Supporting Information

Photoinduced Reversible Assembly of Polynuclear Complexes from Ru-Containing Ionic Liquids with Accompanying Ionic Conductivity Modulations

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Table S1. Crystallographic parameters for $[CpRu(C_6H_6)][(CpRu)_2\{BF_2(CN)_2\}_3]$

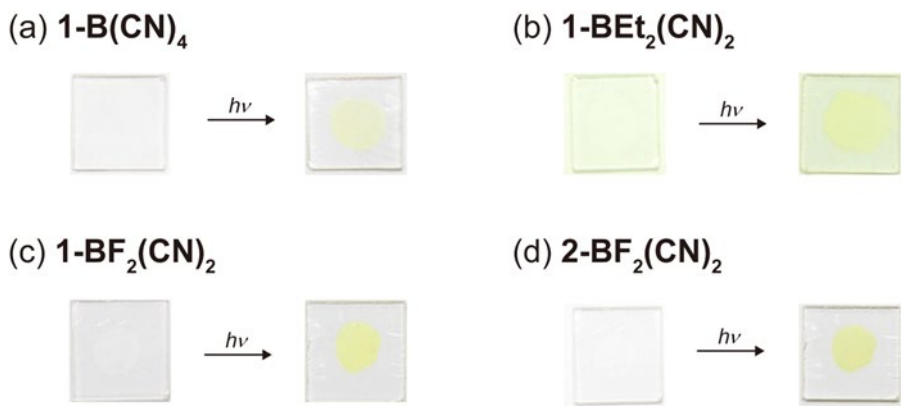


Figure S1. Photographs of samples sandwiched between quartz plates before and after UV irradiation (365 nm).

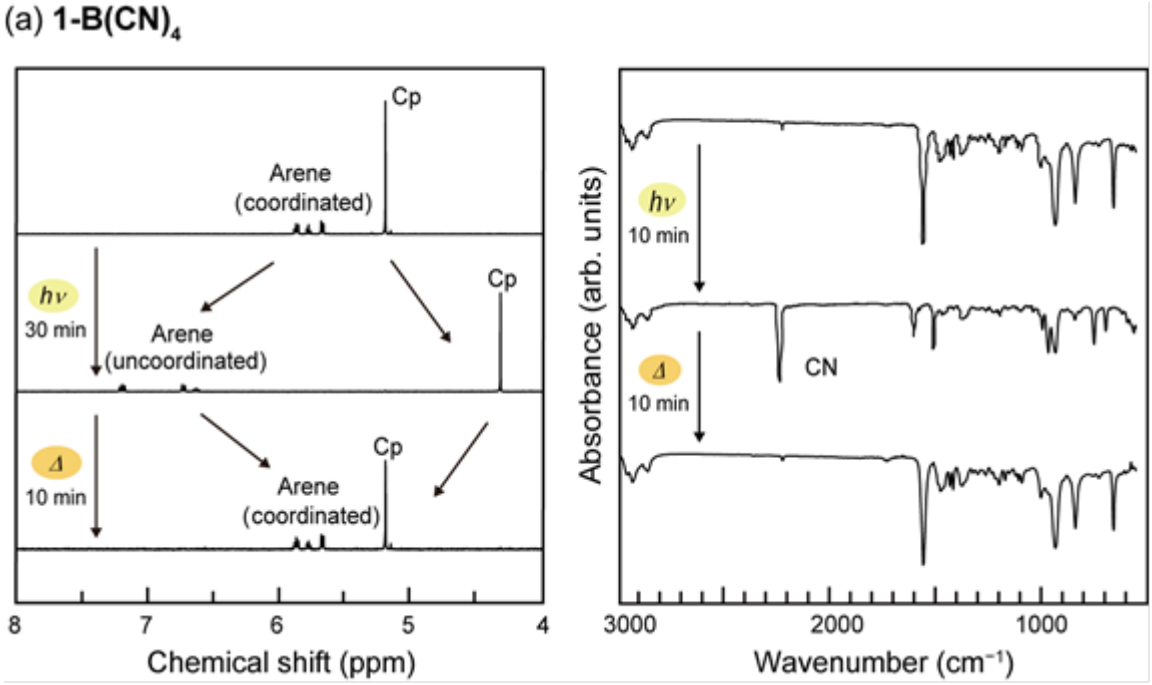


Figure S2. ^{1}H NMR spectra in CD_3CN (left) and FT-IR spectra (right) of (a) **1-B(CN)2**, (b) **1-BEt2(CN)2**, (c) **1-BF2(CN)2**, and (d) **2-BF2(CN)2** before photoirradiation, after photoirradiation, and after subsequent heating to 393 K.

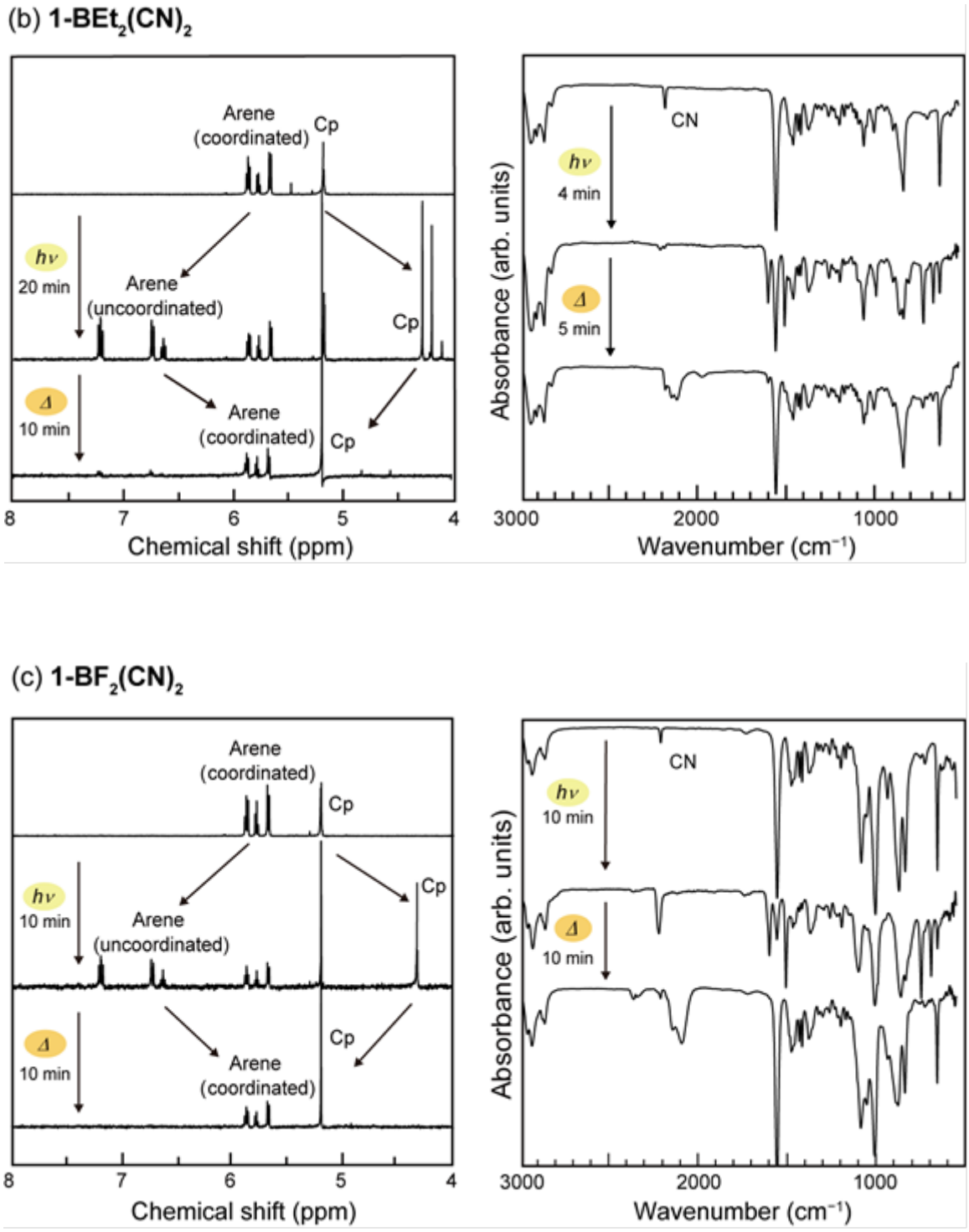


Figure S2. (Continued)

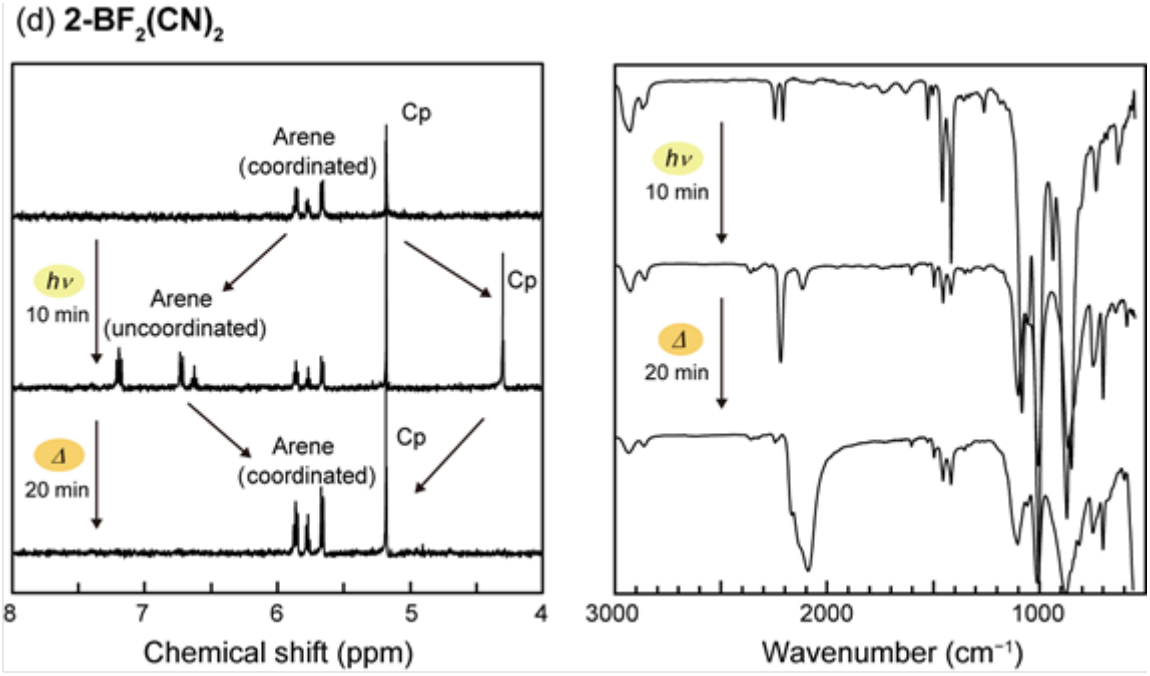


Figure S2. (Continued)

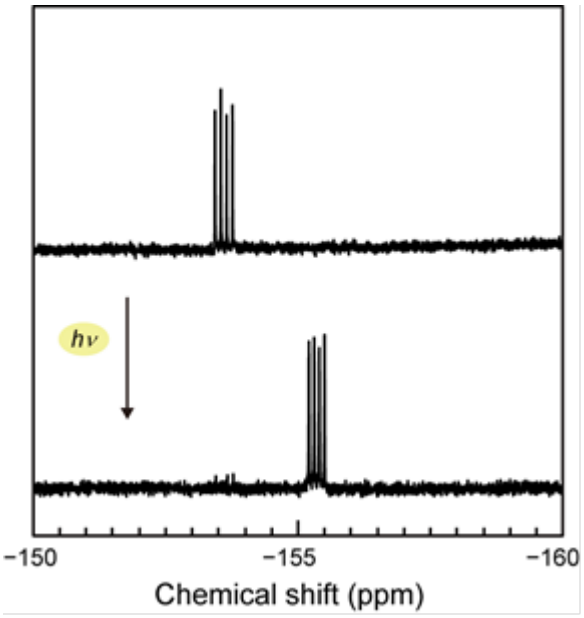


Figure S3. ^{19}F NMR spectra of **1-$BF_2(CN)_2$** before (top) and after (bottom) photoirradiation in $CDCl_3$.

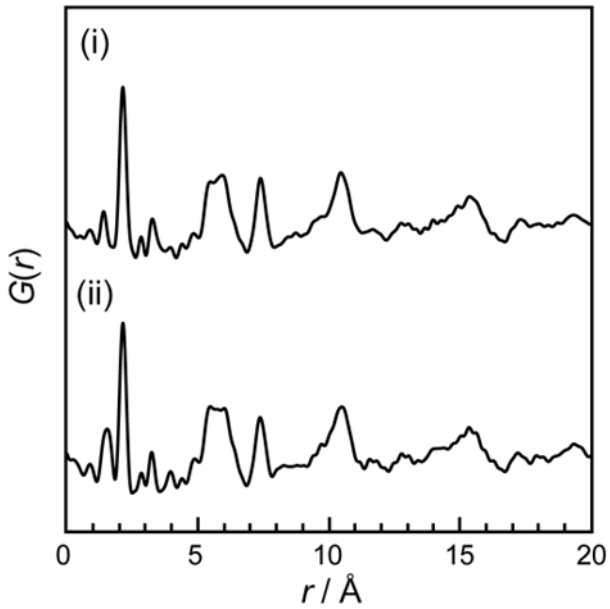


Figure S4. PDF patterns of (i) **1-B(CN)$_4$** and (ii) **Bu-B(CN)$_4$** photoproducts prepared by LED photoirradiation.

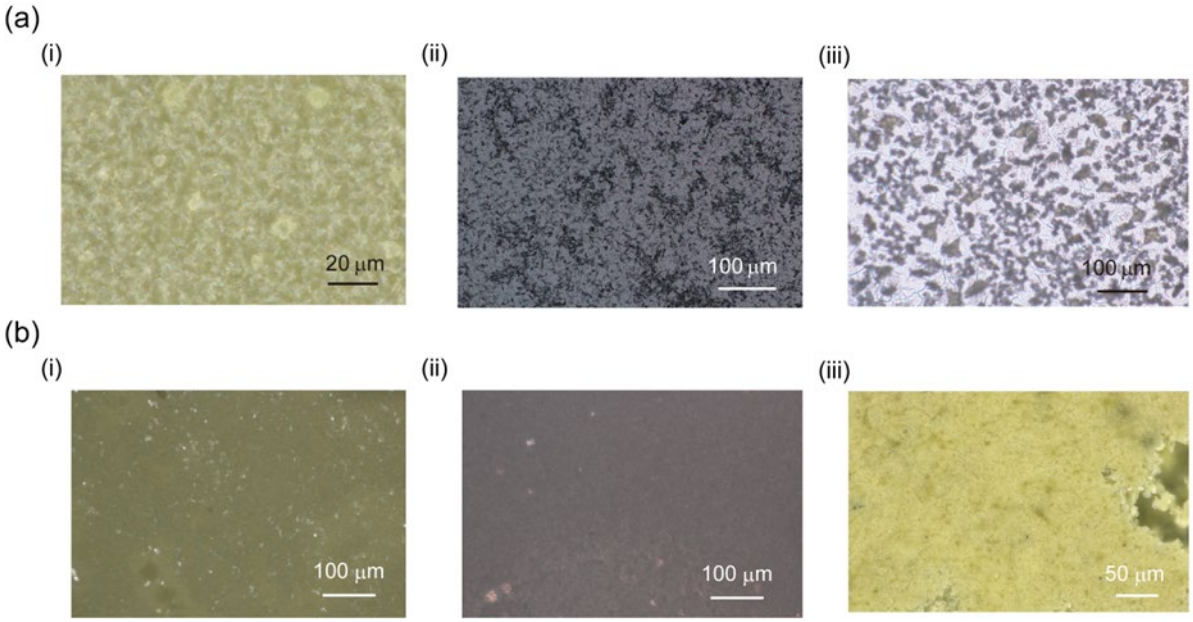


Figure S5. Optical microscope images of (a) **1-B(CN)$_4$** and (b) **Bu-B(CN)$_4$** photoproducts obtained under (i) LED, (ii) deep UV, and (iii) xenon UV light.

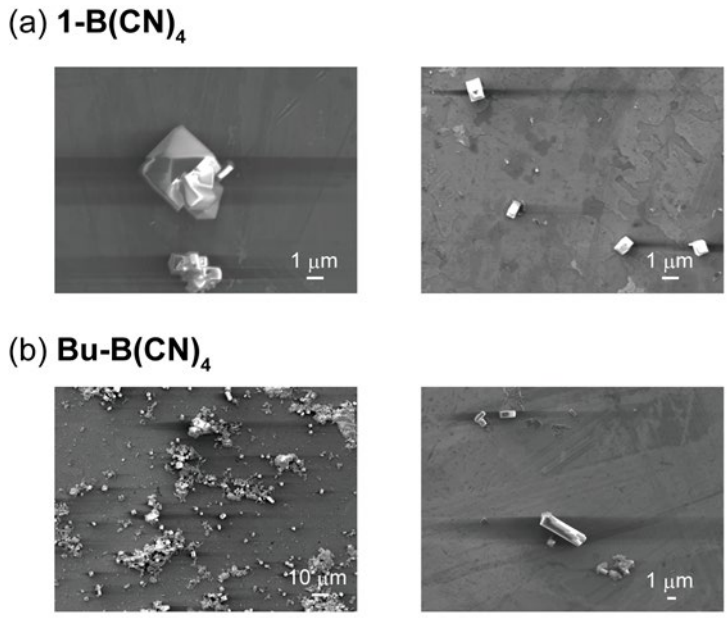


Figure S6. SEM images of the photoproducts of (a) **1-B(CN)$_4$** and (b) **Bu-B(CN)$_4$**, obtained by LED photoirradiation.

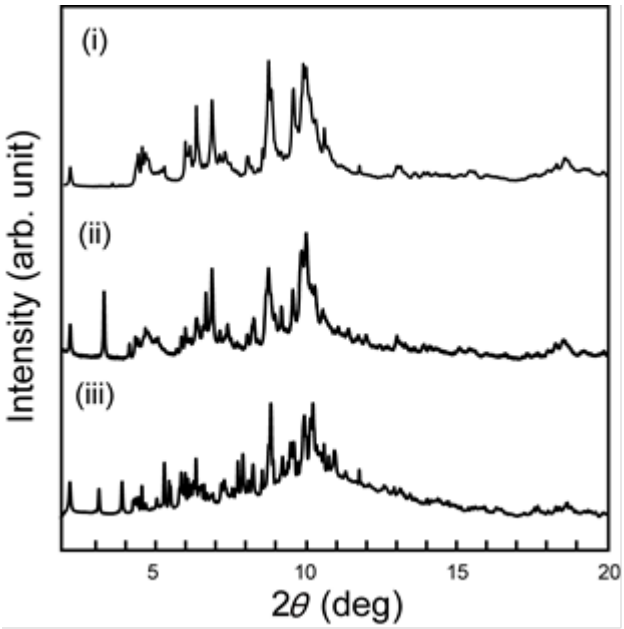


Figure S7. PXRD patterns of **Bu-B(CN)$_4$** photoproducts obtained under (i) LED, (ii) deep UV, and (iii) xenon UV light, measured using synchrotron radiation at room temperature.

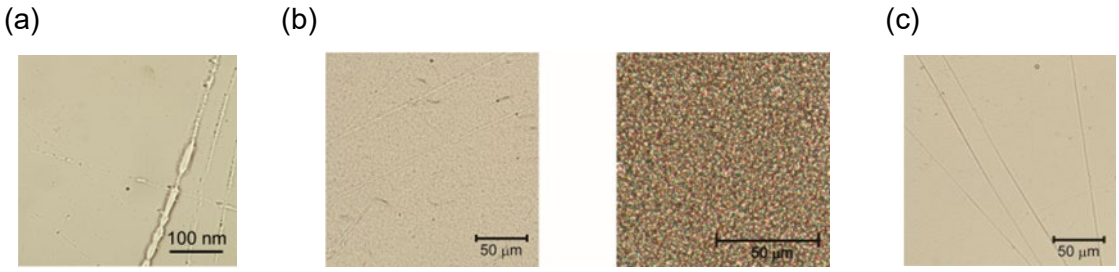


Figure S8. Microscopic images of photoproducts sandwiched between quartz plates:(a) **1-BEt$_2$(CN)$_2$**, (b) **1-BF$_2$(CN)$_2$**, and (c) **2-BF$_2$(CN)$_2$**. The right panel in (b) shows the photoproduct of **1**–**BF$_2$(CN)$_2$** after washing with hexane, observed by polarized optical microscopy under crossed Nicols.

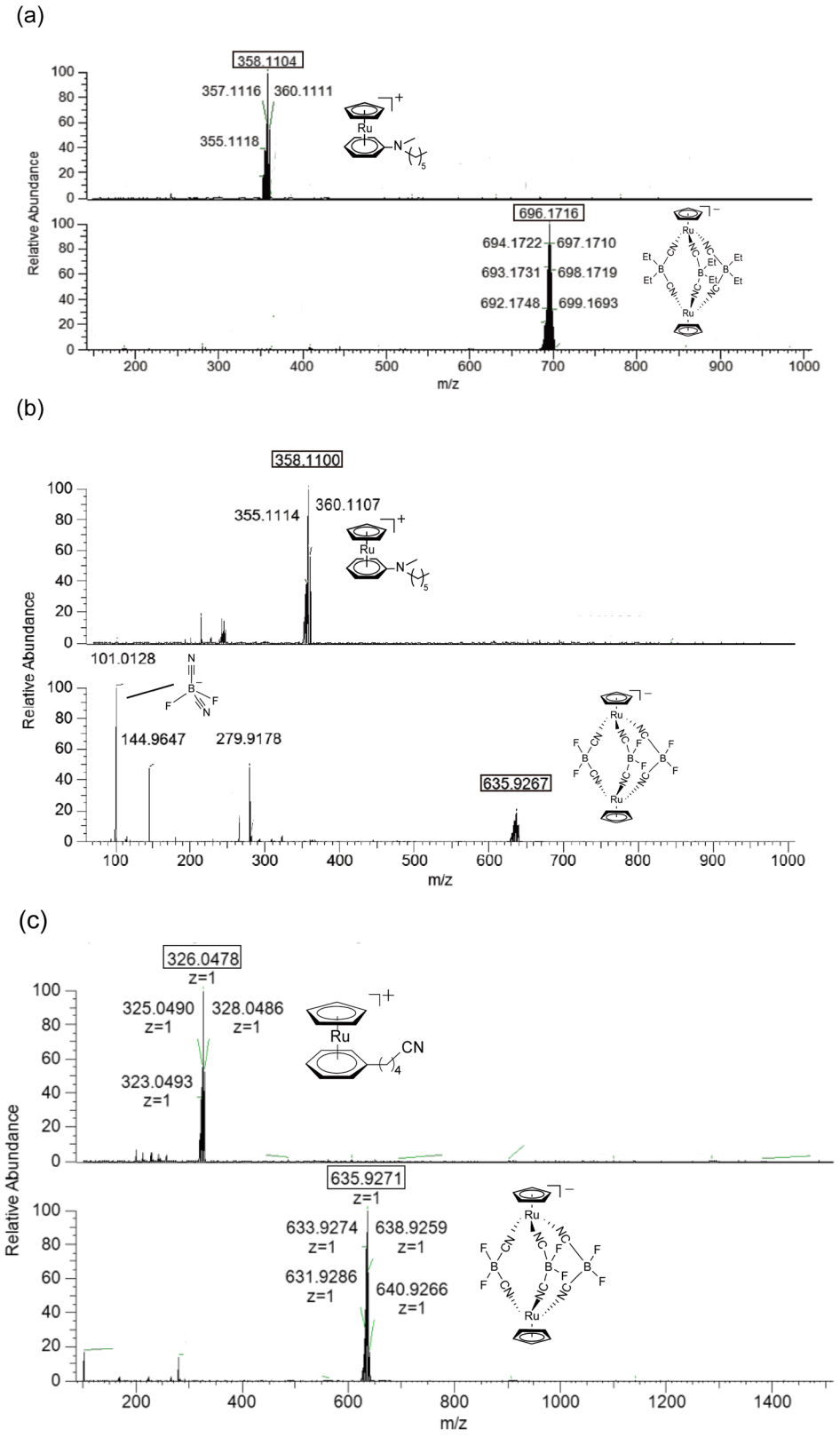


Figure S9. ESI-MS spectra of acetone solutions of the photoproducts of (a) **1-BEt$_2$(CN)$_2$**, (b) **1-BF$_2$(CN)$_2$**, and (c) **2-BF$_2$(CN)$_2$**.

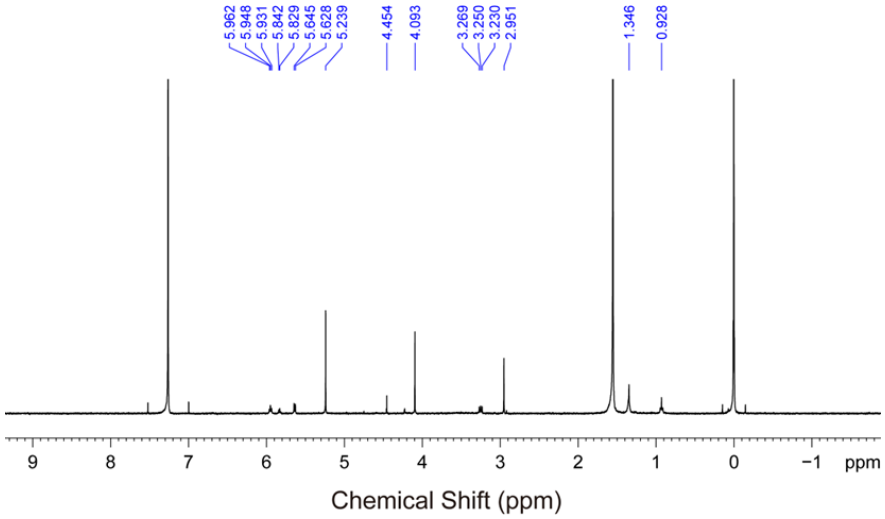


Figure S10. ^{1}H NMR spectrum of the photoproducts of **1-BF$_2$(CN)$_2$** in $CDCl_3$.

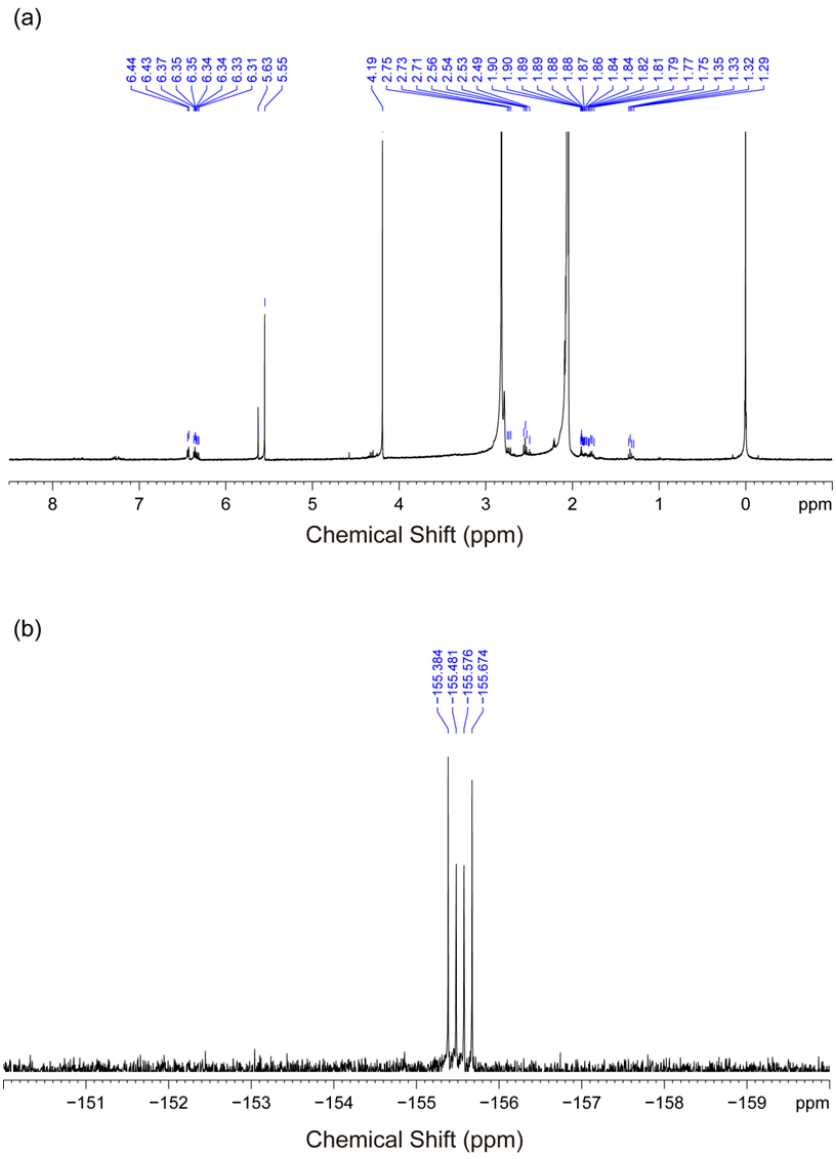


Figure S11. (a) ^{1}H and (b) ^{19}F NMR spectra of the photoproduct of **2-BF$_2$(CN)$_2$** in acetone-d_6.

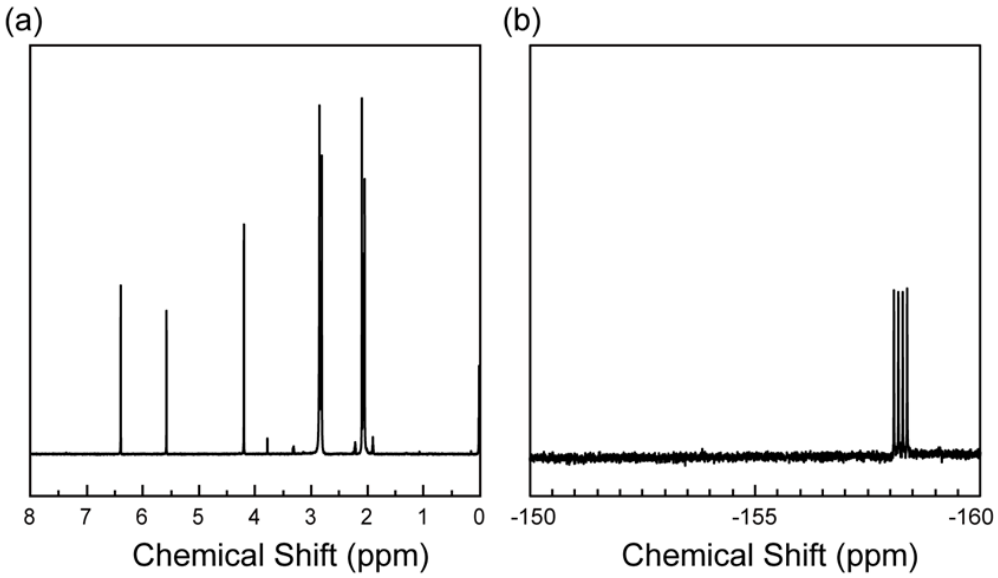


Figure S12. (a) ^{1}H and (b) ^{19}F NMR spectra in acetone-d_6 of crystals obtained by photoirradiation of **3-BF$_2$(CN)$_2$** in methanol.

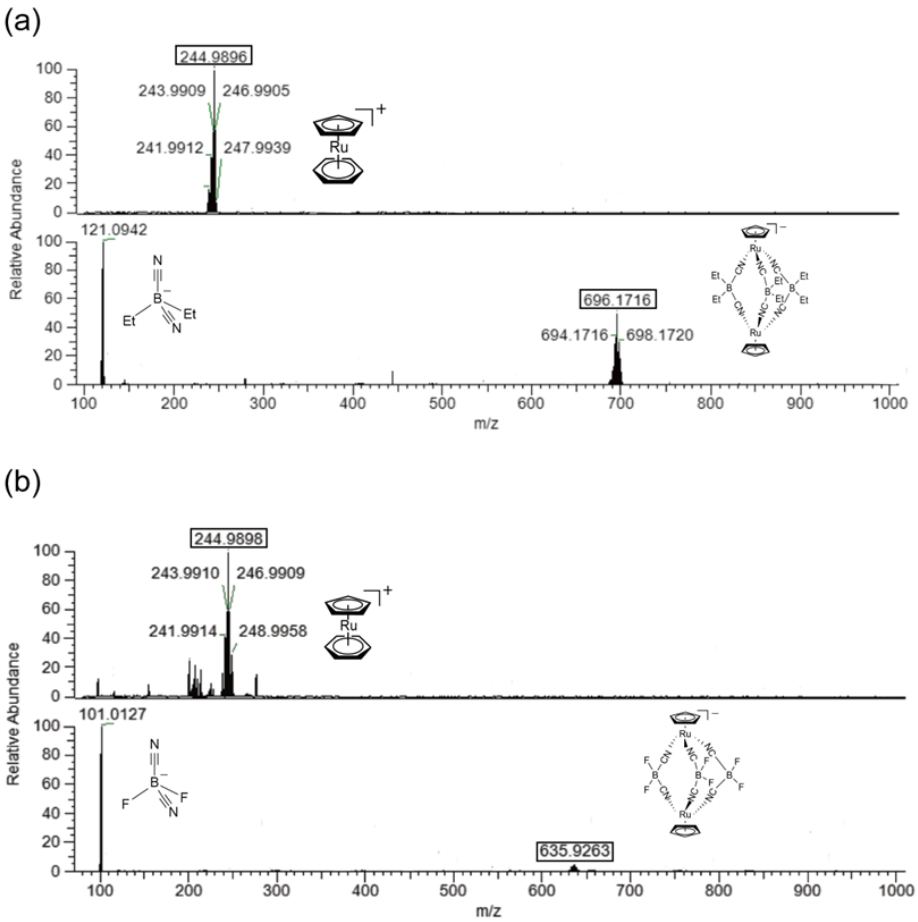


Figure S13. ESI–MS spectra of the photoproducts of (a) **3-BEt$_2$(CN)$_2$** obtained by photoirradiation in acetone-d_6 and (b) **3-BF$_2$(CN)$_2$**, whose crystals were obtained by photoirradiation in methanol and subsequently dissolved in acetone.

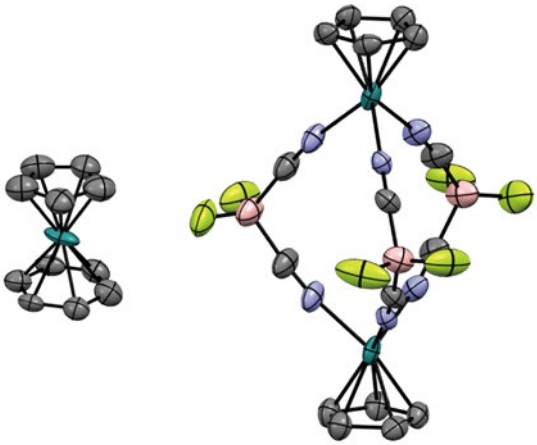


Figure S14. Molecular structures of the cation and anion in $[CpRu(C_6H_6)][(CpRu)_2\{BF_2(CN)_2\}_3]$ determined at 100 K. Hydrogen atoms are omitted.

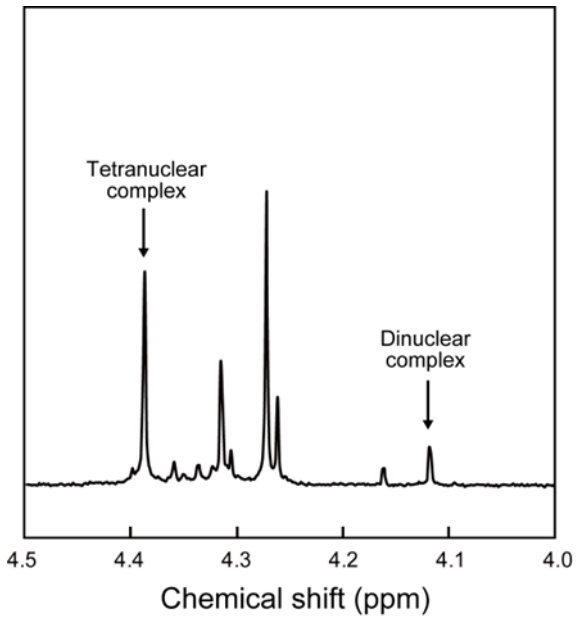


Figure S15. ^1H NMR spectrum ($CDCl_3$) of the photoproducts obtained from a mixture of **1-B(CN)$_4$** and **1-BF$_2$(CN)$_2$** after 1 h of photoirradiation.

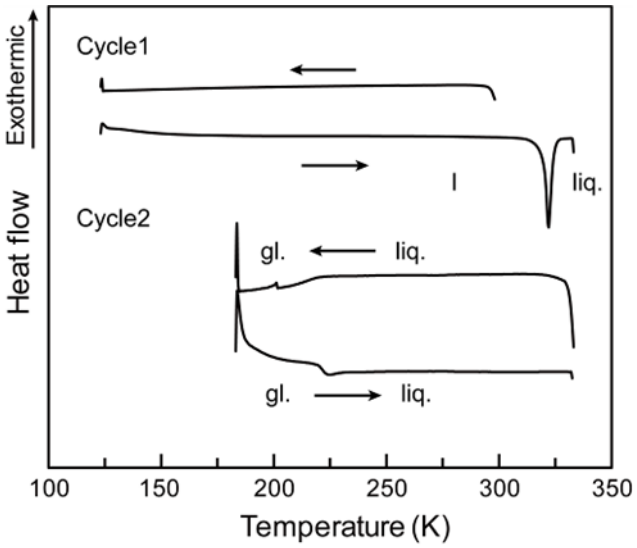
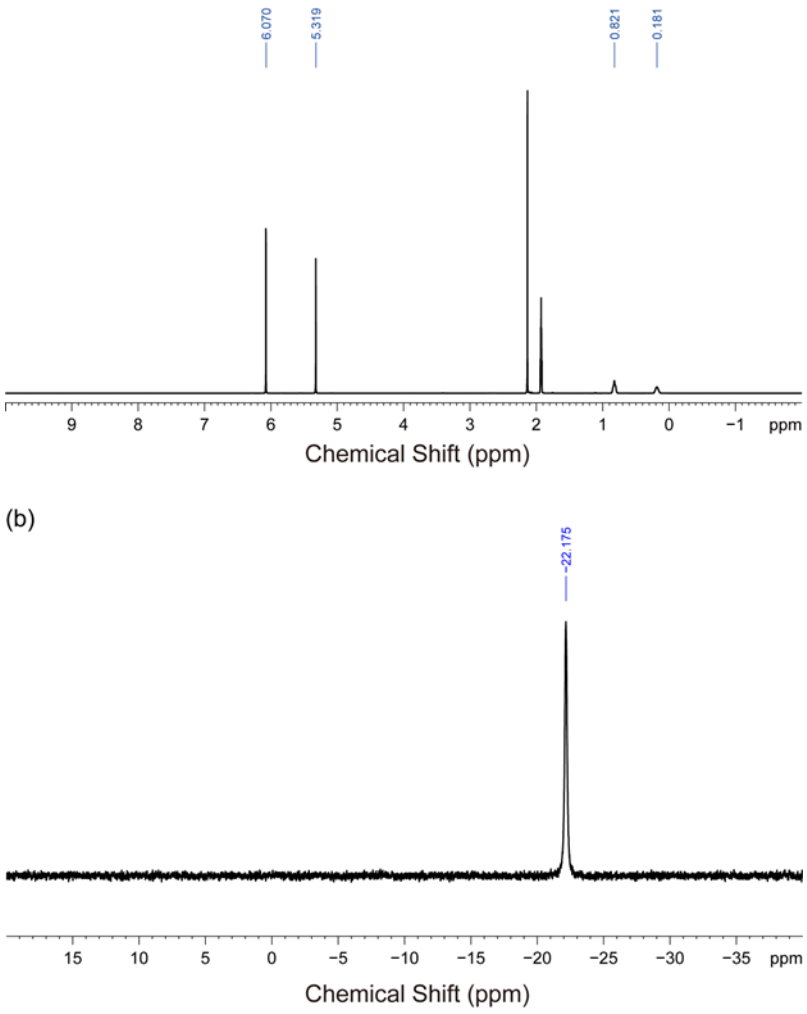


Figure S16. DSC curves of **1-B(CN)$_4$**.



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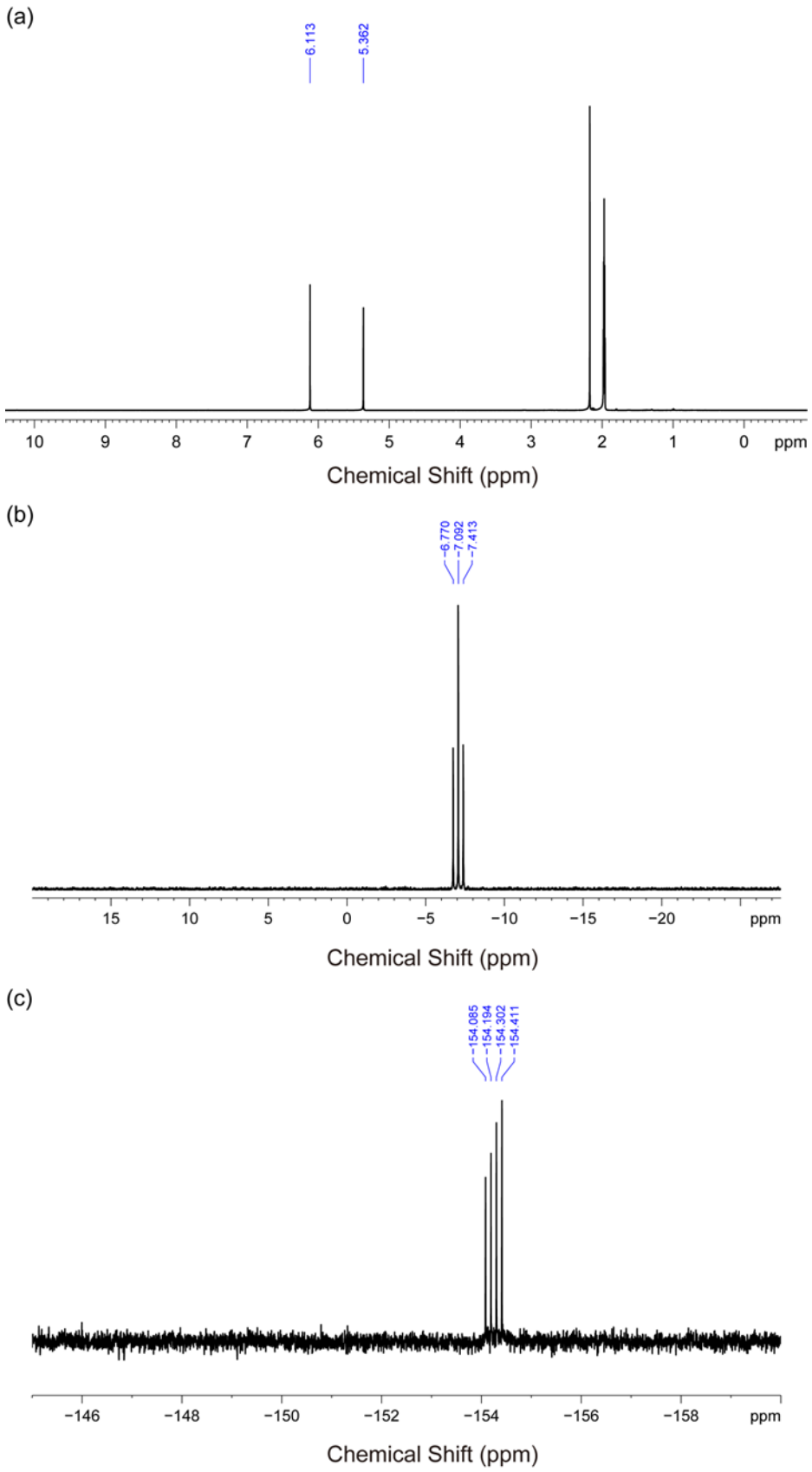

Figure S18. (a) ^{1}H, (b) ^{11}B, and (c) ^{19}F NMR spectra of **3-BF$_2$(CN)$_2$** in CD_3CN.

Table S1. Crystallographic parameters for $[CpRu(C_6H_6)][(CpRu)_2\{BF_2(CN)_2\}_3]$[a]

Empirical formula	$C_{81}H_{63}B_9F_{18}N_{18}Ru_9$
Formula weight	2637.41
Crystal system	Monoclinic
Space group	*I*2/*a*
a [Å]	16.5027(3)
b [Å]	31.2640(7)
c [Å]	19.0958(4)
b [°]	109.534(2)
V [Å^3]	9285.2(3)
Z	4
Temperature [K]	100

[a]Refinement not satisfactory owing to extensive disorder