Supporting Information

A Highly Stable, Au/Ru Heterobimetallic Photoredox Catalyst with a [2.2]Paracyclophane backbone

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Contents

1 General Information

^{1}H NMR spectra were recorded on a Bruker AM 400 (400 MHz), a Bruker DRX 500 (500 MHz) or on a Bruker Avance 600 (600 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm) as internal standard. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of dd, dt = doublet of triplet, td = triplet of doublet, bs = broad singlet, m = multiplet. The spectra were analyzed according to first order. – ^{13}C NMR spectra were recorded on a Bruker AM 400 (100 MHz), a Bruker DRX 500 (125 MHz) or on a Bruker Avance 600 (150 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CDCl_3$ (77.0 ppm) as internal standard. – MS (EI) (electron impact mass spectrometry) and MS (FAB) (fast atom bombardment): Finnigan MAT 90 (70 eV). The peaks are given as mass-to-charge-ratio (*m*/*z*). The molecule peak is given as $[M]^+$. For the high resolution mass, the following abbreviations were used: calc.= theoretical calculated mass; found = mass found in analysis. – IR (infrared spectroscopy): FT-IR Bruker IFS 88 and Bruker alpha. IR spectra of solids were recorded in KBr or by ATR technique (ATR = Attenuated Total Reflection), and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1} between 3600 cm^{-1} and 500 cm^{-1}. Band intensities were characterized as follows: vs = very strong (0 - 10% transmission (T)), s = strong (11 - 30% T), m = medium (31 - 70% T), w = weak (71 - 90% T), vw = very weak (91 - 100% T).– Routine monitoring of reactions was performed using Silica gel coated aluminum plates (*Merck*, silica gel 60, F254), which were analyzed under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from *Aldrich*, *Fluka*, *Carbolution*, *ChemPur*, *ABCR*, *TCI* and *Fisher Scientific*. Dry solvents were obtained from an mbraun SPS800. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried and/or flame dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise. Air- or moisture- sensitive reactions were carried out under an argon atmosphere in previously evacuated and heated glass ware. Liquids were transferred with plastic syringes and steel cannula. Solids were used as powders. Reaction control was performed by thin layer chromatography. Solvents were removed at 40 °C at the rotavapor. If not stated otherwise, crude products were purified by flash chromatography with Silica gel 60 (0.040 × .063 mm, Geduran®) (*Merck*) which was used as stationary phase and solvents of *p.a*. quality were used as mobile phase.

2 Experimental Procedures and Analytical Data

Materials

(*rac*)-4-phenylpyridine[2.2]paracyclophane,[1] 4-bromo[2.2]paracyclophane,[1] **1**,[3] and (tht)AuCl[4] were synthesized according to literature procedures. All other chemicals were purchased from Sigma Aldrich, Merck, Fluorochem, abcr, Alfa Aesar, TCI or fisher chemicals and used without further purification. # All procedures were carried out following standard Schlenk techniques.

4-diphenylphosphine gold(I) chloride[2.2]paracyclophane (PCP-Au)
In a flame-dried Schlenk tube, 4-bromo[2.2]paracyclophane (100 mg, 348 µmol, 1.00 equiv.) was dissolved in dry and degassed THF (70.0 mM). A solution of n-BuLi in n-hexanes (139 µL, 348 µmol, 1.00 equiv.) was added dropwise at –78 °C. After 30 minutes, chlorodiphenylphosphine (77 µL, 62.5 µmol, 1.00 equiv.) was added dropwise. The reaction was slowly allowed to warm up to r.t. over 2 h. In an argon counter-current (tht)gold(I)chloride (112 mg, 348 µmol, 1.00 equiv.) was added to the mixture and stirred for 2 hours at r.t. in the

dark. After removal of the solvent the crude residue was purified by column chromatography to afford the title compound as a white solid (115 mg, 53%).

R_f = 0.16 (pentane/ethyl acetate 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 – 7.52 (m, 4H), 7.51 – 7.44 (m, 5H), 7.37 (td, *J* = 7.7, 2.8 Hz, 2H), 6.65 – 6.57 (m, 3H), 6.52 (dd, *J* = 7.7, 5.4 Hz, 1H), 6.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.93 (dd, *J* = 14.8, 1.8 Hz, 1H), 3.82 (ddd, *J* = 12.8, 10.7, 4.0 Hz, 1H), 3.73 (dddd, *J* = 12.1, 10.8, 2.8, 1.3 Hz, 1H), 3.13 – 2.84 (m, 5H), 2.71 (ddd, *J* = 13.3, 10.3, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.5, 144.4, 140.6, 140.5, 139.3, 137.0, 136.9, 136.4, 136.4, 136.3, 136.2, 135.2, 135.1, 134.1, 134.0, 133.0, 132.4, 132.2, 132.1, 132.0, 132.0, 131.9, 131.9, 131.9, 130.6, 130.1, 129.3, 129.2, 129.0, 128.9, 128.7, 126.4, 125.9, 35.1, 35.1, 34.7, 34.6. IR (ATR: $\tilde{\nu}$ = 2948, 2922, 2890, 2850, 1479, 1435, 1409, 1392, 1181, 1099, 1027, 997, 899, 847, 793, 747, 718, 708, 691, 637, 579, 547, 507, 490, 463, 442, 429 cm^{-1}.

4-(((Bis(2,2'-bipyridyl)4-(2'-pyridyl)phenyl) ruthenium (II))[2.2]paracyclophane (PCP-Ru)
A solution of [Ru(bpy)$_2$Cl$_2$] (100 mg, 199 µmol, 1.00 equiv.), (*rac*)-4-phenylpyridine[2.2]paracyclophane (216 mg, 597 µmol, 3.00 equiv.) and silver tetrafluoroborate (80.2 mg, 412 µmol, 2.07 equiv.) in dichloromethane (16 mL) was heated to reflux for 5 h. The solution was cooled to room temperature, filtered through Celite and the solvent was removed under reduced pressure. The solid was taken up in acetonitrile and ammonium hexafluorophosphate (97.3 mg, 597 µmol, 3.00 equiv.) in methanol (1.40 mL) was added. The solvent was removed under reduced pressure and the crude solid was purified by column chromatography (silica, DCM/MeCN, 15:1) to yield [Ru(bpy)$_2$(PCP-ppy)]PF$_6$ (85.0 mg, 46%) as a diastereomeric mixture of a deep red solid.
^{1}H NMR [diastereomeric mixture – double signal set] (500 MHz, Acetonitrile-d_3): δ = 8.52 – 8.48 (m, 2H), 8.47 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.45 – 8.39 (m, 3H), 8.27 – 8.21 (m, 3H), 8.18 – 8.15 (m, 1H), 8.06 – 7.89 (m, 9H), 7.88 – 7.75 (m, 7H), 7.75 – 7.65 (m, 4H), 7.57 (t, *J* = 5.5 Hz, 2H), 7.47 (qd, *J* = 5.9, 5.3, 2.7 Hz, 2H), 7.35 – 7.23 (m, 5H), 7.19 (ddd, *J* = 7.2, 5.5, 1.3 Hz, 1H), 6.88 (q, *J* = 7.9, 7.5 Hz, 2H), 6.68 (d, *J* = 23.6 Hz, 2H), 6.57 (ddd, *J* = 7.8, 4.5, 1.9 Hz, 2H), 6.53 – 6.41 (m, 6H), 6.37 (d, *J* = 1.8 Hz, 1H), 6.33 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.16 (d, *J* = 1.8 Hz, 1H), 6.06 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.00 (dd, *J* = 7.8, 1.9 Hz, 1H), 5.94 (dd, *J* = 7.8, 1.9 Hz, 1H), 3.36 – 3.20 (m, 2H), 3.10 – 2.93 (m, 6H), 2.89 – 2.68 (m, 6H), 2.46 – 2.37 (m, 1H), 2.30 – 2.21 (m, 1H). ^{13}C NMR: δ = [diastereomeric mixture – double signal set] (126 MHz, CD_3CN) δ 159.0, 159.0, 158.2, 158.1, 158.0, 157.9, 156.3, 156.2, 155.5, 155.4, 151.7, 151.6, 151.4, 151.3, 151.1, 151.0, 143.7, 143.6, 140.6, 140.6, 140.6, 140.5, 140.4, 138.0, 137.8, 137.4, 136.8, 136.8, 136.5, 136.5, 136.0, 136.0, 134.9, 134.9, 134.7, 133.9, 133.8, 133.6, 133.5, 133.0, 132.9, 132.7, 132.7, 132.5, 132.3, 130.6, 130.4, 129.9, 129.2, 128.2, 128.1, 127.5, 127.4, 127.2, 126.8, 126.7, 124.5, 124.4, 124.2, 124.1, 124.1, 124.0, 123.8, 123.6, 123.4, 122.2, 120.1, 120.1, 35.9, 35.9, 35.7, 35.6, 35.4, 35.3, 35.3, 35.2. IR (ATR: cm^{-1}) $\tilde{\nu}$ = 2921, 2851, 1596, 1572, 1554, 1459, 1441, 1419, 1360, 1309, 1256, 1242, 1157, 1057, 1027, 1014, 1001, 878, 832, 782, 755, 727, 673, 652, 555, 518, 510, 487, 419. HRMS ($C_{47}H_{38}N_5Ru$) calc.: 774.2165; found: 774.2153.

4,16-dibromo[2.2]paracyclophane (1)
In a 500 mL three-necked flask iron powder (241 mg , 4.32 mmol, 4.5 mol%) was placed. In a dropping funnel a mixture of bromine (10.3 mL, 201 mmol, 2.10 equiv.) in dichloromethane (80 mL) was placed. Then 15 mL of this solution was added to the iron powder and stirred for 2 hours. The solution was diluted with dichloromethane (100 mL). and [2.2]paracyclophane (20.0 g 96.0 mmol, 1.00 equiv.) was added portion-wise. After 30 minutes, the remaining bromine solution was added over 5 hours and the resulting solution was stirred for 3 days. Then saturated aqueous sodium sulfite solution (100 mL) was added and stirred until the organic phase turned colourless. The precipitate was filtered, washed with water, re-dissolved in boiling toluene (150 mL), filtered and left for crystallization overnight. After filtration and drying at 60 °C the title compound was obtained as a white solid (6.82 g, 18.6 mmol, 19%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 3.49 (ddd, *J* = 12.8, 10.3, 2.0 Hz, 1H), 3.16 (ddd, *J* = 12.1, 10.2, 4.6 Hz, 1H), 3.02 – 2.78 (m, 2H).

The analytical data is in agreement with the data reported in literature.[3]

4-Bromo-16-diphenylphosphoryl[2.2]paracyclophane (2)
A 500 mL Schlenk flask was charged with 4,16-dibromo[2.2.]paracyclophane (1.50 g, 4.10 mmol, 1.00 equiv.) and dry THF (100 mL). The reaction mixture was cooled to –78 °C and *n*-BuLi (2.00 mL, 4.92 mmol, 1.20 equiv.) was added dropwise *via* syringe. The solution became pink in color and faded to a pale yellow. This step was allowed to proceed for 30 min. Then chlorodiphenylphosphine (1.51 mL, 1,81 g, 8.20 mmol, 2.00 equiv.) was added. The mixture was stirred overnight and allowed to warm slowly to room temperature.

After the mixture was quenched with a saturated solution of NH_4Cl, the mixture was extracted with ethyl acetate (3×50 mL). The organic layers were washed with brine, dried over $MgSO_4$ and the solvents removed under reduced pressure. The residue was resolved in dichloromethane (100 mL) and H_2O_2 (35% aq. solution, 7.50 mL, 73.8 mmol, 18.0 equiv.) was added and stirred overnight. Purification *via* column chromatography (silica, CH/EA 3:1) yielded the title compound as a white solid (1.42 g, 71%).

m.p. 211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 – 7.63 (m, 2H), 7.58 – 7.43 (m, 6H), 7.42 – 7.34 (m, 2H), 7.29 (td, J = 7.9, 1.9 Hz, 2H), 6.60 (d, J = 1.7 Hz, 1H), 6.55 (dd, J = 7.7, 4.2 Hz, 1H), 6.28 – 6.25 (m, 1H), 6.25 – 6.20 (m, 1H), 3.62 – 3.51 (m, 1H), 3.50 – 3.35 (m, 2H), 3.26 – 3.04 (m, 1H), 2.98 – 2.68 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.0, 145.9, 142.4, 139.5, 139.4, 138.4, 137.3, 137.2, 137.0, 135.5, 135.4, 134.7, 133., 132.7, 132.3, 132.2, 131.7, 131.6, 131.5, 128.6, 128.5, 128.40, 126.4, 35.4, 35.1, 35.1, 35.0, 33.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.2 (s). IR (ATR): $\tilde{\nu}$ = 3043, 1596, 1491, 1478, 1448, 1334, 1311, 1224, 1152, 1120, 1044, 1028, 946, 744, 722, 617, 596, 578, 552, 528, 486, 442, 423, 381 cm^{-1}. HRMS ($C_{28}H_{24}BrOP$) calc. 486.0743; found 486.0741.

4-diphenylphosphoryl-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (3)
In a vial with a magnetic stirring bar, 4-bromo-16-diphenylphosphoryl[2.2]paracyclophane (100 mg, 0.205 mmol, 1.00 equiv.), 4-bromo-(2'-pyridyl)phenyl (61.3 mg, 0.308 mmol, 1.50 equiv.), palladium(II) acetate (2.3 mg, 10.2 µmol, 5 mol%), RuPhos (14.3 mg, 30.8 µmol, 15 mol%) and potassium phosphate (174 mg, 0.820 mmol, 4.00 equiv.) were placed. The vial was capped and evacuated and backfilled with argon three times. Then, toluene (2 mL) and water (0.2 mL) were added with a syringe. The mixture was stirred and heated to 80 °C overnight. The next day, the mixture was passed over a celite pad and the solvent removed under reduced pressure. The crude mixture was subjected to column chromatography (silica, pentane/ethyl acetate 2:1 to 1:1) to yield the title compound as an off-white solid (88 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.7 (dt, J = 4.8, 1.4 Hz, 1H), 8.1 – 8.0 (m, 2H), 7.8 (dt, J = 4.4, 1.6 Hz, 2H), 7.8 – 7.7 (m, 2H), 7.6 – 7.5 (m, 5H), 7.5 (tq, J = 6.7, 1.7 Hz, 3H), 7.4 (ddd, J = 8.4, 6.7, 2.9 Hz, 2H), 7.3 – 7.2 (m, 2H), 6.7 (dd, J = 8.8, 1.6 Hz, 2H), 6.7 (dd, J = 7.8, 4.1 Hz, 1H), 6.4 (d, J = 7.8 Hz, 1H), 6.4 (dd, J = 14.5, 1.8 Hz, 1H), 3.7 – 3.5 (m, 2H), 3.3 (ddd, J = 13.6, 10.1, 5.1 Hz, 1H), 3.1 – 2.9 (m, 3H), 2.8 (ddd, J = 13.6, 10.0, 3.6 Hz, 1H), 2.6 (ddd, J = 13.4, 10.2, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.4, 149.9, 146.1, 146.1, 142.1, 141.2, 140.3, 140.0, 139.8, 138.0, 137.3, 137.2, 136.9, 136.7, 135.9, 135.4, 135.3, 135.2, 134.9, 134.1, 133.9, 133.9, 133.4, 132.4, 132.3, 132.2, 131.6, 131.6, 131.6, 131.5, 131.1, 130.3, 130.1, 128.6, 128.5, 128.4, 128.4, 127.3, 122.2, 120.7, 35.6, 35.6, 35.4, 34.9, 33.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.0 (s). IR (ATR, $\tilde{\nu}$) = 3053, 3024, 3006, 2968, 2924, 2890, 2846, 1584, 1572, 1459, 1434, 1394, 1179, 1160, 1116, 1103, 1067, 853, 846, 788, 768, 747, 731, 717, 694, 654, 643, 615, 557, 537, 524, 507, 496, 490, 443, 398 cm^{-1}. HRMS ($C_{39}H_{33}ONP$) calc. 562.2300; found 562.2299.

4-(diphenylphosphinyl)-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (4)
Triethylamine (0.35 mL, 2.50 mmol, 2.00 equiv.) was added dropwise to a stirred solution of 4-diphenylphosphoryl-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (700 mg, 1.00 mmol, 1.00 equiv.) in toluene (7.0 mL) under argon. To this solution was added trichlorosilane (0.25 mL, 2.50 mmol, 2.00 equiv.) and stirring was continued at 120 °C overnight. The reaction was carefully quenched with sat. aq. ammonium chloride and extractive workup was conducted with ethyl acetate. The organic extracts were washed with brine and dried over anhydrous sodium sulphate and used without further purification in the next step. The conversion was determined to be 83% by peak integration of the ^{31}P NMR spectrum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 – 8.68 (m, 1H), 8.09 (d, J = 7.8 Hz, 2H), 7.78 (d, J = 5.4 Hz, 2H), 7.58 (d, J = 7.7 Hz, 2H), 7.41 (s, 4H), 7.25 (dd, J = 6.1, 3.5 Hz, 6H), 7.17 (d, J = 7.7 Hz, 1H), 6.70 (d, J = 2.0 Hz, 1H), 6.66 – 6.52 (m, 2H), 6.32 (d, J = 7.9 Hz, 1H), 5.99 – 5.70 (m, 1H), 3.71 – 3.44 (m, 2H), 3.34 (ddd, J = 14.1, 10.0, 4.6 Hz, 1H), 3.13 – 3.02 (m, 1H), 2.91 (dp, J = 13.7, 6.5, 4.3 Hz, 1H), 2.80 (ddd, J = 13.7, 10.2, 4.1 Hz, 1H), 2.63 (ddd, J = 13.9, 10.0, 4.2 Hz, 1H), 2.52 (ddd, J = 13.8, 10.2, 4.4 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ = -3.53.

4-(diphenylphosphinyl gold(I) chloride)-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (5)
In a round bottom flask, crude 4-(diphenylphosphinyl)-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (420 mg, 0.770 mmol, 1.00 equiv.) and (tht)AuCl (381 mg, 0.770 mmol, 1.00 equiv.) were placed. The round bottom flask was closed with a rubber septum and evacuated and backfilled with argon three times. Degassed DCM (7 mL) was added with a syringe. The mixture was stirred for 2 hours at r.t. in the dark. The solvent was removed under

reduced pressure and the residue subjected to column chromatography (silica, pentane/ethyl acetate 2:1) to yield the title compound as a white solid (277 mg, 46%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.7 (dt, J = 4.7, 1.4 Hz, 1H), 8.2 – 8.1 (m, 2H), 7.9 – 7.8 (m, 2H), 7.6 – 7.6 (m, 5H), 7.6 – 7.5 (m, 2H), 7.5 – 7.5 (m, 4H), 7.4 (td, J = 7.7, 2.7 Hz, 2H), 7.3 – 7.3 (m, 1H), 6.8 (d, J = 1.9 Hz, 1H), 6.7 (dt, J = 7.7, 1.5 Hz, 1H), 6.6 (dd, J = 7.8, 5.5 Hz, 1H), 6.3 (d, J = 7.9 Hz, 1H), 6.0 (dd, J = 14.7, 1.7 Hz, 1H), 3.9 – 3.8 (m, 2H), 3.3 (ddd, J = 13.8, 10.2, 5.0 Hz, 1H), 3.1 (ddd, J = 12.4, 11.0, 2.3 Hz, 1H), 3.0 (dddd, J = 17.3, 13.9, 10.3, 3.4 Hz, 2H), 2.8 (ddd, J = 13.6, 10.1, 3.6 Hz, 1H), 2.6 (ddd, J = 13.5, 10.3, 5.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.1, 149.7, 144.4, 144.3, 141.8, 141.6, 141.0, 140.9, 139.6, 138.0, 137.2, 137.0, 136.6, 136.6, 135.6, 135.5, 135.4, 135.3, 135.0, 134.2, 134.1, 133.8, 133.8, 132.2, 132.2, 132.0, 132.0, 131.4, 130.8, 130.2, 129.5, 129.4, 129.3, 129.2, 129.1, 128.8, 127.4, 126.8, 126.3, 122.4, 120.8, 34.9, 34.9, 34.7, 34.6, 33.1, 30.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.8 (d, J = 14.3 Hz). IR (ATR, $\tilde{\nu}$) = 3050, 3003, 2921, 2851, 1732, 1608, 1584, 1572, 1463, 1434, 1412, 1391, 1309, 1296, 1238, 1183, 1153, 1098, 1011, 993, 911, 849, 782, 742, 710, 691, 652, 616, 571, 548, 523, 510, 490, 443, 426, 401 cm^{-1}. HRMS ($C_{39}H_{32}AuClNP + H^+$) calc. 778.1699; found 778.1685.

4-(((Bis(2,2'-bipyridyl)-4-(2'-pyridyl)phenyl) ruthenium (II))-16-(chloro(diphenylphosphinyl)-gold(I))[2.2]paracyclophane (pAuRu)
In a vial under argon, 4-(4-(2'-pyridyl)phenyl))16-(chloro(diphenylphosphinyl)-gold(I))[2.2]paracyclophane (30.0 mg, 38.6 µmol, 1.00 equiv.), (benzene)ruthenium dichloride dimer (9.6 mg, 19.3 µmol, 0.500 equiv.), sodium hydroxide (1.5 mg, 38.6 µmol, 1.00 equiv.) and potassium hexafluorophosphate (14.2 mg, 77.1 µmol, 2.00 equiv.) were dissolved in degassed acetonitrile (2.0 mL) and stirred at 50 °C overnight. The next day, the solvent was removed under reduced pressure. The crude was purified on silica gel with dichloromethane/acetonitrile 10:1 as eluent and the yellow band was collected. This intermediate and 2,2'-bipyridine (12.0 mg, 0.771 mmol, 2.00 equiv.) were dissolved in degassed methanol (4.0 mL) under argon and refluxed overnight. The solution changed from canary yellow to dark berry-red. The solvent was removed, and the crude purified on silica gel with dichloromethane/acetonitrile 10:1. The first red band was collected to afford the title compound as a reddish black solid (28.0 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (dd, J = 4.7, 1.5 Hz, 1H), 8.55 (dd, J = 18.4, 8.0 Hz, 1H), 8.41 (q, J = 7.7 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.3 Hz, 2H), 8.06 – 7.89 (m, 3H), 7.85 – 7.76 (m, 2H), 7.67 – 7.43 (m, 12H), 7.39 (td, J = 7.6, 3.9 Hz, 2H), 7.21 (d, J = 6.9 Hz, 1H), 7.04 (d, J = 7.7 Hz, 2H), 6.76 (d, J = 1.9 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.63 (dd, J = 7.8, 5.4 Hz, 1H), 6.57 (t, J = 2.2 Hz, 1H), 6.34 (d, J = 7.9 Hz, 1H), 6.29 – 6.19 (m, 2H), 6.11 (dd, J = 7.9, 4.6 Hz, 1H), 6.00 (dd, J = 14.7, 1.7 Hz, 1H), 5.95 – 5.86 (m, 2H), 3.92 – 3.76 (m, 1H), 3.76 – 3.62 (m, 1H), 3.33 (ddd, J = 14.3, 10.2, 5.0 Hz, 1H), 3.11 – 2.70 (m, 4H), 2.60 – 2.52 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.2, 156.6, 156.0, 155.8, 150.1, 149.9, 149.8, 144.4, 144.3, 144.0, 143.9, 141.7, 141.6, 141.0, 140.9, 140.9, 140.8, 140.7, 139.6, 139.4, 139.3, 138.2, 137.4, 137.2, 137.1, 137.0, 136.6, 136.5, 136.2, 135.7, 135.6, 135.5, 135.5, 135.4, 135.3, 135.2, 135.2, 135.1, 135.1, 135.0, 134.2, 134.1, 134.0, 133.8, 133.8, 132.3, 132.2, 132.1, 132.0, 131.3, 130.9, 130.8, 130.7, 130.5, 130.2, 130.1, 130.0, 129.5, 129.4, 129.3, 129.3, 129.2, 129.2, 129.1, 128.8, 128.7, 128.4, 127.4, 126.8, 126.6, 126.6, 126.3, 126.2, 126.2, 126.1, 126.0, 125.9, 123.1, 123.0, 122.9, 122.8, 122.7, 122.3, 121.3, 120.7, 34.9, 34.9, 34.8, 34.7, 34.6, 34.5, 34.2, 33.7, 33.1. IR (ATR, $\tilde{\nu}$) = 2917, 2849, 1737, 1715, 1462, 1438, 1421, 1375, 1258, 1239, 1183, 1098, 1041, 1037, 1026, 841, 805, 764, 728, 720, 694, 557 cm^{-1}. HRMS ($C_{59}H_{47}AuClN_5PRu$) calc. 1190.1961; found 1190.1958.

Ethyl 4-carboxybenzenediazonium tetrafluoroborate (10)
Ethyl 4-Aminobenzoate (3.00 g, 18.2 mmol, 1.00 equiv.) was dissolved in a mixture of 50% fluoroboric acid (3.5 mL, 54.5 mmol, 3.00 equiv.) and distilled water (4 mL). After cooling to 0 °C, sodium nitrite (1.25 g, 18.2 mmol, 1.00 equiv.) in 1.5 mL of distilled water was added dropwise. The mixture was stirred mechanically and the thick precipitate was collected and re-dissolved in acetone (10 mL). The diazonium tetrafluoroborate was then precipitated by the addition of diethyl ether (50 mL) and collected by filtration as an off-white needle forming crystalline substance (2.77 g, 58%).

m.p. 92 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 8.94 (d, J = 9.0 Hz, 1H), 8.54 (d, J = 9.0 Hz, 1H), 4.47 (q, J = 7.1 Hz, 1H), 1.41 (t, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ = 206.6, 164.1, 141.7, 134.2, 132.5, 120.4, 63.4, 14.3. IR (ATR, $\tilde{\nu}$) = 3104, 2306, 1714, 1679, 1473, 1421, 1373, 1309, 1283, 1184, 1154, 1128, 1106, 1052, 1011, 973, 873, 860, 806, 761, 670, 637, 530, 476, 378 cm^{-1}. HRMS ($C_9H_9O_2N_2$): calc. 177.0664; found 177.0665.

Ethyl 4-(3-methyl-1-oxo-1-phenylbut-2-en-2-yl)benzoate (11)

In a glass vial under argon, alkynol (1.00 equiv.)**,** diazonium salt (4.00 equiv.) and the catalyst (2.5 mol%) were placed. Under an argon counter-current, degassed solvent (MeOH or MeCN/MeOH 3:1, 0.1 M) was added with a syringe. The solution was stirred and irradiated with a green 30W LED light-source for 12 h under vigorous stirring. The solvent was removed under reduced pressure and the residue subjected to column chromatography (silica, pentane/ethyl acetate 15:1) to afford the title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 – 7.97 (m, 2H), 7.96 – 7.93 (m, 2H), 7.46 – 7.35 (m, 5H), 4.34 (q, J = 7.1 Hz, 2H), 1.89 (s, 3H), 1.80 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 198.4, 166.5, 141.9, 137.3, 136.9, 136.3, 133.5, 130.3, 129.8, 129.8, 129.4, 129.3, 129.3, 128.8, 128.6, 61.1, 22.9, 21.6, 14.5. IR HRMS ($C_{20}H_{20}O_3 + H^+$): calc. 309.1485; found 309.1477.

3 Time-resolved reaction monitoring

By ESI MS supported time-resolved reaction monitoring, it could be determined that the reaction is complete after 25 minutes. An induction period is observed which could be due to the slight increase in temperature by the LED irradiation (T_{max} < 30 °C).

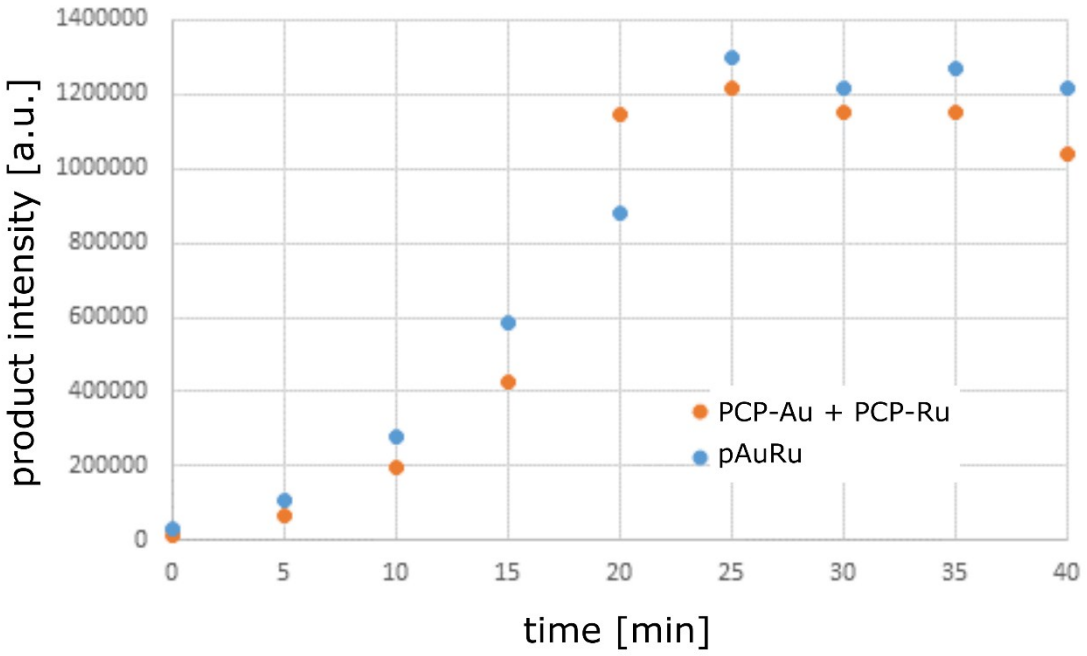
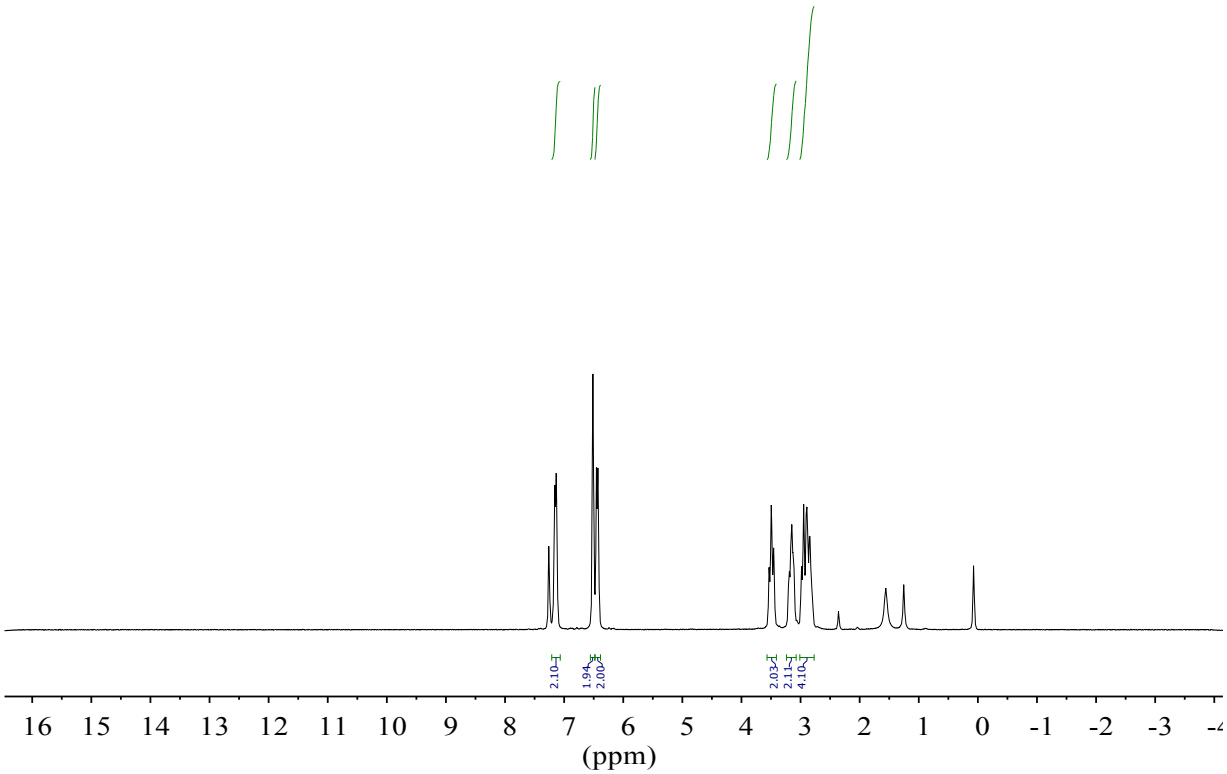


Fig. 1 Time-resolved product intensity by ESI mass spectrometry.

4 Spectra

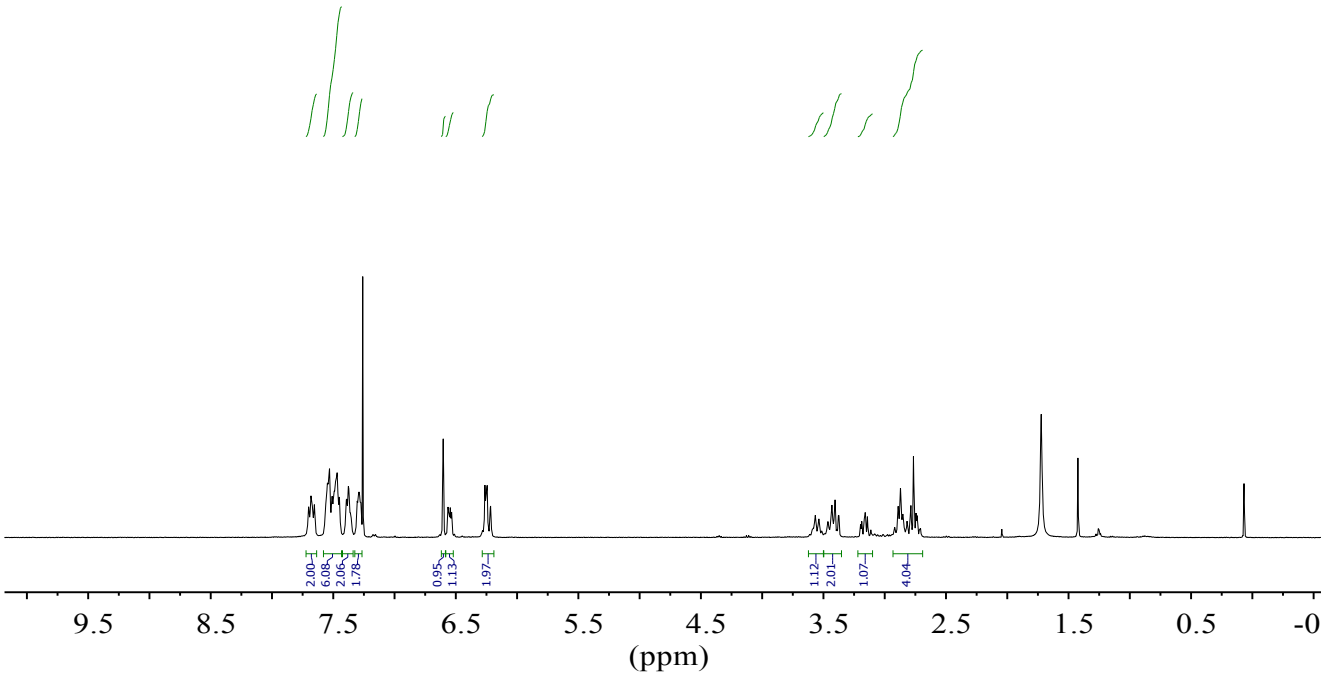
4,16-dibromo[2.2]paracyclophane (1)

^{1}H spectrum

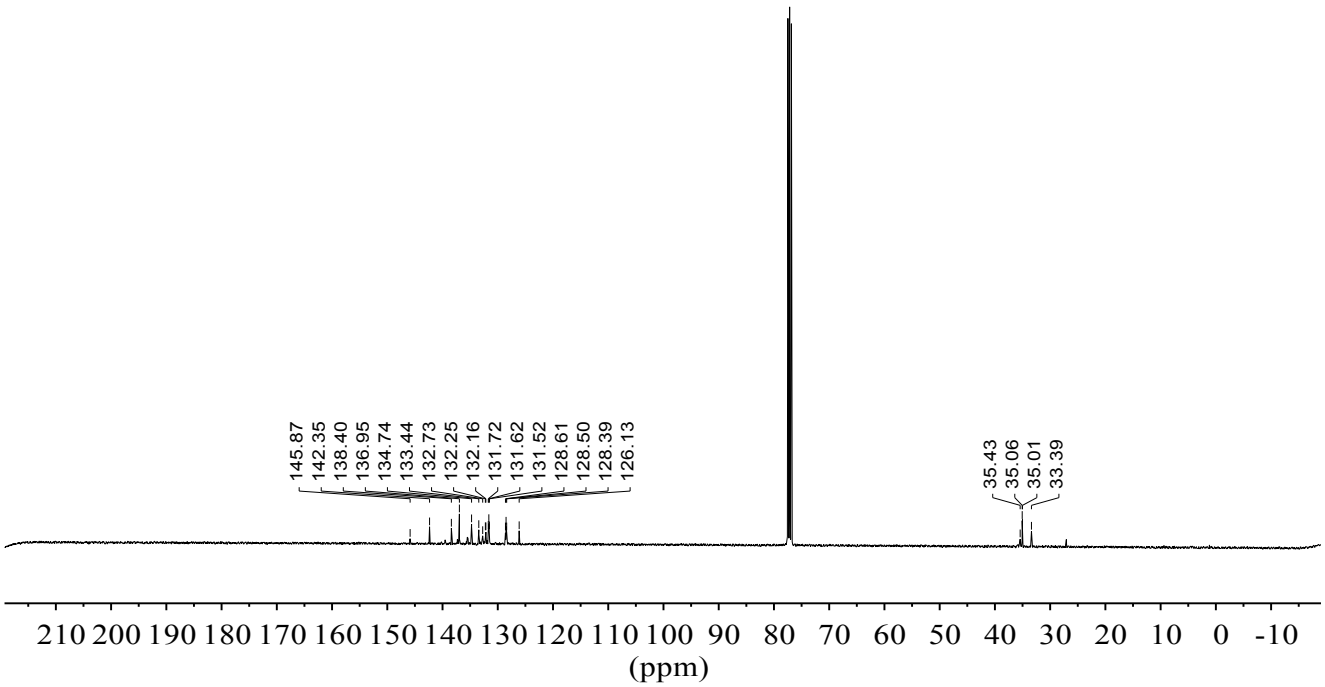


4-Bromo-16-diphenylphosphoryl[2.2]paracyclophane (2)

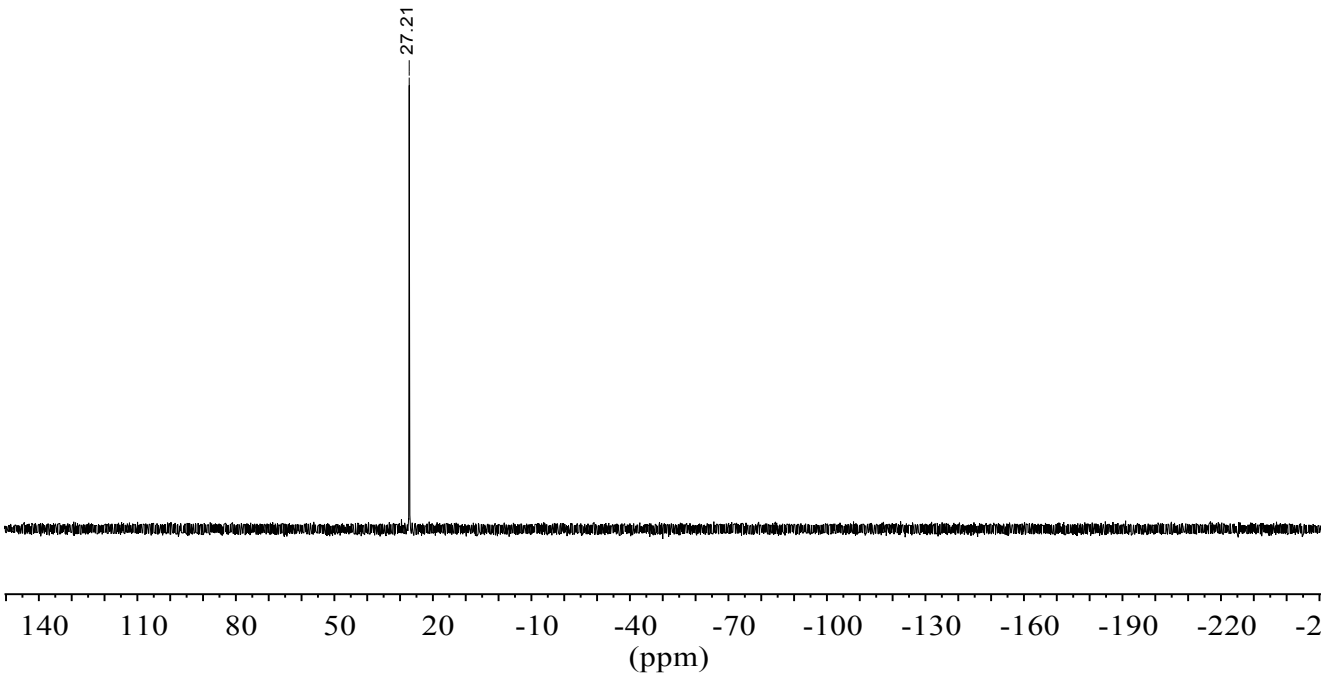
^{1}H spectrum



^{13}C spectrum

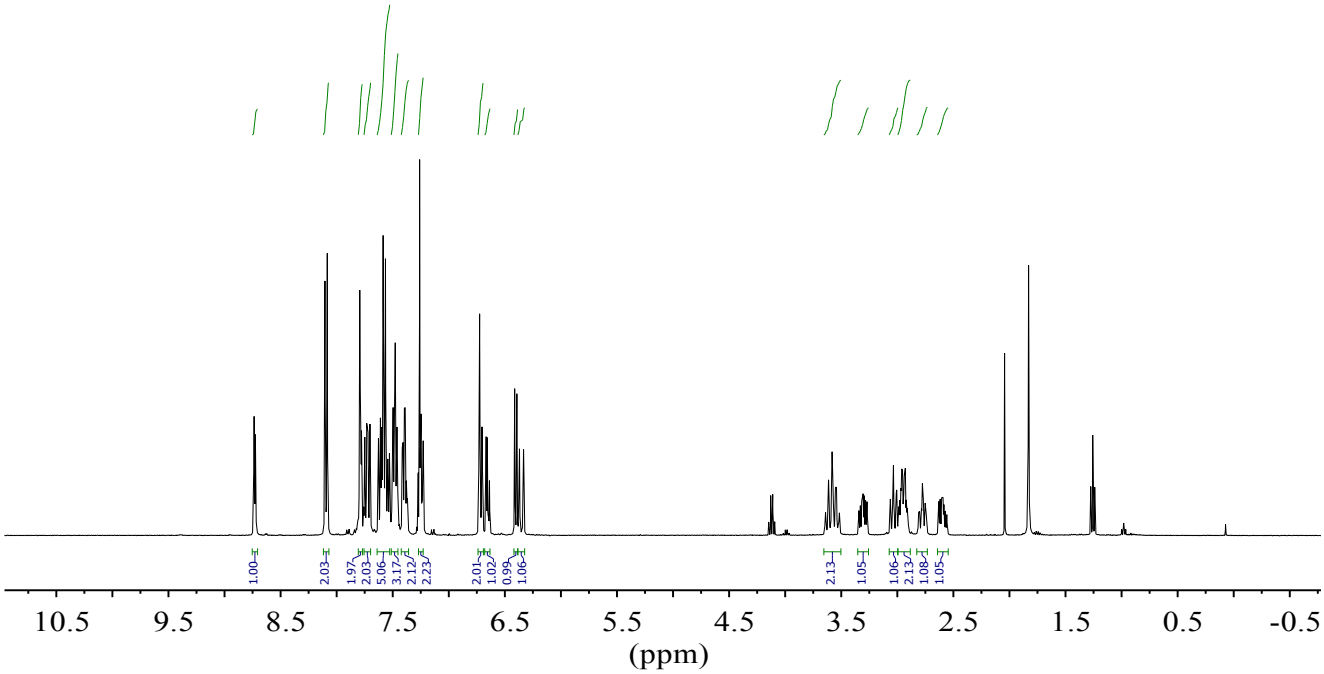


^{31}P spectrum

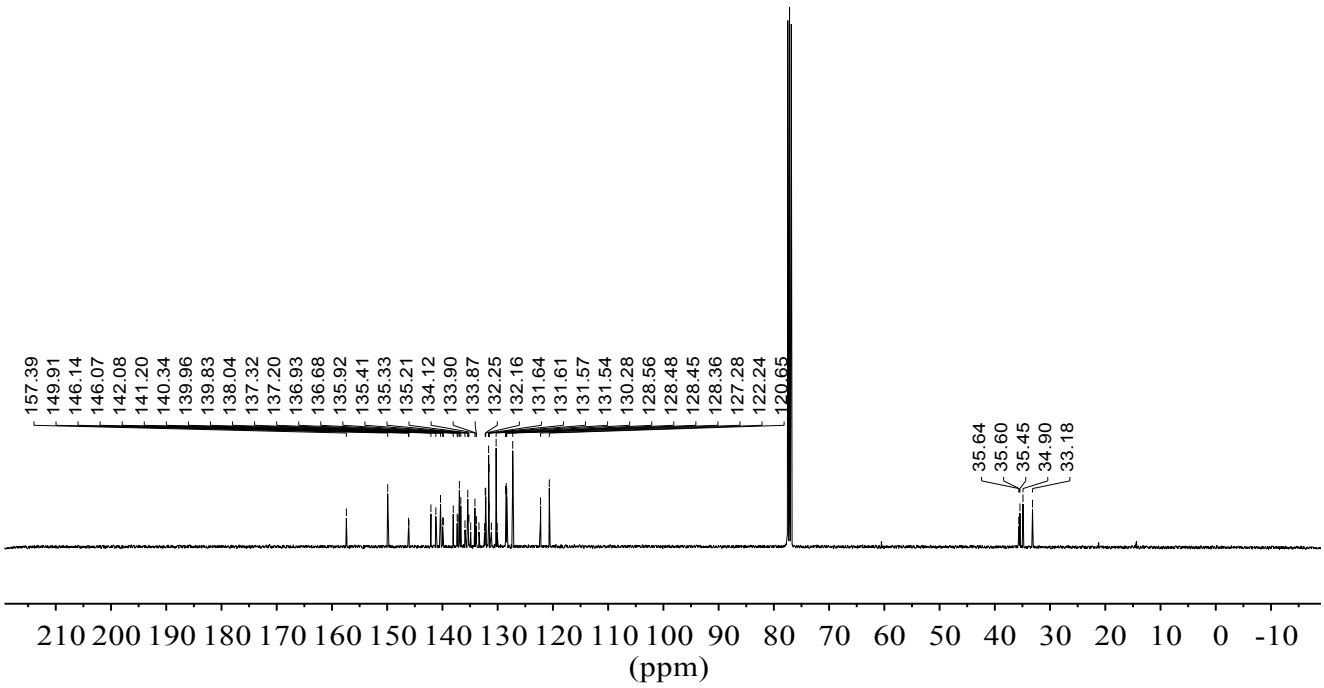


4-diphenylphosphoryl-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (3)

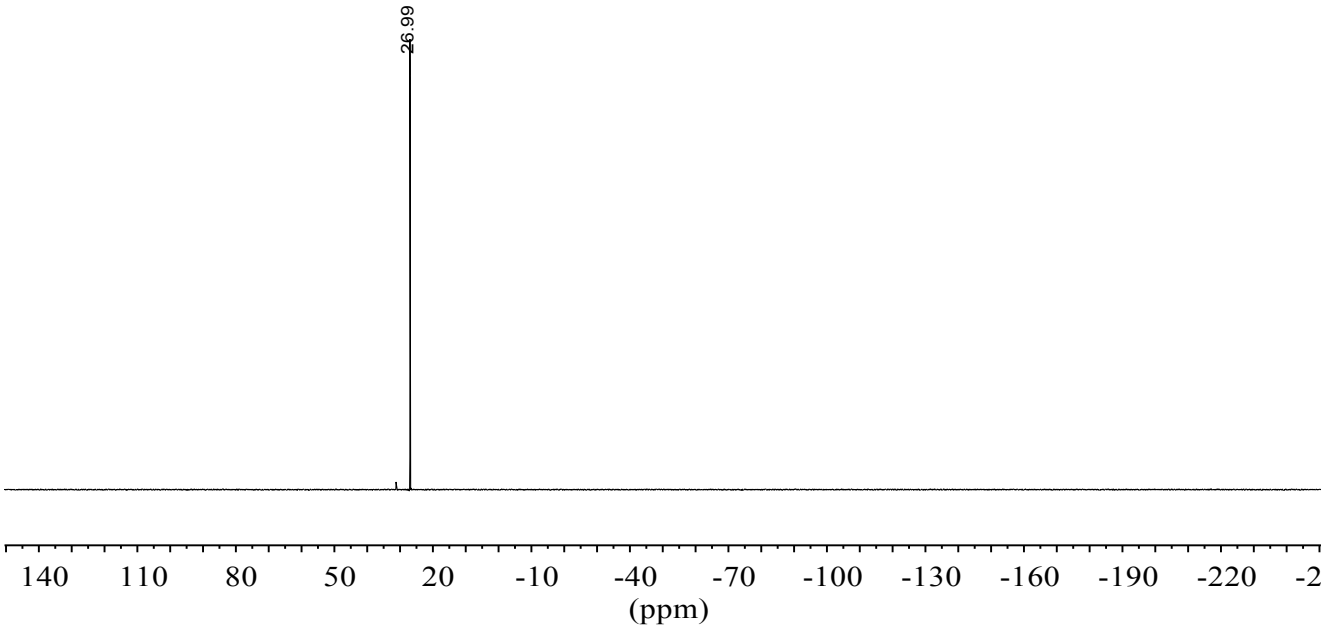
^{1}H spectrum



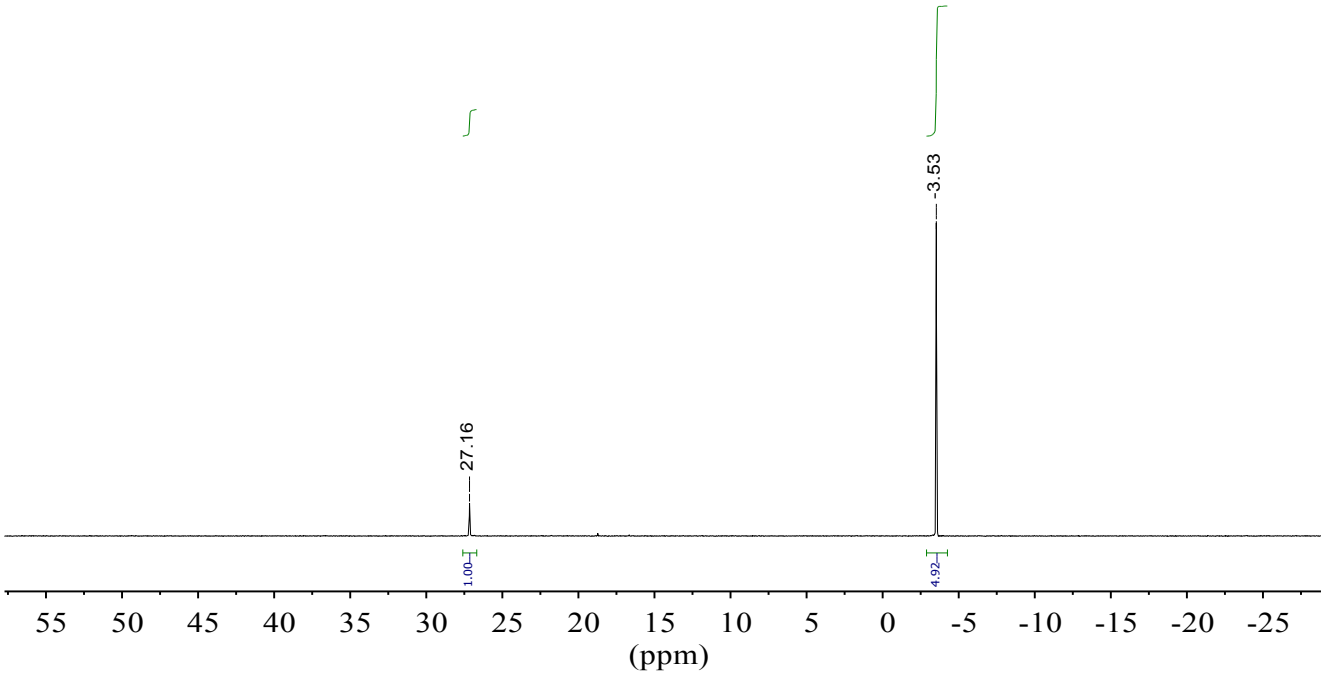
^{13}C spectrum



^{31}P spectrum

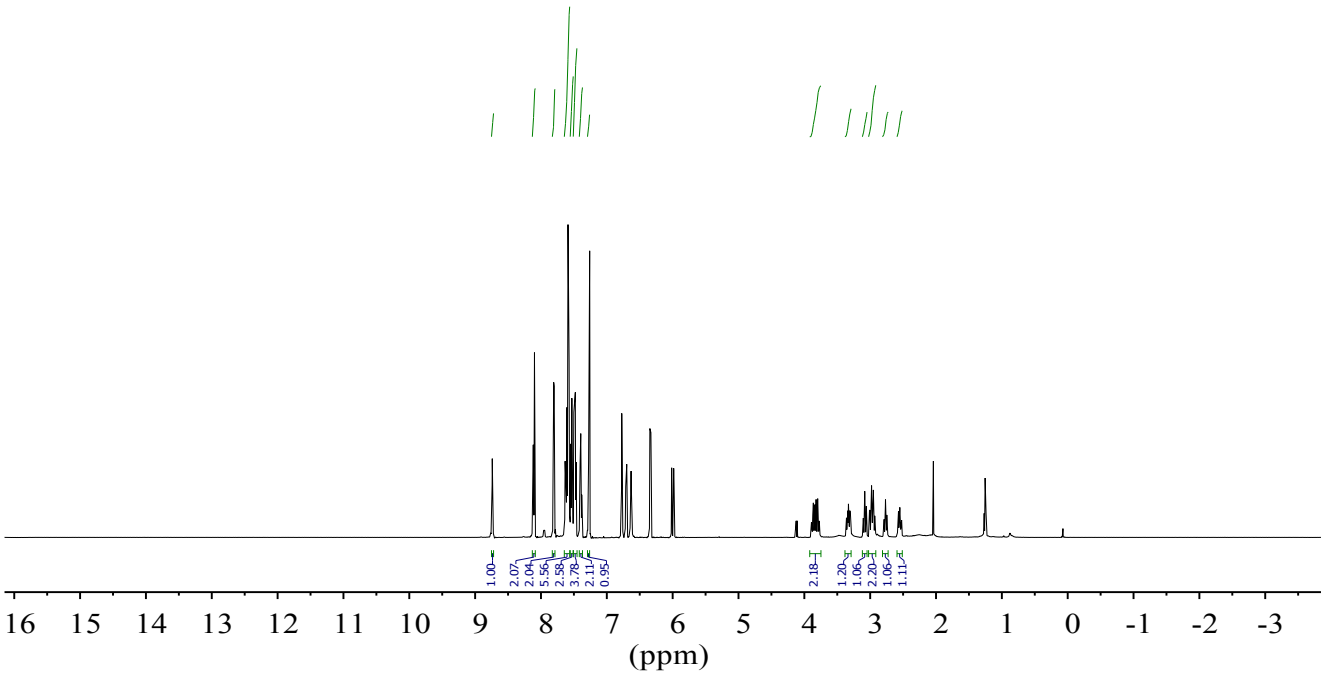


4-(diphenylphosphinyl)-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (4)
^{31}P spectrum

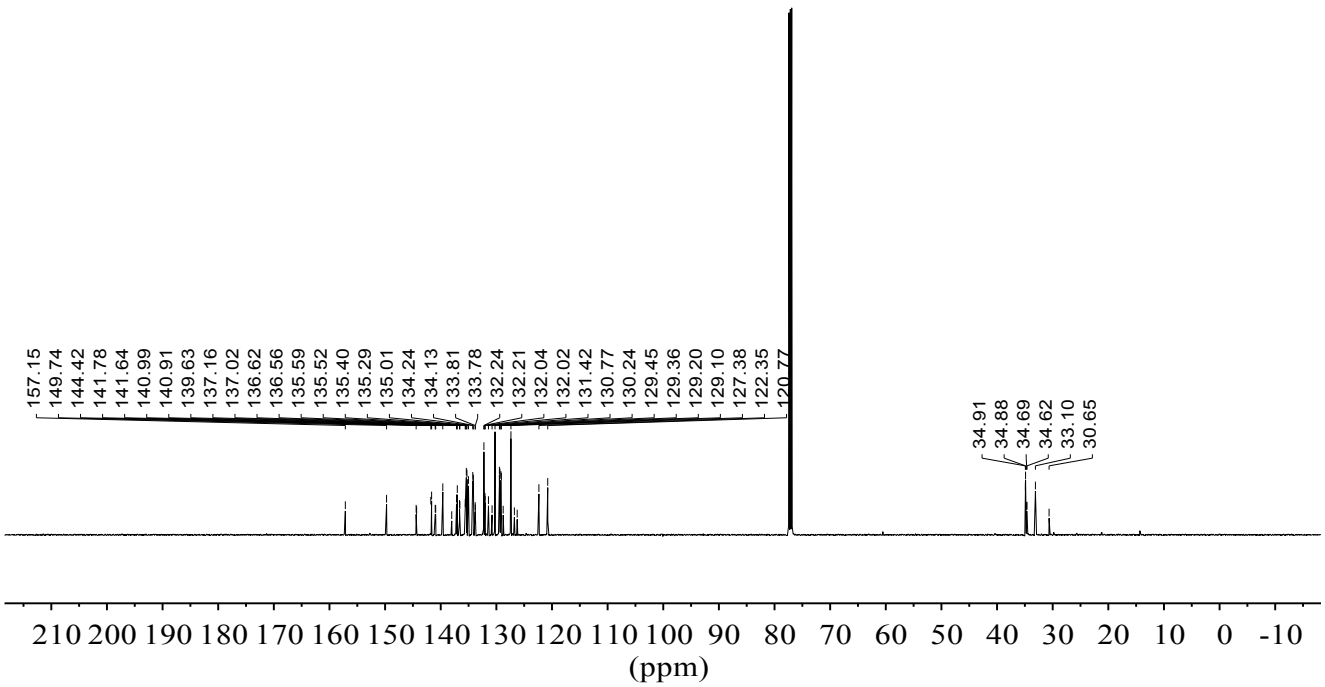


4-(diphenylphosphinyl gold(I) chloride)-16-(4-(2'-pyridyl)phenyl)[2.2]paracyclophane (5)

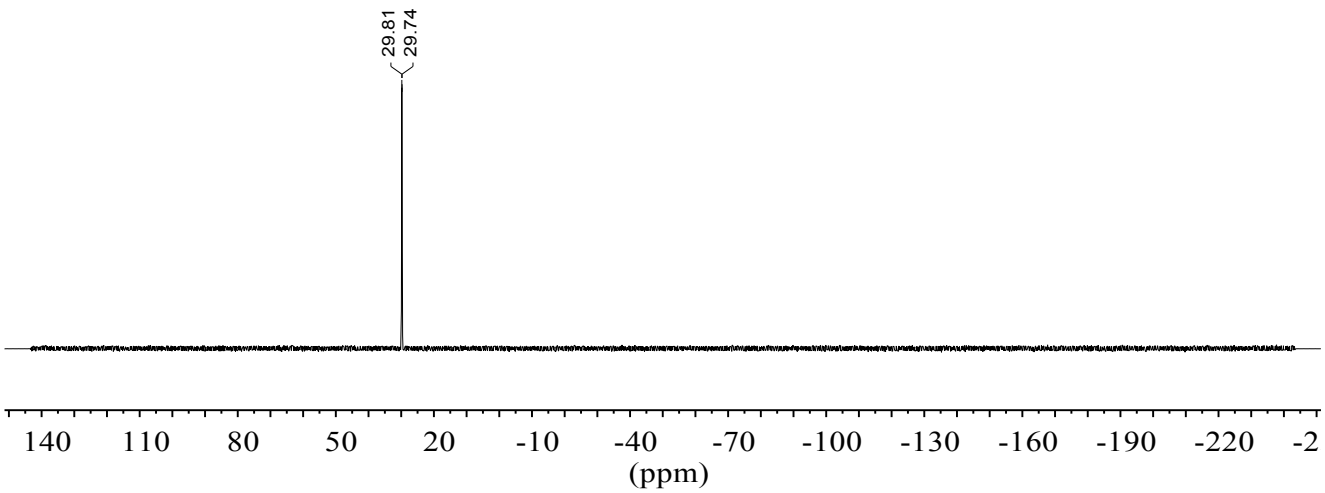
^{1}H spectrum



^{13}C spectrum

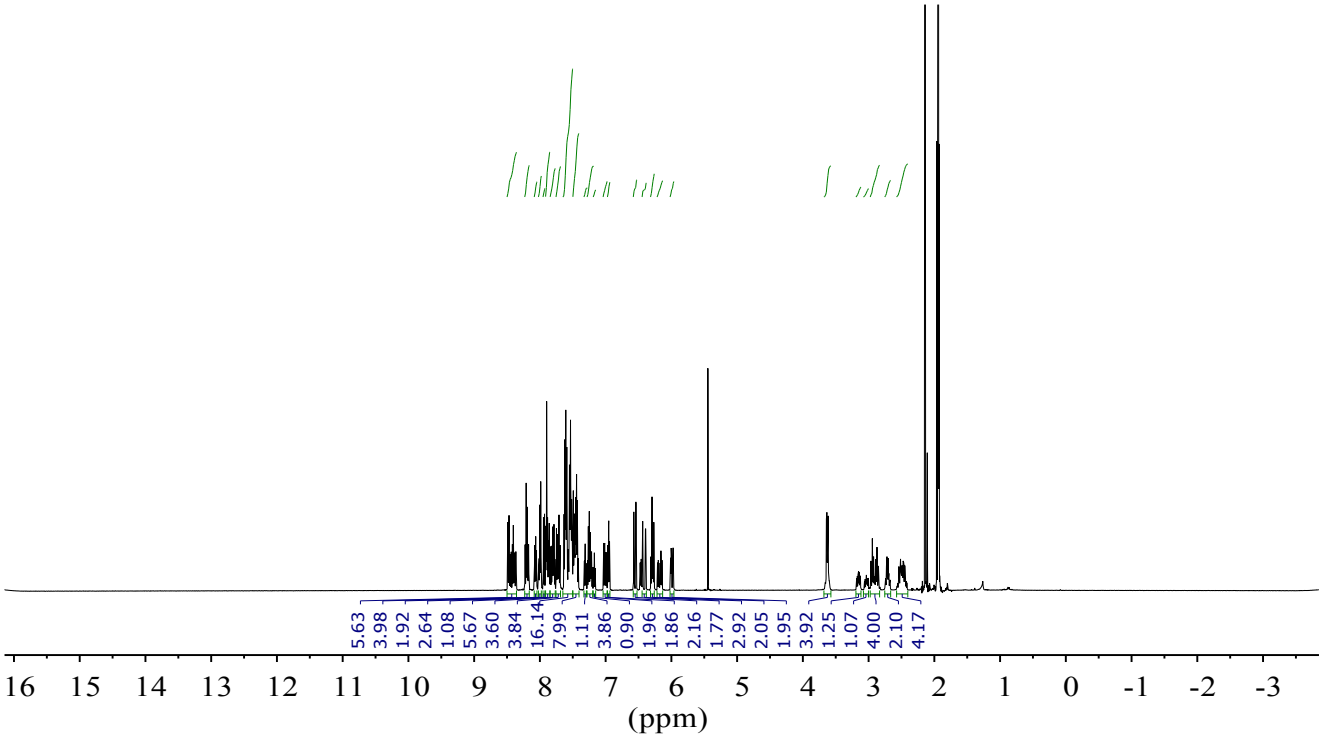


^{31}P spectrum

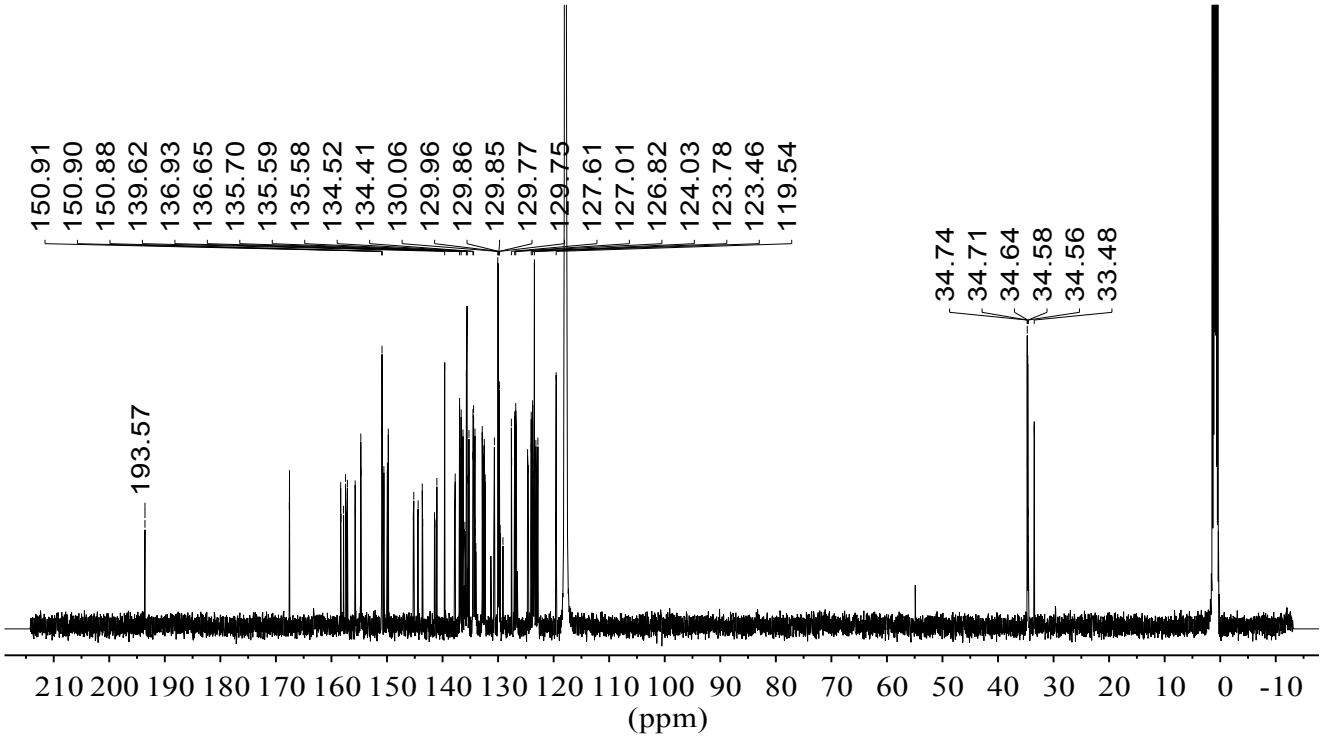


4-(((Bis(2,2'-bipyridyl)-4-(2'-pyridyl)phenyl) ruthenium (II))-16-(chloro(diphenylphosphinyl)-gold(I))[2.2]paracyclophane (pAuRu)

^{1}H spectrum

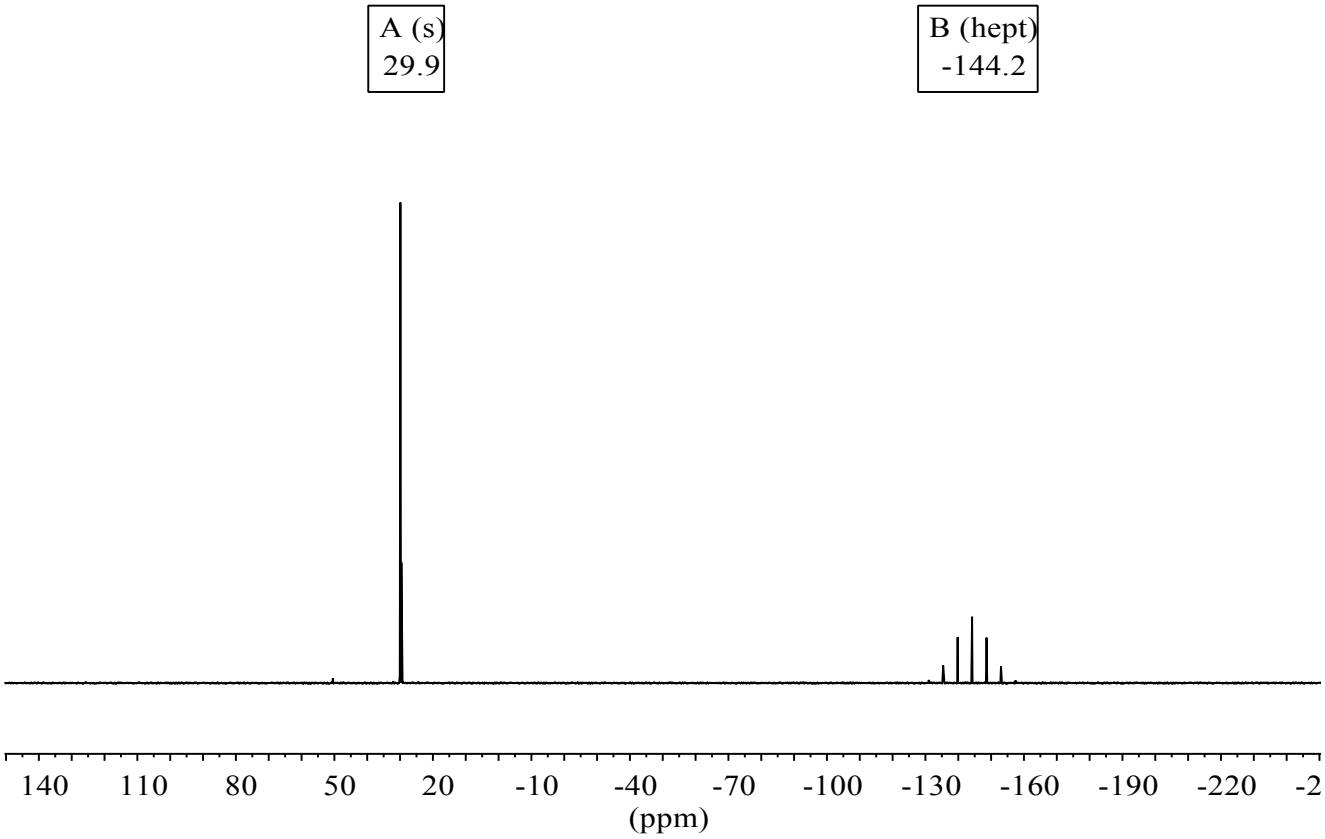


^{13}C spectrum



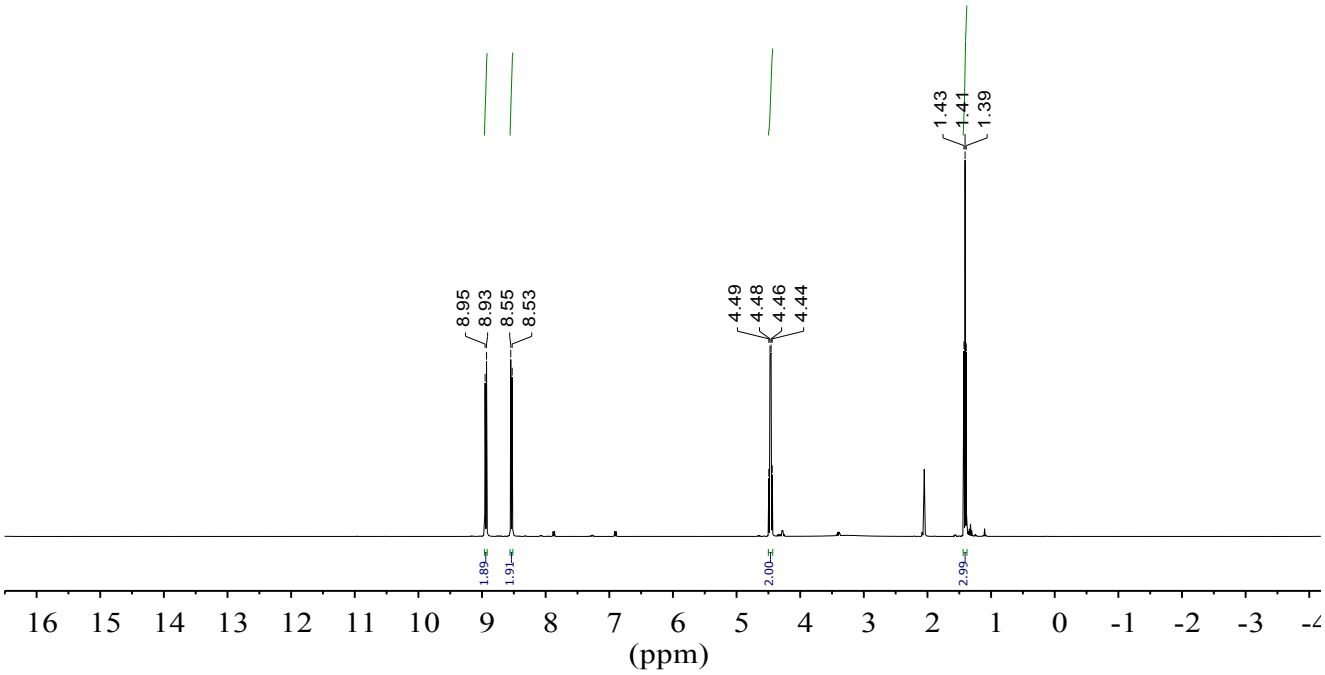
^{31}P spectrum

The ^{31}P NMR of **pAuRu** shows a heptet at δ = –144.2 ppm that corresponds to the PF_6-anion and a singlet at δ = 29.9 ppm that corresponds to the *P–Au* phosphorous. Upon closer examination, a second singlet at δ = 29.6 ppm is found. This probably originates from the presence of two diastereomeric species.

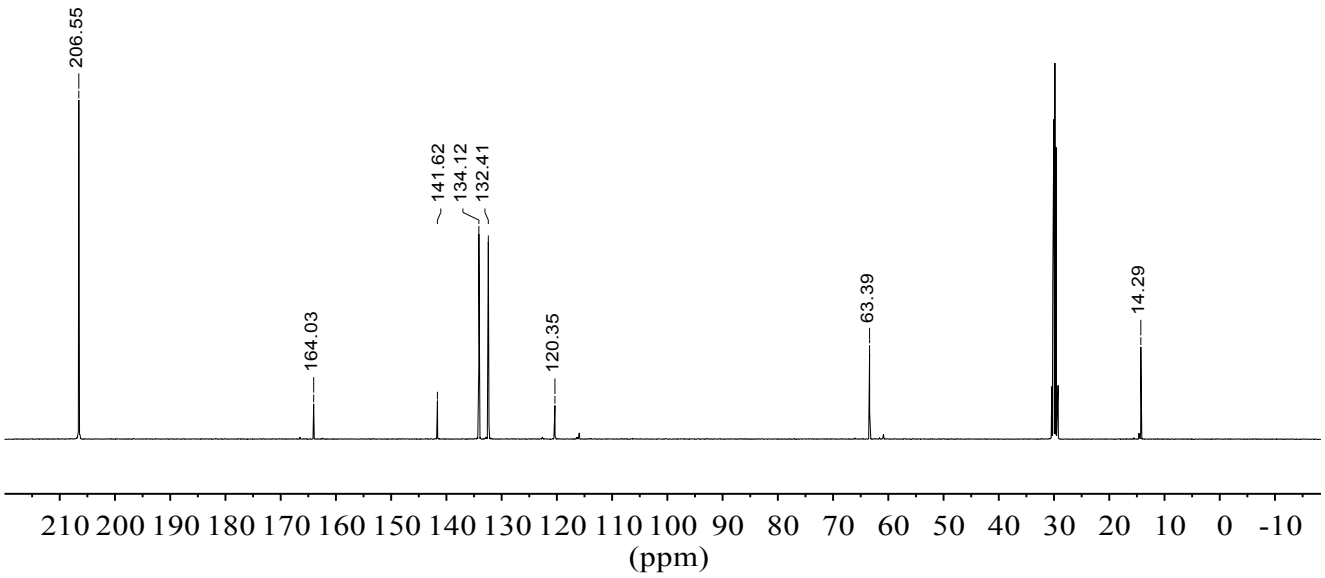

A (s)
29.9
B (hept)
-144.2
140
110
80
50
20
-10
-40
-70
-100
-130
-160
-190
-220
-2
(ppm)

Ethyl 4-carboxybenzenediazonium tetrafluoroborate (10)

^{1}H spectrum

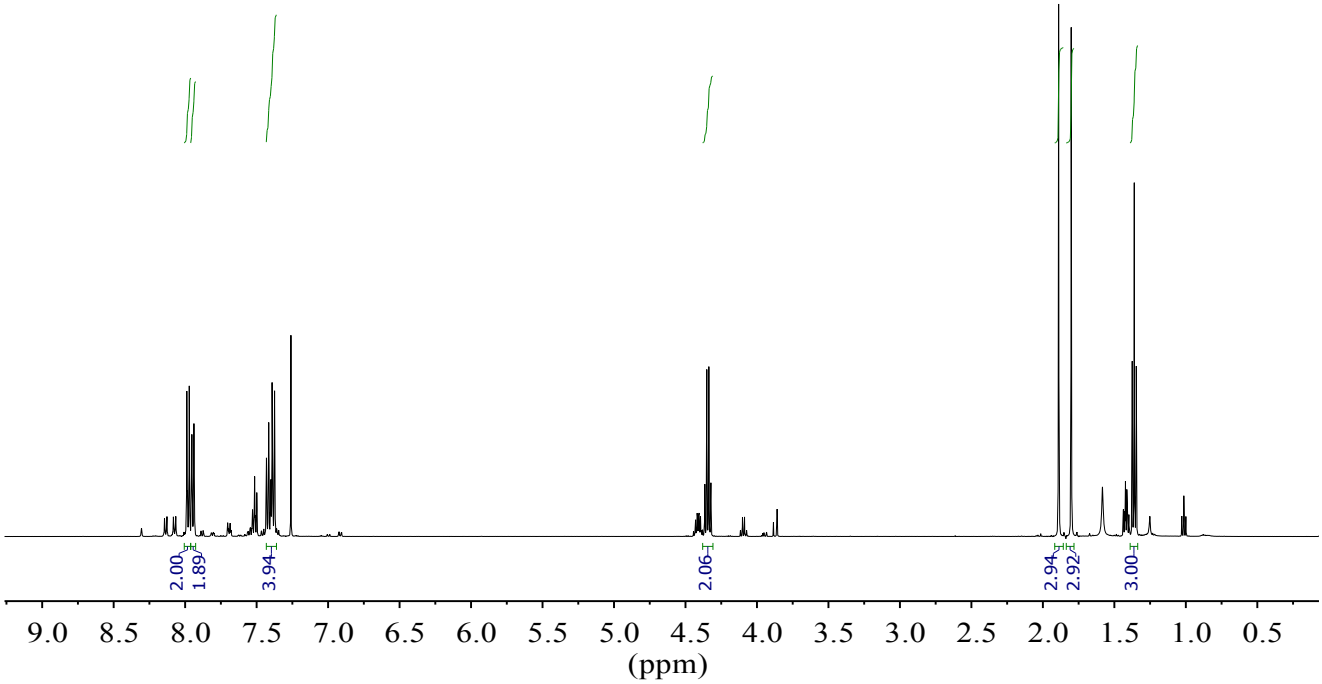


^{13}C spectrum

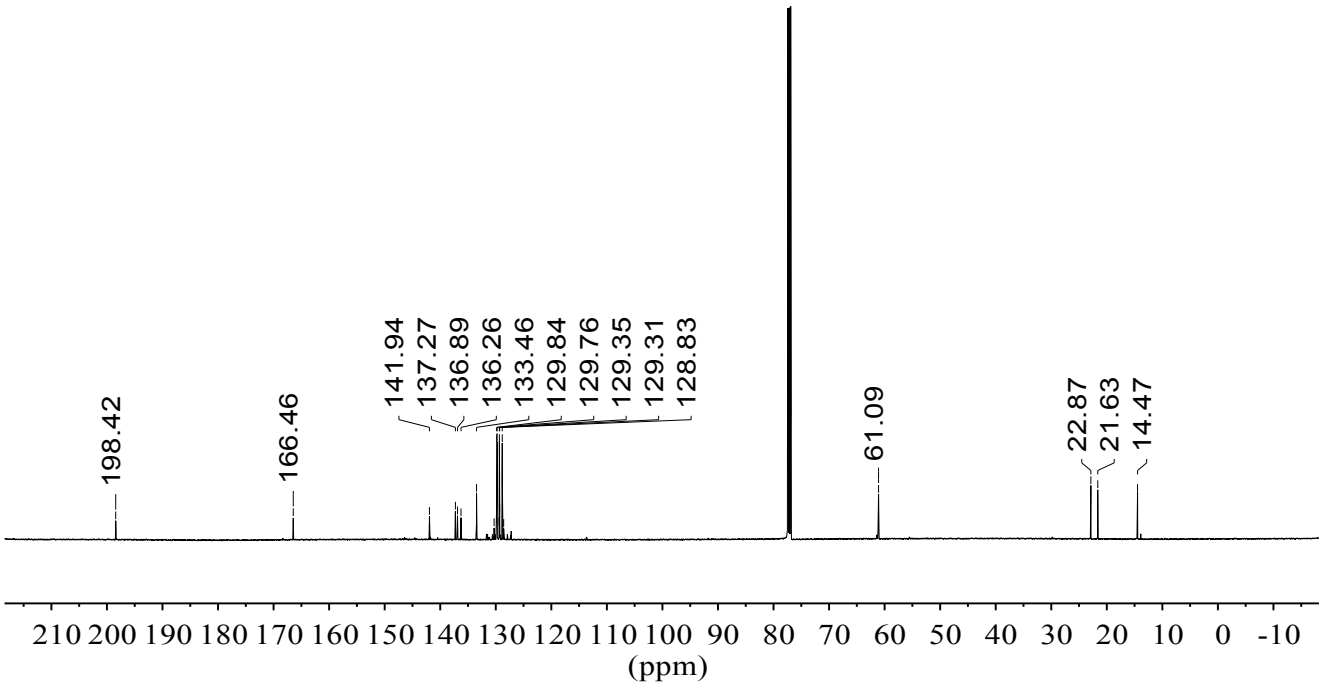


Ethyl 4-(3-methyl-1-oxo-1-phenylbut-2-en-2-yl)benzoate (11)

^{1}H spectrum



^{13}C spectrum



5 X-Ray data

Crystal Structure Determination of compound 5

The single-crystal X-ray diffraction study of **5** was carried out on a Bruker D8 Venture diffractometer with PhotonII detector at 123(2) K using Cu-Kα radiation (λ = 1.54178 Å. Dual space methods (SHELXT) [G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3-8] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2) [G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3-8]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption correction was applied. The refinement with the listed atoms shows residual electron density due to a heavily disordered cyclohexane solvent molecule in one void, which could not be refined with split atoms. Therefore, the option "SQUEEZE" of the program package PLATON (A. L. Spek, *Acta Crystallogr.* 2009, **D65**, 148-155; A. L. Spek, *Acta Crystallogr.* 2015, **C71**, 9-18.) was used to create a hkl file taking into account the residual electron density in the void areas. Therefore, the atoms list and unit card do not agree (see cif-file for details).

5: colourless crystals, $C_{39}H_{32}AuClNP \cdot 0.5\ C_6H_{12}$, M_r = 820.12, crystal size 0.16 × 0.06 × 0.04 mm, triclinic, space group *P-1* (No. 2), a = 9.9785(4) Å, b = 13.0028(5) Å, c = 15.0193(5) Å, α = 114.068(1)°, β = 104.088(1)°, γ = 97.102(1)°, V = 1670.23(11) Å^3, Z = 2, ρ = 1.631 Mg/m^{-3}, μ(Cu-K$_\alpha$) = 9.70 mm^{-1}, F(000) = 816, $2\theta_{max}$ = 144.8°, 29481 reflections, of which 6556 were independent (R_{int} = 0.035), 388 parameters, R_1 = 0.029 (for 6445 I > 2σ(I)), wR_2 = 0.074 (all data), S = 1.17, largest diff. peak / hole = 2.40 (close to Au1) / -0.52 e Å^{-3}.

CCDC 1958713 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

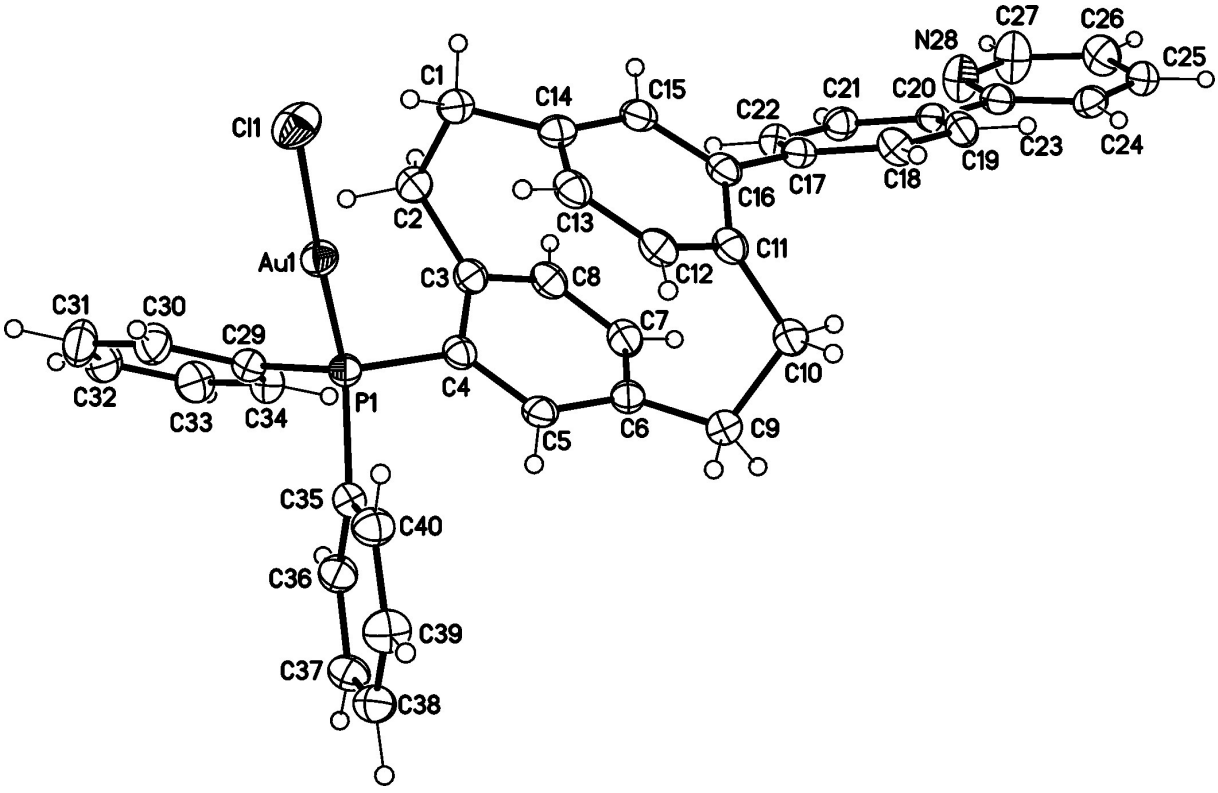


Fig. 2 Molecular structure of **5** (displacement parameters are drawn at 50% probability level).

6 Collision Induced Dissociation ESI MS Analysis

When subjected to collision induced dissociation ESI MS analysis, further insight can be gained regarding the structure of **pAuRu** (**Fig. 3**). The base spectrum at E = 0 eV only shows fragment **e**, which corresponds to **pAuRu**. When the energy is raised to 60 eV, two new fragments appear. Fragment **d** corresponds to the formal loss of a bipyridine ligand. The PCP typical homolytical separation of the decks by cleavage of the ethylene bridges corresponds to the ruthenium complex fragment **a**. When the energy is raised further to 80 eV **a** and **d** become more pronounced. Finally, raising the collision energy to 100 eV leads to fragment **c**, which corresponds to the formal loss of two bipyridine ligands and fragment **b**, that additionally shows the formal loss of a chlorine atom.

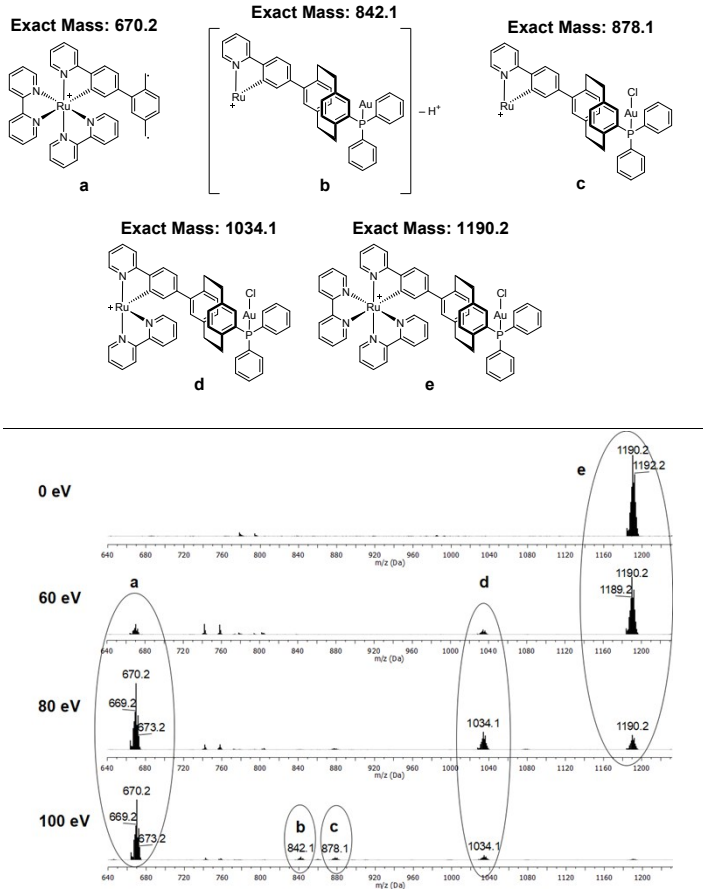


Fig. 3 CID ESI MS analysis of **pAuRu** at collision energies of E = 0, 60, 80 and 100 eV. Fragments a-e correspond to dissociation fragments of **pAuRu**.