Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Solid-Phase Synthesis and Photoactivity of Ru-Polypyridyl Visible Light Chromophores Bonded Through Carbon to Semiconductor Surfaces

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Materials

Chemicals used without any purification unless mentioned otherwise; anhydrous ethanol (Commercial Alcohols); triply distilled water; dichloromethane, distilled (Sigma Aldrich, ACS reagent, ≥ 99.5 %); hexanes, distilled (Caledon, ACS); acetonitrile, distilled (≥ 99.5 %); methanol (Sigma Aldrich, ACS reagent, ≥ 99.8 %); silver trifluoromethanesulfonate (Sigma Aldrich, 99 %); silver tetrafluoroborate (Sigma Aldrich, 98 %); tetrahydrofuran, distilled (Sigma Aldrich, ACS reagent, ≥ 99.0 %); $Ru(COD)Cl_2$ (Strem Chemicals, polymer, ≥ 97 %); 4,4'-methyl 2,2'-bipyridine (Sigma Aldrich, 99 %); 4,4'-tert-butyl 2,2'-bipyridine (Sigma Aldrich, 98 %); 1,10-phenanthroline (Sigma Aldrich, ≥ 99 %); $Ru(DMSO)_4Cl_2$ (Sigma Aldrich, 96 %); Hydrochloric acid (Caledon, 37 %); diethyl ether (Anachemia, ≥ 99.0 %); 1,10-phenanthroline-5,6-diamine (Shanghai Uchem, ≥ 98 %); 1,10-phenanthroline-5,6-dione (Sigma Aldrich, 97 %); dimethylformamide (Fisher Chemicals, 99.9 %).

Synthesis of $Ru(Mebipy)_2Cl_2$ & $Ru(^tBubipy)_2Cl_2$ complexes

A literature procedure with slight modification was used to prepare both $Ru(Mebipy)_2Cl_2$ and $Ru(^tBubipy)_2Cl_2$ complexes.[1] $Ru(COD)Cl_2$ (1 equivalent) and ligand (2 equivalents) were weighed into a 100 ml side-arm flask. The flask then connected to a Schlenk line, and then evacuated and refilled with N_2 (3 cycles). 1,2-dichlorobenzene (0.04 M based on [$Ru(COD)Cl_2$]), bubbled with N_2 for 30 minutes, was added to the flask, then connected to a condenser. The flask was placed in an oil bath preheated to 140 °C and stirred overnight. During the reaction, the color of the solution turned to dark purple with precipitate forming. After 16 hours, the flask was cooled to room temperature, added 20 ml of hexane and allowed for precipitates to settle down. The dark purple product was collected by filtration through a Buchner funnel and by washing with copious amount

of hexane. The yield of the product after dried under suction was > 90% with some 1,2-dichlorobenzene present, which was used for the next step without further purifications. The ^{1}H NMR data were consistent with reported values:[2]

Ru(Mebipy)$_2$Cl$_2$ **^{1}H NMR** (399.978 MHz, CD_2Cl_2, 27.0 °C): 2.41 (s, 6H), 2.61 (s, 6H), 6.72 (d, 2H, J = 5.0 Hz), 7.39 (d, 2H, J = 4.9 Hz), 7.47 (s, 2H), 7.82 (s, 2H), 7.95 (s, 2 H), 10.12 (d, 2H, J = 4.8 Hz).

Ru(^{t}Bubipy)$_2$Cl$_2$ **^{1}H NMR** (498.119 MHz $CDCl_3$, 27.0 °C): 1.31 (s, 18H), 1.51 (s, 18H), 6.95 (d, 2H, J = 4.5 Hz), 7.55–7.59 (m, 4H), 7.95 (d, 2H, J = 1.5 Hz), 8.09 (d, 2H, J = 1.0 Hz), 10.17 (d, 2H, J = 3.9 Hz).

General procedure for the synthesis of [Ru(bipyridine)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$ complexes[3]

Both Ru(bis-bipyridine)$_2$Cl$_2$ (1 equivalent) and $AgBF_4$ (2 equivalents) were weighed into a 100 ml side arm flask inside the glove box. The flask was wrapped in aluminum foil, connected to a Schlenk line, and then evacuated and refilled with N_2 (3 cycles). Freshly distilled MeCN (0.02 M based on Ru(bis-bipyridine)$_2$Cl$_2$) was then added using a gas tight syringe and the resulted suspension was stirred at room temperature for overnight. After 20 hours, the stirring was stopped, and the precipitates were allowed to settle down. After an hour, the orange-reddish solution was transferred into another side-arm flask by cannula filtration. The greyish-white precipitate was washed with additional MeCN (2 × 10 ml) and filtrate transferred to the same flask. Combined filtrate was concentrated using rotavap and a reddish-orange product was obtained, which was dissolved using minimum DCM. Upon dissolving in DCM, greyish-white precipitate (AgCl) started to form again, which was removed by filtering through a Celite plug. Additional DCM was

passed until no more orange/reddish color was observed on the Celite plug. The filtrate was then concentrated again using rotavap and purified by crystallization with DCM/Et_2O.

$[Ru(Mebipy)_2(CH_3CN)_2](BF_4)_2$:**^{1}H NMR** (498.121 MHz, CD_3CN, 27.0 °C): δ 2.26 (6H, s, CH_3), 2.45 (6H, s, CH_3), 2.69 (6H, s, CH_3), 7.08 (2H, dd J=5.5 Hz, aromatic CH), 7.37 (2H, d, J=6.0 Hz, aromatic CH), 7.66 (2H, d, J=5.5 Hz, aromatic CH), 8.21 (2H, s, aromatic CH), 8.35 (2H, s, aromatic CH), 9.09 (2H, d, J=6.0 Hz, aromatic CH). **^{13}C{^{1}H} NMR** (125.686 MHz, CD_3CN, 27.0 °C): δ 3.5 (CH_3), 20.1 (CH_3), 20.4 (CH_3), 124.2 (CH), 124.5 (CH), 125.4 (C), 127.4 (CH), 128.2 (CH), 150.4 (C), 150.7 (C), 151.0 (CH), 152.5 (CH), 156.7 (C), 157.6 (C). **HRMS (ESI)** m/z Calcd. for $C_{28}H_{30}N_6{}^{102}Ru$ (M^{2+}): 276.0782. Found: 276.0787

$[Ru(^tBubipy)_2(CH_3CN)_2](BF_4)_2$:**^{1}H NMR** (498.121 MHz, CD_3CN, 27.0 °C): δ 1.34 (18H, s, CH_3), 1.55 (18H, s, CH_3), 2.29 (6H, s, CH_3), 7.26 (2H, dd J=6.0 Hz, J=2.0 Hz aromatic CH), 7.42 (2H, d, J=6.0 Hz, 2 aromatic CH), 7.83 (2H, dd, J=6.0 Hz, J=2.0 Hz, 2 aromatic CH), 8.34 (2H, d, J=1.5 Hz, 2 aromatic CH), 8.48 (2H, d, J=1.5 Hz, 2 aromatic CH), 9.18 (2H, d, J=8.1 Hz, 2 aromatic CH). **^{13}C{^{1}H} NMR** (125.685 MHz, CD_3CN, 27.0 °C): δ 3.5 (CH_3), 29.4 (CH_3), 29.6 (CH_3), 35.2 (aliphatic C), 35.5 (aliphatic C), 120.8 (CH), 121.1 (CH), 123.6 (CH), 124.5 (CH), 125.3 (C), 151.3 (CH), 152.7 (CH), 156.9 (C), 157.8 (C), 162.7 (C), 163.1 (C). **HRMS (ESI)** m/z Calcd. for $C_{40}H_{54}N_6{}^{102}Ru$ (M^{2+}): 360.1712. Found: 360.1724

Synthesis of Ru(1,10-phenanthroline-5,6-dione)(bipy)Cl_2

Following a similar literature procedure,[4] $Ru(pheno)(DMSO)_2Cl_2$ (590.2 mg, 1.1 mmol, 1 equiv.) and 2,2'-bipyridine (194.1 mg, 1.2 mmol, 1.1 equiv.), were added to 30 ml of DCB under N_2 atmosphere in a dry Schlenk flask. The yellow suspension was refluxed at 150 ºC for 12 hours under N_2 and minimum exposure to light by covering the reaction mixture with aluminum foil.

After cooling the reaction mixture to room temperature, a dark purple solid precipitated. Then, the solvent was removed using a cannula and the solid was thoroughly washed with hexanes (3 x 20 ml) followed by diethyl ether (3 x 20 ml) and dried under high vacuum. The dark purple microcrystalline solid needed no further purification (560.6 mg, 95 % yield), the ^{1}H NMR data confirmed the product. The **^{1}H NMR** data is as follows and consistent with reported values: (ppm, in DMSO-d_6, 599.929 MHz, *J*-values in Hz): 7.12 (t, 1 H, *J* = 6.6), 7.28 (dd, 1 H, *J* = 6.0), 7.49 (d, 1 H, *J* = 6), 7.71 (t, 1 H, *J* = 7.8), 7.81-7.79 (m, 1 H), 7.95 (dd, 1 H, *J* = 5.4), 8.10-8.04 (m, 2 H), 8.42 (d, 1 H, *J* = 7.8), 8.50-8.46 (m, 1 H), 8.65 (d, 1 H, *J* = 7.8), 9.99 (d, 1 H, *J* = 5.4), 10.06 (d, 1 H, *J* = 5.4).

(ppm, in CD_3CN, 399.98 MHz, *J*-values in Hz): 10.09 (d, 1 H, *J* = 5.2), 7.05 (t, 1 H, *J* = 5.6), 7.20 (dd, 1 H, *J* = 6.0, 1.6), 7.70-7.66 (m, 2 H), 7.74 (t, 1 H, *J* = 6.4), 7.89 (dd, 1 H, *J* = 6.0, 2.0), 7.95 (d, 1 H, *J* = 5.6), 8.03-8.08 (m, 2 H), 8.25 (d, 1 H, *J* =8.0), 8.44 (dd, 2 H, *J* = 7.2, 6.4), 10.28 (d, 1 H, *J* = 4.8).

Synthesis Ru(pheno)(bipy)(CH$_3$CN)$_2$](OTf)$_2$

Ru(pheno)(bipy)Cl_2 (165.0 mg, 0.3 mmol, 1 equiv.) and AgOTf (181.1 mg, 0.7 mmol, 2.3 equiv.) were dissolved in 10 ml acetonitrile forming a black purple solution, and refluxed for 16 hours under N_2. After cooling to room temperature, the red brick solution was cannula filtered into a different flask to separate it from the white precipitate, AgCl. The mixture reaction was passed through a celite column into a dry and clean flask three times. The last celite filtration column was washed with DCM to collect all remaining product. Then, the solvents were removed using high vacuum. The red-brown solid was washed with ether (3 × 30 ml) and vacuum dried again. The solid was recrystallized from acetonitrile/diethyl ether (249.0 mg, 98 % yield). The **^{1}H NMR** data

is as follows: (ppm, CD_3CN-d_3, 498.121 MHz, *J*-values in Hz): 2.29 (s, 3 H), 2.31 (s, 3 H), 7.30 (t, 1 H, *J* = 12.9), 7.47 (dd, 1 H, *J* = 6.0, 2.0), 7.76 (d, 1 H, *J* = 5.5), 7.83 (d, 1 H, *J* = 5.0), 7.87 (t, 1 H, *J* = 6.0), 7.98 (t, 1 H, *J* = 7.5), 8.10-8.04 (m, 1 H), 8.31 (t, 1 H, *J* = 7.5), 8.41 (t, 2 H, *J* = 8.5), 8.56 (d, 1 H, *J* = 8.0), 8.71 (d, 1 H, *J* = 8.0), 9.33 (d, 1 H, *J* = 5.5), 9.53 (d, 1 H, *J* = 5.5). **^{13}C{^{1}H} NMR** (ppm, CD_3CN-d_3, 125 MHz): δ = 175.2, 158.0, 157.9, 157.2, 156.9, 153.6, 152.7, 138.7, 138.4, 136.5, 136.2, 128.8, 127.8, 127.6, 126.7, 124.0, 123.7, 117.4, 3.5, 3.4. **HRMS (ESI) m/z** Calcd. for $C_{30}H_{30}N_6O_2{}^{102}Ru$ (M^{2+}): 608.1463. Found: 608.1451.

Synthesis of Ru(bipy)$_2$(5,6-diamino-1,10-phenanthroline)(OTf)$_2$

Inside a glove box, $[Ru(CH_3CN)_2(bipy)_2](OTf)_2$ (following a reported procedure,[5,6] 199.5 mg, 0.2514 mmol) and 1,10-phenanthroline-5,6-diamine (52.8 mg, 0.251 mmol, 1 equivalent) were weighed into a 500 ml Schlenk flask. The flask was sealed with a 24/40 septum, brought out of the box, and attached to an Argon Schlenk line. A minimum volume of anhydrous, bubbled MeOH was added and the solution was transferred through a double-ended needle to a triply evacuated and refilled screw top Schlenk flask. The flask was heated to 75 °C under Argon bubbler line pressure. The flask was sealed, and the temperature set to 70 °C. The reaction was stirred for 3 days, cooled to room temperature, and solvent removed under reduced pressure. The crude product was sonicated in DCM and the black liquid removed via filtration through a double-ended needle to leave a reddish orange solid (129.6 mg, 56.0 %).

^{1}H NMR (399.796 MHz, CD_3OD, 27.0 °C): δ 7.30 (ddd, *J* = 7.6, 5.6, 1.1 Hz, 2H), 7.50 (ddd, *J* = 7.6, 5.6, 1.1 Hz, 2H), 7.56 (d, *J* = 5.6 Hz, 2H), 7.63 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.84 (d, *J* = 5.1 Hz, 2H), 7.91 (d, *J* = 5.6 Hz, 2H), 8.03 (ddd, *J* = 7.9, 7.6, 1.4 Hz, 2H), 8.13 (ddd, *J* = 7.9, 7.6, 1.4 Hz, 2H), 8.66-8.71 (m, 6H). **^{13}C{^{1}H} NMR** (125.688 MHz, CD_3OD, 27.0 °C): δ 125.4, 125.5,

125.6, 128.7, 128.8, 131.0, 138.9, 139.0, 143.2, 148.5, 152.5, 152.8, 158.6, 158.8. **HRMS (ESI) *m/z***: Calcd for $C_{33}H_{26}F_3N_8O_3RuS$ $[M]^+$: 773.0847. Found: 773.0835.

Synthesis of [Ru(pheno)(phen)(bipy)](BF$_4$)$_2$

Synthesis of Ru(pheno)(Phen)Cl$_2$

Ru(Pheno)(DMSO)$_2$Cl$_2$ was prepared according to a reported procedure.[3] Ru(Pheno)(DMSO)$_2$Cl$_2$ (1 equivalent) and phen ligand (1 equivalent) were weighed into a 100 ml side-arm flask. The flask then connected to a Schlenk line, and then evacuated and refilled with N_2 (3 cycles). 1,2-dichlorobenzene (0.016 M based on Ru(pheno)(DMSO)$_2$Cl$_2$) bubbled with N_2 for 30 minutes was added to the flask, and the flask was connected to a condenser. The flask was then placed in an oil bath preheated to 150 °C and stirred overnight. During the reaction, the color of the solution turned to dark brownish-black with precipitate forming. After 18 hours, the flask was cooled to room temperature, and 20 ml of hexane was added and precipitates were allowed to settle down. The dark purple product was collected by filtration through a Buchner funnel and by washing with copious amount of hexane. The yield of the product after being dried under suction was > 85% with some 1,2-dichlorobenzene still present, which was used for the next step without further purifications: **^{1}H NMR** (498.120 MHz, DMSO, 27.0 °C): δ 7.14 (1H, dd, *J*=6.0 Hz, *J*=6.0 Hz, aromatic CH), 7.50 (1H, dd, *J*=5.4 Hz, *J*=5.5 Hz, aromatic CH), 7.69 (1H, d, *J*=5.5 Hz, aromatic CH), 7.86 (1H, d *J*=5.1 Hz, aromatic CH), 7.98–8.00 (2H, m, aromatic CH), 8.14 (1H, d, *J*=8.9 Hz, aromatic CH), 8.19 (1H, dd, *J*=5.3 Hz, *J*=5.3 Hz, aromatic CH), 8.27 (1H, d, *J*=8.8 Hz, aromatic CH), 8.32 (1H, d, *J*=8.0 Hz, aromatic CH), 8.46 (1H, d, *J*=7.1 Hz, aromatic CH), 8.70 (1H, d, *J*=7.8 Hz, aromatic CH), 10.15 (1H, d, *J*=4.8 Hz, aromatic CH), 10.20 (1H, d, *J*=4.7 Hz, aromatic CH). **^{13}C{^{1}H} NMR** (125.686 MHz, DMSO, 27.7 °C): δ 124.4, 124.9, 126.1, 126.2, 127.1, 127.5,

129.5, 129.6, 130.4, 130.6, 130.7, 132.1, 132.8, 134.0, 148.9, 150.2, 153.1, 153.9, 156.0, 157.0, 157.8, 159.4, 174.8, 175.0. **HRMS (ESI)** m/z Calcd. for $C_{24}H_{14}Cl_2N_4O_2{}^{102}Ru$ (M^+): 561.9532. Found: 561.9529

Synthesis of [Ru(pheno)(phen)(MeCN)$_2$](BF$_4$)$_2$

Both Ru(pheno)(phen)Cl_2 (1 equivalent) and $AgBF_4$ (2 equivalents) were weighed into a 100 ml side arm flask inside the glove box. The flask was wrapped in aluminum foil, connected to a Schlenk line, and then evacuated and refilled with N_2 (3 cycles). Freshly distilled MeCN (0.02 M based on Ru-(bis-bipyridine)$_2Cl_2$) was then added using a gas tight syringe and the resulted suspension was stirred at room temperature. After 48 hours, the stirring was stopped and the precipitates were allowed to settle down. After an hour, the dark reddish-brown solution was transferred into another side arm flask by cannula filtration. The greyish-white precipitate was washed with additional MeCN (2 × 10 ml) and filtrate transferred to the same flask. Combined filtrate was concentrated using rotavap resulting in a dark brown product, which was dissolved using minimum MeCN and passed through a Celite plug. Additional MeCN was passed until no further brown color on the Celite plug was observed. The filtrate was then concentrated again using rotavap, and purified by crystallization with MeCN/Et_2O to give 83% of the target compound: **^{1}H NMR** (498.120 MHz, CD_3CN, 27.0 °C): δ 2.19 (3H, s, CH_3), 2.35 (3H, s, CH_3), 7.30–7.33 (1H, m, aromatic CH), 7.62–7.65 (1H, m, aromatic CH), 7.68 (1H, d, *J*=5.3 Hz, aromatic CH), 8.08–8.12 (2H, m, aromatic CH), 8.19–8.23 (2H, m, aromatic CH), 8.31 (1H, d, *J*=8.8 Hz, aromatic CH), 8.35 (1H, d, *J*=7.8 Hz, aromatic CH), 8.55 (1H, d, *J*=8.1 Hz, aromatic CH), 8.76 (1H, d, *J*=7.7 Hz, aromatic CH), 8.88 (1H, d, *J*=8.1 Hz, aromatic CH), 9.63 (1H, d, *J*=5.1 Hz, aromatic CH), 9.67 (1H, d, *J*=5.1 Hz, aromatic CH). **^{13}C{^{1}H} NMR** (125.685 MHz, CD_3CN, 27.0 °C): δ 3.5 (2 CH_3),

125.3, 126.2, 126.4, 126.7, 127.7, 127.8, 127.9, 128.7, 130.1, 130.6, 131.0, 136.1, 136.6, 137.4, 137.7, 147.8, 148.5, 153.5, 154.2, 156.7, 157.4, 158.3, 175.2, 175.4. **HRMS (ESI)** m/z Calcd. for $C_{28}H_{20}N_6O_2{}^{102}Ru$ (M^{2+}): 287.034. Found: 287.034

Synthesis of [Ru(pheno)(phen)(bipy)](BF$_4$)$_2$

[Ru(pheno)(phen)(MeCN)$_2$](BF$_4$)$_2$ (31 mg, 0.0402 mmol) and bipy ligand (6.1 mg, 0.0402 mmol) were weighed into a 15 ml side arm flask. The flask was then connected to a Schlenk line, and then evacuated and refilled with N_2 (3 cycles). To the flask, 3.0 ml of absolute ethanol and 1.0 ml of distilled water (both solvents were bubbled with N_2 before use) were added and then connected to a condenser. The content in the flask was then refluxed overnight under N_2 atmosphere. After 16 hours, heating was stopped and the reaction mixture was cooled down. The content was concentrated under reduced pressure using rotavap giving a reddish brown solid product. Purification attempts by recrystallization were unsuccessful. However, both ^{1}H NMR and HRMS analysis showed that [Ru(pheno)(phen)(MeCN)$_2$](BF$_4$)$_2$ is predominantly (~ 85 %) present in the product.

^{1}H NMR (498.120 MHz, CD_3CN, 26.9 °C): δ 7.25 (1H, t *J*=6.4 Hz m, aromatic CH), 7.43 (1H, dd, *J*=5.7 Hz, *J*=5.7 Hz, aromatic CH), 7.49 (1H, t, *J*=6.6 Hz aromatic CH), 7.57 (1H, d, *J*=5.4 Hz, aromatic CH), 7.61–7.63 (1H, m, aromatic CH), 7.67 (1H, dd, *J*=5.8 Hz, *J*=5.7 Hz, aromatic CH), 7.76–7.79 (2H, m, aromatic CH), 7.98–8.04 (2H, m, aromatic CH), 8.10–8.16 (4H, m, aromatic CH), 8.22 (1H, d, *J*=7.9 Hz, aromatic CH), 8.44–8.45 (2H, m, aromatic CH), 8.52–8.58 (3H, m, aromatic CH), 8.66 (1H, d, *J*=8.1 Hz, aromatic CH), 8.74 (1H, d, *J*=4.5 Hz, aromatic CH). **^{13}C{^{1}H} NMR** (125.685 MHz, CD_3CN, 27.7 °C): δ 121.6, 124.3, 124.4, 125.3, 126.1, 126.2, 127.5, 128.6, 128.7, 130.6, 130.7, 131.2, 135.8, 135.9, 137.3, 137.4, 138.1, 138.3, 139.5, 147.4, 147.5, 148.1, 152.1,

152.5, 152.7, 153.0, 156.3, 156.6, 156.7, 156.8, 157.0, 157.3, 175.3, 175.4. **HRMS (ESI)** m/z Calcd. for $C_{34}H_{22}N_6O_2{}^{102}Ru$ (M^{2+}): 324.0418. Found: 324.0415.

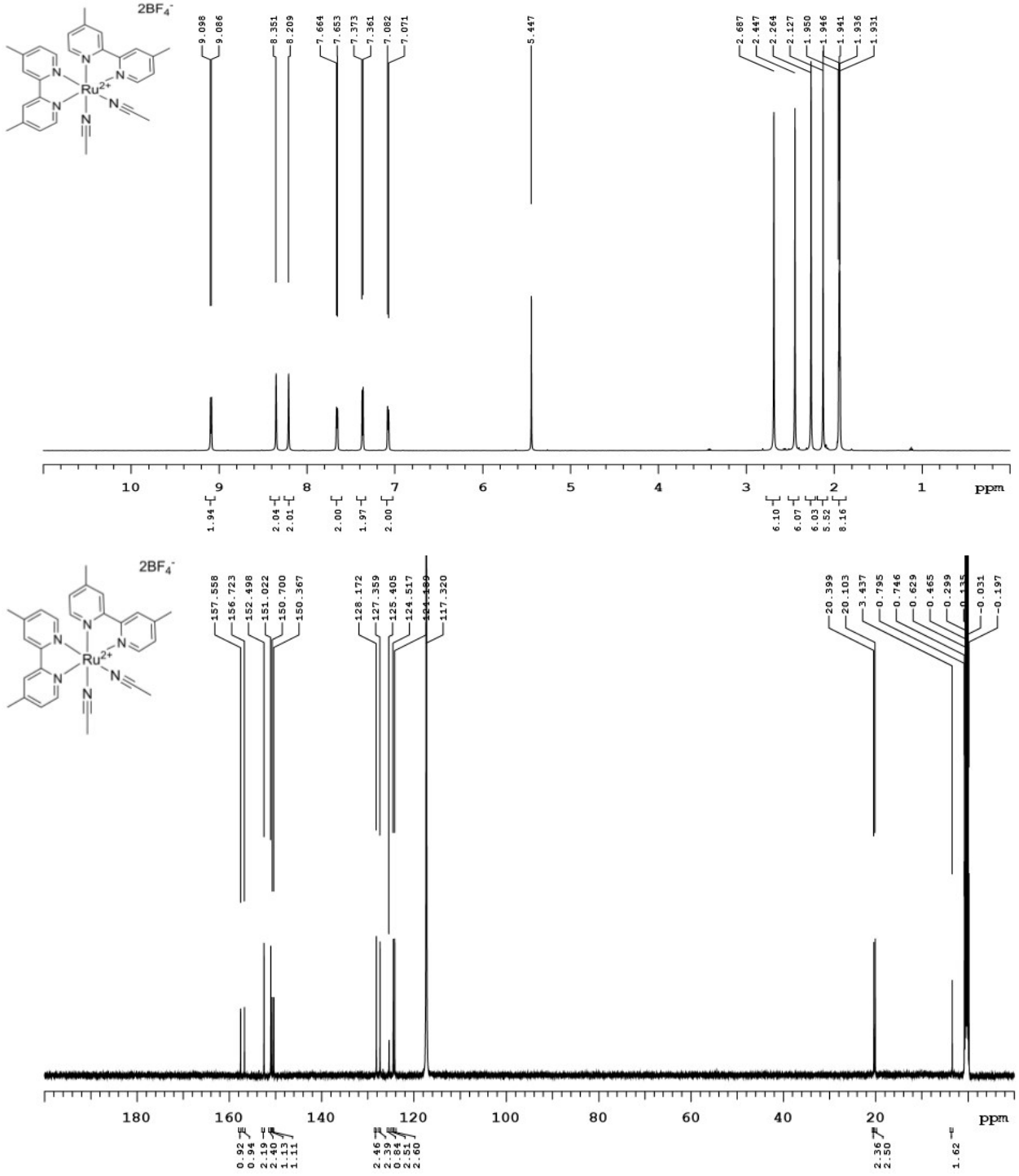

Figure S1. NMR spectra of $[Ru(Mebipy)_2(CH_3CN)_2](BF_4)_2$

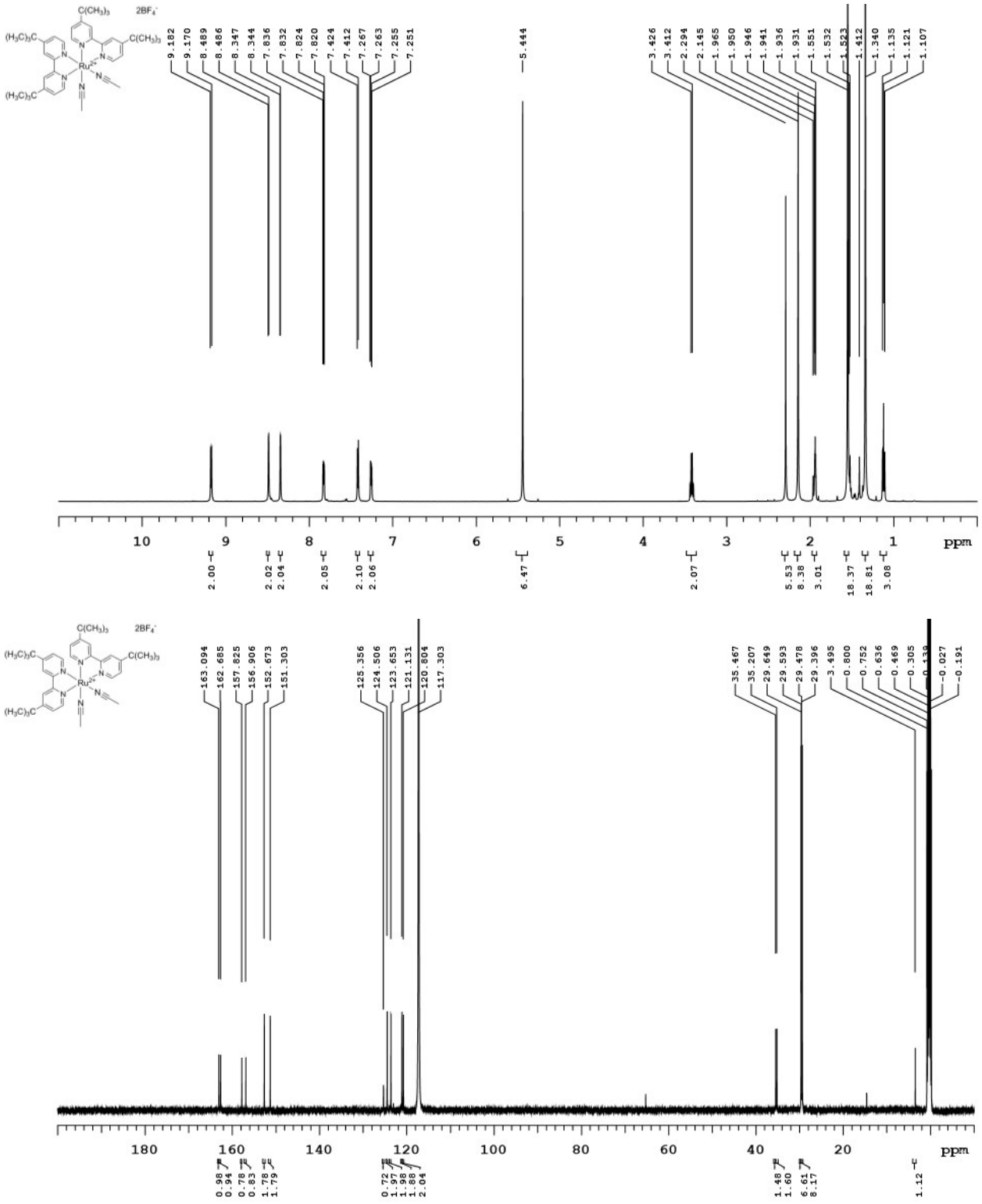

Figure S2. NMR spectra of $[Ru(^{t}Bubipy)_2(CH_3CN)_2](BF_4)_2$

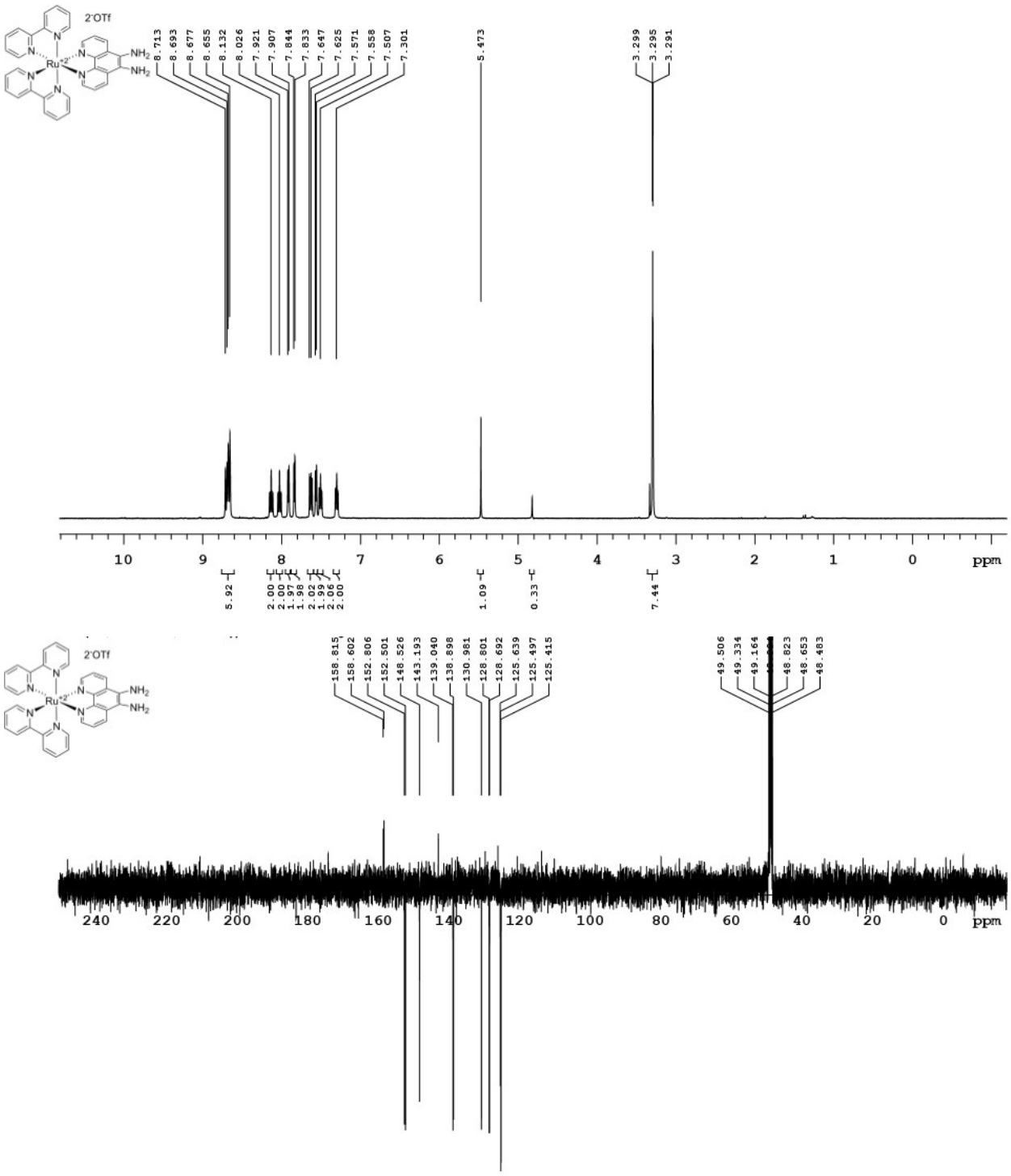

Figure S3. NMR spectra of $[Ru(bipy)_2(phen\text{-}diamine)](OTf)_2$

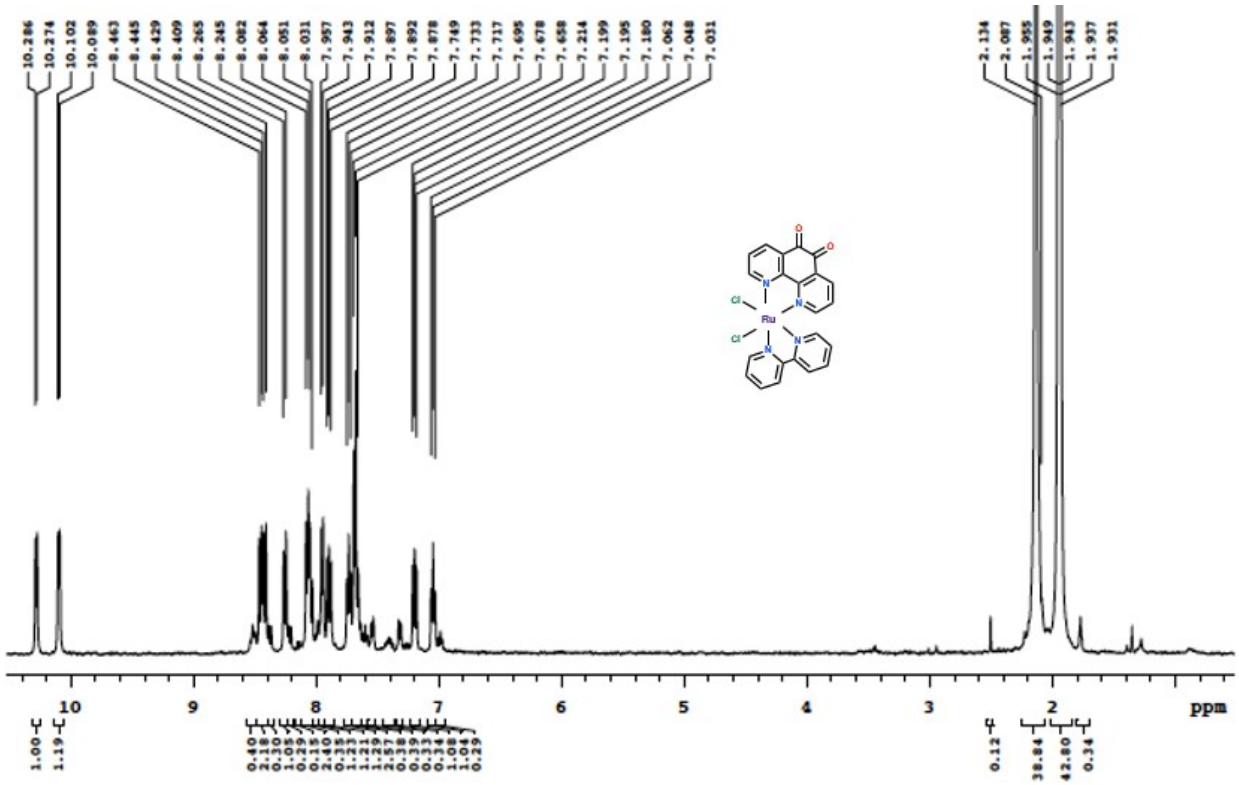

Figure S4. NMR spectra of [Ru(bipy)(pheno)]Cl_2

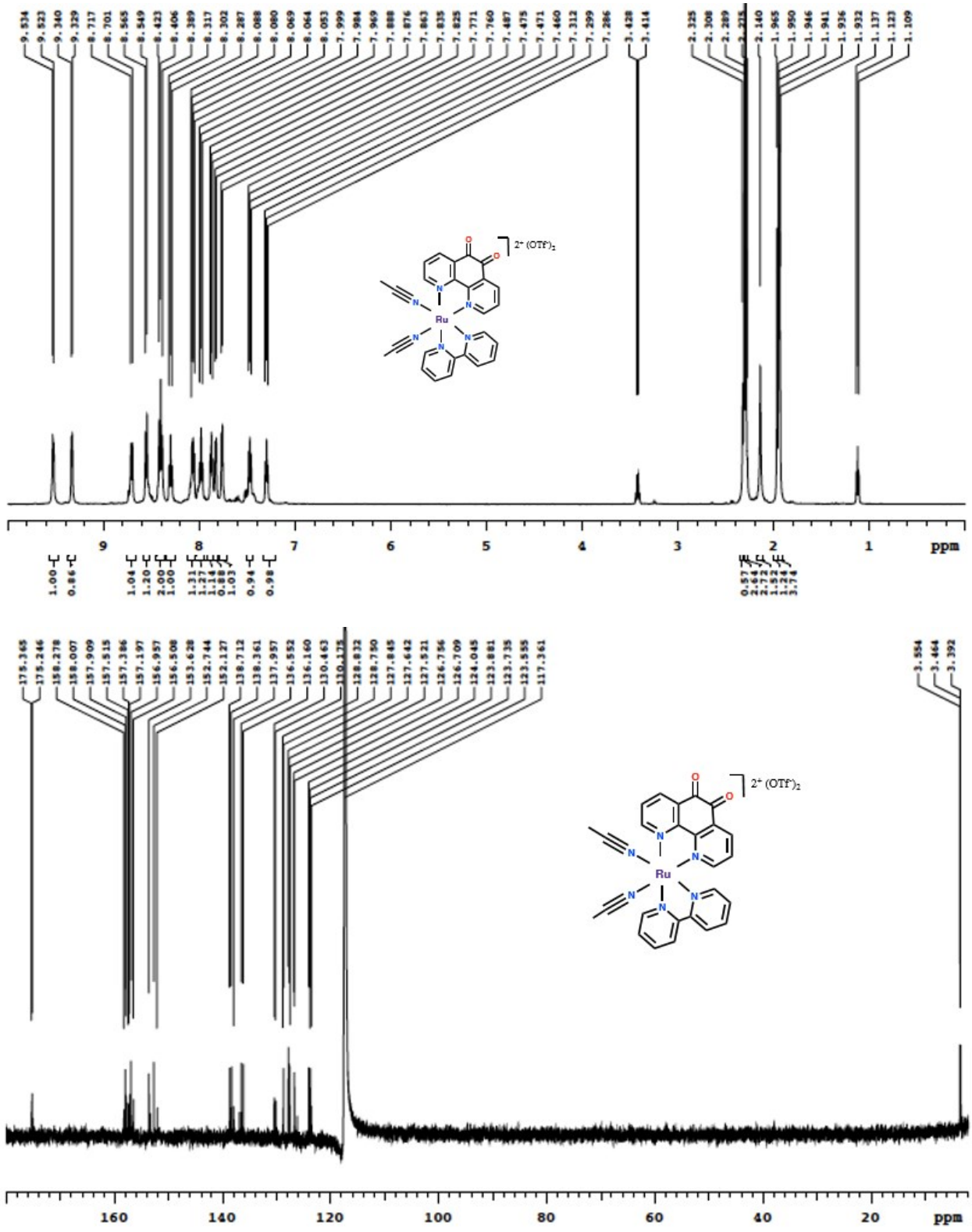

Figure S5. NMR spectra of [Ru(pheno)(bipy) $(CH_3CN)_2$]$(OTf)_2$

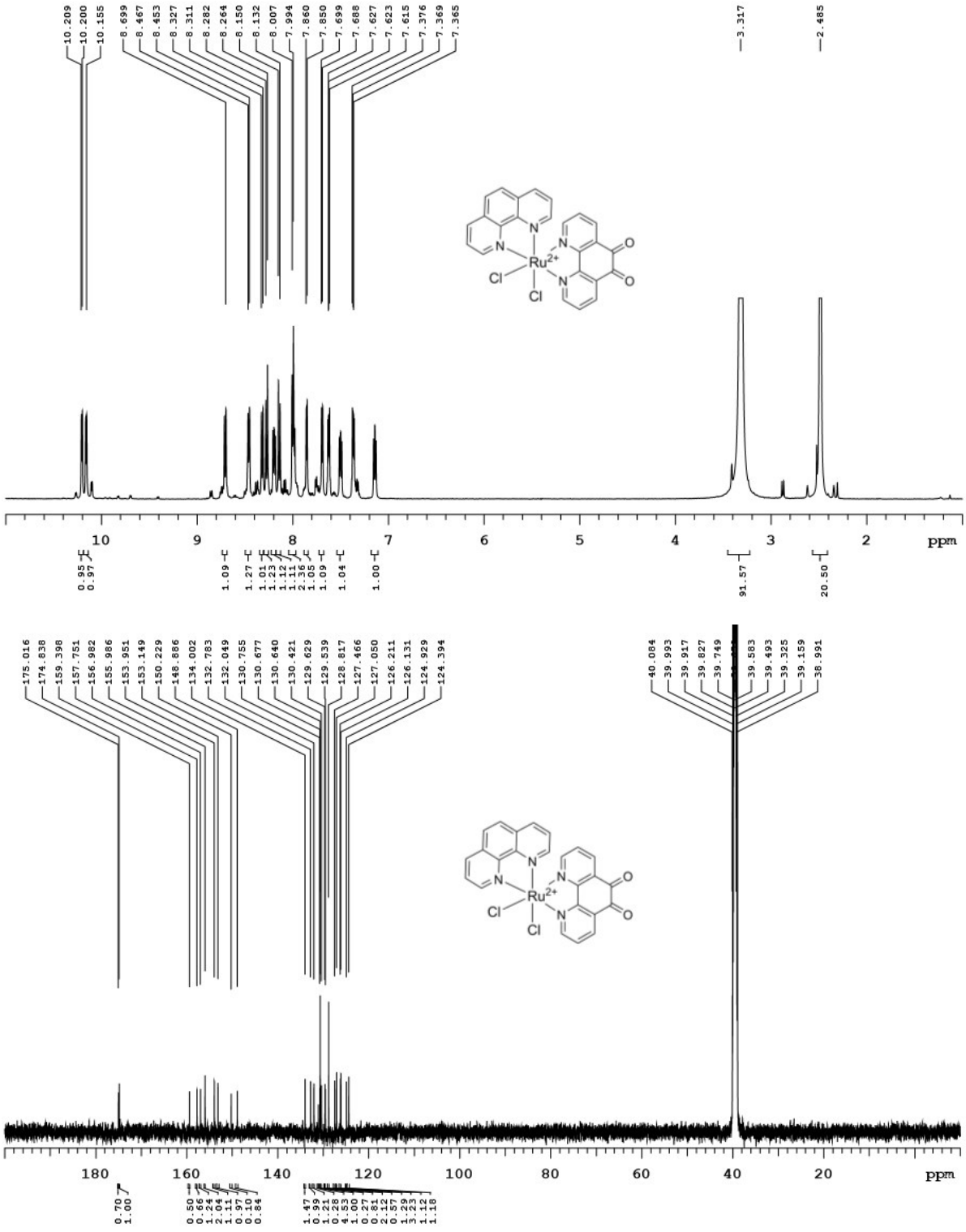

Figure S6. NMR spectra of [Ru(phen)(pheno)]Cl_2

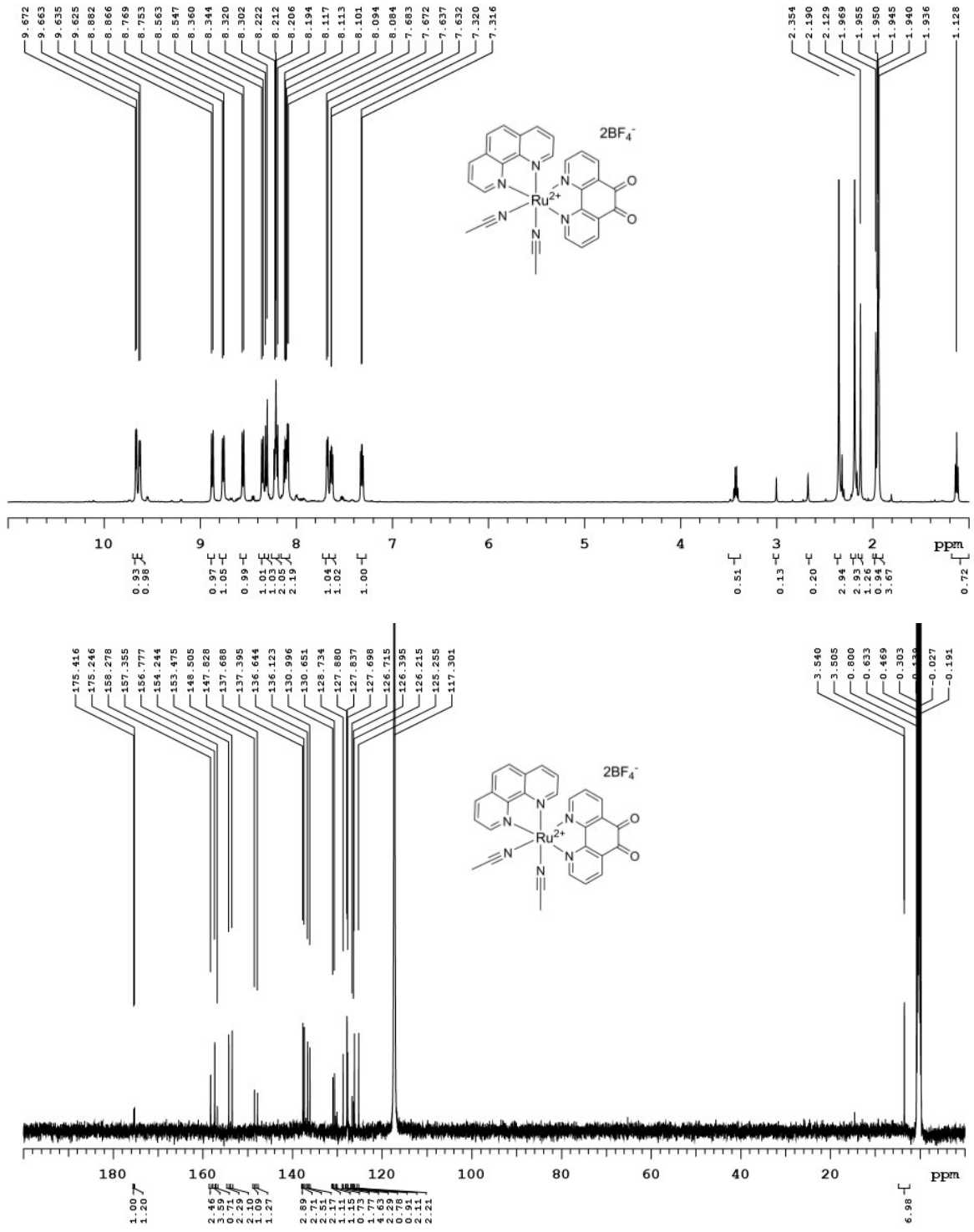

Figure S7. NMR spectra of $[Ru(phen)(pheno)(CH_3CN)_2](BF_4)_2$

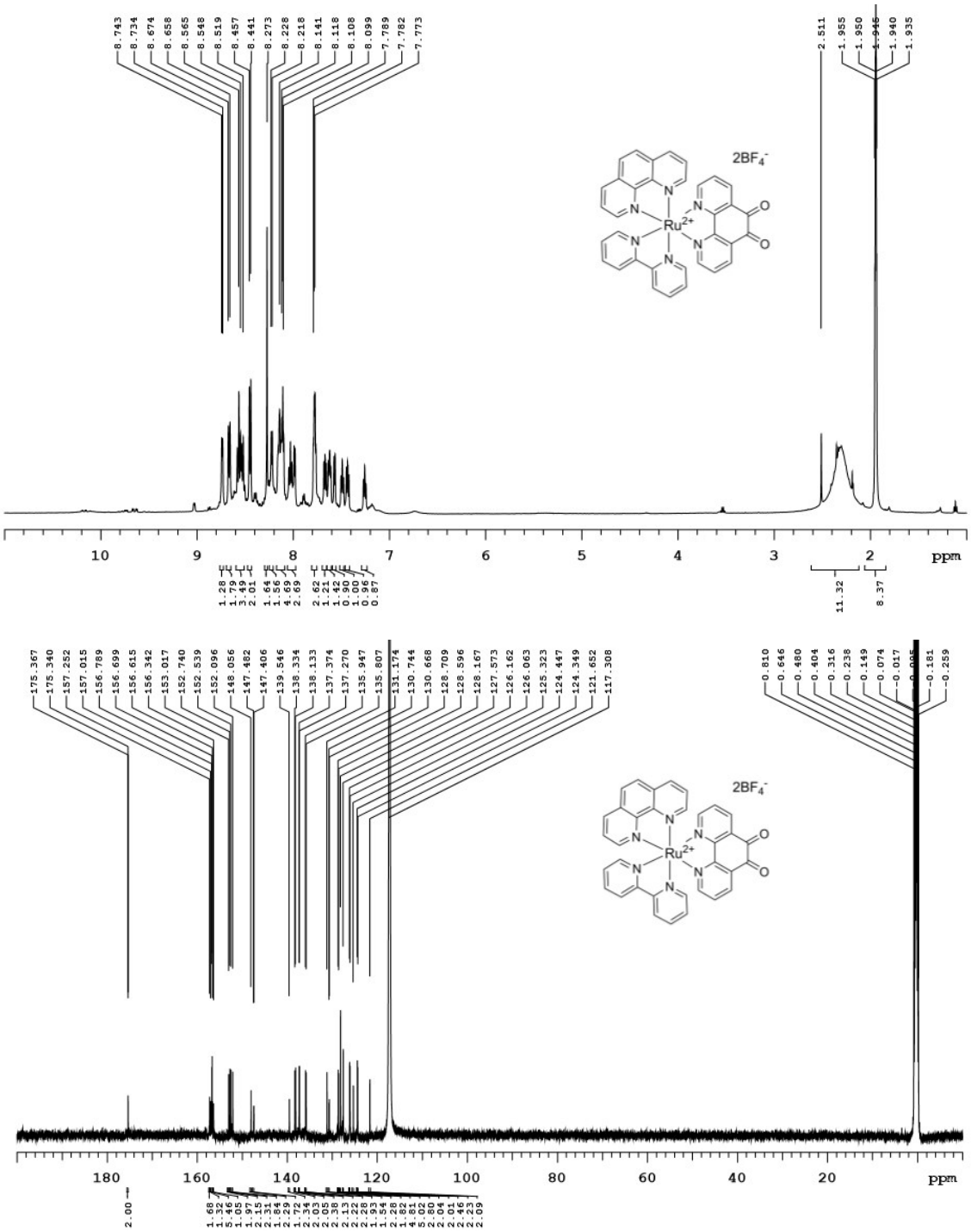

Figure S8. NMR spectra of $[Ru(phen)(pheno)(bipy)](BF_4)_2$

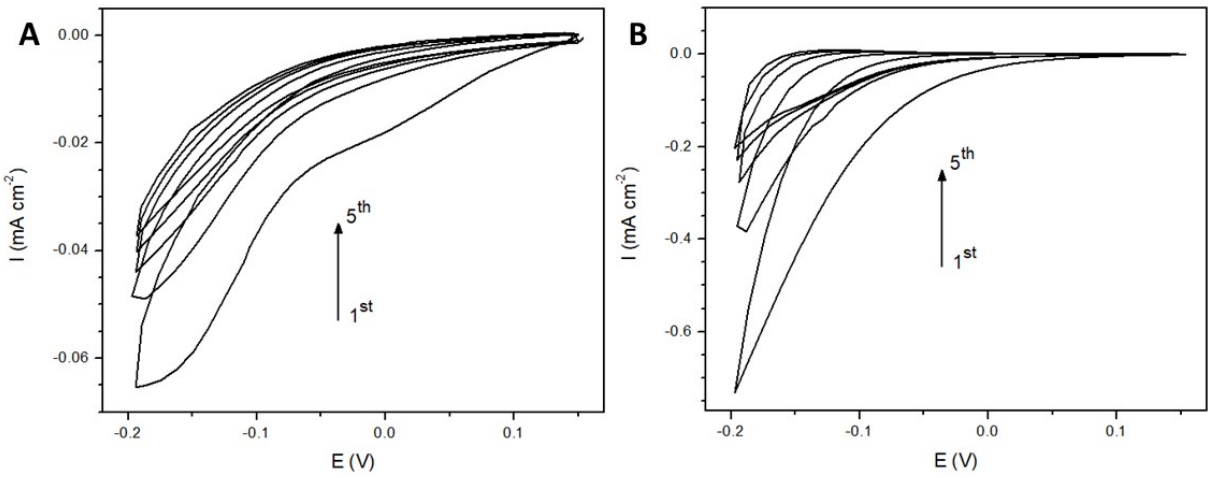

Figure S9. Cyclic voltammogram of the (A) FTO, and (B) TiO_2 electrodes in 0.1 M H_2SO_4 solution containing 5-amino-1,10-phenanthroline (1 mM) and $NaNO_2$ (2 mM), scan rate 50 mV s^{-1};

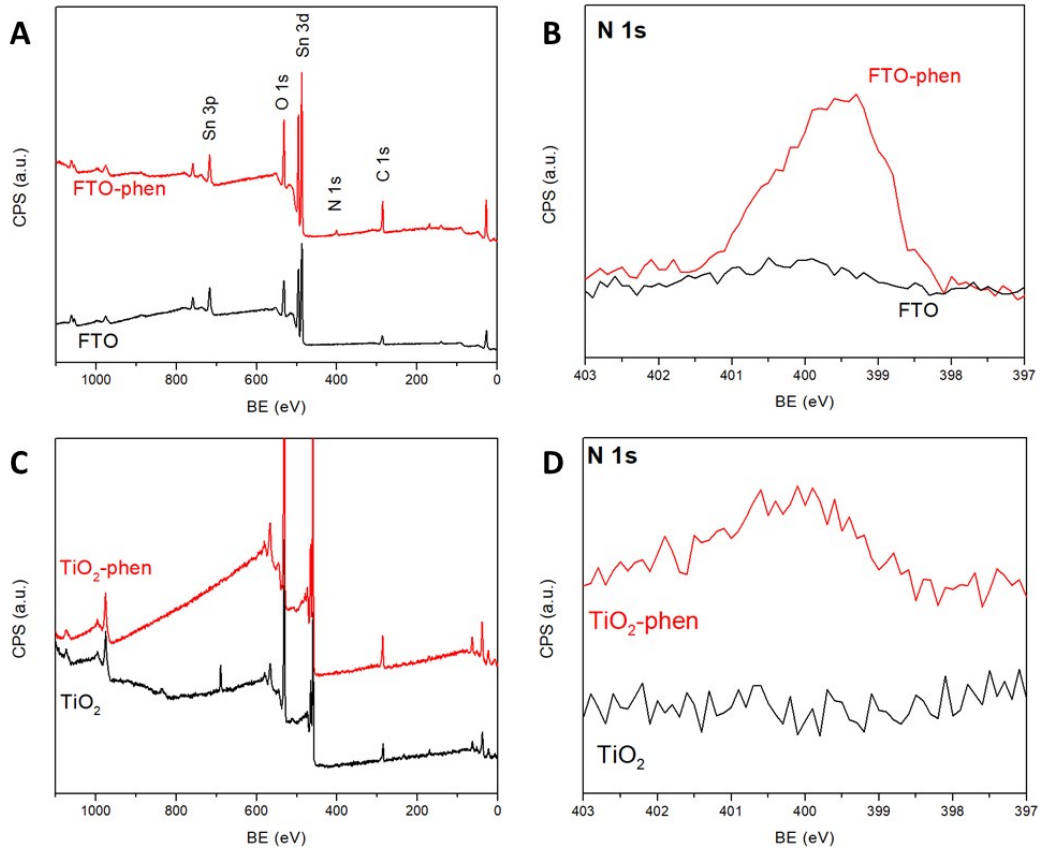

Figure S10. XPS survey scan (A and C), and high-resolution N 1s region spectra (B and D) of bare and phen-modified FTO and TiO_2, respectively.

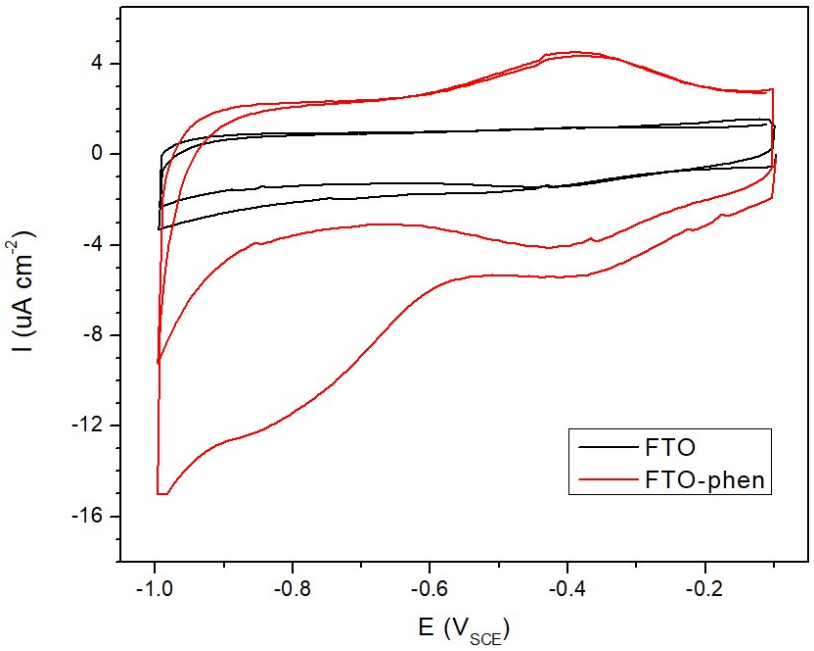

Figure S11. Cyclic voltammograms of the bare FTO and 1,10-phenanthroline modified FTO electrodes in N_2-saturated 0.1 M Na_2SO_4 solution and scan rate of 50 mV s^{-1}.

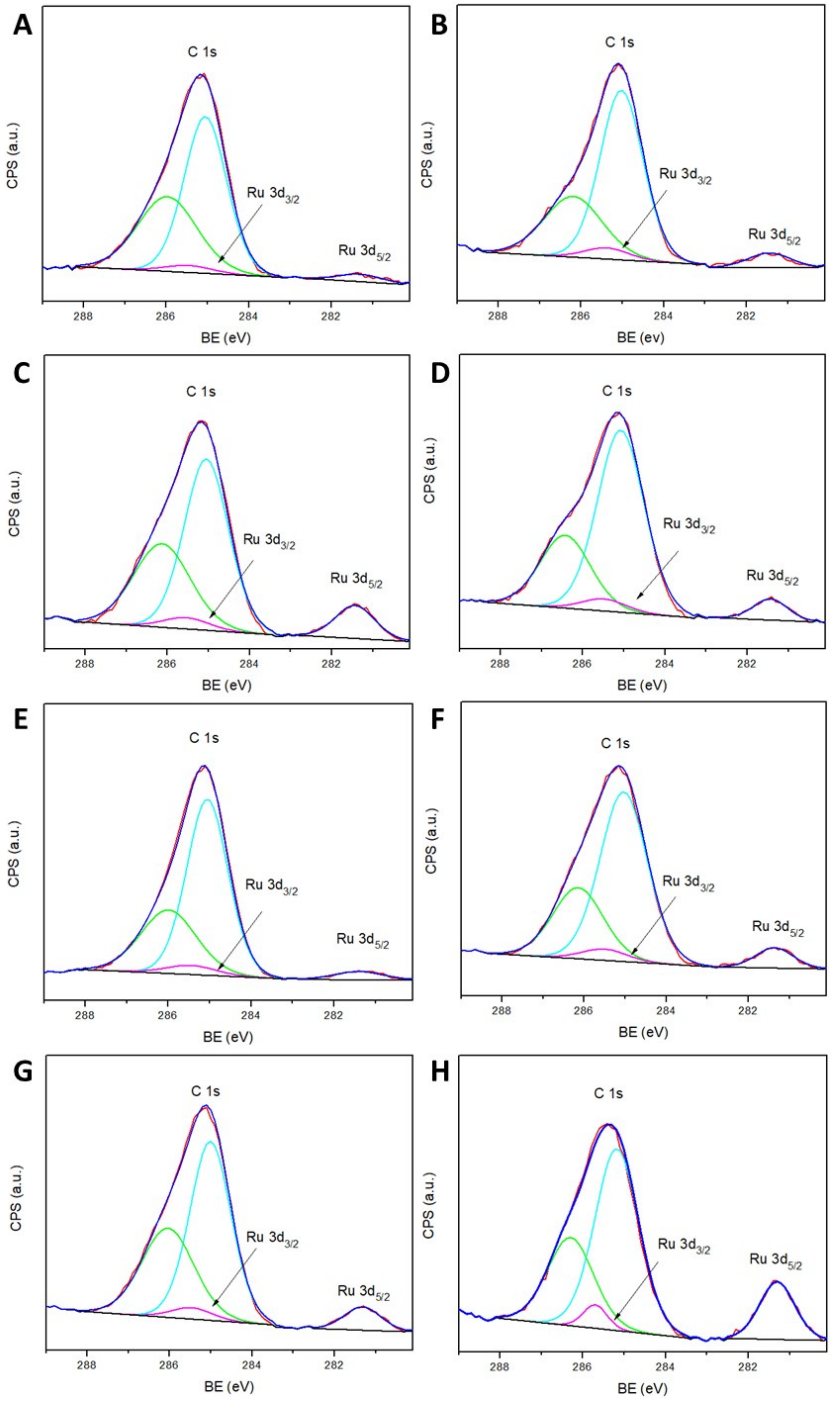

Figure S12. High resolution C 1s and Ru 3d region XPS spectra of (A) FTO-RuMePhen; (B) TiO_2-RuMePhen; (C) FTO-RuOPhen; (D) TiO_2-RuOPhen; (E) FTO-Ru^{t}BuPhen; (F) TiO_2-Ru^{t}BuPhen; (G) FTO-RuRu; and (H) TiO_2-RuRu electrodes. The cyan and green curves could be ascribed to sp^2 carbon, and carbon to nitrogen or oxygen, respectively.

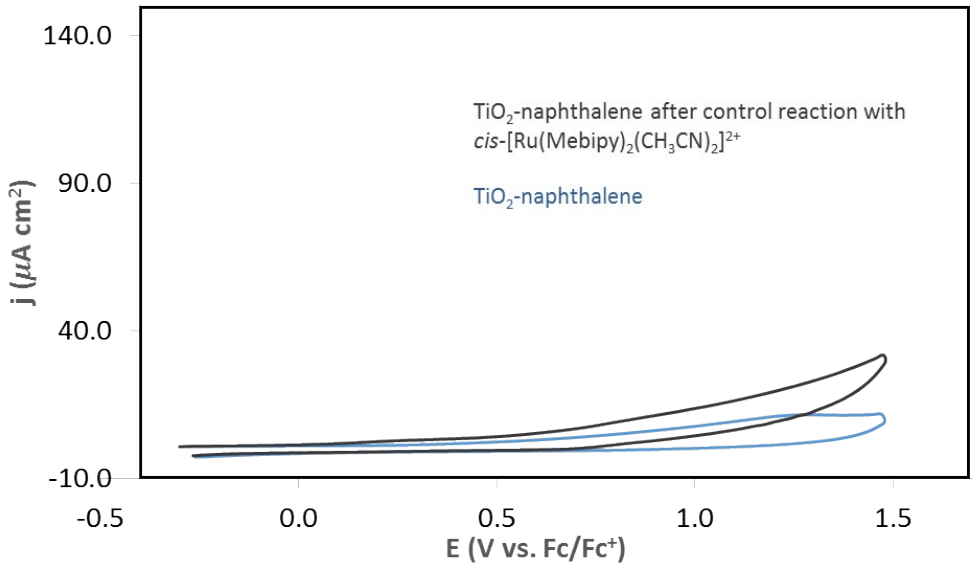

Figure S13. Cyclic voltammograms of TiO_2 modified by 1-naphthalene by diazonium grafting of 1-amino-naphthalene before, and after control reaction with *cis*-$[Ru(Mebipy)_2(CH_3CN)_2]^{2+}$ (in N_2-saturated 0.1 M $TBAPF_6$ in CH_2Cl_2, 100 mV s^{-1}).

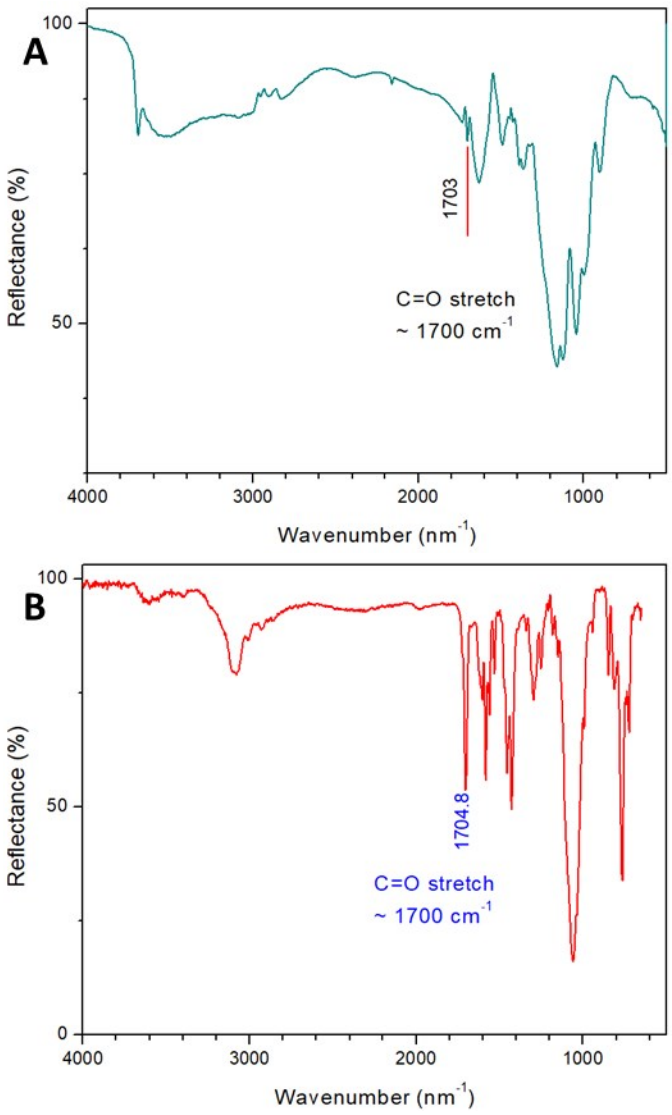

Figure S14. IR spectra of (A) TiO_2-RuOPhen electrode (with TiO_2 reflectance subtracted); and (B) $[(phen)Ru(pheno)(bipy)]^{2+}$ solid.

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