Supplementary Information

Isomerization Reaction of Head-to-Head α-Pyridonato-Bridged Ethylenediamine-palladium(II) Binuclear Complex, [Pd₂(en)₂(C₅H₄NO)₂]²⁺, in Aqueous Solution

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Table S1. Observed rate constants for the reaction of $[Pd(en)(H_2O)_2]^{2+}$ with α-pyridone ($I = 0.10$ mol dm^{-3}, 20°C, $C_L = 4 \times 10^{-4}$ mol dm^{-3})

[H⁺] / mmol dm⁻³	C_{Pd} / mmol dm⁻³	$10^2\, k_{obs}$ / s⁻¹
2.50	16	1.89
	20	2.20
	24	2.53
	28	2.84
5.00	16	1.65
	20	1.92
	24	2.18
	28	2.46
7.50	16	1.59
	20	1.83
	24	2.09
	28	2.35
10.0	16	1.55
	20	1.80
	24	2.07
	28	2.31

Table S2. The concentrations of the dimers (HH and HT) and monomers (A, B, C, and their deprotonated species) estimated by the ^{1}H NMR peak integrals at $I = 0.1$ M and 26°C after completion of the reaction [a]

pD	$C_{L(add)}$ / mmol dm^{-3}	[species] / mmol dm^{-3} [b]							
		[HH]	[HT]	[A'] ([A$_1$]+[A$_2$])	[A''] ([A$_3$])	[B'] ([B$_1$]+[B$_2$])	[B''] ([B$_3$])	[C'] ([C$_1$]+[C$_2$])	[L'] ([L]+[HL$^+$])
1.16	0	c	c	0.9	c	6.2	c	8.9	8.0
2.26	0	c	c	1.5	c	7.6	c	7.0	5.4
3.21	0	0.7	0.4	1.3	c	6.5	c	6.0	4.8
3.41	0	1.3	0.8	1.0	c	5.4	0.2	5.2	4.3
3.55	0	1.5	0.9	0.9	c	4.9	0.2	5.2	4.2
3.67	0	1.9	1.2	0.8	c	4.3	0.3	4.4	3.9
4.19	0	3.1	1.9	0.3	c	2.0	0.6	3.1	2.7
5.21	0	3.8	2.2	0.2	c	1.0	1.1	1.7	1.6
6.1	0	3.7	2.2	c	0.5	0.7	1.4	1.6	1.1
3.36	8.0	1.2	0.7	2.3	c	6.5	c	3.4	9.1
3.49	8.0	1.7	1.0	2.1	c	5.8	c	2.7	8.6
4.05	8.0	3.3	1.9	1.1	c	2.7	0.3	1.5	8.3
5.39	8.0	4.3	2.5	0.8	c	1.0	0.3	0.3	7.5

[a] $C_{HH} = 8.0$ mmol dm^{-3}. [b] HH = HH-[Pd$_2$(en)$_2$(α-pyridonato)$_2$]$^{2+}$, HT = HT-[Pd$_2$(en)$_2$(α-pyridonato)$_2$]$^{2+}$, A$_1$ = [Pd(en)(α-pyridone)$_2$]$^{2+}$, A$_2$ = [Pd(en)(α-pyridone)(α-pyridonato)]$^{+}$, A$_3$ = [Pd(en)(α-pyridonato)$_2$]^{0}, B$_1$ = [Pd(en)(OH$_2$)(α-pyridone)]$^{2+}$, B$_2$ = [Pd(en)(OH$_2$)(α-pyridonato)]$^{+}$, B$_3$ = [Pd(en)(OH)(α-pyridonato)]^{0}, C$_1$ = [Pd(en)(OH$_2$)$_2$]$^{2+}$, C$_2$ = [Pd(en)(OH$_2$)(OH)]$^{+}$, L = α-pyridone, and HL^{+} = protonated α-pyridone. [c] Not observed.
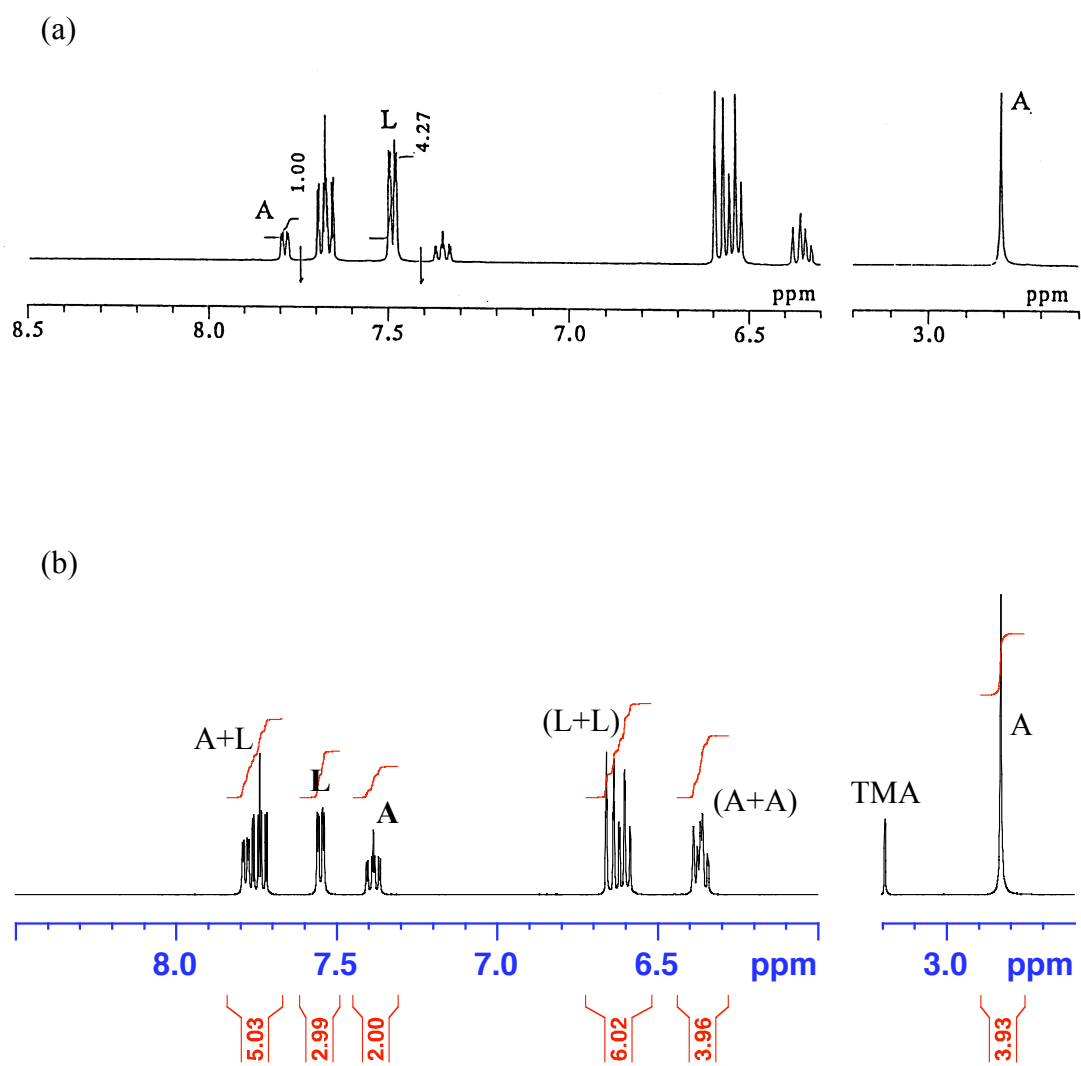
Fig. S1. ^{1}H NMR spectra of the solution containing [Pd(en)(H$_2$O)$_2$](ClO$_4$)$_2$ and α-pyridone at $C_M:C_L$ = 1:10 and pH = 6.06 (a), and $C_M:C_L$ = 1:5 and pD 7.6 (b). The chemical shifts are referenced to TSP-d_4 as an external reference (a) and TMA as an internal reference (b).

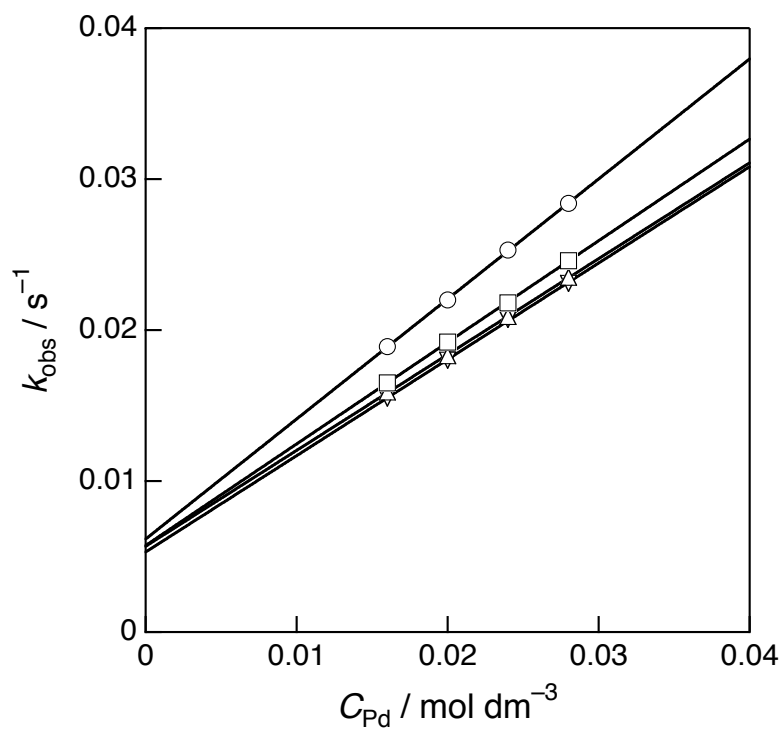**Fig. S2.** The dependence of the conditional pseudo first-order rate constant (k_{obs}) on C_{Pd} for the reaction of $[Pd(en)(H_2O)_2]^{2+}$ with α-pyridone (L) in acidic aqueous solution at 20°C. C_L = 4 x 10^{-4} mol dm^{-3}. [H$^+$] / mol dm^{-3} = 2.50 x 10^{-3} (○), 5.00 x 10^{-3} (□), 7.50 x 10^{-3} (▽), and 1.00 x 10^{-2} (△).
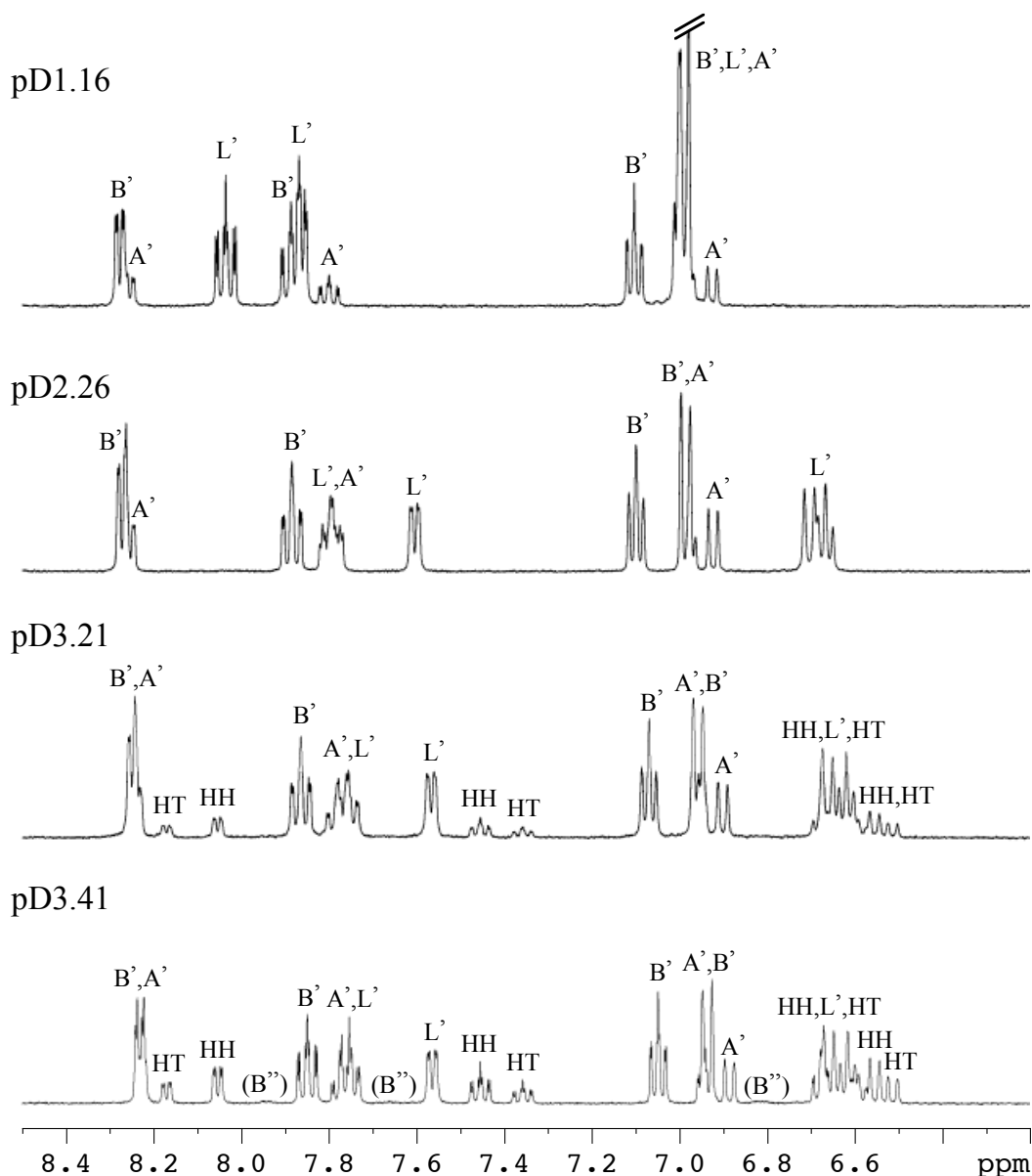
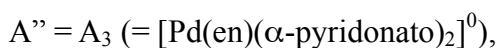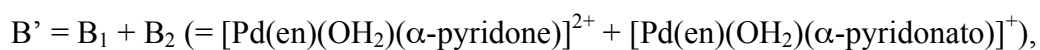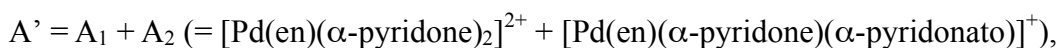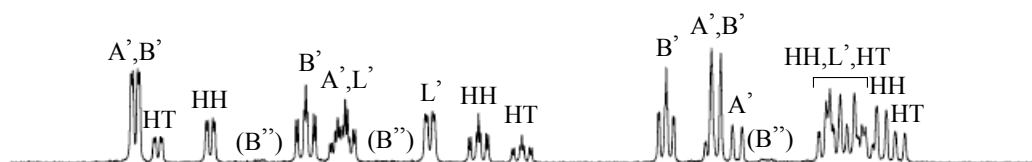**Fig. S3.** Detailed assignments of the ^1H NMR signals in the region of α-pyridone moiety (8.5–6.2 ppm). $C_{HH} = 8.0$ mM, $C_{L(add)} = 0$ M, $I = 0.1$ M, and $T = 26°C$. Symbol notations used in this figure are as follows;
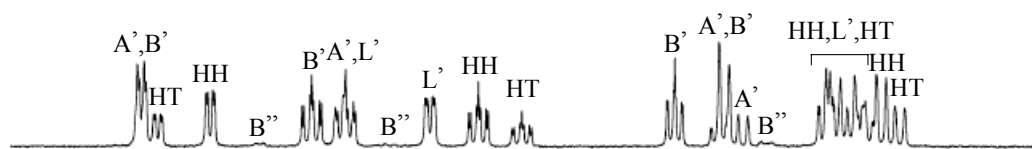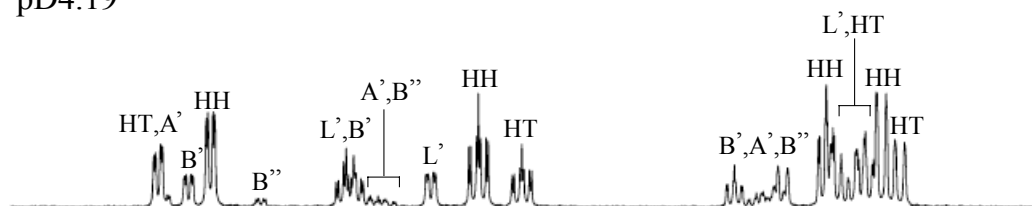
HH and HT = HH- and HT-$[Pd_2(en)_2(\alpha\text{-pyridonato})_2]^{2+}$,

A' = $A_1 + A_2$ (= $[Pd(en)(\alpha\text{-pyridone})_2]^{2+}$ + $[Pd(en)(\alpha\text{-pyridone})(\alpha\text{-pyridonato})]^+$),

B' = $B_1 + B_2$ (= $[Pd(en)(OH_2)(\alpha\text{-pyridone})]^{2+}$ + $[Pd(en)(OH_2)(\alpha\text{-pyridonato})]^+$),

A" = A_3 (= $[Pd(en)(\alpha\text{-pyridonato})_2]^0$),

B" = B_3 (= $[Pd(en)(OH)(\alpha\text{-pyridonato})]^0$),
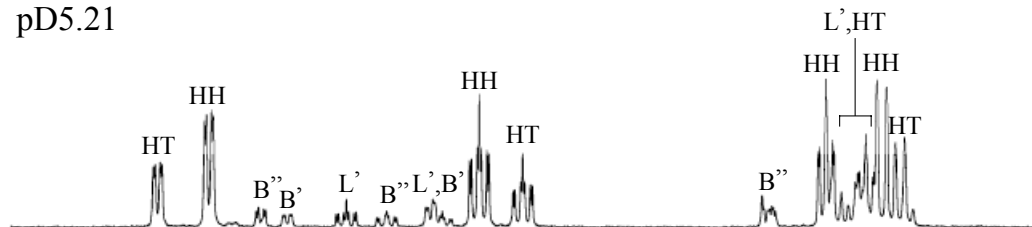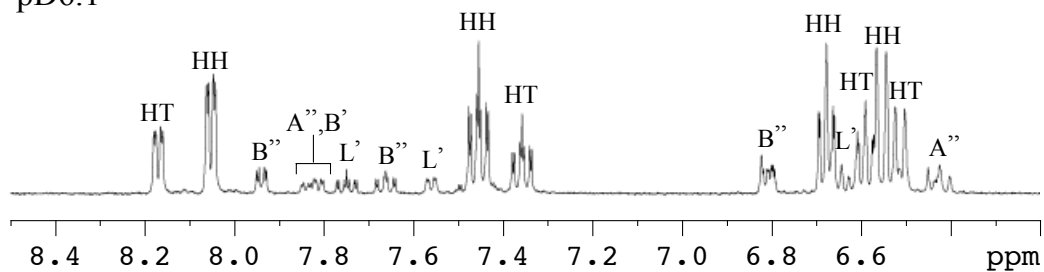
L' = L + HL$^+$ (= α-pyridone and protonated α-pyridone).
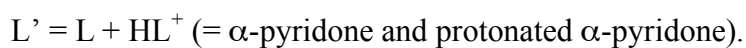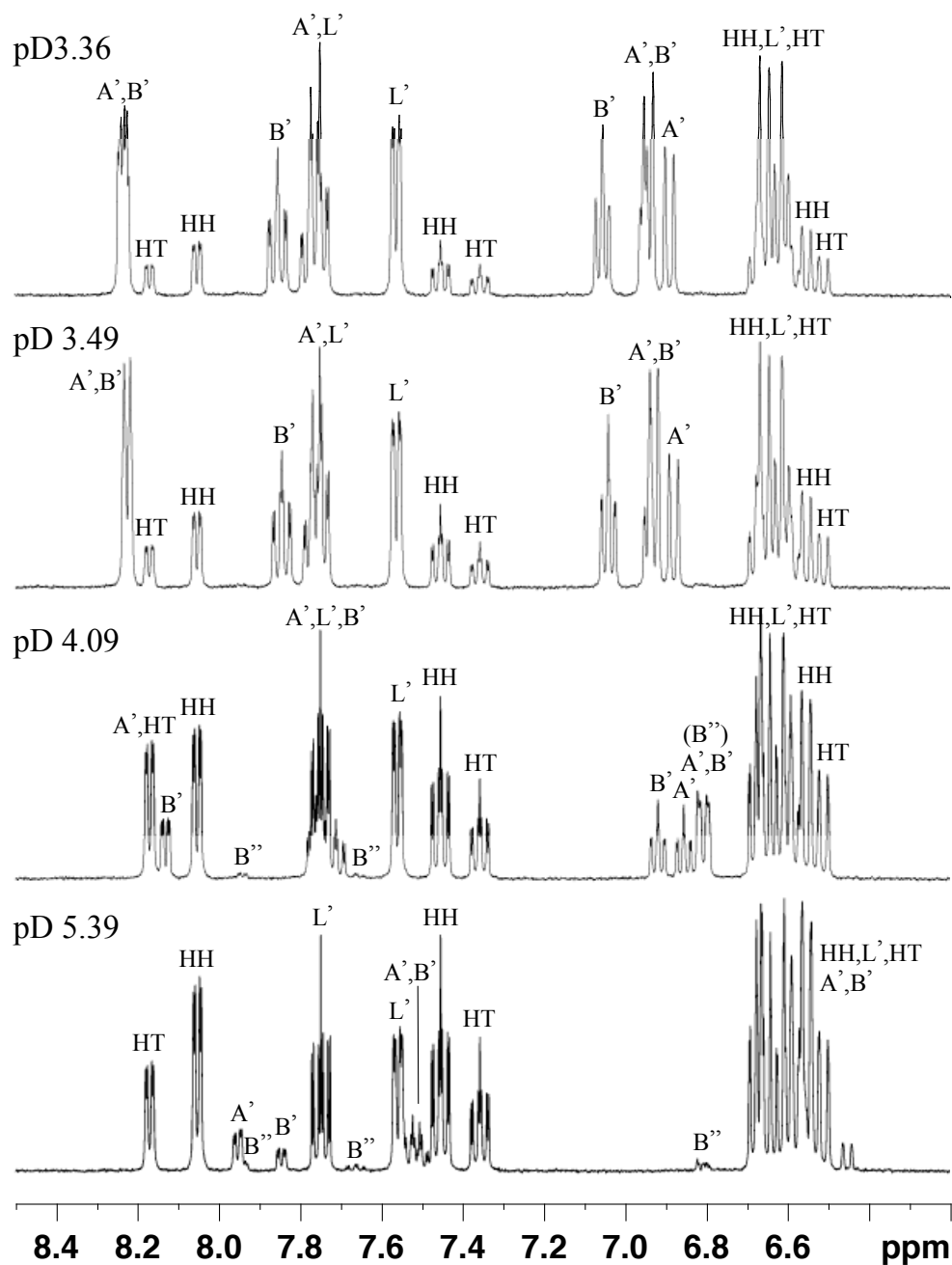
(**Fig. S3**, continued.)

Fig. S4. Detailed assignments of the ^{1}H NMR signals in the region of α-pyridone moiety (8.5–6.2 ppm) in the presence of excess free ligand ($C_{L(add)}$ = 8.0 mmol dm^{-3}). C_{HH} = 8.0 mmol dm^{-3}, I = 0.1 mol dm^{-3}, and T = 26°C. Symbol notations used in this figure are same as those in Fig. S3.
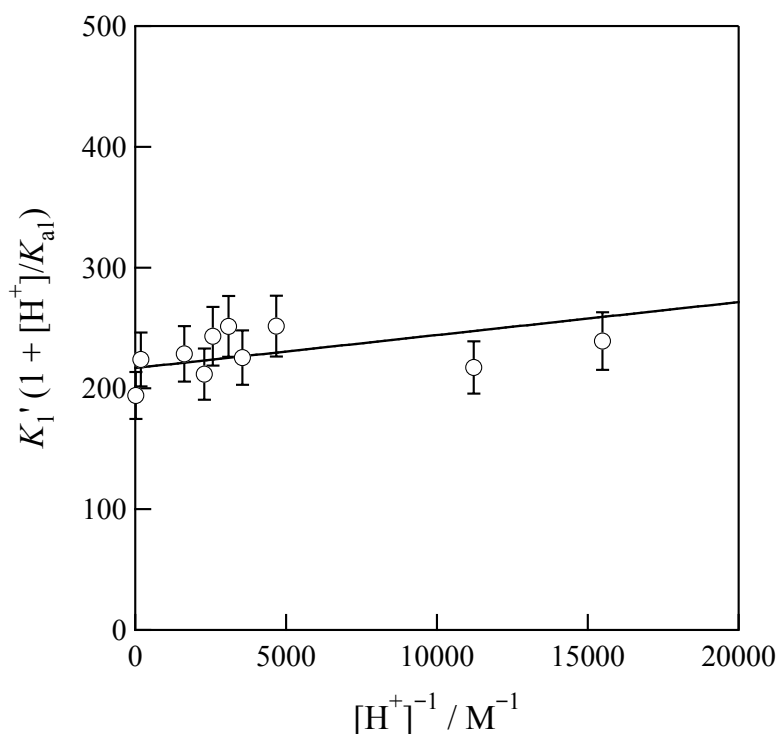
Fig. S5. The plot of K_1'$(1+[H^+]/K_{a1})$ against $[H^+]^{-1}$ in Scheme 2. The unavoidable error of each plot (~10%) comes from the peak integration analysis of the NMR data.
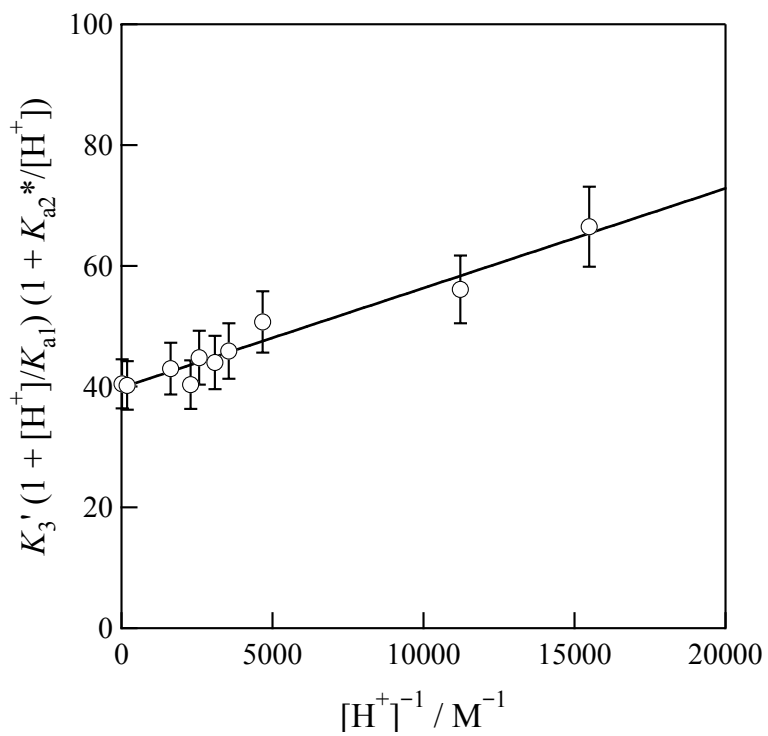
Fig. S6. The plot of K_3'$(1+[H^+]/K_{a1})(1+K_{a2}*/[H^+])$ against $[H^+]^{-1}$ in Scheme 2. The unavoidable error of each plot (~10%) comes from the peak integration analysis of the NMR data.
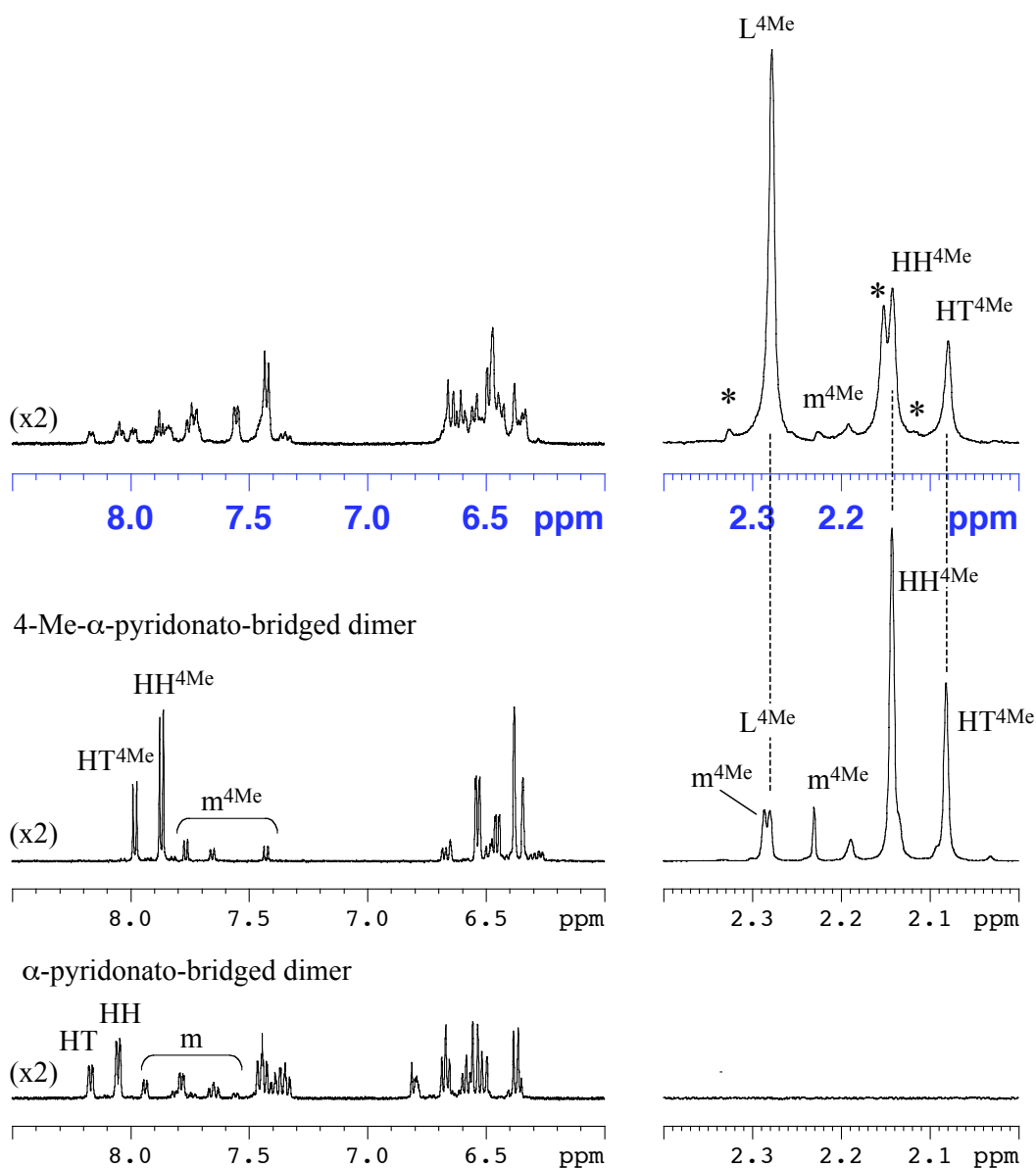
Fig. S7. The ^{1}H NMR spectrum of the reaction mixture of the α-pyridonato-bridged dimer (C_{HH} = 0.0144 mol dm^{-3}) and 4-methyl-α-pyridone (L^{4Me}, C_{L4Me} = 0.034 mol dm^{-3}) (top). For reference, the ^{1}H NMR spectra of the 4-methyl-α-pyridonato-bridged dimer, [Pd$_2$(en)$_2$(4-methyl-α-pyridonato)$_2$]$^{2+}$ (middle), and the α-pyridonato-bridged dimer, [Pd$_2$(en)$_2$(α-pyridonato)$_2$]$^{2+}$ in D$_2$O (bottom) are also shown in this Figure. The symbol "*" denotes the signals of the mixed-ligand dimers and monomers.