Supporting Information

Synthesis of Ferrocenyl Alkyne-Cu(I) π-Complexes via Copper-Promoted 8-Aminoquinoline Directed C-H Bond Alkynylations

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1. X-ray Crystal Data for Compounds 3a:

Table S1. Crystal data and structure refinement for 3a ·H_2O.

Identification code	s (CCDC **1905737**)
Empirical formula	$C_{30}H_{23}CuFeN_2O_1 \cdot H_2O$
Formula weight	564.91
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.9611(6)
b/Å	8.9351(3)
c/Å	20.0367(7)
α/°	90
β/°	112.372(3)
γ/°	90
Volume/$Å^3$	2476.88(16)
Z	4
ρ_{calc}g/cm^3	1.515
μ/mm^{-1}	1.475
F(000)	1160.0
Crystal size/mm^3	0.15 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.396 to 55.3
Index ranges	$-19 \leq h \leq 18$, $-11 \leq k \leq 9$, $-20 \leq l \leq 26$
Reflections collected	20039
Independent reflections	5665 [Rint = 0.0310, Rsigma = 0.0462]
Data/restraints/parameters	5665/16/339
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R1 = 0.0394, wR2 = 0.0908
Final R indexes [all data]	R1 = 0.0866, wR2 = 0.1057
Largest diff. peak/hole / e $Å^{-3}$	0.45/-0.34

Table S2. Bond Lengths for 3a ·H_2O.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N1	1.945(2)	C7	C8	1.413(4)
Cu1	N2	1.941(2)	C8	C9	1.344(5)
Cu1	C21	1.895(3)	C15	C16	1.485(4)
Cu1	C22	1.967(3)	C16	C17	1.422(4)
Fe1	C16	2.042(3)	C16	C20	1.438(4)
Fe1	C17	2.029(3)	C17	C18	1.399(5)
Fe1	C18	2.043(3)	C18	C19	1.410(5)
Fe1	C19	2.031(3)	C19	C20	1.426(4)
Fe1	C20	2.034(3)	C20	C21	1.431(4)

Fe1	C11	2.007(4)	C21	C22	1.244(4)
Fe1	C10	2.032(4)	C22	C23	1.440(4)
Fe1	C14	2.033(4)	C23	C24	1.392(4)
Fe1	C13	2.028(4)	C23	C28	1.381(4)
Fe1	C12	2.011(3)	C24	C25	1.365(5)
O1	C15	1.253(3)	C25	C26	1.370(5)
N1	C1	1.321(3)	C26	C27	1.352(5)
N1	C5	1.367(3)	C26	C29	1.484(4)
N2	C6	1.399(3)	C27	C28	1.384(4)
N2	C15	1.334(3)	C29	C30	1.428(7)
C1	C2	1.378(4)	C29	C31	1.443(8)
C2	C3	1.346(4)	C11	C10	1.378(5)
C3	C4	1.410(4)	C11	C12	1.413(5)
C4	C5	1.411(4)	C10	C14	1.382(5)
C4	C9	1.403(4)	C14	C13	1.385(6)
C5	C6	1.440(4)	C13	C12	1.381(6)
C6	C7	1.380(4)			

Table S3 Bond Angles for 3a·H_2O.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Cu1	C22	133.39(11)	C4	C5	C6	121.4(3)
N2	Cu1	N1	86.28(10)	N2	C6	C5	114.8(2)
N2	Cu1	C22	140.30(12)	C7	C6	N2	128.3(3)
C21	Cu1	N1	170.89(12)	C7	C6	C5	116.8(3)
C21	Cu1	N2	102.79(12)	C6	C7	C8	120.7(3)
C21	Cu1	C22	37.52(12)	C9	C8	C7	22.4(3)
C16	Fe1	C18	68.51(13)	C8	C9	C4	119.8(3)
C17	Fe1	C16	40.88(11)	O1	C15	N2	125.8(3)
C17	Fe1	C18	40.18(13)	O1	C15	C16	117.0(3)
C17	Fe1	C19	68.31(14)	N2	C15	C16	117.1(3)
C17	Fe1	C20	68.72(12)	C15	C16	Fe1	126.60(18)
C17	Fe1	C10	162.74(17)	C17	C16	Fe1	69.09(18)
C17	Fe1	C14	154.42(17)	C17	C16	C15	122.8(3)
C19	Fe1	C16	69.21(12)	C17	C16	C20	106.6(3)
C19	Fe1	C18	40.50(13)	C20	C16	Fe1	69.06(17)
C19	Fe1	C20	41.07(12)	C20	C16	C15	130.6(3)
C19	Fe1	C10	123.01(16)	C16	C17	Fe1	70.03(17)
C19	Fe1	C14	109.31(16)	C18	C17	Fe1	70.4(2)
C20	Fe1	C16	41.31(12)	C18	C17	C16	109.2(3)
C20	Fe1	C18	68.47(13)	C17	C18	Fe1	69.38(18)
C11	Fe1	C16	107.13(14)	C17	C18	C19	108.5(3)
C11	Fe1	C17	124.77(16)	C19	C18	Fe1	69.30(18)
C11	Fe1	C18	161.25(19)	C18	C19	Fe1	70.20(19)
C11	Fe1	C19	156.83(19)	C18	C19	C20	108.0(3)

C11	Fe1	C20	121.11(16)	C20	C19	Fe1	69.58(16)
C11	Fe1	C10	39.91(15)	C16	C20	Fe1	69.63(16)
C11	Fe1	C14	67.65(16)	C19	C20	Fe1	69.34(17)
C11	Fe1	C13	67.97(18)	C19	C20	C16	107.7(3)
C11	Fe1	C12	41.19(16)	C19	C20	C21	126.5(3)
C10	Fe1	C16	126.89(15)	C21	C20	Fe1	127.7(2)
C10	Fe1	C18	156.75(18)	C21	C20	C16	125.7(3)
C10	Fe1	C20	110.21(14)	C20	C21	Cu1	116.8(2)
C10	Fe1	C14	39.76(16)	C22	C21	Cu1	74.4(2)
C14	Fe1	C16	164.18(16)	C22	C21	C20	168.6(3)
C14	Fe1	C18	121.30(17)	C21	C22	Cu1	68.12(19)
C14	Fe1	C20	127.32(16)	C21	C22	C23	154.4(3)
C13	Fe1	C16	153.81(16)	C23	C22	Cu1	137.4(2)
C13	Fe1	C17	119.26(16)	C24	C23	C22	119.8(3)
C13	Fe1	C18	107.41(17)	C28	C23	C22	123.0(3)
C13	Fe1	C19	125.49(17)	C28	C23	C24	117.2(3)
C13	Fe1	C20	163.38(17)	C25	C24	C23	120.5(3)
C13	Fe1	C10	66.80(17)	C24	C25	C26	122.6(3)
C13	Fe1	C14	39.89(16)	C25	C26	C29	120.8(4)
C12	Fe1	C16	119.26(16)	C27	C26	C25	116.8(3)
C12	Fe1	C17	106.06(16)	C27	C26	C29	122.4(4)
C12	Fe1	C18	123.67(19)	C26	C27	C28	122.6(3)
C12	Fe1	C19	160.93(19)	C23	C28	C27	120.4(3)
C12	Fe1	C20	155.75(18)	C30	C29	C26	116.5(5)
C12	Fe1	C10	67.44(17)	C31	C29	C26	120.7(6)
C12	Fe1	C14	67.43(17)	C10	C11	Fe1	71.0(2)
C12	Fe1	C13	39.98(16)	C10	C11	C12	107.0(4)
C1	N1	Cu1	131.1(2)	C12	C11	Fe1	69.6(2)
C1	N1	C5	118.4(3)	C11	C10	Fe1	69.1(2)
C5	N1	Cu1	110.59(18)	C11	C10	C14	109.1(4)
C6	N2	Cu1	110.87(16)	C14	C10	Fe1	70.2(2)
C15	N2	Cu1	126.1(2)	C10	C14	Fe1	70.1(2)
C15	N2	C6	122.9(2)	C10	C14	C13	107.7(4)
N1	C1	C2	123.9(3)	C13	C14	Fe1	69.9(2)
C3	C2	C1	118.9(3)	C14	C13	Fe1	70.3(2)
C2	C3	C4	120.4(3)	C12	C13	Fe1	69.4(2)
C3	C4	C5	117.3(3)	C12	C13	C14	108.5(4)
C9	C4	C3	123.9(3)	C11	C12	Fe1	69.2(2)
C9	C4	C5	118.8(3)	C13	C12	Fe1	70.7(2)
N1	C5	C4	121.2(3)	C13	C12	C11	107.6(4)
N1	C5	C6	117.4(2)				

2. CV Anaiysis

The cyclic voltammetry was performed at CHI760E electrochemical workstation, in separate CH_3COCH_3 solutions at room temperature containing **3l** (1 mM) and 10 mM *n*-Bu_4NBF_4 with Ag/AgCl as reference electrode, Pt wire as counter electrode and glassy carbon disk as working electrode; scan rate: 100 mV s^{-1}.

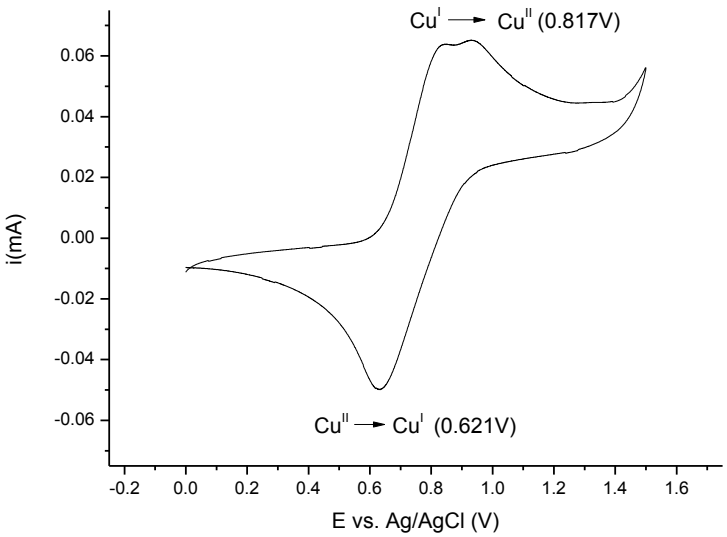

Fig S1: Cyclic voltammogram of **3l**: The oxidation peak of Cu(I)/Cu(II) appears at +0.817 V, and the reversible reduction peak appears at +0.621 V.

6. NMR Spectra of all New Compounds (Figures S2–S51)

The 1H NMR spectra of **3** indicate the presence of some impurities (between 4.20 to 4.50 ppm), which may be the corresponding **4**. The solvent peak: for the ^{1}H NMR spectra, $CDCl_3$ in 7.26 ppm and DMSO-d_6 in 2.50 ppm; for the ^{1}C NMR spectra, $CDCl_3$ in 77.0 ppm and DMSO-d_6 in 39.6 ppm.

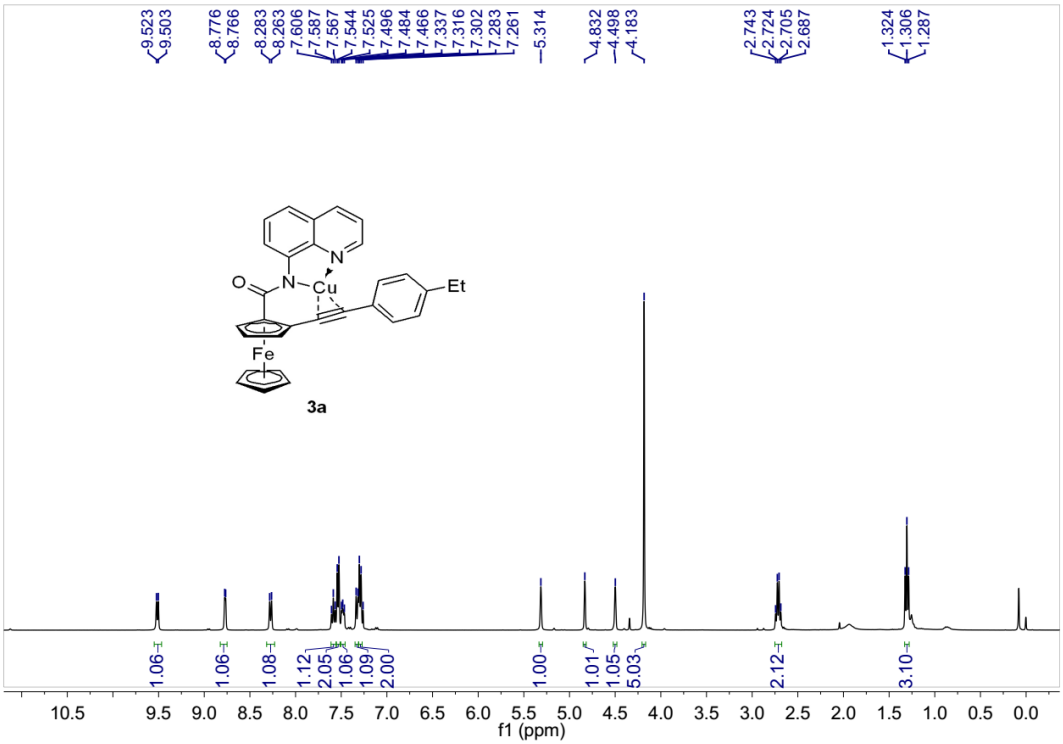

Fig S2: ^{1}H NMR Spectrum of **3a**

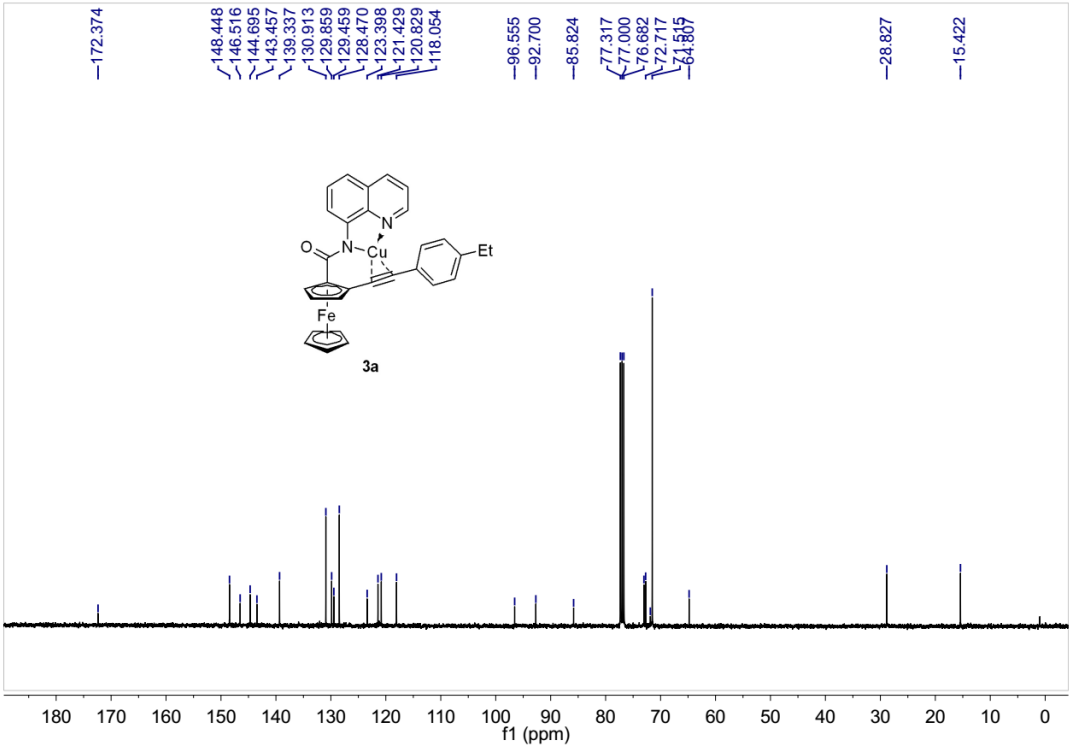

Fig S3: ^{13}C NMR Spectrum of **3a**

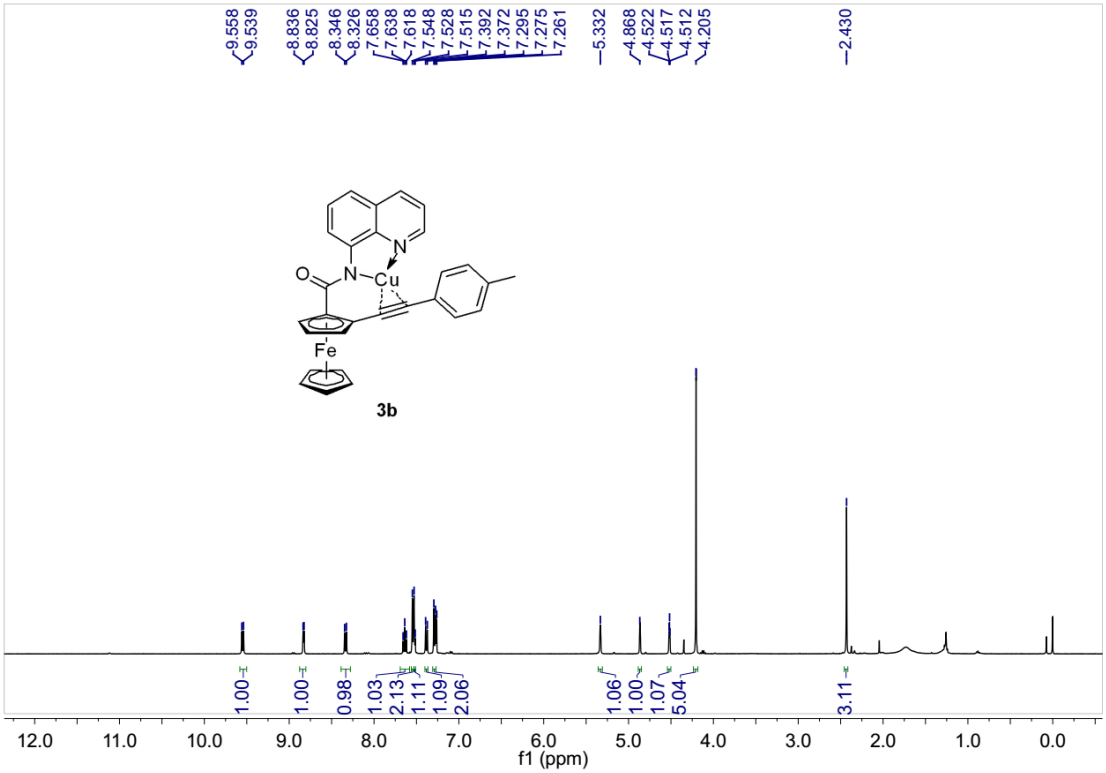

Fig S4: ^{1}H NMR Spectrum of **3b**

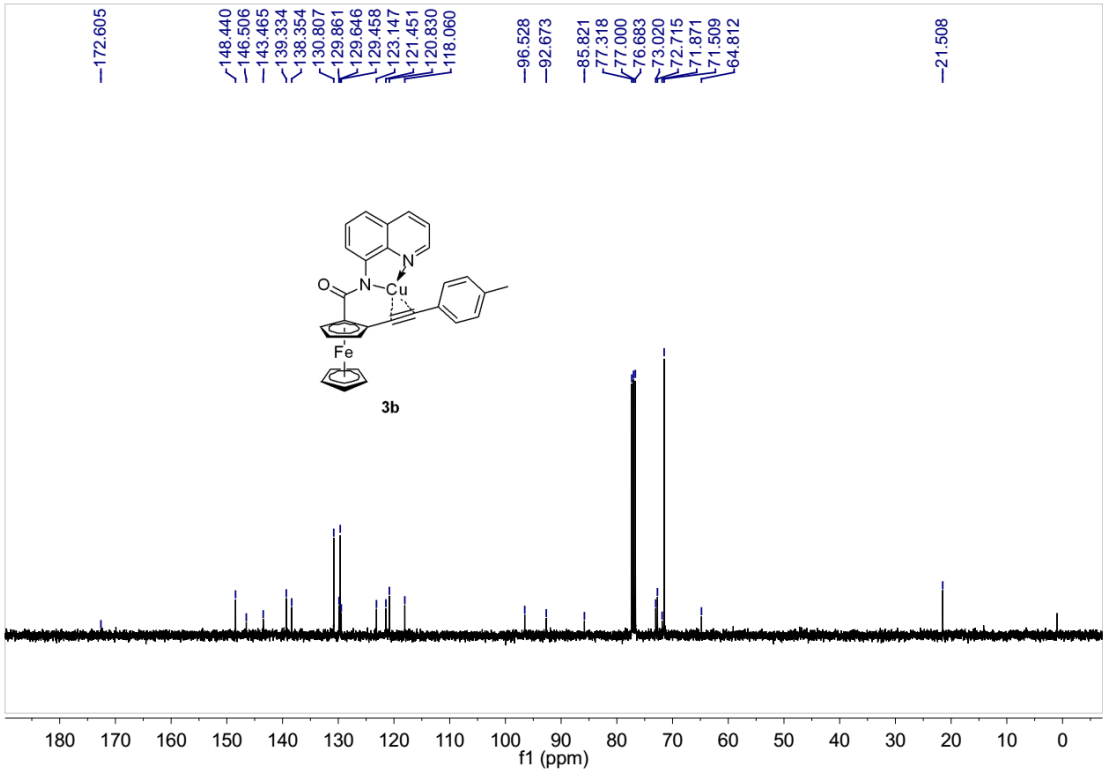

Fig S5: ^{13}C NMR Spectrum of **3b**

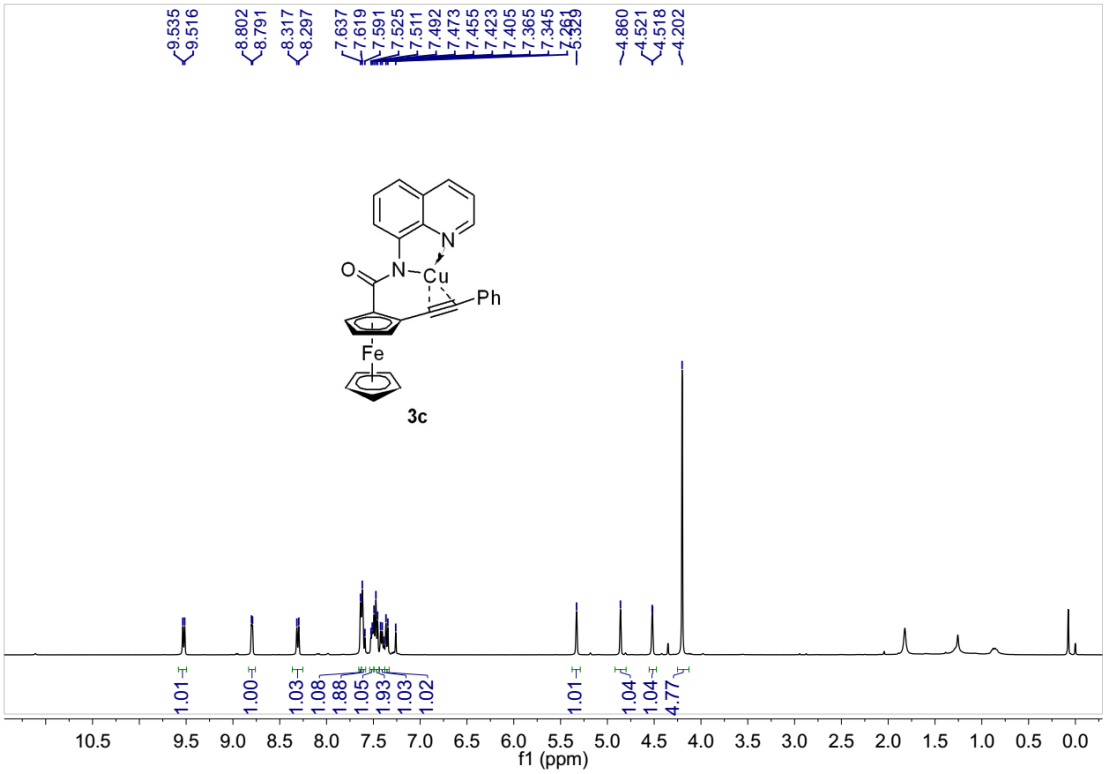

Fig S6: ^{1}H NMR Spectrum of **3c**

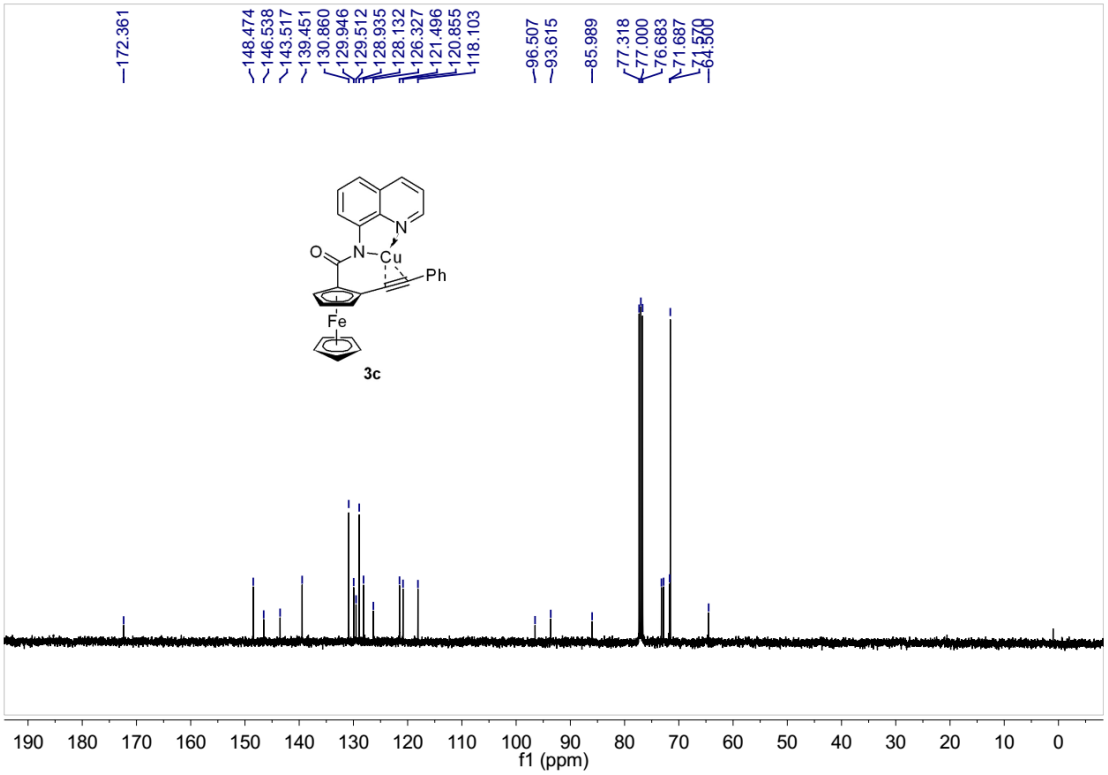

Fig S7: ^{13}C NMR Spectrum of **3c**

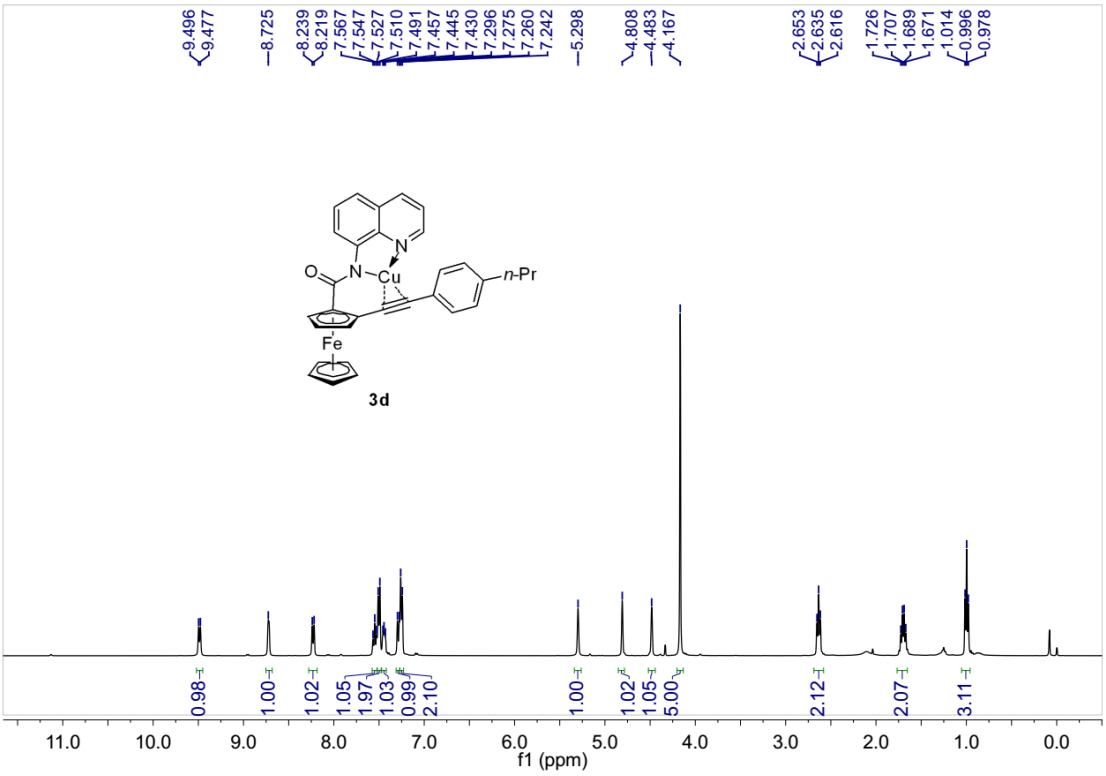

Fig S8: ^{1}H NMR Spectrum of **3d**

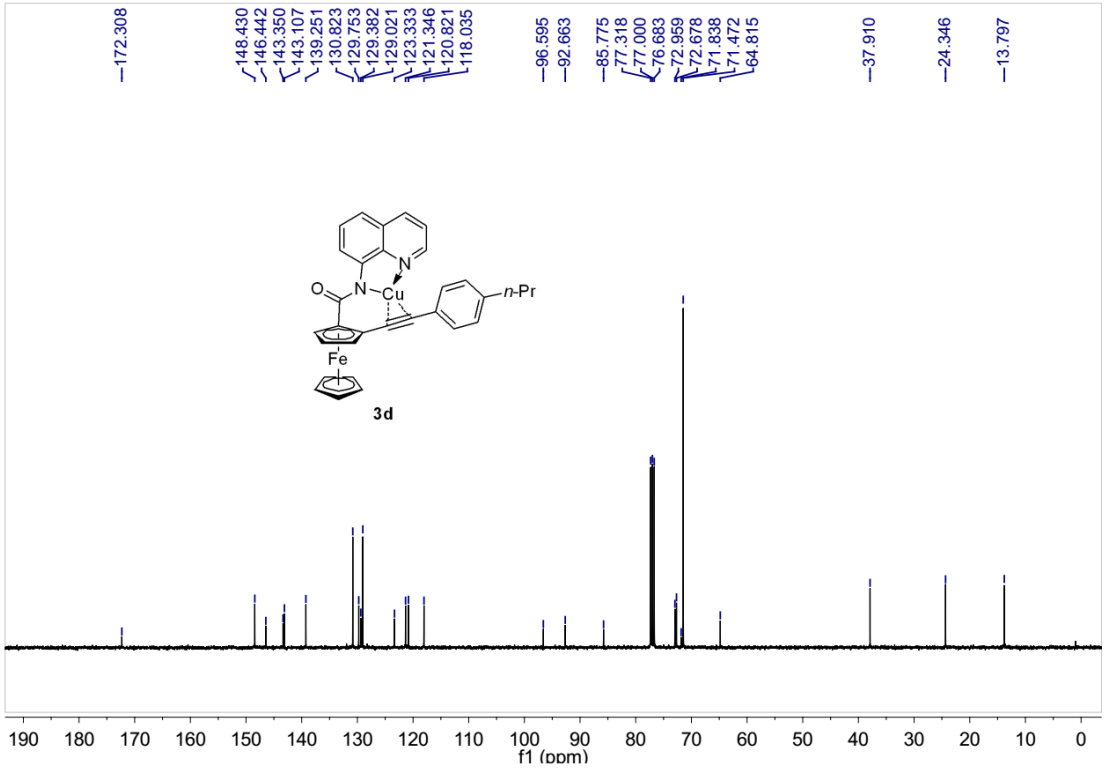

Fig S9: ^{13}C NMR Spectrum of **3d**

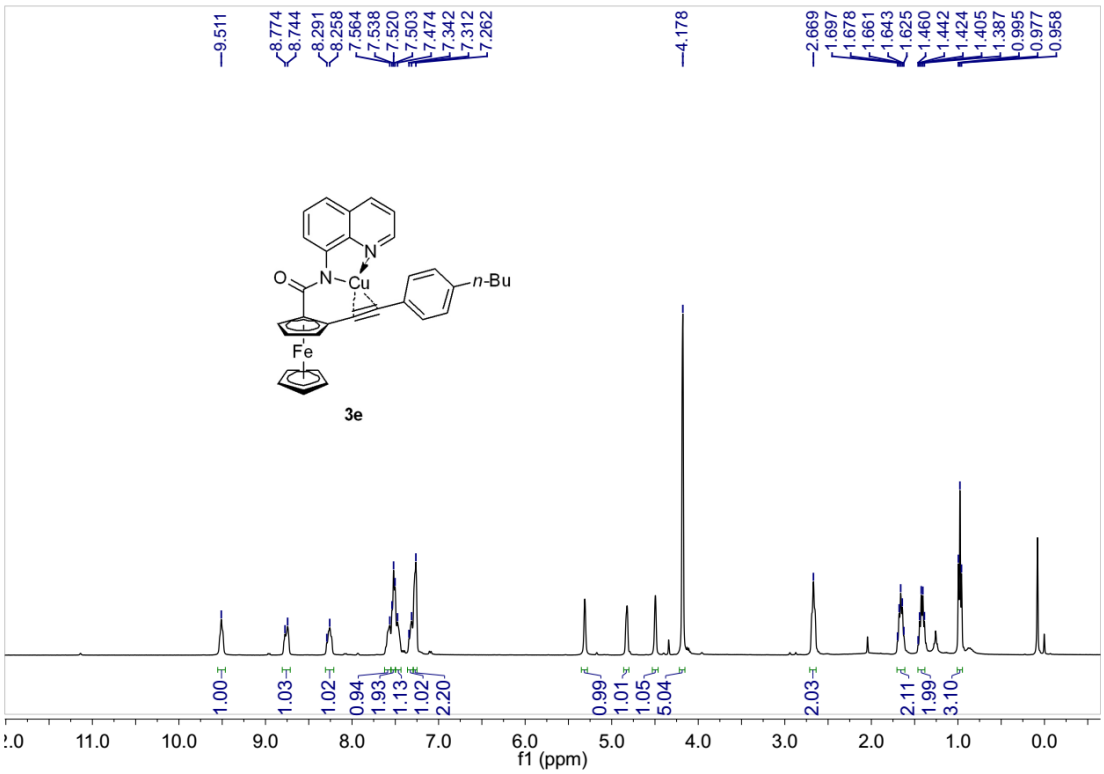

Fig S10: ^{1}H NMR Spectrum of **3e**

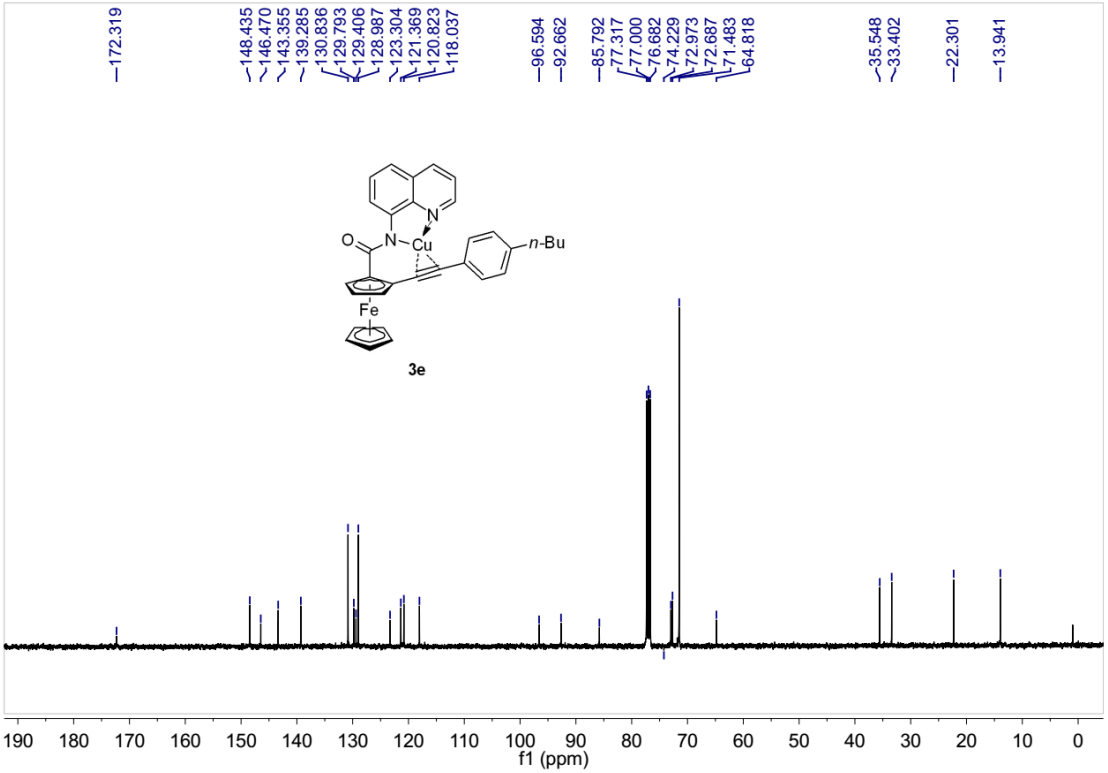

Fig S11: ^{13}C NMR Spectrum of **3e**

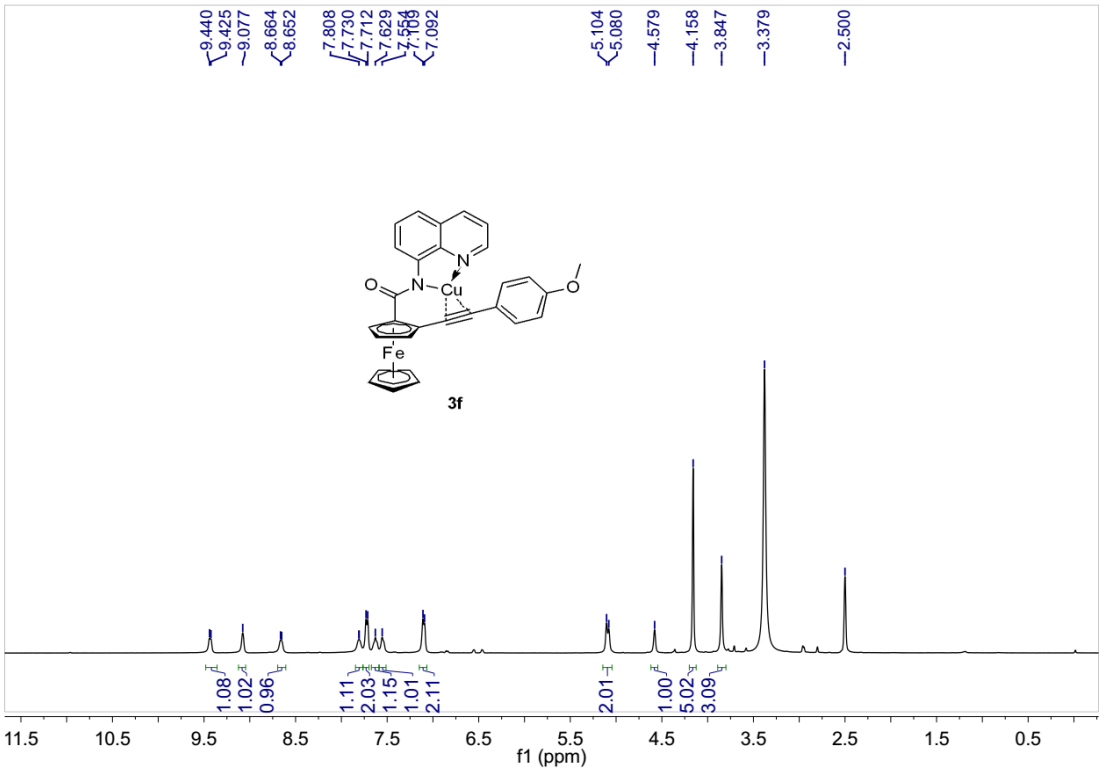

Fig S12: ^{1}H NMR Spectrum of **3f**

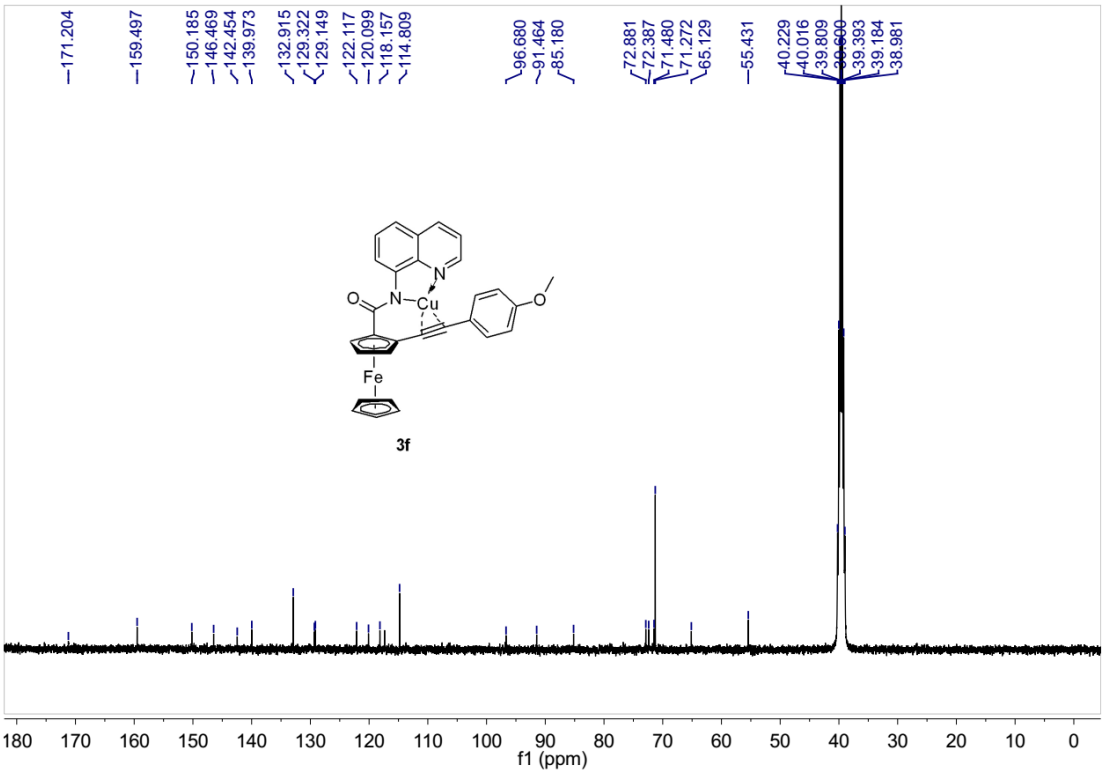

Fig S13: ^{13}C NMR Spectrum of **3f**

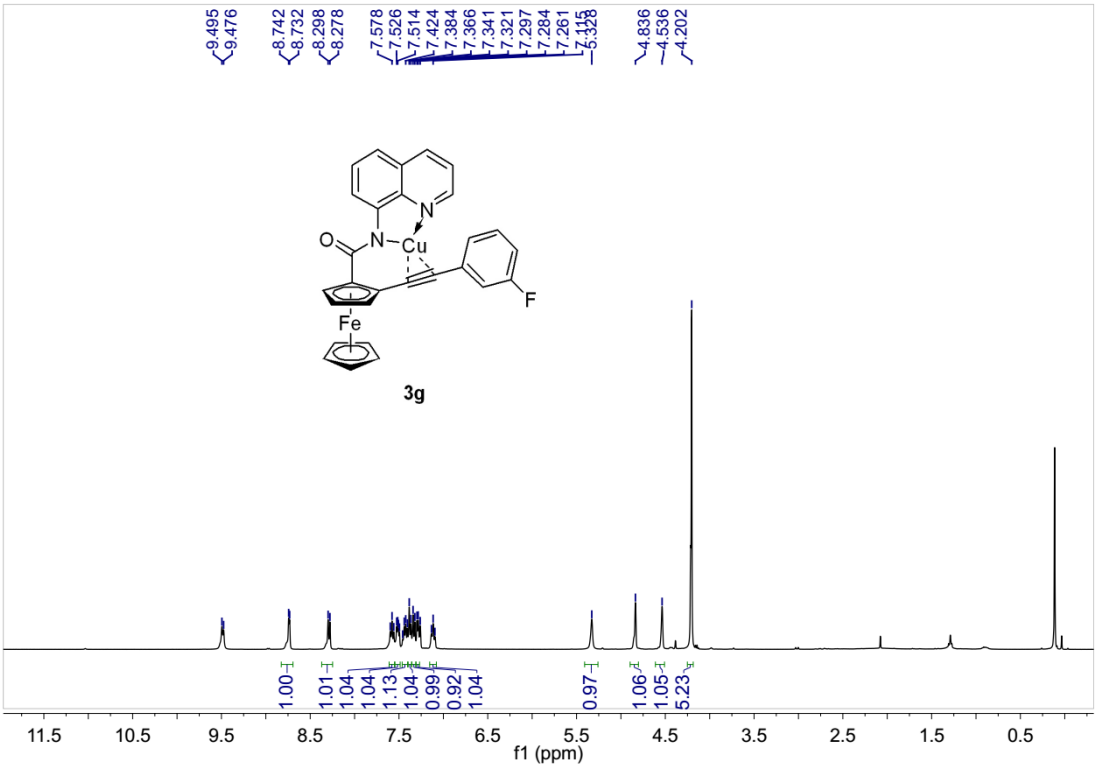

Fig S14: ^{1}H NMR Spectrum of **3g**

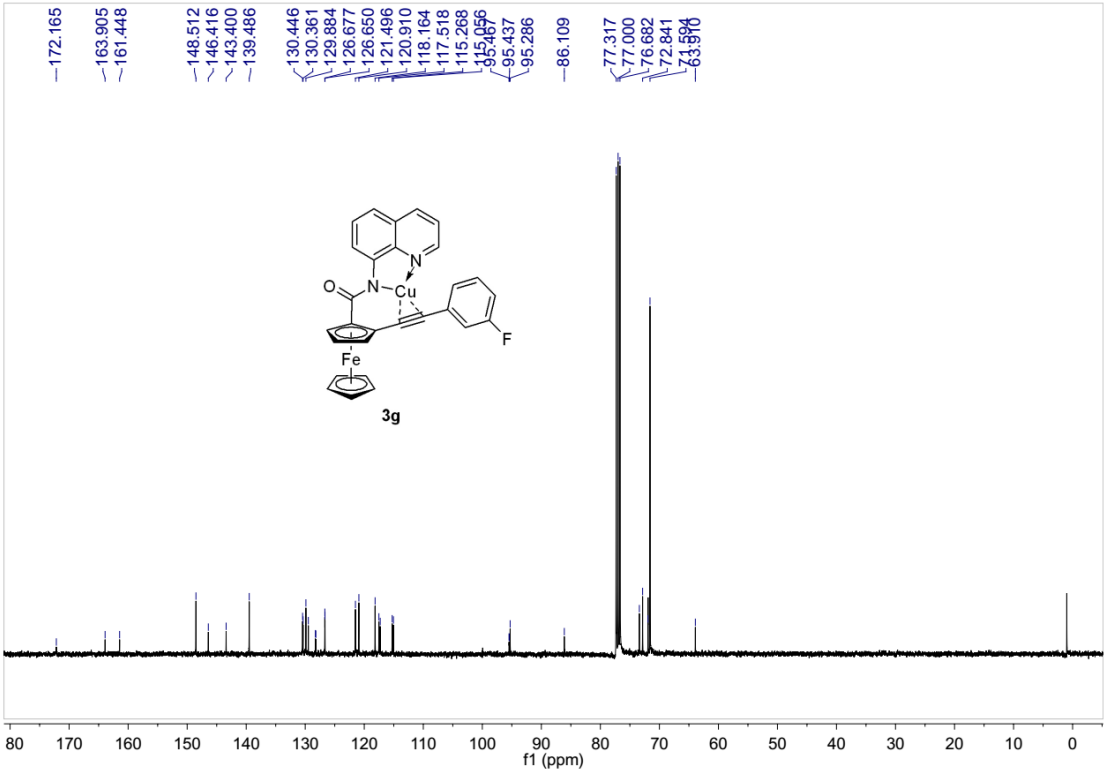

Fig S15: ^{13}C NMR Spectrum of **3g**

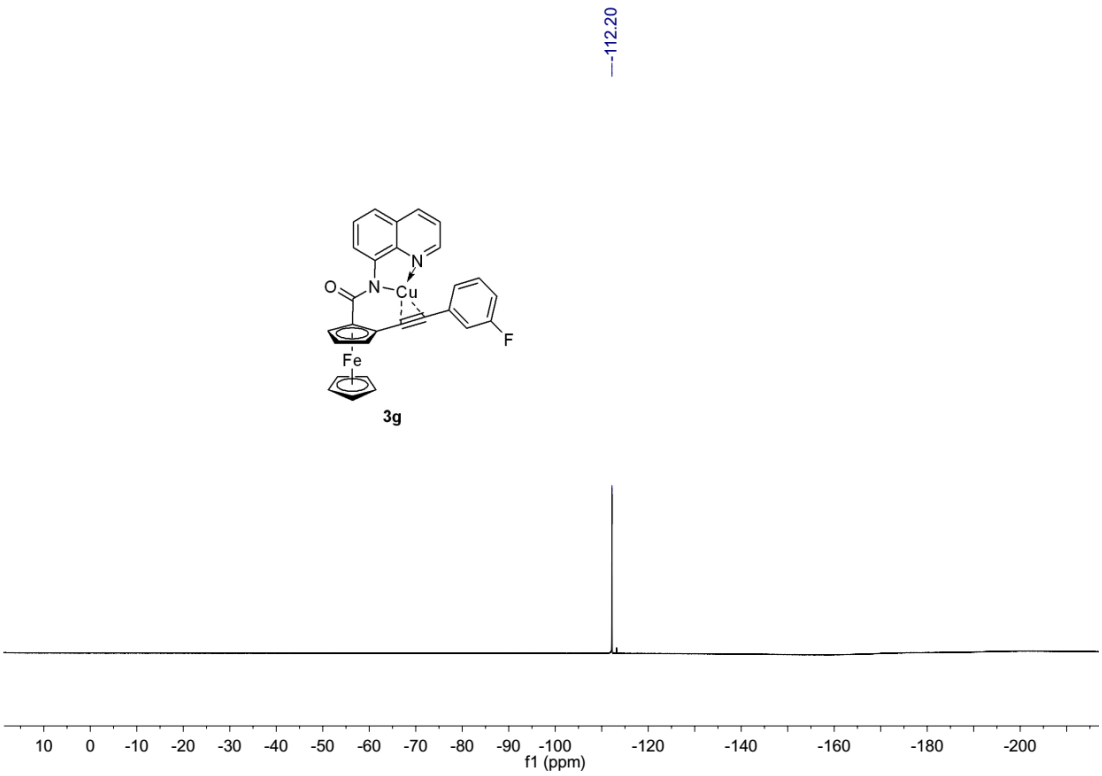

Fig S16: ^{19}F NMR Spectrum of **3g**

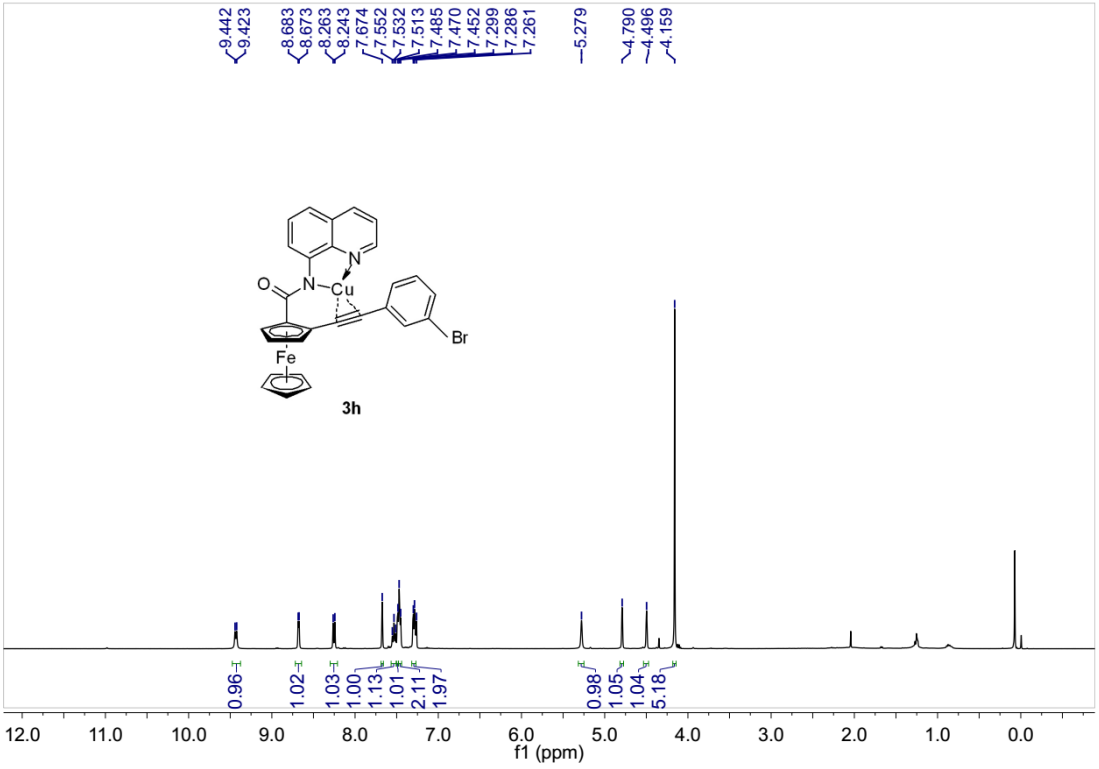

Fig S17: ^{1}H NMR Spectrum of **3h**

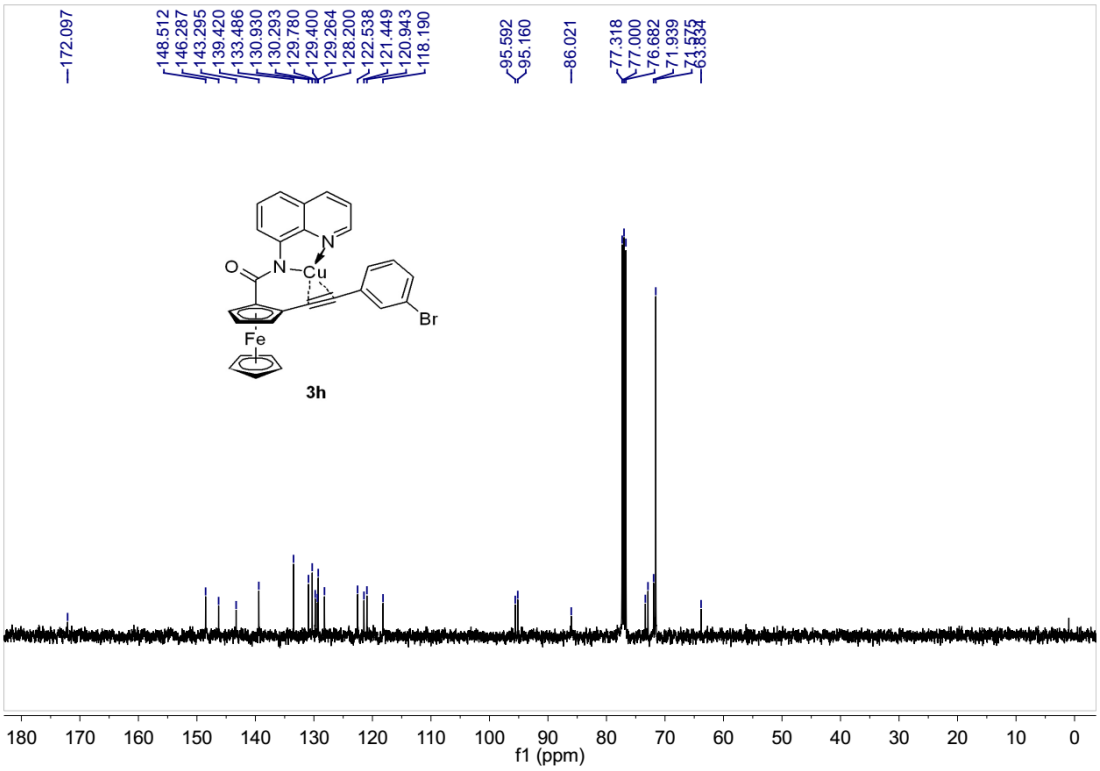

Fig S18: ^{13}C NMR Spectrum of **3h**

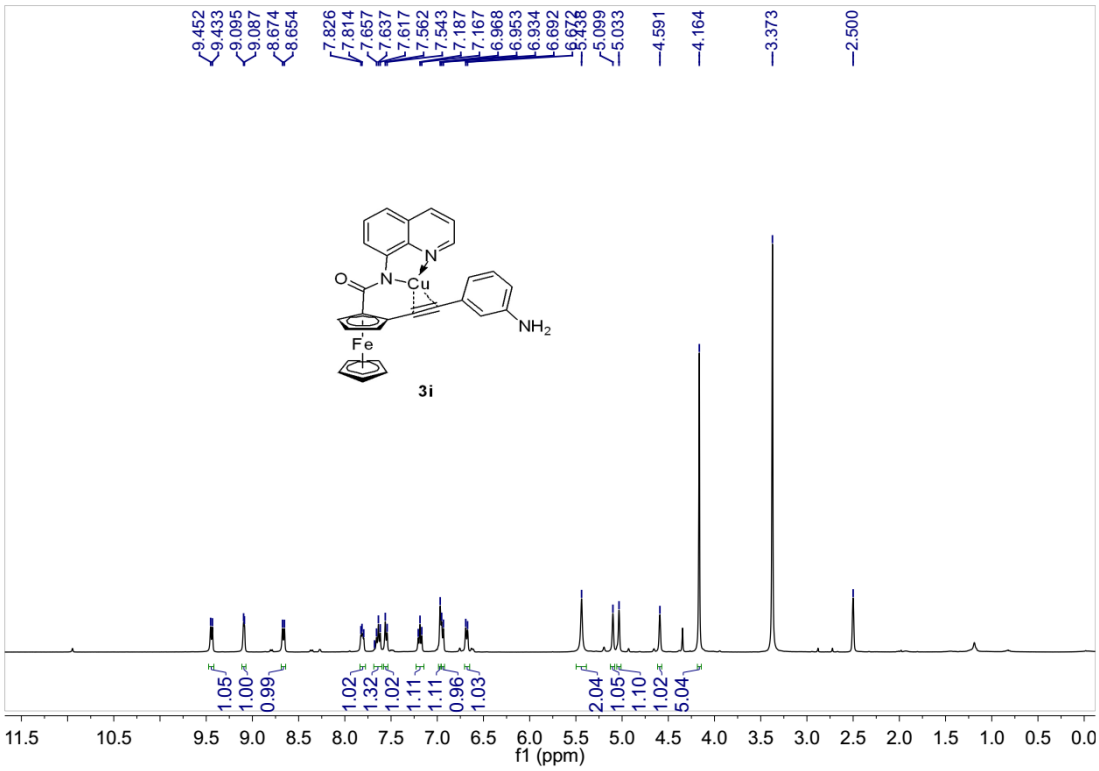

Fig S19: ^{1}H NMR Spectrum of **3i**

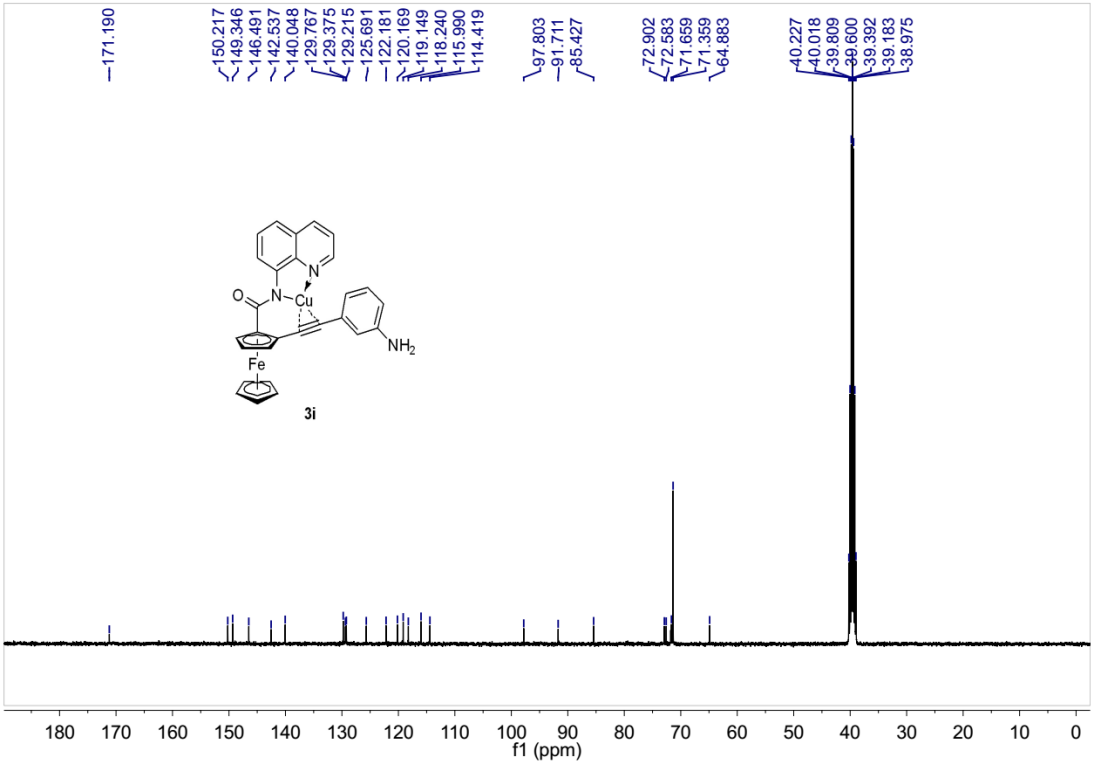

Fig S20: ^{13}C NMR Spectrum of **3i**

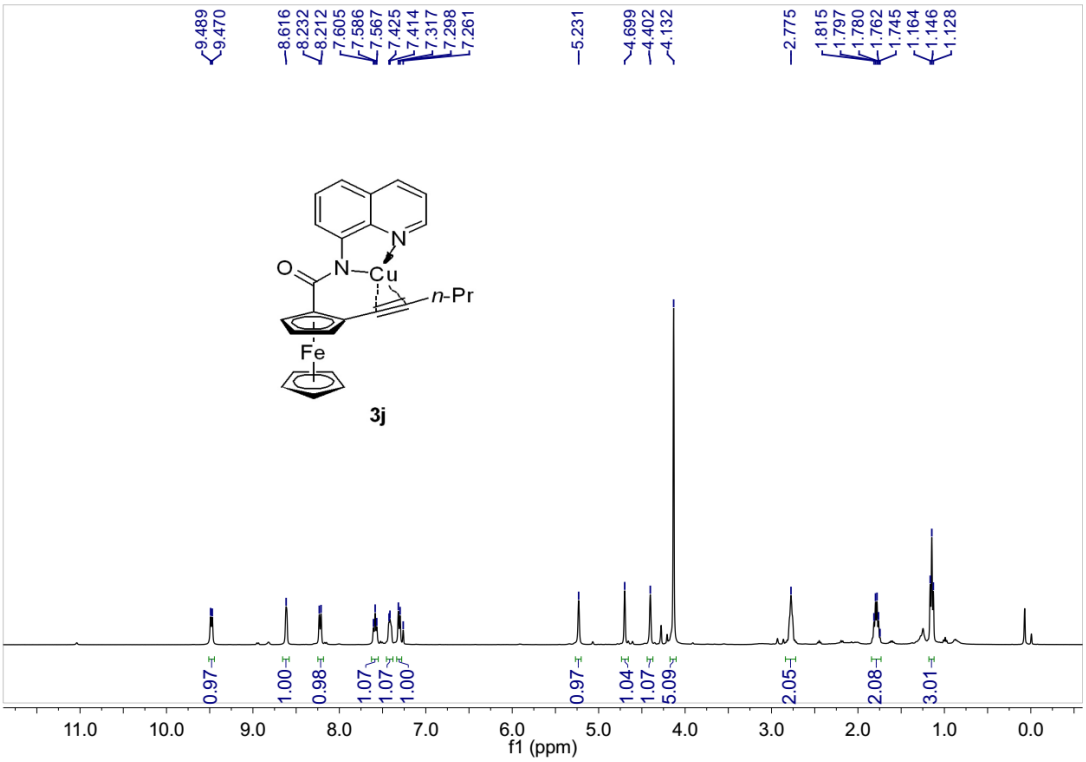

Fig S21: ^{1}H NMR Spectrum of **3j**

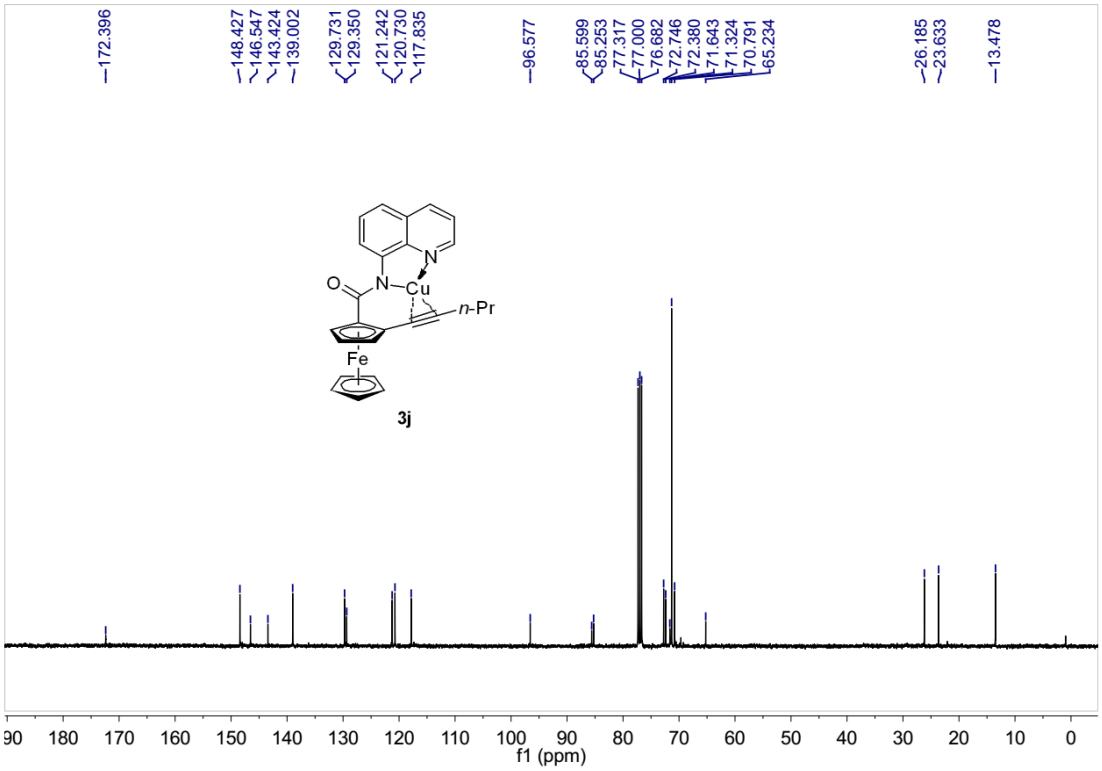

Fig S22: ^{13}C NMR Spectrum of **3j**

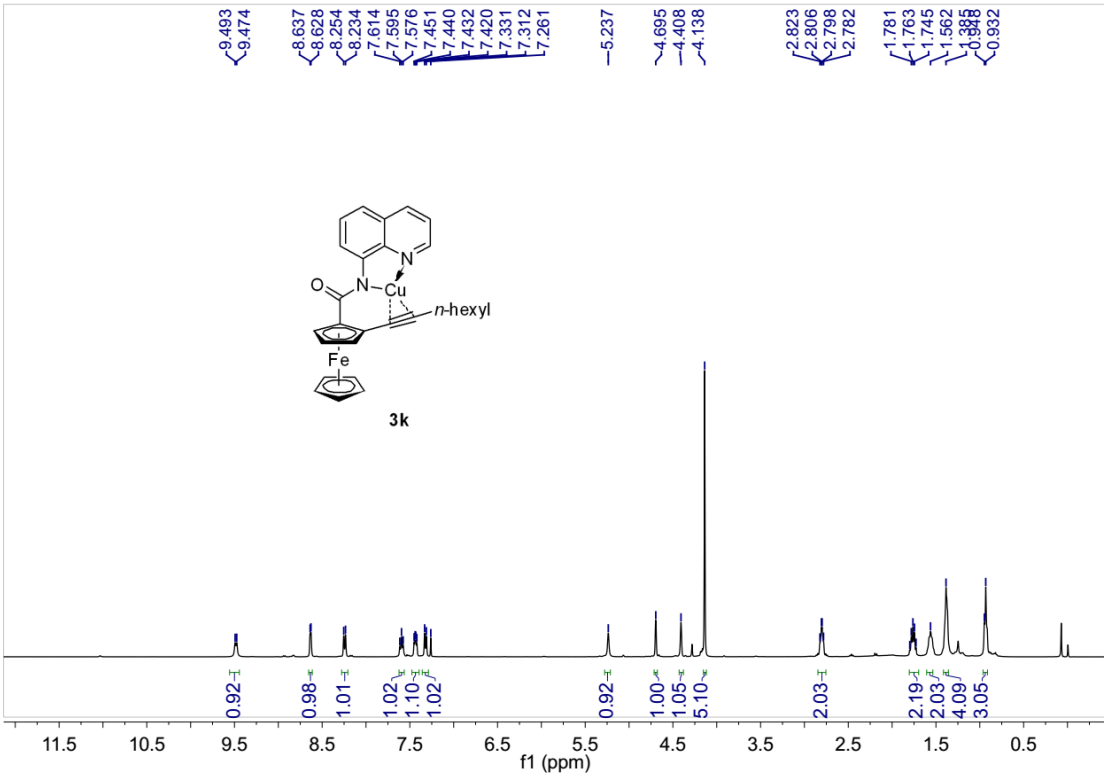

Fig S23: ^{1}H NMR Spectrum of **3k**

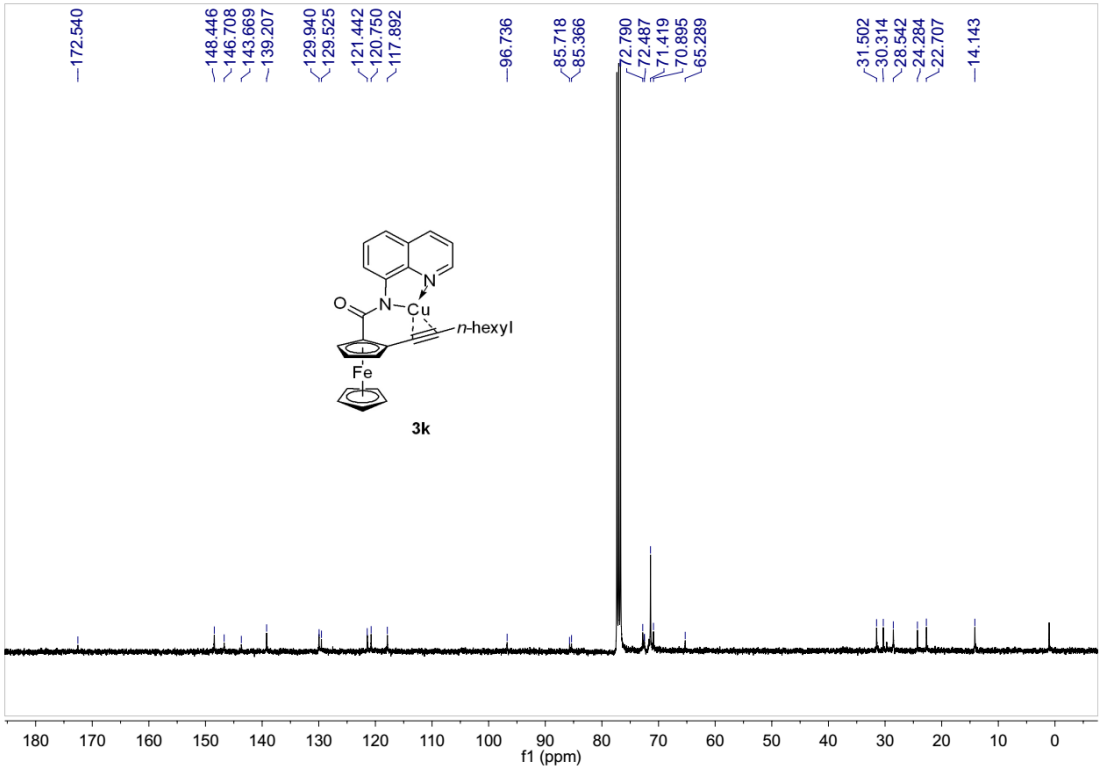

Fig S24: ^{13}C NMR Spectrum of **3k**

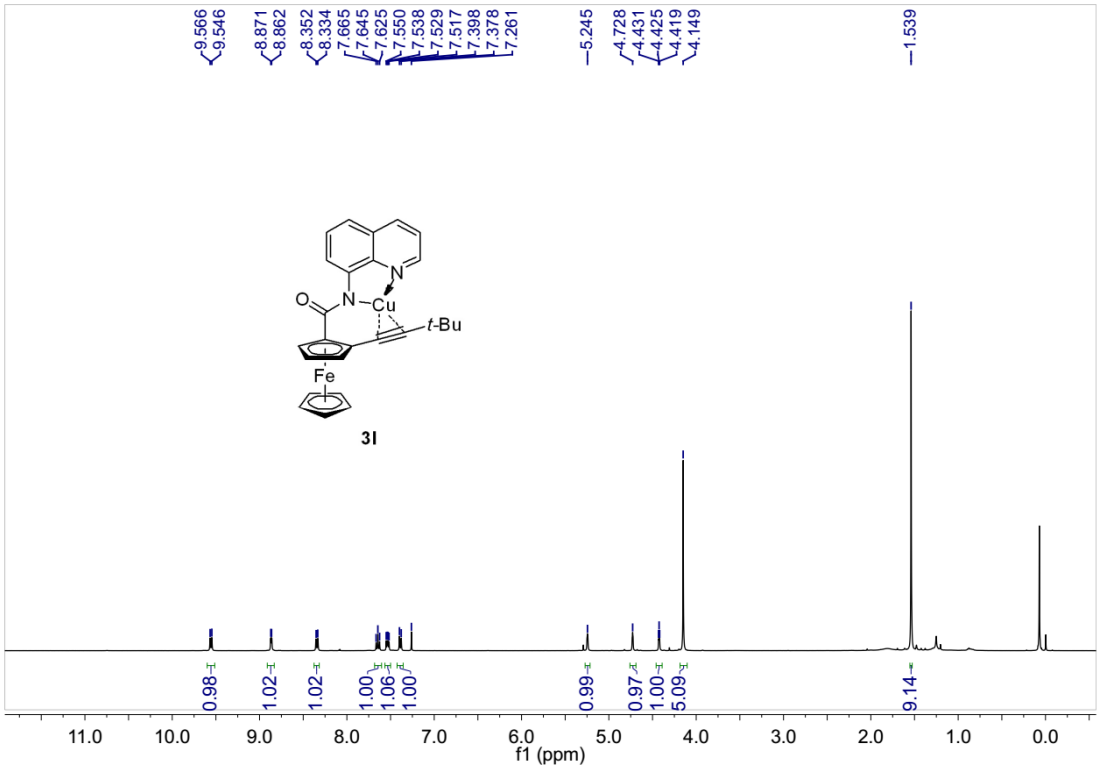

Fig S25: ^{1}H NMR Spectrum of **3l**

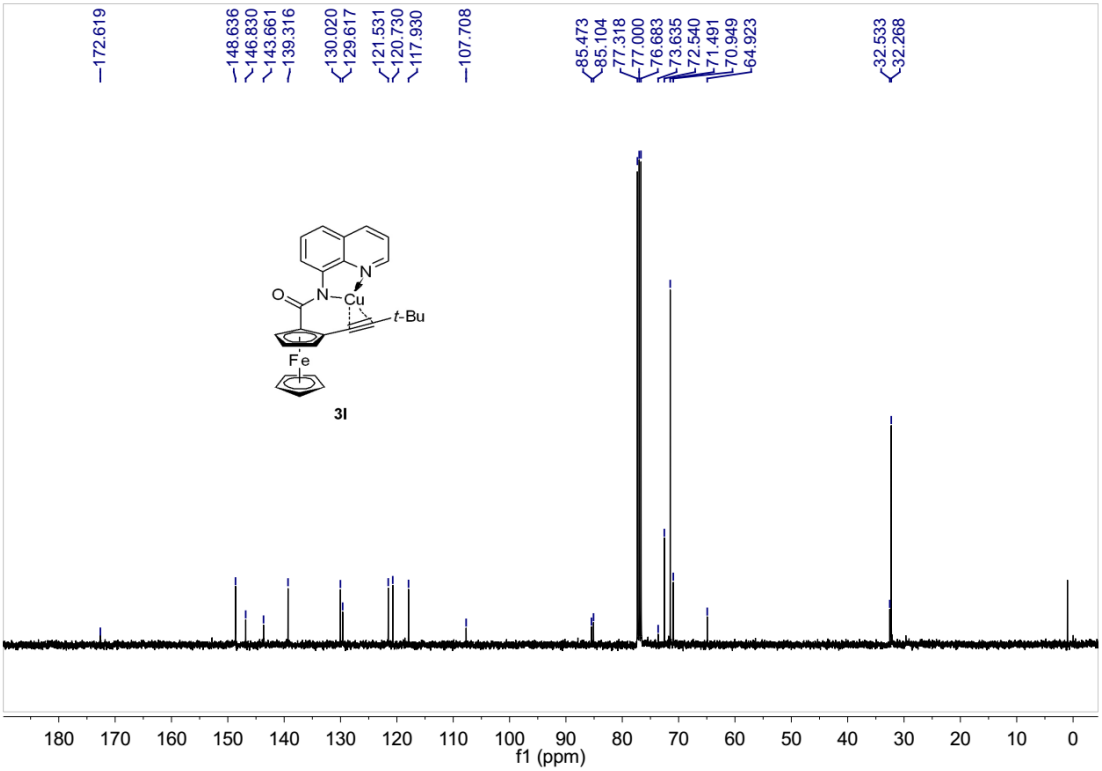

Fig S26: ^{13}C NMR Spectrum of **3l**

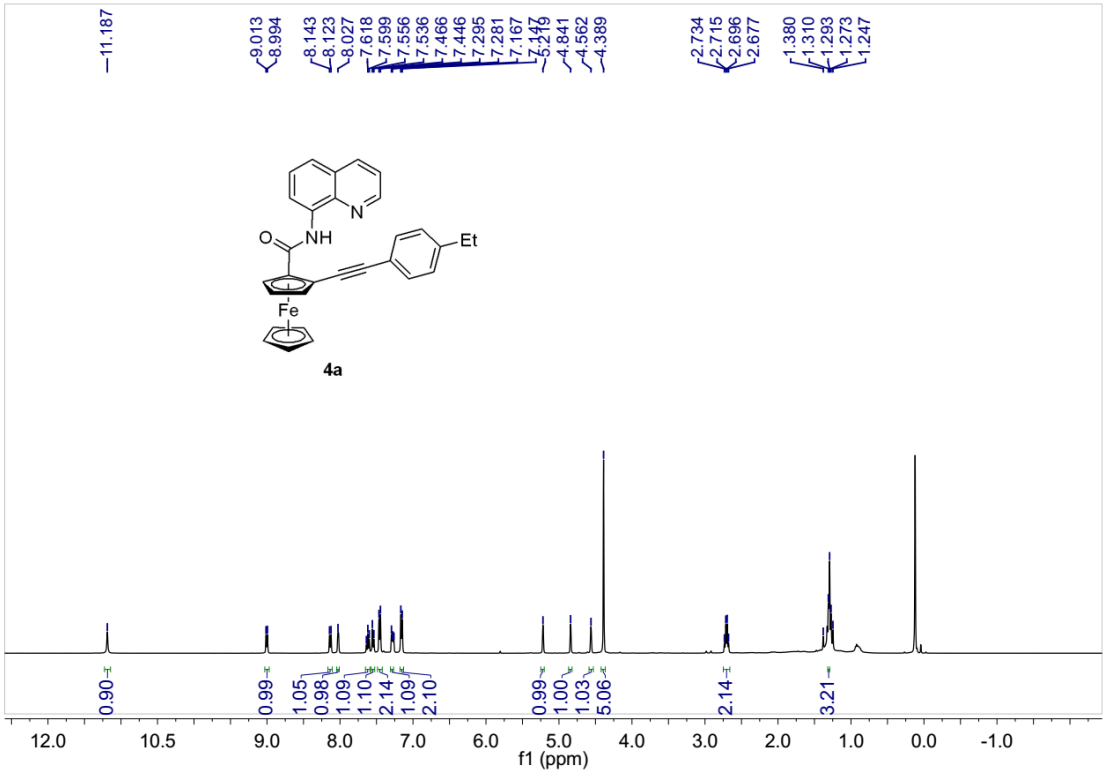

Fig S27: ^{1}H NMR Spectrum of **4a**

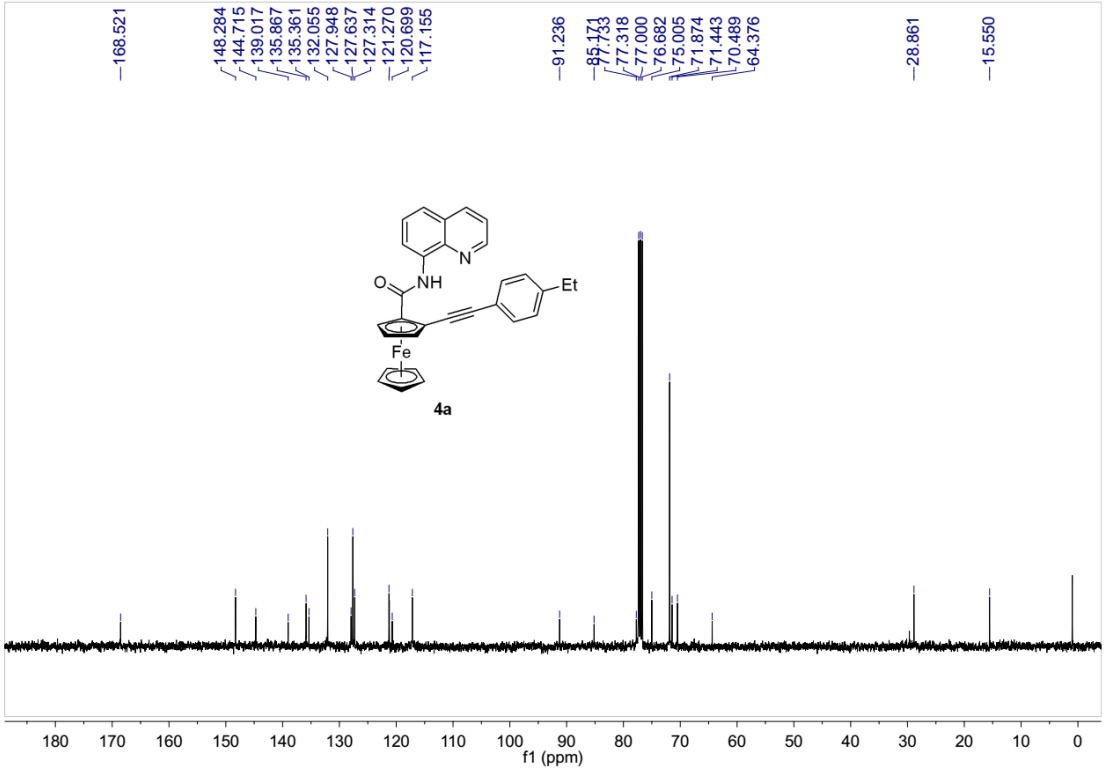

Fig S28: ^{13}C NMR Spectrum of **4a**

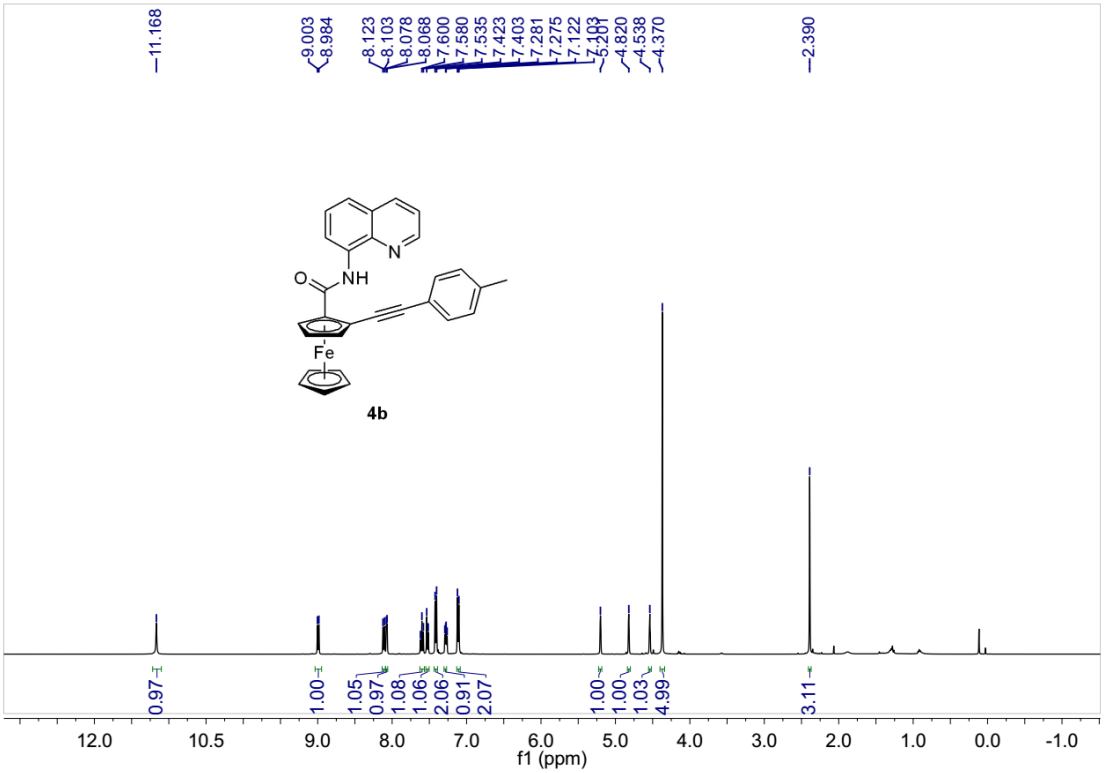

Fig S29: ^{1}H NMR Spectrum of **4b**

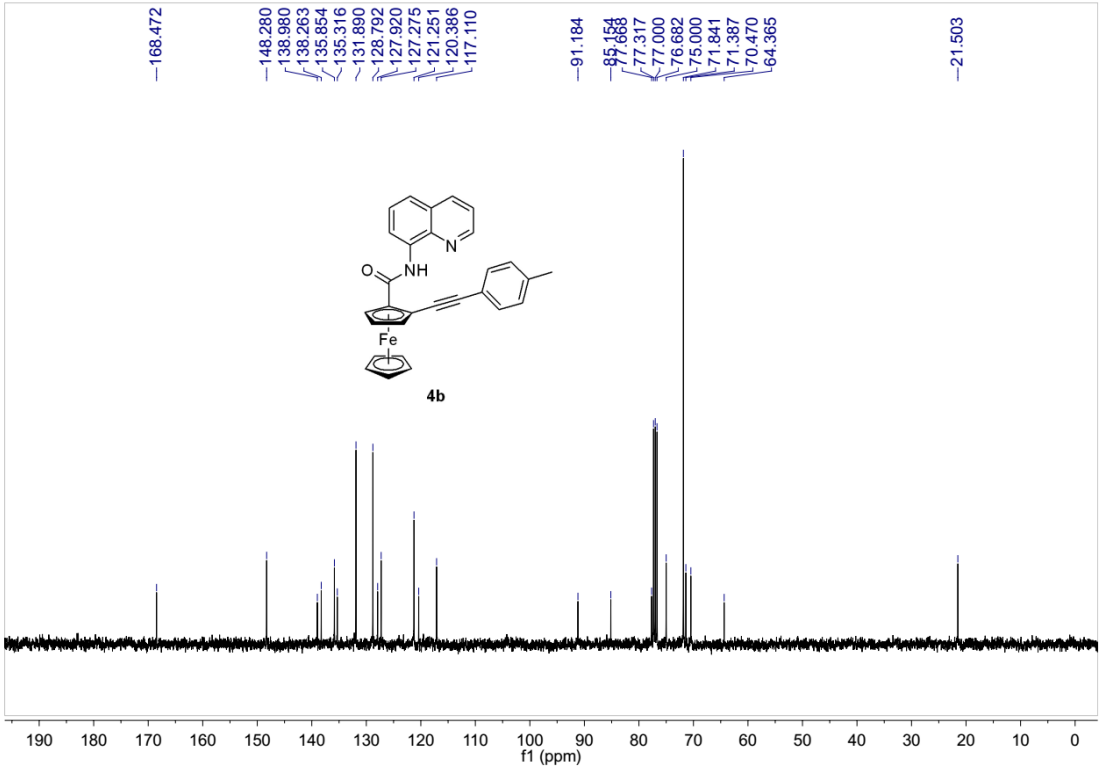

Fig S30: ^{13}C NMR Spectrum of **4b**

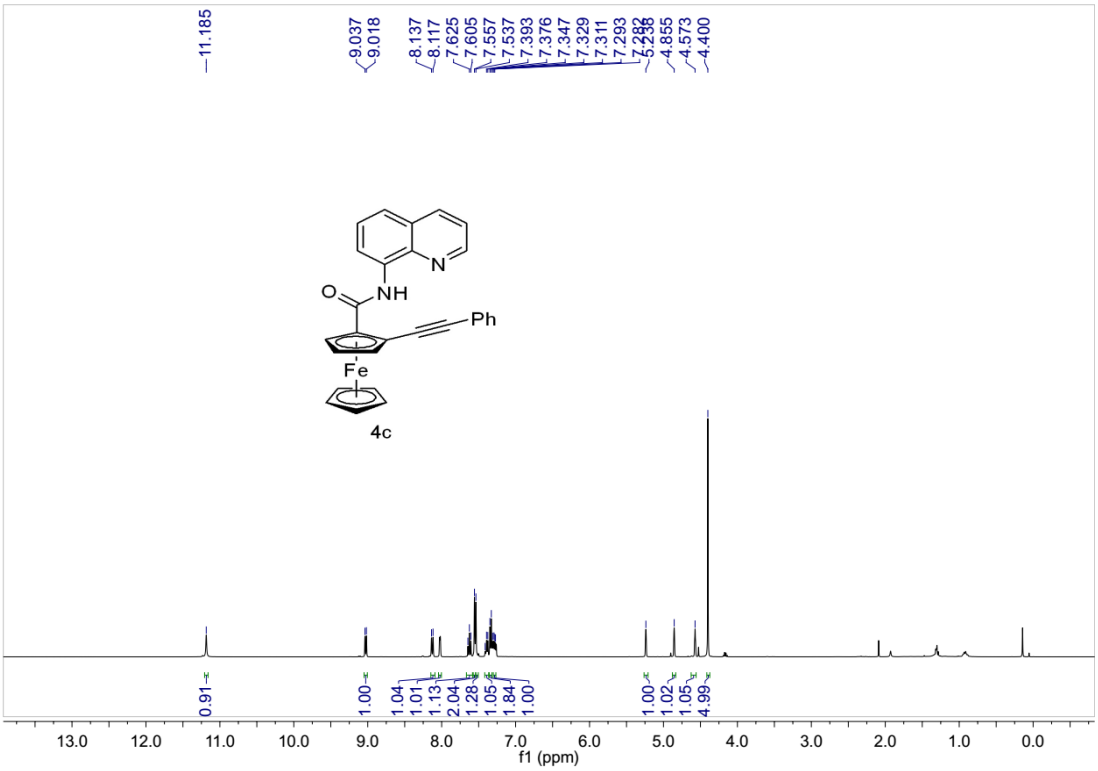

Fig S31: ^{1}H NMR Spectrum of **4c**

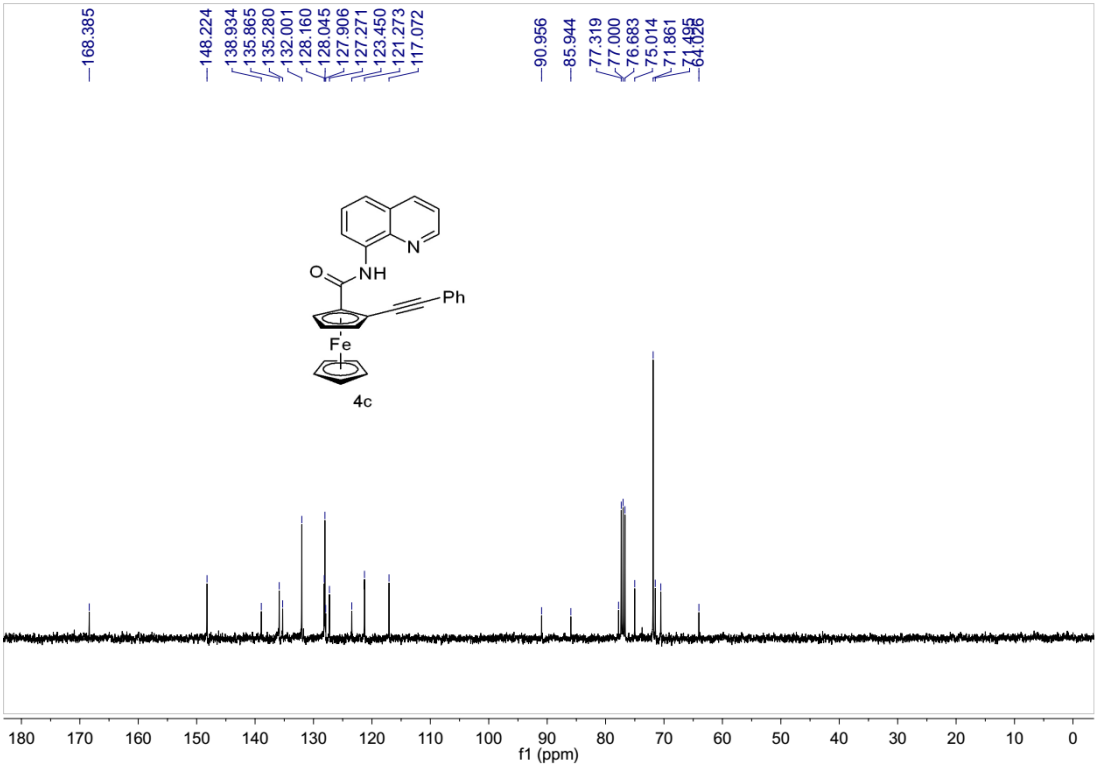

Fig S32: ^{13}C NMR Spectrum of **4c**

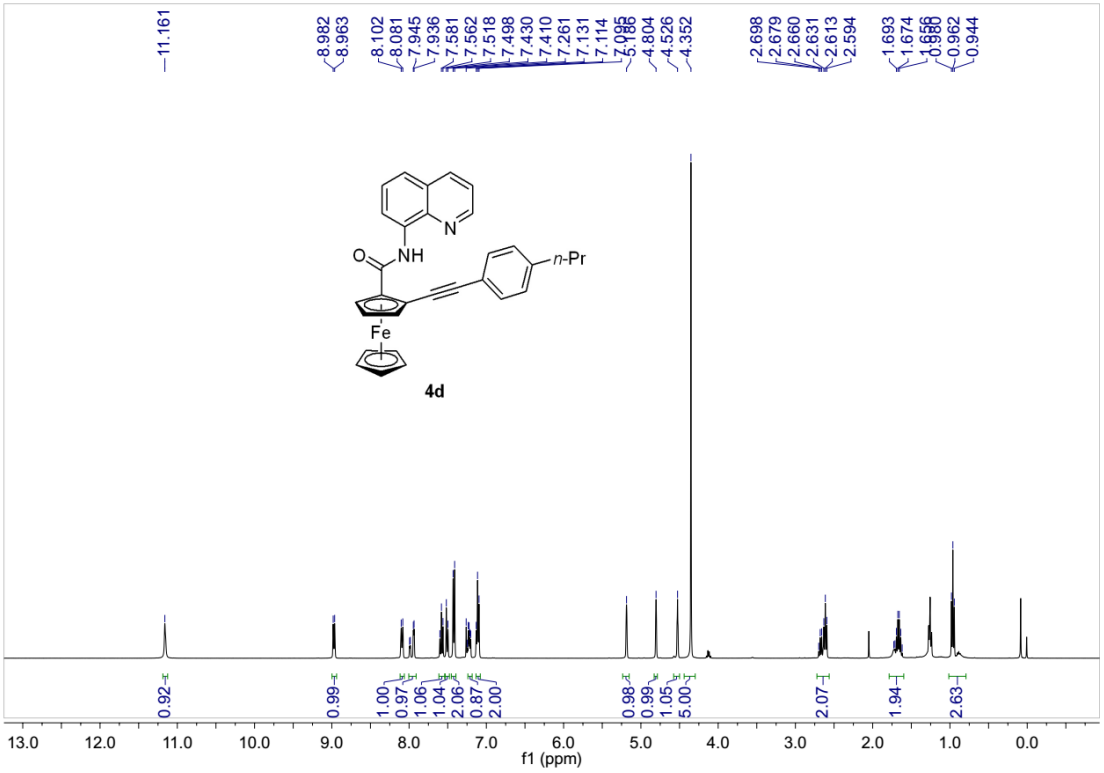

Fig S33: ^{1}H NMR Spectrum of **4d**

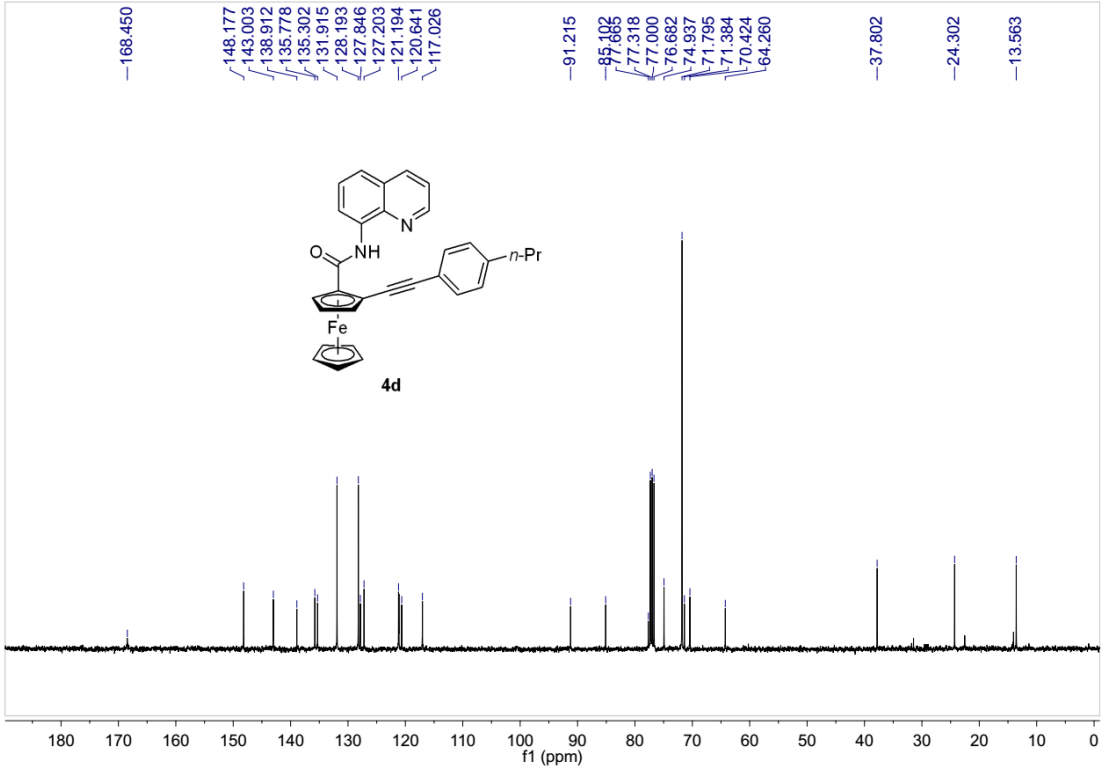

Fig S34: ^{13}C NMR Spectrum of **4d**

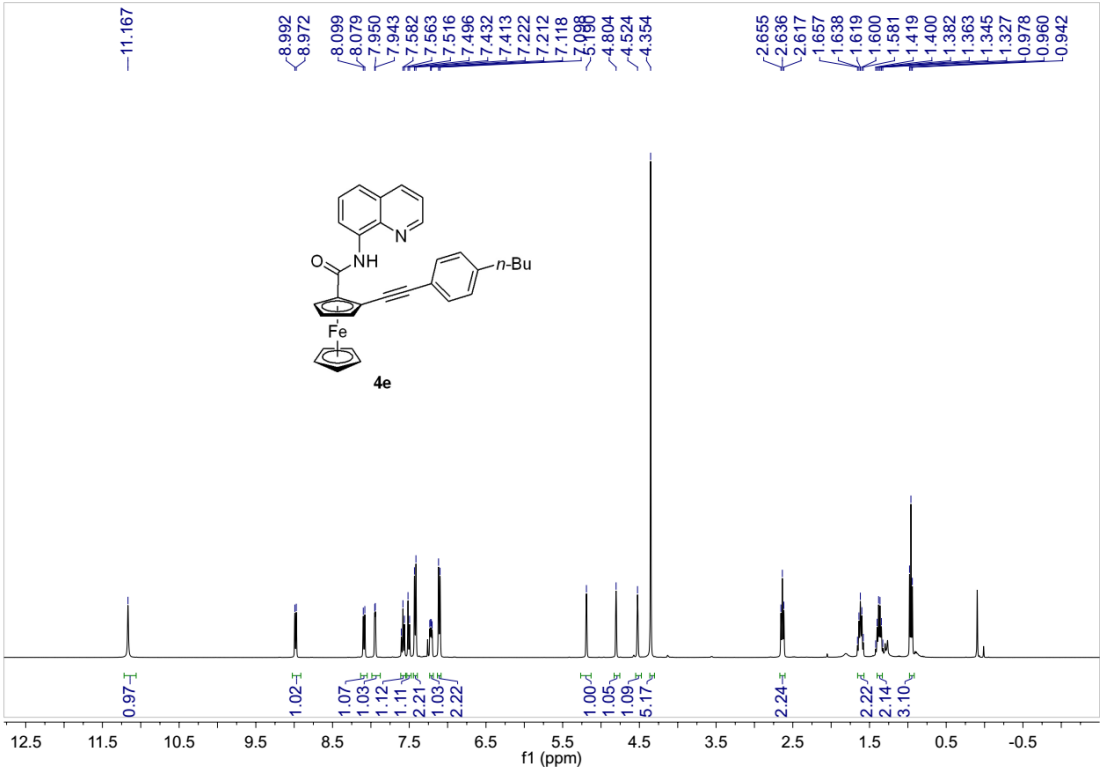

Fig S35: ^{1}H NMR Spectrum of **4e**

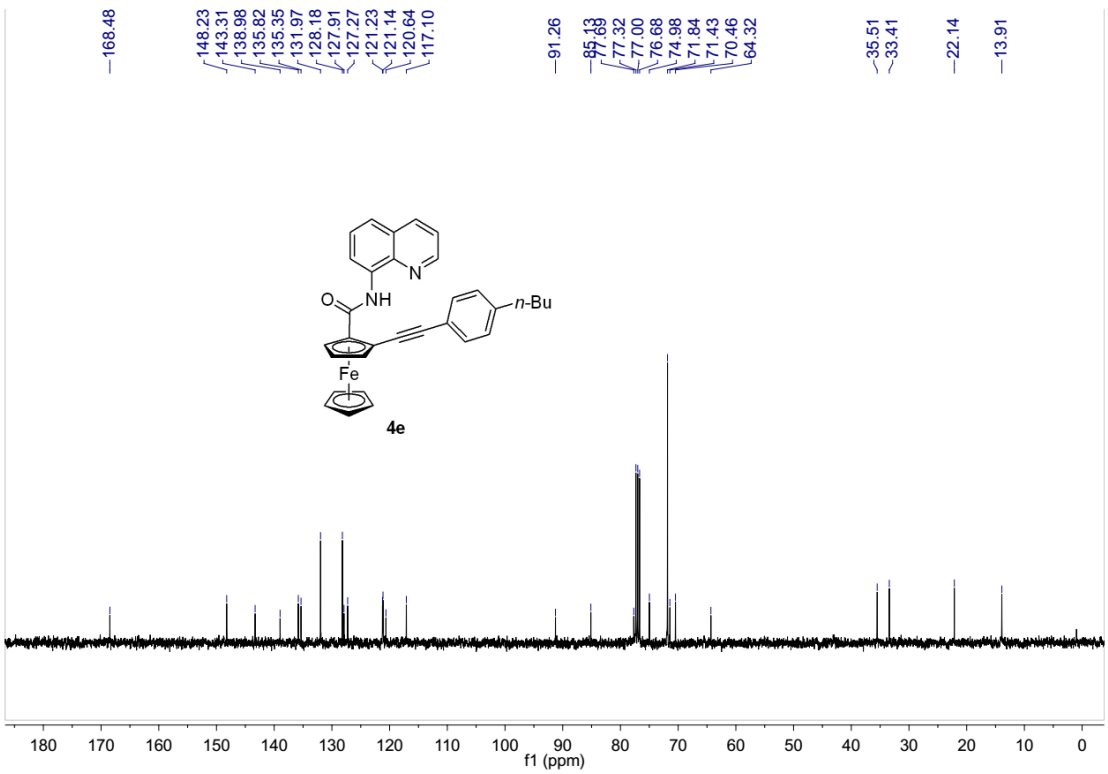

Fig S36: ^{13}C NMR Spectrum of **4e**

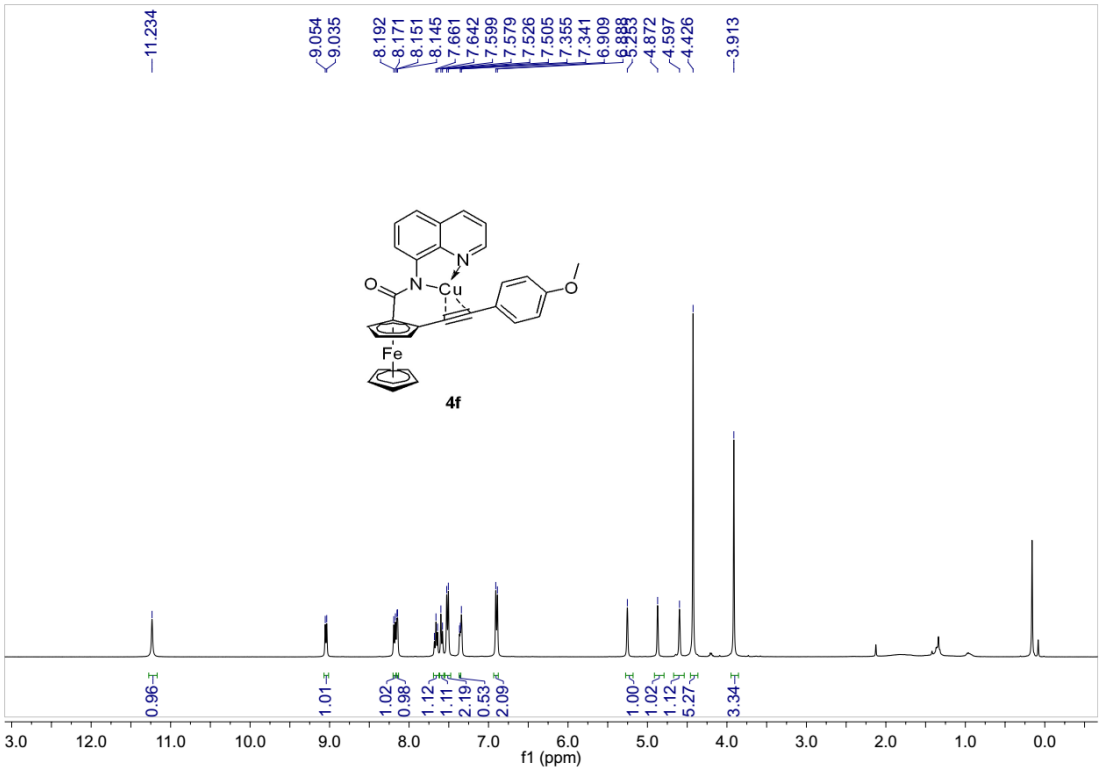

Fig S37: ^{1}H NMR Spectrum of **4f**

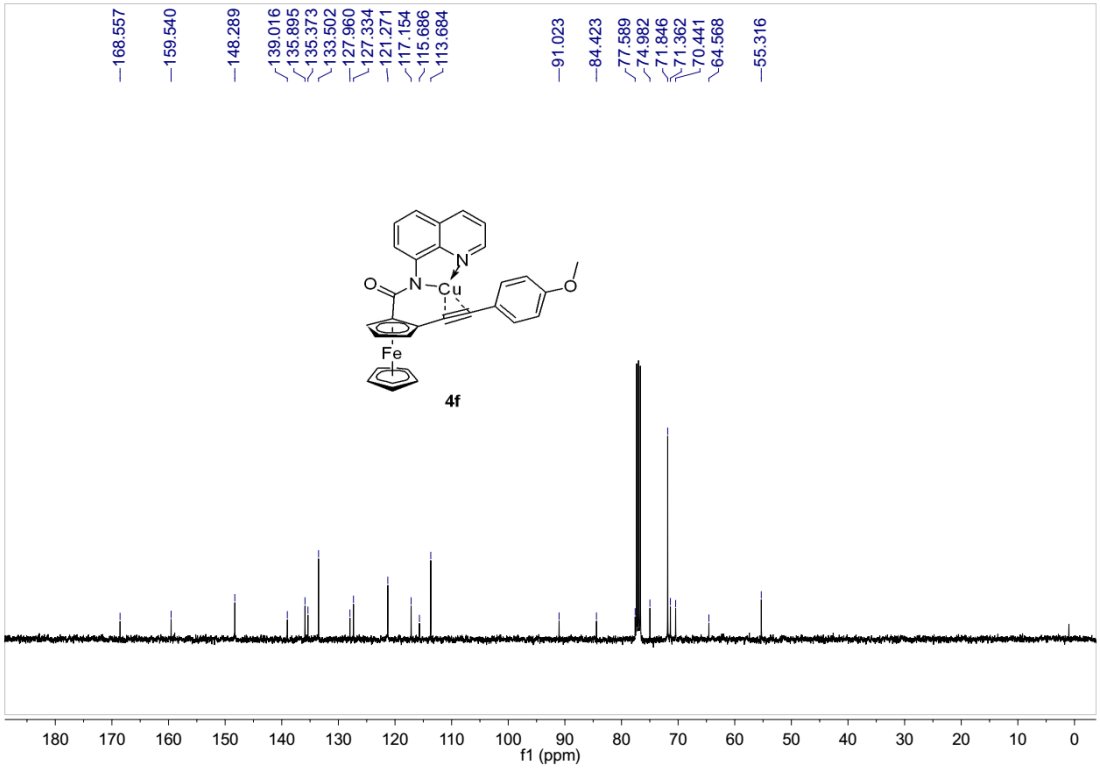

Fig S38: ^{13}C NMR Spectrum of **4f**

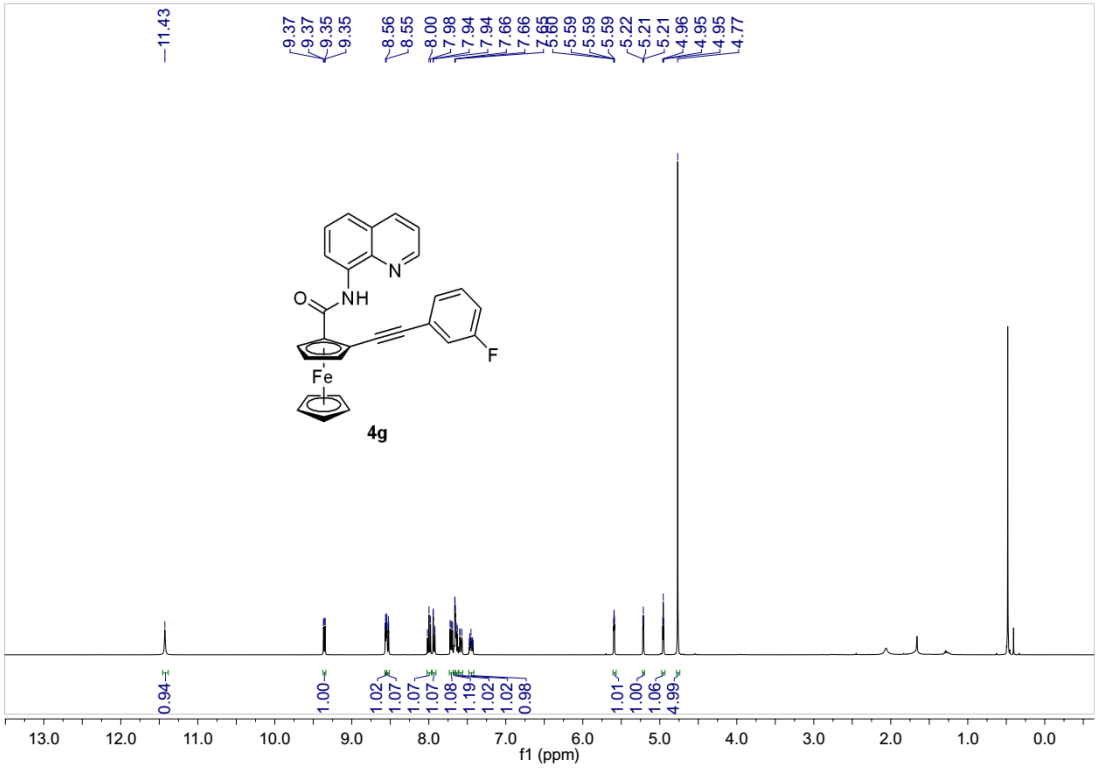

Fig S39: ^{1}H NMR Spectrum of **4g**

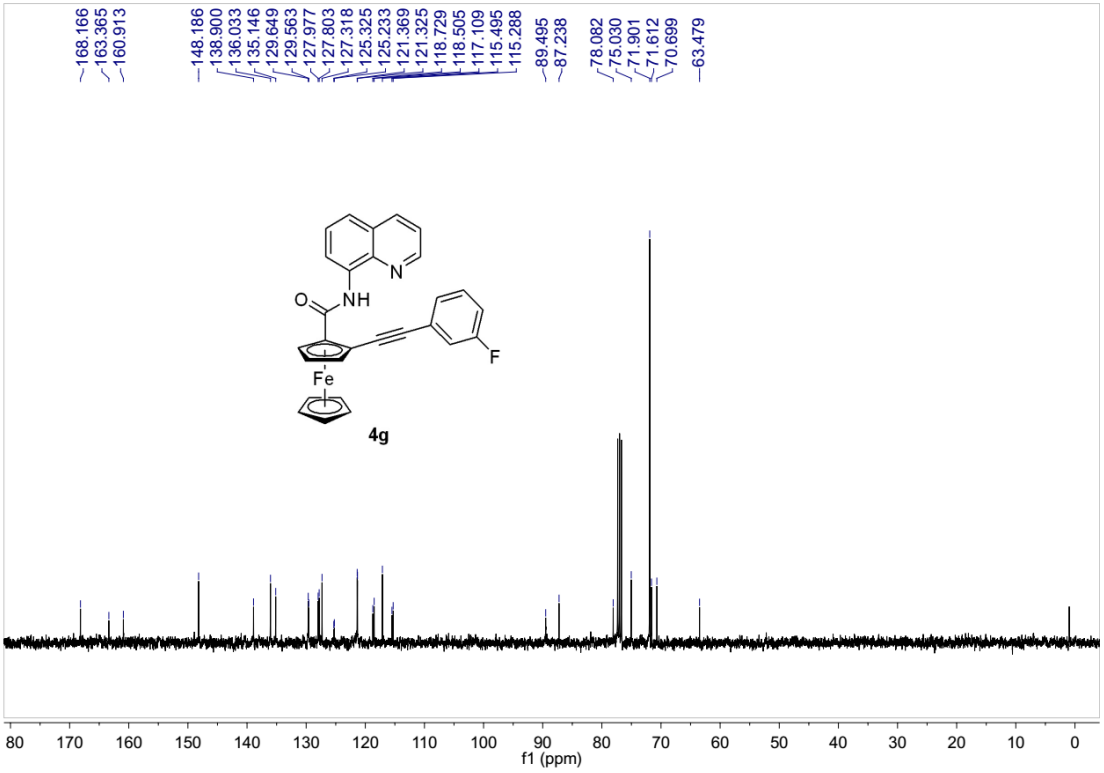

Fig S40: ^{13}C NMR Spectrum of **4g**

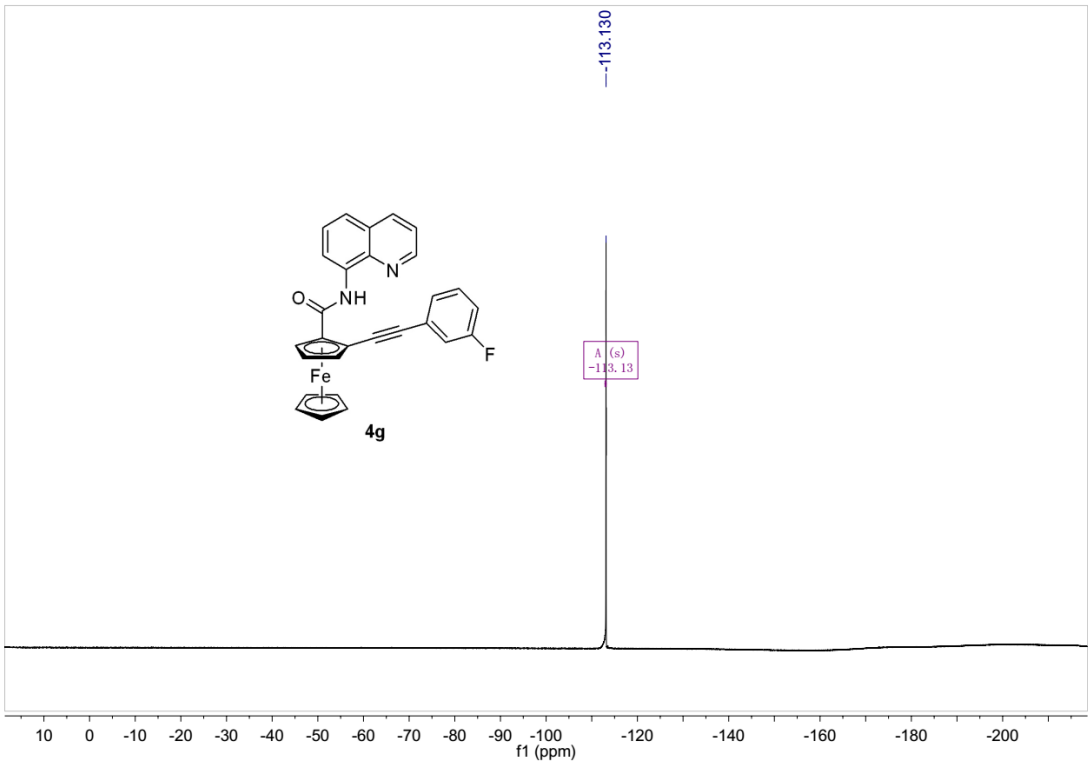

Fig S41: ^{19}F NMR Spectrum of **4g**

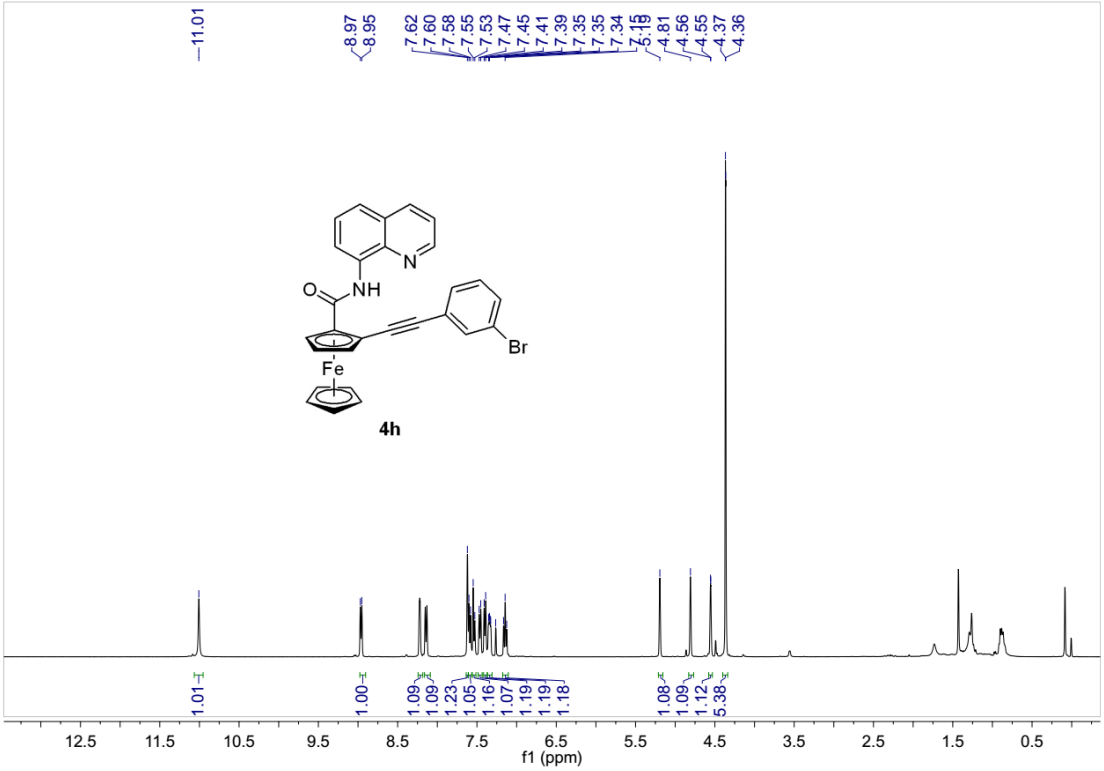

Fig S42: ^{1}H NMR Spectrum of **4h**

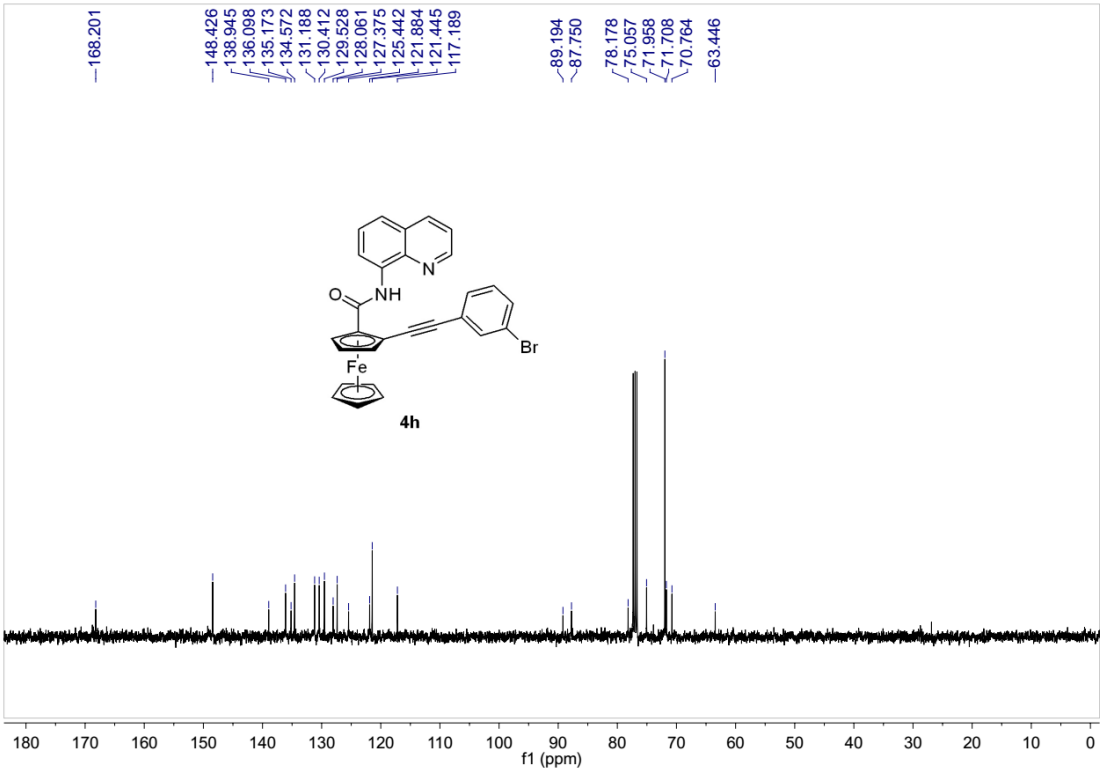

Fig S43: ^{13}C NMR Spectrum of **4h**

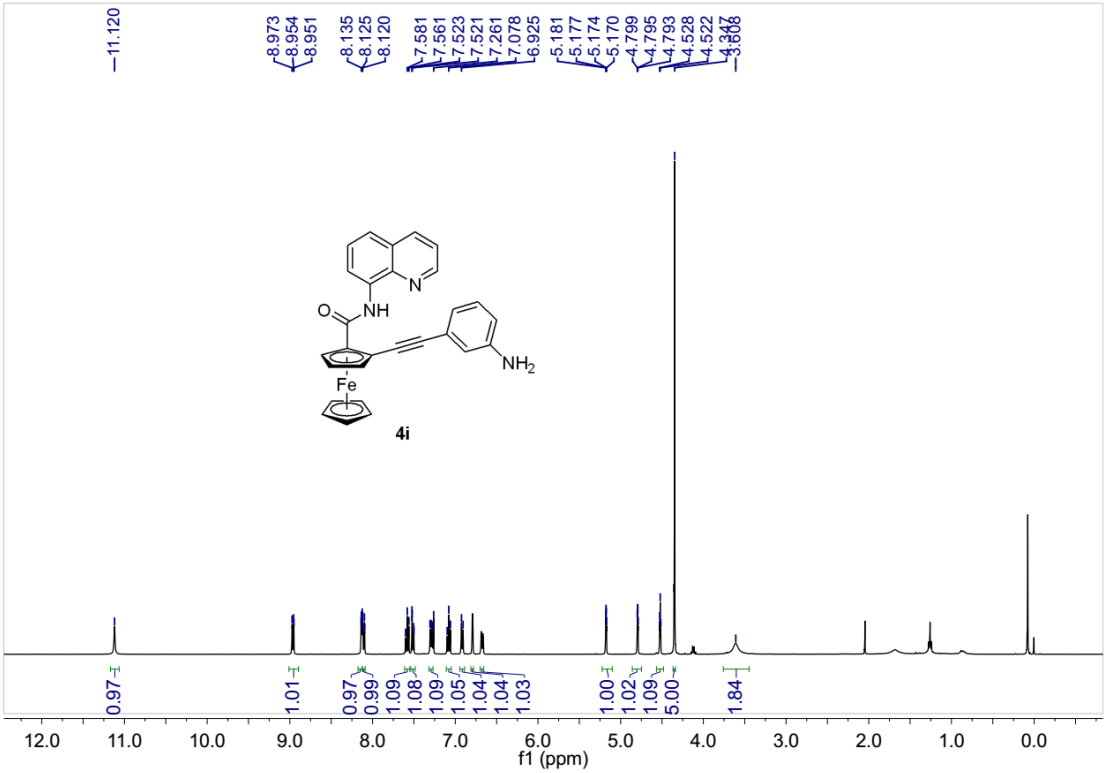

Fig S44: ^{1}H NMR Spectrum of **4i**

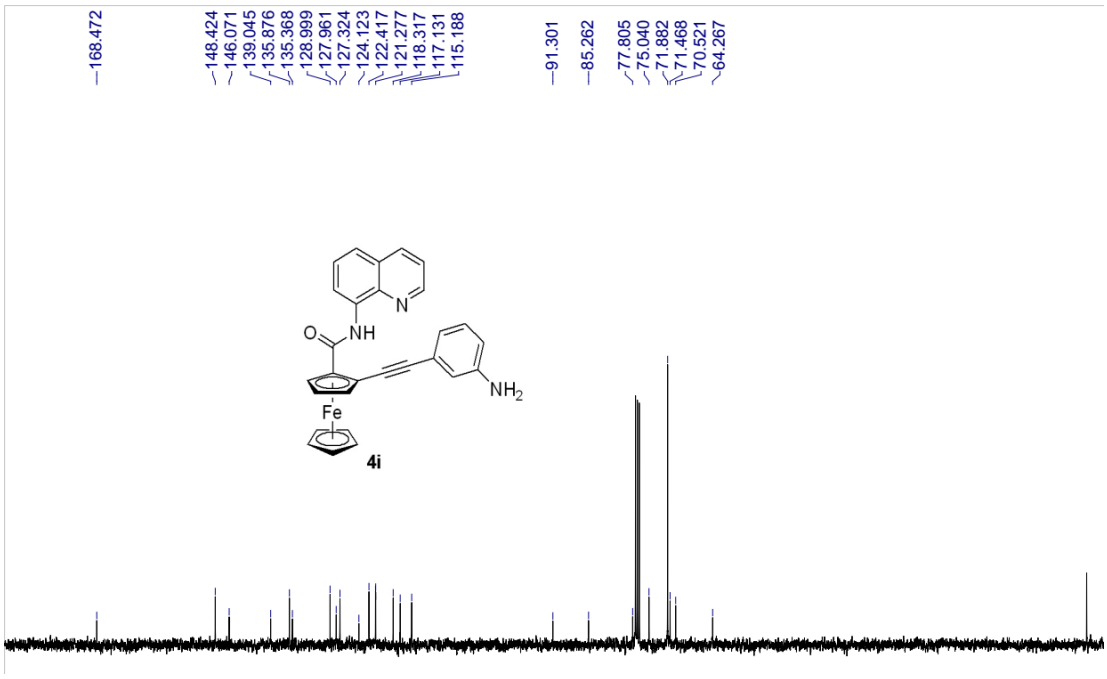

Fig S45: ^{13}CNMR Spectrum of **4i**

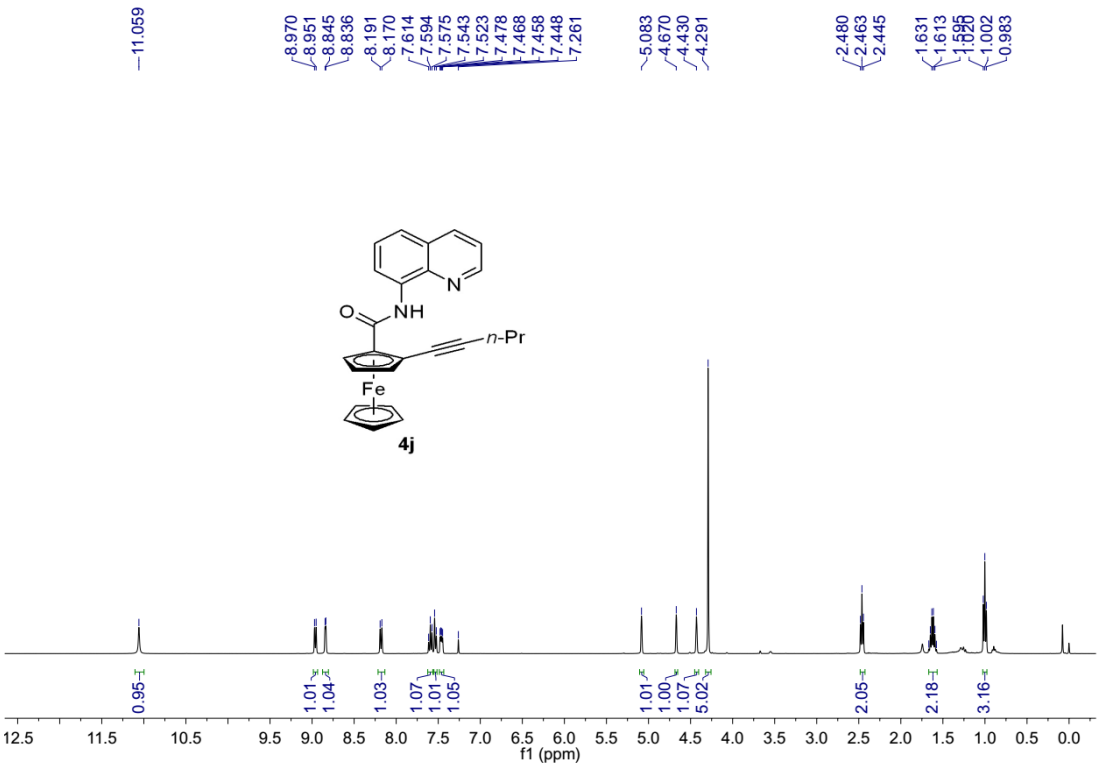

Fig S46: ^{1}H NMR Spectrum of **4j**

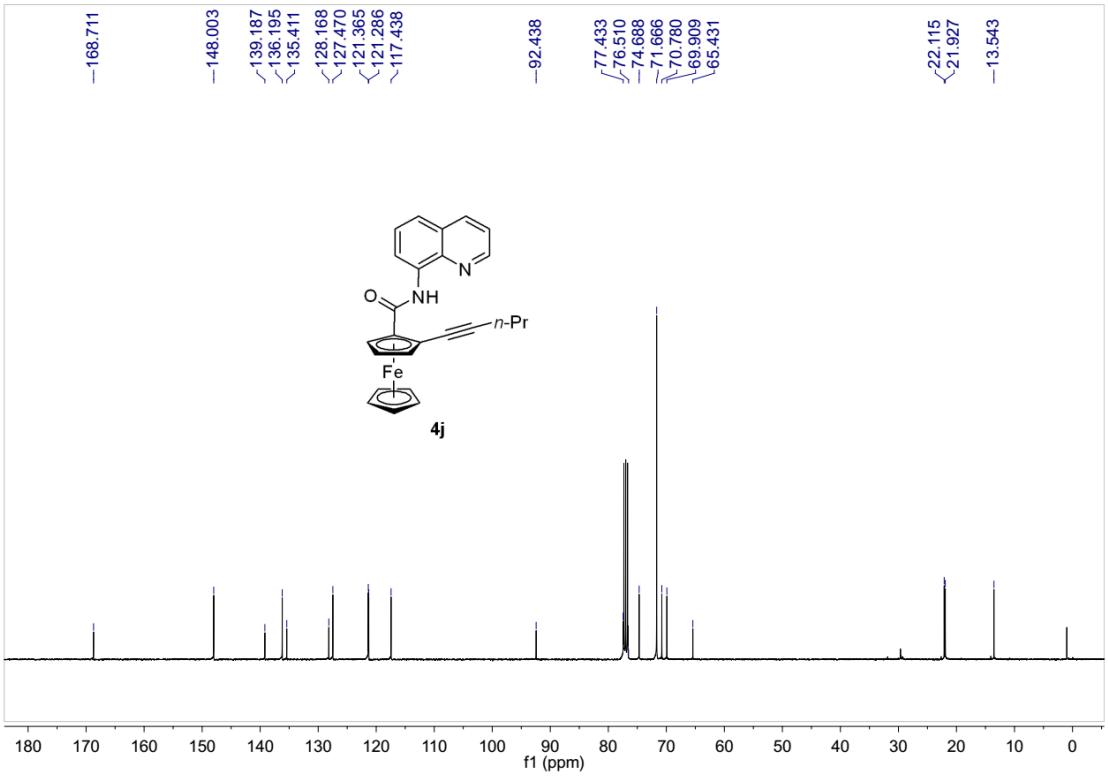

Fig S47: ^{13}C NMR Spectrum of **4j**

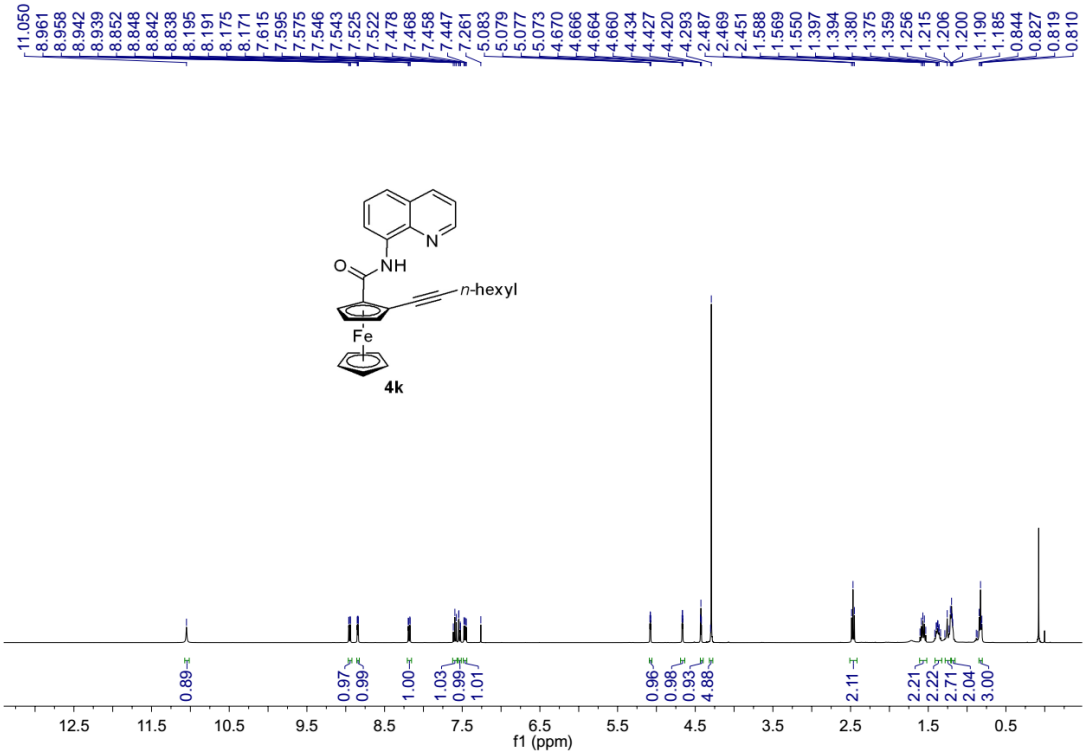

Fig S48: ^{1}H NMR Spectrum of **4k**

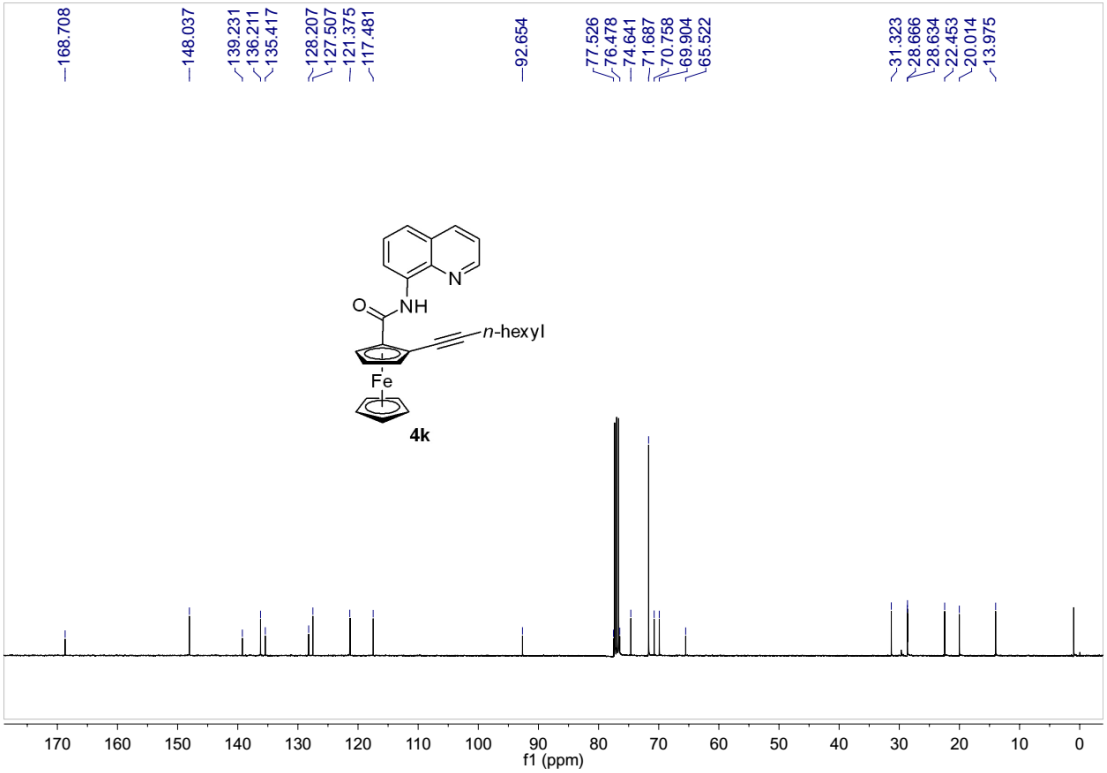

Fig S49: ^{13}H NMR Spectrum of **4k**

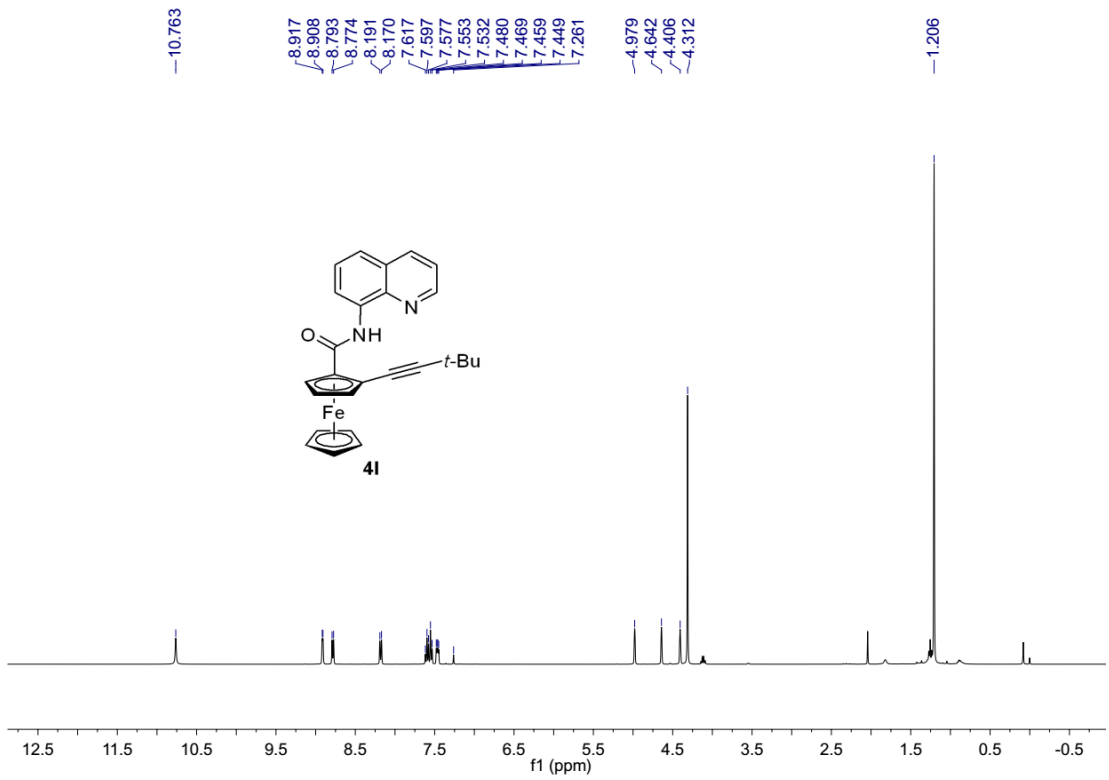

Fig S50: ^{1}H NMR Spectrum of **4l**

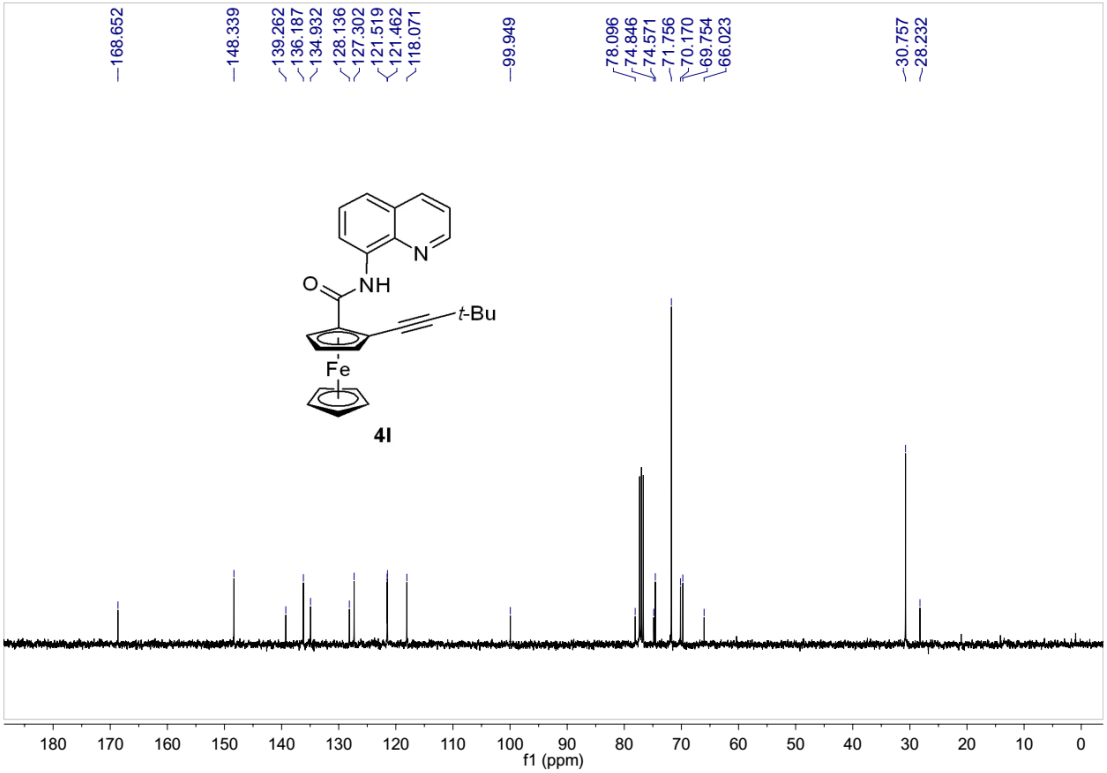

Fig S51: ^{13}C NMR Spectrum of **4l**