 (4)	97.86 (2)
γ [˚]	90	118.581 (3)	90
V [Å^3]	6018.9(7)	2520.8 (6)	6841(9)
Z	4	2	4
μ [mm^{-1}]	0.733	0.87	4.134
D_x [g cm^{-3}]	1.400	1.490	1.489
F(000)	2616.0	1152	3104.0
Radiation	Mo $K\alpha$ (λ = 0.71073 Å)	Mo $K\alpha$ (λ = 0.71073 Å)	Mo $K\alpha$ (λ = 0.71073 Å)
T [K]	173	170	173
No of measured reflections	11298	77554	70382
No of independent reflections	6025	34140	12160
Restraints	0	561	62
R_{int} [%]	0.1403	0.072	0.0897
R [$F^2 > 2\sigma(F^2)$]	0.0727	0.055	0.0445
wR [F^2]	0.1829	0.130	0.0985
CCDC	2353065	2053114	2353067

Table S2. Crystallographic data of **3**, **4** and **5**.

	3·0.5DCE	**4·MeCN**	**5**
Formula	$C_{72}H_{54}N_6Pd_2\cdot0.5(C_2H_4Cl_2)$	$C_{46}H_{40}N_8Pd_2\cdot C_2H_3N$	$C_{52}H_{42}N_{10}Pd_2$
Formula weight	1265.48	958.71	1019.75
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*	$P2_1/c$	*C*2/*c*
a [Å]	13.1747 (15)	20.022 (3)	19.9715 (11)
b [Å]	15.0320 (17)	13.1386 (19)	17.5055 (10)
c [Å]	15.0828 (18)	17.551 (2)	13.1183 (8)
α [°]	87.387 (3)	90	90
β [°]	80.397 (3)	114.783 (4)	109.737 (3)
γ [°]	77.998 (3)	90	90
V [Å^3]	2880.6 (6)	4191.8(10)	4316.9 (4)
Z	2	4	4
μ [mm^{-1}]	0.72	0.90	4.82
D_x [g cm^{-3}]	1.459	1.519	1.569
F(000)	1290.0	1944.0	2064
Radiation	Mo *Kα* (λ = 0.71073 Å)	Mo *Kα* (λ = 0.71073 Å)	Ga *Kα* (λ = 1.34138 Å)
T [K]	187	173	173
No of measured reflections	43428	50512	17688
No of independent reflections	11552	8517	5304
Restraints	74	0	0
R_{int} [%]	0.068	0.071	0.070
R [$F^2 > 2\sigma(F^2)$]	0.0581	0.032	0.043
wR [F^2]	0.1500	0.074	0.118
CCDC	1976305	2353099	2018758

Table S3. Selected bond lengths (Å) and angles (deg) of **1**.

1			
Bond lengths (Å)		Bond angles (deg)	
Pd(1)–Pd(1)	2.789(1)	N(1)–Pd(1)–N(2)	94.5(3)
Pd(1)–N(1)	2.007(5)	N(1)–Pd(1)–C(1)	80.7(3)
Pd(1)–N(2)	2.111(5)	N(1)–Pd(1)–N(3)	169.7(3)
Pd(1)–C(1)	1.996(6)	N(2)–Pd(1)–C(1)	168.0(3)
Pd(1)–N(3)	2.095(5)	N(2)–Pd(1)–N(3)	88.1(2)

Table S4. Selected bond lengths (Å) and angles (deg) of **2** and **Ref-Pt1**.

2		**Ref-Pt1**	
Bond lengths (Å)			
Pd(1)–Pd(2)	3.395	Pt(1)–Pt(2)	2.898(2)
Pd(1)–N(1)	1.984(3)	Pt(1)–N(1)	1.996(6)
Pd(1)–C(11)	2.044(8)	Pt(1)–N(3)	2.110(7)
Pd(1)–N(2)	2.048(7)	Pt(1)–N(5)	2.039(6)
Pd(1)–N(2)	2.049(0)	Pt(1)–C(11)	1.985(7)
Pd(2)–N(1)	1.977(7)	Pt(2)–N(2)	1.990(6)
Pd(2)–C(11)	2.052(1)	Pt(2)–N(4)	2.119(6)
Pd(2)–N(3)	2.061(1)	Pt(2)–N(6)	2.067(6)
Pd(2)–N(3)	2.081(4)	Pt(2)–C(34)	1.987(7)
Bond angles (deg)			
N(1)–Pd(1)–N(2)	96.6(5)	N(1)–Pt(1)–N(3)	98.1(2)
N(1)–Pd(1)–C(11)	80.7(4)	N(1)–Pt(1)–N(5)	173.8(2)
N(1)–Pd(1)–N(2)	176.5(5)	N(1)–Pt(1)–C(11)	80.5(3)
C(11)–Pd(1)–N(2)	177.3(6)	N(3)–Pt(1)–N(5)	86.4(2)
N(2)–Pd(1)–N(2)	86.5(6)	N(3)–Pt(1)–C(11)	175.2(3)
N(1)–Pd(2)–N(3)	95.0(7)	N(2)–Pt(2)–N(4)	94.1(2)
N(1)–Pd(2)–N(3)	175.6(8)	N(2)–Pt(2)–N(6)	173.9(2)
N(1)–Pd(2)–C(11)	80.6(9)	N(2)–Pt(2)-C(34)	80.3(3)
N(3)–Pd(2)–C(11)	175.0(0)	N(4)–Pt(2)–N(6)	86.3(2)
N(3)–Pd(2)–N(3)	89.1(3)	N(4)–Pt(2)–C(34)	173.5(3)

Table S5. Selected bond lengths (Å) and angles (deg) of **3** and **4**.

3		**4**	
Bond lengths (Å)			
Pd(1)–Pd(2)	2.855(9)	Pd(1)–Pd(2)	2.8850(7)
Pd(1)–N(1)	2.128(8)	Pd(1)–N(5)	2.140(2)
Pd(1)–N(3)	2.041(5)	Pd(1)–N(7)	2.079(2)
Pd(1)–N(5)	2.037(4)	Pd(1)–C(2)	1.995(3)
Pd(1)–C(37)	1.980(3)	Pd(1)–C(6)	2.006(3)
Pd(2)–N(2)	2.037(2)	Pd(2)–N(6)	2.082(2)
Pd(2)–N(4)	2.122(2)	Pd(2)–N(8)	2.142(3)
Pd(2)–N(6)	2.024(5)	Pd(2)–C(12)	1.988(3)
Pd(2)–C(60)	1.986(6)	Pd(2)–C(16)	2.004(3)
Bond angles (deg)			
N(1)–Pd(1)–N(3)	89.2(7)	N(5)–Pd(1)–N(7)	86.39(9)
N(1)–Pd(1)–N(5)	96.1(3)	N(5)–Pd(1)–C(2)	101.2(1)
N(1)–Pd(1)–C(37)	175.1(3)	N(5)–Pd(1)–C(6)	177.8(1)
N(3)–Pd(1)–N(5)	173.5(1)	N(7)–Pd(1)–C(2)	170.9(1)
N(3)–Pd(1)–C(37)	93.9(1)	N(7)–Pd(1)–C(6)	92.7(1)
N(5)–Pd(1)–C(37)	80.9(4)	C(2)–Pd(1)–C(6)	79.9(1)
N(2)–Pd(2)–N(4)	89.5(2)	N(6)–Pd(2)–N(8)	87.10(9)
N(2)–Pd(2)–N(6)	172.4(1)	N(6)–Pd(2)–C(16)	92.1(1)
N(2)–Pd(2)–C(60)	93.6(5)	N(8)–Pd(2)–C(12)	101.1(1)
N(4)–Pd(2)–N(6)	95.9(1)	N(8)–Pd(2)–C(16)	178.1(1)
N(4)–Pd(2)–C(60)	176.3(6)	N(6)–Pd(2)–C(12)	170.9(1)
N(6)–Pd(1)–C(60)	81.1(1)	C(12)–Pd(2)–C(16)	79.9(1)
N(1)–C(1)–N(2)	124.5(7)	N(7)–C(34)–N(8)	125.5(3)

Table S6. Selected bond lengths (Å) and angles (deg) of **5**.

Bond lengths (Å)			
Pd(1)–Pd(1A)	2.854(7)	Pd(1A)–N(4A)	2.091(9)
Pd(1)–N(5A)	2.156(8)	Pd(1A)–C(1A)	1.991(8)
Pd(1)–N(4)	2.091(7)	Pd(1A)–C(13A)	2.004(7)
Pd(1)–C(1)	1.992(0)	Pd(1A)–N(5)	2.156(9)
Pd(1)–C(13)	2.004(8)		
Bond angles (deg)			

N(4)–Pd(1)–C(1)	171.1(6)	N(5)–Pd(1A)–N(4A)	85.6(8)
N(4)–Pd(1)–C(13)	92.7(7)	N(5)–Pd(1A)–C(1A)	101.5(6)
N(4)–Pd(1)–N(5A)	85.6(9)	N(5)–Pd(1A)–C(13A)	177.3(7)
C(1)–Pd(1)–C(13)	80.1(6)	N(4A)–Pd(1A)–C(1A)	171.1(6)
C(1)–Pd(1)–N(5A)	101.5(6)	N(4A)–Pd(1A)–C(13A)	92.7(7)
C(13)–Pd(1)–N(5A)	177.3(8)	C(1A)–Pd(1A)–C(13A)	80.1(7)
		N(4A)–C(14A)–N(5A)	125.4(0)

UV-Vis Absorption and Steady-State Emission

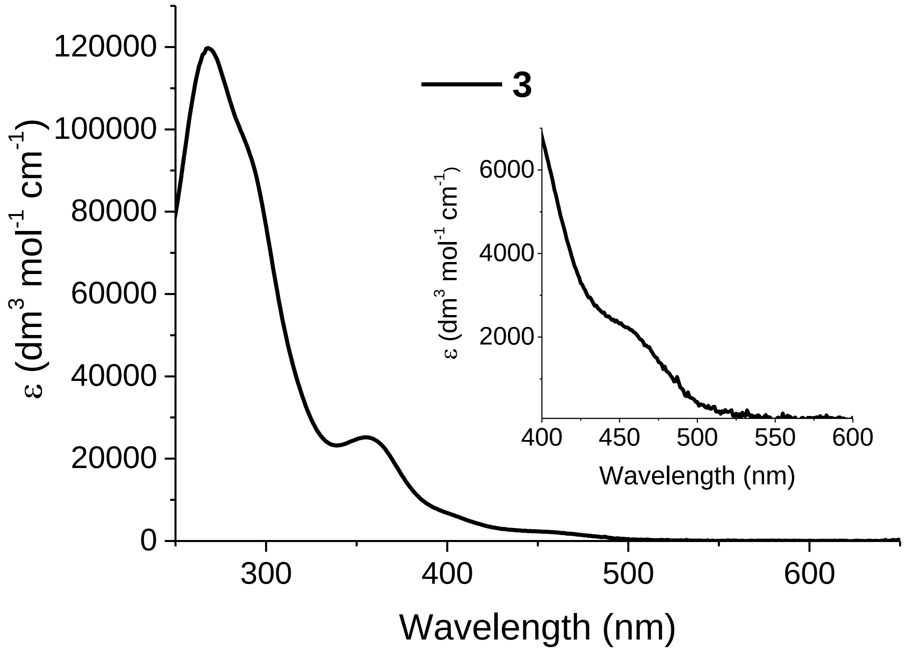


Figure S5. UV-visible absorption spectrum of complex **3** in CH_2Cl_2 (1×10^{-5} M). Inset shows the absorption features in the region of 400–600 nm.

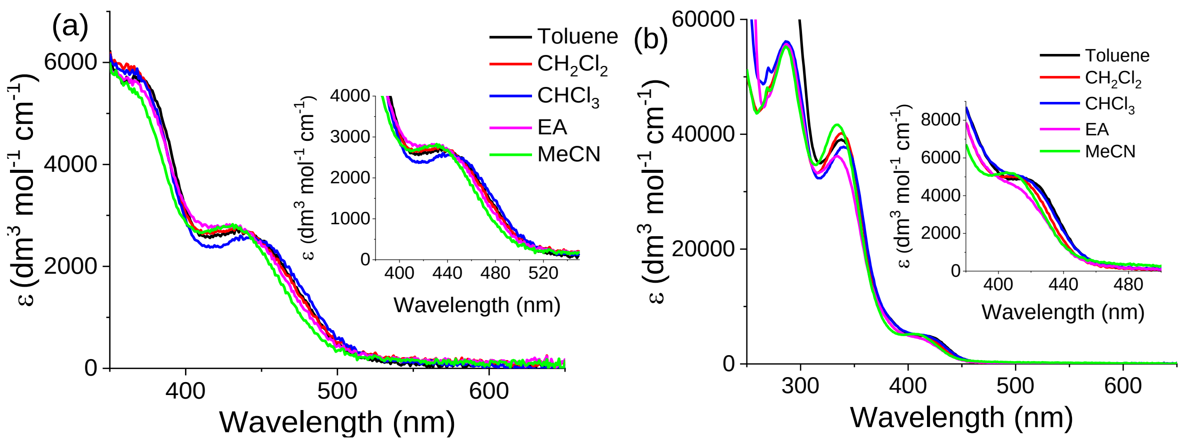


Figure S6. UV-visible absorption spectra of (a) **1** and (b) **5** in various organic solvents (1×10^{-5} M). Inset shows the absorption features in the region of 350–550 nm.

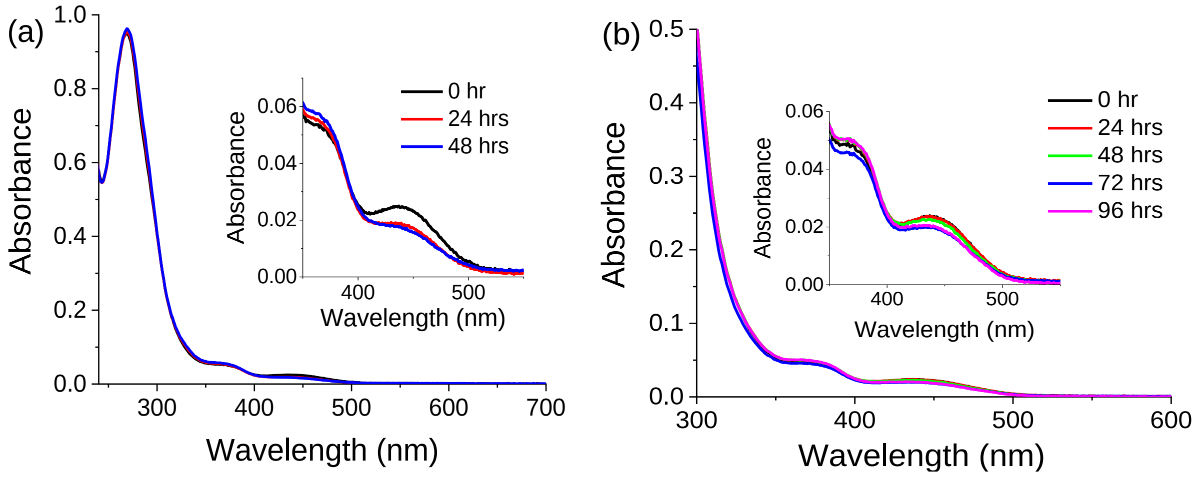


Figure S7. UV-visible absorption spectra of complex **1** in (a) CH_2Cl_2 and (b) toluene (1×10^{-5} M) at different time intervals. Inset shows the absorption features in the region of 350–550 nm.

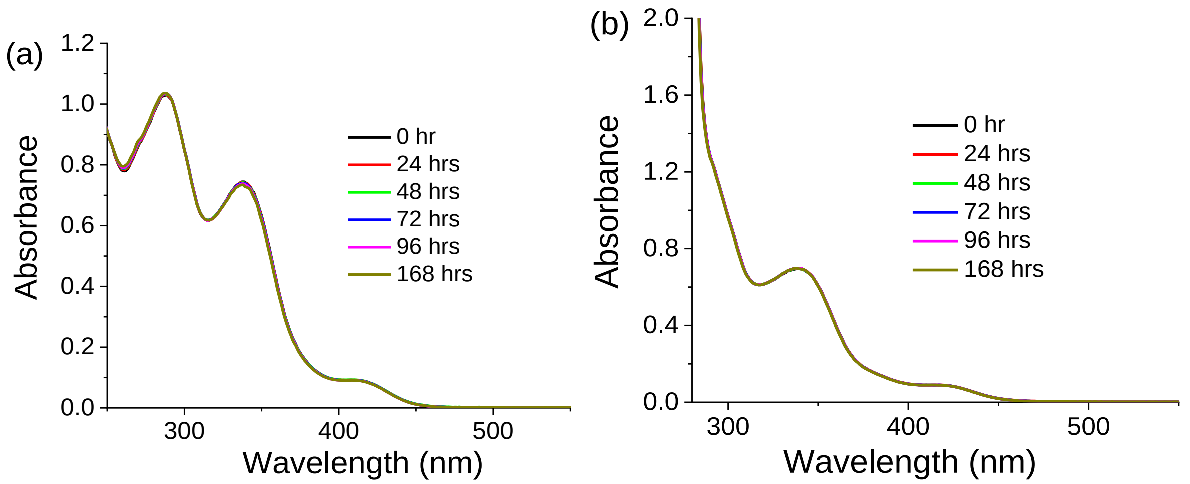


Figure S8. UV-visible absorption spectra of complex **5** in (a) CH_2Cl_2 and (b) toluene (1×10^{-5} M) at different time intervals.

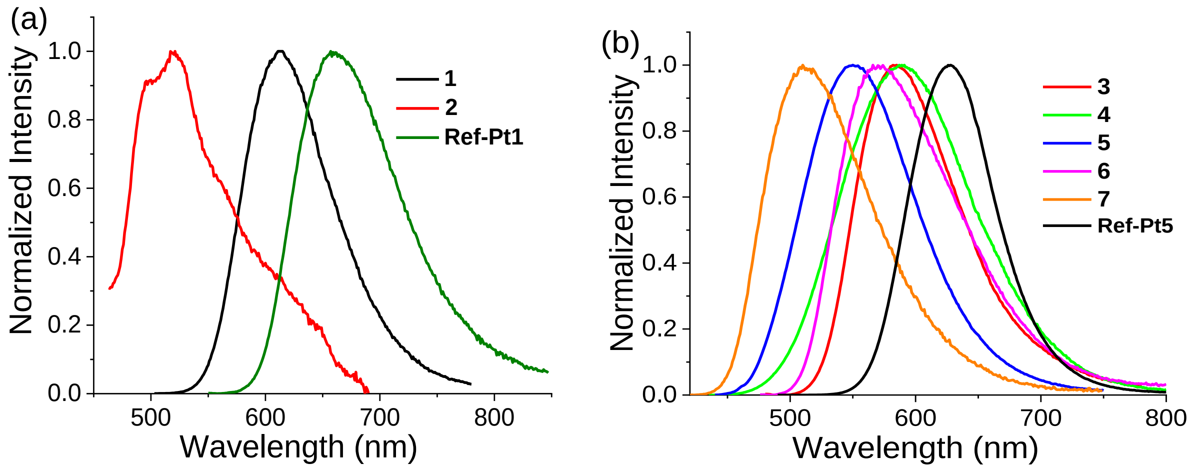


Figure S9. Emission spectra of (a) **1**, **2** and **Ref-Pt1**, (b) **3–7** and **Ref-Pt5** in solid state at RT.

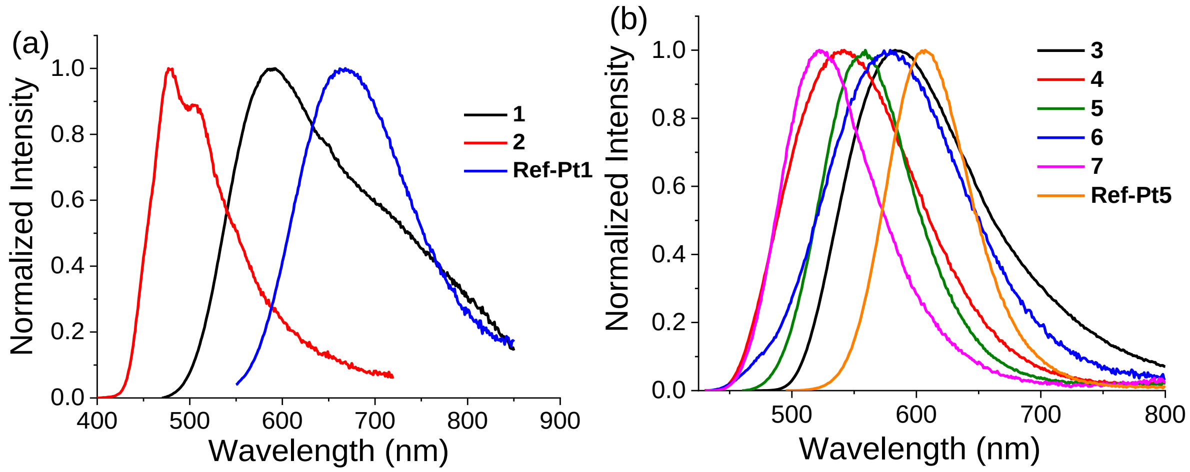


Figure S10. Emission spectra of (a) **1**, **2** and **Ref-Pt1** and (b) **3–7** and **Ref-Pt5** in 2 wt. % PMMA thin films at RT.

Table S7. Photophysical data of complexes **1** and **5** in various organic solvents.

	Solvent	UV-vis absorption[a]	Emission at 298 K[b]
		λ_{max} [nm] (ε [10^3 M^{-1} cm^{-1}])	λ_{em} [nm] (τ^c[us]; Φ_{em} [%]; k_r^f [10^3 s^{-1}]; k_{nr}^g [10^4 s^{-1}])
1	CH_2Cl_2	269 (102.1), 365 (sh, 5.9), 433 (br, 2.8)	609 (0.30; 0.016[d]; 0.53; 333)
	Toluene	366 (sh, 5.8), 433 (br, 2.7)	609 (0.29; 0.030[d]; 1.0; 345)
	$CHCl_3$	269 (100.5), 365 (5.9), 444 (br, 2.6)	608 (0.32; 0.036[d]; 1.1; 312)

	EA	268 (sh, 101.3), 366 (sh, 5.7), 433 (br, 2.8)	598 (0.15; 0.013[d]; 0.87; 667)
	MeCN	268 (106.5), 366 (5.5), 431 (br, 2.8)	Too weak to be detected
5	CH_2Cl_2	286 (55.7), 338 (40.2), 410 (br, 5.0)	532 (0.45; 3.0[e]; 67; 216)
	Toluene	338 (39.1), 417 (sh, 4.9)	530 (0.65; 4.3[e]; 66; 147)
	$CHCl_3$	286 (56.2), 338 (37.7), 414 (5.0)	530 (0.46; 2.8[e]; 61; 211)
	EA	287 (55.7), 334 (36.2), 405 (4.8)	533 (0.42; 1.6[e]; 38; 234)
	MeCN	286 (55.3), 334 (41.7), 405 (sh, 5.2)	537 (0.18; 0.7[e]; 39; 552)

[a] At a concentration of 1×10^{-5} M. [b] At a concentration of 2×10^{-5} M. [c] Emission lifetime. [d] Emission quantum yield was calculated using $[Ru(bpy)_3](PF_6)_2$ as reference (in MeCN, Φ_{em}: 0.062, λ_{em} = 619 nm). [e] Emission quantum yield was obtained by integrating sphere. [f] Radiative decay rate constant estimated from the equation $k_r = \Phi_{em}/\tau$. [g] Non-radiative decay rate constant estimated from the equation $k_{nr} = (1-\Phi_{em})/\tau$.

Time-Resolved Spectroscopy

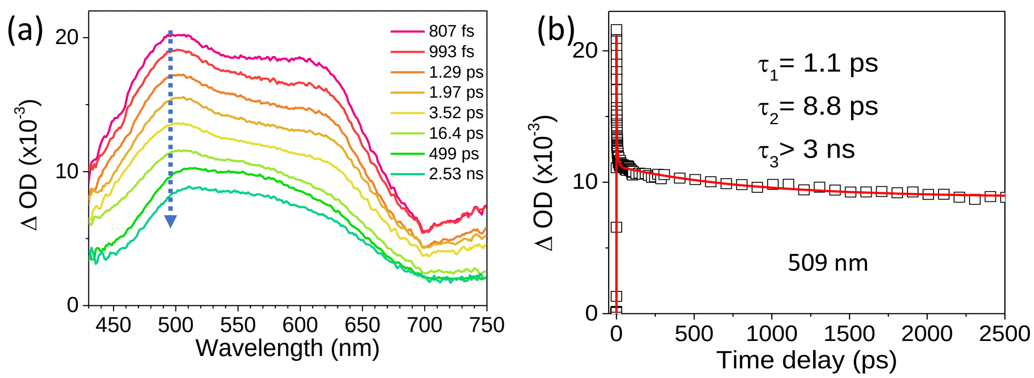


Figure S11. (a) fs-TA spectra of complex **1** in toluene. (b) Kinetics of fs-TA absorption signal at 509 nm of complex **1** (excitation wavelength = 355 nm).

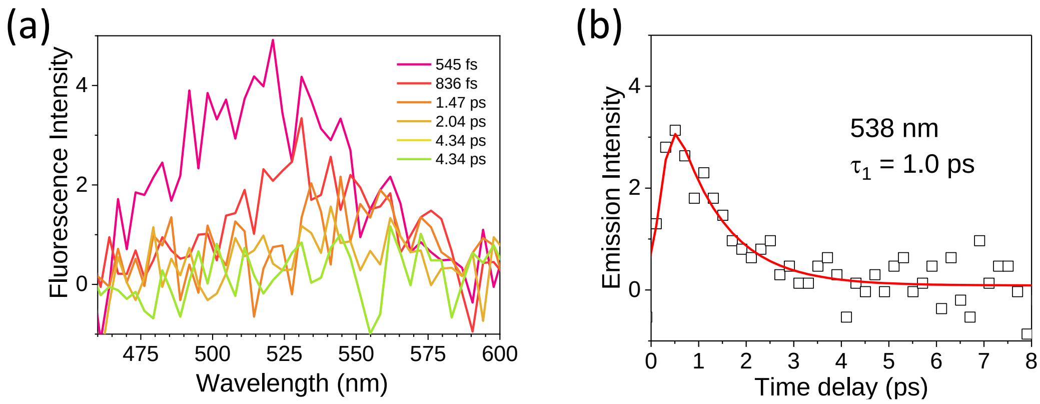


Figure S12. (a) fs-TRF spectra of complex **1** in toluene. (b) Kinetics of fs-TRF signal at 538 nm of complex **1** (excitation wavelength = 355 nm).

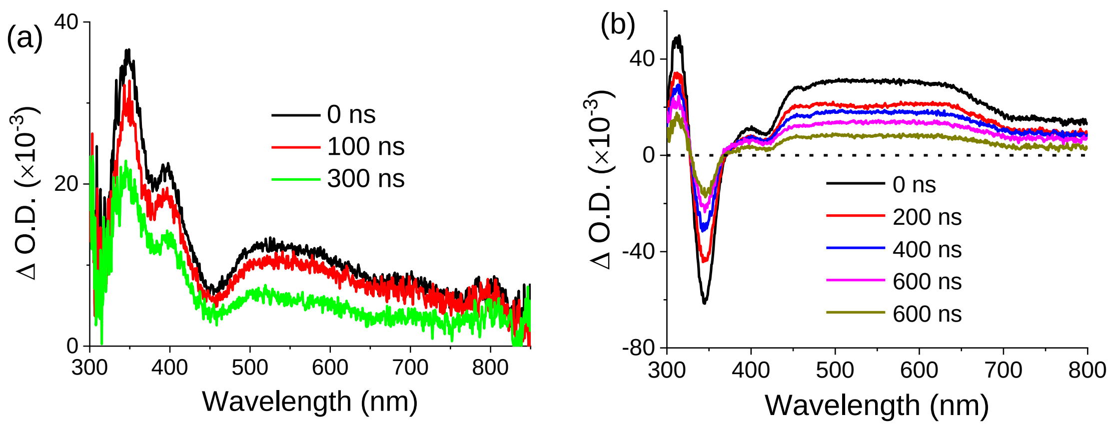


Figure S13. ns-TA spectra of (a) complex **1** and (b) **5** in deoxygenated toluene (excitation wavelength = 355 nm).

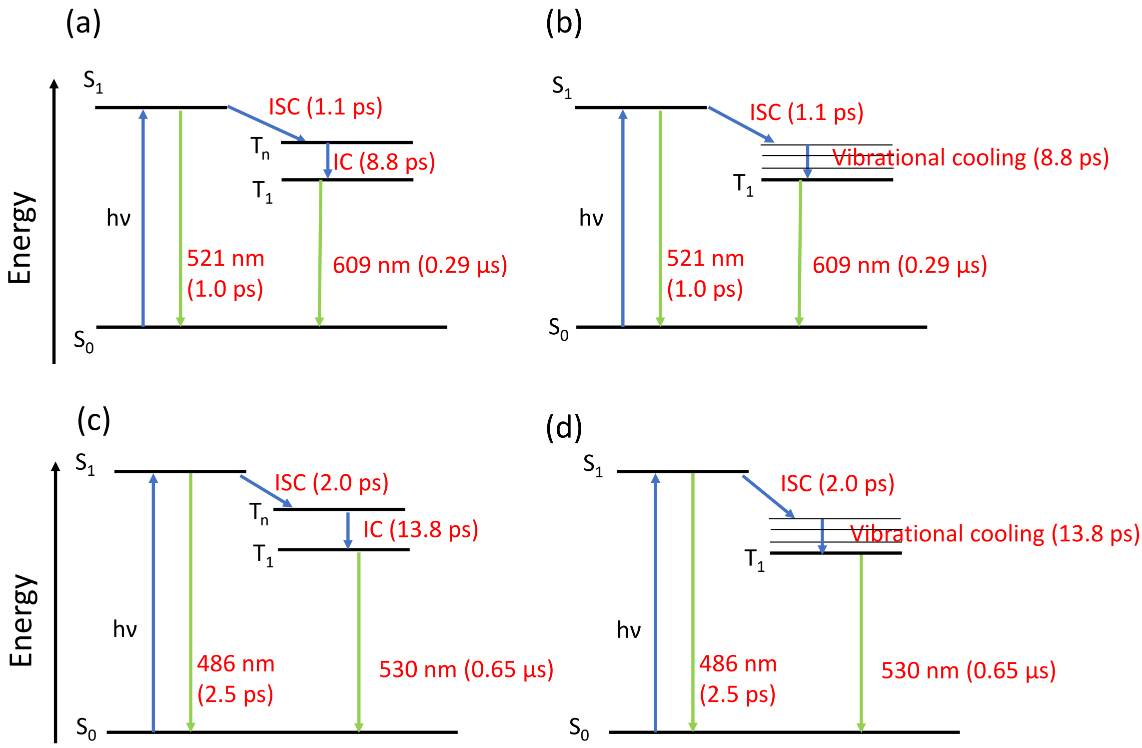


Figure S14. Two possible excited state dynamics of (a), (b) complex **1** and (c), (d) complex **5** in toluene.

Electrochemical Data

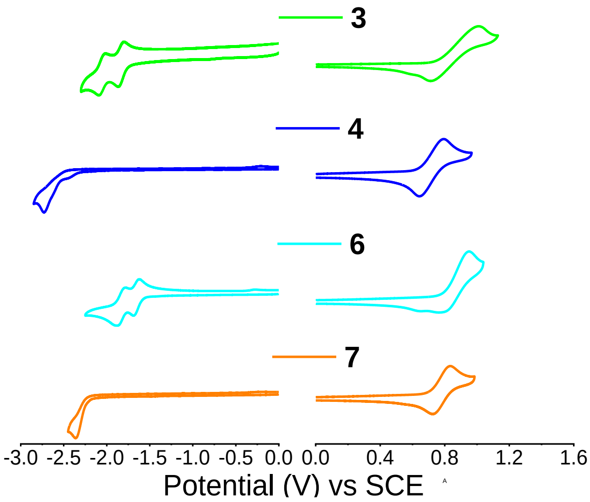


Figure S15. Cyclic voltammograms of complexes **3**, **4**, **6** and **7** in CH_2Cl_2 for anodic sweeps and in DMF for cathodic sweeps. $E_{1/2}$ ($Cp^2Fe^{+/0}$) is recorded at the range of 0.43–0.52 V vs SCE in CH_2Cl_2 or DMF solution.

Spectroelectrochemistry

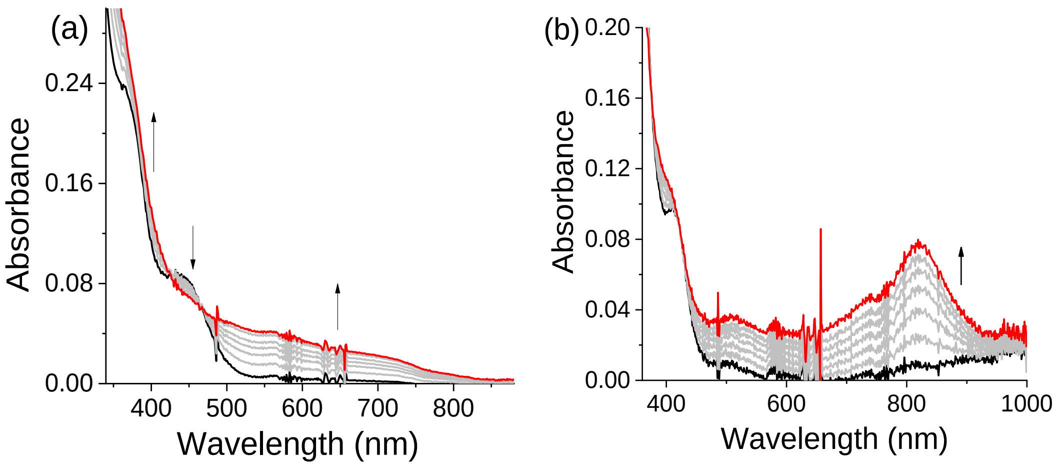


Figure S16. Spectroelectrochemistry of (a) **1** at 1.0 V vs Ag/AgCl and (b) **5** at 0.85 V vs Ag/AgCl in CH_2Cl_2 with 0.1 M NBu_4PF_6 as electrolyte.

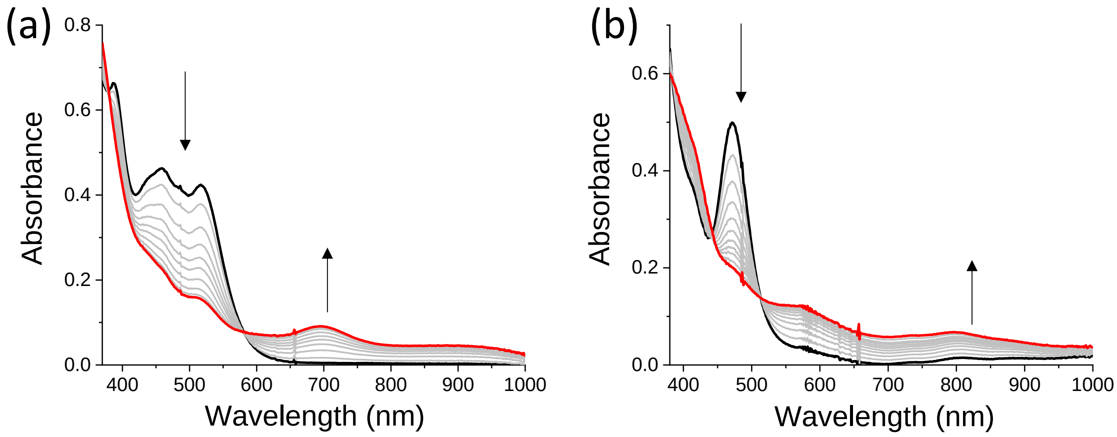


Figure S17. Spectroelectrochemistry of (a) **Ref-Pt1** at 0.7 V vs Ag/AgCl and (b) **Ref-Pt5** at 0.8 V vs Ag/AgCl in CH_2Cl_2 with 0.1 M NBu_4PF_6 as electrolyte.

DFT/TDDFT Calculations

Table S8. The energy difference calculated between the *trans* and *cis* isomers.

	1	**Ref-Pt1**
ΔE(*cis-trans*) (eV)	0.06	0.04

Gaussian functions have been adopted to simulate the absorption spectrum according to the equation:[35]

$$\varepsilon(\vartheta') = \frac{2.175.10^{8} L.mol^{-1}cm^{-2}}{\Delta_{1/2}\vartheta'} f.\exp\left[-2.772\left(\frac{\vartheta' - \vartheta'_{i\to f}}{\Delta_{1/2}\vartheta'}\right)^{2}\right]$$

where the values of f and $\vartheta'_{i\to f}$ are derived from a quantum mechanical calculation. $\Delta_{1/2}\vartheta'$, which is the full-width half-maximum (FWHM) of the band, was set as 3000 cm^{-1} when convoluting the spectra.

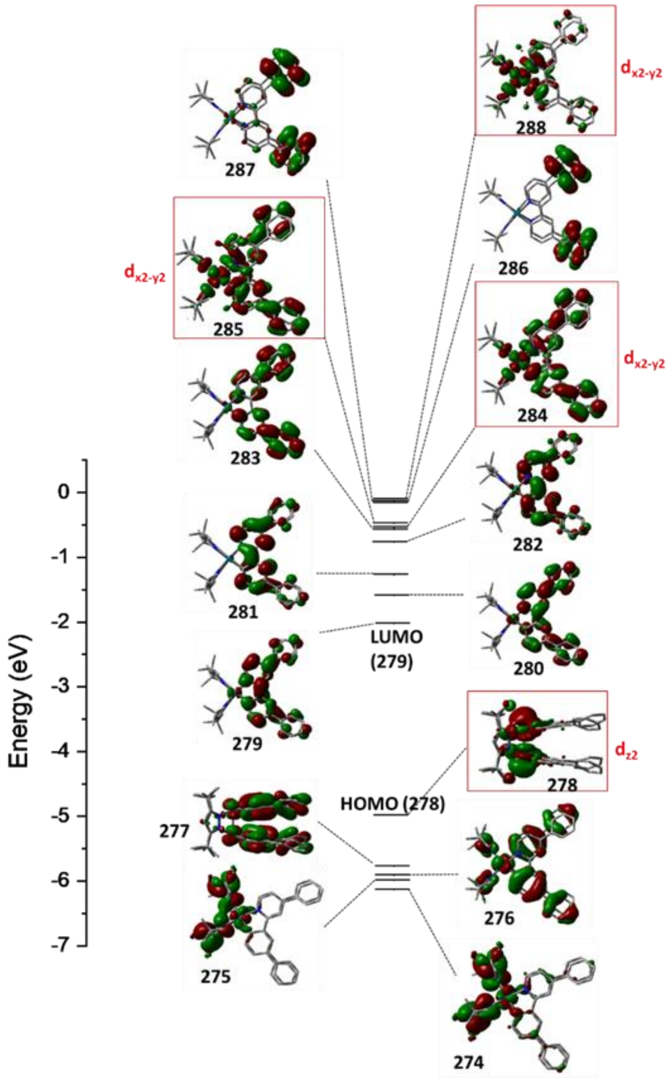


Figure S18. Calculated MO diagram of complex **1** based on the optimized T_1 structure.

Table S9. Energy, contribution and natures of selected excited states of complex **1**.

T_1	Contribution (%)	Energy (eV)	Nature
278→279	69	1.96	MMLCT
278→288	11		dd
T_2			
278→284	47	2.23	dd&MLCT
278→285	46		dd&MLCT
T_3			
277→279	54	2.35	IL

In the T_1 state of complex **1**, 10% ^{3}dd state is mixed with ^{3}MMLCT excited state. The ^{3}dd state also has a major contribution to the T_2 state where the T_1-T_2 energy difference was calculated to be 0.27 eV.

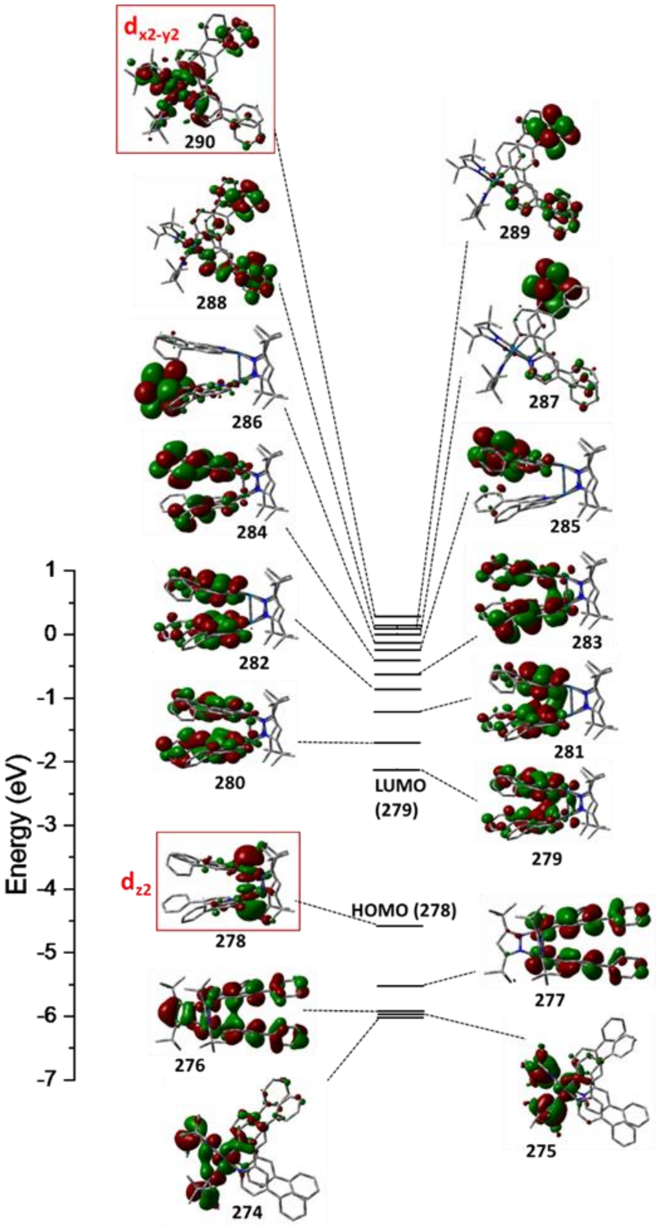


Figure S19. Calculated MO diagram of **Ref-Pt1** based on the optimized T_1 structure.

Table S10. Energy, contribution, and natures of selected excited states of complex **Ref-Pt1**.

T_1	Contribution (%)	Energy(eV)	Nature
278→279	69	1.52	MMLCT
T_8			
278→290	42	2.92	dd&MLCT
278→282	28		MLCT

For **Ref-Pt1**, the ^{3}dd state has a major contribution to the T_8 state where the T_1-T_8 energy difference was calculated to be 1.4 eV.

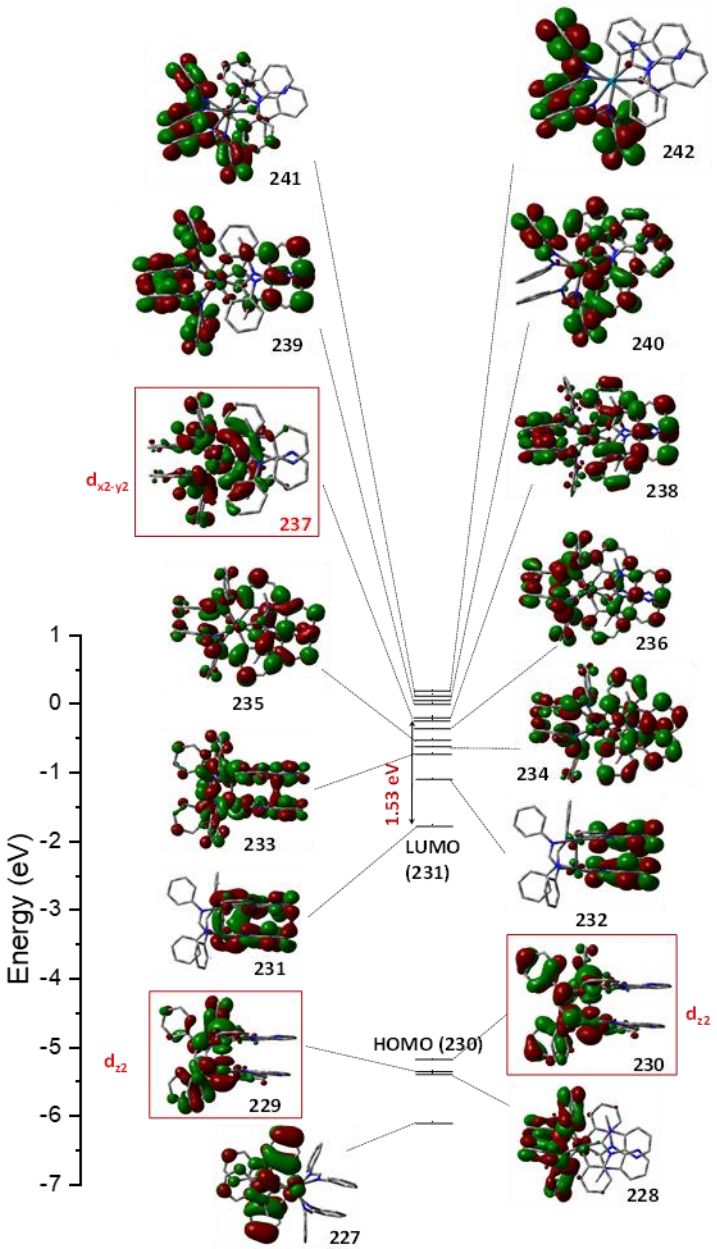


Figure S20. Calculated MO diagram of complex **5** based on the optimized T_1 structure.

Table S11. Energy, contribution, and natures of selected excited states of complex **5**.

T_1	Contribution (%)	Energy (eV)	Nature
229→231	40	2.26	MMLCT&LLCT
230→231	53		MMLCT&LLCT
T_2			
229→231	45	2.77	MMLCT&LLCT
230→231	43		MMLCT&LLCT
T_3			

229→231	31	2.81	MMLCT&LLCT
230→233	38		LLCT
T_4			
228→231	63	2.87	LLCT
T_5			
230→237	42	2.92	dd
229→237	39		

At T_1 state of complex **5**, no ^{3}dd state is mixed with the ^{3}MMLCT (T_1) excited state. The ^{3}dd state has a major contribution to the T_5 state where the T_1-T_5 energy difference was calculated to be 0.66 eV.

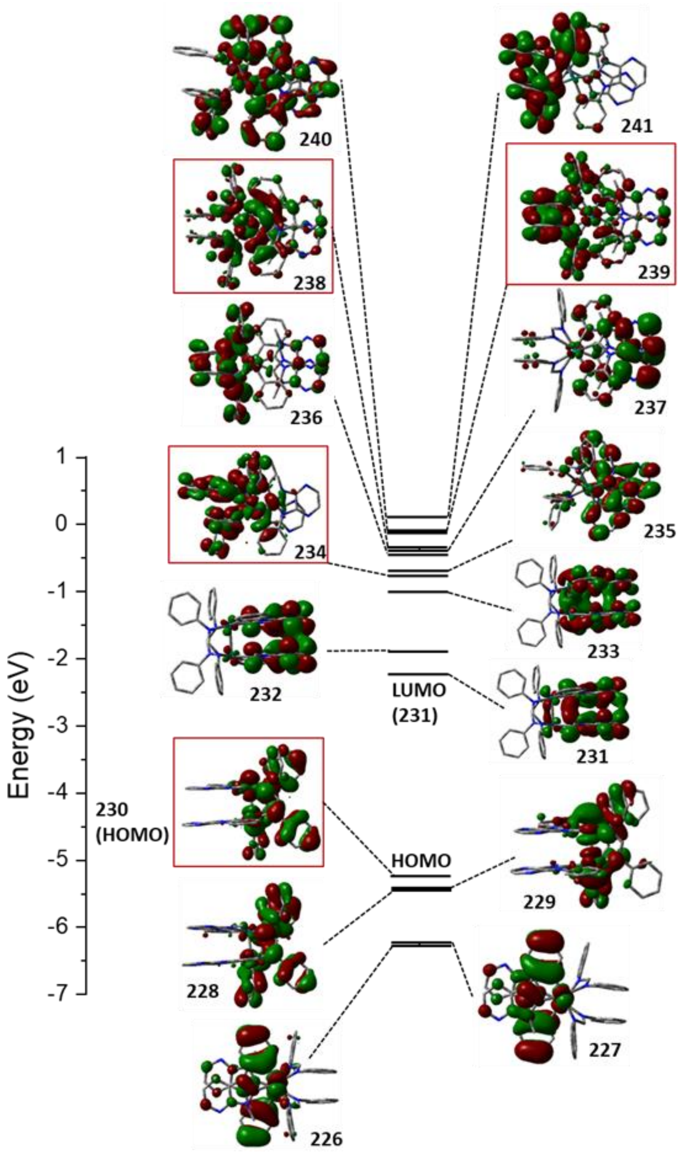


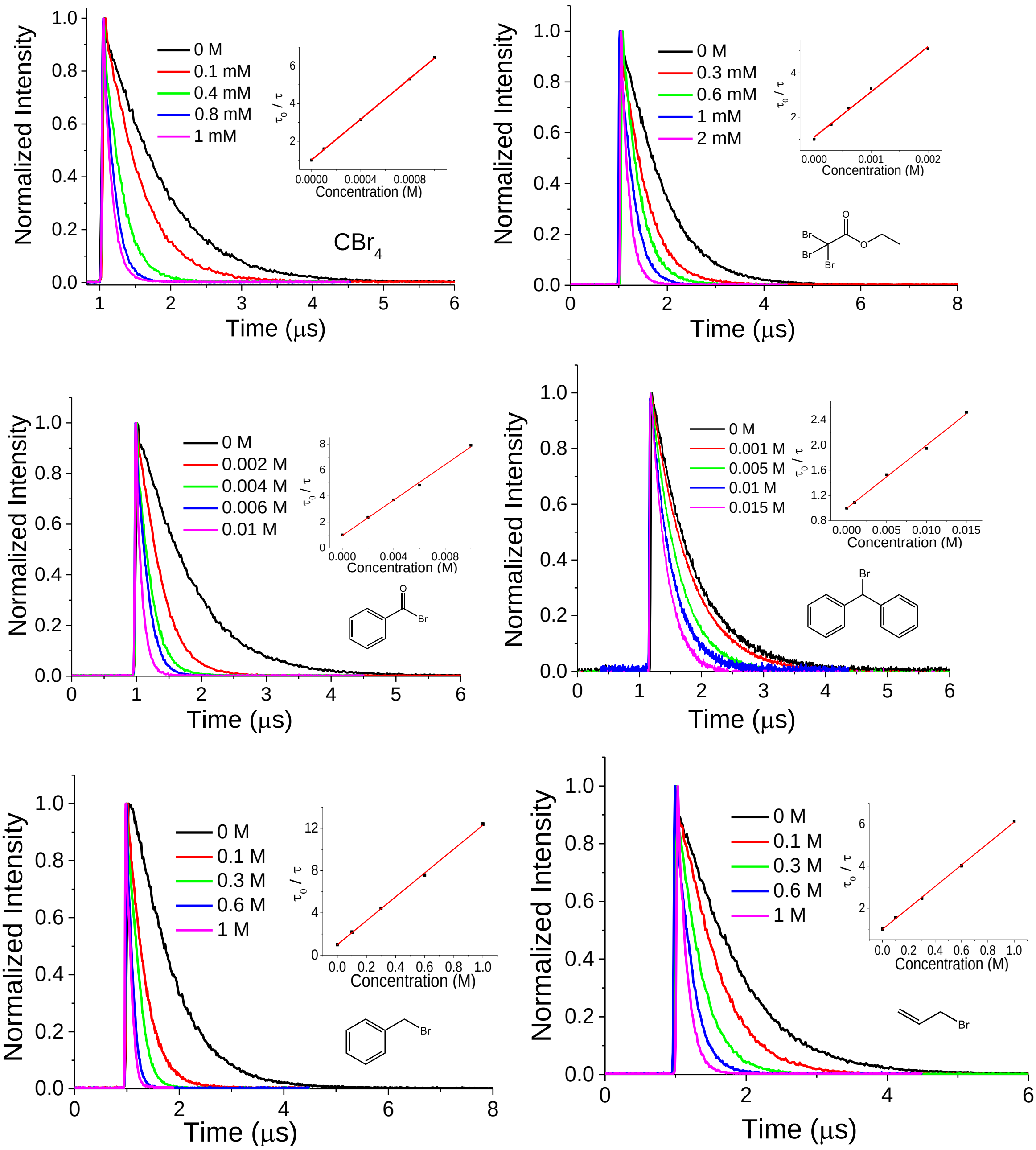
Figure S21. Calculated MO diagram of complex **6** based on the optimized T_1 structure.

Table S12. Energy, contribution, and natures of selected excited states of complex **6**.

T_1	Contribution (%)	Energy (eV)	Nature
229→231	50	2.08	MMLCT&LLCT
230→231	47		MMLCT&LLCT
T_5		2.77	
229→234	40		dd&MLCT
230→234	40		dd&MLCT

At T_1 state of complex **6**, no ^{3}dd state is mixed with the ^{3}MMLCT (T_1) excited state. The ^{3}dd state has a major contribution to the T_5 state where the T_1-T_5 energy difference was calculated to be 0.69 eV.

Quenching and Photochemical Studies of Complex 5 with Alkyl Bromides



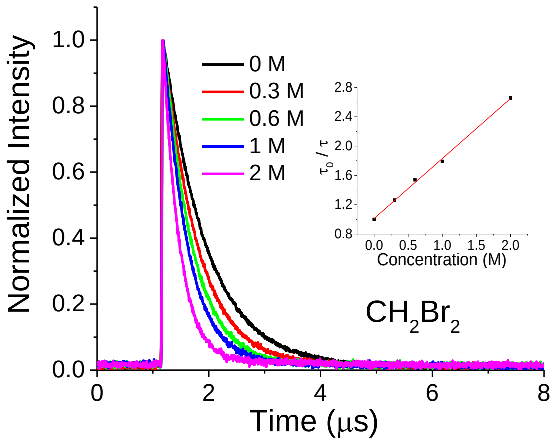


Figure S22. Stern-Volmer studies of complex **5** with various alkyl bromides in deoxygenated toluene.

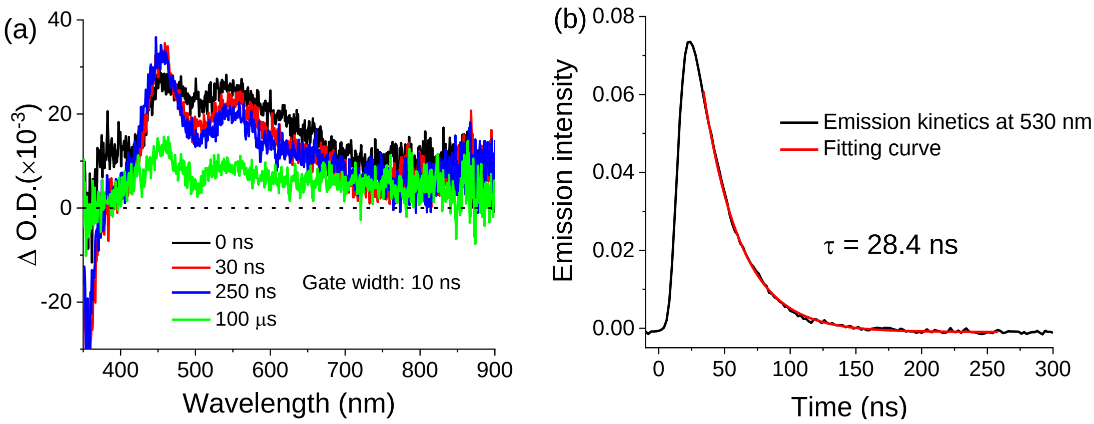
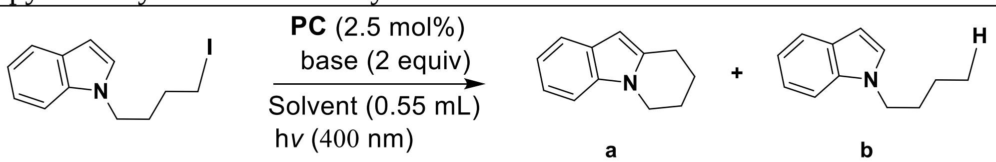
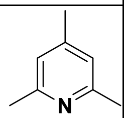


Figure S23. (a) ns-TA spectra of complex **5** in the presence of benzyl bromide (3 M) in deoxygenated toluene at RT. (b) Emission kinetics at 530 nm of complex **5** in the presence of benzyl bromide (3 M).

Table S13. Optimization of reaction conditions for photo-induced functionalization of indoles/pyrroles by intramolecular cyclization.[a]



Entry	PC	Solvent	Base	Irradiation time (hr)	Substrate conversion (%)	Yield (%)	
						a	**b**
1	**5**	MeCN	DIPEA	12	100	59	5.6
2	**5**	MeCN		12	100	23	trace
3	**5**	MeCN	Na_2CO_3	12	26	20	trace
4	**5**	DMA	DIPEA	12	35	22	trace

5	**5**	Benzene-d_6	DIPEA	2	100	83	13
6	**7**	Benzene-d_6	DIPEA	2	100	73	8.7
7	**Ru(bpy)$_3$Cl$_2$**	Benzene-d_6	DIPEA	6	0	0	0
8	***fac*-Ir(ppy)$_3$**	Benzene-d_6	DIPEA	6	52	37	trace
9[b]	**5**	Benzene-d_6	--	2	0	0	0
10[c]	--	Benzene-d_6	DIPEA	2	6.7	6.3	trace
11[d]	**5**	Benzene-d_6	DIPEA	--	0	0	0

[a] Reaction conditions: indole/pyrrole (0.05 mmol), base (0.10 mmol), **PC** (2.5 mol%) in 0.55 mL solvent, light (blue LED lamp, λ_{max} = 400 nm). Substrate conversion and product yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] In the absence of base. [c] In the absence of **PC**. [d] In dark.

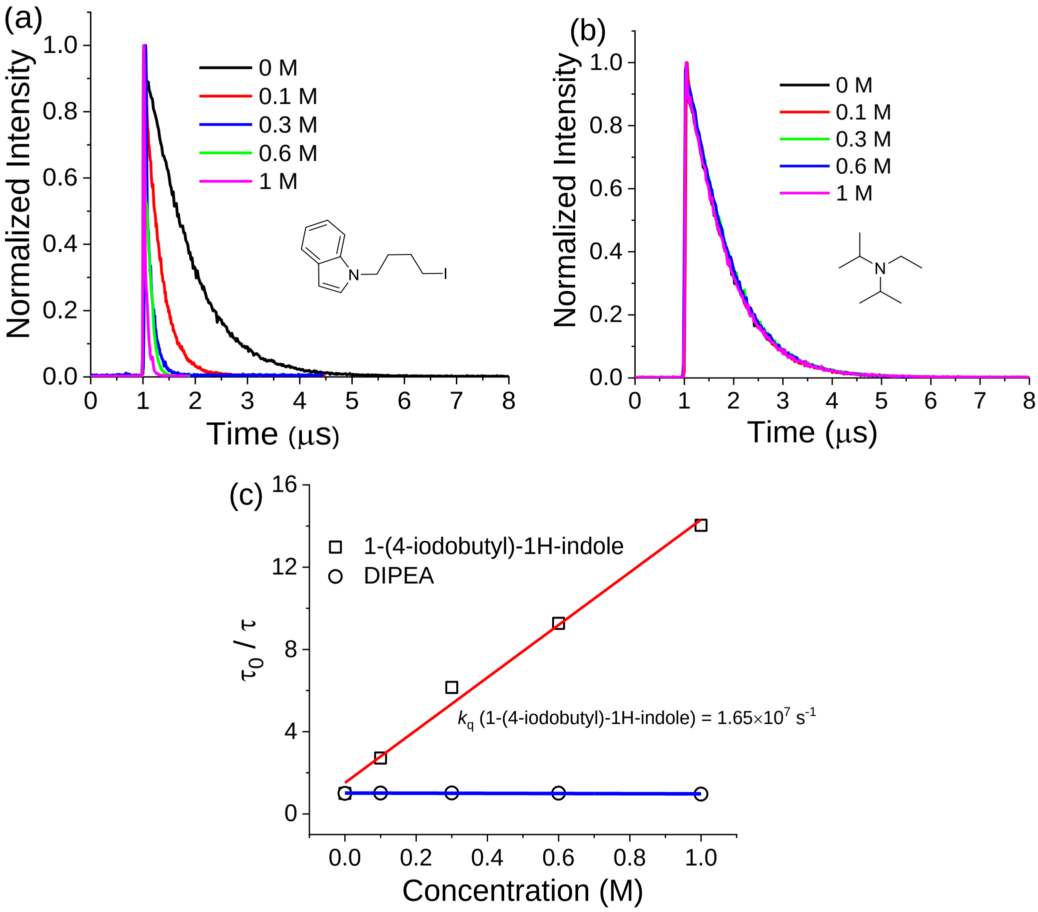


Figure S24. Stern-Volmer studies of **5** (2×10^{-5} M) with (a) 1-(4-iodobutyl)-1H-indole and (b) DIPEA in deoxygenated toluene. (c) Stern-Volmer plots of **5** with 1-(4-iodobutyl)-1H-indole and DIPEA.

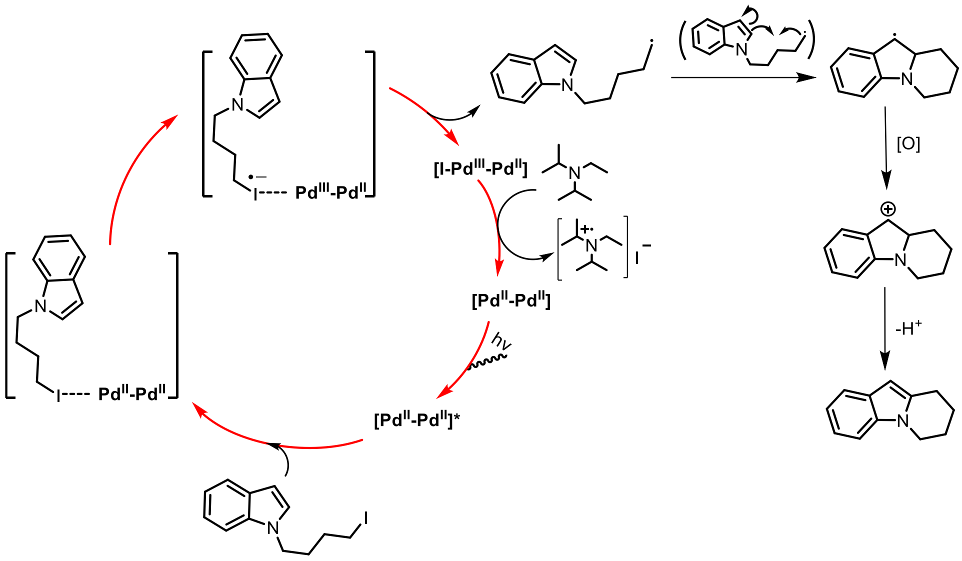


Figure S25. Plausible reaction pathways for photo-driven functionalization of indoles using complex **5** as a photocatalyst.

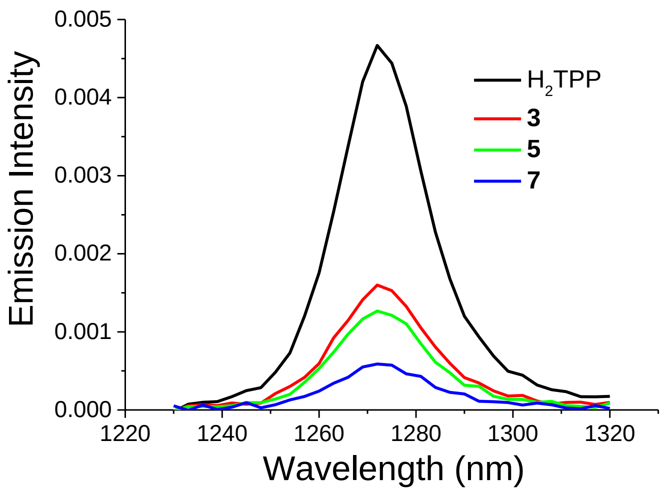


Figure S26. Singlet oxygen emission spectra produced by H_2TPP and binuclear Pd^{II} complexes as photosensitizers in aerated $CHCl_3$.

Electroluminescence

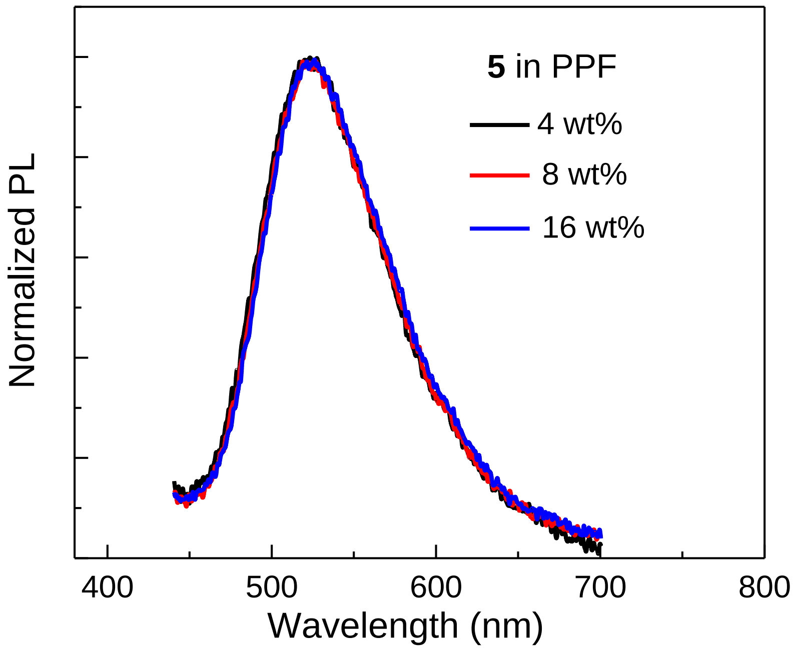


Figure S27. Normalized PL spectra of complex **5** in PPF thin films with various doping concentrations.

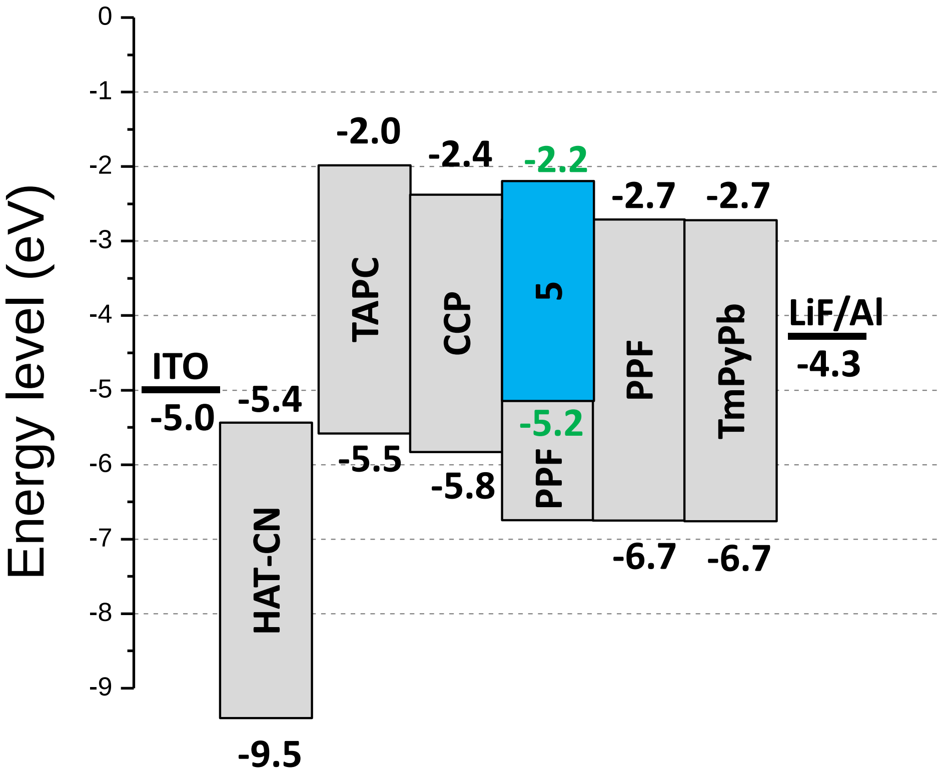


Figure S28. Energy level diagram of a vacuum-deposited OLED with complex **5** as an emitting dopant.

NMR Spectra

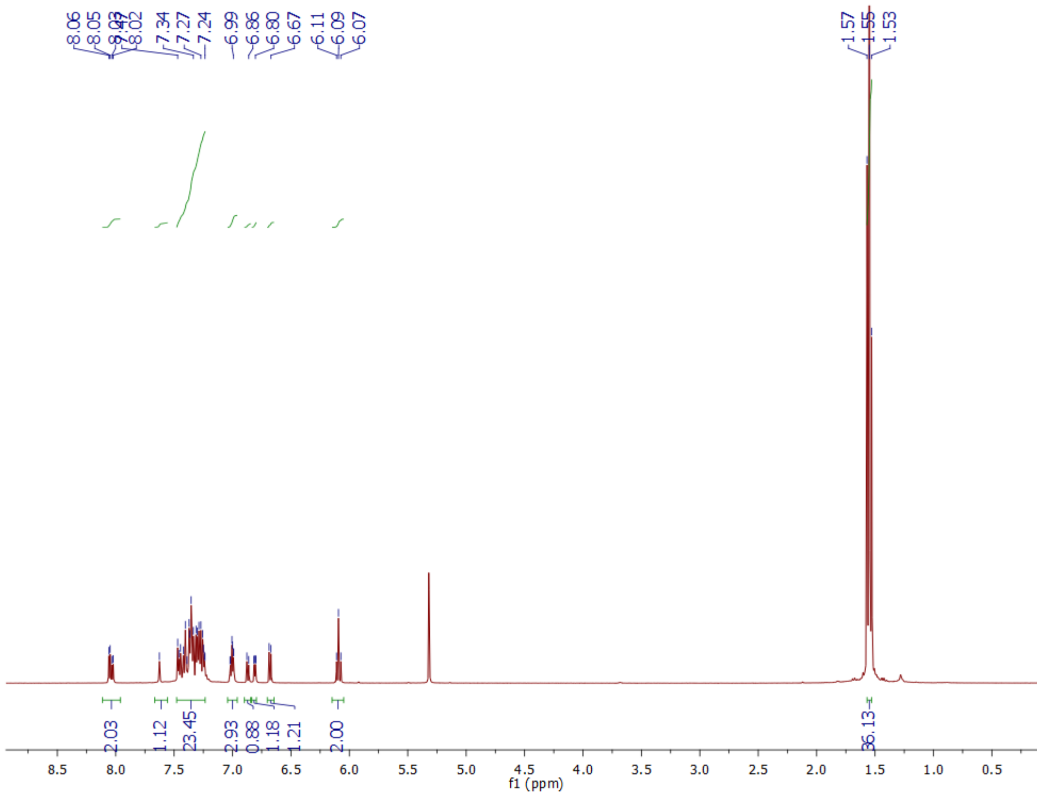


Figure S29. ^{1}H NMR spectrum of complex **1** in CD_2Cl_2.

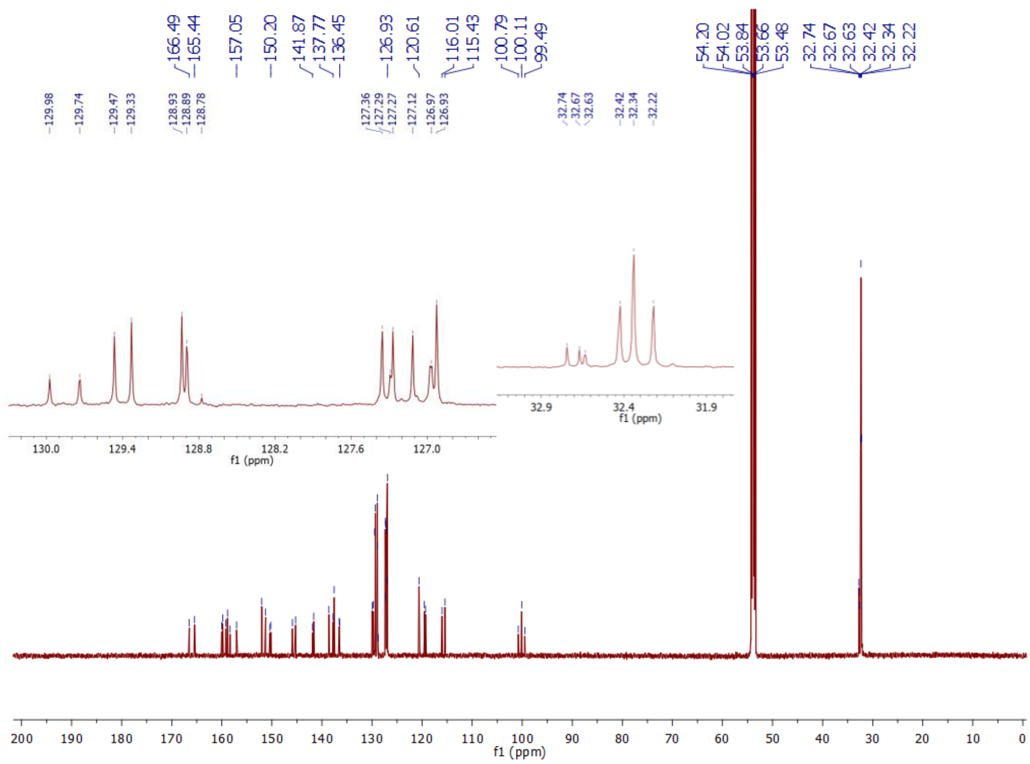


Figure S30. ^{13}C NMR spectrum of complex **1** in CD_2Cl_2.

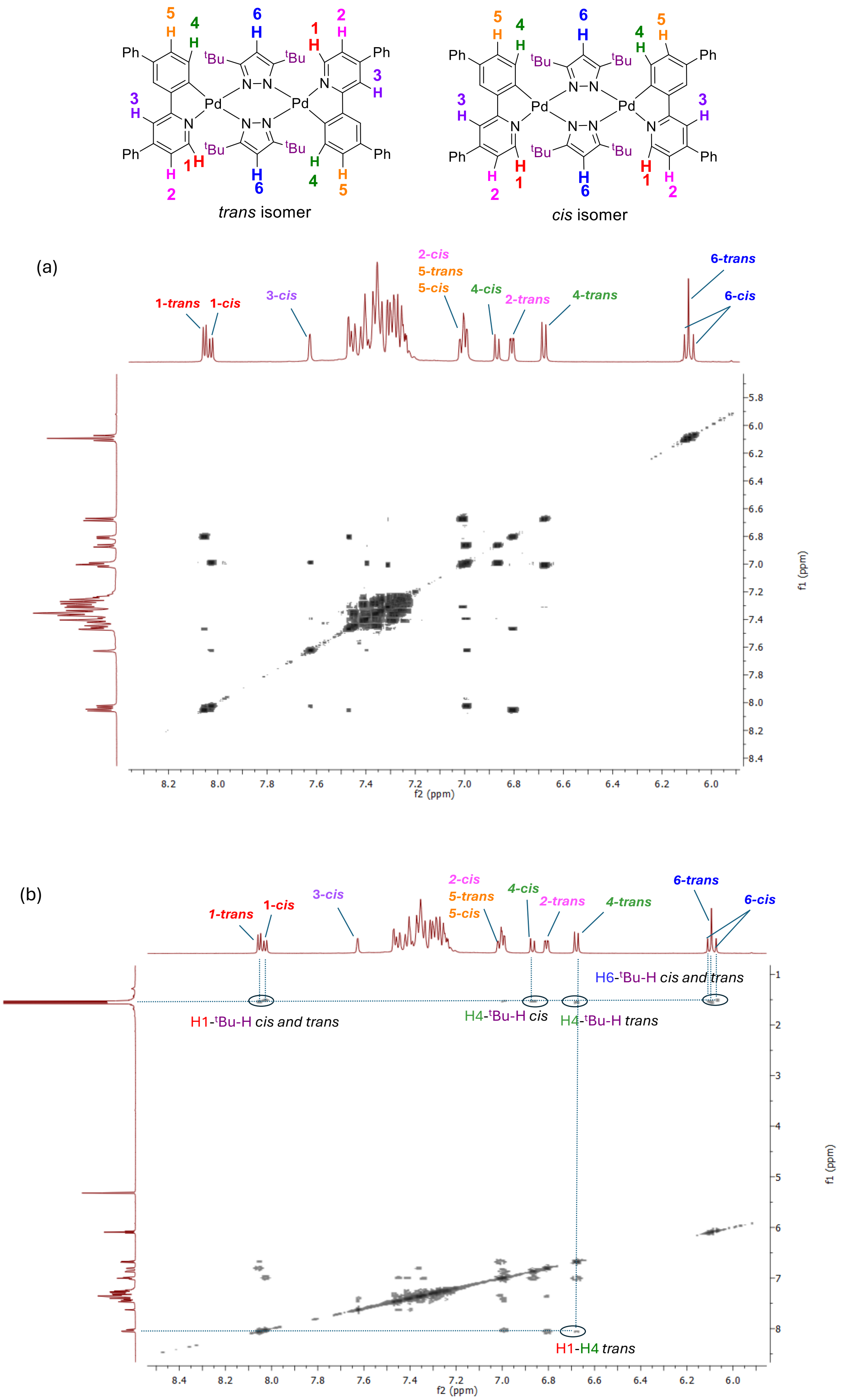


Figure S31. (a) ^1H-^1H COSY and (b) ^1H-^1H NOESY spectra of complex **1** in CD_2Cl_2.

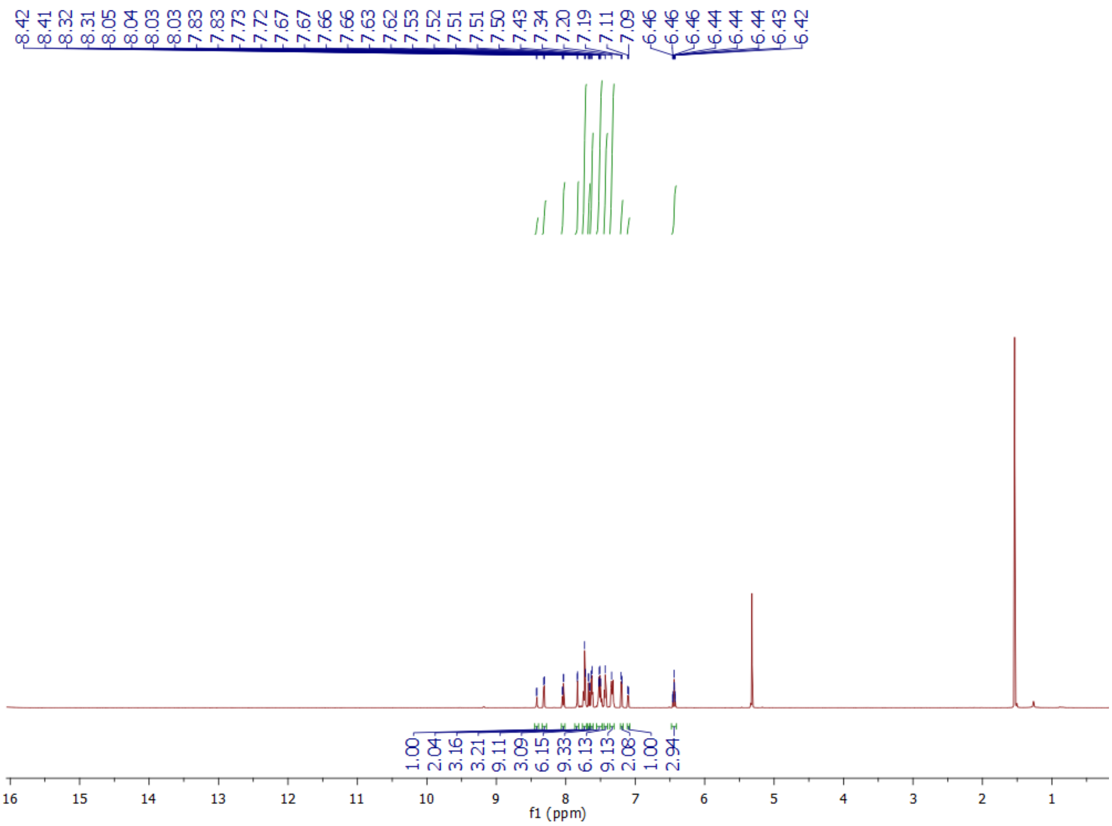


Figure S32. ^{1}H NMR spectrum of complex **2** in CD_2Cl_2.

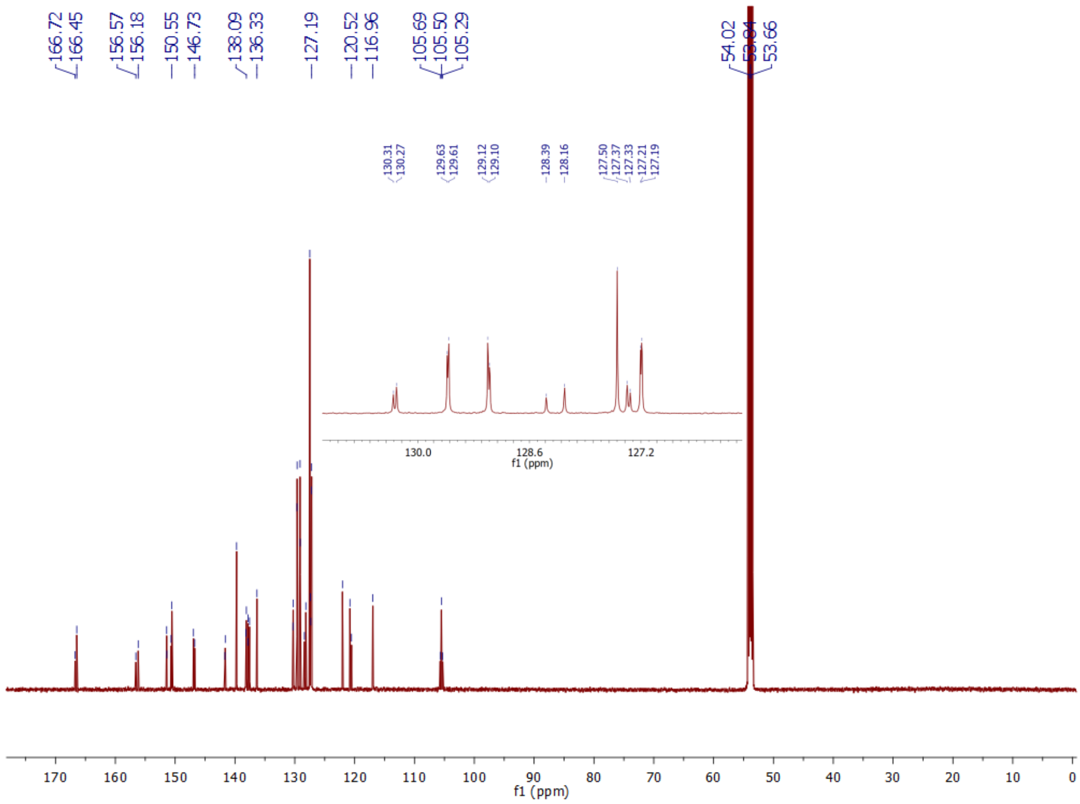


Figure S33. ^{13}C NMR spectrum of complex **2** in CD_2Cl_2.

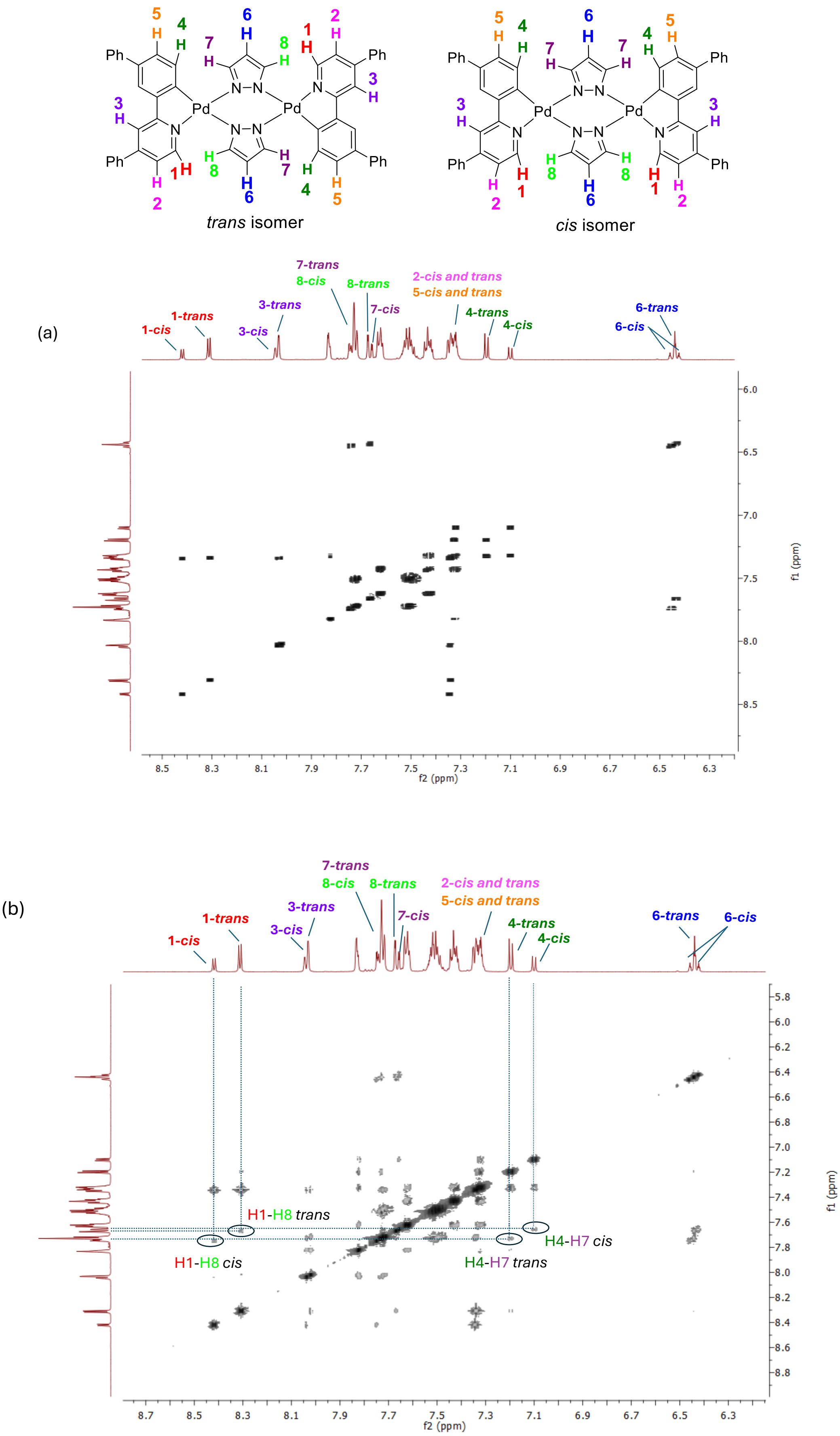


Figure S34. (a) ^{1}H-^{1}H COSY and (b) ^{1}H-^{1}H NOESY spectra of complex **2** in CD_2Cl_2.

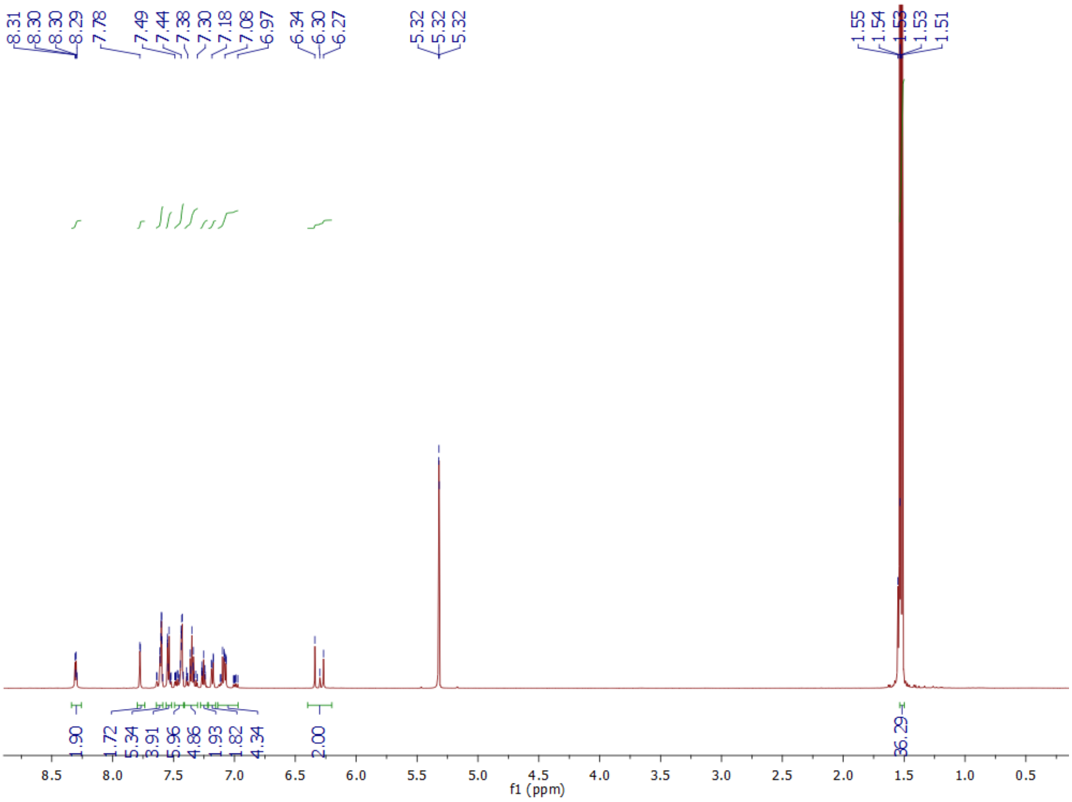


Figure S35. ^{1}H NMR spectrum of complex **Ref-Pt1** in CD_2Cl_2.

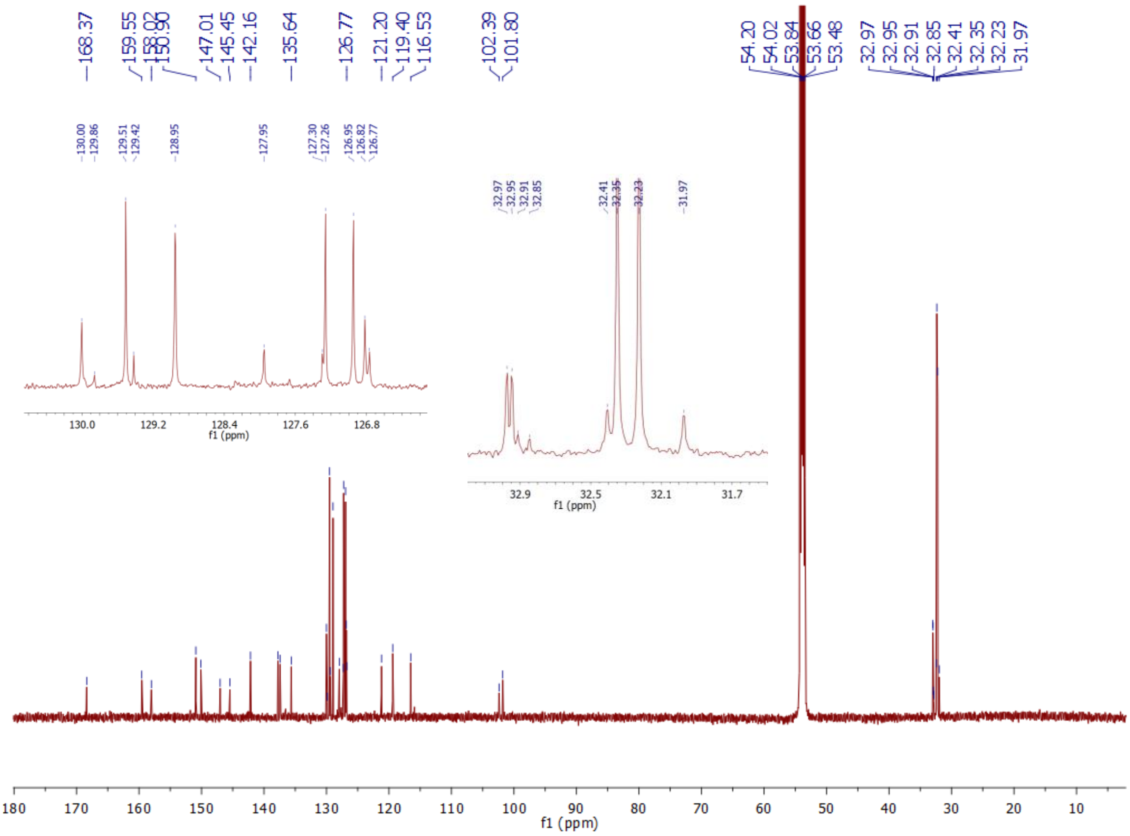


Figure S36. ^{13}C NMR spectrum of complex **Ref-Pt1** in CD_2Cl_2.

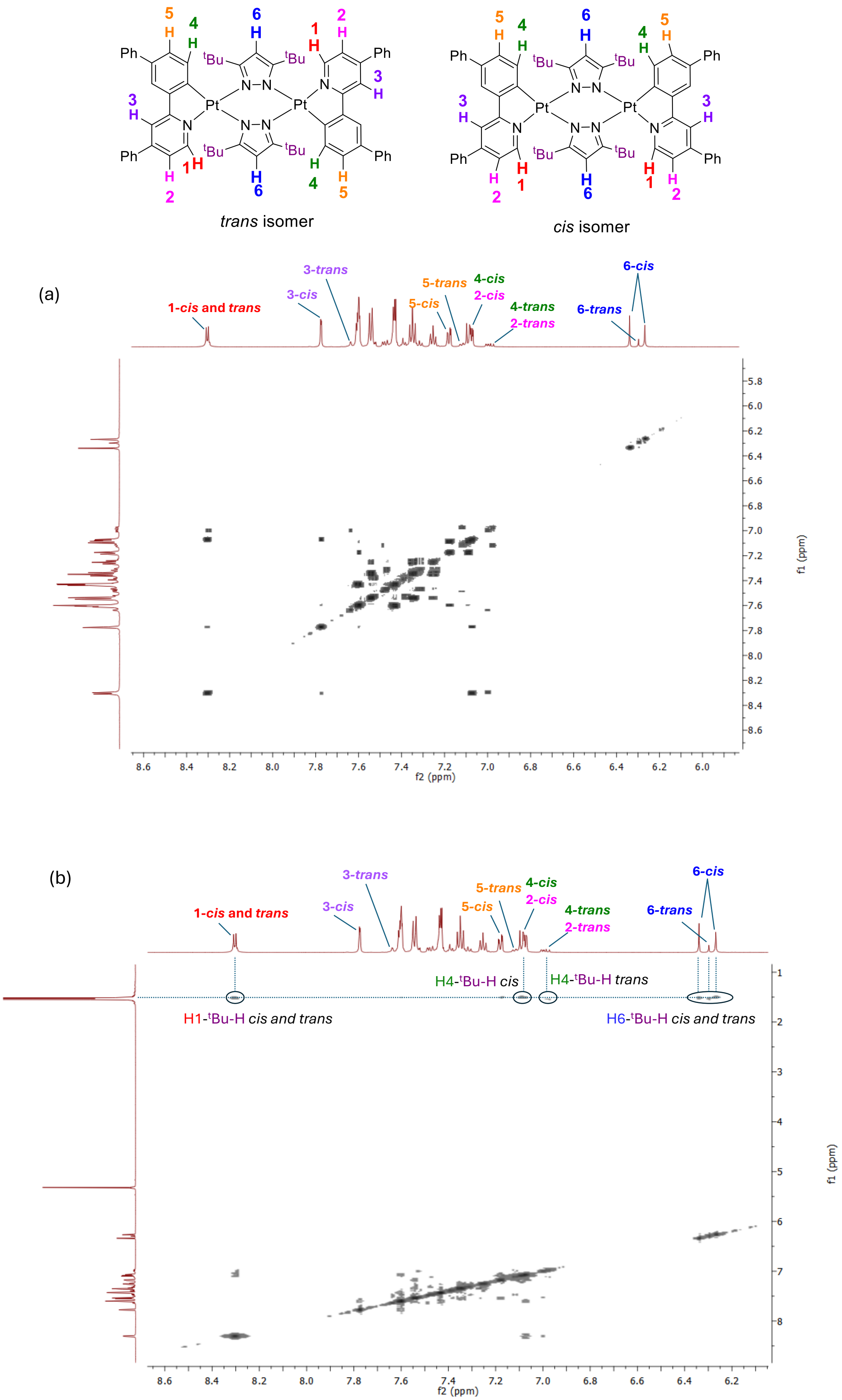


Figure S37. (a) ^{1}H-^{1}H COSY and (b) ^{1}H-^{1}H NOESY spectra of complex **Ref-Pt1** in CD_2Cl_2.

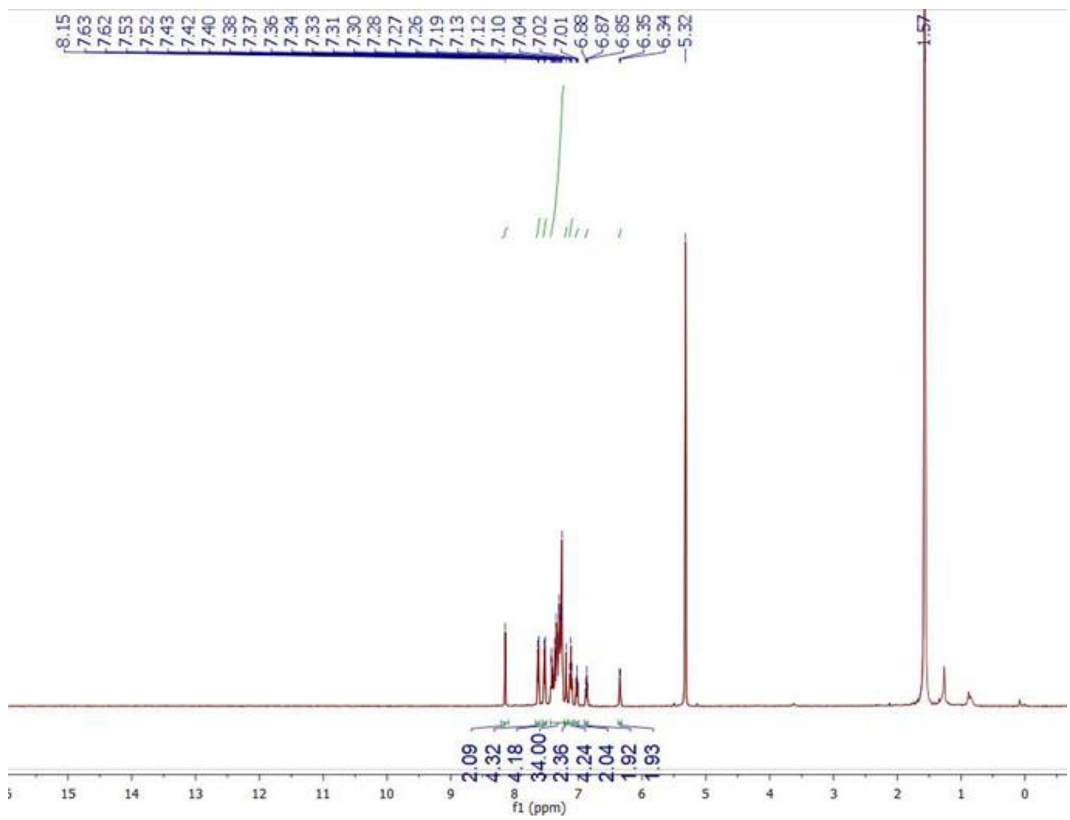


Figure S38. ^{1}H NMR spectrum of complex **3** in CD_2Cl_2.

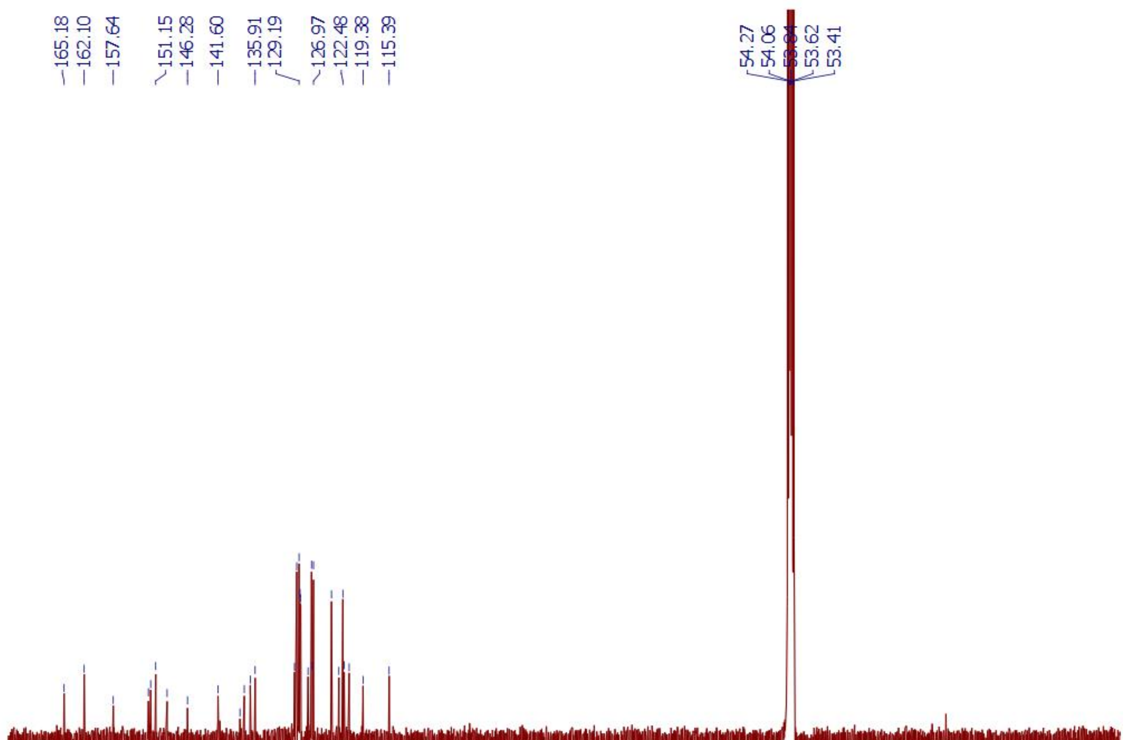


Figure S39. ^{13}C NMR spectrum of complex **3** in CD_2Cl_2.

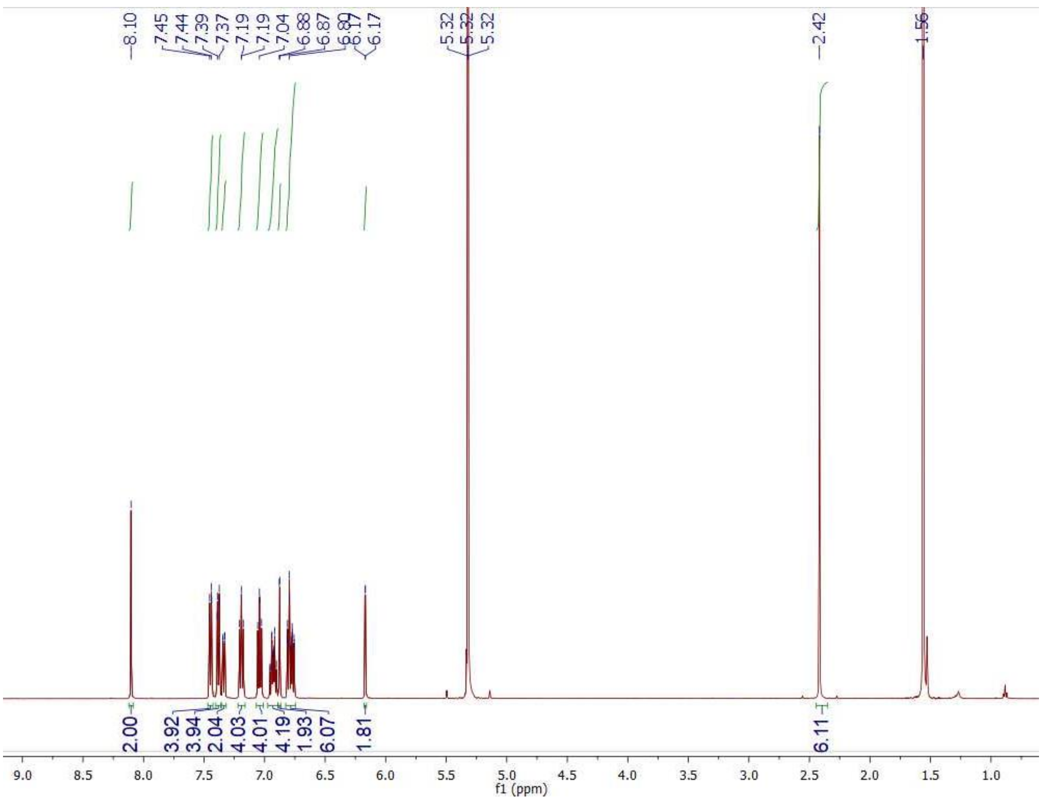


Figure S40. ^{1}H NMR spectrum of complex **4** in CD_2Cl_2.

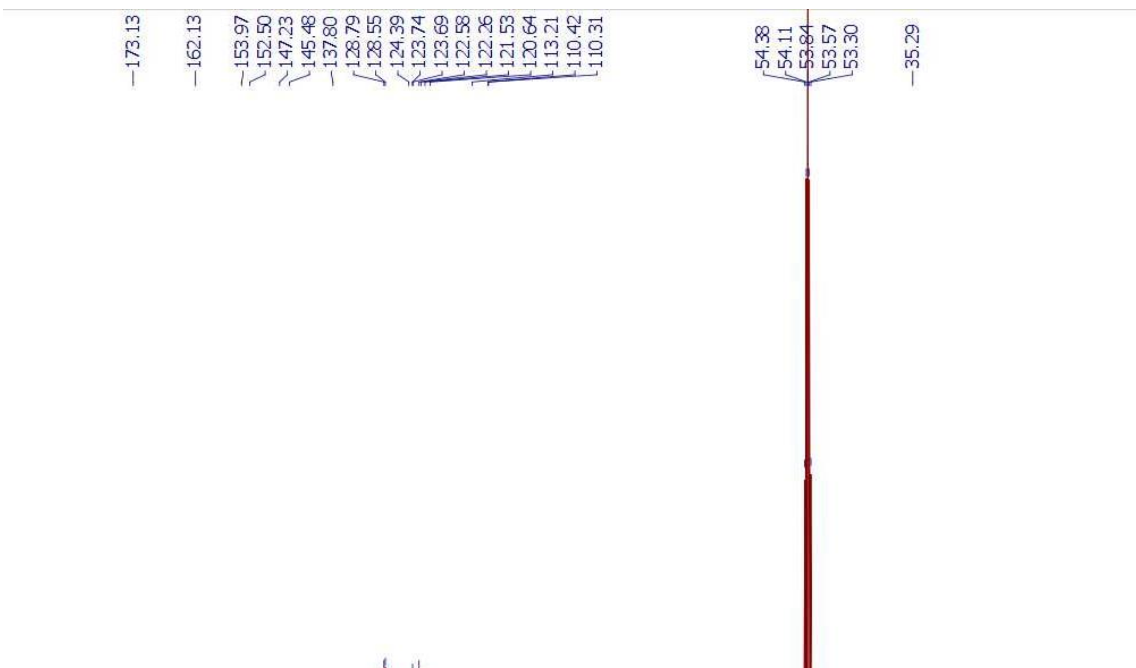


Figure S41. ^{13}C NMR spectrum of complex **4** in CD_2Cl_2.

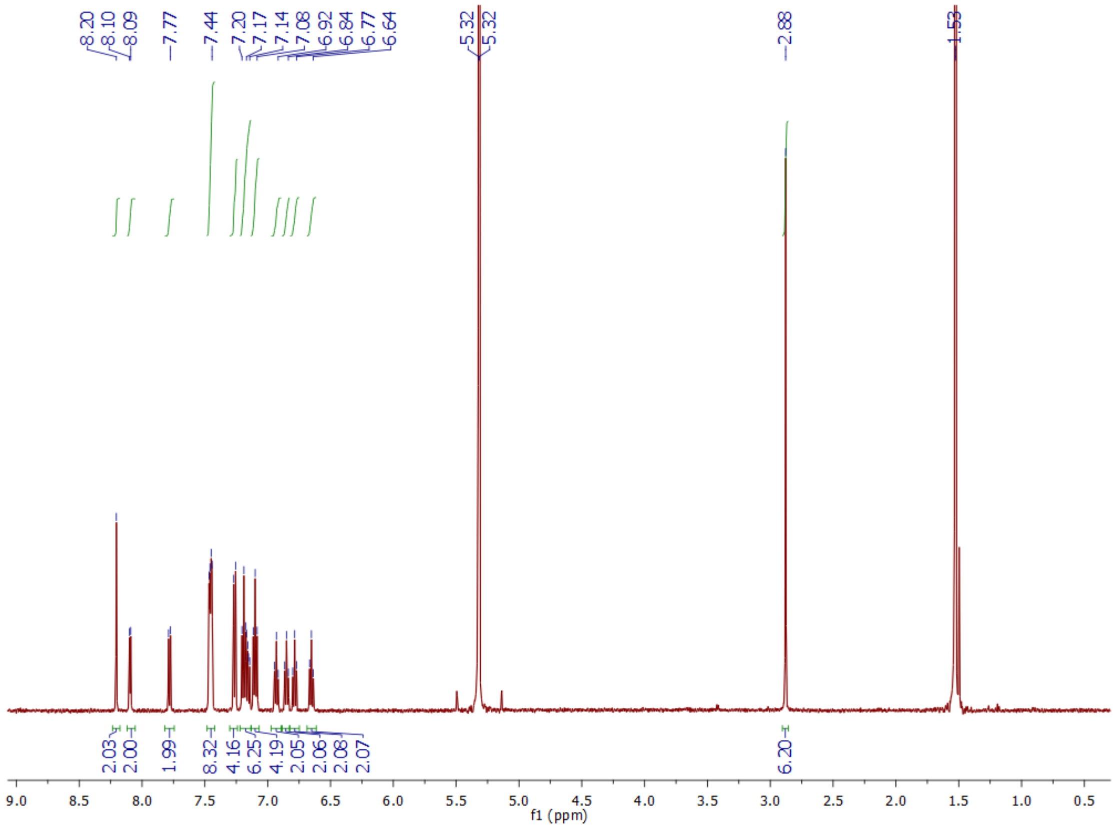


Figure S42. ^{1}H NMR spectrum of complex **5** in CD_2Cl_2.

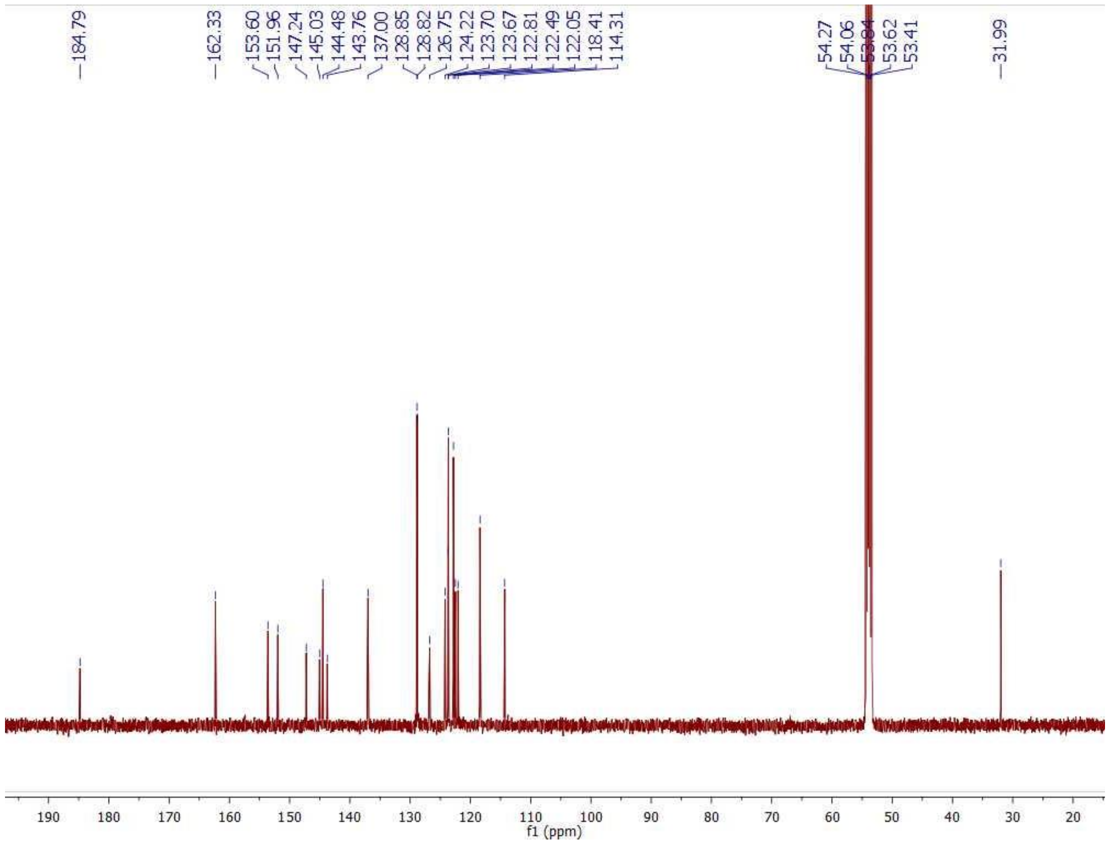


Figure S43. ^{13}C NMR spectrum of complex **5** in CD_2Cl_2.

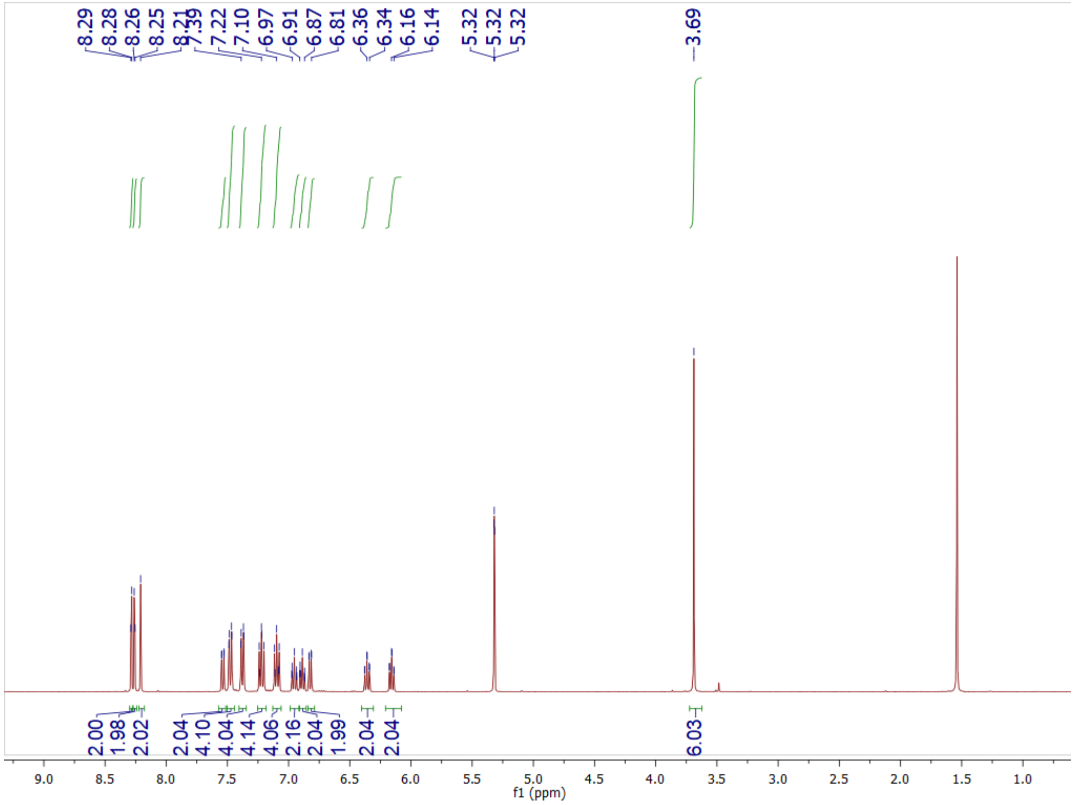


Figure S44. ^{1}H NMR spectrum of complex **6** in CD_2Cl_2.

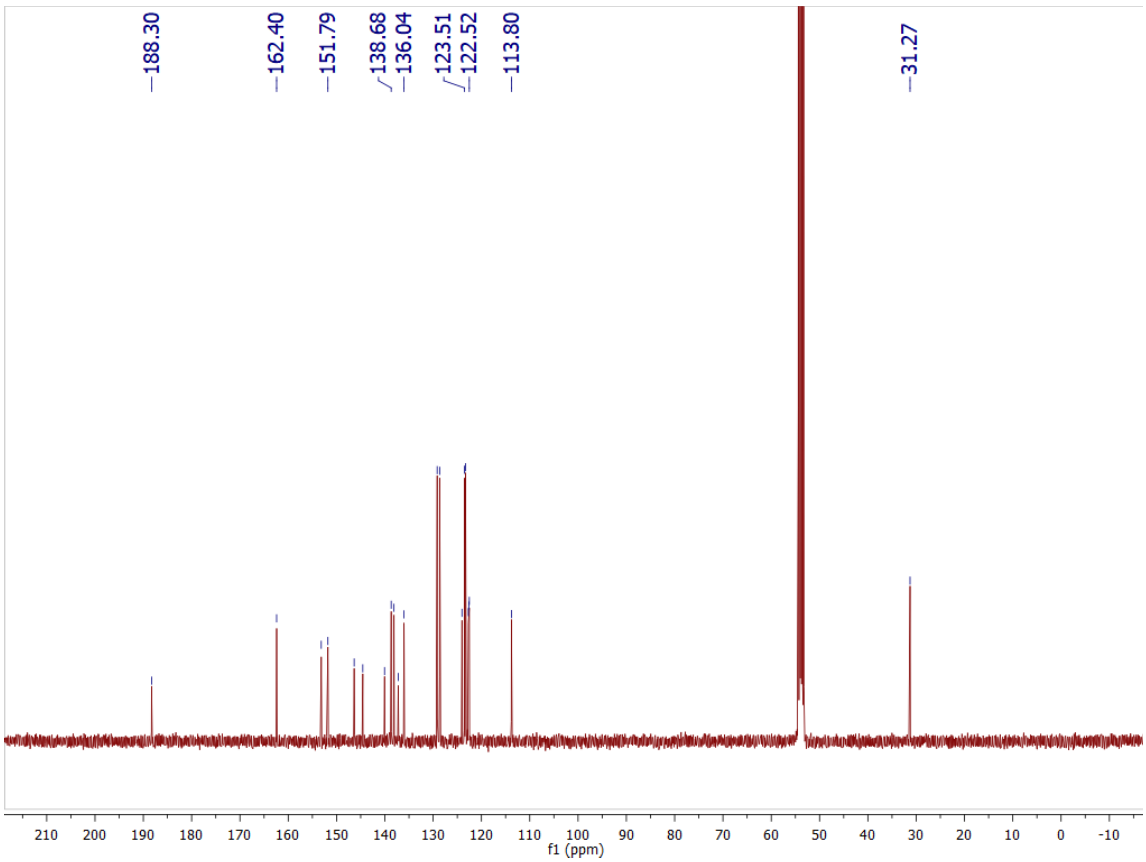


Figure S45. ^{13}C NMR spectrum of complex **6** in CD_2Cl_2.

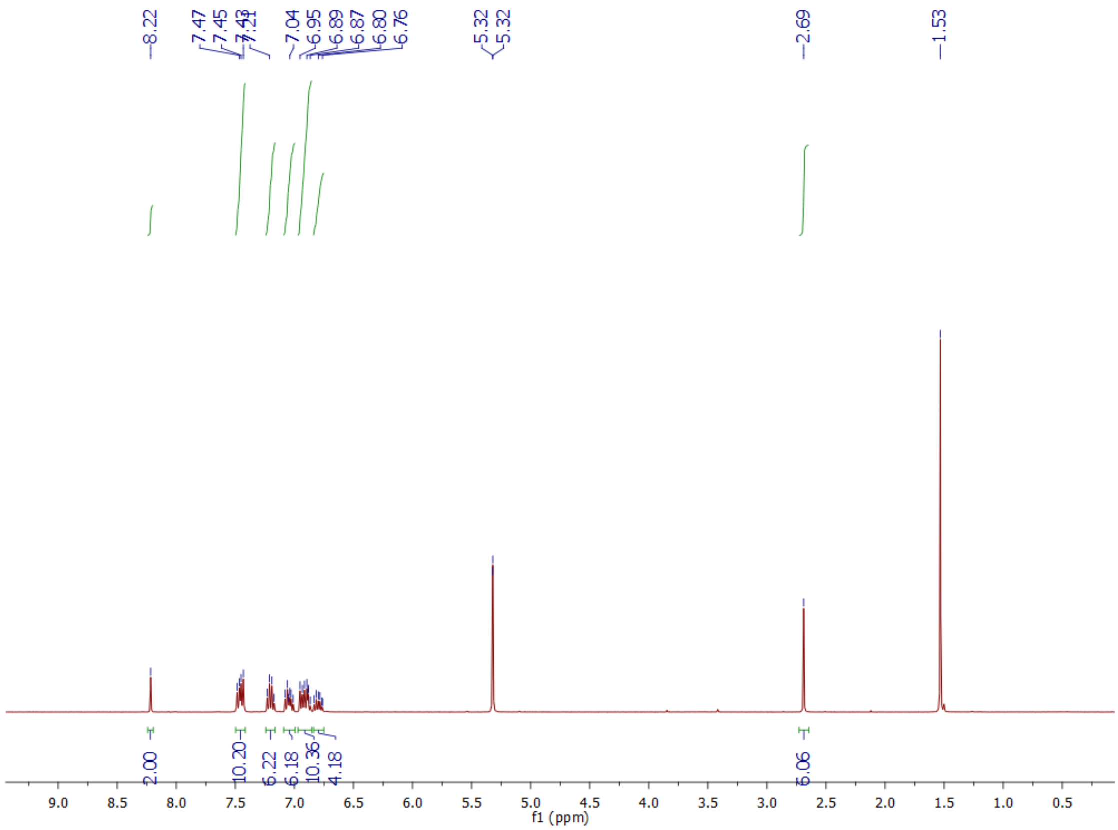


Figure S46. ^{1}H NMR spectrum of complex **7** in CD_2Cl_2.

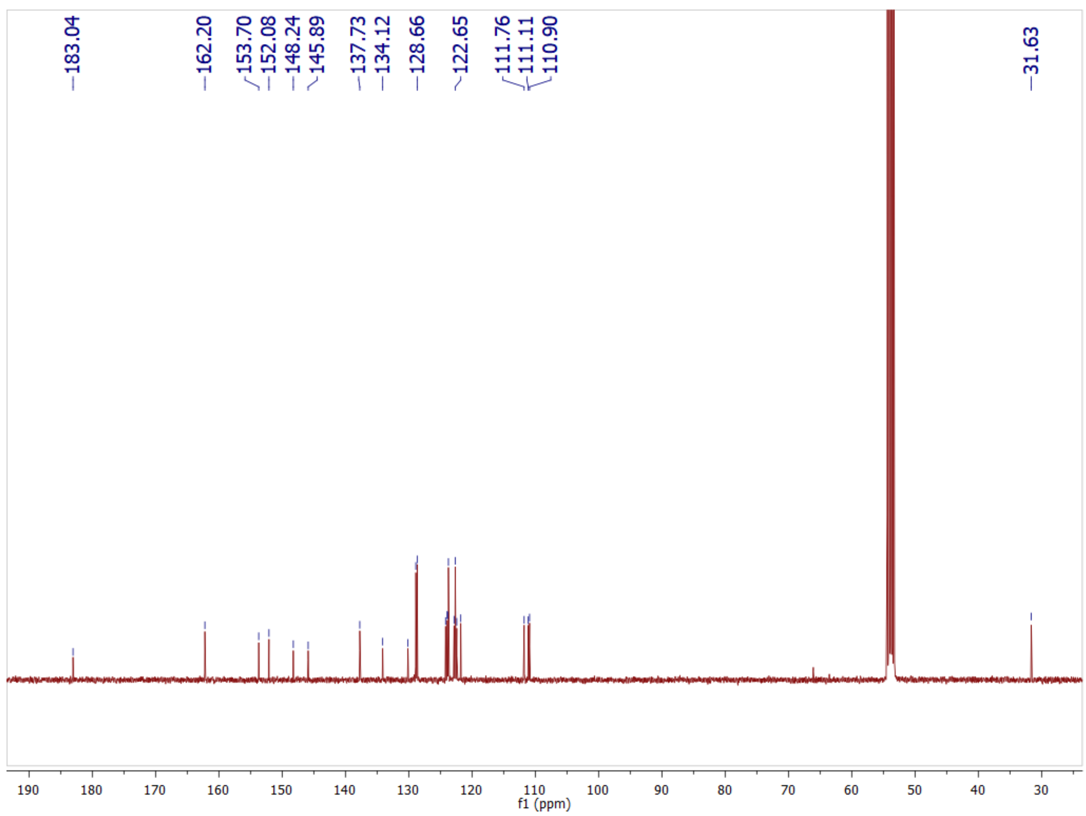


Figure S47. ^{13}C NMR spectrum of complex **7** in CD_2Cl_2.

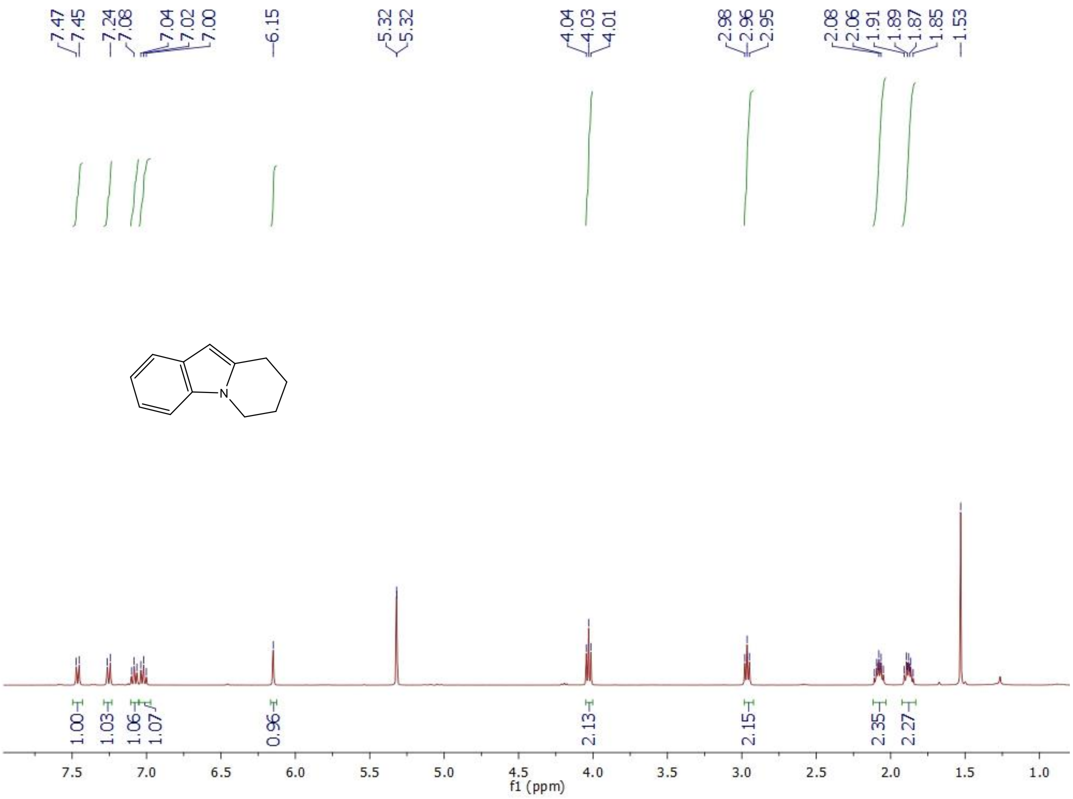


Figure S48. ^{1}H NMR spectrum of **8a** in CD_2Cl_2.

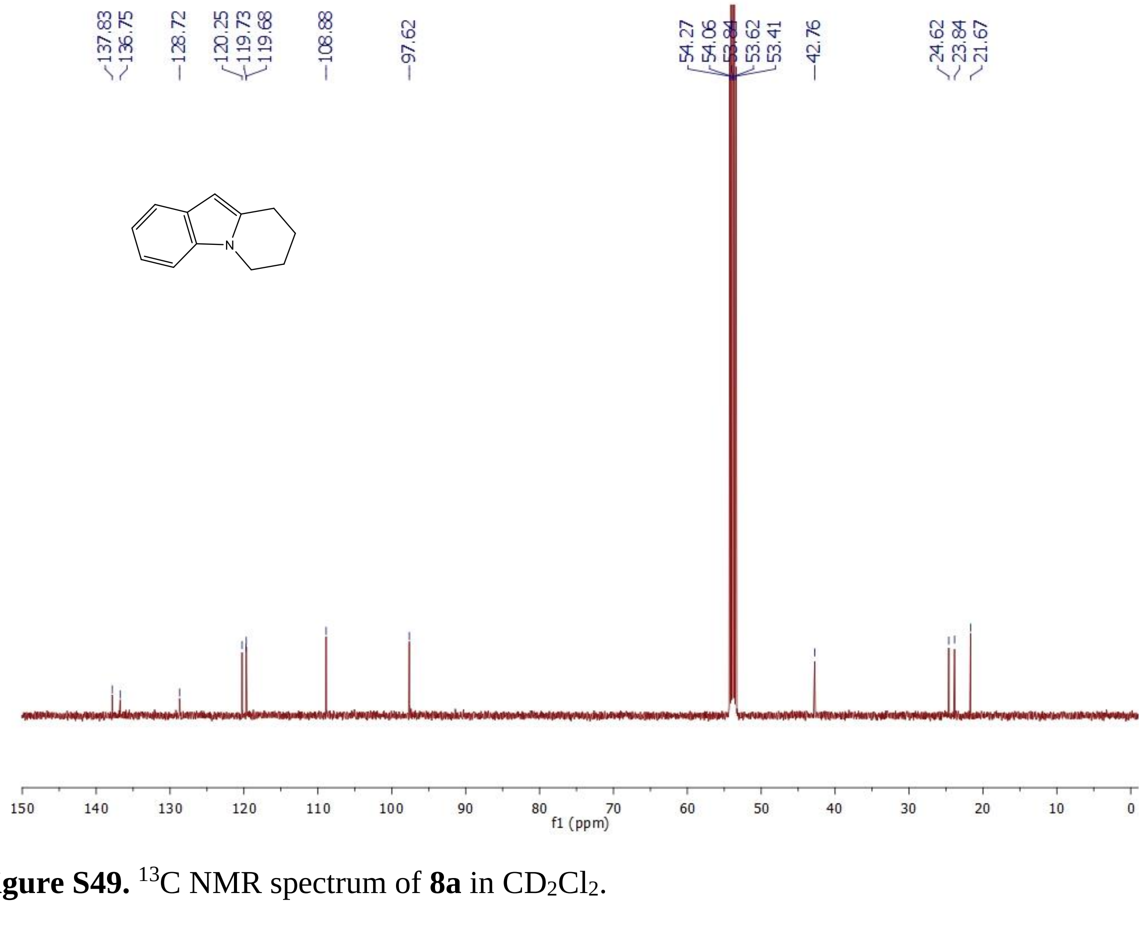


Figure S49. ^{13}C NMR spectrum of **8a** in CD_2Cl_2.

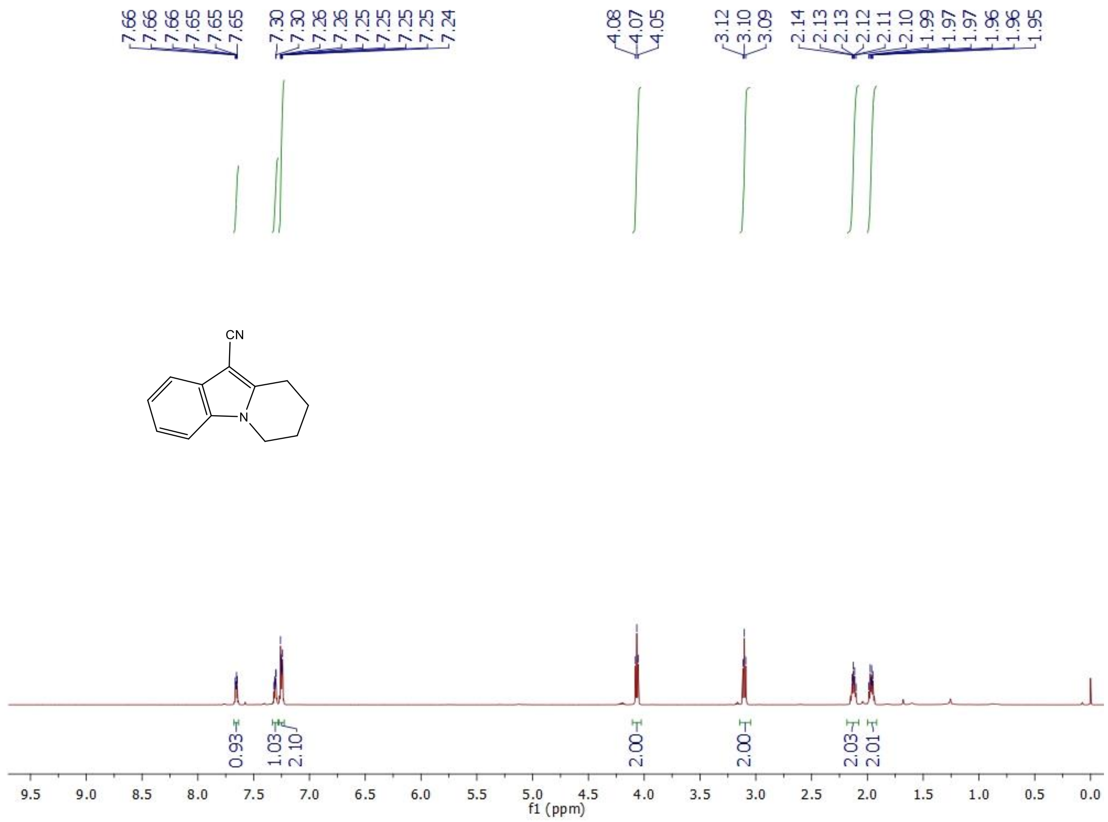


Figure S50. ^{1}H NMR spectrum of **8b** in $CDCl_3$.

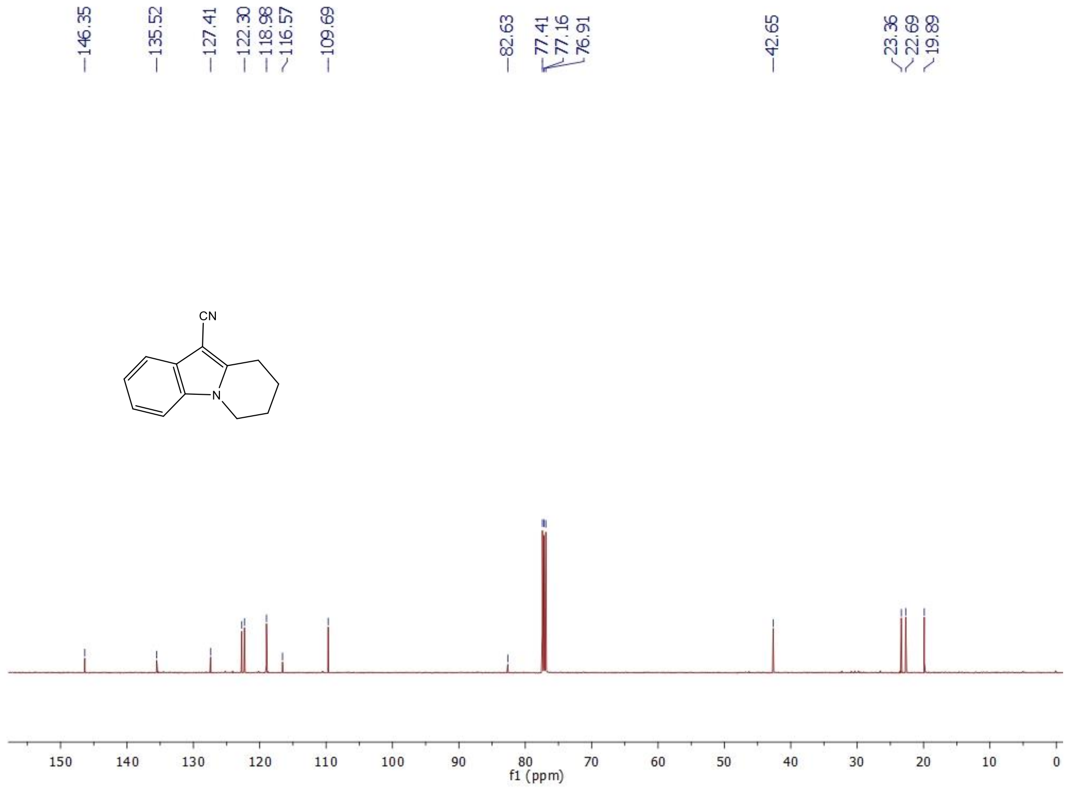


Figure S51. ^{13}C NMR spectrum of **8b** in $CDCl_3$.

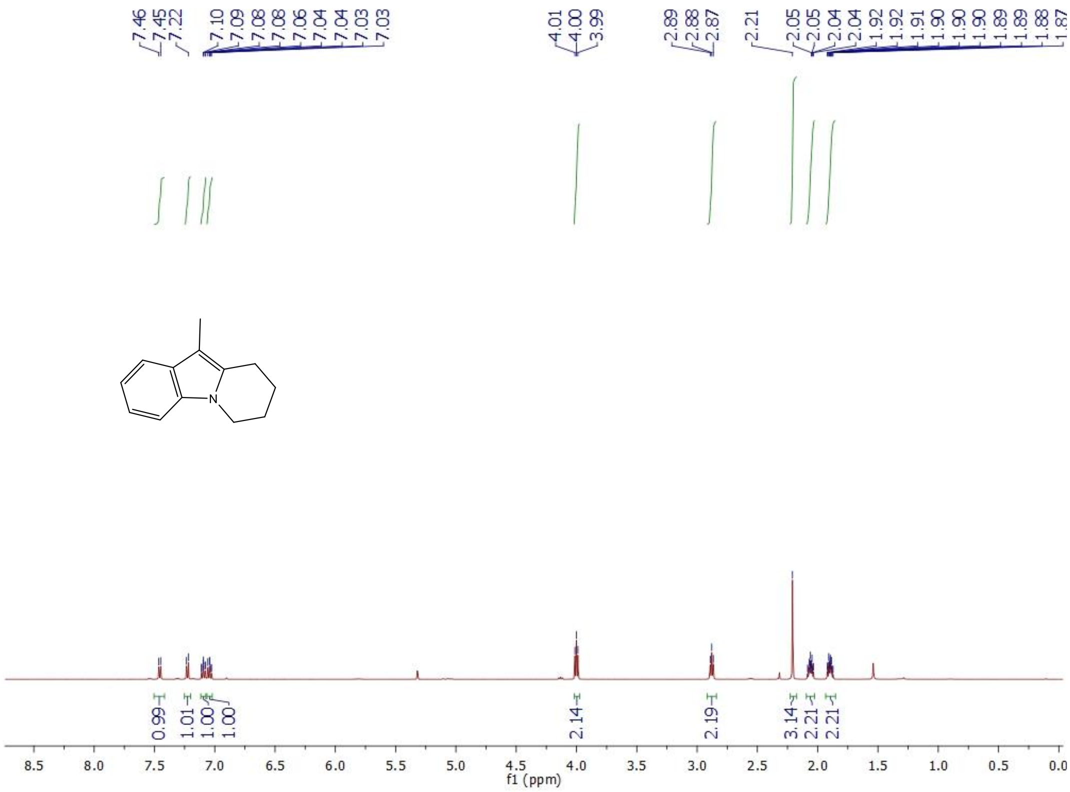


Figure S52. ^{1}H NMR spectrum of **8c** in CD_2Cl_2.

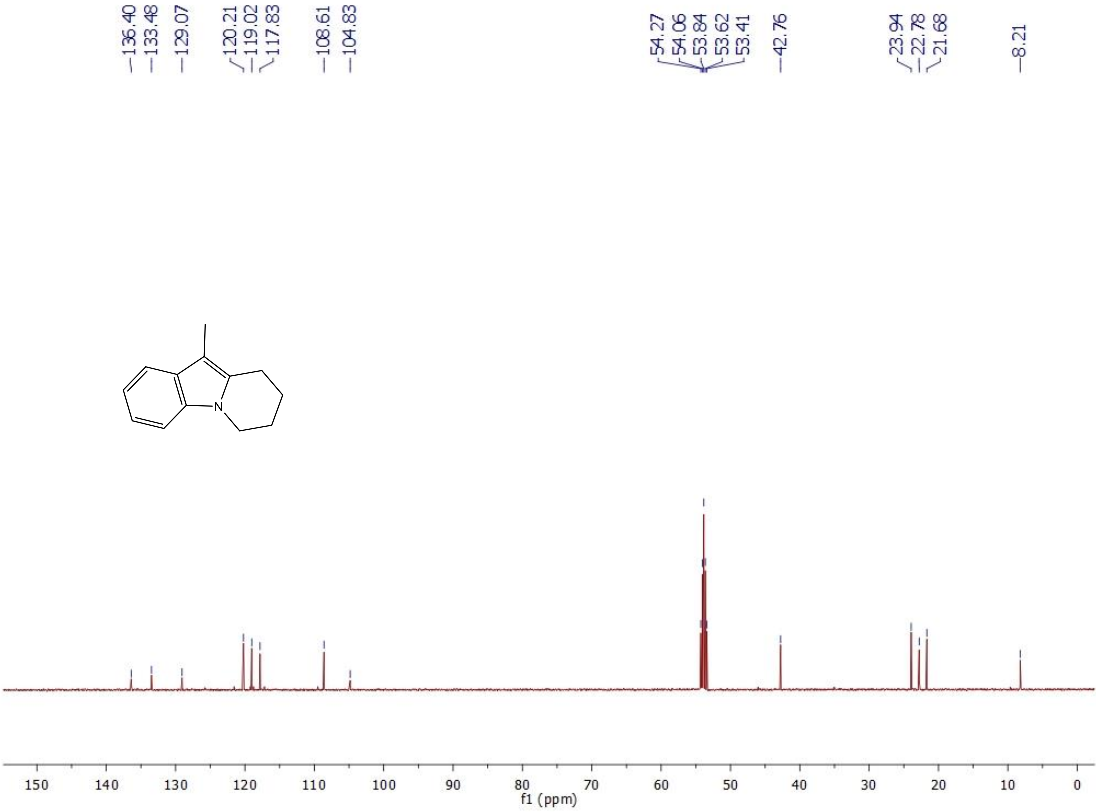


Figure S53. ^{13}C NMR spectrum of **8c** in CD_2Cl_2.

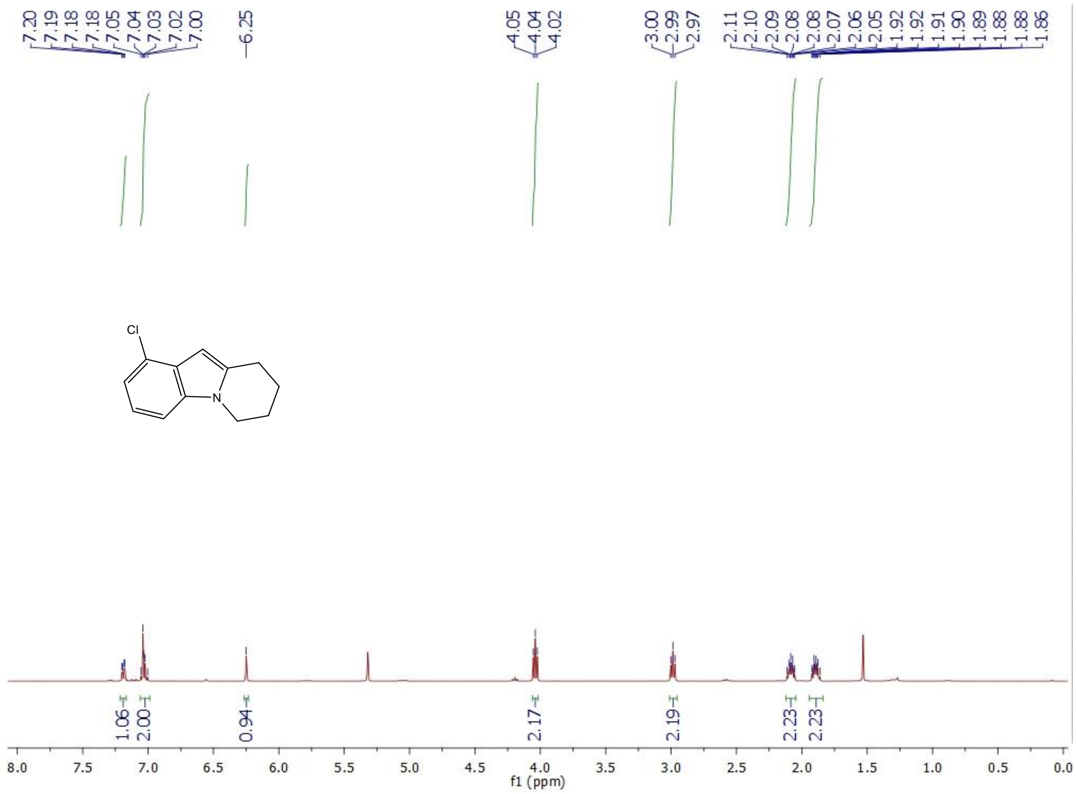


Figure S54. ^{1}H NMR spectrum of **8d** in CD_2Cl_2.

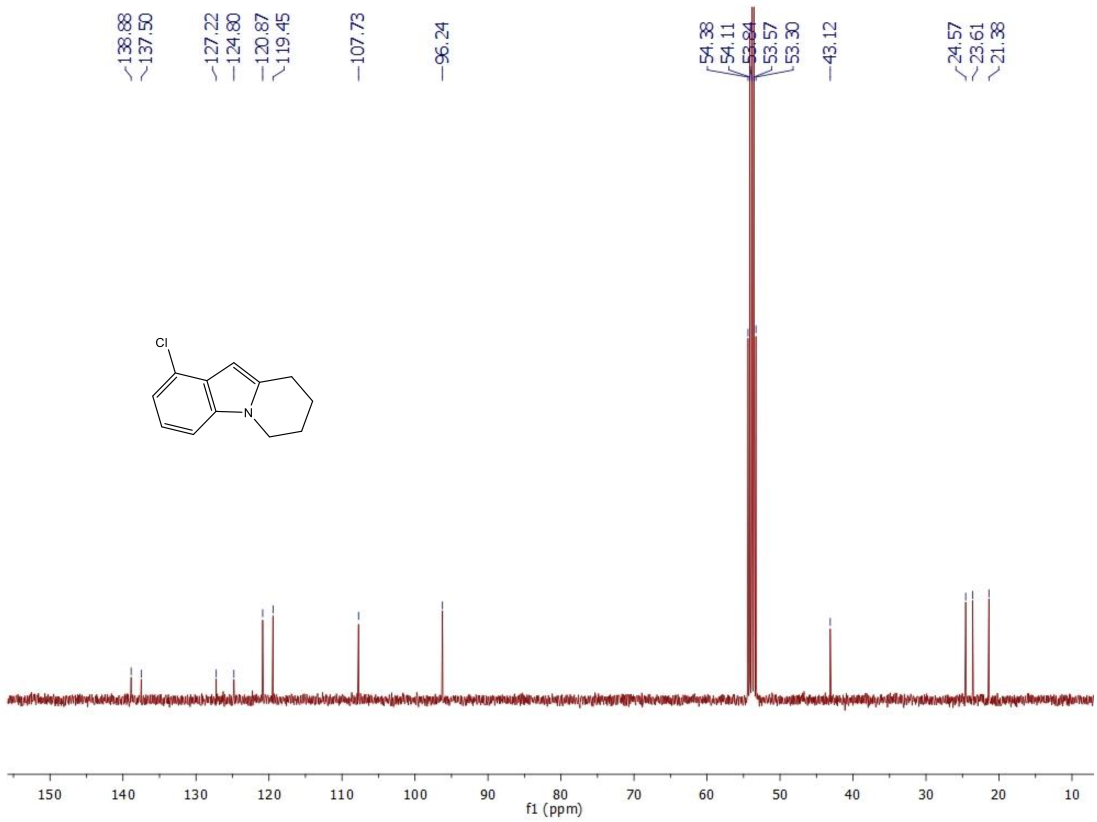


Figure S55. ^{13}C NMR spectrum of **8d** in CD_2Cl_2.

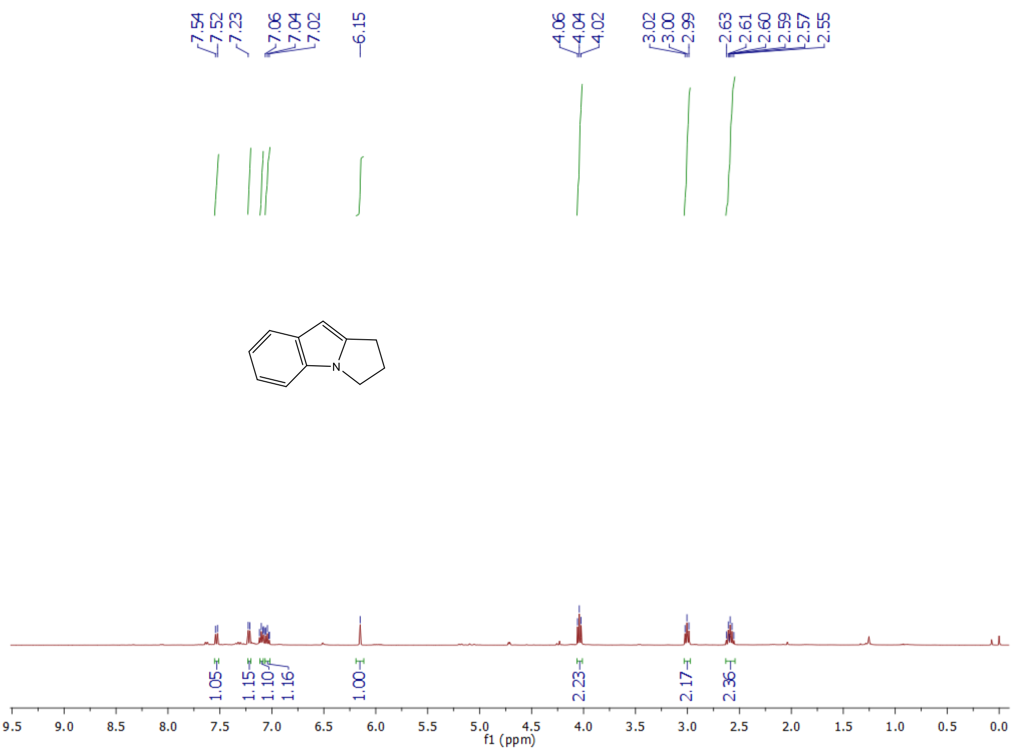


Figure S56. [1]H NMR spectrum of **8e** in $CDCl_3$.

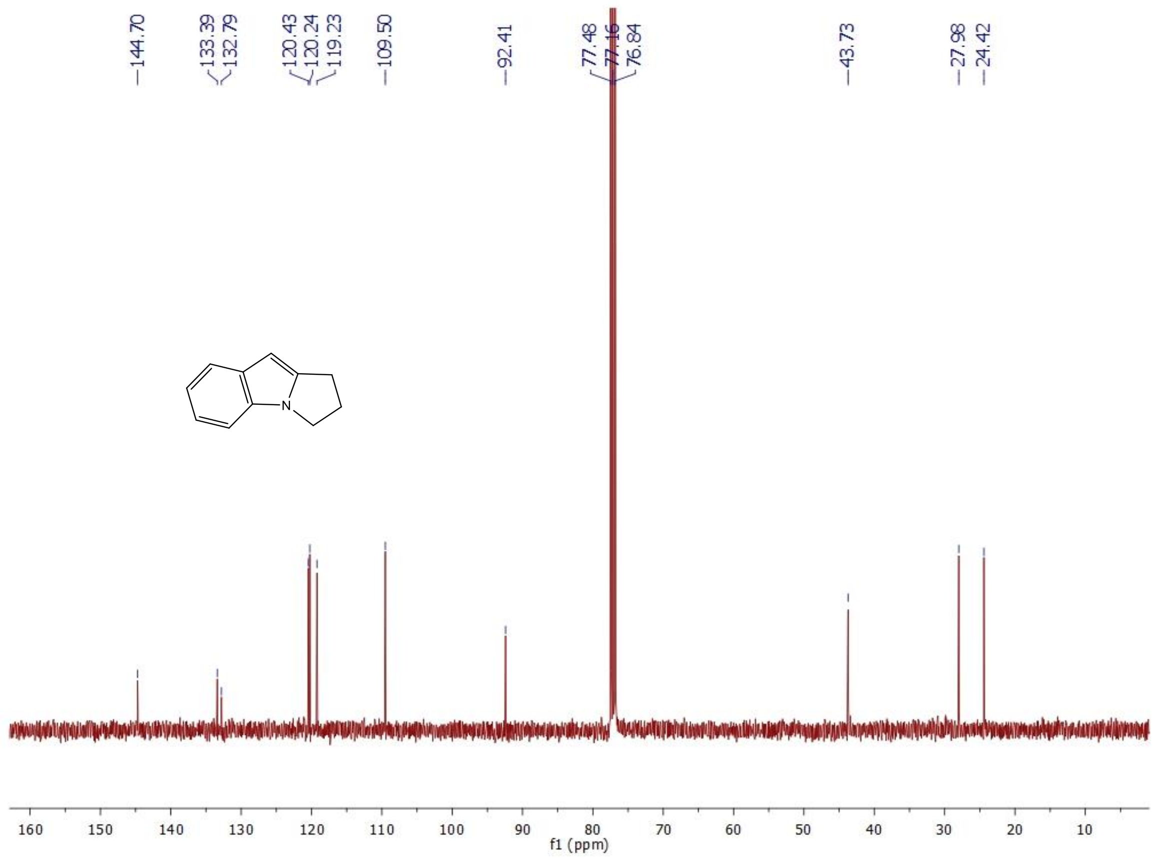


Figure S57. [13]C NMR spectrum of **8e** in $CDCl_3$.

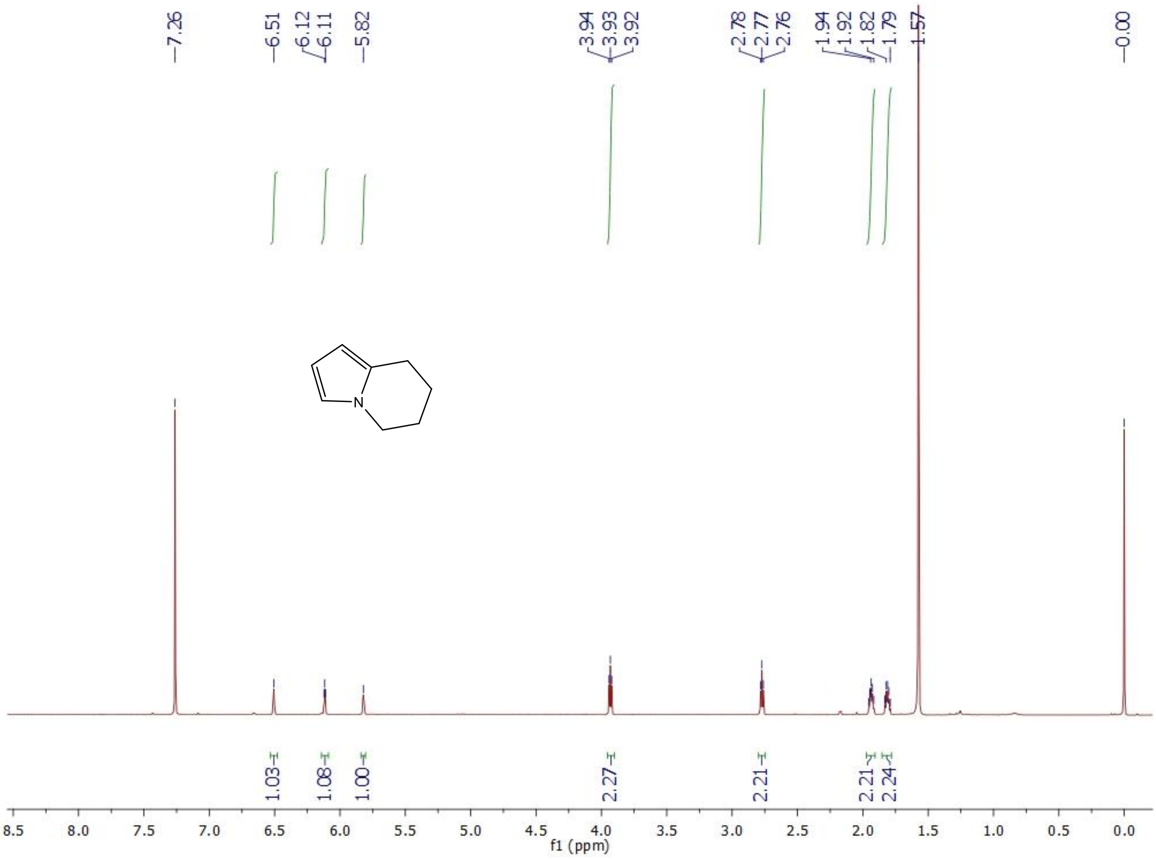


Figure S58. ^{1}H NMR spectrum of **8f** in $CDCl_3$.

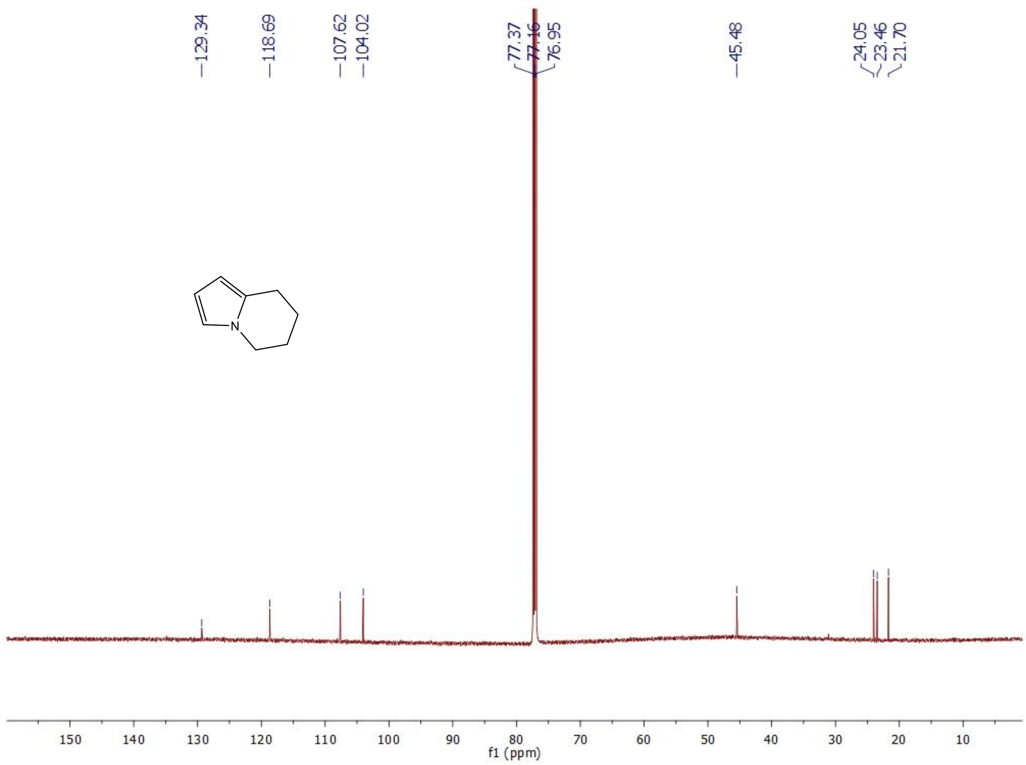


Figure S59. ^{13}C NMR spectrum of **8f** in $CDCl_3$.

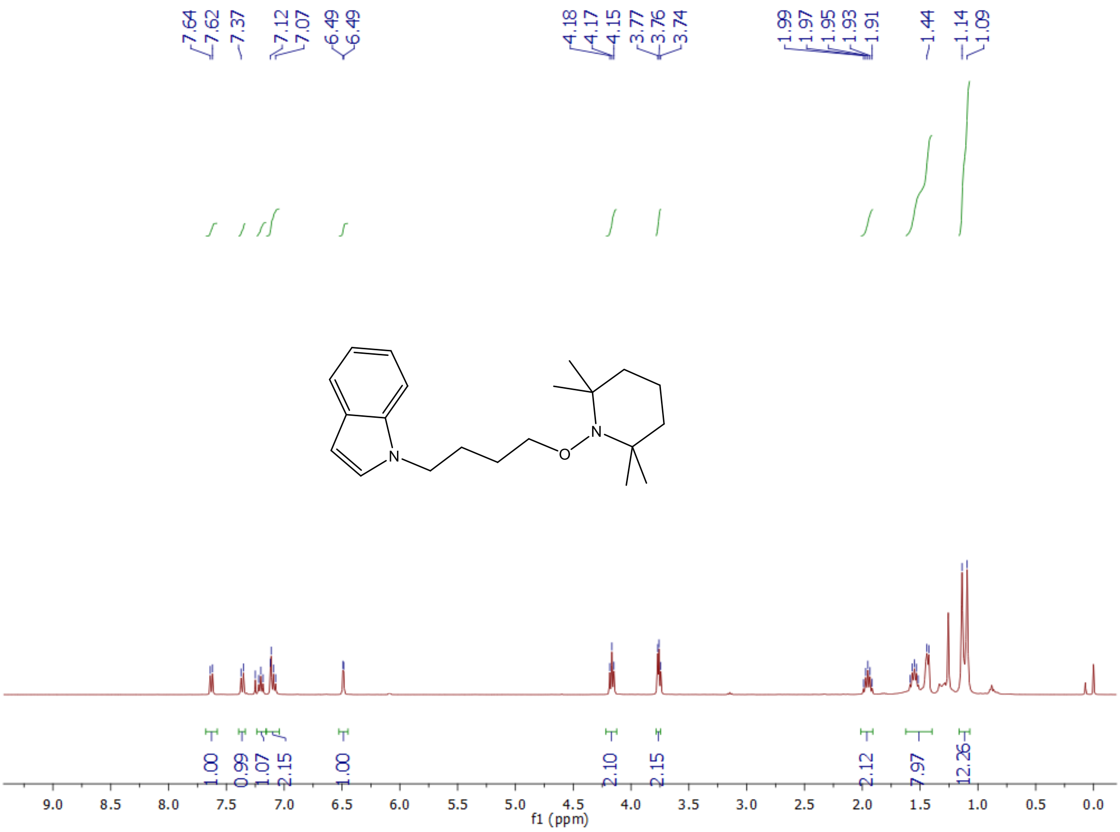


Figure S60. ^{1}H NMR spectrum of **8g** in $CDCl_3$.

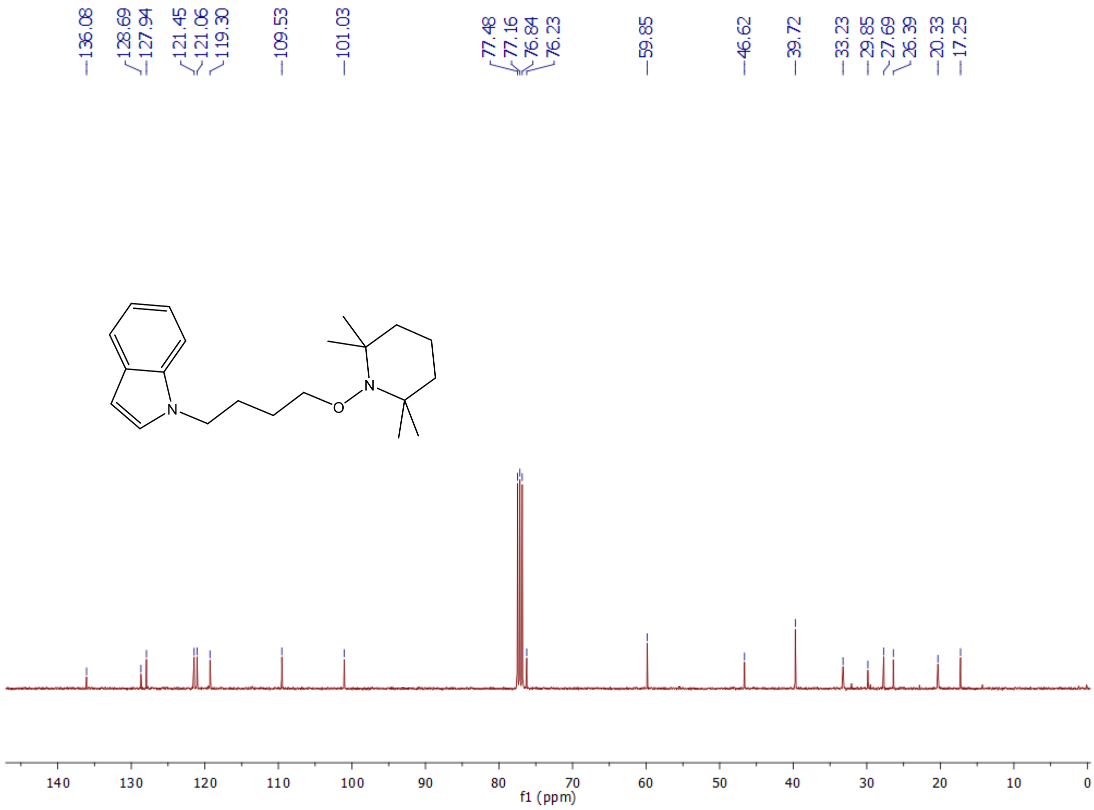


Figure S61. ^{13}C NMR spectrum of **8g** in $CDCl_3$.

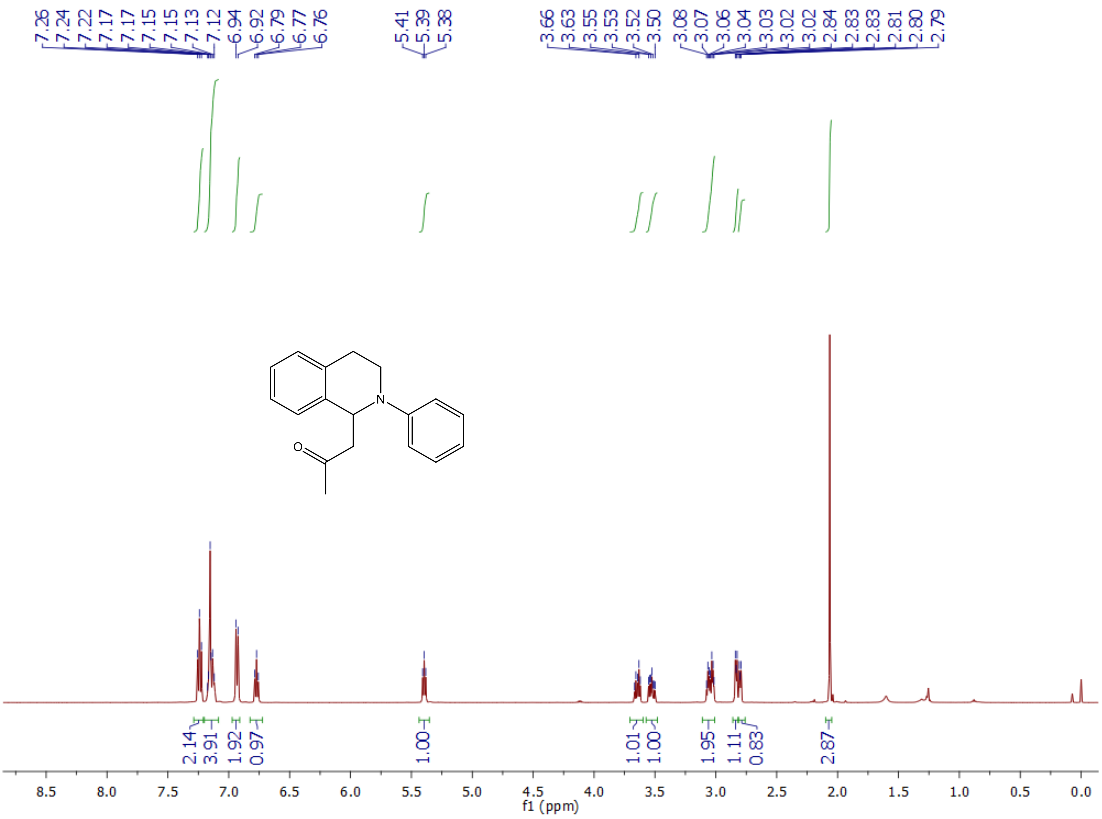


Figure S62. ^{1}H NMR spectrum of **9** in $CDCl_3$.

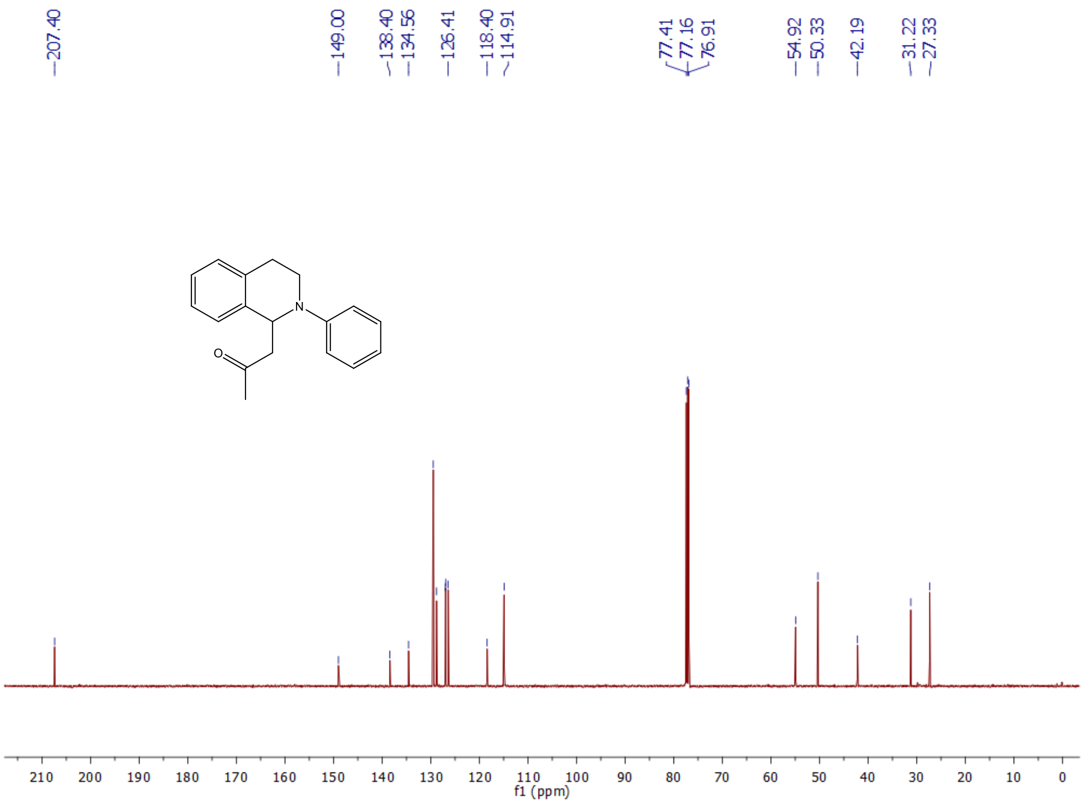


Figure S63. ^{13}C NMR spectrum of **9** in $CDCl_3$.

Cartesian Coordinates

Complex Ref-Pt1 at S_0 state

Pt	-1.36138000	-0.50101400	1.34669500
N	0.27993500	0.46710600	2.04514100
N	-2.61151900	1.27014100	1.08435800
N	-2.78120100	1.48675100	-0.24769500
C	-0.10037800	-2.02449800	1.37465300
C	-0.31376000	-3.33864600	0.93949100
H	-1.29243300	-3.62434600	0.56539700
C	0.70926000	-4.27976800	0.95156700
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C	2.23383200	-2.64355500	1.81764700
H	3.22290500	-2.37468100	2.17973700
C	1.21139800	-1.69267400	1.79555000
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Complex Ref-Pt1 at T_1 state

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C	1.28779500	-1.11684400	1.81414100
C	1.41316900	0.32192600	1.93599800
C	2.59153900	1.03363700	2.14024500
H	3.52211500	0.48093400	2.21455100
C	2.60772300	2.42826100	2.19237100
C	1.36364400	3.08633100	2.01203700
H	1.28809000	4.16711000	2.04136800
C	0.22623800	2.34743600	1.80664600
H	-0.73204400	2.81742900	1.62520900
C	3.30271800	-4.32506000	1.86556800
C	3.13220600	-5.60678200	2.40977700
H	2.15542000	-5.90216800	2.78437800
C	4.20143900	-6.49260100	2.50237400

H	4.04697900	-7.47846400	2.93335200
C	5.46739300	-6.11508500	2.05617900
H	6.30238400	-6.80683600	2.12789900
C	5.65123900	-4.84470900	1.51350800
H	6.62777100	-4.54538200	1.14234500
C	4.58061600	-3.96182500	1.41684800
H	4.72584500	-2.99167000	0.94929900
C	3.85367800	3.17830100	2.39702800
C	4.91869000	2.63149800	3.13456600
H	4.80871500	1.65217200	3.59273000
C	6.09901100	3.34108100	3.31856500
H	6.90481700	2.90044400	3.89975000
C	6.24644200	4.61697800	2.77261200
H	7.16974400	5.17136000	2.91654400
C	5.19849800	5.17291200	2.04099000
H	5.30643100	6.15642200	1.59192500
C	4.01622400	4.46490800	1.85700000
H	3.22863600	4.89619000	1.24613300
C	-3.54714800	2.42337400	1.22693200
C	-4.19145600	2.99163600	0.11894600
H	-4.92917700	3.78091900	0.13665000
C	-3.70944500	2.32288200	-1.00679600
C	-3.71531300	2.82837900	2.67647700
C	-3.23196800	4.28076100	2.83263300
H	-2.16597300	4.37310100	2.59495800
H	-3.37884900	4.61902000	3.86540500
H	-3.78509800	4.95494100	2.16988500
C	-2.92972300	1.94216200	3.64570300
H	-3.22977800	0.89186000	3.57745400
H	-3.11661900	2.27760600	4.67251100
H	-1.85125200	1.99560200	3.47063800
C	-5.20715700	2.76448000	3.04078400
H	-5.59555600	1.74564500	2.93938000
H	-5.80320000	3.41943100	2.39632700
H	-5.35432700	3.08612400	4.07879100

C	-4.18102200	2.42907000	-2.43852100
C	-3.02624200	2.38335000	-3.44407100
H	-2.47582800	1.43743000	-3.39231900
H	-2.30901600	3.19181100	-3.26983600
H	-3.42189600	2.48294200	-4.46171400
C	-4.94448800	3.74269800	-2.63442800
H	-5.29173900	3.81831500	-3.67097000
H	-4.30526800	4.60763700	-2.42370300
H	-5.82421400	3.79832200	-1.98416200
C	-5.13147600	1.24776500	-2.69345400
H	-5.46870500	1.23883200	-3.73731700
H	-6.01239600	1.31161000	-2.04466200
H	-4.62699400	0.30102700	-2.47907300
Pt	-1.37461900	0.15375900	-1.31768500
N	0.22242500	-0.99919300	-1.79080200
N	-2.72008700	-1.46971100	-0.77589700
N	-2.81510400	-1.41292100	0.57568000
C	-0.01707300	1.59401700	-1.52757900
C	-0.19809900	2.96392900	-1.34191500
H	-1.17939300	3.34864800	-1.07931900
C	0.87225100	3.84737000	-1.44709400
H	0.71152800	4.90693400	-1.26365900
C	2.16547900	3.38693300	-1.75463400
C	2.35333200	2.01689400	-1.93639100
H	3.34574900	1.65290500	-2.18994700
C	1.28774200	1.11690400	-1.81420600
C	1.41312200	-0.32186500	-1.93608000
C	2.59149900	-1.03357000	-2.14029800
H	3.52207300	-0.48086100	-2.21457500
C	2.60770100	-2.42819700	-2.19238300
C	1.36361400	-3.08626800	-2.01209600
H	1.28806100	-4.16704800	-2.04141700
C	0.22619900	-2.34737800	-1.80675200
H	-0.73208500	-2.81737900	-1.62534400
C	3.30265700	4.32511600	-1.86572500

C	3.13211400	5.60683900	-2.40991800
H	2.15529600	5.90224100	-2.78442600
C	4.20135200	6.49264200	-2.50261100
H	4.04686700	7.47851000	-2.93356900
C	5.46734200	6.11510400	-2.05653600
H	6.30233800	6.80684000	-2.12833700
C	5.65121800	4.84472500	-1.51388200
H	6.62778000	4.54538300	-1.14281000
C	4.58059000	3.96185800	-1.41712300
H	4.72584300	2.99170000	-0.94958800
C	3.85367700	-3.17823200	-2.39691800
C	4.91873700	-2.63146500	-3.13441300
H	4.80878500	-1.65217200	-3.59265300
C	6.09907900	-3.34104500	-3.31827900
H	6.90492100	-2.90043800	-3.89943700
C	6.24649000	-4.61690400	-2.77222600
H	7.16981100	-5.17128100	-2.91605200
C	5.19850100	-5.17280100	-2.04064100
H	5.30641600	-6.15627500	-1.59149400
C	4.01620300	-4.46480000	-1.85678800
H	3.22857800	-4.89605000	-1.24594700
C	-3.54702700	-2.42349500	-1.22687800
C	-4.19124600	-2.99180100	-0.11886100
H	-4.92887400	-3.78117200	-0.13652300
C	-3.70928200	-2.32295500	1.00684500
C	-3.71516600	-2.82857400	-2.67640500
C	-3.23165400	-4.28090500	-2.83251200
H	-2.16564300	-4.37311300	-2.59485800
H	-3.37852000	-4.61922200	-3.86526700
H	-3.78469200	-4.95512200	-2.16972500
C	-2.92969200	-1.94229300	-3.64566400
H	-3.22991500	-0.89203800	-3.57746100
H	-3.11652600	-2.27781200	-4.67245800
H	-1.85121700	-1.99555100	-3.47057700
C	-5.20702200	-2.76485900	-3.04070100

H	-5.59553700	-1.74606600	-2.93932200
H	-5.80298600	-3.41986100	-2.39622500
H	-5.35416000	-3.08654600	-4.07869900
C	-4.18074400	-2.42915900	2.43859900
C	-3.02584900	-2.38318200	3.44400300
H	-2.47554500	-1.43720700	3.39203300
H	-2.30855800	-3.19158900	3.26977300
H	-3.42135600	-2.48268500	4.46171200
C	-4.94398300	-3.74289900	2.63465000
H	-5.29112000	-3.81851000	3.67123000
H	-4.30465100	-4.60775300	2.42391600
H	-5.82376200	-3.79869500	1.98447000
C	-5.13135900	-1.24798500	2.69355100
H	-5.46849300	-1.23903800	3.73744500
H	-6.01233100	-1.31200600	2.04484600
H	-4.62705100	-0.30118100	2.47906000

Complex 1 at S_0 state

Pd	1.55550110	0.05211097	-1.41551709
N	0.06348399	1.41546508	-1.78703212
N	2.93168521	1.50486408	-0.55848403
N	2.86874521	1.41571807	0.79400508
C	0.07078798	-1.21052212	-1.76171012
C	0.09709798	-2.60501222	-1.69439011
H	1.04046005	-3.11767527	-1.52985810
C	-1.07453611	-3.35189328	-1.78240012
H	-1.02432912	-4.43450936	-1.68707612
C	-2.32470021	-2.73443022	-1.93462713
C	-2.35996320	-1.34041412	-2.01361514
H	-3.32043627	-0.84914408	-2.14850415
C	-1.18765811	-0.58542807	-1.92471513
C	-1.17401710	0.87775004	-1.92547413
C	-2.29355919	1.70359411	-1.99422014
H	-3.28103627	1.25977808	-2.05445114
C	-2.16276817	3.09212022	-1.92132613
C	-0.86877907	3.61086825	-1.78771212

H	-0.69333205	4.67998033	-1.73900312
C	0.20393701	2.74211218	-1.71112111
H	1.21511409	3.10169421	-1.56180810
C	-3.57163331	-3.52759628	-1.97169714
C	-3.61989531	-4.76899938	-2.62010618
H	-2.73595325	-5.13843741	-3.13399322
C	-4.79171140	-5.52003844	-2.63777919
H	-4.80923041	-6.47725150	-3.15251623
C	-5.94066747	-5.04290539	-2.00988414
H	-6.85497156	-5.63001841	-2.02161914
C	-5.90605546	-3.81029829	-1.36049609
H	-6.79029255	-3.43819626	-0.84994305
C	-4.73384239	-3.06262124	-1.33978609
H	-4.70500538	-2.12118117	-0.79683804
C	-3.34484626	3.97411929	-1.95011313
C	-4.45563734	3.66225627	-2.74486120
H	-4.43427535	2.77963720	-3.37889324
C	-5.57250541	4.49183934	-2.75463820
H	-6.42232449	4.24291433	-3.38421224
C	-5.59776542	5.64049945	-1.96568714
H	-6.47295649	6.28440047	-1.96838714
C	-4.49959134	5.95656644	-1.16794307
H	-4.52146533	6.83617153	-0.53156702
C	-3.38060226	5.13257638	-1.16261107
H	-2.54525919	5.36512037	-0.50852502
C	3.78712728	2.48846315	-0.88266105
C	4.27935032	3.04938919	0.30003904
H	5.00295338	3.84830325	0.38446204
C	3.68149227	2.33894714	1.34418912
C	4.17854931	2.88690818	-2.29071216
C	3.86894829	4.37778829	-2.49836818
H	2.79355722	4.57580531	-2.41842217
H	4.19731632	4.69956231	-3.49432525
H	4.38105834	4.99736234	-1.75439612
C	3.45796726	2.07513612	-3.36664124

H	3.66701027	1.00676703	-3.26657923
H	3.80268928	2.39565114	-4.35726032
H	2.37208117	2.20839213	-3.33156724
C	5.69317344	2.66965815	-2.44859117
H	5.95429447	1.61664607	-2.29392016
H	6.25713848	3.26533920	-1.72264512
H	6.01851547	2.95999018	-3.45534725
C	4.00890430	2.46790815	2.81915023
C	2.89811021	1.96843911	3.74480830
H	2.63920219	0.92285703	3.55039028
H	1.98294514	2.55664116	3.62988229
H	3.23134924	2.05061012	4.78664038
C	4.27985433	3.94105126	3.15342726
H	4.52197535	4.04347926	4.21796933
H	3.40011526	4.55984031	2.94199024
H	5.12396139	4.34083028	2.58173921
C	5.28835539	1.65455508	3.08346625
H	5.57866541	1.72417508	4.13948733
H	6.11802143	2.02446310	2.47086820
H	5.13532537	0.59851000	2.83742823
Pd	1.55550410	-0.05200004	1.41555612
N	0.06346598	-1.41539413	1.78695315
N	2.93175620	-1.50467915	0.55854706
N	2.86878920	-1.41554315	-0.79394005
C	0.07074799	1.21060007	1.76167515
C	0.09704800	2.60509217	1.69437215
H	1.04041308	3.11775921	1.52988913
C	-1.07460309	3.35195523	1.78231215
H	-1.02439408	4.43456932	1.68697514
C	-2.32477618	2.73448419	1.93450016
C	-2.36001619	1.34046809	2.01348117
H	-3.32048427	0.84918105	2.14835518
C	-1.18769911	0.58549602	1.92461916
C	-1.17404111	-0.87768409	1.92537716
C	-2.29358120	-1.70352715	1.99414917

H	-3.28105527	-1.25970411	2.05438317
C	-2.16279620	-3.09205425	1.92130416
C	-0.86880710	-3.61079730	1.78765515
H	-0.69335009	-4.67990838	1.73895415
C	0.20391399	-2.74204524	1.71105315
H	1.21508906	-3.10165327	1.56175314
C	-3.57172228	3.52764026	1.97156917
C	-3.61992328	4.76914035	2.61980822
H	-2.73594421	5.13864638	3.13358025
C	-4.79173236	5.52018444	2.63749621
H	-4.80919636	6.47746651	3.15210726
C	-5.94075944	5.04296039	2.00979917
H	-6.85506252	5.63007344	2.02155517
C	-5.90621744	3.81026029	1.36059312
H	-6.79051152	3.43808127	0.85019308
C	-4.73400237	3.06258623	1.33984712
H	-4.70523537	2.12107216	0.79702308
C	-3.34487429	-3.97404631	1.95017616
C	-4.45558237	-3.66224429	2.74506323
H	-4.43416237	-2.77966722	3.37915227
C	-5.57245244	-4.49182734	2.75489922
H	-6.42219252	-4.24294833	3.38459727
C	-5.59783046	-5.64040542	1.96582716
H	-6.47303253	-6.28428945	1.96855816
C	-4.49974639	-5.95640446	1.16793110
H	-4.52169039	-6.83594853	0.53146906
C	-3.38073030	-5.13245140	1.16259910
H	-2.54544923	-5.36496342	0.50842205
C	3.78674926	-2.48866523	0.88271308
C	4.27877530	-3.04975328	-0.30000501
H	5.00208935	-3.84892734	-0.38444801
C	3.68118625	-2.33906622	-1.34414309
C	4.17811229	-2.88718527	2.29075519
C	3.86807226	-4.37795838	2.49845920
H	2.79260318	-4.57561839	2.41860320

H	4.19642028	-4.69981840	3.49439428
H	4.37991830	-4.99772443	1.75446815
C	3.45779824	-2.07523120	3.36673227
H	3.66718126	-1.00692312	3.26678626
H	3.80239626	-2.39594623	4.35733035
H	2.37186715	-2.20812920	3.33162727
C	5.69282238	-2.67039825	2.44853420
H	5.95428642	-1.61749518	2.29373119
H	6.25652246	-3.26633930	1.72259315
H	6.01813944	-2.96074228	3.45529628
C	4.00858628	-2.46800923	-2.81911320
C	2.89781020	-1.96854419	-3.74479127
H	2.63887018	-0.92297211	-3.55036925
H	1.98265012	-2.55676223	-3.62992226
H	3.23110022	-2.05067920	-4.78661035
C	4.27956729	-3.94113934	-3.15342022
H	4.52173931	-4.04354435	-4.21795131
H	3.39981522	-4.55993039	-2.94204221
H	5.12364435	-4.34093138	-2.58169618
C	5.28802038	-1.65459617	-3.08342622
H	5.57840838	-1.72432618	-4.13941730
H	6.11766445	-2.02438320	-2.47072517
H	5.13491737	-0.59852309	-2.83752420

Complex 1 at T_1 state

Pd	-1.53244810	-0.06274508	1.30556706
N	0.02342826	1.17785119	1.73949134
N	-2.91793045	1.51723796	0.67572918
N	-2.93594047	1.42397999	-0.67290179
C	-0.11098699	-1.43356128	1.50548229
C	-0.25554393	-2.81166107	1.39726607
H	-1.22809233	-3.24647438	1.18758223
C	0.85400794	-3.64776642	1.50983318
H	0.72693185	-4.71925245	1.37830035
C	2.13741094	-3.12222938	1.74618226
C	2.27443398	-1.73965592	1.86324103

H	3.25543017	-1.32489896	2.07991319
C	1.17435227	-0.88243799	1.73344338
C	1.24696597	0.56011083	1.81688510
C	2.40437610	1.32664736	1.93819105
H	3.36363051	0.81976224	1.94054589
C	2.35309512	2.71910533	1.99953804
C	1.06831785	3.31464934	1.92381225
H	0.93946425	4.38894530	1.98700501
C	-0.04173092	2.51932028	1.77652211
H	-1.03225706	2.94364635	1.66498901
C	3.31887799	-4.00426413	1.85570131
C	3.21759029	-5.28473337	2.41829029
H	2.26182739	-5.62324171	2.81003121
C	4.33015741	-6.11642644	2.50862243
H	4.22859242	-7.10303879	2.95347846
C	5.57111722	-5.68305356	2.04492822
H	6.43956535	-6.33246570	2.11526434
C	5.68653343	-4.41211215	1.48465016
H	6.64305570	-4.07081505	1.09810312
C	4.57292753	-3.58585903	1.38736516
H	4.66556953	-2.61782715	0.90253085
C	3.56965721	3.53695141	2.10770505
C	4.73497854	3.03637831	2.71278536
H	4.73261735	2.03939197	3.14518509
C	5.88469126	3.81266017	2.80036631
H	6.77118750	3.40559215	3.27967549
C	5.89850649	5.11151726	2.29146714
H	6.79763472	5.71758661	2.36074914
C	4.74937957	5.62275540	1.69131611
H	4.75287637	6.62417730	1.27003704
C	3.60040929	4.84663335	1.60044208
H	2.73154734	5.24506254	1.08531820
C	-3.76006048	2.49441243	1.04583416
C	-4.32476721	3.04475836	-0.11214218
H	-5.05309715	3.84216021	-0.15997875

C	-3.78085132	2.33826122	-1.18633390
C	-4.03508236	2.91909146	2.47256694
C	-3.57146541	4.37344253	2.65706511
H	-2.48916194	4.46911248	2.51300137
H	-3.80932212	4.72164645	3.66955847
H	-4.06638849	5.03893425	1.94157091
C	-3.32983937	2.03288097	3.49930733
H	-3.66678928	0.99507284	3.42472138
H	-3.56136447	2.38794038	4.51024913
H	-2.24143819	2.04613316	3.38271212
C	-5.55020149	2.84707203	2.72206607
H	-5.92090338	1.82493918	2.58590136
H	-6.09878261	3.49949201	2.03440712
H	-5.78036872	3.16329935	3.74663842
C	-4.14943333	2.44450731	-2.64892213
C	-3.00930507	2.01765337	-3.57551044
H	-2.72985027	0.96948288	-3.41933224
H	-2.11355404	2.62751321	-3.42517912
H	-3.32676115	2.11688098	-4.62023016
C	-4.52444114	3.89424342	-2.97975634
H	-4.80001231	3.97592828	-4.03754727
H	-3.68360230	4.57122728	-2.79089722
H	-5.37947145	4.23622051	-2.38708894
C	-5.36924139	1.53909986	-2.89176845
H	-5.66435561	1.56472632	-3.94811843
H	-6.22173853	1.86534398	-2.28589702
H	-5.14244925	0.50247814	-2.62017299
Pd	-1.53247509	0.06269322	-1.30558029
N	0.02341186	-1.17786600	-1.73954902
N	-2.91788811	-1.51733691	-0.67570696
N	-2.93587696	-1.42406889	0.67292031
C	-0.11104097	1.43354487	-1.50549710
C	-0.25562701	2.81164308	-1.39729411
H	-1.22818124	3.24644051	-1.18760604
C	0.85390793	3.64776906	-1.50987022

H	0.72681596	4.71925457	-1.37834322
C	2.13731727	3.12225531	-1.74622618
C	2.27436836	1.73968502	-1.86329024
H	3.25537408	1.32495188	-2.07997192
C	1.17430517	0.88244328	-1.73347619
C	1.24694533	-0.56010395	-1.81691633
C	2.40437028	-1.32662090	-1.93819528
H	3.36361517	-0.81971884	-1.94053319
C	2.35311893	-2.71908204	-1.99953698
C	1.06834695	-3.31464828	-1.92383024
H	0.93951399	-4.38894636	-1.98702406
C	-0.04171716	-2.51933933	-1.77656921
H	-1.03223907	-2.94368445	-1.66506309
C	3.31876634	4.00431335	-1.85574894
C	3.21744636	5.28477835	-2.41833897
H	2.26167234	5.62326129	-2.81007619
C	4.32999337	6.11650052	-2.50866423
H	4.22840933	7.10311076	-2.95352132
C	5.57096164	5.68315728	-2.04496209
H	6.43939231	6.33259164	-2.11529609
C	5.68640748	4.41222011	-1.48468192
H	6.64293664	4.07094946	-1.09812799
C	4.57282117	3.58593946	-1.38740114
H	4.66548010	2.61790811	-0.90256789
C	3.56969319	-3.53690643	-2.10769129
C	4.73502616	-3.03630528	-2.71272715
H	4.73266921	-2.03930624	-3.14509619
C	5.88474841	-3.81257550	-2.80030546
H	6.77125153	-3.40548314	-3.27957918
C	5.89856046	-5.11145058	-2.29145232
H	6.79769452	-5.71751146	-2.36073326
C	4.74942137	-5.62271941	-1.69135103
H	4.75291553	-6.62415666	-1.27010795
C	3.60044421	-4.84660848	-1.60047489
H	2.73156904	-5.24506466	-1.08539598

C	-3.76009011	-2.49445635	-1.04579712
C	-4.32481008	-3.04476524	0.11218981
H	-5.05317652	-3.84213428	0.16004384
C	-3.78084127	-2.33829033	1.18636830
C	-4.03512205	-2.91915443	-2.47251931
C	-3.57143313	-4.37348221	-2.65701696
H	-2.48912542	-4.46909449	-2.51296010
H	-3.80928137	-4.72170360	-3.66950714
H	-4.06631758	-5.03899457	-1.94151323
C	-3.32993939	-2.03291113	-3.49927134
H	-3.66693904	-0.99511993	-3.42467005
H	-3.56146502	-2.38797742	-4.51021156
H	-2.24153503	-2.04611040	-3.38269836
C	-5.55024859	-2.84720803	-2.72199516
H	-5.92099546	-1.82509106	-2.58582727
H	-6.09879161	-3.49965129	-2.03432721
H	-5.78041529	-3.16344911	-3.74656116
C	-4.14939311	-2.44450096	2.64896447
C	-3.00921723	-2.01767136	3.57550250
H	-2.72970104	-0.96952416	3.41927033
H	-2.11350218	-2.62758518	3.42516536
H	-3.32664314	-2.11684023	4.62023651
C	-4.52444855	-3.89421749	2.97983519
H	-4.79999537	-3.97587007	4.03763617
H	-3.68364252	-4.57123840	2.79096707
H	-5.37950849	-4.23617024	2.38719795
C	-5.36916255	-1.53904429	2.89182508
H	-5.66423760	-1.56462419	3.94818616
H	-6.22169249	-1.86528101	2.28599597
H	-5.14234818	-0.50244110	2.62018411

Complex 5 at S_0 state

Pd	-0.35681612	-1.03024303	-1.01245409
N	2.09445303	-2.27252220	0.46980403
N	2.47312309	-1.15480913	-1.36263511
N	4.91032228	-1.18099320	-1.34675111

N	-2.12748823	-0.04980690	-1.57839713
N	-1.54530112	1.97095524	-0.54959505
C	1.48224500	-1.63834413	-0.55052105
C	3.46880713	-2.19816224	0.32371002
C	4.53631820	-2.65455831	1.08067008
H	4.39973617	-3.20875234	2.00352315
C	5.80058631	-2.34816532	0.58171303
H	6.69069435	-2.66497037	1.11456008
C	5.93441635	-1.62527527	-0.60988106
H	6.92578140	-1.38958928	-0.98872209
C	3.71839818	-1.47912419	-0.85633107
C	1.43617396	-2.92871023	1.58052311
H	1.97568301	-2.69286523	2.50000218
H	1.41118192	-4.01025131	1.42139510
H	0.42630989	-2.53469517	1.65392312
C	2.05950808	-0.40777406	-2.48887520
C	2.93772116	0.10803996	-3.43500527
H	4.00706324	-0.03646409	-3.32625226
C	2.39800315	0.81106803	-4.51444035
H	3.06143821	1.22188304	-5.27053241
C	1.01947005	0.97689508	-4.62187036
H	0.60358603	1.51995013	-5.46719343
C	0.16314596	0.45772507	-3.64382529
H	-0.90818211	0.61062511	-3.73685429
C	0.66521898	-0.24083500	-2.54621220
C	-2.31852220	1.23007320	-1.32343211
H	-3.18631325	1.71029426	-1.79210015
C	-3.15372733	-0.76776592	-2.20391817
C	-2.82525333	-1.77543001	-3.12431825
H	-1.77516126	-1.95607906	-3.34242726
C	-3.82062043	-2.51524604	-3.75073029
H	-3.54271743	-3.28909711	-4.46190335
C	-5.16663753	-2.26877398	-3.47579427
H	-5.94301363	-2.85197200	-3.96289631
C	-5.50186152	-1.27505589	-2.55892620

H	-6.54496058	-1.08314984	-2.32007818
C	-4.50931543	-0.53583086	-1.92012815
H	-4.78063642	0.20515220	-1.17277310
C	-1.73238209	3.35909534	-0.58824405
C	-2.05197610	4.03787641	-1.77742915
H	-2.13827112	3.48023537	-2.70677121
C	-2.21051407	5.42096450	-1.78616314
H	-2.45658607	5.92211954	-2.71910121
C	-2.02881703	6.16302658	-0.62117805
H	-2.14284100	7.24332966	-0.63277306
C	-1.68271302	5.50050953	0.55719304
H	-1.53181899	6.06417453	1.47459710
C	-1.53411306	4.11863540	0.57544704
H	-1.27824105	3.60221235	1.49668611
Pd	-0.35661306	1.03024613	1.01253807
N	2.09469517	2.27222815	-0.46986104
N	2.47334716	1.15458005	1.36262110
N	4.91054435	1.18045098	1.34657509
N	-2.12737823	0.04997911	1.57851811
N	-1.54554324	-1.97087306	0.54968903
C	1.48247810	1.63819712	0.55054804
C	3.46905027	2.19771110	-0.32385603
C	4.53657837	2.65393410	-1.08089809
H	4.40002637	3.20811015	-2.00376716
C	5.80083746	2.34740104	-0.58200605
H	6.69095153	2.66406803	-1.11492509
C	5.93465046	1.62455198	0.60961404
H	6.92600752	1.38875093	0.98840307
C	3.71862727	1.47871903	0.85621906
C	1.43635214	2.92850122	-1.58049313
H	1.97607717	2.69310018	-2.49995620
H	1.41092617	4.00998730	-1.42106612
H	0.42663905	2.53414722	-1.65416013
C	2.05970811	0.40764400	2.48891418
C	2.93790116	-0.10815906	3.43507025

H	4.00725024	0.03627092	3.32629524
C	2.39815110	-0.81107910	4.51455934
H	3.06156813	-1.22187815	5.27067539
C	1.01960899	-0.97682107	4.62201235
H	0.60370294	-1.51979310	5.46737843
C	0.16330294	-0.45765800	3.64394727
H	-0.90803315	-0.61048998	3.73699728
C	0.66540699	0.24080603	2.54628719
C	-2.31863128	-1.22986399	1.32354109
H	-3.18650536	-1.70993600	1.79220513
C	-3.15351028	0.76810719	2.20402616
C	-2.82488722	1.77569526	3.12445523
H	-1.77477114	1.95615824	3.34260425
C	-3.82014728	2.51567835	3.75084328
H	-3.54213223	3.28946740	4.46204133
C	-5.16619838	2.26945537	3.47585126
H	-5.94248741	2.85278444	3.96293530
C	-5.50156645	1.27581630	2.55895019
H	-6.54469155	1.08410532	2.32005617
C	-4.50912939	0.53642522	1.92017714
H	-4.78055143	-0.20448983	1.17279108
C	-1.73293130	-3.35897217	0.58824204
C	-2.05282734	-4.03775921	1.77734213
H	-2.13911933	-3.48016716	2.70671320
C	-2.21168740	-5.42081130	1.78596213
H	-2.45799343	-5.92197036	2.71883620
C	-2.03001641	-6.16284036	0.62095104
H	-2.14429445	-7.24311746	0.63246104
C	-1.68360736	-5.50032532	-0.55733105
H	-1.53272337	-6.06396238	-1.47475412
C	-1.53468631	-4.11848523	-0.57547305
H	-1.27857327	-3.60205820	-1.49664312

Complex 5 at T_1 state

Pd	-0.37422707	-0.89437207	-0.98602409
N	2.14335808	-2.16555126	0.39469002

N	2.47119915	-0.92246118	-1.38135311
N	4.89779233	-1.01975528	-1.48691512
N	-2.17469217	0.03586807	-1.54613413
N	-1.55777405	2.00279720	-0.47168904
C	1.49464105	-1.41987118	-0.54090005
C	3.50519718	-2.11491331	0.18320701
C	4.59664424	-2.64396639	0.85775406
H	4.48952121	-3.25828343	1.74540413
C	5.84898534	-2.32826041	0.31869702
H	6.75290538	-2.69909847	0.79105805
C	5.95065241	-1.53581035	-0.82329707
H	6.92834950	-1.30029837	-1.23592510
C	3.72597423	-1.31908226	-0.95804608
C	1.52036000	-2.95450530	1.43233810
H	2.06704004	-2.81539431	2.36772617
H	1.51525796	-4.01294838	1.15296608
H	0.50157393	-2.60172523	1.56604611
C	2.02820614	-0.16567610	-2.46829420
C	2.86548423	0.38531191	-3.43581227
H	3.93993230	0.26357086	-3.35328126
C	2.28174321	1.08388198	-4.49211735
H	2.91666327	1.51727199	-5.26011541
C	0.89544311	1.22284504	-4.56750336
H	0.44702809	1.75920810	-5.39992441
C	0.07532603	0.67960704	-3.57402428
H	-1.00044805	0.80870209	-3.63943728
C	0.62716304	-0.02672704	-2.50609920
C	-2.35969713	1.31009418	-1.25496010
H	-3.22675418	1.81438724	-1.69711414
C	-3.19314427	-0.68186695	-2.18081017
C	-2.85291729	-1.65902603	-3.12895925
H	-1.80338521	-1.80570008	-3.37407927
C	-3.83983739	-2.40772105	-3.75877429
H	-3.55480840	-3.15930912	-4.49035135
C	-5.18655848	-2.19274698	-3.46416727

H	-5.95654755	-2.78038000	-3.95579831
C	-5.53312145	-1.22102490	-2.52730820
H	-6.57769956	-1.05114384	-2.27930418
C	-4.54949137	-0.47640488	-1.88244515
H	-4.82648937	0.25027719	-1.12361009
C	-1.69500201	3.39705231	-0.44521804
C	-2.00306100	4.13167938	-1.60295113
H	-2.12040803	3.61343934	-2.55137020
C	-2.11033696	5.51865851	-1.55511313
H	-2.34830595	6.06522955	-2.46418120
C	-1.88843592	6.20596852	-0.36388704
H	-1.96147088	7.28928463	-0.33158803
C	-1.55473692	5.48547047	0.78340205
H	-1.37274288	6.00623951	1.72009012
C	-1.45629496	4.09950335	0.74536705
H	-1.20946397	3.54493930	1.64628812
Pd	-0.37424200	0.89440007	0.98596507
N	2.14344924	2.16547107	-0.39471704
N	2.47116022	0.92234396	1.38133510
N	4.89774241	1.01970888	1.48710411
N	-2.17476618	-0.03580193	1.54603611
N	-1.55782520	-2.00271711	0.47158003
C	1.49465016	1.41972404	0.54077803
C	3.50526034	2.11485701	-0.18311802
C	4.59675345	2.64387901	-0.85761207
H	4.48969146	3.25818007	-1.74528114
C	5.84906154	2.32817795	-0.31846803
H	6.75301159	2.69899993	-0.79078507
C	5.95065251	1.53575988	0.82355005
H	6.92831859	1.30025682	1.23625509
C	3.72595933	1.31901995	0.95815207
C	1.52049822	2.95441315	-1.43240212
H	2.06716826	2.81523813	-2.36779019
H	1.51544126	4.01286723	-1.15307510
H	0.50169313	2.60167517	-1.56608812

C	2.02811316	0.16563592	2.46829818
C	2.86535220	-0.38536115	3.43585026
H	3.93980529	-0.26365218	3.35334225
C	2.28156912	-1.08388718	4.49215833
H	2.91646016	-1.51727824	5.26018040
C	0.89526202	-1.22281514	4.56751834
H	0.44681496	-1.75914916	5.39994039
C	0.07518297	-0.67957207	3.57401026
H	-1.00059711	-0.80862304	3.63941127
C	0.62706004	0.02674696	2.50609618
C	-2.35975224	-1.31002802	1.25486009
H	-3.22678832	-1.81434903	1.69702412
C	-3.19319022	0.68189116	2.18080216
C	-2.85290216	1.65907022	3.12890823
H	-1.80335307	1.80578019	3.37392525
C	-3.83978421	2.40773132	3.75882328
H	-3.55470416	3.15933236	4.49036833
C	-5.18652832	2.19270935	3.46435926
H	-5.95648738	2.78031642	3.95606730
C	-5.53315140	1.22097129	2.52753719
H	-6.57774845	1.05105332	2.27963917
C	-4.54956233	0.47638419	1.88257514
H	-4.82662339	-0.25030385	1.12376908
C	-1.69505426	-3.39697621	0.44509903
C	-2.00311232	-4.13160225	1.60283211
H	-2.12045731	-3.61335721	2.55125119
C	-2.11039638	-5.51857934	1.55499311
H	-2.34836841	-6.06515139	2.46405918
C	-1.88849739	-6.20588740	0.36376402
H	-1.96154143	-7.28920250	0.33146302
C	-1.55479433	-5.48539035	-0.78352207
H	-1.37280434	-6.00616040	-1.72021214
C	-1.45634827	-4.09942327	-0.74548706
H	-1.20952623	-3.54485724	-1.64640813

Complex 6 at T_1 state

Pd	-0.38272502	0.84755105	1.02801107
N	2.16381112	2.20516124	-0.23542302
N	2.45402419	0.83368215	1.45162810
N	4.89472936	0.88988823	1.54735411
N	-2.18137512	-0.10079407	1.53366511
N	-1.53308901	-2.01653819	0.39041703
C	1.49383610	1.43101316	0.65956005
C	3.52174123	2.09008427	-0.03278600
C	5.72253738	2.31719536	-0.22100402
H	6.58203241	2.74576042	-0.72927305
C	5.91201141	1.46914730	0.86393206
H	6.91634950	1.24296532	1.20974209
C	3.71448727	1.21770621	1.05806708
C	1.56803605	3.08852928	-1.21495009
H	2.25588110	3.18009031	-2.05601515
H	1.38169901	4.07161434	-0.77347705
H	0.63171700	2.65118622	-1.55254811
C	1.99265618	-0.00149293	2.47713218
C	2.82072626	-0.61917895	3.40882625
H	3.89619033	-0.49459190	3.34704824
C	2.22605825	-1.39268402	4.40519731
H	2.85283131	-1.88609004	5.14260137
C	0.84014015	-1.52533607	4.46085932
H	0.38190214	-2.11845713	5.24796838
C	0.02859407	-0.90569506	3.50493325
H	-1.04799800	-1.02708010	3.56125726
C	0.59449308	-0.14087999	2.48602518
C	-2.34502709	-1.36893017	1.20002609
H	-3.19662313	-1.90652024	1.63263412
C	-3.20880021	0.58256594	2.19120716
C	-2.88324222	1.53417802	3.17032323
H	-1.83684515	1.68585907	3.42580225
C	-3.88160531	2.24837004	3.82166728
H	-3.60836432	2.98037210	4.57704133
C	-5.22453140	2.02157598	3.51937525

H	-6.00355447	2.58129699	4.02885229
C	-5.55636741	1.07309890	2.55351518
H	-6.59825444	0.89388185	2.30117916
C	-4.56174830	0.36427688	1.88628313
H	-4.82746630	-0.34350618	1.10592908
C	-1.63300497	-3.41328630	0.32202502
C	-1.87565096	-4.18831036	1.46765611
H	-1.97114198	-3.69983733	2.43410818
C	-1.94051392	-5.57616748	1.38264810
H	-2.12622791	-6.15648452	2.28276117
C	-1.74127388	-6.22077051	0.16380801
H	-1.77999285	-7.30451858	0.10197401
C	-1.47708089	-5.45780746	-0.97395307
H	-1.31647986	-5.94544747	-1.93202414
C	-1.42208093	-4.07077633	-0.89835206
H	-1.23281093	-3.48302128	-1.79171813
Pd	-0.38290896	-0.84755607	-1.02791607
N	2.16351627	-2.20552108	0.23543602
N	2.45383224	-0.83411397	-1.45165211
N	4.89451942	-0.89070090	-1.54753711
N	-2.18138012	0.10114094	-1.53355011
N	-1.53262314	2.01673910	-0.39034003
C	1.49359519	-1.43128305	-0.65951604
C	3.52144836	-2.09065303	0.03271200
C	5.72221654	-2.31810297	0.22079502
H	6.58167659	-2.74679698	0.72901505
C	5.91175449	-1.47010391	-0.86416706
H	6.91610460	-1.24408486	-1.21004709
C	3.71425934	-1.21832596	-1.05816707
C	1.56770625	-3.08876017	1.21505109
H	2.25533831	-3.17992615	2.05633515
H	1.38172027	-4.07201824	0.77380805
H	0.63120917	-2.65152616	1.55226911
C	1.99254218	0.00115107	-2.47711918
C	2.82066322	0.61877614	-3.40880524

H	3.89611530	0.49406717	-3.34705224
C	2.22606415	1.39238718	-4.40513532
H	2.85288018	1.88575624	-5.14252737
C	0.84016005	1.52519314	-4.46077232
H	0.38197400	2.11838817	-5.24785538
C	0.02856401	0.90561807	-3.50484425
H	-1.04801607	1.02713305	-3.56113325
C	0.59440008	0.14071104	-2.48597018
C	-2.34474917	1.36931303	-1.19990609
H	-3.19618525	1.90712604	-1.63254911
C	-3.20893617	-0.58199114	-2.19113016
C	-2.88355612	-1.53356820	-3.17034323
H	-1.83719604	-1.68536117	-3.42590525
C	-3.88204917	-2.24754728	-3.82172127
H	-3.60894612	-2.97951633	-4.57717633
C	-5.22493127	-2.02056931	-3.51937425
H	-6.00405533	-2.58012238	-4.02888029
C	-5.55659231	-1.07211826	-2.55343018
H	-6.59844643	-0.89276427	-2.30104917
C	-4.56184628	-0.36350717	-1.88616414
H	-4.82743932	0.34423987	-1.10573608
C	-1.63208319	3.41351820	-0.32205302
C	-1.87447823	4.18855224	-1.46773110
H	-1.97014322	3.70004621	-2.43414918
C	-1.93889228	5.57643635	-1.38280410
H	-2.12443232	6.15675938	-2.28294917
C	-1.73942529	6.22104441	-0.16400401
H	-1.77778833	7.30480847	-0.10223201
C	-1.47545424	5.45806136	0.97379707
H	-1.31467125	5.94570439	1.93183614
C	-1.42090820	4.07100825	0.89827806
H	-1.23179716	3.48322921	1.79166513
N	4.50650645	-2.66113404	0.70408105
N	4.50684927	2.66042235	-0.70420505

Complex 5^{+}

N	2.12889383	-2.30887495	0.11085946
N	2.43857047	-0.93068837	-1.54886106
N	4.87359546	-0.90968691	-1.60396429
N	-2.18353350	0.15107164	-1.45543111
N	-1.50294964	2.07886806	-0.33932803
C	1.48246360	-1.54400956	-0.79090408
C	3.49918456	-2.19277981	-0.06460196
C	4.59765440	-2.73719578	0.58437732
H	4.50247975	-3.42782818	1.41557137
C	5.83940638	-2.33467340	0.10090087
H	6.75003999	-2.71084381	0.55419887
C	5.92648250	-1.43782803	-0.97212612
H	6.90182443	-1.12800640	-1.33817972
C	3.70338453	-1.30403879	-1.13028080
C	1.51648600	-3.12912879	1.13757392
H	2.17810837	-3.15613853	2.00437366
H	1.33756111	-4.14046325	0.76444787
H	0.58047622	-2.66587962	1.43627807
C	1.98415697	-0.03410812	-2.53994390
C	2.82507730	0.62657603	-3.42711009
H	3.89868745	0.48465915	-3.37223123
C	2.24306964	1.46576224	-4.37910049
H	2.87761137	1.99256931	-5.08591937
C	0.86035225	1.61552364	-4.42923210
H	0.41098286	2.25978424	-5.18043624
C	0.03883685	0.94411889	-3.51593778
H	-1.03693658	1.07916598	-3.57550885
C	0.58815194	0.11548764	-2.53870245
C	-2.31824033	1.44137034	-1.14994820
H	-3.15294124	1.98657849	-1.59835342
C	-3.25544975	-0.50876635	-2.04843243
C	-2.99139348	-1.58391852	-2.91639266
H	-1.95650164	-1.82173978	-3.14866337
C	-4.03218141	-2.29939474	-3.48867404
H	-3.81045614	-3.12263685	-4.16149910

C	-5.35718462	-1.95993389	-3.20754757
H	-6.17149474	-2.52406118	-3.65222262
C	-5.63028559	-0.89306440	-2.34987508
H	-6.65843465	-0.63164184	-2.11655553
C	-4.59540063	-0.16989024	-1.77230298
H	-4.82113177	0.62759046	-1.07054780
C	-1.58741903	3.47719566	-0.28041949
C	-1.93328611	4.25136186	-1.40123807
H	-2.12233785	3.77028101	-2.35692213
C	-1.97294106	5.63799941	-1.30963749
H	-2.23474357	6.22255982	-2.18707899
C	-1.65401916	6.27725293	-0.11257029
H	-1.67865872	7.36097989	-0.04772332
C	-1.28174562	5.51433439	0.99538029
H	-1.01868261	6.00174156	1.92995229
C	-1.23994961	4.12907271	0.91213647
H	-0.94289331	3.53169509	1.76910622
Pd	-0.38345030	0.89858636	1.10806911
N	2.12897850	2.30878340	-0.11082824
N	2.43861122	0.93057089	1.54887958
N	4.87363674	0.90942709	1.60392777
N	-2.18354197	-0.15097374	1.45545440
N	-1.50308088	-2.07880720	0.33933068
C	1.48252605	1.54394659	0.79094060
C	3.49926658	2.19260571	0.06459878
C	4.59775494	2.73695924	-0.58440272
H	4.50260464	3.42760117	-1.41559148
C	5.83949370	2.33436119	-0.10095538
H	6.75013948	2.71047868	-0.55427242
C	5.92654071	1.43750682	0.97206686
H	6.90187259	1.12762486	1.33809664
C	3.70343851	1.30384988	1.13027180
C	1.51657490	3.12909281	-1.13750354
H	2.17822903	3.15619991	-2.00427418
H	1.33759604	4.14039128	-0.76430605

H	0.58059211	2.66583041	-1.43628072
C	1.98416438	0.03401551	2.53996930
C	2.82506090	-0.62670038	3.42713496
H	3.89867740	-0.48483907	3.37224287
C	2.24302043	-1.46584109	4.37914547
H	2.87754205	-1.99266773	5.08596752
C	0.86029510	-1.61552893	4.42929507
H	0.41090137	-2.25975196	5.18051721
C	0.03880457	-0.94409613	3.51600022
H	-1.03697468	-1.07908343	3.57558823
C	0.58815141	-0.11551093	2.53874320
C	-2.31833347	-1.44125763	1.14995138
H	-3.15308888	-1.98640704	1.59832643
C	-3.25542541	0.50892299	2.04845519
C	-2.99131463	1.58402436	2.91646039
H	-1.95641168	1.82176624	3.14876444
C	-4.03206711	2.29955138	3.48874336
H	-3.81030056	3.12275485	4.16160388
C	-5.35708725	1.96019160	3.20757562
H	-6.17136880	2.52435857	3.65225278
C	-5.63024167	0.89337079	2.34986026
H	-6.65840290	0.63202549	2.11650950
C	-4.59539163	0.17014636	1.77228552
H	-4.82115929	-0.62729624	1.07049965
C	-1.58769209	-3.47712422	0.28036763
C	-1.93365759	-4.25130207	1.40114864
H	-2.12267970	-3.77024185	2.35684804
C	-1.97345119	-5.63793220	1.30948985
H	-2.23532778	-6.22250266	2.18690224
C	-1.65457163	-6.27716720	0.11240148
H	-1.67931807	-7.36088940	0.04750848
C	-1.28220388	-5.51424019	-0.99551100
H	-1.01917369	-6.00163519	-1.93009887
C	-1.24027135	-4.12898539	-0.91221003
H	-0.94314150	-3.53160196	-1.76914961

Pd	-0.38348893	-0.89857366	-1.10803207

Complex 5-Br

N	1.65035567	-2.34019907	1.04620088
N	2.22054574	-1.50753761	-0.88670104
N	4.60217516	-2.01968541	-0.85347083
N	-2.15657986	0.22343292	-1.44907887
N	-1.07379007	2.22165225	-0.87925657
C	1.17596996	-1.70032535	-0.03207185
C	3.01087461	-2.55810579	0.90205194
C	3.97889273	-3.12847526	1.71380296
H	3.74854717	-3.54498961	2.68873796
C	5.27186960	-3.12673215	1.19556169
H	6.09017343	-3.55154294	1.76678154
C	5.52954241	-2.57470291	-0.06587728
H	6.54292849	-2.57745251	-0.45889986
C	3.38272958	-2.02876503	-0.34329633
C	0.86830631	-2.75670178	2.18998417
H	1.39144512	-2.47150858	3.10480939
H	0.71043157	-3.83804903	2.16002639
H	-0.08584737	-2.23839595	2.14386373
C	1.92741436	-0.91035685	-2.12794872
C	2.86069940	-0.72886334	-3.14249793
H	3.89345283	-1.02326846	-2.99203220
C	2.42213000	-0.17440835	-4.34555700
H	3.13105976	-0.02746324	-5.15538923
C	1.08528909	0.17959958	-4.50934583
H	0.74745387	0.60474535	-5.45093313
C	0.16701681	-0.00451812	-3.46973161
H	-0.87208781	0.27142824	-3.61375884
C	0.58282894	-0.54214050	-2.25719656
C	-2.05146356	1.53713555	-1.44728020
H	-2.83917882	2.09878894	-1.96387573
C	-3.37876446	-0.33034842	-1.86806342
C	-3.38571943	-1.41294188	-2.75684995
H	-2.43887105	-1.81675810	-3.09965150

C	-4.59010992	-1.97839053	-3.16126467
H	-4.57836800	-2.82180963	-3.84691381
C	-5.80456165	-1.47195785	-2.69646183
H	-6.74256166	-1.91994872	-3.01234784
C	-5.80256453	-0.39110379	-1.81761431
H	-6.74042484	0.00866316	-1.44058928
C	-4.60002934	0.17387494	-1.40027338
H	-4.59695271	0.99852783	-0.69255014
C	-0.95574862	3.58002538	-1.20211873
C	-1.20762905	4.06003254	-2.49898347
H	-1.48845707	3.36230387	-3.28394806
C	-1.04920185	5.40988115	-2.79921800
H	-1.24888953	5.75689918	-3.80988886
C	-0.61104203	6.30623438	-1.82650608
H	-0.47734963	7.35717193	-2.06654617
C	-0.33426063	5.83333143	-0.54349414
H	0.01034594	6.51810690	0.22731655
C	-0.50420537	4.48895451	-0.23308194
H	-0.30688100	4.12841917	0.77234213
Pd	-0.01312730	1.35932141	0.79431410
N	2.59490584	1.95662759	-0.85400635
N	2.81232572	1.05166623	1.11563106
N	5.22690118	0.72722289	1.14139670
N	-1.87818394	0.99022822	1.63238799
N	-1.95545546	-1.27785987	1.04182300
C	1.90261552	1.55037504	0.22561895
C	3.94559637	1.70866677	-0.67495764
C	5.06672346	1.89450747	-1.46958343
H	5.01300244	2.33434796	-2.45992066
C	6.27188337	1.47303896	-0.91362928
H	7.19688150	1.57823992	-1.47015547
C	6.30229095	0.90889209	0.36852380
H	7.24930656	0.58432651	0.79213601
C	4.09135136	1.12727772	0.59387393
C	2.03137334	2.56626729	-2.04128907

H	2.58095778	2.21133383	-2.91410979
H	2.08777358	3.65555220	-1.97132178
H	0.99554116	2.24972511	-2.12506841
C	2.31058419	0.58152240	2.35004230
C	3.11879978	0.10649269	3.37606618
H	4.19373287	0.05182815	3.24523557
C	2.50387253	-0.28478467	4.56706107
H	3.11380646	-0.65515583	5.38619041
C	1.12201875	-0.19003231	4.70539330
H	0.64811513	-0.48567623	5.63803486
C	0.33278475	0.27291205	3.64607993
H	-0.74391261	0.32910433	3.77014342
C	0.91137710	0.65764667	2.43798838
C	-2.41053043	-0.21906721	1.67554398
H	-3.30157602	-0.34705243	2.30154003
C	-2.59220068	2.06251913	2.18135170
C	-1.89751214	3.08317186	2.84999838
H	-0.81865678	2.99685776	2.95712449
C	-2.57712919	4.17067239	3.38593057
H	-2.01784916	4.94829359	3.89982042
C	-3.96480074	4.26235605	3.27697986
H	-4.49407959	5.11372763	3.69520451
C	-4.66327026	3.25192490	2.61917444
H	-5.74347872	3.31440221	2.51545887
C	-3.98795277	2.16693850	2.06752779
H	-4.54055935	1.40485817	1.52512217
C	-2.59931018	-2.49141994	1.38045358
C	-2.61409804	-2.93716604	2.70939228
H	-2.10303188	-2.35035186	3.47001049
C	-3.26447699	-4.12024920	3.05359509
H	-3.26398379	-4.45142526	4.08895895
C	-3.90609646	-4.87531635	2.07490135
H	-4.41082361	-5.80054255	2.33953654
C	-3.89799899	-4.43126837	0.75217519
H	-4.40652034	-5.00583421	-0.01802589

C	-3.25180954	-3.25013470	0.40323941
H	-3.25545398	-2.89799475	-0.62121070
Pd	-0.57938294	-0.95637252	-0.66307444
Br	-0.64314774	-3.47265002	-1.76547077

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