Supplementary Information

Formation, reactivity and redox properties of carbon- and sulfur-bridged diiron complexes derived from dibenzothienyl Schiff bases: effect of N,N- and N,P-chelating moieties

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In all of the following NMR spectra, residual solvent signals are marked with an asterisk.

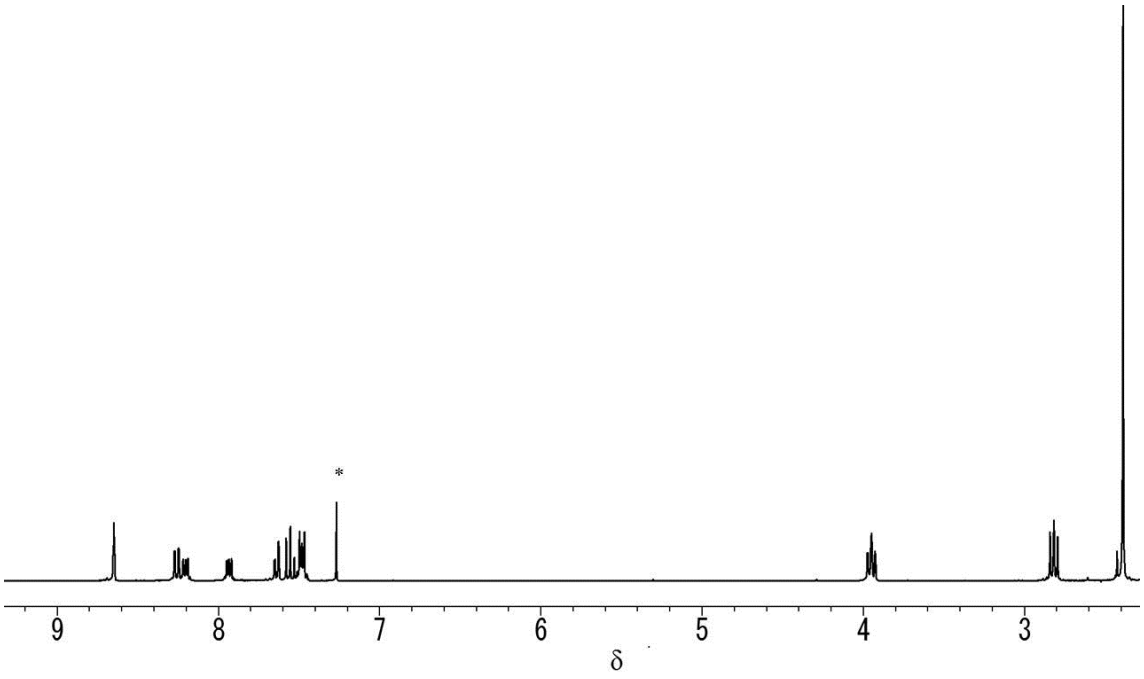


Figure S1. ^{1}H NMR spectrum (300 MHz) of DBT-NN in $CDCl_3$.

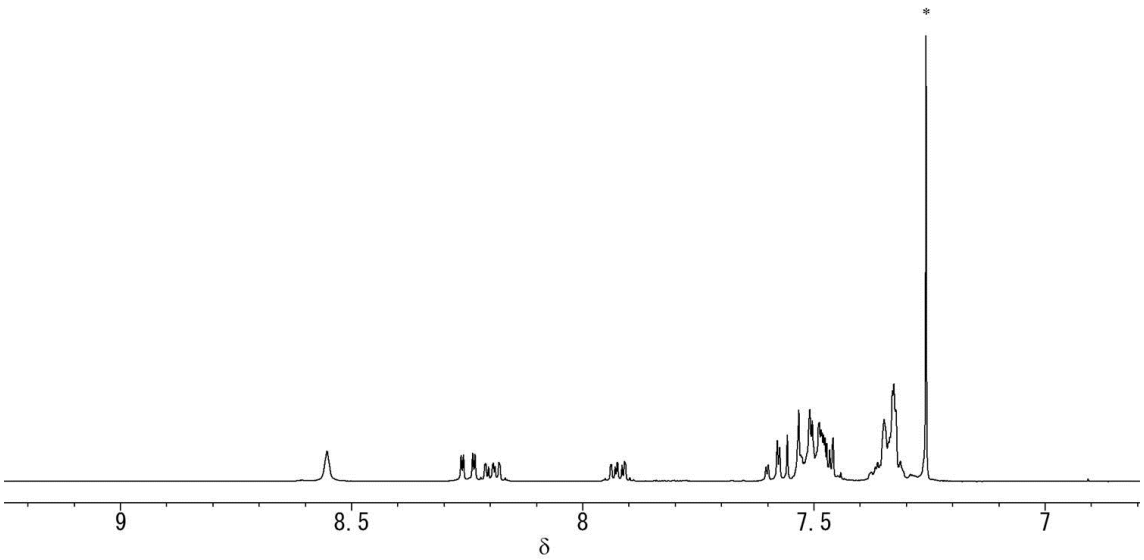


Figure S2. ^{1}H NMR spectrum (300 MHz) of DBT-NP in $CDCl_3$.

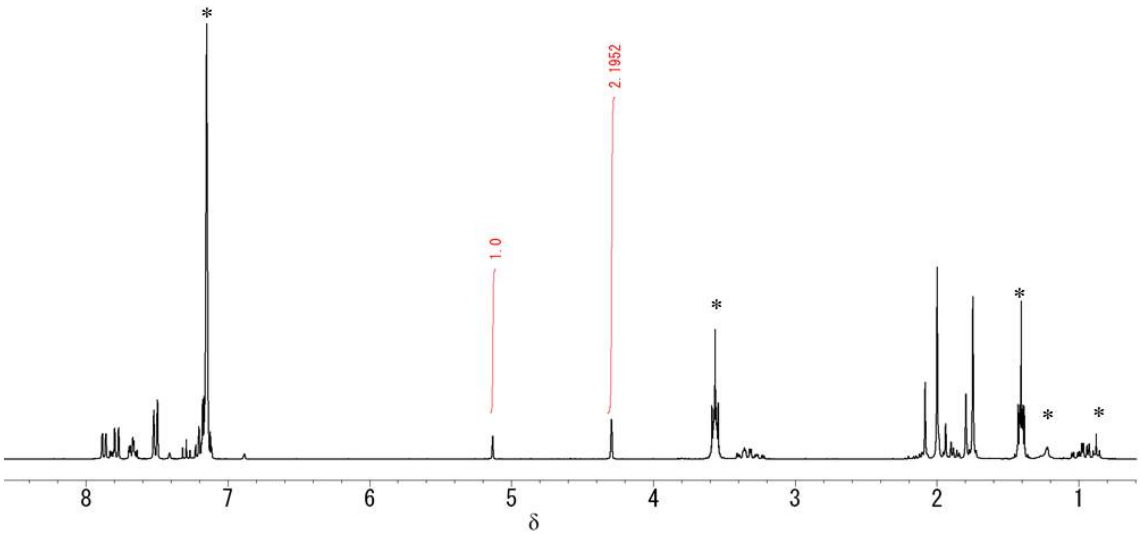


Figure S3. ^{1}H NMR spectrum (300 MHz) of **1** in C_6D_6.

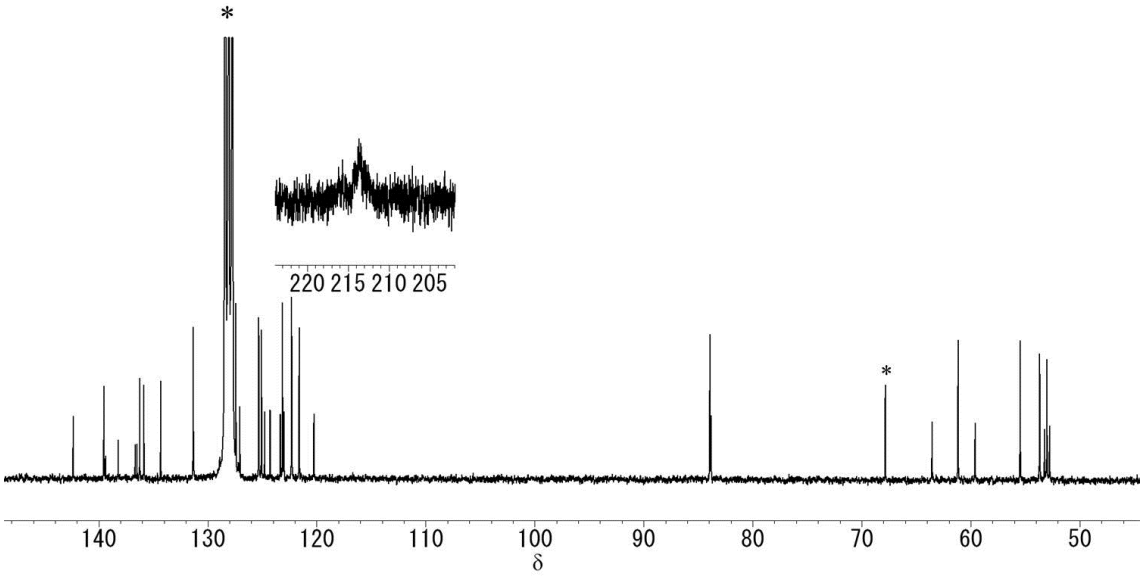
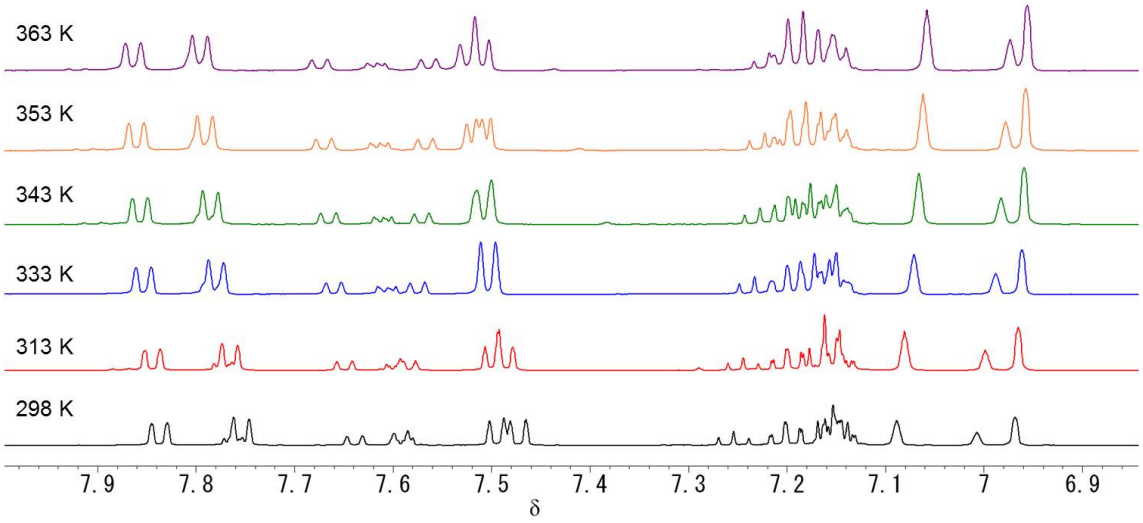


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **1** in C_6D_6. Residual solvent signals are marked with an asterisk.

(a)



(b)

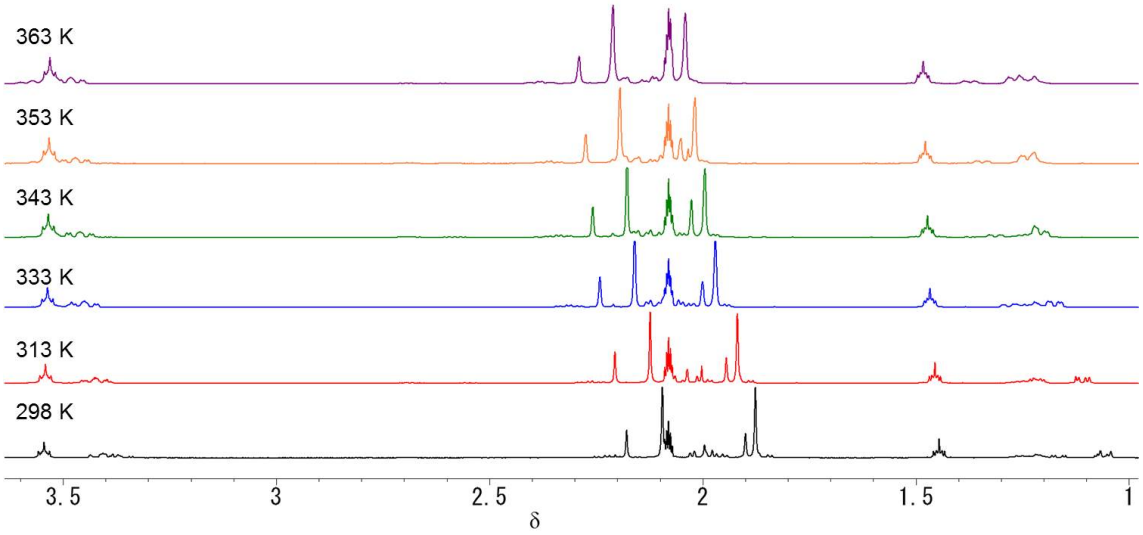
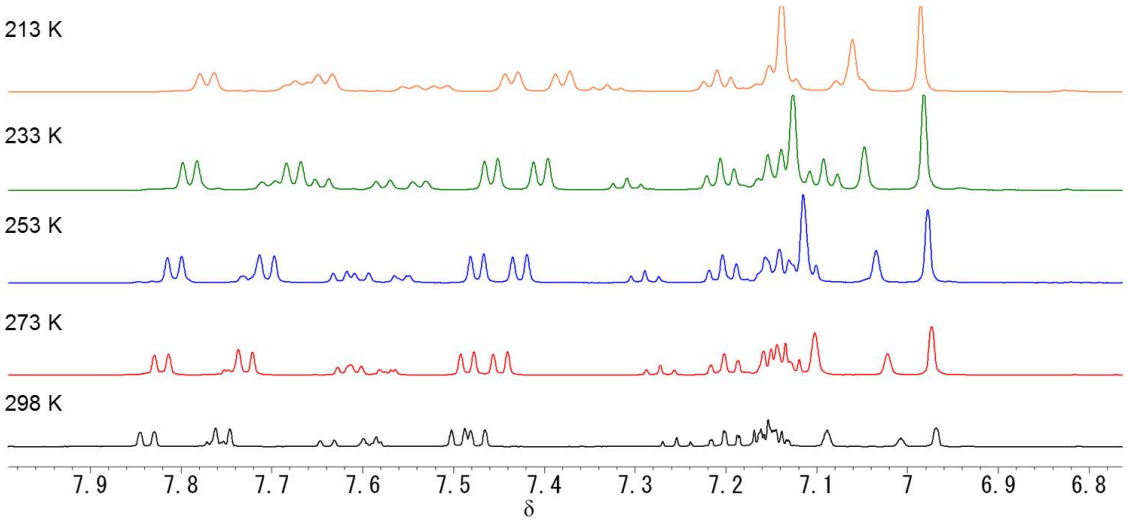


Figure S5. Variable temperature ^{1}H NMR spectra (500 MHz) of **1** in toluene-d^{8} (298—363 K).

(a)



(b)

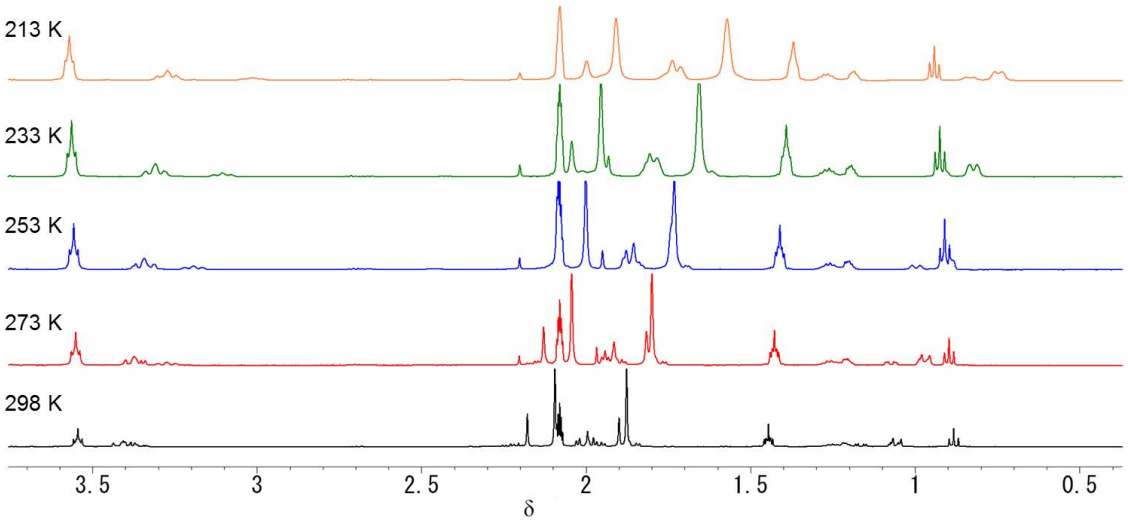


Figure S6. Variable temperature ^{1}H NMR spectra (500 MHz) of **1** in toluene-d^{8} (213—298 K).

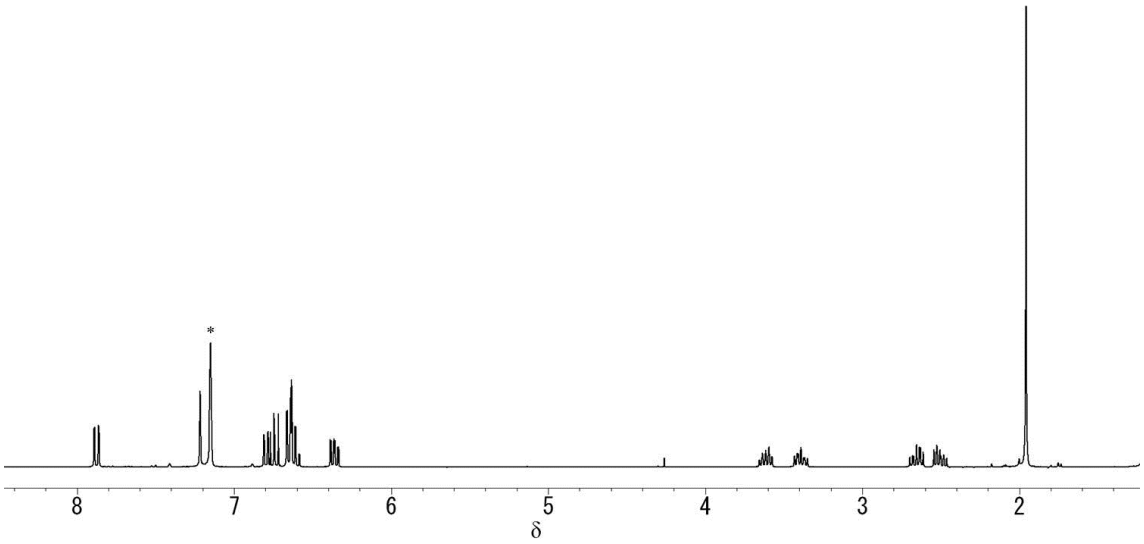


Figure S7. ^{1}H NMR spectrum (300 MHz) of **2** in C_6D_6.

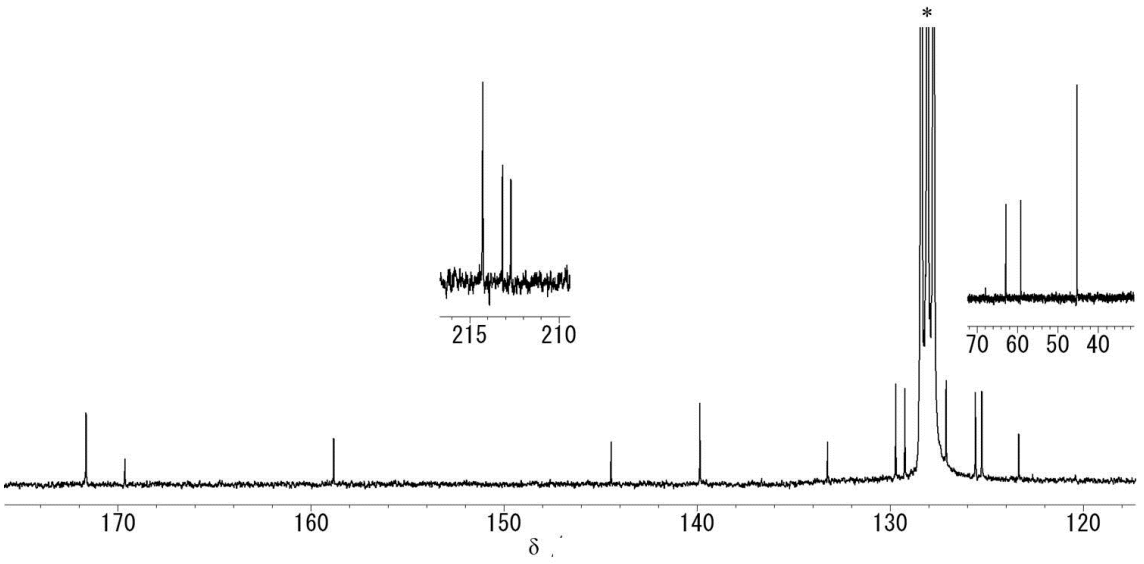


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **2** in C_6D_6.

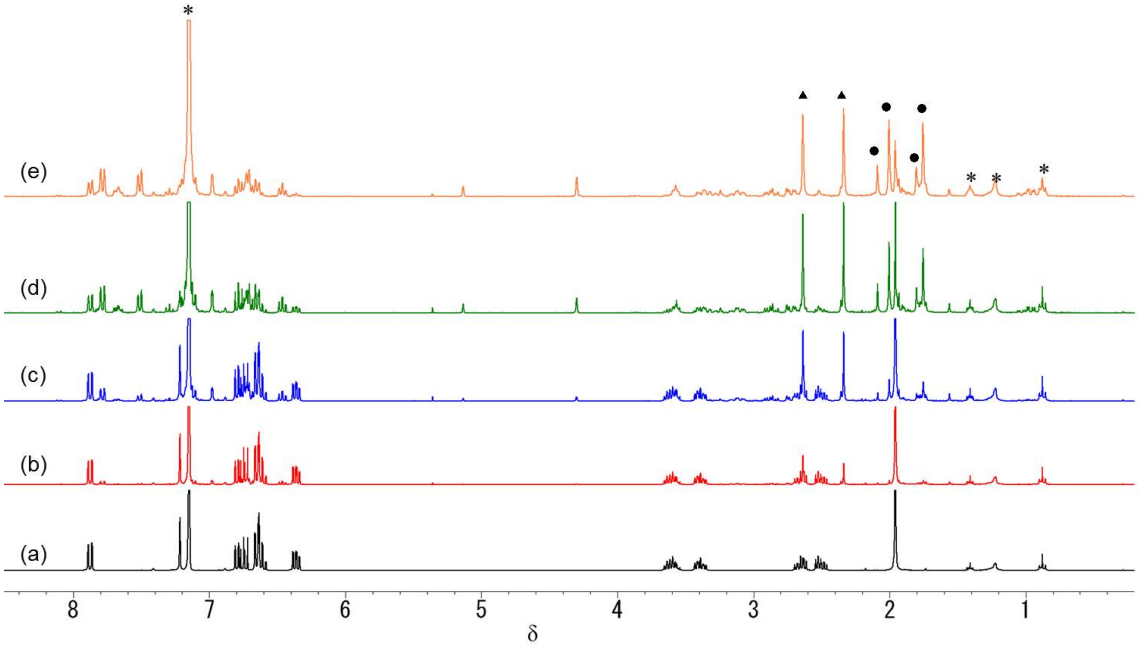


Figure S9. ^{1}H NMR spectra (300 MHz) of **2** in C_6D_6: (a) A solution of **2**. The solution was irradiated with a high pressure Hg lamp for (b) 1 h, (c) 2 h, (d) 5 h, and then (e) 3 h. Solid triangles denote N*Me*$_2$ of [{Fe(μ-BPT-NN-κ^4*S,C,N,N'*)(CO)}Fe(CO)$_3$]. Solid circles denote N*Me*$_2$ of **1a**, **1b**.

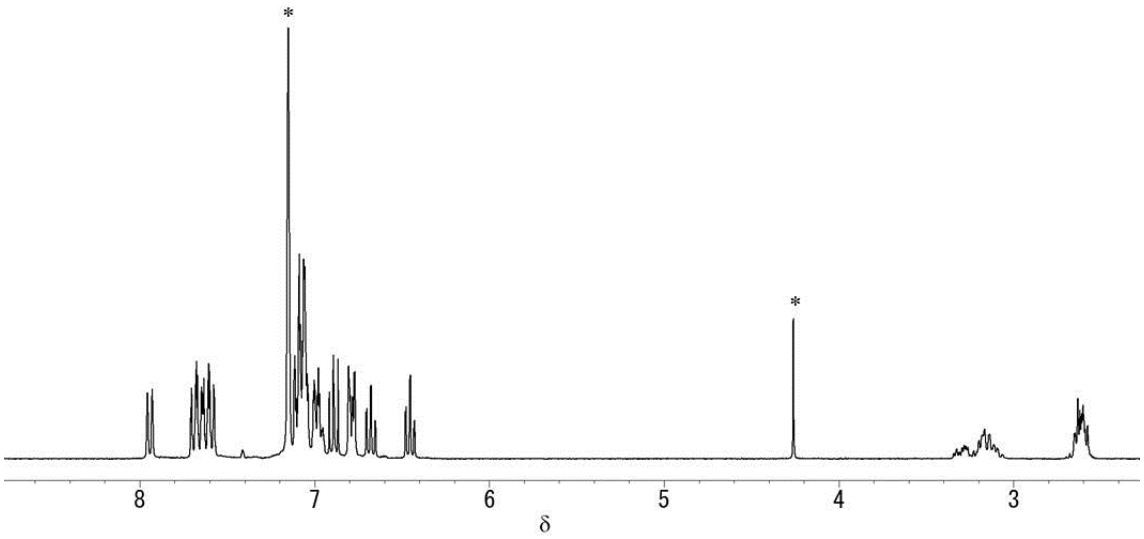


Figure S10. ^{1}H NMR spectrum (300 MHz) of **3** in C_6D_6.

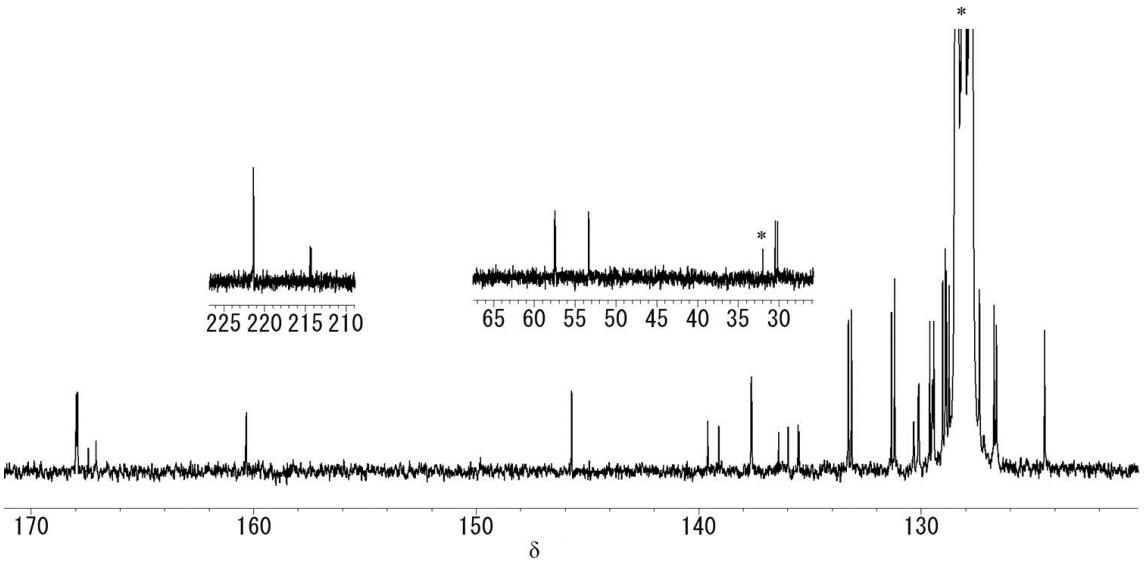


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **3** in C_6D_6. Residual solvent signals are marked with an asterisk.

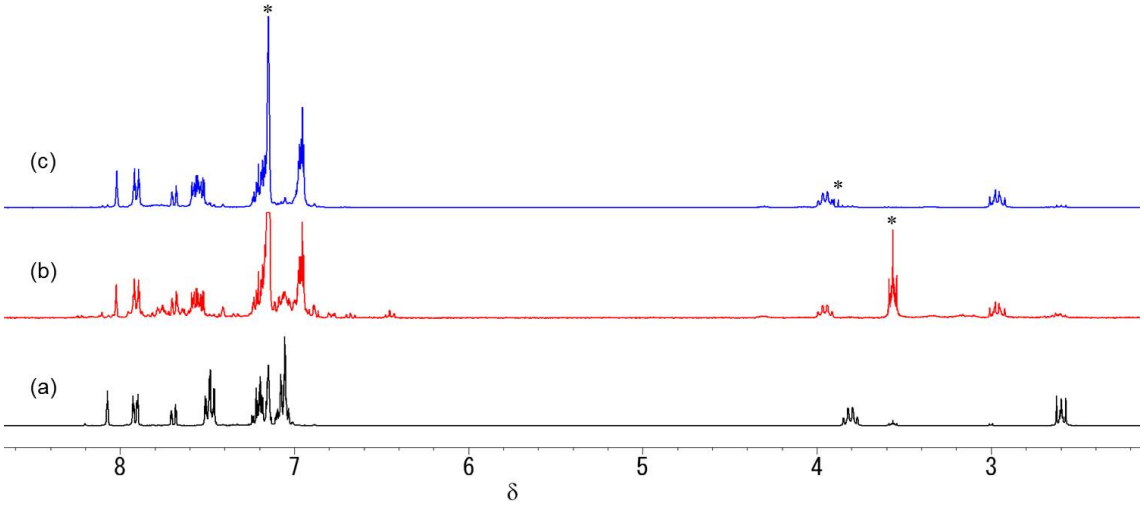


Figure S12. ^{1}H NMR spectra (300 MHz, C_6D_6). (a) DBT-NP. (b) A THF solution of DBT-NP and $Fe(CO)_5$ was irradiated with a high pressure Hg lamp for 30 min. (c) The reaction solution was purified by column chromatography to afford complex **4**.

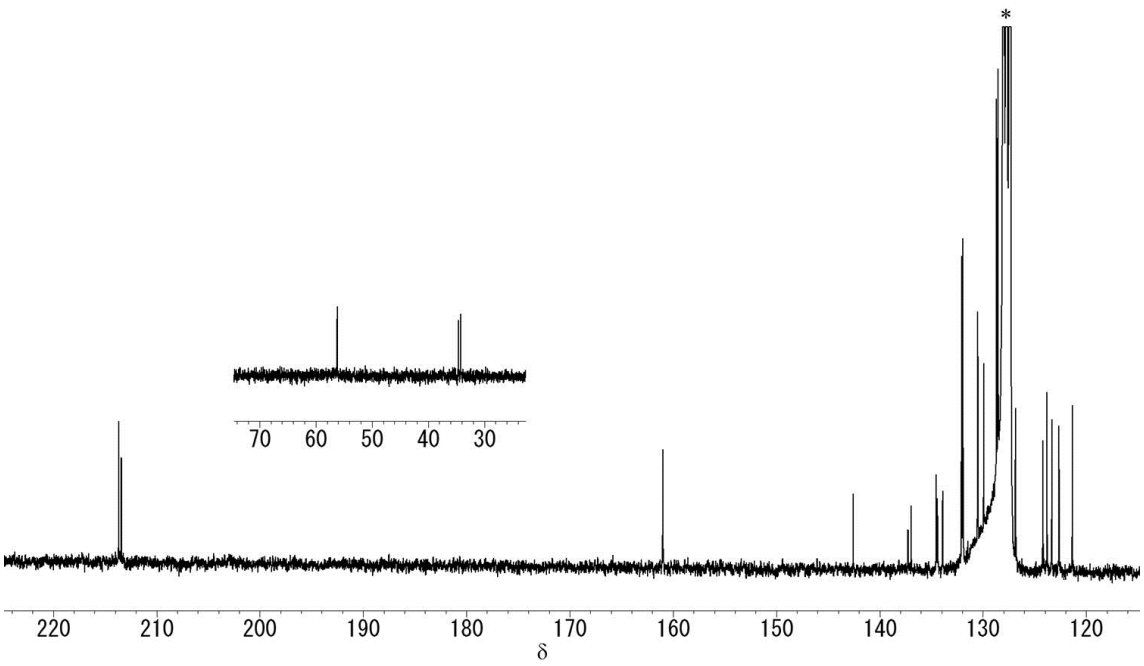


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **4** in C_6D_6.

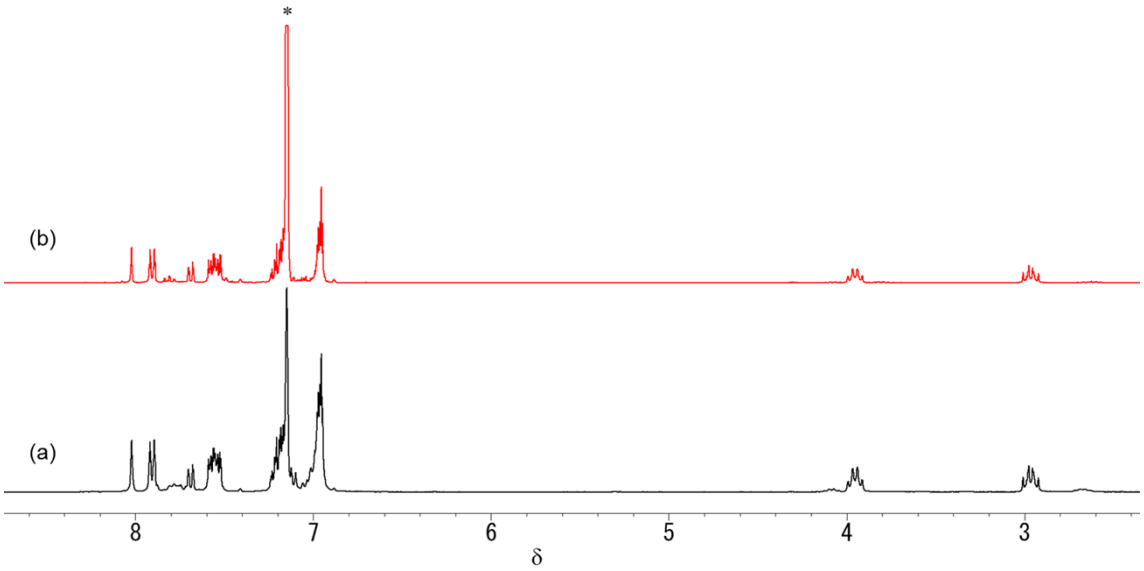


Figure S14. ^{1}H NMR spectra (300 MHz, C_6D_6): (a) A toluene solution of **3** was heated at 100 °C for 2 h under an atmosphere of CO. (b) Complex **4**.

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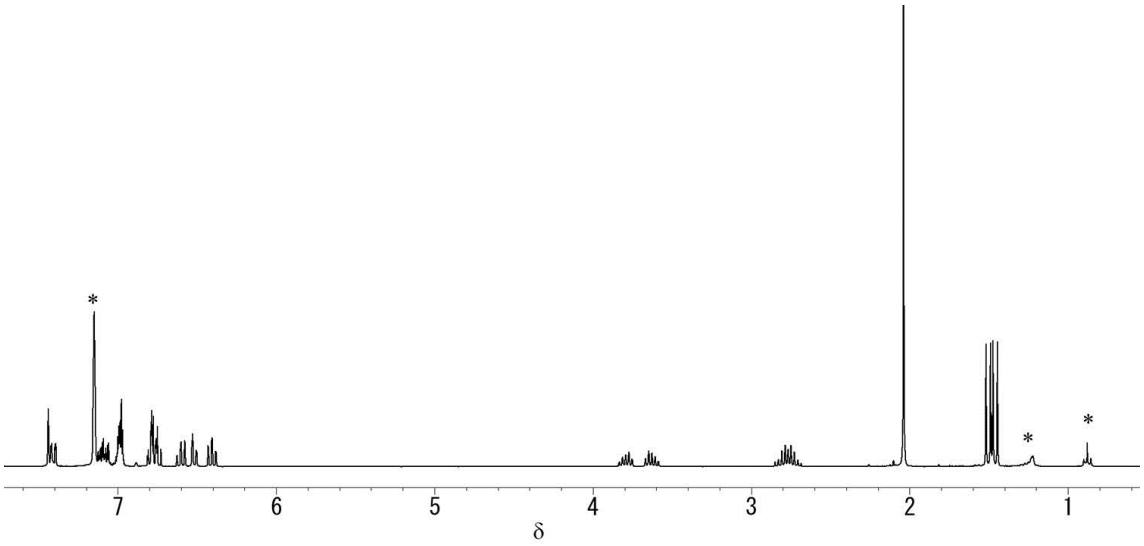

Figure S15. ^{1}H NMR spectrum (300 MHz) of **5** in C_6D_6.

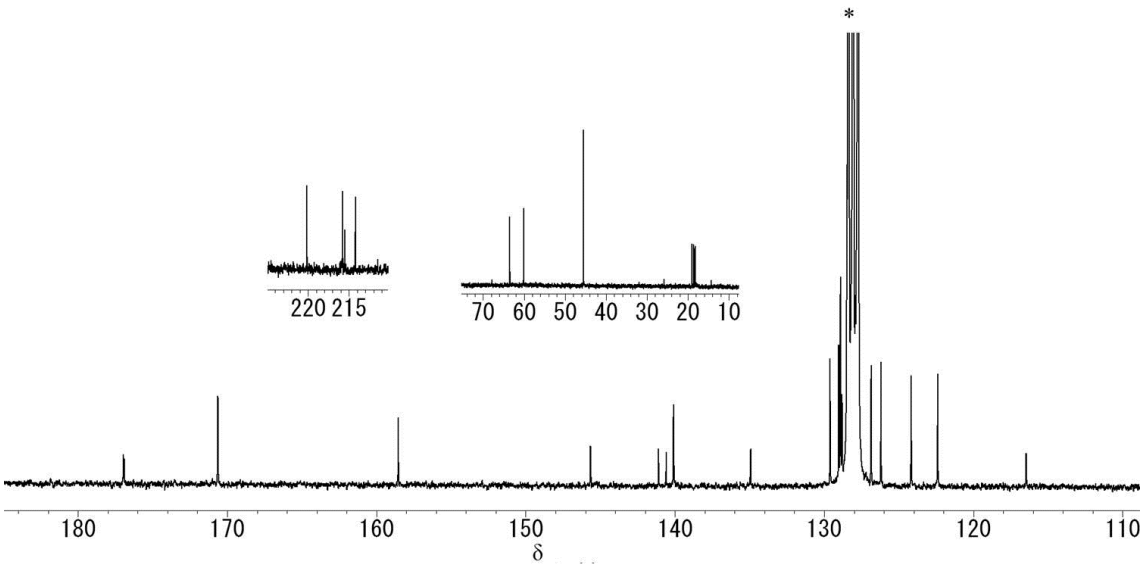

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **5** in C_6D_6.

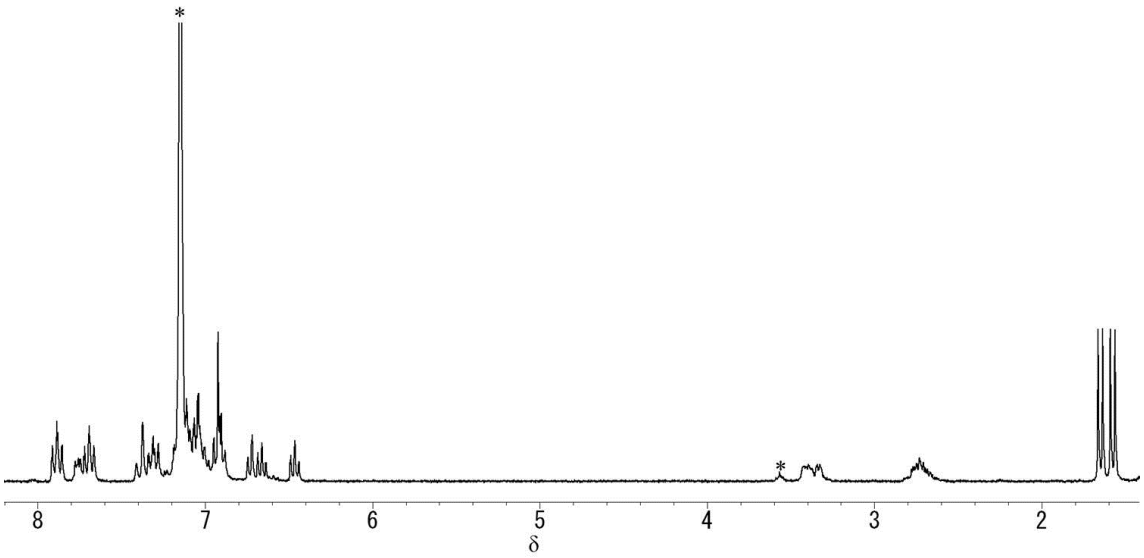

Figure S17. ^{1}H NMR spectrum (300 MHz) of **6** in C_6D_6.

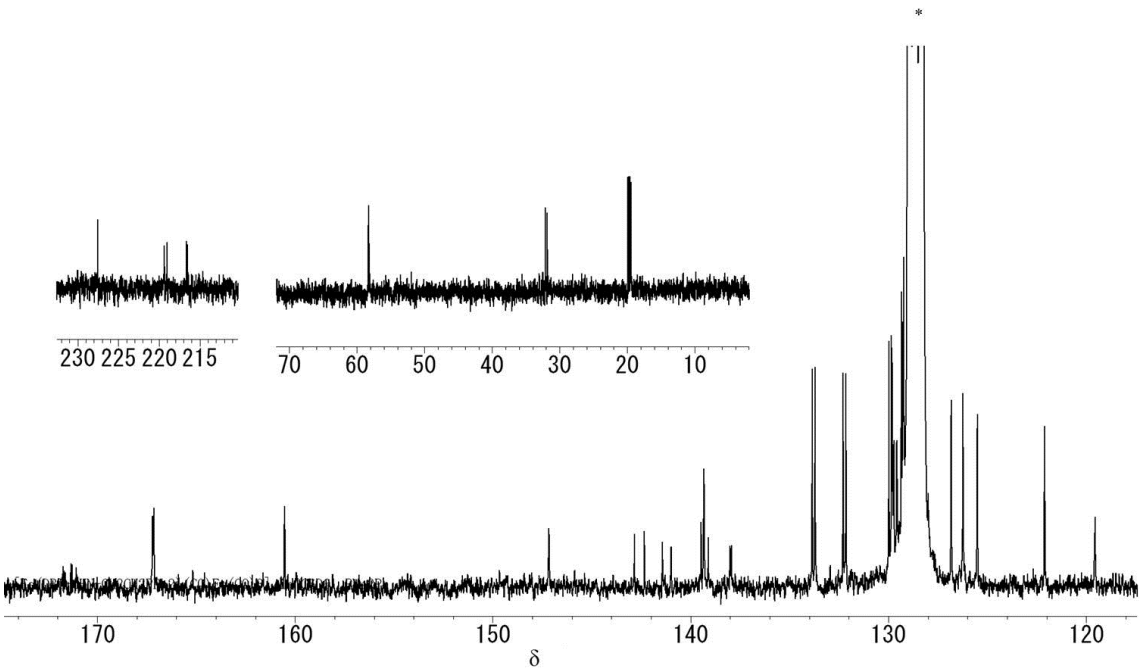

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **6** in C_6D_6.

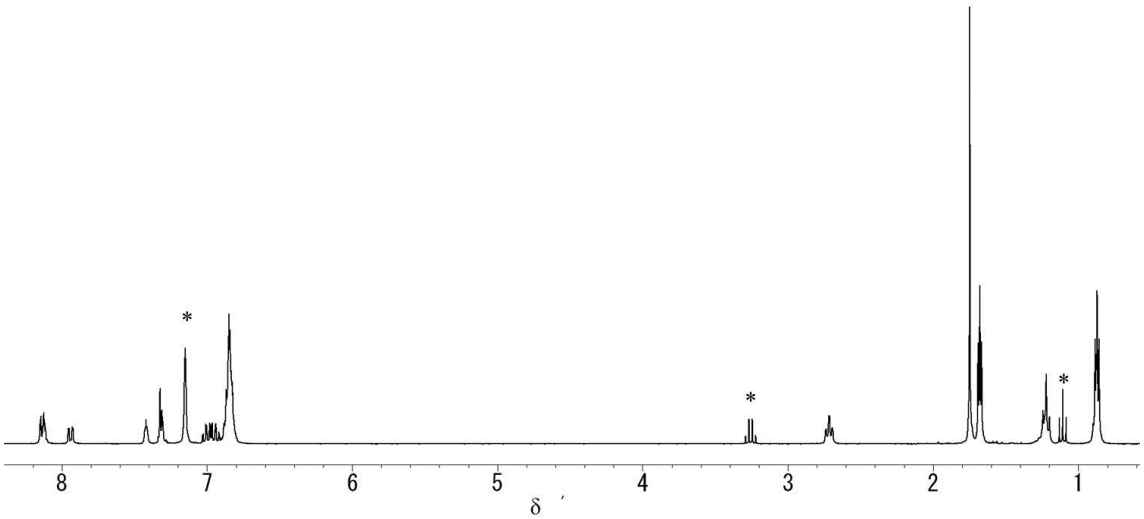

Figure S19. ^{1}H NMR spectrum (300 MHz) of **7** in C_6D_6.

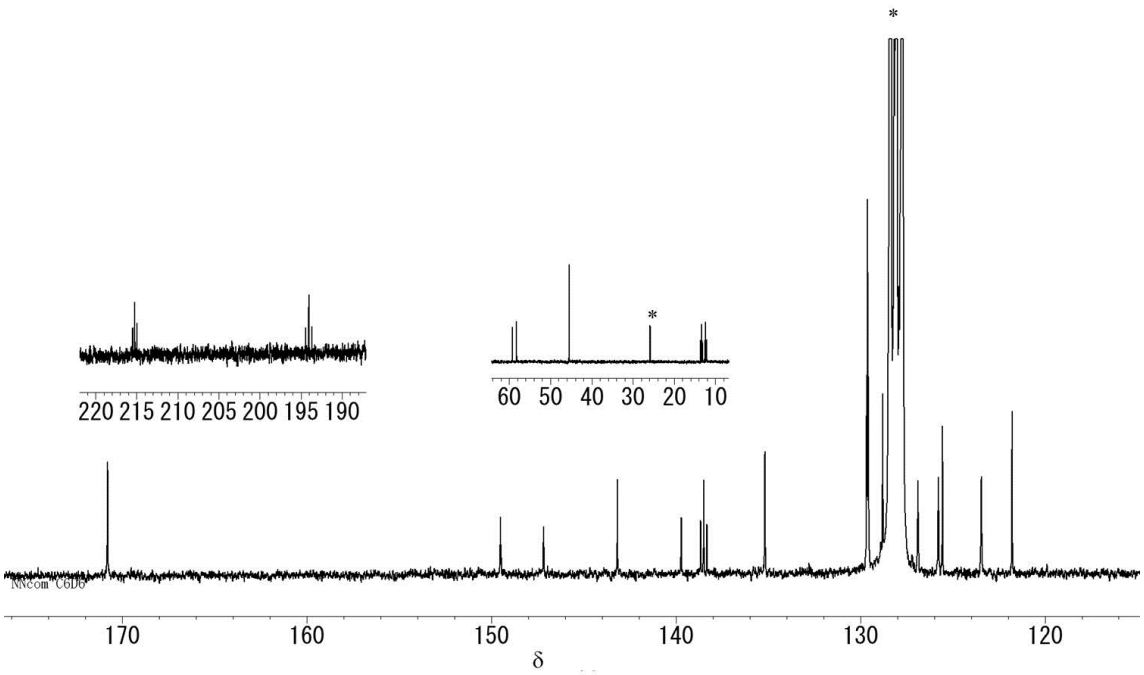

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **7** in C_6D_6.

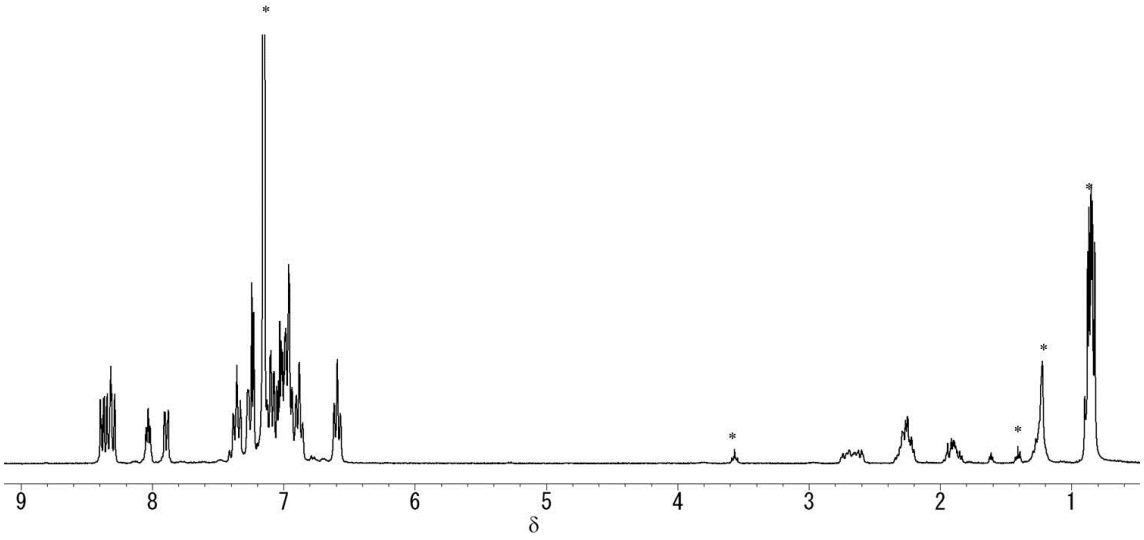

Figure S21. ^{1}H NMR spectrum (300 MHz) of **8** in C_6D_6.

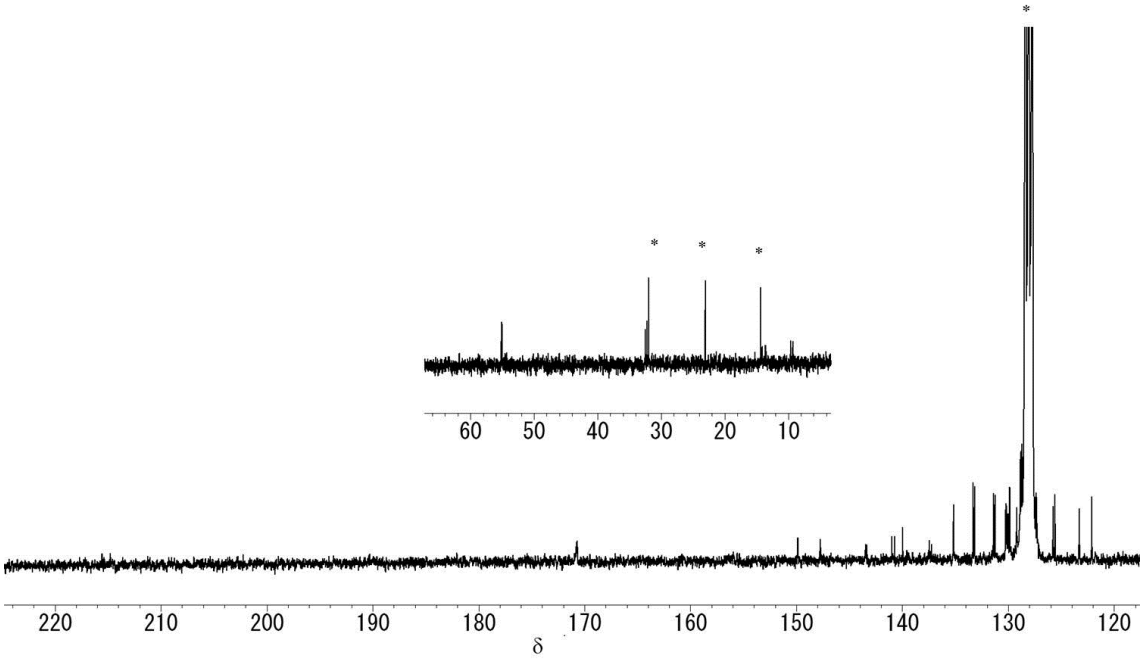

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz) of **8** in C_6D_6.

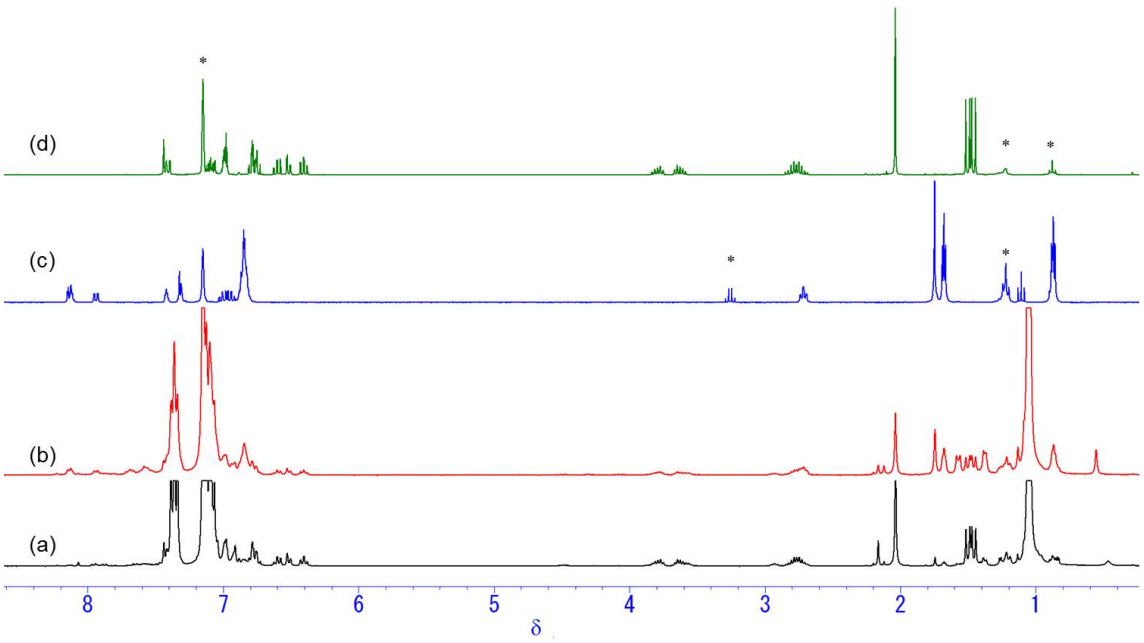

Figure S23. ^{1}H NMR spectra (300 MHz). (a) A C_6D_6 solution of **5** and PMe_2Ph. (b) After 20 hours at room temperature. (c) A C_6D_6 solution of **7**. (d) A C_6D_6 solution of **5**.

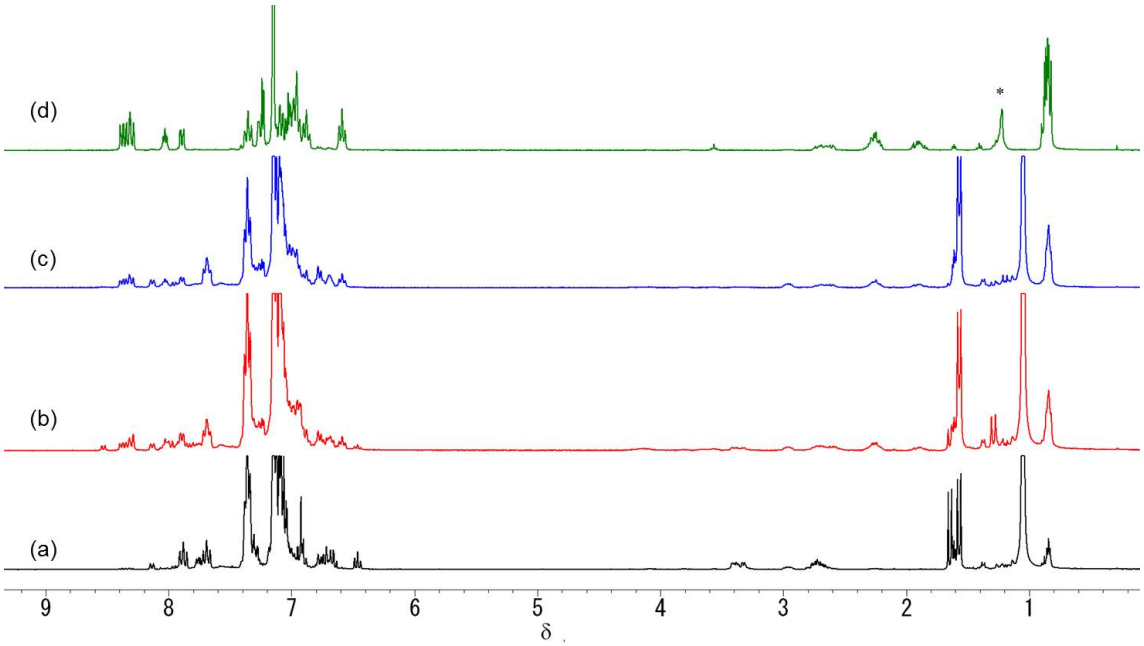

Figure S24. ^{1}H NMR spectra (300 MHz). (a) A C_6D_6 solution of **6** and PMe_2Ph were heated at 60 °C for 5 h. (b) CO gas was introduced. (c) The solution was heated at 40 °C for 1 h under an atmosphere of CO. (d) A C_6D_6 solution of **8**.

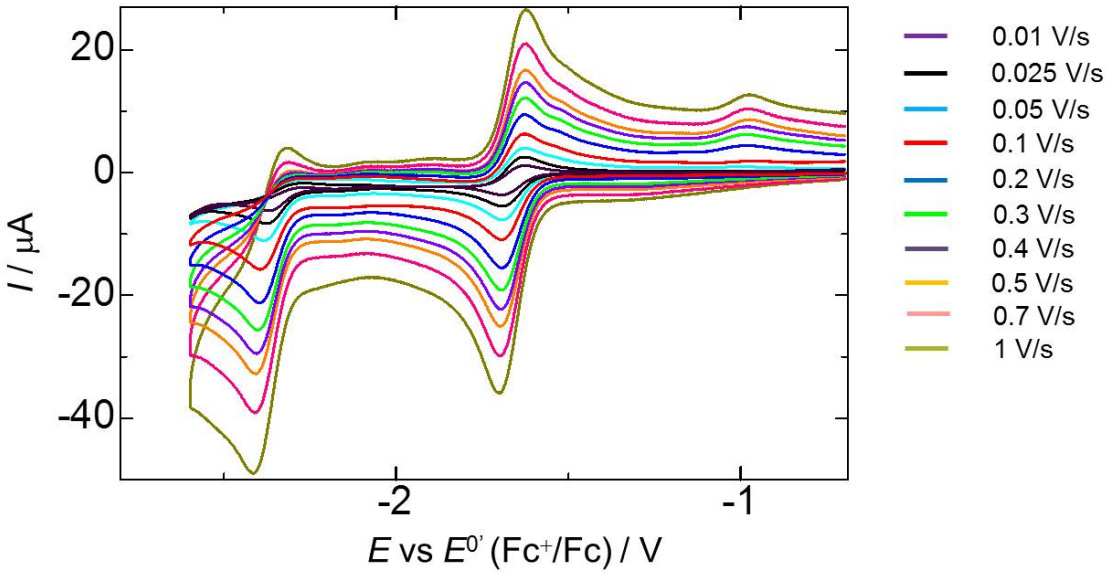

Figure S25. The reduction processes of **5** (5.0×10^{-4} M) in CH_3CN containing 0.10 M Bu_4NPF_6 recorded at scan rates from 0.01 to 1 V s^{-1}: working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).

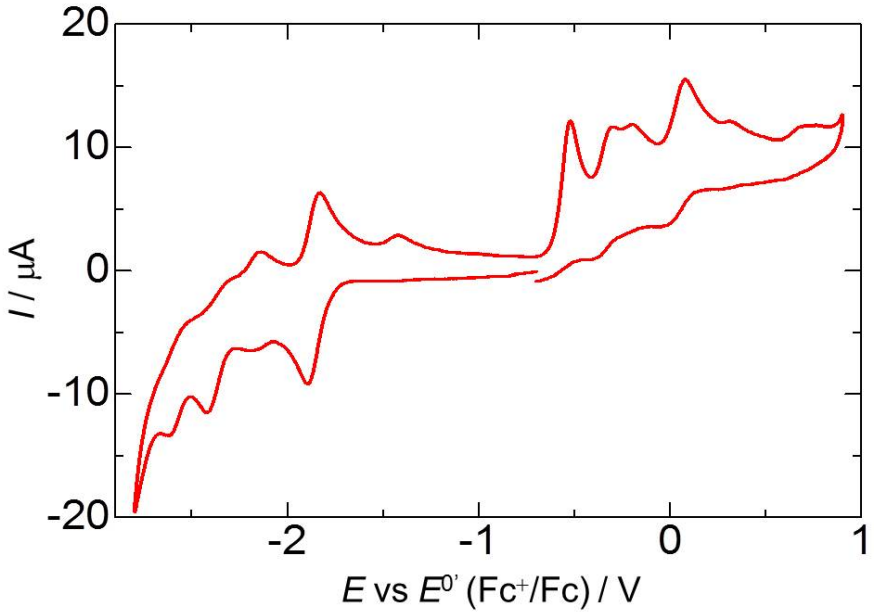

Figure S26. The reduction processes of **6** (5.0×10^{-4} M) in CH_3CN containing 0.10 M Bu_4NPF_6 recorded in the scan range of 0.9 to –2.8 V: working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).