Electronic Supplementary Material (ESI) for Chemical Science.
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Supporting information

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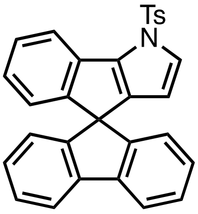
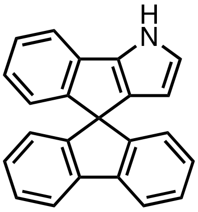
1. General Information

All solvents were dried and used after distillation: dichloromethane and 1,2-dichloroethane dried over CaH_2; THF dried over sodium, dimethylacetamide distilled over CaH_2; methanol distilled over K_2CO_3; acetone distilled over CaO. All mentioned solvents were stored over molecular sieves 4Å after distillation. All reagents were used as purchased for the reactions without further purification. 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. Column chromatography was performed on silica 60 (Machery-Nagel GmbH & Co.KG, 0.063-0.2 mm) with the indicated eluent mixtures. Filtration processes were performed using filter paper 310 with particle retention 10 – 20 μm or SCHOTT-DURAN glass filter Por.4. High vacuum denotes pressure range 0.1 – 10^{-3} mbar. ^{1}H, ^{13}C, and ^{19}F 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). 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 Finnigan MAT95 spectrometer using electrospray ionization (ESI). UV-Vis spectra were recorded on Analytik Jena Specord 600 UV-Vis spectrometer. Emission spectra were recorded on corrected J&M TIDAS S700/CCD UV/NIR 2098 spectrometer combined with J&M TIDAS LSM monochromator with 75 W Xenon light source. The following compounds were synthesized according to known literature procedures: 9-(2-Bromophenyl)-9H-fluoren-9-ol[1], [Ag(bdpSO_3)][2], 8-Chloro Bodipy[3], 8-SMe Bodipy[4], 11[5], 13[5], [AuCl(NHC_green)][5], **9**·HBr[5], [AuCl(**9**)][5]**,** [Au(NTf_2)(NHC_green)][5].

2. Synthesis and Experimental Procedures



Synthesis of pyrrole 2. A mixture of 9-(2-bromophenyl)-9H-fluoren-9-ol[1] (14.6 g, 27.0 mmol), $Pd(OAc)_2$ (1.0 g, 4.5 mmol), and K_2CO_3 (7.8 g, 56.4 mmol) in dry DMF (150 mL) was stirred at 100 °C for 20 h. After the solvent was distilled off under low vacuum, the residue was dissolved in CH_2Cl_2 (150 mL) and washed with brine (100 mL) and water (150 mL). The organic layer was separated, dried over $MgSO_4$, and filtered. Evaporation of the solution in a rotavap gave the product as a brown solid. The crude product was slurried with a mixture of CH_2Cl_2 and cyclohexane (ca. 20 mL, 1:1), and the resulting precipitate was collected by suction filtration to provide **2** as a white solid (8.7 g, 18.9 mmol, 70%). The characterization data of **2** match with literature data. [1]



Synthesis of pyrrole 3. A mixture of **2** (4.2 g, 9.0 mmol) and Cs_2CO_3 (9.1 g, 27.8 mmol) in THF/MeOH (3:1, 145 mL) was stirred for 24 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL). The organic layer was washed with H_2O, dried over $MgSO_4$, filtered over a paper filter and evaporated in a rotavap to provide a dark orange solid. Recrystallization from CH_2Cl_2 and cyclohexane afforded **3** as a white crystalline solid (2.4 g, 7.7 mmol, 85 %). The characterization data of **3** match with literature data. [1]

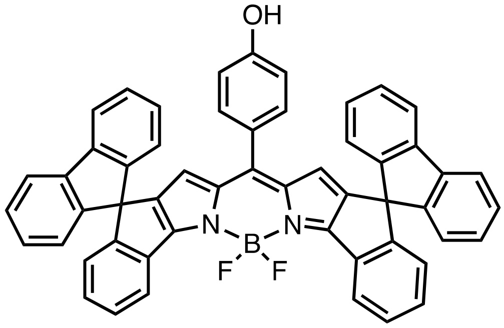
General Procedure A. Synthesis of Bodipy derivatives. To a solution of pyrrole **3** (0.33 mmol, 2.0 eq.) and aldehyde (0.16 mmol, 1.0 eq.) in dry CH_2Cl_2 (3.0 mL) was added a catalytic amount of TFA (1 drop), and the solution was stirred at rt for 15 h under nitrogen atmosphere. The reaction mixture was poured into 5% aq. solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with brine (100 mL), followed by drying of the organic layer over $MgSO_4$ and filtration over a paper filter. After evaporation of the volatiles in a rotavap, the residue was dissolved in dry CH_2Cl_2 (3.0 mL) and treated with DDQ (36 mg, 0.16 mmol). After stirring for 1 h, Et_3N (0.2 mL, 1.4 mmol) and $BF_3 \cdot OEt_2$ (0.3 mL, 2.4 mmol) were added at 0 °C, and the resulting mixture was stirred at rt for another 15 h at rt. The reaction mixture was poured into 5% aq. solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with brine (100 mL), followed by drying over $MgSO_4$ and filtration over paper filter. After evaporation of the volatiles in a rotavap under reduced pressure, the crude product was purified by column chromatography. The product may be recrystallized from CH_2Cl_2 and MeOH.

General procedure B. Synthesis of alkoxy substituted products. A mixture of alkyl bromide (0.3 mmol, 1.5 eq.), alcohol (0.2 mmol, 1.0 eq.), K_2CO_3 (0.4 mmol, 2.0 eq.), and KI (0.6 mmol, 3.0 eq.) in dry acetone (3.0 mL) was heated to reflux for 15 h under nitrogen atmosphere. The mixture was poured into CH_2Cl_2 (200 mL), and washed with brine (100 mL). After drying over $MgSO_4$ and filtration over a paper filter, the volatiles were evaporated in a rotavap under reduced pressure. The remaining solid was purified by column chromatography (silica, CH_2Cl_2 100%→ CH_2Cl_2/EtOH = 50/1).

General Procedure C. Synthesis of NHC-metal complexes. A mixture of imidazolium salt (0.06 mmol, 1 eq.), K_2CO_3 (0.18 mmol, 3 eq.), and the corresponding metal source, $[AuCl(SMe_2)]$ (0.06 mmol, 1 eq.) or $[CuCl(SMe_2)]$ (0.06 mmol, 1 eq.) or $[RhCl(cod)]_2$ (0.03 mmol, 0.5 eq.) or $[IrCl(cod)]_2$ (0.03 mmol, 0.5 eq.) or $[Pd(allyl)Cl]_2$ (0.03 mmol, 0.5 eq.) in dry acetone (2.0 mL) was heated to reflux for 15 h under nitrogen atmosphere. CH_2Cl_2 (ca. 10 mL) was added to the reaction mixture and the solution filtered through a celite plug. The crude mixture obtained after evaporation of the volatiles was purified by column chromatography (EtOAc/cyclohexane) to afford the desired complex.

General procedure D. Synthesis of 8-Amino Bodipy derivatives B1, B2, B3 and B4: To a solution of the corresponding 8-Chloro-Bodipy[3] (0.5 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL) propylamine (1.0 mmol, 2.0 eq.) was added. The reaction mixture was stirred at rt for 2 h. After the addition of water (50 mL), the reaction mixture was poured into CH_2Cl_2 (30 mL) and the organic layer separated. The organic solution was washed with brine (25 mL) and water, dried over $MgSO_4$, filtered over a paper filter and evaporated on the rotavap under reduced pressure. The crude product was purified by column chromatography on silica (CH_2Cl_2/MeOH = 30/1).

Synthesis of individual compounds

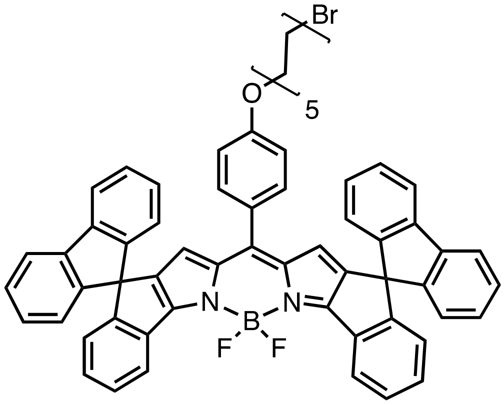


Synthesis of 10. General Procedure A: Pyrrole **3** (100 mg, 0.33 mmol), 4-Hydroxybenzaldehyde (20 mg, 0.16 mmol), DDQ (36 mg, 0.16 mmol), Et_3N (0.2 mL, 1.4 mmol), BF_3OEt_2 (0.3 mL, 2.4 mmol) were placed in 25 mL Schlenk flask and dissolved in dry CH_2Cl_2 (5.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/4) and gave Bodipy **10** (46 mg, 38%) as a dark red powder.

^1H NMR ($CDCl_3$, 500 MHz): δ / ppm = 8.51 (d, J = 7.7 Hz, 2H), 7.82 (dt, J = 7.7, 0.9 Hz, 4H), 7.52 (td, J = 7.6, 1.1 Hz, 2H), 7.39 (td, J = 7.5, 1.1 Hz, 4H), 7.28 – 7.24 (m, 2H), 7.20 (dtd, J = 11.1, 7.5, 1.2 Hz, 6H), 6.97 (dt, J = 7.6, 1.0 Hz, 4H), 6.73 – 6.69 (m, 2H), 6.64 (d, J = 7.7 Hz, 2H), 6.23 (s, 2H), 4.99 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 161.4, 157.1, 156.7, 148.2, 143.0, 142.0, 141.3, 141.1, 132.5, 132.2, 130.5, 128.8, 128.0, 127.9, 126.7, 124.3, 124.3, 124.2, 120.6, 120.1, 115.1, 59.7, 53.4.

HRMS (ESI positive): *m*/*z* calcd. for $C_{53}H_{32}BF_2N_2O$ $[M+H]^+$ 761.25758, found 761.25657, calcd. for $C_{53}H_{31}BF_2N_2NaO$ $[M+Na]^+$ 783.23952, found 783.24024, calcd. for $C_{53}H_{31}BFN_2O$ $[M-F]^+$ 741.25135, found 741.25217.

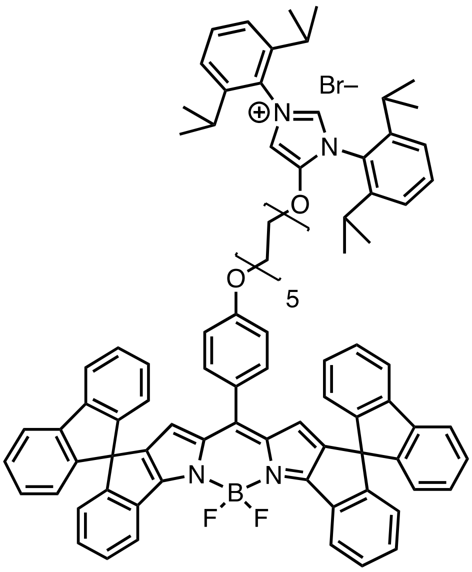


Synthesis of 4. General Procedure B: Bodipy **10** (153 mg, 0.2 mmol, 1 eq.), 1,10-Dibromodecane (90 mg, 0.3 mmol, 1.5 eq.), K_2CO_3 (55 mg, 0.4 mmol, 2 eq.), KI (100 mg, 0.6 mmol, 4 eq.) were placed in 10 mL round flask and dissolved in dry acetone (3.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/4) and gave **4** (55 mg, 28%) as a dark red powder.

^{1}H NMR ($CDCl_3$, 500 MHz) δ / ppm = 8.52 (d, J = 7.7 Hz, 2H), 7.82 (d, J = 7.6 Hz, 4H), 7.53 (td, J = 7.6, 1.1 Hz, 2H), 7.39 (td, J = 7.5, 1.1 Hz, 4H), 7.34 – 7.29 (m, 2H), 7.21 (dtd, J = 15.1, 7.5, 1.1 Hz, 6H), 6.98 (d, J = 7.6 Hz, 4H), 6.77 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 7.7 Hz, 2H), 3.86 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.9 Hz, 2H), 1.85 (p, J = 6.9 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.44 – 1.34 (m, 4H), 1.28 (d, J = 2.4 Hz, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm = 161.2, 160.6, 156.6, 148.3, 142.9, 142.3, 141.3, 141.1, 132.6, 131.9, 130.4, 128.7, 127.97, 127.93, 126.2, 124.29, 124.23, 124.20, 120.7, 120.1, 114.2, 68.0, 59.8, 34.0, 32.8, 29.38, 29.30, 29.2, 29.0, 28.7, 28.1, 25.9.

HRMS (ESI positive): m/z calcd. for $C_{63}H_{51}BBrF_2N_2O$ $[M+H]^+$ 981.32254, found 981.32330, calcd. for $C_{63}H_{50}BBrF_2N_2NaO$ $[M+Na]^+$ 1003.30449, found 1003.30674, calcd. for $C_{63}H_{50}BBrFN_2O$ $[M-F]^+$ 961.31631, found 961.31873.

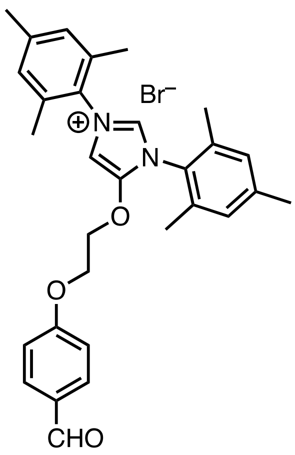


Synthesis of 5·HBr. General Procedure B: 1,3-bis(2,6-diisopropylphenyl)-4-hydroxy-1H-imidazol-3-ium chloride (97 mg, 0.2 mmol, 1 eq.), Bodipy **4** (294 mg, 0.3 mmol), K_2CO_3 (55 mg, 0.4 mmol, 2 eq.), KI (100 mg, 0.6 mmol, 4 eq.) were placed in 10 mL round flask and dissolved in dry acetone (3.0 mL). The crude red product was purified by column chromatography (MeOH/CH_2Cl_2= 1/20) and gave **5·HBr** (64 mg, 23%) as a dark red powder.

^{1}H NMR ($CDCl_3$, 500 MHz): δ / ppm = 8.90 (dt, *J* = 4.6, 2.1 Hz, 1H), 8.52 (d, *J* = 7.6 Hz, 2H), 7.98 (dq, *J* = 7.4, 2.4 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 4H), 7.59 (q, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.32 (m, 8H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.20 (dt, *J* = 17.5, 7.5 Hz, 6H), 6.98 (d, *J* = 7.5 Hz, 4H), 6.79 – 6.73 (m, 2H), 6.66 (d, *J* = 7.7 Hz, 2H), 6.25 (s, 2H), 4.52 (t, *J* = 6.3 Hz, 2H), 3.84 (t, *J* = 6.4 Hz, 2H), 2.57 (hept, *J* = 6.9 Hz, 2H), 2.46 (hept, *J* = 7.0 Hz, 2H), 1.70 (ddt, *J* = 21.5, 14.2, 6.6 Hz, 4H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.37 – 1.15 (m, 30H).

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 161.3, 160.6, 156.6, 148.5, 148.3, 145.7, 145.1, 142.9, 142.3, 141.3, 141.1, 132.6, 132.31, 132.21, 132.0, 130.5, 130.4, 130.2, 128.8, 128.0, 127.9, 126.3, 126.1, 124.8, 124.7, 124.3, 124.3, 124.2, 120.7, 120.1, 114.2, 104.3, 75.9, 68.1, 59.8, 29.41, 29.32, 29.25, 29.23, 29.18, 29.12, 29.01, 28.6, 25.9, 25.5, 25.0, 24.37, 24.14, 23.5.

HRMS (ESI positive): *m*/*z* calcd. for $C_{90}H_{86}BF_2N_4O_2$ [M-Br]$^+$ 1303.68119, found 1303.68127.

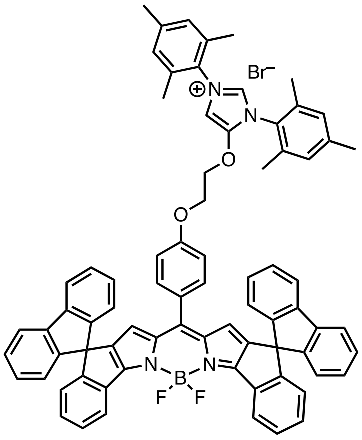


Synthesis of 7·HBr. General Procedure B: 1,3-bis(2,4,6-trimethylphenyl)-4-hydroxy-1H-imidazol-3-ium chloride (71 mg, 0.2 mmol, 1.0 eq.), 4-(2-bromoethoxy)benz aldehyde (69 mg, 0.3 mmol, 1.5 eq.), K_2CO_3 (55 mg, 0.4 mmol, 2 eq.), KI (100 mg, 0.6 mmol, 4 eq.) were placed in 10 mL round flask and dissolved in dry acetone (3.0 mL). The crude red product was purified by column chromatography ($MeOH/CH_2Cl_2$= 1/25) and gave **7·HBr** (55 mg, 50%) as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 9.78 (s, 1H), 9.04 (d, J = 1.8 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.57 (d, J = 1.9 Hz, 1H), 6.96 – 6.92 (m, 4H), 6.91 – 6.85 (m, 2H), 5.26 (s, 1H), 4.85 – 4.80 (m, 2H), 4.38 – 4.33 (m, 2H), 2.27 (s, 6H), 2.16 (s, 6H), 2.05 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 190.7, 163.0, 147.2, 141.6, 141.3, 134.8, 134.0, 132.0, 130.9, 130.7, 130.2, 129.88, 129.82, 126.6, 114.8, 103.3, 73.3, 66.1, 53.6, 21.2, 21.1, 17.85, 17.71.

HRMS (ESI positive): m/z calcd. for $C_{30}H_{33}N_2O_3$ $[M-Br]^+$ 469.24857, found 469.24878.

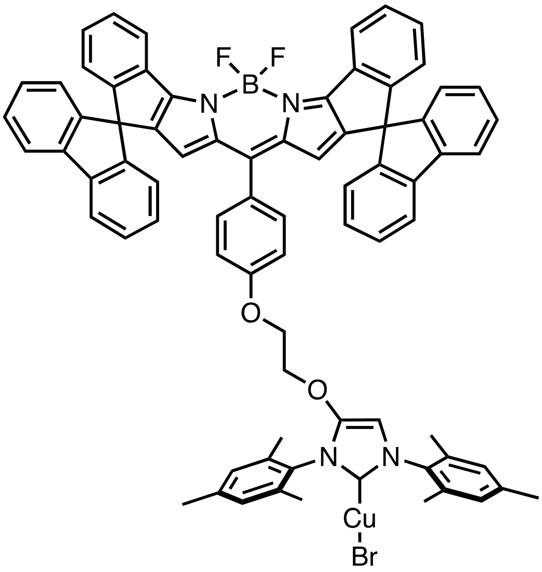


Synthesis of 8·HBr General Procedure A: Pyrrole **3** (100 mg, 0.33 mmol), aldehyde **7·HBr** (88 mg, 0.16 mmol), DDQ (36 mg, 0.16 mmol), Et_3N (0.2 mL, 1.4 mmol), BF_3OEt_2 (0.3 mL, 2.4 mmol) were placed in 25 mL Schlenk flask and dissolved in dry CH_2Cl_2 (5.0 mL). The crude red product was purified by column chromatography ($MeOH/CH_2Cl_2$= 1/20) and gave **8·HBr** (82 mg, 43%) as a dark red powder.

^{1}H NMR ($CDCl_3$, 300 MHz): δ / ppm = 8.50 (d, J = 7.7 Hz, 2H), 8.09 (s, 1H), 7.80 (d, J = 7.6 Hz, 4H), 7.51 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.5 Hz, 4H), 7.24 – 7.13 (m, 9H), 7.00 – 6.92 (m, 6H), 6.90 (s, 2H), 6.64 (dd, J = 8.1, 5.6 Hz, 4H), 6.16 (s, 2H), 4.62 – 4.57 (m, 2H), 4.17 – 4.11 (m, 2H), 2.32 (s, 3H), 2.21 (s, 3H), 2.11 (s, 6H), 2.00 (s, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ / ppm = 159.6, 157.6, 154.7, 146.3, 145.7, 141.2, 139.79, 139.67, 139.64, 139.41, 139.06, 132.9, 132.2, 130.6, 130.0, 128.87, 128.63, 127.98, 127.89, 126.9, 126.15, 126.05, 125.3, 124.7, 122.44, 122.37, 122.25, 118.5, 118.2, 112.3, 100.8, 75.4, 75.11, 74.9, 70.8, 63.8, 57.8, 19.24, 19.20, 15.39, 15.22.

HRMS (ESI positive): *m*/*z* calcd. for $C_{76}H_{58}BF_2N_4O_2$ $[M\text{-}Cl]^+$ 1107.46154, found 1107.46219.

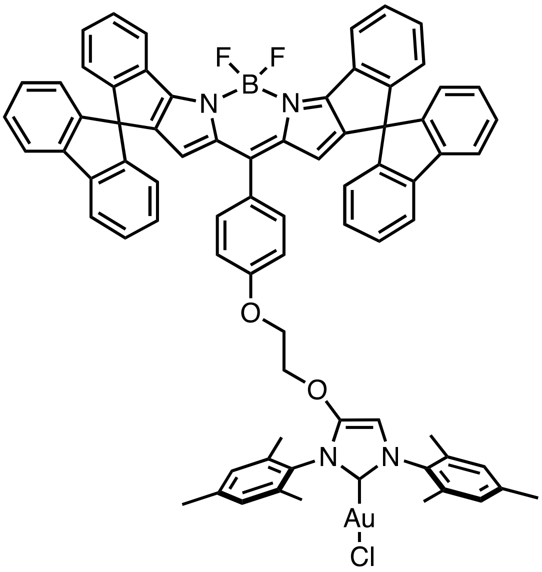


Synthesis of [CuBr(**8**)]. General Procedure C: Imidazolium salt **8·HBr** (71 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), [CuBr(SMe_2)] (12.6 mg, 0.06 mmol, 1 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/5) and gave [CuBr(**8**)] (52 mg, 69%) as a microcrystalline dark red powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 8.36 (d, J = 7.7 Hz, 2H), 7.75 (dt, J = 7.5, 1.0 Hz, 4H), 7.44 (td, J = 7.6, 1.1 Hz, 2H), 7.29 (td, J = 7.5, 1.1 Hz, 4H), 7.12 (dtd, J = 20.6, 7.5, 1.0 Hz, 8H), 6.92 (q, J = 0.7 Hz, 2H), 6.85 (dt, J = 7.6, 0.9 Hz, 4H), 6.80 (dd, J = 1.3, 0.7 Hz, 2H), 6.60 – 6.52 (m, 4H), 6.31 (s, 1H), 6.11 (s, 2H), 4.16 – 4.09 (m, 2H), 4.02 – 3.95 (m, 2H), 2.27 (s, 3H), 2.14 (s, 3H), 2.00 (d, J = 0.6 Hz, 6H), 1.90 (d, J = 0.6 Hz, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ / ppm = 174.5 (C_{NHC}), 161.3, 159.7, 156.8, 148.1, 147.9, 143.2, 141.9, 141.4, 141.0, 139.6, 139.5, 135.8, 135.4, 134.8, 132.5, 132.0, 131.4, 130.6, 129.24, 129.14, 128.8, 128.1, 127.9, 127.1, 124.2, 124.0, 120.4, 120.2, 114.3, 99.4, 71.5, 66.3, 59.8, 29.7, 29.1, 20.9, 17.6.

HRMS (ESI positive): m/z calcd. for $C_{76}H_{57}BCuF_2N_4O_2$ [M-Cl]$^+$ 1169.38332, found 1169.38430.

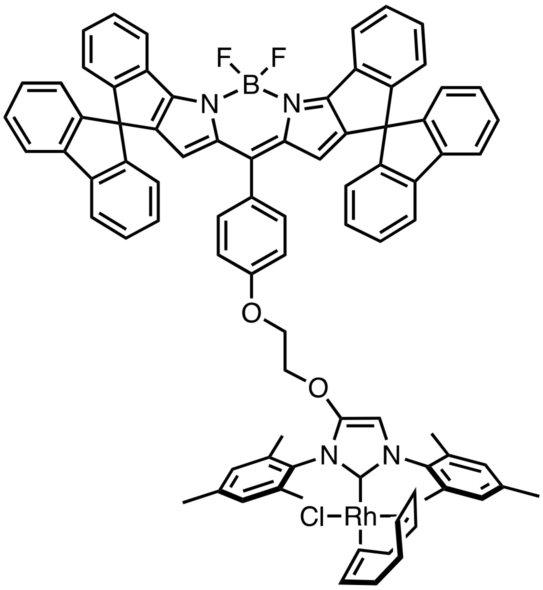


Synthesis of [AuCl(**8**)]. General Procedure C: Imidazolium salt **8·HBr** (71 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), [AuCl(SMe_2)] (17.7 mg, 0.06 mmol, 1 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/5) and gave [AuCl(**8**)] (30 mg, 37%) as a microcrystalline dark red powder.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ / ppm = 8.49 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 7.6 Hz, 4H), 7.58 (td, J = 7.6, 1.0 Hz, 2H), 7.43 (t, J = 7.5 Hz, 4H), 7.35 – 7.26 (m, 4H), 7.22 (td, J = 7.5, 1.1 Hz, 4H), 7.06 (s, 2H), 6.99 (d, J = 7.6 Hz, 4H), 6.94 (d, J = 4.5 Hz, 2H), 6.74 – 6.65 (m, 4H), 6.47 (d, J = 3.0 Hz, 1H), 6.25 (d, J = 2.3 Hz, 2H), 4.31 – 4.25 (m, 2H), 4.18 – 4.10 (m, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 2.13 (d, J = 9.8 Hz, 6H), 2.03 (d, J = 5.0 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 178.3 (C_{NHC}), 168.0, 161.3, 159.6, 156.8, 148.1, 147.5, 147.3, 141.9, 141.4, 141.0, 140.0, 139.92, 139.86, 139.82, 135.50, 135.47, 135.30, 135.19, 134.95, 134.91, 132.5, 132.0, 130.92, 130.79, 130.6, 129.26, 129.22, 129.18, 129.13, 128.8, 128.1, 127.9, 127.1, 124.22, 124.07, 123.97, 120.39, 120.22, 114.3, 99.29, 99.22, 71.53, 71.51, 66.24, 66.22, 59.8, 53.9, 53.7, 53.4, 53.2, 53.00, 20.9, 17.56, 17.52, 17.40, 17.38.

HRMS (ESI positive): m/z calcd. for $C_{76}H_{57}AuBF_2N_4O_2$ [M-Cl]$^+$ 1303.42082, found 1303.42138.

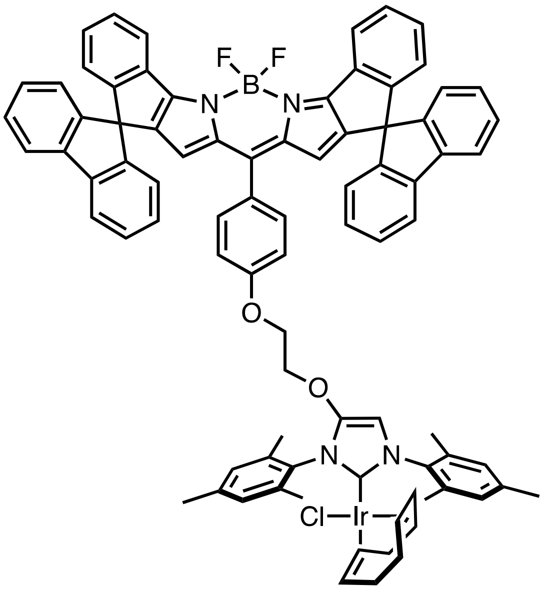


Synthesis of [RhCl(cod)(**8**)]. General Procedure C: Imidazolium salt **8·HBr** (71 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), $[RhCl(cod)]_2$ (14.8 mg, 0.03 mmol, 0.5 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/3) and gave [RhCl(cod)(**8**)] (54 mg, 67%) as a microcrystalline dark red powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 8.36 (d, J = 7.7 Hz, 2H), 7.73 (dt, J = 7.7, 1.0 Hz, 4H), 7.43 (td, J = 7.6, 1.1 Hz, 2H), 7.27 (td, J = 7.5, 1.1 Hz, 4H), 7.17 – 7.02 (m, 8H), 6.93 (s, 1H), 6.89 (s, 1H), 6.84 (dt, J = 7.6, 0.9 Hz, 4H), 6.80 (s, 1H), 6.72 (s, 1H), 6.59 – 6.44 (m, 4H), 6.17 (s, 1H), 6.11 (s, 2H), 4.28 (s, 2H), 3.99 (dt, J = 4.6, 2.8 Hz, 2H), 3.90 (dt, J = 6.6, 3.0 Hz, 2H), 3.47 (s, 1H), 3.20 (s, 1H), 3.11 (s, 1H), 2.51 (s, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.04 (s, 3H), 2.02 (s, 1H), 1.98 (s, 3H), 1.84 (s, 3H), 1.69 (s, 4H), 1.50 – 1.39 (m, 4H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ / ppm = 180.7 (C_{NHC}) (d, $J(^{13}C - ^{103}Rh)$ = 53.0 Hz), 163.2, 161.7, 158.7, 150.6, 150.0, 145.0, 144.0, 143.3, 142.9, 140.59, 140.46, 140.0, 139.3, 138.7, 137.4, 136.5, 134.5, 134.3, 133.8, 132.4, 131.2, 131.0, 130.6, 130.0, 129.84, 128.80, 126.1, 125.9, 122.4, 122.1, 116.3, 102.8, 97.6, 97.2, 72.7, 71.2, 70.0, 69.7, 68.1, 61.7, 34.8, 34.3, 33.5, 32.5, 31.6, 31.0, 30.4, 30.0, 28.8, 22.7, 21.3, 19.8.

HRMS (ESI positive): m/z calcd. for $C_{84}H_{69}BF_2N_4O_2Rh$ $[M-Cl]^+$ 1317.45367, found 1317.45457.

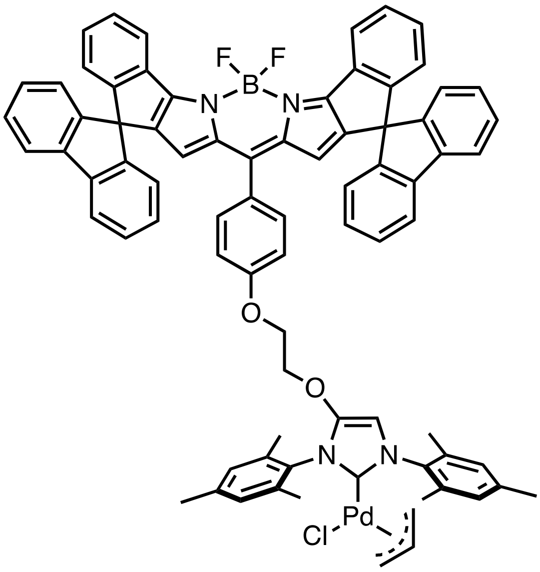


Synthesis of [IrCl(cod)(**8**)]. General Procedure C: Imidazolium salt **8·HBr** (71 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), $[IrCl(cod)]_2$ (20.2 mg, 0.03 mmol, 0.5 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/3) and gave [IrCl(cod)(**8**)] (40 mg, 67%) as a microcrystalline dark red powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 8.36 (d, J = 7.7 Hz, 2H), 7.74 (dt, J = 7.6, 1.0 Hz, 4H), 7.44 (td, J = 7.6, 1.1 Hz, 2H), 7.29 (td, J = 7.5, 1.1 Hz, 4H), 7.11 (dtd, J = 20.1, 7.6, 1.1 Hz, 8H), 6.85 (dt, J = 7.5, 1.0 Hz, 6H), 6.75 (s, 1H), 6.69 (s, 1H), 6.59 – 6.45 (m, 4H), 6.18 (s, 1H), 6.12 (s, 2H), 4.02 (dt, J = 4.0, 2.5 Hz, 2H), 3.98 – 3.82 (m, 4H), 2.89 (d, J = 6.4 Hz, 1H), 2.81 (s, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 2.10 (d, J = 3.3 Hz, 6H), 2.03 (s, 3H), 1.89 (s, 3H), 1.66 – 1.47 (m, 4H), 1.26 – 1.11 (m, 4H).

^{13}C NMR (75 MHz, CD_2Cl_2): δ / ppm = 176.1 (C_{NHC}), 161.3, 156.8, 148.4, 148.1, 143.1, 142.1, 141.4, 141.0, 138.6, 138.5, 137.9, 137.1, 136.6, 135.5, 134.6, 132.5, 132.1, 132.0, 130.5, 129.1, 128.9, 128.7, 128.2, 128.1, 127.9, 126.9, 124.2, 124.1, 124.0, 120.4, 120.2, 114.4, 100.6, 82.1, 81.4, 70.8, 66.2, 59.8, 53.9, 53.7, 53.4, 53.2, 53.0, 51.8, 51.3, 33.7, 33.1, 31.9, 29.7, 29.4, 29.1, 28.5, 22.7, 20.8, 19.3, 18.0, 13.9.

HRMS (ESI positive): m/z calcd. for $C_{84}H_{69}BF_2IrN_4O_2$ $[M\text{-}Cl]^+$ 1407.51109, found 1407.51211, calcd. for $C_{86}H_{72}BF_2IrN_5O_2$ $[M\text{-}Cl+CH_3CN]^+$ 1448.53764, found 1448.53865.

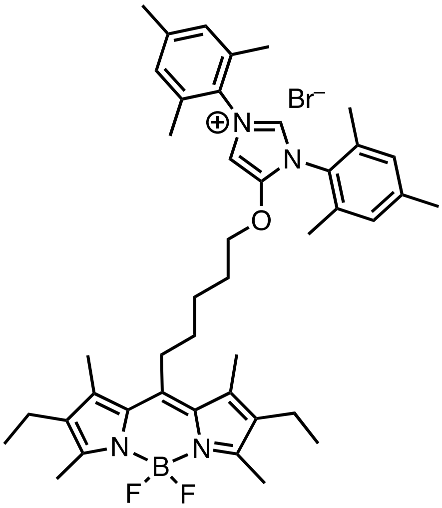


Synthesis of [Pd(allyl)Cl(**8**)]. General Procedure C: Imidazolium salt **8·HBr** (71 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), $[Pd(allyl)Cl]_2$ (11 mg, 0.03 mmol, 0.5 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/2) and gave [Pd(allyl)Cl(**8**)] (37 mg, 48%) as a microcrystalline dark red powder.

^{1}H NMR (300 MHz, CD_2Cl_2): *δ* / ppm = δ 8.36 (d, *J* = 7.7 Hz, 2H), 7.74 (dt, *J* = 7.7, 1.0 Hz, 4H), 7.44 (td, *J* = 7.6, 1.1 Hz, 2H), 7.29 (td, *J* = 7.5, 1.1 Hz, 4H), 7.19 – 7.12 (m, 4H), 7.08 (td, *J* = 7.5, 1.1 Hz, 4H), 6.85 (dt, *J* = 7.5, 1.0 Hz, 6H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.61 – 6.51 (m, 4H), 6.31 (s, 1H), 6.13 (s, 2H), 4.73 (ddd, *J* = 18.8, 13.3, 7.4 Hz, 1H), 4.08 (dd, *J* = 5.8, 2.9 Hz, 2H), 4.02 – 3.92 (m, 2H), 3.60 (dd, *J* = 7.5, 1.7 Hz, 1H), 3.06 (d, *J* = 6.6 Hz, 1H), 2.57 (d, *J* = 13.4 Hz, 1H), 2.23 (s, 3H), 2.10 (s, 3H), 2.08 (d, *J* = 2.6 Hz, 6H), 1.99 (s, 3H), 1.94 (s, 3H), 1.62 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2): *δ* / ppm = 178.4 (C_{NHC}), 161.3, 159.8, 156.8, 148.6, 148.1, 143.1, 142.0, 141.4, 141.0, 138.9, 138.7, 136.5, 136.3, 136.1, 135.7, 132.5, 132.2, 131.9, 130.5, 128.7, 128.1, 127.9, 120.0, 124.2, 124.0, 120.5, 120.2, 114.4, 114.1, 100.2, 71.1, 70.9, 66.2, 59.8, 49.8, 29.7, 26.9, 20.8, 18.0, 17.9.

HRMS (ESI positive): *m*/*z* calcd. for $C_{79}H_{62}BF_2N_4O_2Pd$ [M-Cl]$^+$ 1253.39687, found 1253.39942.

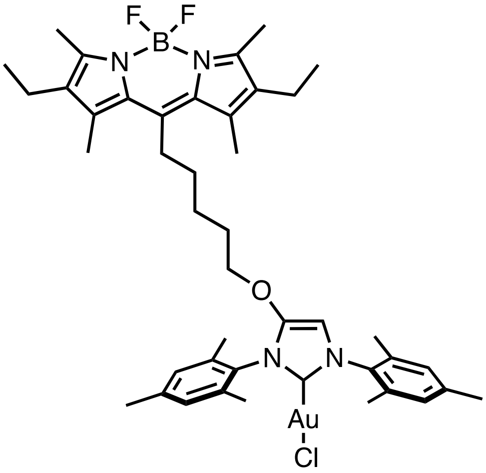


Synthesis of 9·HBr.[5] General Procedure B: Imidazolium salt·HCl (71 mg, 0.2 mmol, 1.0 eq.), Bodipy **11**[5] (136 mg, 0.3 mmol), K_2CO_3 (55 mg, 0.4 mmol, 2 eq.), KI (100 mg, 0.6 mmol, 4 eq.) were placed in dried 10 mL Schlenk flask and dissolved in dry acetone (4.0 mL). The crude orange product was purified by column chromatography ($MeOH/CH_2Cl_2$= 1/20) and gave **9·HBr** (77 mg, 50%) as an orange powder.

^1H NMR (500 MHz, $CDCl_3$): δ / ppm = 9.19 (d, J = 1.7 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.06 (s, 4H), 4.44 (t, J = 6.3 Hz, 2H), 2.96 (t, J = 7.7 Hz, 2H), 2.51 (s, 6H), 2.42 (q, J = 7.6 Hz, 4H), 2.37 (s, 3H), 2.36 (s, 3H), 2.29 (s, 6H), 2.27 (s, 6H), 2.16 (s, 6H), 1.86 (t, J = 6.6 Hz, 2H), 1.06 (t, J = 7.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 152.3, 147.5, 144.1, 141.7, 141.5, 135.5, 134.7, 134.1, 132.7, 130.9, 130.8, 130.6, 130.0, 129.9, 126.7, 102.6, 74.9, 31.3, 28.5, 28.2, 26.2, 21.19, 21.16, 17.9, 17.8, 17.2, 14.7, 13.5, 12.42, 12.40, 12.38.

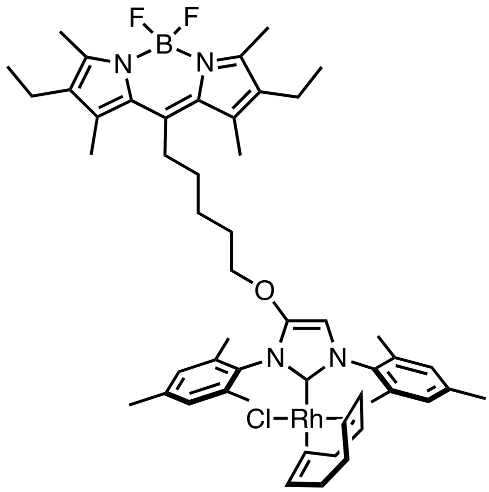
HRMS (ESI positive): m/z calcd. for $C_{34}H_{56}BF_2N_4O$ $[M\text{-}Br]^+$ 693.45098, found 693.45194.



Synthesis of [AuCl(**9**)].[5] General Procedure C: Imidazolium salt **9·HBr** (46 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), [AuCl(SMe_2)] (17.7 mg, 0.06 mmol, 1 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/5) and gave [AuCl(**9**)] (38 mg, 69%) as a microcrystalline, orange powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 7.08 (d, *J* = 2.9 Hz, 4H), 6.42 (s, 1H), 4.04 (t, *J* = 6.2 Hz, 2H), 3.07 – 2.88 (m, 2H), 2.51 – 2.42 (m, 10H), 2.40 (s, 3H), 2.38 (s, 3H), 2.30 (s, 6H), 2.20 (s, 6H), 2.15 (s, 6H), 1.84 – 1.73 (m, 2H), 1.68 – 1.47 (m, 6H), 1.08 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ / ppm = 178.0 (C_{NHC}), 152.1, 147.5, 144.4, 139.9, 139.8, 135.8, 135.5, 135.3, 134.9, 132.8, 131.0, 130.8, 129.22, 129.15, 98.6, 72.6, 31.2, 29.7, 28.4, 28.2, 26.9, 26.2, 20.9, 17.6, 17.4, 17.1, 14.6, 13.1, 12.1.

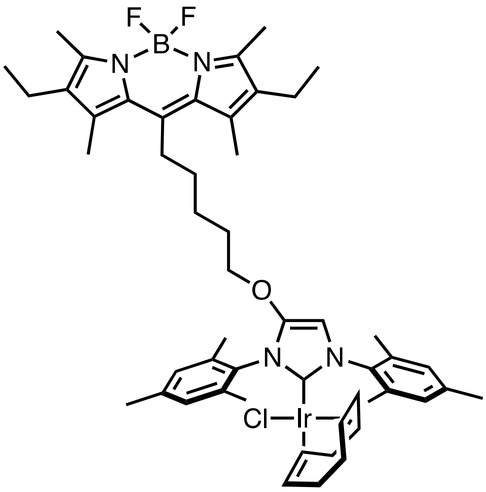


Synthesis of [RhCl(cod)(**9**)]. General Procedure C: Imidazolium salt **9·HBr** (46 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), $[RhCl(cod)]_2$ (14.8 mg, 0.03 mmol, 0.5 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/3) and gave [RhCl(cod)(**9**)] (41 mg, 72%) as a microcrystalline orange powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 6.92 (d, J = 4.0 Hz, 4H), 6.17 (d, J = 1.6 Hz, 1H), 4.61 (d, J = 4.2 Hz, 2H), 3.80 (t, J = 6.2 Hz, 2H), 3.62 – 3.48 (m, 1H), 3.45 (dd, J = 7.1, 3.3 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.42 – 2.22 (m, 24H), 2.18 (s, 6H), 2.12 (s, 3H), 2.06 (d, J = 3.0 Hz, 3H), 1.76 – 1.70 (m, 2H), 1.68 – 1.55 (m, 4H), 1.54 – 1.41 (m, 6H), 0.97 (t, J = 7.5 Hz, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ / ppm = 177.3 (C_{NHC}) (d, $J(^{13}C - {}^{103}Rh)$ = 52.3 Hz), 152.0, 149.2, 144.5, 138.7, 138.6, 137.7, 137.0, 136.9, 135.6, 135.7, 134.8, 132.6, 130.6, 129.5, 129.3, 128.3, 128.1, 101.0, 93.6, 93.5, 93.4, 93.3, 71.9, 71.6, 71.5, 71.3, 37.1, 32.4, 31.8, 31.2, 30.0, 29.7, 29.3, 28.8, 28.5, 28.3, 26.9, 26.3, 22.7, 21.7, 21.5, 20.8, 18.19, 18.14, 17.1, 14.6, 13.9, 13.1, 12.1.

HRMS (ESI positive): m/z calcd. for $C_{51}H_{67}BF_2N_4ORh$ $[M-Cl]^+$ 903.44310, found 903.44289.

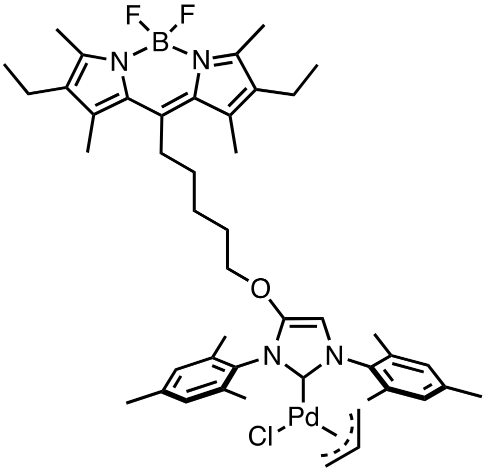


Synthesis of [IrCl(cod)(**9**)]. General Procedure C: Imidazolium salt **9·HBr** (46 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), $[IrCl(cod)]_2$ (20.2 mg, 0.03 mmol, 0.5 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/3) and gave [IrCl(cod)(**9**)] (33 mg, 53%) as a microcrystalline orange powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 6.96 – 6.84 (m, 4H), 6.16 (s, 1H), 4.17 (dq, J = 5.8, 3.0 Hz, 2H), 3.82 (td, J = 6.2, 1.1 Hz, 2H), 3.04 (dtd, J = 23.7, 7.4, 2.9 Hz, 2H), 2.89 – 2.75 (m, 2H), 2.39 – 2.33 (m, 8H), 2.33 – 2.27 (m, 6H), 2.26 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H), 2.19 (s, 6H), 2.15 (s, 3H), 2.09 (s, 3H), 1.67 – 1.55 (m, 4H), 1.52 – 1.41 (m, 5H), 1.26 – 1.16 (m, 4H), 0.97 (t, J = 7.6 Hz, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ / ppm = 174.7 (C_{NHC}), 152.1, 148.9, 144.5, 138.7, 138.6, 137.5, 136.8, 136.7, 135.9, 135.8, 134.8, 132.8, 132.5, 130.8, 129.4, 129.2, 128.3, 128.0, 100.7, 80.2, 79.6, 71.9, 55.2, 55.0, 33.1, 32.4, 31.2, 30.0, 29.7, 29.4, 28.5, 28.3, 26.9, 26.3, 21.4, 21.2, 20.80, 20.76, 18.26, 18.20, 17.1, 14.6, 13.1, 12.1.

HRMS (ESI positive): m/z calcd. for $C_{51}H_{67}BF_2N_4OIr$ $[M\text{-}Cl]^+$ 993.50052, found 993.49966, calcd. for $C_{51}H_{67}BF_2N_4OIr$ $[M\text{-}Cl+CH_3CN]^+$ 1034.52707, found 1034.52568.

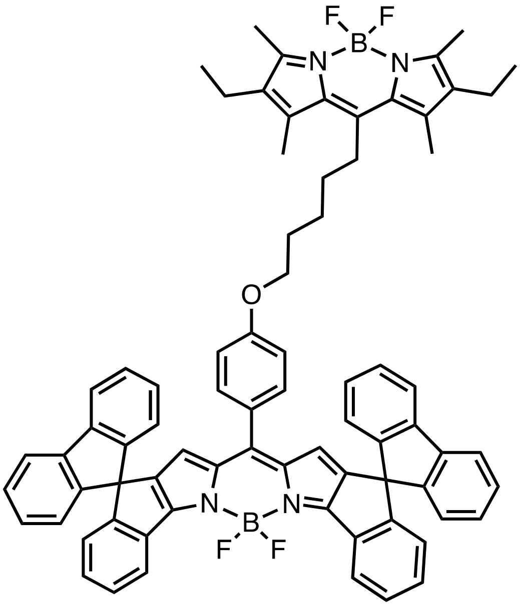


Synthesis of [Pd(allyl)Cl(**9**)]. General Procedure C: Imidazolium salt **9·HBr** (46 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), $[Pd(allyl)Cl]_2$ (11 mg, 0.03 mmol, 0.5 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/2) and gave [Pd(allyl)Cl(**9**)] (38 mg, 72%) as a microcrystalline orange powder.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ / ppm = 6.86 (ddq, J = 3.5, 1.3, 0.7 Hz, 4H), 6.31 (s, 1H), 4.65 (dddd, J = 13.2, 12.4, 7.4, 6.8 Hz, 1H), 3.87 (t, J = 6.2 Hz, 2H), 3.78 – 3.64 (m, 2H), 2.93 – 2.77 (m, 2H), 2.38 – 2.28 (m, 11H), 2.23 (s, 3H), 2.22 (s, 3H), 2.19 (s, 6H), 2.18 – 2.15 (m, 6H), 2.14 (s, 3H), 2.10 (s, 3H), 1.93 (dq, J = 12.3, 0.9 Hz, 1H), 1.72 – 1.59 (m, 2H), 1.43 (s, 6H), 0.97 (t, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 177.1 (C_{NHC}), 152.1, 149.1, 144.5, 138.9, 138.7, 136.6, 136.2, 136.0, 135.9, 135.4, 132.8, 132.4, 130.8, 128.94, 128.89, 128.86, 128.71, 112.7, 100.0, 72.1, 67.3, 58.5, 31.2, 29.7, 28.5, 28.3, 26.9, 26.3, 20.8, 18.79, 18.75, 18.65, 17.1, 14.6, 13.1, 12.1.

HRMS (ESI positive): *m*/*z* calcd. for $C_{46}H_{60}BF_2N_4OPd$ $[M-Cl]^+$ 839.38631, found 839.38840, calcd. for $C_{48}H_{63}BF_2N_5OPd$ $[M-Cl+CH_3CN]^+$ 880.41286, found 880.41527.

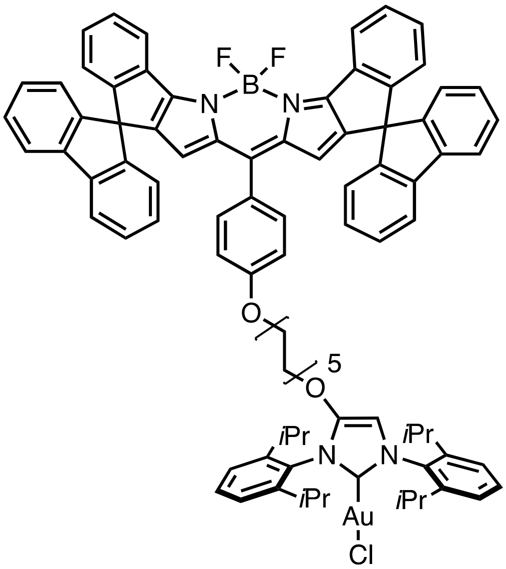


Synthesis of 12. General Procedure B: Bodipy **10** (153 mg, 0.2 mmol, 1 eq.), Bodipy **11** (136 mg, 0.3 mmol, 1.5 eq.), K_2CO_3 (55 mg, 0.4 mmol, 2 eq.), KI (100 mg, 0.6 mmol, 4 eq.) were placed in 10 mL round flask and dissolved in dry acetone (4.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/4) and gave **12** (110 mg, 49%) as a dark red powder.

^{1}H NMR ($CDCl_3$, 500 MHz): δ / ppm = 8.52 (d, *J* = 7.7 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 4H), 7.53 (td, *J* = 7.6, 1.1 Hz, 2H), 7.40 (td, J = 7.5, 1.1 Hz, 4H), 7.35 – 7.29 (m, 2H), 7.23 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.19 (td, *J* = 7.5, 1.2 Hz, 4H), 6.98 (d, *J* = 7.6 Hz, 4H), 6.80 – 6.75 (m, 2H), 6.66 (d, *J* = 7.7 Hz, 2H), 6.25 (s, 2H), 3.89 (t, *J* = 6.2 Hz, 2H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.49 (s, 6H), 2.34 (p, *J* = 7.7 Hz, 4H), 2.29 (s, 6H), 1.80 (q, *J* = 6.3 Hz, 2H), 1.64 (t, *J* = 6.1 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 161.3, 160.4, 156.6, 152.1, 148.3, 144.4, 142.9, 142.1, 141.3, 141.1, 135.6, 132.6, 132.0, 130.8, 130.4, 128.8, 128.0, 127.9, 126.5, 124.3, 124.2, 124.2, 120.6, 120.0, 114.1, 67.4, 59.8, 53.4, 31.2, 28.7, 28.4, 26.5, 17.1, 14.8, 13.3, 12.4.

HRMS (ESI): *m/z* calcd. for $C_{75}H_{63}B_2F_4N_4O$ $[M+H]^+$ 1133.51241, found 1133.51382, calcd. for $C_{75}H_{62}B_2F_3N_4O$ $[M-F]^+$ 1113.50618, found 1113.50802, calcd. for $C_{75}H_{62}B_2F_4N_4NaO$ $[M+Na]^+$ 1155.49436, found 1155.49631.

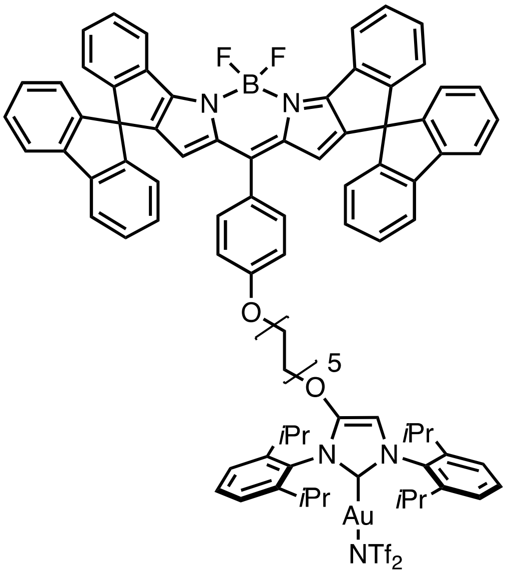


Synthesis of [AuCl(NHC_red)]. General Procedure C: Imidazolium salt **5·HBr** (83 mg, 0.06 mmol, 1 eq.), K_2CO_3 (25 mg, 0.18 mmol, 3 eq.), [AuCl(SMe_2)] (17.7 mg, 0.06 mmol, 1 eq.) were placed in dried 5 mL Schlenk flask and dissolved in dry acetone (2.0 mL). The crude red product was purified by column chromatography (EtOAc/cyclohexane = 1/5) and gave [AuCl(NHC_red)] (54 mg, 59%) as a microcrystalline dark red powder.

^{1}H NMR (500 MHz, CD_2Cl_2): δ / ppm = 8.48 (d, *J* = 7.7 Hz, 2H), 7.87 (dd, *J* = 7.6, 1.0 Hz, 4H), 7.62 – 7.51 (m, 4H), 7.42 (td, *J* = 7.5, 1.1 Hz, 4H), 7.39 – 7.31 (m, 6H), 7.28 (td, *J* = 7.6, 1.1 Hz, 2H), 7.21 (td, *J* = 7.5, 1.1 Hz, 4H), 6.98 (d, *J* = 7.6 Hz, 4H), 6.82 – 6.77 (m, 2H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.47 (s, 1H), 6.31 (s, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 2.72 (h, *J* = 6.7 Hz, 2H), 2.63 (h, *J* = 6.9 Hz, 2H), 1.73 – 1.64 (m, 4H), 1.37 (dd, *J* = 13.1, 6.9 Hz, 12H), 1.34 – 1.25 (m, 12H), 1.23 (q, *J* = 5.7, 5.1 Hz, 12H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 179.4 (C_{NHC}), 161.1, 160.8, 156.8, 148.5, 148.1, 146.4, 145.9, 143.0, 142.5, 141.4, 141.0, 134.7, 132.6, 132.00, 130.55, 130.47, 130.44, 130.36, 128.7, 128.0, 127.9, 126.1, 124.15, 124.12, 124.04, 123.98, 120.6, 120.1, 114.2, 99.2, 72.8, 68.2, 59.8, 29.26, 29.22, 29.20, 29.00, 28.99, 28.70, 28.58, 25.8, 25.6, 24.4, 23.86, 23.84, 23.3, 0.8.

HRMS (ESI positive): m/z calcd. For $C_{90}H_{86}BF_2N_4O_2$: 1303.68064 [M-AuCl]$^+$; found 1303.68222.

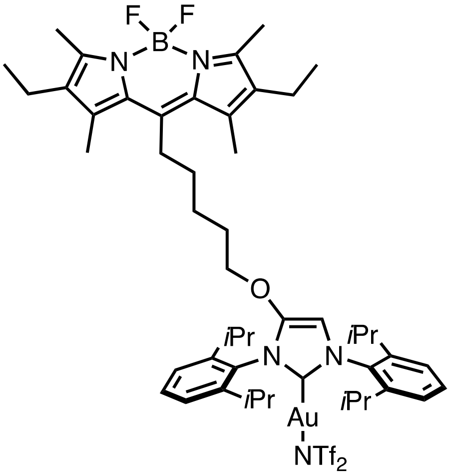


Synthesis of 14. A mixture of [AuCl(NHC_red)] complex (20 mg, 0.013 mmol, 1.0 eq.) and Ag(NTf$_2$) (5.4 mg, 0.014 mmol, 1.05 eq.) were dissolved in dry CH_2Cl_2 (1.5 mL), and reaction mixture was stirred for 30 min in the dark at rt under nitrogen atmosphere. The mixture was filtered *via* celite, and the filtrate was evaporated on the rotavap under reduced pressure. The crude material was rinsed with pentane (1 mL), dried *in high vacuum* and gave **14** (22 mg, 95%) as a dark red solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ / ppm = 8.49 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 7.6 Hz, 4H), 7.57 (qd, J = 7.8, 1.7 Hz, 4H), 7.42 (td, J = 7.6, 1.1 Hz, 4H), 7.35 (dd, J = 7.9, 6.1 Hz, 6H), 7.28 (td, J = 7.5, 1.1 Hz, 2H), 7.21 (td, J = 7.6, 1.1 Hz, 4H), 6.99 (d, J = 7.6 Hz, 4H), 6.79 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 7.7 Hz, 2H), 6.57 (s, 1H), 6.31 (s, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.86 (t, J = 6.5 Hz, 2H), 2.64 (p, J = 6.8 Hz, 2H), 2.56 (h, J = 6.8 Hz, 2H), 1.75 – 1.66 (m, 4H), 1.34 (dd, J = 11.3, 6.9 Hz, 14H), 1.29 (d, J = 6.9 Hz, 10H), 1.23 (d, J = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 162.0, 161.1, 160.8, 156. 8, 149.0, 148.1, 146.3, 145.9, 142.9, 142.5, 141.4, 141.0, 134.4, 132.6, 132.0, 130.7, 130.6, 130.5, 130.1, 128.7, 128.0, 127.9, 126.1, 124.16, 124.10, 124.03, 123.98, 120.6, 120.1, 117.6, 114.2, 100.0, 73.0, 68.2, 59.8, 29.36, 29.28, 29.23, 29.21, 29.08, 29.01, 28.99, 28.77, 28.58, 25.8, 25.6, 24.1, 23.9, 23.6, 23.3.

High-resolution mass could not be obtained for this complex.

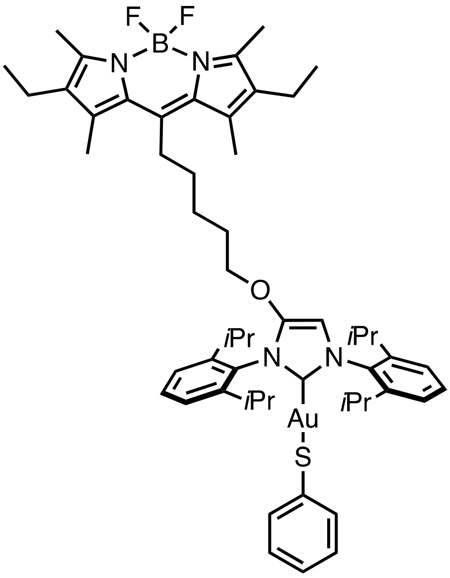


Synthesis of [Au(NTf$_2$)(NHC_green)].[5] A mixture of [AuCl(NHC_green)][5] complex (13 mg, 0.013 mmol, 1.0 eq.), and Ag(NTf$_2$) (5.4 mg, 0.014 mmol, 1.05 eq.) were dissolved in dry CH_2Cl_2 (1.0 mL), and reaction mixture was stirred for 30 min in the dark at rt under nitrogen atmosphere. The mixture was filtered through a celite plug, and the filtrate evaporated on the rotavap under reduced pressure. The crude material was rinsed with pentane (1 mL), dried *in high vacuum* and gave [Au(NTf$_2$)(NHC_green)] (15 mg, 91%) as an orange solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ / ppm = 7.55 (dt, J = 11.5, 7.8 Hz, 2H), 7.35 (t, J = 8.4 Hz, 4H), 6.60 (s, 1H), 4.11 (t, J = 6.3 Hz, 2H), 2.96 (dd, J = 10.7, 5.8 Hz, 2H), 2.58 (dt, J = 13.8, 7.2 Hz, 2H), 2.49 (s, 3H), 2.45 (q, J = 7.5 Hz, 6H), 2.29 (s, 6H), 1.82 (p, J = 6.6 Hz, 2H), 1.63 – 1.53 (m, 4H), 1.35 (d, J = 6.9 Hz, 6H), 1.33 (d, J = 6.8 Hz, 6H), 1.29 (d, J = 6.9 Hz, 6H), 1.24 (d, J = 6.9 Hz, 6H), 1.09 (t, J = 7.6 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 162.2, 152.1, 148.8, 146.2, 145.9, 144.3, 135.8, 134.4, 132.8, 130.7, 130.6, 130.0, 124.1, 124.0, 122.7, 120.2, 117.6, 115.0, 100.1, 72.6, 31.3, 29.7, 29.1, 28.8, 28.7, 28.2, 26.31, 24.1, 23.9, 23.6, 23.3, 17.1, 14.6, 13.2, 12.2.

High-resolution mass could not be obtained for this complex.

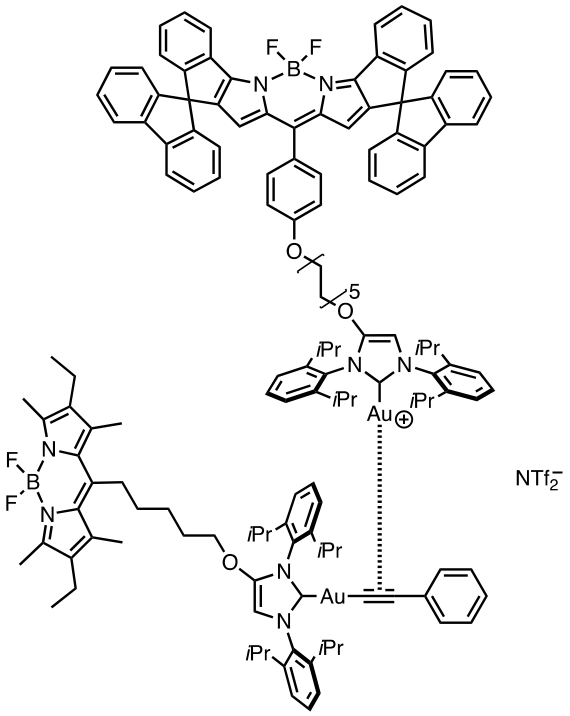


Synthesis of 15. To a solution of [AuCl(NHC_green)] [5] (51.4 mg, 0.041 mmol) in dry EtOH (2.5 mL) and dry CH_2Cl_2 (1.5 mL), were added thiophenol (30 μL, 0.28 mmol) and Et_3N (30 μL, 0.21 mmol), and the resulting mixture was stirred for 30 min (open vessel). After evaporation of the solvent on the rotavap under reduced pressure, the residue was purified by dissolution/precipitation using CH_2Cl_2 and pentane to afford **15** as an orange solid (44.4 mg, 0.042 mmol, 82%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ / ppm = 7.59 (td, J = 7.8, 5.2 Hz, 2H), 7.38 (dd, J = 7.8, 4.9 Hz, 4H), 6.78 (s, 5H), 6.53 (s, 1H), 4.09 (t, J = 6.3 Hz, 2H), 3.01 – 2.94 (m, 2H), 2.74 (dp, J = 31.2, 6.9 Hz, 4H), 2.49 (s, 6H), 2.44 (t, J = 7.6 Hz, 4H), 2.30 (s, 6H), 1.81 (p, J = 6.5 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.52 (d, J = 7.4 Hz, 2H), 1.37 (dd, J = 11.0, 6.8 Hz, 12H), 1.27 (dd, J = 23.2, 6.9 Hz, 12H), 1.09 (t, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 181.0 (C_{NHC}), 152.1, 148.6, 146.5, 146.1, 144.40, 144.35, 135.8, 134.9, 132.8, 131.3, 130.7, 130.6, 130.5, 130.4, 127.2, 124.2, 124.0, 121.6, 99.2, 72.4, 53.9, 53.6, 53.4, 53.2, 53.0, 31.3, 29.1, 28.8, 28.7, 28.2, 26.3, 24.3, 23.91, 23.84, 23.4, 17.1, 14.6, 13.2, 12.17, 12.15, 12.12.

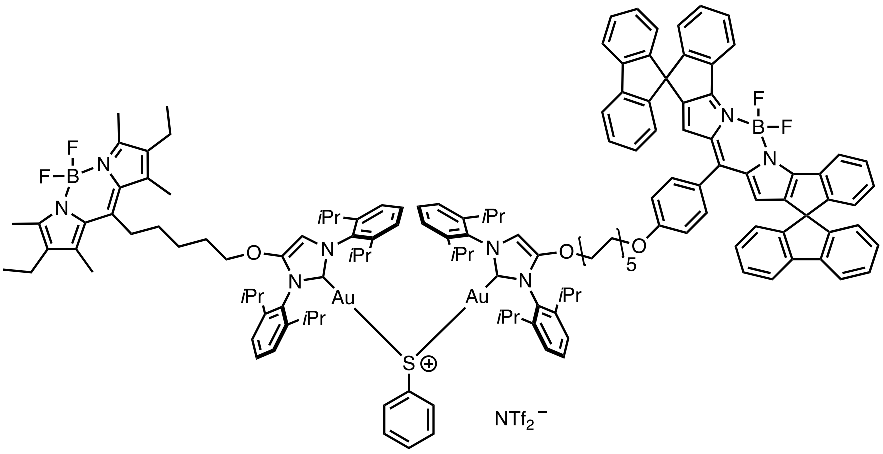
HRMS (ESI positive): m/z calcd. $C_{55}H_{73}AuBF_2N_4OS$: 1083.52264 [M+H] $^+$; found 1083.52334.



Synthesis of 16. A solution of **13** (16.4 mg, 0.015 mmol, 1 eq.) and **14** (27.1 mg, 0.015 mmol, 1 eq.) in dry CH_2Cl_2 (1.5 mL) was stirred for 40 min in the dark. After the solvent was evaporated on the rotavap under reduced pressure, the resulting solid was rinsed with Et_2O (ca. 1 mL) and pentane (ca. 1.5 mL) and dried in high vacuum to give a dark violet solid **16** (34.6 mg, 0.012 mmol, 80%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ / ppm = 8.48 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 7.6 Hz, 4H), 7.62 – 7.45 (m, 6H), 7.44 – 7.34 (m, 7H), 7.31 – 7.24 (m, 9H), 7.21 (tt, J = 7.5, 1.3 Hz, 5H), 7.15 – 7.09 (m, 2H), 6.98 (d, J = 7.6 Hz, 4H), 6.79 (dd, J = 8.6, 2.4 Hz, 2H), 6.74 – 6.69 (m, 2H), 6.67 (d, J = 7.7 Hz, 2H), 6.50 (d, J = 19.6 Hz, 2H), 6.31 (d, J = 1.8 Hz, 2H), 4.06 (t, J = 6.3 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.86 (td, J = 6.6, 2.1 Hz, 2H), 3.44 (q, J = 7.3 Hz, 1H), 2.97 – 2.91 (m, 2H), 2.69 – 2.55 (m, 4H), 2.49 (s, 9H), 2.45 (q, J = 7.6 Hz, 4H), 2.28 (s, 6H), 1.77 (p, J = 6.5 Hz, 2H), 1.68 (dt, J = 14.2, 6.7 Hz, 4H), 1.52 (d, J = 7.2 Hz, 4H), 1.45 – 1.27 (m, 14H), 1.24 (dd, J = 7.0, 3.0 Hz, 16H), 1.18 (dd, J = 6.9, 2.2 Hz, 12H), 1.15 – 1.07 (m, 24H).

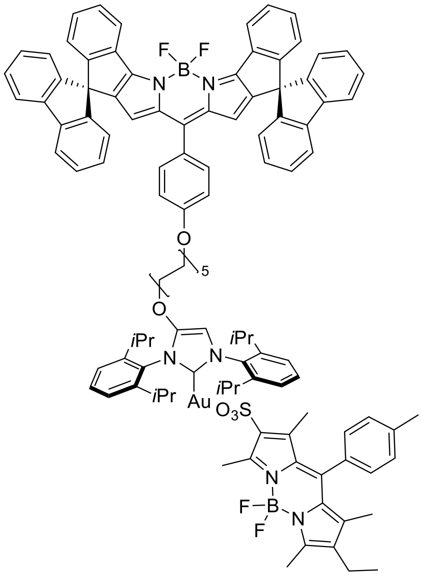
^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 177.1 (C_{NHC}), 160.8, 156.8, 152.1, 148.9, 148.7, 148.1, 146.2, 146.1, 145.7, 142.9, 141.4, 141.0, 135.8, 134.3, 132.8, 132.5, 132.0, 131.7, 130.7, 130.5, 130.0, 129.4, 128.7, 128.3, 128.0, 127.9, 126.1, 124.23, 124.15, 124.04, 123.98, 121.2, 120.6, 120.1, 118.7, 114.2, 100.25, 100.16, 73.1, 72.8, 68.2, 59.8, 31.2, 29.26, 29.21, 28.97, 28.93, 28.71, 28.66, 28.53, 28.23, 26.3, 25.8, 25.5, 24.5, 23.9, 23.8, 23.29, 23.27, 22.3, 17.1, 14.6, 13.8, 13.2, 12.2, 7.3.



Synthesis of 17. A solution of **15** (10.4 mg, 0.01 mmol, 1 eq.) and **14** (17.1 mg, 0.01 mmol, 1 eq.) in dry CH_2Cl_2 (2.0 mL) was stirred for 30 min in the dark under nitrogen atmosphere. After the solvent was evaporated on the rotavap under reduced pressure, the remaining solid was purified by dissolution/precipitation using CH_2Cl_2 (ca. 0.5 mL) and pentane (1.5 mL) to give **17** as a black solid (27.0 mg, 0.010 mmol, 98%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ / ppm = 8.48 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 4H), 7.60 – 7.46 (m, 6H), 7.42 (t, J = 7.6 Hz, 4H), 7.39 – 7.33 (m, 2H), 7.31 – 7.18 (m, 14H), 6.98 (d, *J* = 7.7 Hz, 5H), 6.81 – 6.74 (m, 4H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.51 (s, 1H), 6.47 (s, 1H), 6.31 (s, 2H), 6.24 (d, *J* = 7.7 Hz, 2H), 4.06 (t, *J* = 6.3 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.89 – 3.83 (m, 2H), 2.97 – 2.91 (m, 2H), 2.54 (q, *J* = 6.9 Hz, 4H), 2.51 – 2.41 (m, 14H), 2.27 (s, 6H), 1.77 (p, *J* = 6.7 Hz, 2H), 1.73 − 1.62 (m, 4H), 1.56 – 1.45 (m, 4H), 1.34 (dq, *J* = 12.6, 6.7 Hz, 4H), 1.30 – 1.20 (m, 20H), 1.18 (t, *J* = 7.8 Hz, 14H), 1.07 (dd, *J* = 12.3, 7.0 Hz, 28H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 173.71 (C_{NHC}), 173.58 (C_{NHC}), 161.1, 160.8, 156.8, 152.1, 148.8, 148.7, 148.1, 146.2, 146.1, 145.7, 144.3, 143.0, 141.4, 141.0, 135.8, 134.3, 134.3, 132.8, 132.54 132.3, 132.0, 131.6, 130.7, 130.5, 129.9, 128.7, 128.4, 128.0, 127.9, 126.2, 126.1, 124.20, 124.18, 124.15, 124.03, 123.98, 120.6, 120.1, 114.2, 100.01, 99.91, 73.1, 72.7, 68.2, 59.8, 53.9, 53.6, 53.4, 53.2, 53.0, 31.2, 29.3, 29.21, 29.19, 29.0, 28.9, 28.7, 28.63, 28.62, 28.53, 28.2, 26.3, 25.8, 25.5, 24.5, 23.9, 23.8, 23.28, 23.25, 17.1, 14.59, 13.1, 12.2.



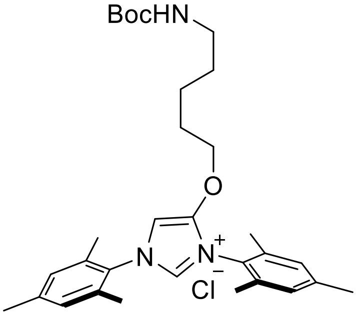
Synthesis of 18. In 25 mL round flask **14** (6.15 mg, 4.0·μmol) was dissolved in CH_2Cl_2 (10 mL) and a solution of [Ag(bdpSO$_3$)] (2.22 mg, 4.0·μmol) in acetonitrile (5 mL) was added. The AgCl precipitate formed immediately was separated by filtration through celite. The celite was washed with dichloromethane (10 mL) to extract the product completely. The combined filtrates were evaporated and dried overnight in high vacuum. Yield: 7.8 mg (99 %).

^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm = 8.44 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 7.6 Hz, 4H), 7.53 (t, J = 7.5 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.38 (t, J = 7.5 Hz, 4H), 7.32 (d, J = 8.0 Hz, 4H), 7.29 – 7.22 (m, 6H), 7.17 (t, J = 7.5 Hz, 4H), 7.11 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 7.6 Hz, 4H), 6.75 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 7.7 Hz, 2H), 6.46 (s, 1H), 6.27 (s, 2H), 3.97 (t, J = 6.4 Hz, 2H), 3.83 (t, J = 6.4 Hz, 2H), 2.60 – 2.39 (m, 12H), 2.33 (q, J = 7.2 Hz, 2H), 1.68 – 1.61 (m, 4H), 1.34 – 1.13 (m, 42H), 0.99 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 161.69 (d, J = 4.4 Hz), 161.3, 159.2, 158.6, 157.4, 149.3, 148.7, 146.8, 146.4, 143.5, 143.0, 141.9, 141.6, 139.8, 139.7, 135.6, 135.1, 133.1, 132.6, 131.3, 131.2, 131.1, 131.0, 130.7, 130.4, 130.3, 129.5, 129.3, 128.62, 128.55, 128.47, 126.7, 124.80, 124.72, 124.66, 124.55, 121.2, 120.7, 114.7, 100.3, 73.4, 68.7, 60.3, 29.84, 29.79, 29.77, 29.73, 29.61, 29.55, 29.31, 29.25, 29.12, 26.4, 26.1, 24.9, 24.5, 24.3, 24.0, 21.8, 17.6, 14.7, 14.0, 13.3, 13.1, 12.4.

^{19}F NMR (471 MHz, CD_2Cl_2) δ / ppm = -144, 26 (q, $J(^{11}B-^{19}F)$ = 33 Hz) (green Bodipy), -146.43 (q, $J(^{11}B-^{19}F)$ = 33 Hz) (red Bodipy).

HRMS (ESI positive): m/z calcd. for $C_{90}H_{85}AuBF_2N_4O_2$: 1499.63992 [M+H]$^+$; found 1499.64152. HRMS (ESI negative): m/z calcd. for $C_{22}H_{24}BF_2N_2O_3S$: 445.1569 [M-H]$^-$; found 445.1570.

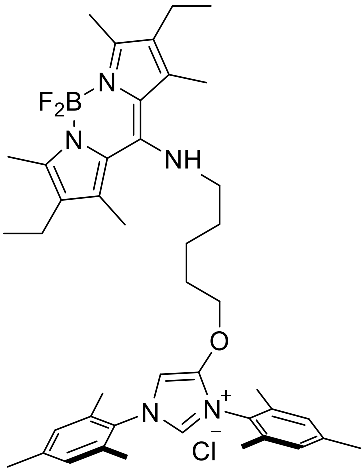


Synthesis of IMes·HCl. General Procedure B: BocNH$(CH_2)_5$OTs (90 mg, 0.25 mmol, 1.2 eq.), 4-hydroxy-1,3-dimesityl-1H-imidazol-3-ium chloride (75 mg, 0.21 mmol, 1.0 eq.), K_2CO_3 (29 mg, 0.21 mmol, 1.0 eq.), KI (105 mg, 0.63 mmol, 3 eq) were placed in a dried 5 mL Schlenk flask and dissolved in dry acetone (3 mL). The crude product was purified by column chromatography (MeOH/CH_2Cl_2 = 1/15) and gave IMes·HCl (55 mg, 48%) as a white powder.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm = 9.28 (s, 1H), 7.30 (s, 1H), 7.02 (d, J = 10.4 Hz, 4H), 4.57 (s, 1H), 4.32 (t, J = 6.5 Hz, 2H), 3.03 (q, J = 6.7 Hz, 2H), 2.34 (d, J = 8.7 Hz, 6H), 2.22 (s, 6H), 2.14 (s, 6H), 1.84 – 1.60 (m, 3H), 1.50 – 1.14 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm = 156.2, 147.7, 141.7, 141.5, 134.9, 134.2, 131.3, 130.9, 130.1, 126.8, 102.2, 74.9, 29.6, 28.5, 28.0, 22.7, 21.3, 18.0.

HRMS (ESI positive): m/z calcd. for $C_{31}H_{44}N_3O_3$: 506.33772 [M-Cl]$^+$; found 506.33840.



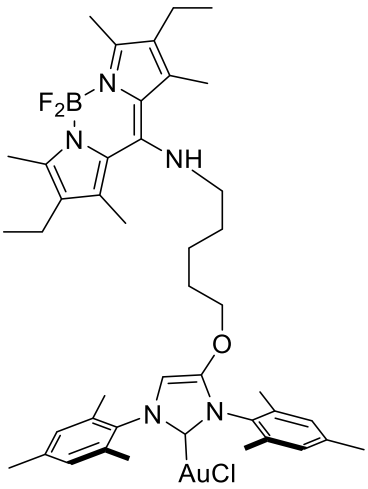
Synthesis of 19. The imidazolium salt (40 mg, 0.074 mmol) was dissolved in freshly distilled CH_2Cl_2 (2 mL) in a dried 10 mL Schlenk flask, cooled to 0°C and treated with a solution of HCl in dioxane (4M, 28 μL, 0.11 mmol, 1.5 eq) and stirred at rt for 15 h under nitrogen atmosphere. The volatiles was evaporated on the rotavap under reduced pressure, Et_3N (17.5 μL, 0.11 mmol, 1.7 eq) and *meso*-Cl Bodipy[3] (25 mg, 0.074 mmol) were added to the crude product, and the mixture dissolved in CH_2Cl_2:CH_3CN (1:1) (2 mL). The solution was stirred for 15 h at rt. Removal of the solvent on the rotavap under reduced pressure and purification of the residue by silica gel column chromatography (CH_2Cl_2/MeOH = 1/1) as an eluent provides **19** as a yellow solid. Yield: 27 mg (49%).

^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm = 9.26 (d, J = 1.7 Hz, 1H), 7.56 (d, J = 1.8 Hz, 1H), 7.00 (s, 4H), 5.39 (t, J = 5.3 Hz, 1H), 4.31 (t, J = 6.6 Hz, 2H), 3.47 (q, J = 6.3 Hz, 2H), 2.42 (s, 6H), 2.40 – 2.37 (m, 4H), 2.32 (d, J = 2.2 Hz, 6H), 2.26 (s, 6H), 2.20 (s, 6H), 2.09 (s, 6H), 1.71 – 1.64 (m, 6H), 1.37 – 1.31 (m, 2H), 1.03 (t, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 151.4, 147.5, 145.0, 141.5, 141.3, 134.8, 134.1, 131.3, 131.0, 129.9, 129.8, 129.6, 128.6, 126.9, 122.7, 102.6, 74.3, 52.1, 31.7, 27.9, 22.5, 21.20, 21.16, 17.6, 17.2, 15.1, 13.2, 12.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ / ppm = -144.43 (q, $J(^{11}B-^{19}F)$ = 33 Hz).

HRMS (ESI positive): m/z calcd. for $C_{43}H_{57}BF_2N_5O$: 708.46310 $[M-Cl]^+$; found 708.46187.



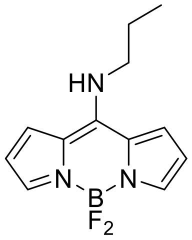
Synthesis of 20. General Procedure C**:** To a 5 mL dried Schlenk flask equipped with a stirring bar containing **19** (15 mg, 0.02 mmol, 1.0 eq) and Ag_2O (2.3 mg, 0.01 mmol, 0.5 eq) under a flow of the nitrogen gas, dry 1,2-dichloroethane (2 mL) was added and the flask was sealed. After stirring in the dark for 90 min at 55 °C, $[AuCl(SMe_2)]$ (5.9 mg, 0.02 mmol, 1.0 eq) was added and the mixture was stirred for an additional 2 h at 60 °C. The resulting suspension was filtered through a short celite plug. The filtrate was collected and evaporated on the rotavap under reduced pressure. The product was purified by column chromatography (CH_2Cl_2) obtaining the product as a yellow solid. Yield: 9.6 mg (51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm = 6.95 (d, J = 7.0 Hz, 4H), 6.30 (s, 1H), 5.18 (t, J = 5.7 Hz, 1H), 3.88 (t, J = 6.3 Hz, 2H), 3.42 (q, J = 6.6 Hz, 2H), 2.45 (s, 6H), 2.40 (q, J = 7.6 Hz, 4H), 2.32 (d, J = 7.0 Hz, 6H), 2.24 (s, 6H), 2.12 (s, 6H), 2.06 (s, 6H), 1.64 – 1.57 (m, 4H), 1.31 – 1.25 (m, 4H), 1.04 (t, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 168.2 (C_{NHC}), 151.3, 147.7, 145.7, 139.79, 139.75, 135.42, 135.39, 134.9, 131.1, 129.9, 129.55, 129.47, 128.7, 98.8, 72.6, 52.3, 32.0, 28.2, 22.9, 21.34, 21.27, 18.0, 17.8, 17.3, 15.2, 13.2, 12.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ / ppm = -145.17 (q, $J(^{11}B\text{-}^{19}F)$ = 28 Hz).

HRMS (ESI negative): m/z calcd. for $C_{43}H_{55}AuBClF_2N_5O$: 938.38274 $[M\text{-}H]^-$; found 938.38084.

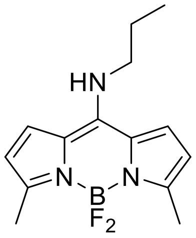


Synthesis of B1. General Procedure D:

^{1}H NMR (500 MHz, CDCl$_3$) δ / ppm = 7.68 (s, 1H), 7.44 (s, 1H), 7.09 (s, 1H), 6.80 (s, 1H), 6.58 (s, 1H), 6.51 (s, 1H), 6.29 (s, 1H), 3.50 (q, *J* = 6.5 Hz, 3H), 1.81 (h, *J* = 7.3 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 4H).

^{13}C NMR (126 MHz, CDCl$_3$) δ / ppm = 148.3, 135.0, 132.2, 125.0, 123.9, 122.4, 114.9, 114.7, 113.8, 49.0, 22.3, 11.5.

HRMS (ESI positive): m/z calcd. for $C_{12}H_{15}BF_2N_3$: 250.13216 [M+H]$^+$; found 250.13233. Yield: 108 mg (87%).

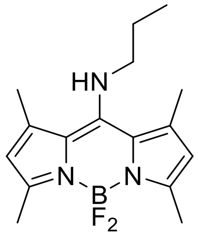


Synthesis of B2. General Procedure D:

^{1}H NMR (500 MHz, CDCl$_3$) δ / ppm = 6.83 (s, 2H), 6.13 (s, 2H), 6.02 (s, 1H), 3.41 (q, *J* = 6.5 Hz, 2H), 2.56 (s, 5H), 1.75 (h, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ / ppm = 147.5, 145.8, 123.3, 114.9, 48.8, 29.8, 22.6, 14.2, 11.5.

HRMS (ESI positive): m/z calcd. for $C_{14}H_{19}BF_2N_3$: 278.16346 [M+H]$^+$; found 278.16357. Yield: 118 mg (85%).

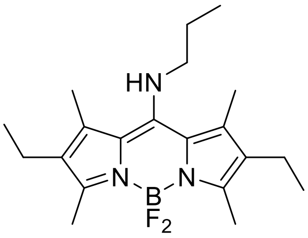


Synthesis of B3. General Procedure D:

^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm = 6.01 (s, 2H), 5.46 (s, 1H), 3.50 (q, *J* = 6.4 Hz, 2H), 2.50 (s, 6H), 2.36 (s, 6H), 1.70 (h, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 152.3, 147.4, 131.8, 123.2, 118.2, 54.4, 25.7, 15.7, 14.3, 11.3.

HRMS (ESI positive): m/z calcd. for $C_{16}H_{23}BF_2N_3$: 306.19476 $[M+H]^+$; found 306.19482. Yield: 113 mg (74%).

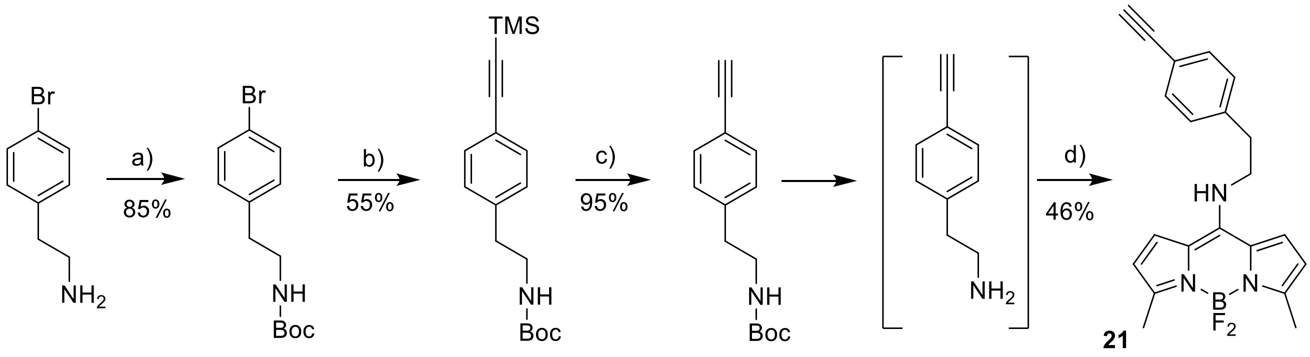


Synthesis of B4. General Procedure D:

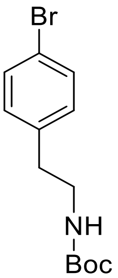
^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm = 5.38 (s, 1H), 3.47 (q, *J* = 6.3 Hz, 3H), 2.47 (s, 6H), 2.42 (q, *J* = 7.5 Hz, 4H), 2.29 (s, 6H), 1.69 (h, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.5 Hz, 6H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 151.5, 145.2, 129.7, 128.6, 122.9, 54.5, 25.7, 17.3, 15.2, 13.3, 12.2, 11.4.

HRMS (ESI positive): m/z calcd. for $C_{20}H_{31}BF_2N_3$: 362.25736 $[M+H]^+$; found 362.25743. Yield: 137 mg (76%).



Scheme S 1 Synthesis of blue Bodipy acetylene **21**. Reagents and conditions: a) Et_3N, Boc_2O, CH_2Cl_2, rt, 3 h; b) TMS-acetylene, CuI, $[PdCl_2(PPh_3)_2]$, HN*i*Pr_2, rt, 24 h; c) TBAF, THF, rt, 60 min. d) TFA, CH_2Cl_2, 0°C, 60 min; then 8-SMe Bodipy[4], Et_3N, CH_2Cl_2/ACN, rt, 24 h.

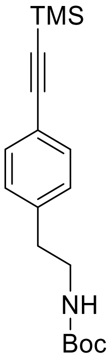


Synthesis of *tert*-butyl (4-bromophenethyl)carbamate. 2-(4-Bromophenyl)ethylamine (1.0 g, 5 mmol) was dissolved in CH_2Cl_2 (20 mL) and treated with Et_3N (1.05 mL, 7.5 mmol) and di-*tert*-butyl dicarbonate (1.43 g, 6.5 mmol). The solution was stirred at rt for 3 h. The reaction mixture was poured into 50 mL of water and washed with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL), dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuum. The crude product was purified by column chromatography on silica (EtOAc/cyclohexane = 3/1) to obtain the product as a white solid (1.28 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm = 7.35 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 4.80 (bs, 1H), 3.28 (q, J = 6.5 Hz, 2H), 2.69 (t, J = 7.0 Hz, 2H), 1.38 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm = 155.9, 138.1, 131.7, 130.6, 120.3, 41.7, 35.7, 28.5.

HRMS (ESI positive): m/z calcd. for $C_{13}H_{19}BrNO_2$: 300.05937 $[M+H]^+$; found 300.05902.

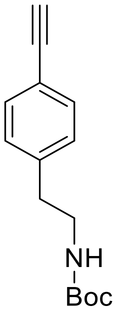


Synthesis of *tert*-butyl (4-((trimethylsilyl)ethynyl)phenethyl)carbamate. A solution of *tert*-butyl (4-bromophenethyl) carbamate (500 mg, 1.67 mmol), CuI (29 mg, 0.15 mmol) and dichlorobis(triphenylphosphine)palladium (II) (50 mg, 0.07 mmol) in degassed HN*i*Pr$_2$ (10 mL) was treated with TMS-acetylene (0.28 mL, 2.0 mmol) under nitrogen atmosphere, and stirred at rt for 3 h. The volatiles were evaporated on the rotavap under reduced pressure, the residue was dissolved in Et$_2$O (50 mL) and filtered through a celite plug, and the filtrate was concentrated in vacuum. The crude product was purified by column chromatography (EtOAc/cyclohexane = 1/ 10) to yield *tert*-butyl (4-((trimethylsilyl)ethynyl)phenethyl)carbamate (291 mg, 55%) as a yellow solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ / ppm = 7.44 – 7.37 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 4.57 (s, 1H), 3.35 (q, J = 6.4 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H), 1.44 (s, 9H), 0.26 (s, 9H).

^{13}C NMR (75 MHz, chloroform-*d*) δ / ppm = 155.9, 139.7, 132.3, 128.8, 121.3, 105.1, 94.0, 41.7, 36.2, 28.5, 0.1.

HRMS (ESI positive): m/z calcd. for $C_{18}H_{28}NO_2Si$: 318.18838 $[M+H]^+$; found 318.18887.

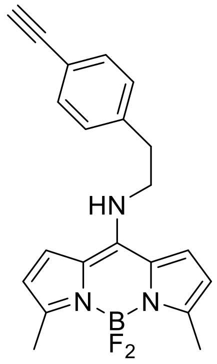


Synthesis of *tert*-butyl (4-ethynylphenethyl)carbamate. *Tert*-butyl(4-((trimethylsilyl)ethynyl)phenethyl)carbamate (250 mg, 0.79 mmol) was dissolved in freshly distilled THF (3 mL) and treated with a solution of TBAF in THF (1.58 mL, 1.58 mmol, 1 M in THF) and stirred at rt for 1 h. After evaporation of the solution on the rotavap under reduced pressure, the residue was purified by column chromatography (EtOAc/cyclohexane = 1/3) to yield tert-butyl (4-ethynylphenethyl)carbamate (184 mg, 95%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm = 7.44 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 4.60 (s, 1H), 3.37 (q, J = 7.1 Hz, 2H), 3.07 (s, 1H), 2.81 (t, J = 6.8 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 156.0, 140.2, 132.5, 129.0, 120.3, 83.7, 79.5, 54.0, 41.7, 36.3, 28.6, 20.9, 14.3.

HRMS (ESI positive): m/z calcd. for $C_{15}H_{19}NNaO_2$: 268.13080 $[M+Na]^+$; found 268.13092.

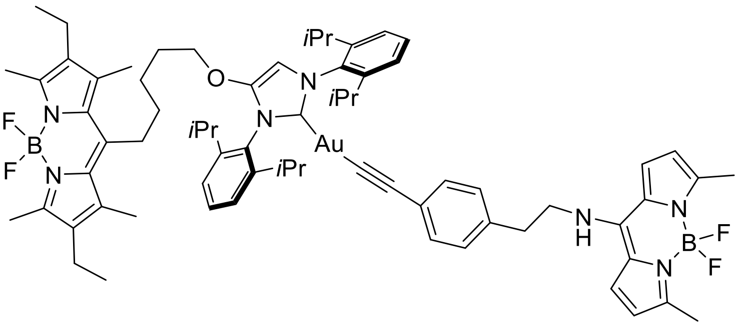


Synthesis of 21. *Tert*-butyl (4-ethynylphenethyl)carbamate (100 mg, 0.41 mmol) was dissolved in 3 mL of CH_2Cl_2, the reaction mixture was cooled to 0°C and treated with trifluoroacetic acid (200 μL) and stirred at rt for 1 h. The solution was evaporated and to the crude material was added 8-SMe Bodipy[4] (110 mg, 0.41 mmol) and Et_3N (112 μL, 0.8 mmol) in the solvent mixture 1:1 of CH_2Cl_2 and CH_3CN (2 mL), and the solution was stirred for 24 h at rt. Solvent removal on the rotavap under reduced pressure and purification by column chromatography on silica using CH_2Cl_2 as an eluent gave Bodipy **21** as a yellow solid (68 mg, 46%).

^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm = 7.51 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.79 (s, 2H), 6.16 (s, 2H), 5.99 (s, 1H), 3.83 (q, J = 6.5 Hz, 2H), 3.10 (s, 1H), 3.07 (t, J = 6.9 Hz, 2H), 2.56 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm = 147.9, 145.5, 137.6, 133.1, 128.8, 123.3, 121.6, 115.3, 83.1, 78.0, 47.3, 34.9, 27.1, 14.3.

HRMS (ESI positive): m/z calcd. for $C_{21}H_{21}BF_2N_3$: 364.17911 $[M+H]^+$; found 364.17939.

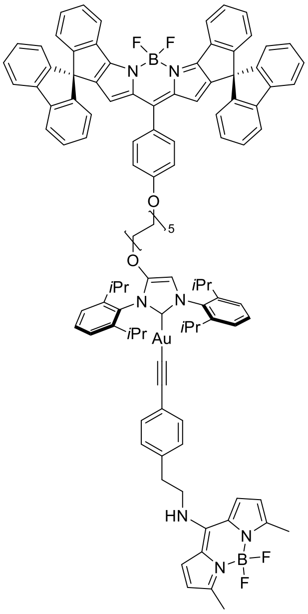


Synthesis of 22·dbu. A vial was charged with [AuCl(NHC_green)][5] (4.0 mg, 0.004 mmol, 1.0 eq) and **21** (1.5 mg, 0.004 mmol, 1.0 eq) and dissolved in a minimum amount of CH_2Cl_2 ~200 μL. To the reaction mixture, DBU (3.0 μL, 0.02 mmol, 5.0 eq) was added and the solution stirred at rt for 15 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed two times with brine (50 mL) and two times with water (50 mL). The organic layer was dried over $MgSO_4$, filtered and the volatiles evaporated on the rotavap under reduced pressure. The remaining orange solid **22·dbu** was used in further experiments without additional purification (5.9 mg, 99%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm = 7.55 (m, 2H, *p*-H_{Ar}), 7.35 (m, 4H, *m*-H_{Ar}), 7.23 (d, J = 8.0 Hz, 2H, *m*-$H_{Ar\text{-}bdp}$), 7.06 (d, J = 8.0 Hz, 2H, *o*-$H_{Ar\text{-}bdp\text{-}blue}$), 6.89 (br. s, 2H, γ-H bpd-blue), 6.45 (s, 1H, NC(OR)CHN), 6.17 (bs, 2H, β-H bdp-blue), 4.02 (t, J = 6.3 Hz, 2H, alkyl chain -CH_2O-), 3.86 (t, J = 7.0 Hz, 2H, alkyl chain -CH_2-Ar bdp-blue), 3.46 – 3.28 (m, 6H, DBU), 3.03 (t, J = 6.9 Hz, 2H, alkyl chain -CH_2-NH-bdp-blue), 2.91 (m, 4H, DBU + alkyl chain CH_2 bdp-green), 2.75 – 2.56 (m, 4H, CH *i*Pr), 2.48 (s, 6H, CH_3 bdp-blue), 2.45 (s, 6H, CH_3 bdp-green), 2.43 – 2.37 (m, 4H, $\underline{CH_2}CH_3$ bdp-green), 2.25 (s, 6H, CH_3 bdp-green), 2.12 – 1.89 (m, 2H, alkyl chain CH_2), 1.81 – 1.45 (m, 12H, DBU + alkyl chain), 1.41 – 1.31 (m, 12H, CH_3 *i*Pr), 1.26 (d, J = 6.7 Hz, 6H, CH_3 *i*Pr), 1.21 (d, J = 6.8 Hz, 6H, CH_3 *i*Pr), 1.05 (t, J = 7.5 Hz, 6H, $CH_2\underline{CH_3}$ bdp-green).

^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm = 185.1 (C_{NHC}), 166.2, 152.1, 148.7, 148.5, 146.4, 146.0, 145.9, 145.7, 144.3, 135.8, 135.0, 134.2, 132.8, 132.4, 130.7, 130.6, 130.5, 130.4, 130.4, 128.3, 125.4, 124.2, 124.2, 124.1, 124.0, 99.6, 72.4, 48.7, 47.4, 43.9, 41.1, 37.9, 34.5, 32.0, 31.9, 31.3, 29.6. 29.6, 29.4, 29.1, 29.0, 28.7, 28.2, 26.6, 26.3, 24.6, 24.4, 24.1, 24.0, 23.88, 23.84, 23.77, 23.37, 23.29, 22.7.

^{19}F NMR (471 MHz, CD_2Cl_2) δ / ppm = -145.40 (q, $J(^{11}B\text{-}^{19}F)$ = 33 Hz) (green Bodipy), -147.51 (q, $J(^{11}B\text{-}^{19}F)$ = 28 Hz) (blue Bodipy).

HRMS (ESI positive): m/z calcd. for $C_{70}H_{87}AuB_2F_4N_7O$: 1336.67545 $[M+H]^+$; found 1336.67735.



Synthesis of 24·dbu. A vial was charged with [AuCl(NHC_red)] (6.1 mg, 0.004 mmol, 1.0 eq) and **21** (1.5 mg, 0.004 mmol, 1.0 eq) and dissolved in a minimum amount of CH_2Cl_2 ~200 µL. To the reaction mixture, DBU (6.0 µL, 0.02 mmol, 10 eq) was added and the solution was stirred at rt for 48 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), and washed two times with brine (50 mL) and two times with water (50 mL). The organic layer was dried over $MgSO_4$, filtered and the volatiles evaporated on the rotavap under reduced pressure. The remaining **24·dbu** as a red solid was used in further experiments without additional purification (8.0 mg, 99%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.44 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 4H), 7.57 – 7.50 (m, 4H), 7.40 – 7.32 (m, 10H), 7.27 – 7.22 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 4H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 4H), 6.75 (d, *J* = 7.7 Hz, 2H), 6.63 (d, *J* = 7.7 Hz, 2H), 6.42 (s, 1H), 6.27 (s, 2H), 6.23 – 6.13 (m, 3H), 3.97 (t, *J* = 6.2 Hz, 2H), 3.91 – 3.80 (m, 4H), 3.46 – 3.32 (m, 6H, DBU) 3.02 (t, *J* = 6.7 Hz, 2H), 2.72 – 2.55 (m, 4H), 2.48 (s, 6H), 2.31 – 2.29 (m, 2H, DBU) 1.89 – 1.61 (m, 12H, DBU + alkyl chain), 1.38 – 1.19 (m, 40H, CH_3 *i*Pr + alkyl chain).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -146.44 (q, *J*(^{11}B-^{19}F) = 31 Hz), -147.52 (q, *J*(^{11}B-^{19}F) = 31 Hz) (blue Bodipy).

HRMS (ESI positive): m/z calcd. for $C_{111}H_{104}AuB_2F_4N_7O_2$: 1862.8112 $[M+H]^+$; found 1862.8116.

3. UV/Vis and Fluorescence Data

3.1 Evaluation of red-green FRET

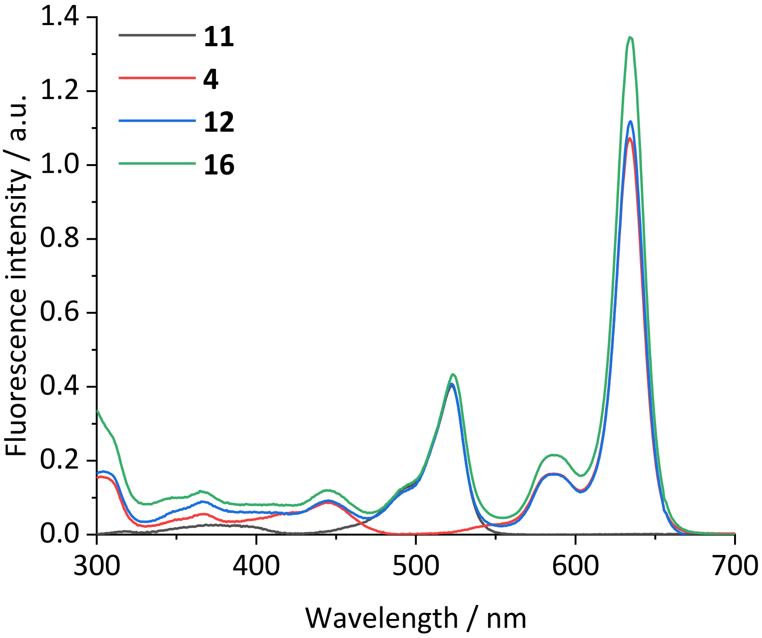


Figure S 1 Individual absorbance spectra of Bodipys **11** and **4**, Bodipy dyad **12**, and Widenhoefer complex **16** in CH_2Cl_2 (5.0 μM).

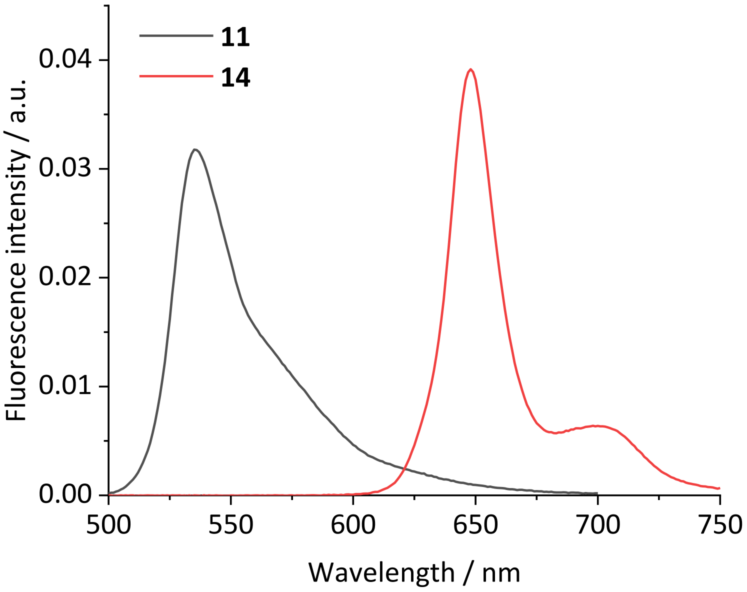


Figure S 2 Emission spectra of compounds **11** (λ_{ex} = 500 nm) and **14** (λ_{ex} = 620 nm) in CH_2Cl_2 (5.0 μM).

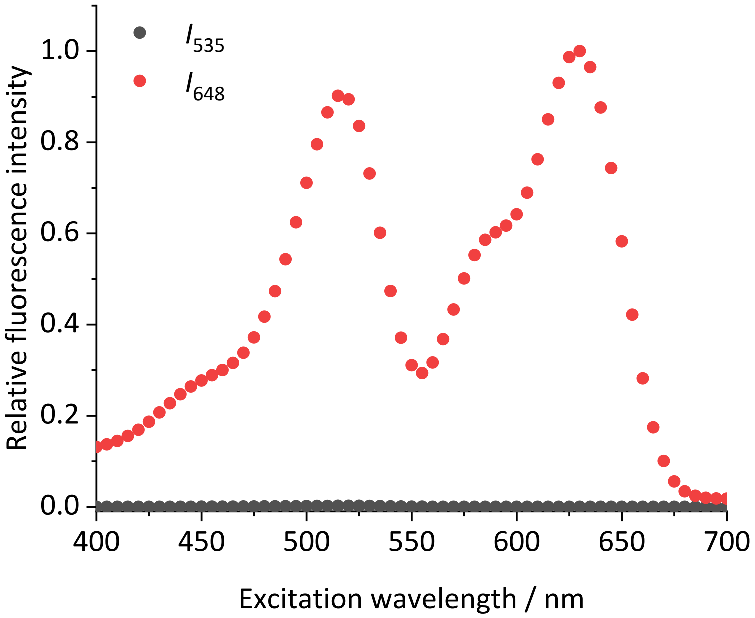
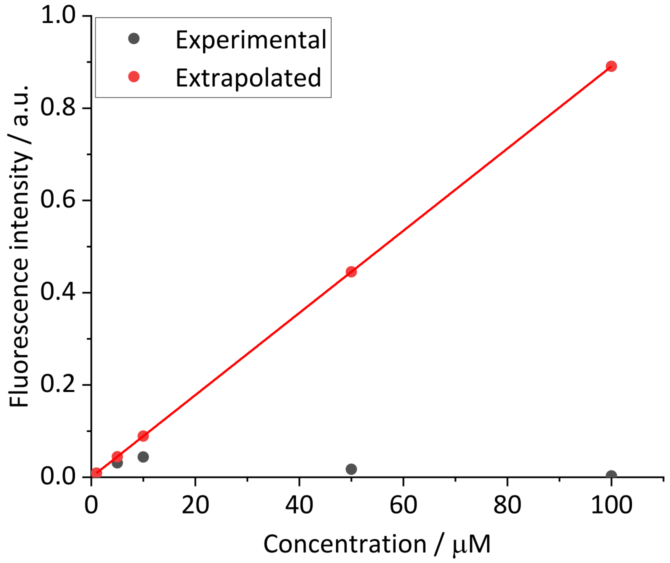


Figure S 3 Excitation spectrum of Bodipy dyad **12** in CH_2Cl_2 (5.0 μM).

(a)



(b)

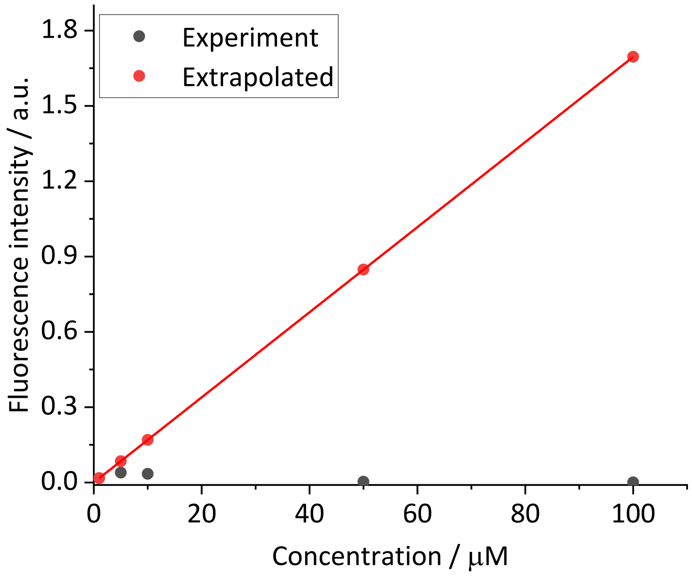


Figure S 4 Concentration dependence of emission intensity for (a) **11** (λ_{ex} = 500 nm, $\lambda_{em,max}$ = 535 nm) and (b) Bodipy **4** (λ_{ex} = 620 nm, $\lambda_{em,max}$ = 648 nm) in CH_2Cl_2 (5.0 μM). Red circles represent extrapolated emission intensities at the respective concentrations.

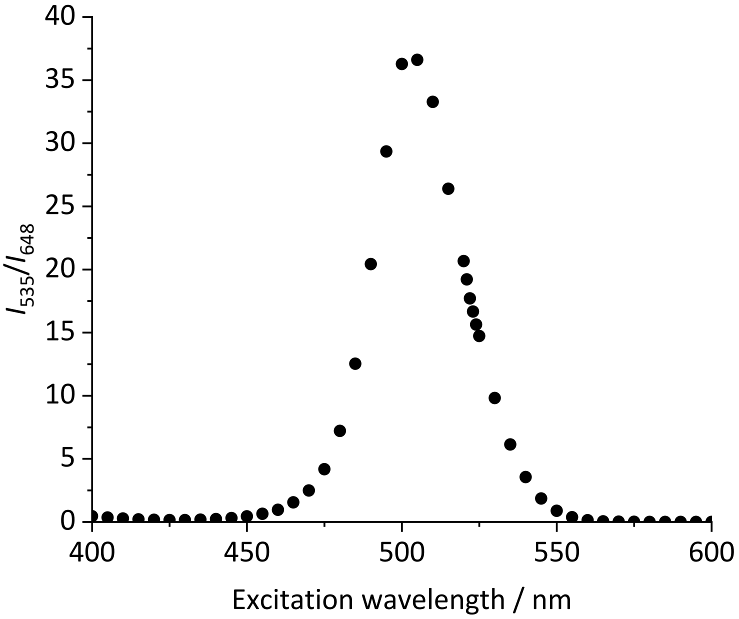


Figure S 5 Plot of excitation wavelength *vs*. ratio of emission intensities of individual compound **11** ($\lambda_{\mathrm{em,max}}$ = 535 nm) and **4** ($\lambda_{\mathrm{em,max}}$ = 648 nm) in CH_2Cl_2 (5.0 μM). The maximum I_{535}/I_{648} value is 36.6 at 505 nm.

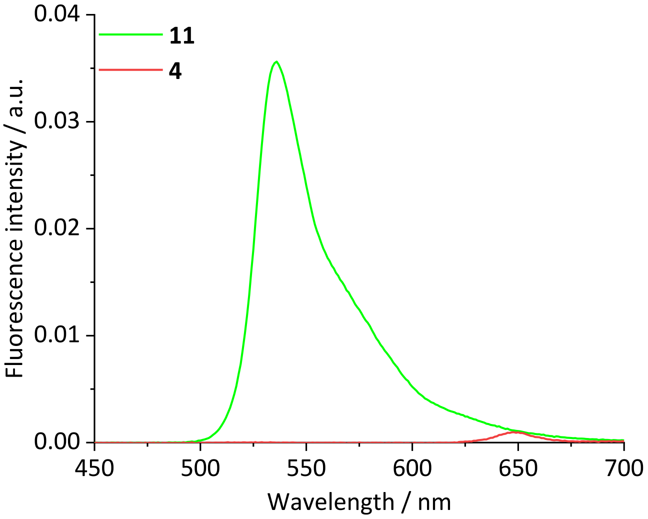
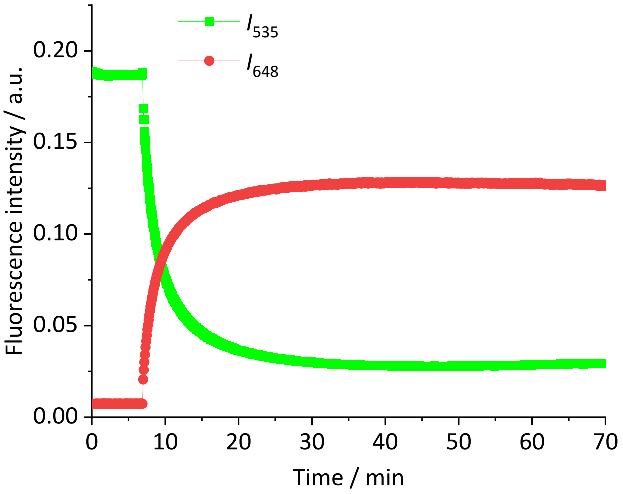


Figure S 6 Emission spectrum of individual compounds **11** and **4** in CH_2Cl_2 solution (5.0 μM) photo-excited at 505 nm showed the maximum I_{535}/I_{648} value.

Procedure of FRET experiments. To a quartz cuvette containing a solution of gold acetylide complex **13** (5.0 μM) or gold thiolate **15** (5.0 μM) in CH_2Cl_2, a stock solution of gold-NTf_2 complex **14** (1.0 eq.) (stored at -20 °C until use), was added dropwise in one portion. The emission intensities at 535 and 648 nm were monitored every interval 5 seconds over the measurement time.

(a)



(b)

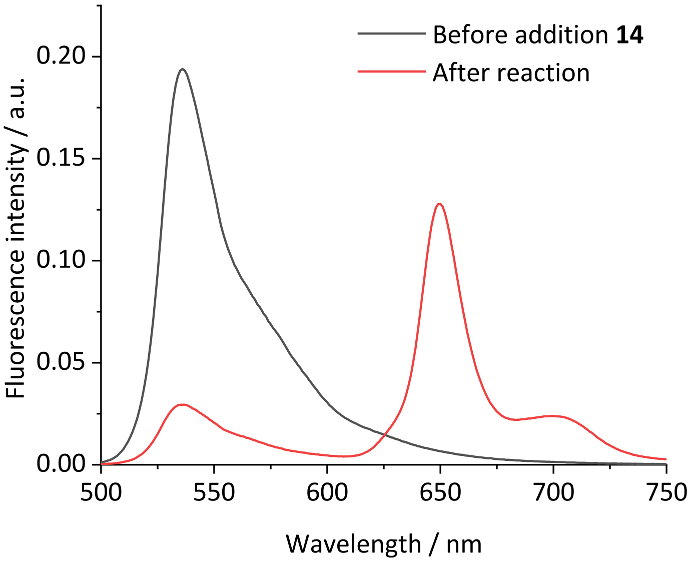
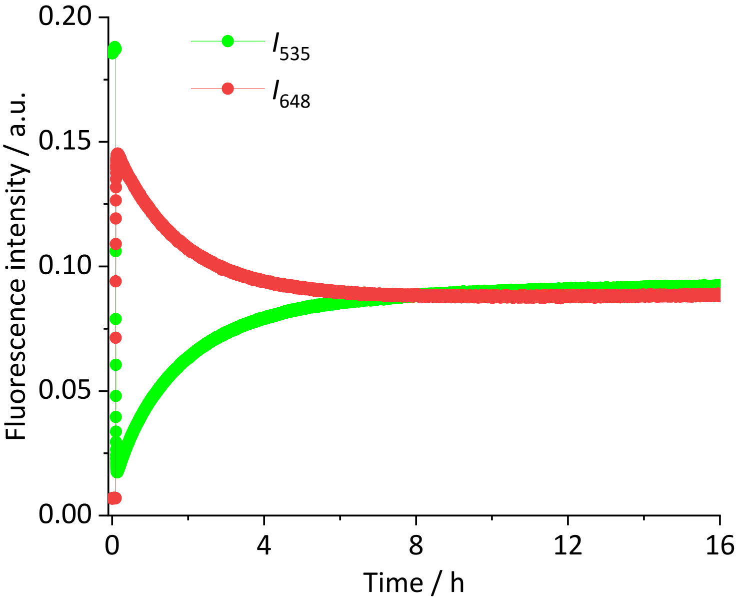
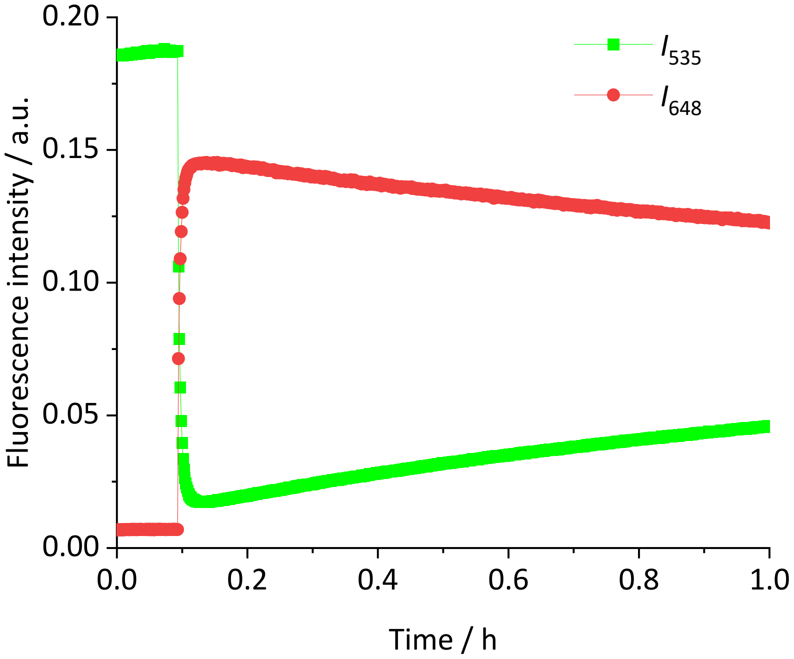


Figure S 7 (a) Time profile of emission intensities at 535 and 648 nm for a mixture of gold acetylide complex **13** (5.0 μM) and gold-NTf_2 complex **14** (5.0 μM) in CH_2Cl_2 (λ_{ex} = 505 nm). (b) Emission spectrum of **13** (5.0 μM) in CH_2Cl_2 before and after addition of **14** (5.0 μM) in (a).

(a)


0.20
0.15
0.10
0.05
0.00
Fluorescence intensity / a.u.
0
4
8
12
16
Time / h
I_{535}
I_{648}

(b)


0.20
0.15
0.10
0.05
0.00
Fluorescence intensity / a.u.
0.0
0.2
0.4
0.6
0.8
1.0
Time / h
I_{535}
I_{648}

(c)

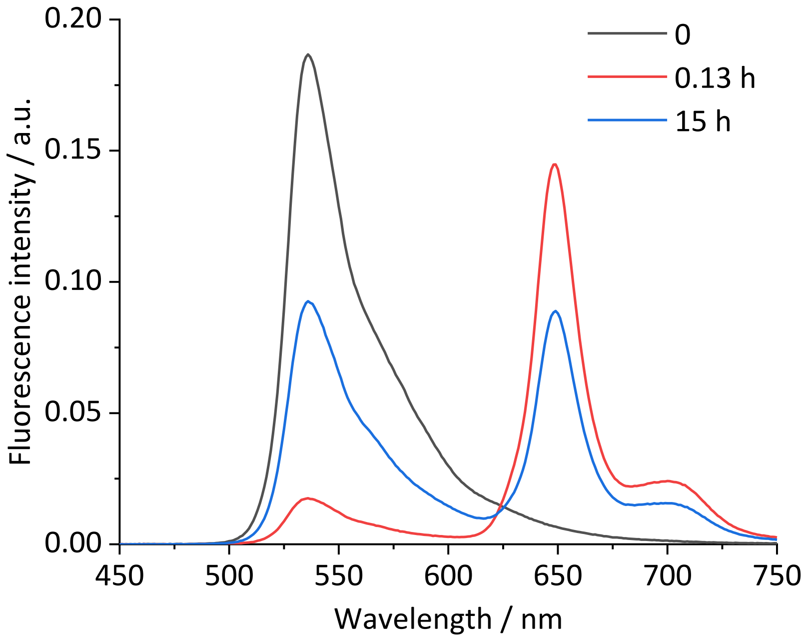
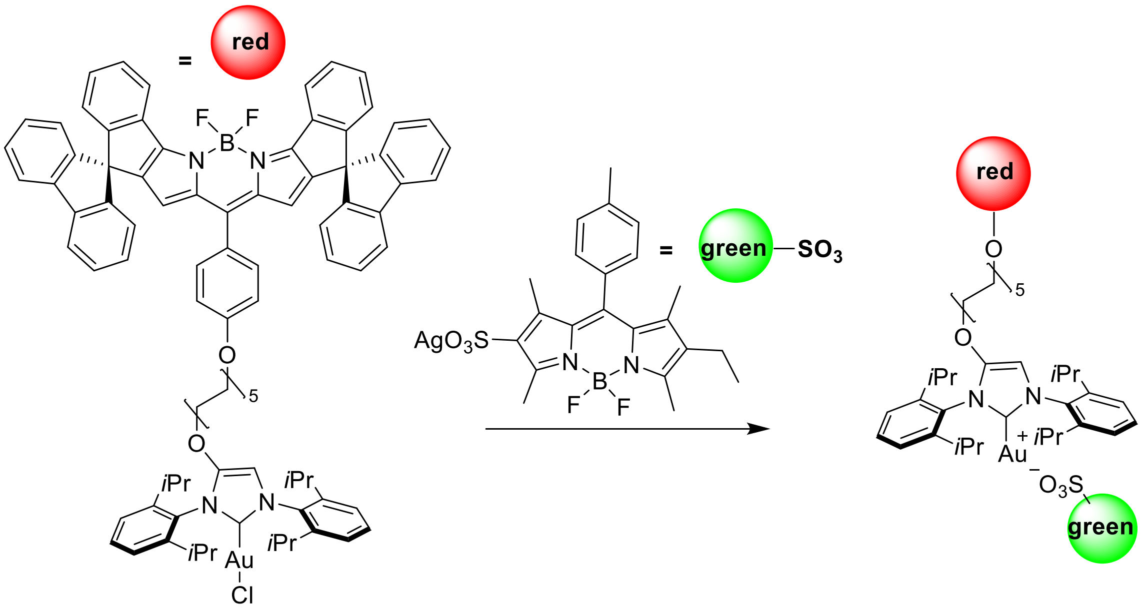


Figure S 8 (a) Time profile of emission intensities at 535 and 648 nm for a mixture of gold thiolate complex **17** (5.0 μM) and gold-NTf2 complex **14** (5.0 μM) in CH_2Cl_2 (λ_{ex} = 505 nm). (b) displayed range from 0 to 1 h of (a). (c) Emission spectrum of **17** (5.0 μM) in CH_2Cl_2 before (0 h) and after addition of **14** (5.0 μM) in (a).

3.2 Monitoring ion pairing using red-green FRET



FRET experiments. All experiments were carried out in quartz cuvettes with path lengths of 10.0 mm. A cuvette was charged with the respective Bodipy ion-paired dyad **18** (2.0 mL, 1.00 μM) in toluene or 1,2-dichloroethane solution. Next, the measurement was started and the fluorescence intensity at the designated wavelength was observed (530 nm for the green emission and 648 nm for the red emission). After approximately 1 min (when the intensity of fluorescence signal remains constant), portions of freshly distilled DMAc or phenylacetylene in toluene solution (0.18M) were added to the cuvette (typical range 5 μL - 100 μL). After each aliquot, the fluorescence intensity at the specific wavelength was monitored. The next aliquot was added when the fluorescence level was found to remain constant after 30 s. The titration was terminated when addition of a new aliquot did not lead to further change in the fluorescence signal. The fluorescence data were finally corrected for dilution of the sample. In order to obtain the respective fluorescence intensity for the fully separated ion pair an (8M) solution of NBu_4Br in 1,2-dichloroethane was added (10 μL, 0.08 mmol).

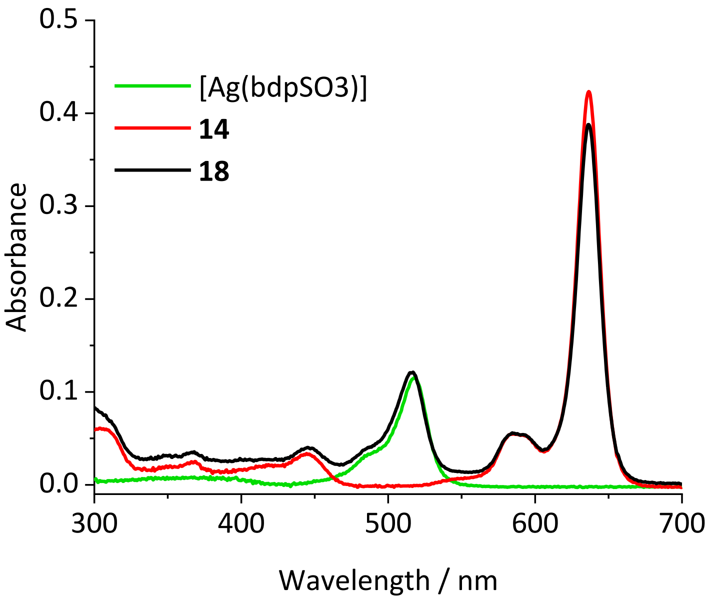


Figure S 9 Absorbance spectra of [Ag(bdpSO$_3$)] (green), (red) **14** and **18** (black) in toluene solution (2.0 μM).

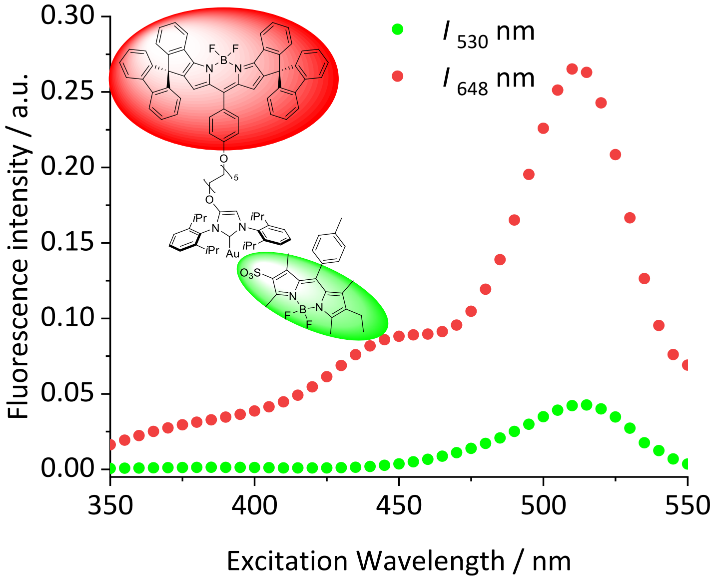


Figure S 10 Plot of excitation wavelength *vs*. observed fluorescence intensity for the corresponding [Ag(bdpSO$_3$)] ($I_{em,max}$ = 530 nm) and for the red Bodipy ($I_{em,max}$ = 648 nm) in **18** (close pair) in toluene solution (2.0 μM).

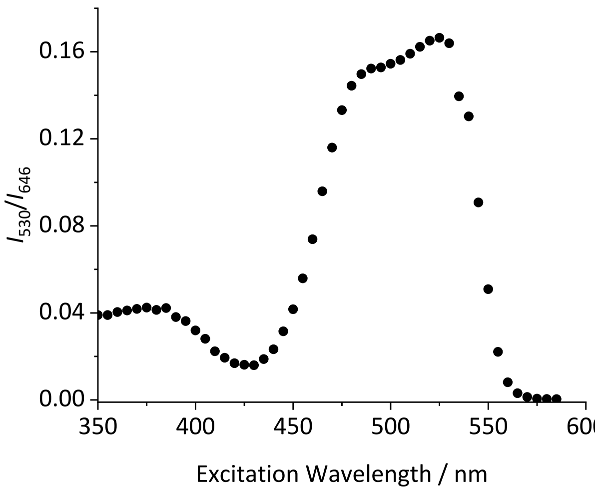


Figure S 11 Plot of excitation wavelength *vs*. ratio of emission intensities of green Bodipy (*l*$_{\mathrm{em,max}}$ = 530 nm) and red Bodipy (*l*$_{\mathrm{em,max}}$ = 648 nm) components in **18** (close pair) in toluene solution (2.0 μM).

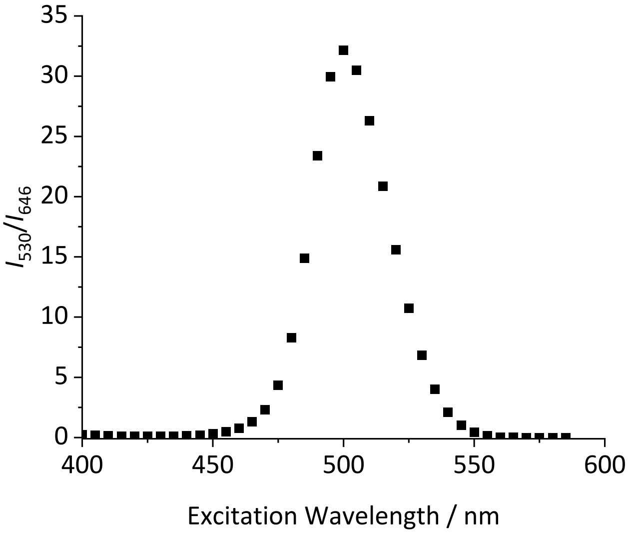


Figure S 12 Plot of excitation wavelength *vs*. ratio of individual fluorophore emission intensities of [Ag(bdpSO$_3$)] (at *l*$_{\mathrm{em,max}}$ = 530 nm) and **14** (at *l*$_{\mathrm{em,max}}$ = 648 nm) in toluene solution (2.0 μM).

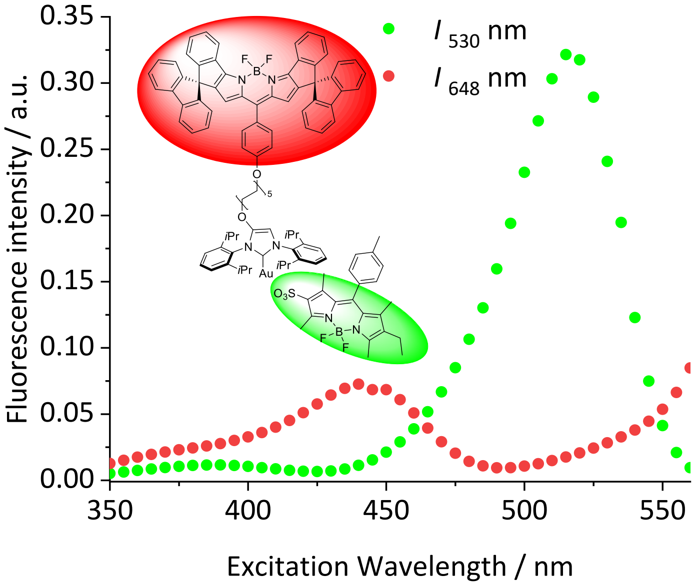


Figure S 13 Plot of excitation wavelength *vs*. observed fluorescence intensity for the corresponding green Bodipy (at $I_{\mathrm{em,max}}$ = 530 nm) and for the red Bodipy (at $I_{\mathrm{em,max}}$ = 648 nm) components in **18** (not close pair) in toluene solution (2.0 μM) after addition of NBu_4Br solution in 1,2-dichloroethane (8M, 10 μL, 8.00 mmol).

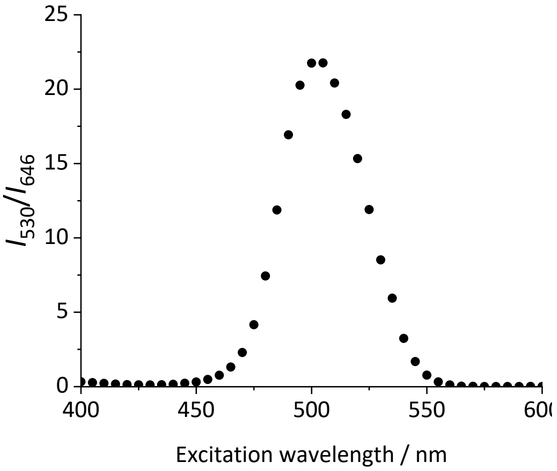
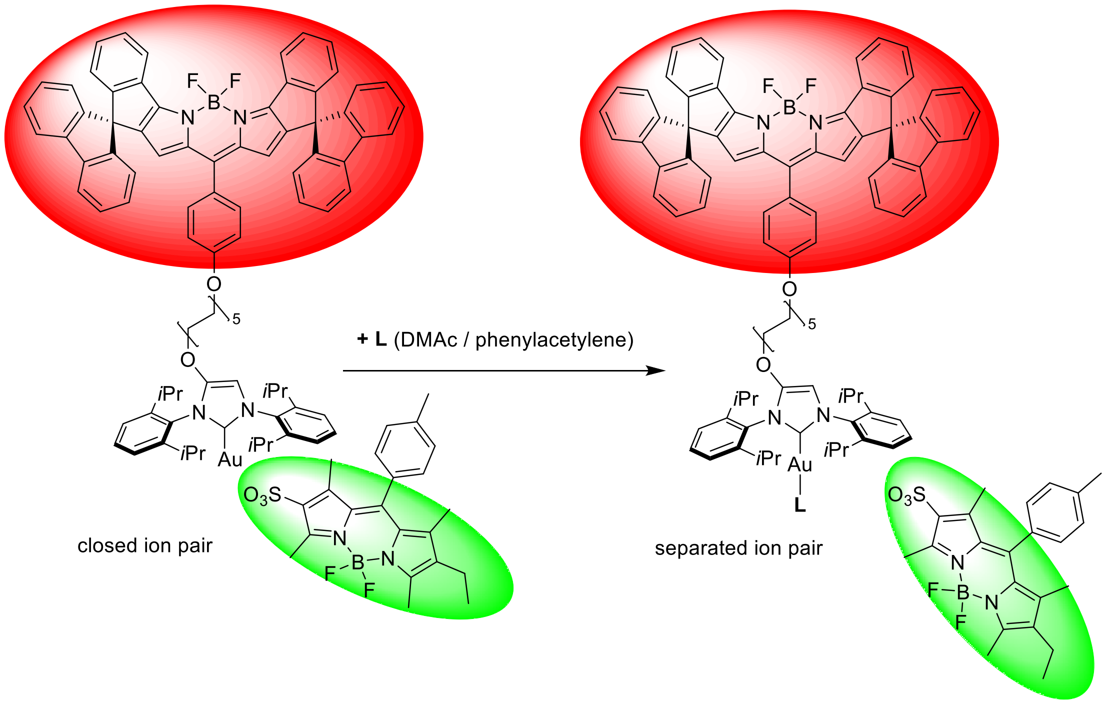


Figure S 14 Plot of excitation wavelength *vs*. ratio of emission intensities for the corresponding green Bodipy (at $I_{\mathrm{em,max}}$ = 530 nm) and for the red Bodipy (at $I_{\mathrm{em,max}}$ = 648 nm) components in the separated cation and anion in dyad **18** in toluene solution (2.0 μM) after addition (8M) solution of NBu_4Br in 1,2-dichloroethane (10 μL, 8.00 mmol).



Scheme S 2 General reaction scheme for the FRET ion pair titration experiment.

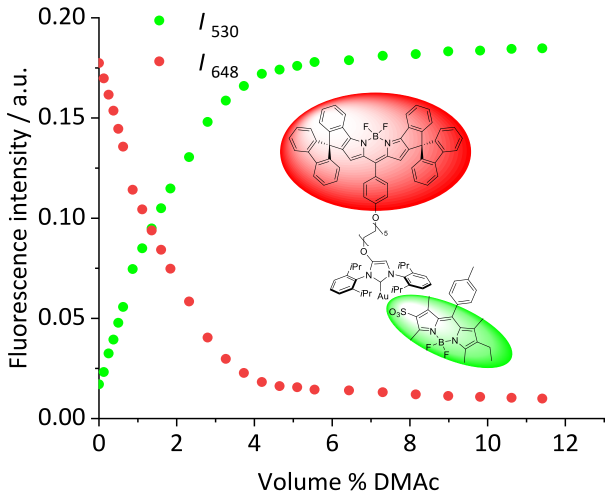


Figure S 15 Plot of added volume of DMAc *vs*. change of fluorescence intensity (λ_{exc} = 500 nm) for the corresponding green Bodipy (at $I_{em,max}$ = 530 nm) and for the red Bodipy (at $I_{em,max}$ = 648 nm) components in **18** in toluene solution (1.0 μM) after addition of DMAc. Simultaneous drop of the FRET fluorescence intensity signal at 648 nm and corresponding gain of intensity at 530 indicates a separation of **18** complex and separation of the FRET pair after the addition of the specific amount of DMAc.

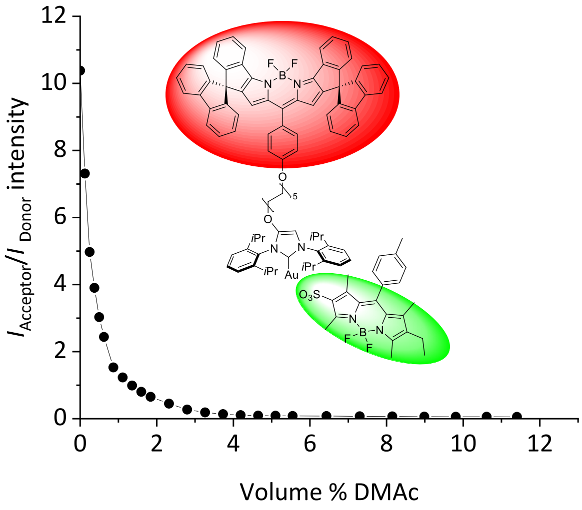


Figure S 16 Plot of changes of the relative fluorescence intensity (λ_{exc} = 500 nm) of acceptor red Bodipy (at $I_{em,max}$ = 648 nm) to donor green Bodipy (at $I_{em,max}$ = 530 nm) components in **18** in toluene solution (1.0 μM) *vs.* volume of added dimethylacetamide.

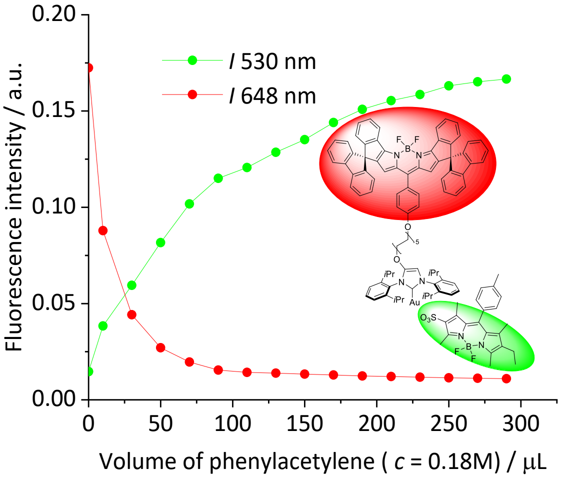
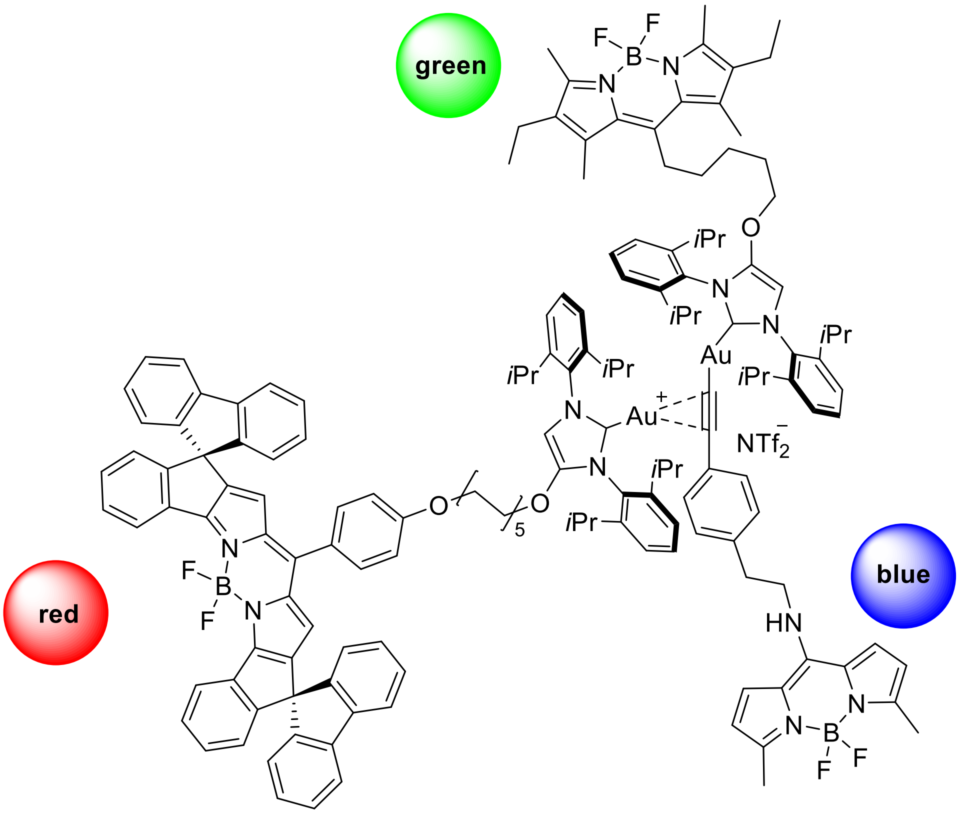


Figure S 17 Plot of added volume of phenylacetylene solution (μL) in toluene (*c* = 0.18 M, 10μL = 900 eq) *vs*. change of fluorescence intensity (λ_{exc} = 500 nm) for the corresponding green Bodipy (at $I_{em,max}$ = 530 nm) and for the red Bodipy (at $I_{em,max}$ = 648 nm) components in the **18** in toluene solution (1.0 μM) .

3.3 Evaluation of the blue-green-red triad



FRET experiments. A quartz cuvette was filled with blue-green dyad **22·dbu** in 2 mL of 1,2-dichloroethane solution (5.0 µM). Next, the measurement was started and the fluorescence intensity at the emission maximum of the corresponding fluorophore was observed at the designated wavelength (at 535 nm for the green emission and at 652 nm for the red emission). After approximately 1 min (once the fluorescence signal intensity remained constant), a solution of **14** (5 µM, 1.0 eq) in 1,2-dichloroethane was added. The time of addition is indicated with arrows. After approx. 1-2 min more of the **14** complex solution (5 µM, 1.0 eq) in 1,2-dichloroethane was added and a formation of the Widenhoefer dimer was observed.

The reported fluorescence are peak intensities. For selected examples, it was shown that changes in peak intensities are the same as changes in integrated intensities. This is possible since the Bodipy units are remote tags, which are not influenced to a significant extent by the nature of the organometallic complex.

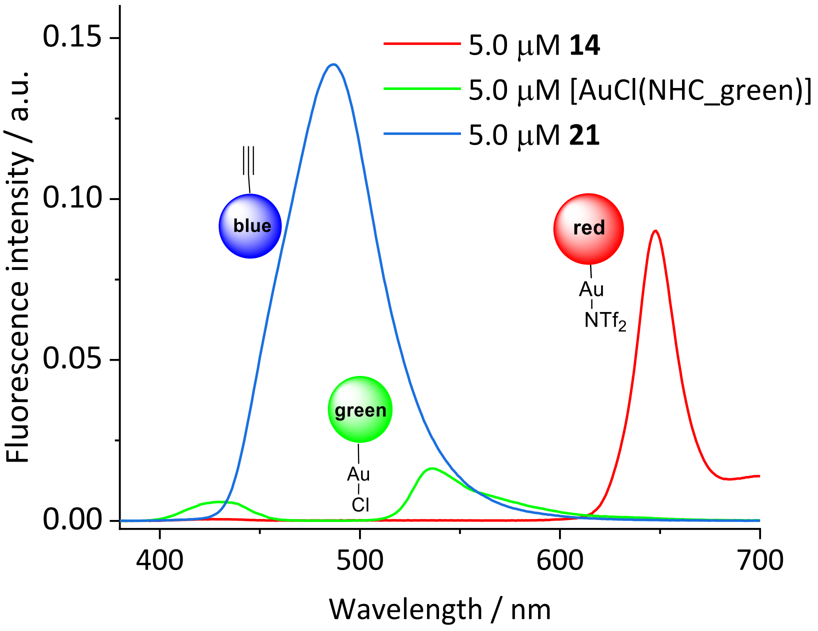


Figure S 18 Emission spectra of **21**, [AuCl(NHC_green)] and **14** (at λ_{ex} = 423 nm) in 1,2-DCE (5.0 μM).

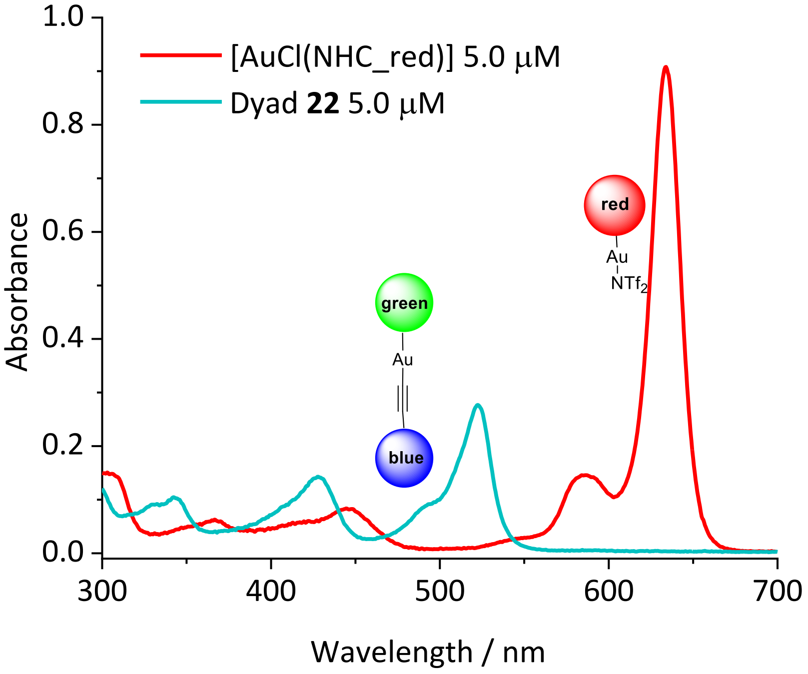


Figure S 19 Absorbance spectra of blue-green dyad **22** (cyan) and **14** in 1,2-DCE (5.0 μM).

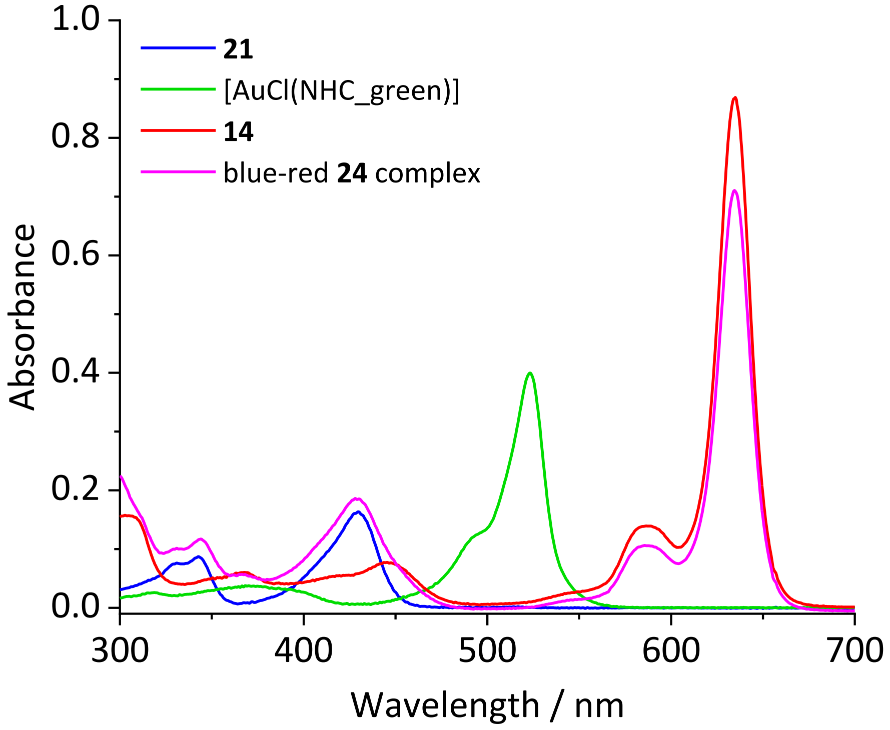


Figure S 20 Absorbance spectra of blue-red **24** (**pink**), **14**, **21** and [AuCl(NHC_green)] in 1,2-DCE (5.0 μM).

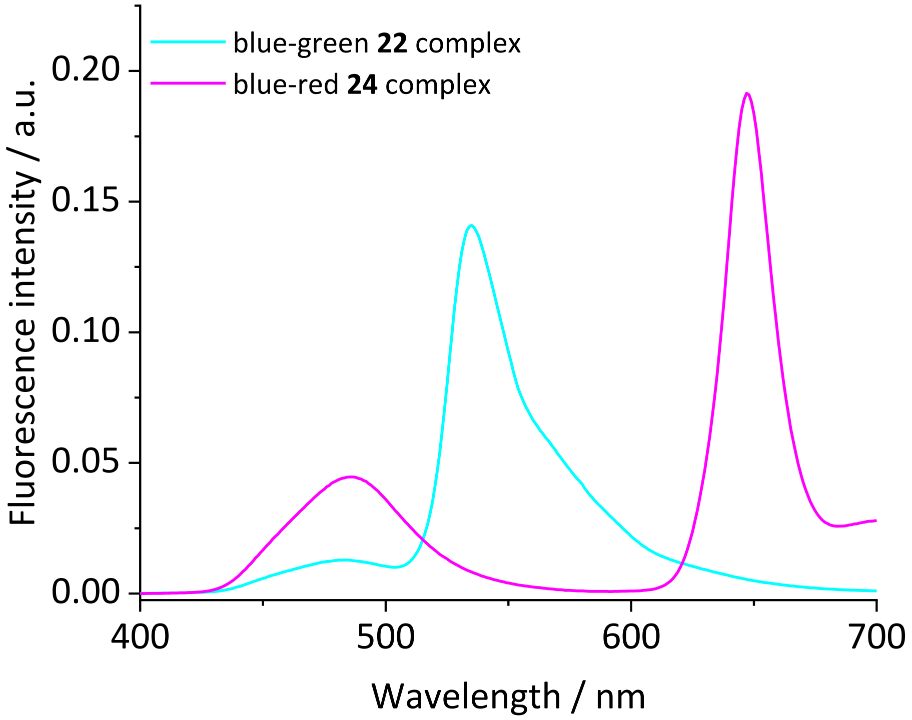


Figure S 21 Plot of emission spectra of blue-red **24** complex (**pink**) and blue-green **22** (**cyan**) (at λ_{ex} = 423 nm) in 1,2-DCE (5.0 μM).

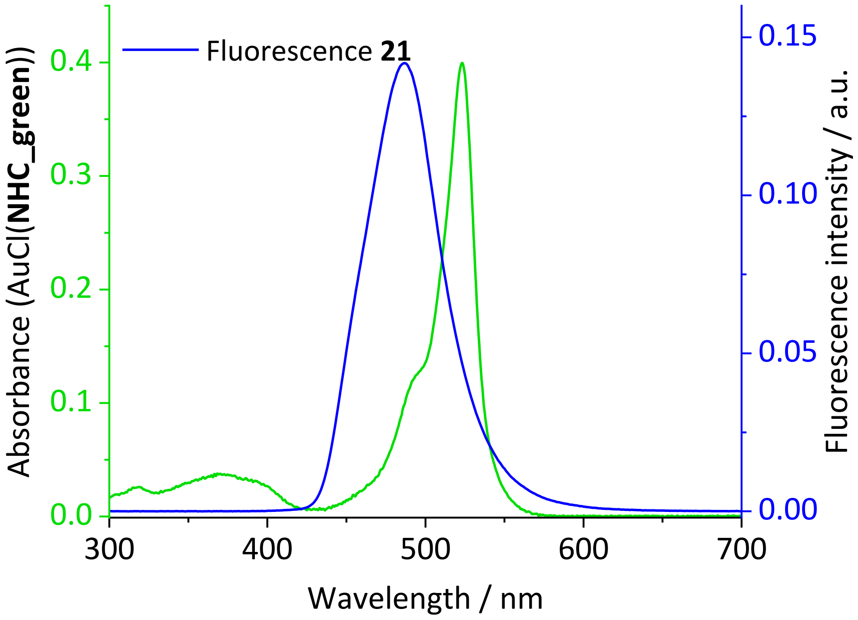


Figure S 22 Plot of emission spectra (at λ_{ex} = 423 nm) of **21** (**blue**) and absorbance spectra of [AuCl(NHC_green)] (**green**) in 1,2-DCE (5.0 μM).

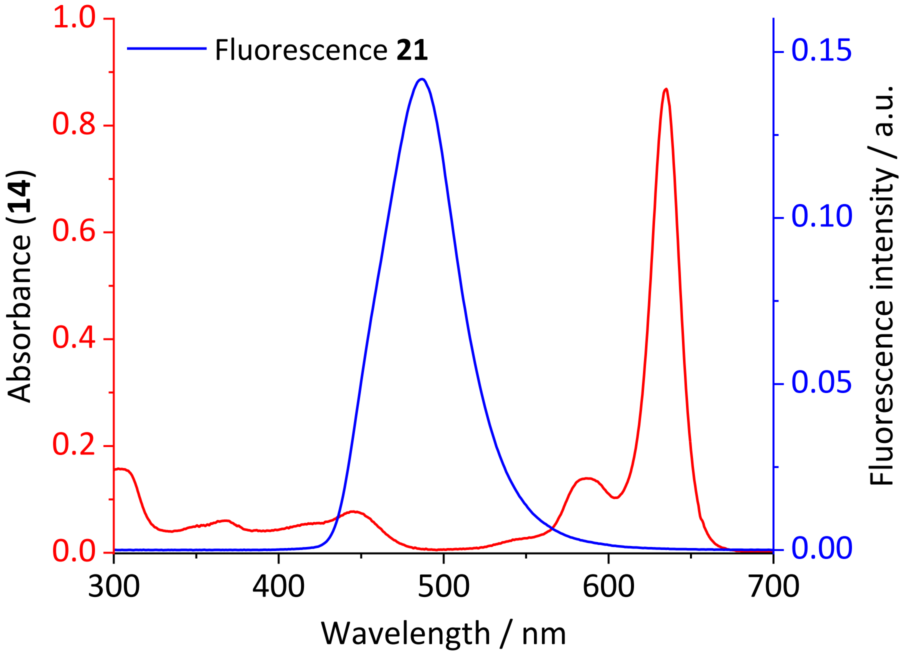


Figure S 23 Plot of emission spectra (at λ_{ex} = 423 nm) of **21** (**blue**) and absorbance spectra of **14** (**red**) in 1,2-DCE (5.0 μM).

Triad or Dyad-Dyad. Convincing evidence for the chemical formation of the triad was presented. However, the absorption and emission spectra of the red and the blue Bodipy show some overlap and based on this, excitation energy can also be transferred from the blue Bodipy directly to the red Bodipy. If this were the predominant energy transfer mechanism, the triad would be better described as a dyad-dyad from a photophysical point of view. However, the overlap of the emission spectrum of the blue Bodipy with the absorption spectrum of the green Bodipy is much larger than the overlap with the absorption spectrum of the red Bodipy (Figs. S22, 23). Based on this it is likely, that the majority of the excitation energy is channeled along the blue-green-red triad. A simple experiment provides additional information. Blue phenyl acetylene **21** and [AuCl(NHC_red)] were reacted in the presence of dbu (analogous to the synthesis of **22**) to provide **24**·dbu (scheme 8) and the fluorescence monitored. The red fluorescence observed directly after mixing represents the cross-talk intensity, any additional red fluorescence observed during the slow formation of the dyad corresponds to the formation of the blue-red dyad and blue-red FRET, as does any decrease in the blue fluorescence. The formation of the dyad leads to an approx. 30% increase in the red emission, but the blue emission is at ca. 50% of the initial value. Based on this it is concluded, that the direct blue-red FRET is the minor pathway and the blue-green-red system reported is best described as a triad.

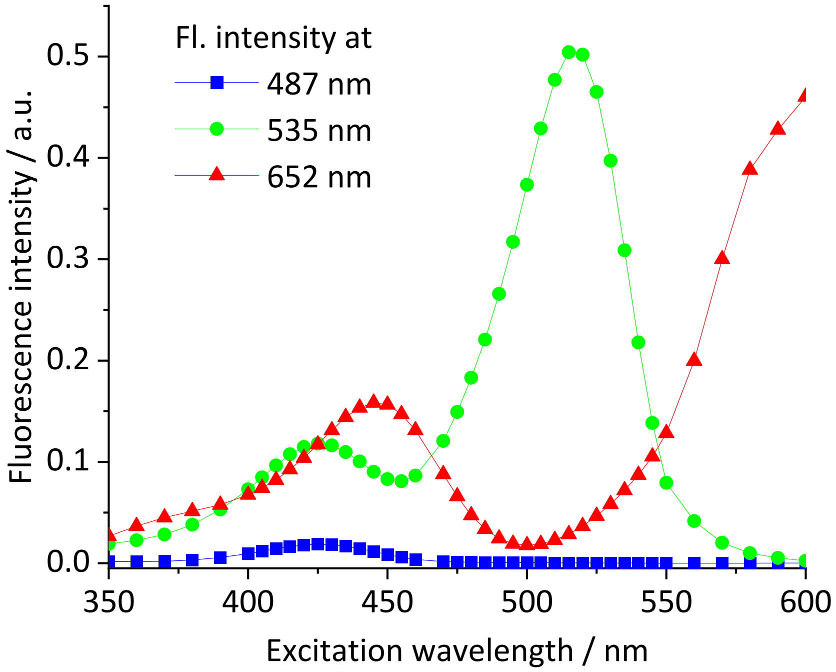


Figure S 24 Plot of excitation wavelength *vs*. observed fluorescence intensities for the corresponding blue-green dyad **22** system for the blue Bodipy component (at $l_{em,max}$ = 487 nm) and for the green Bodipy component (at $l_{em,max}$ = 535 nm) and for **14** (at $l_{em,max}$ = 652 nm) in 1,2-DCE solution (5.0 μM).

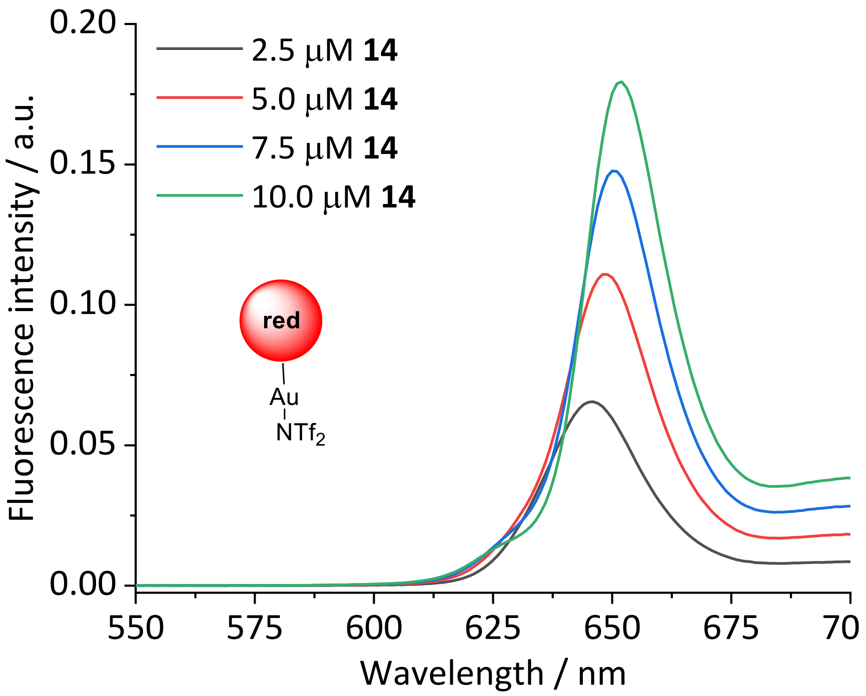


Figure S 25 Plot of emission spectra of **14** complex in 1,2-DCE solution (λ_{ex} = 423 nm) at different concentrations (2.5 - 10.0 μM).

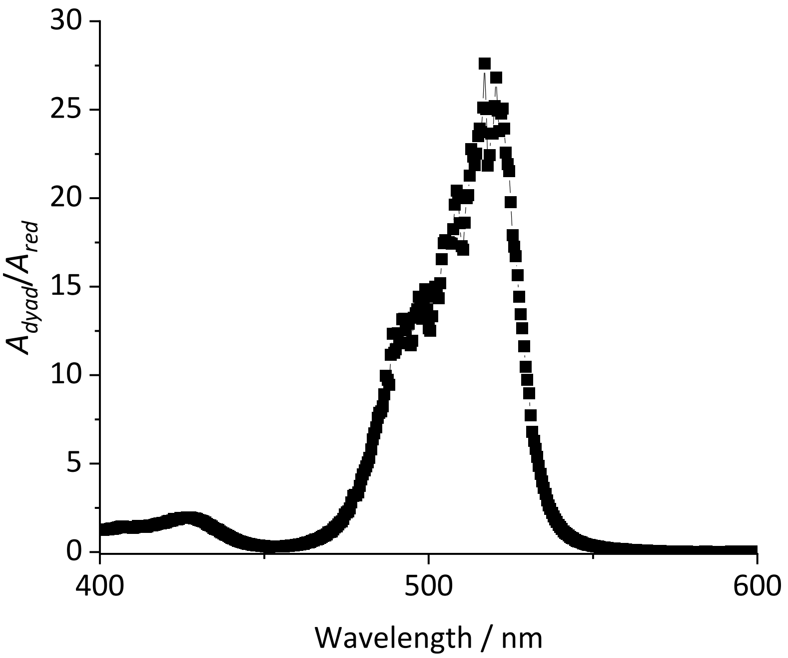


Figure S 26 Plot of absorbance ratio of blue-green dyad **22** system to individual **14** complex ($\lambda_{ex,max}$ = 636 nm) in 1,2-DCE solution (5.0 μM).

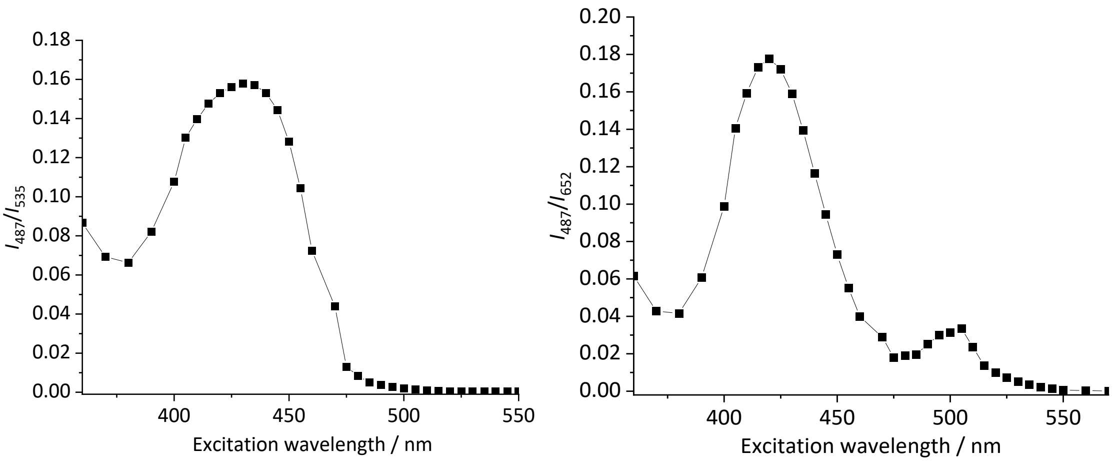
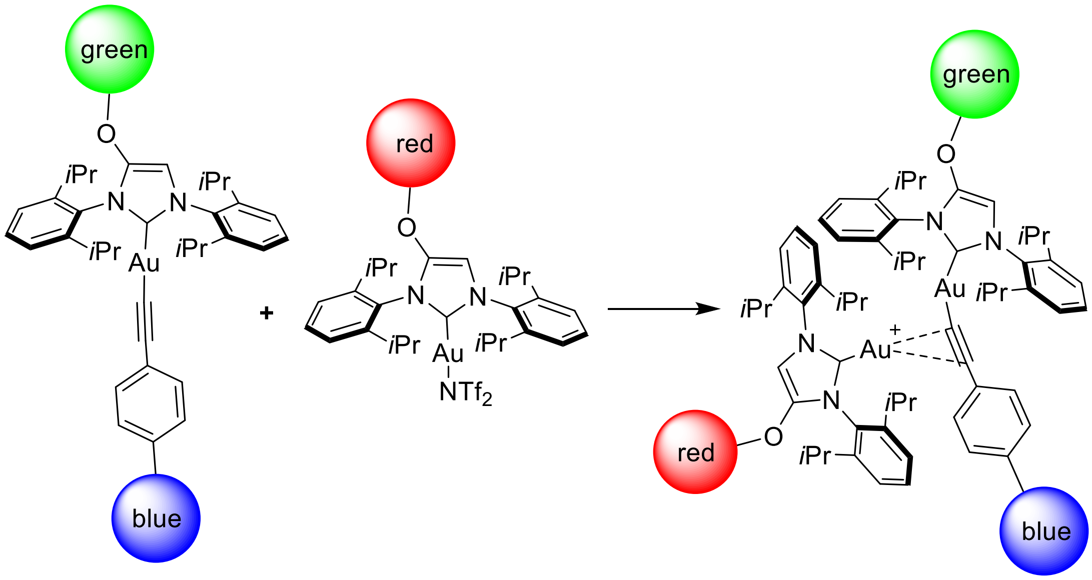


Figure S 27 Left: Plot of excitation wavelength *vs*. ratio of emission intensities of blue Bodipy component (at $I_{em,max}$ = 487 nm) relatively to green Bodipy component (at $I_{em,max}$ = 535 nm) within the blue-green dyad **22** system in 1,2-DCE solution (5.0 μM). Right: Plot of excitation wavelength *vs*. ratio of emission intensities of blue Bodipy component (at $I_{em,max}$ = 487 nm) within the blue-green dyad **22** system relatively to the individual **14** complex (at $I_{em,max}$ = 652 nm) in 1,2-DCE solution (5.0 μM).



Scheme S 3 Reaction of the formation of the blue-green-red triad FRET system **23** via gold acetylide system **22**.

Excitation wavelength 423 nm

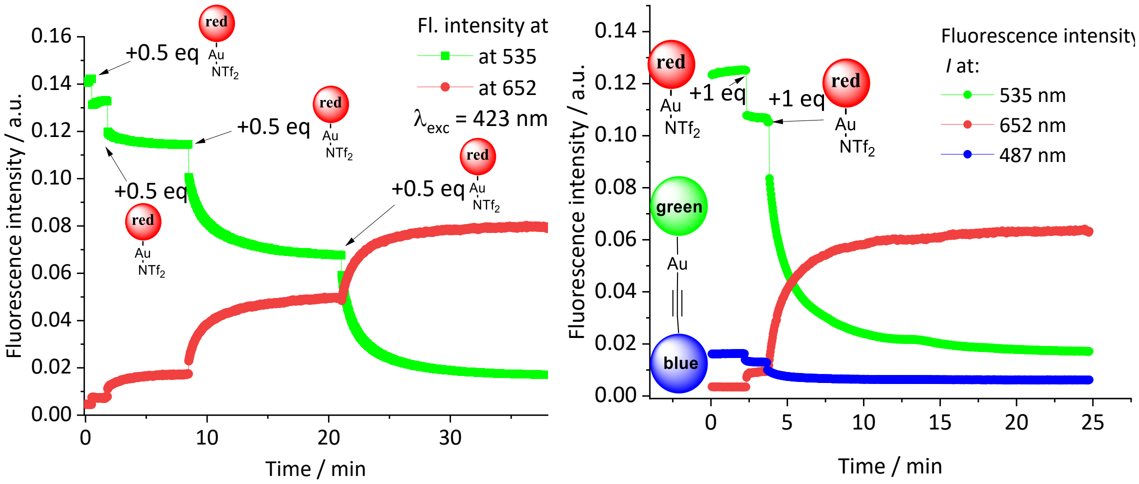


Figure S 28 Plot of the time-dependent fluorescence intensities (subtracted values of red cross-talk intensity) for the green Bodipy (at $I_{em,max}$ = 535 nm) and (at $I_{em,max}$ = 652 nm) for the red Bodipy components at λ_{exc} = 423 nm within the formed blue-green-red triad **23** after additions of **14** complex (n eq). Initial concentration of complexes in 1,2-DCE solution (5.0 μM).

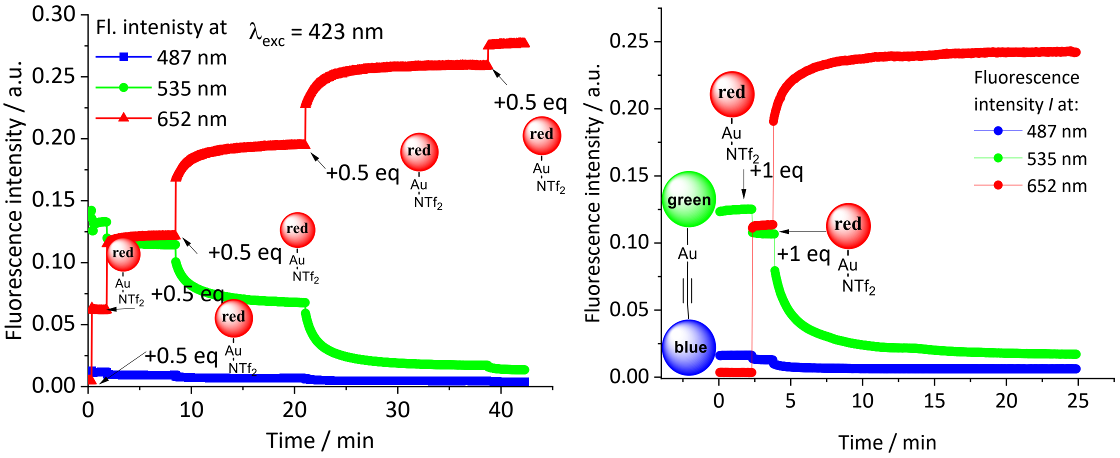


Figure S 29 Plot of the time-dependent fluorescence intensities for the blue Bodipy (at $l_{\mathrm{em,max}}$ = 487 nm), for the green Bodipy (at $l_{\mathrm{em,max}}$ = 535 nm) and for the red Bodipy (at $l_{\mathrm{em,max}}$ = 652 nm) components at λ_{exc} = 423 nm within the formed blue-green-red triad **23** after additions of **14** complex (n eq). Initial concentration of complexes in 1,2-DCE (5.0 µM).

Excitation wavelength 500 nm

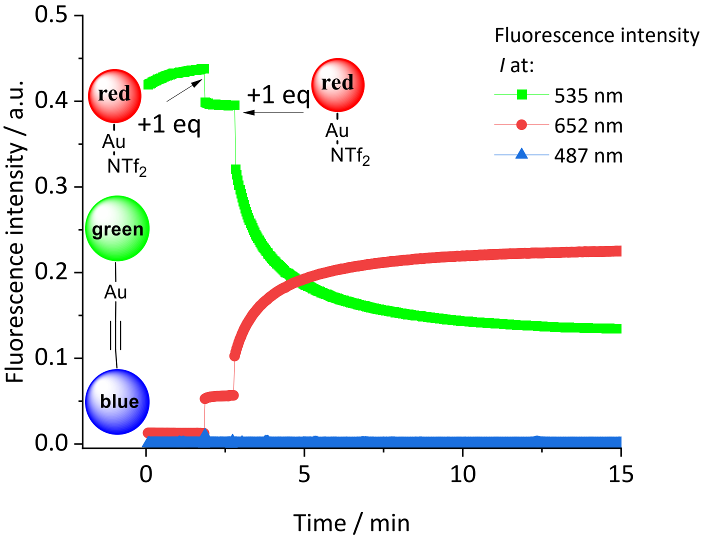


Figure S 30 Plot of the time-dependent fluorescence intensities for the green Bodipy (at $l_{\mathrm{em,max}}$ = 535 nm) and for the green Bodipy (at $l_{\mathrm{em,max}}$ = 652 nm) components at λ_{exc} = 500 nm within the blue-green-red triad **23** after additions of **14** complex (1.0 eq). Initial concentration of complexes in 1,2-DCE (5.0 µM).

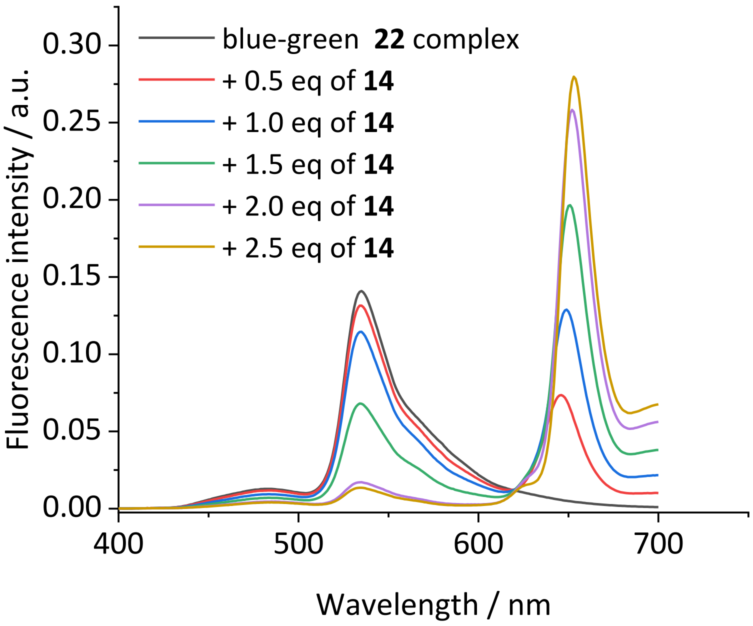


Figure S 31 Emission spectra (λ_{ex} = 423 nm) of triad system **23** in 5.0 μM 1,2-DCE solution before (black = blue-green dyad **22**) and after addition of **14** solution (2.5 - 12.5 μM / 0.5 – 2.5 eq) in 1,2-DCE.

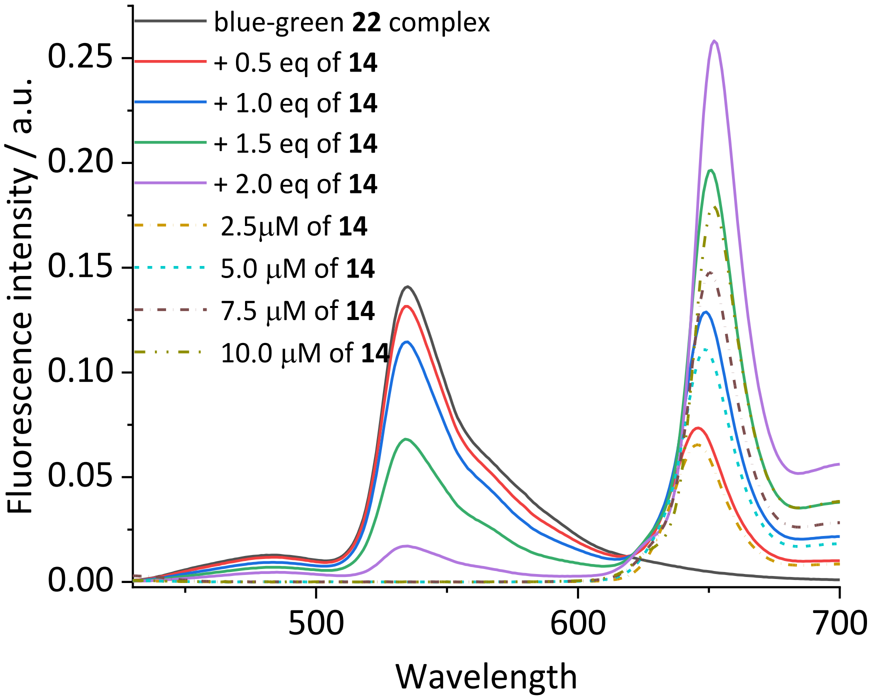


Figure S 32 Emission spectra (λ_{ex} = 423 nm) of dyad system **22** (solid line) in 5.0 μM 1,2-DCE solution before and after addition of (2.5 - 10 μM / 0.5 **–** 2.0 eq) **14** solution in 1,2-DCE. Emission spectra of individual **14** in different concentrations (2.5 - 10.0 μM) (dashed line) in 1,2-DCE solution.

3.4 Fluorescence and absorbance spectra for synthesized complexes

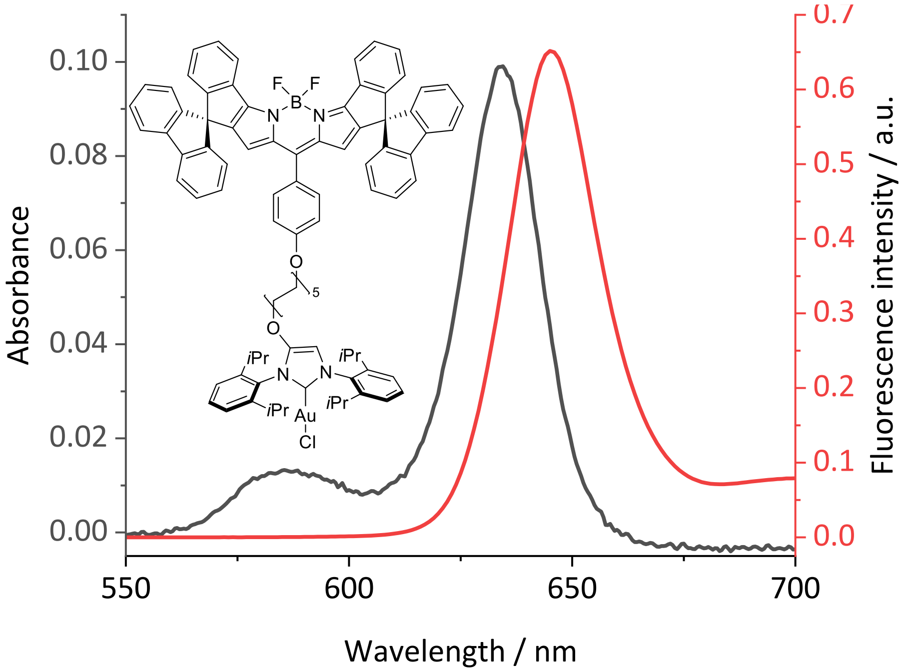


Figure S 33 Absorbance (black) and emission (red, λ_{exc} = 636 nm) spectra of [AuCl(NHC_red)] complex in 1,2-dichloroethane solution.

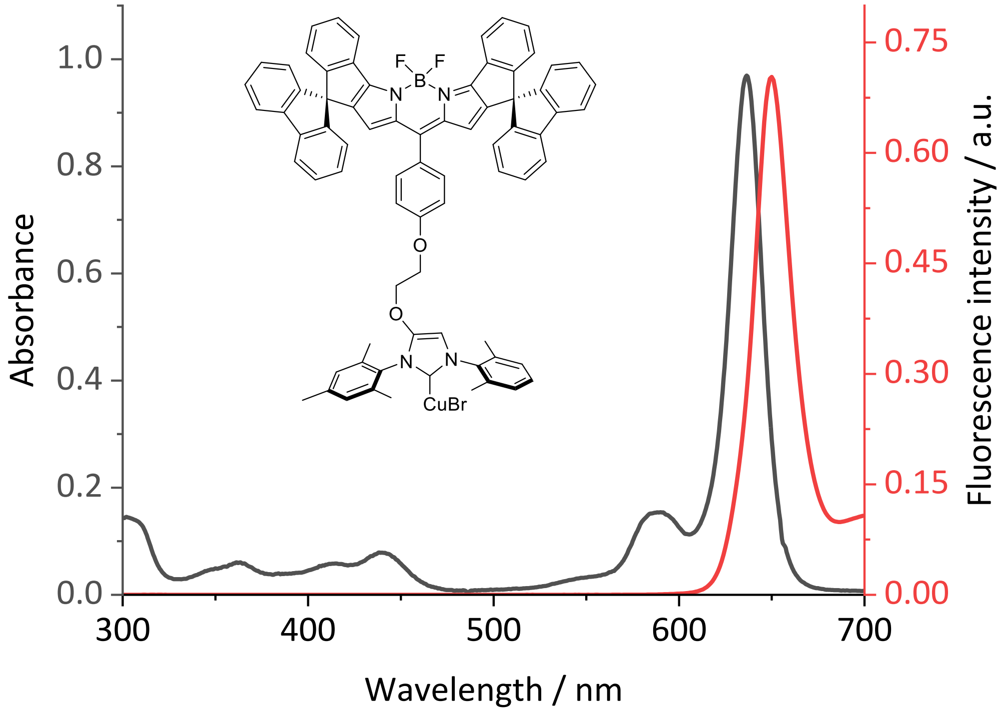


Figure S 34 Absorbance (black) and emission (red, λ_{exc} = 636 nm) spectra of [CuBr(**8**)] complex in 1,2-dichloroethane solution (5.0 μM).

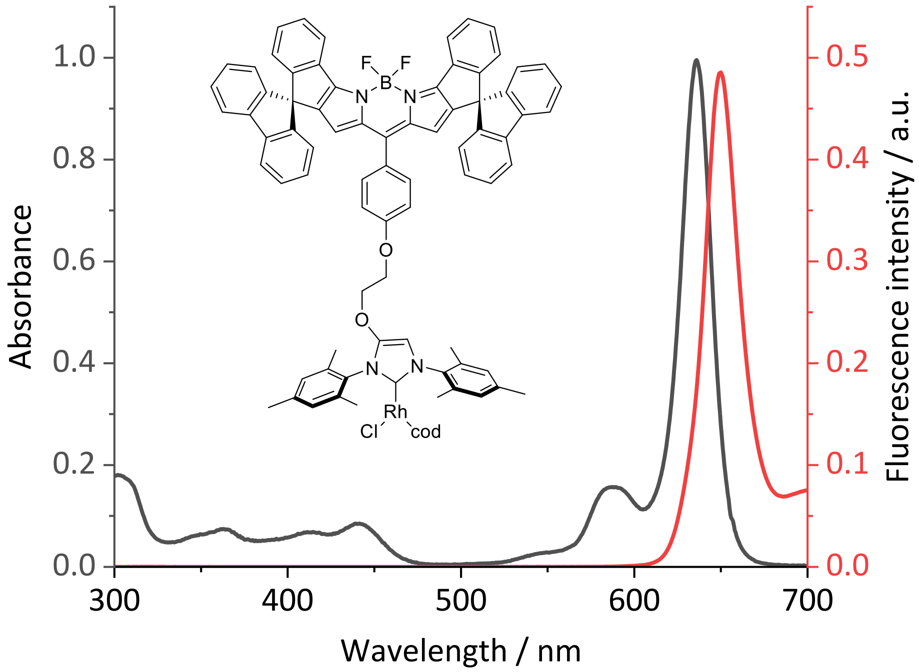


Figure S 35 Absorbance (black) and emission (red, λexc = 636 nm) spectra of [RhCl(cod)(**8**)] complex in 1,2-dichloroethane solution (5.0 μM).

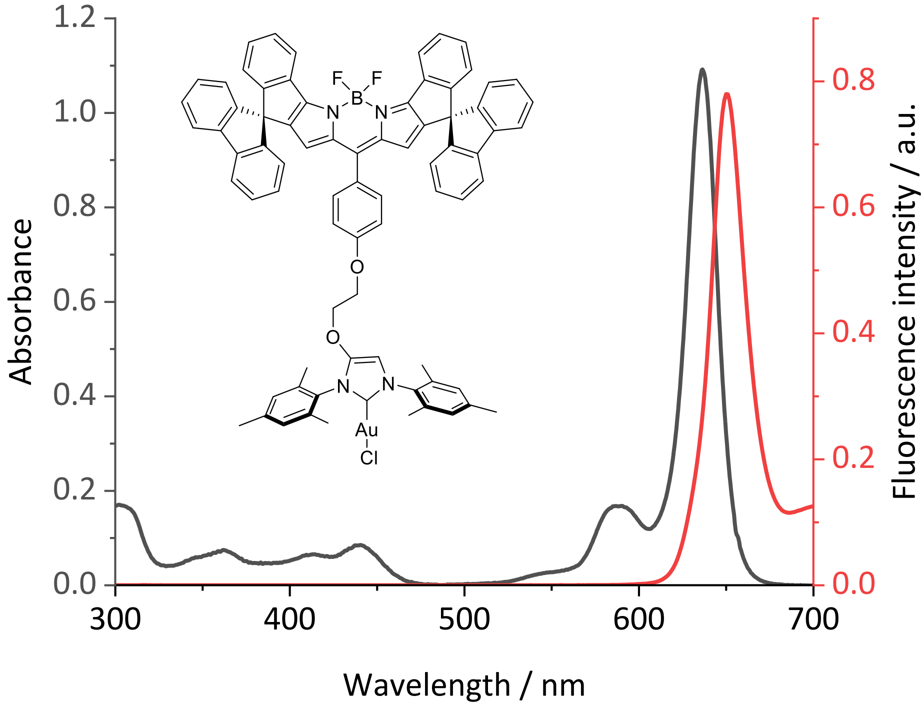


Figure S 36 Absorbance (black) and emission (red, λexc = 636 nm) spectra of [AuCl(**8**)] complex in 1,2-dichloroethane solution (5.0 μM).

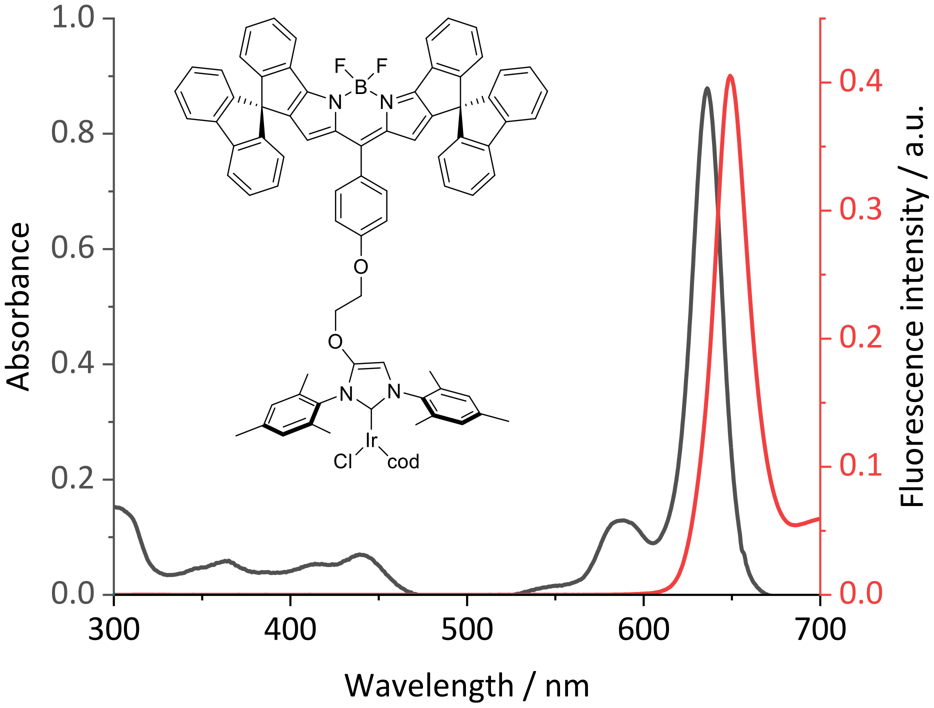


Figure S 37 Absorbance (black) and emission (red, λexc = 636 nm) spectra of [IrCl(cod)(**8**)] complex in 1,2-dichloroethane solution (5.0 μM).

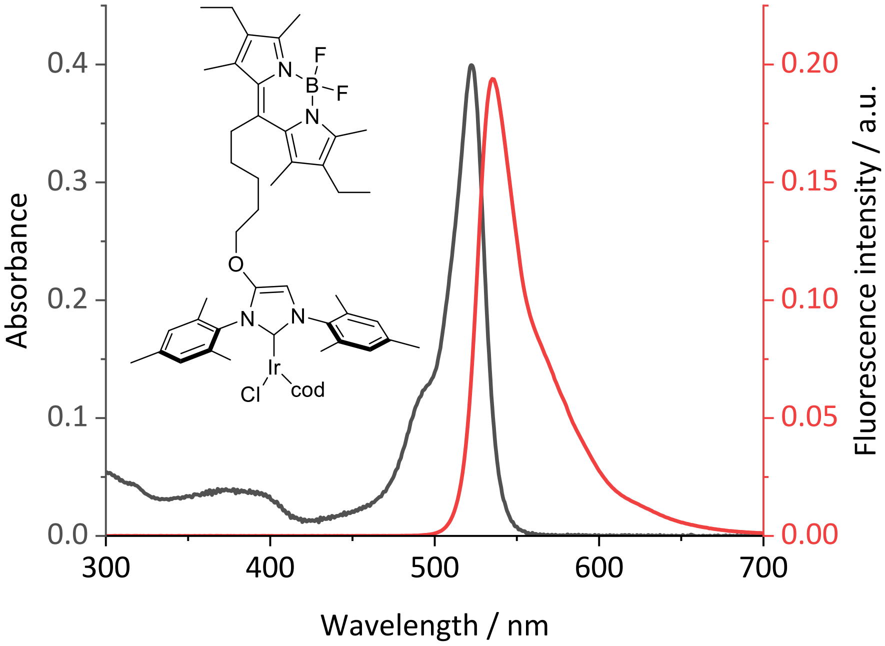


Figure S 38 Absorbance (black) and emission (red, λexc = 523 nm) spectra of [IrCl(cod)(**9**)] in 1,2-dichloroethane solution (5.0 μM).

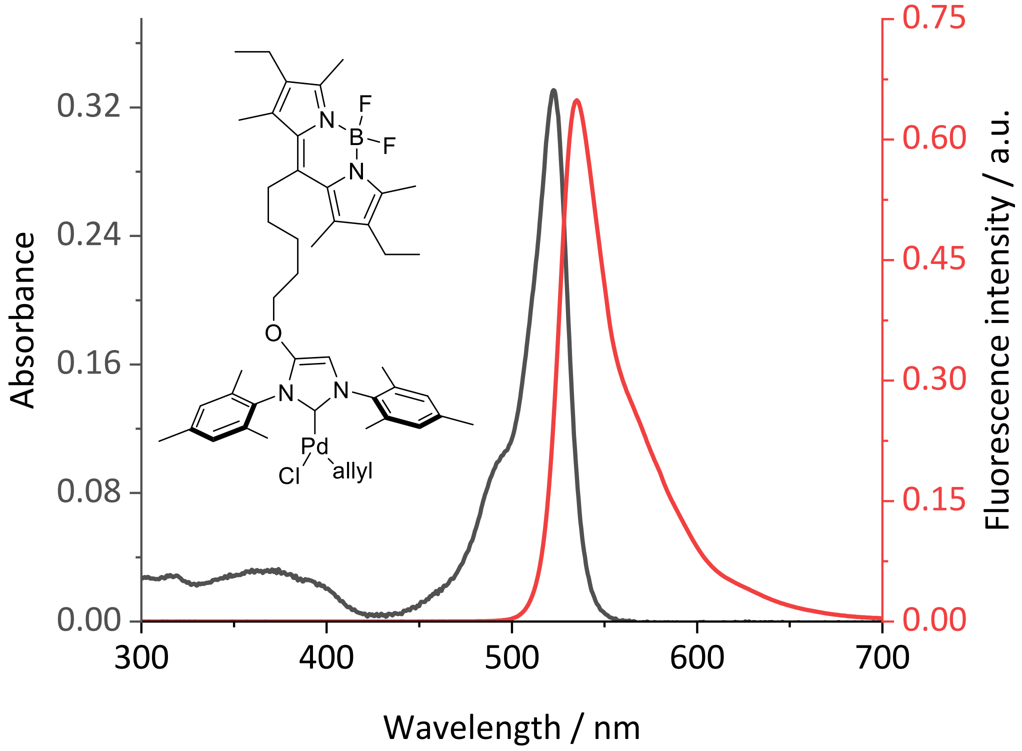
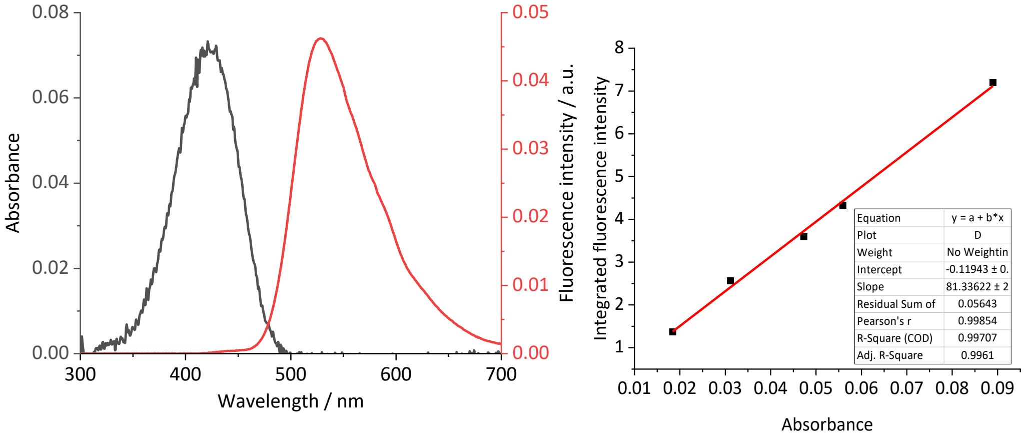


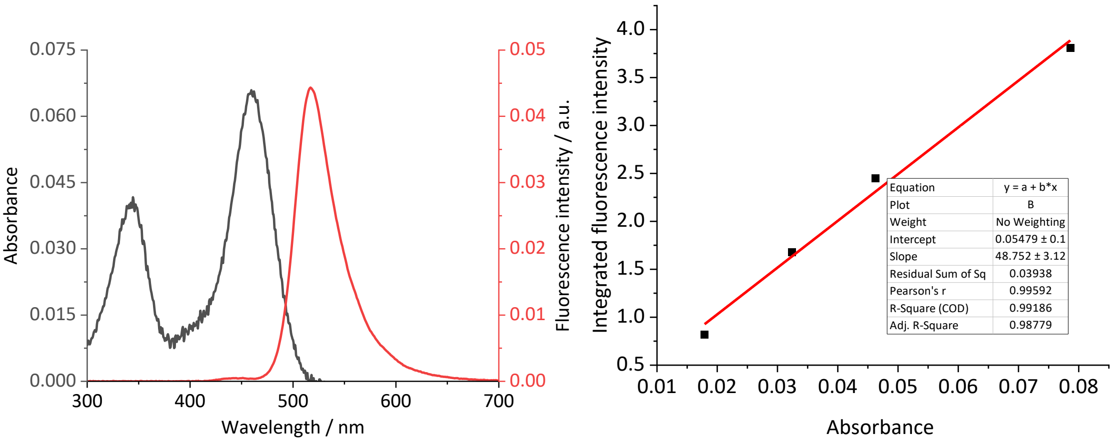
Figure S 39 Absorbance (black) and emission (red, λ$_{exc}$ = 523 nm) spectra of [Pd(allyl)Cl(**9**)] in 1,2-dichloroethane solution (5.0 μM).



Equation	y = a + b*x
Plot	D
Weight	No Weightin
Intercept	-0.11943 ± 0.
Slope	81.33622 ± 2
Residual Sum of	0.05643
Pearson's r	0.99854
R-Square (COD)	0.99707
Adj. R-Square	0.9961

Figure S 40 Left: absorbance (black) and emission (red, λ$_{exc}$ = 444 nm) spectra of Coumarin 153 in ethanol solution. Right: integrated fluorescence intensity *vs.* absorbance plot for Coumarin 153.

3.5 Fluorescence quantum yield



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0.05479 ± 0.1
Slope	48.752 ± 3.12
Residual Sum of Sq	0.03938
Pearson's r	0.99592
R-Square (COD)	0.99186
Adj. R-Square	0.98779

Figure S 41 Left: absorbance (black) and emission (red, λ_{exc} = 444 nm) spectra of **20** complex in 1,2-dichloroethane solution. Right: integrated fluorescence intensity *vs.* absorbance plot for **20** complex.

Quantum yield was determined according to the literature procedure (U. Resch-Genger, K. Rurack, *Pure Appl. Chem.*, **2013**, 85, 2005–2026) using Coumarin 153 (from Sigma-Aldrich, BioReagent, suitable for fluorescence) as the standard. Absorption and emission spectra were obtained over a range of concentrations (100 nM to 0.5 μM, in 1,2-dichloroethane), where a linear correlation between concentration and absorption was observed. The absorbance was within the range of 0.01 to 0.10. The quantum yield was calculated according to the equation:

$$\varphi_x = \varphi_{st}(\frac{r_x}{r_{st}})(\frac{\eta_x}{\eta_{st}})^2$$

where the subscripts *st* and *x* denote standard and test respectively, φ_x is the fluorescence quantum yield, *r* is the gradient from the plot of integrated fluorescence intensity vs. absorbance, and η is the refractive index of the solvent. φ_{st} = 0.95 in EtOH.

φ (**20**) = 0.35

4. NMR Spectra

Red Bodipy derivatives

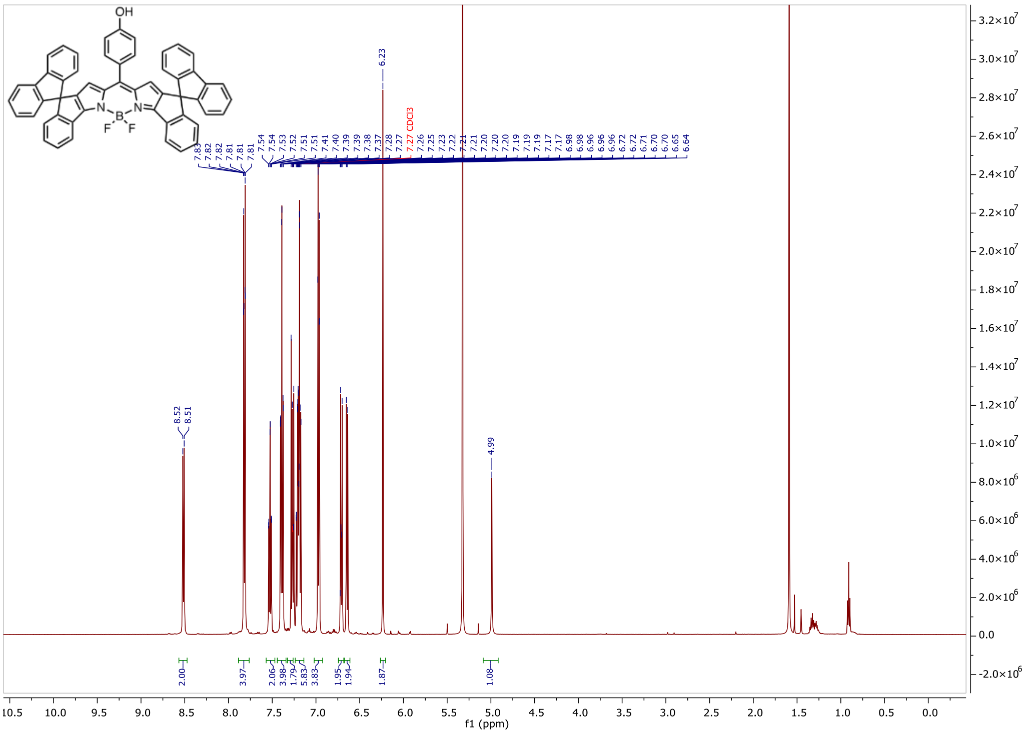


Figure S 42 ^{1}H-NMR spectrum of **10** in CDCl$_3$.

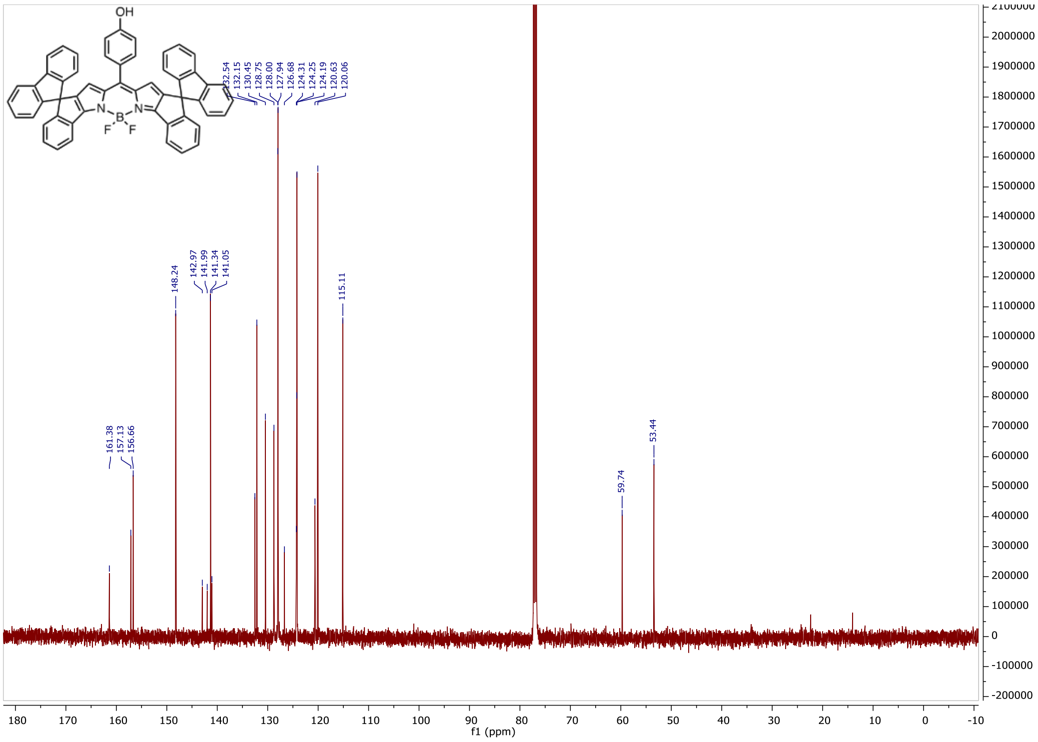


Figure S 43 ^{13}C-NMR spectrum of **10** in CDCl$_3$.

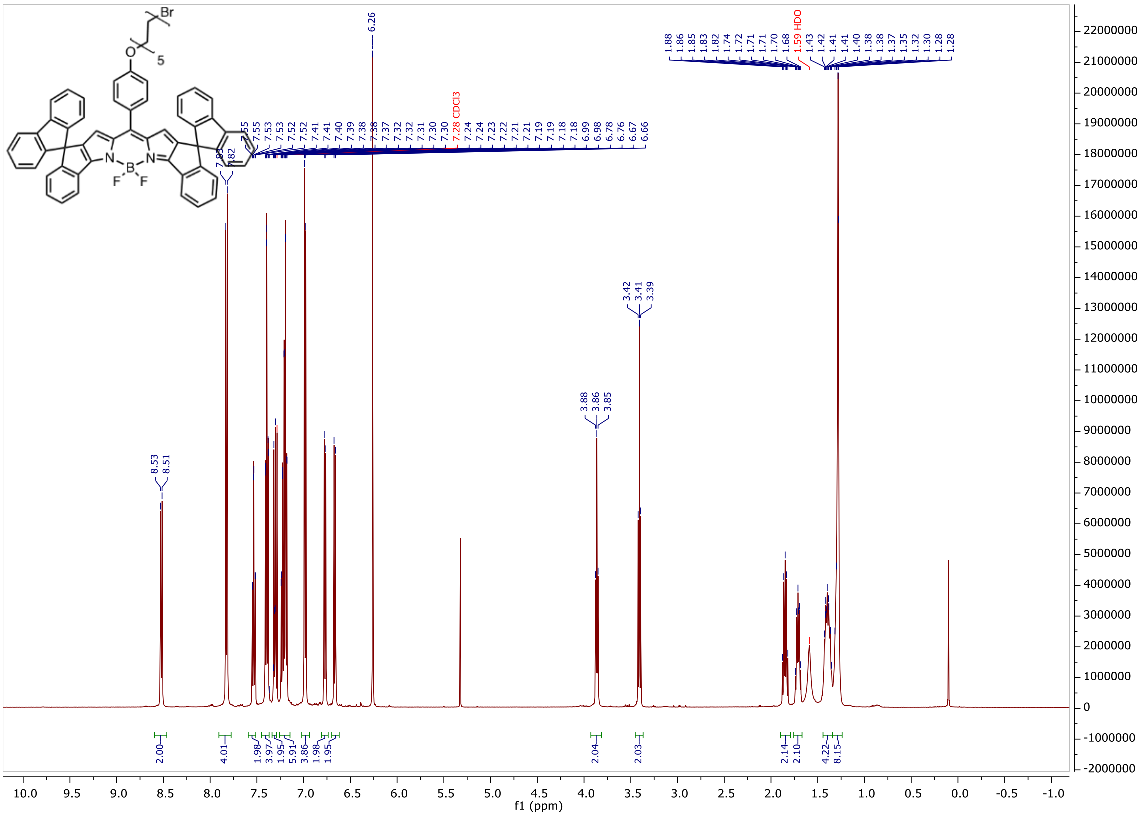


Figure S 44 ^{1}H-NMR spectrum of **4** in CDCl$_3$.

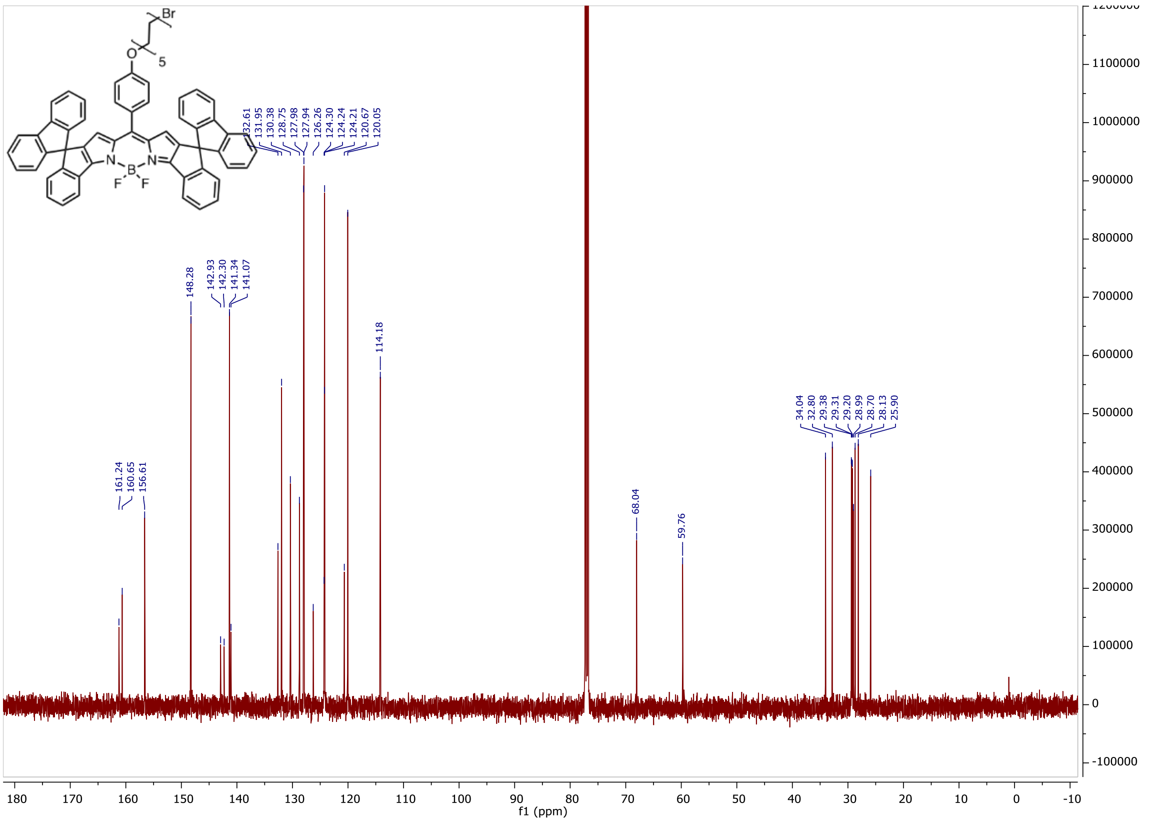


Figure S 45 ^{13}C-NMR spectrum of **4** in CDCl$_3$.

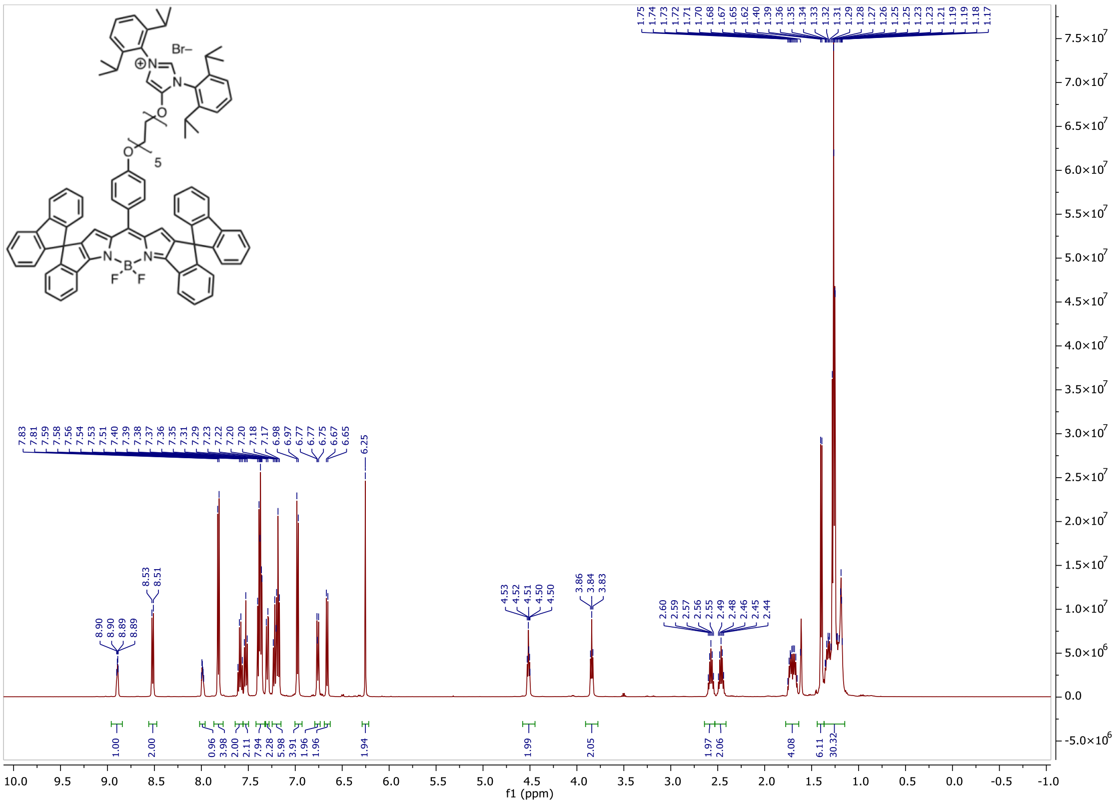


Figure S 46 ^{1}H-NMR spectrum of **5**·HBr in $CDCl_3$.

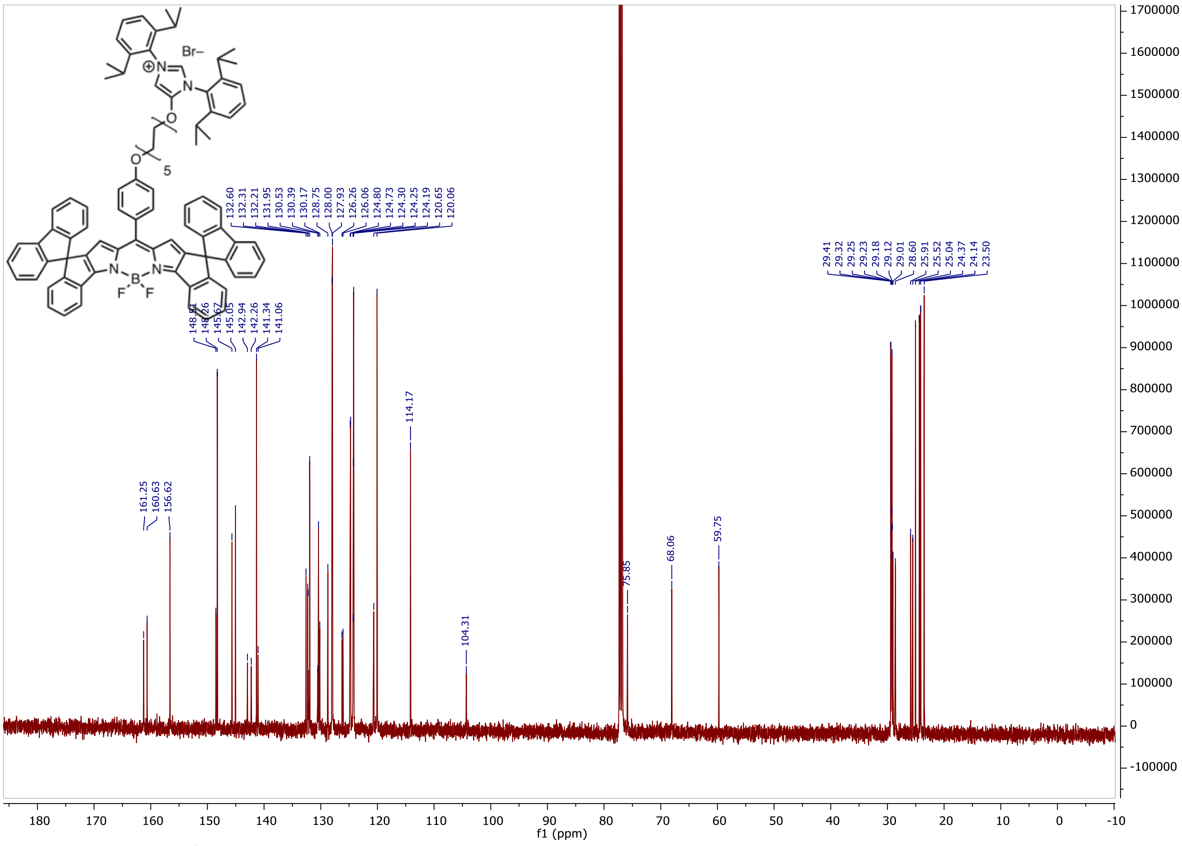


Figure S 47 ^{13}C-NMR spectrum of **5**·HBr in $CDCl_3$.

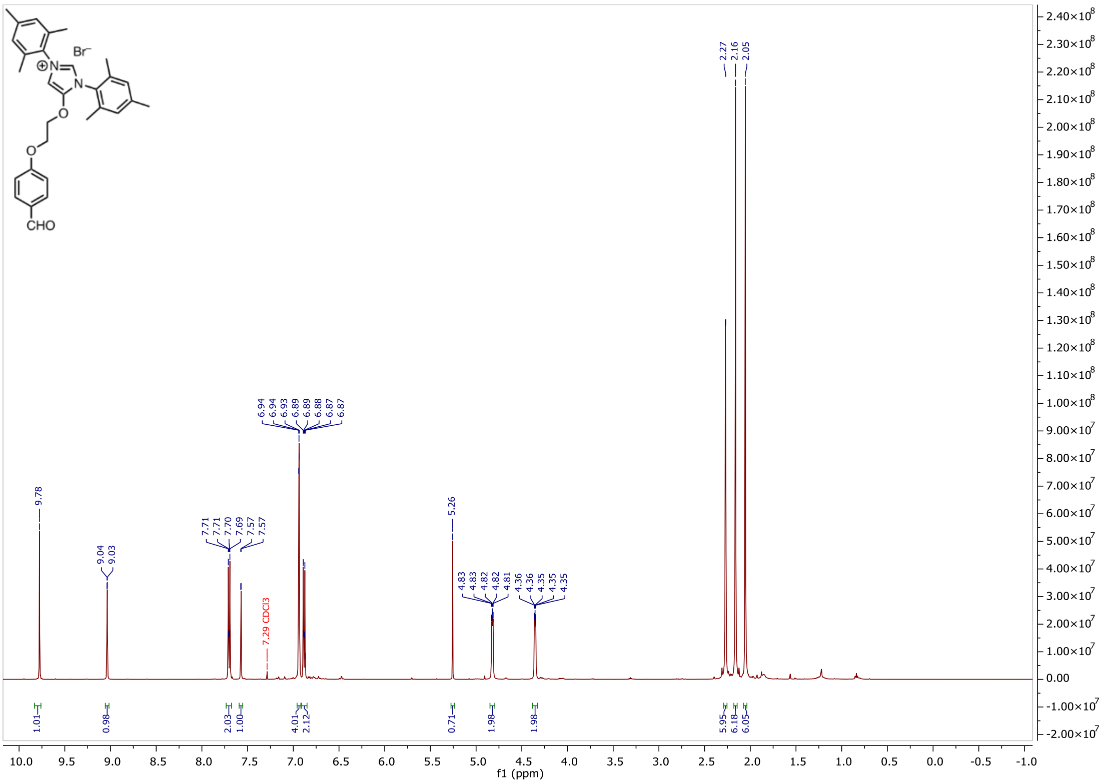


Figure S 48 ^{1}H-NMR spectrum of **7**·HBr in CDCl3.

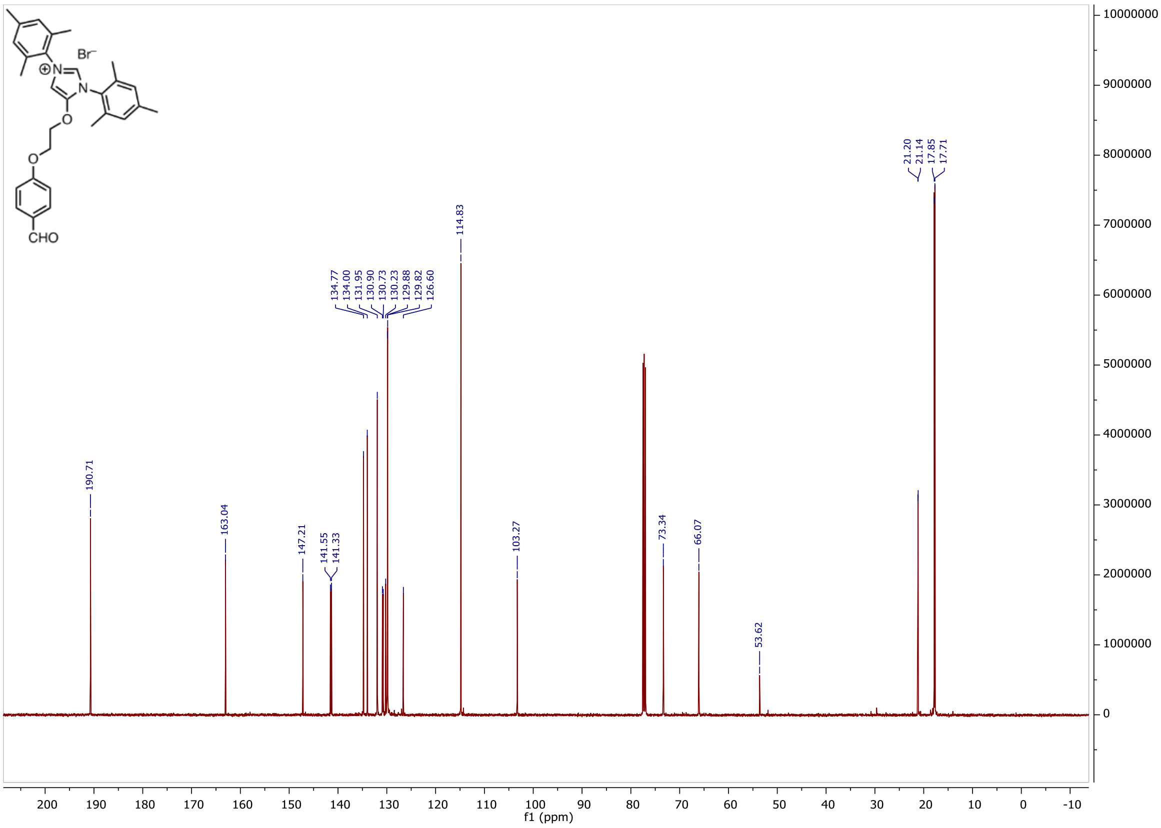


Figure S 49 ^{13}C-NMR spectrum of **7**·HBr in CDCl3.

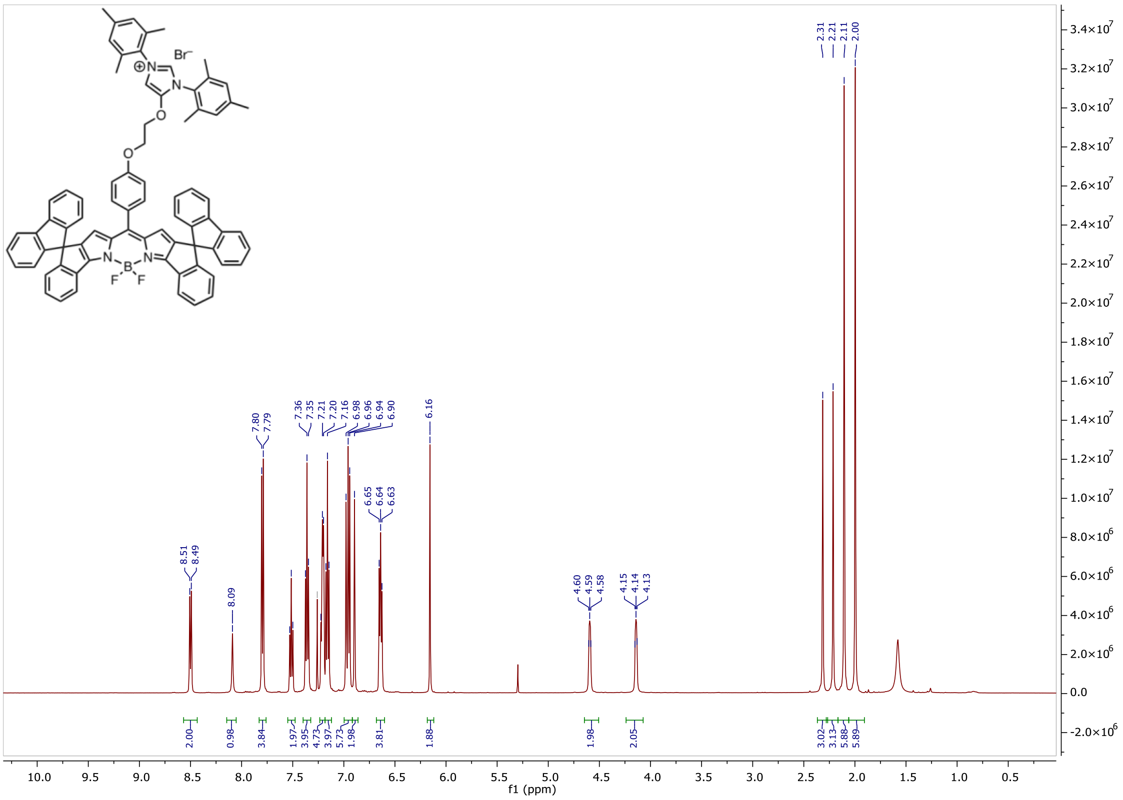


Figure S 50 ^{1}H-NMR spectrum of **8**·HBr in CDCl$_3$.

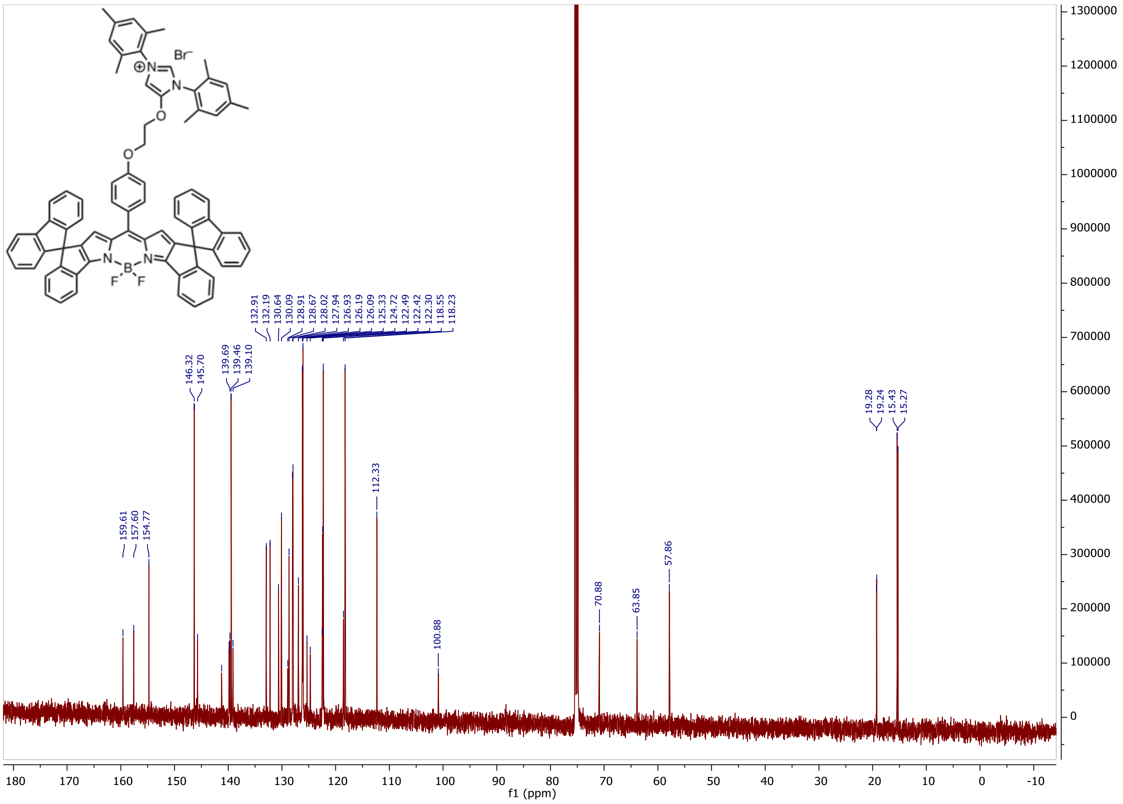


Figure S 51 ^{13}C-NMR spectrum of **8**·HBr in CDCl$_3$.

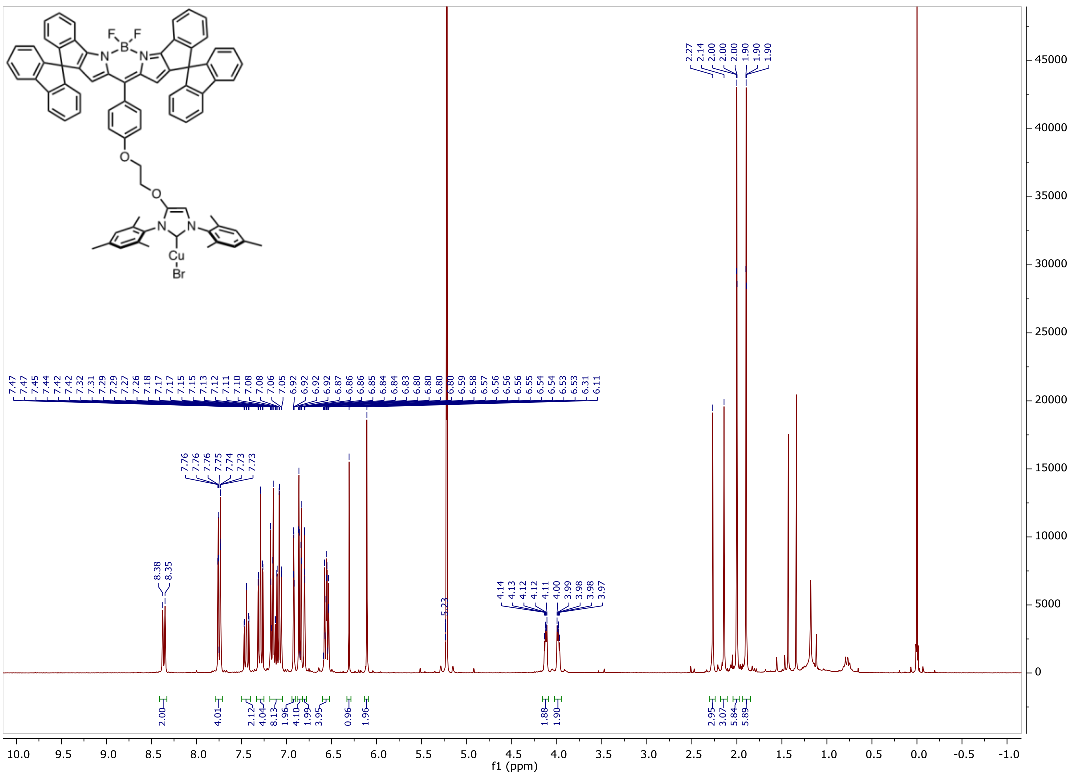


Figure S 52 ^{1}H-NMR spectrum of [CuBr(**8**)] in CD_2Cl_2.

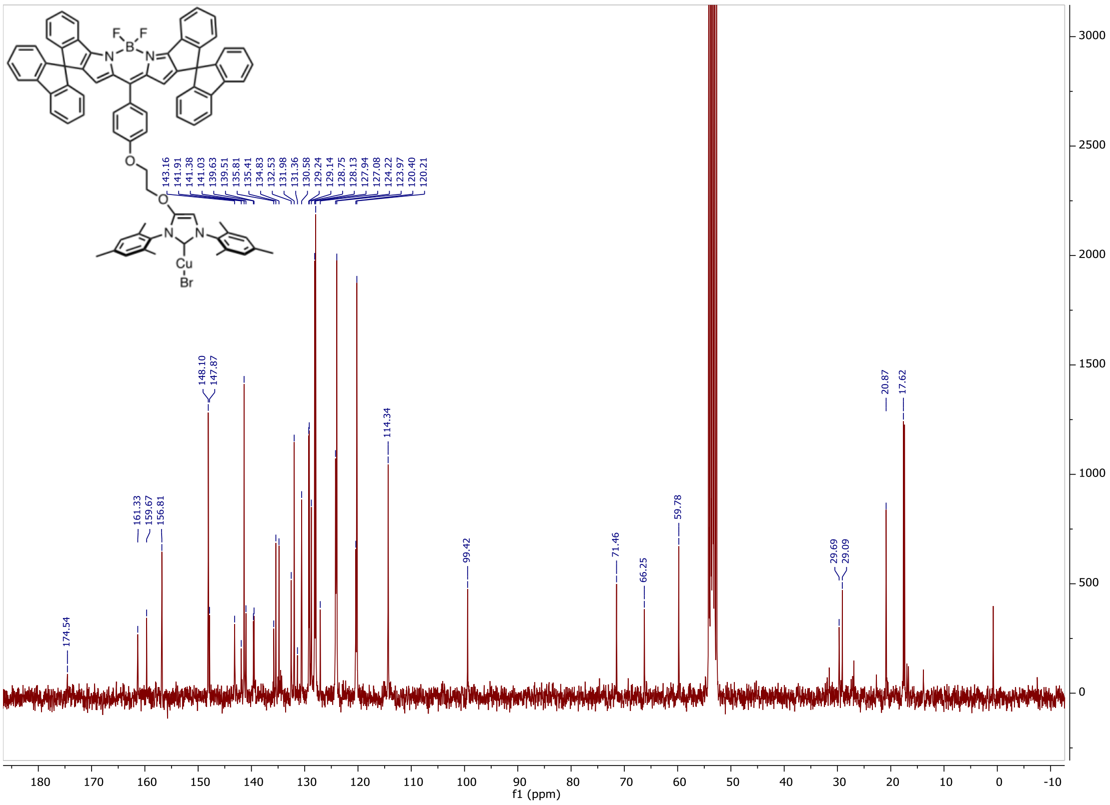


Figure S 53 ^{13}C-NMR spectrum of [CuBr(**8**)] in CD_2Cl_2.

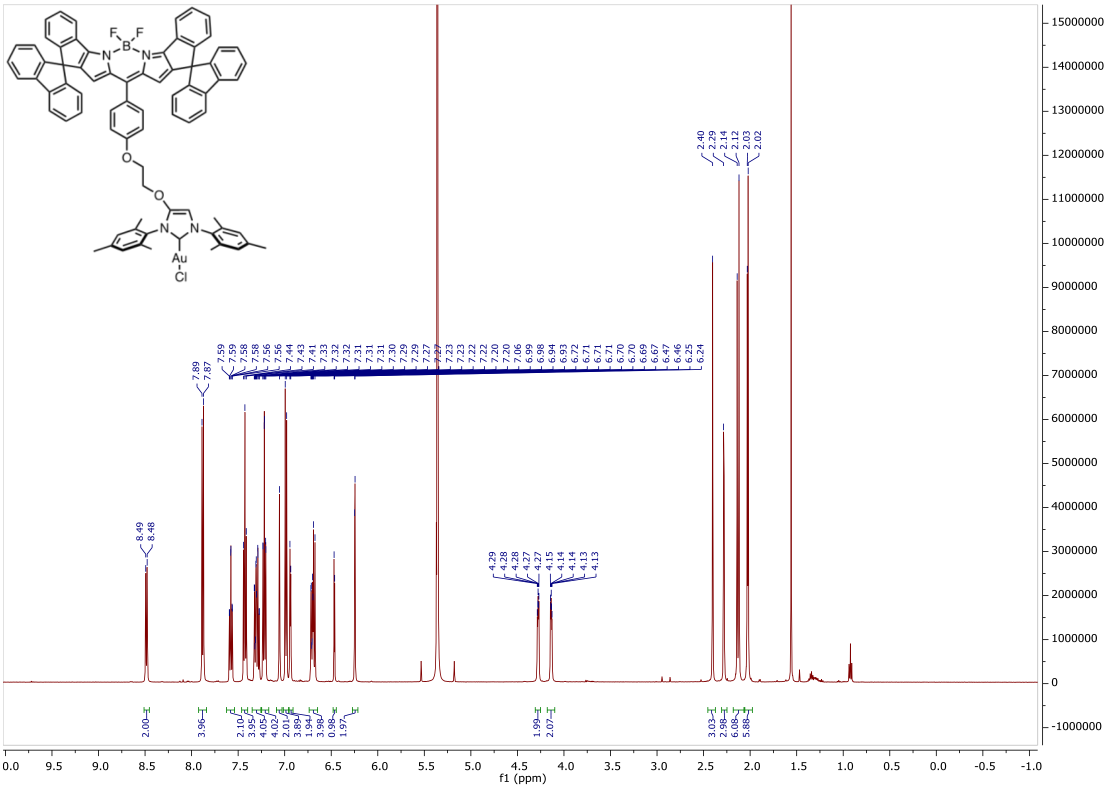


Figure S 54 ^{1}H-NMR spectrum of [AuCl(**8**)] in CD_2Cl_2.

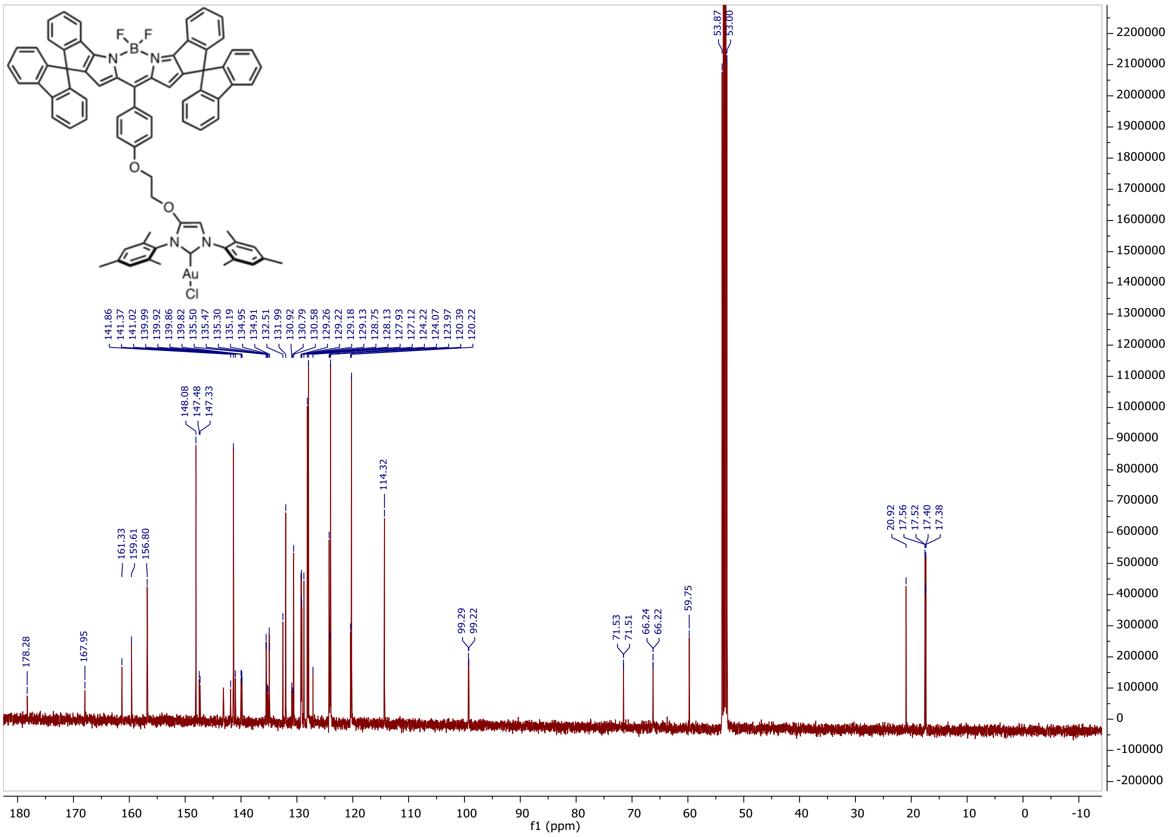


Figure S 55 ^{13}C-NMR spectrum of [AuCl(**8**)] in CD_2Cl_2.

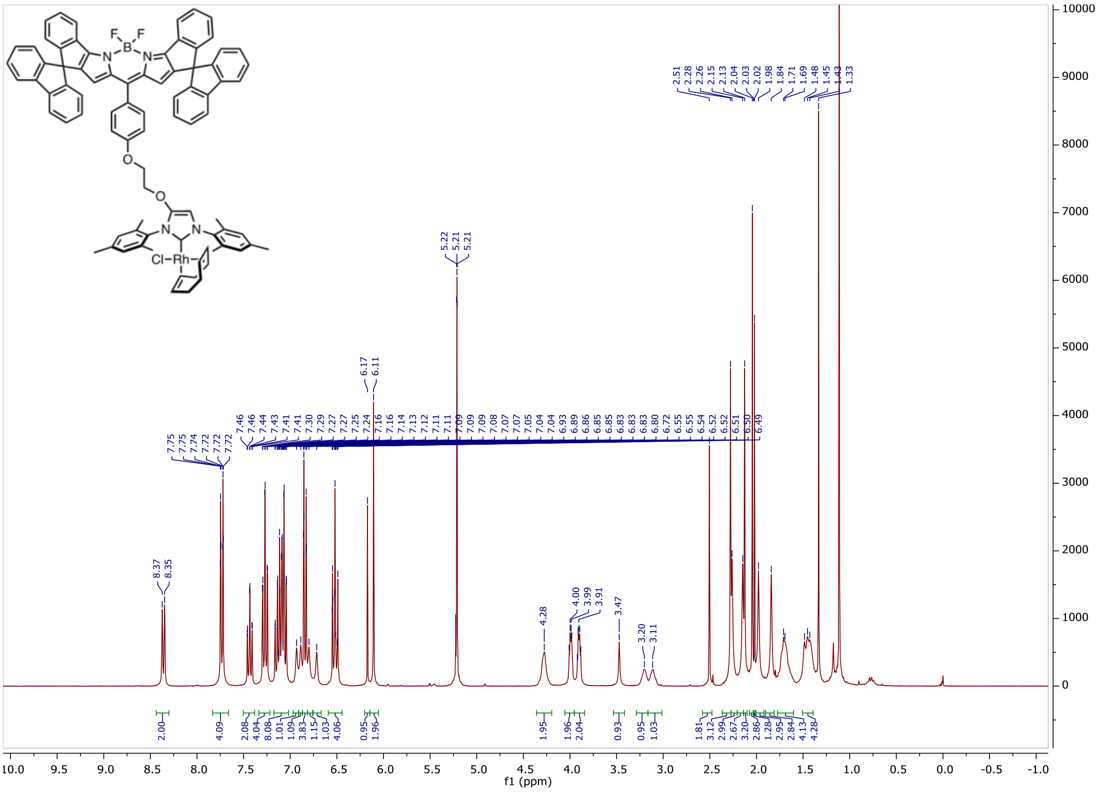


Figure S 56 ^{1}H-NMR spectrum of [RhCl(cod)(**8**)] in CD_2Cl_2.

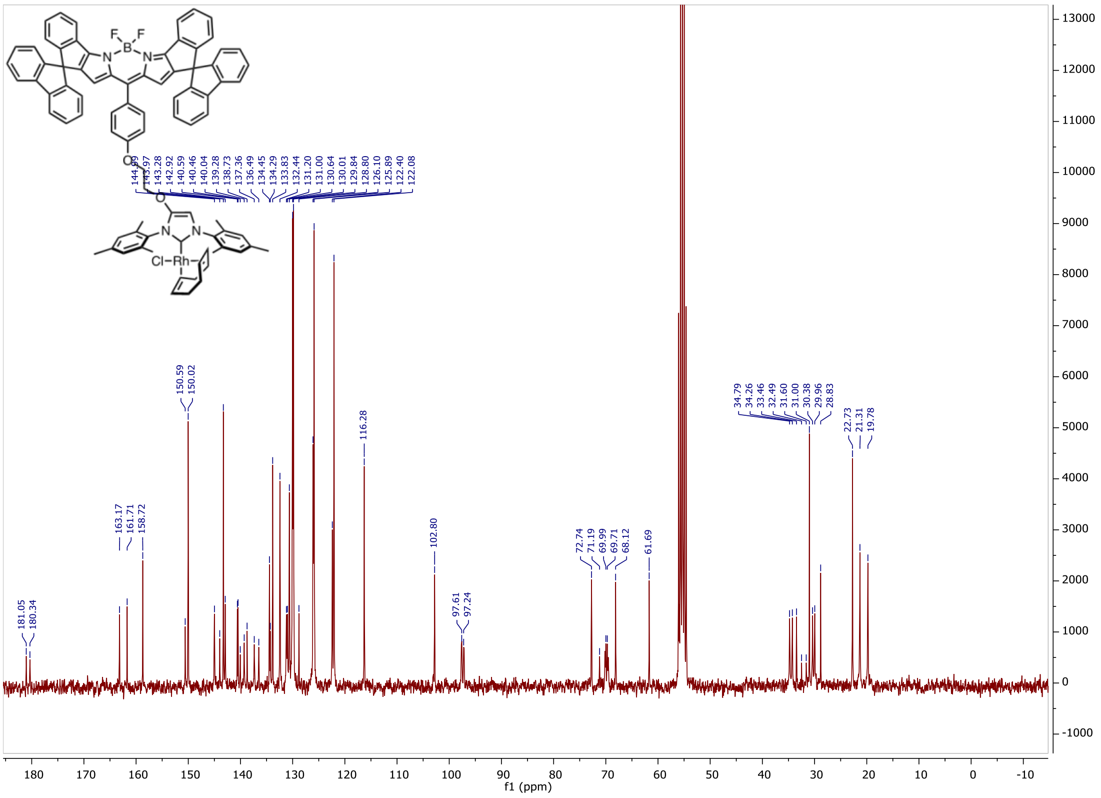


Figure S 57 ^{13}C-NMR spectrum of [RhCl(cod)(**8**)] in CD_2Cl_2.

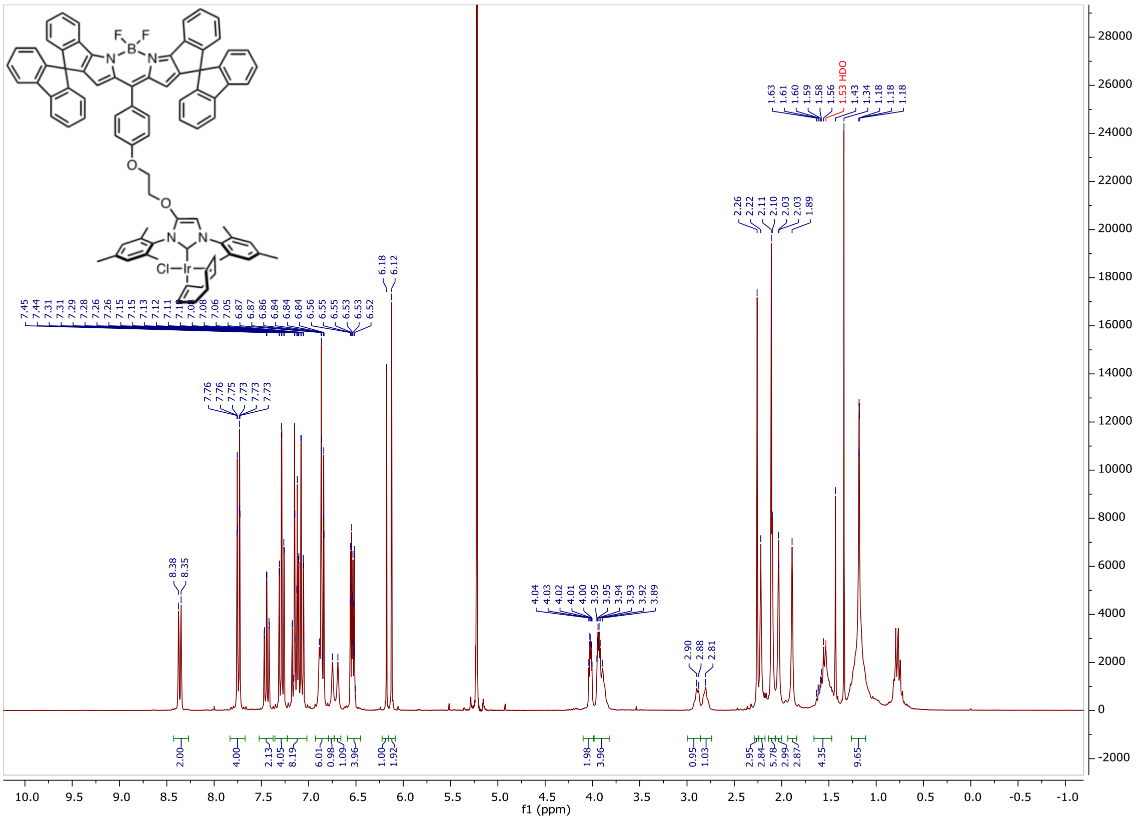


Figure S 58 ^{1}H-NMR spectrum of [IrCl(cod)(**8**)] in CD_2Cl_2.

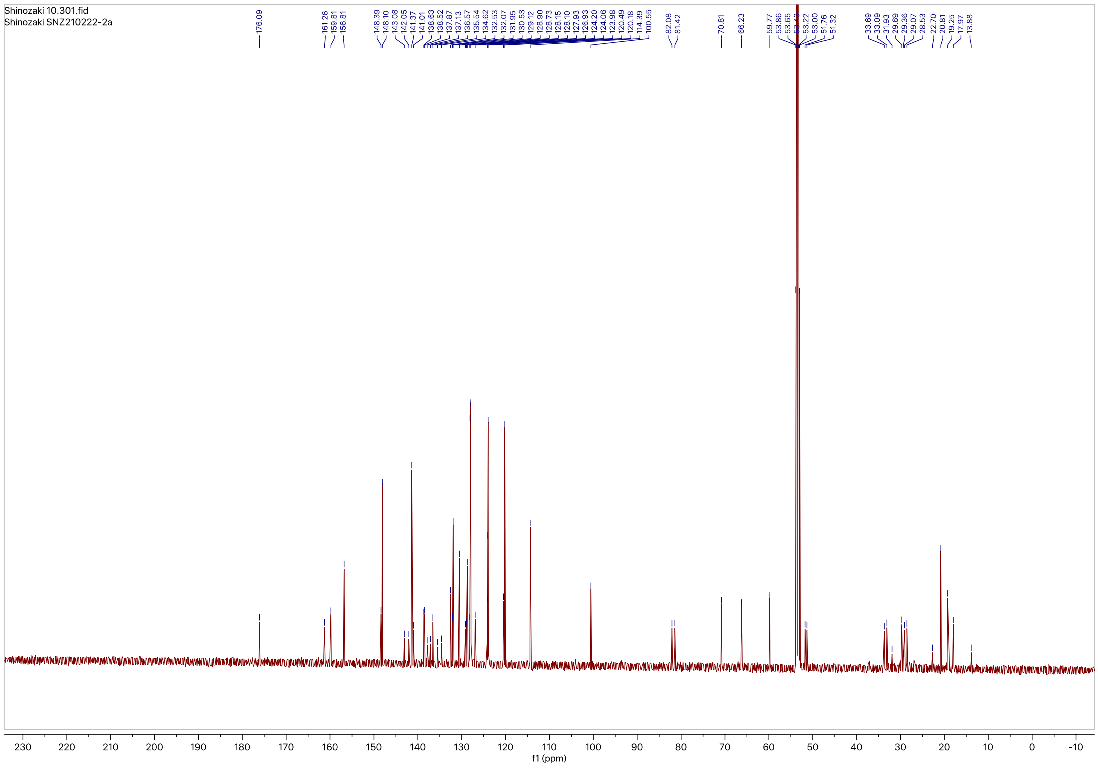


Figure S 59 ^{13}C-NMR spectrum of [IrCl(cod)(**8**)] in CD_2Cl_2.

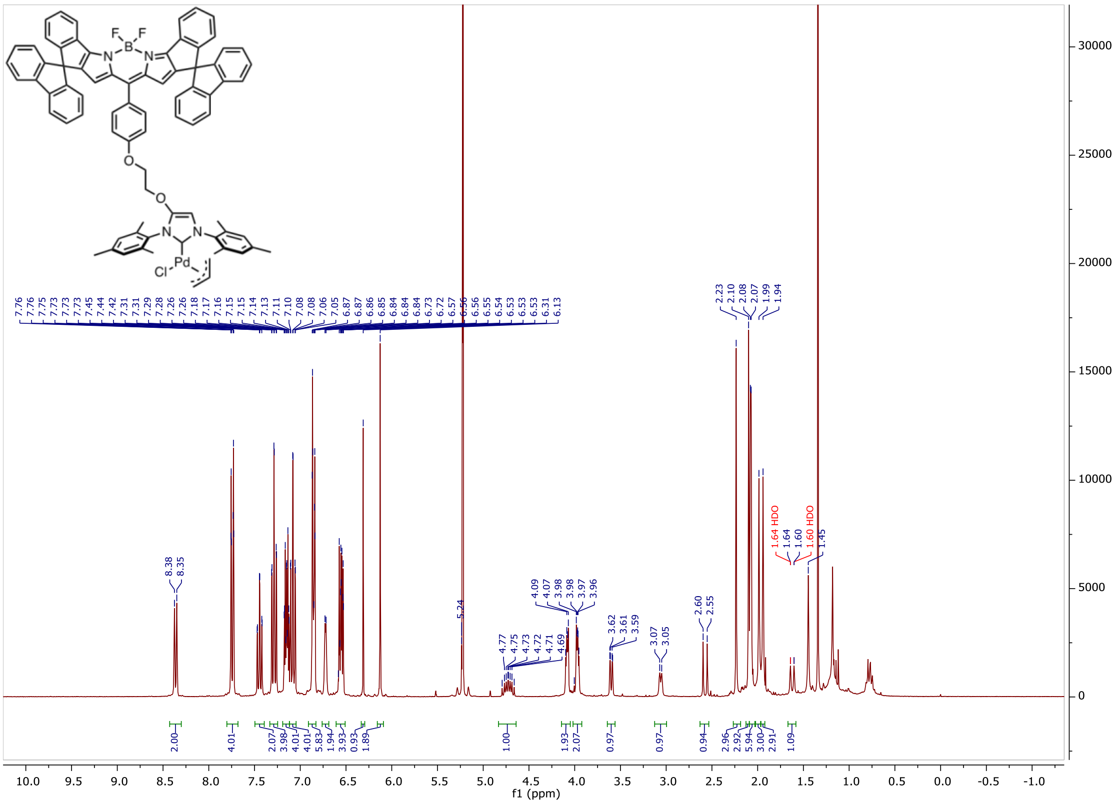


Figure S 60 ^{1}H-NMR spectrum of [Pd(allyl)Cl(**8**)] in CD_2Cl_2.

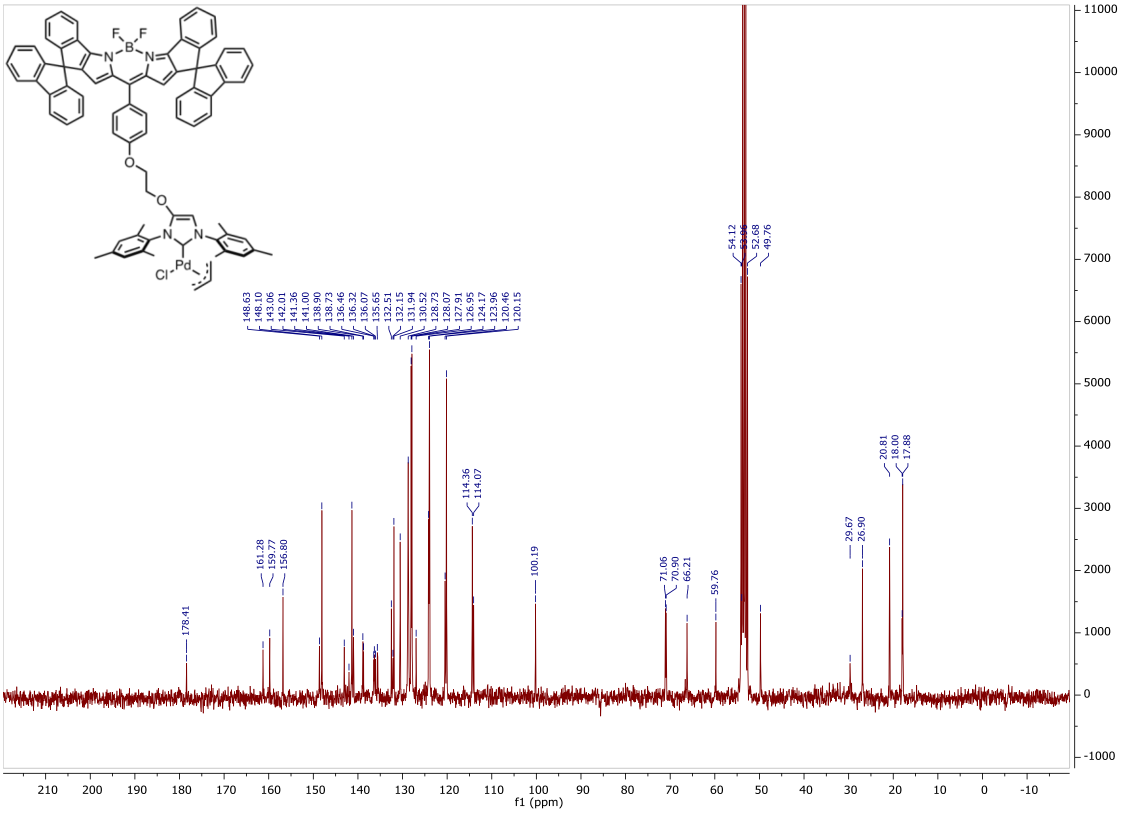


Figure S 61 ^{13}C-NMR spectrum of [Pd(allyl)Cl(**8**)] in CD_2Cl_2.

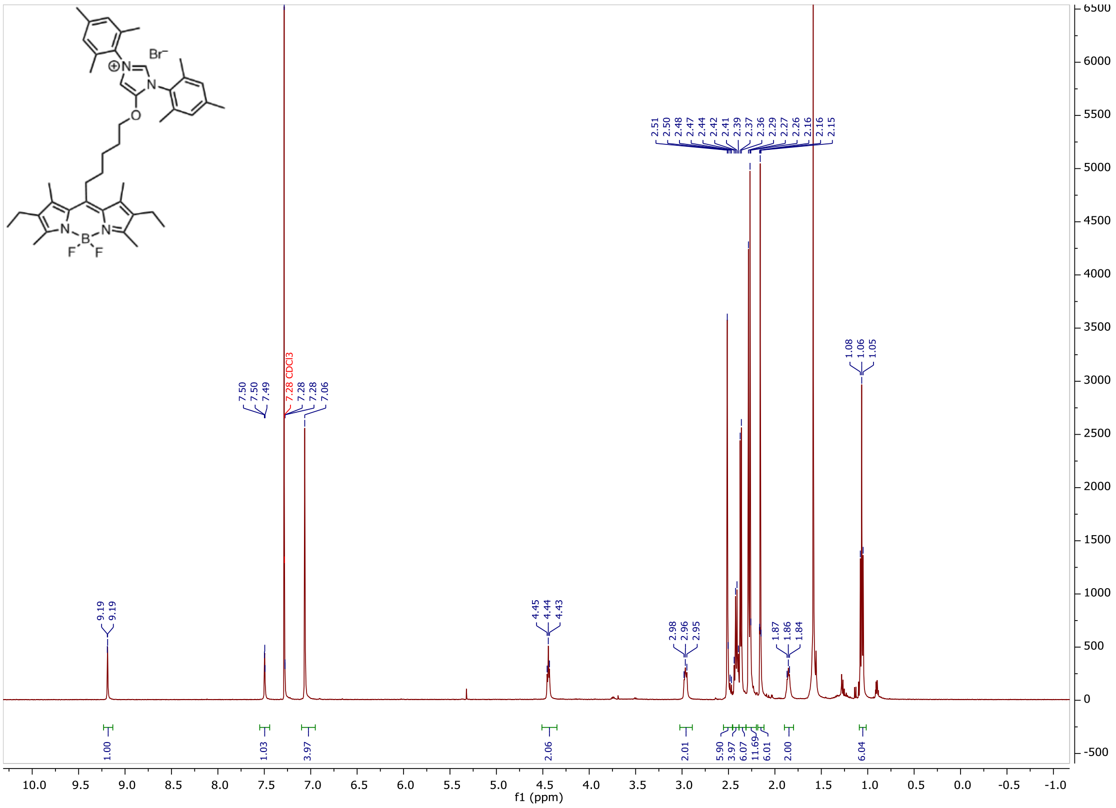


Figure S 62 ^{1}H-NMR spectrum of **9** in $CDCl_3$.

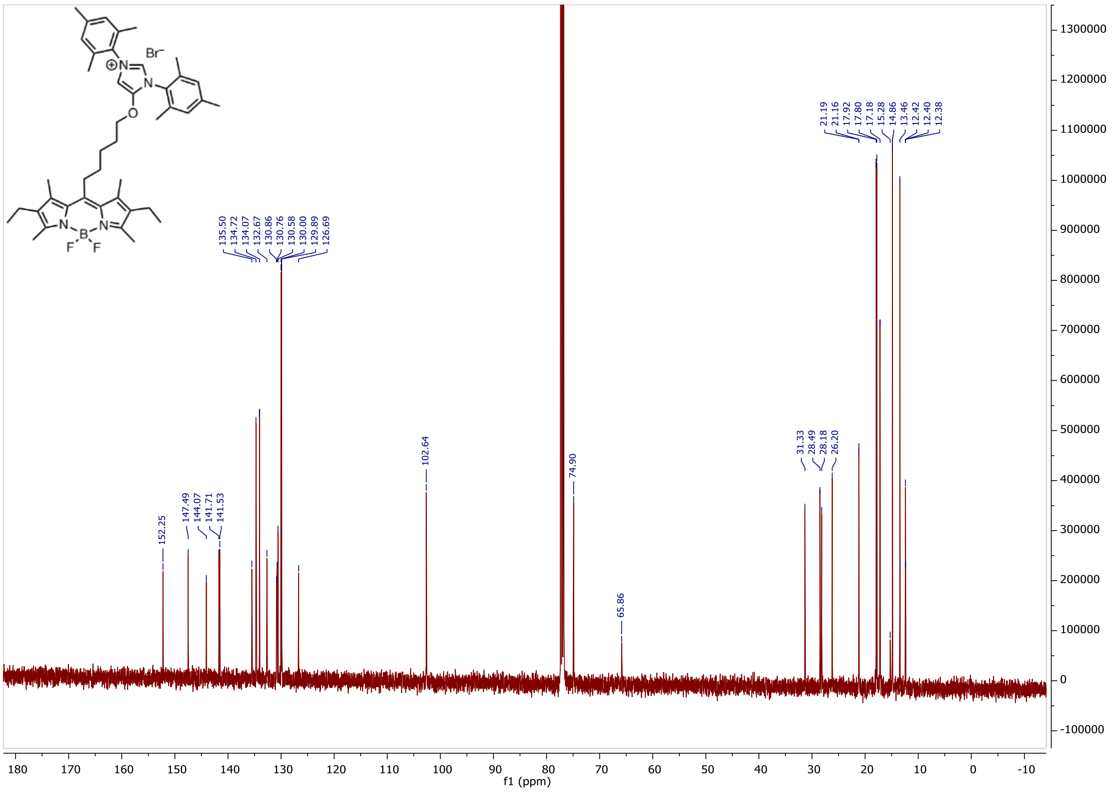


Figure S 63 ^{13}C-NMR spectrum of **9** in $CDCl_3$.

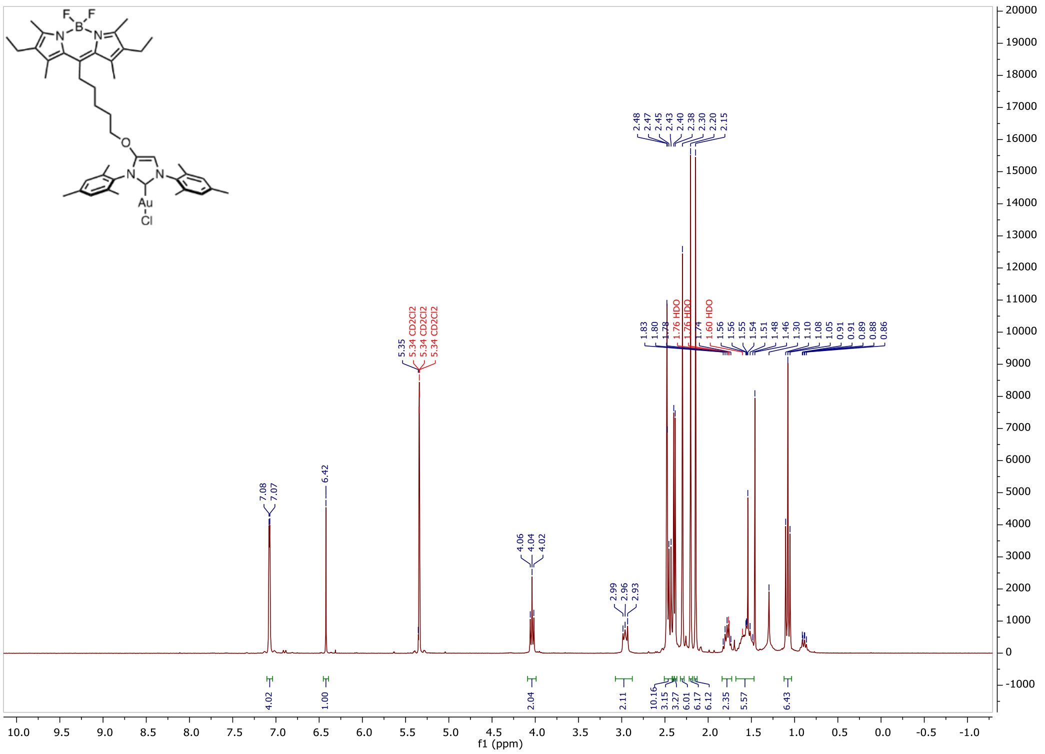


Figure S 64 ^{1}H-NMR spectrum of [AuCl(**9**)] in CD_2Cl_2.

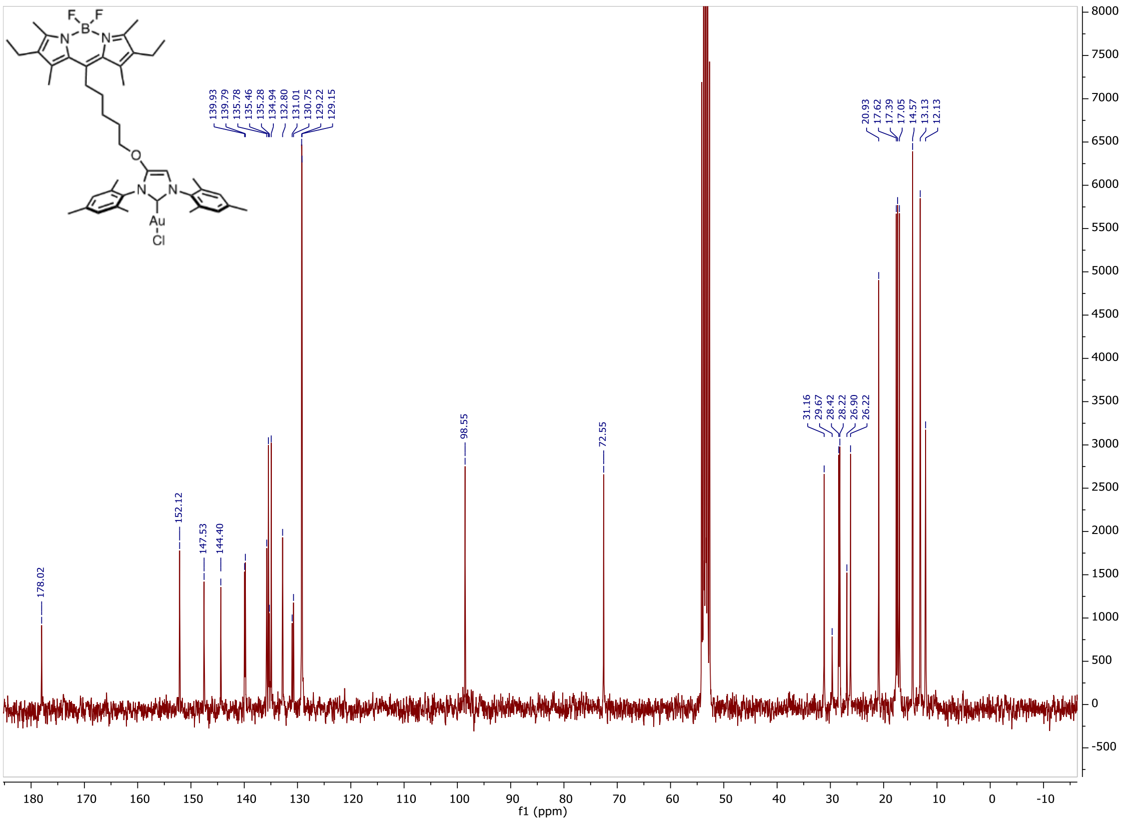


Figure S 65 ^{13}C-NMR spectrum of [AuCl(**9**)] in CD_2Cl_2.

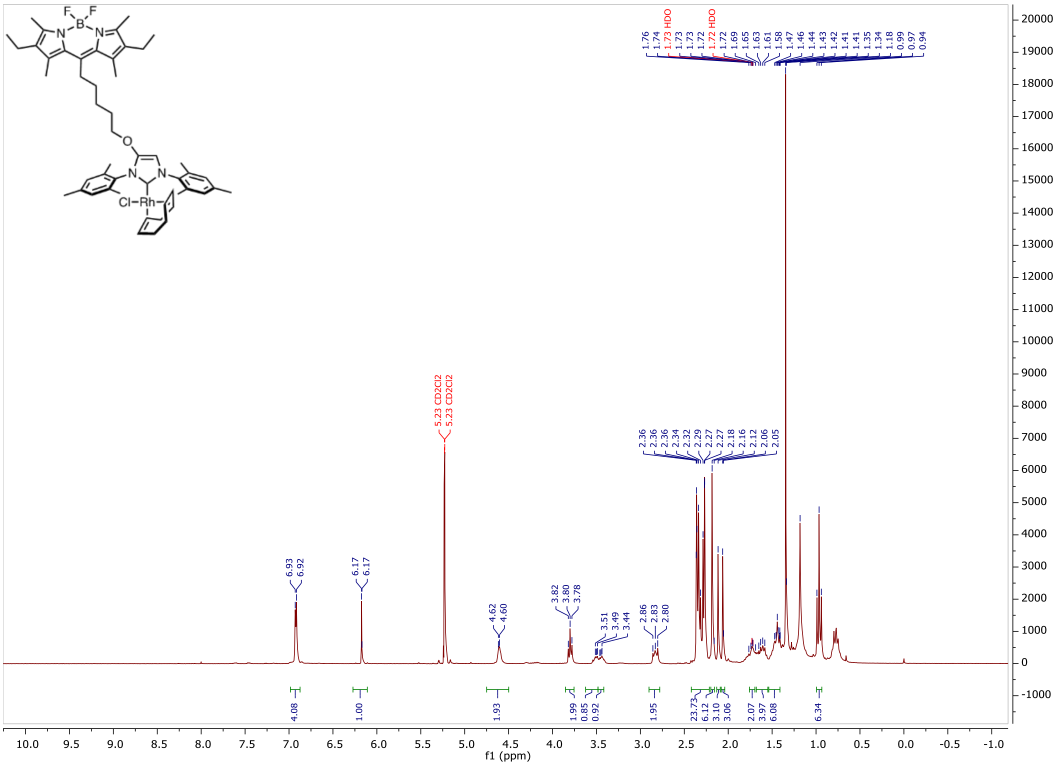


Figure S 66 ^{1}H-NMR spectrum of [RhCl(cod)(**9**)] in CD_2Cl_2.

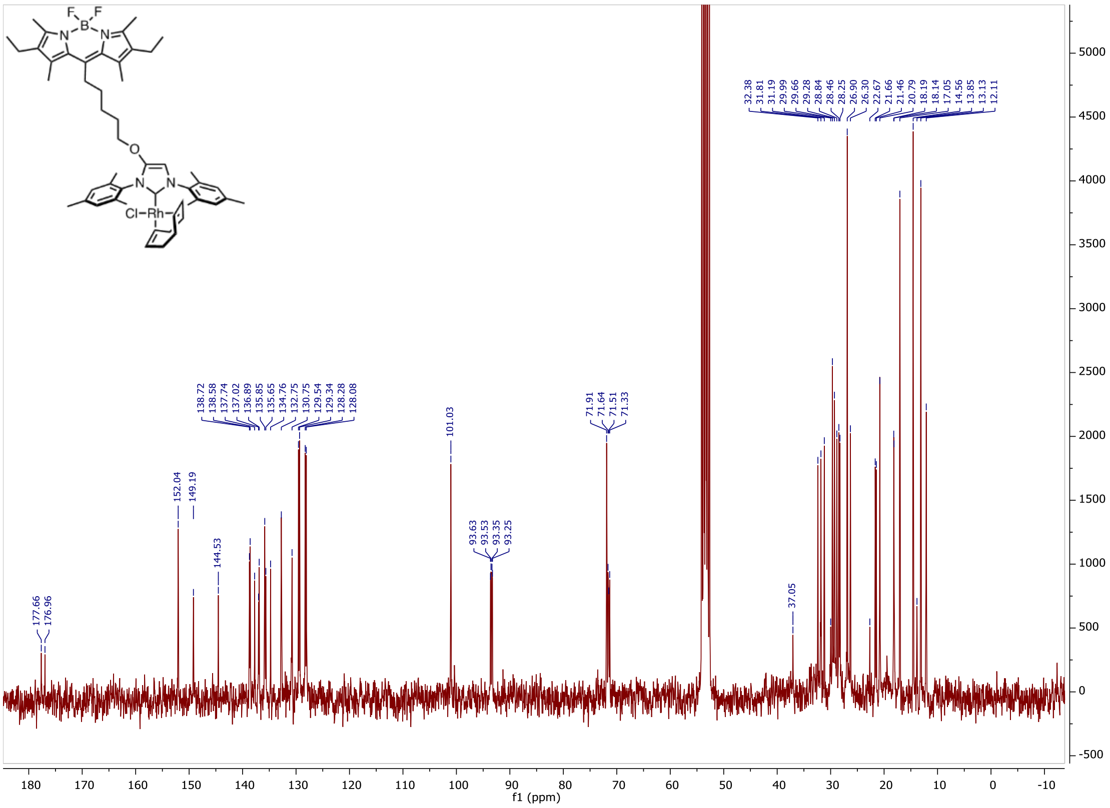


Figure S 67 ^{13}C-NMR spectrum of [RhCl(cod)(**9**)] in CD_2Cl_2.

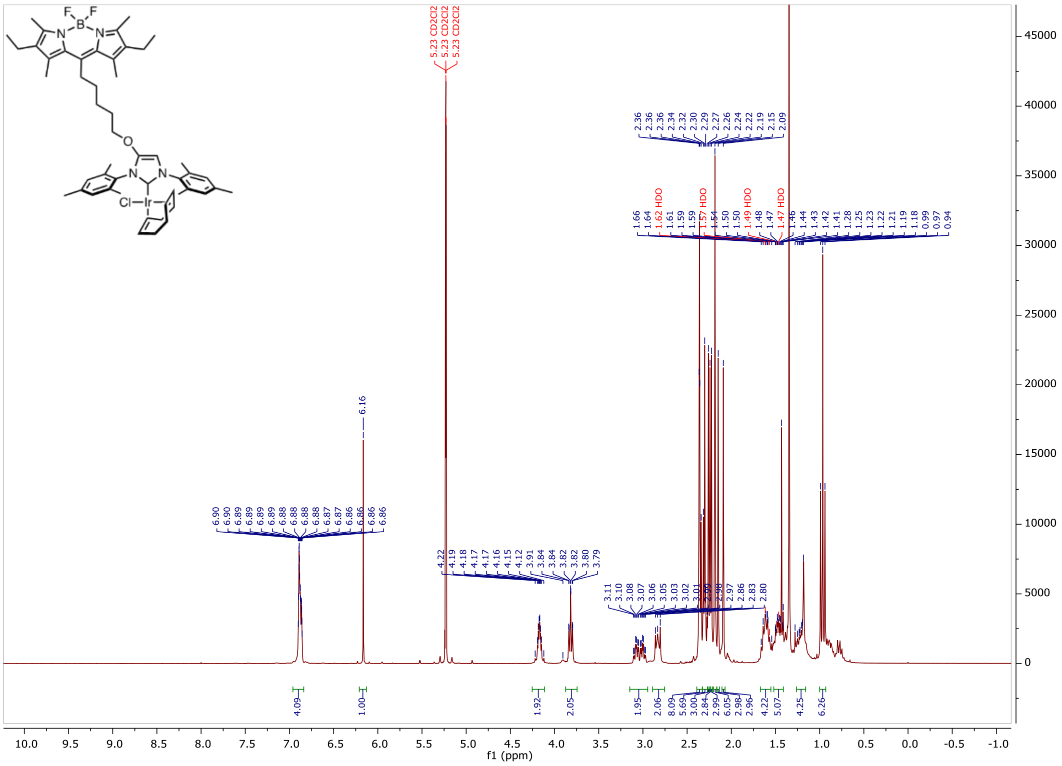


Figure S 68 ^{1}H-NMR spectrum of [IrCl(cod)(**9**)] in CD_2Cl_2.

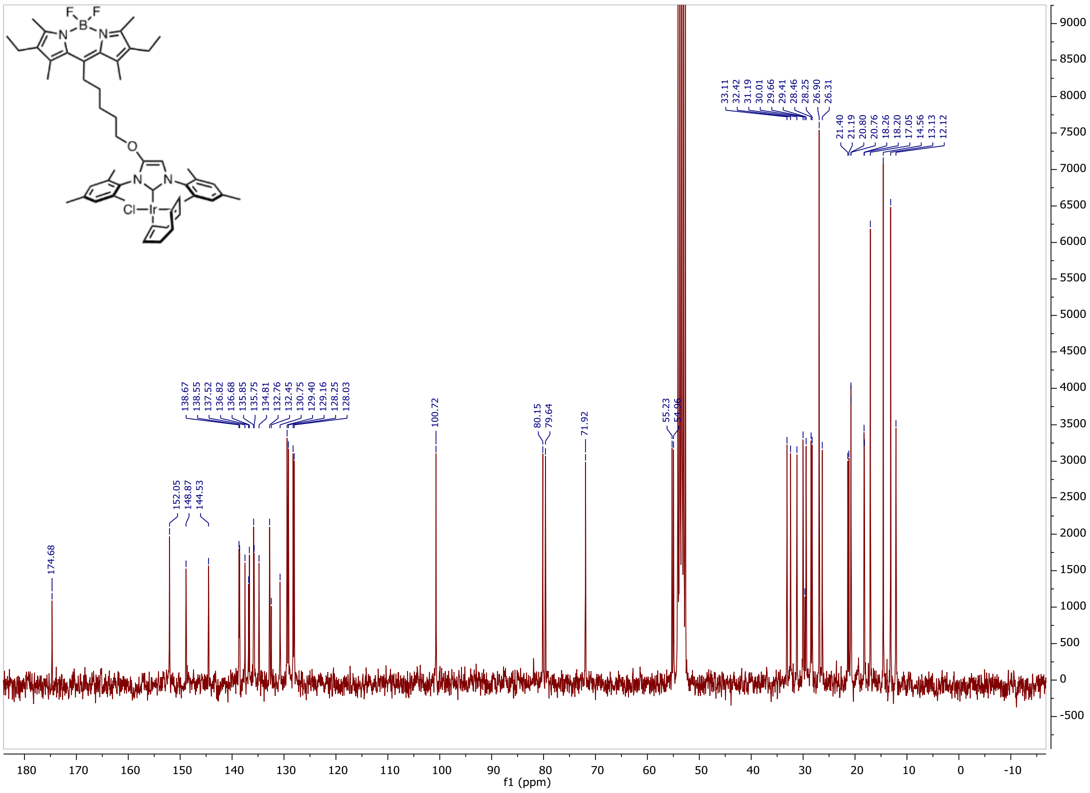


Figure S 69 ^{13}C-NMR spectrum of [IrCl(cod)(**9**)] in CD_2Cl_2.

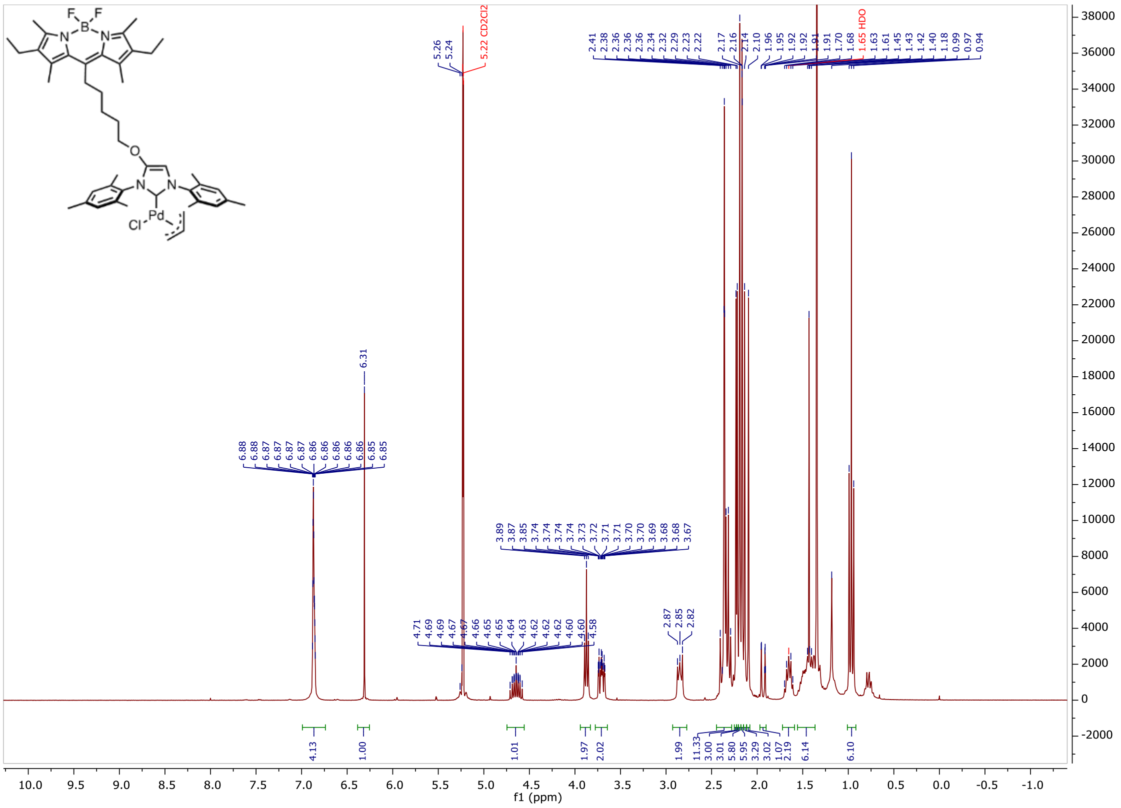


Figure S 70 ^{1}H-NMR spectrum of [Pd(allyl)Cl(**9**)] in CD_2Cl_2.

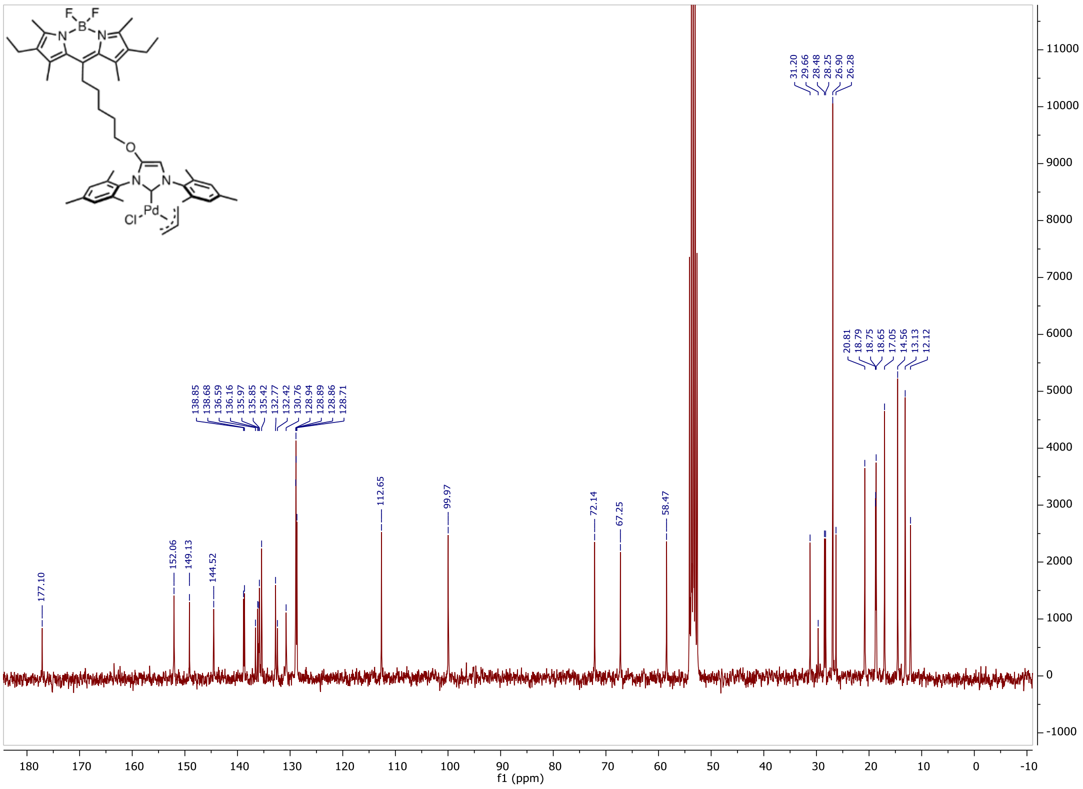


Figure S 71 ^{13}C-NMR spectrum of [Pd(allyl)Cl(**9**)] in CD_2Cl_2.

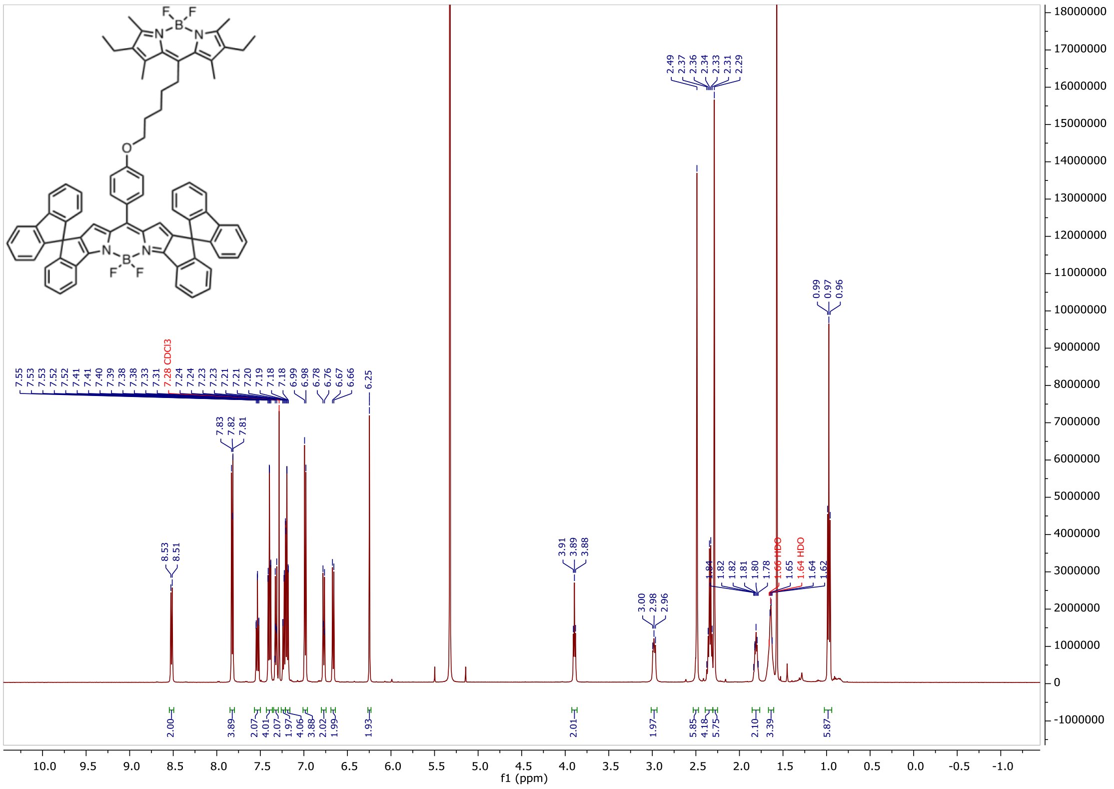


Figure S 72 ^{1}H-NMR spectrum of **12** in CDCl$_3$.

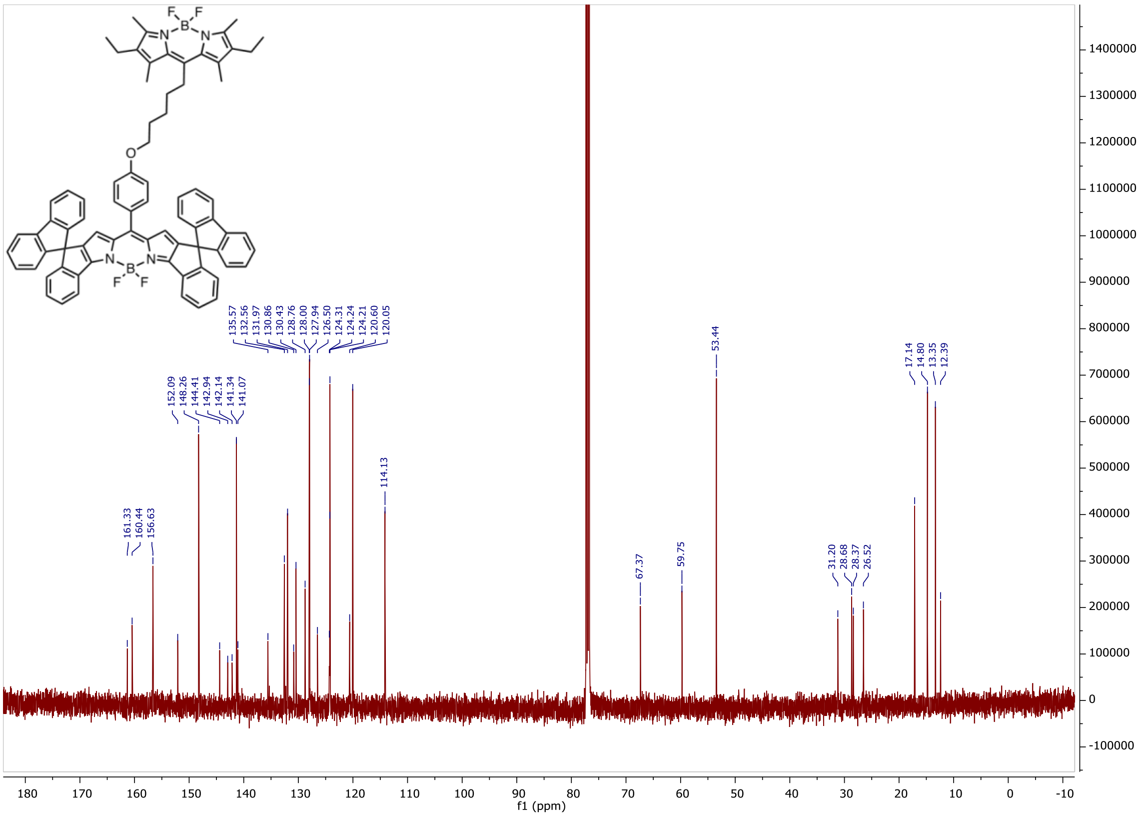


Figure S 73 ^{13}C-NMR spectrum of **12** in CDCl$_3$.

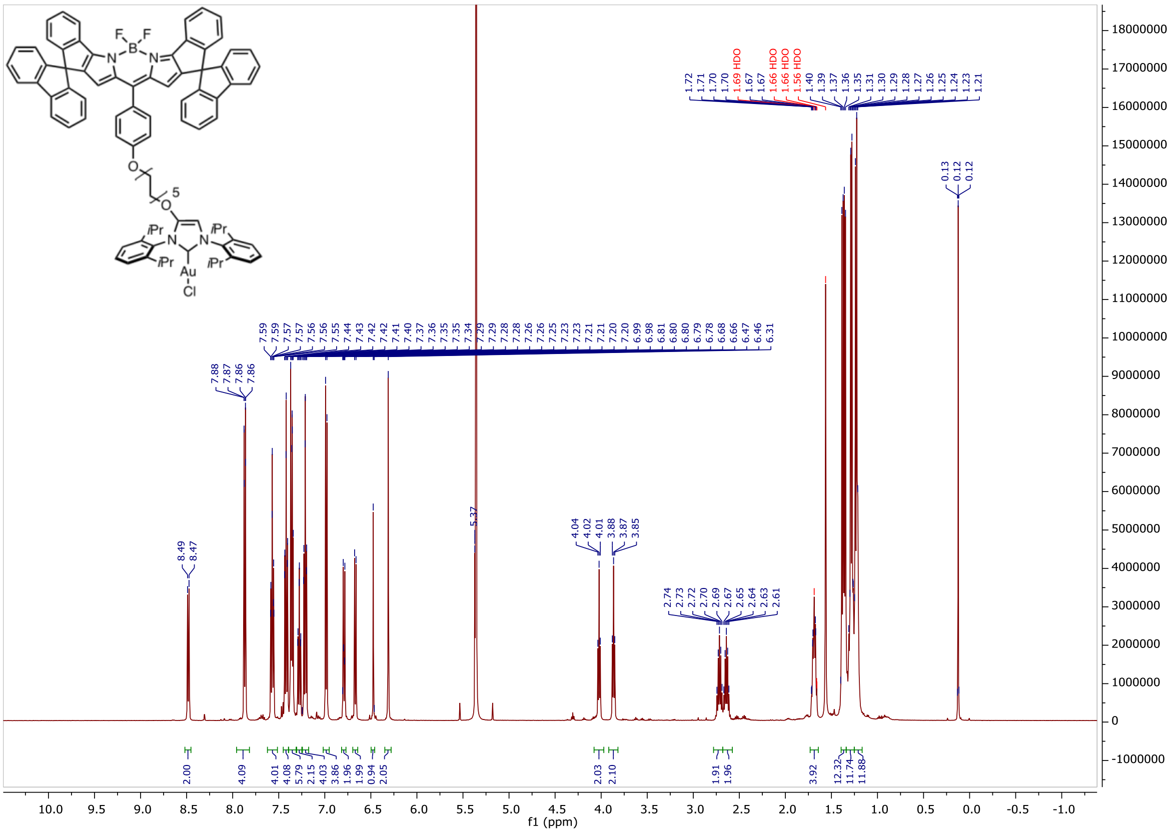


Figure S 74 ^{1}H-NMR spectrum of [AuCl(NHC_red)] in CD_2Cl_2.

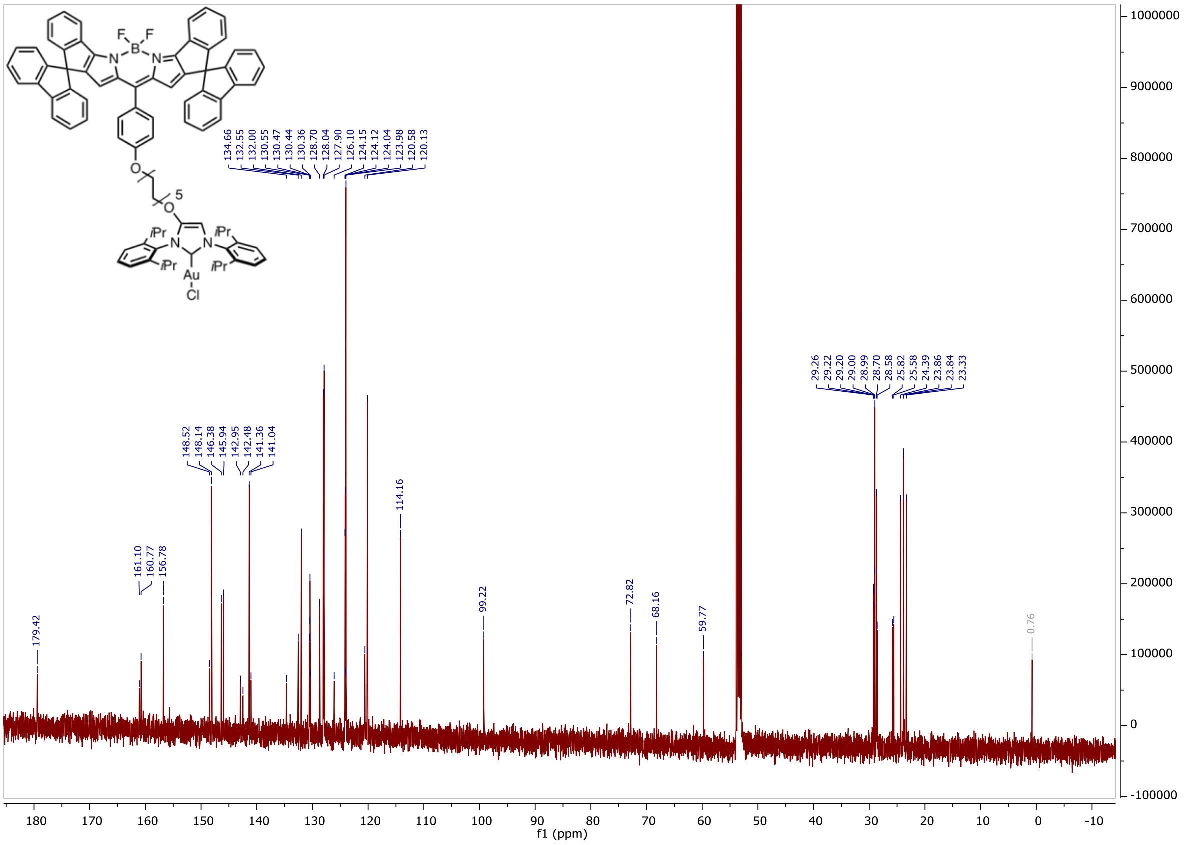


Figure S 75 ^{13}C-NMR spectrum of [AuCl(NHC_red)] in CD_2Cl_2.

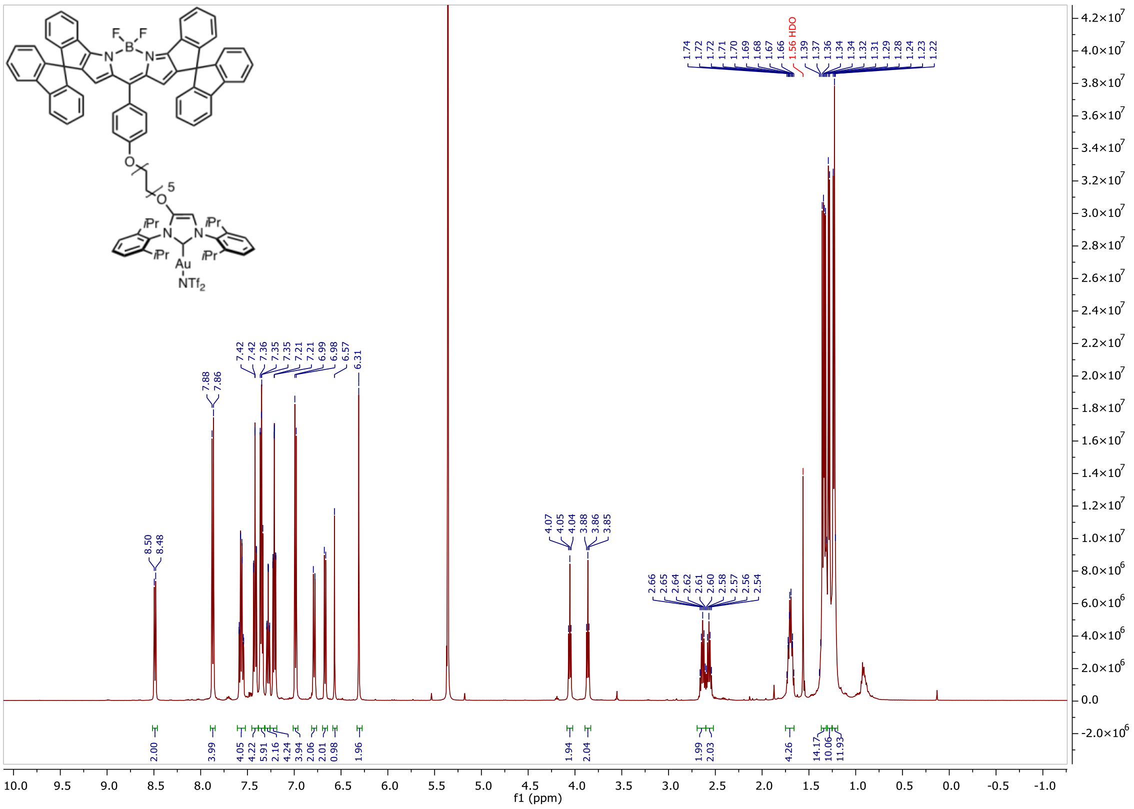


Figure S 76 ^{1}H-NMR spectrum of **14** in CD_2Cl_2.

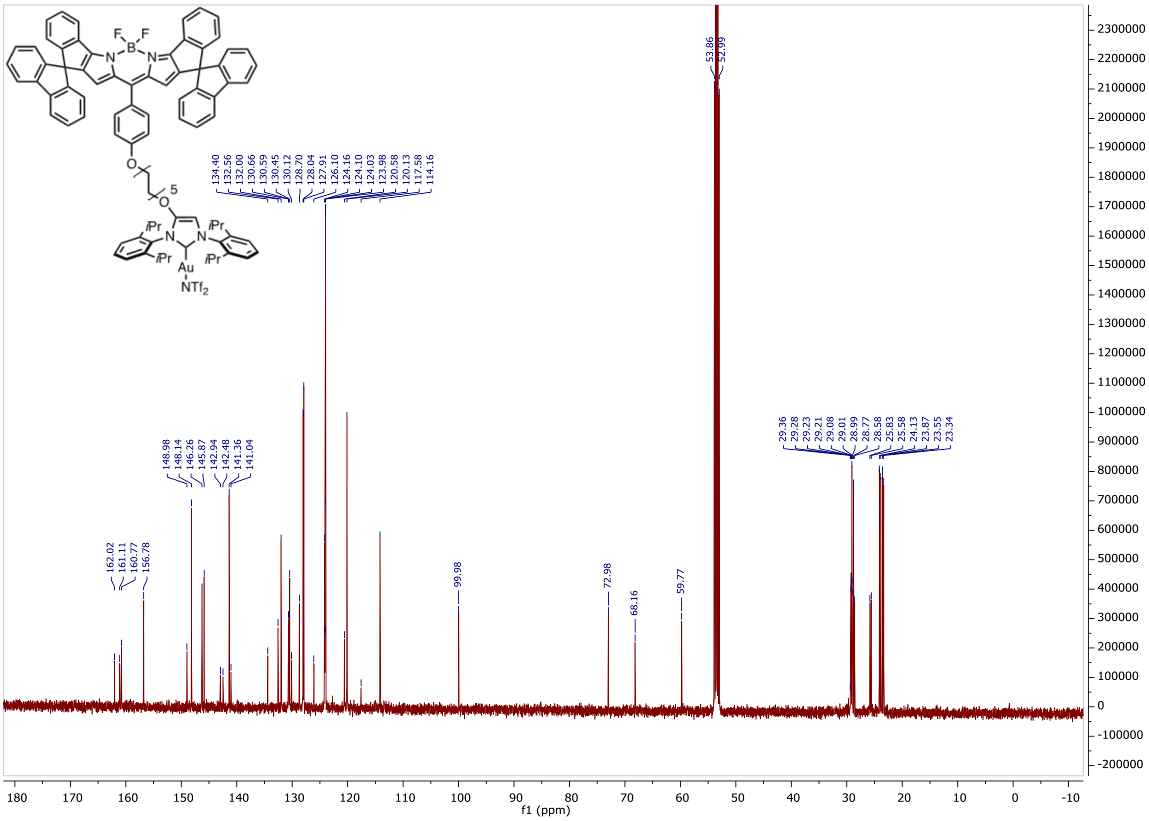


Figure S 77 ^{13}C-NMR spectrum of **14** in CD_2Cl_2.

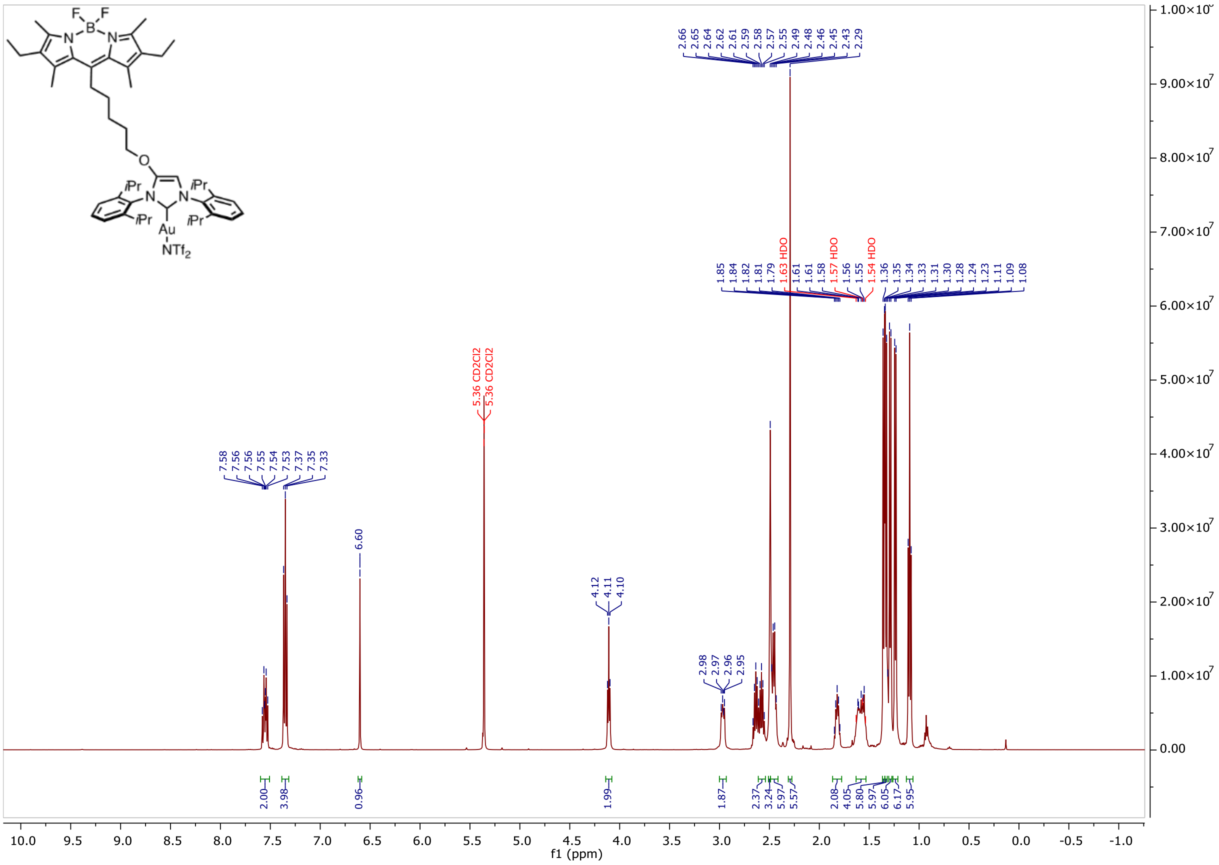


Figure S 78 ^{1}H-NMR spectrum of [AuCl(NHC_green)] in CD_2Cl_2.

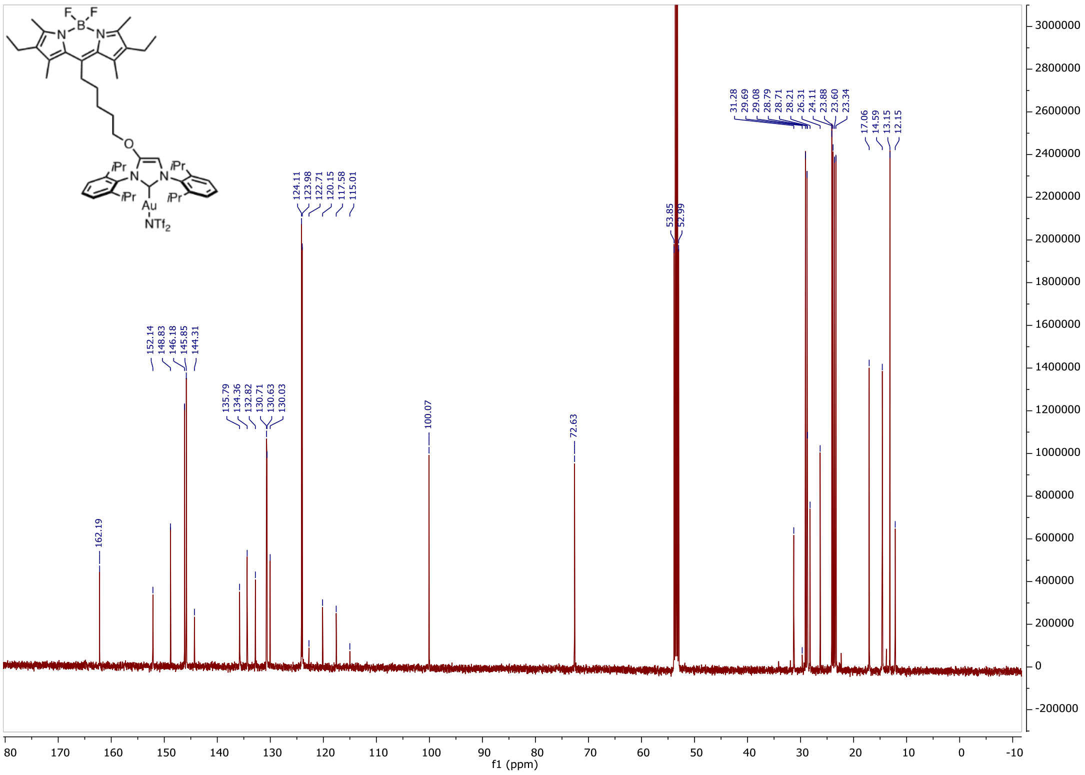


Figure S 79 ^{13}C-NMR spectrum of [AuCl(NHC_green)] in CD_2Cl_2.

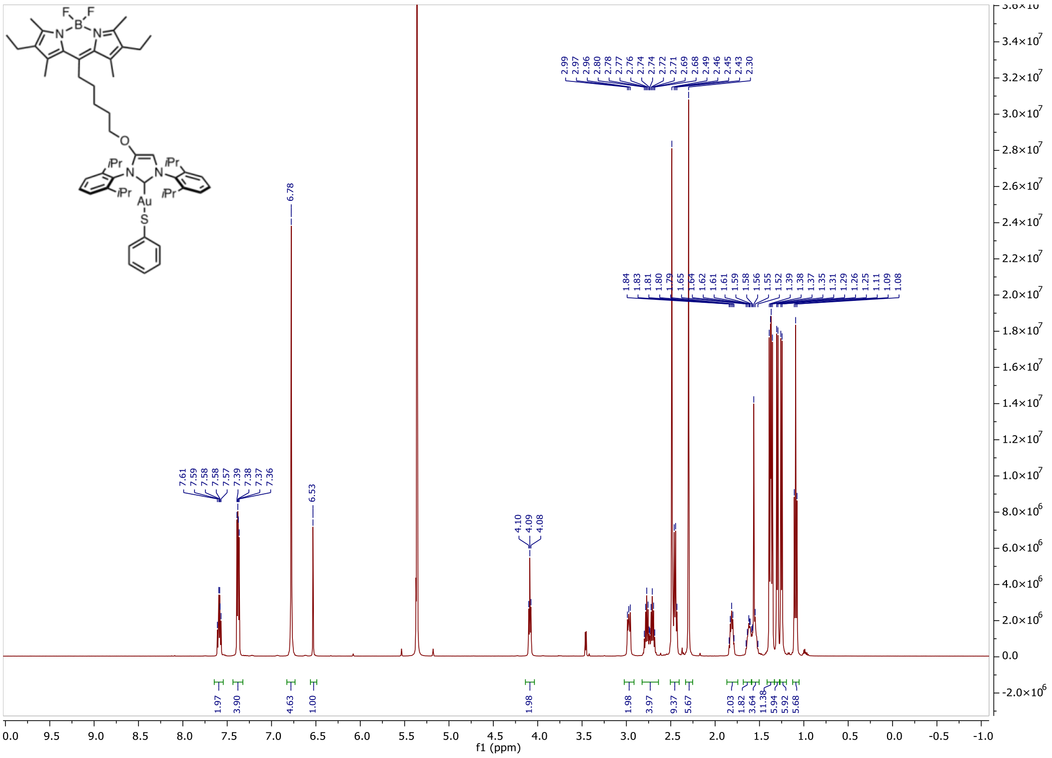


Figure S 80 ^{1}H-NMR spectrum of **15** in CD_2Cl_2.

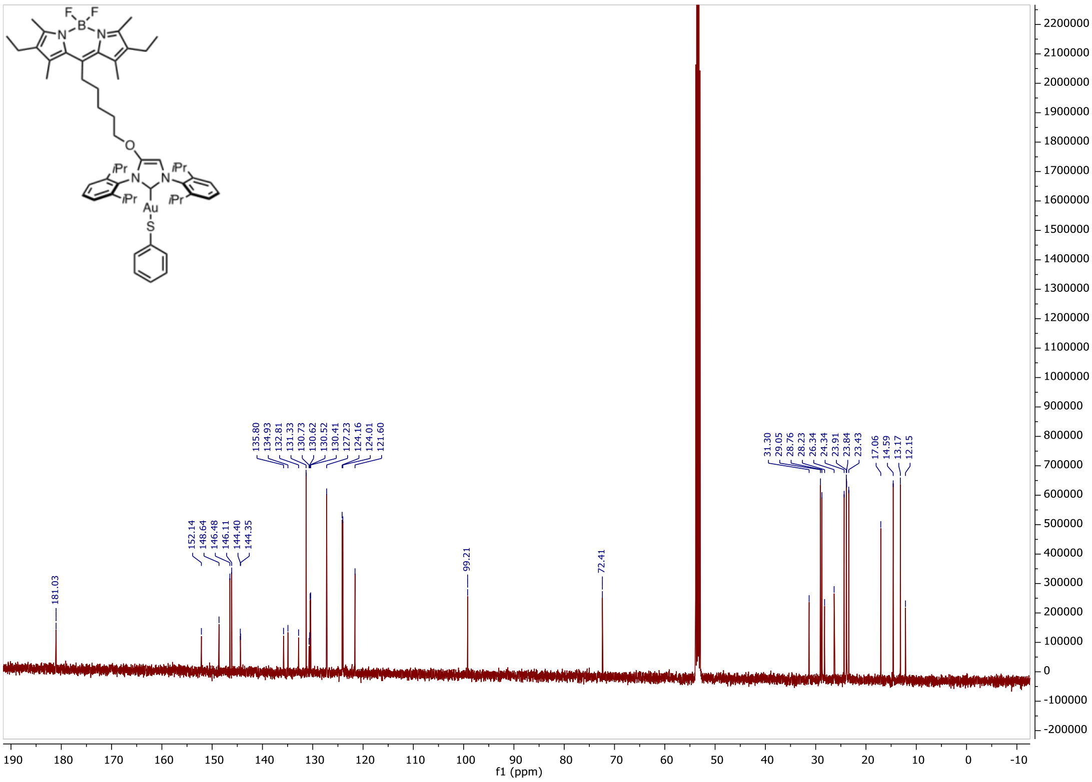


Figure S 81 ^{13}C-NMR spectrum of **15** in CD_2Cl_2.

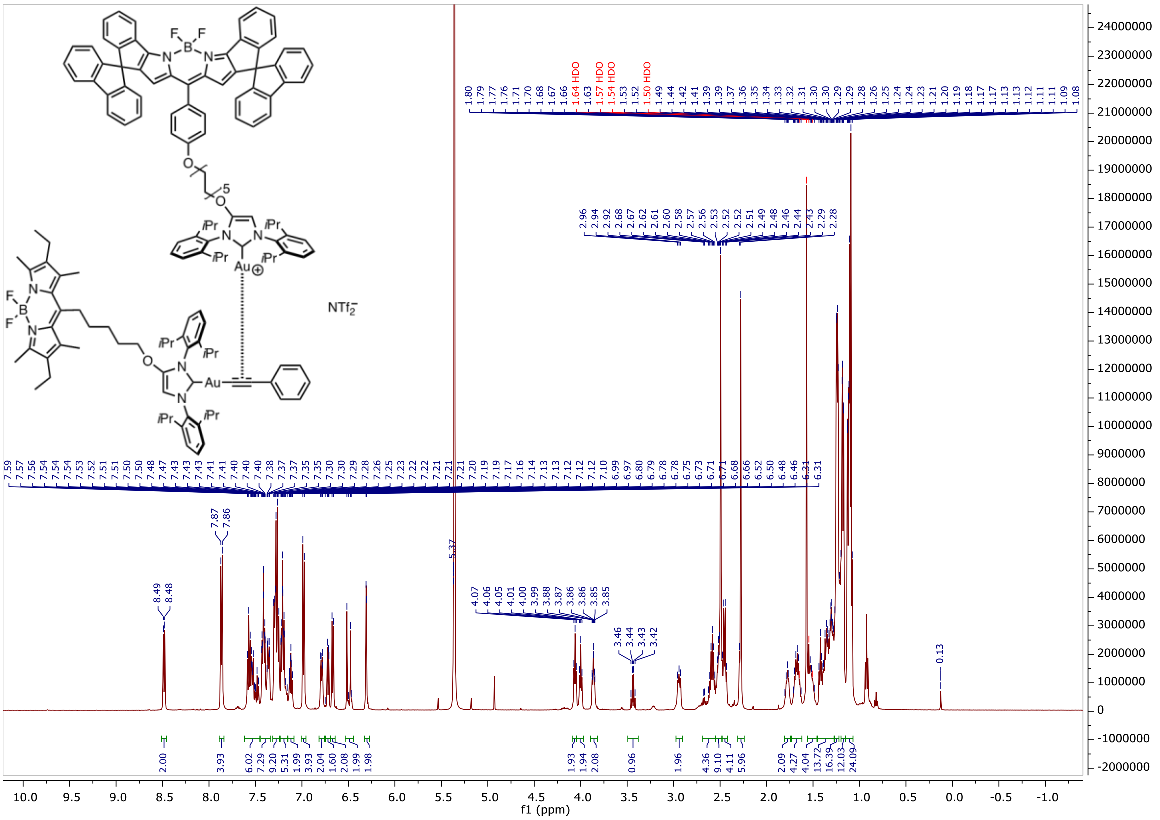


Figure S 82 ^{1}H-NMR spectrum of **16** in CD_2Cl_2.

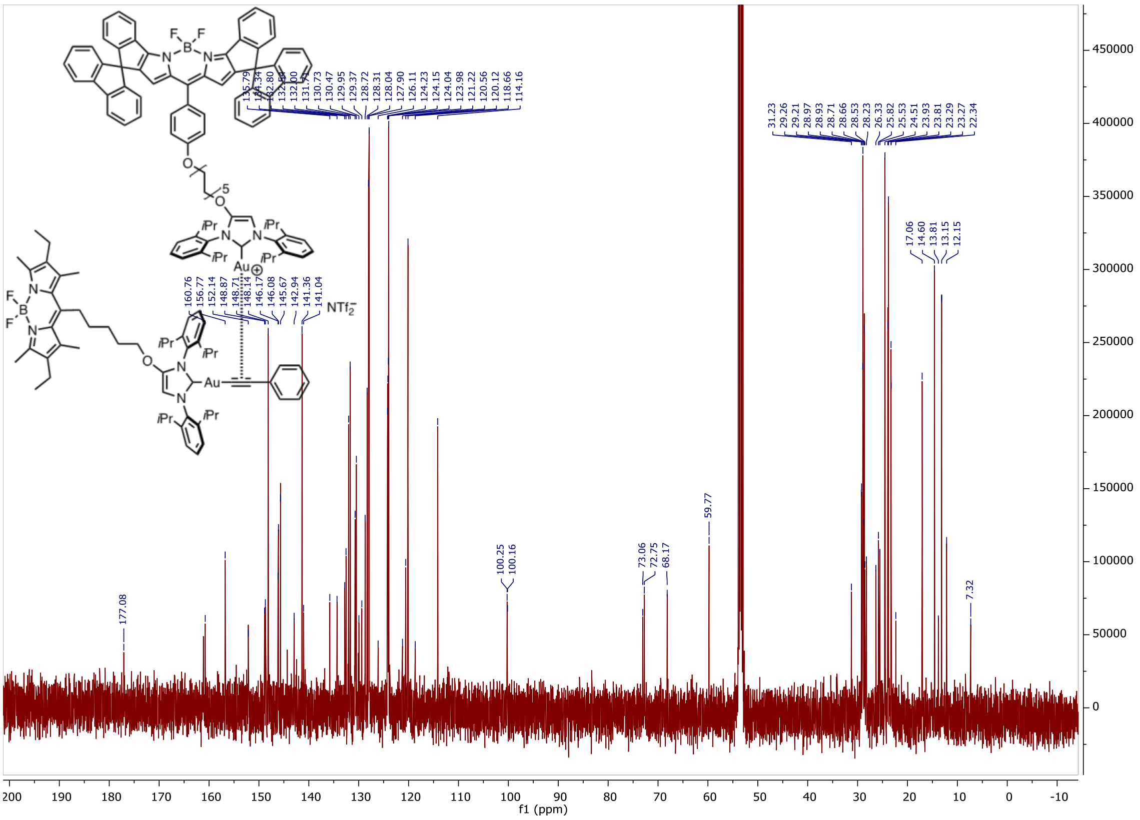


Figure S 83 ^{13}C-NMR spectrum of **16** in CD_2Cl_2.

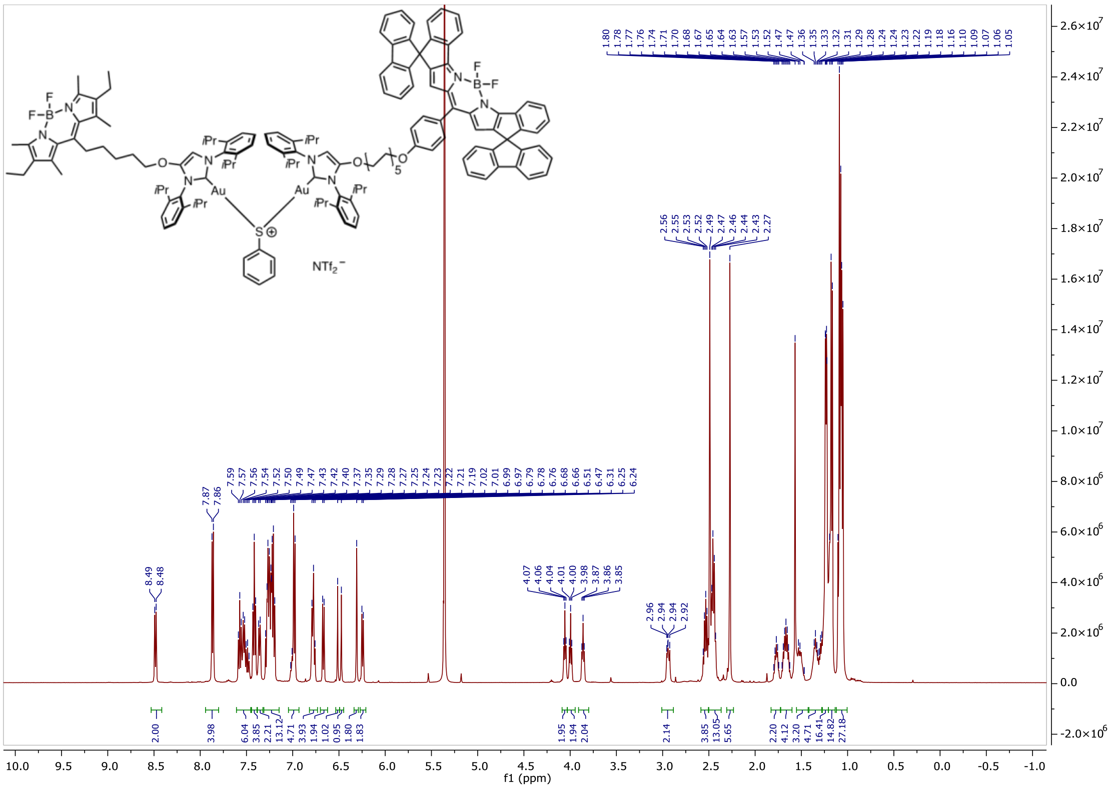


Figure S 84 ^{1}H-NMR spectrum of **17** in CD_2Cl_2.

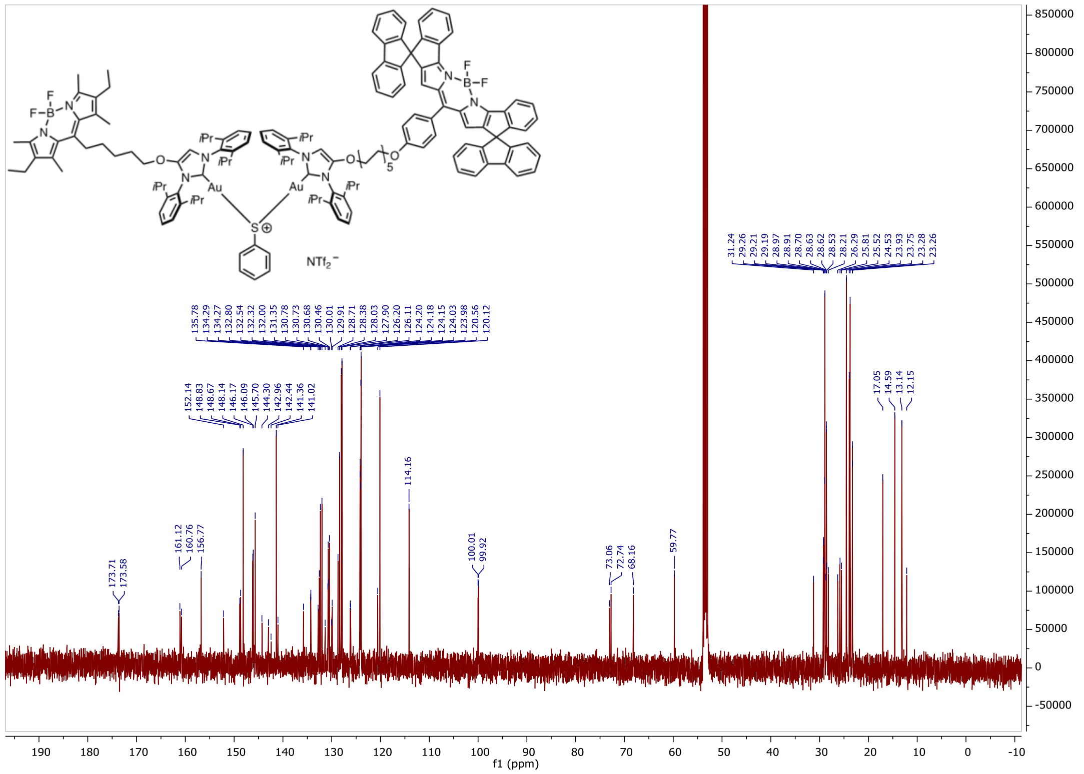


Figure S 85 ^{13}C-NMR spectrum of **17** in CD_2Cl_2.

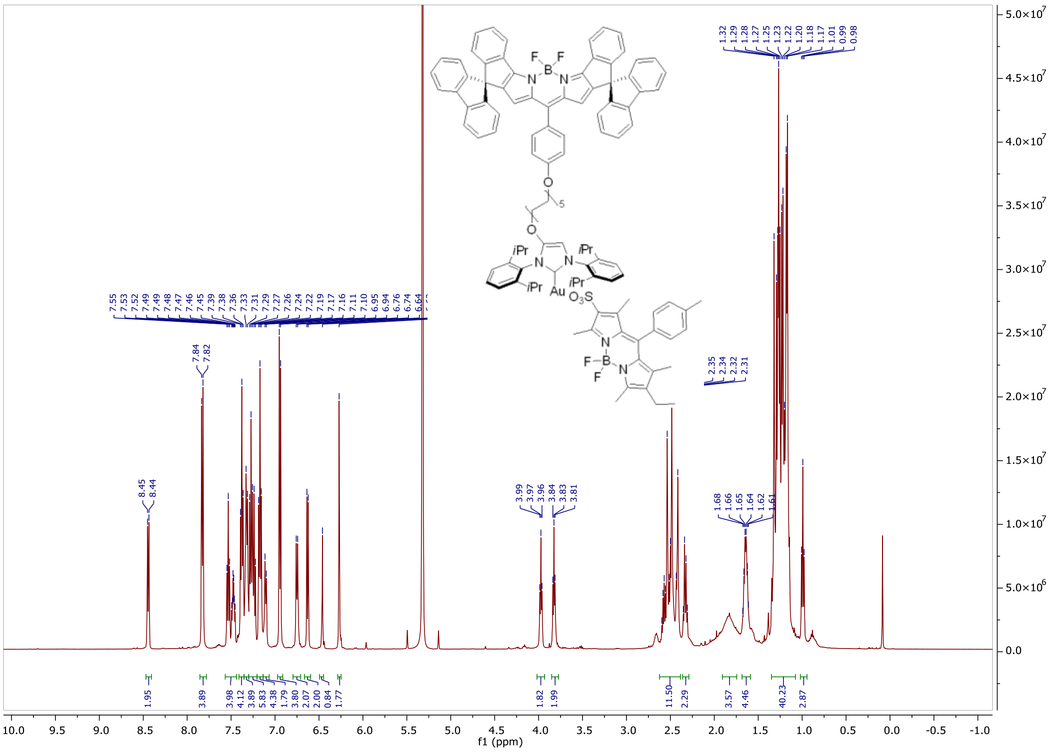


Figure S 86 ^{1}H-NMR spectrum of **18** in CD_2Cl_2.

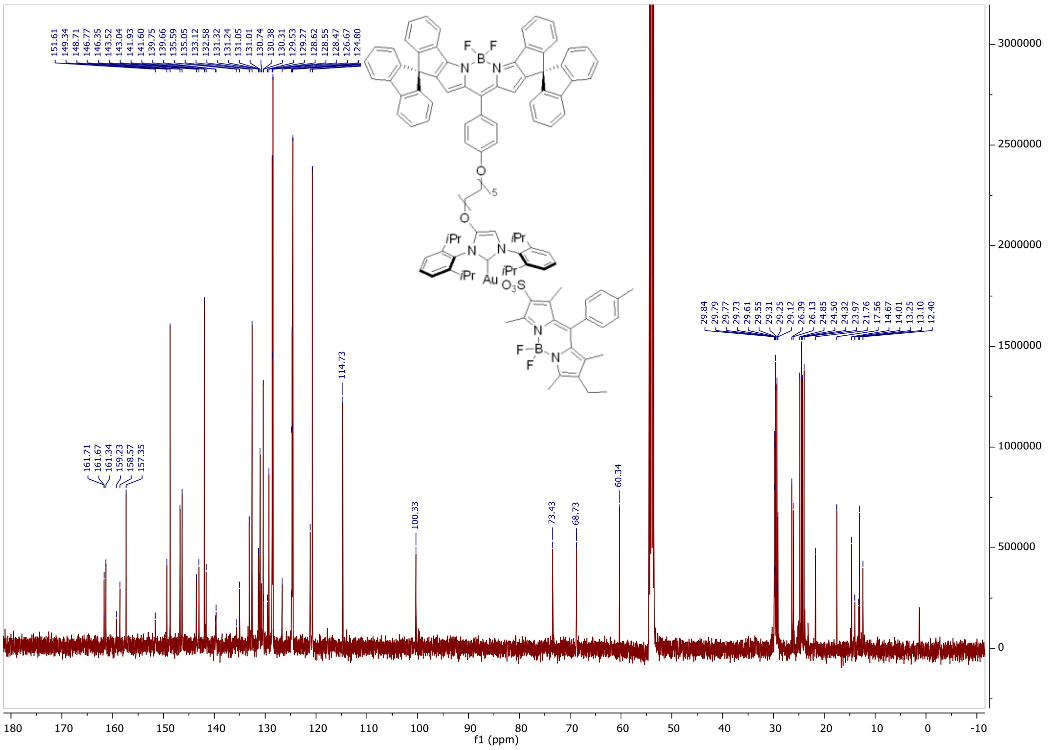


Figure S 87 ^{13}C-NMR spectrum of **18** in CD_2Cl_2.

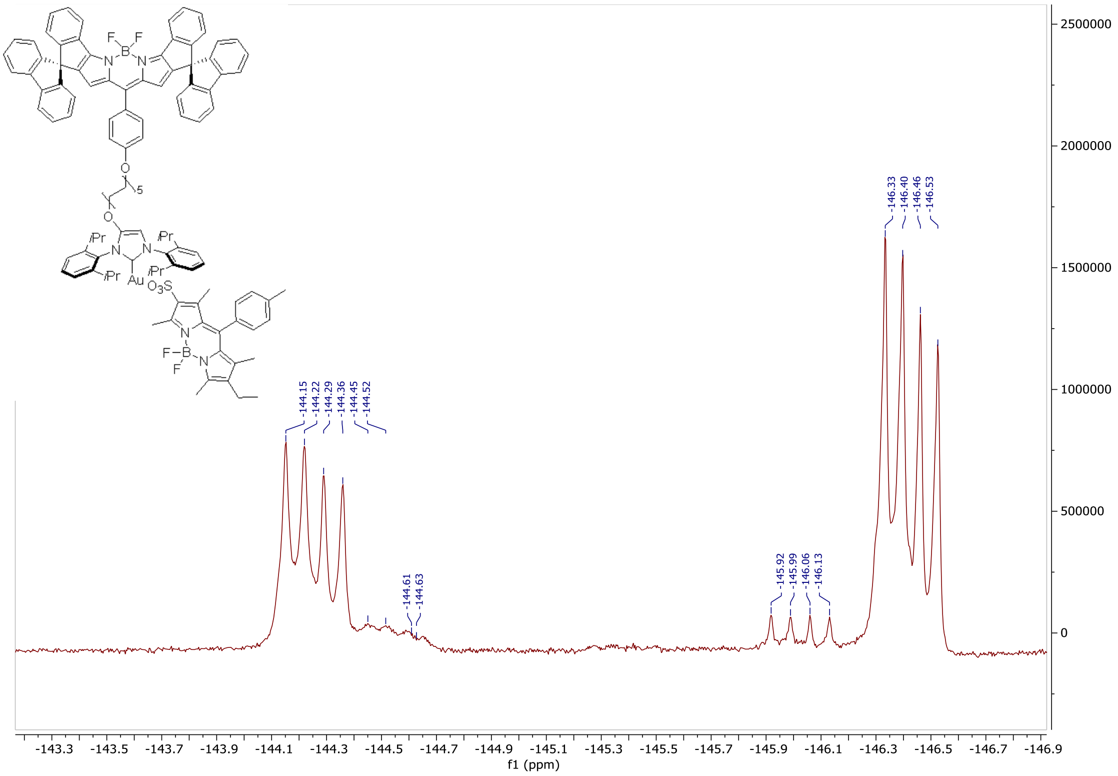


Figure S 88 ^{19}F-NMR spectrum of **18** in CD_2Cl_2.

Blue Bodipy derivatives

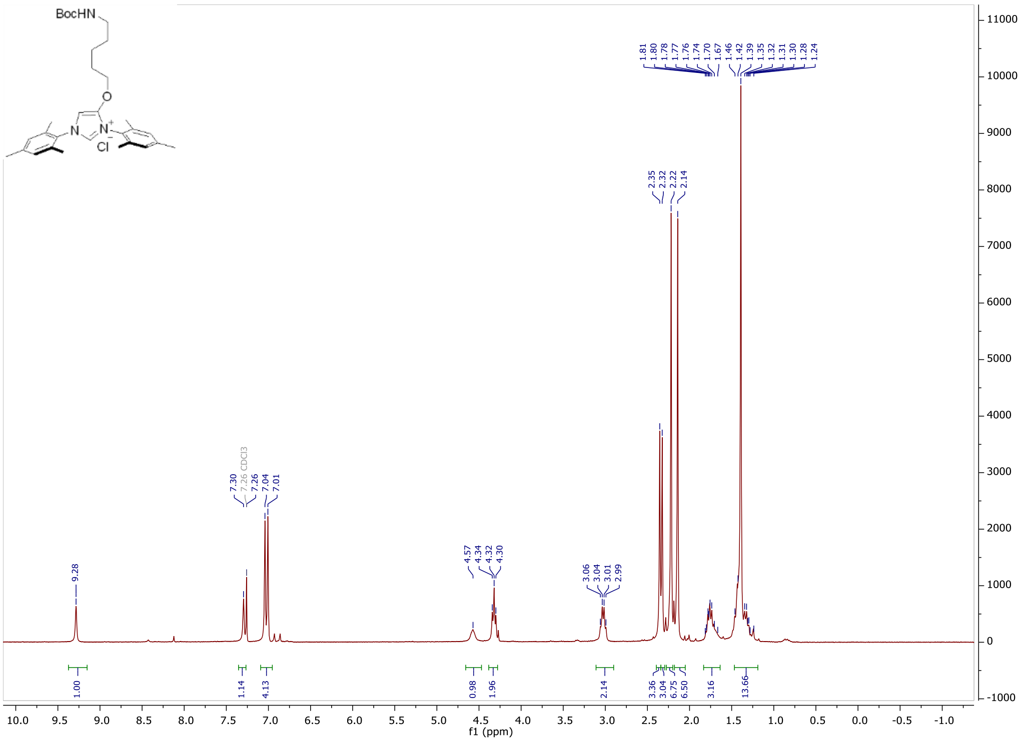


Figure S 89 ^{1}H-NMR spectrum of **IMes·HCl** in $CDCl_3$.

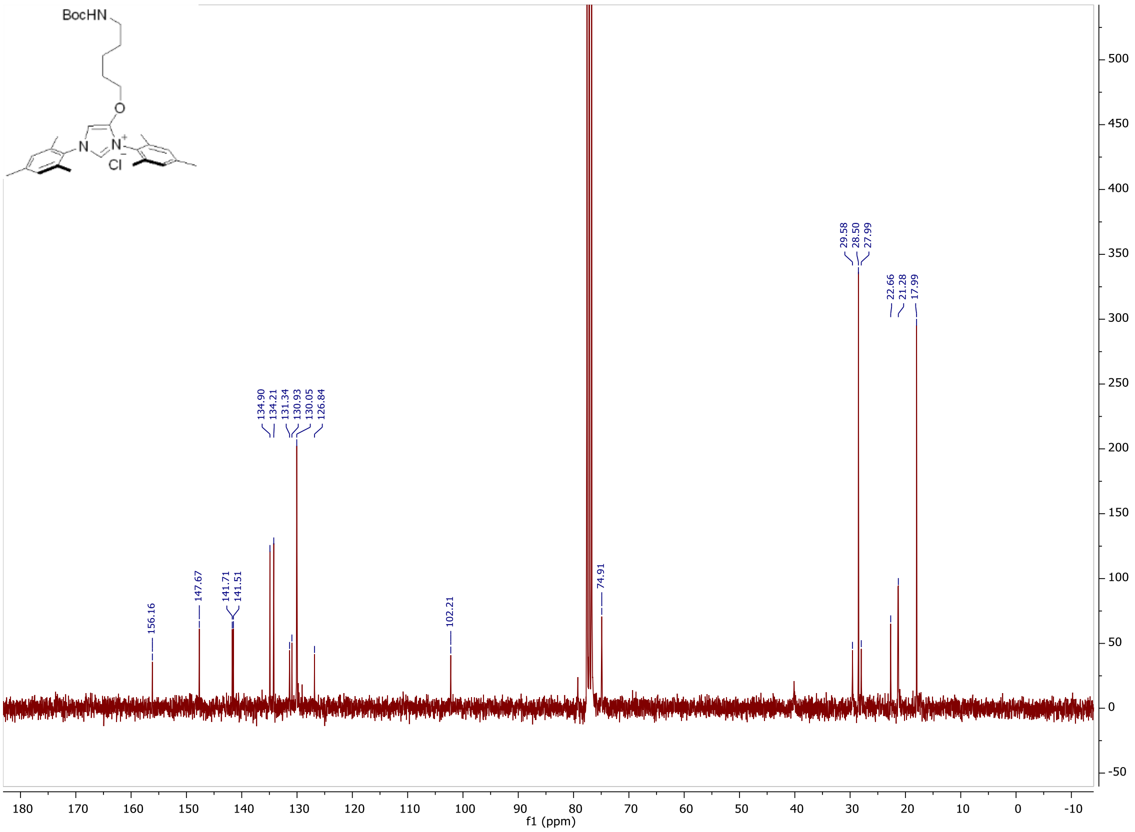


Figure S 90 ^{13}C-NMR spectrum of **IMes·HCl** in CDCl$_3$.

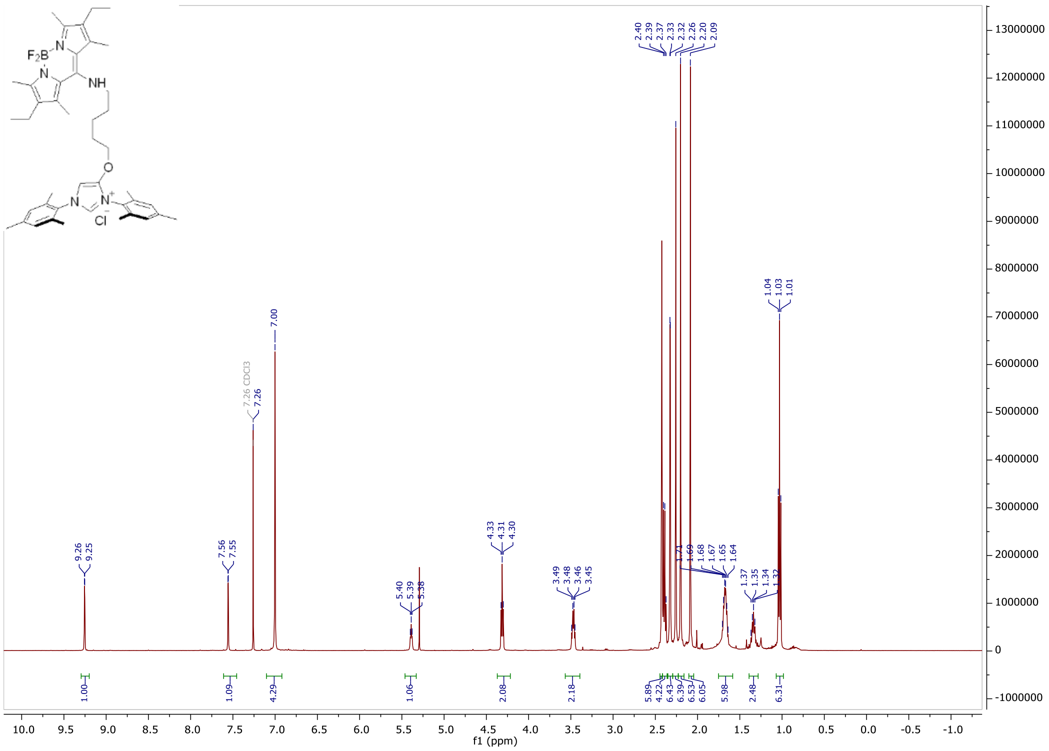


Figure S 91 ^{1}H-NMR spectrum of **19** in CDCl$_3$.

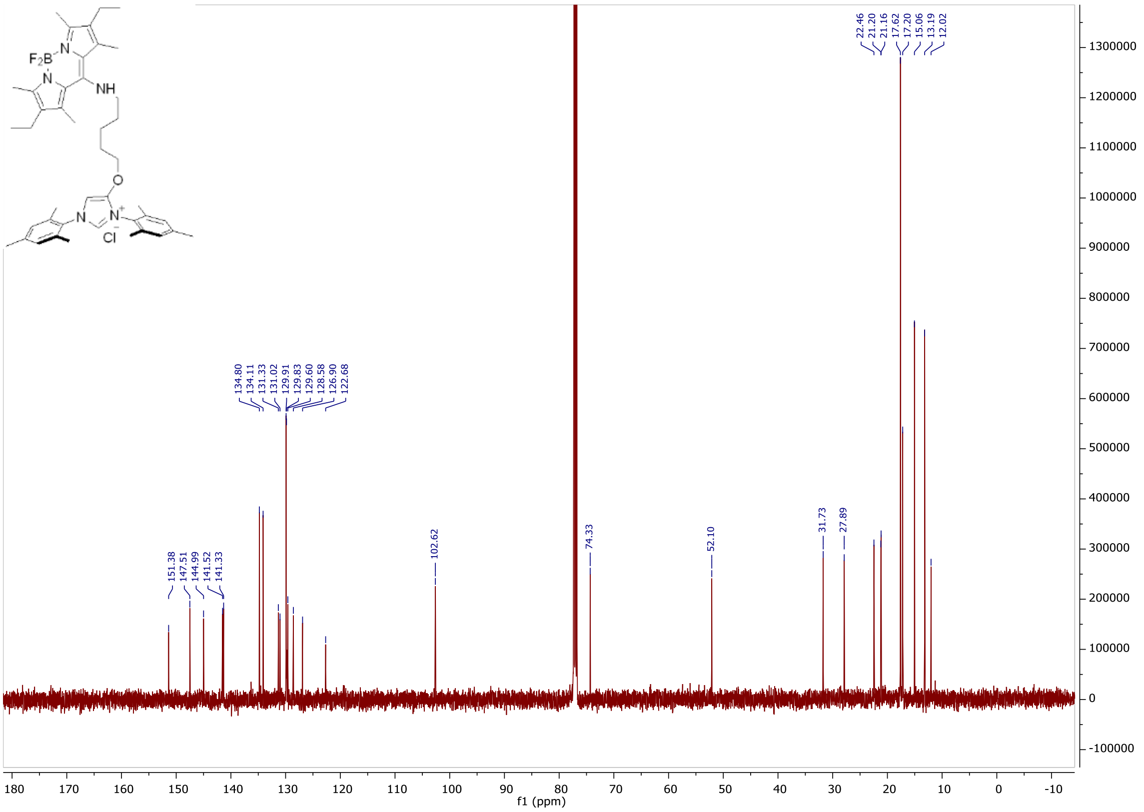


Figure S 92 ^{13}C-NMR spectrum of **19** in $CDCl_3$.

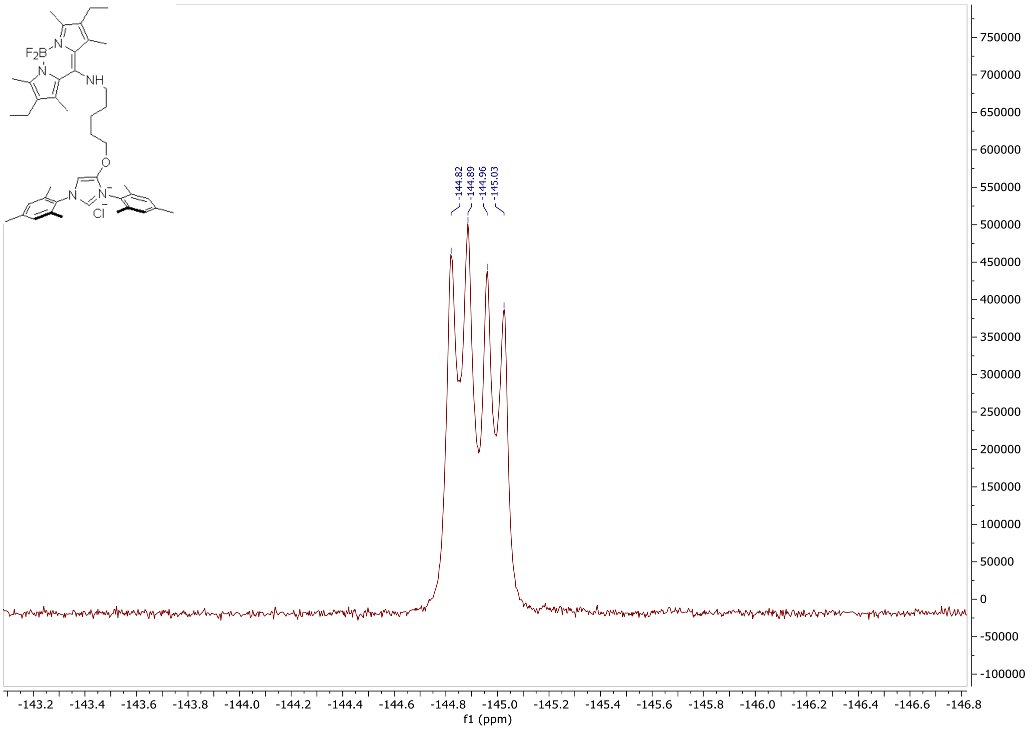


Figure S 93 ^{19}F-NMR spectrum of **19** in $CDCl_3$.

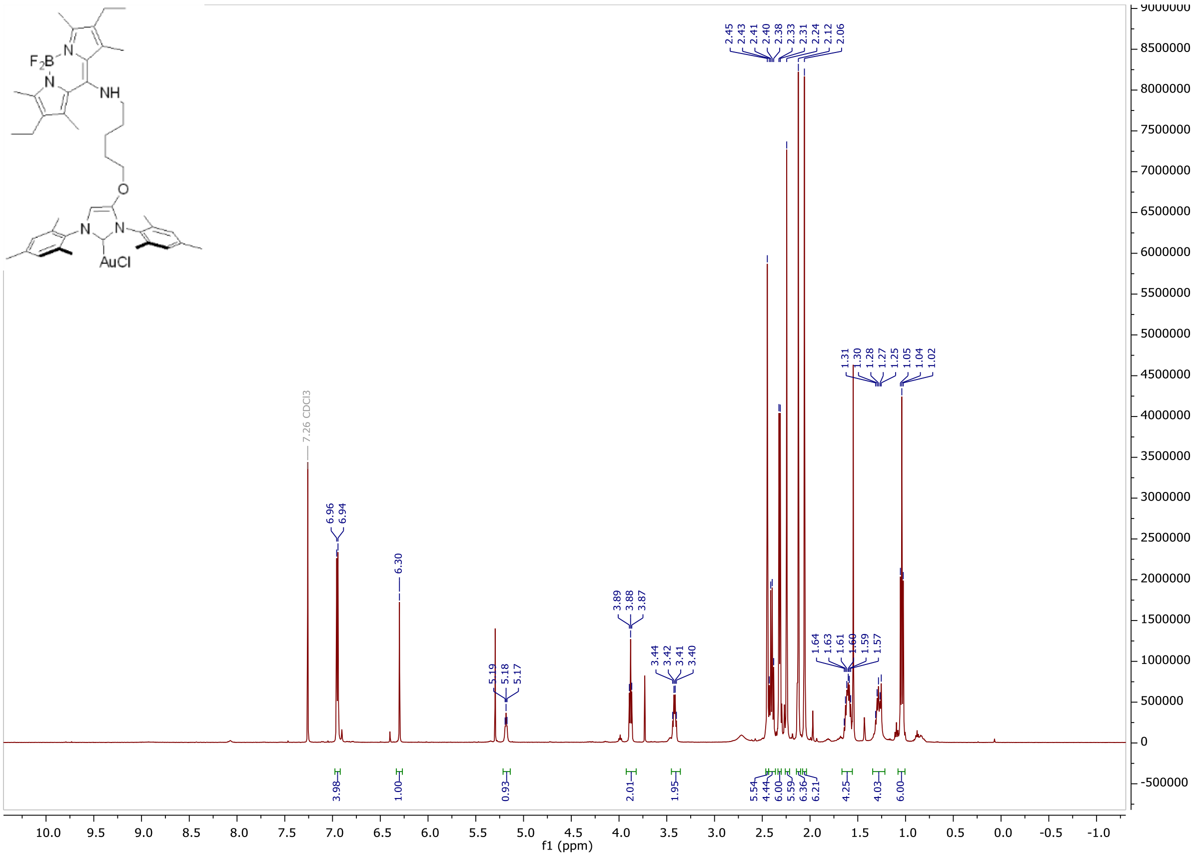


Figure S 94 ^{1}H-NMR spectrum of **20** in CDCl$_3$.

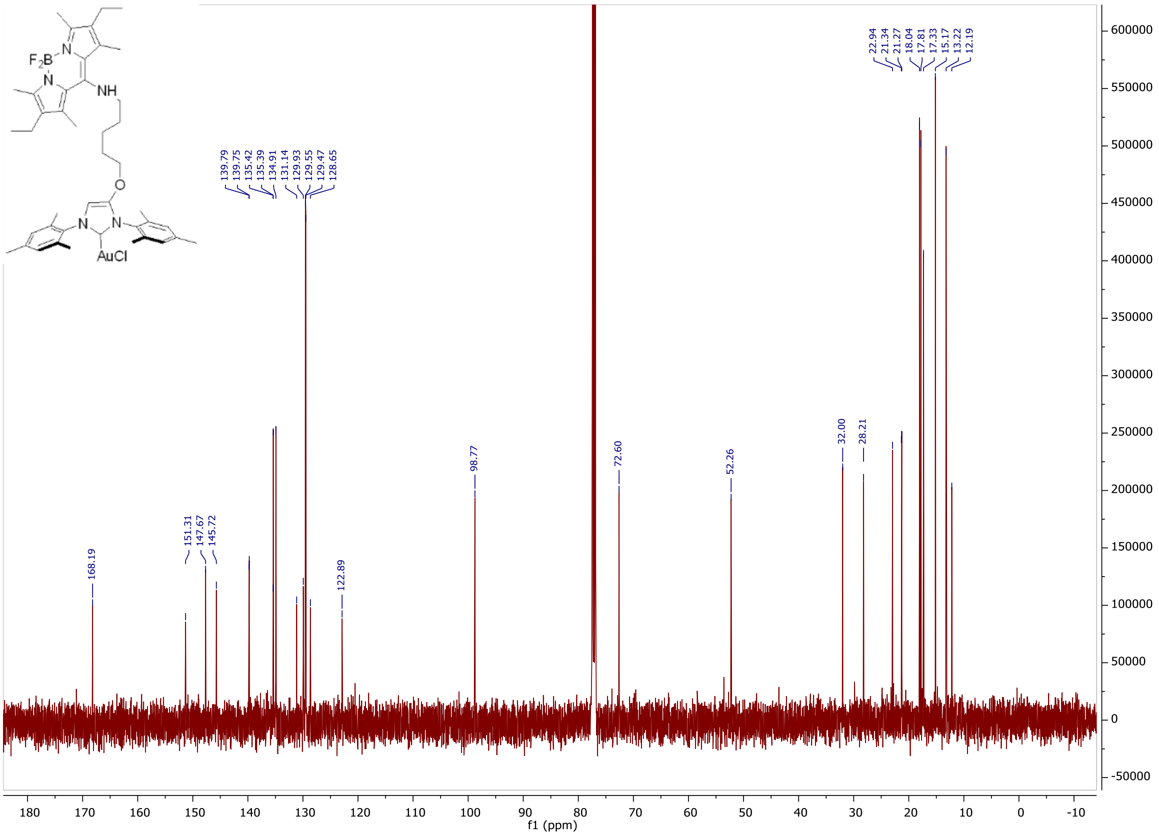


Figure S 95 ^{13}C-NMR spectrum of **20** in CDCl$_3$.

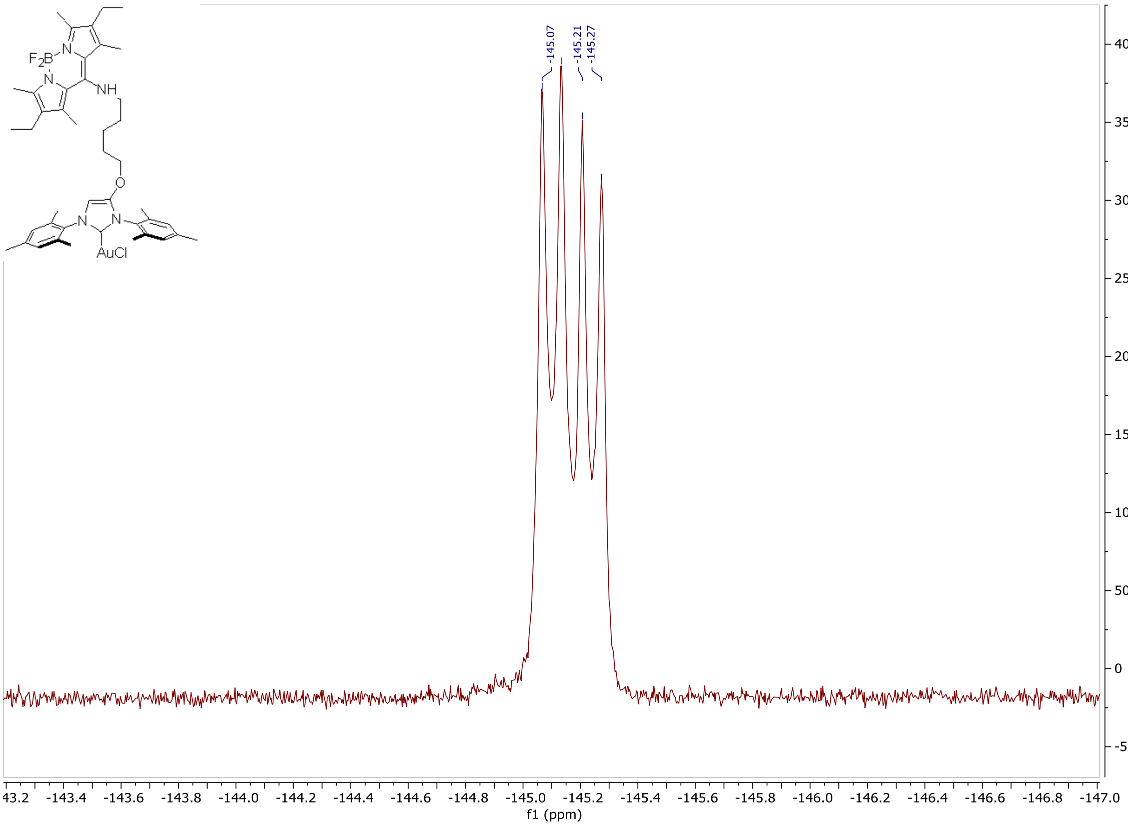


Figure S 96 ^{19}F-NMR spectrum of **20** in CDCl$_3$.

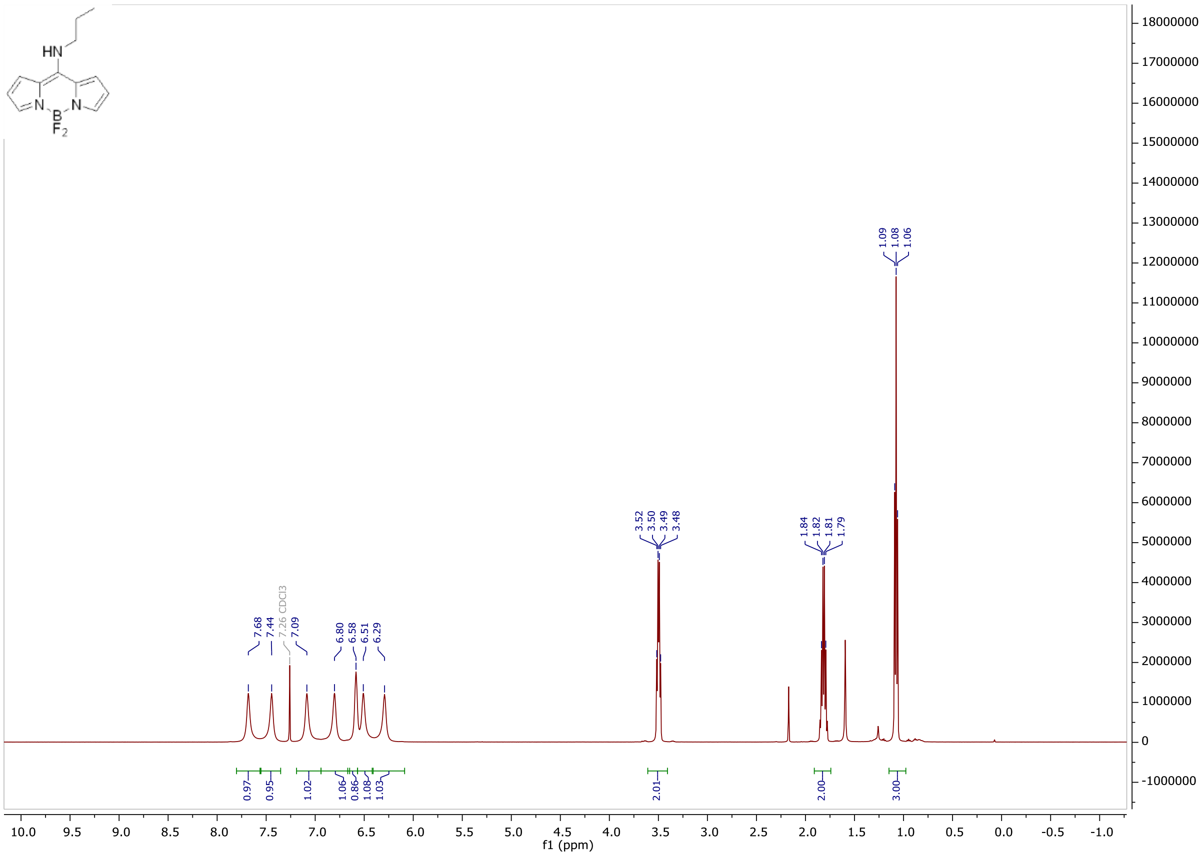


Figure S 97 ^{1}H-NMR spectrum of **B1** in CDCl$_3$.

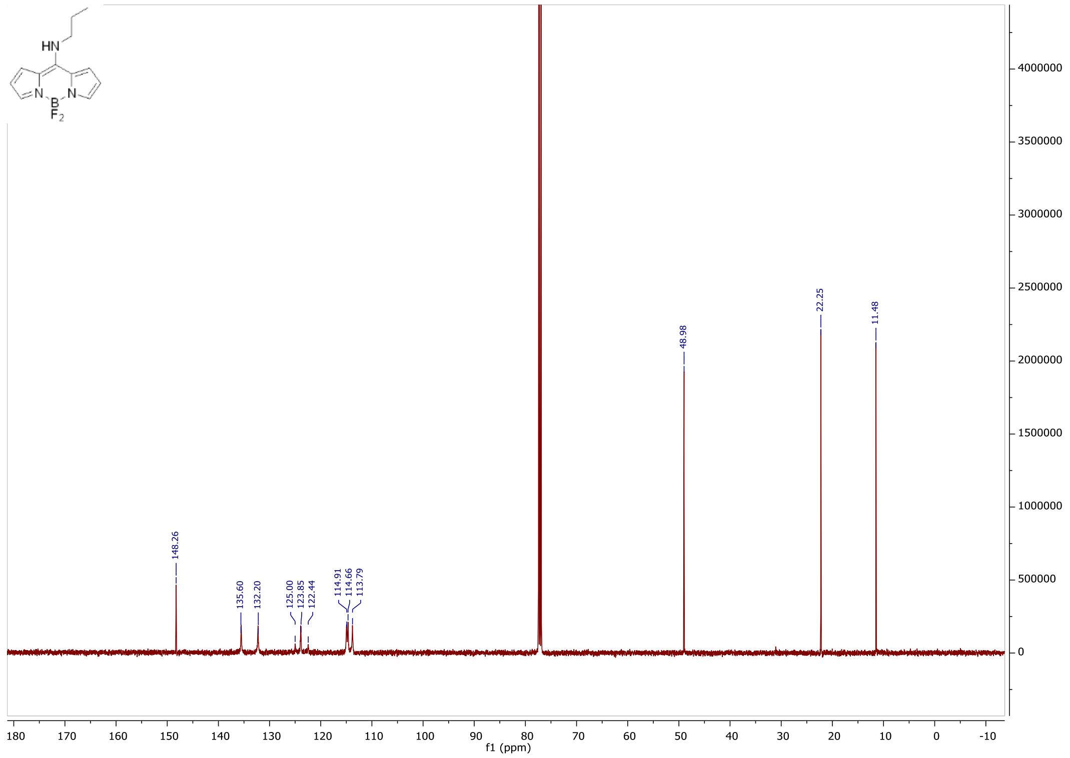


Figure S 98 ^{13}C-NMR spectrum of **B1** in $CDCl_3$.

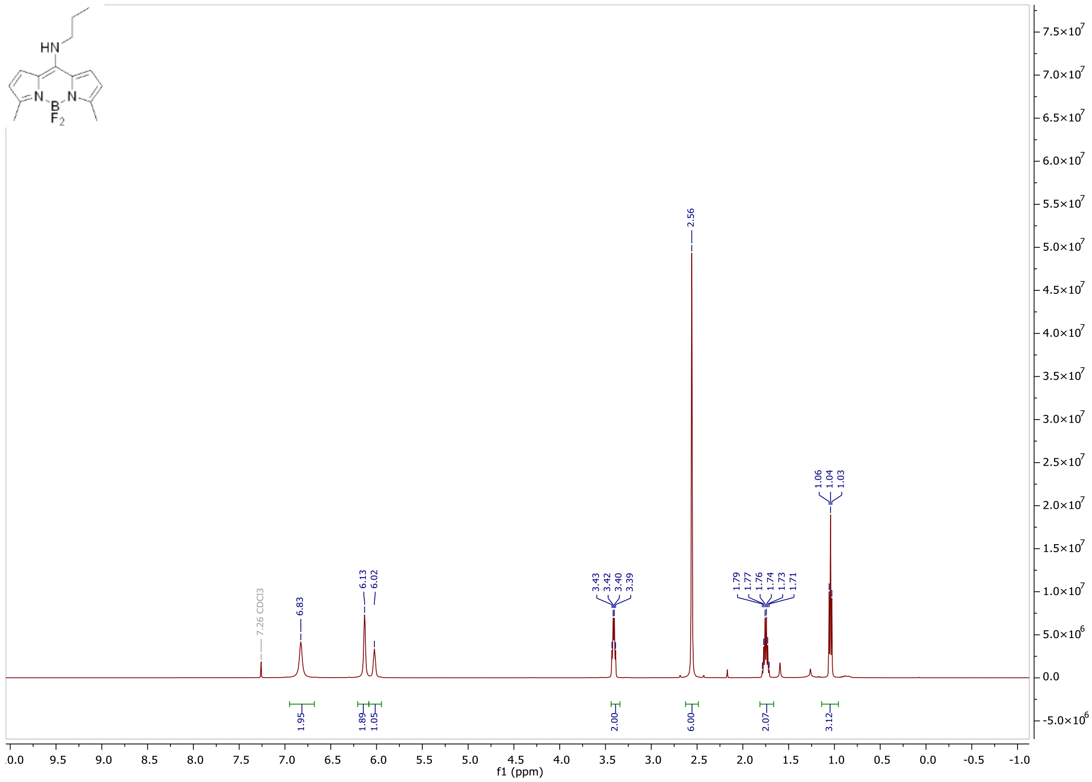


Figure S 99 ^{1}H-NMR spectrum of **B2** in $CDCl_3$.

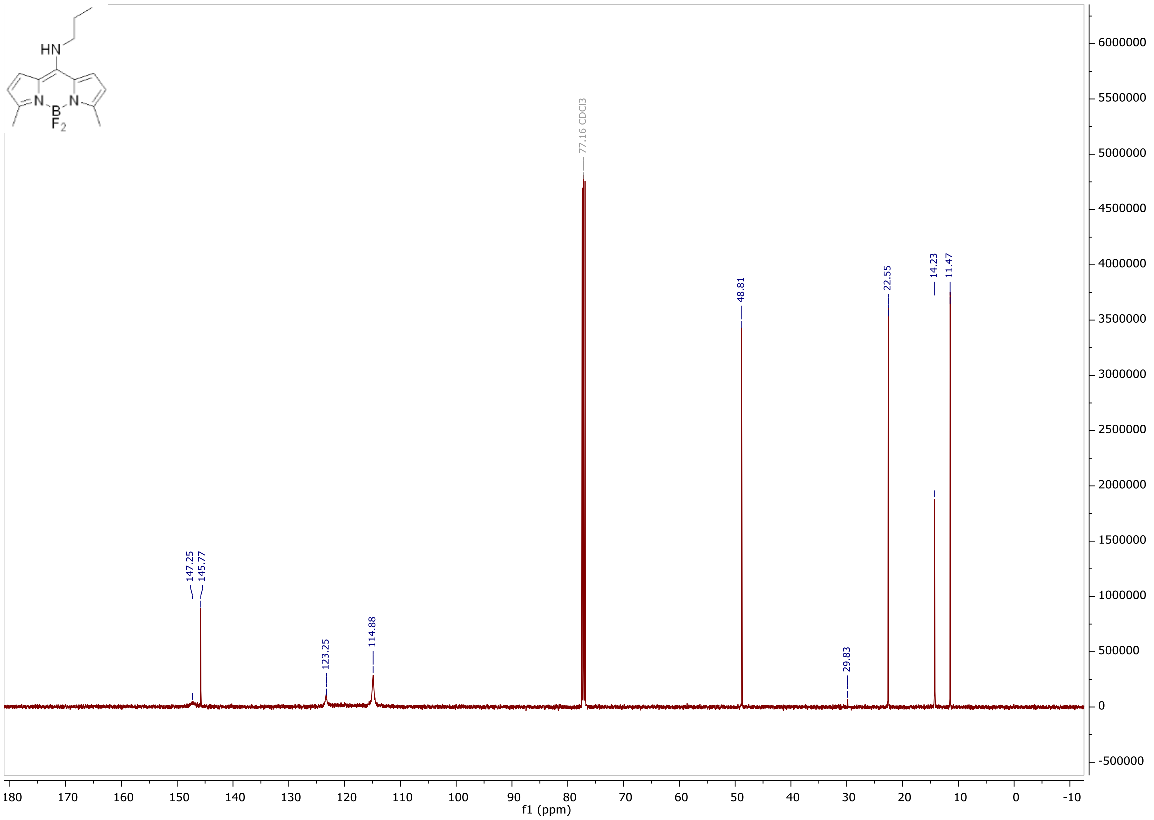


Figure S 100 ^{13}C-NMR spectrum of **B2** in CDCl$_3$.

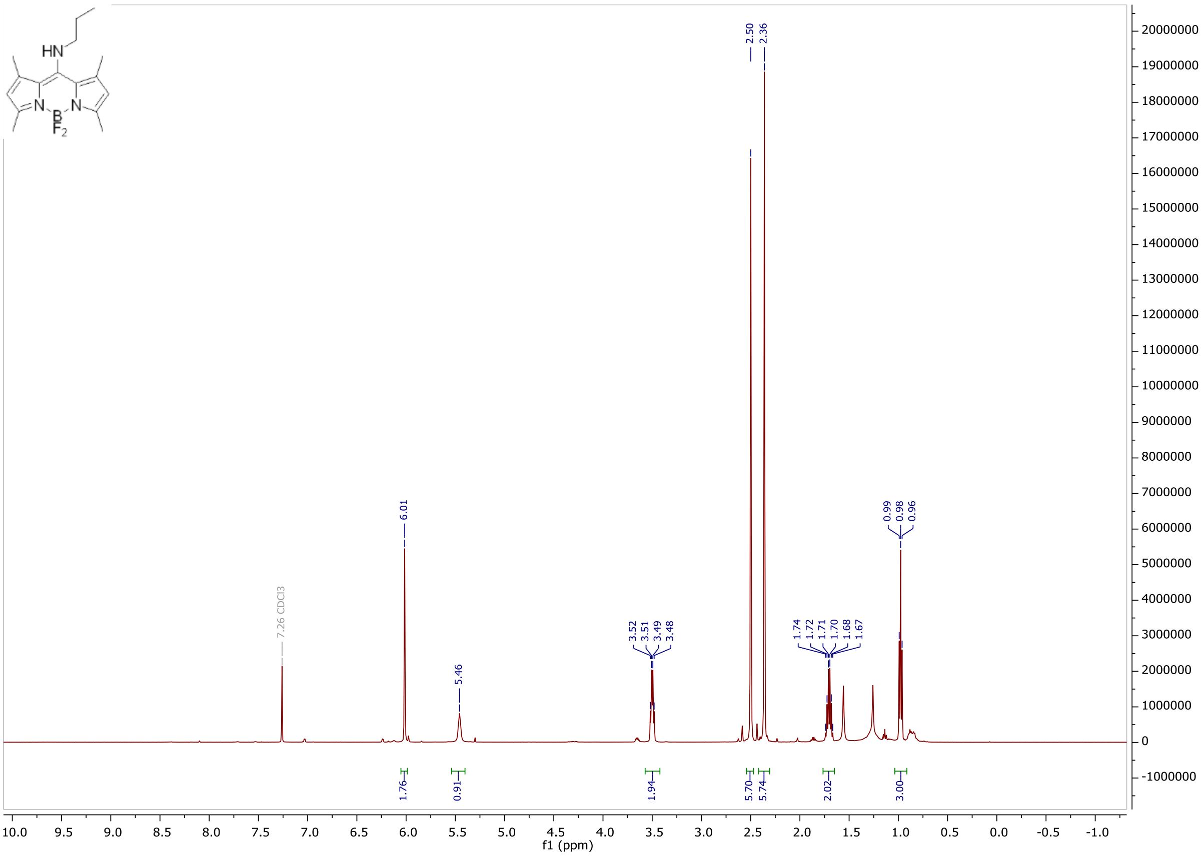


Figure S 101 ^{1}H-NMR spectrum of **B3** in CDCl$_3$.

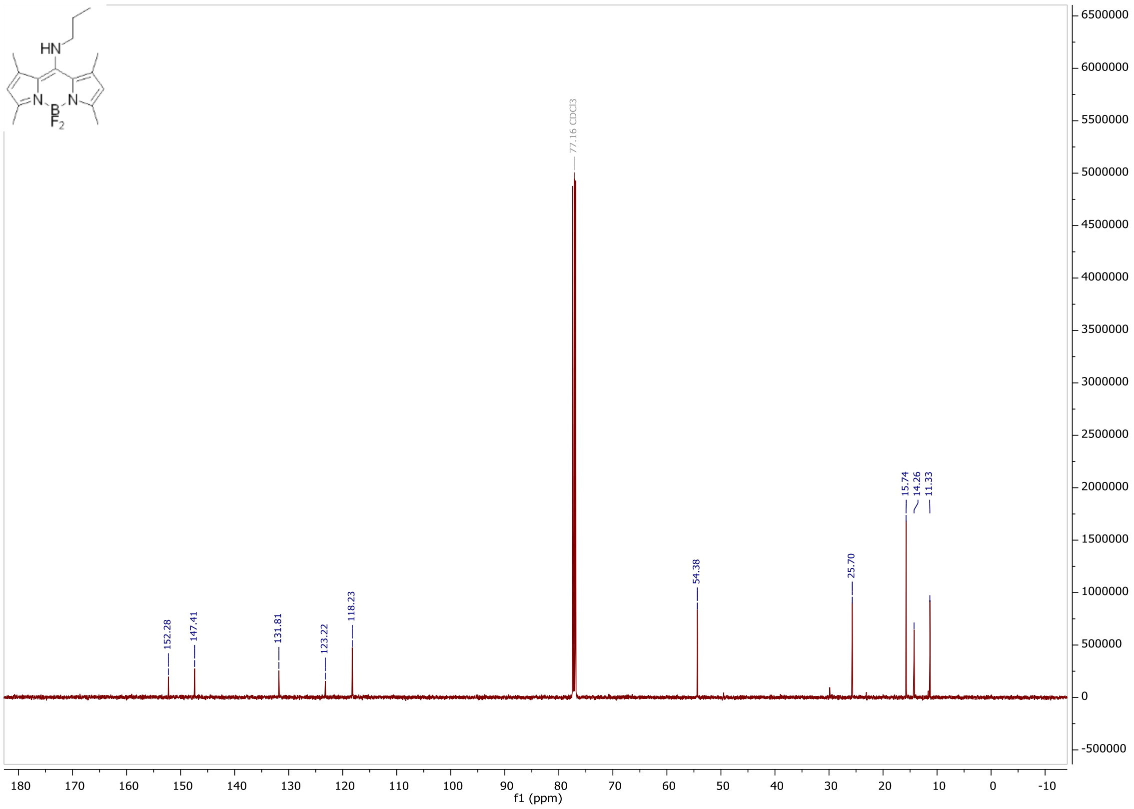


Figure S 102 ^{13}C-NMR spectrum of **B3** in CDCl3.

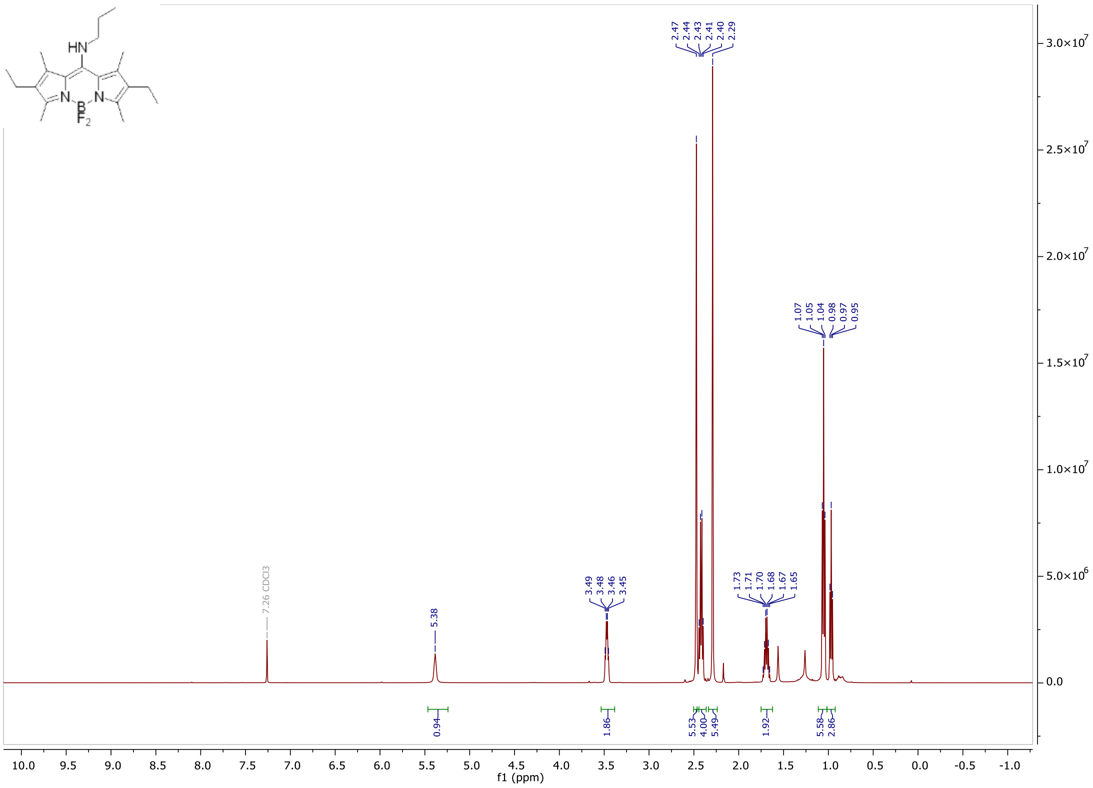


Figure S 103 ^{13}H-NMR spectrum of **B4** in CDCl3.

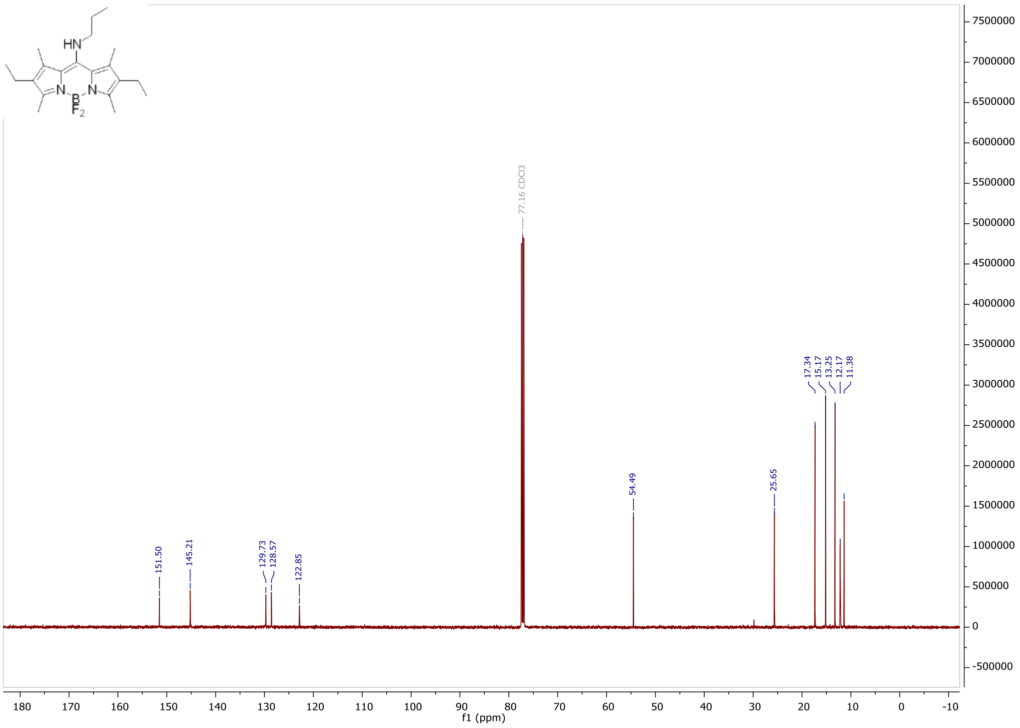


Figure S 104 ^{13}C-NMR spectrum of **B4** in CDCl$_3$.

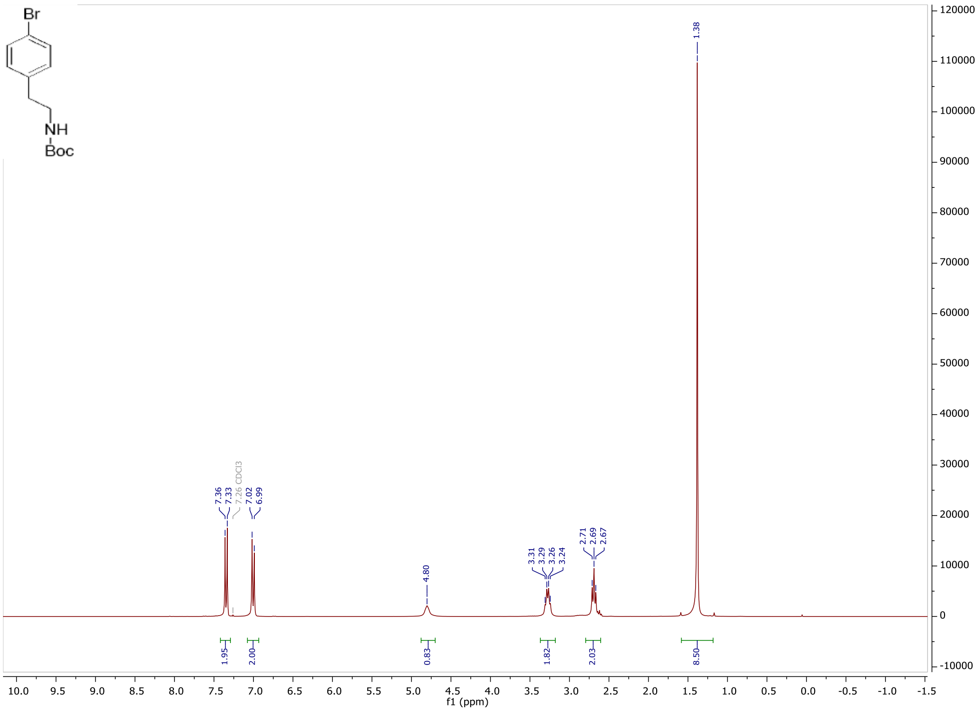


Figure S 105 ^{1}H-NMR spectrum of *tert*-butyl (4-bromophenethyl)carbamate in CDCl$_3$.

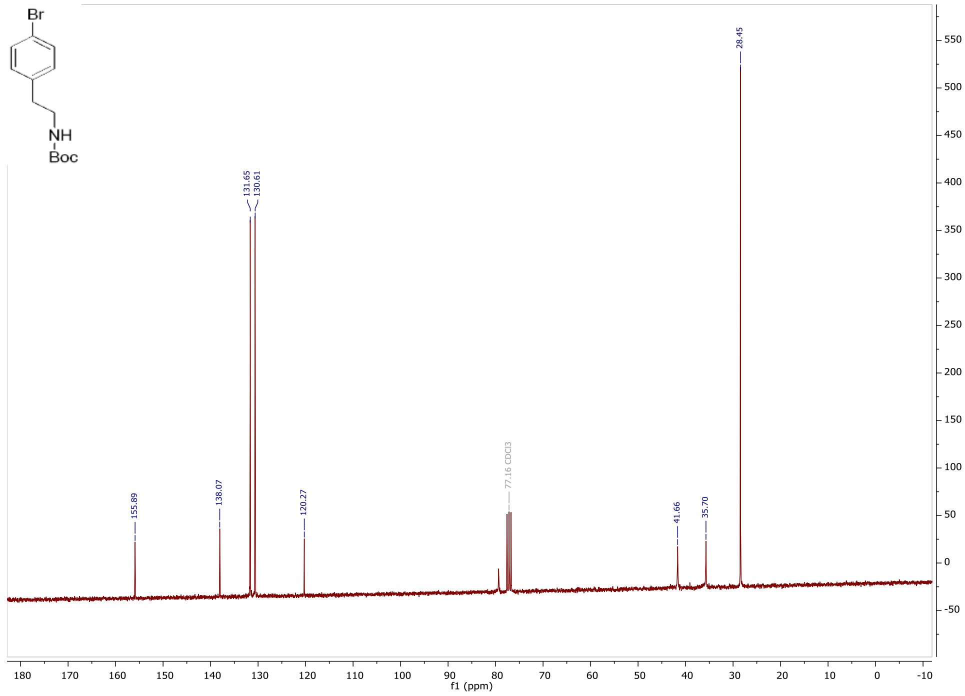


Figure S 106 ^{13}C-NMR spectrum of *tert*-butyl (4-bromophenethyl)carbamate in $CDCl_3$.

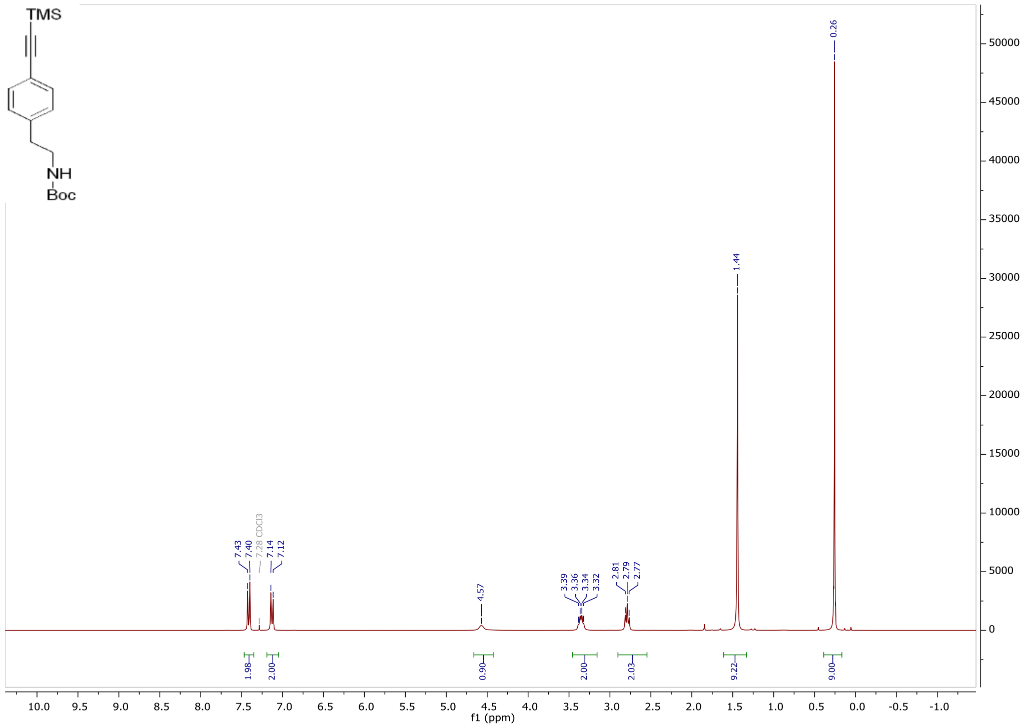


Figure S 107 ^{1}H-NMR spectrum of *tert*-butyl (4-((trimethylsilyl)ethynyl)phenethyl) carbamate in $CDCl_3$.

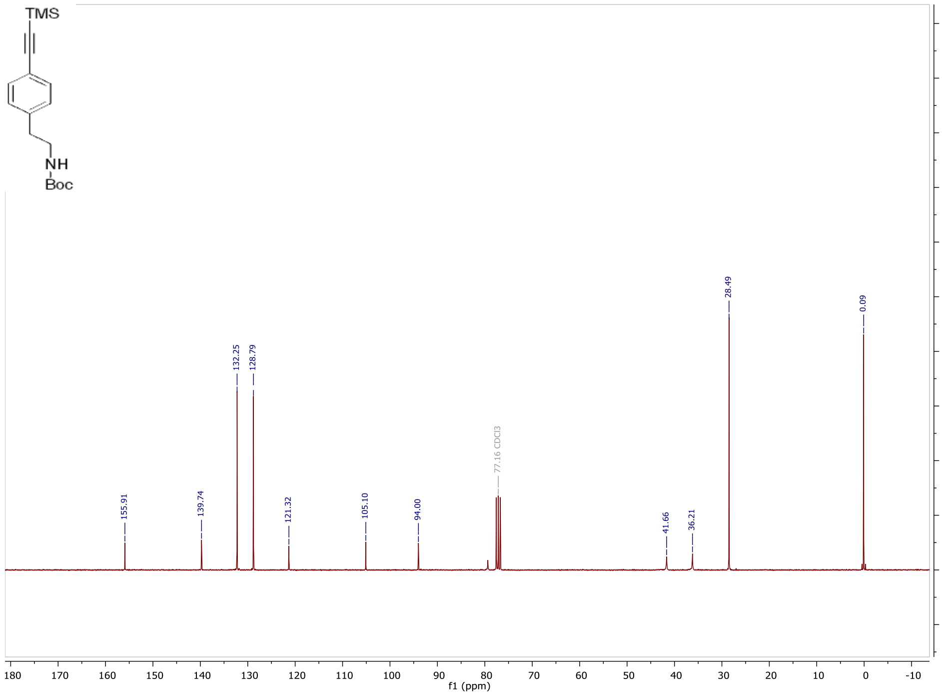


Figure S 108 ^{13}C-NMR spectrum of *tert*-butyl (4-((trimethylsilyl)ethynyl)phenethyl) carbamate in $CDCl_3$.

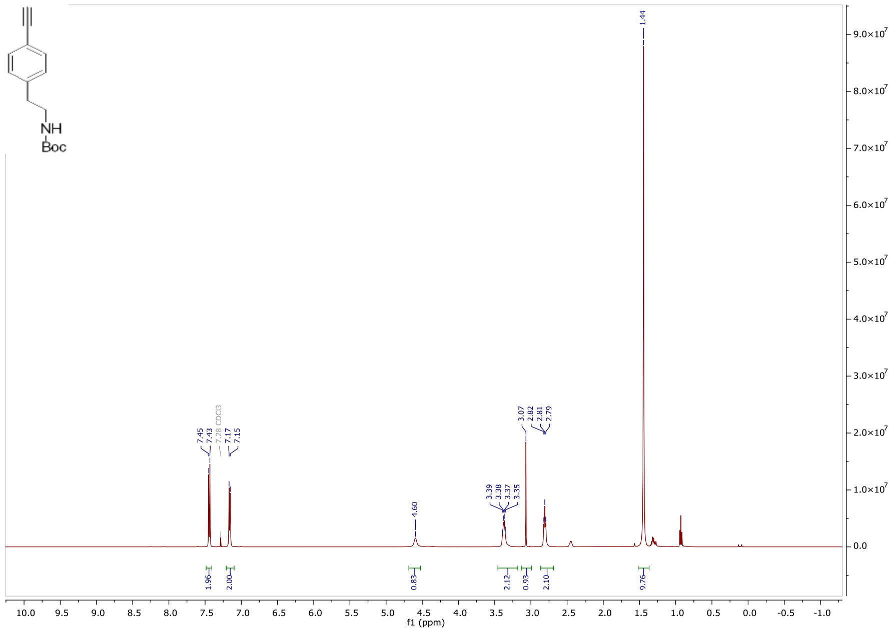


Figure S 109 ^{1}H-NMR spectrum of *tert*-butyl (4-ethynylphenethyl)carbamate in $CDCl_3$.

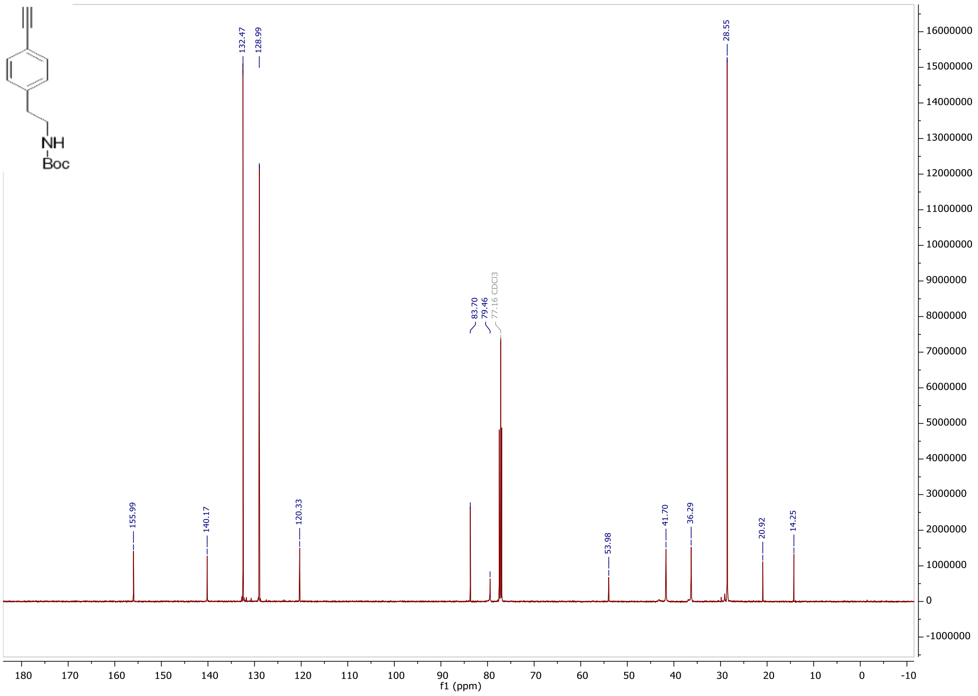


Figure S 110 ^{13}C-NMR spectrum of *tert*-butyl (4-ethynylphenethyl)carbamate in $CDCl_3$.

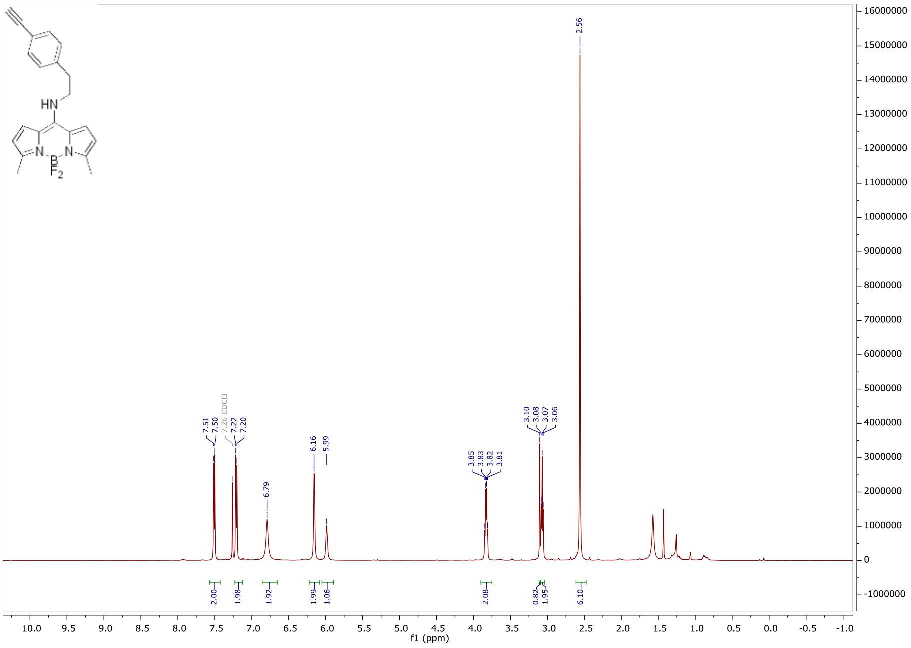


Figure S 111 ^{1}H-NMR spectrum of **21** in $CDCl_3$.

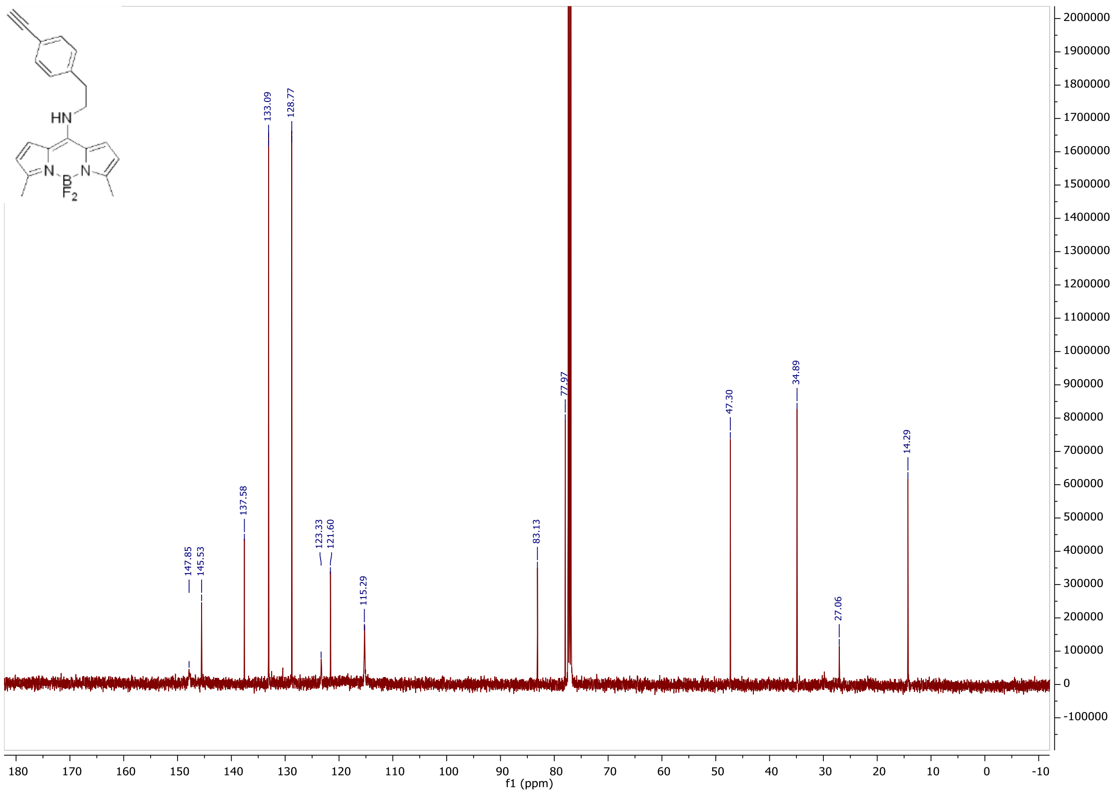


Figure S 112 ^{13}C-NMR spectrum of **21** in $CDCl_3$.

Blue-green-red triad

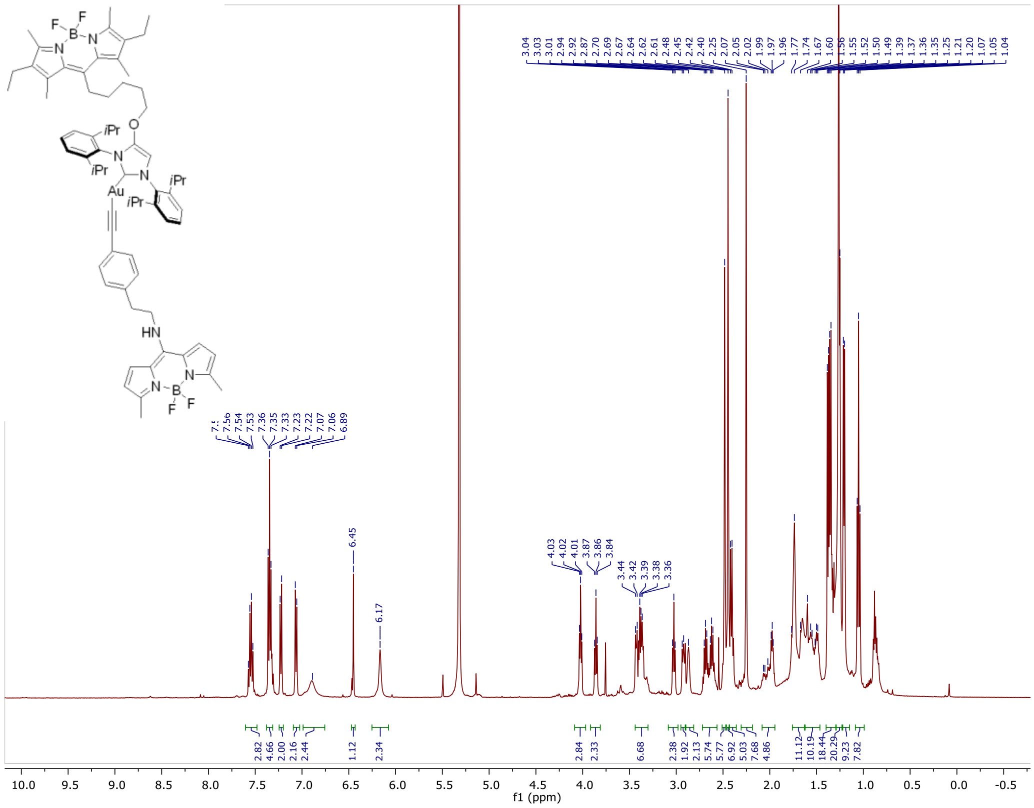


Figure S 113 ^{1}H-NMR spectrum of **22·dbu** in CD_2Cl_2.

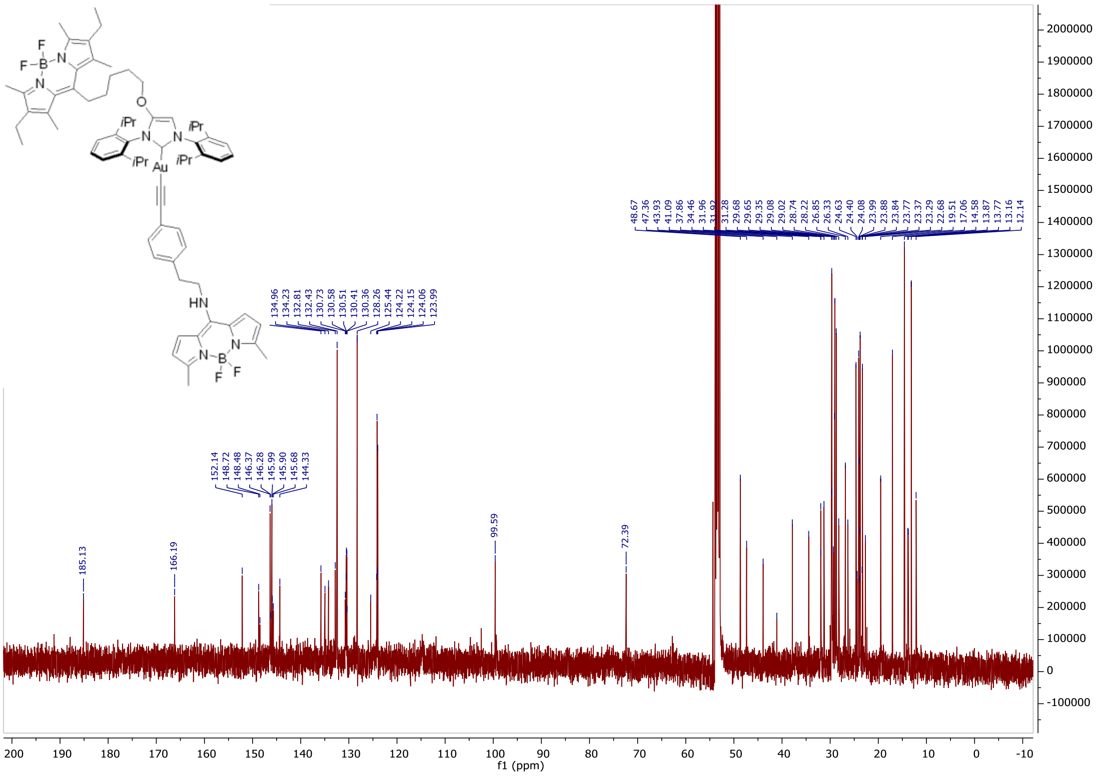


Figure S 114 ^{13}C-NMR spectrum of **22·dbu** in CD_2Cl_2.

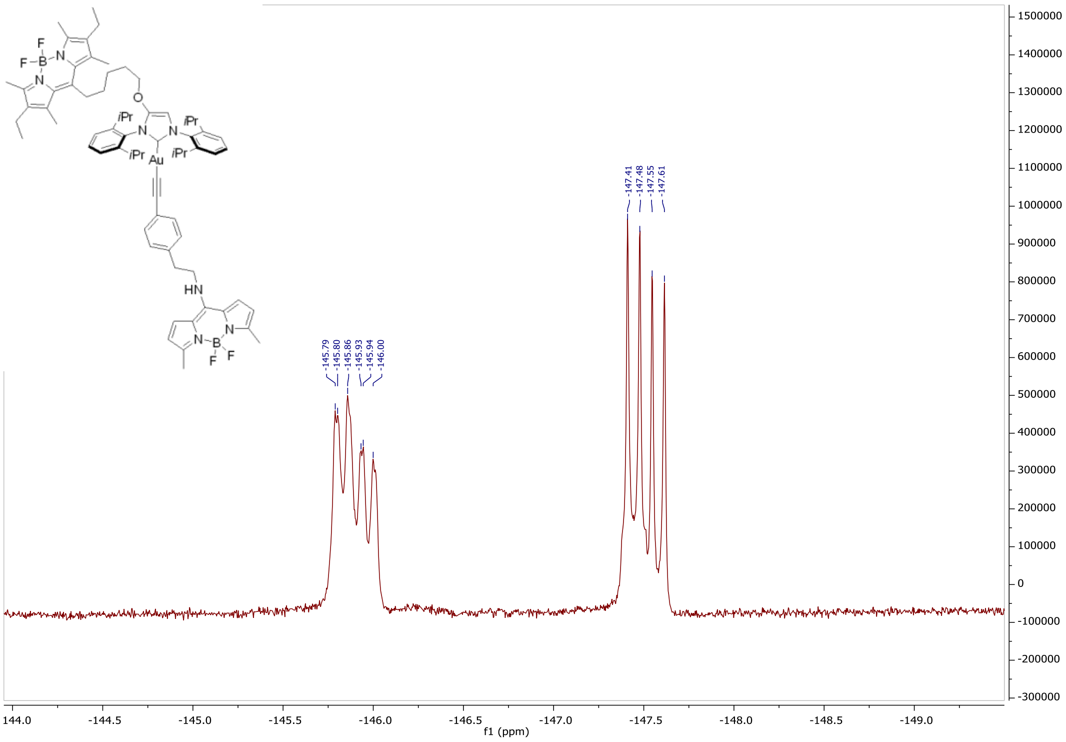


Figure S 115 ^{19}F-NMR spectrum of **22·dbu** in CD_2Cl_2.

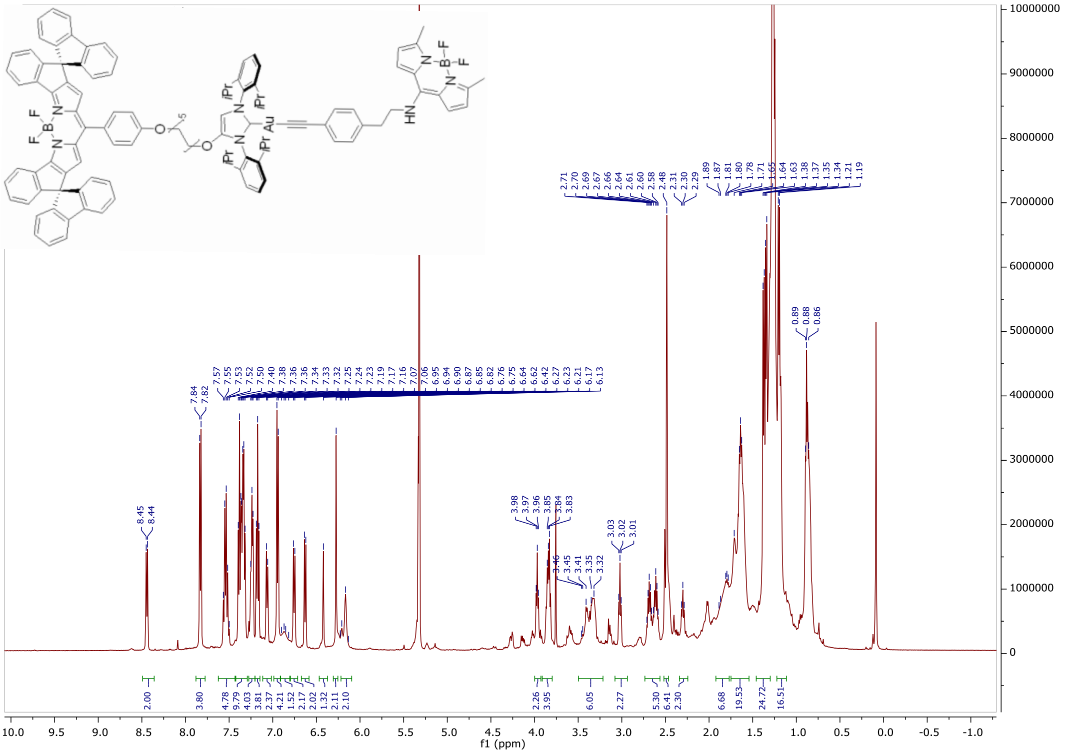


Figure S 116 ^{1}H-NMR spectrum of **24·dbu** in CD_2Cl_2.

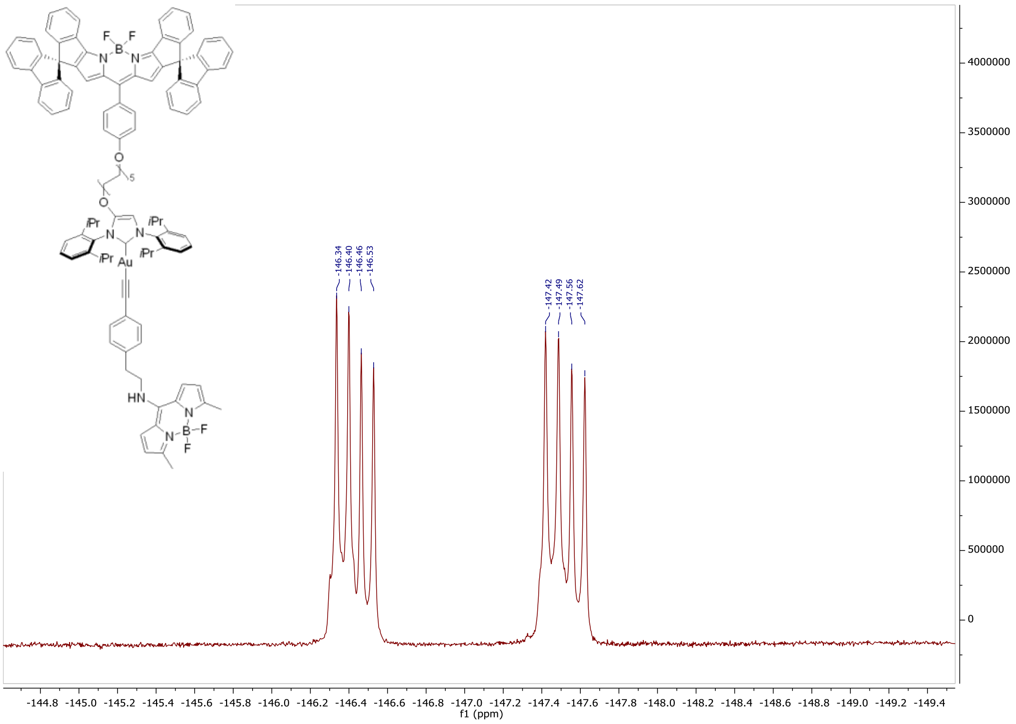


Figure S 117 ^{19}F-NMR spectrum of **24·dbu** in CD_2Cl_2.

IPrAuNTf2 + DBU interaction

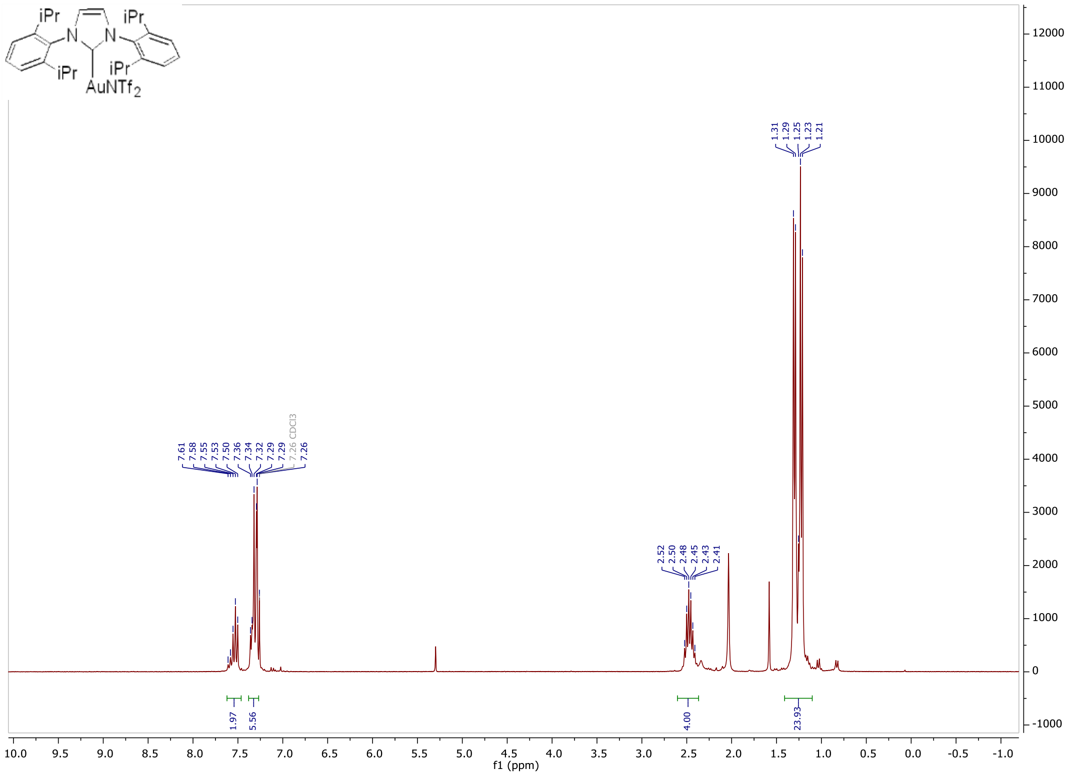


Figure S 118 ^{1}H-NMR spectrum of IPrAuNTf$_2$ in CDCl$_3$.

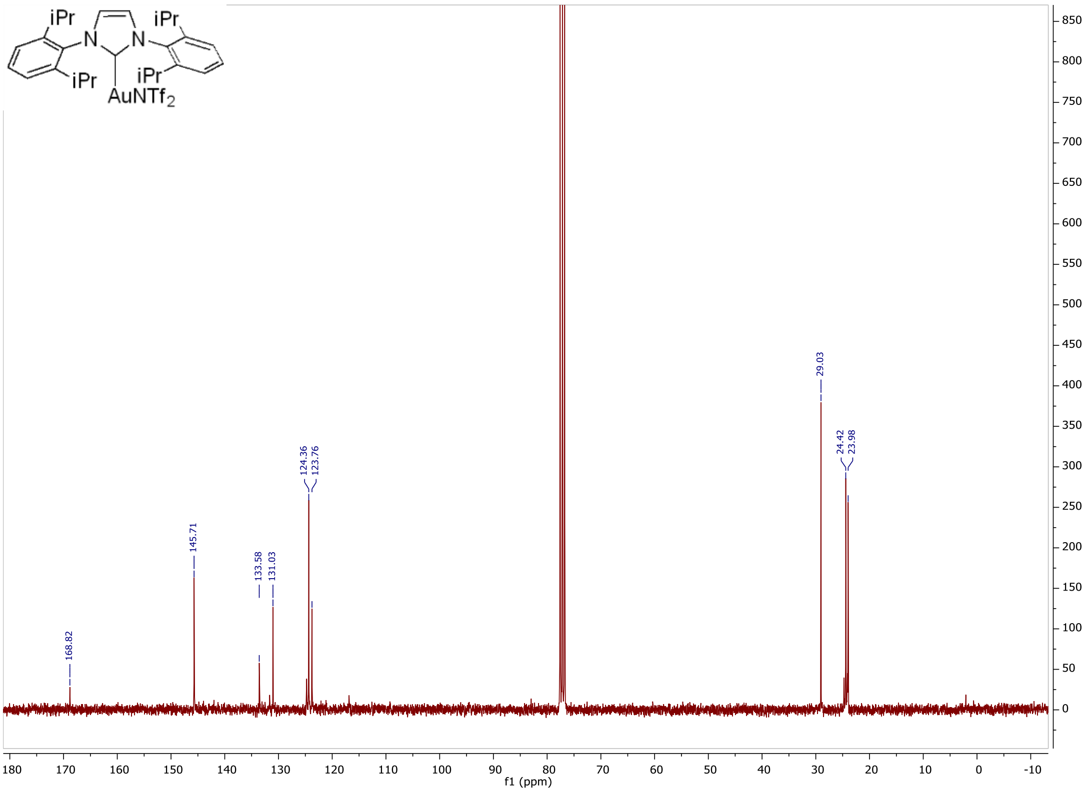


Figure S 119 ^{13}C-NMR spectrum of IPrAuNTf$_2$ in CDCl$_3$.

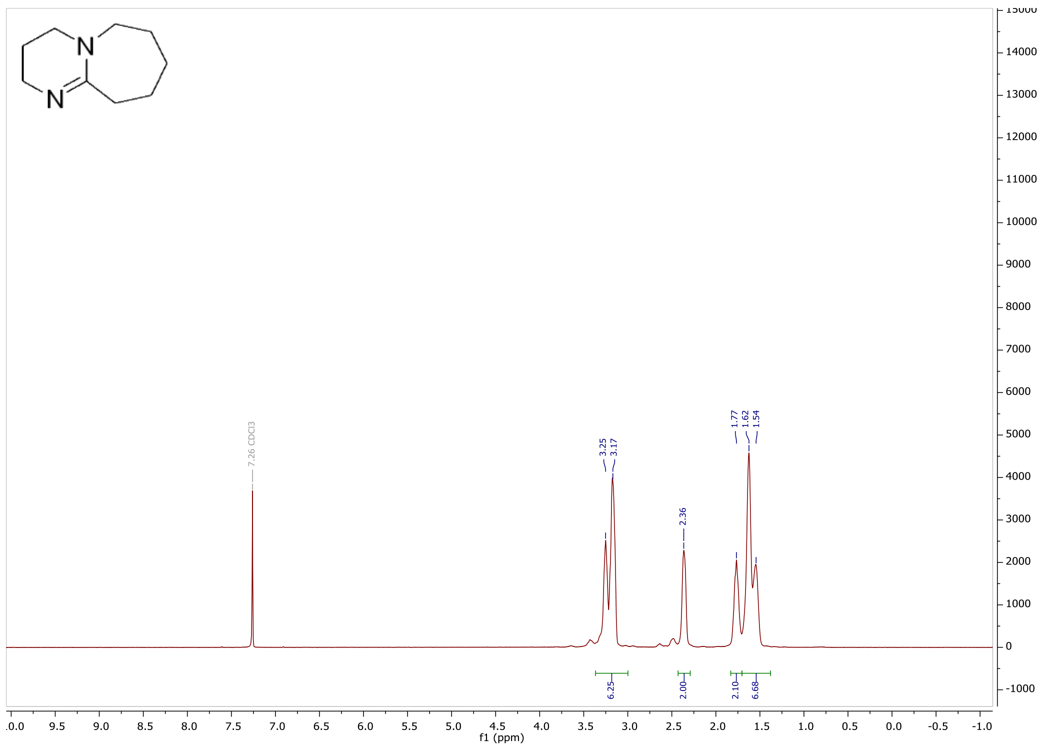


Figure S 120 ^{1}H-NMR spectrum of DBU in CDCl$_3$.

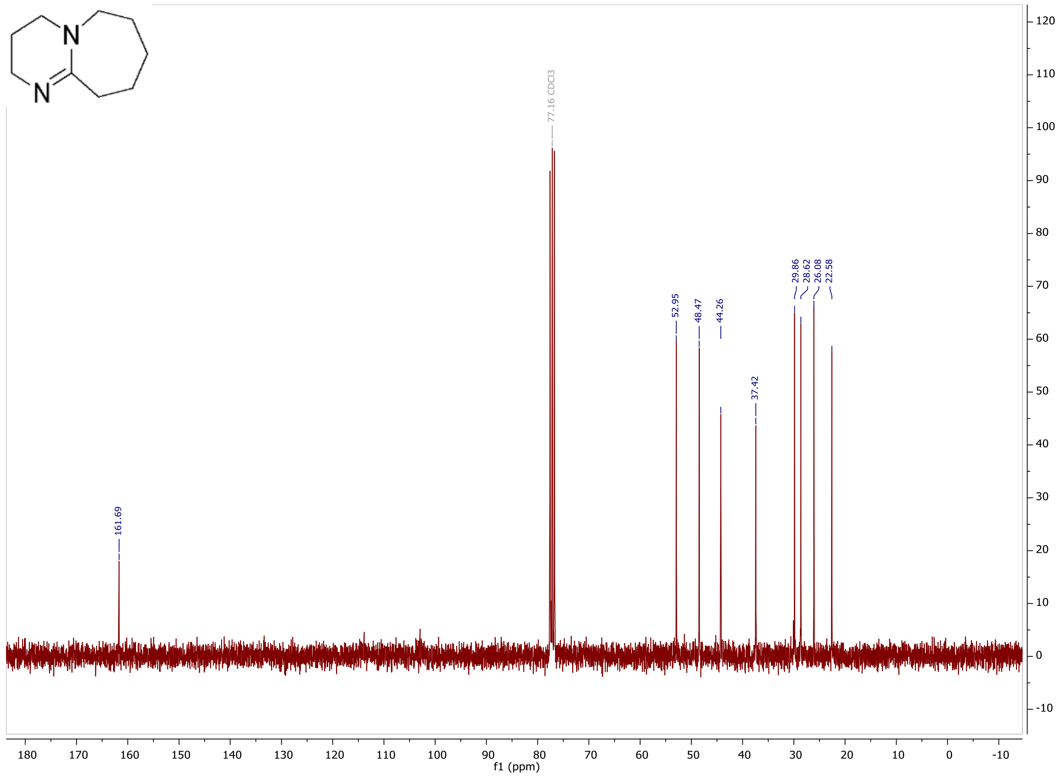


Figure S 121 ^{13}C-NMR spectrum of DBU in CDCl$_3$.

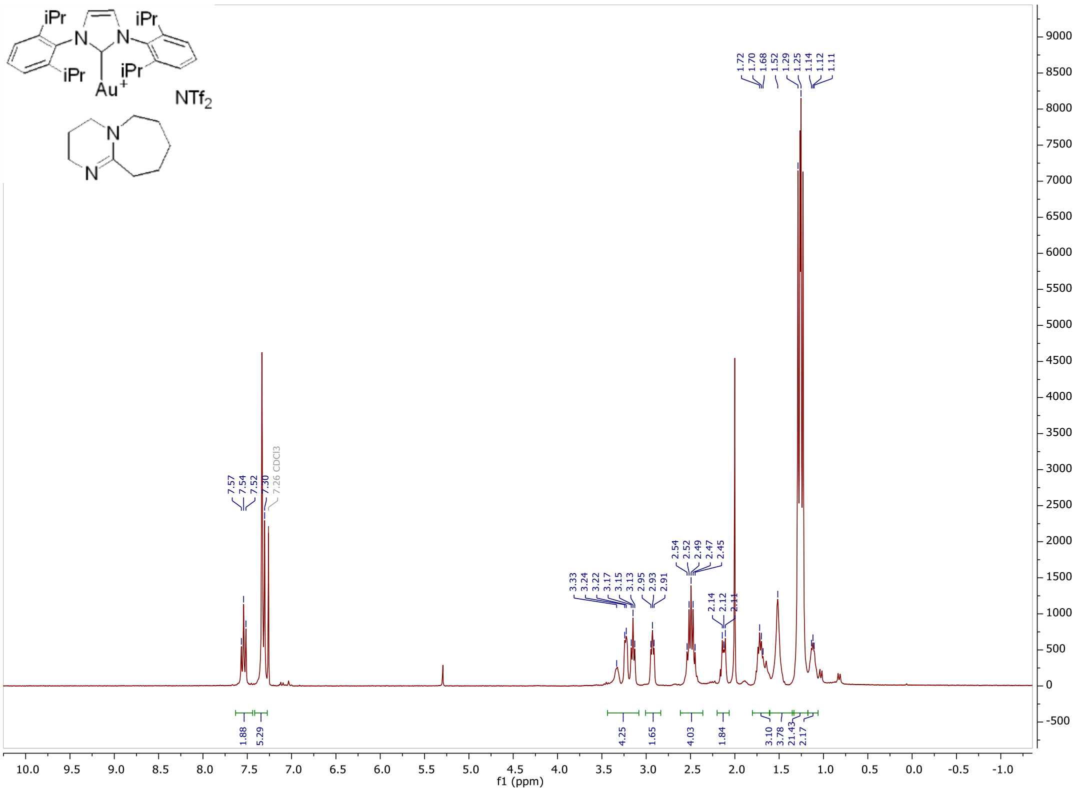


Figure S 122 ^{1}H-NMR spectrum of IPrAuNTf$_2$ + DBU (1:1 mixture) in CDCl$_3$.

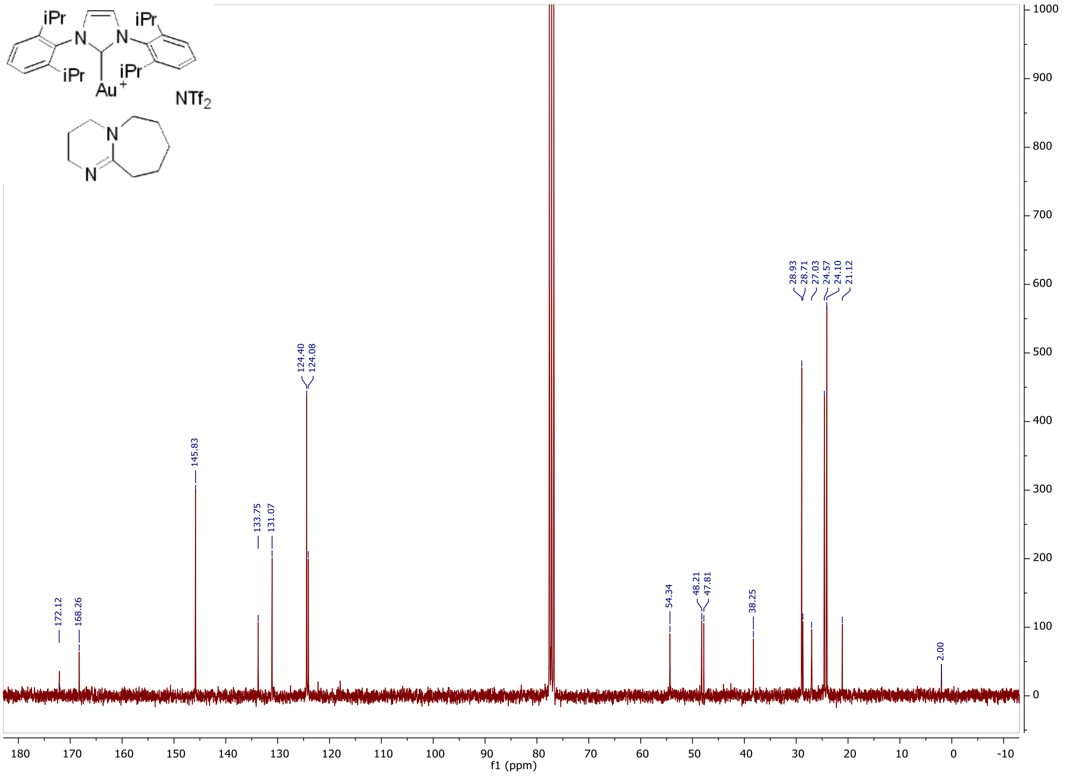


Figure S 123 ^{13}C-NMR spectrum of IPrAuNTf$_2$ + DBU (1:1 mixture) in CDCl$_3$.

5. High-resolution mass spectrometry

Analysis	D:\Data\Plenio\87421_ESI_HR_P1-E-4_01_13632.d	Acquisition Date	23.11.2021 18:02:25
Sample Name	87421_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinozaki SNZ 210126 2a	Operator	Rudolph

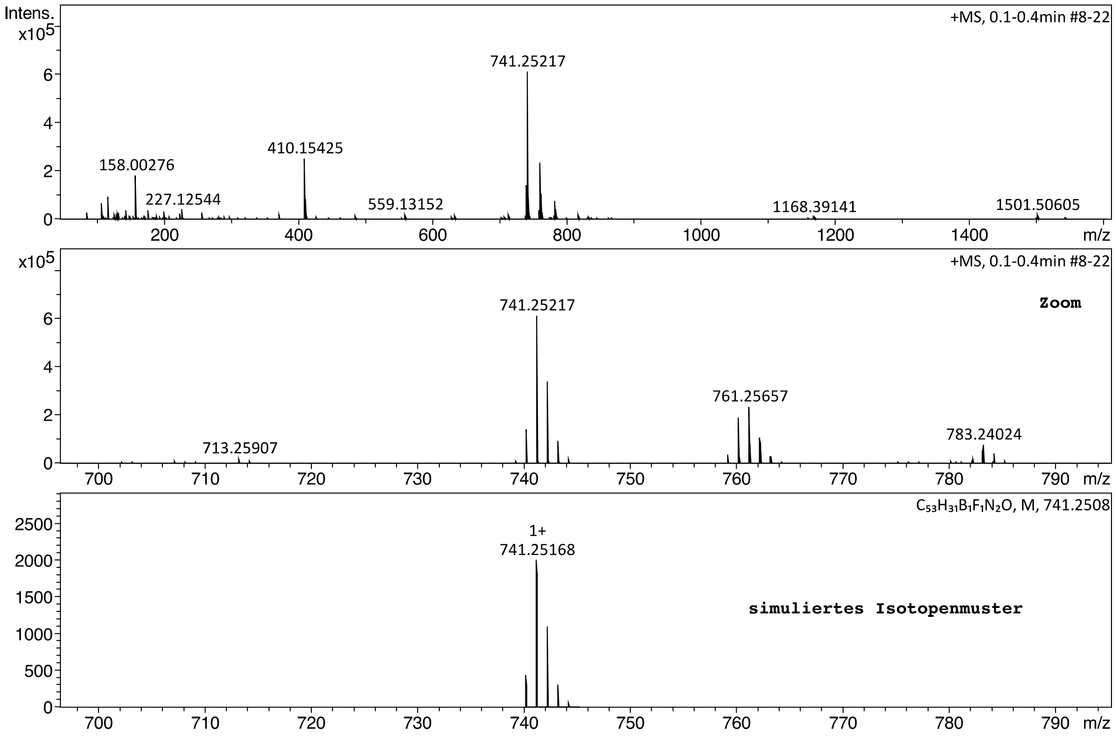


Figure S 124 HRMS spectrum of **10**. (ESI Positive)

Analysis	D:\Data\Plenio\87417_ESI_HR_P1-E-3_01_13631.d	Acquisition Date	23.11.2021 17:40:05
Sample Name	87417_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinozaki SNZ 2101110 3a	Operator	Rudolph

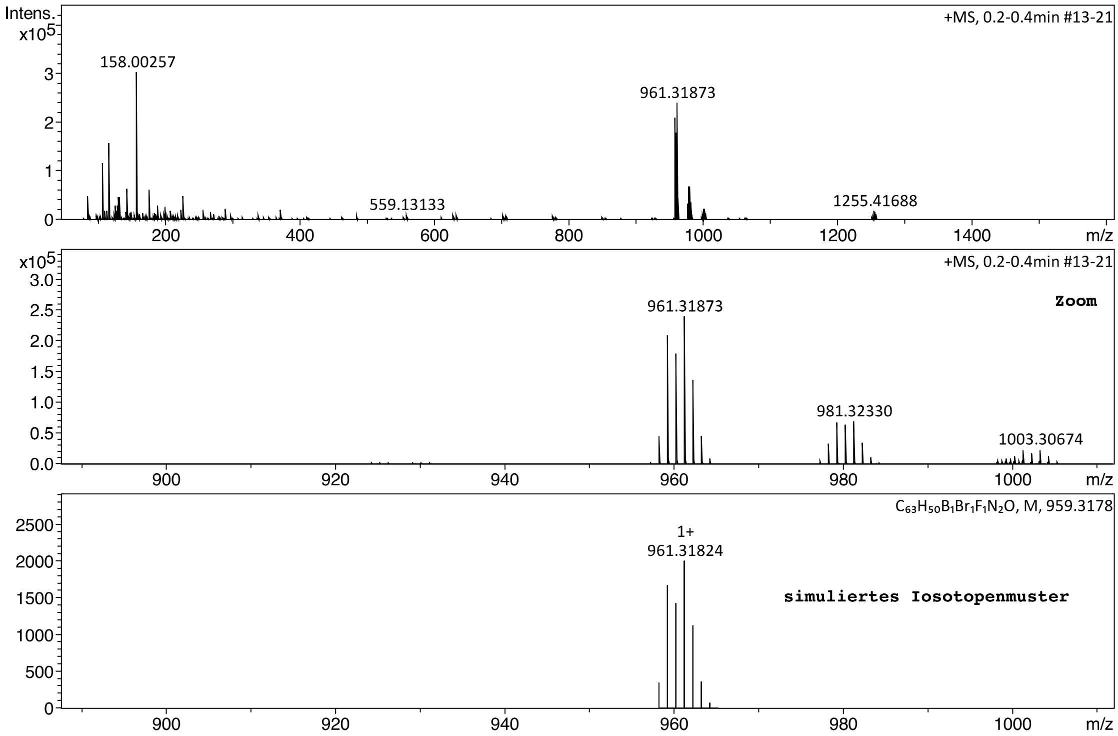


Figure S 125 HRMS spectrum of **14**. (ESI Positive)

Analysis	D:\Data\Plenio\87418_ESI_HR_P1-E-2_01_13641.d	Acquisition Date	23.11.2021 19:53:16
Sample Name	87418_ESI_HR	Ionisation	ES Positive
Method	as 50-2500 1hz.m	Mass Range	50 m/z - 2500 m/z
Client	Shinozaki SNZ 211108 a	Operator	Rudolph

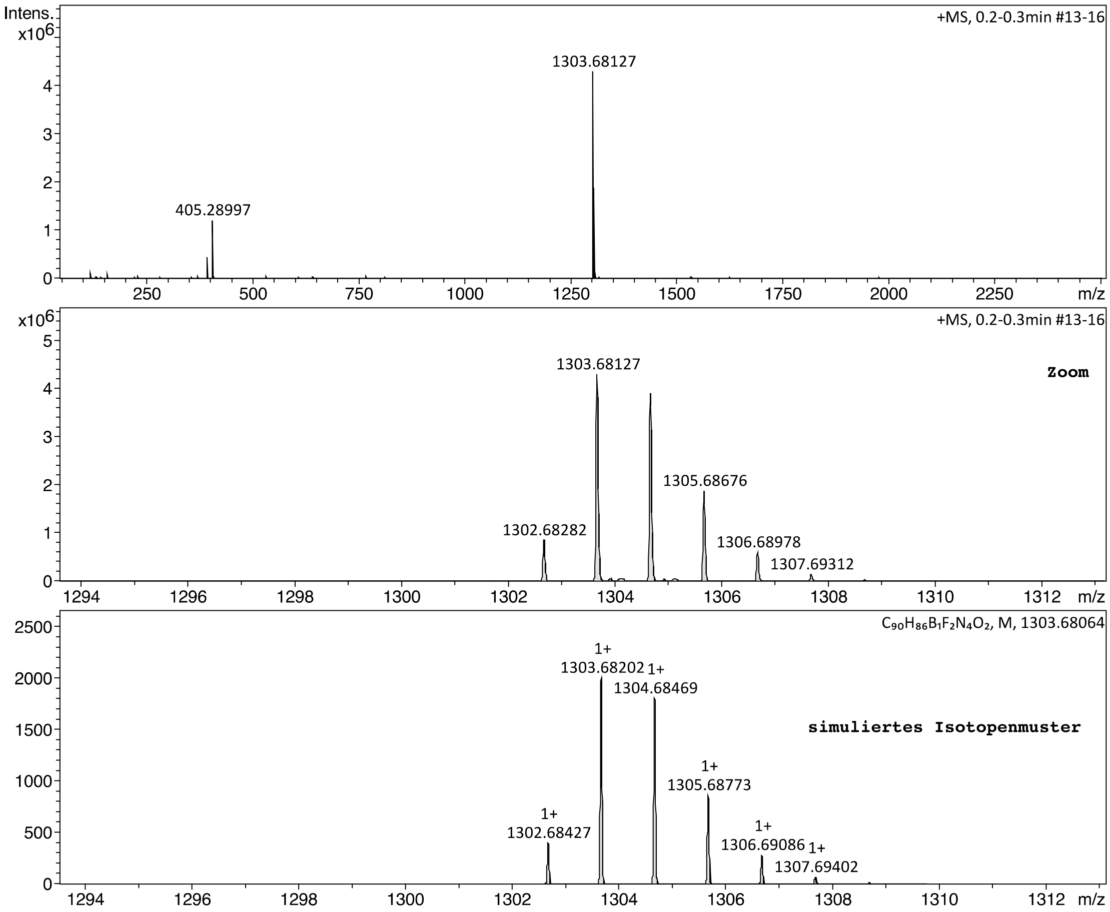


Figure S 126 HRMS spectrum of **5**·HBr. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85994_ESI_HR_P1-D-3_01_8704.d	Acquisition Date	04.03.2021 14:43:11
Sample Name	85994_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinzaki SNZ 21020 7a	Operator	Rudolph

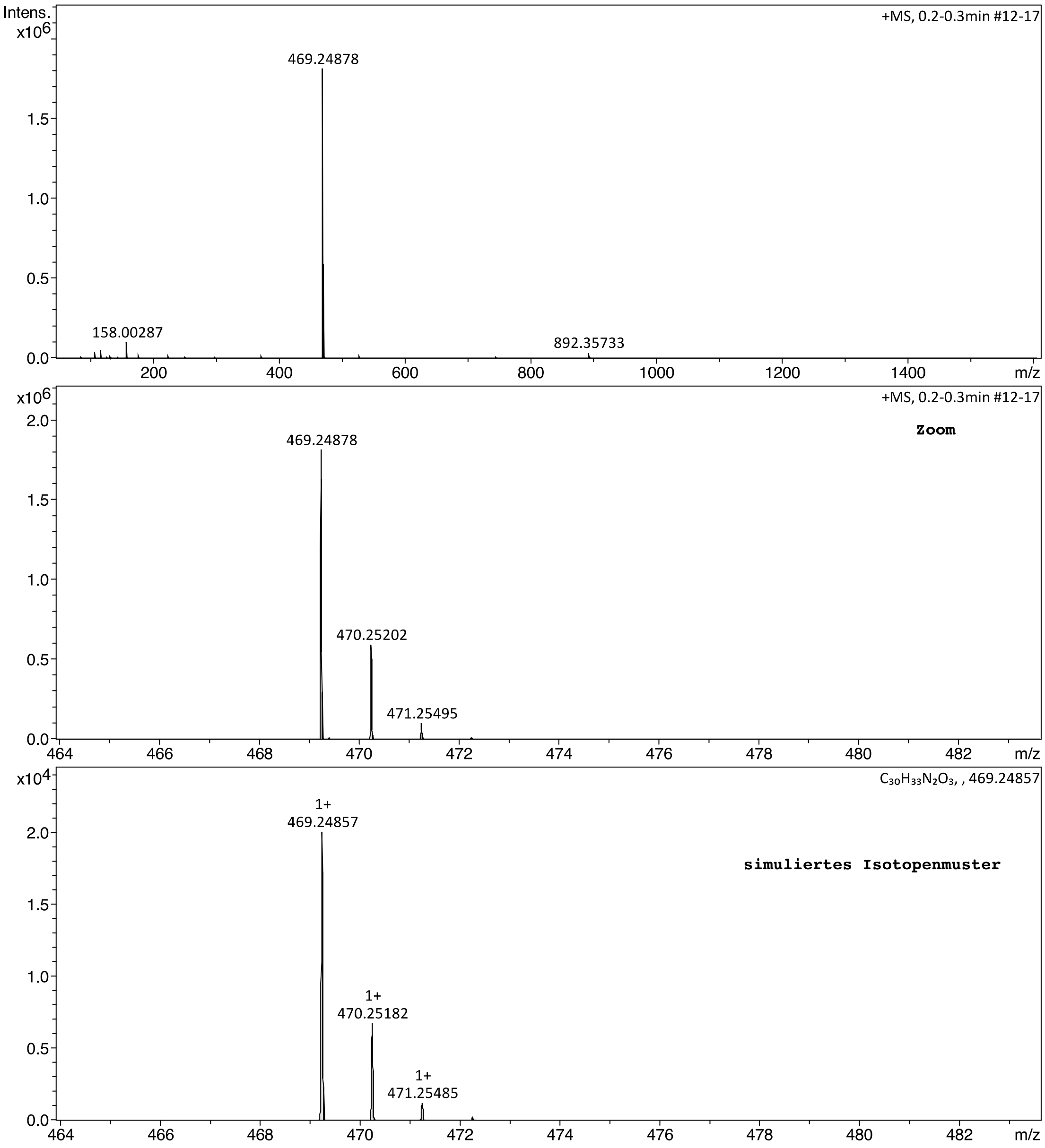
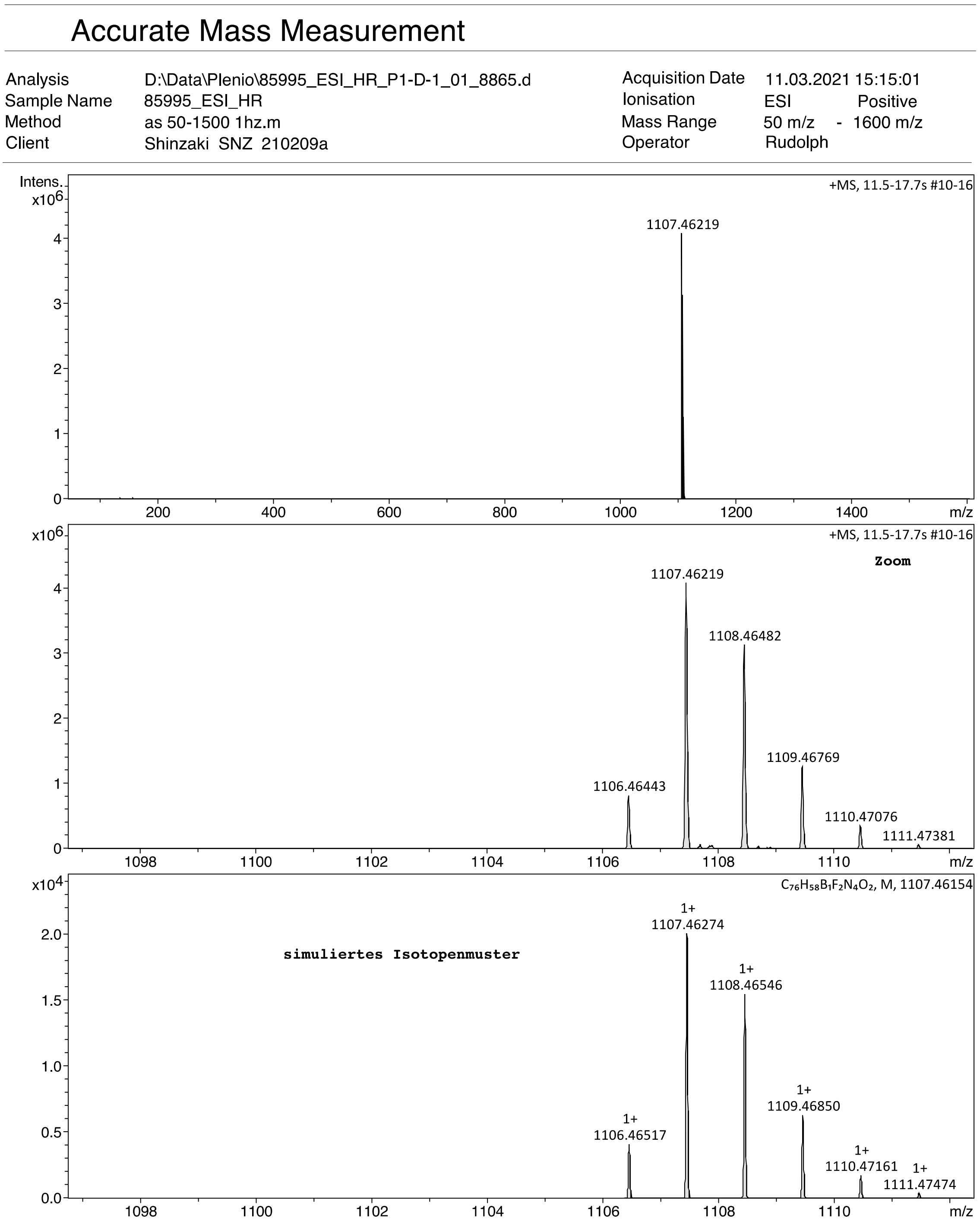


Figure S 127 HRMS spectrum of **7·**HBr. (ESI Positive)



Accurate Mass Measurement

Analysis	D:\Data\Plenio\85995_ESI_HR_P1-D-1_01_8865.d	Acquisition Date	11.03.2021 15:15:01
Sample Name	85995_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinzaki SNZ 210209a	Operator	Rudolph

Figure S 128 HRMS spectrum of **8**·HBr. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86034_ESI_HR_P1-C-2_01_8999.d	Acquisition Date	17.03.2021 15:46:57
Sample Name	86034_ESI_HR	Ionisation	ESI Positive
Method	as 50-2000a 1hz.m	Mass Range	50 m/z - 2000 m/z
Client	Shinozaki SNZ 210310-2a	Operator	Rudolph

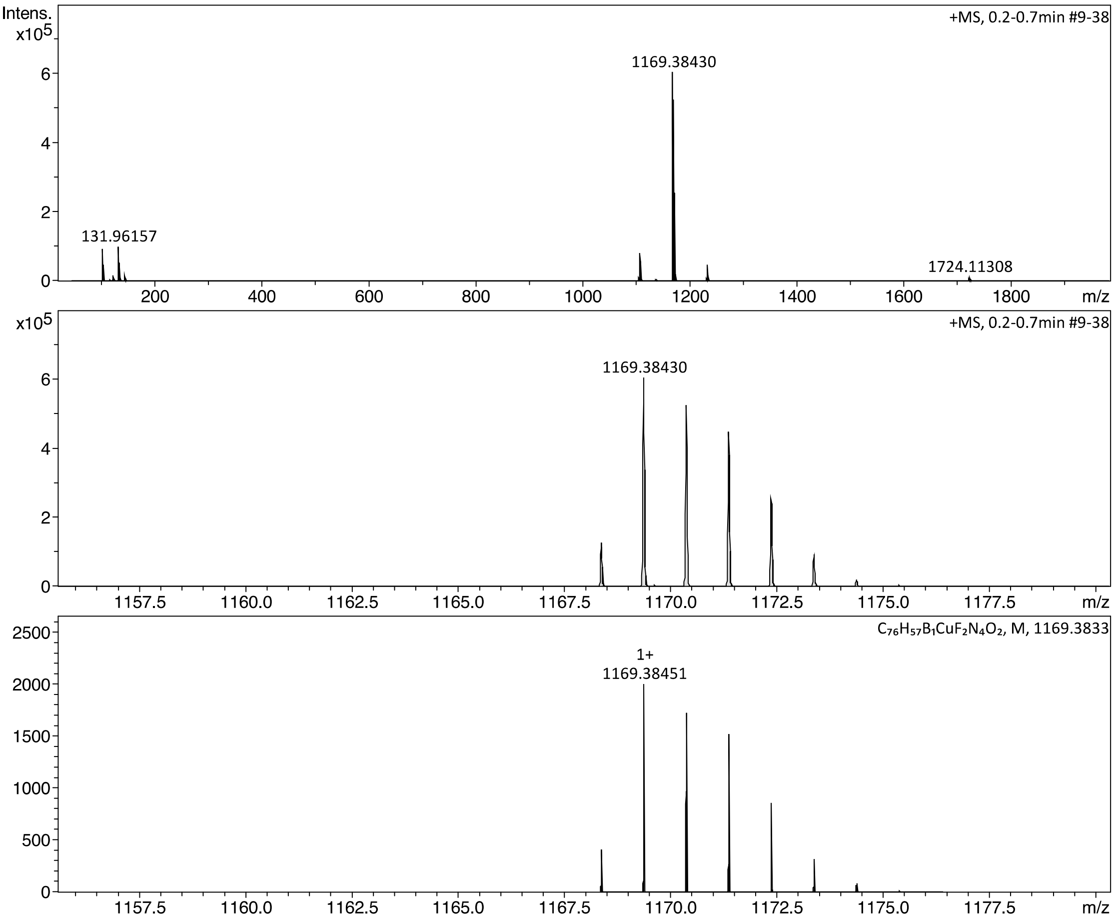


Figure S 129 HRMS spectrum of [CuBr(**8**)]. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85992_ESI_HR_P1-C-2_01_8875.d	Acquisition Date	11.03.2021 18:05:50
Sample Name	85992_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000.m	Mass Range	50 m/z - 3000 m/z
Client	Shinzaki SNZ 210218-2a	Operator	Rudolph

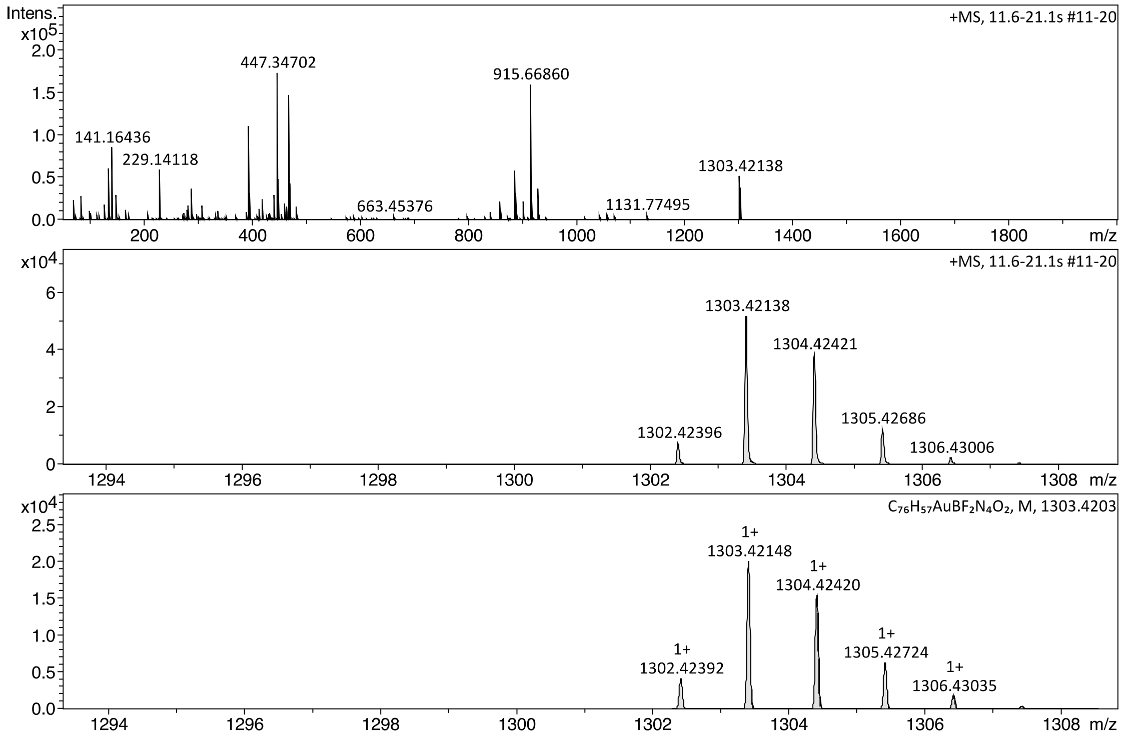


Figure S 130 HRMS spectrum of [AuCl(**8**)]. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85990_ESI_HR_P1-D-3_01_8715.d	Acquisition Date	04.03.2021 18:58:12
Sample Name	85990_ESI_HR	Ionisation	ESI Positive
Method	as 50-2000a 1hz.m	Mass Range	50 m/z - 2000 m/z
Client	Shinzaki SNZ 210220 - 2a	Operator	Rudolph

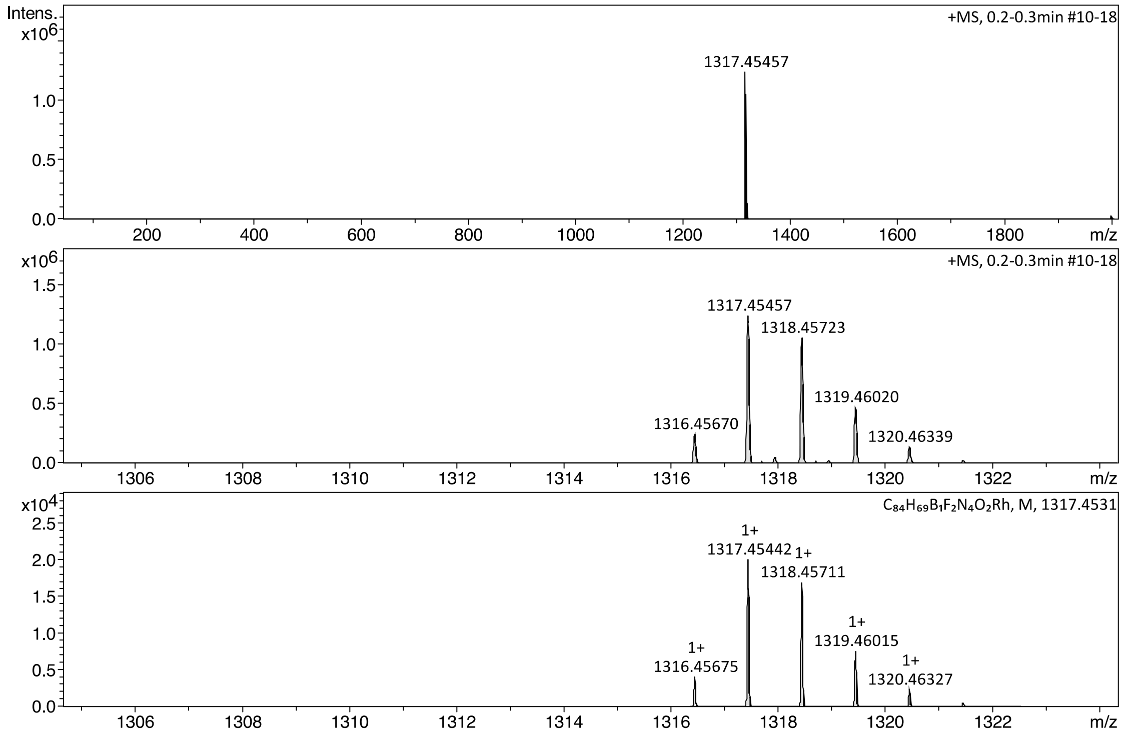


Figure S 131 HRMS spectrum of [RhCl(cod)(**8**)]. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85988_ESI_HR_P1-C-1_01_8873.d	Acquisition Date	11.03.2021 17:00:42
Sample Name	85988_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000.m	Mass Range	50 m/z - 3000 m/z
Client	Shinzaki SNZ 210222-2a	Operator	Rudolph

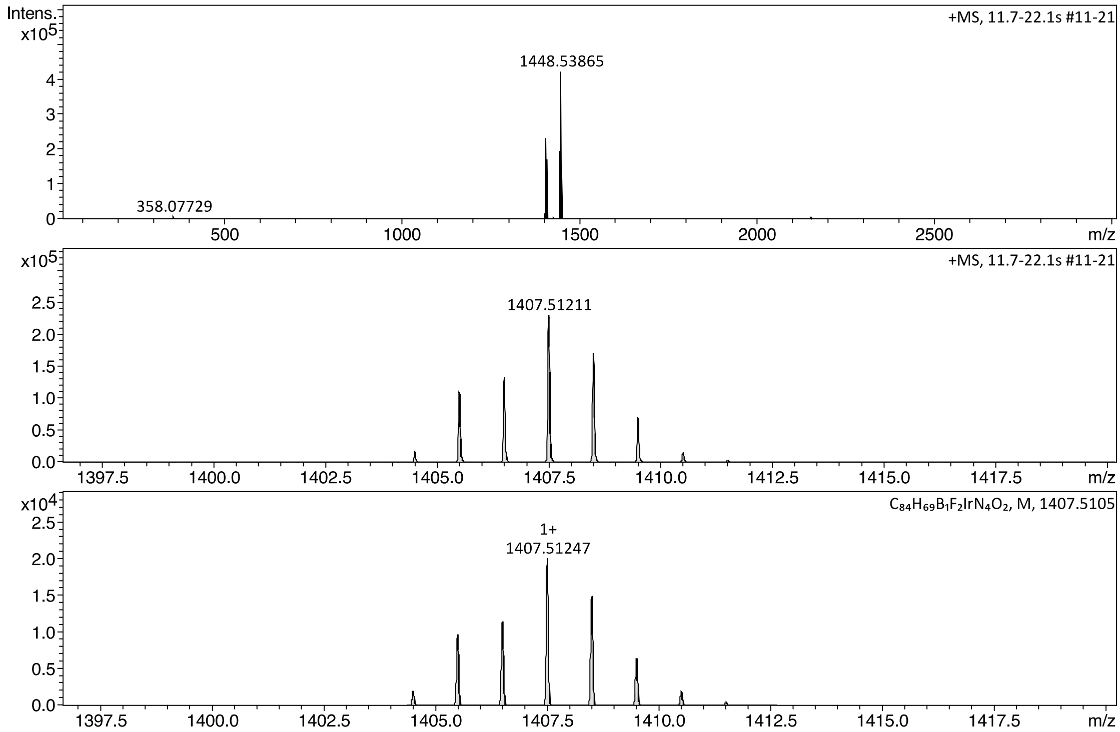


Figure S 132 HRMS spectrum of [IrCl(cod)(**8**)]. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85986_ESI_HR_P1-D-1_01_8871.d	Acquisition Date	11.03.2021 16:43:41
Sample Name	85986_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000.m	Mass Range	50 m/z - 3000 m/z
Client	Shinzaki SNZ 210223-2a	Operator	Rudolph

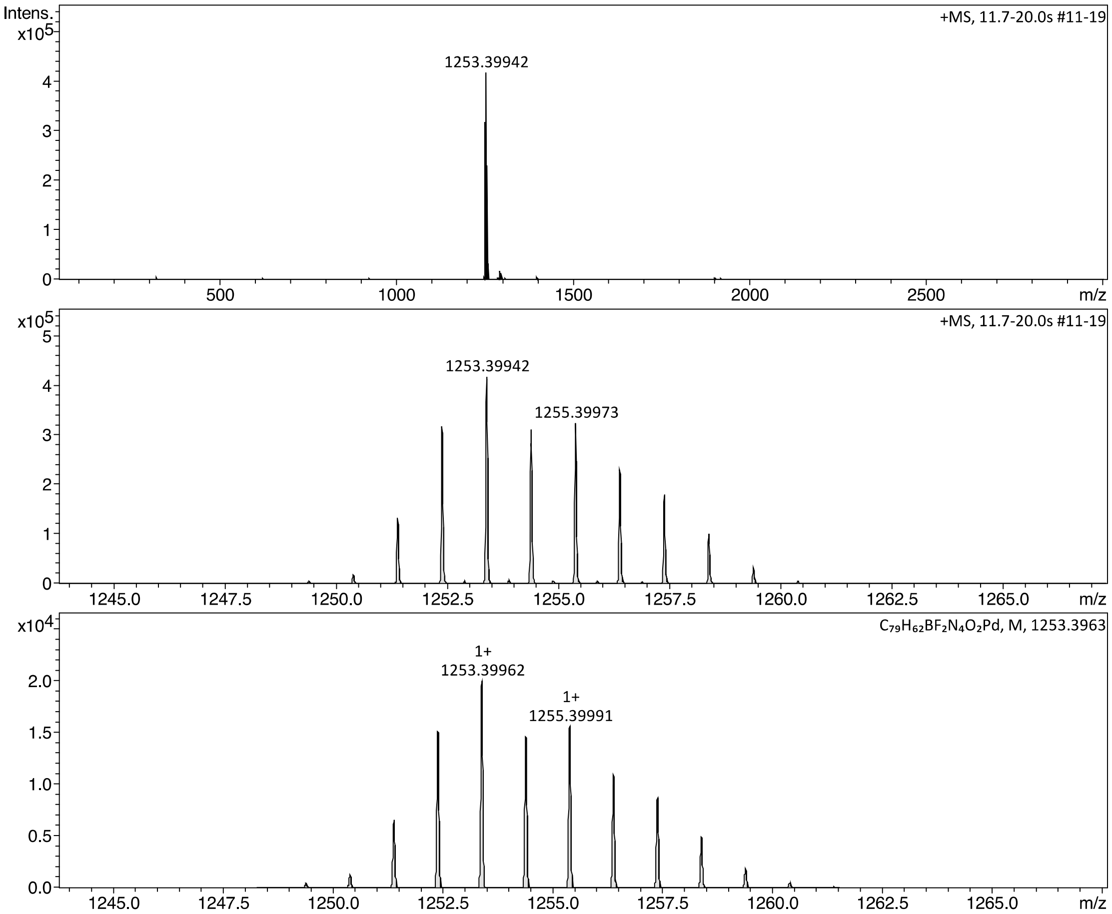


Figure S 133 HRMS spectrum [Pd(allyl)Cl(**8**)]. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85996_ESI_HR_P1-D-4_01_8705.d	Acquisition Date	04.03.2021 14:48:07
Sample Name	85996_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinzaki SNZ 21021 6a	Operator	Rudolph

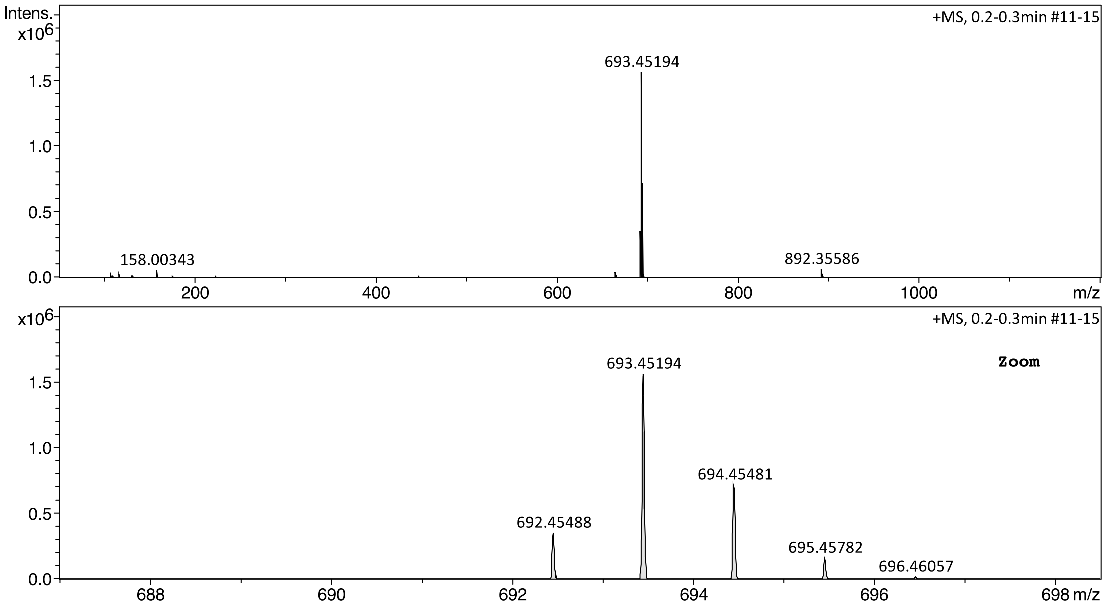


Figure S 134 HRMS spectrum of **9·HBr**. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85991_ESI_HR_P1-D-2_01_8708.d	Acquisition Date	04.03.2021 17:18:31
Sample Name	85991_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinzaki SNZ 210220 - 1a	Operator	Rudolph

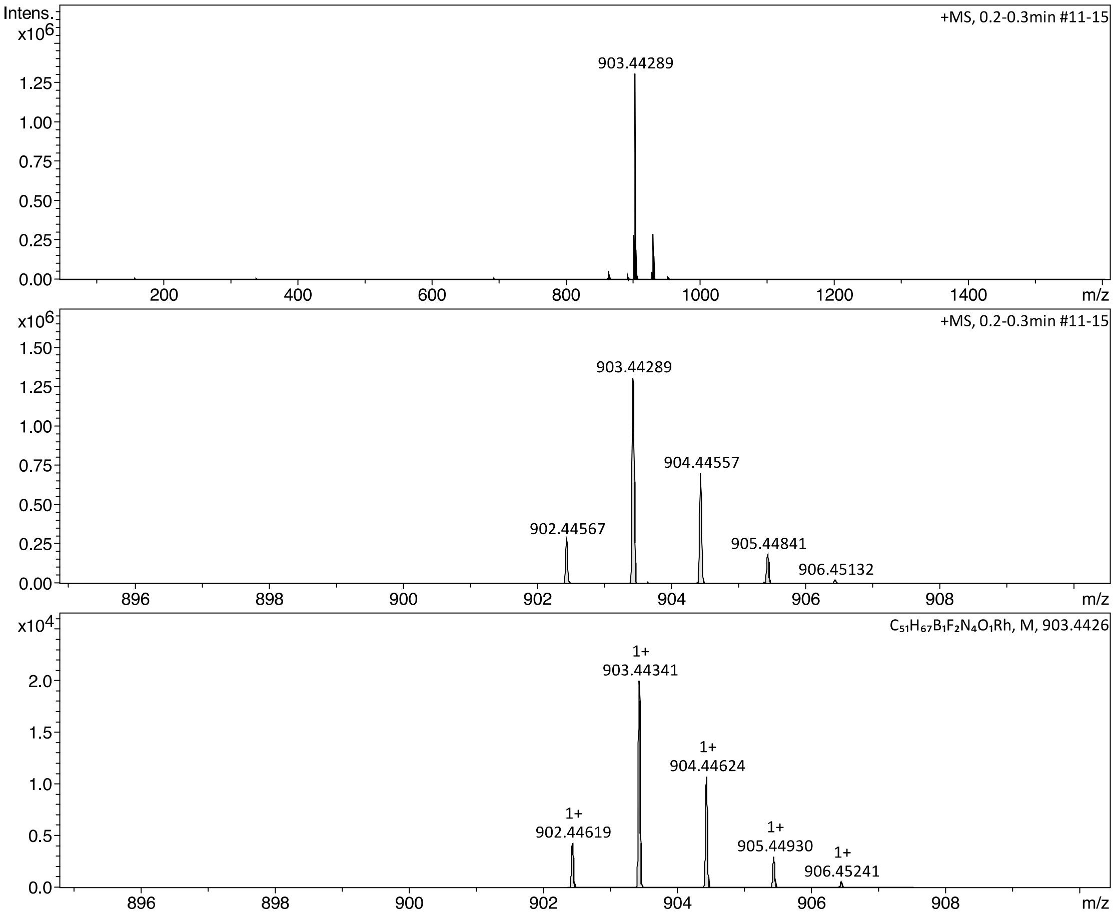
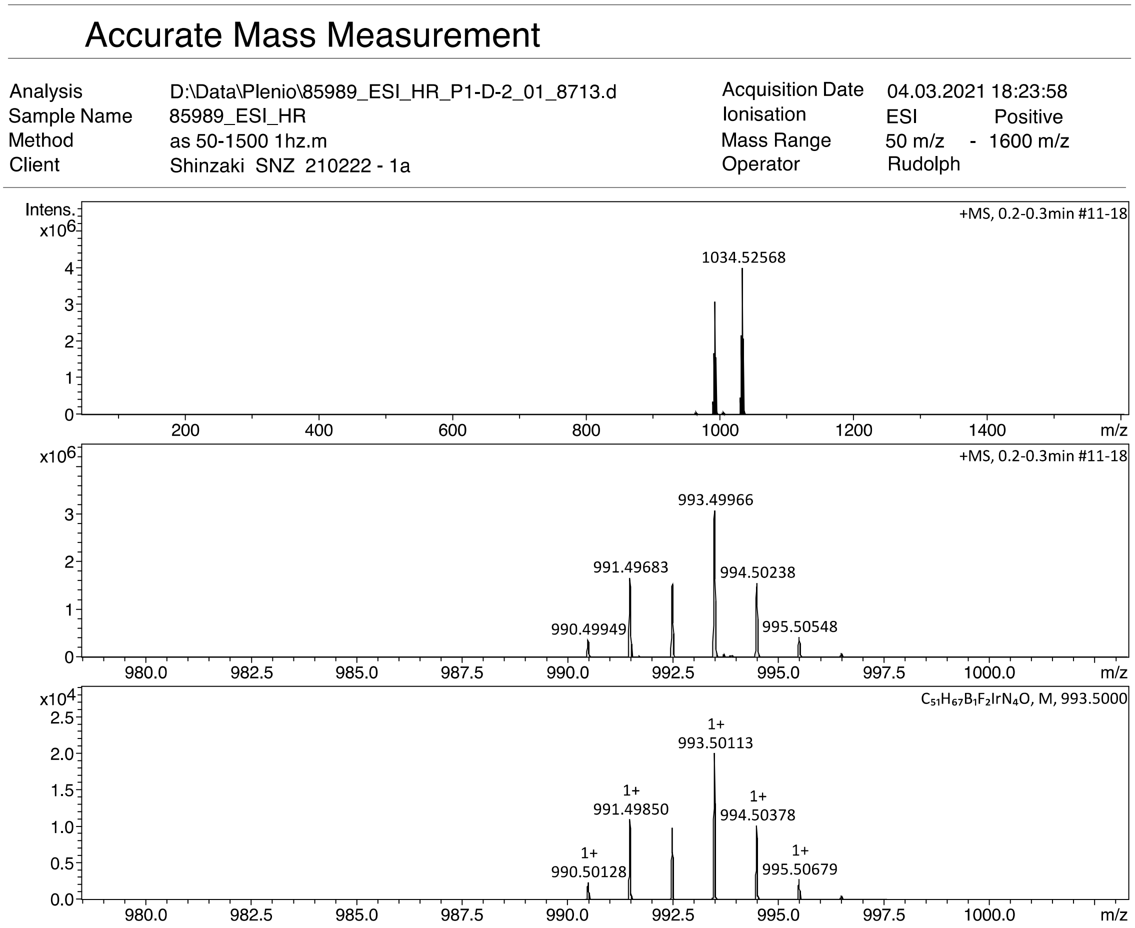


Figure S 135 HRMS spectrum of [RhCl(cod)(**9**)]. (ESI Positive)



Accurate Mass Measurement

Analysis	D:\Data\Plenio\85989_ESI_HR_P1-D-2_01_8713.d	Acquisition Date	04.03.2021 18:23:58
Sample Name	85989_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinzaki SNZ 210222 - 1a	Operator	Rudolph

Figure S 136 HRMS spectrum of [IrCl(cod)(**9**)]. (ESI Positive)

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85987_ESI_HR_P1-D-1_01_8706.d	Acquisition Date	04.03.2021 15:06:41
Sample Name	85987_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Shinzaki SNZ 210223-1a	Operator	Rudolph

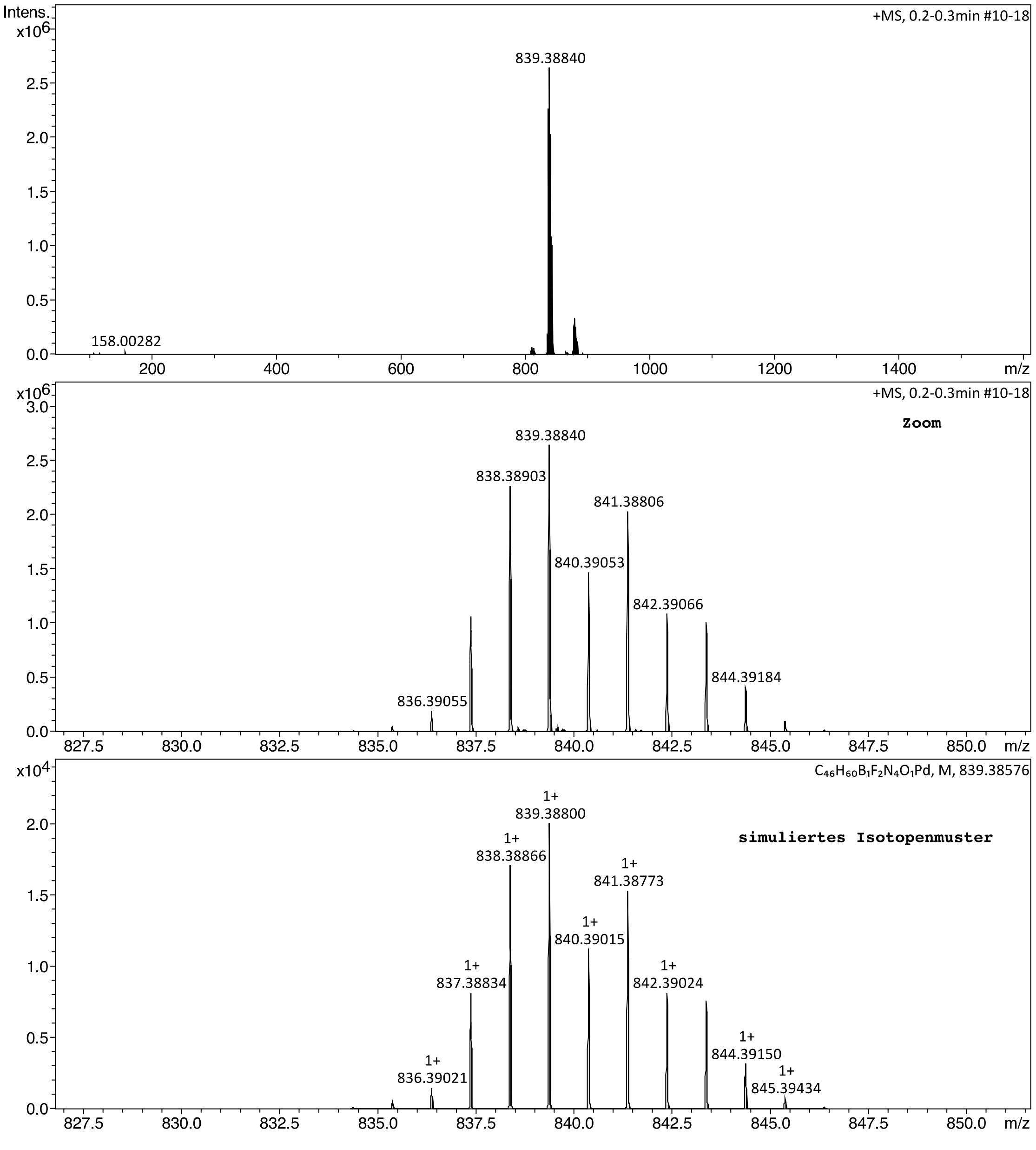


Figure S 137 HRMS spectrum of [Pd(allyl)Cl(**9**)]. (ESI Positive)

Analysis	D:\Data\Plenio\87415_ESI_HR_P1-E-1_01_13626.d	Acquisition Date	23.11.2021 16:15:11
Sample Name	87415_ESI_HR	Ionisation	ESI Positive
Method	as 50-2500 1hz.m	Mass Range	50 m/z - 2500 m/z
Client	Shinozaki SNZ 211025 b	Operator	Rudolph

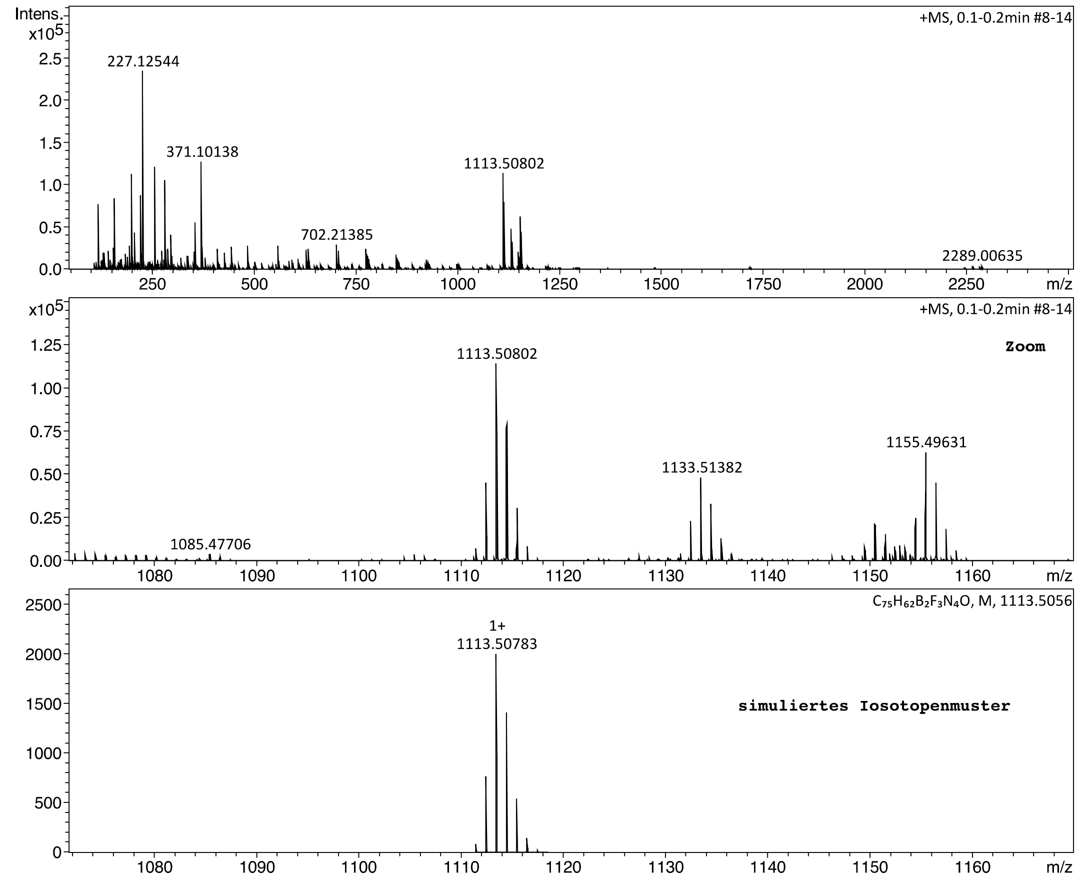
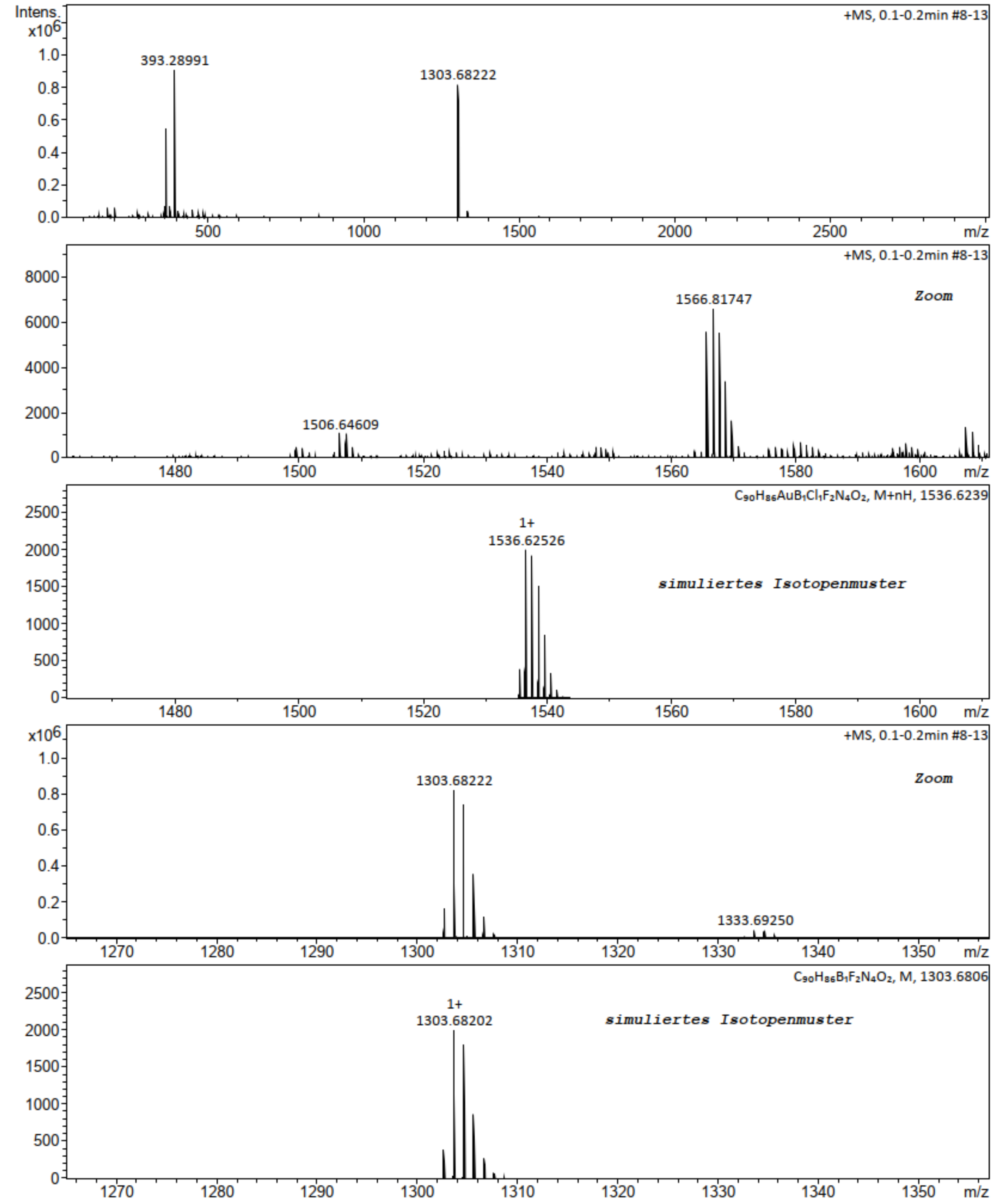


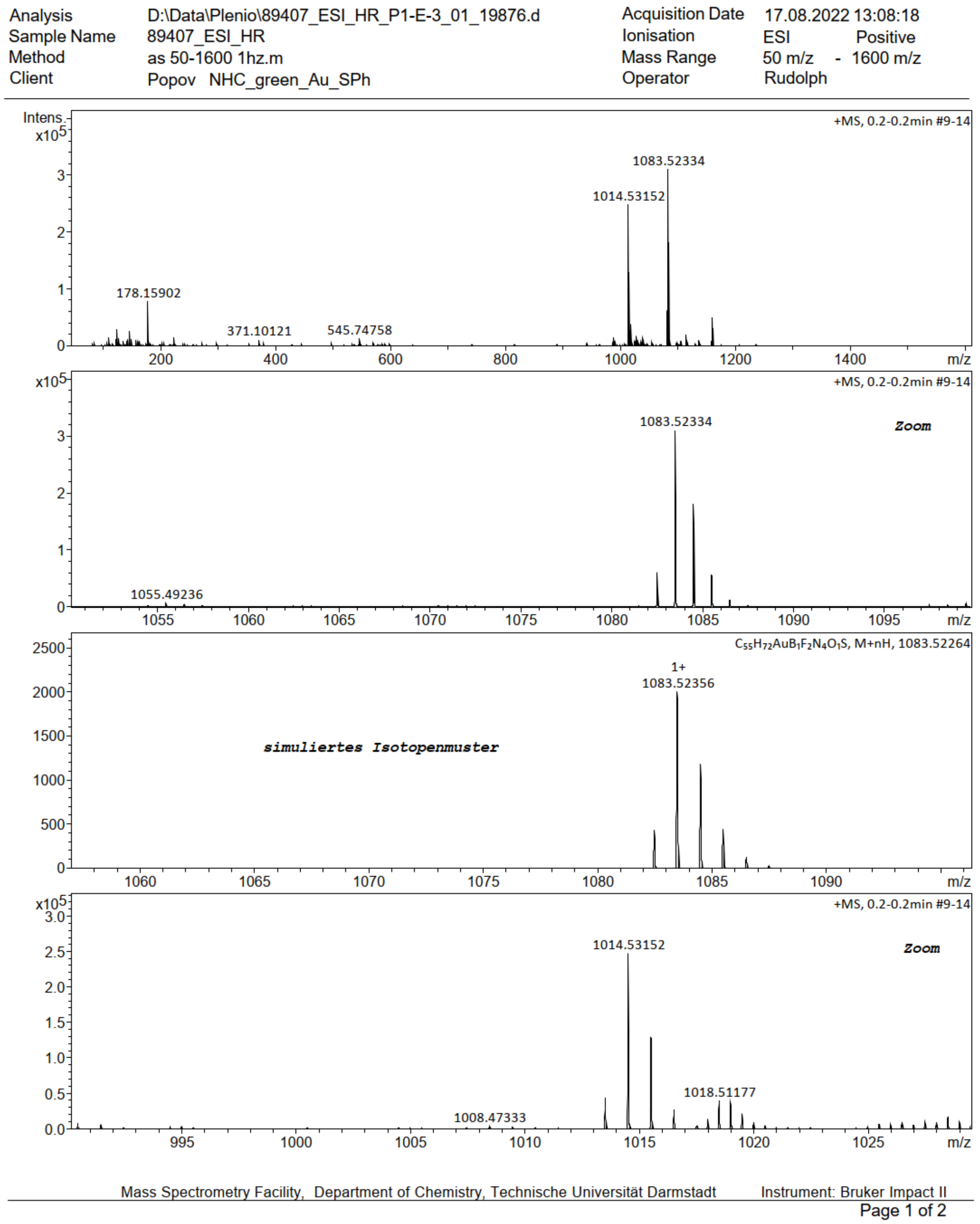
Figure S 138 HRMS spectrum of **12**. (ESI Positive)

Analysis	D:\Data\Plenio\89408_ESI_HR_P1-E-2_01_20295.d	Acquisition Date	30.08.2022 14:15:19
Sample Name	89408_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000_tune.m	Mass Range	50 m/z - 3000 m/z
Client	Popov AuCl_NHC_red	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e^- Conf	z
1	1303.68222	1303.68064	C90H86BF2N4O2	M	C90H86BF2N4O2	0.20	0.16	3.3	even	1+

Figure S 139 HRMS spectrum of **[AuCl (NHC_red)]**. (ESI Positive)



Analysis	D:\Data\Plenio\89407_ESI_HR_P1-E-3_01_19876.d	Acquisition Date	17.08.2022 13:08:18
Sample Name	89407_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Popov NHC_green_Au_SPh	Operator	Rudolph

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#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	1083.52334	1083.52264	C55H73AuBF2N4OS	M+H	C55H72AuBF2N4OS	0.22	0.20	19.4	even	1+
2	1083.52334	1083.52284	C60H74AuBFNOS	M+H	C60H73AuBFNOS	0.49	0.45	34.5	odd	1+
3	1083.52334	1083.52398	C57H75AuBF2NO2S	M+H	C57H74AuBF2NO2S	1.59	1.47	663.4	odd	1+

Figure S 140 HRMS spectrum of **15**. (ESI Positive)

Mass spectrum

Analysis	D:\Data\Plenio\89122_neg_ESI_HR_P1-E-1_01_18795.d	Acquisition Date	24.06.2022 16:16:58
Sample Name	89122_neg_ESI_HR	Ionisation	ESI Negative
Method	as 50-3000_neg.m	Mass Range	50 m/z - 3000 m/z
Client	Popov green-red IPrAu ion pair	Operator	Rudolph

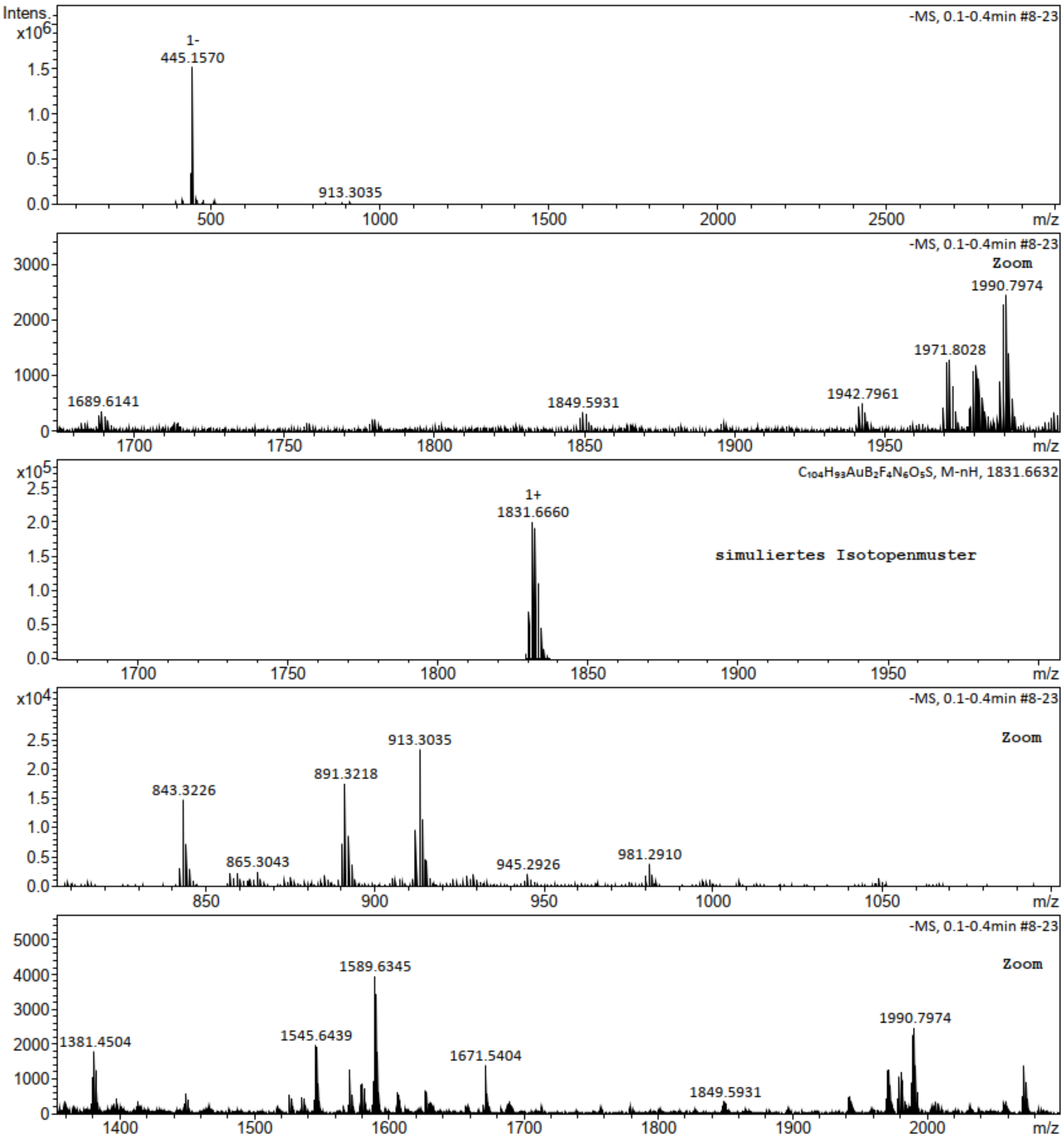
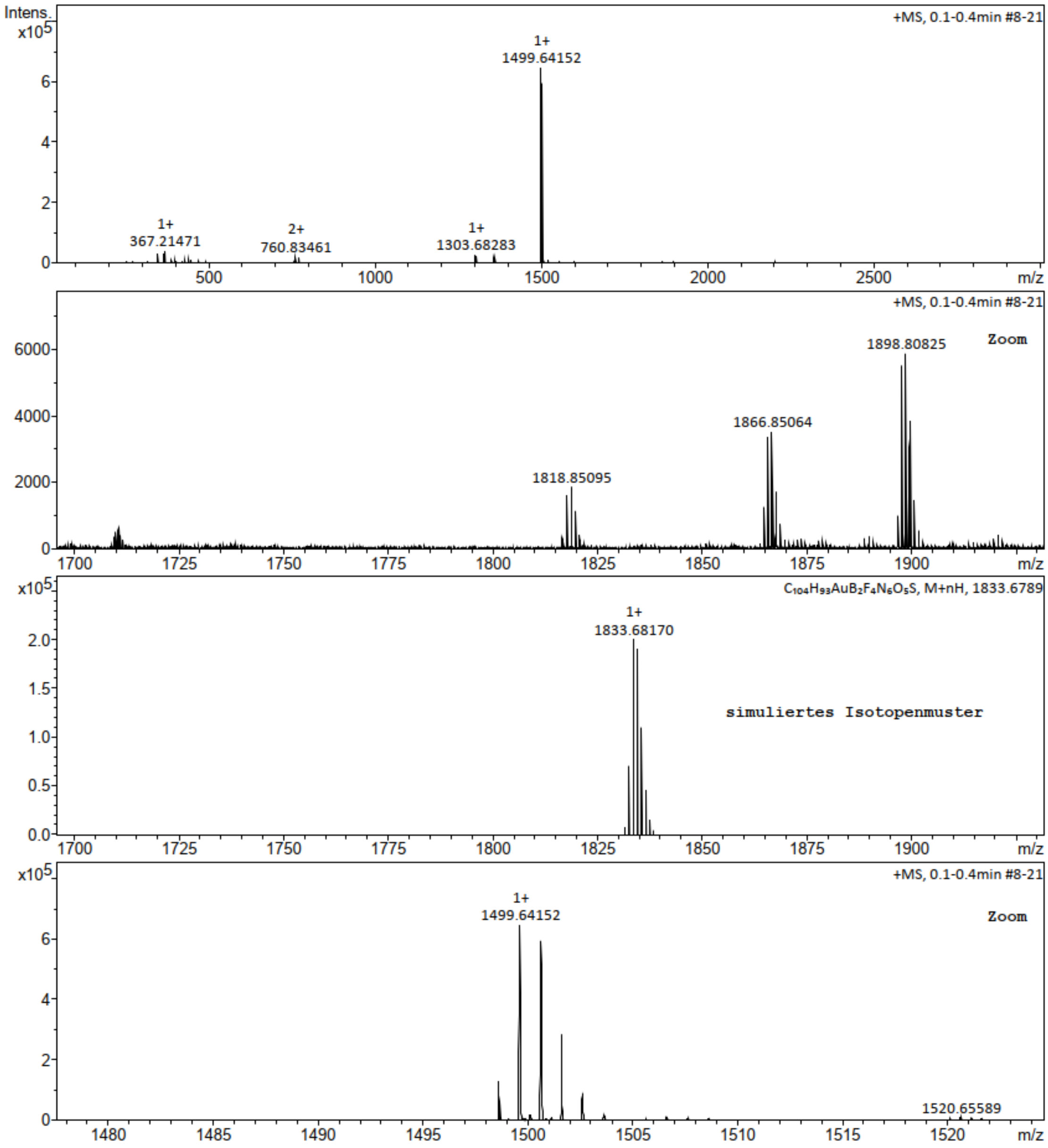


Figure S 141 HRMS spectrum of **18**. (ESI Negative)

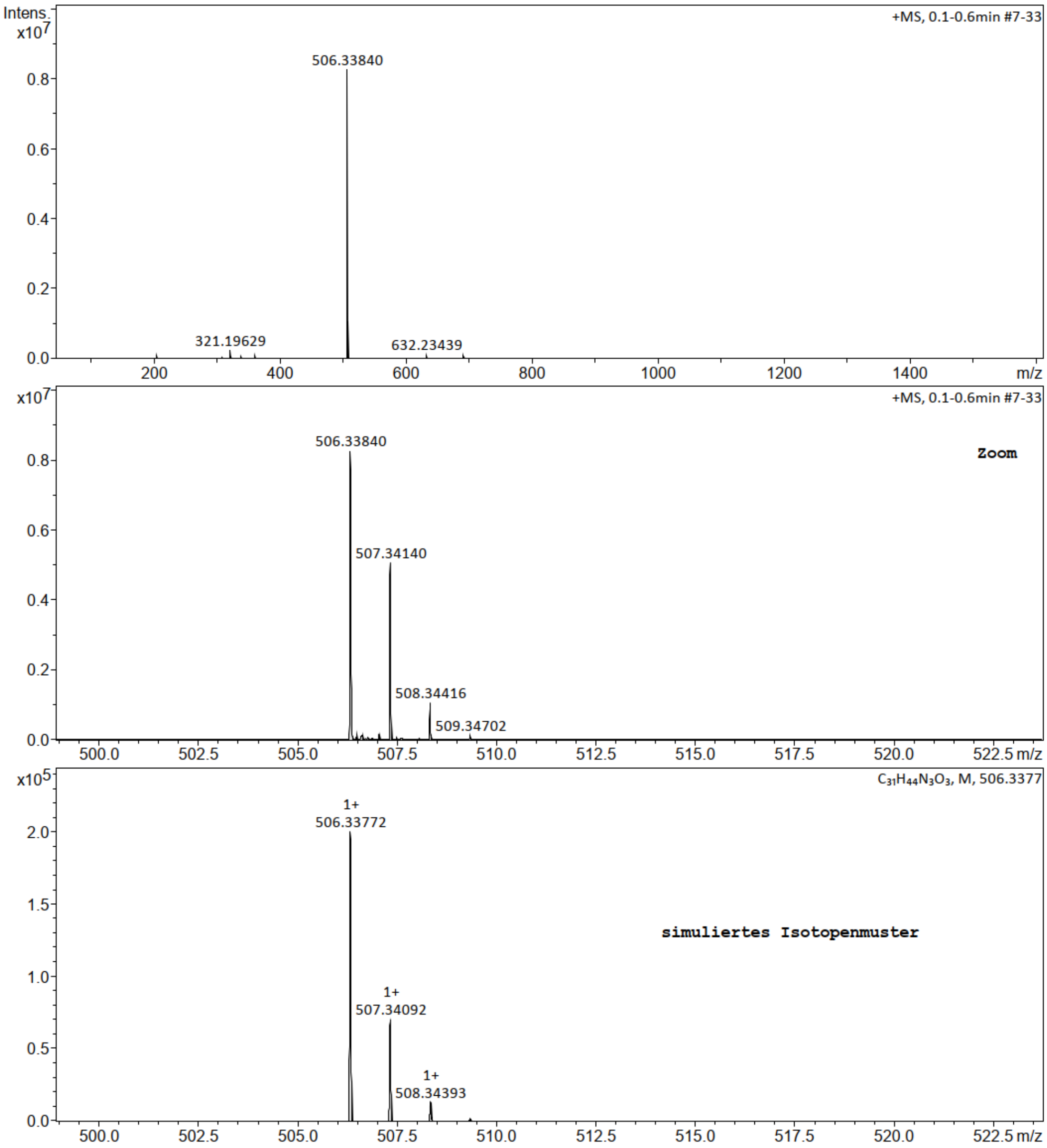
Analysis	D:\Data\Plenio\89122_ESI_HR_P1-E-1_01_18732.d	Acquisition Date	23.06.2022 13:41:44
Sample Name	89122_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000.m	Mass Range	50 m/z - 3000 m/z
Client	Popov green-red IPrAu ion pair	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	1499.64152	1499.63988	C79H90AuBF3N6O5S	M+H	C79H89AuBF3N6O5S	0.39	0.26	41.3	even	1+
2	1499.64152	1499.63816	C75H89AuB2F5N6O5S	M+H	C75H88AuB2F5N6O5S	1.14	0.76	104.9	even	1+

Figure S 142 HRMS spectrum of **18**. (ESI Positive)

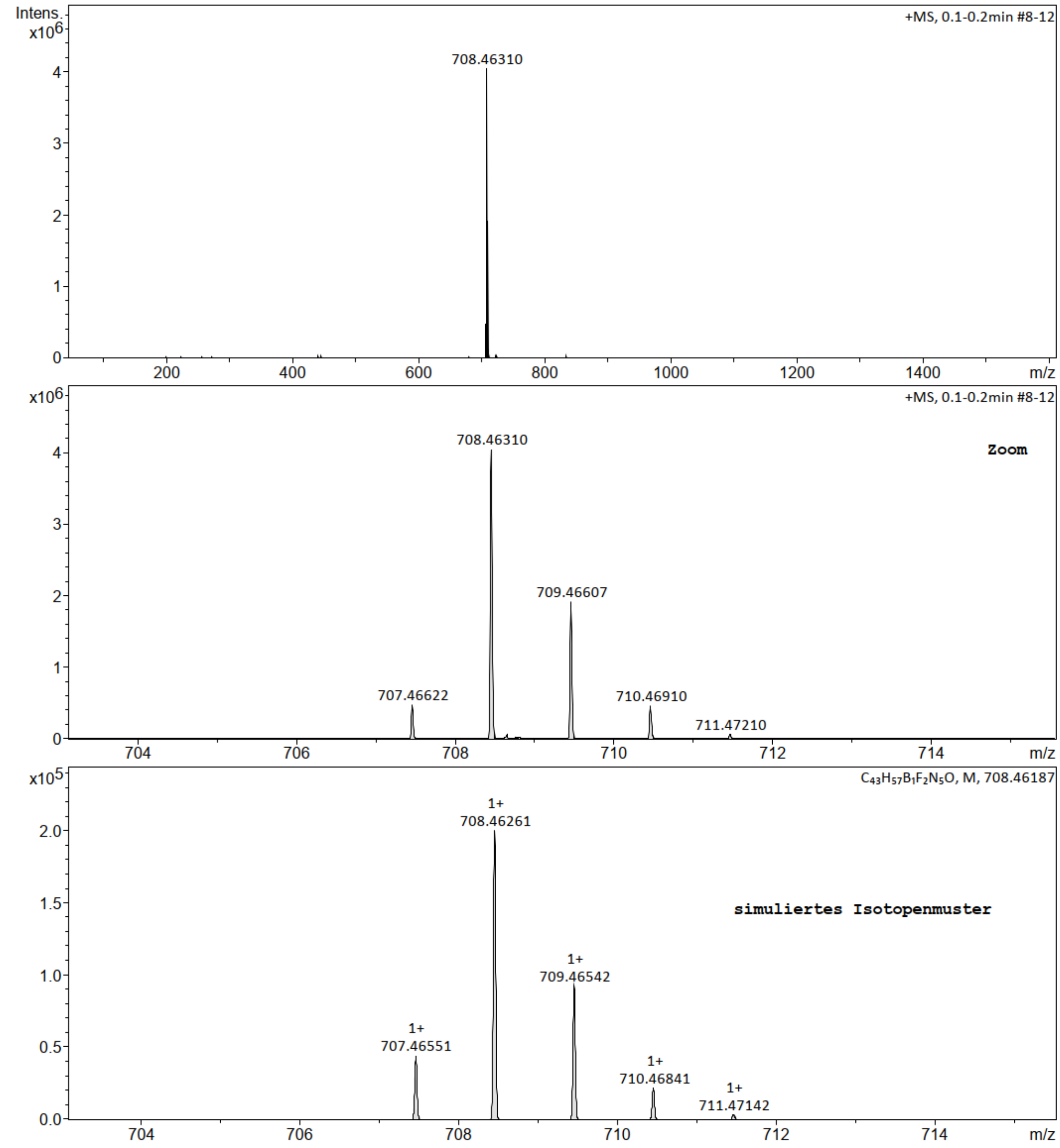
Analysis	D:\Data\Plenio\89125_ESI_HR_P1-E-2_01_18724.d	Acquisition Date	23.06.2022 12:34:17
Sample Name	89125_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Popov IMes OalkylNHBoc	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e^- Conf	z
1	506.33840	506.33772	C31H44N3O3	M	C31H44N3O3	0.68	1.35	133.8	even	1+

Figure S 143 HRMS spectrum of **IMes·HCl**. (ESI Positive)

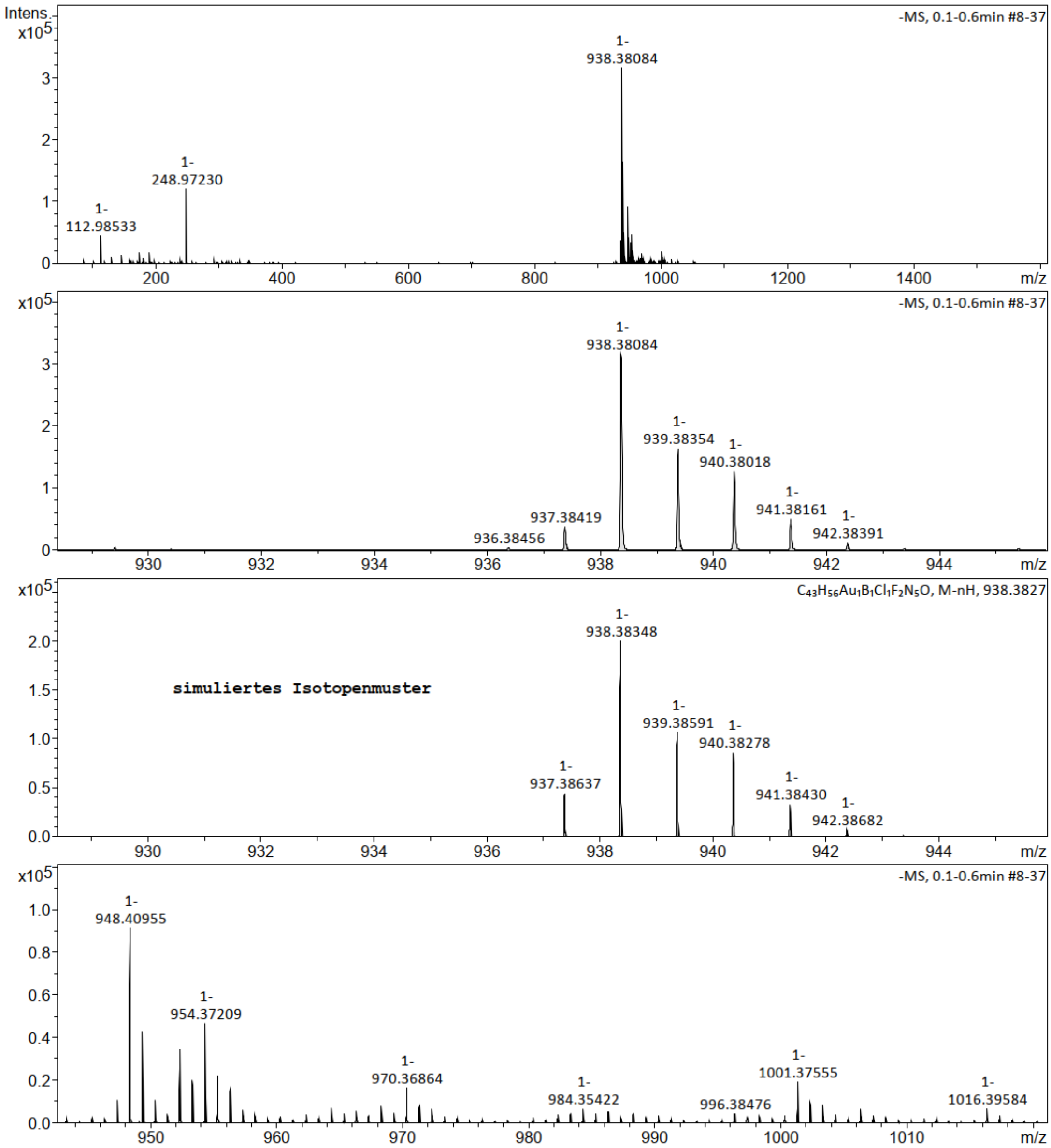
Analysis	D:\Data\Plenio\89124_ESI_HR_P1-E-1_01_18721.d	Acquisition Date	23.06.2022 12:14:14
Sample Name	89124_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Popov IMes salt with NHbodipy	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e^- Conf	z
1	708.46310	708.46187	C43H57BF2N5O	M	C43H57BF2N5O	0.49	0.69	46.2	even	1+

Figure S 144 HRMS spectrum of **19**. (ESI Positive)

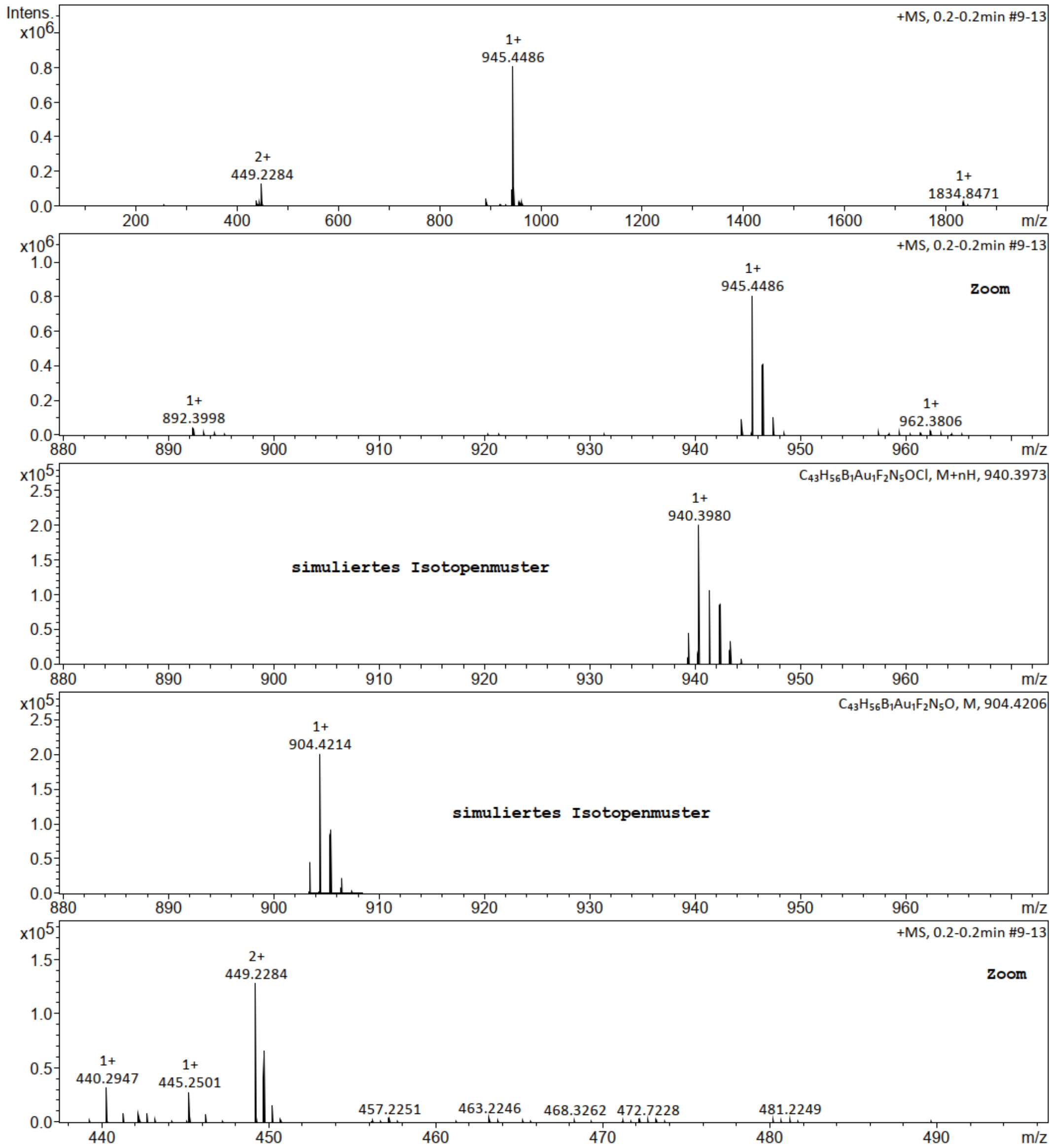
Analysis	D:\Data\Plenio\89123_neg_ESI_HR_P1-E-3_01_18780.d	Acquisition Date	24.06.2022 13:50:22
Sample Name	89123_neg_ESI_HR	Ionisation	ESI Negative
Method	as 50-1600 1hz negative.m	Mass Range	50 m/z - 1600 m/z
Client	Popov IMesAuCl comp.w. alkyl-NH-bodipy	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e^- Conf	z
1	938.38084	938.38140	C41H53AuBClF2N8	M-H	C41H54AuBClF2N8	1.27	1.35	43.6	odd	1-
2	938.38084	938.38141	C42H59AuBClF2NO5	M-H	C42H60AuBClF2NO5	1.29	1.38	44.3	even	1-
3	938.38084	938.38006	C40H57AuBClF2N4O4	M-H	C40H58AuBClF2N4O4	0.08	0.08	44.4	odd	1-
4	938.38084	938.38274	C43H55AuBClF2N5O	M-H	C43H56AuBClF2N5O	2.64	2.82	44.5	even	1-
5	938.38084	938.37873	C39H61AuBClF2O8	M-H	C39H62AuBClF2O8	1.43	1.52	46.7	odd	1-

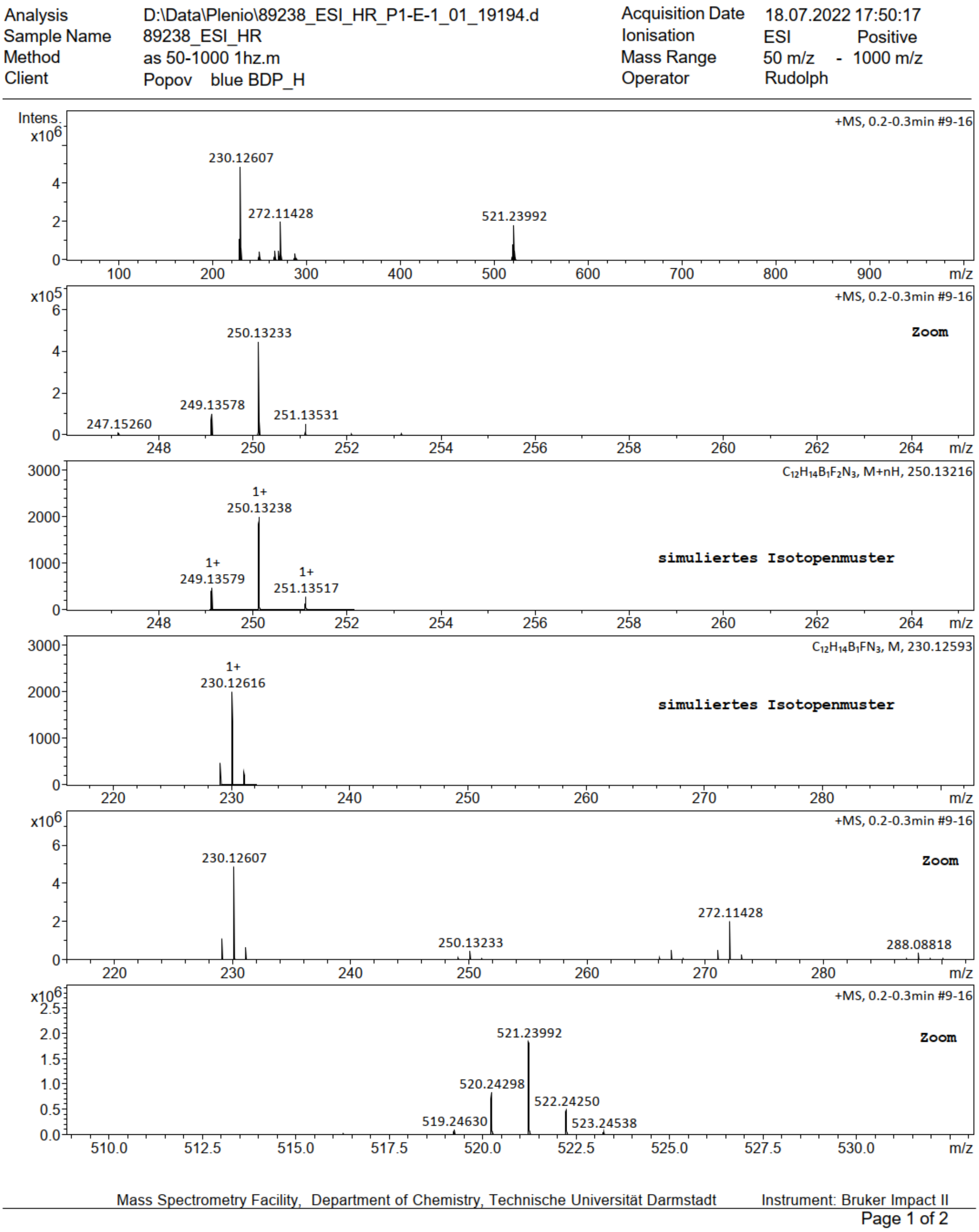
Figure S 145 HRMS spectrum of **20**. (ESI Negative)

Analysis	D:\Data\Plenio\89123_ESI_HR_P1-E-1_01_18728.d	Acquisition Date	23.06.2022 13:09:59
Sample Name	89123_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000.m	Mass Range	50 m/z - 3000 m/z
Client	Popov IMesAuCl comp.w. alkyl-NH-bodipy	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e$^-$ Conf	z
1	945.4486	945.4487	C44H59AuFN9O	M+H	C44H58AuFN9O	0.1	0.1	5.3	odd	1+
2	945.4486	945.4475	C47H58AuN9	M+H	C47H57AuN9	1.0	1.1	22.6	odd	1+
3	945.4486	945.4485	C40H64AuF2N5O6	M+H	C40H63AuF2N5O6	0.1	0.1	24.2	odd	1+
4	945.4486	945.4489	C49H60AuN6O	M+H	C49H59AuN6O	0.3	0.3	29.5	even	1+
5	945.4486	945.4485	C47H61AuBF2N3O2	M+H	C47H60AuBF2N3O2	0.7	0.8	45.4	odd	1+
6	945.4486	945.4496	C55H57F2N9O4	M+H	C55H56F2N9O4	1.0	1.1	76.3	odd	1+
7	945.4486	945.4483	C61H58BF2N3O4	M+H	C61H57BF2N3O4	0.7	0.7	80.0	odd	1+
8	945.4486	945.4485	C58H56FN9O3	M+H	C58H55FN9O3	0.1	0.1	85.0	odd	1+
9	945.4486	945.4487	C63H57N6O3	M+H	C63H56N6O3	0.1	0.1	108.8	even	1+
10	945.4486	945.4496	C62H54BF2N7	M+H	C62H53BF2N7	2.1	2.2	580.1	odd	1+

Figure S 146 HRMS spectrum of **20**. (ESI Positive)



Analysis	D:\Data\Plenio\89238_ESI_HR_P1-E-1_01_19194.d	Acquisition Date	18.07.2022 17:50:17
Sample Name	89238_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Popov blue BDP_H	Operator	Rudolph

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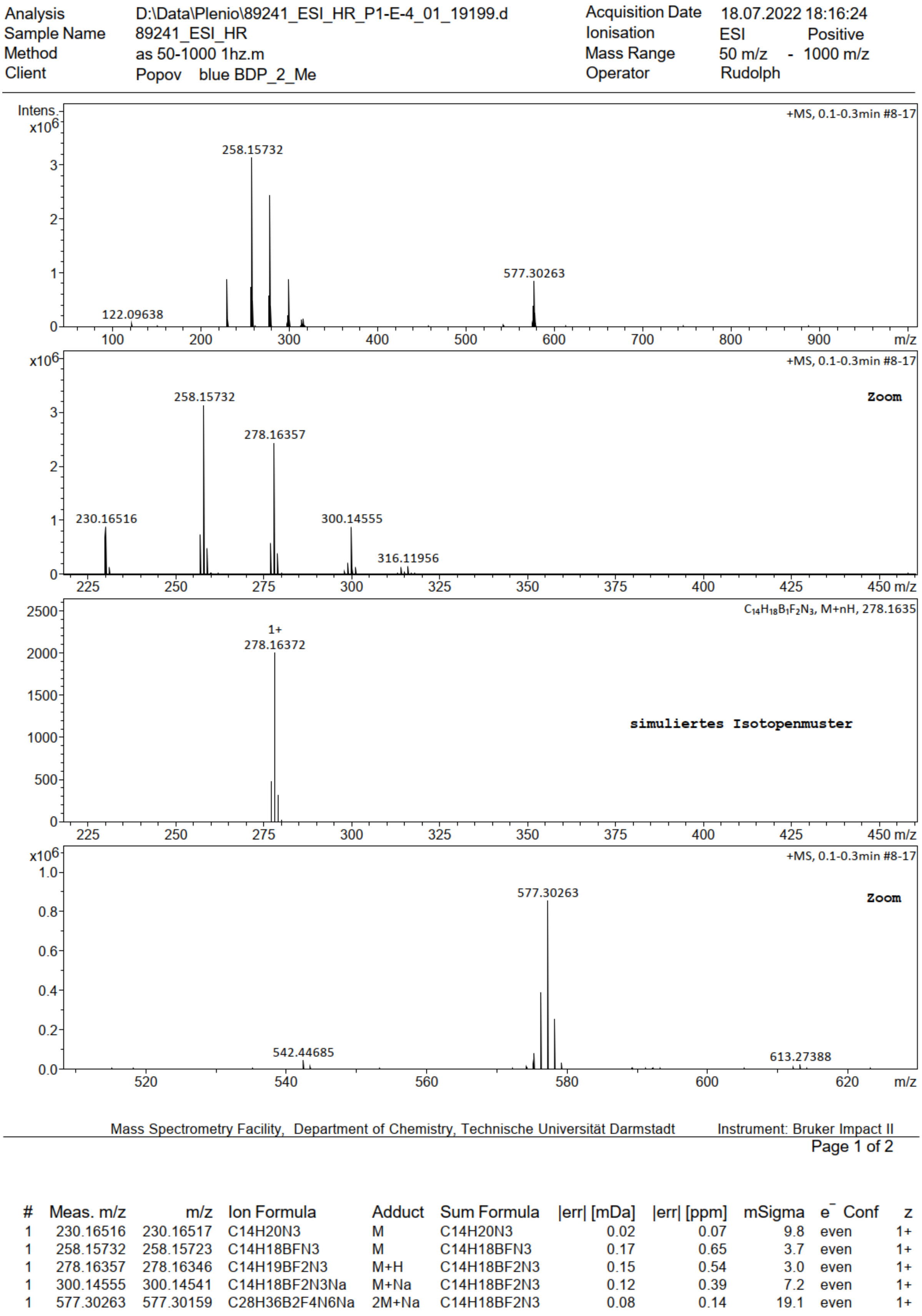
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	230.12607	230.12593	C12H14BFN3	M	C12H14BFN3	0.09	0.37	7.0	even	1+
1	250.13233	250.13216	C12H15BF2N3	M+H	C12H14BF2N3	0.06	0.23	11.7	even	1+
1	272.11428	272.11411	C12H14BF2N3Na	M+Na	C12H14BF2N3	0.05	0.17	4.6	even	1+
1	521.23992	521.23899	C24H28B2F4N6Na	2M+Na	C12H14BF2N3	0.10	0.18	2.2	even	1+

Figure S 147 HRMS spectrum of **B1**. (ESI Positive)



Analysis	D:\Data\Plenio\89241_ESI_HR_P1-E-4_01_19199.d	Acquisition Date	18.07.2022 18:16:24
Sample Name	89241_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Popov blue BDP_2_Me	Operator	Rudolph

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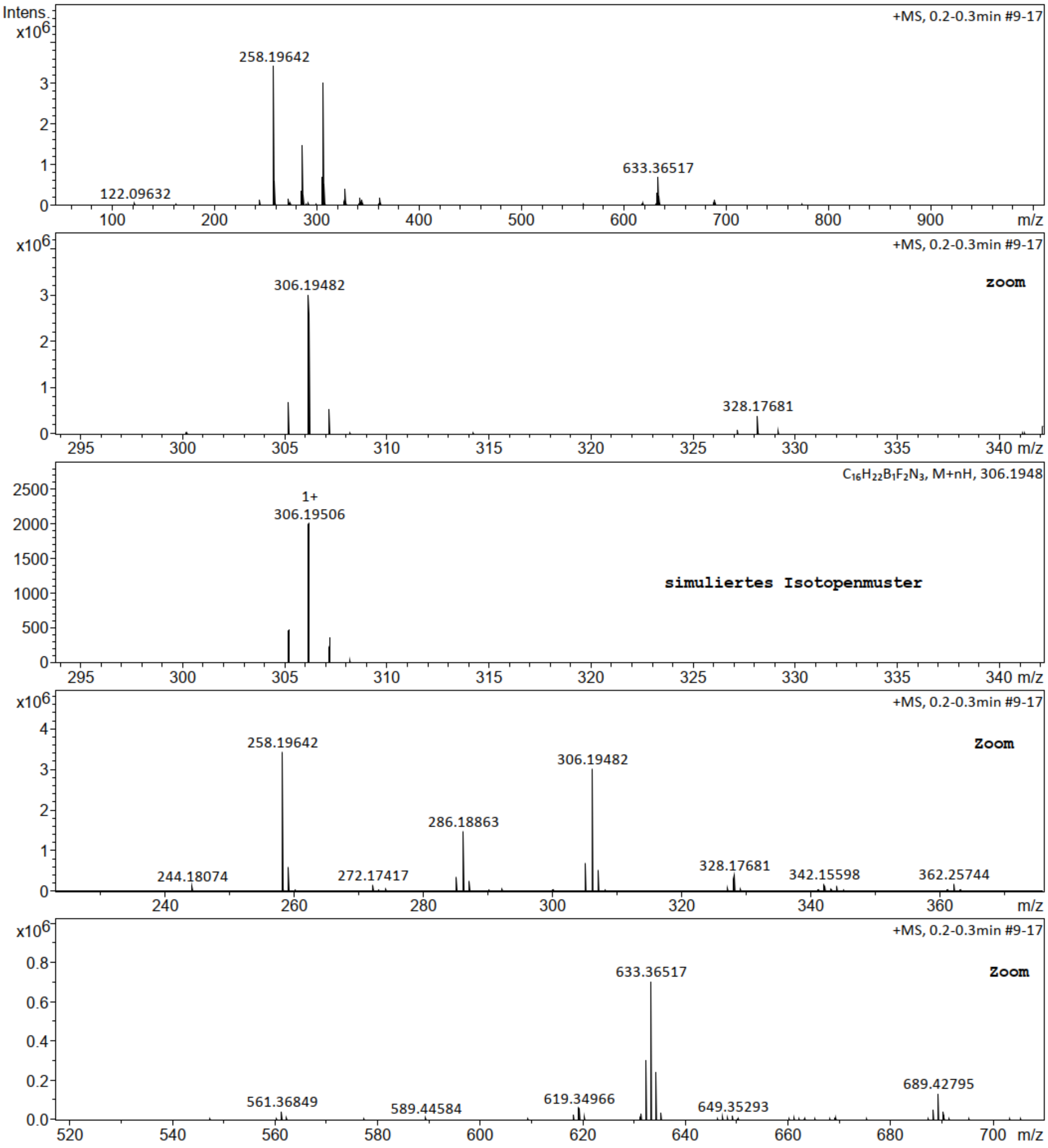
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	230.16516	230.16517	C14H20N3	M	C14H20N3	0.02	0.07	9.8	even	1+
1	258.15732	258.15723	C14H18BFN3	M	C14H18BFN3	0.17	0.65	3.7	even	1+
1	278.16357	278.16346	C14H19BF2N3	M+H	C14H18BF2N3	0.15	0.54	3.0	even	1+
1	300.14555	300.14541	C14H18BF2N3Na	M+Na	C14H18BF2N3	0.12	0.39	7.2	even	1+
1	577.30263	577.30159	C28H36B2F4N6Na	2M+Na	C14H18BF2N3	0.08	0.14	19.1	even	1+

Figure S 148 HRMS spectrum of **B2**. (ESI Positive)

Analysis D:\Data\Plenio\89240_ESI_HR_P1-E-3_01_19198.d
Sample Name 89240_ESI_HR
Method as 50-1000 1hz.m
Client Popov blue BDP_4_Me

Acquisition Date 18.07.2022 18:13:16
Ionisation ESI Positive
Mass Range 50 m/z - 1000 m/z
Operator Rudolph



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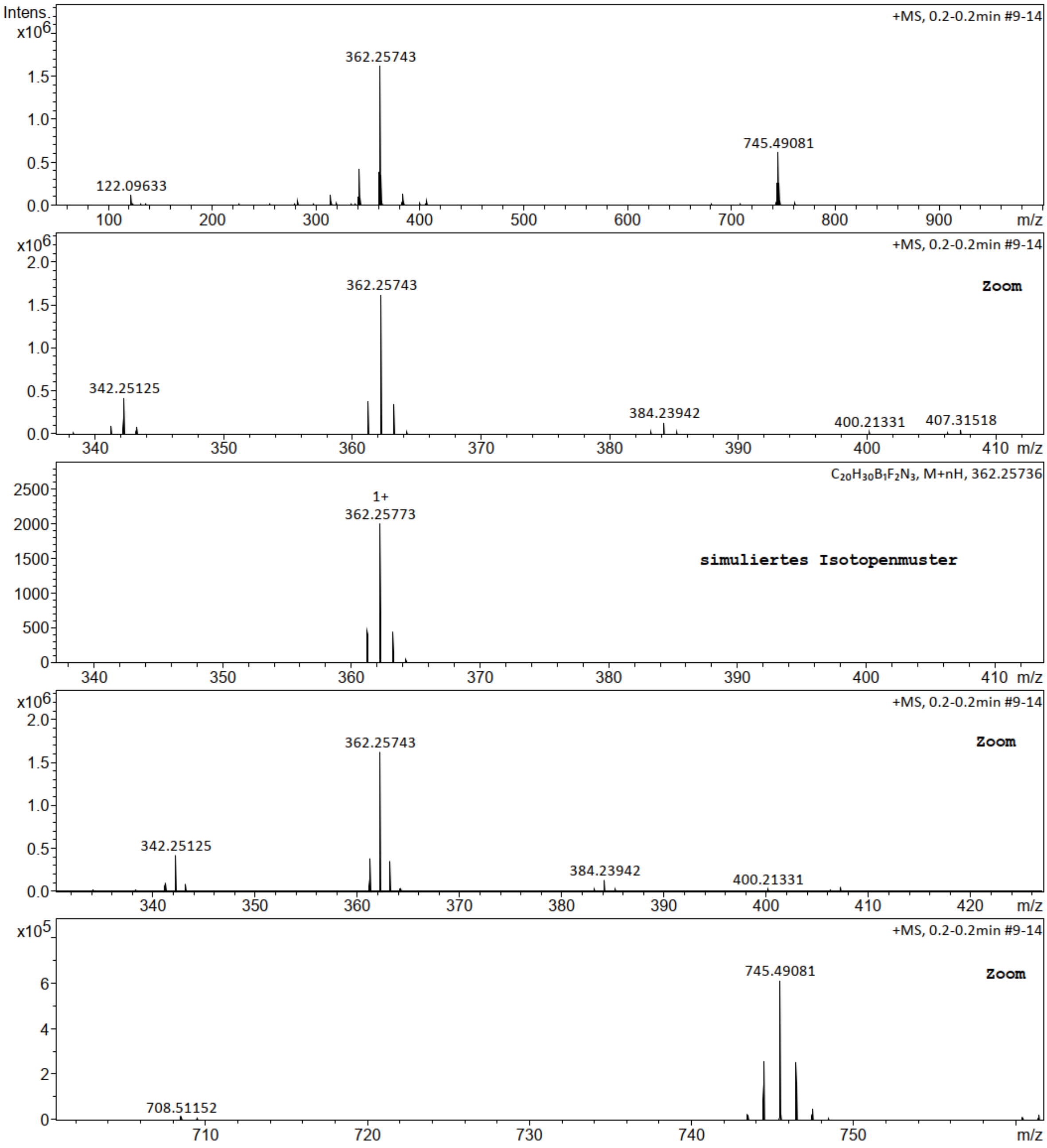
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	258.19642	258.19647	C16H24N3	M	C16H24N3	0.06	0.22	6.3	even	1+
1	286.18863	286.18853	C16H22BFN3	M	C16H22BFN3	0.20	0.70	5.1	even	1+
1	306.19482	306.19476	C16H23BF2N3	M+H	C16H22BF2N3	0.24	0.78	2.6	even	1+
1	328.17681	328.17671	C16H22BF2N3Na	M+Na	C16H22BF2N3	0.19	0.59	9.3	even	1+
1	633.36517	633.36419	C32H44B2F4N6Na	2M+Na	C16H22BF2N3	0.10	0.16	5.4	even	1+

Figure S 149 HRMS spectrum of **B3**. (ESI Positive)

Analysis	D:\Data\Plenio\89239_ESI_HR_P1-E-2_01_19197.d	Acquisition Date	18.07.2022 18:11:45
Sample Name	89239_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Popov NH_BDP_(dimethylethyl)	Operator	Rudolph



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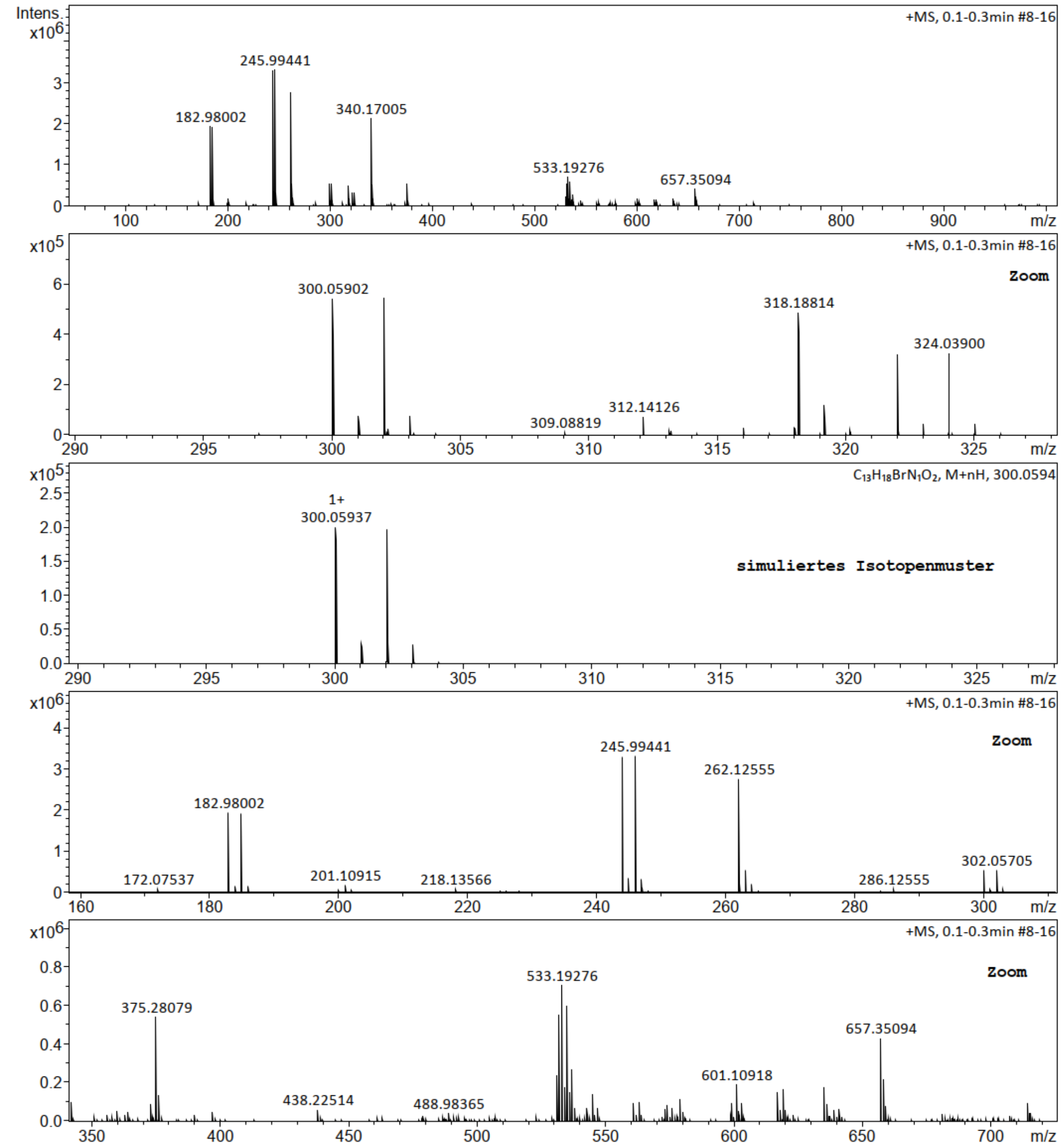
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e^- Conf	z
1	342.25125	342.25113	C20H30BFN3	M	C20H30BFN3	0.25	0.72	8.8	even	1+
1	362.25743	362.25736	C20H31BF2N3	M+H	C20H30BF2N3	0.29	0.81	5.5	even	1+
1	384.23942	384.23931	C20H30BF2N3Na	M+Na	C20H30BF2N3	0.25	0.64	20.4	even	1+
1	745.49081	745.48939	C40H60B2F4N6Na	2M+Na	C20H30BF2N3	0.10	0.14	6.9	even	1+

Figure S 150 HRMS spectrum of **B4**. (ESI Positive)

Analysis	D:\Data\Plenio\88985_ESI_HR_P1-E-4_01_18308.d	Acquisition Date	03.06.2022 12:54:48
Sample Name	88985_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Popov 4_Bromo_phenethyl_carbamate	Operator	Rudolph



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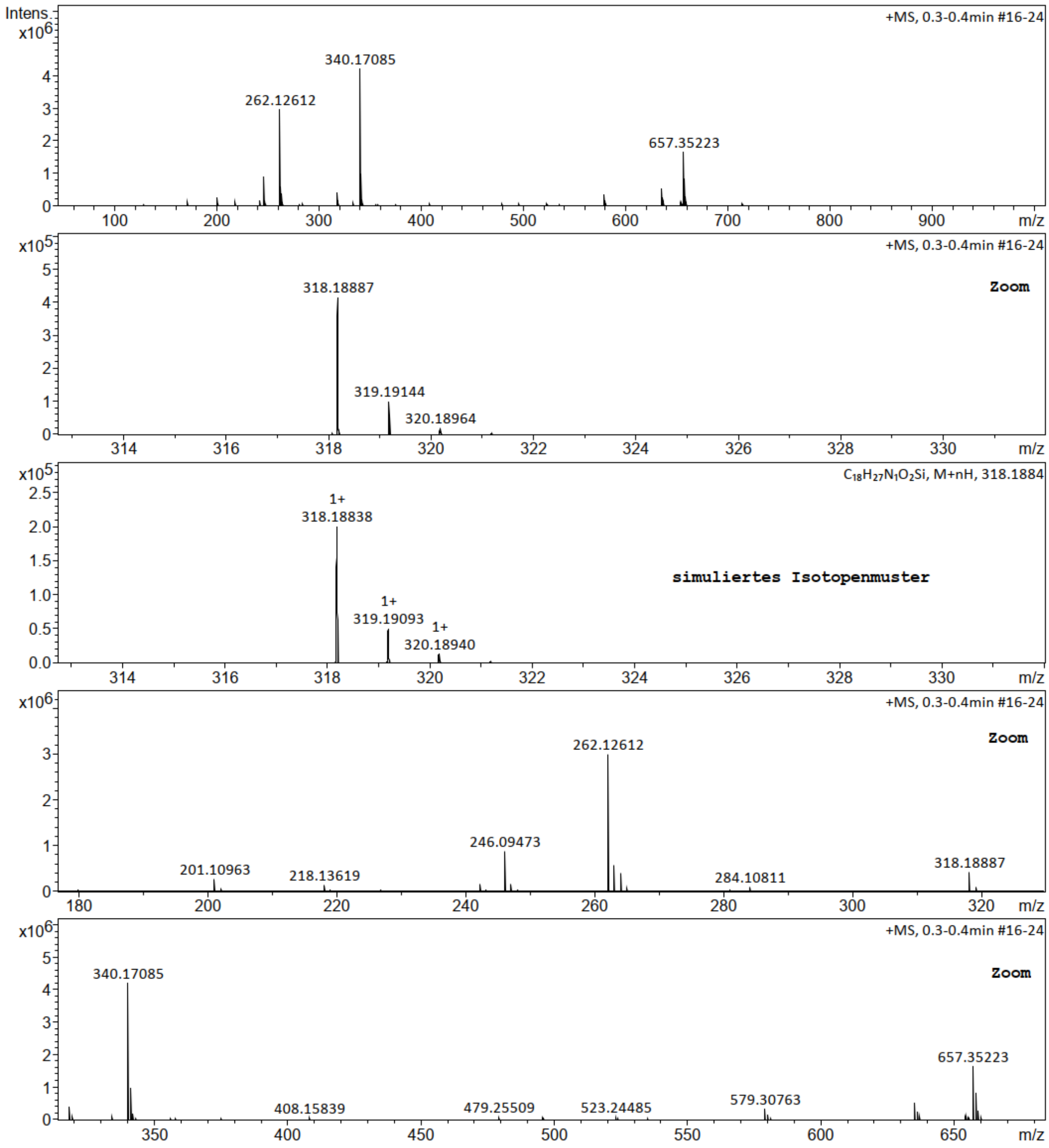
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	182.98002	182.98039	C8H8Br	M	C8H8Br	0.37	2.02	1.7	even	1+
1	243.99639	243.99677	C9H11BrNO2	M	C9H11BrNO2	0.38	1.56	10.2	even	1+
1	300.05902	300.05937	C13H19BrNO2	M+H	C13H18BrNO2	0.35	1.16	7.2	even	1+
1	322.04094	322.04131	C13H18BrNNaO2	M+Na	C13H18BrNO2	0.37	1.16	10.1	even	1+

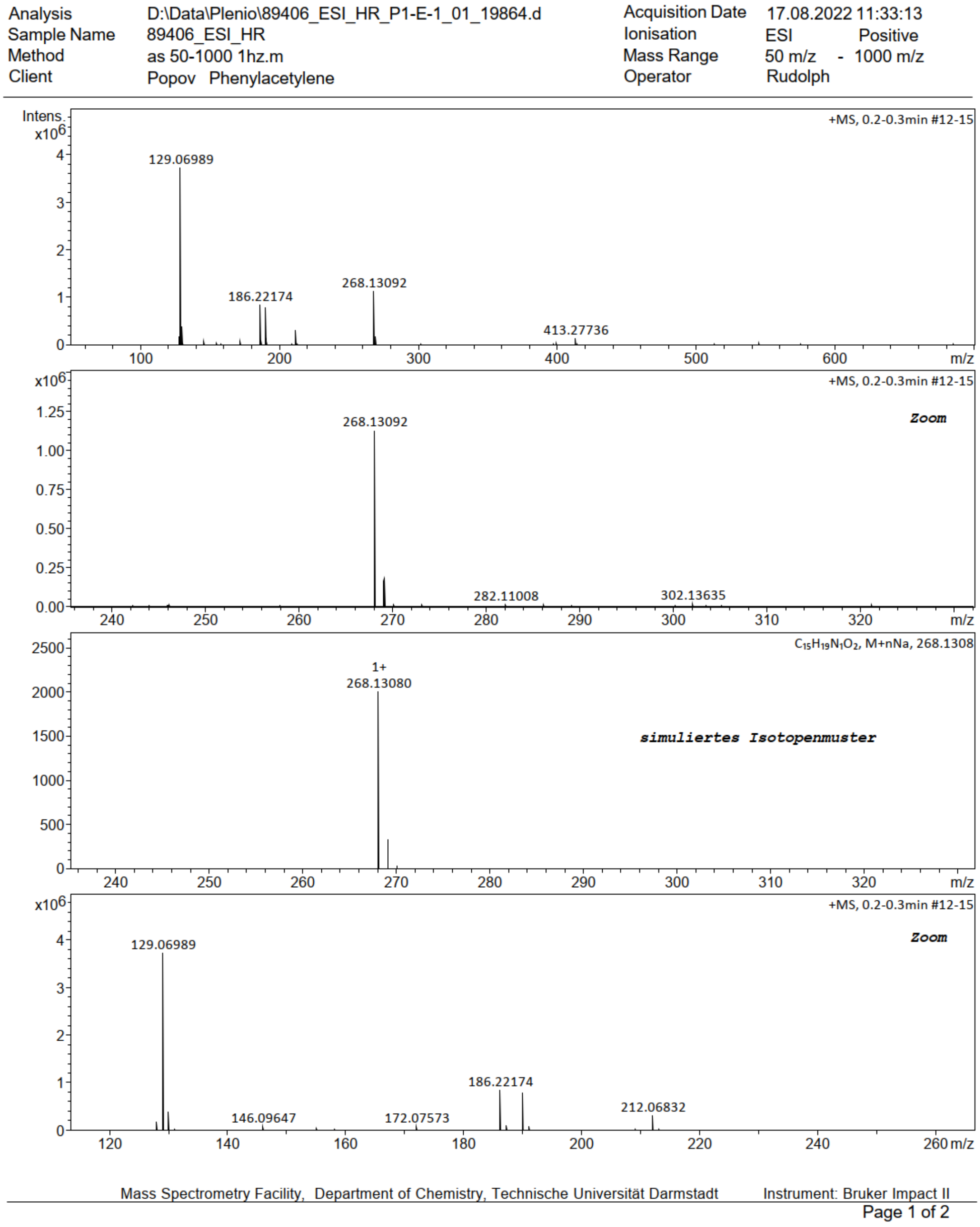
Figure S 151 HRMS spectrum of *tert*-butyl (4-bromophenethyl)carbamate. (ESI Positive)

Analysis	D:\Data\Plenio\88984_ESI_HR_P1-E-2_01_18310.d	Acquisition Date	03.06.2022 13:06:32
Sample Name	88984_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Popov 4_TMS ethynyl_phenethyl_carbamate	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	262.12612	262.12578	C14H20NO2Si	M	C14H20NO2Si	0.34	1.30	13.3	even	1+
1	318.18887	318.18838	C18H28NO2Si	M+H	C18H27NO2Si	0.49	1.53	13.4	even	1+
1	340.17085	340.17033	C18H27NNaO2Si	M+Na	C18H27NO2Si	0.52	1.53	12.9	even	1+
1	657.35223	657.35143	C36H54N2NaO4Si2	2M+Na	C18H27NO2Si	0.80	1.22	9.1	even	1+

Figure S 152 HRMS spectrum of *tert*-butyl (4-((trimethylsilyl)ethynyl)phenethyl)carbamate. (ESI Positive)



Analysis	D:\Data\Plenio\89406_ESI_HR_P1-E-1_01_19864.d	Acquisition Date	17.08.2022 11:33:13
Sample Name	89406_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Popov Phenylacetylene	Operator	Rudolph

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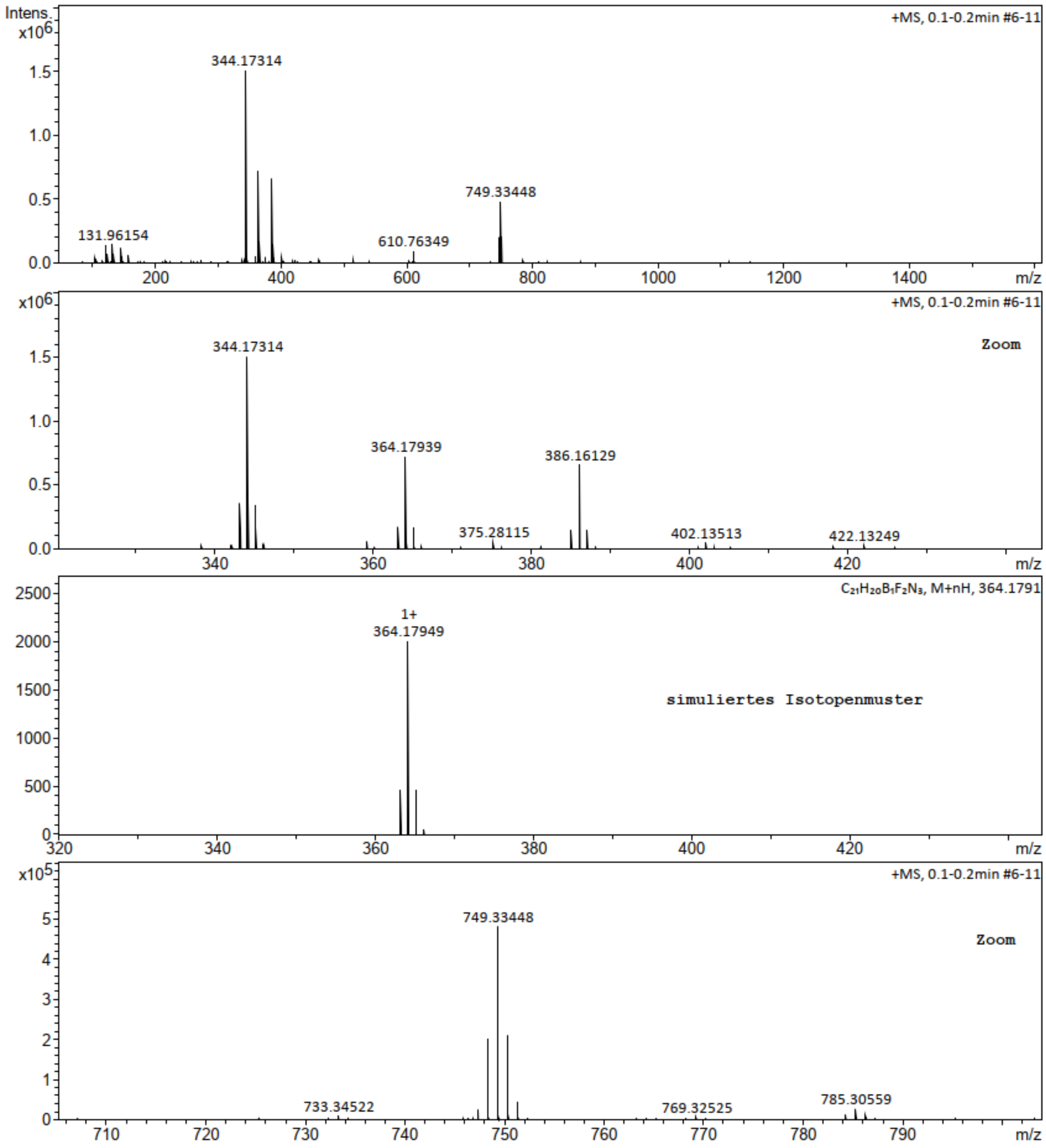
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e¯ Conf	z
1	268.13092	268.13080	C15H19NNaO2	M+Na	C15H19NO2	0.12	0.45	4.2	even	1+

Figure S 153 HRMS spectrum of *tert*-butyl (4-ethynylphenethyl)carbamate. (ESI Positive)

Analysis	D:\Data\Plenio\88712_ESI_HR_P1-E-3_01_17583.d	Acquisition Date	05.05.2022 15:50:14
Sample Name	88712_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Popov Blue BODipy_acetylene	Operator	Rudolph



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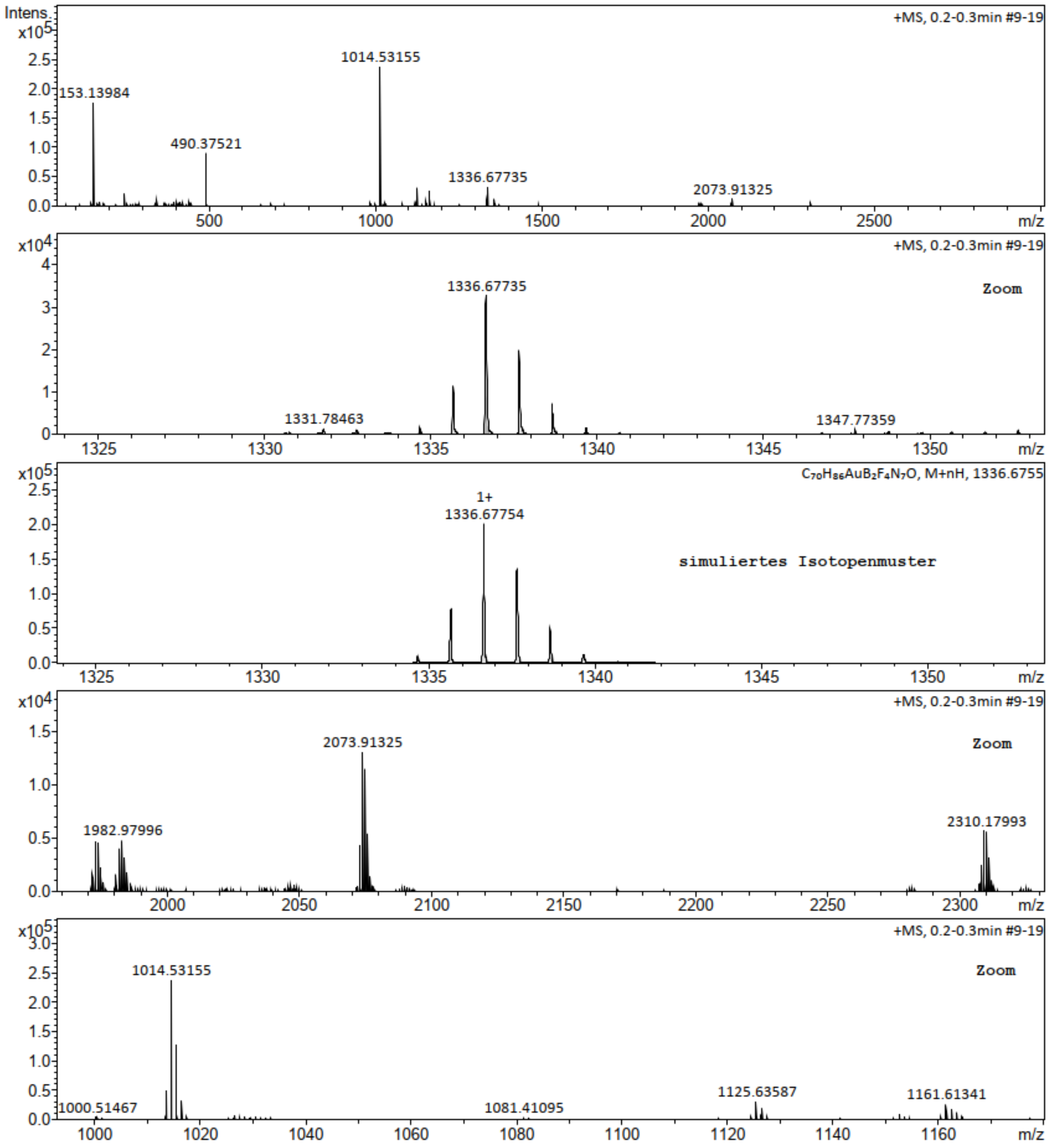
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	344.17314	344.17288	C21H20BFN3	M	C21H20BFN3	0.12	0.35	3.9	even	1+
1	364.17939	364.17911	C21H21BF2N3	M+H	C21H20BF2N3	0.10	0.29	2.9	even	1+
1	386.16129	386.16106	C21H20BF2N3Na	M+Na	C21H20BF2N3	0.14	0.36	4.2	even	1+
1	749.33448	749.33289	C42H40B2F4N6Na	2M+Na	C21H20BF2N3	0.23	0.31	2.4	even	1+

Accurate Mass Measurement

Figure S 154 HRMS spectrum of **21**. (ESI Positive)

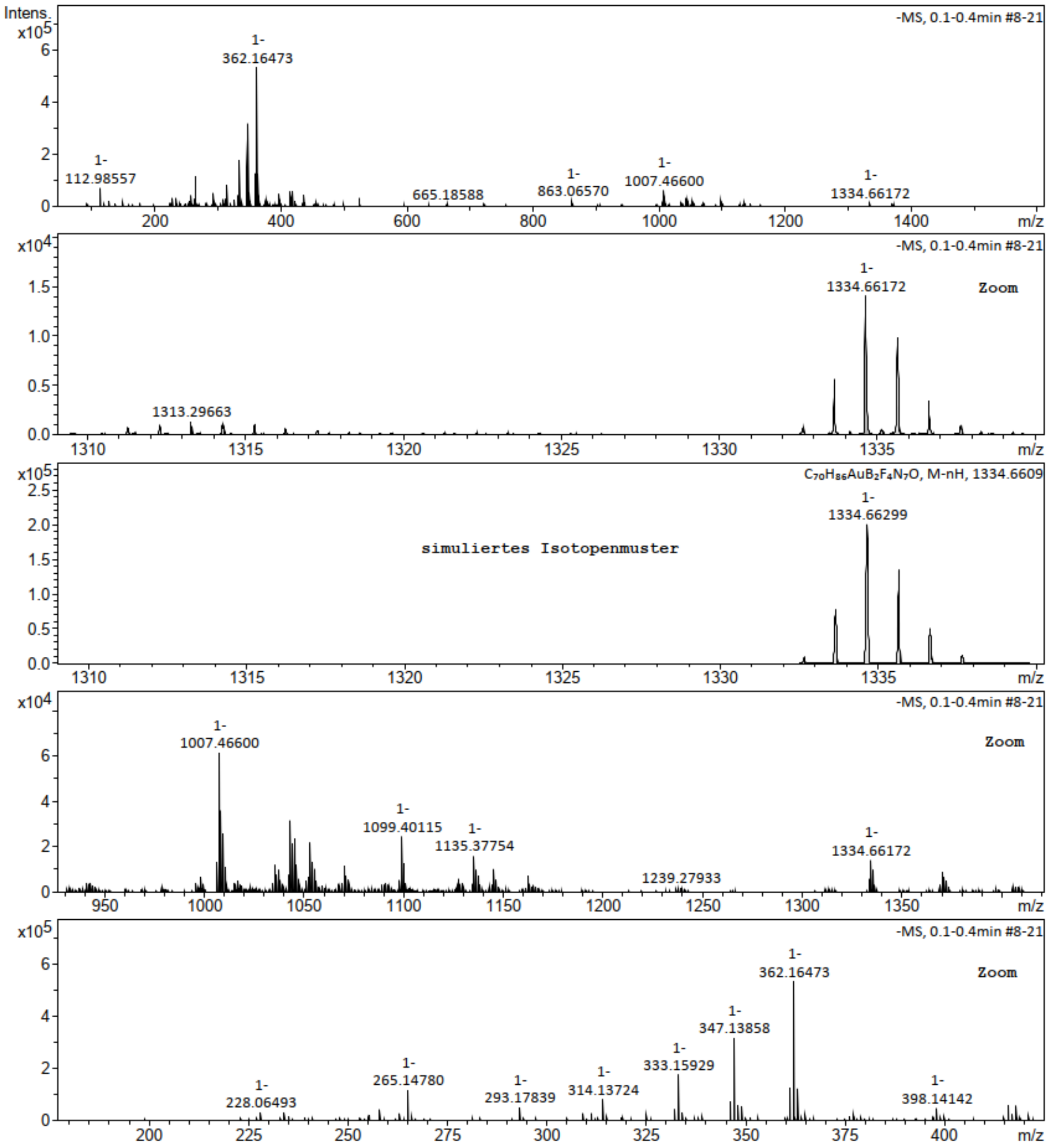
Analysis	D:\Data\Plenio\89121_ESI_HR_P1-E-2_01_18733.d	Acquisition Date	23.06.2022 13:46:34	
Sample Name	89121_ESI_HR	Ionisation	ESI	Positive
Method	as 50-3000.m	Mass Range	50 m/z -	3000 m/z
Client	Popov blue-green acetylide	Operator	Rudolph	



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e$^-$ Conf	z
1	1336.67735	1336.67730	C58H91AuB2F4N9O8	M+H	C58H90AuB2F4N9O8	1.77	1.32	24.6	even	1+
2	1336.67735	1336.67545	C70H87AuB2F4N7O	M+H	C70H86AuB2F4N7O	0.19	0.14	30.4	even	1+

Figure S 155 HRMS spectrum of **22·dbu**. (ESI Positive)

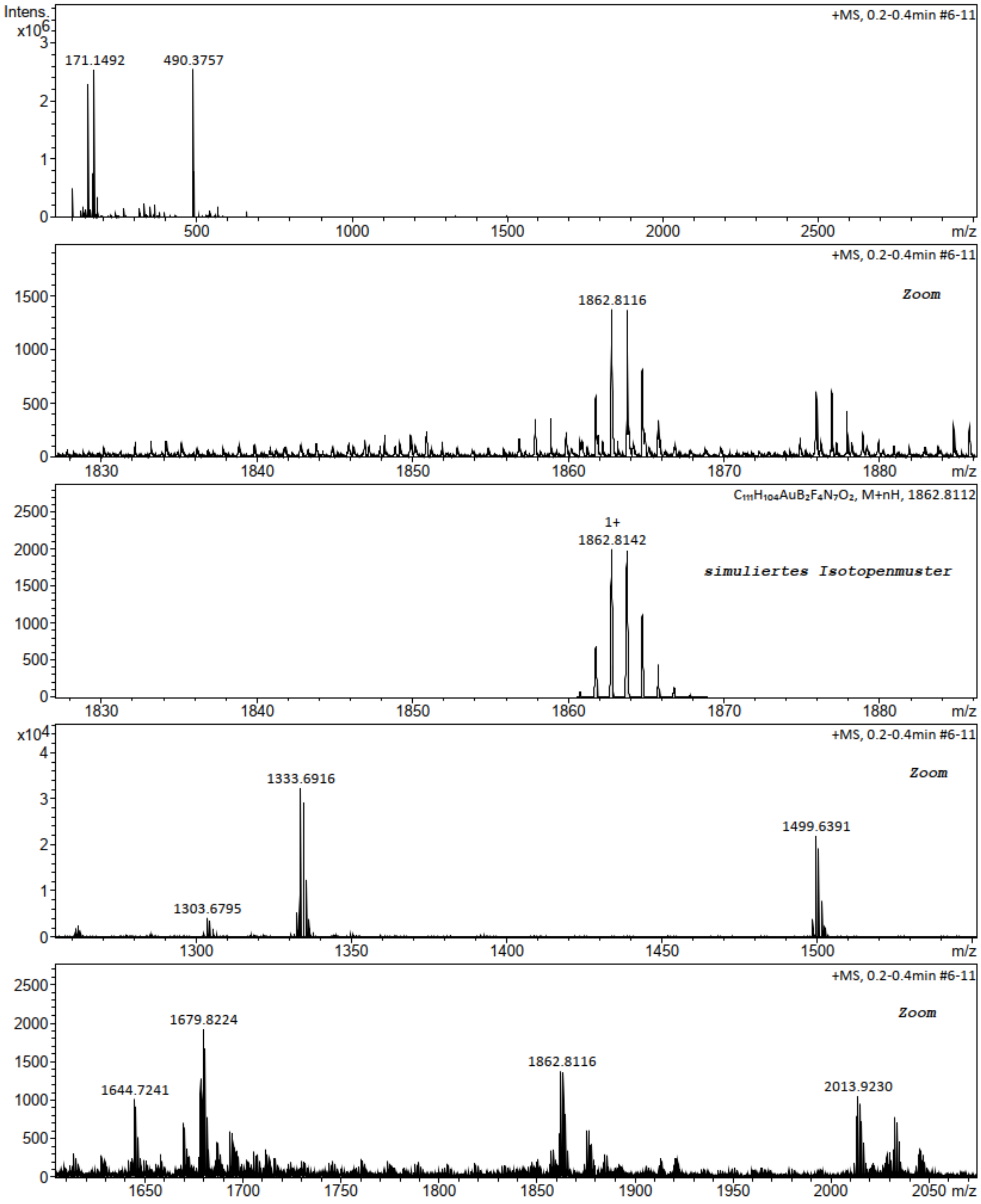
Analysis	D:\Data\Plenio\89121_neg_ESI_HR_P1-E-2_01_18781.d	Acquisition Date	24.06.2022 14:01:29
Sample Name	89121_neg_ESI_HR	Ionisation	ESI Negative
Method	as 50-1600 1hz negative.m	Mass Range	50 m/z - 1600 m/z
Client	Popov blue-green acetylide	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	1334.66172	1334.66090	C70H85AuB2F4N7O	M-H	C70H86AuB2F4N7O	1.26	0.95	13.5	even	1-
2	1334.66172	1334.65688	C65H85AuB2F4N9O3	M-H	C65H86AuB2F4N9O3	2.87	2.15	24.4	even	1-

Figure S 141 HRMS spectrum of **22·dbu.** (ESI Negative)

Analysis	D:\Data\Plenio\89477_ESI_HR_P1-E-1_01_20287.d	Acquisition Date	30.08.2022 13:35:12
Sample Name	89477_ESI_HR	Ionisation	ESI Positive
Method	as 50-3000_tune.m	Mass Range	50 m/z - 3000 m/z
Client	Popov blue_red 24 dbu	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e^- Conf	z
1	1862.8116	1862.8112	C111H105AuB2F4N7O2	M+H	C111H104AuB2F4N7O2	2.5	1.4	409.4	even	1+

Figure S 156 HRMS spectrum of **24·dbu**. (ESI Positive)

[1] T. Kowada, S. Yamaguchi and K. Ohe, *Org. Lett.* **2010**, *12*, 296–299.

[2] S. Popov, H. Plenio, *Eur. J. Inorg. Chem*. **2021**, *22*, 3708-3718.

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