A solution of TPA (0.41 g, 1.4 mmol) and cis-[RuCl₂(Me₂SO)₄] (0.68 g, 1.4 mmol) in 80 mL of methanol was refluxed for 2 h. The reaction mixture was concentrated to dryness, and resulting solid was dissolved in a small amount of methanol. After adding ethyl acetate, the solution was kept in a refrigerator overnight. Yellow precipitates were collected and dried in vacuo. The crude complex was a mixture of an approximately equal amount of the trans and cis isomers, which was isolated by fractional recrystallization from methanol and ethyl acetate. The cis isomer (5) and the trans isomer (1) were obtained as yellow powder and pale orange powder, respectively. The complex 5 was less soluble.

Yield 0.24 g (32%) for 5 and 0.39 g (52%) for 1. Anal. For 5: Found: C, 43.01; H, 4.69; N, 10.03. Calcd for C₂₀H₂₄Cl₂N₄O₁₃RuS·H₂O: C, 42.72; H, 4.80; N, 9.76. For 1: Found: C, 43.01; H, 4.69; N, 10.03. Calcd for C₂₀H₂₄Cl₂N₄O₁₃RuS·H₂O: C, 42.72; H, 4.80; N, 9.76. FAB-MS: (M-Cl)⁺ 505 for 1 and 5.

trans(Cl, N amino)-[RuCl(5-(MeOCO)₃-TPA)(Me₂SO)]Cl (2) The complex 2 was obtained in the procedure similar to the complex 1 using 5-(MeOCO)₃-TPA and cis-[RuCl₂(Me₂SO)₄] except that the resulting product was recrystallized from methanol-ethyl acetate and orange crystals obtained were the trans(Cl, N amino) isomer. Yield 88%. FAB-MS: (M- Cl)⁺ 679, (M- Cl -Me₂SO)⁺ 601. ¹H NMR: δ(CDCl₃, 270MHz) 2.93 (6H, s, Me₂SO), 3.95 (6H, s, Me₂OCO), 3.98 (3H, s, CH₃OCO), 5.38 (2H, s, CH₂(ax)), 5.42 (2H, d, J=15.5Hz, CH₂(eq)), 5.81 (2H, d, J=15.5Hz, CH₂(eq)), 7.64 (1H, d, J=8.2Hz, py-H3(ax)), 7.82 (2H, J=8.2Hz, py-H3(eq)), 8.17 (1H, dd, J=2.0, 8.2Hz, py-H4(ax)), 8.29 (2H, dd, J=2.0, 8.2Hz, py-H4(eq)), 9.33 (2H, d, J=2.0Hz, py-H6(eq)), 10.29 (1H, d, J=2.0Hz, py-H6(ax)). The pyridyl protons having small J values of about 5.5 Hz were easily assigned as H6 and other protons were determined from it. The assignment of the pyridyl groups was confirmed by COSY measurements.

trans(Cl, N amino)-[RuCl(TPA)(Me₂SO)]Cl (1) The structure of trans(Cl,
N\textsubscript{amino})-\text{[RuCl(TPA)(Me\textsubscript{2}SO)]}[\text{RuCl\textsubscript{3}(Me\textsubscript{2}SO\textsubscript{3})\textsubscript{3}}] 3 and cis(Cl, N\textsubscript{amino})-\text{[RuCl(TPA)(Me\textsubscript{2}SO)]Cl} (5) has been confirmed by X-ray structure analysis.\textsuperscript{6a,6e}

**trans(Cl, N\textsubscript{amino})-\text{[RuCl\{5-(MeOCO)\textsubscript{3}-TPA\}(Me\textsubscript{2}SO)]PF\textsubscript{6} (4)** The complex 4 was obtained by adding ammonium hexafluorophosphate to a solution of complex 2 in water. Yield 98%. FAB-MS: (M-PF\textsubscript{6}\textsuperscript{+}) \textsubscript{679}, (M-PF\textsubscript{6} -Me\textsubscript{2}SO\textsuperscript{+}) \textsubscript{601}. \textsuperscript{1}H NMR: \(\delta\) (CD\textsubscript{3}CN, 270MHz) 2.86 (6H, s, Me\textsubscript{2}SO), 3.89 (6H, s, CH\textsubscript{3}OCO), 3.93 (3H, s, CH\textsubscript{3}OCO), 4.59 (2H, s, CH\textsubscript{2}(ax)), 4.87 (2H, d, J=15.5Hz, CH\textsubscript{2}(eq)), 5.39 (2H, d, J=15.5Hz, CH\textsubscript{2}(eq)), 7.24 (1H, d, J=8.2Hz, py-H3(ax)), 7.57 (2H, J=8.2Hz, py-H3(eq)), 8.16 (1H, dd, J=2.0, 8.2Hz, py-H4(ax)), 8.27 (2H, dd, J=2.0, 8.2Hz, py-H4(eq)), 9.20 (2H, d, J=2.0Hz, py-H6(eq)), 10.22 (1H, d, J=2.0Hz, py-H6(ax)).

**Table S-1. Crystallographic Data for trans(Cl, N\textsubscript{amino})-\text{[RuCl\{5-(MeOCO)\textsubscript{3}-TPA\}(Me\textsubscript{2}SO)]PF\textsubscript{6} (4).**
Figure S-1. $^1$H NMR spectra of trans(Cl, N_{amine})-[RuCl(TPA)(DMSO)]Cl (1) in Me$_2$SO-d$_6$. Concentration: ca. 1.0 x $10^{-3}$ mol/l. a) Before irradiation. $\delta$(Me$_2$SO-d$_6$, 270MHz) 2.81 (6H, s, CH$_3$), 4.66 (2H, s, CH$_2$(ax)), 4.83 (2H, d, J=15 Hz, CH$_2$(eq)), 5.26 (2H, d, J=15, CH$_2$(ax)), 7.25 (1H, d, J=7.9, py-H3(ax)), 7.40-7.45 (3H, m, py-H5(ax + eq)), 7.55 (2H, d, J=7.9, py-H3(eq)), 7.77 (1H, t, J=7.9, py-H4(ax)), 7.88 (2H, t, J=7.8, py-H4(eq)), 8.67 (2H, d, J=5.3, py-H6(eq)), 9.62 (1H, d, J=5.6, py-H6(ax)). b) After 600-min irradiation. The peak of DMSO(*) at 2.81 ppm collapsed.
Figure S-2. $^1$H NMR spectra of trans(Cl, N$_{amino}$)-[RuCl(TPA)(DMSO)]Cl (I) in MeCN-d$_3$.
Concentration: ca. 1.0 x $10^{-3}$ mol/l. a) Before irradiation. $^1$H NMR: $\delta$(CD$_3$CN, 270MHz) 2.85 (6H, s, CH$_3$), 4.49 (2H, s, CH$_2$(ax)), 4.67 (2H, d, J=15 Hz, CH$_2$(eq)), 5.41 (2H, d, J=15, CH$_2$(ax)), 7.12 (1H, d, J=7.9, py-H3(ax)), 7.27-7.32 (3H, m, py-H5(ax + eq)), 7.43 (2H, d, J=7.9, py-H3(eq)), 7.63 (1H, t, J=7.9, py-H4(ax)), 7.77 (2H, t, J=7.8, py-H4(eq)), 8.76 (2H, d, J=5.3, py-H6(eq)), 9.70 (1H, d, J=5.6, py-H6(ax)). b) After 150-min irradiation. The peak of DMSO(*) at 2.85 ppm collapsed, and a free DMSO(O) appeared at 2.55 ppm.
Figure S-3. $^1$H NMR spectra of trans(Cl, Namino)-[RuCl{5-(MeOCO)$_3$-TPA}(DMSO)]Cl (2) in Me$_2$SO-$d_6$. Concentration: ca. $1.0 \times 10^{-3}$ mol/l. a) Before irradiation. $^1$H NMR: $\delta$(Me$_2$SO-$d_6$, 270MHz) 2.90 (6H, s, (CH$_3$)$_2$SO), 3.92 (6H, s, CH$_3$OCO), 3.95 (3H, s, CH$_3$OCO), 4.88 (2H, s, CH$_2$(ax)), 5.04 (2H, d, J=15.5Hz, CH$_2$(eq)), 5.32 (2H, d, J=15.5Hz, CH$_2$(eq)), 7.43 (1H, d, J=8.2Hz, py-H$_3$(ax)), 7.76 (2H, d, J=8.2Hz, py-H$_3$(eq)), 8.26 (1H, dd, J=2.0, 8.2Hz, py-H$_4$(ax)), 8.40 (2H, dd, J=2.0, 8.2Hz, py-H$_4$(eq)), 9.18 (2H, d, J=2.0Hz, py-H$_6$(eq)), 10.20 (1H, d, J=2.0Hz, py-H$_6$(ax)). b) After 110-min irradiation. The peak of DMSO(*) at 2.90 ppm collapsed.
**Figure S-4.** UV-vis spectral change of trans(Cl, N$_{\text{amine}}$)-[RuCl\{5-(MeOCO)$_3$-TPA\}(Me$_2$SO)]Cl (2), under photoirradiation in MeCN. Isosbestic points at 274 nm and 340 nm. $\lambda_{\text{max}}$ (before irradiation): 334 nm; 379 nm. $\lambda_{\text{max}}$ (after irradiation): 368 nm; 433 nm. 3.95 x 10$^{-5}$ mol/l. 0, 3, 15, 30 sec, 1, 1.5, 2 min.
Figure S-5. ¹H NMR spectra of trans(Cl, Namino)-[RuCl{(5-(MeOCO))₃-TPA}](DMSO)]Cl (2) in MeCN-d₃. a) Before irradiation. ¹H NMR: δ(CD₃CN, 270MHz) 2.86 (6H, s, (CH₃)₂SO), 3.89 (6H, s, CH₃OCO), 3.93 (3H, s, CH₃OCO), 4.59 (2H, s, CH₃(ax)), 4.82 (2H, d, J=15.5Hz, CH₂(eq)), 5.44 (2H, d, J=15.5Hz, CH₂(eq)), 7.24 (1H, d, J=8.2Hz, py-H₃(ax)), 7.57 (2H, d, J=8.2Hz, py-H₃(eq)), 8.16 (1H, dd, J=2.0, 8.2Hz, py-H₄(ax)), 8.27 (2H, dd, J=2.0, 8.2Hz, py-H₄(eq)), 9.20 (2H, d, J=2.0Hz, py-H₆(eq)), 10.22 (1H, d, J=2.0Hz, py-H₆(ax)). b) After 110-min irradiation. The peak of DMSO(*) at 2.86 ppm collapsed, and a free DMSO(O) appeared at 2.47 ppm.
Figure S-6. UV-vis spectral change of trans(Cl, Naminο)-[RuCl{5-(MeOCO)3-(TPA)(Me2S0)]PF6 (4), under photoirradiation in the presence of 4-picoline (10 equiv.) in 1,2-dichloroethane. Isosbestic points at 348 nm. \( \lambda_{\text{max}} \) (before irradiation): 332 nm; 383 nm. \( \lambda_{\text{max}} \) (after irradiation): 381 nm; 483 nm(sh). \( 8.10 \times 10^{-5} \) mol/l. 0, 5, 15, 30sec, 1.5, 3, 5, 8 min.