Electronic Supplementary Material (ESI) for Dalton Transactions.

Coinage metal-ethylene complexes of sterically demanding 1,10-phenanthroline ligands

Deepika V. Karade, Vo Quang Huy Phan, H. V. Rasika Dias*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Box 19065, Arlington, Texas 76019-0065, United States

Supplementary Information

Table S1. Selected peaks from ^{1}H and ^{13}C NMR for complexes **1-4** and several related in the literature. The chemical shift (Δδ) from free ethylene represents Δδ = δ (metal complex) – δ (free ethylene). For comparison, free ethylene has chemical shifts of δ 5.40 (^{1}H) and 123.1 (^{13}C) ppm in $CDCl_3$. [a]Data acquired at -90 °C.

Compound	δ_H (H_2C=) (ppm)	$\Delta\delta_H$ (ppm)	δ_C (H_2C=) (ppm)	$\Delta\delta_C$ (ppm)	Ref.
Free ethylene	5.40	-	123.1	-	
[a]Free ethylene	5.44	-	-	-	[1]
[**L1**Cu(C_2H_4)]$^+$	3.23	-2.17	86.21	-36.89	This work
[**L1**Ag(C_2H_4)]$^+$	3.50	-1.90	101.92	-21.18	This work
[**L1**Au(C_2H_4)]$^+$	2.34	-3.04	61.08	-62.02	This work
[**L2**Cu(C_2H_4)]$^+$	3.53	-1.87	-	-	This work
[a][(5-Clphen)Cu(C_2H_4)]$^+$	5.34	-0.1	-	-	[1]
[a][(phen)Cu(C_2H_4)]$^+$	5.02	-0.42	-	-	[1]
[a][(2,9-Me_2phen)Cu(C_2H_4)]$^+$	4.92	-0.52	-	-	[1]
[a][(3,4,7,8-Me_4phen)Cu(C_2H_4)]$^+$	4.72	-0.72	-	-	[1]
[a][(4,7-Me_2phen)Cu(C_2H_4)]$^+$	4.89	-0.55	-	-	[1]
[(phen)Au(C_2H_4)]$^+$	3.97	-1.43	61.91	-61.03	[2]
[(2,9-*n*-Bu_2phen)Au(C_2H_4)]$^+$	3.88	-1.52	60.60	-62.5	[2]

Table S2. Selected bond distances (Å) and angles (°) for [**L1**M(C_2H_4)][SbF_6] (M **=** Cu (**1**), Ag (**2**), Au (**3**)) and [**L2**Cu(C_2H_4)][BArF] (**4**)**.** [a]There are two chemically identical molecules in the asymmetric unit. Metrical parameters of the second molecules are given in *italics*. [b]Sum of the angles at the metal ion.

Complex	C=C (Å)	M-N (Å)	M-C (Å)	∠NMN (°)	∠CMC (°)	∑ at M[b] (°)	Ref.
[**L1**Cu(C_2H_4)]$^+$	1.364(6)	2.011(2), 2.013(2)	2.027(3) 2.024(3)	83.90(10)	39.34(16)	360.1	This work
[**L1**Ag(C_2H_4)]$^+$	1.326(4)	2.2843(15) 2.2842(15)	2.283(2) 2.283(2)	73.42(8)	33.77(11)	360	This work
[a][**L1**Au(C_2H_4)]$^+$	1.394(5)	2.208(3) 2.214(3)	2.099(4) 2.112(3)	75.31(10)	38.99(15)	360.1	This work
	1.405(5)	*2.206(3)* *2.216(3)*	*2.099(4)* *2.112(3)*	*75.15(11)*	*38.66(15)*	*360.0*	
[**L2**Cu(C_2H_4)]$^+$	1.339(3)	2.0059(14) 2.0179(14)	2.024(2) 2.0011(19)	83.59(6)	38.86(9)	360.6	This work
[(phen)Cu(C_2H_4)]$^+$	1.36(2)	2.002(8) 2.004(9)	1.998(13) 2.022(12)	85.6(3)	39.6(6)	360	3
[a][(2,9-*n*-Bu_2phen)Au(C_2H_4)]$^+$	1.383(8)	2.192(5) 2.196(5)	2.086(6) 2.096(7)	76.29(18)	38.6(2)	360	2
	1.411(10)	*2.201(5)* *2.189(5)*	*2.104(7)* *2.106(7)*	*76.61(18)*	*39.2(3)*	*360*	

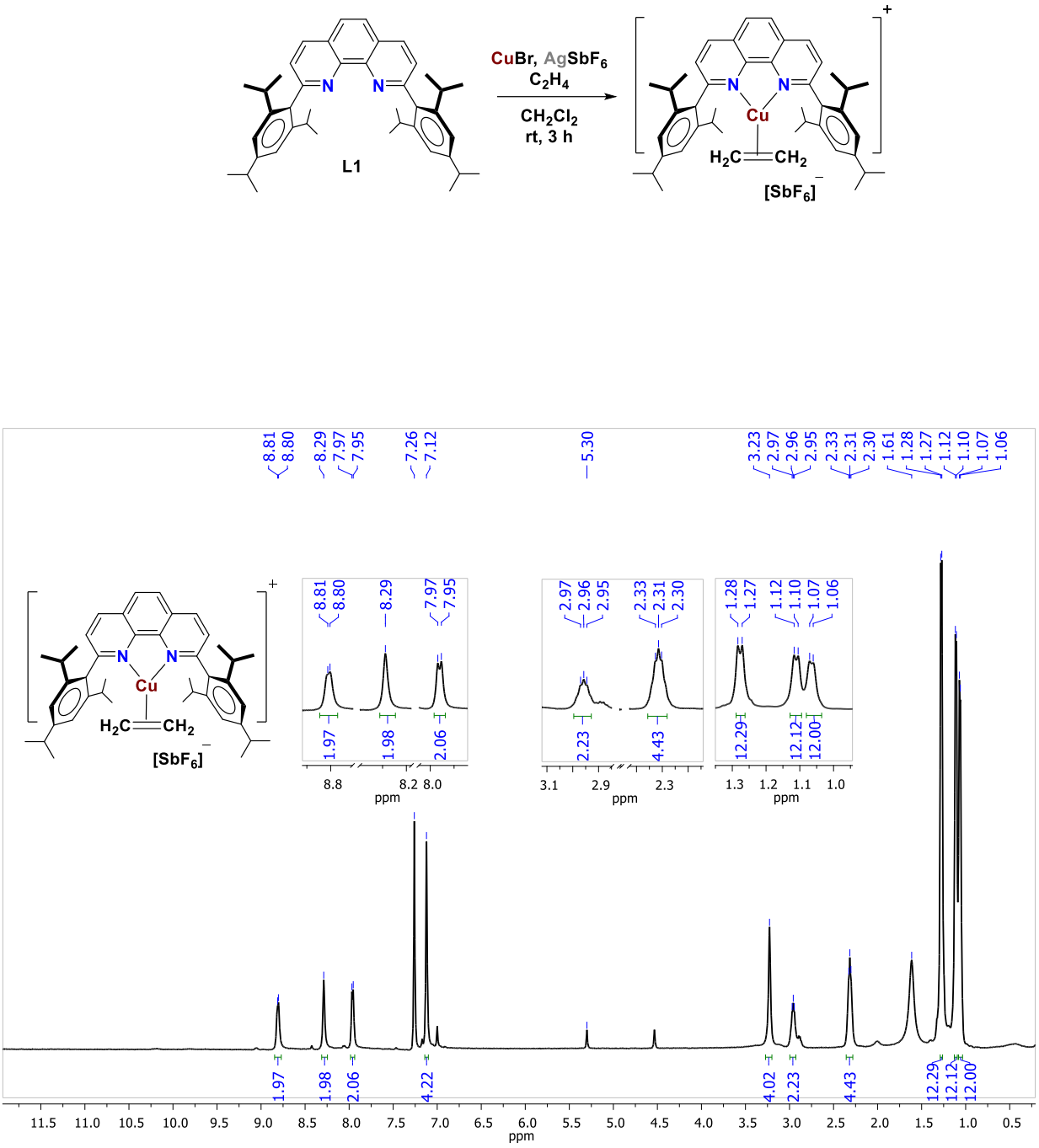


Figure S1. ^{1}H NMR spectrum of [**L1**Cu(C_2H_4)][SbF_6] (**1**) in $CDCl_3$

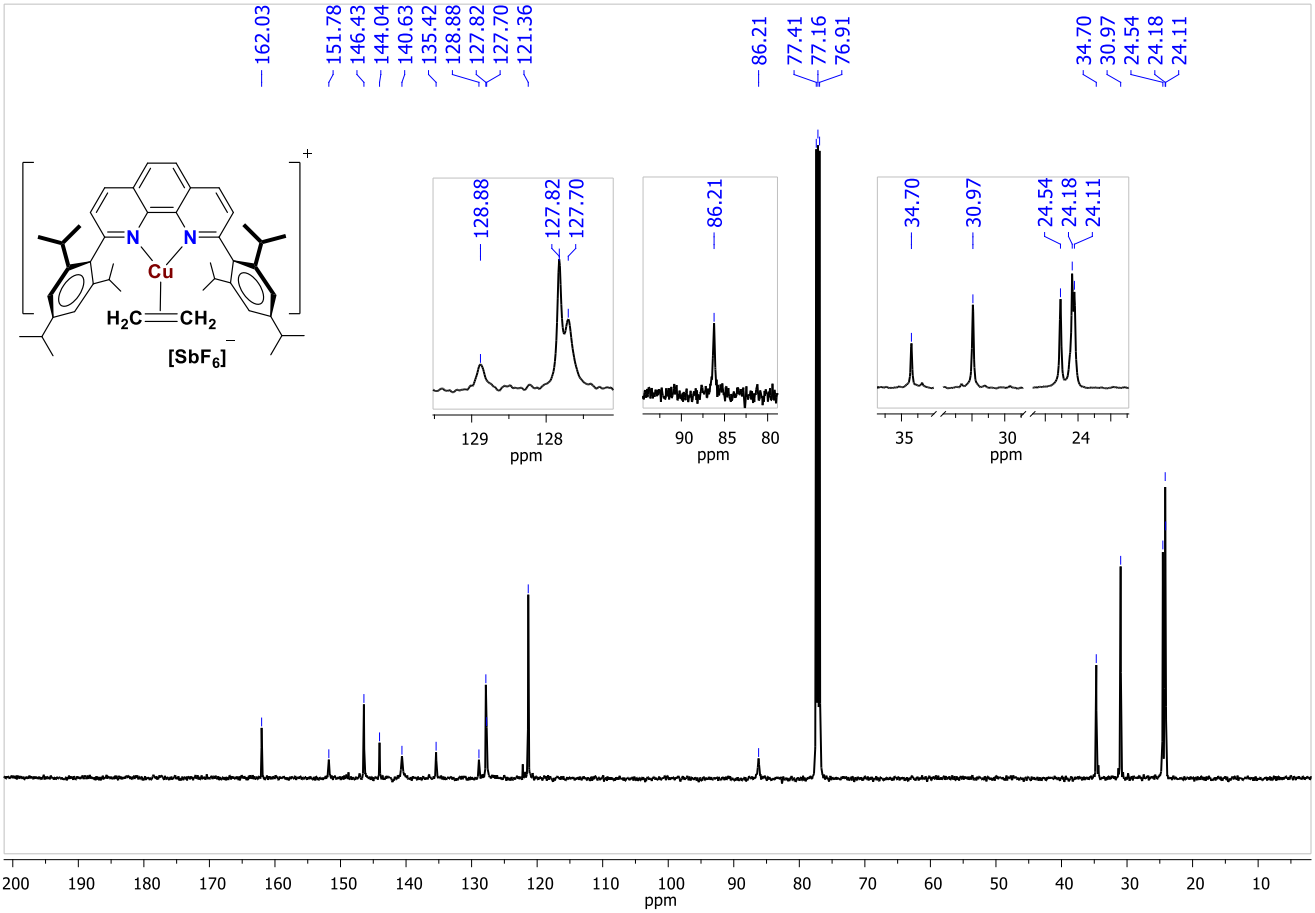
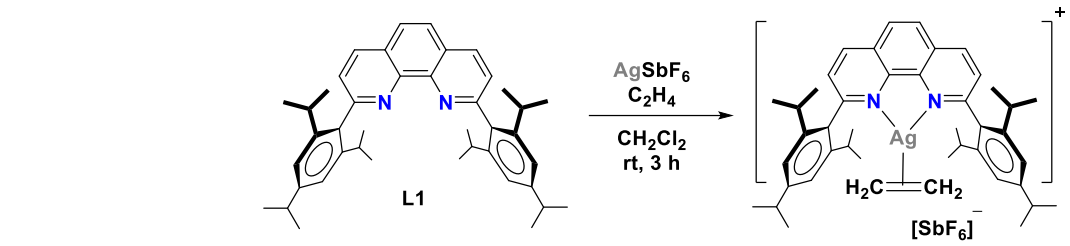


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of [**L1**Cu(C_2H_4)][SbF_6] (**1**) in $CDCl_3$



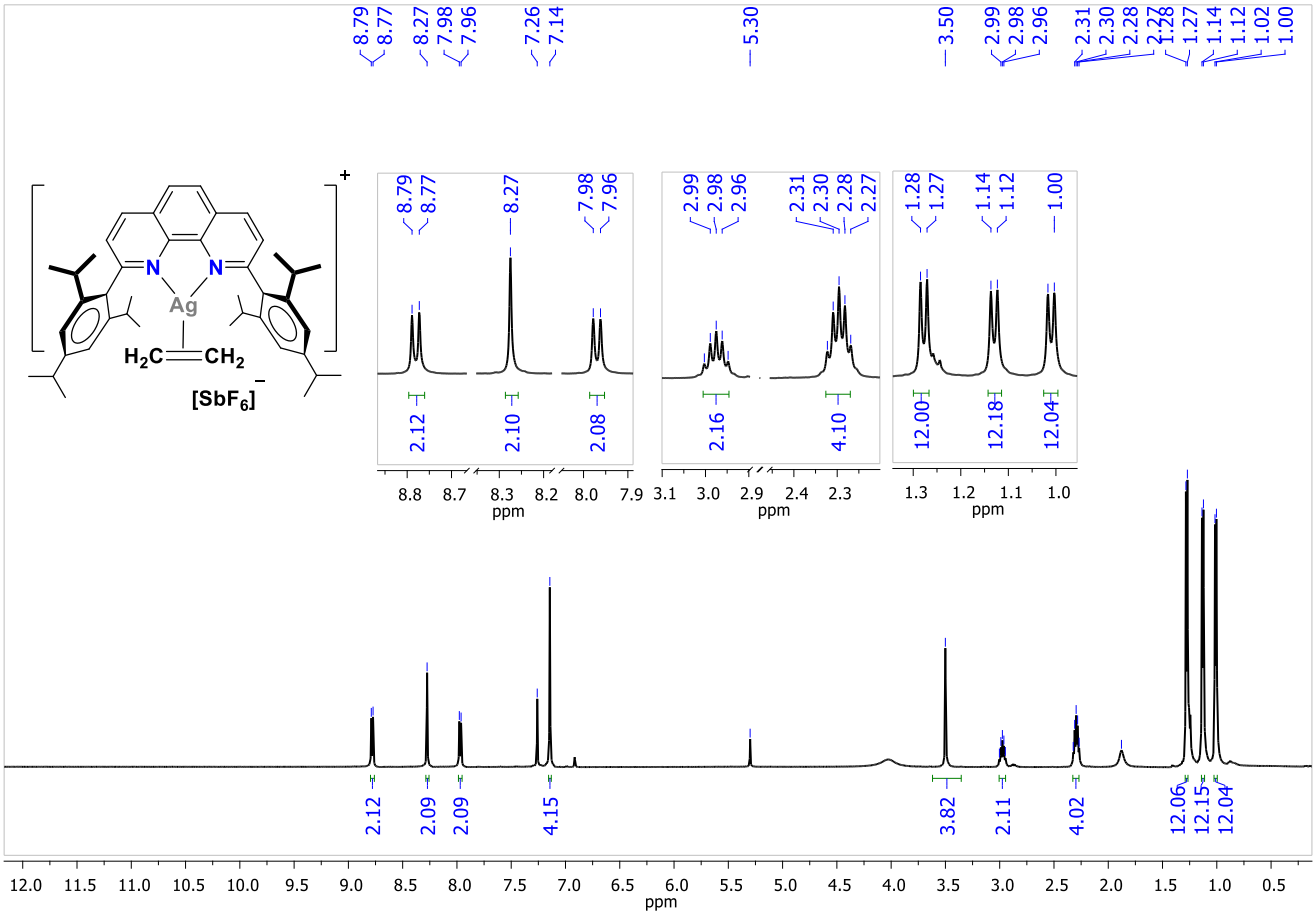


Figure S3. ^{1}H NMR spectrum of [**L1**Ag(C_2H_4)][SbF_6] (**2**) in $CDCl_3$

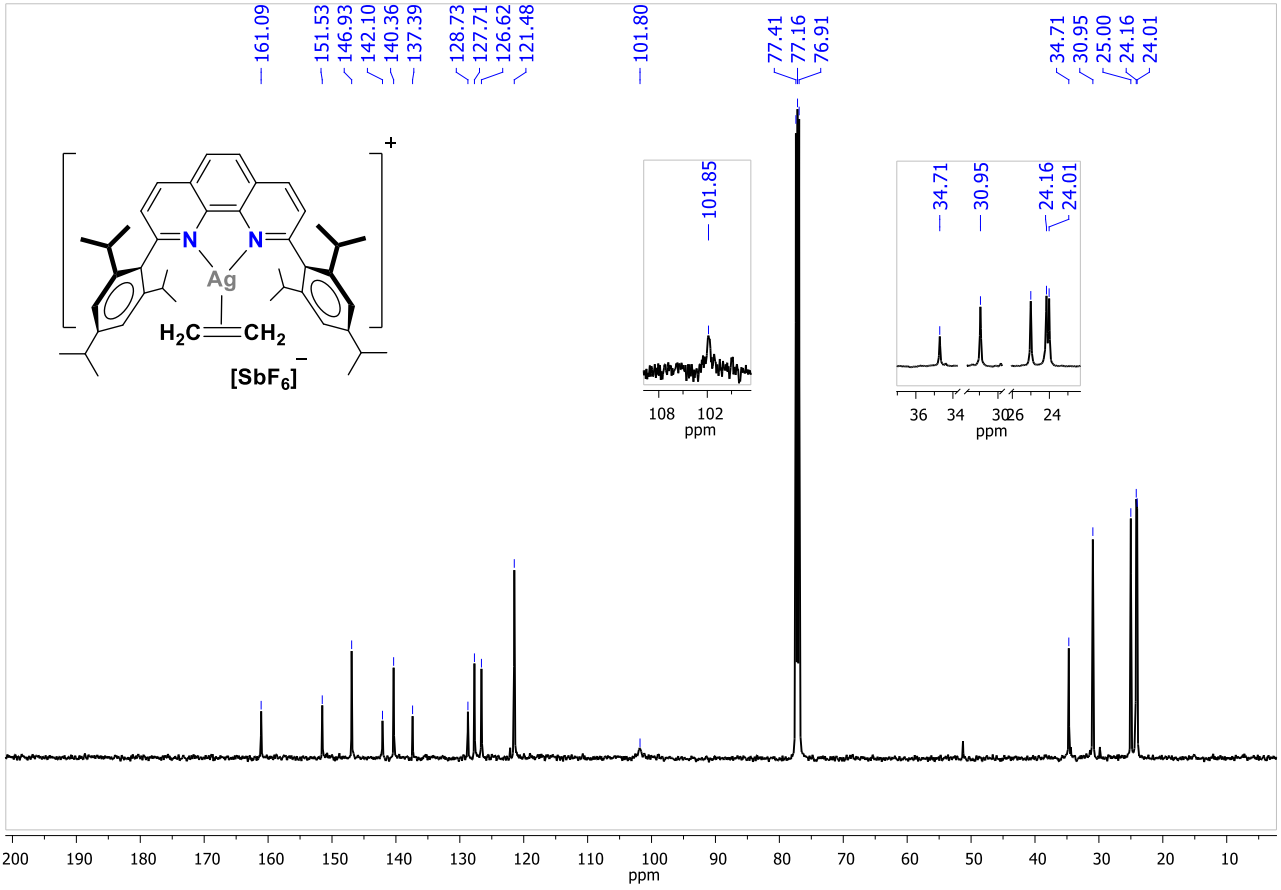
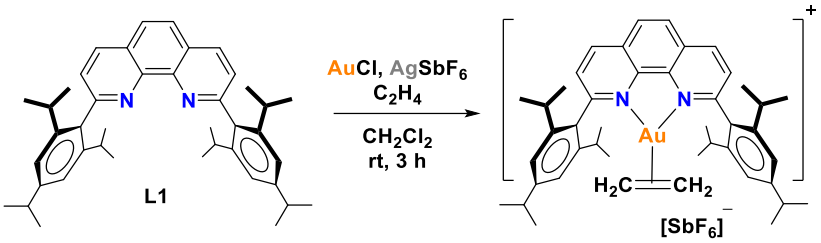


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of [**L1**Ag(C_2H_4)][SbF_6] (**2**) in $CDCl_3$



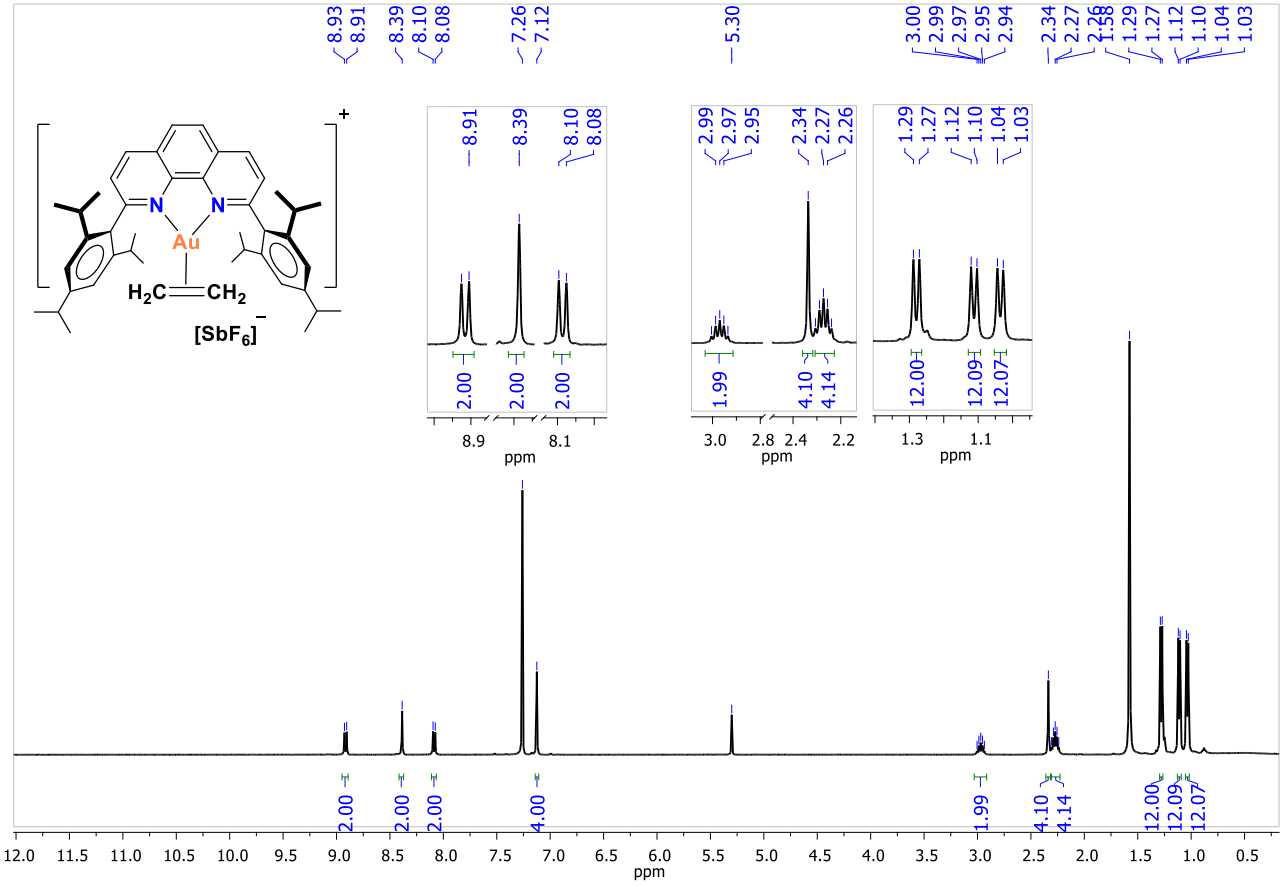


Figure S5. ^{1}H NMR spectrum of [**L1**Au(C_2H_4)][SbF_6] (**3**) in $CDCl_3$

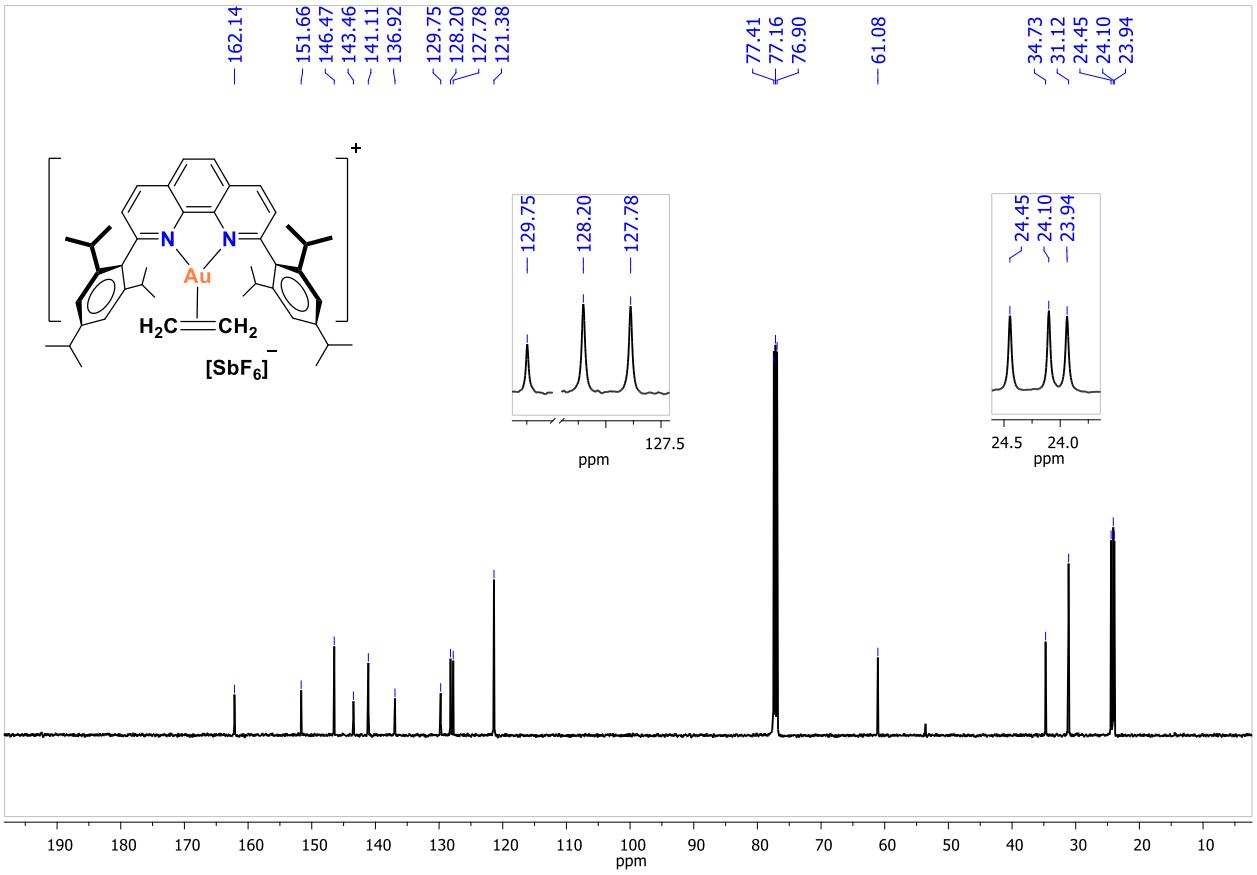
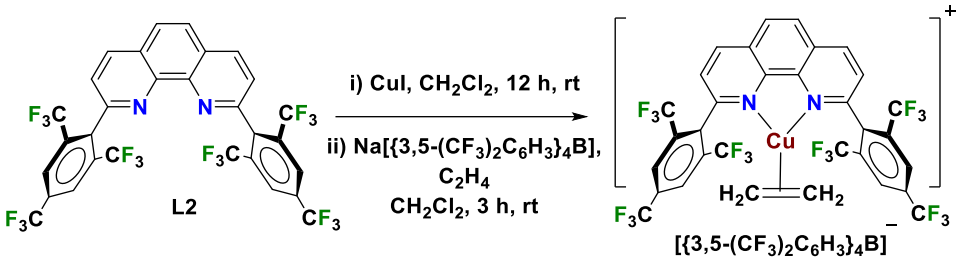


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of [**L1**Au(C_2H_4)][SbF_6] (**3**) in $CDCl_3$



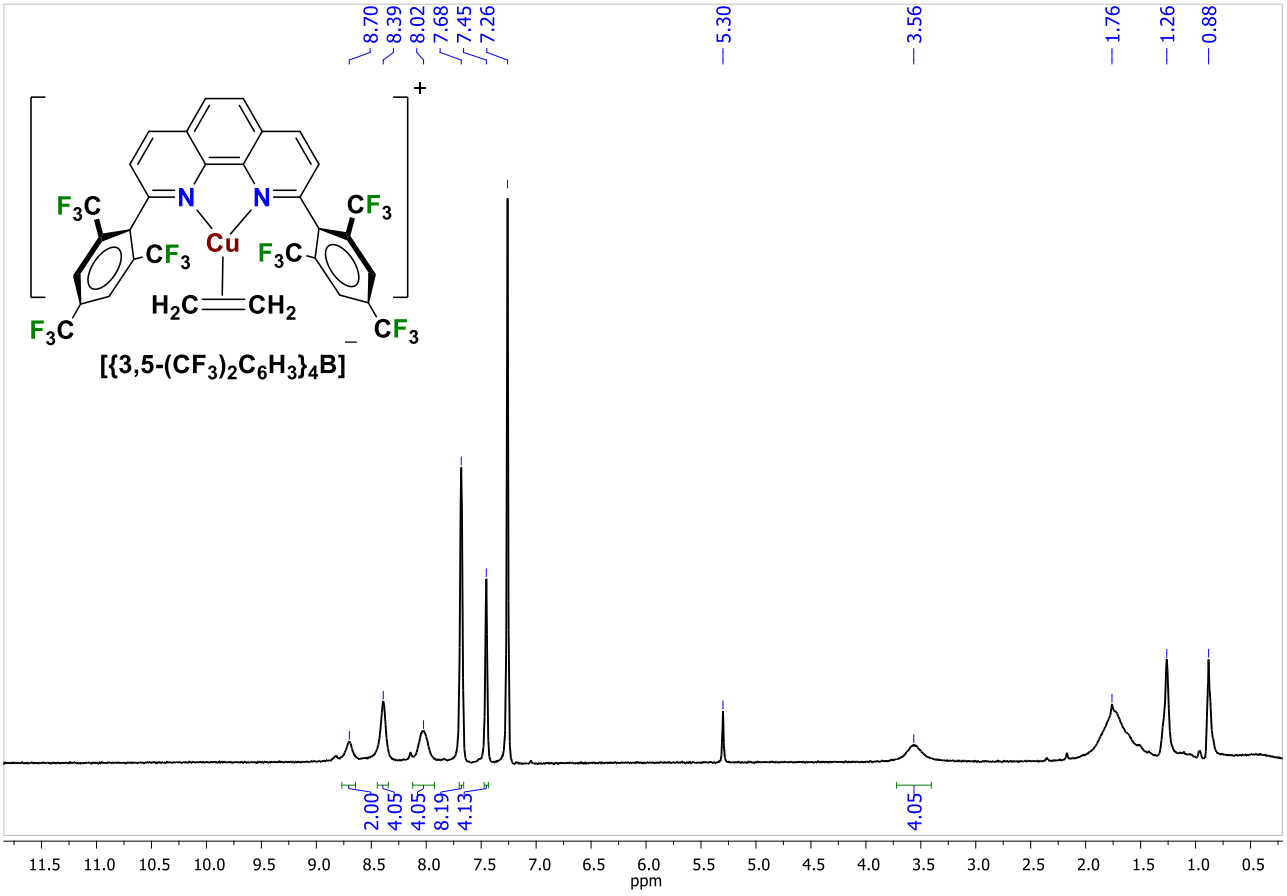


Figure S7. ^{1}H NMR spectrum of [**L2**Cu(C_2H_4)][BArF] (**4**) in $CDCl_3$. Signal at 1.76 ppm belongs to some moisture present in $CDCl_3$. Signal at 1.26 and 0.88 ppm belong to some grease present in the sample.

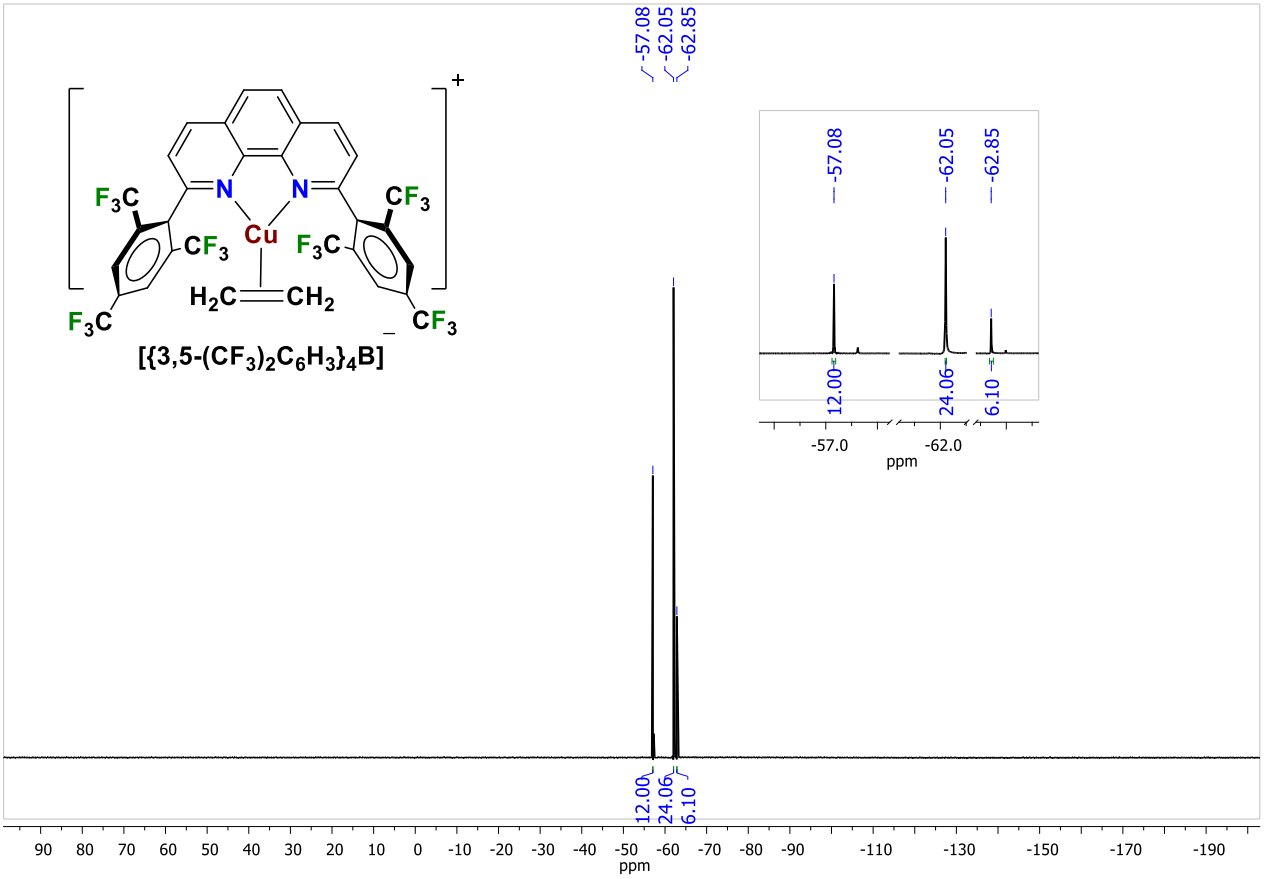


Figure S8. ^{19}F NMR spectrum of [**L2**Cu(C_2H_4)][BArF] (**4**) in $CDCl_3$. Tiny peaks present near -57.08 ppm and -62.85 ppm correspond to very small amount of unreacted ligand.

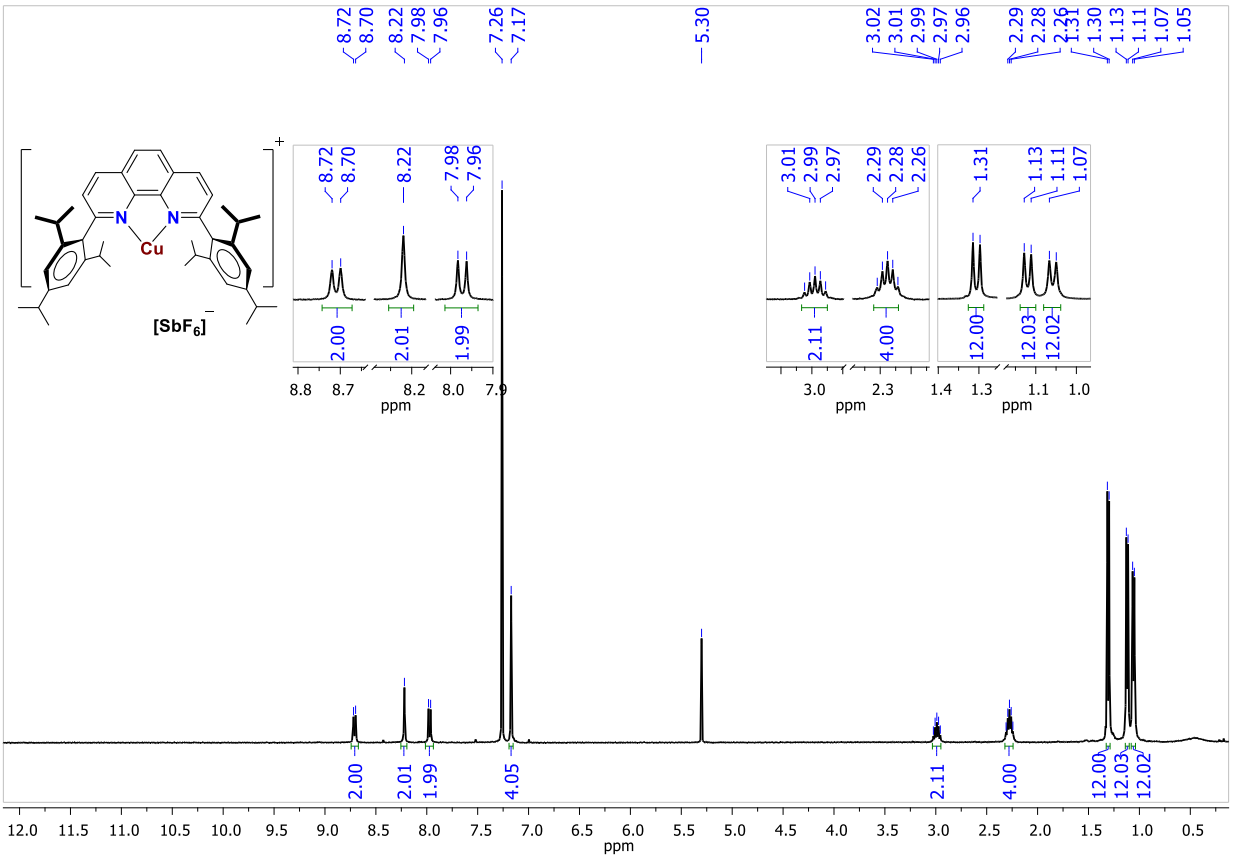


Figure S9. ^{1}H NMR spectrum of [**L1**Cu][SbF_6] in $CDCl_3$

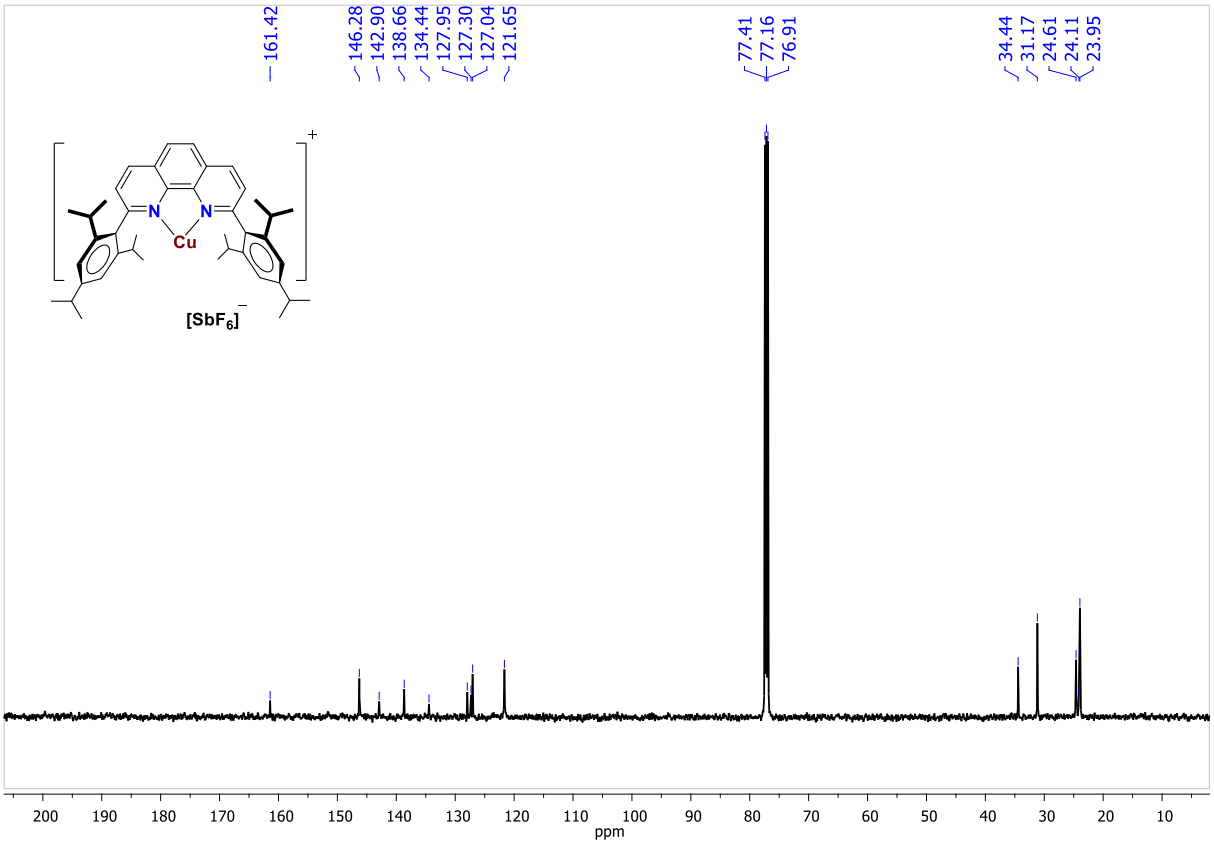


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of [**L1**Cu][SbF_6] in $CDCl_3$

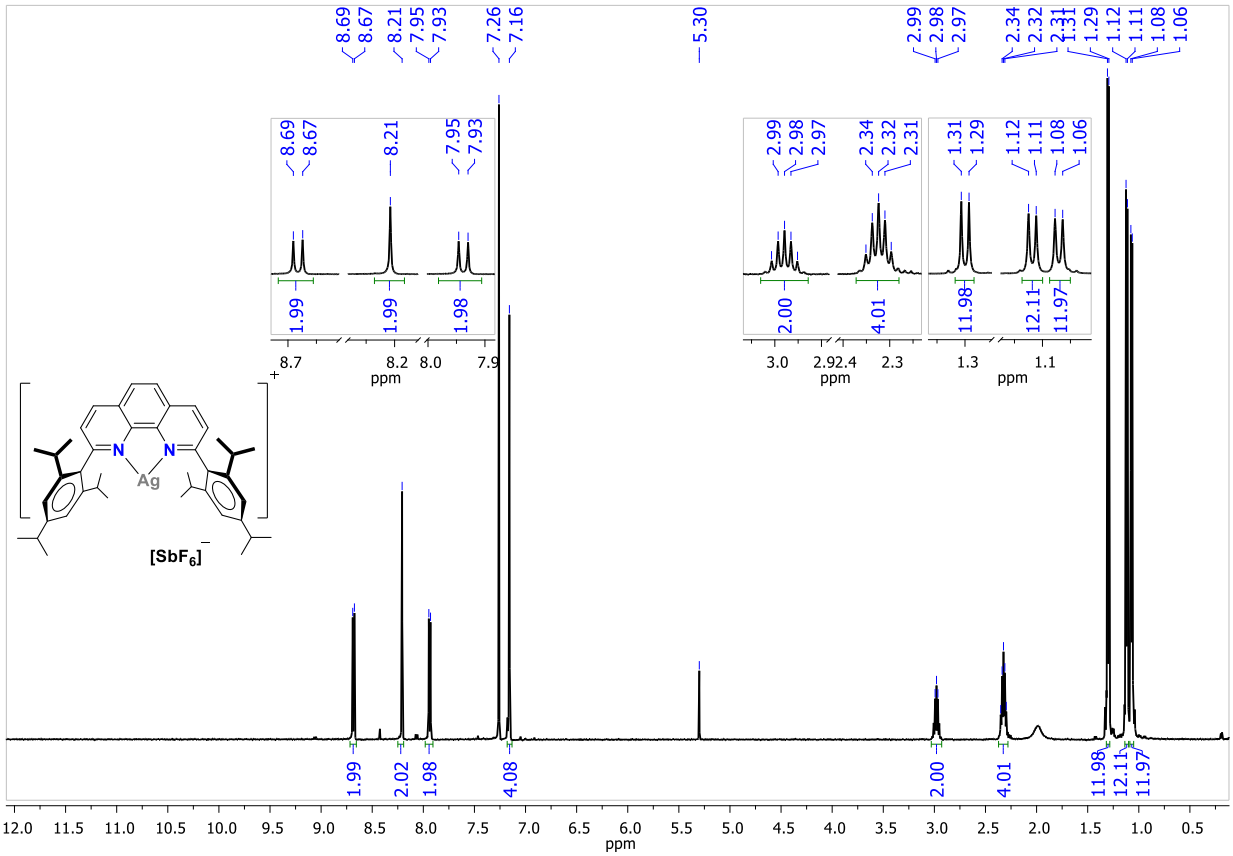


Figure S11. ^{1}H NMR spectrum of [**L1**Ag][SbF_6] in $CDCl_3$

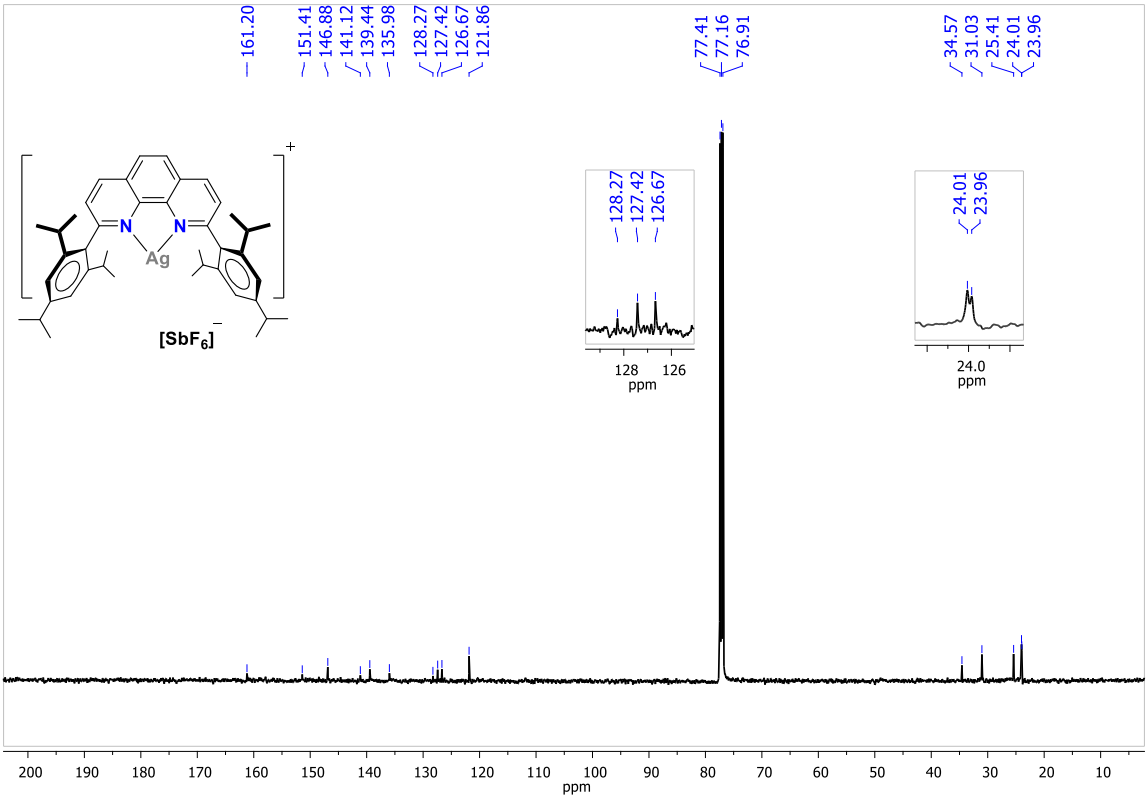


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of [**L1**Ag][SbF_6] in $CDCl_3$

Table S3. Crystal data and structure refinement for [**L1**Cu(C_2H_4)][SbF_6]•CH_2Cl_2.

Identification code	dia94_0m_a
Empirical formula	$C_{45}H_{58}Cl_2CuF_6N_2Sb$
Formula weight	997.12
Temperature/K	99.98
Crystal system	triclinic
Space group	P-1
a/Å	9.1342(9)
b/Å	12.9011(12)
c/Å	19.4966(19)
α/°	88.4970(10)
β/°	87.2490(10)
γ/°	78.8350(10)
Volume/Å^3	2251.1(4)
Z	2
ρ_{calc}g/cm^3	1.471
μ/mm^{-1}	1.249
F(000)	1020.0
Crystal size/mm^3	0.355 × 0.146 × 0.132
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.218 to 61.078

Index ranges	$-12 \leq h \leq 13, -18 \leq k \leq 18, -27 \leq l \leq 27$
Reflections collected	26077
Independent reflections	12957 [R_{int} = 0.0208, R_{sigma} = 0.0352]
Data/restraints/parameters	12957/253/636
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1525
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1650
Largest diff. peak/hole / e $Å^{-3}$	1.63/-1.61

Table S4. Crystal data and structure refinement for [**L1**Ag(C_2H_4)][SbF_6].

Identification code	dia105_0m_a
Empirical formula	$C_{44}H_{56}AgF_6N_2Sb$
Formula weight	956.52
Temperature/K	100.28
Crystal system	monoclinic
Space group	C2/c
a/Å	12.259(4)
b/Å	24.606(9)
c/Å	15.700(6)
α/°	90
β/°	99.591(5)
γ/°	90
Volume/Å^3	4670(3)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	1.051
F(000)	1944.0
Crystal size/mm^3	0.257 × 0.178 × 0.16
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.31 to 61.994

Index ranges	$-16 \leq h \leq 17$, $-35 \leq k \leq 34$, $-22 \leq l \leq 21$
Reflections collected	27107
Independent reflections	6998 [R_{int} = 0.0427, R_{sigma} = 0.0412]
Data/restraints/parameters	6998/15/288
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0687
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0724
Largest diff. peak/hole / e $Å^{-3}$	0.59/-0.61

Table S5. Crystal data and structure refinement for [**L1**Au(C_2H_4)][SbF_6]•CH_2Cl_2.

Identification code	HRD64_0m_a
Empirical formula	$C_{45}H_{58}AuCl_2F_6N_2Sb$
Formula weight	1130.55
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	30.8326(8)
b/Å	22.8905(6)
c/Å	13.0504(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9210.6(4)
Z	8
ρ_{calc}g/cm^3	1.631
μ/mm^{-1}	3.941
F(000)	4480.0
Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.328 to 63.01

Index ranges	$-44 \leq h \leq 45$, $-33 \leq k \leq 33$, $-19 \leq l \leq 19$
Reflections collected	165465
Independent reflections	30564 [R_{int} = 0.0289, R_{sigma} = 0.0234]
Data/restraints/parameters	30564/1/1052
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0216, wR_2 = 0.0439
Final R indexes [all data]	R_1 = 0.0237, wR_2 = 0.0444
Largest diff. peak/hole / e $Å^{-3}$	1.16/-0.98
Flack parameter	0.489(2)

Table S6. Crystal data and structure refinement for [**L2**Cu(C_2H_4)] [{3,5-$(CF_3)_2C_6H_3$}$_4$B] •CH_2Cl_2.

Identification code	HRD132_0m_a
Empirical formula	$C_{65}H_{28}BCl_2CuF_{42}N_2$
Formula weight	1780.14
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	14.4451(4)
b/Å	14.7271(4)
c/Å	17.4381(4)
α/°	79.7320(10)
β/°	73.2900(10)
γ/°	79.6100(10)
Volume/Å^3	3463.18(16)
Z	2
ρ_{calc}g/cm^3	1.707
μ/mm^{-1}	0.549
F(000)	1756.0
Crystal size/mm^3	0.344 × 0.32 × 0.16
Radiation	Mo Kα (λ = 0.71073)

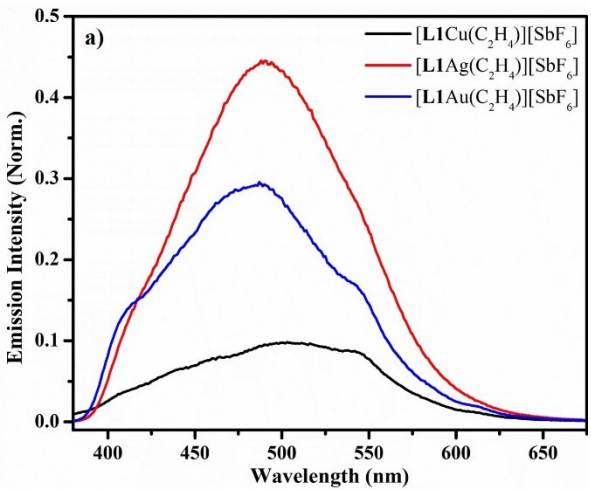
2Θ range for data collection/°	5.676 to 61.038
Index ranges	$-20 \leq h \leq 20$, $-21 \leq k \leq 20$, $-24 \leq l \leq 24$
Reflections collected	58212
Independent reflections	20956 [R_{int} = 0.0214, R_{sigma} = 0.0245]
Data/restraints/parameters	20956/54/1046
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1255
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.1306
Largest diff. peak/hole / e $Å^{-3}$	1.06/-1.42

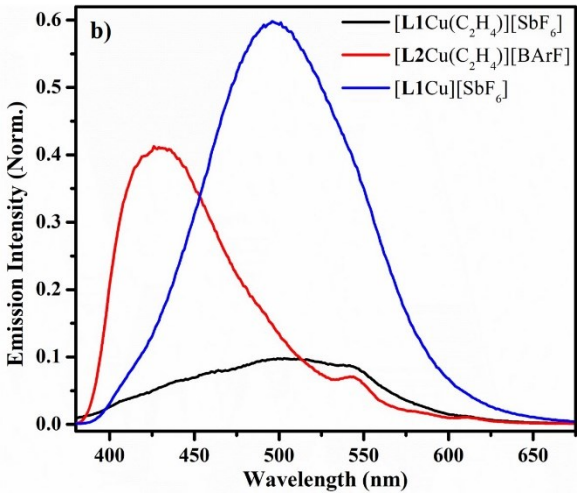
Photoluminescence studies:

Experimental procedure: The $1x10^{-3}$ M to $1.5x10^{-3}$ M stock solutions of the compound of interest were prepared in anhydrous dichloromethane under nitrogen. These solutions were diluted to $4x10^{-4}$ M solution for data collection. The photoluminescence studies were done under nitrogen.

Table S7. Comparison of photoluminescence data of **1-4** complexes, [**L1**Cu][SbF_6] and [**L1**Ag][SbF_6] in dichloromethane ($4x10^{-4}$ M solution) at 360 nm.

Complex	Emission wavelength, λ_{max} (nm)
[**L1**Cu(C_2H_4)][SbF_6] (**1**)	502
[**L1**Ag(C_2H_4)][SbF_6] (**2**)	490
[**L1**Au(C_2H_4)][SbF_6] (**3**)	487
[**L2**Cu(C_2H_4)][BArF] (**4**)	428, 544 (sh)
[**L1**Cu][SbF_6]	497
[**L1**Ag][SbF_6]	495





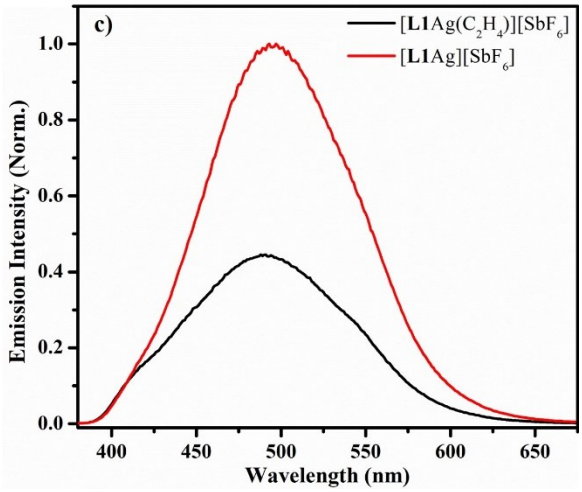


Figure S13. Emission spectra acquired for (a) compounds **1-3** ([**L1**M(C_2H_4)][SbF_6] (M = Cu (**1**), Ag (**2**), Au (**3**)) (b) compounds [**L1**Cu(C_2H_4)][SbF_6] (**1**), [**L2**Cu(C_2H_4)][BArF] (**4**) and [**L1**Cu][SbF_6] (c) compound [**L1**Ag(C_2H_4)][SbF_6] (**2**) and [**L1**Ag][SbF_6] in dichloromethane (4 X 10^{-4} M) by photoexcitation at 360 nm**.**

References.

1. Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. Studies of Copper(I) Olefin Complexes. Formation Constants of Copper Olefin Complexes with 2,2′-Bipyridine, 1,10-Phenanthroline, and Their Derivatives. *Inorg. Chem.* **1986**, *25* (15), 2622–2627.
2. Yang, Y.; Antoni, P.; Zimmer, M.; Sekine, K.; Mulks, F. F.; Hu, L.; Zhang, L.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. Dual Gold/Silver Catalysis Involving Alkynylgold(III) Intermediates Formed by Oxidative Addition and Silver-Catalyzed C–H Activation for the Direct Alkynylation of Cyclopropenes. *Angew. Chem., Int. Ed.* **2019**, *58* (15), 5129–5133.
3. Masuda, H.; Yamamoto, N.; Taga, T.; Machida, K.; Kitagawa, S.; Munakata, M. Structural Studies of Copper(I) Complexes with Ethylene. Crystal Structures of [Cu(2,2′-Bipyridine)(Ethylene)]ClO_4 and [Cu(1,10-Phenanthroline)(Ethylene)]ClO_4. *J. Organomet. Chem.* **1987**, *322* (1), 121–129.