Supporting Information

Fluorescence Resonance Energy Transfer (FRET) for the verification of Dual Gold Catalysis

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1. General experimental, materials and instrumentations

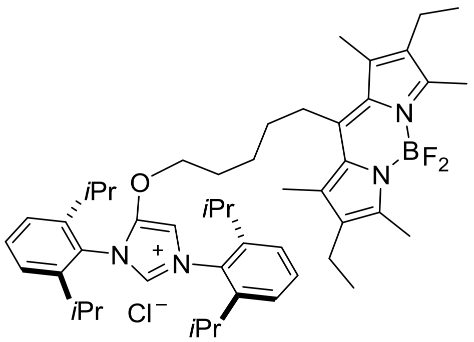
General experimental. All reactions involving transition metal complexes were conducted in oven-dried glassware. Reactions were performed in Schlenk flasks under a positive pressure of argon or nitrogen. The flasks were fitted with rubber septa and gas-tight syringes with stainless steel needles or double-cannula were used to transfer air- and moisture-sensitive liquids.

Materials. All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. CH_2Cl_2 (99.5%) and pentane (99%) were obtained from Grüssing GmbH, toluene from Sigma-Aldrich (Lab. Reagent grade, 99.3%). These solvents were dried and degassed by using a column purification system from Innovative Technology Inc. Tetrahydrofuran was dried under sodium and distilled under argon atmosphere. All solvents were stored over molecular sieves (4 Å). Preparative chromatography was performed using Merck silica 60 (0.063 – 0.2 mm).

Instrumentations. ^{1}H, ^{19}F and ^{13}C-NMR spectra were recorded on a Bruker DRX 500 or Bruker ARX 300 spectrometer. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (^{1}H, ^{13}C-NMR = 0.0 ppm) or the residual peaks of $CDCl_3$ (^{1}H-NMR = 7.26 ppm, ^{13}C-NMR = 77.23 ppm), DMSO (^{1}H-NMR = 2.50 ppm, ^{13}C-NMR = 39.51 ppm), CD_2Cl_2 (^{1}H-NMR = 5.32 ppm) or hexafluorobenzene (^{19}F-NMR = -164.90 ppm). Abbreviations for NMR data: s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = multiplet; bs = broad signal. Mass spectra were recorded on the Impact II, Quadrupol-Time-of-Flight Massenspektrometer (ESI, APCI, APPI). UV-Vis spectra were recorded on Analytik Jena Specord 600 UV-Vis spectrometer, fluorescence spectra were recorded on *J*&M TIDAS S700/CCD UV/NIR 2098 spectrometer combined with *J*&M TIDAS LSM monochromator with 75 W Xenon light source and thermo-controlled cuvette holder. Samples for emission and absorption measurements were contained in 1.00 cm quartz cuvette (Hellma Analytics).

2. Experimental procedures and compounds characterization

Synthesis of 3d·HCl



In a 5 mL round-bottom flask equipped with a stirring bar, bdp$(CH_2)_5$Br (bodipy **d**) [1,2,3] (135 mg, 0.298 mmol, 1.2eq) 1,3-bis(2,6-diisopropylphenyl)-5-hydroxy-1*H*-imidazol-3-ium chloride (110 mg, 0.249 mmol, 1eq), K_2CO_3 (34.4 mg, 0.249 mmol, 1eq) and KI (124 mg, 0.747 mmol, 3eq) were suspended in acetone (3 mL). The reaction mixture was heated under reflux for 24 h. The product was extracted with CH_2Cl_2. The organic phase were combined, washed with brine, and dried over magenesium sulfate. The solvent was removed in vacuo. The residue was dissolved in a small amount of CH_2Cl_2. Diethyl ether was added, and the resulting precipitate was filtered off and washed with diethyl ether. Product **3d**·HCl is an orange solid (141 mg, 0.173 mmol, yield 69.5%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.9 Hz, 1H, N*CH*N), 8.23 (d, *J* = 1.9 Hz, 1H, NC(OR)*CH*N), 7.55 (t, *J* = 7.8 Hz, 1H, *p*-H Ar), 7.49 (t, *J* = 7.8 Hz, 1H, *p*-H Ar), 7.31 (dd, *J* = 12.3, 7.8 Hz, 4H, *m* - H Ar), 4.66–4.63 (t, *J* = 6.4 Hz, 2H,alkyl chain CH_2O-), 2.92–2.85 (m, 2H, alkyl chain CH_2 BODIPY), 2.58–2.50 (sept, *J*= 7.5 Hz, *i*Pr-group CH), 2.46 (s, 6H, CH_3 BODIPY), 2.44–2.40 (m, 2H, *i*Pr-group), 2.38 (q, *J* = 7.6, 6.4 Hz, 4H, CH_2 BODIPY), 2.23 (s, 6H, CH_3 BODIPY), 1.83–1.78 (m, 2H, alkyl chain CH_2), 1.59–1.54 (m, 2H, alkyl chain CH_2), 1.52–1.47 (m, 2H, alkyl chain CH_2), 1.38–1.37 (d, *J* = 6.8 Hz, 6H, *i*Pr-group CH_3), 1.22–1.18 (m, 18H, *i*Pr-group CH_3), 1.05–1.02 (t, *J* = 7.5 Hz, 6H, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.19, 148.55, 145.69, 145.19, 144.34, 135.74, 132.69, 132.46, 132.35, 130.98, 130.24, 129.93, 126.09, 124.93, 124.81, 105.29, 76.18, 31.59, 29.47, 29.26, 28.94, 28.39, 26.44, 25.08, 24.41, 24.27, 23.57, 17.28, 14.96, 13.59, 12.48. ^{19}F NMR (282 MHz, $CDCl_3$) δ -148.82- -149.24 (m, 2F)

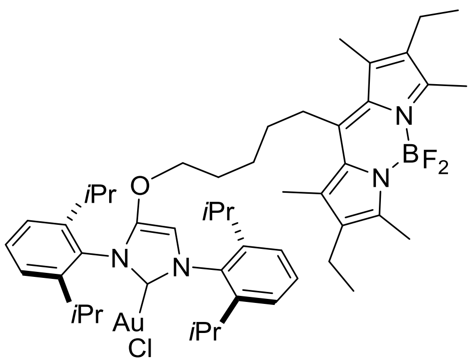
HRMS (APCI): m/z calcd. for $C_{49}H_{68}BF_2N_4O$ $[M\text{-}Cl]^+$ 777.54488, found 777.54469.

[1] Carrascoso, L.; Sastre, R.; Amat-guerri, F.; Liras, M. *Photochem. Photobiol.* **2003**, *77*, 577–584.

[2] Heisig, F.; Gollos, S.; Freudenthal, S. J.; El-Tayeb, A.; Iqbal, J.; Müller, C. E. *J. Fluoresc.* **2014**, 213–230.

[3] Kajiwara, Y.; Chujo, Y. *J. Mater. Chem.* **2009**, 2985–2992.

Synthesis of [AuCl(3d)]

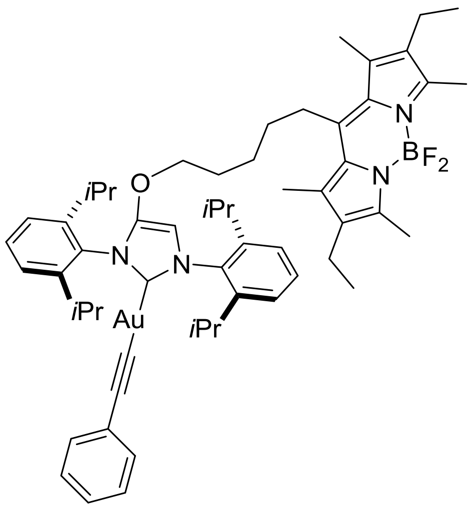


In a 5 mL round-bottom flask equipped with a stirring bar, **3d**·HCl (50 mg, 0.061 mmol, 1 eq), [AuCl(Me_2S)] (18.1 mg, 0.061 mmol, 1 eq) and K_2CO_3 (8.43 mg, 0.061 mmol, 1 eq) were suspended in acetone (1 mL). The flask was heated under reflux for 12 h. The reaction mixture was filtered, evaporated and purified by column chromatography (Cy:EA= 2:1). The volatiles were evaporated in vacuo to provide complex [AuCl(**3d**)] as an orange solid (46.5 mg, 0.046 mmol, yield 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.44 (td, *J* = 7.8, 2.7 Hz, 2H, *p*-H Ar), 7.27 (d, *J* = 2.2 Hz, 2H, *m* - H Ar), 7.25 (d, *J* = 2.1 Hz, 2H, *m* - H Ar), 6.40 (s, 1H, NC(OR)*CH*N), 4.02–3.99 (t, *J* = 6.3 Hz, 2H, alkyl chain CH_2 O-), 2.94–2.86 (m, 2H, alkyl chain CH_2 BODIPY), 2.68–2.63 (m, 2H, *i*Pr-group CH), 2.62–2.57 (m, 2H, *i*Pr-group CH), 2.49 (s, 6H, CH_3 BODIPY), 2.39 (q, *J* = 7.6 Hz, 4H, CH_2 BODIPY), 2.22 (s, 6H, CH_3 BODIPY), 1.76–1.73 (m, 2H, alkyl chain CH_2), 1.58–1.52 (m, 2H, alkyl chain CH_2), 1.51–1.46 (m, 2H, alkyl chain CH_2), 1.36–1.33 (m, 12H, *i*Pr-group CH_3), 1.24 (d, *J* = 6.9 Hz, 6H, *i*Pr-group CH_3), 1.19 (d, *J* = 6.8 Hz, 6H, *i*Pr-group CH_3), 1.04 (t, *J* = 7.5 Hz, 6H, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.25, 152.46, 148.40, 146.22, 145.85, 143.99, 135.42, 134.67, 132.81, 130.97, 130.77, 130.68, 130.30, 124.27, 124.07, 99.23, 77.41, 77.36, 76.91, 72.38, 31.47, 29.16, 28.93, 28.88, 28.28, 26.40, 24.81, 24.29, 24.26, 23.80, 17.30, 14.95, 13.46, 12.53. ^{19}F NMR (282 MHz, $CDCl_3$) δ -148.96- -149.41(m, 2F).

HRMS (APCI): m/z calcd. for $C_{49}H_{67}BF_2AuN_4O$ [M-Cl]$^+$ 973.5036, found 973.5056.

Synthesis of [Au(CCPh)(3d)]

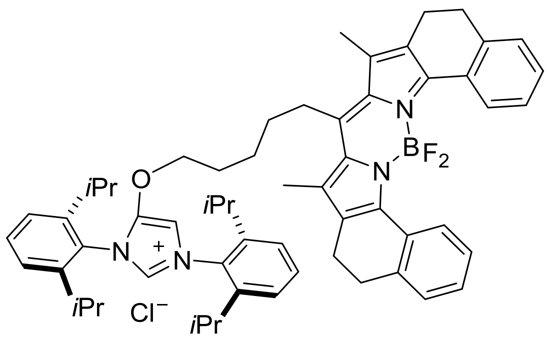


An ovendried Schlenk flask was loaded with a stirring bar, [AuCl(**3d**)] (25 mg, 0.0248 mmol, 1eq) dissolved in CH_2Cl_2 (1 ml) and Et_3N (1 ml), followed by the addition of phenylacetylene (93 mg, 0.911 mmol, 37 eq). The flask was sealed and stirred at 40°C for 24 h. The reaction mixture was cooled to room temperature and diethyl ether added. The organic phase was washed with water, brine and dried over $MgSO_4$. After filtration and removal of the volatiles, the residue was dissolved in a small amount of CH_2Cl_2. Pentane was added, and the resulting precipitate was filtered off and washed with pentane. The product is an orange solid (24 mg, 0.0223 mmol, yield 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H, *p*-H Ar), 7.31 – 7.23 (m, 6H, *m*-H Ar, *o*-CH H C_8H_5), 7.08 (t, *J* = 7.4 Hz, 2H, *m*-H C_8H_5), 7.03 (t, *J* = 7.3 Hz, 1H, *p*-H C_8H_5), 6.36 (s, 1H, NC(OR)*CH*N)), 3.97 (t, *J* = 6.2 Hz, 2H, alkyl chain CH_2 O), 2.94 – 2.83 (m, 2H, alkyl chain CH_2 BODIPY), 2.75 – 2.67 (m, 2H, *i*Pr-group CH), 2.67 – 2.60 (m, 2H, *i*Pr-group CH), 2.49 (s, 6H, CH_3 BODIPY), 2.39 (q, *J* = 7.5 Hz, 4H, CH_2 BODIPY), 2.23 (s, 6H, CH_3 BODIPY), 1.77 – 1.69 (m, 2H, alkyl chain CH_2), 1.59 – 1.52 (m, 2H, alkyl chain CH_2), 1.49 – 1.43 (m, 2H, alkyl chain CH_2), 1.38 (dd, *J* = 11.5, 6.9 Hz, 12H, *i*Pr-group CH_3), 1.24 (d, *J* = 6.9 Hz, 6H, *i*Pr-group CH_3), 1.19 (d, *J* = 6.9 Hz, 6H, *i*Pr-group CH_3), 1.05 (t, *J* = 7.5 Hz, 6H, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.01, 152.34, 148.56, 146.12, 145.75, 143.86, 135.28, 135.02, 132.68, 132.25, 130.84, 130.55, 130.43, 130.33, 129.38, 127.46, 126.09, 125.63, 124.12, 123.89, 103.56, 99.45, 72.07, 31.33, 29.04, 28.80, 28.77, 28.17, 26.31, 24.86, 24.33, 24.15, 23.60, 17.17, 14.81, 13.32, 12.41. ^{19}F NMR (471 MHz, $CDCl_3$) δ -148.97- -149.30(m, 2F).

HRMS (APCI): m/z calcd. for $C_{57}H_{73}BF_2AuN_4O$ $[M+H]^+$ 1075.55204, found 1075.55057.

Synthesis of 3a·HCl

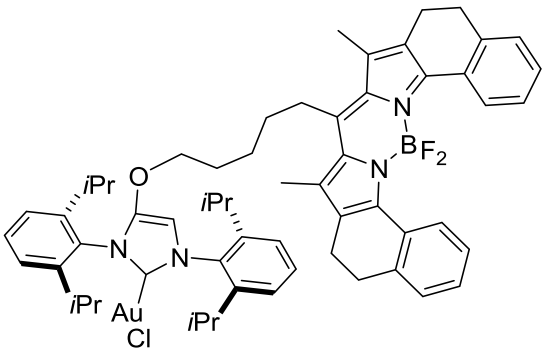


A 5 mL round-bottom flask was loaded with a stirring bar, bdp$(CH_2)_5$Br (bodipy **a**) (155 mg, 0.271 mmol, 1.1eq), 1,3-bis(2,6-diisopropyl-phenyl)-5-hydroxy-1*H*-imidazol-3-ium chloride (109 mg, 0.247 mmol, 1eq), K_2CO_3 (34.05 mg, 0.247 mmol, 1eq) and KI (123 mg, 0.739 mmol, 3eq) and acetone (3 mL). The reaction mixture was heated under reflux for 24 h. The product was extracted with CH_2Cl_2. The organic phase were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed in vacuo. The residue was dissolved in a small amount of CH_2Cl_2. Diethyl ether was added, and the resulting precipitate filtered off and washed with diethyl ether. The crude product was purified by column chromatography ($CHCl_3$: MeOH= 10:1). The product **3a**·HCl (101 mg, 0.108 mmol, yield 44%) is a blue violet solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, 2H, Ar BODIPY), 8.33 – 8.30 (m, 1H, N*CH₂*N), 8.13 – 8.10 (m, 1H, NC(OR)*CH*N), 7.44 (dt, *J* = 26.3, 7.8 Hz, 2H, *p*-H Ar), 7.30 (ddd, *J* = 8.3, 7.0, 1.9 Hz, 2H, Ar BODIPY), 7.23 (m, 4H, *p*-H Ar), 7.19 – 7.14 (m, 4H, Ar BODIPY), 4.56 (t, *J* = 6.3 Hz, 2H, alkyl chain CH_2O), 3.02 – 2.93 (m, 2H, alkyl chain CH_2 BODIPY), 2.82 (t, *J* = 7.0 Hz, 4H, CH_2 BODIPY), 2.64 – 2.50 (m, 4H, CH_2 BODIPY), 2.50 – 2.43 (m, 2H, *i*Pr-group CH), 2.40 – 2.30 (m, 2H, *i*Pr-group CH), 2.26 (s, 6H, CH_3 BODIPY), 1.81 – 1.71 (m, 2H, alkyl chain CH_2), 1.56 – 1.49 (m, 4H, alkyl chain CH_2), 1.30 (d, *J* = 6.8 Hz, 6H, *i*Pr-group), 1.17 – 1.07 (m, 18H, *i*Pr-group). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.52, 148.58, 145.66, 145.18, 144.17, 140.51, 134.19, 133.58, 132.51, 132.35, 132.05, 130.24, 129.85, 129.21, 128.61, 128.56, 128.09, 127.31, 126.05, 124.92, 124.81, 105.17, 76.13, 32.04, 30.73, 29.46, 29.25, 28.98, 28.84, 26.35, 25.10, 24.40, 24.22, 23.58, 20.77, 14.19. ^{19}F NMR (471 MHz, $CDCl_3$) δ -134.43- -134.83 (m, 1F), -135.84- -136.23 (m,1F).

HRMS (ESI): m/z calcd. for $C_{59}H_{67}AuBF_2N_4O^+$ $[M-Cl]^+$ 897.5468, found 897.54488.

Synthesis of [AuCl(3a]

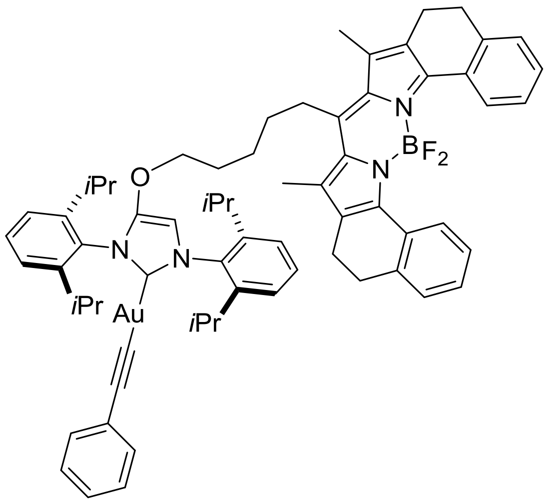


A 5 mL round-bottom flask was loaded with a stirring bar, **3a**·HCl (42 mg, 0.045 mmol, 1 eq), [AuCl(Me_2S)] (13.3 mg, 0.045 mmol, 1eq), K_2CO_3 (6.2 mg, 0.045 mmol, 1 eq) and acetone (1 mL). The reaction mixture was heated under reflux for 12 h. The solution was filtered, evaporated and the residue purified by column chromatography (Cy: EA = 4:1). [AuCl(**3a)**] was obtained as a blue solid (31 mg, 0.0274 mmol, yield 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.1 Hz, 2H, Ar BODIPY), 7.53 – 7.43 (m, 2H, Ar BODIPY), 7.37 (t, J = 8.2 Hz, 2H, *p*-H Ar), 7.28 – 7.22 (m, 8H, *o*-H Ar, Ar BODIPY), 6.40 (s, 1H, NC(OR)*CH*N), 4.00 (t, J = 6.2 Hz, 2H, alkyl chain CH_2 O-), 3.09 – 2.99 (m, 2H, alkyl chain CH_2 BODIPY), 2.88 (t, J = 7.0 Hz, 4H, CH_2 BODIPY), 2.71 – 2.55 (m, 8H, CH_2 BODIPY, *i*Pr-group CH), 2.31 (s, 6H, CH_3 BODIPY), 1.81 – 1.70 (m, 2H, alkyl chain CH_2), 1.70 – 1.60 (m, 2H, alkyl chain CH_2), 1.55 – 1.48 (m, 2H, alkyl chain CH_2), 1.34 (m, 12H, *i*Pr-group CH_3), 1.21 (m, 12H, *i*Pr-group CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.33, 149.76, 148.43, 146.26, 145.87, 143.73, 140.49, 134.69, 134.17, 133.18, 132.16, 130.82, 130.72, 130.33, 129.36, 128.68, 128.48, 128.11, 127.39, 124.30, 124.11, 99.26, 72.35, 31.94, 30.71, 29.84, 29.20, 29.01, 28.91, 28.71, 27.07, 26.30, 24.83, 24.32, 24.28, 23.85, 20.81, 14.06, 1.16. ^{19}F NMR (471 MHz, $CDCl_3$) δ -137.21--137.62 (m, 1F), -139.81- -140.14 (m, 2F).

HRMS (APCI): m/z calcd. for $C_{59}H_{67}AuBF_2N_4O^+$ [M-Cl]$^+$ 1093.50362, found 1093.50429.

Synthesis of [Au(CCPh)(3a)]

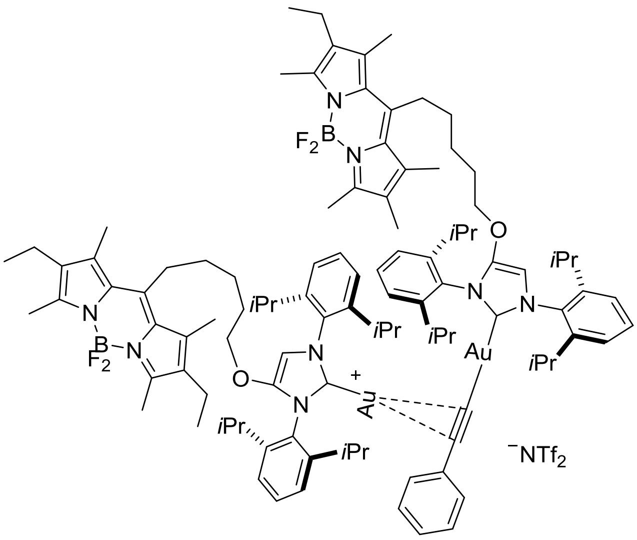


An ovendried Schlenk flask was loaded with a stirring bar, [AuCl(**3a**)] (25 mg, 0.0221 mmol, 1eq) dissolved in CH_2Cl_2 (1 mL) and Et_3N (1 mL). Phenylacetylene (84 mg, 0.818 mmol, 37 eq) was added. The flask was sealed and stirred at 40°C for 24 h. The solution was cooled to room temperature and diethyl ether added. The organic solution was washed with water, brine and dried over $MgSO_4$. After filtration and removal of solvent, the residue was dissolved in a small amount of CH_2Cl_2. Pentane was added, the resulting precipitate was filtered off and the solid washed with pentane. The product [Au(CCPh)(**3a**)] is a blue solid (22 mg, 0.0184 mmol, yield 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 8.0 Hz, 2H, Ar BODIPY), 7.50 – 7.43 (m, 2H, Ar BODIPY), 7.39 (t, J = 7.6 Hz, 2H, 2H, *p*-H Ar), 7.31 – 7.23 (m, 10H, 2H, *m*-H Ar, Ar BODIPY, *o*-CH C_8H_5), 7.08 (t, J = 7.4 Hz, 2H, *m*-CH C_8H_5), 7.03 (t, J = 7.3 Hz, 1H, *p*-CH C_8H_5), 6.37 (s, 1H, NC(OR)*CH*N), 3.98 (t, J = 6.2 Hz, 2H, alkyl chain CH_2 O-), 3.09 – 3.00 (m, 2H, alkyl chain CH_2 BODIPY), 2.89 (t, J = 7.1 Hz, 4H, CH_2 BODIPY), 2.76 – 2.56 (m, 8H, CH_2 BODIPY, *i*Pr-group CH), 2.32 (s, 6H, CH_3 BODIPY), 1.78 – 1.70 (m, 2H, alkyl chain CH_2), 1.69 – 1.60 (m, 2H, alkyl chain CH_2), 1.54 – 1.46 (m, 2H, alkyl chain CH_2), 1.39 (dd, J = 11.0, 6.9 Hz, 12H, *i*Pr-group CH_3), 1.25 – 1.19 (m, 12H, *i*Pr-group CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.16, 149.75, 148.71, 146.29, 145.89, 143.76, 140.50, 135.17, 134.18, 133.19, 132.40, 132.16, 130.71, 130.59, 130.48, 129.35, 128.78, 128.69, 128.49, 128.11, 127.61, 127.39, 126.23, 125.78, 124.27, 124.05, 103.71, 99.62, 72.20, 31.94, 30.72, 29.20, 29.01, 28.92, 28.74, 26.35, 25.02, 24.49, 24.31, 23.78, 20.81, 14.06. ^{19}F NMR (282 MHz, $CDCl_3$) δ -137.33- -137.78 (m, 1F), -139.51- -139.86 (m, 1F).

HRMS (APCI): m/z calcd. for $C_{67}H_{73}AuBF_2N_4O$ $[M-H]^+$ 1195.55158, found 1195.55057.

Synthesis of [(Au(3d))(Au(CCPh)(3d))]NTf$_2$

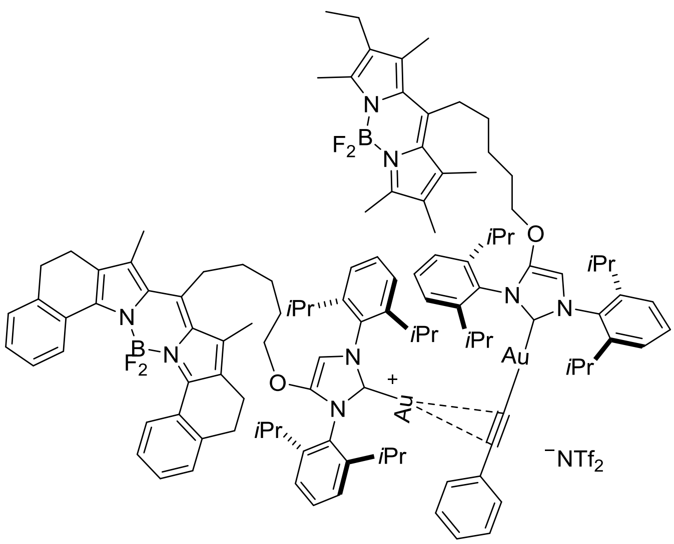


A solution of [Au(CCPh)(**3d**)] (0.01 M, 1000 µl, 0.0100 mmol, 1eq) in CH_2Cl_2 was added to a stirred solution of [(Au(NTf$_2$)(**3d**)] (1000 µl, 0.01 M, 0.0100 mmol, 1eq) in a Schlenk flask in CH_2Cl_2. The solution was stirred at -10°C for 20 min. The volatiles were evaporated under reduced pressure. The remaining orange solid [(Au(**3d**))(Au(CCPh)(**3d**))]NTf$_2$ (21.4 mg, 0.0092 mmol, 92 %) was used without additional purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H, *p*-H Ar), 7.41 (t, *J* = 7.8 Hz, 2H, *p*-H Ar), 7.28 – 7.24 (m, 1H, *p*-H C_8H_5), 7.24 – 7.16 (m, 4H, *m*-H Ar), 7.04 (t, *J* = 7.8 Hz, 2H, *m*-H C_8H_5), 6.67 – 6.62 (m, 2H, *o*-H C_8H_5), 6.52 (s, 2H, NC(OR)*CH*N), 4.04 (t, *J* = 6.2 Hz, 4H, alkyl chain CH_2 O-), 2.93 – 2.84 (m, 4H, alkyl chain CH_2 BODIPY), 2.57 – 2.43 (m, 20H, *i*Pr-group CH, CH_3 BODIPY), 2.39 (q, *J* = 7.6 Hz, 8H, CH_2 BODIPY), 2.22 (s, 6H, CH_3 BODIPY), 1.72 (p, *J* = 6.3 Hz, 4H, alkyl chain CH_2), 1.53 – 1.41 (m, 8H, alkyl chain CH_2), 1.20 (d, *J* = 6.9 Hz, 12H, *i*Pr-group CH_3), 1.13 (d, *J* = 6.9 Hz, 12H, *i*Pr-group CH_3), 1.09 – 1.02 (m, 36H, *i*Pr-group CH_3, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.33, 152.33, 148.83, 146.18, 145.74, 144.29, 135.65, 134.52, 132.77, 131.82, 131.05, 130.85, 130.80, 130.17, 129.31, 128.35, 125.00, 124.33, 124.10, 121.17, 118.88, 112.15, 100.52, 72.99, 31.50, 29.07, 28.96, 28.82, 28.37, 26.47, 24.87, 24.23, 24.14, 23.65, 17.32, 14.97, 13.45, 12.55.

HRMS (ESI): m/z calcd. for $C_{106}H_{139}Au_2B_2F_4N_8O_2$ [M] 2048.05118, found 2048.05339.

Synthesis of [(Au(3a))(Au(CCPh)(3d))]NTf_2

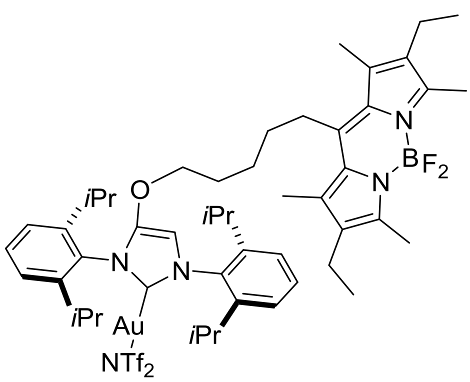


A solution of [Au(CCPh)(**3a**)] (0.01 M, 1000 µl, 0.01 mmol, 1eq) in CH_2Cl_2 was added to a solution of [(Au(NTf_2)(**3d**)] (1000 µl, 0.01 M, 0.01 mmol, 1eq) in CH_2Cl_2 at -10 °C. Stirring was continued for 20 min, followed by evaporation of the volatiles under reduced pressure. The remaining dark violet amorphous solid [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2 (22.5mg, 0.0092 mmol, 92 %) was isolated as a mixture of three isomers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, J = 8.2 Hz, 8H, Ar BODIPY), 7.52 – 7.43 (m, 8H, *p*-H Ar), 7.41 – 7.36 (m, 14H, Ar BODIPY, *p*-H C_8H_5), 7.30 –7.14 (m, 48H, Ar BODIPY, *m*-H Ar), 7.08 – 7.00 (m, 8H, *o*-H C_8H_5), 6.67 – 6.60 (m, 8H, *m*-H C_8H_5), 6.54 – 6.49 (m, 8H, NC(OR)*CH*N), 4.08 – 4.00 (m, 16H, alkyl chain CH_2 O-), 3.09 – 3.01 (m, 8H, alkyl chain CH_2 BODIPY), 2.94 – 2.85 (m, 24H, chain CH_2 BODIPY), 2.68 – 2.58 (m, 16H, CH_2 BODIPY), 2.56 – 2.44 (m, 58H, *i*Pr-group CH, CH_3 BODIPY), 2.39 (q, J = 7.5 Hz, 16H, CH_2 BODIPY), 2.32 (s, 24H, CH_3 BODIPY), 2.22 (s, 24H, CH_3 BODIPY), 1.77 – 1.68 (m, 16H, alkyl chain CH_2), 1.61 – 1.44 (m, 32H, alkyl chain CH_2), 1.22 – 1.17 (m, 48H, *i*Pr-group CH_3), 1.15 – 1.10 (m, 48H, *i*Pr-group CH_3), 1.07 – 1.01 (m, 120H, *i*Pr-group CH_3, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.32, 152.34, 149.62, 148.83, 146.17, 145.75, 144.12, 140.54, 139.27, 135.64, 134.52, 134.24, 133.49, 132.78, 132.12, 131.81, 131.04, 130.87, 130.80, 130.16, 129.28, 128.59, 128.34, 128.12, 127.36, 125.01, 124.33, 124.10, 121.45, 121.16, 112.14, 100.51, 72.97, 31.94, 31.49, 30.75, 29.86, 29.06, 28.96, 28.82, 28.36, 26.45, 24.86, 24.23, 24.13, 23.65, 20.80, 17.32, 14.97, 14.04, 13.45, 12.55. ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.82 (s, 6F, NTf_2), -137.45- -137.80 (m, 1F, BODIPY 1b), -139.34 - -139.71 (m, 1F, BODIPY 1b), -148.92- -149.20 (m, 2F, BODIPY 2a).

APCI HR-MS: m/z calcd for $C_{116}H_{139}Au_2B_2F_4N_8O_2$ $C_{116}H_{139}Au_2B_2F_4N_8O_2$ $[M+H]^+$ 2168.04691, found 2168.05008.

Synthesis of [(Au(NTf_2)(3d)]

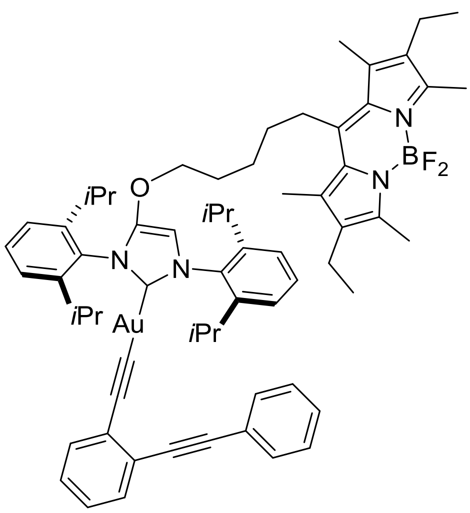


To a solution of [AuCl(**3d**)] (26.8 mg, 0.0266mmol, 1eq) in CH_2Cl_2 (1 mL) was added [Ag(NTf_2)] (10.33 mg, 0.0266 mmol, 1eq)). The resulting suspension was stirred at room temperature for 20 minutes and then filtered through celite. Evaporation of the CH_2Cl_2 under reduced pressure gave [(Au(NTf_2)(**3d**)] (31 mg, 0.0247mmol, 93%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, *p* - H Ar), 7.29 (d, *J* = 4.0 Hz, 2H, *m* - H Ar), 7.27 (d, *J* = 3.9 Hz, 2H, *m* - H Ar), 6.51 (s, 1H, NC(OR)*CH*N), 4.05 (t, *J* = 6.3 Hz, 2H, alkyl chain CH_2 O-), 2.96 – 2.84 (m, 2H, alkyl chain CH_2 BODIPY), 2.61 – 2.55 (m, 2H, , *i*Pr-group CH), 2.50 – 2.47 (m, 8H, *i*Pr-group CH, CH_3 BODIPY), 2.39 (q, *J* = 7.6 Hz, 4H, CH_2 BODIPY), 2.22 (s, 6H, CH_3 BODIPY), 1.83 – 1.71 (m, 2H, alkyl chain CH_2), 1.62 – 1.46 (m, 4H, alkyl chain CH_2), 1.30 (dd, *J* = 9.1, 6.8 Hz, 12H, *i*Pr-group CH_3), 1.24 (d, *J* = 6.9 Hz, 6H, *i*Pr-group CH_3), 1.19 (d, *J* = 6.9 Hz, 6H, iPr-group CH_3), 1.04 (t, *J* = 7.6 Hz, 6H, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.11, 152.48, 148.88, 146.13, 145.81, 143.95, 135.43, 134.37, 132.83, 130.94, 130.88, 130.05, 124.30, 124.14, 122.85, 119.0 (q, J = 323.8 Hz, CF_3) 115.15, 99.88, 72.57, 31.47, 29.27, 28.97, 28.92, 28.27, 26.40, 24.53, 24.25, 24.00, 23.66, 17.31, 14.96, 13.44, 12.55. ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.11 (s, 6F, NTf_2), -149.00, -149.11 (m, 2F, BODIPY 2d).

APCI HR-MS: m/z calcd for $C_{51}H_{67}AuBF_8N_5O_5S_2$ $[M+H]^+$ 1254.42840, found 1254.42874.

Synthesis of [Au(CCPh'')(3d)]

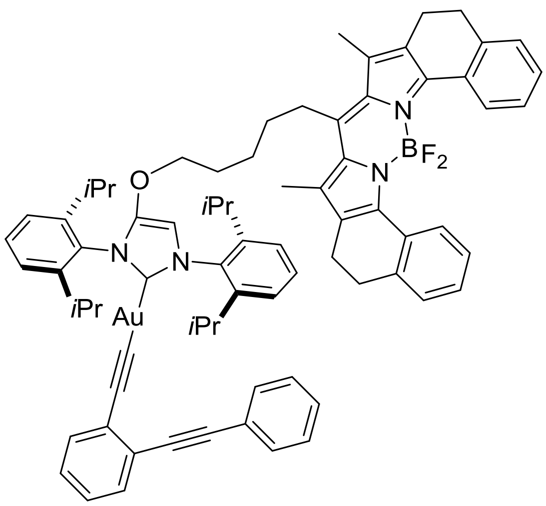


To an ovendried Schlenk flask equipped with a stirring bar a solution of [AuCl(**3d**)] (97.2 mg, 0.0963mmol, 1eq) CH_2Cl_2 (1ml) and triethylamine (1ml) as well as 1-ethynyl-2-(phenylethynyl)benzene (50.6 mg, 0.250 mmol, 2.6 eq) were added. The flask was sealed and stirred at 40°C for 24 h. The solution was cooled to room temperature and diethylether added. The organic phase was washed with water, brine and dried over $MgSO_4$. After filtration and removal of solvent, the residue was dissolved in small amount of CH_2Cl_2. Pentane was added, and the resulting precipitate was filtered off and washed with pentane. The product [Au(CCPh´´)(**3d**)] is an orange solid (90.5 mg, 0.077 mmol, yield 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.35 (d, J = 8.7 Hz, 2H), 7.32 – 7.23 (m, 8H), 7.08 – 6.99 (m, 2H), 6.38 (s, 1H, NC(OR)*CH*N), 3.99 (t, J = 6.2 Hz, 2H), 2.95 – 2.87 (m, 2H), 2.77 – 2.60 (m, 4H), 2.51 (s, 6H), 2.41 (q, J = 7.5 Hz, 4H), 2.24 (s, 6H), 1.80 – 1.69 (m, 4H), 1.64 – 1.52 (m, 4H), 1.52 – 1.44 (m, 4H), 1.44 – 1.32 (m, 12H), 1.28 – 1.16 (m, 12H), 1.06 (t, J = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.25, 152.48, 148.71, 146.21, 145.85, 144.02, 135.54, 135.43, 135.13, 132.89, 132.00, 131.48, 130.98, 130.67, 130.52, 130.42, 128.92, 127.96, 127.57, 127.45, 125.59, 125.40, 124.23, 124.01, 101.72, 99.54, 92.19, 89.94, 72.23, 65.97, 31.47, 29.18, 28.90, 28.31, 26.45, 24.95, 24.29, 23.75, 17.32, 14.95, 13.46, 12.55.

APCI HR-MS: m/z calcd for $C_{65}H_{77}AuBF_2N_4O$ $[M+H]^+$ 1175.581468, found 1175.581870.

Synthesis of [Au(CCPh'')(3a)]

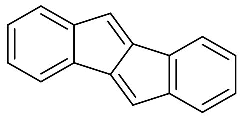


To an ovendried Schlenk flask equipped with a stirring bar a solution of [AuCl(**3a**)] (25.5 mg, 0.0226mmol, 1eq) in CH_2Cl_2 (1 mL) and Et_3N (1 mL) and 1-ethynyl-2-(phenyl-ethynyl)benzene (11.9 mg, 0.0588 mmol, 2.6 eq) were added. The flask was sealed and stirred at 40°C for 60 h. The solution was cooled down to room temperature, diethyl ether was added. The organic phase was washed with water, brine and dried over $MgSO_4$. After filtration and removal of solvent, the residue was dissolved in a small amount of CH_2Cl_2. Pentane was added, and the resulting precipitate was filtered off and washed with pentane. The product [Au(CCPh´´)(**3a**)] is a blue solid (24.4 mg, 0.0188 mmol, yield 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 – 8.65 (m, 2H), 7.44 – 7.31 (m, 8H), 7.31 – 7.12 (m, 11H), 7.04 – 7.00 (m, 2H), 6.40 – 6.37 (m, 1H), 4.00 – 3.98 (m, 2H), 3.06 – 3.03(m, 2H), 2.90 – 2.88 (m, 4H), 2.70 – 2.62 (m, 8H), 2.32 (s, 6H), 1.76 – 1.73 (m, 2H), 1.66 – 1.63 (m, 2H), 1.53 – 1.48 (m, 2H), 1.36 – 1.34 (m, 12H), 1.23 – 1.20 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.23, 149.73, 148.71, 146.24, 145.86, 143.78, 140.49, 135.56, 135.13, 134.17, 133.20, 132.89, 132.16, 132.00, 131.48, 130.70, 130.53, 130.43, 129.35, 128.92, 128.76, 128.67, 128.58, 128.49, 128.11, 127.97, 127.59, 127.46, 127.38, 125.59, 125.41, 124.41, 124.29, 124.23, 124.10, 124.02, 101.73, 99.57, 92.20, 89.95, 72.34, 31.93, 30.71, 29.19, 29.00, 28.91, 28.73, 26.34, 26.29, 24.96, 24.84, 24.42, 24.30, 23.84, 23.78, 20.80, 14.05, 10.88, 1.16.

APCI HR-MS: m/z calcd for $C_{75}H_{76}AuBF_2N_4O$ $[M+H]^+$ 1295.581979, found 1295.581870.

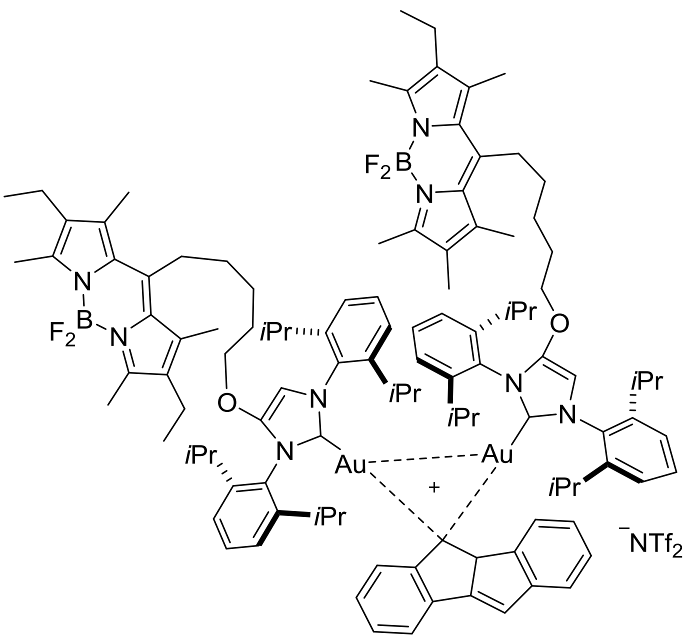
Synthesis of Dibenzopentalene



In a round bottom flask 1-ethynyl-2-(phenylethynyl)benzene (1eq), [(Au(NTf_2)(**3d**)] (5 mol%) and [Au(CCPh'')(**3d**)] (5 mol%) were dissolved in 1,2-dichloroethane and heated to 80°C for 24 h. The solvent was removed under reduced pressure. Without further purification the orange-brownish crude product was dissolved in $CDCl_3$, insoluble impurities were filtered off. NMR measurements show the desired product signals. The spectroscopic data are in accord with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 – 7.00 (m, 2H), 6.90 – 6.82 (m, 6H), 6.40 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.33, 149.15, 134.96, 128.46, 127.99, 127.35, 126.38, 123.30, 122.24.

Synthesis of [(Au(3d))(Au(CCPh'')(3d))]NTf_2



A solution of [Au(CCPh'')(**3a**)] (0.01 M, 1276 µl, 0.01276 mmol, 1eq) in $C_2H_4Cl_2$ was added to a solution of [(Au(NTf_2)(**3d**)] (1276 µl, 0.01 M, 0.01276 mmol, 1eq) in $C_2H_4Cl_2$ at -10 ^{o}C. Stirring was continued for 20 min, followed by evaporation of the volatiles under reduced pressure. A dark orange amorphous solid [(Au(**3d**))(Au(CCPh'')(**3d**))]NTf_2 (21.7mg, 0.0101 mmol, 79 %) was isolated.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H, 2x *p* - H Ar), 7.09 – 7.01 (m, 8H, 2x *m* - H Ar), 6.76 – 6.68 (m, 3H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.44 (s, 2H, , NC(OR)*CH*N), 6.38 (t, *J* = 7.8 Hz, 1H), 6.26 (t, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 5.49 (d, *J* = 7.0 Hz, 1H), 5.25 (d, *J* = 7.2 Hz, 1H), 3.98 (t, *J* = 6.2 Hz, 4H, alkyl chain CH_2 O-), 2.90 – 2.82 (m, 4H, 2x alkyl chain CH_2 BODIPY), 2.48 (s, 12H, 2x CH_2 BODIPY), 2.40 – 2.34 (m, 16H, 2x (*i*Pr-group CH, CH_2 BODIPY)), 2.18 (s, 12H, 2x CH_2 BODIPY), 1.72 – 1.64 (m, 4H, 2x alkyl chain CH_2), 1.53 –

[4] B. Eliasson and U. Edlund**,** *Org. Magn. Res.*, **1983**, *21*, 322-327.

1.39 (m, 8H, 2x alkyl chain 2xCH_2), 1.10 (d, *J* = 6.8 Hz, 12H, 2x *i*Pr-group CH_3), 1.05 – 1.00 (m, 24H, 2x *i*Pr-group CH_3), 0.92 – 0.85 (m, 24H, 2x (*i*Pr-group CH_3, CH_3 BODIPY). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.17, 152.32, 148.76, 145.98, 145.75, 145.60, 145.33, 144.23, 135.60, 134.53, 132.75, 131.00, 130.56, 130.24, 128.48, 124.23, 124.15, 124.07, 123.98, 123.12, 121.65, 121.15, 100.48, 77.16, 72.79, 31.48, 29.05, 29.03, 28.87, 28.79, 28.27, 26.34, 24.41, 24.36, 24.21, 23.75, 23.66, 17.30, 14.94, 13.46, 13.42, 12.53. ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.83, -148.95- -149.28 (m, 4F, 2x BODIPY d).

APPI HR-MS: m/z calcd for $C_{114}H_{144}Au_2B_2F_4N_8O_2$ $[M+H]^+$ 2148.078213, found 2148.081300.

3. NMR spectra

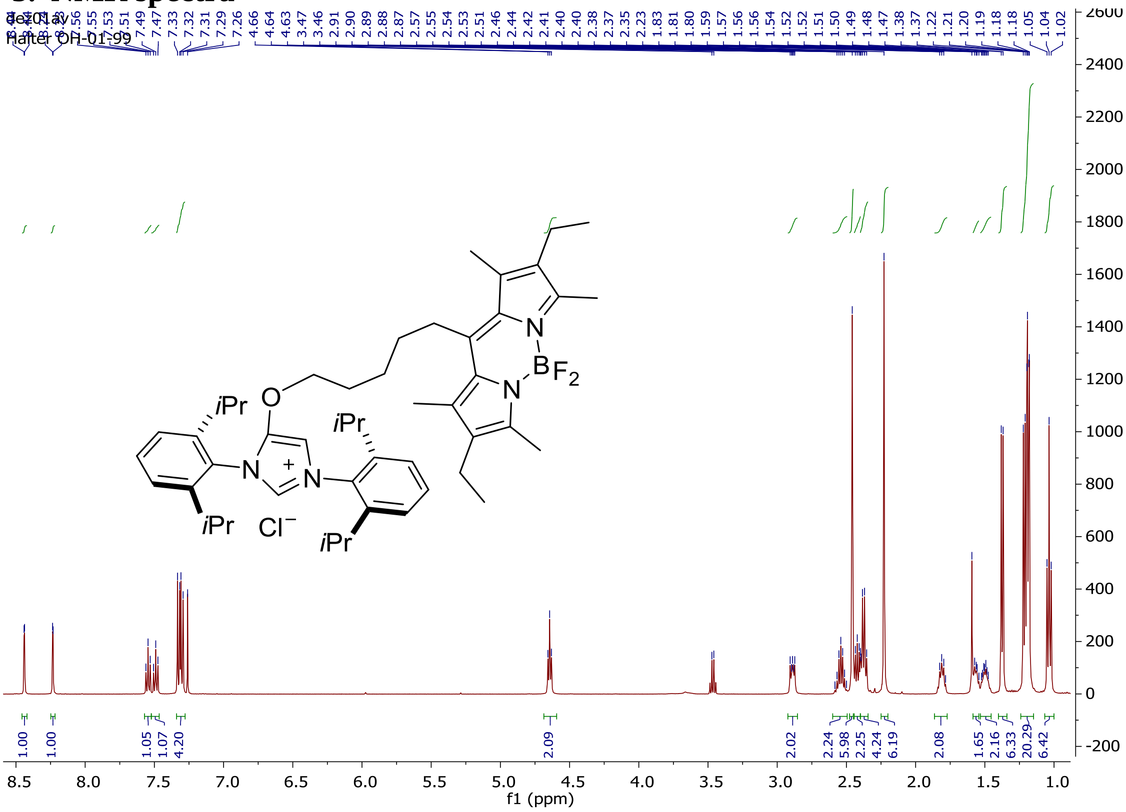


Figure S1 ^{1}H NMR of **3d**·HCl in $CDCl_3$.

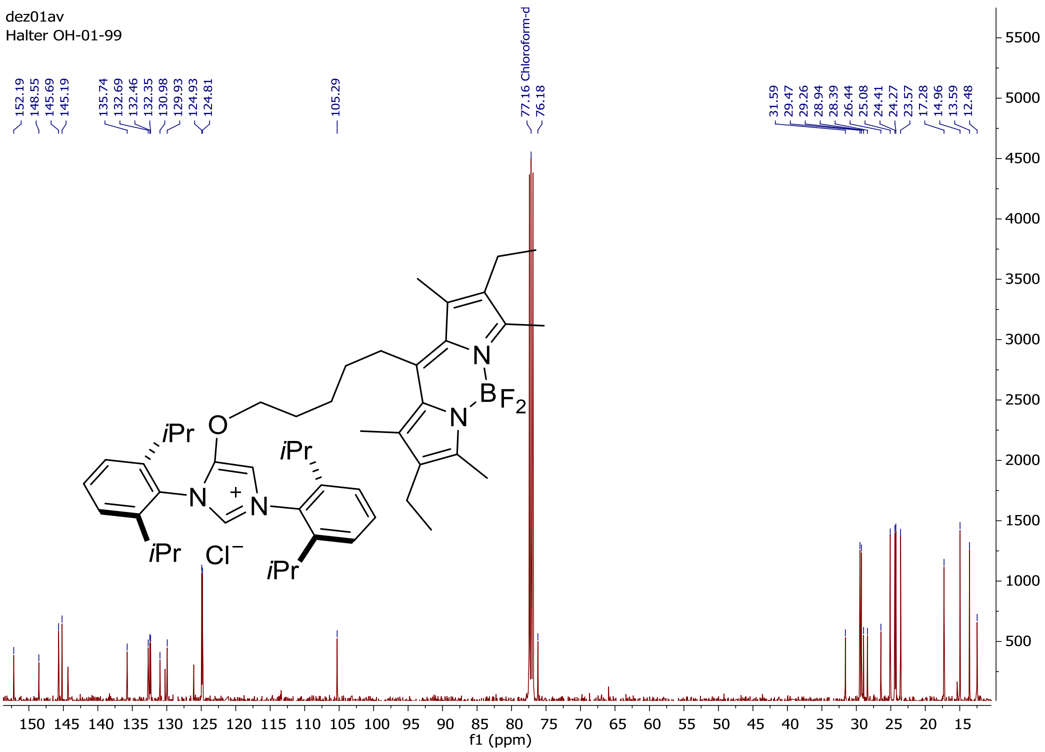


Figure S2 ^{13}C NMR of **3d**·HCl in $CDCl_3$.

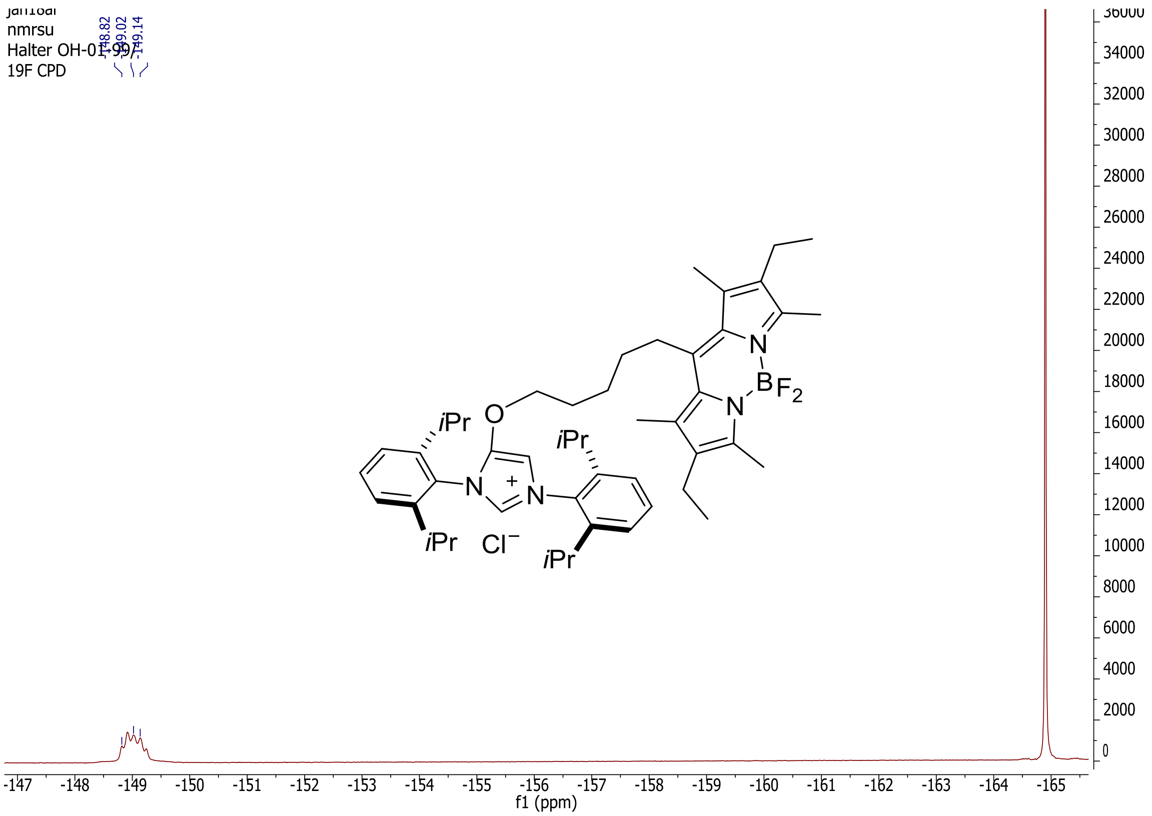


Figure S3 [19]F-NMR spectrum of **3d**·HCl in $CDCl_3$.

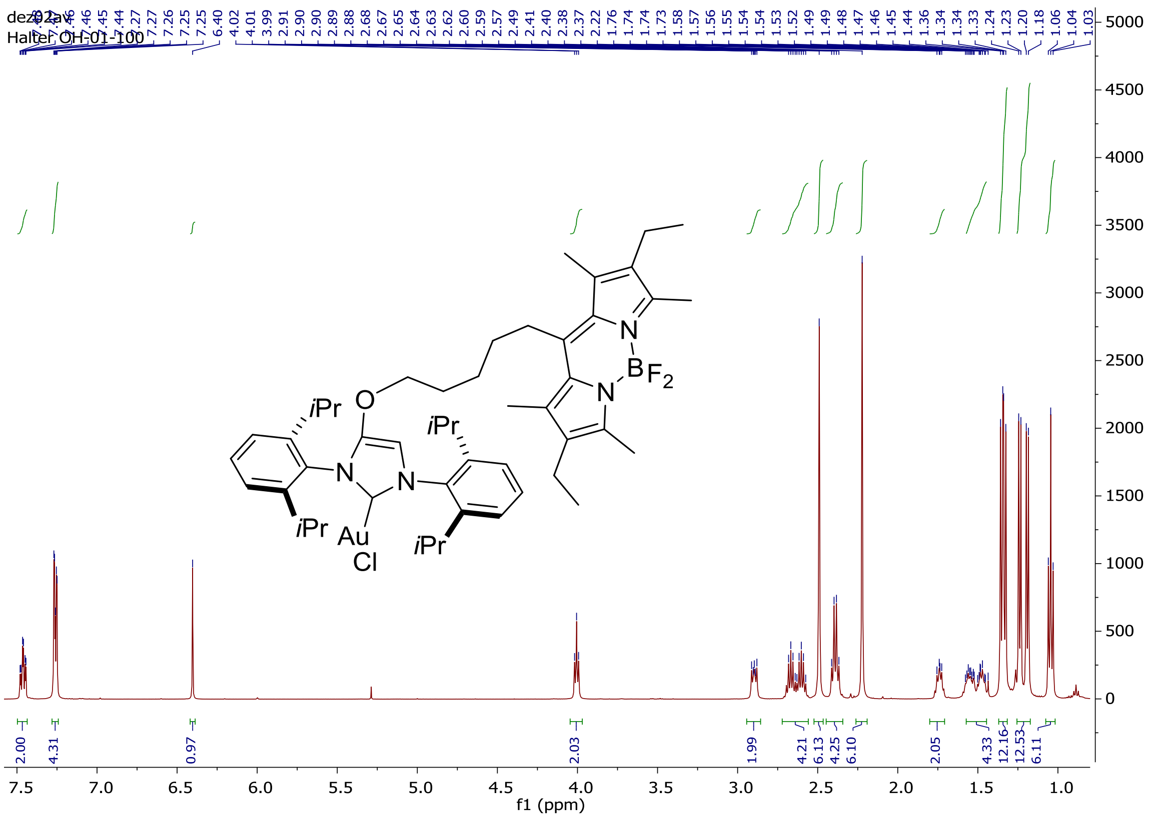


Figure S 4 [1]H NMR of [AuCl(**3d**)] in $CDCl_3$.

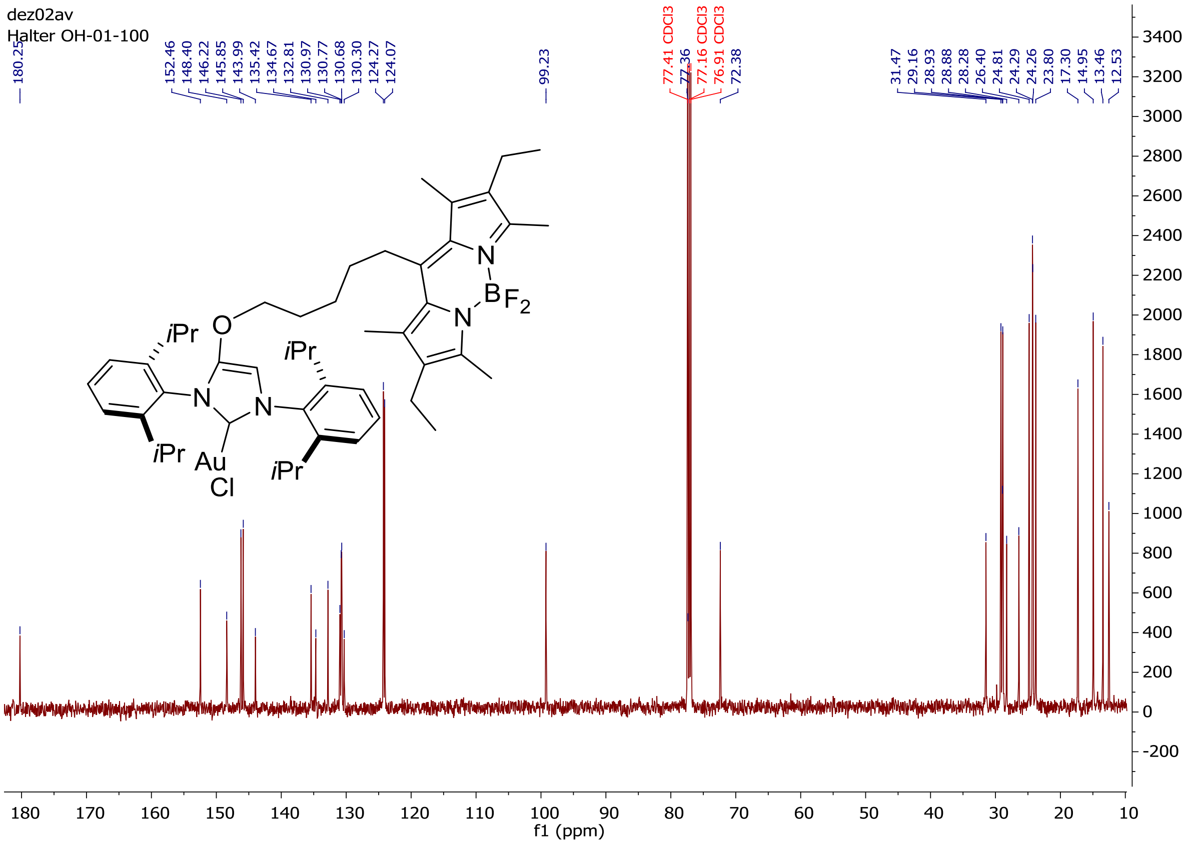


Figure S5 ^{13}C NMR of [AuCl(**3d**)] in $CDCl_3$.

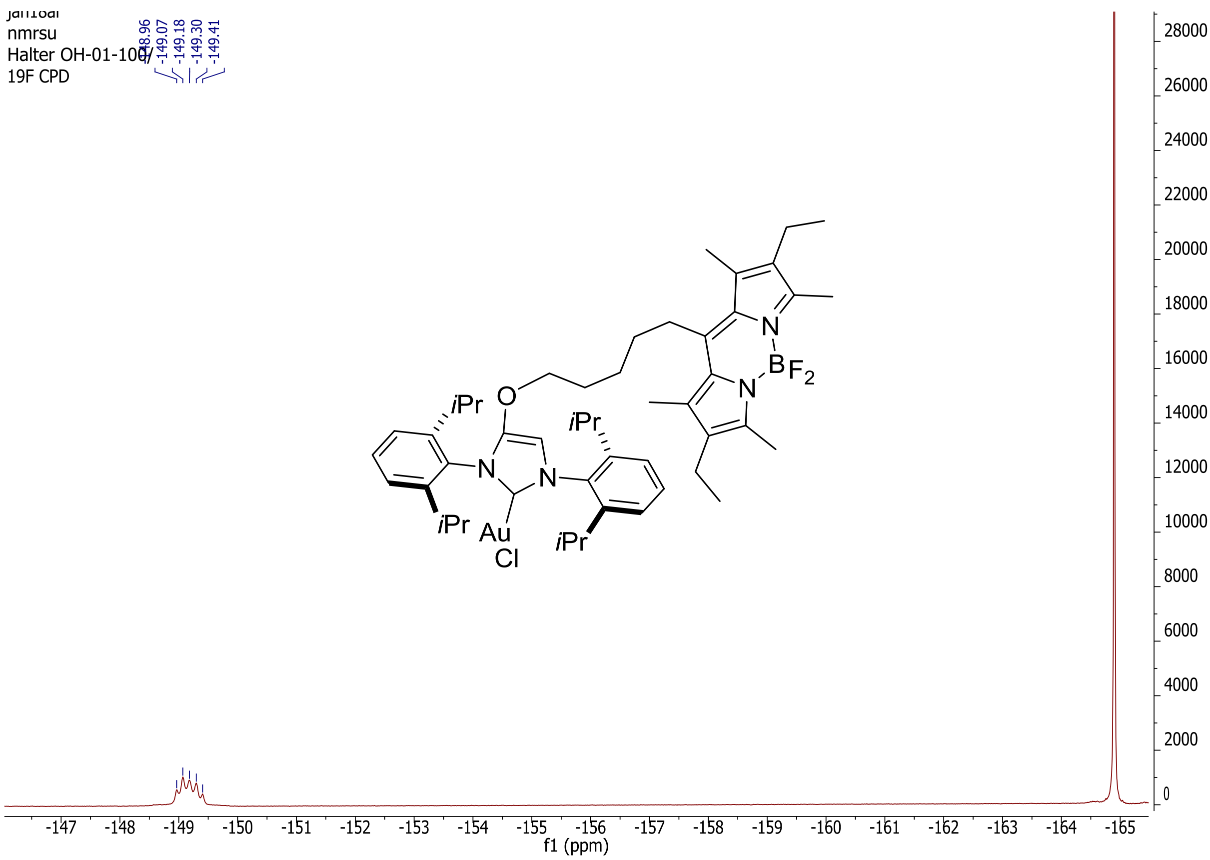


Figure S6 ^{19}F-NMR spectrum of [AuCl(**3d**)] in $CDCl_3$.

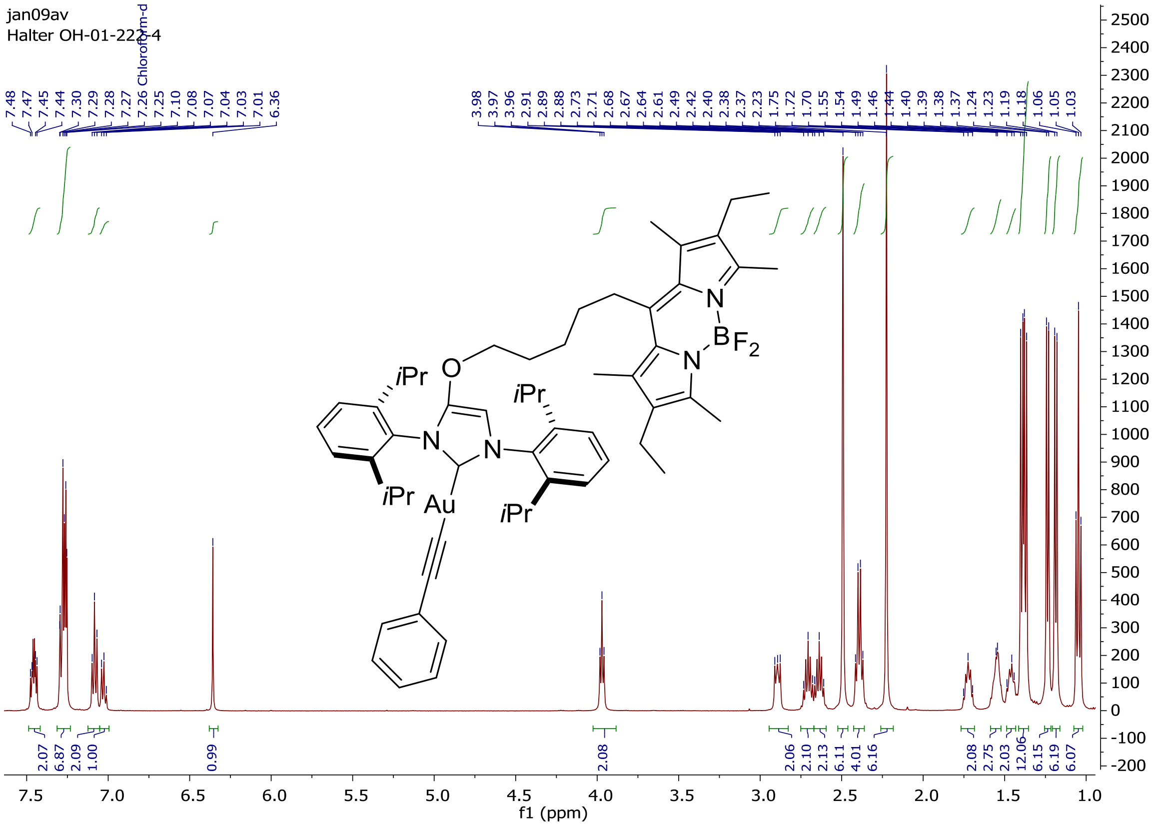


Figure S 7 ^{1}H NMR of [Au(CCPh)(**3d**)] in $CDCl_3$.

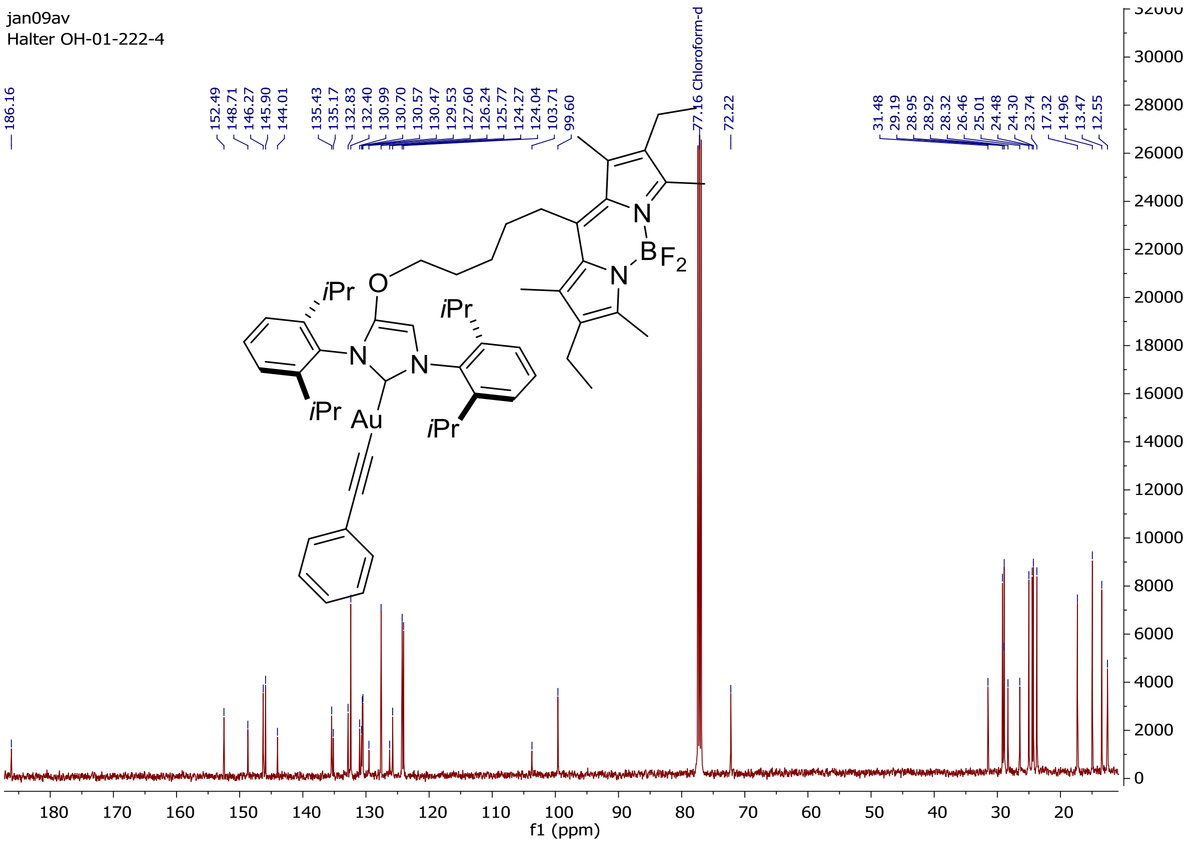


Figure S 8 ^{13}C NMR of [Au(CCPh)(**3d**)] in $CDCl_3$.

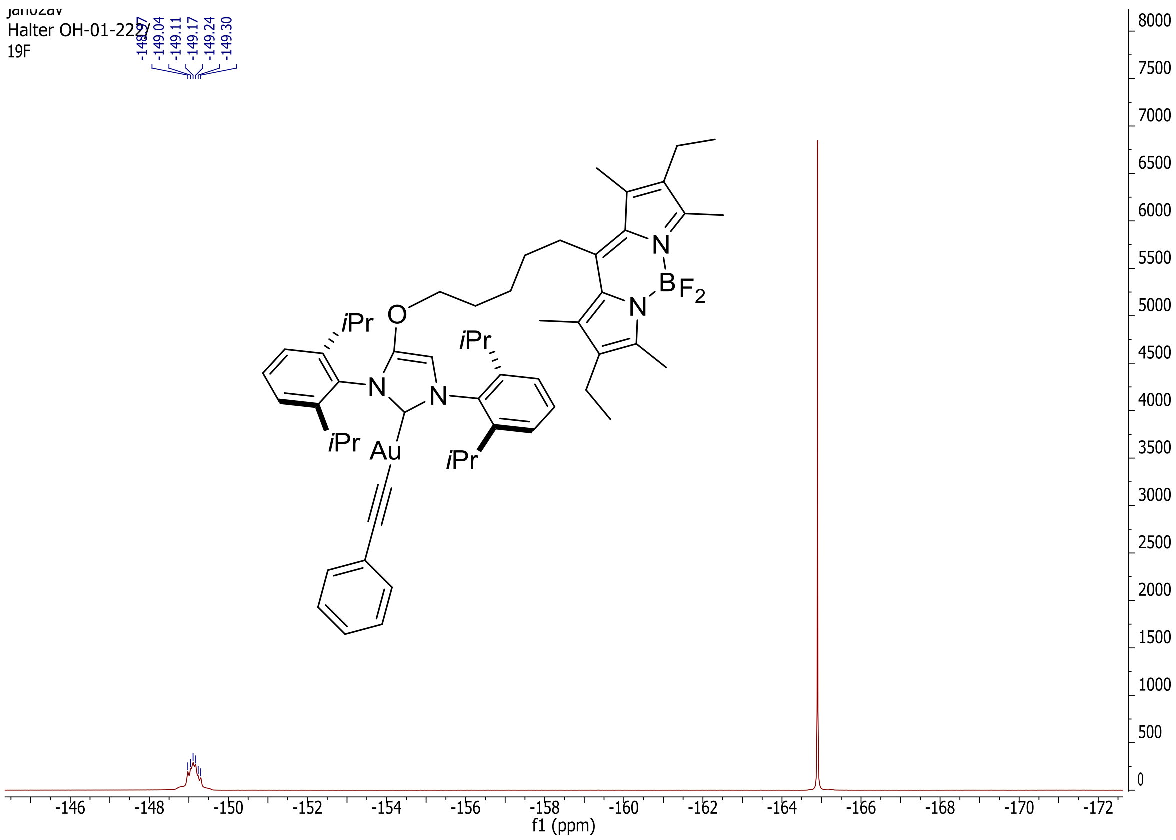


Figure S 9 ^{19}F NMR of [Au(CCPh)(**3d**)] in $CDCl_3$.

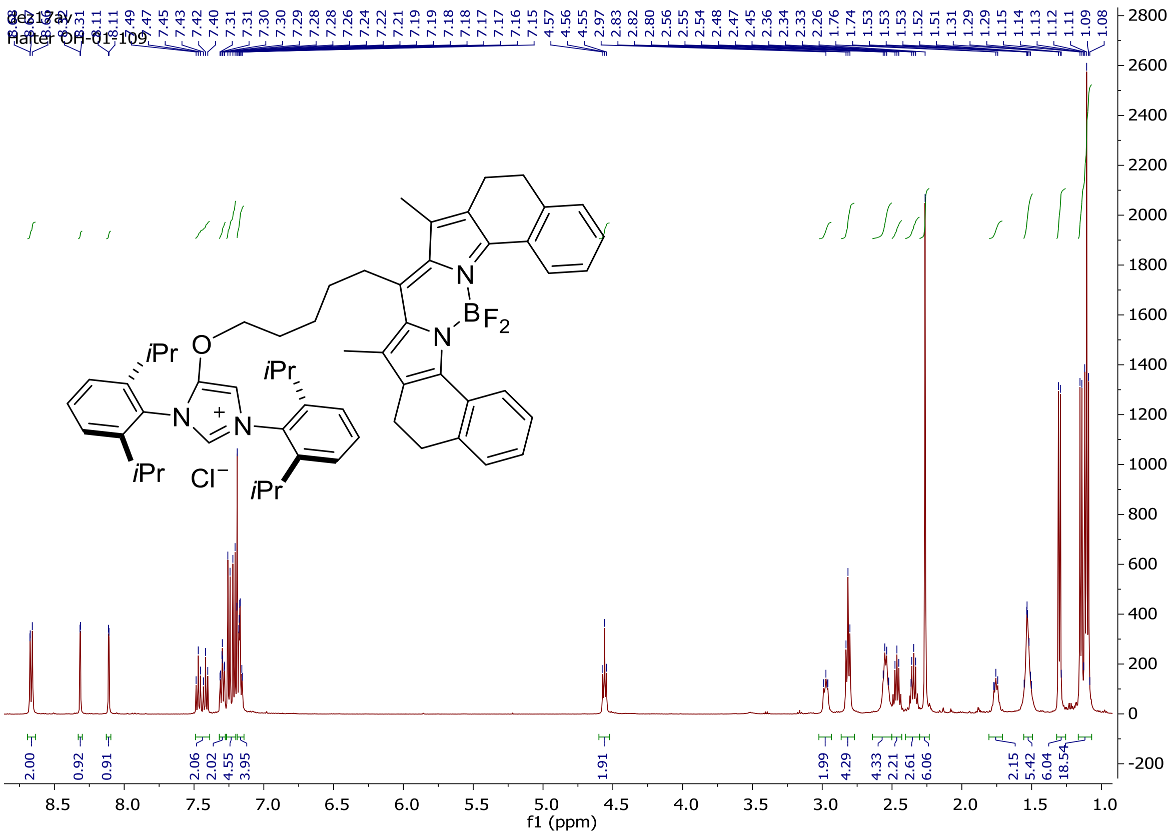


Figure S10 ^{1}H NMR of **3a**·HCl in $CDCl_3$.

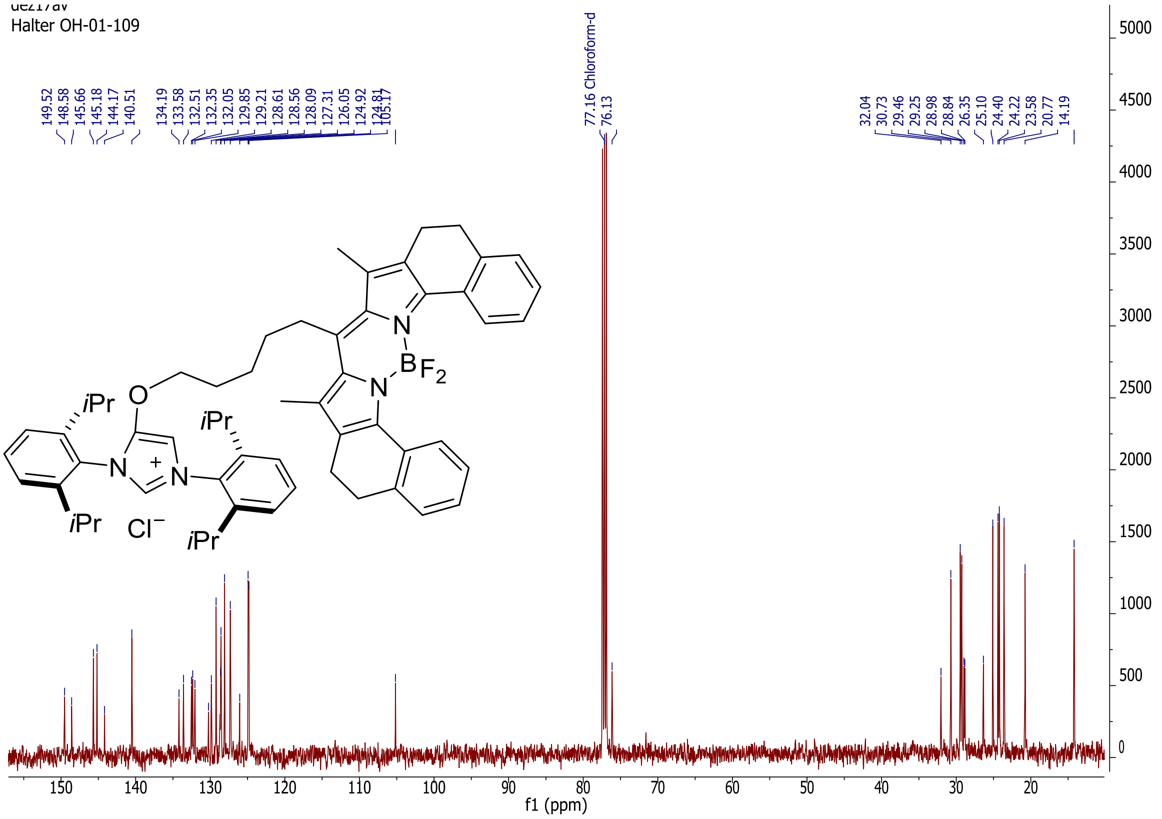


Figure S11 ^{13}C NMR of **3a**·HCl in $CDCl_3$.

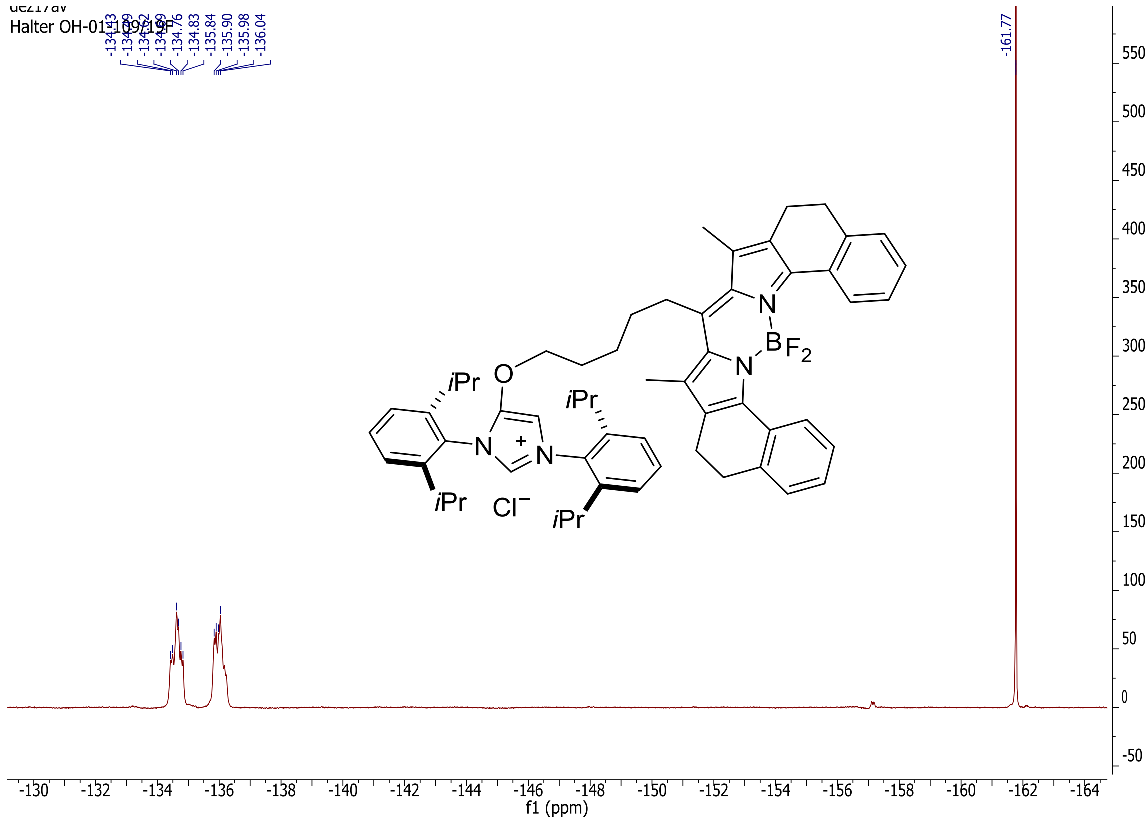


Figure S12 ^{19}F NMR of **3a**·HCl in $CDCl_3$.

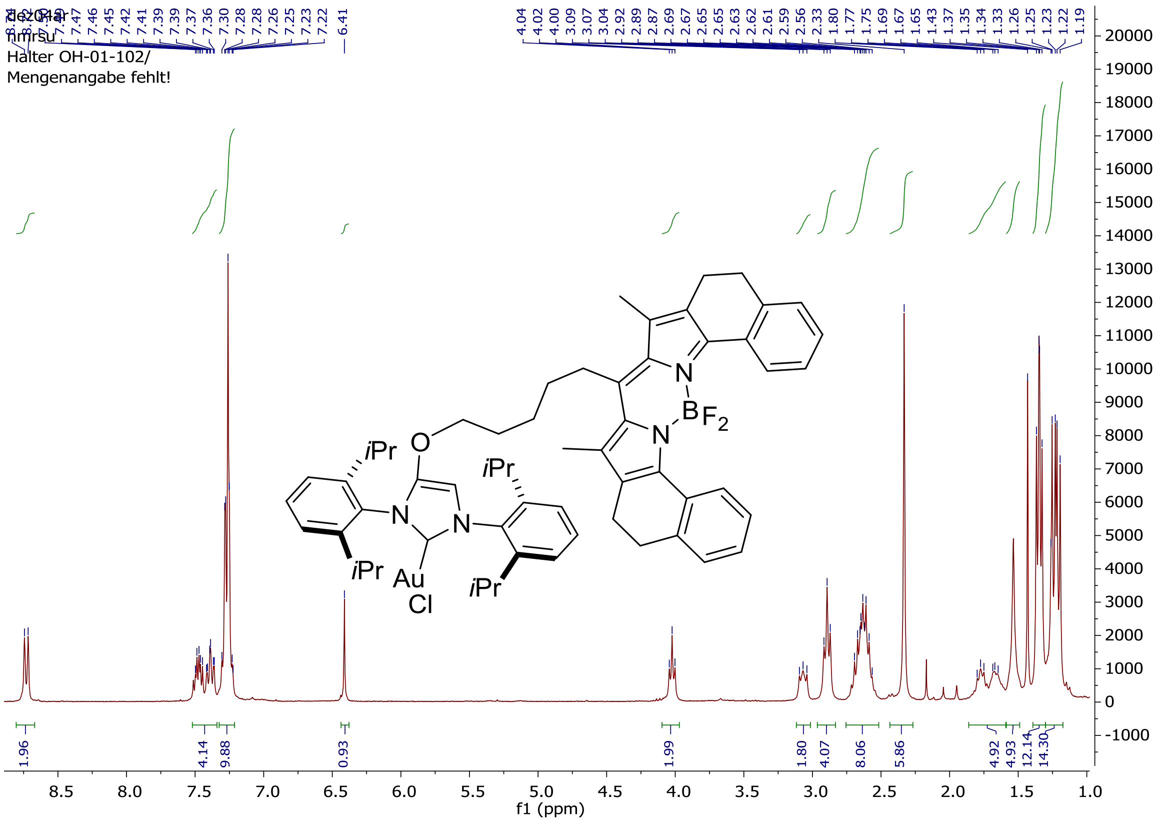


Figure S 13 ^{1}H NMR of [AuCl(**3a)**] in $CDCl_3$.

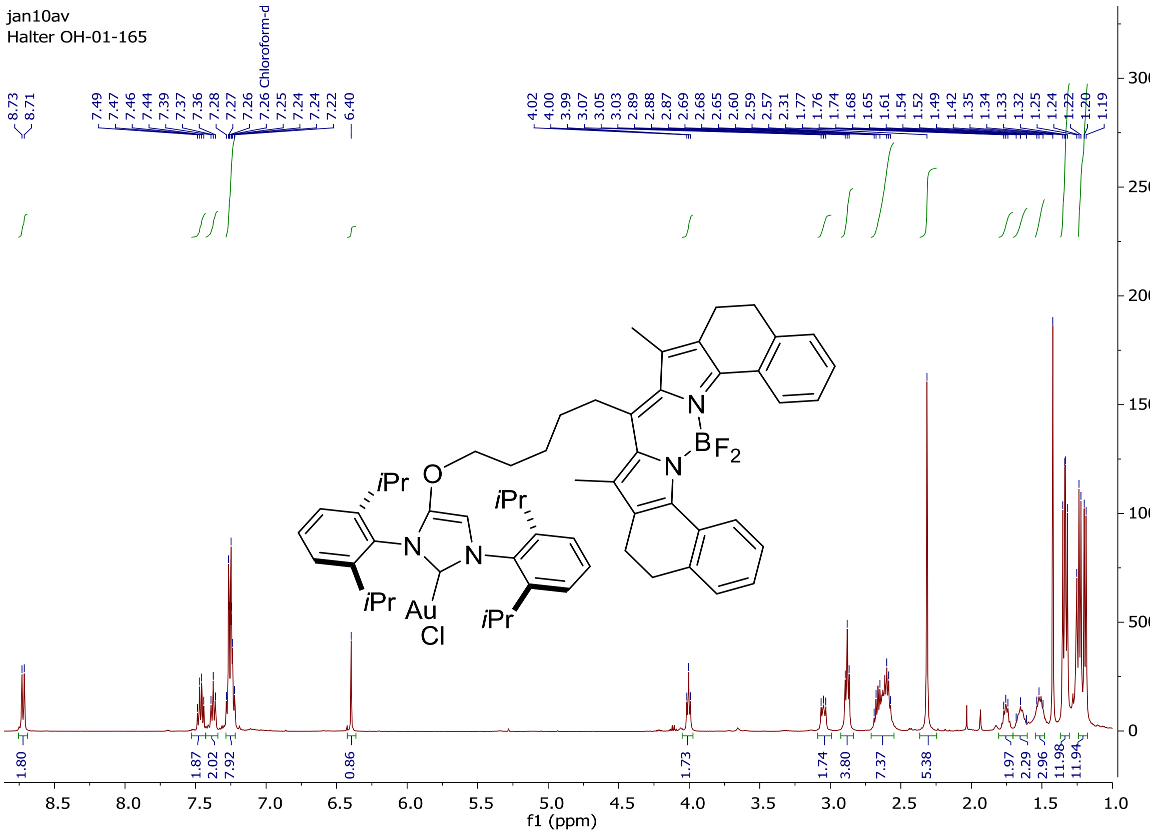


Figure S 14 ^{1}H NMR of [AuCl(**3a)**] in $CDCl_3$.

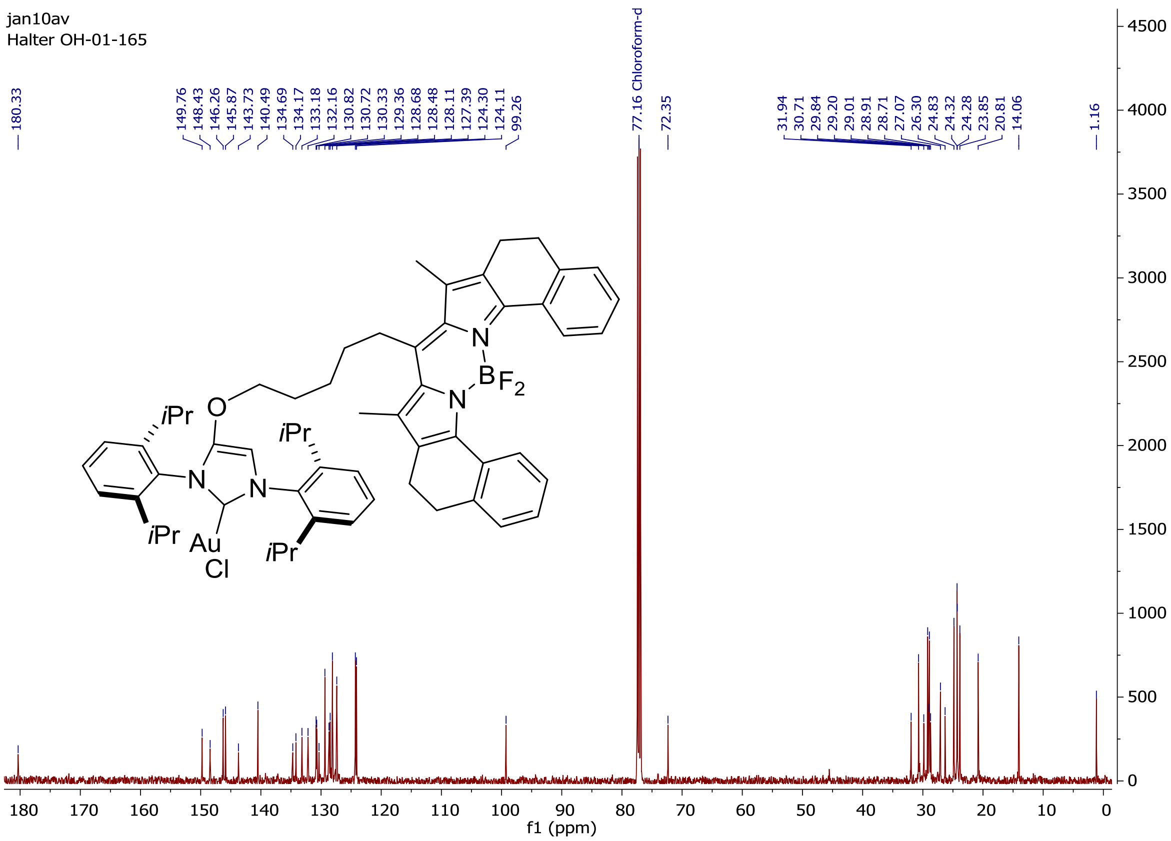


Figure S 15 ^{13}C NMR of [AuCl(**3a)**] in $CDCl_3$.

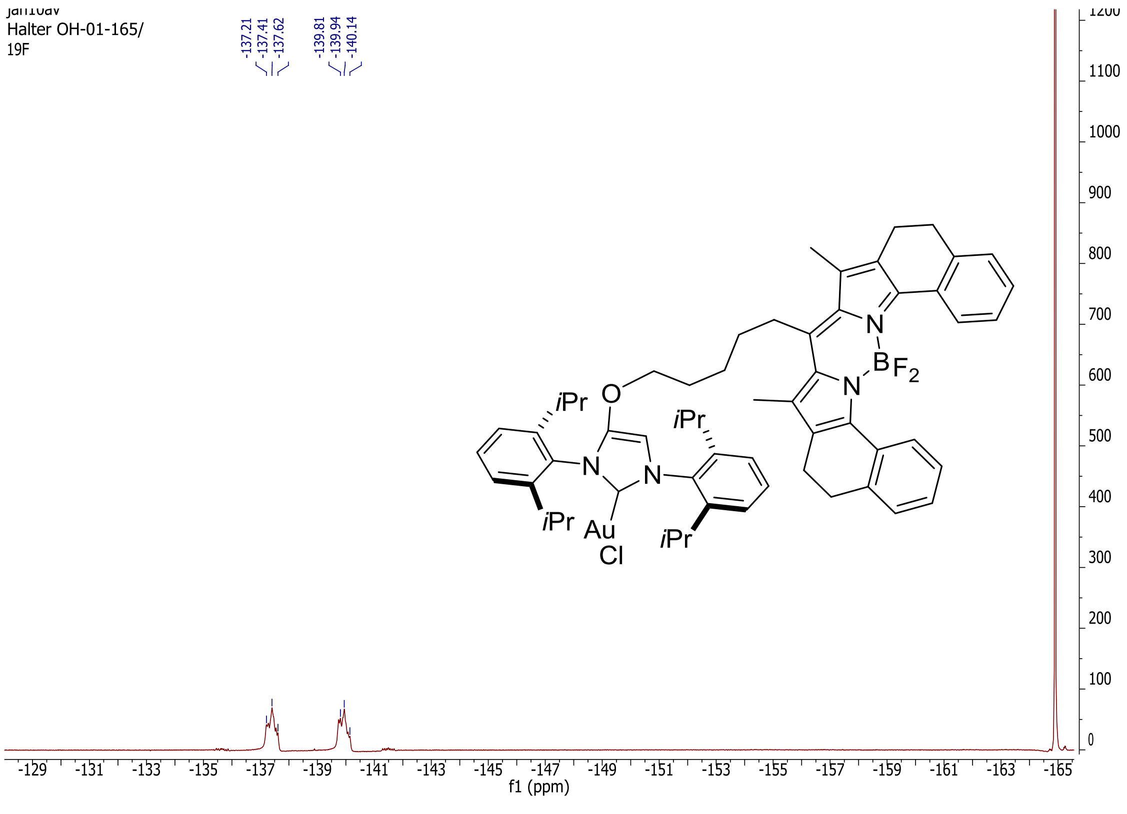


Figure S 16 ^{19}F NMR of [AuCl(**3a)**] in $CDCl_3$.

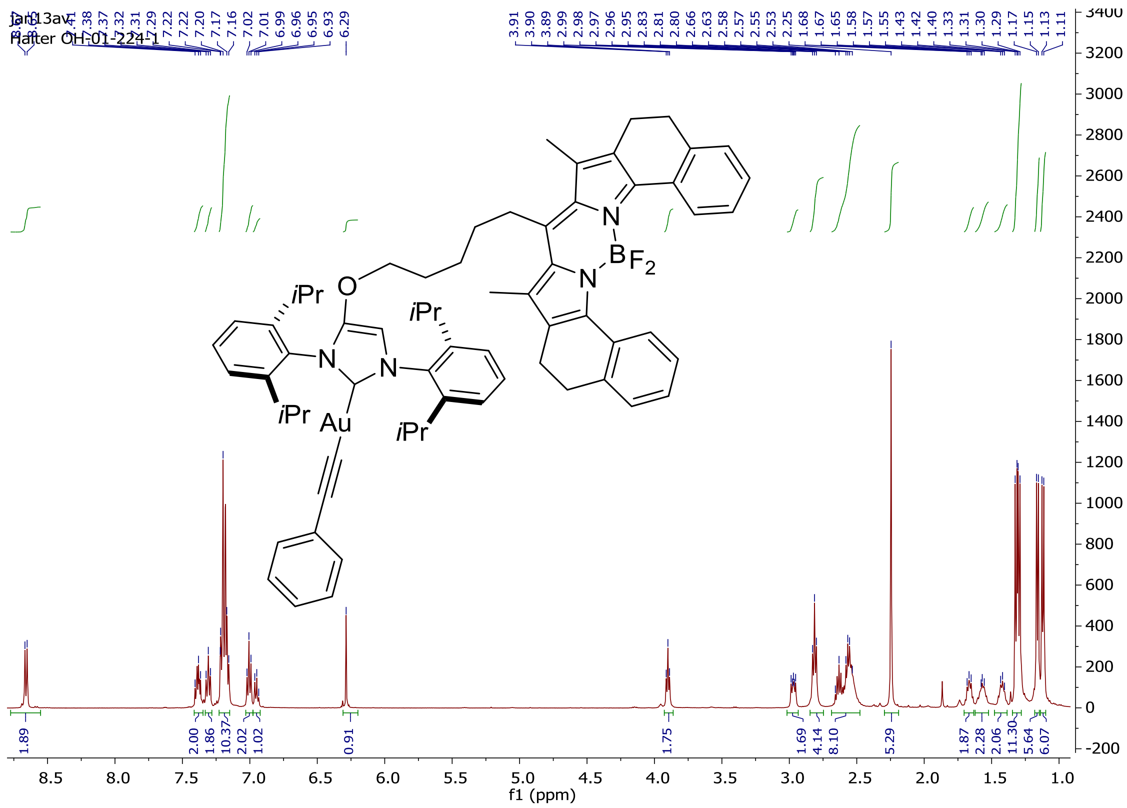


Figure S 17 ^{1}H NMR of [Au(CCPh)(**3a**)] in $CDCl_3$.

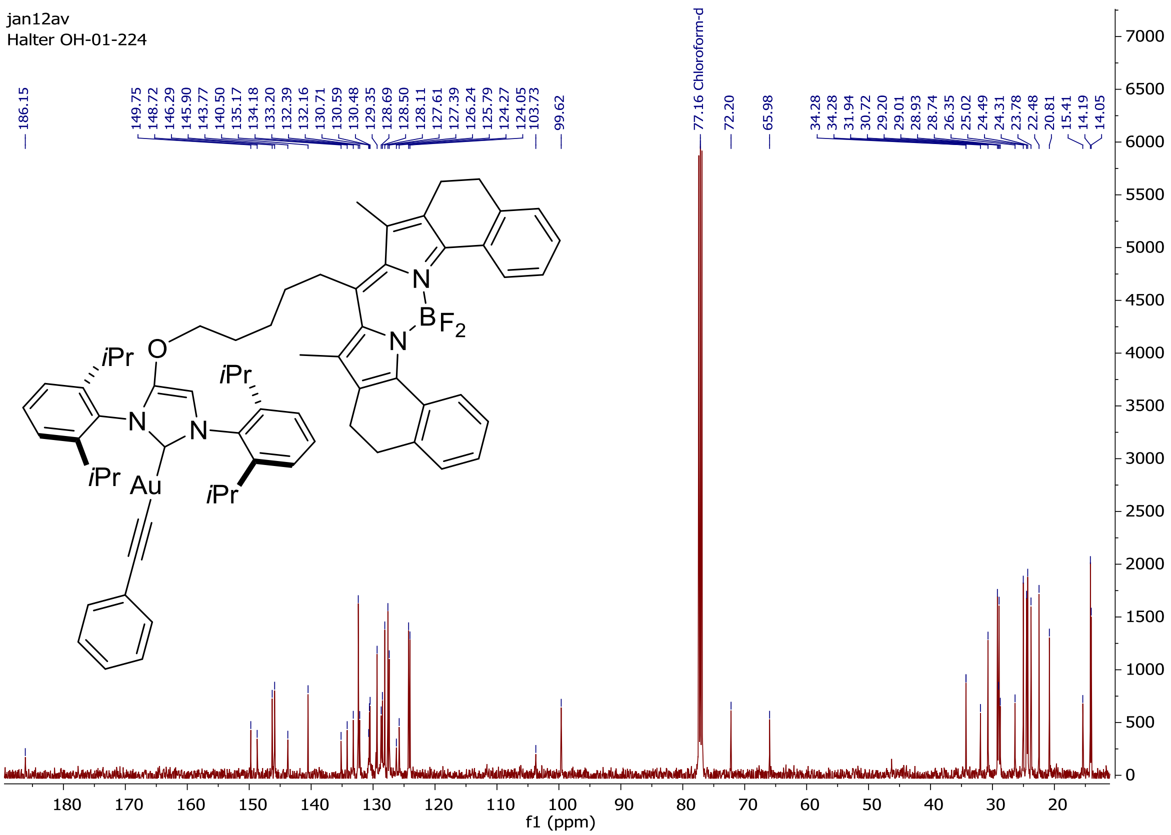


Figure S 18 ^{13}C NMR of [Au(CCPh)(**3a**)] in $CDCl_3$.

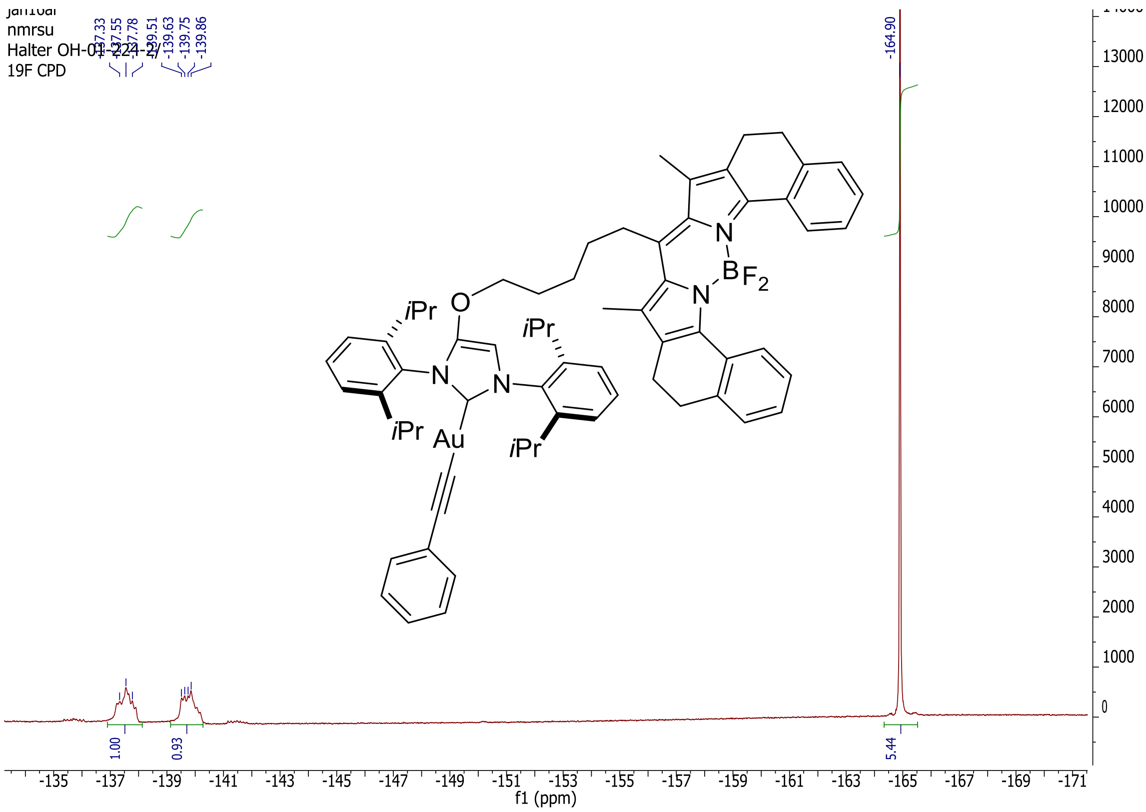


Figure S 19 ^{19}F NMR of [Au(CCPh)(**3a**)] in $CDCl_3$.

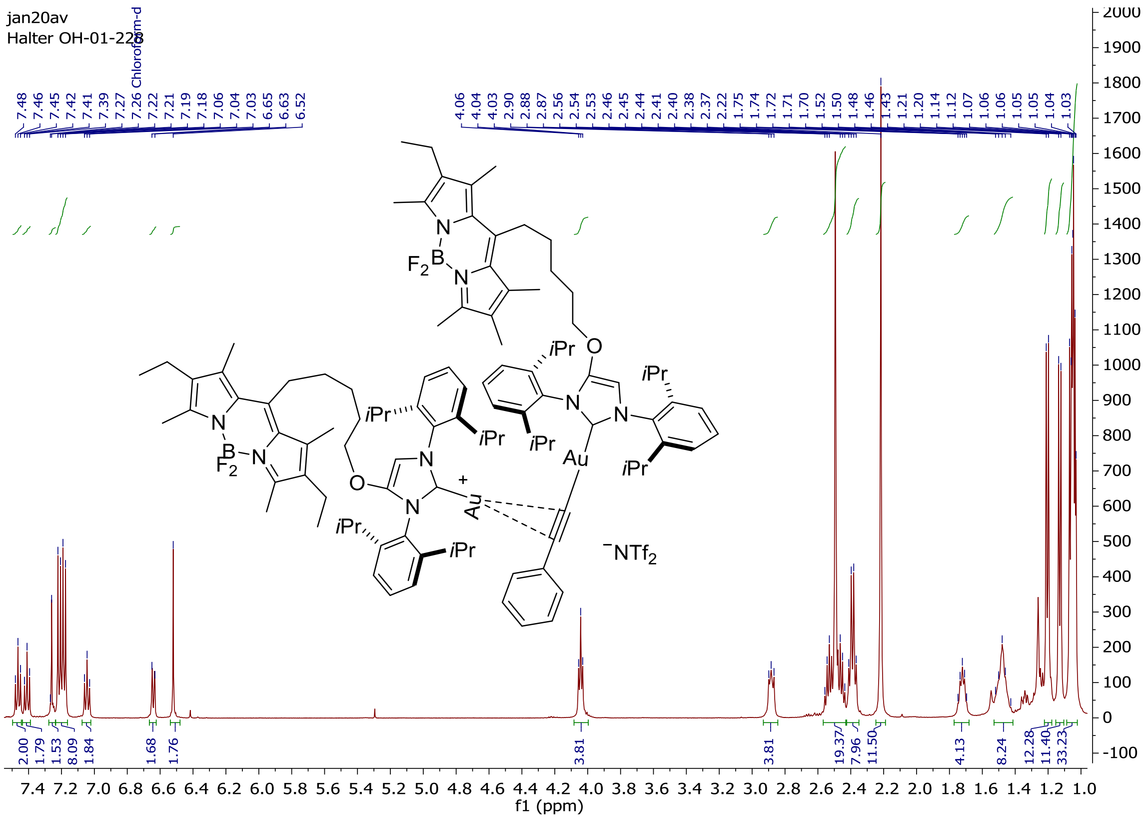


Figure S 20 ^{1}H NMR of [(Au(**3d**))(Au(CCPh)(**3d**))]NTf_2 in $CDCl_3$.

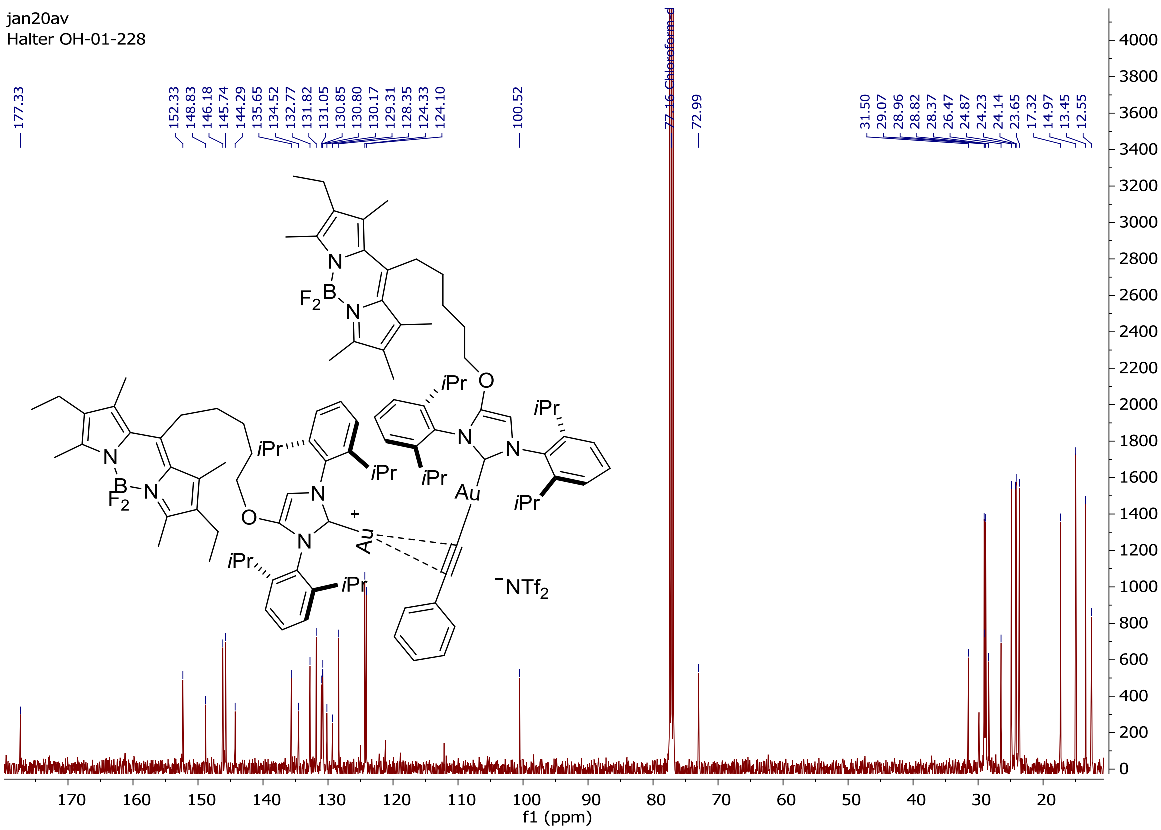


Figure S 21 ^{13}C NMR of [(Au(**3d**))(Au(CCPh)(**3d**))]NTf_2 in $CDCl_3$.

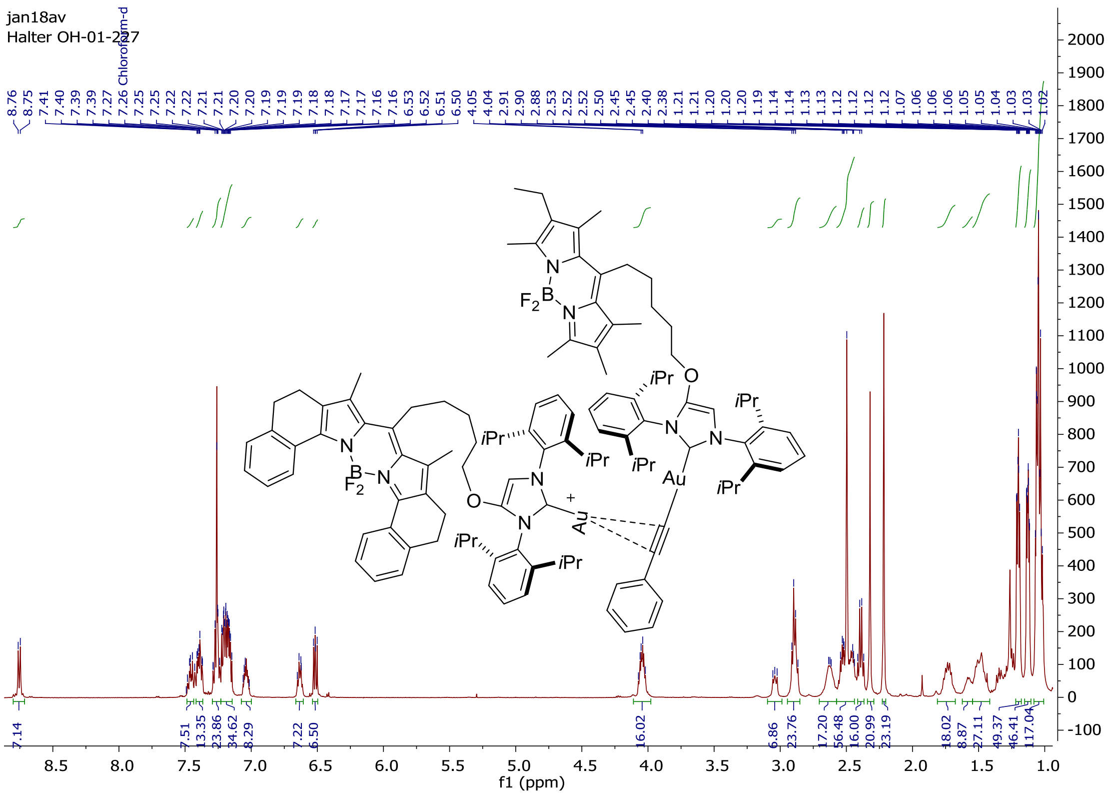


Figure S 22 ^{1}H NMR of [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2 in $CDCl_3$.

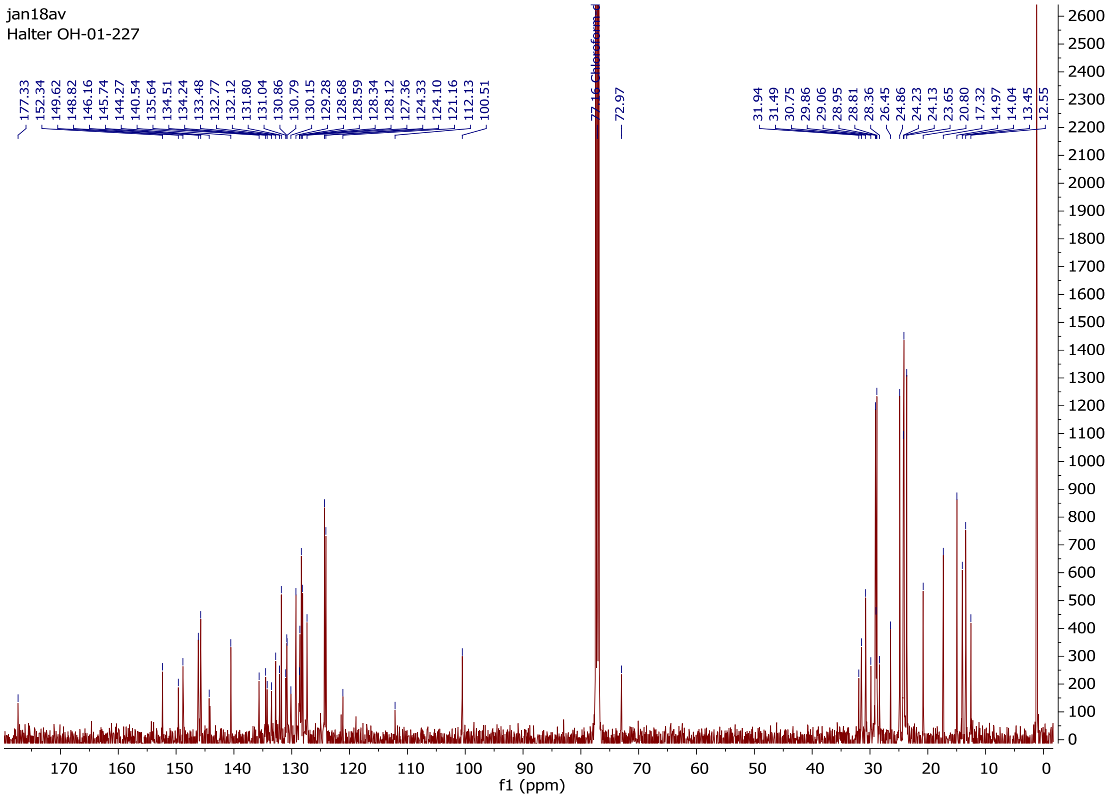


Figure S 23 ^{13}C NMR of [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2 in $CDCl_3$.

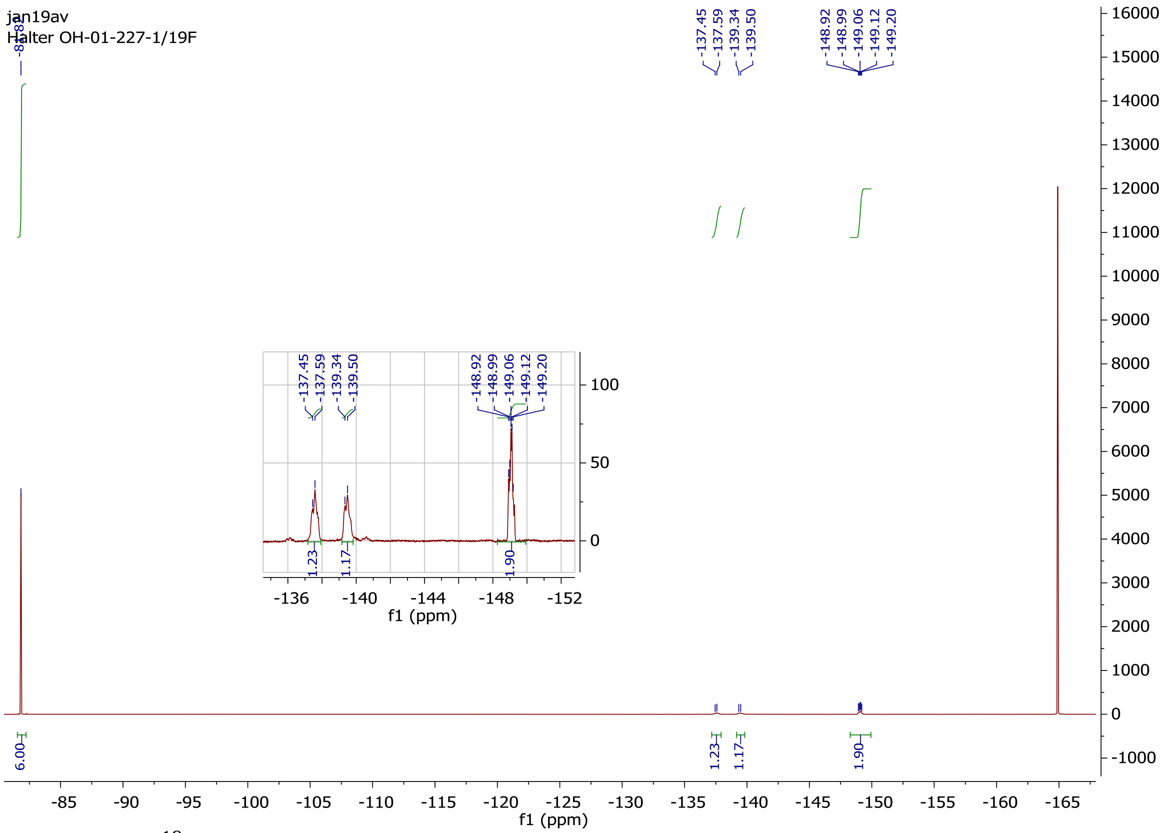


Figure S 24 ^{19}F NMR of [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2 in $CDCl_3$.

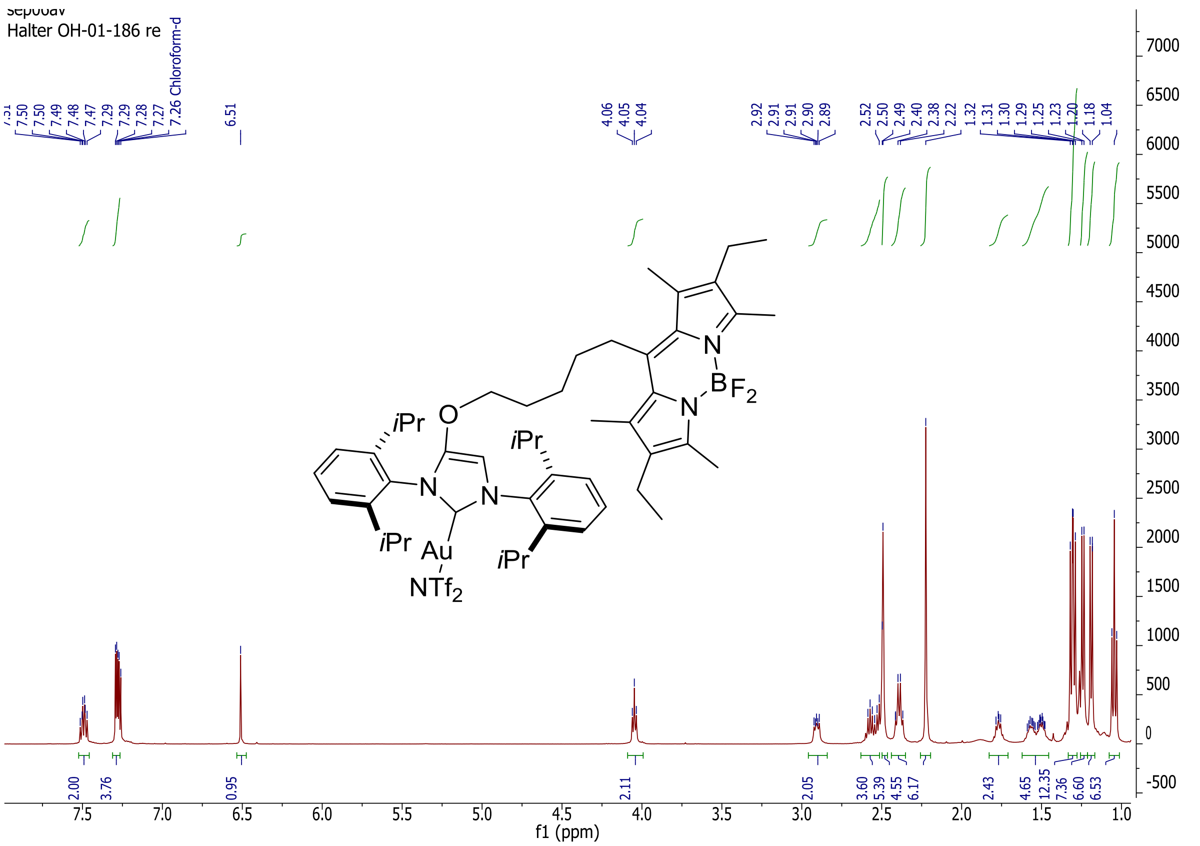


Figure S 25 ^{1}H NMR of [Au(NTf$_2$)(**3d**)] in $CDCl_3$.

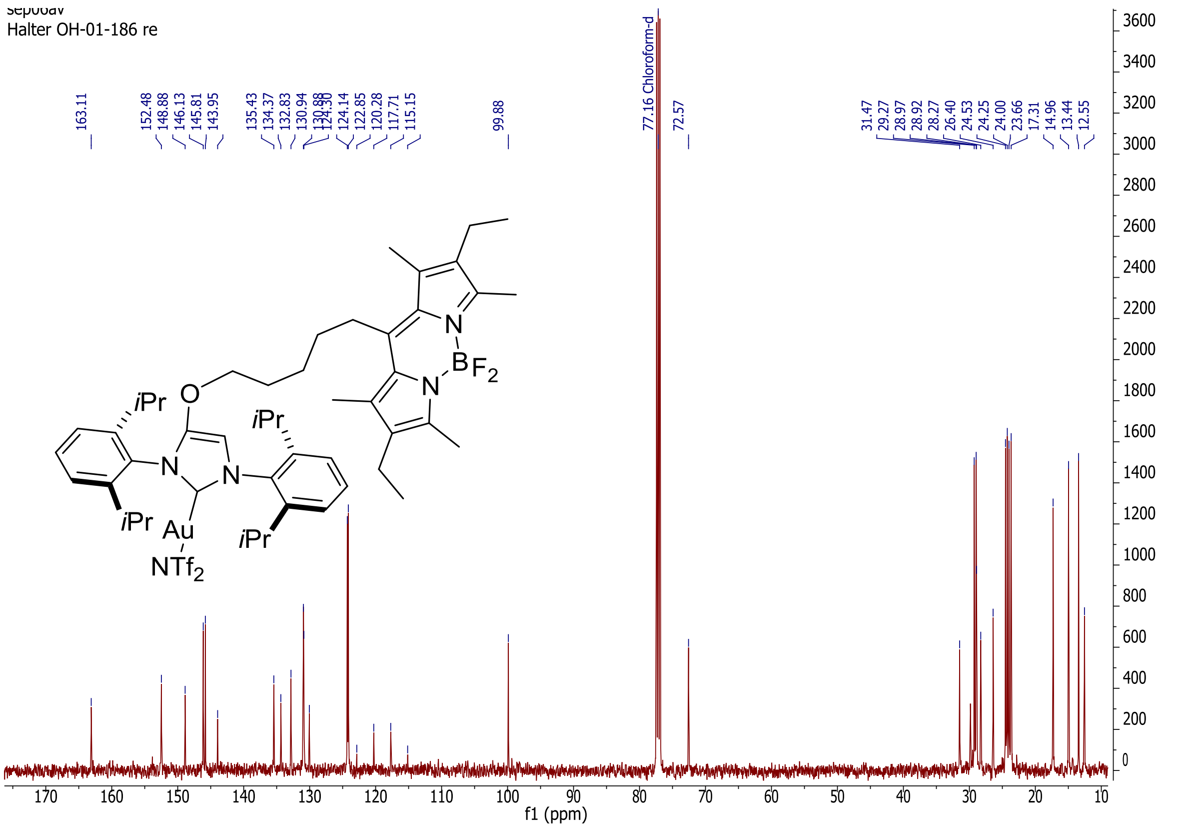


Figure S 26 ^{13}C NMR of [Au(NTf$_2$)(**3d**)] in $CDCl_3$.

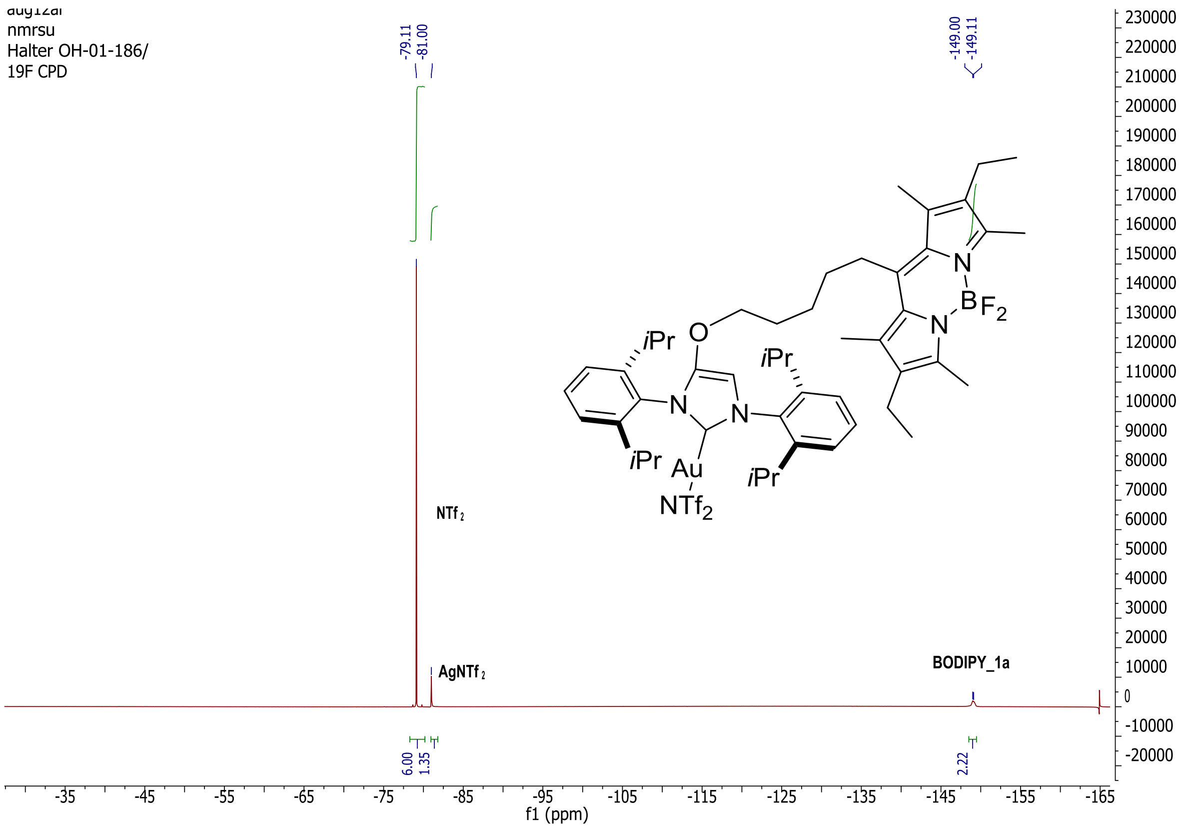


Figure S 27 ^{19}F NMR of [Au(NTf$_2$)(**3d**)] in CDCl$_3$.

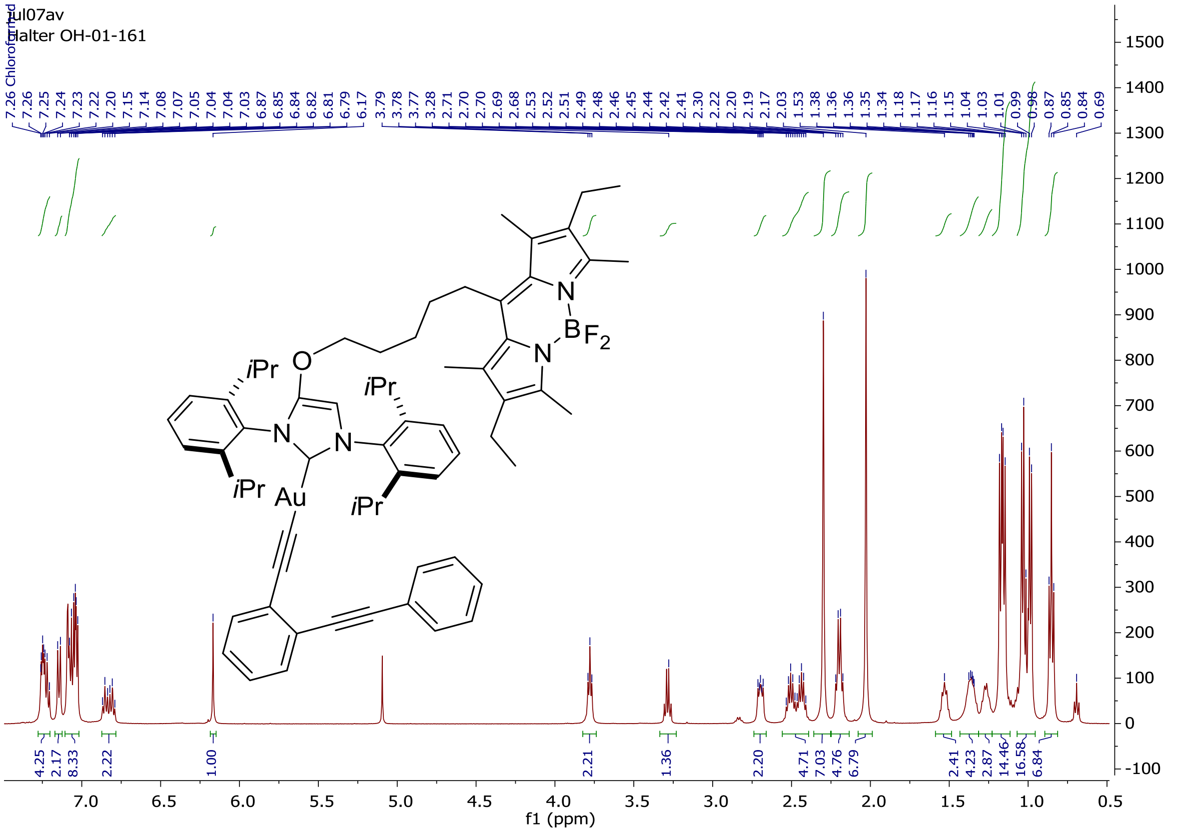


Figure S 28 ^{1}H NMR of [Au(CCPh´´)(**3d**)] in CDCl$_3$.

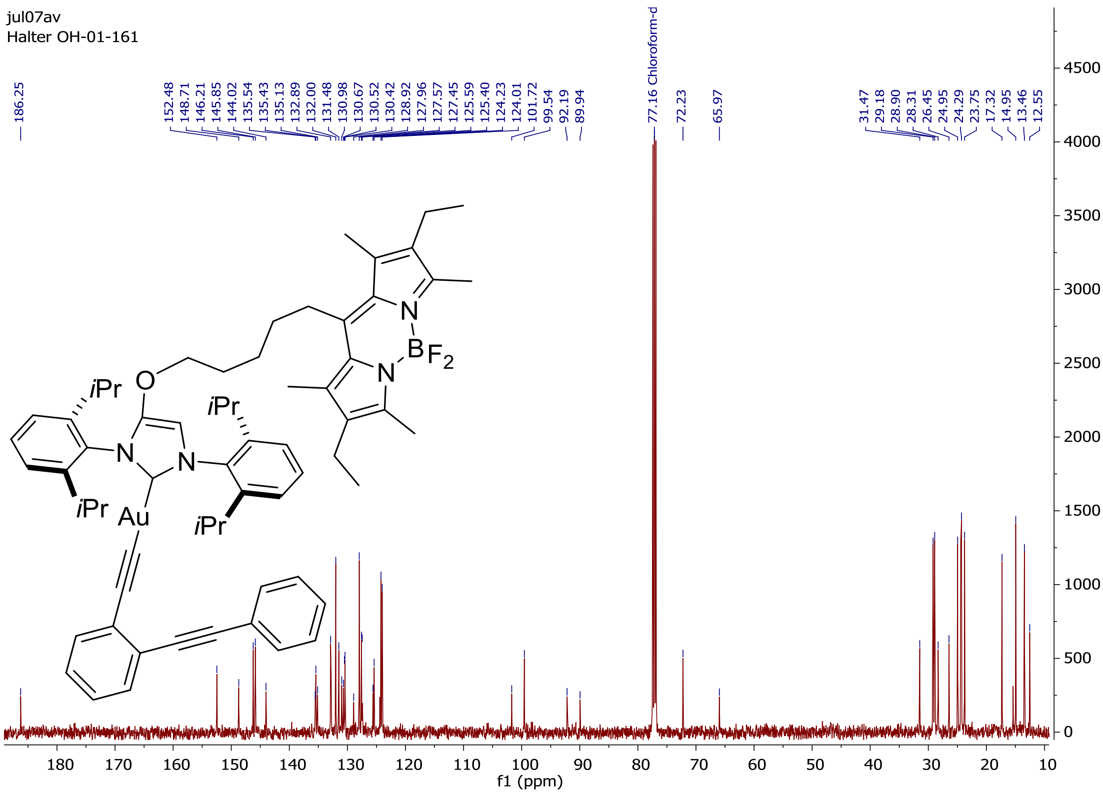


Figure S 29 ^{13}C NMR of [Au(CCPh´´)(**3d**)] in $CDCl_3$.

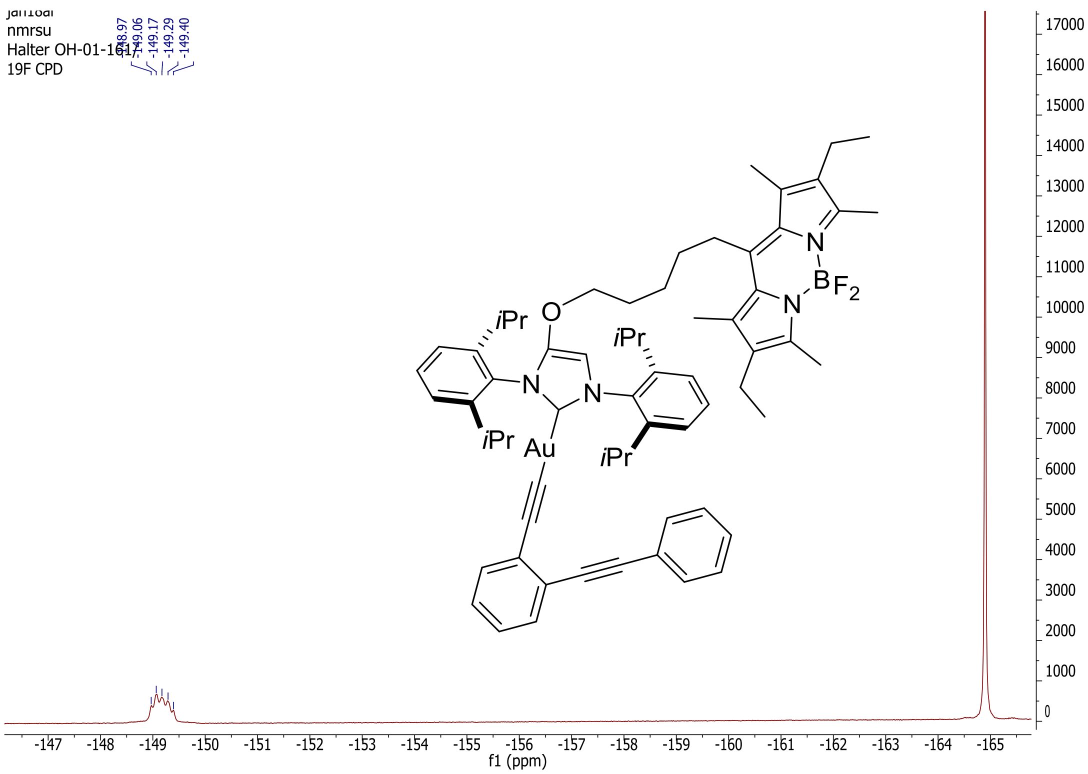


Figure S 30 ^{19}F NMR of [Au(CCPh´´)(**3d**)] in $CDCl_3$.

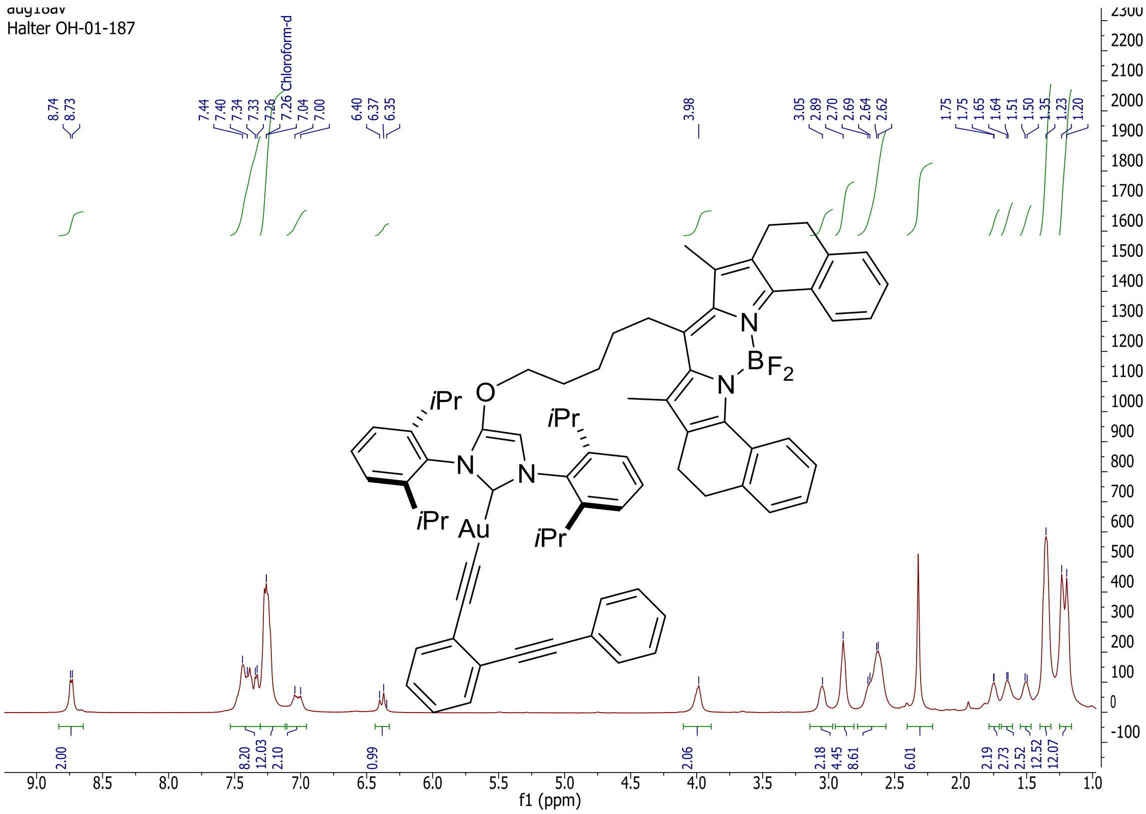


Figure S 31 ^{1}H NMR of [Au(CCPh´´)(**3a**)] in $CDCl_3$.

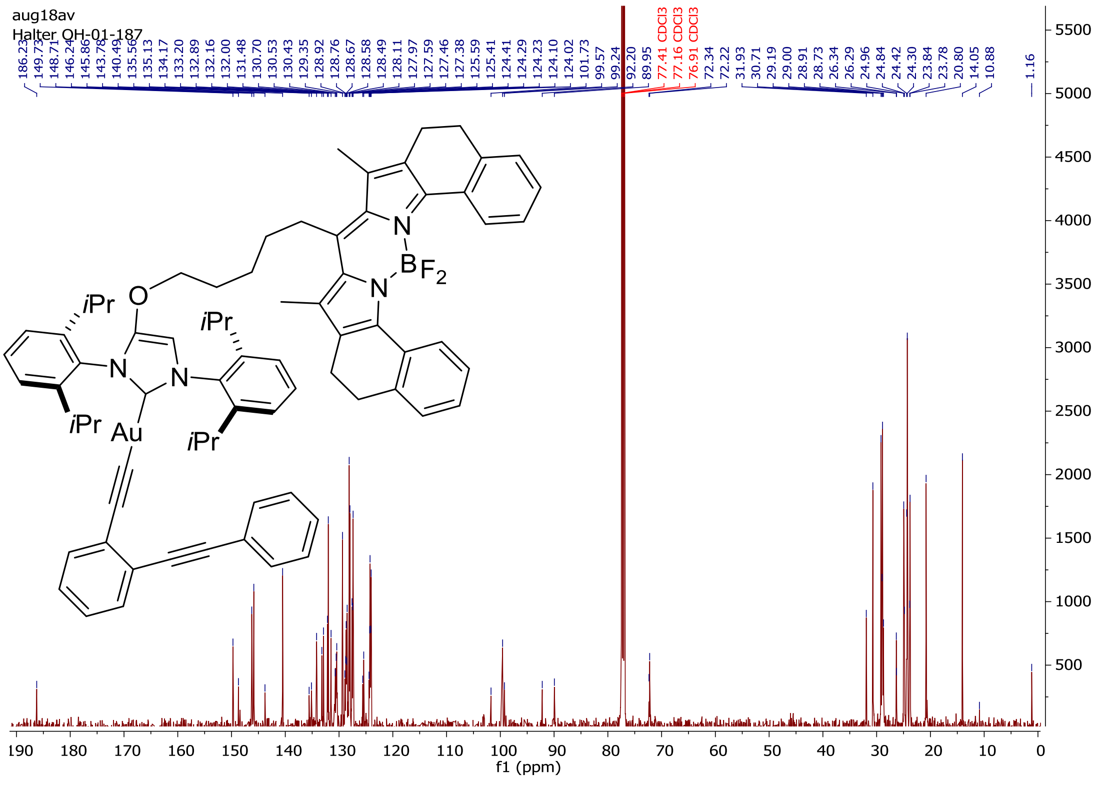


Figure S 32 ^{13}C NMR of [Au(CCPh´´)(**3a**)] in $CDCl_3$.

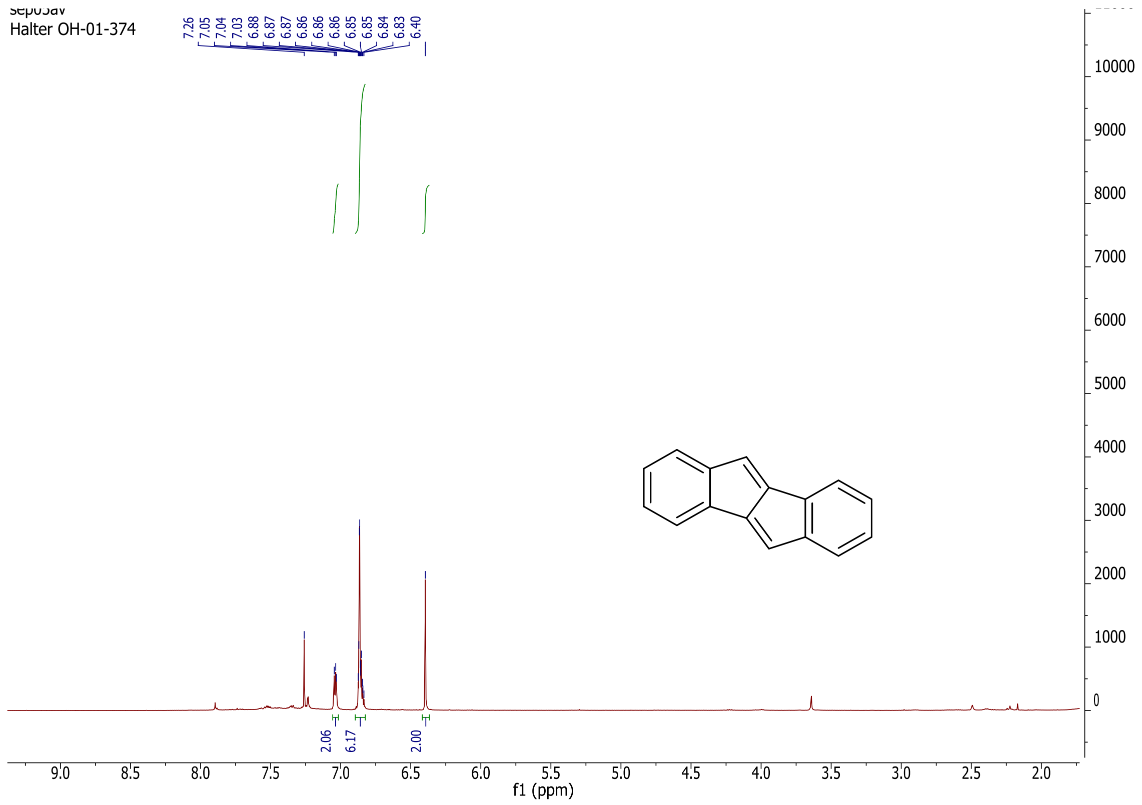


Figure S 33 ^{1}H NMR of Dibenzopentalene (crude material).

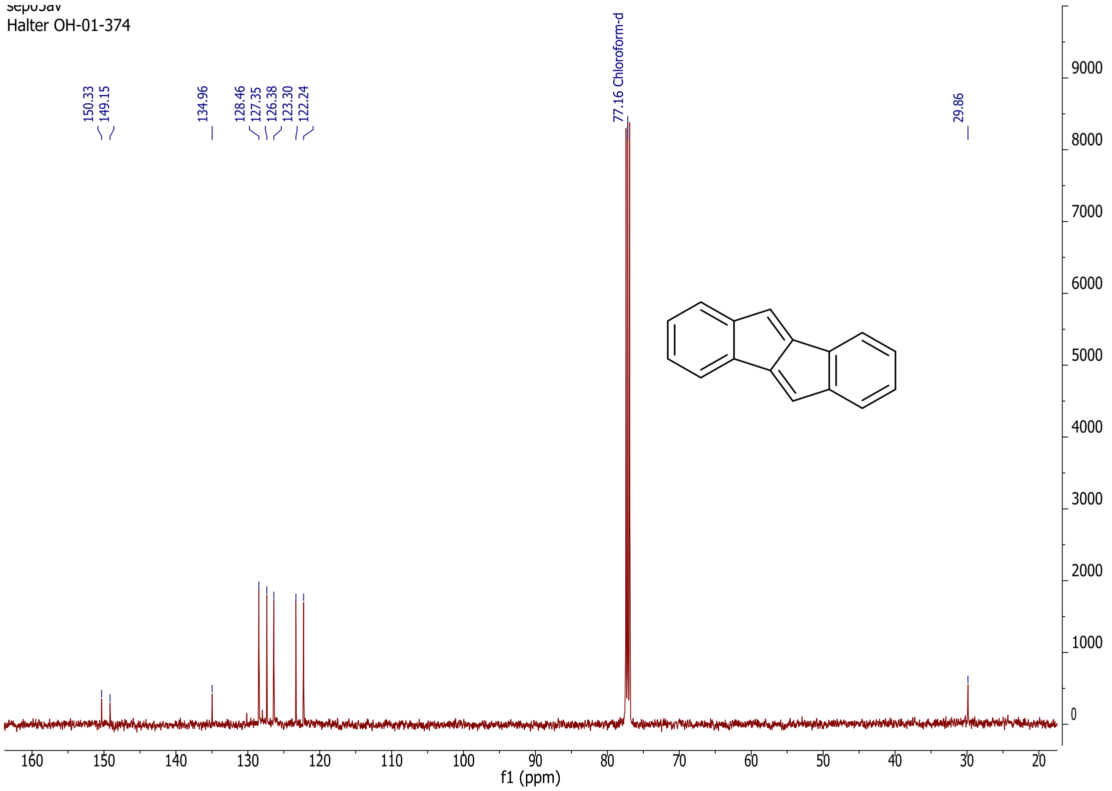


Figure S 34 ^{13}C NMR of Dibenzopentalene (crude material).

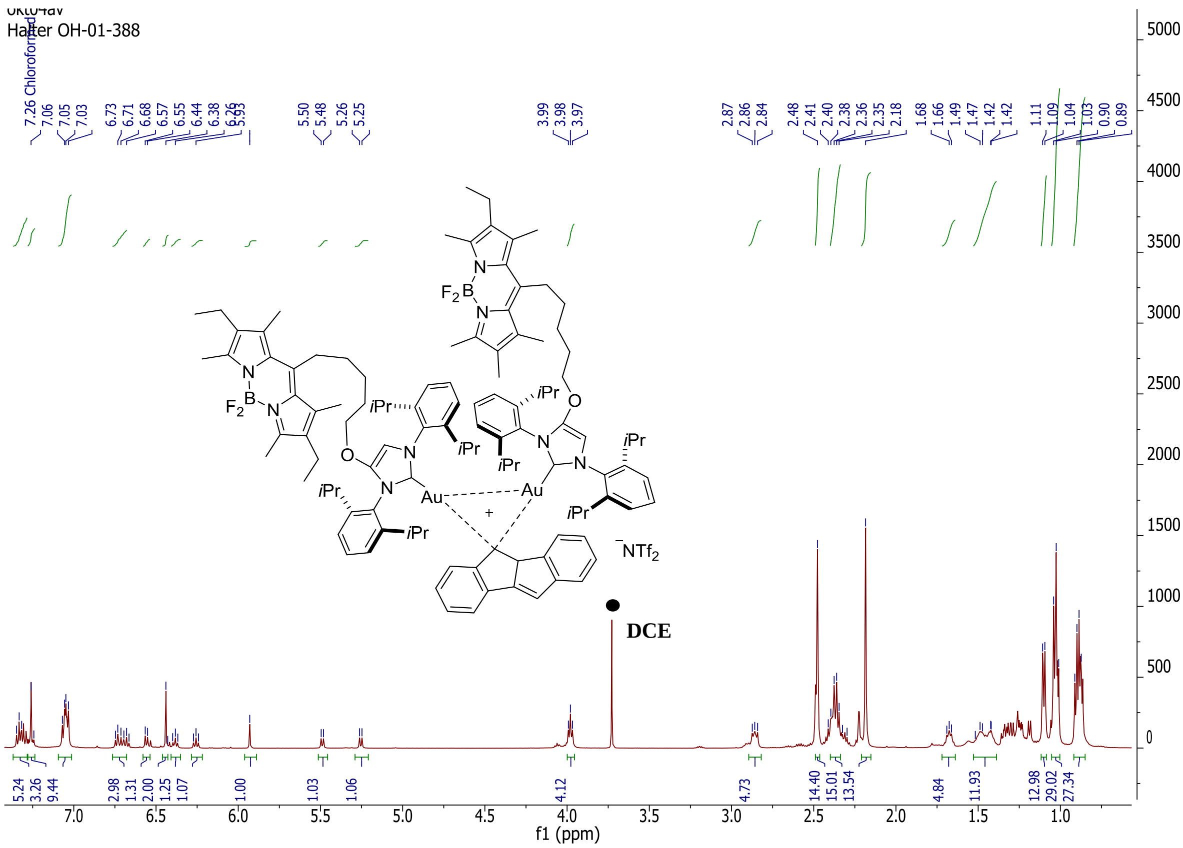


Figure S 35 ^{1}H NMR of [(Au(**3d**))(Au(Au(CCPh´´)(**3d**))]NTf_2.

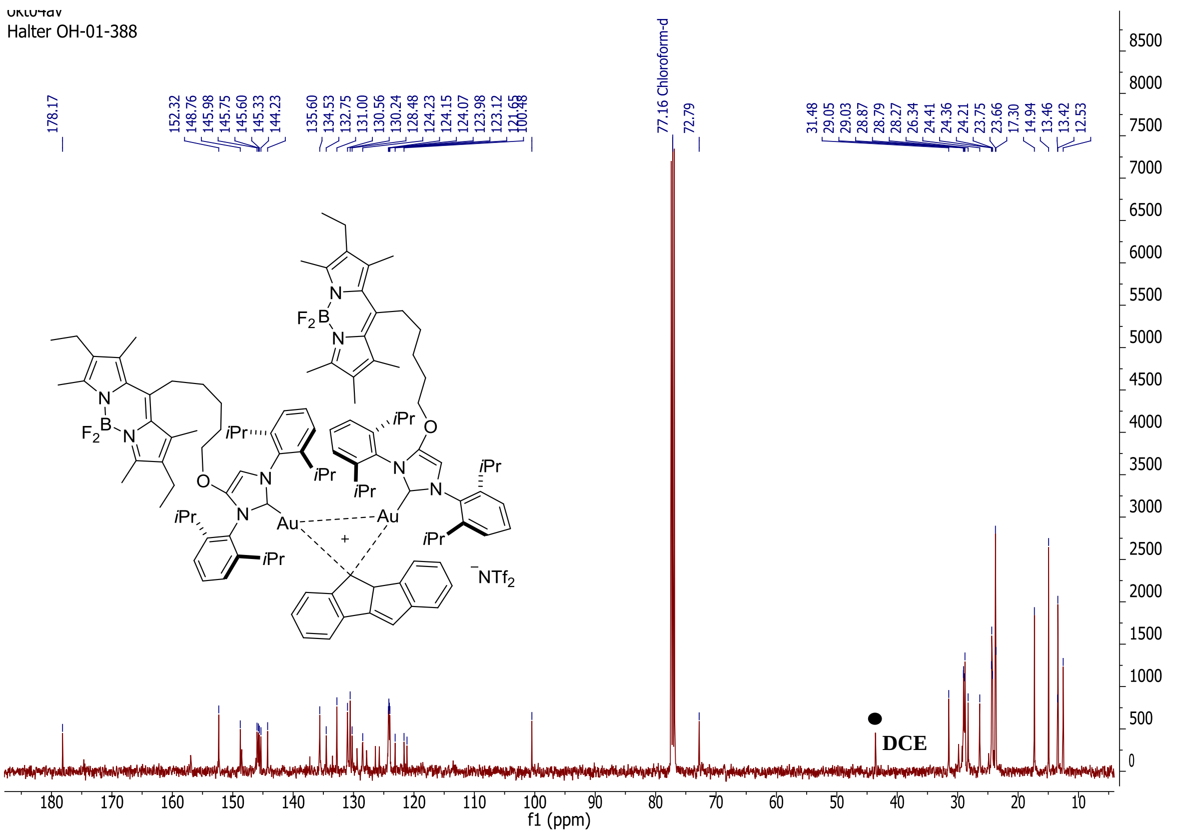


Figure S 36 ^{13}C NMR of [(Au(**3d**))(Au(Au(CCPh´´)(**3d**))]NTf_2.

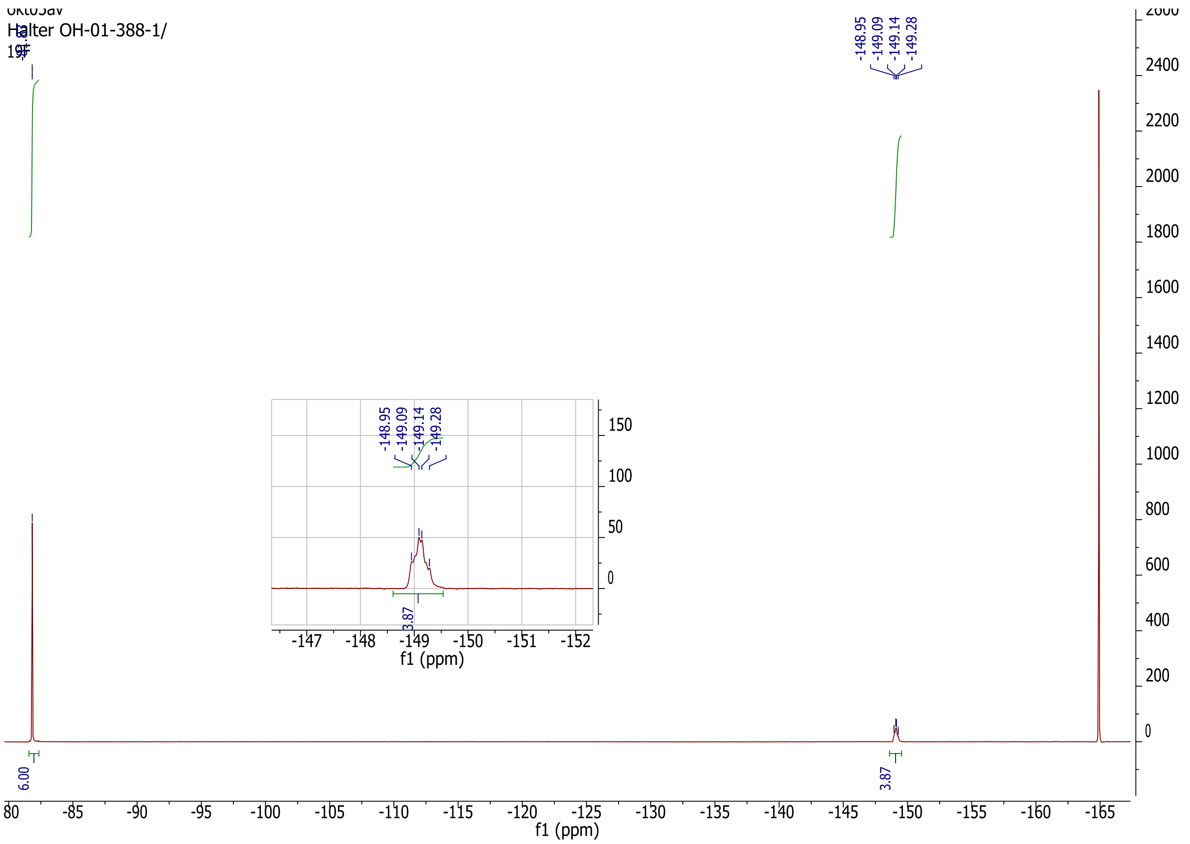


Figure S 37 ^{19}F NMR of [(Au(**3d**))(Au(Au(CCPh´´)(**3d**))]NTf_2.

4. Fluorescence measurements of BODIPY tagged metal complexes

Fluorescence quantum yield

Quantum yields were determined according to the literature procedure[5] using rhodamine 6G (from Sigma-Aldrich, BioReagent, suitable for fluorescence) as the standard. Absorption and emission spectra for all compounds and standard were obtained over a range of concentrations (250 nM to 1.0 µM, in 1,2-dichloroethane) where a linear correlation between concentration and absorption was observed. The absorbance was within the range from 0.01 to 0.1. The quantum yield was calculated according to the equation $\Phi_x = \Phi_{st}\left(\frac{Grad_x}{Grad_{st}}\right)\left(\frac{\eta_x}{\eta_{st}}\right)^2$ where the subscripts *st* and *x* denote standard and test respectively, Φ is the fluorescence quantum yield, *Grad* the gradient from the plot of integrated fluorescence intensity *vs* absorbance, and η the refractive index of the solvent. Φ_{st} = 0.95 in EtOH.

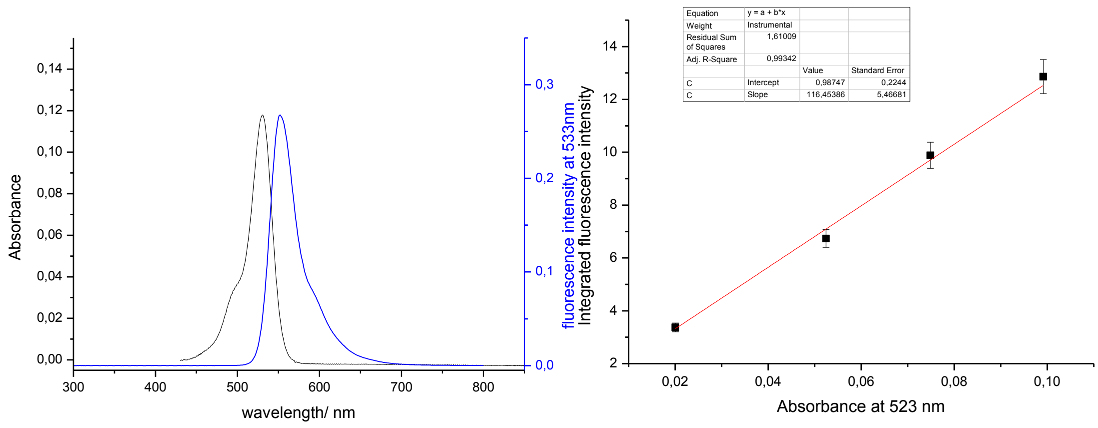


Figure S 38Left: absorbance (black) and emission (blue, λ_{exc} = 523 nm) spectra of 1 µM solution of Rhodamine 6G in ethanol. Right: integrated fluorescence intensity vs absorbance plot for Rhodamine 6G.

[5] U. Resch-Genger, K. Rurack, Pure Appl. Chem., **2013**, *85*, 2005–2026.

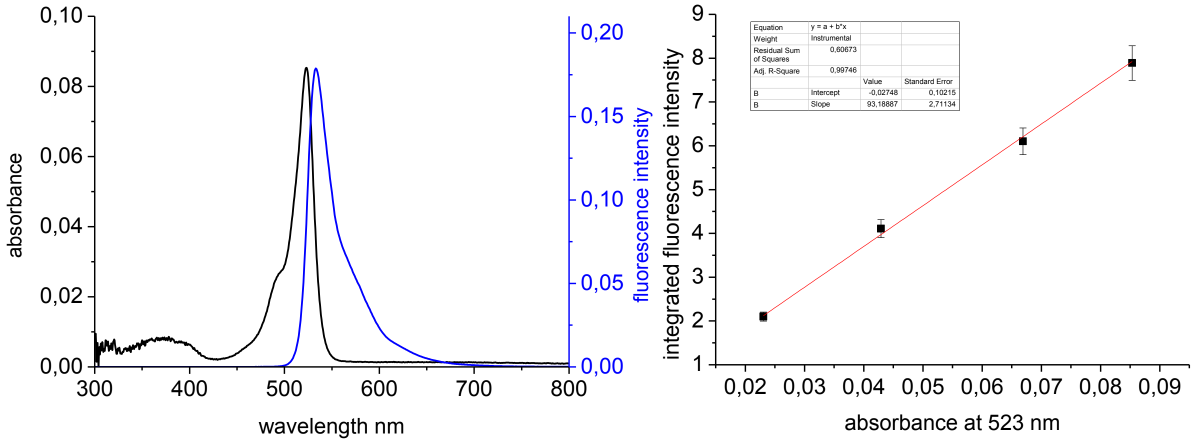


Figure S 39 Left: absorbance (black) and emission (blue, λ_{exc} = 523 nm) spectra of 1 μM solution of [AuCl(**3d**)] in 1,2-dichloroethane. Right: integrated fluorescence intensity vs absorbance plot for [AuCl(**3d**)] complex.

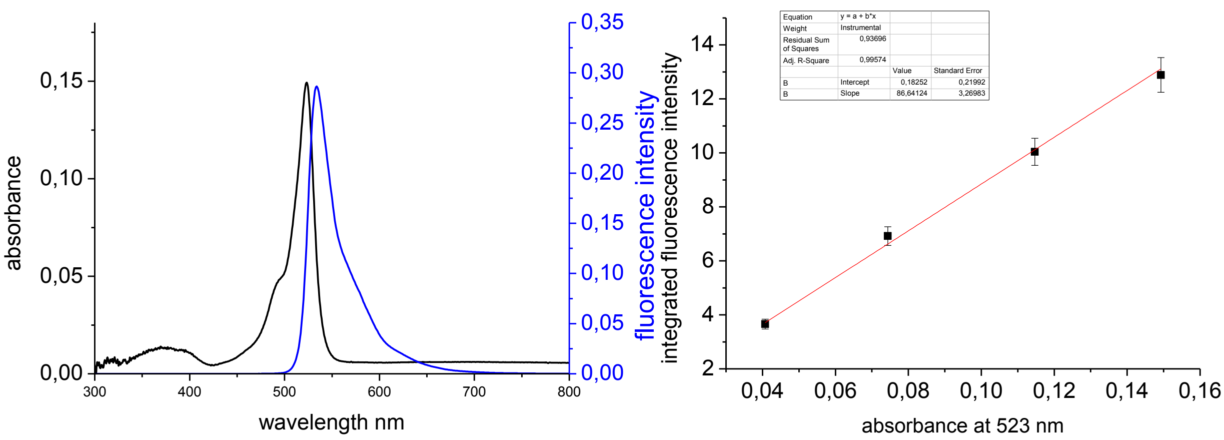


Figure S 40 Left: absorbance (black) and emission (blue, λ_{exc} = 523 nm) spectra of 1 μM solution of [Au(NTf_2)(**3d**)] in 1,2-dichloroethane. Right: integrated fluorescence intensity vs absorbance plot for [Au(NTf_2)(**3d**)] complex.

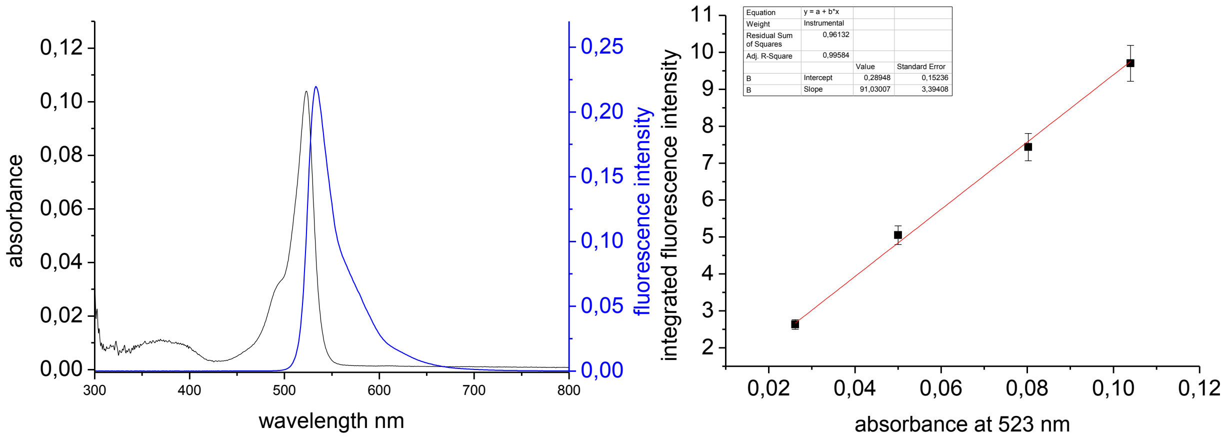


Figure S 41 Left: absorbance (black) and emission (blue, λ_{exc} = 523 nm) spectra of 1 µM solution of [Au(CCPh)(**3d**)] in 1,2-dichloroethane. Right: integrated fluorescence intensity vs absorbance plot for [Au(CCPh)(**3d**)] complex.

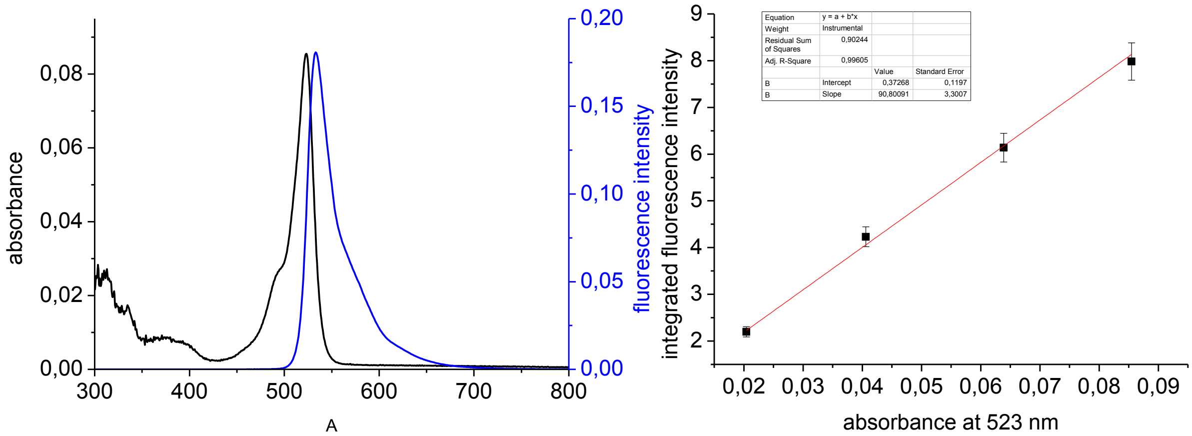


Figure S 42 Left: absorbance (black) and emission (blue, λ_{exc} = 523 nm) spectra of 1 µM solution of [Au(CCPh´´)(**3d**)] in 1,2-dichloroethane. Right: integrated fluorescence intensity vs absorbance plot for [Au(CCPh´´)(**3d**)] complex.

Compound	Fluorescence quantum yield	Absorbance λ_{max}., nm	Emission λ_{max}., nm
[AuCl(**3d**)]	0.86	523	534
[Au(NTf_2)(**3d**)]	0.80	523	534
[Au(CCPh)(**3d**)]	0.84	523	534
[Au(CCPh´´)(**3d**)]	0.83	523	534

Table S 1 Fluorescence quantum yields and spectroscopic data of synthesized compounds

UV/Vis [[AuCl(3a)]

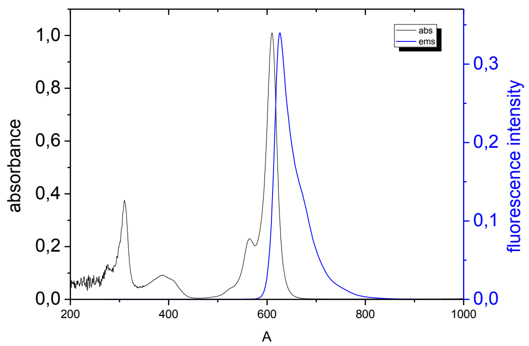


Figure S 43 Absorbance (black, λ_{abs} = 610 nm) and emission (blue, λ_{ems} = 626 nm, λ_{exc}= 523 nm) spectra of $5{\cdot}10^{-5}$ M solution of [[AuCl(**3a**)].

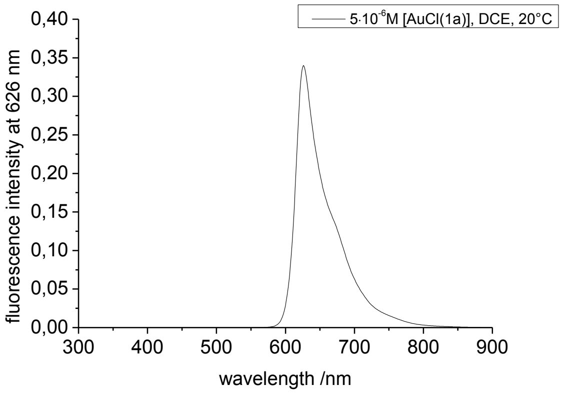


Figure S 44 Emission (blue, λ_{abs} = 610 nm; λ_{ems} = 626 nm, λ_{exc}= 523 nm) spectra of $5.0\cdot10^{-6}$ M solution of [AuCl(**3a**)].

Fluorescence measurements of BODIPY tagged NHC gold complexes

For all FRET reaction monitoring experiments on gold complexes, (λ_{exc}= 500 nm) was chosen. At this excitation wavelength the best relative FRET intensity relative to the emission from the unwanted direct excitation of the acceptor fluorophore by green light was observed. This approach was reported in detail in: O. Halter, I. Fernández, H. Plenio, *Chem. Eur. J.* **2017**, *23*, 711-719.

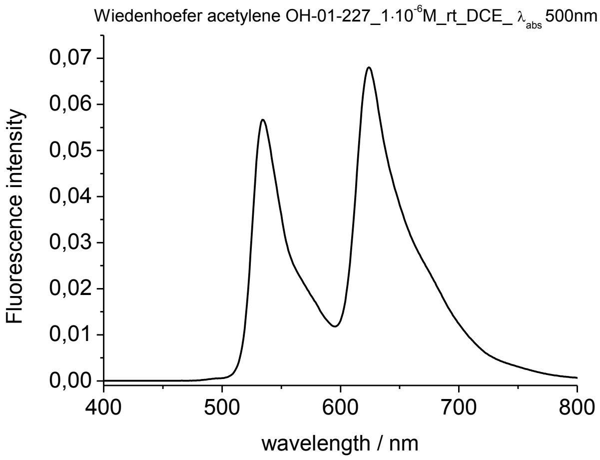


Figure S 45 Fluorescence intensity vs emission wavelength plot of [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2, it was excited at 500 nm. The measurement was carried out in 1,2-dichloroethane (c= $1.0 \cdot 10^{-6}$M) at rt.

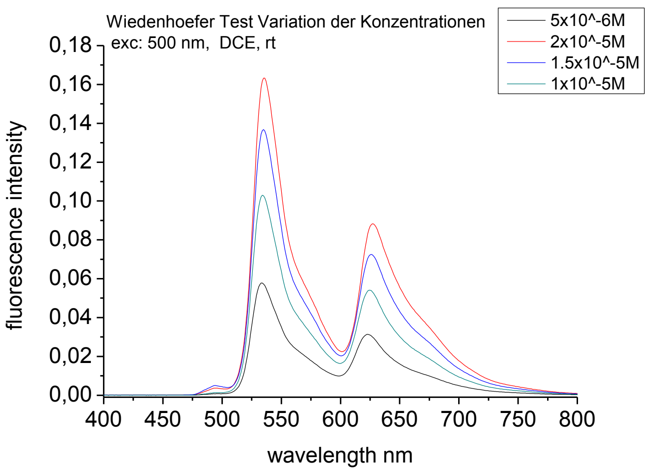


Figure S 46 Variation of concentration for compound [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2. The concentration was within the range from 0.5 to $2.0 \cdot 10^{-5}$ M.

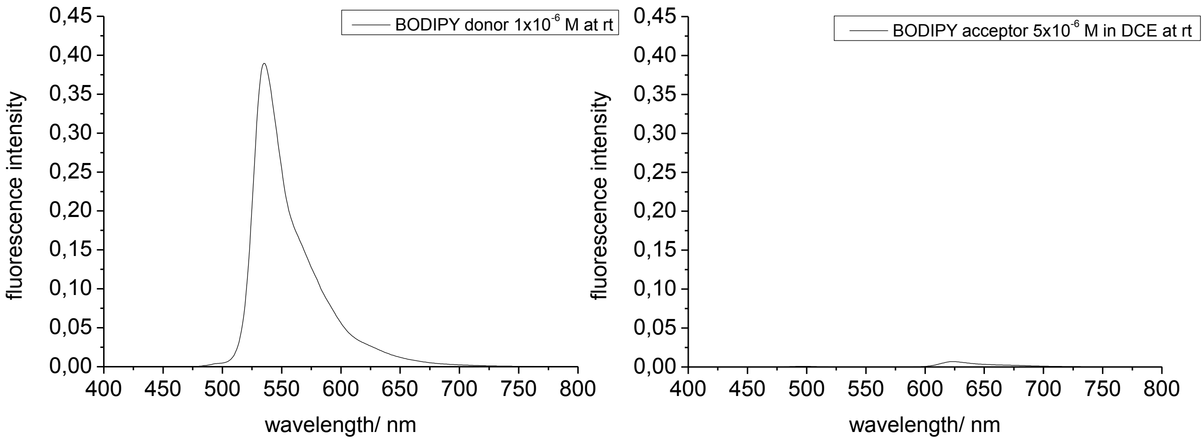


Figure S 47 Left: emission (λ_{exc} = 500 nm) spectra of $5.0{\cdot}10^{-6}$ M solution of BODIPY$_{donor}$ **2d** in 1,2-dichloroethane at rt. Right: emission (λ_{exc} = 500 nm) spectra of $5.0{\cdot}10^{-6}$ M solution of BODIPY$_{acceptor}$ **2a** in 1,2-dichloroethane at r.t.

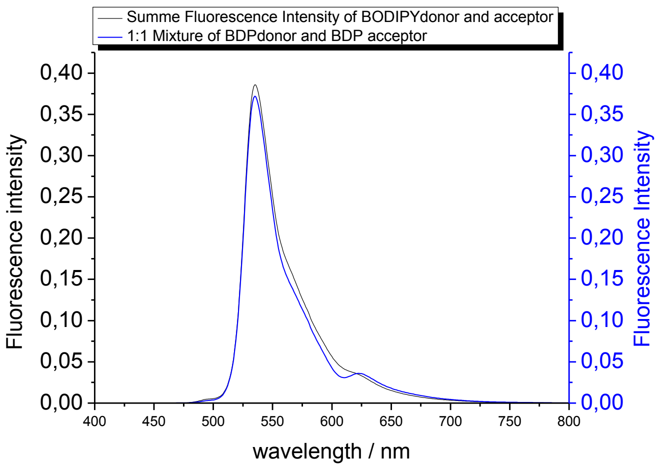


Figure S 48 Black: emission spectra of the sum of the fluorescence intensities of BODIPY$_{donor}$ **2d** and BODIPY$_{acceptor}$ **2a**. Blue: emission (λ_{exc} = 500 nm) spectra of $5.0{\cdot}10^{-6}$ M solution of 1:1 Mixture of BODIPY$_{donor}$ **2d** and BODIPY$_{acceptor}$ **2a** in 1,2-dichloroethane at r.t.

Fluorescence time measurements on “Widenhoefer” and “Hashmi” dimers

General conditions: All experiments were carried out in quartz cuvettes with path length of 10.00 mm equipped with a stirring bar. The temperature (-5°C and 20 °C) was adjusted using a thermostat and controlled with a thermometer. The cuvette was filled with 2 mL of 2.5 and 5 µM solution of the [Au(NTf_2)(**3d**)] in 1,2-dichloroethane. Next the measurement was started and the fluorescence intensity at emission maximum was observed. After approximately 2-3 min 20 and 40 µl of $2.53 \cdot 10^{-4}$ M solution of gold phenylacetylide derivative respectively gold Hashmi acetylide derivative (1eq) in 1,2-dichloroethane was added. The time of addition is indicated with arrows.

Fluorescence time measurements Wiedenhoefer substrates

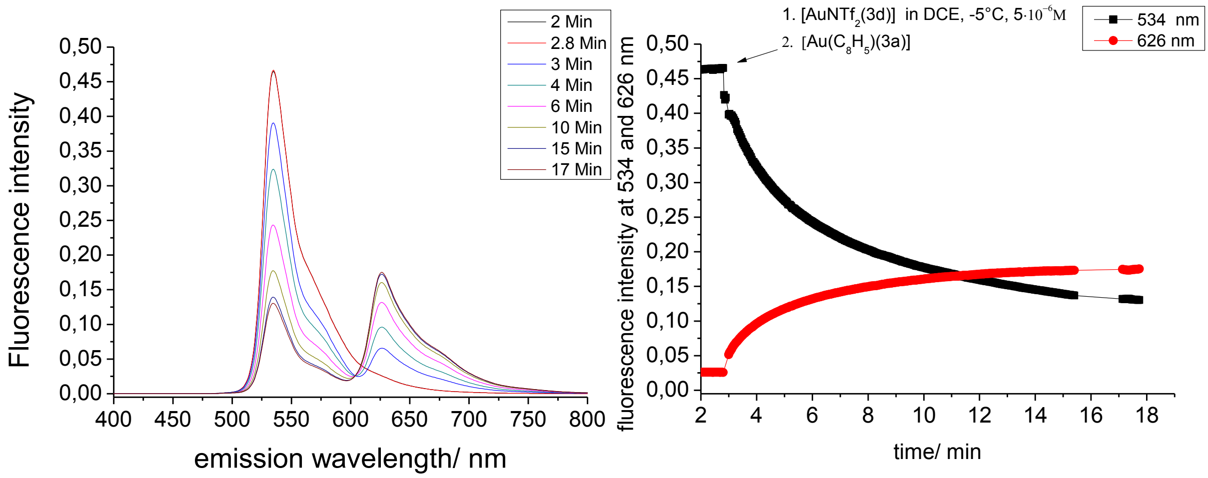
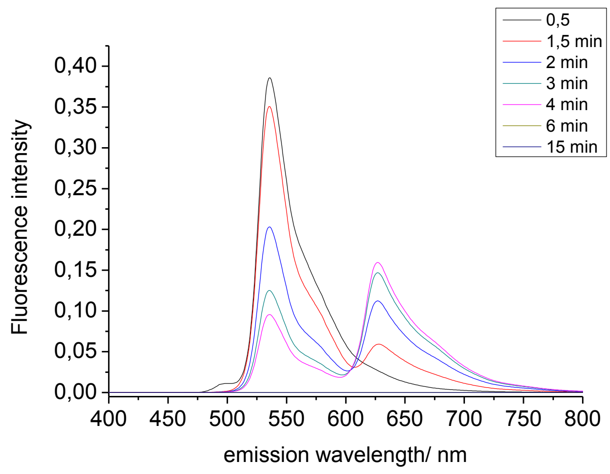


Figure S 49 Left: Plot of the time-dependent fluorescence intensities at 534 nm and 626 nm (λ_{exc}= 500 nm). Right: Fluorescence intensity vs. time plot for the reactions of [Au(NTf_2)(**3d**)] ($c = 5.0 \times 10^{-6}$ mol·L^{-1}) in 1,2-dichloroethane with [Au(CCPh)(**3a**)] (1eq) at -5°C.



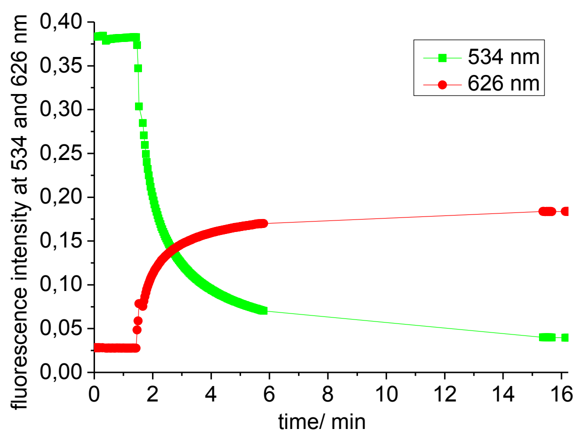
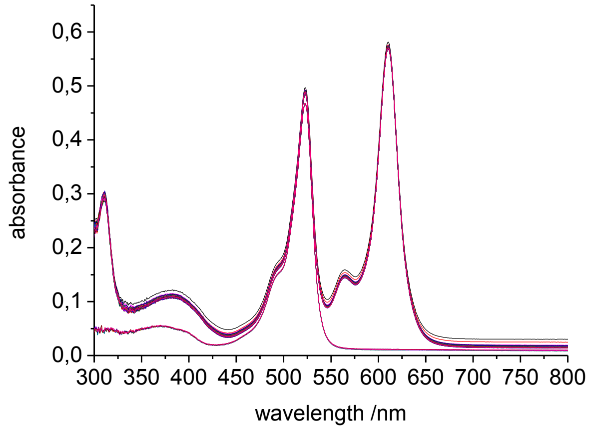


Figure S 50 Left: Plot of the time-dependent fluorescence intensities at 534 nm and 626 nm (λ_{exc}= 500 nm). Right: Fluorescence intensity vs. time plot for the reactions of [Au(NTf$_2$)(**3d**)] (c = 5.0 × 10^{-6} mol·L^{-1}) in 1,2-dichloroethane with [Au(CCPh)(**3a**)] (1eq) at 20°C.

Absorbance time measurements Wiedenhoefer substrates



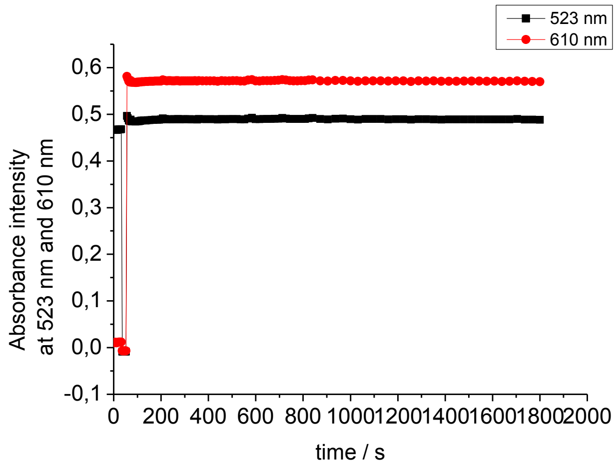


Figure S 51 Left: Plot of the time-dependent absorbance intensities at 526 nm and 610 nm. Right: Absorbance intensity vs. time plot for the reactions of [Au(NTf$_2$)(**3d**)] (c = 5.0 × 10^{-6} mol·L^{-1}) in 1,2-dichloroethane with [Au(CCPh)(**3a**)] (1eq) at 20°C.

Fluorescence time measurements Hashmi substrates

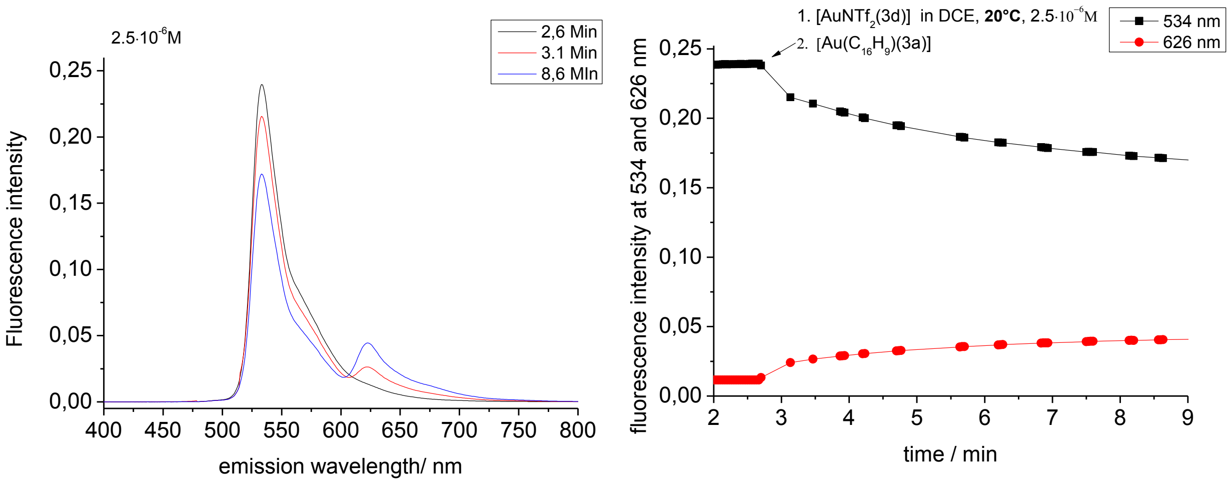


Figure S 52 Left: Plot of the time-dependent fluorescence intensities at 534 nm and 626 nm (λ_{exc}= 500 nm). Right: Fluorescence intensity vs. time plot for the reactions of [Au(NTf$_2$)(**3d**)] (c = 2.5 × 10^{-6} mol·L^{-1}) in 1,2-dichloroethane with [Au(CCPh´´)(**3a**)] (1eq) at 20°C.

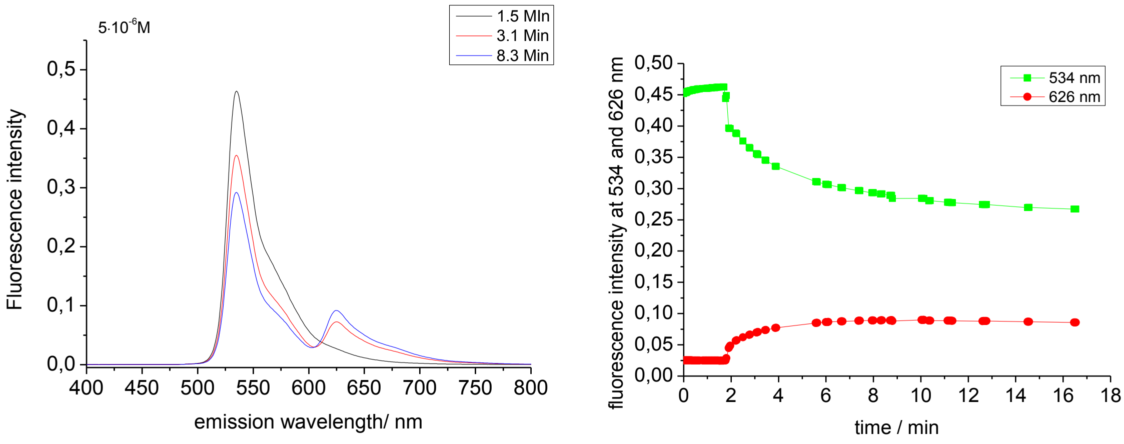
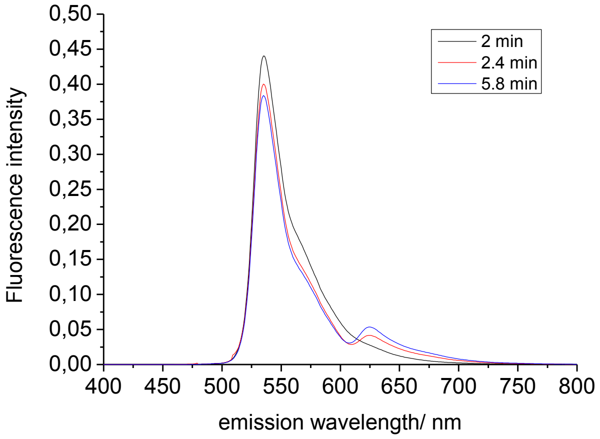


Figure S 53 Left: Plot of the time-dependent fluorescence intensities at 534 nm and 626 nm (λ_{exc}= 500 nm). Right: Fluorescence intensity vs. time plot for the reactions of [Au(NTf$_2$)(**3d**)] (c = 5.0 × 10^{-6} mol·L^{-1}) in 1,2-dichloroethane with [Au(CCPh´´)(**3a**)] (1eq) at -5°C.



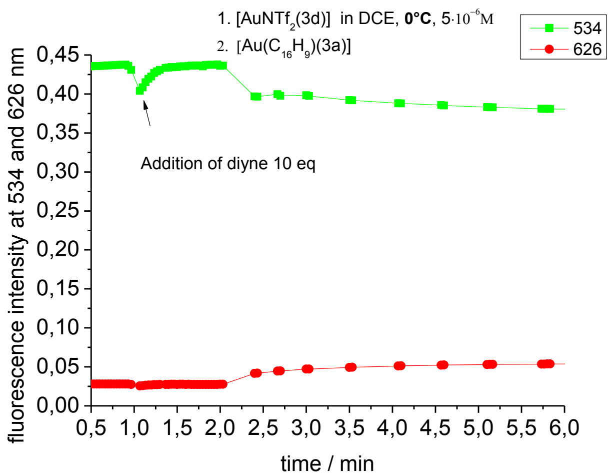


Figure S 54 Left: Plot of the time-dependent fluorescence intensities at 534 nm and 626 nm (λ_{exc}= 500 nm). Right: Fluorescence intensity vs. time plot for the catalytic reactions of [Au(NTf$_2$)(**3d**)] (1eq) (c = 5.0 × 10^{-6} mol·L^{-1}) and 1-Ethynyl-2-(phenylethynyl)benzene (c = 5.0 × 10^{-5} mol·L^{-1} in 1,2-dichloroethane) with [Au(CCPh´´)(**3a**)] (1eq) at 0°C.

5. Mass spectrometry

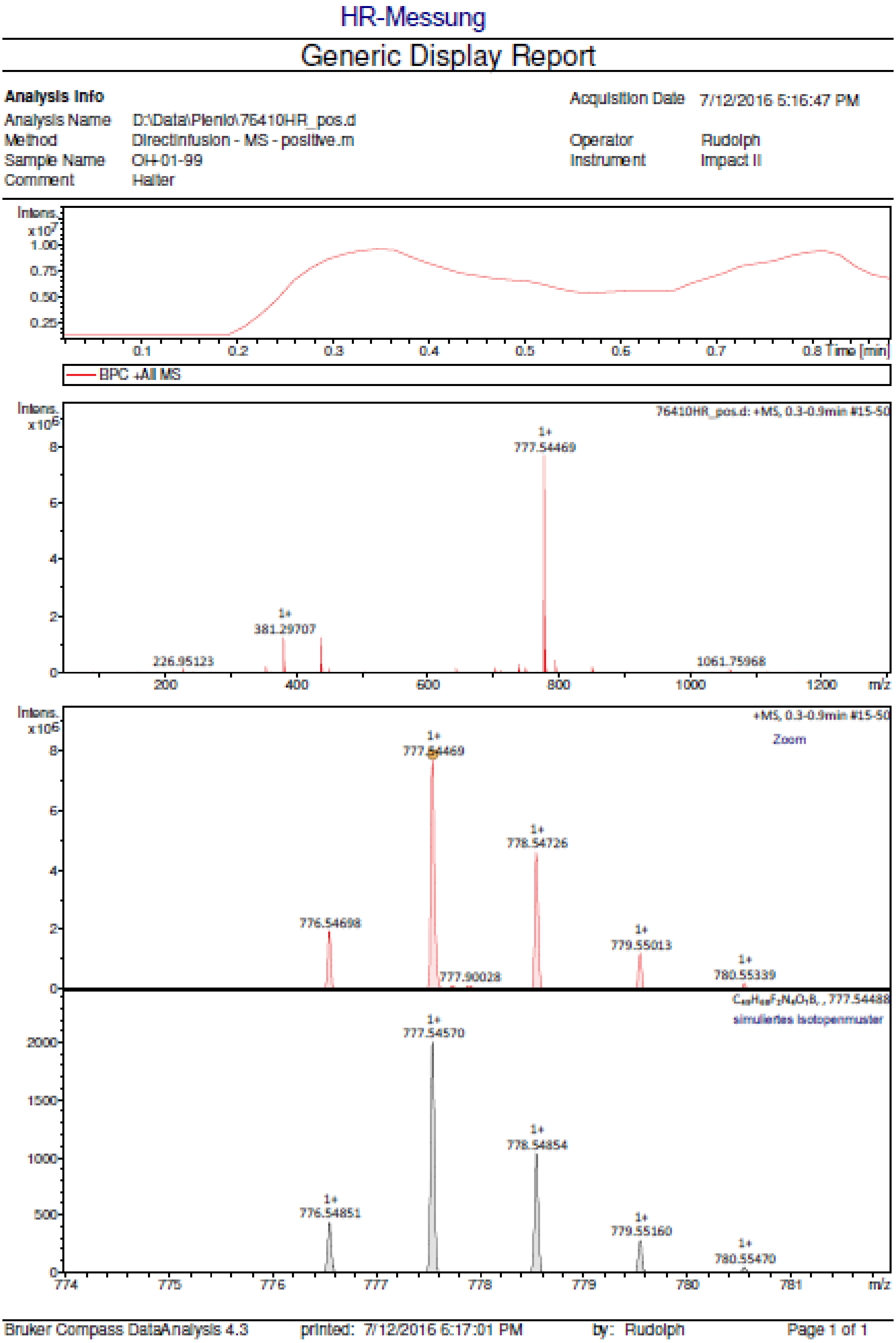


Figure S 55 mass spectrum of **3d**·HCl.

HR-Messung

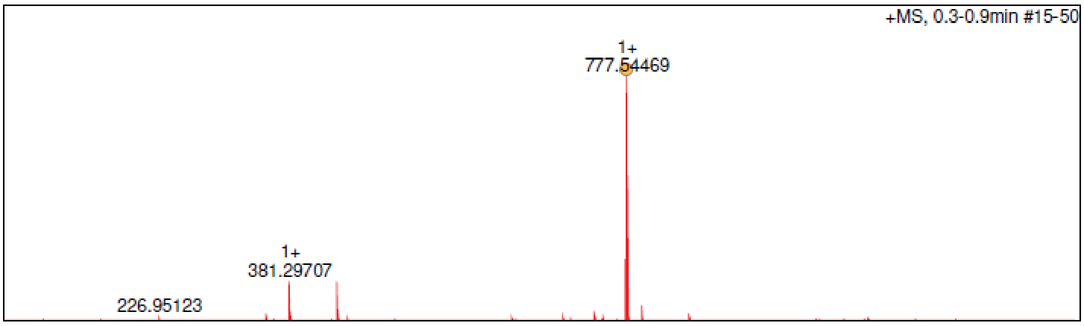
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Plenio\76410HR_pos.d	Acquisition Date	7/12/2016 5:16:47 PM
Method	DirectInfusion - MS - positive.m	Operator	Rudolph
Sample Name	OH-01-99	Instrument	impact II 1825265.10135
Comment	Halter		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1300 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
777.54469	1	C49H68BF2N4O	100.00	777.54488	1.01	1.30	38.5	17.5	even	ok	M

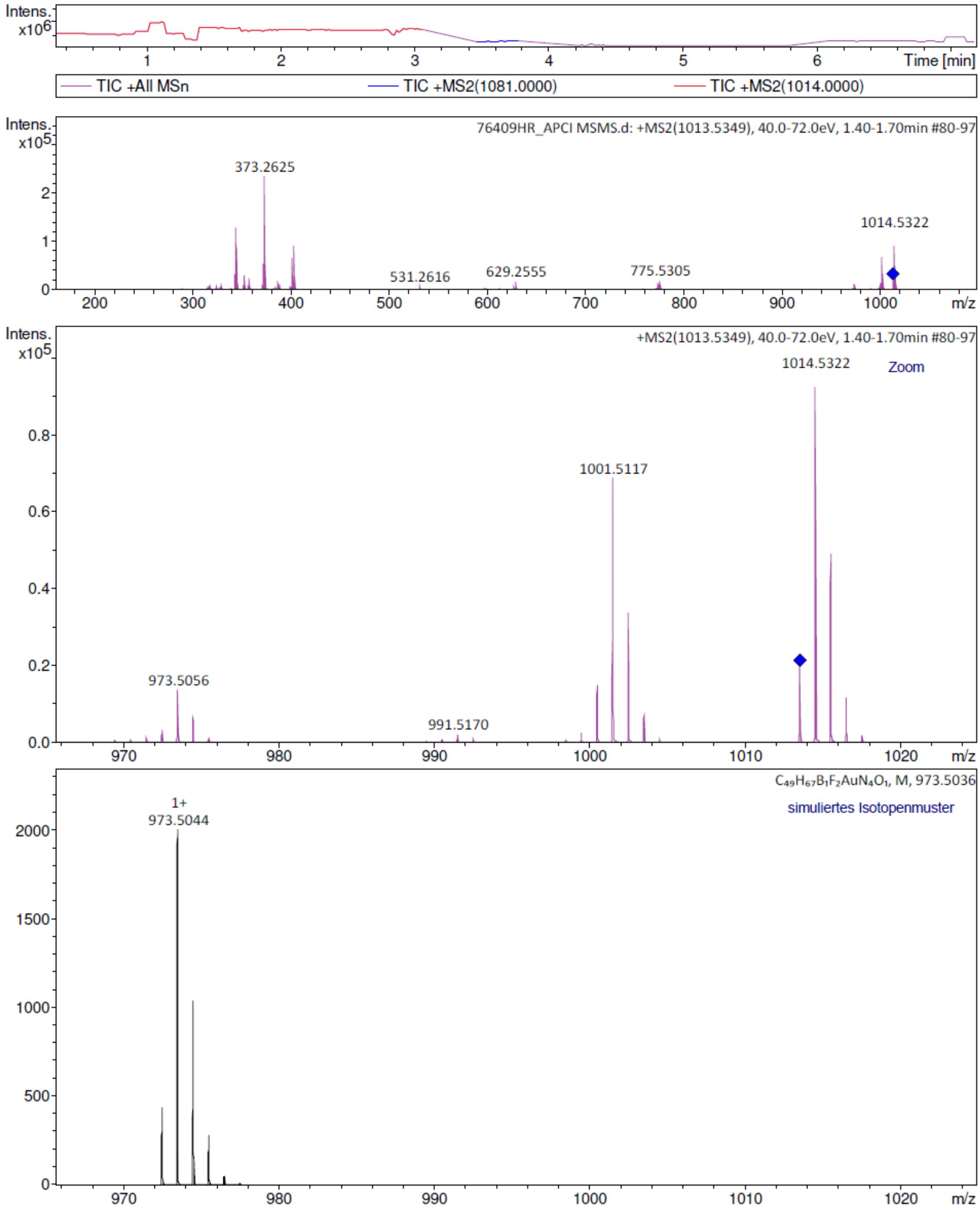
Figure S 56 mass spectrum of **3d**·HCl.

MSMS-APCI-Messung

Generic Display Report

Analysis Info

Analysis Name	D:\Data\Plenio\76409HR_APCI MSMS.d	Acquisition Date	7/13/2016 4:29:37 PM
Method	APCI_pos.m	Operator	Rudolph
Sample Name	OH-01-137	Instrument	impact II
Comment	Halter		



Bruker Compass DataAnalysis 4.3 printed: 7/18/2016 5:58:34 PM by: Rudolph Page 1 of 1

Figure S 57 mass spectrum [AuCl(**3d**)].

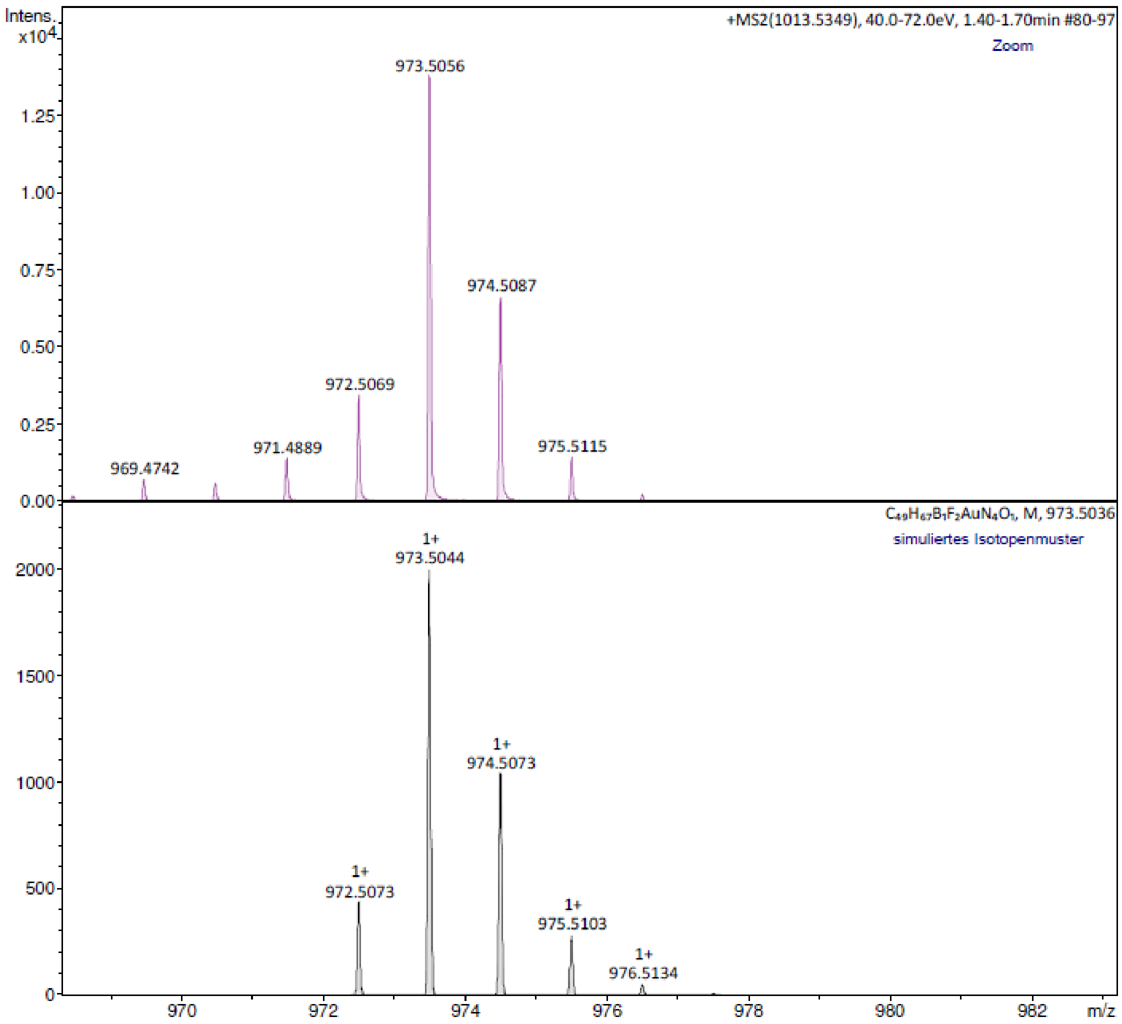
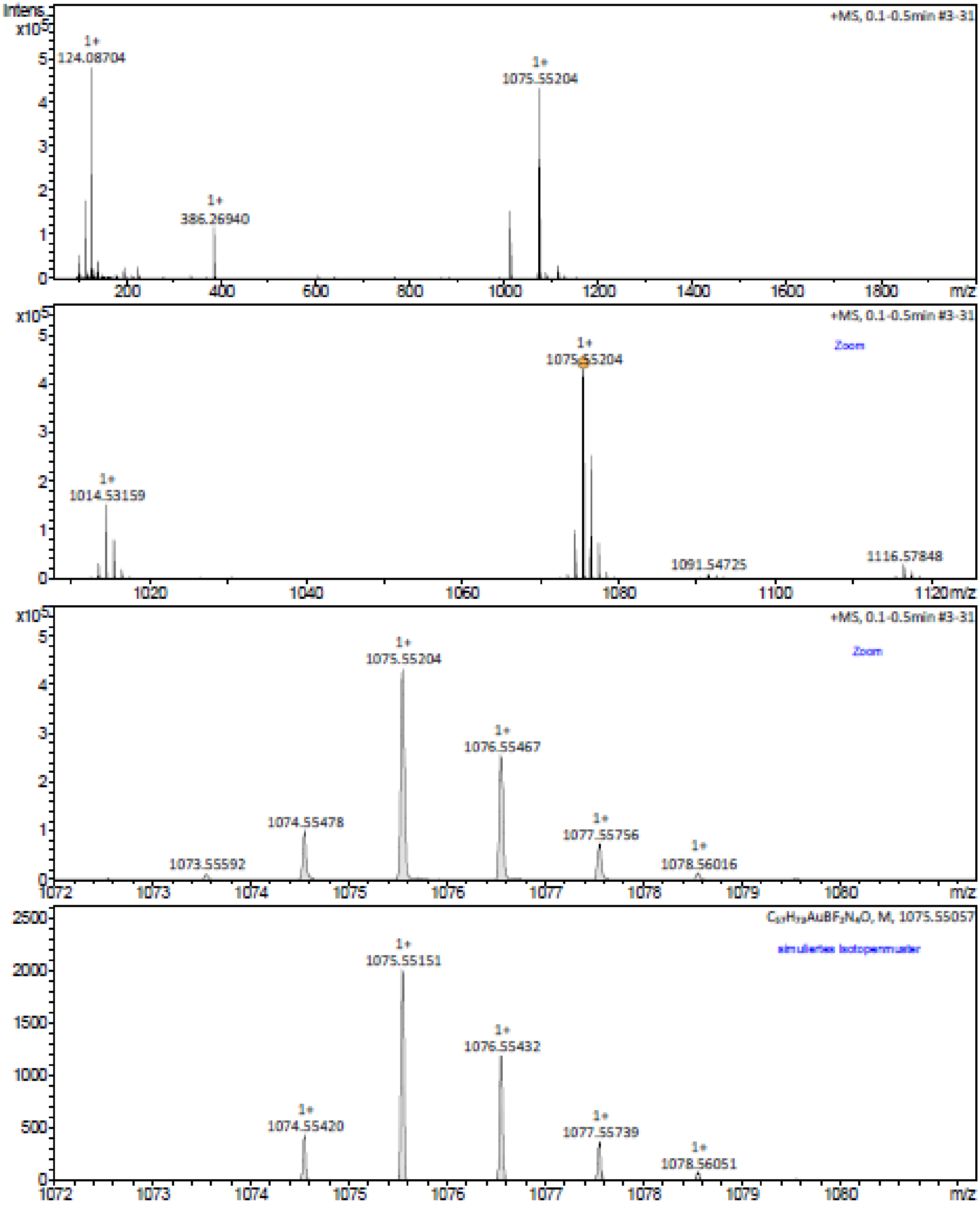


Figure S 58 mass spectrum [AuCl(**3d**)].

Accurate Mass Measurement

Analysis	D:\Data\Plenio\77065APCI-HR000001.d	Acquisition Date	1/17/2017 11:39:15 AM
Sample Name	OH-01-222-4	Ionisation	APCI Positive
Method	APCI_pos.m	Mass Range	50 m/z - 3000 m/z
Client	Halter	Operator	Rudolph



Mass Spectrometry Facility, Department of Chemistry, Technische Universität Darmstadt Instrument: Bruker Impact II

Figure S 59 mass spectrum [Au(CCPh)(**3d**)].

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Sum Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
1075.55204	1	C57H73AuBF2N4O	C57H73AuBF2N4O	1075.55057	-0.52	-0.48		11.1	22.5 even	ok	M
	2	C59H75AuBF2NO2	C59H75AuBF2NO2	1075.55191	0.85	0.79		15.8	22.0 odd	ok	M
	3	C62H74AuBFNO	C62H74AuBFNO	1075.55077	-0.25	-0.23		28.8	26.0 odd	ok	M
	1	C57H73AuBF2N4O	C57H72AuBF2N4O	1075.55057	-0.52	-0.48		11.1	22.5 even	ok	M+H
	2	C59H75AuBF2NO2	C59H74AuBF2NO2	1075.55191	0.85	0.79		15.8	22.0 odd	ok	M+H
	3	C62H74AuBFNO	C62H73AuBFNO	1075.55077	-0.25	-0.23		28.8	26.0 odd	ok	M+H

Figure S 60 mass spectrum [Au(CCPh)(**3d**)].

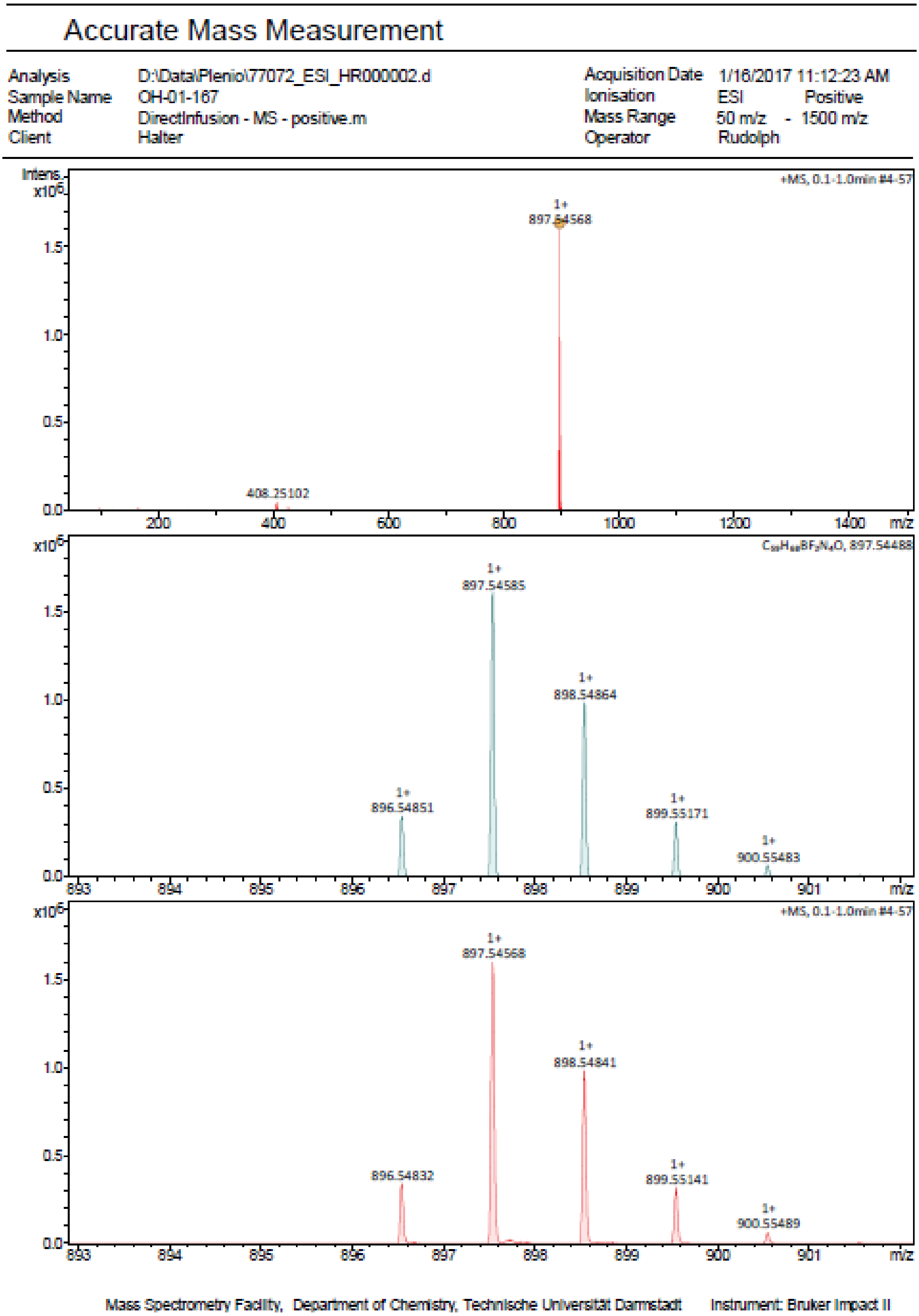


Figure S 61 mass spectrum **3a**·HCl.

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
897.54568	1	C59H68BF2N4O	100.00	897.54488	0.17	0.19	1.6	27.5	even	ok	M
	2	C63H69N4O	25.16	897.54659	0.91	1.01	46.5	31.5	even	ok	M

Figure S 62 mass spectrum **3a**·HCl.

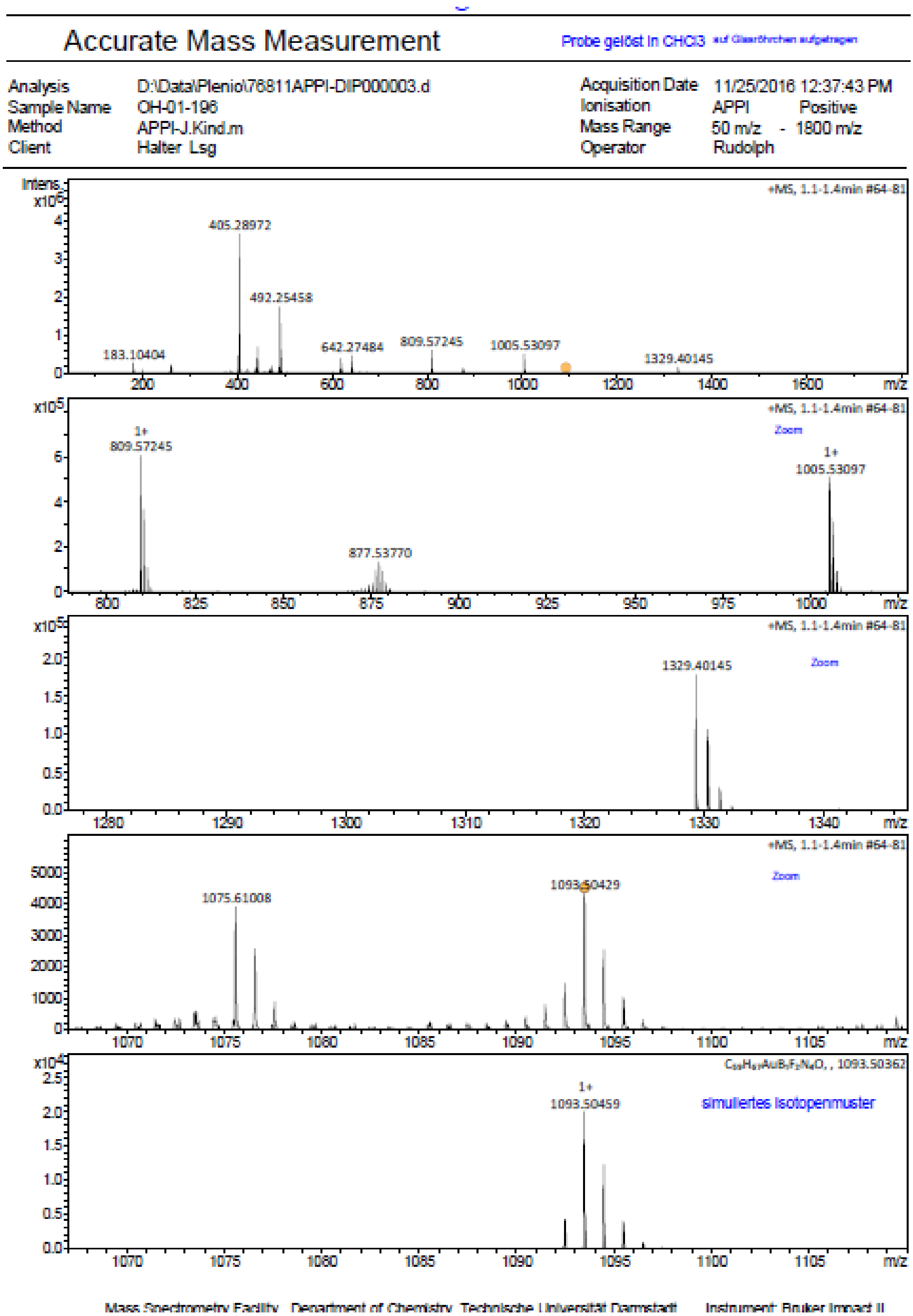


Figure S63 mass spectrum [AuCl(**3a**].

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Sum Formula	m/z	err [mDa]	err [ppm]	e⁻ Conf	N-Rule	Adduct
1093.50429	1	C59H67AuBF2N4O	C59H67AuBF2N4O	1093.50362	0.30	0.27	even	ok	M
	2	C76H62BF2N5	C76H62BF2N5	1093.50609	2.99	2.73	odd	ok	M
	3	C65H191BF2N4O	C65H191BF2N4O	1093.50736	4.14	3.79	odd	ok	M
	4	C78H64BF2N2O	C78H64BF2N2O	1093.50743	4.36	3.98	even	ok	M
	5	C71H191BF2	C71H191BF2	1093.50014	-2.99	-2.74	odd	ok	M
	6	C53H196AuBF2N	C53H196AuBF2N	1093.50891	5.53	5.06	even	ok	M

Figure S64 mass spectrum [AuCl(**3a**].

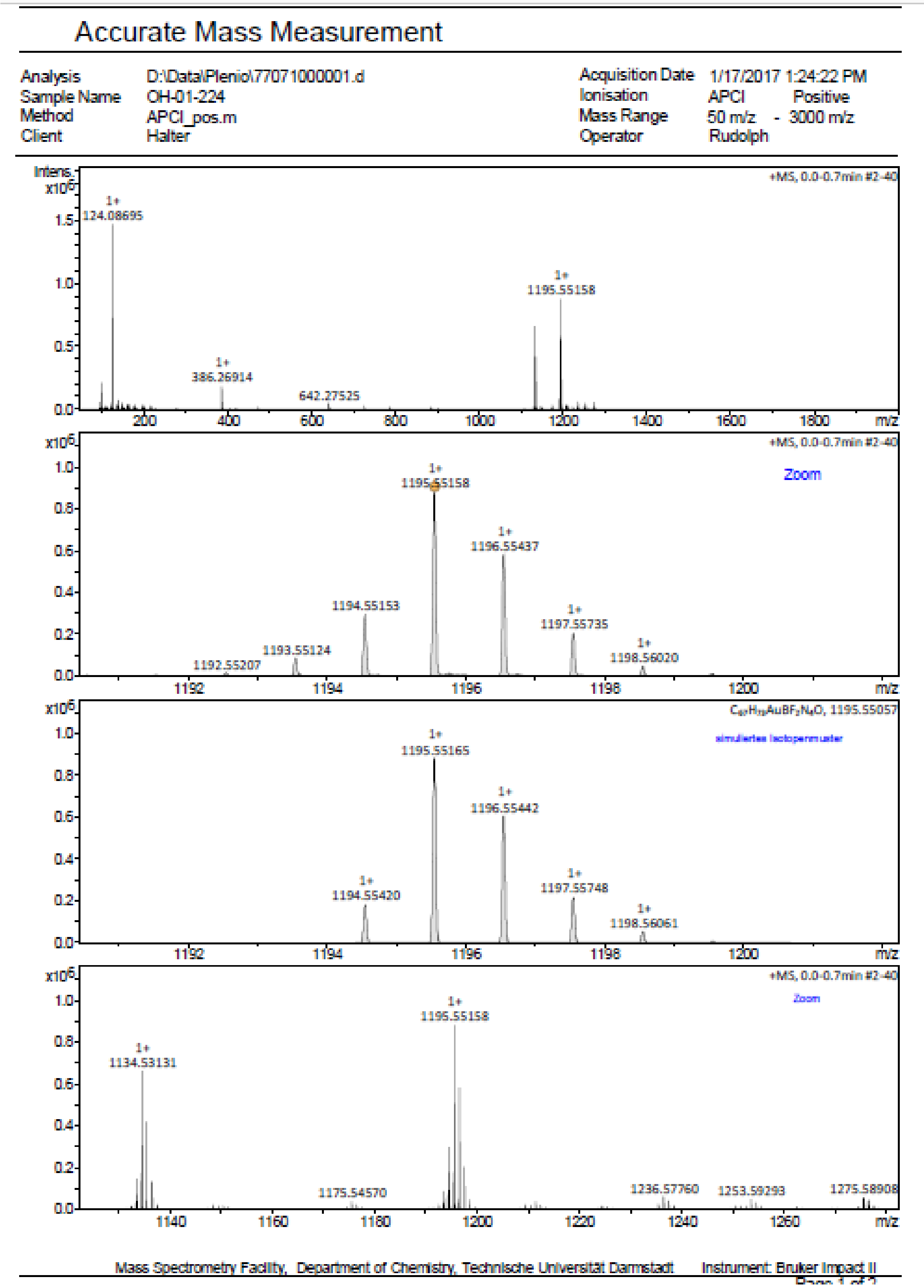


Figure S 65 mass spectrum [Au(CCPh)(**3a**)].

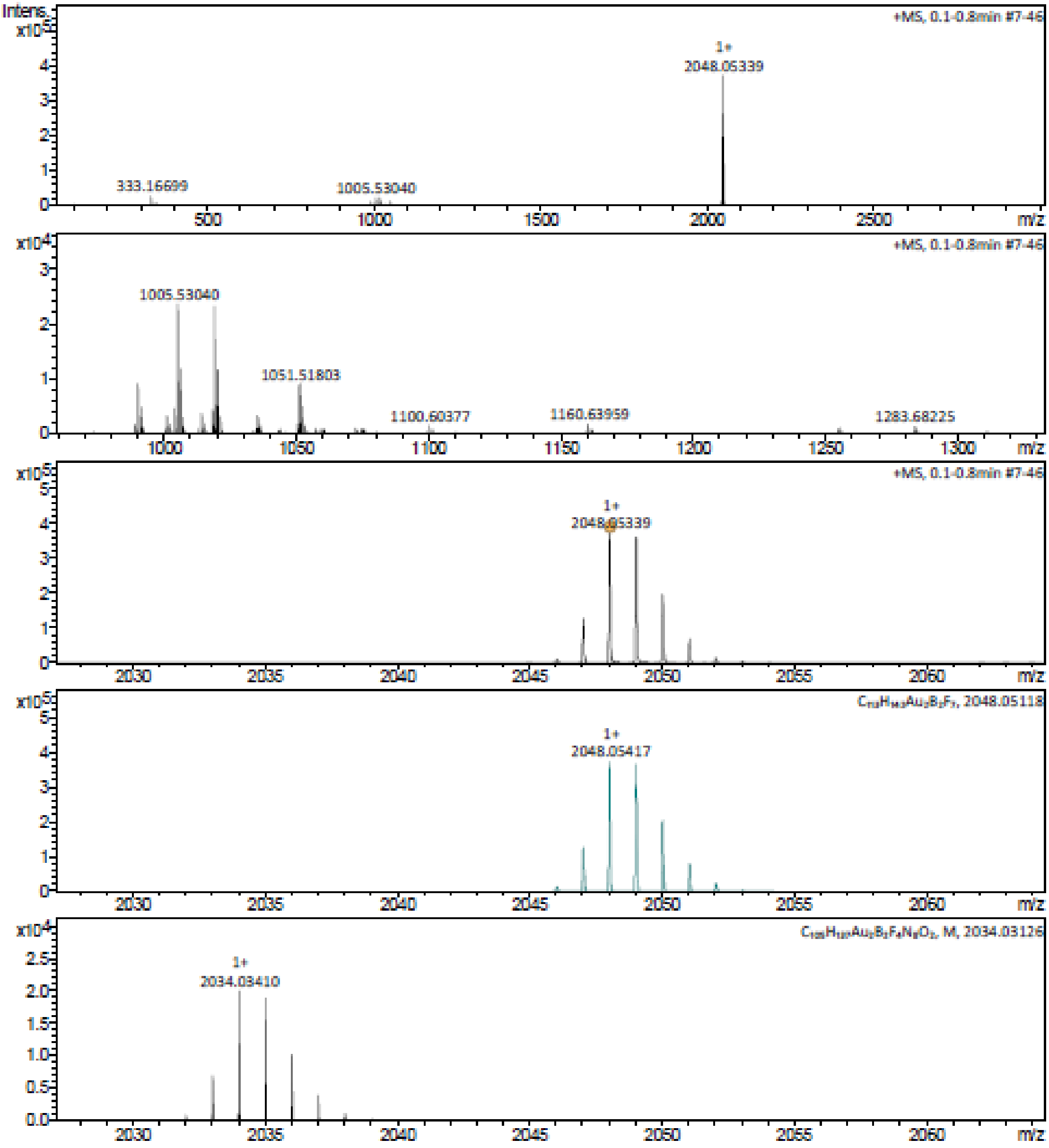
Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Sum Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
1195.55158	1	C67H73AuBF2N4O	C67H73AuBF2N4O	1195.55057	0.07	0.06	53.8	32.5	even	ok	M
	2	C69H75AuBF2NO2	C69H75AuBF2NO2	1195.55191	1.44	1.21	55.7	32.0	odd	ok	M
	3	C72H74AuBFNO	C72H74AuBFNO	1195.55077	0.34	0.28	62.3	36.0	odd	ok	M
	1	C67H73AuBF2N4O	C67H72AuBF2N4O	1195.55057	0.07	0.06	53.8	32.5	even	ok	M+H
	2	C69H75AuBF2NO2	C69H74AuBF2NO2	1195.55191	1.44	1.21	55.7	32.0	odd	ok	M+H
	3	C72H74AuBFNO	C72H73AuBFNO	1195.55077	0.34	0.28	62.3	36.0	odd	ok	M+H

Figure S 66 mass spectrum [Au(CCPh)(**3a**)].

Accurate Mass Measurement

Analysis	D:\Data\Plenio\77286000002.d	Acquisition Date	3/16/2017 1:52:44 PM
Sample Name	77286	Ionisation	ESI Positive
Method	DirectInfusion 50-3000 - MS - positive.m	Mass Range	50 m/z - 3000 m/z
Client	Halter	Operator	Rudolph



Mass Spectrometry Facility, Department of Chemistry, Technische Universität Darmstadt Instrument: Bruker Impact II

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Figure S 67 mass spectrum [(Au(**3d**))(Au(CCPh)(**3d**))]NTf_2.

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
2048.05339	1	C113H142Au2B2F7	100.00	2048.05118	0.78	0.38	17.5	39.5	even	ok	M+H
	2	C110H146Au2B2F7S	4.15	2048.05455	4.10	2.00	32.1	34.5	even	ok	M+H

Figure S 68 mass spectrum [(Au(**3d**))(Au(CCPh)(**3d**))]NTf_2.

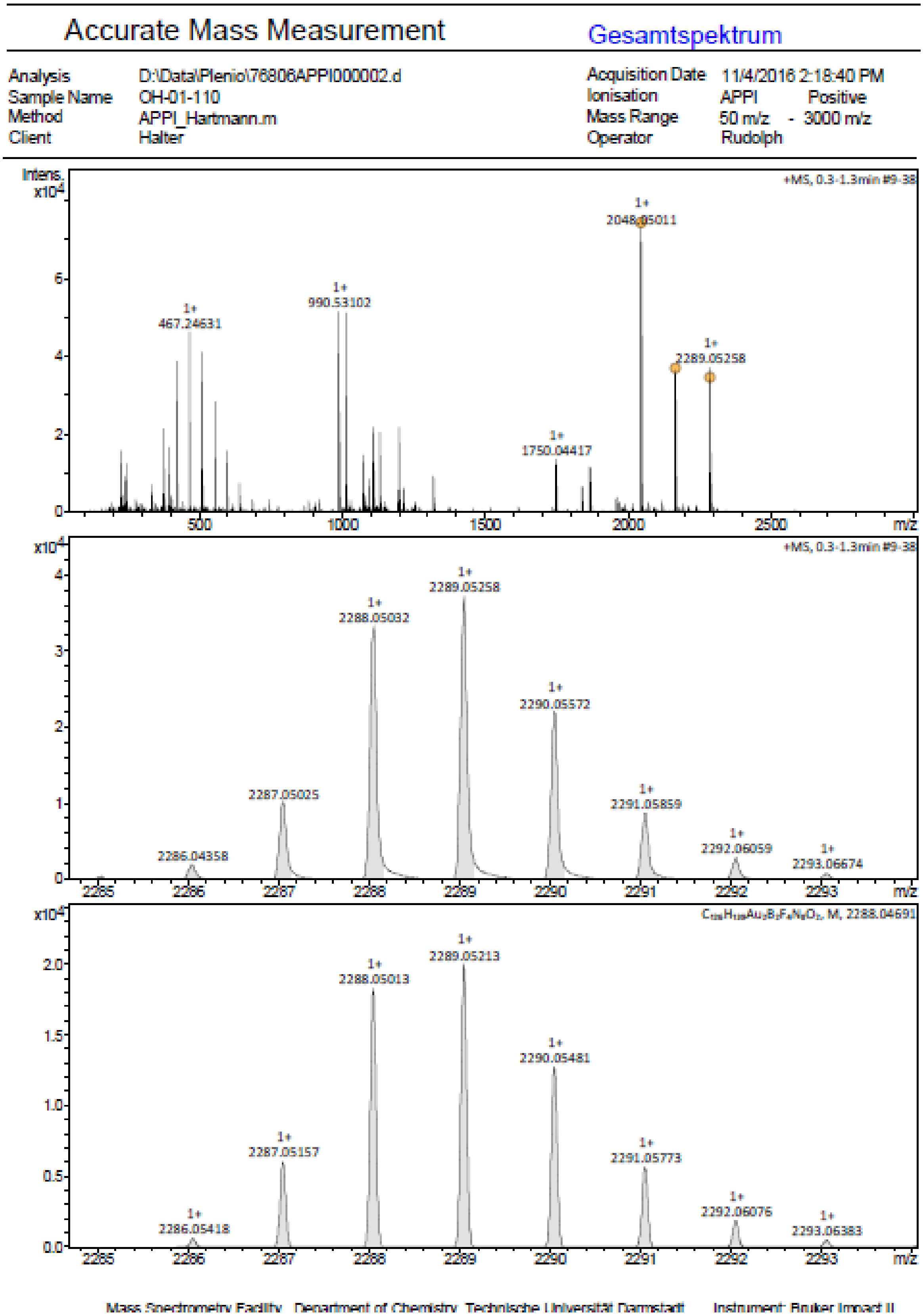

Figure S69 mass spectrum [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2.

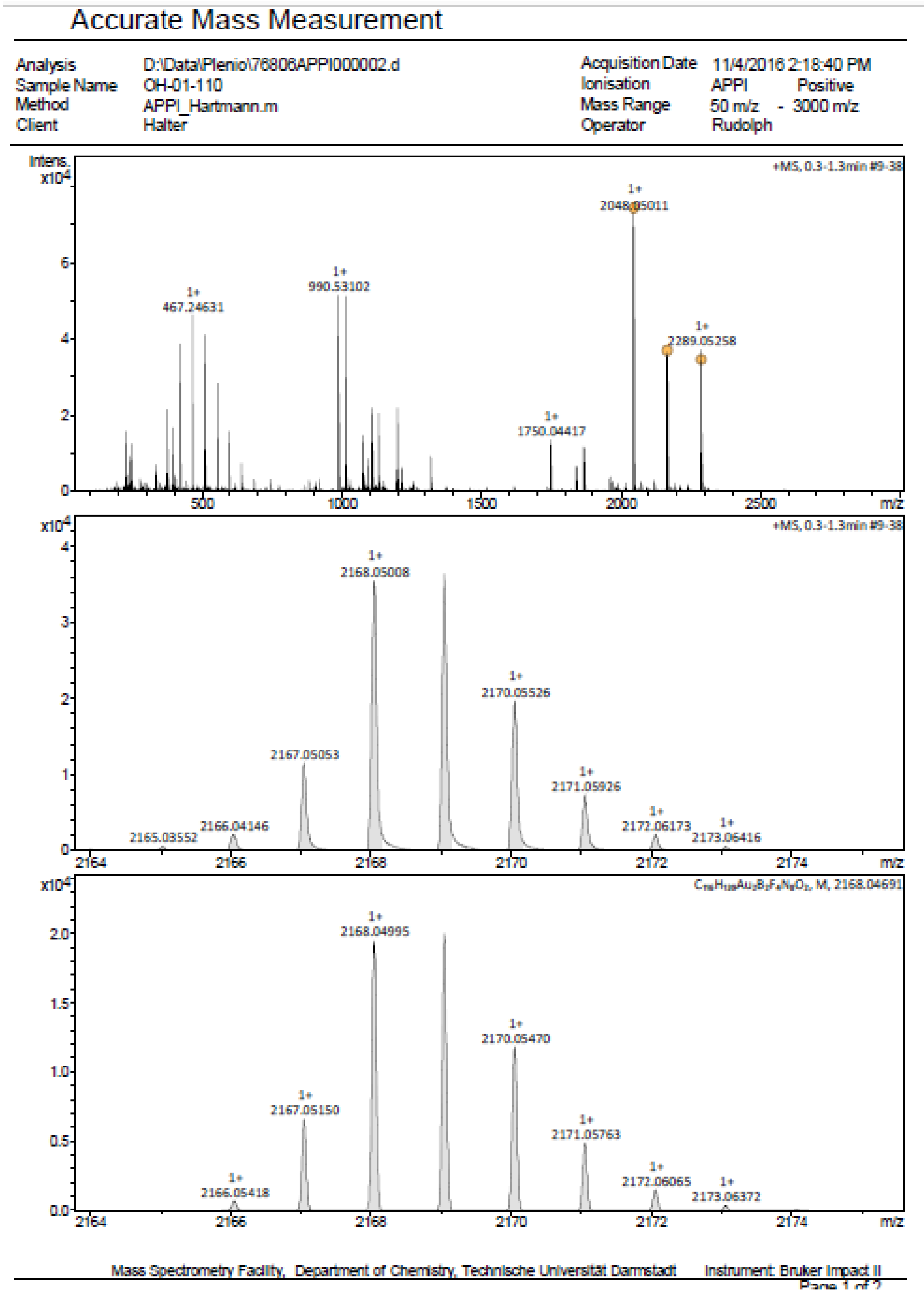

Figure S70 mass spectrum [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2.

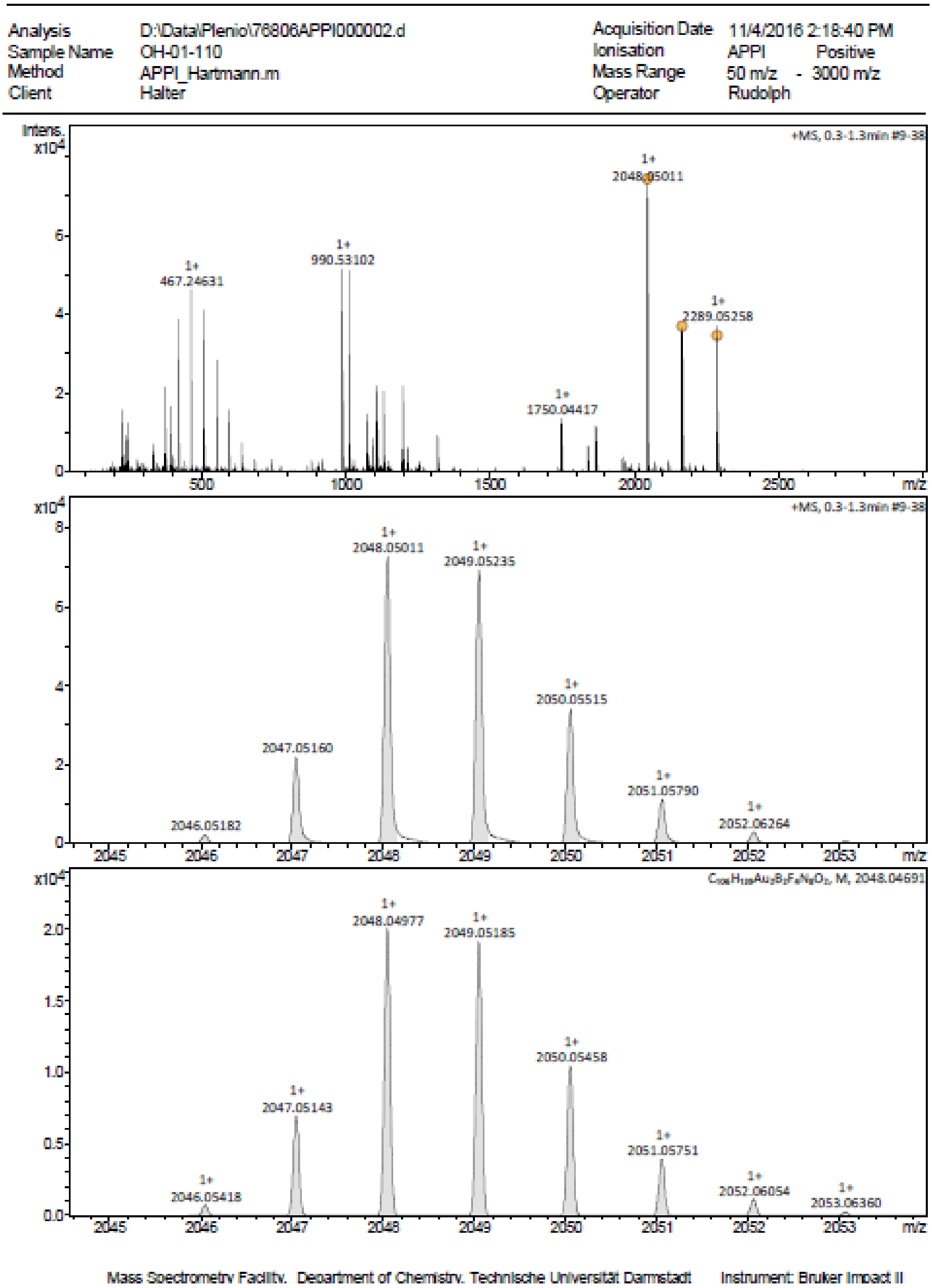

Figure S71 mass spectrum [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2.

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Sum Formula	m/z	err [mDa]	err [ppm]	rdb	e¯ Conf	Adduct
2048.05011	1	C106H139Au2B2F4N8O2	C106H139Au2B2F4N8O2	2048.04691	-0.34	-0.17	39.5	even	M
	2	C108H141Au2B2F4N5O3	C108H141Au2B2F4N5O3	2048.04826	1.04	0.51	39.0	odd	M
	3	C114H139Au2B2F2N5O	C114H139Au2B2F2N5O	2048.04597	-1.13	-0.55	47.0	odd	M
2168.05008	1	C116H139Au2B2F4N8O2	C116H139Au2B2F4N8O2	2168.04691	-0.13	-0.06	49.5	even	M
	2	C118H141Au2B2F4N5O3	C118H141Au2B2F4N5O3	2168.04826	1.26	0.58	49.0	odd	M
	3	C120H143Au2B2F4N2O4	C120H143Au2B2F4N2O4	2168.04960	2.64	1.22	48.5	even	M
2288.05032	1	C126H139Au2B2F4N8O2	C126H139Au2B2F4N8O2	2288.04691	-0.19	-0.08	59.5	even	M
	2	C128H141Au2B2F4N5O3	C128H141Au2B2F4N5O3	2288.04826	1.19	0.52	59.0	odd	M
	3	C130H143Au2B2F4N2O4	C130H143Au2B2F4N2O4	2288.04960	2.57	1.13	58.5	even	M

Figure S72 mass spectrum [(Au(**3a**))(Au(CCPh)(**3d**))]NTf_2.

APPI-HR-Messung

Mass spectrum

Analysis	D:\Data\Plenio\76806APPI000002.d	Acquisition Date	11/4/2016 2:18:40 PM
Sample Name	OH-01-110	Ionisation	APPI Positive
Method	APPI_Hartmann.m	Mass Range	50 m/z - 3000 m/z
Client	Halter	Operator	Rudolph

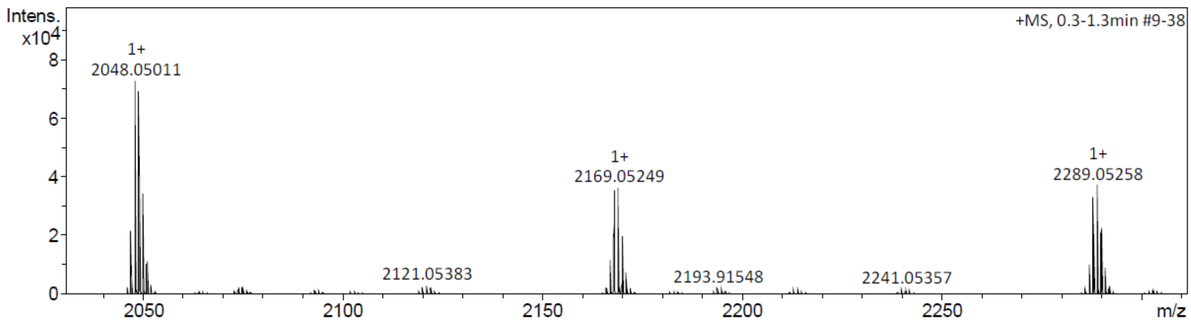

Figure S 73 mass spectrum [(Au(**3a**))(Au(Au(CCPh)(**3d**))]NTf_2.

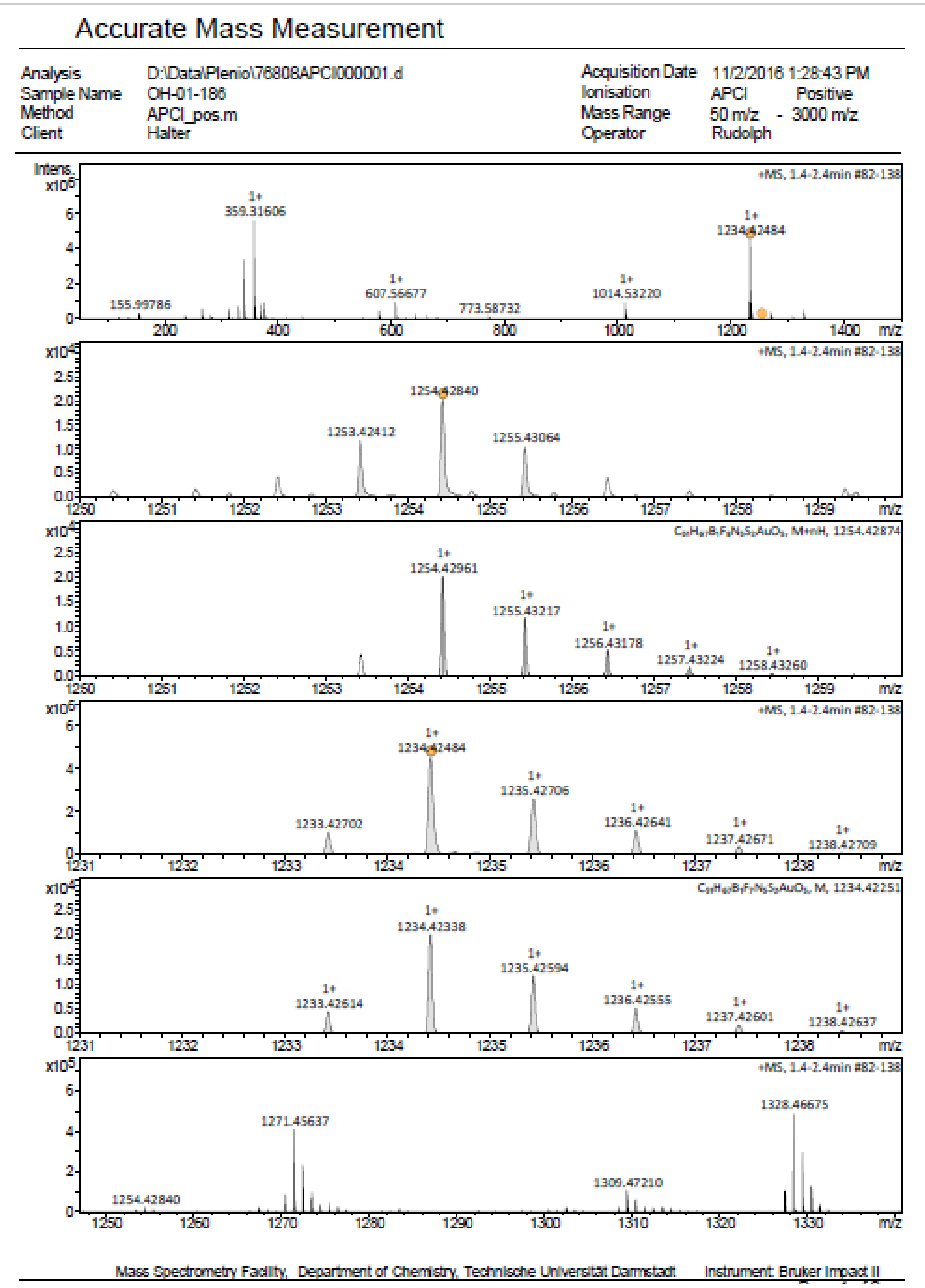

Figure S 74 mass spectrum of [(Au(NTf$_2$)(3**d**)].

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Sum Formula	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule	Adduct
1234.42484	1	C51H67AuBF7N5O5S2	C51H67AuBF7N5O5S2	1234.42251	-1.46	-1.18	17.5	even	ok	M
	2	C54H65AuBF7N6O2S2	C54H65AuBF7N6O2S2	1234.42519	1.26	1.02	22.0	odd	ok	M
	3	C52H69AuF6N5O6S2	C52H69AuF6N5O6S2	1234.42537	0.53	0.43	17.5	even	ok	M
	4	C55H64AuF7N6O4S	C55H64AuF7N6O4S	1234.42582	0.98	0.79	23.0	odd	ok	M
	5	C55H68AuF5N5O5S2	C55H68AuF5N5O5S2	1234.42422	-0.61	-0.50	21.5	even	ok	M
	6	C53H64AuBF6N6O6S	C53H64AuBF6N6O6S	1234.42655	2.60	2.11	22.0	odd	ok	M
1254.42840	1	C55H69AuF6N5O5S2	C55H68AuF6N5O5S2	1254.43045	2.05	1.64	20.5	even	ok	M+H
	2	C51H68AuBF8N5O5S2	C51H67AuBF8N5O5S2	1254.42874	1.21	0.96	16.5	even	ok	M+H
	3	C54H67AuBF7N5O4S2	C54H66AuBF7N5O4S2	1254.42760	0.11	0.09	20.5	even	ok	M+H

Figure S 75 mass spectrum of [(Au(NTf_2)(3**d**)].

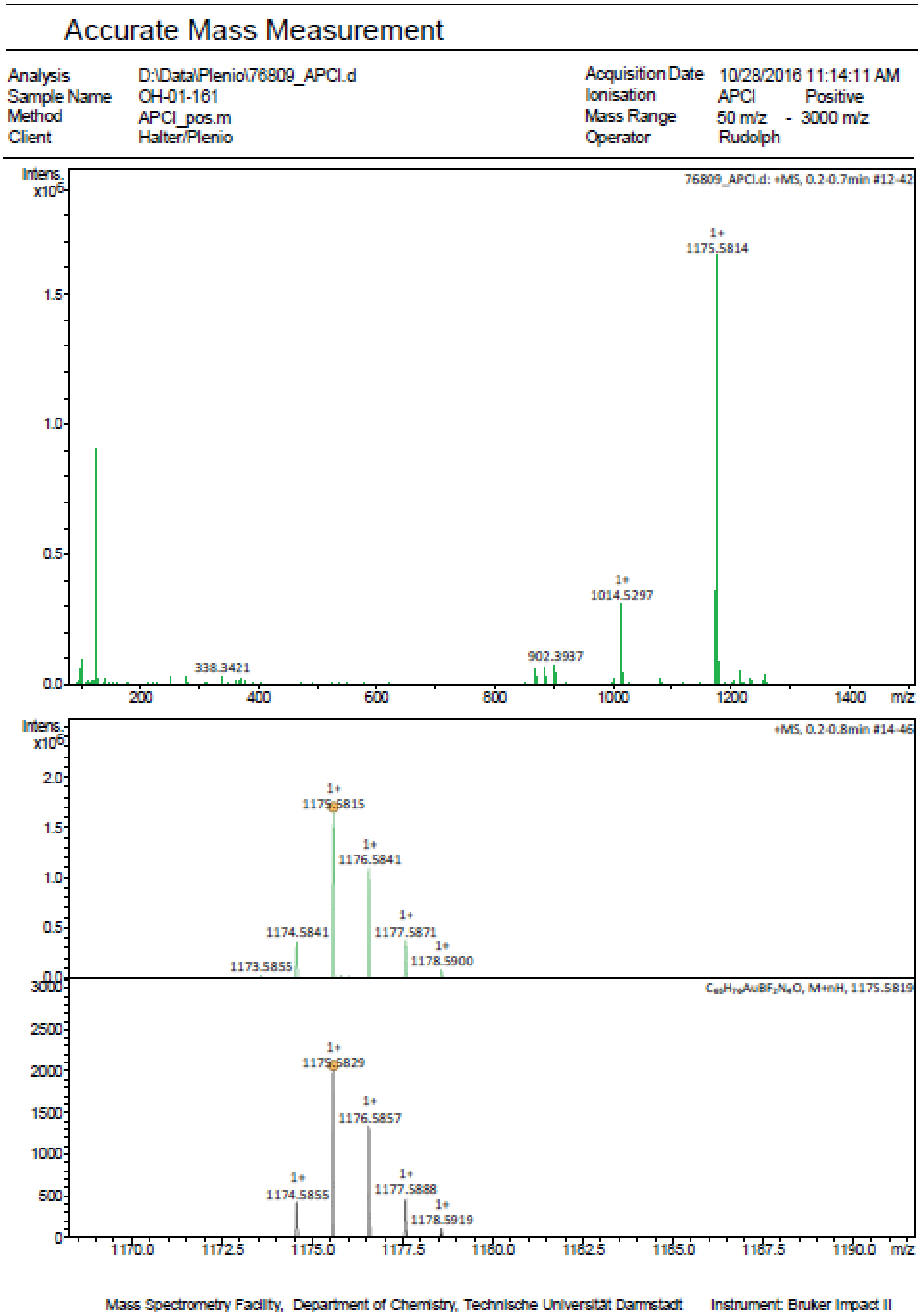

Figure S 76 Mass spectrum of [Au(CCPh´´)(3**d**)].

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
1175.581468	1	C68H76AuBFN4	100.00	1175.580727	0.4	0.3	16.5	32.5	even	ok	M+H
	2	C73H202F2N3O	9.20	1175.581051	-0.4	-0.4	86.3	-26.5	even	ok	M+H
	3	C65H77AuBF2N4O	0.00	1175.581870	1.5	1.2	659.5	28.5	even	ok	M+H

Figure S 77 mass spectrum of [Au(CCPh´´)(3**d**)].

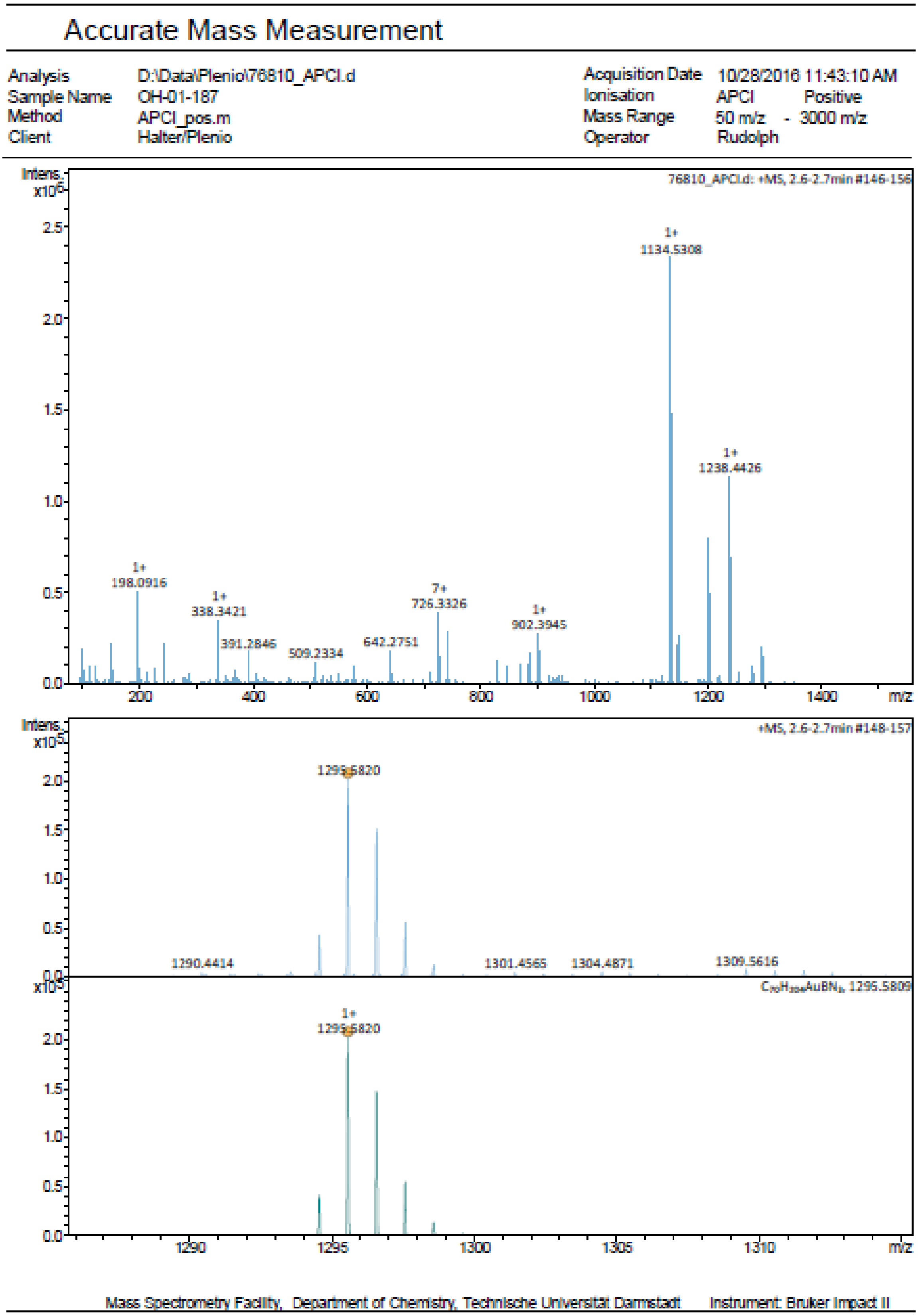

Figure S 78 mass spectrum of [Au(CCPh´´)(3**a**)].

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
1295.581979	1	C70H204AuBN3	100.00	1295.580854	0.0	0.0	9.5	-29.5	even	ok	M+H
	2	C75H77AuBF2N4O	53.39	1295.581870	1.1	0.8	15.2	38.5	even	ok	M+H

Figure S 79 mass spectrum of [Au(CCPh´´)(3**a**)].

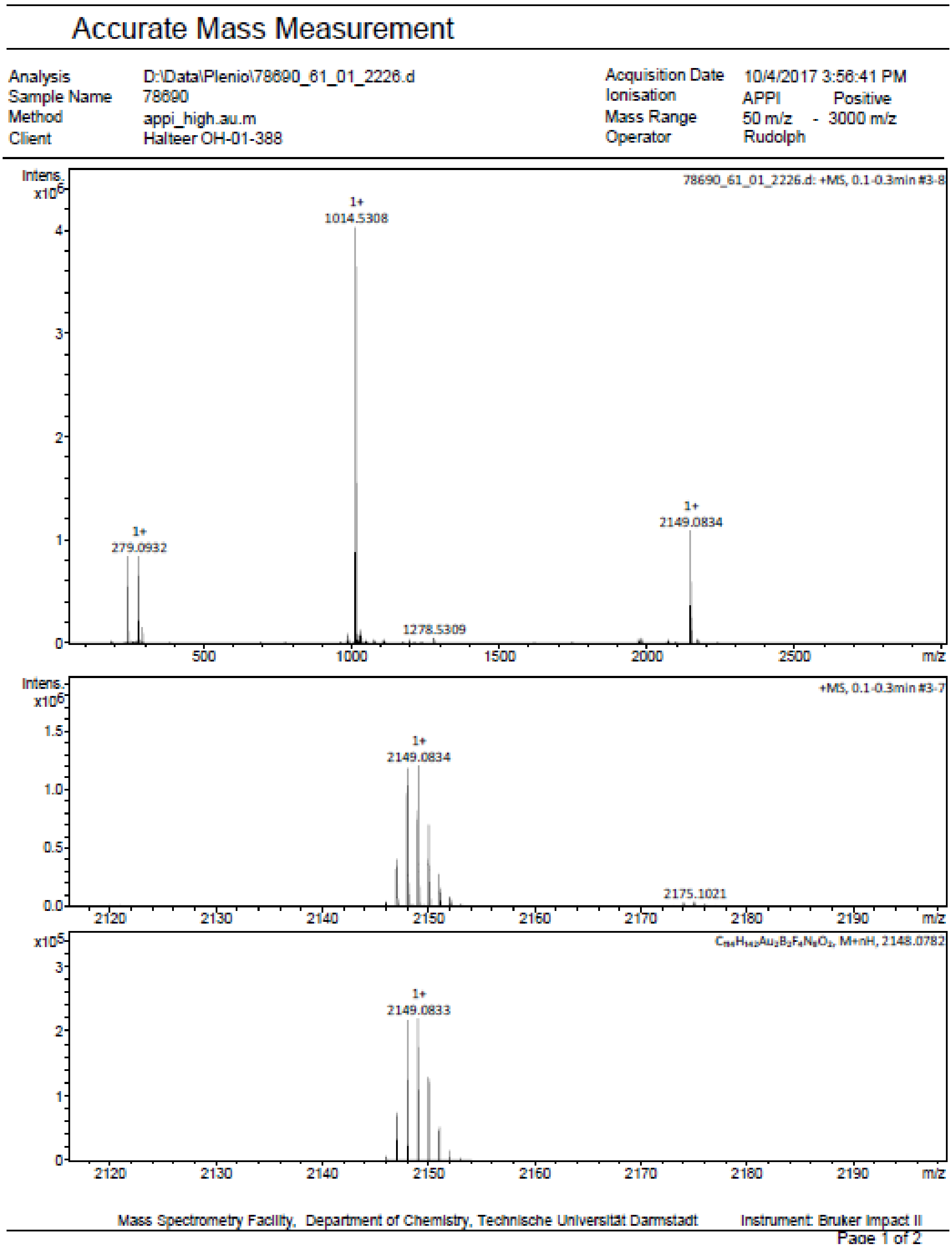

Figure S 80 mass spectrum of [(Au(**3d**))(Au(Au(CCPh´´)(**3d**))]NTf$_2$.

Accurate Mass Measurement

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
2148.081300	1	C114H143Au2B2F4N8O2	100.00	2148.078213	-0.1	-0.0	2.9	45.5	even	ok	M+H
	2	C103H143Au2B2F4N14O5	8.45	2148.081401	2.9	1.3	31.6	37.5	even	ok	M+H
	3	C98H143Au2B2F4N16O7	15.87	2148.077378	-1.2	-0.6	50.8	33.5	even	ok	M+H
	4	C108H143Au2B2F4N12O3	0.00	2148.085424	1.$	1.$	621.4	41.5	even	ok	M+H
2149.083404	1	C114H144Au2B2F4N8O2	-1.#J	2149.086038	-992.8	-462.0	614.7	45.0	odd	ok	M+H
	1	C98H144Au2B2F4N16O7	100.00	2149.085204	4.5	2.1	311.7	33.0	odd	ok	M+H

Figure S 81 mass spectrum of [(Au(**3d**))(Au(Au(CCPh´´)(**3d**))]NTf_2.