Electronic Supplementary Information

Influence of perhalophenyl groups in the TADF mechanism of diphosphino gold(I) complexes

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I. Synthesis of [AuR(tht)] (R = *o*-C_6BrF_4, *p*-C_6BrF_4, *o*-C_6F_4I, *p*-C_6F_4I; tht = tetrahydrothiophene)

To a solution of 5 mmol (R=*o*-C_6F_4I, *p*-C_6F_4I) or 8 mmol (R = *o*-C_6BrF_4, *p*-$C6BrF_4$) of LiR in 100ml of diethyl ether at -78˚C was added the equimolecular amount of ClAu(tht). The reaction was stirred for 3 hours at -78˚C and after that, the mixture was allowed to warm to room temperature around 1 or 2 hours. The solid fraction was eliminated by filtration through celite and the filtrate was concentrate ca. 5ml giving rise to the precipitation of [AuR(tht)] (R = *o*-C_6BrF_4, *p*-C_6BrF_4, *o*-C_6F_4I, *p*-C_6F_4I) which was isolated by filtration. Another fraction of this complex can be obtained by addition of *n*-hexane to the diethyl ether solution and subsequent filtration. The complex [AuR(tht)] (R = *o*-C_6BrF_4, *p*-C_6BrF_4, *o*-C_6F_4I, *p*-C_6F_4I) is isolated as a white solid.

Experimental Data for:

[Au(*o*-C_6BrF_4)(tht)]. ^1H (298 K, toluene-*d*$_8$): δ 2.42 (m, 4H, H_1), 1.28 (m, 4H, H_2). ^{19}F (298, toluene-*d*$_8$): δ -115.41 (dd, 4F, F_1) ($^3J(F_1\text{-}F_2)$ = 30.4 Hz, $^5J(F_1\text{-}F_4)$ = 12.3 Hz), δ -156.66 (ddd, 4F, F_2) ($^3J(F_2\text{-}F_1)$ = 30.4 Hz, $^4J(F_2\text{-}F_3)$ = 19.2 Hz), $^4J(F_2\text{-}F_4)$ = 1.6 Hz), δ -157.45 (dd, 4F, F_3) ($^3J(F_3\text{-}F_4)$ = 21.3 Hz, $^4J(F_3\text{-}F_2)$ = 19.2 Hz), δ -126.43 (ddd, 4F, F_4) ($^3J(F_4\text{-}F_3)$ = 21.3 Hz, $^5J(F_4\text{-}F_1)$ = 13.9 Hz), $^4J(F_4\text{-}F_2)$ = 1.6 Hz). MS(ESI-): *m/z* 652.83 [Au(*o*-C_6BrF_4)$_2$]$^-$. ESI(+) *m/z* 373.02 [Au(C_4H_8S)]$^+$. ATR-IR: ν 1614, 1596, 1082, 824 cm^{-1} (Au-(*o*-C_6BrF_4)).

[Au(*p*-C_6BrF_4)(tht)]. ^1H (298 K, toluene-*d*$_8$): δ 2.36 (m, 4H, H_1), 1.21 (m, 4H, H_2). ^{19}F (298, toluene-*d*$_8$): δ -114.55 (m, 4F, F_1), δ -134.61 (m, 4F, F_2). MS(ESI-): *m/z* 652.84 [Au(*p*-C_6BrF_4)$_2$]$^-$. ESI(+) *m/z* 373.02 [Au(C_4H_8S)]$^+$. ATR-IR: ν 1578, 1532, 1075, 764 cm^{-1} (Au-(*p*-C_6BrF_4)).

[Au(*o*-C_6F_4I)(tht)]. ^1H (298 K, toluene-*d*$_8$): δ 2.46 (m, 4H, H_1), 1.32 (m, 4H, H_2). ^{19}F (298, toluene-*d*$_8$): δ -116.14 (dd, 4F, F_1) ($^3J(F_1\text{-}F_2)$ = 30.8 Hz, $^5J(F_1\text{-}F_4)$ = 12.8 Hz), δ -155.53 (ddd, 4F, F_2) ($^3J(F_2\text{-}F_1)$ = 30.8 Hz, $^4J(F_2\text{-}F_3)$ = 19.5 Hz), $^4J(F_2\text{-}F_4)$ = 2.0 Hz), δ -157.37 (dd, 4F, F_3) ($^3J(F_3\text{-}F_4)$ = 22.4 Hz, $^4J(F_3\text{-}F_2)$ = 19.5 Hz), δ -111.87 (ddd, 4F, F_4) ($^3J(F_4\text{-}F_3)$ = 22.4 Hz, $^5J(F_4\text{-}F_1)$ = 12.8 Hz), $^4J(F_4\text{-}F_2)$ = 2.0 Hz). MS(ESI-): *m/z* 746.81 [Au(*o*-C_6F_4I)$_2$]$^-$. ESI(+) *m/z* 373.03 [Au(C_4H_8S)]$^+$. ATR-IR: ν 1578, 1606, 1589, 1083, 812 cm^{-1} (Au-(*o*-C_6F_4I))

[Au(*p*-C_6F_4I)(tht)]. ^1H (298 K, toluene-*d*$_8$): δ 2.37 (m, 4H, H_1), 1.22 (m, 4H, H_2). ^{19}F (298, toluene-*d*$_8$): δ -114.25 (m, 4F, F_1), δ -122.21 (m, 4F, F_2). MS(ESI-): *m/z* 746.82 [Au(*p*-C_6F_4I)$_2$]$^-$. ESI(+) *m/z* 373.02 [Au(C_4H_8S)]$^+$. ATR-IR: ν 1640, 1565, 1092, 874 cm^{-1} (Au-(*p*-C_6F_4I)).

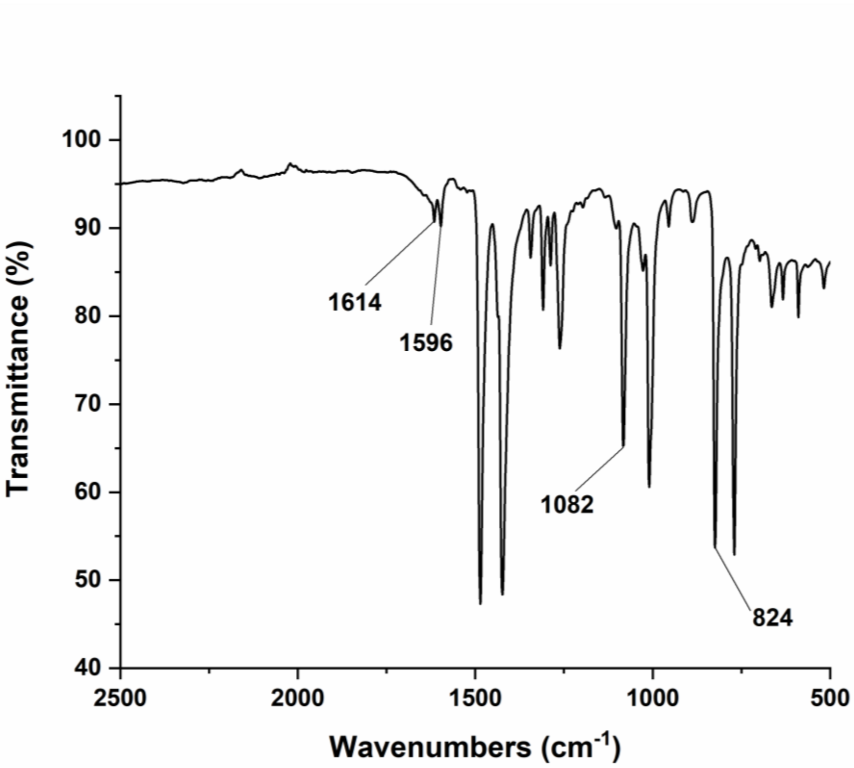

Figure S1. FT-IR spectrum of complex [Au(o-C_6BrF_4)(tht)].

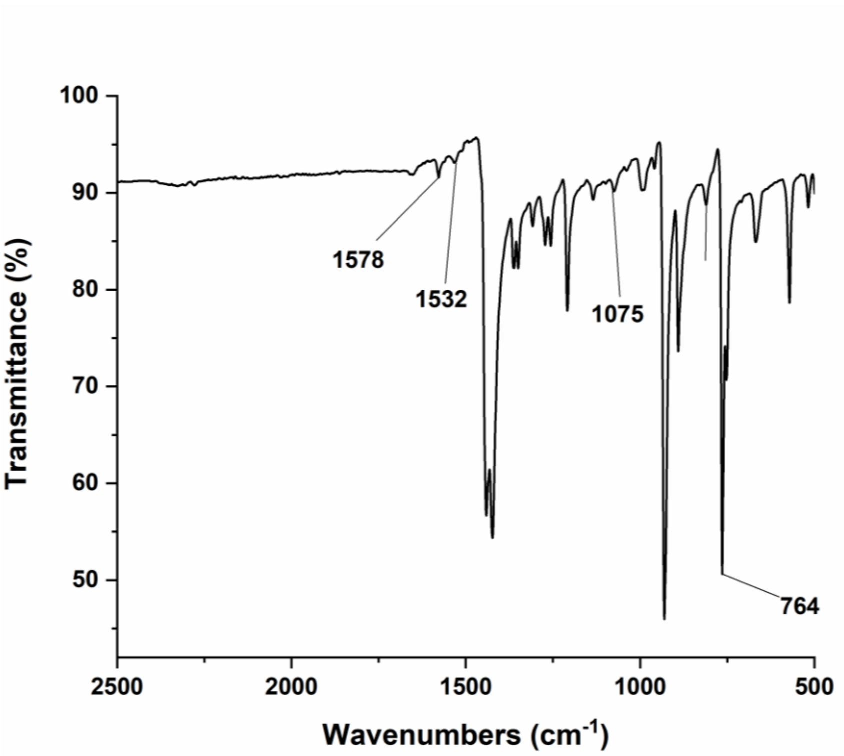

Figure S2. FT-IR spectrum of complex [Au(p-C_6BrF_4)(tht)].

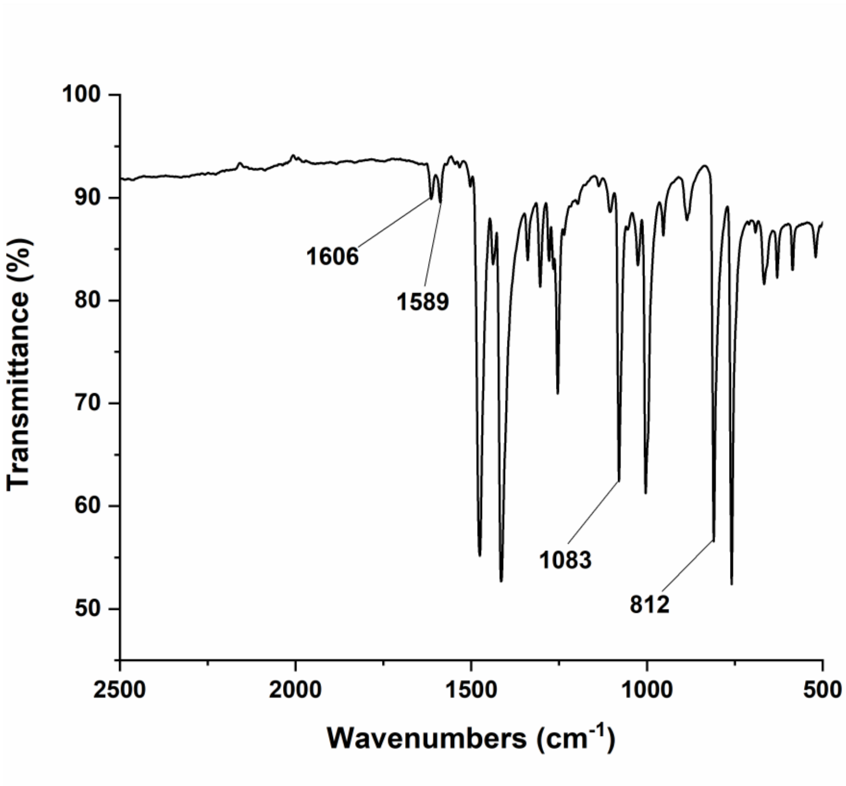

Figure S3. FT-IR spectrum of complex [Au(o-C_6F_4I)(tht)].

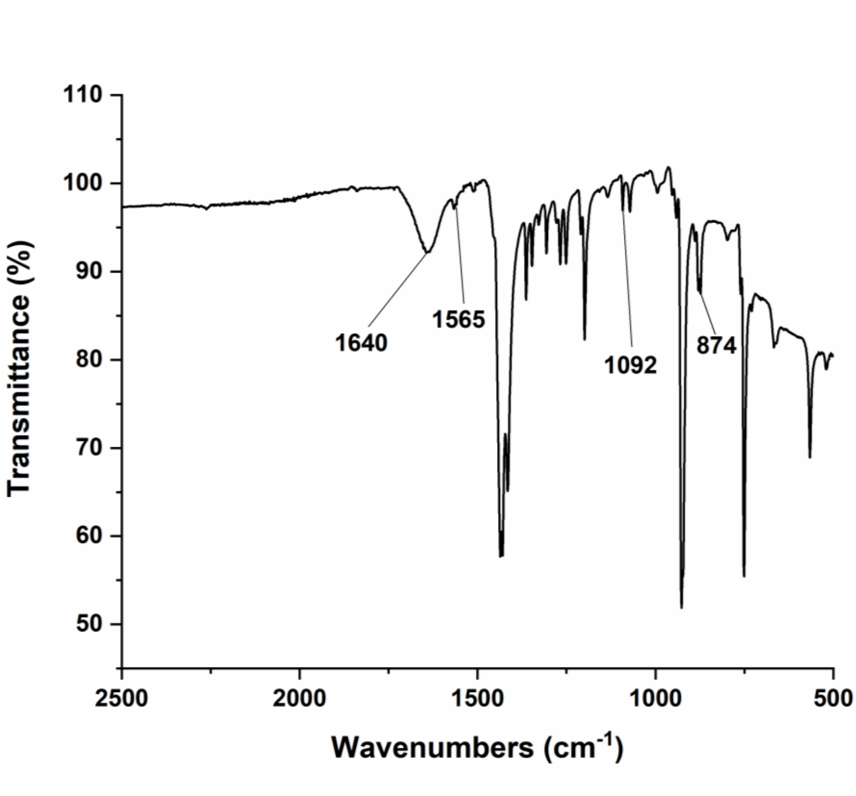

Figure S4. FT-IR spectrum of complex [Au(p-C_6F_4I)(tht)].

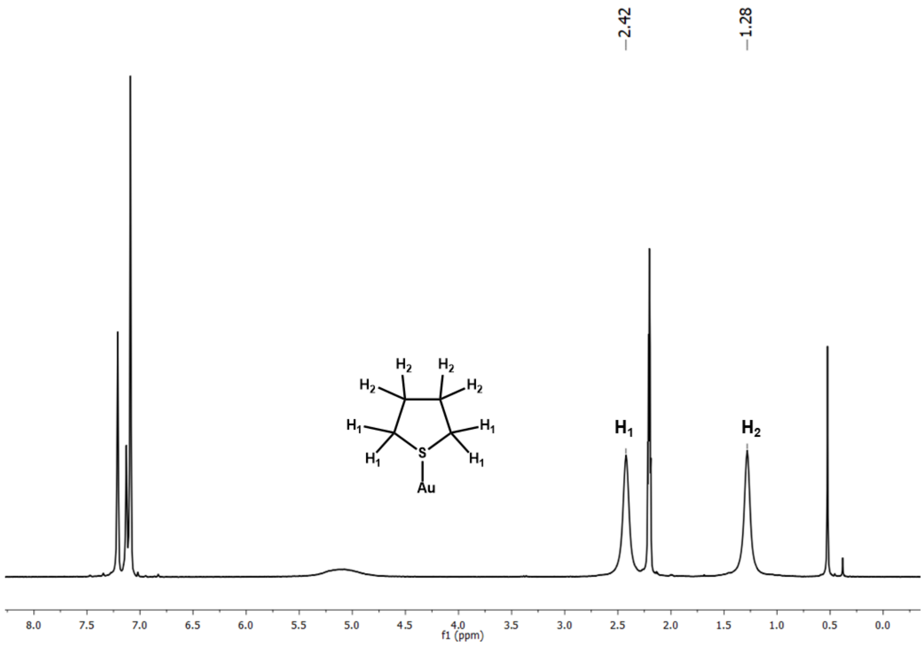

Figure S5. ^{1}H NMR spectrum of complex [Au(*o*-C_6BrF_4)(tht)] in toluene-d8

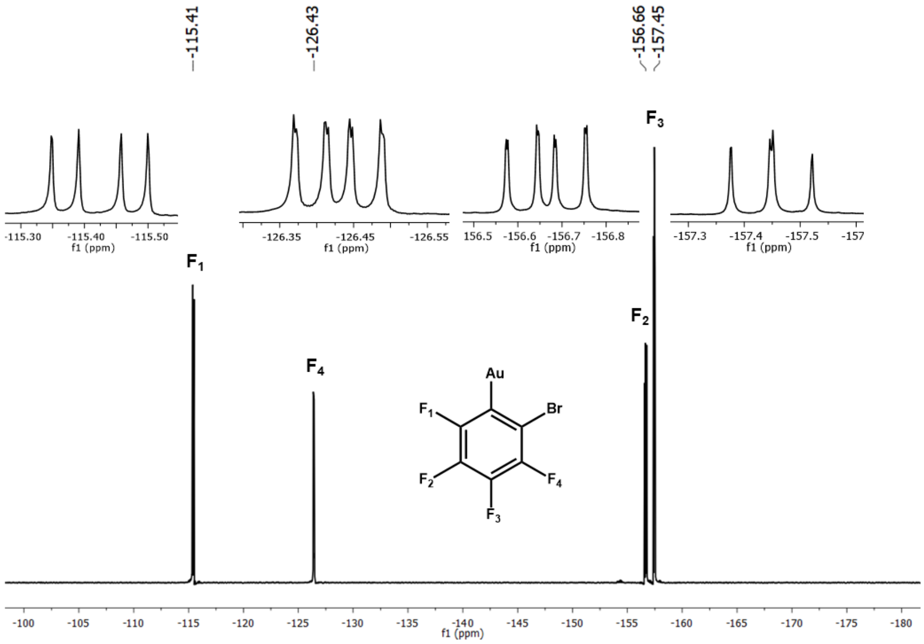

Figure S6. ^{19}F NMR spectrum of complex [Au(*o*-C_6BrF_4)(tht)] in toluene-d8

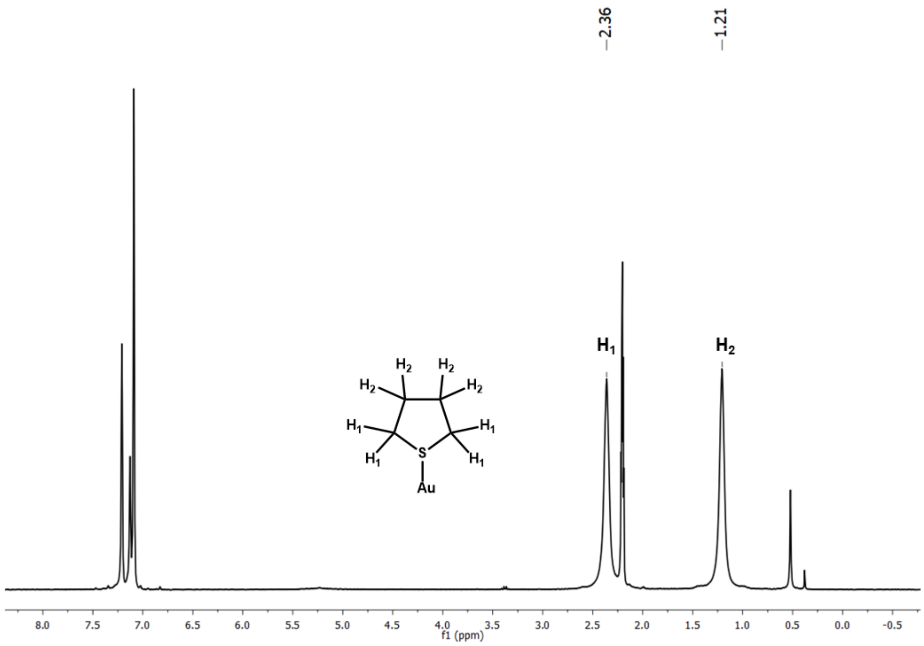

Figure S7. ^{1}H NMR spectrum of complex [Au(p-C_6BrF_4)(tht)] in toluene-d8

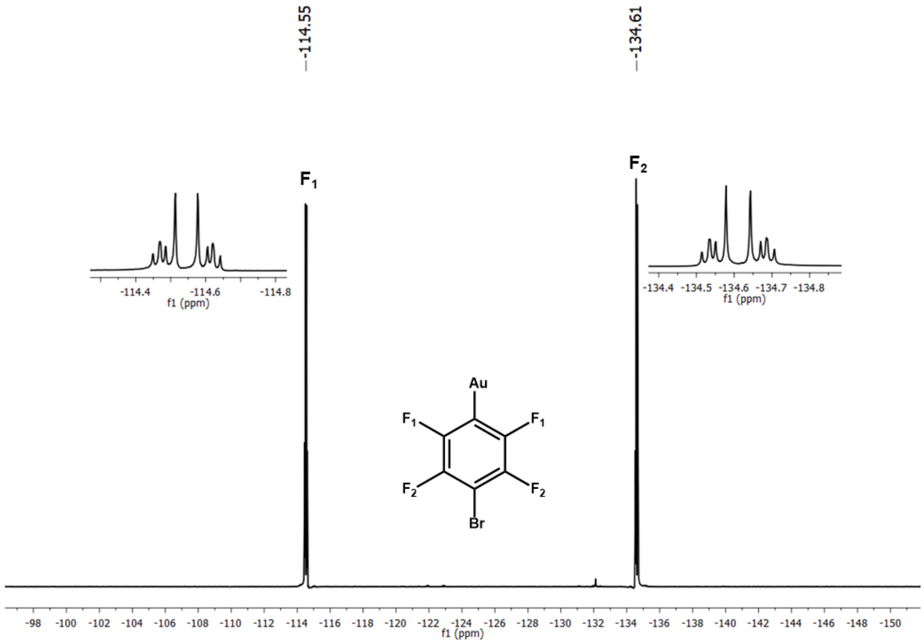

Figure S8. ^{19}F NMR spectrum of complex [Au(p-C_6BrF_4)(tht)] in toluene-d8

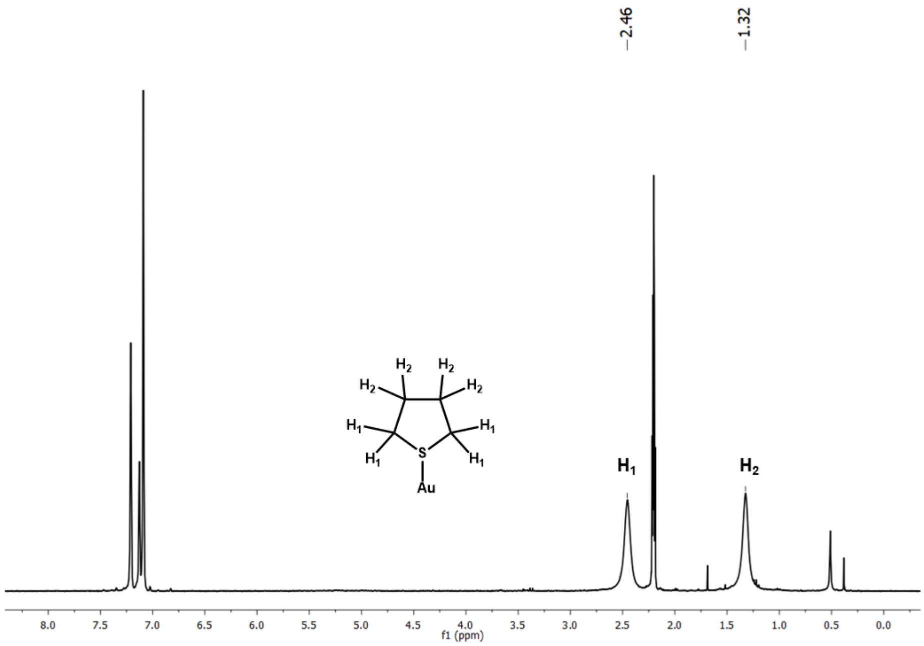

Figure S9. ^{1}H NMR spectrum of complex [Au(o-C_6F_4I)(tht)] in toluene-d8

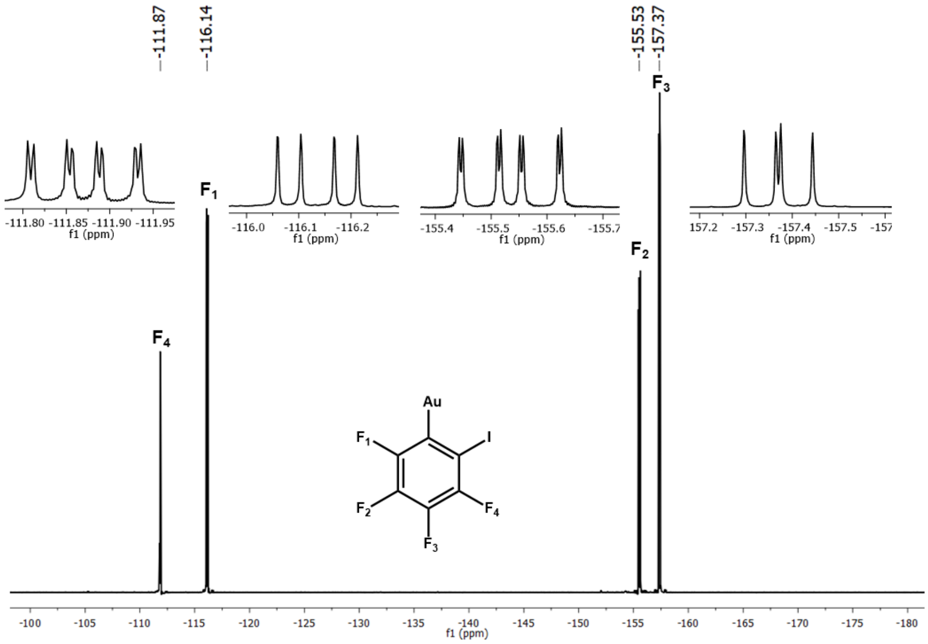

Figure S10. ^{19}F NMR spectrum of complex [Au(o-C_6F_4I)(tht)] in toluene-d8

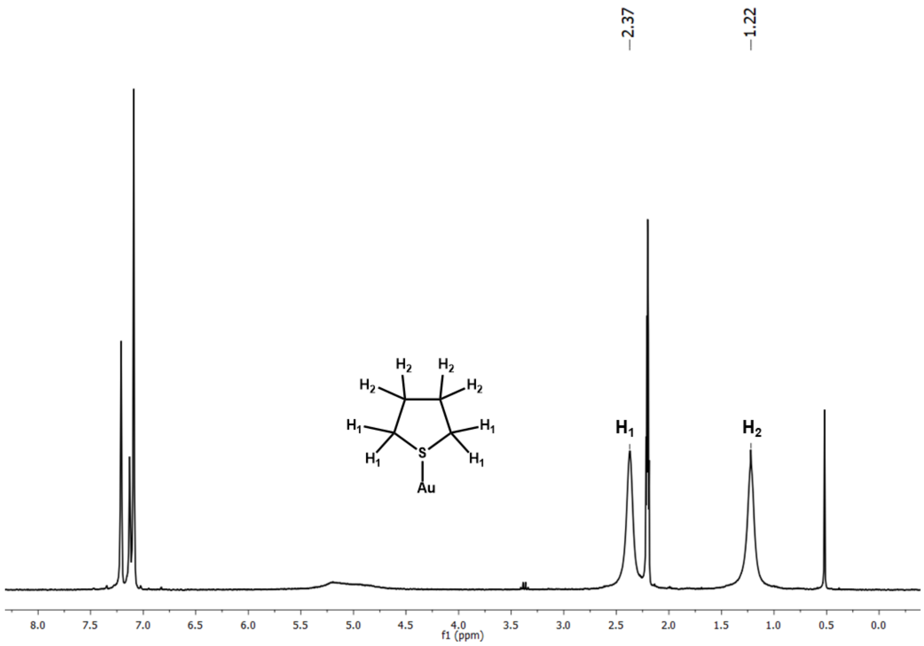

Figure S11. ^{1}H NMR spectrum of complex [Au(p-C_6F_4I)(tht)] in toluene-d8

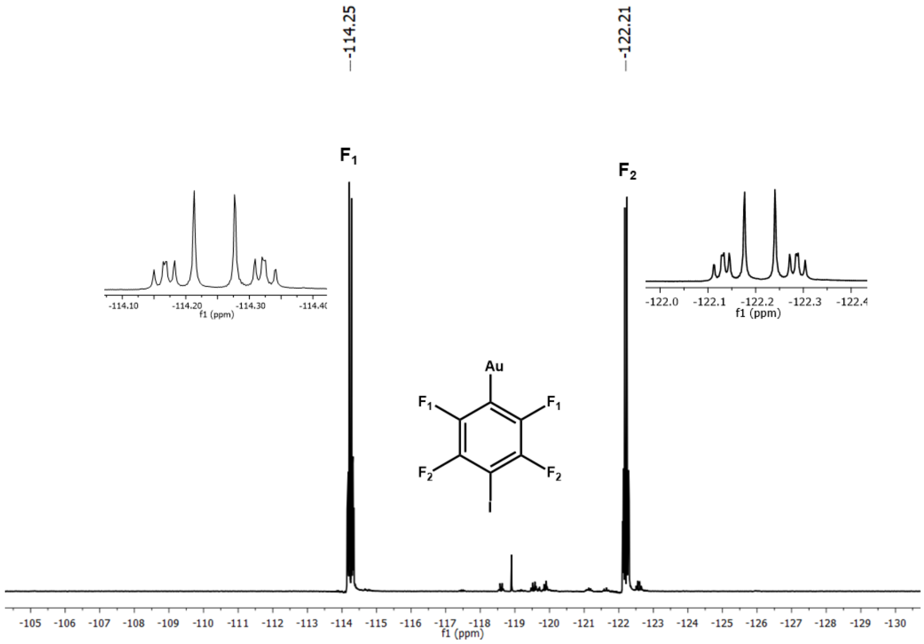

Figure S12. ^{19}F NMR spectrum of complex [Au(p-C_6F_4I)(tht)] in toluene-d8

II. Characterization of complexes **2**-**5**

1. IR spectra

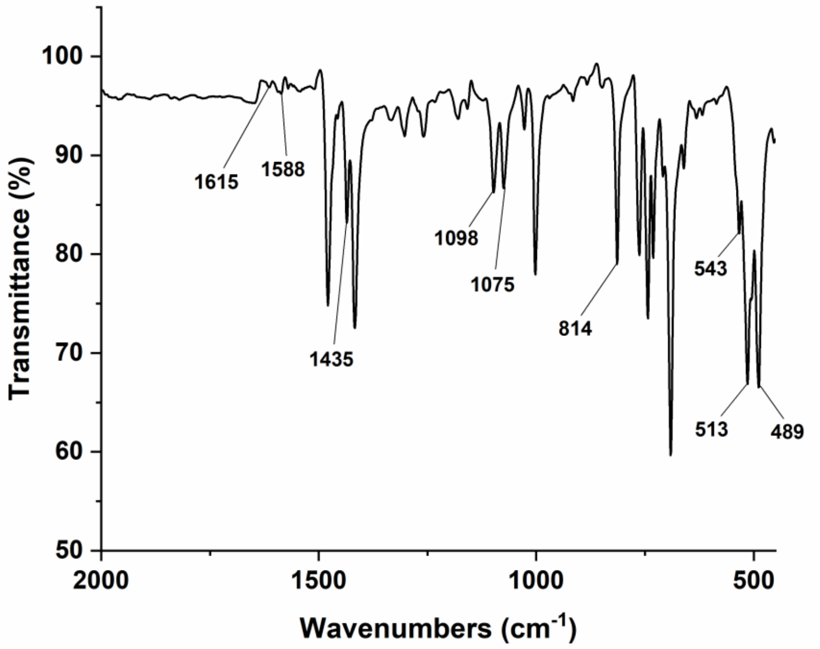

Figure S13. FT-IR spectrum of complex **2**.

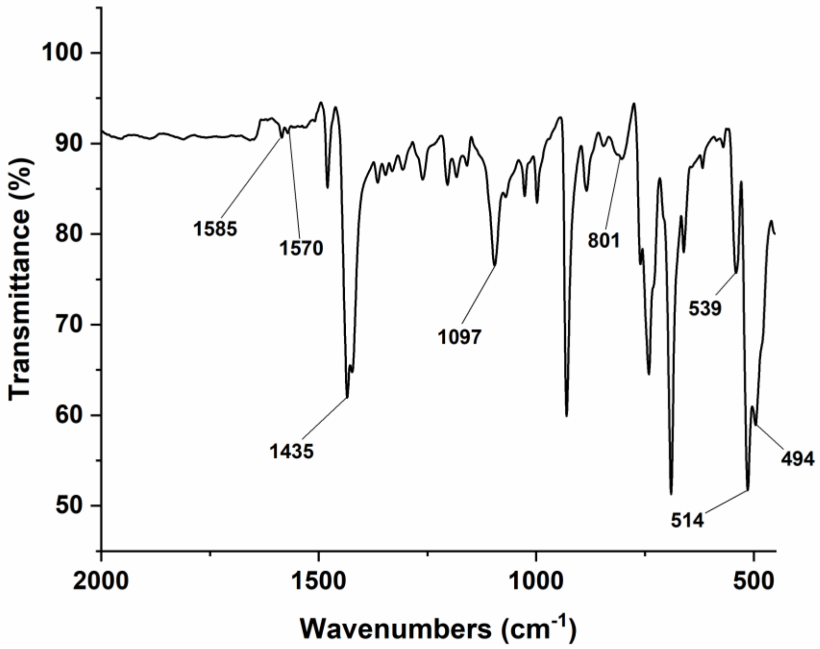

Figure S14. FT-IR spectrum of complex **3**.

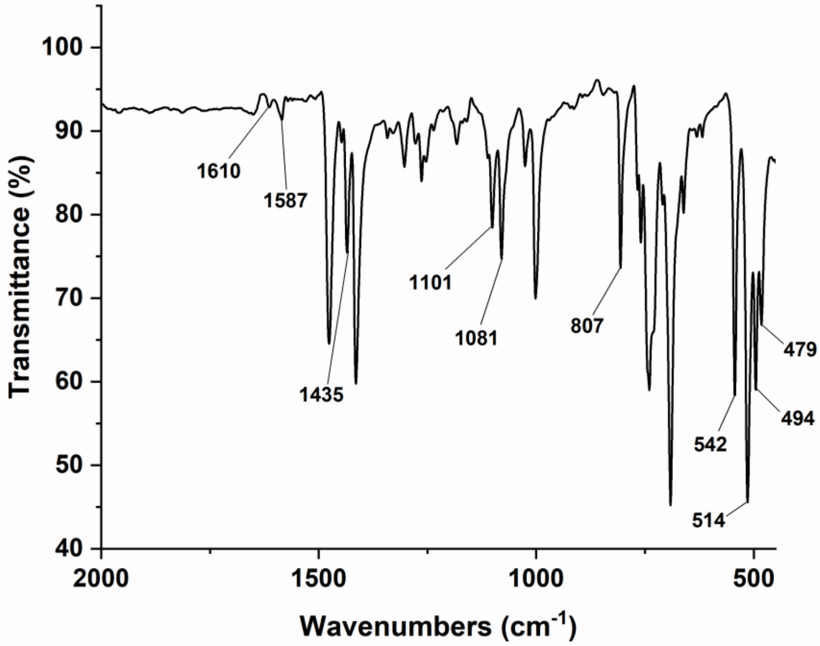

Figure S15. FT-IR spectrum of complex **4**.

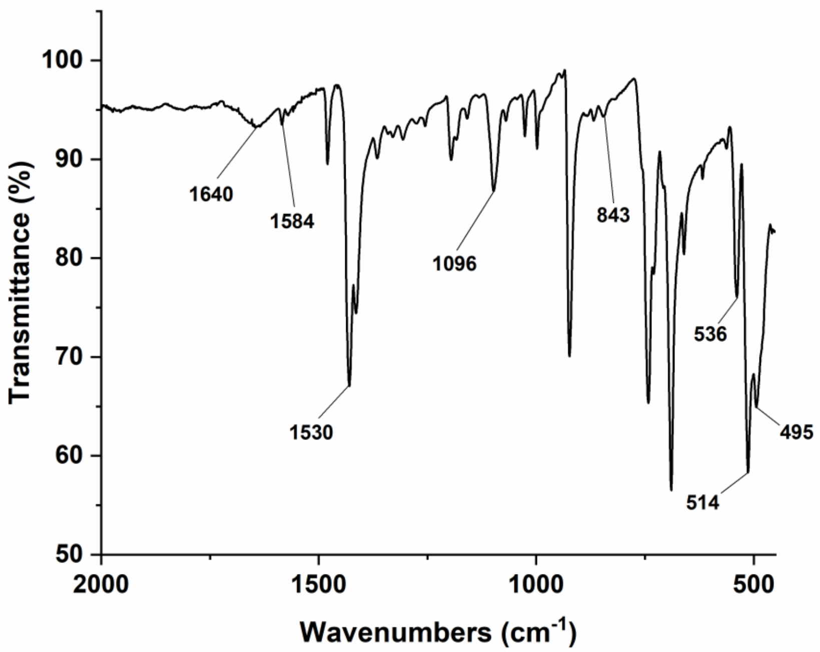

Figure S16. FT-IR spectrum of complex **5**.

2 TGA spectra of complexes **1**-**5**

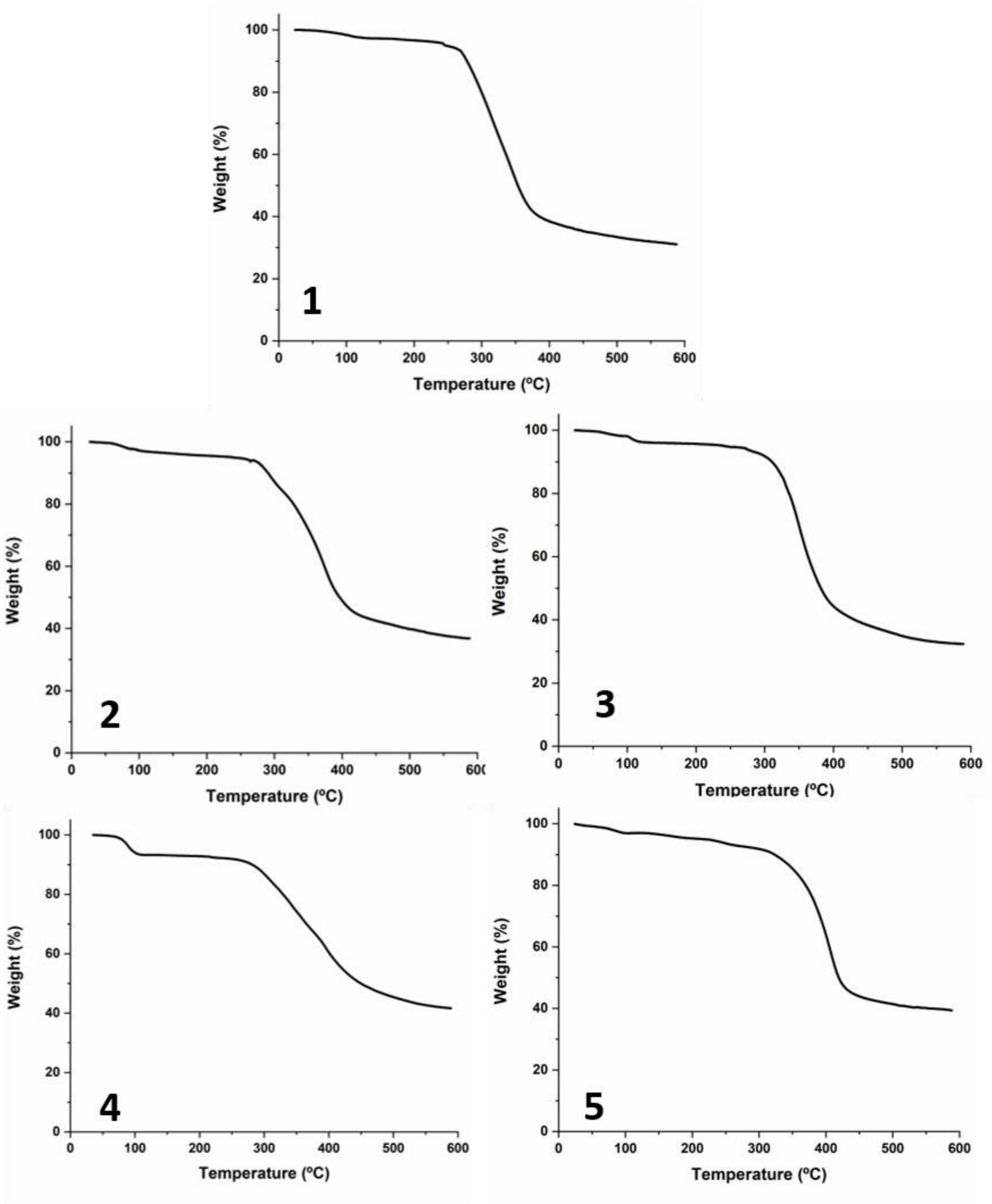

Figure S17. TGA spectra of complexes **1**-**5**.

3 ^{1}H NMR spectra (300 MHz, 298K)

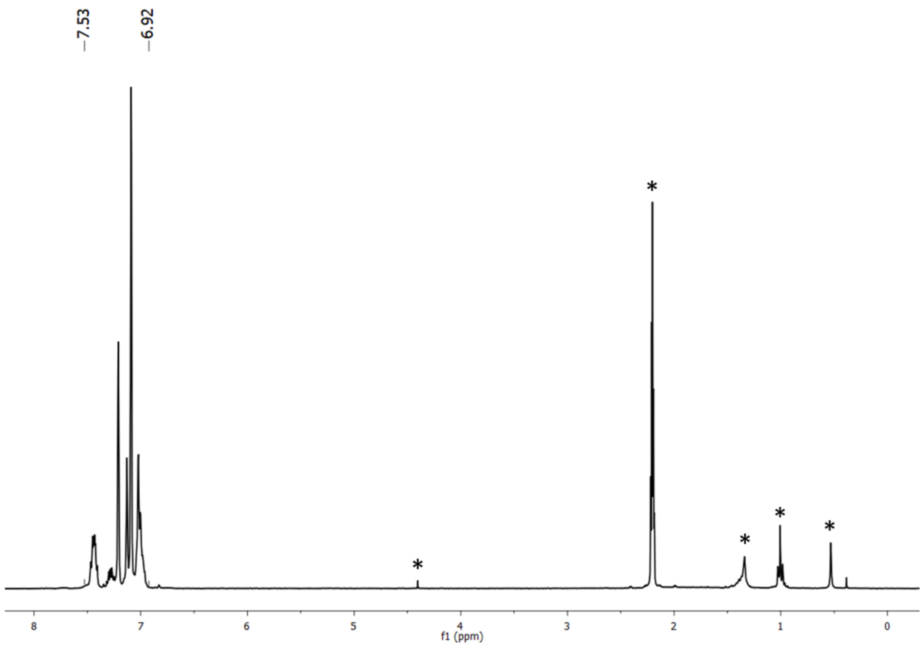

Figure S18. ^{1}H NMR spectrum of complex **2** in toluene-d8

(* Solvent residual peaks)

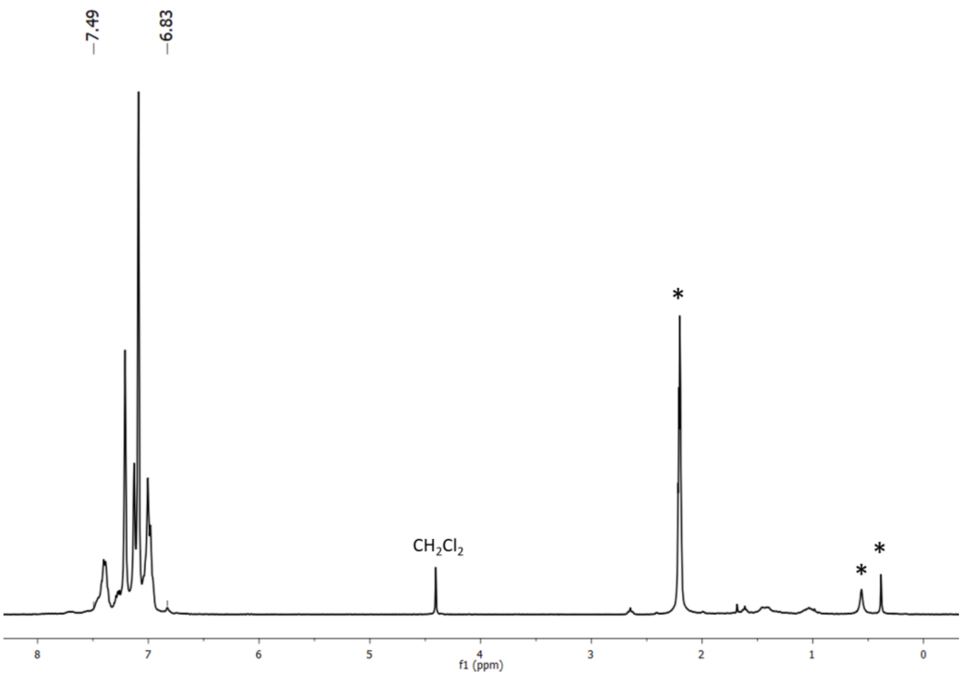

Figure S19. ^{1}H NMR spectrum of complex **3** in toluene-d8

(* Solvent residual peaks)

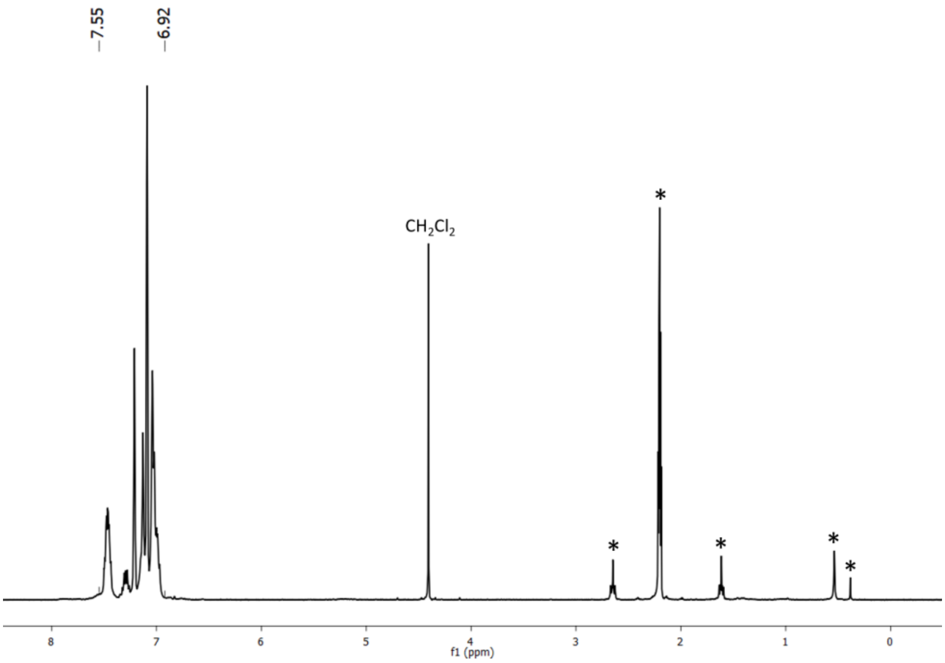

Figure S20. ^{1}H NMR spectrum of complex **4** in toluene-d8

(* Solvent residual peaks)

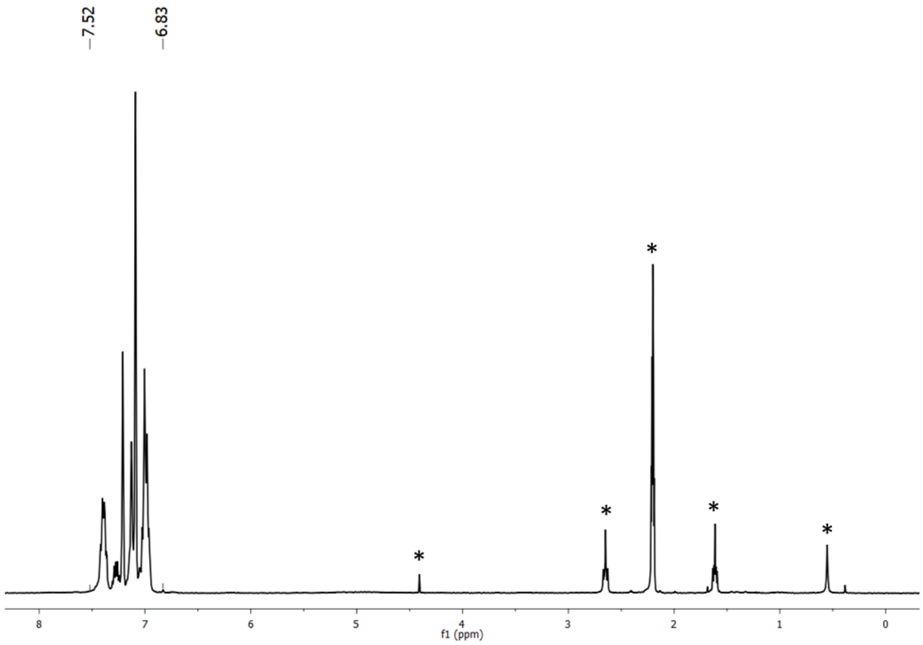

Figure S21. ^{1}H NMR spectrum of complex **5** in toluene-d8

(* Solvent residual peaks)

4 ^{19}F NMR spectra (282 MHz, 298K)

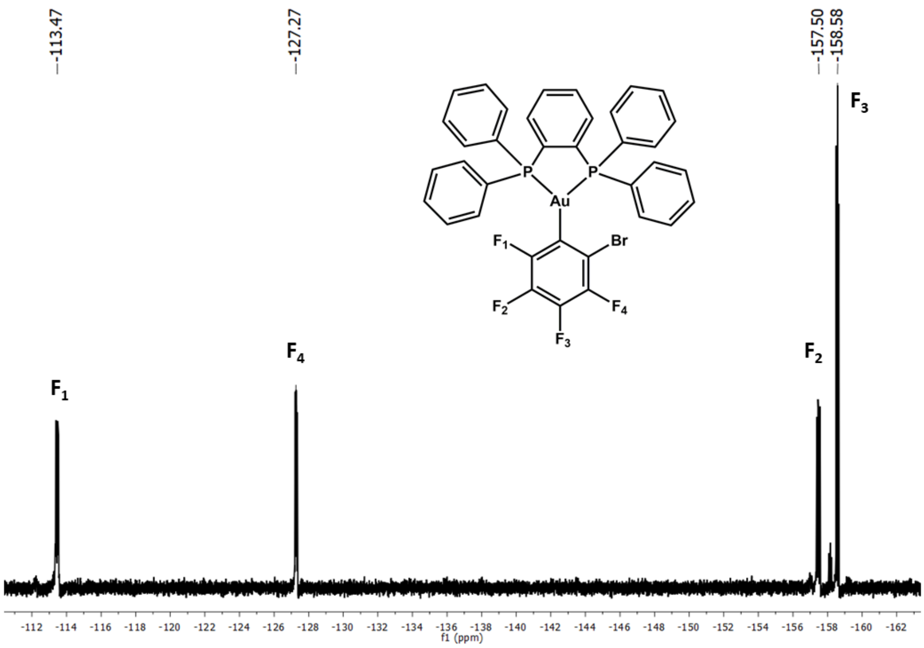

Figure S22. ^{19}F NMR spectrum of complex **2** in toluene-d8

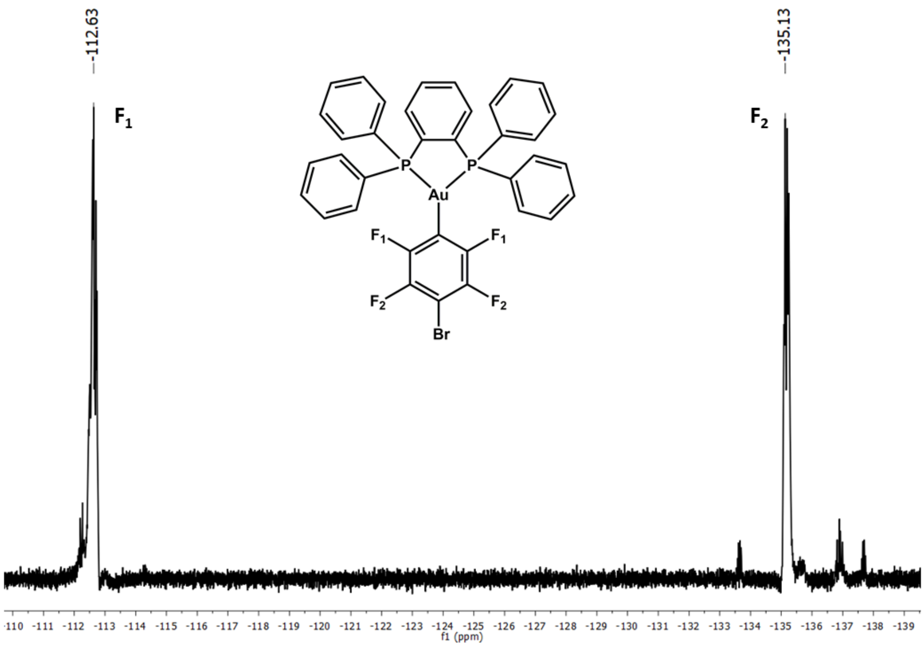

Figure S23. ^{19}F NMR spectrum of complex **3** in toluene-d8

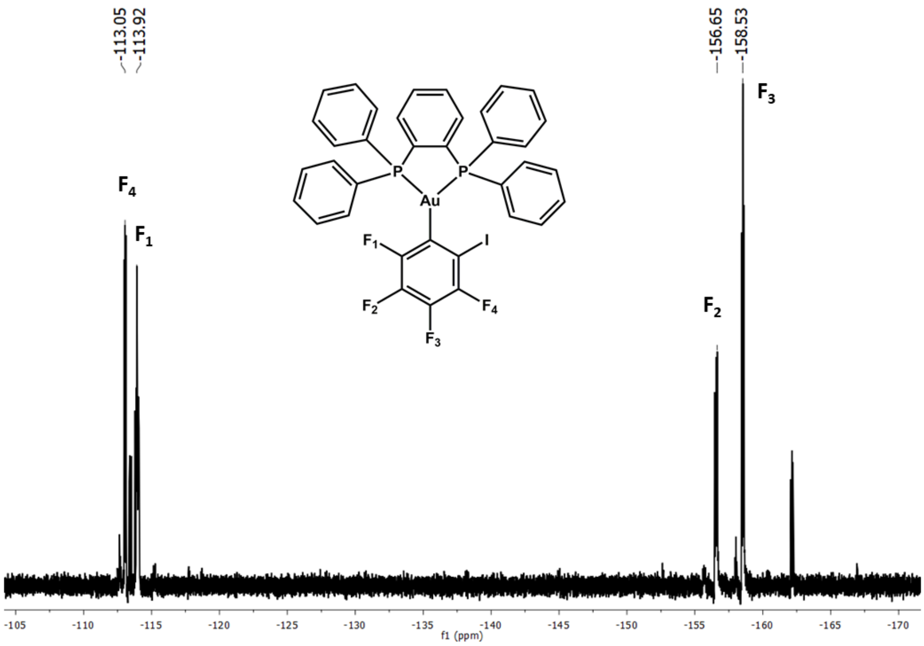

Figure S24. ^{19}F NMR spectrum of complex **4** in toluene-d8

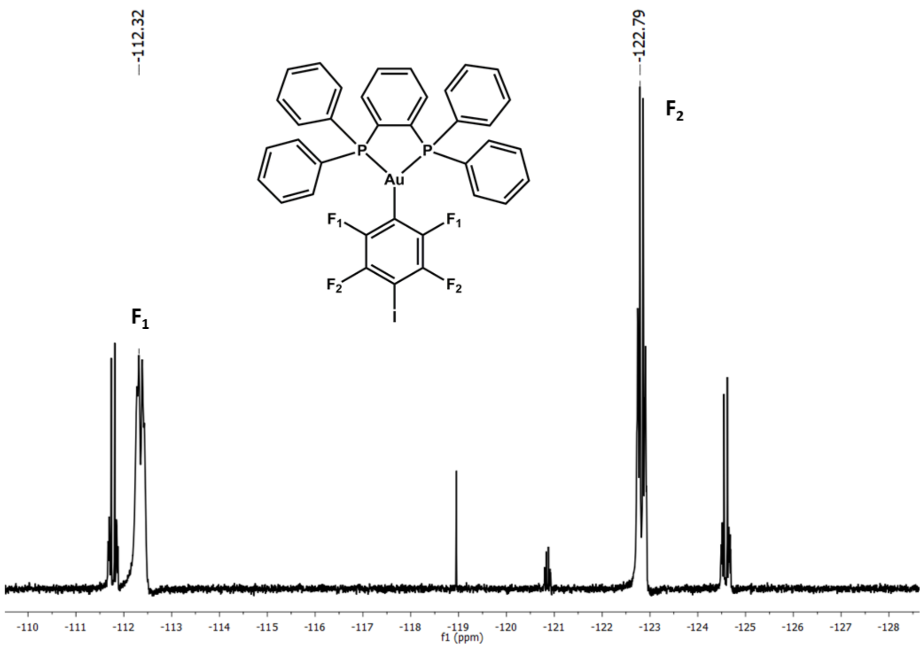

Figure S25. ^{19}F NMR spectrum of complex **5** in toluene-d8

5 $^{31}P\{^1H\}$ NMR spectra (122 MHz, 298K)

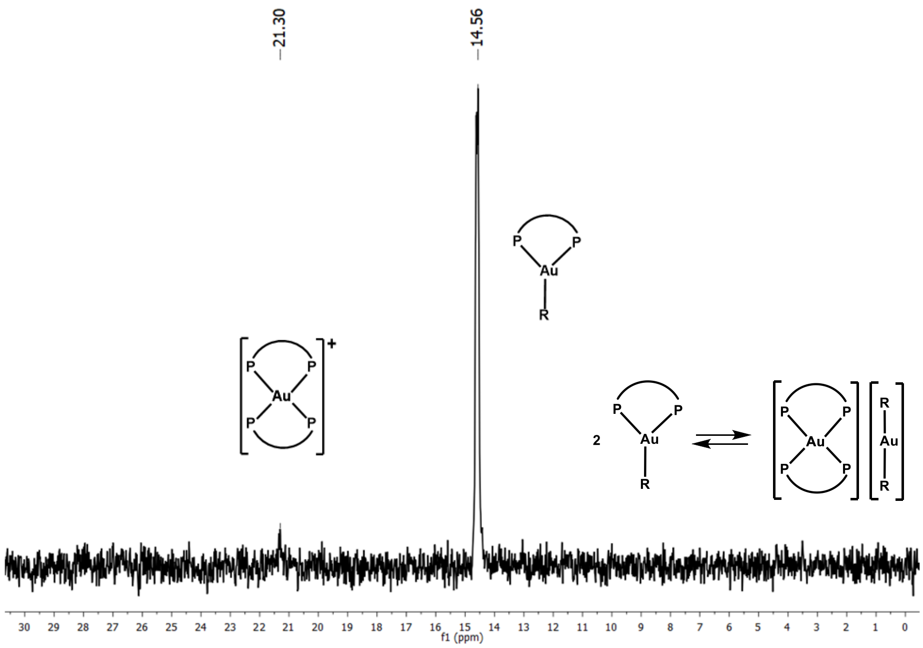

Figure S26. $^{31}P\{^1H\}$ NMR spectrum of complex **2** in toluene-d8

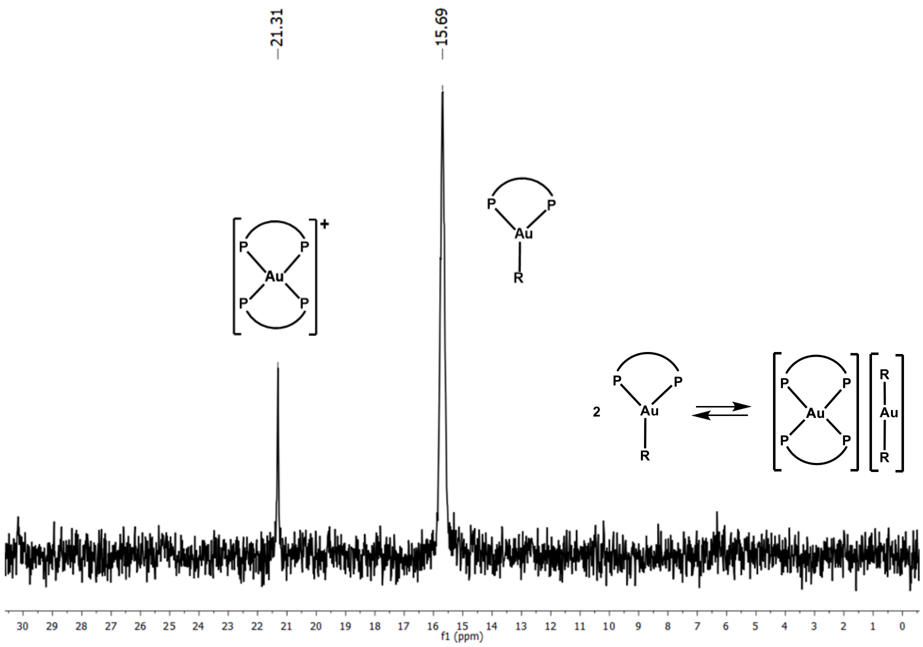

Figure S27. $^{31}P\{^1H\}$ NMR spectrum of complex **3** in toluene-d8

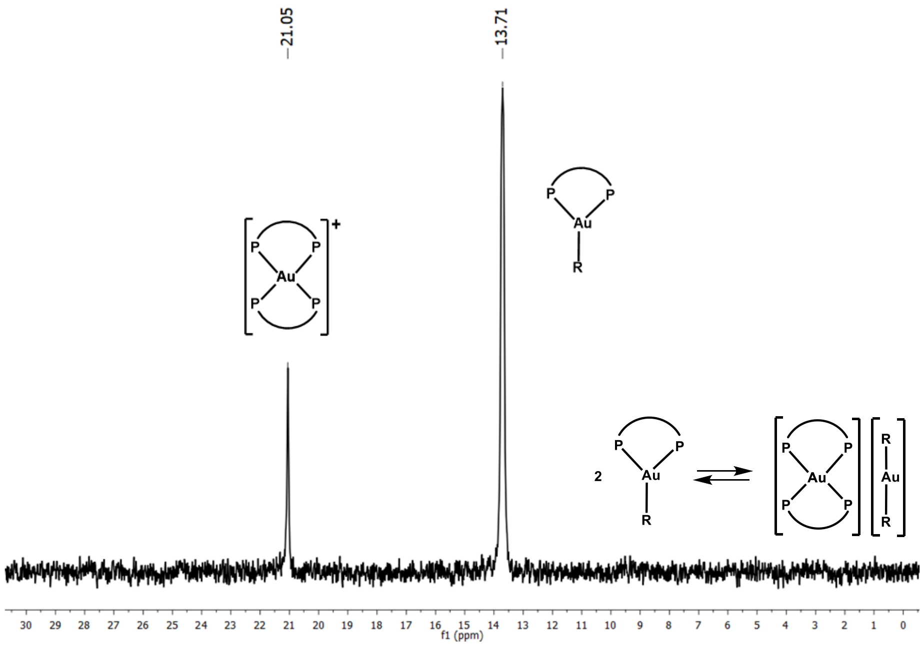

Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** in toluene-d8

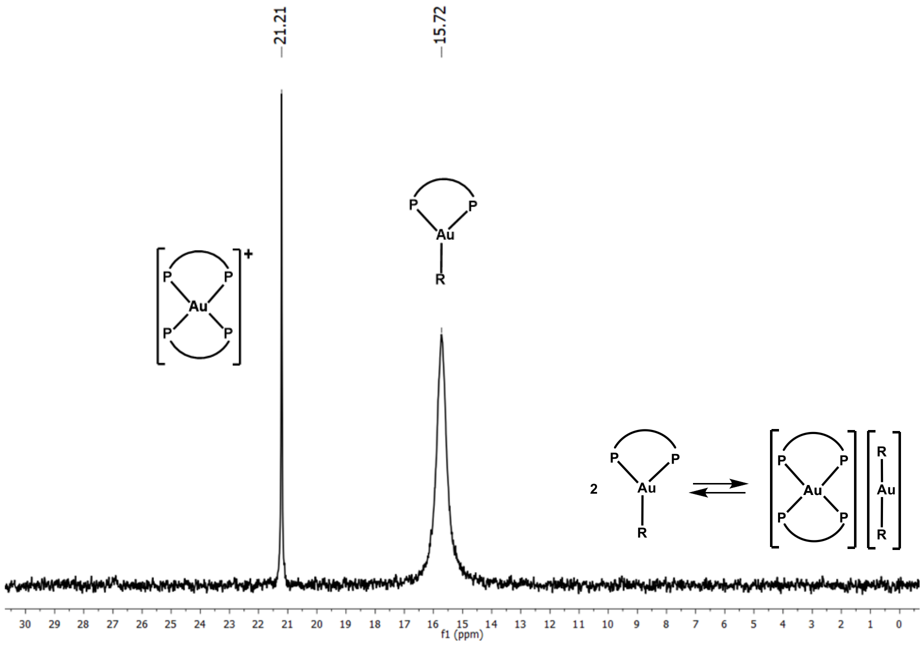

Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of complex **5** in toluene-d8

6 Single crystals X-ray diffraction analyses

Table S1. Data collection and structure refinement details for **1** and **2**

	1	**2**
Chemical Formula	$C_{36}H_{24}AuF_5P_2$	$C_{36}H_{24}AuBrF_4P_2$
Crystal habit	Yellow prism	Colourless prism
Crystal size/mm	0.061 x 0.053 x 0.023	0.106 x 0.059 x 0.057
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
a/Å	9.3057(7)	9.5296(7)
b/Å	13.6833(10)	13.7464(9)
c/Å	14.0638(9)	14.1548(9)
α/°	117.397(2)	65.383(2)
β/°	96.580(2)	71.256(2)
γ/°	102.952(3)	75.683(2)
V/Å^3	1499.62(19)	1582.40(19)
Z	2	2
D_c/g cm^{-3}	1.795	1.829
M	810.46	871.37
F(000)	788	840
T/ºC	-173	26
2θmax/°	68	55
μ(Mo-$K\alpha$)/mm^{-1}	5.069	6.061
No. refl. Measured	46032	46803
No. unique refl.	10486	7517
R_{int}	0.0839	0.0430
$R[F>2\sigma(F)]$[a]	0.0501	0.0456
$wR[F^2$, all refl.][b]	0.1031	0.1314
No. of refl. Used [$F>2\sigma$(F)]	10486	7517
No. of parameters	397	391
No. of restrains	87	0
S [c]	1.142	1.057
Max. residual electron density/e·Å^{-3}	2.075	1.996

[a] R: $(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] wR: $(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

[c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters

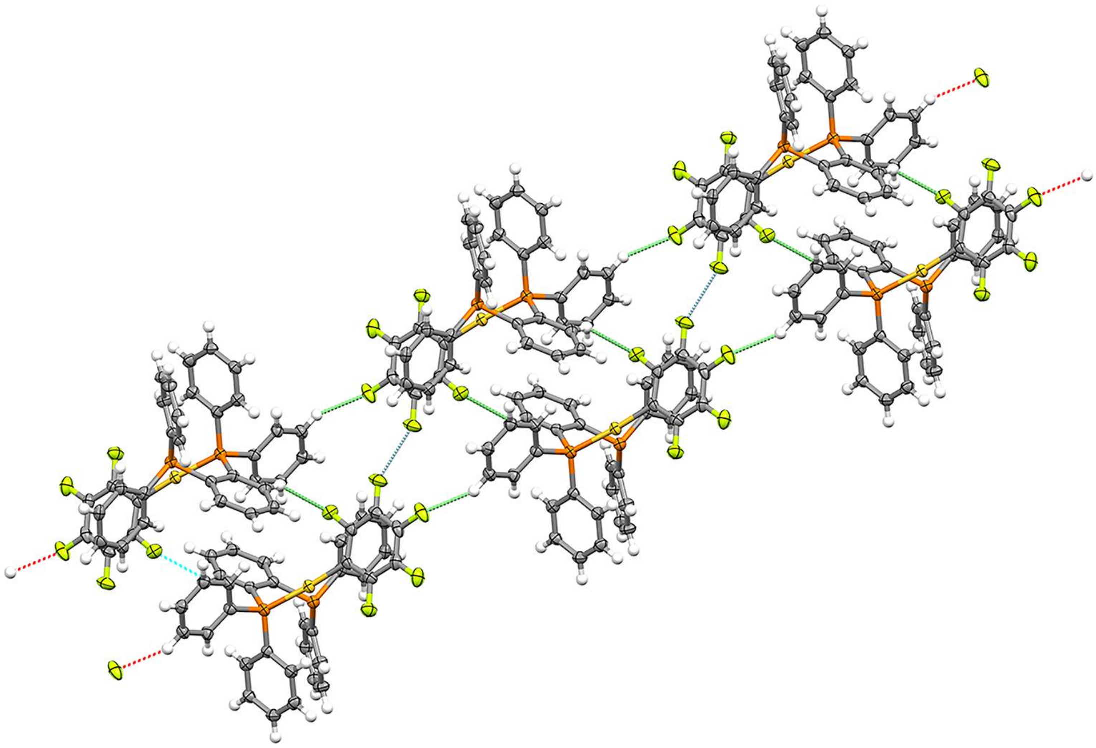

Figure S30. Crystal structure of complex **1** showing the polymeric double chain formed *via* C-H···F hydrogen bonds and F···F contacts. Colour code: C, grey; H, white; Au, yellow; F, green; P, orange.

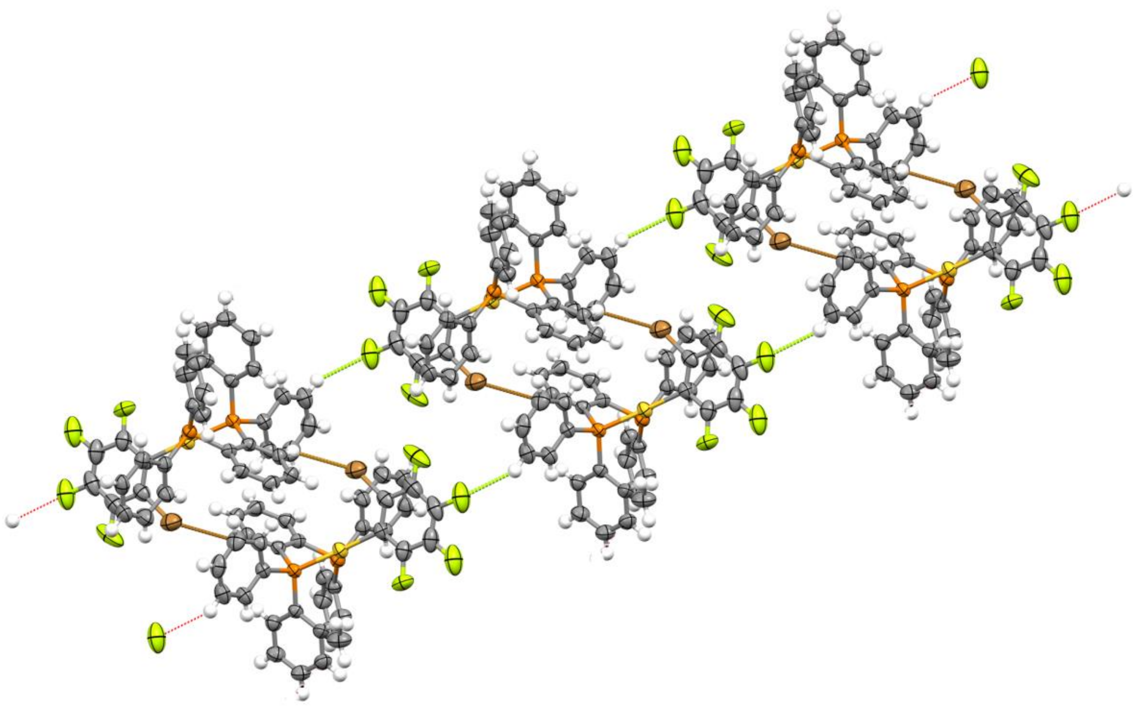

Figure S31. Crystal structure of complex **2** showing the polymeric double chain formed *via* C-H···F and C-H···Br hydrogen. Colour code: C, grey; H, white; Au, yellow; Br, brown; F, green; P, orange.

Table S2. Selected hydrogen bond lengths (Å) and angles (°) for **1**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(D-H···A)
C(8)-H(8)…F(1)#1	0.95	2.575	3.342(7)	138.0
C(33)-H(33)…F(3)#2	0.95	2.435	3.286(7)	149.0

Symmetry transformations used to generate equivalent atoms:

#1 –x+1,-y+1,-z+1; #2 x,y+1,z+1

Table S3. Selected hydrogen bond lengths (Å) and angles (°) for **2**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(D-H···A)
C(8)-H(8)…Br(1)#1	0.93	3.11	3.902(7)	143.6
C(33)-H(33)…F(2)#2	0.93	2.545	3.347(7)	144.7

Symmetry transformations used to generate equivalent atoms:

#1 –x+1,-y,-z+2; #2 x,y,z+1

III Optical properties

1. UV-Vis absorption spectra in solid state

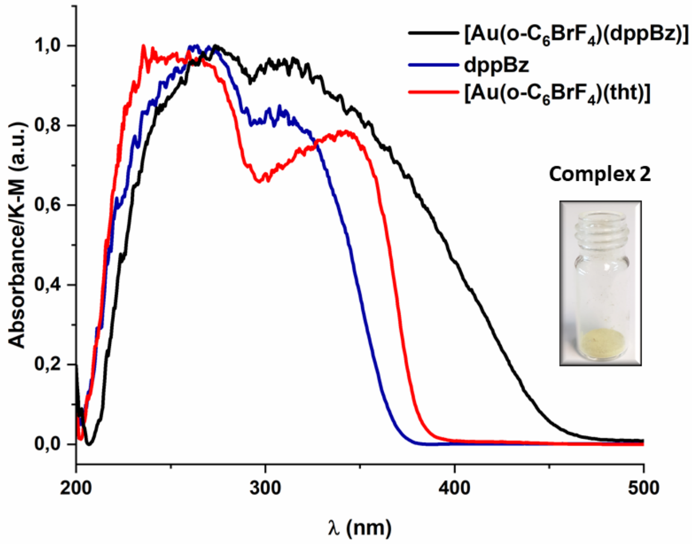

Figure S32. UV-Vis absorption spectra in solid state for complexes [Au(*o*-C_6BrF_4)(dppBz)] (**2**) (black), dppBz (blue) and [Au(*o*-C_6BrF_4)(tht)] (red).

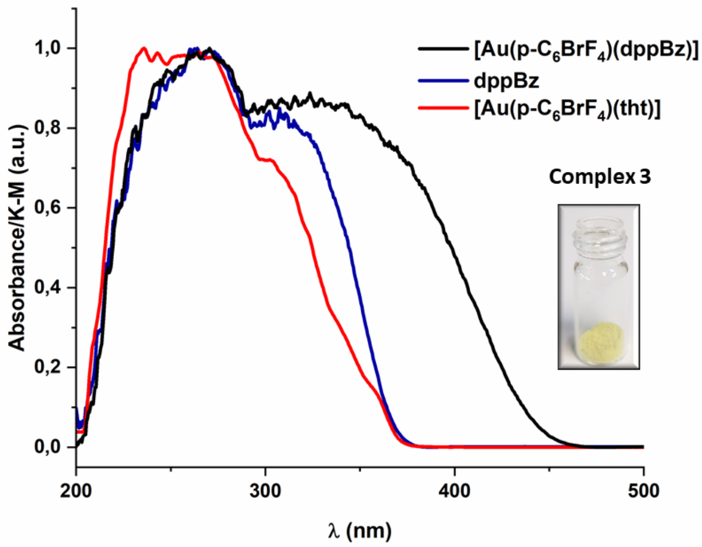

Figure S33. UV-Vis absorption spectra in solid state for complexes [Au(*p*-C_6BrF_4)(dppBz)] (**3**) (black), dppBz (blue) and [Au(*p*-C_6BrF_4)(tht)] (red).

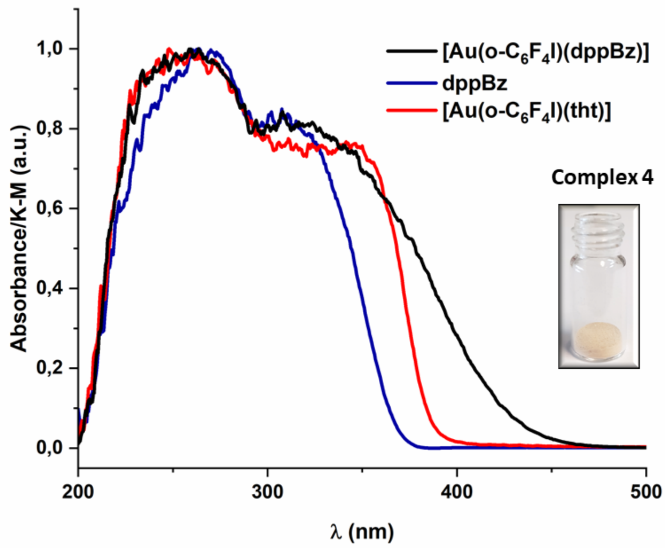

Figure S34. UV-Vis absorption spectra in solid state for complexes [Au(*o*-C_6F_4I)(dppBz)] (**4**) (black), dppBz (blue) and [Au(*o*-C_6F_4I)(tht)] (red).

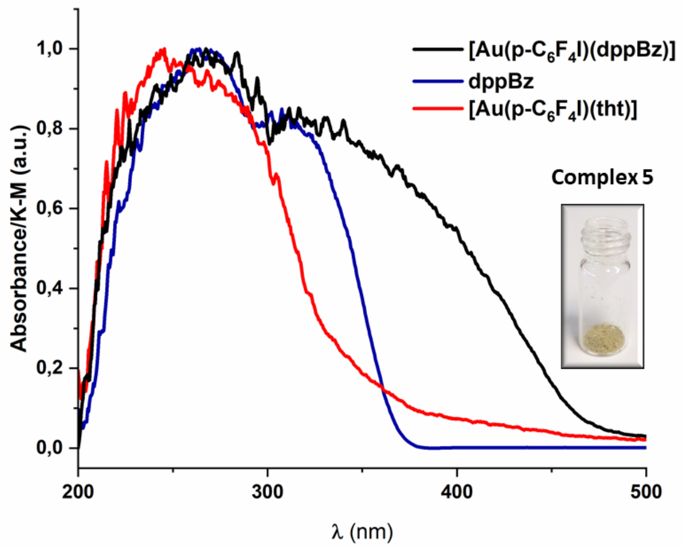

Figure S35. UV-Vis absorption spectra in solid state for complexes [Au(*p*-C_6F_4I)(dppBz)] (**5**) (black), dppBz (blue) and [Au(*p*-C_6F_4I)(tht)] (red).

2. Temperature-dependent emission spectra for complexes **2**-**5**

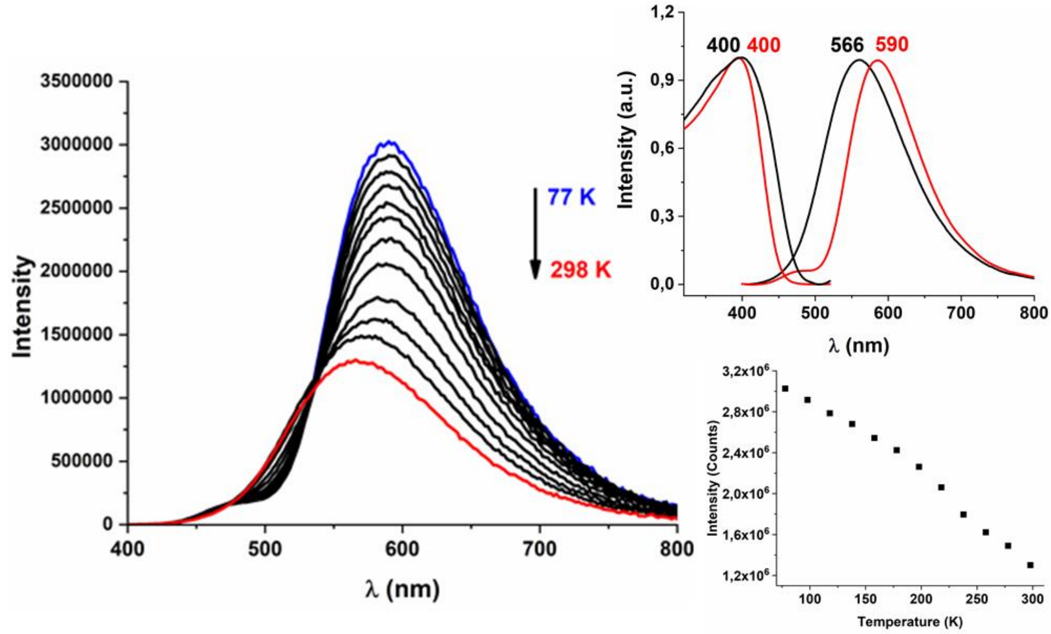

Figure S36. **Left**: Temperature-dependent change of emission energies and intensities for complex **2** in the 77-300K range. **Right**: (up) Excitation and emission spectra in solid state for complex **2** at room temperature (black) and 77K (red); (bottom) Emission intensities *vs* temperature.

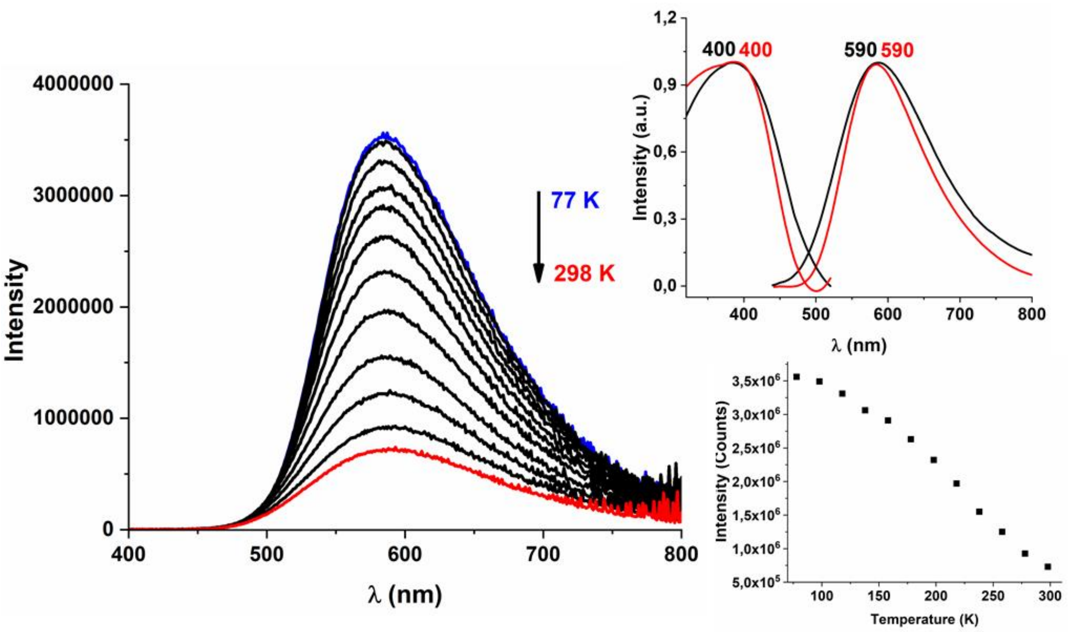

Figure S37. **Left**: Temperature-dependent change of emission energies and intensities for complex **3** in the 77-300K range. **Right**: (up) Excitation and emission spectra in solid state for complex **3** at room temperature (black) and 77K (red); (bottom) Emission intensities *vs* temperature.

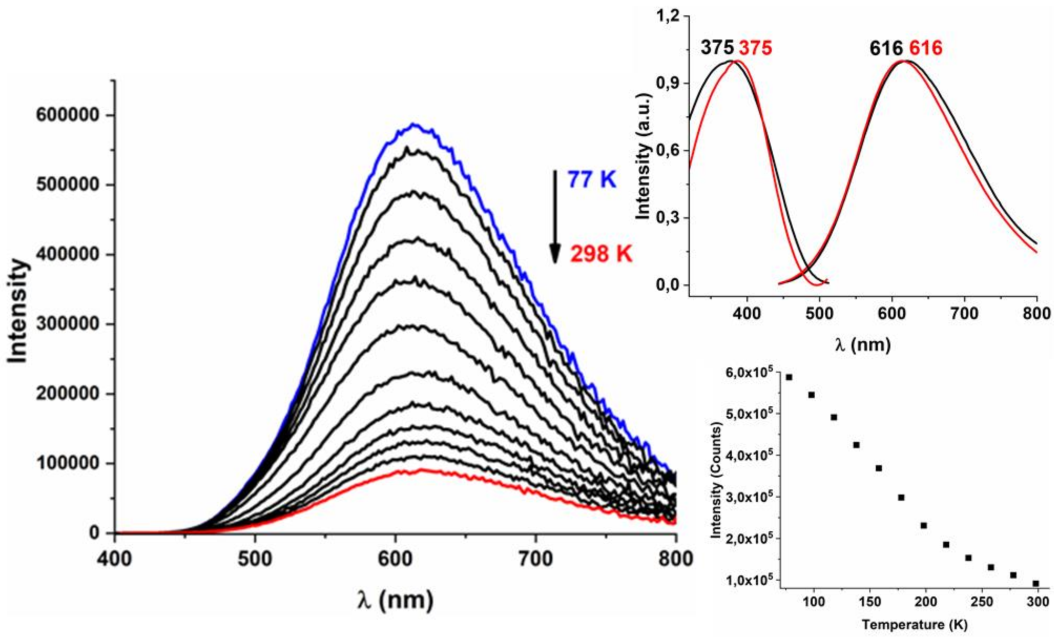

Figure S38. **Left**: Temperature-dependent change of emission energies and intensities for complex **4** in the 77-300K range. **Right**: (up) Excitation and emission spectra in solid state for complex **4** at room temperature (black) and 77K (red); (bottom) Emission intensities *vs* temperature.

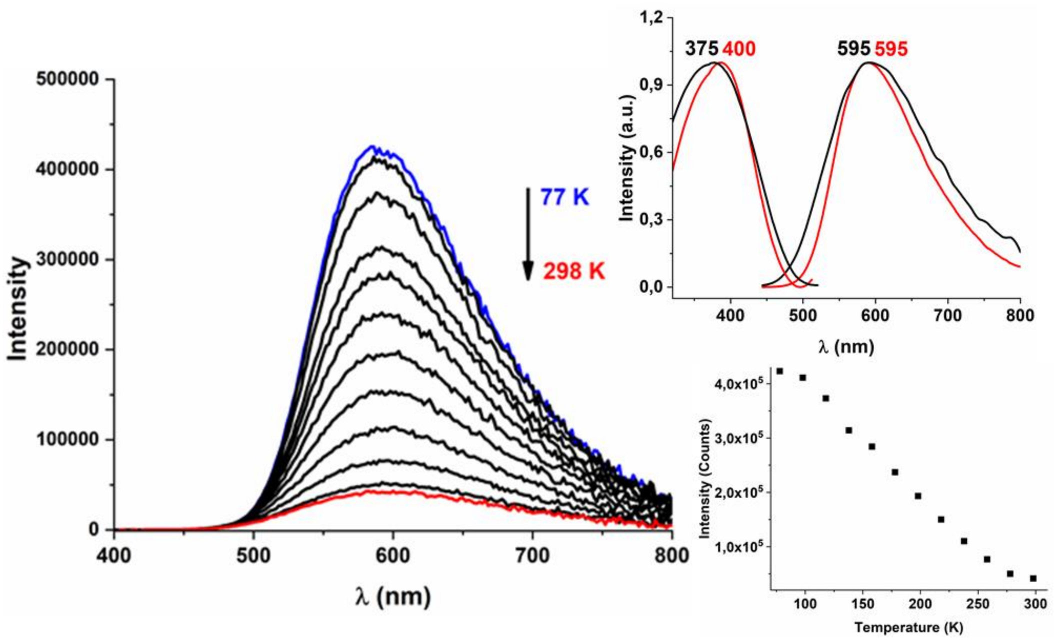

Figure S39. **Left**: Temperature-dependent change of emission energies and intensities for complex **5** in the 77-300K range. **Right**: (up) Excitation and emission spectra in solid state for complex **5** at room temperature (black) and 77K (red); (bottom) Emission intensities *vs* temperature.

3. Lifetimes at RT and at 77K

Complex 2:

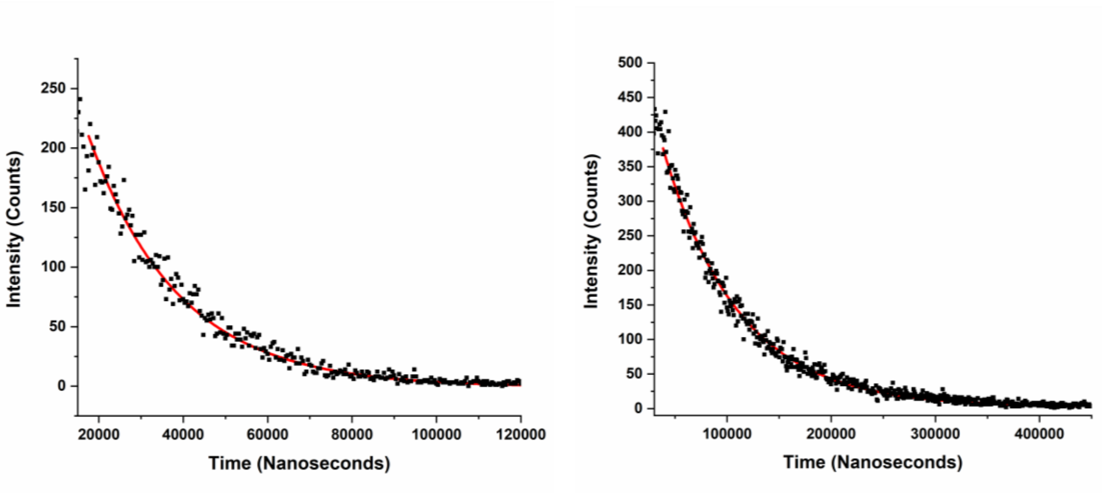

Figure S40. Lifetime decay for complex **2** at room temperature: τ = 22.60 ± 0.27 μs (χ^2 = 1.13) (left) and at 77K: τ = 70.85 ± 0.41 μs (χ^2 = 1.16) (right).

Complex 3:

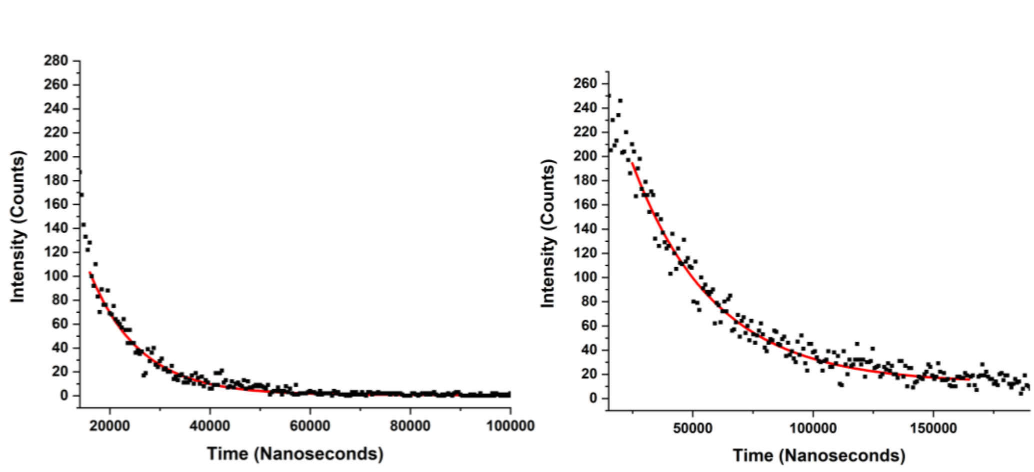

Figure S41. Lifetime decay for complex **3** at room temperature: τ = 9,92 ± 0.30 μs (χ^2 = 1.14) (left) and at 77K: τ = 32.76 ± 1.72 μs (χ^2 = 1.06) (right).

Complex 4:

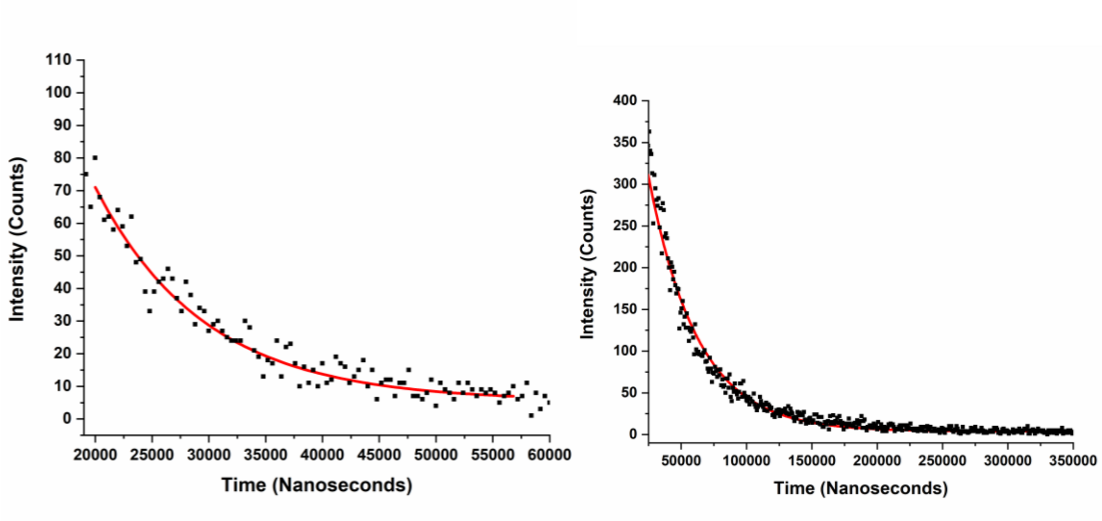

Figure S42. Lifetime decay for complex **4** at room temperature: τ = 9.63 ± 0.75 μs (χ^2 = 0.76) (left) and at 77K: τ = 37.37 ± 0.42 μs (χ^2 = 1.56) (right).

Complex 5:

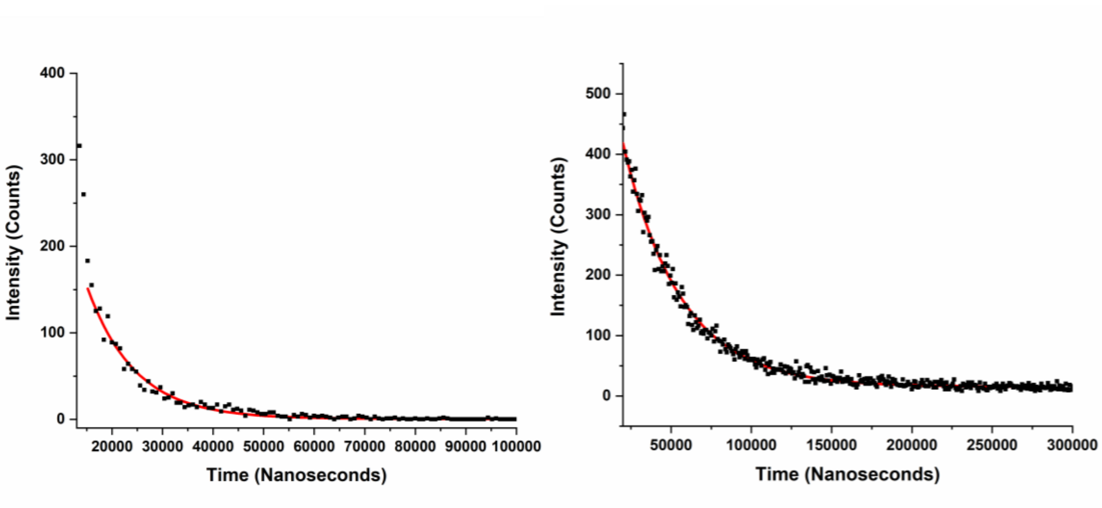

Figure S43. Lifetime decay for complex **5** at room temperature: τ = 9.42 ± 0.28 μs (χ^2 = 1.05) (left) and at 77K: τ = 34.40 ± 0.65 μs (χ^2 = 1.16) (right).

4. TADF studies

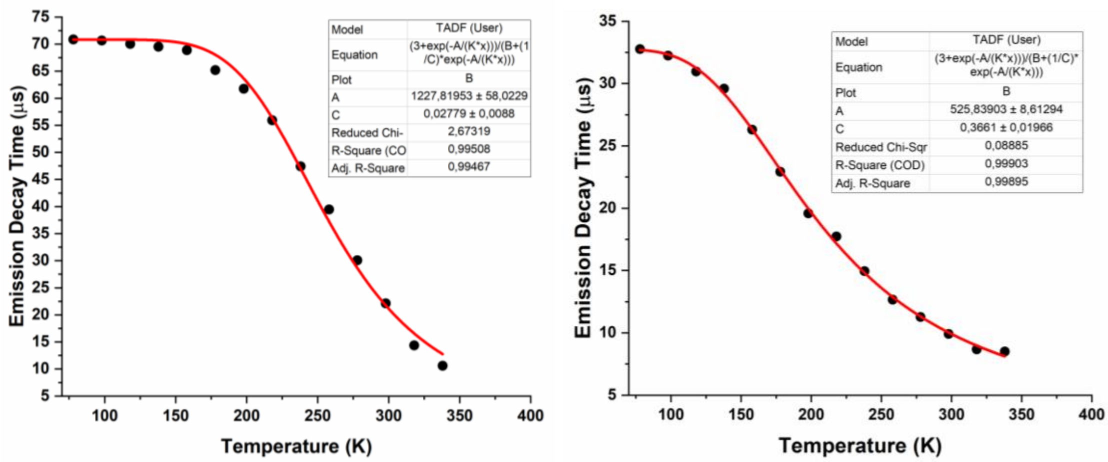

Figure S44. Temperature dependence of the emission decay time for complexes **2** (left) and **3** (right). The solid red lines represent the fit of the experimental data according to Eq. 1 (main text). The fit parameters are showed in the attached tables.

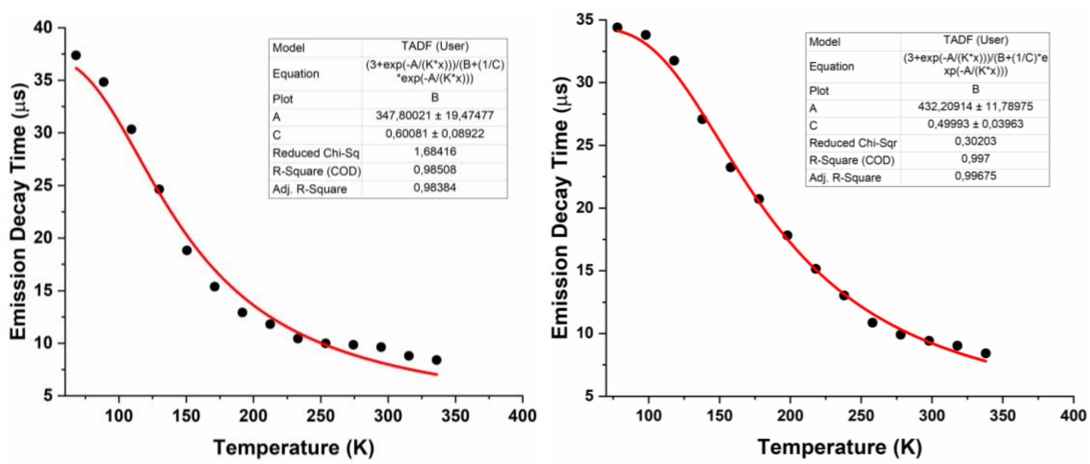

Figure S45. Temperature dependence of the emission decay time for complexes **4** (left) and **5** (right). The solid red lines represent the fit of the experimental data according to Eq. 1 (main text). The fit parameters are showed in the attached tables.

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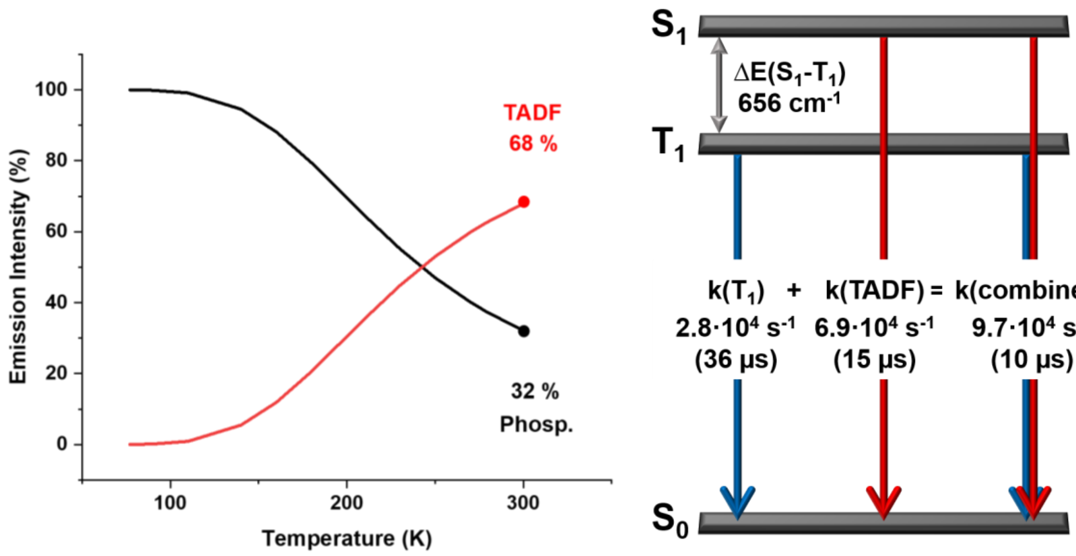

Figure S46. Left: Fractional emission intensities (simulation results) stemming from TADF (red) and direct phosphorescence (black) as a function of temperature calculated on the basis of the experimental data and Equations 3 and 4 (main text) for complex **1**; Right: Schematic energy level diagram and decay times of **1** in powder.

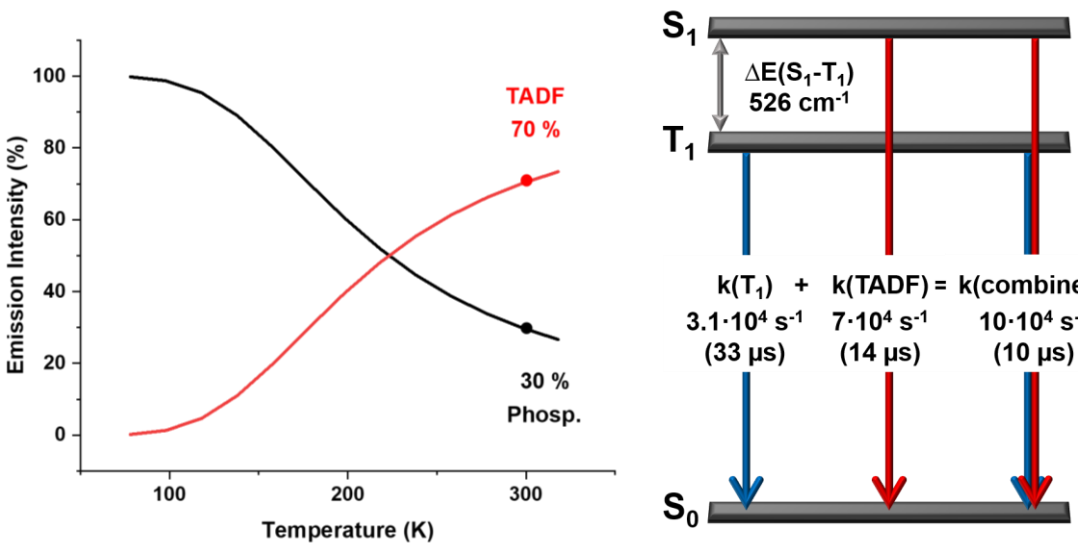

Figure S47. Left: Fractional emission intensities (simulation results) stemming from TADF (red) and direct phosphorescence (black) as a function of temperature calculated on the basis of the experimental data from figure 6 (main text) and Equations. 3 and 4 (main text) for complex **3**; Right: Schematic energy level diagram and decay times of **3** in powder.

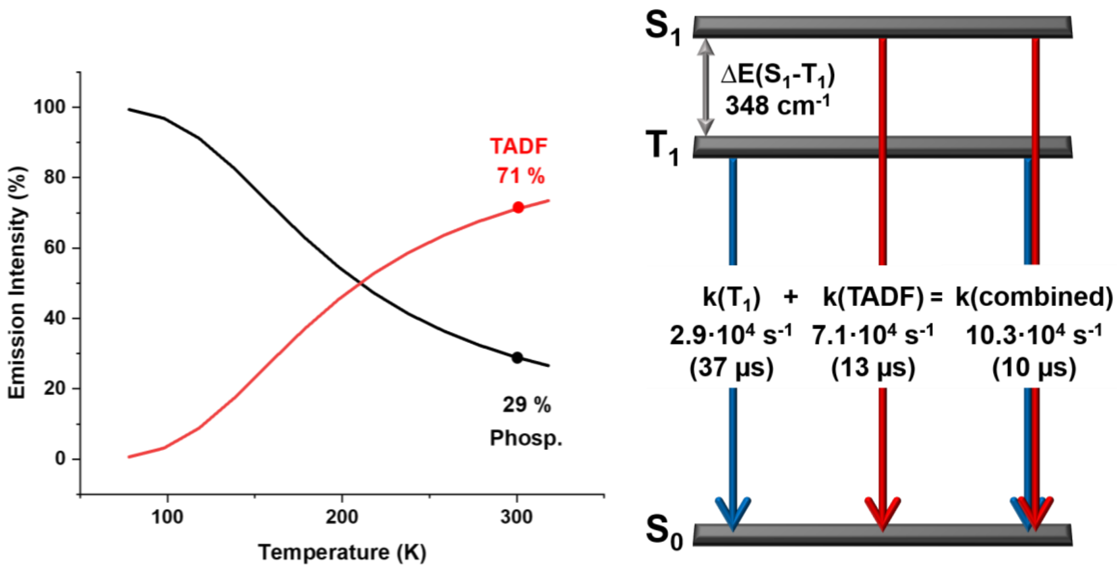

Figure S48. Left: Fractional emission intensities (simulation results) stemming from TADF (red) and direct phosphorescence (black) as a function of temperature calculated on the basis of the experimental data from figure 7 (main text) and Equations. 3 and 4 (main text) for complex **4**; Right: Schematic energy level diagram and decay times of **4** in powder.

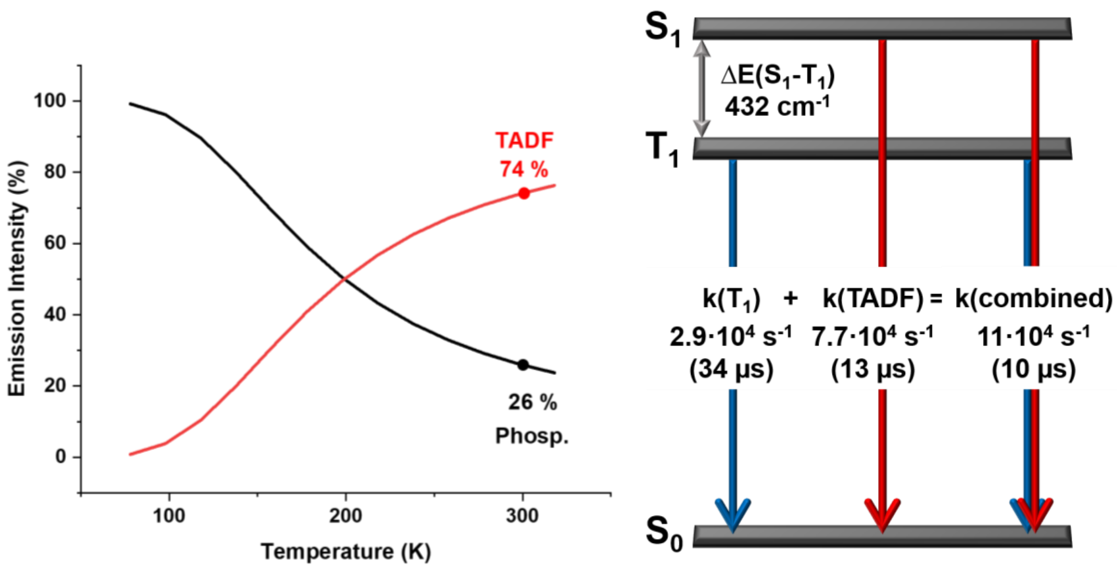

Figure S49. Left: Fractional emission intensities (simulation results) stemming from TADF (red) and direct phosphorescence (black) as a function of temperature calculated on the basis of the experimental data from figure 7 (main text) and Equations. 3 and 4 (main text) for complex **5**; Right: Schematic energy level diagram and decay times of **5** in powder.

IV Computational Methods

1. Results of DFT optimization of complexes **2-5** in the S_0 state

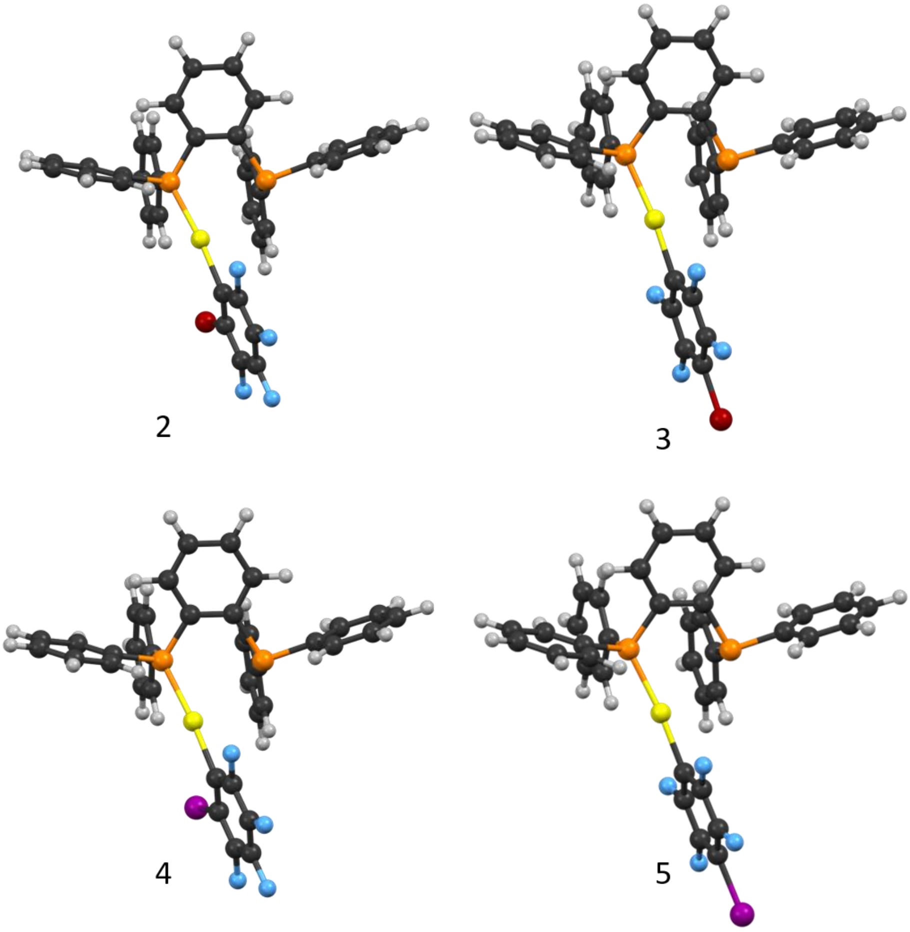

Figure S50. Model Systems of complexes **2**-**5** in the ground state S_0

2. xyz coordinates for model **2-5** in the S_0 state

```
68
Model_2 S0
P       12.289851  7.541646   7.851496
C       9.975455   5.437777   5.149464
C       10.904249  6.299120   5.718317
H       11.441986  6.987658   5.082463
C       11.156348  6.298898   7.093152
C       13.744827  6.518553   8.281974
C       12.872402  8.480744   6.387079
C       14.060233  5.312245   7.655218
H       13.421466  4.931838   6.869035
C       14.012367  8.162887   5.647238
H       14.611412  7.304902   5.920775
C       12.126448  9.606459   6.026015
H       11.255245  9.877574   6.611160
C       13.626061  10.049288  4.196808
```

H	13.920297	10.656830	3.350304
C	12.492937	10.379088	4.932376
H	11.902495	11.245881	4.663101
C	14.386855	8.944414	4.560966
H	15.275702	8.688201	3.997633
C	15.177066	4.587475	8.046500
H	15.403847	3.646512	7.561718
C	14.563247	6.978189	9.316160
H	14.308331	7.895159	9.831936
C	15.992391	5.060319	9.068274
H	16.857677	4.488176	9.378913
C	15.684381	6.257488	9.703052
H	16.302147	6.622996	10.513076
P	10.754237	5.256478	9.695885
C	10.441769	5.385261	7.899079
C	9.502746	4.532215	7.316349
H	8.941586	3.851358	7.942037
C	9.265950	4.553192	5.949336
C	9.215856	4.552654	10.366911
C	8.121650	5.412067	10.501922
H	8.221119	6.453822	10.222679
C	12.004186	3.945139	9.862459
C	6.918132	4.938643	11.001539
H	6.076207	5.611384	11.102160
C	9.094434	3.221461	10.760576
H	9.938805	2.552177	10.675064
C	12.045995	2.849274	8.998033
H	11.345248	2.778280	8.177068
C	12.932429	4.037303	10.899074
H	12.917908	4.898945	11.553403
C	7.888176	2.752242	11.270255
H	7.803528	1.717685	11.577788
C	13.914308	1.947521	10.219022
H	14.660279	1.174299	10.353553
C	12.996018	1.854586	9.178460
H	13.024745	1.010046	8.501591
C	6.799223	3.606078	11.386760
H	5.861897	3.238895	11.784911
C	13.882700	3.040362	11.075504
H	14.606022	3.128355	11.875728
Au	11.332915	7.219030	10.763606
C	11.836561	8.891085	11.893959
C	11.120473	10.067258	11.749417
C	12.897825	8.931078	12.795480
C	11.416055	11.229239	12.446441
C	12.479422	11.230919	13.335393
C	13.225971	10.074995	13.509574
F	14.250677	10.107607	14.372101
F	10.696477	12.345270	12.276003
F	10.073976	10.123872	10.895586
H	9.805960	5.465816	4.080330
H	8.530935	3.885791	5.518245
F	12.782698	12.339458	14.019670
Br	13.992149	7.387392	13.100705

68

Model_3 S0

Au	6.701641	2.489392	3.547797
P	8.596732	2.909499	4.796297
P	7.523007	5.380281	2.864591
C	4.927482	1.971014	2.606433
C	9.754473	4.154115	4.125573
C	11.117471	4.019350	4.396626
H	11.466884	3.159749	4.952349
C	7.508223	6.930927	1.884682
C	3.723357	1.978444	3.288048
C	4.856039	1.615375	1.271207
C	8.212008	3.481633	6.480053
C	6.944637	3.221623	7.001600
H	6.205124	2.725568	6.386478
C	12.033475	4.961694	3.951730
H	13.086447	4.835955	4.168508
C	9.292620	5.257561	3.374801
C	3.667342	1.280118	0.639948
C	6.705037	5.880456	4.423837
C	2.513080	1.649613	2.697465
C	9.620623	1.419692	5.007322
C	5.347752	5.576419	4.557763
H	4.835613	5.056693	3.758270
C	2.475745	1.294370	1.354838
C	7.735826	6.809379	0.510411
H	7.905663	5.827759	0.083787
C	9.939836	0.691787	3.857579
H	9.567089	1.019485	2.894746
C	8.830761	4.549377	8.554068
H	9.564242	5.073762	9.153414
C	7.362807	6.515910	5.477580
H	8.418625	6.738141	5.396390
C	10.074055	0.975116	6.247643
H	9.820604	1.521922	7.144979
C	11.584835	6.056470	3.226409
H	12.285007	6.803476	2.873875
C	9.151526	4.155186	7.263097
H	10.129358	4.383406	6.861063
C	7.255157	8.196645	2.416033
H	7.060810	8.308204	3.473969
C	10.719531	-0.450912	3.947388
H	10.961564	-1.008086	3.051500
C	10.849094	-0.176618	6.334885
H	11.194187	-0.517134	7.302830
C	7.568373	4.279800	9.072021
H	7.316689	4.594829	10.076892
C	11.176153	-0.887682	5.187914
H	11.777621	-1.785074	5.258583
C	7.496366	9.188048	0.231310
H	7.489539	10.062144	-0.407397
C	6.676377	6.848430	6.637384
H	7.201608	7.327712	7.453561
C	7.741285	7.930200	-0.309365
H	7.922951	7.820202	-1.371092
C	6.626825	3.618683	8.293884

H	5.636994	3.421674	8.684373
C	10.232835	6.196806	2.941987
H	9.902033	7.050728	2.368926
C	7.247430	9.316774	1.593115
H	7.046909	10.292470	2.018164
C	5.324082	6.550440	6.756749
H	4.793157	6.799681	7.666852
C	4.659125	5.915512	5.714261
H	3.610167	5.664802	5.806483
F	3.689822	2.323407	4.599019
F	1.386352	1.676705	3.422608
F	3.671256	0.944403	-0.656892
F	5.978630	1.583999	0.519294
Br	0.843931	0.843520	0.520841

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Model_4 S0

P	12.322208	7.527527	7.886340
C	9.950973	5.496013	5.179625
C	10.895841	6.337677	5.751314
H	11.432354	7.032156	5.120978
C	11.165502	6.310565	7.122420
C	13.770992	6.481838	8.280948
C	12.897660	8.486487	6.432312
C	14.060942	5.278363	7.636891
H	13.404714	4.914529	6.857379
C	14.023386	8.168411	5.671052
H	14.613632	7.296554	5.918605
C	12.163209	9.630085	6.105388
H	11.304295	9.901138	6.708396
C	13.645603	10.090980	4.266623
H	13.937771	10.712547	3.429684
C	12.526840	10.420860	5.023828
H	11.945734	11.301635	4.781114
C	14.395126	8.967923	4.596993
H	15.273067	8.711725	4.016877
C	15.174204	4.535169	8.003040
H	15.380725	3.596369	7.505275
C	14.611780	6.920268	9.306179
H	14.377069	7.834917	9.835731
C	16.012140	4.987128	9.015944
H	16.875546	4.401404	9.305709
C	15.730160	6.182034	9.666826
H	16.366207	6.532387	10.469415
P	10.776433	5.235822	9.714751
C	10.451322	5.390872	7.921957
C	9.496786	4.557185	7.336323
H	8.935508	3.872129	7.957265
C	9.243205	4.604236	5.973008
C	9.236404	4.537122	10.387830
C	8.148502	5.402462	10.535683
H	8.253263	6.445860	10.264780
C	12.015447	3.912023	9.857351
C	6.944729	4.932792	11.038079
H	6.107891	5.610215	11.148862

C	9.108323	3.203650	10.771457
H	9.947848	2.529665	10.676101
C	12.040230	2.825156	8.981130
H	11.331536	2.768703	8.165804
C	12.953949	3.986511	10.885604
H	12.952601	4.841195	11.549088
C	7.901732	2.738073	11.283666
H	7.811953	1.701641	11.583238
C	13.913090	1.896695	10.174607
H	14.654097	1.116272	10.293962
C	12.983763	1.821215	9.142481
H	12.998874	0.982963	8.457395
C	6.819040	3.597918	11.412928
H	5.881473	3.233598	11.813056
C	13.897840	2.980509	11.042822
H	14.629205	3.054384	11.837214
Au	11.358722	7.198593	10.782781
C	11.822546	8.902966	11.882175
C	11.095319	10.061775	11.666037
C	12.854066	8.993621	12.817389
C	11.351880	11.255803	12.322587
C	12.383057	11.309919	13.246775
C	13.137117	10.171913	13.493383
F	14.128327	10.259647	14.392688
F	10.624600	12.352630	12.078786
F	10.076907	10.070007	10.776090
H	9.768038	5.544539	4.113476
H	8.495920	3.952018	5.539851
F	12.646521	12.450903	13.893975
I	14.075559	7.320313	13.262888

68

Model_5 S0

P	12.270696	7.551790	7.844683
C	10.012353	5.411558	5.123304
C	10.923677	6.286558	5.699530
H	11.459679	6.979720	5.067308
C	11.160003	6.294146	7.077157
C	13.729654	6.544230	8.298209
C	12.861728	8.489863	6.383170
C	14.061333	5.337077	7.681770
H	13.434546	4.947217	6.890579
C	14.013007	8.179172	5.657989
H	14.617498	7.328883	5.943407
C	12.108194	9.605386	6.006573
H	11.227453	9.870804	6.579958
C	13.623434	10.052490	4.191433
H	13.920631	10.657572	3.344195
C	12.478827	10.375087	4.912265
H	11.882401	11.233899	4.630798
C	14.391418	8.957797	4.570996
H	15.288897	8.707186	4.018958
C	15.179668	4.623215	8.089025
H	15.419291	3.681730	7.611411
C	14.533517	7.016481	9.338609
H	14.267293	7.935176	9.845423

C	15.980009	5.107810	9.116876
H	16.846607	4.544466	9.439718
C	15.656141	6.306433	9.741426
H	16.263897	6.681859	10.554717
P	10.736895	5.259406	9.680004
C	10.448324	5.374297	7.878100
C	9.526653	4.507453	7.287855
H	8.966637	3.822144	7.909700
C	9.305391	4.520387	5.918183
C	9.191144	4.554584	10.332751
C	8.090393	5.409511	10.440224
H	8.188267	6.448736	10.151019
C	11.991409	3.955511	9.871724
C	6.881664	4.935271	10.926250
H	6.034998	5.604793	11.006027
C	9.070403	3.227317	10.739747
H	9.919577	2.561701	10.675239
C	12.045748	2.852494	9.016928
H	11.351305	2.771019	8.191718
C	12.913308	4.061502	10.913135
H	12.890933	4.929319	11.559558
C	7.858690	2.757381	11.235673
H	7.774707	1.725988	11.553830
C	13.911841	1.971972	10.256189
H	14.661926	1.204715	10.401387
C	13.000524	1.864977	9.210922
H	13.038121	1.015077	8.541253
C	6.763574	3.606584	11.324997
H	5.822006	3.239003	11.712636
C	13.868473	3.071590	11.103494
H	14.586305	3.170343	11.907261
Au	11.300888	7.225686	10.754452
C	11.804992	8.881388	11.897652
C	11.032958	10.029336	11.930255
C	12.959485	8.917896	12.659413
C	11.376771	11.150601	12.670947
C	12.542139	11.156852	13.427493
C	13.336842	10.017690	13.414839
F	14.471648	9.974055	14.129613
F	10.578688	12.228419	12.649898
F	9.887731	10.091984	11.213989
H	9.854661	5.433817	4.052227
H	8.583525	3.842504	5.481270
F	13.784740	7.841711	12.686609
I	13.085711	12.833630	14.550317

3. Results of DFT optimization of complexes **2-5** in the T_1 state

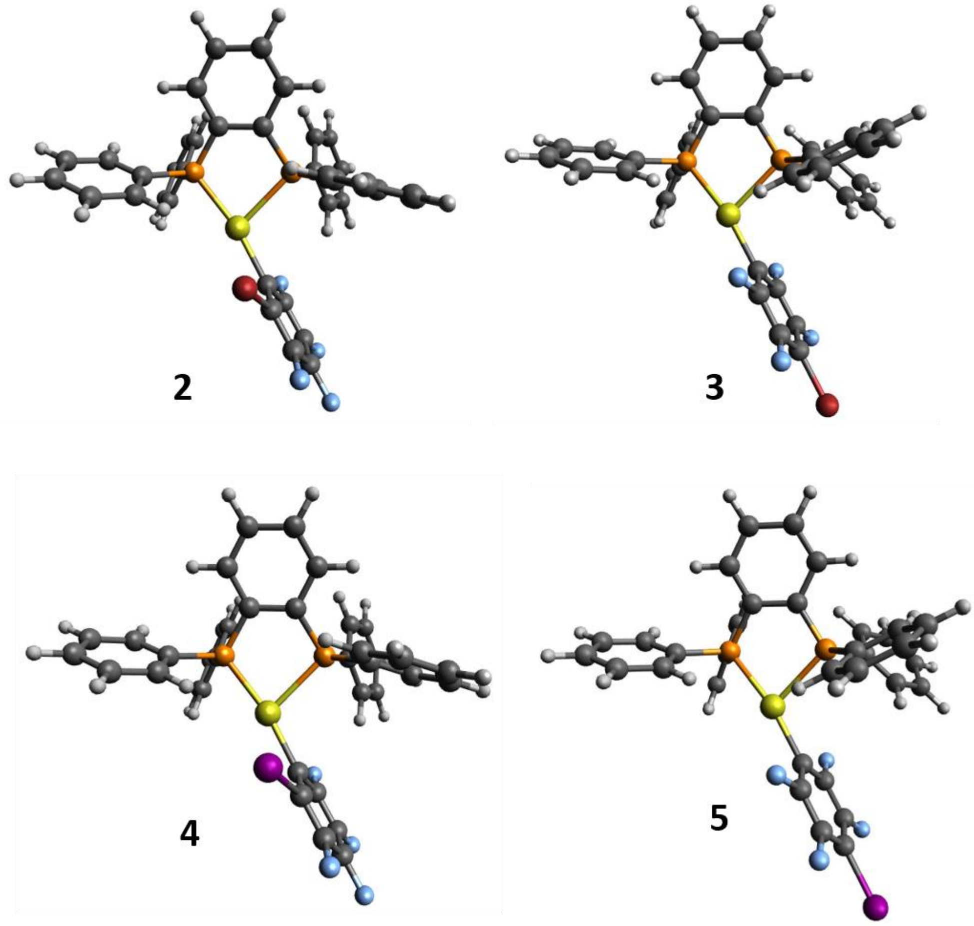

Figure S51. Model Systems of complexes **2**-**5** in the lowest triplet excited state T_1

4. xyz coordinates for model **2-5** in the T_1 state

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Model_2 T1

Au	12.108502258	6.865840068	10.593343919
P	12.936854781	6.859436473	8.202881044
C	10.907539397	4.831357147	5.340395650
C	11.713023890	5.731404873	5.989134218
H	12.269848534	6.454767952	5.404175881
C	11.820603328	5.763799718	7.403726855
C	14.679211948	6.301853127	8.103562454
C	12.866696763	8.500042343	7.429156335
C	15.024028220	5.244818815	7.256349970
H	14.264304525	4.781082260	6.641149466
C	14.010821003	9.222978249	7.073993341
H	14.992721131	8.794243520	7.216142977
C	11.607190462	9.077734160	7.220437975
H	10.714667831	8.525503378	7.483505241
C	12.640764833	11.056891325	6.317307367
H	12.553786339	12.046648592	5.886571613
C	11.497467739	10.344435192	6.668149576

H	10.517521276	10.778002977	6.513622157
C	13.894406643	10.491677412	6.519578253
H	14.788389205	11.036751188	6.242870179
C	16.335204589	4.787270178	7.204978554
H	16.591900577	3.973399628	6.538046624
C	15.663242226	6.867476332	8.921789245
H	15.408055346	7.659299945	9.612750018
C	17.310929917	5.365985821	8.009047254
H	18.330433581	5.001977021	7.973473647
C	16.971375683	6.404728957	8.870050802
H	17.722394322	6.848461480	9.511772500
P	11.103006159	4.812355180	9.941870903
C	11.041481117	4.789800794	8.173764473
C	10.218538538	3.891819181	7.468318479
H	9.610641506	3.189179038	8.027358570
C	10.140581447	3.887050644	6.094176320
C	9.417919078	4.597333234	10.609089959
C	8.590629328	5.717225738	10.751016699
H	8.976432770	6.703905453	10.526081522
C	12.048907512	3.373202929	10.578216398
C	7.281320204	5.575706448	11.186093104
H	6.656168797	6.452879345	11.297225486
C	8.904585121	3.333882033	10.918279404
H	9.530679638	2.455691962	10.829323179
C	12.617154695	2.441500407	9.710601522
H	12.469246178	2.545463834	8.643590721
C	12.256480098	3.239929274	11.955243938
H	11.830177663	3.963943024	12.640212827
C	7.589723630	3.195411142	11.350896421
H	7.205165210	2.210189416	11.584486070
C	13.566789357	1.253962243	11.581221475
H	14.156506759	0.433020679	11.970284865
C	13.371640959	1.384995203	10.212084459
H	13.807659506	0.666446103	9.528916033
C	6.775655041	4.312847365	11.486361769
H	5.753880428	4.203666986	11.828249622
C	13.007360902	2.184609814	12.453176012
H	13.162829384	2.090799986	13.520934381
F	11.697286085	12.102154587	12.138385919
F	14.833001366	7.668629578	12.065708710
F	15.731363425	9.941687913	13.180405599
F	14.169165838	12.169146542	13.207051139
C	12.758436200	8.656474065	11.479506252
C	11.983648003	9.816502944	11.524777995
C	14.014320690	8.745940877	12.057471981
C	12.443761827	10.992640206	12.099592289
C	13.714489183	11.039772875	12.657448495
C	14.507707009	9.903475797	12.641127298
H	10.834018362	4.854878456	4.261046506
H	9.487288114	3.187215187	5.591005169
Br	10.208993244	9.851124566	10.808351535

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Model_3 T1

Au	12.164704412	6.766000361	10.619676848

P	12.995975850	6.841186250	8.244153906
C	11.475173460	4.482331513	5.336630787
C	12.303595331	5.315379166	6.037120095
H	13.082574664	5.849029979	5.505031249
C	12.157099775	5.516928398	7.443565091
C	14.796922204	6.620738385	8.151480941
C	12.664945561	8.466151938	7.476767772
C	15.339034154	5.361879739	7.874750244
H	14.677628221	4.537831808	7.642875262
C	13.375381247	8.885555923	6.343449650
H	14.218886591	8.309821882	5.984623484
C	11.587755766	9.240997693	7.920506121
H	11.032485977	8.942489082	8.800129855
C	11.940993370	10.811157799	6.127617755
H	11.663069886	11.719584524	5.607729445
C	11.232940695	10.405724237	7.254977205
H	10.406137143	11.000998608	7.622407972
C	13.011075060	10.046970272	5.675391393
H	13.569334869	10.357682922	4.800440881
C	16.715056538	5.171957114	7.889086582
H	17.123883370	4.195162483	7.662195555
C	15.658920737	7.678016595	8.471088812
H	15.254099856	8.654752419	8.704164000
C	17.563573121	6.229371343	8.197488336
H	18.635910821	6.078221192	8.215064689
C	17.031650168	7.482069821	8.491270040
H	17.688222124	8.305914109	8.741994326
P	11.029091035	4.812360234	9.885366362
C	11.100655712	4.765622278	8.115680449
C	10.255016038	3.947275042	7.357960426
H	9.458435830	3.408853786	7.859702978
C	10.408772689	3.796771359	5.992865864
C	9.286967781	4.692420416	10.413008192
C	8.500867595	5.849274988	10.411802594
H	8.940164237	6.800097997	10.135424229
C	11.862136567	3.343700805	10.604503087
C	7.160417929	5.790143103	10.765747237
H	6.564088368	6.693904099	10.763687737
C	8.706405807	3.477347076	10.782952409
H	9.301417045	2.573836847	10.800590114
C	12.375965024	2.337362981	9.786710995
H	12.262002433	2.410273308	8.713028804
C	12.021358137	3.246173883	11.990899864
H	11.639220317	4.027906446	12.637126358
C	7.361632715	3.420614507	11.136090178
H	6.922405110	2.471842224	11.418461200
C	13.176120634	1.149603584	11.726084688
H	13.686957689	0.299377287	12.160969913
C	13.030043445	1.244622043	10.347770845
H	13.425156014	0.468718325	9.703644471
C	6.587666167	4.574018203	11.128791797
H	5.542401604	4.528625405	11.408538127
C	12.669310998	2.152649212	12.548079586
H	12.787456566	2.086645505	13.622605365
F	12.240776790	11.833344276	12.521875374
F	15.006678355	7.178408829	12.090880344

F	16.104987799	9.237892174	13.376044327
C	13.030346044	8.392862418	11.612419363
C	12.378846971	9.606812072	11.758634593
C	14.293623469	8.321502358	12.177738915
C	12.932939007	10.692035809	12.420208756
C	14.202702700	10.588193321	12.976284799
C	14.882703720	9.382333416	12.849663156
H	11.623594390	4.354601641	4.271578694
H	9.729628735	3.170242742	5.431948702
F	11.137381227	9.771697750	11.245490261
Br	14.981820693	12.046814754	13.884691357

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Model_4 T1

I	9.962789085	9.941737230	10.732563503
Au	12.049907852	6.915881030	10.589628701
P	12.941992220	6.844944492	8.213877291
C	10.905409759	4.828383787	5.347369300
C	11.735375756	5.706234259	5.993348512
H	12.330252277	6.396139183	5.405622369
C	11.817914603	5.761732559	7.412182647
C	14.677317948	6.256137553	8.141498827
C	12.918737394	8.475418095	7.413123217
C	15.019483044	5.206158235	7.284166340
H	14.263102786	4.763028375	6.649957625
C	14.082976870	9.196535456	7.124707348
H	15.053858993	8.772353755	7.337983621
C	11.675409707	9.047144818	7.112033295
H	10.768342565	8.495603334	7.320797126
C	12.764272153	11.015721102	6.250617741
H	12.705002723	11.998460052	5.799553036
C	11.601461506	10.305595592	6.534508435
H	10.633434855	10.733746925	6.306809459
C	14.002500913	10.456685812	6.545817336
H	14.912351260	10.999903102	6.322349910
C	16.323524752	4.727732914	7.247476840
H	16.578070633	3.920395324	6.571777887
C	15.656240428	6.791733833	8.985134141
H	15.403052419	7.576047514	9.684863344
C	17.294907657	5.276857826	8.077507844
H	18.308655281	4.896147632	8.053581276
C	16.957278737	6.307029481	8.949109089
H	17.703970444	6.727932894	9.611021051
P	11.059147833	4.850112602	9.948646451
C	10.988623893	4.827636439	8.178942513
C	10.142362748	3.954432914	7.477067493
H	9.499843082	3.285096821	8.038142517
C	10.084519140	3.930399692	6.099689122
C	9.381531084	4.589286548	10.616603815
C	8.521808324	5.684629081	10.752545500
H	8.876030676	6.680137547	10.515137944
C	12.044093958	3.432439374	10.575277152
C	7.220444360	5.507227516	11.198192637
H	6.568739756	6.365515628	11.304215974
C	8.910595078	3.314057372	10.942863228

H	9.563068978	2.454963706	10.857801464
C	12.585719584	2.487746334	9.704700495
H	12.400641097	2.572609703	8.641773885
C	12.298152603	3.323236257	11.946544835
H	11.893101911	4.058184657	12.632853419
C	7.603497204	3.139524158	11.386340837
H	7.251183254	2.145513323	11.633064081
C	13.602221985	1.335258152	11.562042957
H	14.207849502	0.522896886	11.944647934
C	13.361084320	1.442646566	10.198175160
H	13.777359754	0.714564535	9.512790717
C	6.756524068	4.232734625	11.515655966
H	5.741006410	4.095839702	11.866237175
C	13.068610784	2.278294724	12.436795110
H	13.259668814	2.202545028	13.500218068
F	11.680764729	12.177796252	12.106581194
F	14.770304204	7.713057746	12.043021674
F	15.695704943	9.981791027	13.136028104
F	14.156618405	12.225914861	13.158009107
C	12.702126484	8.717207523	11.455494440
C	11.935590026	9.885490262	11.498669570
C	13.961163383	8.798073062	12.028570342
C	12.413996616	11.057335223	12.065680934
C	13.687967809	11.098028395	12.616769821
C	14.469249967	9.953948948	12.602965142
H	10.854540676	4.834580310	4.266218729
H	9.409937930	3.251717779	5.596106226

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Model_5 T1

Au	12.157687320	6.775710229	10.619533891
P	12.993645327	6.838870401	8.243739227
C	11.429471432	4.507787183	5.336406802
C	12.268856993	5.332586677	6.033658514
H	13.045111397	5.865865124	5.497248163
C	12.135798575	5.527377293	7.442347152
C	14.791714518	6.592010839	8.152447954
C	12.686076889	8.466032412	7.472470123
C	15.314613153	5.327059860	7.866720556
H	14.640651215	4.515027354	7.628698355
C	13.414252179	8.880528850	6.348773591
H	14.257248449	8.297988642	6.000020208
C	11.609470390	9.249082769	7.903173545
H	11.040124863	8.954131563	8.774921153
C	11.998248983	10.817656403	6.116282196
H	11.734172644	11.728619723	5.593604382
C	11.272655379	10.417031453	7.234254883
H	10.445947264	11.018550952	7.591579291
C	13.067747874	10.045367267	5.677065022
H	13.639438710	10.352007549	4.809374251
C	16.687562187	5.115989169	7.879925476
H	17.081359972	4.134672025	7.646080854
C	15.669568482	7.633564298	8.480219279

H	15.279517250	8.614572699	8.720567897
C	17.552053642	6.158116082	8.195841103
H	18.621991121	5.990571145	8.212165289
C	17.039197193	7.416598430	8.498900014
H	17.708160364	8.228463039	8.755890764
P	11.031874238	4.813790393	9.891088392
C	11.082842087	4.776910189	8.120337384
C	10.226117922	3.966940617	7.366402724
H	9.431882425	3.429481051	7.872793601
C	10.365977527	3.823773639	5.998864157
C	9.296881504	4.678943907	10.437650479
C	8.504563390	5.831276099	10.460572310
H	8.935725963	6.788189488	10.192416137
C	11.882074468	3.345056642	10.590200940
C	7.168534212	5.759756460	10.828774115
H	6.567265336	6.660081052	10.845496545
C	8.727447307	3.455813811	10.798436622
H	9.327854100	2.555665017	10.797758888
C	12.376178156	2.338574829	9.760492427
H	12.238260642	2.412458831	8.689679599
C	12.072247282	3.246549154	11.972525603
H	11.705517902	4.028335841	12.627574719
C	7.387078526	3.386737013	11.165756235
H	6.956335278	2.431901179	11.440675855
C	13.218525930	1.148860413	11.680648905
H	13.738233404	0.297892141	12.103422643
C	13.041348322	1.244672669	10.306021702
H	13.420860857	0.468621851	9.652743472
C	6.606656031	4.535724752	11.182106378
H	5.564868612	4.480769668	11.472939490
C	12.731529013	2.152002393	12.514406138
H	12.873813985	2.085271772	13.585961719
F	12.155419007	11.855155666	12.473128185
F	14.986614219	7.234716188	12.113430401
F	16.046860891	9.313162435	13.388001045
C	12.999735871	8.419401557	11.604686665
C	12.332768010	9.626889941	11.734951000
C	14.258290389	8.369714808	12.182945892
C	12.869034716	10.723535487	12.392581539
C	14.133622124	10.644924313	12.963400010
C	14.825800153	9.444995607	12.851129617
H	11.566640657	4.386007903	4.269140541
H	9.678255425	3.204034213	5.440865989
F	11.093527817	9.772660297	11.209716587
I	14.965786924	12.279599349	13.965596181

5. Coordination environment for the gold(I) centers for complexes **2**-**5** at the ground state S_0 and the first triplet excited state T_1

Table S4. Selected bond lengths (Å) and angles (°) for the coordination environment of the gold(I) centers for complexes **2-3**

	2			**3**	
	X-Ray	**S_0**	**T_1**	**S_0**	**T_1**
Au-C (Å)	2.084	2.08	2.10	2.07	2.09
Au-P (Å)	2.2794	2.31	2.38	2.31	2.38
Au-P (Å)	3.4398	3.08	2.53	3.08	2.52
C-Au-P (°)	177.16	174.63	169.29	173.37	169.50
C-Au-P (°)	118.29	110.74	107.42	111.21	106.72
P-Au-P (°)	64.29	74.32	82.96	74.36	83.73

Table S5. Selected bond lengths (Å) and angles (°) for the coordination environment of the gold(I) centers for complexes **4-5**

	4		**5**	
	S_0	**T_1**	**S_0**	**T_1**
Au-C (Å)	2.08	2.10	2.07	2.09
Au-P (Å)	2.31	2.38	2.31	2.38
Au-P (Å)	3.07	2.54	3.08	2.52
C-Au-P (°)	175.51	169.79	174.21	169.47
C-Au-P (°)	109.92	107.48	110.05	106.90
P-Au-P (°)	74.56.70	82.53	74.22	83.62

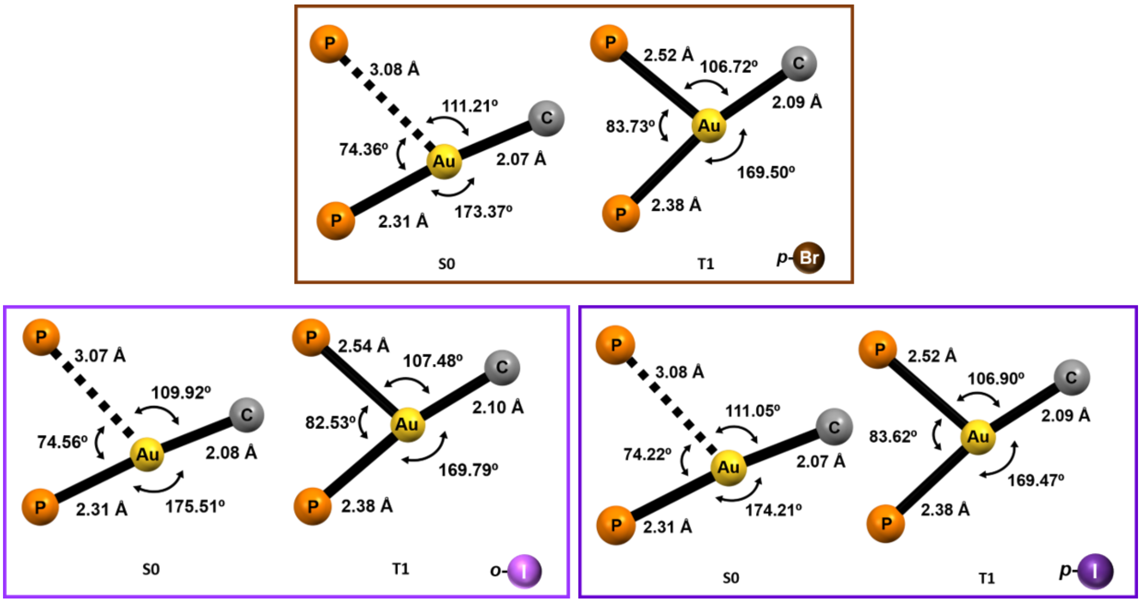

Figure S52. Coordination environment for the gold(I) centers for complexes **3**-**5** at the ground state S_0 and the first triplet excited state T_1

6. Computational calculation of the energy difference between S_0 and T_1

Table S6. The energy difference between the ground singlet state and the lowest excited triplet state calculated at the B3LYP/def2-TZVP level are compared to the experimental data. Spin-orbit coupling matrix element (SOC in cm^{-1}); rate constant for intersystem crossing (K_{ISC} ($S_0 \rightarrow T_1$) are also reported for complexes **2-5**

	SOC(S_0-T_1)	ΔE(S_0-T_1) Theory	ΔE(S_0-T_1) Exp.	E(S_0-T_1) Exp.	k_{ISC} (S_0-T_1) (Theor. Energy)	k_{ISC} (S_0-T_1) (Exp. Energy)
2	46.8 cm^{-1}	10730 cm^{-1}	17668 cm^{-1}	566 nm	$1{\cdot}10^4$ s^{-1}	$3{\cdot}10^{-4}$ s^{-1}
3	59.5 cm^{-1}	9491 cm^{-1}	16949 cm^{-1}	590 nm	$4{\cdot}10^5$ s^{-1}	$3{\cdot}10^{-3}$ s^{-1}
4	56.5 cm^{-1}	10920 cm^{-1}	16234 cm^{-1}	616 nm	$1{\cdot}10^4$ s^{-1}	$2{\cdot}10^{-2}$ s^{-1}
5	60.2 cm^{-1}	9618 cm^{-1}	16807 cm^{-1}	595 nm	$3{\cdot}10^5$ s^{-1}	$5{\cdot}10^{-3}$ s^{-1}

7. Frontier HOMO and LUMO for complexes **3**-**5**.

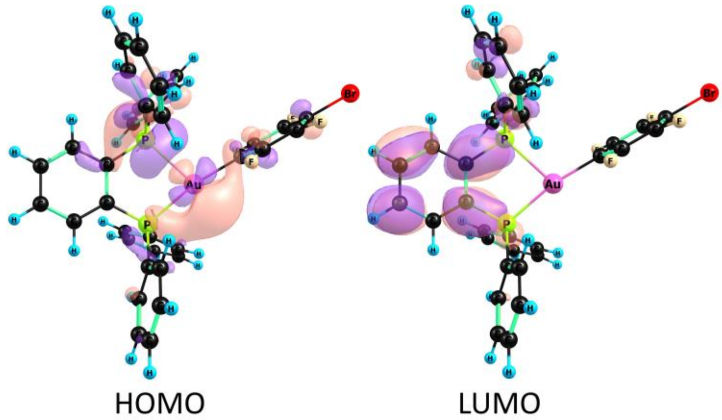

Figure S53. The orbitals obtained in the CASSCF calculation that correspond to the HOMO (left) and the LUMO (right) of complex [Au(*p*-C_6BrF_4)(dppBz)] (**3**)

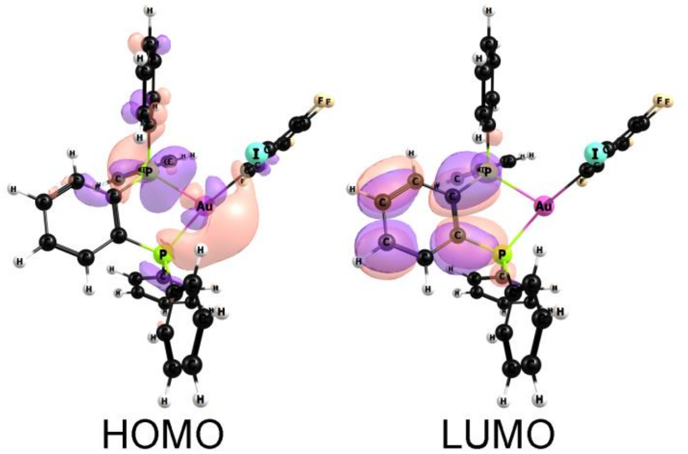

Figure S54. The orbitals obtained in the CASSCF calculation that correspond to the HOMO (left) and the LUMO (right) of complex [Au(*o*-C_6F_4I)(dppBz)] (**4**)

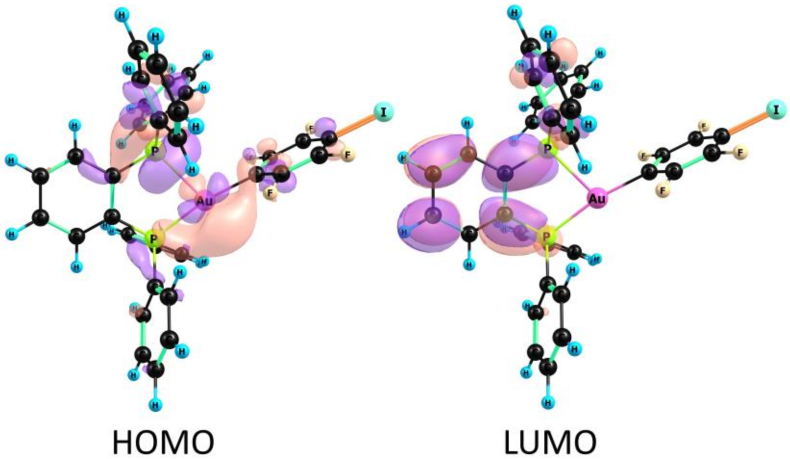

Figure S55. The orbitals obtained in the CASSCF calculation that correspond to the HOMO (left) and the LUMO (right) of complex [Au(p-C_6F_4I)(dppBz)] (**5**)

8. Transition densities calculations

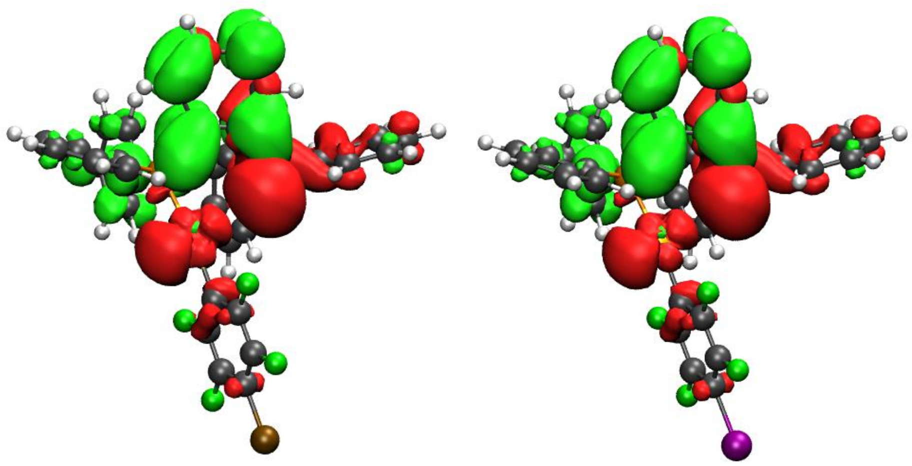

Figure S56. Transition densities for complexes [Au(p-C_6BrF_4)(dppBz)] (**3**) (left) and [Au(p-C_6F_4I)(dppBz)] (**5**) (right). During the transition the electron density increases in the green areas and decreases in the red ones.