Supporting Information for:

Developing Red-Emissive Ruthenium(II) Complex-Based Luminescent Probes for Cellular Imaging

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1. Syntheses and Characterizations of the Ru(II) Complexes

All the new Ru(II) complexes were synthesized according to the procedures shown in Scheme 2. Their ^{1}H NMR, ^{13}C NMR and MS spectra are shown in Figure S12 to Figure S38. The starting materials, 4-(4-methoxylphenyl)-2,2'-bipyridine (MeO-ph-bpy)[1] and cis-Ru(II)$(bpy)_2Cl_2\cdot 2H_2O$[2] were synthesized by using the literature methods.

References

1. Hayes, M. A., Meckel, C., Schatz, E., and Ward, M. D. (1992) Derivatives of tris(2,2'-bipyridine)ruthenium(II) with pendant pyridyl or phenol ligands. *J. Chem. Soc. Dalton*

Trans. 703-708.

2. Marmion, M. E., and Takeuchi, K. J. (1988) Ruthenium(IV)-oxo complexes: the novel utilization of tertiary pnictogen ligands. *J. Am. Chem. Soc. 110*, 1472-1480.

Synthesis of bis(2,2'-bipyridine)(4-(4-methoxylphenyl)-2,2'-bipyridine)Ru(II) hexafluorophosphate (1). A mixture of MeO-ph-bpy (52.4 mg, 0.2 mmol), cis-Ru(II)$(bpy)_2Cl_2 \cdot 2H_2O$ (104.1 mg, 0.2 mmol), and 20 mL of ethanol was refluxed for 6 h. After the solvent was evaporated, the residue was purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:9:0.5, v/v/v) as the eluent. The fractions containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give Compound **1** as a red precipitate. Compound **1** was filtered, washed with small amount of water, and dried (131.4 mg, 68% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 3.88 (s, 3H), 7.13 (d, J(H,H) = 12 Hz, 2H), 7.40 (m, 5H), 7.60 (m, 1H), 7.66 (d, J(H,H) = 8 Hz, 1H), 7.74-7.80(m, 5H), 7.86 (d, J(H,H) = 8 Hz, 2H), 8.04-8.10 (m, 5H), 8.51 (m, 4H), 8.68 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ = 55.31, 114.86, 121.08, 124.05, 124.25, 124.36, 127.56, 127.58, 128.85, 137.69, 137.76, 149.06, 151.40, 151.63, 151.68, 157.01, 157.04, 157.14, 157.19, 161.86. ESI-MS (m/z): 821.4 ($[M\text{-}PF_6]^+$), 338.2 ($[M\text{-}2PF_6]^{2+}$).

Synthesis of $[Ru(bpy)_2(HP\text{-}bpy)](PF_6)_2$. Under an argon atmosphere, BBr_3 (100.2 mg, 0.4 mmol) in 5 mL of dry CH_2Cl_2 was added dropwise to a solution of Compound **1** (96.6 mg, 0.1 mmol) in 25 mL of dry CH_2Cl_2 at 0 ^{o}C. After stirring for 4 h at room temperature, 30 mL of water was added for collecting the crude product. The residue was dried and then purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:10:1, v/v/v) as eluent. The fractions

containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give $[Ru(bpy)_2(HP\text{-}bpy)](PF_6)_2$ as a red precipitate. $[Ru(bpy)_2(HP\text{-}bpy)](PF_6)_2$ was filtered, washed with small amount of water, and dried (72.4 mg, 76% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.00 (d, J(H,H) = 8.8 Hz, 2H), 7.40 (t, 5H), 7.58 (m, 1H), 7.64 (d, J(H,H) = 6 Hz, 1H), 7.73-7.81 (m, 7H), 8.06 (t, 5H), 8.50 (m, 4H), 8.66 (d, J(H,H) = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ = 116.24, 120.94, 123.91, 124.25, 124.33, 126.91, 127.57, 128.99, 137.68, 137.75, 149.24, 151.35, 151.67, 157.01, 157.10, 157.22, 159.48. ESI-MS (m/z): 807.2 ($[M\text{-}PF_6]^+$), 331.1 ($[M\text{-}2PF_6]^{2+}$). Elemental analysis calcd for $C_{36}H_{28}F_{12}N_6OP_2Ru$ (%): C 45.44, H 2.97, N 8.83; found: C 45.67, H 2.85, N 8.69.

Synthesis of $[Ru(bpy)_2(DNP\text{-}bpy)](PF_6)_2$. After a mixture of 47.6 mg $[Ru(bpy)_2(HP\text{-}bpy)](PF_6)_2$ (0.05 mmol), 2 mg NaH (60% in purity, 0.05 mmol), and 10 mL anhydrous acetonitrile was stirred at room temperature for 90 min under an nitrogen atmosphere, a solution of 11.2 mg 2,4-dinitrofluorobenzene (0.06 mmol) in 2 mL anhydrous acetonitrile was added. The mixture was further stirred for 3 h at 45 ^{o}C. After the solvent was evaporated, the residue was purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:9:1, v/v/v) as eluent. The fractions containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give $[Ru(bpy)_2(DNP\text{-}bpy)](PF_6)_2$ as a red precipitate. $[Ru(bpy)_2(DNP\text{-}bpy)](PF_6)_2$ was filtered, washed with small amount of water, and dried (31.8 mg, 57% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.25 (d, J(H,H) = 8 Hz, 1H), 7.38 (m, 7H), 7.66 (d, J(H,H) = 4 Hz, 1H), 7.76 (m, 6H), 8.00 (d, J(H,H) = 8 Hz, 2H), 8.07 (t, 5H), 8.41 (m, 1H), 8.52 (m, 4H), 8.69 (d, J(H,H) = 4 Hz, 1H), 8.75 (s, 1H), 8.83 (s, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ =

120.47, 120.66, 121.76, 122.04, 124.30, 124.53, 124.73, 127.60, 127.63, 127.72, 129.44, 129.86, 133.30, 137.77, 137.85, 142.60, 148.17, 151.67, 151.74, 151.79, 154.67, 156.27, 156.98, 157.00, 157.50. ESI-MS (m/z): 973.1 ($[M-PF_6]^+$), 414.1 ($[M-2PF_6]^{2+}$). Elemental analysis calcd for $C_{42}H_{30}F_{12}N_8O_5P_2Ru \cdot 1.5H_2O$ (%): C 44.07, H 2.91, N 9.79; found: C 44.51, H 2.91, N 9.35.

Synthesis of bis(4-(4-methoxylphenyl)-2,2'-bipyridine)$RuCl_2$ (2). Under an argon atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (0.78 g, 2.98 mmol), MeO-ph-bpy (1.57 g, 6 mmol), and LiCl (0.84 g, 0.2 mmol) in 5 mL of DMF was refluxed for 8 h with stirring. After the reaction mixture was cooled to room temperature, 25 mL of acetone was added and the resultant solution was cooled at 0 ^oC overnight. The precipitated compound **2,** as fine black crystals, was washed with three portions of water (10 mL) and two portions of cooled diethyl ether (10 mL) and dried (0.89 g, 43% yield). Compound **2** was directly used for the next step without further characterization.

Synthesis of bis(4-(4-methoxylphenyl)-2,2'-bipyridine)(2,2'-bipyridine)Ru(II) hexafluorophosphate (3). A mixture of compound **2** (104.4 mg, 0.15 mmol), 2,2'-bipyridine (23.4 mg, 0.15 mmol), and 20 mL of ethanol was refluxed for 10 h with stirring. After the solvent was evaporated, the residue was purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:8:0.5, v/v/v) as the eluent. The fractions containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give compound **3** as a red precipitate. Compound **3** was filtered, washed with small amount of water, and dried (110.9 mg, 69% yield). ^1H NMR (400 MHz, CD_3CN): δ = 3.88 (s, 6H), 7.12 (dd, J(H,H) = 2.4 Hz, 4H), 7.41 (m, 4H), 7.62 (m, 2H), 7.68 (t, 2H), 7.73-7.87 (m, 8H), 8.07 (m, 4H), 8.52 (m, 2H), 8.68 (m, 4H). ^{13}C NMR (100 MHz, CD_3CN): δ = 55.31, 114.50, 114.87, 121.07, 124.05, 124.24, 124.35, 127.56, 127.63, 128.85, 129.10, 137.66, 137.73, 149.03, 151.38, 151.67, 157.04, 157.18, 157.24, 161.86. ESI-MS (m/z):

927.5 ([M-PF_6]$^+$), 391.2 ([M-2PF_6]$^{2+}$).

Synthesis of [Ru(bpy)(HP-bpy)$_2$](PF_6)$_2$. Under an argon atmosphere, BBr_3 (200.4 mg, 0.8 mmol) in 10 mL of dry CH_2Cl_2 was added dropwise to a solution of compound **3** (107.2 mg, 0.1 mmol) in 25 mL of dry CH_2Cl_2 at 0 ^oC. After stirring for 5 h at room temperature, 30 mL of water was added for collecting the crude product. The residue was dried and then purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:10:1, v/v/v) as eluent. The fractions containing the target product were collected. After the solvent was evaporated, the resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give [Ru(bpy)(HP-bpy)$_2$](PF_6)$_2$ as a red precipitate. [Ru(bpy)(HP-bpy)$_2$](PF_6)$_2$ was filtered, washed with small amount of water, and dried (73.1 mg, 70% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.00 (d, J(H,H) = 8.8 Hz, 4H), 7.41 (m, 4H), 7.59 (m, 2H), 7.66 (d, J(H,H) = 6 Hz, 2H), 7.75-7.83 (m, 8H), 8.07 (m, 4H), 8.52 (m, 2H), 8.67 (m, 4H). ^{13}C NMR (100 MHz, CD_3CN): δ = 116.25, 120.92, 123.91, 124.23, 124.31, 126.90, 127.51, 127.56, 128.98, 137.63, 137.69, 149.19, 151.33, 151.68, 157.03, 157.14, 157.28, 159.50. ESI-MS (m/z): 899.4 ([M-PF_6]$^+$), 377.2 ([M-2PF_6]$^{2+}$). Elemental analysis calcd for $C_{42}H_{32}F_{12}N_6O_2P_2Ru\cdot 2H_2O$(%): C 46.72, H 3.36, N 7.78; found: C 46.95, H 3.31, N 7.96.

Synthesis of [Ru(bpy)(DNP-bpy)$_2$](PF_6)$_2$. After a mixture of [Ru(bpy)(HP-bpy)$_2$](PF_6)$_2$ (54.0 mg, 0.05 mmol), NaH (2 mg, 60% in purity, 0.05 mmol), and 10 mL of anhydrous acetonitrile was stirred at room temperature for 90 min under an nitrogen atmosphere, a solution of 2,4-dinitrofluorobenzene (22.3 mg, 0.12 mmol) in 2 mL of anhydrous acetonitrile was added. The mixture was further stirred for 6 h at 45 ^oC. After the solvent was evaporated, the residue was purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:9:1, v/v/v) as eluent. The fractions containing the target product were collected, and the solvent was evaporated.

The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give $[Ru(bpy)(DNP\text{-}bpy)_2](PF_6)_2$ as a red precipitate. $[Ru(bpy)(DNP\text{-}bpy)_2](PF_6)_2$ was filtered, washed with small amount of water, and dried (35.1 mg, 51% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.25 (d, J(H,H) = 12 Hz, 2H), 7.38 (d, J(H,H) = 8 Hz, 4H), 7.44 (m, 4H), 7.66 (d, J(H,H) = 4 Hz, 2H), 7.79 (m, 4H), 7.85 (d, J(H,H) = 4 Hz, 2H), 8.01 (d, J(H,H) = 8 Hz, 4H), 8.09 (m, 4H), 8.42 (m, 2H), 8.55 (m, 2H), 8.70 (d, J(H,H) = 8 Hz, 2H), 8.76 (s, 2H), 8.83 (s, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ = 120.46, 120.65, 121.76, 122.05, 124.32, 124.53, 124.76, 127.66, 127.71, 129.43, 129.86, 133.28, 137.80, 137.89, 140.31, 142.61, 148.20, 151.76, 154.65, 156.30, 157.02, 151.07, 157.48, 157.51. ESI-MS (m/z): 1231.0 ($[M\text{-}PF_6]^+$), 543.1 ($[M\text{-}2PF_6]^{2+}$). Elemental analysis calcd for $C_{54}H_{36}F_{12}N_{10}O_{10}P_2Ru\cdot H_2O$(%): C 46.53, H 2.75, N 10.05; found: C 46.48, H 2.80, N 10.09.

Synthesis of tris(4-(4-methoxylphenyl)-2,2'-bipyridine)Ru(II) hexafluorophosphate (4). Under an argon atmosphere, MeO-ph-bpy (471.8 mg, 1.8 mmol) in 80 mL of ethanol was added to a solution of $RuCl_3\cdot 3H_2O$ (117.4 mg, 0.45 mmol) in 40 mL of 3:1 ethanol-H_2O. The reaction mixture was refluxed for 24 h with stirring, and then cooled to room temperature. After the solvent was evaporated, the residue was purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:7:1, v/v/v) as the eluent. The fractions containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give compound **4** as a red precipitate. Compound **4** was filtered, washed with small amount of water, and dried (259.8 mg, 49% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 3.88 (s, 9H), 7.12 (d, J(H,H) = 8.4 Hz, 6H), 7.44 (m, 3H), 7.62 (t, 3H), 7.71-7.88 (m, 12H), 8.08 (t, 3H), 8.69 (m, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ = 55.31, 114.87, 121.06, 124.05, 124.35, 127.57, 127.65, 128.86, 137.62, 148.98, 149.00, 151.36, 151.64,

157.24, 161.86. ESI-MS (m/z): 1033.6 ($[M-PF_6]^+$), 444.3 ($[M-2PF_6]^{2+}$).

Synthesis of $[Ru(HP\text{-}bpy)_3](PF_6)_2$. Under an argon atmosphere, BBr_3 (300.6 mg, 1.2 mmol) in 15 mL of dry CH_2Cl_2 was added dropwise to a solution of compound **4** (117.8 mg, 0.1 mmol) in 25 mL of dry CH_2Cl_2 at 0 ^oC. After stirring for 6 h at room temperature, 30 mL of water was added for collecting the crude product. The residue was dried and then purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:9:1, v/v/v) as eluent. The fractions containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give $[Ru(HP\text{-}bpy)_3](PF_6)_2$ as a red precipitate. $[Ru(HP\text{-}bpy)_3](PF_6)_2$ was filtered, washed with small amount of water, and dried (65.9 mg, 58% yield). ^1H NMR (400 MHz, CD_3CN): δ = 7.00 (d, J(H,H) = 7.6 Hz, 6H), 7.43 (m, 3H), 7.60 (t, 3H), 7.70-7.84 (m, 12H), 8.08 (m, 3H), 8.69 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ = 116.25, 120.90, 123.90, 124.31, 126.91, 127.52, 128.98, 137.58, 149.14, 151.32, 151.64, 157.18, 157.31, 159.52. ESI-MS (m/z): 991.5 ($[M-PF_6]^+$), 423.2 ($[M-2PF_6]^{2+}$). Elemental analysis calcd for $C_{48}H_{36}F_{12}N_6O_3P_2Ru \cdot 2.5H_2O$ (%): C 48.82, H 3.50, N 7.12; found: C 48.56, H 3.49, N 7.47.

Synthesis of $[Ru(DNP\text{-}bpy)_3](PF_6)_2$. After a mixture of $[Ru(HP\text{-}bpy)_3](PF_6)_2$ (59.1 mg, 0.05 mmol), NaH (2 mg, 60% in purity, 0.05 mmol), and 10 mL of anhydrous acetonitrile was stirred at room temperature for 90 min under an nitrogen atmosphere, a solution of 2,4-dinitrofluorobenzene (33.5 mg, 0.18 mmol) in 2 mL of anhydrous acetonitrile was added. The mixture was further stirred overnight at 45 ^oC. After the solvent was evaporated, the residue was purified by silica gel column chromatography using MeCN-H_2O-KNO_3 (sat.) (100:8:1, v/v/v) as eluent. The fractions containing the target product were collected, and the solvent was evaporated. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and then a saturated solution of NH_4PF_6 was added to give

$[Ru(DNP\text{-}bpy)_3](PF_6)_2$ as a red precipitate. $[Ru(DNP\text{-}bpy)_3](PF_6)_2$ was filtered, washed with small amount of water, and dried (37.6 mg, 46% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.25 (d, J(H,H) = 9.2 Hz, 3H), 7.37 (d, J(H,H) = 8 Hz, 6H), 7.46 (s, 3H), 7.68 (s, 3H), 7.85 (d, J(H,H) = 16 Hz, 6H), 8.01 (d, J(H,H) = 7.2 Hz, 6H), 8.12 (m, 3H), 8.41 (d, J(H,H) = 8.4 Hz, 3H), 8.77 (m, 9H). ^{13}C NMR (100 MHz, CD_3CN): δ = 120.48, 120.65, 121.76, 122.05, 124.56, 124.78, 127.76, 129.43, 129.88, 133.29, 137.85, 140.31, 142.61, 148.22, 151.76, 154.65, 156.30, 157.06, 157.51. ESI-MS (m/z): 671.6 ($[M\text{-}2PF_6]^{2+}$). Elemental analysis calcd for $C_{66}H_{42}F_{12}N_{12}O_{15}P_2Ru \cdot 2H_2O$(%): C 47.46, H 2.78, N 10.06; found: C 47.14, H 2.70, N 10.09.

2. Supplementary Figures

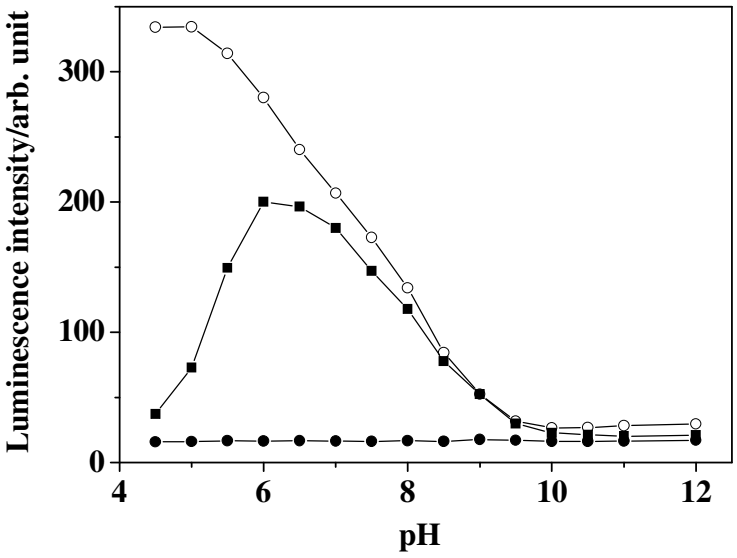

Figure S1. Effects of pH on the luminescence intensities of $[Ru(bpy)_2(DNP\text{-}bpy)]^{2+}$ (10 μM, ●), $[Ru(bpy)_2(HP\text{-}bpy)]^{2+}$ (10 μM, ○), and the product (■) of $[Ru(bpy)_2(DNP\text{-}bpy)]^{2+}$ (10 μM) reacted with thiophenol (50 μM) in 50 mM phosphate buffers with different pHs.

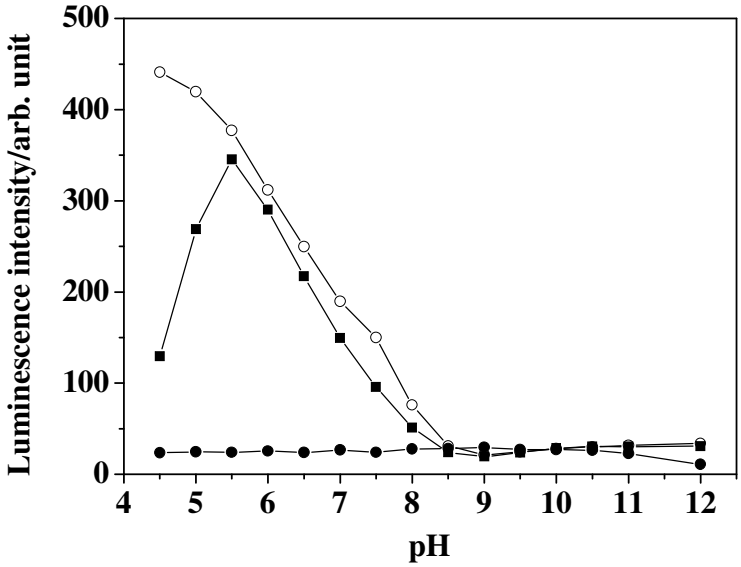

Figure S2. Effect of pH on the luminescence intensities of $[Ru(DNP\text{-}bpy)_3]^{2+}$ (10 μM, ●), $[Ru(HP\text{-}bpy)_3]^{2+}$ (10 μM, ○), and the product (■) of $[Ru(DNP\text{-}bpy)_3]^{2+}$ (10 μM) reacted with thiophenol (50 μM) in 50 mM phosphate buffers with different pHs.

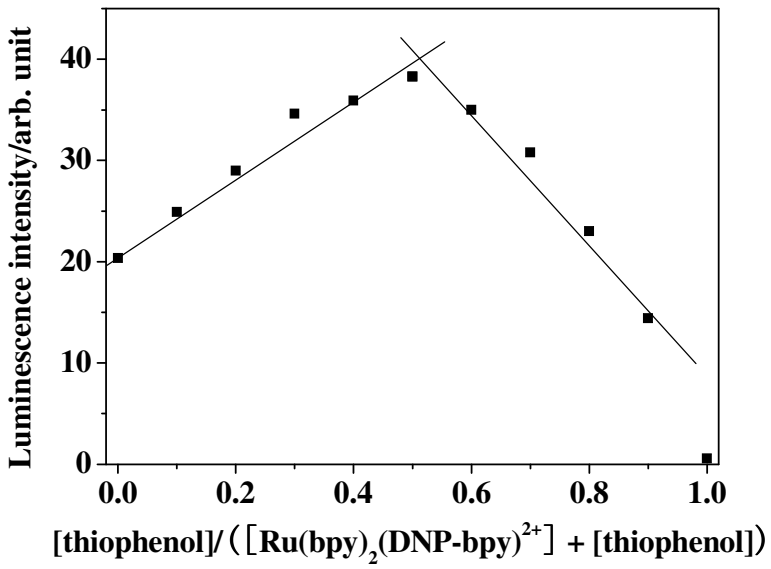

Figure S3. The job's plot of the reaction between $[Ru(bpy)_2(DNP\text{-}bpy)]^{2+}$ and thiophenol in 20 mM HEPES buffer at pH 7.0. The total concentration of $[Ru(bpy)_2(DNP\text{-}bpy)]^{2+}$ and thiophenol was kept at 10 μM.

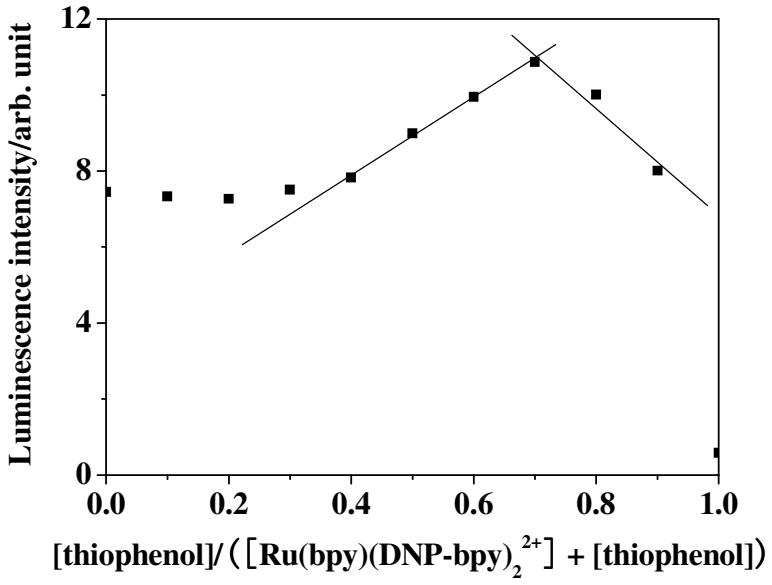

Figure S4. The Job's plot of the reaction between $[Ru(bpy)(DNP\text{-}bpy)_2]^{2+}$ and thiophenol in 20 mM HEPES buffer at pH 7.0. The total concentration of $[Ru(bpy)(DNP\text{-}bpy)_2]^{2+}$ and thiophenol was kept at 10 μM.

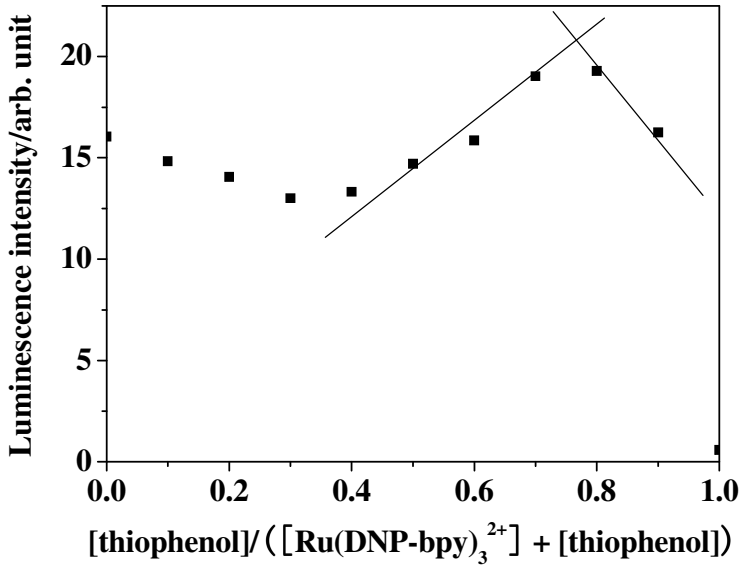

Figure S5. The job's plot of the reaction between $[Ru(DNP\text{-}bpy)_3]^{2+}$ and thiophenol in 20 mM HEPES buffer at pH 7.0. The total concentration of $[Ru(DNP\text{-}bpy)_3]^{2+}$ and thiophenol was kept at 10 μM.

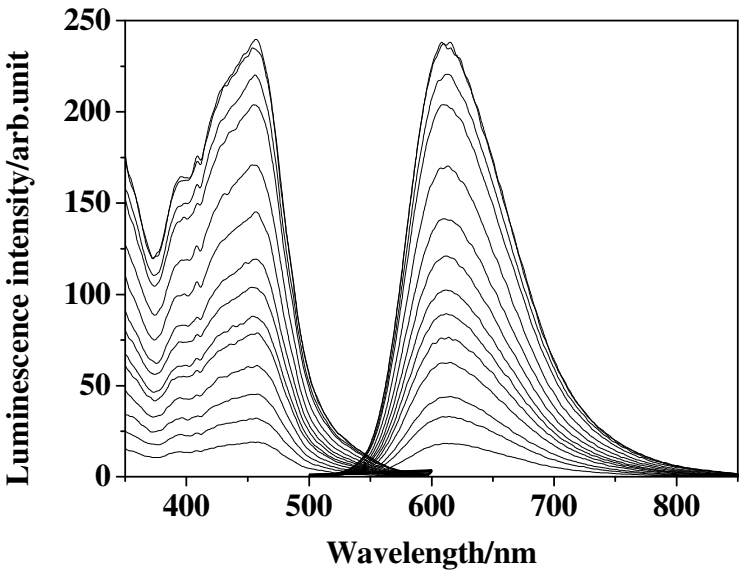

Figure S6. Excitation and emission spectra of $[Ru(bpy)_2(DNP\text{-}bpy)]^{2+}$ (10 μM) in the presence of different concentrations of thiophenol in 20 mM HEPES buffer at pH 7.0. The concentrations of thiophenol are 0.0, 2.0, 4.0, 6.0, 8.0, 10, 12, 15, 20, 30, 40, 50, 75 and 100 μM, respectively.

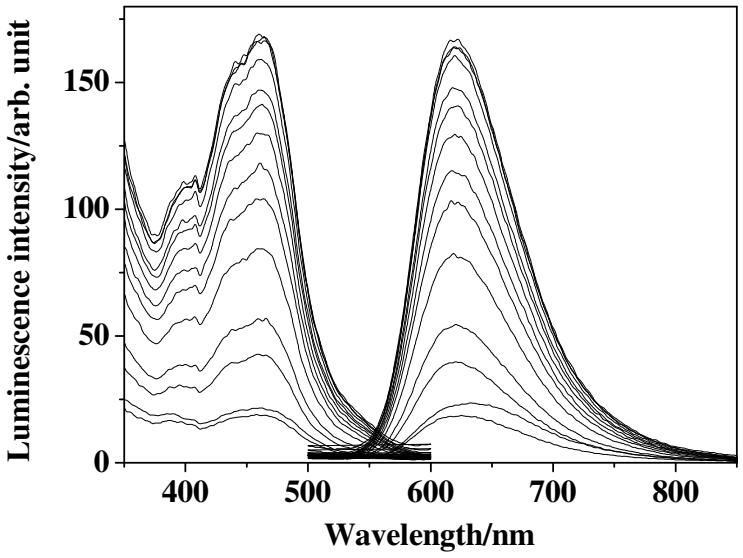

Figure S7. Excitation and emission spectra of $[Ru(DNP\text{-}bpy)_3]^{2+}$ (10 μM) in the presence of different concentrations of thiophenol in 20 mM HEPES buffer at pH 7.0. The concentrations of thiophenol are 0.0, 10, 20, 22.5, 25, 27.5, 30, 32.5, 35, 37.5, 40, 50, 75 and 100 μM, respectively.

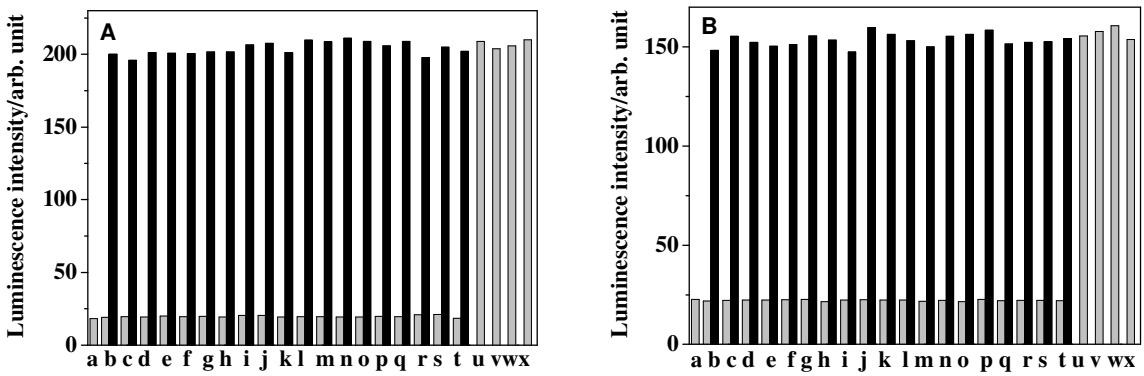

Figure S8. Luminescence intensities of the products of the Ru(II) complex (10 μM) reacted with various species (100 μM) and thiophenol or its derivatives (40 μM) in 20 mM HEPES buffer at pH 7.0 (gray bars). The black bars show the luminescence intensities of the products of the Ru(II) complex (10 μM) reacted with thiophenol (40 μM) in the presence of various possibly interfering species (100 μM) in 20 mM HEPES buffer at pH 7.0. A: $[Ru(bpy)_2(DNP\text{-}bpy)]^{2+}$ (λ_{em}=612 nm); B: $[Ru(DNP\text{-}bpy)_3]^{2+}$ (λ_{em}=620 nm). (a) blank, (b) Val, (c) Lys, (d) Asp, (e) His, (f) Arg, (g) Met, (h) Leu, (i) GSH, (j) Cys, (k) Hcy, (l) Ser, (m) Tyr, (n) Na_2S, (o) KI, (p) PhOH, (q) Vc, (r) aniline, (s) $NH_2CH_2CH_2SH$, (t) the mixture of all possibly interfering species (10 μM for each), (u) thiophenol, (v) 4-bromo-thiophenol, (w) 4-amino-thiophenol, (x) 2-amino-thiophenol.

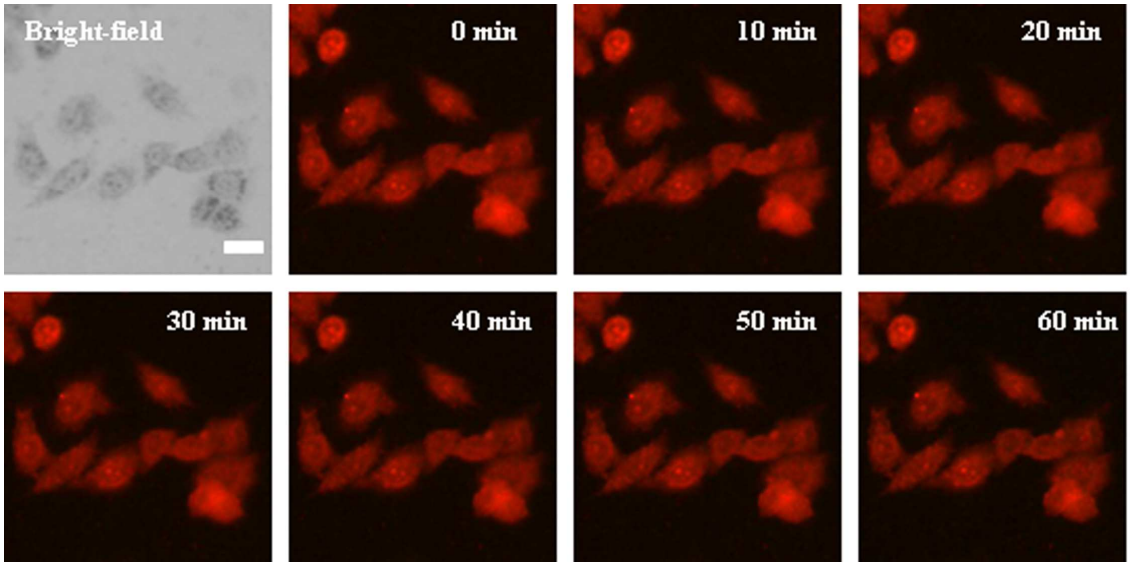

Figure S9. Bright-field and luminescence images of the thiophenol-treated $[Ru(bpy)(DNP\text{-}bpy)_2]^{2+}$-loaded HeLa cells in the isotonic saline solution within 60 min. The images were recorded at 10 min intervals. Scale bar: 10 μm.

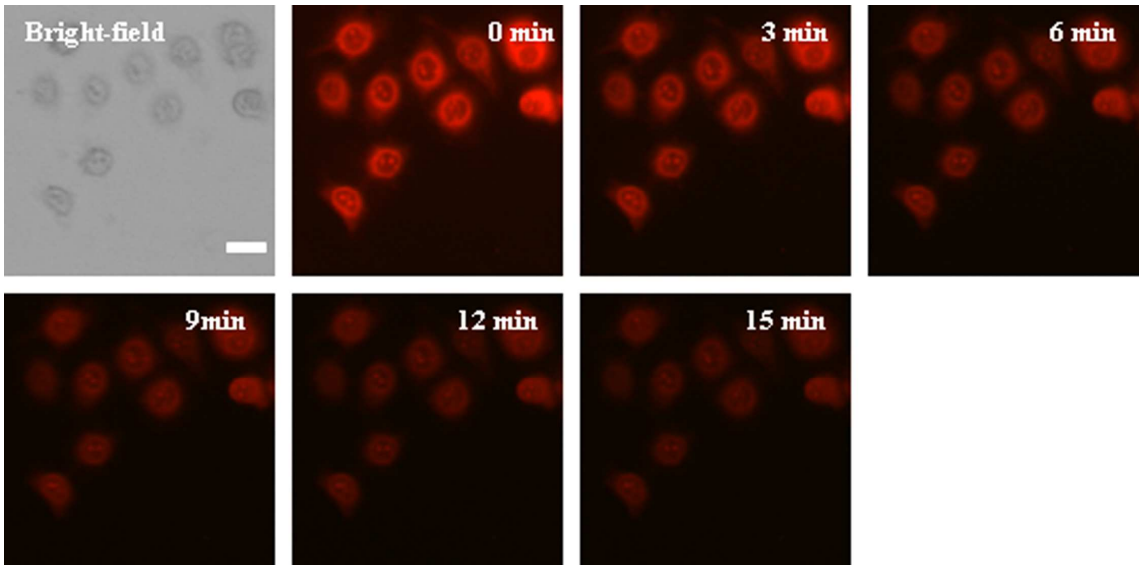

Figure S10. Photostability of the thiophenol-treated $[Ru(bpy)(DNP\text{-}bpy)_2]^{2+}$-loaded HeLa cells under the irradiation of 450-490 nm light from a 100 W Hg lamp. The images were recorded at 3 min intervals for 15 min. Scale bar: 10 μm.

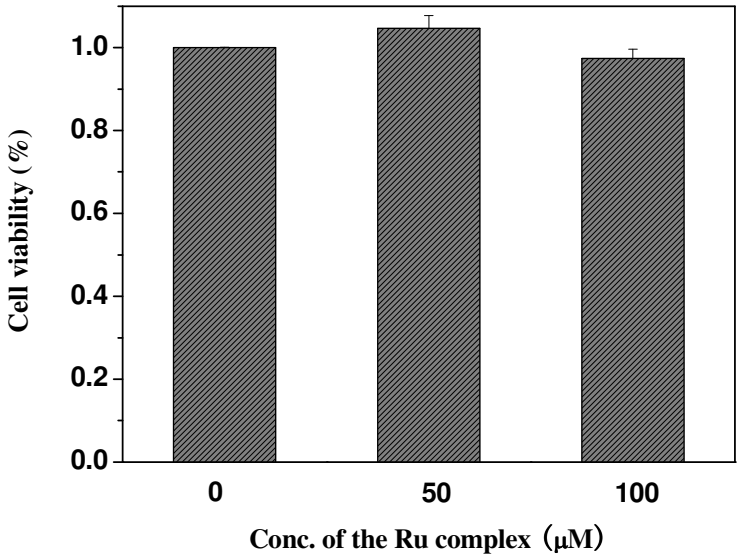

Figure S11. Cell viability of HeLa cells incubated with different concentrations of $[Ru(bpy)(DNP\text{-}bpy)_2]^{2+}$ for 4 h.

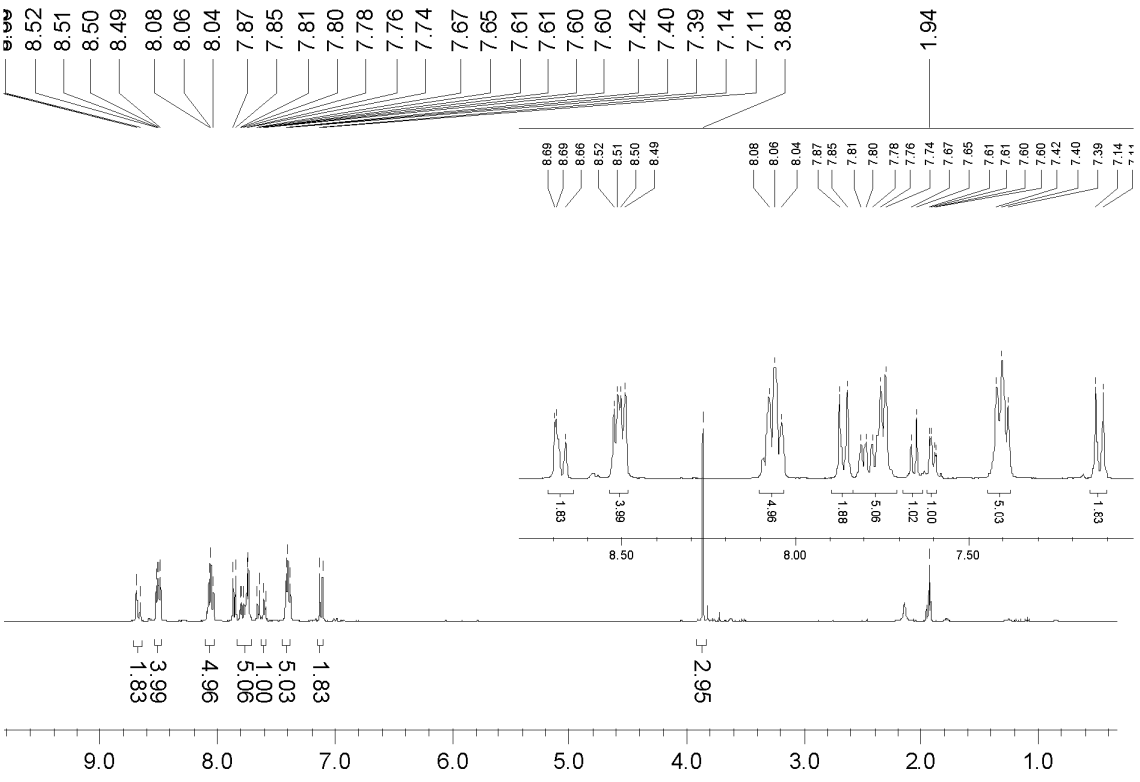

Figure S12. ^{1}H NMR of compound **1** (CD_3CN, 400 MHz).

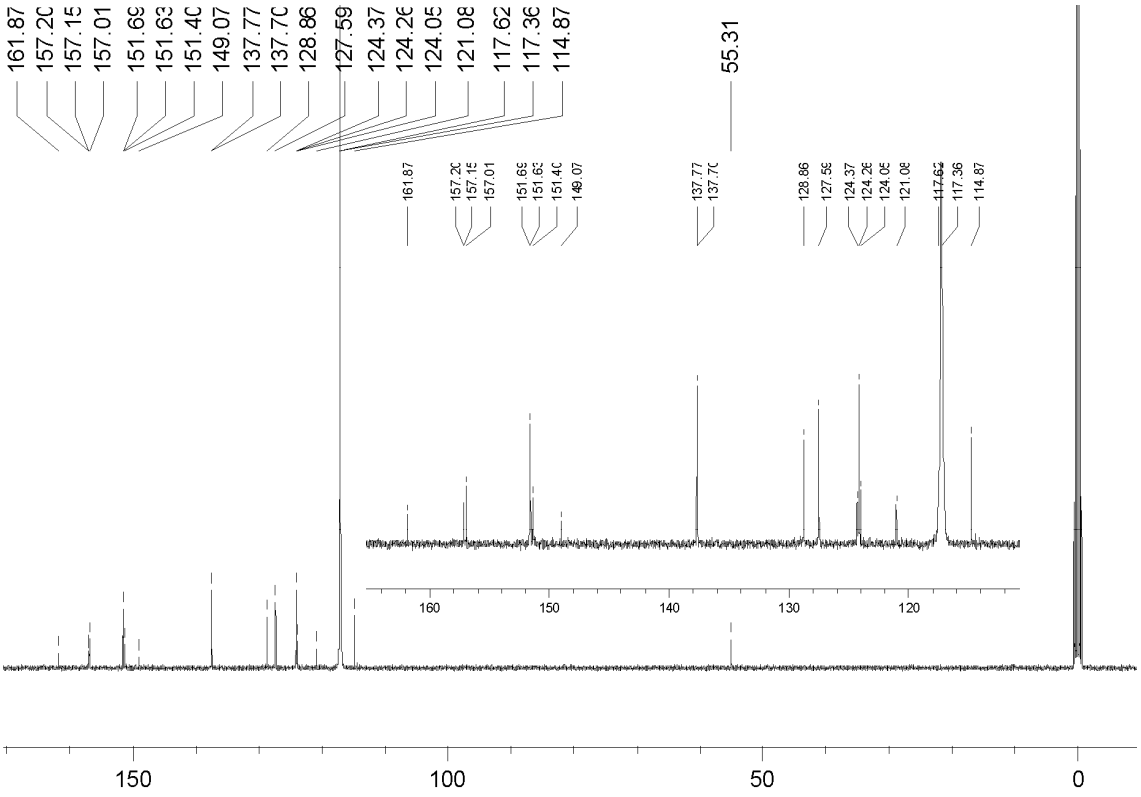

Figure S13. ^{13}C NMR of compound **1** (CD_3CN, 100 MHz).

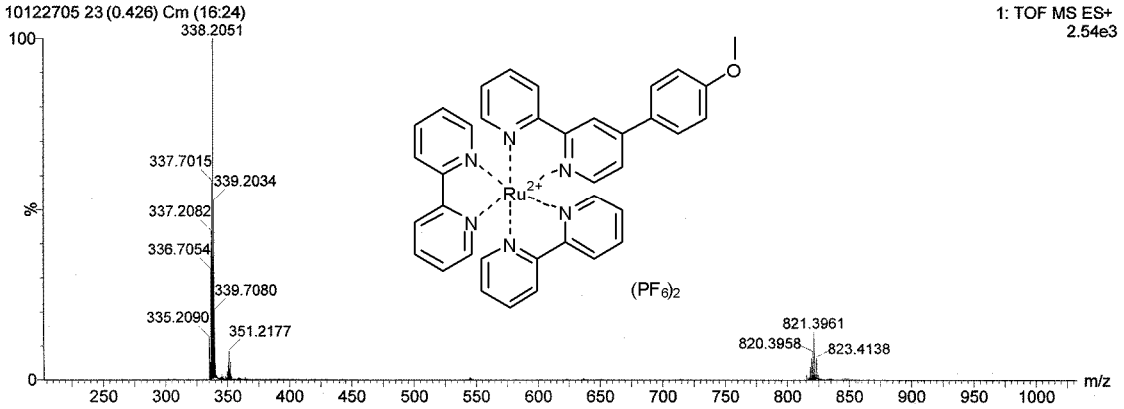

Figure S14. TOF ESI MS of compound **1**.

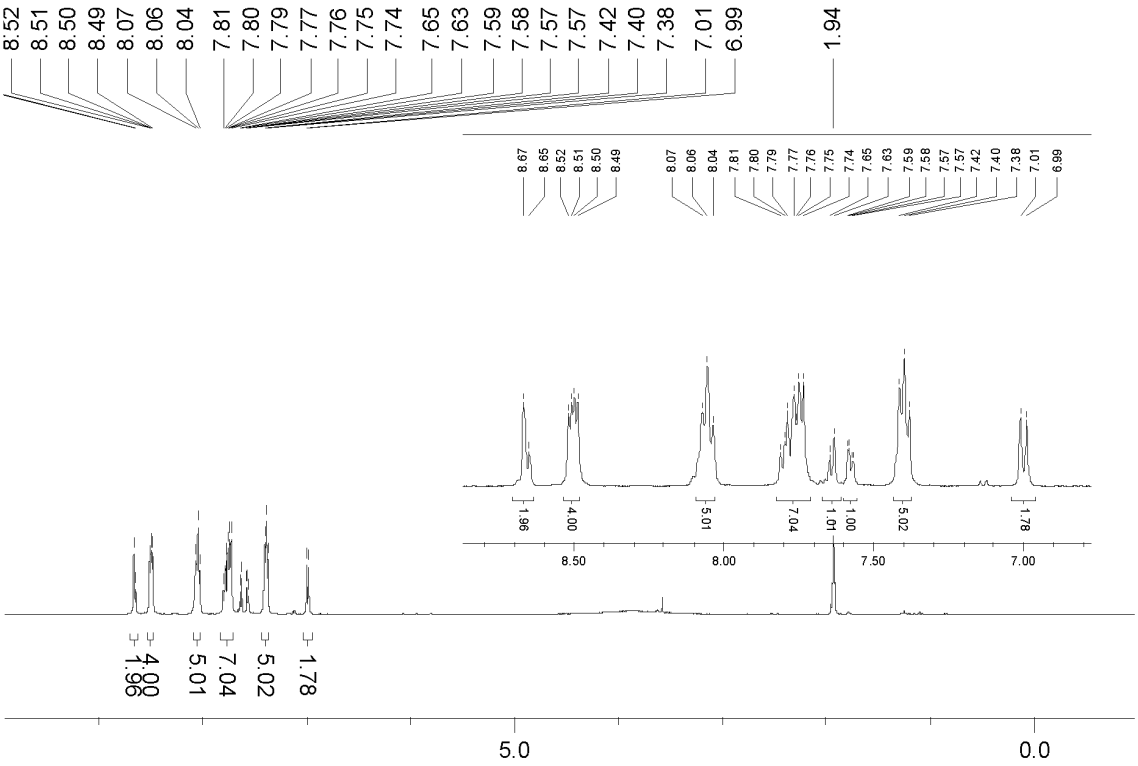

Figure S15. ^{1}H NMR of [Ru(bpy)$_2$(HP-bpy)](PF$_6$)$_2$ (CD$_3$CN, 400 MHz).

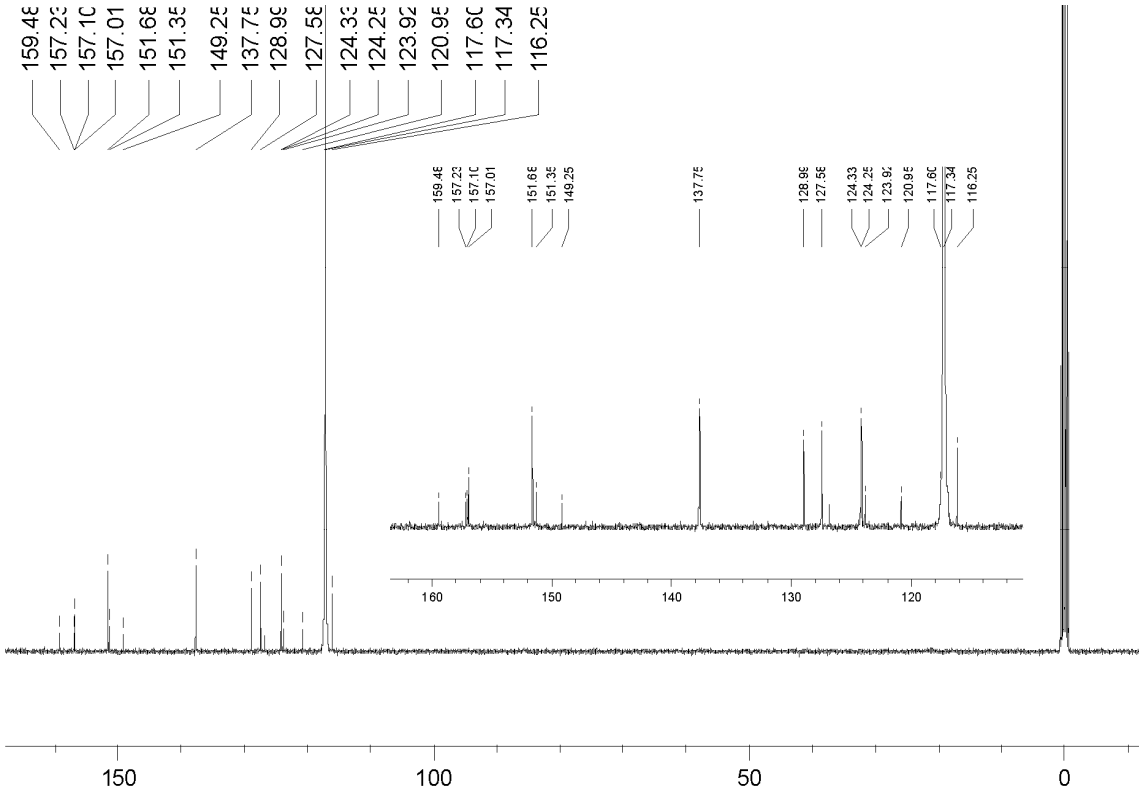

Figure S16. ^{13}C NMR of $[Ru(bpy)_2(HP\text{-}bpy)](PF_6)_2$ (CD_3CN, 100 MHz).

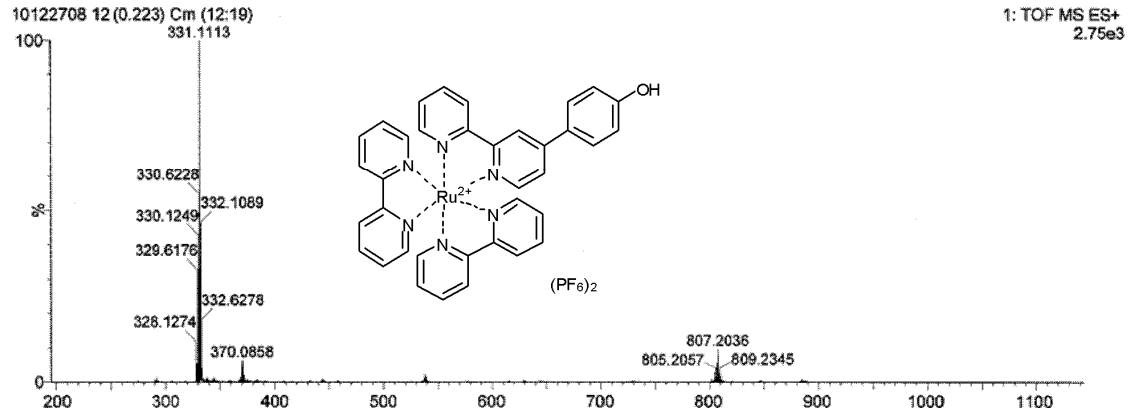

Figure S17. TOF ESI MS of $[Ru(bpy)_2(HP\text{-}bpy)](PF_6)_2$.

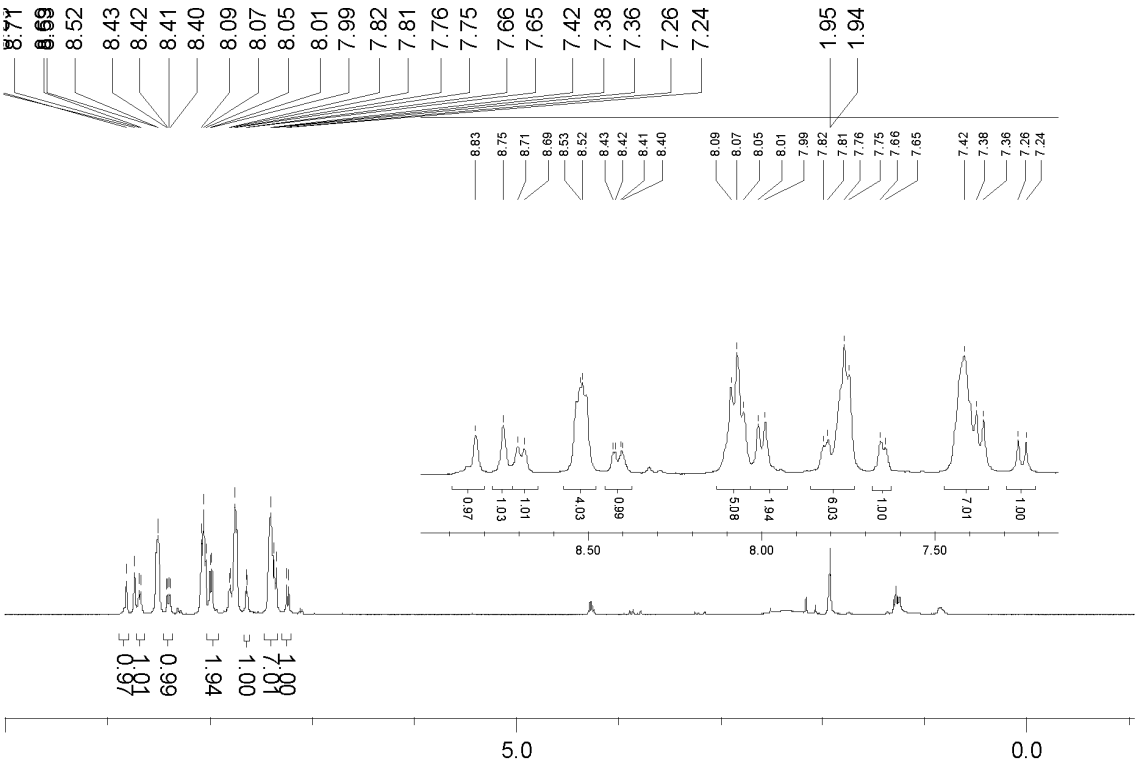

Figure S18. ^{1}H NMR of [Ru(bpy)$_2$(DNP-bpy)](PF$_6$)$_2$ (CD$_3$CN, 400 MHz).

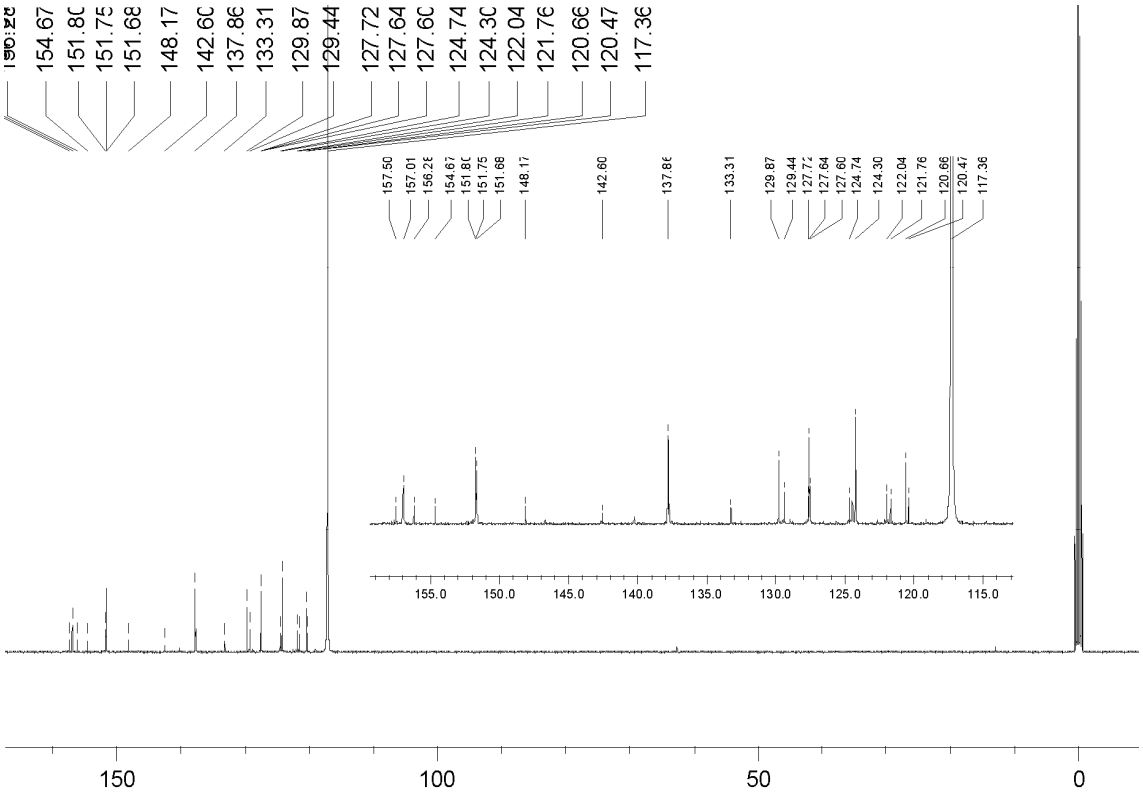

Figure S19. ^{13}C NMR of [Ru(bpy)$_2$(DNP-bpy)](PF$_6$)$_2$ (CD$_3$CN, 100 MHz).

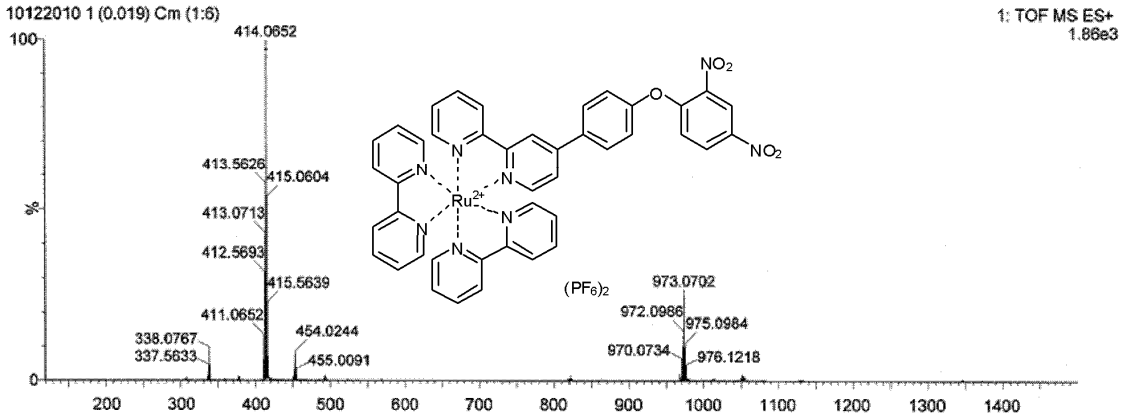

Figure S20. TOF ESI MS of $[Ru(bpy)_2(DNP\text{-}bpy)](PF_6)_2$.

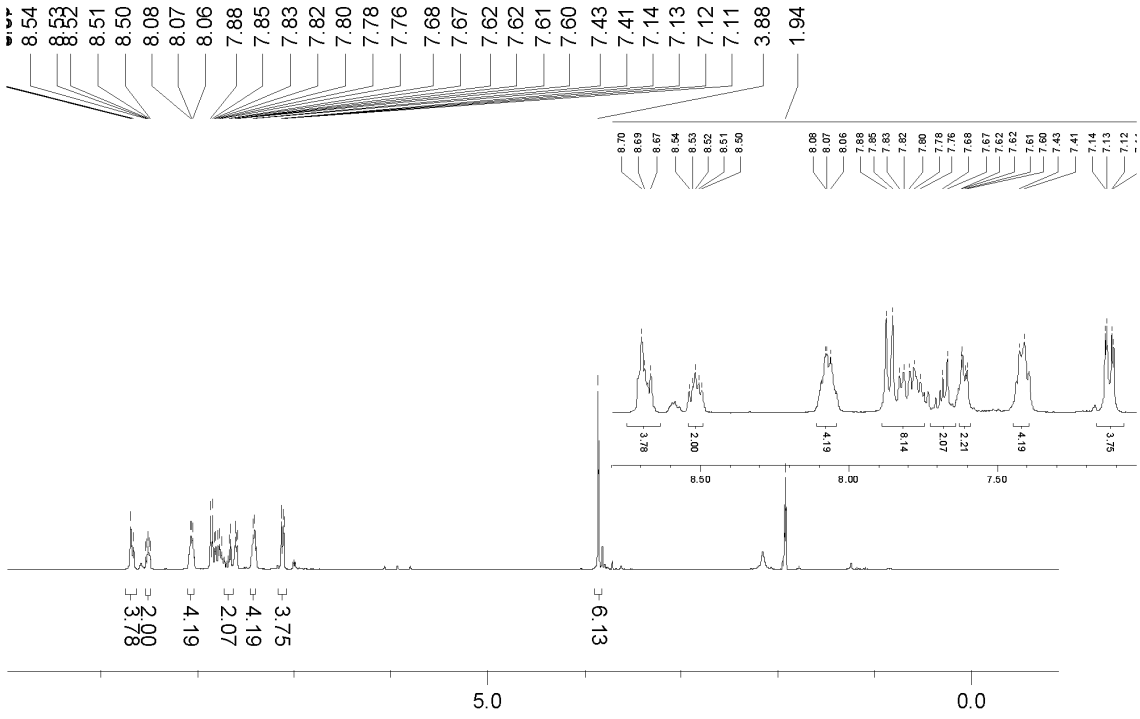

Figure S21. ^1H NMR of compound **3** (CD_3CN, 400 MHz).

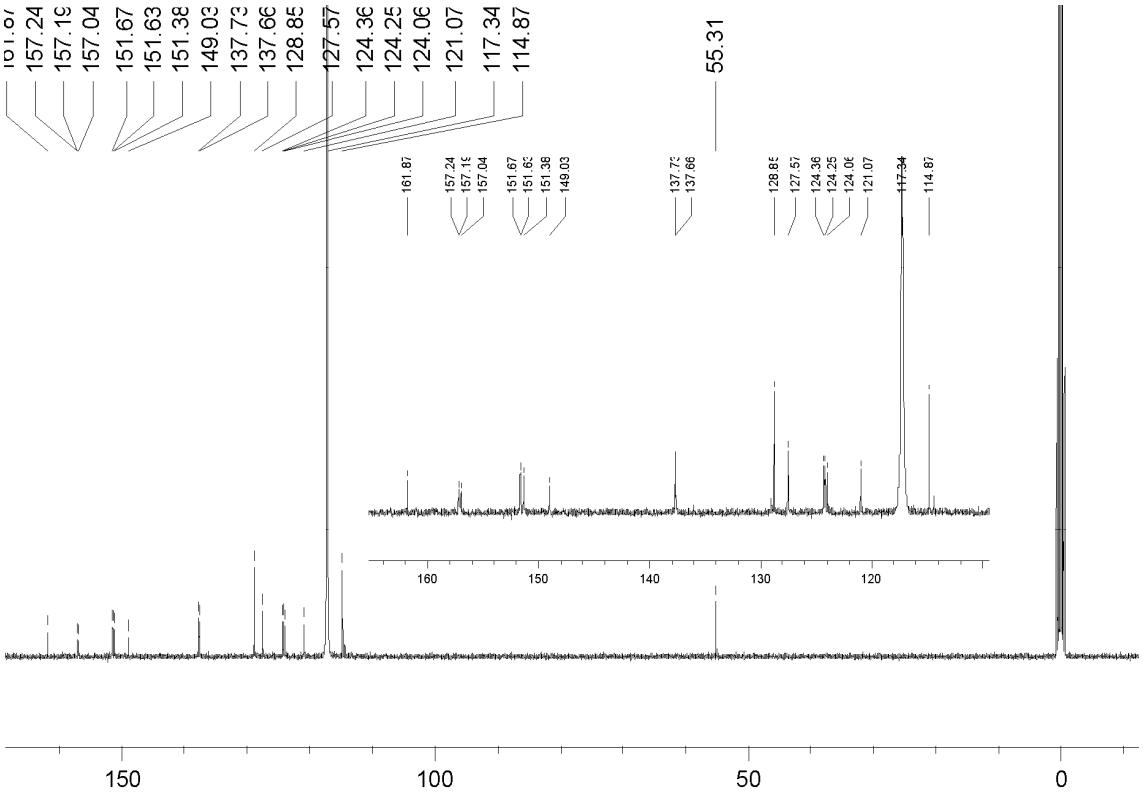

Figure S22. ^{13}C NMR of compound **3** (CD_3CN, 100 MHz).

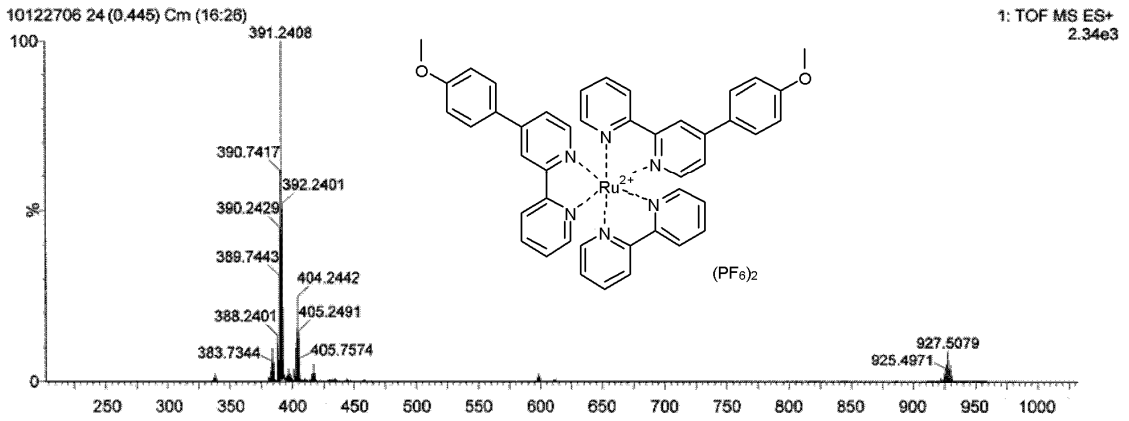

Figure S23. TOF ESI MS of compound **3**.

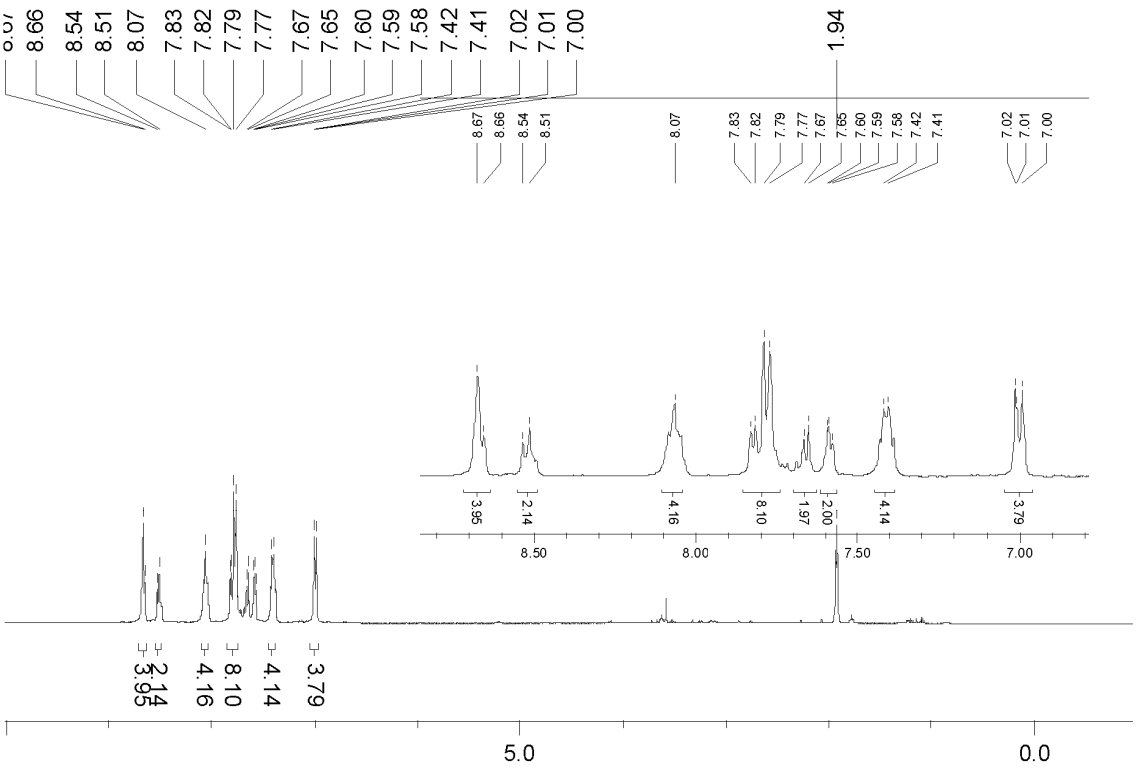

Figure S24. ^{1}H NMR of [Ru(bpy)(HP-bpy)$_2$](PF$_6$)$_2$ (CD$_3$CN, 400 MHz).

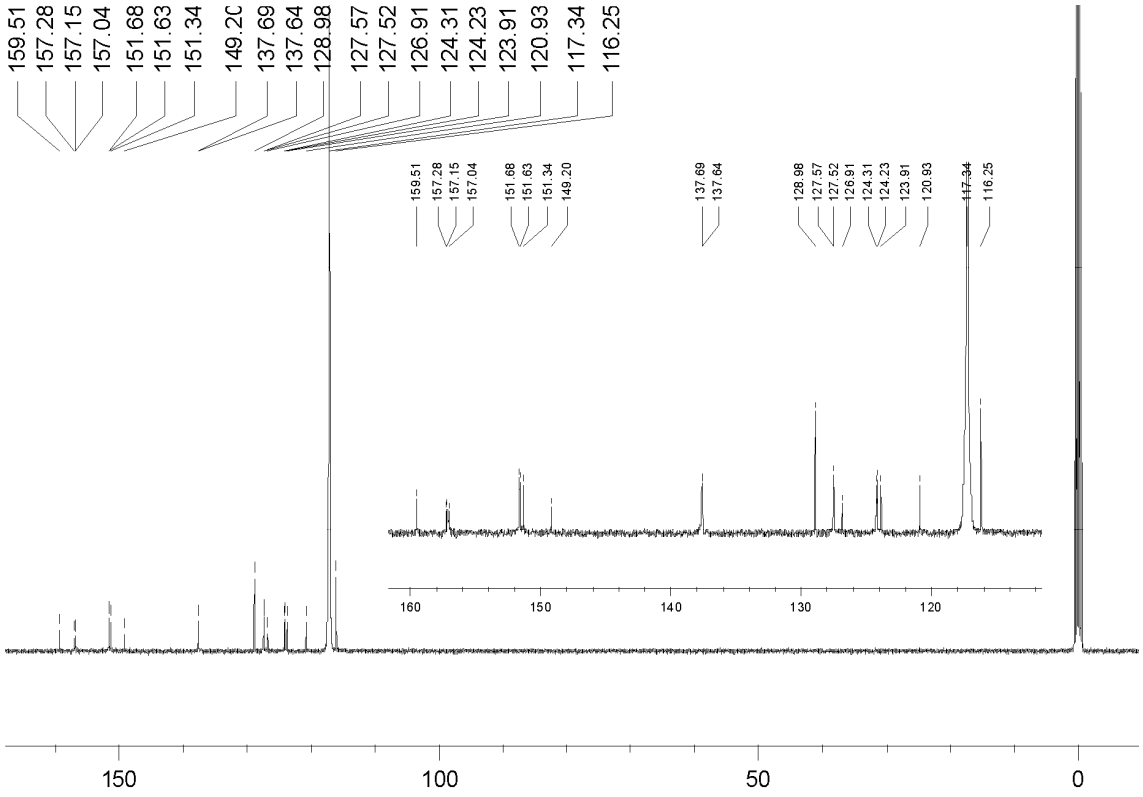

Figure S25. ^{13}C NMR of [Ru(bpy)(HP-bpy)$_2$](PF$_6$)$_2$ (CD$_3$CN, 100 MHz).

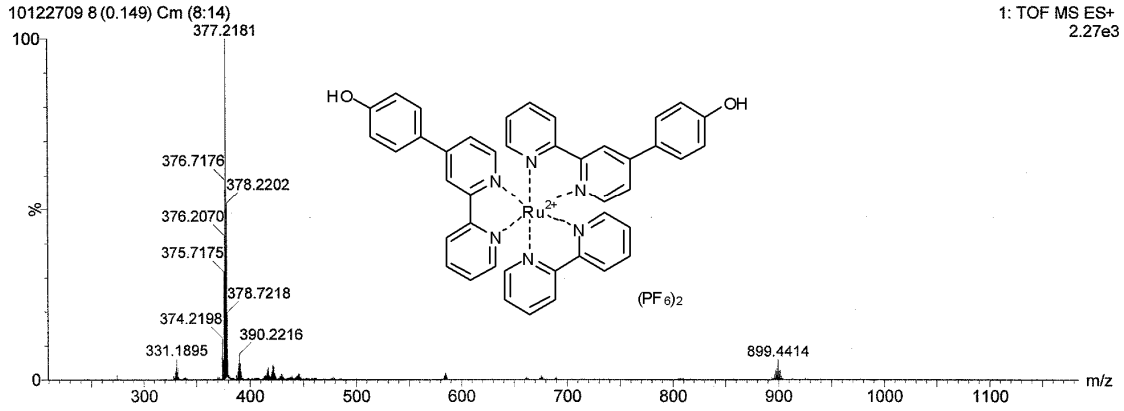

Figure S26. TOF ESI MS of $[Ru(bpy)(HP\text{-}bpy)_2](PF_6)_2$.

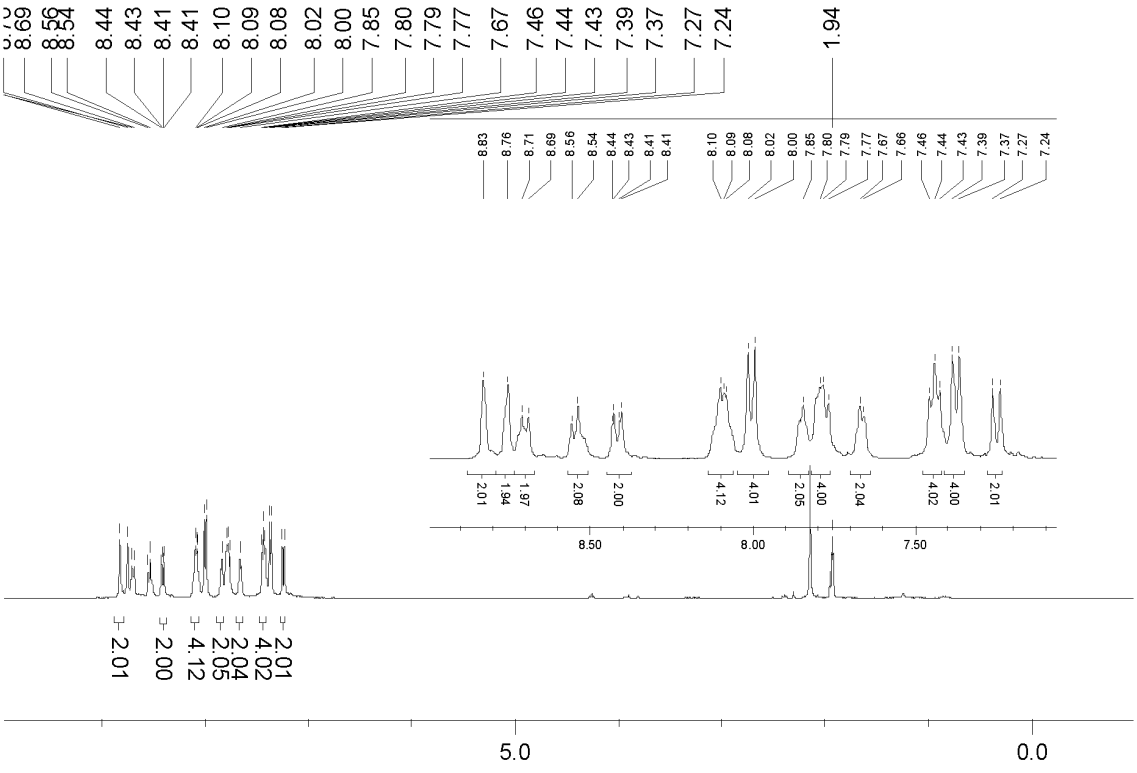

Figure S27. ^1H NMR of $[Ru(bpy)(DNP\text{-}bpy)_2](PF_6)_2$ (CD_3CN, 400 MHz).

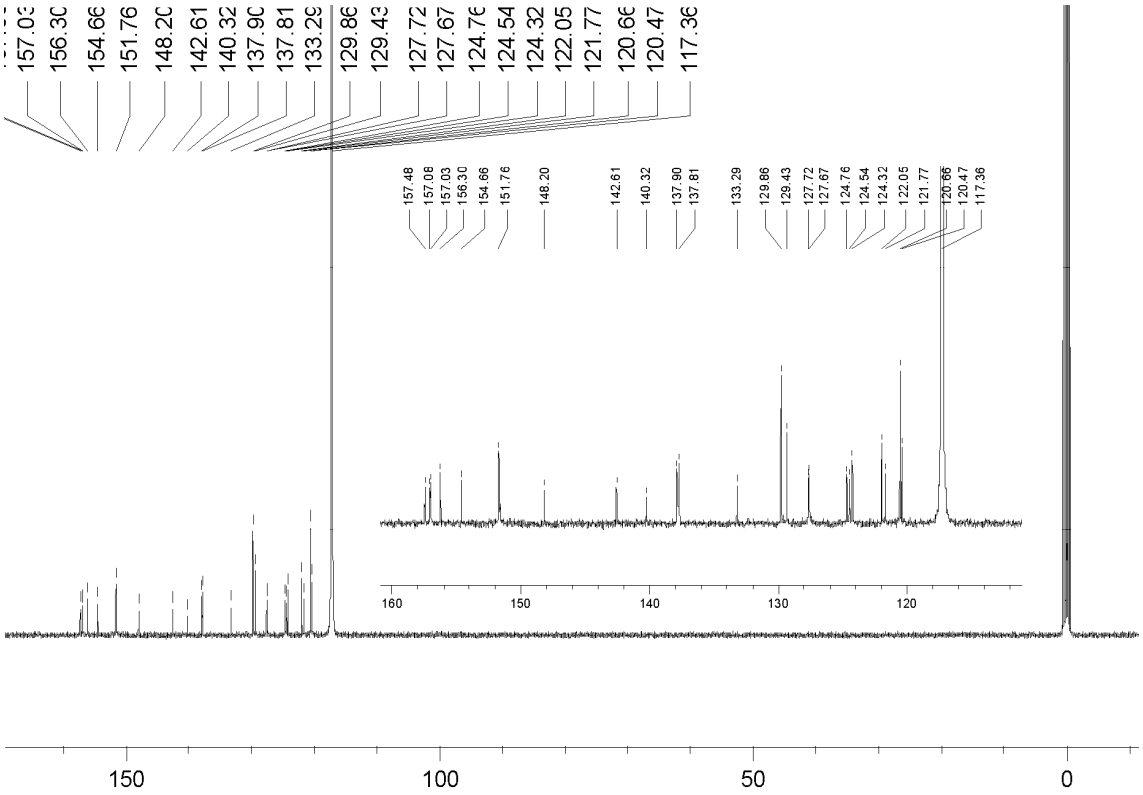

Figure S28. ^{13}C NMR of [Ru(bpy)(DNP-bpy)$_2$](PF$_6$)$_2$ (CD$_3$CN, 100 MHz).

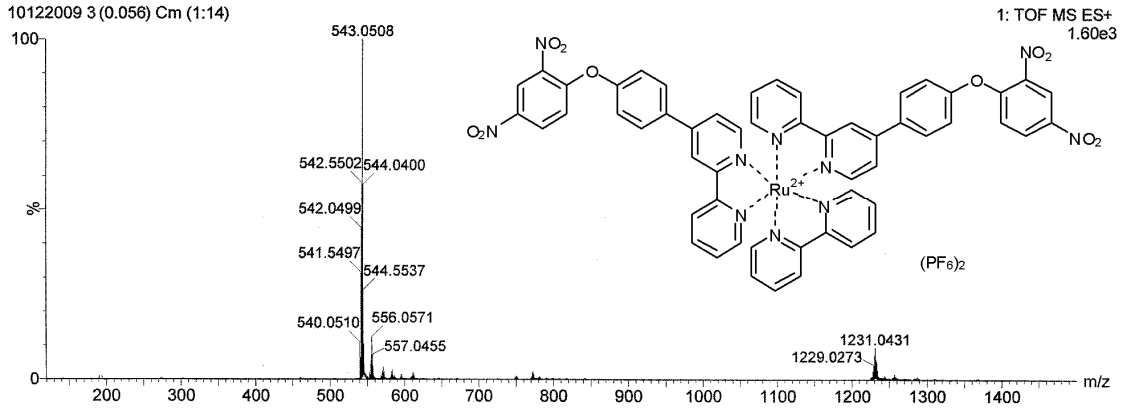

Figure S29. TOF ESI MS of [Ru(bpy)(DNP-bpy)$_2$](PF$_6$)$_2$.

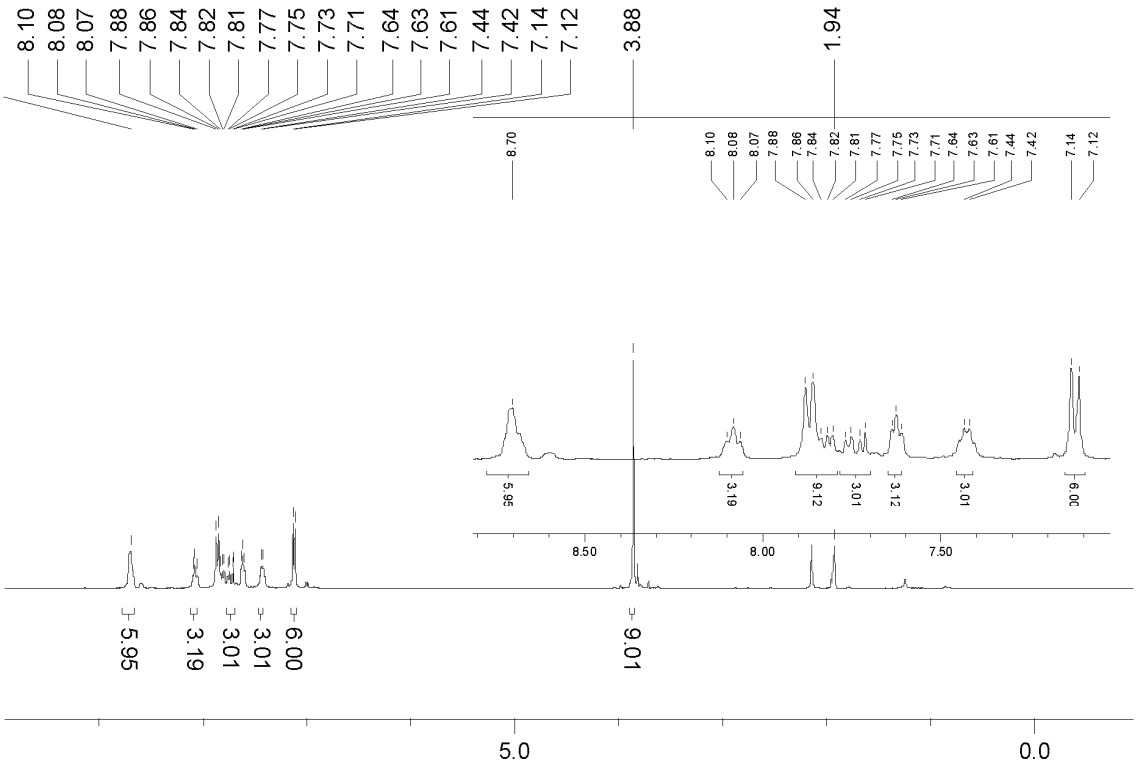

Figure S30. ^{1}H NMR of compound **4** (CD_3CN, 400 MHz).

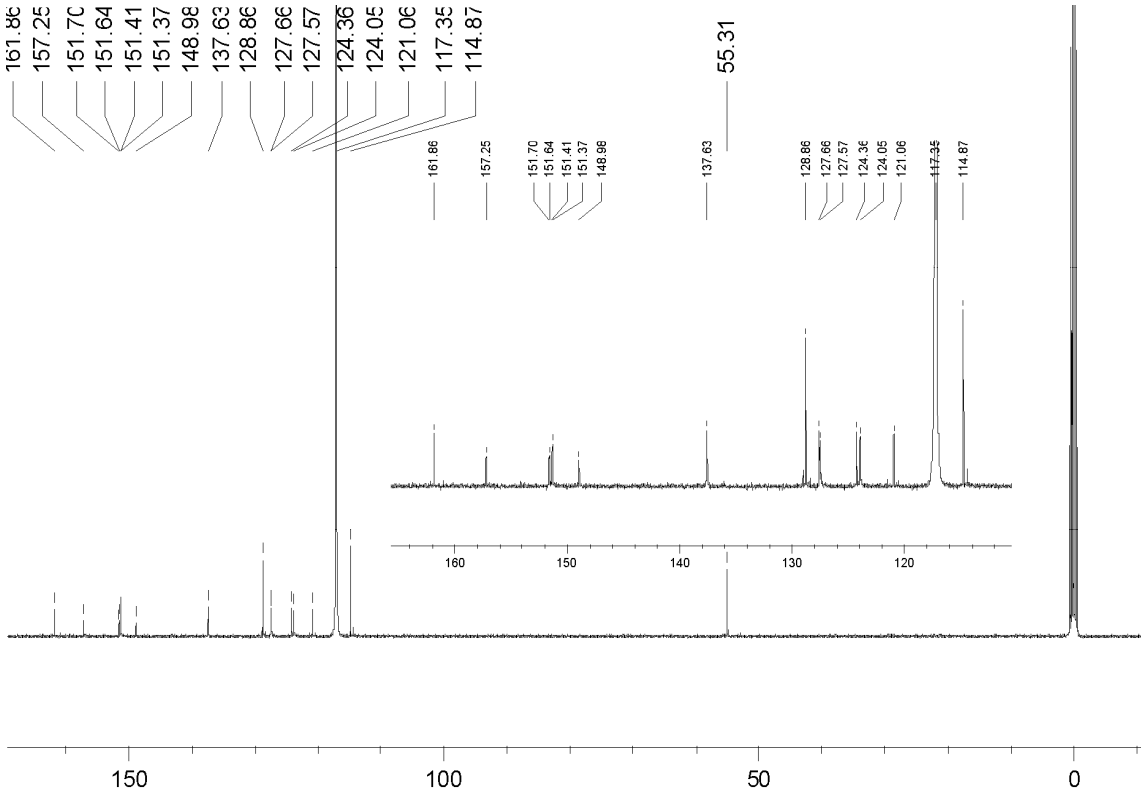

Figure S31. ^{13}C NMR of compound **4** (CD_3CN, 100 MHz).

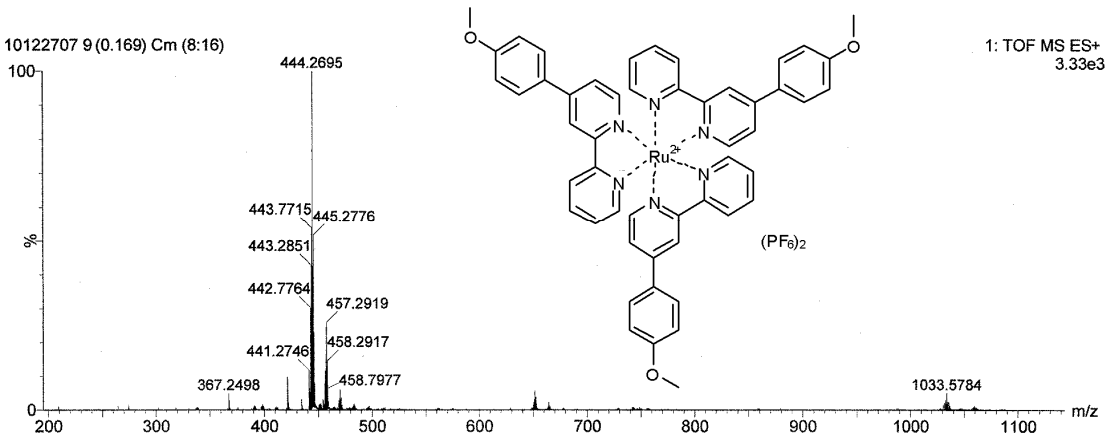

Figure S32. TOF ESI MS of compound **4**.

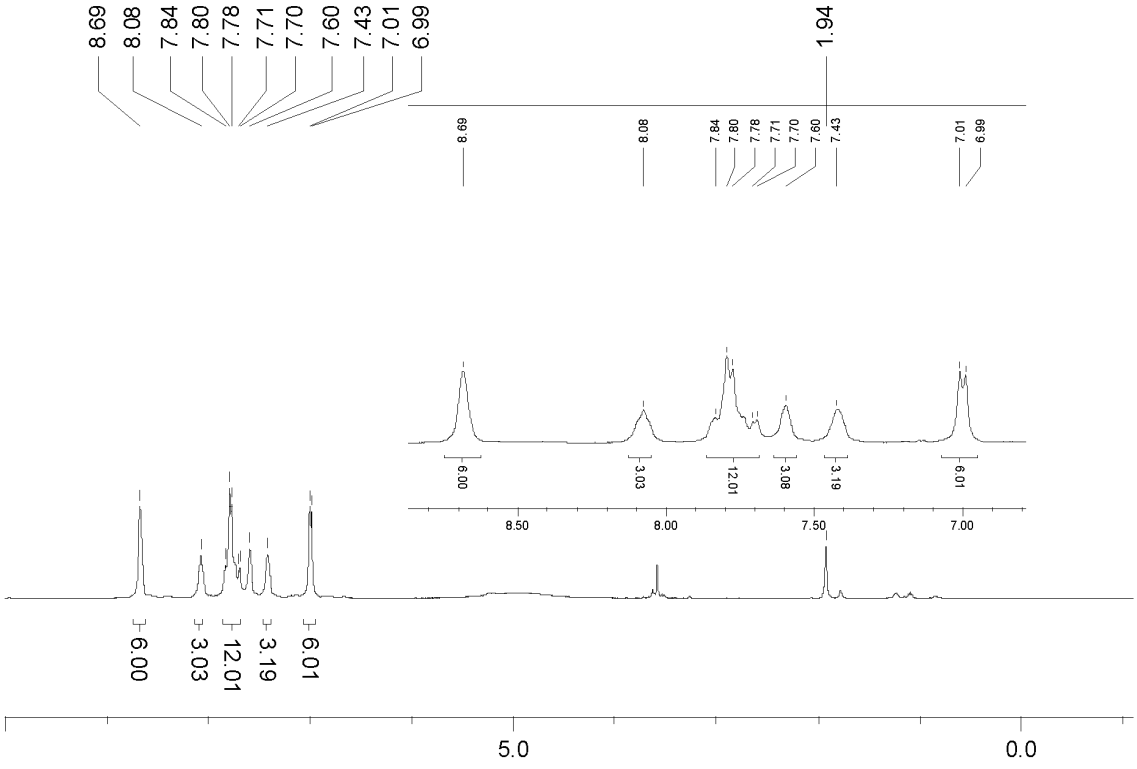

Figure S33. ^{1}H NMR of $[Ru(HP\text{-}bpy)_3](PF_6)_2$ (CD_3CN, 400 MHz).

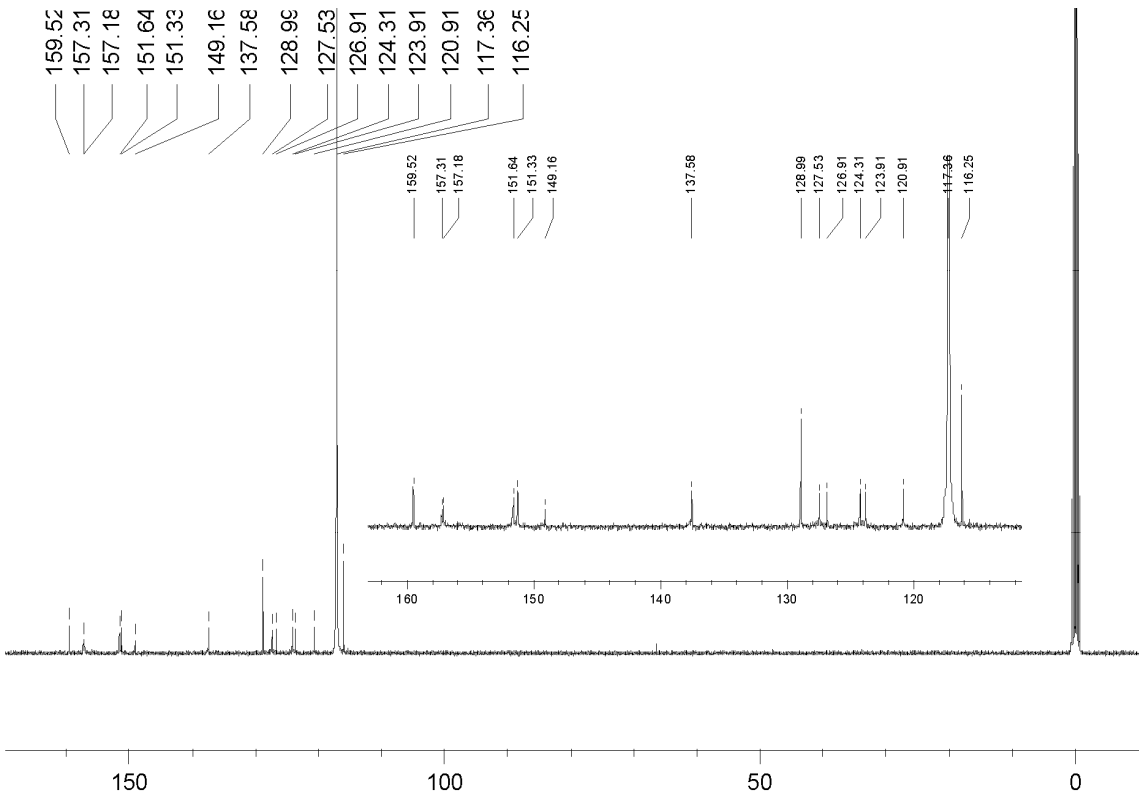

Figure S34. ^{13}C NMR of [Ru(HP-bpy)$_3$](PF$_6$)$_2$ (CD$_3$CN, 100 MHz).

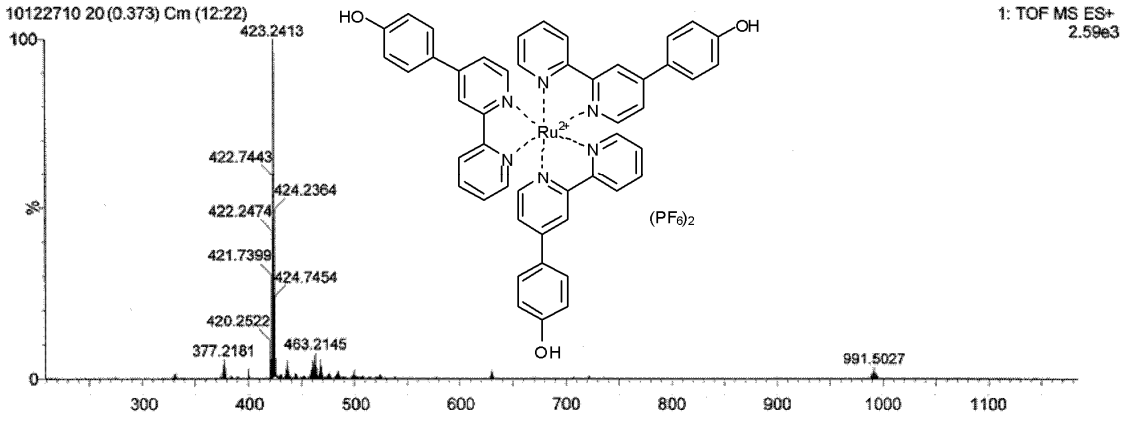

Figure S35. TOF ESI MS of [Ru(HP-bpy)$_3$](PF$_6$)$_2$.

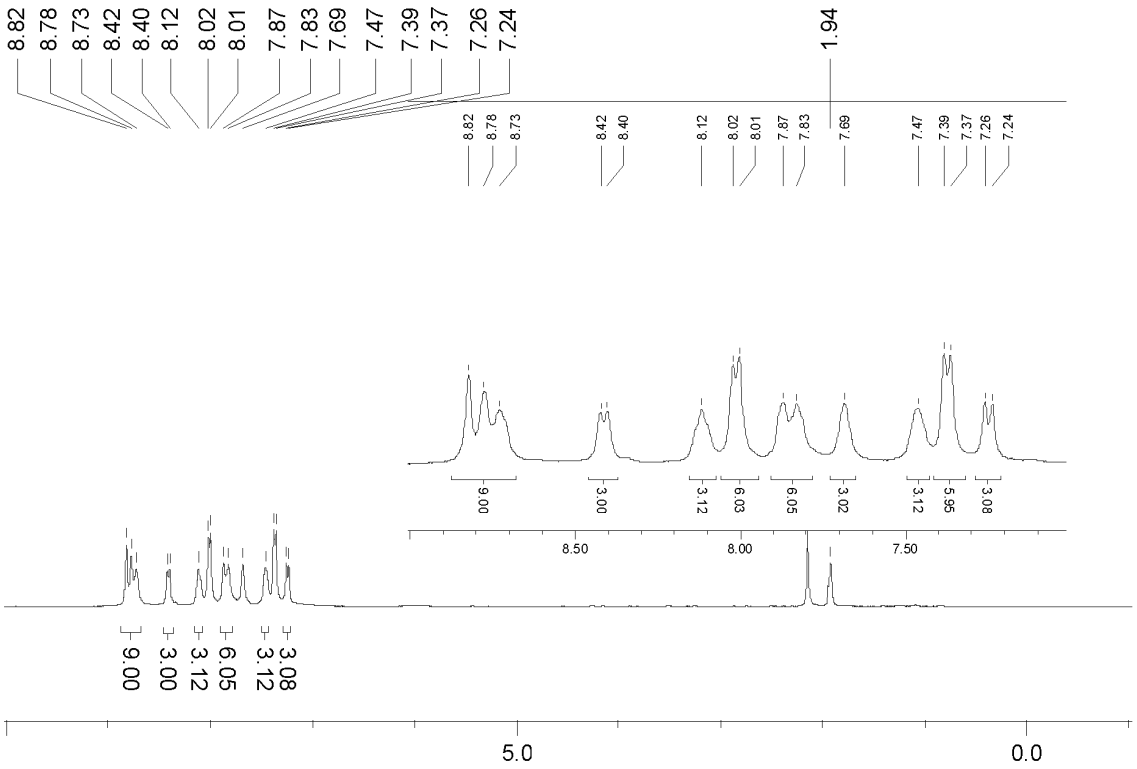

Figure S36. ^{1}H NMR of $[Ru(DNP\text{-}bpy)_3](PF_6)_2$ (CD_3CN, 400 MHz).

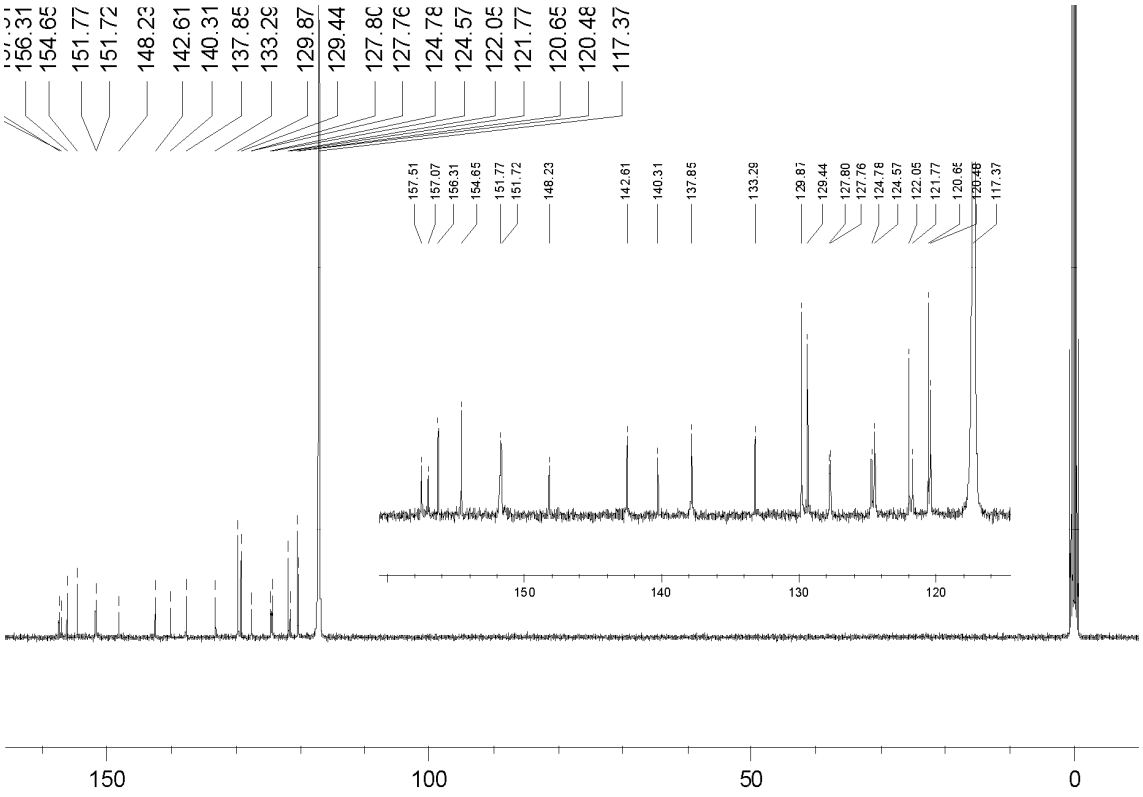

Figure S37. ^{13}C NMR of $[Ru(DNP\text{-}bpy)_3](PF_6)_2$ (CD_3CN, 100 MHz).

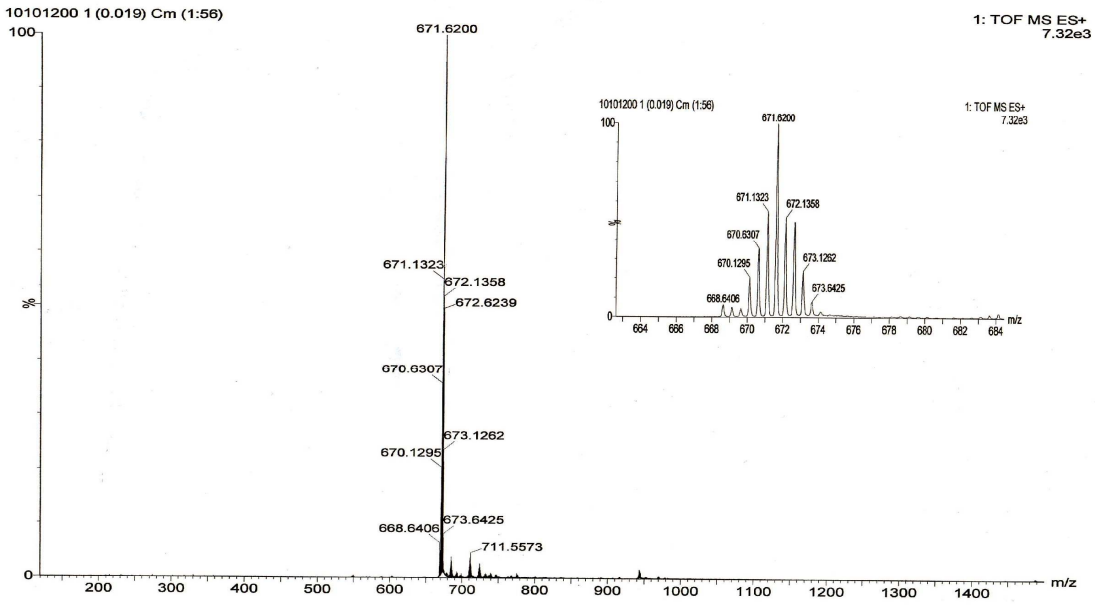

Figure S38. TOF ESI MS of $[Ru(DNP\text{-}bpy)_3](PF_6)_2$.