Supporting Information:

cis(Cl, N_{amino})-[RuCl(TPA)(Me_2SO)]Cl (5) and trans(Cl, N_{amino})-[RuCl(TPA)(Me_2SO)]Cl (1). A solution of TPA (0.41 g, 1.4 mmol) and cis-[$RuCl_2(Me_2SO)_4$] (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 $C_{20}H_{24}Cl_2N_4ORuS\ H_2O$: C, 42.72; H, 4.80; N, 9.76. For **1**: Found: C, 43.01; H, 4.69; N, 10.03. Calcd for $C_{20}H_{24}Cl_2N_4ORuS\ H_2O$: C, 42.72; H, 4.80; N, 9.76. FAB-MS: $(M\text{-}Cl)^+$ 505 for **1** and **5**. ^{1}H NMR: δ(CD_3CN, 270MHz) For **5**: 3.42 (6H, s, C*H*$_3$), 4.69 (2H, s, C*H*$_2$(ax)), 4.79 (2H, d, J=15 Hz, C*H*$_2$(eq)), 5.76 (2H, d, J=15, C*H*$_2$(eq)), 6.95 (1H, d, J=7.9, py-H3(ax)), 7.16-7.25 (3H, m, py-H5(ax + eq)), 7.46-7.51 (3H, m, py-H4(ax) + py-H3(eq)), 7.73 (2H, t, J=7.8, py-H4(eq)), 8.70 (2H, d, J=5.6, py-H6(eq)), 9.81 (1H, d, J=5.6, py-H6(ax)). For **1**: 2.84 (6H, s, C*H*$_3$), 4.53 (2H, s, C*H*$_2$(ax)), 4.72 (2H, d, J=15 Hz, C*H*$_2$(eq)), 5.39 (2H, d, J=15, C*H*$_2$(eq)), 7.13 (1H, d, J=7.9, py-H3(ax)), 7.26-7.36 (3H, m, py-H5(ax + eq)), 7.43 (2H, d, J=7.9, py-H3(eq)), 7.64 (1H, t, J=7.9, py-H4(ax)), 7.76 (2H, t, J=7.8, py-H4(eq)), 8.75 (2H, d, J=5.3, py-H6(eq)), 9.69 (1H, d, J=5.6, 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{5-$(MeOCO)_3$-TPA}(Me_2SO)]Cl (2) The complex **2** was obtained in the procedure similar to the complex **1** using 5-$(MeOCO)_3$-TPA and cis-[$RuCl_2(Me_2SO)_4$] 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: $(M\text{- }Cl)^+$ 679, $(M\text{- Cl -}Me_2SO)^+$ 601. ^{1}H NMR: δ($CDCl_3$, 270MHz) 2.93 (6H, s, Me_2SO), 3.95 (6H, s, CH_3OCO), 3.98 (3H, s, CH_3OCO), 5.38 (2H, s, CH_2(ax)), 5.42 (2H, d, J=15.5Hz, CH_2(eq)), 5.81 (2H, d, J=15.5Hz, CH_2(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 complex **2** is assumed to be trans isomer, since the chemical shift of DMSO methyl groups is similar to that of trans(Cl, N_{amino})-[RuCl(TPA)(Me_2SO)]Cl **(1)**. The structure of trans(Cl,

N_{amino})-[RuCl(TPA)(Me_2SO)][$RuCl_3(Me_2SO)_3$] **3** and cis(Cl, N_{amino})-[RuCl(TPA)(Me_2SO)]Cl (**5)** has been confirmed by X-ray structure analysis.[6a,6e]

trans(Cl, N_{amino})-[RuCl{5-$(MeOCO)_3$-TPA}(Me_2SO)]PF_6 (4) The complex **4** was obtained by adding ammonium hexafluorophosphate to a solution of complex **2** in water. Yield 98%. FAB-MS: $(M-PF_6)^+$ 679, $(M- PF_6 -Me_2SO)^+$ 601. ^{1}H NMR: δ(CD_3CN, 270MHz) 2.86 (6H, s, Me_2SO), 3.89 (6H, s, CH_3OCO), 3.93 (3H, s, CH_3OCO), 4.59 (2H, s, CH_2(ax)), 4.87 (2H, d, J=15.5Hz, CH_2(eq)), 5.39 (2H, d, J=15.5Hz, CH_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_{amino})-[RuCl{5-$(MeOCO)_3$-TPA}(Me_2SO)]PF_6 (**4**).

	4
empirical formula	$C_{26}H_{30.4}ClF_6N_4O_{7.2}PRuS$
fw	827.69
crystal system	triclinic
a, Å	11.5045 (9)
b, Å	14.2950 (11)
c, Å	11.4761 (8)
α, deg	104.455 (3)
β, deg	106.799 (3)
γ, deg	97.201 (2)
V, Å ^{3}	1709.4 (2)
space group	P-1
Z	2
D_{calc} , g cm^{-3}	1.608
Temperature, K	293
μ(Mo Kα), cm^{-1}	7.25
no. of reflections used	7097
no. of variables	506
R	0.033
R_w	0.092
goodness of fit	1.18

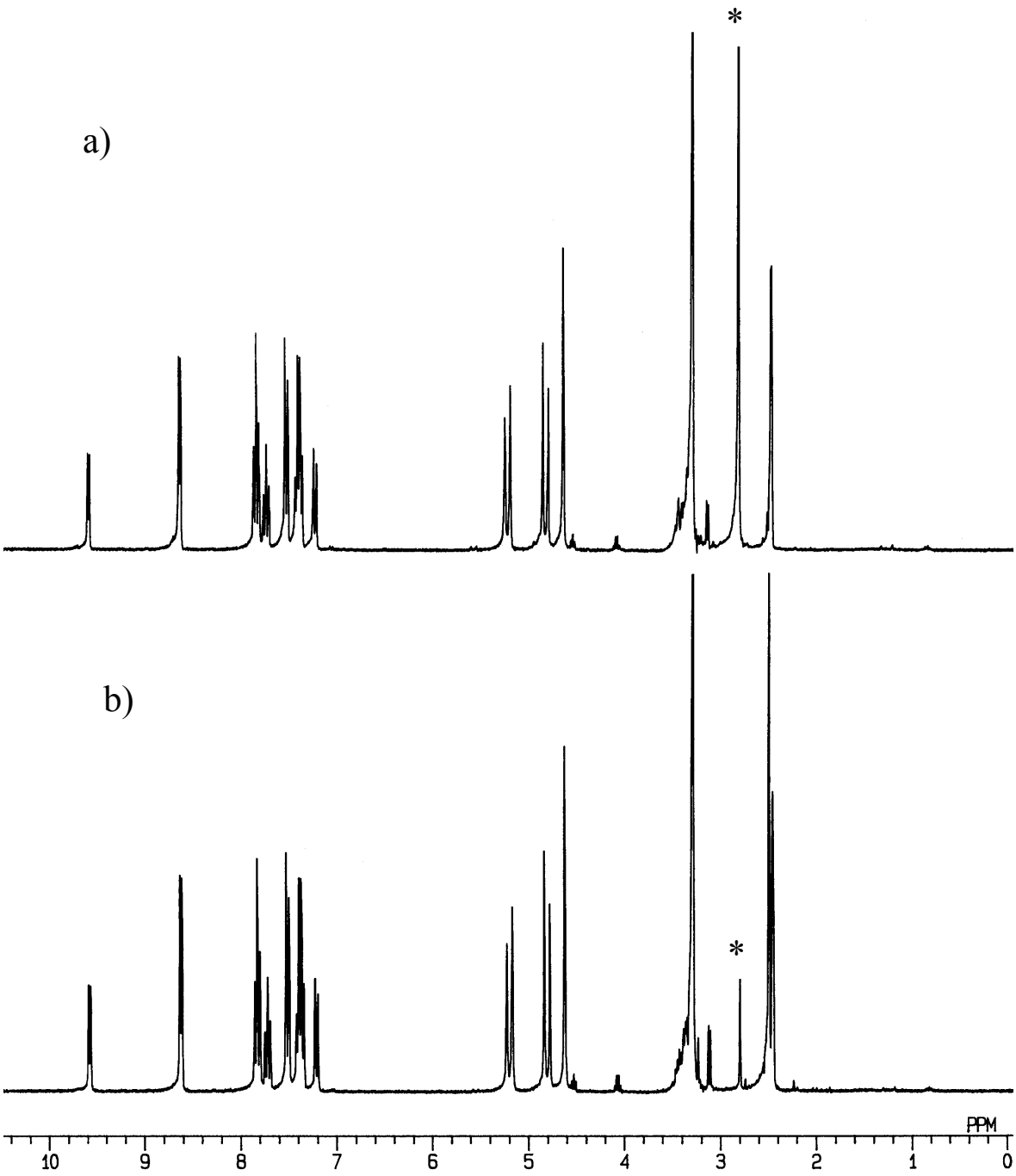

Figure S-1. ^{1}H NMR spectra of trans(Cl, N_{amino})-[RuCl(TPA)(DMSO)]Cl (**1**) in Me_2SO-d_6. Concentration: ca. 1.0 x 10^{-3} mol/l. a) Before irradiation. δ(Me_2SO-d_6, 270MHz) 2.81 (6H, s, CH_3), 4.66 (2H, s, CH_2(ax)), 4.83 (2H, d, J=15 Hz, CH_2(eq)), 5.26 (2H, d, J=15, CH_2(ax)), 7.25 (1H, d, 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.

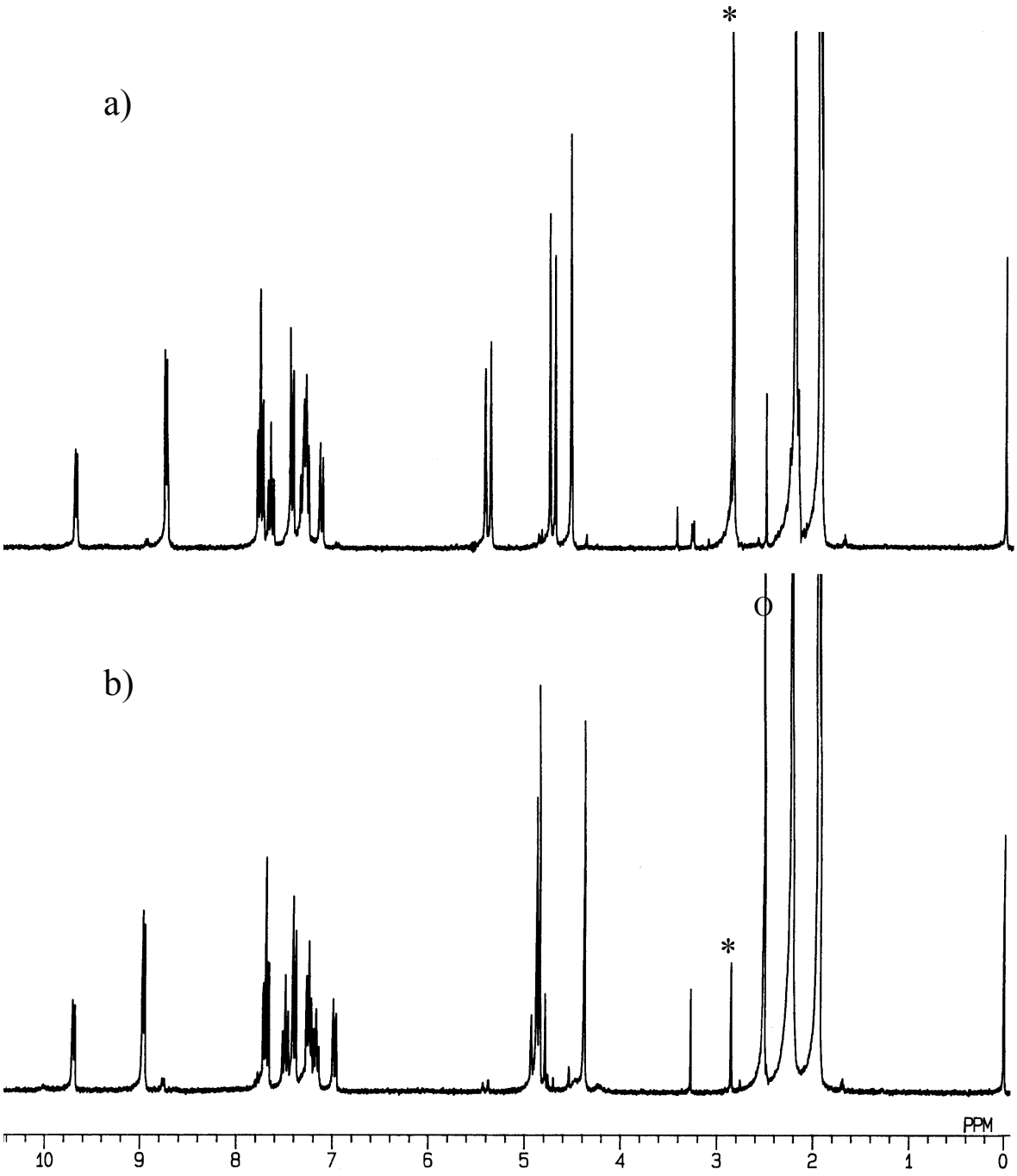

Figure S-2. ^{1}H NMR spectra of trans(Cl, N_{amino})-[RuCl(TPA)(DMSO)]Cl (**1**) in MeCN-d_3. Concentration: ca. 1.0 x 10^{-3} mol/l. a) Before irradiation. ^{1}H NMR: δ(CD_3CN, 270MHz) 2.85 (6H, s, CH_3), 4.49 (2H, s, CH_2(ax)), 4.67 (2H, d, J=15 Hz, CH_2(eq)), 5.41 (2H, d, J=15, CH_2(ax)), 7.12 (1H, 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.

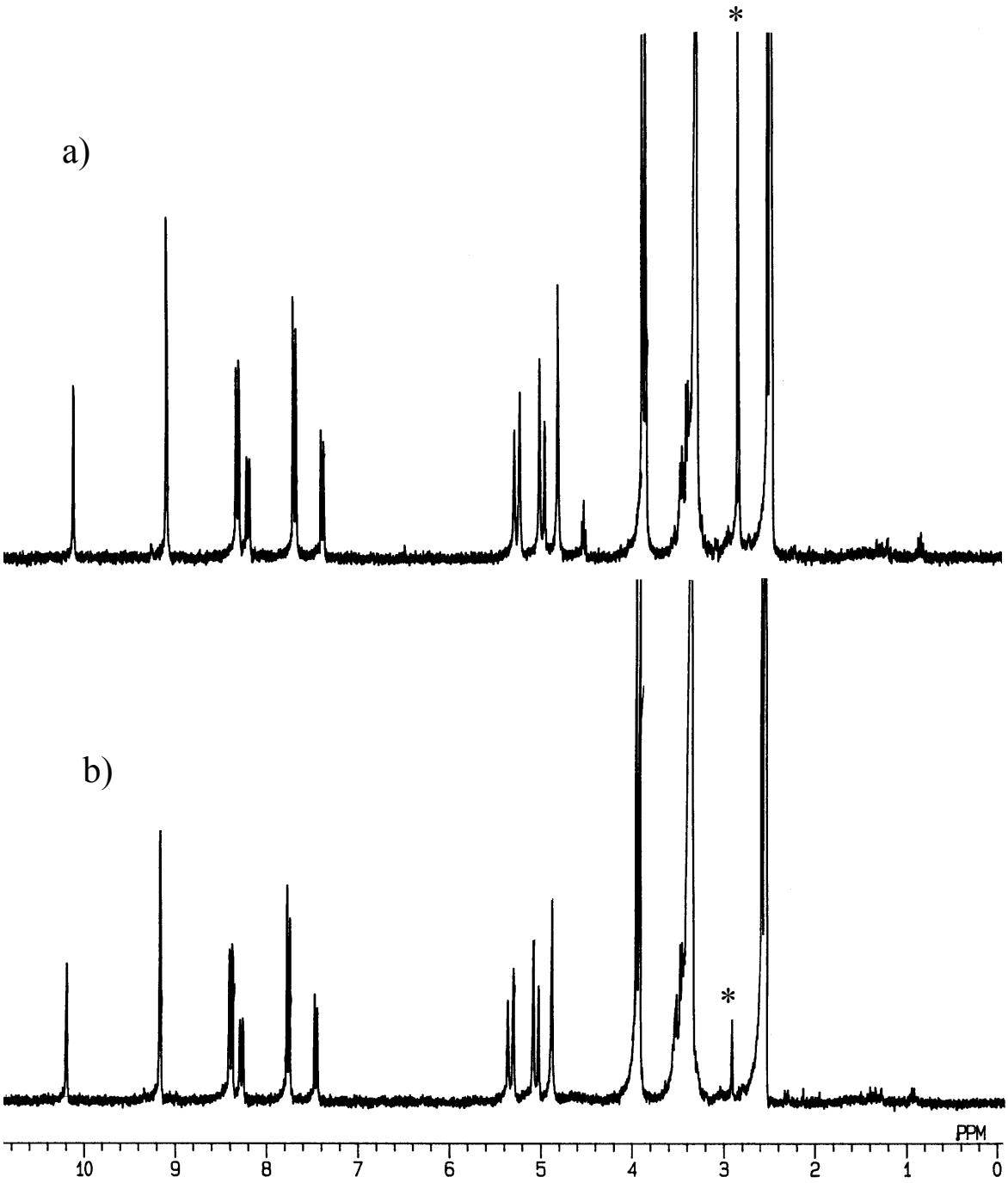

Figure S-3. ^{1}H NMR spectra of trans(Cl, Namino)-[RuCl{5-(MeOCO)$_3$-TPA}(DMSO)]Cl (**2**) in Me_2SO-d_6. Concentration: ca. 1.0 x 10^{-3} mol/l. a) Before irradiation. ^{1}H NMR: δ(Me_2SO-d_6, 270MHz) 2.90 (6H, s, $(CH_3)_2SO$), 3.92 (6H, s, CH_3OCO), 3.95 (3H, s, CH_3OCO), 4.88 (2H, s, CH_2(ax)), 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-H3(ax)), 7.76 (2H, d, J=8.2Hz, py-H3(eq)), 8.26 (1H, dd, J=2.0, 8.2Hz, py-H4(ax)), 8.40 (2H, dd, J=2.0, 8.2Hz, py-H4(eq)), 9.18 (2H, d, J=2.0Hz, py-H6(eq)), 10.20 (1H, d, J=2.0Hz, py-H6(ax)). b) After 110-min irradiation. The peak of DMSO(*) at 2.90 ppm collapsed.

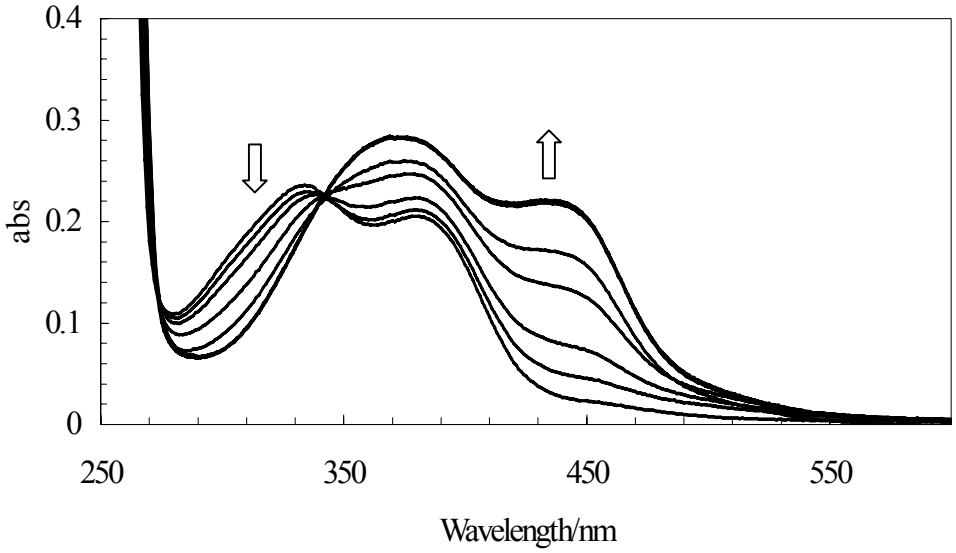

Figure S-4. UV-vis spectral change of trans(Cl, N_{amino})-[RuCl{5-$(MeOCO)_3$-TPA}(Me_2SO)]Cl (**2**), under photoirradiation in MeCN. Isosbestic points at 274 nm and 340 nm. λ_{max} (before irradiation): 334 nm; 379 nm. λ_{max} (after irradiation): 368 nm; 433 nm. 3.95 x 10^{-5} mol/l. 0, 3, 15, 30 sec, 1, 1.5, 2 min.

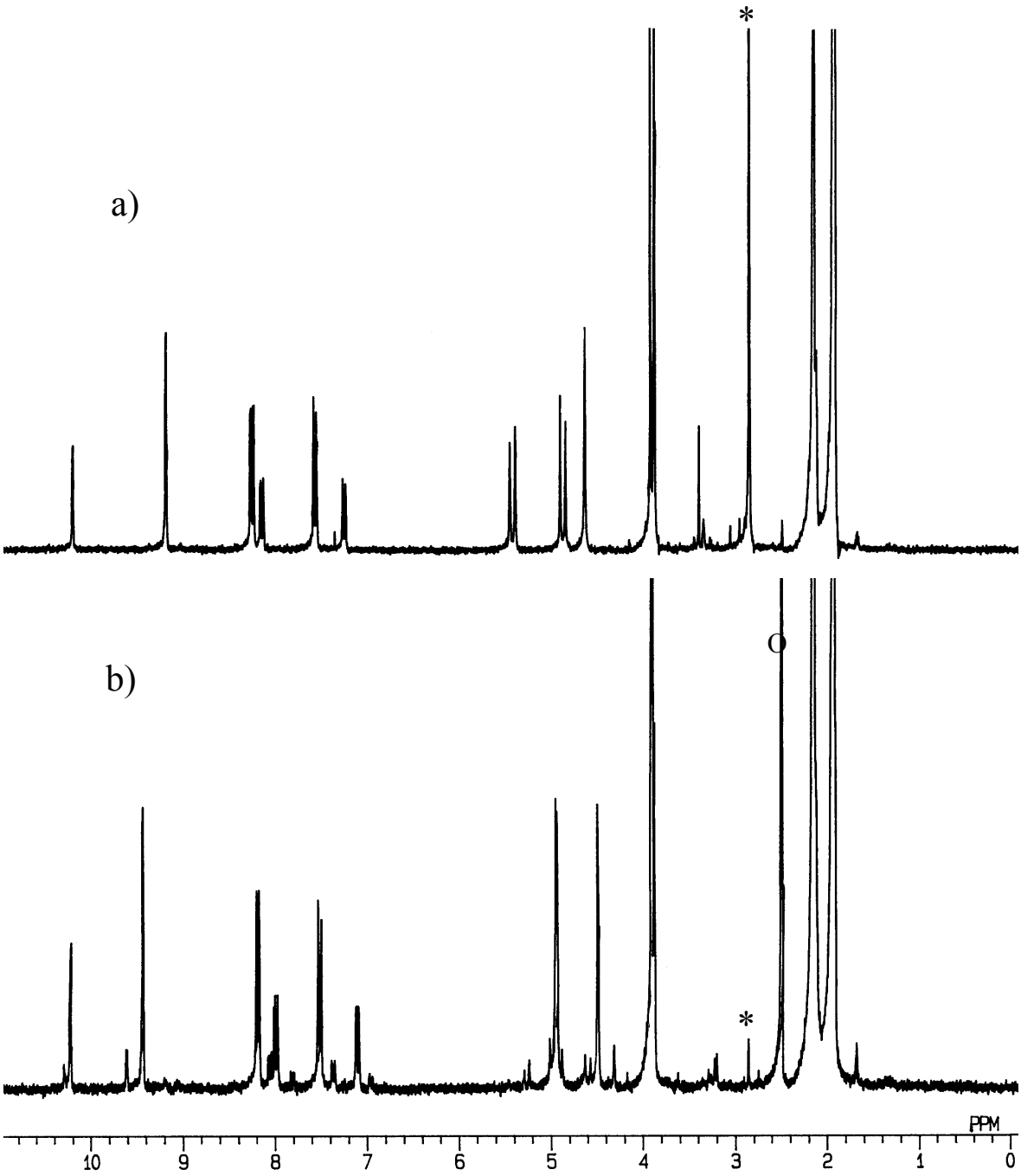

Figure S-5. ^{1}H NMR spectra of trans(Cl, Namino)-[RuCl{5-(MeOCO)$_3$-TPA}(DMSO)]Cl (**2**) in MeCN-d$_3$. a) Before irradiation. ^{1}H NMR: δ(CD$_3$CN, 270MHz) 2.86 (6H, s, (C*H*$_3$)$_2$SO), 3.89 (6H, s, CH$_3$OCO), 3.93 (3H, s, CH$_3$OCO), 4.59 (2H, s, CH$_2$(ax)), 4.82 (2H, d, J=15.5Hz, CH$_2$(eq)), 5.44 (2H, d, J=15.5Hz, CH$_2$(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.

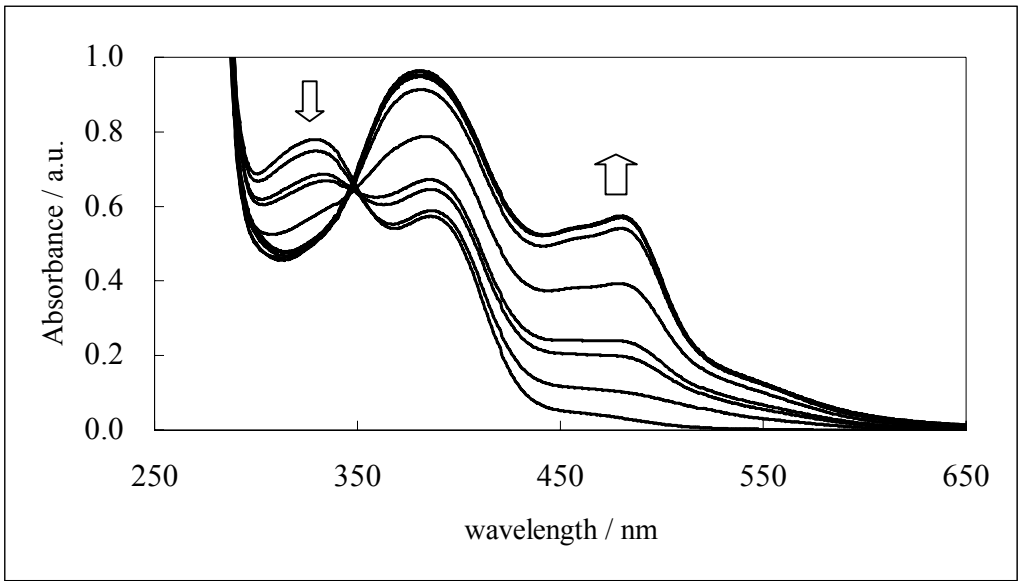

Figure S-6. UV-vis spectral change of trans(Cl, N_{amino})-[RuCl{5-$(MeOCO)_3$-(TPA}(Me_2SO)]PF_6 (**4**), under photoirradiation in the presence of 4-picoline (10 equiv.) in 1,2-dichloroethane. Isosbestic points at 348 nm. λ_{max} (before irradiation): 332 nm; 383 nm. λ_{max} (after irradiation): 381 nm; 483 nm(sh). 8.10 x 10^{-5} mol/l. 0, 5, 15, 30sec, 1.5, 3, 5, 8 min.