

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. *N^{1,N¹'}*-(ethane-1,2-diyl)diethane-1,2-diamine (**5e**) was obtained by treatment of commercially available tetraethylenepentamine dihydrochloride with 2.5 M solution of KOH in methanol. [(2-Bromoacetyl amino)methyl]phosphonic acid diethyl ester (**1**) was synthesized according to a known procedure [25]. Pd(dba)₂ was synthesized according to a known method [26] and used without recrystallization. 3-Bromo-1,10-phenanthroline (**2**) was synthesized according to the procedure [27] and purified by column chromatography followed by recrystallization from boiling acetone. Starting complex *cis*-Ru(bpy)₂Cl₂ was synthesized from RuCl₃·3H₂O according to a known method [28]. 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, CH₂Cl₂ and CH₃CN were distilled over CaH₂, chloroform was distilled over P₂O₅, MeOH was used freshly distilled.

¹H, ³¹P and ¹³C NMR spectra were registered with Bruker Avance-400 spectrometer in CDCl₃, CD₃OD or CD₃CN, using the residual signals of CHCl₃, CHD₂OD or CHD₂CN as internal standards.

MALDI-TOF mass-spectra were obtained on a Bruker Daltonics Autoflex II mass-spectrometer in positive ion mode with a dithranol matrix and polyethyleneglycols as internal standards. Accurate mass measurements (ESI-HRMS) were performed with a Thermo Scientific Orbitrap Elite high-field orbitrap hybrid mass spectrometer. FTIR spectra were registered on Nicolet iS 5 and Bruker Vector 22 spectrophotometers. Micro-ATR accessory (Pike) was used in order to obtain FTIR spectra of polycrystalline solid complexes.

Protonation and complexation studies were performed at room temperature. The solutions were prepared with double-deionized high-purity water (18.2 MΩ cm) obtained from a «Millipore Simplicity» apparatus. Solution concentrations and other experiment conditions are given in the title of the corresponding figures and tables. pH measurements were carried out using «Mettler Toledo» apparatus with a combined electrode LE438. The electrode was calibrated with commercial buffers (pH = 4.01 and 7.00). UV-vis spectra were registered with Agilent Cary 60 device in quartz cuvette (Hellma, *l* = 1 cm).

Fluorescence spectra were obtained with Horiba Jobin Yvon Fluoromax-2 apparatus in quartz cuvette (Hellma, *l* = 1 cm). Luminescence quantum yields were determined relative to Ru(bpy)₃(PF₆)₂ in aerated acetonitrile according to a standard procedure [29].

Protonation studies were conducted in a glass beaker equipped with magnetic stirrer and pH-electrode adding HCl (4 M or 0.01M) or KOH (5 M or 0.01M) to the solutions of complexes. Metal-binding experiments were conducted by a manual addition of the aliquots of metal salt solutions by a Hamilton syringe to a solution of chemosensor placed in a quartz cuvette. All metal salts used were perchlorates of general M(ClO₄)_n·xH₂O formula. *Caution! Although no problems were experienced,*

perchlorate salts are potentially explosive when combined with organic ligands and should be manipulated with care and used only in very small quantities.

Hg(ClO₄)₂ solution was prepared in acetonitrile (HPLC, Merck) to avoid hydrolysis of the salt. Aqueous solutions of metal perchlorates were prepared with concentrations of about 1000-fold of that of the ligands in order to decrease the influence of the medium changes on the spectra of the studied solutions. Stability constants were calculated using nonlinear least-squares analysis by means of HYPERQUAD algorithm [31] after factor analysis of the combined data sets [32]. The goodness of fit was assessed through the scaled standard deviation of the residuals (*s*), which has an expectation value of unity in the absence of systematic errors assuming a correct weighting scheme. The results were checked by plotting calculated molar extinction graphs.

2. Synthesis

2.1 Palladium-catalyzed amination of 3-bromo-1,10-phenanthroline

General Procedure. A flask flushed with dry argon and equipped with a magnetic stirrer, a condenser and a gas outlet was charged with 3-bromo-1,10-phenanthroline (**2**) (0.5 mmol), Pd(dba)₂ (2–10 mol%), ligand (2.5–20 mol%), amine (0.33–5 mmol), and absolute 1,4-dioxane (5 mL). *t*-BuONa (0.75 mmol) was added, and the reaction mixture was stirred under reflux for 24 h. After cooling to r.t., the mixture was concentrated under reduced pressure. The solid residue was taken up in dichloromethane and subjected to column chromatography on silica gel using a CH₂Cl₂/MeOH/ NH₃(aq) mixtures as eluents (gradual elution using pure CH₂Cl₂, CH₂Cl₂/MeOH, 200:1 to 3:1, and then CH₂Cl₂/MeOH/NH₃(aq), 100:20:1 to 10:4:1 v/v).

Table S1. Optimization of the amination reaction conditions.^a

The reaction scheme illustrates the amination of compound **2** (3-bromo-1,10-phenanthroline) with phenylalanine (NCCc1ccccc1) using Pd(dba)2 and a P-Ligand in dioxane. The products are **3** (3-phenylamino-1,10-phenanthroline) and **4** (3-bromo-1,10-phenanthroline).

Optimized conditions: **L5** (BINAP), **Pd(dba)₂**, **tBuONa**, **11 h**, **60 (54) %** yield for **3**.

Ligands:

- BINAP:** 1,1'-bis(diphenylphosphino)-ferrocene
- dppf:** 1,1'-bis(diphenylphosphino)-binaphthyl
- XantPhos:** 2-dimesitylphosphino-4,4-dimethyl-2H-chromene
- JohnPhos:** 2-(dimethylaminophenyl)diphenylphosphine
- DavePhos:** 2-(diisopropylphosphino)phenylbenzene
- BrettPhos:** 2-(dimethylaminophenyl)diphenylphosphine with methoxy substituents
- RuPhos:** 2-(dimethylaminophenyl)diphenylphosphine with isopropoxy substituents

Josiphos series:

- L1:** 2-(dicyclohexylphosphino)phenylbenzene
- L2:** 2-(diphenylphosphino)phenylbenzene
- L3:** 2-(bis(diphenylphosphino)methoxy)phenylbenzene
- L4:** 2-(bis(2,6-trifluorophenyl)diphenylphosphino)phenylbenzene
- L5:** 2-(diphenylphosphino)-2-ferrocenylbenzene
- L6:** 2-(tert-butyl(diphenylphosphino)methyl)phenylbenzene

Entry	Ligand	Pd(dba)₂/Ligand (mol%)	Base	Time, h	Yield, % ^b	
					3	4
1 ^c	-	-	<chem>Cs2CO3</chem> ^d	16	0 ^e	0
2 ^{c,f}	-	-	<chem>Cs2CO3</chem> ^d	16	0	100
3	BINAP	2 / 4	<chem>tBuONa</chem> ^c	16	traces	100
4	BINAP	2 / 25	<chem>tBuONa</chem> ^c	16	traces	100
5	BINAP	10 / 10.5	<chem>tBuONa</chem>	11	30 (28)	70
6	BINAP	10 / 25	<chem>tBuONa</chem>	11	30	70
7	BINAP	10 / 10.5	<chem>Cs2CO3</chem> ^d	11	< 15	85
8	BINAP	10 / 10.5	<chem>K3PO4</chem> ^g	11	0	100
9 ⁱ	BINAP	10 / 10.5	<chem>tBuONa</chem>	11	16	80
10	DPPF	10 / 10.5	<chem>tBuONa</chem>	11	0	100
11	JohnPhos	10 / 20	<chem>tBuONa</chem>	16	0	100
12	DavePhos	10 / 10.5	<chem>tBuONa</chem>	11	0	100
13	XantPhos	10 / 10.5	<chem>tBuONa</chem>	11	0	100
14	BrettPhos	10 / 10.5	<chem>tBuONa</chem>	16	0	100
15	RuPhos	10 / 10.5	<chem>tBuONa</chem>	16	0	100
16	L1	10 / 10.5	<chem>tBuONa</chem>	11	35	60
17	L2	10 / 10.5	<chem>tBuONa</chem>	11	0	100
18	L3	10 / 10.5	<chem>tBuONa</chem>	11	35	65
19	L4	10 / 10.5	<chem>tBuONa</chem>	11	< 15	85
20	L5	10 / 10.5	<chem>tBuONa</chem>	11	60 (54)	30
21	L6	10 / 10.5	<chem>tBuONa</chem>	11	60 (50)	30

^a Reaction conditions: 3-bromo-1,10-phenanthroline (0.25 mmol), Pd(dba)2, ligand and base (1.5 equivalents) were vigorously stirred in dioxane (2.5 ml) under reflux until a complete conversion of the starting bromide (NMR monitoring) under inert atmosphere.

^b Determined by NMR spectroscopy. The isolated yields are given in parenthesis.

^c The reaction was performed in DMF at 140°C.

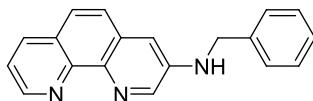
^d 2 equivalents of Cs2CO3;

^e no conversion of the bromide was observed.

^f CuI (200 equivalents) was added.

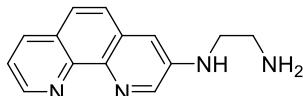
^g 2 equivalents of K3PO4

ⁱ Reaction was performed in toluene using 3 equivalents of amine.



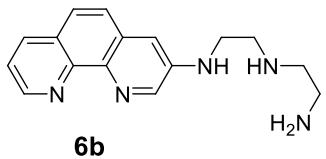
3

N-benzyl-1,10-phenanthrolin-3-amine (3). Compound **3** was obtained according to the general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), benzylamine (54 mg, 0.5 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 86 mg (60%); yellowish oil; chromatography (CH₂Cl₂/MeOH, 20:3 v/v). IR (cm⁻¹): 3247, 3028, 2960, 2922, 2851, 2201, 1603, 1584, 1536, 1505, 1494, 1475, 1452, 1419, 1406, 1378, 1351, 1296, 1265, 1248, 1200, 1182, 1138, 1099, 1071, 1054, 1027, 948, 906, 858, 828, 813, 793, 776, 728, 697, 639, 609. ¹H NMR (400 MHz, CDCl₃): δ = 4.46 (s, 2H, CH₂N), 7.09 (d, ⁴J = 2.9 Hz, 1H, H4(Phen)), 7.26–7.43 (m, 5H, H(Ph)), 7.45 (dd, ³J = 8.0 Hz, ³J = 4.4 Hz, 1H, H8(Phen)), 7.54 (d, ³J = 8.9 Hz, 1H, H5(Phen)), 7.62 (d, ³J = 8.9 Hz, 1H, H6(Phen)), 8.11 (dd, ³J = 8.0 Hz, ⁴J = 1.8 Hz, 1H, H7(Phen)), 8.72 (d, ⁴J = 2.9 Hz, 1H, H2(Phen)), 9.05 (dd, ³J = 4.4 Hz, ⁴J = 1.8 Hz, 1H, H9(Phen)). NH proton was not unambiguously assigned. ¹³C NMR (100.6 MHz, CDCl₃): δ = 47.6 (1C, CH₂N), 111.8 (1C), 121.1 (1C), 126.2 (1C), 126.3 (1C), 126.5 (1C), 127.3 (2C), 127.5 (1C), 128.7 (2C), 129.9 (1C), 135.9 (1C), 137.5 (1C), 137.9 (1C), 141.1 (1C), 143.5 (1C), 146.1 (1C), 149.7 (1C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₁₉H₁₆N₃: 286.134; found: 286.138.



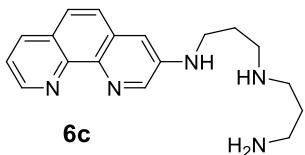
6a

N¹-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine (6a). Compound **6a** was obtained according to the general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), ethylenediamine **5a** (300 mg, 5 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 55 mg (46%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:20:2 v/v). IR (cm⁻¹): 3282, 3141, 2910, 2858, 1655, 1620, 1591, 1575, 1534, 1499, 1480, 1466, 1394, 1363, 1282, 1232, 1143, 1112, 1097, 1079, 1026, 929, 837, 811, 769, 733, 715, 664, 627, 578, 481, 447, 419 ¹H NMR (400 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 2.94 (t, ³J = 5.5 Hz, 2H, CH₂NH₂), 3.24 (t, ³J = 5.5 Hz, 2H, CH₂NH), 5.55 (br. m, 1H, NH), 6.97 (d, ⁴J = 2.6 Hz, 1H, H4(Phen)), 7.36 (dd, ³J = 7.8 Hz, ³J = 4.4 Hz, 1H, H8(Phen)), 7.46 (d, ³J = 8.8 Hz, 1H, H5(Phen)), 7.53 (d, ³J = 8.8 Hz, 1H, H6(Phen)), 8.03 (dd, ³J = 7.8 Hz, ⁴J = 1.8 Hz, 1H, H7(Phen)), 8.47 (d, ⁴J = 2.6 Hz, 1H, H2(Phen)), 8.86 (dd, ³J = 4.4 Hz, ⁴J = 1.8 Hz, 1H, H9(Phen)). Two NH protons were not unambiguously assigned. ¹³C NMR (100.6 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 39.7 (1C, CH₂), 44.7 (1C, CH₂), 110.9 (1C), 121.0 (1C), 126.1 (1C), 126.2 (1C), 126.4 (1C), 130.0 (1C), 135.9 (1C), 136.8 (1C), 140.7 (1C), 144.0 (1C), 145.9 (1C), 149.3 (1C). HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₅N₄: 239.1296; found: 239.1291.



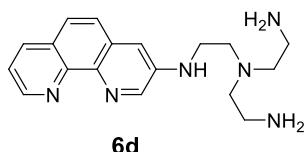
N¹-(2-aminoethyl)-N²-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine (6b). Compound **6b** was obtained according to the general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), triamine **5b** (258 mg, 2.5 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 77 mg (55%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:20:3 v/v). IR (cm⁻¹): 3356, 3051, 2965, 2938, 2907, 2831, 1636, 1605, 1589, 1508, 1478, 1457, 1433, 1425, 1410, 1360, 1340, 1251, 1222, 1204, 1179, 1140, 1103, 1022, 949, 910, 864, 832, 816, 775, 729, 700, 669. ¹H NMR (400 MHz, CD₃OD): δ = 2.69–2.74 (m, 2H, CH₂N), 2.75–2.80 (m, 2H, CH₂N), 2.86 (t, ³J = 6.2 Hz, 2H, CH₂N), 3.32 (t, ³J = 6.2 Hz, 2H, CH₂NPhen), 6.09 (br. s, 1H, NHPhen), 7.14 (d, ⁴J = 2.5 Hz, 1H, H4(Phen)), 7.46 (dd, ³J = 7.8 Hz, ³J = 4.3 Hz, 1H, H8(Phen)), 7.58 (d, ³J = 8.8 Hz, 1H, H5(Phen)), 7.62 (d, ³J = 8.8 Hz, 1H, H6(Phen)), 8.16 (d, ³J = 7.8 Hz, 1H, H7(Phen)), 8.49 (d, ⁴J = 2.5 Hz, 1H, H2(Phen)), 8.85 (d, ³J = 4.3 Hz, 1H, H9(Phen)). Three NH-protons were not unambiguously assigned. ¹³C NMR (100.6 MHz, CD₃OD): δ = 41.7 (1C, CH₂), 43.5 (1C, CH₂), 48.9 (1C, CH₂), 52.2 (1C, CH₂), 111.9 (1C), 122.4 (1C), 127.6 (1C), 127.8 (1C), 127.9 (1C), 131.9 (1C), 137.5 (1C), 137.6 (1C), 141.9 (1C), 146.2 (1C), 147.1 (1C), 150.4 (1C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₁₆H₂₀N₅: 282.1718; found: 282.1736.

When the load of amine **5b** was 155 mg (1.5 mmol, 3 equivalents) the yield of the product **6b** was 32%. In this case **N¹-(2-(1,10-phenanthrolin-3-ylamino)ethyl)-N²-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine (7b)** was also isolated from the reaction mixture in 34% yield using CH₂Cl₂/MeOH/NH₃(aq) (100:20:1 v/v) as eluent.

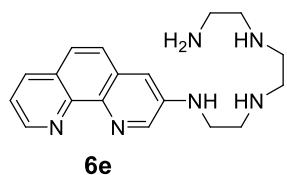


N¹-(3-aminopropyl)-N³-(1,10-phenanthrolin-3-yl)propane-1,3-diamine (6c). Compound **6c** was obtained according to general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), triamine **5c** (197 mg, 1.5 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 56 mg (36%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:20:3 v/v) IR (cm⁻¹): 3279, 2935, 2822, 1604, 1588, 1540, 1506, 1474, 1422, 1376, 1314, 1249, 1201, 1115, 1026, 858, 830, 814, 729, 586. ¹H NMR (400 MHz, CD₃OD): δ = 1.69 (quint, ³J = 7.3 Hz, 2H, CH₂CH₂NH₂), 1.90 (quint, ³J = 7.0 Hz, 2H, CH₂CH₂NPhen), 2.66 (t, ³J = 7.4 Hz, 2H, CH₂N), 2.71 (t, ³J = 7.2 Hz, 2H, CH₂N), 2.75 (t, ³J = 7.2 Hz, 2H, CH₂N), 3.26

(t, $^3J = 6.8$ Hz, 2H, CH₂NPhen), 7.16 (d, $^4J = 2.7$ Hz, 1H, H4(Phen)), 7.50 (dd, $^3J = 8.1$ Hz, $^3J = 4.5$ Hz, 1H, H8(Phen)), 7.63 (d, $^3J = 8.8$ Hz, 1H, H5(Phen)), 7.68 (d, $^3J = 8.8$ Hz, 1H, H6(Phen)), 8.23 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 1H, H7(Phen)), 8.53 (d, $^4J = 2.7$ Hz, 1H, H2(Phen)), 8.89 (dd, $^3J = 4.5$ Hz, $^4J = 1.5$ Hz, 1H, H9(Phen)). Three NH-protons were not unambiguously assigned. ¹³C NMR (100.6 MHz, CD₃OD): $\delta = 29.5$ (1C, CH₂CH₂CH₂), 32.8 (1C, CH₂CH₂CH₂), 40.5 (1C, CH₂N), 42.1 (1C, CH₂N), 48.3 (1C, CH₂N), 48.4 (1C, CH₂N), 111.8 (1C), 122.4 (1C), 127.7 (2C), 127.8 (1C), 132.0 (1C), 137.4 (1C), 137.5 (1C), 141.9 (1C), 146.4 (1C), 147.2 (1C), 150.4 (1C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₁₈H₂₄N₅: 310.2032; found: 310.2049.



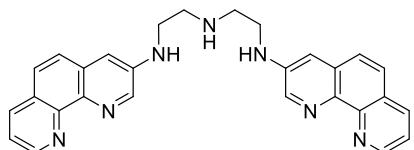
N¹,N¹-bis(2-aminoethyl)-N²-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine (6d). Compound **6d** was obtained according to the general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), tetraamine **5d** (219 mg, 1.5 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 55 mg (34%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:30:5 v/v). IR (cm⁻¹): 3276, 3046, 2946, 2839, 1656, 1604, 1587, 1537, 1506, 1472, 1422, 1408, 1375, 1354, 1338, 1298, 1265, 1248, 1201, 1171, 1139, 1099, 1030, 858, 829, 814, 727, 699. ¹H NMR (400 MHz, CD₃OD): $\delta = 2.60$ (t, $^3J = 5.8$ Hz, 4H, CH₂NH₂), 2.72–2.72 (m, 6H, CH₂N), 3.28 (t, $^3J = 6.2$ Hz, 2H, CH₂NPhen), 7.16 (d, $^4J = 2.9$ Hz, 1H, H4(Phen)), 7.49 (dd, $^3J = 8.1$ Hz, $^3J = 4.4$ Hz, 1H, H8(Phen)), 7.62 (d, $^3J = 8.9$ Hz, 1H, H5(Phen)), 7.69 (d, $^3J = 8.9$ Hz, 1H, H6(Phen)), 8.22 (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 1H, H7(Phen)), 8.57 (d, $^4J = 2.9$ Hz, 1H, H2(Phen)), 8.89 (dd, $^3J = 4.4$ Hz, $^4J = 1.6$ Hz, 1H, H9(Phen)). NH-protons were not unambiguously assigned. ¹³C NMR (100.6 MHz, CD₃OD): $\delta = 39.8$ (2C, CH₂), 41.9 (1C, CH₂), 54.3 (1C, CH₂), 56.6 (2C, CH₂), 112.3 (1C), 122.5 (1C), 127.7 (1C), 127.8 (1C), 127.9 (1C), 131.9 (1C), 137.6 (1C), 137.7 (1C), 142.0 (1C), 146.2 (1C), 147.2 (1C), 150.4 (1C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₁₈H₂₅N₆: 325.2141; found: 325.2112.



N¹-(2-(1,10-phenanthrolin-3-ylamino)ethyl)-N²-(2-aminoethyl)ethane-1,2-diamine (6e). Compound **6e** was obtained according to general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), tetraamine **5e** (219 mg, 1.5 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 57 mg (35%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:30:5 v/v). IR (cm⁻¹): 3286, 2935, 2825, 1654, 1604, 1588, 1506, 1424, 1357, 1250, 1203, 1172, 1118, 1025, 860, 831, 814, 729, 533. ¹H NMR

(400 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 2.64 (t, ³J = 5.5 Hz, 2H, CH₂N), 2.70–2.85 (m, 10H, CH₂, NH, NH₂), 2.93 (t, ³J = 5.6 Hz, 2H, CH₂), 3.32 (t, ³J = 5.6 Hz, 2H, CH₂NPhen), 5.44 (br. s, 1H, NHPhen), 7.06 (d, ⁴J = 2.5 Hz, 1H, H4(Phen)), 7.43 (dd, ³J = 7.9 Hz, ³J = 4.4 Hz, 1H, H8(Phen)), 7.56 (d, ³J = 8.8 Hz, 1H, H5(Phen)), 7.61 (d, ³J = 8.8 Hz, 1H, H6(Phen)), 8.08 (dd, ³J = 7.9 Hz, ⁴J = 1.6 Hz, 1H, H7(Phen)), 8.60 (d, ⁴J = 2.5 Hz, 1H, H2(Phen)), 8.96 (dd, ³J = 4.4 Hz, ⁴J = 1.6 Hz, 1H, H9(Phen)). ¹³C NMR (100.6 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 40.7 (1C, CH₂), 42.5 (1C, CH₂), 47.7 (1C, CH₂), 48.5 (2C, CH₂), 51.2 (1C, CH₂), 111.2 (1C), 121.1 (1C), 126.1 (1C), 126.3 (1C), 126.5 (1C), 130.1 (1C), 135.8 (1C), 137.3 (1C), 141.1 (1C), 144.0 (1C), 146.3 (1C), 149.7 (1C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₁₈H₂₅N₆: 325.2141; found: 325.2165.

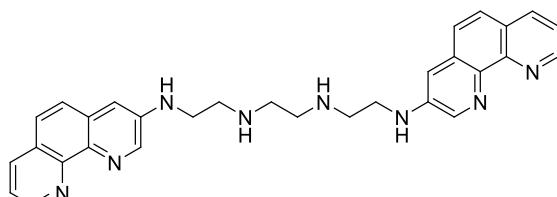
N¹,N^{1'}-(ethane-1,2-diyl)bis(N²-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine) (7e) was also isolated from the reaction mixture in 12% yield using CH₂Cl₂/MeOH/NH₃(aq) (100:20:1 v/v) as eluent.



7b

N¹-(2-(1,10-phenanthrolin-3-ylamino)ethyl)-N²-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine

(7b). Compound **7b** was obtained according to general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5 mmol), triamine **5b** (25.8 mg, 0.25 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 60 mg (52%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:20:1 v/v). IR (cm⁻¹): 3257, 3043, 2923, 2849, 1603, 1586, 1559, 1540, 1534, 1522, 1507, 1472, 1458, 1420, 1406, 1374, 1336, 1296, 1264, 1247, 1199, 1170, 1138, 1098, 1055, 976, 909, 857, 828, 813, 775, 727, 696, 669. ¹H NMR (400 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 3.29 (br. s, 4H, CH₂), 3.32 (br. s, 4H, CH₂NPhen), 6.47 (br. s, 2H, H4(Phen), 6.95 (d, ³J = 8.8 Hz, 2H, H5(Phen)), 7.16–7.22 (m, 4H, H6(Phen), H8(Phen)), 7.82 (d, ³J = 7.9 Hz, 2H, H7(Phen)), 8.25 (d, ⁴J = 1.9 Hz, 2H, H2(Phen)), 8.65 (d, ³J = 4.4 Hz, 2H, H9(Phen)). NH-protons were not unambiguously assigned. ¹³C NMR (100.6 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 39.6 (2C, CH₂), 46.5 (2C, CH₂), 111.0 (2C), 120.9 (2C), 125.8 (2C), 125.9 (2C), 126.0 (2C), 129.5 (2C), 135.9 (4C), 139.6 (2C), 142.9 (2C), 145.0(2C), 148.7 (2C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₂₈H₂₆N₇: 460.224; found: 460.226.



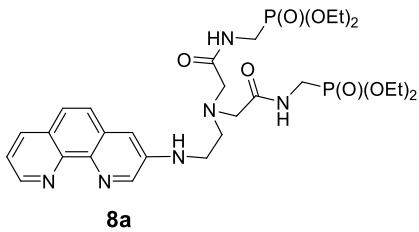
7e

N¹,N^{1'}-(ethane-1,2-diyl)bis(N²-(1,10-phenanthrolin-3-yl)ethane-1,2-diamine) (7e) Compound **7e** was obtained according to general procedure from 3-bromo-1,10-phenanthroline (**2**) (130 mg, 0.5

mmol), tetraamine **5e** (36.5 mg, 0.25 mmol) and *t*-BuONa (72 mg, 0.75 mmol) in the presence of Pd(dba)₂ (29 mg, 10 mol%) and phosphine **L5** (28 mg, 10.5 mol%). Yield: 49 mg (39%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:20:1 v/v).

Yield: 24 mg (39%); yellow oil; chromatography (CH₂Cl₂/MeOH/NH₃(aq), 100:20:1 v/v). IR (cm⁻¹): 3290, 3051, 2918, 2848, 1653, 1604, 1588, 1540, 1507, 1473, 1422, 1413, 1375, 1270, 1250, 1200, 1173, 1139, 1112, 1100, 1029, 860, 831, 815, 729, 680, 669, 649. ¹H NMR (400 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 2.60–2.90 (br. s, 2H, NH) 2.82 (s, 4H, CH₂), 2.96 (t, ³J = 5.5 Hz, 4H, CH₂), 3.26 (br. s, 4H, CH₂NHPhen), 5.24 (br. s, 2H, NHPhen), 6.96 (br. s, 2H, H4(Phen)), 7.40 (dd, ³J = 8.0 Hz, ³J = 4.4 Hz, 2H, H8(Phen)), 7.48 (d, ³J = 8.8 Hz, 2H, H5(Phen)), 7.54 (d, ³J = 8.8 Hz, 2H, H6(Phen)), 8.05 (dd, ³J = 8.0 Hz, ⁴J = 1.6, 1H, H7(Phen)), 8.64 (br. s, 1H, H2(Phen)), 9.00 (dd, ³J = 4.4 Hz, ⁴J = 1.6 Hz, 1H, H9(Phen)). ¹³C NMR (100.6 MHz, CDCl₃+CD₃OD, 2:1 v/v): δ = 42.5 (2C, CH₂), 47.8 (4C, CH₂), 48.6 (2C, CH₂), 111.2 (2C), 121.0 (2C), 126.1 (2C), 126.2 (2C), 126.4 (2C), 130.0 (2C), 135.7 (2C), 137.4 (2C), 141.2 (2C), 143.9 (2C), 146.4(2C), 149.7 (2C). HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₃₀H₃₁N₈: 503.2671; found: 503.2702.

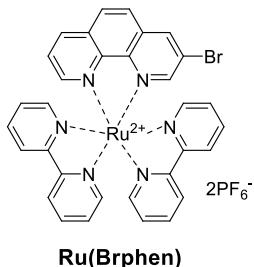
2.2. Synthesis of the compound 8a



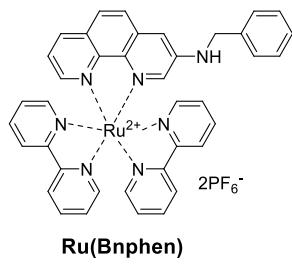
A 15 mL flask equipped with a magnetic stirrer, a condenser and a gas outlet was charged with **6a** (61 mg, 0.26 mmol), chloroform (7 mL) and DIPEA (109 mg, 0.85 mmol). [(2-bromoacetylamino)methyl]phosphonic acid diethyl ester **2** (162 mg, 0.56 mmol) was added, and the reaction mixture was stirred at 40 °C for 48 h under argon. The solution was evaporated under reduced pressure and the residue was chromatographed on silica gel using pure CH₂Cl₂, and then CH₂Cl₂/MeOH (200:1 to 3:1 v/v) as eluents. Yield: 85 mg (50%); brown oil; chromatography (CH₂Cl₂/MeOH, 10:1 v/v). IR (cm⁻¹): 3276, 3056, 2982, 2924, 2851, 1667, 1654, 1605, 1589, 1533, 1524, 1474, 1457, 1422, 1393, 1375, 1339, 1299, 1216, 1162, 1141, 1099, 1047, 1016, 971, 861, 830, 816, 779, 731, 681, 669. ¹H NMR (400 MHz, CDCl₃): δ = 1.24 (t, ³J = 7.1 Hz, 12H, CH₃), 2.92 (t, ³J = 5.3 Hz, 2H, CH₂N), 2.92 (t, ³J = 5.3 Hz, 2H, CH₂NHPhen), 3.28 (s, 4H, CH₂C(O)), 2.92 (t, ³J = 5.3 Hz, 2H, CH₂N), 3.55–3.65 (m, 4H, CH₂P(O)), 4.06 (dq, ³J_{PH} = ³J_{HH} = 7.1 Hz, 8H, CH₂OP), 6.17 (br. s, 1H, NHPhen), 7.09 (d, ³J = 1.9 Hz, 1H, H4(Phen)), 7.43 (dd, ³J = 8.1 Hz, ³J = 4.4 Hz, 1H, H8(Phen)), 7.58 (d, ³J = 8.8 Hz, 1H, H5(Phen)), 7.63 (d, ³J = 8.8 Hz, 1H, H6(Phen)), 8.11 (dd, ³J = 8.1 Hz, ⁴J = 1.7 Hz, 1H, H7(Phen)), 8.18 (br. t, ³J = 5.7 Hz, 2H, C(O)NH), 8.83 (br. s, 1H, H2(Phen)), 8.99 (m, 1H, H9(Phen)). ¹³C NMR (100.6 MHz, CDCl₃): δ = 16.2 (d, ³J_{PC} = 6.0 Hz, 4C, CH₃), 34.3 (d, ¹J_{PC} = 156.7 Hz, 2C, CH₂P(O)), 40.78 (1C, CH₂N), 54.4 (1C, CH₂N), 59.1 (2C, CH₂C(O)), 62.8 (d, ²J_{PC} = 6.5 Hz, 4C, CH₂OP), 111.2 (1C), 121.1 (1C), 126.2 (1C), 126.3 (1C), 126.5 (1C), 130.7 (1C), 135.9 (1C), 137.3 (1C), 141.5 (1C), 144.1 (1C), 146.3 (1C), 149.7 (1C), 170.4 (2C, C(O)). ³¹P NMR (162.5 MHz, CDCl₃): δ = 23.7. HRMS (MALDI-TOF): *m/z* [M+H]⁺ calcd for C₂₈H₄₃N₆O₈P₂: 653.2618; found: 653.2629.

2.3 Synthesis of the ruthenium complexes

General procedure. A two-neck flask equipped with a magnetic stirrer and a reflux condenser was charged with *cis*-Ru(bpy)₂Cl₂, phenanthroline ligand (1.1 equivalents) and MeOH ($C_{Ru} = 0.03M$). The reaction mixture was refluxed for 20 h in the dark. The hot reaction mixture was passed through a glass filter and cooled down to r. t.. A saturated aqueous solution of NH₄PF₆ (0.3 mL) was added to this filtrate. After 5 min, the solution was diluted with distilled water (15 mL). In the case of complexes **Ru(Brphen)**, **Ru(Bnphen)** and **Ru(N₂Phen)** the product was obtained as a solid precipitate, which was washed with distilled water and diethyl ether, then dried under reduced pressure. In the case of water-soluble complex **Ru(N₂P₂phen)** the product was extracted by CH₂Cl₂ (3 × 20 mL) and combined organic phases were dried over molecular sieves 3Å. Then the solution was evaporated under reduced pressure and the residue was chromatographed (on silica gel using pure CH₂Cl₂, and then CH₂Cl₂/MeOH (200:1 to 3:1 v/v) as eluents. After chromatography the product was dissolved in CH₂Cl₂ (20 mL), washed with distilled water (3 × 20 mL) to eliminate an excess of NH₄PF₆, and dried over sieves 3Å. Then the solution was evaporated under reduced pressure.

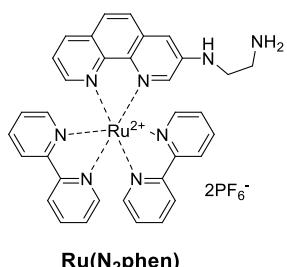


Complex Ru(Brphen). The complex **Ru(Brphen)** was obtained according to the general procedure from 3-bromo-1,10-phenanthroline (**1**) (200 mg, 0.77 mmol), *cis*-Ru(bpy)₂Cl₂ (339 mg, 0.7 mmol), NH₄PF₆ (3 mL of saturated (r.t.) aqueous solution) in 23 mL of MeOH. Yield: 633 mg (94%); red powder. ¹H NMR (400 MHz, CD₃CN): δ = 7.23 (ddt, ³J = 7.6 Hz, ³J = 5.6 Hz, ⁴J = 1.6 Hz, 2H), 7.41–7.47 (m, 2H), 7.47–7.50 (m, 1H), 7.62 (d, ³J = 5.6 Hz, 1H), 7.72–7.79 (m, 2H), 7.84 (d, ³J = 5.0 Hz, 1H), 7.96–8.05 (m, 2H), 8.05–8.13 (m, 4H), 8.17 (d, ³J = 8.8 Hz, 1H, H6(Phen)), 8.27 (d, ³J = 8.8 Hz, 1H, H5(Phen)), 8.45–8.55 (m, 4H), 8.62 (dd, ³J = 8.3 Hz, ⁴J = 1.3 Hz, 1H, H9(Phen)), 8.83 (d, ⁴J = 1.9 Hz, 1H, H2(Phen)). HRMS (MALDI-TOF): *m/z* [M-PF₆]⁺ calcd for C₃₂H₂₃BrF₆N₆PRu: 816.9841; found: 816.9881. The compound was reported previously in *J. Am. Chem. Soc.* **1997**, *119*, 852–853.



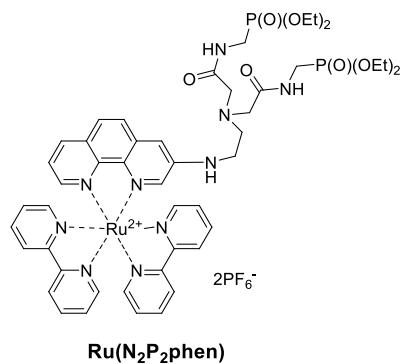
Complex Ru(Bnphen) was obtained according to the general procedure from **3** (30 mg, 0.105 mmol), *cis*-Ru(bpy)₂Cl₂ (45 mg, 0.093 mmol), NH₄PF₆ (0.3 mL of saturated (r.t.) aqueous solution) in 1.5 mL of MeOH. Yield: 83 mg (88%); red powder.

This compound was also obtained according to the palladium-catalyzed amination procedure from **Ru(Brphen)** (97 mg, 0.1 mmol) and benzylamine (11 mg, 0.1 mmol) in the presence of *t*BuONa (15 mg, 0.15 mmol), Pd(dba)₂ (6 mg, 10 mol%) and BINAP (7 mg, 10.5 mol%) in 1 mL of dioxane. After chromatography (silica gel, CH₂Cl₂/MeOH, 10:1 v/v), the product was dissolved in methanol, 0.3 mL of NH₄PF₆ (saturated (r.t.) aqueous solution) was added to precipitate the complex. The solid was filtered, washed with distilled water to eliminate an excess of NH₄PF₆ and dried under reduced pressure. Yield: 59 mg (60%). IR (cm⁻¹): 3735, 3730, 3604, 3431, 3116, 3079, 2926, 2855, 1653, 1624, 1591, 1584, 1559, 1540, 1522, 1507, 1465, 1446, 1432, 1389, 1355, 1331, 1313, 1301, 1267, 1243, 1207, 1179, 1111, 1099, 1068, 1027, 1000, 947, 827, 762, 728, 699. ¹H NMR (400 MHz, CD₃CN): δ = 4.35 (d, ³J = 6.1 Hz, 2H, CH₂), 5.99 (t, ³J = 6.1 Hz, 1H, NH), 7.15–7.35 (m, 7H), 7.35–7.45 (m, 3H), 7.45–7.54 (m, 3H), 7.58 (d, ³J = 5.7 Hz, 1H), 7.74 (d, ³J = 5.4 Hz, 1H), 7.78–7.95 (m, 3H), 7.95–8.12 (m, 5H), 8.37–8.56 (m, 5H). UV/Vis (CH₃CN, λ_{max}, nm (ε, cm⁻¹M⁻¹)): 447 (12000), 420 (13000), 354 (21000), 290 (70000). Fluorescence (CH₃CN): λ_{ex} = 450 nm; λ_{em} = 603 nm. HRMS (MALDI-TOF): *m/z* [M-PF₆]⁺ calcd for C₃₉H₃₁F₆N₇PRu: 844.132; found: 844.128; [M-H-2PF₆]⁺ calcd for C₃₉H₃₀N₇Ru: 698.1606; found: 698.1600



Complex Ru(N₂phen). The complex **Ru(N₂phen)** was obtained according to the general procedure from **6a** (55 mg, 0.23 mmol), *cis*-Ru(bpy)₂Cl₂ (102 mg, 0.21 mmol), NH₄PF₆ (0.3 mL of saturated (r.t.) aqueous solution) in 3.5 mL of MeOH. Yield: 140 mg (71%); red powder. IR (cm⁻¹): 3649, 3421, 3282, 2924, 2855, 2360, 2343, 1602, 1539, 1507, 1362, 1314, 1271, 1243, 1209, 1185, 1162, 1124, 1110, 1070, 1030, 831, 761, 731, 718, 668, 660. ¹H NMR (400 MHz, CD₃CN): δ = 3.12 (t, ³J = 6.0 Hz, 2H, CH₂), 3.46 (q, ³J = 6.0 Hz, 2H, CH₂), 5.42 (t, ³J = 5.9 Hz, 1H, NH), 7.22–7.30 (m, 2H), 7.39–7.47 (m, 3H), 7.49–7.60 (m, 3H), 7.63 (d, ³J = 5.7 Hz, 1H), 7.82 (d, ³J = 5.7 Hz, 1H), 7.84 (d, ³J = 5.6 Hz,

1H), 7.84 (d, $^3J = 5.3$ Hz, 1H), 7.94–8.13 (m, 7H), 8.43–8.55 (m, 5H). HRMS (ESI): m/z [M-H-2PF₆]⁺ calcd for C₃₄H₂₉N₈Ru: 651.1558; found: 651.1545.



Complex Ru(N₂P₂phen). The complex **Ru(N₂P₂phen)** was obtained according to the general procedure from **8a** (57 mg, 0.087 mmol), *cis*-Ru(bpy)₂Cl₂ (38 mg, 0.079 mmol), NH₄PF₆ (0.3 mL of saturated (r.t.) aqueous solution) in 2 mL of MeOH. Yield: 75 mg (70%); red glassy compound, chromatography (silica gel, CH₂Cl₂/MeOH, 20:1 v/v).

This compound was also obtained from complex **Ru(N₂phen)** according to the following procedure. A 10mL flask equipped with a magnetic stirrer a condenser and a gas outlet was charged with **Ru(N₂phen)** (47 mg, 0.05 mmol), CH₂Cl₂ (3 mL) and DIPEA (20 mg, 0.15 mmol). [(2-bromoacetylamino)methyl]phosphonic acid diethyl ester (**2**) (32 mg, 0.11 mmol) was added, and the reaction mixture was stirred at reflux for 48 h under argon. Then the solution was evaporated under reduced pressure and the residue was chromatographed on silica gel using a gradual elution with pure CH₂Cl₂ and then CH₂Cl₂/MeOH, 200:1 to 3:1 v/v. The fractions containing the product (CH₂Cl₂/MeOH, 20:1 v/v) were evaporated, dissolved in 10 mL of distilled water and NH₄PF₆ (0.3 mL of saturated (r.t.) aqueous solution) was added. The product was extracted with CH₂Cl₂ (3 × 10 ml). The combined organic layers were washed with distilled water (3 × 10 ml) to eliminate an excess of NH₄PF₆ and dried over sieves 3Å. The solution was evaporated under reduced pressure. Yield: 24 mg (35%). IR (cm⁻¹): 3299, 3083, 2985, 2933, 2644, 2382, 2349, 2337, 2325, 2114, 2082, 2051, 1981, 1944, 1667, 1600, 1531, 1466, 1445, 1434, 1391, 1369, 1300, 1217, 1184, 1161, 1100, 1020, 975, 876, 829, 763, 730, 717, 660, 647, 599, 579, 555. ¹H NMR (400 MHz, CD₃CN): δ = 1.24 (dt, $^3J_{HH} = ^4J_{HP}$ = 7.1 Hz, 12H, CH₃), 2.71–2.79 (m, 2H, CH₂N), 3.14–3.21 (m, 2H, CH₂N), 3.24 (s, 4H, C(O)CH₂N), 3.49–3.56 (m, 4H, CH₂P(O)), 4.06 (dq, $^3J_{PH} = ^3J_{HH}$ = 7.1 Hz, 8H, CH₂OP), 6.41 (br. s, 1H, NHPhen), 7.22–7.31 (m, 2H), 7.40–7.53 (m, 6H), 7.56 (d, 3J = 5.5 Hz, 1H), 7.59 (d, 3J = 2.3 Hz, 1H), 7.74 (d, 3J = 5.5 Hz, 1H), 7.81 (d, 3J = 5.5 Hz, 1H), 7.84–7.91 (m, 2H), 7.94 (d, 3J = 8.9 Hz, 1H, H5(Phen)), 7.96–8.03 (m, 3H), 8.04–8.12 (m, 2H), 8.40–8.57 (m, 5H). ³¹P NMR (162.5 MHz, CD₃CN): δ = -144.5 (m, $^1J_{PF}$ = 706.5 Hz, 2P, PF₆⁻), 22.7 (2P, P(O)(OEt)₂). UV/Vis (H₂O, pH = 7.4, λ_{max} , nm (ε, cm⁻¹M⁻¹)): 450 (12000), 354 (20000), 285 (66000). Fluorescence (H₂O, pH = 7.4): λ_{ex} = 450 nm; λ_{em} = 603 nm. HRMS (ESI): m/z [M-PF₆]⁺ calcd for C₄₈H₅₈F₆N₁₀O₈P₃Ru: 1211.2594; found: 1211.2589; m/z [M-2PF₆]²⁺ calcd for C₄₈H₅₈N₁₀O₈P₂Ru: 1066.2946; found: 1066.2926.

3. Protonation studies of complexes Ru(N₂phen) and Ru(N₂P₂phen)

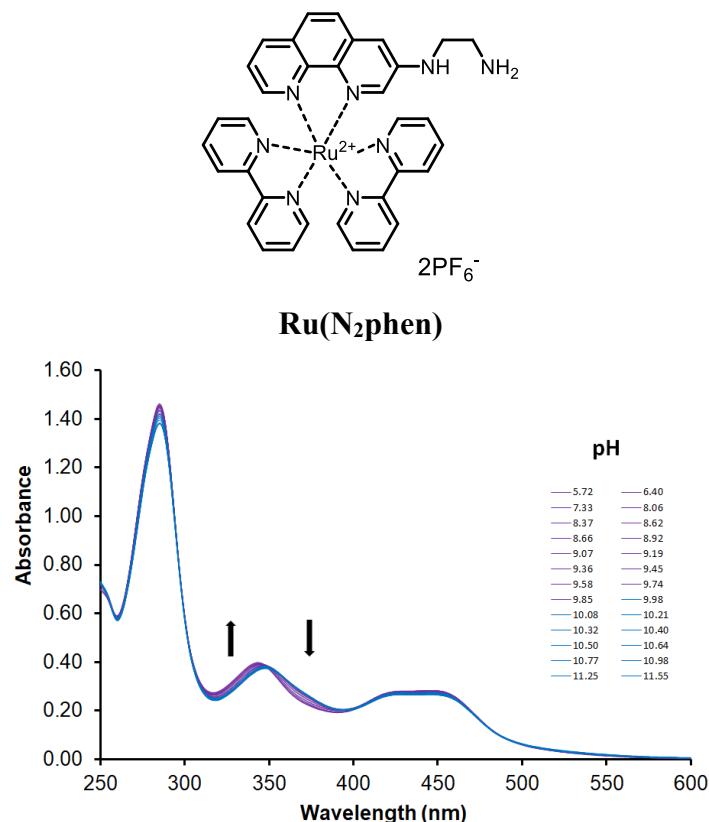


Figure S1. Spectrophotometric titration of **Ru(N₂phen)** ($[Ru(N_2phen)] = 33 \mu M$, $I = 0.1 M$ KCl, pH = 5.7–11.6).

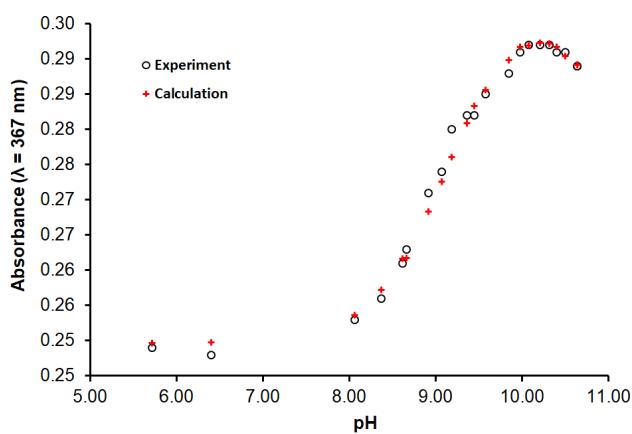


Figure S2. Absorbance changes with pH at $\lambda = 367 \text{ nm}$ for **Ru(N₂phen)**.

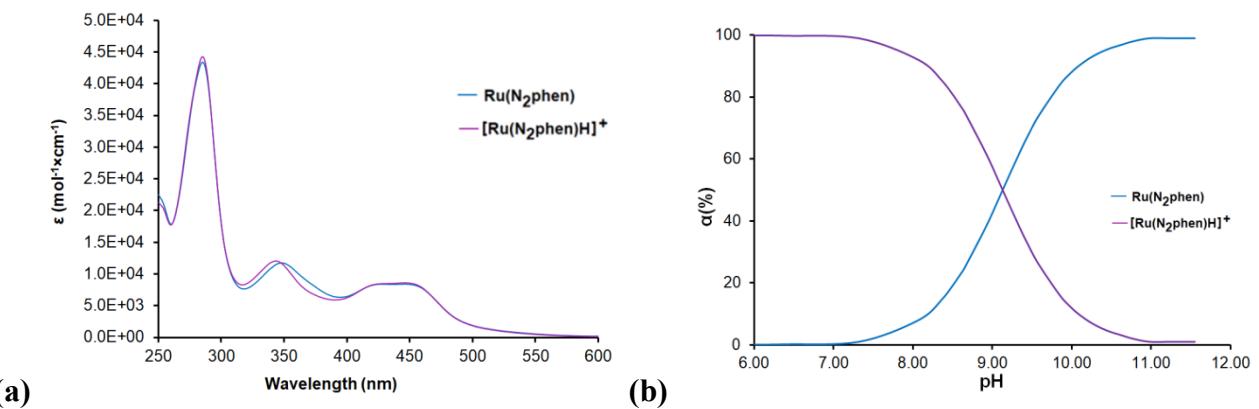


Figure S3. (a) UV–vis spectra of **Ru(N₂phen)** and **[Ru(N₂phen)H]⁺** in water calculated using Hyperquad program [31]. (b) Species distribution diagram for the **Ru(N₂phen)/H⁺** system in water calculated using Hyperquad program [31].

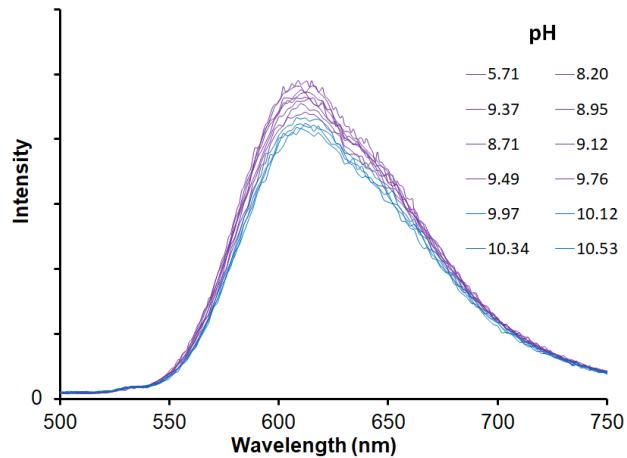


Figure S4. Fluorimetric titration of **Ru(N₂phen)** ($[\text{Ru(N}_2\text{phen)}] = 11 \mu\text{M}$, $I = 0.1 \text{ M KCl}$, $\lambda_{\text{ex}} = 450 \text{ nm}$, pH = 5.7–10.5).

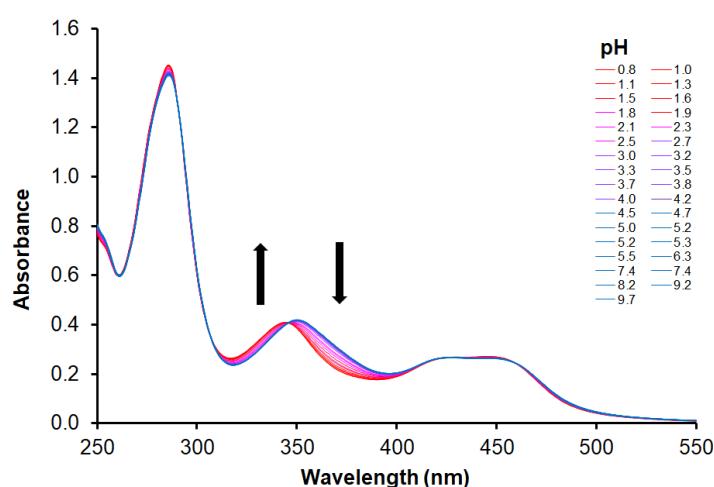
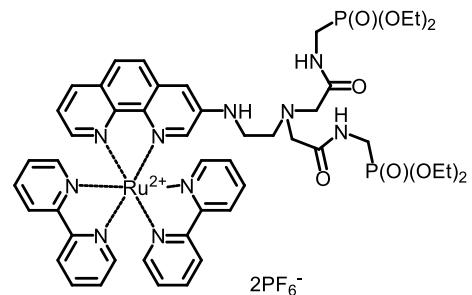


Figure S5. Spectrophotometric titration of **Ru(N₂P₂phen)** ($[Ru(N_2P_2phen)] = 21 \mu M$, $I = 0.1 \text{ M KCl}$, pH = 1.0–9.2).

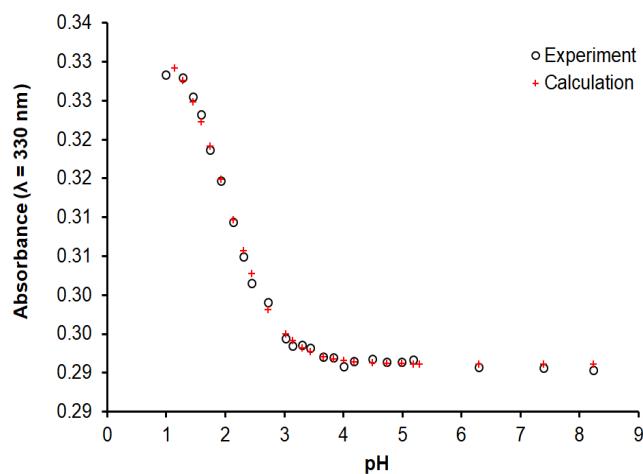


Figure S6. Absorbance changes with pH at $\lambda = 330 \text{ nm}$ for **Ru(N₂P₂phen)**.

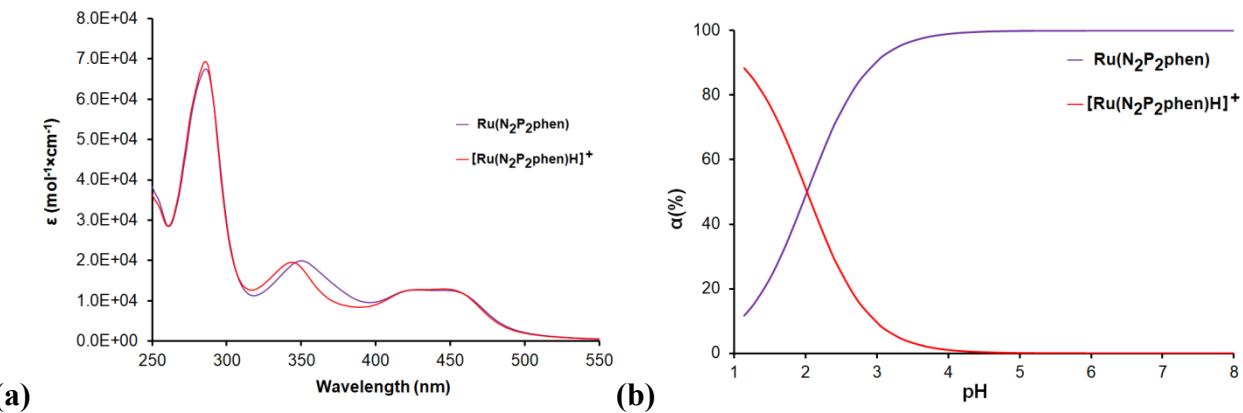


Figure S7. (a) UV–vis spectra of **Ru(N₂P₂phen)** and **[Ru(N₂P₂phen)H]⁺** in water calculated using Hyperquad program [31]. (b) Species distribution diagram for the **Ru(N₂P₂phen)/H⁺** system in water calculated using Hyperquad program [31].

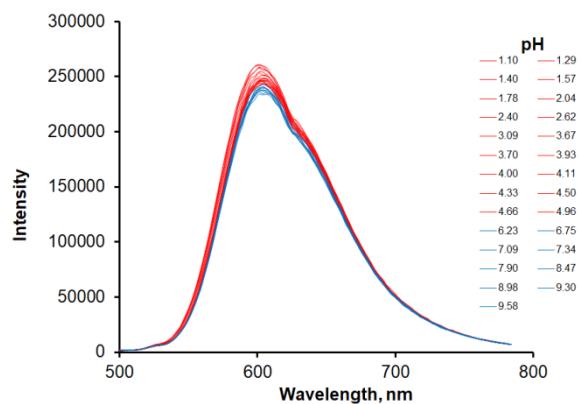


Figure S8. Fluorimetric titration of **Ru(N₂P₂phen)** ($[\text{Ru(N}_2\text{P}_2\text{phen})] = 6.6 \mu\text{M}$, $I = 0.1 \text{ M KCl}$, $\lambda_{\text{ex}} = 450 \text{ nm}$, pH = 1.1–9.3).

4. Metal ion-sensing properties of complexes Ru(N₂phen) and Ru(N₂P₂phen)

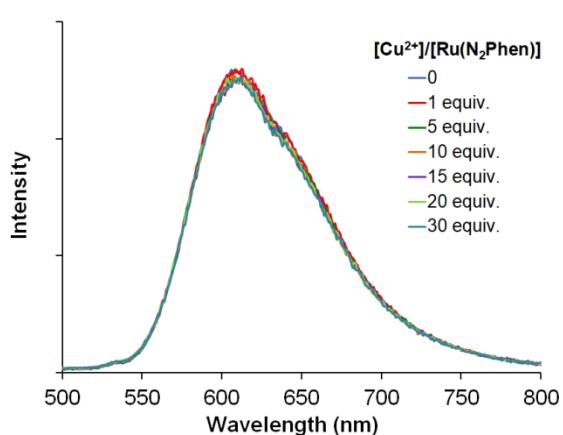
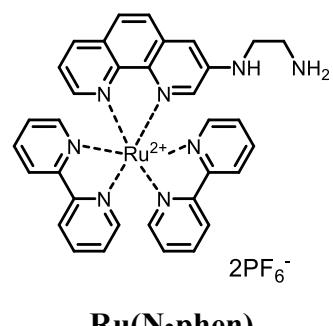


Figure S9. Evolution of fluorescence spectrum of **Ru(N₂phen)** upon addition of Cu(ClO₄)₂ (0–30 equivalents) ([Ru(N₂phen)] = 11 μM, 0.03M HEPES buffer, pH=7.4, $\lambda_{\text{ex}} = 450$ nm).

Point	[Ru(N ₂ phen)] _{tot} , μM	[Cu(ClO ₄) ₂] _{tot} , μM	[Cu ²⁺] _{tot} /[Ru(N ₂ phen)] _{tot} , equivalents
1	11	0	0
2	11	11	1
3	11	55	5
4	11	110	10
5	11	165	15
6	11	220	20
7	11	330	30

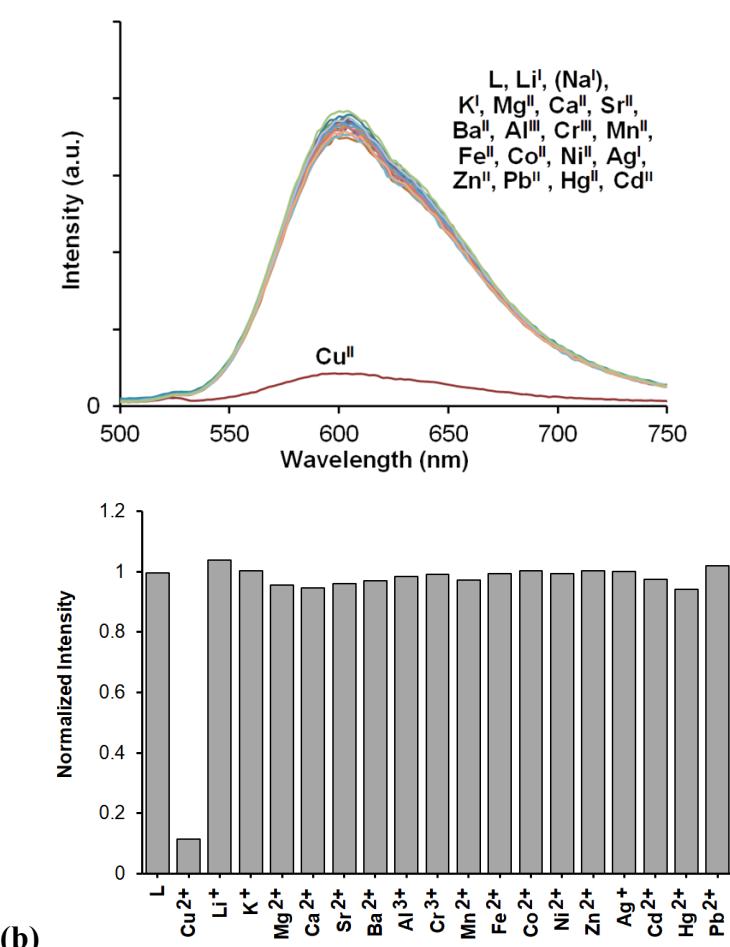
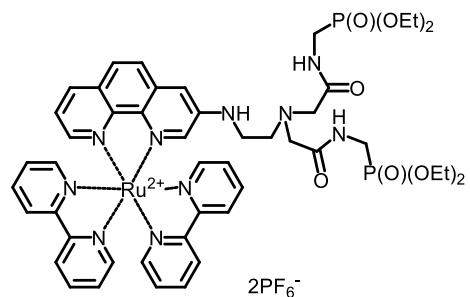


Figure S10. (a) Fluorescence spectra of **Ru(N₂P₂phen)** ($[Ru(N_2P_2phen)] = 5.4 \mu M$, 0.03M HEPES buffer, pH=7.4, $\lambda_{ex} = 450$ nm) before and after addition of 15 equivalents of metal perchlorates ($[M^{n+}]_{tot} = 81 \mu M$ for each metal ion); (b) Normalized fluorescence intensity of the studied solutions at $\lambda_{em} = 600$ nm.

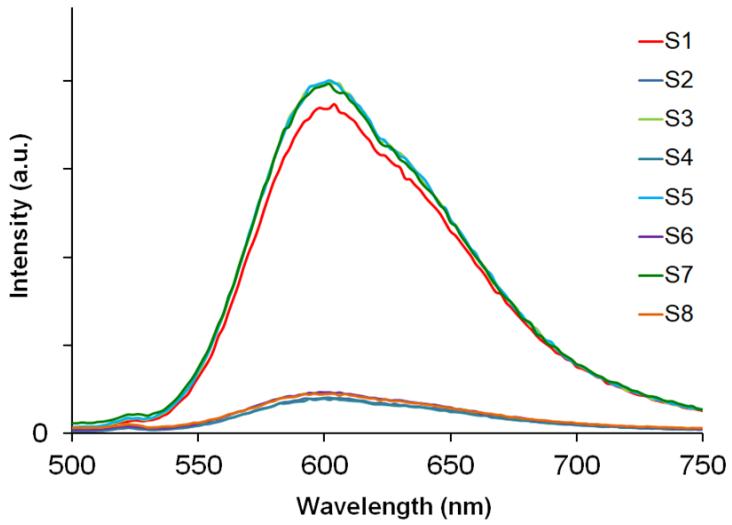


Figure S11. Cross-selectivity studies of metal ion binding by ligand **Ru(N₂P₂phen)** ($[\text{Ru(N}_2\text{P}_2\text{phen}]\right] = 5.4 \mu\text{M}$, 0.03M HEPES buffer, pH=7.4, $\lambda_{\text{ex}} = 450 \text{ nm}$) using fluorescence spectroscopy:

- (S1) emission spectrum of **Ru(N₂P₂phen)**;
- (S2) emission spectrum of **Ru(N₂P₂phen)** after addition of Cu²⁺ (15 equivalents, $[\text{Cu}^{2+}]_{\text{tot}} = 81 \mu\text{M}$);
- (S3) emission spectrum of **Ru(N₂P₂phen)** after addition of Li⁺, (Na⁺), K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺ ($[\text{M}^{n+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents of each metal ion);
- (S4) emission spectrum of **Ru(N₂P₂phen)** after addition of Li⁺, (Na⁺), K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺ ($[\text{M}^{n+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents of each metal ion) and Cu²⁺ ($[\text{Cu}^{2+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents);
- (S5) emission spectrum of **Ru(N₂P₂phen)** after addition of Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ ($[\text{M}^{n+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents of each metal ion);
- (S6) emission spectrum of **Ru(N₂P₂phen)** after addition of Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ ($[\text{M}^{n+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents of each metal ion) and Cu²⁺ (15 equivalents, $[\text{Cu}^{2+}]_{\text{tot}} = 81 \mu\text{M}$);
- (S7) emission spectrum of **Ru(N₂P₂phen)** after addition of Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺ ($[\text{M}^{n+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents of each metal ion);
- (S8) emission spectrum of **Ru(N₂P₂phen)** after addition of Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺ ($[\text{M}^{n+}]_{\text{tot}} = 81 \mu\text{M}$, 15 equivalents of each metal ion) and Cu²⁺ (15 equivalents, $[\text{Cu}^{2+}]_{\text{tot}} = 81 \mu\text{M}$).

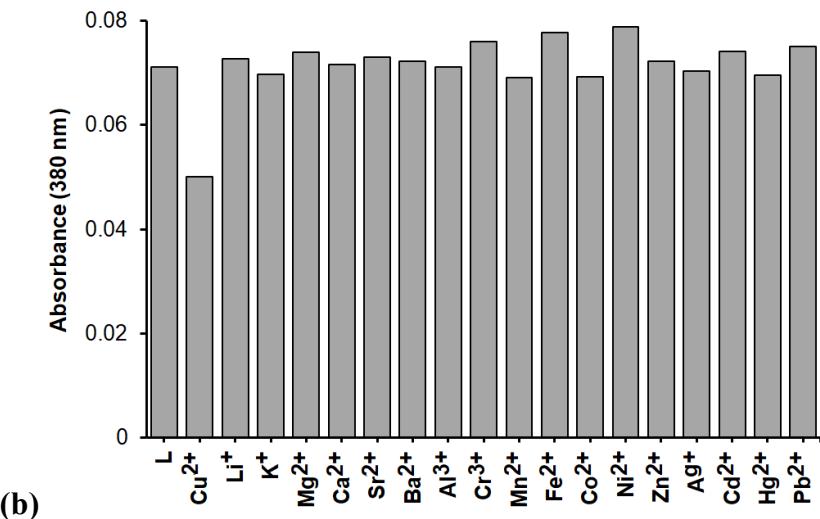
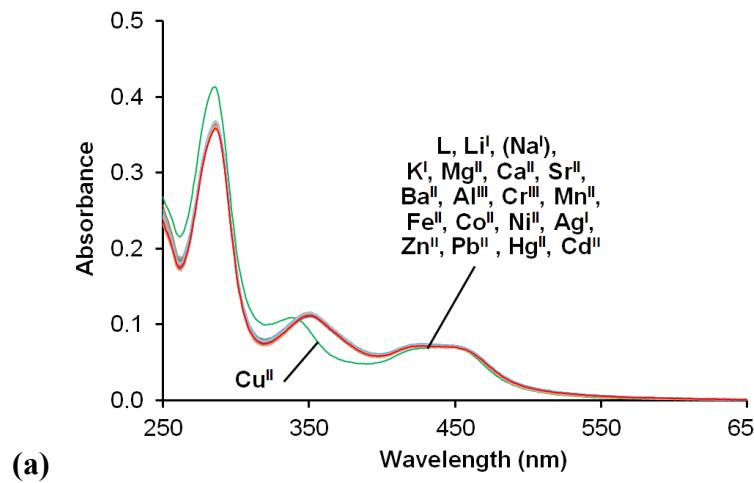


Figure S12. a) Absorption spectra of **Ru(N₂P₂phen)** ($[Ru(N_2P_2phen)] = 5.4 \mu M$, 0.03M HEPES buffer, pH=7.4) before and after addition of 15 equivalents of metal perchlorates ($[M^{n+}]_{tot} = 81 \mu M$); (b) Absorbance of the studied solutions at $\lambda = 380$ nm.

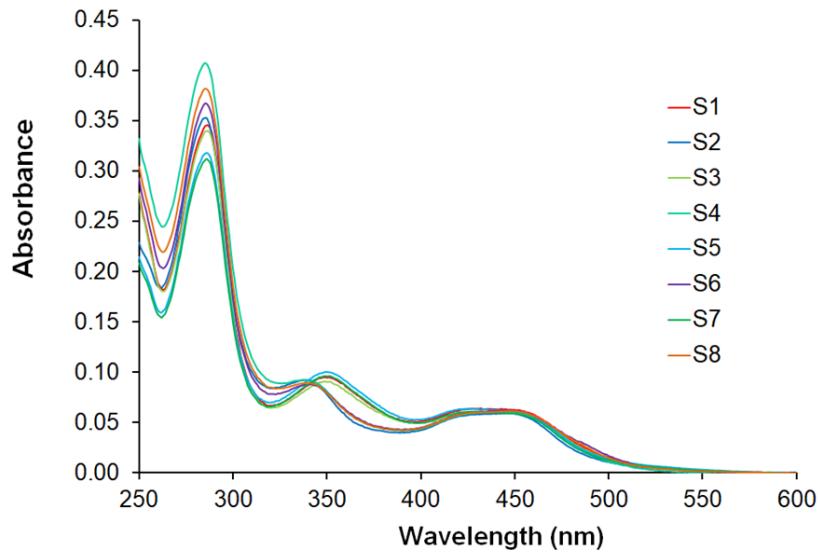


Figure S13. Cross-selectivity studies of metal ion binding by ligand **Ru(N₂P₂phen)** ([Ru(N₂P₂phen)]) = 5.4 μM, 0.03M HEPES buffer, pH=7.4) using UV-vis spectroscopy:

- (S1) emission spectrum of **Ru(N₂P₂phen)**;
- (S2) emission spectrum of **Ru(N₂P₂phen)** after addition of Cu²⁺ ([Cu²⁺]_{tot} = 81 μM, 15 equivalents);
- (S3) emission spectrum of **Ru(N₂P₂phen)** after addition of Li⁺, (Na⁺), K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺ ([Mⁿ⁺]_{tot} = 81 μM, 15 equivalents of each metal ion);
- (S4) emission spectrum of **Ru(N₂P₂phen)** after addition of Li⁺, (Na⁺), K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺ ([Mⁿ⁺]_{tot} = 81 μM, 15 equivalents of each metal ion) and Cu²⁺ ([Cu²⁺]_{tot} = 81 μM, 15 equivalents);
- (S5) emission spectrum of **Ru(N₂P₂phen)** after addition of Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ ([Mⁿ⁺]_{tot} = 81 μM, 15 equivalents of each metal ion);
- (S6) emission spectrum of **Ru(N₂P₂phen)** after addition of Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ ([Mⁿ⁺]_{tot} = 81 μM, 15 equivalents of each metal ion) and Cu²⁺ ([Cu²⁺]_{tot} = 81 μM, 15 equivalents);
- (S7) emission spectrum of **Ru(N₂P₂phen)** after addition of Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺ ([Mⁿ⁺]_{tot} = 81 μM, 15 equivalents of each metal ion);
- (S8) emission spectrum of **Ru(N₂P₂phen)** after addition of Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺ ([Mⁿ⁺]_{tot} = 81 μM, 15 equivalents of each metal ion) and Cu²⁺ ([Cu²⁺]_{tot} = 81 μM, 15 equivalents).

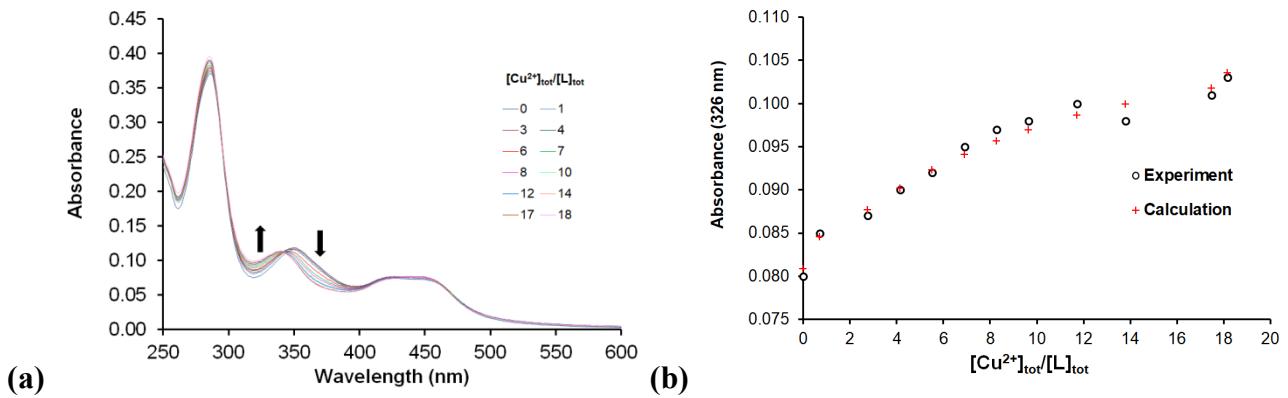


Figure S14. (a) Evolution of UV–vis spectrum of **Ru(N₂P₂phen)** upon addition of $Cu(ClO_4)_2$ (0–18) equivalents ($[Ru(N_2P_2phen)] = 5.6 \mu M$, 0.03M HEPES buffer, pH=7.4). (b) Changes of absorbance with $[Cu^{2+}]_{tot}/[Ru(N_2P_2phen)]_{tot}$ ratio at $\lambda = 326$ nm upon addition of $Cu(ClO_4)_2$ (0–18).

Point	$[Ru(N_2P_2phen)]_{tot}, \mu M$	$[Cu^{2+}]_{tot}, \mu M$	$[Cu^{2+}]_{tot}/[Ru(N_2P_2phen)]_{tot}$, equivalents
1	5.6	0	0.0
2	5.6	8.0	1.4
3	5.6	15.9	2.8
4	5.6	23.9	4.3
5	5.6	31.7	5.7
6	5.6	39.6	7.1
7	5.6	47.4	8.5
8	5.6	55.2	9.9
9	5.6	66.9	11.9
10	5.6	78.4	14.0
11	5.6	98.8	17.6
12	5.6	129.0	18.1

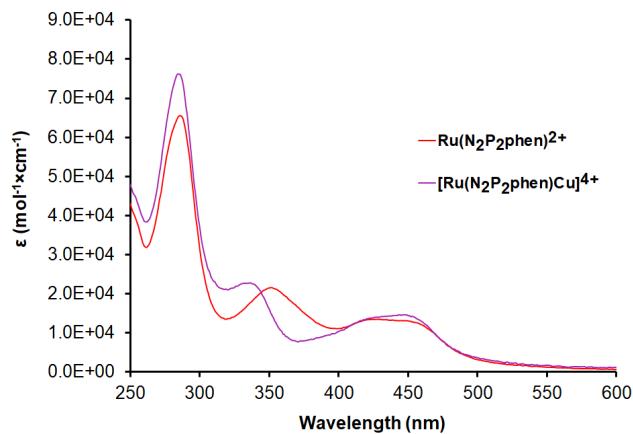


Figure S15. (a) UV–vis spectra of $Ru(N_2P_2phen)^{2+}$ and $[Ru(N_2P_2phen)Cu]^{4+}$ in water calculated using Hyperquad program [31].

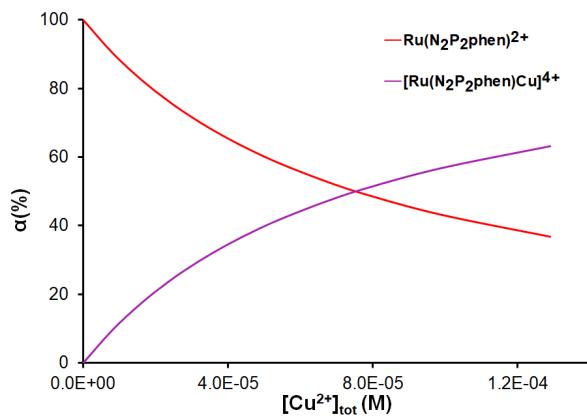


Figure S16. Species distribution diagram for the $Ru(N_2P_2phen)/Cu^{2+}$ system in water calculated using Hyperquad program [31] (Model for calculation: $L \rightleftharpoons LH^+$; $Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$; $Cu^{2+} \rightleftharpoons Cu(OH)^+ \rightleftharpoons Cu_2(OH)_2^{2+} \rightleftharpoons Cu(OH)_2$).

5. Structural studies of copper(II) complex with Ru(N₂P₂phen) chelator

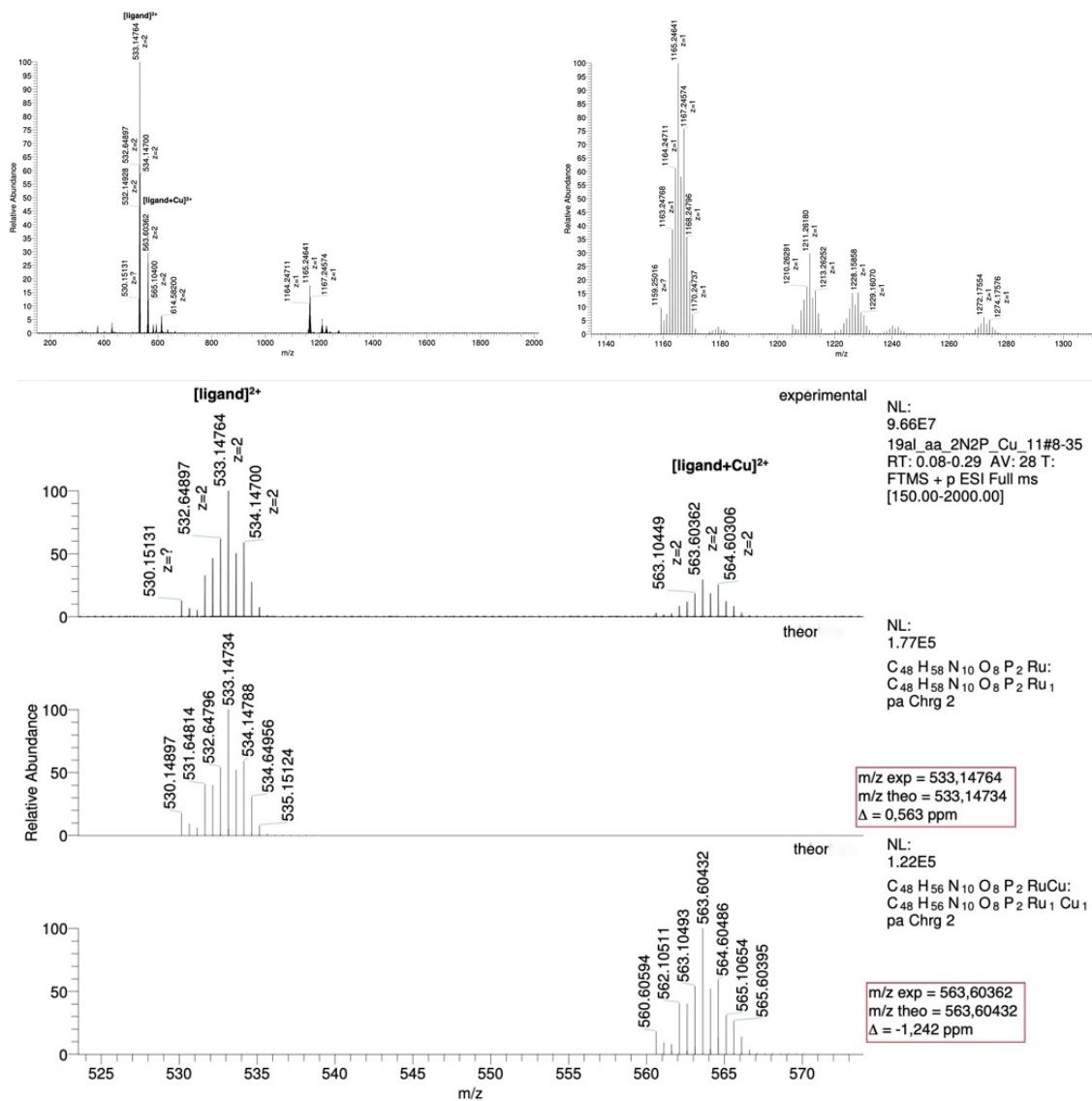


Figure S17. HRMS (ESI) spectrum of the $\{\text{Cu}[\text{Ru}(\text{N}_2\text{P}_2\text{phen})]\}\text{(ClO}_4)_2$ complex.

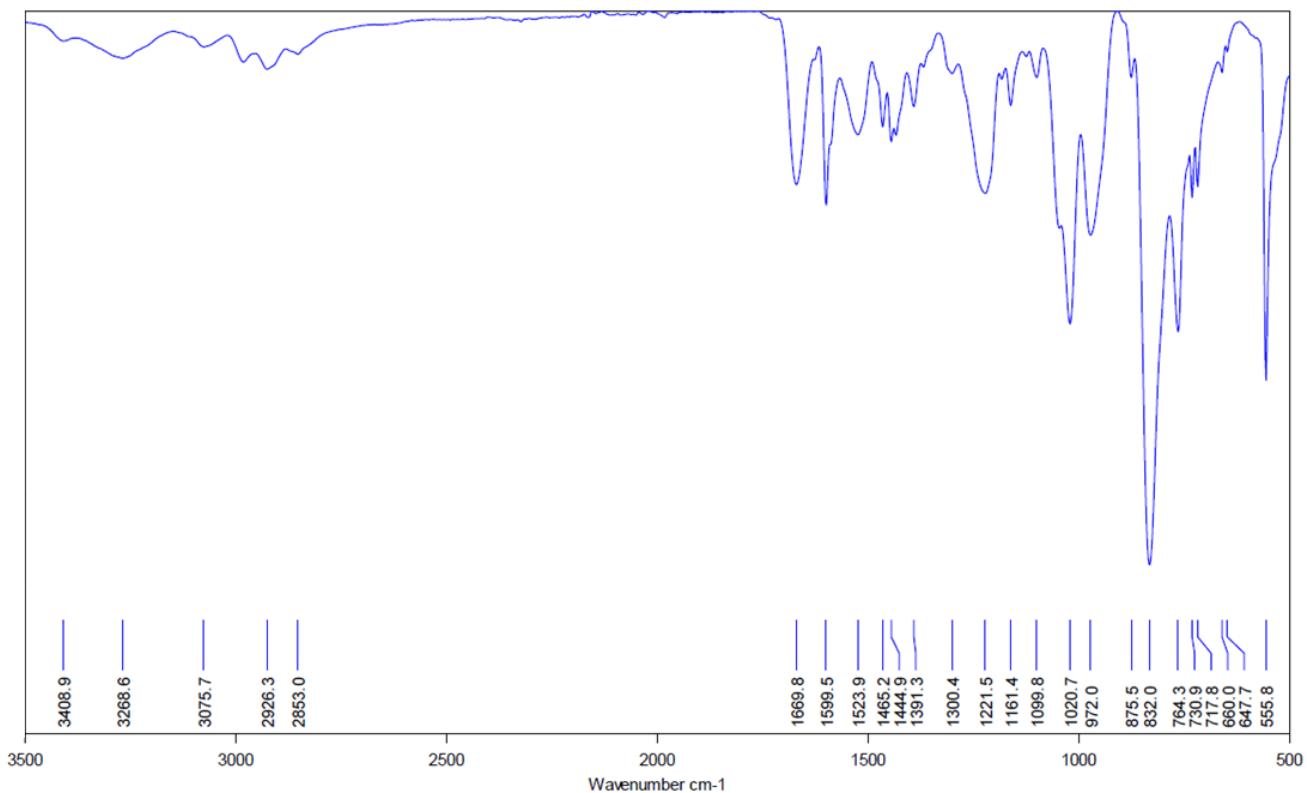


Figure S18. FTIR spectrum of **Ru(N₂P₂phen)** (neat).

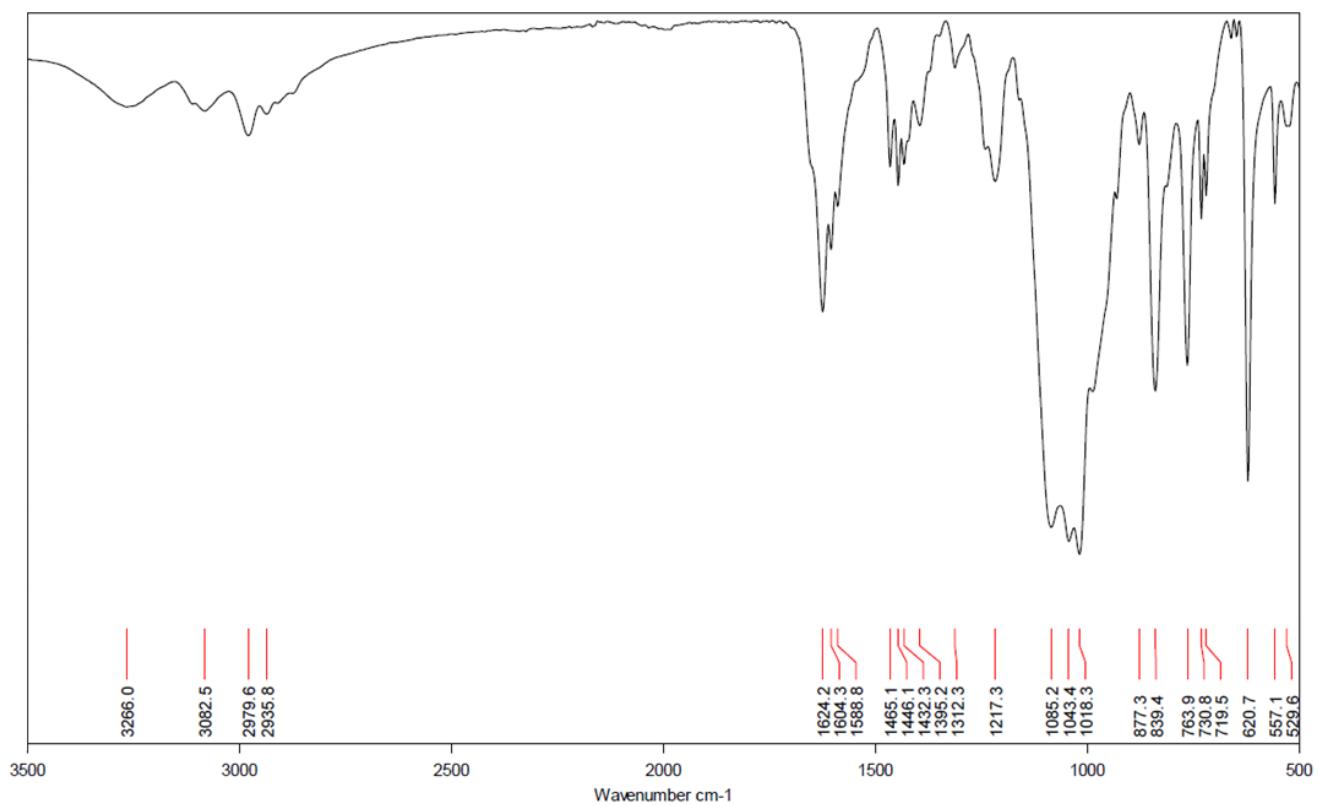
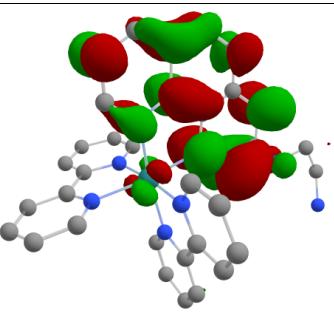
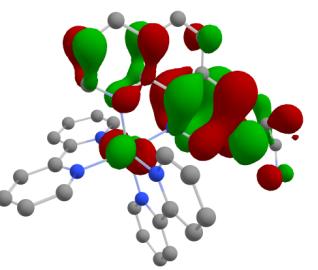
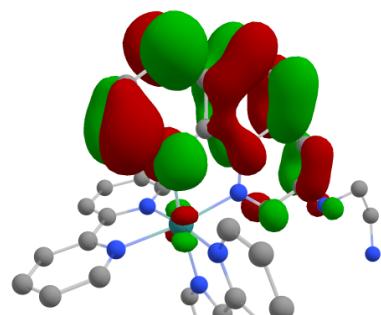
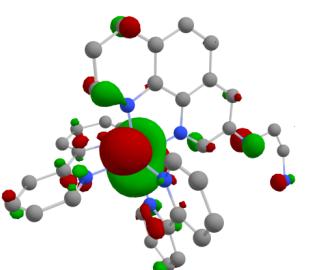
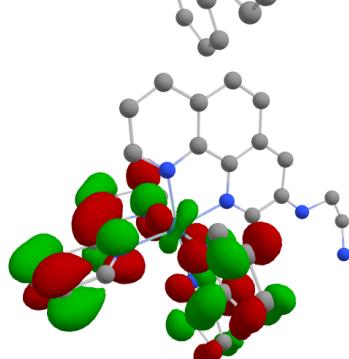
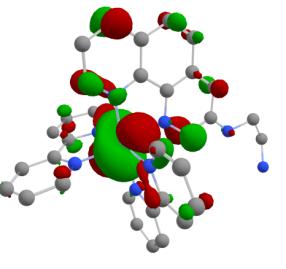
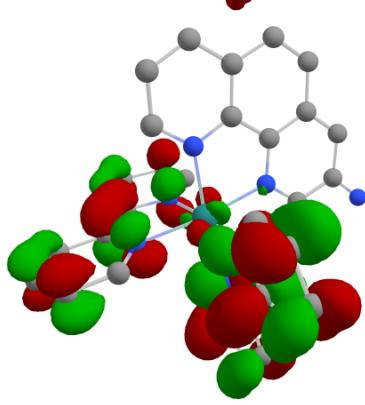
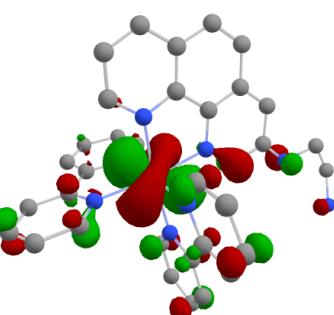


Figure S19. FTIR spectrum of complex $\{\text{Cu}[\text{Ru}(\text{N}_2\text{P}_2\text{phen})]\}(\text{ClO}_4)_2$ (neat).

6. DFT-studies of Ru(N₂phen) and Ru(N₂P₂phen) complexes

DFT-studies of **Ru(phen)** were previously published [24].

Table S2. Calculated isodensity plot of the HOMO and LUMO orbitals for complex **Ru(N₂phen)**

Orbital E(eV)	The electron-cloud distribution	Orbital E(eV)	The electron-cloud distribution
LUMO+3 -6.65		HOMO -10.33	
LUMO+2 -6.68		HOMO-1 -10.69	
LUMO+1 -7.14		HOMO-2 -10.77	
LUMO -7.23		HOMO-3 -10.85	

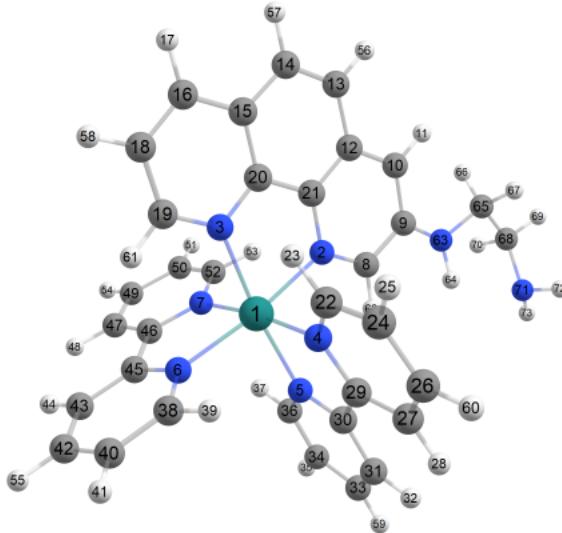


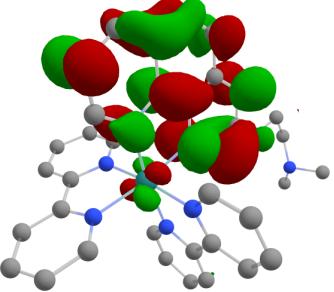
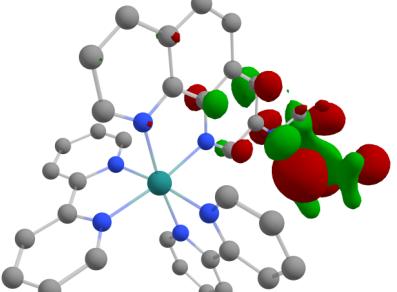
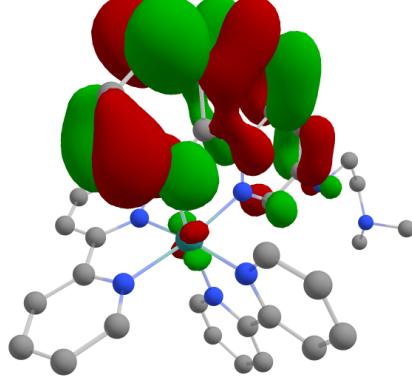
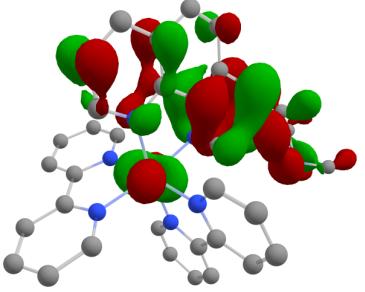
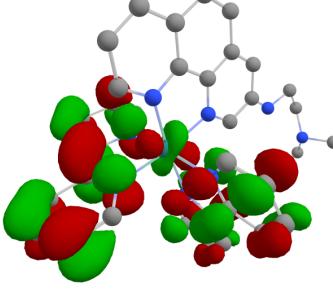
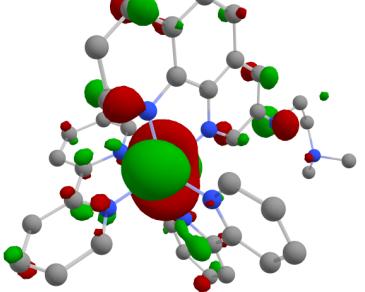
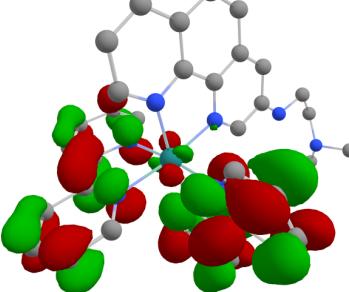
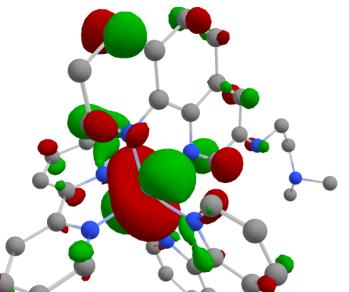
Figure S20. The structure of **Ru(N₂phen)** complex obtained by full geometry optimization at B3LYP/6-31G(d,p) level.

1	44	8.419781437	24.245451317	0.319524873
2	7	10.404433117	24.875906739	0.714328876
3	7	8.690523211	23.519938896	2.287258550
4	7	9.199170521	22.560034843	-0.659119223
5	7	8.385669593	24.851601110	-1.691631450
6	7	6.392942049	23.715431546	0.173412402
7	7	7.466256333	25.930623932	1.136463837
8	6	11.225749846	25.549967204	-0.081560071
9	6	12.555623768	25.926988626	0.287613320
10	6	13.000092250	25.538679446	1.562037014
11	1	14.002508142	25.781372993	1.894632210
12	6	12.143014710	24.829713091	2.415484845
13	6	12.522043403	24.402383990	3.738253655
14	6	11.657615789	23.717801342	4.537794608
15	6	10.328866212	23.392057798	4.095411214
16	6	9.390849916	22.689929265	4.876608204
17	1	9.657405910	22.362497985	5.876857077
18	6	8.134551214	22.424619710	4.356210408
19	6	7.821866286	22.855312584	3.060360825
20	6	9.931315344	23.795413922	2.795635745
21	6	10.840253555	24.509939453	1.960655275
22	6	9.607546543	21.425480128	-0.056168030
23	1	9.504319585	21.398945908	1.021361573
24	6	10.125794523	20.343350633	-0.757586510

25	1	10.436029782	19.454115184	-0.220805525
26	6	10.233625299	20.432751210	-2.144691166
27	6	9.819127075	21.601955475	-2.775085098
28	1	9.897125551	21.688028965	-3.851570089
29	6	9.304162433	22.657307729	-2.015771492
30	6	8.834949627	23.931570748	-2.593806394
31	6	8.836718422	24.209289481	-3.964391859
32	1	9.191561697	23.470591993	-4.672022037
33	6	8.376008993	25.439394935	-4.422971612
34	6	7.918116450	26.373469116	-3.494617095
35	1	7.547828462	27.344699129	-3.802583289
36	6	7.938457206	26.039693737	-2.145725570
37	1	7.590640489	26.734526616	-1.391195141
38	6	5.918963570	22.567432443	-0.351387375
39	1	6.663503831	21.864142408	-0.703337472
40	6	4.561983958	22.281587262	-0.440863278
41	1	4.237548420	21.341157860	-0.871756814
42	6	3.646837333	23.222276442	0.029512718
43	6	4.125974125	24.411050789	0.570981912
44	1	3.427992634	25.152816557	0.938353510
45	6	5.503931095	24.642119689	0.635085698
46	6	6.104484478	25.869414530	1.193391278
47	6	5.359920692	26.914067013	1.749782977
48	1	4.279635142	26.854468222	1.792109451
49	6	6.010628498	28.034549043	2.257053598
50	6	7.402510023	28.087618841	2.197268021
51	1	7.954391382	28.937551612	2.582488829
52	6	8.088565389	27.018820860	1.632667758
53	1	9.169473124	27.017350234	1.565854091
54	1	5.440641147	28.848403993	2.692157647
55	1	2.579678384	23.035912578	-0.024291501
56	1	13.520774859	24.639497419	4.090763614
57	1	11.962156824	23.404127347	5.531325446
58	1	7.389426524	21.888654945	4.932654452
59	1	8.373119574	25.661755344	-5.484600586
60	1	10.632865497	19.608854724	-2.726442319

61	1	6.848000705	22.656657466	2.627904323
62	1	10.841850593	25.825806220	-1.058128173
63	7	13.296072519	26.651172551	-0.584306978
64	1	13.019017583	26.713132698	-1.562800926
65	6	14.700765431	26.989240830	-0.410696398
66	1	14.859636038	27.484818238	0.553442204
67	1	15.325857334	26.082280973	-0.424011909
68	6	15.107261129	27.938714449	-1.547291880
69	1	16.191468608	28.106056929	-1.494677015
70	1	14.620422993	28.905960509	-1.388752312
71	7	14.632512559	27.402036263	-2.830379587
72	1	15.262243599	26.677278648	-3.168512189
73	1	14.631421216	28.131508334	-3.537631472

Table S3. Calculated isodensity plot of the HOMO and LUMO orbitals for complex Ru(N₂Me₂phen)

Orbital E(eV)	The electron-cloud distribution	Orbital E(eV)	The electron-cloud distribution
LUMO+3 -6.65		HOMO -10.08	
LUMO+2 -6.68		HOMO-1 -10.40	
LUMO+1 -7.15		HOMO-2 -10.70	
LUMO -7.23		HOMO-3 -10.77	

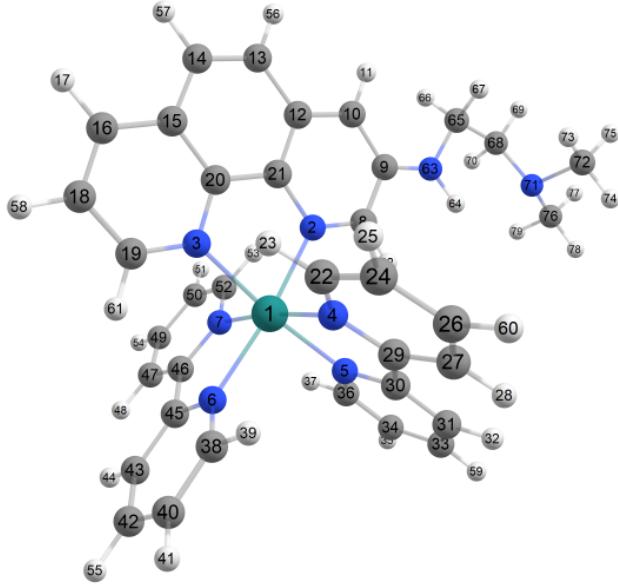


Figure S21. The structure of **Ru(N₂Me₂phen)** complex obtained by full geometry optimization at B3LYP/6-31G(d,p) level.

1	44	8.430109094	24.236288643	0.316158089
2	7	10.414180919	24.864681832	0.710811253
3	7	8.698549510	23.510840895	2.284058946
4	7	9.213407120	22.558109878	-0.673171421
5	7	8.388705771	24.851996387	-1.691411361
6	7	6.400965542	23.710811101	0.174512753
7	7	7.482929251	25.920727406	1.140137264
8	6	11.237978670	25.531923663	-0.088226291
9	6	12.564154956	25.917805723	0.284696508
10	6	13.000634260	25.548834756	1.567997525
11	1	13.998247539	25.804152915	1.905398816
12	6	12.142137734	24.843570500	2.423117533
13	6	12.512795545	24.435271357	3.754461744
14	6	11.645474281	23.756298901	4.555852354
15	6	10.323060556	23.414466762	4.106276582
16	6	9.383610849	22.714486027	4.887834102
17	1	9.643883588	22.401923932	5.894462228
18	6	8.133986940	22.432857137	4.359836005
19	6	7.828707828	22.847551661	3.057071585
20	6	9.933606389	23.799839141	2.798687189
21	6	10.844203423	24.511650049	1.962955822
22	6	9.637220600	21.425971438	-0.076324910

23	1	9.538009401	21.393959704	1.001542404
24	6	10.167567343	20.353809652	-0.784199924
25	1	10.490768701	19.465939834	-0.252634059
26	6	10.271590906	20.451390676	-2.171093883
27	6	9.841767647	21.618418252	-2.795236784
28	1	9.919476702	21.712035132	-3.871225082
29	6	9.314879891	22.663319878	-2.029670298
30	6	8.833013847	23.936304548	-2.600360224
31	6	8.819352981	24.217631041	-3.970250790
32	1	9.168746430	23.481845501	-4.683661885
33	6	8.349718064	25.447459679	-4.420500845
34	6	7.900352297	26.378372428	-3.484831499
35	1	7.524957091	27.349656894	-3.786419568
36	6	7.935127677	26.040830357	-2.137258580
37	1	7.593988030	26.732732931	-1.376955992
38	6	5.921276243	22.566020075	-0.351981209
39	1	6.662319037	21.860785846	-0.707690767
40	6	4.562791802	22.285914679	-0.438707222
41	1	4.233419159	21.348128684	-0.871577766
42	6	3.652356171	23.228524210	0.037015868
43	6	4.137483625	24.413192783	0.581764237
44	1	3.444000404	25.156714296	0.954133119
45	6	5.516318176	24.638642166	0.642324348
46	6	6.121422088	25.863045667	1.201462671
47	6	5.381048687	26.909707003	1.759733301
48	1	4.300886313	26.852691728	1.806906666
49	6	6.036027041	28.029811940	2.262017913
50	6	7.427768899	28.079943728	2.196390232
51	1	7.982604702	28.930248964	2.576276469
52	6	8.109591352	27.008197980	1.632296613
53	1	9.190195130	27.004137790	1.561062357
54	1	5.469327372	28.845897768	2.697195395
55	1	2.584331762	23.046881282	-0.015363829
56	1	13.506990568	24.683362989	4.112391782
57	1	11.942597403	23.459417091	5.556768997
58	1	7.387764594	21.897302520	4.935464279

59	1	8.333526190	25.672478234	-5.481459318
60	1	10.680501385	19.635485218	-2.757281932
61	1	6.859327762	22.637614357	2.619889174
62	1	10.859030149	25.796073485	-1.069899762
63	7	13.309667027	26.631054919	-0.590646344
64	1	13.032991173	26.704180533	-1.568717480
65	6	14.703273915	27.004506662	-0.400688989
66	1	14.830557266	27.540910513	0.546540772
67	1	15.345841418	26.112987097	-0.360357187
68	6	15.105092131	27.933253576	-1.557585359
69	1	16.192690710	28.110115879	-1.515886739
70	1	14.613070044	28.899578331	-1.408641116
71	7	14.661230852	27.400381978	-2.849541938
72	6	15.499636456	26.286816254	-3.306038423
73	1	15.492387886	25.473892823	-2.574412152
74	1	15.102892487	25.893238570	-4.245707065
75	1	16.547038310	26.587405991	-3.475342050
76	6	14.594645930	28.450817673	-3.871451038
77	1	15.577426390	28.899792724	-4.089858706
78	1	14.202494941	28.029367068	-4.801195958
79	1	13.919377726	29.246530277	-3.544496911

7. NMR spectra of newly synthesized compounds

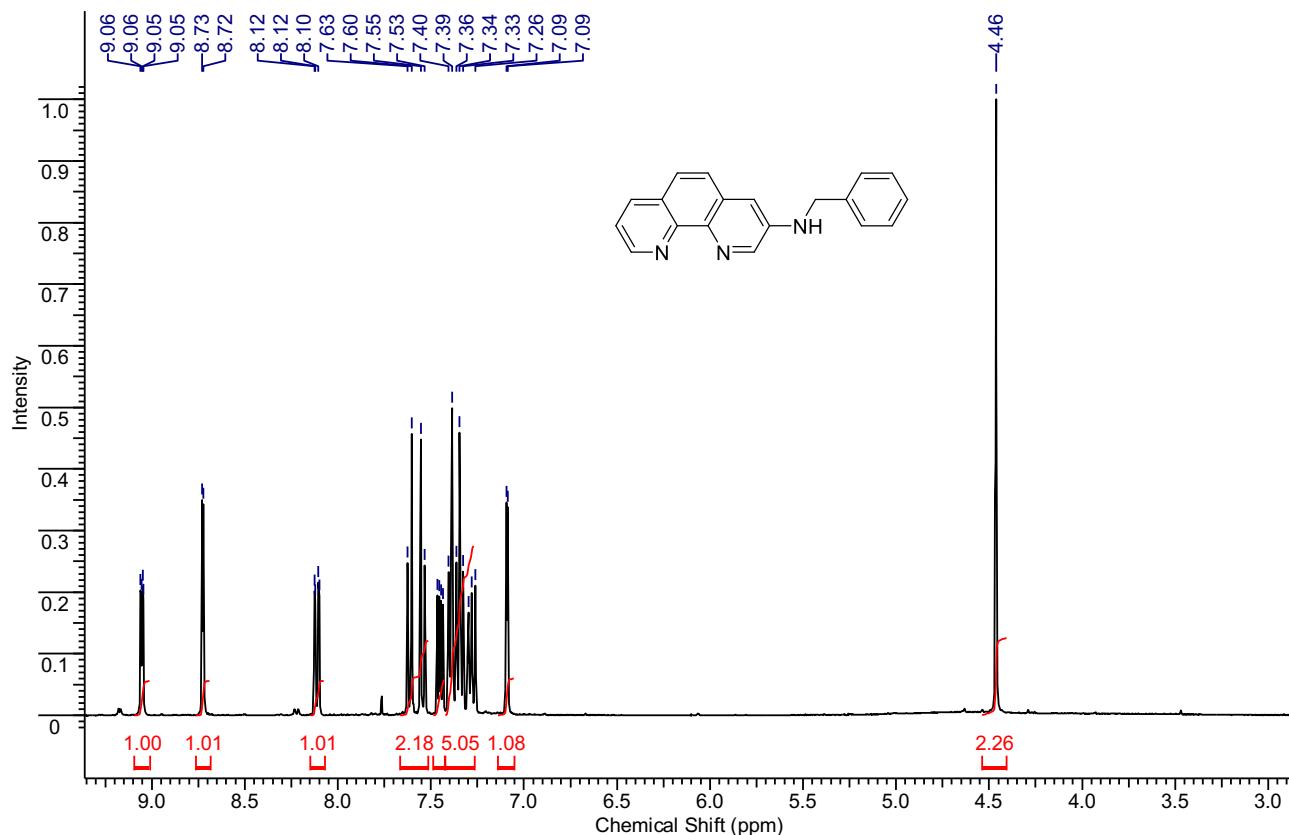


Figure S22. ¹H NMR spectrum of 3 (CDCl₃, 400MHz, 300K).

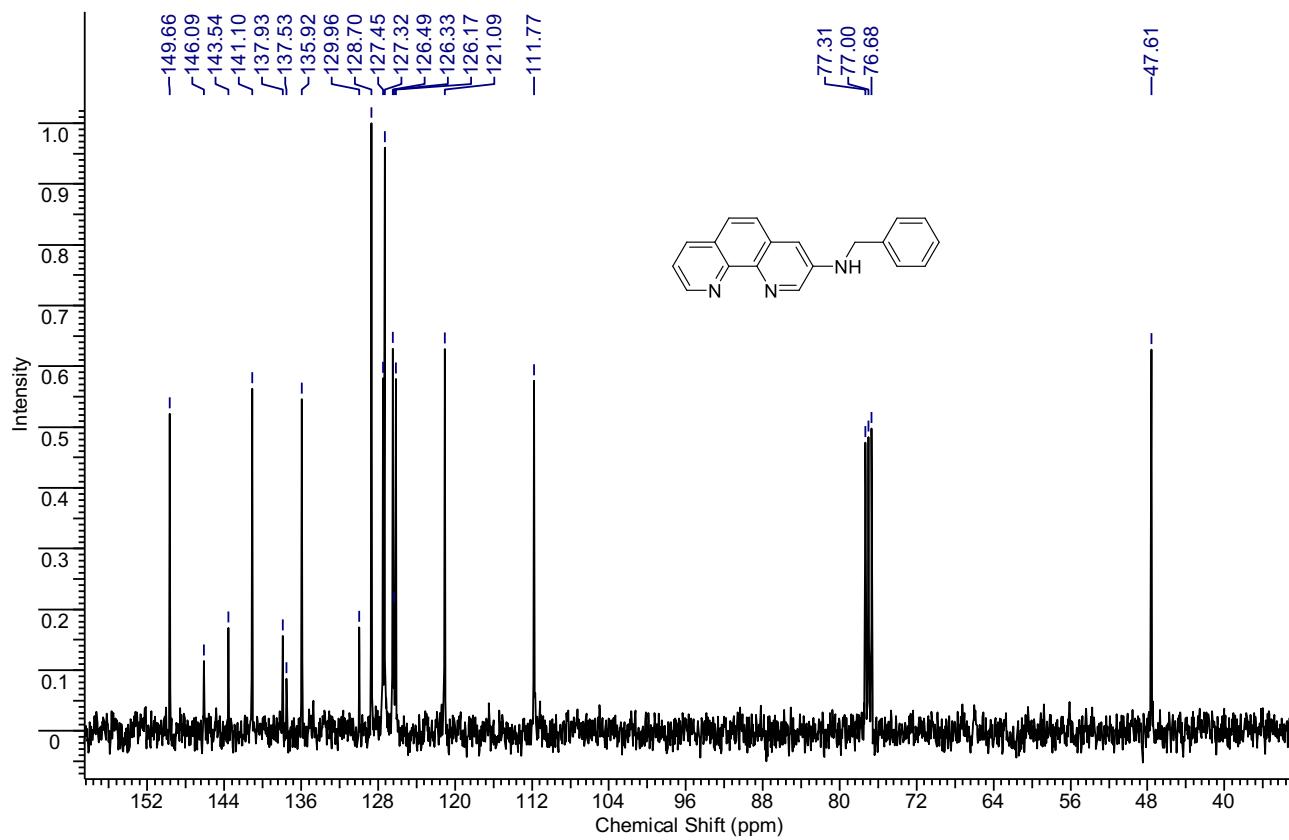


Figure S23. ¹³C NMR spectrum of 3 (CDCl₃, 100.6 MHz, 300K).

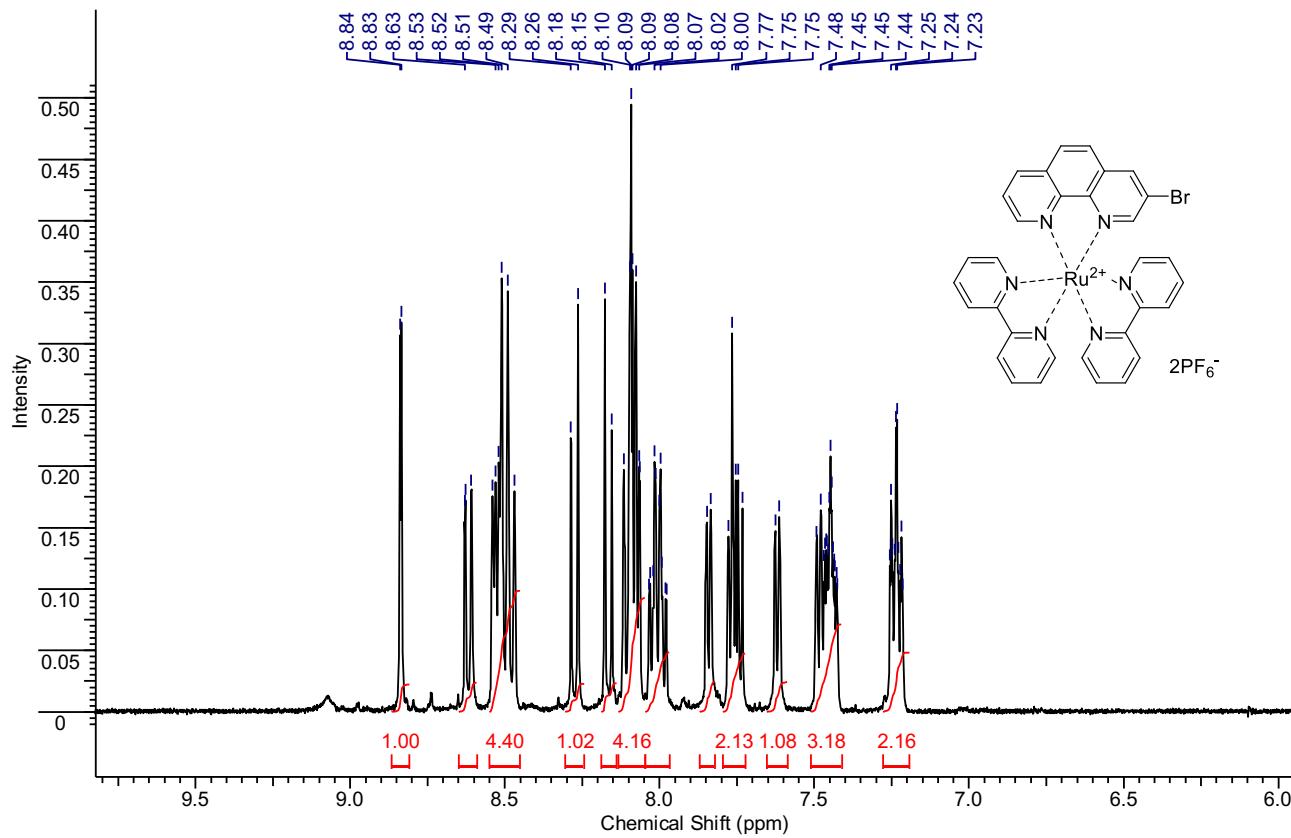


Figure S24. ^1H NMR spectrum of Ru(Brphen) (CD_3CN , 400MHz, 300K).

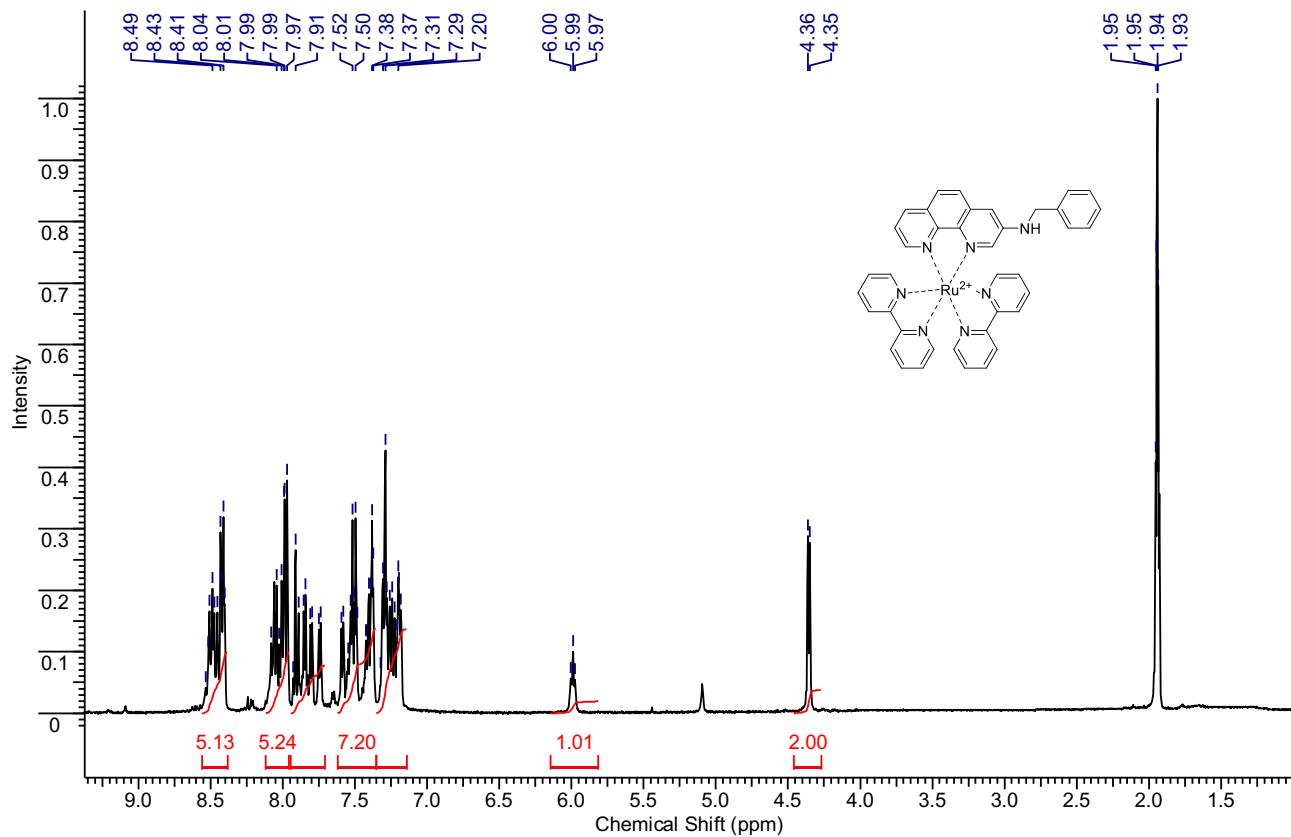


Figure S25. ^1H NMR spectrum of Ru(Bnphen) (CD_3CN , 400MHz, 300K).

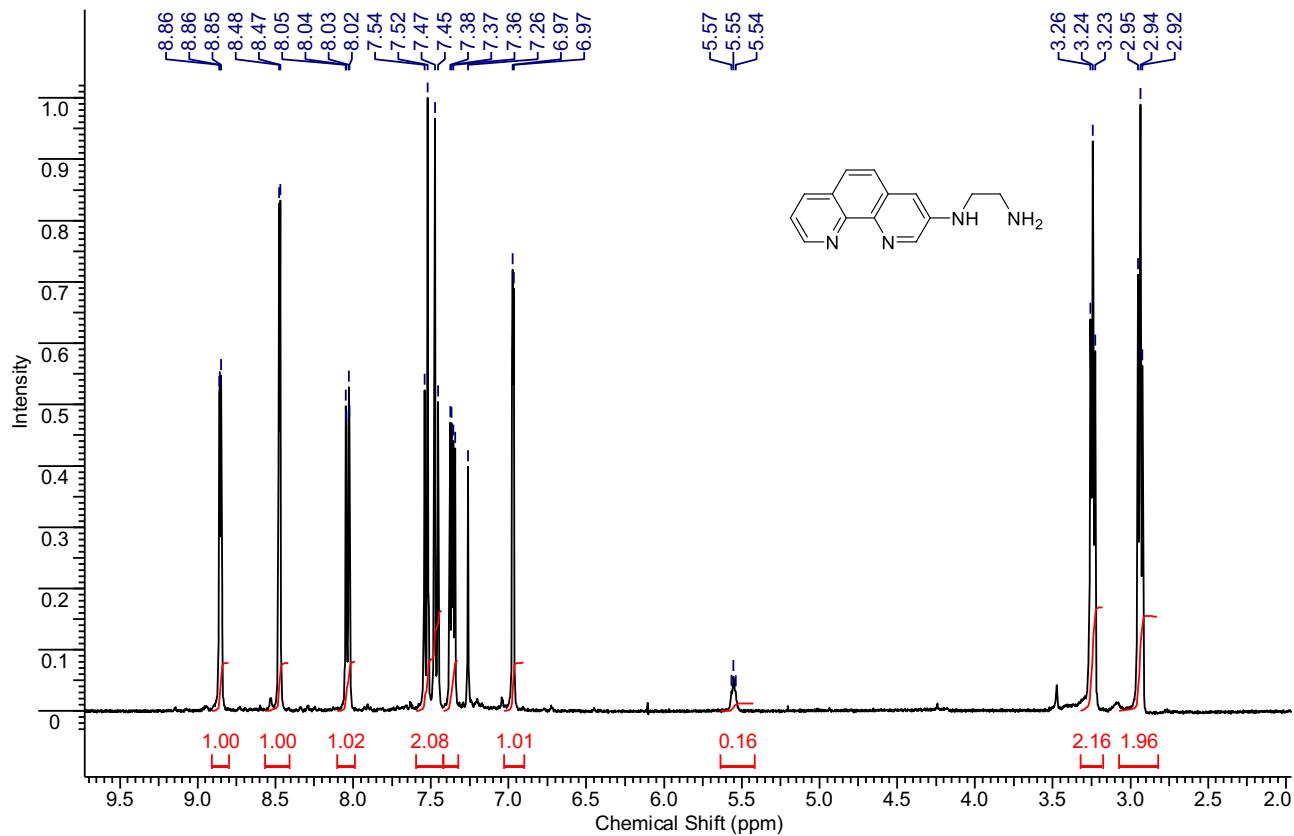


Figure S26. ^1H NMR spectrum of **6a** ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 400MHz, 300K).

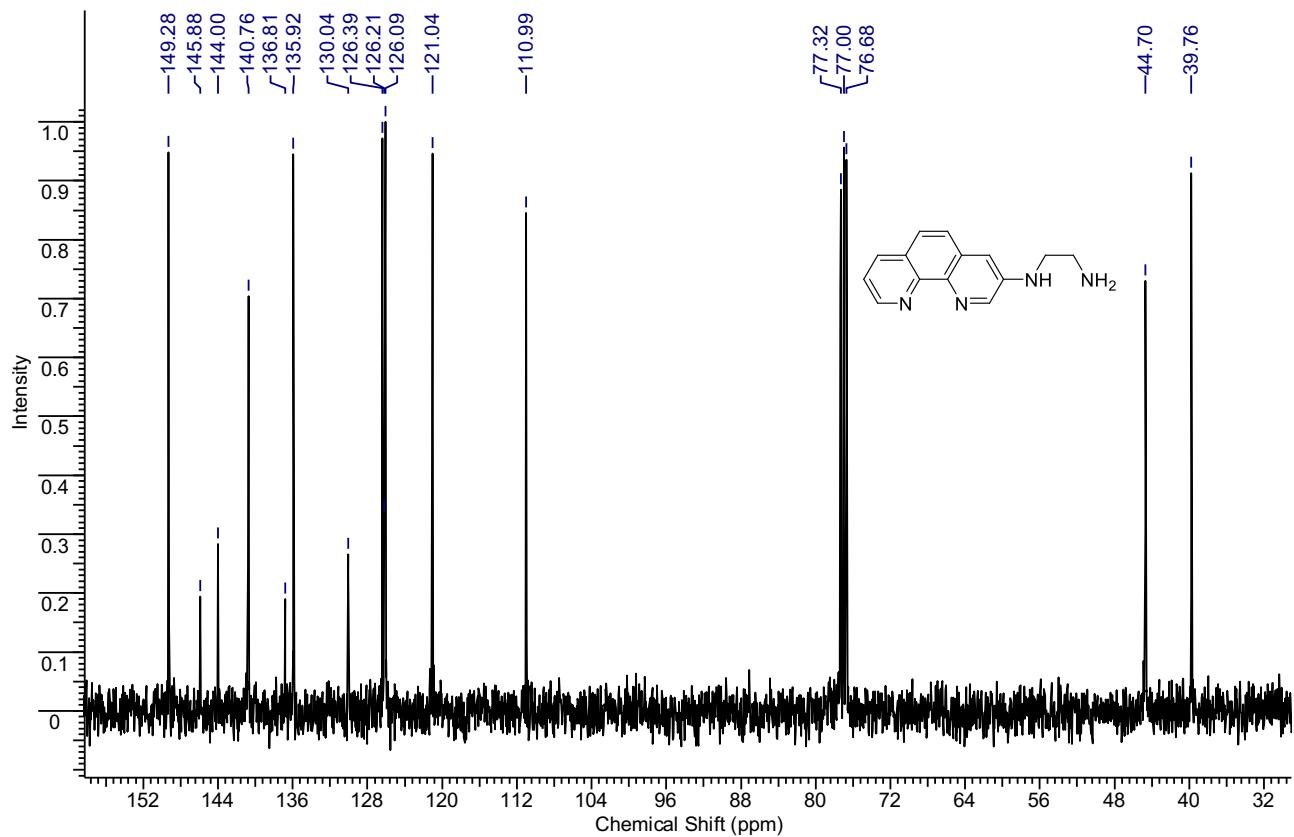


Figure S27. ^{13}C NMR spectrum of **6a** ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 100.6 MHz, 300K).

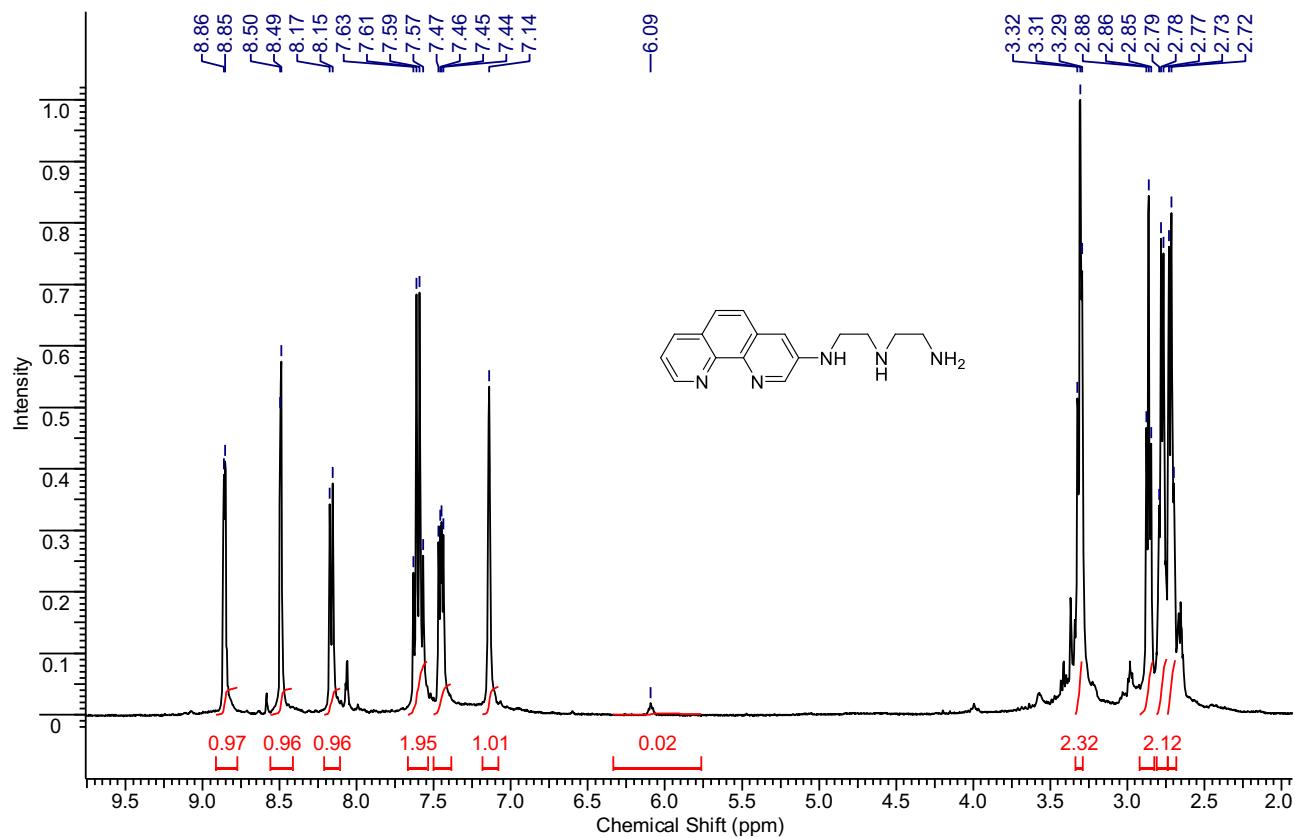


Figure S28. ^1H NMR spectrum of **6b** (CD_3OD , 400MHz, 300K).

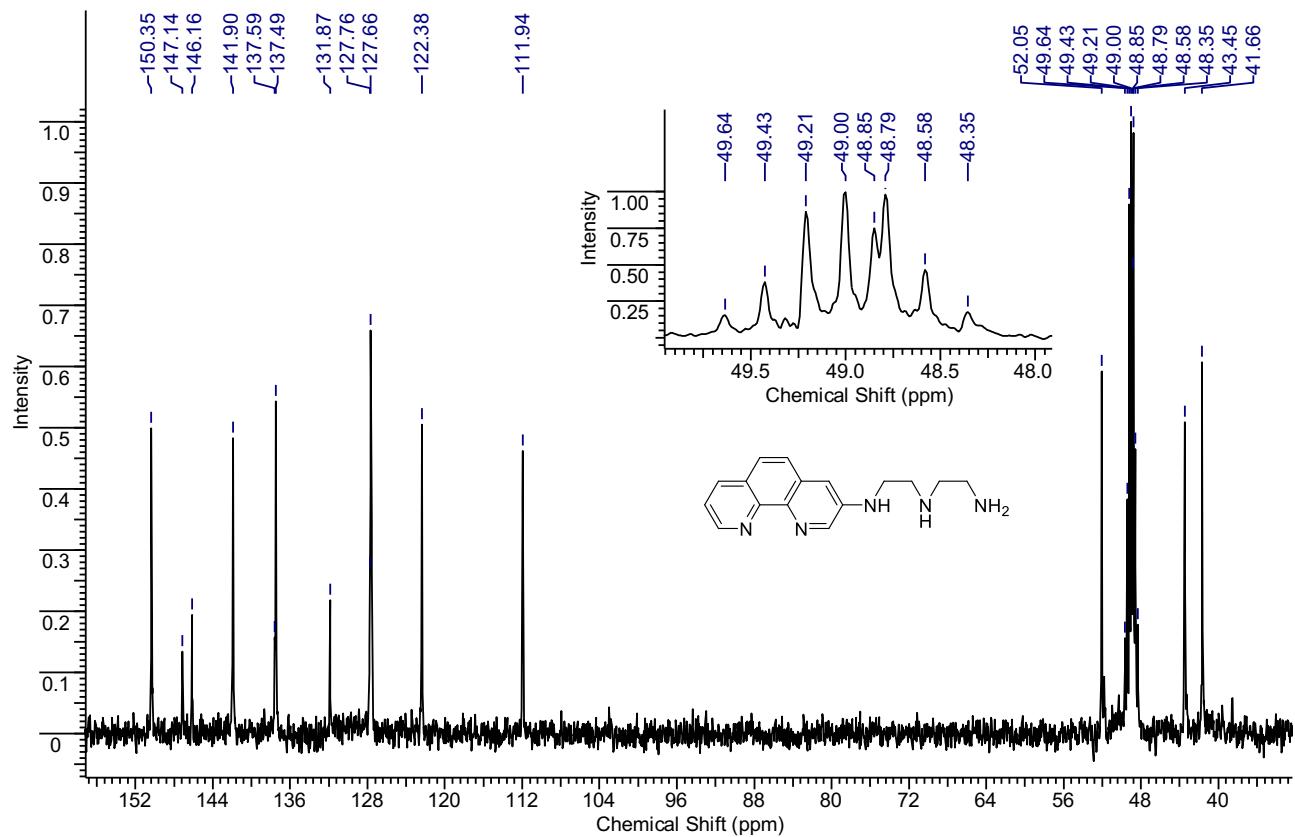


Figure S29. ^{13}C NMR spectrum of **6b** (CD_3OD , 100.6 MHz, 300K).

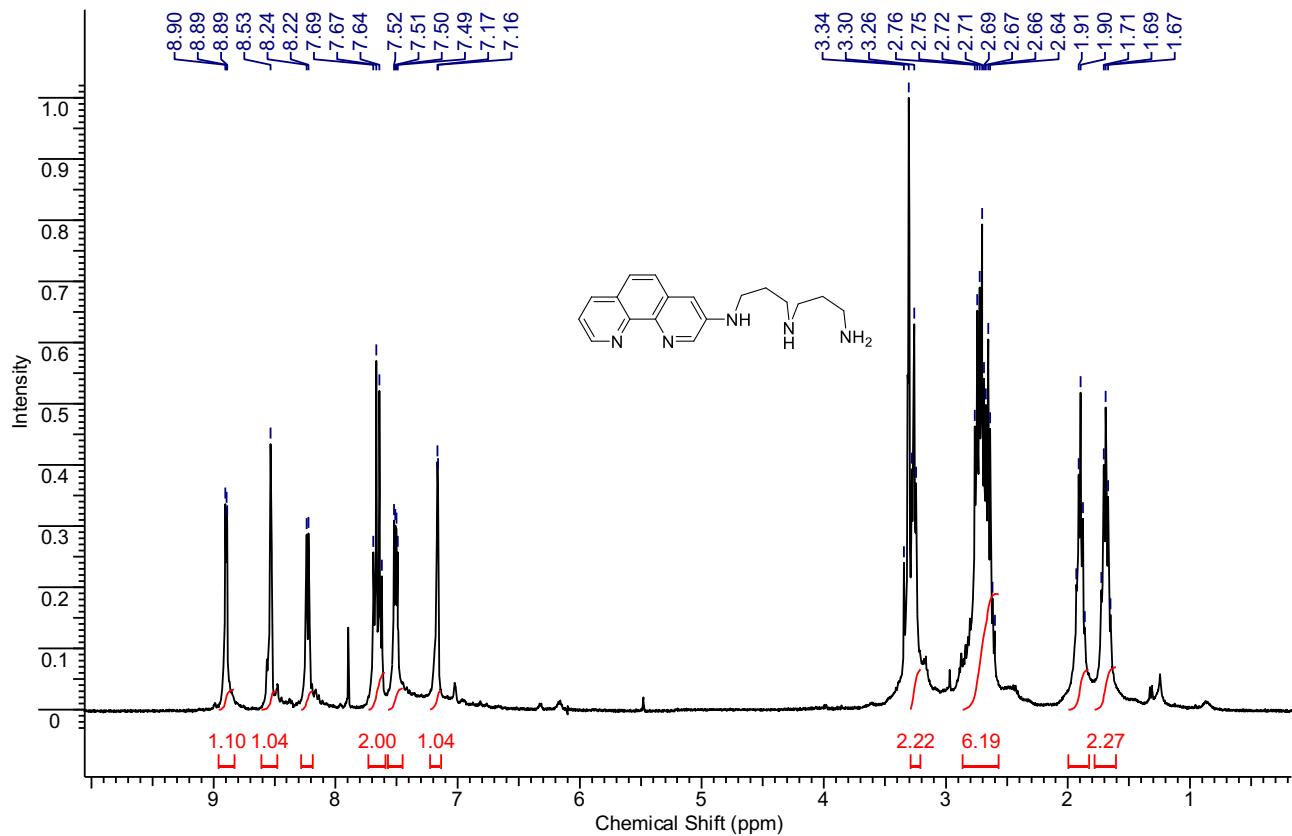


Figure S30. ^1H NMR spectrum of **6c** (CD_3OD , 400MHz, 300K).

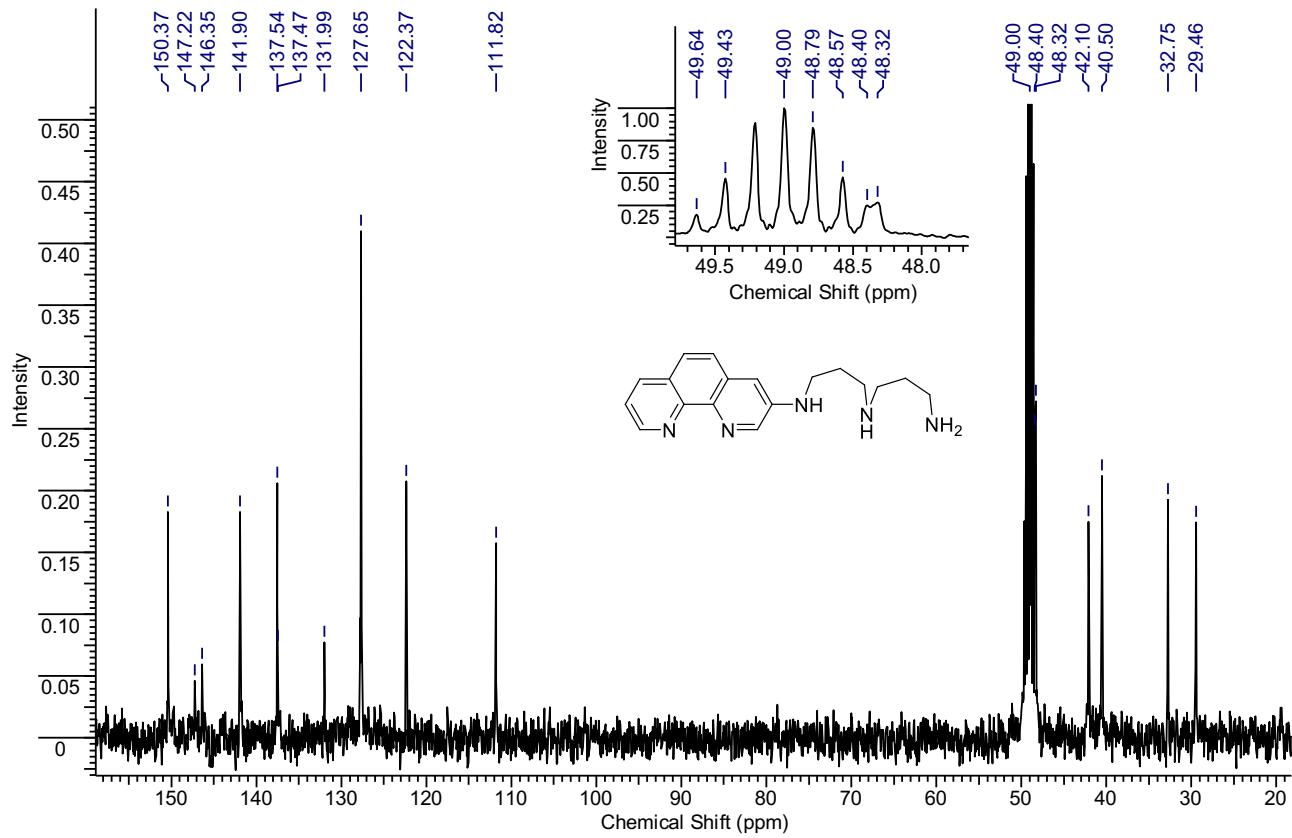


Figure S31. ^{13}C NMR spectrum of **6c** (CD_3OD , 100.6 MHz, 300K).

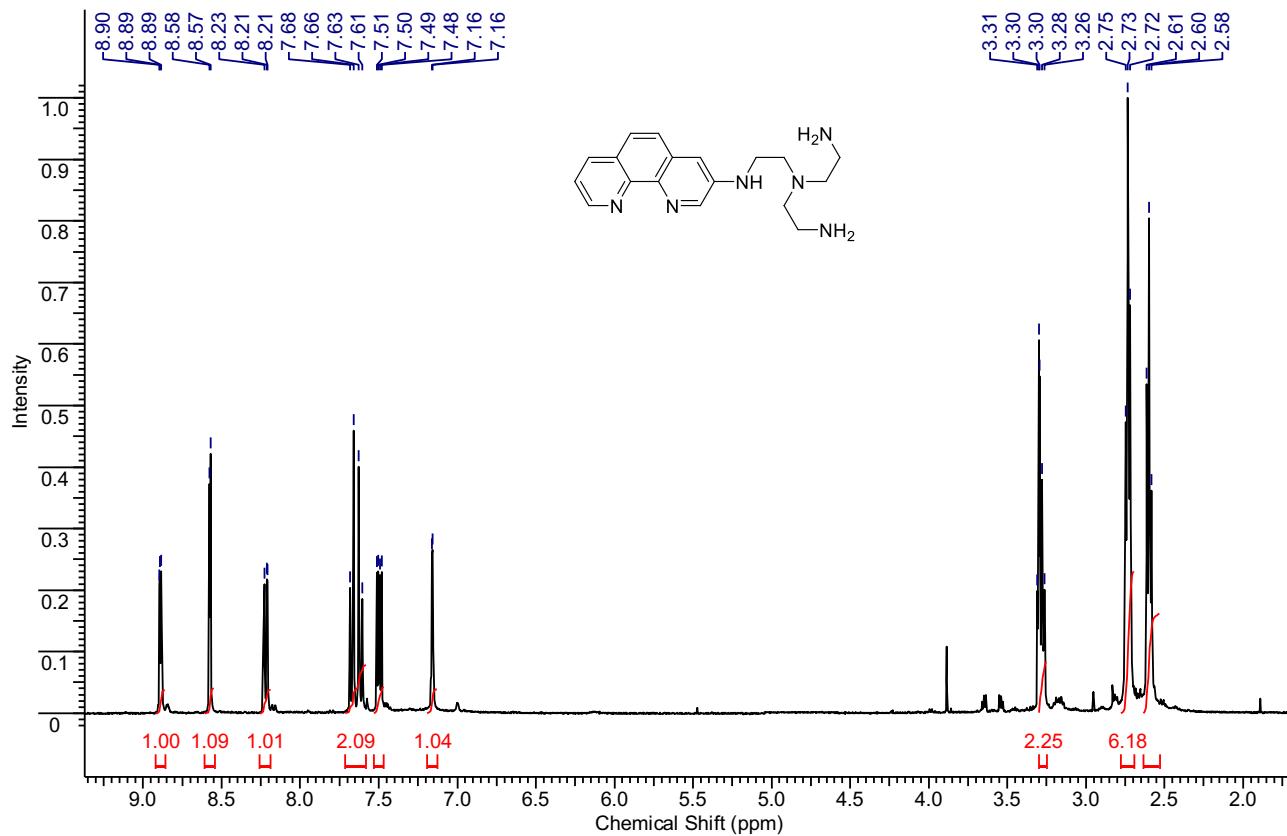


Figure S32. ¹H NMR spectrum of **6d** (CD₃OD, 400MHz, 300K).

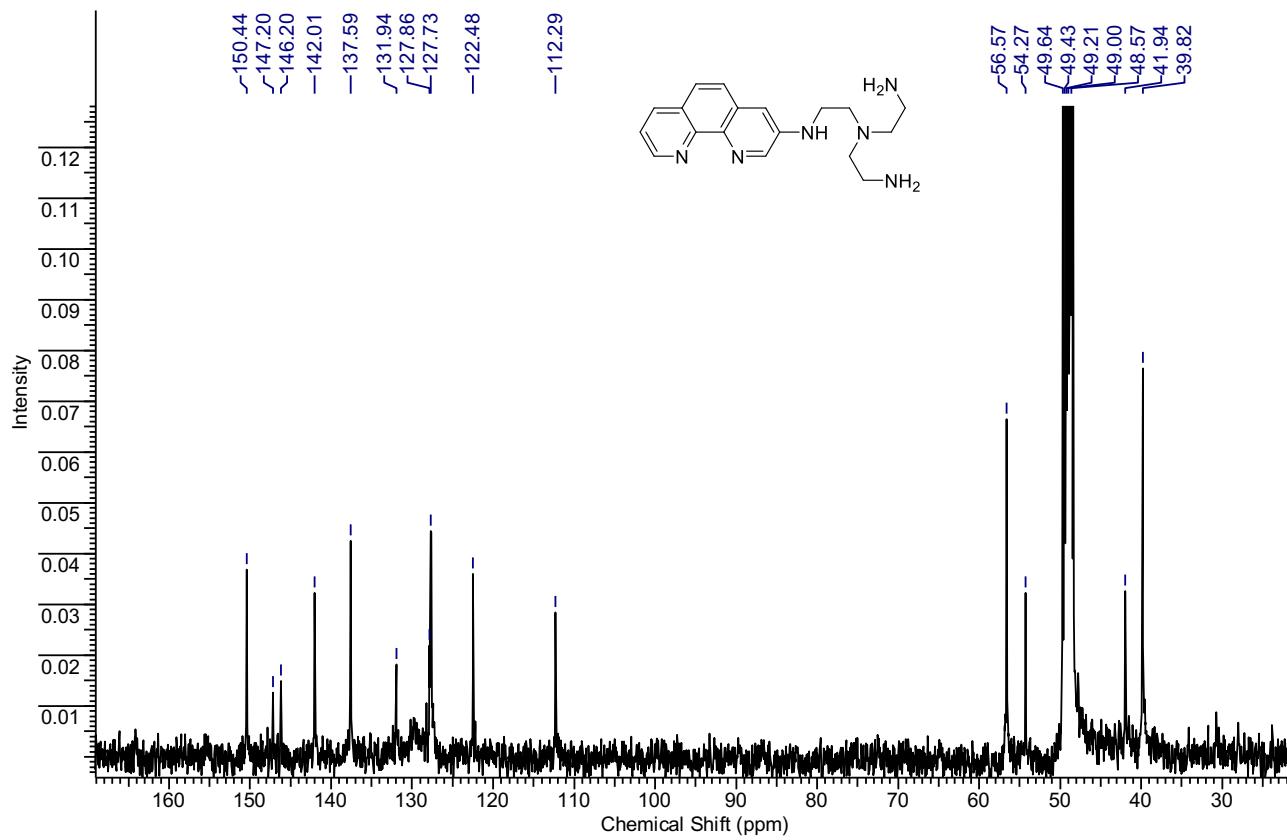


Figure S33. ¹³C NMR spectrum of **6d** (CD₃OD, 100.6 MHz, 300K).

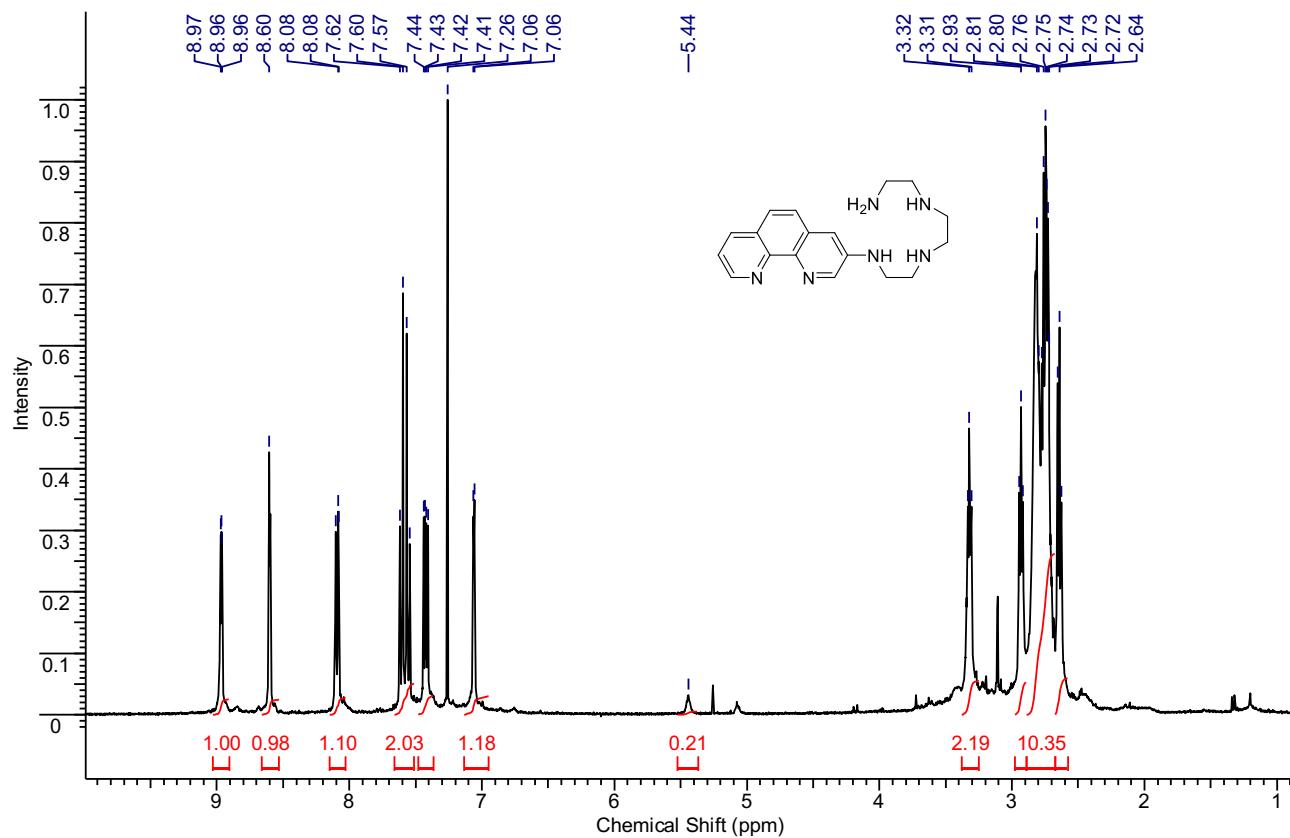


Figure S34. ^1H NMR spectrum of **6e** ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 400MHz, 300K).

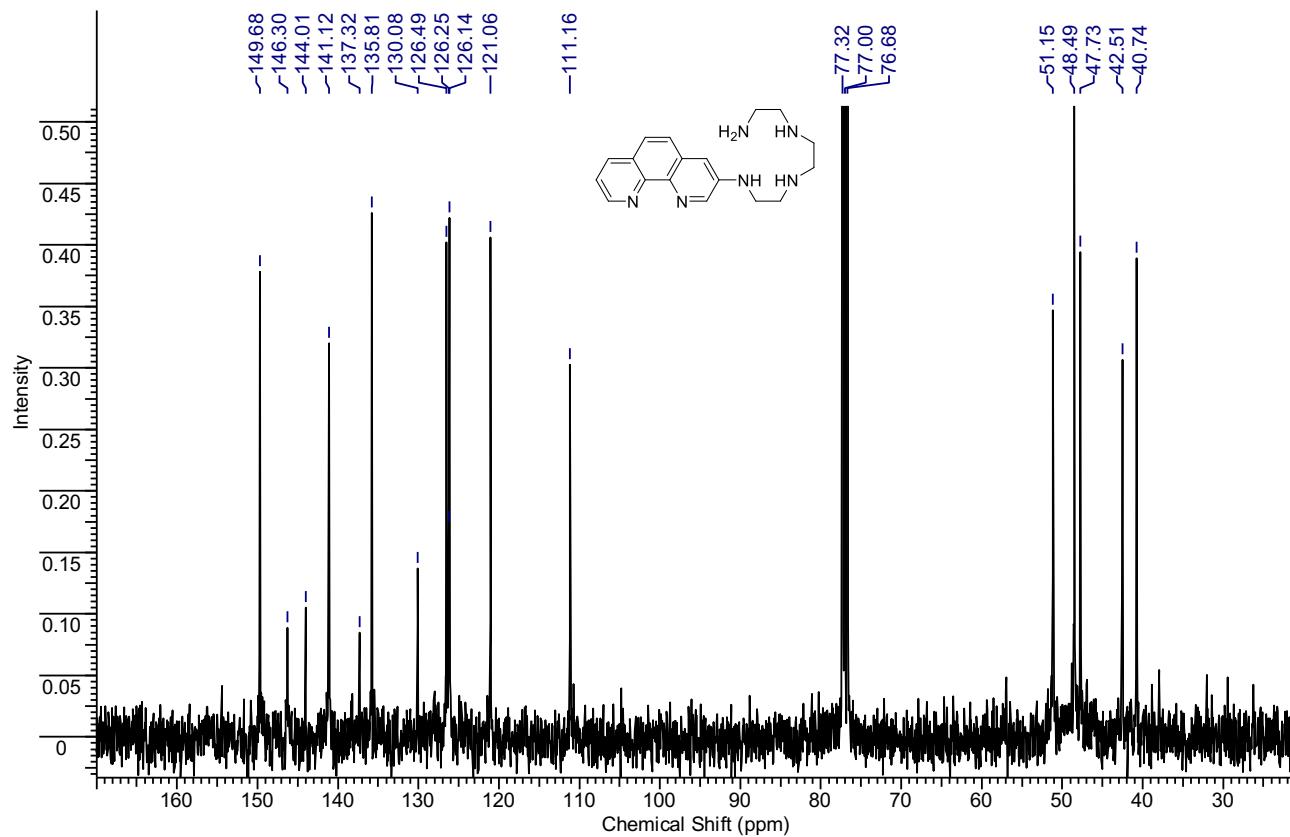


Figure S35. ^{13}C NMR spectrum of **6e** ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 100.6 MHz, 300K).

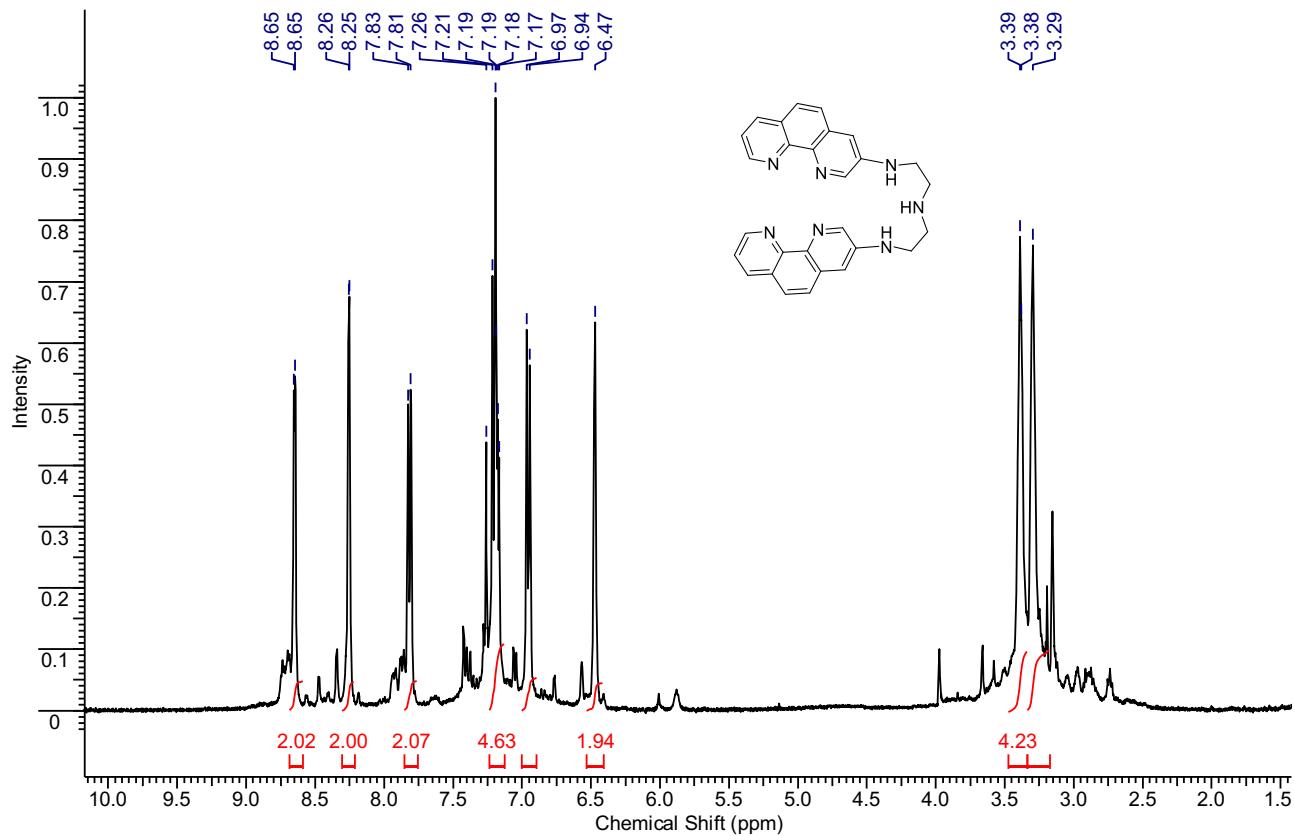


Figure S36. ^1H NMR spectrum of **7b** ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 400MHz, 300K).

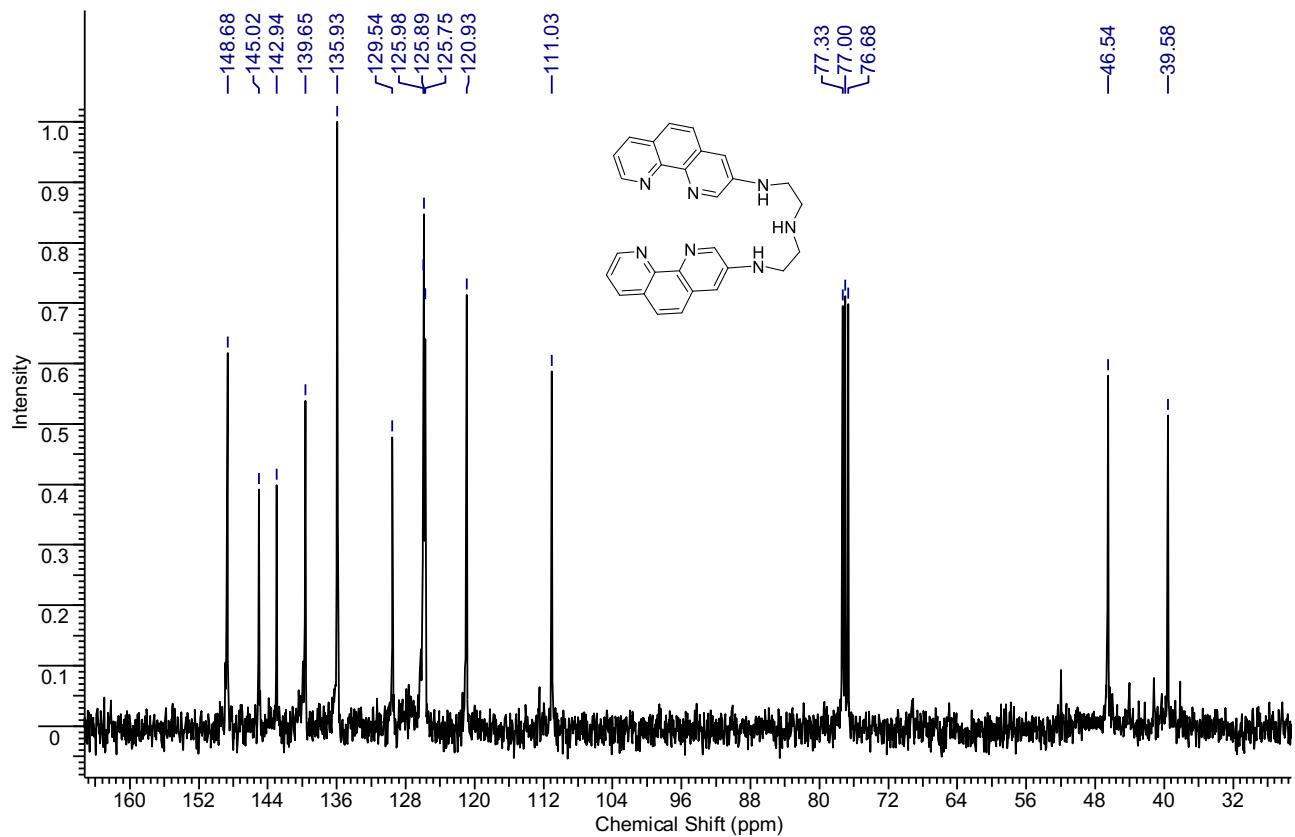


Figure S37. ^{13}C NMR spectrum of **7b** ($\text{CDCl}_3 + \text{CD}_3\text{OD}$, 100.6 MHz, 300K).

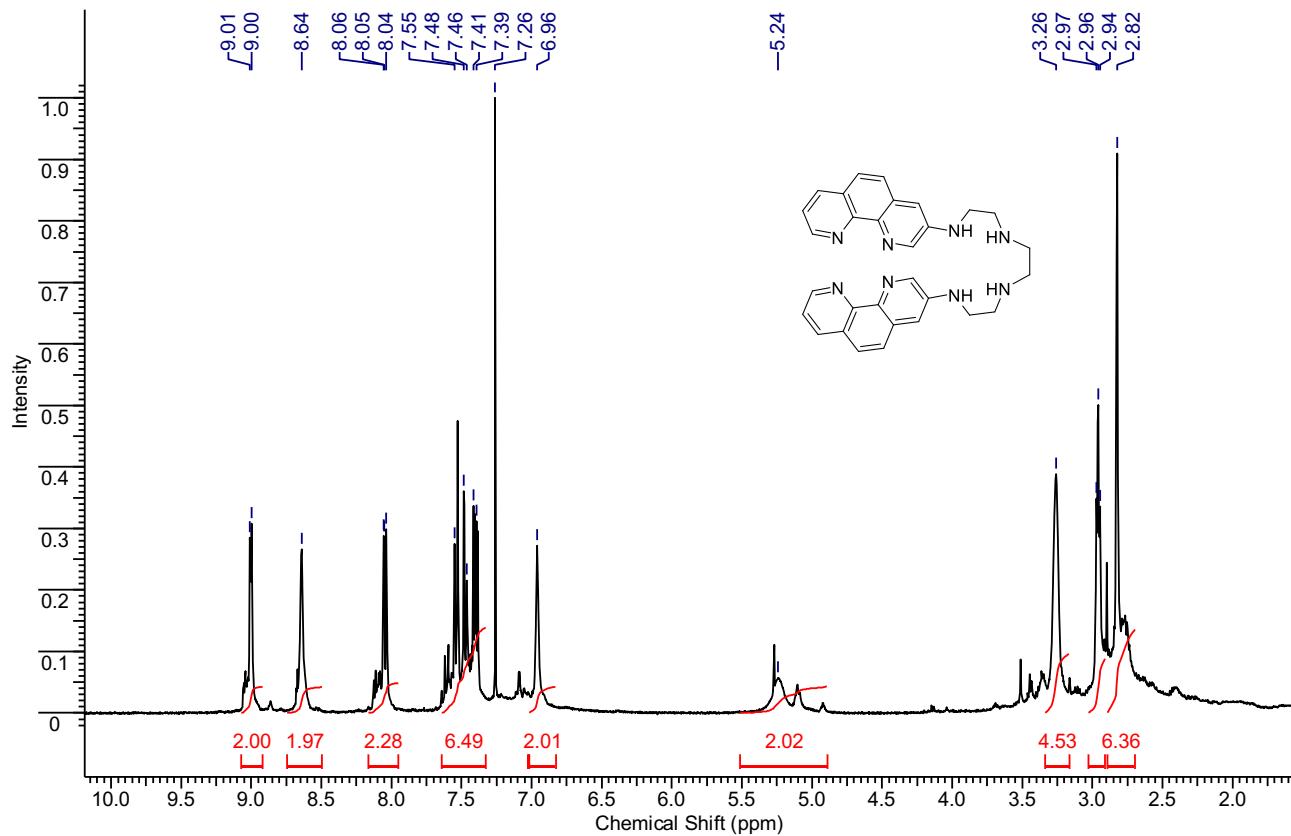


Figure S38. ^1H NMR spectrum of **7e** (CDCl_3 , 400MHz, 300K).

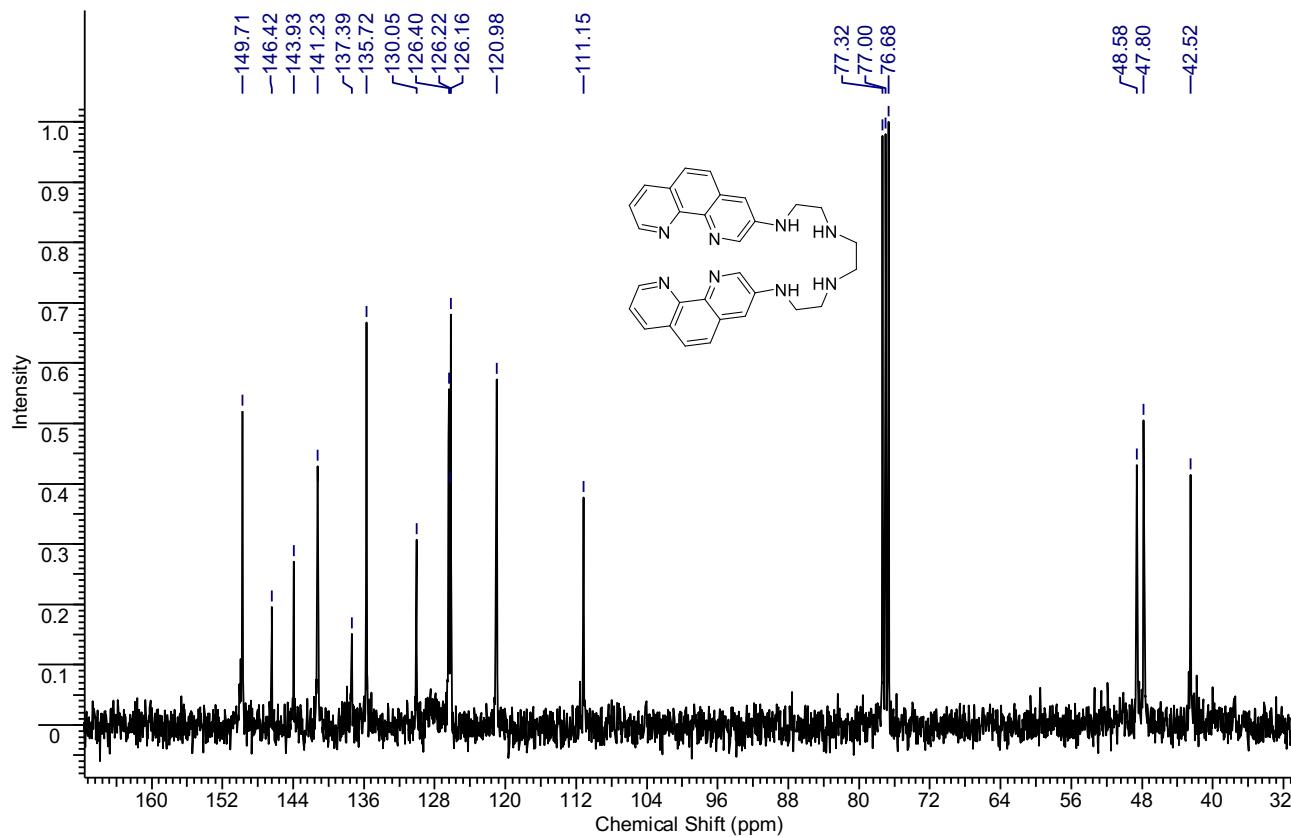


Figure S39. ^{13}C NMR spectrum of **7e** (CDCl_3 , 100.6 MHz, 300K).

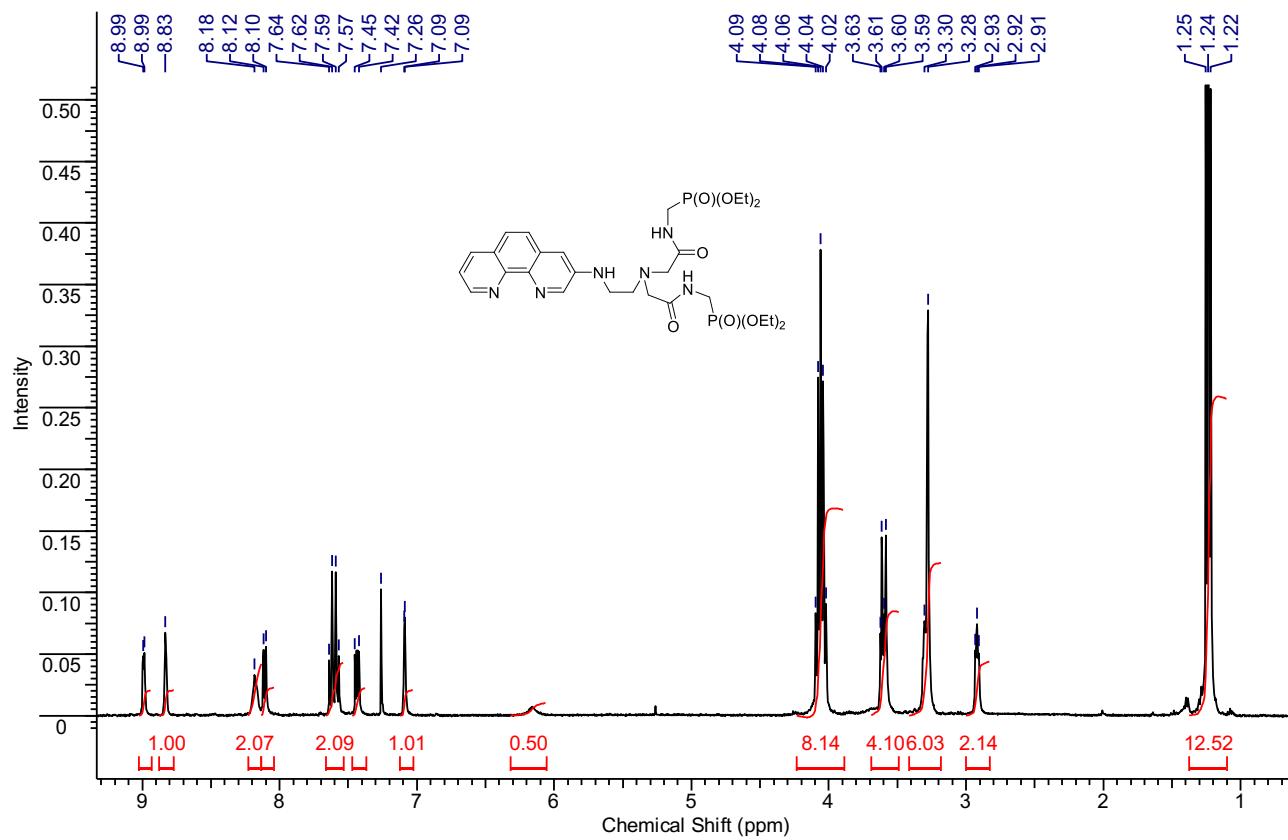


Figure S40. ^1H NMR spectrum of **8a** (CDCl_3 , 400MHz, 300K).

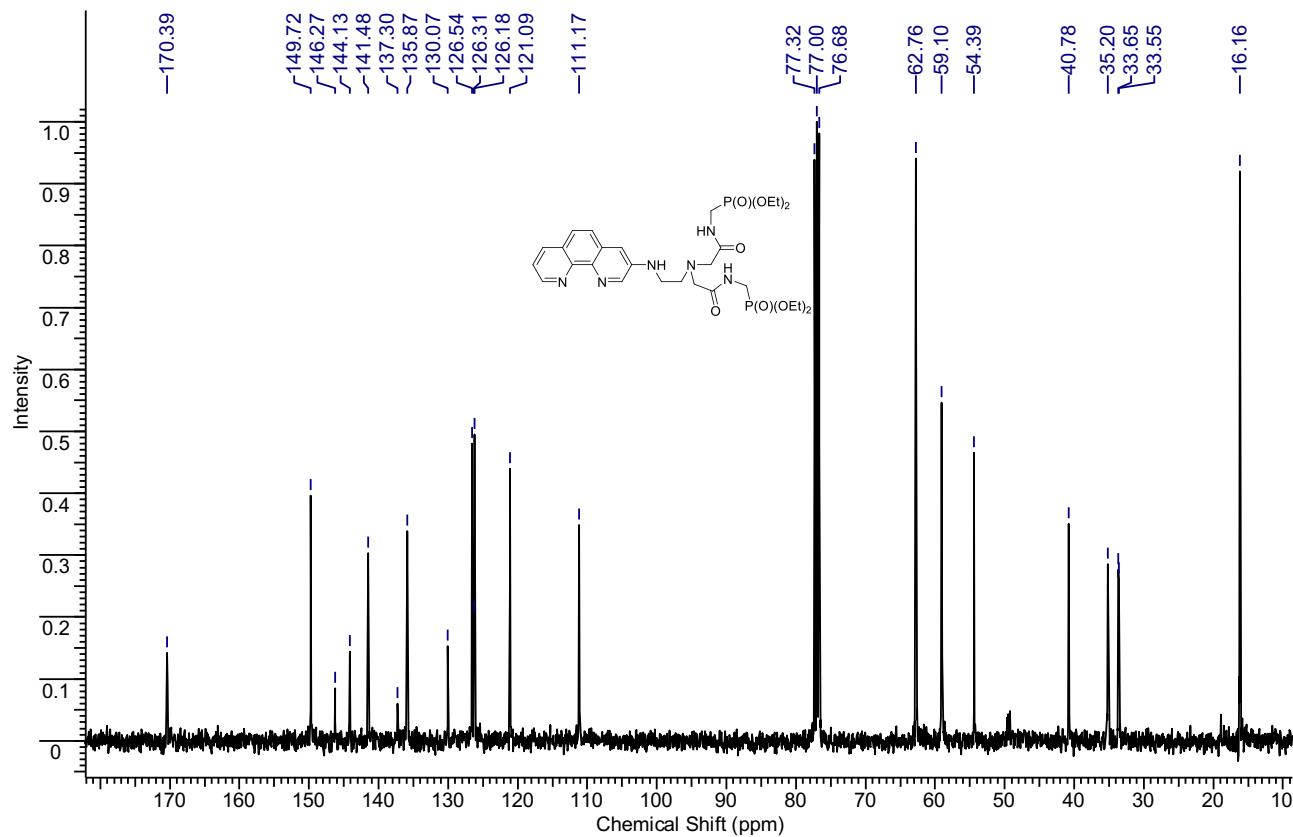


Figure S41. ^{13}C NMR spectrum of **8a** (CDCl_3 , 100.6 MHz, 300K).

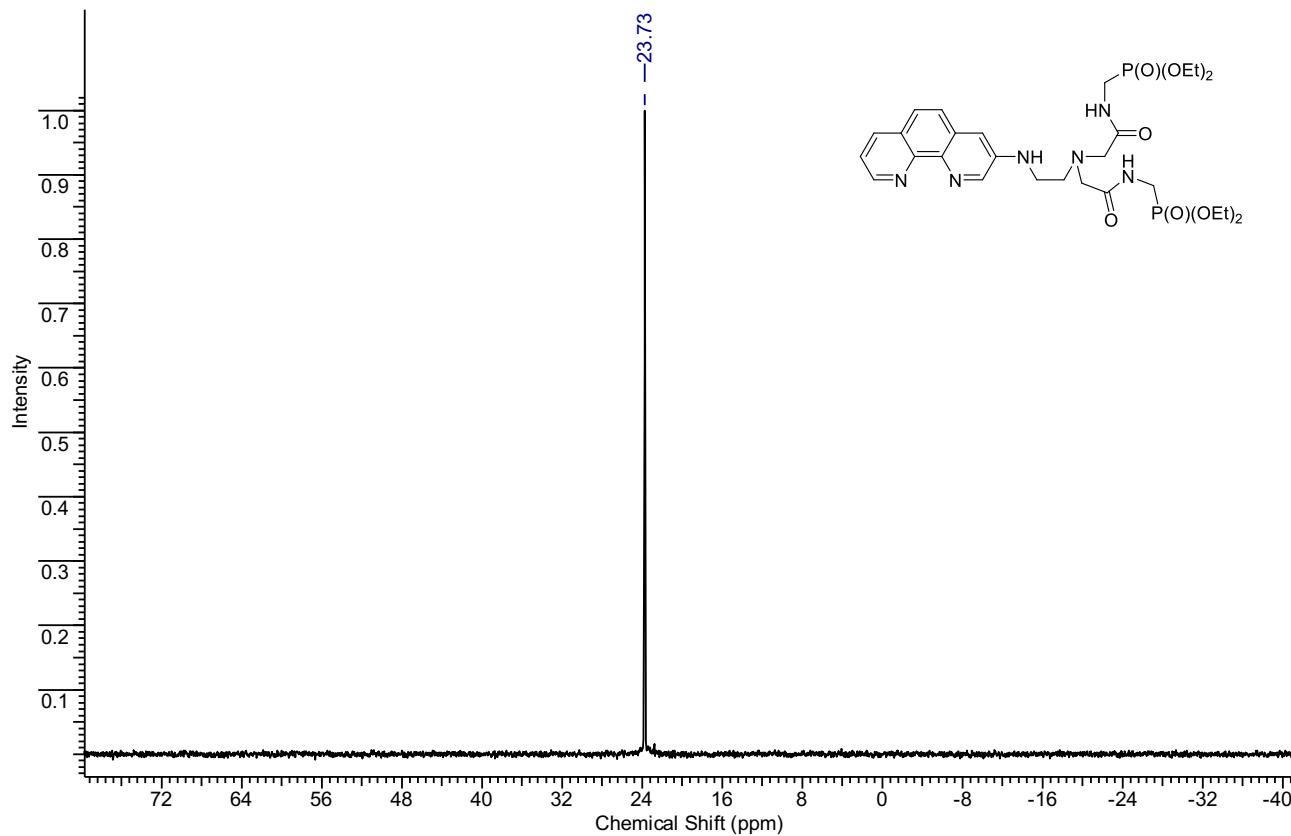


Figure S42. ^{31}P NMR spectrum of **8a** (CDCl_3 , 162.5MHz, 300K).

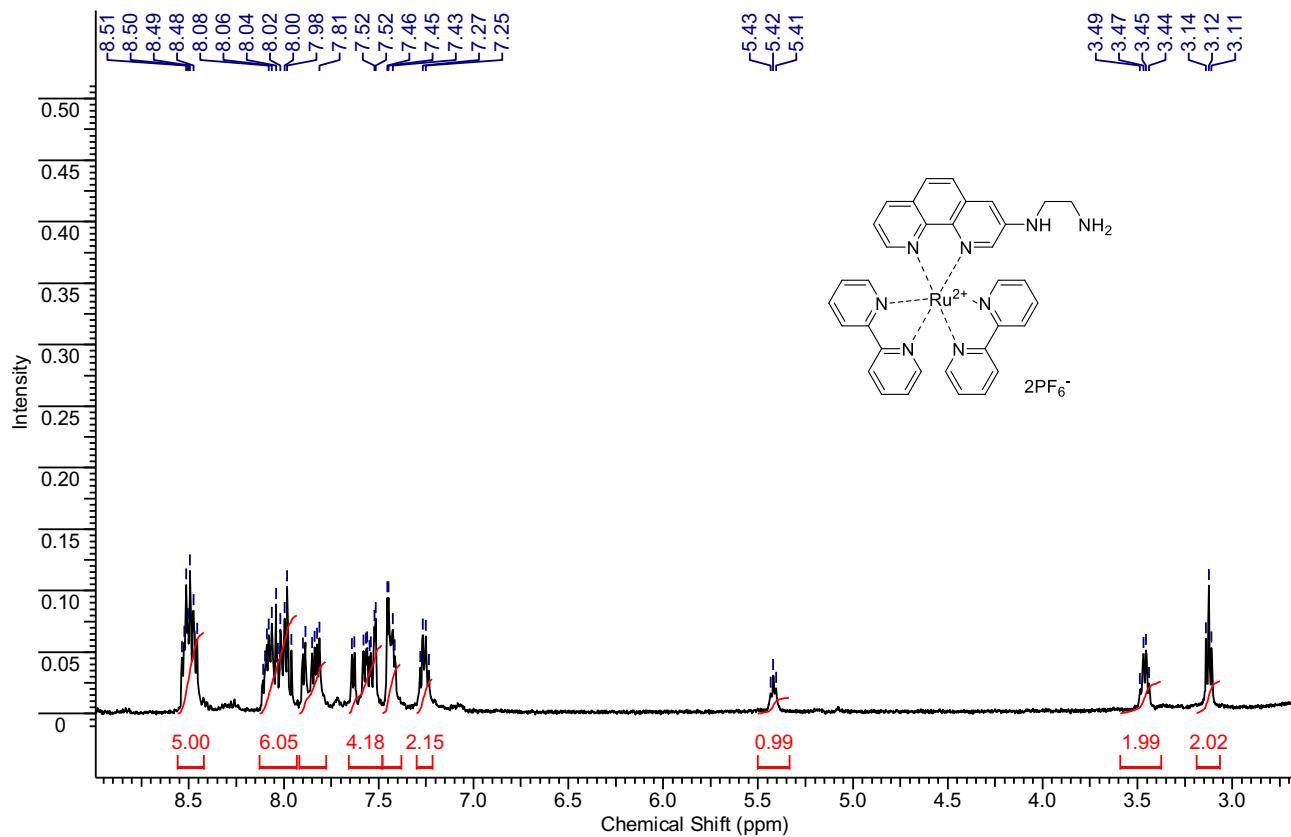


Figure S43. ^1H NMR spectrum of $\text{Ru}(\text{N}_2\text{phen})$ (CD_3CN , 400MHz, 300K).

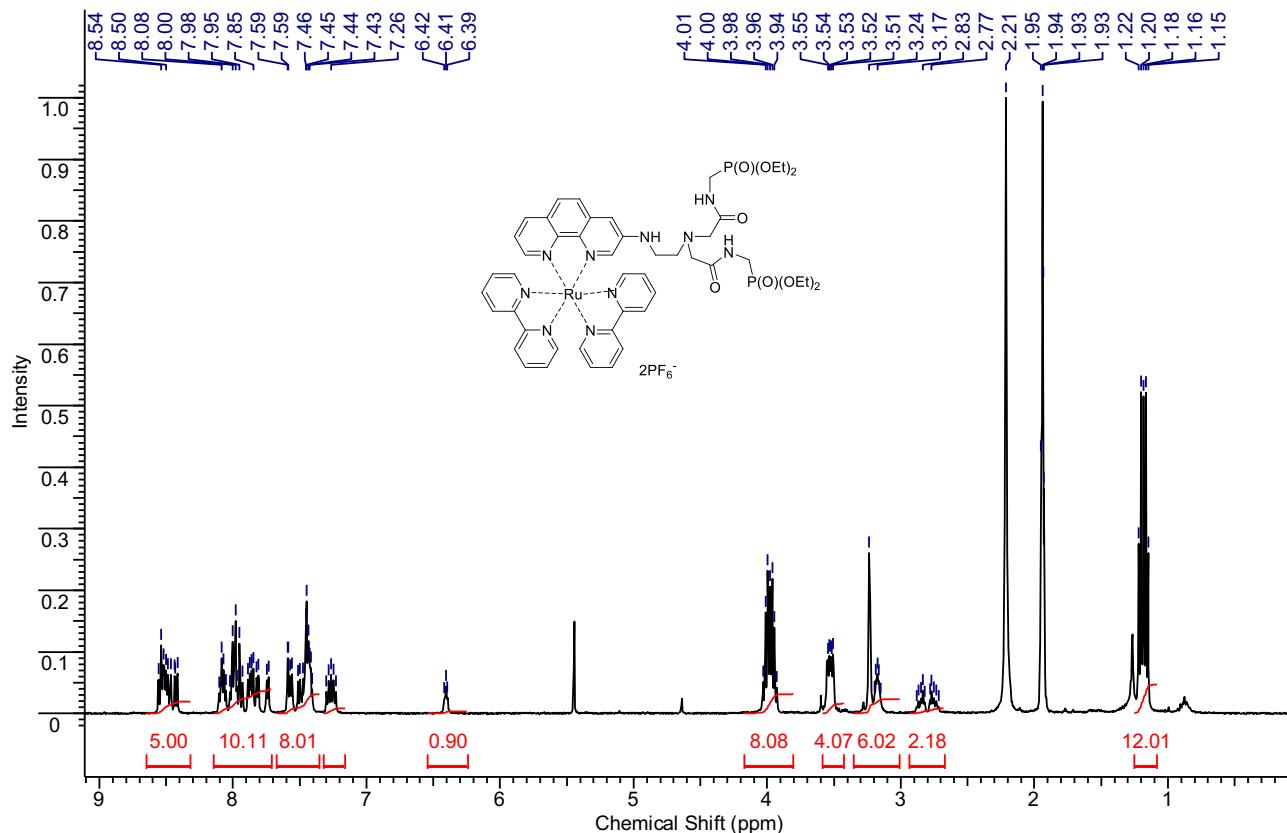


Figure S44. ¹H NMR spectrum of Ru(N₂P₂phen) (CD₃CN, 400MHz, 300K).

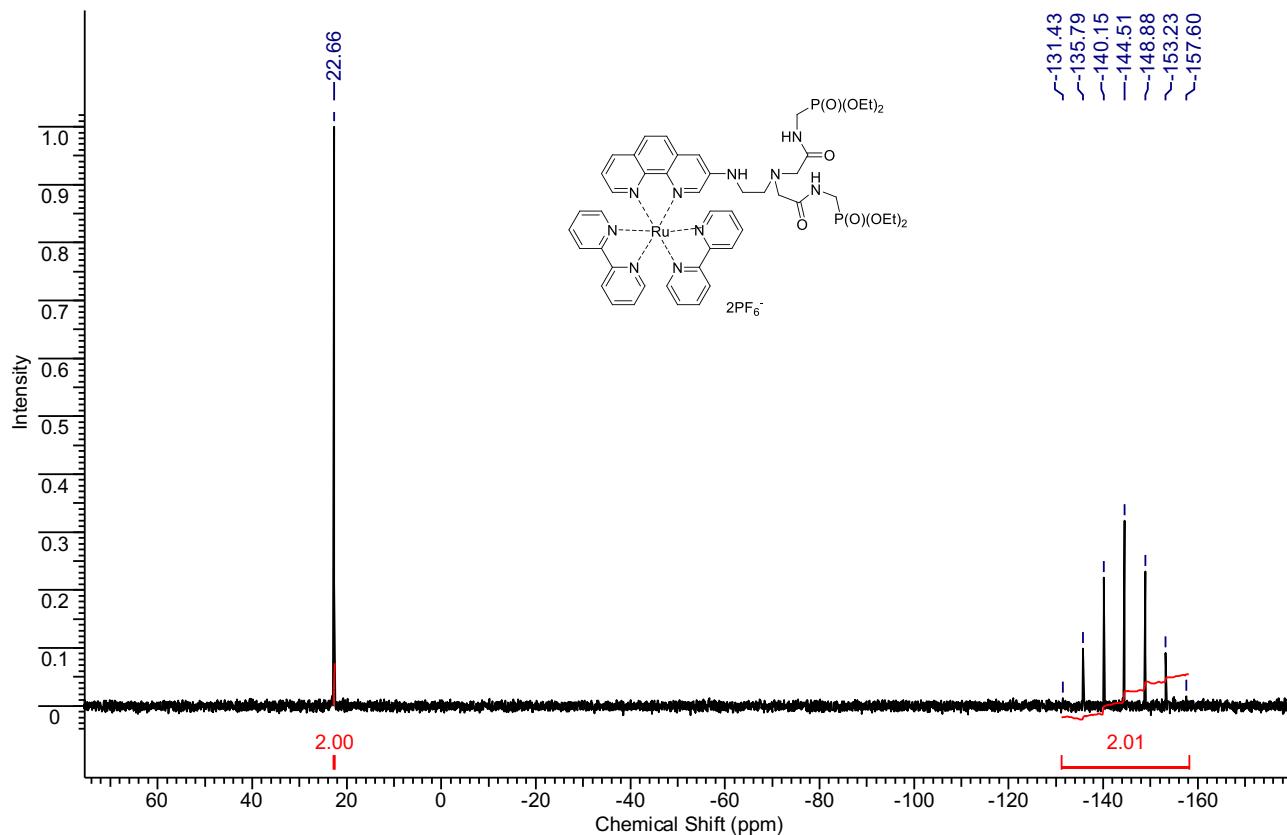


Figure S45. ³¹P NMR spectrum of Ru(N₂P₂phen) (CD₃CN, 162.5MHz, 300K).

8. FTIR spectra of Ru(Bnphen) and Ru(N₂phen)

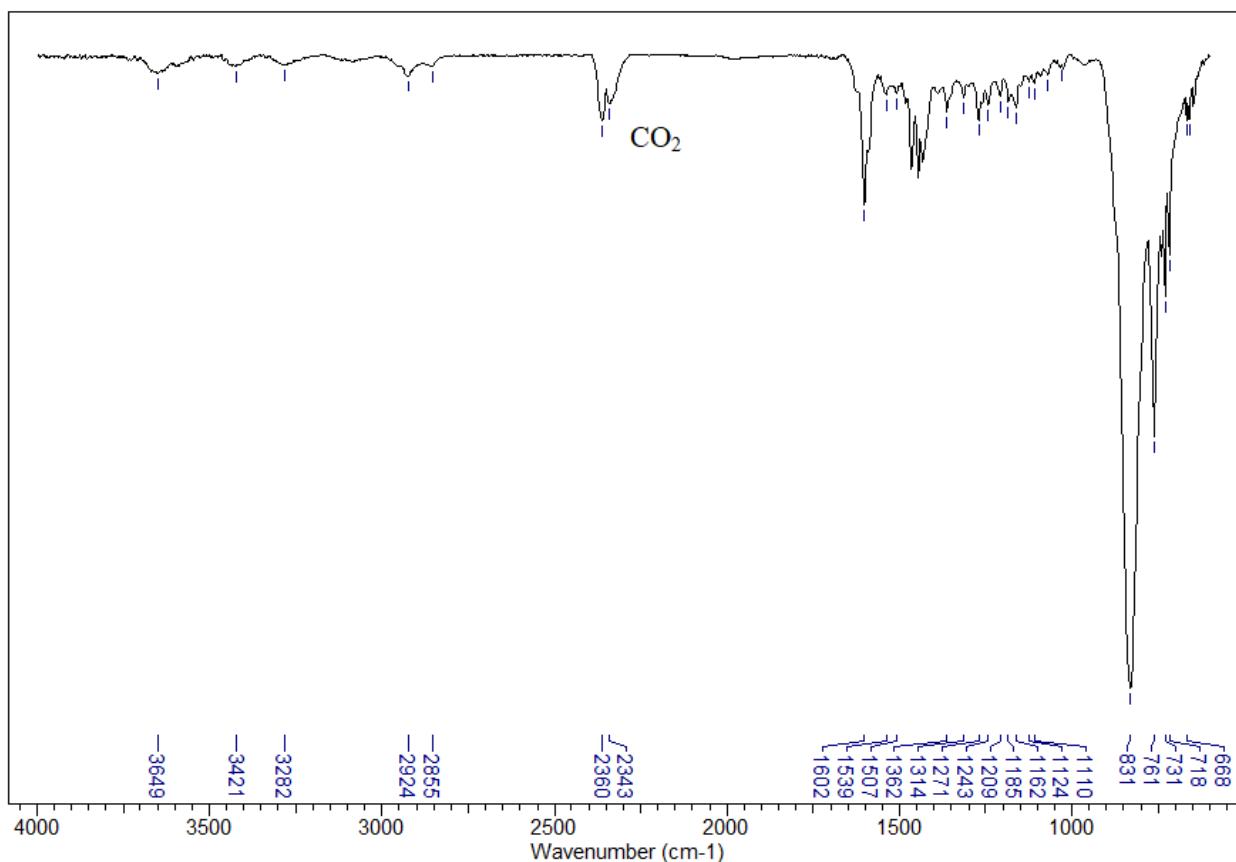


Figure S46. FTIR spectrum of Ru(Bnphen) (neat).

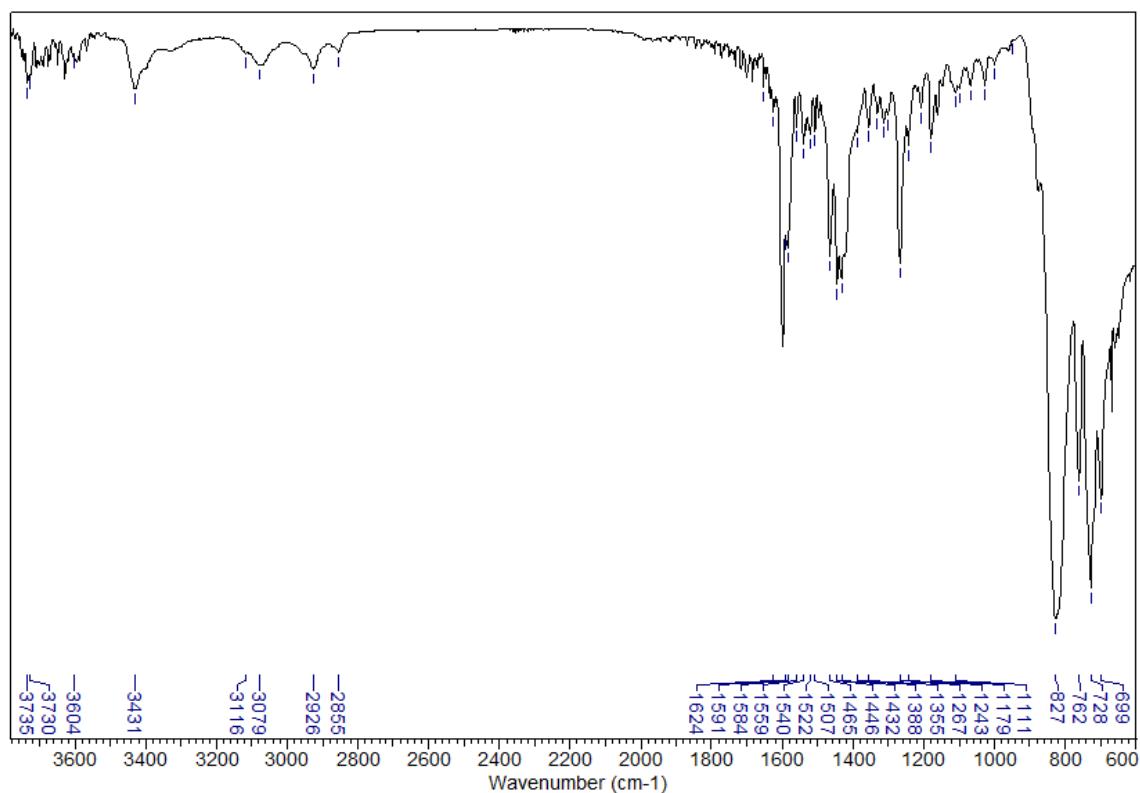


Figure S47. FTIR spectrum of Ru(N₂phen) (neat).