Supporting Information

Additional experimental methods:

Materials: $Na_2WO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 2H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $Y(NO_3)_3 \cdot 9H_2O$, $H_3[\alpha\text{-}PMo_{12}O_{40}] \cdot nH_2O$, conc. HCl, cyanoacetic acid, acetone, methanol, butanol, toluene, benzaldehyde and distilled water were purchased from Kanto Chemical Co. Inc. and used as received. $H_3[\alpha\text{-}PW_{12}O_{40}] \cdot nH_2O$ was synthesized according to the literature.[S1] Allyltributyltin and 1,2-dimethoxybenzene (internal standard) were purchased from TCI Co. Ltd. and used as received. $InCl_3 \cdot 4H_2O$ was purchased from FUJIFILM Wako Pure Chemical Corporation.

Synthesis of $[Cr_3O(OOCCH_2CN)_6(H_2O)_3](NO_3)$: $Cr(NO_3)_3 \cdot 9H_2O$ (40 g, 0.10 mol) and cyano acetic acid (25 g, 0.29 mol) were dissolved in 300 mL of acetone, and the solution was stirred at 333 K for 6 h. The solution was concentrated by evaporation, water was added as a poor solvent, and $[Cr_3O(OOCCH_2CN)_6(H_2O)_3](NO_3)$ was obtained as a green powder (22 g, yield 90 % based on cyanoacetic acid).

[S1] J. C. Bailar Jr., H. S. Booth and M. Grennert, *Inorg. Synth.*, 1939, **1**, 132.

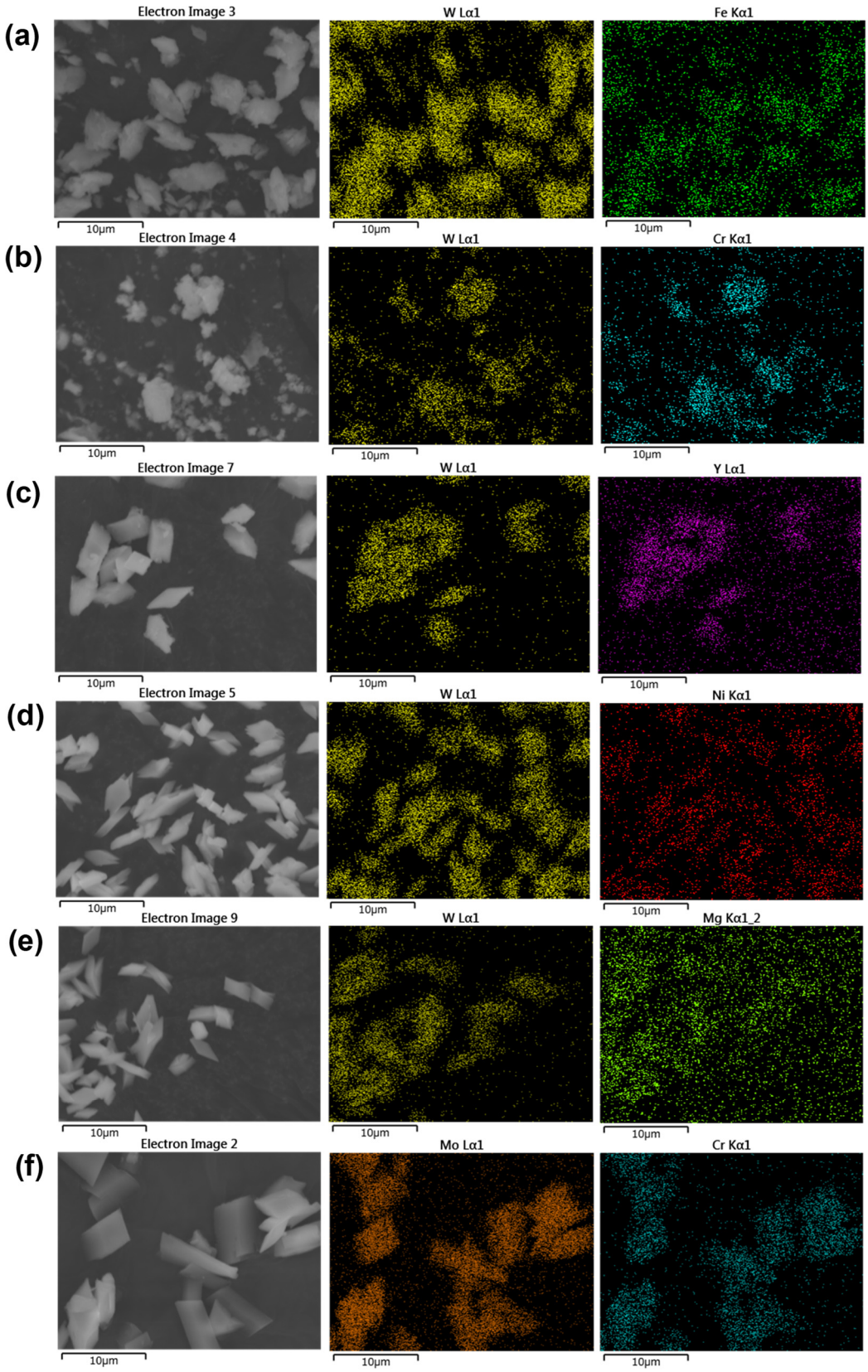

Figure S1. SEM-EDX images: (a) **I-Fe^{3+}**, (b) **I-Cr^{3+}**, (c) **I-Y^{3+}**, (d) **I-Ni^{2+}**, (e) **I-Mg^{2+}**, and (f) **II-Cr^{3+}**. SEM images (left), elemental maps of tungsten or molybdenum in the POMs (middle), and elemental maps of the incorporated metals (right).

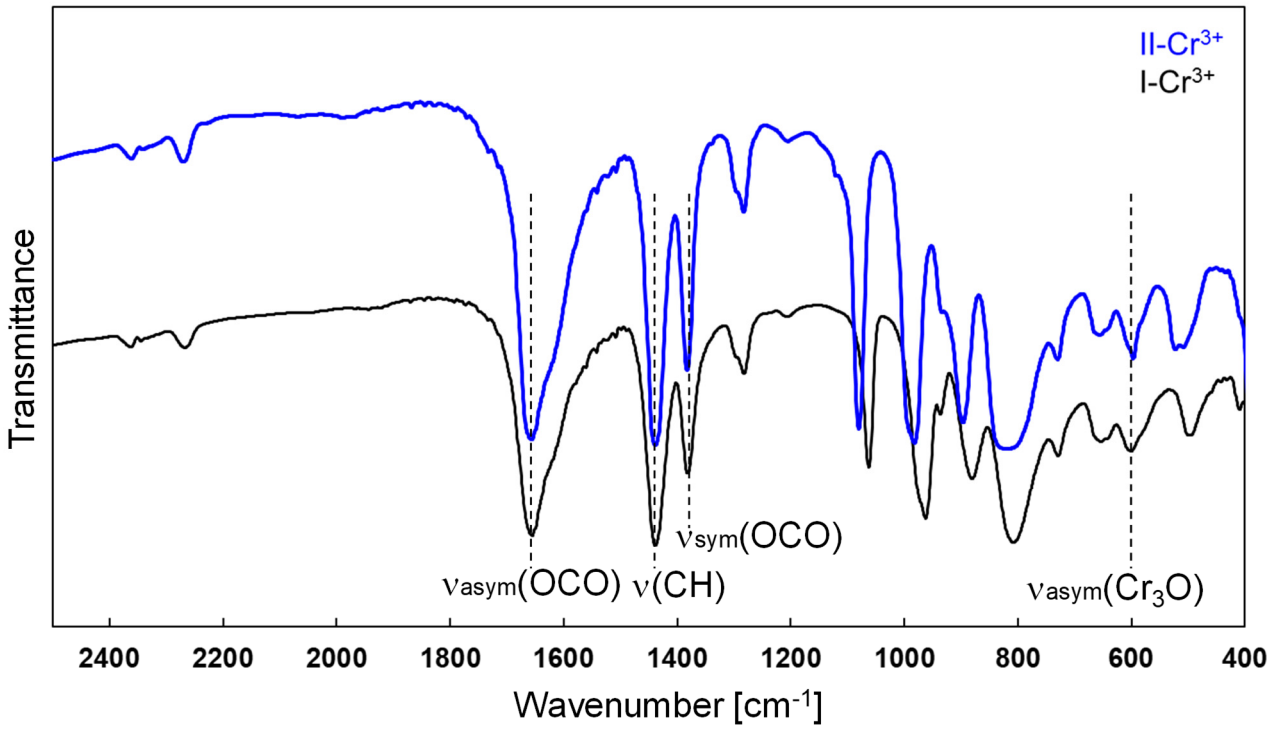

Figure S2. IR spectra of **I-Cr^{3+}** and **II-Cr^{3+}** measured by KBr method. Band assignments of the macrocation are shown.

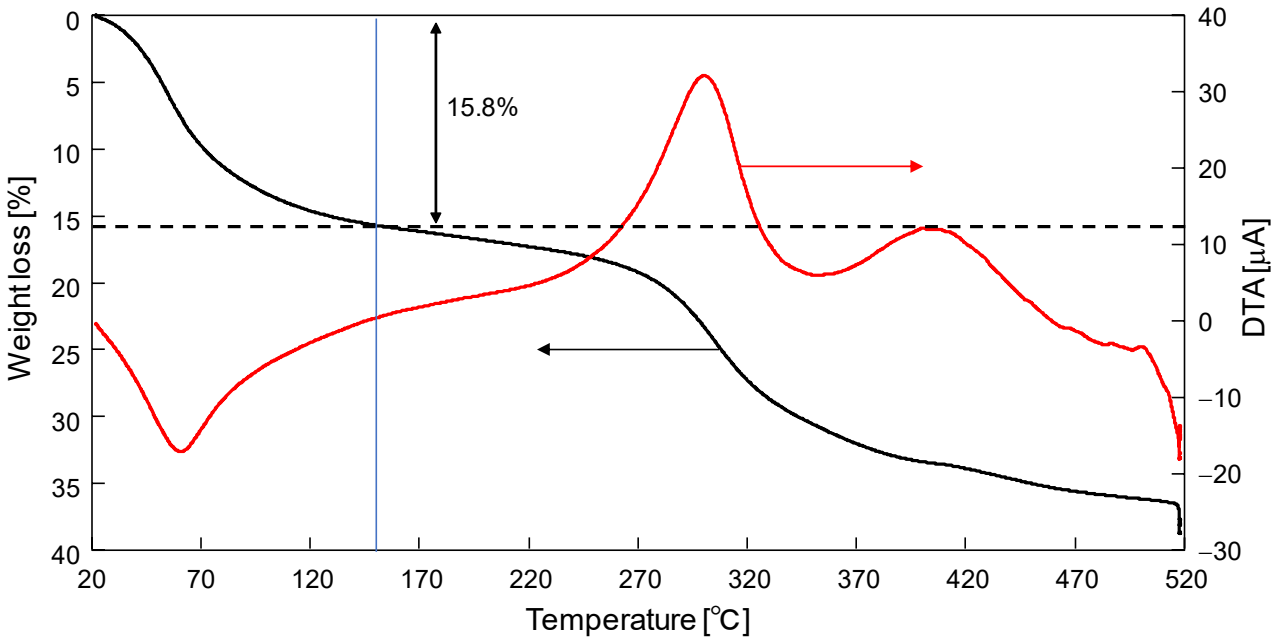

Figure S3. Thermogravimetry of **II-Cr**$^{3+}$. The weight loss up to 150 °C is 15.8% and is equal to the weight of 50 water of crystallization and 9 water ligands of the macrocation.

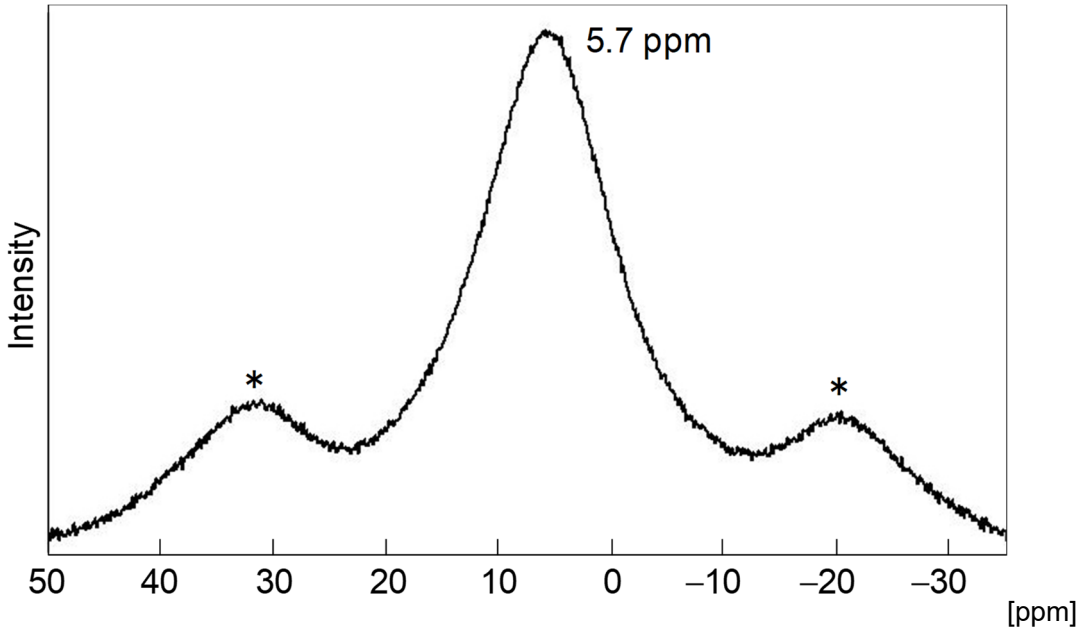

Figure S4. Solid-state ^{1}H-MASNMR spectrum of **II-Cr^{3+}** (MAS = 10kHz). Asterisks denote the spinning side bands.

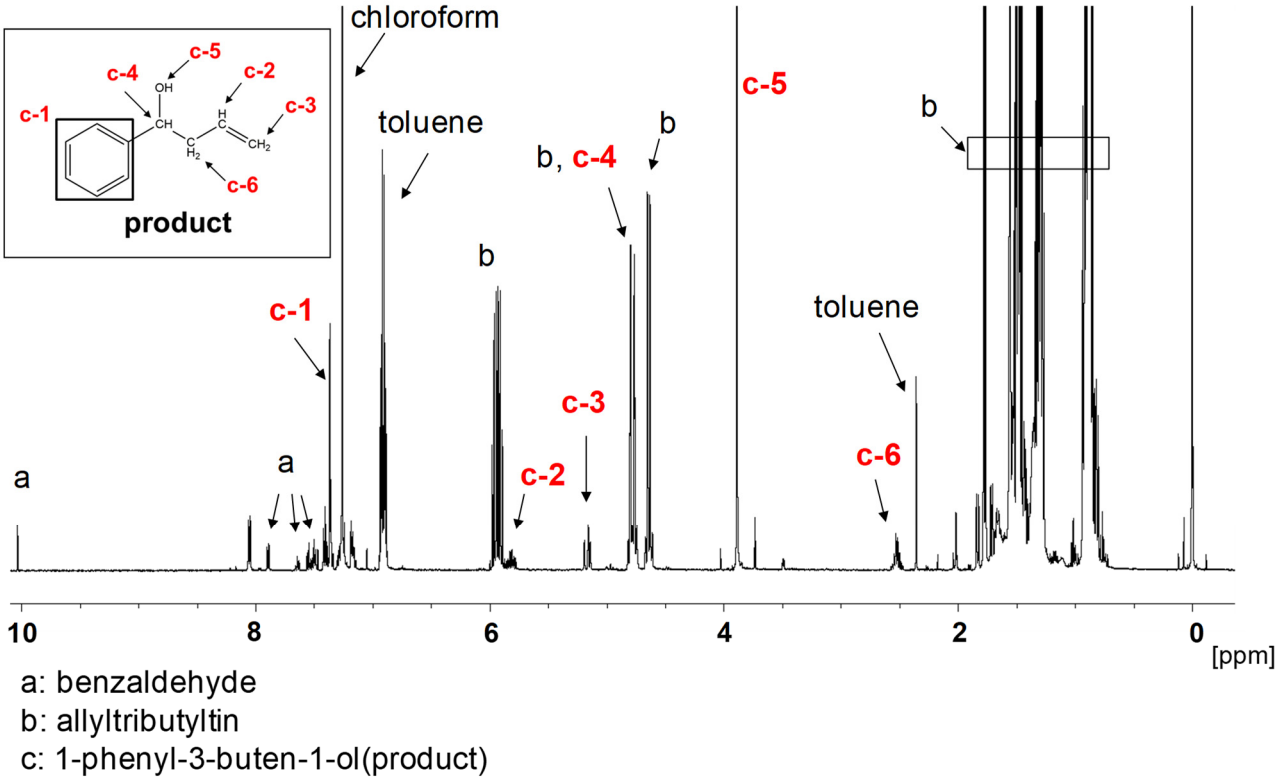

Figure S5. ^{1}H-NMR spectrum of the reaction solution.

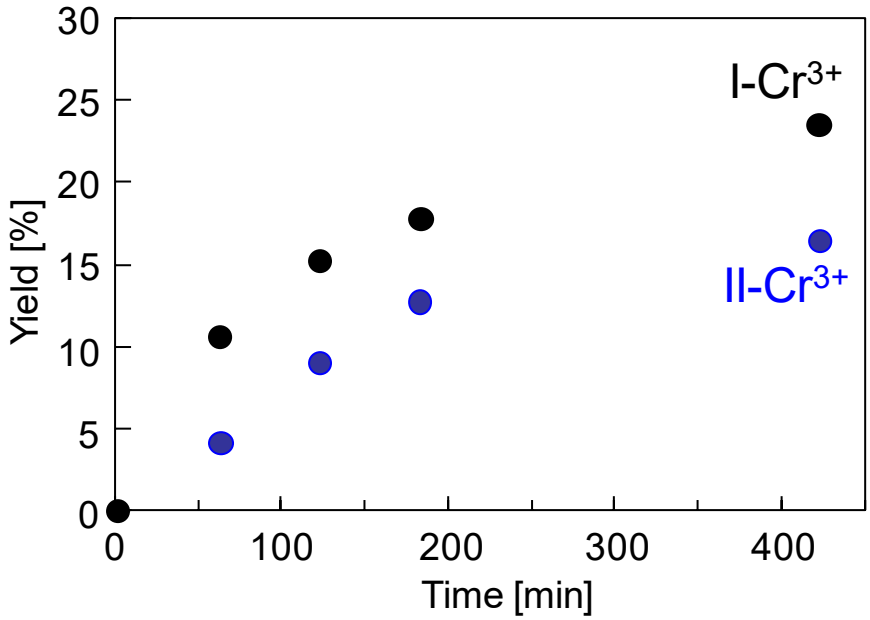

Figure S6. Time courses of the Barbier-Grignard reaction catalyzed by **I-Cr^{3+}** or **II-Cr^{3+}**.