Towards Blue Emitting Gold(III) Complexes – Synthesis, Characterization and Photophysical Investigations

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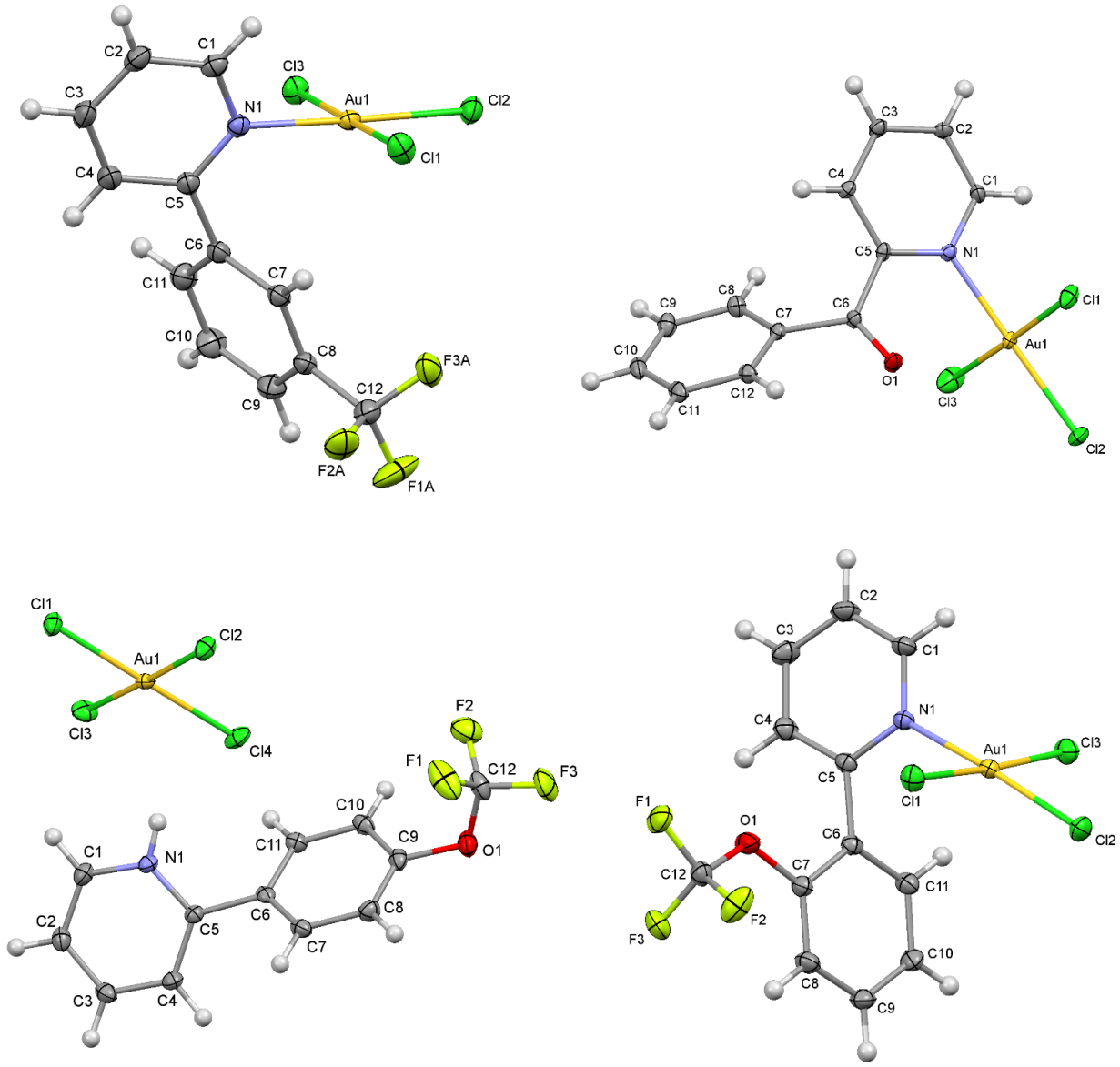

Figure S1. X-ray structures of $LAuCl_3$ and ($L^+AuCl_4^-$) compounds. Thermal ellipsoids were drawn at the 50 % probability level.

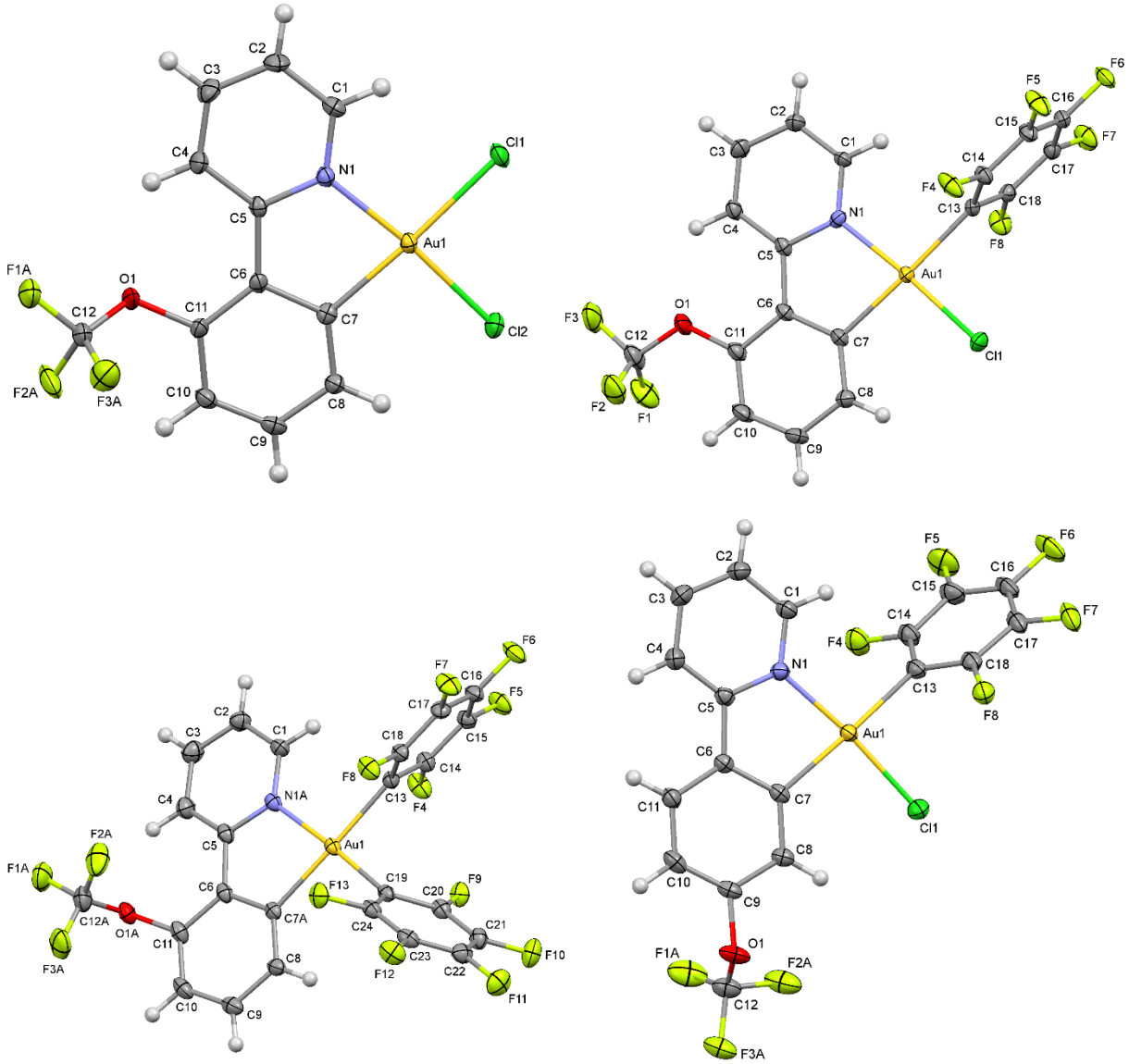

Figure S2. X-ray structures of dichloride precursor, **5**, **6** and **7**. Thermal ellipsoids are drawn at the 30 % probability level. For **5**, only one of the two independent molecules is shown.

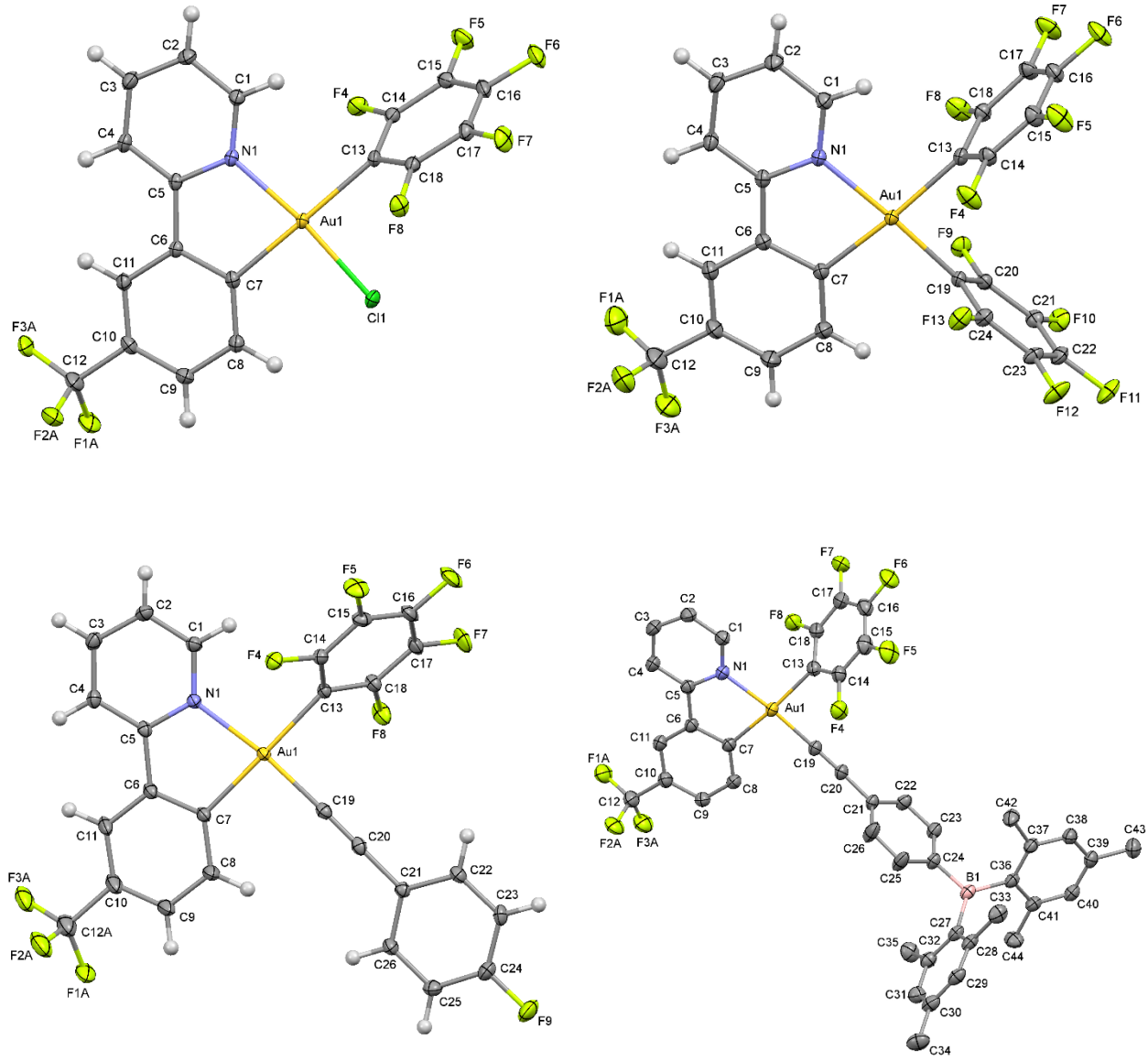

Figure S3. X-ray structures of **1**–**4**. Thermal ellipsoids are drawn at the 30 % probability level.

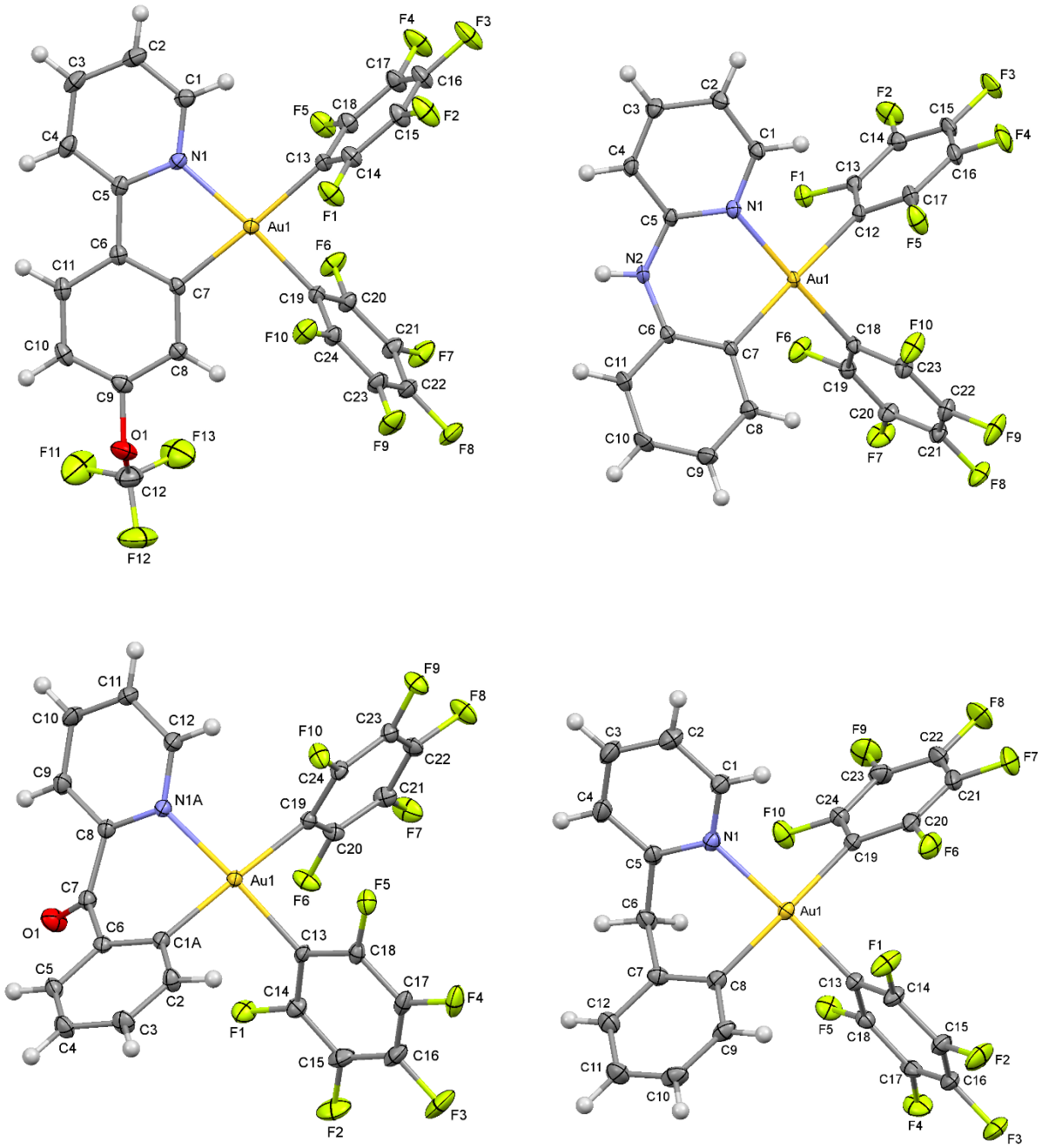

Figure S4. X-ray structures of **8**, **9**, **10** and **11,** ellipsoids were drawn at the 50 % probability level.

Table S1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
CCDC	1869489	1869490
Empirical formula	$C_{18}H_7AuClF_8N$	$C_{24}H_7AuF_{13}N$
Formula weight	621.66	753.27
Temperature/K	183(1)	183(1)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	7.4978(2)	7.46347(12)
b/Å	9.7978(3)	12.3497(2)
c/Å	12.3390(3)	13.5523(2)
α/°	95.658(2)	116.3844(17)
β/°	92.544(2)	91.3367(13)
γ/°	111.090(3)	93.6356(14)
Volume/Å^3	838.49(4)	1114.91(4)
Z	2	2
ρ_{calc}g/cm^3	2.462	2.244
μ/mm^{-1}	9.021	6.721
F(000)	580.0	708.0
Crystal size/mm^3	0.33 × 0.1 × 0.07	0.16 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.252 to 61.012	5.478 to 61.012
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	20382	27509
Independent reflections	5117 [R_{int} = 0.0333, R_{sigma} = 0.0276]	6819 [R_{int} = 0.0218, R_{sigma} = 0.0189]
Data/restraints/parameters	5117/201/320	6819/87/380
Goodness-of-fit on F^2	1.044	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0195, wR_2 = 0.0427	R_1 = 0.0165, wR_2 = 0.0379
Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0435	R_1 = 0.0184, wR_2 = 0.0387
Largest diff. peak/hole / e Å^{-3}	1.24/-0.91	0.82/-0.85

Table S2. Crystal data and structure refinement for **3** and **4**.

	3	**4**
CCDC	1869493	1869498
Empirical formula	$C_{26}H_{11}AuF_9N$	$C_{44}H_{33}AuBF_8N$
Formula weight	705.32	935.49
Temperature/K	183(1)	183(1)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	7.12708(9)	12.19360(10)
b/Å	7.59256(9)	14.5075(2)
c/Å	20.4351(3)	21.3333(2)
α/°	92.6860(10)	90
β/°	90.1522(10)	92.0020(10)
γ/°	94.7363(10)	90
Volume/Å^3	1100.79(2)	3771.53(7)
Z	2	4
ρ_{calc}g/cm^3	2.128	1.648
μ/mm^{-1}	6.775	7.962
F(000)	668.0	1840.0
Crystal size/mm^3	0.21 × 0.09 × 0.04	0.16 × 0.12 × 0.03
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.39 to 61.014	7.254 to 148.954
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -29 ≤ l ≤ 29	-10 ≤ h ≤ 15, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26
Reflections collected	27018	54592
Independent reflections	6721 [R_{int} = 0.0240, R_{sigma} = 0.0211]	7708 [R_{int} = 0.0286, R_{sigma} = 0.0152]
Data/restraints/parameters	6721/158/371	7708/51/530
Goodness-of-fit on F^2	1.050	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0192, wR_2 = 0.0451	R_1 = 0.0261, wR_2 = 0.0724
Final R indexes [all data]	R_1 = 0.0216, wR_2 = 0.0462	R_1 = 0.0287, wR_2 = 0.0748
Largest diff. peak/hole / e Å^{-3}	1.16/-1.06	0.72/-1.14

Table S3. Crystal data and structure refinement for **5** and **6**.

	5	**6**
CCDC	1869496	1869499
Empirical formula	$C_{18}H_7AuClF_8NO$	$C_{25}H_9AuCl_2F_{13}NO$
Formula weight	637.66	854.20
Temperature/K	183(1)	183(1)
Crystal system	orthorhombic	triclinic
Space group	Pbca	P-1
a/Å	13.40689(16)	8.93520(16)
b/Å	15.13771(19)	11.1309(2)
c/Å	35.2684(5)	13.2328(3)
α/°	90	99.6228(17)
β/°	90	94.9371(16)
γ/°	90	95.3130(15)
Volume/Å^3	7157.71(16)	1285.07(4)
Z	16	2
ρ_{calc}g/cm^3	2.367	2.208
μ/mm^{-1}	8.462	6.050
F(000)	4768.0	808.0
Crystal size/mm^3	0.25 × 0.08 × 0.03	0.2 × 0.14 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.62 to 52.742	4.434 to 61.014
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -41 ≤ l ≤ 44	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	49714	31483
Independent reflections	7315 [R_{int} = 0.0333, R_{sigma} = 0.0198]	7838 [R_{int} = 0.0279, R_{sigma} = 0.0251]
Data/restraints/parameters	7315/18/541	7838/41/453
Goodness-of-fit on F^2	1.077	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0232, wR_2 = 0.0517	R_1 = 0.0236, wR_2 = 0.0547
Final R indexes [all data]	R_1 = 0.0302, wR_2 = 0.0545	R_1 = 0.0270, wR_2 = 0.0562
Largest diff. peak/hole / e Å^{-3}	1.75/-0.95	1.22/-1.10

Table S4. Crystal data and structure refinement for **7** and **8**.

	7	**8**
CCDC	1869497	1869491
Empirical formula	$C_{18}H_7AuClF_8NO$	$C_{49}H_{16}Au_2Cl_2F_{26}N_2O_2$
Formula weight	637.66	1623.47
Temperature/K	183(1)	183(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	12.4931(3)	7.52497(10)
b/Å	9.5611(3)	20.3047(3)
c/Å	15.0285(5)	17.2623(3)
α/°	90	90
β/°	94.074(2)	91.7787(12)
γ/°	90	90
Volume/Å^3	1790.59(9)	2636.27(6)
Z	4	2
ρ_{calc}g/cm^3	2.365	2.045
μ/mm^{-1}	8.456	5.794
F(000)	1192.0	1532.0
Crystal size/mm^3	0.16 × 0.12 × 0.07	0.28 × 0.13 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.054 to 61.016	4.656 to 61.01
Index ranges	-17 ≤ h ≤ 17, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21	-10 ≤ h ≤ 10, -29 ≤ k ≤ 29, -24 ≤ l ≤ 22
Reflections collected	43632	42242
Independent reflections	5470 [R_{int} = 0.0589, R_{sigma} = 0.0311]	8035 [R_{int} = 0.0292, R_{sigma} = 0.0213]
Data/restraints/parameters	5470/66/299	8035/18/392
Goodness-of-fit on F^2	1.051	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0681	R_1 = 0.0259, wR_2 = 0.0673
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0748	R_1 = 0.0329, wR_2 = 0.0710
Largest diff. peak/hole / e Å^{-3}	1.35/-1.20	1.76/-1.15

Table S5. Crystal data and structure refinement for **9** and **10**.

	9	**10**
CCDC	1869492	1869494
Empirical formula	$C_{23.5}H_{10}AuClF_{10}N_2$	$C_{24}H_8AuF_{10}NO$
Formula weight	742.75	713.28
Temperature/K	183(1)	183(1)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	7.52154(19)	8.9720(2)
b/Å	12.3617(3)	26.0250(5)
c/Å	13.5748(4)	9.2820(2)
α/°	67.908(3)	90
β/°	74.915(2)	90.407(2)
γ/°	77.032(2)	90
Volume/Å^3	1117.85(6)	2167.26(9)
Z	2	4
ρ_{calc}g/cm^3	2.207	2.186
μ/mm^{-1}	6.800	6.893
F(000)	702.0	1344.0
Crystal size/mm^3	0.44 × 0.24 × 0.07	0.22 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.642 to 61.016	4.802 to 61.014
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-11 ≤ h ≤ 12, -37 ≤ k ≤ 37, -13 ≤ l ≤ 13
Reflections collected	27592	26976
Independent reflections	6835 [R_{int} = 0.0293, R_{sigma} = 0.0262]	6622 [R_{int} = 0.0387, R_{sigma} = 0.0319]
Data/restraints/parameters	6835/1/329	6622/0/329
Goodness-of-fit on F^2	1.051	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0176, wR_2 = 0.0382	R_1 = 0.0275, wR_2 = 0.0590
Final R indexes [all data]	R_1 = 0.0206, wR_2 = 0.0395	R_1 = 0.0334, wR_2 = 0.0612
Largest diff. peak/hole / e Å^{-3}	0.77/-0.87	1.43/-1.27

Table S6. Crystal data and structure refinement for **11** and **(bpy)AuCl$_3$**.

	11	**(bpy)AuCl$_3$**
CCDC	1869495	1869503
Empirical formula	$C_{24}H_{10}AuF_{10}N$	$C_{12}H_9AuCl_3NO$
Formula weight	699.30	486.52
Temperature/K	183(1)	183(1)
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a/Å	9.9129(3)	22.5415(11)
b/Å	11.1532(3)	7.6492(3)
c/Å	11.4166(3)	16.1518(7)
α/°	103.602(3)	90
β/°	106.404(3)	95.509(5)
γ/°	106.367(2)	90
Volume/Å^3	1091.73(6)	2772.1(2)
Z	2	8
ρ_{calc}g/cm^3	2.127	2.331
μ/mm^{-1}	6.836	11.177
F(000)	660.0	1808.0
Crystal size/mm^3	0.25 × 0.09 × 0.06	0.34 × 0.1 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.062 to 61.016	5.068 to 61.006
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-32 ≤ h ≤ 32, -10 ≤ k ≤ 10, -22 ≤ l ≤ 23
Reflections collected	22916	21616
Independent reflections	6645 [R_{int} = 0.0322, R_{sigma} = 0.0322]	4218 [R_{int} = 0.0440, R_{sigma} = 0.0307]
Data/restraints/parameters	6645/0/325	4218/0/163
Goodness-of-fit on F^2	1.039	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0213, wR_2 = 0.0439	R_1 = 0.0220, wR_2 = 0.0500
Final R indexes [all data]	R_1 = 0.0255, wR_2 = 0.0454	R_1 = 0.0271, wR_2 = 0.0521
Largest diff. peak/hole / e Å^{-3}	0.75/-0.81	0.78/-1.56

Table S7. Crystal data and structure refinement for **cis-[(2-OCF_3-ppy)$AuCl_2$]** and **(3-CF_3-ppy)$AuCl_3$**.

	cis-[(2-OCF_3-ppy)$AuCl_2$]	**(3-CF_3-ppy)$AuCl_3$**
CCDC	1869502	1869501
Empirical formula	$C_{12}H_7AuCl_2F_3NO$	$C_{12}H_8AuCl_3F_3N$
Formula weight	506.05	526.51
Temperature/K	183(1)	183(1)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	7.3933(5)	9.5835(2)
b/Å	9.6720(7)	9.1319(2)
c/Å	9.9155(6)	17.6224(5)
α/°	90.820(5)	90
β/°	110.173(6)	103.788(3)
γ/°	100.635(6)	90
Volume/$Å^3$	651.77(8)	1497.79(7)
Z	2	4
$\rho_{calc}g/cm^3$	2.579	2.335
μ/mm^{-1}	11.723	10.376
F(000)	468.0	976.0
Crystal size/mm^3	0.4 × 0.13 × 0.02	0.17 × 0.13 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.882 to 61.014	4.76 to 61.014
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -25 ≤ l ≤ 25
Reflections collected	4504	35634
Independent reflections	4504 [R_{int} = ?, R_{sigma} = 0.0619]	4560 [R_{int} = 0.0391, R_{sigma} = 0.0232]
Data/restraints/parameters	4504/105/210	4560/66/209
Goodness-of-fit on F^2	0.961	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0715	R_1 = 0.0211, wR_2 = 0.0433
Final R indexes [all data]	R_1 = 0.0384, wR_2 = 0.0736	R_1 = 0.0287, wR_2 = 0.0460
Largest diff. peak/hole / e $Å^{-3}$	1.57/-1.25	1.07/-0.68

Table S8. Crystal data and structure refinement for **(2-OCF_3-ppy)$AuCl_3$** and **(4-OCF_3-ppy)$AuCl_3$**.

	(2-OCF_3-ppy)$AuCl_3$	**[4-OCF_3-ppyH]$^+$[$AuCl_4$]$^-$**
CCDC	1869504	1869500
Empirical formula	$C_{12}H_8AuCl_3F_3NO$	$C_{12}H_9AuCl_4F_3NO$
Formula weight	542.51	578.97
Temperature/K	183(1)	183(1)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	8.32835(10)	7.9515(2)
b/Å	8.52721(13)	9.0911(2)
c/Å	11.14154(18)	11.4209(3)
α/°	80.8251(13)	98.035(2)
β/°	83.4322(12)	94.660(2)
γ/°	75.5789(12)	95.709(2)
Volume/Å^3	754.20(2)	809.63(4)
Z	2	2
ρ_{calc}g/cm^3	2.389	2.375
μ/mm^{-1}	10.311	23.447
F(000)	504.0	540.0
Crystal size/mm^3	0.19 × 0.16 × 0.02	0.19 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.978 to 52.744	7.854 to 136.48
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	28033	11799
Independent reflections	3091 [R_{int} = 0.0212, R_{sigma} = 0.0095]	2953 [R_{int} = 0.0119, R_{sigma} = 0.0109]
Data/restraints/parameters	3091/0/190	2953/1/204
Goodness-of-fit on F^2	1.085	1.204
Final R indexes [I>=2σ (I)]	R_1 = 0.0098, wR_2 = 0.0239	R_1 = 0.0174, wR_2 = 0.0438
Final R indexes [all data]	R_1 = 0.0103, wR_2 = 0.0241	R_1 = 0.0175, wR_2 = 0.0439
Largest diff. peak/hole / e Å^{-3}	0.36/-0.41	0.80/-0.90

Single-crystal X-ray diffraction data were collected at 183(1) K on Rigaku OD SuperNova (CCD Atlas detector) and Xcalibur (CCD Ruby detector) diffractometers using a single wavelength X-ray source (Mo K_α radiation: λ = 0.71073 Å)[1] from a micro-focus sealed X-ray tube and an Oxford liquid-nitrogen Cryostream cooler. The selected suitable single crystals were mounted using polybutene oil on a flexible loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption correction[2] were performed with the program suite *CrysAlisPro*.[3] Using *Olex2*,[4] the structure was solved with the SHELXT[5] small molecule structure solution program and refined with the *SHELXL2018/3* program package[6] by full-matrix least-squares minimization on F^2. *PLATON*[7] was used to check the result of the X-ray analyses. For more details about the data collection and refinement parameters, see the CIF files.

CCDC 1869489 (for **1**), 1869490 (for **2**), 1869493 (for **3**) 1869498 (for **4**), 1869496 (for **5**), 1869499 (for **6**), 1869497 (for **7**), 1869491 (for **8**), 1869492 (for **9**), 1869494 (for **10**), 1869495 (for **11**), 1869503 (for (bpy)$AuCl_3$), 1869502 (for cis-[(2-OCF_3-ppy)$AuCl_2$]), 1869501 (for (3-CF_3-ppy)$AuCl_3$), 1869504 (for (2-OCF_3-ppy)$AuCl_3$) and 1869500 (for (4-OCF_3-ppy)$AuCl_3$).

References

(1) Rigaku Oxford Diffraction, **2015**.

(2) Clark, R. C.; Reid, J. S. *Acta Cryst. A* **1995**, 51, 887.

(3) *CrysAlisPro* (version 1.171.39.13a), Rigaku Oxford Diffraction, **2016**.

(4) "*A complete structure solution, refinement and analysis program*" - Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339.

(5) "*SHELXT - Integrated space-group and crystal-structure determination*" - Sheldrick, G. M. *Acta Cryst. A* **2015**, 71, 3.

(6) "*Crystal structure refinement with SHELXL*" - Sheldrick, G. M. *Acta Cryst. C* **2015**, 71, 3.

(7) "*Structure validation in chemical crystallography*" - Spek, A. L. *Acta Cryst. D* **2009**, *65*, 148.

Excitation Spectra of Complexes at 77 K

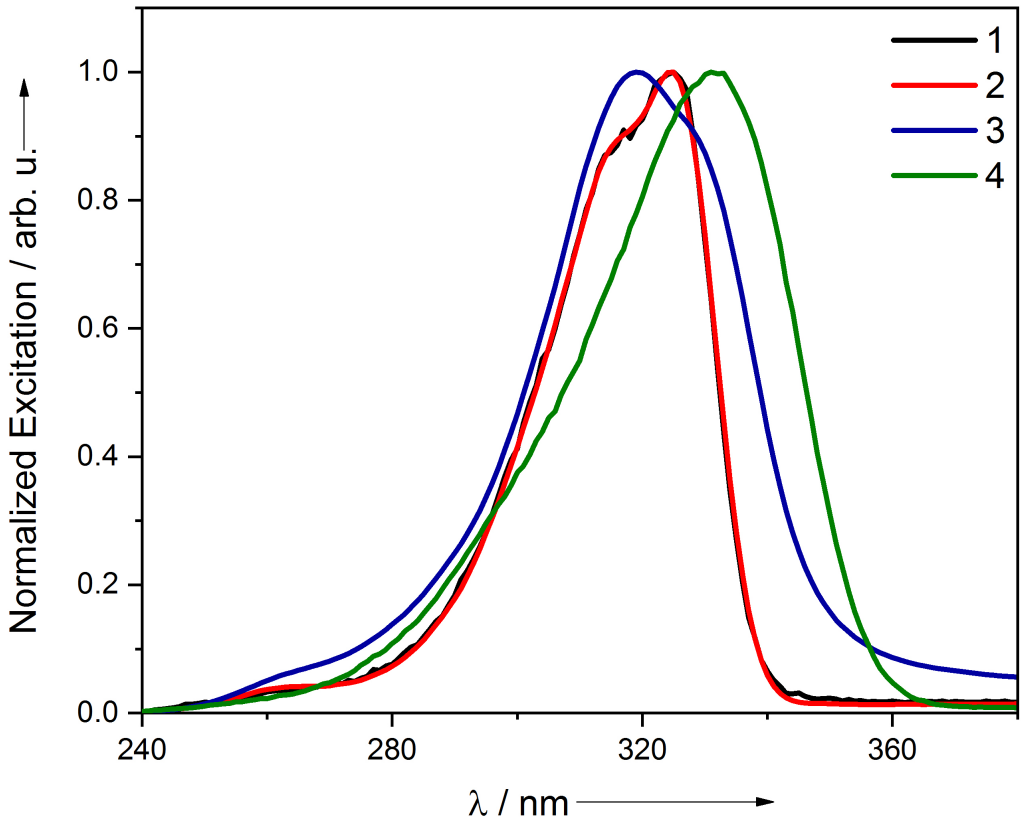

Figure S5. Excitation spectra of complexes 1-4 in 2-MeTHF at 77 K.

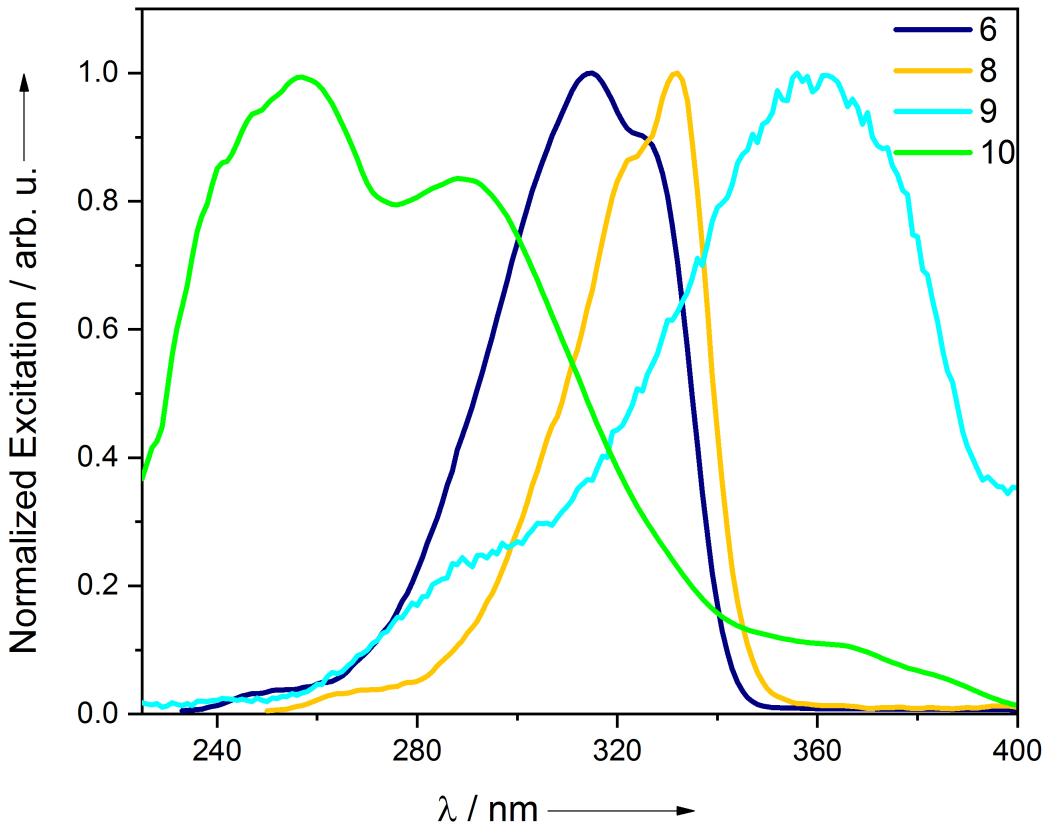

Figure S6. Excitation spectra of complexes 6, 8-10 in 2-MeTHF at 77 K.

Synthesis of precursors

General procedure for the Suzuki-Coupling to obtain the corresponding phenylpyridine (ppy) derivatives (2-(3- trifluoromethylphenyl)pyridine, 2-(2-trifluoromethoxyphenyl)pyridine and 2-(4-trifluoromethoxy- phenyl)pyridine.
To a solution of 2-bromopyridine (1 equivalent), NaOH (2.4 equivalent) and a substituted phenylboronic acid (1.2 equivalent) in a degassed water/1,4-dioxane (3/5) mixture, a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (0.01 equivalent) was added and stirred at 80 °C for 48 h. The product was extracted in dichloromethane and purified by column chromatography using silica gel (eluent: hexane/diethylether = 4/1).

3-trifluoromethylphenylpyridine **(3-CF_3-ppy)**: From 2-bromopyridine (2.19 g, 13.9 mmol) and 3-trifluoromethylphenylboronic acid (3.16 g, 16.6 mmol) in 160 mL water/1,4-dioxane, the product was obtained as a colorless oil (1.97 g, 8.83 mmol, 64%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm) = 8.71 (dt, $^3J_{H-H}$ = 4.8, 1.6 Hz, 1H), 8.34 (s, 1H), 8.22 (d, $^3J_{H-H}$ = 7.6 Hz, 1H), 7.82 – 7. 80 (m, 2H), 7.69 (d, $^3J_{H-H}$ = 7.6 Hz, 1H), 7.62 (t, $^3J_{H-H}$ = 7.6 Hz, 1H), 7.32 – 7.29 (m 1H); ^{19}F NMR (470.70 MHz, CD_2Cl_2, 298 K): δ (ppm) = -64.5 (s).

2-trifluoromethoxyphenylpyridine **(2-OCF_3-ppy)**: From 2-bromopyridine (2.45 g, 15.5 mmol) and 2-trifluoromethoxyphenylboronic acid (3.51 g, 17.0 mmol) in 160 mL water/1,4-dioxane, the product was obtained as a colorless oil (2.39 g, 9.99 mmol, 64%); ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ (ppm) = 8.72 (s, 1H), 7.84 – 7.75 (m, 2H), 7.68 (d, $^3J_{H-H}$ = 7.1 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.32 – 7.28 (m, 1H); ^{19}F NMR (470.70 MHz, CD_2Cl_2, 298 K): δ (ppm) = -59.1 (s).

4-trifluoromethoxyphenylpyridine **(4-OCF_3-ppy)**: From 2-bromopyridine (1 g, 6.33 mmol) and 4-trifluoromethoxyphenylboronic acid (1.56 g, 7.59 mmol) in 160 mL water/1,4-dioxane, the product was obtained as a white solid (0.69 g, 9.99 mmol, 45%); ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ (ppm) = 8.67 – 8.66 (m, 1H), 8.09 – 8.04 (m, 2H), 7.79 – 7.75 (m, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H); ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K): δ (ppm) = -59.1 (s).

General procedure for the substitution reaction on hydrated gold(III)tetrachloroaurate with various phenylpyridine derivatives in order to obtain neutral $LAuCl_3$ (L = 3-CF_3-ppy, 2-OCF_3-ppy, 4-OCF_3-ppy).
To an aqeuous solution of $NaAuCl_4 \cdot 2H_2O$, a solution of corresponding *ppy* derivative in acetonitrile was added and the mixture was stirred at RT for 24 h. The solution was filtered and the filter cake was washed with water and hexane. The product was dried *in vacuo*.

N-2-(3-trifluoromethylphenyl)pyridine$AuCl_3$ **((3-CF_3-ppy)$AuCl_3$)**: From 3-CF_3-ppy (600 mg, 2.69 mmol) in acetonitrile (15 mL) and $NaAuCl_4 \cdot 2H_2O$ (891 mg, 2.24 mmol) in water (15 mL) a yellow solid was obtained **(3-CF_3-ppy)$AuCl_3$** (1.09 g, 2.07 mmol, 92%); ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ (ppm) = 8.75 (s, 1H), 8.43 (s, 1H), 8.39 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 8.16 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 8.04 (t, $^3J_{H-H}$ = 8.4 Hz, 1H), 7.84 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.77 (t, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.51 (t, $^3J_{H-H}$ = 6 Hz, 1H); ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ (ppm) = -63.2 (s, 3F).

N-2-(2-trifluoromethoxyphenyl)pyridine$AuCl_3$ **((2-OCF_3-ppy)$AuCl_3$)**: From 2-OCF_3-ppy (388 mg, 1.62 mmol) in acetonitrile (10 mL) and $NaAuCl_4 \cdot 2H_2O$ (5382.0 mg, 1.35 mmol) in water (15 mL), **(2-OCF_3-ppy)$AuCl_3$** was collected as a yellow solid (247 mg, 0.455 mmol, 34%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm) = 8.90 (d, $^3J_{H-H}$ = 6 Hz, 1H), 8.26 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.99 (d, $^3J_{H-H}$ = 7.6 Hz, 1H), 7.88 (d, $^3J_{H-H}$ = 7.6 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.63 (t, $^3J_{H-H}$ = 7.6 Hz, 1H), 7.55 (d, $^3J_{H-H}$ =8.4 Hz, 1H); ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K): δ (ppm) = -58.2.

N-4-(2-trifluoromethoxyphenyl)pyridine$H^+AuCl_4^-$ **[4-OCF_3-ppyH]$^+$[$AuCl_4$]$^-$**: From 4-OCF_3-ppy 700 mg, 2.92 mmol) in acetonitrile (40 mL) and $NaAuCl_4 \cdot 2H_2O$ (970 mg, 2.44 mmol) in water (40

mL) a yellow solid was obtained **[4-OCF$_3$-ppyH]$^+$[AuCl$_4$]$^-$** (1.30 g, 0.240 mmol, 98%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm) = 9.04 (d, $^3J_{H-H}$ = 6 Hz, 1H), 8,68 (t, $^3J_{H-H}$ = 8 Hz, 1H), 8.26 (d, $^3J_{H-H}$ = 8 Hz, 1H), 8.10 – 8.05 (m, 3H); ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ (ppm) = -58.0 (s, 3F).

N-2-benzylpyridineAuCl$_3$ **(bepyAuCl$_3$)**: From bpy (234.0 mg, 1.383 mmol) in acetonitrile (25 mL) and $NaAuCl_4 \cdot 2H_2O$ (500 mg, 1.257 mmol) in water (25 mL) a yellow solid was obtained (bpyAuCl$_3$) (463.3 mg, 0.980 mmol, 78%); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm) = 8.70 (d, $^3J_{(H-H)}$ = 6.0 Hz, 1H), 8.00 (td, $^3J_{(H-H)}$ = 7.8 Hz, $^4J_{(H-H)}$ = 1.4 Hz, 1H), 7.56-7.60 (m, 1H), 7.36-7.45 (m, 4H), 7.30-7.32 (m, 2H), 4.73 (s, 2H).

Cis-(2-(3-trifluoromethylphenyl)pyridine)AuCl$_2$ **((3-CF$_3$-ppy)AuCl$_2$)**: A suspension of **((3-CF$_3$-ppy)AuCl$_3$)** (501 mg, 0.923 mmol) in water (20 mL) was subjected to microwave irradiation and was kept stirring at 180 °C for 10 min. Thereafter, the solid was filtered and washed with water. This procedure was repeated four times and the product was washed with water and diethylether and dried *in vacuo* to obtain ***cis*-[(3-CF$_3$-ppy)AuCl$_2$]** as a white solid (257 mg, 0.524 mmol, 55%); ^{1}H NMR (500.25 MHz, CD_2Cl_2, 298 K): δ (ppm) = 9.83 (d, $^3J_{(H-H)}$ = 7.0 Hz, 1H), 8.26 – 8.22 (m, 2H), 8.03 (d, $^3J_{(H-H)}$ = 8.0 Hz, 1H), 7.87 (s, 1H), 7.66 – 7.63 (m, 2H); ^{19}F NMR (470.70 MHz, $(CD_3)_2SO$, 298 K): δ (ppm) = -62.0 (s).

Cis-(2-(2-trifluoromethoxyphenyl)pyridine)AuCl$_2$ **(*cis*-[(2-OCF$_3$-ppy)AuCl$_2$])**: A suspension of **((2-OCF$_3$-ppy)AuCl$_3$)** (206 mg, 0.378 mmol) in water (20 mL) was subjected to microwave irradiation and was kept stirring at 180 °C for 15 min. Thereafter, the reaction mixture was filtered and washed with water and acetonitrile and dried *in vacuo* to afford ***cis*-[(2-OCF$_3$-ppy)AuCl$_2$]** as a white solid (71 mg, 0.140 mmol, 37%); ^{1}H NMR (500.25 MHz, CD_2Cl_2, 298 K): δ (ppm) = 9.85 (dd, $^3J_{(H-H)}$ = 6 Hz, 1.5 Hz, 1H), 8.38 (d, $^3J_{(H-H)}$ = 8.5 Hz, 1H), 8.16 (t, $^3J_{(H-H)}$ = 8.0 Hz, 1.5 Hz, 1H), 7.04 (d, $^3J_{(H-H)}$ = 8.0 Hz, 1H), 7.54 (td, $^3J_{(H-H)}$ = 6.8 Hz, 1.5 Hz, 1H), 7.37 (t, $^3J_{(H-H)}$ = 8.0 Hz, 1H), 7.29 (d, $^3J_{(H-H)}$ = 8.5 Hz, 1H); ^{19}F NMR (470.70 MHz, CD_2Cl_2, 298 K): δ (ppm) = -58.6 (s).

Cis-(2-(4-trifluoromethoxyphenyl)pyridine)AuCl$_2$ **(*cis*-[(4-OCF$_3$-ppy)AuCl$_2$])**: A suspension of **[4-OCF$_3$-ppyH]$^+$[AuCl$_4$]$^-$** (1.593 g, 2.75 mmol) in water (5 mL) was subjected to microwave irradiation and was kept stirring at 180 °C for two times 15 min. Thereafter, the reaction mixture was filtered and washed with a mixture of dichloromethane/hexane (2/1) to afford ***cis*-[(4-OCF$_3$-ppy)AuCl$_2$]** as a white solid (581 mg, 1.15 mmol, 42%); ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ (ppm) = 9.47 – 9.43 (m, 1H), 8.40 – 8.38 (m, 2H), 8.17-8.13 (m, 1H), 7.80 – 7.69 (m, 2H), 7.52 – 7.48) m, 1H); ^{19}F NMR (470.70 MHz, $(CD_3)_2SO$, 298 K): δ (ppm) = -57.6 (s).

2-anilinopyridineAuCl$_2$ **(*cis*-[(apy)AuCl$_2$])**: 2-anilinopyridine (245 mg, 1.44 mmol) was dissolved in acetonitrile (40 mL) and transferred to $NaAuCl_4 \cdot 2H_2O$ (500 mg, 1.26 mmol) in water (40 mL). This mixture was stirred for 24 h. The solvents were decanted and the remaining solid was washed with water and acetonitrile. After drying *in vacuo*, **cis-[(apy)AuCl$_2$]** was collected as an orange solid (406 mg, 0.929 mmol, 74%); ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ (ppm) = 8.80 (dd, $^3J_{(H-H)}$ = 6.8 Hz, 1.7 Hz, 1H), 7.96 (td, $^3J_{(H-H)}$ = 9.0 Hz, 1.5 Hz, 1H), 7.55 (dd, $^3J_{(H-H)}$ = 8.3 Hz, 1.4 Hz, 1H), 7.39 (dd, $^3J_{(H-H)}$ = 8.6 Hz, 1.7 Hz, 1H), 7.25 (td, $^3J_{(H-H)}$ = 7.8 Hz, 1.2 Hz, 1H), 7.14 – 7.06 (m, 2H), 7.00 (td, $^3J_{(H-H)}$ = 7.5 Hz, 1.8 Hz, 1H).

2-benzoylpyridineAuCl$_2$ **(*cis*-[(bpy)AuCl$_2$])**: A suspension of **(bpy)AuCl$_3$** (75 mg, 0.15 mmol) in water (20 mL) was subjected to microwave irradiation and kept stirring at 170 °C for 10 min. The mixture was then filtered and the filter cake washed with water, ethanol and cold acetonitrile (-32 °C). The crude was dissolved in dichloromethane and dried over $MgSO_4$ to afford ***cis*-[(bpy)AuCl$_2$]** as an off-white solid (40 mg, 0.089 mmol, 58%); ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ (ppm) = 9.48 (d, $^3J_{(H-H)}$ = 6.0 Hz, 1H), 8.56 (td, $^3J_{(H-H)}$ = 7.7 Hz, 1.5 Hz, 1H), 8.36 (dd, $^3J_{(H-H)}$ = 7.8 Hz, 1.6 Hz, 1H), 8.09 (td, $^3J_{(H-H)}$ = 6.8 Hz, 1.8 Hz, 1H), 7.78 – 7.67 (m, 2H), 7.50 – 7.45 (m, 2H).

Cis-(2-benzylpyridine)AuCl₂ **(cis-[(bepy)AuCl₂]):** A suspension of **(bepy)AuCl₃** (400 mg, 0.846 mmol) in water (20 mL) was was subjected to microwave i r radiation and kept stirring at 180 °C for 20 min. Thereafter, the reaction mixture was filtered and washed with water and acetonitrile and dried *in vacuo* to afford ***cis*-[(bpy)AuCl₂]** as an off-white solid (300 mg, 0.688 mmol, 81.3%); ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ (ppm) = 9.16-9.18 (m, 1H), 8.26 (1 H, td, $^{3}J_{(H-H)}$ = 7.7 Hz, $^{3}J_{(H-H)}$ = 1.5 Hz, 1H), 7.99 (dd, $^{3}J_{(H-H)}$ = 7.8 Hz, $^{3}J_{(H-H)}$ = 1.1 Hz, 1H), 7.71 (ddd, $^{3}J_{(H-H)}$ = 7.5 Hz, $^{3}J_{(H-H)}$ = 6.1 Hz, $^{4}J_{(H-H)}$ = 1.5 Hz, 1H), 7.41 (dd, $^{3}J_{(H-H)}$ = 8.0 Hz, $^{4}J_{(H-H)}$ = 1.0 Hz, 1H), 7.25 (dd, $^{3}J_{(H-H)}$ = 7.3 Hz, $^{3}J_{(H-H)}$ = 1.7Hz, 1H), 7.18 (td, $^{3}J_{(H-H)}$ = 7.3 Hz, $^{4}J_{(H-H)}$ = 1.1 Hz, 1H), 7.04-7.09 (m, 1H), 4.33-4.63 (m, 2H).

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