Supporting Information

Synthesis and cytotoxicity studies of Cu(I) and Ag(I) complexes based on sterically hindered β-diketonates with different degrees of fluorination

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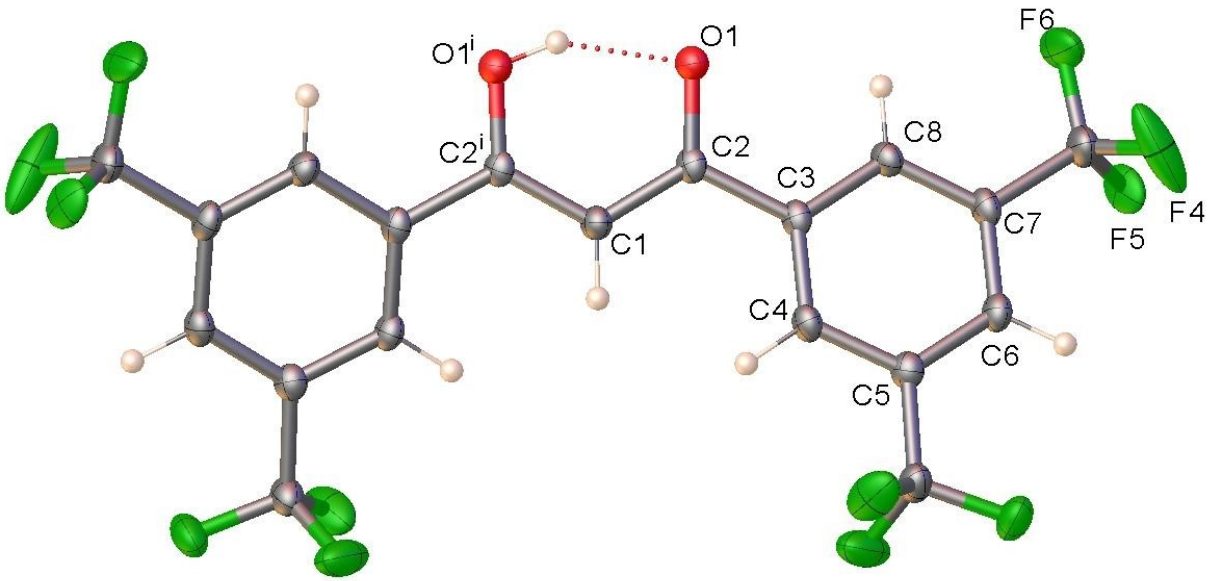

Figure S1. Molecular structure of HL^{CF3}.

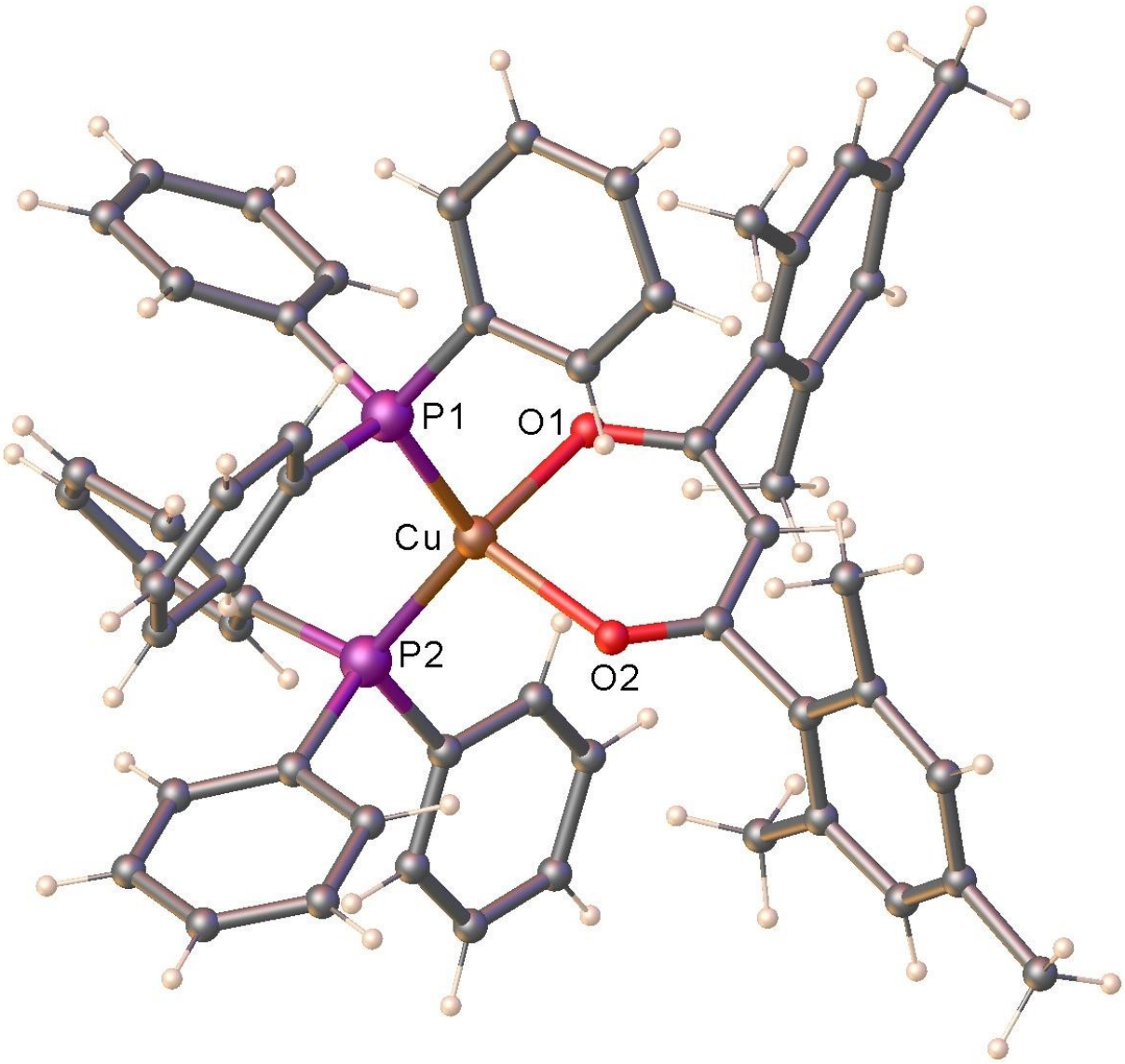

Figure S2. Molecular structure of [Cu(L^{Mes})(PPh_3)$_2$] (**6**). It crystallizes with a molecule of CH_2Cl_2. Crystal Data for $C_{58}H_{55}Cl_2CuO_2P_2$ (*M* =980.40 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 23.368(14) Å, *b* = 15.832(9) Å, *c* = 13.601(8) Å, *β* = 98.943(10)°, *V* = 4971(5) Å^3, *Z* = 4, *T* = 99.96 K, μ(Mo Kα) = 0.654 mm^{-1}, *Dcalc* = 1.310 g/cm^3, 10374 reflections measured (1.764° ≤ 2Θ ≤ 55.282°), 10374 unique (R_{int} = merged, R_{sigma} = 0.1200) which were used in all calculations. The final R_1 was 0.0887 (I > 2σ(I)) and wR_2 was 0.2455 (all data).

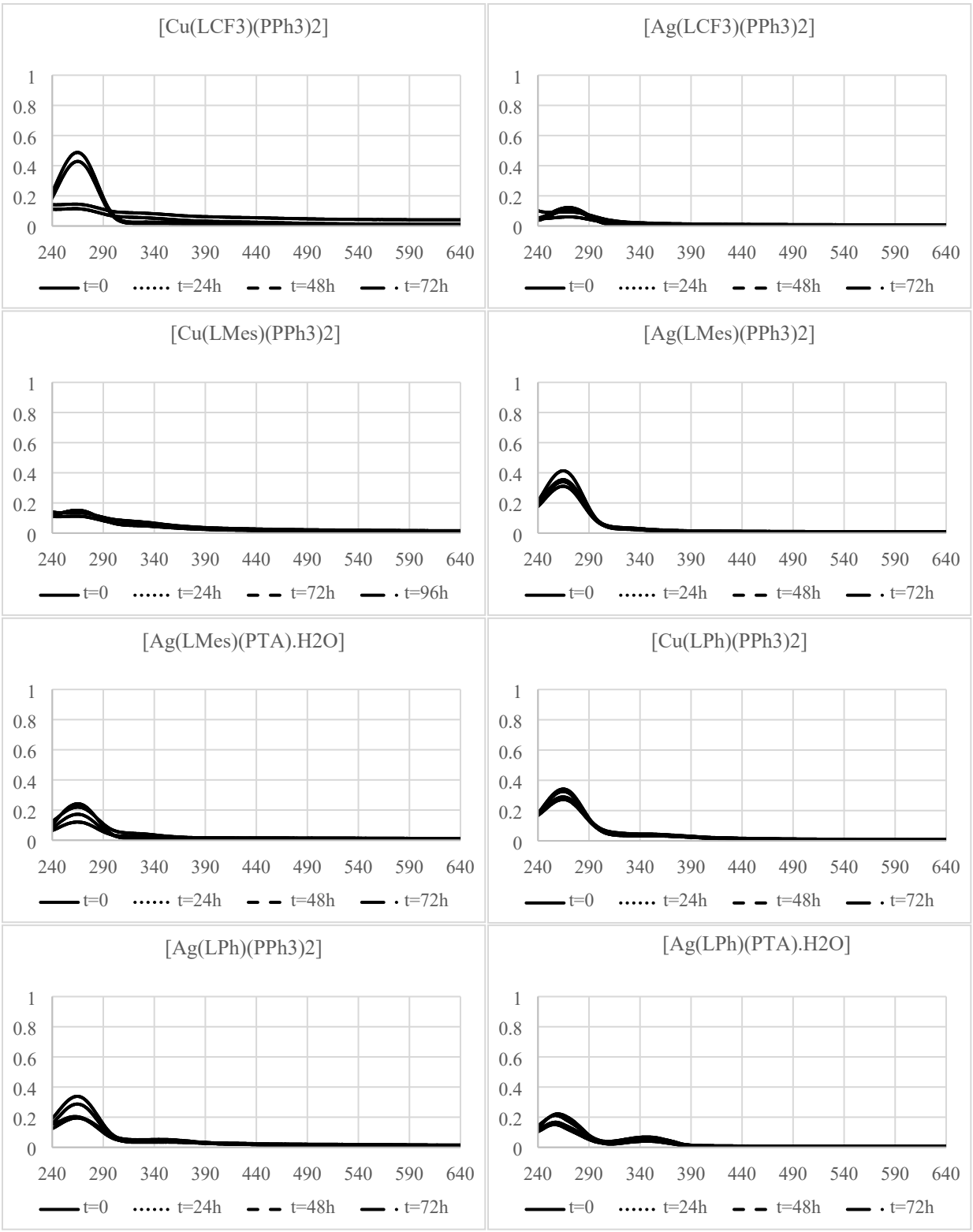

Figure S3. Stability studies. All complexes were dissolved at 50 μM in 0.5% DMSO/ physiological solution. UV-Visible spectra were recorded at t = 0 min, t = 24 h, t = 48 h and t = 72 h.

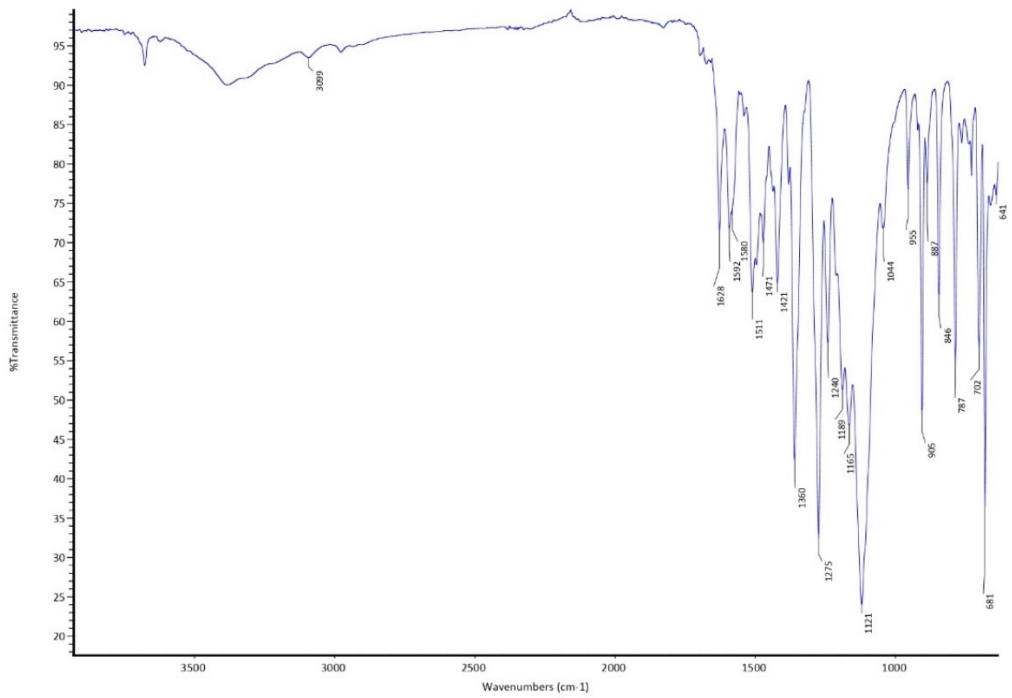

Figure S4. FT-IR spectrum of NaL^{CF3} (**1**).

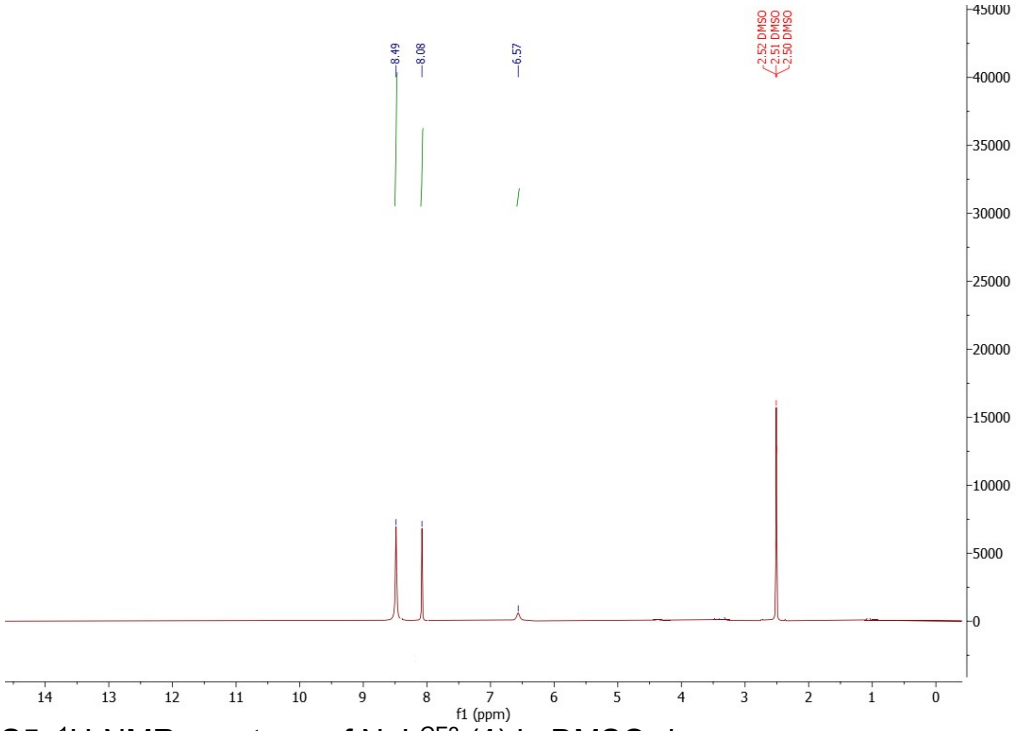

Figure S5. ^{1}H-NMR spectrum of NaL^{CF3} (**1**) in DMSO-d_6.

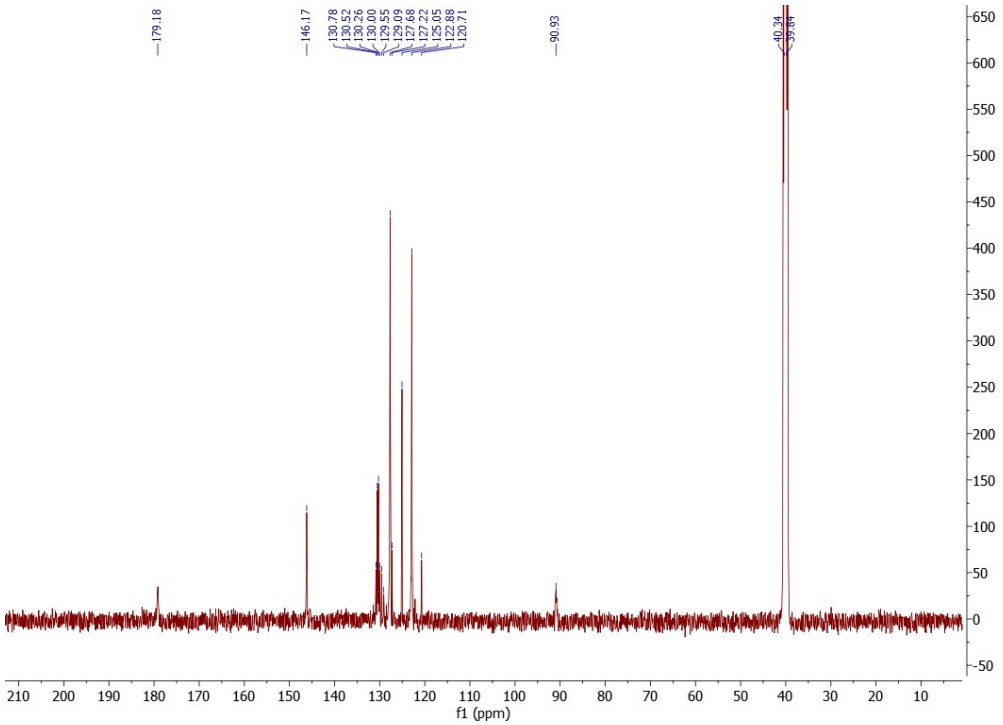

Figure S6. $^{13}C\{^{1}H\}$-NMR spectrum of NaL^{CF3} (**1**) in DMSO-d_6.

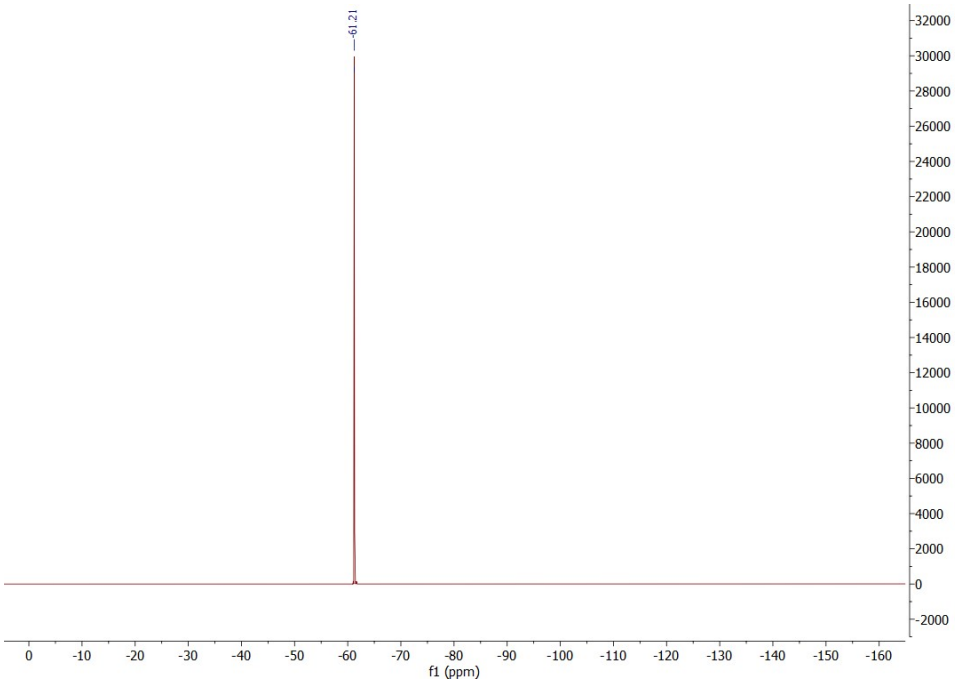

Figure S7. $^{19}F\{^{1}H\}$-NMR spectrum of NaL^{CF3} (**1**) in DMSO-d_6.

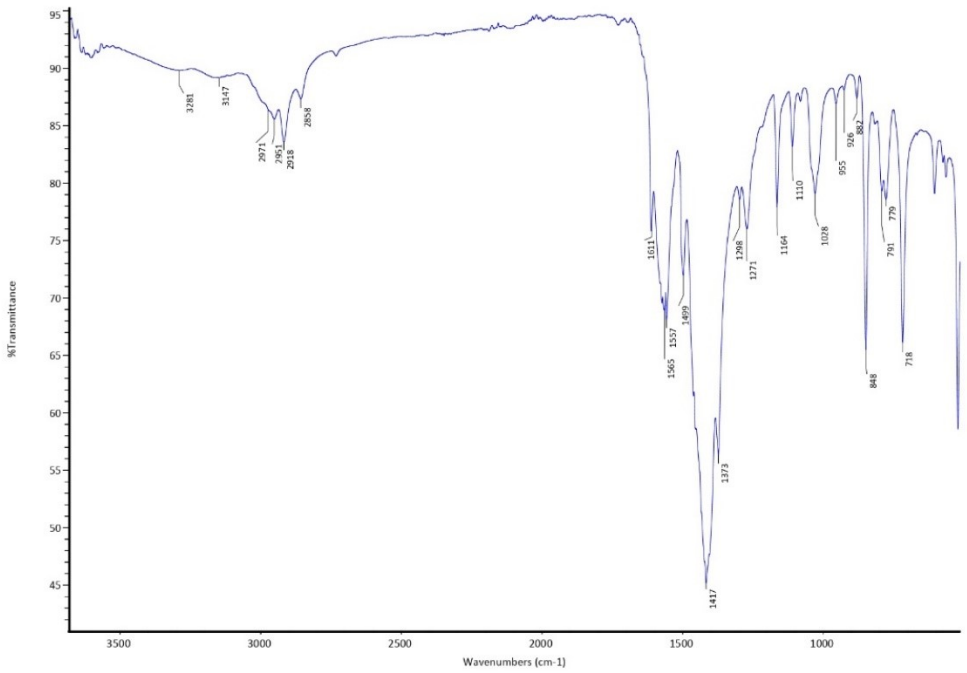

Figure S8. FT-IR spectrum of NaL^{Mes} (**2**).

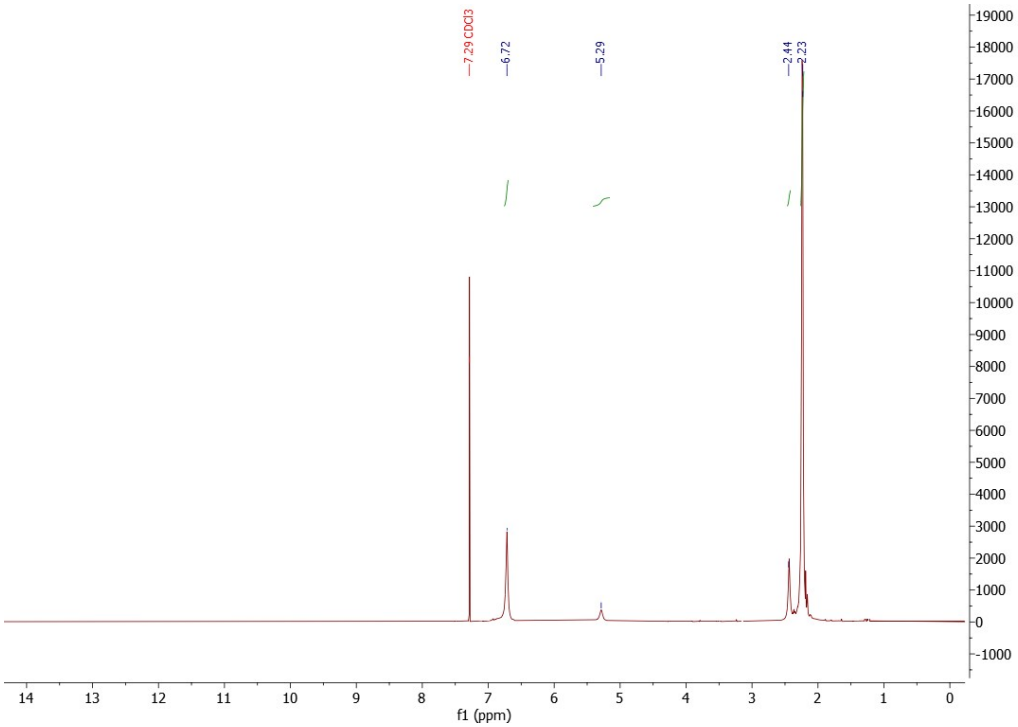

Figure S9. ^{1}H-NMR spectrum of NaL^{Mes} (**2**) in $CDCl_3$.

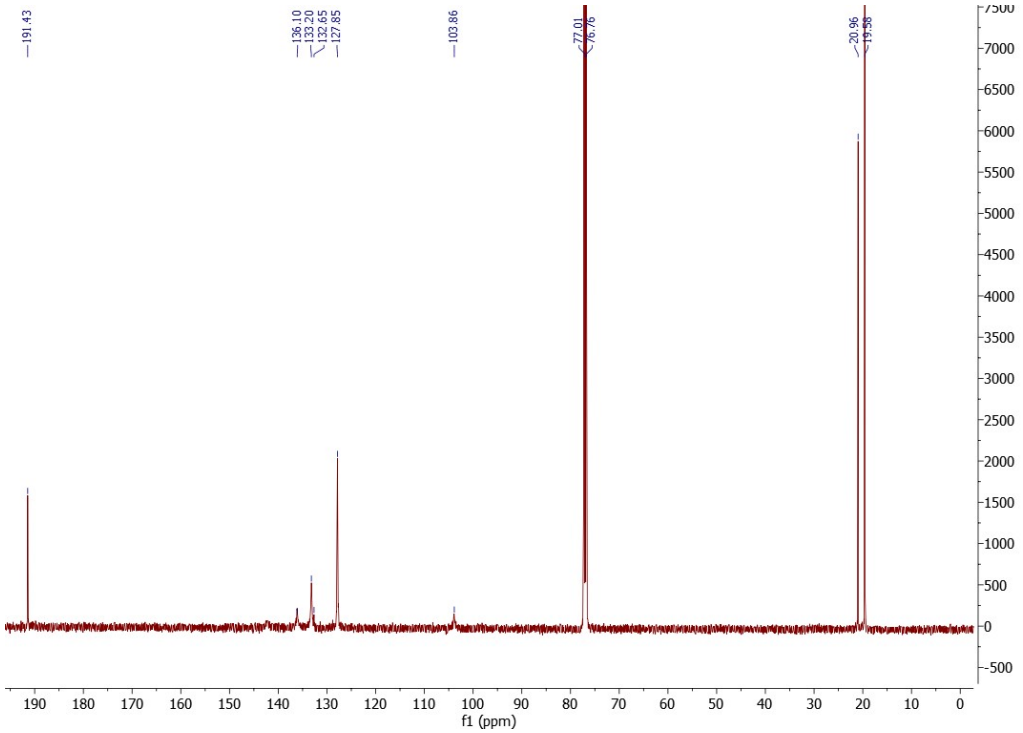

Figure S10. $^{13}C\{^{1}H\}$-NMR of NaL^{Mes} (**2**) in $CDCl_3$.

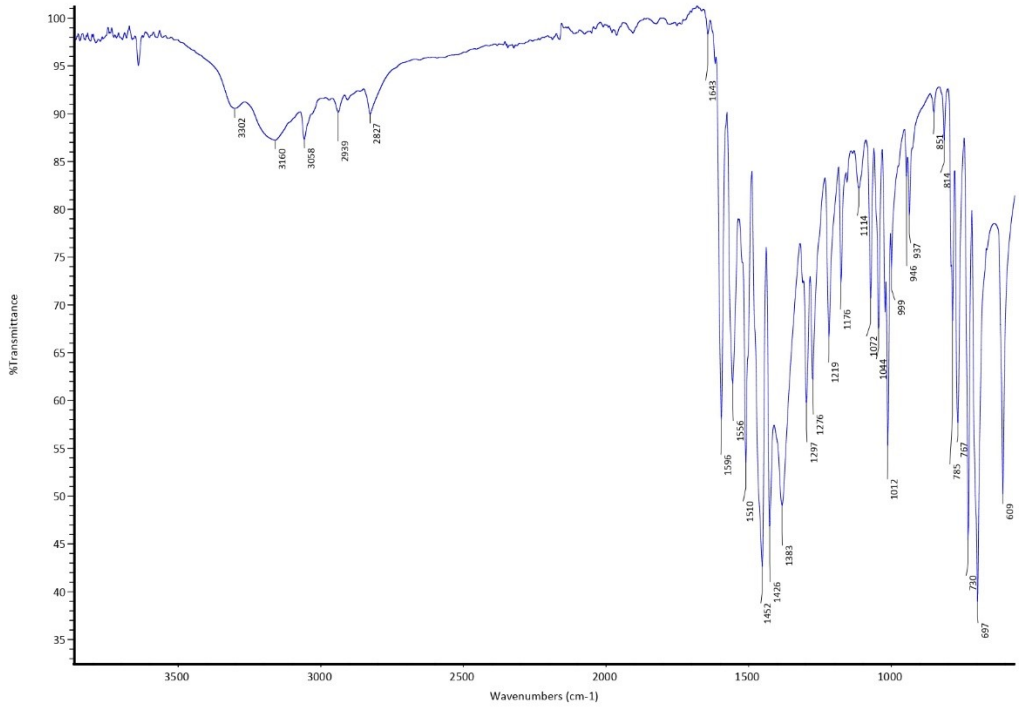

Figure S11. FT-IR spectrum of NaL^{Ph} (**3**).

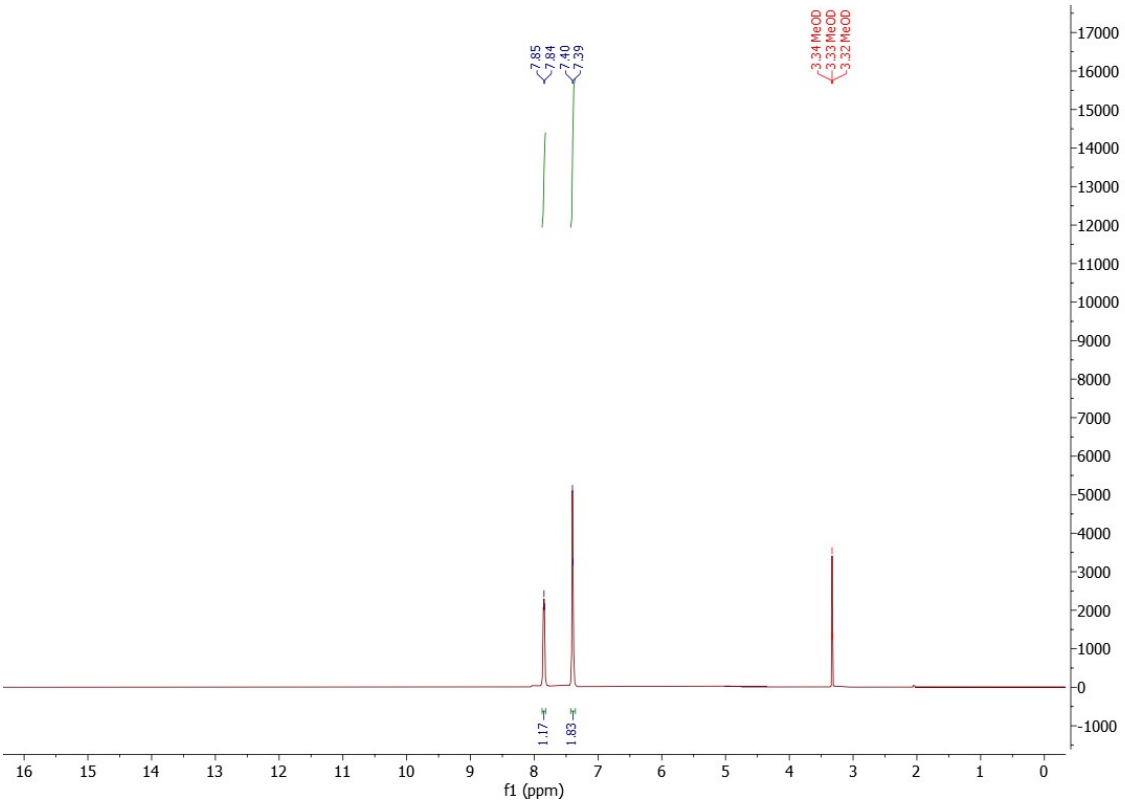

Figure S12. ^{1}H-NMR of NaL^{Ph} (**3**) in CD_3OD.

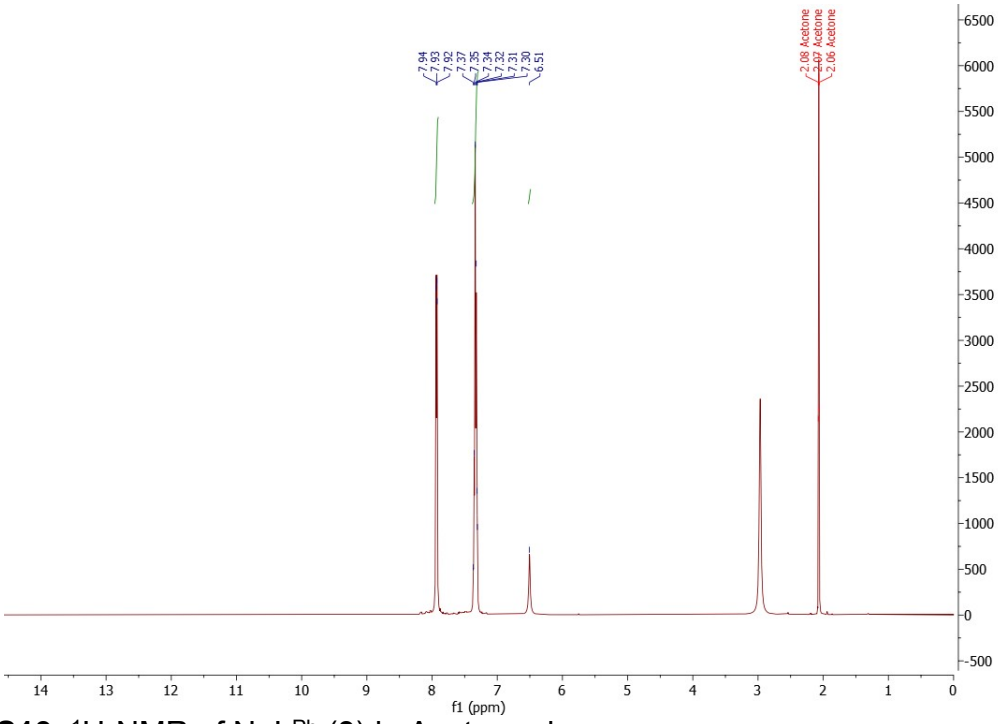

Figure S13. ^{1}H-NMR of NaL^{Ph} (**3**) in Acetone-d_6.

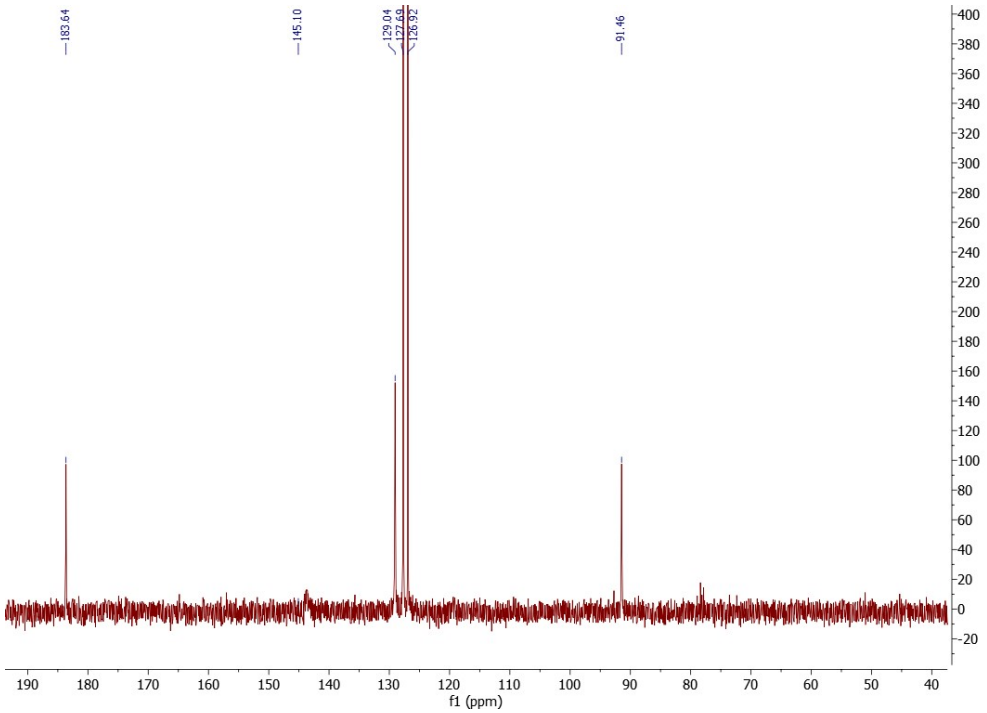

Figure S14. $^{13}C\{^{1}H\}$-NMR of NaL^{Ph} (**3**) in Acetone-d_6.

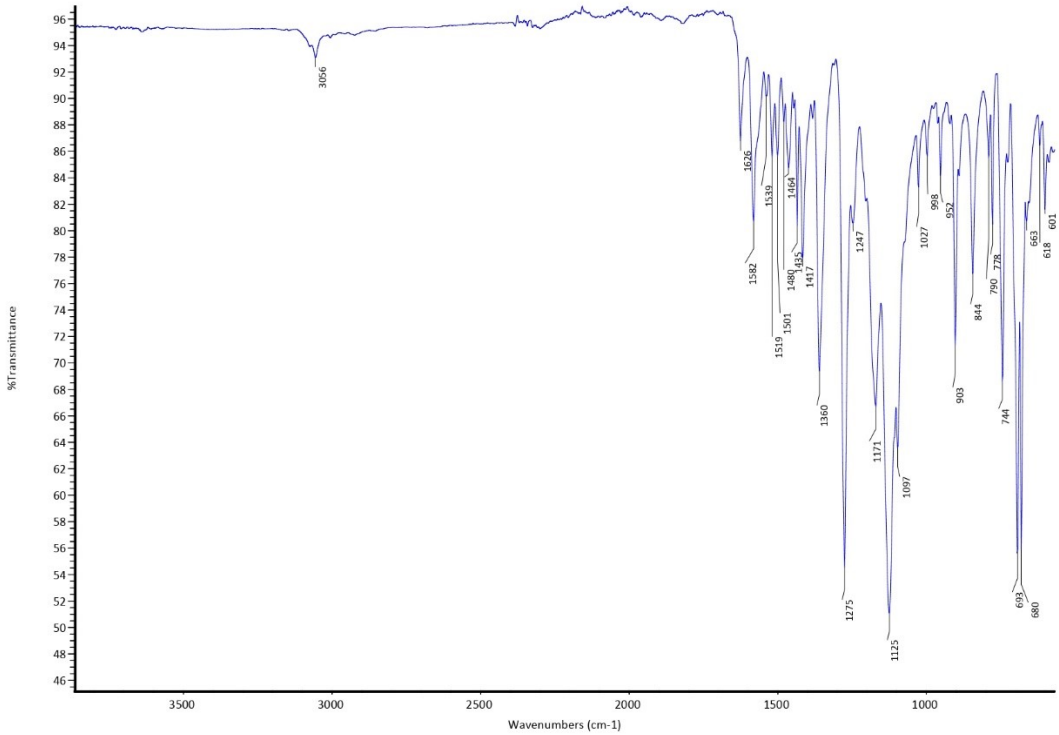

Figure S15. FT-IR spectrum of $[Cu(L^{CF3})(PPh_3)_2]$ (**4**).

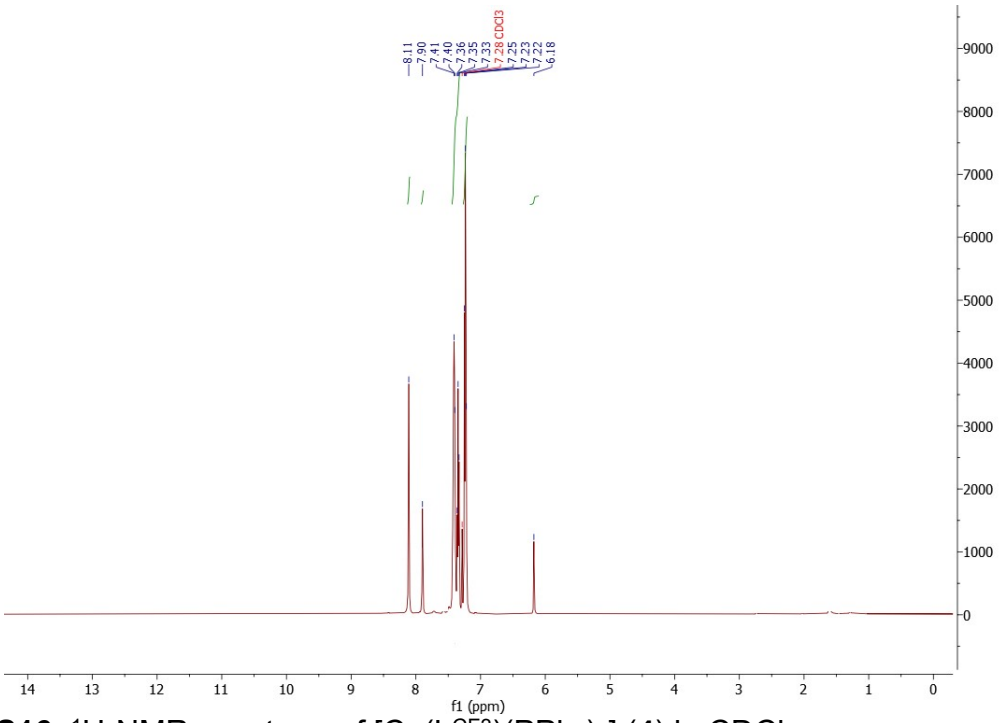

Figure S16. ^{1}H-NMR spectrum of [Cu(L^{CF3})(PPh_3)$_2$] (**4**) in $CDCl_3$.

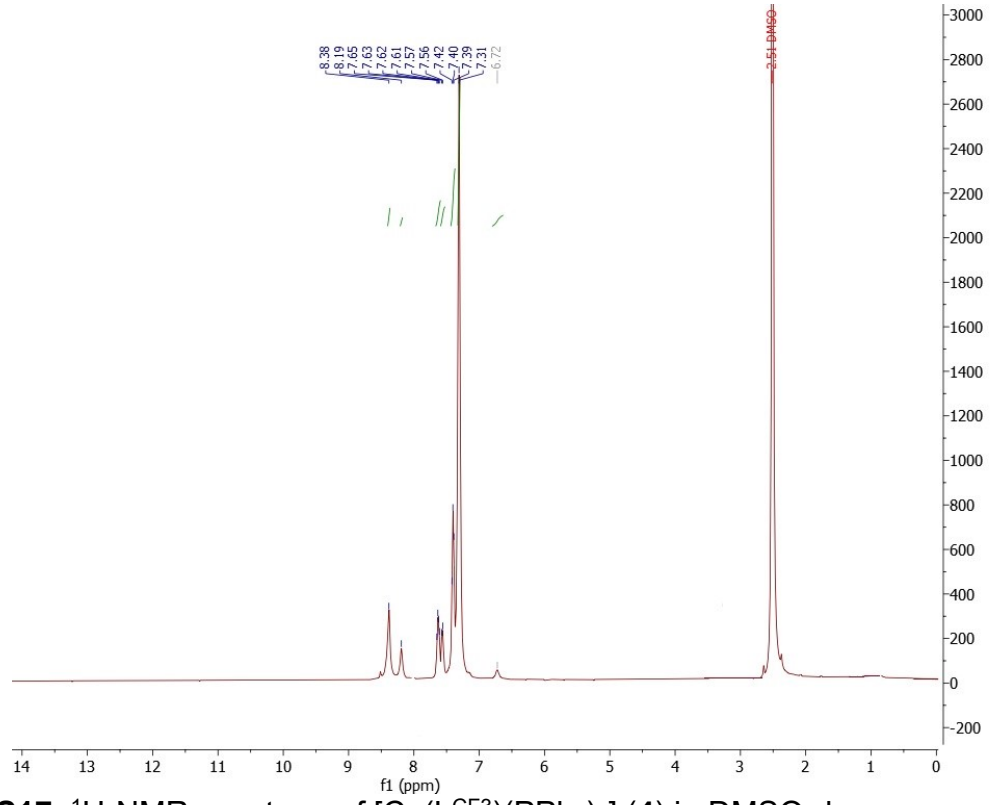

Figure S17. ^{1}H-NMR spectrum of [Cu(L^{CF3})(PPh_3)$_2$] (**4**) in DMSO-d_6

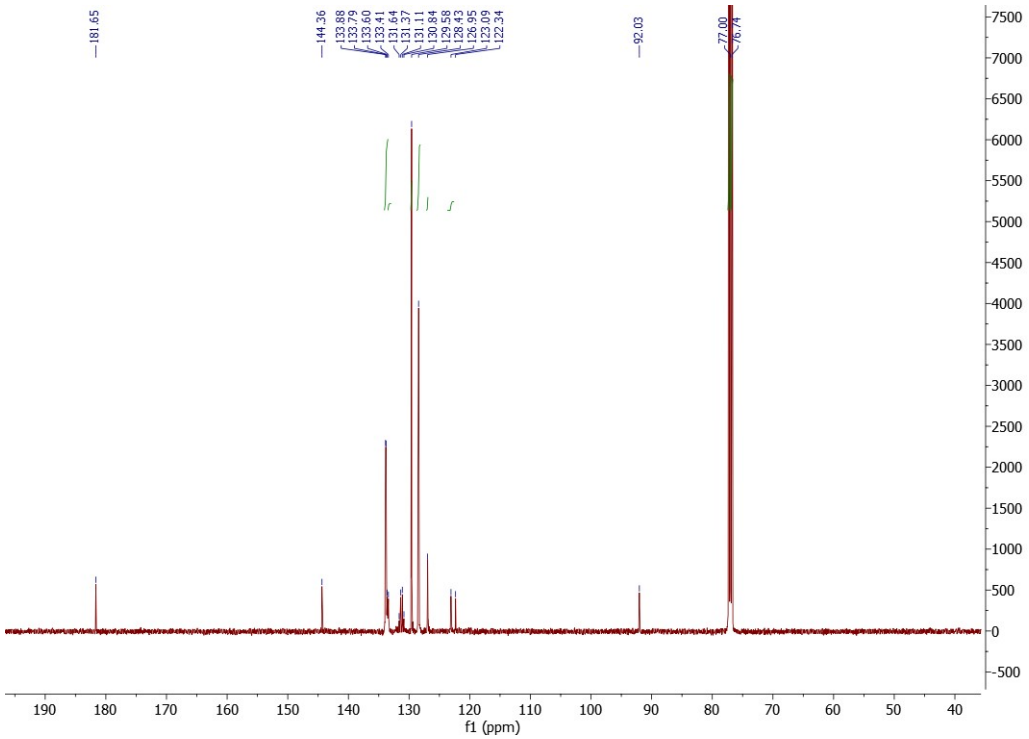

Figure S18. $^{13}C\{^{1}H\}$-NMR of $[Cu(L^{CF3})(PPh_3)_2]$ (**4**) in $CDCl_3$.

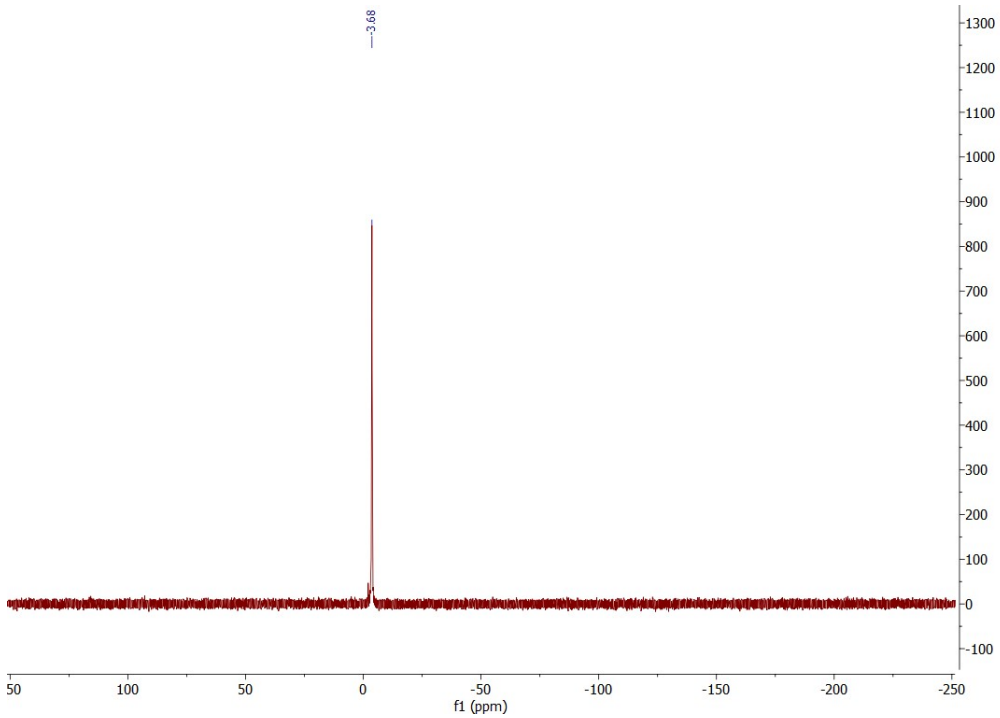

Figure S19. $^{31}P\{^{1}H\}$-NMR spectrum of $[Cu(L^{CF3})(PPh_3)_2]$ (**4**) in $CDCl_3$ at 223 K.

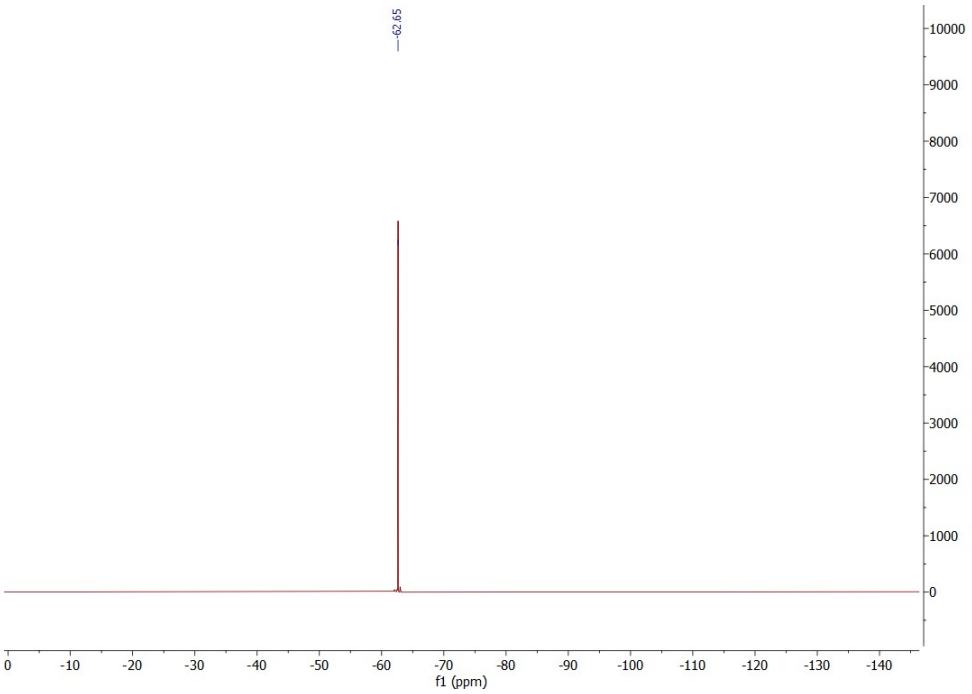

Figure S20. $^{19}F\{^{1}H\}$-NMR spectrum of $[Cu(L^{CF3})(PPh_3)_2]$ (**4**) in $CDCl_3$.

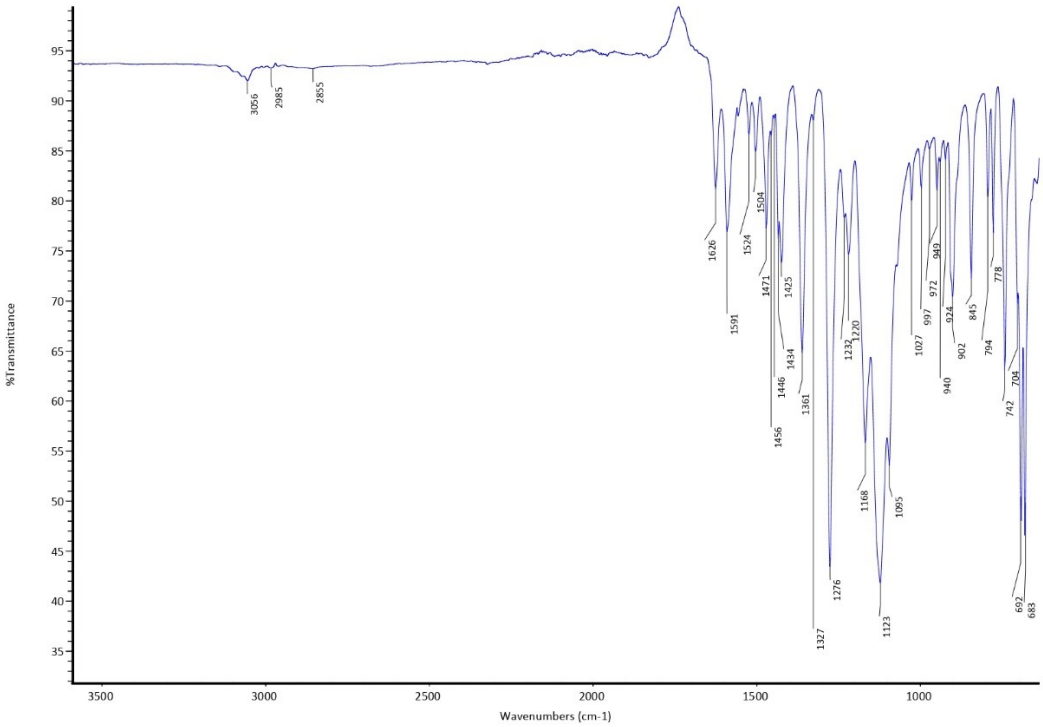

Figure S21. FT-IR spectrum of $[Ag(L^{CF3})(PPh_3)_2]$ (**5**).

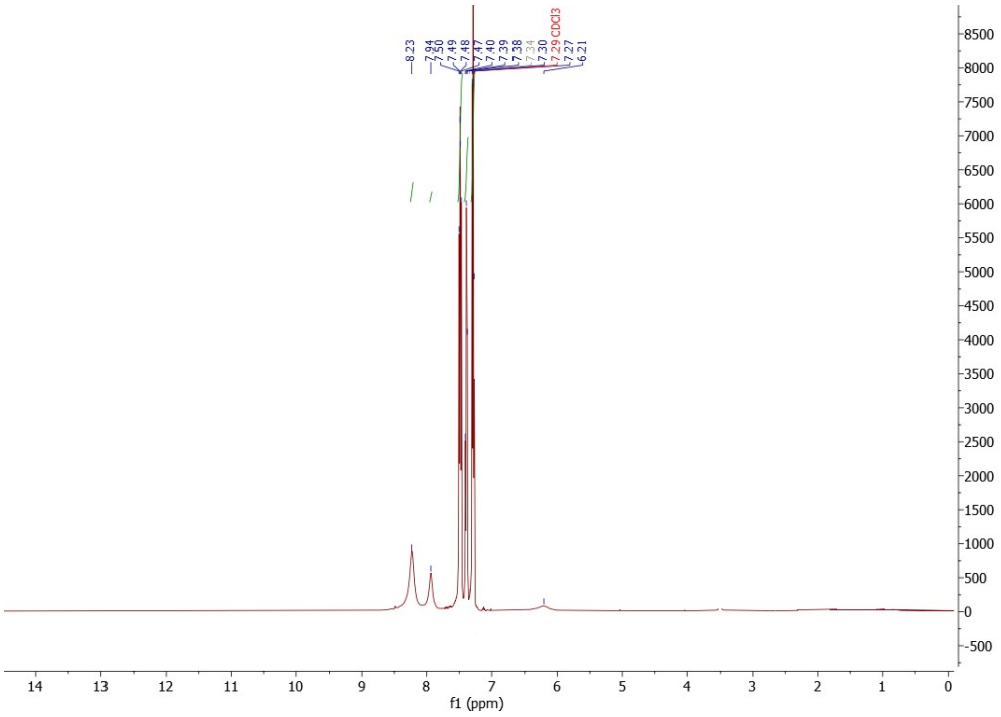

Figure S22. ^{1}H-NMR spectrum of [Ag(L^{CF3})(PPh_3)$_2$] (**5**) in $CDCl_3$.

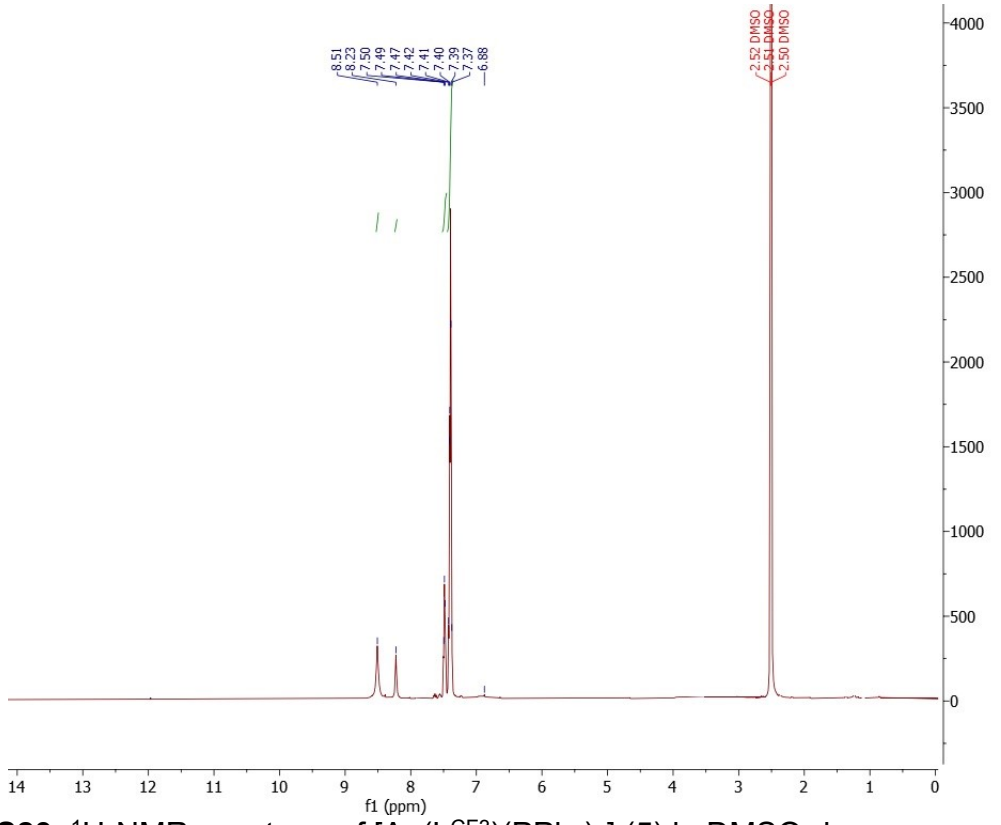

Figure S23. ^{1}H-NMR spectrum of [Ag(L^{CF3})(PPh_3)$_2$] (**5**) in DMSO-d_6.

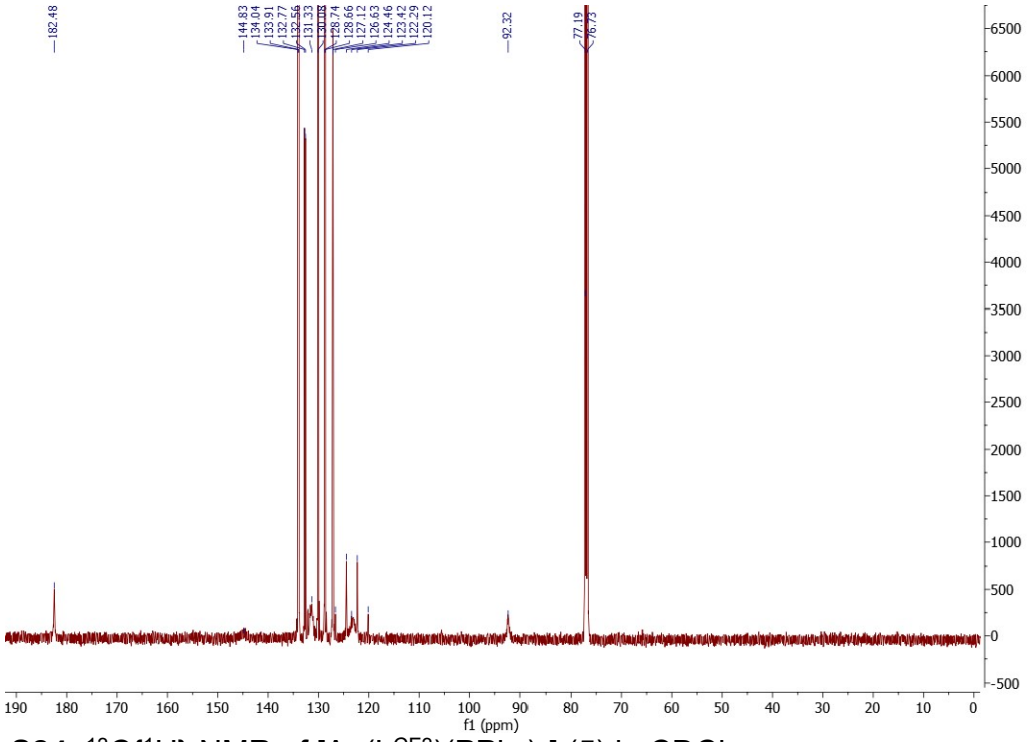

Figure S24. $^{13}C\{^{1}H\}$-NMR of $[Ag(L^{CF3})(PPh_3)_2]$ (**5**) in $CDCl_3$.

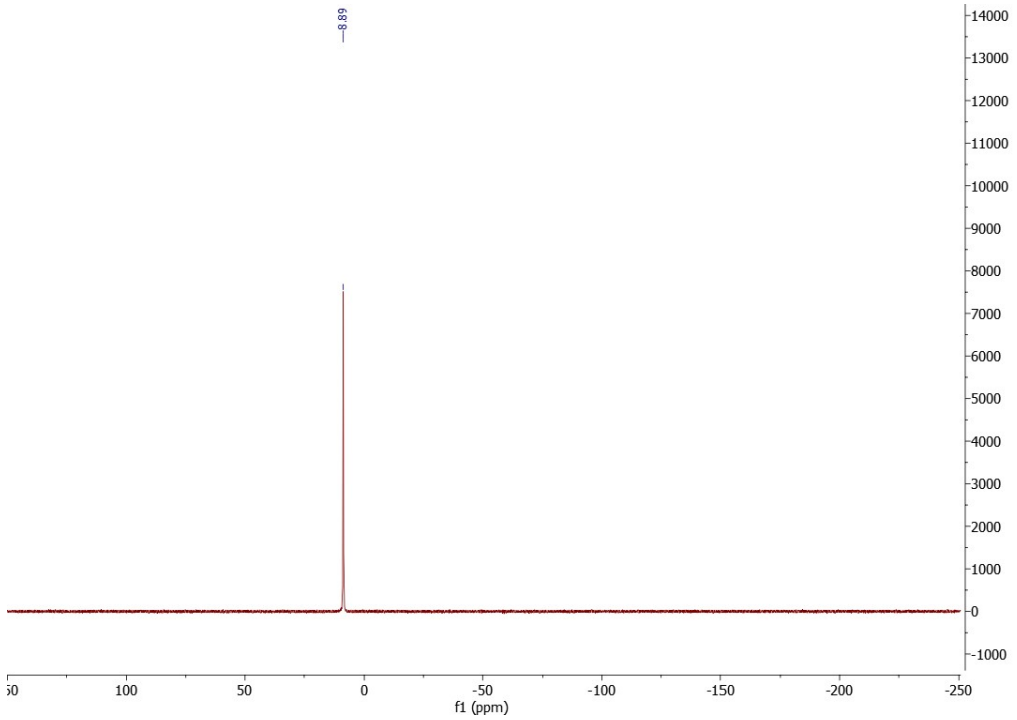

Figure S25. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{CF3})(PPh_3)_2]$ (**5**) in $CDCl_3$.

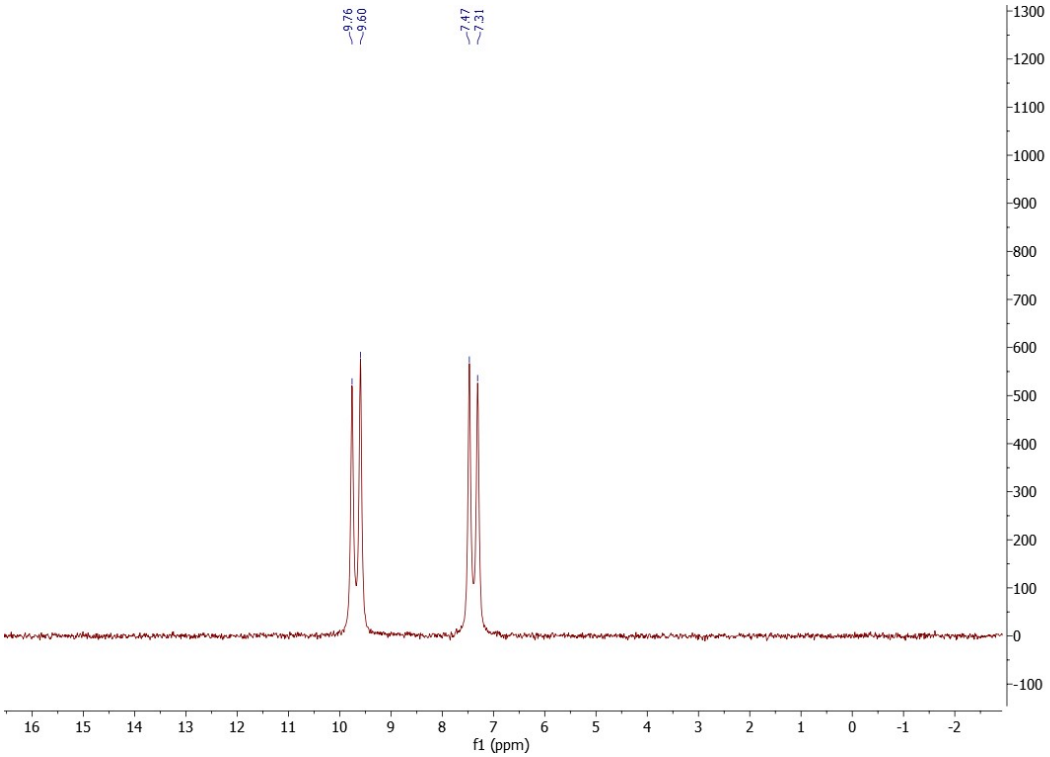

Figure S26. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{CF3})(PPh_3)_2]$ (**5**) in $CDCl_3$ at 223K.

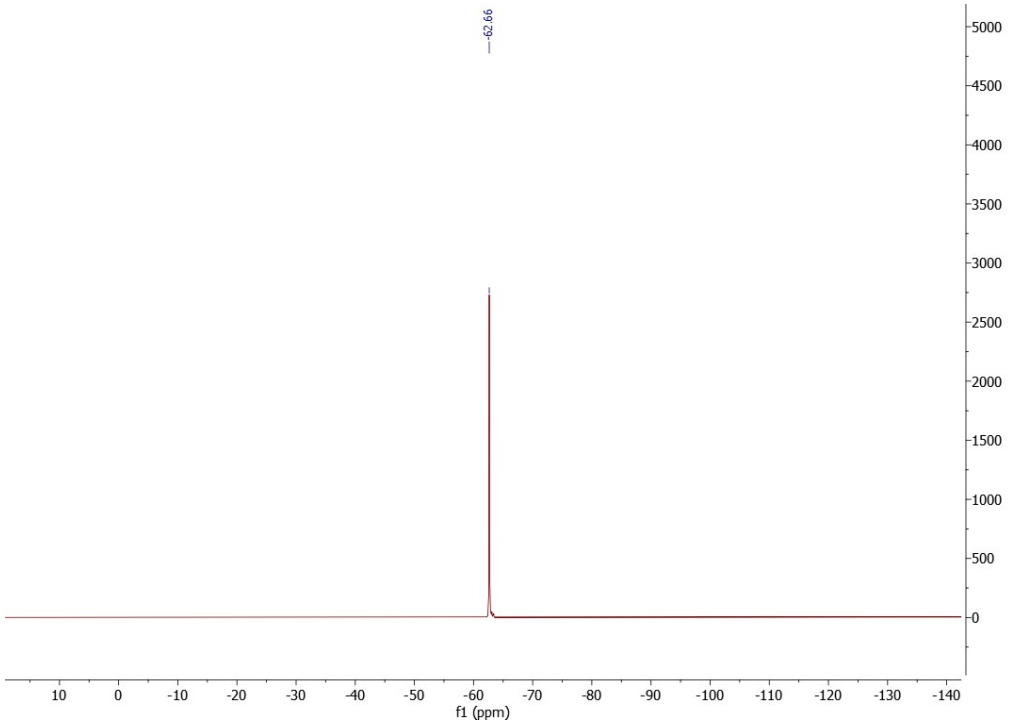

Figure S27. $^{19}F\{^{1}H\}$-NMR spectrum of $[Ag(L^{CF3})(PPh_3)_2]$ (**5**) in $CDCl_3$.

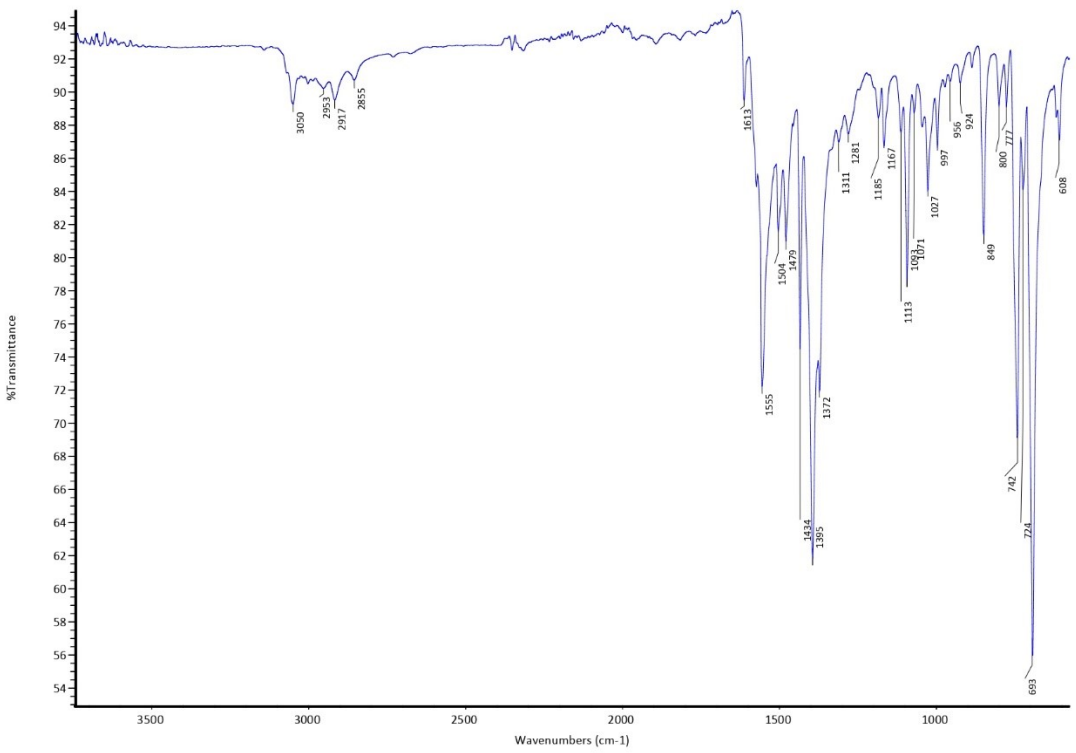

Figure S28. FT-IR spectrum of [Cu(L^{Mes})(PPh_3)$_2$] (**6**).

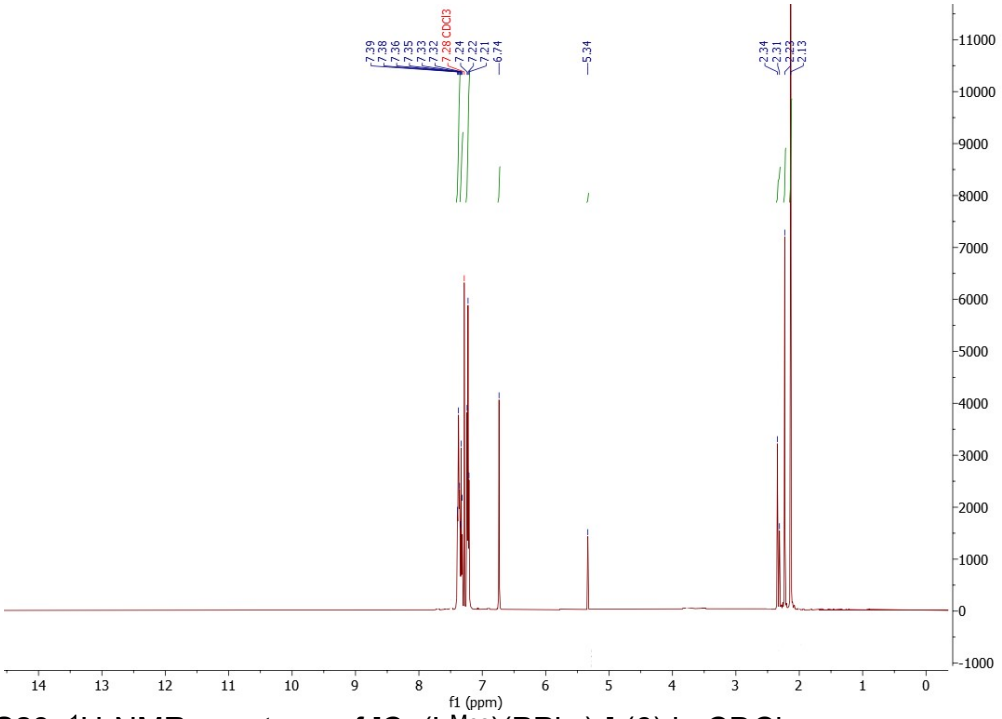

Figure S29. ^{1}H-NMR spectrum of [Cu(L^{Mes})(PPh_3)$_2$] (**6**) in $CDCl_3$.

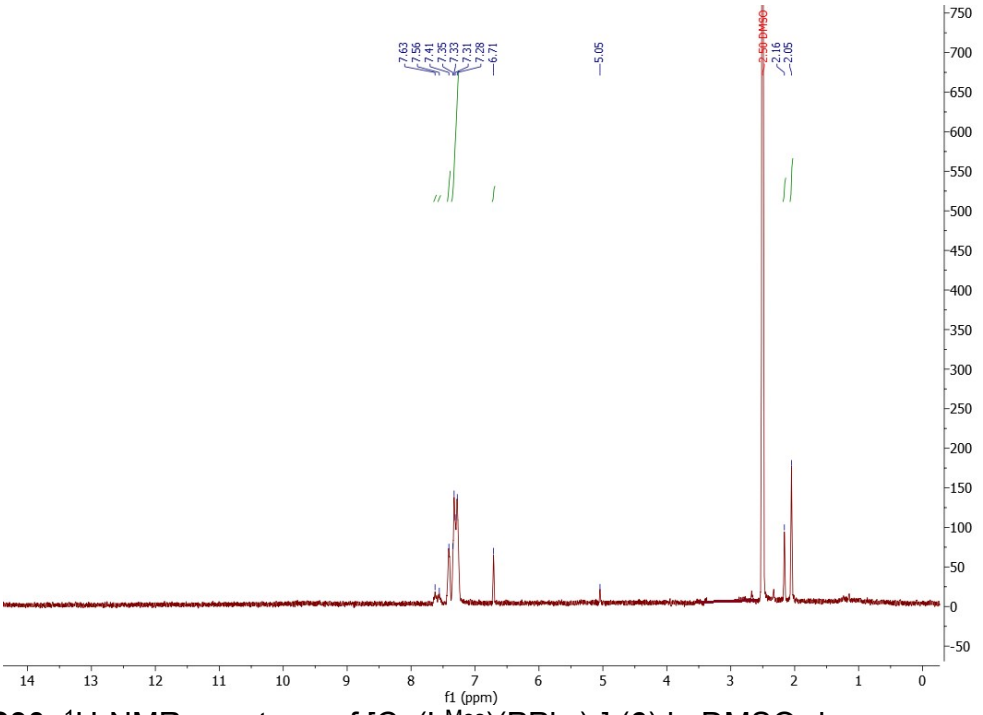

Figure S30. ^{1}H-NMR spectrum of [Cu(L^{Mes})(PPh_3)$_2$] (**6**) in DMSO-d_6.

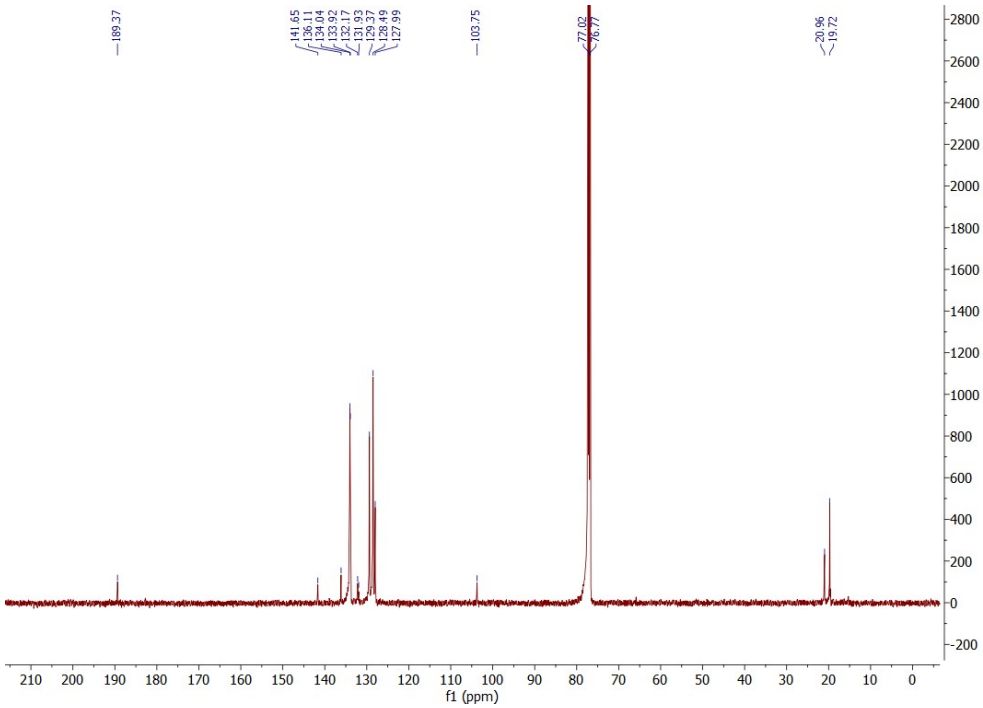

Figure S31. ^{13}C{^{1}H}-NMR of [Cu(L^{Mes})(PPh_3)$_2$] (**6**) in $CDCl_3$.

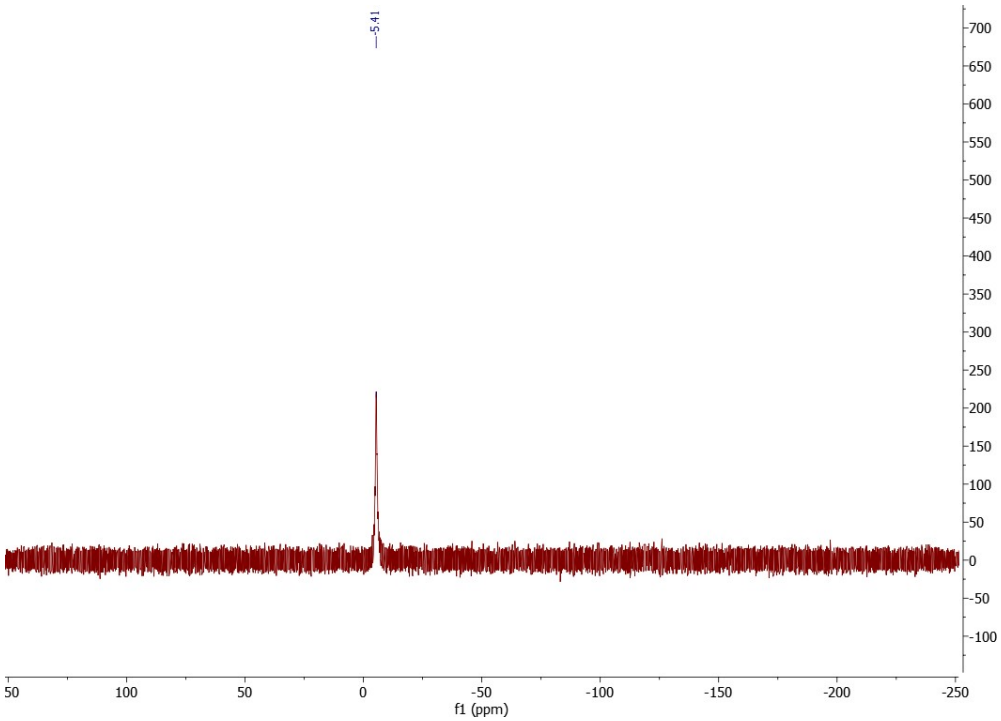

Figure S32. $^{31}P\{^{1}H\}$-NMR spectrum of $[Cu(L^{Mes})(PPh_3)_2]$ (**6**) in CD_2Cl_2.

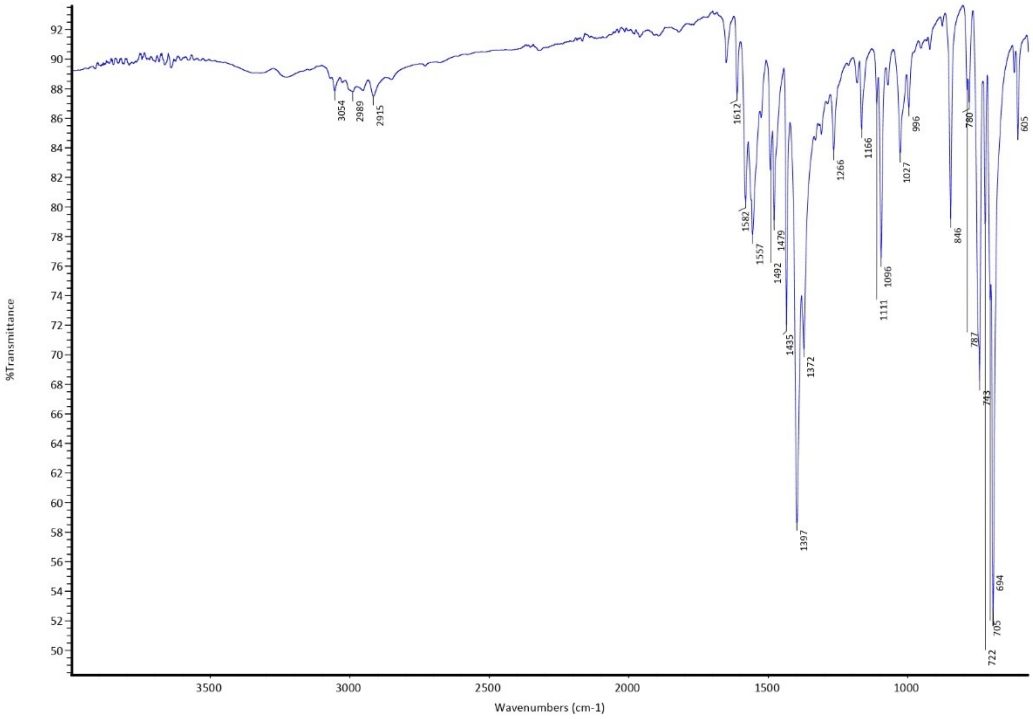

Figure S33. FT-IR spectrum of $[Ag(L^{Mes})(PPh_3)_2]$ (**7**).

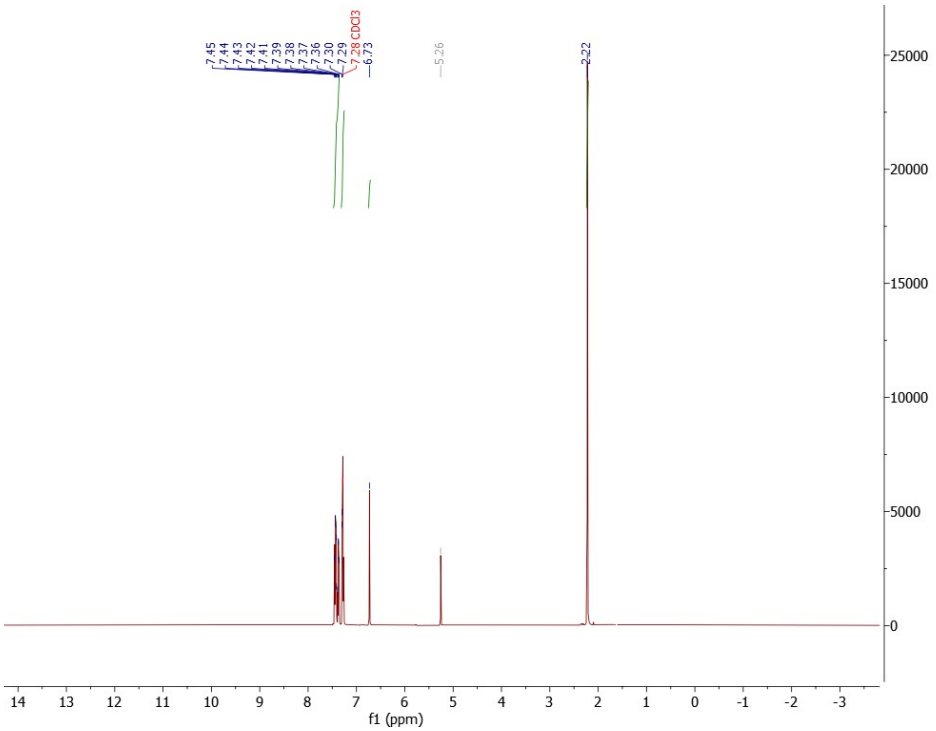

Figure S34. ^{1}H-NMR spectrum of [Ag(L^{Mes})(PPh_3)$_2$] (**7**) in $CDCl_3$.

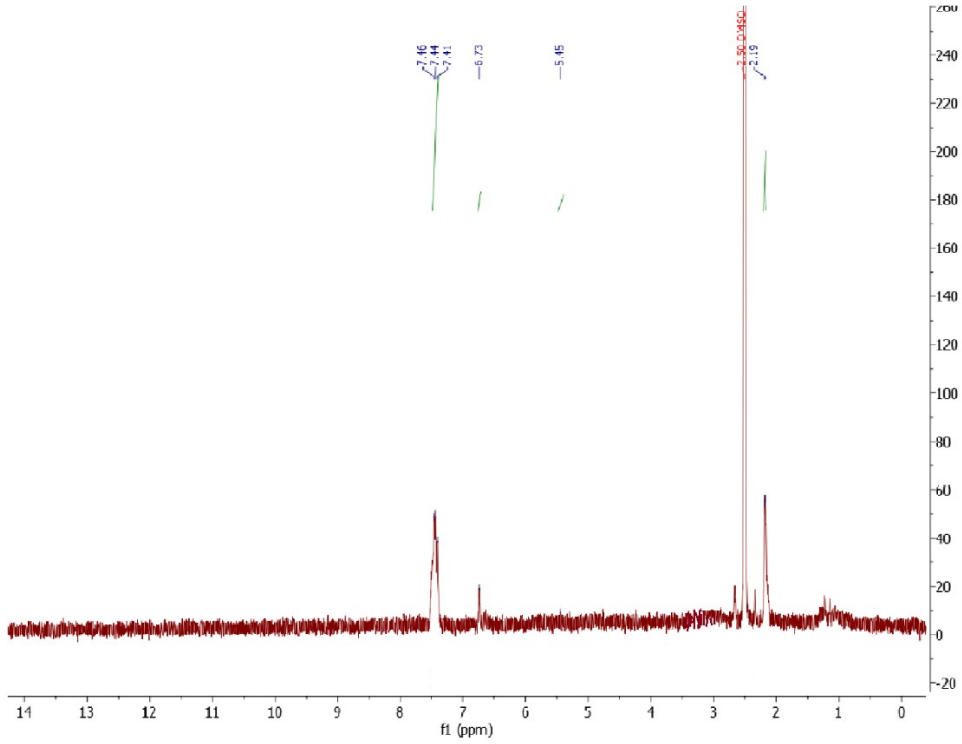

Figure S35. ^{1}H-NMR spectrum of [Ag(L^{Mes})(PPh_3)$_2$] (**7**) in DMSO-d_6.

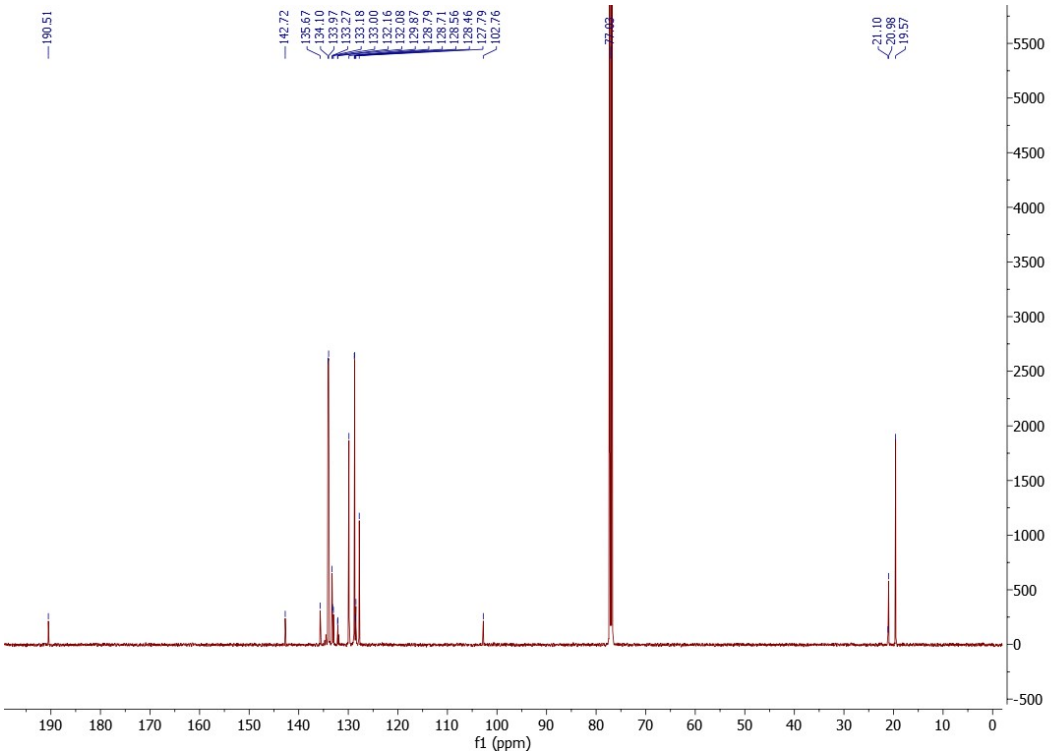

Figure S36. $^{13}C\{^{1}H\}$-NMR of $[Ag(L^{Mes})(PPh_3)_2]$ (**7**) in $CDCl_3$.

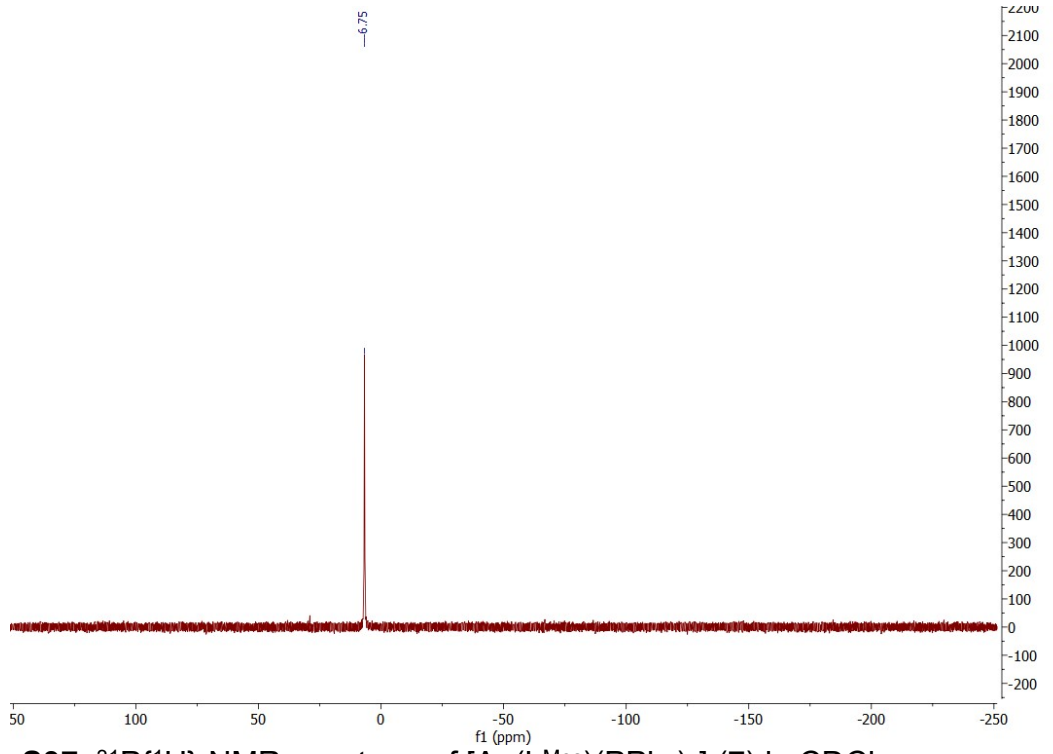

Figure S37. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{Mes})(PPh_3)_2]$ (**7**) in $CDCl_3$.

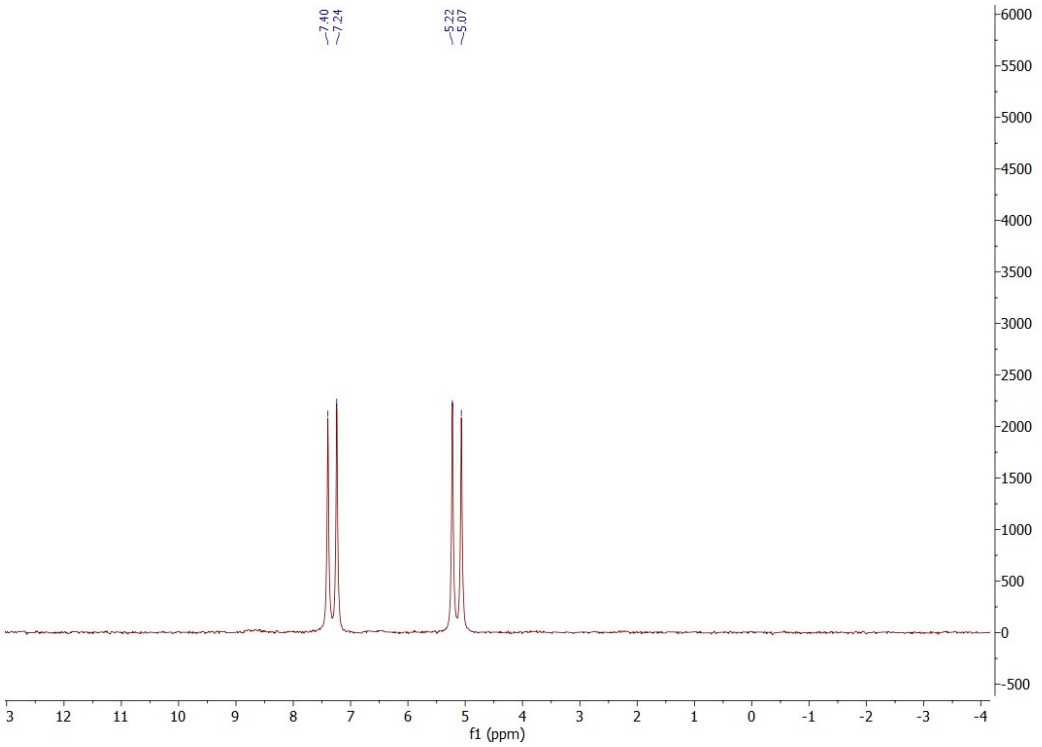

Figure S38. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{Mes})(PPh_3)_2]$ (**7**) in $CDCl_3$ at 223K.

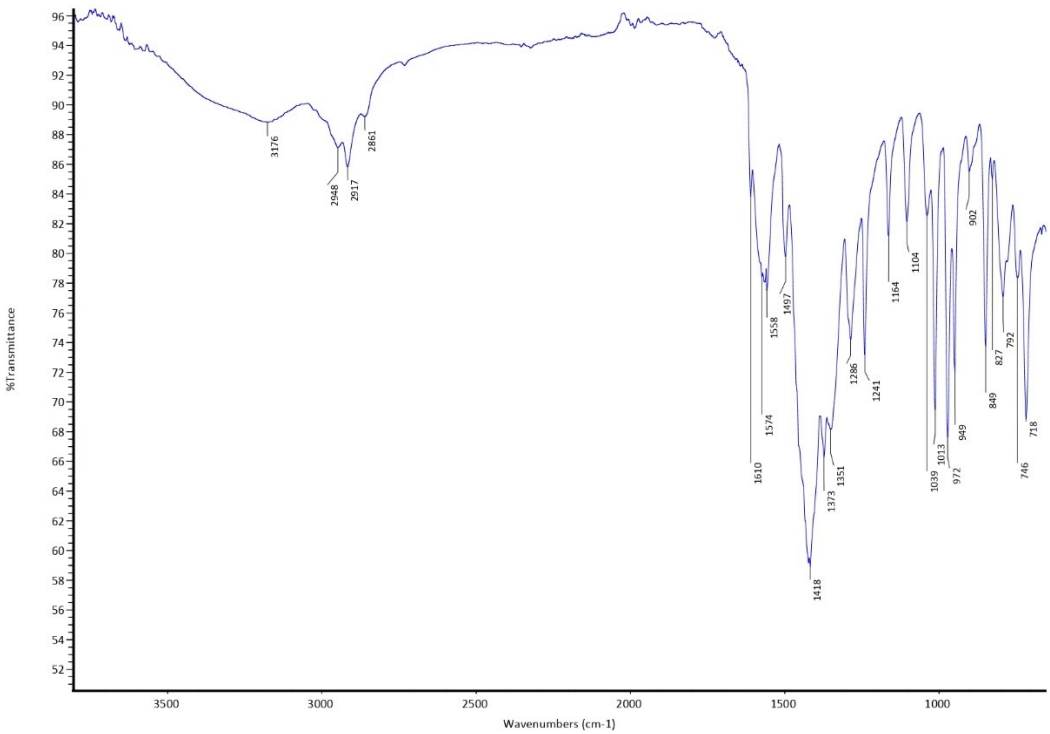

Figure S39. FT-IR spectrum of $[Ag(L^{Mes})(PTA)]$ (**8**).

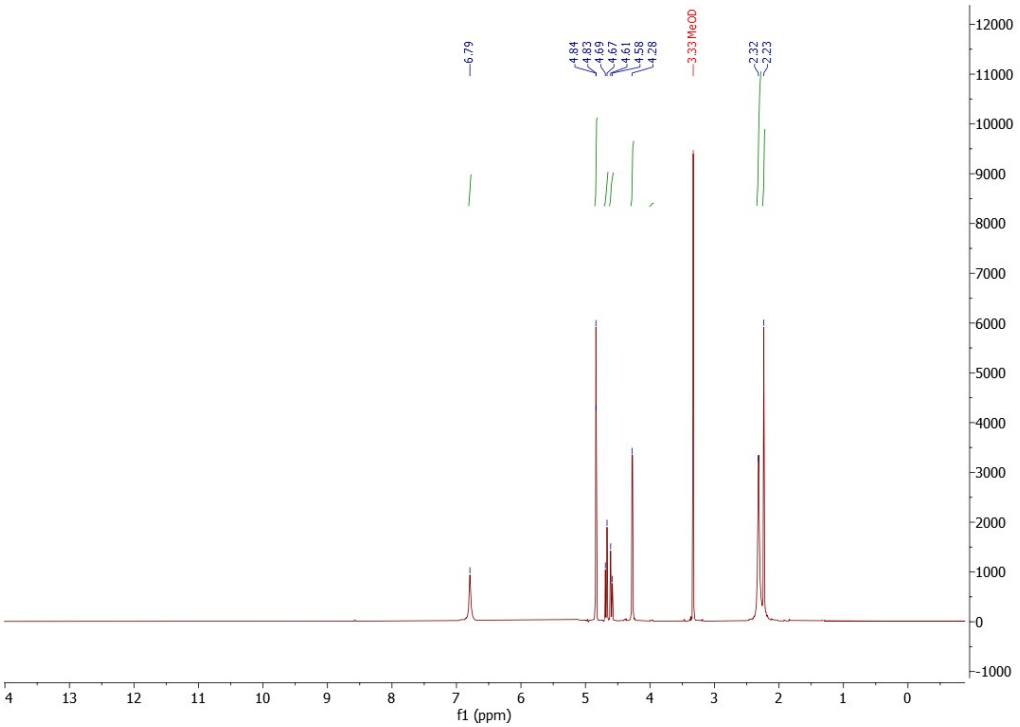

Figure S40. ^{1}H-NMR spectrum of [Ag(L^{Mes})(PTA)] (**8**) in CD_3OD.

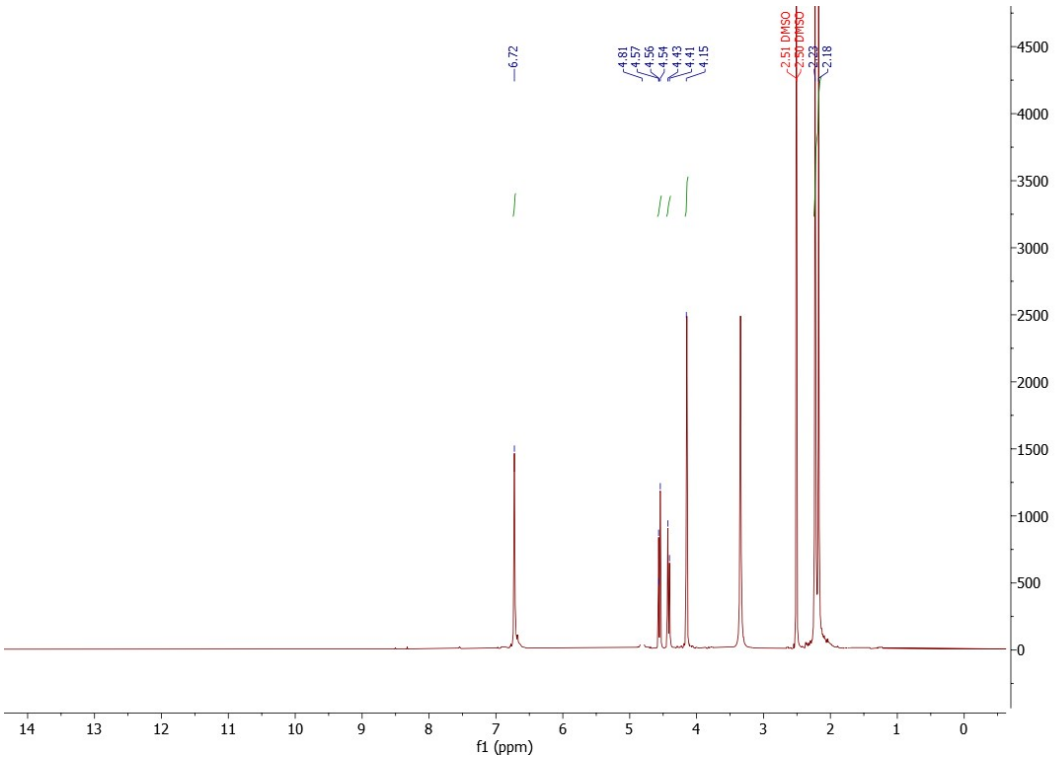

Figure S41. ^{1}H-NMR spectrum of [Ag(L^{Mes})(PTA)] (**8**) in DMSO-d_6.

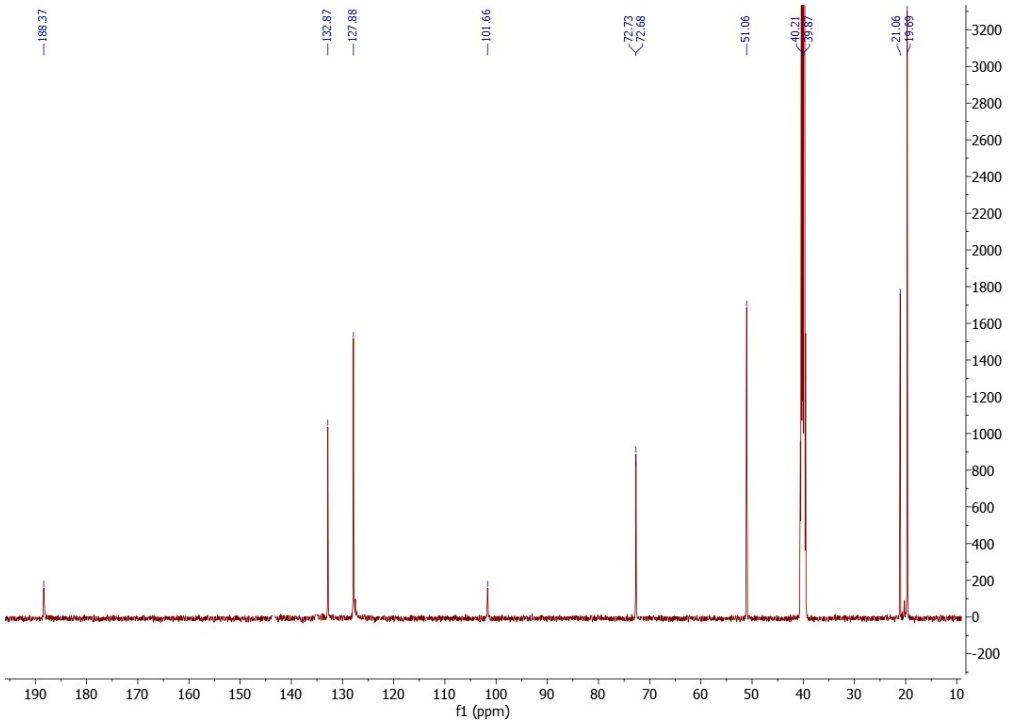

Figure S42. $^{13}C\{^{1}H\}$-NMR of [Ag(L^{Mes})(PTA)] (**8**) in DMSO-d_6.

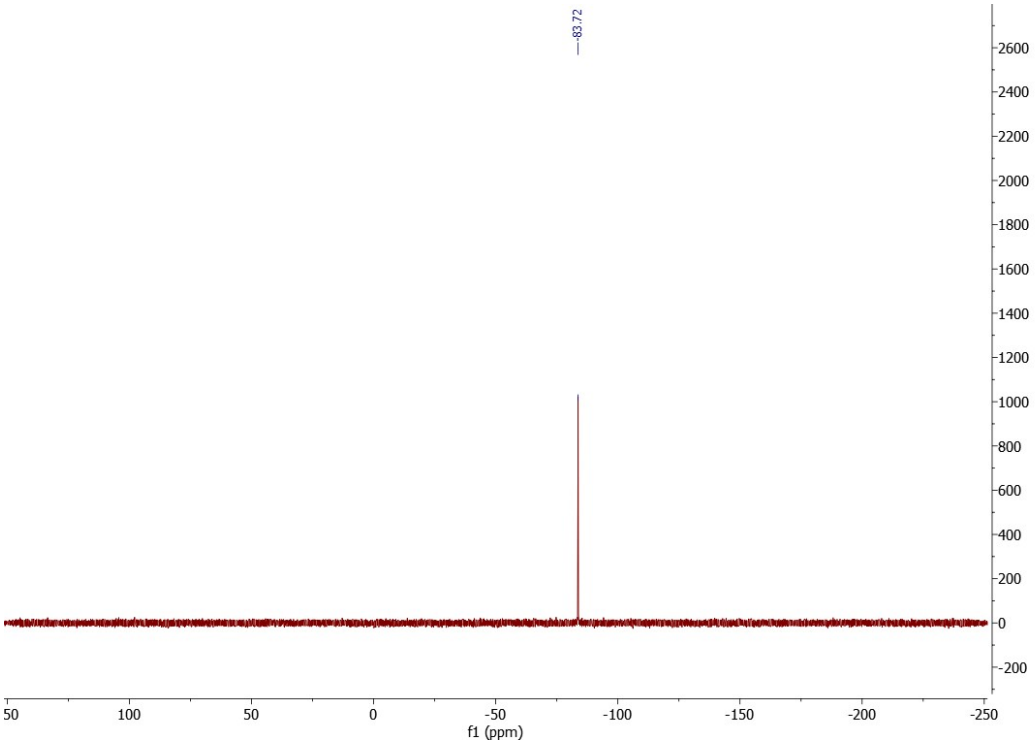

Figure S43. $^{31}P\{^{1}H\}$-NMR spectrum of [Ag(L^{Mes})(PTA)] (**8**) in CD_3OD.

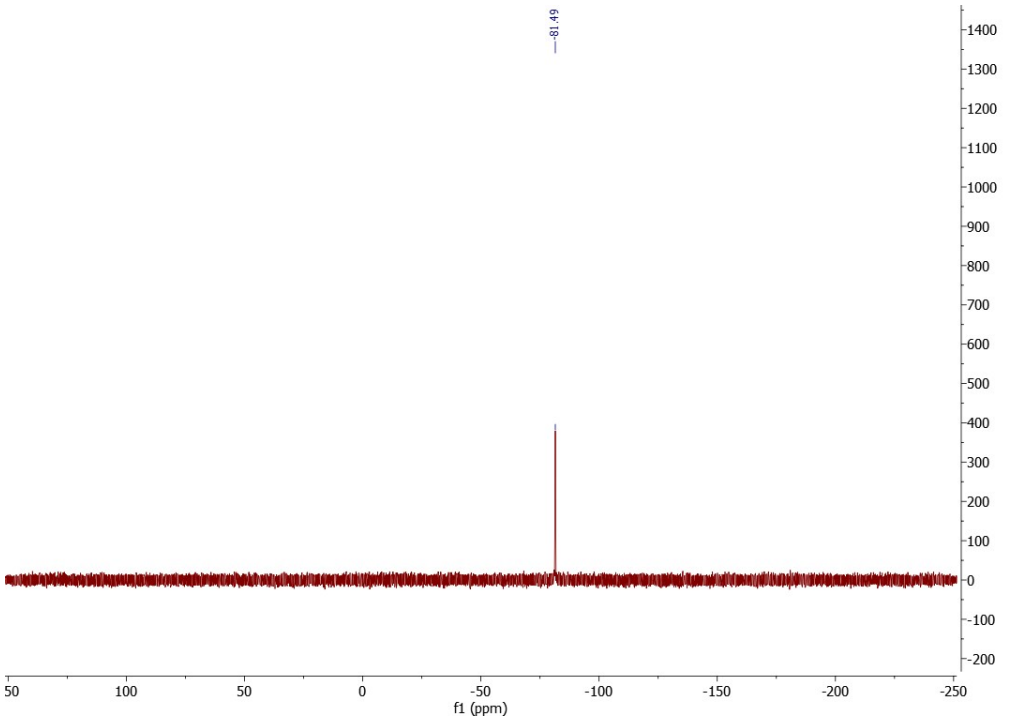

Figure S44. $^{31}P\{^{1}H\}$-NMR spectrum of [Ag(L^{Mes})(PTA)] (**8**) in D_2O.

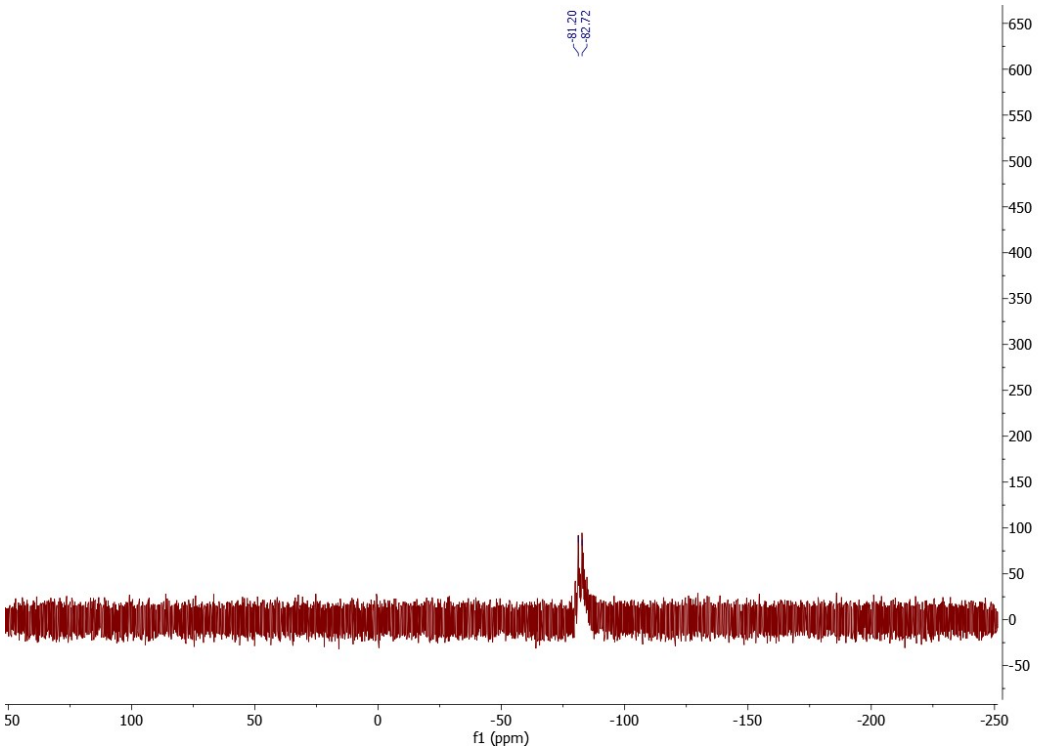

Figure S45. $^{31}P\{^{1}H\}$-NMR spectrum of [Ag(L^{Mes})(PTA)] (**8**) in CD_3OD at 223 K.

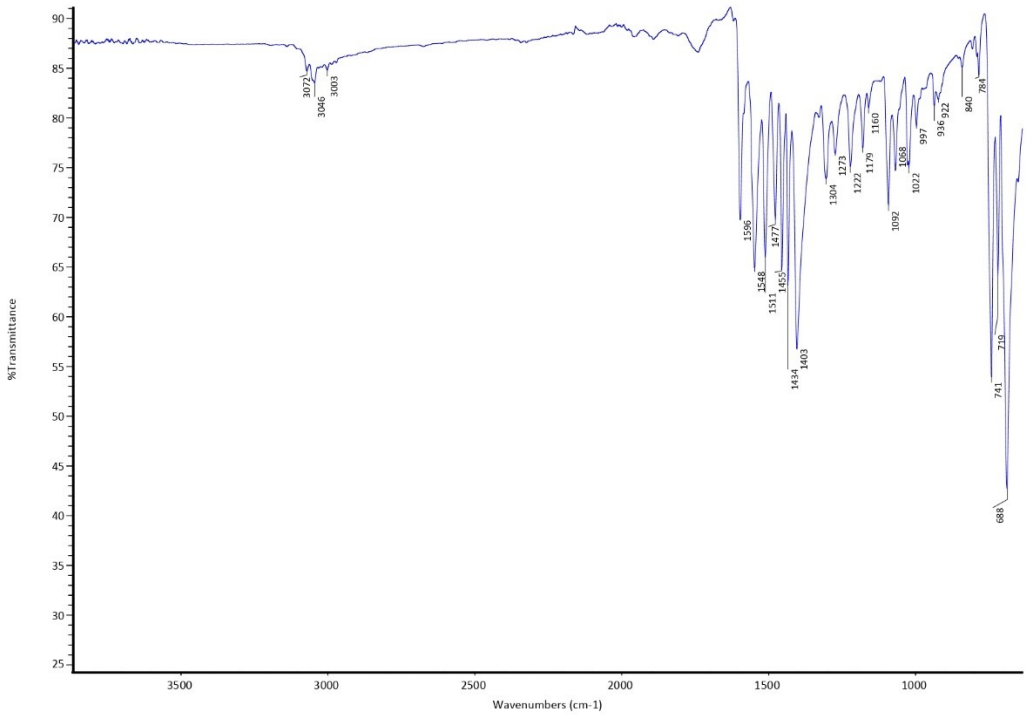

Figure S46. FT-IR spectrum of $[Cu(L^{Ph})(PPh_3)_2]$ (**9**).

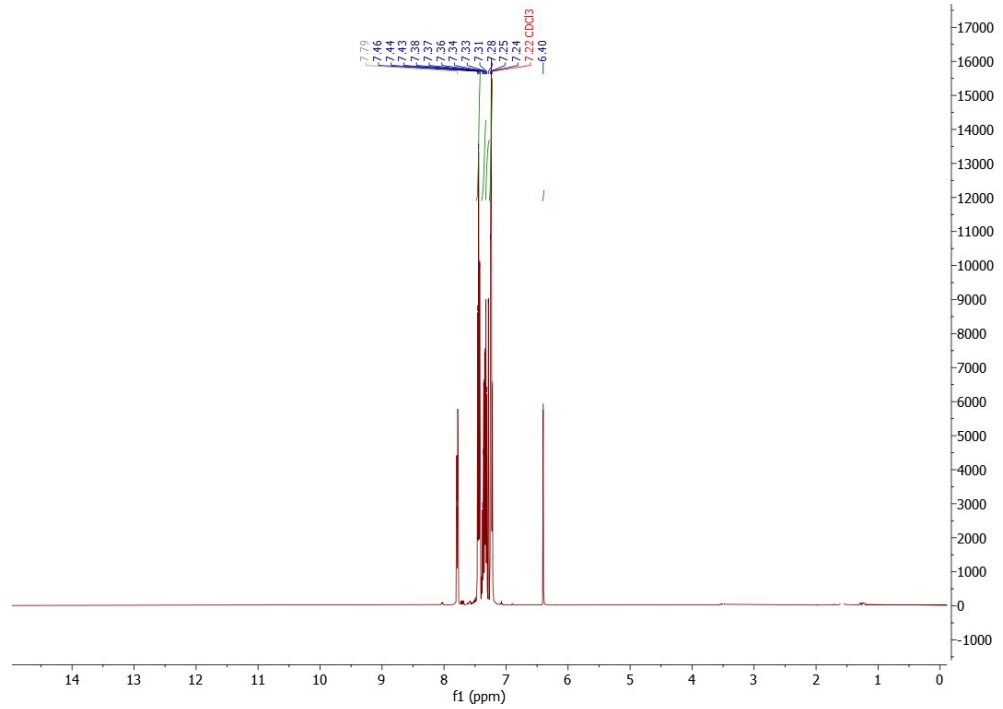

Figure S47. ^{1}H-NMR spectrum of $[Cu(L^{Ph})(PPh_3)_2]$ (**9**) in $CDCl_3$.

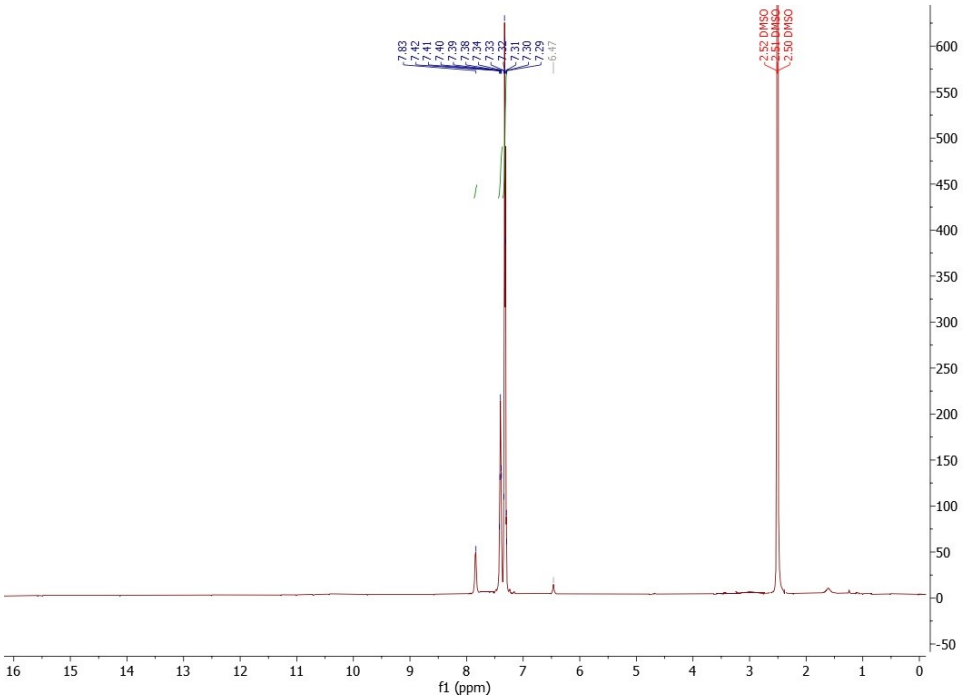

Figure S48. ^{1}H-NMR spectrum of [Cu(L^{Ph})(PPh_3)$_2$] (**9**) in DMSO-d_6.

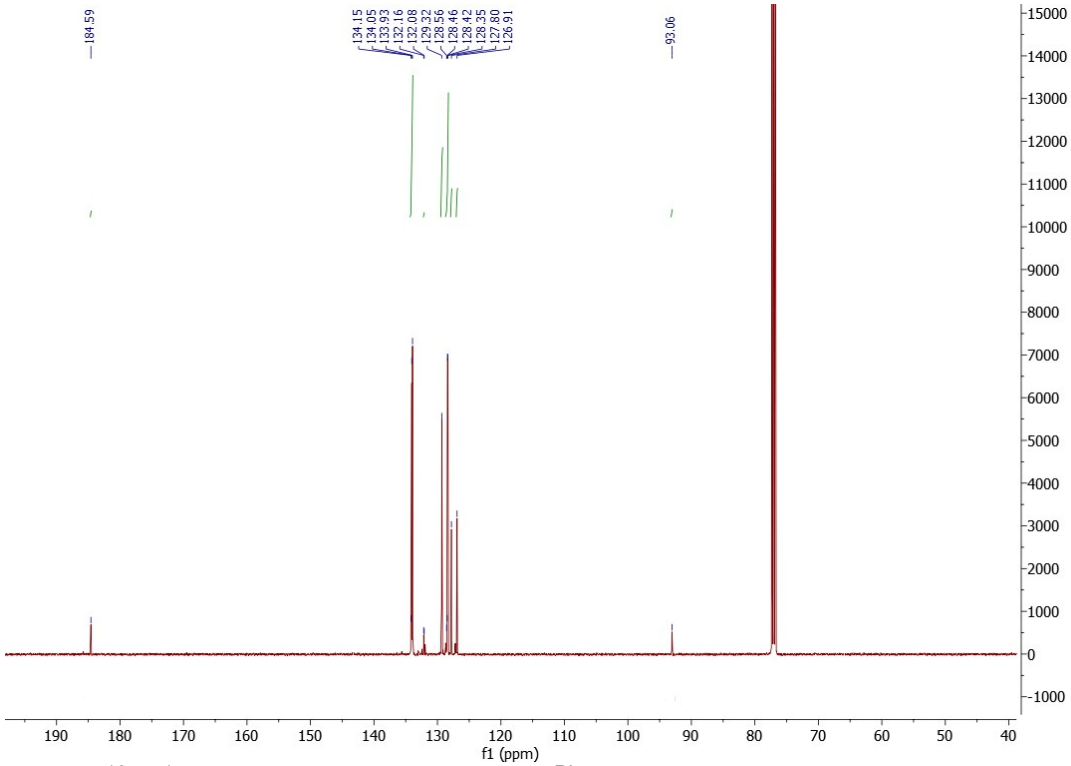

Figure S49. ^{13}C{^{1}H}-NMR spectrum of [Cu(L^{Ph})(PPh_3)$_2$] (**9**) in $CDCl_3$.

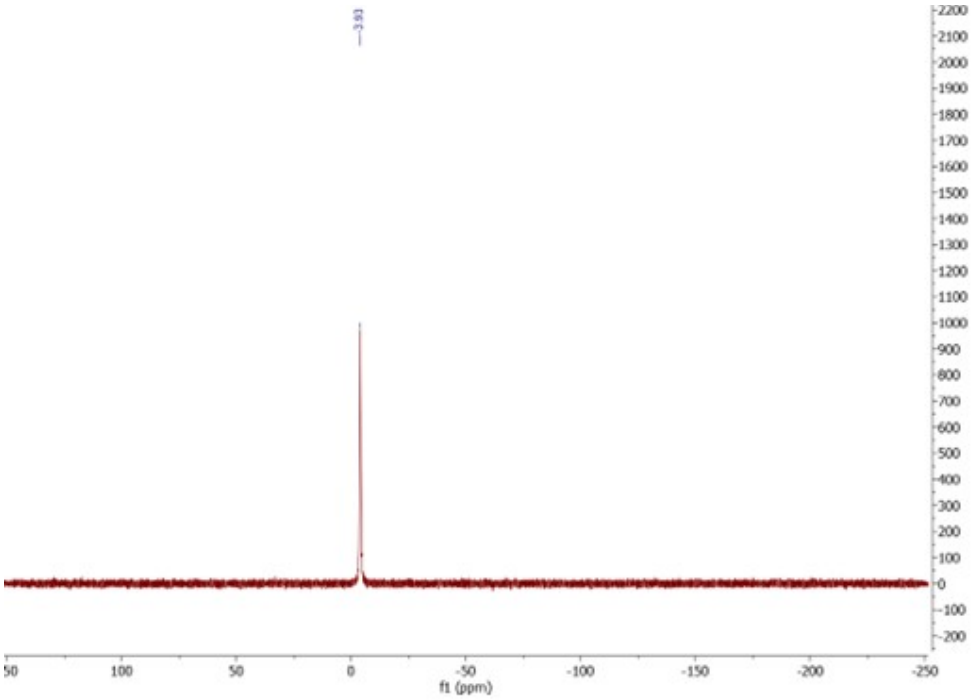

Figure S50. $^{31}P\{^{1}H\}$-NMR spectrum of $[Cu(L^{Ph})(PPh_3)_2]$ (**9**) in $CDCl_3$.

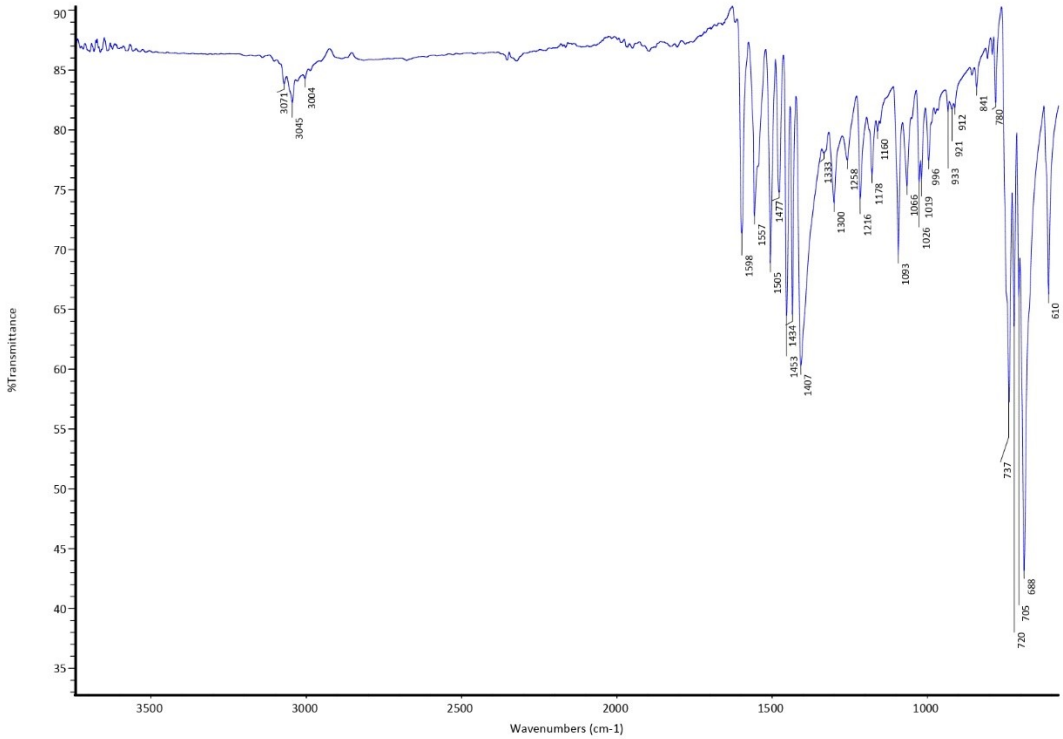

Figure S51. FT-IR spectrum of $[Ag(L^{Ph})(PPh_3)_2]$ (**10**).

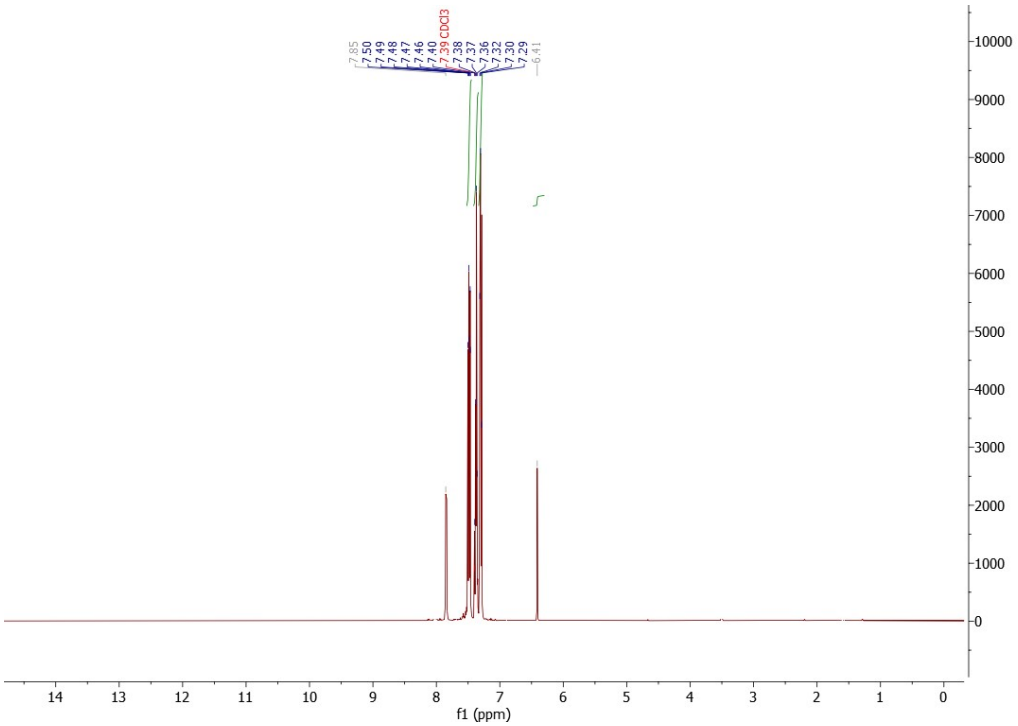

Figure S52. ^{1}H-NMR spectrum of [Ag(L^{Ph})(PPh_3)$_2$] (**10**) in $CDCl_3$.

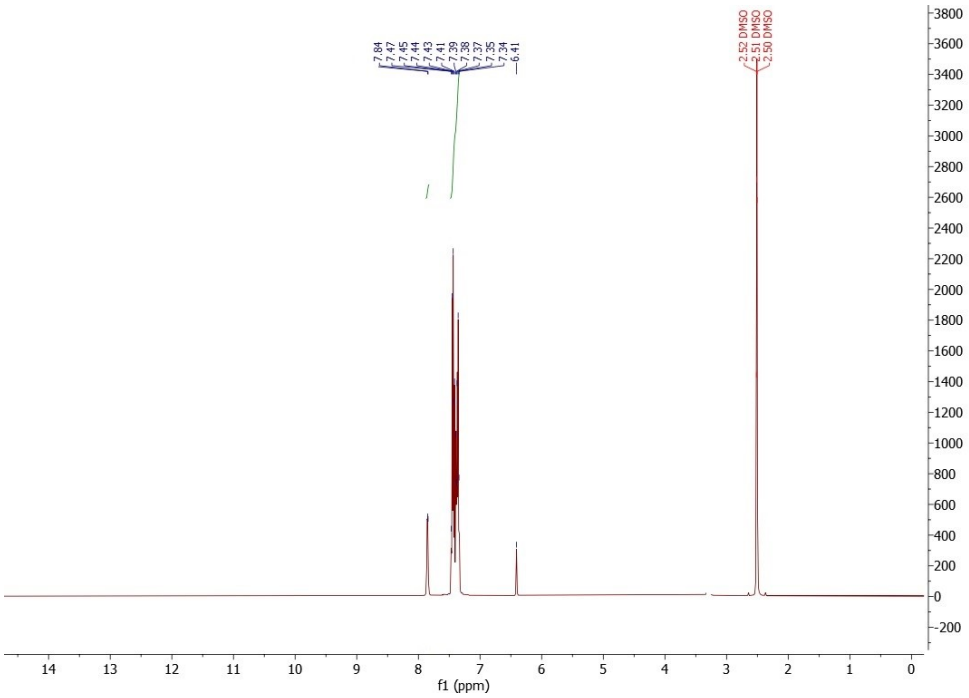

Figure S53. ^{1}H-NMR spectrum of [Ag(L^{Ph})(PPh_3)$_2$] (**10**) in DMSO-d_6.

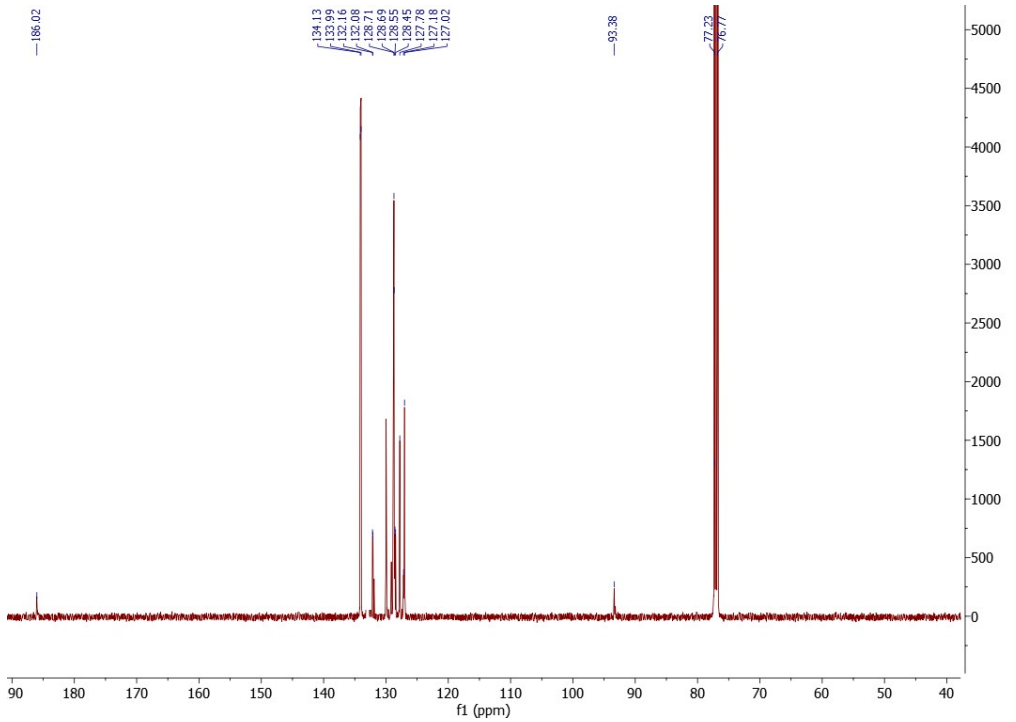

Figure S54. $^{13}C\{^{1}H\}$-NMR spectrum of $[Ag(L^{Ph})(PPh_3)_2]$ (**10**) in $CDCl_3$.

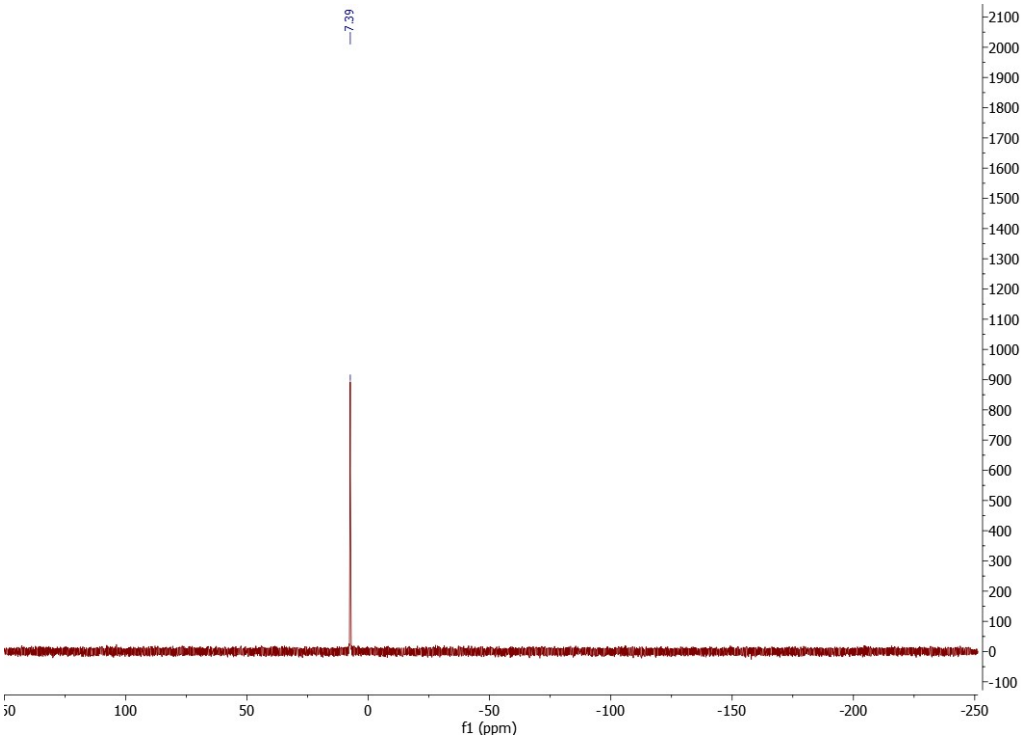

Figure S55. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{Ph})(PPh_3)_2]$ (**10**) in $CDCl_3$.

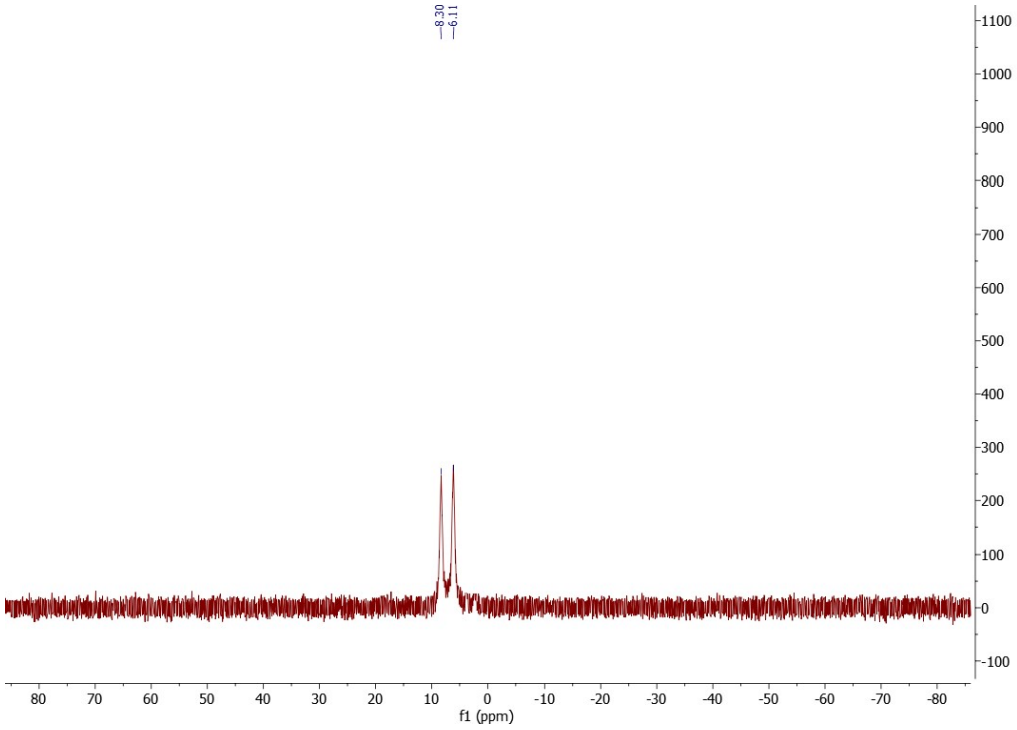

Figure S56. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{Ph})(PPh_3)_2]$ (**10**) in $CDCl_3$ at 223K.

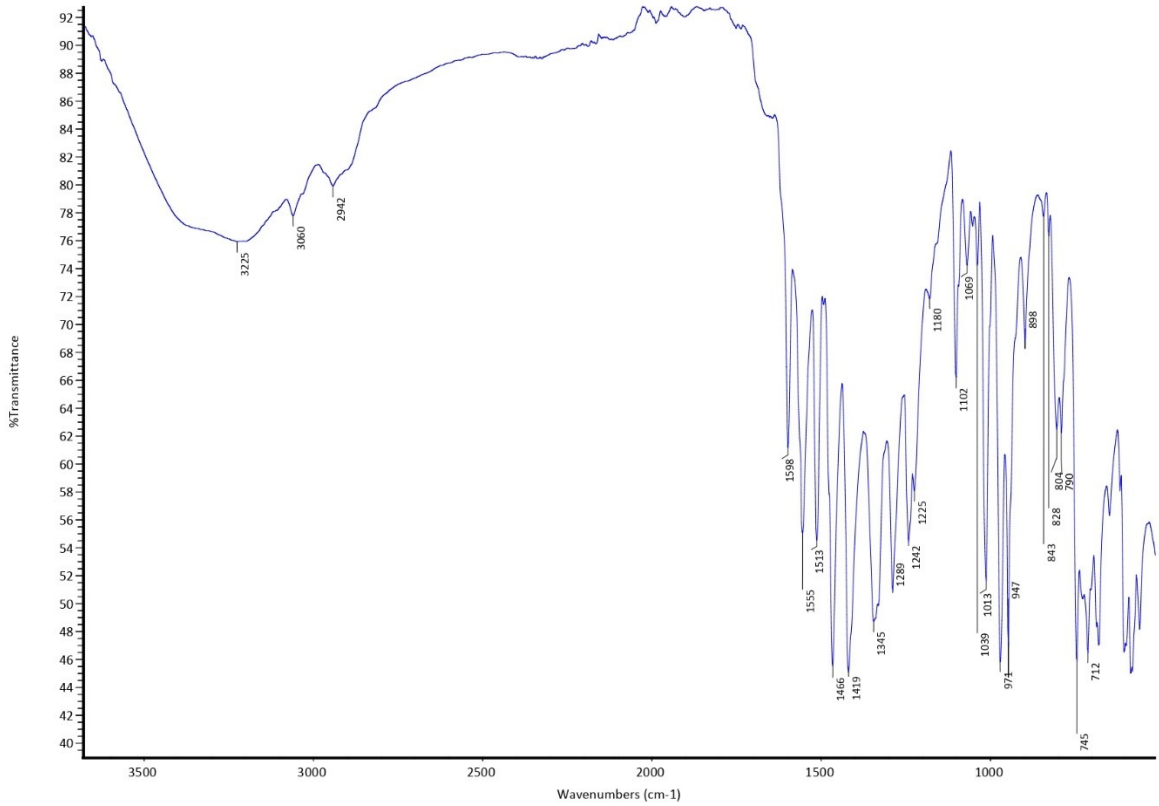

Figure S57. FT-IR spectrum of $[Ag(L^{Ph})(PTA)]\cdot H_2O$ (**11**).

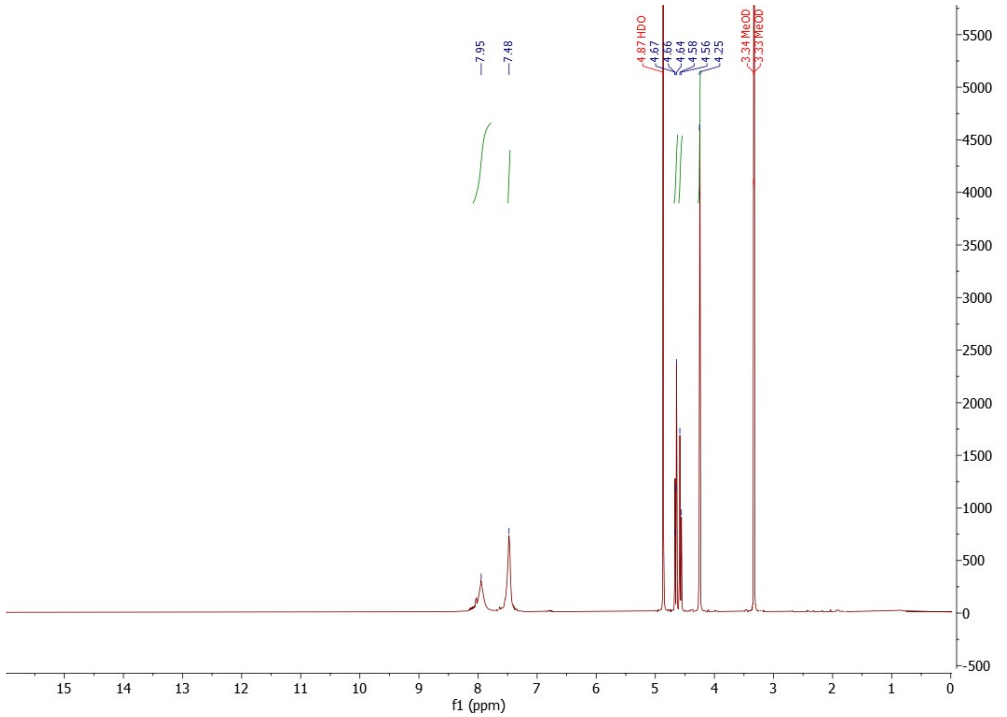

Figure S58. ^{1}H-NMR spectrum of [Ag(L^{Ph})(PTA)]·H_2O (**11**) in CD_3OD.

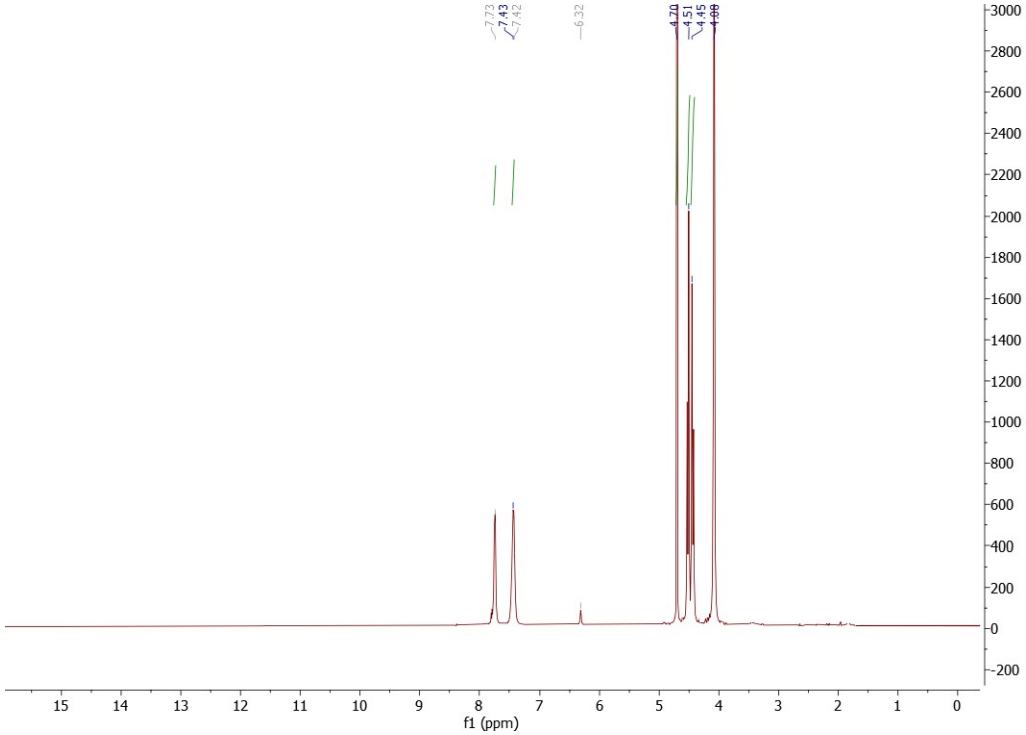

Figure S59. ^{1}H-NMR spectrum of [Ag(L^{Ph})(PTA)]·H_2O (**11**) in D_2O.

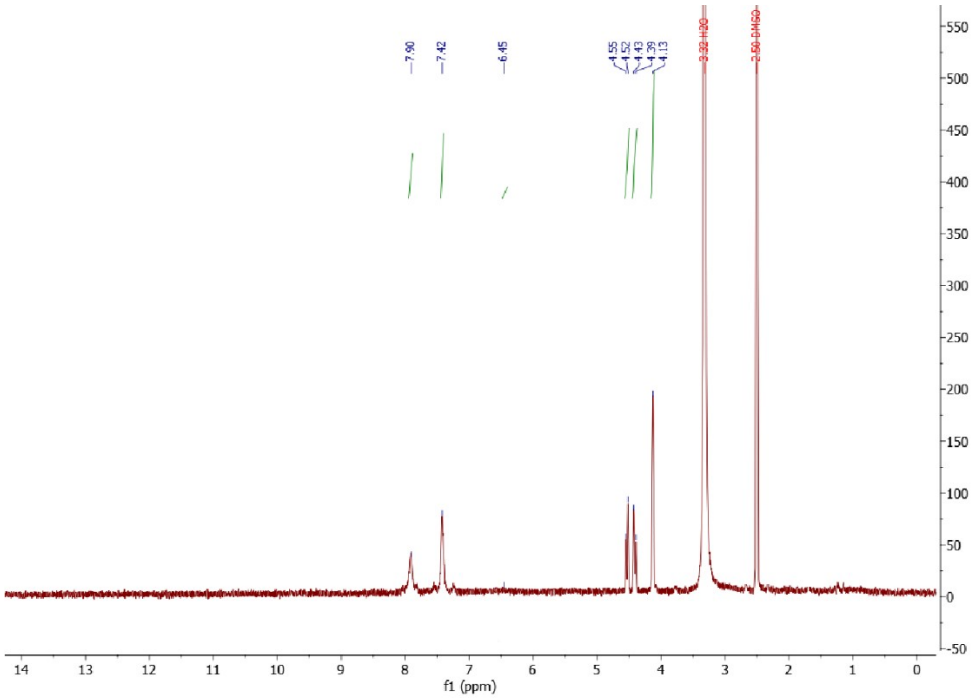

Figure S60. ^{1}H-NMR spectrum of [Ag(L^{Ph})(PTA)]·H_2O (**11**) in DMSO-d_6.

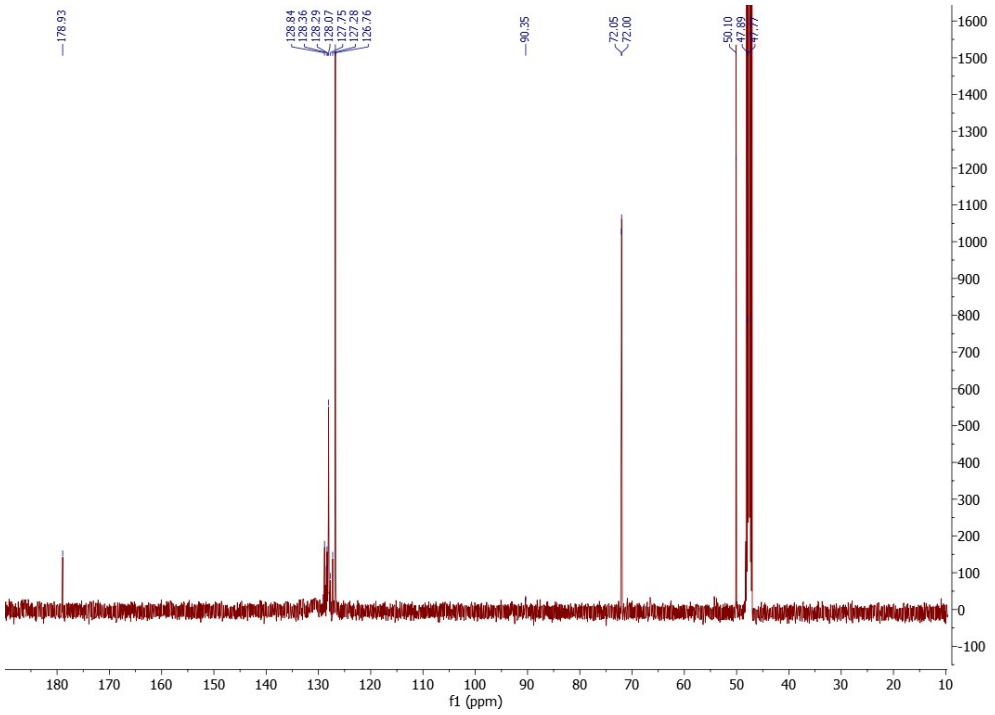

Figure S61. ^{13}C{^{1}H}-NMR spectrum of [Ag(L^{Ph})(PTA)]·H_2O (**11**) in CD_3OD.

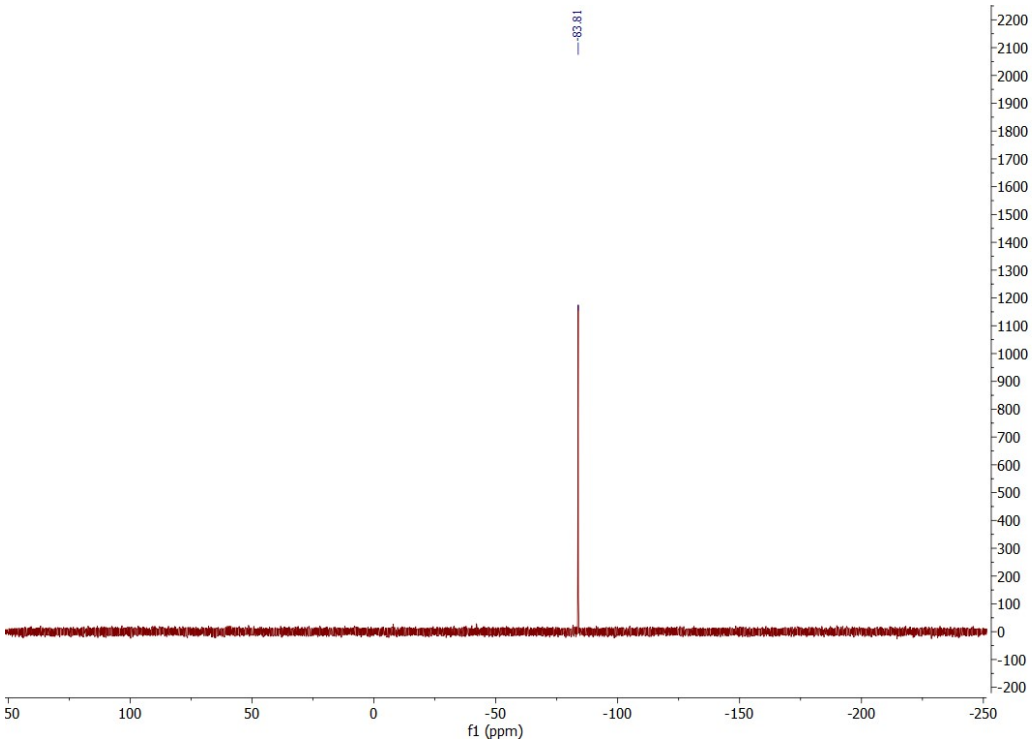

Figure S62. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{Ph})(PTA)]\cdot H_2O$ (**11**) in CD_3OD.

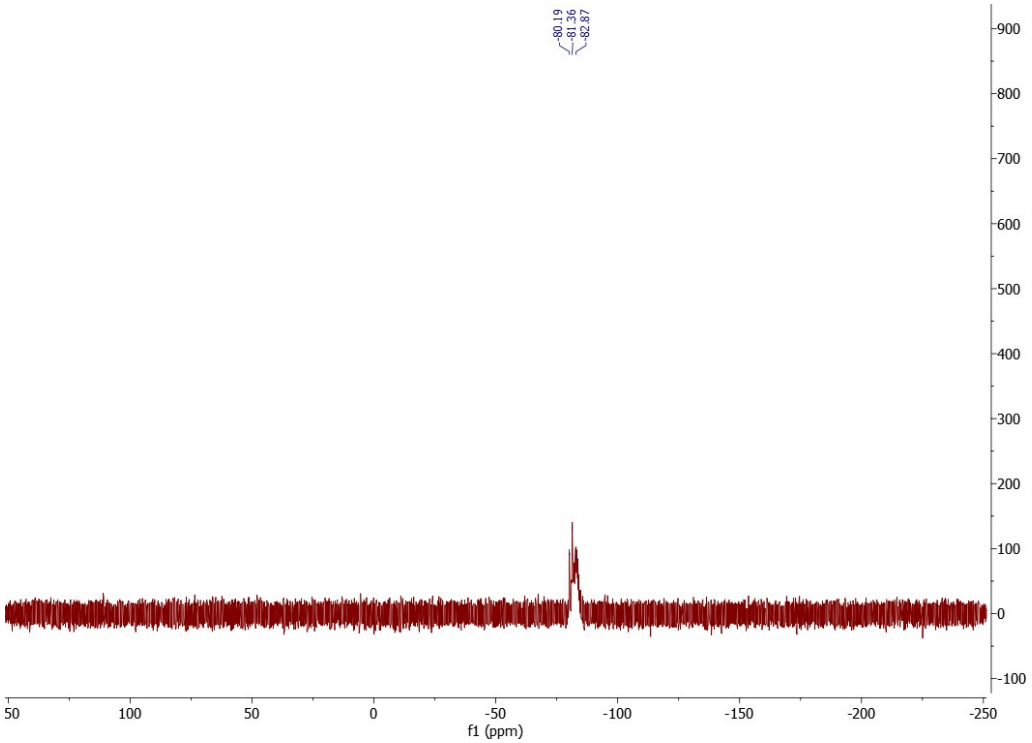

Figure S63. $^{31}P\{^{1}H\}$-NMR spectrum of $[Ag(L^{Ph})(PTA)]\cdot H_2O$ (**11**) in CD_3OD at 223 K.

Table S1. Crystal data and structure refinement for HL^{CF3}.

Identification code	dia99_0m
Empirical formula	$C_{19}H_8F_{12}O_2$
Formula weight	496.25
Temperature/K	99.96
Crystal system	monoclinic
Space group	C2/c
a/Å	24.898(7)
b/Å	8.400(2)
c/Å	9.239(2)
α/°	90
β/°	110.682(4)
γ/°	90
Volume/Å^3	1807.8(8)
Z	4
ρ_{calc}g/cm^3	1.823
μ/mm^{-1}	0.201
F(000)	984.0
Crystal size/mm^3	0.42 × 0.12 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.496 to 61.826
Index ranges	-34 ≤ h ≤ 34, -8 ≤ k ≤ 12, -12 ≤ l ≤ 10
Reflections collected	4933
Independent reflections	2578 [R_{int} = 0.0225, R_{sigma} = 0.0374]
Data/restraints/parameters	2578/87/179
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1225
Final R indexes [all data]	R_1 = 0.0717, wR_2 = 0.1351
Largest diff. peak/hole / e Å^{-3}	0.40/-0.35

Table S2. Bond Lengths for HL^{CF3}.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C9	1.349(2)	C3	C8	1.403(2)
F2	C9	1.333(2)	C4	C5	1.398(2)
F3	C9	1.3313(19)	C5	C6	1.386(2)
F4	C10	1.267(7)	C5	C9	1.494(2)
F5	C10	1.377(5)	C6	C7	1.383(2)
F6	C10	1.336(5)	C7	C8	1.386(2)
O1	C2	1.286(2)	C7	C10	1.506(2)
C1	C2	1.4045(19)	C10	F6A	1.348(6)
C1	C2[1]	1.4045(19)	C10	F4A	1.367(6)
C2	C3	1.487(2)	C10	F5A	1.251(7)
C3	C4	1.384(2)			

[1]1-X,+Y,1/2-Z

Table S3. Bond Angles for HL^{CF3}.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2[1]	C1	C2	119.6(2)	F2	C9	F1	106.49(14)
O1	C2	C1	121.46(15)	F2	C9	C5	112.27(15)
O1	C2	C3	116.58(13)	F3	C9	F1	106.44(14)
C1	C2	C3	121.96(16)	F3	C9	F2	106.75(15)
C4	C3	C2	122.05(13)	F3	C9	C5	113.35(13)
C4	C3	C8	119.41(14)	F4	C10	F5	104.6(6)
C8	C3	C2	118.54(15)	F4	C10	F6	111.8(5)
C3	C4	C5	120.31(14)	F4	C10	C7	115.7(5)
C4	C5	C9	118.33(14)	F5	C10	C7	109.9(3)
C6	C5	C4	120.34(16)	F6	C10	F5	100.0(4)
C6	C5	C9	121.32(14)	F6	C10	C7	113.3(3)
C7	C6	C5	119.09(14)	F6A	C10	C7	111.3(3)
C6	C7	C8	121.35(14)	F6A	C10	F4A	99.7(7)
C6	C7	C10	118.53(14)	F4A	C10	C7	110.2(4)
C8	C7	C10	120.11(15)	F5A	C10	C7	115.5(4)
C7	C8	C3	119.47(16)	F5A	C10	F6A	111.1(4)
F1	C9	C5	111.11(14)	F5A	C10	F4A	107.8(6)

[1]1-X,+Y,1/2-Z

Table S4. Crystal data and structure refinement for $[Cu(L^{CF3})(PPh_3)_2]$ (4).

Identification code	dia97_0m
Empirical formula	$C_{55}H_{37}CuF_{12}O_2P_2$
Formula weight	1083.32
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	13.5755(6)
b/Å	19.2736(8)
c/Å	20.1001(9)
α/°	102.5570(10)
β/°	94.3400(10)
γ/°	97.1660(10)
Volume/Å^3	5064.5(4)
Z	4
ρ_{calc}g/cm^3	1.421
μ/mm^{-1}	0.580
F(000)	2200.0
Crystal size/mm^3	0.412 × 0.155 × 0.152
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.04 to 58.26
Index ranges	-18 ≤ h ≤ 18, -26 ≤ k ≤ 26, -27 ≤ l ≤ 27
Reflections collected	56923
Independent reflections	27098 [R_{int} = 0.0285, R_{sigma} = 0.0476]
Data/restraints/parameters	27098/0/1297
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0414, wR_2 = 0.0974
Final R indexes [all data]	R_1 = 0.0606, wR_2 = 0.1061
Largest diff. peak/hole / e Å^{-3}	0.64/-0.72

Table S5. Bond Lengths for [Cu(L^{CF3})(PPh_3)$_2$] (**4**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	P1	2.2266(5)	Cu2	P3	2.2250(5)
Cu1	P2	2.2309(5)	Cu2	P4	2.2198(5)
Cu1	O1	2.1042(13)	Cu2	O3	2.0774(12)
Cu1	O2	2.0335(13)	Cu2	O4	2.0705(12)
P1	C20	1.8211(19)	P3	C74	1.8192(18)
P1	C26	1.8252(19)	P3	C80	1.8271(19)
P1	C32	1.8228(19)	P3	C86	1.8252(19)
P2	C38	1.8192(18)	P4	C92	1.8309(18)
P2	C44	1.8243(19)	P4	C98	1.8215(18)
P2	C50	1.8283(18)	P4	C104	1.8273(18)
F1	C10	1.285(4)	F13	C65	1.314(3)
F2	C10	1.329(4)	F14	C65	1.321(3)
F3	C10	1.341(4)	F15	C65	1.327(3)
F4	C11	1.334(3)	F16	C66	1.324(3)
F5	C11	1.346(3)	F17	C66	1.330(2)
F6	C11	1.325(4)	F18	C66	1.344(3)
F7	C18	1.321(3)	F19	C72	1.337(3)
F8	C18	1.332(3)	F20	C72	1.324(3)
F9	C18	1.336(3)	F21	C72	1.321(3)
F10	C19	1.312(3)	F22	C73	1.332(2)
F11	C19	1.326(3)	F23	C73	1.330(3)
F12	C19	1.331(4)	F24	C73	1.321(3)
O1	C1	1.254(2)	O3	C56	1.264(2)
O2	C3	1.258(2)	O4	C58	1.258(2)
C1	C2	1.403(3)	C01D	C70	1.387(3)
C1	C4	1.513(3)	C01D	C71	1.388(3)
C2	C3	1.405(3)	C01D	C73	1.495(3)
C3	C12	1.511(3)	C56	C57	1.399(2)
C4	C5	1.386(3)	C56	C59	1.508(2)
C4	C9	1.393(3)	C57	C58	1.410(2)
C5	C6	1.389(3)	C58	C67	1.510(2)
C6	C7	1.375(4)	C59	C60	1.397(2)
C6	C10	1.496(4)	C59	C64	1.385(2)
C7	C8	1.384(4)	C60	C61	1.382(3)
C8	C9	1.394(3)	C61	C62	1.388(3)
C8	C11	1.487(4)	C61	C65	1.499(3)
C12	C13	1.396(3)	C62	C63	1.387(3)
C12	C17	1.388(3)	C63	C64	1.394(3)
C13	C14	1.393(3)	C63	C66	1.492(3)
C14	C15	1.383(3)	C67	C68	1.393(2)

Table S5. Bond Lengths for [Cu(L^{CF3})(PPh_3)$_2$] (**4**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C14	C18	1.503(3)	C67	C71	1.390(2)
C15	C16	1.382(3)	C68	C69	1.386(3)
C16	C17	1.386(3)	C69	C70	1.388(3)
C16	C19	1.494(3)	C69	C72	1.500(3)
C20	C21	1.392(3)	C74	C75	1.395(3)
C20	C25	1.395(3)	C74	C79	1.392(3)
C21	C22	1.382(3)	C75	C76	1.387(3)
C22	C23	1.379(3)	C76	C77	1.380(3)
C23	C24	1.386(3)	C77	C78	1.381(3)
C24	C25	1.383(3)	C78	C79	1.392(3)
C26	C27	1.388(3)	C80	C81	1.397(3)
C26	C31	1.399(3)	C80	C85	1.388(3)
C27	C28	1.384(3)	C81	C82	1.388(3)
C28	C29	1.381(3)	C82	C83	1.378(3)
C29	C30	1.378(3)	C83	C84	1.374(3)
C30	C31	1.389(3)	C84	C85	1.389(3)
C32	C33	1.391(3)	C86	C87	1.396(3)
C32	C37	1.401(3)	C86	C91	1.397(2)
C33	C34	1.395(3)	C87	C88	1.389(3)
C34	C35	1.377(3)	C88	C89	1.385(3)
C35	C36	1.391(3)	C89	C90	1.385(3)
C36	C37	1.382(3)	C90	C91	1.389(3)
C38	C39	1.397(3)	C92	C93	1.389(2)
C38	C43	1.395(3)	C92	C97	1.396(3)
C39	C40	1.384(3)	C93	C94	1.393(3)
C40	C41	1.385(3)	C94	C95	1.387(3)
C41	C42	1.381(3)	C95	C96	1.387(3)
C42	C43	1.393(3)	C96	C97	1.388(3)
C44	C45	1.390(3)	C98	C99	1.392(2)
C44	C49	1.395(3)	C98	C103	1.394(2)
C45	C46	1.389(3)	C99	C100	1.389(3)
C46	C47	1.379(3)	C100	C101	1.382(3)
C47	C48	1.385(3)	C101	C102	1.386(3)
C48	C49	1.389(3)	C102	C103	1.389(3)
C50	C51	1.390(3)	C104	C105	1.399(2)
C50	C55	1.391(3)	C104	C109	1.394(3)
C51	C52	1.388(3)	C105	C106	1.387(3)
C52	C53	1.378(3)	C106	C107	1.385(3)
C53	C54	1.389(3)	C107	C108	1.386(3)
C54	C55	1.387(3)	C108	C109	1.389(3)

Table S6. Bond Angles for [Cu(L^{CF3})(PPh_3)$_2$] (**4**).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
P1	Cu1	P2	129.02(2)	P4	Cu2	P3	128.009(19)
O1	Cu1	P1	100.28(4)	O3	Cu2	P3	119.12(4)
O1	Cu1	P2	106.77(4)	O3	Cu2	P4	94.19(4)
O2	Cu1	P1	113.60(4)	O4	Cu2	P3	97.20(4)
O2	Cu1	P2	109.90(4)	O4	Cu2	P4	124.30(4)
O2	Cu1	O1	87.76(5)	O4	Cu2	O3	88.37(5)
C20	P1	Cu1	113.73(6)	C74	P3	Cu2	109.50(6)
C20	P1	C26	104.15(9)	C74	P3	C80	102.20(8)
C20	P1	C32	102.99(8)	C74	P3	C86	105.10(8)
C26	P1	Cu1	110.99(6)	C80	P3	Cu2	110.92(6)
C32	P1	Cu1	118.66(6)	C86	P3	Cu2	122.60(6)
C32	P1	C26	104.93(8)	C86	P3	C80	104.52(8)
C38	P2	Cu1	108.12(6)	C92	P4	Cu2	107.92(6)
C38	P2	C44	103.12(8)	C98	P4	Cu2	121.55(6)
C38	P2	C50	105.36(8)	C98	P4	C92	103.20(8)
C44	P2	Cu1	122.26(6)	C98	P4	C104	106.31(8)
C44	P2	C50	104.30(8)	C104	P4	Cu2	113.47(6)
C50	P2	Cu1	112.20(6)	C104	P4	C92	102.25(8)
C1	O1	Cu1	126.02(12)	C56	O3	Cu2	125.04(11)
C3	O2	Cu1	127.98(12)	C58	O4	Cu2	126.23(11)
O1	C1	C2	126.63(18)	C70	C01D	C71	120.84(18)
O1	C1	C4	115.34(17)	C70	C01D	C73	118.70(18)
C2	C1	C4	118.00(18)	C71	C01D	C73	120.45(18)
C1	C2	C3	124.58(18)	O3	C56	C57	126.61(16)
O2	C3	C2	126.30(17)	O3	C56	C59	114.04(15)
O2	C3	C12	114.68(16)	C57	C56	C59	119.34(15)
C2	C3	C12	119.02(17)	C56	C57	C58	124.35(16)
C5	C4	C1	118.15(19)	O4	C58	C57	126.46(16)
C5	C4	C9	119.3(2)	O4	C58	C67	115.46(15)
C9	C4	C1	122.56(19)	C57	C58	C67	118.00(15)
C4	C5	C6	119.9(2)	C60	C59	C56	117.18(16)
C5	C6	C10	120.3(3)	C64	C59	C56	123.53(16)
C7	C6	C5	121.0(2)	C64	C59	C60	119.20(16)
C7	C6	C10	118.7(2)	C61	C60	C59	120.34(17)
C6	C7	C8	119.5(2)	C60	C61	C62	120.72(17)
C7	C8	C9	120.2(2)	C60	C61	C65	119.47(18)
C7	C8	C11	118.9(2)	C62	C61	C65	119.81(17)
C9	C8	C11	120.9(3)	C63	C62	C61	118.94(17)
C4	C9	C8	120.2(2)	C62	C63	C64	120.73(18)
F1	C10	F2	107.7(4)	C62	C63	C66	119.77(18)

Table S6. Bond Angles for [Cu(L^{CF3})(PPh_3)$_2$] (**4**).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
F1	C10	F3	108.5(3)	C64	C63	C66	119.41(18)
F1	C10	C6	114.2(2)	C59	C64	C63	120.07(17)
F2	C10	F3	102.7(2)	F13	C65	F14	106.02(19)
F2	C10	C6	111.9(3)	F13	C65	F15	107.7(2)
F3	C10	C6	111.1(3)	F13	C65	C61	112.7(2)
F4	C11	F5	105.6(2)	F14	C65	F15	104.7(2)
F4	C11	C8	112.4(2)	F14	C65	C61	113.30(17)
F5	C11	C8	111.5(3)	F15	C65	C61	111.95(18)
F6	C11	F4	107.4(3)	F16	C66	F17	106.85(18)
F6	C11	F5	105.9(3)	F16	C66	F18	105.55(19)
F6	C11	C8	113.5(2)	F16	C66	C63	112.75(18)
C13	C12	C3	124.25(18)	F17	C66	F18	105.71(18)
C17	C12	C3	117.17(17)	F17	C66	C63	113.00(18)
C17	C12	C13	118.55(18)	F18	C66	C63	112.39(18)
C14	C13	C12	120.0(2)	C68	C67	C58	117.77(16)
C13	C14	C18	119.2(2)	C71	C67	C58	123.06(16)
C15	C14	C13	121.1(2)	C71	C67	C68	119.11(16)
C15	C14	C18	119.6(2)	C69	C68	C67	120.23(17)
C16	C15	C14	118.8(2)	C68	C69	C70	120.80(18)
C15	C16	C17	120.7(2)	C68	C69	C72	120.07(18)
C15	C16	C19	120.6(2)	C70	C69	C72	119.08(18)
C17	C16	C19	118.6(2)	C01D	C70	C69	118.81(18)
C16	C17	C12	120.9(2)	C01D	C71	C67	120.21(18)
F7	C18	F8	107.0(2)	F19	C72	C69	111.54(19)
F7	C18	F9	106.0(2)	F20	C72	F19	106.28(19)
F7	C18	C14	111.8(2)	F20	C72	C69	112.24(19)
F8	C18	F9	106.9(2)	F21	C72	F19	105.5(2)
F8	C18	C14	112.8(2)	F21	C72	F20	107.9(2)
F9	C18	C14	112.0(2)	F21	C72	C69	112.90(18)
F10	C19	F11	106.4(2)	F22	C73	C01D	112.00(18)
F10	C19	F12	105.9(2)	F23	C73	F22	105.77(19)
F10	C19	C16	113.4(2)	F23	C73	C01D	113.18(17)
F11	C19	F12	105.8(2)	F24	C73	F22	105.82(19)
F11	C19	C16	113.1(2)	F24	C73	F23	107.2(2)
F12	C19	C16	111.7(3)	F24	C73	C01D	112.36(19)
C21	C20	P1	117.08(14)	C75	C74	P3	117.28(13)
C21	C20	C25	119.12(18)	C79	C74	P3	123.52(14)
C25	C20	P1	123.80(15)	C79	C74	C75	119.12(17)
C22	C21	C20	120.40(19)	C76	C75	C74	120.53(18)
C23	C22	C21	120.3(2)	C77	C76	C75	119.70(19)

Table S6. Bond Angles for [Cu(L^{CF3})(PPh_3)$_2$] (**4**).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C22	C23	C24	119.7(2)	C76	C77	C78	120.59(19)
C25	C24	C23	120.4(2)	C77	C78	C79	119.87(19)
C24	C25	C20	120.03(19)	C74	C79	C78	120.16(19)
C27	C26	P1	122.60(15)	C81	C80	P3	117.44(14)
C27	C26	C31	119.08(17)	C85	C80	P3	123.50(15)
C31	C26	P1	118.30(14)	C85	C80	C81	119.03(18)
C28	C27	C26	120.4(2)	C82	C81	C80	120.3(2)
C29	C28	C27	120.1(2)	C83	C82	C81	119.9(2)
C30	C29	C28	120.38(19)	C84	C83	C82	120.1(2)
C29	C30	C31	119.9(2)	C83	C84	C85	120.6(2)
C30	C31	C26	120.18(19)	C80	C85	C84	120.0(2)
C33	C32	P1	123.40(14)	C87	C86	P3	122.93(14)
C33	C32	C37	118.96(17)	C87	C86	C91	118.98(17)
C37	C32	P1	117.50(14)	C91	C86	P3	118.08(14)
C32	C33	C34	120.10(18)	C88	C87	C86	120.09(18)
C35	C34	C33	120.53(19)	C89	C88	C87	120.61(18)
C34	C35	C36	119.73(18)	C90	C89	C88	119.61(19)
C37	C36	C35	120.20(18)	C89	C90	C91	120.30(18)
C36	C37	C32	120.49(18)	C90	C91	C86	120.37(18)
C39	C38	P2	117.91(14)	C93	C92	P4	123.55(14)
C43	C38	P2	122.67(14)	C93	C92	C97	119.13(17)
C43	C38	C39	118.80(17)	C97	C92	P4	117.29(13)
C40	C39	C38	120.73(18)	C92	C93	C94	120.38(18)
C39	C40	C41	120.03(19)	C95	C94	C93	120.04(18)
C42	C41	C40	119.96(19)	C96	C95	C94	119.95(18)
C41	C42	C43	120.35(18)	C95	C96	C97	119.97(18)
C42	C43	C38	120.11(18)	C96	C97	C92	120.49(18)
C45	C44	P2	118.97(15)	C99	C98	P4	117.53(13)
C45	C44	C49	118.82(18)	C99	C98	C103	119.20(16)
C49	C44	P2	122.17(15)	C103	C98	P4	123.17(13)
C46	C45	C44	120.58(19)	C100	C99	C98	120.37(17)
C47	C46	C45	120.3(2)	C101	C100	C99	119.84(18)
C46	C47	C48	119.64(19)	C100	C101	C102	120.47(17)
C47	C48	C49	120.33(19)	C101	C102	C103	119.71(17)
C48	C49	C44	120.29(19)	C102	C103	C98	120.38(17)
C51	C50	P2	124.15(15)	C105	C104	P4	122.89(14)
C51	C50	C55	119.06(17)	C109	C104	P4	118.02(14)
C55	C50	P2	116.73(14)	C109	C104	C105	118.98(16)
C52	C51	C50	120.12(19)	C106	C105	C104	120.48(18)
C53	C52	C51	120.54(19)	C107	C106	C105	119.99(19)

Table S6. Bond Angles for [Cu(L^{CF3})(PPh_3)$_2$] (**4**).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C52	C53	C54	119.86(19)	C106	C107	C108	120.13(19)
C55	C54	C53	119.69(19)	C107	C108	C109	120.08(19)
C54	C55	C50	120.71(18)	C108	C109	C104	120.34(18)

Table S7. Crystal data and structure refinement for $[Ag(L^{Ph})(PPh_3)_2]$ (**10**).

Identification code	HRD108_0m
Empirical formula	$C_{51}H_{41}AgO_2P_2$
Formula weight	855.65
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.9503(3)
b/Å	22.1429(6)
c/Å	16.6953(5)
α/°	90
β/°	98.0050(10)
γ/°	90
Volume/Å^3	4008.7(2)
Z	4
ρ_{calc}g/cm^3	1.418
μ/mm^{-1}	0.624
F(000)	1760.0
Crystal size/mm^3	0.28 × 0.15 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.258 to 64.924
Index ranges	-15 ≤ h ≤ 16, -30 ≤ k ≤ 31, -25 ≤ l ≤ 25
Reflections collected	35007
Independent reflections	13384 [R_{int} = 0.0173, R_{sigma} = 0.0199]
Data/restraints/parameters	13384/0/506
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0237, wR_2 = 0.0585
Final R indexes [all data]	R_1 = 0.0271, wR_2 = 0.0611
Largest diff. peak/hole / e Å^{-3}	0.50/-0.54

Table S8. Bond Lengths for [Ag(L^{Ph})(PPh_3)$_2$] (**10**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag	P1	2.4290(3)	C19	C20	1.3898(18)
Ag	P2	2.4188(3)	C20	C21	1.3890(17)
Ag	O1	2.3259(8)	C22	C23	1.3975(16)
Ag	O2	2.3610(9)	C22	C27	1.3949(16)
P1	C16	1.8221(11)	C23	C24	1.3931(16)
P1	C22	1.8165(11)	C24	C25	1.388(2)
P1	C28	1.8218(11)	C25	C26	1.383(2)
P2	C34	1.8243(11)	C26	C27	1.3922(16)
P2	C40	1.8243(11)	C28	C29	1.3963(16)
P2	C46	1.8244(11)	C28	C33	1.3997(15)
O1	C1	1.2641(14)	C29	C30	1.3935(17)
O2	C3	1.2601(14)	C30	C31	1.3869(18)
C1	C2	1.4138(15)	C31	C32	1.3899(18)
C1	C4	1.5055(15)	C32	C33	1.3883(17)
C2	C3	1.4102(15)	C34	C35	1.3882(17)
C3	C10	1.5131(15)	C34	C39	1.3782(17)
C4	C5	1.3966(15)	C35	C36	1.387(2)
C4	C9	1.4010(16)	C36	C37	1.372(2)
C5	C6	1.3927(15)	C37	C38	1.373(2)
C6	C7	1.3904(18)	C38	C39	1.3966(19)
C7	C8	1.3920(17)	C40	C41	1.3977(16)
C8	C9	1.3913(16)	C40	C45	1.3969(16)
C10	C11	1.3953(16)	C41	C42	1.3928(16)
C10	C15	1.3932(16)	C42	C43	1.3886(18)
C11	C12	1.3889(17)	C43	C44	1.3892(18)
C12	C13	1.3870(18)	C44	C45	1.3931(15)
C13	C14	1.384(2)	C46	C47	1.3995(16)
C14	C15	1.3913(17)	C46	C51	1.3978(16)
C16	C17	1.3966(15)	C47	C48	1.3893(17)
C16	C21	1.3996(15)	C48	C49	1.3909(19)
C17	C18	1.3934(17)	C49	C50	1.3882(18)
C18	C19	1.3902(18)	C50	C51	1.3926(17)

Table S9. Bond Angles for [Ag(L^{Ph})(PPh_3)$_2$] (**10**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P2	Ag	P1	129.195(10)	C18	C17	C16	120.37(11)
O1	Ag	P1	105.84(2)	C19	C18	C17	120.29(11)
O1	Ag	P2	119.64(2)	C20	C19	C18	119.75(11)
O1	Ag	O2	77.70(3)	C21	C20	C19	120.03(11)
O2	Ag	P1	110.94(2)	C20	C21	C16	120.78(11)
O2	Ag	P2	100.26(2)	C23	C22	P1	123.04(9)
C16	P1	Ag	112.82(4)	C27	C22	P1	117.30(9)
C22	P1	Ag	115.40(4)	C27	C22	C23	119.66(10)
C22	P1	C16	104.24(5)	C24	C23	C22	119.88(12)
C22	P1	C28	104.27(5)	C25	C24	C23	120.12(12)
C28	P1	Ag	111.90(4)	C26	C25	C24	120.10(11)
C28	P1	C16	107.44(5)	C25	C26	C27	120.32(12)
C34	P2	Ag	115.84(4)	C26	C27	C22	119.92(12)
C40	P2	Ag	111.78(4)	C29	C28	P1	124.68(9)
C40	P2	C34	104.98(5)	C29	C28	C33	119.22(10)
C40	P2	C46	105.63(5)	C33	C28	P1	116.10(8)
C46	P2	Ag	114.42(4)	C30	C29	C28	120.03(11)
C46	P2	C34	103.14(5)	C31	C30	C29	120.19(11)
C1	O1	Ag	124.88(7)	C30	C31	C32	120.24(11)
C3	O2	Ag	121.59(7)	C33	C32	C31	119.73(11)
O1	C1	C2	127.09(10)	C32	C33	C28	120.57(11)
O1	C1	C4	115.70(9)	C35	C34	P2	117.92(9)
C2	C1	C4	117.22(10)	C39	C34	P2	123.71(9)
C3	C2	C1	126.08(10)	C39	C34	C35	118.31(11)
O2	C3	C2	125.40(10)	C36	C35	C34	121.13(13)
O2	C3	C10	116.04(10)	C37	C36	C35	120.19(13)
C2	C3	C10	118.56(10)	C36	C37	C38	119.22(13)
C5	C4	C1	118.89(10)	C37	C38	C39	120.85(13)
C5	C4	C9	118.79(10)	C34	C39	C38	120.25(12)
C9	C4	C1	122.16(10)	C41	C40	P2	118.09(8)
C6	C5	C4	121.07(11)	C45	C40	P2	122.90(8)
C7	C6	C5	119.56(11)	C45	C40	C41	119.00(10)
C6	C7	C8	120.02(10)	C42	C41	C40	120.46(11)
C9	C8	C7	120.33(11)	C43	C42	C41	120.12(11)
C8	C9	C4	120.22(10)	C42	C43	C44	119.84(11)
C11	C10	C3	124.17(10)	C43	C44	C45	120.21(11)
C15	C10	C3	117.53(10)	C44	C45	C40	120.36(11)
C15	C10	C11	118.19(10)	C47	C46	P2	123.02(9)
C12	C11	C10	120.59(11)	C51	C46	P2	117.51(8)
C13	C12	C11	120.55(12)	C51	C46	C47	119.44(10)

Table S9. Bond Angles for [Ag(L^{Ph})(PPh_3)$_2$] (**10**).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C14	C13	C12	119.47(12)	C48	C47	C46	120.35(11)
C13	C14	C15	119.95(12)	C47	C48	C49	119.87(11)
C14	C15	C10	121.21(12)	C50	C49	C48	120.19(11)
C17	C16	P1	123.40(8)	C49	C50	C51	120.21(12)
C17	C16	C21	118.77(10)	C50	C51	C46	119.95(11)
C21	C16	P1	117.42(8)				