Supporting Information for

Gold(I)-BODIPY-imidazole bimetallic complexes as new potential anti-inflammatory and anticancer trackable agents

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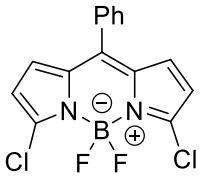
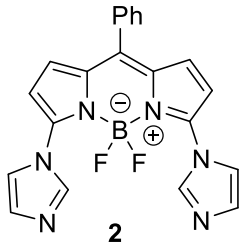
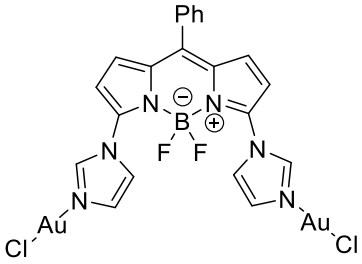
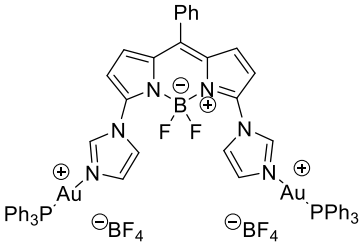
General Information

Otherwise specified, all reactions were carried out under Argon using conventional Schlenk techniques. CH_2Cl_2, MeCN, MeOH and DMF were dried using an MBRAUN SPS 800 solvent purification system or distilled under argon from appropriate drying agents and either used directly or stored under argon. The precursors [AuCl(tht)] and [AuCl(PPh_3)] have been synthesized according to literature procedure.[1,2] All other reagents were commercially available and used as received.

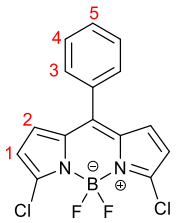
All of the analyses were performed at the "Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne" (PACSMUB). The identity and purity of the compounds were unambiguously established using high-resolution mass spectrometry and NMR. High resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL ESI-MS spectrometer. NMR spectra (^{1}H, ^{31}P, ^{19}F, ^{13}C) were recorded on Bruker 300 Avance III, 500 Avance III, or 600 Avance II spectrometers. Chemical shifts are given relative to TMS and were referenced to the residual solvent signal ^{1}H, ^{13}C. The list of abbreviations for signals in NMR are the following: s = singlet, d = doublet, hept = heptuplet, m = multiplet, ps = pseudo-singlet, pt = pseudo-triplet, pq = pseudo-quadruplet, brs = broad singlet. Far-IR spectrum was recorded on a Bruker Vertex 70v (Platinum ATR).

Compounds Chart

Compound	Chemistry		Photophysics		Biology
 **1**	Data	^{1}H-NMR ^{19}F-NMR	Data	UV-Vis Fluo	Antiproliferative properties Imaging Gold Uptake Anti-inflammatory properties
 **2**	Data	^{1}H-NMR ^{19}F-NMR ^{13}C-NMR XRD	Data	UV-Vis Fluo	
 **BODI-Au-5**	Data	^{1}H-NMR ^{19}F-NMR ^{13}C-NMR Far-IR	Data	UV-Vis Fluo	
 **BODI-Au-6**	Data	^{1}H-NMR ^{19}F-NMR ^{31}P-NMR ^{13}C-NMR	Data	UV-Vis Fluo	

Synthetic procedures

Compound 1



The compound **1** was synthesized following a reported procedure.[3] ^{1}H and ^{19}F data are in agreement with literature data.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm): 6.44 (d, 2H, $^{3}J_{H\text{-}H}$ = 4.1 Hz, H_1), 6.84 (d, 2H, $^{3}J_{H\text{-}H}$ = 4.1 Hz , H_2), 7.56 (m, 5H, $H_{3\text{-}5}$).

^{19}F-NMR (282.4 MHz, $CDCl_3$): δ (ppm): -148.2 (pq, $^{1}J_{F\text{-}^{11}B}$ = 27.6 Hz).

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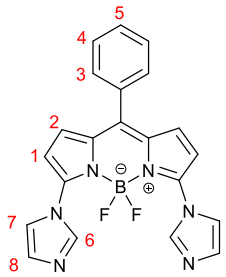
Compound 2



A round-bottom flask was charged with compound **1** (1 eq., 250 mg, 0.742 mmol), **imidazole** (2 eq., 101 mg, 1.484 mmol), and **Na_2CO_3** (2.5 eq., 197 mg, 1.855 mmol) in acetonitrile (250 mL). The solution was stirred for 72 h at room temperature. The solvent was removed under reduced pressure, then the residue was dissolved in dichloromethane (100 mL), washed with water (3 x 50 mL) and dried over Na_2SO_4. After filtration, the solvent was removed under vacuum to give a red-green solid. The product was then purified by silica gel column chromatography (eluent: DCM/MeOH (95/5 v/v)), to afford the pure red-green solid (140 mg, 47 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 6.54 (d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H_1), 6.97 (d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz , H_2), 7.20 (brs, 2H, $H_{7 \text{ or } 8}$), 7.56 (m, 5H, $H_{3\text{-}5}$), 7.63 (pt, 2H, $H_{7 \text{ or } 8}$), 8.15 (s, 2H, H_6).

^{19}F{^{1}H} NMR (470.5 MHz, $CDCl_3$): δ (ppm): -137.0 (pq, $^1J_{F\text{-}11B}$ = 31.8 Hz), -136.9 (hept, $^1J_{F\text{-}10B}$ = 11.2 Hz).

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ (ppm): 113.3 (s, CH), 120.4 (pt, CH), 128.8 (s, CH), 130.7 (s, CH), 130.8 (s, CH), 131.1 (s, CH), 132.3 (s, CH), 132.9 (s, Cq), 133.0 (s, Cq), 138.2 (pt, CH), 145.8 (s, Cq), 148.1 (s, Cq).

HR-MS (ESI): (DCM), *positive mode exact mass for* $[M+H]^+$ ($[C_{21}H_{16}BF_2N_6]^+$) calculated: 401.14921 / measured *m/z*: 401.14880.

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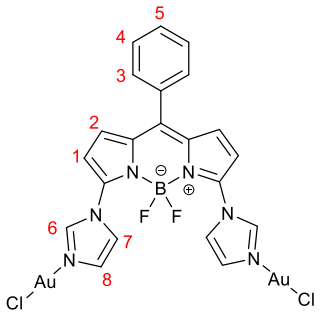
BODI-Au-5



A Schlenk tube was charged with **compound 2** (1 eq., 100 mg, 0.250 mmol) and **Au(tht)Cl** (2 eq., 160 mg, 0.500 mmol) in dichloromethane (6 mL). The solution was stirred for 4h at room temperature. The formation of a red-violet precipitate was obtained in the mixture. The solvent was partially removed and diethyl ether was added (20 mL). Then the precipitate was filtered with canula and washed with diethyl ether (2 x 10 mL). Finally, the solvent was removed under vacuum to form a violet powder (151 mg, 70 % yield).

^{1}H NMR (600 MHz, DMSO): δ (ppm) = 6.96 (d, 2H, $^{3}J_{H\text{-}H}$ = 4.41 Hz, H_1), 7.10 (d, 2H, $^{3}J_{H\text{-}H}$ = 4.41 Hz, H_2), 7.26 (s, 2H, $H_{7 \text{ or } 8}$), 7.68 (m, 5H, $H_{3\text{-}5}$), 7.80 (s, 2H, $H_{7 \text{ or } 8}$), 8.41 (brs, 2H, H_6).

^{19}F{^{1}H} NMR (282.4 MHz, DMSO): δ (ppm) = -136.0 (pq, $^{1}J_{F\text{-}11B}$ = 32.2 Hz).

^{13}C{^{1}H} NMR (125.7 MHz, DMSO): δ (ppm): 116.1 (s, CH), 122.3 (s, CH), 127.0 (brs, CH), 129.4 (s, CH), 131.3 (s, CH), 131.9 (s, CH), 132.4 (s, Cq), 133.0 (s, Cq), 133.2 (s, CH), 138.7 (pt, CH), 146.3 (s, Cq), 146.5 (s, Cq).

HR-MS (ESI): (DCM), *positive mode exact mass for* $[M\text{-}Cl]^+$ ($[C_{21}H_{15}Au_2BF_2N_6Cl]^+$) calculated: 829.04389 / measured *m/z*: 829.04311.

Elemental analysis (C, N, H): calculated [C: 29.16%, H: 1.75%, N: 9.72%]; experimental [C: 29.06%, H: 1.76%, N: 9.69%]

FT-IR FIR (ATR, cm^{-1}): 346, 120.

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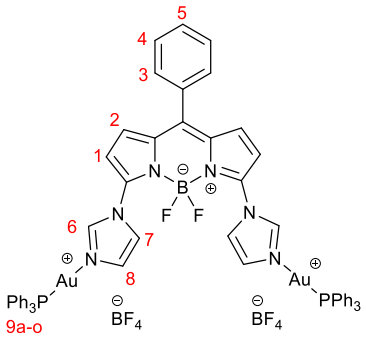
BODI-Au-6



A Schlenk tube was charged with **AuCl(PPh$_3$)** (2 eq., 124 mg, 0.250 mmol) and **AgBF$_4$** (2.2 eq., 53 mg, 0.275 mmol) in dichloromethane (10 mL). The solution was stirred for 30 min at room temperature in the dark. The resulting purple solution was filtered and transferred by canula onto a solution of **2** (1 eq., 50 mg, 0.125 mmol) in dichloromethane (2 mL). The mixture was stirred for 3 h at room temperature in the dark. After centrifugation, the supernatant was isolated and the solvent was removed under vacuum to form a red product (171 mg, 92 % yield).

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm): 7.11 (d, 2H, $^3J_{H\text{-}H}$ = 4.41 Hz, H_2), 7.16 (d, 2H, $^3J_{H\text{-}H}$ = 4.41 Hz , H_1), 7.32 (s, 2H, $H_{7 \text{ or } 8}$), 7.57 (m, 35H, $H_{3\text{-}5,\ 9a\text{-}o}$), 8.10 (s, 2H, $H_{7 \text{ or } 8}$), 9.03 (s, 2H, H_6).

^{31}P{^{1}H} NMR (202.4 MHz, CDCl$_3$): δ (ppm): 30.2.

^{19}F{^{1}H} NMR (470.5 MHz, CDCl$_3$): δ (ppm): -135.8 (pq, $^1J_{F\text{-}11B}$ = 32.4 Hz), -151.5 (ps, $^{10}BF_4^-$), -151.5 (ps, $^{11}BF_4^-$).

^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ (ppm): 115.7 (s, CH), 122.0 (pt, CH), 127.3 (d, $J_{C\text{-}P}$ = 65 Hz, Cq), 128.7 (s, CH), 128.9 (s, CH), 129.7 (d, $J_{C\text{-}P}$ = 12 Hz, CH), 130.8 (s, CH), 131.9 (s, CH), 132.1 (s, Cq), 132.5 (d, $J_{C\text{-}P}$ = 2 Hz, CH), 133.1 (s, Cq), 134.1 (s, CH), 134.5 (d, $J_{C\text{-}P}$ = 14 Hz, CH), 141.7 (s, CH), 145.9 (s, Cq), 149.4 (s, Cq).

HR-MS (ESI): (DCM), *positive mode exact mass for* $[M\text{-}BF_4]^+$ ($[C_{57}H_{45}Au_2B_2F_6N_6P_2]^+$) calculated: 1405.25968 / measured *m/z*: 1405.26122.

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NMR Characterization

Indication of $CDCl_3$ on the different spectra corresponds to the $CHCl_3$ residual signal.

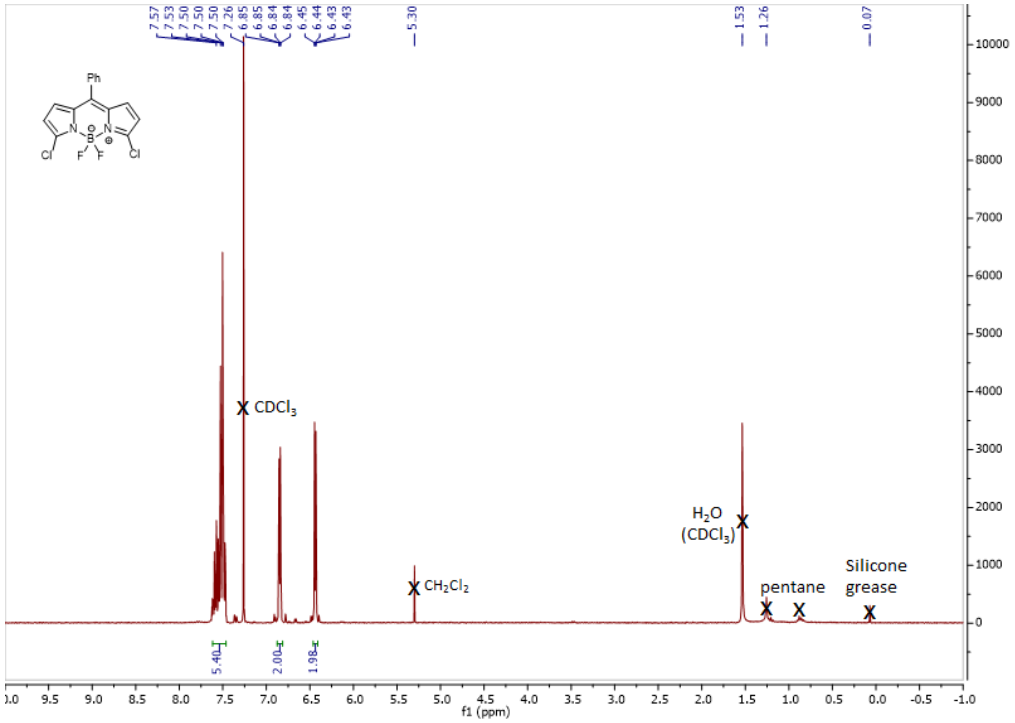

Figure S 1: ^{1}H-NMR spectrum of compound 1 ($CDCl_3$, 300 MHz)

Back to Compounds Chart - **Data compound 1**

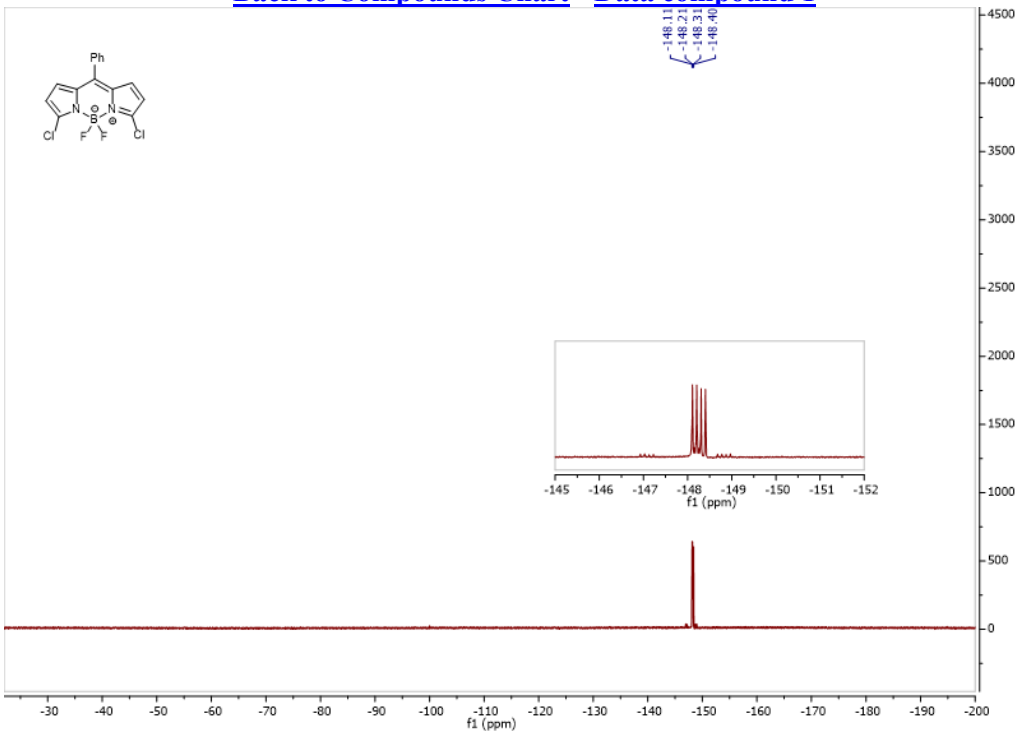

Figure S 2: ^{19}F-NMR spectrum of compound 1 ($CDCl_3$, 282.4 MHz)

Back to Compounds Chart - **Data compound 1**

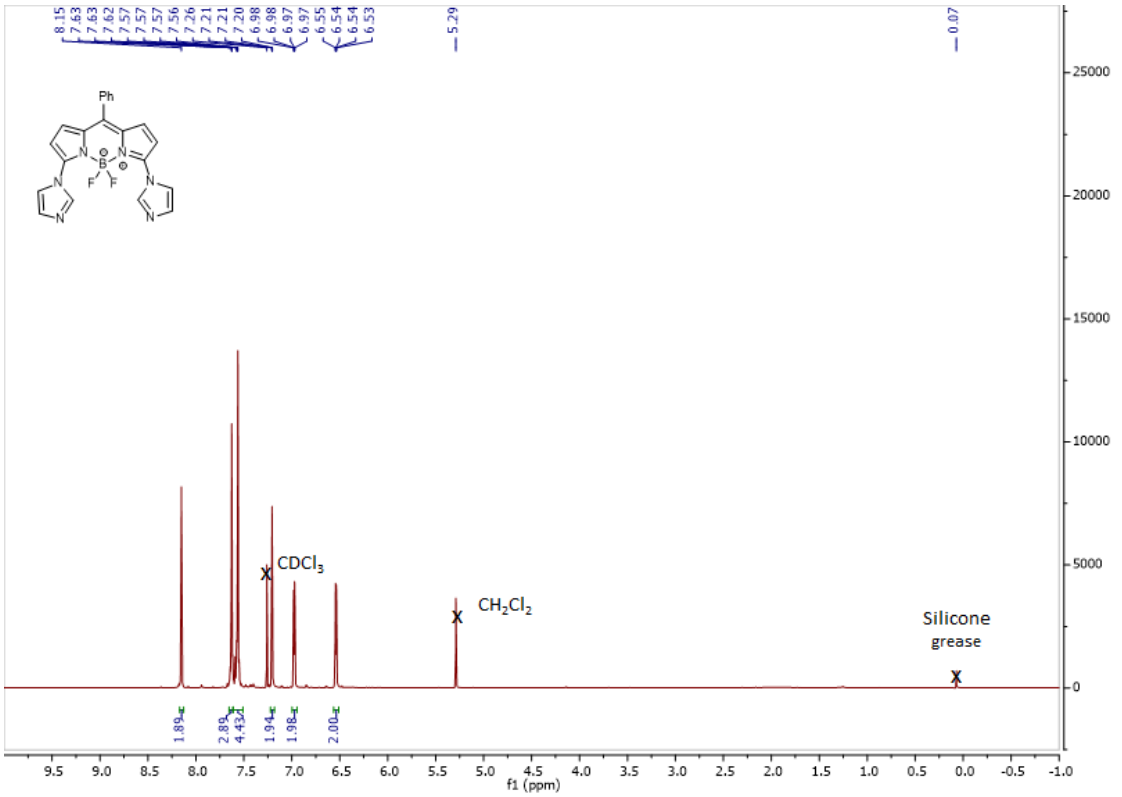

Figure S 3: ^{1}H-NMR spectrum of compound 2 ($CDCl_3$, 500 MHz)

Back to Compounds Chart - Data compound 2

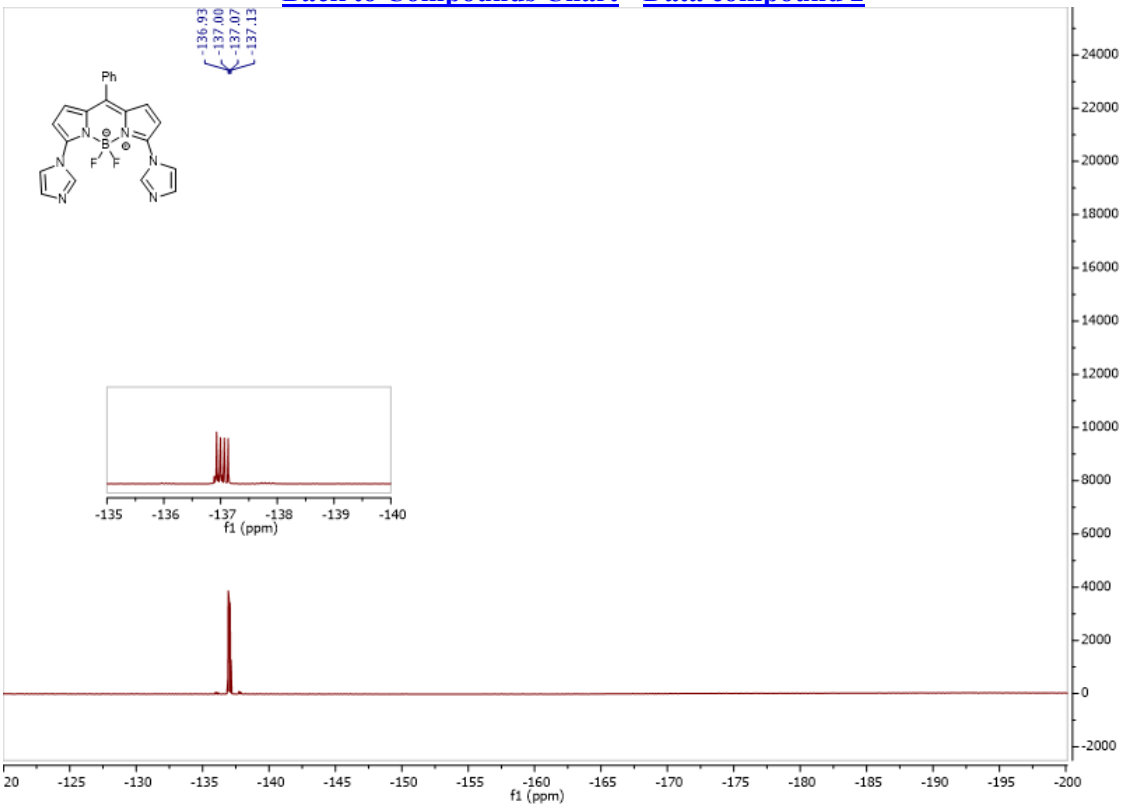

Figure S 4: ^{19}F-NMR spectrum of compound 2 ($CDCl_3$, 470.5 MHz)

Back to Compounds Chart - Data compound 2

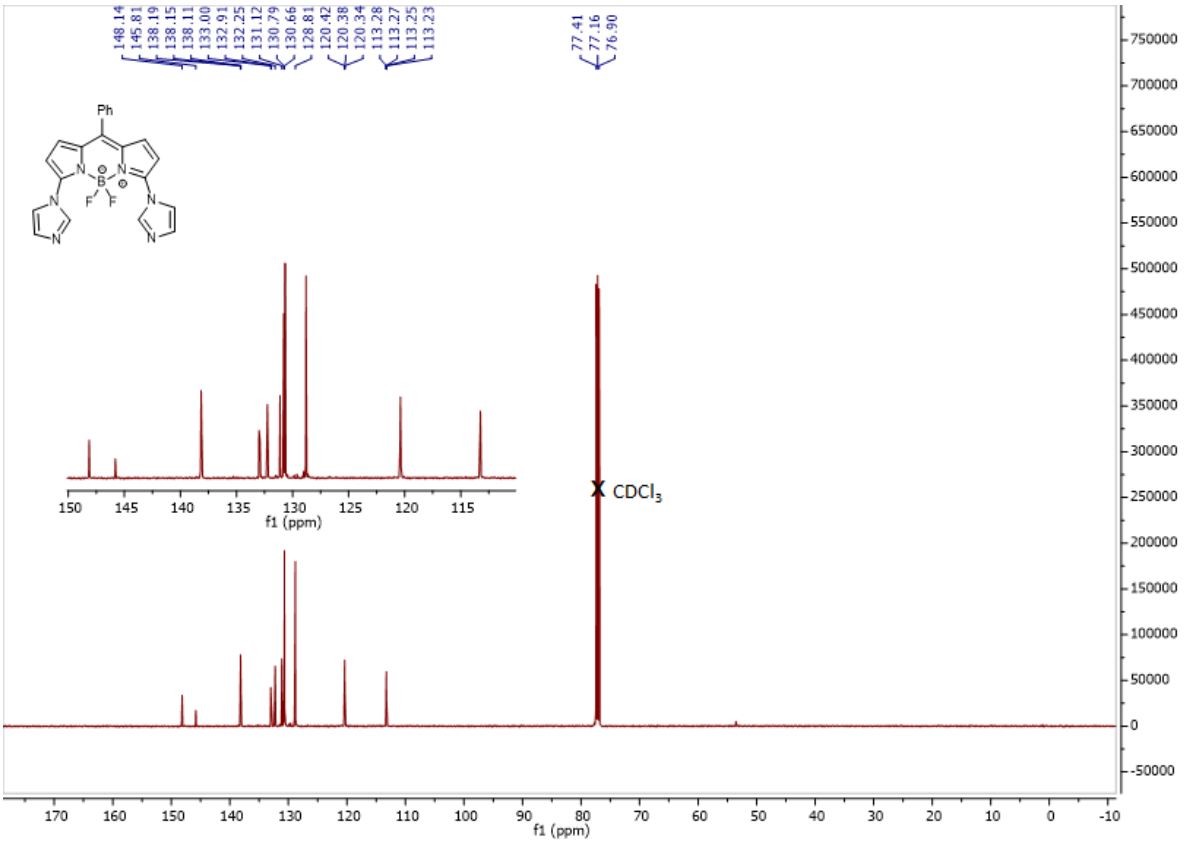

Figure S 5: ^{13}C-NMR spectrum of compound 2 ($CDCl_3$, 125.7 MHz)

Back to Compounds Chart - **Data compound 2**

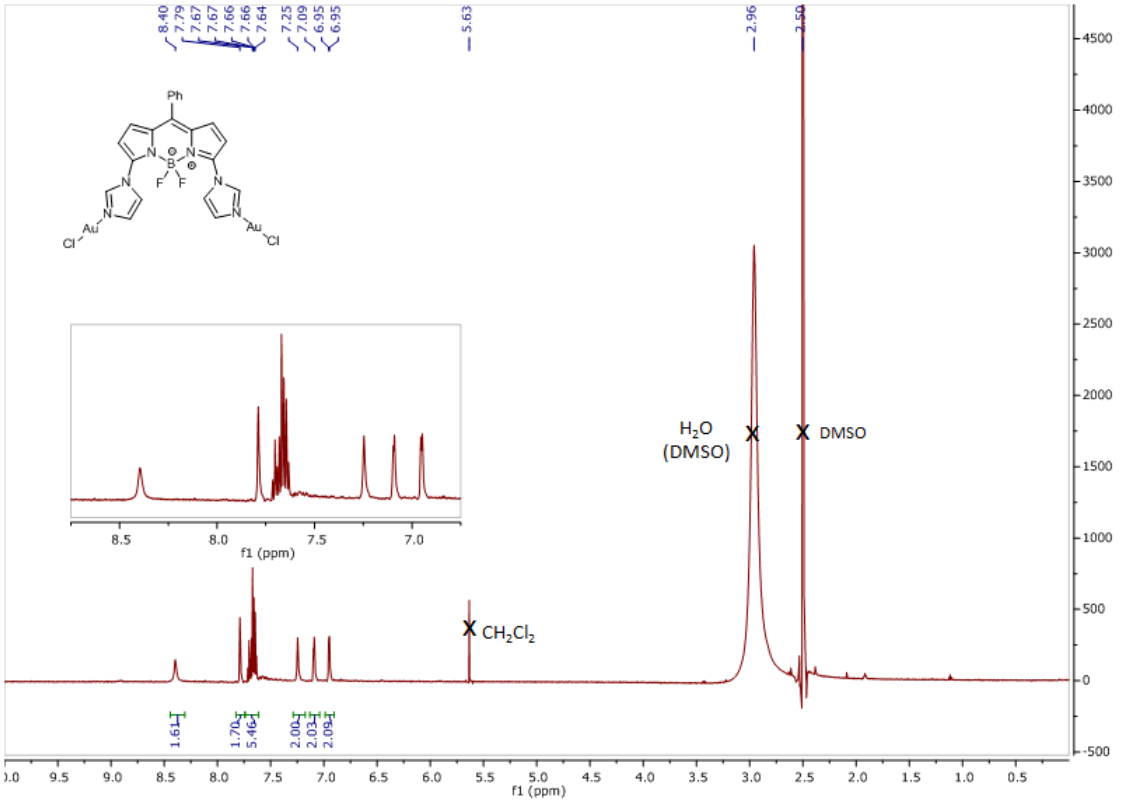

Figure S 6: ^{1}H-NMR spectrum of BODI-Au-5 (DMSO, 600 MHz, 400K)

Back to Compounds Chart – Data BODI-Au-5

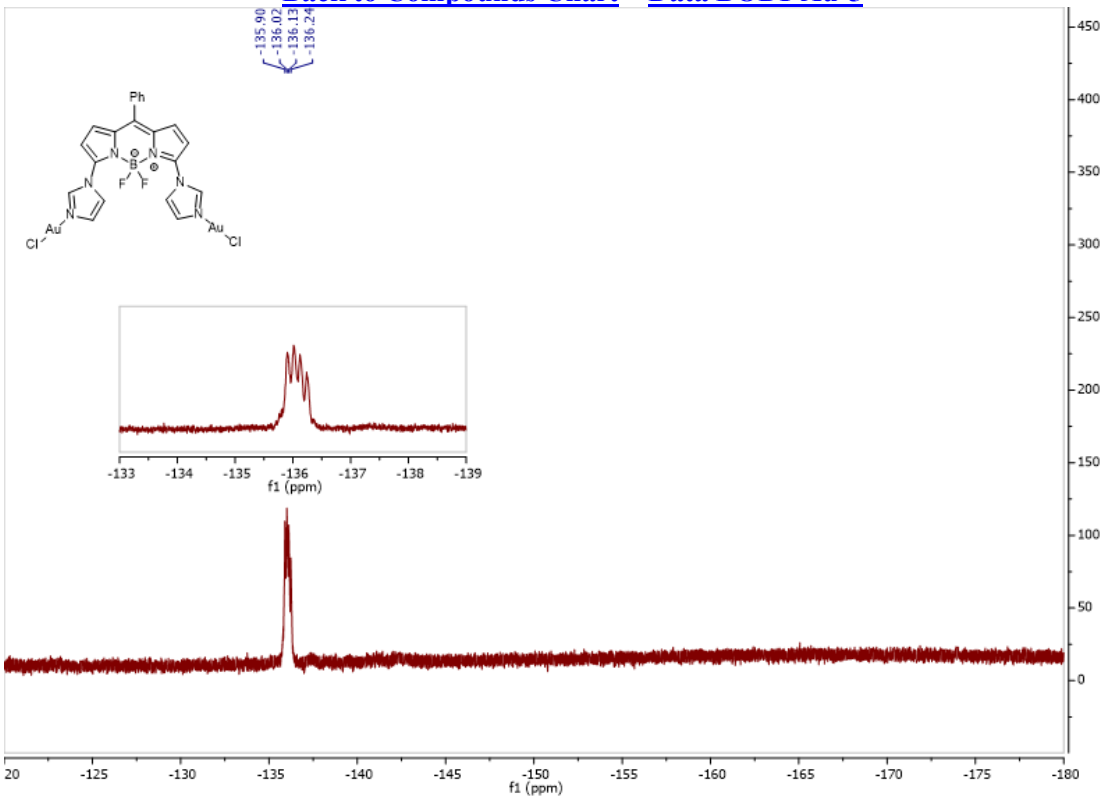

Figure S 7: ^{19}F-NMR spectrum of BODI-Au-5 (DMSO, 282.4 MHz)

Back to Compounds Chart – Data BODI-Au-5

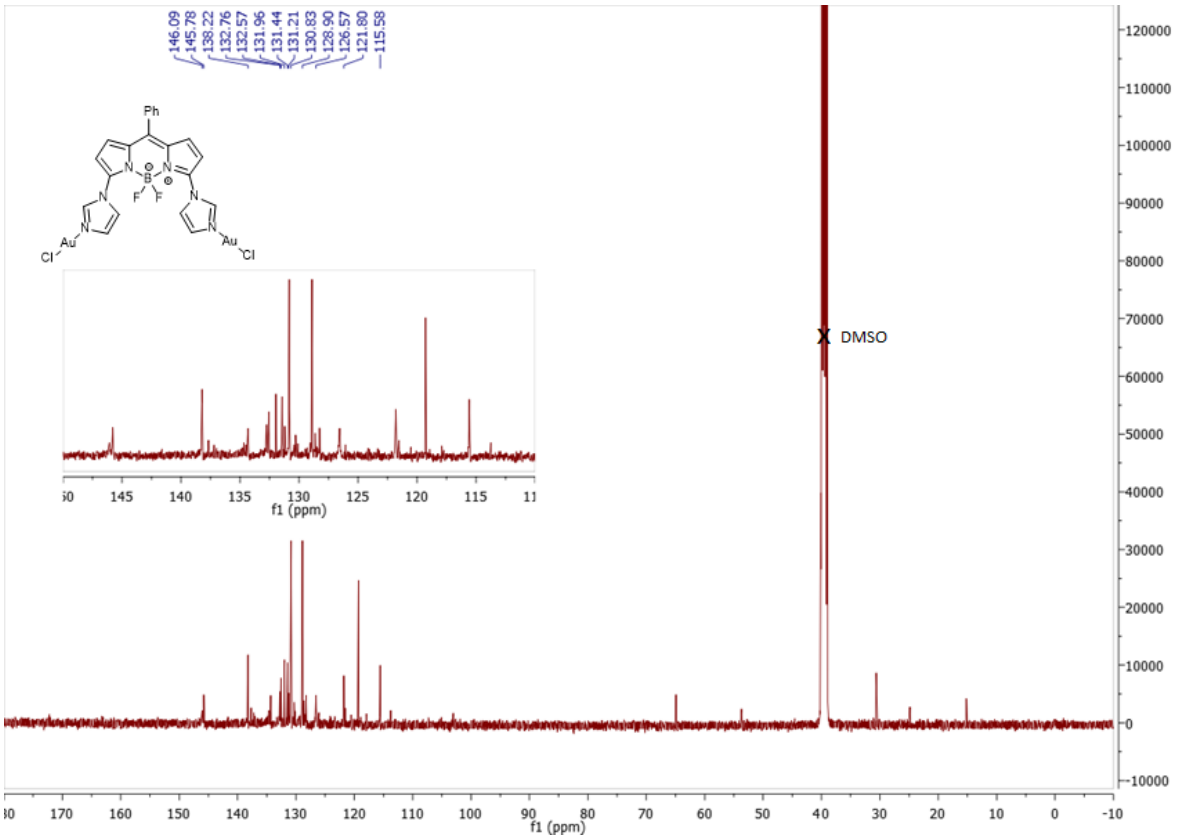

Figure S 8: ^{13}C-NMR spectrum of BODI-Au-5 ($CDCl_3$, 75.5 MHz)

Back to Compounds Chart– Data BODI-Au-5

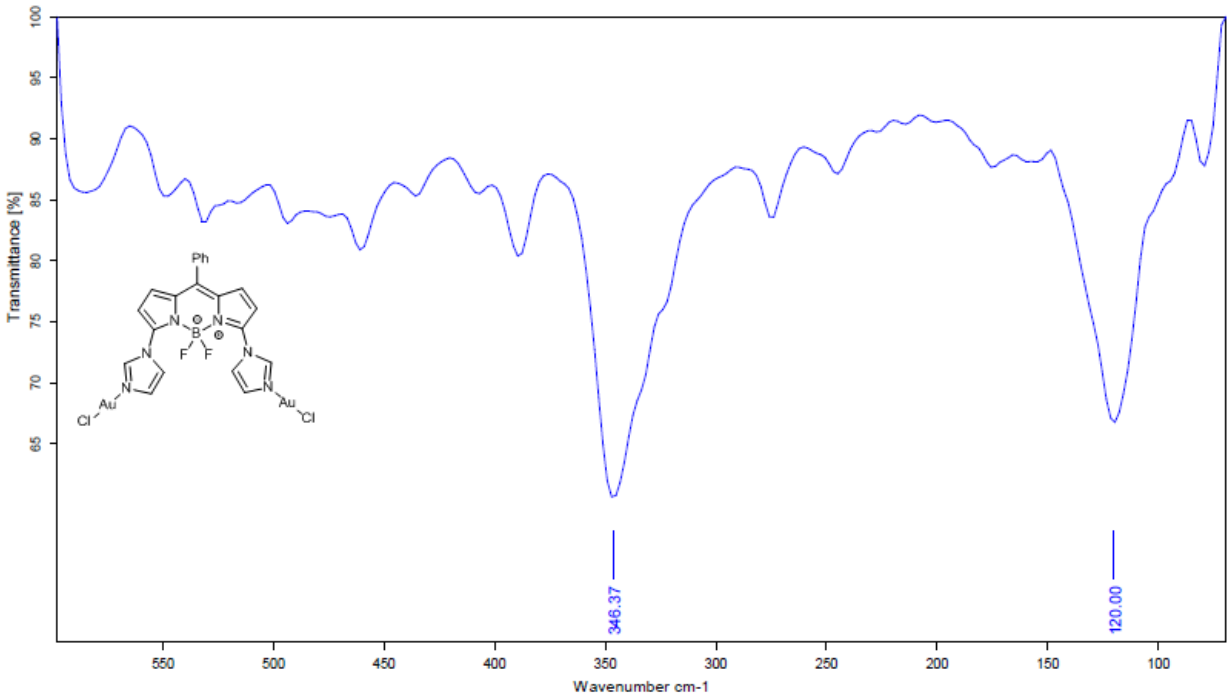

Figure S 9: Far-IR spectrum of BODI-Au-5

Back to Compounds Chart– Data BODI-Au-5

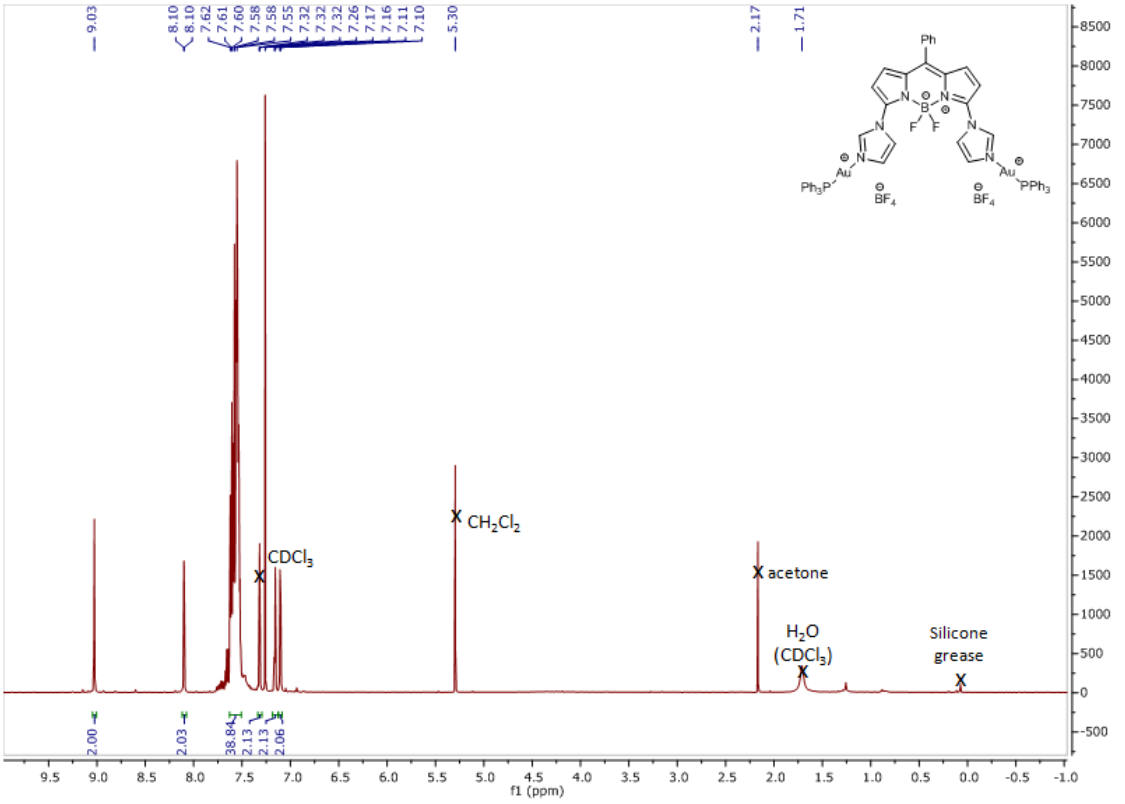

Figure S 10: ^{1}H-NMR spectrum of BODI-Au-6 ($CDCl_3$, 500 MHz)

Back to Compounds Chart – **Data BODI-Au-6**

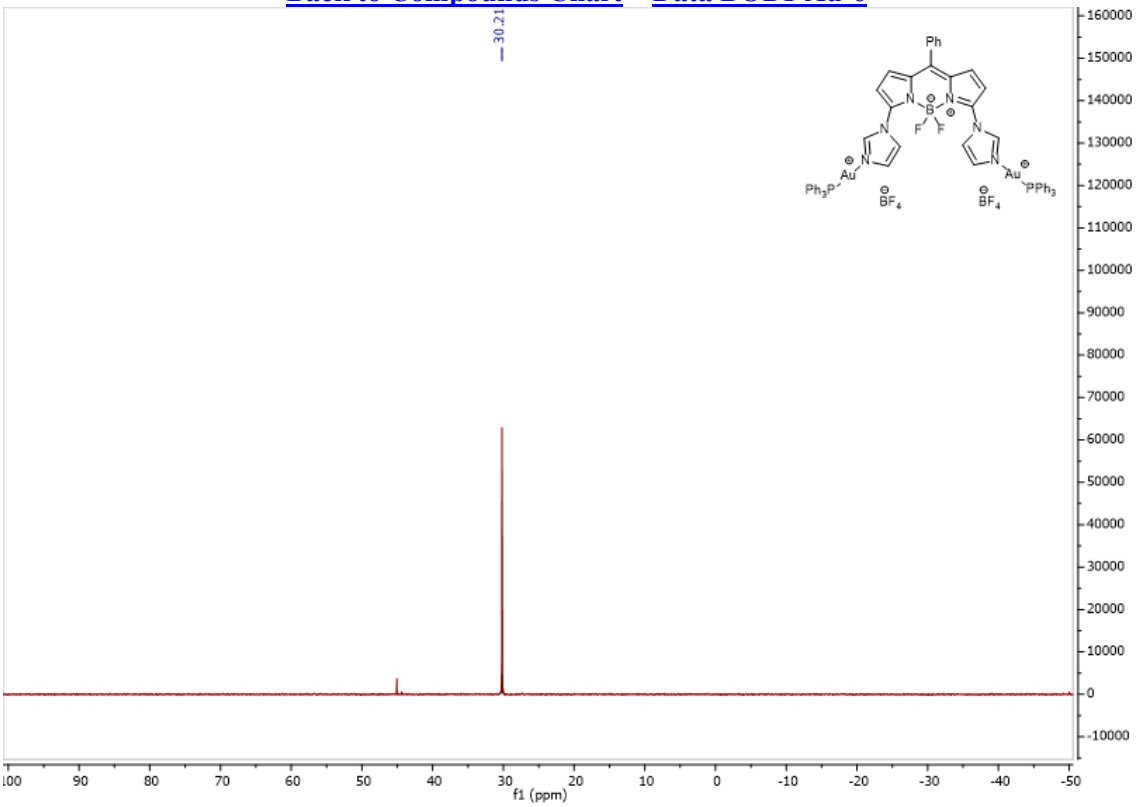

Figure S 11: ^{31}P-NMR spectrum of BODI-Au-6 ($CDCl_3$, 202.4 MHz)

Back to Compounds Chart – **Data BODI-Au-6**

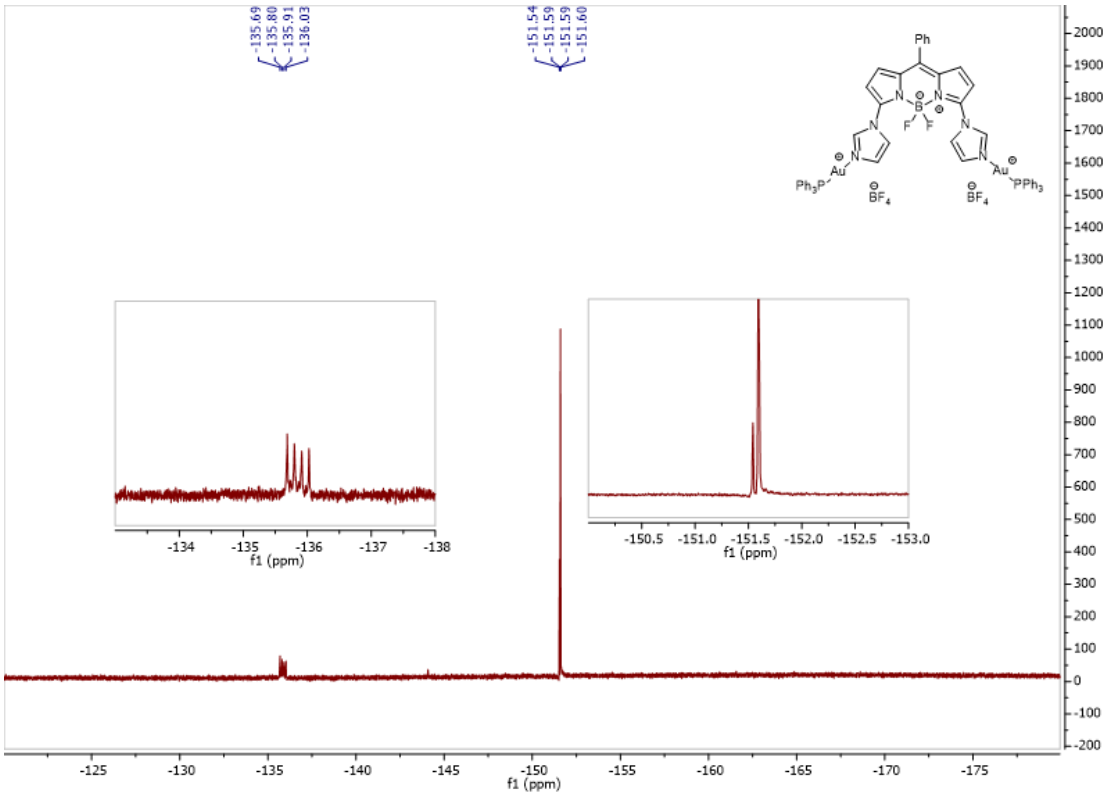

Figure S 12: ^{19}F-NMR spectrum of BODI-Au-6 ($CDCl_3$, 470.5 MHz)

[Back to Compounds Chart](#) – [Data BODI-Au-6](#)

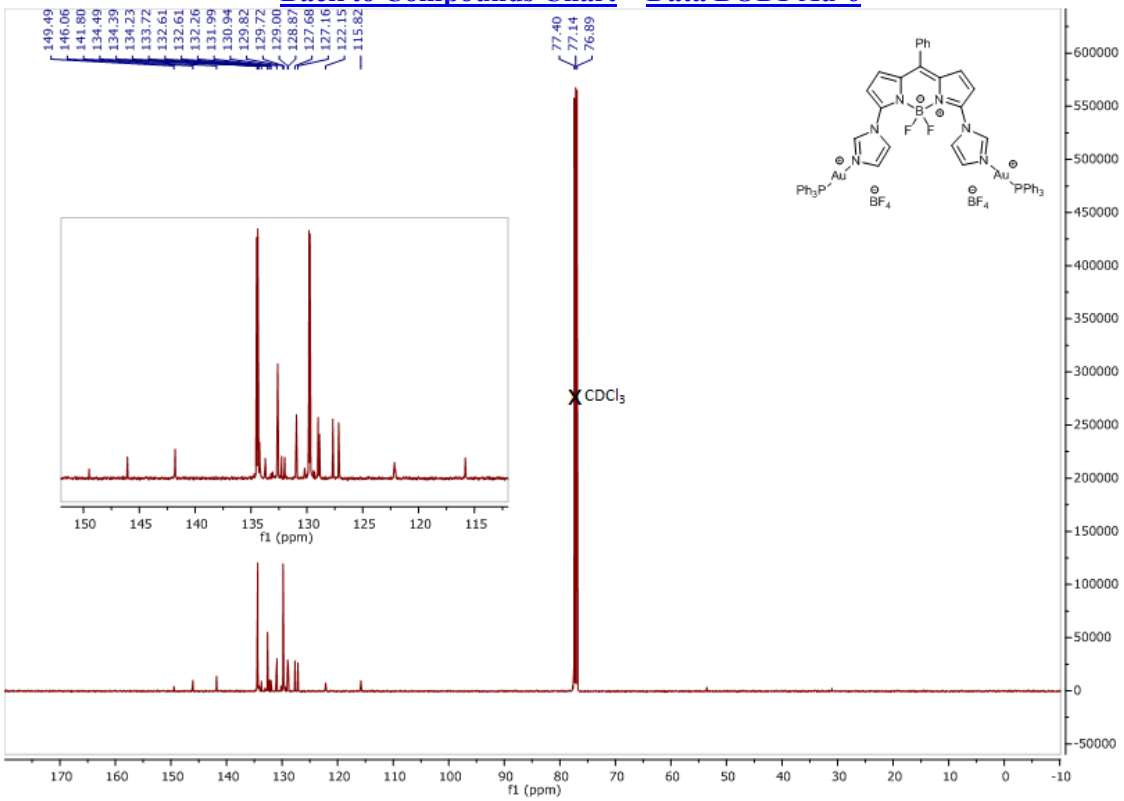

Figure S 13: ^{13}C-NMR spectrum of BODI-Au-6 ($CDCl_3$, 125.7 MHz)

[Back to Compounds Chart](#) – [Data BODI-Au-6](#)

X-ray diffraction

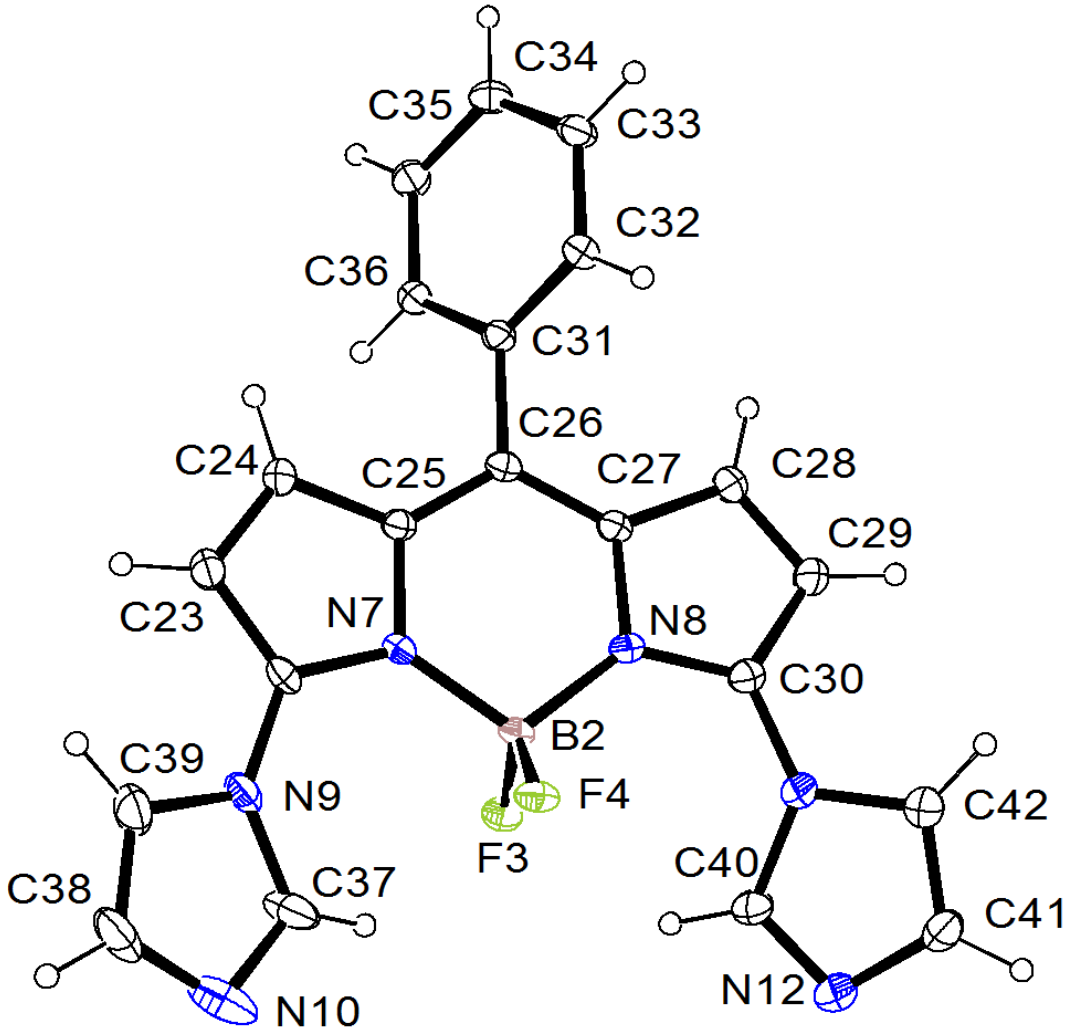

Figure S 14: ORTEP view of 2. For clarity, only one molecule is represented.

Table S 1: Crystal data and structure refinement for 2.

Identification code	**2**
Empirical formula	$C_{53}H_{38.5}B_{2.5}ClF_5N_{15}$
Formula weight	1042.96
Temperature/K	150
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	12.0671(5)
b/Å	32.4681(14)
c/Å	12.0173(5)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	4708.3(3)
Z	4
ρ_{calc}g/cm^3	1.471
μ/mm^{-1}	0.160
F(000)	2144.0
Crystal size/mm^3	0.5 × 0.3 × 0.075
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.05 to 55.032
Index ranges	-15 ≤ h ≤ 15, -42 ≤ k ≤ 42, -15 ≤ l ≤ 15
Reflections collected	144944
Independent reflections	10767 [R_{int} = 0.0722, R_{sigma} = 0.0357]
Data/restraints/parameters	10767/60/730
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1300
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1380
Largest diff. peak/hole / e Å^{-3}	0.91/-0.49
Flack parameter	-0.01(4)
CCDC	1538131

Table S 2: Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 2. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
B1	2696(3)	3923.9(13)	4606(3)	27.1(8)
C1	3202(3)	4008.6(11)	6723(3)	30.3(8)
C2	4129(3)	3949.6(13)	7406(3)	33.4(8)
C3	5001(3)	3854.8(12)	6721(3)	32.6(8)
C4	4597(3)	3846.8(11)	5619(3)	25.4(7)
C5	5167(3)	3810.1(10)	4610(3)	24.6(7)
C6	4596(3)	3847.2(11)	3595(3)	24.5(7)
C7	4991(3)	3847.4(11)	2492(3)	27.7(7)
C8	4097(3)	3905.7(11)	1802(3)	30.4(8)
C9	3163(3)	3931.5(11)	2477(3)	27.9(7)
C10	6385(3)	3741.3(11)	4610(3)	28.4(7)
C11	7072(3)	3987.3(12)	3959(3)	31.6(8)
C12	8210(3)	3919.1(14)	3962(4)	39.1(9)

C13	8665(3)	3609.2(16)	4601(4)	43.9(11)
C14	7987(4)	3362.7(15)	5243(3)	44.3(10)
C15	6841(3)	3426.4(13)	5252(3)	34.1(8)
C19	1133(3)	3773.8(16)	2396(4)	43.8(10)
C20	719(4)	4117.5(18)	945(4)	54.4(13)
C21	1800(4)	4200.2(16)	1142(4)	47.6(11)
F1	2044.7(18)	3565.8(7)	4679.0(18)	34.8(5)
F2	2009.3(18)	4261.9(7)	4537.4(18)	34.1(5)
N1	3465(2)	3943.7(9)	5641(2)	25.8(6)
N2	3452(2)	3900.4(9)	3568(2)	24.2(6)
N3	2086(8)	4136(5)	7017(13)	30(3)
C18	1076(9)	4025(4)	6636(10)	35(2)
C16	1906(10)	4414(4)	7855(12)	47(3)
C17	797(11)	4459(3)	7940(12)	52(4)
N4	276(8)	4213(3)	7172(10)	46(3)
N5	2070(3)	3980.0(11)	2096(3)	34.4(7)
N6	301(3)	3850.1(16)	1727(3)	54.9(11)
N3B	2242(9)	4153(7)	7180(15)	31(3)
C18B	2173(9)	4382(5)	8114(13)	36(3)
C16B	1187(11)	4125(7)	6763(12)	52(5)
C17B	533(8)	4340(6)	7467(10)	52(4)
N4B	1156(11)	4501(4)	8314(11)	46(4)
B2	4912(3)	3007.5(12)	264(3)	24.4(8)
C22	6979(3)	3141.3(11)	879(3)	25.7(7)
C23	7615(3)	3111.3(12)	1851(3)	32.2(8)
C24	6938(3)	2951.2(11)	2655(3)	27.5(7)
C25	5883(3)	2886(1)	2179(3)	23.6(7)
C26	4894(3)	2769.4(10)	2675(3)	23.9(7)
C27	3903(3)	2782.6(11)	2075(3)	26.1(7)
C28	2805(3)	2697.0(13)	2417(3)	34.1(9)
C29	2119(3)	2786.9(14)	1536(3)	38.1(9)
C30	2789(3)	2918.3(12)	664(3)	29.6(8)
C31	4871(3)	2657.2(10)	3882(3)	23.6(7)
C32	4114(3)	2850.3(11)	4596(3)	26.7(7)
C33	4092(3)	2755.1(12)	5719(3)	31.2(8)
C34	4826(3)	2467.7(12)	6142(3)	34.1(8)
C35	5583(3)	2274.6(12)	5452(3)	32.7(8)
C36	5609(3)	2368.7(11)	4313(3)	27.0(7)
C37	7002(4)	3253.4(15)	-1196(4)	48.6(11)
C38	8489(4)	3631.9(16)	-1247(5)	54.5(13)
C39	8324(3)	3540.8(15)	-194(4)	45.5(11)
C40	2846(3)	3000.0(13)	-1428(3)	35.1(9)

C41	1215(4)	3225.7(15)	-1664(4)	43.2(10)
C42	1318(4)	3174.2(16)	-561(4)	44.9(11)
F3	5037.5(18)	2696.5(7)	-532.9(17)	32.5(5)
F4	4810.5(18)	3385.5(6)	-265.0(16)	30.7(5)
N7	5933(2)	3009.0(9)	1059(2)	23.6(6)
N8	3865(2)	2916.8(9)	968(2)	25.3(6)
N9	7377(3)	3294.5(10)	-129(3)	32.0(7)
N10	7634(5)	3448.7(15)	-1906(4)	67.5(14)
N11	2388(3)	3035.6(10)	-384(3)	30.8(7)
N12	2161(3)	3114.9(11)	-2205(3)	38.3(8)
B3	5000	5000	8779(5)	29.6(12)
C43	6813(3)	4605.0(13)	8296(3)	34.9(9)
C44	7433(4)	4488.1(16)	7363(4)	46.2(11)
C45	6842(3)	4615.1(13)	6455(3)	38.5(9)
C46	5876(3)	4817.4(12)	6832(3)	31.0(8)
C47	5000	5000	6249(4)	29.5(11)
C48	5000	5000	5015(4)	31.7(11)
C49	4041(4)	4899.9(11)	4424(4)	38.4(9)
C50	4056(5)	4903.1(13)	3269(4)	52.4(13)
C51	5000	5000	2683(5)	59(2)
C52	6550(4)	4309(2)	10179(5)	61.8(15)
C53	7987(5)	4541.0(17)	10998(4)	55.8(13)
C54	8047(4)	4683.5(15)	9934(4)	47.4(11)
F5	5514.5(19)	5296.3(8)	9430(2)	41.8(6)
N13	5881(3)	4805.2(10)	8002(2)	28.4(6)
N14	7102(3)	4542.9(11)	9421(3)	36.1(7)
N15	7053(3)	4300.7(16)	11148(4)	62.9(13)
Cl1	9086(2)	4862.9(10)	15297(3)	77.7(9)
Cl2	10362(4)	4948.6(15)	13232(3)	106.8(16)
C55	10257(7)	5080(4)	14650(4)	75(4)

Table S 3: Anisotropic Displacement Parameters (Å2×103) for 2. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	27.2(19)	30(2)	24.2(18)	3.8(16)	2.9(16)	-1.3(16)
C1	37(2)	30.7(19)	23.4(17)	2.1(14)	7.3(15)	-8.4(16)
C2	38(2)	42(2)	19.4(16)	-1.8(15)	3.3(15)	-9.2(17)
C3	37(2)	37(2)	24.2(17)	-1.7(15)	-2.7(16)	-4.4(17)
C4	28.1(17)	25.9(17)	22.3(16)	-1.5(13)	2.2(14)	-2.0(14)
C5	29.6(18)	20.1(15)	24.2(16)	-1.0(13)	-0.9(15)	-1.7(13)

C6	25.8(17)	25.5(17)	22.3(16)	-1.1(13)	0.9(13)	-2.1(14)
C7	30.1(18)	28.5(18)	24.5(16)	-3.4(14)	2.4(15)	4.5(15)
C8	38(2)	32.1(19)	21.4(16)	-2.0(14)	4.3(15)	3.1(16)
C9	33.3(19)	27.5(18)	22.8(16)	-0.4(14)	-2.0(15)	2.1(15)
C10	30.0(18)	34.5(19)	20.7(16)	-7.1(15)	-0.6(14)	1.4(14)
C11	33(2)	34.2(19)	27.6(18)	-6.5(15)	0.2(16)	0.5(16)
C12	30(2)	48(2)	39(2)	-7.8(19)	4.5(17)	-4.3(18)
C13	25.0(19)	71(3)	36(2)	-13(2)	-1.1(17)	6.2(19)
C14	39(2)	64(3)	30(2)	-5.3(19)	-7.4(18)	14(2)
C15	30.9(19)	47(2)	24.5(18)	-1.2(16)	-2.2(15)	5.7(17)
C19	31(2)	68(3)	32(2)	6(2)	-1.5(17)	-4(2)
C20	38(3)	82(4)	44(3)	16(2)	-7(2)	10(2)
C21	46(3)	61(3)	36(2)	15(2)	0.9(19)	8(2)
F1	33.2(11)	40.3(12)	30.9(11)	5.9(9)	-2.4(9)	-10.7(10)
F2	30.5(11)	40.5(12)	31.2(11)	4.0(9)	7.3(9)	9.7(9)
N1	26.9(15)	27.0(15)	23.5(14)	2.6(12)	3.0(12)	-2.0(12)
N2	26.1(15)	26.2(15)	20.4(14)	-0.1(12)	-1.2(11)	1.4(12)
N3	33(5)	36(5)	19(5)	-3(3)	8(4)	-2(4)
C18	28(4)	51(5)	26(5)	-2(4)	6(3)	-10(4)
C16	38(6)	64(6)	38(7)	-24(6)	17(4)	-15(5)
C17	31(6)	73(6)	53(8)	-23(6)	21(5)	-10(5)
N4	35(5)	62(6)	41(5)	-8(4)	11(4)	-8(4)
N5	33.0(17)	45.4(19)	24.7(15)	2.2(14)	-2.8(13)	7.7(15)
N6	30.6(19)	98(3)	36(2)	5(2)	-6.5(16)	-2(2)
N3B	23(4)	49(7)	22(6)	0(5)	-3(4)	-16(4)
C18B	34(5)	55(7)	21(5)	-10(4)	4(4)	-16(5)
C16B	29(6)	103(13)	25(5)	-16(7)	1(4)	-18(6)
C17B	23(5)	98(13)	34(8)	-14(6)	7(5)	-13(6)
N4B	29(5)	69(7)	40(6)	-9(5)	1(4)	-9(5)
B2	26.7(19)	31.3(19)	15.3(16)	-2.8(14)	3.5(15)	0.2(16)
C22	22.3(16)	27.3(17)	27.5(17)	-0.5(13)	9.2(14)	3.2(14)
C23	23.6(18)	39(2)	34(2)	3.8(16)	2.8(15)	0.3(15)
C24	22.3(17)	32.1(18)	28.0(17)	0.9(14)	-0.2(14)	2.5(14)
C25	25.9(17)	25.3(16)	19.6(15)	-0.8(13)	1.9(13)	1.4(13)
C26	27.3(17)	24.4(16)	19.9(15)	-1.9(12)	2.9(13)	1.3(13)
C27	25.2(18)	32.2(18)	20.9(16)	1.3(14)	2.4(14)	-2.6(14)
C28	23.6(18)	51(2)	27.5(18)	5.2(17)	3.0(15)	-7.8(16)
C29	24.4(19)	60(3)	30.1(19)	3.8(18)	-1.8(16)	-7.3(18)
C30	28.2(19)	37.1(19)	23.5(17)	-1.4(15)	-0.8(14)	-2.8(15)
C31	23.9(17)	25.9(16)	21.1(16)	1.7(13)	1.7(13)	-2.6(13)
C32	27.7(17)	27.3(17)	25.0(16)	-0.3(14)	4.2(15)	0.7(14)
C33	34(2)	37(2)	22.2(17)	0.0(14)	6.5(15)	1.6(16)

C34	41(2)	41(2)	21.0(17)	6.9(15)	2.3(16)	-0.6(17)
C35	33(2)	34.3(19)	30.3(19)	7.5(16)	-0.5(16)	4.0(15)
C36	25.7(18)	30.6(18)	24.8(17)	0.9(14)	1.5(13)	2.4(14)
C37	60(3)	57(3)	29(2)	-4.5(19)	18(2)	-15(2)
C38	39(3)	62(3)	62(3)	26(3)	26(2)	8(2)
C39	27(2)	57(3)	52(3)	13(2)	5.0(18)	-6.0(19)
C40	36(2)	46(2)	23.2(17)	-7.7(16)	-3.9(16)	3.7(18)
C41	38(2)	59(3)	33(2)	-0.4(19)	-8.7(18)	13(2)
C42	34(2)	67(3)	33(2)	-1(2)	-0.9(18)	12(2)
F3	35.2(11)	38.6(11)	23.6(10)	-10.0(9)	2.4(9)	2.7(9)
F4	39.4(12)	34.0(11)	18.7(9)	3.2(8)	3.7(9)	1.3(9)
N7	22.3(14)	29.0(15)	19.4(13)	0.8(11)	4.9(12)	0.6(12)
N8	26.1(15)	31.8(15)	18.1(13)	-0.7(11)	-0.9(11)	-1.1(12)
N9	25.2(15)	37.0(17)	33.8(17)	8.7(13)	11.4(13)	3.0(13)
N10	91(4)	63(3)	49(2)	7(2)	38(3)	-5(3)
N11	26.9(15)	40.6(17)	25.0(14)	-3.4(13)	-2.8(13)	1.2(13)
N12	37.7(19)	50(2)	27.5(17)	-3.8(15)	-5.7(14)	0.2(16)
B3	25(3)	36(3)	28(3)	0	0	3(2)
C43	28.7(19)	40(2)	37(2)	-1.4(17)	-2.7(16)	3.8(16)
C44	34(2)	61(3)	43(2)	-10(2)	-0.4(19)	13(2)
C45	37(2)	45(2)	34(2)	-10.6(18)	1.6(17)	4.0(18)
C46	32.1(19)	30.3(18)	30.5(19)	-3.8(15)	0.2(16)	-4.0(16)
C47	35(3)	28(2)	26(2)	0	0	-4(2)
C48	43(3)	23(2)	30(3)	0	0	-4(2)
C49	52(2)	25.2(19)	38(2)	2.3(15)	-6.4(19)	-1.3(17)
C50	90(4)	28(2)	39(2)	-3.4(17)	-20(3)	4(2)
C51	113(7)	34(3)	29(3)	0	0	7(4)
C52	34(2)	90(4)	62(3)	33(3)	2(2)	4(2)
C53	61(3)	69(3)	37(2)	1(2)	-14(2)	9(3)
C54	44(2)	53(3)	45(2)	3(2)	-7(2)	-5(2)
F5	35.2(12)	52.8(14)	37.5(13)	-15.4(11)	-7.8(10)	6.5(11)
N13	25.5(15)	32.5(16)	27.4(15)	-2.1(12)	0.6(12)	-1.0(13)
N14	27.0(16)	48.5(19)	32.8(17)	2.2(15)	1.0(14)	8.5(15)
N15	36(2)	104(4)	48(2)	28(2)	6.4(19)	15(2)
Cl1	59.4(16)	71.3(18)	102(2)	35.5(17)	9.6(17)	-0.7(14)
Cl2	147(5)	106(3)	67.6(19)	28(2)	29(2)	39(3)
C55	46(8)	80(10)	99(9)	-24(7)	16(6)	-24(5)

Table S 4: Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
B1	F1	1.406(5)	C25	N7	1.405(4)
B1	F2	1.377(5)	C26	C27	1.398(5)
B1	N1	1.553(5)	C26	C31	1.495(4)
B1	N2	1.547(5)	C27	C28	1.414(5)
C1	C2	1.401(6)	C27	N8	1.401(4)
C1	N1	1.355(5)	C28	C29	1.376(5)
C1	N3	1.453(9)	C29	C30	1.390(5)
C1	N3B	1.365(9)	C30	N8	1.349(5)
C2	C3	1.371(6)	C30	N11	1.401(5)
C3	C4	1.411(5)	C31	C32	1.402(5)
C4	C5	1.398(5)	C31	C36	1.392(5)
C4	N1	1.402(5)	C32	C33	1.385(5)
C5	C6	1.407(5)	C33	C34	1.383(6)
C5	C10	1.486(5)	C34	C35	1.384(6)
C6	C7	1.408(5)	C35	C36	1.402(5)
C6	N2	1.392(5)	C37	N9	1.366(6)
C7	C8	1.373(5)	C37	N10	1.309(6)
C8	C9	1.392(5)	C38	C39	1.315(7)
C9	N2	1.360(4)	C38	N10	1.431(8)
C9	N5	1.406(5)	C39	N9	1.397(5)
C10	C11	1.393(5)	C40	N11	1.375(5)
C10	C15	1.394(5)	C40	N12	1.302(5)
C11	C12	1.390(6)	C41	C42	1.341(6)
C12	C13	1.380(7)	C41	N12	1.362(6)
C13	C14	1.380(7)	C42	N11	1.384(5)
C14	C15	1.397(6)	B3	F5^{1}	1.386(4)
C19	N5	1.363(6)	B3	F5	1.386(4)
C19	N6	1.310(6)	B3	N13	1.550(5)
C20	C21	1.353(7)	B3	N13^{1}	1.550(5)
C20	N6	1.375(7)	C43	C44	1.400(6)
C21	N5	1.390(5)	C43	N13	1.346(5)
N3	C18	1.3503	C43	N14	1.411(5)
N3	C16	1.3702	C44	C45	1.368(6)
C18	N4	1.3108	C45	C46	1.413(6)
C16	C17	1.3499	C46	C47	1.400(5)
C17	N4	1.3712	C46	N13	1.406(5)
N3B	C18B	1.3495	C47	C46^{1}	1.400(5)
N3B	C16B	1.3711	C47	C48	1.482(7)
C18B	N4B	1.3086	C48	C49	1.397(5)
C16B	C17B	1.3507	C48	C49^{1}	1.397(5)

C17B	N4B	1.3690	C49	C50	1.388(6)
B2	F3	1.400(4)	C50	C51	1.376(7)
B2	F4	1.388(4)	C51	C50[1]	1.376(7)
B2	N7	1.558(5)	C52	N14	1.360(6)
B2	N8	1.550(5)	C52	N15	1.313(7)
C22	C23	1.401(5)	C53	C54	1.361(7)
C22	N7	1.351(4)	C53	N15	1.382(7)
C22	N9	1.395(4)	C54	N14	1.374(6)
C23	C24	1.368(5)	Cl1	C55	1.7603
C24	C25	1.412(5)	Cl2	C55	1.7606
C25	C26	1.387(5)			

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

Table S 5: Bond Angles for 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F1	B1	N1	108.5(3)	N7	C25	C24	107.9(3)
F1	B1	N2	109.8(3)	C25	C26	C27	120.4(3)
F2	B1	F1	109.1(3)	C25	C26	C31	120.0(3)
F2	B1	N1	112.0(3)	C27	C26	C31	119.5(3)
F2	B1	N2	110.2(3)	C26	C27	C28	130.2(3)
N2	B1	N1	107.2(3)	C26	C27	N8	121.8(3)
C2	C1	N3	129.5(7)	N8	C27	C28	107.9(3)
N1	C1	C2	110.8(3)	C29	C28	C27	107.3(3)
N1	C1	N3	119.7(7)	C28	C29	C30	107.2(3)
N1	C1	N3B	129.7(9)	C29	C30	N11	124.1(3)
N3B	C1	C2	119.3(8)	N8	C30	C29	110.7(3)
C3	C2	C1	106.9(3)	N8	C30	N11	125.2(3)
C2	C3	C4	107.6(4)	C32	C31	C26	119.8(3)
C5	C4	C3	130.2(3)	C36	C31	C26	120.9(3)
C5	C4	N1	121.0(3)	C36	C31	C32	119.3(3)
N1	C4	C3	108.4(3)	C33	C32	C31	120.7(3)
C4	C5	C6	120.3(3)	C34	C33	C32	119.7(3)
C4	C5	C10	119.9(3)	C33	C34	C35	120.6(3)
C6	C5	C10	119.8(3)	C34	C35	C36	120.0(3)
C5	C6	C7	130.6(3)	C31	C36	C35	119.7(3)
N2	C6	C5	121.1(3)	N10	C37	N9	111.8(5)
N2	C6	C7	108.3(3)	C39	C38	N10	109.3(4)
C8	C7	C6	107.6(3)	C38	C39	N9	107.8(4)
C7	C8	C9	107.0(3)	N12	C40	N11	112.1(4)
C8	C9	N5	125.3(3)	C42	C41	N12	111.2(4)

N2	C9	C8	110.5(3)	C41	C42	N11	106.2(4)
N2	C9	N5	124.2(3)	C22	N7	B2	129.9(3)
C11	C10	C5	120.2(3)	C22	N7	C25	106.5(3)
C11	C10	C15	119.7(3)	C25	N7	B2	123.6(3)
C15	C10	C5	120.1(3)	C27	N8	B2	123.5(3)
C12	C11	C10	119.7(4)	C30	N8	B2	129.5(3)
C13	C12	C11	120.7(4)	C30	N8	C27	106.9(3)
C12	C13	C14	119.9(4)	C22	N9	C39	122.3(4)
C13	C14	C15	120.3(4)	C37	N9	C22	131.8(3)
C10	C15	C14	119.7(4)	C37	N9	C39	106.0(3)
N6	C19	N5	112.3(4)	C37	N10	C38	105.1(4)
C21	C20	N6	111.0(4)	C40	N11	C30	131.2(3)
C20	C21	N5	105.6(4)	C40	N11	C42	105.2(3)
C1	N1	B1	129.4(3)	C42	N11	C30	123.3(3)
C1	N1	C4	106.3(3)	C40	N12	C41	105.4(3)
C4	N1	B1	123.9(3)	F5	B3	F5[1]	111.3(5)
C6	N2	B1	124.9(3)	F5	B3	N13[1]	111.33(15)
C9	N2	B1	128.5(3)	F5	B3	N13	108.41(15)
C9	N2	C6	106.5(3)	F5[1]	B3	N13[1]	108.41(15)
C18	N3	C1	132.7(7)	F5[1]	B3	N13	111.33(15)
C18	N3	C16	106.4	N13[1]	B3	N13	105.9(4)
C16	N3	C1	120.9(7)	C44	C43	N14	126.5(4)
N4	C18	N3	111.9	N13	C43	C44	111.6(4)
C17	C16	N3	106.4	N13	C43	N14	121.8(3)
C16	C17	N4	110.0	C45	C44	C43	106.1(4)
C18	N4	C17	105.3	C44	C45	C46	108.3(4)
C19	N5	C9	129.6(3)	C47	C46	C45	131.2(4)
C19	N5	C21	106.0(4)	C47	C46	N13	121.0(4)
C21	N5	C9	123.1(4)	N13	C46	C45	107.7(3)
C19	N6	C20	105.0(4)	C46[1]	C47	C46	119.9(5)
C1	N3B	C16B	128.2(10)	C46	C47	C48	120.0(2)
C18B	N3B	C1	125.2(10)	C46[1]	C47	C48	120.0(2)
C18B	N3B	C16B	106.5	C49[1]	C48	C47	120.6(3)
N4B	C18B	N3B	111.9	C49	C48	C47	120.6(3)
C17B	C16B	N3B	106.2	C49[1]	C48	C49	118.8(5)
C16B	C17B	N4B	110.0	C50	C49	C48	119.8(5)
C18B	N4B	C17B	105.4	C51	C50	C49	121.6(5)
F3	B2	N7	109.7(3)	C50[1]	C51	C50	118.5(6)
F3	B2	N8	108.9(3)	N15	C52	N14	112.3(5)
F4	B2	F3	109.5(3)	C54	C53	N15	111.0(5)
F4	B2	N7	110.4(3)	C53	C54	N14	105.3(4)
F4	B2	N8	110.2(3)	C43	N13	B3	127.7(3)

N8	B2	N7	108.1(3)	C43	N13	C46	106.2(3)
N7	C22	C23	110.9(3)	C46	N13	B3	126.0(3)
N7	C22	N9	125.1(3)	C52	N14	C43	126.9(4)
N9	C22	C23	124.0(3)	C52	N14	C54	106.9(4)
C24	C23	C22	106.7(3)	C54	N14	C43	126.0(4)
C23	C24	C25	108.0(3)	C52	N15	C53	104.5(4)
C26	C25	C24	130.0(3)	Cl1	C55	Cl2	112.9
C26	C25	N7	121.7(3)				

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

Table S 6: Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 2.

Atom	*x*	*y*	*z*	U(eq)
H2	4150	3971	8194	40
H3	5743	3804	6947	39
H7	5740	3813	2266	33
H8	4114	3925	1013	37
H11	6766	4201	3514	38
H12	8679	4088	3520	47
H13	9443	3566	4600	53
H14	8300	3149	5680	53
H15	6376	3256	5693	41
H19	1088	3595	3020	53
H20	303	4229	345	65
H21	2275	4373	717	57
H18	959	3834	6050	42
H16	2454	4549	8290	56
H17	431	4634	8456	62
H18B	2789	4449	8572	44
H16B	961	3983	6110	63
H17B	-245	4374	7386	62
H23	8371	3187	1935	39
H24	7142	2894	3403	33
H28	2583	2596	3125	41
H29	1335	2764	1525	46
H32	3612	3049	4307	32
H33	3574	2887	6197	37
H34	4810	2402	6912	41
H35	6086	2078	5750	39

H36	6127	2236	3839	32
H37	6360	3101	-1397	58
H38	9083	3794	-1526	65
H39	8770	3627	415	55
H40	3576	2903	-1565	42
H41	567	3326	-2021	52
H42	767	3223	-12	54
H44	8126	4349	7362	55
H45	7045	4574	5699	46
H49	3381	4830	4811	46
H50	3398	4837	2874	63
H51	5000	5000	1893	71
H52	5878	4168	10026	74
H53	8516	4599	11562	67
H54	8620	4846	9615	57
H55A	10932	4984	15042	90
H55B	10222	5383	14720	90

Table S 7: Atomic Occupancy for 2.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
N3	0.55(3)	C18	0.55(3)	H18	0.55(3)
C16	0.55(3)	H16	0.55(3)	C17	0.55(3)
H17	0.55(3)	N4	0.55(3)	N3B	0.45(3)
C18B	0.45(3)	H18B	0.45(3)	C16B	0.45(3)
H16B	0.45(3)	C17B	0.45(3)	H17B	0.45(3)
N4B	0.45(3)	Cl1	0.5	Cl2	0.5
C55	0.5	H55A	0.5	H55B	0.5

Experimental

Single crystals of $C_{53}H_{38.5}B_{2.5}ClF_5N_{15}$ **2** were grown from a CH_2Cl_2 solution. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 150 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of 2

Crystal Data for 2.5($C_{21}H_{15}BF_2N_6$), 0.5(CH_2Cl_2) (M =1042.96 g/mol): orthorhombic, space group $P2_12_12$ (no. 18), a = 12.0671(5) Å, b = 32.4681(14) Å, c = 12.0173(5) Å, V = 4708.3(3) Å^3, Z = 4, T = 150 K, μ(MoKα) = 0.160 mm^{-1}, *Dcalc* = 1.471 g/cm^3, 144944 reflections measured (6.05° ≤ 2Θ ≤ 55.032°), 10767 unique (R_{int} = 0.0722, R_{sigma} = 0.0357) which were used in all calculations. The final R_1 was 0.0538 (I > 2σ(I)) and $wR_2$was 0.1380 (all data).

Refinement model description

The compound crystallized in the P21212 orthorhombic space group. The asymmetric unit contains two and half bodipy molecules and one half of a dichloromethane molecule, these two halves of molecules are located on a twofold symmetry axis. For one of the bodipy molecules, an imidazole group occupies two positions (rotation of 180°). This disorder was handled by using a rigid group refinement with occupation factors converged to 0.55/0.45.
Number of restraints - 60.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2. Rigid body (RIGU) restrains
 N3B, N3, C16B, C18, N4, C17B, C17, N4B, C16, C18B
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
3. Others
 Sof(N3B)=Sof(C18B)=Sof(H18B)=Sof(C16B)=Sof(H16B)=Sof(C17B)=Sof(H17B)=Sof(N4B)=
 1-FVAR(1)
 Sof(N3)=Sof(C18)=Sof(H18)=Sof(C16)=Sof(H16)=Sof(C17)=Sof(H17)=Sof(N4)=FVAR(1)
 Fixed Sof: Cl1(0.5) Cl2(0.5) C55(0.5) H55A(0.5) H55B(0.5)
4.a Free rotating group:
 N3(C18,C16,C17,N4), N3B(C18B,C16B,C17B,N4B), Cl1(Cl2,C55)
4.b Secondary CH2 refined with riding coordinates:
 C55(H55A,H55B)
4.c Aromatic/amide H refined with riding coordinates:
 C2(H2), C3(H3), C7(H7), C8(H8), C11(H11), C12(H12), C13(H13), C14(H14),
 C15(H15), C19(H19), C20(H20), C21(H21), C18(H18), C16(H16), C17(H17),
 C18B(H18B), C16B(H16B), C17B(H17B), C23(H23), C24(H24), C28(H28), C29(H29),
 C32(H32), C33(H33), C34(H34), C35(H35), C36(H36), C37(H37), C38(H38), C39(H39),
  C40(H40), C41(H41), C42(H42), C44(H44), C45(H45), C49(H49), C50(H50),
 C51(H51), C52(H52), C53(H53), C54(H54)
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This report has been created with Olex2, compiled on 2017.02.23 svn.r3390 for OlexSys.

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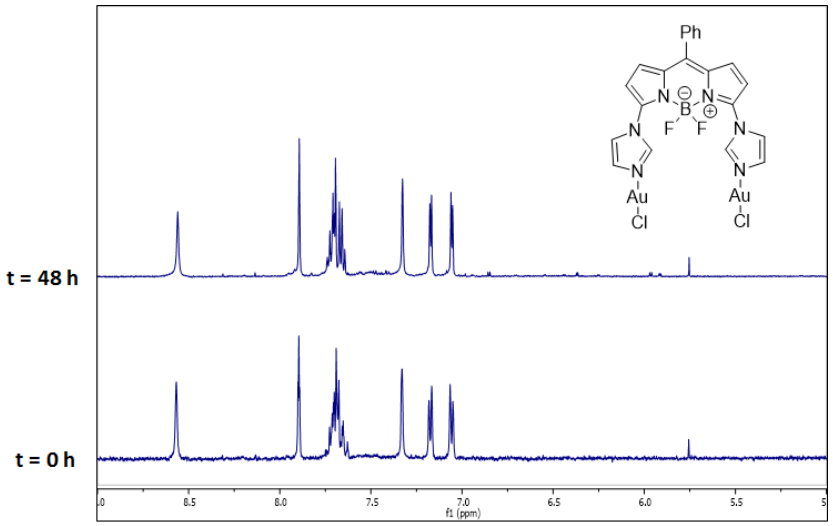
NMR stability studies

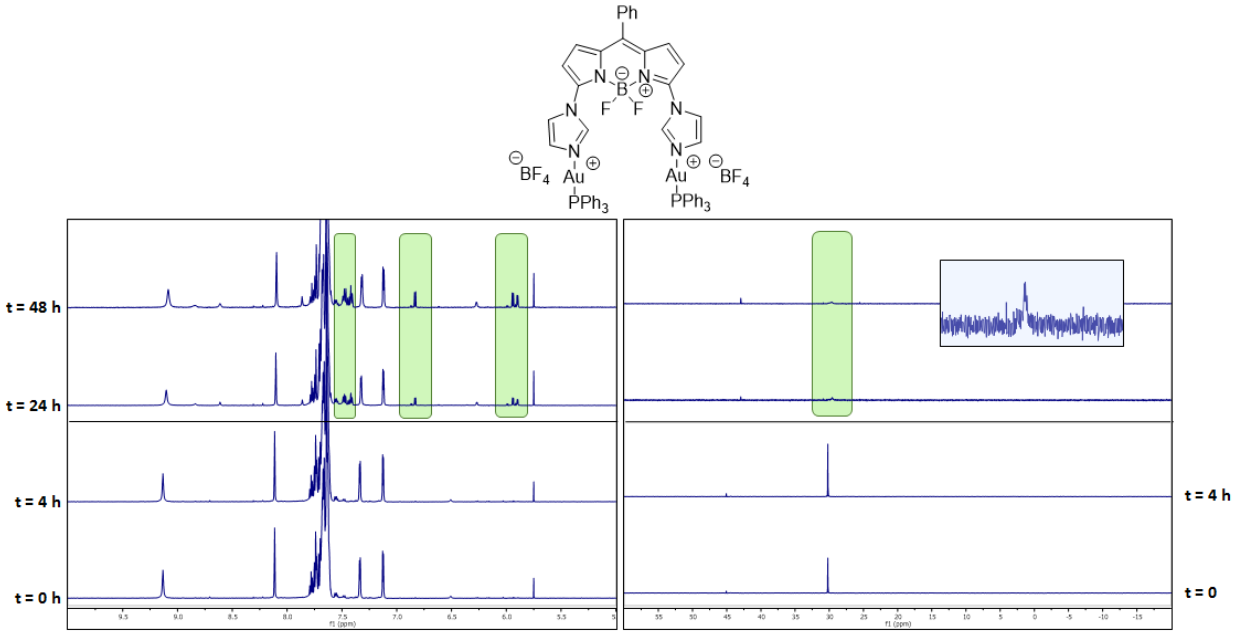
Stability studies have been performed in a mixture DMSO/water in order to have enough complex in solution to perform NMR experiment.

In the case of **BODI-Au-5**, the ^{1}H-NMR spectra at t = 0 h and t = 48 h are very similar. Thus, it seems that the presence of water did not degrade the complex.



^{1}H NMR 25°C, t = 0 h (500 MHz), t = 48 h (300 MHz)

In the case of **BODI-Au-6**, new signals appeared on ^{1}H-NMR spectra. At 48 h, the percentage of the side product is significant, but **BODI-Au-6** is still the major product. On ^{31}P{^{1}H}-NMR spectra, we did not see the apparition of a new signal but the singlet corresponding to the phosphorus of our complex became very broad, which suggest equilibrium reaction(s) occurring in the surrounding of the phosphorus. It may be the coordination of a water/DMSO molecule on gold(I) centers).



^{1}H NMR, 600 MHz, 25 °C.

^{31}P {^{1}H} NMR, 600 MHz, 25 °C.

Photophysical measurements

UV-Visible absorption spectra were recorded on a JASCO V630BIO spectrometer. The steady-state fluorescence emission spectra were obtained by using a JASCO FP8500 spectrofluorometer instrument. All fluorescence spectra were corrected for instrument response. The fluorescence quantum yields (Φ_F) were calculated from equation:

$$\frac{\Phi_F}{\Phi_{FR}} = \frac{n^2}{n_R^2} \times \frac{\int_0^\infty I_F(\lambda_E, \lambda_F) d\lambda_F}{\int_0^\infty I_{FR}(\lambda_E, \lambda_F) d\lambda_F} \times \frac{1-10^{-A_R(\lambda_E)}}{1-10^{-A(\lambda_E)}}$$

Φ_F and Φ_{FR} are fluorescence quantum yields of the compound and the reference respectively. $A(\lambda_E)$ and $A_R(\lambda_E)$ are the absorbance at the excitation wavelength, and n is the refractive index of the medium. I_F and I_{FR} are fluorescent intensities of the compound and the reference respectively. Rhodamine 6G ($\Phi_F = 0.92$ in water) was used as standard.[4] In all Φ_F determinations, correction for the solvent refractive index (η) was applied.

Table S 8: photophysical data of the different compounds in DMSO at 293K.

Compound	λ_{abs} (nm)	λ_{em} (nm)	ε ($M^{-1}.cm^{-1}$)	Φ_f (%)[a]
1	513	529	69,000	23
2	538	562	58,000	14
BODI-Au-5	539	561	55,000	9
BODI-Au-6	539	560	46,000	10

[a]: rhodamine 6G ($\Phi_f = 0.92$, $\lambda_{exc} = 530$ nm, in water).[4]

Compounds Chart

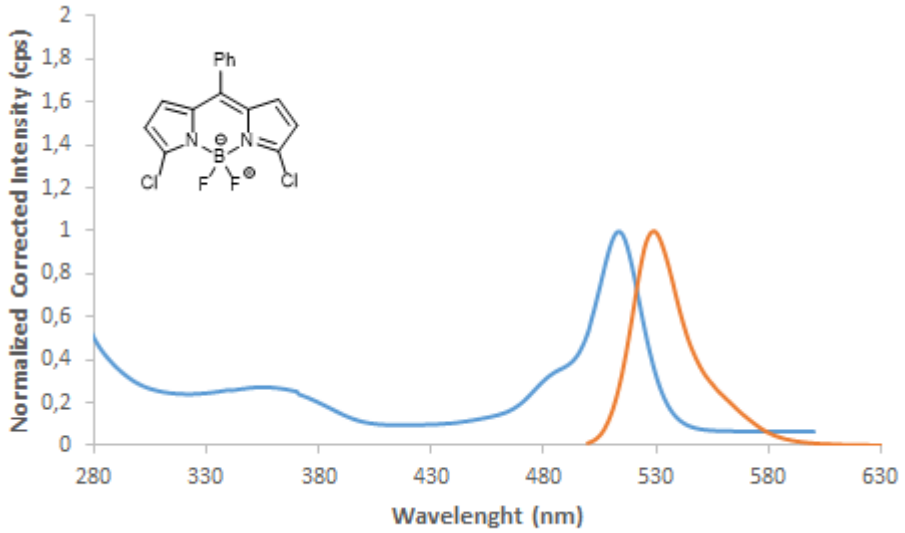


Figure S 15: Absorption (blue) and emission (red, λ_{ex} = 488 nm) spectra of 1 in DMSO, at 293 K.

Back to Compounds Chart - **Data compound 1**

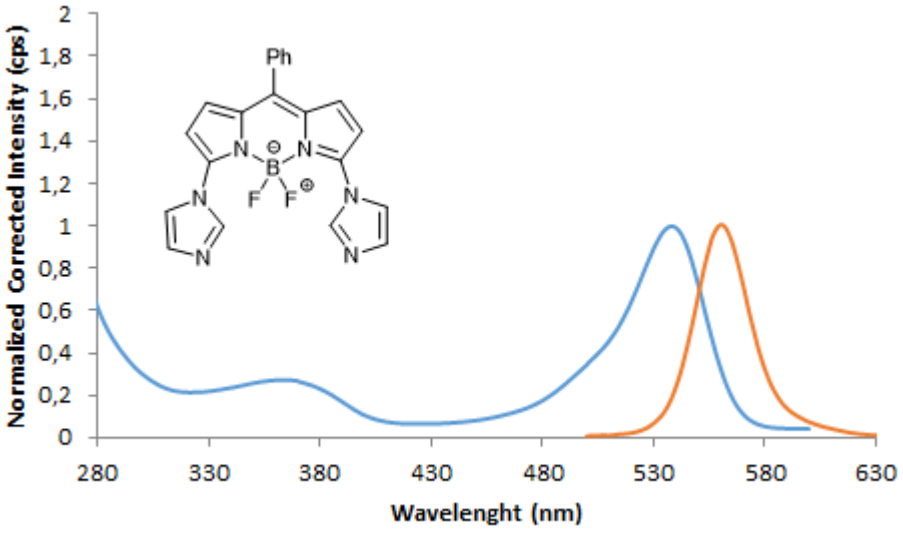


Figure S 16: Absorption (blue) and emission (red, λ_{ex} = 488 nm) spectra of 2 in DMSO, at 293 K.

Back to Compounds Chart - **Data compound 2**

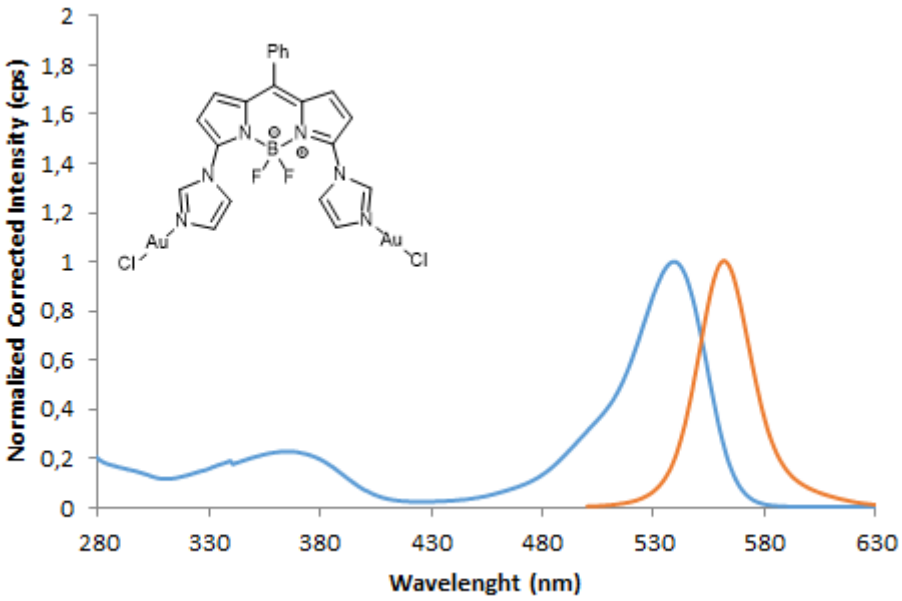


Figure S 17: Absorption (blue) and emission (red, λ_{ex} = 488 nm) spectra of BODI-Au-5 in DMSO, at 293 K.

Back to Compounds Chart - **Data BODI-Au-5**

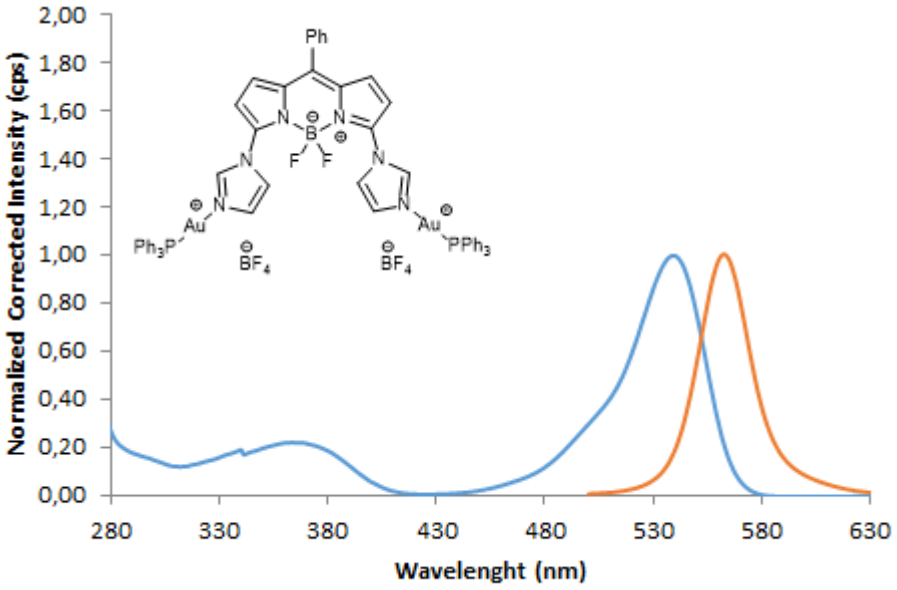


Figure S 18: Absorption (blue) and emission (red, λ_{ex} = 488 nm) spectra of BODI-Au-6 in DMSO, at 293 K.

Back to Compounds Chart - **Data BODI-Au-6**

In vitro tests

Determination of antiproliferative activity in cancer cell line

MDA-MB-231, PC3, SW480 and HEK293T cells were purchased from American Type Culture Collection (ATCC, Manassas, VA). These cells were cultured in DMEM with 10% of foetal bovine serum and grown at 37°C in a humidified atmosphere containing 5% CO_2 .
Cells were seeded in 96-well flat-bottomed microplates (100 µL) and incubated for 24 h to allow cell. The medium was then removed and replaced with fresh medium containing the compounds to be tested at increasing concentrations (from 0.78 to 100 µM) at 37°C for 48 h. Etoposide and 5-fluorouracil were used as anti-cancer references.
Each treatment was performed in triplicate. The anti-cancer activity of compounds and drug references were determined using the MTS assay (Promega). This assay is based on the conversion of a tetrazolium compound [3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium, inner salt] in the presence of an electron coupling reagent (phenazine ethosulfate; PES) to formazan product by metabolically active cells. The amount of formazan produced was detected by measurement of the absorbance at 490 nm on a microplate reader ClarioStar.
IC50 (i.e., the half maximal inhibitory concentration representing the concentration of a substance required for 50% in vitro inhibition) values were calculated using GraphPad7.0 Prism software.

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In vitro confocal microscopy experiments:

Cells were seeded on chambered coverglass (24 well-plate) and allowed to recover. After 24h, cells were incubated with 1 µM of each compound during 1hour, then wash with PBS1X.
For co-localization experiments, cells were fixed and permeabilized with iced methanol for 10 min at room temperature. Methanol was eliminated, then, cells were incubated with a blocking buffer (PBS1X-0.3% Triton 100X-1% BSA) for 1hours. While blocking, the primary antibodies dilution was prepared as indicated on antibodies datasheet: Na, K-ATPase (D4Y7E) rabbit mAB (#23565-Cell Signaling TECHNOLOGY) and AIF (D39D2) rabbit mAB (#5318-Cell Signaling TECHNOLOGY).
The blocking buffer was eliminated and the diluted antibodies was applied. Cells were incubated during 2hrs at room temperature in a humid light-tight box. Cells were rinsed thrice with PBS (5min each), then incubated with the fluorochrome-conjugated (Alexa647) secondary antibodies diluted as indicated on antibodies datasheet: anti Rabbit IgG (H+L), F(ab')2 Fragment (Alexa Fluor®647 conjugate) (#4414-Cell Signaling TECHNOLOGY) for 1hours at room temperature in a humid light-tight box.
Cells were then washed thrice with PBS (5min each) and incubated with a DAPI solution (5min) then mounted with Fluoromount-G® (Southern Biotech).

Confocal imaging was performed using a confocal laser-scanning microscope (Leica TCS SP8) with a × 63 HCX PL APO oil immersion (ON 1.4) objective lens, that allowed to simultaneously obtain DIC (Differential Interference Contrast) and fluorescent images (1024 pixels × 1024 pixels), and LASX software (Leica Microsystems, Ltd).

The samples were excited using internal microscope lasers and emission intensity was recorded at the appropriate emission wavelength. Fluorescence images were sequentially acquired. For co-localization experiments, each compound (green) was excited at 488 nm and its emission was recorded from 493 to 600 nm, whereas fluorochrome-conjugated (Alexa647) secondary antibodies (red) was excited at 638 nm and its emission was recorded from 643nm to 778 nm and DAPI was excited at 405 nm and its emission was recorded from 410 nm to 490 nm.

Image processing and analyses were carried out using Fiji/ImageJ

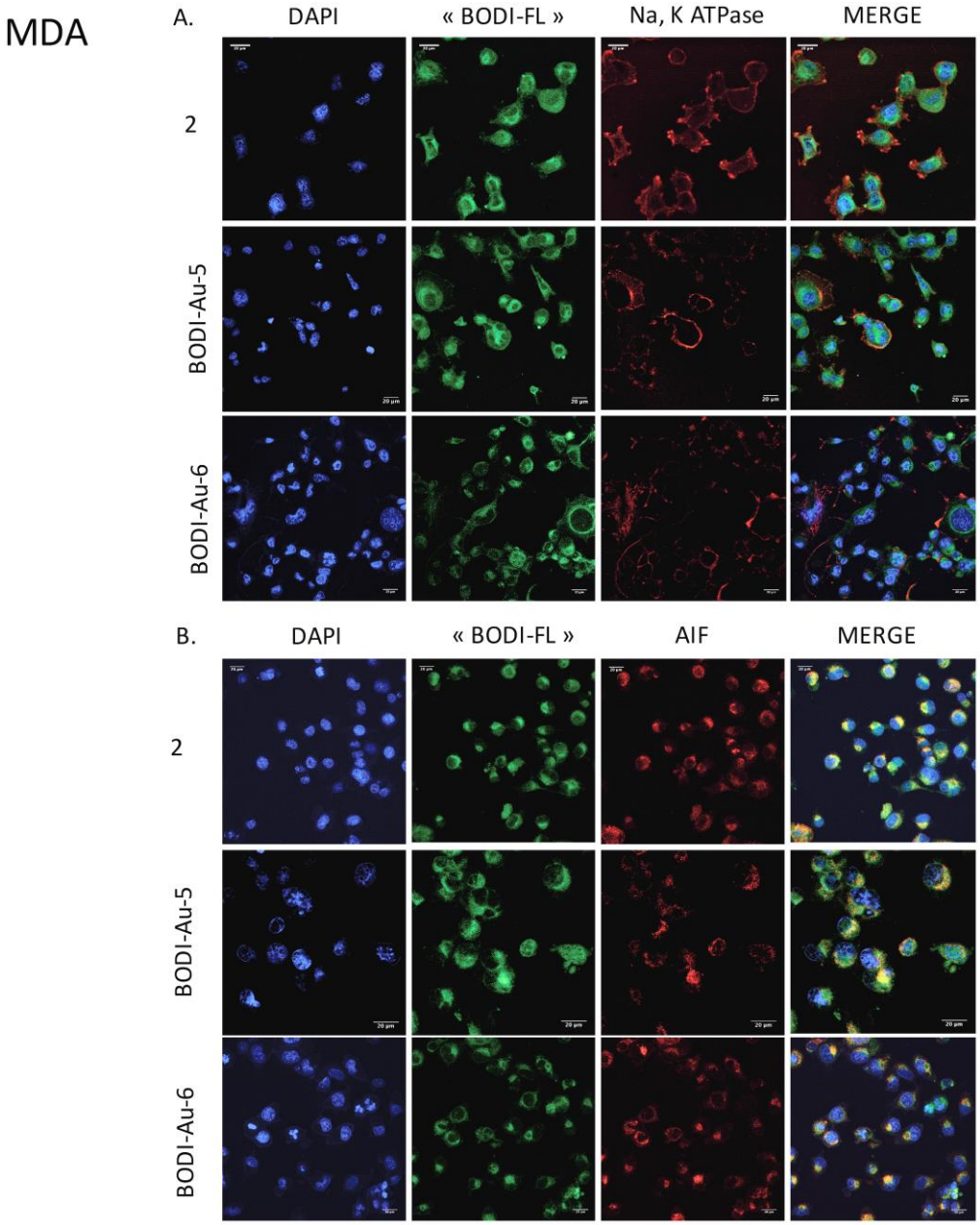

Figure S 19: Confocal images of the ligand 2, complexes BODI-Au-5 and BODI-Au-6 in MDA-MB231. Cells are incubated with 1µM of compound for 1h at 37°C, then according to supplier cells are immunolabelled with (A.) Na, K-ATPase (D4Y7E) rabbit mAB (Alexa 647 red) or (B.) AIF (D39D2) rabbit mAB (Alexa 647 red) respectively showing the membrane and a colocalization with mitochondria.

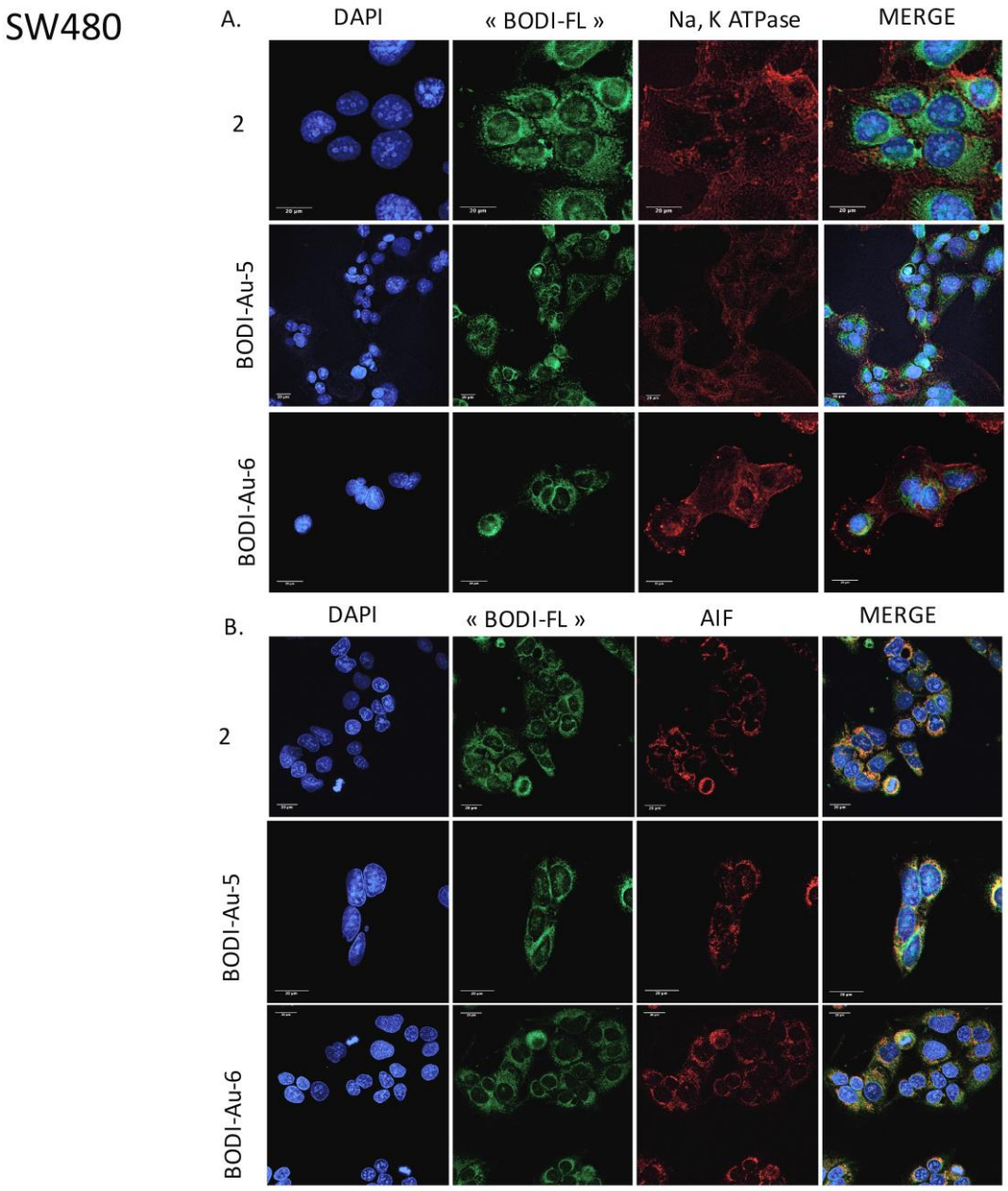

Figure S 20: Confocal images of the ligand 2, complexes BODI-Au-5 and BODI-Au-6 in SW480. Cells are incubated with 1µM of compound for 1h at 37°C, then according to supplier cells are immunolabelled with (A.) Na, K-ATPase (D4Y7E) rabbit mAB (Alexa 647 red) or (B.) AIF (D39D2) rabbit mAB (Alexa 647 red) respectively showing the membrane and a colocalization with mitochondria.

Another protocol was used to image the compounds but lead to images of weaker quality: SW480 cells ($4x10^5$ cells) were treated 1 hour at 37°C with 500 nM of DMSO or bimetallic complexes **BODI-Au-5**, **BODI-Au-6**, rinsed two times with PBS before paraformaldhéhyde fixation, and visualization by confocal microscopy (Nikon Eclipse TE 2000). The transmitted light images and confocal epifluorescence images are acquired simultaneously using the same illumination beam. Excitation was provided by a 405 nm laser diode. Fluorescence emission was collected in the 503-568 nm range (Bodipy fluorescence) or 408-488 nm (Dapi fluorescence, present in ProLong® reagent) using the Nikon spectral imaging system. Image analysis was performed with Image J software.

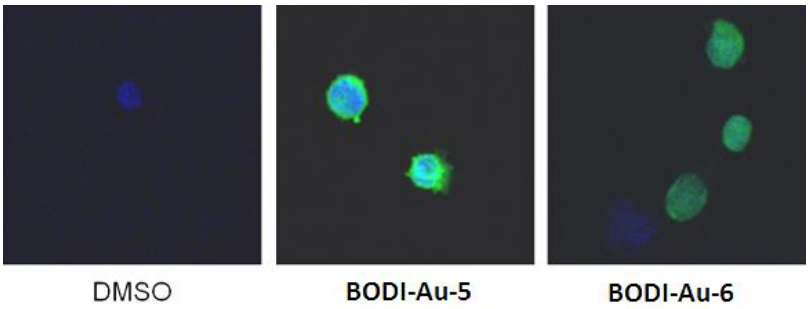

Figure S 21: Confocal microscopy experiments of BODI-Au-5 and BODI-Au-6 in SW480 cell line treated with 500 nM of metal complexes for 1 h at 37 °C (exc. 488 nm, detection 503-568 nm range for BODIPY complexes – green – and exc. 405 nm, detection 408-488 nm for DAPI – blue –).

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Uptake of gold(I) in PBMC and SW480 cell lines:

Uptake of gold in cells by ICP-MS. The study targeted PBMC cells ($1x10^5$ cells per well) and SW480 cells ($1x10^4$ cells per well). All of these cells were incubated at 37 °C for 1 hour with 5 µM of **BODI-Au-5**, **BODI-Au-6**, or Auranofin. Then, cells were rinsed two times with phosphate buffer saline (PBS) and lysed in water. All samples were digested in ICP-MS grade concentrated hydrochloric acid (OPTIMA Grade, Fisher Chemical) for 3 h at room temperature and filled to a total volume of 10 mL with ultrapure water. Indium was added as an internal standard at a concentration of 1 ppb. Determinations of total metal contents were achieved using a Thermo Element 2 ICP-MS. The instrument was tuned daily using a solution provided by the manufacturer containing 1 ppb each of Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Tl, U, Y (Tune-Up Solution ELEMENT, Thermo Fisher Scientific, Bremen, Germany). The external standard was prepared gravimetrically in an identical matrix to the samples (with regard to the internal standard and hydrochloric acid) with a gold solution single element standard at 1000 ppm (ASSURANCE, SPEX CertiPrep).

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Determination of pro-inflammatory IL-1β cytokine production in PBMCs

Human peripheral blood mononuclear cells (PBMCs) were isolated from buffy coats from healthy donors by density gradient centrifugation (Pancoll human, d.1.077 g/mL). Recovered PBMCs were washed three times in Dulbecco's phosphate buffered saline, seeded in a 96-well microplate at $6.67x10^5$ cells/mL in RPMI-1640 containing 10 % fetal bovine serum, penicillin (100 U/mL), streptomycin (100 µg/mL), amphotericin B (250 ng/mL), and incubated at 5 % CO_2 and 37 °C.

PBMCs were treated with compounds **2**, **BODI-Au-5**, **BODI-Au-6** (1, 3, 10 µM), or auranofin (0.1, 0.3, 1, 3 µM) then were stimulated for 24 h with 10 ng/mL of LPS (E. coli, 0128:B12, Sigma). Two anti-inflammatory references were tested in the same conditions: ZVAD (5µM) and dexamethasone (DEXA, 1µM). After incubation, the supernatants were harvested and kept at −20 °C until use. Viability of PBMCs was assessed by XTT assay. Secretion IL-1β was measured only in the culture supernatants of PBMCs treated with compounds that showed no or low toxicity, using a sandwich enzyme-linked immunosorbent assay (ELISA) method (eBioscience, San Diego, USA), according to manufacturer instructions.

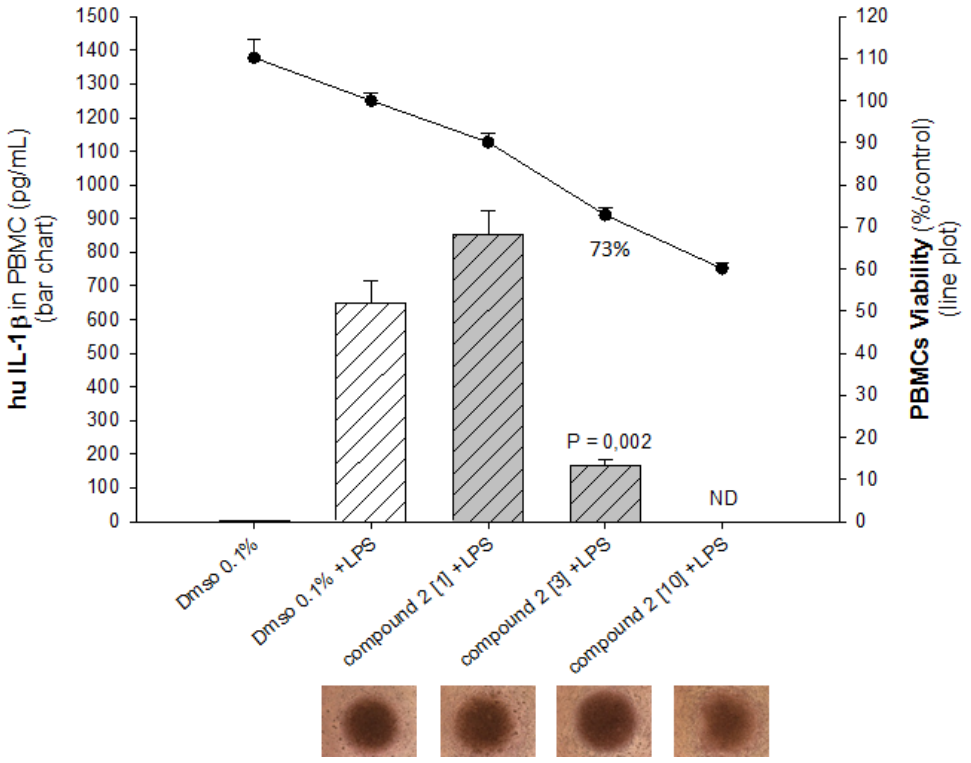

Figure S 22: Effect of compound 2 on viability (line plot) and inflammatory cytokine (IL-1β) production (bar chart) in LPS-stimulated PBMC.

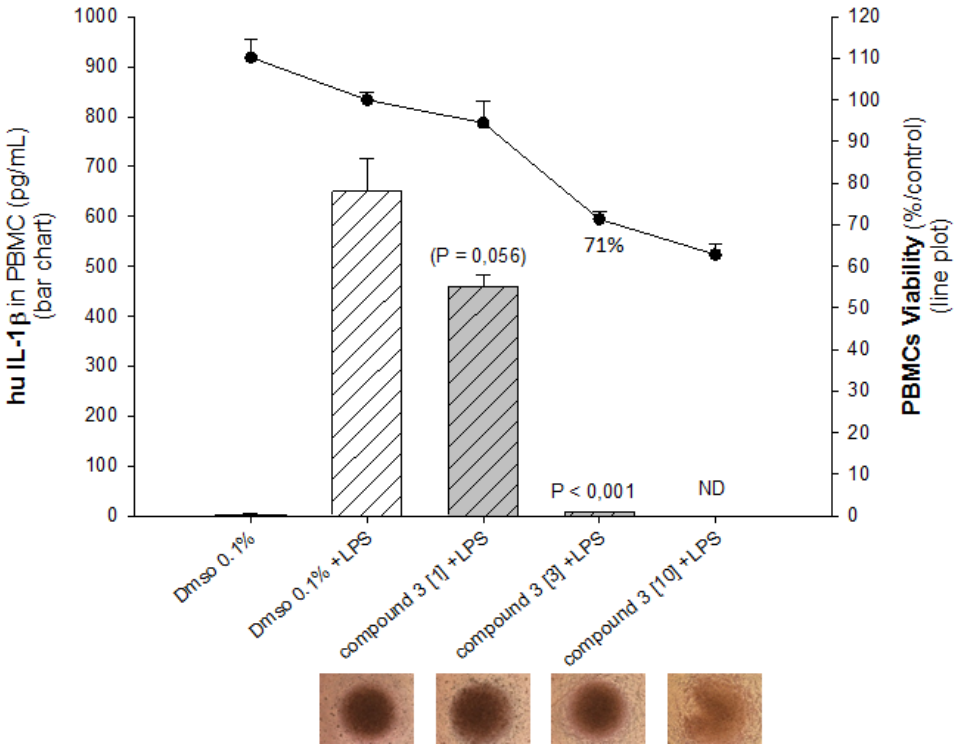

Figure S 23: Effect of BODI-Au-5 on viability (line plot) and inflammatory cytokine (IL-1β) production (bar chart) in LPS-stimulated PBMC.

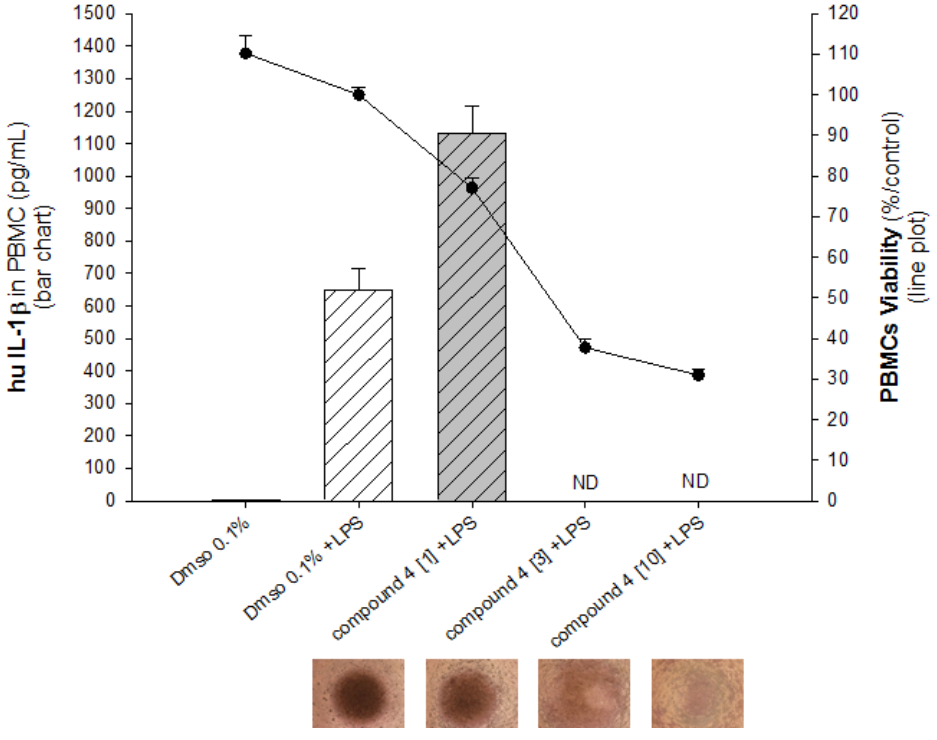

Figure S 24: Effect of BODI-Au-6 on viability (line plot) and inflammatory cytokine (IL-1β) production (bar chart) in LPS-stimulated PBMC.

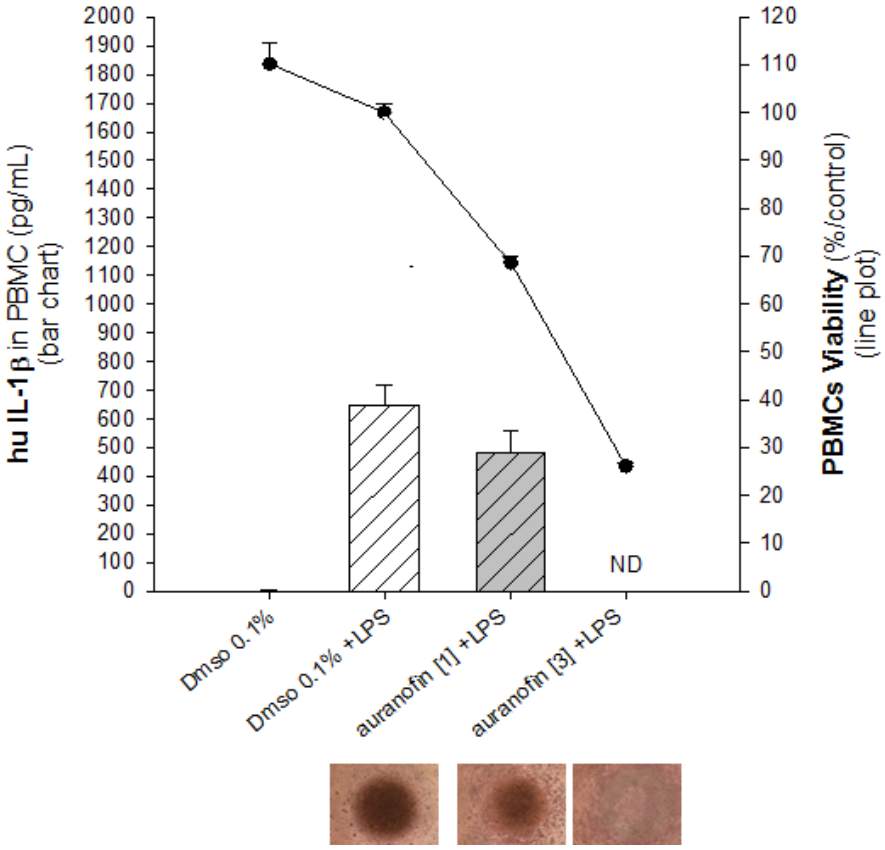

Figure S 25: Effect of auranofin on viability (line plot) and inflammatory cytokine (IL-1β) production (bar chart) in LPS-stimulated PBMC.

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