Supporting Information.

Synthesis and Linkage Isomerization of Thiolato-Bridged $Ru^{II}Ag^{I}Ru^{II}$ Trinuclear Complex with D-Penicillaminate

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Table S1. Crystallographic data of $\Delta_D\Delta_D$-[Ag{Ru(D-pen)(bpy)$_2$}{Ru(D-Hpen)(bpy)$_2$}](PF$_6$)$_{1.5}$(NO$_3$)$_{0.5}$, ([**2a** – H$^+$](PF$_6$)$_{1.5}$(NO$_3$)$_{0.5}$).

	([**2a** – H$^+$](PF$_6$)$_{1.5}$(NO$_3$)$_{0.5}$)
formula	$C_{50}H_{65.25}AgF_9N_{10.5}O_{13.125}P_{1.5}Ru_2S_2$
fw	1614.96
crystal color, habit	red, block
crystal system	Orthorhombic
space group	$C222_1$
a (Å)	19.036(11)
b (Å)	24.229(13)
c (Å)	58.24(3)
V (Å^3)	26863(26)
Z	8
T (K)	100
radiation λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	1.597
crystal size (mm)	0.20 × 0.10 × 0.20
μ (Mo $K\alpha$) (cm^{-1})	9.19
R^a ($I > 2\sigma(I)$)	0.122
$R_w{}^b$ (all data)	0.309

[a] $R = \Sigma\ |(|Fo| - |Fc|)| / \Sigma\ (|Fo|)$.

[b] $R_w = [\Sigma\ w\ (Fo^2 - Fc^2)^2 / \Sigma\ w\ (Fo^2)^2]^{1/2}$, $w = 1/(\sigma^2(Fo^2)+(0.1463P)^2+1022.6P)$, $P = (Fo^2+2Fc^2)/3$.

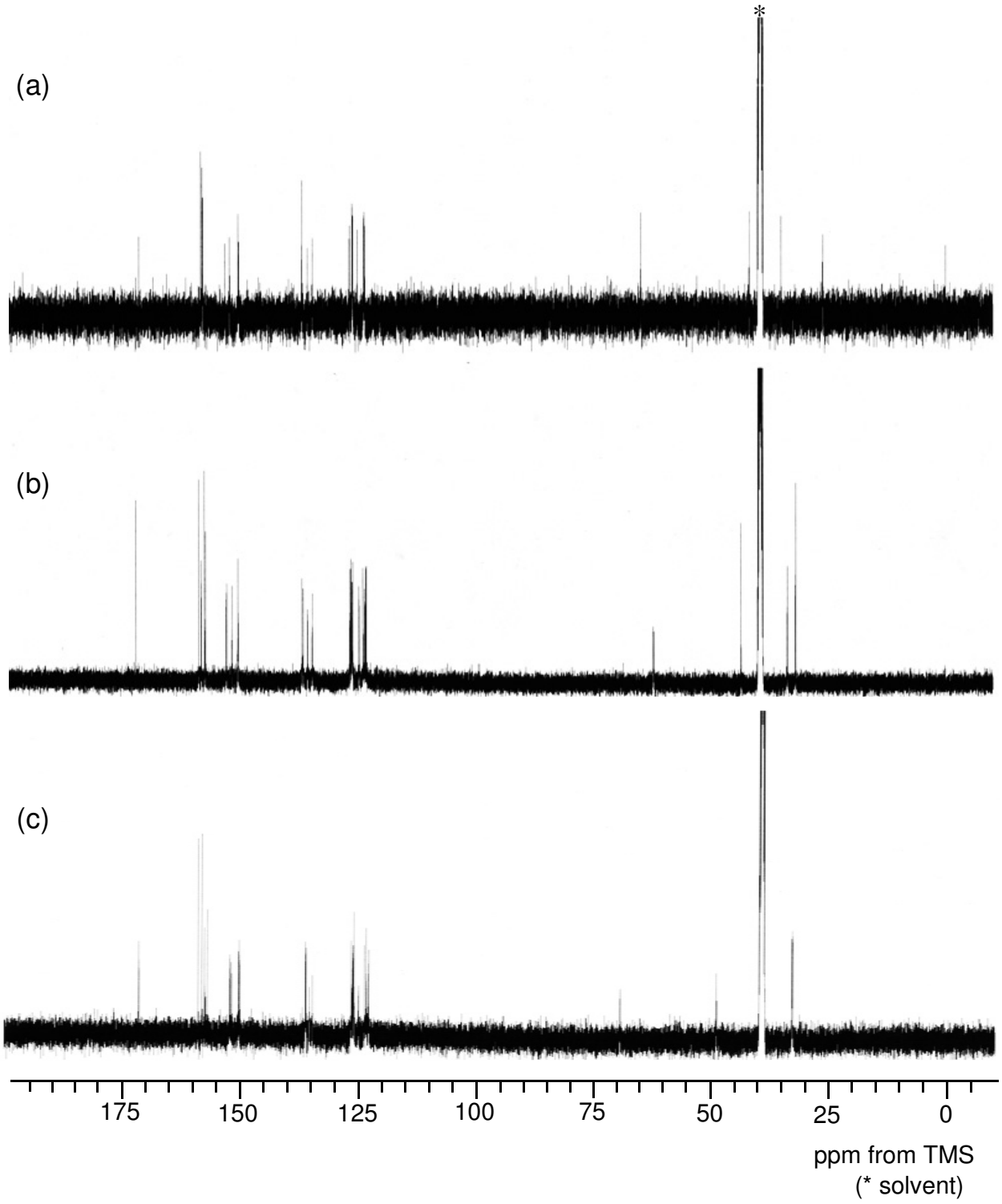

Figure S1. ^{13}C NMR spectra of (a) $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1a**](ClO$_4$)$_3$), (b) $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1b**](ClO$_4$)$_3$), and (c) $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*N*,*S*)-(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**2a**](ClO$_4$)$_3$) in DMSO-d_6.

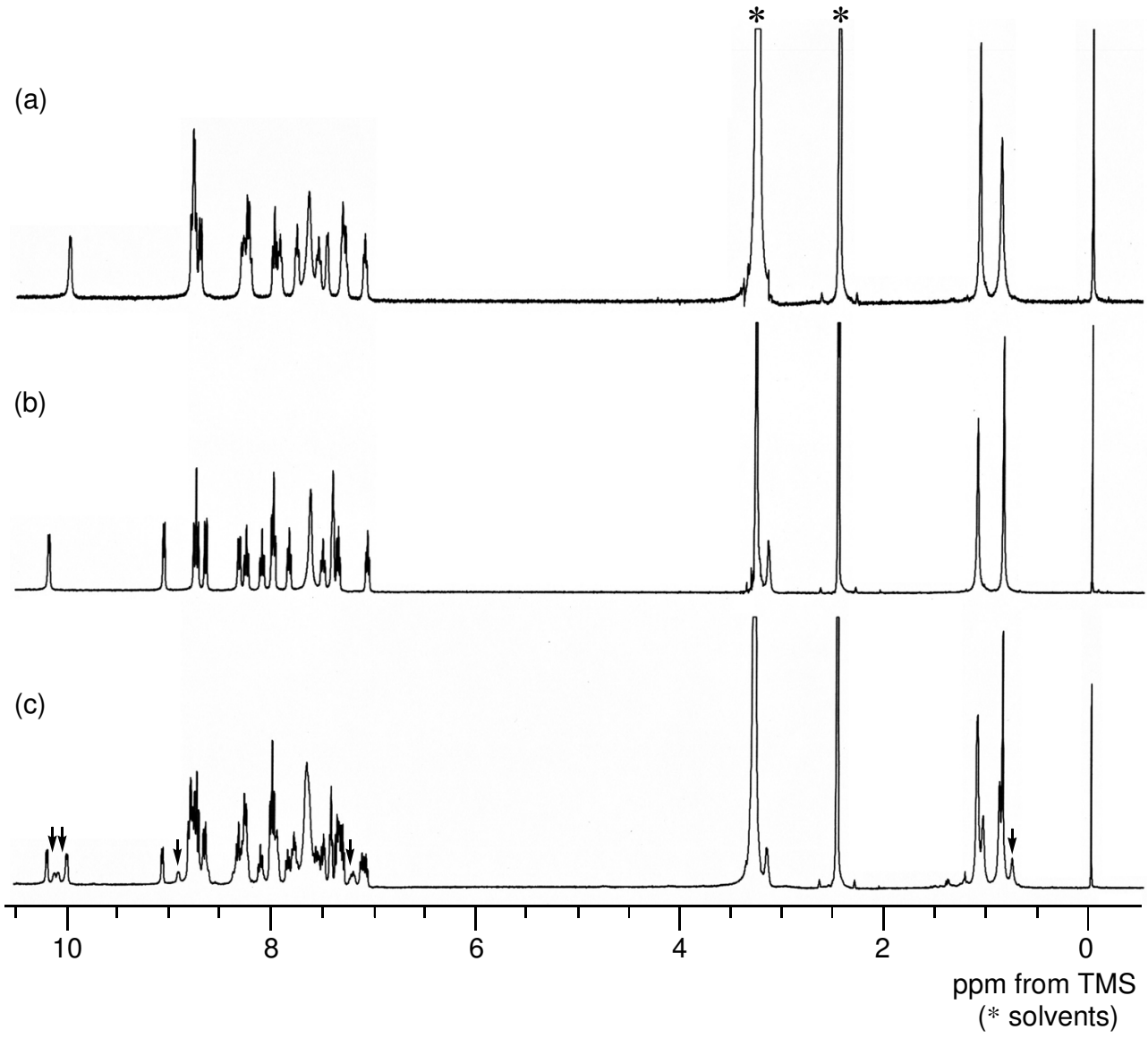

Figure S2. ^{1}H NMR spectra of (a) $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1a**](ClO$_4$)$_3$), (b) $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1b**](ClO$_4$)$_3$), and (c) mixture of [**1a**](ClO$_4$)$_3$) and [**1b**](ClO$_4$)$_3$ (1:1) in DMSO-d_6.

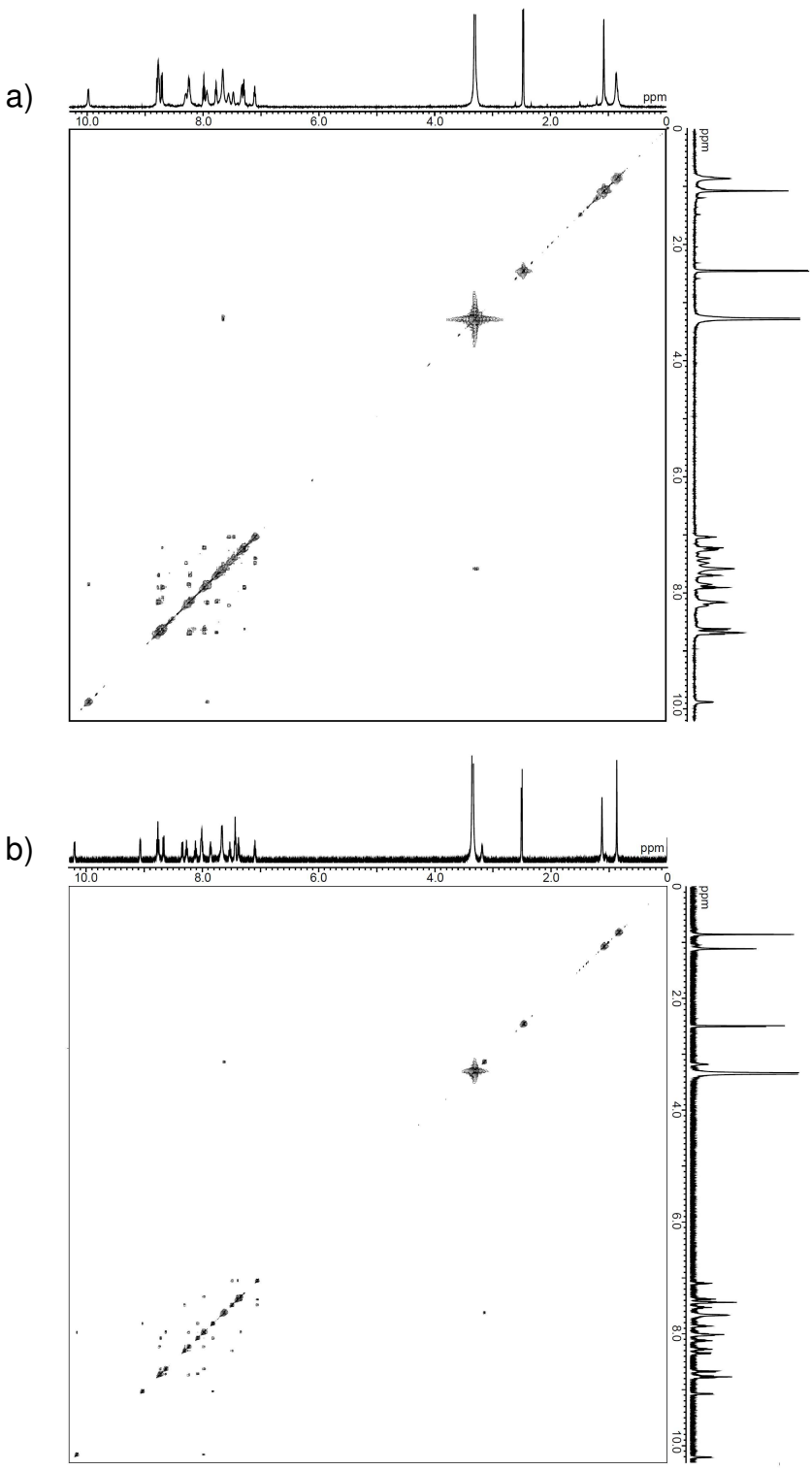

Figure S3. ^{1}H-^{1}H COSY spectra of (a) $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1a**](ClO$_4$)$_3$) and (b) $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1b**](ClO$_4$)$_3$) in DMSO-d_6.

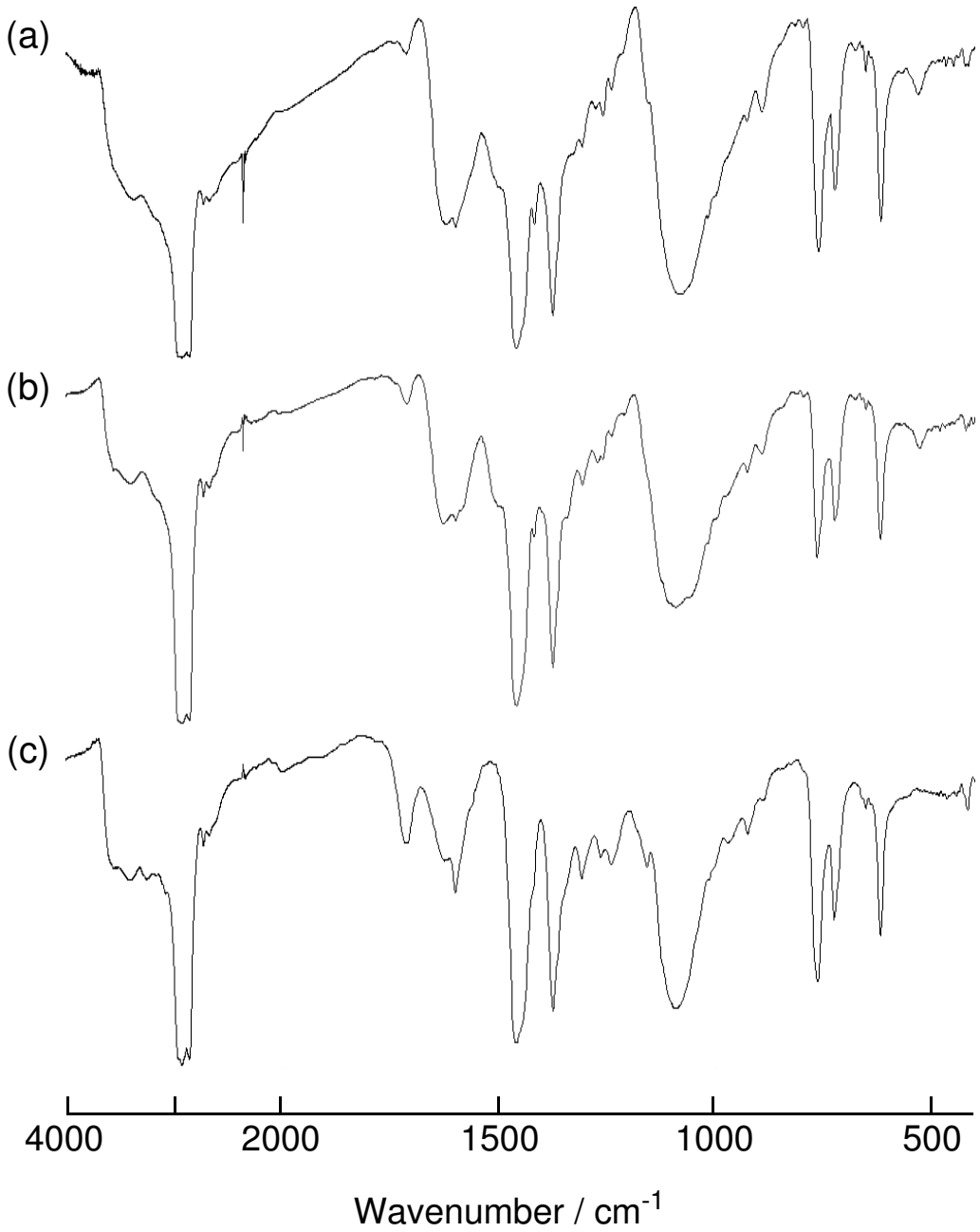

Figure S4. IR spectra (nujol mull) of (a) $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1a**](ClO$_4$)$_3$), (b) $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**1b**](ClO$_4$)$_3$), and (c) $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*N*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$ ([**2a**](ClO$_4$)$_3$).

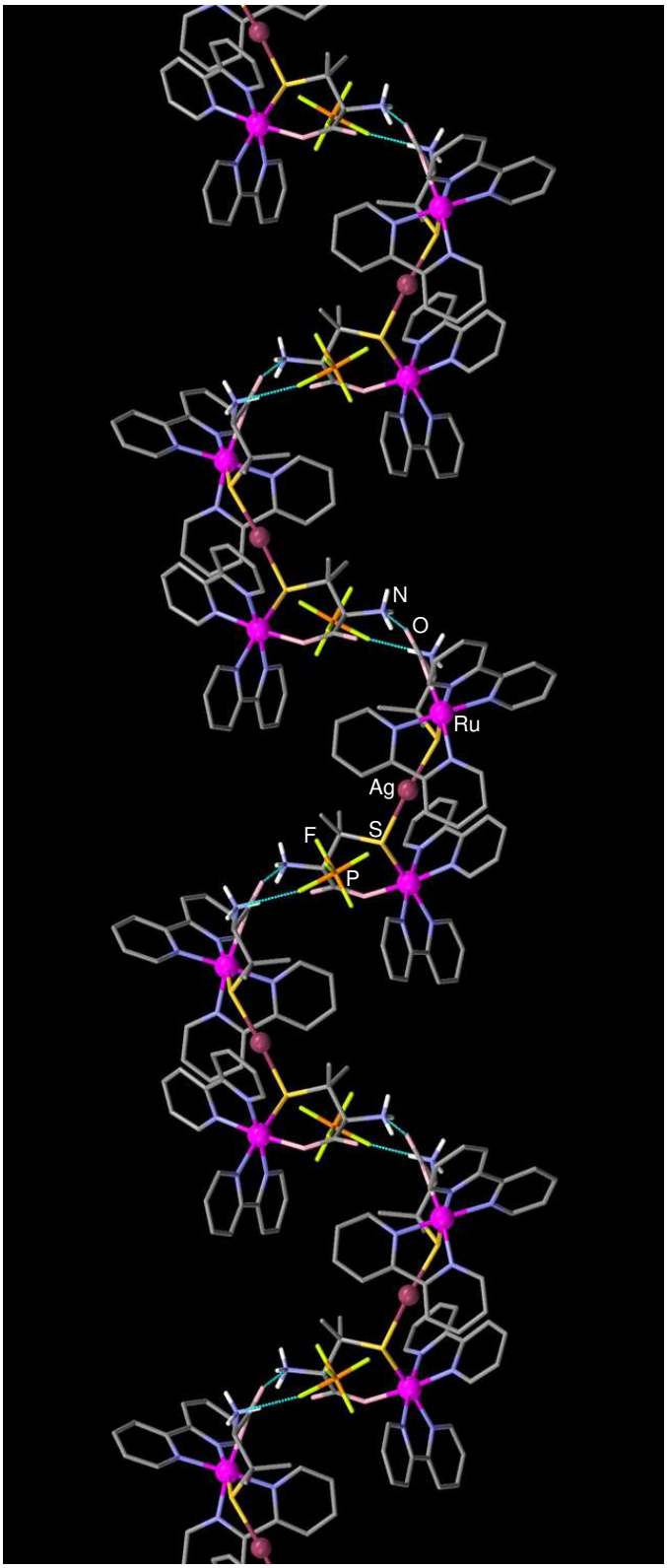

Figure S5. 1D helix structure of [**1b**]$(PF_6)_2(NO_3)$. Nitrate and hexaphosphate anions that do not participate in hydrogen bonding interaction are omitted.

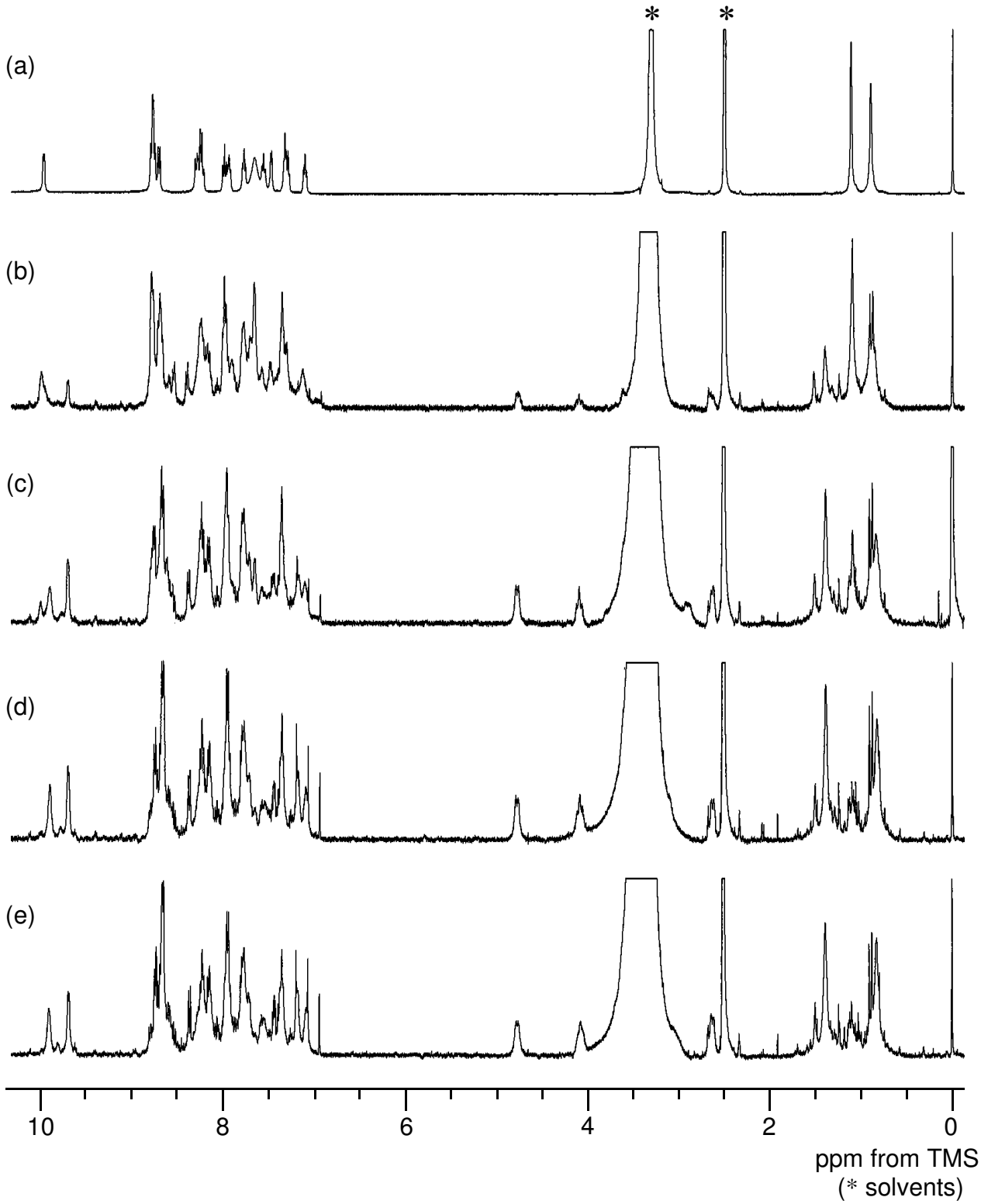

Figure S6. ^{1}H NMR spectra of [**1a**]$(ClO_4)_3$ heated at 85 °C in DMSO-d_6 under N_2; (a) 0 hour, (b) 1 hour, (c) 3 hours, (d) 6 hours, and (e) 9 hours.

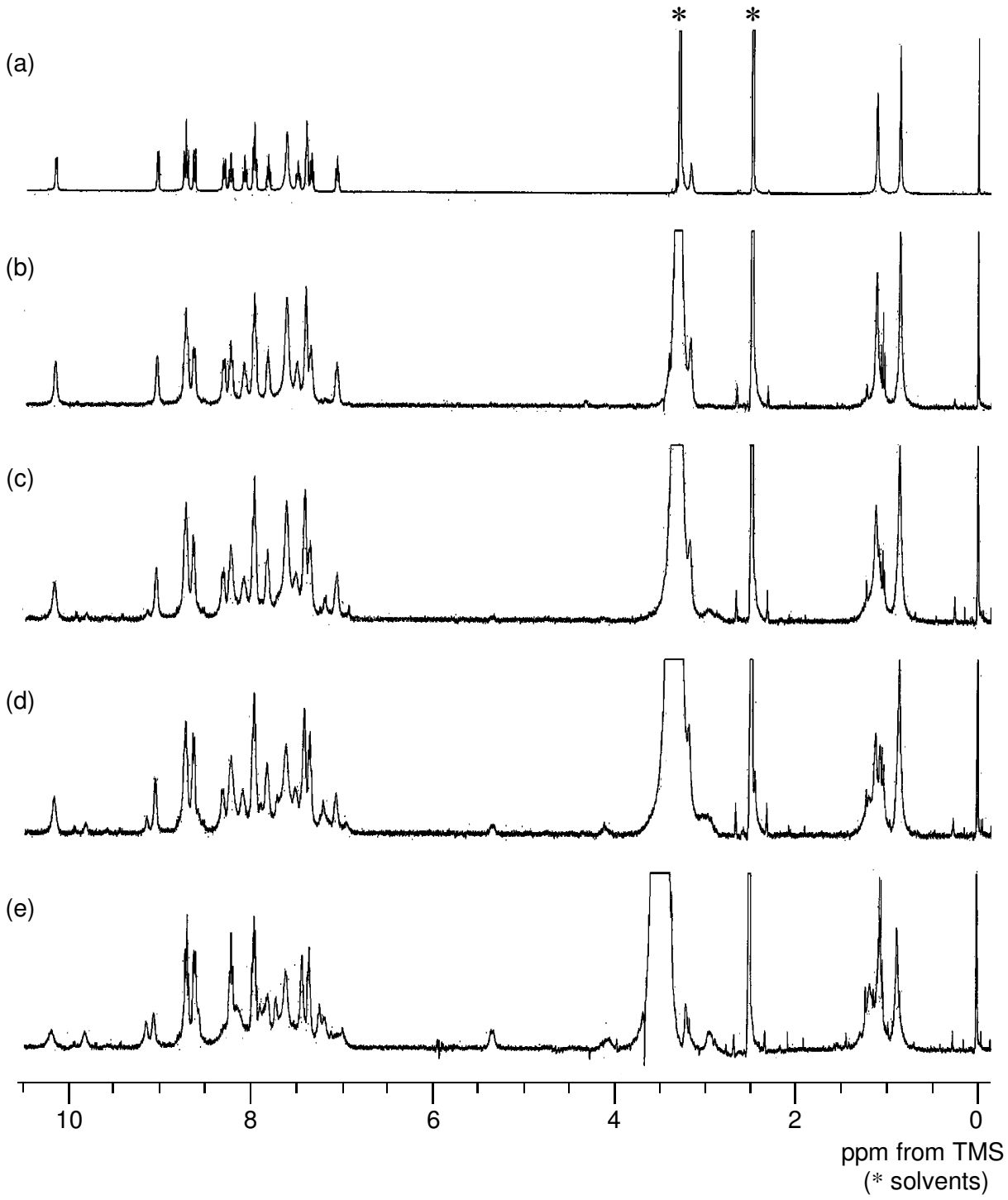

Figure S7. ^{1}H NMR spectra of [**1b**]$(ClO_4)_3$ heated at 85 °C in DMSO-d_6 under N_2; (a) 0 hour, (b) 1 hour, (c) 3 hours, (d) 6 hours, and (e) 9 hours.

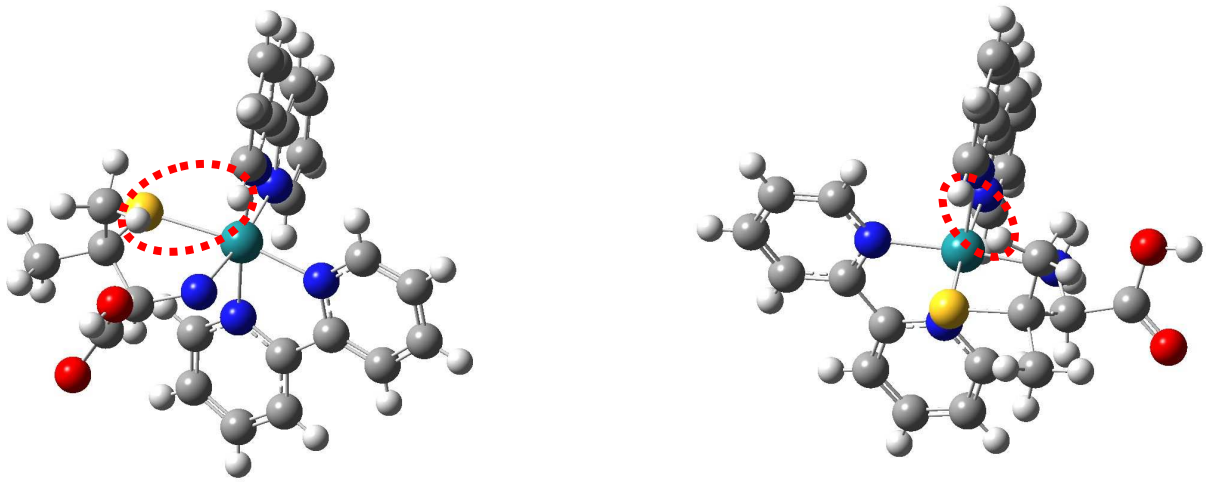

Figure S8. Schematic representation of steric hindrance in the $\Lambda_D\Lambda_D$ (a) and $\Delta_D\Delta_D$ (b) isomers with N,S chelating D-pen ligands. A Ru^{II} octahedral unit of each isomer is shown for clarity.