Ruthenium tri(2-pyridylmethyl)amine is an effective photocaging group for nitriles.

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Supporting Information

(36 Pages)

Part A. General Considerations

All reagents were purchased from commercial suppliers and used as received. NMR spectra were recorded on a Varian FT-NMR Mercury-400 MHz Spectrometer. Mass spectra were recorded on a Time-of-Flight Micromass LCT Premier XE Spectrometer. IR spectra were recorded on a Nicolet FT-IR spectrophotometer (KBr pellet). UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer. The UV lamp used in all experiments was a long wavelength (UV-365 nm) Black Ray® Lamp. Lamp specifications are 8W, 115 V, 60 Hz and 0.16 amps. All reactions were performed under ambient atmosphere unless otherwise noted. Anaerobic reactions were performed by purging the reaction solutions with Ar or N_2

Part B. Experimental Procedures

Synthesis of [Ru(TPA)(CH_3CN)$_2$](PF_6)$_2$. [Ru(TPA)(DMSO)Cl)]Cl[1,2] (200.0 mg, 0.370 mmol) as a 2:1 mixture of stereoisomers, was dissolved in a 1:1 mixture of H_2O and CH_3CN (20 mL) under argon atmosphere and the resulting solution was refluxed for 2 h under inert atmosphere. Ice cold water (20 mL) was added to the reaction mixture followed by a saturated solution of aqueous NH_4PF_6 (5 mL), resulting in a pale yellow precipitate that was isolated by filtration, washed with ice-cold H_2O and dried under reduced pressure to get the title complex as a yellow solid (136 mg, 48%). Crystals suitable for X-ray crystallographic analysis were obtained by diffusing Et_2O into a solution of **1** in MeCN: mp = 190 °C (decomp); ^{1}H NMR (400MHz C_3D_6O:D_2O - 9:1) δ 9.18 (d, 1H, *J* = 5.9 Hz), 8.83 (d, 2H, *J* = 5.9 Hz), 7.85 (t, 2H, *J* = 7.8 Hz), 7.68-7.56 (m,

3H), 7.41 (t, 2H, J = 6.8 Hz), 7.25 (t, 1H, J = 6.8 Hz), 7.18 (d, 1H, J = 7.8 Hz), 5.25 (d, 2H, J = 15.6 Hz), 5.15 (d, 2H, J = 15.6 Hz), 4.86 (s, 2H), 2.88 (s, 3H), 2.47 (s, 3H); IR (KBr) ν_{max} (cm^{-1}) 3666, 3592, 3418, 3119, 2935, 2856, 2276, 1729, 1609, 1481, 1461, 1448, 1311, 1289, 1160, 992, 838, 767, 739. ESMS calcd for $C_{22}H_{24}F_6N_6PRu$ (M^{+1}) 619.1, found 619.3; UV-vis λ_{max} = 380 (ε = 11200 $M^{-1}cm^{-1}$); Anal. Calcd for $C_{22}H_{24}F_{12}N_6P_2Ru$: C, 34.61; H, 3.17; N, 11.01. Found: C, 34.70; H, 3.20; N, 10.82.

Synthesis of [Ru(TPA)(RCN)$_2$](PF$_6$)$_2$. A solution of $[Ru(TPA)(H_2O)_2](CF_3SO_3)_2$[3] (540 mg, 0.72 mmol) and dry EtOH (40 mL) was deoxygenated by bubbling Ar through a submerged needle for 10 min. Cbz-Leu-$NHCH_2CN$ (1.09 g, 3.6 mmol) was added and the reaction mixture was refluxed for 24 h at 80 °C under Ar atmosphere. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The green oil was extracted with Et_2O (3 × 20 mL) to get a dark green solid, which was dissolved in minimum amount of CH_2Cl_2 and washed with water (3 × 30 mL). The organic layer was dried ($NaSO_4$) and concentrated under reduced pressure to get a dark green solid (501 mg). The dark green solid was dissolved in MeOH (10 mL) and H_2O (10 mL) was added. The insoluble green oil was removed by centrifugation. A saturated solution aqueous solution of NH_4PF_6 (2 mL) was added to the clear pale green supernatant solution, resulting in formation of a precipitate that was isolated by filtration, washed with water (3 × 20 mL) and dried under reduced pressure to get the title compound as a pale yellow solid in analytically pure form (290 mg, 53%): mp = 210 °C (decomp); ^{1}H NMR (400MHz C_3D_6O) δ 9.19 (d, 1H, J = 5.6 Hz), 8.85 (d, 1H, J = 6.1 Hz), 8.84 (d, 1H, J = 6.1 Hz), 8.50 (t, 1H, J = 5.1 Hz), 8.16 (t, 1H, J = 4.7 Hz), 7.92-

7.87 (m, 2H), 7.71-7.62 (m, 3H), 7.43-7.22 (m, 14H), 6.96 (d, 1H, J = 7.3 Hz), 6.79 (d, 1H, J = 7.1 Hz), 5.32 (d, 1H, J = 15.7 Hz), 5.31 (d, 1H, J = 15.7 Hz), 5.20-5.14 (m, 3H), 5.07-4.96 (m, 4H), 4.90-4.88 (m, 2H), 4.81 (d, 1H, J = 12.7 Hz), 4.57-4.45 (m, 2H), 4.36-4.32 (m, 1H), 4.16-4.11 (m, 1H), 1.86-1.65 (m, 3H), 1.61-1.42 (m, 3H), 0.97-0.84 (m, 12H); IR (KBr) ν_{max} (cm^{-1}) 3417, 3319, 2959, 2873, 2265, 1717, 1684, 1608, 1519, 1451, 1406, 1340, 1312, 1254, 1160, 1121, 1044, 844, 769, 740, 699; ESMS calcd for $C_{50}H_{60}F_6N_{10}O_6PRu$ (M^{+1}) 1143.3, found 1143.9; UV-vis λ_{max} = 375 (ε = 12000 $M^{-1}cm^{-1}$); Anal. Calcd for $C_{50}H_{61}F_{12}N_{10}O_{6.5}P_2Ru$ (**2**·0.5 H_2O): C, 46.30; H, 4.74; N, 10.80. Found: C, 46.21; H, 4.79; N, 10.78.

Photochemical Quantum Yields. Photosubstitution quantum yields were determined using ferrioxalate actinometry as previously described in detail.[4] A 150 W Xe lamp housed in a Milliarc compact arc lamp housing (PTI) and powered by a PTI model LPS-220 power supply was used in the steady-state photolysis experiments; the wavelength of the light reaching the sample was controlled with colored glass long-pass (295 nm) and band-pass (350 nm) filters (Newport).

Stability of 1 and 2 in Buffer. Solutions of **1** or **2** in 0.1M pH 6.5 phosphate buffer (1.0% DMSO) were monitored by UV-Vis spectroscopy for 24 h. Ln A_{380} was plotted vs. time and the line was fit to give a first order reaction rate constants.

Table S1. Observed rate constants for decomposition of **1** and **2** in 100% DMSO or pH 6.5 phosphate buffer (1.0% DMSO) at 298±2K.

Compound and Condition	**1** (DMSO)	**1** (PBS)	**2** (DMSO)	**2** (PBS)
Rate constant k (s^{-1})	$8(2)\times10^{-9}$	$6(2)\times10^{-9}$	$7(3)\times10^{-9}$	$1.2(2)\times10^{-8}$
$t_{1/2}$ (days)	1.07×10^{3}	1.33×10^{3}	1.25×10^{3}	7.35×10^{3}

Cathepsin K inhibition studies. Cathepsin enzyme activity was determined from kinetic measurements performed by fluorimetric detection of the hydrolysis product AMC at 37°C every 2 min for 14 min (8 measures). The excitation and emission wavelengths were 360 and 485 nm respectively. Excitation pulses were kept to a minimum to avoid photochemical ligand loss by **2**. The selective fluorescent substrate Z-Gly-Pro-Arg-AMC was used at a final concentration of 100 μM (obtained from Bachem, Torrance, CA). Enzyme activities are expressed as a percentage, with 100% equal to activity in the absence of inhibitor.

Recombinant cathepsin K (human) was obtained from Enzo Life Sciences (Farmingdale, NY). An 880 nM stock solution was prepared in 50 mM sodium acetate, pH 5.5, 50 mM NaCl, 0.5 mM EDTA and 5 mM DTT and kept at –80 °C. For each experiment the stock solution was diluted 110 times and activated for 15 min at 37°C

with a 400 mM sodium acetate, pH 5.5, 4 mM EDTA, 8 mM DTT assay buffer solution. The inhibitor was prepared as a 1% DMSO solution in the buffer solution (400 mM sodium acetate, pH 5.5, 4 mM EDTA, 0.01 % Triton X -100) and plated (Corning® 96 Well Flat Clear Bottom Black Polystyrene TC-Treated Microplates, 50 μL/well). Three experiments in triplicates (**2** or **3,** light or dark) were carried out on 96 well plates, with "dark" and "light" experiments on separate plates. The plate containing "dark" was carefully wrapped in aluminum foil and the other plate was exposed to 365 nm light (8W) for the same time period. The photolysis was conducted for 15 min (with gentle shaking of the plate every 2-3 min) using a long wavelength (UV-365 nm) Black Ray® Lamp (8W) held at distance of 18 cm from the plate. After photolysis, the reaction was initiated by addition of 50 μL of 200 μM Z-Gly-Pro-Arg-AMC solution in the assay buffer (final volume 100 μL, final enzyme concentration 2 nM). Cathepsin enzyme activity was determined from kinetic measurements performed by fluorimetric detection of the hydrolysis product AMC at 37°C every 2 min for 14 min (8 measures) and MAX RFU slope values used for plotting.

Part C. X-ray Crystallographic Analysis.

A specimen of $C_{49.50}H_{57}F_{24}N_{15.50}P_4Ru_2$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 56.65 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 65934 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 12628 were independent (average redundancy 5.221, completeness = 95.9%, R_{int} = 3.66%) and 10076 (79.79%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.1129(8) Å, b = 12.2928(8) Å, c = 21.8490(15) Å, α = 94.436(3)°, β = 97.000(3)°, γ = 91.324(3)°, volume = 3217.7(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9922 reflections above 20 σ(I) with 4.669° < 2θ < 58.65°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.923.

The final anisotropic full-matrix least-squares refinement on F^2 with 863 variables converged at R1 = 5.79%, for the observed data and wR2 = 19.52% for all data. The goodness-of-fit was 1.413. The largest peak in the final difference electron density synthesis was 1.728 $e^-/Å^3$ and the largest hole was -1.368 $e^-/Å^3$ with an RMS deviation of 0.130 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.704 g/cm^3 and F(000), 1653 e^-.

Table S2. Crystal data and structure refinement for $[Ru^{II}(TPA)(CH_3CN)_2](PF_6)_2$.

Identification code	rs01147_rework	
Chemical formula	$C_{49.50}H_{57}F_{24}N_{15.50}P_4Ru_2$	
Formula weight	1651.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.1129(8) Å	α = 94.436(3)°
	b = 12.2928(8) Å	β = 97.000(3)°
	c = 21.8490(15) Å	γ = 91.324(3)°
Volume	3217.7(4) $Å^3$	
Z	2	
Density (calculated)	1.704 g/cm^3	
Absorption coefficient	0.688 mm^{-1}	
F(000)	1653	
Theta range for data collection	0.94 to 26.37°	
Index ranges	-15<=h<=15, -15<=k<=15, -26<=l<=27	
Reflections collected	65934	
Independent reflections	12628 [R(int) = 0.0366]	
Coverage of independent reflections	95.9%	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	12628 / 0 / 863	
Goodness-of-fit on F2	1.413	
Δ/σ_{max}	0.001	
Final R indices	10076 data; I>2σ(I)	R1 = 0.0579, wR2 = 0.1853
	all data	R1 = 0.0771, wR2 = 0.1952
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2+0.5098P$	
	where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.728 and -1.368 $eÅ^{-3}$	
R.M.S. deviation from mean	0.130 $eÅ^{-3}$	

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$)
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x /a	y/b	z/c	U(eq)
Ru1	0.34193(3)	0.02767(3)	0.71876(2)	0.01620(14)
Ru2	0.12463(3)	0.48193(3)	0.22502(2)	0.01489(13)
P1	0.37972(15)	0.73310(15)	0.44715(8)	0.0404(4)
P2	0.28898(12)	0.70587(12)	0.94526(7)	0.0277(4)
P3	0.88862(12)	0.78405(12)	0.06745(7)	0.0257(3)
P4	0.93103(12)	0.79375(12)	0.55563(7)	0.0264(3)
F1	0.4210(4)	0.8474(4)	0.4811(2)	0.0693(14)
F2	0.4994(4)	0.7224(4)	0.4218(3)	0.0834(17)
F3	0.3461(5)	0.6162(4)	0.4136(3)	0.0880(18)
F4	0.3476(6)	0.7906(4)	0.3881(3)	0.115(3)
F5	0.4298(7)	0.6761(5)	0.5073(3)	0.120(3)
F6	0.2729(5)	0.7372(6)	0.4762(4)	0.148(4)
F7	0.3609(3)	0.7878(3)	0.99661(16)	0.0380(9)
F8	0.1842(3)	0.7210(3)	0.98206(18)	0.0399(9)
F9	0.2158(3)	0.6253(3)	0.89461(18)	0.0459(10)
F10	0.3934(3)	0.6912(3)	0.9086(2)	0.0549(11)
F11	0.3242(3)	0.6056(3)	0.98446(19)	0.0448(10)
F12	0.2524(3)	0.8083(3)	0.90713(18)	0.0468(10)
F13	0.8923(4)	0.9144(3)	0.0769(2)	0.0526(11)
F14	0.9894(3)	0.7860(4)	0.02752(19)	0.0589(13)
F15	0.9728(3)	0.7802(3)	0.12922(17)	0.0486(10)
F16	0.7868(3)	0.7824(3)	0.10735(17)	0.0429(9)
F17	0.8828(3)	0.6543(3)	0.05812(19)	0.0463(10)
F18	0.8035(3)	0.7885(3)	0.00615(16)	0.0327(8)
F19	0.0131(3)	0.6939(3)	0.5556(2)	0.0549(11)
F20	0.0171(3)	0.8643(4)	0.52577(17)	0.0530(11)
F21	0.9894(3)	0.8369(3)	0.62285(16)	0.0383(9)
F22	0.8449(3)	0.7215(3)	0.58718(18)	0.0445(9)

F23	0.8496(3)	0.8925(3)	0.55660(19)	0.0499(10)
F24	0.8735(3)	0.7499(3)	0.48833(16)	0.0354(8)
N1	0.3677(3)	0.0445(3)	0.8127(2)	0.0181(9)
N2	0.4968(3)	0.9698(3)	0.7064(2)	0.0175(9)
N3	0.3176(3)	0.9989(4)	0.6242(2)	0.0197(9)
N4	0.1820(3)	0.0846(3)	0.7047(2)	0.0180(9)
N5	0.2782(3)	0.8705(3)	0.7151(2)	0.0172(9)
N6	0.4043(3)	0.1828(4)	0.7180(2)	0.0199(10)
N7	0.0664(3)	0.3229(3)	0.2107(2)	0.0171(9)
N8	0.1535(4)	0.4530(4)	0.1348(2)	0.0215(10)
N9	0.1947(3)	0.6320(3)	0.2138(2)	0.0152(9)
C57	0.2406(4)	0.7078(5)	0.2576(3)	0.0242(12)
N11	0.2788(3)	0.4218(3)	0.2439(2)	0.0171(9)
N12	0.9689(3)	0.5378(3)	0.2050(2)	0.0197(9)
N13	0.0982(3)	0.5129(3)	0.3146(2)	0.0185(9)
N14	0.7548(6)	0.5979(6)	0.3667(4)	0.0591(18)
N15	0.5099(5)	0.4123(6)	0.8779(3)	0.0523(17)
N16	0.3473(5)	0.0853(6)	0.1038(3)	0.0565(18)
C1	0.3849(4)	0.0464(4)	0.8657(3)	0.0184(11)
C2	0.4082(5)	0.0460(5)	0.9327(3)	0.0284(13)
C3	0.5182(4)	0.9722(4)	0.6470(3)	0.0241(12)
C4	0.4302(4)	0.0213(5)	0.6038(3)	0.0260(12)
C5	0.2341(5)	0.0768(5)	0.6002(3)	0.0291(13)
C6	0.1449(4)	0.0898(5)	0.6437(3)	0.0233(12)
C7	0.1134(4)	0.1090(4)	0.7464(2)	0.0202(11)
C8	0.0048(4)	0.1401(5)	0.7293(3)	0.0245(12)
C9	0.9645(5)	0.1411(4)	0.6673(3)	0.0273(13)
C10	0.0393(5)	0.1152(5)	0.6237(3)	0.0298(13)
C11	0.2795(5)	0.8834(5)	0.6044(3)	0.0337(14)
C12	0.2610(4)	0.8206(4)	0.6585(3)	0.0211(12)
C13	0.2592(4)	0.8185(4)	0.7643(3)	0.0242(12)
C14	0.2195(4)	0.7095(5)	0.7570(3)	0.0289(13)
C15	0.2006(4)	0.6559(5)	0.6994(3)	0.0282(13)
C16	0.2232(4)	0.7115(5)	0.6488(3)	0.0280(13)
C17	0.6185(5)	0.9368(5)	0.6295(3)	0.0299(13)
C18	0.6991(5)	0.9016(5)	0.6724(3)	0.0297(14)
C19	0.6775(5)	0.8995(4)	0.7324(3)	0.0250(12)
C20	0.5748(4)	0.9316(4)	0.7483(3)	0.0212(11)

C21	0.4421(4)	0.2689(4)	0.7190(3)	0.0221(12)
C22	0.4892(5)	0.3799(5)	0.7204(3)	0.0290(13)
C23	0.0531(4)	0.2511(4)	0.2533(3)	0.0183(11)
C24	0.0232(4)	0.1414(4)	0.2366(3)	0.0222(12)
C25	0.0051(4)	0.1065(4)	0.1745(3)	0.0246(12)
C26	0.0160(4)	0.1805(4)	0.1305(3)	0.0244(12)
C27	0.0481(4)	0.2893(4)	0.1499(2)	0.0203(11)
C28	0.0636(4)	0.3730(4)	0.1051(3)	0.0235(12)
C29	0.1466(4)	0.5599(4)	0.1070(2)	0.0233(12)
C30	0.2047(4)	0.6462(4)	0.1536(3)	0.0211(11)
C31	0.2941(4)	0.8008(4)	0.2436(3)	0.0220(12)
C32	0.3064(5)	0.8149(5)	0.1823(3)	0.0298(13)
C33	0.2608(5)	0.7364(4)	0.1368(3)	0.0262(13)
C34	0.2675(4)	0.4052(5)	0.1313(3)	0.0254(13)
C35	0.3290(4)	0.3898(4)	0.1937(3)	0.0175(11)
C36	0.3316(4)	0.4090(4)	0.3009(3)	0.0226(12)
C37	0.4346(4)	0.3636(4)	0.3093(3)	0.0289(14)
C38	0.4865(5)	0.3319(4)	0.2583(3)	0.0301(14)
C39	0.4331(4)	0.3445(4)	0.1999(3)	0.0288(14)
C40	0.8781(4)	0.5651(5)	0.2009(3)	0.0251(12)
C41	0.7630(5)	0.5956(5)	0.1984(3)	0.0395(17)
C42	0.0771(4)	0.5367(4)	0.3638(3)	0.0217(12)
C43	0.0503(5)	0.5689(6)	0.4250(3)	0.0357(15)
C44	0.6871(7)	0.5614(7)	0.4713(4)	0.063(2)
C45	0.7249(6)	0.5799(6)	0.4128(4)	0.050(2)
C46	0.4140(5)	0.3682(5)	0.9730(3)	0.0404(16)
C47	0.4678(5)	0.3930(5)	0.9197(4)	0.0400(16)
C48	0.1739(5)	0.9740(5)	0.0515(3)	0.0364(15)
C49	0.2709(5)	0.0371(5)	0.0807(3)	0.0335(14)

Table S4. Bond lengths (Å).

Ru1-N1	2.031(5)	Ru1-N6	2.037(5)
Ru1-N3	2.053(4)	Ru1-N5	2.056(4)
Ru1-N2	2.062(4)	Ru1-N4	2.071(4)

Ru2-N13	2.030(5)	Ru2-N12	2.031(4)
Ru2-N11	2.032(4)	Ru2-N8	2.048(4)
Ru2-N7	2.051(4)	Ru2-N9	2.057(4)
P1-F6	1.510(5)	P1-F4	1.532(6)
P1-F1	1.579(4)	P1-F3	1.583(5)
P1-F5	1.599(6)	P1-F2	1.618(5)
P2-F10	1.583(4)	P2-F8	1.590(4)
P2-F11	1.592(4)	P2-F9	1.594(4)
P2-F12	1.604(4)	P2-F7	1.605(4)
P3-F14	1.585(4)	P3-F17	1.591(4)
P3-F18	1.593(4)	P3-F15	1.594(4)
P3-F16	1.595(4)	P3-F13	1.598(4)
P4-F20	1.574(4)	P4-F23	1.582(4)
P4-F21	1.596(4)	P4-F24	1.596(4)
P4-F19	1.597(4)	P4-F22	1.606(4)
N1-C1	1.151(7)	N2-C20	1.353(7)
N2-C3	1.357(7)	N3-C5	1.487(7)
N3-C11	1.498(7)	N3-C4	1.511(6)
N4-C7	1.327(7)	N4-C6	1.360(7)
N5-C12	1.328(7)	N5-C13	1.333(7)
N6-C21	1.141(7)	N7-C23	1.351(7)
N7-C27	1.352(7)	N8-C29	1.490(7)
N8-C28	1.501(7)	N8-C34	1.521(7)
N9-C57	1.342(7)	N9-C30	1.359(7)
C57-C31	1.375(8)	C57-H57	0.95
N11-C36	1.350(7)	N11-C35	1.355(7)
N12-C40	1.152(7)	N13-C42	1.152(7)
N14-C45	1.146(11)	N15-C47	1.137(9)
N16-C49	1.130(8)	C1-C2	1.456(7)
C2-H1	0.98	C2-H3	0.98
C2-H2	0.98	C3-C17	1.387(7)
C3-C4	1.503(8)	C4-H17	0.99
C4-H16	0.99	C5-C6	1.526(7)
C5-H8	0.99	C5-H9	0.99
C6-C10	1.352(7)	C7-C8	1.393(7)
C7-H7	0.95	C8-C9	1.384(8)
C8-H4	0.95	C9-C10	1.417(8)
C9-H5	0.95	C10-H6	0.95

C11-C12	1.498(8)	C11-H14	0.99
C11-H15	0.99	C12-C16	1.398(8)
C13-C14	1.404(8)	C13-H13	0.95
C14-C15	1.365(8)	C14-H10	0.95
C15-C16	1.396(9)	C15-H11	0.95
C16-H12	0.95	C17-C18	1.371(8)
C17-H21	0.95	C18-C19	1.370(8)
C18-H20	0.95	C19-C20	1.389(7)
C19-H19	0.95	C20-H18	0.95
C21-C22	1.463(8)	C22-H24	0.98
C22-H23	0.98	C22-H22	0.98
C23-C24	1.397(7)	C23-H25	0.95
C24-C25	1.381(8)	C24-H26	0.95
C25-C26	1.389(8)	C25-H42	0.95
C26-C27	1.402(8)	C26-H41	0.95
C27-C28	1.498(7)	C28-H39	0.99
C28-H40	0.99	C29-C30	1.511(8)
C29-H27	0.99	C29-H32	0.99
C30-C33	1.383(8)	C31-C32	1.388(8)
C31-H28	0.95	C32-C33	1.385(8)
C32-H30	0.95	C33-H29	0.95
C34-C35	1.500(8)	C34-H37	0.99
C34-H38	0.99	C35-C39	1.386(7)
C36-C37	1.377(7)	C36-H36	0.95
C37-C38	1.379(9)	C37-H33	0.95
C38-C39	1.380(9)	C38-H35	0.95
C39-H34	0.95	C40-C41	1.448(7)
C41-H43	0.98	C41-H44	0.98
C41-H45	0.98	C42-C43	1.442(8)
C43-H47	0.98	C43-H46	0.98
C43-H48	0.98	C44-C45	1.442(13)
C44-H49	0.98	C44-H51	0.98
C44-H50	0.98	C46-C47	1.450(10)
C46-H52	0.98	C46-H53	0.98
C46-H54	0.98	C48-C49	1.446(9)
C48-H58	0.98	C48-H55	0.98
C48-H56	0.98		

Table S5. Bond angles (°)

N1-Ru1-N6	88.80(17)	N1-Ru1-N3	175.88(16)
N6-Ru1-N3	94.79(17)	N1-Ru1-N5	93.86(17)
N6-Ru1-N5	177.34(17)	N3-Ru1-N5	82.55(17)
N1-Ru1-N2	96.35(16)	N6-Ru1-N2	89.14(16)
N3-Ru1-N2	81.70(17)	N5-Ru1-N2	90.43(16)
N1-Ru1-N4	99.50(16)	N6-Ru1-N4	89.73(16)
N3-Ru1-N4	82.57(17)	N5-Ru1-N4	89.96(15)
N2-Ru1-N4	164.09(18)	N13-Ru2-N12	84.79(17)
N13-Ru2-N11	95.87(17)	N12-Ru2-N11	178.38(17)
N13-Ru2-N8	178.94(17)	N12-Ru2-N8	95.59(17)
N11-Ru2-N8	83.77(18)	N13-Ru2-N7	99.34(17)
N12-Ru2-N7	91.47(16)	N11-Ru2-N7	86.96(16)
N8-Ru2-N7	81.64(17)	N13-Ru2-N9	97.26(17)
N12-Ru2-N9	91.30(16)	N11-Ru2-N9	90.08(15)
N8-Ru2-N9	81.75(17)	N7-Ru2-N9	163.35(17)
F6-P1-F4	101.5(5)	F6-P1-F1	91.4(3)
F4-P1-F1	88.6(3)	F6-P1-F3	91.5(3)
F4-P1-F3	92.8(3)	F1-P1-F3	176.4(3)
F6-P1-F5	85.7(5)	F4-P1-F5	172.5(4)
F1-P1-F5	89.0(3)	F3-P1-F5	89.2(3)
F6-P1-F2	174.3(5)	F4-P1-F2	84.2(4)
F1-P1-F2	88.8(3)	F3-P1-F2	88.1(3)
F5-P1-F2	88.6(4)	F10-P2-F8	179.8(2)
F10-P2-F11	90.9(2)	F8-P2-F11	89.2(2)
F10-P2-F9	90.5(2)	F8-P2-F9	89.5(2)
F11-P2-F9	90.2(2)	F10-P2-F12	90.2(2)
F8-P2-F12	89.7(2)	F11-P2-F12	178.7(2)
F9-P2-F12	90.5(2)	F10-P2-F7	90.3(2)
F8-P2-F7	89.6(2)	F11-P2-F7	90.1(2)
F9-P2-F7	179.1(2)	F12-P2-F7	89.2(2)
F14-P3-F17	89.7(2)	F14-P3-F18	89.9(2)
F17-P3-F18	89.6(2)	F14-P3-F15	90.7(2)
F17-P3-F15	90.7(2)	F18-P3-F15	179.4(2)
F14-P3-F16	179.7(3)	F17-P3-F16	90.5(2)
F18-P3-F16	89.9(2)	F15-P3-F16	89.6(2)
F14-P3-F13	91.1(3)	F17-P3-F13	179.1(2)

F18-P3-F13	90.0(2)	F15-P3-F13	89.7(2)
F16-P3-F13	88.7(2)	F20-P4-F23	90.5(2)
F20-P4-F21	89.8(2)	F23-P4-F21	89.8(2)
F20-P4-F24	90.1(2)	F23-P4-F24	90.6(2)
F21-P4-F24	179.5(2)	F20-P4-F19	90.0(3)
F23-P4-F19	179.2(2)	F21-P4-F19	89.6(2)
F24-P4-F19	90.0(2)	F20-P4-F22	178.9(2)
F23-P4-F22	90.1(2)	F21-P4-F22	89.3(2)
F24-P4-F22	90.8(2)	F19-P4-F22	89.5(2)
C1-N1-Ru1	175.1(4)	C20-N2-C3	118.8(4)
C20-N2-Ru1	129.1(4)	C3-N2-Ru1	112.1(3)
C5-N3-C11	111.0(4)	C5-N3-C4	111.8(4)
C11-N3-C4	109.9(4)	C5-N3-Ru1	107.2(3)
C11-N3-Ru1	111.9(3)	C4-N3-Ru1	104.8(3)
C7-N4-C6	119.0(4)	C7-N4-Ru1	128.4(4)
C6-N4-Ru1	112.4(3)	C12-N5-C13	121.1(5)
C12-N5-Ru1	114.2(3)	C13-N5-Ru1	124.7(4)
C21-N6-Ru1	177.7(4)	C23-N7-C27	119.6(4)
C23-N7-Ru2	128.4(4)	C27-N7-Ru2	111.8(3)
C29-N8-C28	112.1(4)	C29-N8-C34	110.7(4)
C28-N8-C34	110.3(4)	C29-N8-Ru2	106.8(3)
C28-N8-Ru2	106.0(3)	C34-N8-Ru2	110.7(3)
C57-N9-C30	118.7(5)	C57-N9-Ru2	128.4(4)
C30-N9-Ru2	112.5(3)	N9-C57-C31	122.3(5)
N9-C57-H57	118.8	C31-C57-H57	118.8
C36-N11-C35	119.1(4)	C36-N11-Ru2	125.8(4)
C35-N11-Ru2	115.1(3)	C40-N12-Ru2	171.3(4)
C42-N13-Ru2	174.4(4)	N1-C1-C2	178.4(6)
C1-C2-H1	109.5	C1-C2-H3	109.5
H1-C2-H3	109.5	C1-C2-H2	109.5
H1-C2-H2	109.5	H3-C2-H2	109.5
N2-C3-C17	120.7(5)	N2-C3-C4	115.7(5)
C17-C3-C4	123.4(5)	C3-C4-N3	109.0(4)
C3-C4-H17	109.9	N3-C4-H17	109.9
C3-C4-H16	109.9	N3-C4-H16	109.9
H17-C4-H16	108.3	N3-C5-C6	109.6(4)
N3-C5-H8	109.8	C6-C5-H8	109.8
N3-C5-H9	109.8	C6-C5-H9	109.8

H8-C5-H9	108.2	C10-C6-N4	122.4(5)
C10-C6-C5	122.2(5)	N4-C6-C5	115.1(4)
N4-C7-C8	121.8(5)	N4-C7-H7	119.1
C8-C7-H7	119.1	C9-C8-C7	119.8(5)
C9-C8-H4	120.1	C7-C8-H4	120.1
C8-C9-C10	117.4(5)	C8-C9-H5	121.3
C10-C9-H5	121.3	C6-C10-C9	119.5(5)
C6-C10-H6	120.2	C9-C10-H6	120.2
N3-C11-C12	111.7(5)	N3-C11-H14	109.3
C12-C11-H14	109.3	N3-C11-H15	109.3
C12-C11-H15	109.3	H14-C11-H15	107.9
N5-C12-C16	121.0(5)	N5-C12-C11	119.2(5)
C16-C12-C11	119.8(5)	N5-C13-C14	120.2(6)
N5-C13-H13	119.9	C14-C13-H13	119.9
C15-C14-C13	120.2(5)	C15-C14-H10	119.9
C13-C14-H10	119.9	C14-C15-C16	118.5(5)
C14-C15-H11	120.8	C16-C15-H11	120.8
C15-C16-C12	119.1(6)	C15-C16-H12	120.5
C12-C16-H12	120.5	C18-C17-C3	120.5(6)
C18-C17-H21	119.8	C3-C17-H21	119.8
C19-C18-C17	118.7(5)	C19-C18-H20	120.6
C17-C18-H20	120.6	C18-C19-C20	119.7(5)
C18-C19-H19	120.2	C20-C19-H19	120.2
N2-C20-C19	121.5(5)	N2-C20-H18	119.3
C19-C20-H18	119.3	N6-C21-C22	179.2(6)
C21-C22-H24	109.5	C21-C22-H23	109.5
H24-C22-H23	109.5	C21-C22-H22	109.5
H24-C22-H22	109.5	H23-C22-H22	109.5
N7-C23-C24	122.1(5)	N7-C23-H25	118.9
C24-C23-H25	118.9	C25-C24-C23	118.4(5)
C25-C24-H26	120.8	C23-C24-H26	120.8
C24-C25-C26	119.7(5)	C24-C25-H42	120.1
C26-C25-H42	120.1	C25-C26-C27	119.4(5)
C25-C26-H41	120.3	C27-C26-H41	120.3
N7-C27-C26	120.6(5)	N7-C27-C28	117.0(5)
C26-C27-C28	122.4(5)	C27-C28-N8	107.9(4)
C27-C28-H39	110.1	N8-C28-H39	110.1
C27-C28-H40	110.1	N8-C28-H40	110.1

H39-C28-H40	108.4	N8-C29-C30	108.2(4)
N8-C29-H27	110.1	C30-C29-H27	110.1
N8-C29-H32	110.1	C30-C29-H32	110.1
H27-C29-H32	108.4	N9-C30-C33	121.6(5)
N9-C30-C29	115.5(5)	C33-C30-C29	122.9(5)
C57-C31-C32	119.2(5)	C57-C31-H28	120.4
C32-C31-H28	120.4	C33-C32-C31	118.8(5)
C33-C32-H30	120.6	C31-C32-H30	120.6
C30-C33-C32	119.3(5)	C30-C33-H29	120.4
C32-C33-H29	120.4	C35-C34-N8	112.9(4)
C35-C34-H37	109.0	N8-C34-H37	109.0
C35-C34-H38	109.0	N8-C34-H38	109.0
H37-C34-H38	107.8	N11-C35-C39	121.1(5)
N11-C35-C34	117.4(4)	C39-C35-C34	121.4(5)
N11-C36-C37	121.8(5)	N11-C36-H36	119.1
C37-C36-H36	119.1	C36-C37-C38	119.3(6)
C36-C37-H33	120.4	C38-C37-H33	120.4
C37-C38-C39	119.3(5)	C37-C38-H35	120.3
C39-C38-H35	120.3	C38-C39-C35	119.3(5)
C38-C39-H34	120.3	C35-C39-H34	120.3
N12-C40-C41	176.8(6)	C40-C41-H43	109.5
C40-C41-H44	109.5	H43-C41-H44	109.5
C40-C41-H45	109.5	H43-C41-H45	109.5
H44-C41-H45	109.5	N13-C42-C43	178.7(6)
C42-C43-H47	109.5	C42-C43-H46	109.5
H47-C43-H46	109.5	C42-C43-H48	109.5
H47-C43-H48	109.5	H46-C43-H48	109.5
C45-C44-H49	109.5	C45-C44-H51	109.5
H49-C44-H51	109.5	C45-C44-H50	109.5
H49-C44-H50	109.5	H51-C44-H50	109.5
N14-C45-C44	178.0(9)	C47-C46-H52	109.5
C47-C46-H53	109.5	H52-C46-H53	109.5
C47-C46-H54	109.5	H52-C46-H54	109.5
H53-C46-H54	109.5	N15-C47-C46	179.9(10)
C49-C48-H58	109.5	C49-C48-H55	109.5
H58-C48-H55	109.5	C49-C48-H56	109.5
H58-C48-H56	109.5	H55-C48-H56	109.5
N16-C49-C48	179.1(7)		

Table S6. Anisotropic displacement parameters ($Å^2$).
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru1	0.0147(2)	0.0168(2)	0.0175(3)	0.00155(18)	0.00313(15)	0.00220(16)
Ru2	0.0125(2)	0.0153(2)	0.0171(2)	-0.00021(17)	0.00365(15)	0.00086(16)
P1	0.0521(11)	0.0404(10)	0.0282(10)	-0.0096(8)	0.0145(8)	-0.0165(8)
P2	0.0273(8)	0.0273(8)	0.0293(9)	0.0024(7)	0.0063(6)	0.0020(6)
P3	0.0241(8)	0.0286(8)	0.0239(8)	-0.0033(7)	0.0036(6)	0.0044(6)
P4	0.0287(8)	0.0282(8)	0.0229(8)	0.0020(7)	0.0056(6)	0.0038(6)
F1	0.099(4)	0.059(3)	0.050(3)	-0.023(2)	0.037(3)	-0.035(3)
F2	0.076(3)	0.059(3)	0.126(5)	0.012(3)	0.051(3)	0.010(3)
F3	0.150(5)	0.043(3)	0.075(4)	-0.026(3)	0.054(3)	-0.034(3)
F4	0.214(7)	0.061(3)	0.054(4)	0.003(3)	-0.046(4)	-0.007(4)
F5	0.199(7)	0.086(4)	0.071(4)	0.032(4)	-0.001(4)	-0.046(5)
F6	0.087(4)	0.148(6)	0.209(9)	-0.104(6)	0.102(5)	-0.070(4)
F7	0.033(2)	0.046(2)	0.033(2)	0.0027(17)	-0.0022(15)	-0.0098(16)
F8	0.0267(19)	0.046(2)	0.049(2)	0.0016(19)	0.0120(16)	-0.0003(16)
F9	0.055(2)	0.045(2)	0.036(2)	-0.0081(18)	0.0052(17)	-0.0148(18)
F10	0.035(2)	0.065(3)	0.069(3)	-0.004(2)	0.028(2)	-0.0010(19)
F11	0.043(2)	0.029(2)	0.062(3)	0.0117(19)	-0.0014(18)	0.0074(16)
F12	0.063(3)	0.034(2)	0.043(3)	0.0136(19)	-0.0018(19)	0.0001(18)
F13	0.073(3)	0.030(2)	0.048(3)	-0.0107(19)	-0.007(2)	-0.0065(19)
F14	0.029(2)	0.099(3)	0.045(3)	-0.028(2)	0.0174(17)	-0.023(2)
F15	0.042(2)	0.068(3)	0.032(2)	-0.007(2)	-0.0090(16)	0.0236(19)
F16	0.036(2)	0.056(2)	0.039(2)	0.0004(19)	0.0152(16)	0.0021(17)
F17	0.054(2)	0.0281(19)	0.056(3)	0.0042(19)	-0.0013(19)	0.0150(17)
F18	0.041(2)	0.0268(18)	0.028(2)	-0.0003(15)	-0.0015(14)	-0.0050(15)
F19	0.052(2)	0.057(3)	0.051(3)	-0.011(2)	-0.0071(19)	0.028(2)
F20	0.054(2)	0.079(3)	0.025(2)	0.006(2)	0.0051(17)	-0.022(2)
F21	0.054(2)	0.037(2)	0.023(2)	-0.0015(16)	0.0051(16)	-0.0046(17)
F22	0.049(2)	0.047(2)	0.038(2)	0.0033(18)	0.0114(17)	-0.0122(18)
F23	0.064(3)	0.041(2)	0.047(3)	0.0077(19)	0.0077(19)	0.0254(19)
F24	0.0323(19)	0.043(2)	0.032(2)	0.0049(17)	0.0033(14)	0.0038(15)

N1	0.010(2)	0.017(2)	0.027(3)	-0.001(2)	0.0022(17)	0.0018(17)
N2	0.015(2)	0.014(2)	0.024(3)	0.0007(19)	0.0070(17)	0.0009(17)
N3	0.019(2)	0.021(2)	0.020(2)	0.004(2)	0.0058(17)	0.0017(18)
N4	0.018(2)	0.013(2)	0.023(3)	0.0029(19)	0.0027(17)	0.0010(17)
N5	0.0050(19)	0.019(2)	0.028(3)	0.002(2)	0.0018(16)	0.0027(16)
N6	0.017(2)	0.022(3)	0.021(3)	0.002(2)	0.0059(17)	0.0027(19)
N7	0.013(2)	0.017(2)	0.021(3)	-0.0020(19)	0.0028(16)	-0.0004(17)
N8	0.029(3)	0.019(2)	0.017(2)	0.0022(19)	0.0024(18)	0.0007(19)
N9	0.013(2)	0.012(2)	0.021(2)	-0.0004(18)	0.0028(16)	0.0036(16)
C57	0.021(3)	0.031(3)	0.020(3)	-0.001(3)	0.000(2)	0.007(2)
N11	0.014(2)	0.010(2)	0.027(3)	0.0013(19)	0.0048(17)	0.0006(16)
N12	0.020(2)	0.020(2)	0.020(3)	0.0003(19)	0.0041(17)	0.0003(18)
N13	0.016(2)	0.016(2)	0.024(3)	0.0009(19)	0.0022(18)	-0.0012(17)
N14	0.058(4)	0.053(4)	0.062(5)	-0.008(4)	-0.004(3)	0.015(3)
N15	0.027(3)	0.069(5)	0.062(5)	0.012(4)	0.000(3)	0.014(3)
N16	0.060(4)	0.070(5)	0.036(4)	0.019(3)	-0.015(3)	-0.012(3)
C1	0.011(2)	0.020(3)	0.024(3)	0.001(2)	0.002(2)	0.003(2)
C2	0.035(3)	0.032(3)	0.017(3)	0.003(3)	0.000(2)	0.005(3)
C3	0.026(3)	0.020(3)	0.027(3)	0.002(2)	0.006(2)	0.001(2)
C4	0.019(3)	0.037(3)	0.024(3)	0.002(3)	0.010(2)	0.002(2)
C5	0.026(3)	0.042(4)	0.020(3)	0.007(3)	0.004(2)	0.010(3)
C6	0.020(3)	0.028(3)	0.022(3)	0.006(2)	0.001(2)	0.006(2)
C7	0.022(3)	0.020(3)	0.018(3)	0.002(2)	0.002(2)	-0.004(2)
C8	0.023(3)	0.026(3)	0.026(3)	0.000(3)	0.006(2)	0.006(2)
C9	0.020(3)	0.023(3)	0.040(4)	0.008(3)	0.003(2)	0.007(2)
C10	0.028(3)	0.041(4)	0.021(3)	0.008(3)	-0.003(2)	0.002(3)
C11	0.044(4)	0.035(3)	0.023(3)	0.001(3)	0.005(3)	-0.010(3)
C12	0.010(2)	0.025(3)	0.027(3)	0.001(3)	0.003(2)	0.002(2)
C13	0.018(3)	0.022(3)	0.033(3)	0.005(3)	0.003(2)	0.008(2)
C14	0.024(3)	0.030(3)	0.035(4)	0.013(3)	0.010(2)	0.003(2)
C15	0.021(3)	0.018(3)	0.045(4)	0.001(3)	0.004(2)	0.000(2)
C16	0.024(3)	0.025(3)	0.033(4)	-0.005(3)	0.000(2)	-0.001(2)
C17	0.025(3)	0.034(3)	0.033(4)	0.001(3)	0.014(2)	0.008(3)
C18	0.023(3)	0.028(3)	0.039(4)	-0.007(3)	0.014(2)	0.004(2)
C19	0.023(3)	0.017(3)	0.035(4)	0.005(2)	0.005(2)	0.002(2)
C20	0.016(3)	0.019(3)	0.028(3)	0.001(2)	0.002(2)	0.000(2)
C21	0.015(3)	0.020(3)	0.032(3)	0.002(2)	0.004(2)	0.005(2)
C22	0.025(3)	0.022(3)	0.040(4)	0.002(3)	0.006(2)	-0.002(2)

C23	0.016(3)	0.016(3)	0.024(3)	0.002(2)	0.005(2)	0.002(2)
C24	0.022(3)	0.020(3)	0.025(3)	0.001(2)	0.005(2)	-0.001(2)
C25	0.025(3)	0.017(3)	0.031(3)	-0.006(3)	0.005(2)	0.000(2)
C26	0.026(3)	0.024(3)	0.022(3)	-0.002(2)	0.001(2)	0.000(2)
C27	0.015(3)	0.027(3)	0.018(3)	0.001(2)	0.0034(19)	0.002(2)
C28	0.024(3)	0.023(3)	0.023(3)	-0.003(2)	0.004(2)	-0.003(2)
C29	0.029(3)	0.024(3)	0.017(3)	0.004(2)	0.003(2)	0.001(2)
C30	0.019(3)	0.019(3)	0.026(3)	0.002(2)	0.006(2)	0.006(2)
C31	0.024(3)	0.014(3)	0.027(3)	0.000(2)	0.000(2)	0.000(2)
C32	0.033(3)	0.026(3)	0.029(4)	-0.004(3)	0.005(2)	-0.003(2)
C33	0.034(3)	0.021(3)	0.026(3)	0.011(3)	0.010(2)	-0.001(2)
C34	0.018(3)	0.032(3)	0.028(3)	-0.003(3)	0.012(2)	-0.001(2)
C35	0.016(3)	0.006(2)	0.033(3)	0.003(2)	0.008(2)	-0.0014(19)
C36	0.021(3)	0.015(3)	0.031(3)	0.002(2)	0.000(2)	0.000(2)
C37	0.020(3)	0.018(3)	0.047(4)	0.007(3)	-0.002(3)	-0.003(2)
C38	0.018(3)	0.010(3)	0.063(5)	0.005(3)	0.004(3)	0.004(2)
C39	0.022(3)	0.017(3)	0.050(4)	0.000(3)	0.016(3)	-0.001(2)
C40	0.022(3)	0.027(3)	0.028(3)	0.008(3)	0.005(2)	0.007(2)
C41	0.015(3)	0.044(4)	0.062(5)	0.023(4)	0.004(3)	0.008(3)
C42	0.012(3)	0.024(3)	0.029(3)	0.000(3)	0.005(2)	-0.001(2)
C43	0.035(3)	0.048(4)	0.025(4)	-0.006(3)	0.011(3)	-0.003(3)
C44	0.055(5)	0.050(5)	0.081(7)	0.016(5)	-0.007(4)	-0.010(4)
C45	0.037(4)	0.041(4)	0.066(6)	-0.001(4)	-0.016(4)	0.002(3)
C46	0.020(3)	0.038(4)	0.062(5)	-0.001(3)	0.002(3)	-0.003(3)
C47	0.029(4)	0.035(4)	0.052(5)	-0.003(3)	-0.005(3)	0.005(3)
C48	0.034(3)	0.029(3)	0.046(4)	0.003(3)	0.004(3)	0.005(3)
C49	0.036(4)	0.031(3)	0.035(4)	0.015(3)	0.001(3)	0.003(3)

Table S7. Hydrogen coordinates (x) and isotropic atomic displacement parameters ($Å^2$).

	x	y	z	U(eq)
H57	0.2359	0.6968	0.2998	0.029
H1	0.3901	-0.0266	0.9451	0.043
H3	0.3631	0.1002	0.9525	0.043

H2	0.4873	0.0639	0.9456	0.043
H17	0.4318	-0.0111	0.5610	0.031
H16	0.4446	0.1010	0.6045	0.031
H8	0.1993	0.0494	0.5584	0.035
H9	0.2710	0.1486	0.5972	0.035
H7	0.1391	0.1052	0.7890	0.024
H4	-0.0414	0.1605	0.7602	0.029
H5	-0.1104	0.1584	0.6545	0.033
H6	0.0154	0.1157	0.5807	0.036
H14	0.3361	-0.1529	0.5816	0.04
H15	0.2094	-0.1168	0.5759	0.04
H13	0.2725	-0.1446	0.8045	0.029
H10	0.2057	-0.3271	0.7922	0.035
H11	0.1727	-0.4175	0.6939	0.034
H12	0.2131	-0.3242	0.6083	0.034
H21	0.6314	-0.0631	0.5875	0.036
H20	0.7686	-0.1209	0.6608	0.036
H19	0.7325	-0.1238	0.7630	0.03
H18	0.5591	-0.0734	0.7896	0.025
H24	0.4315	0.4280	0.7038	0.044
H23	0.5507	0.3799	0.6952	0.044
H22	0.5168	0.4061	0.7631	0.044
H25	0.0645	0.2760	0.2959	0.022
H26	0.0156	0.0920	0.2673	0.027
H42	-0.0148	0.0323	0.1619	0.03
H41	0.0019	0.1576	0.0877	0.029
H39	-0.0066	0.4111	0.0951	0.028
H40	0.0853	0.3375	0.0663	0.028
H27	0.0677	0.5781	0.0963	0.028
H32	0.1828	0.5562	0.0687	0.028
H28	0.3223	0.8549	0.2754	0.026
H30	0.3454	0.8774	0.1718	0.036
H29	0.2679	0.7443	0.0946	0.031
H37	0.2582	0.3338	0.1067	0.031
H38	0.3124	0.4542	0.1095	0.031
H36	0.2968	0.4321	0.3361	0.027
H33	0.4696	0.3540	0.3498	0.035
H35	0.5583	0.3018	0.2633	0.036

H34	0.4674	0.3224	0.1643	0.035
H43	-0.2849	0.5379	0.1747	0.059
H44	-0.2467	0.6639	0.1783	0.059
H45	-0.2572	0.6058	0.2405	0.059
H47	0.1035	0.6262	0.4447	0.054
H46	0.0545	0.5057	0.4498	0.054
H48	-0.0251	0.5968	0.4221	0.054
H49	0.6848	0.6312	0.4959	0.094
H51	0.7384	0.5135	0.4938	0.094
H50	0.6125	0.5267	0.4641	0.094
H52	0.4131	0.2892	0.9765	0.061
H53	0.3375	0.3933	0.9680	0.061
H54	0.4551	0.4053	1.0105	0.061
H58	0.1974	0.9098	0.0276	0.055
H55	0.1282	1.0189	0.0239	0.055
H56	0.1302	0.9503	0.0833	0.055

Part D. Spectral Data for 1 and 2.

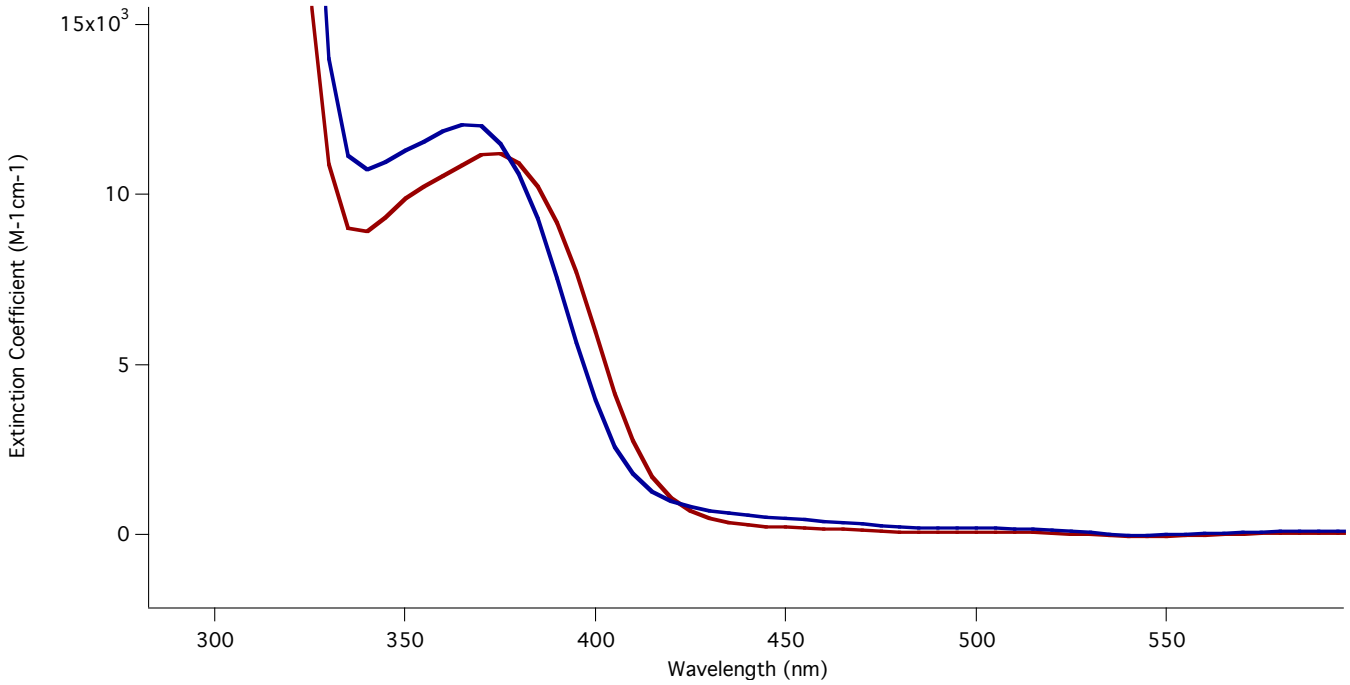


Figure S1 : Overlap plot of UV -Vis spectra (Extinction coefficient ($M^{-1}cm^{-1}$ Vs wavelength (nm)) of **1** (red) and **2** (blue) in DMSO.

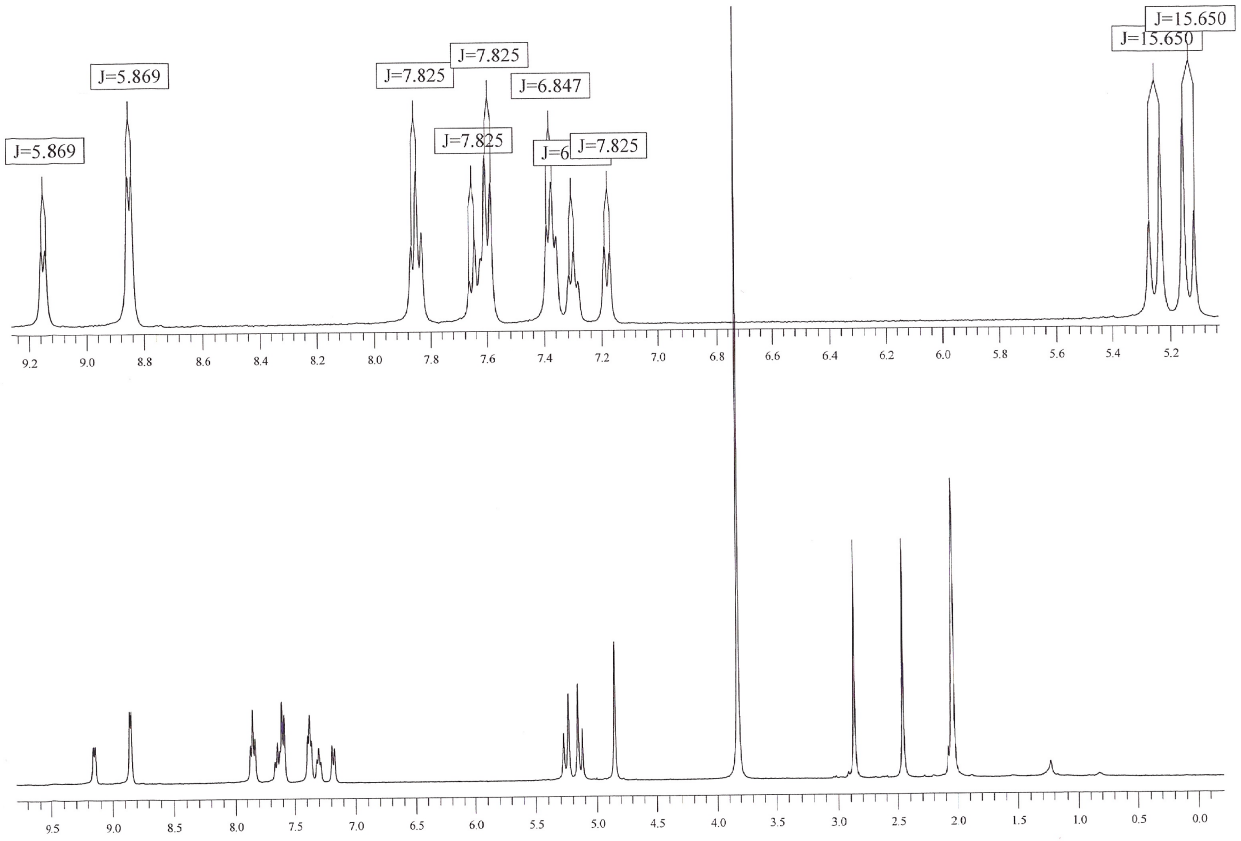


Figure S2: ^{1}H NMR spectra of **1** in 9:1 C_3D_6O:D_2O. The peak at ~3.8 ppm corresponds to D_2O in the solvent mixture.

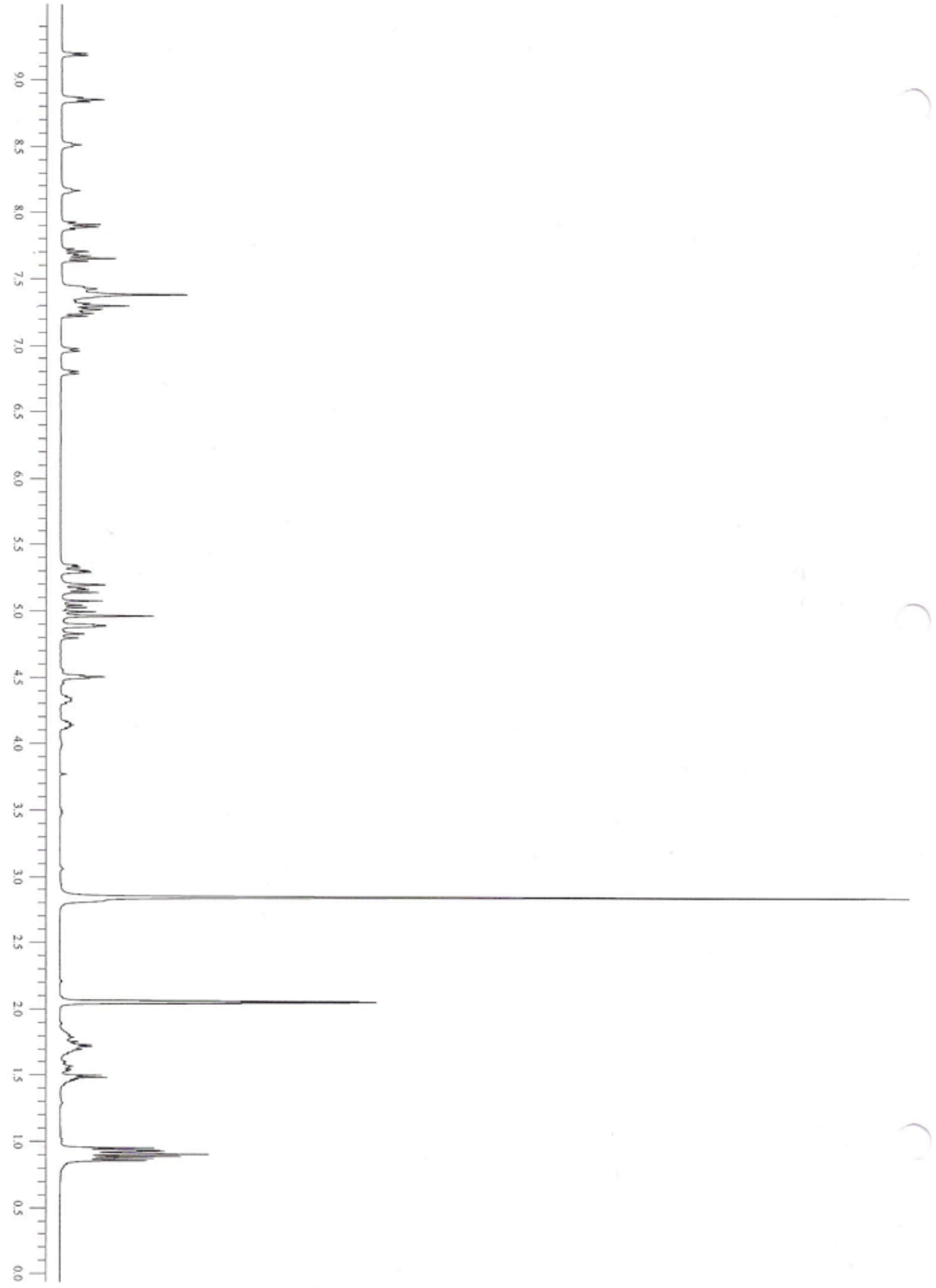


Figure S3: ^{1}H NMR spectrum of **2** in 100% C_3D_6O.

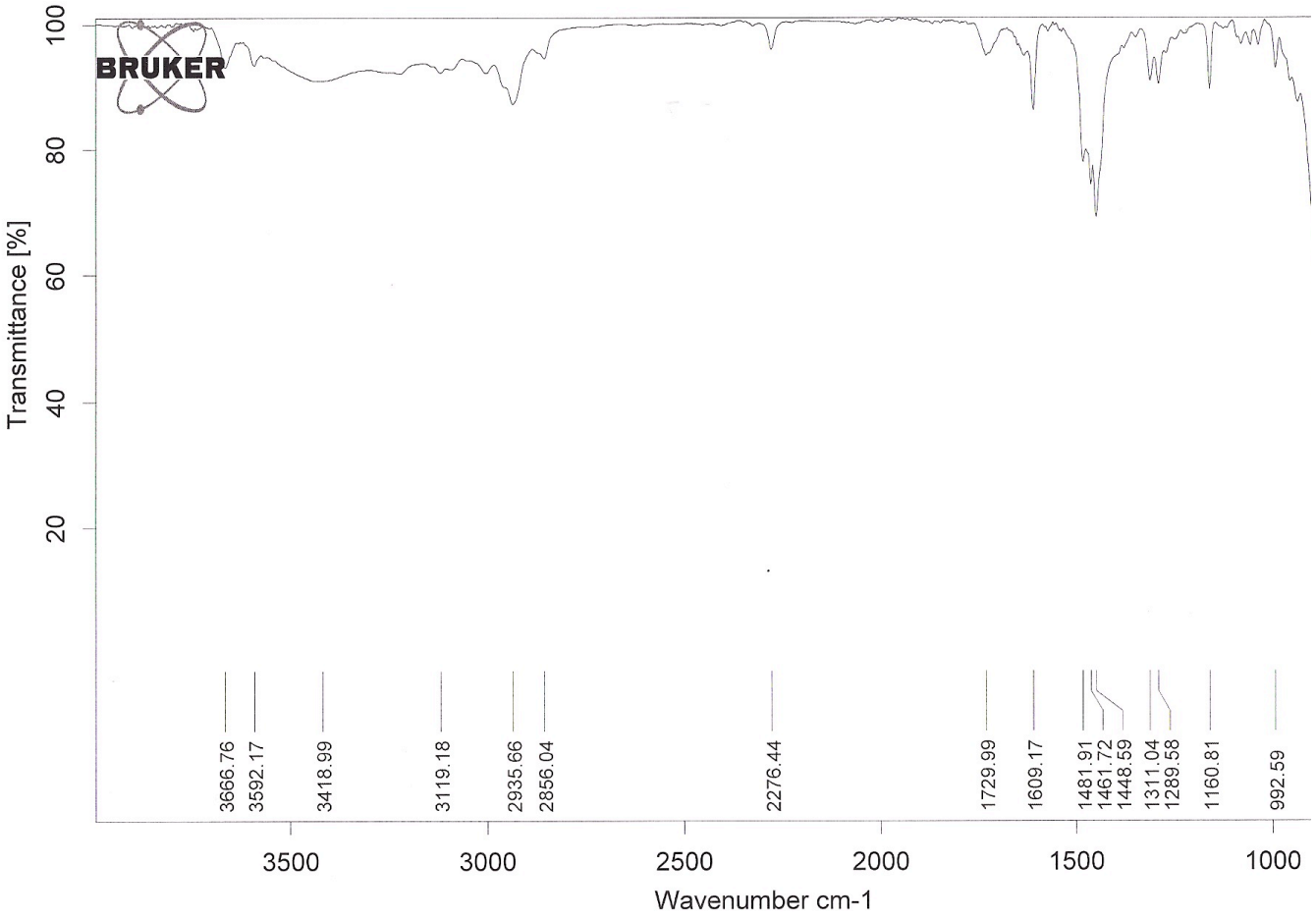


Figure S4 : IR spectrum of **1** (KBr)

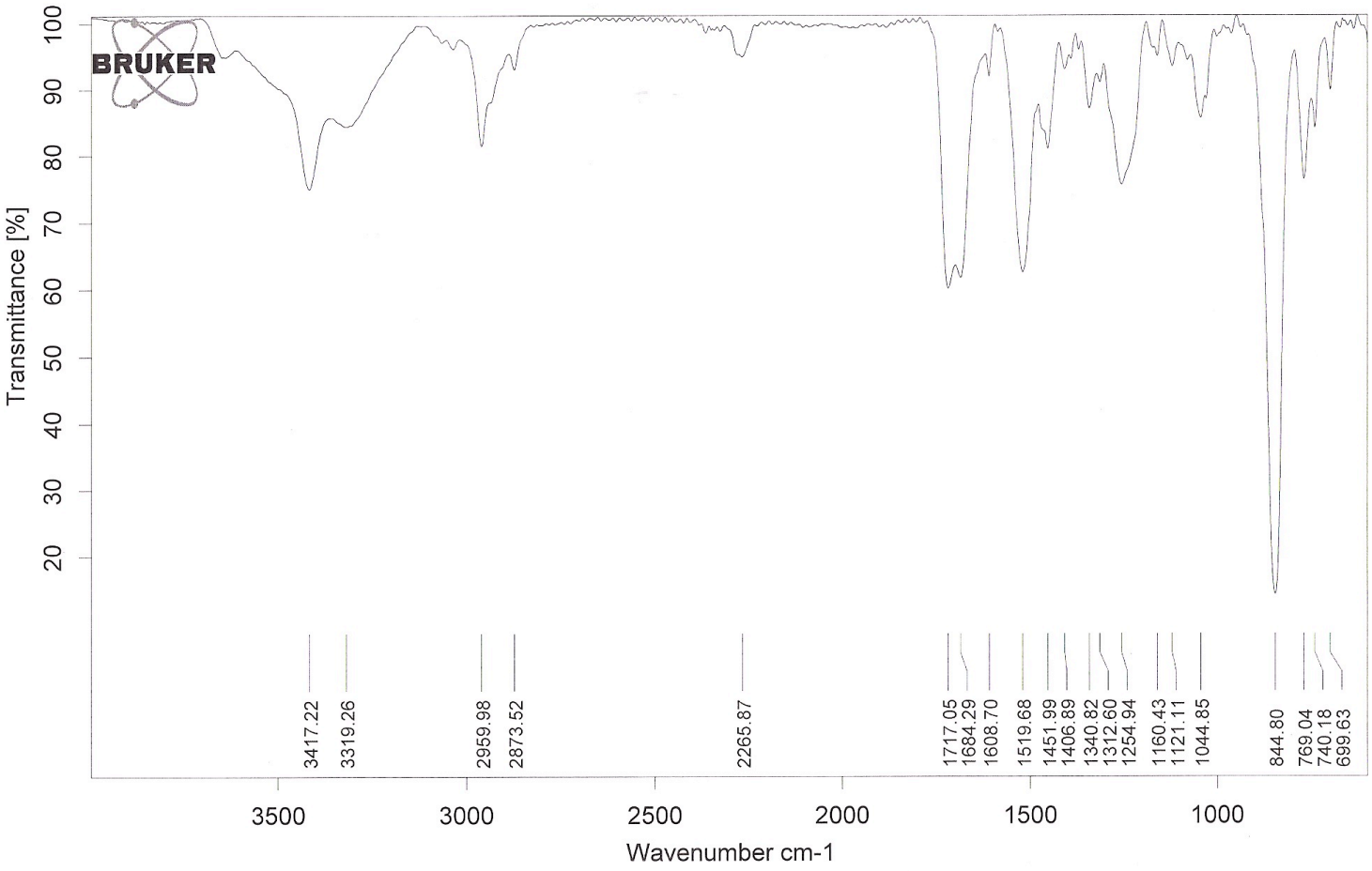


Figure S5 : IR spectrum of **2** (KBr)

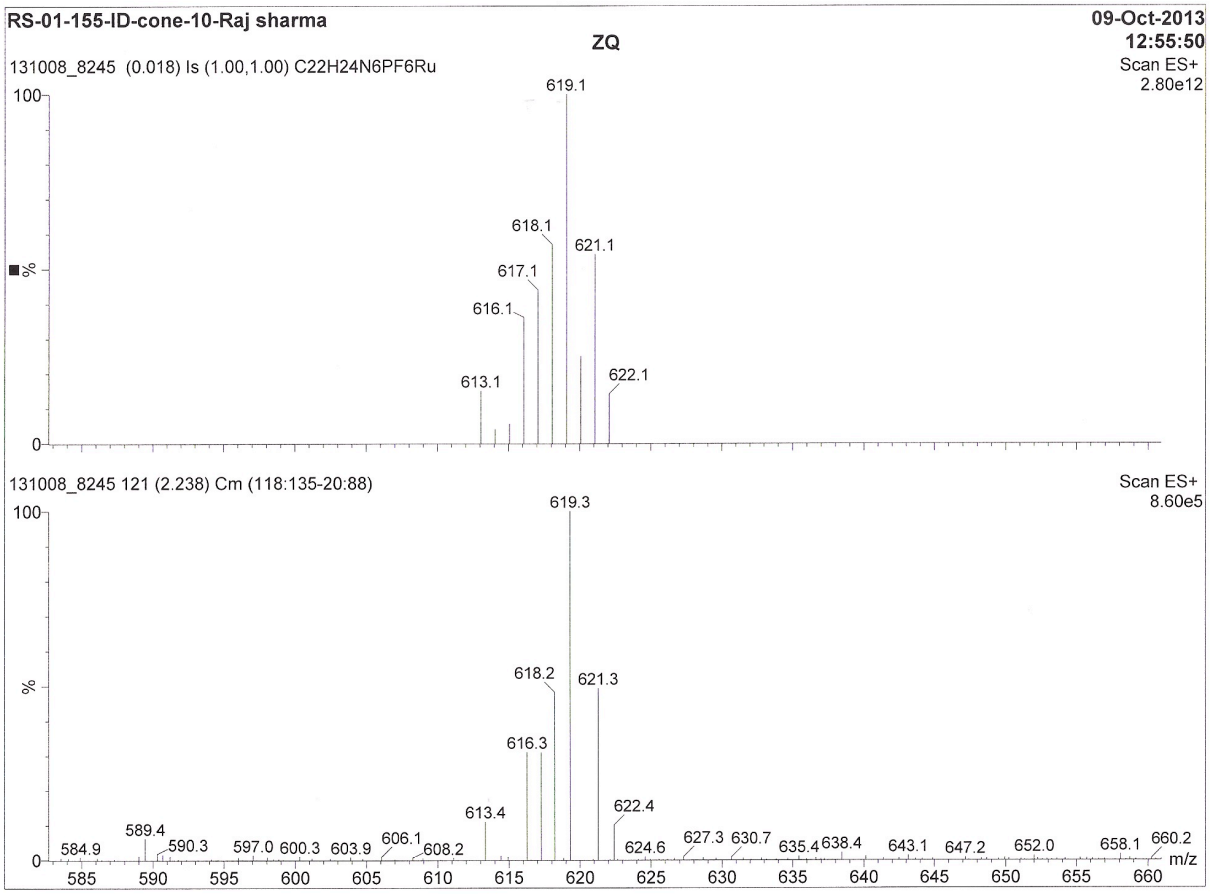


Figure S6 : Mass spectrum calculated (above) and observed (below) of the cation $[Ru(TPA)(CH_3CN)_2](PF_6)\}^+$ of **1**

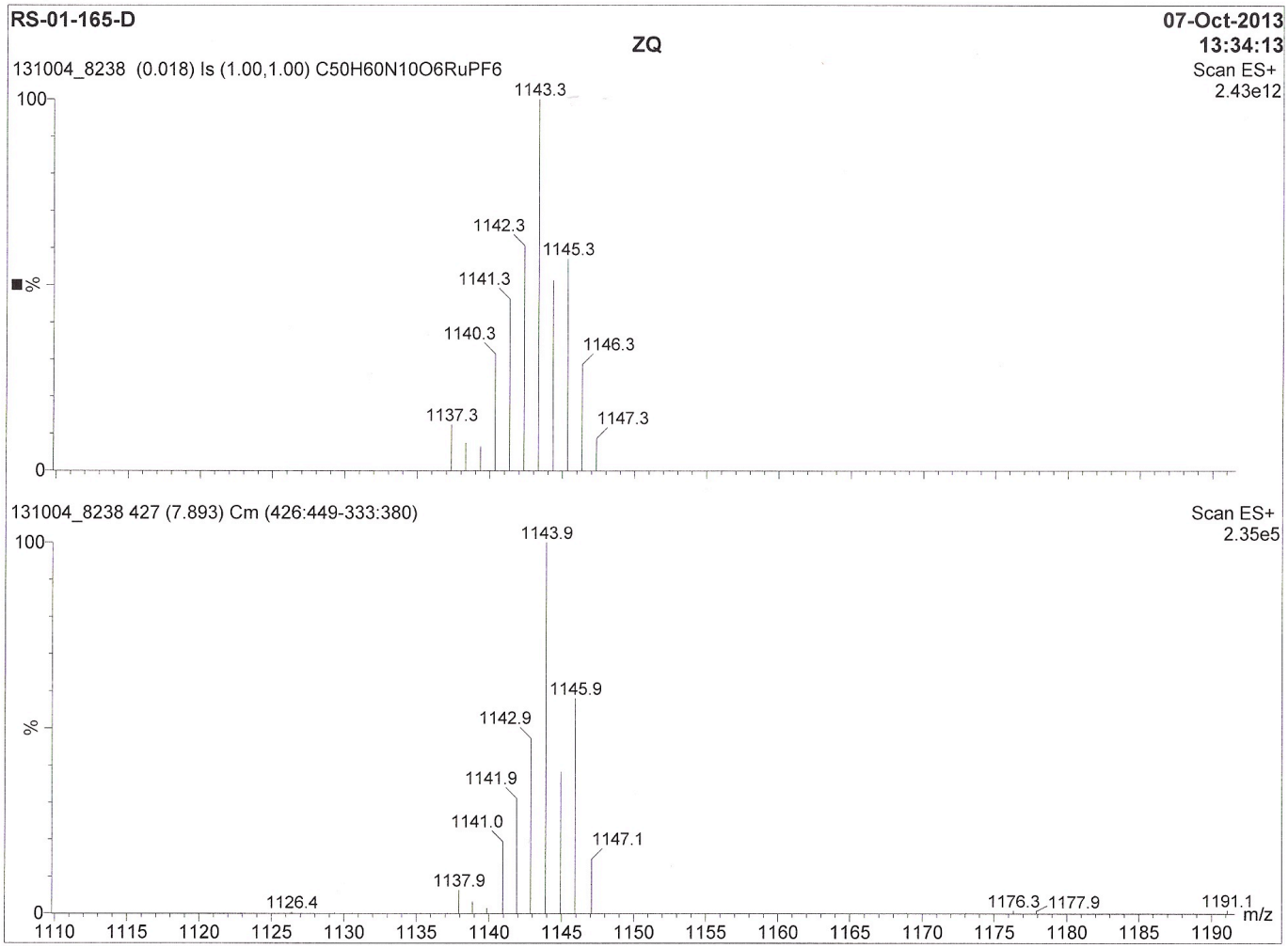


Figure S7 : Mass spectrum calculated (above) and observed (below) of the cation $[Ru(TPA)(RCN)_2](PF_6)\}^+$ of **2**

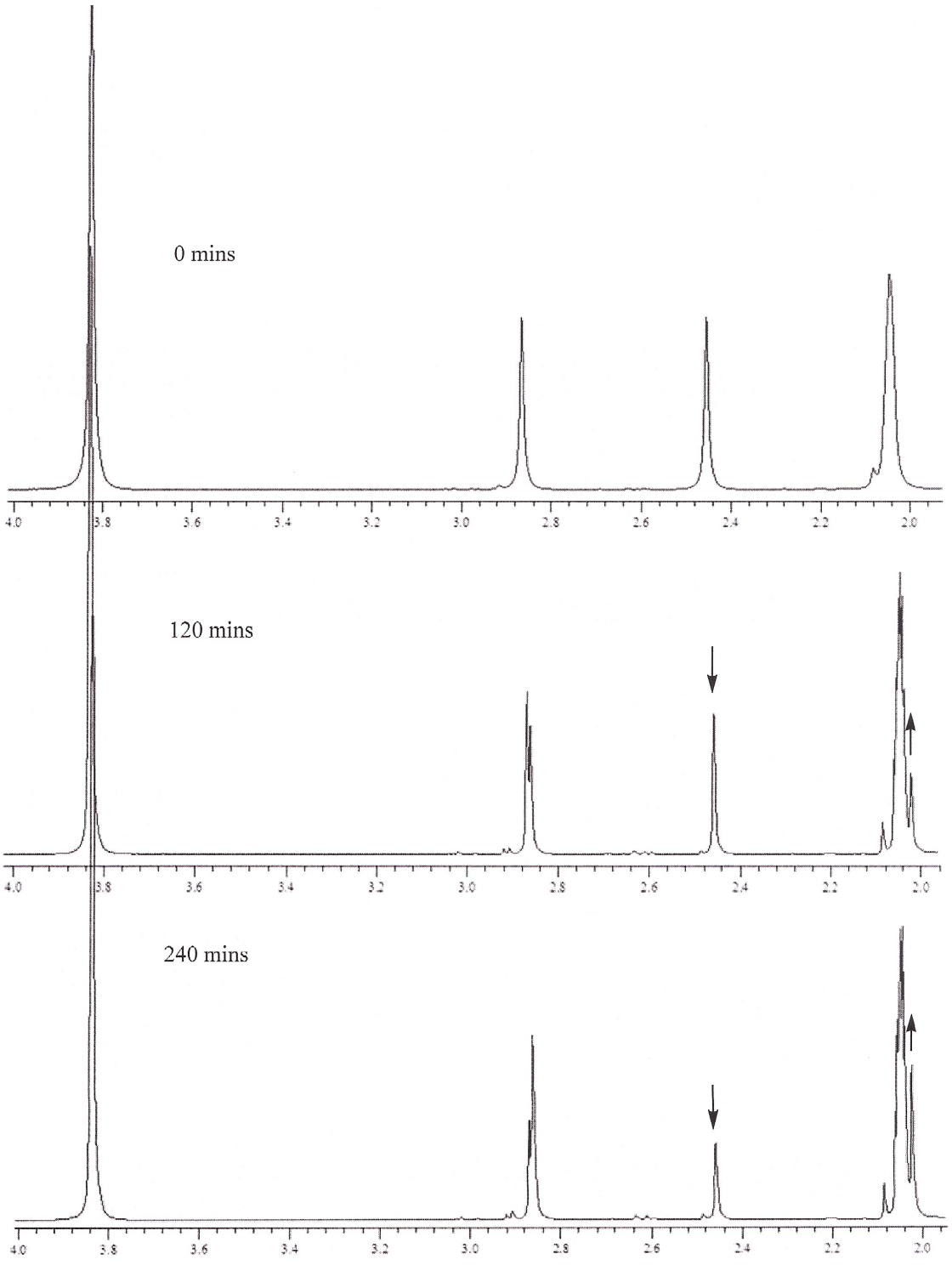


Figure S8 : Photochemical reaction of **1** in 9:1 C_3D_6O:D_2O. Compound **1** was irradiated with 365 nm light (8W) in an NMR tube. Timescales are longer than reported in Figure 3A because of the higher concentration of this sample.

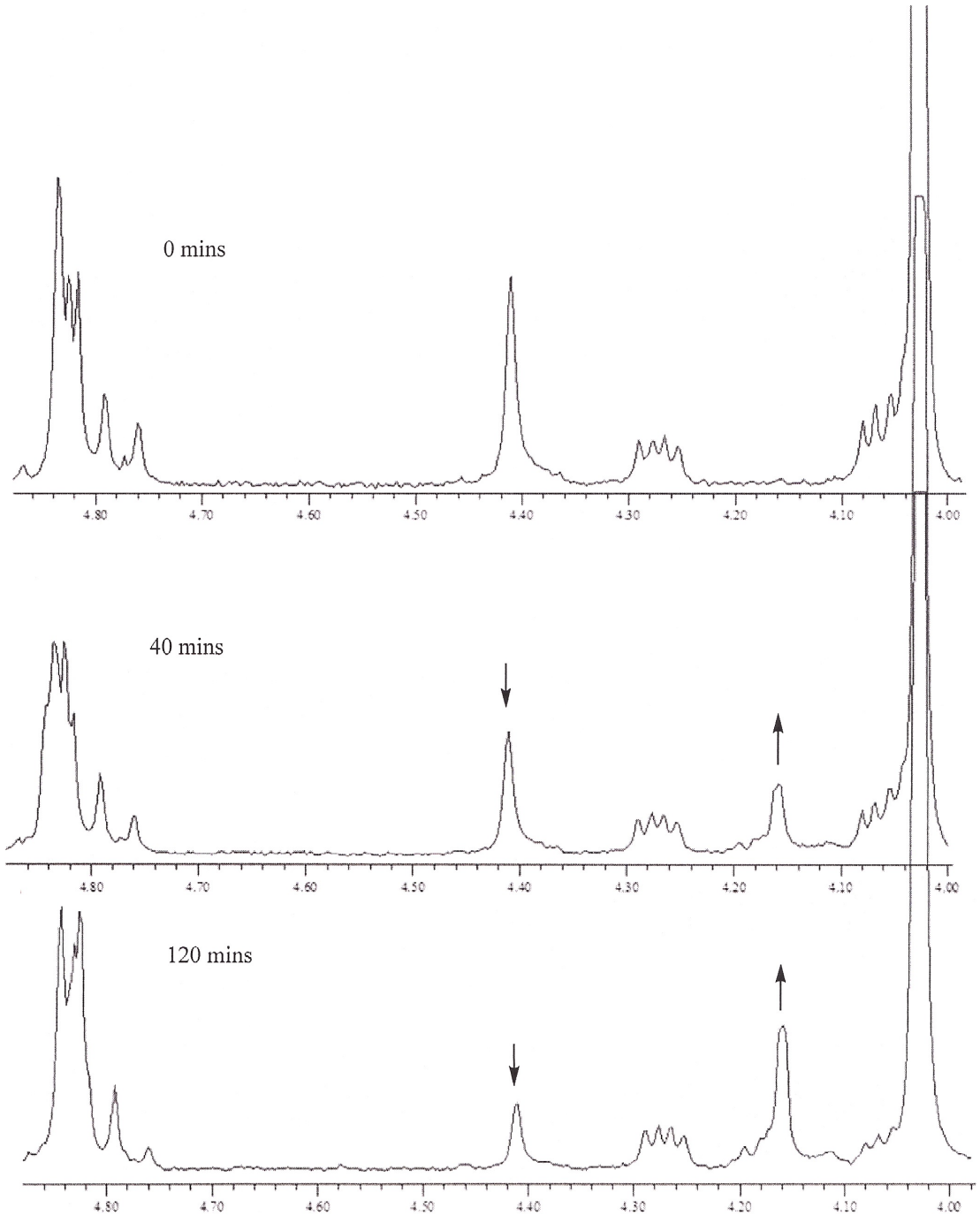


Figure S9 : Photochemical reaction of **2** in 9:1 C_3D_6O:D_2O. Compound **2** was irradiated with 365 nm light (8W) in an NMR tube. Timescales are longer than reported in Figure 3B because of the higher concentration of this sample.

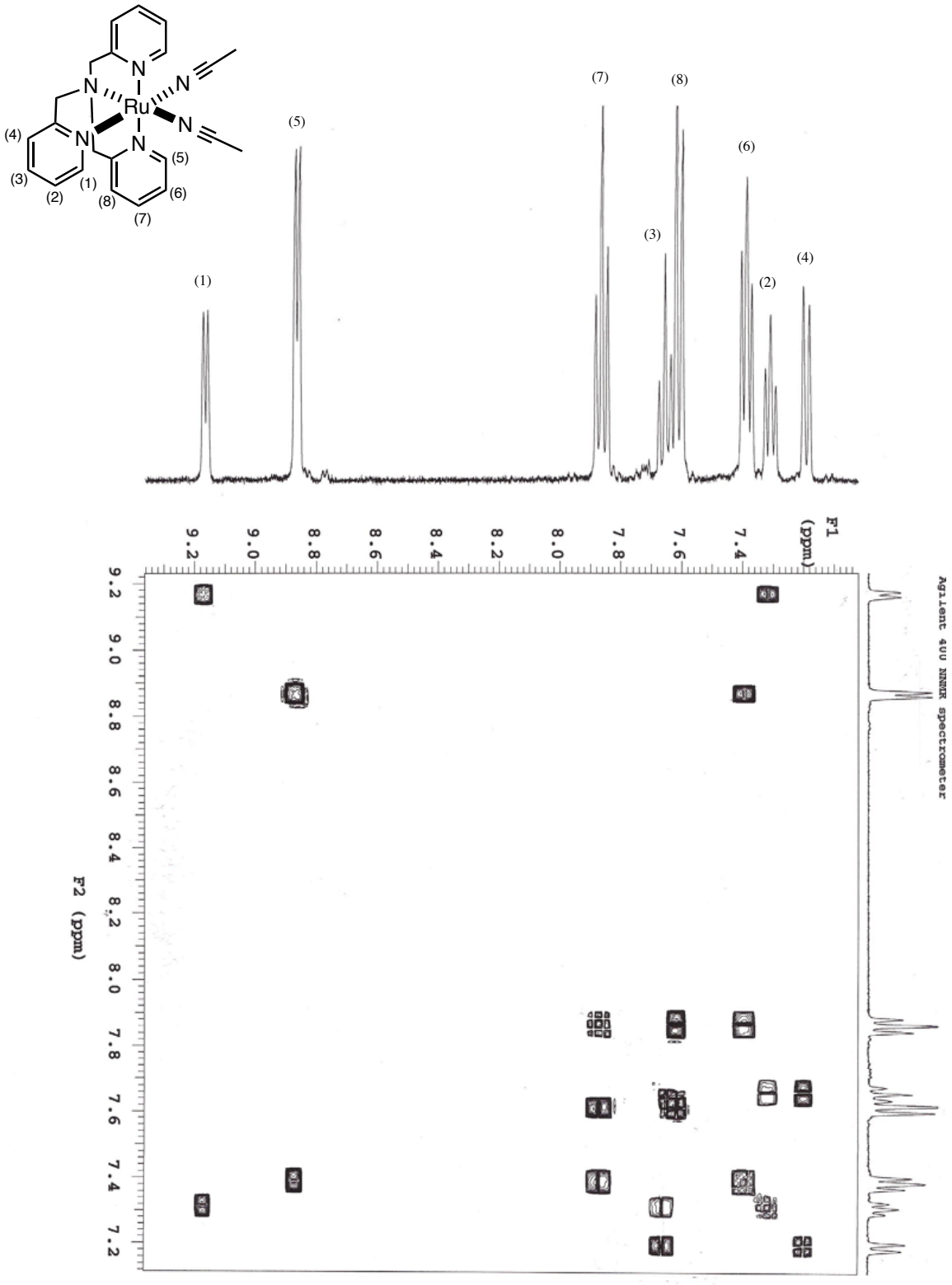


Figure S10 : COSY spectrum of **1**

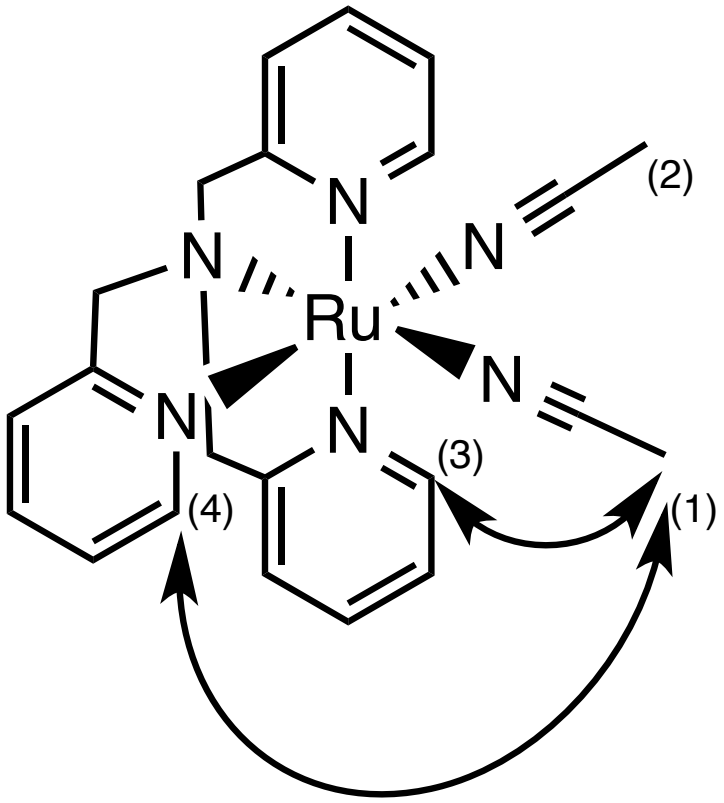
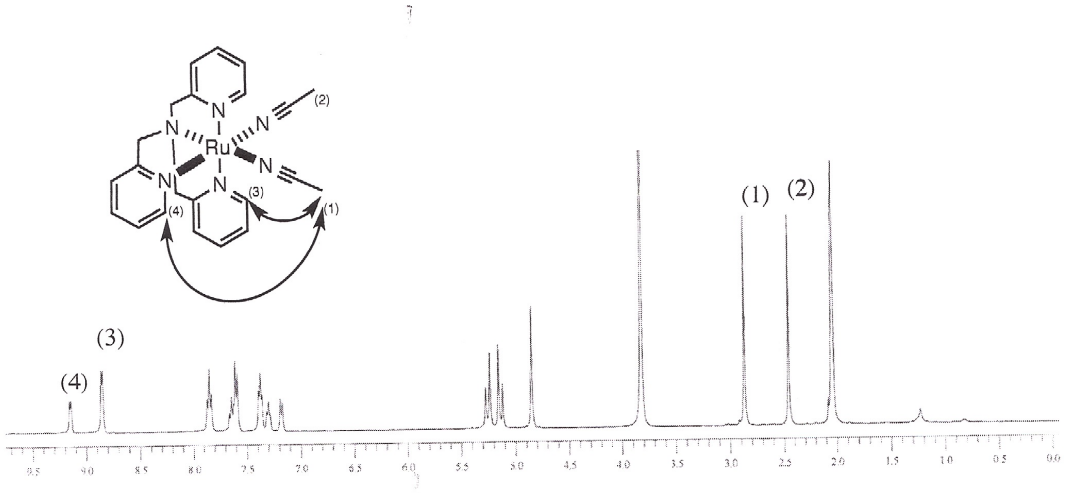


Figure S11 : NOESY data for **1** with peak assignment. See following two pages for spectra.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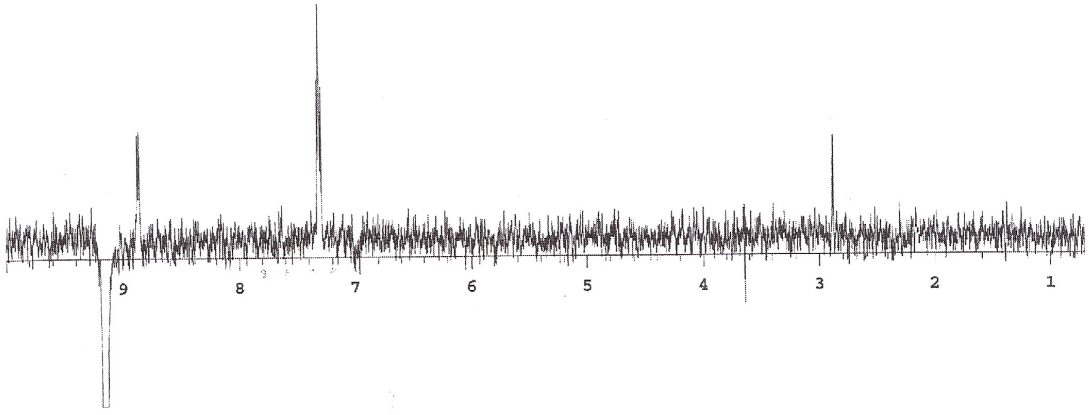
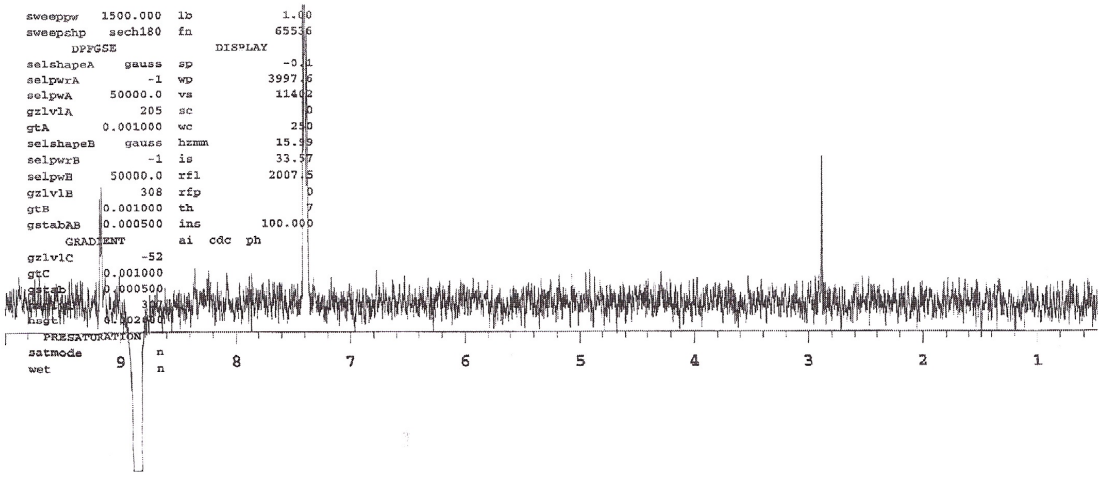
(2)
(3)
(4)


9
8
7
6
5
4
3
2
1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gtC 0.001000
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fn 65536
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sc 0
wc 250
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rfl 2007.5
rfp 0
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8
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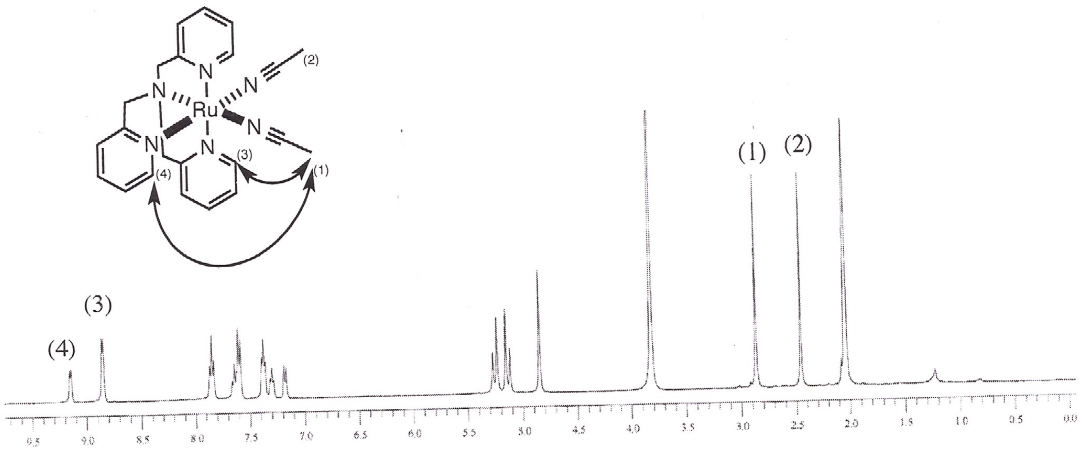
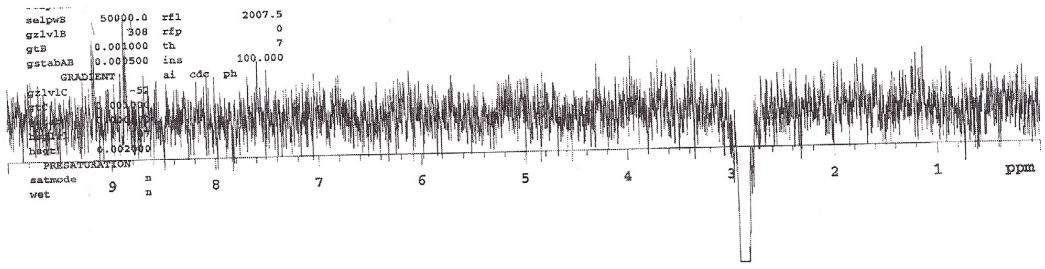
5
4
3
2
1


(1)
(2)
(3)
(4)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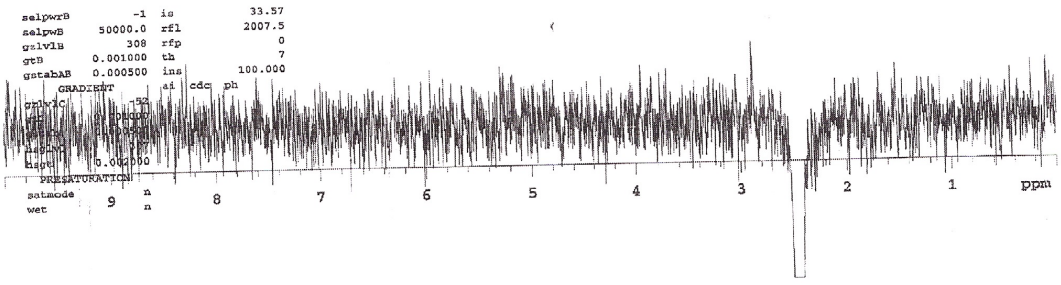
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ppm

References:

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