Supplementary material:

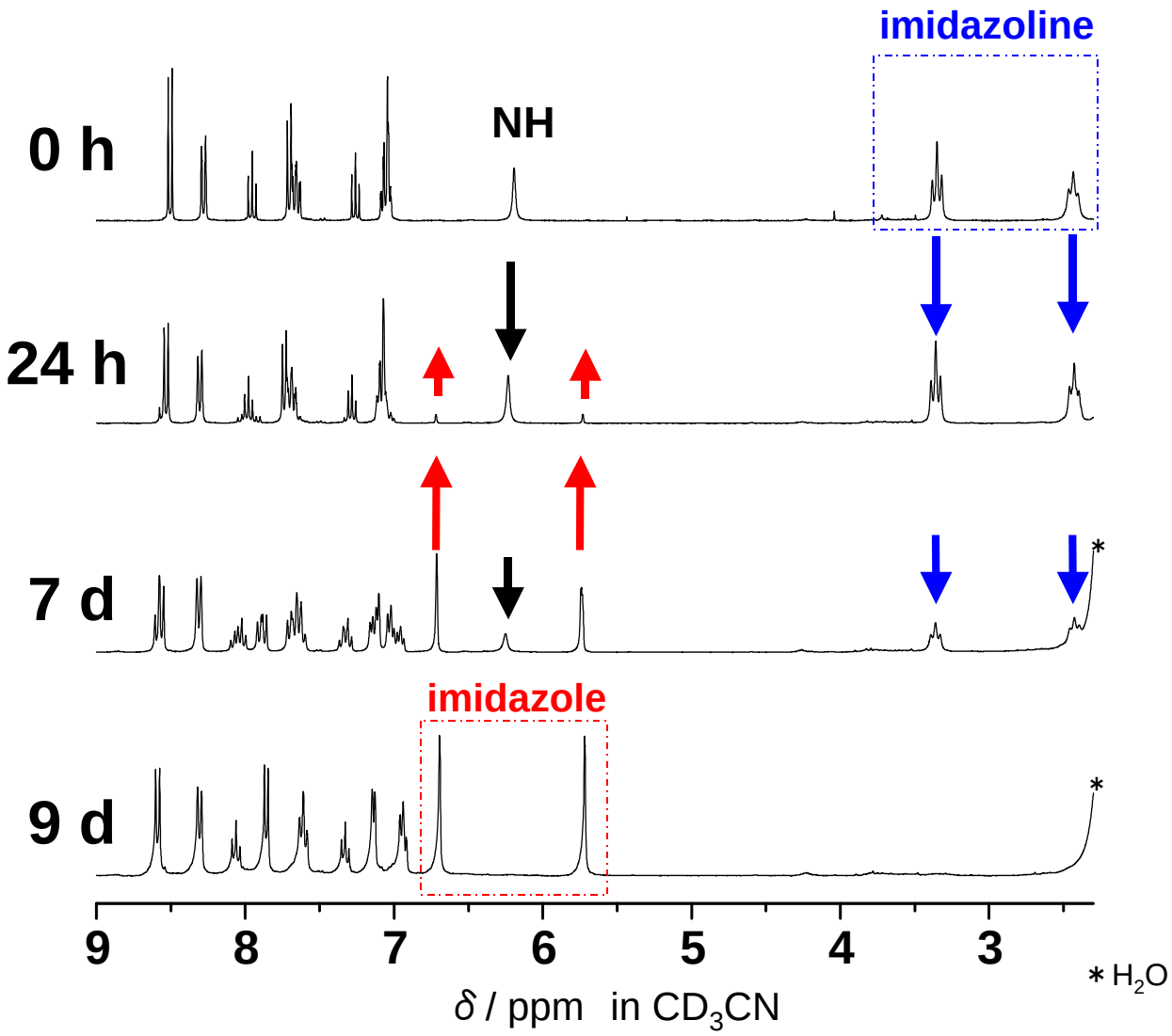

Figure S1 Time course of ^{1}H NMR spectrum of **1** in CD_3CN at 70 °C in air. A peak marked with an asterisk * is due to solvated water.

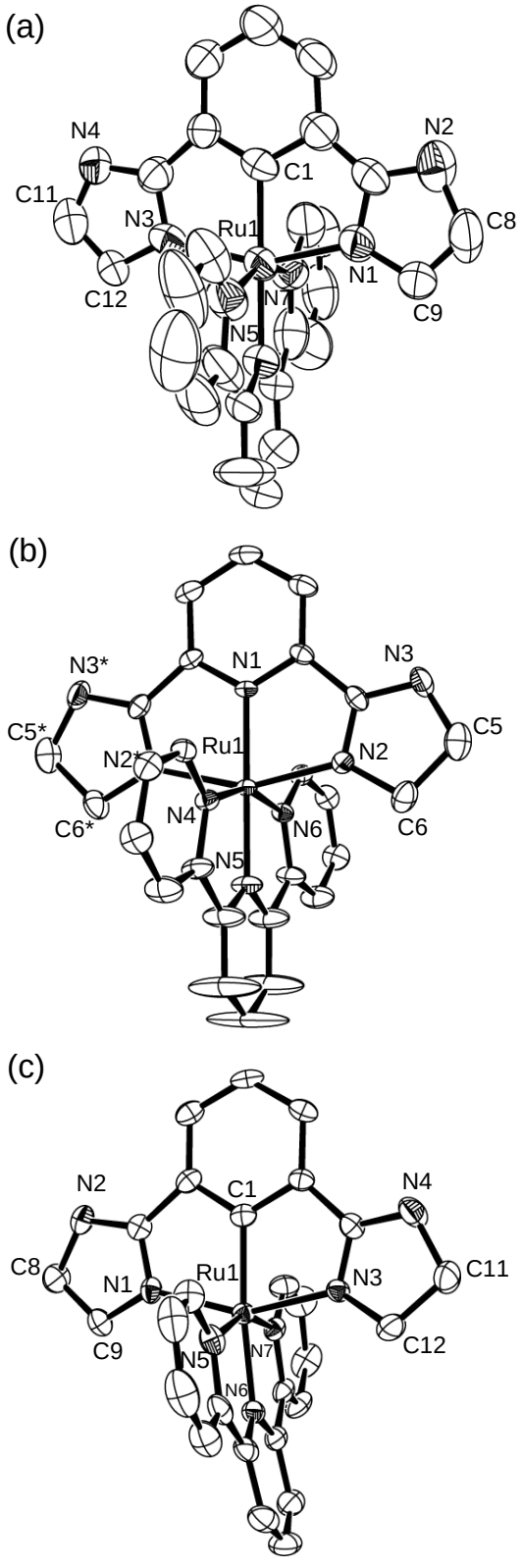

Figure S2 X-ray crystal structures of (a) **2** (b) **3**, and (c) **5** with thermal ellipsoids drawn at the 50% probability level. One of the two crystallographically independent molecules of **2** and one of the two crystallographically independent molecules of **5** are shown. Hydrogen atoms and PF_6^- anions and solvated

ether molecules are omitted for simplicity.

Selected bond lengths (Å) and angles (deg):

(a) Ru1-C1, 2.008(6); Ru1-N1, 2.100(7); Ru1-N3, 2.084(7); Ru1-N5, 2.071(7); Ru1-N6, 1.998(7); Ru1-N7, 2.067(6); C8-C9, 1.320(13); C11-C12, 1.357(12); N1-Ru1-N3, 155.2(2); N5-Ru1-N7, 155.5(2); N6-Ru1-C1, 179.1(3).

(b) Ru1-N1, 2.004(3); Ru1-N2, 2.070(3); Ru1-N4, 2.070(2); Ru1-N5, 1.972(4); C5-C6, 1.512(7); N2-Ru1-N2*, 155.23(11); N4-Ru1-N4*, 158.11(11); N1-Ru1-N5, 0.0.

(c) Ru1-C1, 1.988(4); Ru1-N1, 2.099(3); Ru1-N3, 2.084(2); Ru1-N5, 2.068(3); Ru1-N6, 2.009(3); Ru1-N7, 2.055(2); C8-C9, 1.376(7); C11-C12, 1.468(7); N1-Ru1-N3, 154.18(12); N5-Ru1-N7, 156.53(13); N6-Ru1-C1, 174.24(13).

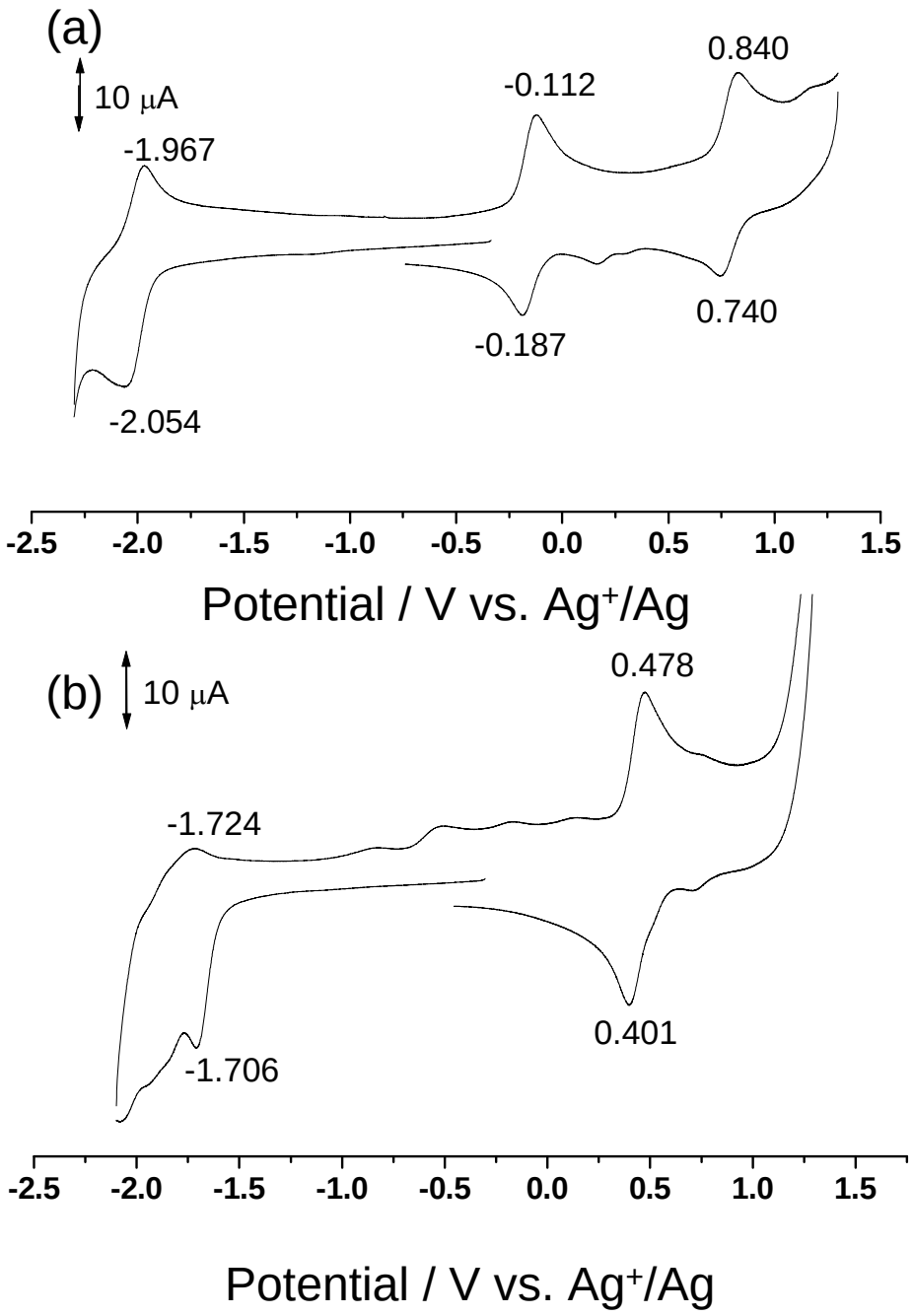

Figure S3 Cyclic voltammograms of (a) **1** and (b) **3** (1.0 mM) in CH_3CN containing $[(n\text{-}Bu)_4N][PF_6]$ (0.1 M) under N_2. Sweep rate = 50 mV s^{-1}.

Table S1 Crystal data and details of the structure refinements for **1**, **2**, **3**, and **5**

	1·0.5MeCN	**2**·1.5Et_2O [a]	**3**	**5**
Formula	$C_{28}H_{25.5}F_6N_{7.5}PRu$	$C_{33}H_{35}F_6N_7O_{1.5}PRu$	$C_{26}H_{24}F_{12}N_8P_2Ru$	$C_{27}H_{22}F_6N_7PRu$
Formula Weight	713.09	799.72	839.53	690.55
Crystal Color	red	red	red	red
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Lattice Parameters				
a/Å	15.7319(19)	14.580(7)	17.595(7)	17.876(5)
b/Å	27.039(3)	14.084(6)	20.288(8)	13.583(4)
c/Å	26.819(3)	36.532(17)	9.032(4)	22.628(6)
β/°	92.1710(5)	103.512(5)	113.6524(15)	97.1482(17)
V/ Å^3	11400(2)	7294(6)	2953(2)	5452(3)
Space Group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
Z value	16	8	4	8
μ(MoKα) / cm^{-1}	6.800	5.426	7.516	7.075
F(000)	5744	3256	1672	2768
No. Reflections Measured				
Total	86254	38231	10128	39968
Unique	25335	38200	3318	12138
Observations	25335	38200	3318	12138
	all data	all data	all data	all data
D_{calc}/g cm^{-3}	1.662	1.518	1.888	1.683
Structure Solution	Direct Methods (SIR92)	Direct Methods (SIR92)	Direct Methods (SIR92)	Direct Methods (SIR92)
Reflection/Parameter Ratio	15.19 [b]	45.86 [c]	13.77	13.01
R_1	0.0464 ($I > 2.0\sigma(I)$)	0.1552 ($I > 2.0\sigma(I)$)	0.0483 ($I > 2.0\sigma(I)$)	0.0397 ($I > 2.0\sigma(I)$)
R	0.0797 (all data)	0.1788 (all data)	0.0524 (all data)	0.0739 (all data)
*R*w	0.1122 (all data)	0.3160 (all data)	0.0726 (all data)	0.0442 (all data)
Goodness of Fit Indicator	1.001	1.264	0.938	0.942

[a] Despite several attempts, X-ray quality single crystals of **2** could not be obtained.

[b] Involving the four crystallographically independent molecules of **1**.

[c] Involving the two crystallographically independent molecules of **2**.