Supplementary Information

Luminescent heterometallic gold-copper alkynyl complexes stabilized by tridentate phosphine

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Table S1. Atomic coordinates and displacement parameters (Å^2) for **2**.

Atom	***x***	***y***	***z***	U_{eq}
Au1	0.21156(1)	0.57773(1)	0.08590(1)	0.04990(5)
Cu1	0.3333	0.6667	0.21409(6)	0.0629(3)
P1	0.21496(8)	0.61319(9)	–0.03761(7)	0.0420(3)
C1	0.3333	0.6667	–0.0733(4)	0.0405(18)
H1	0.3333	0.6667	–0.1281	0.049*
C2	0.2094(3)	0.5446(4)	0.1939(3)	0.0567(14)
C3	0.2181(4)	0.5264(4)	0.2583(3)	0.0550(14)
C4	0.2202(3)	0.4902(3)	0.3296(3)	0.0514(13)
C5	0.2116(4)	0.5232(4)	0.3960(3)	0.0686(15)
H5	0.2051	0.5739	0.3973	0.082*
C6	0.2127(4)	0.4805(4)	0.4637(3)	0.0703(17)
H6	0.2076	0.5036	0.5094	0.084*
C7	0.2211(4)	0.4055(4)	0.4618(3)	0.0620(15)
C8	0.2322(4)	0.3755(4)	0.3952(4)	0.0782(18)
H8	0.2402	0.3257	0.3941	0.094*
C9	0.2320(4)	0.4154(4)	0.3295(3)	0.0706(17)
H9	0.2398	0.3929	0.2845	0.085*
C10	0.1731(3)	0.6922(3)	–0.0513(3)	0.0452(11)
C11	0.1564(3)	0.7283(4)	0.0112(3)	0.0574(14)
H11	0.1682	0.7138	0.0585	0.069*
C12	0.1221(4)	0.7864(4)	0.0045(4)	0.0667(16)
H12	0.1102	0.8102	0.0468	0.080*
C13	0.1062(4)	0.8078(4)	–0.0652(4)	0.0739(17)
H13	0.0843	0.8475	–0.0704	0.089*
C14	0.1219(4)	0.7721(4)	–0.1268(4)	0.0701(17)
H14	0.1101	0.7872	–0.1738	0.084*
C15	0.1550(3)	0.7133(4)	–0.1215(3)	0.0545(13)
H15	0.1650	0.6887	–0.1643	0.065*
C16	0.1483(3)	0.5202(3)	–0.0990(3)	0.0450(12)
C17	0.0815(3)	0.4406(4)	–0.0677(3)	0.0625(14)
H17	0.0747	0.4357	–0.0160	0.075*
C18	0.0248(4)	0.3685(4)	–0.1125(5)	0.088(2)
H18	–0.0208	0.3160	–0.0910	0.105*
C19	0.0358(5)	0.3743(5)	–0.1876(5)	0.091(2)
H19	–0.0014	0.3250	–0.2174	0.109*
C20	0.1025(5)	0.4535(4)	–0.2208(4)	0.083(2)
H20	0.1088	0.4575	–0.2726	0.100*
C21	0.1583(4)	0.5247(4)	–0.1771(3)	0.0574(14)
H21	0.2035	0.5770	–0.1992	0.069*
C22	0.2184(4)	0.3548(5)	0.5319(4)	0.0735(18)
C23	0.1959(6)	0.3377(6)	0.6590(4)	0.124(3)
H23A	0.1923	0.2816	0.6460	0.186*
H23B	0.1441	0.3261	0.6879	0.186*
H23C	0.2495	0.3736	0.6878	0.186*
O2	0.1989(3)	0.3855(4)	0.5914(2)	0.1000(16)
O1	0.2352(4)	0.2947(4)	0.5307(3)	0.1044(16)
B1	0.3333	0.6667	–0.3384(13)	0.29(2)
F1A	0.3333	0.6667	–0.2754(9)	0.118(5)
F2A	0.3713(9)	0.7525(10)	–0.3737(7)	0.183(5)
F1B	0.3333	0.6667	–0.409(2)	0.244(12)
F2B	0.4161(10)	0.7411(9)	–0.3077(9)	0.194(5)

* keep fixed during refinement

Table S2. Atomic coordinates and displacement parameters (Å^2) for **3**.

Atom	***x***	***y***	***z***	U_{eq}
Au1	0.63881(1)	0.21395(1)	0.18213(1)	0.02664(4)
Cu1	0.6667	0.3333	0.04341(5)	0.0316(2)
P1	0.60355(7)	0.21444(7)	0.31438(6)	0.0229(2)
C1	0.6667	0.3333	0.3549(4)	0.0213(13)
H1	0.6667	0.3333	0.4137	0.026*
C2	0.6737(3)	0.2141(3)	0.0665(3)	0.0331(10)
C3	0.7002(3)	0.2207(3)	–0.0017(3)	0.0312(10)
C4	0.7354(3)	0.2202(3)	–0.0802(2)	0.0285(9)
C5	0.8234(3)	0.2369(3)	–0.0885(3)	0.0383(11)
H5	0.8609	0.2519	–0.0437	0.046*
C6	0.8563(3)	0.2313(3)	–0.1643(3)	0.0407(11)
H6	0.9144	0.2394	–0.1692	0.049*
C7	0.8031(3)	0.2138(3)	–0.2308(3)	0.0339(11)
C8	0.7163(3)	0.2003(3)	–0.2232(3)	0.0406(11)
H8	0.6806	0.1897	–0.2686	0.049*
C9	0.6815(3)	0.2025(3)	–0.1474(3)	0.0393(11)
H9	0.6225	0.1921	–0.1424	0.047*
C10	0.8365(4)	0.2071(3)	–0.3086(3)	0.0438(12)
C11	0.6306(3)	0.1439(3)	0.3778(3)	0.0245(9)
C12	0.6397(3)	0.0766(3)	0.3404(3)	0.0328(10)
H12	0.6368	0.0721	0.2847	0.039*
C13	0.6530(3)	0.0166(3)	0.3847(3)	0.0418(12)
H13	0.6578	–0.0295	0.3592	0.050*
C14	0.6592(4)	0.0243(4)	0.4669(3)	0.0470(14)
H14	0.6684	–0.0166	0.4969	0.056*
C15	0.6520(3)	0.0911(3)	0.5045(3)	0.0437(12)
H15	0.6579	0.0966	0.5600	0.052*
C16	0.6359(3)	0.1516(3)	0.4610(3)	0.0337(10)
H16	0.6289	0.1961	0.4870	0.040*
C17	0.4832(3)	0.1712(3)	0.3313(2)	0.0259(8)
C18	0.4257(3)	0.1487(3)	0.2654(3)	0.0293(9)
H18	0.4499	0.1588	0.2139	0.035*
C19	0.3332(3)	0.1114(3)	0.2758(3)	0.0363(11)
H19	0.2947	0.0951	0.2316	0.044*
C20	0.2989(3)	0.0988(3)	0.3530(3)	0.0406(12)
H20	0.2368	0.0746	0.3604	0.049*
C21	0.3542(3)	0.1211(3)	0.4184(3)	0.0367(11)
H21	0.3299	0.1125	0.4698	0.044*
C22	0.4459(3)	0.1565(3)	0.4081(3)	0.0303(9)
H22	0.4835	0.1707	0.4527	0.036*
N1	0.8623(3)	0.1985(3)	–0.3705(3)	0.0559(14)
B1	0.6667	0.3333	0.6236(5)	0.0313(18)
F1	0.6667	0.3333	0.5393(5)	0.124(3)
F2	0.6513(4)	0.4012(3)	0.6384(4)	0.1225(19)

* keep fixed during refinement

Table S3. Atomic coordinates and displacement parameters (Å^2) for **4**.

Atom	***x***	***y***	***z***	U_{eq}
Au1	0.11661(1)	0.09514(1)	0.62031(1)	0.04469(4)
Cu1	0.0000	0.0000	0.48465(5)	0.0568(2)
P1	0.11831(6)	0.05835(7)	0.75091(6)	0.0373(2)
C1	0.0000	0.0000	0.7914(4)	0.0360(13)
H1	0.0000	0.0000	0.8499	0.043*
C2	0.1127(3)	0.1302(3)	0.5061(3)	0.0528(10)
C3	0.1094(3)	0.1518(3)	0.4384(3)	0.0499(10)
C4	0.1127(3)	0.1848(3)	0.3594(2)	0.0465(9)
C5	0.1122(3)	0.2638(3)	0.3470(3)	0.0567(11)
H5	0.1083	0.2950	0.3907	0.068*
C6	0.1174(3)	0.2986(3)	0.2697(3)	0.0620(11)
H6	0.1161	0.3517	0.2627	0.074*
C7	0.1242(3)	0.2542(3)	0.2059(3)	0.0609(12)
C8	0.1218(4)	0.1742(3)	0.2172(3)	0.0699(13)
H8	0.1229	0.1419	0.1731	0.084*
C9	0.1179(3)	0.1404(3)	0.2927(3)	0.0626(11)
H9	0.1188	0.0869	0.2988	0.075*
C10	0.1341(4)	0.3637(4)	0.1131(4)	0.107(2)
H10A	0.1421	0.3758	0.0568	0.160*
H10B	0.1836	0.4113	0.1415	0.160*
H10C	0.0789	0.3602	0.1300	0.160*
C11	0.1845(2)	0.1539(2)	0.8156(2)	0.0403(9)
C12	0.2514(3)	0.2324(3)	0.7812(3)	0.0523(10)
H12	0.2584	0.2356	0.7260	0.063*
C13	0.3071(3)	0.3050(3)	0.8267(4)	0.0721(14)
H13	0.3517	0.3573	0.8028	0.087*
C14	0.2969(4)	0.3005(3)	0.9073(4)	0.0810(17)
H14	0.3354	0.3500	0.9382	0.097*
C15	0.2320(4)	0.2254(3)	0.9433(3)	0.0769(15)
H15	0.2253	0.2240	0.9984	0.092*
C16	0.1755(3)	0.1506(3)	0.8981(3)	0.0581(11)
H16	0.1318	0.0984	0.9228	0.070*
C17	0.1637(2)	–0.0168(2)	0.7658(2)	0.0430(9)
C18	0.1835(3)	–0.0514(3)	0.6994(3)	0.0561(11)
H18	0.1722	–0.0372	0.6488	0.067*
C19	0.2199(3)	–0.1069(3)	0.7072(4)	0.0704(15)
H19	0.2339	–0.1294	0.6624	0.084*
C20	0.2353(3)	–0.1285(3)	0.7832(5)	0.089(2)
H20	0.2574	–0.1678	0.7894	0.107*
C21	0.2182(3)	–0.0926(3)	0.8484(4)	0.0759(15)
H21	0.2314	–0.1056	0.8988	0.091*
C22	0.1817(3)	–0.0374(3)	0.8415(3)	0.0587(11)
H22	0.1692	–0.0142	0.8868	0.070*
O1	0.1305(3)	0.2818(3)	0.1290(2)	0.0905(12)
B1	0.6667	0.3333	0.3831(5)	0.053(2)
F1	0.7480(4)	0.3520(5)	0.4003(5)	0.221(3)
F2	0.6667	0.3333	0.3129(8)	0.246(6)

* keep fixed during refinement

Table S4. Selected bond lengths (Å) and angles (°) for **2**.

Bond		**Angle**	
Au1–C2	2.007(6)	C2–Au1–P1	178.74(18)
Au1–P1	2.2816(13)	C2–Au1–Cu1	46.31(15)
Au1–Cu1	2.9565(9)	P1–Au1–Cu1	133.97(4)
Au1–Au1	3.2388(3)	C16–P1–C10	105.2(2)
Cu1–C2	2.138(5)	C16–P1–C1	106.2(2)
Cu1–C3	2.357(5)	C10–P1–C1	108.72(17)
Cu1–Au1	2.9564(9)	C16–P1–Au1	115.73(17)
P1–C16	1.797(5)	C10–P1–Au1	110.96(16)
P1–C10	1.838(5)	C1–P1–Au1	109.7(2)
P1–C1	1.871(3)	P1–C1–P1	109.0(2)
C2–C3	1.220(7)	C3–C2–Au1	172.6(5)
C3–C4	1.425(7)	C2–C3–C4	170.7(6)
C4–C5	1.354(7)	C5–C4–C9	118.8(5)
C4–C9	1.394(8)	C4–C5–C6	120.0(6)
C5–C6	1.418(7)	C7–C6–C5	120.0(5)
C6–C7	1.364(8)	C8–C7–C6	119.0(5)
C7–C8	1.347(8)	C7–C8–C9	122.3(6)
C7–C22	1.511(8)	C8–C9–C4	120.0(6)
C8–C9	1.360(8)	C11–C10–C15	119.7(5)
C10–C11	1.375(6)	C10–C11–C12	120.6(5)
C10–C15	1.382(7)	C13–C12–C11	118.9(6)
C11–C12	1.392(7)	C14–C13–C12	120.7(5)
C12–C13	1.364(8)	C13–C14–C15	121.4(6)
C13–C14	1.349(8)	C10–C15–C14	118.7(5)
C14–C15	1.384(7)	C17–C16–C21	118.2(5)
C16–C17	1.387(7)	C18–C17–C16	120.8(6)
C16–C21	1.402(7)	C19–C18–C17	119.9(7)
C17–C18	1.382(8)	C18–C19–C20	120.6(6)
C18–C19	1.351(10)	C21–C20–C19	119.7(6)
C19–C20	1.396(10)	C20–C21–C16	120.7(6)
C20–C21	1.358(8)	O1–C22–O2	125.5(7)
C22–O1	1.201(7)	O1–C22–C7	121.8(7)
C22–O2	1.302(8)	O2–C22–C7	112.6(6)
C23–O2	1.446(8)	C22–O2–C23	113.3(6)
B1–F1A	1.13(2)	F1A–B1–F2A	116.2(11)
B1–F2A	1.424(16)	F2A–B1–F2A	101.9(13)

Table S5. Selected bond lengths (Å) and angles (°) for **3**.

Bond		**Angle**	
Au1–C2	2.016(5)	C2–Au1–P1	178.25(14)
Au1–P1	2.2851(11)	C2–Au1–Cu1	45.94(12)
Au1–Cu1	2.9538(7)	P1–Au1–Cu1	134.80(3)
Au1–Au1	3.1843(3)	C17–P1–C11	104.31(18)
Cu1–C2	2.123(4)	C17–P1–C1	107.53(14)
Cu1–C3	2.376(4)	C11–P1–C1	107.7(2)
Cu1–Au1	2.9537(7)	C17–P1–Au1	113.13(14)
P1–C17	1.817(4)	C11–P1–Au1	113.86(14)
P1–C11	1.821(4)	C1–P1–Au1	109.94(19)
P1–C1	1.876(3)	P1–C1–P1	107.8(2)
C1–P1	1.876(3)	C3–C2–Au1	175.0(4)
C2–C3	1.207(6)	C2–C3–C4	172.7(5)
C3–C4	1.440(6)	C9–C4–C5	119.7(4)
C4–C9	1.381(6)	C4–C5–C6	120.2(4)
C4–C5	1.384(6)	C7–C6–C5	120.1(5)
C5–C6	1.404(6)	C6–C7–C8	119.9(4)
C6–C7	1.367(7)	C7–C8–C9	120.5(4)
C7–C8	1.381(7)	C4–C9–C8	119.6(4)
C7–C10	1.442(7)	N1–C10–C7	177.5(5)
C8–C9	1.403(6)	C12–C11–C16	120.0(4)
C10–N1	1.159(6)	C13–C12–C11	120.3(5)
C11–C12	1.377(6)	C12–C13–C14	120.0(5)
C11–C16	1.392(6)	C15–C14–C13	120.4(4)
C12–C13	1.367(6)	C14–C15–C16	120.8(5)
C13–C14	1.375(8)	C11–C16–C15	118.5(4)
C14–C15	1.354(7)	C18–C17–C22	118.8(4)
C15–C16	1.392(6)	C19–C18–C17	120.6(4)
C17–C18	1.390(6)	C18–C19–C20	118.8(4)
C17–C22	1.393(6)	C21–C20–C19	121.5(4)
C18–C19	1.381(6)	C20–C21–C22	119.7(5)
C19–C20	1.384(7)	C21–C22–C17	120.6(4)
C20–C21	1.364(7)	F2–B1–F2	116.7(3)
C21–C22	1.372(6)	F2–B1–F1	100.7(5)
B1–F2	1.327(4)		
B1–F1	1.405(11)		

Table S6. Selected bond lengths (Å) and angles (°) for **4**.

Bond		**Angle**	
Au1–C2	2.018(5)	C2–Au1–P1	177.84(13)
Au1–P1	2.2828(10)	C2–Au1–Cu1	46.69(12)
Au1–Cu1	2.9278(7)	P1–Au1–Cu1	133.67(3)
Au1–Au1	3.1938(3)	C11–P1–C17	105.10(17)
Cu1–C2	2.130(4)	C11–P1–C1	106.60(19)
Cu1–C3	2.453(4)	C17–P1–C1	107.59(13)
Cu1–Au1	2.9278(7)	C11–P1–Au1	114.37(13)
P1–C11	1.814(4)	C17–P1–Au1	113.27(13)
P1–C17	1.826(4)	C1–P1–Au1	109.47(17)
P1–C1	1.884(2)	P1–C1–P1	107.76(19)
C2–C3	1.204(6)	C3–C2–Au1	178.8(4)
C3–C4	1.431(6)	C2–C3–C4	174.9(5)
C4–C5	1.375(6)	C5–C4–C9	117.2(4)
C4–C9	1.380(6)	C4–C5–C6	121.6(4)
C5–C6	1.412(6)	C7–C6–C5	119.6(4)
C6–C7	1.350(7)	C6–C7–C8	119.3(4)
C7–O1	1.359(5)	C7–C8–C9	121.3(4)
C7–C8	1.365(7)	C4–C9–C8	120.9(4)
C8–C9	1.381(6)	C7–O1–C10	119.0(5)
C10–O1	1.402(8)	C12–C11–C16	118.4(4)
C11–C12	1.386(5)	C13–C12–C11	121.1(5)
C11–C16	1.389(6)	C14–C13–C12	119.6(5)
C12–C13	1.362(6)	C15–C14–C13	121.2(5)
C13–C14	1.359(8)	C14–C15–C16	120.0(5)
C14–C15	1.353(8)	C15–C16–C11	119.7(4)
C15–C16	1.384(6)	C18–C17–C22	119.4(4)
C17–C18	1.382(5)	C19–C18–C17	120.8(5)
C17–C22	1.394(6)	C18–C19–C20	118.9(5)
C18–C19	1.381(7)	C21–C20–C19	120.3(5)
C19–C20	1.387(8)	C20–C21–C22	121.4(5)
C20–C21	1.357(8)	C21–C22–C17	119.0(5)
C21–C22	1.376(6)	F2–B1–F1	102.9(6)
B1–F2	1.177(14)	F1–B1–F1	115.2(4)
B1–F1	1.299(6)		

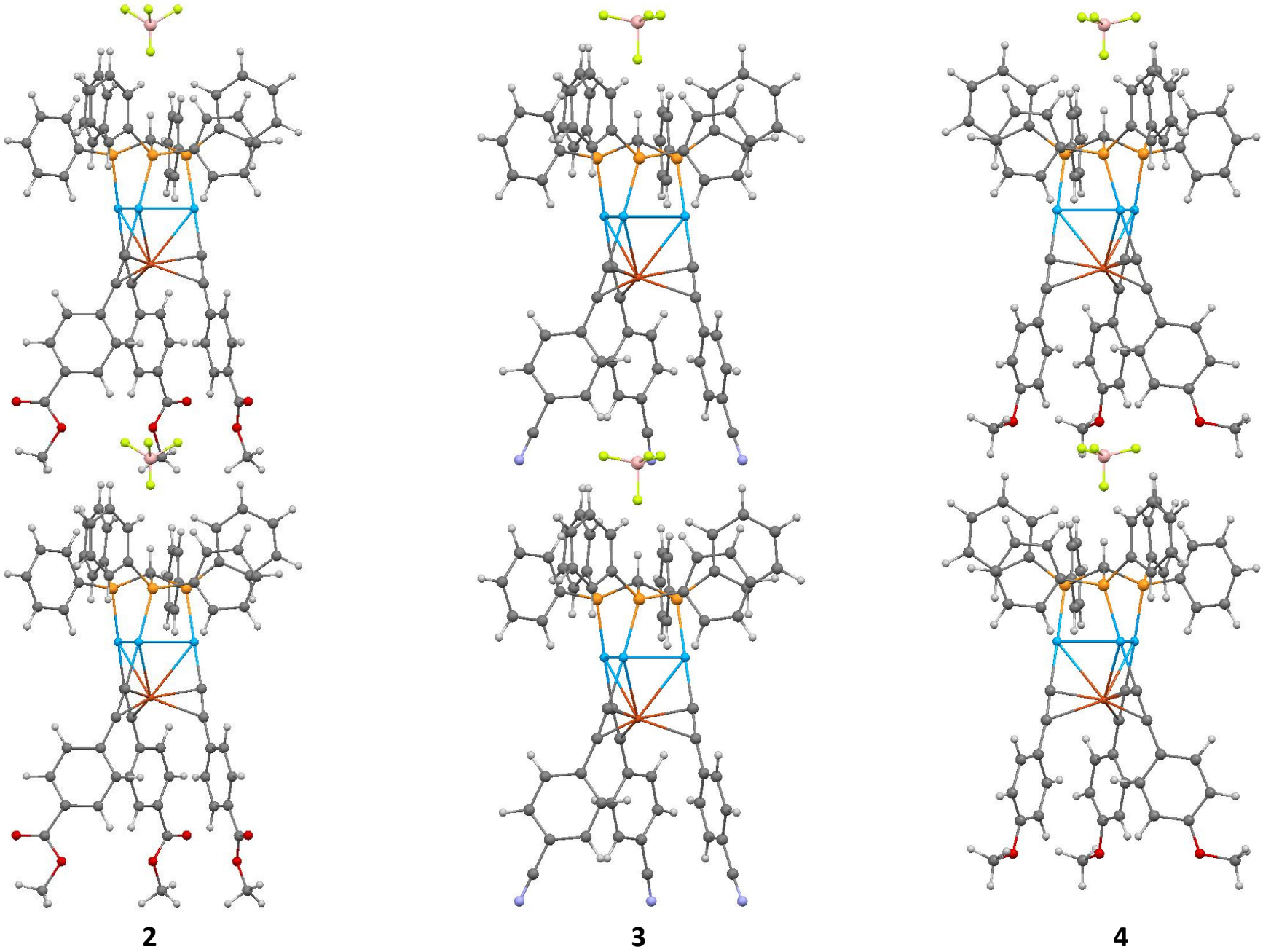

Figure S1. Column packing of the cluster molecule **2**-**4** in crystalline state.

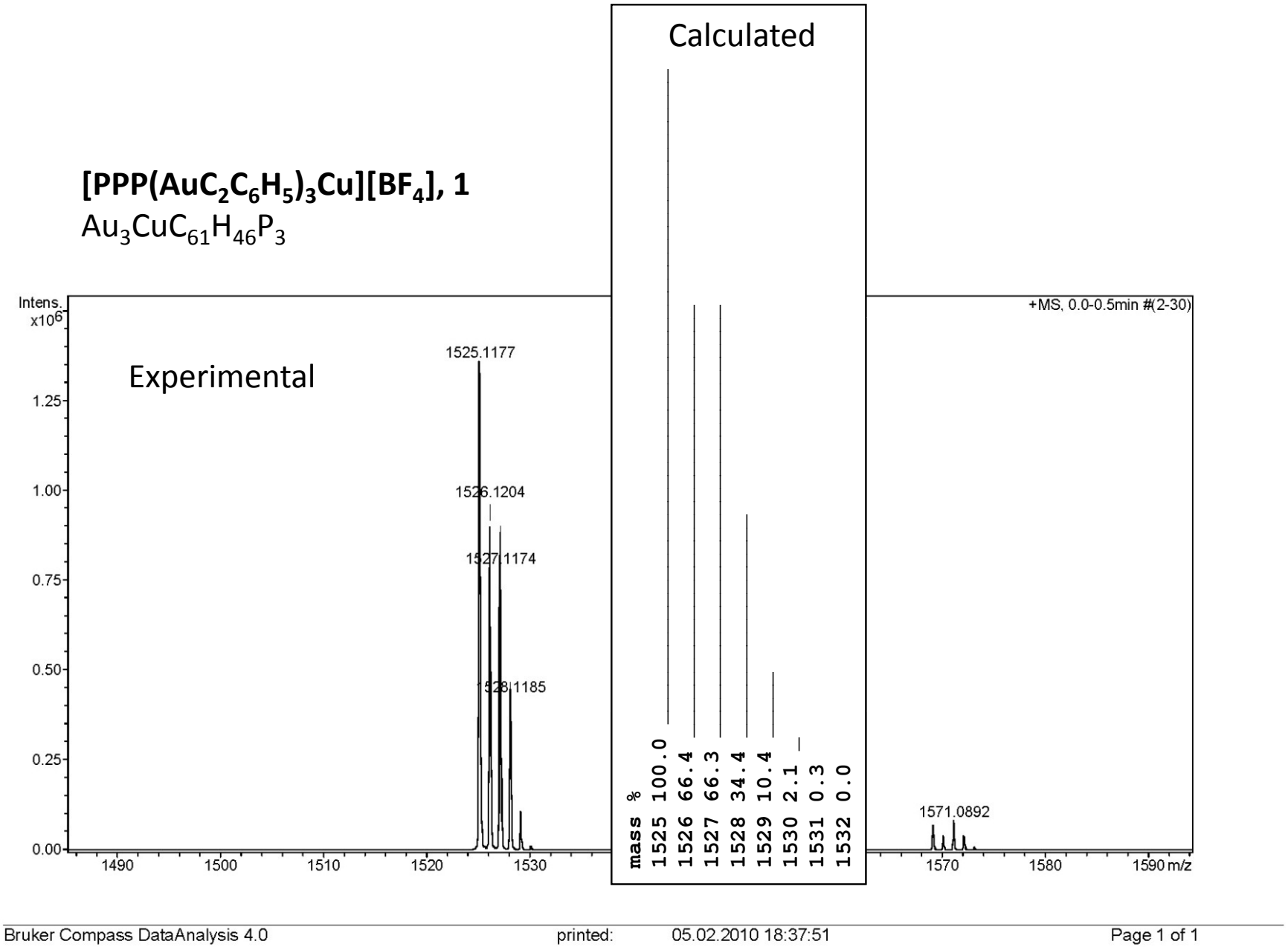

Figure S2. The ESI+ mass spectra of **1**.

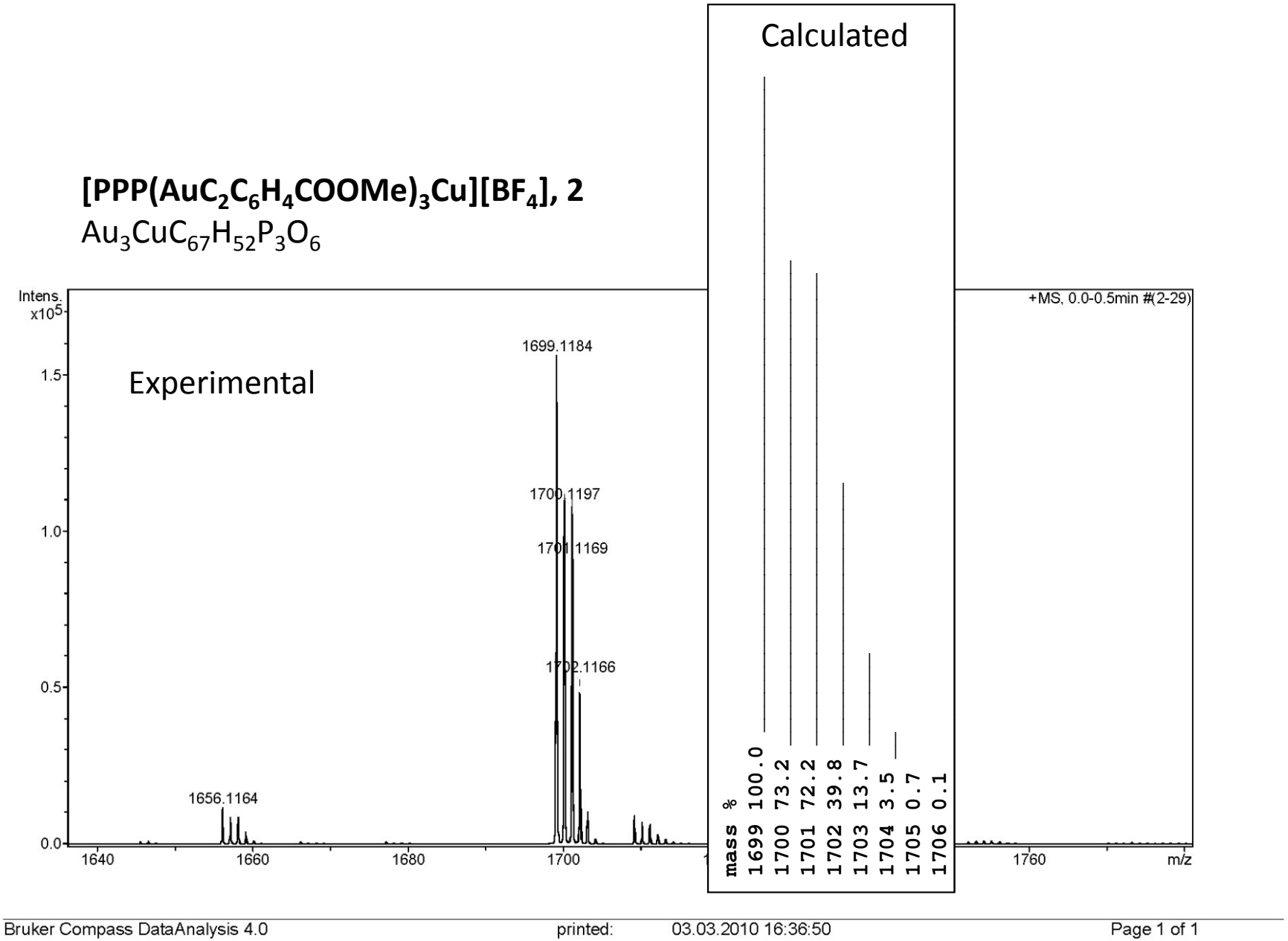

Figure S3. The ESI$^+$ mass spectra of **2**.

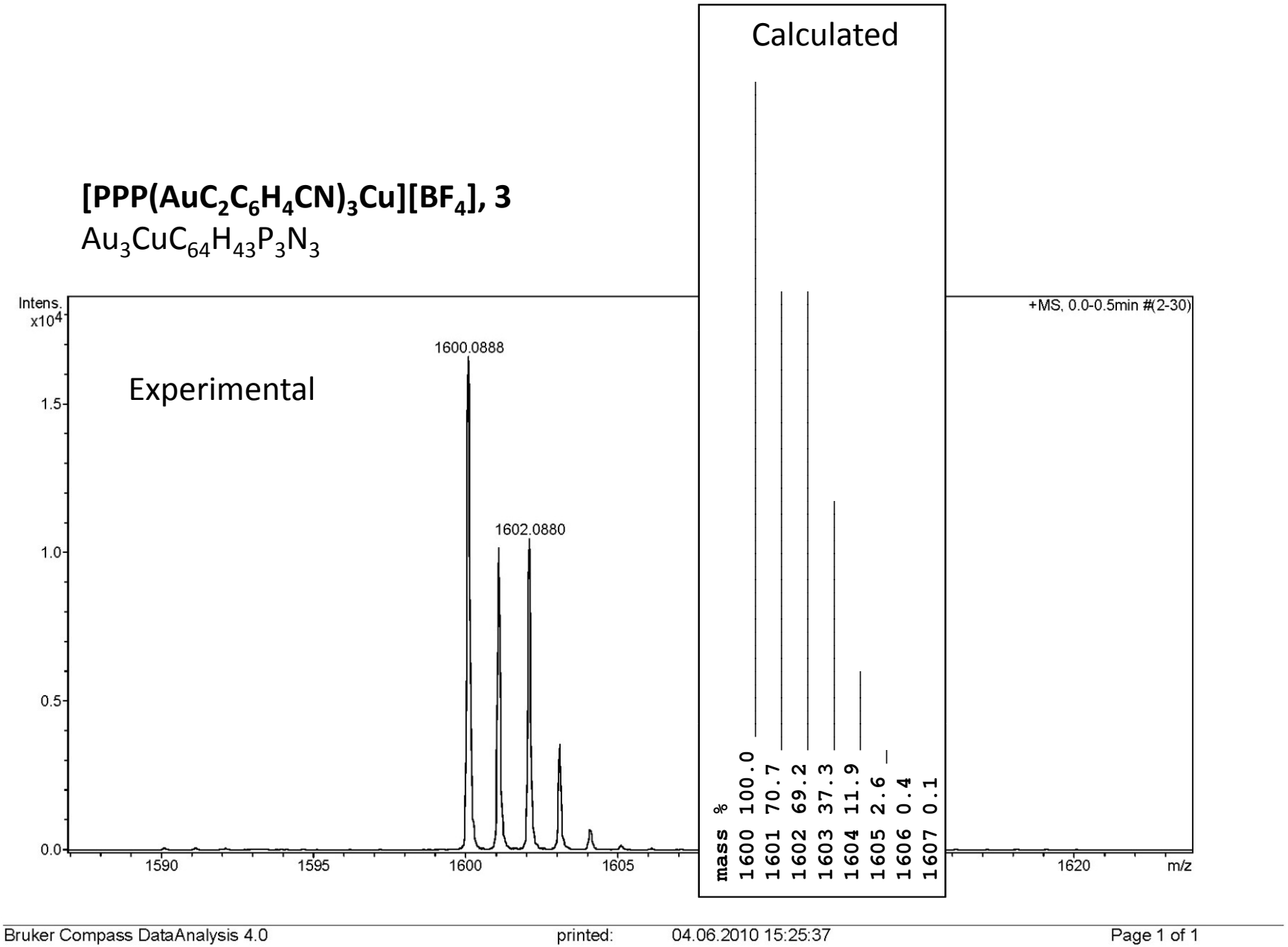

Figure S4. The ESI$^+$ mass spectra of **3**.

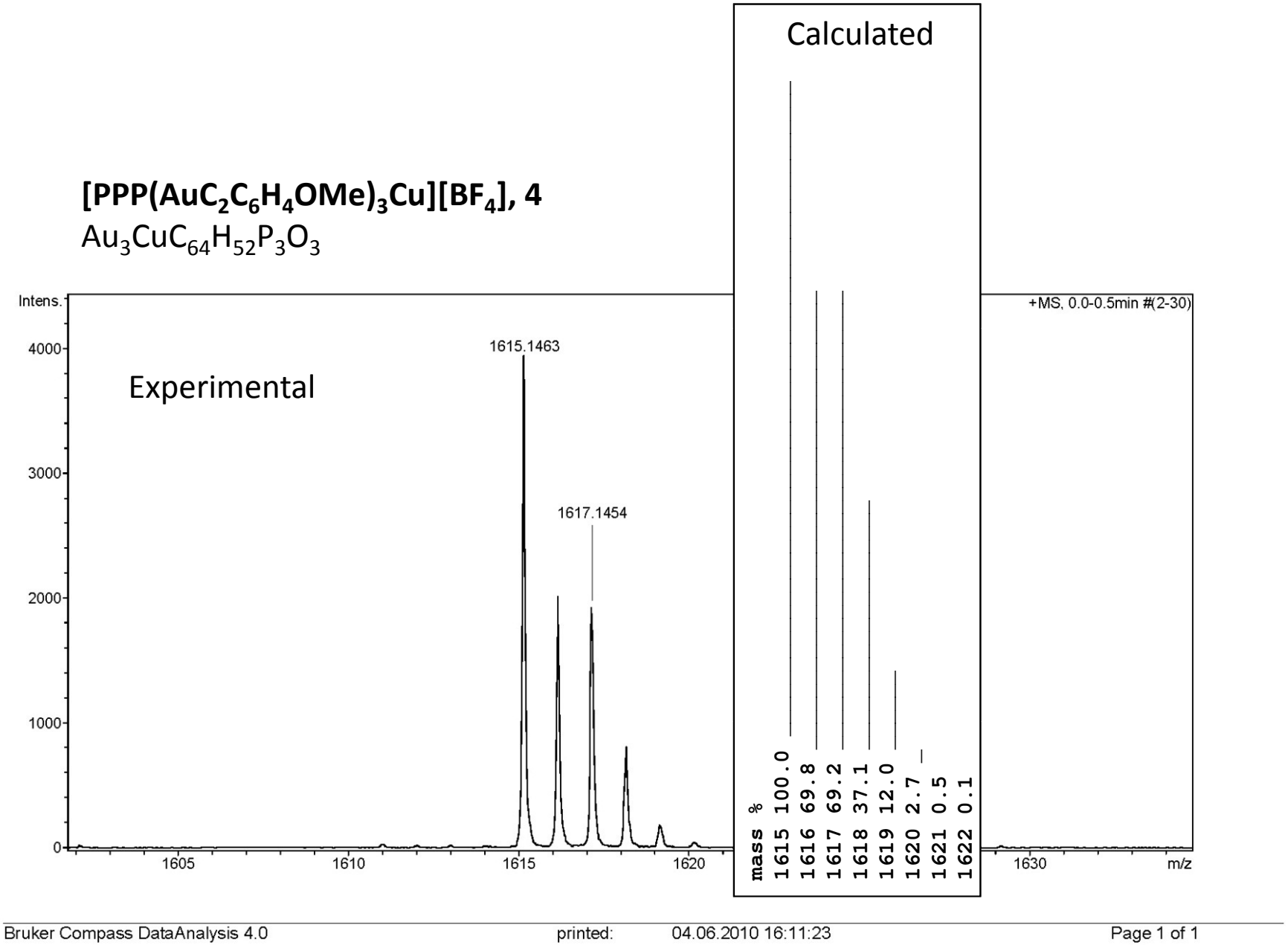

Figure S5. The ESI+ mass spectra of **4**.

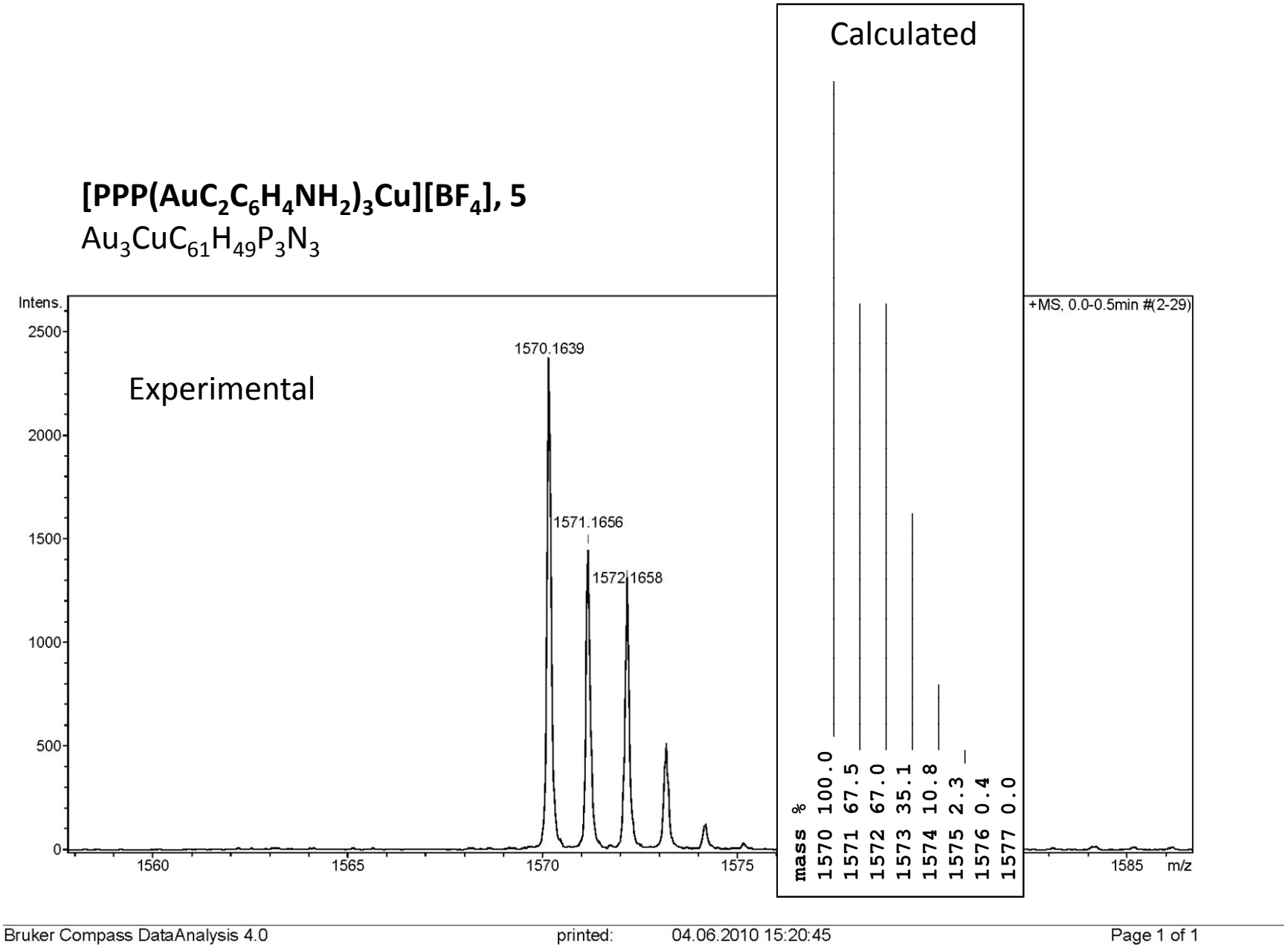

Figure S6. The ESI+ mass spectra of **5**.

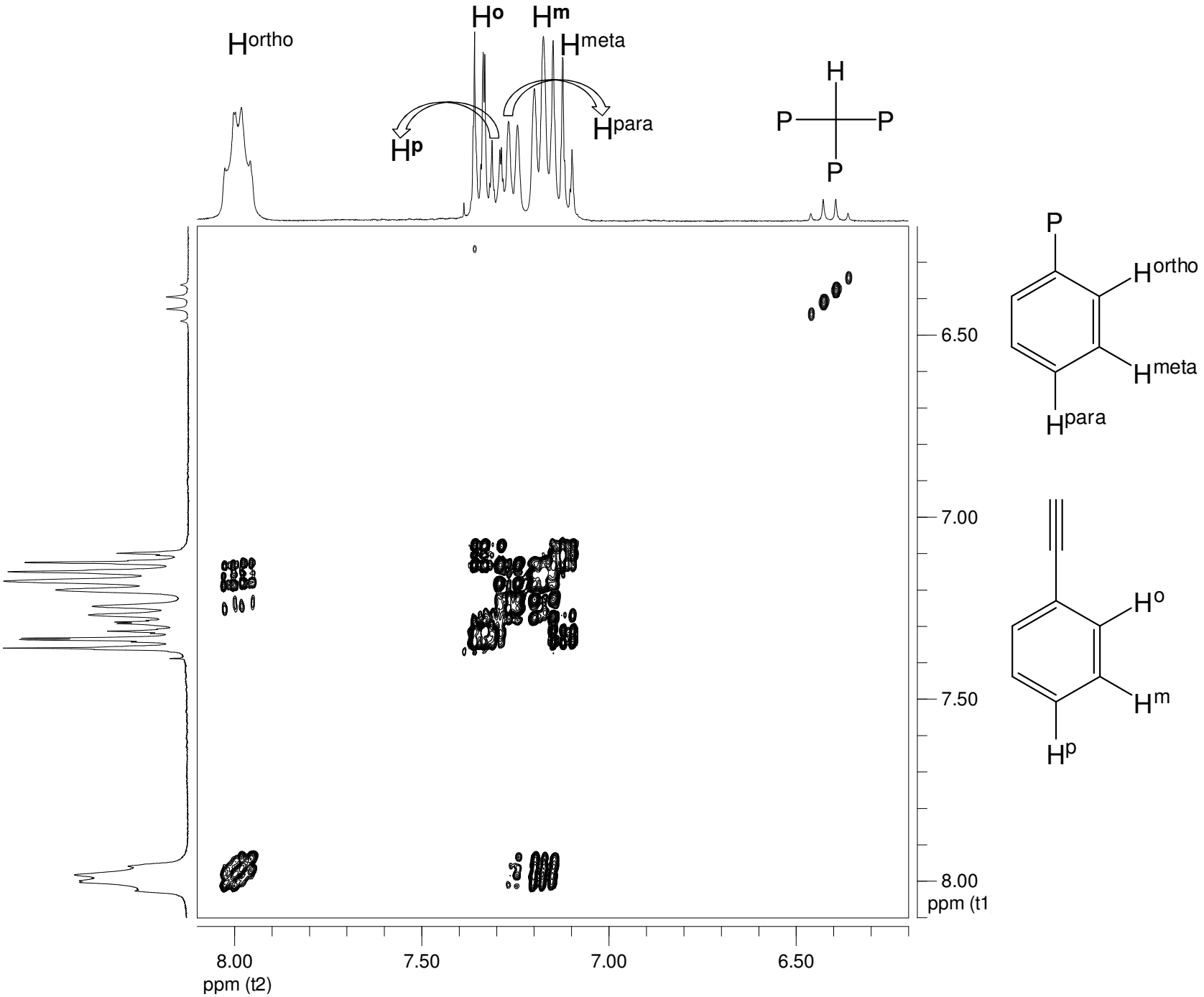

Figure S7. 300 MHz ^{1}H-^{1}H COSY NMR spectrum of **1** (aromatic range), CD_2Cl_2, ambient temperature. Assignment of the signals is given in the upper part of the figure.

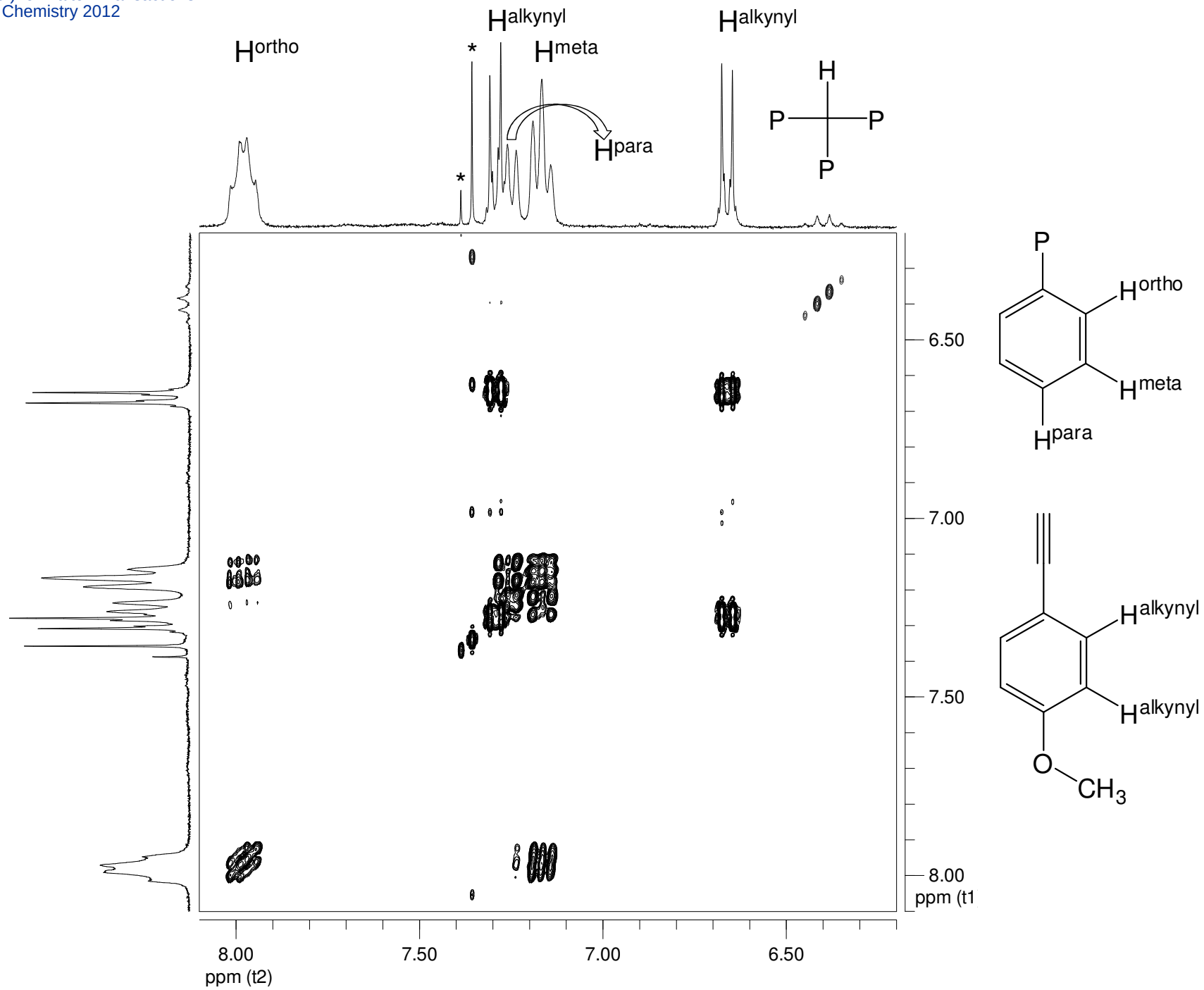

Figure S8. 300 MHz ^{1}H-^{1}H COSY NMR spectrum of **4** (aromatic range), CD_2Cl_2, ambient temperature. Assignment of the signals is given in the upper part of the figure. Resonances of admixtures are marked with *.

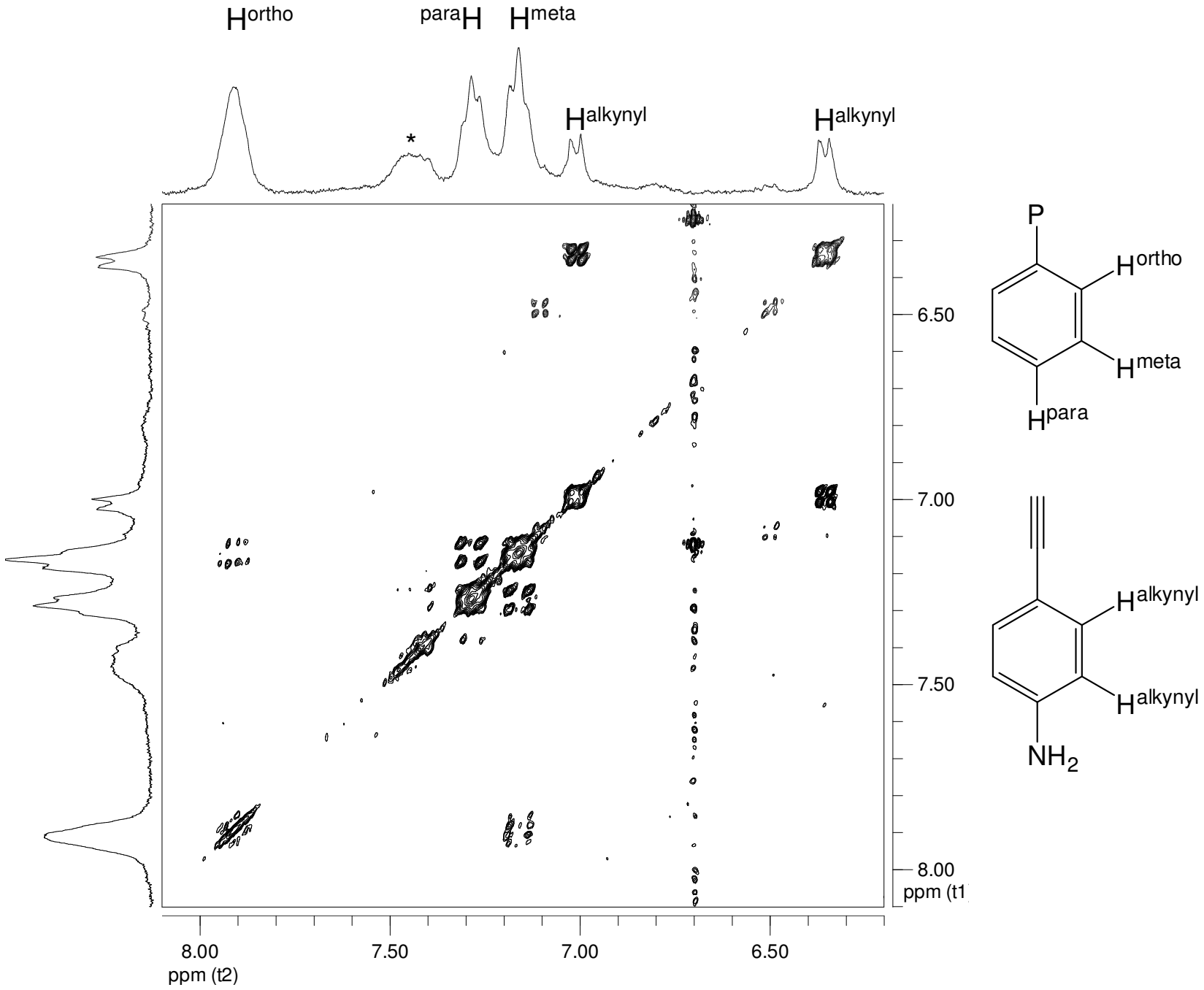

Figure S9. 300 MHz ^{1}H-^{1}H COSY NMR spectrum of **5** (aromatic range), $(CD_3)_2SO$, ambient temperature. Assignment of the signals is given in the upper part of the figure. Resonances of admixtures are marked with *.

Complex	**3**	**5**	**3a**
Number of atoms	117	120	116
Electron number	568	556	550
Basis function number	1222	1192	1186

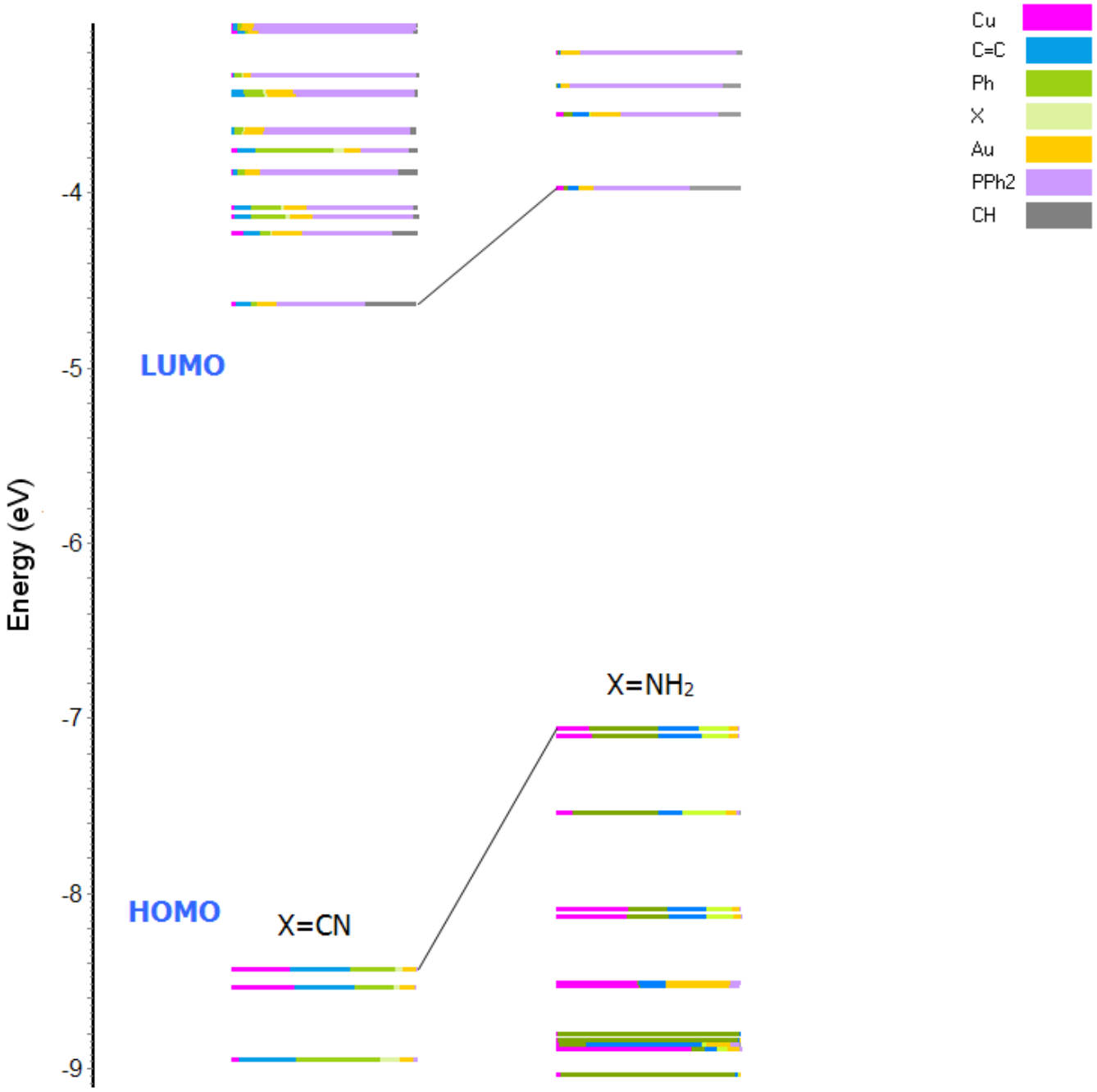

Figure S10. Diagram of the selected Kohn-Sham molecular orbitals for the complexes **3** (left) and **5** (right).

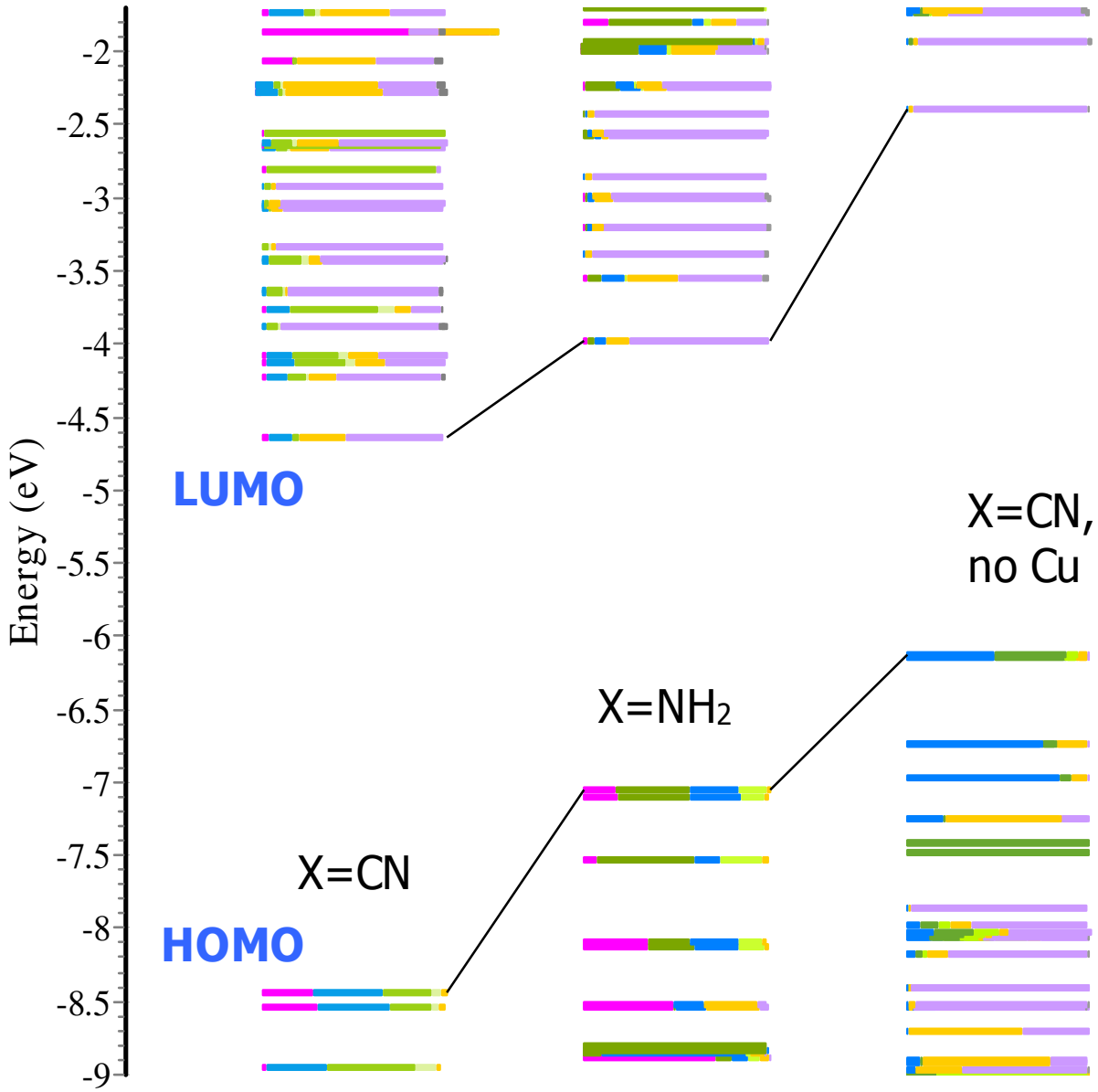

Figure S11. Diagram of the selected Kohn-Sham molecular orbitals for the complexes **3** (left), **5** (center), and **3a** (right).

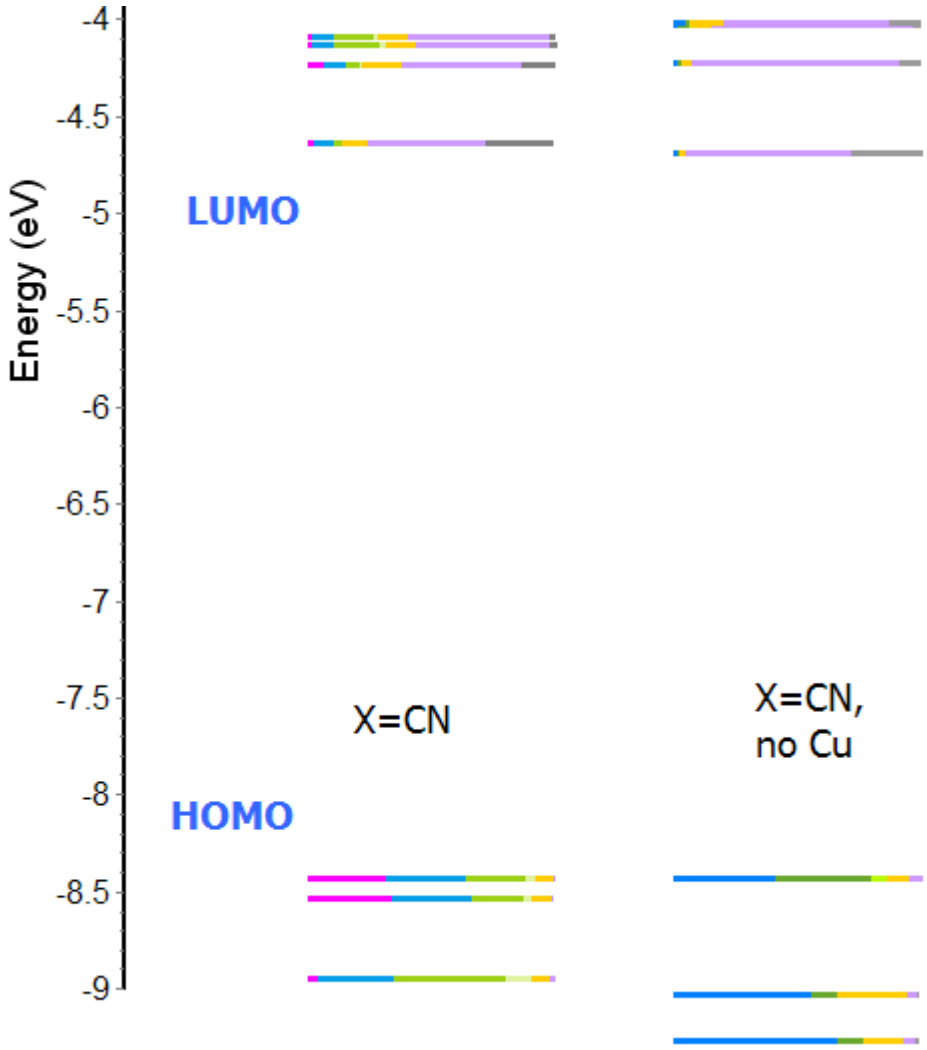

Figure S12. Diagram of the selected Kohn-Sham molecular orbitals for the complexes **3** (left) and **3a** (right).

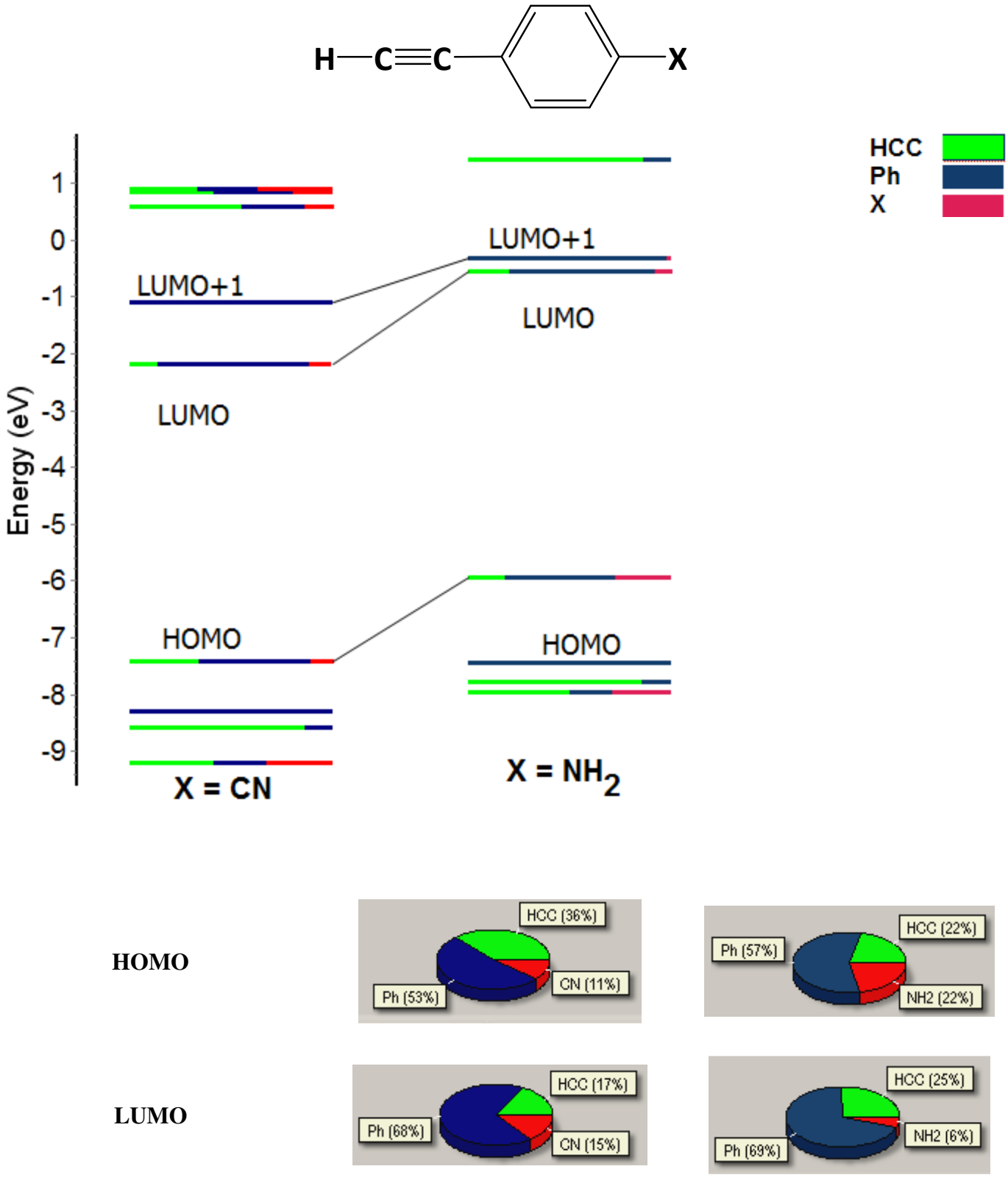

Figure S13. Diagram of the selected Kohn-Sham molecular orbitals for the alkynyl ligands $HC_2C_6H_4CN$ (left) and $HC_2C_6H_4NO_2$ (right).

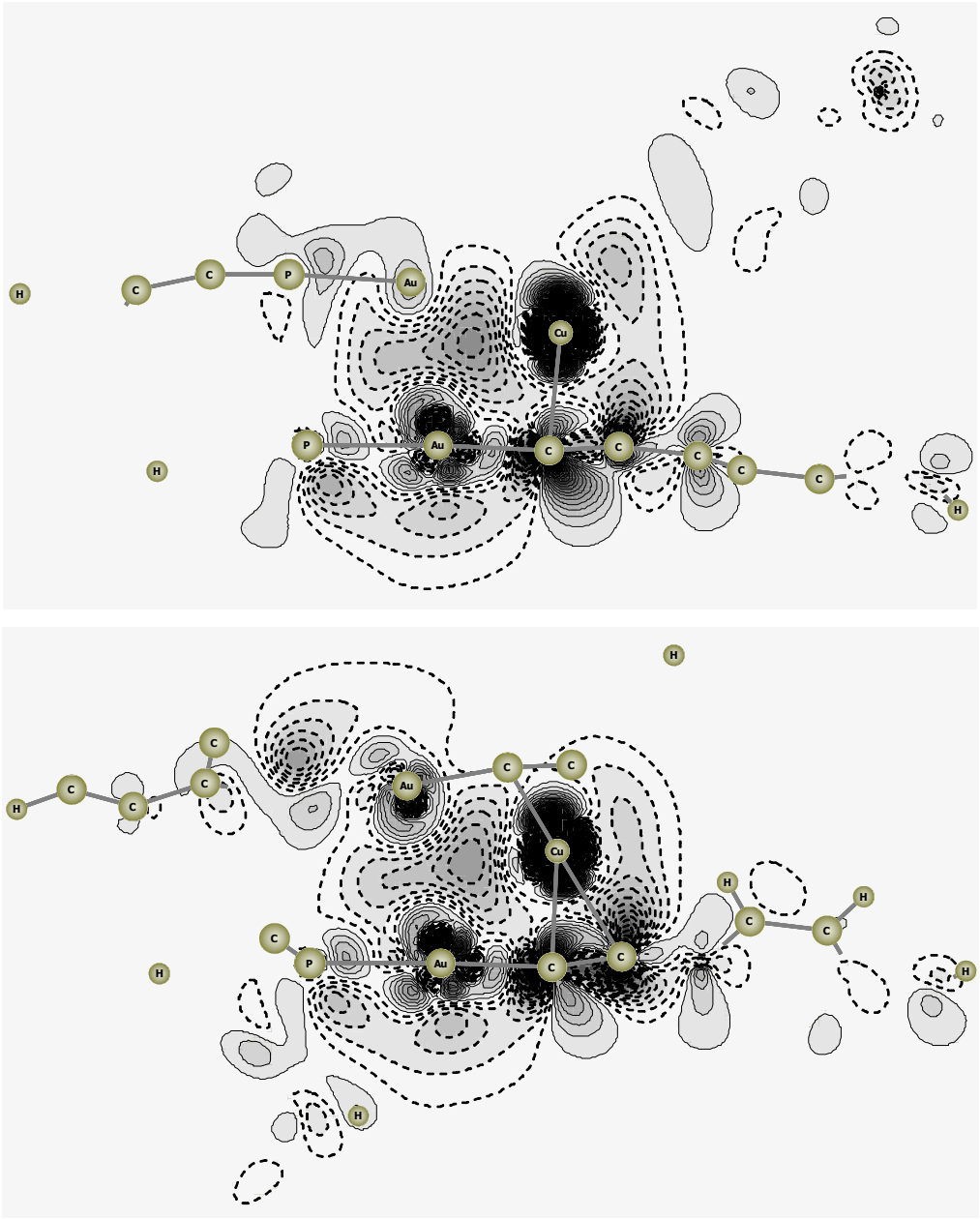

Figure S14. Contour project the deformation of electron density $\rho(S_0) - \rho(T_1)$ into a plane P–Au–Cu for the complexes **3** (top) and **5** (bottom); optimized T_1 geometry. Solid lines (plus sign) enclose the regions where the electron density is higher in the S_0 state, dashed lines (minus sign) show the regions, in which the electron density is higher in the T_1 state. The atoms located close to the cross-section plane are also shown.

Table S7. Energies and Mulliken composition of frontier KS molecular orbitals of **3, 5** and **3a** (%).

		ε, eV	**Cu**	**3{C≡C}**	**3{C_6H_4}**	**3{X}**	**3{Au}**	**3{PPh_2}**
HOMO	**3a**	–6.13	-	48	39	7	5	-
	3	–8.43	28	38	26	5	3	-
	5	–7.06	17	26	40	14	1	-
LUMO	**3a**	–2.40	-	-	-	-	3	90
	3	–4.64	4	13	5	-	25	53
	5	–3.97	1	6	-	-	13	75

Table S8. Selected Wiberg bond indices (symbols C1 and C2 denote the carbon atoms of {–C≡C–} fragments).

Complex	**State**	**Au–Au**	**Au–Cu**	**Au–C1**	**Au–P**	**Cu–C1**	**Cu–C2**	**C1≡C2**
3	**S_0(S_0)**	0.01	0.04	0.52	0.49	0.14	0.06	2.67
	T_1(T_1)	0.12	0.10	0.56	0.55	0.25	0.15	2.40
5	**S_0(S_0)**	0.01	0.04	0.53	0.49	0.14	0.06	2.67
	T_1(T_1)	0.13	0.13	0.56	0.57	0.27	0.09	2.42