Electronic Supporting Information for

Gold(I) Dimers with Hemilabile Azophosphine Ligands in Catalysis

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Experimental

General Considerations

Commercial reagents were purchased, suitably stored as specified by the supplier, and used as received, unless otherwise stated, from Sigma-Aldrich (silver hexafluoroantimonate(V), 98%, stored and handled in the glovebox), Acros Organics (potassium tetrachloroaurate(III), 98%) or Alfa Aesar (dimethyl sulfide, 99+%). Solvents were purchased and used as received, unless otherwise stated, from Sigma-Aldrich (diethyl ether, puriss, p.a., ACS reagent, reag. Ph. Eur., 99+ (GC); methanol, 99.8%, HPLC grade; chloroform-*d*, 99.8 atom % D, dried by overnight reaction with CaH_2, degassed and stored in an air-tight ampoule over 3 Å molecular sieves; dichloromethane-d_2, 99.5 atom % D, dried by overnight reaction with CaH_2, degassed and stored in an air-tight ampoule over 3 Å molecular sieves; acetonitrile-d_3, 99.8 atom % D, dried by overnight reaction with CaH_2, degassed and stored in an air-tight ampoule over 3 Å molecular sieves) or Fisher Scientific (dichloromethane (DCM), 99.8%, HPLC grade, degassed and stored in air-tight ampoules over 3 Å molecular sieves). Me_2SAuCl and 4-(OMe)-$C_6H_4N_2P^tBu_2$ (**1**) were synthesised according to literature procedures.[1,2]

All NMR spectra were collected on a Bruker 400 MHz Avance NEO NMR Spectrometer or a Bruker 400 MHz AV_NEO NMR Spectrometer. Chemical shifts are reported in ppm, coupling constants (*J*) are reported in Hz. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced internally to the most up-field solvent peak; ^{31}P and $^{31}P\{^{1}H\}$ NMR spectra are externally referenced to 85% H_3PO_4; $^{11}B\{^{1}H\}$ NMR spectra are externally referenced to $BF_3.OEt_2$.

All UV/Vis absorption spectra were collected on a Cary50 UV/Vis Spectrometer. The samples were prepared as 50 mM solutions in DCM to a volume of 3 mL and irradiated in a quartz glass High Precision Cell cuvette (10 x 10 mm) from Hellma Analytics. Air-sensitive UV-Vis samples were collected using a sealable cuvette, with solutions made up in the glovebox.

All IR spectra were collected on a Perkin Elmer Spectrum Two FT-IR spectrometer using attenuated total reflection (ATR) sampling technique.

All mass spectra were collected on a Waters Xevo G2-XS TOF mass spectrometer using electrospray ionisation (ESI) positive ion mode or atmospheric solids analysis

probe (ASAP) with atmospheric pressure ionisation positive ion mode. Using ESI, samples were dissolved in dry DCM/acetonitrile and directly injected into the ESI ionisation chamber via a 250 µL glass syringe. Using ASAP, samples were run neat by dipping a glass capillary into the sample vial, before insertion into the ASAP source.

Single-crystal X-ray diffraction data were collected at 100 K on an Agilent SuperNova A diffractometer using an Atlas detector, using Cu-Kα radiation (λ = 1.54184). The data collections were driven and processed, and absorption corrections were applied using CrysalisPro.[3] Using OLEX2[4] the structures were solved using SHELXT[5] and were refined by a full-matrix least-squares procedure on F^2 in SHELXL.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters.

NMR Spectra

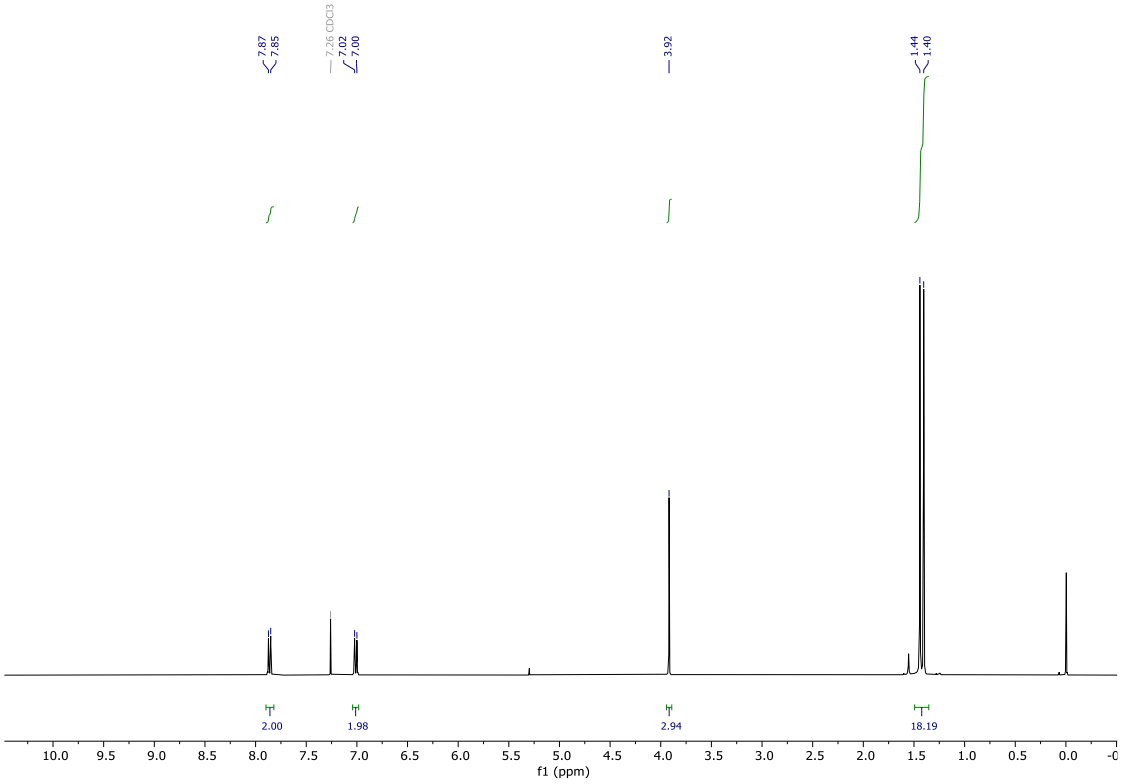

Figure S1: ^{1}H NMR Spectrum of Compound **2** in $CDCl_3$

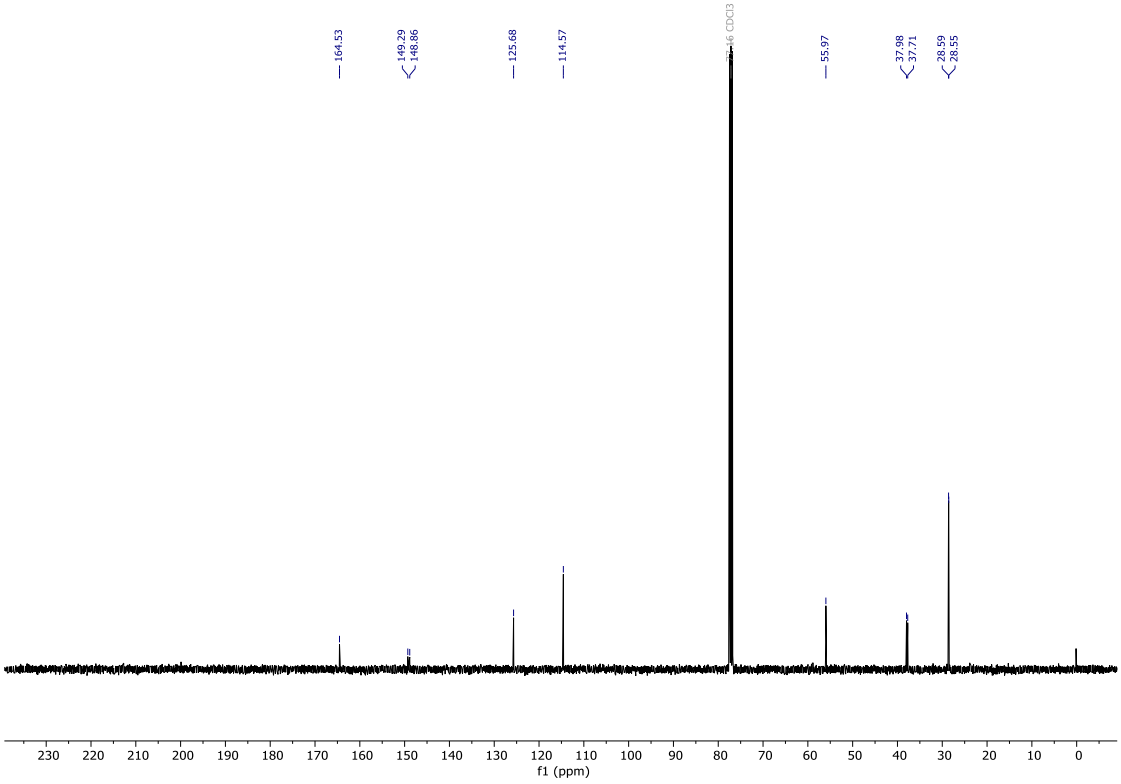

Figure S2: $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **2** in $CDCl_3$

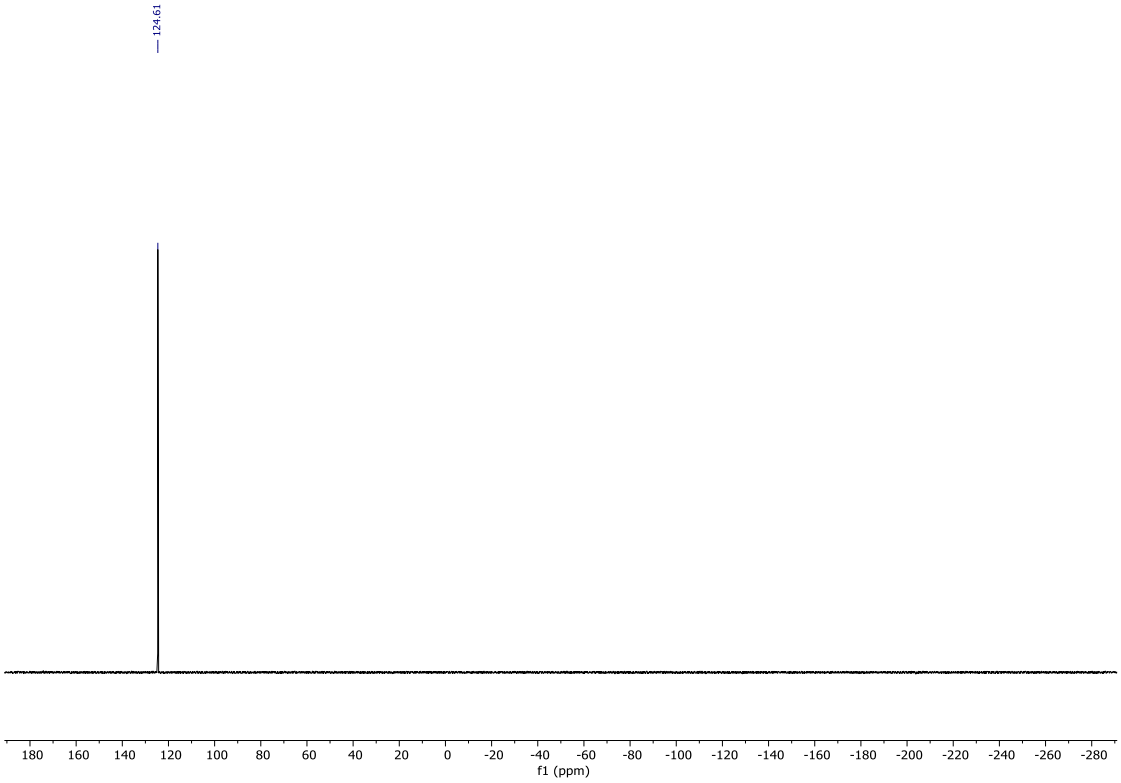

Figure S3: $^{31}P\{^{1}H\}$ NMR Spectrum of Compound **2** in $CDCl_3$

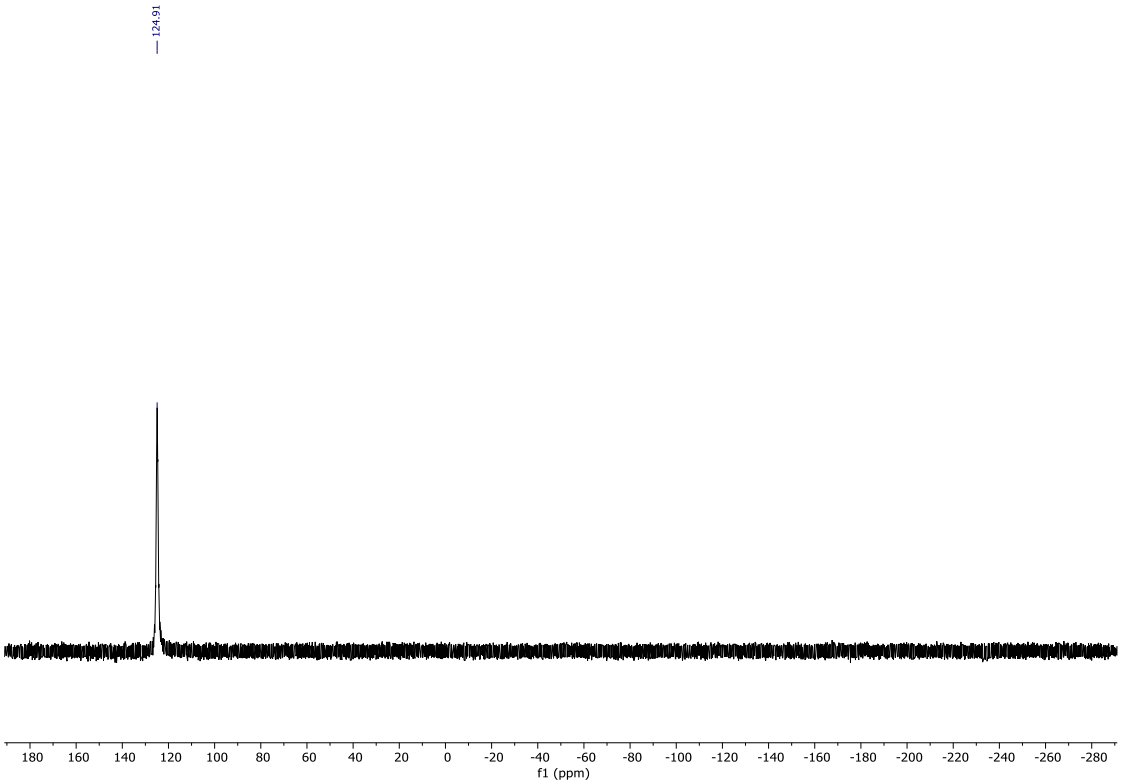

Figure S4: ^{31}P NMR Spectrum of Compound **2** in $CDCl_3$

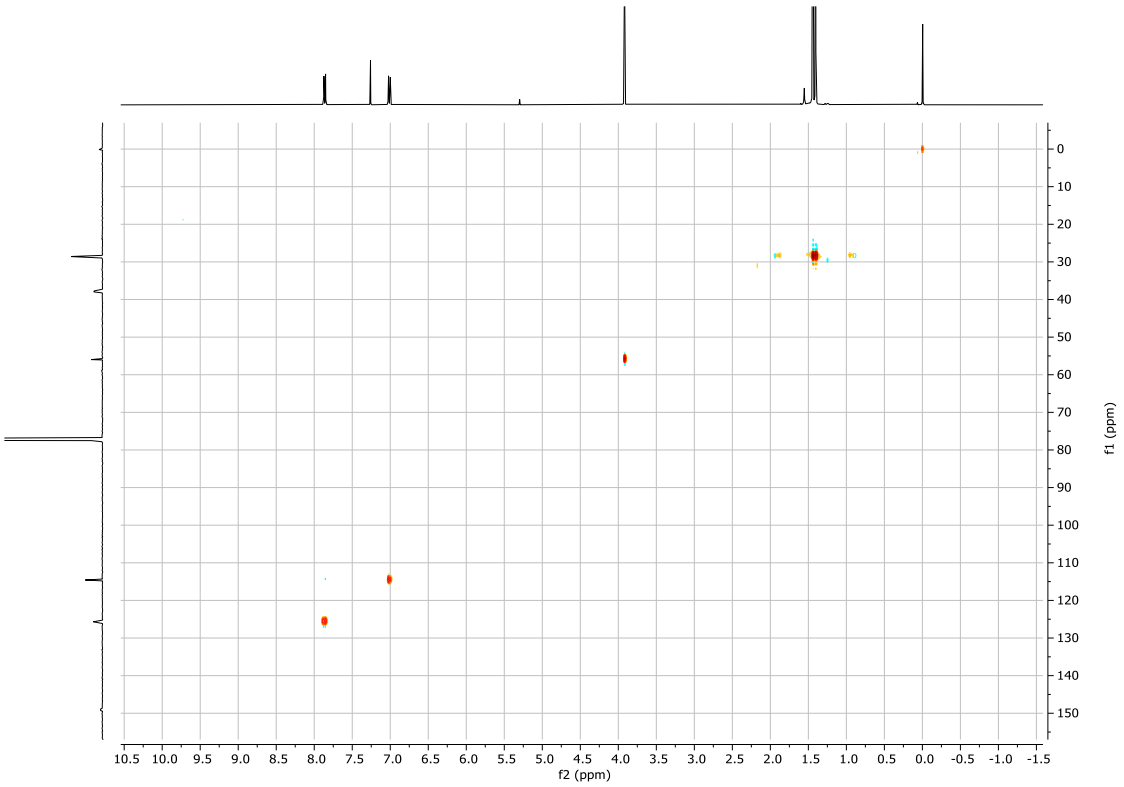

Figure S5: HSQC Spectrum of Compound **2** in $CDCl_3$

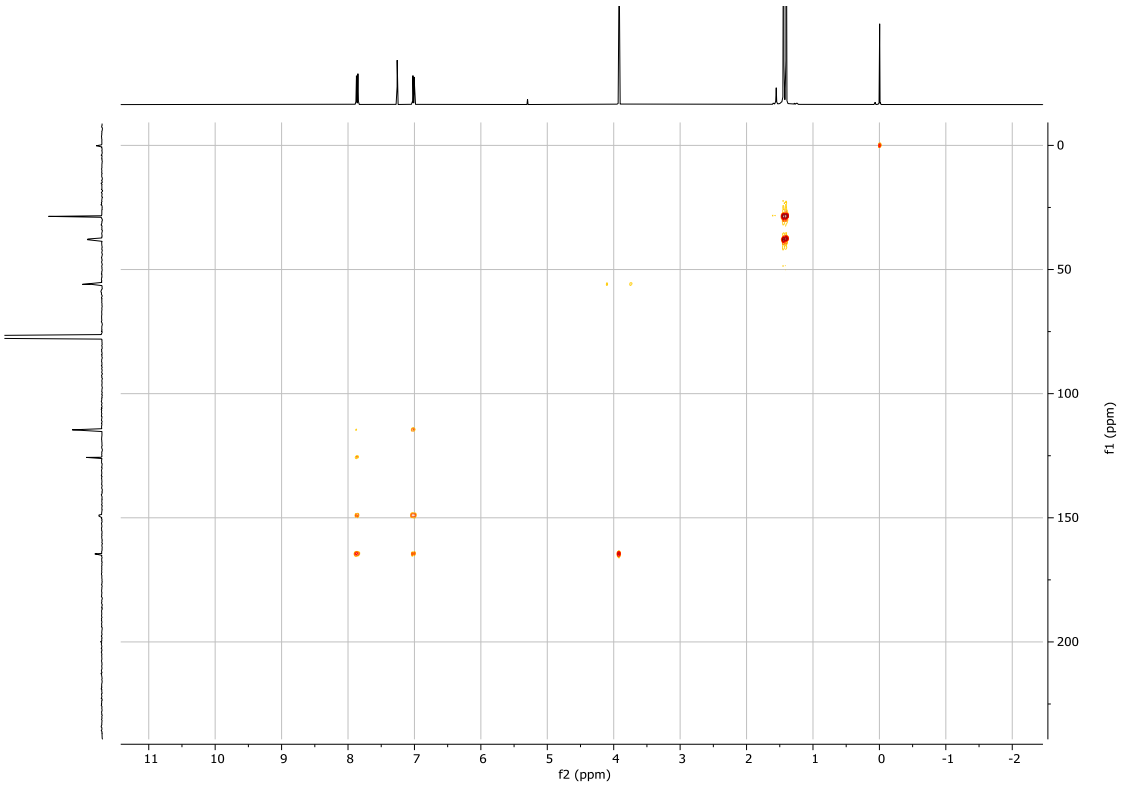

Figure S6: HMBC Spectrum of Compound **2** in $CDCl_3$

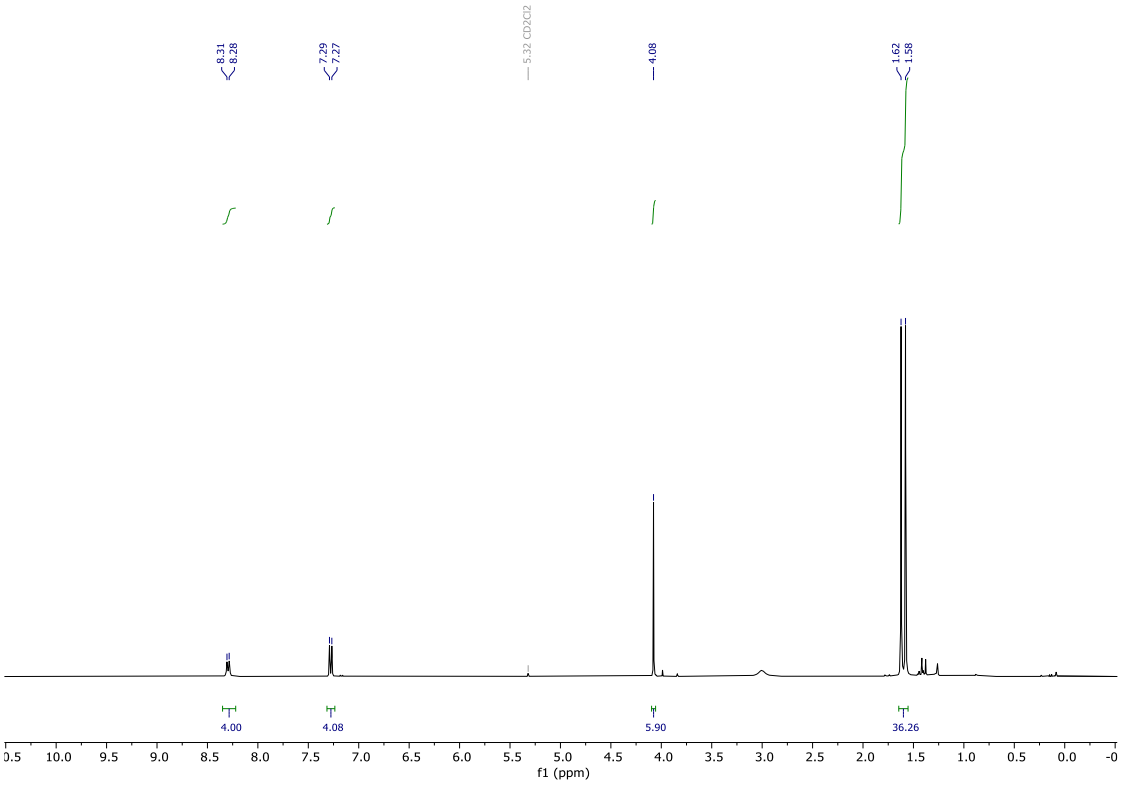

Figure S7: ^{1}H NMR Spectrum of Compound **3** in CD_2Cl_2

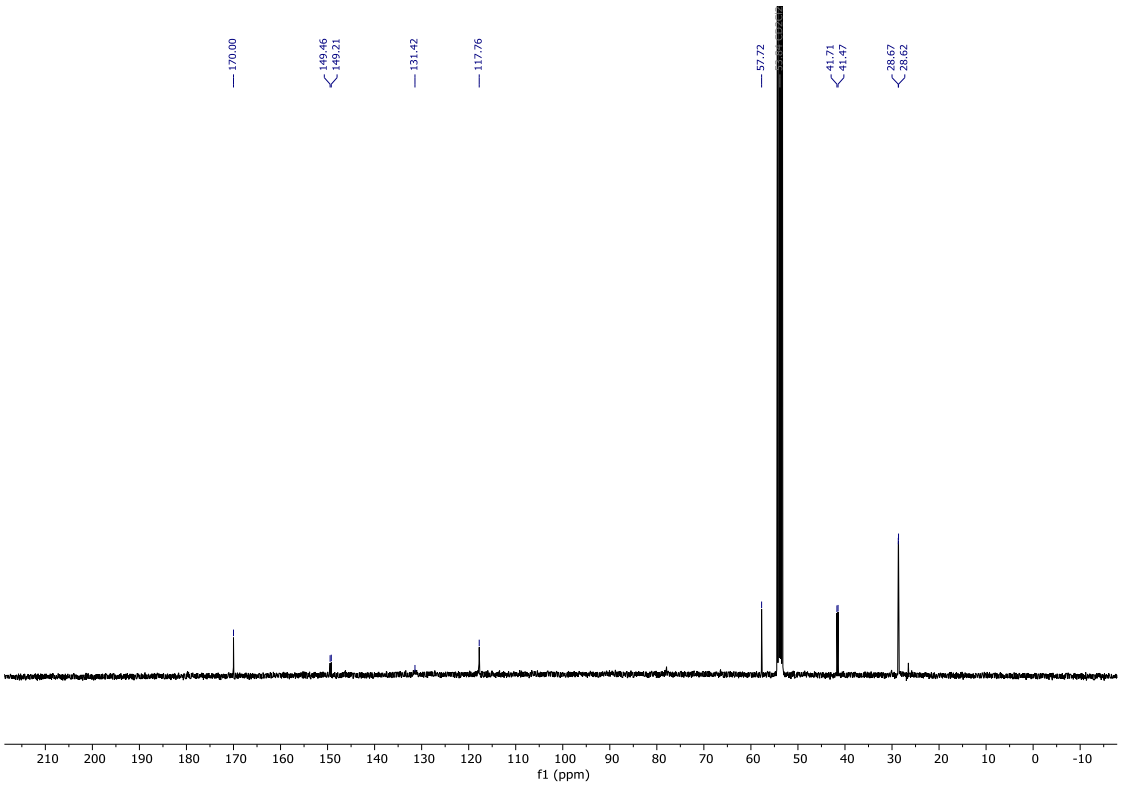

Figure S8: $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **3** in CD_2Cl_2

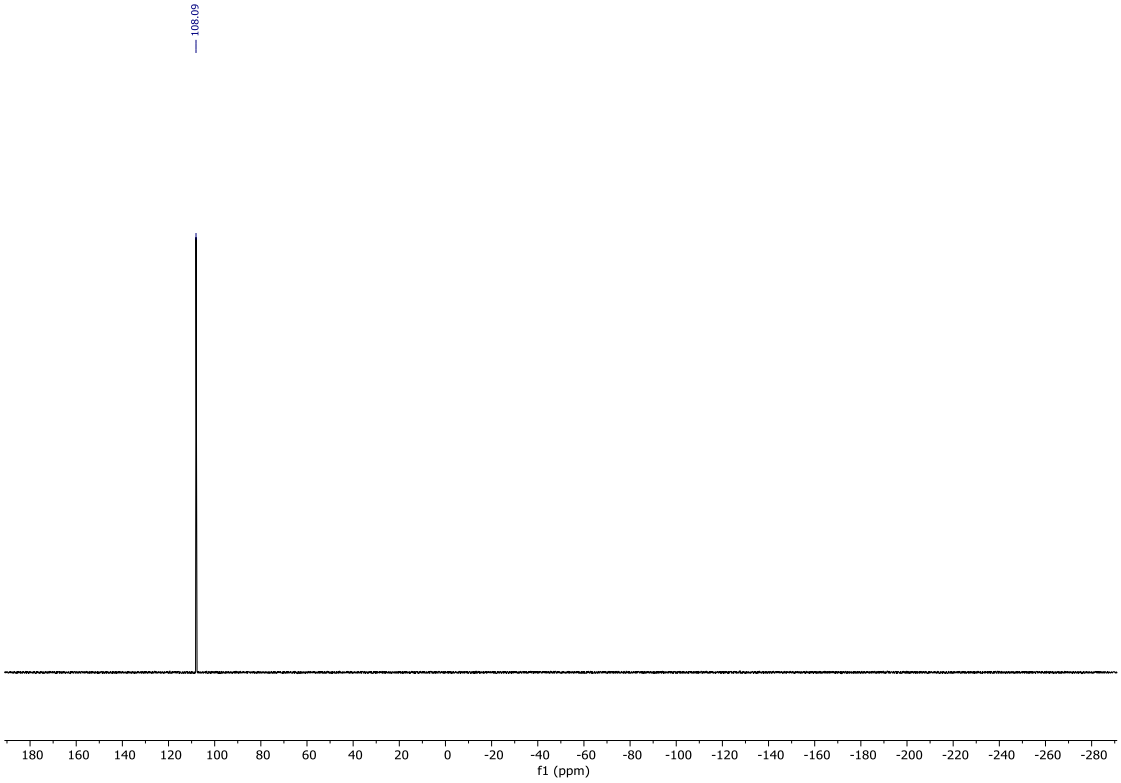

Figure S9: $^{31}P\{^{1}H\}$ NMR Spectrum of Compound **3** in CD_2Cl_2

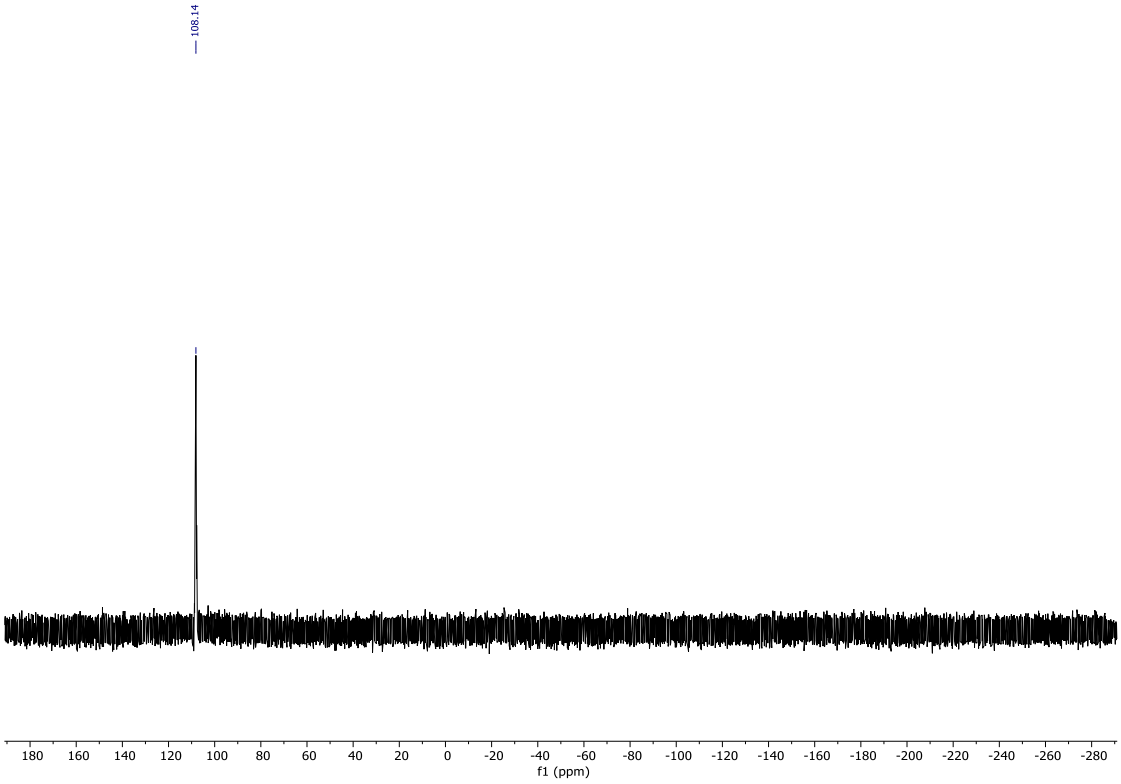

Figure S10: ^{31}P NMR Spectrum of Compound **3** in CD_2Cl_2

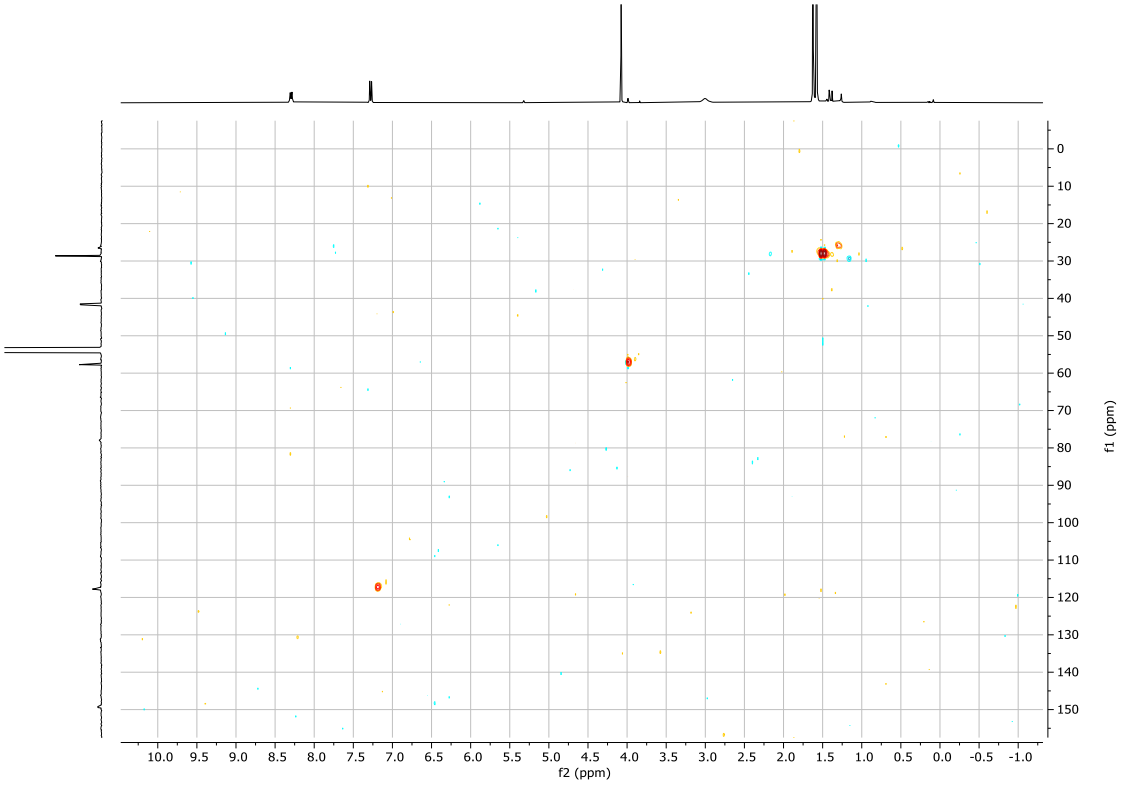

Figure S11: HSQC Spectrum of Compound **3** in CD_2Cl_2

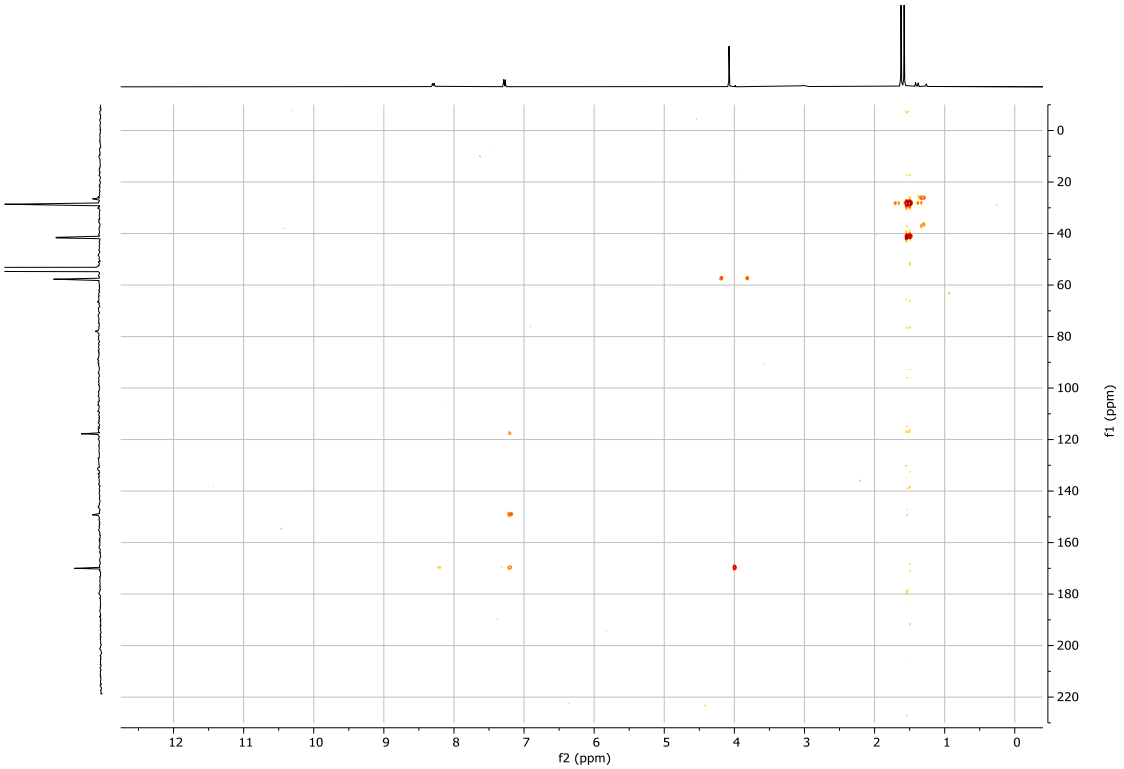

Figure S12: HMBC Spectrum of Compound **3** in CD_2Cl_2

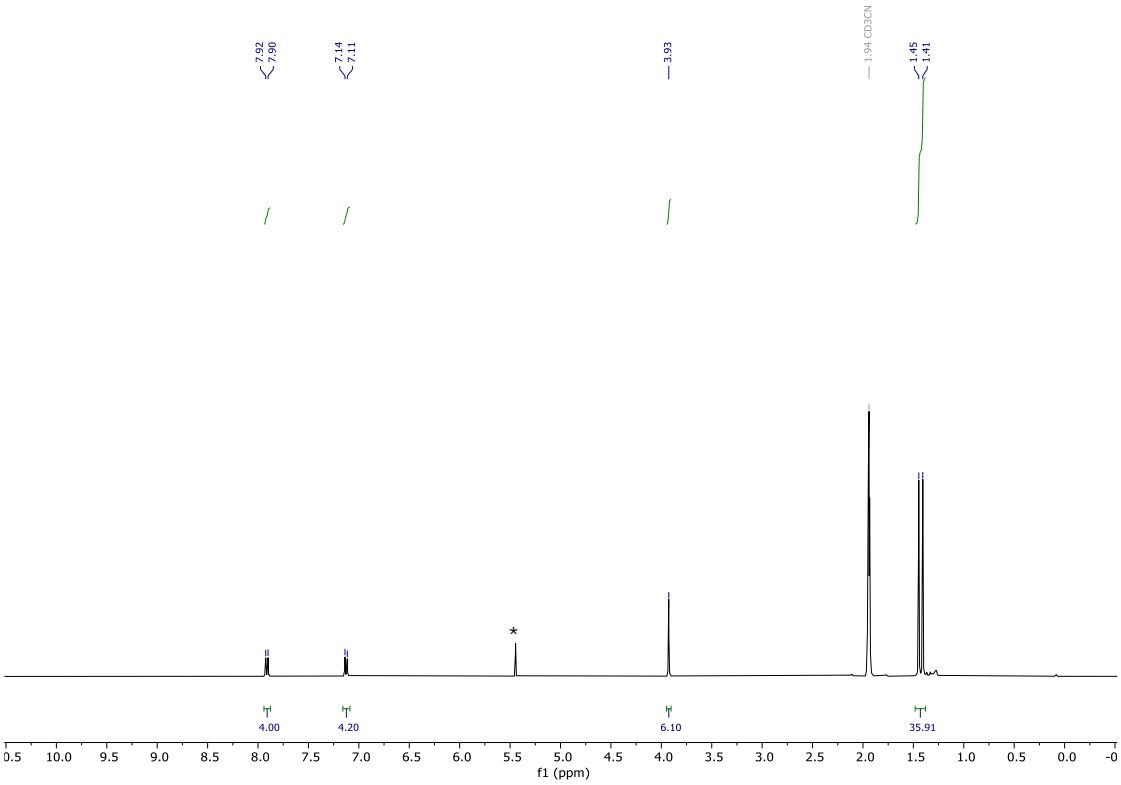

Figure S13: ^{1}H NMR Spectrum of Compound **3** in CD_3CN, *denotes CD_2Cl_2 impurity

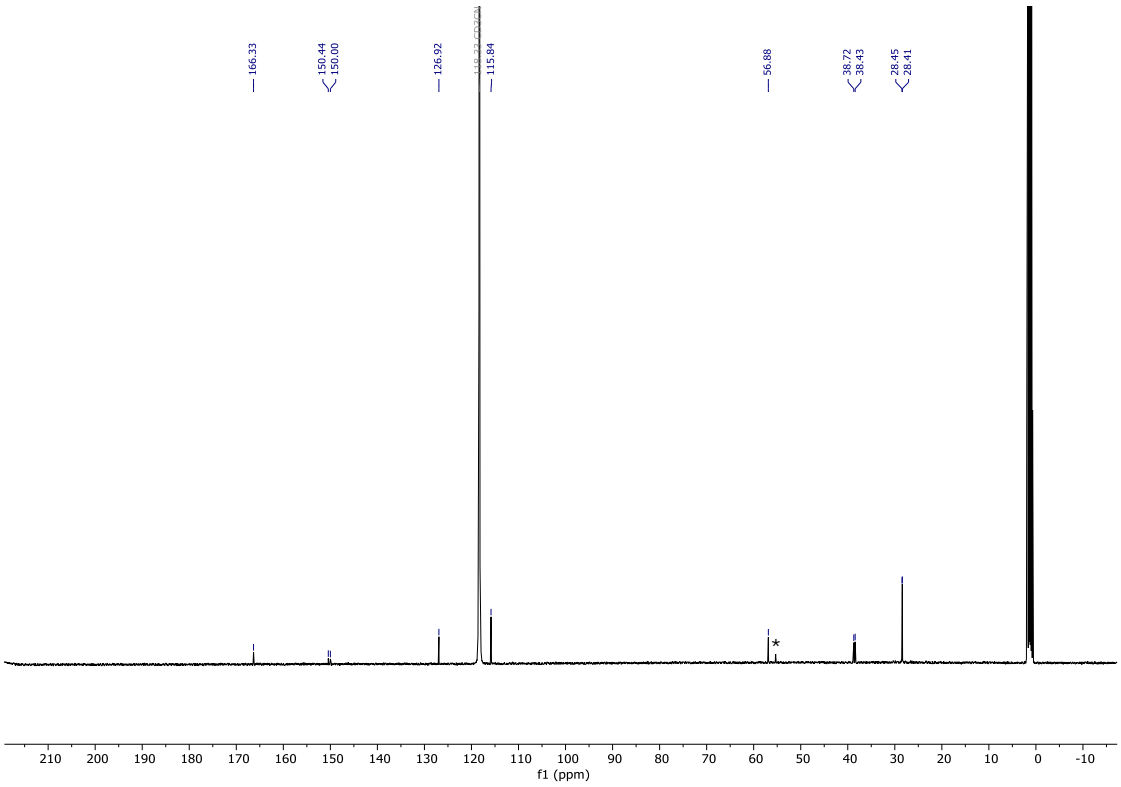

Figure S14: $^{13}C\{^{1}H\}$ NMR Spectrum of Compound **3** in CD_3CN, *denotes CD_2Cl_2 impurity

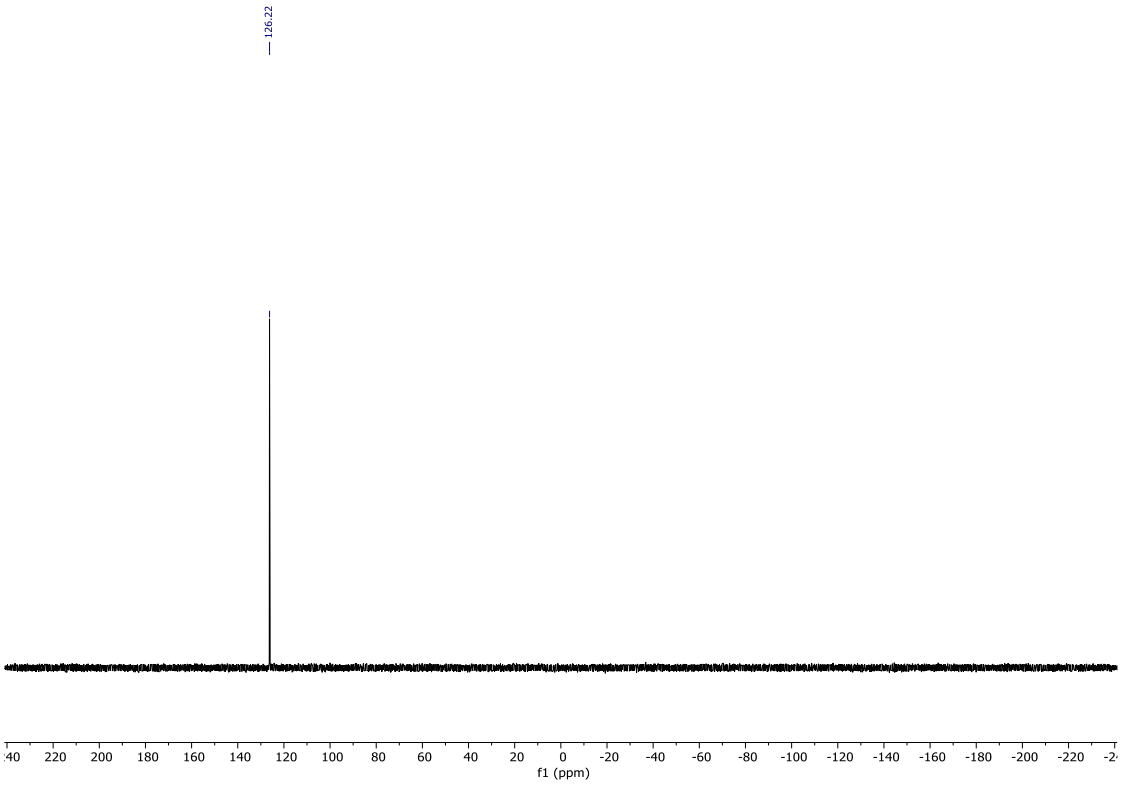

Figure S15: ^{31}P NMR Spectrum of Compound **3** in CD_3CN

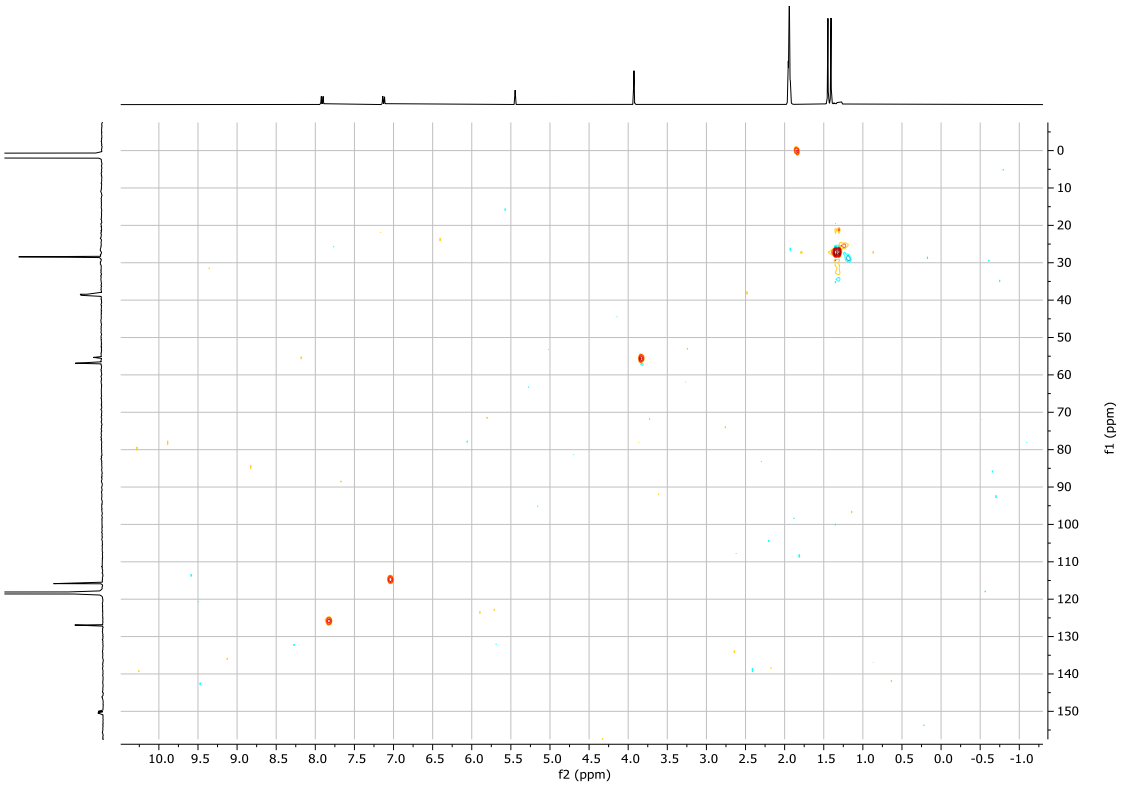

Figure S16: HSQC Spectrum of Compound **3** in CD_3CN

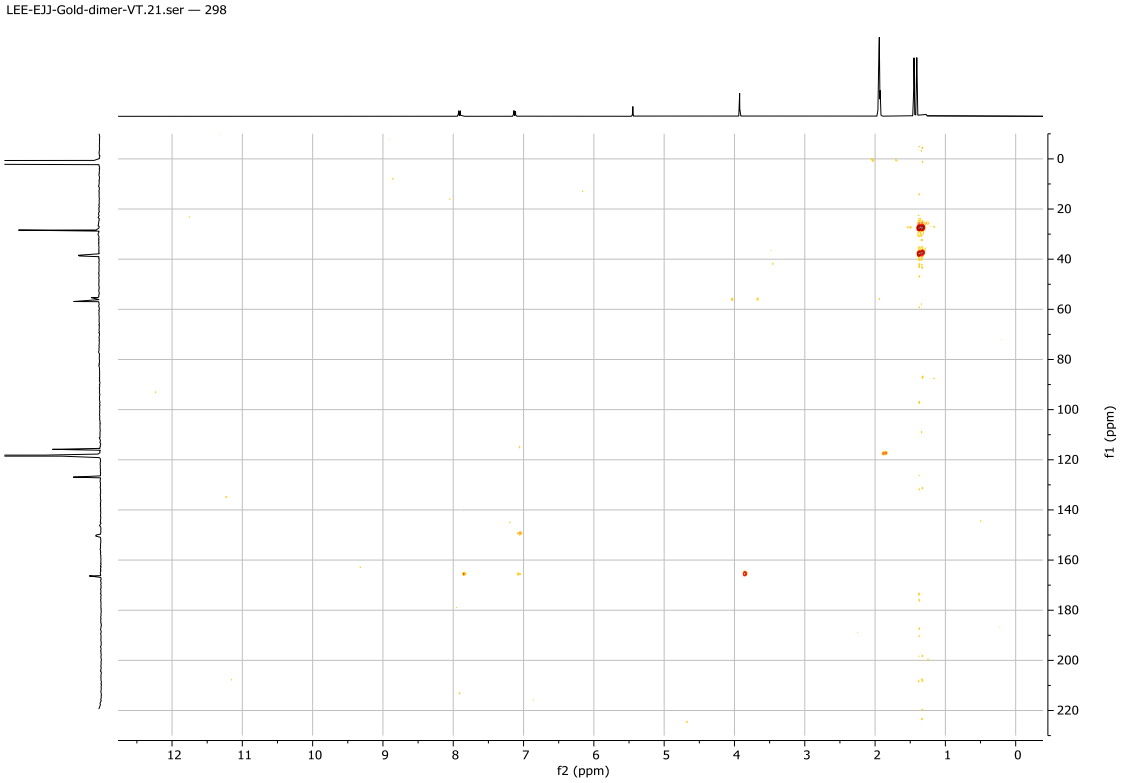

Figure S17: HMBC Spectrum of Compound **3** in CD_3CN

VT NMR Spectra

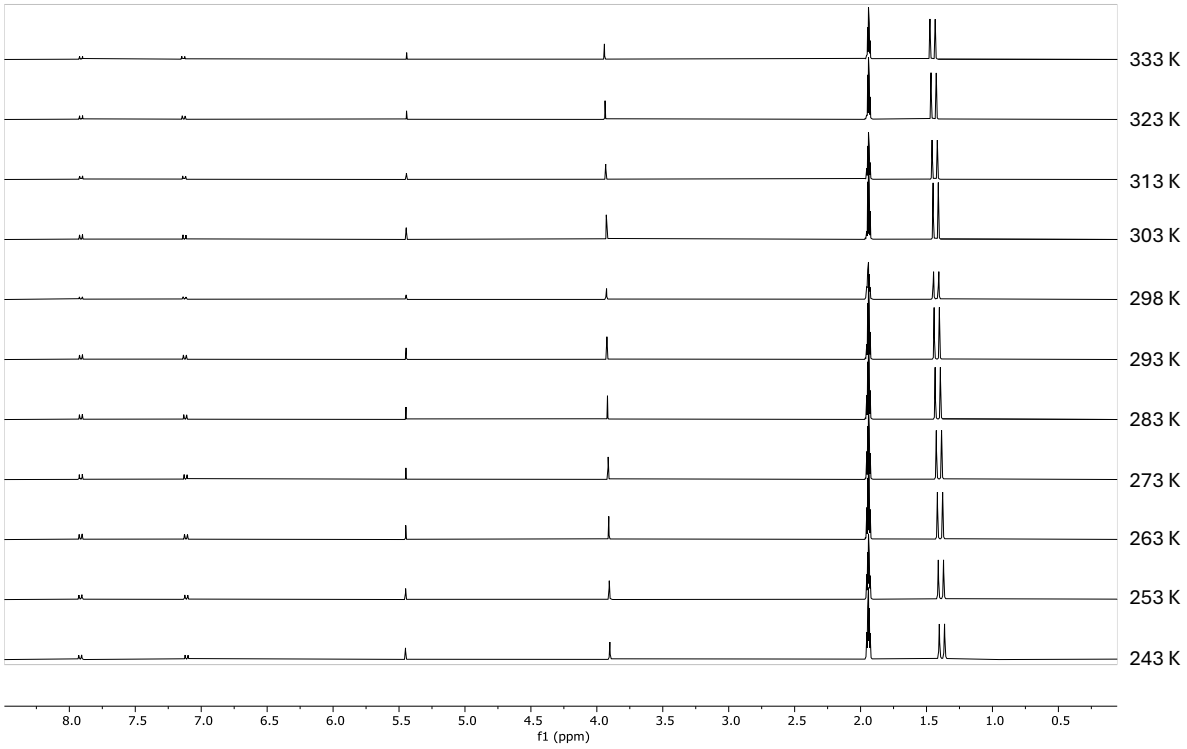

Figure S18: Stacked ^{1}H NMR Spectra of Compound **3** in CD_3CN. The change in the chemical shifts for the resonances from 243 K to 333 K are:

1.38 to 1.45 ppm

3.90 to 3.94 ppm

5.45 to 5.44 ppm

7.11 to 7.13 ppm

7.91 to 7.91 ppm

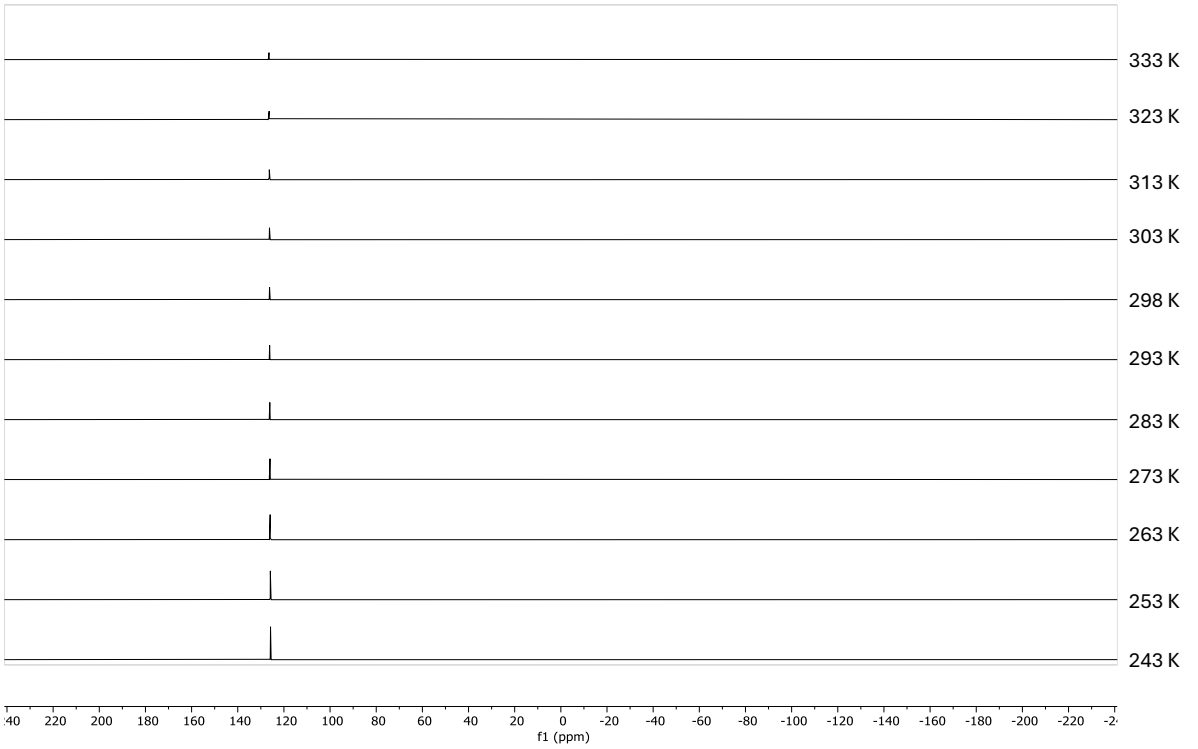

Figure S19: ^{31}P NMR Spectra of Compound **3** in CD_3CN

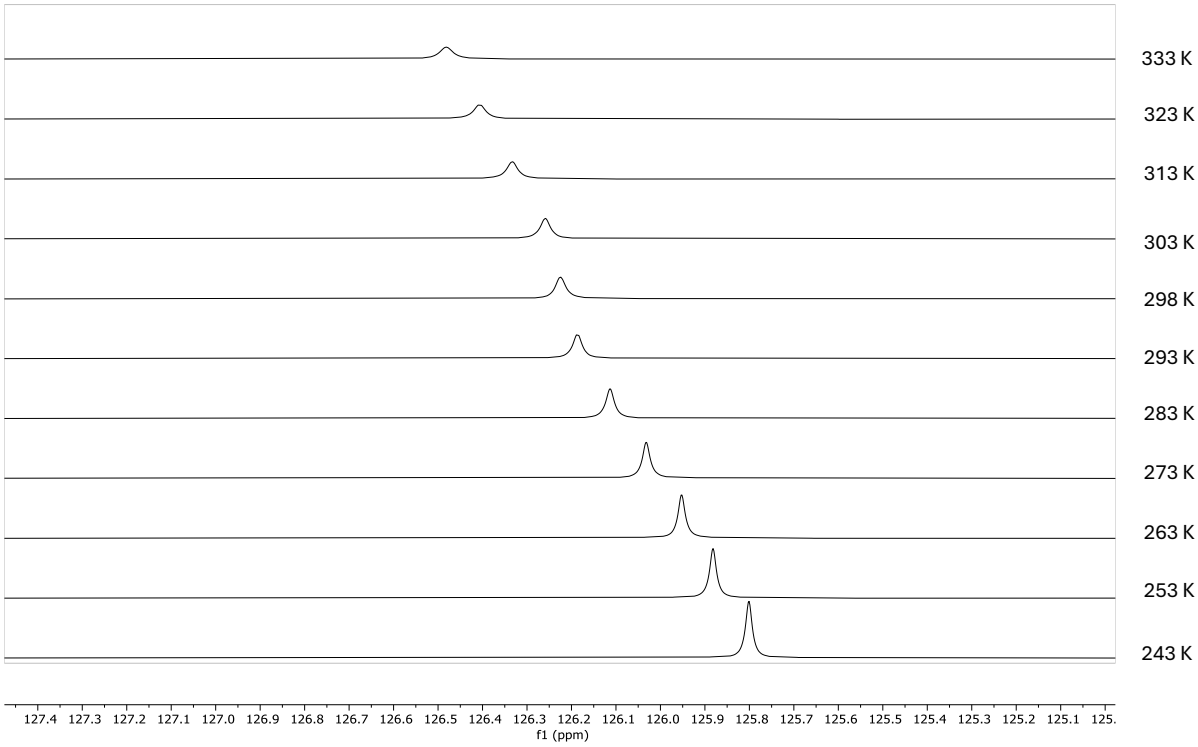

Figure S20: ^{31}P NMR Spectra of Compound **3** in CD_3CN

Mass Spectrometry Data

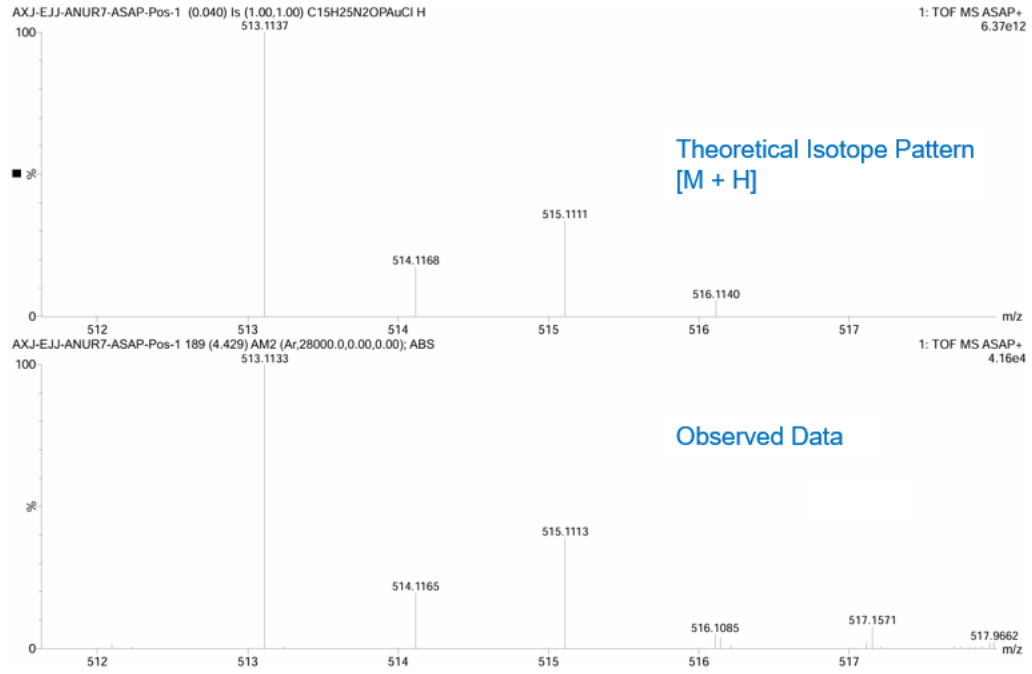

Figure S21: High-resolution Mass Spectrum of Compound **2** [M + H] = $C_{15}H_{25}N_2OPAuCl\ H$

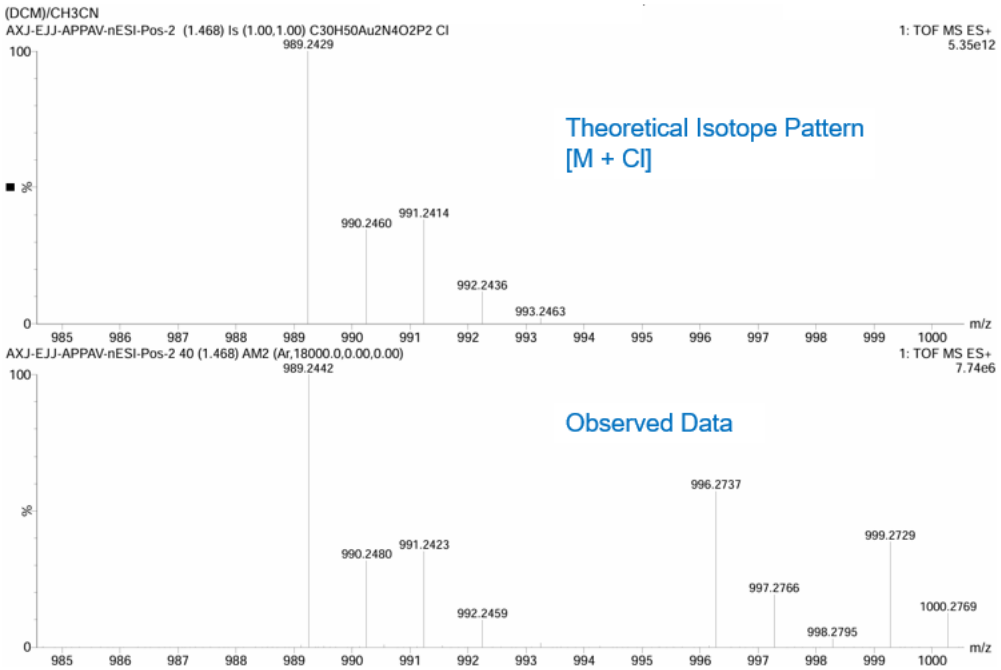

Figure S22: High-resolution Mass Spectrum of Compound **3** (positive mode) [M + Cl] = $C_{30}H_{50}Au_2N_4O_2P_2\,Cl$

UV-Vis Spectra

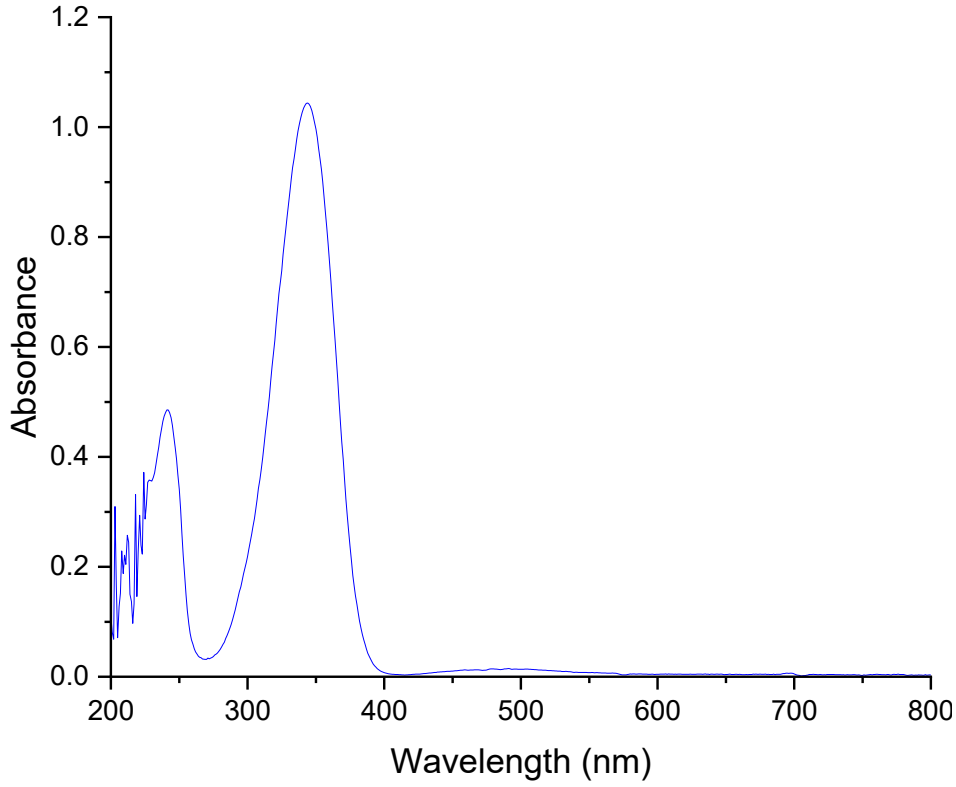

Figure S23: UV-Vis Spectrum of Compound **2** in DCM

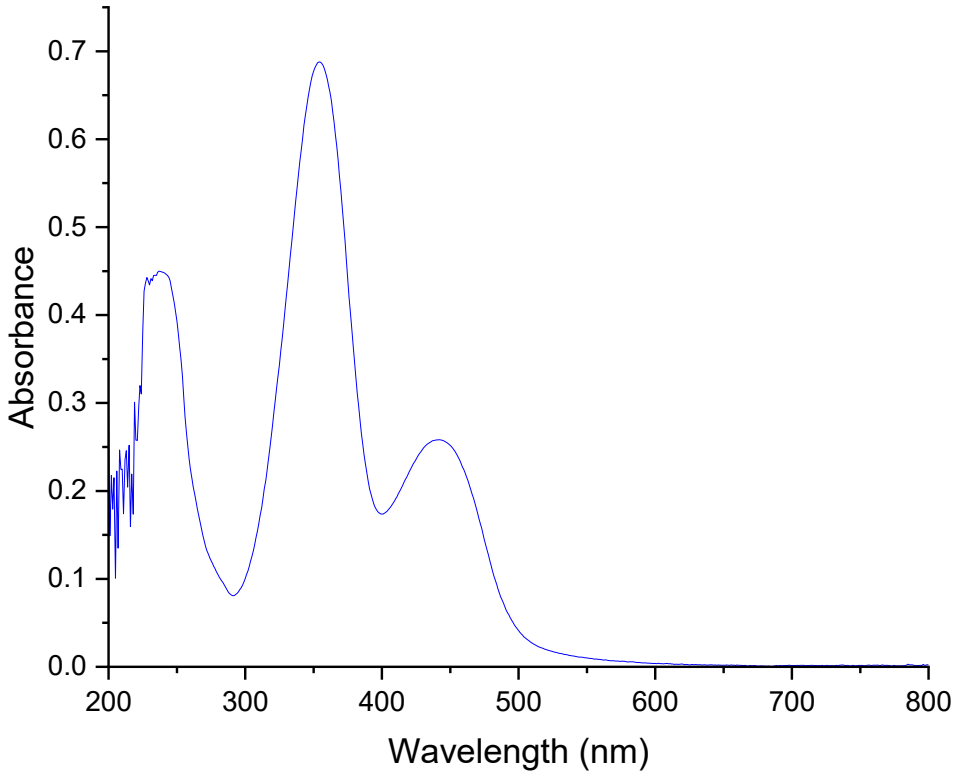

Figure S24: UV-Vis Spectrum of Compound **3** in DCM

IR Spectra

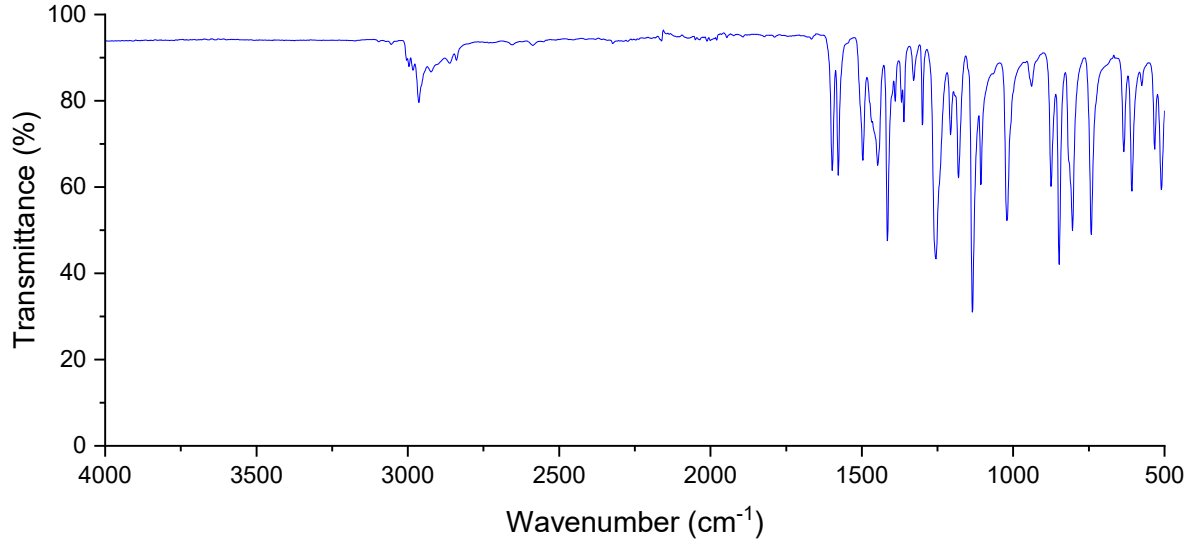

Figure S25: IR Spectrum of Compound **2**

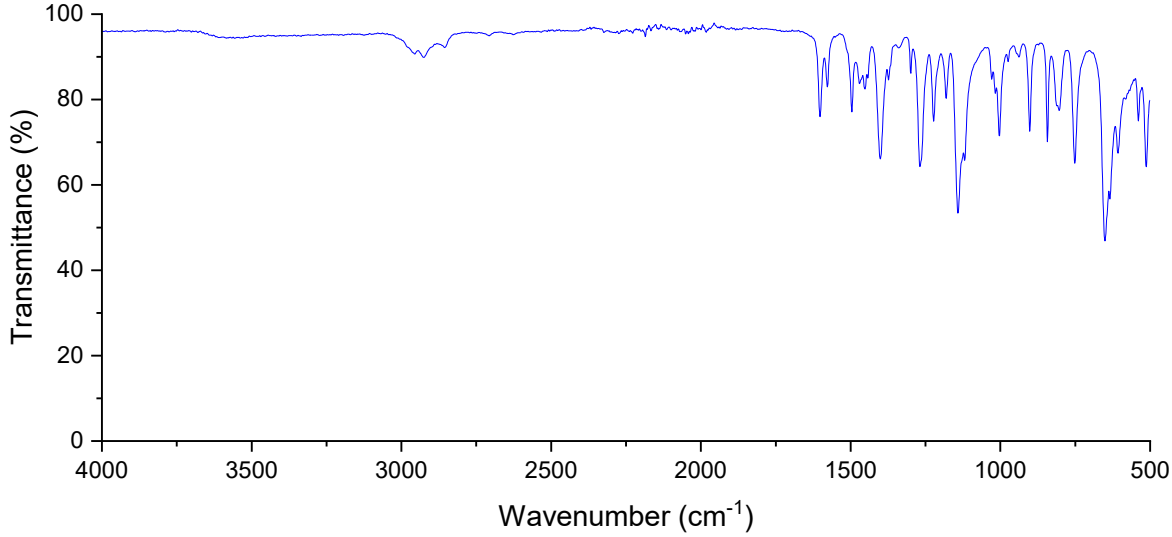

Figure S26: IR Spectrum of Compound **3**

NMR Spectra for catalysis runs

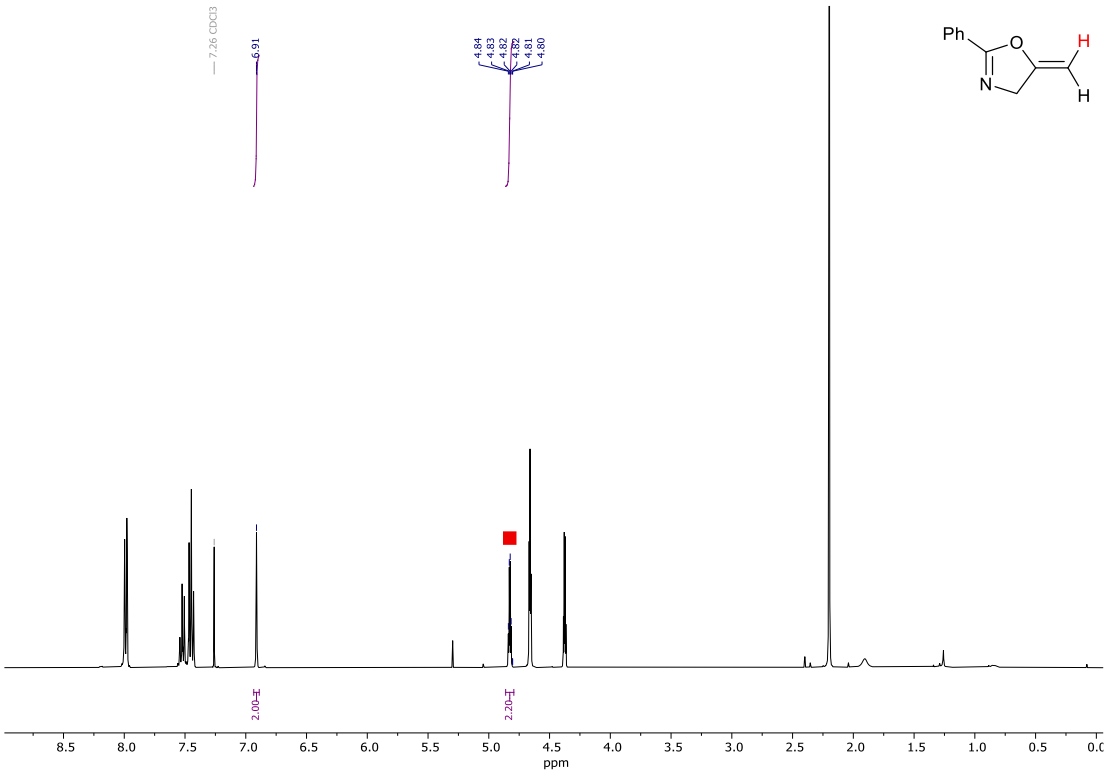

Figure S27: ^{1}H NMR Spectrum of the reaction of compound **4** using PPh_3AuCl run 1.

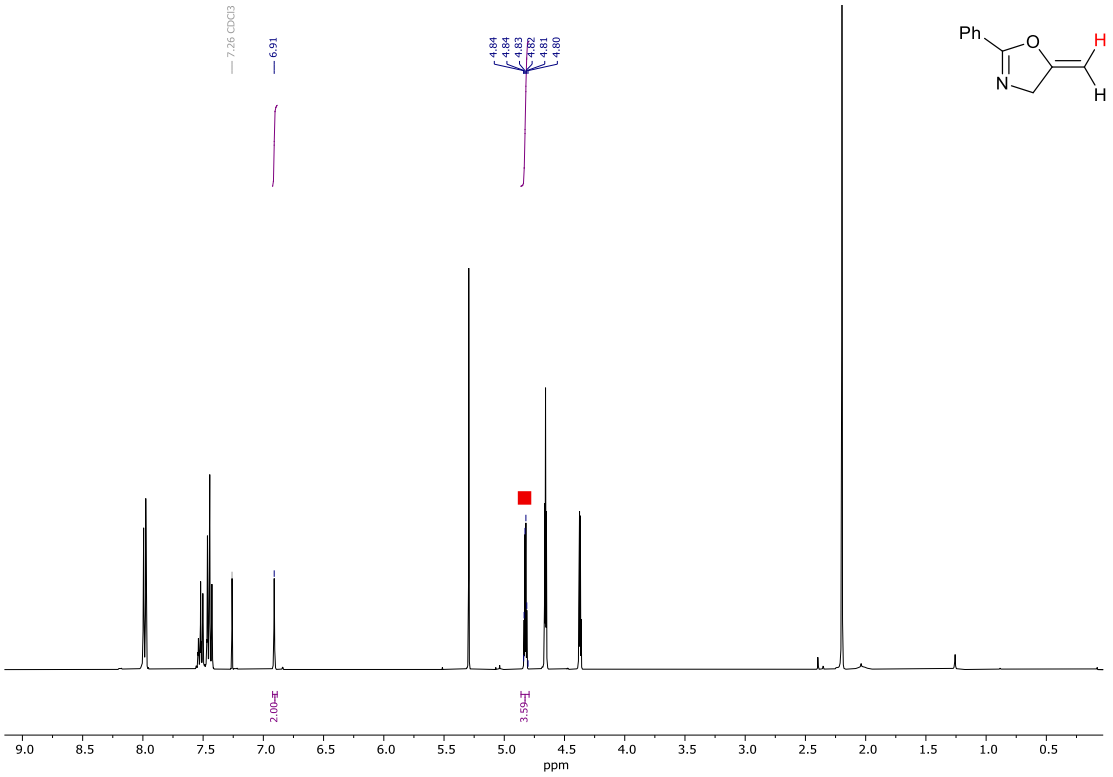

Figure S28: ^{1}H NMR Spectrum of the reaction of compound **4** using PPh_3AuCl run 2.

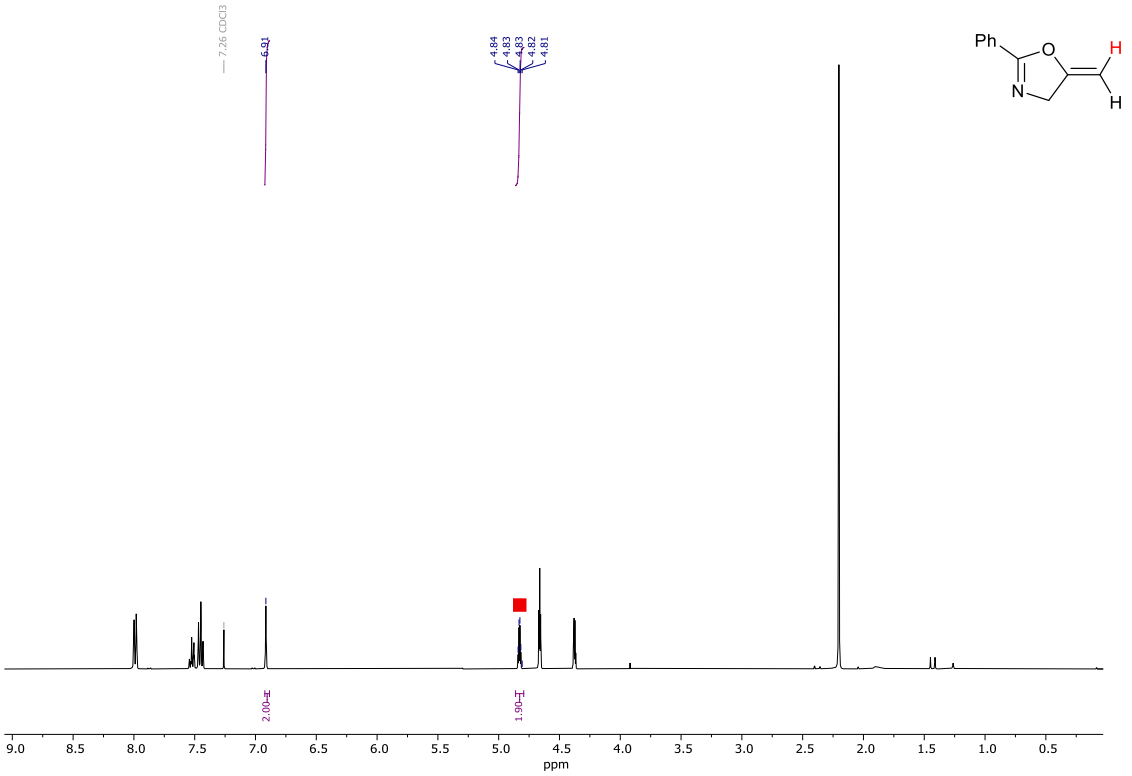

Figure S29: ^{1}H NMR Spectrum of the reaction of compound **4** using complex **2** run 1.

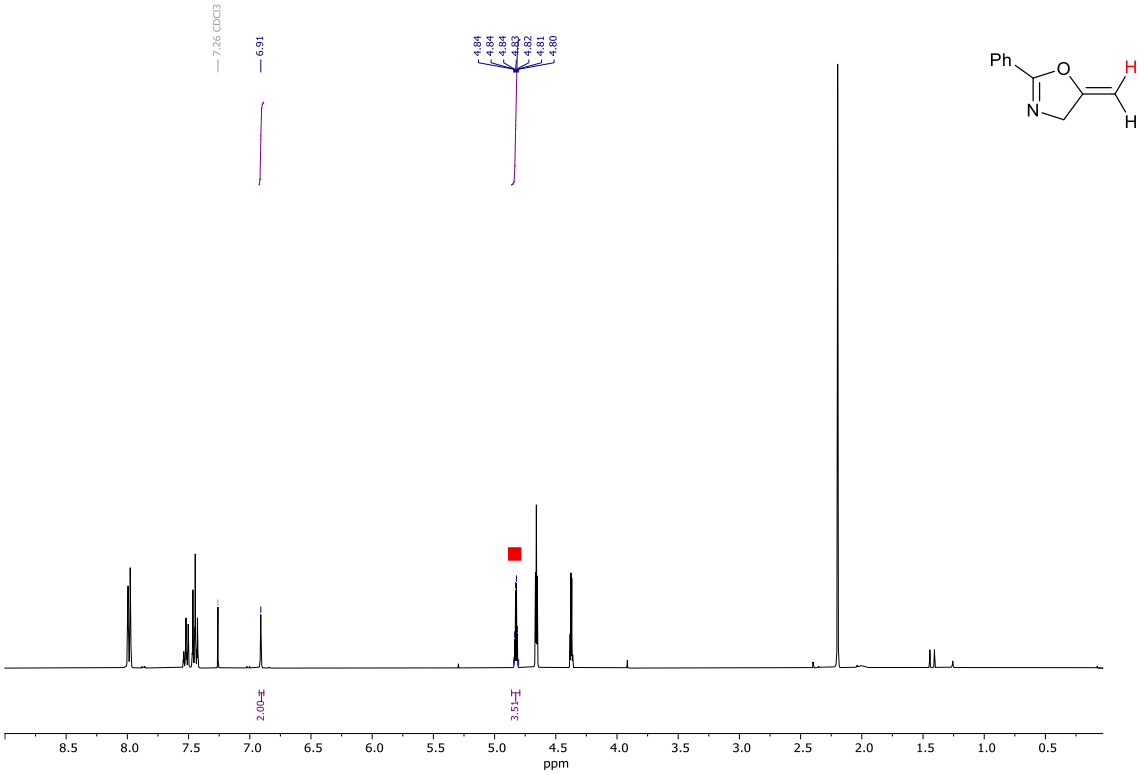

Figure S30: ^{1}H NMR Spectrum of the reaction of compound **4** using complex **2** run 2.

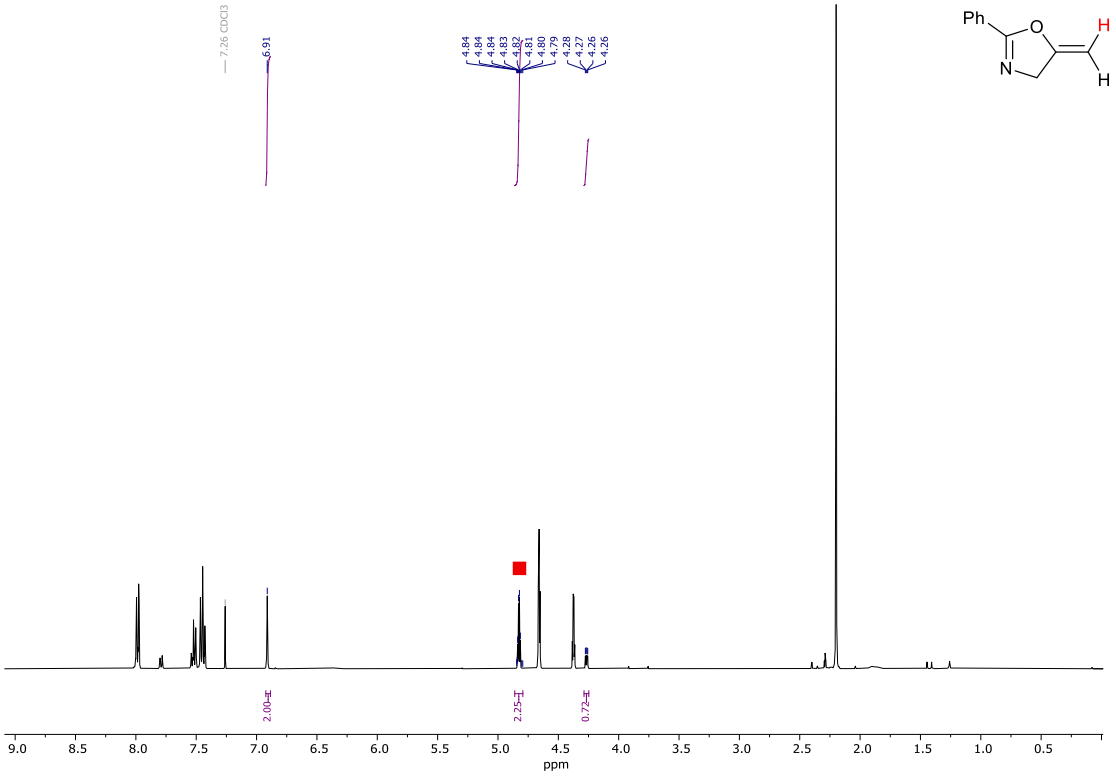

Figure S31: ^{1}H NMR Spectrum of the reaction of compound **4** using complex **3** run 1.

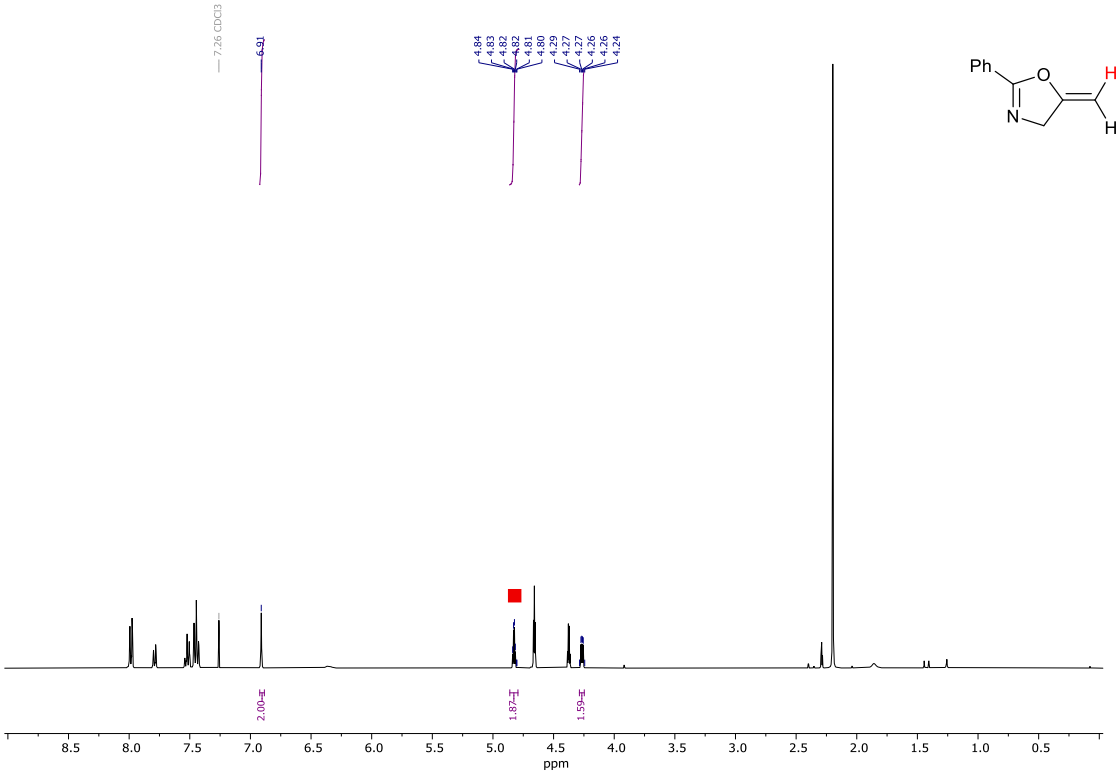

Figure S32: ^{1}H NMR Spectrum of the reaction of compound **4** using complex **3** run 2.

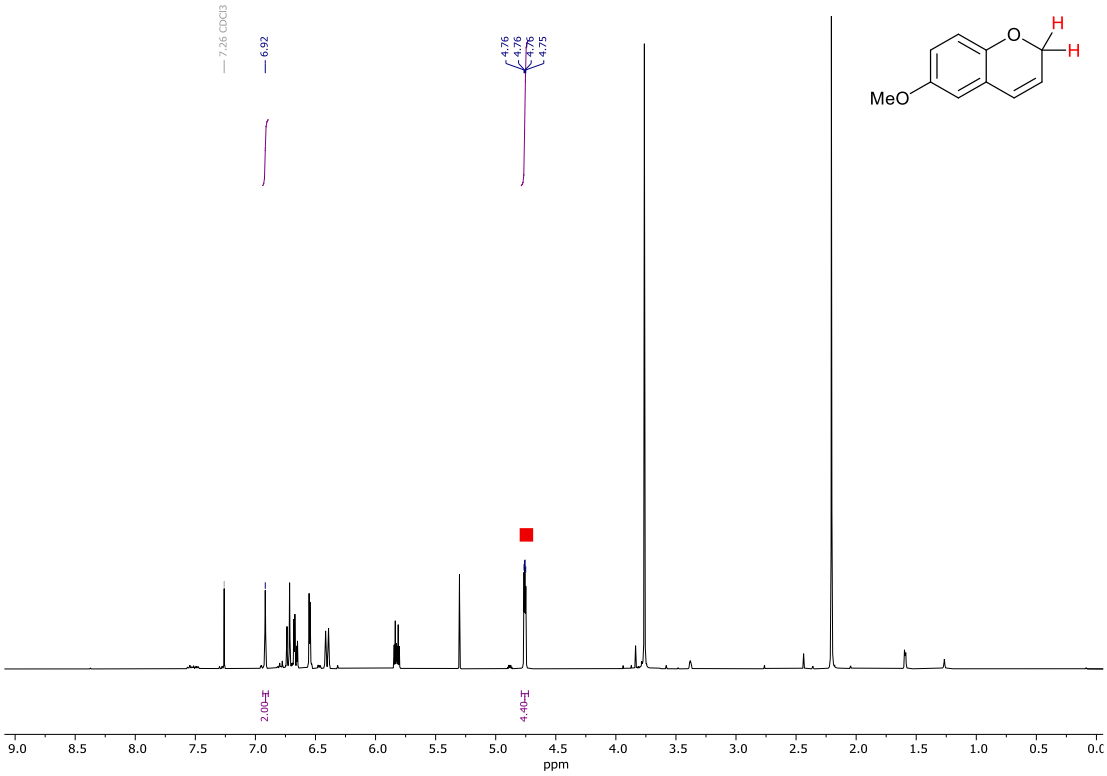

Figure S33: ^{1}H NMR Spectrum of the reaction of compound **7** using PPh_3AuCl run 1.

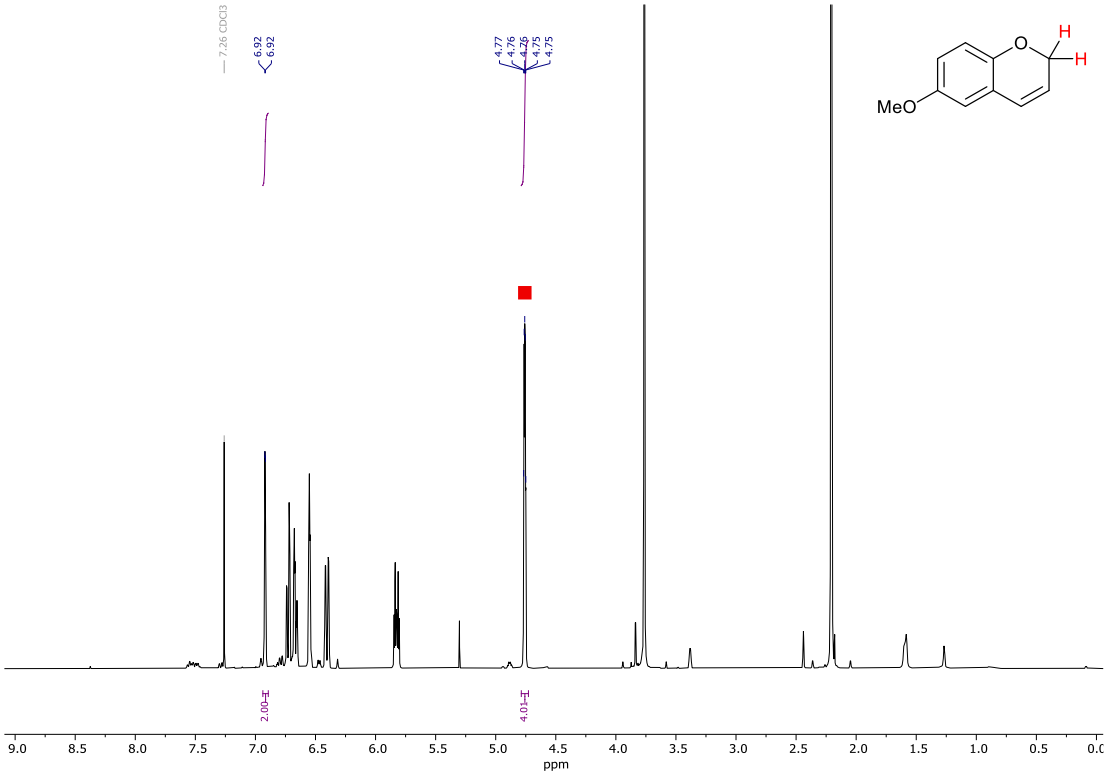

Figure S34: ^{1}H NMR Spectrum of the reaction of compound **7**using PPh_3AuCl run 2.

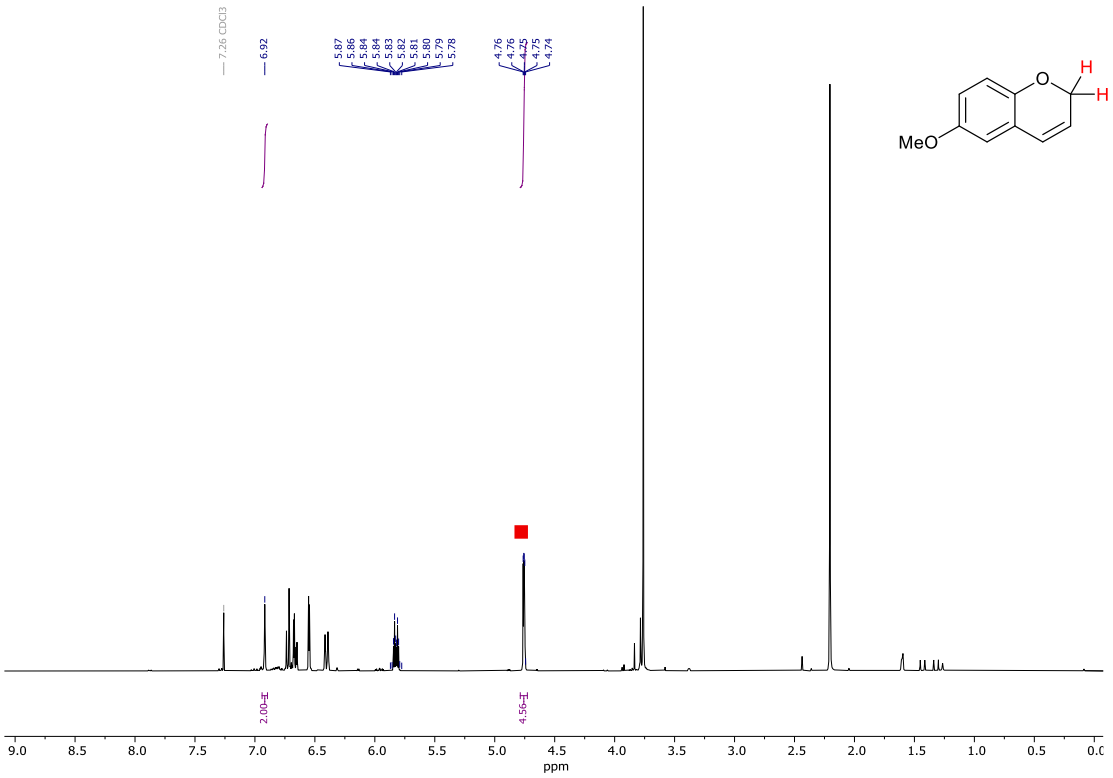

Figure S35: ^{1}H NMR Spectrum of the reaction of compound **7** using complex **2** run 1.

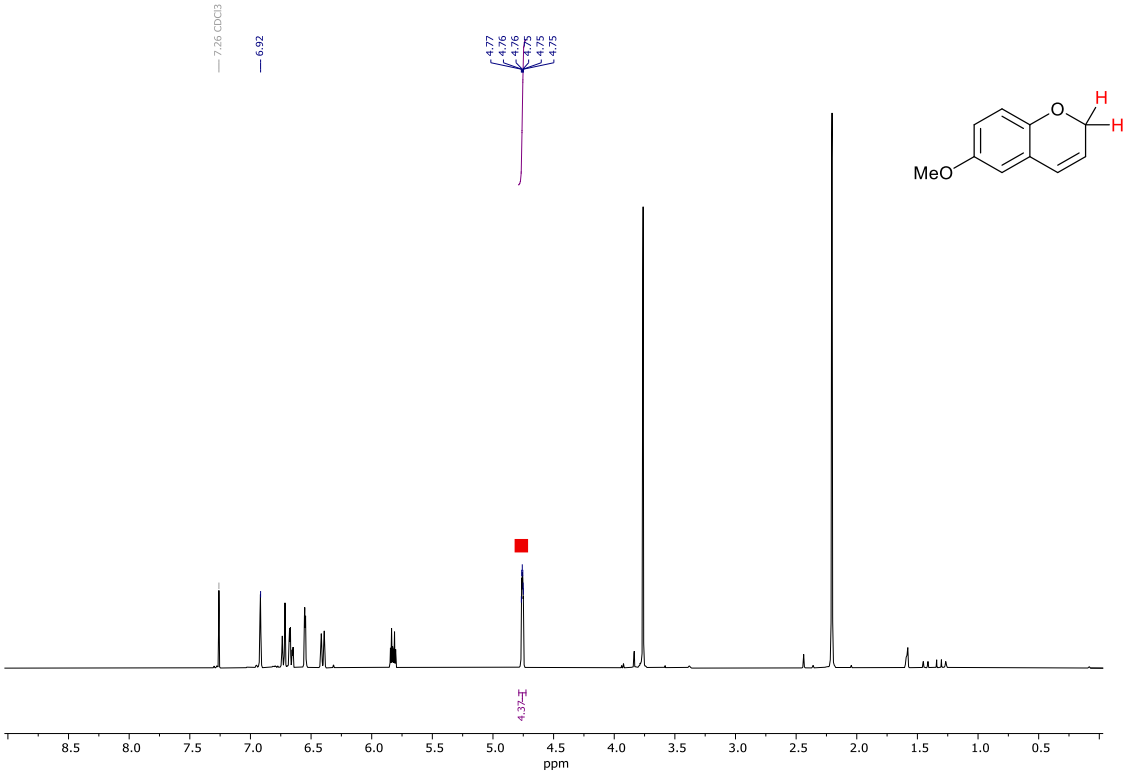

Figure S36: ^{1}H NMR Spectrum of the reaction of compound **7** using complex **2** run 2.

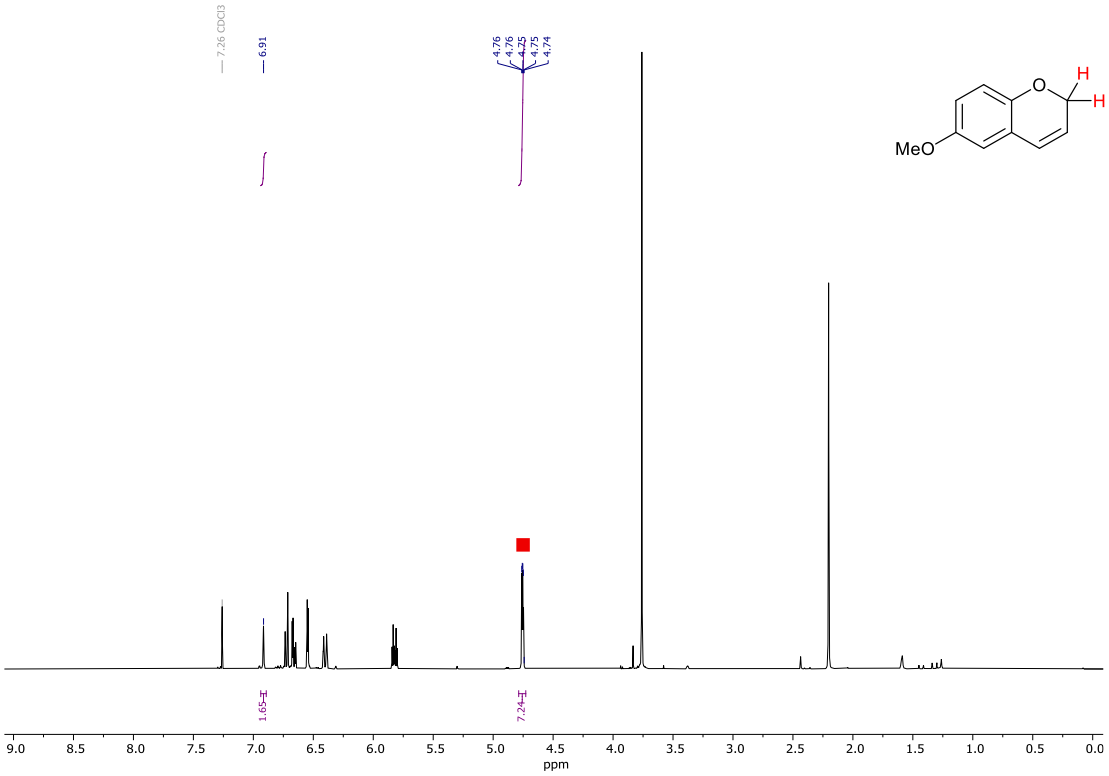

Figure S37: ^{1}H NMR Spectrum of the reaction of compound **7** using complex **3** run 1.

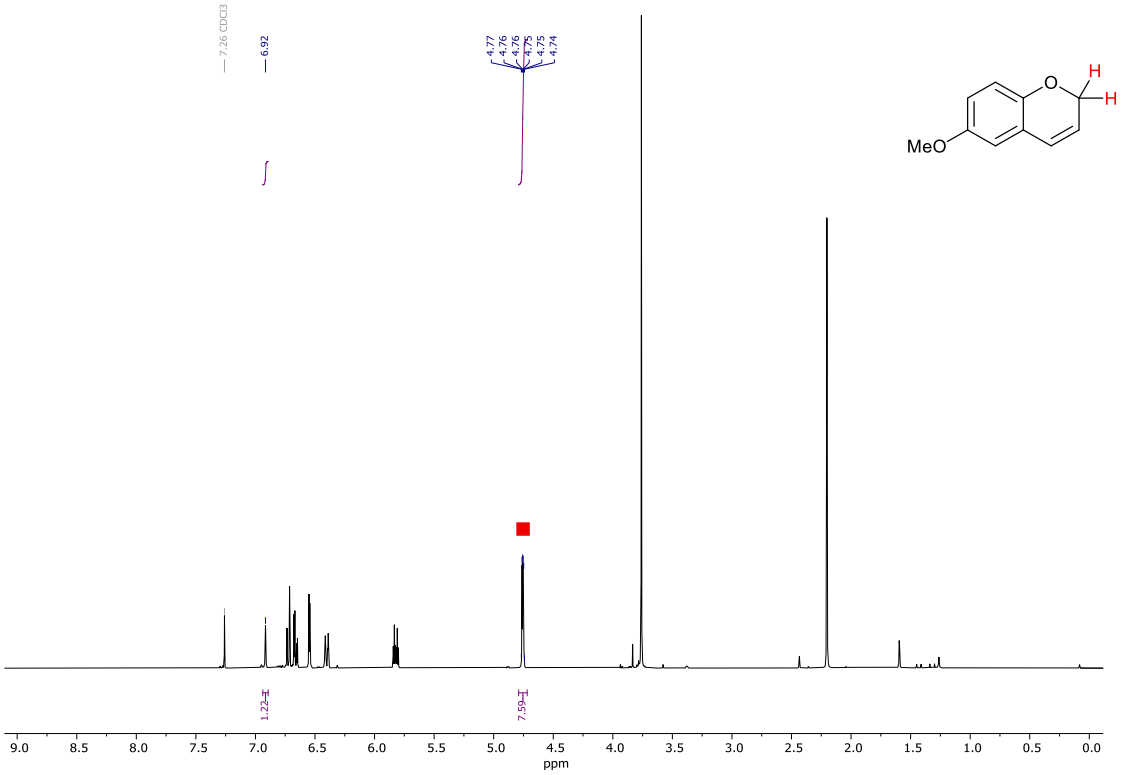

Figure S38: ^{1}H NMR Spectrum of the reaction of compound **7** using complex **3** run 2.

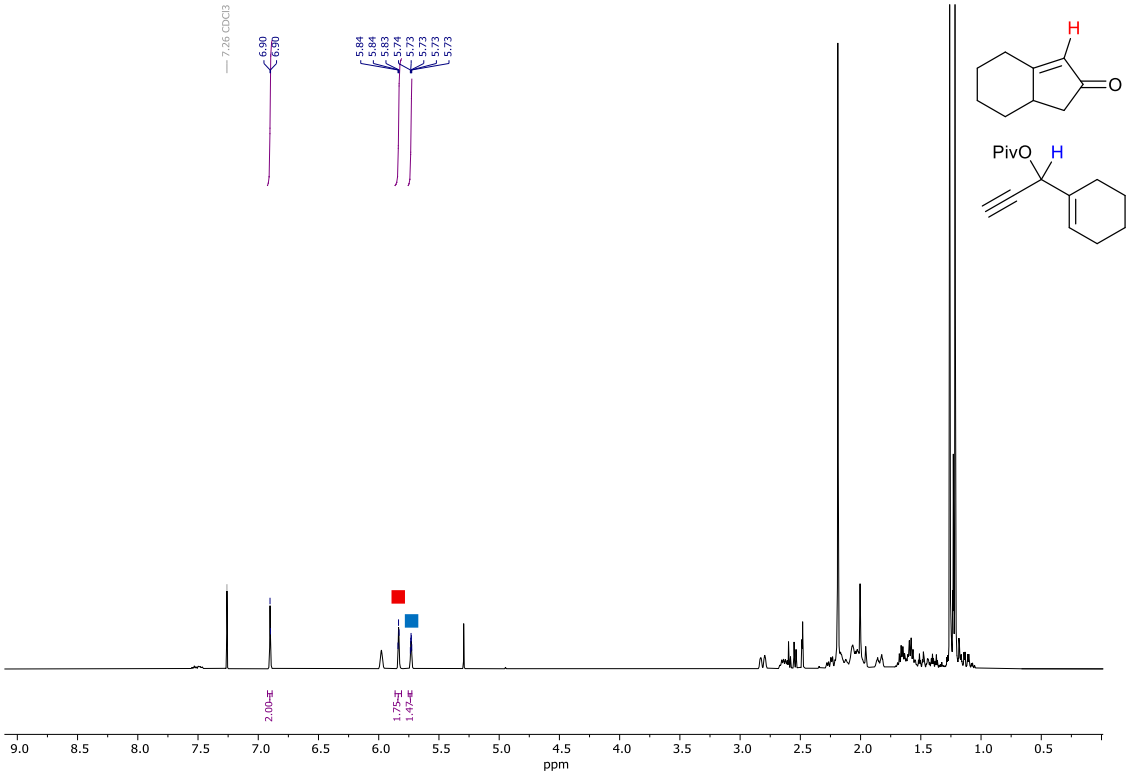

Figure S39: ^{1}H NMR Spectrum of the reaction of compound **9** using PPh_3AuCl run 1.

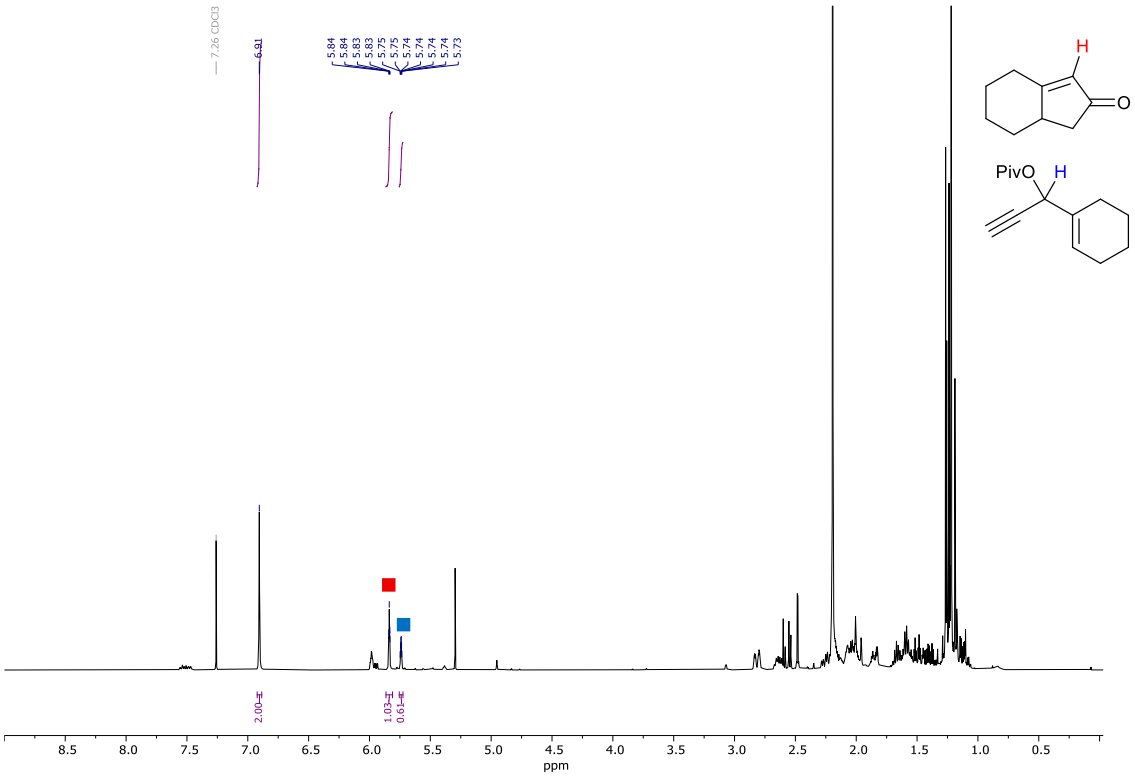

Figure S40: ^{1}H NMR Spectrum of the reaction of compound **9** using PPh_3AuCl run 2.

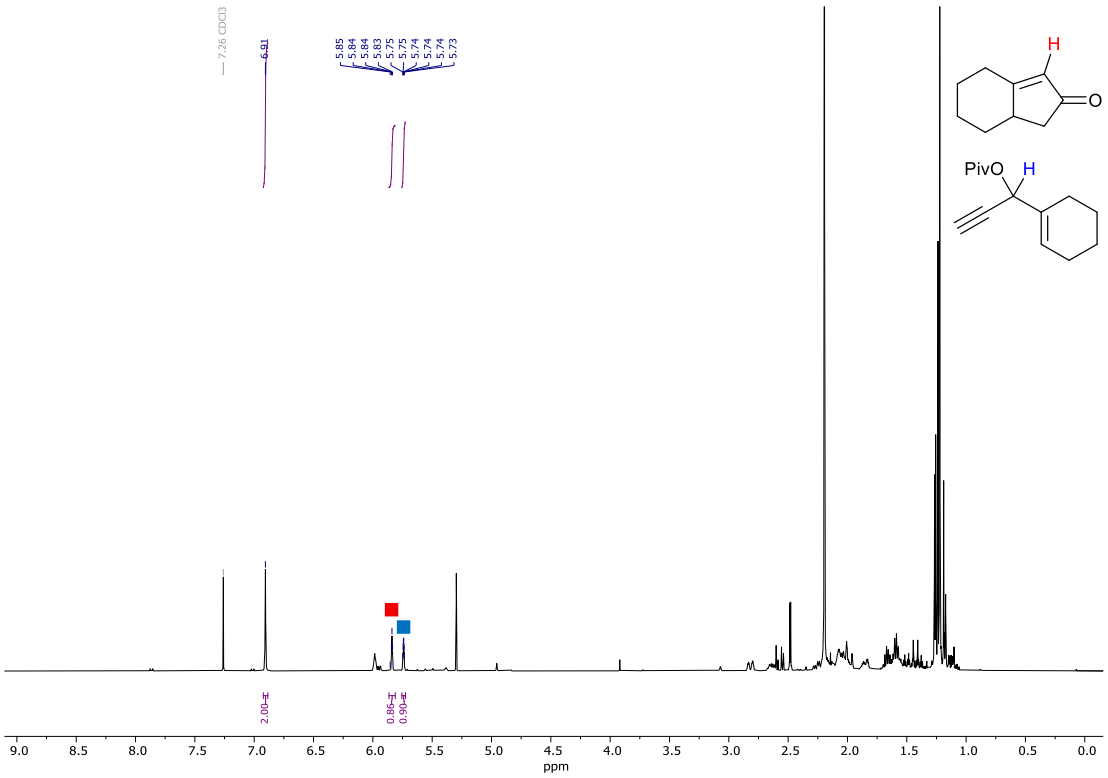

Figure S41: ^{1}H NMR Spectrum of the reaction of compound **7** using complex **2** run 1.

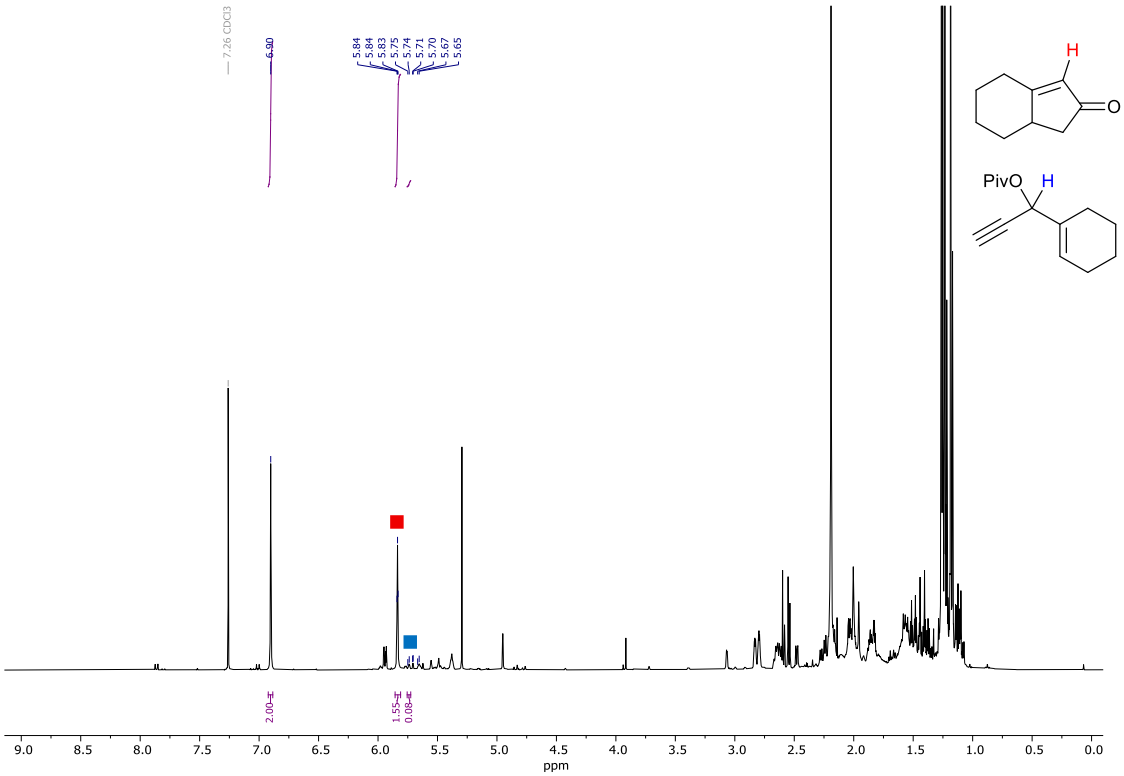

Figure S42: ^{1}H NMR Spectrum of the reaction of compound **9** using complex **2** run 2.

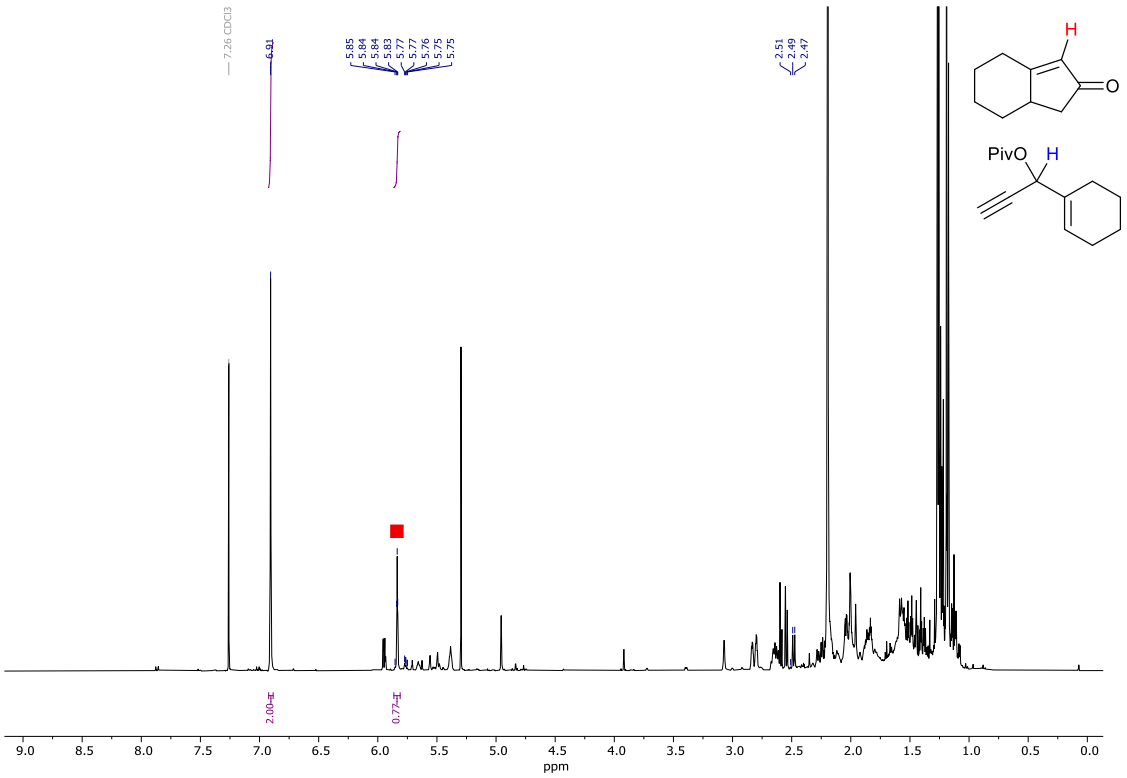

Figure S43: ^{1}H NMR Spectrum of the reaction of compound **9** using complex **3** run 1.

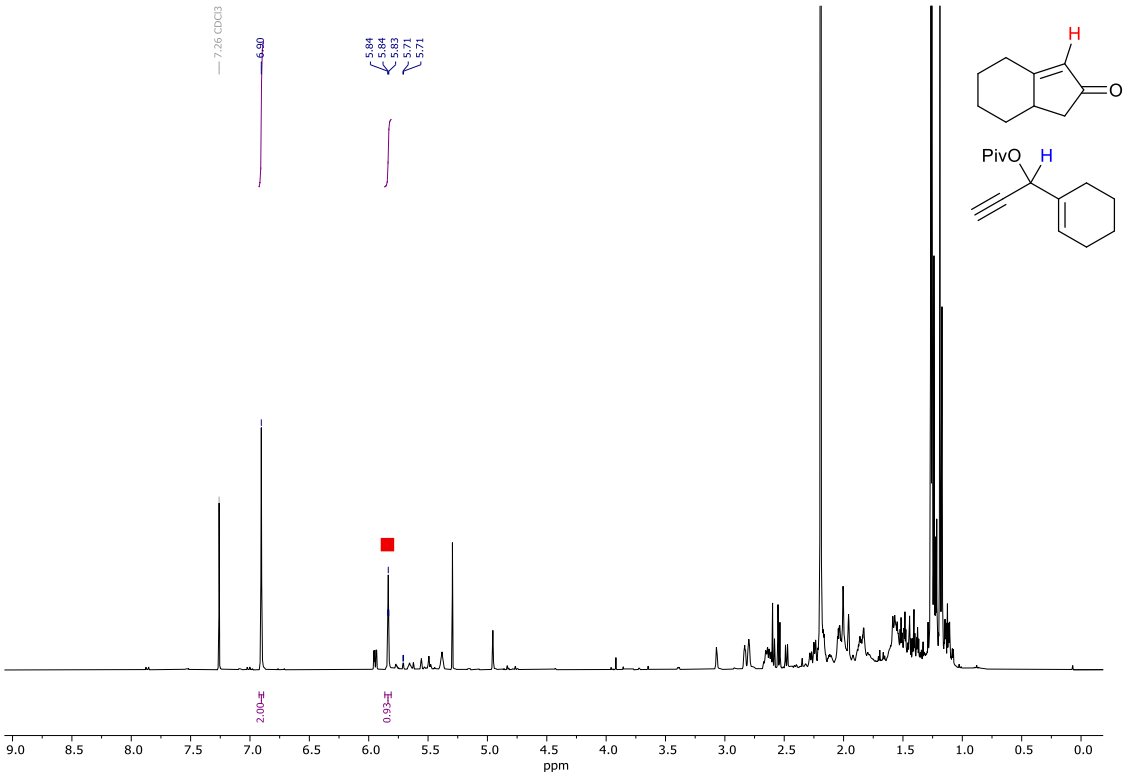

Figure S44: ^{1}H NMR Spectrum of the reaction of compound **9** using complex **3** run 2.

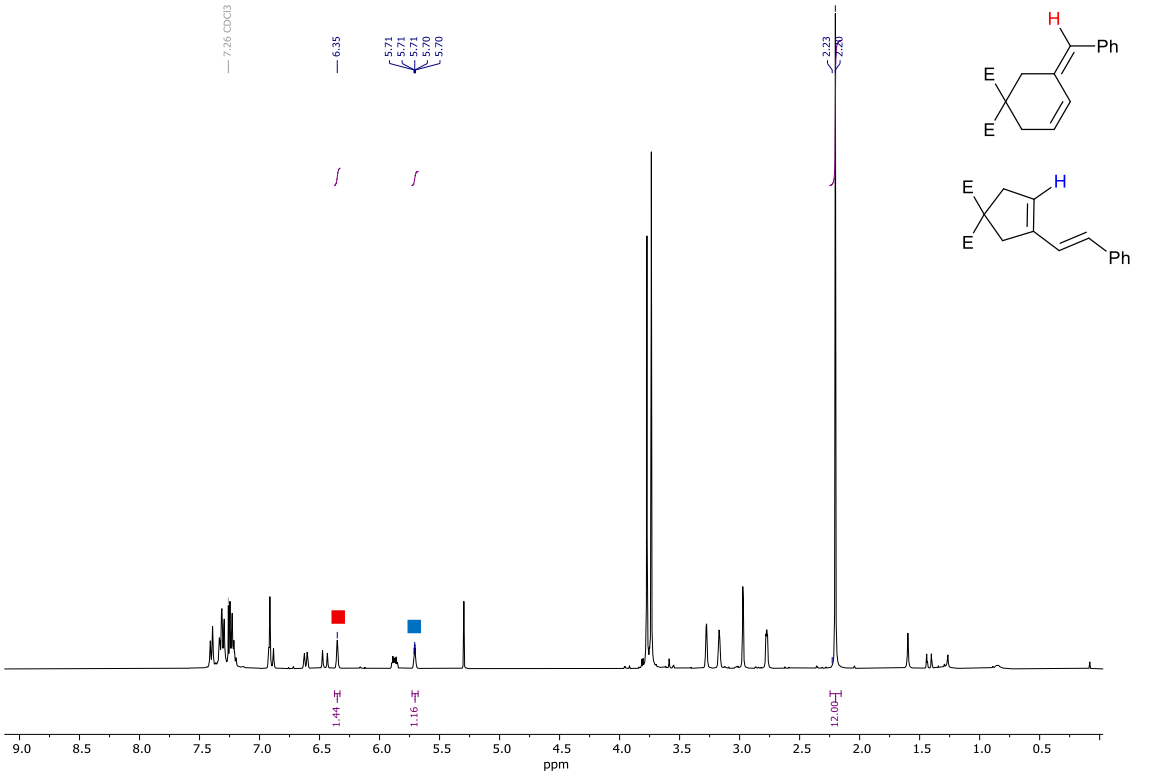

Figure S45: ^{1}H NMR Spectrum of the reaction of compound **11** using JohnPhosAuCl run 1.

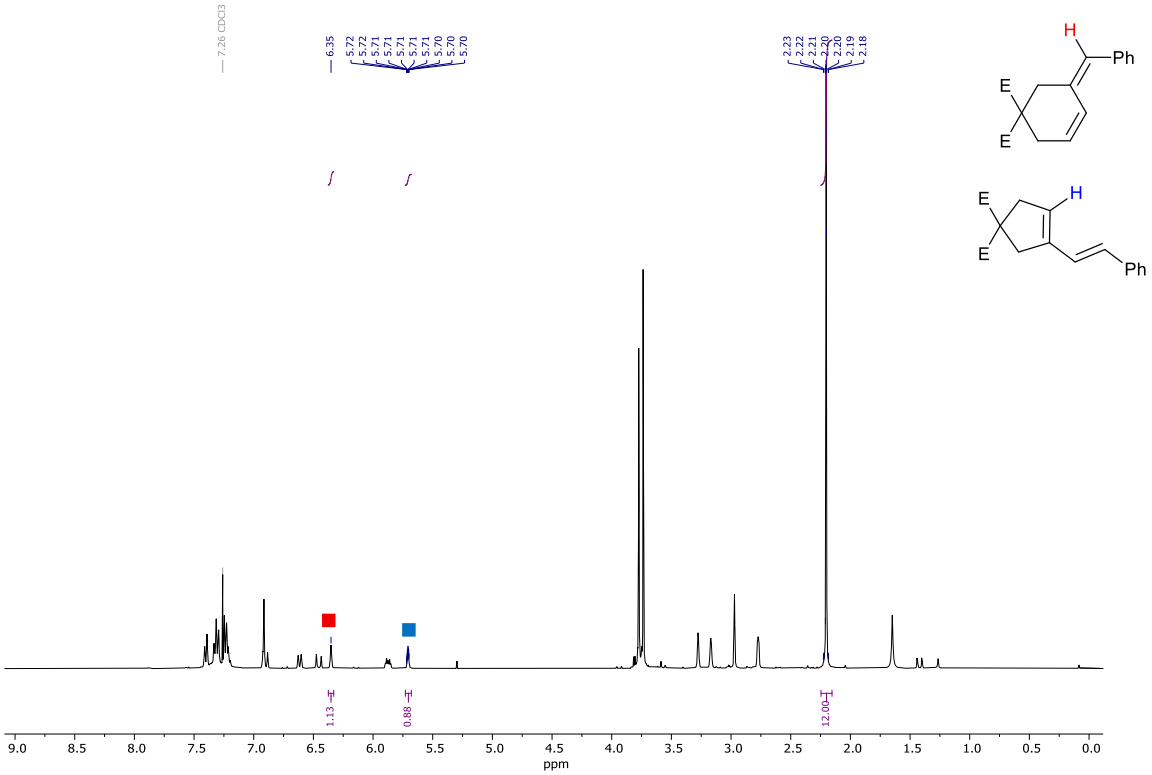

Figure S46: ^{1}H NMR Spectrum of the reaction of compound **11** using JohnPhosAuCl run 2.

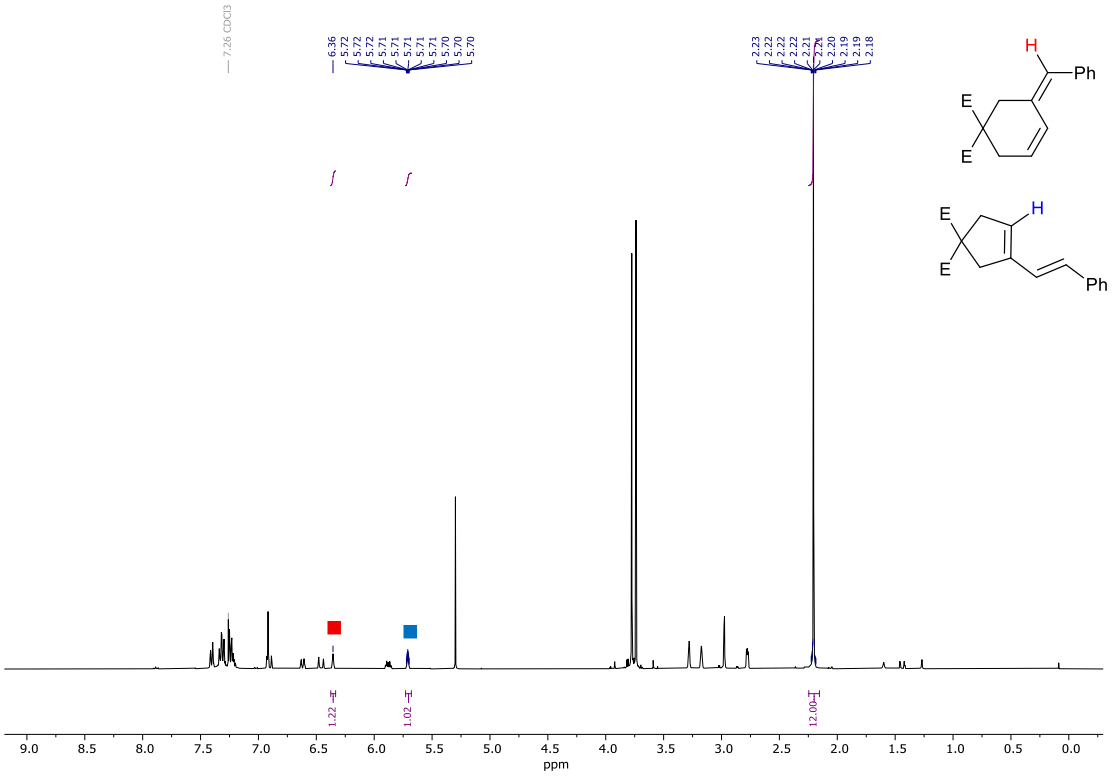

Figure S47: ^{1}H NMR Spectrum of the reaction of compound **11** using complex **2** run 1.

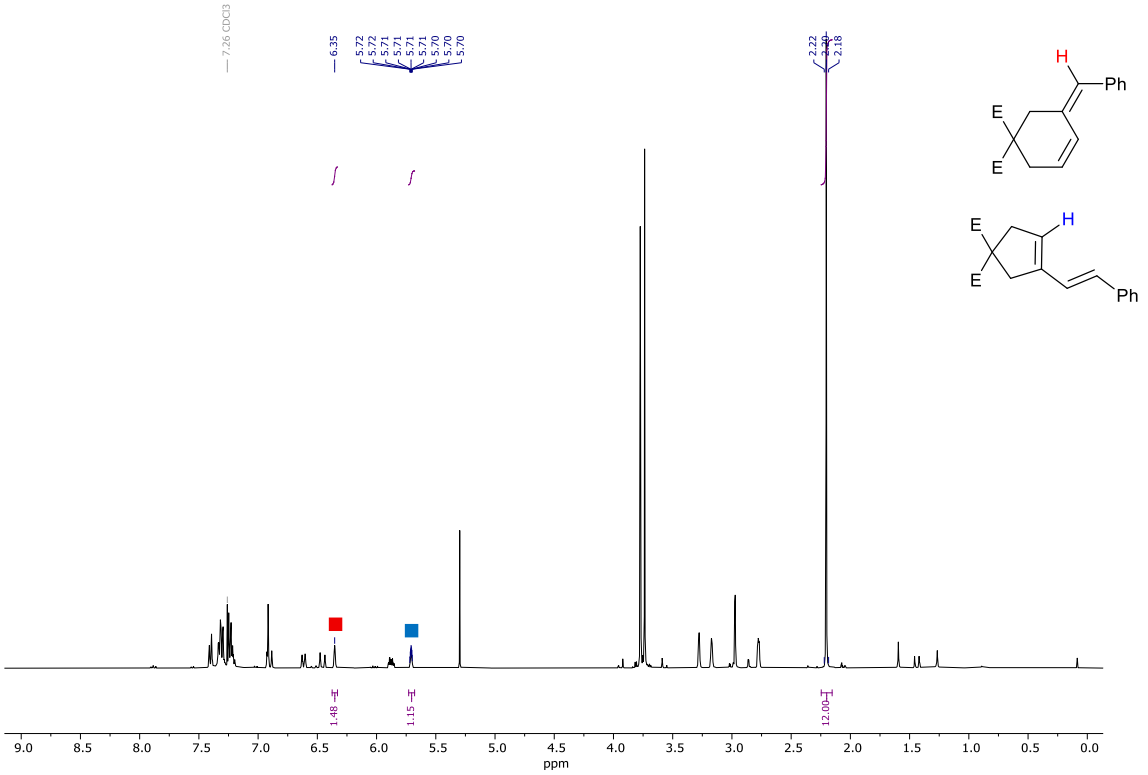

Figure S48: ^{1}H NMR Spectrum of the reaction of compound **11** using complex **2** run 2.

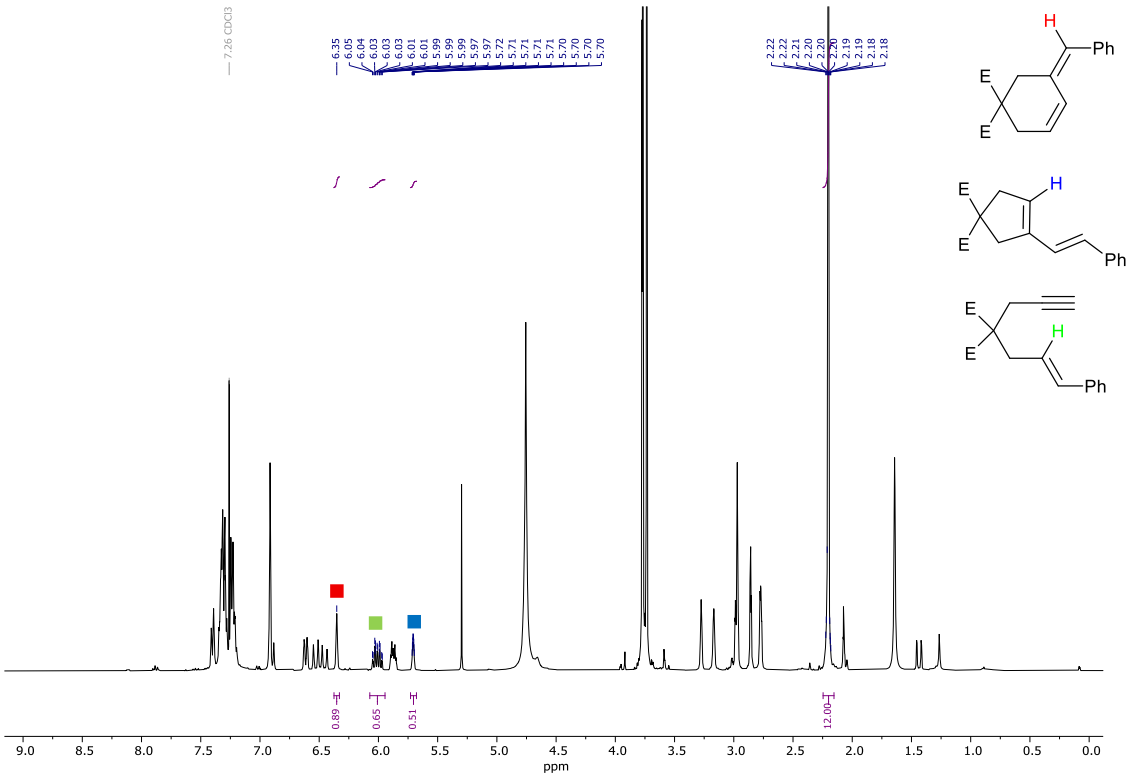

Figure S49: ^{1}H NMR Spectrum of the reaction of compound 11 using complex **3** run 1.

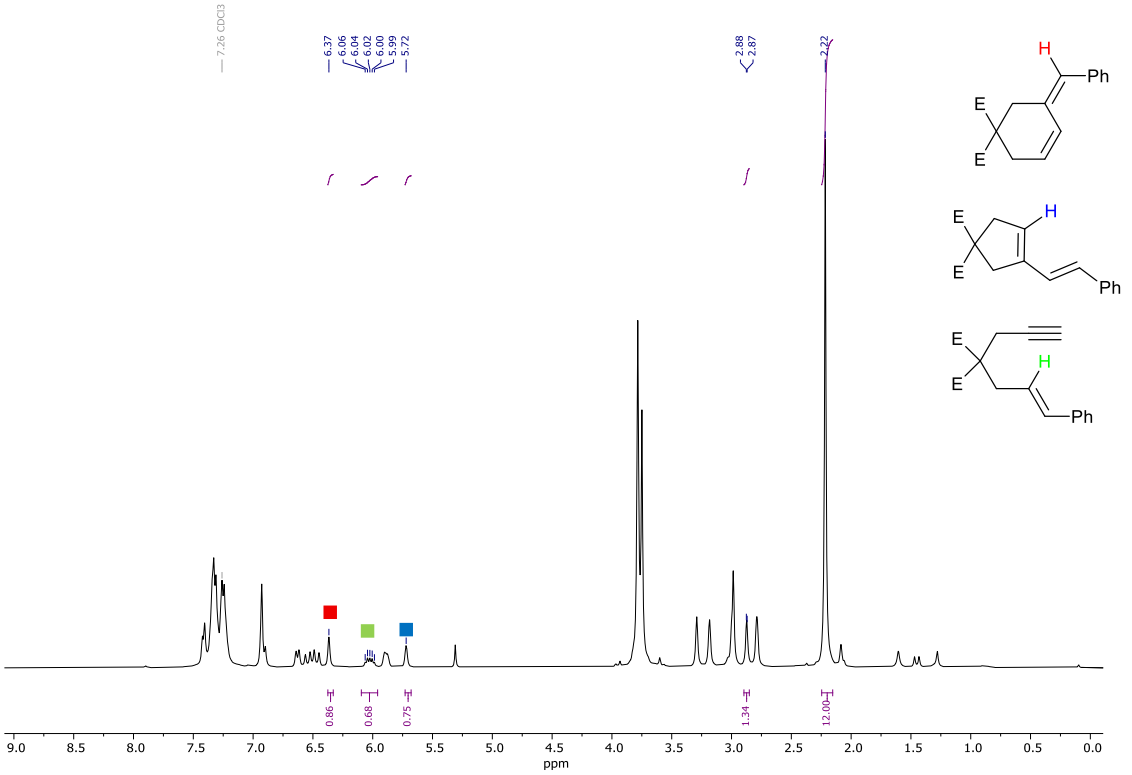

Figure S50: ^{1}H NMR Spectrum of the reaction of compound **11** using complex **3** run 2.

Crystallographic Data

Table S1: Crystallographic Data for **2** and **3**

Compound	2	2
Crystallographic Parameter		
CCDC Identification	2465038	2465037
Empirical formula	$C_{15}H_{25}AuClN_2OP$	$C_{30}H_{50}Au_2F_{12}N_4O_2P_2Sb_2$
Formula weight	512.76	1426.11
Temperature/K	99.95(15)	99.97(12)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	12.2138(3)	12.4548(6)
b/Å	11.6076(3)	12.6126(5)
c/Å	14.2495(4)	14.7731(6)
α/°	90	90
β/°	114.331(3)	112.161(5)
γ/°	90	90
Volume/$Å^3$	1840.76(9)	2149.23(17)
Z	4	2
$\rho_{calc}g/cm^3$	1.850	2.204
μ/mm^{-1}	17.174	23.875
F(000)	992.0	1344.0
Crystal size/mm^3	0.129 × 0.1 × 0.075	0.122 × 0.095 × 0.039
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.944 to 145.508	7.664 to 146.212
Index ranges	-15 ≤ h ≤ 13, -13 ≤ k ≤ 14, -17 ≤ l ≤ 17	-14 ≤ h ≤ 15, -15 ≤ k ≤ 14, -15 ≤ l ≤ 18
Reflections collected	33476	12151
Independent reflections	3631 [R_{int} = 0.0448, R_{sigma} = 0.0208]	4194 [R_{int} = 0.0511, R_{sigma} = 0.0485]
Data/restraints/parameters	3631/0/197	4194/0/251
Goodness-of-fit on F^2	1.059	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0227, wR_2 = 0.0519	R_1 = 0.0356, wR_2 = 0.0897
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0559	R_1 = 0.0438, wR_2 = 0.0958
Largest diff peak/hole / e $Å^{-3}$	0.86/-1.16	2.25/-1.47
Flack parameter	-	-

Computational Data

Cartesian Coordinates and Computed Energies [in Hartrees]

Azophosphine Gold Dimer (3) (DCM)

SCF (TPSS-D3/Def2TZVP) Energy = -2497.655802

Enthalpy Correction 298K = 0.802217

Free Energy Correction 298K = 0.669128

Lowest Frequency = 15.2064 cm^{-1}

Second Frequency = 25.1119 cm^{-1}

79	-1.892748000	7.101386000	6.094229000
6	-1.291998000	3.439591000	8.816547000
6	-1.009196000	3.280519000	7.303551000
1	-1.900450000	3.474176000	6.696348000
1	-0.692025000	2.247204000	7.124205000
1	-0.205782000	3.943761000	6.968516000
6	-0.001700000	3.161995000	9.608062000
1	0.778536000	3.892912000	9.381500000
1	0.363472000	2.169733000	9.318849000
1	-0.175076000	3.151326000	10.685260000
6	-2.415560000	2.473394000	9.239106000
1	-2.576446000	2.480362000	10.319888000
1	-2.119739000	1.458063000	8.951030000
1	-3.362987000	2.705201000	8.739735000
6	-2.222912000	5.867050000	10.722320000
6	-1.048075000	5.636611000	11.688928000
1	-0.957083000	4.587955000	11.979138000
1	-1.240452000	6.216507000	12.599075000
1	-0.099564000	5.973774000	11.263284000
6	-3.518391000	5.238963000	11.270179000

1	-4.364562000	5.408719000	10.595858000
1	-3.749245000	5.715165000	12.230001000
1	-3.417259000	4.164970000	11.443289000
6	-2.437463000	7.385511000	10.517035000
1	-1.524647000	7.880313000	10.172164000
1	-2.720484000	7.823583000	11.480541000
1	-3.242218000	7.589796000	9.801718000
6	0.915495000	7.391070000	7.389534000
6	1.977468000	7.221386000	8.309538000
1	1.834068000	6.594862000	9.181851000
6	3.176487000	7.851413000	8.085113000
1	4.008013000	7.738733000	8.772856000
6	3.354084000	8.668685000	6.940049000
6	2.300246000	8.838663000	6.020684000
1	2.417816000	9.459366000	5.141318000
6	1.096270000	8.199672000	6.253869000
1	0.271839000	8.326743000	5.552904000
6	4.831999000	10.087019000	5.680978000
1	4.738818000	9.514416000	4.753427000
1	5.858685000	10.421445000	5.817575000
1	4.150447000	10.942793000	5.678415000
7	-0.470260000	6.069249000	8.615487000
7	-0.332625000	6.774915000	7.567420000
8	4.562730000	9.235714000	6.823789000
15	-1.918793000	5.202085000	8.997227000
79	-3.698772000	5.550933000	7.618616000
6	-4.264790000	9.161477000	4.698462000
6	-4.651798000	9.410892000	6.174957000

1	-3.824157000	9.191732000	6.859243000
1	-4.913797000	10.469120000	6.284636000
1	-5.519383000	8.814689000	6.472475000
6	-5.491839000	9.402660000	3.801425000
1	-6.285162000	8.675474000	3.991840000
1	-5.881606000	10.402150000	4.026560000
1	-5.233409000	9.378142000	2.741505000
6	-3.105584000	10.095429000	4.301496000
1	-2.828929000	9.981402000	3.250492000
1	-3.435256000	11.129946000	4.451422000
1	-2.217920000	9.929905000	4.921587000
6	-3.307538000	6.591282000	3.004263000
6	-4.469280000	6.731558000	2.004981000
1	-4.579365000	7.758489000	1.650424000
1	-4.246386000	6.100633000	1.136878000
1	-5.417889000	6.399277000	2.434686000
6	-2.010263000	7.191030000	2.427950000
1	-1.182817000	7.128912000	3.143571000
1	-1.733505000	6.615717000	1.537106000
1	-2.137135000	8.233936000	2.127696000
6	-3.080787000	5.096675000	3.332966000
1	-3.989169000	4.624186000	3.718464000
1	-2.796204000	4.583341000	2.407693000
1	-2.274225000	4.956953000	4.061766000
6	-6.520603000	5.313827000	6.356815000
6	-7.578160000	5.460169000	5.427921000
1	-7.421828000	6.043538000	4.528173000
6	-8.787670000	4.860714000	5.678097000

1	-9.615957000	4.954333000	4.983657000
6	-8.980460000	4.099703000	6.859070000
6	-7.931418000	3.955403000	7.788386000
1	-8.061420000	3.379917000	8.696302000
6	-6.716353000	4.562259000	7.528475000
1	-5.895843000	4.457095000	8.238286000
6	-10.481268000	2.758766000	8.174444000
1	-10.379722000	3.367295000	9.077917000
1	-11.512917000	2.434854000	8.050550000
1	-9.812777000	1.893514000	8.212275000
7	-5.114020000	6.568936000	5.084910000
7	-5.261453000	5.897926000	6.154274000
8	-10.198325000	3.558142000	6.997912000
15	-3.647123000	7.387916000	4.666874000

Azophosphine Gold Monomer (2) (DCM)

SCF (TPSS-D3/Def2TZVP) Energy = -1248.780835

Enthalpy Correction 298K = 0.398833

Free Energy Correction 298K = 0.316677

Lowest Frequency = 11.7473 cm^{-1}

Second Frequency = 28.801 cm^{-1}

79	-2.053610000	6.876714000	6.132725000
1	-4.950670000	7.632457000	1.876983000
6	-4.058654000	9.208708000	4.760092000
6	-4.664035000	9.454394000	6.160292000
1	-3.986362000	9.120313000	6.954068000
1	-4.346206000	6.124110000	1.180374000
1	-5.429730000	6.077634000	2.586333000

6	-2.196102000	7.389891000	2.335097000
1	-1.321228000	7.468508000	2.989815000
1	-1.898004000	6.837255000	1.436799000
1	-4.823439000	10.532128000	6.278028000
1	-5.625748000	8.947719000	6.280460000
6	-5.063816000	9.632083000	3.672416000
1	-5.970828000	9.022287000	3.697841000
1	-5.345275000	10.674794000	3.860681000
1	-2.500428000	8.393080000	2.024355000
6	-2.927000000	5.163366000	3.276564000
1	-3.695442000	4.611201000	3.827058000
1	-2.782182000	4.671047000	2.308118000
1	-4.623215000	9.583281000	2.673213000
6	-2.749029000	10.008781000	4.625734000
1	-2.276983000	9.877134000	3.649616000
1	-2.986986000	11.071945000	4.745270000
1	-2.029742000	9.730622000	5.403243000
1	-1.987419000	5.107639000	3.835441000
6	-6.513975000	5.246050000	6.254056000
6	-3.347900000	6.626060000	3.011586000
6	-7.703114000	5.594629000	5.568946000
1	-7.666622000	6.345902000	4.786910000
6	-8.886429000	4.978646000	5.900963000
1	-9.814487000	5.224021000	5.394225000
6	-8.917838000	3.998678000	6.923736000
6	-7.740345000	3.645270000	7.608114000
1	-7.751448000	2.896659000	8.390965000
6	-6.551634000	4.271318000	7.266967000

1	-5.627113000	4.018561000	7.777559000
6	-10.248778000	2.454797000	8.196607000
1	-9.958455000	2.867418000	9.167925000
1	-11.302803000	2.181672000	8.203535000
1	-9.633840000	1.583522000	7.950522000
7	-5.210860000	6.691594000	5.100307000
7	-5.260438000	5.800402000	6.004061000
8	-10.129637000	3.462707000	7.165275000
15	-3.692453000	7.372493000	4.701182000
6	-4.607729000	6.625851000	2.119522000

Azophosphine Gold Dimer (3) (Impl. MeCN)

SCF (TPSS-D3/Def2TZVP) Energy = -2497.671269

Enthalpy Correction 298K = 0.800385

Free Energy Correction 298K = 0.663694

Lowest Frequency = 7.8298 cm^{-1}

Second Frequency = 19.707 cm^{-1}

79	-1.932498000	7.212832000	6.176052000
6	-1.311573000	3.316015000	8.964464000
6	-0.731662000	3.060478000	7.553569000
1	-1.453010000	3.315236000	6.768269000
1	-0.496465000	1.993559000	7.468218000
1	0.187366000	3.629672000	7.385503000
6	-0.239873000	3.045355000	10.033054000
1	0.600106000	3.740406000	9.951114000
1	0.141527000	2.028407000	9.884001000
1	-0.654133000	3.099080000	11.043423000
6	-2.537915000	2.406520000	9.178068000

1	-3.006304000	2.559236000	10.153162000
1	-2.201186000	1.364901000	9.123524000
1	-3.292183000	2.561696000	8.399503000
6	-2.203918000	5.938345000	10.573313000
6	-0.934181000	6.093492000	11.431052000
1	-0.506870000	5.133293000	11.723371000
1	-1.213866000	6.629795000	12.345443000
1	-0.166982000	6.675346000	10.914161000
6	-3.282068000	5.136313000	11.325452000
1	-4.158837000	4.945122000	10.696540000
1	-3.607473000	5.724871000	12.190925000
1	-2.893766000	4.183201000	11.695067000
6	-2.746763000	7.340865000	10.214645000
1	-2.040858000	7.909061000	9.599594000
1	-2.904249000	7.894725000	11.147361000
1	-3.702223000	7.282727000	9.683668000
6	0.951294000	7.288957000	7.331010000
6	2.057878000	6.992649000	8.160817000
1	1.939538000	6.293066000	8.979963000
6	3.267095000	7.598337000	7.920243000
1	4.131884000	7.392501000	8.542413000
6	3.408905000	8.514931000	6.848569000
6	2.310375000	8.810527000	6.018867000
1	2.400609000	9.505540000	5.193360000
6	1.096058000	8.196452000	6.268319000
1	0.239086000	8.414274000	5.631861000
6	4.858777000	10.004428000	5.641880000
1	4.677241000	9.536135000	4.670062000

1	5.905826000	10.286720000	5.736067000
1	4.215486000	10.879252000	5.775154000
7	-0.400966000	5.866995000	8.479632000
7	-0.311190000	6.707371000	7.531659000
8	4.632267000	9.049276000	6.708787000
15	-1.887686000	5.096479000	8.922345000
79	-3.640155000	5.400071000	7.505920000
6	-4.260925000	9.296807000	4.716844000
6	-4.840799000	9.552840000	6.127673000
1	-4.119421000	9.298359000	6.913030000
1	-5.076018000	10.619784000	6.212663000
1	-5.759810000	8.983680000	6.295956000
6	-5.332649000	9.567150000	3.648195000
1	-6.172681000	8.872201000	3.730434000
1	-5.713956000	10.584186000	3.796891000
1	-4.918433000	9.513021000	2.637831000
6	-3.034587000	10.206224000	4.502904000
1	-2.566237000	10.053191000	3.527847000
1	-3.371323000	11.247857000	4.557117000
1	-2.280289000	10.051335000	5.281496000
6	-3.368744000	6.673982000	3.108810000
6	-4.638562000	6.518401000	2.251260000
1	-5.066357000	7.478423000	1.959081000
1	-4.358799000	5.982279000	1.336784000
1	-5.405419000	5.936167000	2.768233000
6	-2.290785000	7.475945000	2.356331000
1	-1.414055000	7.667588000	2.985159000
1	-1.965245000	6.887100000	1.491103000

1	-2.679304000	8.428814000	1.986323000
6	-2.825696000	5.271630000	3.467780000
1	-3.531287000	4.703649000	4.083392000
1	-2.668632000	4.717391000	2.535217000
1	-1.869994000	5.330007000	3.998283000
6	-6.523887000	5.323846000	6.350947000
6	-7.630359000	5.619723000	5.520839000
1	-7.511975000	6.319066000	4.701492000
6	-8.839521000	5.013898000	5.761353000
1	-9.704204000	5.219350000	5.138910000
6	-8.981390000	4.097617000	6.833284000
6	-7.882961000	3.802421000	7.663264000
1	-7.973240000	3.107639000	8.488958000
6	-6.668689000	4.416595000	7.413843000
1	-5.811783000	4.199045000	8.050491000
6	-10.431227000	2.608208000	8.040121000
1	-10.249977000	3.076805000	9.011847000
1	-11.478201000	2.325683000	7.945801000
1	-9.787737000	1.733474000	7.907216000
7	-5.171758000	6.746080000	5.202483000
7	-5.261464000	5.905592000	6.150373000
8	-10.204692000	3.563114000	6.972999000
15	-3.684942000	7.516333000	4.759589000

Azophosphine Gold Monomer (2) (Impl. MeCN)

SCF (TPSS-D3/Def2TZVP) Energy = -1248.787336

Enthalpy Correction 298K = 0.398721

Free Energy Correction 298K = 0.317127

Lowest Frequency = 15.9918 cm^{-1}

Second Frequency = 28.0805 cm^{-1}

79	-2.053472000	6.873556000	6.132022000
1	-4.945654000	7.636511000	1.873652000
6	-4.057936000	9.206962000	4.760113000
6	-4.666458000	9.452499000	6.159223000
1	-3.991955000	9.115906000	6.954579000
1	-4.345726000	6.124759000	1.180362000
1	-5.430899000	6.084580000	2.585165000
6	-2.193523000	7.388324000	2.336942000
1	-1.319529000	7.463409000	2.993178000
1	-1.896123000	6.836086000	1.438042000
1	-4.824282000	10.530520000	6.277344000
1	-5.629558000	8.947399000	6.275849000
6	-5.061979000	9.630443000	3.671642000
1	-5.967974000	9.018982000	3.694498000
1	-5.345697000	10.672335000	3.861373000
1	-2.494854000	8.392893000	2.027692000
6	-2.928813000	5.162961000	3.274780000
1	-3.697732000	4.611324000	3.825216000
1	-2.785197000	4.671566000	2.305565000
1	-4.620089000	9.584241000	2.672878000
6	-2.749446000	10.009539000	4.628118000
1	-2.273108000	9.874273000	3.654545000
1	-2.990846000	11.072700000	4.741832000
1	-2.032489000	9.736379000	5.409376000
1	-1.989355000	5.106313000	3.833581000
6	-6.515917000	5.246682000	6.251035000

6	-3.347808000	6.626640000	3.011766000
6	-7.705829000	5.596171000	5.568867000
1	-7.670817000	6.347864000	4.787204000
6	-8.889236000	4.980227000	5.903060000
1	-9.817714000	5.226841000	5.397527000
6	-8.919147000	4.000009000	6.925054000
6	-7.740838000	3.646147000	7.606888000
1	-7.750306000	2.897598000	8.389782000
6	-6.552114000	4.271903000	7.263192000
1	-5.626983000	4.018206000	7.772231000
6	-10.245912000	2.454056000	8.199979000
1	-9.950969000	2.865273000	9.170446000
1	-11.299885000	2.180678000	8.211652000
1	-9.631938000	1.583060000	7.950522000
7	-5.213740000	6.692967000	5.096590000
7	-5.260852000	5.801110000	5.998811000
8	-10.131510000	3.463207000	7.169174000
15	-3.687422000	7.371085000	4.703847000
6	-4.606401000	6.629159000	2.118384000

MeCN Bound Azophosphine Gold Monomer (4) (Impl. MeCN)

SCF (TPSS-D3/Def2TZVP) Energy = -1381.665664

Enthalpy Correction 298K = 0.449889

Free Energy Correction 298K = 0.352961

Lowest Frequency = 8.8494 cm^{-1}

Second Frequency = 13.9758 cm^{-1}

79	-1.853396000	6.915091000	5.688635000
1	-5.228395000	7.822219000	1.752925000

6	-4.026902000	9.297990000	4.564644000
6	-4.478955000	9.505237000	6.028688000
1	-3.724968000	9.144864000	6.737905000
1	-4.717318000	6.326199000	0.961458000
1	-5.640250000	6.256049000	2.475753000
6	-2.446565000	7.562118000	1.909237000
1	-1.505753000	7.620252000	2.468030000
1	-2.248941000	7.036381000	0.967556000
1	-4.620172000	10.579259000	6.196800000
1	-5.425229000	8.996189000	6.234078000
6	-5.141731000	9.759521000	3.610669000
1	-6.039683000	9.143204000	3.708428000
1	-5.405790000	10.793017000	3.865266000
1	-2.775537000	8.575565000	1.663440000
6	-3.077990000	5.313411000	2.856081000
1	-3.780310000	4.743005000	3.472729000
1	-3.042484000	4.848843000	1.863596000
1	-4.812634000	9.750812000	2.568071000
6	-2.739247000	10.108506000	4.318101000
1	-2.371590000	10.004797000	3.294510000
1	-2.962317000	11.168007000	4.490702000
1	-1.940174000	9.812710000	5.006167000
1	-2.082249000	5.242273000	3.305321000
6	-6.284051000	5.258034000	6.191556000
6	-3.523068000	6.784127000	2.686761000
6	-7.558789000	5.646374000	5.719486000
1	-7.635659000	6.450032000	4.994652000
6	-8.684348000	5.002898000	6.182646000

1	-9.675764000	5.279755000	5.837405000
6	-8.569013000	3.955416000	7.127089000
6	-7.305368000	3.562556000	7.600593000
1	-7.201972000	2.763045000	8.324234000
6	-6.176319000	4.217668000	7.128059000
1	-5.187695000	3.934149000	7.477071000
6	-9.697961000	2.311571000	8.466832000
1	-9.264785000	2.650735000	9.413228000
1	-10.738164000	2.023653000	8.611704000
1	-9.125651000	1.469032000	8.065853000
7	-5.162644000	6.786163000	4.953353000
7	-5.071985000	5.839808000	5.795286000
8	-9.737159000	3.396085000	7.511718000
15	-3.651214000	7.467597000	4.433094000
6	-4.867828000	6.808830000	1.934642000
6	1.854583000	5.817423000	8.291176000
6	0.701184000	6.157891000	7.484583000
7	-0.217897000	6.433552000	6.842543000
1	2.164072000	6.755653000	8.894033000
1	2.707751000	5.487938000	7.581302000
1	1.558141000	4.953610000	9.002115000

MeCN

SCF (TPSS-D3/Def2TZVP) Energy = -132.8369622

Enthalpy Correction 298K = 0.049122

Free Energy Correction 298K = 0.020541

Lowest Frequency = 384.3166 cm^{-1}

Second Frequency = 385.1322 cm^{-1}

6	0.493445000	-0.007961000	0.000248000
6	-0.963177000	0.015664000	-0.000473000
7	-2.123004000	0.034242000	-0.001143000
1	0.867631000	0.227938000	1.000218000
1	0.876768000	0.730802000	-0.708929000
1	0.848338000	-1.000686000	-0.289920000

References

1. F. Sánchez-Cantalejo, J. D. Priest, P. W. Davies, *Chem. - A Eur. J.* **2018**, *24*, 17215–17219.
2. E. J. Jordan, E. D. E. Calder, B. L. Greene, H. V. Adcock, L. Male, P. W. Davies, A. R. Jupp, *Organometallics* **2024**, *43*, 2674-2685.
3. CrysAlisPro, Rigaku Oxford Diffraction, 2021.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.
5. G. M. Sheldrick, Acta Crystallogr., 2015, A71, 3-8.
6. G. M. Sheldrick, Acta Crystallogr., 2015, C71, 3-8.