Supporting information

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1. Materials and methods

Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros and Aldrich–Sigma Co and used without further purification. 3-Bromo-1,10-phenanthroline was synthesized according to previously reported procedure [1] from 1,10-phenanthroline hydrochloride. 5-Bromo-1,10-phenathroline was obtained from 1,10-phenanthroline by bromination in oleum.[2] 4,7-Dibromo-1,10-phenanthroline was prepared *via* three–step procedure from *o*-phenylenediamine and Meldrum's acid.[3] 4-Bromo-1,10-phenanthroline was synthesized according to the same method from 8-aminoquinoline.[4, 5] *cis*-$[Ru(bpy)_2]Cl_2$ was prepared from $RuCl_3 \cdot H_2O$ as reported previously.[6] Complexes $[(phen)Ru(bpy)_2](PF_6)_2$ (**Ru(phen)**) [7] and $[(phendione)Ru(bpy)_2](PF_6)_2$ (**Ru[Phen(O)$_2$]**) [8] were synthesized as reported in the previous works. Preparative column chromatography was carried out using Silica gel 60 (40–63 μm) from Merck Co. Dioxane was distilled successively over NaOH and sodium under argon; CH_2Cl_2 was distilled over CaH_2; DMF was distilled over CaH_2 under reduced pressure; EtOH was distilled over CaO; MeOH was used freshly distilled. All reactions were performed in argon. Preparation of Ru(II) complexes was conducted in Monowave 300 Microwave reactor (Anton Paar Co).

^1H and ^{13}C NMR spectra were recorded with Bruker Avance-400 spectrometer in $CDCl_3$ or CD_3CN, using the residual signals of $CHCl_3$ or CHD_2CN as internal standards. MALDI TOF mass-spectra were obtained with Bruker Daltonics Autoflex II mass spectrometer in positive ion mode with dithranol matrix and polyethyleneglycols as internal standards. ESI mass measurements were obtained with were performed with a Thermo Scientific Orbitrap Elite high-field orbitrap hybrid mass spectrometer. FTIR spectra were registered on Nicolet iS 5 with iD3 ATR accessory (ZnSe). Elemental analysis was performed with a Thermo Electron Flash EA1112 CHNS analyzer.

UV–vis spectra were registered with a Hitachi U-2900 device in a quartz cuvette (Hellma, l = 1 cm). Emission spectra were recorded in argon-saturated acetonitrile (HPLC grade) with Horiba Jobin Yvon Fluoromax-2 apparatus in a quartz cuvette (Hellma, l = 1 cm), (excitation and emission slits 3 nm). All fluorescence spectra were corrected. Luminescence quantum yields were determined in argon-saturated acetonitrile relative to $[Ru(bpy)_3](PF_6)_2$ (Φ = 9.4% in argon-saturated acetonitrile) as a standard according to a standard procedure [9].

$$\Phi_x = \Phi_{st} \times ((F_x \times A_{st} \times \eta_x^2)/(F_{st} \times A_x \times \eta_{st}^2)),$$

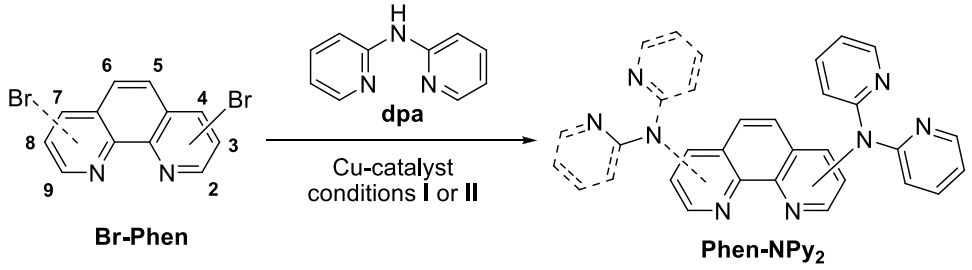
where A is the absorbance (in the range of 0.01–0.1 A.U., λ_{ex}=450 nm), F is the area under the emission curve, η is the refractive index of the solvents (at 293 K) used in measurements, and the subscripts *st* and *x* represent the standard and studied compounds, respectively. At least 4 points were used for each sample.

2. Synthesis

2.1. Synthesis of the ligands

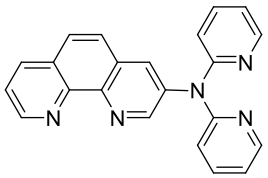
Cu-catalyzed synthesis of Phen-NPy$_2$ ligands. General procedure A. A glass vial (5 mL) equipped with a magnetic stirrer was charged with corresponding bromo-1,10-phenanthroline (0.4–0.8 mmol), di(pyridin-2-yl)amine (1–2 equiv.), $CuSO_4$ (10–20 mol%), Cs_2CO_3 (2–4 equiv.), evacuated and backfilled with dry argon for three times. Then the vial was sealed with a plastic screw cap, containing a teflon-lined silicone septum. The reaction mixture was stirred at 210 ºC for 24 h. After cooling to room temperature, the mixture was diluted with dichloromethane (50 mL) and washed with a concentrated NH_3(aq.) (3 × 30 mL). Combined water layers were extracted with dichloromethane (3 × 30 mL). Combined organic layers were washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel using a CH_2Cl_2/MeOH mixtures as eluents (gradual elution using pure CH_2Cl_2, CH_2Cl_2 : MeOH, 100:1 to 5:1 v/v). The products were obtained as yellow oils.

Table S1. Cu-catalyzed arylation of bis(pyridine-2-yl)amine with bromophenanthrolines.

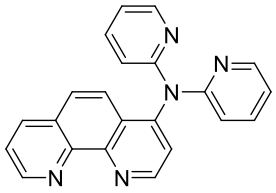


Entry	Substrate	Equiv. of dpa	Catalyst (mol%)	Conditions	Product	Yield [a], %
1	**3-Br-Phen**	1	$CuSO_4$ (10)	**I**	**Phen-3NPy$_2$**	15
2	**3-Br-Phen**	1.5	$CuSO_4$ (10)	**I**	**Phen-3NPy$_2$**	32
3	**3-Br-Phen**	1	CuI (10)	**I**	**Phen-3NPy$_2$**	-
4	**4-Br-Phen**	1	$CuSO_4$ (10)	**I**	**Phen-4NPy$_2$**	36
5	**4-Br-Phen**	1.5	$CuSO_4$ (10)	**I**	**Phen-4NPy$_2$**	4
6	**4-Br-Phen**	1	$CuSO_4$ (20)	**I**	**Phen-4NPy$_2$**	61
7	**5-Br-Phen**	1	$CuSO_4$ (10)	**I**	**Phen-5NPy$_2$**	31
8	**5-Br-Phen**	1	CuI (20)	**II**	**Phen-5NPy$_2$**	8
9	**5-Br-Phen**	1	CuI (40)	**II**	**Phen-5NPy$_2$**	-
10	**4,7-diBr-Phen**	4	$CuSO_4$ (10)	**I**	**Phen-4,7(NPy$_2$)$_2$**	9

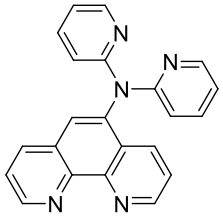
Conditions I: Br-Phen (0.4 mmol), dpa (1–4 equiv.), Cs_2CO_3 (2–4 equiv.), Cu-catalyst (10–20 mol%), 210°C, neat, 24 h. **Conditions II**: Br-Phen (0.5 mmol), dpa (1 equiv.), Cs_2CO_3 (2 equiv.), CuI (20–40 mol%), dry DMF (1 mL), 140°C, 48 h. [a] Preparative yields are given.



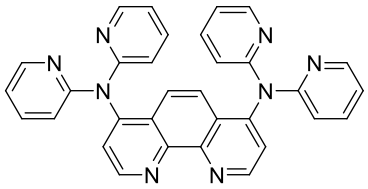
N,N-di(pyridin-2-yl)-1,10-phenanthrolin-3-amine (***Phen-3NPy₂***) was synthesized according to the general procedure **A** from 3-bromo-1,10-phenanthroline (207 mg, 0.80 mmol), di(pyridin-2-yl)amine (205 mg, 1.2 mmol) in the presence of $CuSO_4$ (13 mg, 10 mol%) and Cs_2CO_3 (522 mg, 1.6 mmol). Yield: 89 mg (32%); yellow oil; the product was eluted with CH_2Cl_2–MeOH (33:1 v/v) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.32 (m, 1H, H9 (Phen)), 9.03 (d, 1H, ^4J=2.4 Hz, H2 (Phen)), 8.42 (d, 1H, ^3J = 7.8 Hz, H7 (Phen)), 8.38 (dd, 2H, ^3J = 4.8 Hz, ^4J = 1.7 Hz, H6, H6' (Py)), 8.01 (d, 1H, ^4J = 2.4 Hz, H4 (Phen)), 7.81 (d, 1H, ^3J = 8.9 Hz, H5 (Phen)), 7.73 (d, 2H, ^3J = 8.3 Hz, H3, H3'(Py)), 7.67 (dd, 2H, ^3J = 8.3 Hz, ^4J = 1.7 Hz, H4, H4'(Phen)), 7.15–7.04 (m, 4H, H6, H8 (Phen), H5, H5' (Py)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 156.6 (2C), 149.0 (1C), 148.6 (2C), 148.3 (2C), 141.3 (1C), 138.2 (3C), 129.5 (2C), 129.4 (1C), 127.9 (1C), 126.8 (1C), 126.1 (1C), 122.3 (1C), 119.4 (2C), 117.5 (2C). IR (neat): 3047–2852, 1586, 1465, 1427, 1317, 1271 (C=C, C=N), 1150 (CH, Py), 1050 (CH, Py), 997, 833, 733, 669 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{16}N_5$ 350.1406; Found 350.1373.



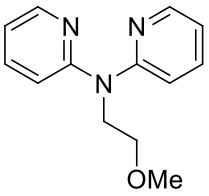
N,N-di(pyridin-2-yl)-1,10-phenanthrolin-4-amine (***Phen-4NPy₂***) was synthesized according to the general procedure **A** from 4-bromo-1,10-phenanthroline (207 mg, 0.80 mmol), di(pyridin-2-yl)amine (137 mg, 0.80 mmol) in the presence of $CuSO_4$ (26 mg, 20 mol%) and Cs_2CO_3 (522 mg, 1.6 mmol). Yield: 170 mg (61%); yellow oil; the product was eluted with CH_2Cl_2–MeOH (20:1 v/v) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.20 (m, 2H, H2, H9 (Phen)), 8.31 (ddd, 2H, ^3J = 4.9 Hz, ^4J = 2.0 Hz, ^5J = 0.9 Hz, H6, H6'(Py)), 8.17 (d, 1H, ^3J = 7.4 Hz, H7(Phen)), 7.72 (d, 1H, ^3J = 9.1 Hz, H5 (Phen)), 7.67–7.51 (m. 4H, H4, H4' (Py), H6, H8 (Phen)), 7.45 (d, 1H, ^3J = 4.8 Hz, H3 (Phen)), 7.10–6.81 (m, 4H, H3, H3', H5, H5' (Py)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 157.5 (2C), 150.9 (1C), 150.4 (1C), 148.8 (3C), 147.5 (1C), 145.6 (1C), 138.1 (2C), 135.9 (1C), 128.4 (1C), 126.8 (1C), 126.5 (1C), 123.5 (1C), 122.4 (1C), 122.1 (1C), 119.2 (2C), 116.8 (2C). IR (neat): 3038–2852 (ν_{CH}), 1582, 1564, 1556, 1427, 1318 (ν_{CNC}), 1213 ($\nu_{CC,}$ $\nu_{CN,}$ Phen), 1150 ($\delta_{CH,}$ Py), 1096 ($\delta_{CH,}$ Py), 992, 835, 774, 728, 693 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{16}N_5$ 350.1406; Found 350.1451.



N,N-di(pyridin-2-yl)-1,10-phenanthrolin-5-amine ***(Phen-5NPy$_2$)*** was synthesized according to the general procedure **A** from 5-bromo-1,10-phenanthroline (130 mg, 0.50 mmol), di(pyridin-2-yl)amine (86 mg, 0.50 mmol) in the presence of $CuSO_4$ (8 mg, 10 mol%) and Cs_2CO_3 (326 mg, 1.00 mmol). Yield: 54 mg (31%); yellow oil; the product was eluted with CH_2Cl_2–MeOH (33:1 v/v) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.17-9.15 м. (m, 2H, H2, H9 (Phen)), 8.27 (ddd, 2H, ^3J = 4.9 Hz, ^4J = 2.0 Hz, ^5J = 1.0 Hz, H6, H6'(Py)), 8.20 (d, 1H, ^3J = 8.3 Hz, H4 (Phen)), 8.15 (d, 1H, J = 8.3 Hz, H7 (Phen)), 7.74 (s, 1H, H6 (Phen)), 7.60 (dd, 1H, ^3J = 8.3 Hz, ^3J = 4.0 Hz, H3 (Phen)), 7.57–7.51 (m, 2H, H4, H4'(Phen)), 7.48 (dd, 1H, ^3J = 8.3 Hz, ^3J = 4.0 Hz, H8 (Phen)), 7.04 (dd, 2H, ^3J = 8.4 Hz, ^4J = 1.0 Hz, H3, H3'(Py)), 6.96-6.87 (m, 2H, H5, H5'(Py)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 157.9 (1C), 150.6 (1C), 149.0 (1C), 148.9 (1C), 148.6 (1C), 147.8 (1C), 145.9 (1C), 139.9 (1C), 137.9 (1C), 136.1 (1C), 132.7 (1C), 128.9 (1C), 127.9 (1C), 127.1 (1C), 123.4 (1C), 123.3 (1C), 119.9 (1C), 119.7 (1C), 118.4 (1C), 118.3 (1C), 116.2 (1C), 115.9 (1C). IR (neat): 3029 (ν_{CH}), 1586, 1465, 1423, 1320 (ν_{CNC}), 1264 ($\nu_{CC,}$ $\nu_{CN,}$ Phen), 1151 ($\delta_{CH,}$ Py), 990, 772, 732 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{16}N_5$ 350.1406; Found 350.1445.

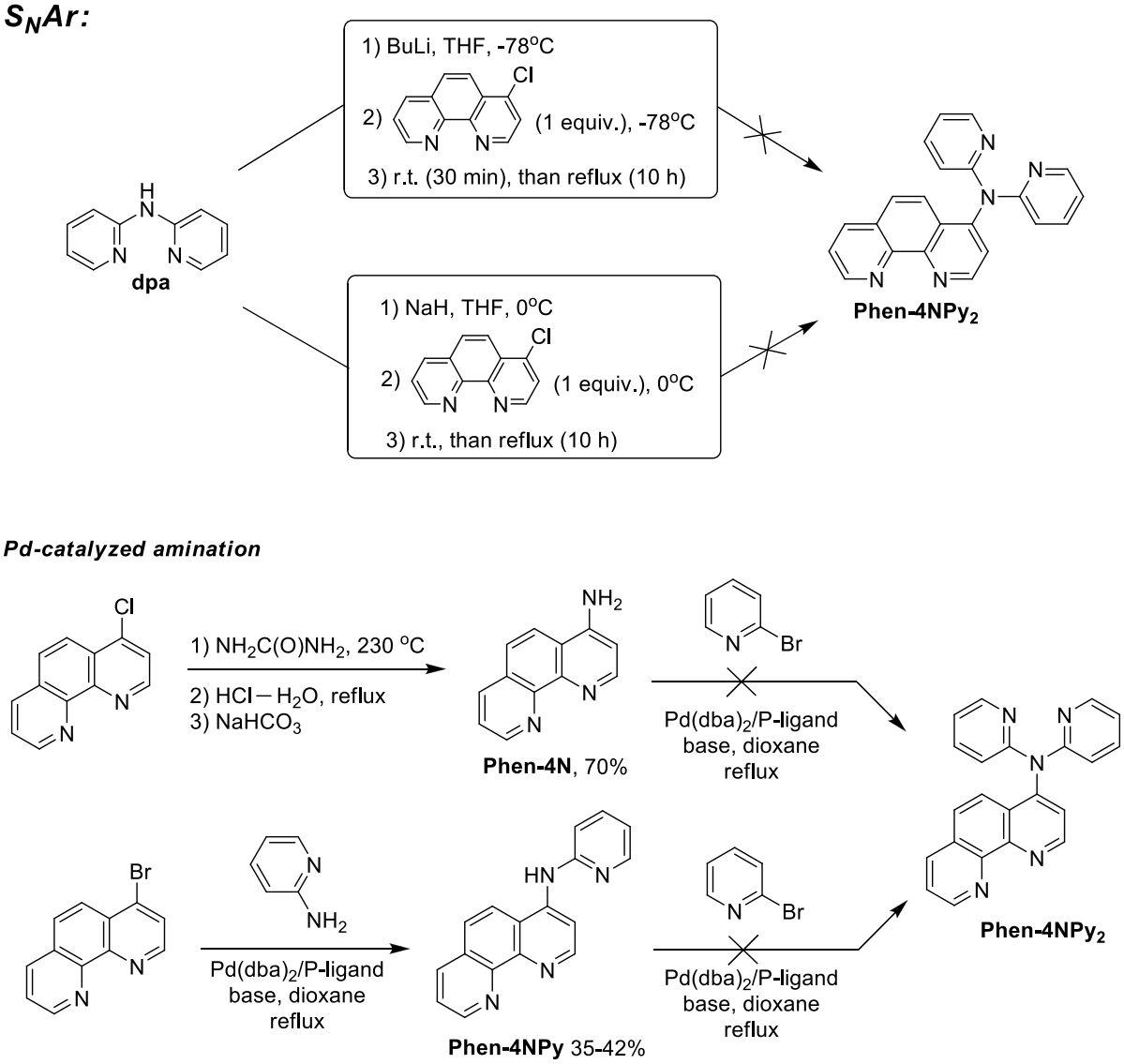


N^4,N^4,N^7,N^7-tetra(pyridin-2-yl)-1,10-phenanthroline-4,7-diamine ***(Phen-4,7(NPy$_2$)$_2$)*** was synthesized according to the general procedure **A** from 4,7-dibromo-1,10-phenanthroline (270 mg, 0.8 mmol), di(pyridin-2-yl)amine (574 mg, 3.4 mmol) in the presence of $CuSO_4$ (26 mg, 20 mol%) and Cs_2CO_3 (1043 mg, 3.2 mmol). Yield: 39 mg (9%); yellow oil; the product was eluted with CH_2Cl_2–MeOH (10:1 v/v) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.34 (d, 2H, ^3J = 5.4 Hz, H2, H9 (Phen)), 8.31 (d, 4H, ^3J = 4.1 Hz, H6, H6', H6'', H6'''(Py)), 7.74–7.70 (m, 4H, H4, H4', H4'', H4'''(Py)), 7.52 (d, 2H, ^3J = 5.4 Hz, H3(Phen)), 7.30 (s, 2H, H5, H6 (Phen)), 7.16–7.12 (m, 4H, H3, H'3, H3'', H3'''(Py)), 7.03 (d, 4H, ^3J = 8.1 Hz, H5, H5', H5'', H5'''(Py)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 157.3 (2C), 152.3 (2C), 149.7 (2C), 149.1 (4C), 138.5 (4C), 126.2 (2C), 122.6 (4C), 122.5 (4C), 119.9 (4C), 117.3 (4C). IR (neat): 3050 (ν_{CH}), 2357, 2342, 1583, 1563, 1507, 1463, 1424, 1350 (ν_{CNC}), 1270 ($\nu_{CC,}$ $\nu_{CN,}$ Phen), 1150 ($\delta_{CH,}$ Py), 1099, 1013, 999, 840, 771, 728, 668, 646 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{23}N_8$ 519.2046; Found 519.2068.

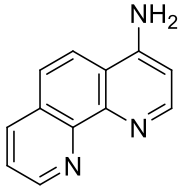


*N-(2-methoxyethyl)-N-(pyridin-2-yl)pyridin-2-amine (**NPy$_2$**).* A two-neck flask equipped with condenser and magnetic stirrer was charged with Pd(dba)$_2$ (46 mg, 4 mol%) and *rac*-BINAP (56 mg, 4.5 mol%). The flask was flushed with dry argon and absolute dioxane (20 mL) was added. The mixture was stirred for 2–3 min, then 2-bromopyridine (696 mg, 4.4 mmol), 2-methoxyethylamine (150 mg, 2 mmol) and *t*-BuONa (769 mg, 8 mmol) were in stream of argon. The reaction mixture was refluxed for 24 h under argon atmosphere. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, the solution was filtered, the filtrate evaporated under reduced pressure. The residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2/MeOH 200:1–20:1 v/v. Yield: 266 mg (58%); colorless oil; the product was eluted with CH_2Cl_2–MeOH (100:1 v/v) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (dd, 2H, ^3J = 4.8 Hz, ^4J = 1.4 Hz, H6, H6'(Py)), 7.52 (td, 2H, ^3J = 8.2 Hz, ^3J = 7.5 Hz, ^4J = 1.9 Hz, H4, H4'(Py)), 7.15 (d, 2H, J = 8.2 Hz, H3, H3'(Py)), 6.85 (dd, 2H, ^3J = 7.5 Hz, ^3J = 4.8 Hz, H5, H5'(Py)), 4.39 (t, 2H, ^3J = 6.0 Hz, CH_2N), 3.69 (t, 2H, ^3J = 6.0 Hz, CH_2O), 3.30 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 156.5 (2C), 147.2 (2C), 137.3 (2C), 116.9 (2C), 114.9 (2C), 70.3 (1C, CH_2O), 58.5 (1C, CH_3), 48.0 (1C, CH_2N). IR (neat): 3053, 2812 (CH), 1582, 1560, 1467, 1421, 1372 (C=N), 1320, 1273 (C=C, C=N), 1218, 1115 (CH, Py), 1082, 1019, 984, 771, 723, 703 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3O$ 230.1293; Found 230.1263.

Alternative attempts of synthesis of ***Phen-4NPy$_2$*** *ligand*



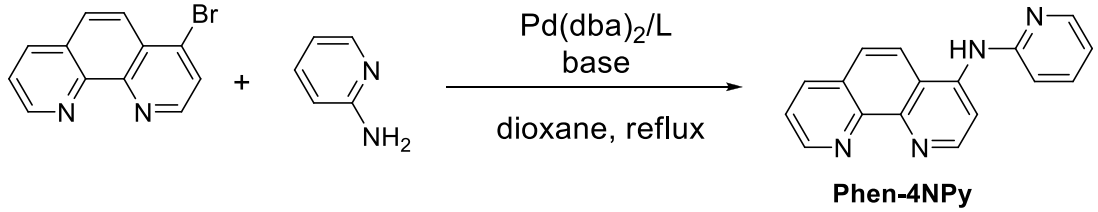
Scheme S1. Alternative attempts of synthesis of **Phen-4NPy$_2$** ligand.



1,10-Phenanthrolin-4-amine ***(Phen-4N)****.* The mixture of 4-chloro-1,10-phenanthroline (430 mg, 2 mmol) and urea (1.1 g, 18.3 mmol) was finely powdered in mortar and placed into pressure resistant tube with a screw cap (Synthware ®) and magnetic stir bar. The mixture was melted in sealed vessel and stirred at 230°C in sand bath for 30 min until yellow solid formed in the tube. After cool to room temperature the solid was washed with methanol and dried under reduced pressure. The residue than was refluxed in 25 mL of aqueous HCl (6 M) for 48 h. The mixture was cooled to 0°C in ice bath and cold $NaHCO_3$ saturated aqueous solution was added to achieve pH 9. The mixture was kept in refrigerator (4 °C) for 2 h. The precipitate was collected, washed with cold distilled water and dried at 80°C under reduced pressure. Yield 273 mg (70%), pale-yellow powder, m.p. >300°. ^{1}H NMR (DMSO-D6, 400 MHz): δ 8.92 (d, 1H, ^3J = 4.4, H9), 8.41–8.38 (m, 2H, H2, H7), 8.18 (d,

1H, ^3J = 9.2 Hz, H6), 7.73 (d, 1H, ^3J = 9.2 Hz, H5), 7.68 (dd, 1H, ^3J = 7.9 Hz, ^3J = 4.4 Hz, H8), 6.78 (d, 1H, ^3J = 5.7, H4). NH-protons were not assigned because of exchange. ^{13}C NMR (DMSO-D6, 100.6 MHz): 155.1 (1C), 149.8 (1C), 149.7 (1C), 146.1 (1C), 145.4 (1C), 136.6 (1C), 128.3 (1C), 123.2 (1C), 122.9 (1C), 121.4 (1C), 116.9 (1C), 105.7 (1C). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{10}N_3$ 196.0875; Found 196.0866.

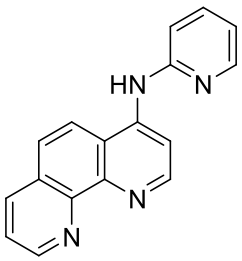
Table S2. Pd-catalyzed arylation of 2-aminopyridine with 4-bromo-1,10-phenanthroline.



Phen-4NPy

Entry	L	[Pd]/L, mol%	Equiv. of 2-aminopyridine	Base (equiv.)	Yield [a], %
1	*rac*-BINAP [b]	4/4.5	1	*t*-BuONa (1.5)	40 (35 [c])
2	*rac*-BINAP [b]	8/9	2	*t*-BuONa (1.5)	26[c]
3	*rac*-BINAP [b]	2/2.5	1.5	*t*-BuONa (1.5)	30
4	*rac*-BINAP [b]	4/4.5	1.5	Cs_2CO_3 (2)	39
5	JosiPhos [d]	4/4.5	1.5	*t*-BuONa (1.5)	42 [c]
6	JosiPhos [d]	8/9	2	*t*-BuONa (1.5)	0
7	JosiPhos [d]	2/2.5	2	*t*-BuONa (1.5)	31
8 [e]	*rac*-BINAP [b]	4/4.5	1.5 Cl	Cs_2CO_3 (2)	37
9 [e]	JosiPhos [d]	4/4.5	1.5 Cl	*t*-BuONa (1.5)	32

Conditions: 4-Bromo-1,10-phenanthroline (0.3 mmol), 2-aminopyridine (1–2 equiv.), base (1–2 equiv.), $Pd(dba)_2$ (2–8 mol%), L (2.5–8 mol%), dioxane, reflux, 24 h. [a] Determined by ^{1}H NMR analysis of the reaction mixture. [b] (±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene. [c] Preparative yield. [d] (R)-1-[(SP)-2-(Diphenylphosphino)ferrocenyl]ethyldi-tert-butylphosphine (PhPF-*t*Bu). [e] 4-Chloro-1,10-phenanthroline was used instead of 4-bromo-1,10-phenanthroline.

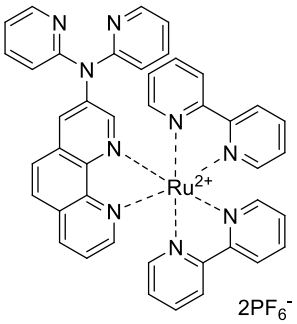


*N-(pyridin-2-yl)-1,10-phenanthrolin-4-amine (**Phen-4NPy**).* A two-neck flask equipped with condenser and magnetic stirrer was charged with 4-bromo-1,10-phenathroline (78 mg, 0.3 mmol), pyridine-2-amine (67 mg, 0.39 mmol), $Pd(dba)_2$ (7 mg, 4 mol%) and JosiPhos (7.5 mg, 4.5 mol%). The flask was flushed with dry argon and absolute dioxane (3 mL) was added. The mixture was stirred for 2–3 min, then *t*BuONa (44 mg, 0.45 mmol) was added and the reaction mixture was refluxed for 24 h under argon atmosphere. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, the solution was filtered, the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel using a sequence of eluents:

CH_2Cl_2, CH_2Cl_2/MeOH 200:1–3:1 v/v. Yield: 34 mg (42%); pale-yellow oil; the product was eluted with CH_2Cl_2–MeOH (20:1 v/v) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.15 (dd, 1H, ^3J = 4.3 Hz, ^4J = 1.8 Hz, H9 (Phen)), 8.95 (d, 1H, ^3J = 5.3 Hz, H2 (Phen)), 8.35 (d, 1H, ^3J = 4.6 Hz, H4 (Py)), 8.21 (d, 1H, ^3J = 8.1 Hz, H7 (Phen)), 8.08 (d, 1H, ^3J = 9.1 Hz, H6 (Phen)), 7.99 (d, 1H, ^3J = 5.3 Hz, H3 (Phen)), 7.76 (d, 1H, ^3J = 9.1 Hz, H5 (Phen)), 7.71–7.64 (m, 1H, H4 (Py)), 7.61 (dd, 1H, ^3J = 8.1 Hz, ^3J = 4.3 Hz, H8 (Phen)), 7.24 (d, 1H, ^3J = 8.5 Hz, H3 (Py)), 7.04–6.92 (m, 1H, H5 (Py)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 154.7 (1C), 150.9 (1C), 150.6 (1C), 148.9 (1C), 145.3 (1C), 138.6 (1C), 136.3 (1C), 128.8 (1C), 126.0 (1C), 123.6 (2C), 120.4 (1C), 119.6 (2C), 118.1(1C), 112.2 (1C), 109.8 (1C). IR (neat): 3259, 2992, 2362 (CH), 1614, 1576, 1562, 1528, 1465, 1471, 1414, 1350 (C=N), 1273 (C=C, C=N), 1170 (CH, Py), 949, 883, 774, 729 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{13}N_4$ 273.1140; Found 273.1107.

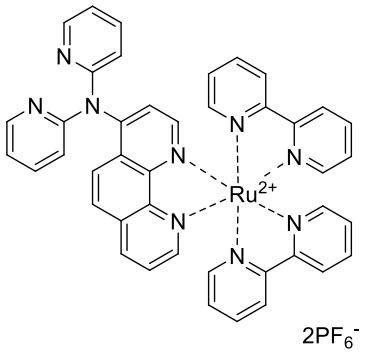
2.2. Synthesis of the ruthenium complexes

General procedure B. A glass vessel G10 (Anton Paar) equipped with a magnetic stirrer was charged with *cis*-Ru(bpy)$_2$Cl$_2$ (1 equiv.), substituted 1,10-phenanthroline ligand (1.1 equiv.) and methanol (to C=0.05 M). The mixture was stirred at 100^{o}C in microwave reactor for 2 h. After cooling to room temperature distilled water (equal volume) and a saturated aqueous solution of NH_4PF_6 (0.5 mL) were added to the reaction mixture. The red-orange precipitate formed was collected by filtration, washed with distilled water twice and dried under reduced pressure at 80^{o}C giving crude product. In case of impurities additional purification by column chromatography was carried out using CH_2Cl_2/MeOH mixtures as eluents (gradual elution using pure CH_2Cl_2, CH_2Cl_2/MeOH, 100:1 to 20:1 v/v). The products were obtained as a red-orange powders.

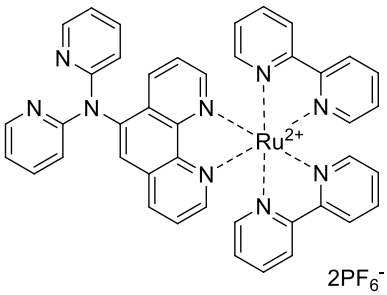


*Complex [(bpy)$_2$Ru(**Phen-3NPy$_2$**)](PF$_6$)$_2$ (**Ru(Phen-3NPy$_2$**))* was obtained according to the general procedure **B** from **Phen-3NPy$_2$** (0.27 mmol, 94 mg), *cis*-Ru(bpy)$_2$Cl$_2$ (0.24 mmol, 118 mg) in methanol (2 mL). Yield: 161 mg (64%); red-orange solid; the product was eluted with CH_2Cl_2/MeOH (33:1 v/v) mixture. ^{1}H NMR (CD_3CN, 400 MHz): δ 8.54 (dd, 2H, *J* = 8.2 Hz, *J* = 1.3 Hz), 8.53–8.48 (m, 3H), 8.34 (d, 1H, *J* = 8.1 Hz), 8.23 (ddd, 1H, *J* = 4.9 Hz, *J* = 2.0 Hz, *J* = 0.8 Hz), 8.14 (d, 1H, *J* = 2.2 Hz), 8.11 (d, 1H, *J* = 8.9 Hz), 8.10–8.03 (m, 2H), 8.10 – 8.00 (m, 2H), 7.98 (d, 1H, *J* = 8.9 Hz), 7.89 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.8 Hz), 7.85 (td, 1H, *J* = 8.0 Hz, *J* = 1.1 Hz), 7.77 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.8 Hz), 7.73 (td, 2H, *J* = 8.0 Hz, *J* = 2.0 Hz), 7.68 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.65 (dd, 1H, *J* = 8.1 Hz, *J* = 5.3 Hz), 7.64 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.62 (d, 1H, *J* = 2.2 Hz), 7.44 (ddd, 1H, *J* = 7.0 Hz, *J* = 5.7 Hz, *J* = 1.1 Hz), 7.37–7.27 (m, 2H), 7.25

– 7.17 (m, 3H), 7.00 (td, 2H, *J* = 8.2 Hz, *J* = 0.9 Hz). ^{13}C NMR (CD_3CN, 100.6 MHz): δ 157.3, 157.1, 156.9, 156.2, 152.1, 151.9, 149.3, 148.8, 147.6, 143.1, 142.3, 138.9, 137.8, 137.8, 137.7, 137.7, 137.5, 136.73, 131.4, 129.9, 128.2, 127.6, 127.6, 127.4, 127.3, 126.9, 125.2, 124.2, 124.1, 124.0, 121.00, 118.3. IR (neat): 3072 (CH), 1582 (C=C), 1567 (C=C), 1467, 1428, 1349, 1309 (C=N), 1268 (C=C, C=N), 1156, 867, 826, 766, 731, 698, 667, 617 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M - PF_6]^+$ Calcd for $C_{42}H_{31}F_6N_9PRu$ 908.1377 ; Found 908.1422.

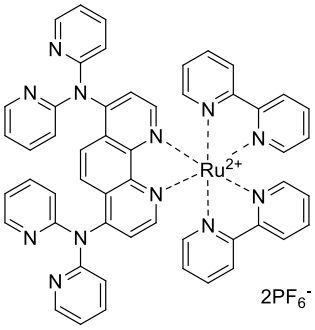


*Complex [(bpy)$_2$Ru(**Phen-4NPy$_2$**)](PF$_6$)$_2$ (**Ru(Phen-4NPy$_2$**))* was obtained according to the general procedure **B** from **Phen-4NPy$_2$** (0.13 mmol, 45 mg), *cis*-Ru(bpy)$_2$Cl$_2$ (0.12 mmol, 59 mg) in methanol (2 mL). Yield 107 mg (84%), red-orange solid, the product was eluted with CH_2Cl_2/MeOH (25:1 v/v) mixture. ^{1}H NMR (CD_3CN, 400 MHz): δ 8.51 (m, 5H), 8.23 (ddd, 2H, *J* = 4.9 Hz, *J* = 1.9 Hz, *J* = 0.8 Hz), 8.13–8.00 (m, 5H), 7.94 (d, 1H, *J* = 9.1 Hz), 7.93 (d, 1H, *J* = 5.8 Hz), 7.85 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.82 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.79 (dd, 1H, *J* = 6.7 Hz, *J* = 1.9 Hz), 7.77 (dd, 1H, *J* = 6.7 Hz, *J* = 1.9 Hz), 7.75 (d, 1H, *J* = 9.1 Hz), 7.71 (dd, 1H, *J* = 8.2 Hz, *J* = 5.3 Hz), 7.67 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.64 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.47–7.39 (m, 2H), 7.37–7.28 (m, 3H), 7.20 – 7.14 (m, 4H). ^{13}C NMR (CD_3CN, 100.6 MHz): δ 157.5, 157.2, 157.1, 152.6, 152.0, 151.9, 151.7, 151.6, 149.2, 148.7, 147.9, 138.7, 137.8, 137.7, 136.7, 128.2, 127.5, 127.2, 126.2, 124.5, 124.3, 124.2, 124.2, 123.3, 120.6, 118.1. IR (neat): 3100, 2800 (CH), 1706 (C=C), 1586 (C=C), 1446 (C=C), 1428 (C=C), 1316 (C=N), 1222 (C=C, C=N), 1155, 828, 762, 669 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M–PF_6]^+$ Calcd for $C_{42}H_{31}F_6N_9PRu$ 908.1377 ; Found 908.1402.



*Complex [(bpy)$_2$Ru(**Phen-5NPy$_2$**)](PF$_6$)$_2$ (**Ru(Phen-5NPy$_2$**))* was obtained according to the general procedure **B** from the ligand (**Phen-5NPy$_2$**) (0.11 mmol, 38 mg), *cis*-Ru(bpy)$_2$Cl$_2$ (0.10 mmol, 48 mg) in methanol (2 mL). Yield 81 mg (77%), red-orange solid. ^{1}H NMR (CD_3CN, 400 MHz): δ 8.57–8.49 (m, 4H), 8.47 (dd, 1H, *J* = 8.5 Hz, *J* = 1.2 Hz), 8.32 (dd, 1H, *J* = 8.5 Hz, *J* = 1.2 Hz), 8.19 (ddd, 2H, *J* = 4.9 Hz, *J* = 1.9 Hz, *J* = 0.9 Hz), 8.14–8.01 (m, 7H), 7.85 (ddd, 2H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.74–7.68 (m, 3H), 7.67 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.61 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.57 (dd, 1H, *J* = 8.5 Hz, *J* = 5.2 Hz), 7.48–7.44 (m, 2H), 7.34–7.30 (m, 2H), 7.21 (td, 2H, *J* = 8.3 Гц, *J* = 0.9 Hz), 7.08 (dd, 1H, *J* = 4.9 Hz, *J* = 0.9 Hz), 7.07

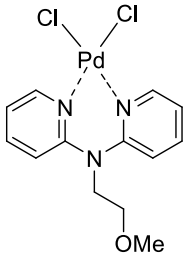
(dd, 1H, J = 4.9 Hz, J = 0.9 Hz). ^{13}C NMR (CD_3CN, 100.6 MHz): δ 157.7, 157.3, 157.1, 157.0, 152.7, 152.2, 151.9, 151.9, 151.8, 148.8, 148.3, 146.6, 142.3, 138.2, 137.9, 137.8, 137.7, 136.3, 133.7, 131.0, 130.5, 128.1, 127.6, 127.5, 127.3, 126.2, 125.9, 124.3, 124.2, 119.2, 116.7. IR (neat): 2363 (CH), 2342, 1590 (C=C), 1466 (C=C), 1428 (C=C), 1319 (C=N), 1266 (C=C, C=N), 876, 830, 761, 722, 695 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M–PF_6]^+$ Calcd for $C_{42}H_{31}F_6N_9PRu$ 908.1377 ; Found 908.1404.



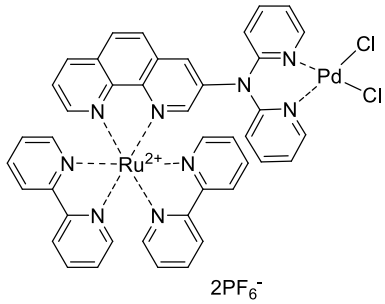
Complex $\{(bpy)_2Ru[$***Phen-4,7(NPy$_2$)$_2$***$]\}(PF_6)_2$ (***Ru[Phen-4,7(NPy$_2$)$_2$]***) was obtained according to the general procedure **B** from **Phen-4,7(NPy$_2$)$_2$** (0.09 mmol, 45 mg), *cis*-$Ru(bpy)_2Cl_2$ (0.07 mmol, 35 mg) in methanol (2 ml). Yield 57 mg (67%), red-orange solid, the product was eluted with CH_2Cl_2/MeOH (20:1 v/v) mixture. ^{1}H NMR (CD_3CN, 400 MHz): δ 8.52 (t, 4H, J = 6.6 Hz), 8.18 (dd, 4H, J = 5.2 Hz, J = 2.0 Hz), 8.08 (td, 2H, J = 8.01 Hz, J = 1.4 Hz), 8.05 (td, 2H, J = 8.01 Hz, J = 1.4 Hz), 7.91 (d, 2H, J = 6.0 Hz), 7.80 (t, 4H, J = 6.0 Hz), 7.73 (ddd, 4H, J = 8.2 Hz, J = 7.4 Hz, J = 2.0 Hz), 7.45–7.40 (m, 4H), 7.39 (s, 2H), 7.26 (dd, 2H, J = 6.0 Hz), 7.16–7.11 (m, 8H). ^{13}C NMR (CD_3CN, 100.6 MHz): δ 158.2, 158.1, 158.0, 153.5, 152.7, 152.6, 152.2, 150.4, 149.5, 139.5, 138.6, 138.5, 128.6, 128.5, 128.4, 125.1, 125.1, 124.5, 124.1, 121.4, 118.9. IR (neat): 2922 (CH), 1706 (C=C), 1590 (C=C), 1567, 1465 (C=C), 1428 (C=C), 1356, 1313 (C=N), 1273, 1221 (C=C, C=N), 1154, 857, 828, 763, 738, 730, 660, 619 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M–PF_6]^+$ calcd for $C_{52}H_{38}F_6N_{12}PRu$, 1077.2022; Found 1077.2035.

2.3. Synthesis of Ru(L)Pd and (NPy$_2$)Pd complexes.

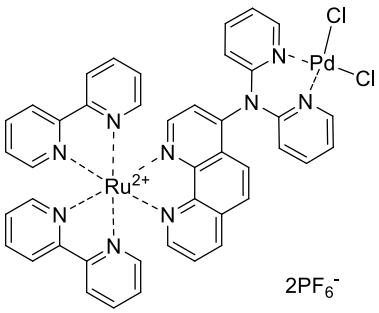
Synthesis of Pd-containing complexes. General procedure C. A round bottom flask, equipped with a magnet stirrer, was charged with a ligand (1 equiv.), $Pd(CH_3CN)_2Cl_2$ (1 equiv.) and dichloromethane. The reaction mixture was stirred at room temperature for 2 hours in the dark. After that, the mixture was concentrated under reduced pressure to *ca.* 5 mL in volume and *n*-hexane (*ca.* 5 mL) was added dropwise to the residue solution. The formed precipitate was collected by centrifugation (1500 rpm, 10 min), washed twice with diethyl ether and dried on air giving target product.



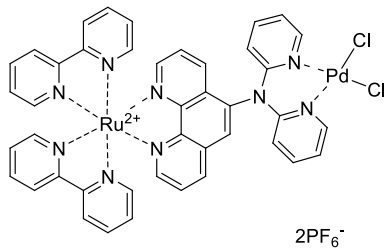
*Complex (**NPy$_2$**)PdCl$_2$ (**(NPy$_2$)Pd**)* was obtained according to the general procedure **C** from **NPy$_2$** (0.5 mmol, 119 mg), Pd(CH$_3$CN)$_2$Cl$_2$ (0.5 mmol, 135 mg) in dichloromethane (104 mL). Yield 178 mg (88%), yellow-green solid. ^{1}H NMR (CD$_3$CN, 400 MHz): δ 8.93 (d, 2H, *J* = 7.2 Hz, H6, H6'(Py)), 7.89 (t, 2H, *J* = 8.9 Hz, H4, H4' (Py)), 7.30 (d, 2H, *J* = 7.2 Hz, H3, H3' (Py)), 7.18 (t, 2H, *J* = 8.9 Hz, H5, H5' (Py)), 4.24 (t, 2H, *J* = 5.7 Hz, CH$_2$N), 3.79 (t, 2H, *J* = 5.7 Hz, CH$_2$O), 3.42 (s, 3H, CH$_3$). IR (neat): 2916 (CH), 2360, 2332, 1707 (C=C), 1598 (C=C), 1576, 1487 (C=C), 1452 (C=C), 1343 (C=N), 1269, 1247 (C=C, C=N), 1195, 1167, 1151, 1057, 961, 907, 830, 782, 722, 695, 657 cm^{-1}. Anal. (%) calcd for found $C_{12}H_{15}N_3OCl_2Pd$: C, 38.29; H, 3.74; N, 10.07; found: C, 38.42; H, 3.69; N, 10.34. HRMS (MALDI TOF) *m/z*: [2M–Cl] calcd for $C_{26}H_{30}Cl_3N_6O_2Pd_2$, 776.9570; Found 776.9515.



*Complex [(bpy)$_2$Ru(**Phen-3NPy$_2$**)PdCl$_2$](PF$_6$)$_2$ (**Ru(Phen-3NPy$_2$)Pd**)* was obtained according to the general procedure **C** from **Ru(Phen-3NPy$_2$)** (0.04 mmol, 40 mg), Pd(CH$_3$CN)$_2$Cl$_2$ (0.04 mmol, 10 mg) in dichloromethane (8 mL). Yield 42 mg (85%); red-orange solid. ^{1}H NMR (CD$_3$CN, 400 MHz): δ 8.87 (dd, 2H, *J* = 5.8 Hz, *J* = 1.6 Hz), 8.56 (dd, 1H, *J* = 8.3 Hz, *J* = 1.3 Hz), 8.51 (dt, 1H, *J* = 8.1 Hz, *J* = 1.1 Hz), 8.46 (d, 1H, *J* = 5.5 Hz), 8.43 (d, 1H, *J* = 5.6 Hz), 8.32 (d, 1H, *J* = 8.2 Hz), 8.16 (d, 1H, *J* = 9.1 Hz), 8.14 (dd, 1H, *J* = 7.6 Hz, *J* = 1.7 Hz), 8.16 (dd, 1H, *J* = 7.8 Hz, *J* = 1.5 Hz), 8.08 (td, 1H, *J* = 8.2 Hz, *J* = 1.5 Hz), 8.04 (d, 1H, *J* = 9.1 Hz), 8.01 (dd, 1H, *J* = 5.3 Hz, *J* = 1.3 Hz), 8.0 (dd, 1H, *J* = 8.1 Hz, *J* = 1.5 Hz), 7.97 (dd, 1H, *J* = 7.8 Hz, *J* = 1.3 Hz), 7.96 (d, 1H, *J* = 2.5 Hz), 7.90 (td, 1H, *J* = 8.3 Hz, *J* = 1.5 Hz), 7.83 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.77 – 7.75 (m, 3H), 7.72 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.69 (ddd, 1H, *J* = 5.6 Hz, *J* = 1.5 Hz, *J* = 0.7 Hz), 7.64 (ddd, 1H, *J* = 6.0 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz), 7.61 (dd, 1H, *J* = 5.9 Hz, *J* = 1.5 Hz), 7.8 (dd, 1H, *J* = 5.8 Hz, *J* = 1.4 Hz), 7.44 (ddd, 1H, *J* = 7.7 Hz, *J* = 5.6 Hz, *J* = 1.3 Hz), 7.35 (ddd, 1H, *J* = 7.6 Hz, *J* = 5.6 Hz, *J* = 1.3 Hz), 7.28 (ddd, 1H, *J* = 7.6 Hz, *J* = 5.6 Hz, *J* = 1.3 Hz), 7.22 (ddd, 1H, *J* = 7.6 Hz, *J* = 5.6 Hz, *J* = 1.3 Hz), 7.11 (d, 1H, *J* = 2.5 Hz). ^{13}C NMR (CD$_3$CN, 100.6 MHz): *δ* 157.3, 156.9, 156.7, 156.6, 154.3, 152.3, 152.22, 152.0, 151.9, 149.2, 147.6, 143.5, 143.4, 142.9, 139.9, 137.9, 137.8, 137.5, 136.9, 131.2, 130.1, 129.2, 128.0, 127.6, 127.5, 127.4, 125.9, 125.5, 124.6, 124.2, 123.9, 119.4. IR (neat): 2360 (CH), 1582 (C=C), 1563 (C=C), 1470 (C=C), 1435 (C=C), 1350 (C=N), 1265, 1245 (C=C, C=N), 885, 834, 772, 747, 714, 641 cm^{-1}. HRMS (MALDI TOF) *m/z*: [M–PF$_6$]$^+$ calcd for $C_{42}H_{31}Cl_2F_6N_9PPdRu$, 1083.9799; Found 1083.9815.



*Complex [(bpy)$_2$Ru(**Phen-4NPy$_2$**)PdCl$_2$](PF$_6$)$_2$ (**Ru(Phen-4NPy$_2$)Pd**)* was obtained according to the general procedure **C** from **Ru(Phen-4NPy$_2$)** (0.04 mmol, 45 mg), Pd(CH$_3$CN)$_2$Cl$_2$ (0.04 mmol, 11 mg) in dichloromethane (9 ml). Yield: 45 mg (86 %); red-orange solid; ^{1}H NMR (CD$_3$CN, 400 MHz): δ 9.42 (d, 1H, *J*=9.1 Hz), 8.81 (ddd, 2H, *J* = 5.9 Hz, *J* = 1.7 Hz, *J* = 0.5 Hz), 8.63 (dd, 1H, *J* = 8.3 Hz, *J* = 1.2 Hz), 8.58 (dt, 1H, *J* = 8.2 Hz, *J* = 1.0 Hz), 8.54 (d, 2H, *J* = 8.2 Hz), 8.50 (dt, 1H, *J* = 8.2 Hz, *J* = 1.0 Hz), 8.37 (d, 1H, *J* = 5.74 Hz), 8.38 (d, 1H, *J* = 9.1 Hz), 8.33 (d, 1H, *J* = 5.74 Hz), 8.18 (dd, 1H, *J* = 5.2 Hz, *J* = 1.3 Hz), 8.14 (td, 1H, *J* = 7.9 Hz, *J* = 1.5 Hz), 8.11 (dt, 1H, *J* = 7.9 Hz, *J* = 1.5 Hz), 8.05 (td, 1H, *J* = 7.9 Hz, *J* = 1.5 Hz), 8.01 (td, 1H, *J* = 7.9 Hz, *J* = 1.5 Hz), 7.89 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.7 Hz, *J* = 0.7 Hz), 7.86 (dd, 1H, *J* = 7.1 Hz, *J* = 1.8 Hz), 7.84 (dd, 1H, *J* = 7.1 Hz, *J* = 1.8 Hz), 7.81–7.77 (m, 2H), 7.64 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.7 Hz, *J* = 0.5 Hz), 7.57 (ddd, 1H, *J* = 5.7 Hz, *J* = 1.7 Hz, *J* = 0.5 Hz), 7.52–7.45 (m, 2H), 7.33 (dd, 1H, *J* = 5.9 Hz, ^{4}*J* = 1.2 Hz), 7.31 (dd, 1H, *J* = 5.9 Hz, *J* = 1.2 Hz), 7.29–7.23 (m, 4H). ^{13}C NMR (CD$_3$CN, 100.6 MHz): *δ* 157.3, 157.2, 156.9, 156.9, 154.0, 153.4, 152.6, 152.3, 152.2, 151.9, 151.8, 150.7, 147.8, 144.0, 141.5, 138.1, 138.0, 137.9, 137.0, 131.3, 130.0, 129.9, 128.2, 127.7 127.6, 127.6, 127.5, 126.8, 124.3, 124.2, 123.2, 122.1, 118.3. IR (neat): 2400 (CH), 1596 (C=C), 1466 (C=C), 1428 (C=C), 1323 (C=N), 1271, 1239 (C=C, C=N), 1221, 1164, 831, 761, 673 cm^{-1}. HRMS (MALDI TOF) *m/z*: [M–PF$_6$]$^+$ calcd for C$_{42}$H$_{31}$Cl$_2$F$_6$N$_9$PPdRu, 1083.9799; Found 1083.9821.

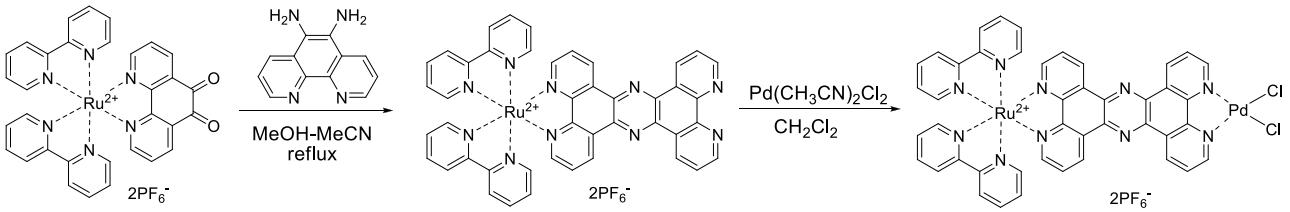


*Complex [(bpy)$_2$Ru(**Phen-5NPy$_2$**)PdCl$_2$](PF$_6$)$_2$ (**Ru(Phen-5NPy$_2$)Pd**)* was obtained according to the general procedure **C** from **Ru(Phen-5NPy$_2$)** (0.04 mmol, 40 mg), Pd(CH$_3$CN)$_2$Cl$_2$ (0.04 mmol, 10 mg) in dichloromethane (8 ml). Yield: 42 mg (86 %); red-orange solid; ^{1}H NMR (CD$_3$CN, 400 MHz): δ 9.91 (d, 1H, *J* = 8.8 Hz), 9.01 (s, 1H), 8.91 (ddd, 2H, *J* = 5.9 Hz, *J* = 1.8 Hz, *J* = 0.6 Hz), 8.81 (dd, 1H, *J* = 8.3 Hz, *J* = 1.3 Hz), 8.55 (d, 1H, *J* = 8.2 Hz), 8.54 (d, 1H, *J* = 8.2 Hz), 8.51 (d, 1H, *J* = 8.0 Hz), 8.50 (d, 1H, *J* = 8.0 Hz), 8.24 (dd, 1H, *J* = 5.3 Hz, *J* = 1.3 Hz), 8.18 (dd, 1H, *J* = 5.3 Hz, *J* = 1.2 Hz), 8.13 (td, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 8.11 (td, 1H, *J* = 8.0 , *J* = 1.5 Hz), 8.02 (td, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.89 – 7.81 (m, 6H), 7.63 (dd, 1H, *J* = 5.6 Hz, *J* = 0.7 Hz), 7.61 (dd, 1H, *J* = 5.6 Hz, *J* = 0.7 Hz), 7.50 – 7.43 (m, 2H), 7.40 (d, 2H, *J* = 8.6 Hz), 7.32–7.21 (m, 4H). ^{13}C NMR (CD$_3$CN, 100.6 MHz): *δ* 157.2, 156.9, 156.9, 154.2, 153.6, 152.4, 152.3, 151.9, 151.9, 151.0, 149.5, 148.0, 141.2, 138.0, 137.9, 137.7, 135.4, 133.5, 132.7, 130.5, 130.0, 127.6, 127.5, 126.9, 126.7, 124.3, 124.2, 121.5. IR (neat): 2360 (CH), 1598 (C=C), 1576, 1487, 1452 (C=C), 1428 (C=C), 1343 (C=N),

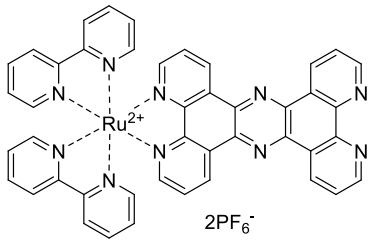
1269, 1247 (C=C, C=N), 1195, 1167, 1151, 1119, 1077, 961, 907, 830, 782, 751, 737, 695, 657 cm^{-1}. HRMS (MALDI TOF) *m/z*: $[M–PF_6]^+$ calcd for $C_{42}H_{31}Cl_2F_6N_9PPdRu$, 1083.9799; Found 1083.9812.

Synthesis of Ru(tpphz)Pd complex

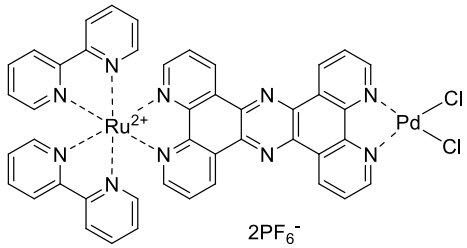
Ru(tpphz)Pd complex was synthesized by known "chemistry on complex" method (Scheme S2). **Ru[Phen(O)$_2$]** starting complex was prepared from *cis*-Ru(bpy)$_2$Cl$_2$ and **Phen(O)$_2$** according previously reported procedure [8].



Scheme S2.



*Synthesis of [(bpy)$_2$Ru(**tpphz**)](PF$_6$)$_2$ complex (**Ru(tpphz)**)* [10]. The two-neck flask equipped with condenser and magnetic stirrer was charged with 91.4 mg (0.1 mmol) of **Ru[Phen(O)$_2$]** and acetonitrile (10 mL). The mixture was heated to boiling and hot solution of 21 mg (0.1 mmol) of 1,10-phenanthroline-5,6-diamine in 5 mL of methanol was added. The mixture was refluxed for 6 hours and allowed to cool. The solution was gravity filtered and saturated NH_4PF_6 aqueous solution was added. The precipitate was collected, washed with water and dried under reduced pressure. Yield 61 mg (56%), red powder. ^{1}H NMR (CD_3CN, 400 MHz): δ 9.59 (dd, 2H, *J* = 8.3 Hz, *J* = 0.8 Hz), 9.38 (d, 2H, *J* = 8.2 Hz), 8.61 (d, 2H, *J* = 8.3 Hz), 8.57 (d, 2H, *J* = 7.9 Hz), 8.47–8.50 (m, 2H), 8.29 (dd, 2H, *J* = 8.3 Hz, *J* = 0.8 Hz), 8.14–8.20 (m, 4H), 8.05 (td, 2H, *J* = 7.9 Hz, *J* = 1.3 Hz), 7.94 (dd, 2H, *J* = 5.6 Hz, *J* = 0.8 Hz), 7.88 (dd, 2H, *J* = 8.2 Hz, *J* = 5.5 Hz), 7.80 (dd, 2H, *J* = 8.2 Hz, *J* = 4.4 Hz), 7.50–7.56 (m, 2H), 7.34–7.40 (m, 2H).



*[(bpy)$_2$Ru(**tpphz**)PdCl$_2$](PF$_6$)$_2$ (**Ru(tpphz)Pd**)* was obtained according to the general procedure **C** from **Ru(tpphz)** (0.012 mmol, 13 mg), Pd(CH$_3$CN)$_2$Cl$_2$ (0.012 mmol, 3 mg) in dichloromethane (4 mL). Yield: 14 mg (92%); red-orange solid; ^{1}H NMR (CD$_3$CN, 400 MHz): δ 9.94 (d, 2H, *J* = 8.1 Hz), 9.71 (d, 2H, *J* = 8.1 Hz), 9.30 (d, 2H *J* = 5.3 Hz), 8.59 (d, 2H *J* = 8.2 Hz), 8.55 (d, 2H *J* = 8.2 Hz), 8.36 (d, 2H, *J* = 5.3 Hz), 8.21 (dd, 2H, *J* = 8.2, Hz, *J* = 5.3 Hz), 8.15 (td, 2H, *J* = 8.2, Hz, *J* = 1.3 Hz), 8.1-8.01 (m, 4H), 7.93 (d, 2H, *J* = 5.5 Hz), 7.89 (d, 2H, *J* = 5.5 Hz), 7.51 (t, 2H, *J* = 6.5 Hz), 7.30 (t, 2H, *J* = 6.5 Hz). HRMS (ESI) *m/z*: [M–2PF$_6$]$^{2+}$ calcd for C$_{44}$H$_{28}$Cl$_2$N$_{10}$PdRu, 486.9971; Found 486.9985.

3. Detailed NMR studies of the complexes

All NMR spectra were recorded with Agilent 400 MR spectrometer in CD_3CN; the residual signal of CHD_2CN was used as an internal standard. δ, ppm

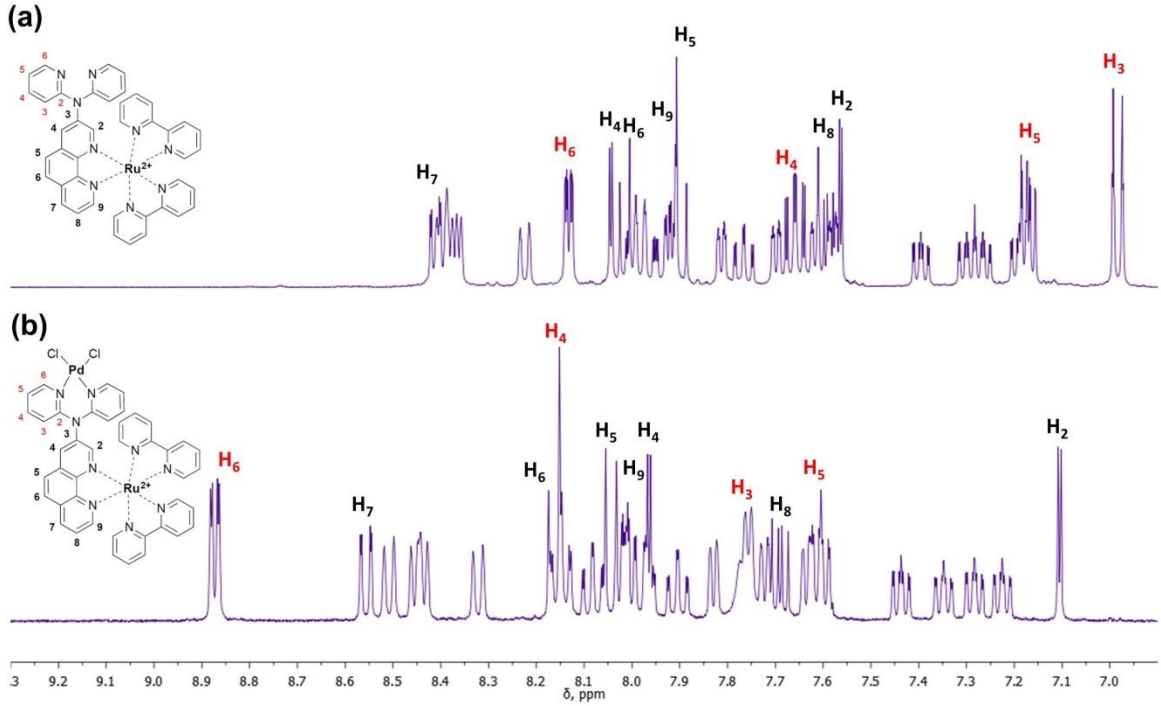


Figure S1. Comparison of ^{1}H NMR spectra of **(a) Ru(Phen-3NPy$_2$)** and **(b) Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

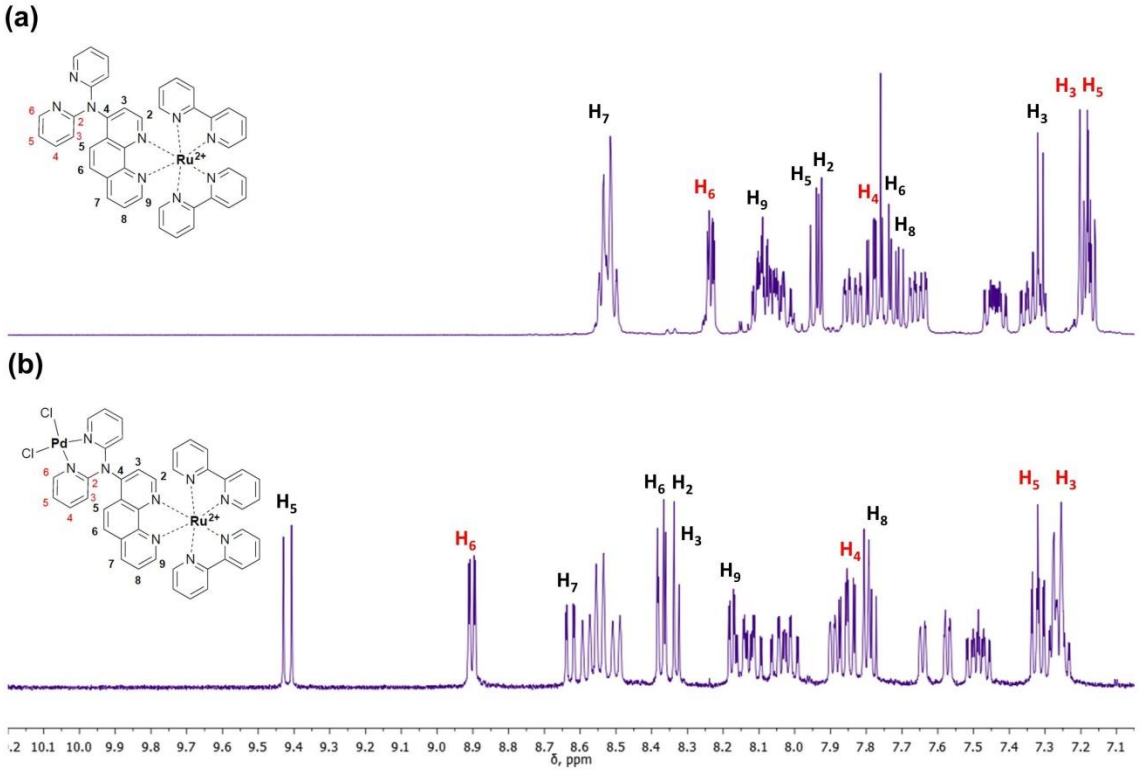
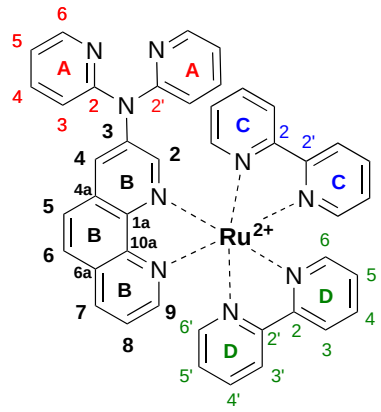


Figure S2. Comparison of ^{1}H NMR spectra of **(a) Ru(Phen-4NPy$_2$)** and **(b) Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

Ru(Phen-3NPy$_2$)

Table S3. Signal assignment in NMR spectra of **Ru(Phen-3NPy$_2$)**.



Assignment		Chemical shift (ppm)		*J* (Hz)	
		^{1}H	^{13}C	H–H (atom)	
A	**2,2'**	-	156.16		
A	**3,3'**	7.00	118.25	8.1 (4,4')	0.9 (6,6')
A	**4,4'**	7.73	138.90	8.1 (3,3')	7.7 (5,5')
A	**5,5'**	7.19	121.01	7.7 (5,5')	4.9 (6,6'), 0.9 (3,3')
A	**6,6'**	8.23	148.78	4.9 (5,5')	2.0 (4,4'), 0.9 (3,3')
B	**1a**	-	131.35		
B	**2**	7.62	149.30	2.2 (4)	
B	**3**	-	143.13		
B	**4**	8.14	126.88	2.2 (2)	
B	**4a**	-	142.30		
B	**5**	7.98	127.55	8.9 (6)	
B	**6**	8.11	128.18	8.9 (5)	
B	**6a**	-	129.88		
B	**7**	8.54	136.73	8.2 (8)	1.3 (9)
B	**8**	7.65	125.14	8.2 (7)	5.3 (9)
B	**9**	8.01	152.20	5.3 (8)	1.3 (7)
B	**10a**	-	147.57		
C	**2,2'**	-	156.98, 157.28		
C	**3,3'**	8.49, 8.52	124.12, 124.21	8.4 (4,4')	1.1(5, 5'), 0.8 (6,6')
C	**4,4'**	8.08, 8.02	137.70, 137.76	8.4 (3,3')	7.0 (5,5'), 1.5(6,6')
C	**5,5'**	7.33, 7.44	127.43, 127.41	7.0 (4,4')	5.6 (6,6'), 1.1 (3,3')
C	**6,6'**	7.77, 7.89	151.91, 152.15	5.6 (5,5')	1.5 (4, 4'), 0.8 (3,3')
D	**2,2'**	-	157.09, 156.91		
D	**3,3'**	8.34, 8.50	124.06, 124.04	8.2 (4,4')	1.1 (5,5'), 0.7 (6, 6')
D	**4,4'**	7.84, 8.06	137.49, 137.84	8.2 (3,3')	7.0 (5,5'), 1.5 (6, 6')
D	**5,5'**	7.21, 7.30	127.28, 127.56	7.0 (4, 4')	5.7 (6, 6'), 1.1(3, 3')
D	**6,6'**	7.68, 7.64	151.91, 152.00	5.7 (5, 5')	1.5 (4, 4'), 0.7 (3,3')

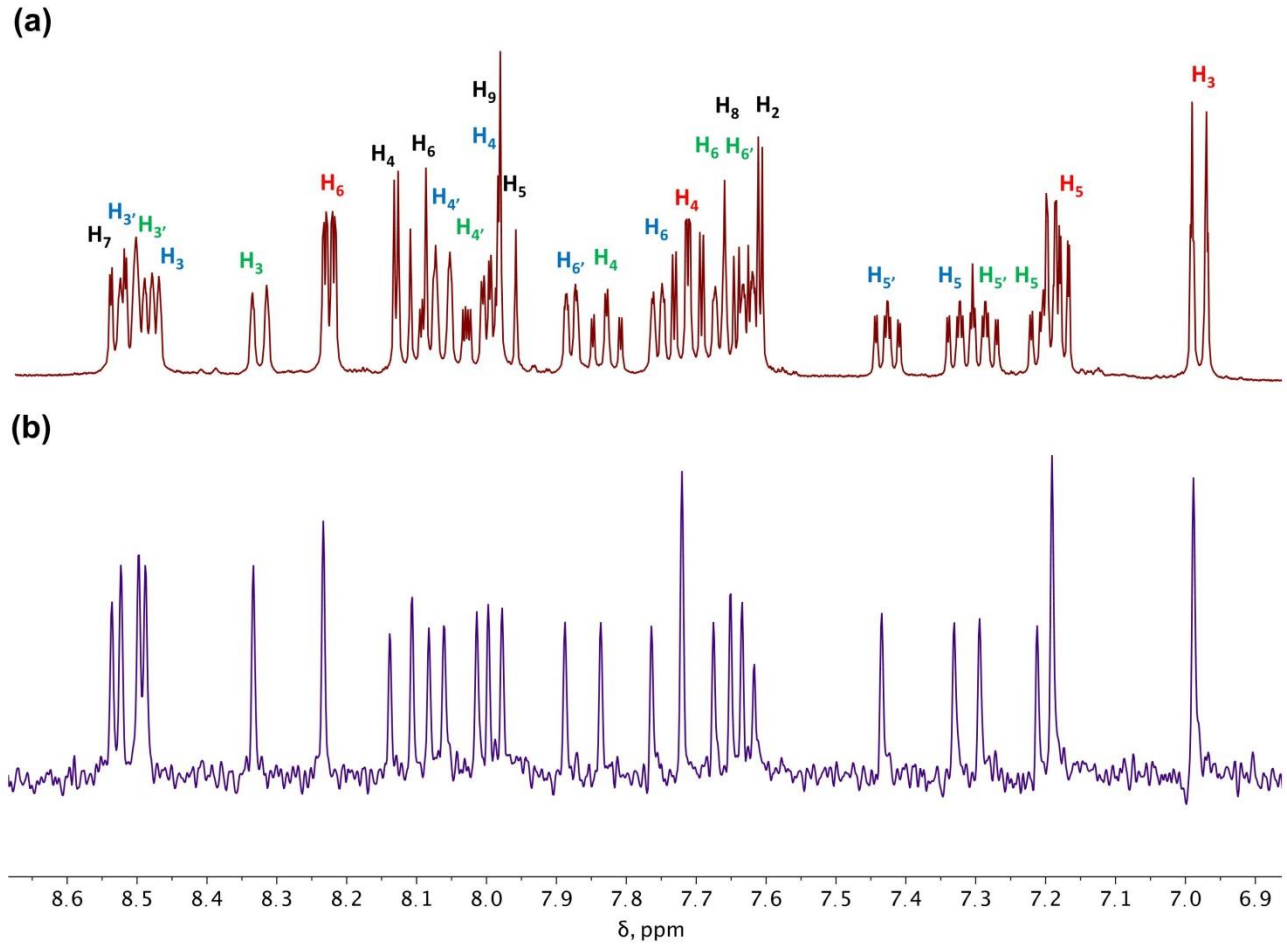


Figure S3. (a) ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K); (b) PSYCHE ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K).

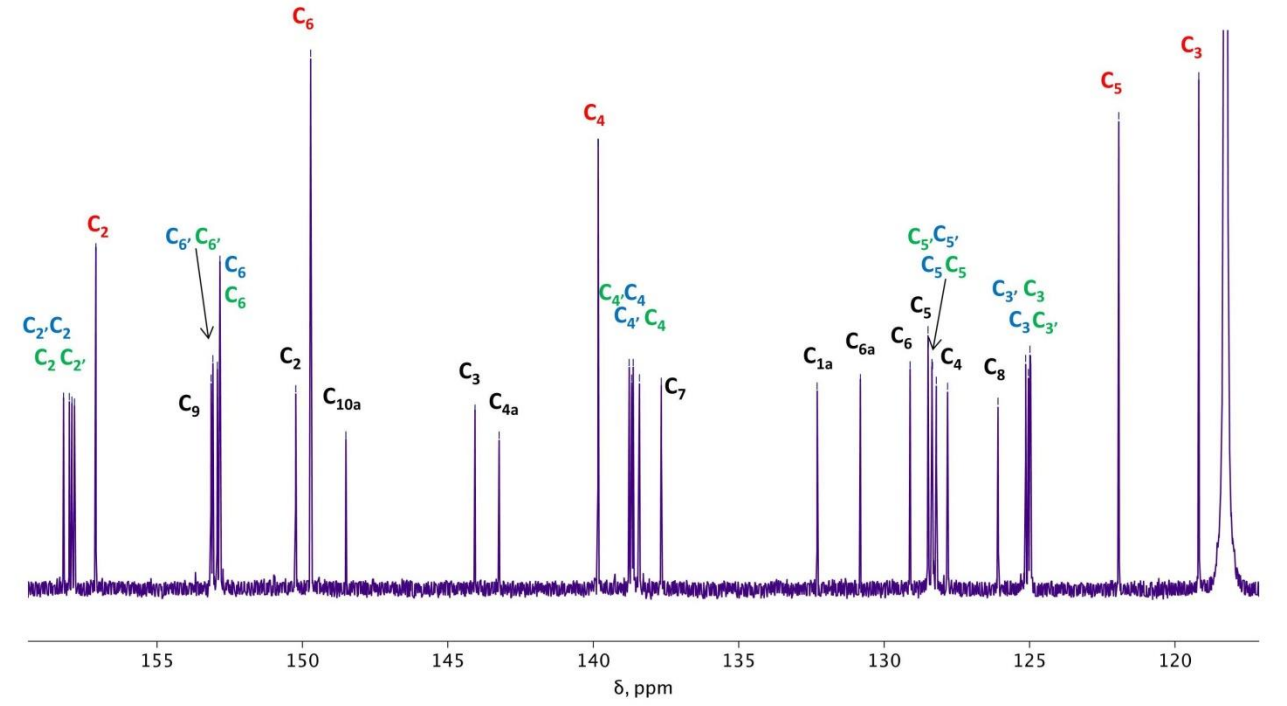


Figure S4. ^{13}C{^{1}H} NMR spectrum of **Ru(Phen-3NPy$_2$)** (100.6 MHz, CD_3CN, 298 K).

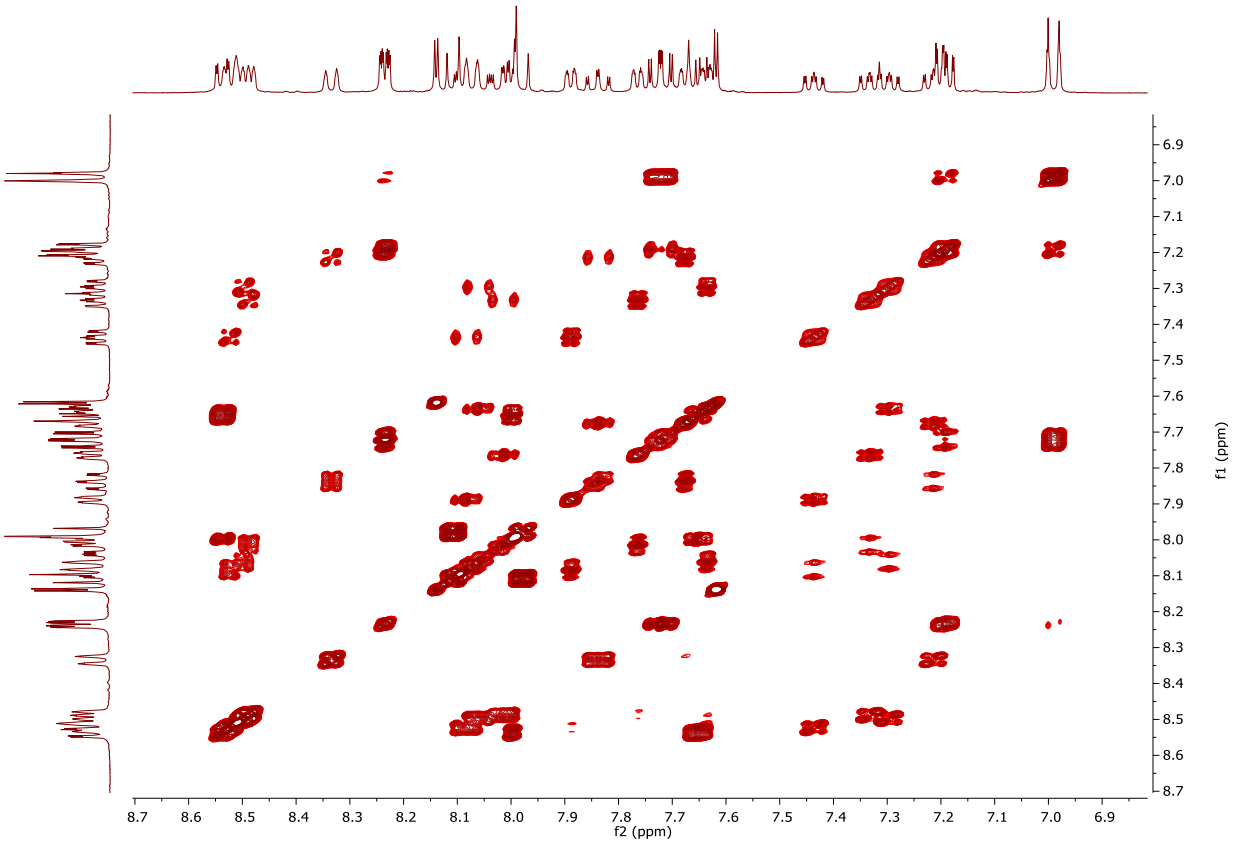


Figure S5. COSY ^{1}H spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K).

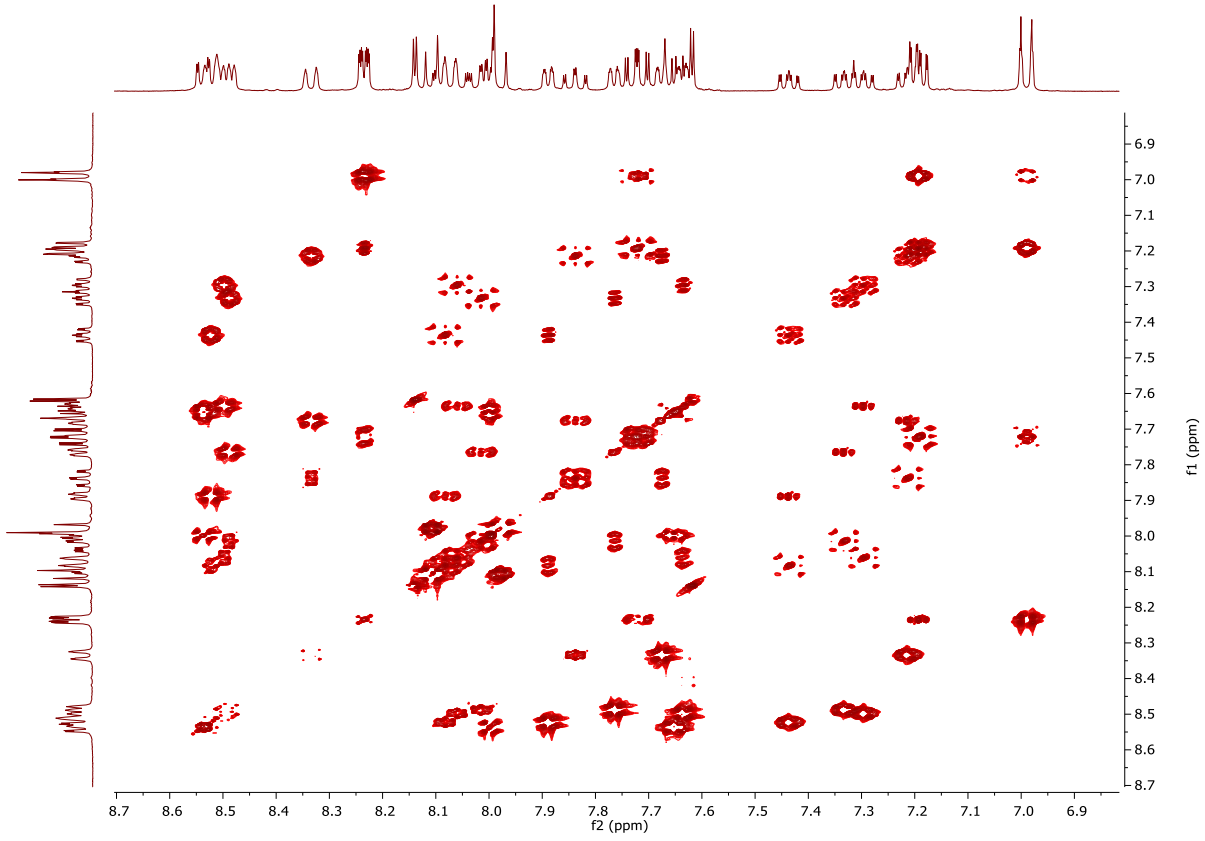


Figure S6. TOCSY ^{1}H spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K, mix. time 150 ms).

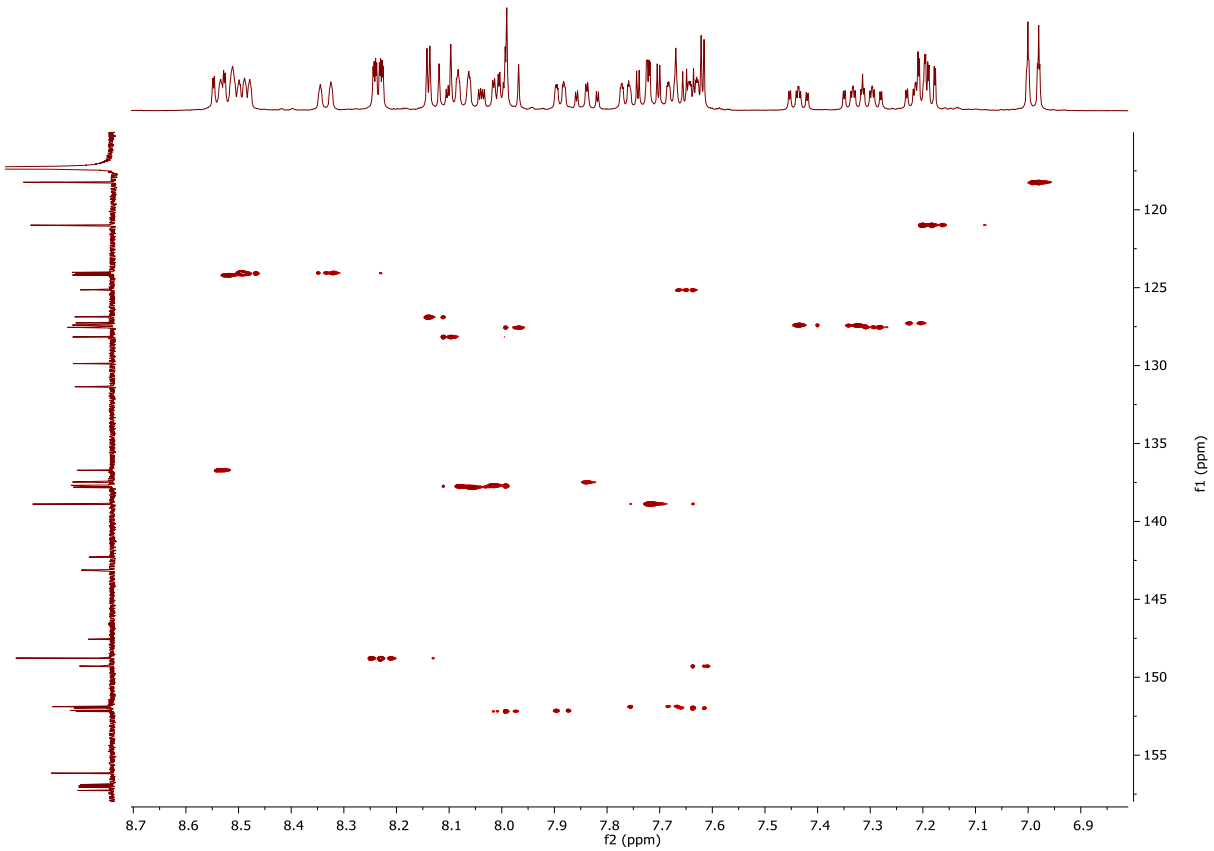


Figure S7. gHSQCAD spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K).

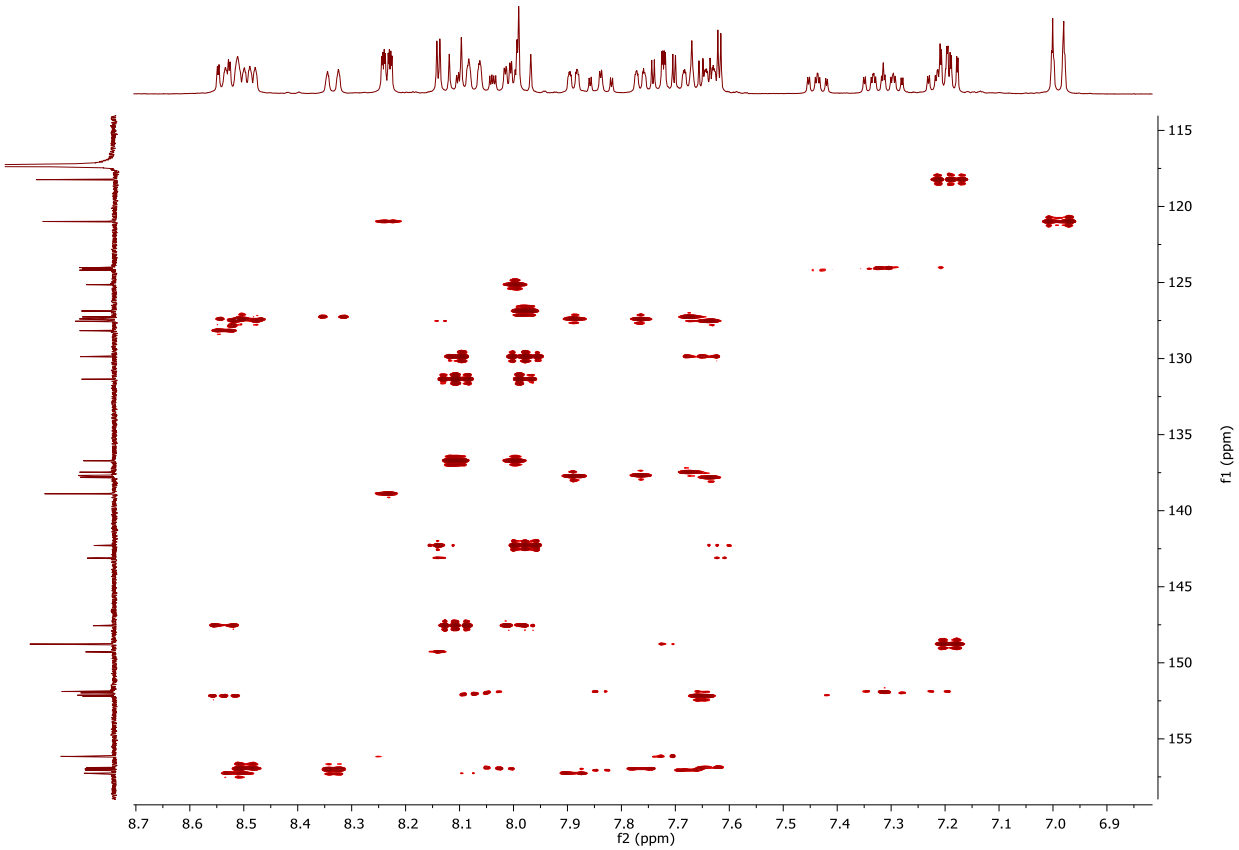


Figure S8. gHMBCAD spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K, J=8 Hz).

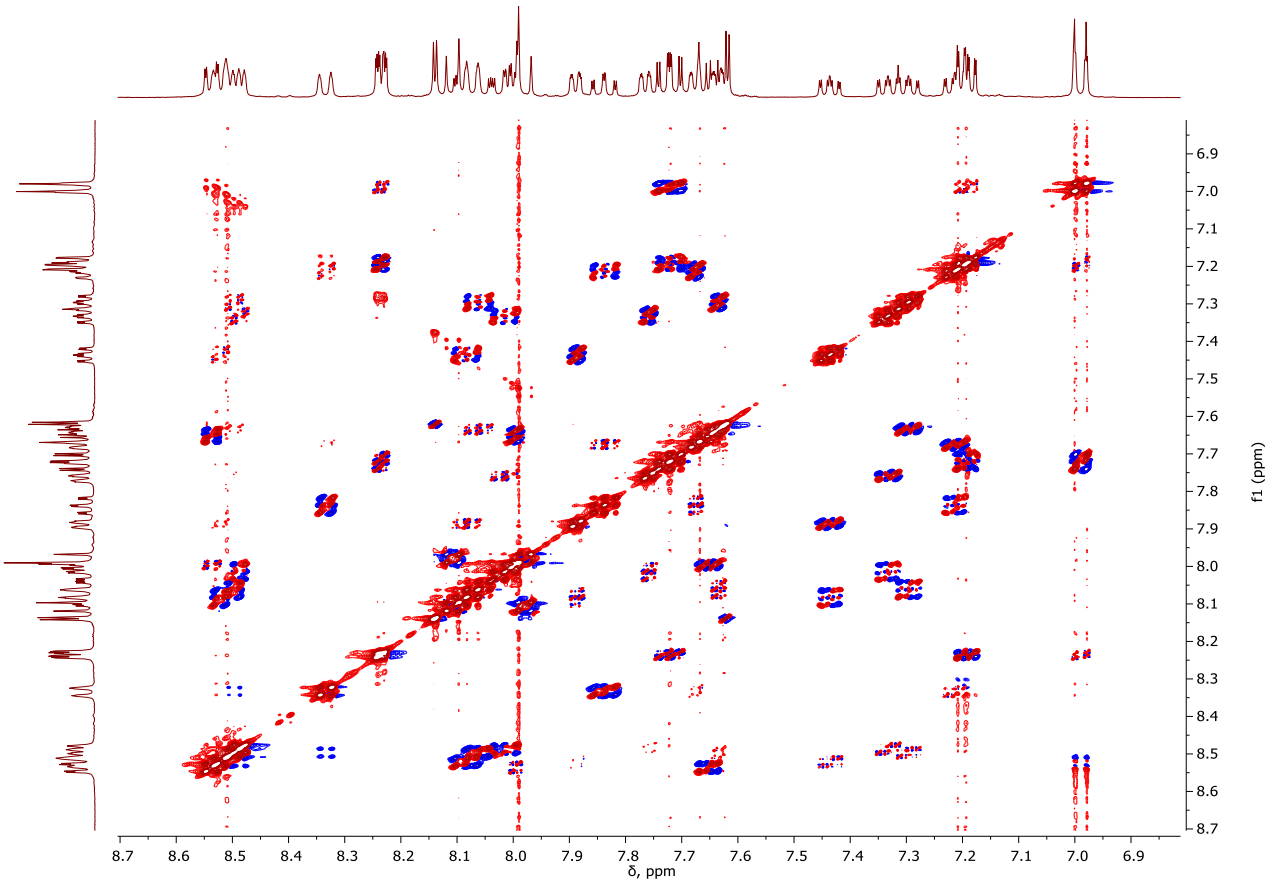
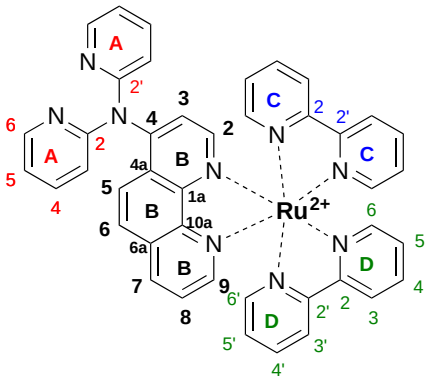


Figure S9. ROESY spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K).

Ru(Phen-4NPy$_2$)

Table S4. Signal assignment in NMR spectra of **Ru(Phen-4NPy$_2$)**.



Assignment		Chemical shift (ppm)		*J* (Hz)	
		^{1}H	^{13}C	H–H (atom)	
A	**2,2'**	-	157.48		
A	**3,3'**	7.19	118.11	8.3 (4, 4')	0.9 (6, 6')
A	**4,4'**	7.78	138.73	8.3 (3, 3')	7.4(5, 5')
A	**5,5'**	7.18	120.56	7.4 (4, 4')	4.9 (6, 6'), 0.9 (3, 3')
A	**6,6'**	8.24	148.72	4.9 (5, 5')	1.9 (4, 4'), 0.9 (3, 3')
B	**1a**	-	149.21		
B	**2**	7.93	152.55	5.9 (3)	
B	**3**	7.31	123.29	5.9 (2)	
B	**4**	-	151.55		
B	**4a**	-	128.18		
B	**5**	7.94	127.22	9.2 (6)	
B	**6**	7.75	124.47	9.2 (5)	
B	**6a**	-	130.73		
B	**7**	8.52	136.66	8.3 (8)	1.3 (9)
B	**8**	7.71	126.21	8.3 (7)	5.3 (9)
B	**9**	8.09	152.59	5.3 (8)	1.3 (7)
B	**10a**	-	147.88		
C [1]	**2,2'**	-	157.33, 157.10		
C [1]	**3,3'**	8.54, 8.53	124.26, 124.22	8.2 (4, 4')	1.3 (5, 5'), 0.8 (6, 6')
C [1]	**4,4'**	8.10, 8.06	137.75, 137.72	8.2 (3, 3')	7.6 (5, 5'), 1.5 (6, 6')
C [1]	**5,5'**	7.45, 7.31	127.53, 127.51	7.6 (4, 4')	5.6 (6, 6'), 1.3 (3, 3')
C [1]	**6,6'**	7.83, 7.64	151.91, 151.91	5.6 (5, 5')	1.5 (4, 4'), 0.8 (3, 3')
D [1]	**2,2'**	-	157.21, 157.05		
D [1]	**3,3'**	8.53, 8.51	124.22, 124.18	8.2 (4, 4')	1.3 (5, 5'), 0.8(6, 6')
D [1]	**4,4'**	8.07, 8.03	137.74, 137.70	8.2 (3, 3')	7.7 (5, 5'), 1.5(6, 6')
D [1]	**5,5'**	7.43, 7.35	127.49, 127.53	7.7 (4, 4'),	5.7 (6, 6') 1.3(3, 3')
D [1]	**6,6'**	7.85, 7.67	151.97, 151.69	5.7 (5, 5')	1.5 (4, 4'), 0.8(3, 3')

[1] Exact assigning the pyridine ring atoms signals to a certain 2,2'-bipyridine ligand is not possible due to the close values of the chemical shifts.

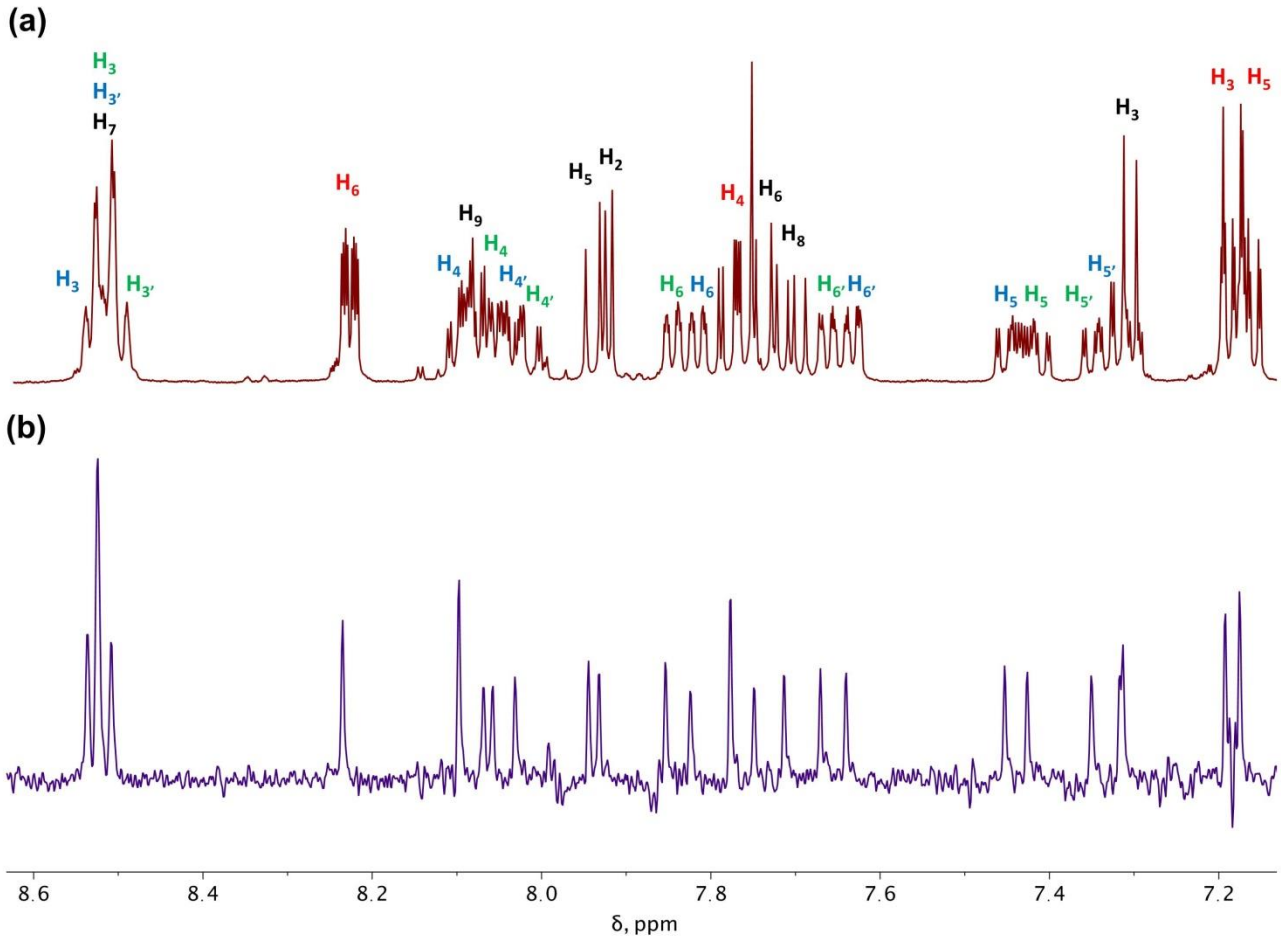


Figure S10. (a) ^{1}H NMR spectrum of **Ru(Phen-4NPy$_2$)** (400 MHz, CD_3CN, 298 K); (b) PSYCHE ^{1}H NMR spectrum of **Ru(Phen-4NPy$_2$)** (400 MHz, CD_3CN, 298 K).

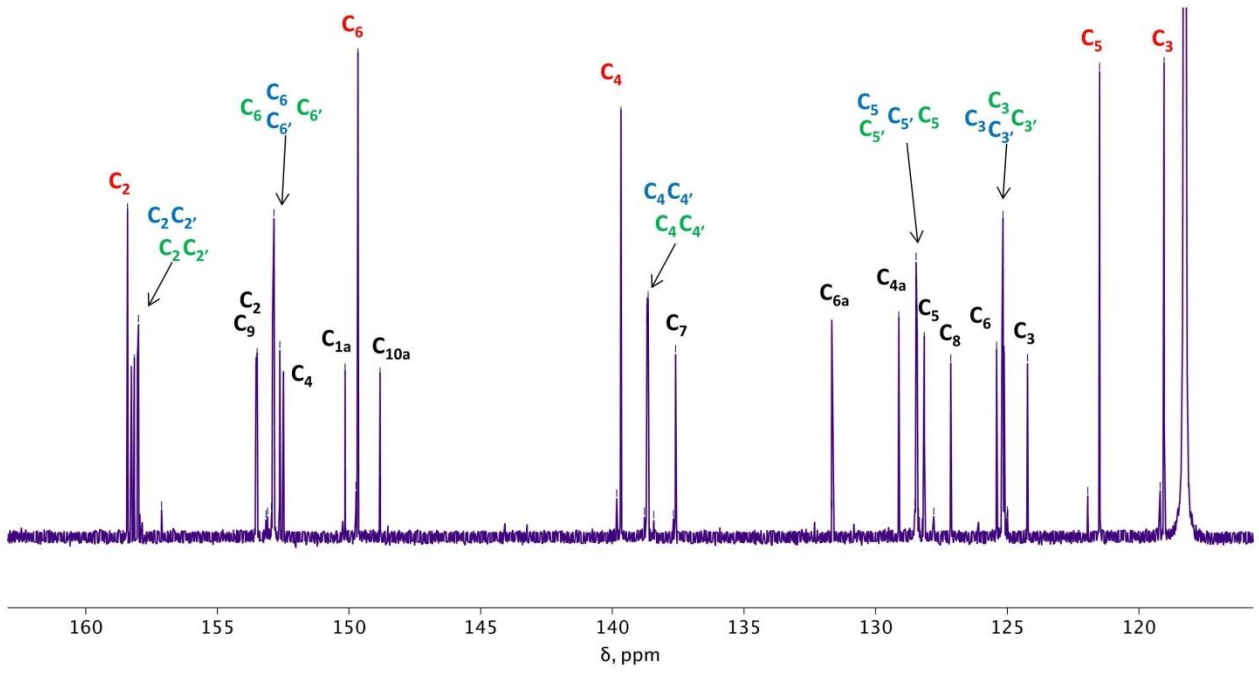


Figure S11. ^{13}C{^{1}H} NMR spectrum of **Ru(Phen-4NPy$_2$)** (100.6 MHz, CD_3CN, 298 K).

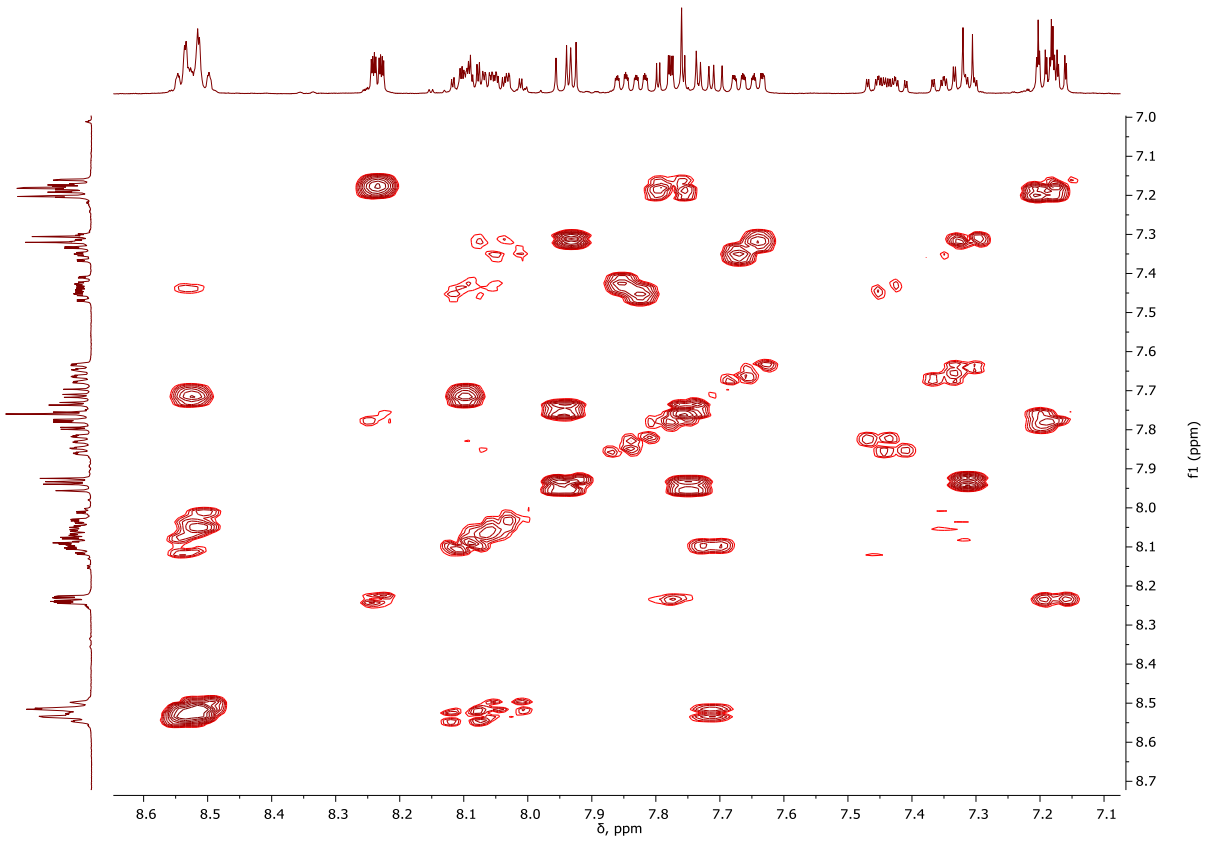


Figure S12. COSY ^{1}H spectrum of **Ru(Phen-4NPy$_2$)** (400 MHz, CD_3CN, 298 K).

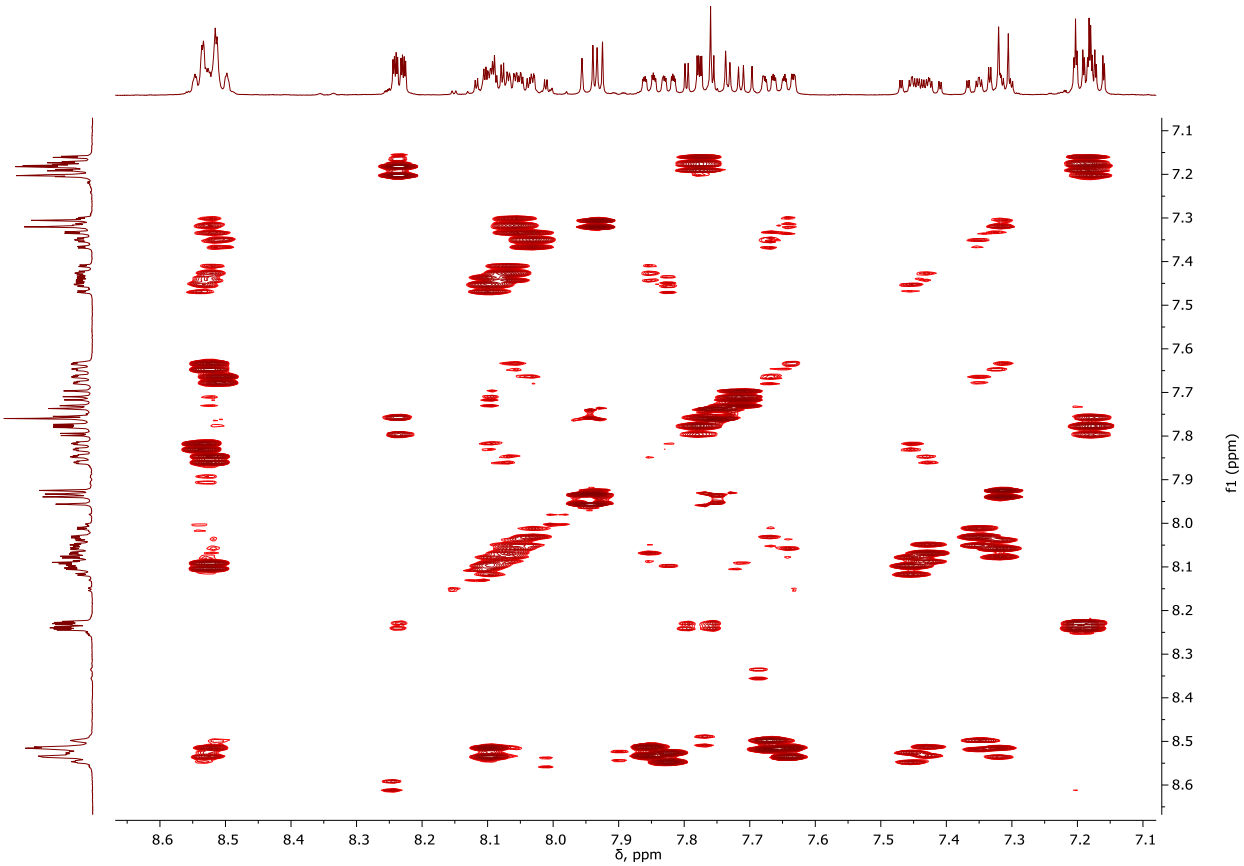


Figure S13. TOCSY ^{1}H spectrum of **Ru(Phen-4NPy$_2$)** (400 MHz, CD_3CN, 298 K).

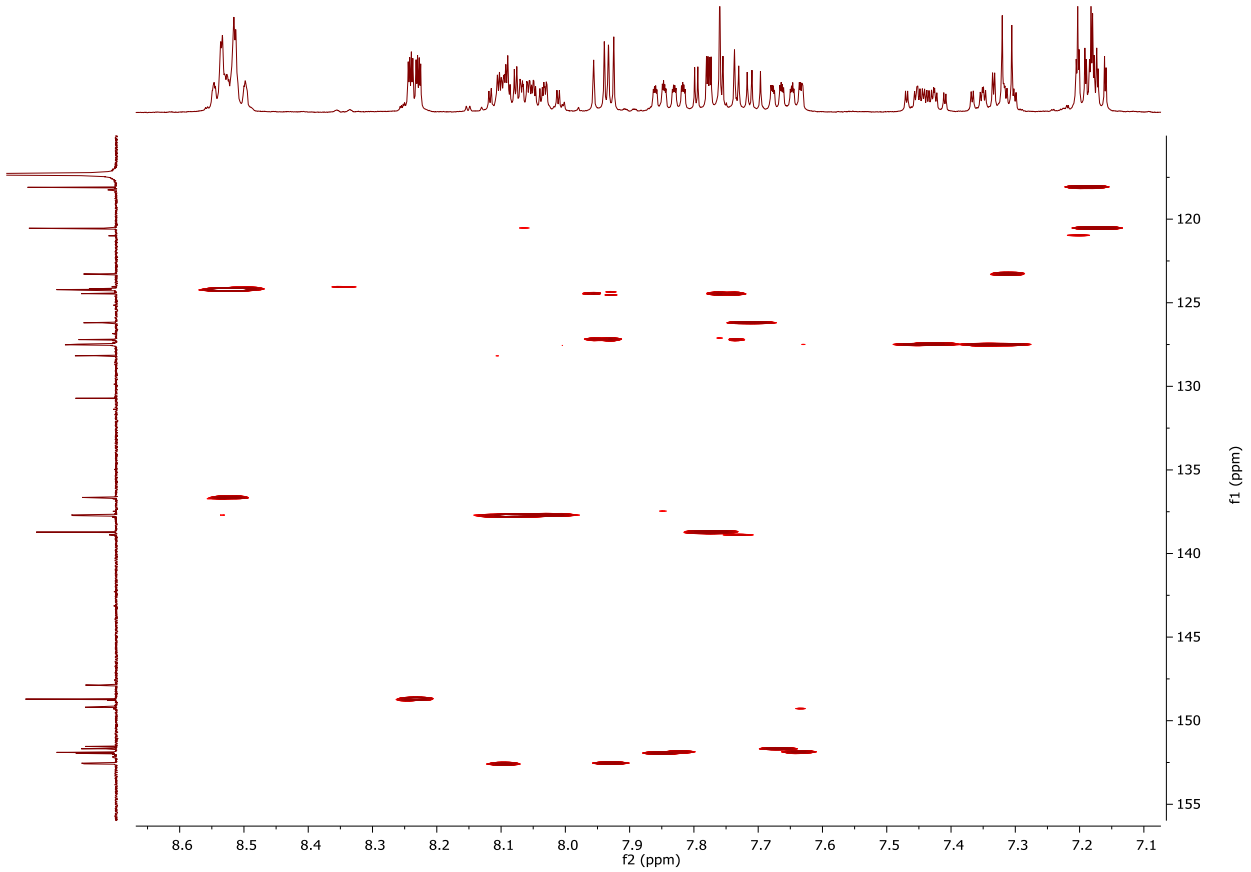


Figure S14. gHSQCAD spectrum of **Ru(Phen-4NPy$_2$)** (400 MHz, CD_3CN, 298 K).

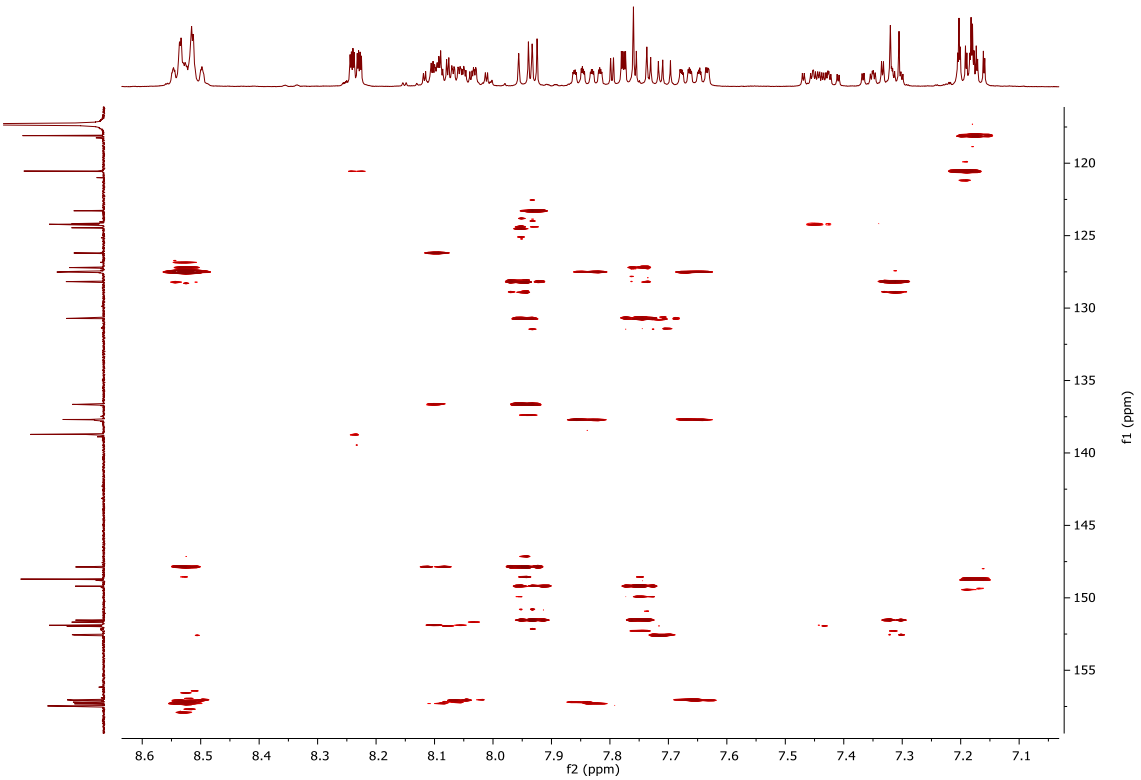
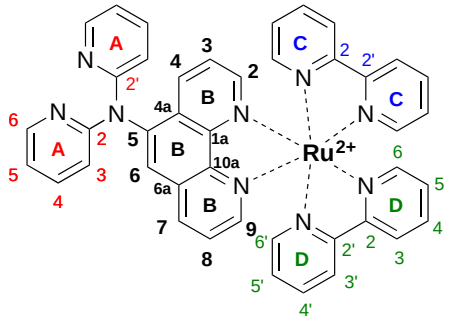


Figure S15. gHMBCAD spectrum of **Ru(Phen-4NPy$_2$)** (400 MHz, CD_3CN, 298 K, *J*=8 Hz).

Ru(Phen-5NPy$_2$)

Table S5. Signal assignment in NMR spectra of **Ru(Phen-5NPy$_2$)**.



Assignment		Chemical shift (ppm)		*J* (Hz)	
		^{1}H	^{13}C	H–H (atom)	
A	**2,2'**	-	157.70		
A	**3,3'**	7.21	116.67	8.3 (4, 4')	1.9 (5, 5'), 0.8 (6, 6')
A	**4,4'**	7.71	138.24	8.3 (3, 3')	7.5 (5, 5'), 1.9 (6, 6')
A	**5,5'**	7.07	119.16	7.5 (4, 4')	4.8 (6, 6'), 0.8 (3, 3')
A	**6,6'**	8.19	148.26	4.8 (5, 5')	1.9 (4, 4'), 0.8 (3, 3')
B	**1a**	-	148.72		
B	**2**	8.06	152.72	5.2 (3)	1.2 (4)
B	**3**	7.56	125.93	8.3 (4)	5.2 (2)
B	**4**	8.32	133.72	8.3 (3)	1.2 (2)
B	**4a**	-	130.45		
B	**5**	-	142.38		
B	**6**	8.07	127.26		
B	**6a**	-	131.02		
B	**7**	8.47	136.27	8.3 (8)	1.3 (9)
B	**8**	7.70	126.23	8.3 (7)	4.3 (9)
B	**9**	8.06	152.21	4.3 (8)	1.3 (7)
B	**10a**	-	146.56		
C [1]	**2,2'**	-	157.27, 157.05		
C [1]	**3,3'**	8.55, 8.52	124.27, 124.25	8.3 (4, 4')	1.3 (5, 5'), 0.7 (6, 6')
C [1]	**4,4'**	8.11, 8.04	137.89, 137,82	8.3 (3, 3')	7.6 (5, 5'), 1.5 (6, 6')
C [1]	**5,5'**	7.46, 7.32	127.56, 127.52	7.6 (4, 4')	5.6 (6, 6'), 1.3 (3, 3')
C [1]	**6,6'**	7.85, 7.62	151.96, 151.92	5.6 (5, 5')	1.5 (4, 4'), 0.7 (3, 3')
D [1]	**2,2'**	-	157.27, 157.08		
D [1]	**3,3'**	8.54, 8.51	124.27, 124.28	8.2 (4, 4')	1.3 (5, 5'), 0.7 (6, 6')
D [1]	**4,4'**	8.10, 8.04	137.87, 137.81	8.2 (3, 3')	7.7 (5, 5'), 1.7 (6, 6')
D [1]	**5,5'**	7.46, 7.32	127.54	7.7 (4, 4')	5.6 (6, 6'), 1.3 (3, 3')
D [1]	**6,6'**	7.85, 7.67	151.94, 151.91	5.6 (5, 5')	1.7 (4, 4'), 0.7 (3, 3')

[1] Exact assigning the pyridine ring atoms signals to a certain 2,2'-bipyridine ligand is not possible due to the close values of the chemical shifts.

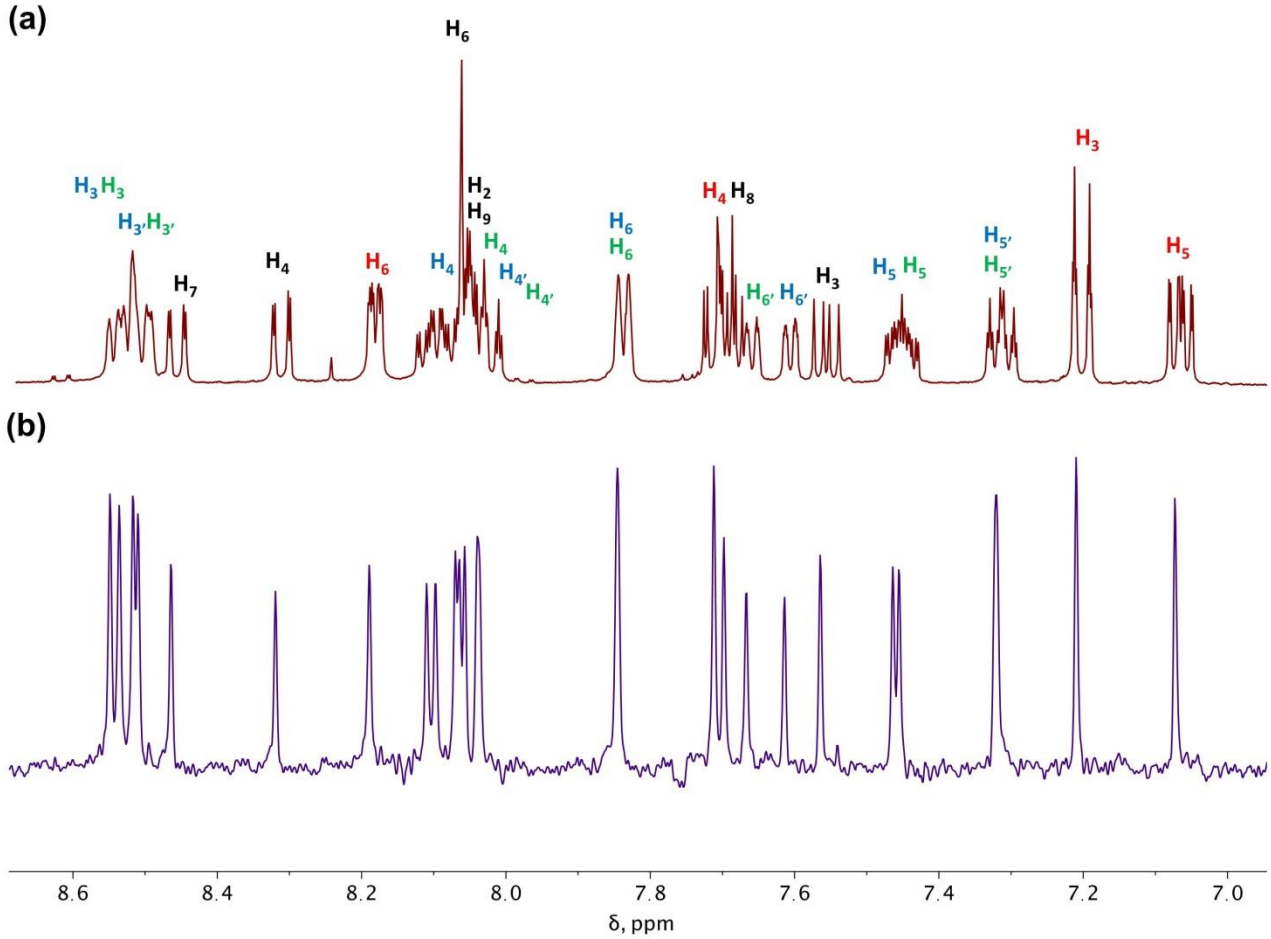


Figure S16. (a) ^{1}H NMR spectrum of **Ru(Phen-5NPy$_2$)** (400 MHz, CD_3CN, 298 K); (b) PSYCHE ^{1}H NMR spectrum of **Ru(Phen-5NPy$_2$)** (400 MHz, CD_3CN, 298 K).

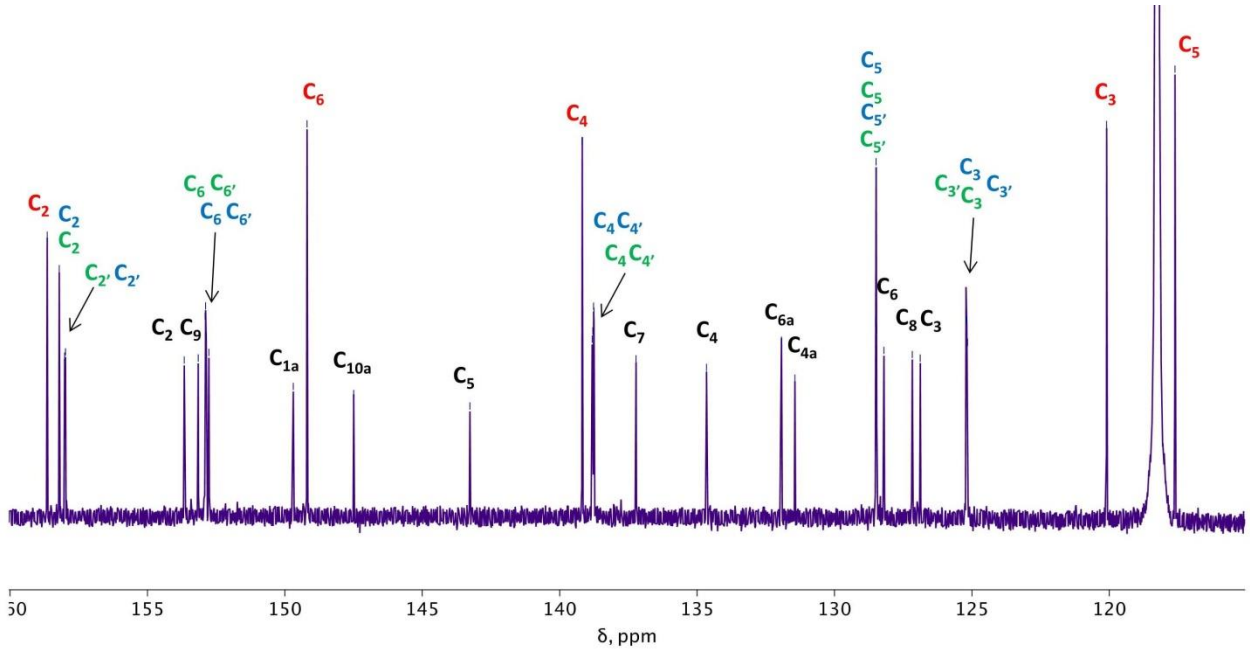


Figure S17. ^{13}C{^{1}H} NMR spectrum of **Ru(Phen-5NPy$_2$)** (100.6 MHz, CD_3CN, 298 K).

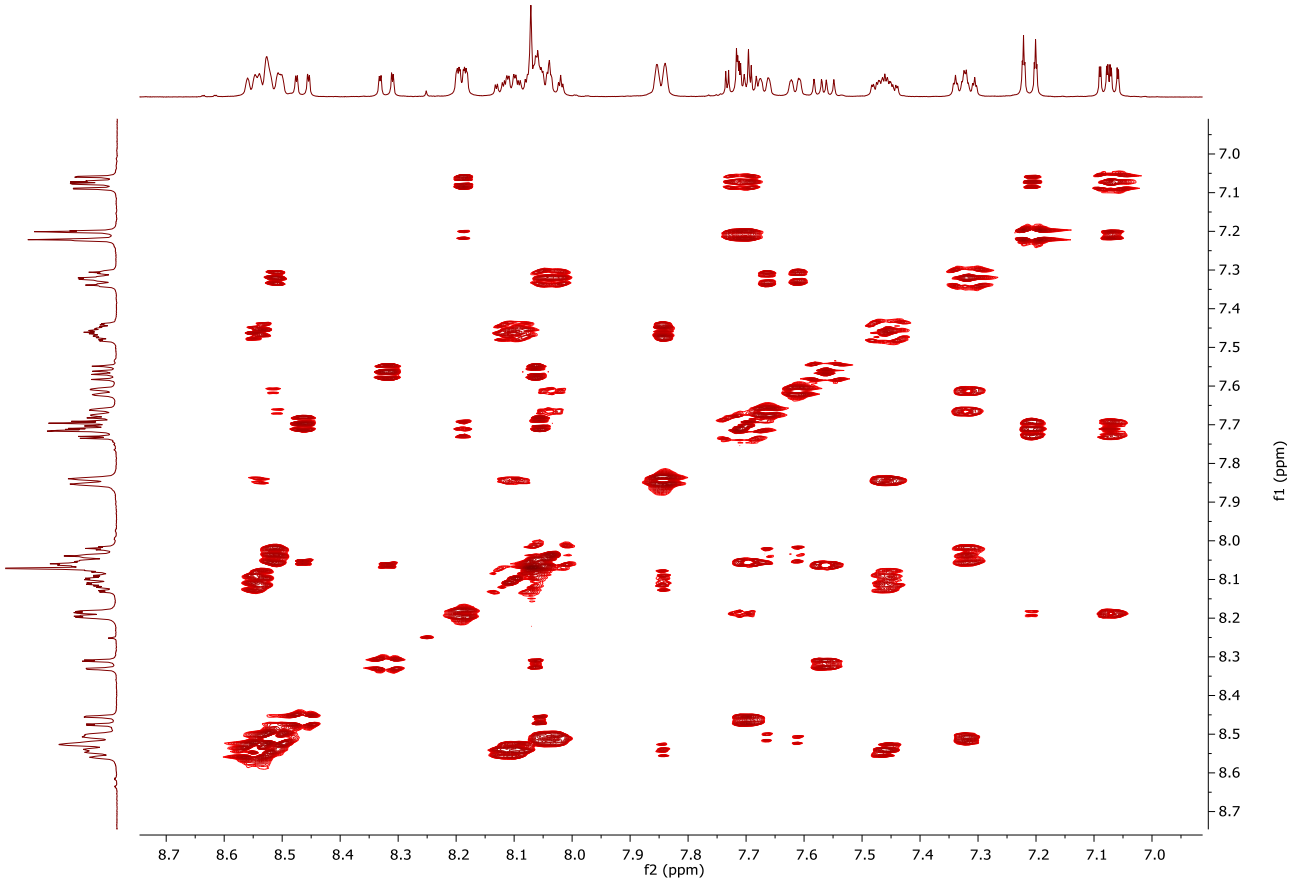


Figure S18. TOCSY ^{1}H spectrum of **Ru(Phen-5NPy$_2$)** (400 MHz, CD_3CN, 298 K).

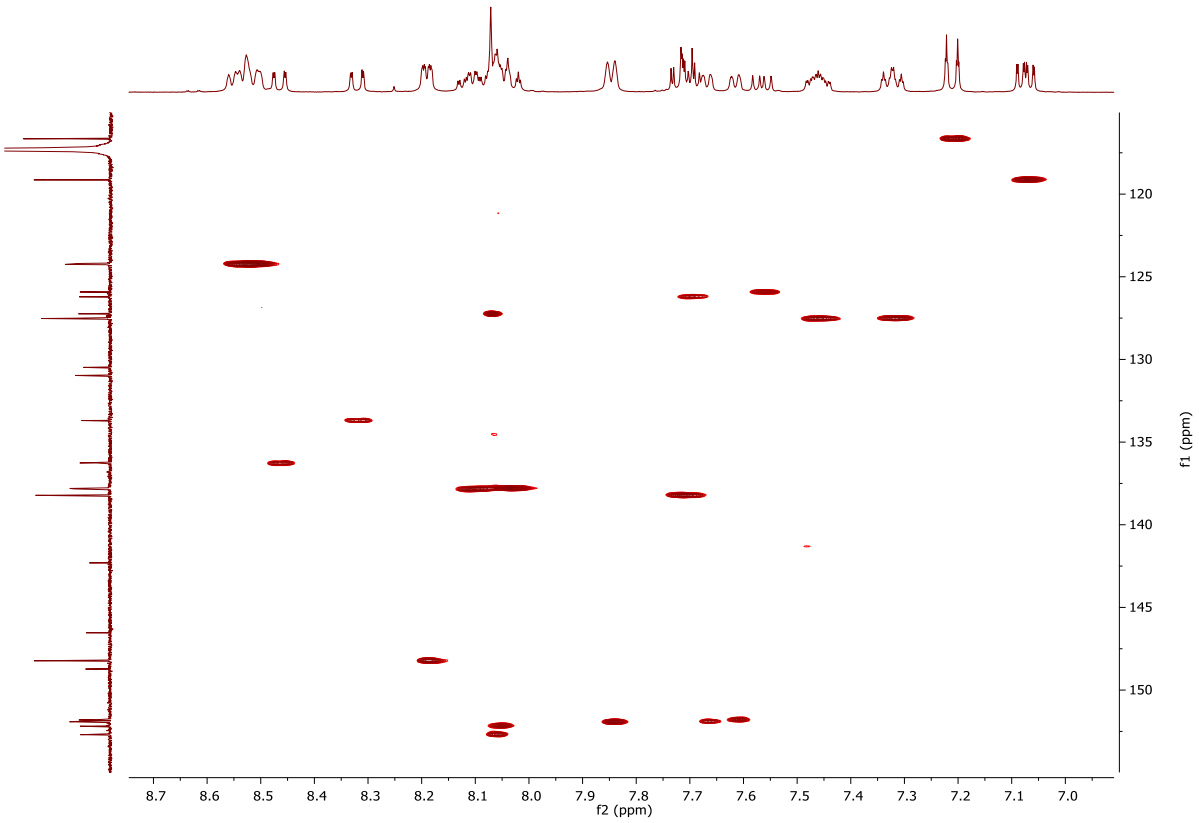


Figure S19. gHSQCAD spectrum of **Ru(Phen-5NPy$_2$)** (400 MHz, CD_3CN, 298 K).

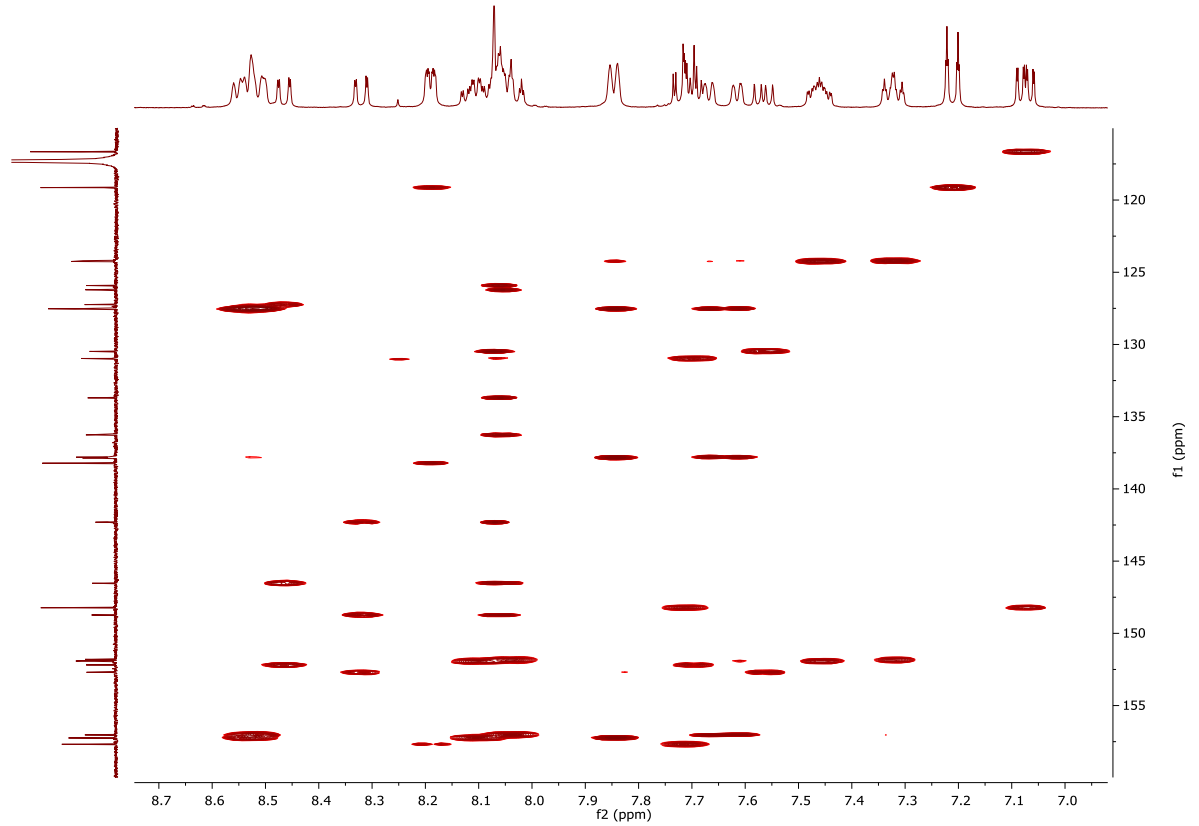
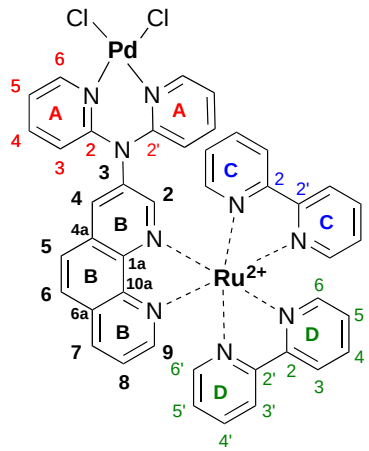


Figure S20. gHMBCAD spectrum of **Ru(Phen-5NPy$_2$)** (400 MHz, CD_3CN, 298 K, *J*=8 Hz).

Ru(Phen-3NPy$_2$)Pd

Table S6. Signal assignment in NMR spectra of **Ru(Phen-3NPy$_2$)Pd**.



Assignment		Chemical shift (ppm)		*J* (Hz)	
		^{1}H	^{13}C	H–H (atom)	
A	**2,2'**	-	149.33		
A	**3,3'**	7.76	125.87	8.6 (4,4')	1.0 (6,6')
A	**4,4'**	8.15	143.38	8.6 (3,3')	7.8 (5,5')
A	**5,5'**	7.60	125.93	7.8 (4,4')	5.9 (6,6'), 1.0 (3,3')
A	**6,6'**	8.87	154.32	5.9 (5,5')	1.7 (4,4'), 1.0 (3,3')
B	**1a**	-	142.89		
B	**2**	7.10	139.98	2.5 (4)	
B	**3**	-	143.51		
B	**4**	7.96	119.33	2.5 (2)	
B	**4a**	-	131.25		
B	**5**	8.04	127.38	9.1 (6)	
B	**6**	8.16	129.19	9.1 (5)	
B	**6a**	-	130.06		
B	**7**	8.56	136.89	8.3 (8)	1.5 (9)
B	**8**	7.69	125.54	8.3(7)	6.8 (9)
B	**9**	8.01	152.31	6.8 (8)	1.5 (7)
B	**10a**	-	147.57		
C	**2,2'**	-	156.94, 156.66		
C	**3,3'**	8.32, 8.44	123.92, 124.57	8.1 (4,4')	1.3 (5, 5'), 0.7 (6, 6')
C	**4,4'**	7.90, 8.02	137.90, 137.84	8.1 (3,3')	7.5 (5, 5'), 1.5 (6, 6')
C	**5,5'**	7.23, 7.28	127.48, 127.57	7.6 (4,4'),	5.6 (6, 6') 1.3 (3, 3')
C	**6,6'**	7.72, 7.64	152.25, 151.92	5.6 (5,5')	1.5 (4, 4'), 0.7 (3, 3')
D	**2,2'**	-	156.56, 157.26		
D	**3,3'**	8.45, 8.51	123.98, 124.18	8.2 (4,4')	1.5 (5, 5'), 0.9 (6, 6')
D	**4,4'**	7.97, 8.08	137.51, 137.84	8.2 (3,3')	7.6 (5, 5'), 1.8 (6, 6')
D	**5,5'**	7.35, 7.44	128.00, 127.39	7.5 (4,4'),	5.6 (6, 6') 1.5 (3, 3')
D	**6,6'**	7.76, 7.83	152.34, 151.98	5.6 (5,5')	1.8 (4, 4'), 0.9 (3, 3')

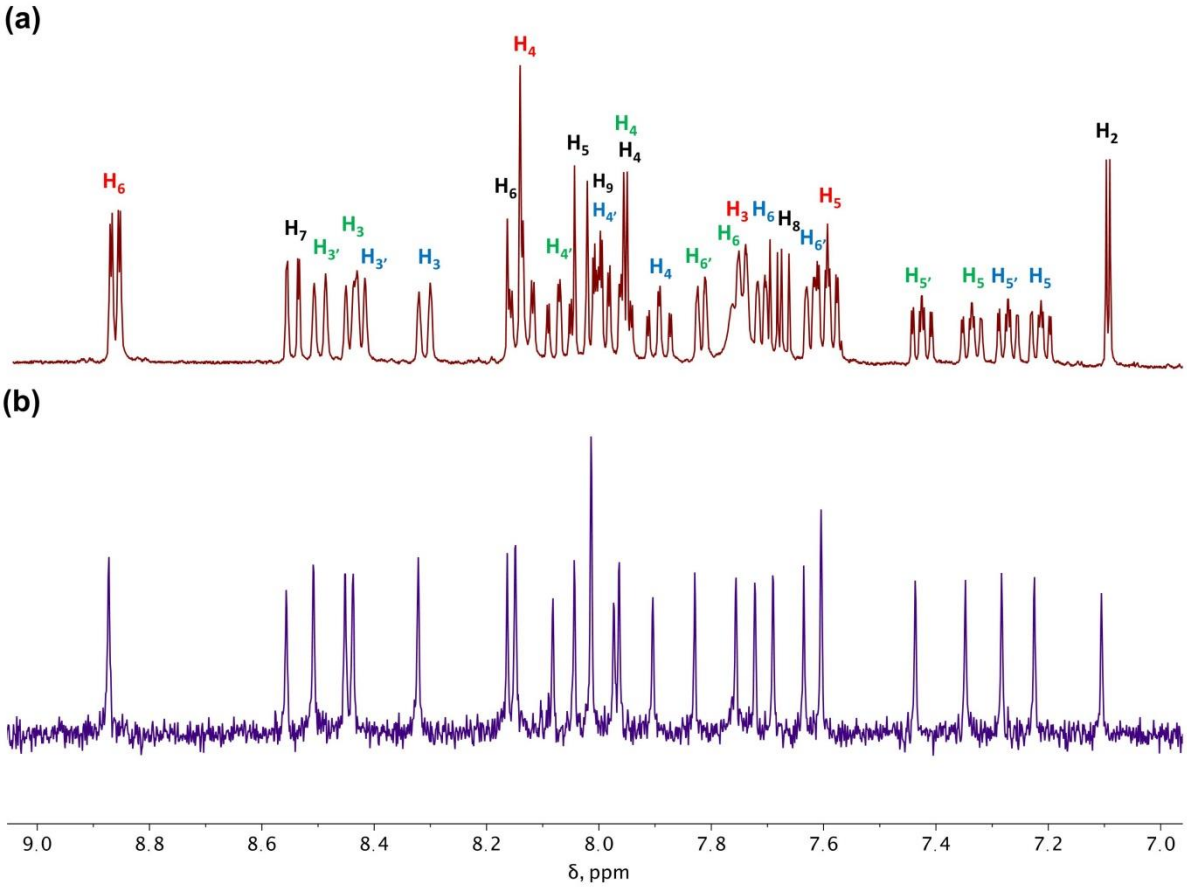


Figure S21. (a) ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K); (b) PSYCHE ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

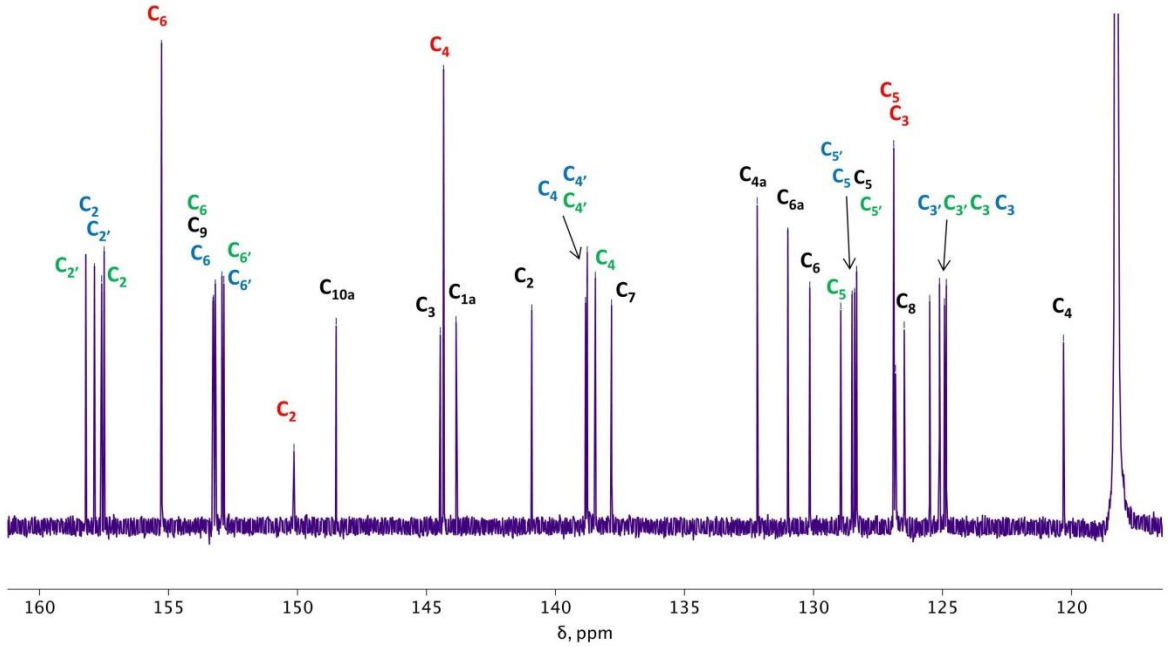


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (100.6 MHz, CD_3CN, 298 K).

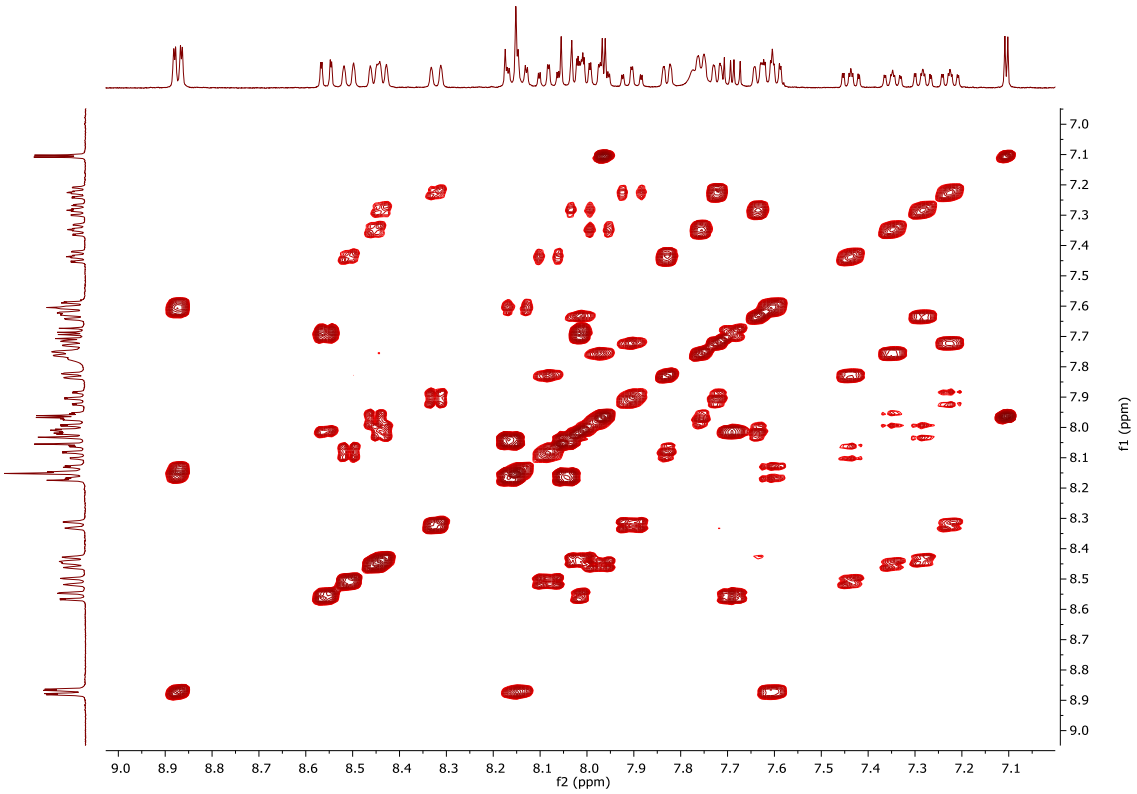


Figure S23. COSY ^{1}H spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

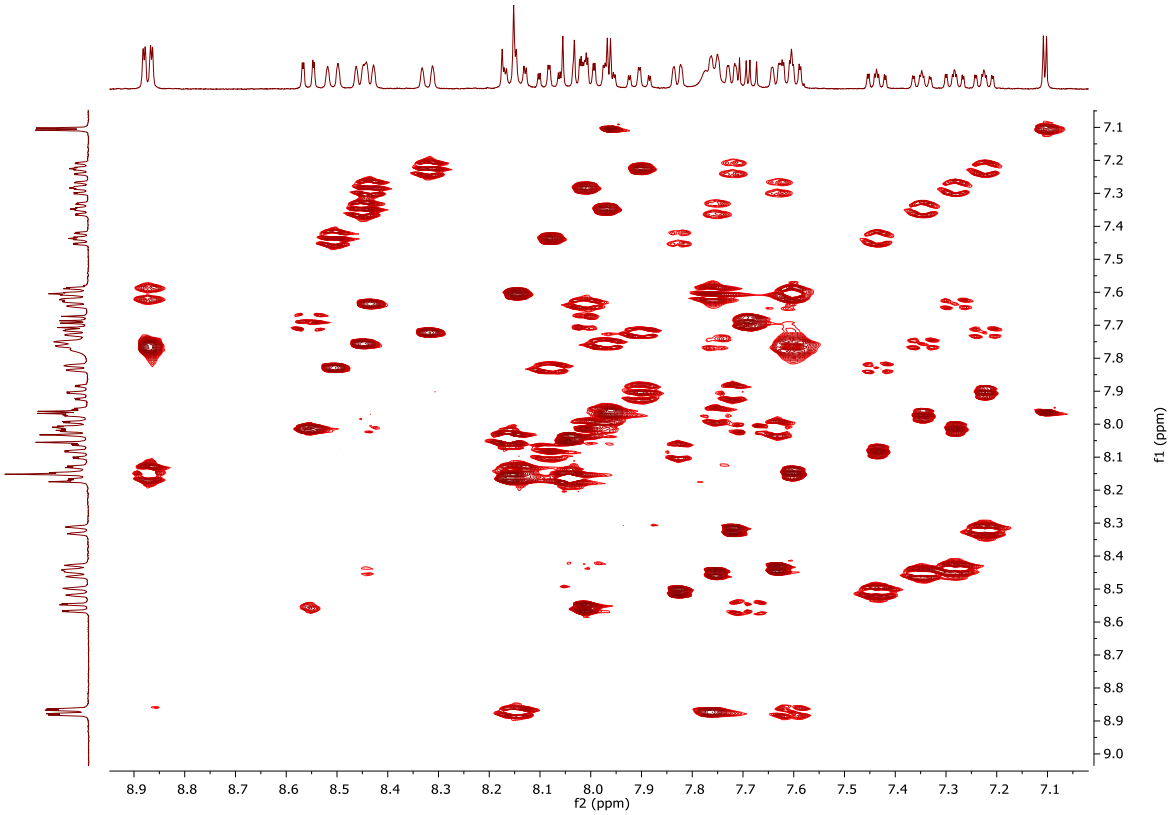


Figure S24. TOCSY ^{1}H spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

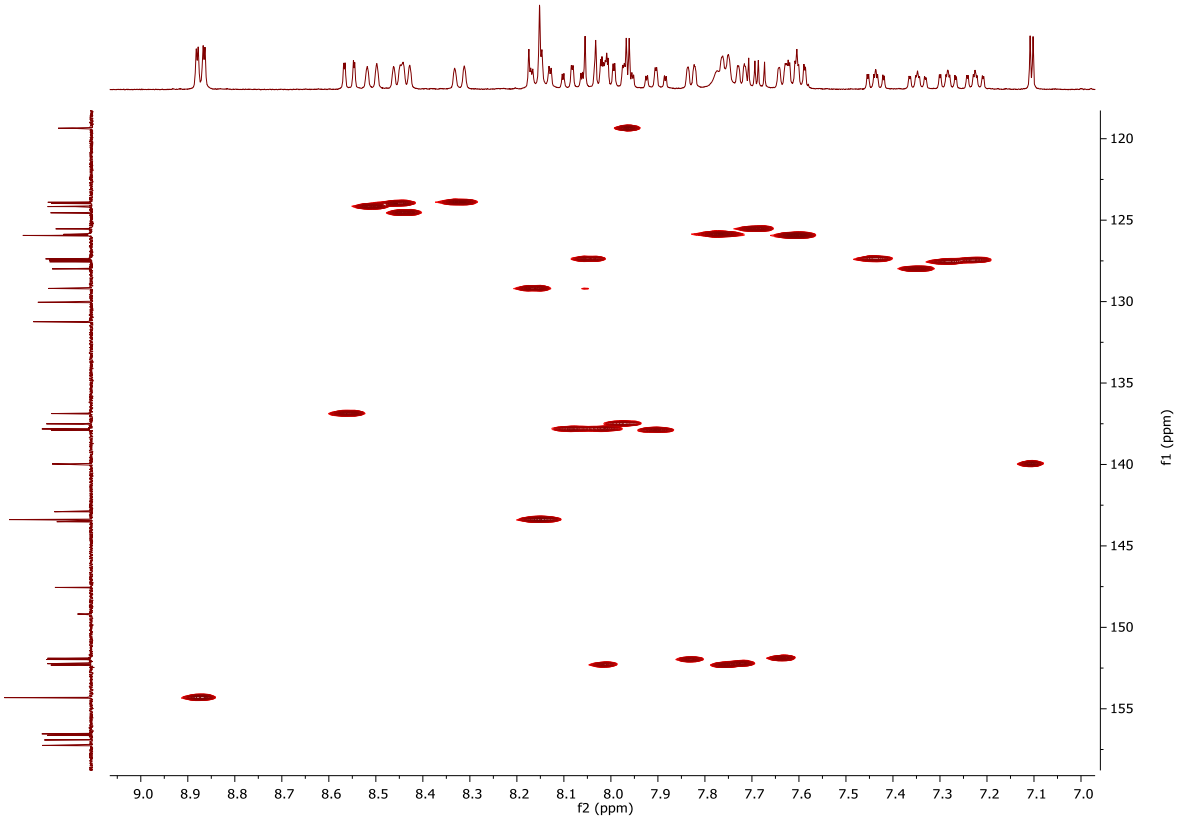


Figure S25. gHSQCAD spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

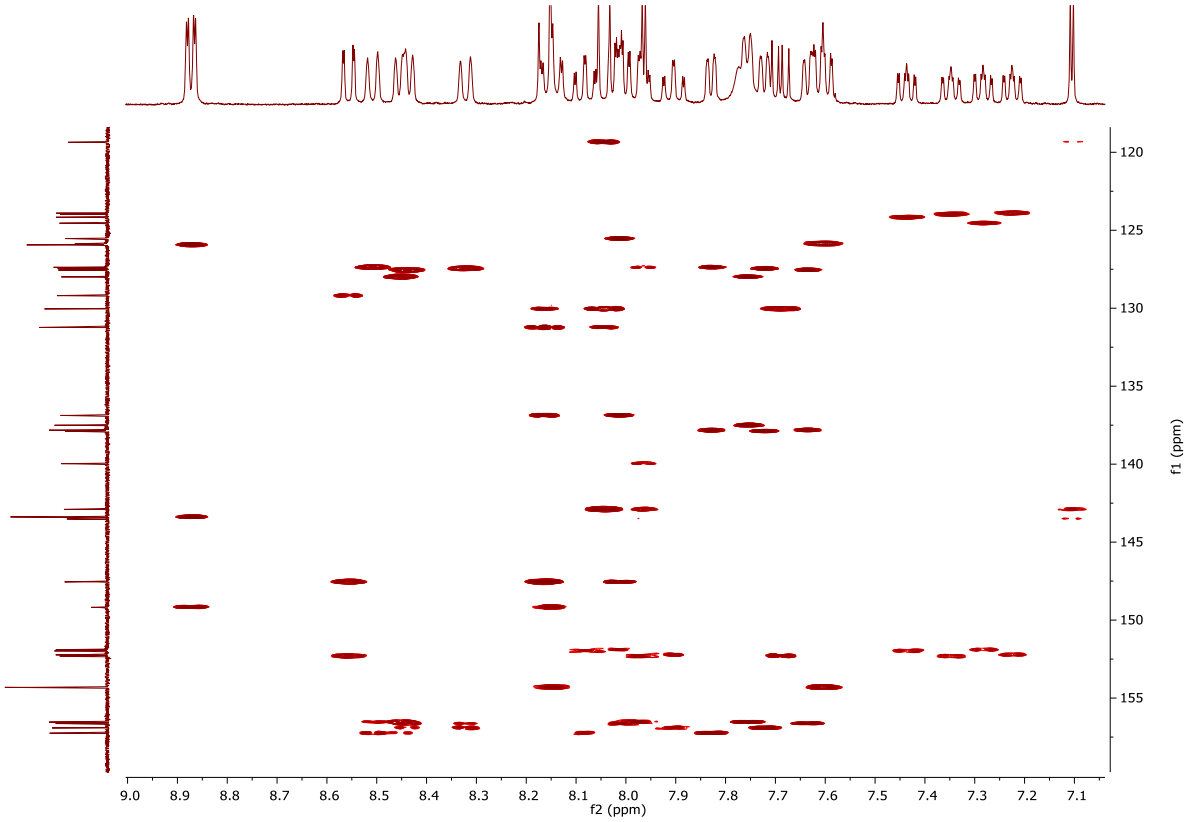
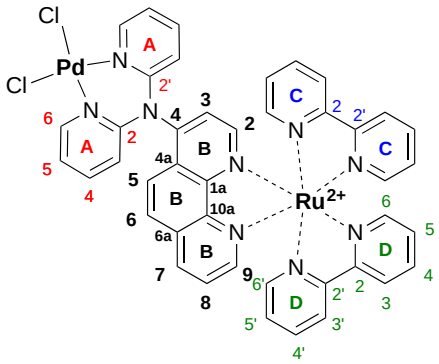


Figure S26. gHMBCAD spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K, *J*=8 Hz).

Ru(Phen-4NPy$_2$)Pd

Table S7. Signal assignment in NMR spectra of **Ru(Phen-4NPy$_2$)Pd**.



Assignment		Chemical shift (ppm)		*J* (Hz)	
		^{1}H	^{13}C	H–H (atom)	
A	**2,2'**	-	151.98		
A	**3,3'**	7.27	118.26	8.4 (4,4')	0.5 (6,6')
A	**4,4'**	7.87	141.45	8.4 (3,3')	7.6 (5,5')
A	**5,5'**	7.32	122.05	7.6 (4,4')	5.9 (6,6'), 0.5 (3,3')
A	**6,6'**	8.91	152.64	5.9 (5,5')	1.6 (4,4'), 0.5 (3,3')
B	**1a**	-	144.00		
B	**2**	8.37	154.02	5.7 (3)	
B	**3**	8.33	128.09	5.7 (2)	
B	**4**	-	150.68		
B	**4a**	-	129.85		
B	**5**	9.42	123.22	9.1 (6)	
B	**6**	8.38	130.04	9.1 (5)	
B	**6a**	-	131.25		
B	**7**	8.63	137.00	8.3 (8)	1.2 (9)
B	**8**	7.79	126.77	8.3 (7)	5.4 (9)
B	**9**	8.18	153.39	5.4 (8)	1.2 (7)
B	**10a**	-	147.76		
C [1]	**2,2'**	-	157.30, 156.93		
C [1]	**3,3'**	8.58, 8.54	124.31, 124.22	9.5 (4, 4')	1.3 (5, 5'), 0.7 (6, 6')
C [1]	**4,4'**	8.14, 8.04	138.15, 137.94	9.5 (3, 3')	7.9 (5, 5'), 1.4 (6, 6')
C [1]	**5,5'**	7.50, 7.29	127.68, 127.60	7.9 (4, 4')	6.0 (6, 6'), 1.2 (3, 3')
C [1]	**6,6'**	7.89, 7.57	151.99, 152.35	6.0 (5, 5')	1.4 (4, 4'), 0.7 (3, 3')
D [1]	**2,2'**	-	157.17, 156.86		
D [1]	**3,3'**	8.55, 8.50	124.31, 124.27	8.9 (4, 4')	1.4 (5, 5'), 0.8 (6, 6')
D [1]	**4,4'**	8.11, 8.01	138.04, 137.92	8.9 (3, 3')	7.8 (5, 5'), 1.5 (6, 6')
D [1]	**5,5'**	7.47, 7.25	127.65, 127.55	7.8 (4, 4'),	5.9 (6, 6') 1.4 (3, 3')
D [1]	**6,6'**	7.80, 7.64	151.79, 152.24	5.9 (5, 5')	1.5 (4, 4'), 0.8 (3, 3')

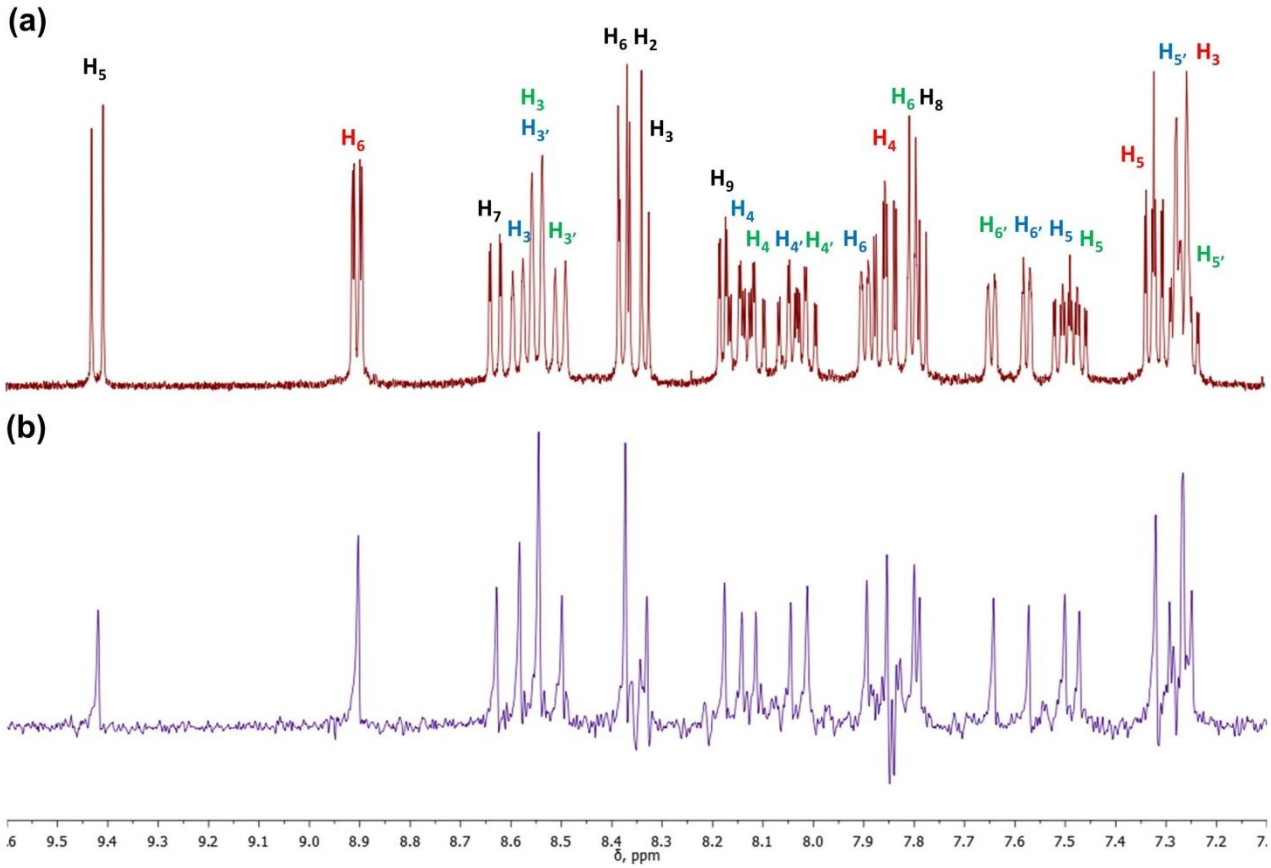


Figure S27. (a) ^{1}H NMR spectrum of **Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K); (b) PSYCHE ^{1}H NMR spectrum of **Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

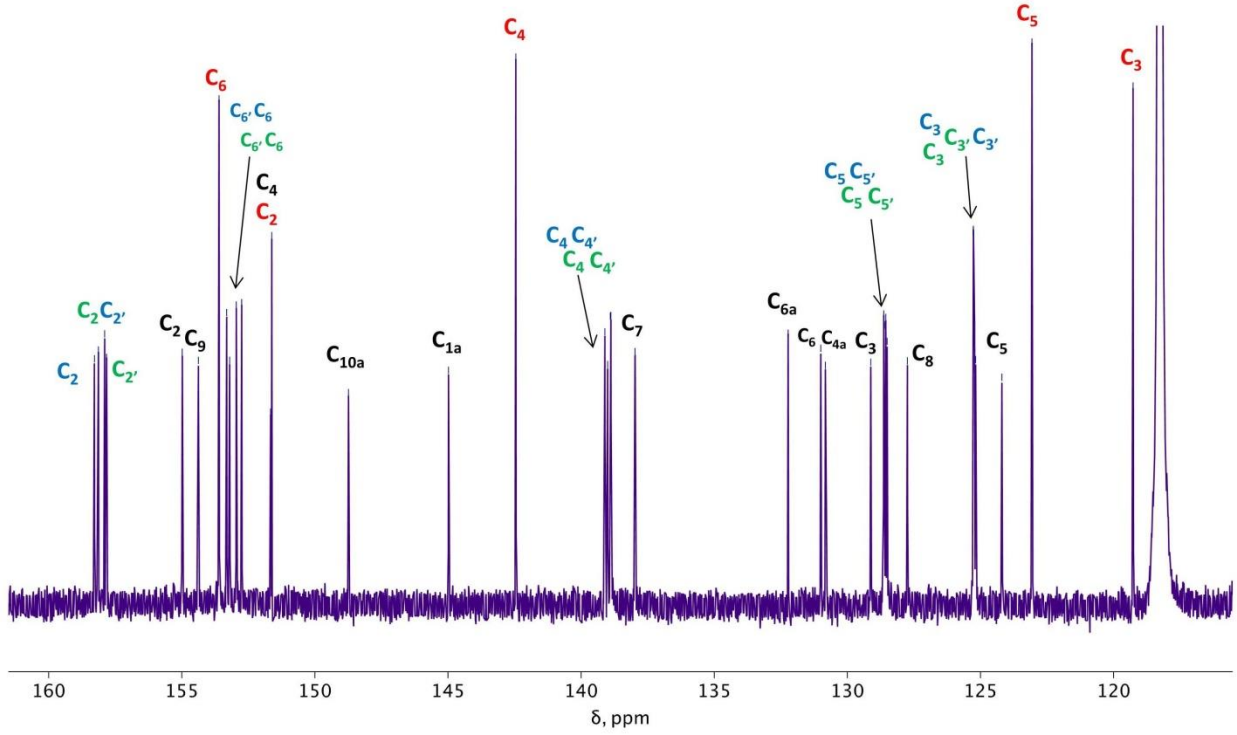


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **Ru(Phen-4NPy$_2$)Pd** (100.6 MHz, CD_3CN, 298 K).

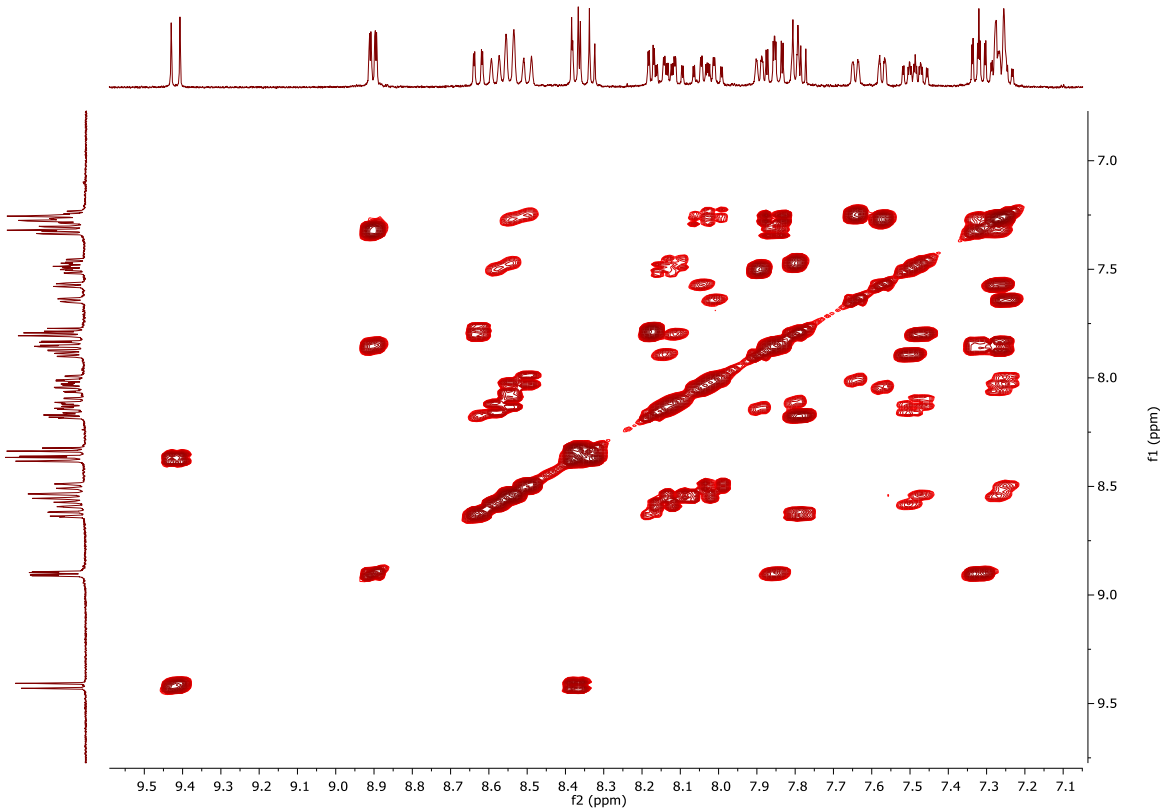


Figure S29. COSY ^{1}H spectrum of **Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

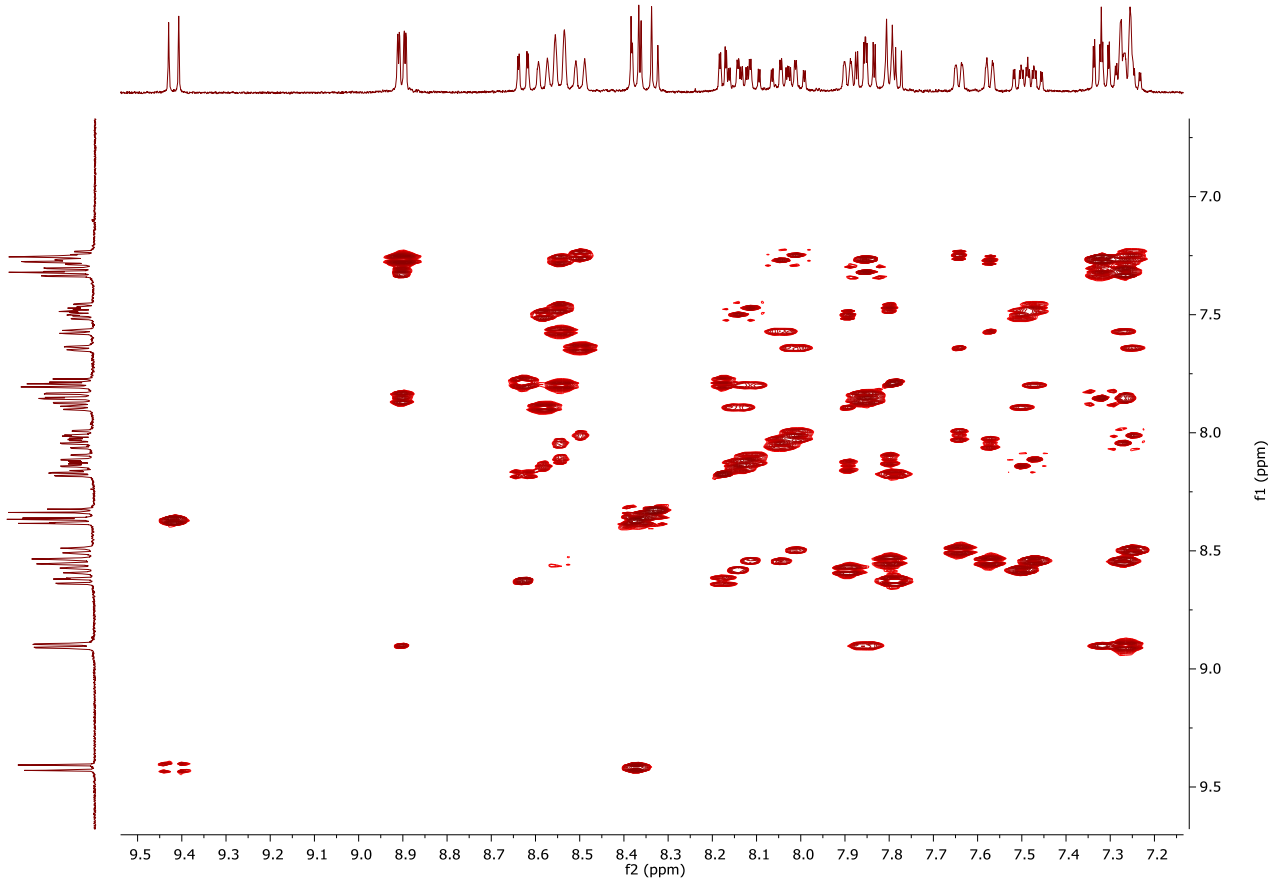


Figure S30. TOCSY ^{1}H spectrum of **Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

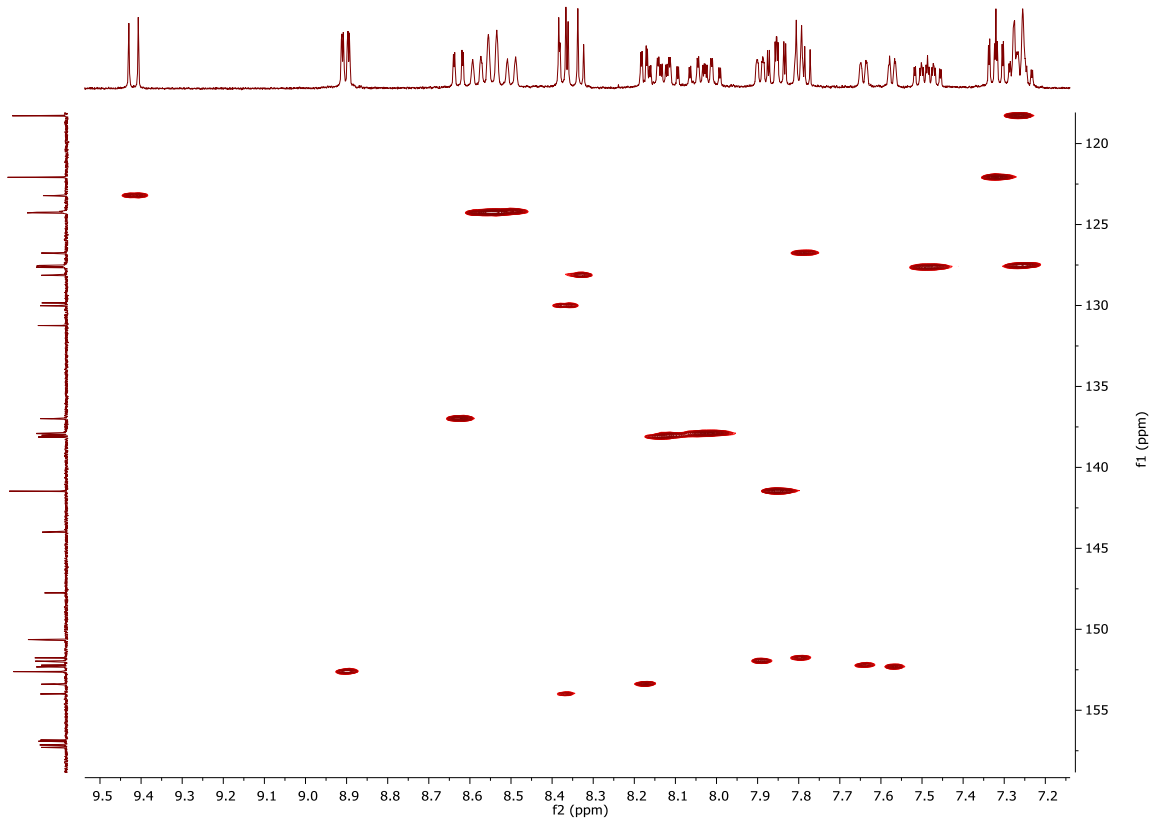


Figure S31. gHSQCAD spectrum of **Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

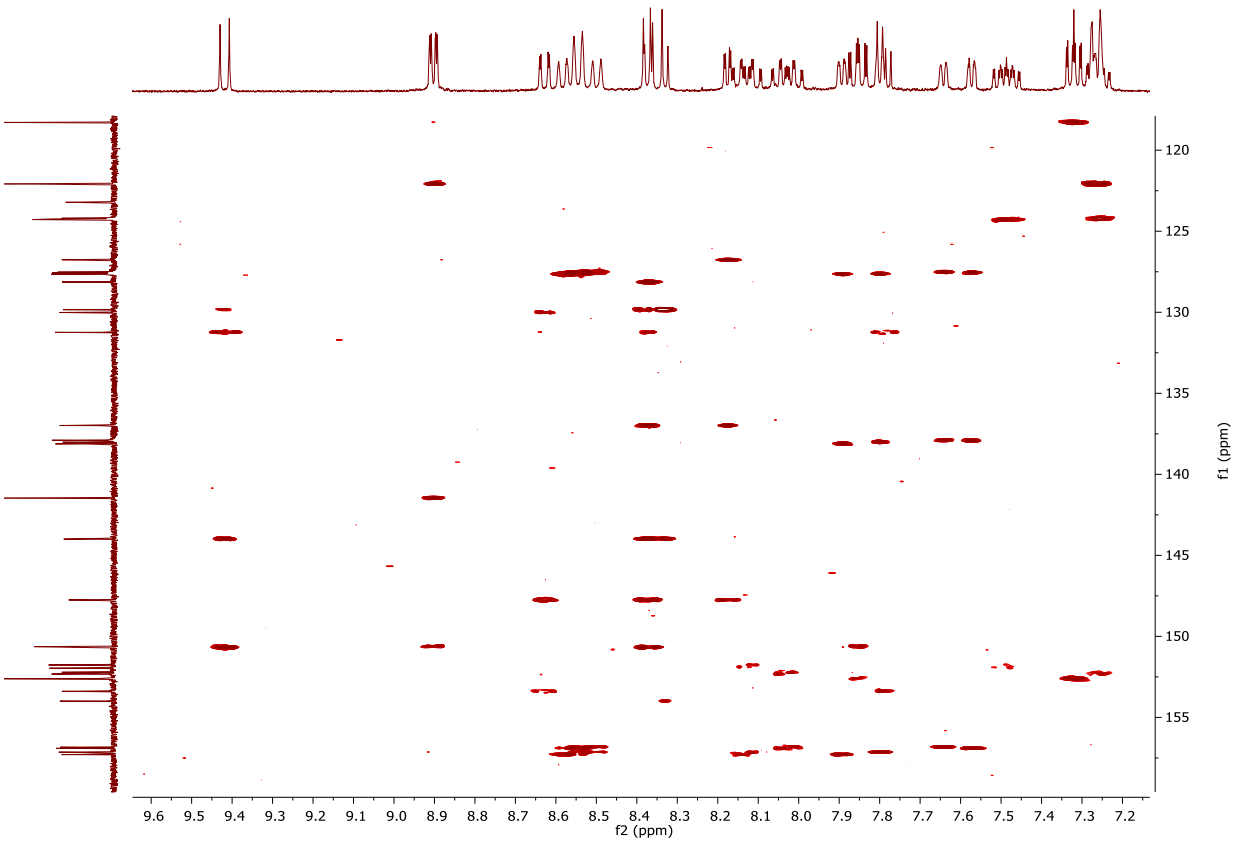
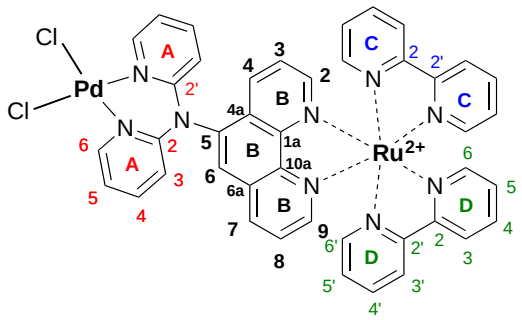


Figure S32. gHMBCAD spectrum of **Ru(Phen-4NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K, J=8 Hz).

Ru(Phen-5NPy$_2$)Pd

Table S8. Signal assignment in NMR spectra of **Ru(Phen-5NPy$_2$)Pd**.



Assignment		Chemical shift (ppm)		*J* (Hz)	
		^{1}H	^{13}C	H–H (atom)	
A	**2,2'**	-	150.96		
A	**3,3'**	7.40	117.31	8.3 (4,4')	0.5 (6,6')
A	**4,4'**	7.84	141.23	8.3 (3,3')	7.5 (5,5'), 1.8 (6,6')
A	**5,5'**	7.29	121.49	7.5 (4,4')	5.9 (6,6'), 0.5 (3,3')
A	**6,6'**	8.91	152.41	5.9 (5, 5')	1.8 (4,4'), 0.5 (3,3')
B	**1a**	-	149.49		
B	**2**	8.18	153.63	5.3 (3)	1.2 (4)
B	**3**	7.87	126.86	8.4 (4)	5.3 (2)
B	**4**	9.91	132.67	8.4 (3)	1.2 (2)
B	**4a**	-	130.46		
B	**5**	-	135.38		
B	**6**	9.01	133.52		
B	**6a**	-	129.98		
B	**7**	8.80	137.68	8.4 (8)	1.2 (9)
B	**8**	7.86	126.64	8.4 (7)	5.3 (9)
B	**9**	8.24	154.19	5.3 (8)	1.2 (7)
B	**10a**	-	148.01		
C [1]	**2,2'**	-	157.22, 156.94		
C [1]	**3,3'**	8.55, 8.49	124.29, 124.19	8.2 (4, 4')	1.3 (5,5'), 0.7 (6,6')
C [1]	**4,4'**	8.13, 8.01	138.00, 137.87	8.2 (3, 3')	7.6 (5,5'), 1.5 (6,6')
C [1]	**5,5'**	7.48, 7.23	127.60, 127.45	7.6 (4, 4')	5.6 (6,6'), 1.3 (3,3')
C [1]	**6,6'**	7.84, 7.60	151.93, 152.25	5.6 (5, 5')	1.5 (4,4'), 0.7 (3,3')
D [1]	**2,2'**	-	157.24, 156.89		
D [1]	**3,3'**	8.54, 8.48	124.31, 124.18	8.0 (4, 4')	1.3 (5, 5'), 0.8 (6, 6')
D [1]	**4,4'**	8.11, 8.01	138.00, 137.87	8.0 (3, 3')	7.7 (5, 5'), 1.5 (6, 6')
D [1]	**5,5'**	7.46, 7.27	127.60, 127.47	7.7 (4, 4')	5.6 (6, 6'), 1.3 (3, 3')
D [1]	**6,6'**	7.84, 7.63	151.96, 152.27	5.6 (5, 5')	1.5 (4, 4'), 0.8 (3, 3')

[1] Exact assigning the pyridine ring atoms signals to a certain 2,2'-bipyridine ligand is not possible due to the close values of the chemical shifts.

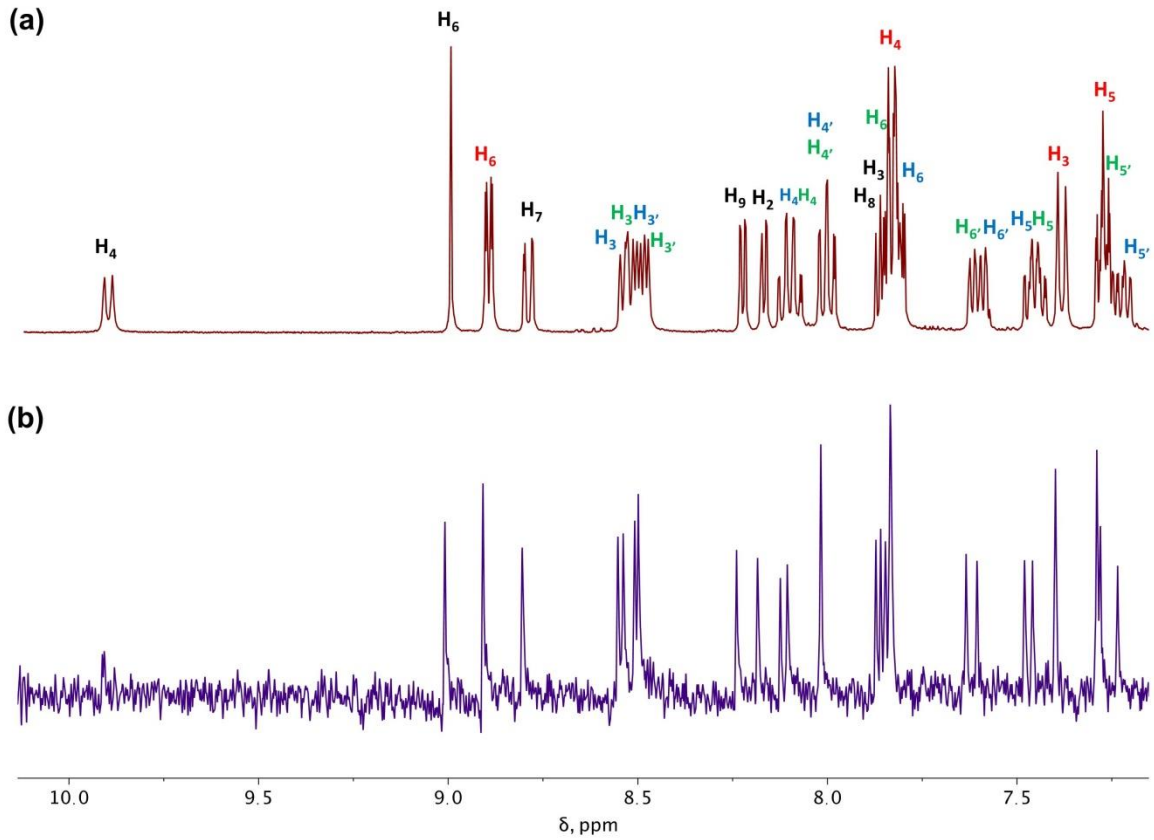


Figure S33. (a) ^{1}H NMR spectrum of **Ru(Phen-5NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K); (b) PSYCHE ^{1}H NMR spectrum of **Ru(Phen-5NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

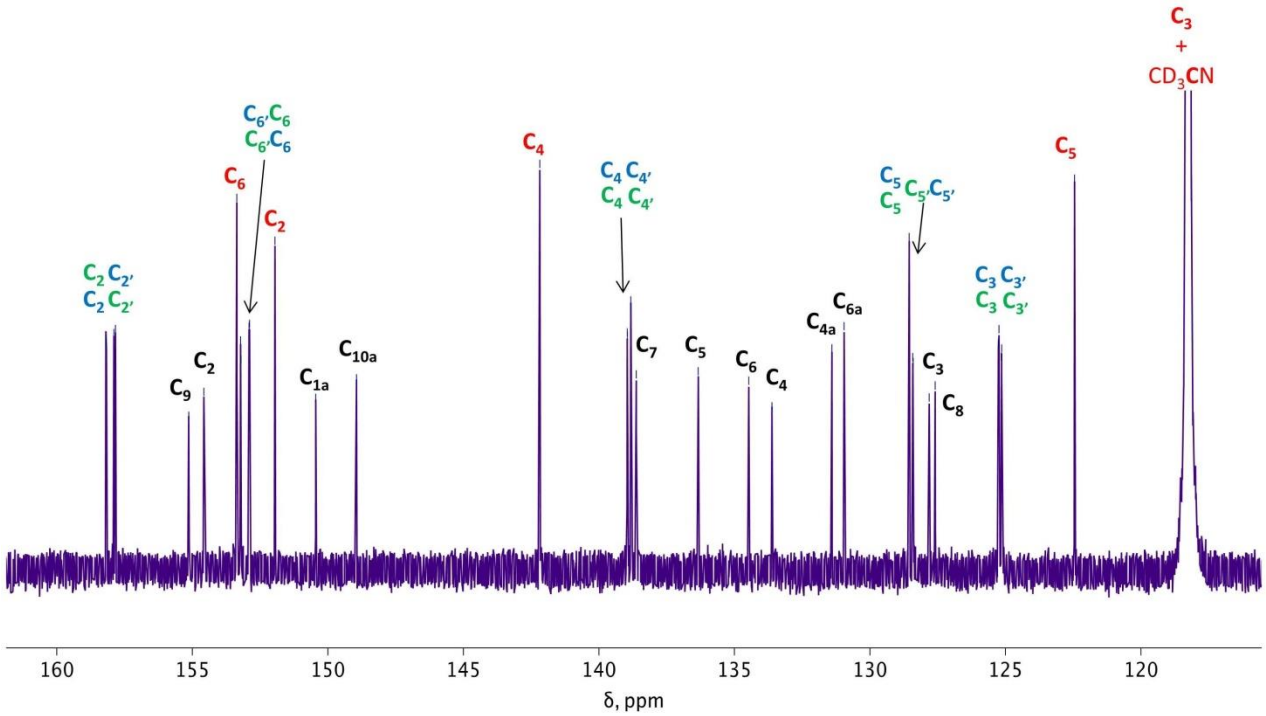


Figure S34. ^{13}C{^{1}H} NMR spectrum of **Ru(Phen-5NPy$_2$)Pd** (100.6 MHz, CD_3CN, 298 K).

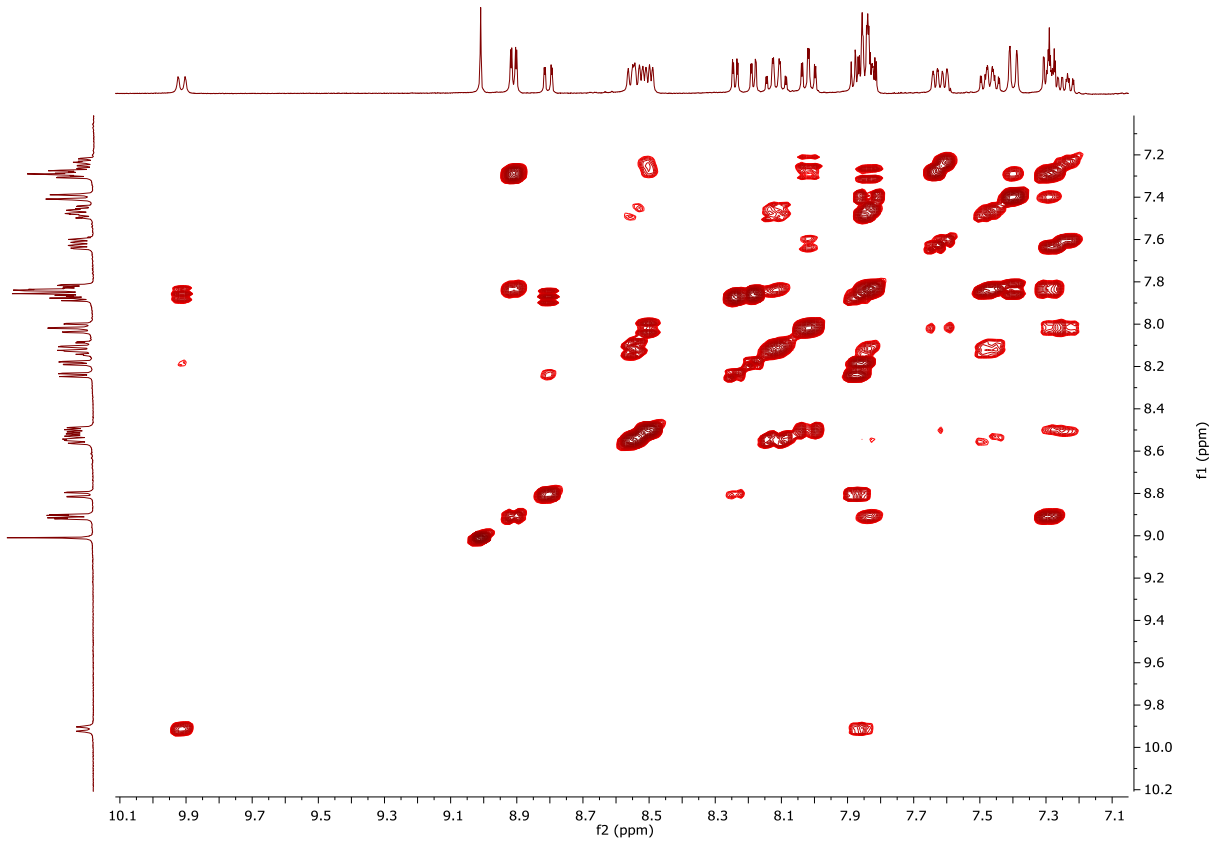


Figure S35. COSY ^{1}H spectrum of **Ru(Phen-5NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

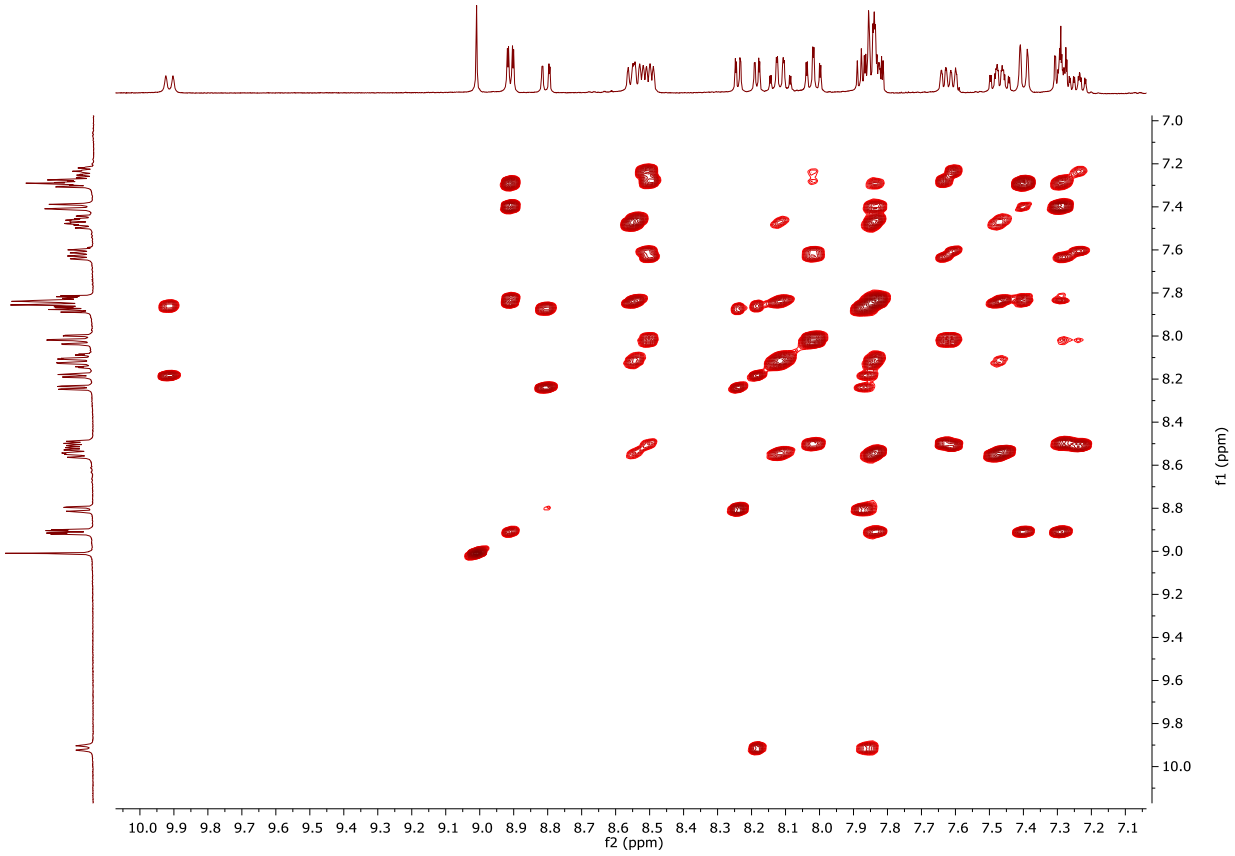


Figure S36. TOCSY ^{1}H spectrum of **Ru(Phen-5NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

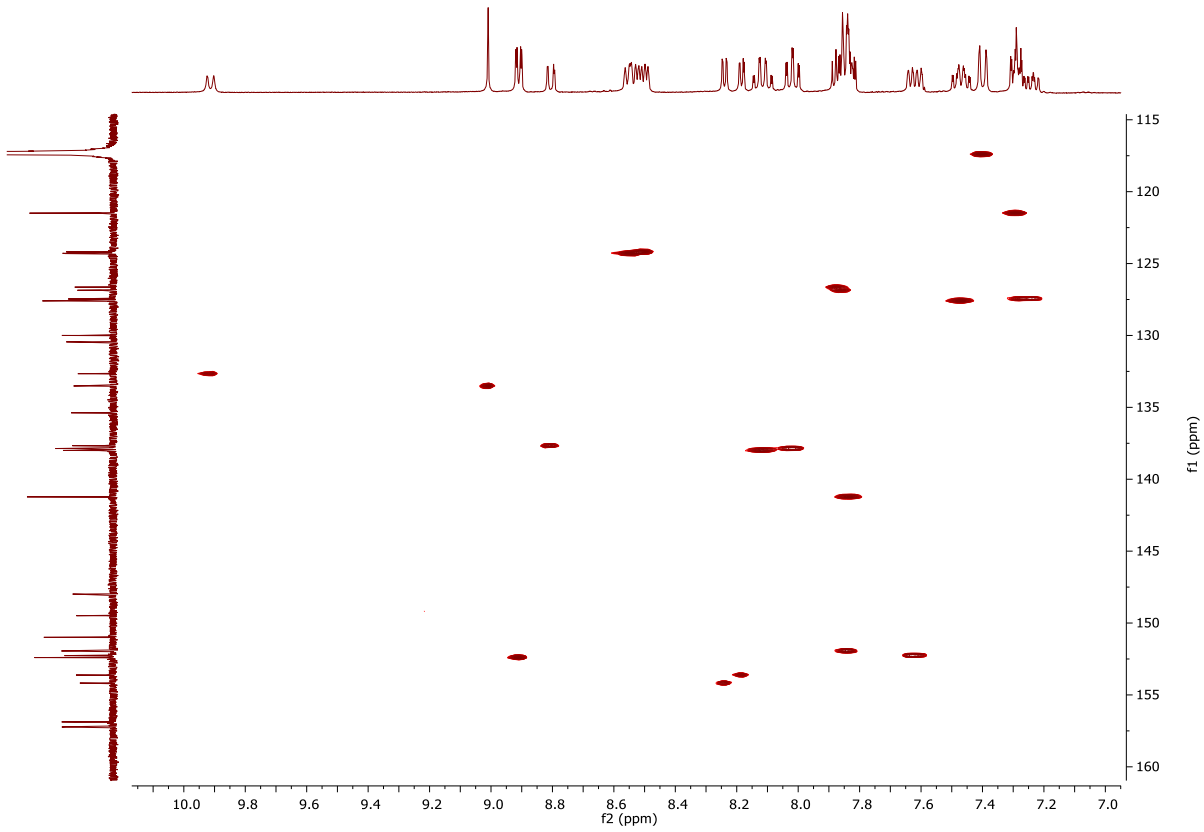


Figure S37. gHSQCAD spectrum of **Ru(Phen-5NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K).

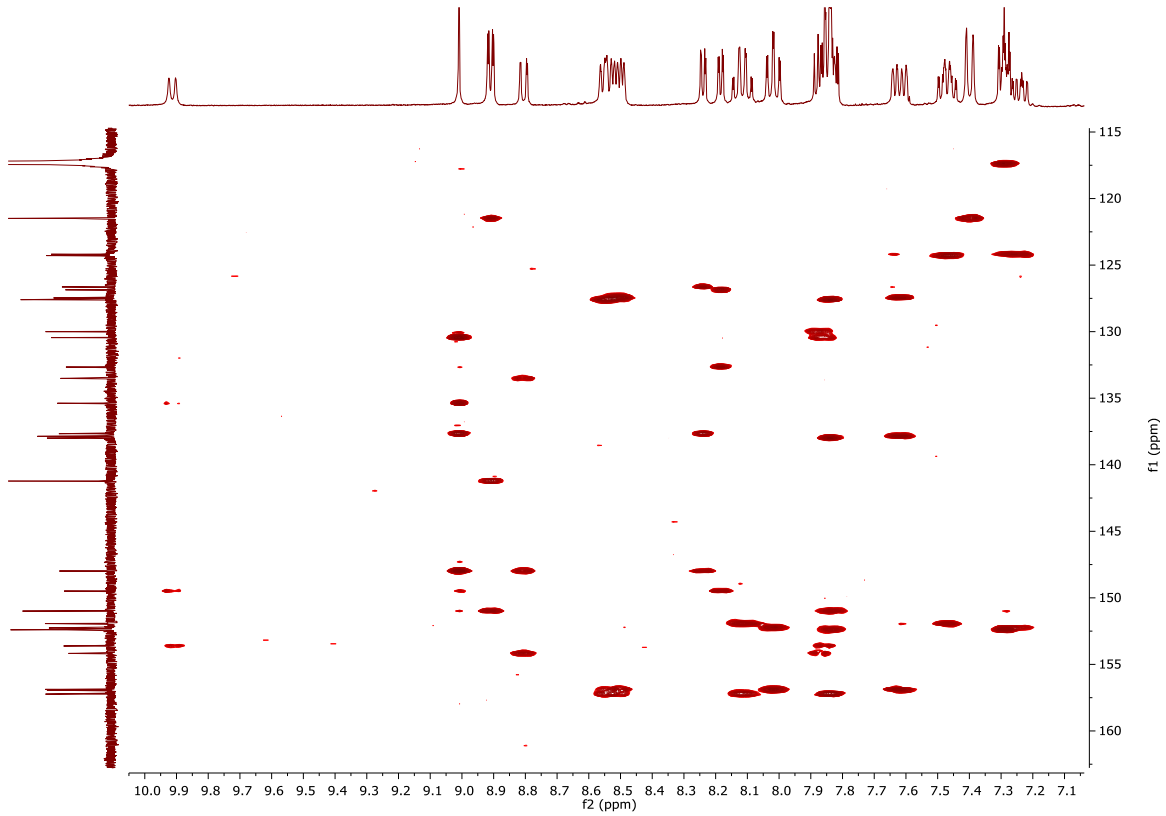


Figure S38. gHMBCAD spectrum of **Ru(Phen-5NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K, J=8 Hz).

4. Single crystal X-ray analysis

Crystals of the complexes suitable for single-crystal X-ray diffraction were obtained by slow diffusion of toluene to the dichloromethane solution (for **Ru(Phen-3NPy$_2$)Pd**, **Ru(Phen-4NPy$_2$)Pd** and **(NPy$_2$)Pd**) or $CHCl_3$/MeOH (1 : 1 v/v, for **Ru(Phen-5NPy$_2$)**) of the compound. SCXRD analysis of **Ru(Phen-3NPy$_2$)Pd**, **Ru(Phen-4NPy$_2$)Pd** and **(NPy$_2$)Pd** was carried out on a Bruker D8 Quest diffractometer (MoKα radiation, ω and φ-scan mode). SCXRD analysis of **Ru(Phen-5NPy$_2$)** was performed using Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromator, MoKα radiation, ω-scan mode).

The crystal data and refinement parameters are listed in Table S9. The structures were solved with direct methods and refined by least-squares method in the full-matrix anisotropic approximation on F^2. All hydrogen atoms were located in calculated positions and refined within riding model. All calculations were performed using the SHELXTL [11, 12] and Olex2 [13] software packages. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2327677 (**Ru(Phen-5NPy$_2$)**), 2327680 (**Ru(Phen-3NPy$_2$)Pd**), 2327678 (**Ru(Phen-4NPy$_2$)Pd**) and 2327679 (**(NPy$_2$)Pd**), which are available free of charge at www.ccdc.cam.ac.uk.

Ru(Phen-3NPy$_2$)Pd. In the crystal structure of **Ru(Phen-3NPy$_2$)Pd** the disorder of PF_6^- anion across inversion center is present. In case of the molecule with P2 atom, we were able to model the disorder as presented in Figure S39, and in case of the molecule with P3 atom, the disorder could not be modelled and the anion was left as is, leading to enlarged ellipsoids of atomic displacement (ADPs).

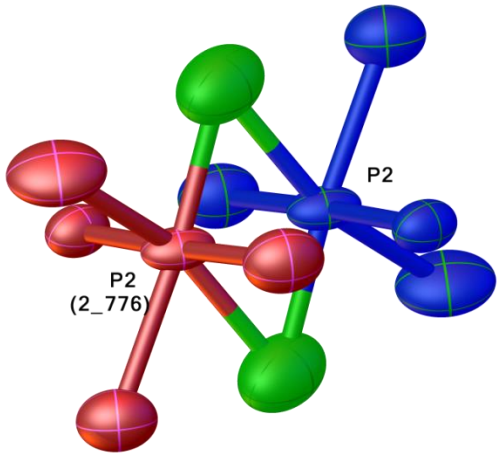


Figure S39. The disorder of PF_6^- anion across inversion center in **Ru(Phen-3NPy$_2$)Pd**. Shared fluorine atoms with occupancy of 100% are painted with green, the phosphorus and fluorine atoms with occupancies of 50% are painted with red and blue. The phosphorus atoms are labelled, and the symmetry operation code is given.

Ru(Phen-4NPy$_2$)Pd. The rather high R-factors of the refinement of **Ru(Phen-4NPy$_2$)Pd** is due to weak X-ray scattering at $2\theta>40^{o}$ which can be best explained as high degree of disorder that affects the whole molecule rather than any discrete substituents. This results in large ADPs of all atoms, including Ru1 atom. For some atoms, such as one bipyridyl ligand and {$PdCl_2$} fragment the disorder could be modelled, but mostly it was left as is due to lack of good quality data. Unfortunately, the data quality cannot be enhanced, as we have conducted the experiment at the lowest possible temperature (120 K) and the highest possible exposure time (100 seconds per frame).

The crystal structures of **Ru(Phen-3NPy$_2$)Pd** and **Ru(Phen-4NPy$_2$)Pd** contained several electron density maxima which could be attributed to solvated molecules of dichloromethane and toluene. However, these molecules could not be properly modelled due to them being disordered, and they were removed from the electron density map using Solvent Mask feature of Olex2 was implemented to deal with this issue. As a result, for **Ru(Phen-3NPy$_2$)Pd** a solvent mask was calculated and 249 electrons were found in a volume of 670 $Å^3$ in 1 void per unit cell. This is consistent with the presence of 2[CH_2Cl_2], 1[C_7H_8] per Asymmetric Unit which account for 268 electrons per unit cell. As for **Ru(Phen-4NPy$_2$)Pd**, a solvent mask was calculated and 181 electrons were found in a volume of 572 $Å^3$ in 1 void per unit cell. This is consistent with the presence of 1[CH_2Cl_2], 1[C_7H_8] per Asymmetric Unit which account for 184 electrons per unit cell.

Table S9. Crystal data and refinement parameters.

Compound	**Ru(Phen-5NPy$_2$)**	**Ru(Phen-3NPy$_2$)Pd**	**Ru(Phen-4NPy$_2$)Pd**	**(NPy$_2$)Pd**
Molecular Formula	$C_{42}H_{31}N_9Ru$, 2(PF_6), 0.5(CH_4O)	$C_{42}H_{31}Cl_2N_9PdRu$, 2(PF_6)	$C_{42}H_{31}Cl_2N_9PdRu$, 2(PF_6)	$C_{13}H_{15}Cl_2N_3OPd$
M	1068.79	1230.07	1230.07	406.58
Temperature, K	296(2)	120(2)	120(2)	120(2)
System	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Pbca
a, Å	10.1007(8)	12.8044(11)	12.689(8)	12.0324(10)
b, Å	13.3932(16)	12.9789(12)	14.266(9)	15.1880(13)
c, Å	17.7896(19)	17.6396(14)	14.621(9)	15.1880(13)
α, deg.	70.753(5)	86.755(3)	84.687(11)	
β, deg.	76.873(4)	71.875(2)	88.882(11)	90
γ, deg.	69.270(4)	76.129(3)	83.021(11)	
V, Å^3	2108.3(4)	2704.3(4)	2616(3)	2978.3(4)
Z, Z’	2, 1	2, 1	2, 1	8, 1
ρ_{calc}, g/cm^3	1.684	1.511	1.562	1.813
μ(MoK_α), mm^{-1}	0.548	0.848	0.877	1.603
F(000)	1074	1216	1216	1616
θmin–θmax, deg.	1.69–25.00	1.72–25.00	1.62–25.00	2.50–25.00
Number of measured reflections	11747	28555	22515	19389
Number of unique reflections (R_{int})	7207 (0.1168)	9481 (0.0599)	9206 (0.1205)	2618 (0.0871)
Number of reflections with $I > 2\sigma(I)$	4517	7223	3821	2172
Number of refined parameters	615	646	679	182
R-factors ($I > 2\sigma(I)$)	R_1=0.1009, ωR_2=0.2775	R_1=0.0678, ωR_2=0.1664	R_1=0.0732, ωR_2=0.1700	R_1=0.0429, ωR_2=0.1070
R-factors (all reflections)	R_1=0.1448, ωR_2=0.3136	R_1=0.0863, ωR_2=0.1801	R_1=0.1637, ωR_2=0.2142	R_1=0.0520, ωR_2=0.1159
GOOF	1.038	1.047	0.907	1.041
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e/Å^3	1.317 / –1.147	2.012 / –1.675	0.742 / –0.892	2.392 / –0.738

5. Electrochemistry

Voltammetric experiments were performed with Biologic BP-300 potentiostat in a three-electrode electrochemical cell (3 ml volume) at a stationary Pt disk electrode (S=0.077 cm^2) with a Pt wire counter electrode and Ag/Ag^+ reference electrode (0.01 M $AgNO_3$, 0.1 M Bu_4NBF_4 in MeCN). Fc^+/Fc couple was used as an internal standard in each experiment. The obtained electrochemical data were converted to Ag/AgCl, $KCl_{(sat.)}$ reference electrode (the standard potential of Fc^+/Fc couple was taken as 475 mV vs. Ag/AgCl, $KCl_{(sat.)}$). Ohmic drop corrections were performed using manual IR compensation procedure implemented in the Biologic software. All solutions were deaerated by passing an argon flow through the solution prior to the CV experiments and above the solution during the measurements. *n*-Bu_4NBF_4 (Aldrich, 99% purity) was used as a supporting electrolyte in all experiments. It was recrystallized from water and dried by heating at 100 °C under high vacuum (0.05 Torr) prior to use. Acetonitrile (AN, Aldrich spectroscopic quality, <0.02% water content) was distilled over P_2O_5. In each case, a freshly distilled portion of the solvent was used.

Table S10. Half-wave and peak potentials (V, *vs* Ag/AgCl, $KCl_{(sat)}$) of the **Ru(L)Pd** complexes and reference compounds in MeCN containing 0.05 M $TBAPF_6$ (Pt electrode).

Complex	Oxidation		Reduction						
	$E_{1/2}$	E_p	$Pd^{2+/0}$	$L^{0/\bullet-}$		$L^{0/\bullet-}$		$L^{0/\bullet-}$	
			E_p	$E_{1/2}$	E_p	$E_{1/2}$	E_p	$E_{1/2}$	E_p
$Ru(bpy)_3$ [a]	1.36		–	–1.25		–1.44		–1.68	–
$Ru(Phen)_3$ [a]	1.37			–1.29	–1.68	–1.41	–1.81	–	
Ru(Phen) [a]	1.37		–	–1.25		–1.43		–1.70	
$(NPy_2)Pd$	–	1.73	–0.88	–	–	–	–	–	–
Ru(Phen-3NPy_2)Pd	1.39	1.42	–0.57	–1.25	–1.28	–1.43	–1.46	–	–1.74
Ru(Phen-4NPy_2)Pd	1.38	1.42	–0.57	–1.24	–1.28	–1.38	–1.45	–	–1.72
Ru(Phen-5NPy_2)Pd	1.40	1.43	–0.72	–1.22	–1.25	–1.39	–1.45	–	–1.73

[a] Values calculated from ref. [14]

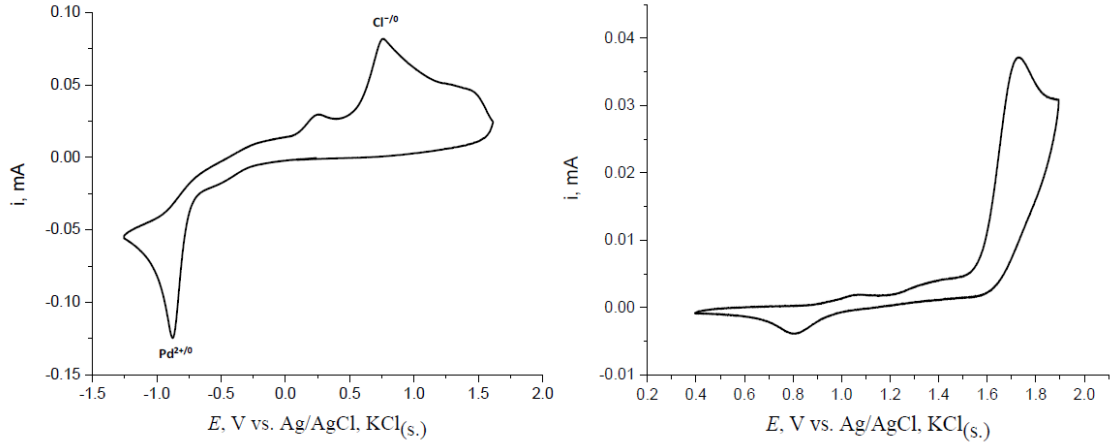


Figure S40. Cyclic voltamperometric curves of **(NPy$_2$)Pd** solution (9.8×10^{-4} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2, 100 $mV\times s^{-1}$).

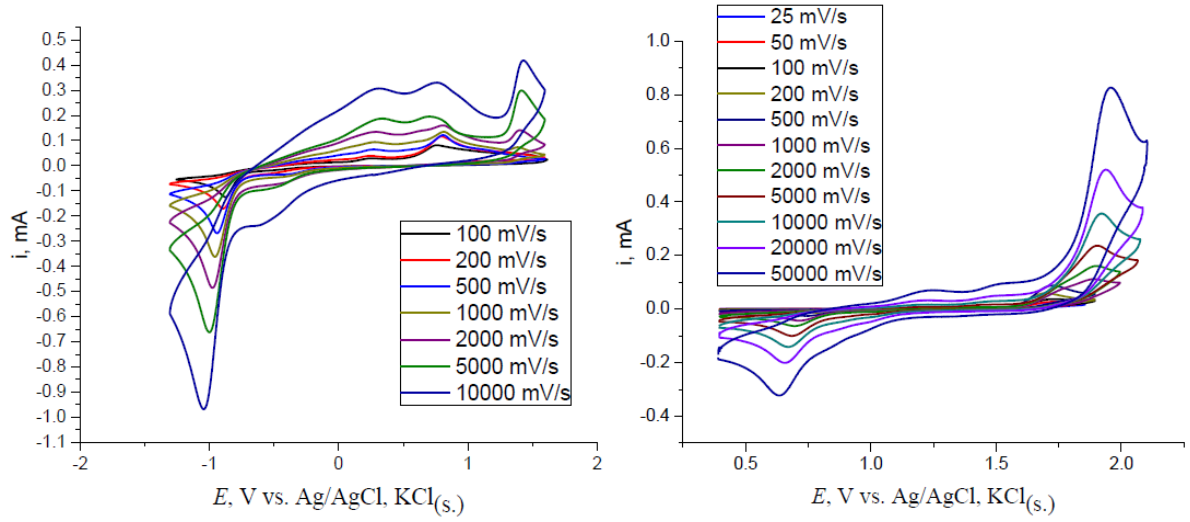


Figure S41. Cyclic voltamperometric curves of **(NPy$_2$)Pd** solution (9.8×10^{-4} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2) at various scan speed.

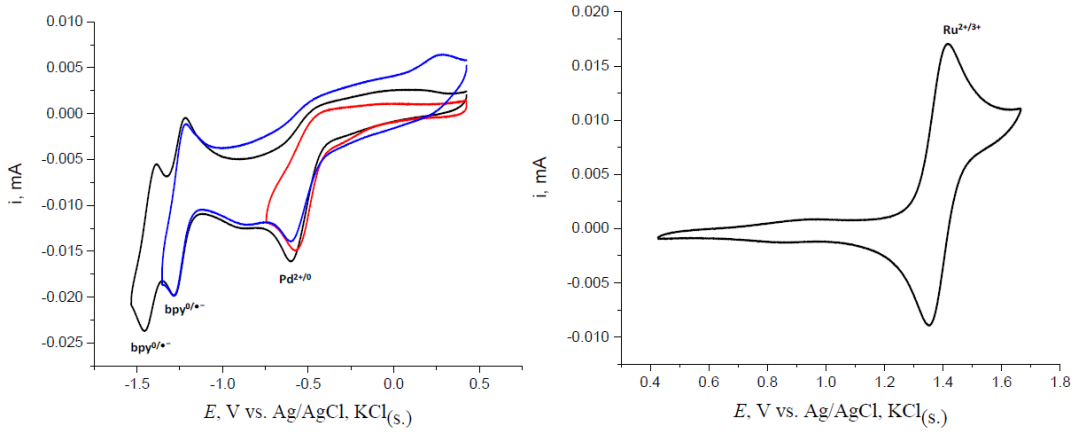


Figure S42. Cyclic voltamperometric curves of **Ru(Phen-3NPy$_2$)Pd** solution (1.08×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2, 100 mV×s^{-1}).

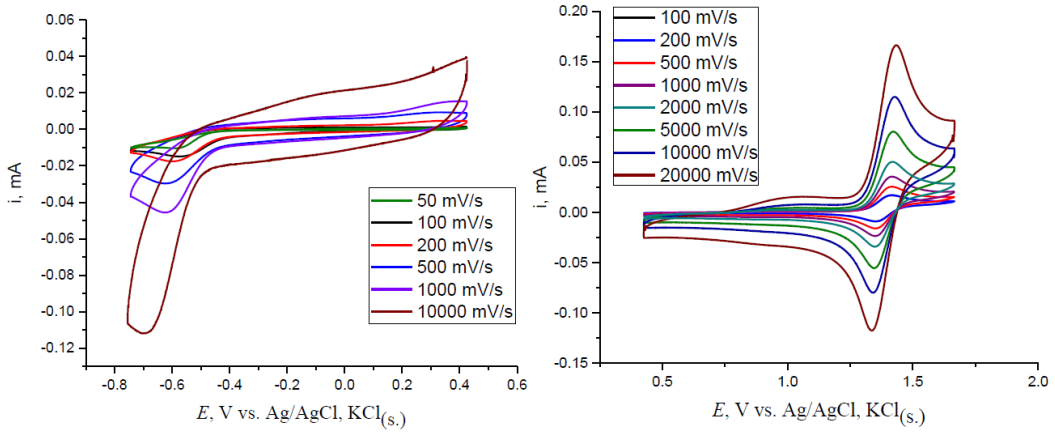
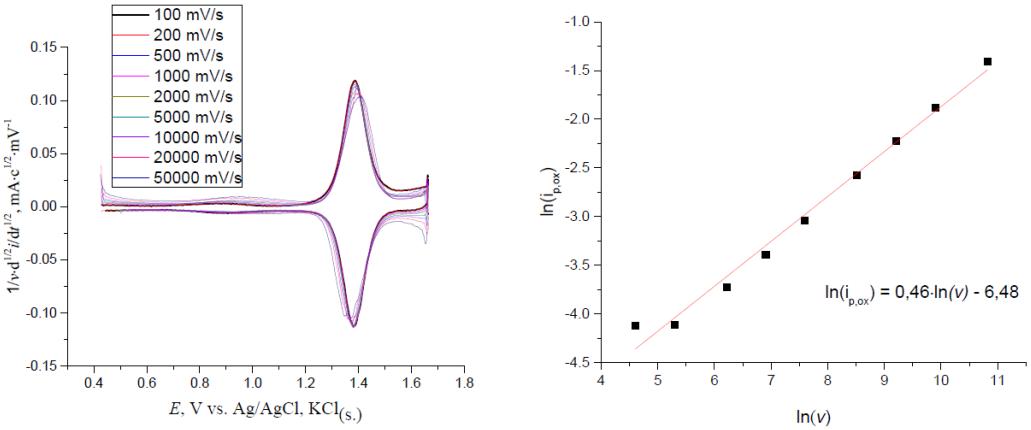


Figure S43. Cyclic voltamperometric curves of **Ru(Phen-3NPy$_2$)Pd** solution (1.08×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2) at various scan rates.



(a) **(b)**

Figure S44. (a) Semi-differential cyclic voltamperometric curves of **Ru(Phen-3NPy$_2$)Pd** solution (1.08×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at different scan rates for oxidation peak. **(b)** Plot of logarithm of the peak oxidation current as a function of the logarithm of the scan rate.

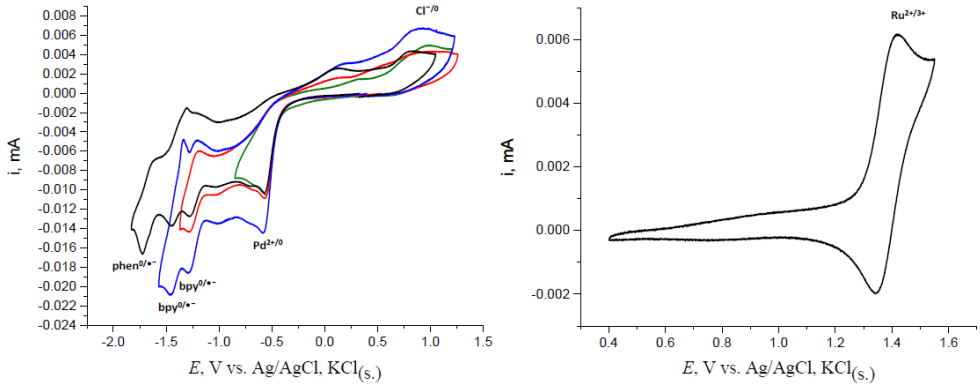


Figure S45. Cyclic voltamperometric curves of **Ru(Phen-4NPy$_2$)Pd** solution (1.41×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2, 100 $mV\times s^{-1}$).

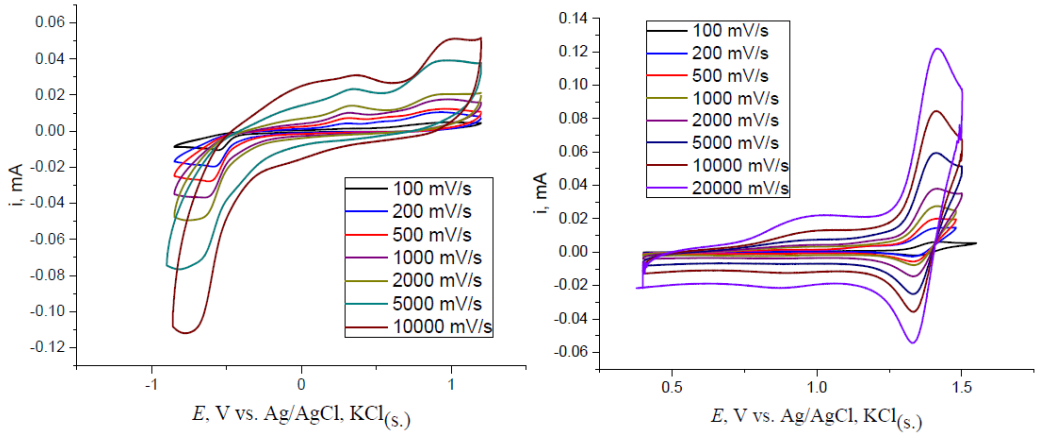
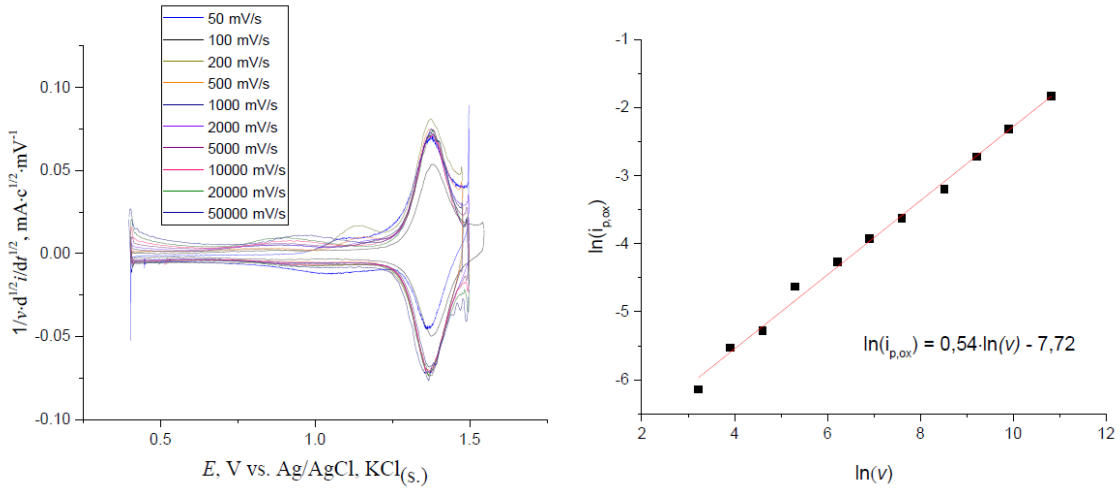


Figure S46. Cyclic voltamperometric curves of **Ru(Phen-4NPy$_2$)Pd** solution (1.41×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2) at various scan rates.



(a) **(b)**

Figure S47. (a) Semi-differential cyclic voltamperometric curves of **Ru(Phen-4NPy$_2$)Pd** solution (1.41×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at different scan rates for oxidation peak. **(b)** Plot of logarithm of the peak oxidation current as a function of the logarithm of the scan rate.

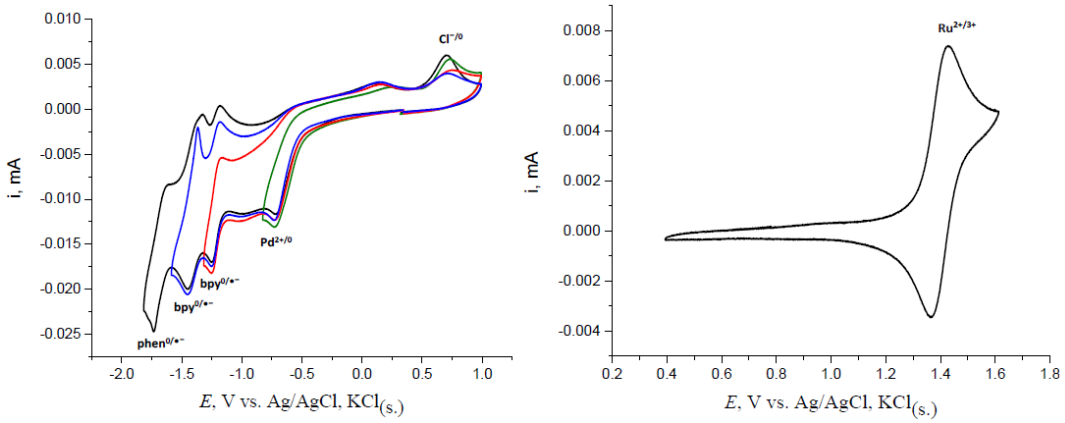


Figure S48. Cyclic voltamperometric curves of **Ru(Phen-5NPy$_2$)Pd** solution (1.08×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2, 100 $mV\times s^{-1}$).

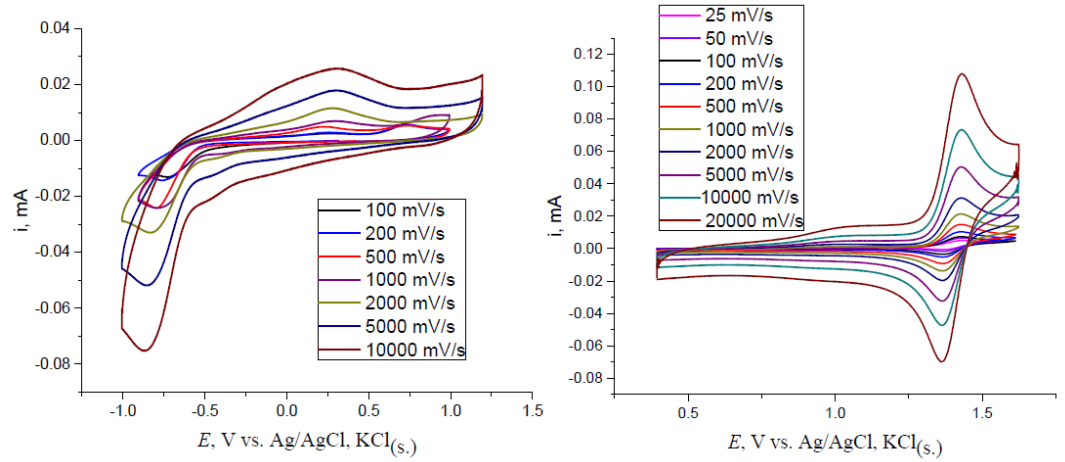
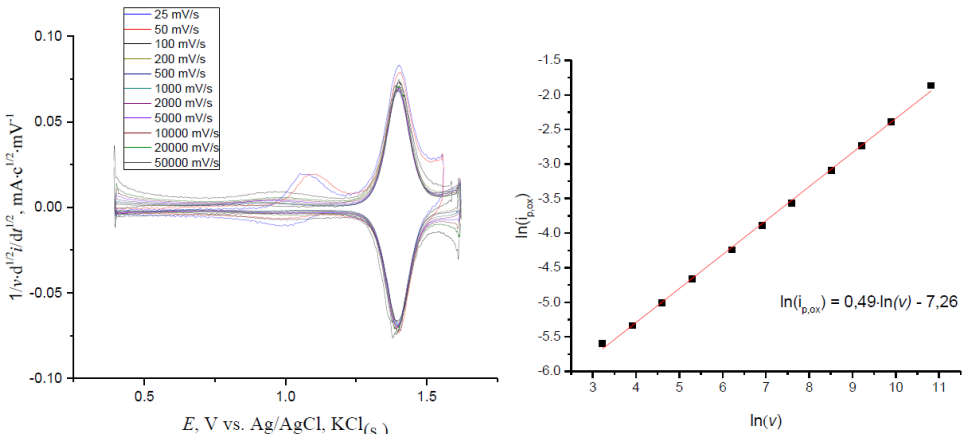


Figure S49. Cyclic voltamperometric curves of **Ru(Phen-5NPy$_2$)Pd** solution (1.08×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at Pt disk electrode (S=0.077 cm^2) at various scan rates.



(a) **(b)**

Figure S50. (a) Semi-differential cyclic voltamperometric curves of **Ru(Phen-5NPy$_2$)Pd** solution (1.08×10^{-3} M, MeCN, 0.05 M Bu_4NBF_4, vs Ag/AgCl, $KCl_{(sat.)}$) recorded at different scan rates for oxidation peak. **(b)** Plot of logarithm of the peak oxidation current as a function of the logarithm of the scan rate.

6. Photophysical studies

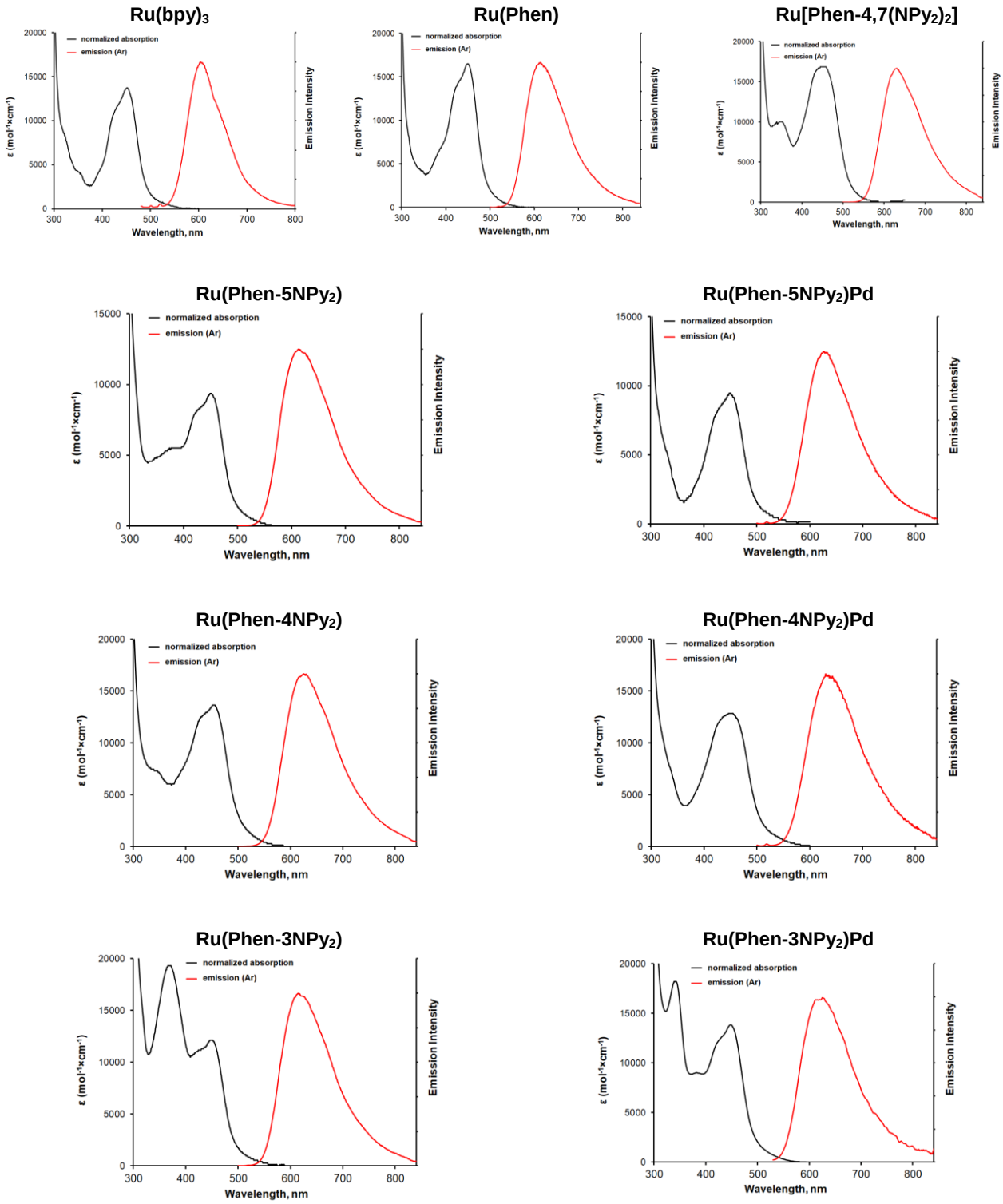


Figure S51. Normalized absorption (black lines) and emission (red lines) spectra of **Ru(Phen-NPy$_2$)** and **Ru(Phen-NPy$_2$)Pd** complexes and the reference compounds **Ru(bpy)$_3$** and **Ru(Phen)** in argon-saturated acetonitrile. Emission was excited at 450 nm.

Photostability studies

General procedure. A solution of complex **Ru(Phen-NPy$_2$)** or **Ru(Phen-NPy$_2$)Pd** in DMF was stirred under irradiation by blue LED (12 W, 455 nm, fig. S53) at room temperature in a Schlenk tube. The solution was diluted in 5–20 times and UV-vis spectra was recorded.

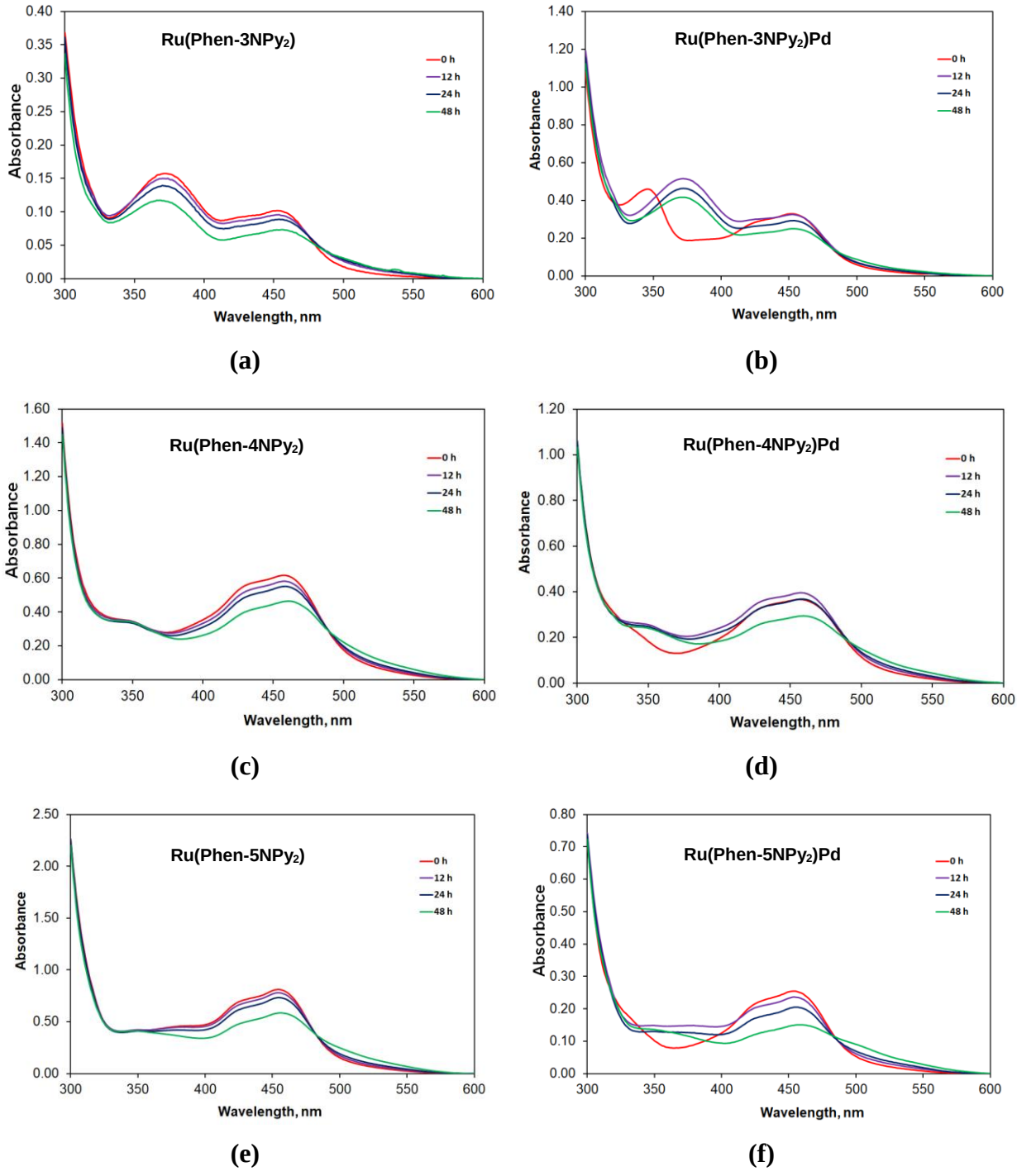


Figure S52. UV–vis spectra of the solutions **Ru(Phen-3NPy$_2$)** (a), **Ru(Phen-3NPy$_2$)Pd** (b), **Ru(Phen-4NPy$_2$)** (c), **Ru(Phen-4NPy$_2$)Pd** (d), **Ru(Phen-5NPy$_2$)** (e), **Ru(Phen-5NPy$_2$)Pd** (f) in DMF before (red) and after irradiation (12 W, blue LED) for 12 hours (violet), 24 hours (blue) and 48 hours (green).

7. DFT-studies

The structures of complexes was modelled using DFT calculations with Firefly quantum chemistry package,[15] which is partially based on the GAMESS (US) [16] source code. The calculations were performed using B3LYP functional with STO 6-31G(d,p) basis set for all elements except Ru and Pd, for which we have used the Jorgedz valence basis set and pseudopotential.[17]

Table S11. Selected bond lengths [Å] and angles [°] for Ru-complexes obtained by DFT calculations and X-Ray analysis.

Complex	**Parameters**								
	Phen			bpy			NPy_2		
	Ru-N	Ru-N	$\theta_{N\text{-}Ru\text{-}N}$	Ru-N_{cis}	Ru-N_{trans}	$\theta_{N\text{-}Ru\text{-}N}$	Pd-N	Pd-Cl	$\theta_{N\text{-}Pd\text{-}N}$
Ru(Phen) (DFT)	2.01	2.01	80.3	2.01	2.01	79.5	-	-	-
Ru(Phen) (X-Ray)[a]	2.07	2.08	79.8	2.07	2.07	78.3	-	-	-
Ru(Phen-3NPy_2) (DFT)	2.03	2.02	80.5	2.00	2.00	79.5	-	-	-
Ru(Phen-4NPy_2) (DFT)	2.02	2.01	79.6	2.00	2.00	79.5	-	-	-
Ru(Phen-5NPy_2) (DFT)	2.02	2.02	80.2	2.00	2.00	79.5	-	-	-
Ru(Phen-5NPy_2) (X-Ray) [b]	2.09	2.06	79.1	2.07	2.05 2.08	78.6	-	-	-
Ru(Phen-3NPy_2)Pd (DFT)	2.02	2.01	80.7	2.00 2.01	2.00 2.01	79.5 79.3	1.95	2.26	88.6
Ru(Phen-3NPy_2)Pd (X-Ray) [b]	2.05	2.07	79.7	2.05	2.05	79.3 79.1	2.02	2.27	87.4
Ru(Phen-4NPy_2)Pd (DFT)	2.01	2.01	80.3	2.00	2.00	79.5	1.96	2.26	89.3
Ru(Phen-4NPy_2)Pd (X-Ray) [b]	2.04	2.06	80.4	2.05	2.08	77.7 79.1	1.92 2.16	2.26 2.28	87.0
Ru(Phen-5NPy_2)Pd (DFT)	2.02	2.02	80.2	2.00	2.00	79.4	1.96	2.26	88.9

[a] experimental values for $[Ru(bpy)_2(Phen)](BF_4)_2.H_2O$ from ref. [18]

[b] experimental values obtained in this work;

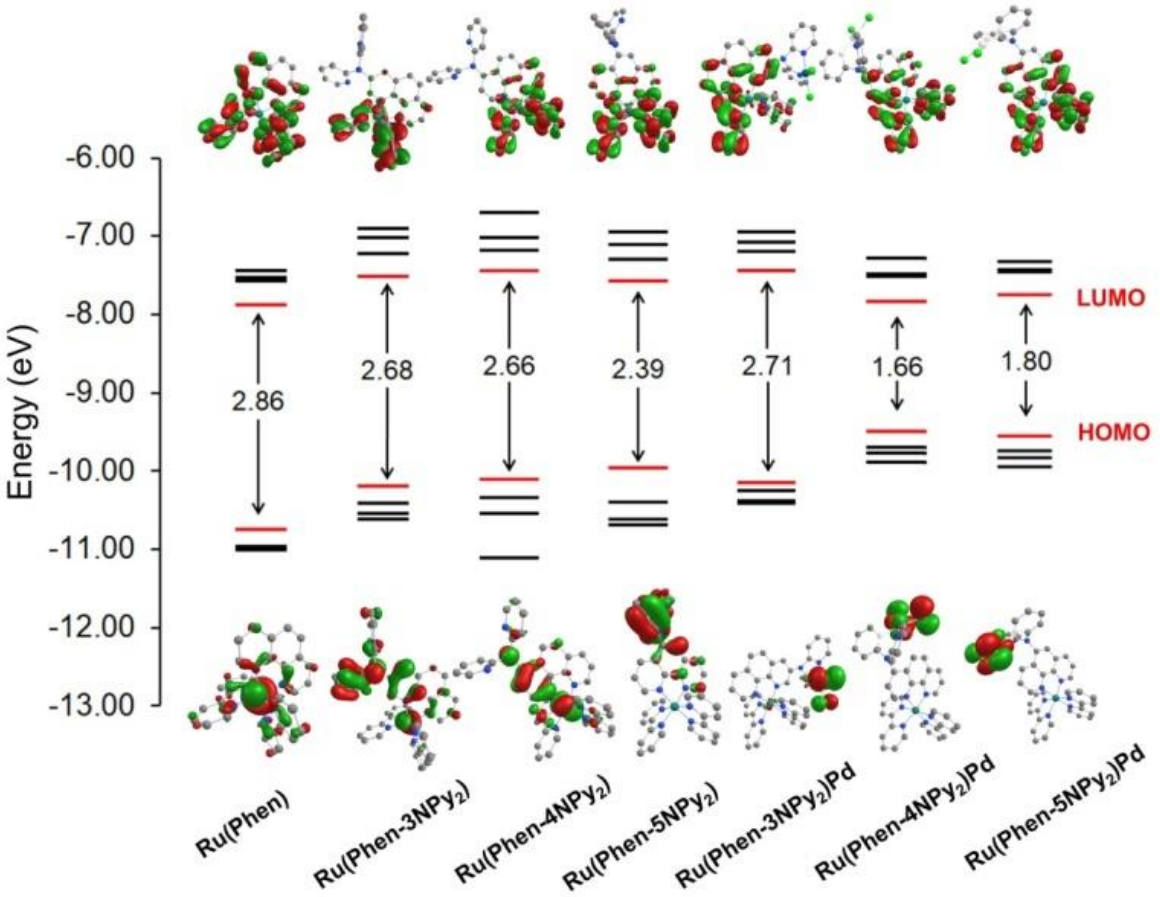


Figure S53. Frontier orbital energies obtained from DFT calculations and HOMO and LUMO orbitals isodensity plots for **Ru(Phen)**, **Ru(Phen-NPy_2)** and **Ru(Phen-NPy_2)Pd** complexes.

In all the complexes modelled $LUMO_{0+3}$ are localized on the ligand π* orbitals of Ru complex, mostly those of bpy peripheral ligands, in a few cases involving also phen ligand. The HOMOs, on the contrary, were calculated to be constructed quite differently for each complex. In **Ru(Phen)**, **Ru(Phen-3NPy_2)** and **Ru(Phen-4NPy_2)** complexes d-orbital of Ru atom are involved in the HOMO. In **Ru(Phen-5NPy_2)** complex HOMO were calculated to be built mostly by π-orbitals of 2-aminopyridine residue. HOMOs of dinuclear Ru–Pd complexes are localized mainly on Pd and Cl atoms. The latter is obviously inconsistent with the optical spectroscopy data, which suggest the location of HOMO on the Ru atom therefore, consideration of these data should be quite careful.

Table S12. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen)** complex.

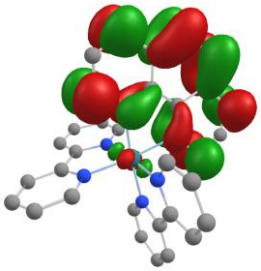
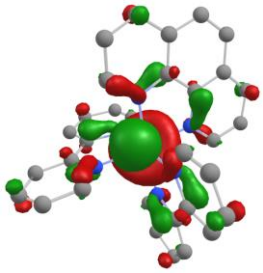
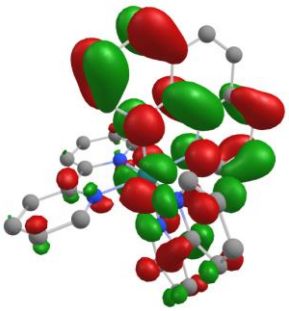
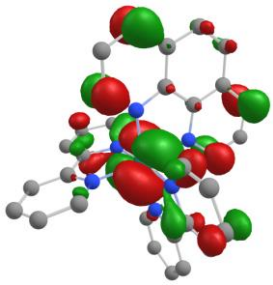
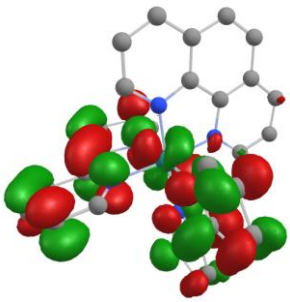
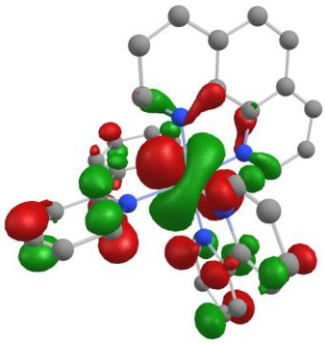
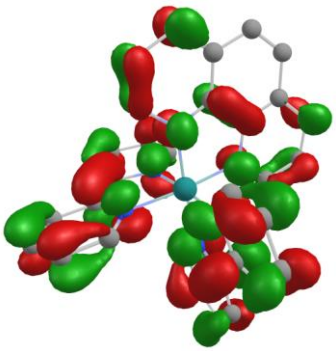
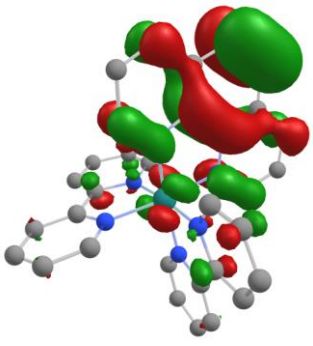
Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–7.44		HOMO	–10.74	
LUMO+2	–7.53		HOMO–1	–10.96	
LUMO+1	– 7.57		HOMO–2	–11.01	
LUMO	–7.88		HOMO–3	–12.26	

Table S13. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen-3NPy$_2$)** complex.

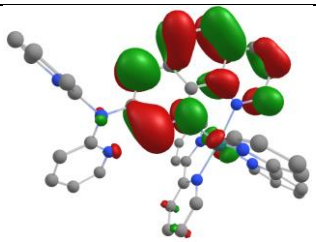
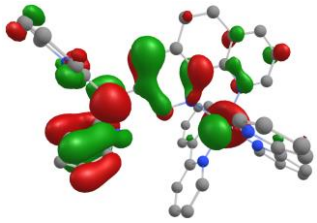
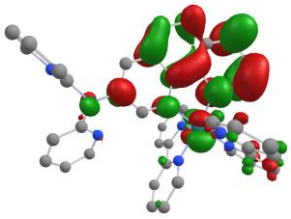
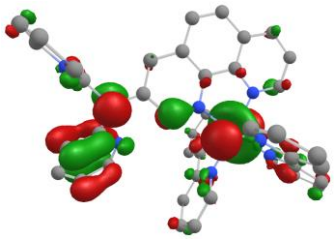
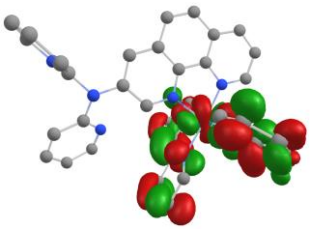
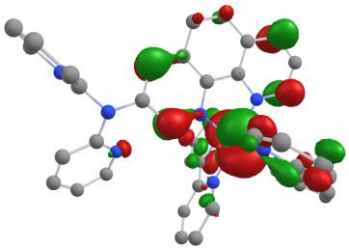
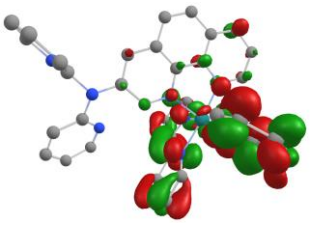
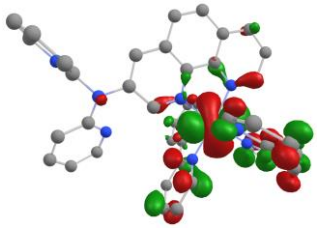
Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–6.90		HOMO	–10.19	
LUMO+2	–7.02		HOMO–1	–10.41	
LUMO+1	–7.11		HOMO–2	–10.54	
LUMO	–7.51		HOMO–3	–10.62	

Table S14. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen-4NPy$_2$)** complex.

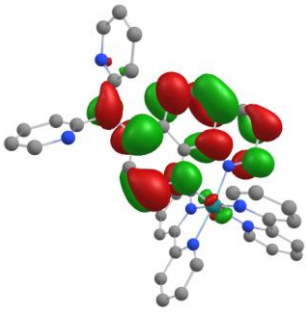
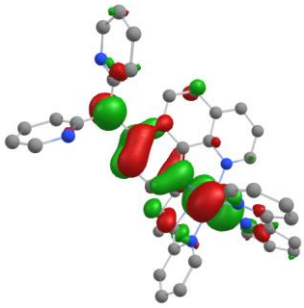
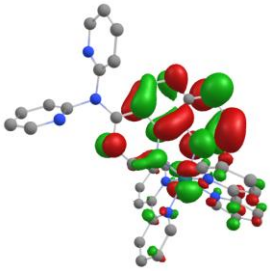
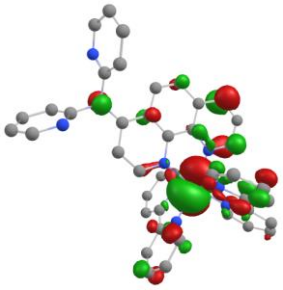
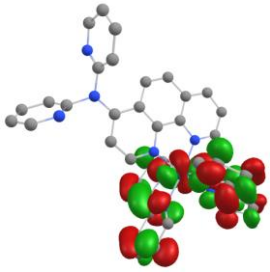
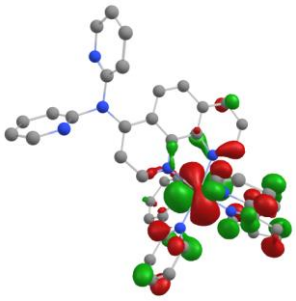
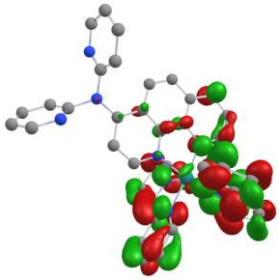
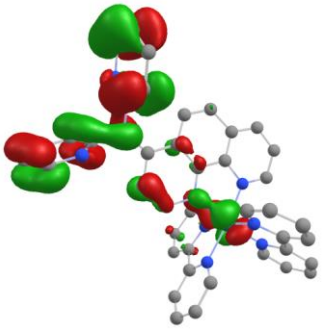
Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–6.70		HOMO	–10.10	
LUMO+2	–7.02		HOMO–1	–10.34	
LUMO+1	–7.18		HOMO–2	–10.54	
LUMO	–7.44		HOMO–3	–11.11	

Table S15. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen-5NPy$_2$)** complex.

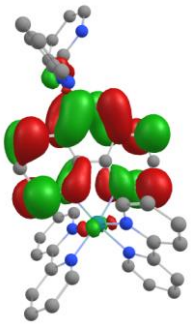
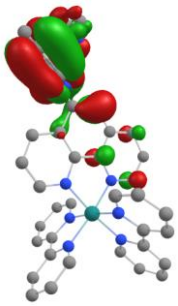
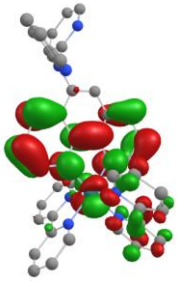
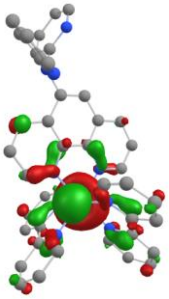
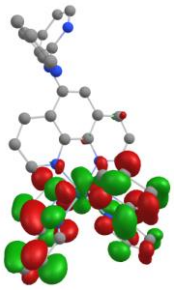
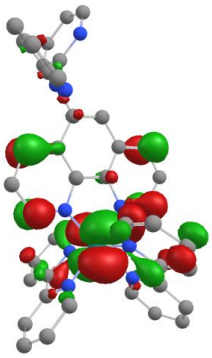
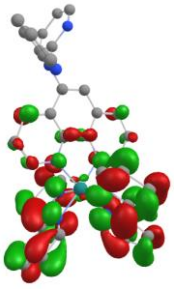
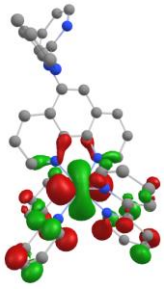
Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–6.95		HOMO	–9.96	
LUMO+2	–7.11		HOMO–1	–10.40	
LUMO+1	–7.29		HOMO–2	–10.61	
LUMO	–7.57		HOMO–3	–10.68	

Table S16. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen-3NPy$_2$)Pd** complex.

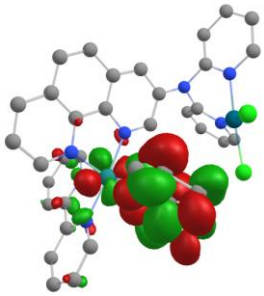
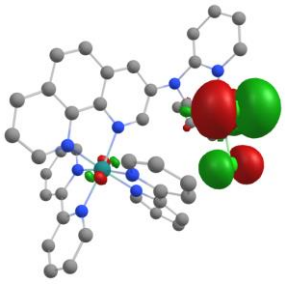
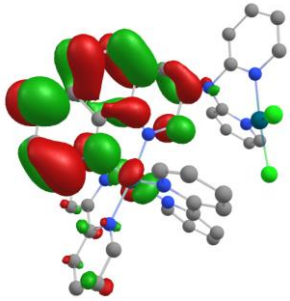
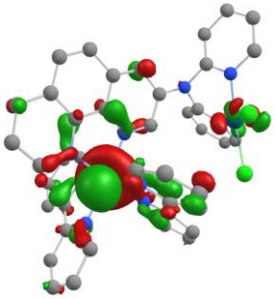
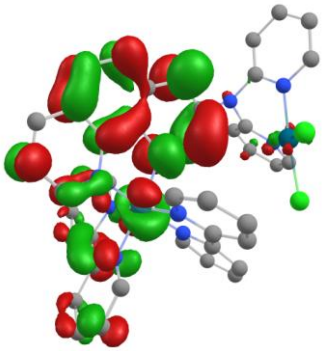
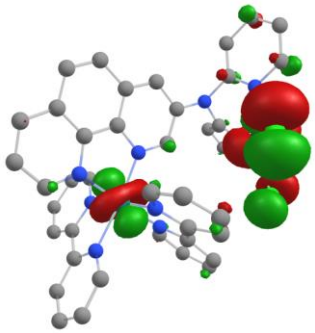
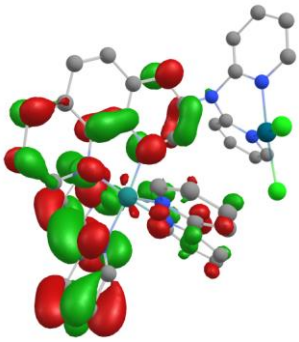
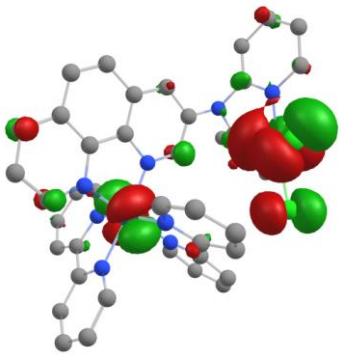
Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–6.94		HOMO	–10.15	
LUMO+2	–7.08		HOMO–1	–10.25	
LUMO+1	–7.19		HOMO–2	–10.38	
LUMO	–7.44		HOMO–3	–10.41	

Table S17. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen-4NPy$_2$)Pd** complex.

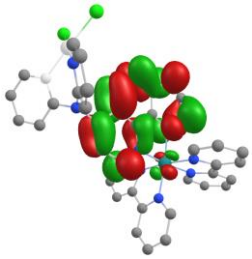
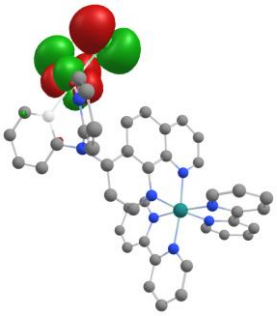
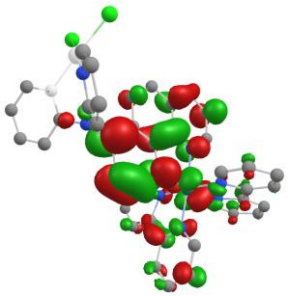
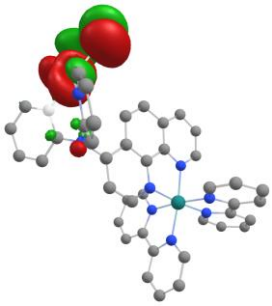
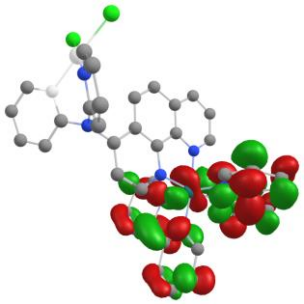
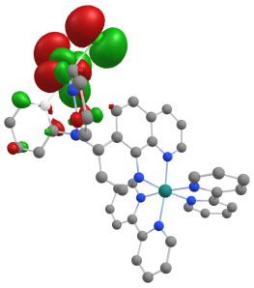
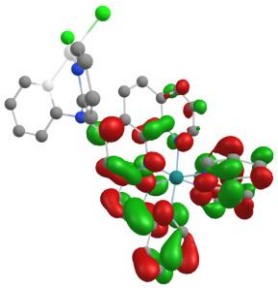
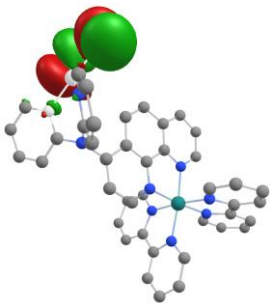
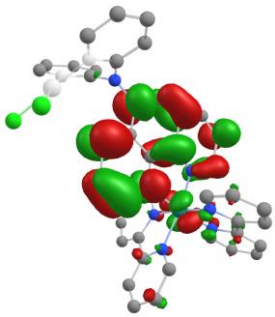
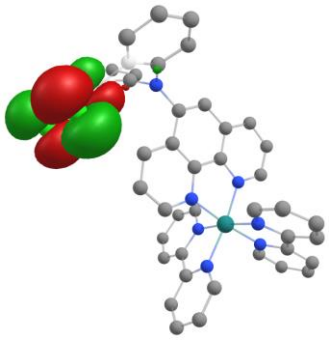
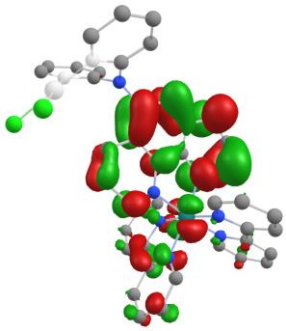
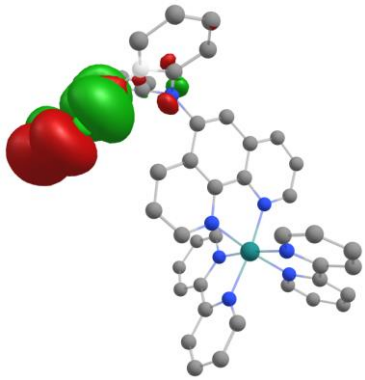
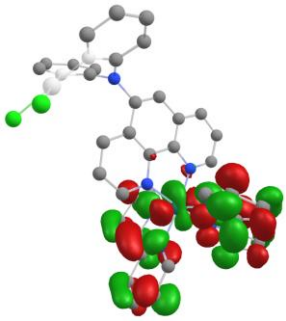
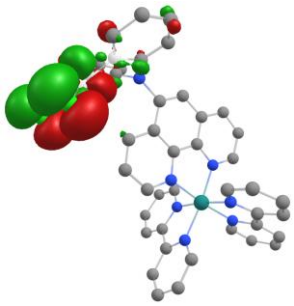
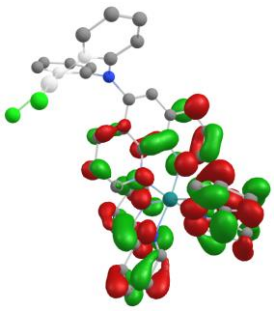
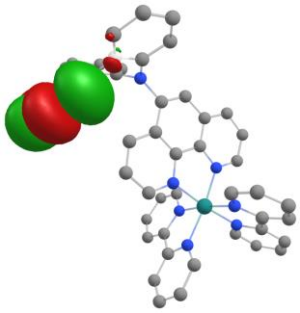
Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–7.28		HOMO	–9.49	
LUMO+2	–7.48		HOMO–1	–9.70	
LUMO+1	–7.52		HOMO–2	–9.77	
LUMO	–7.83		HOMO–3	–9.89	

Table S18. The electron-cloud distribution of the HOMO and LUMO calculated by DFT of the **Ru(Phen-5NPy$_2$)Pd** complex.

Orbital	E(eV)	The electron-cloud distribution	Orbital	E(eV)	The electron-cloud distribution
LUMO+3	–7.32		HOMO	–9.55	
LUMO+2	–7.42		HOMO–1	–9.74	
LUMO+1	–7.45		HOMO–2	–9.83	
LUMO	–7.75		HOMO–3	–9.95	

8. Catalytic studies

Photoreactor setup

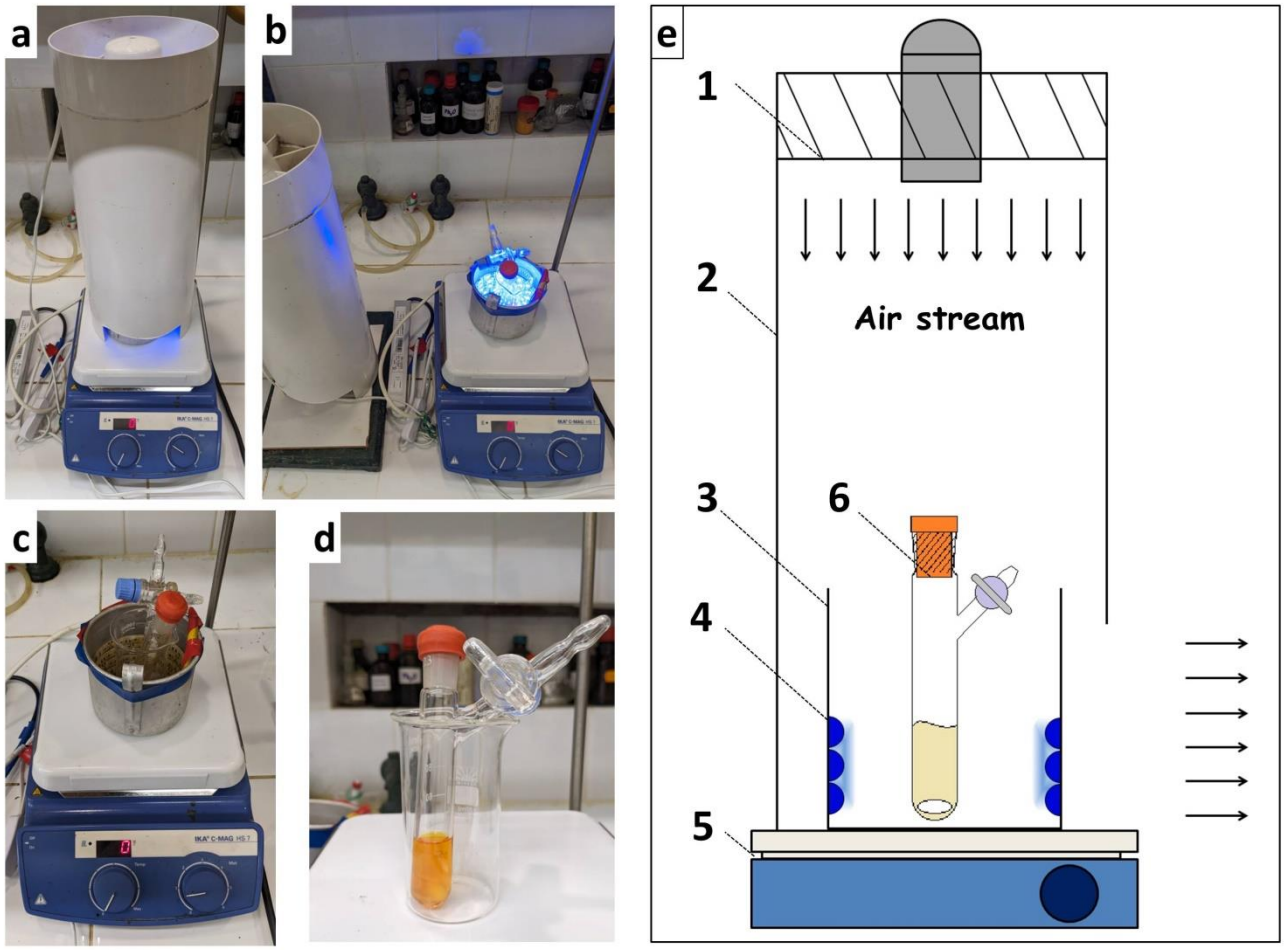
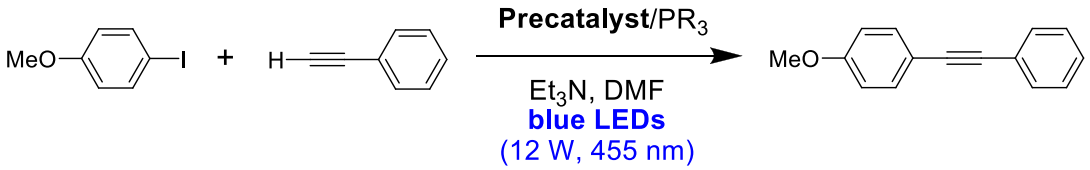


Fig. S54. Photoreactor setup: **a** – front view of the photoreactor; **b, c** – the Schlenk tube between LED; **d** – the Schlenk tube; **e** – schematic representation of photoreactor setup; **1** – electric fan (16 W, 188 m^3/h); **2** – plastic protecting tube (*d* = 150 mm, *h* = 500 mm); **3** – aluminum cup (*d* = 110 mm); **4** – blue LED strip (LP SMD 5050, 300 Led, IP65, 12V, 12 W, 455 nm); **5** – magnetic stirrer (IKA® C-Mag HS 7); **6** – Schlenk tube sealed with rubber septum. The temperature of the reaction vessel did not exceed 25–27^{o}C depending on the ambient temperature.

Cu-free Sonogashira coupling under visible light irradiation.

A Schlenk-tube equipped with a magnetic stirrer was charged with aryliodide (0.2 mmol), photocatalyst (**Ru(bpy)$_3$/(NPy$_2$)Pd** (1/1 mol%) or **Ru(L)Pd** (1 mol %)) and phosphine (2 mol%) and filled with dry argon. The vessel was sealed with a septum and phenylacethylene (or was added earlier in case of solid arylacethylene) (0.25 mmol), triethylamine (1 mL) and DMF (4 mL) were added by syringes. The reaction mixture was stirred under irradiation (Figure S53) the exact time. The probe of the reaction mixture (~50–70 μl) was analyzed by NMR ^{1}H in $CDCl_3$ without solvent evaporation.

Table S19. Photoaccelerated Sonogashira coupling.



Entry [a]	Precatalyst (mol%)	Phosphine (mol%)	Time, h	Conversion of Ar-I, % [b]	Yield, % [b]
1	**Ru(bpy)$_3$/(NPy)$_2$Pd** (8/4)	P(*t*Bu)$_3$ (4)	4	78	36
2 [c]	**Ru(bpy)$_3$/(NPy)$_2$Pd** (8/4)	P(*t*Bu)$_3$ (4)	4	0	0
3	**(NPy)$_2$Pd** (4)	P(*t*Bu)$_3$ (4)	4	0	0
4	**Ru(bpy)$_3$/(NPy)$_2$Pd** (8/4)	PPh$_3$ (4)	24	>95	>95
5	**Ru(bpy)$_3$/(NPy)$_2$Pd** (1/1)	P(*t*Bu)$_3$ (2)	4	40	28
6	**Ru(bpy)$_3$/(NPy)$_2$Pd** (1/1)	JohnPhos (2)	24	86	80
7	**Ru(bpy)$_3$/(NPy)$_2$Pd** (1/1)	PPh$_3$ (2)	24	30	30
8	**Ru(bpy)$_3$/(NPy)$_2$Pd** (1/1)	PPh$_3$ (2)	58	50	50
9	**Ru(Phen-3NPy$_2$)Pd** (1)	-	12	15	15
10	**Ru(Phen-3NPy$_2$)Pd** (1)	-	24	49	49
11	**Ru(Phen-3NPy$_2$)Pd** (1)	P(*t*Bu)$_3$ (2)	4	>95	62
12	**Ru(Phen-4NPy$_2$)Pd** (1)	P(*t*Bu)$_3$ (2)	4	>90	60
13	**Ru(Phen-5NPy$_2$)Pd** (1)	P(*t*Bu)$_3$ (2)	4	>95	52
14	**Ru(Phen-3NPy$_2$)Pd** (1)	PPh$_3$ (2)	4	25	25
15	**Ru(Phen-3NPy$_2$)Pd** (1)	PPh$_3$ (2)	24	60	60
16	**Ru(Phen-3NPy$_2$)Pd** (1)	PPh$_3$ (2)	50	100	>95
17	**Ru(Phen-4NPy$_2$)Pd** (1)	PPh$_3$ (2)	24	75	75
18	**Ru(Phen-4NPy$_2$)Pd** (1)	PPh$_3$ (2)	50	100	>95
19	**Ru(Phen-5NPy$_2$)Pd** (1)	PPh$_3$ (2)	24	35	35
20	**Ru(Phen-5NPy$_2$)Pd** (1)	PPh$_3$ (2)	58	79	79
21	**Ru(tpphz)Pd** (1)	PPh$_3$ (2)	24	30	30
22	**Ru(tpphz)Pd** (1)	PPh$_3$ (2)	48	60	60
23 [c]	**Ru(Phen-3NPy$_2$)Pd** (1)	PPh$_3$ (2)	4	0	0
24 [d]	**Ru(Phen-3NPy$_2$)Pd** (1)	PPh$_3$ (2)	24, 60	0	0

[a] Reaction conditions: phenylacetylene (0.25 mmol), 4-iodoanizole (0.2 mmol), photocatalyst, phosphine, Et_3N (1 mL), DMF (4 mL), argon atmosphere, in Schlenk tube, blue LED (455 nm, 12 W), r.t. The yields were determined from NMR ^{1}H analysis of the reaction mixture. [b] The conversion and yield were determined from NMR ^{1}H analysis of the reaction mixture. [c] The reaction was performed in the dark. [d] Mercury drop was added to the reaction.

1,2-Diphenylethyne, 1-methoxy-4-(phenylethynyl)benzene, 1-(4-(phenylethynyl)phenyl)ethanone and methyl-3-(phenylethynyl)benzoate are known compounds and their spectral data were consistent with those in the literature [19].

1,2-Diphenylethyne. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58–7.56 (m, 4 H), 7.39–7.35 (m, 6 H).

1-Methoxy-4-(phenylethynyl)benzene. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (dd, ^{3}J = 7.9 Hz, ^{4}J = 1.5 Hz, 2H), 7.47 (d, ^{3}J = 8.7 Hz, 2H), 7.36–7.31 (m, 3H), 6.88 (d, ^{3}J=8.7 Hz, 2H), 3.83 (s, 3H, CH_3).

1-(4-(Phenylethynyl)phenyl)ethanone. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, ^{3}J = 7.6 Hz, 2H), 7.61 (d, ^{3}J = 7.6 Hz, 2H), 7.56–7.53 (m, 2H), 7.38–7.35 (m, 3H), 2.60 (s, 3H, CH_3).

Methyl-3-(phenylethynyl)benzoate. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (s, 1H), 8.00 (d, ^{3}J = 7.1 Hz, 1H), 7.69 (d, ^{3}J = 7.1 Hz, 1H), 7.57–7.51 (m, 2H), 7.43 (t, ^{3}J = 7.7 Hz, 1H), 7.38–7.34 (m, 3H), 3.94 (s, 3H, CH_3).

NMR studies of transformations of ***Ru(Phen-3NPy$_2$)Pd***

The NMR-tube was charged with **Ru(Phen-3NPy$_2$)Pd** (0.0025 mmol), flushed with argon, then solvent (650 μL, CD_3CN or DMF-D7) and additional reagent (if required) were added. The tube was sealed with cap and parafilm, thoroughly shacked and NMR spectra were registered. Irradiation experiments were conducted directly in NMR-tube using photoreactor (Fig. S53, 12 W blue LEDs, 455 nm). The NMR spectra are given at Figures S54–S56, the conditions of each experiment are given in the captions.

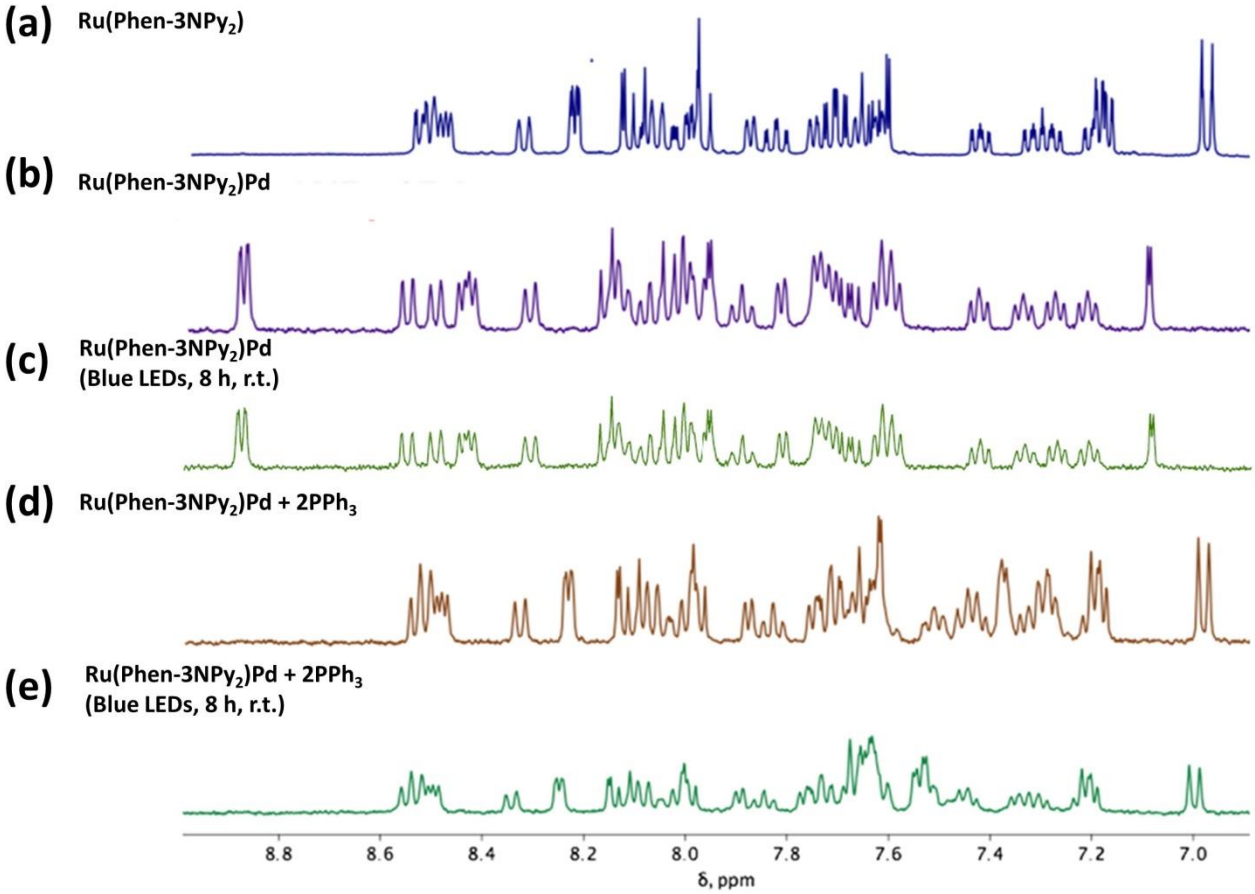


Figure S55. (a) ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)** (400 MHz, CD_3CN, 298 K); (b) ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K); (c) ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (400 MHz, CD_3CN, 298 K) after irradiation (12 W Blue LEDs, 455 nm, 8 h, r.t.); (d) ^{1}H NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd** and PPh_3 (2 equiv.) (400 MHz, CD_3CN, 298 K); (e) ^{1}H NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd** and PPh_3 (2 equiv.) after irradiation (12 W Blue LEDs, 455 nm, 8 h, r.t.) (400 MHz, CD_3CN, 298 K).

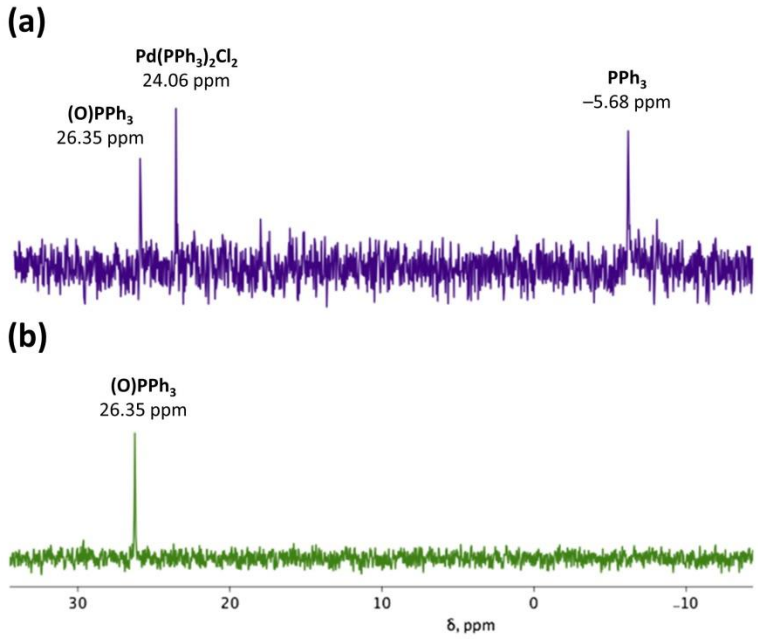


Figure S56. (a) ^{31}P NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd** and PPh_3 (2 equiv.) (162.5 MHz, CD_3CN, 298 K); (b) ^{31}P NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd** and PPh_3 (2 equiv.) after irradiation (12 W Blue LEDs, 455 nm, 8 h, r.t.) (162.5 MHz, CD_3CN, 298 K). Signal assignment was based on the refs. [20-22].

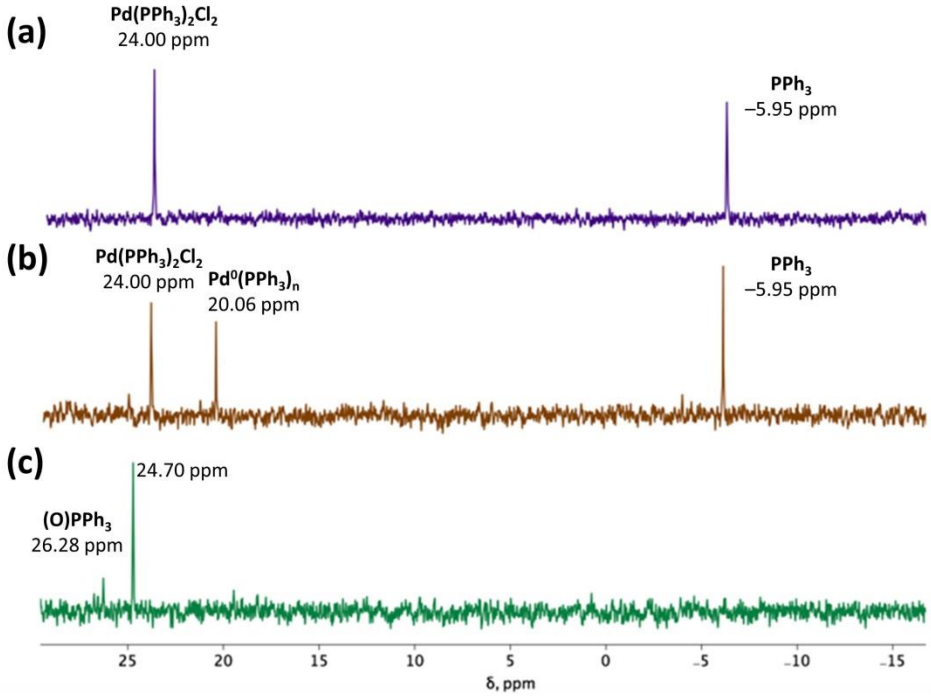


Figure S57. (a) ^{31}P NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd** and PPh_3 (2 equiv.) (162.5 MHz, DMF-D7, 298 K); (b) ^{31}P NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd**, PPh_3 (2 equiv.) and Et_3N (75 equiv.) (162.5 MHz, DMF-D7, 298 K). (c) ^{31}P NMR spectrum of the mixture of **Ru(Phen-3NPy$_2$)Pd**, PPh_3 (2 equiv.) and Et_3N (75 equiv.) after irradiation (12 W Blue LEDs, 455 nm, 8 h, r.t.) (162.5 MHz, DMF-D7, 298 K). Signal assignment was based on the refs. [20-23].

9. NMR-spectra

NMR-spectra of the ligands

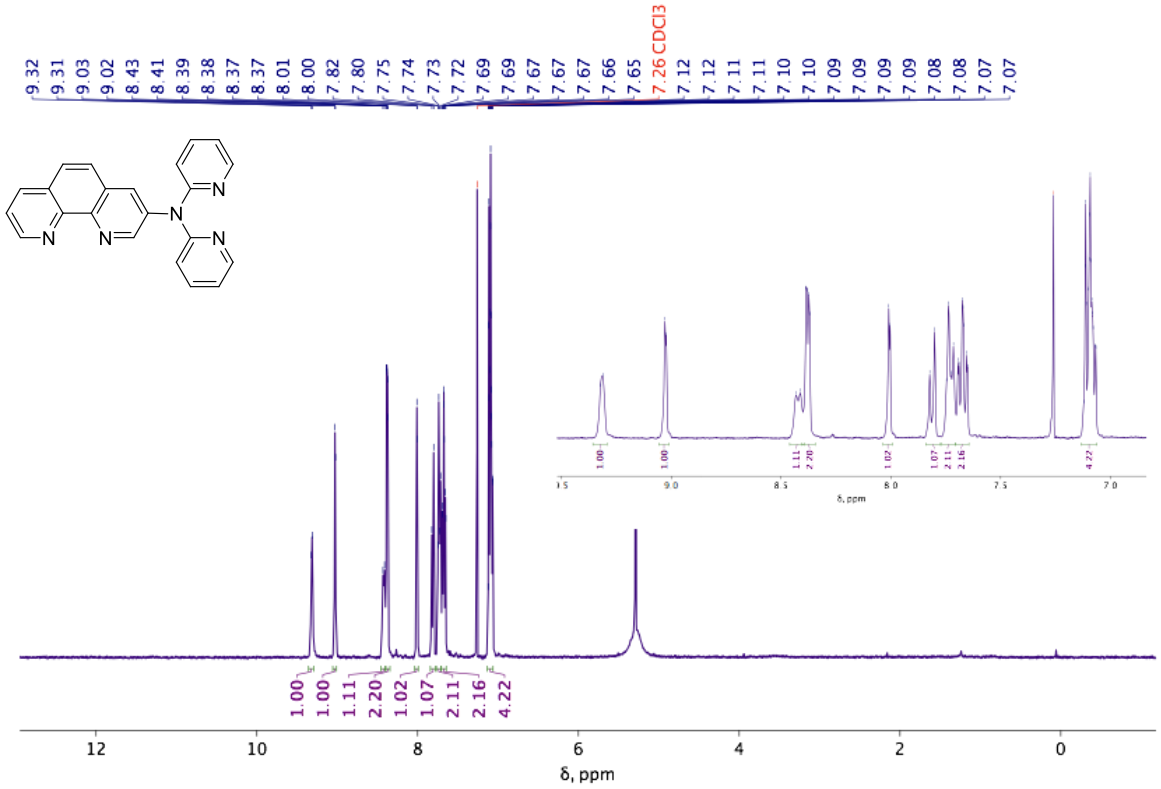


Figure S58. ^{1}H NMR spectrum of **Phen-3NPy$_2$** ($CDCl_3$, 400 MHz, 300 K).

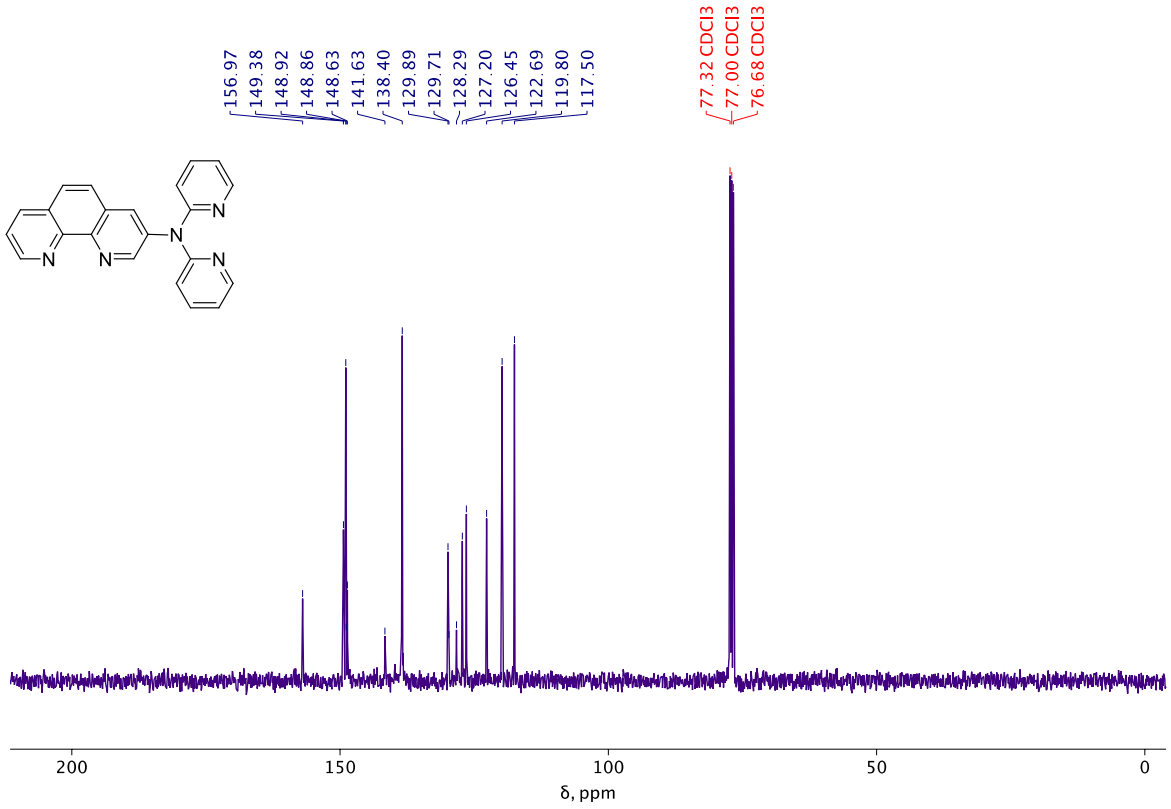


Figure S59. ^{13}C NMR spectrum of **Phen-3NPy$_2$** ($CDCl_3$, 100.6 MHz, 300 K).

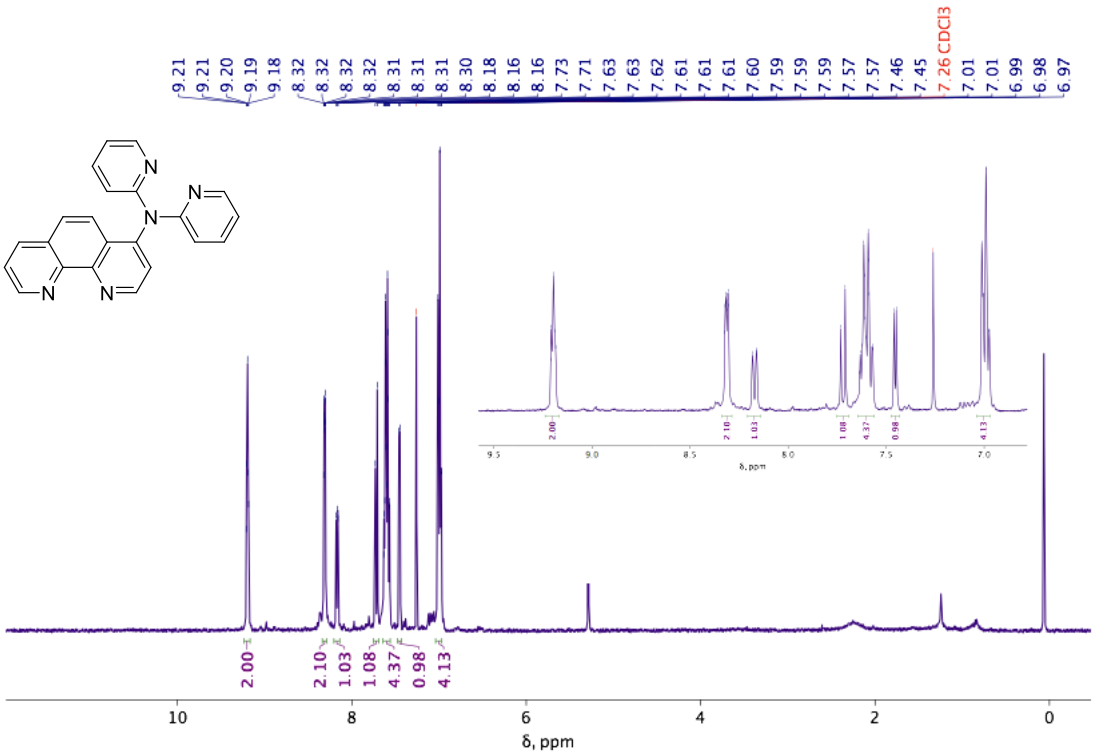


Figure S60. ^{1}H NMR spectrum of **Phen-4NPy$_2$** ($CDCl_3$, 400 MHz, 300 K).

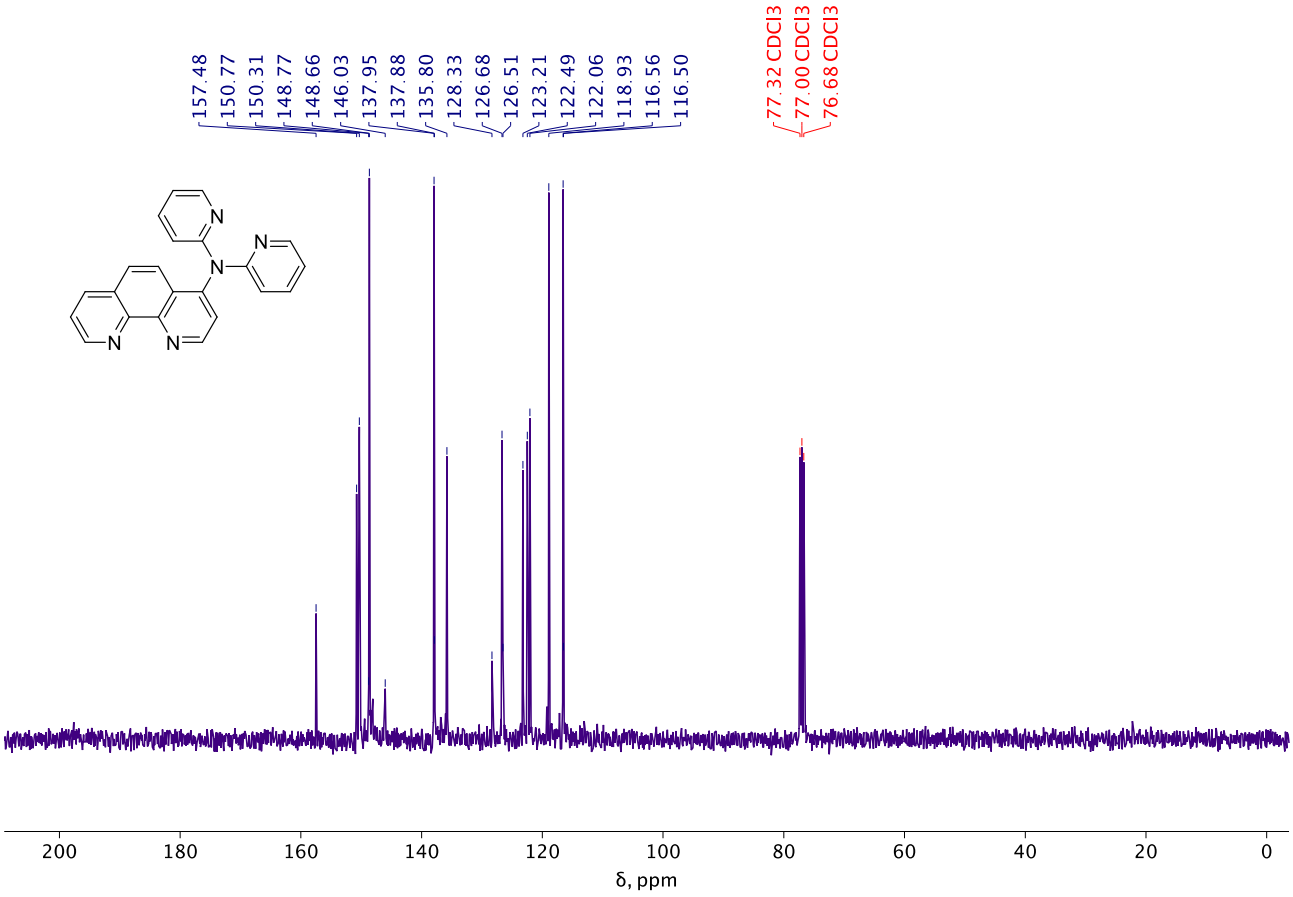


Figure S61. ^{13}C NMR spectrum of **Phen-4NPy$_2$** ($CDCl_3$, 100.6 MHz, 300 K).

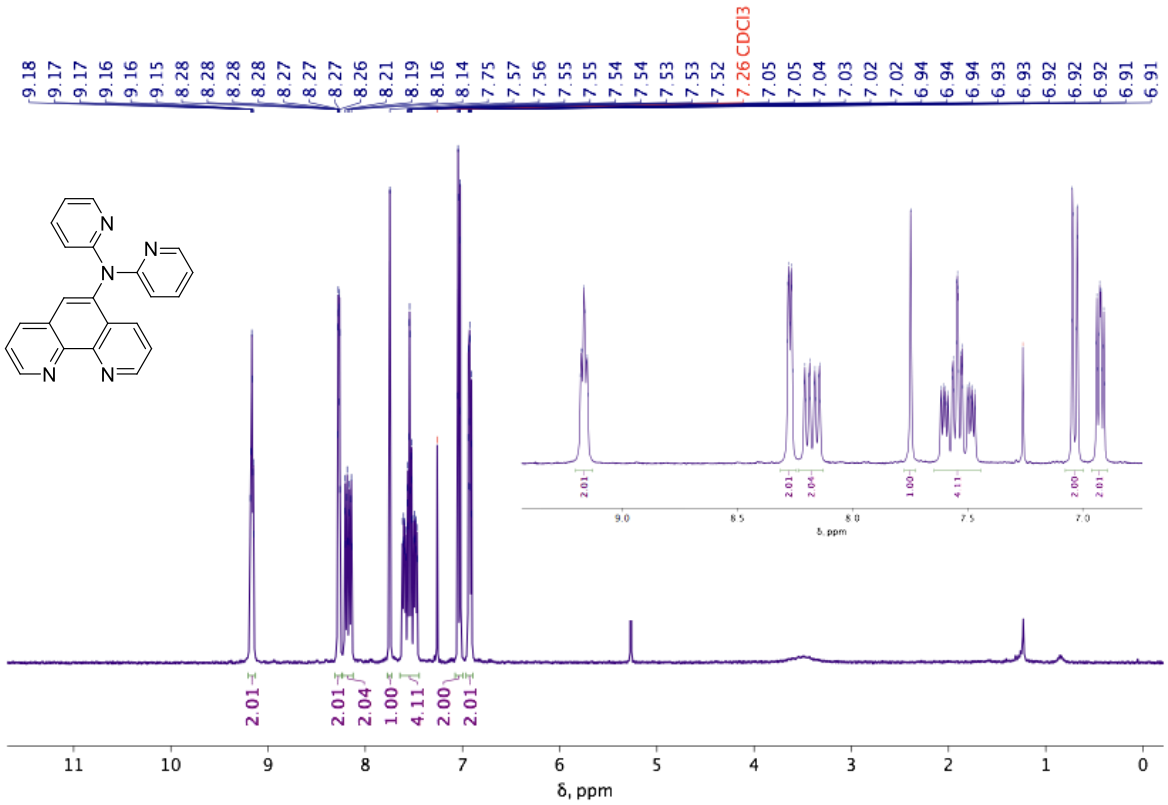


Figure S62. ^{1}H NMR spectrum of **Phen-5NPy$_2$** ($CDCl_3$, 400 MHz, 300 K).

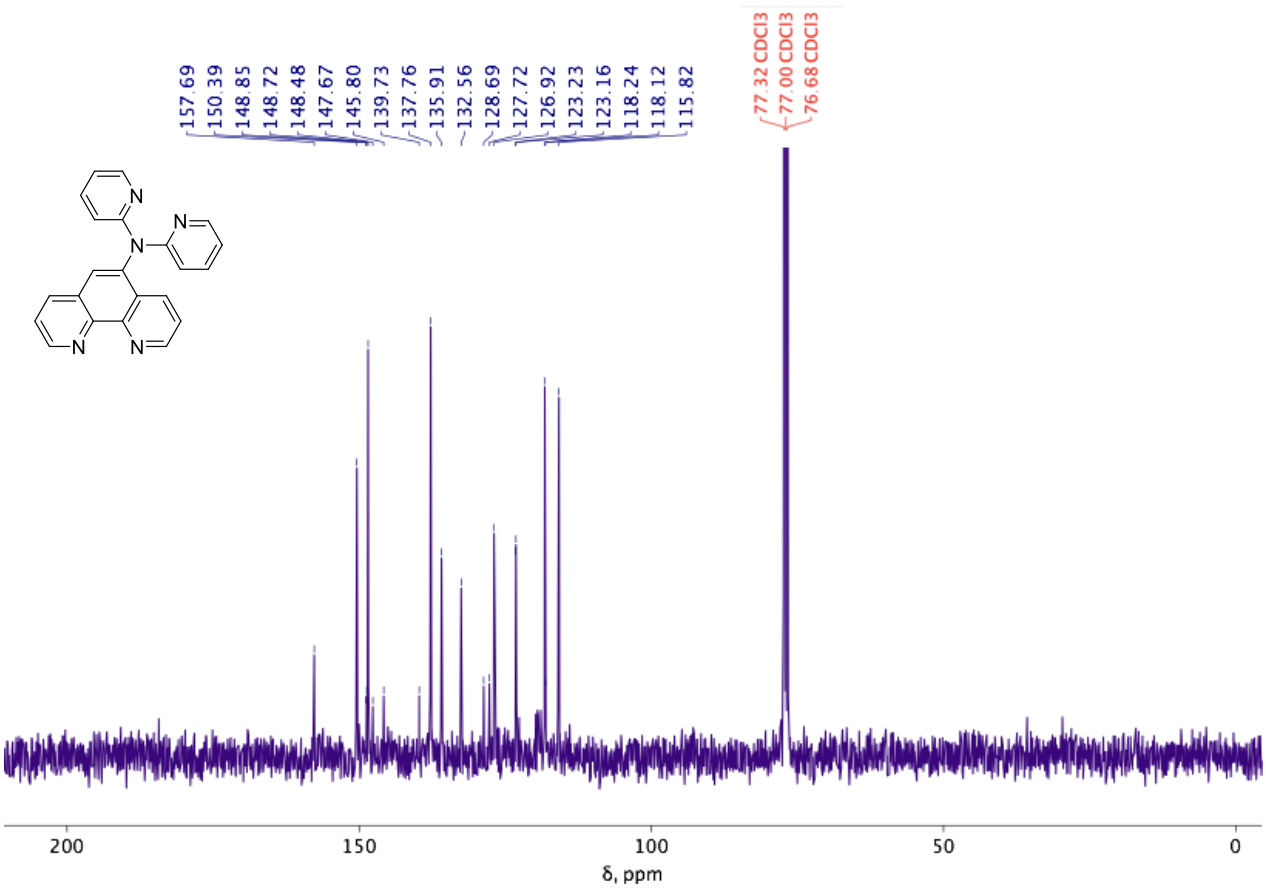


Figure S63. ^{13}C NMR spectrum of **Phen-5NPy$_2$** ($CDCl_3$, 100.6 MHz, 300 K).

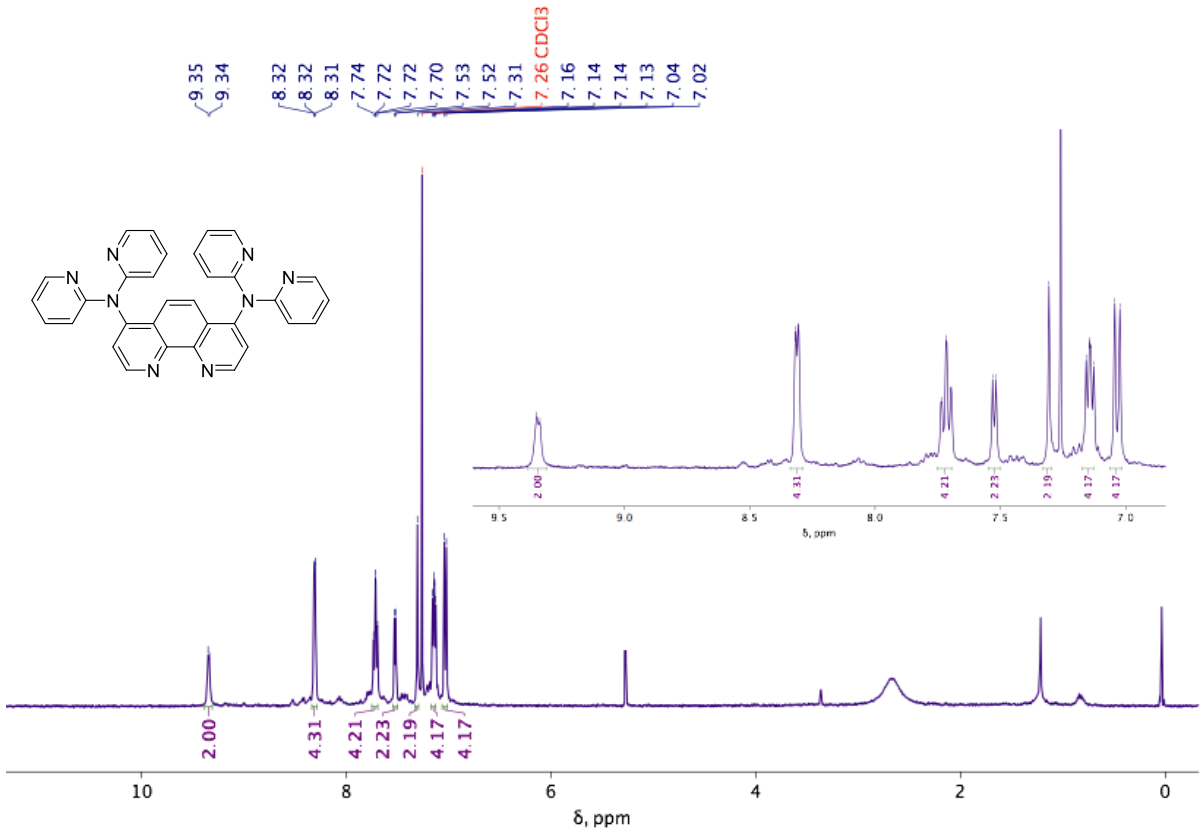


Figure S64. ^{1}H NMR spectrum of **Phen-4,7(NPy$_2$)$_2$,** ($CDCl_3$, 400 MHz, 300 K).

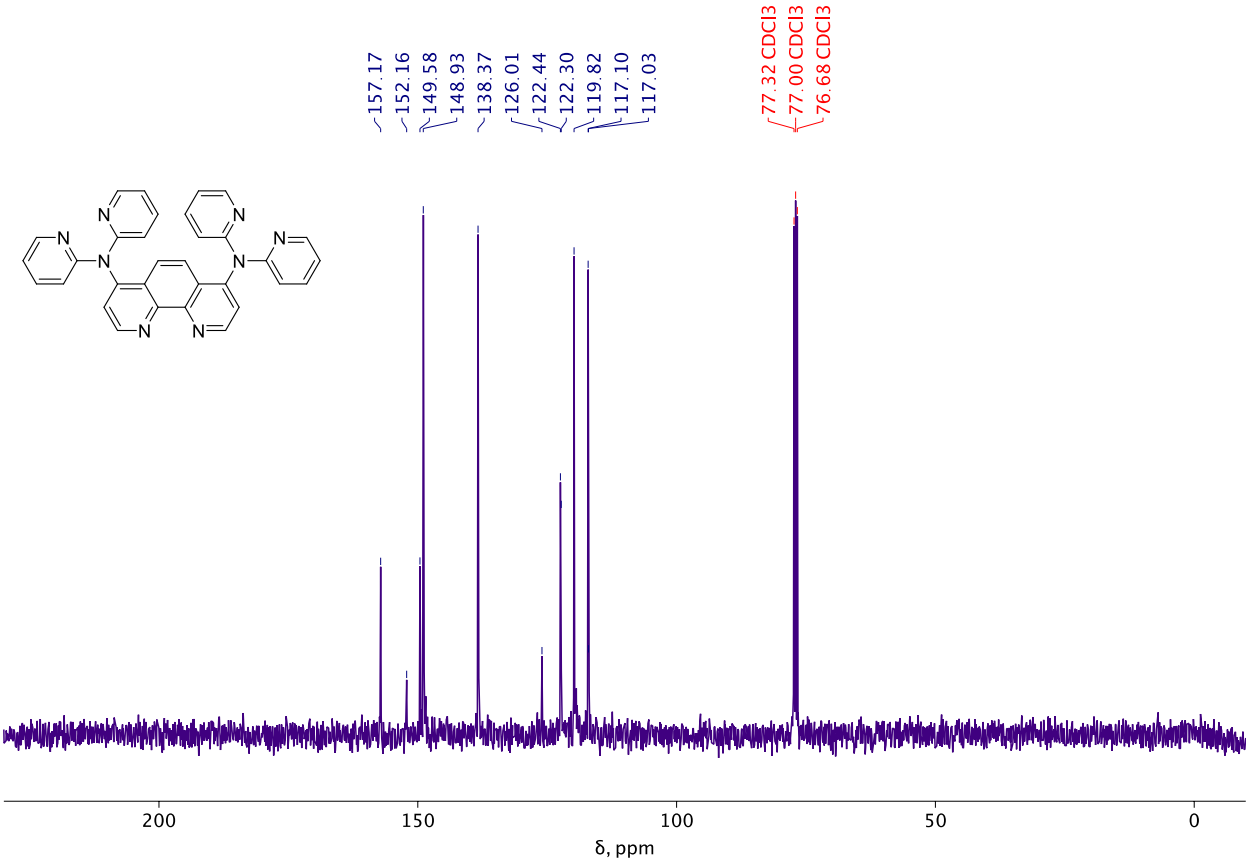


Figure S65. ^{13}C NMR spectrum of **Phen-4,7(NPy$_2$)$_2$** ($CDCl_3$, 100.6 MHz, 300 K).

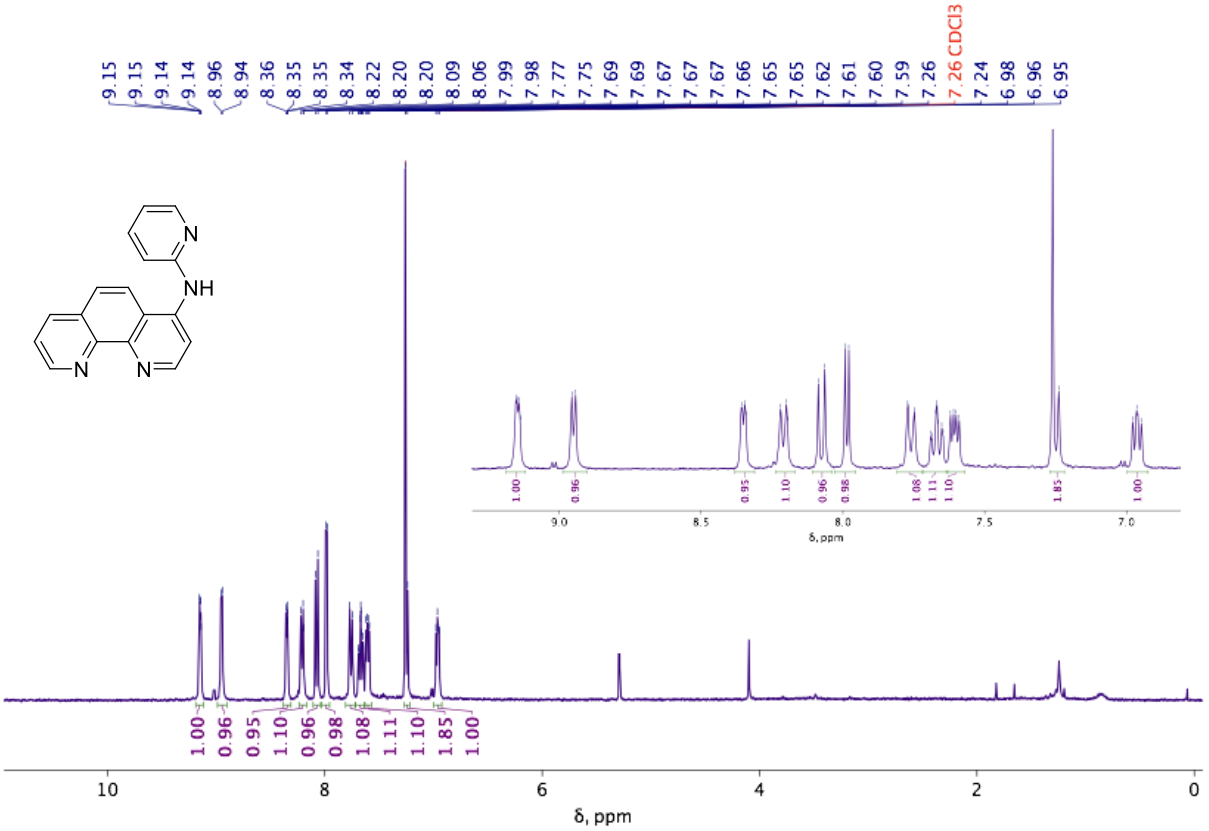


Figure S66. ^{1}H NMR spectrum of **Phen-4NPy** ($CDCl_3$, 400 MHz, 300 K).

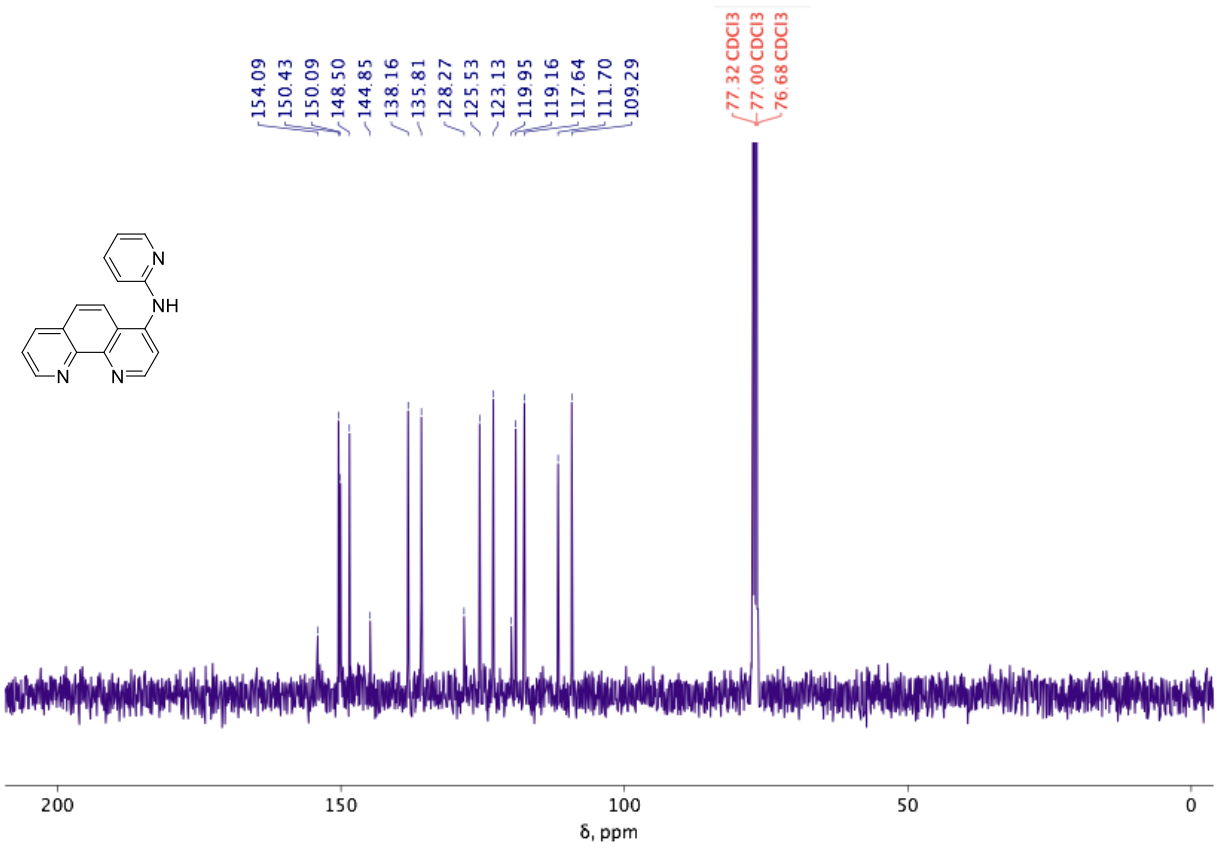


Figure S67. ^{13}C NMR spectrum of **Phen-4NPy** ($CDCl_3$, 100.6 MHz, 300 K).

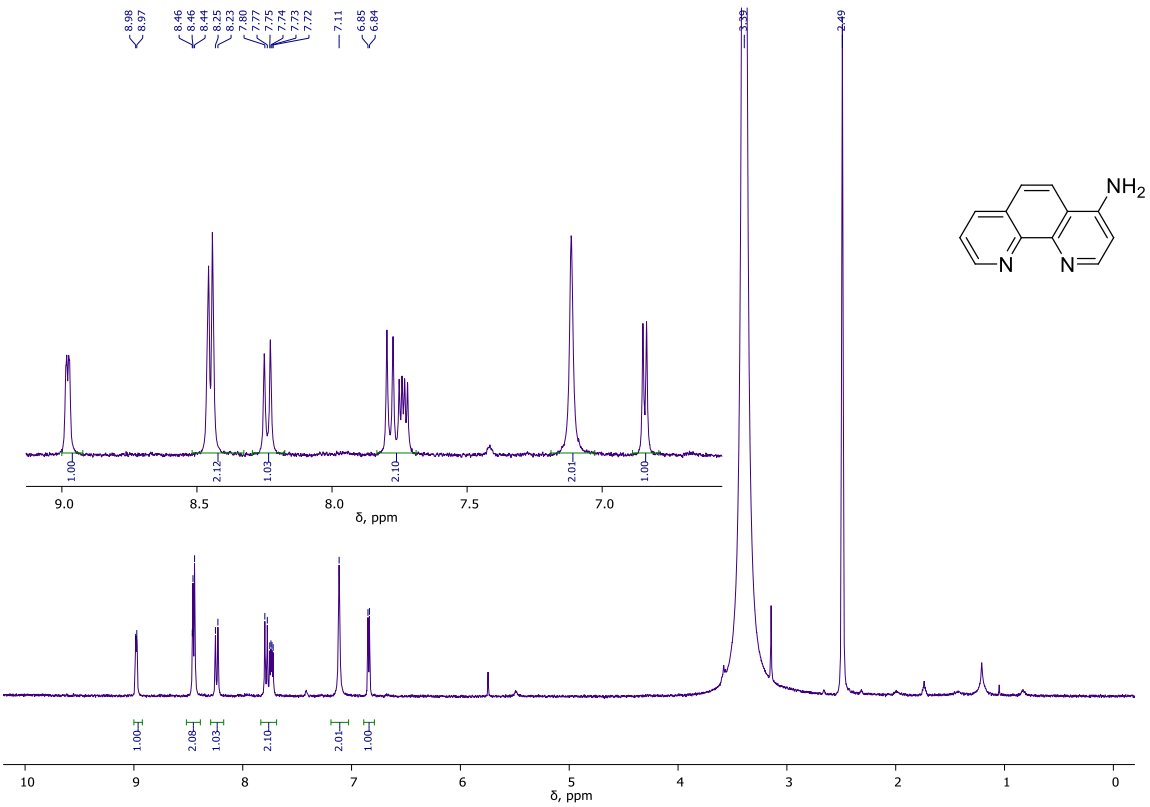


Figure S68. ^{1}H NMR spectrum of **Phen-4N** (DMSO-d6 – D_2O, 400 MHz, 300 K).

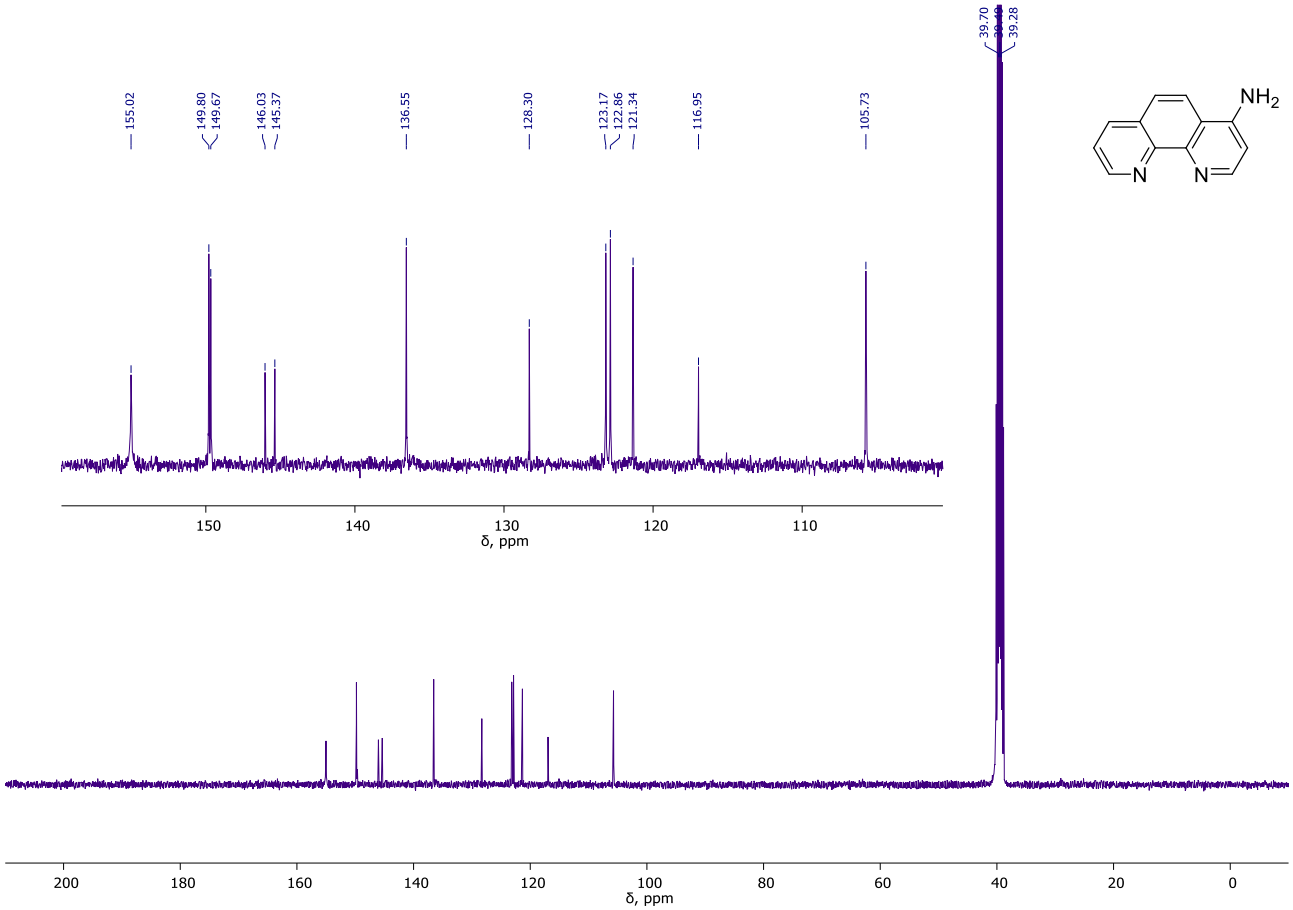


Figure S69. ^{13}C NMR spectrum of **Phen-4N** (DMSO-d6 – D_2O, 100.6 MHz, 300 K).

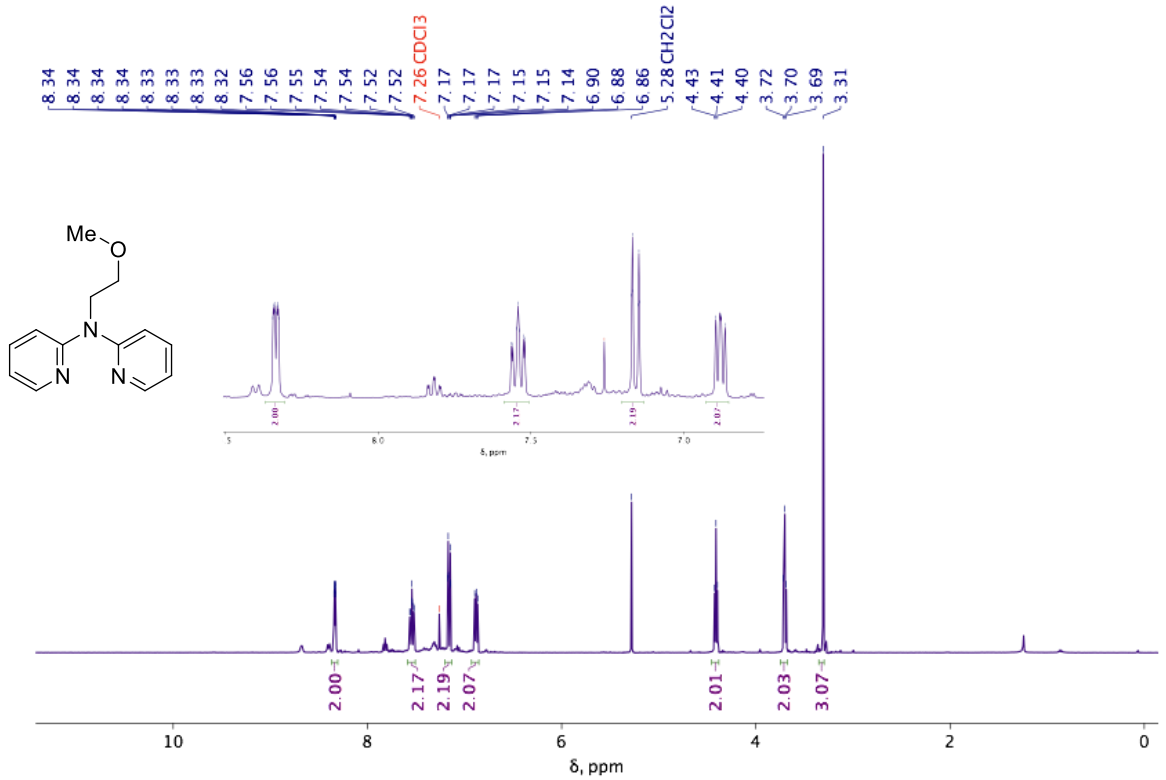


Figure S70. ^{1}H NMR spectrum of **NPy$_2$** ($CDCl_3$, 400 MHz, 300 K).

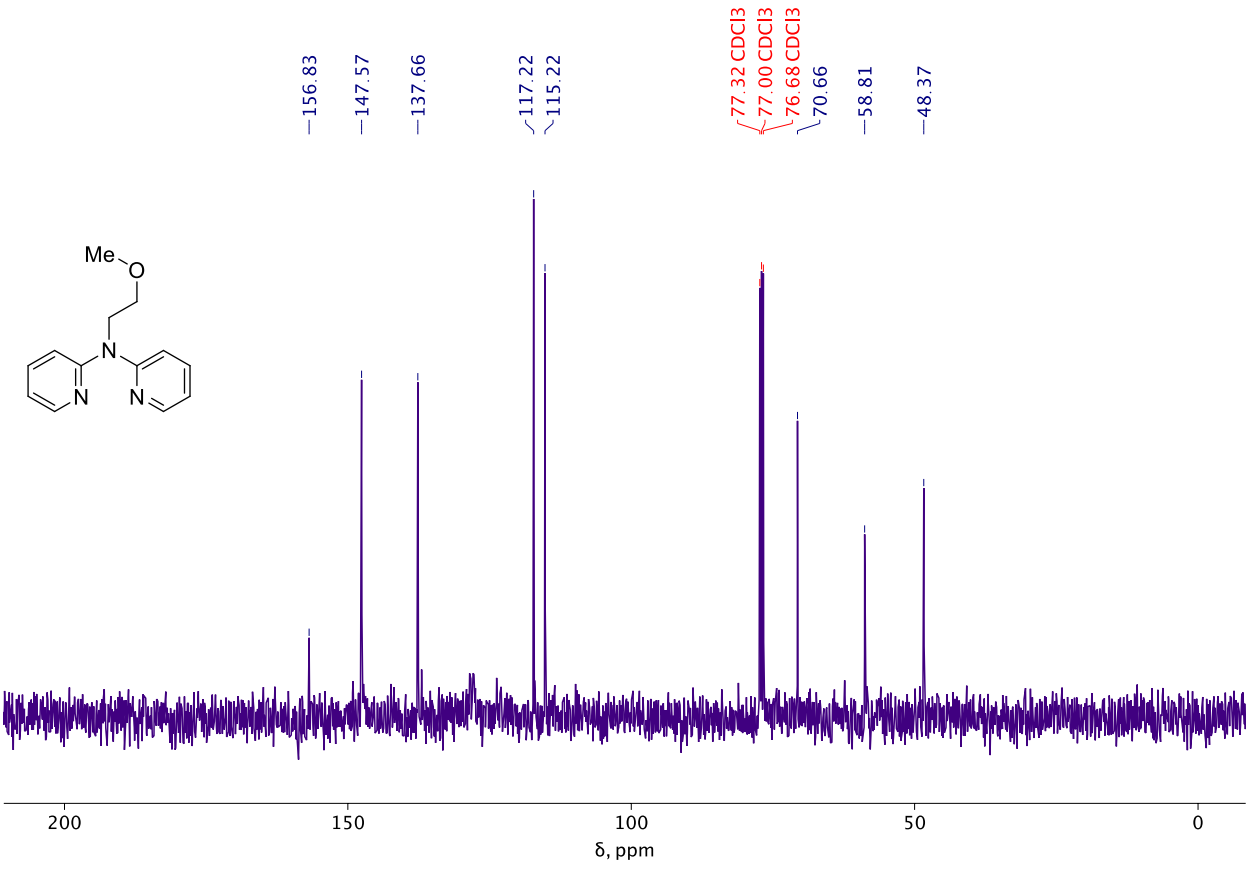


Figure S71. ^{13}C NMR spectrum of **NPy$_2$** ($CDCl_3$, 100.6 MHz, 300 K).

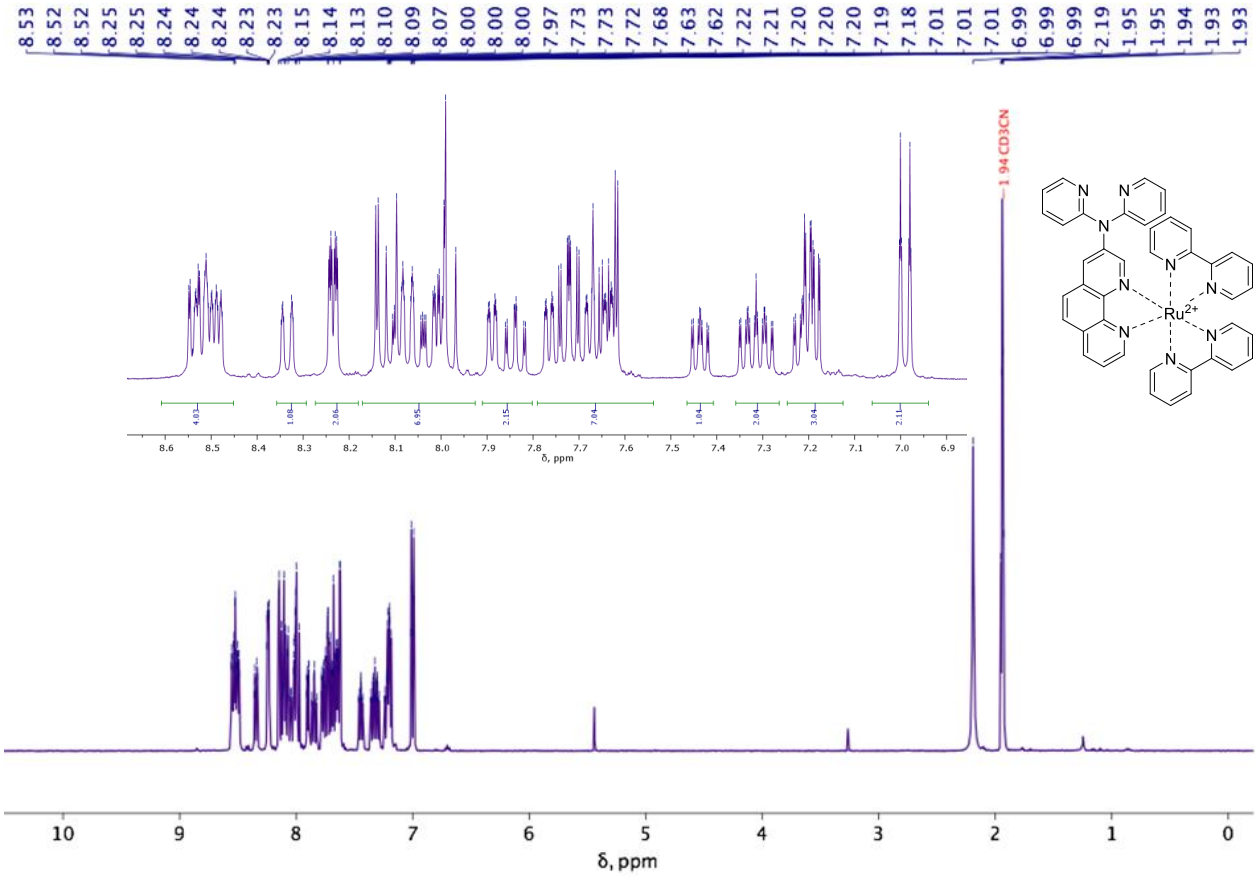


Figure S72. ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)** (CD_3CN, 400 MHz, 300 K).

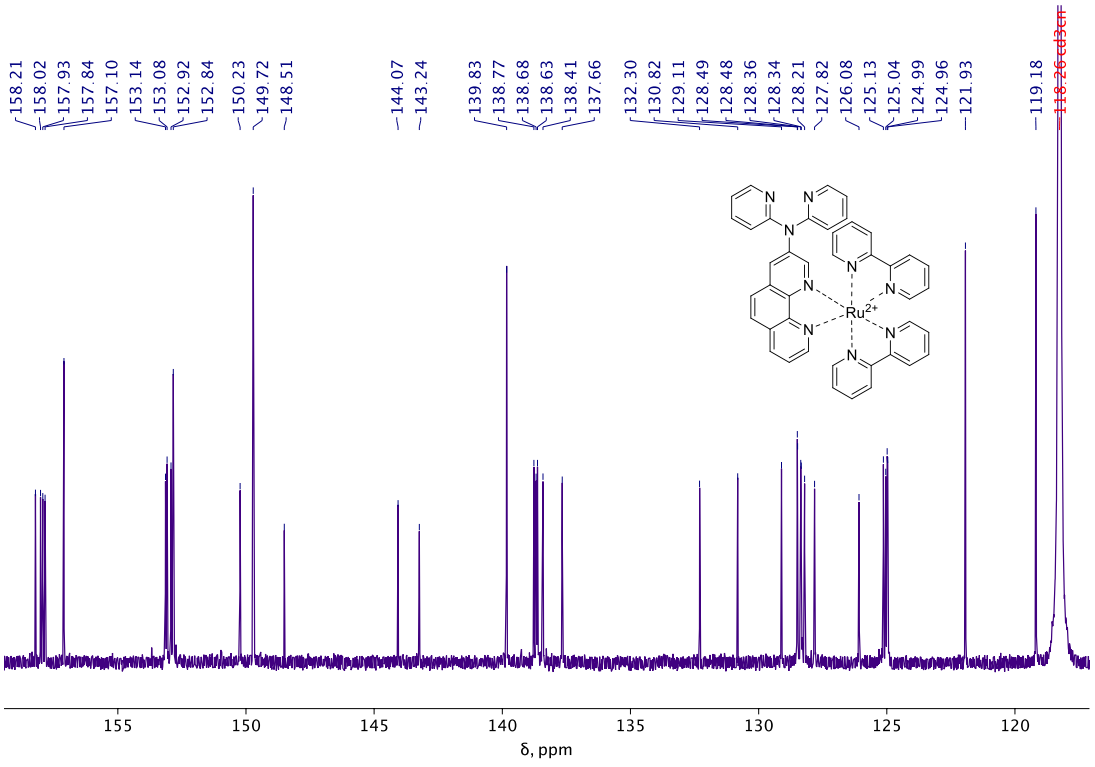


Figure S73. ^{13}C NMR spectrum of **Ru(Phen-3NPy$_2$)** (CD_3CN, 100.6 MHz, 300 K).

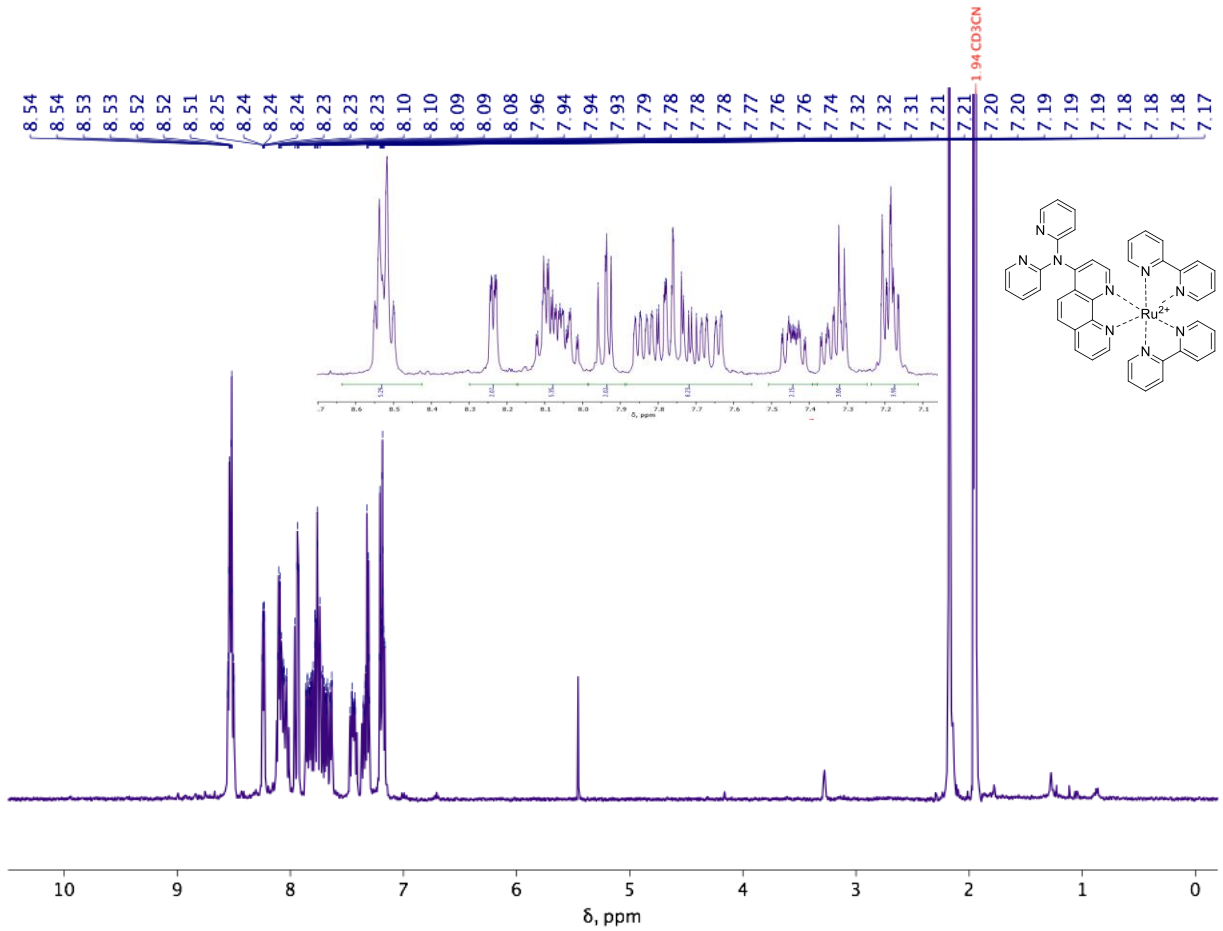


Figure S74. ^{1}H NMR spectrum of **Ru(Phen-4NPy$_2$)** (CD_3CN, 400 MHz, 300 K).

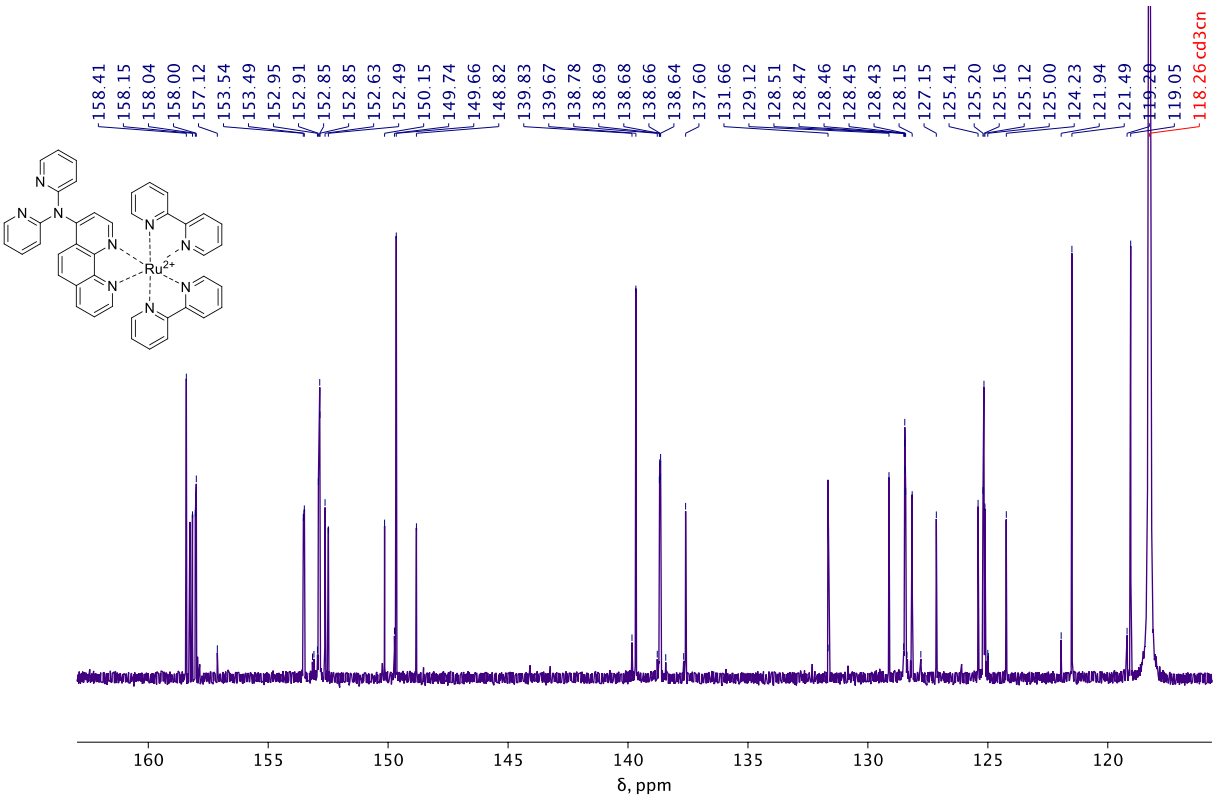


Figure S75. ^{13}C NMR spectrum of **Ru(Phen-4NPy$_2$)** (CD_3CN, 100.6 MHz, 300 K).

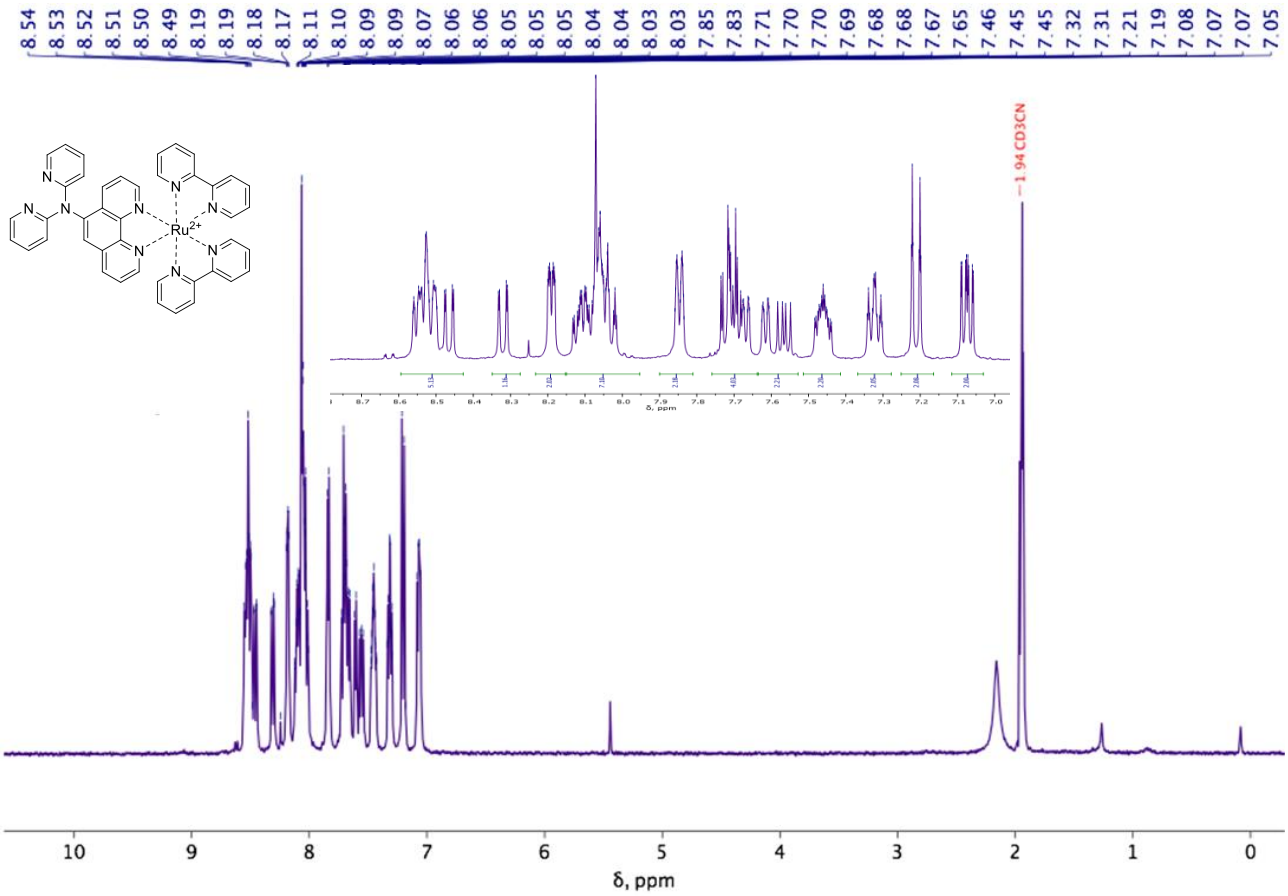


Figure S76. ^{1}H NMR spectrum of **Ru(Phen-5NPy$_2$)** (CD_3CN, 400 MHz, 300 K).

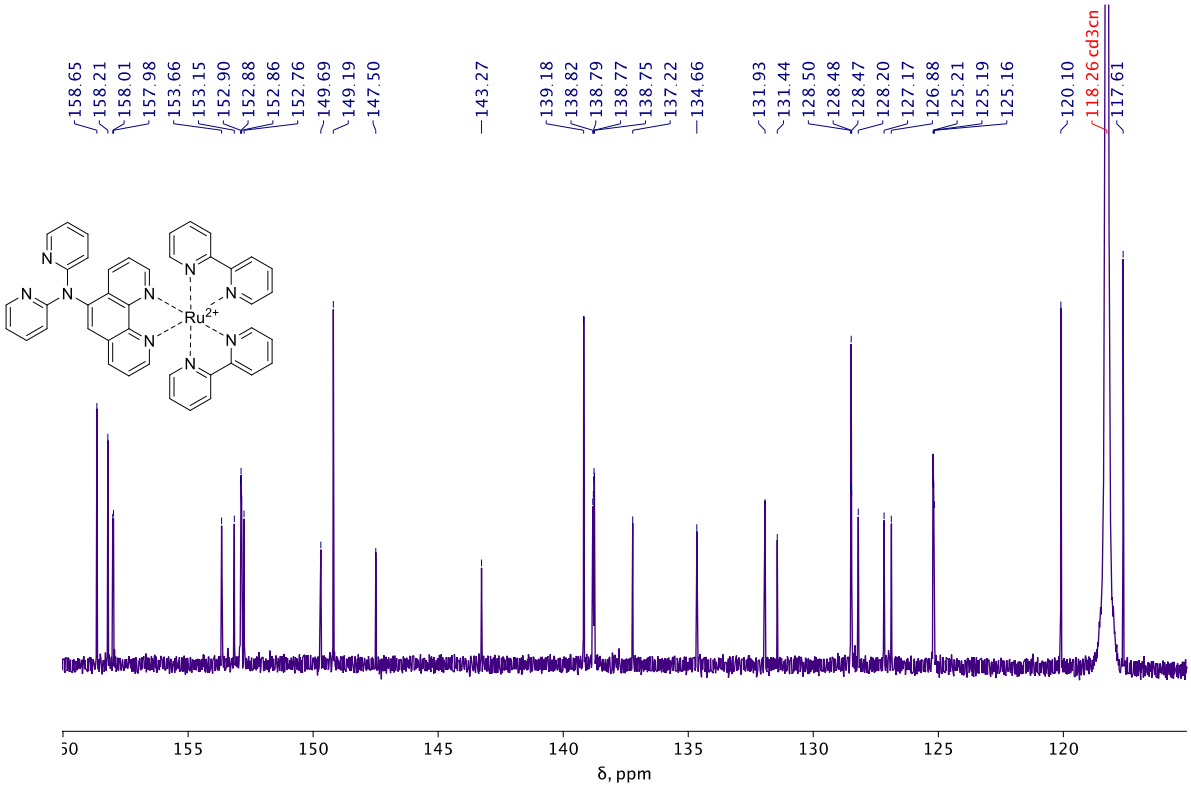


Figure S77. ^{13}C NMR spectrum of **Ru(Phen-5NPy$_2$)** (CD_3CN, 100.6 MHz, 300 K).

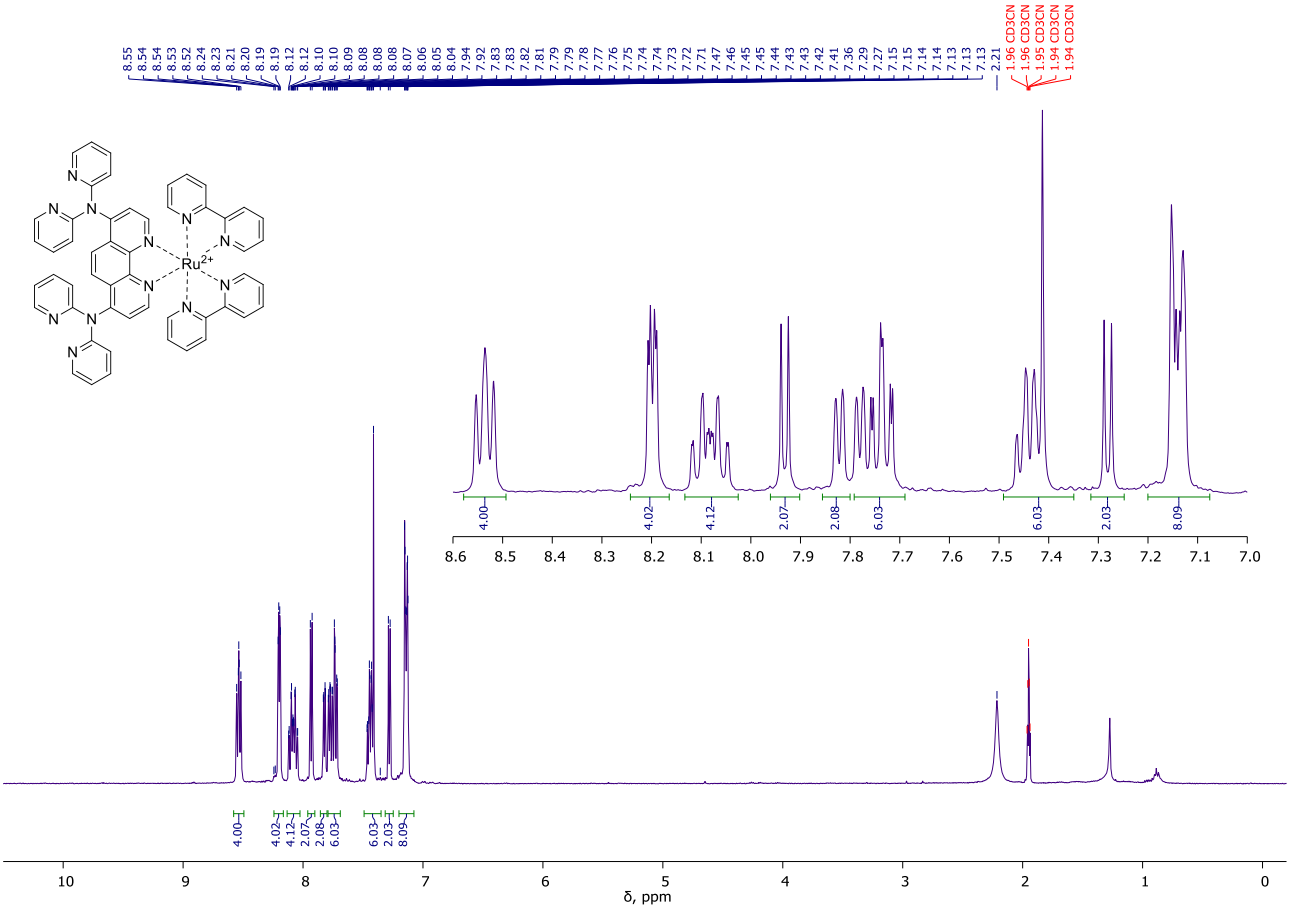


Figure S78. ^{1}H NMR spectrum of **Ru[Phen-4,7(NPy$_2$)$_2$]** (CD_3CN, 400 MHz, 300 K).

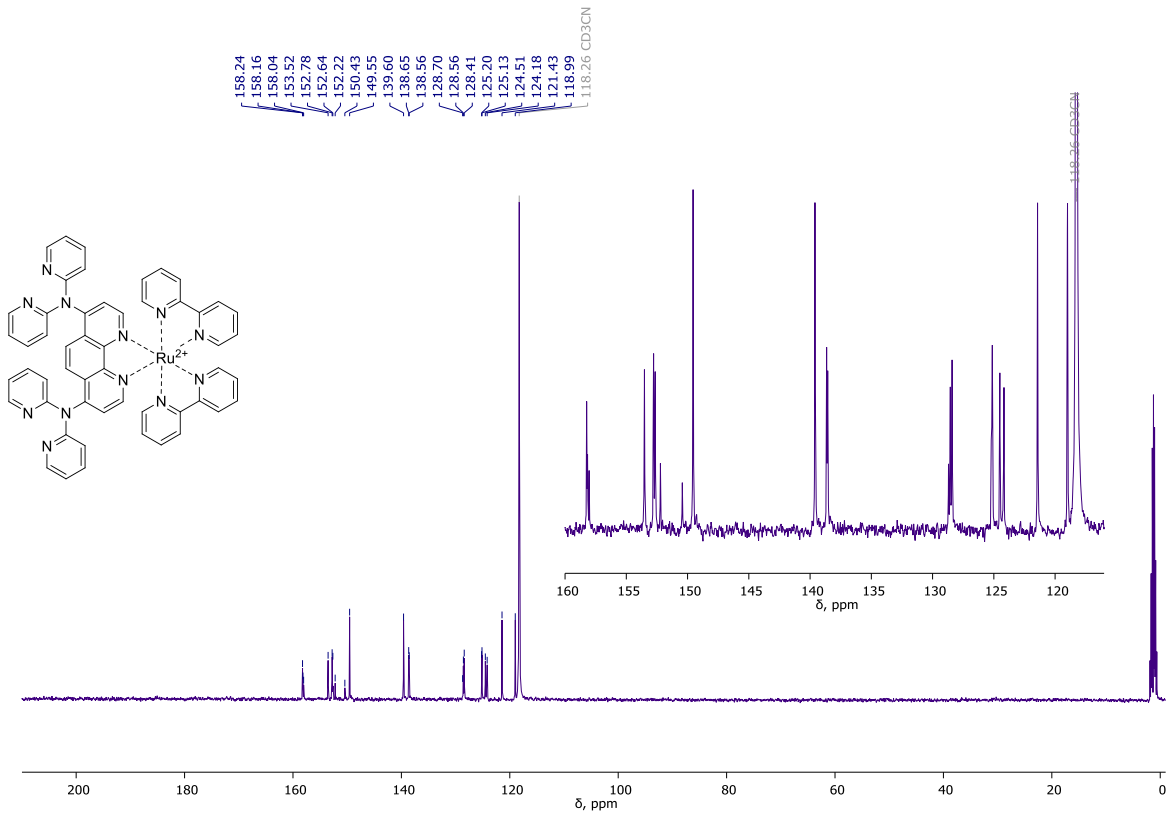


Figure S79. ^{13}C NMR spectrum of **Ru[Phen-4,7(NPy$_2$)$_2$]** (CD_3CN, 100.6 MHz, 300 K).

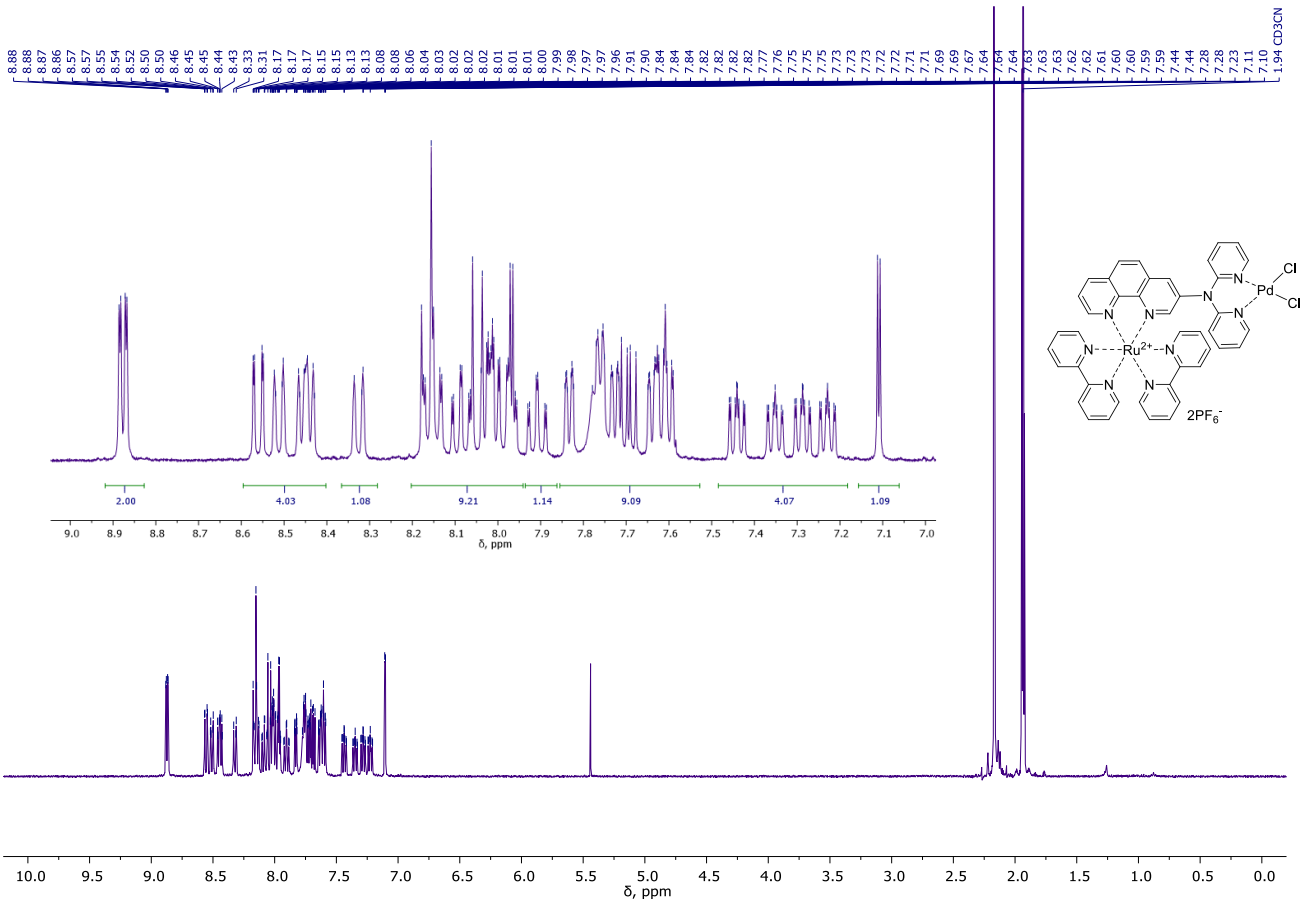


Figure S80. ^{1}H NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (CD_3CN, 400 MHz, 300 K).

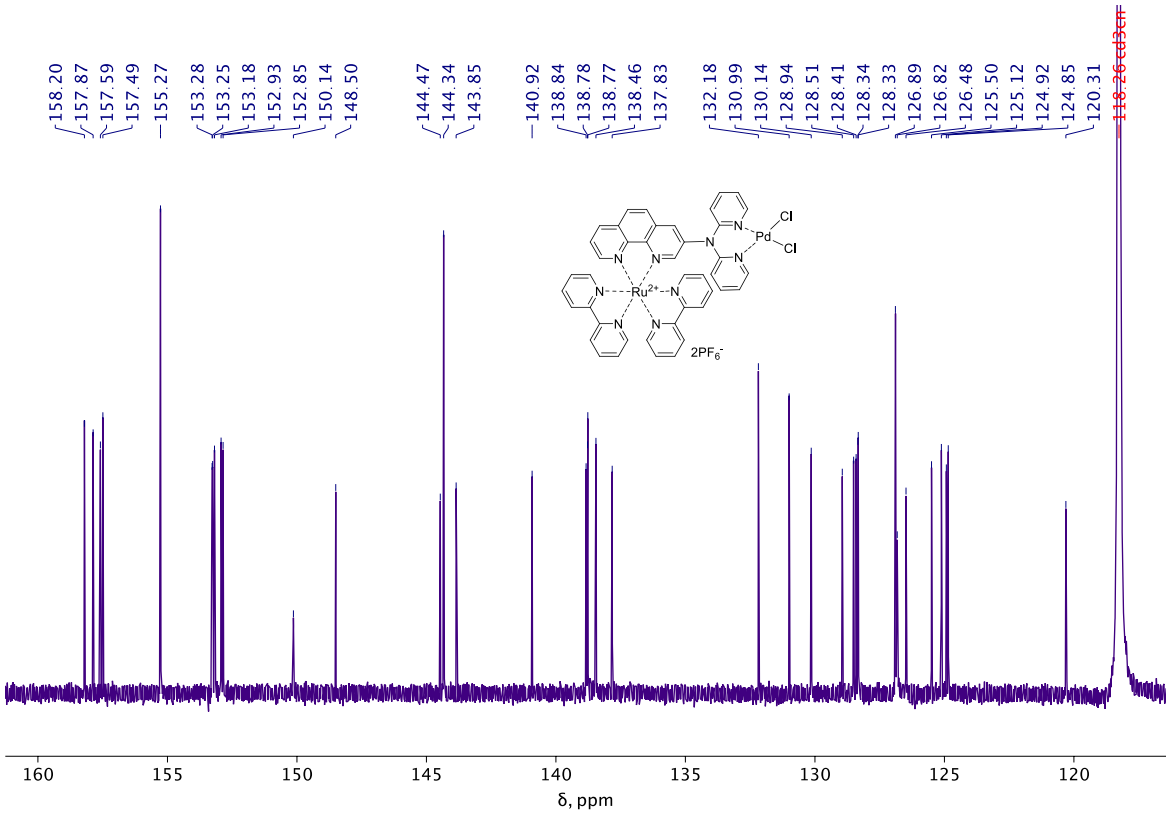


Figure S81. ^{13}C NMR spectrum of **Ru(Phen-3NPy$_2$)Pd** (CD_3CN, 100.6 MHz, 300 K).

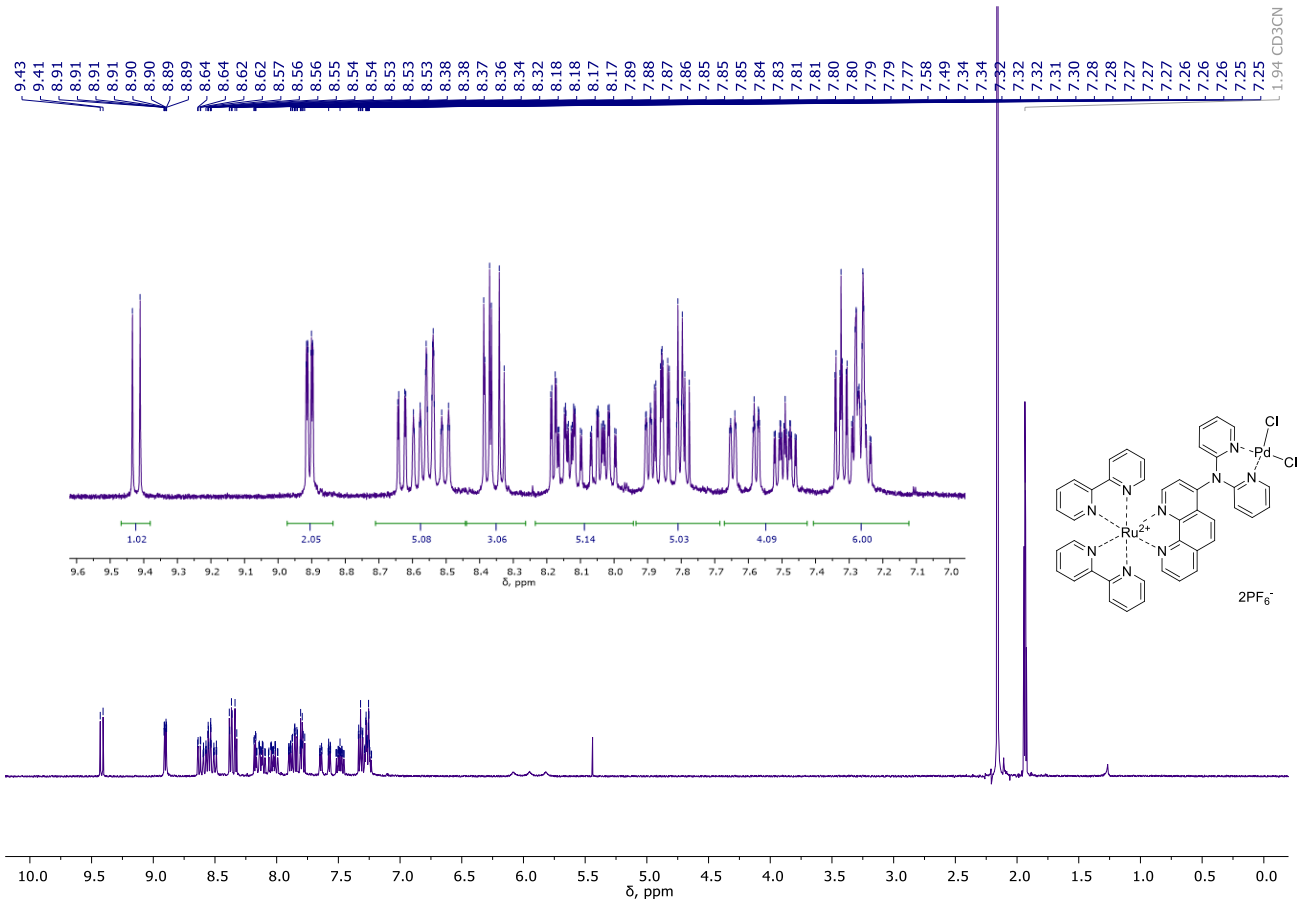


Figure S82. ^{1}H NMR spectrum of **Ru(Phen-4NPy$_2$)Pd** (CD_3CN, 400 MHz, 300 K).

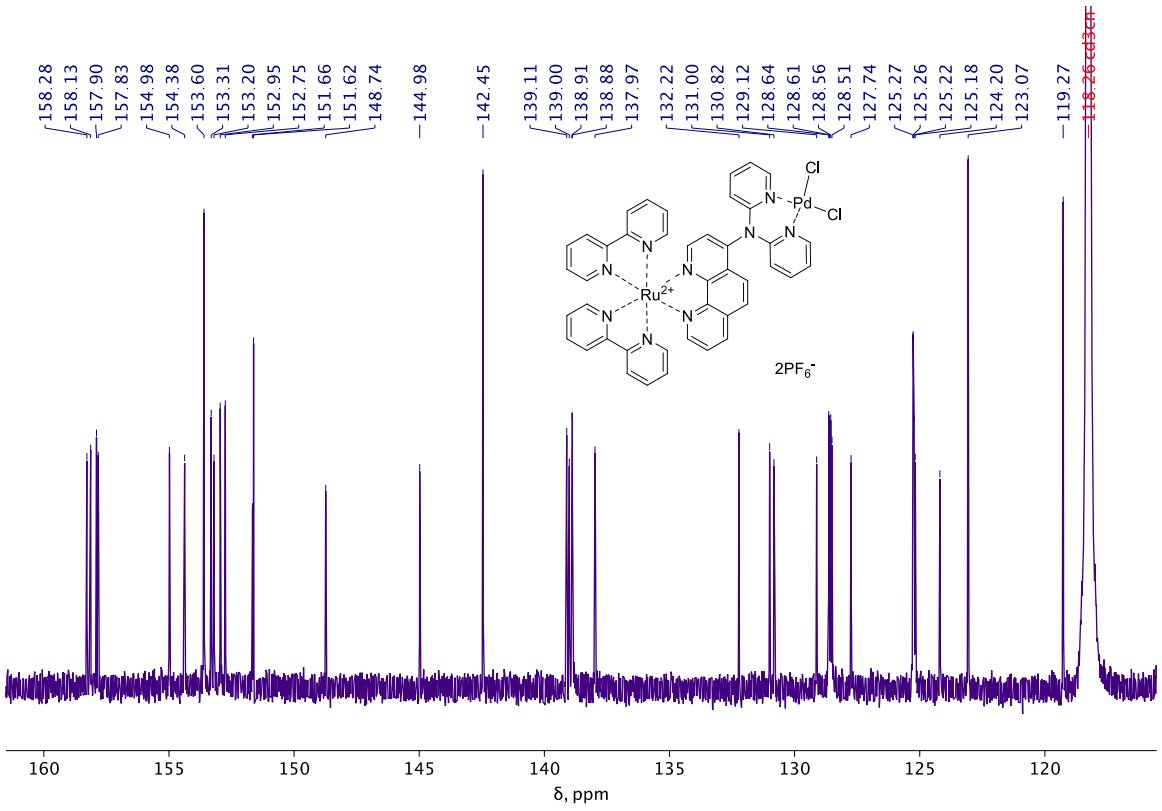


Figure S83. ^{13}C NMR spectrum of **Ru(Phen-4NPy$_2$)Pd** (CD_3CN, 100.6 MHz, 300 K).

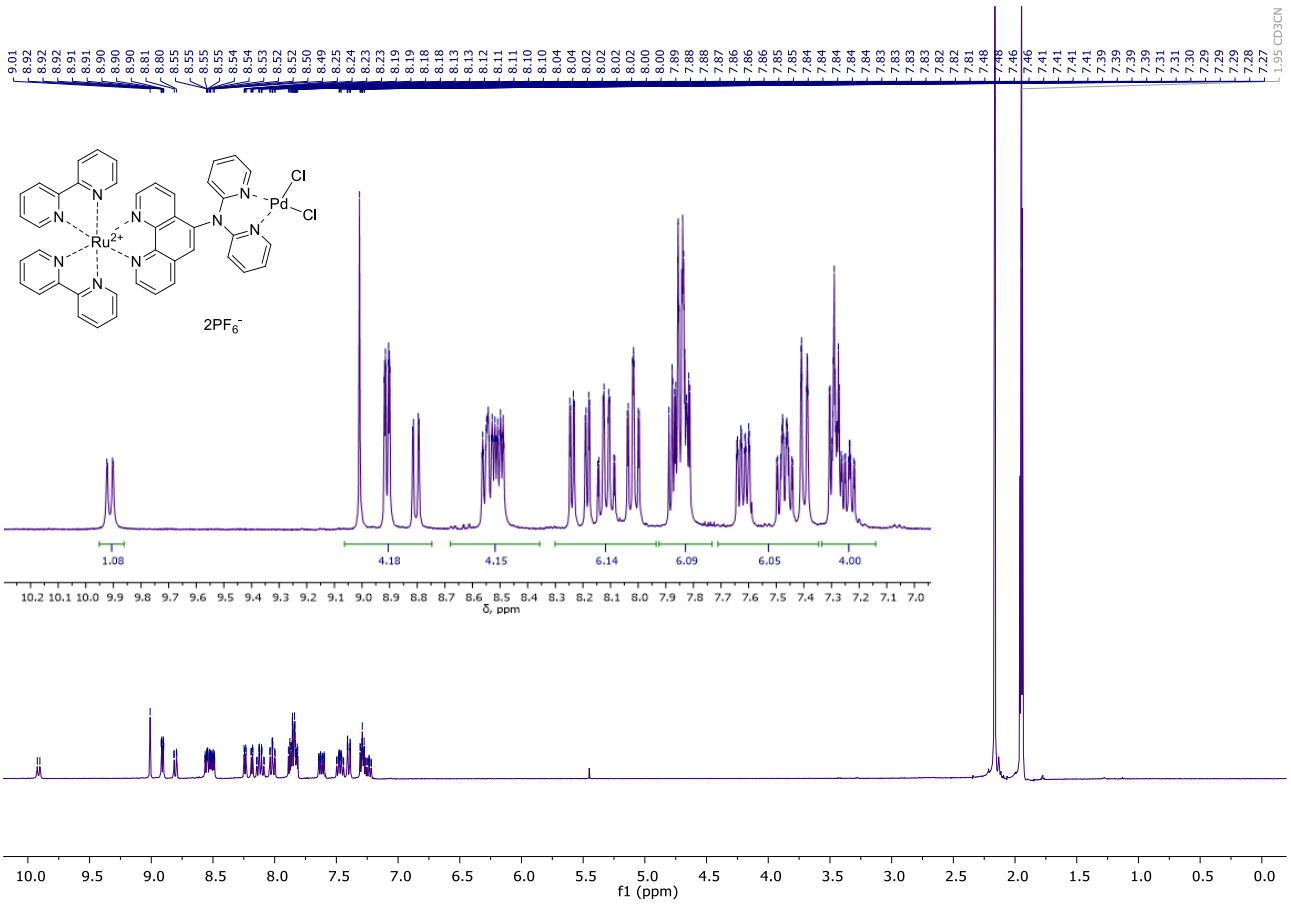


Figure S84. ^{1}H NMR spectrum of **Ru(Phen-5NPy$_2$)Pd** (CD_3CN, 400 MHz, 300 K).

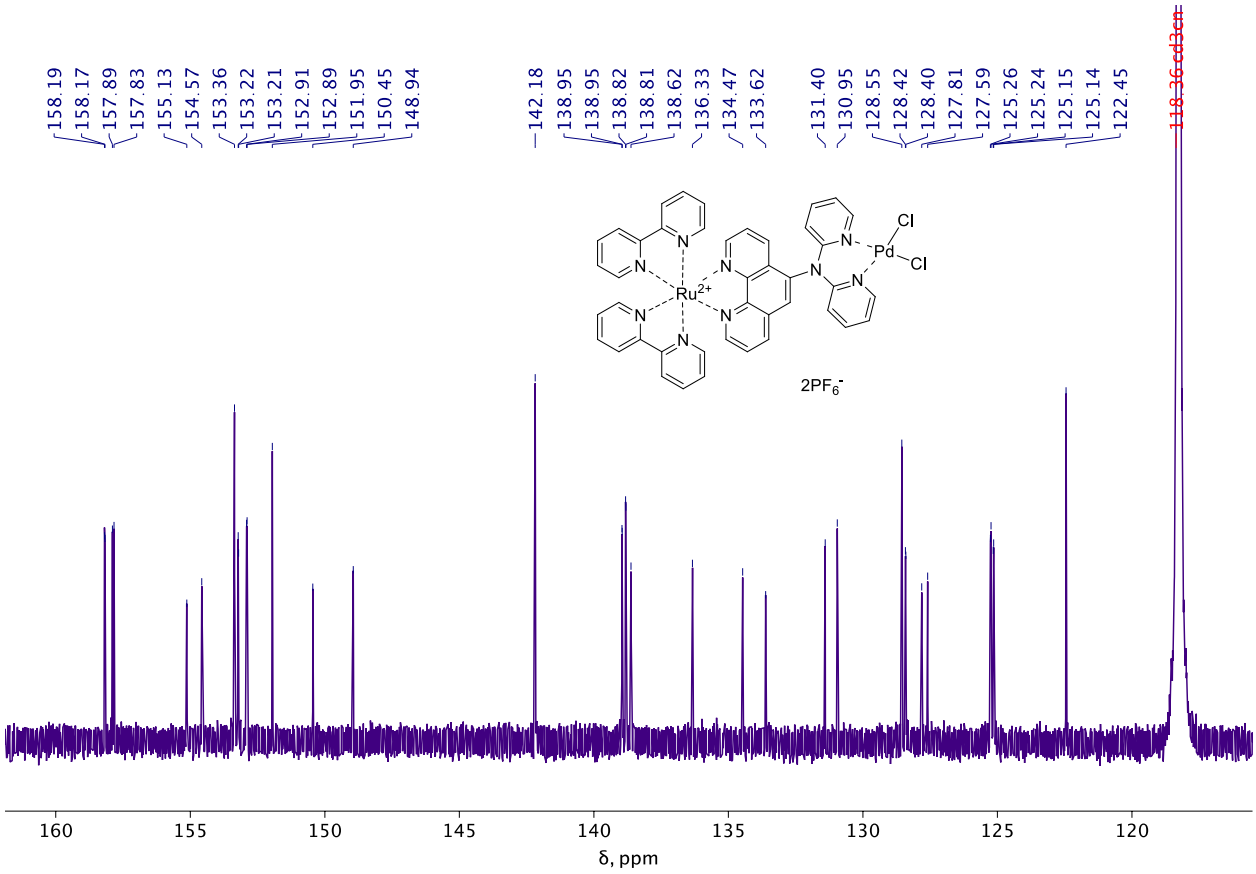


Figure S85. ^{13}C NMR spectrum of **Ru(Phen-5NPy$_2$)Pd** (CD_3CN, 100.6 MHz, 300 K).

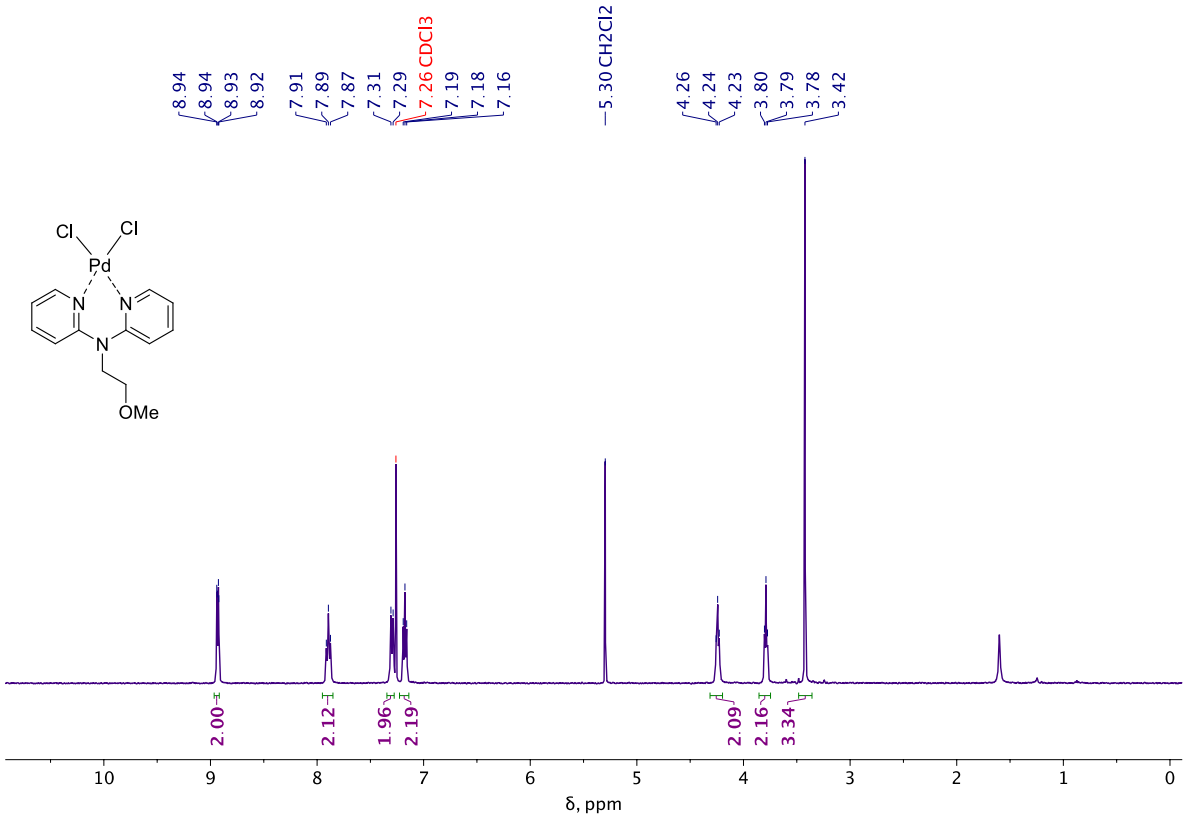


Figure S86. ^{1}H NMR spectrum of **(NPy$_2$)Pd** ($CDCl_3$, 400 MHz, 300 K).

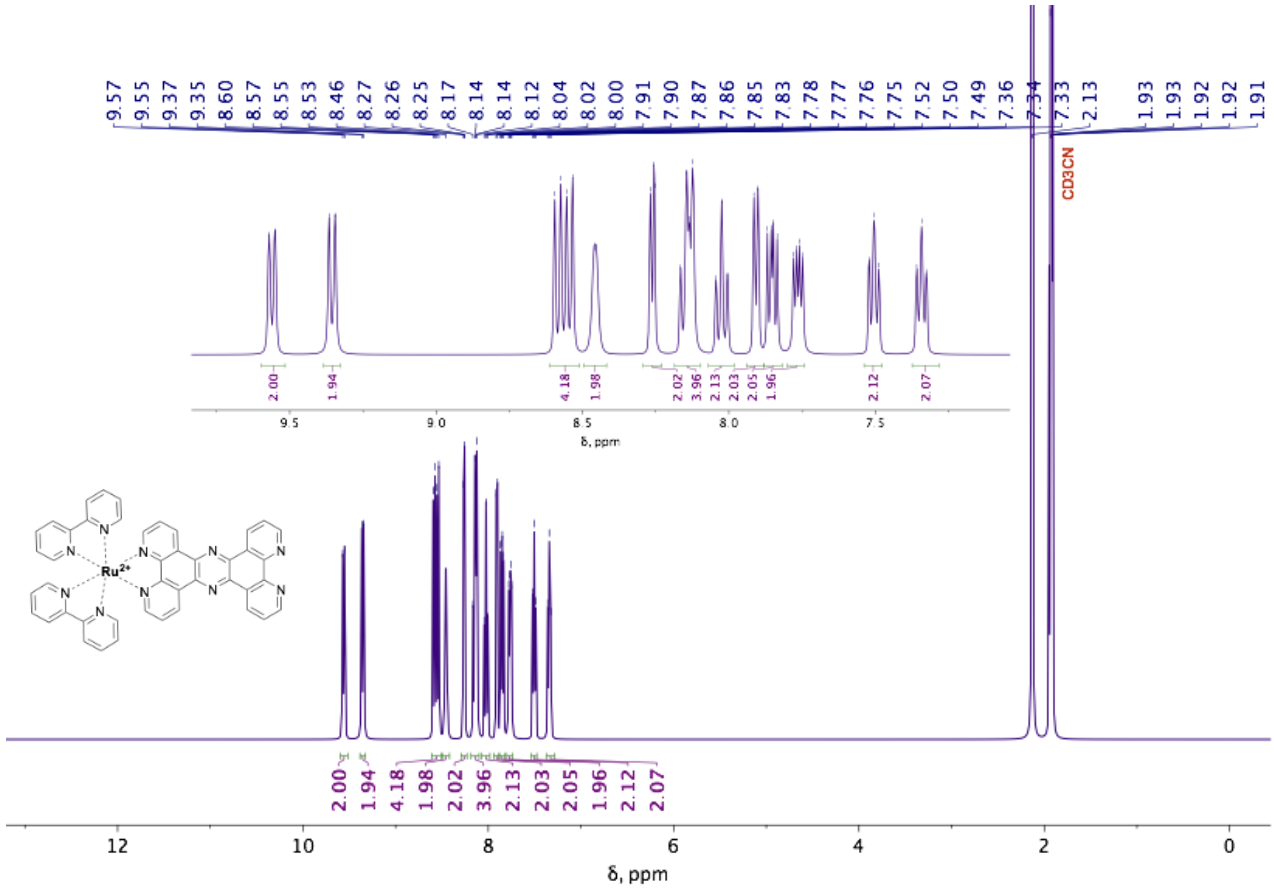


Figure S87. ^{1}H NMR spectrum of **Ru(tpphz)** (CD_3CN, 400 MHz, 300 K).

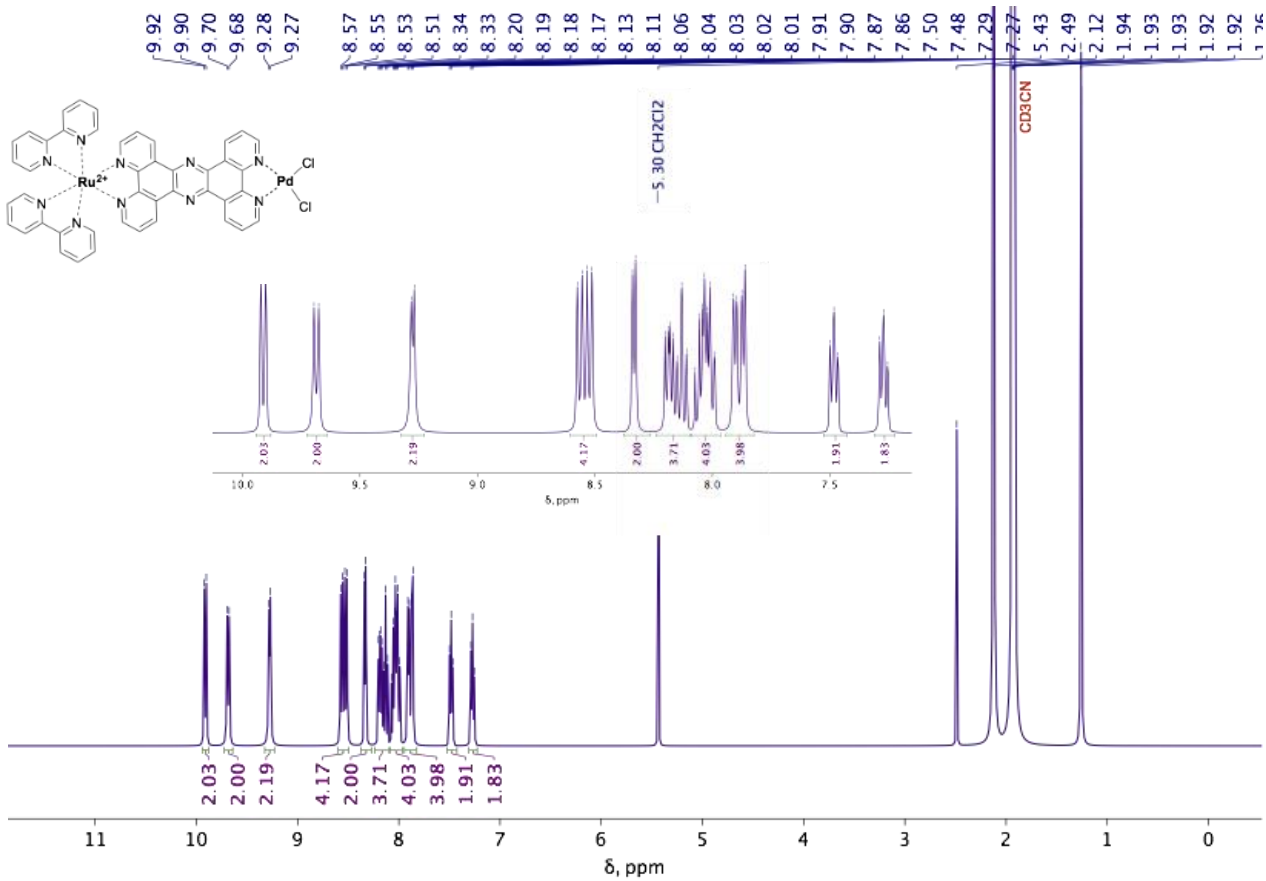


Figure S88. ^{1}H NMR spectrum of **Ru(tpphz)Pd** (CD_3CN, 400 MHz, 300 K).

10. Mass-spectra of the complexes

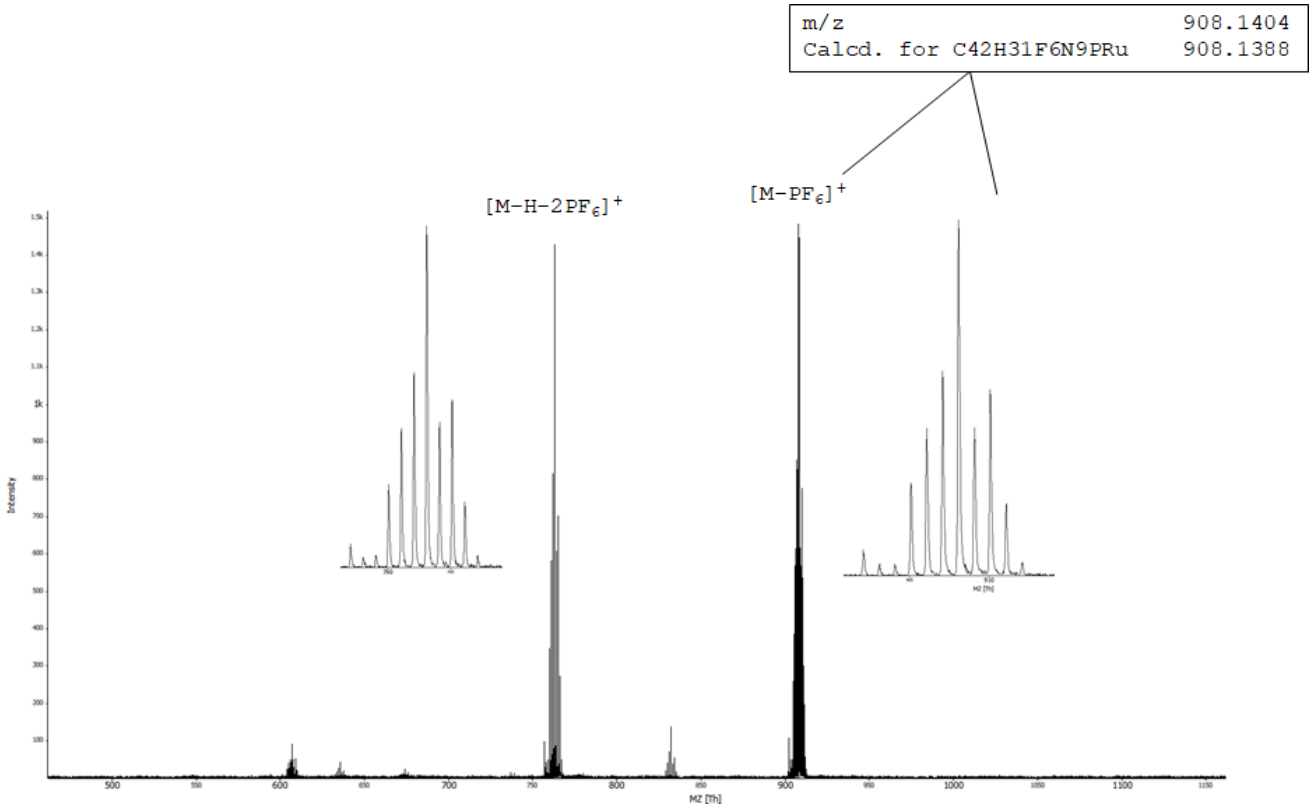


Figure S89. Mass-spectrum (MALDI-TOF) of the complex **Ru(Phen-5NPy$_2$)**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

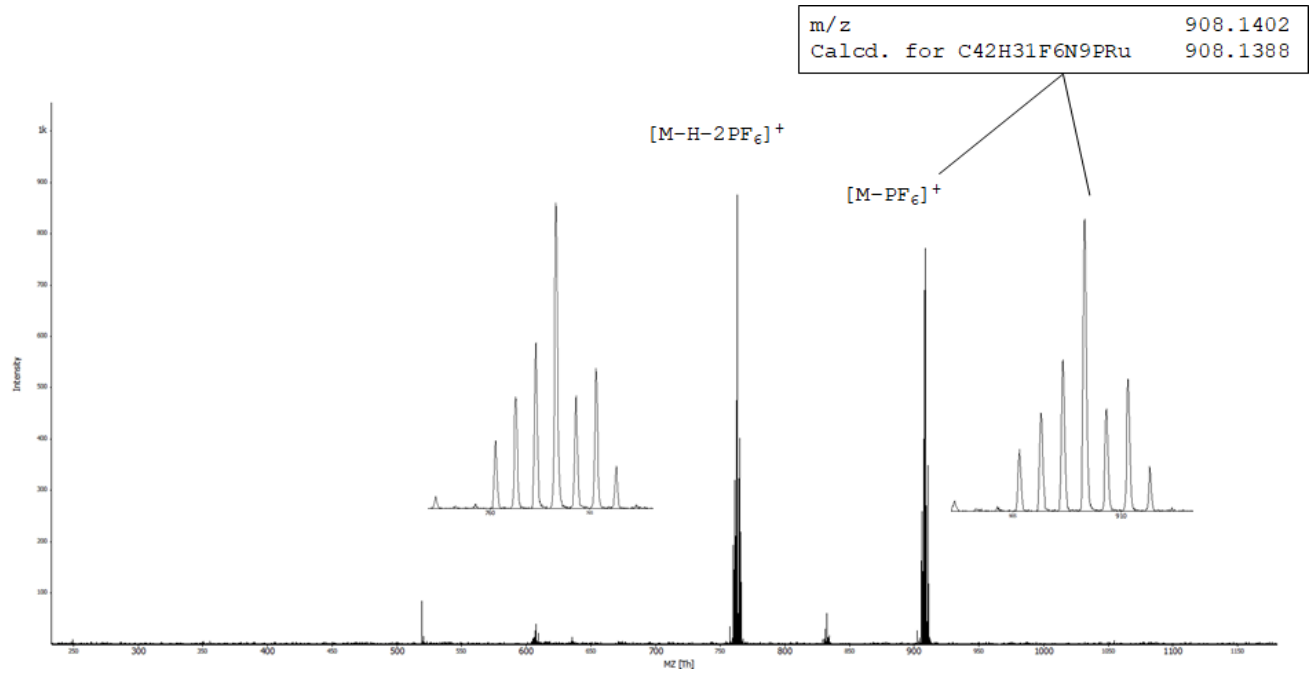


Figure S90. Mass-spectrum (MALDI-TOF) of the complex **Ru(Phen-4NPy$_2$)**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

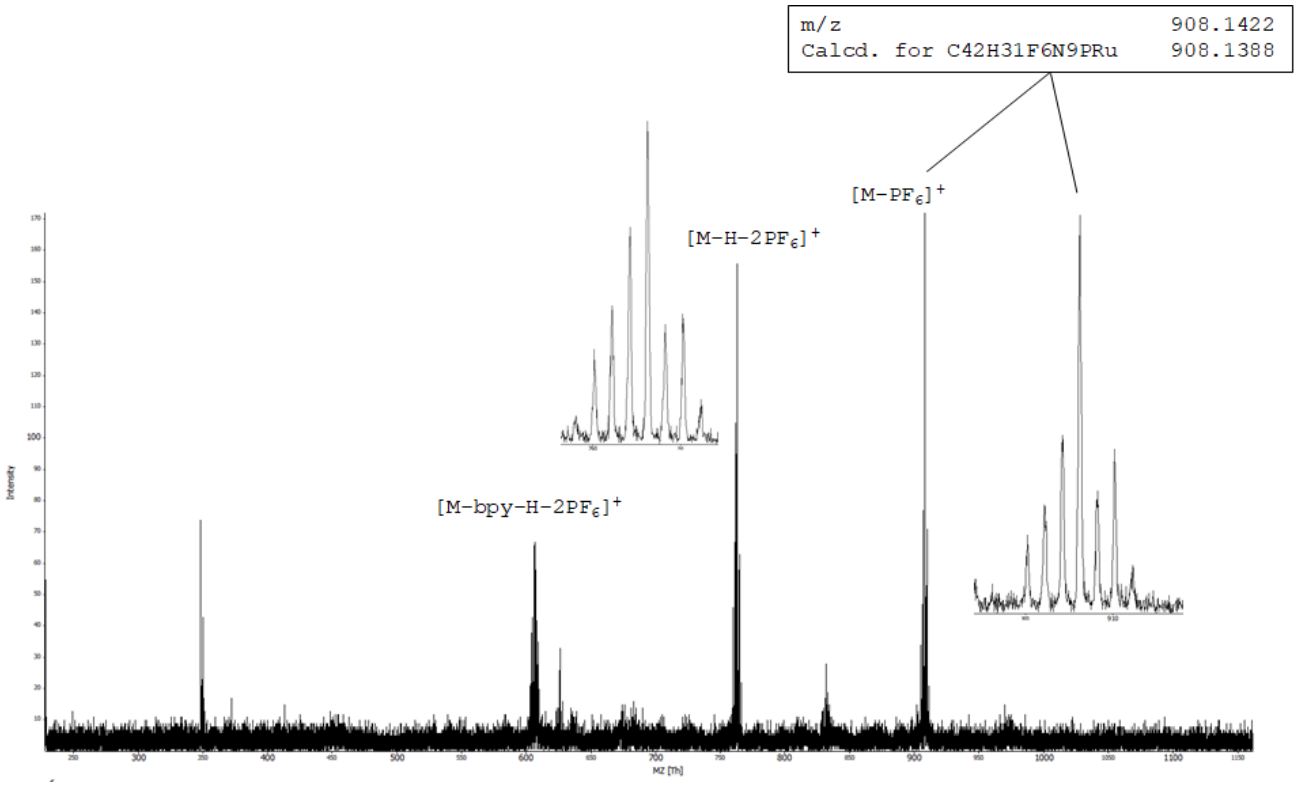


Figure S91. Mass-spectrum (MALDI-TOF) of the complex **Ru(Phen-3NPy$_2$)**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

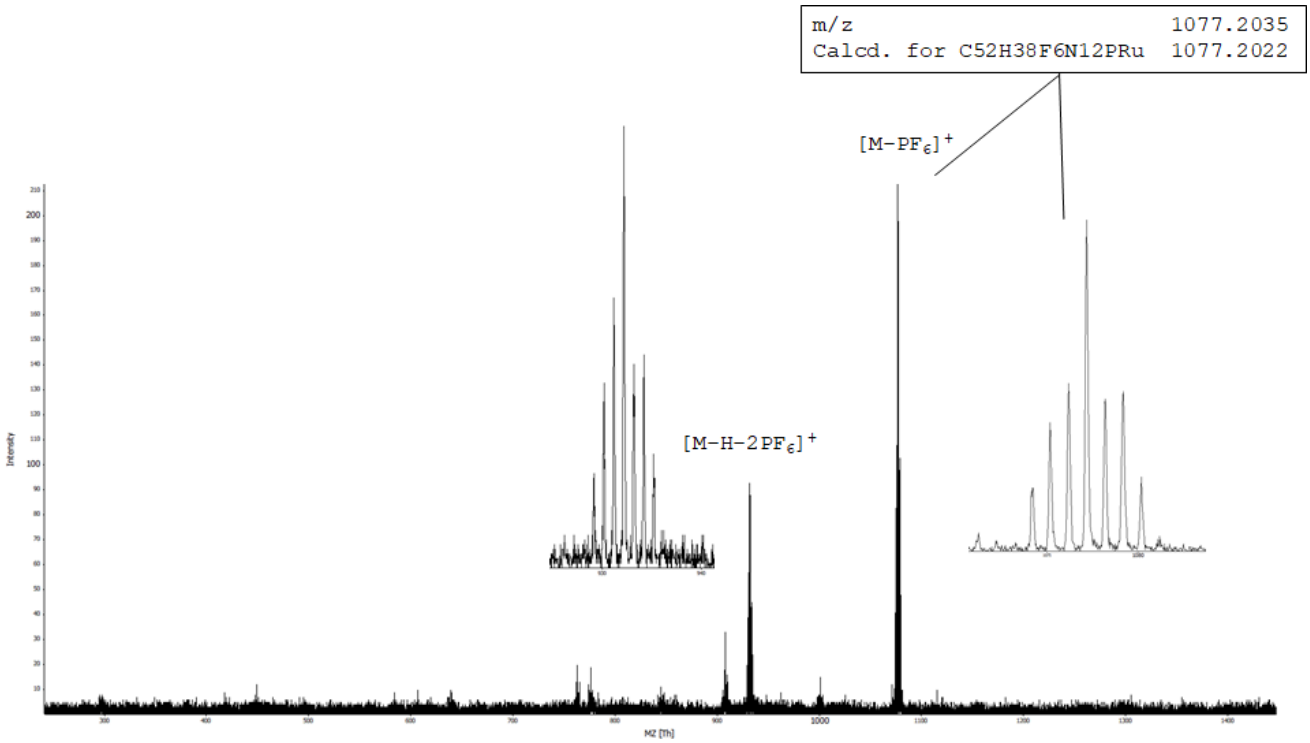


Figure S92. Mass-spectrum (MALDI-TOF) of the complex **Ru[Phen-4,7(NPy$_2$)$_2$]**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

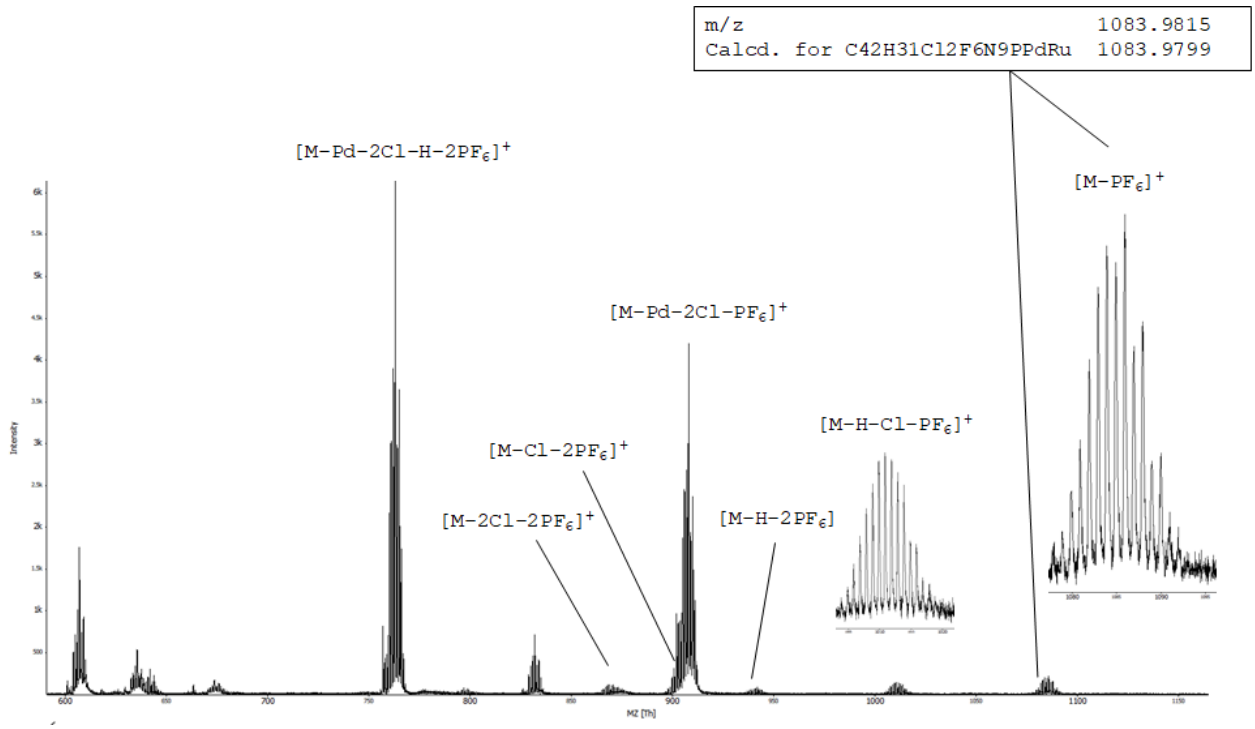


Figure S93. Mass-spectrum (MALDI-TOF) of the complex **Ru(Phen-3NPy$_2$)Pd**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

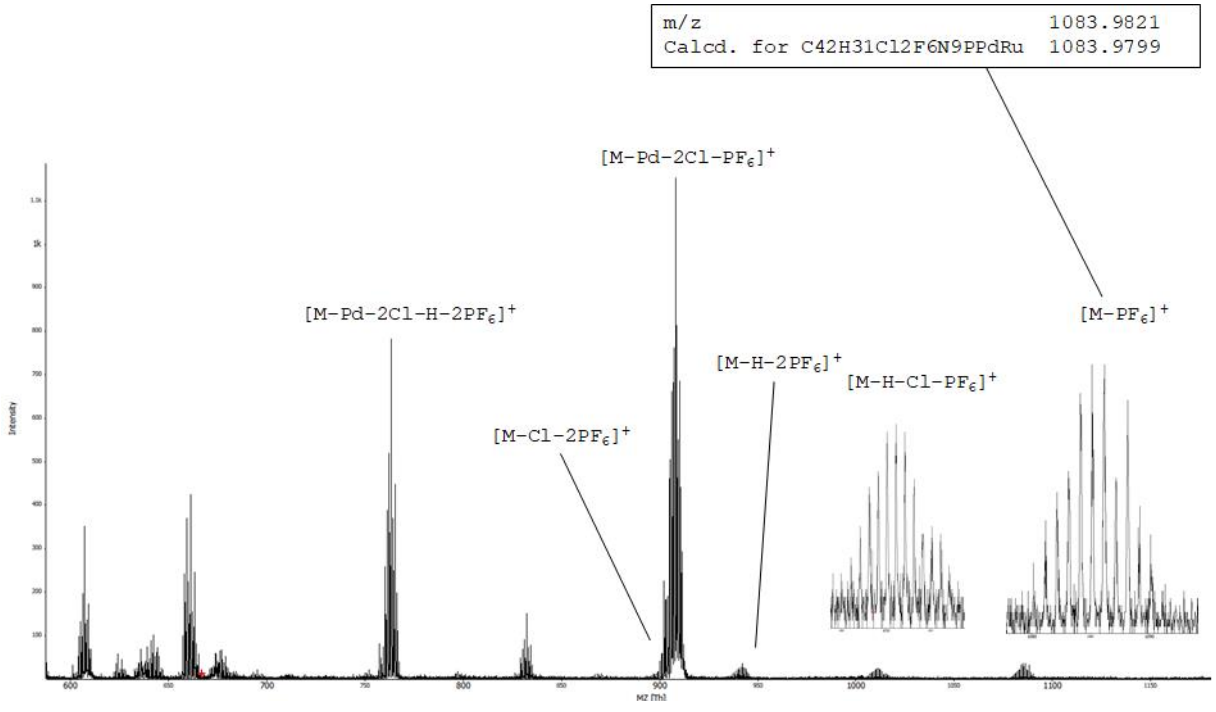


Figure S94. Mass-spectrum (MALDI-TOF) of the complex **Ru(Phen-4NPy$_2$)Pd**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

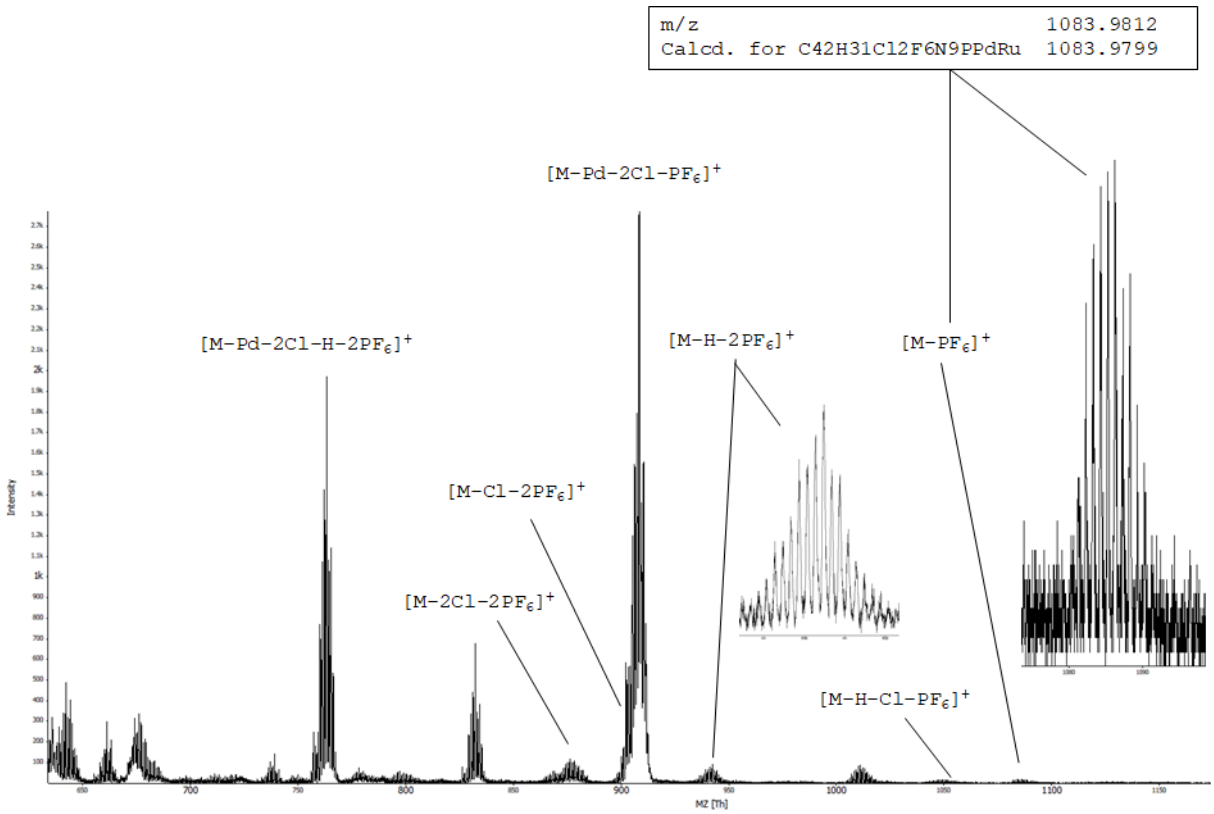


Figure S95. Mass-spectrum (MALDI-TOF) of the complex **Ru(Phen-5NPy$_2$)Pd**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

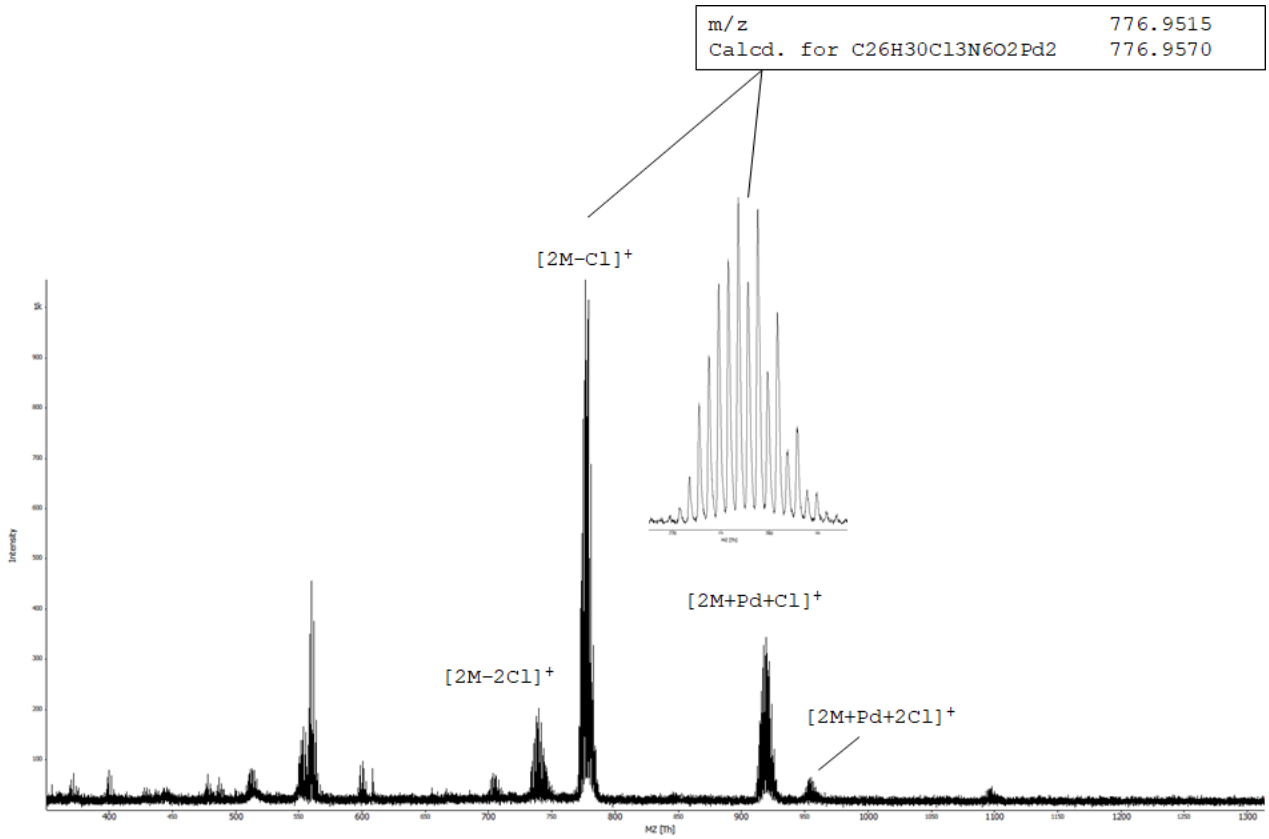


Figure S96. Mass-spectrum (MALDI-TOF) of the complex **(NPy$_2$)Pd**. Matrix: 1,8,9-trihydroxyanthracene. Calibration standard: PEG-600+PEG-1000.

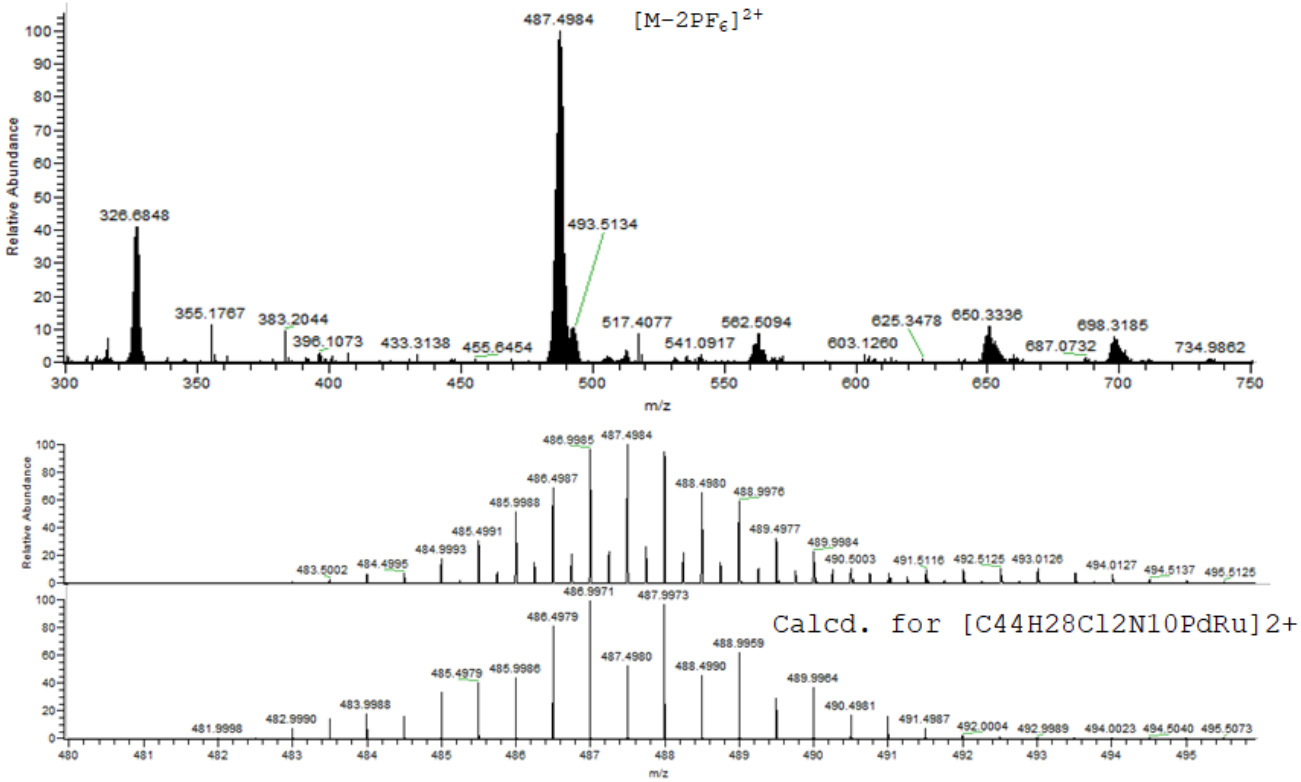
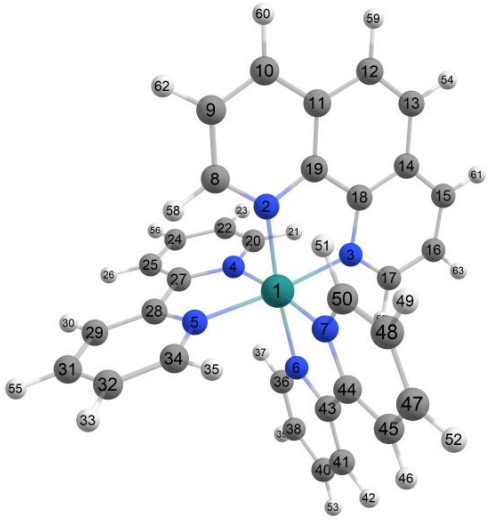


Figure S97. Mass-spectrum (ESI) of the complex **Ru(tpphz)Pd**. Voltage 5.5 kV; ion source gas 15 arb, curtain gas 20 arb; eluent MeCN+0.1% HCOOH.

11. Atomic coordinates obtained by DFT computations

Ru(Phen)



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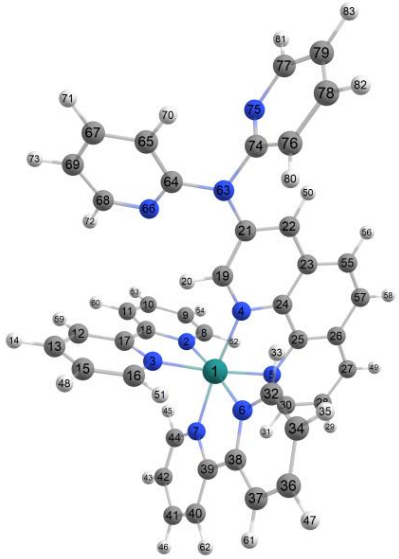
Ru(Phen-3NPy$_2$)



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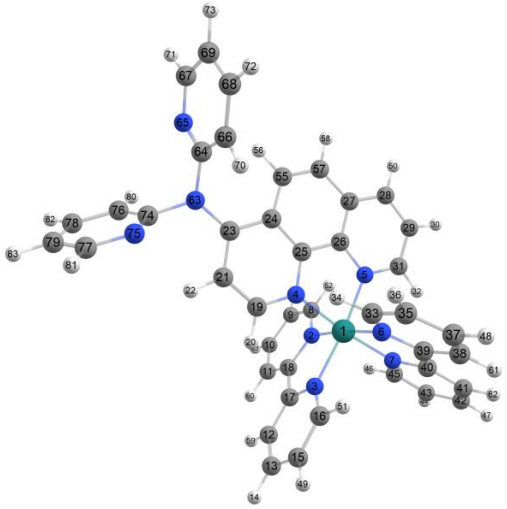
Ru(Phen-4NPy$_2$)



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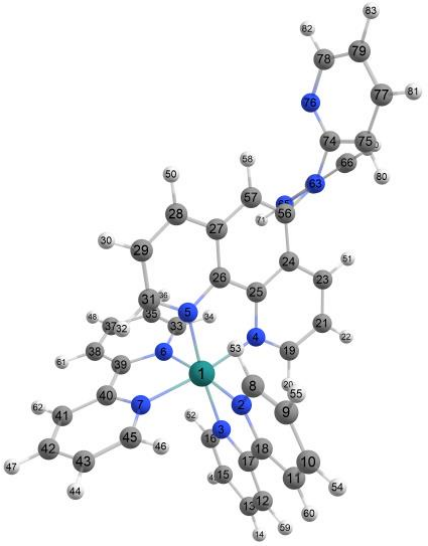

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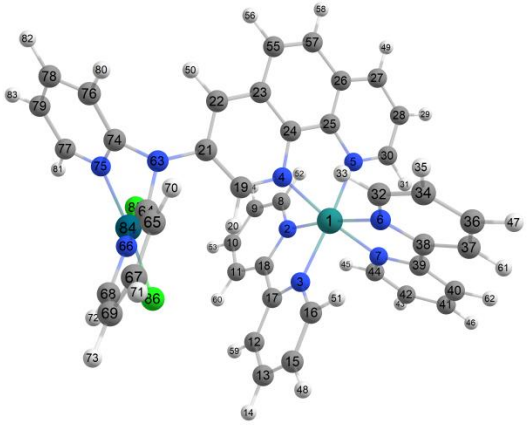

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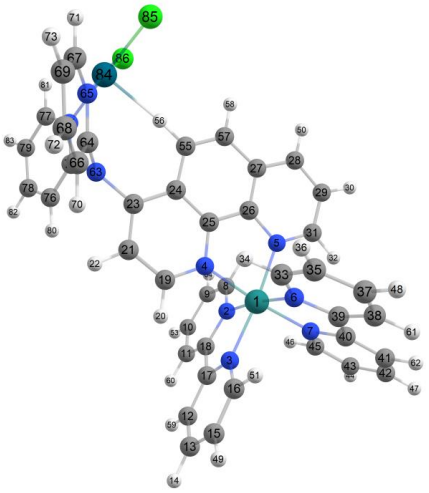

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45	6	10.105225300	27.795842721	3.320381787

46	1	9.161838113	27.795566348	2.772722804
47	1	11.603668614	29.088968981	6.096322293
48	1	16.490805690	24.924711967	3.064181377
49	1	13.910636678	29.708554463	-0.970835341
50	1	9.445295327	20.666547831	3.253224509
51	1	13.497991391	27.594605759	0.256992599
52	1	8.107988525	24.989015459	1.461373413
53	1	5.673898603	27.908066964	-0.597641508
54	1	5.864743400	25.767207916	0.750312009
55	6	10.204419109	21.115096946	-0.800035483
56	1	10.142820247	20.316635834	-1.563563215
57	6	9.932432125	20.841360623	0.512705304
58	1	9.655031826	19.821961383	0.799903809
59	1	9.637806928	30.086570320	-1.509761628
60	1	7.776504203	29.136944181	-1.169921703
61	1	14.899628002	26.414507438	4.291496727
62	1	13.464337717	27.702362310	5.162479801
63	7	10.812460838	21.808689122	-3.621762381
64	6	11.939049914	20.982865548	-3.906078415
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68	6	14.234776821	20.716339822	-4.603501283
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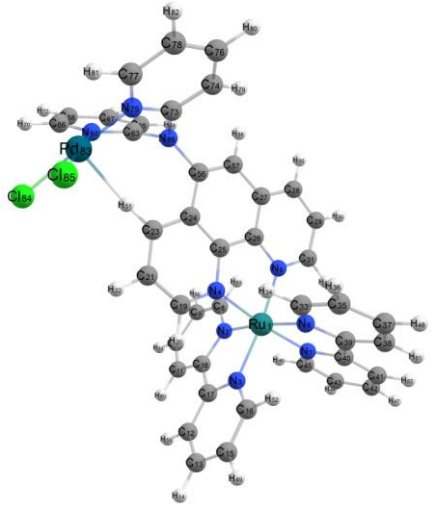
77	6	7.975464584	19.960294349	-4.912268979
78	6	7.689503461	22.246486737	-5.602379027
79	6	7.241269698	20.922916598	-5.599657681
80	1	9.291635360	23.561976845	-4.953649475
81	1	7.652639547	18.919655336	-4.858510154
82	1	7.137849791	23.026849059	-6.135747149
83	1	6.328374077	20.623377605	-6.121370831
84	46	10.067155081	18.919055030	-3.165802876
85	17	11.191275034	17.438218688	-1.879543164
86	17	8.098002412	18.163166463	-2.351141221

Ru(Phen-5NPy$_2$)Pd



1	44	13.107835484	23.208559033	-0.657771501
2	7	15.072556084	23.563741980	-0.872512742
3	7	13.866026344	21.447444494	-0.064868116

4	7	13.029250471	22.700802295	-2.613058753
5	7	12.488253306	24.960214351	-1.442170882
6	7	11.190070724	22.762505064	-0.258089693
7	7	12.983708720	23.805183289	1.252917809
8	6	15.629818650	24.721371012	-1.314309087
9	6	17.000351736	24.897177180	-1.470543606
10	6	17.866609559	23.838260839	-1.168949577
11	6	17.311624090	22.641838257	-0.719272612
12	6	15.877028943	20.135262990	0.278097436
13	6	15.126239056	19.047237849	0.719410197
14	1	15.615437149	18.115592780	1.017691491
15	6	13.732807211	19.181520108	0.771205673
16	6	13.149851182	20.381800354	0.379419823
17	6	15.233777013	21.319958254	-0.104159383
18	6	15.922270044	22.524188371	-0.578839898
19	6	13.337017827	21.520810156	-3.189198687
20	1	13.664064336	20.721128501	-2.521780396
21	6	13.234751417	21.298045225	-4.570385387
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23	6	12.805923109	22.313735272	-5.412328481
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26	6	12.316341561	24.945511184	-2.809325108
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29	6	11.743243795	27.262047507	-1.485680867
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31	6	12.190187938	26.113299365	-0.810324146
32	1	12.319144698	26.126980264	0.273839571
33	6	10.301661266	22.212776887	-1.127266370
34	1	10.685327879	21.966308310	-2.118173175
35	6	8.974972479	21.954437961	-0.799381238
36	1	8.317681657	21.504989763	-1.549172105
37	6	8.510741620	22.275427742	0.482787513
38	6	9.408089486	22.841774151	1.386189971
39	6	10.734936778	23.075872362	1.000533999
40	6	11.765480323	23.651010548	1.870677810
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43	6	13.860248624	24.693060540	3.325835137
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47	1	12.473246695	24.828469673	4.999271216
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54	1	18.949299775	23.943523278	-1.282931010
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85	17	11.337055947	20.059098613	-8.265877777
86	7	11.881495125	24.570391565	-7.046804569

11. References

1 D. Tzalis, Y. Tor, F. Salvatorre and S. Jay Siegel, *Tetrahedron Lett.*, 1995, **36**, 3489–3490.
2 J. Mlochowski, *Rocz. Chem.*, 1974, **48**, 2145–2155.
3 G. I. Graf, D. Hastreiter, L. E. da Silva, R. A. Rebelo, A. G. Montalban and A. McKillop, *Tetrahedron*, 2002, **58**, 9095–9100.
4 F. Ferretti, E. Gallo and F. Ragaini, *J. Organomet. Chem.*, 2014, **771**, 59–67.
5 J. K. Klosterman, A. Linden and J. S. Siegel, *Org. Biomol. Chem.*, 2008, **6**, 2755–2764.
6 P. A. Lay, A. M. Sargeson, H. Taube, M. H. Chou and C. Creutz, *Inorg. Synth.*, 1986, DOI: 10.1002/9780470132555.ch78, 291–299.
7 A. S. Abel, I. S. Zenkov, A. D. Averin, A. V. Cheprakov, A. G. Bessmertnykh-Lemeune, B. S. Orlinson and I. P. Beletskaya, *ChemPlusChem*, 2019, **84**, 498–503.
8 C. A. Goss and H. D. Abruna, *Inorg. Chem.*, 1985, **24**, 4263–4267.
9 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.
10 J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *Inorg. Chem.*, 1996, **35**, 2937–2944.
11 G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.
12 G. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.
13 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
14 G. V. Morozkov, A. S. Abel, M. A. Filatov, S. E. Nefedov, V. A. Roznyatovsky, A. V. Cheprakov, A. Y. Mitrofanov, I. S. Ziankou, A. D. Averin, I. P. Beletskaya, J. Michalak, C. Bucher, L. Bonneviot and A. Bessmertnykh-Lemeune, *Dalton Trans.*, 2022, **51**, 13612–13630.
15 A. A. Granovsky, *Firefly version 8*, *www* http://classic.chem.msu.su/gran/firefly/index.html.
16 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery Jr, *J. Comput. Chem.*, 1993, **14**, 1347–1363.
17 C. L. Barros, P. J. P. de Oliveira, F. E. Jorge, A. Canal Neto and M. Campos, *Mol. Phys.*, 2010, **108**, 1965–1972.
18 W. Huang and T. Ogawa, *Polyhedron*, 2006, **25**, 1379–1385.
19 A. Sagadevan and K. C. Hwang, *Adv. Synth. Catal.*, 2012, **354**, 3421–3427.
20 C. Amatore, A. Jutand and M. A. M'Barki, *Organometallics*, 1992, **11**, 3009–3013.
21 Z. Csákai, R. Skoda-Földes and L. Kollár, *Inorg. Chim. Acta*, 1999, **286**, 93–97.
22 A. F. Shmidt and V. V. Smirnov, *Kinet. Catal.*, 2002, **43**, 195–198.
23 C. Palladino, T. Fantoni, L. Ferrazzano, B. Muzzi, A. Ricci, A. Tolomelli and W. Cabri, *ACS Catalysis*, 2023, **13**, 12048-12061.