Electronic Supplementary Information for

Insertion chemistry of iron(II) boryl complexes

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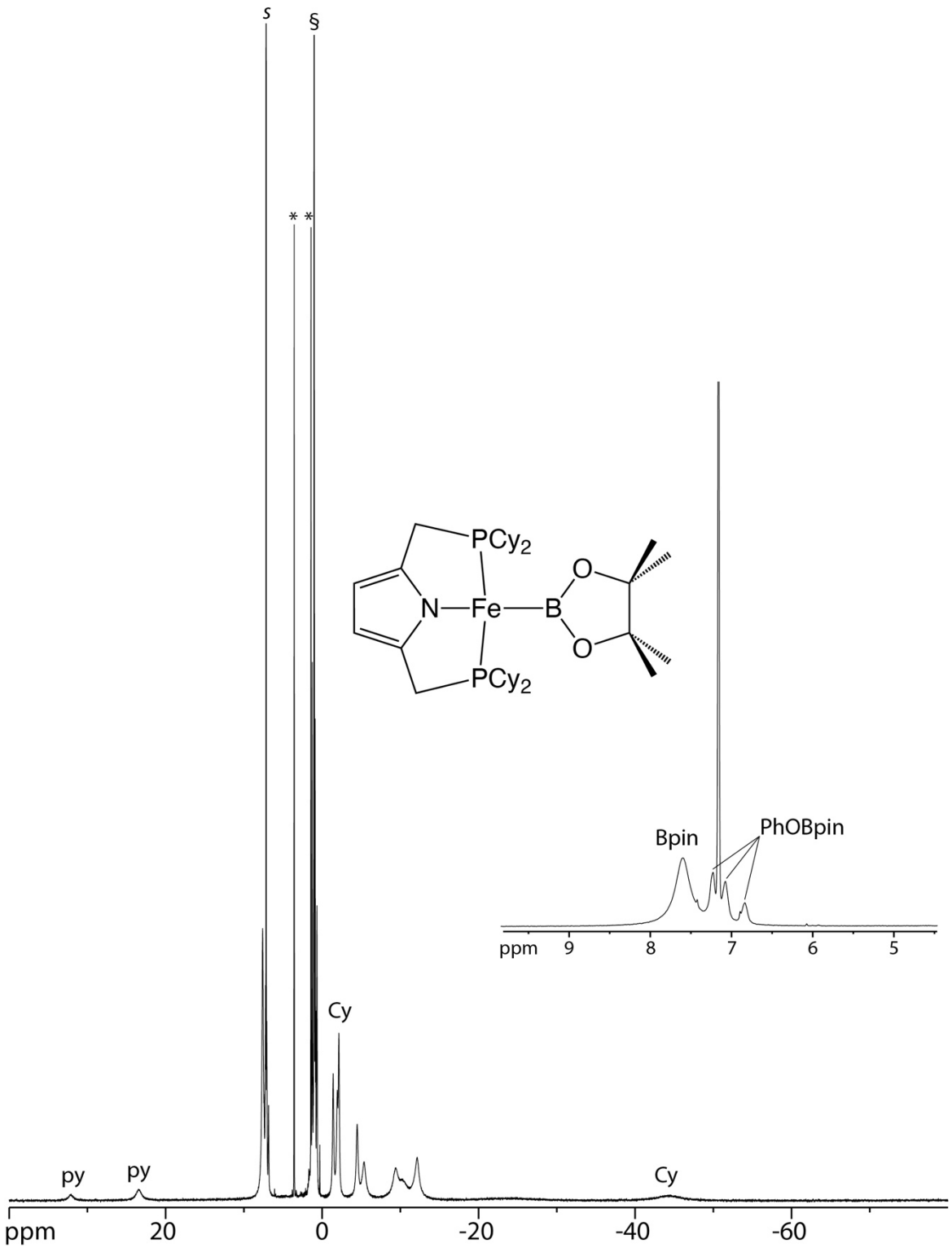

Figure S1. 300 MHz ^{1}H NMR spectrum of [Fe(Bpin)(^{Cy}PNP)] (**3a**) in benzene-d_6(*s*) generated from the reaction of **1·py** and B_2pin_2. Inset displays an expansion of the region from 4 to 10 ppm showing peaks for the expected byproduct, PhOBpin. Asterisks denote resonances for thf used in the preparation of **1·py**. The resonance for excess B_2pin_2 and PhOB*pin* is marked with §.

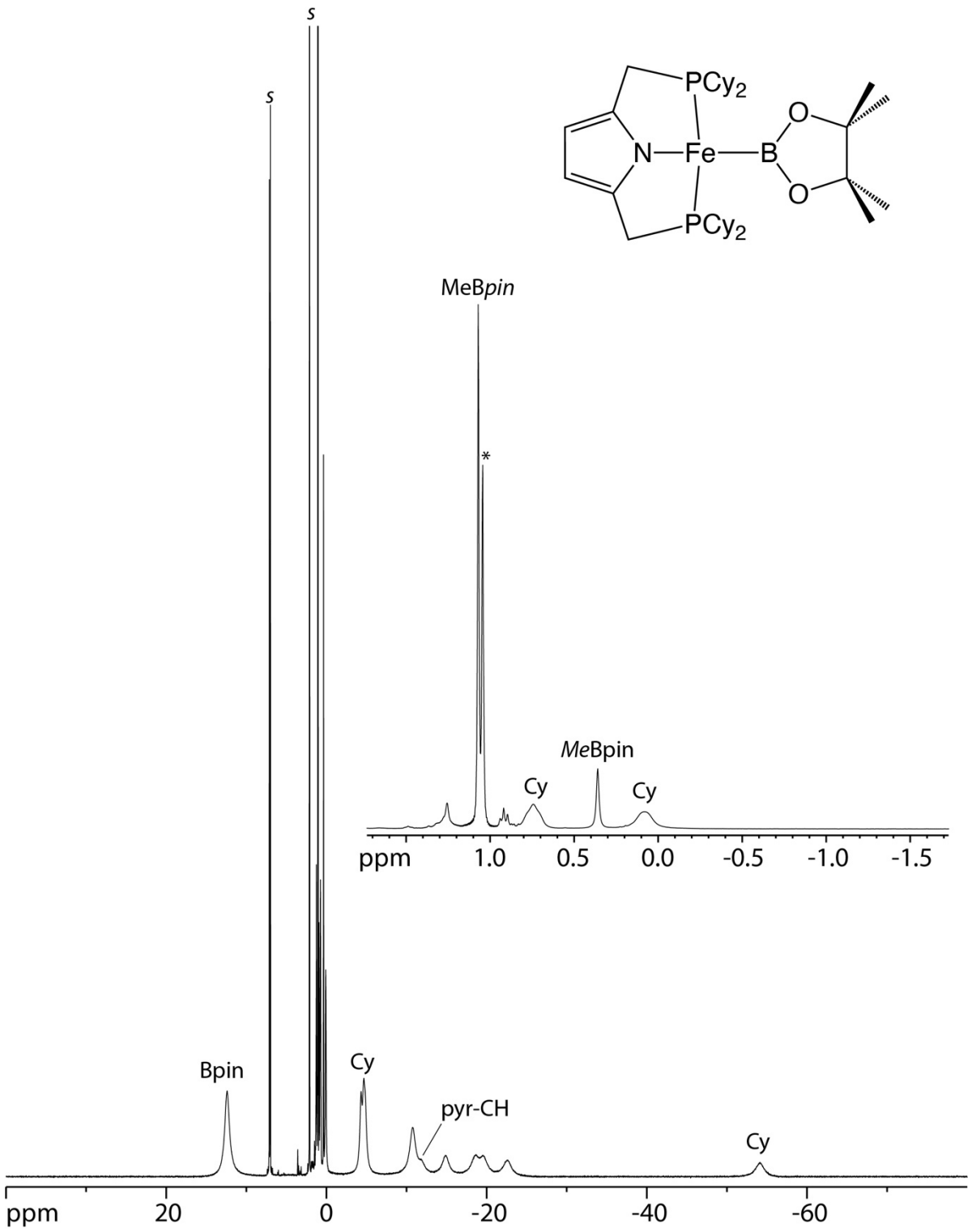

Figure S2. 300 MHz ^{1}H NMR spectrum of [Fe(Bpin)(^{Cy}PNP)] (**3a**) in toluene-d_8(*s*) generated from the reaction of **2** and B_2pin_2. Inset displays an expansion of the region from −2 to 2 ppm showing peaks for the expected byproduct, MeBpin. Asterisk denotes the resonance for excess B_2pin_2.

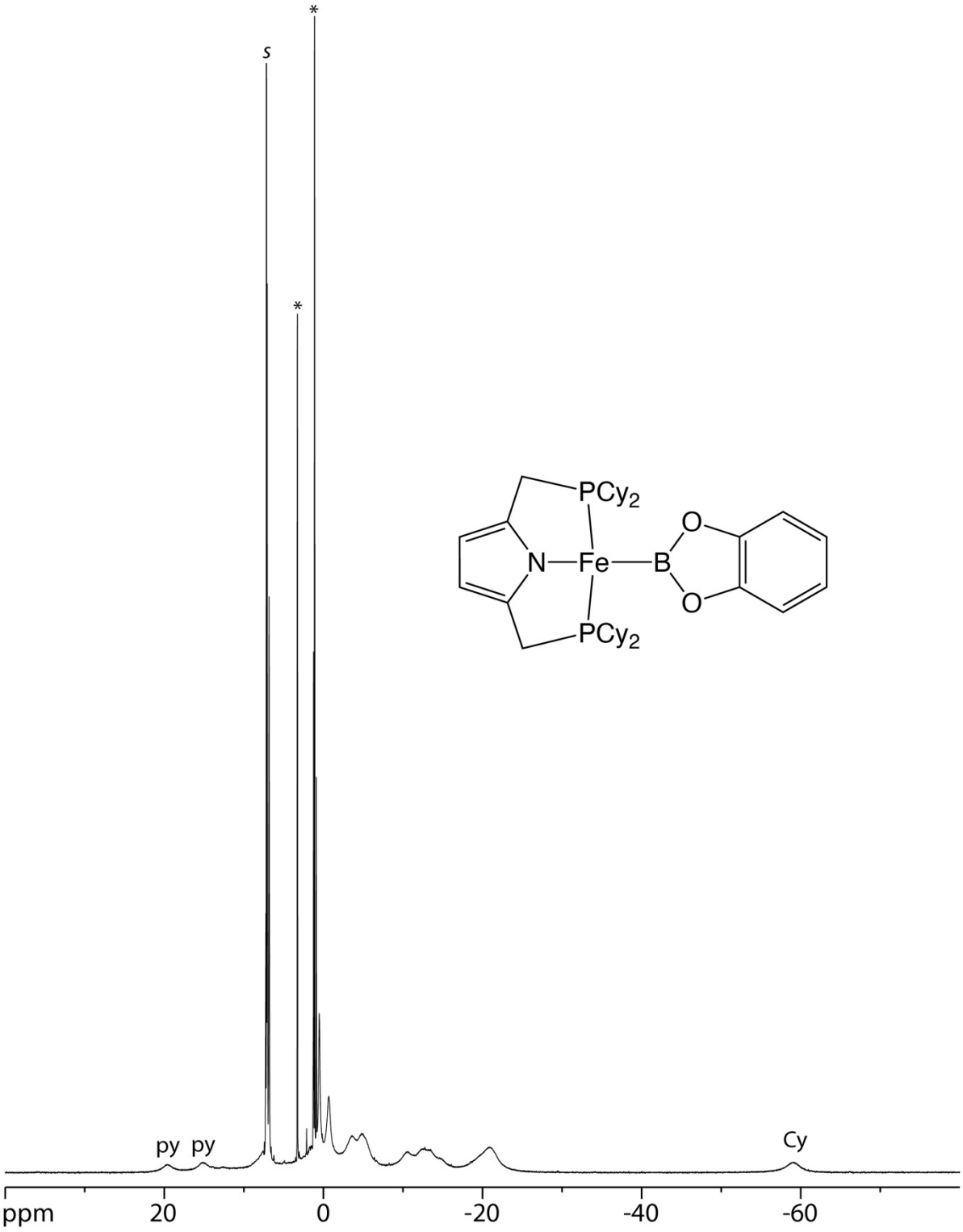

Figure S3. 300 MHz ^{1}H NMR spectrum of [Fe(Bcat)(^{Cy}PNP)] (**3b**) in benzene-d_6(*s*) generated from the reaction of **1·py** and B_2cat_2. Asterisks denotes resonances for Et_2O used in purification of **1·py**.

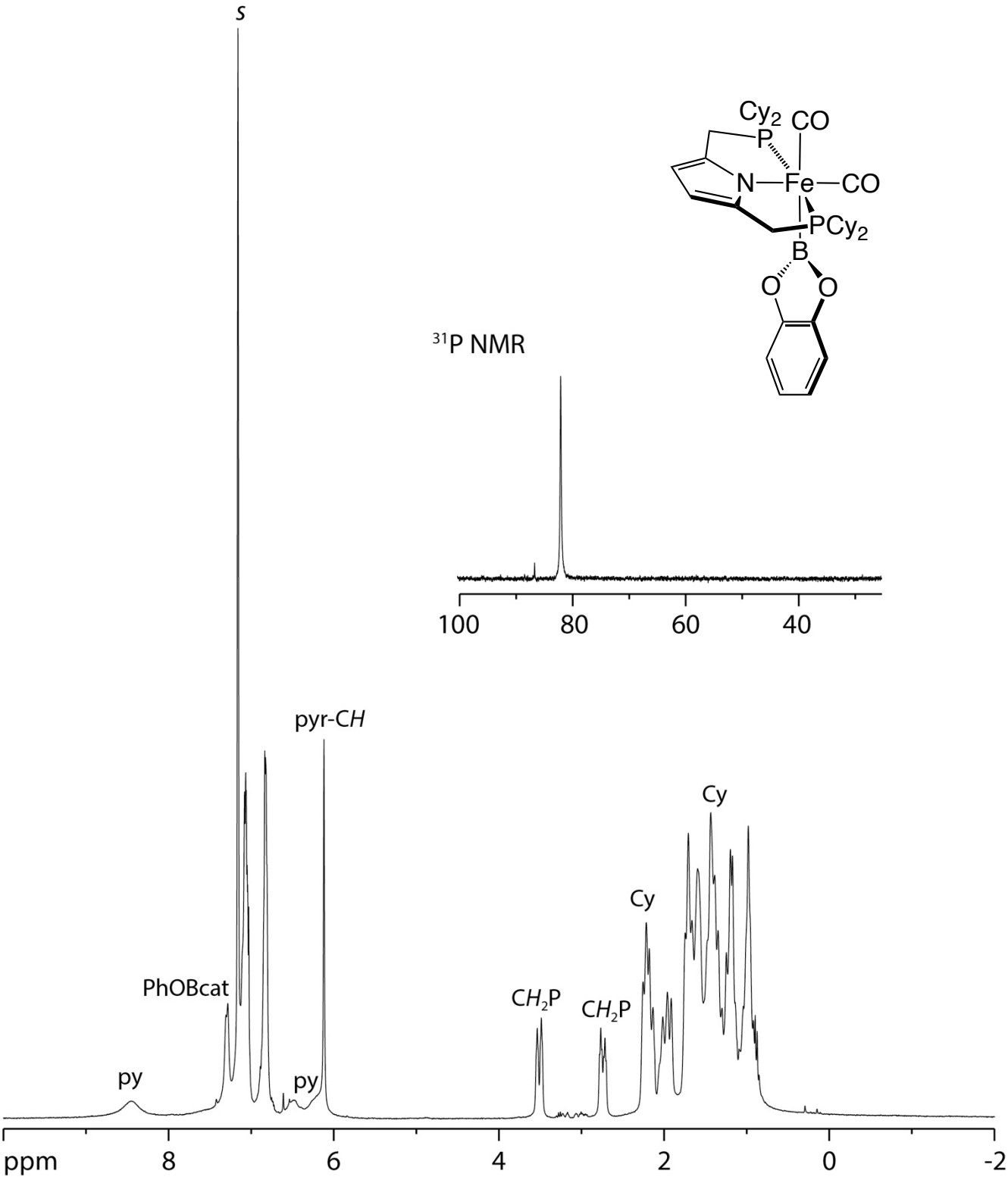

Figure S4. 300 MHz ^{1}H NMR spectrum of putative [Fe(Bcat)(CO)$_2$(^{Cy}PNP)] (**3b·CO**) in benzene-d_6(*s*) generated from the reaction of **1·py** and B_2cat_2 followed by introduction of CO(g).

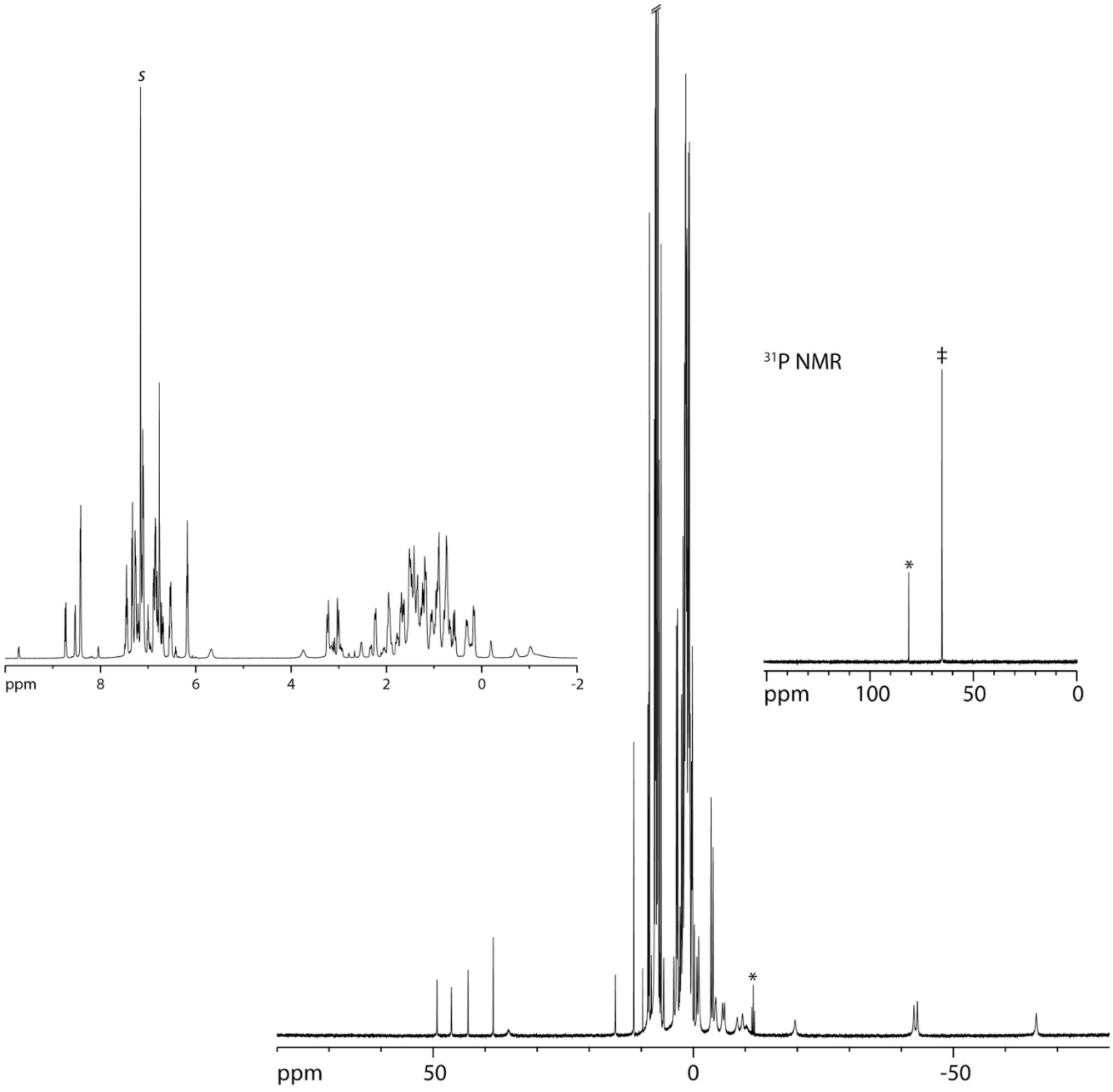

Figure S5. 300 MHz ^{1}H NMR spectrum of the reaction of in situ-generated [Fe(Bcat)(^{Cy}PNP)] (**3b**) with 2,2'-bipyridine in benzene-d_6(*s*). Left inset displays expansion of the diamagnetic region. Asterisks denote resonances for [FeH(bipy)(^{Cy}PNP)]. ^{31}P NMR resonance for putative **3b·bipy** is marked with ‡.

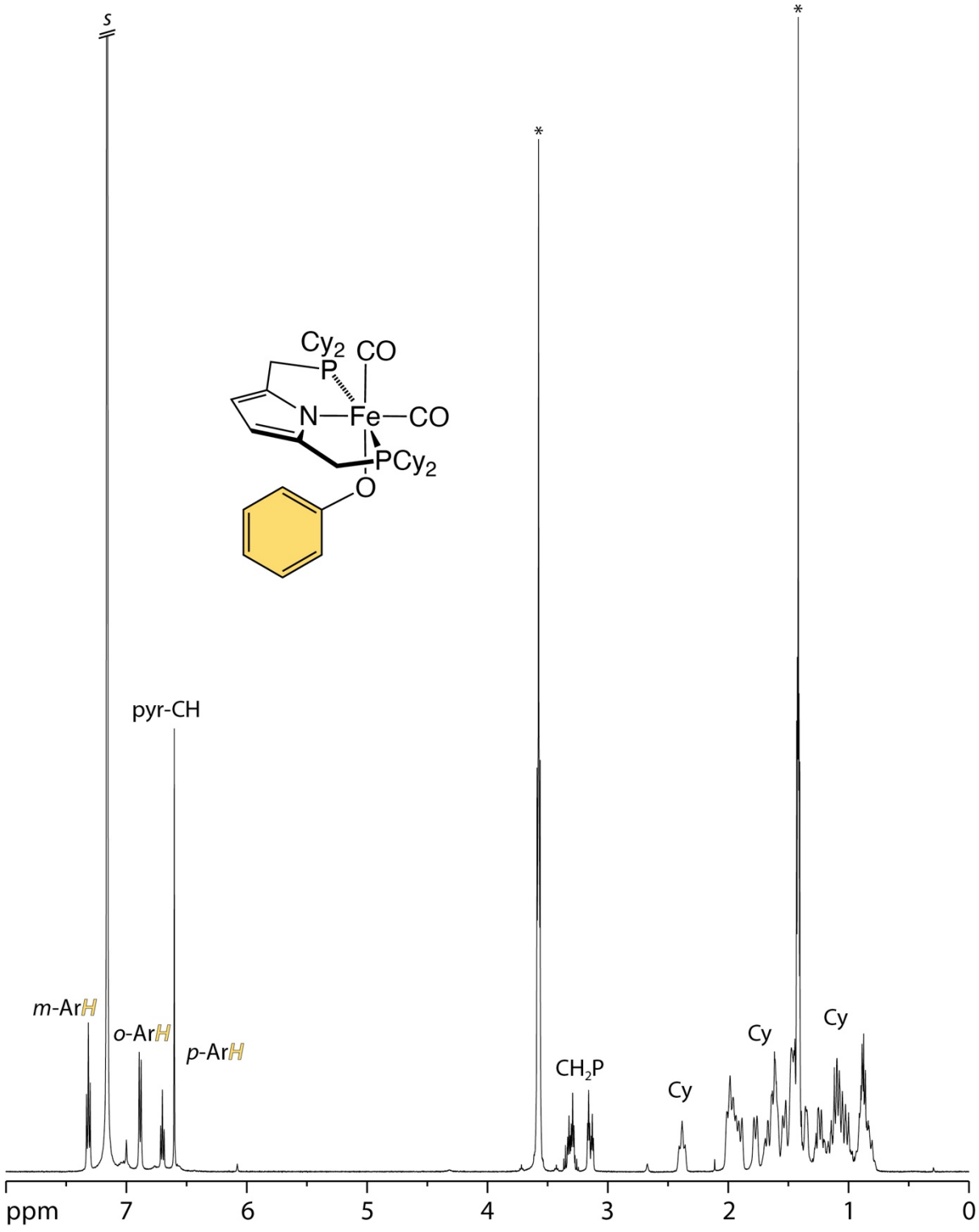

Figure S6. 500 MHz ^{1}H NMR spectrum of [Fe(CO)$_2$(OPh)(^{Cy}PNP)] (**1·CO**) in benzene-d_6(*s*). Asterisks denotes resonances for thf used in preparation of **1·py**.

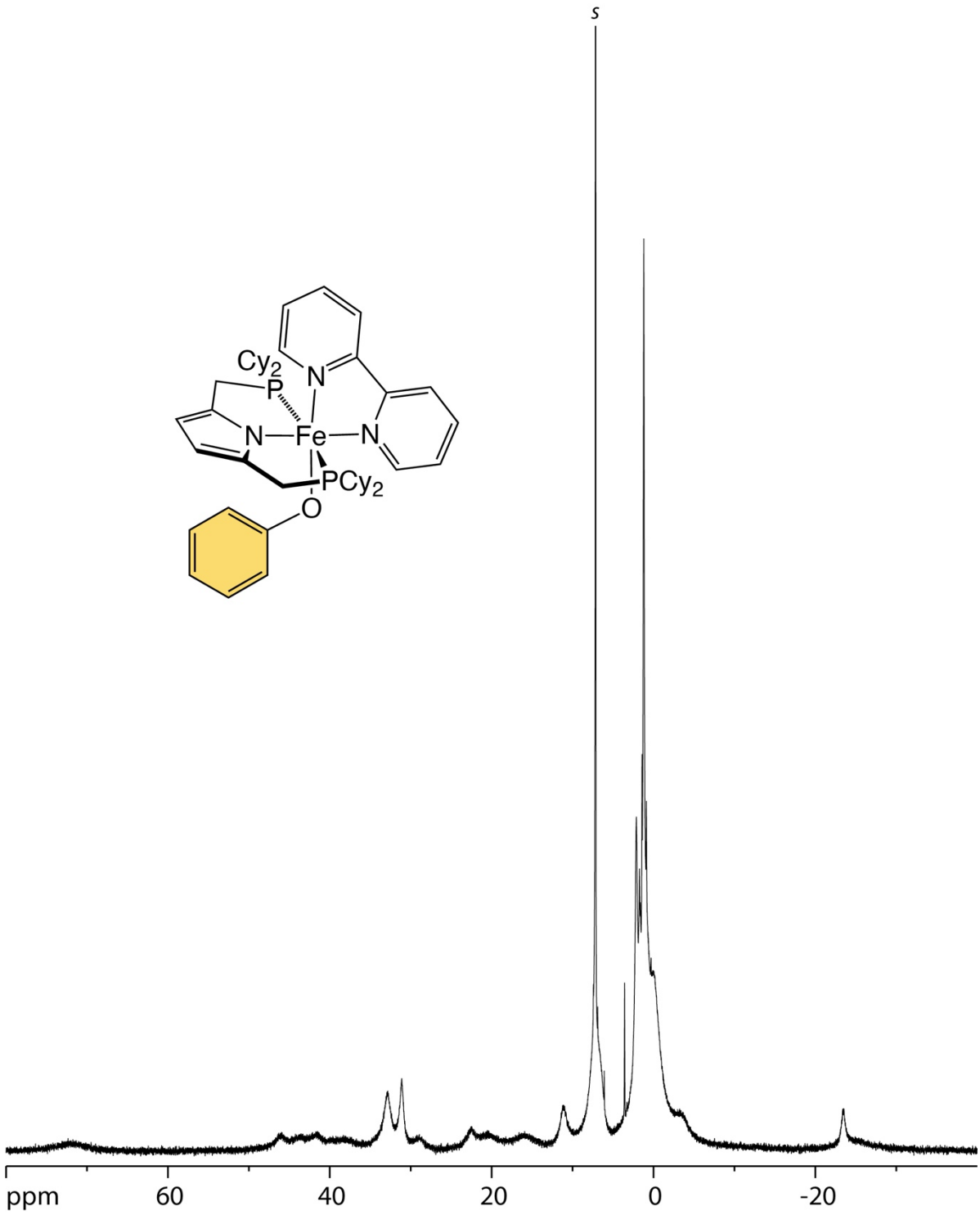

Figure S7. 300 MHz ^{1}H NMR spectrum of [Fe(bipy)(OPh)(^{Cy}PNP)] (**1·bipy**) in benzene-d_6(*s*).

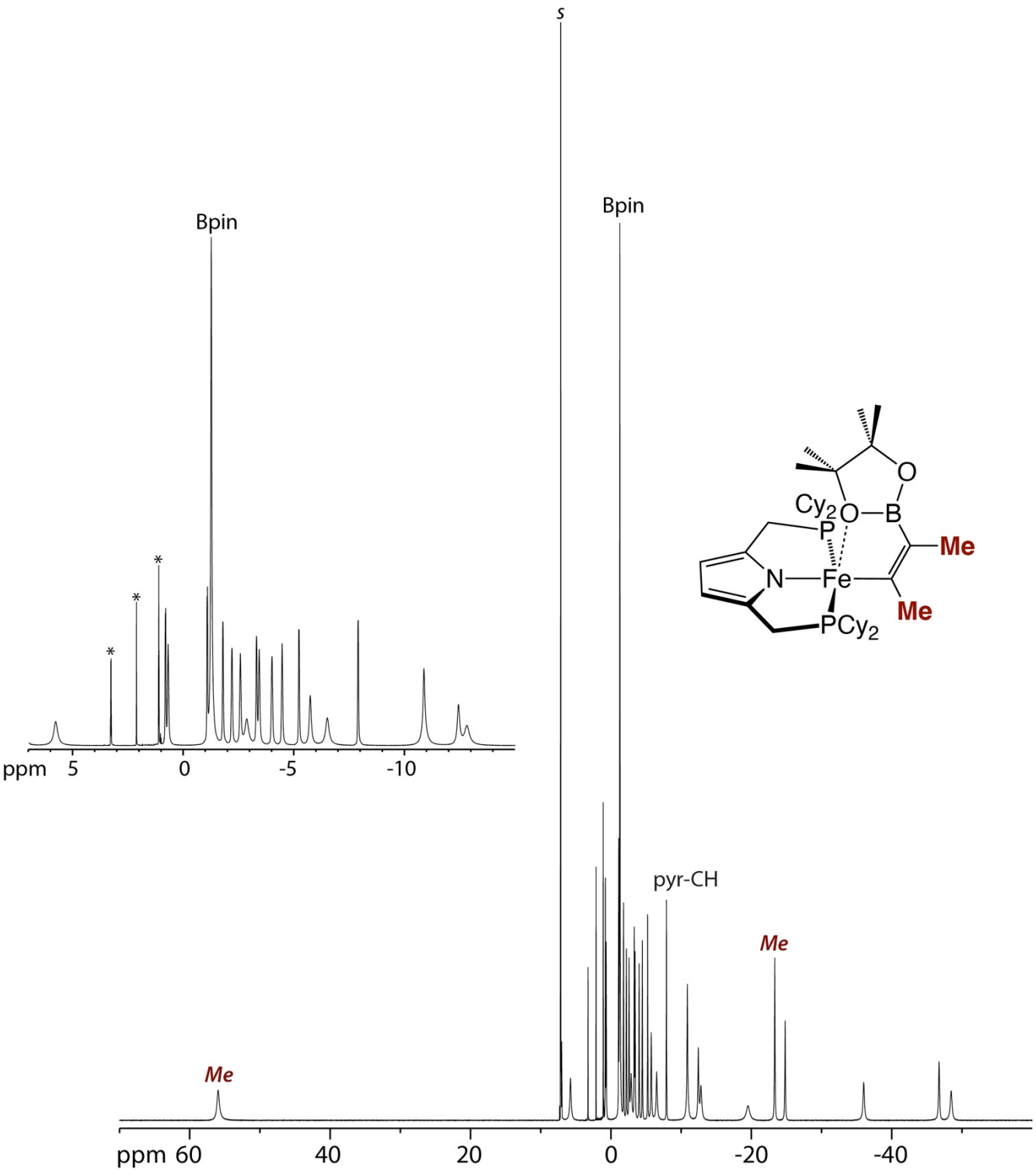

Figure S8. 300 MHz ^{1}H NMR spectrum of [Fe(C{Me}C{Me}Bpin)(^{Cy}PNP)] (**4a**) in benzene-d_6(*s*). Inset displays an expansion of the region from −15 to 7 ppm. Asterisks denote resonances for toluene and ether used in purification.

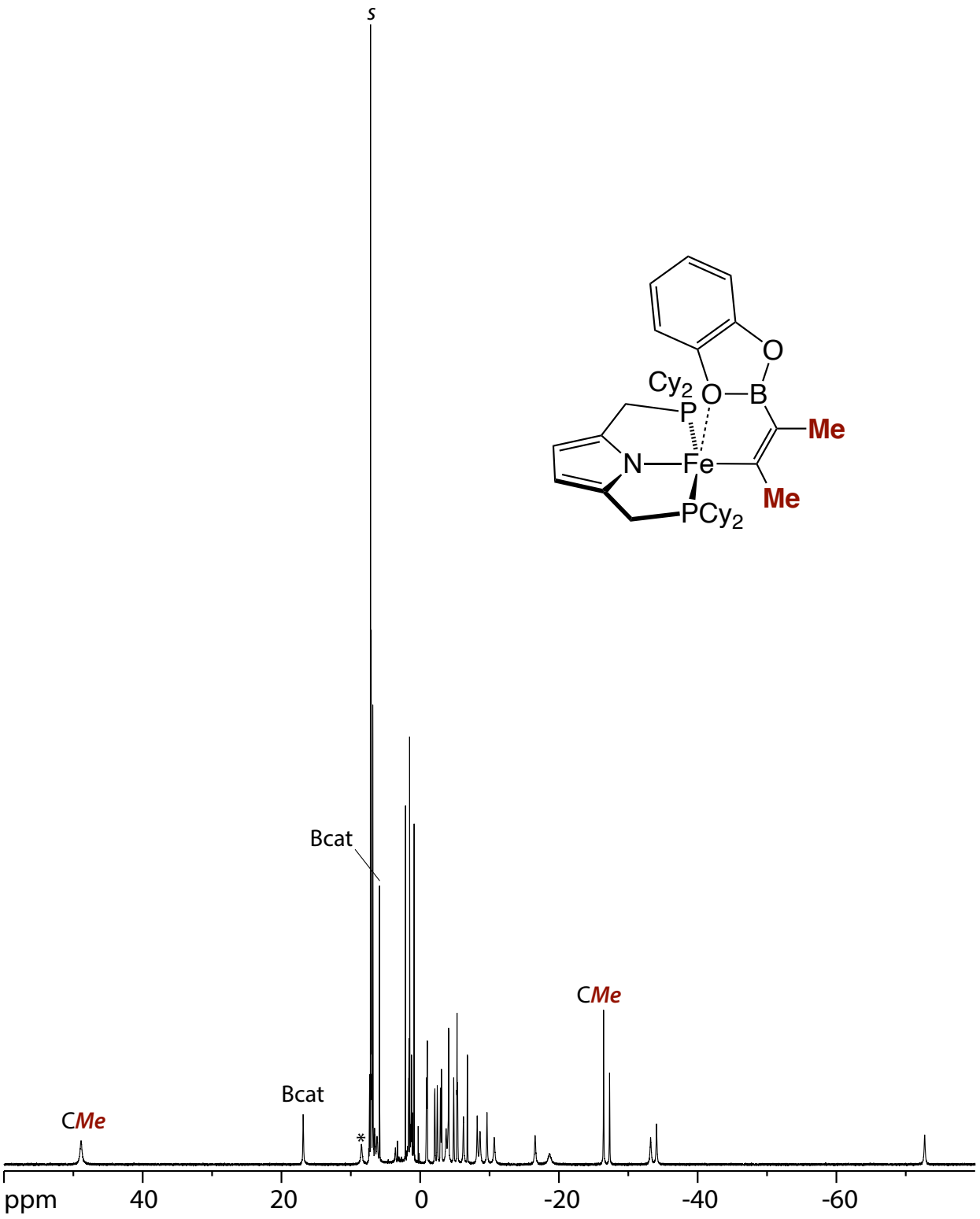

Figure S9. 300 MHz ^{1}H NMR spectrum of [Fe(C{Me}C{Me}Bcat)(^{Cy}PNP)] (**4b**) in benzene-d_6(*s*). Asterisks denote a resonance from the pyridine byproduct, PhOBcat.

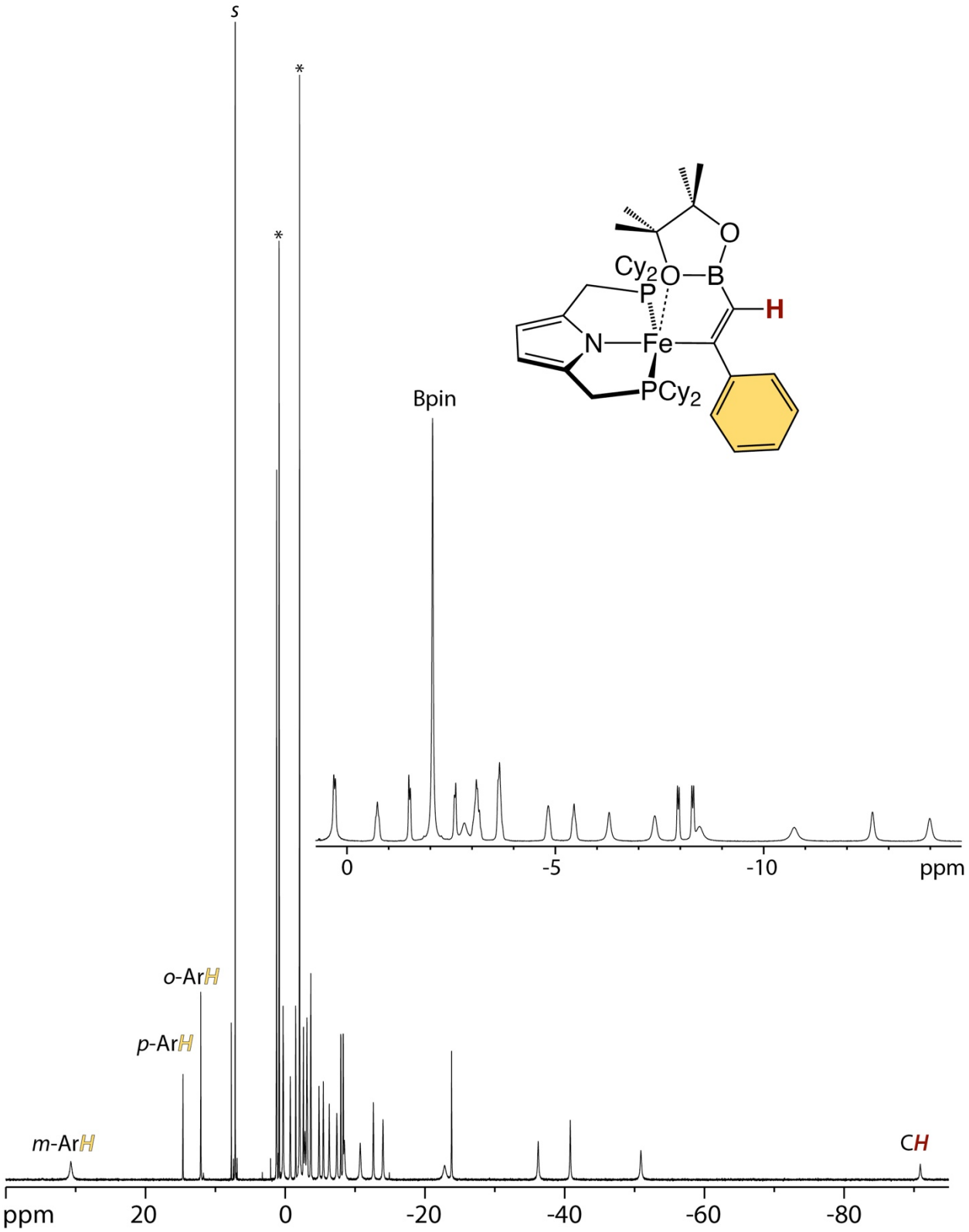

Figure S10. 300 MHz ^{1}H NMR spectrum of [Fe(C{Ph}C{H}Bpin)(^{Cy}PNP)] (**5a**) in benzene-d_6(*s*). Inset displays an expansion of the region from −15 to 1 ppm. Asterisks denote resonances for diethyl ether from purification.

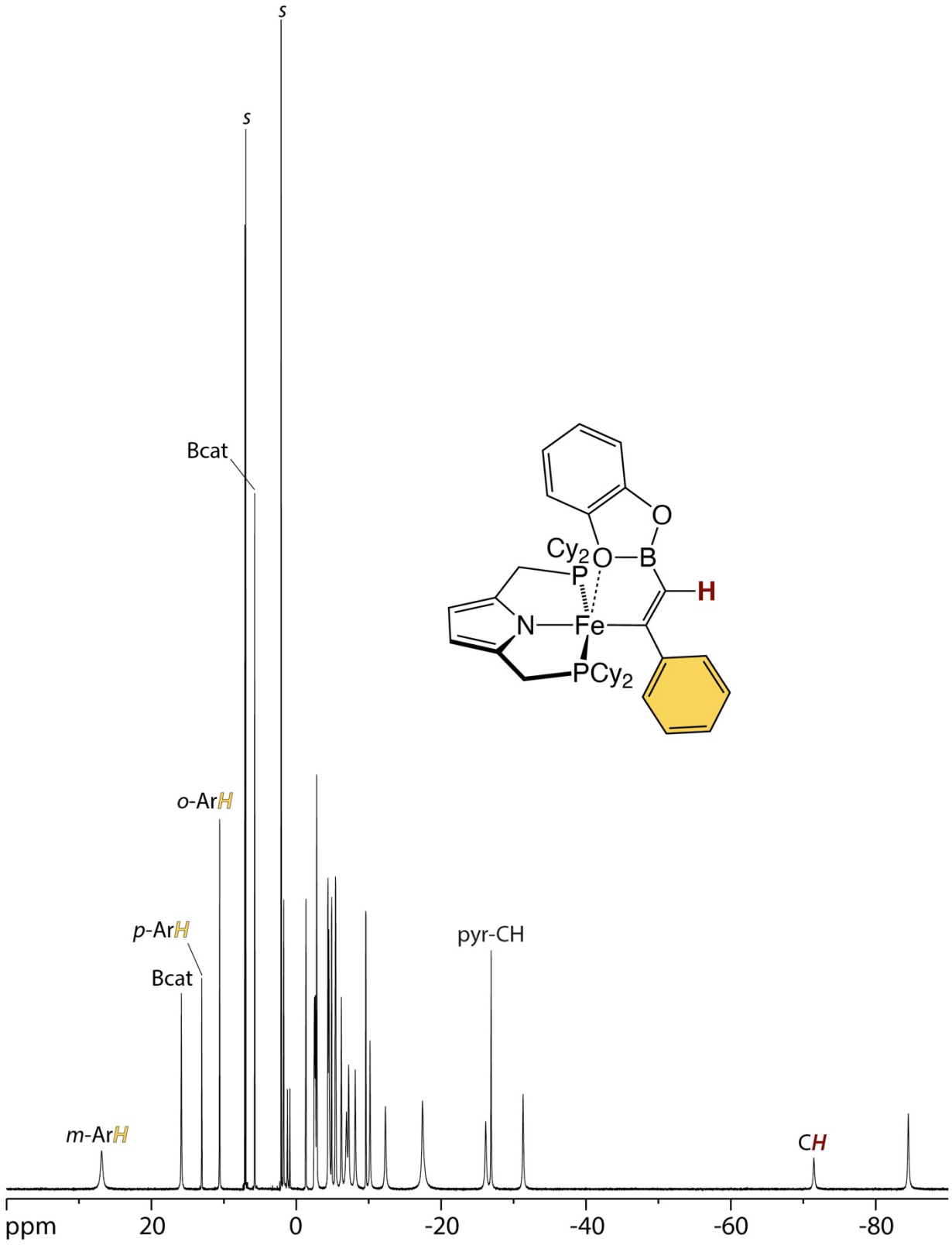

Figure S11. 300 MHz ^{1}H NMR spectrum of [Fe(C{Ph}C{H}Bcat)(^{Cy}PNP)] (**5b**) in toluene-d_8(*s*).

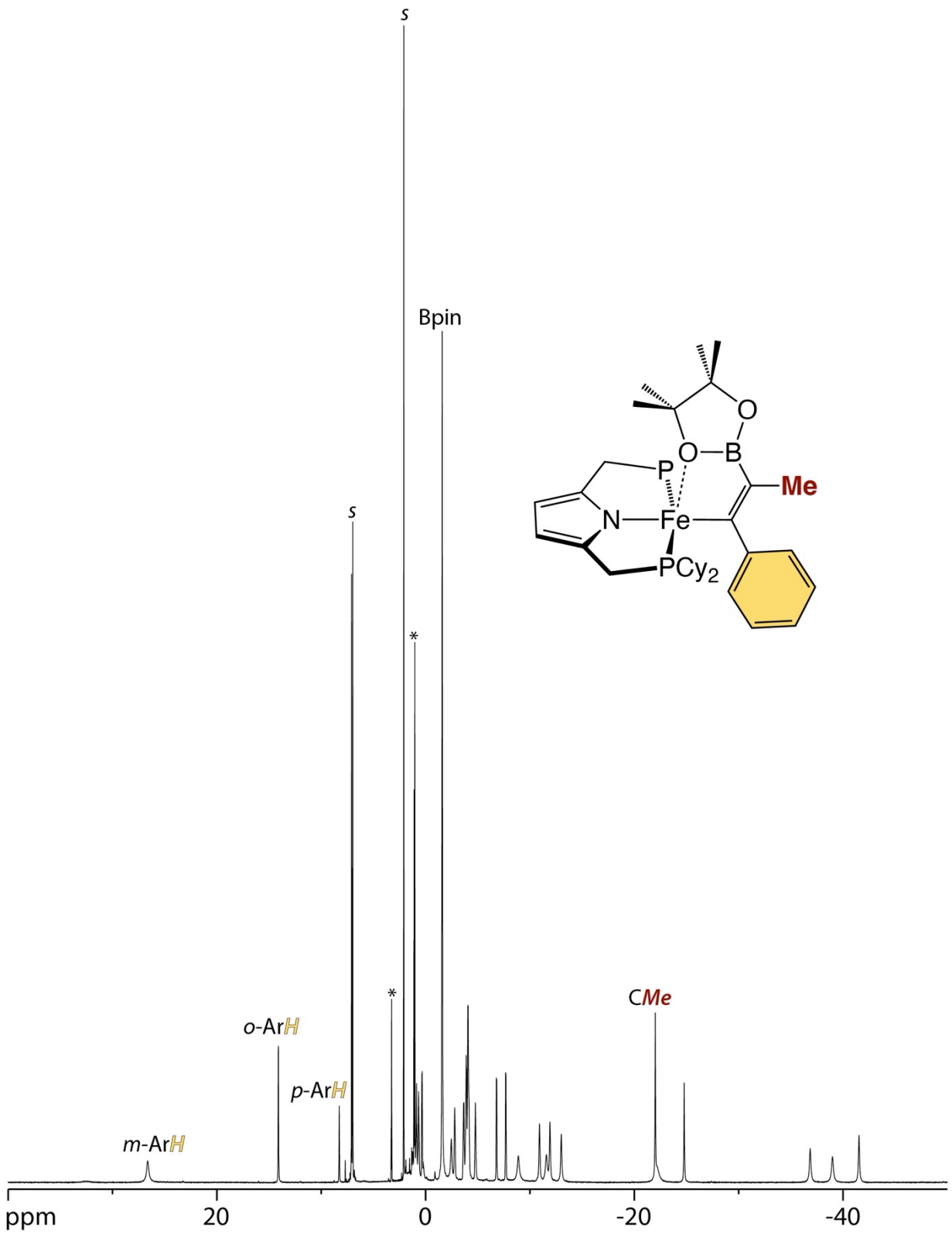

Figure S12. 300 MHz ^{1}H NMR spectrum of [Fe(C{Ph}C{Me}Bpin)(^{Cy}PNP)] (**6a**) in toluene-d_8(*s*). Asterisks denote resonances for diethyl ether from purification.

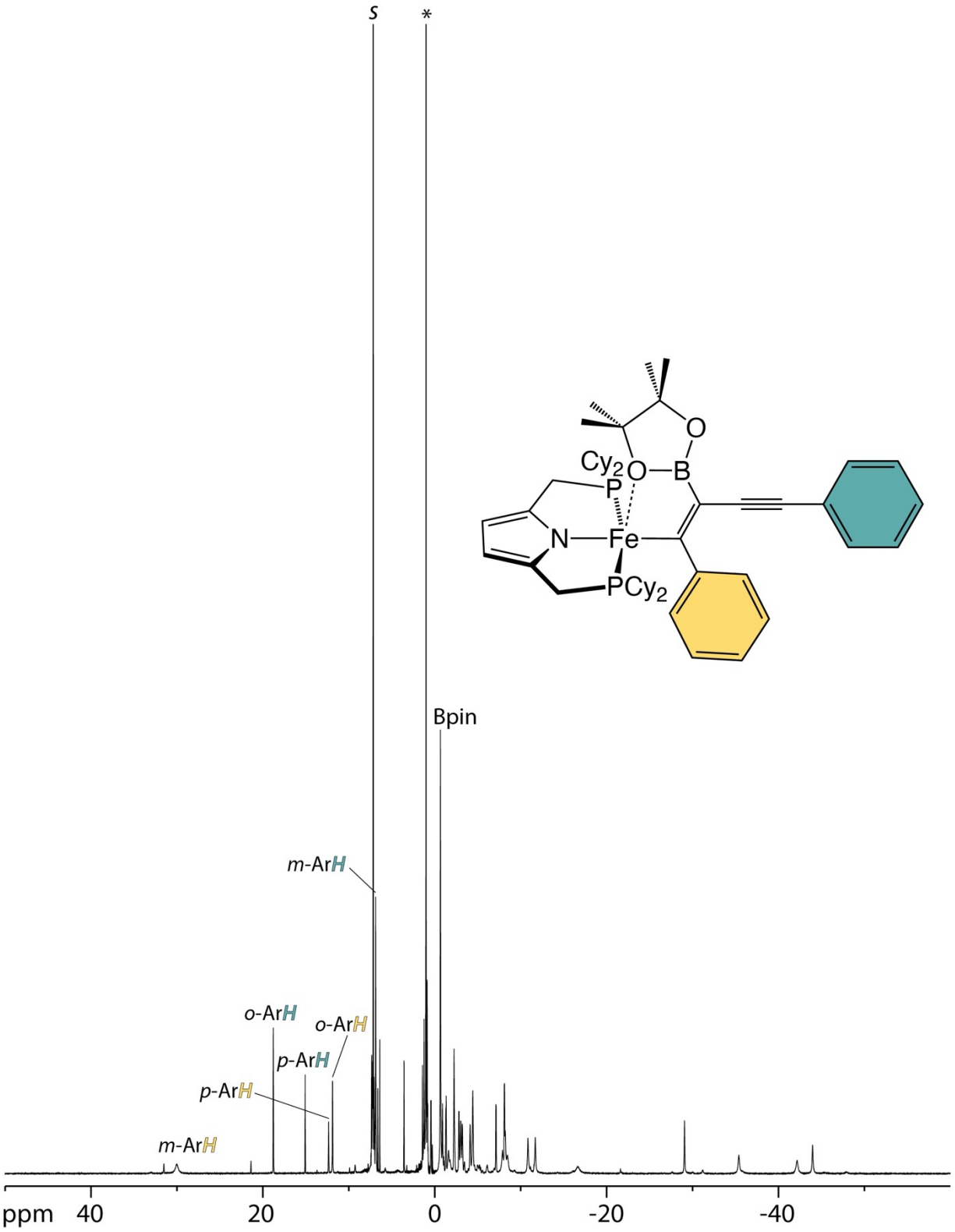

Figure S13. 300 MHz ^{1}H NMR spectrum of [Fe(C{Ph}C{CCPh}Bpin)(^{Cy}PNP)] (**7a**) in benzene-d_6(*s*). Asterisk denotes resonances for residual B_2pin_2 used in preparation of **3a**.

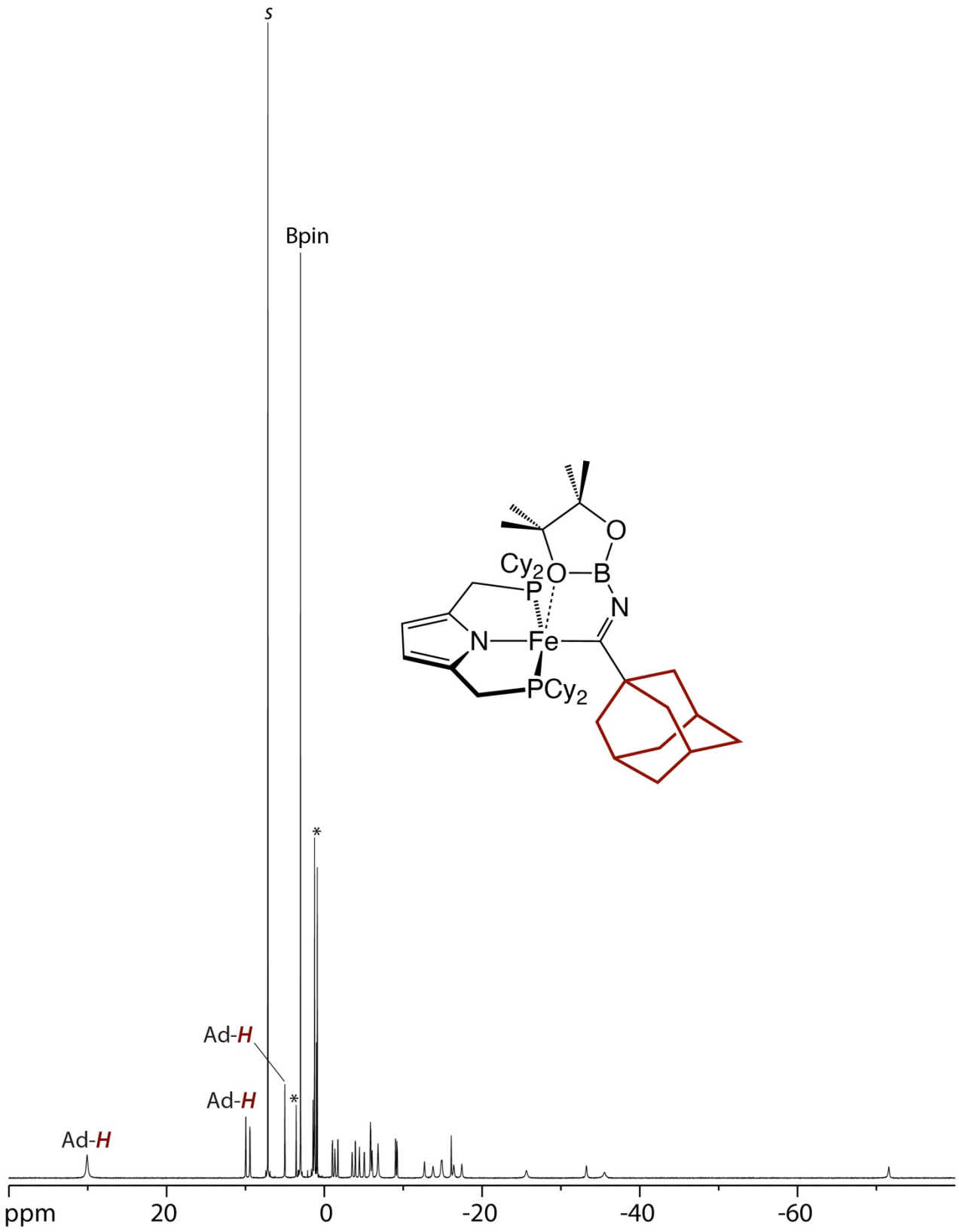

Figure S14. 300 MHz ^{1}H NMR spectrum of [Fe(C{Ad}NBpin)(^{Cy}PNP)] (**8**) in benzene-d_6(*s*).

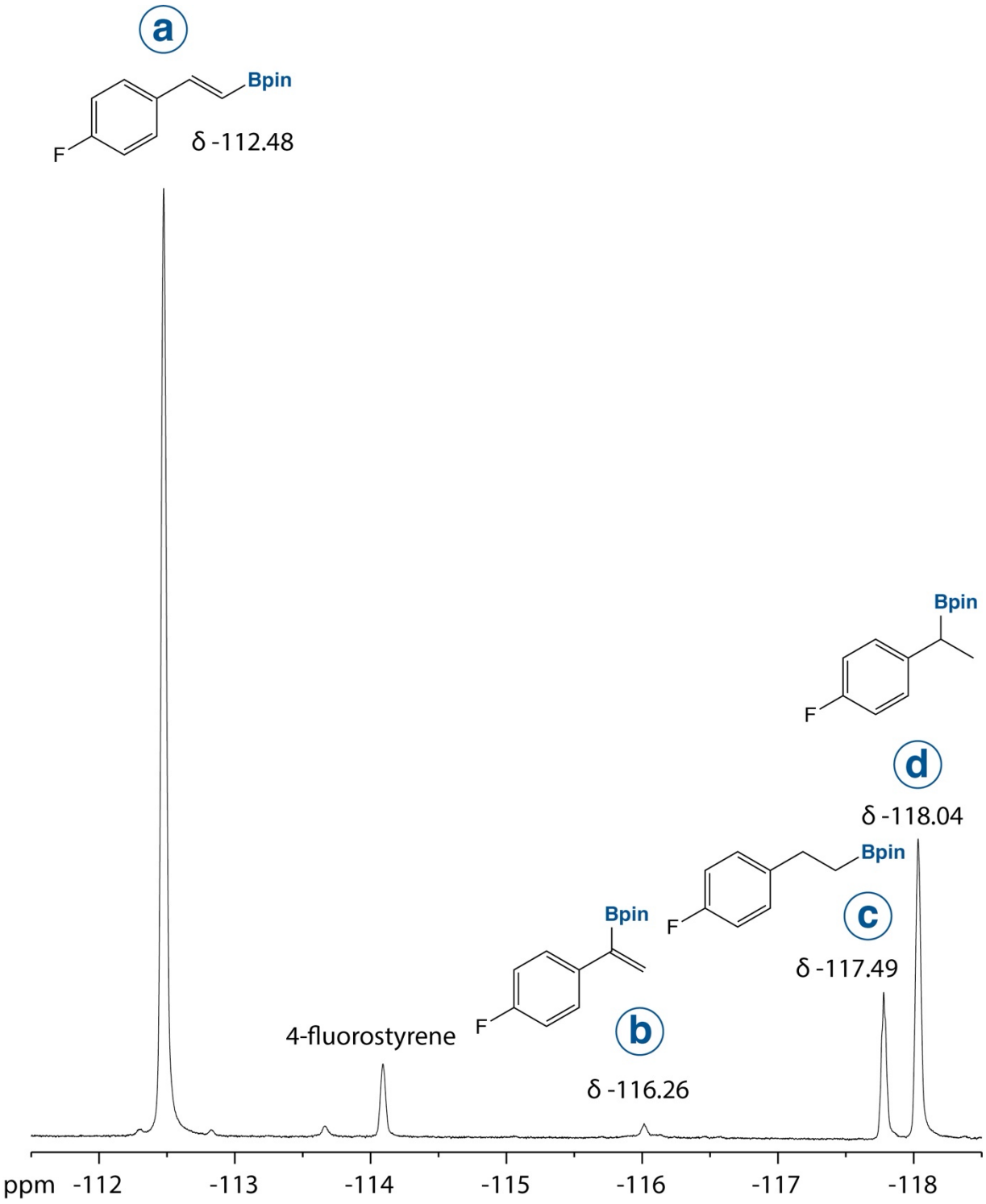

Figure S15. Selected region of the ^{19}F NMR spectrum of the reaction of **3a** and 4-fluorostyrene in benzene-d_6(*s*) showing formation of borylated products. Product assignments (a – d) correspond to those in Scheme 4 of the main text.

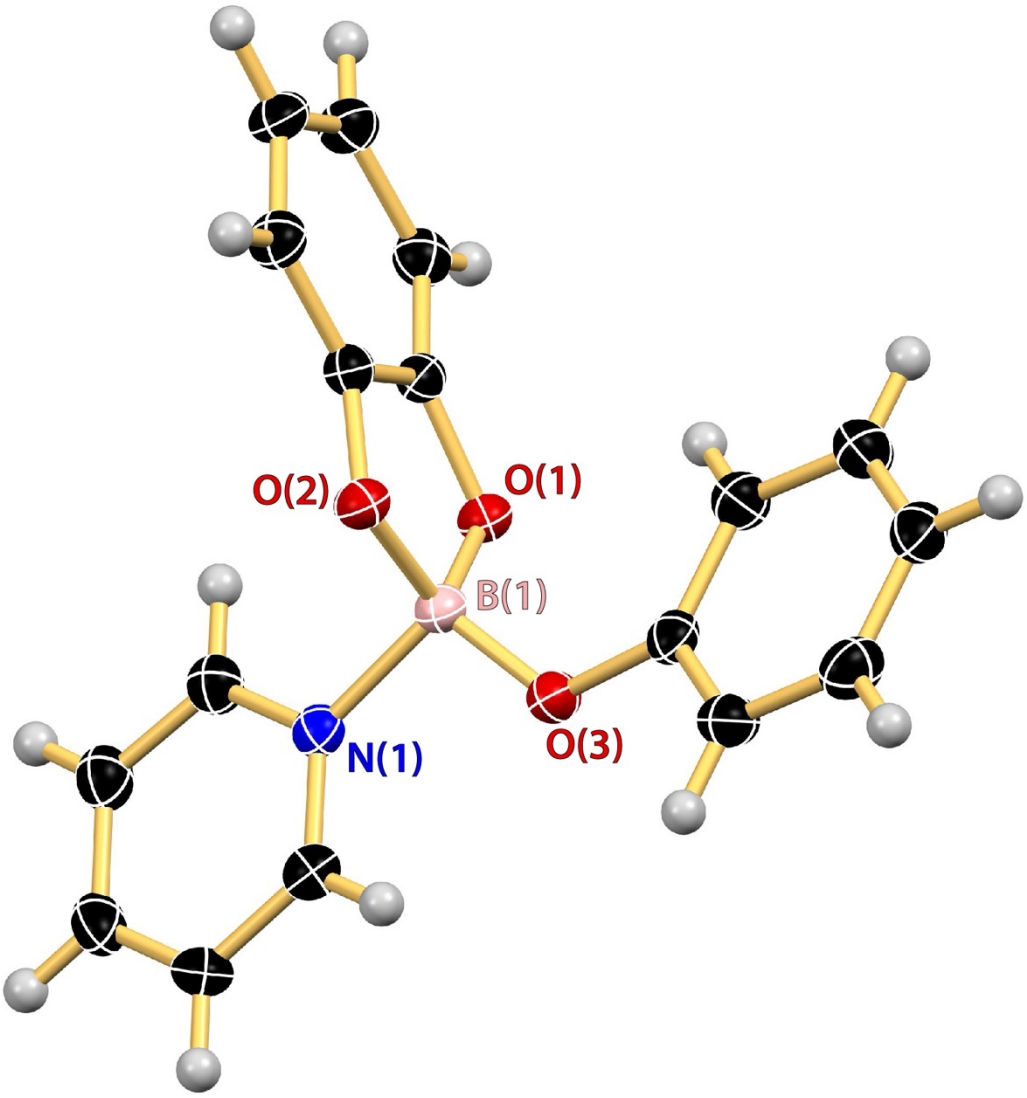

Figure S16. Thermal ellipsoid drawing (50%) of the solid-state structure of PhO(py)Bcat isolated from the synthesis of **3b**.

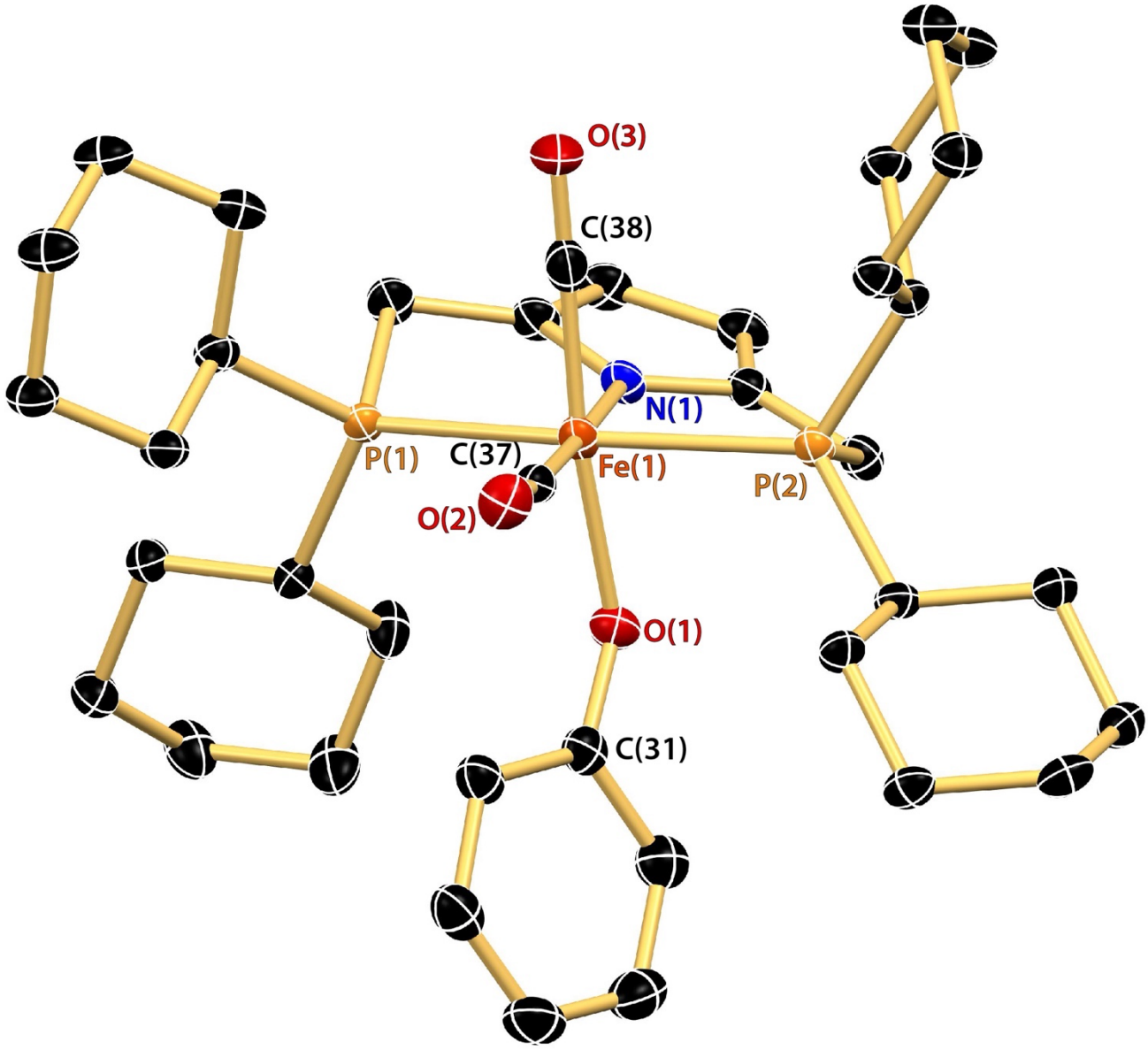

Figure S17. Thermal ellipsoid drawing (50%) of the solid-state structures of **1·CO**. Hydrogen atoms are omitted for clarity.

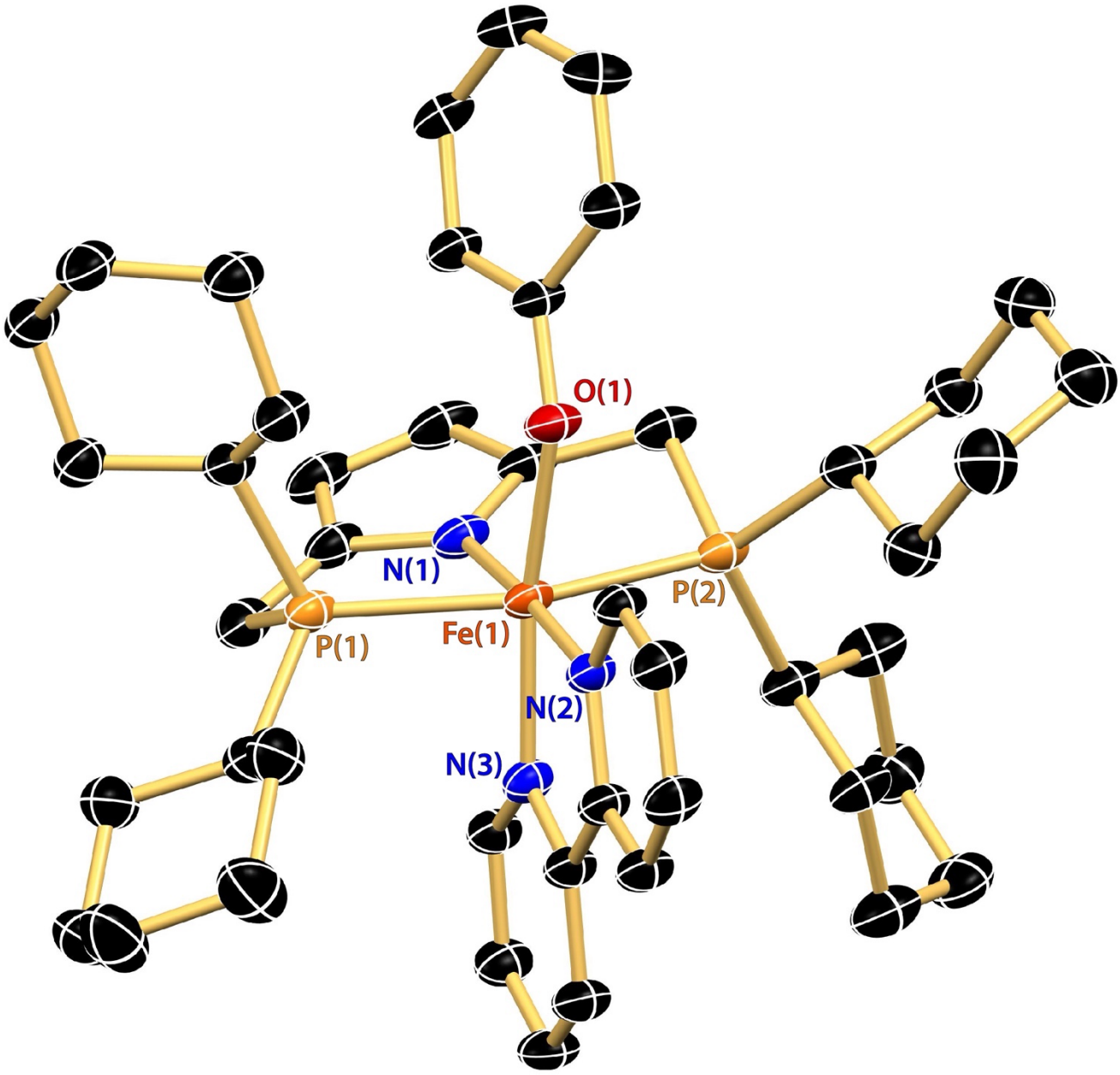

Figure S18. Thermal ellipsoid drawing (50%) of the solid-state structures of **1·bipy**. Hydrogen atoms are omitted for clarity.

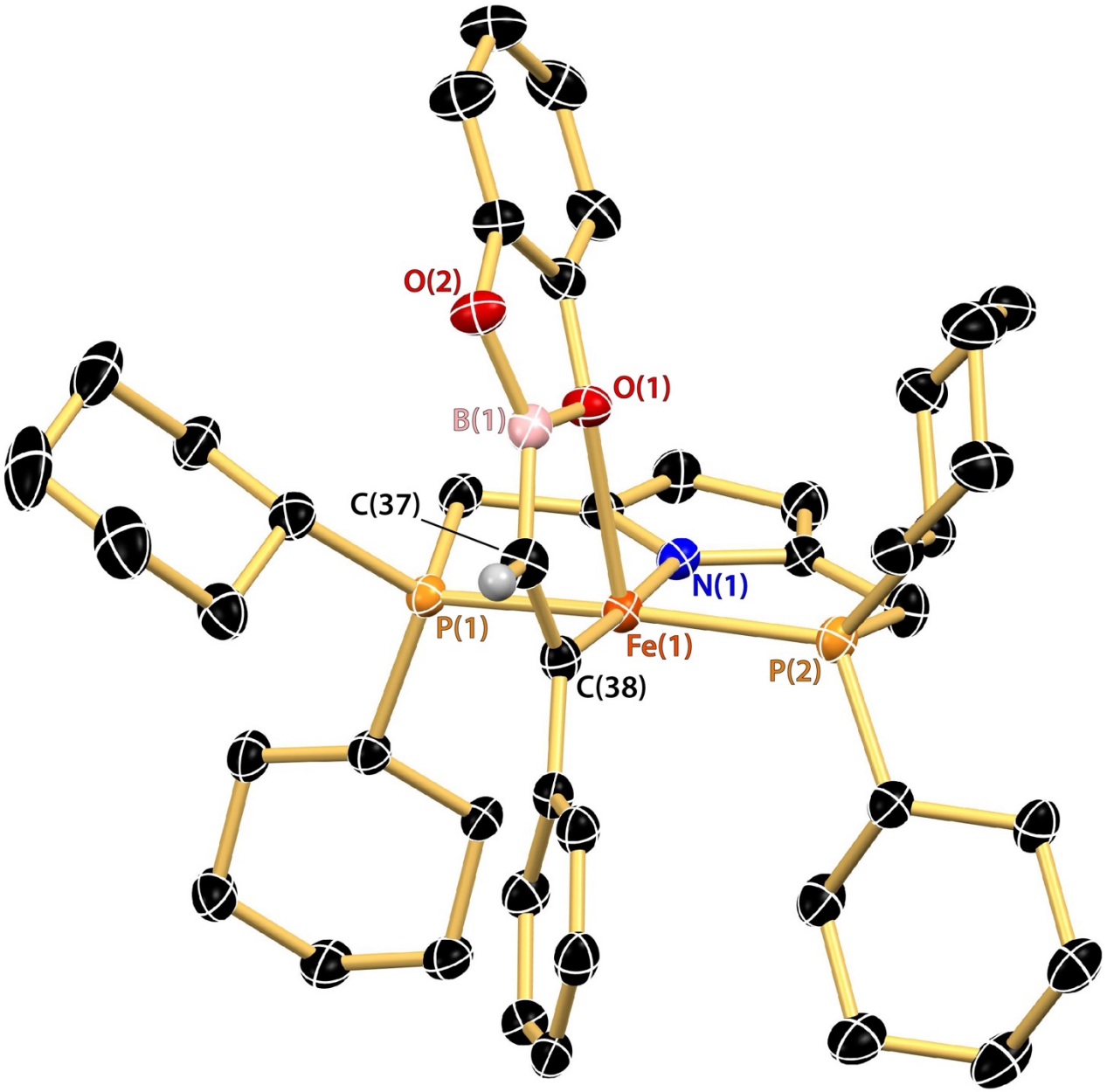

Figure S19. Thermal ellipsoid drawing (50%) of the solid-state structures of **5b**. Hydrogen atoms with the exception of that bound to C(37) are omitted for clarity.

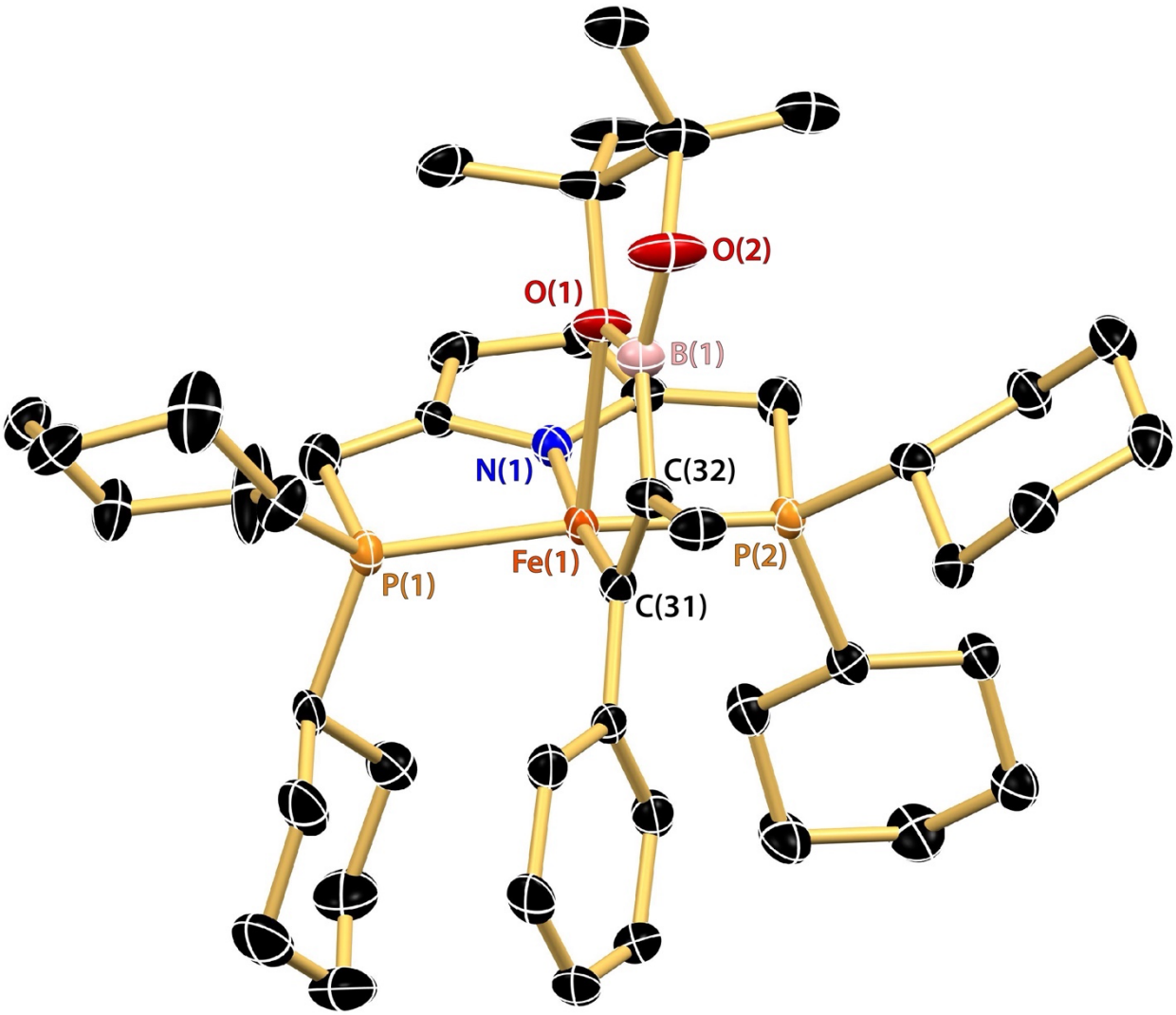

Figure S20. Thermal ellipsoid drawing (50%) of the solid-state structures of **6a**. Hydrogen atoms and minor components of the disorder are omitted for clarity.

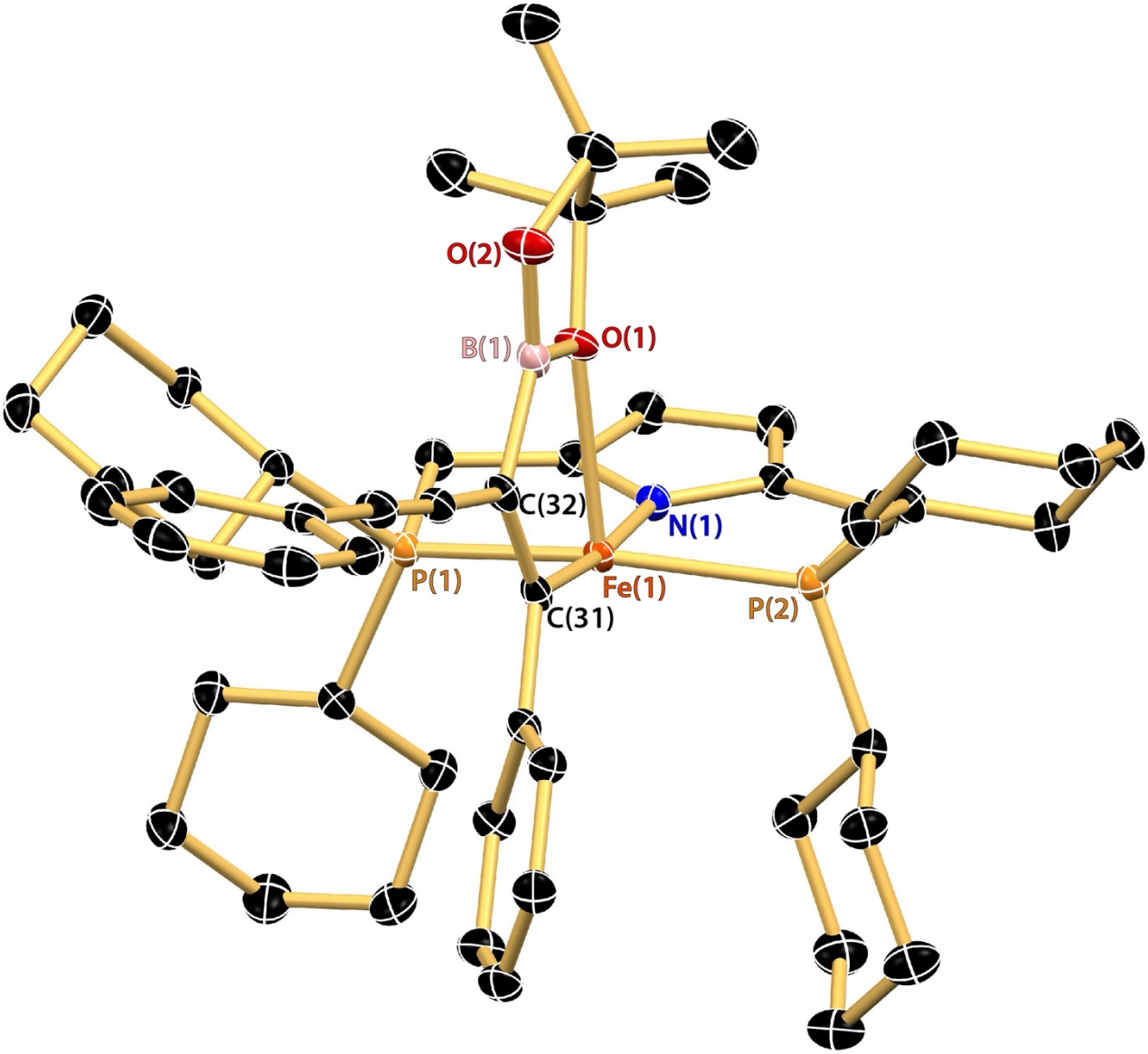

Figure S21. Thermal ellipsoid drawing (50%) of the solid-state structures of **7a**. Hydrogen atoms are omitted for clarity.