Electronic Supplementary Material (ESI) for Dalton Transactions
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Electronic Supplementary Information

Syntheses, Crystal Structures, Reactivity, and Photochemistry of Gold(III) Bromides bearing N-heterocyclic Carbenes

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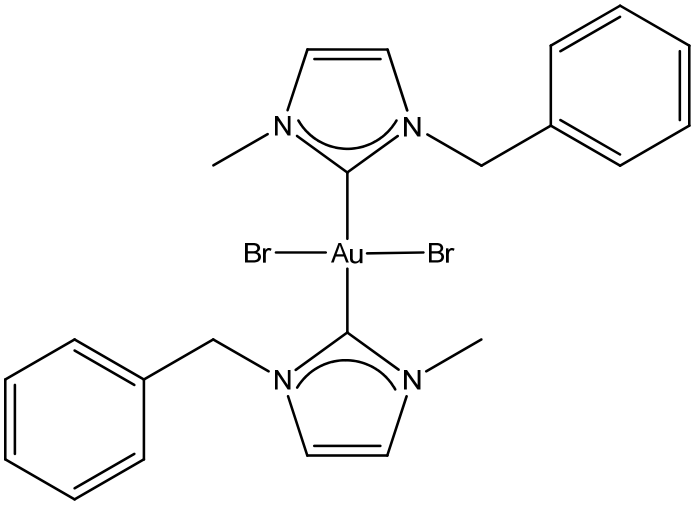
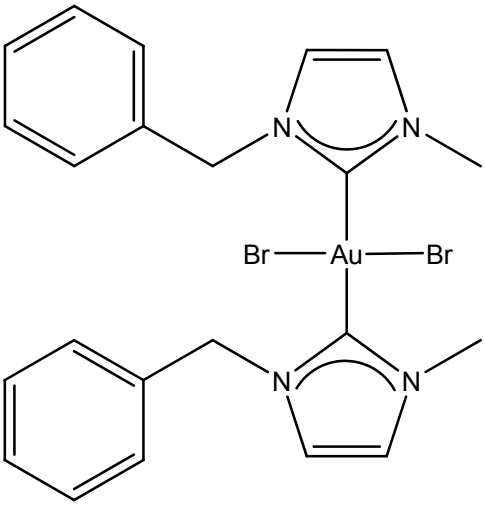
1D- and 2D-NMR spectra of complex **7b**:



= trans-anti - ▼



= trans-syn - Δ

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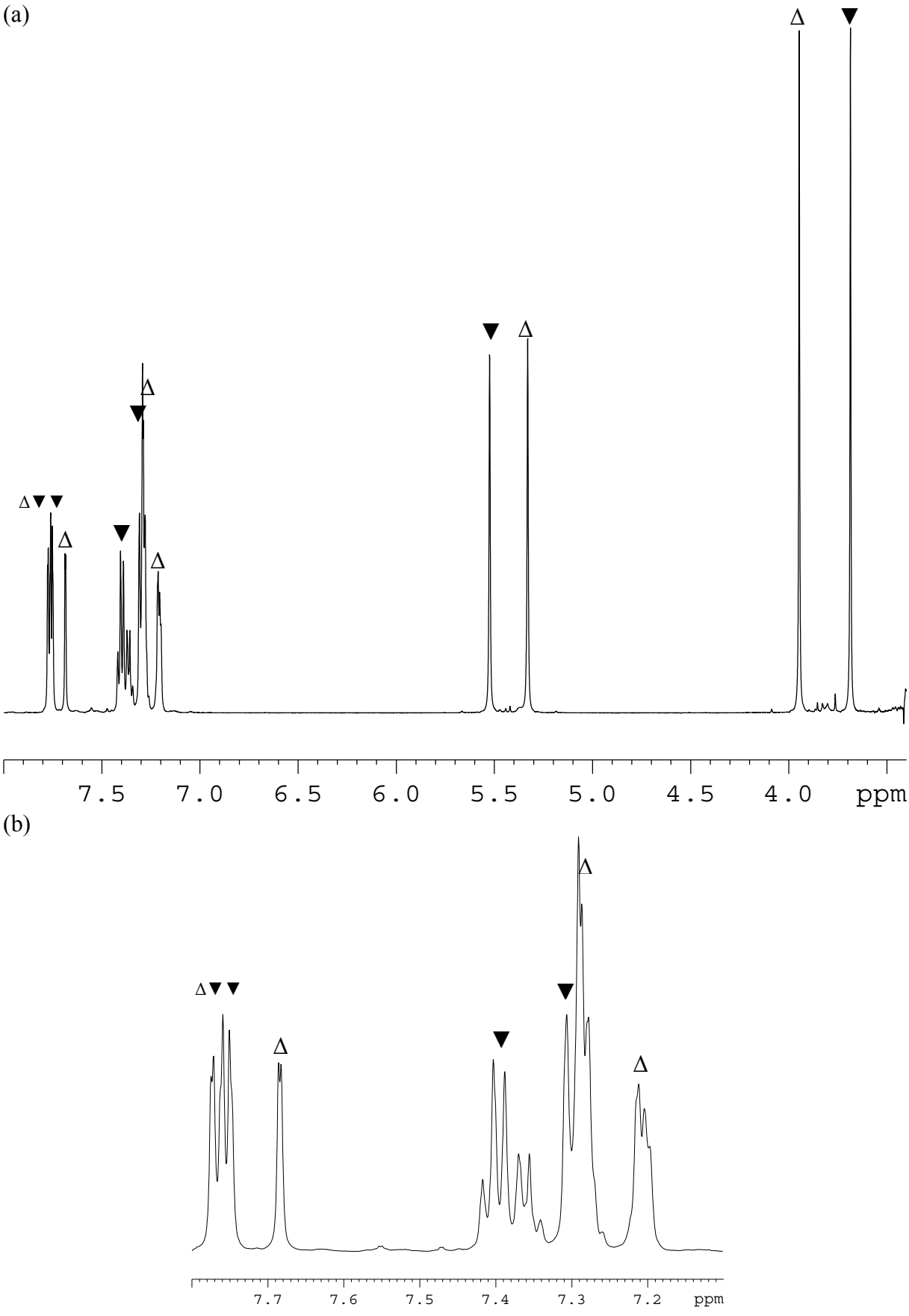

Fig. S1: ^{1}H NMR spectrum of **7b** in DMSO-d_6 a) full region and b) aromatic region

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(▼- trans-anti, Δ – trans-syn)

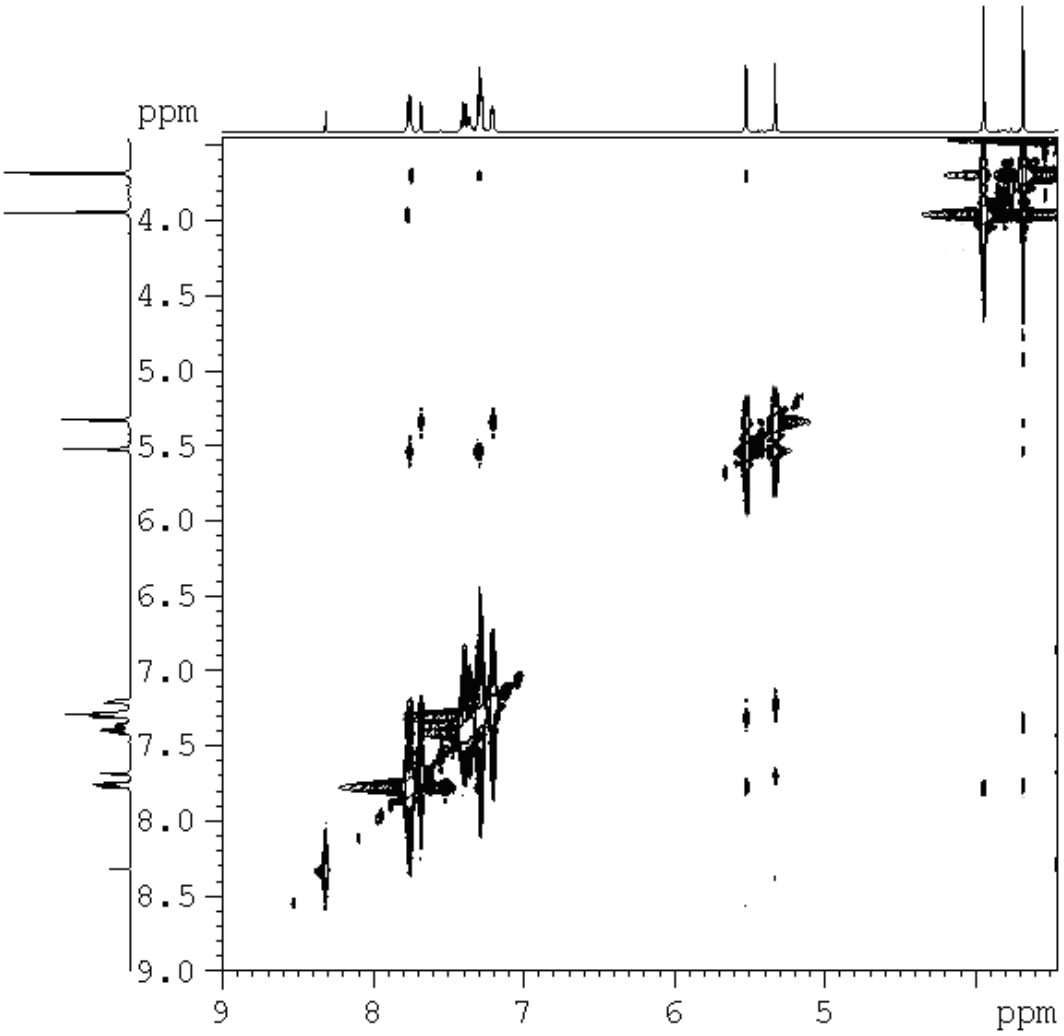

Fig. S2: ^{1}H-^{1}H NOESY spectrum of **7b** in DMSO-d_6 (full region)

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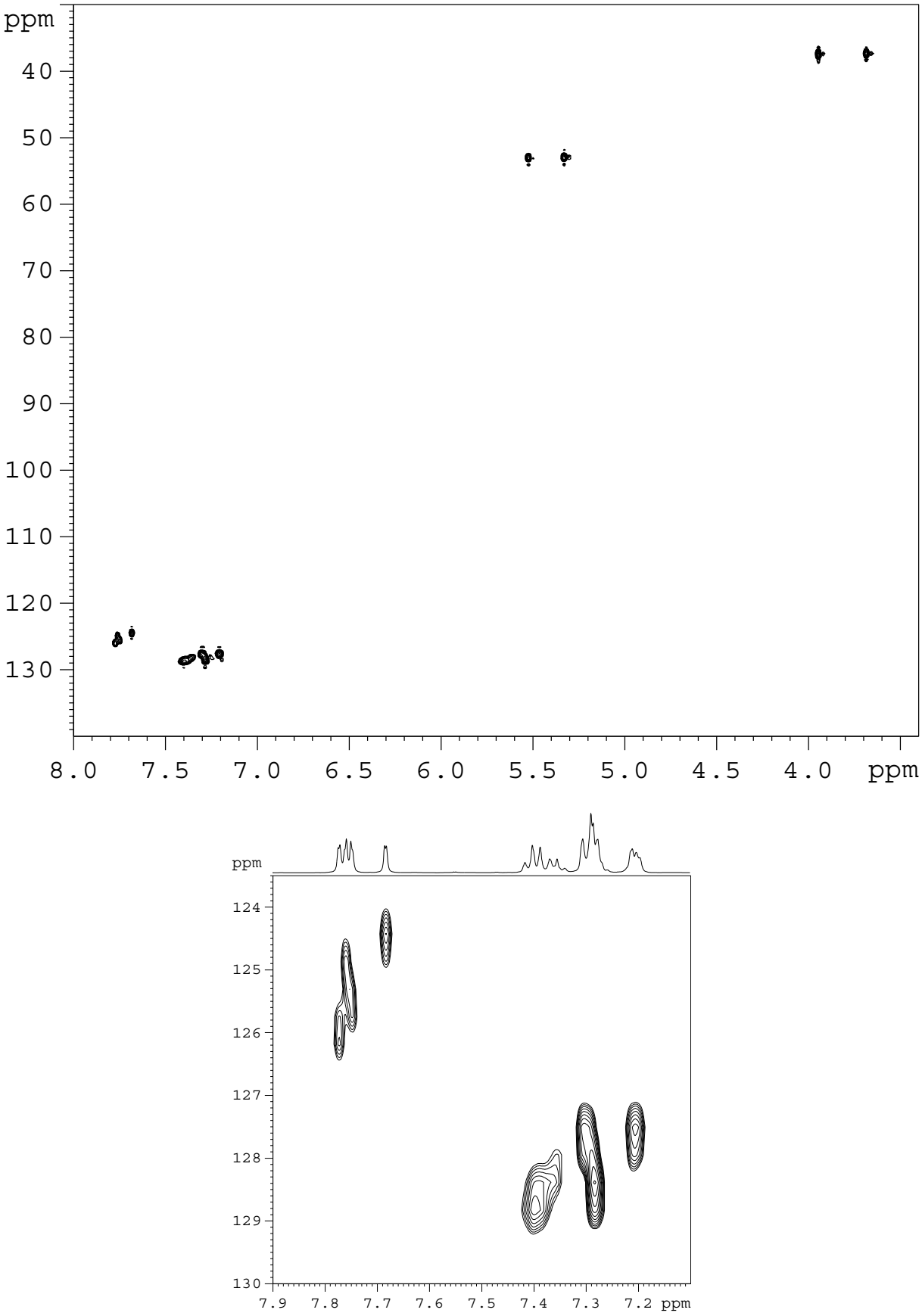

Fig. S3: ^{1}H-^{13}C HSQC spectrum of **7b** in d_6-DMSO (full region)

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Optimized geometry of the cation $[(BnMeIm)_2AuBr_2]^+$

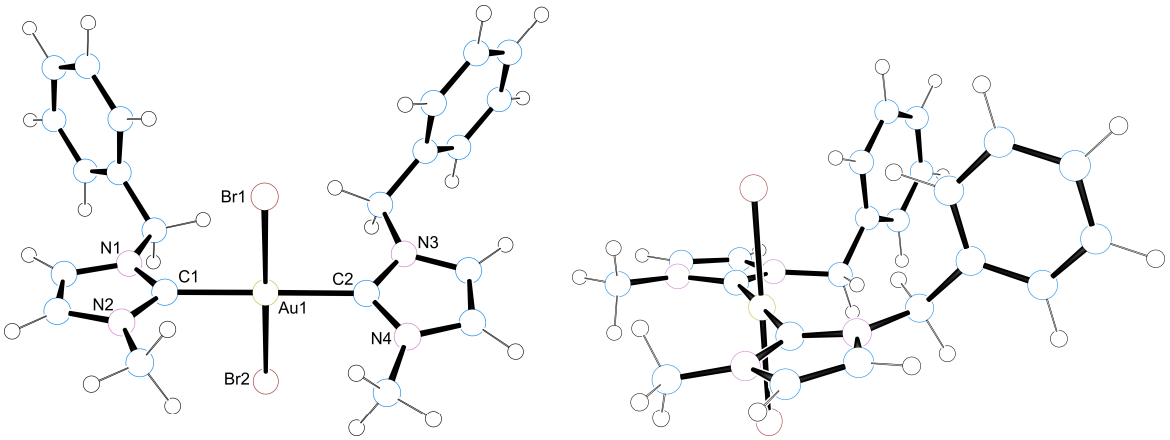

Fig. S4: Optimized geometry of $[(BnMeIm)_2AuBr_2]^+$ (DFT calculation using the COSMO model). Selected bond lengths (Å) and angles (°): Au1–C1 2.047, Au1–C2 2.047, Au1–Br1 2.438, Au1–Br2 2.437, C1–Au1–C2 179.26, Br1–Au1–Br 2 179.64, N1-C1-C2-N3 13.50.

xyz-coordinates of the geometry optimized structure

53

Au	-0.0860481	-0.9625277	0.0290779
Br	-0.2621318	-2.2179293	-2.0522692
Br	0.0890672	0.2803921	2.1194331
N	-2.8879864	-1.7676018	0.8480328
N	-2.9647208	-0.0322837	-0.4100926
N	2.7208593	-2.0855678	0.2413394
N	2.7824872	-0.0999551	-0.5689127
C	-2.1283505	-0.9068717	0.1617475
C	-2.3900257	-2.8834361	1.6309039
C	-4.2131161	-1.4354821	0.7091776
C	-4.2632813	-0.3429590	-0.0832468
C	-2.5841102	1.0730199	-1.2839439
C	-3.1088988	2.3963719	-0.8021411
C	-4.0022556	3.1157046	-1.5860179
C	-4.4839924	4.3451684	-1.1544613
C	-4.0763600	4.8597010	0.0670170
C	-3.1830882	4.1438389	0.8557015
C	-2.7007703	2.9196986	0.4223438
C	1.9553877	-1.0443574	-0.1034141
C	2.2363250	-3.3341441	0.8003238
C	4.0395715	-1.8005669	-0.0128387
C	4.0800669	-0.5513701	-0.5254232
C	2.3739539	1.1956910	-1.1096187
C	3.2639182	2.3169897	-0.6551418
C	4.0700959	2.9803615	-1.5720088
C	4.8891194	4.0245925	-1.1613753
C	4.9074609	4.4083740	0.1711332
C	4.1027975	3.7484657	1.0927559
C	3.2840324	2.7094349	0.6813289
H	-1.7589532	-2.5196253	2.4402539
H	-1.8271053	-3.5645288	0.9945196
H	-3.2392965	-3.4139699	2.0515967
H	-4.9963245	-2.0019297	1.1823369
H	-5.0995020	0.2343875	-0.4374686

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H	-2.9528560	0.8600318	-2.2872812
H	-1.4951484	1.0780473	-1.3307570
H	-4.3228281	2.7133083	-2.5405381
H	-5.1802375	4.8981526	-1.7734993
H	-4.4525531	5.8173408	0.4065090
H	-2.8592573	4.5428940	1.8094201
H	-2.0030172	2.3660456	1.0418978
H	1.6653673	-3.1405351	1.7069181
H	1.6163995	-3.8541836	0.0716563
H	3.0928815	-3.9540929	1.0490307
H	4.8267356	-2.5036800	0.1971619
H	4.9103788	0.0496662	-0.8520526
H	1.3485780	1.3633211	-0.7796359
H	2.3697473	1.1312195	-2.1979546
H	4.0557401	2.6807023	-2.6140097
H	5.5135193	4.5360067	-1.8841326
H	5.5459985	5.2220715	0.4936383
H	4.1108895	4.0481609	2.1338742
H	2.6551599	2.1998333	1.4034962

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Molecular structures obtained from the reactivity studies with 3b and 7c

$[(Bn_2Im)_2Au]NO_3$

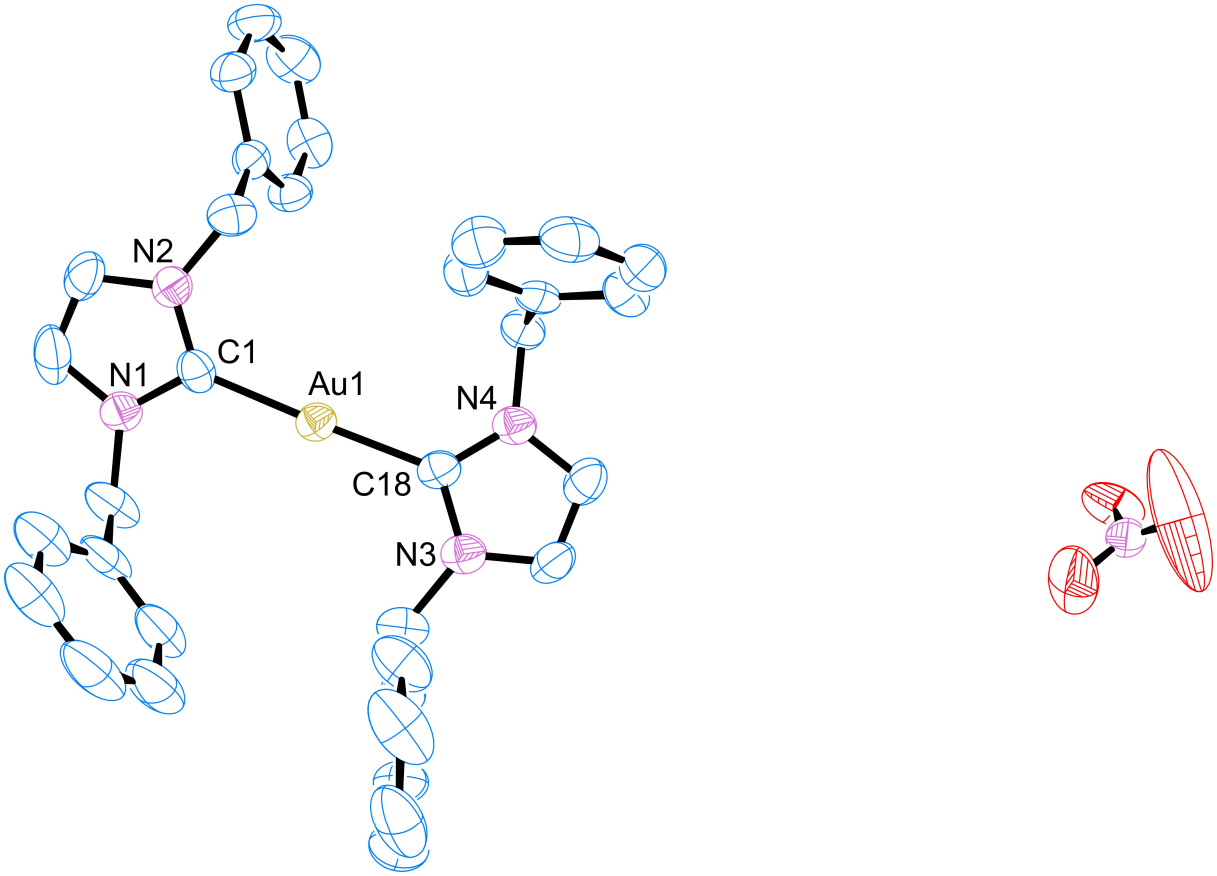

Fig. S5: Molecular structure of $[(Bn_2Im)_2Au]NO_3$.The nitrate anion is disordered over two postions (occupancy 52:48). Only one position is depicted. Selected bond lengths (Å) and angles (deg): Au1–C1 2.006(5), Au1–C18 2.025(5), C1–Au1–C18 178.2(2), N1–C1–C18–N3 10.2(8).

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Bn_2ImAuSPh:

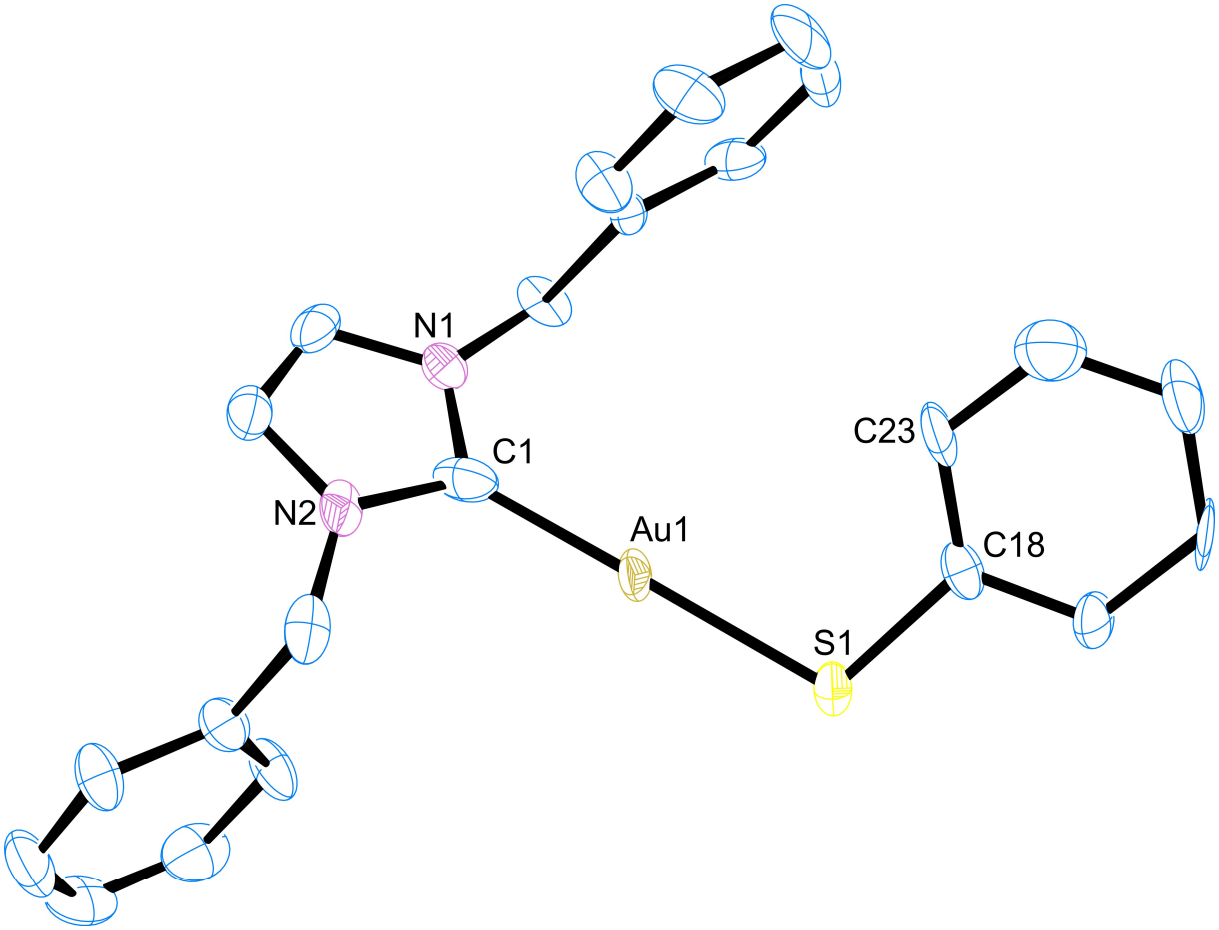

Fig. S6: Molecular structure of (Bn_2Im)AuSPh obtained from the reaction of (Bn_2Im)$AuBr_3$ with three equivalents of NaSPh. Selected bond lengths (Å) and angles (deg): Au1–C1 1.99(2), Au1–S1 2.297(4), C1–Au1–S1 179.5(4), Au1–S1–C18 108.1(5), N1–C1–S1–C18 42(1), Au1–S1–C18–C23 7(1).

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Molecular structure of **[(Bn$_2$Im)$_2$Au]Cl**, **6c**

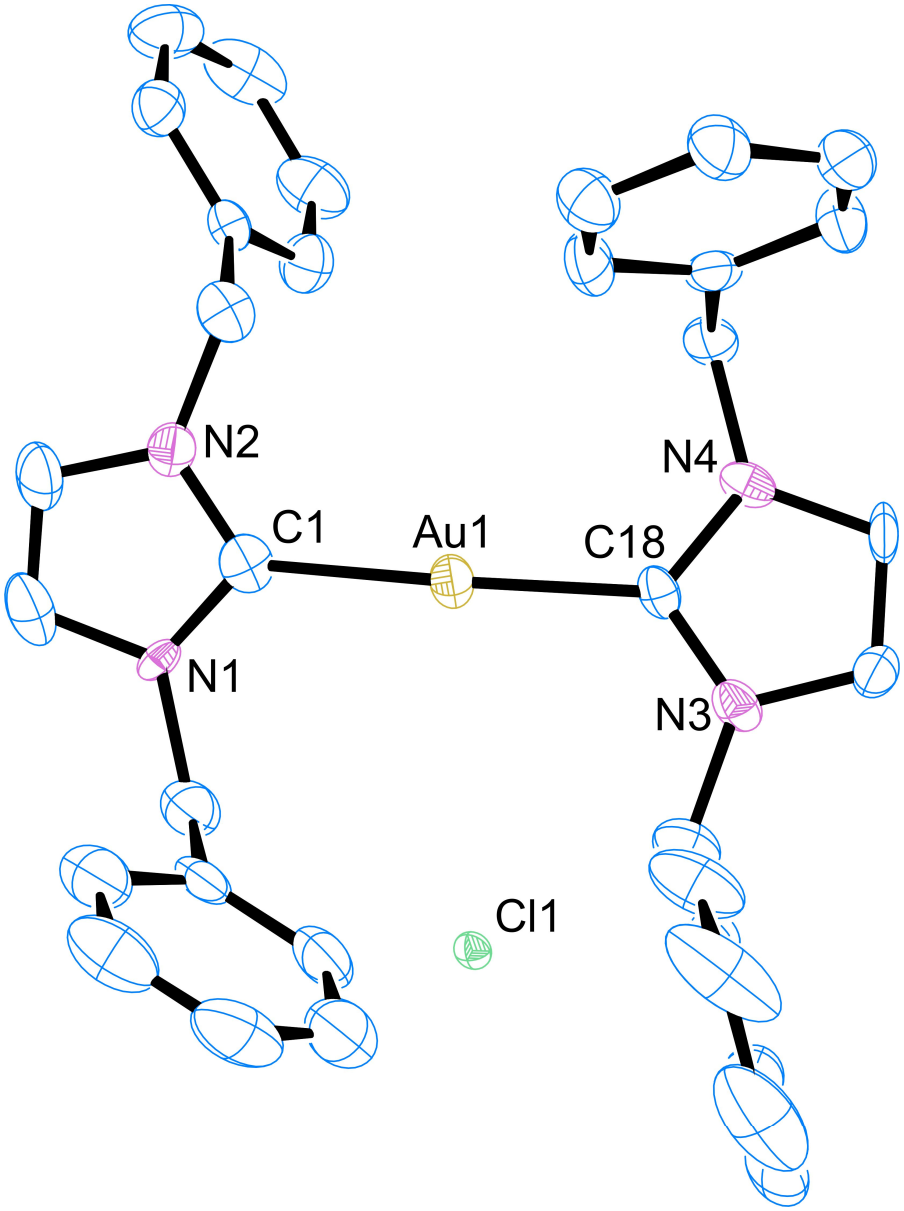

Fig S7: Molecular structure of [(Bn$_2$Im)$_2$Au]Cl. Selected bond lengths (Å) and angles (deg): Au1–C1 2.038(9), Au1–C18 2.032(7), C1–Au1–C18 178.0(3), N1–C1–C18–N3 9.3(9).

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$[(Bn_2Im)_2Au]BF_4$

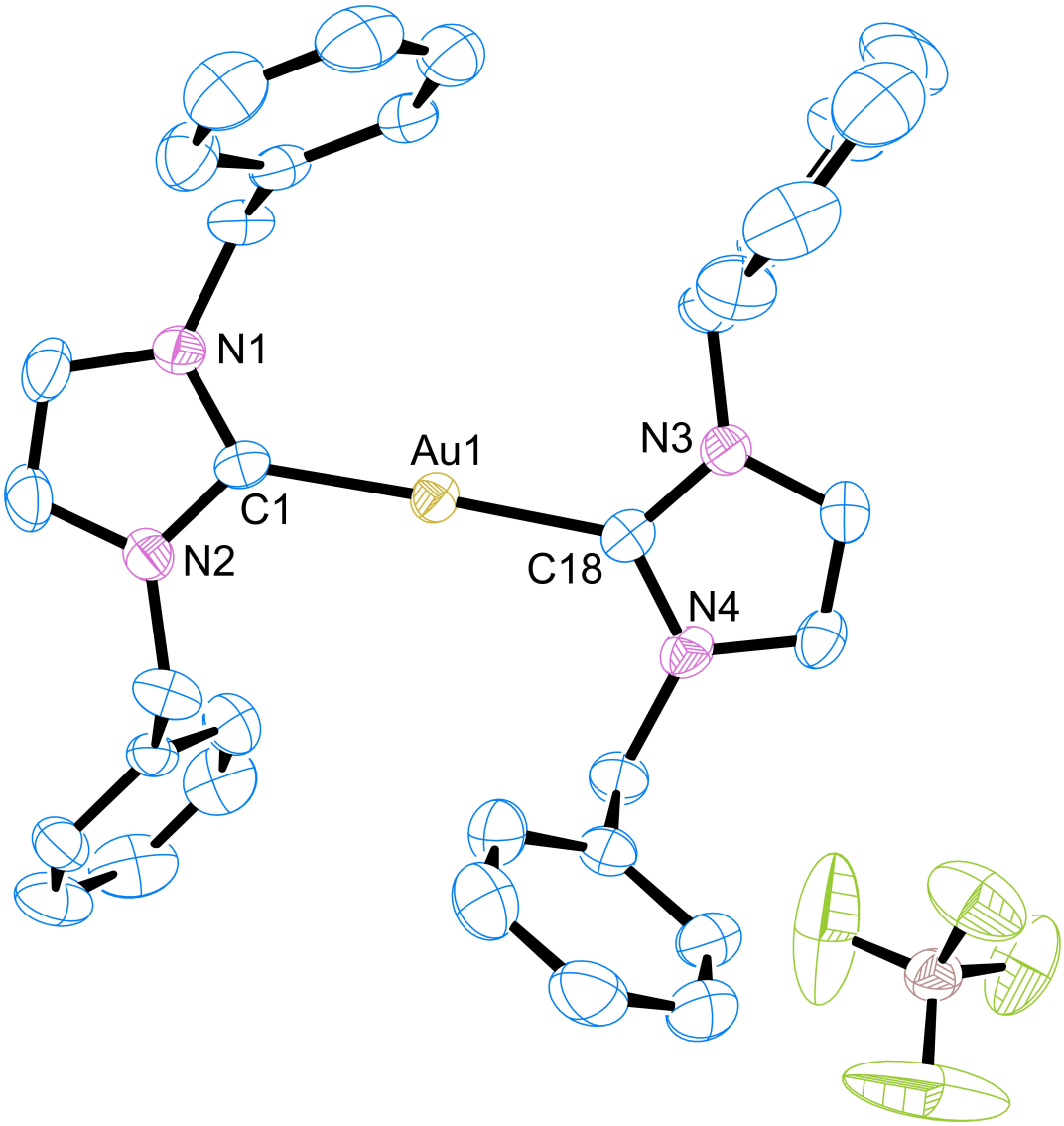

Fig. S8: Molecular structure of $[(Bn_2Im)_2Au]BF_4$. Selected bond lengths (Å) and angles (deg): Au1–C1 2.019(4), Au1–C18 2.033(4), C1–Au1–C18 178.4(2), N1–C1–C18–N3 5.8(5).

Table S1. Crystal data, data collection and structure refinement for compounds (Bn_2Im)AuSPh and [(Bn_2Im)$_2$Au]A (A = Cl^-, BF_4^-, NO_3^-).

	(Bn_2Im)AuSPh	**[(Bn_2Im)$_2$Au]Cl**	**[(Bn_2Im)$_2$Au]BF_4**	**[(Bn_2Im)$_2$Au]NO_3**
Formula	$C_{23}H_{21}N_2SAu$	$C_{34}H_{32}N_4AuCl$	$C_{34}H_{32}N_4AuBF_4$	$C_{34}H_{32}N_5AuO_3$
M_W	554.44	729.05	780.41	755.61
Crystal size [mm]	0.70×0.54×0.47	0.45×0.25×0.22	0.64×0.55×0.50	0.70×0.55×0.42
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	8.1925(5)	14.9584(14)	15.1243(7)	15.1417(14)
b [Å]	9.3756(6)	11.0038(11)	11.4996(5)	11.1604(10)
c [Å]	13.6642(8)	17.8290(15)	18.1831(8)	18.1484(17)
α [°]	73.838(2)	90	90	90
β [°]	81.532(2)	92.788(3)	91.4040(10)	92.617(3)
γ [°]	82.739(2)	90	90	90
V [Å^3]	993.04	2931.2(5)	3161.5(2)	3063.7(5)
ρ_{calc} [g cm^{-3}]	1.854	1.652	1.640	1.638
Z	2	4	4	4
μ [mm^{-1}]	7.52	5.14	4.71	4.85
T [K]	205	300	300	200
Θ range [°]	2.4 – 25.0	2.9 – 25.0	2.9 – 25.0	3.2 – 25.0
Reflections collected	9760	18213	30219	19332
Unique reflections	3463	5110	5579	5405
Observed reflections [I > 2 σ(I)]	3001	3878	4836	4114
Parameters refined */restraint*	220	361	397	411 / 32
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
T_{min}, T_{max}	0.08, 0.13	0.21, 0.40	0.15, 0.20	0.13, 0.24
σ_{fin} (max/min) [eÅ^{-3}]	4.34 / -3.09	3.67 / -1.04	1.15 / -0.88	0.82 / -0.50
R_1 [I≥2σ(I)]	0.081	0.047	0.026	0.031
wR_2	0.207	0.133	0.065	0.072
CCDC number	830166	830164	830163	830165

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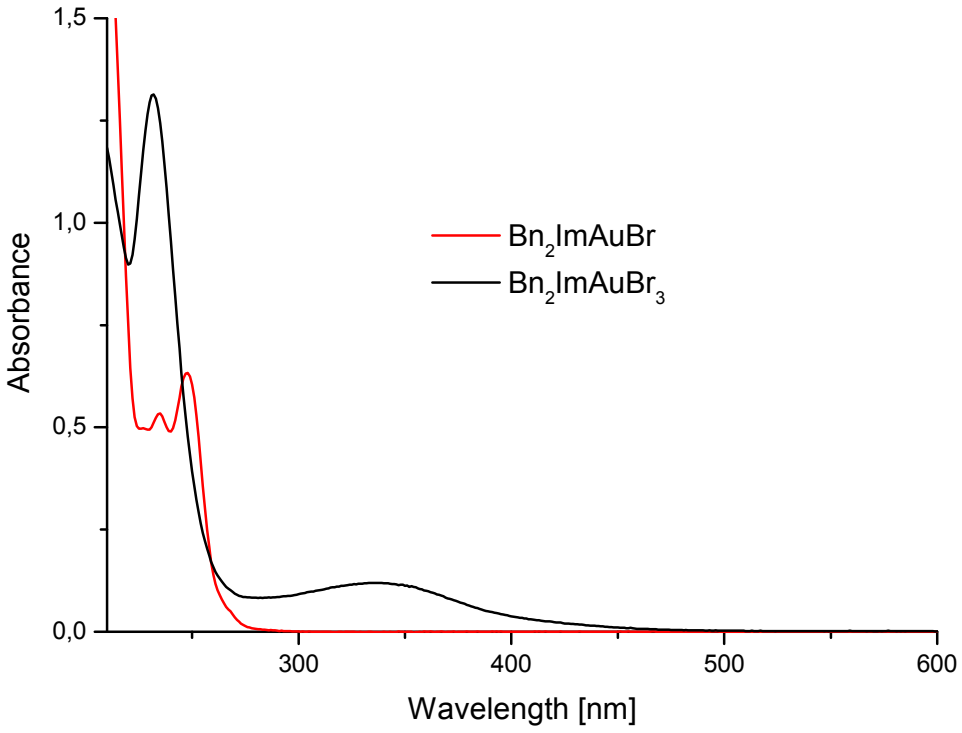

Fig. S9: UV-Vis spectra of methanolic solutions of $Bn_2ImAuBr$ (c = 2.1 10^{-5} mmol/L) and $Bn_2ImAuBr_3$ (c = 1.5 10^{-5} mmol/L).

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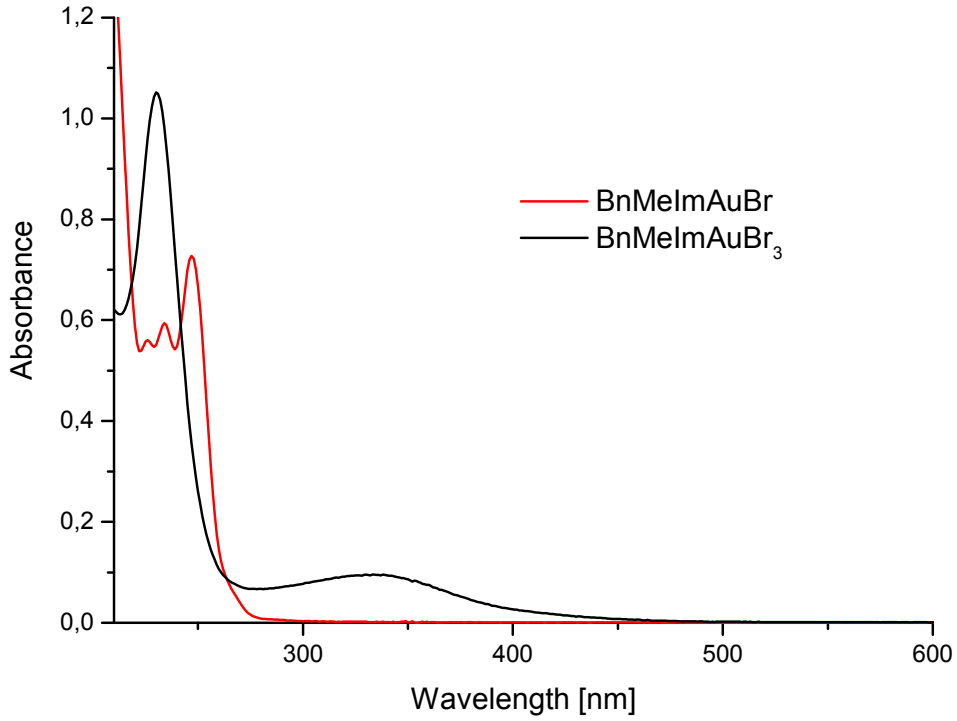

Fig. S10: UV-Vis spectra of methanolic solutions of BnMeImAuBr (c = 5.3 10^{-5} mol/L) and $BnMeImAuBr_3$ (2.5 10^{-5} mol/L).

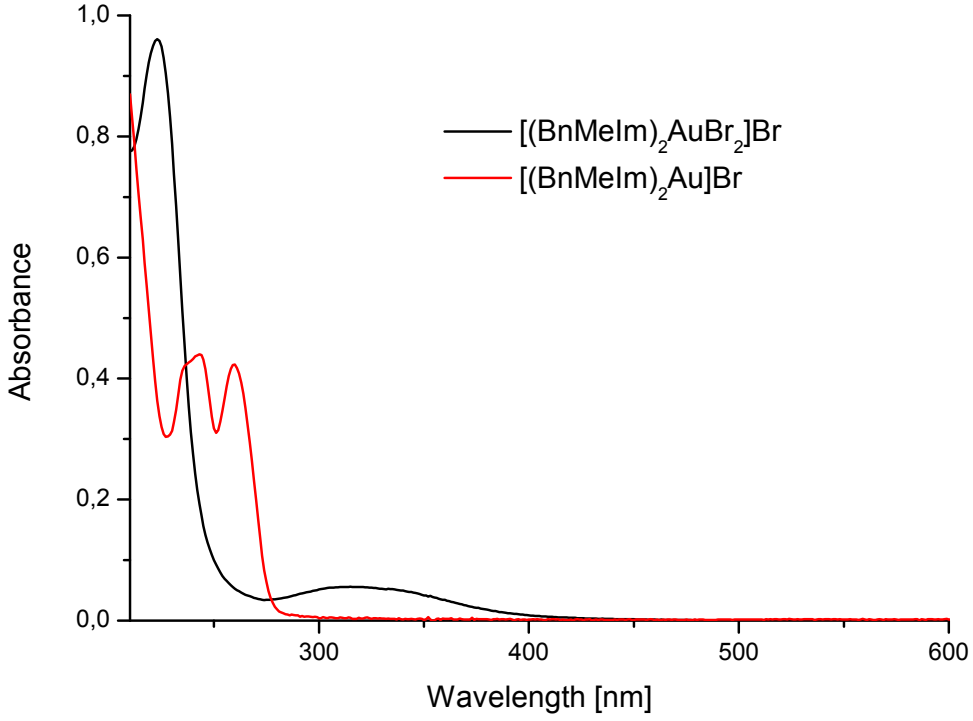

Fig. S11: UV-Vis spectra of methanolic solutions of $[(BnMeIm)_2Au]Br$ (2.4 10^{-5} mol/L) and $[(BnMeIm)_2AuBr_2]Br$ (2.3 10^{-5} mol/L).

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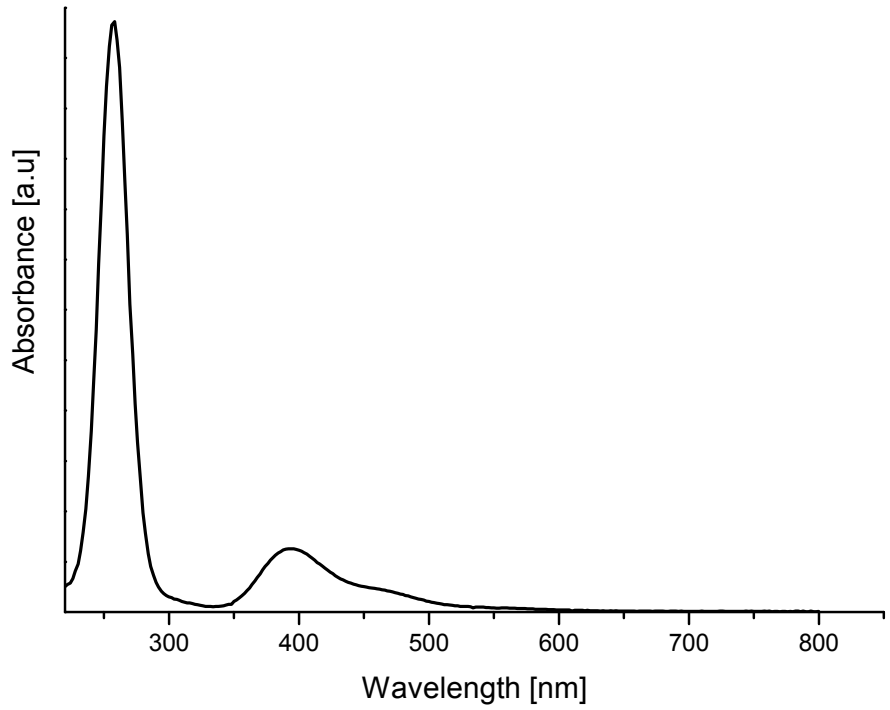

Fig. S12: UV/Vis spectrum of $K[AuBr_4]$ in MeCN.

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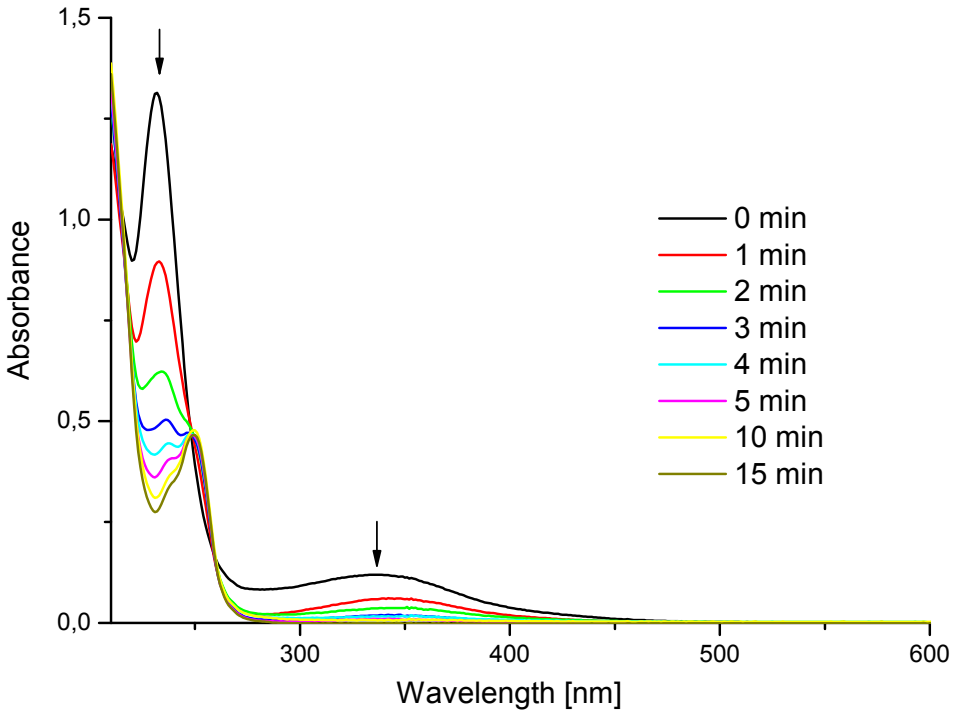

Fig. S13: Irradiation of $Bn_2ImAuBr_3$ in methanolic solution (c = 1.5 10^{-5} mmol/L) with polychromatic light > 280 nm.

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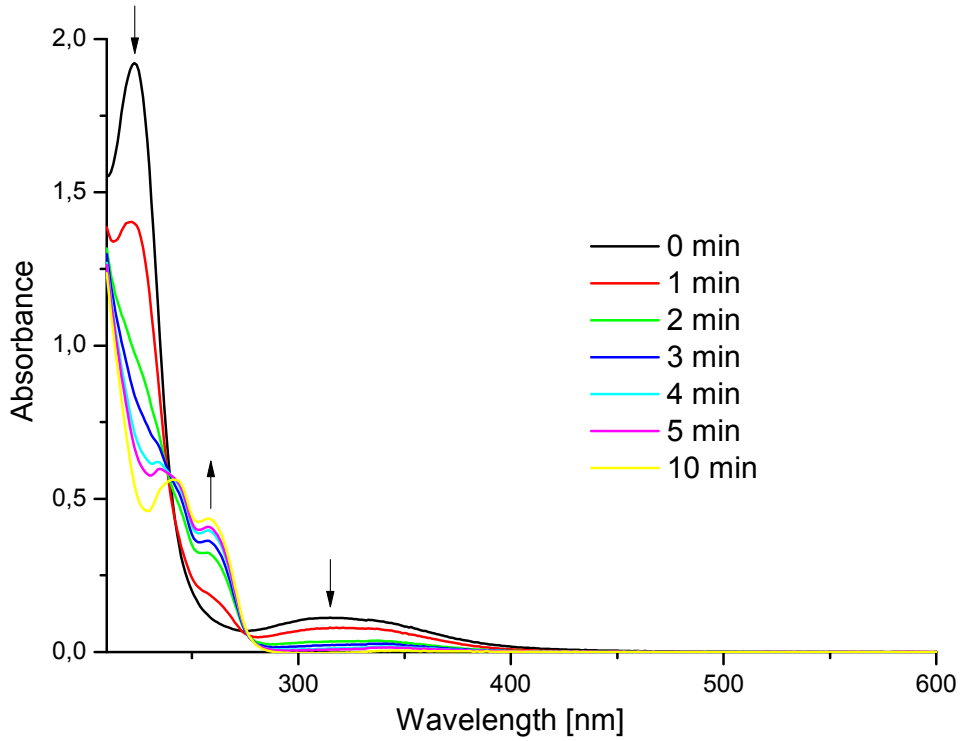

Fig. S14: Irradiation of $[(BnMeIm)_2AuBr_2]Br$ in methanolic solution (c = 2.4 10^{-5} mmol/L) with polychromatic light > 280 nm.

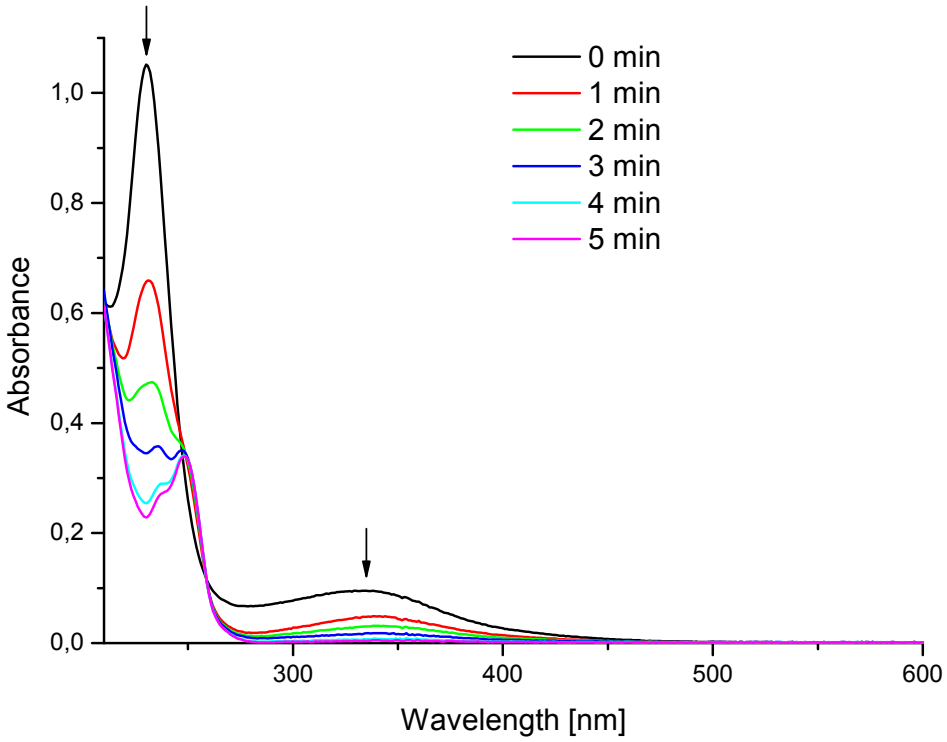

Fig. S15: Irradiation of $BnMeImAuBr_3$ in methanolic solution (c = 2.5 10^{-5} mol/L) with polychromatic light > 280 nm.

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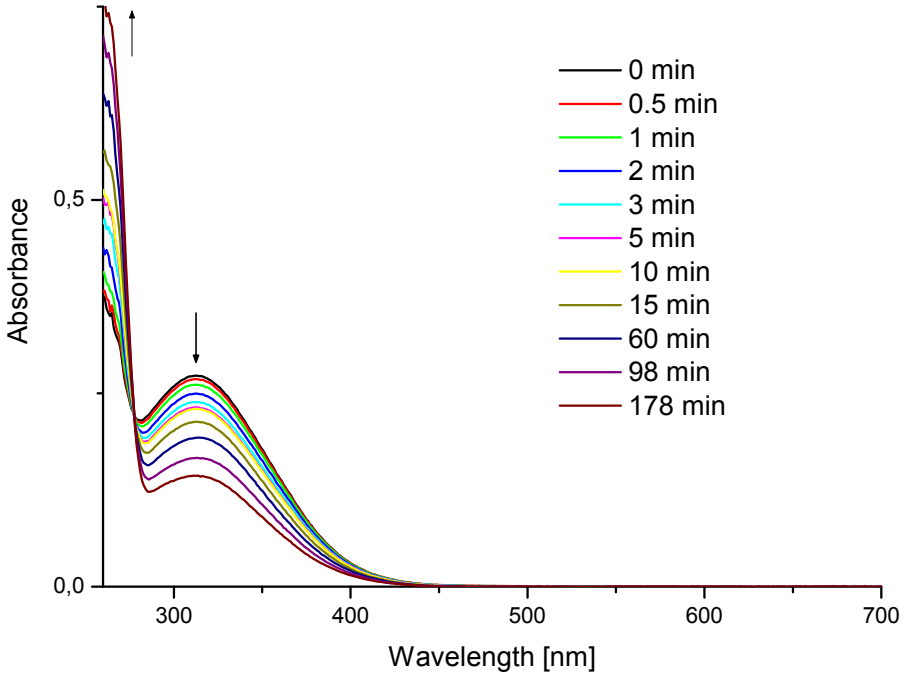

Fig. S16: Irradiation of $Bn_2ImAuBr_3$ in DMSO solution (c = 5.6 10^{-5} mol/L) with polychromatic light > 280 nm.

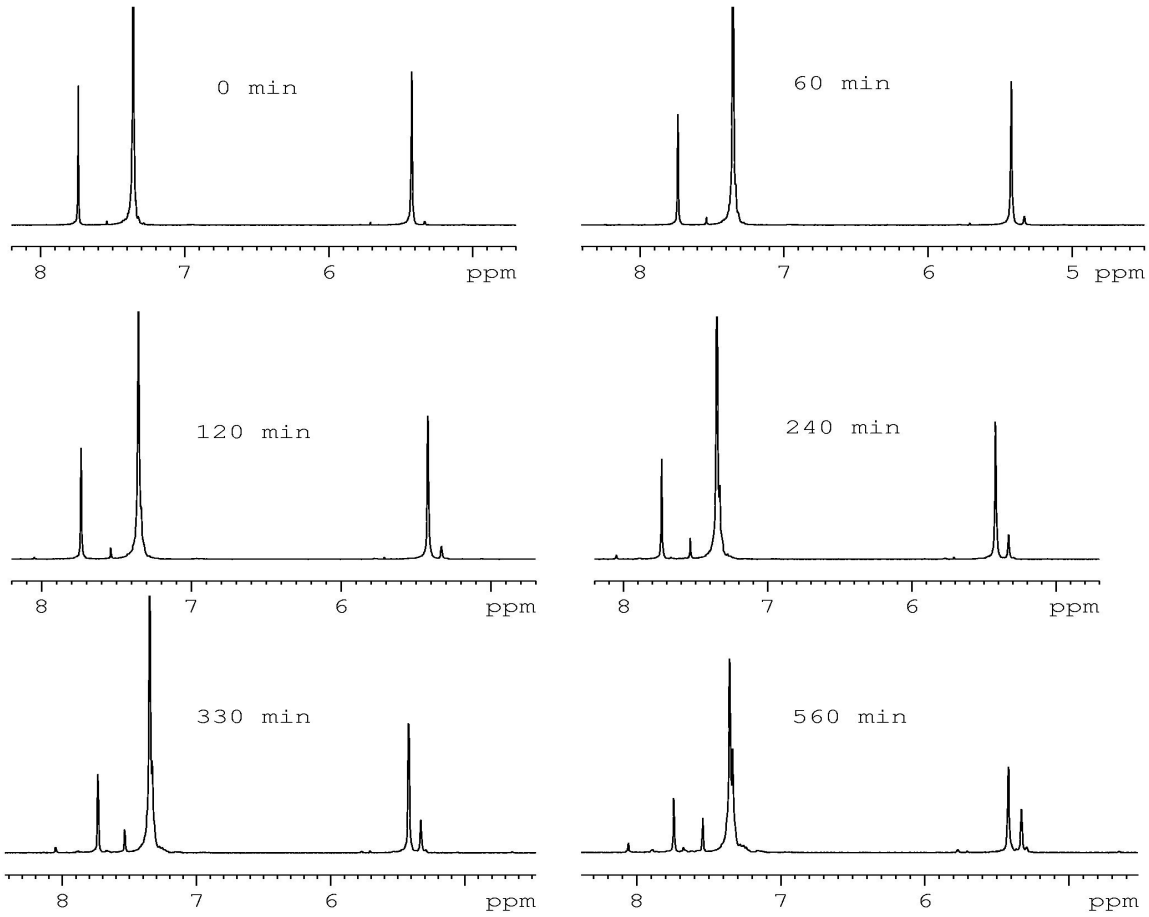

Fig. S17: Excerpt from the ^{1}H-NMR spectrum depicting the photoreduction of the complex **4b** in DMSO upon irradiation with monochromatic light (λ = 300 nm).

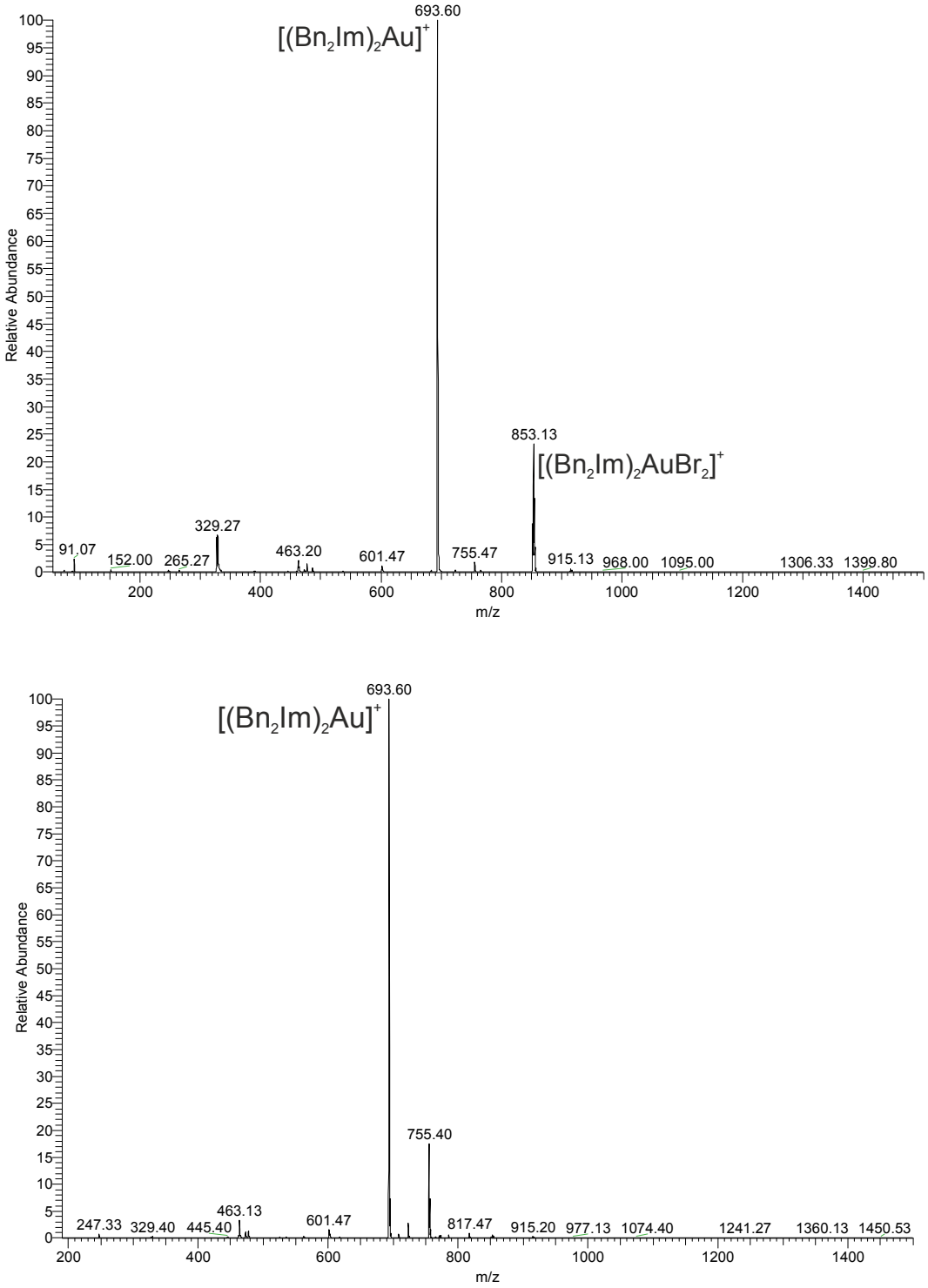

Fig. S18: ESI mass spectra of a solution of compound **7b** in MeOH before (top) and after 18 min (bottom) irradiation at λ = 300 nm.

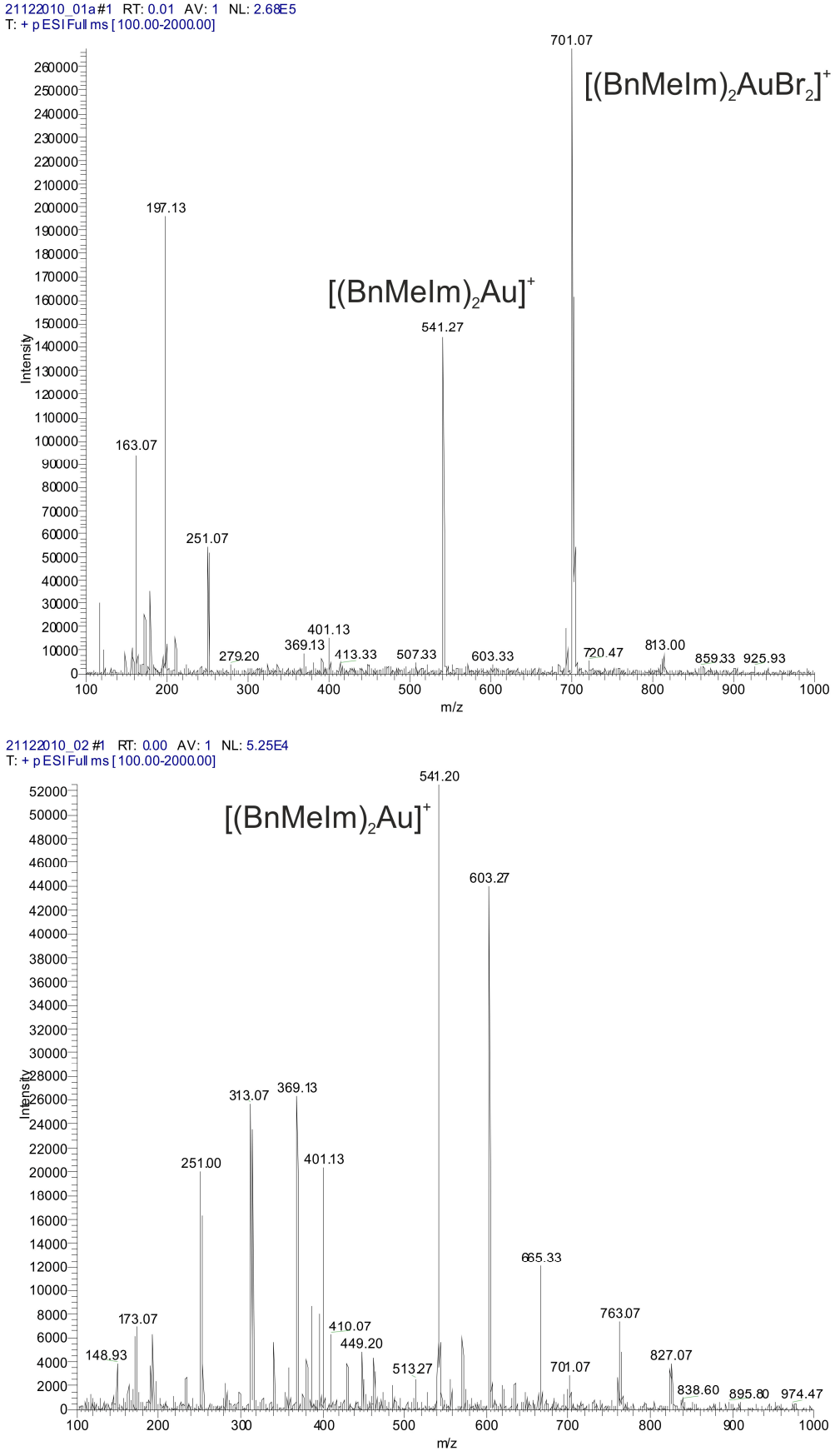

Fig. S19: ESI mass spectra of a solution of compound **7a** in MeOH before (top) and after 15 min (bottom) irradiation at λ = 300 nm.

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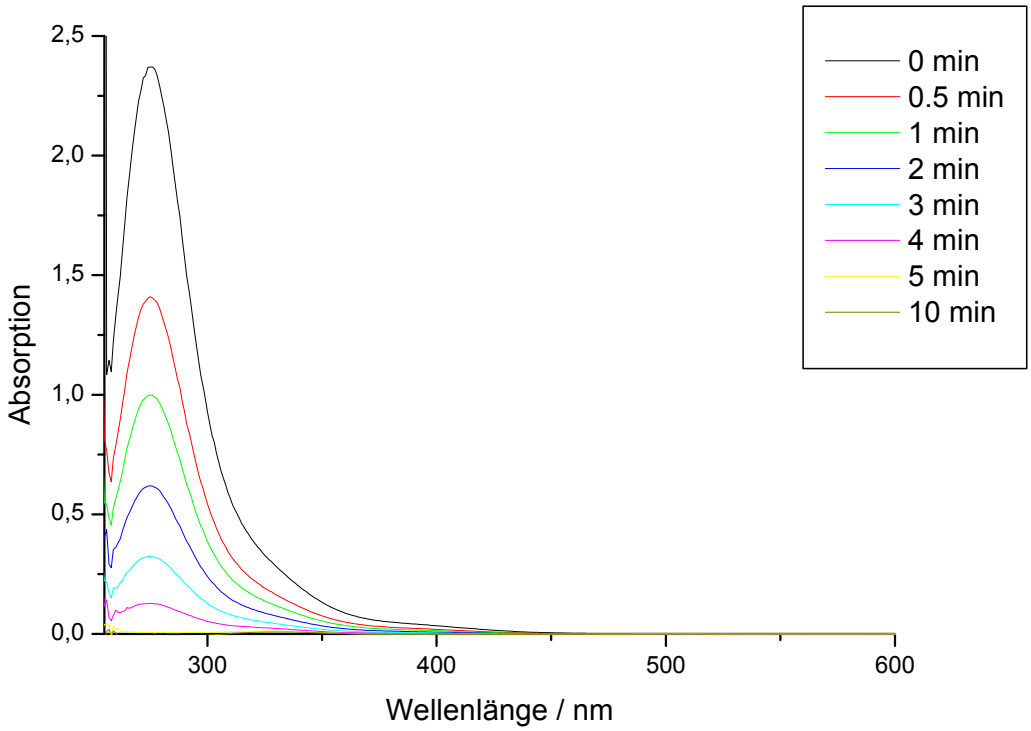

Fig. S20: Spectral changes of the absorptions spectrum of Br_2 in DMSO at r.t.

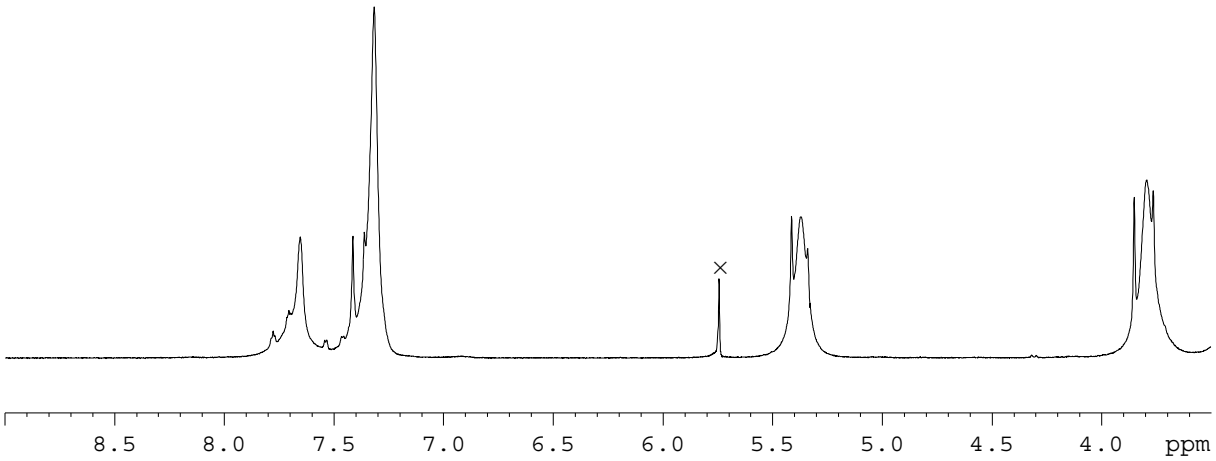

Fig. S21: ^{1}H-NMR spectrum (200 MHz, DMSO) of (BnMeIm)AuI$_2$Br (× - DCM)

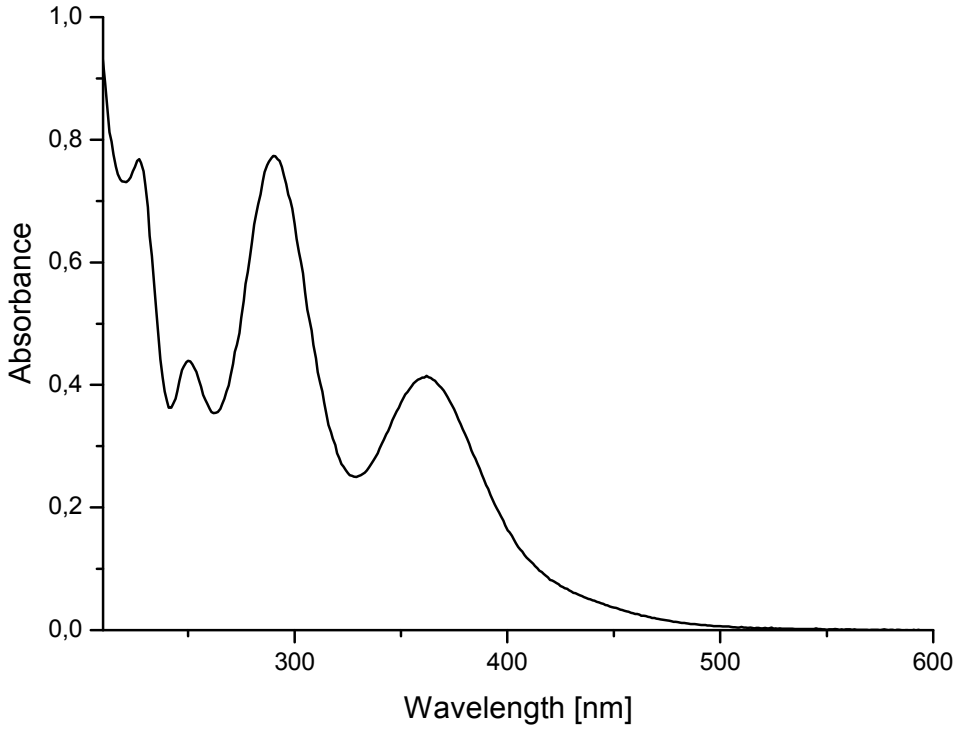

Fig. S22: UV-Vis spectrum of **5** in acetonitrile (c = 1.4 10^{-5} mol/L).