

## Supporting Information

### Janus-faced coordination chemistry of pyridyl- functionalized phosphinines with Cu(I) and Au(I)

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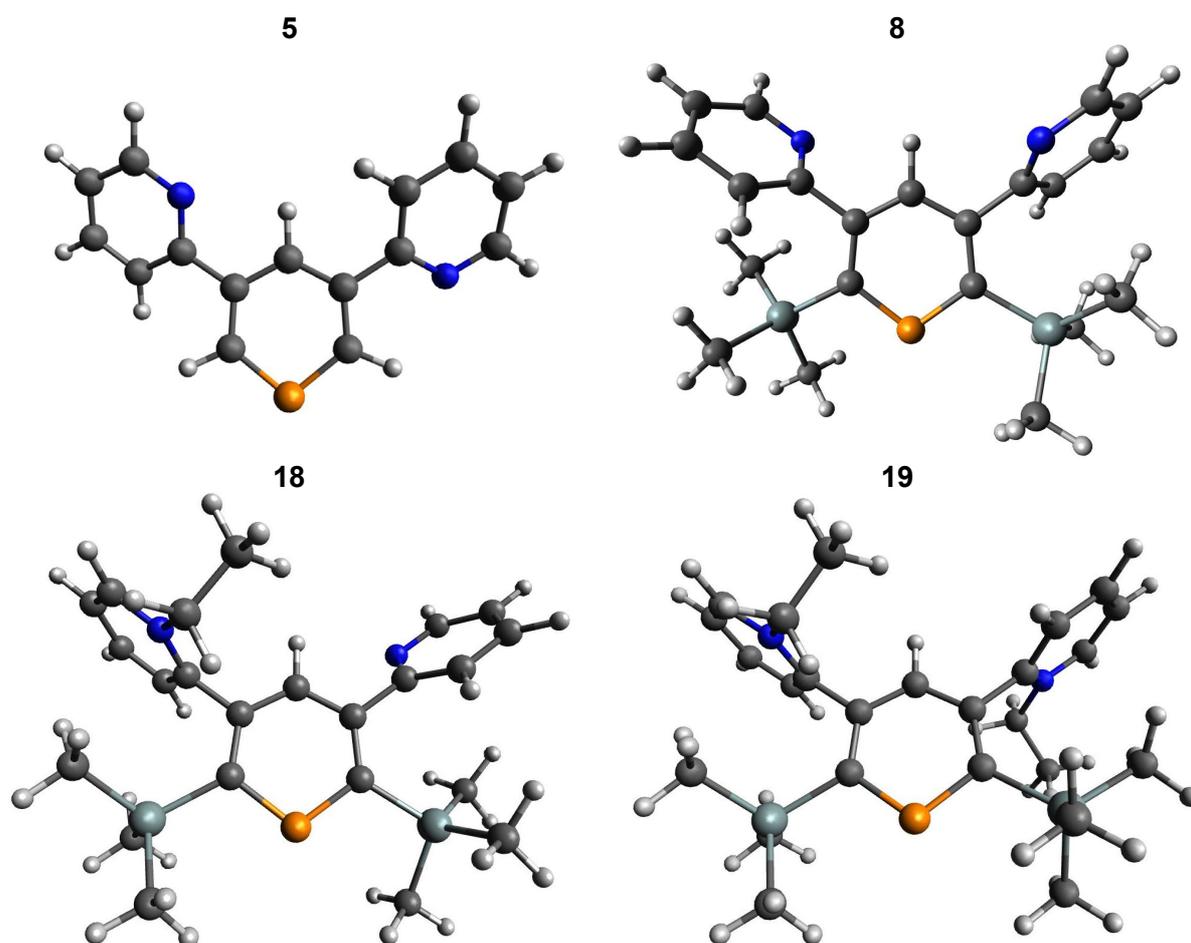
## 1. DFT calculations

### 1.1. Computational details for FMO analysis

DFT calculations were performed using ORCA 5.0.3<sup>[1,2]</sup> Geometry optimizations and vibrational frequency calculations were carried out at the PBEh-3c<sup>[3,4]</sup> composite density functional method. Geometry optimizations were performed without symmetry constraints using the Opt keyword until the default ORCA convergence thresholds were reached. Subsequent frequency calculations confirmed that all optimized structures correspond to local minima without any imaginary frequencies.

DFT calculations on the FMO scheme of phosphinines **5** and **8**, the pyridinium salts **18** and **19** were carried out at the B3LYP-D3/def2-TZVP<sup>[5-9]</sup> level using the RI approximation with the def2/J auxiliary basis. Solvent effects were included via the CPCM model. TIGHTSCF and SLOWCONV settings ensured accurate SCF convergence with the DEFGRID2 integration grid.

### 1.2. Computed Cartesian coordinates (A) and energies (au)



**Figure S1:** Calculated Structures of the H-Py-PP (**5**), TMS-Py-PP (**8**), mono pyridinium salt (**18**) and the bis pyridinium salt (**19**) of the TMS-Py-PP.

## H-Py-PP (5)

Total SCF Energy = -1027.15428407  
Total thermal Energy = -1026.9011502  
Total Enthalpy = -1026.90020604  
Total Free Energy = -1026.954691365

Lowest frequency: 38.34 cm<sup>-1</sup>

Second lowest frequency: 39.80 cm<sup>-1</sup>

C	-0.946201	-2.011009	0.299668
C	0.150819	-1.222813	-0.032623
P	-0.909317	-3.706604	0.594209
C	0.776171	-4.029287	0.404800
C	1.752947	-3.088466	0.104771
C	1.435602	-1.749331	-0.115324
C	-0.060945	0.224172	-0.292219
C	3.180953	-3.484717	0.007661
N	3.954156	-2.735627	-0.773244
C	3.693530	-4.568944	0.719708
C	5.033854	-4.884961	0.588754
C	5.234202	-3.042430	-0.892523
C	5.829141	-4.111352	-0.240474
N	-1.099447	0.792088	0.312365
C	0.773752	0.944794	-1.146722
C	0.528146	2.291775	-1.344093
C	-0.542197	2.882632	-0.693305
C	-1.328673	2.079008	0.118002
H	1.586015	0.458034	-1.668587
H	2.261244	-1.087557	-0.338154
H	5.819670	-2.402209	-1.543354
H	6.881238	-4.320948	-0.373422
H	-2.185652	2.494370	0.636889
H	1.160336	2.869429	-2.005530
H	-0.771040	3.931976	-0.816177
H	5.453055	-5.718933	1.136082
H	3.062648	-5.139979	1.386413
H	-1.906925	-1.515385	0.37124

## TMS-Py-PP (8)

Total SCF Energy = -1843.26906547  
Total thermal Energy = -1842.80203831  
Total Enthalpy = -1842.80109410  
Total Free Energy = -1842.80203831

Lowest frequency: 18.26 cm<sup>-1</sup>

Second lowest frequency: 30.71 cm<sup>-1</sup>

C	-1.120253	-2.166147	-0.465049
C	0.030728	-1.373741	-0.459671
P	-1.025934	-3.895675	-0.369873
C	0.663559	-4.250138	-0.199686
C	1.613335	-3.229859	-0.096527
C	1.308439	-1.881754	-0.252118
C	-0.055793	0.093788	-0.686103
C	3.037159	-3.544920	0.191323
N	3.940667	-3.157685	-0.701651
C	3.384771	-4.185651	1.377488
C	4.717796	-4.473195	1.613883
C	5.212880	-3.439778	-0.468716
C	5.657157	-4.105510	0.664163
N	0.346896	0.889198	0.297761
C	-0.506294	0.584762	-1.908652
C	-0.580385	1.954835	-2.090045
C	-0.198361	2.786193	-1.049571
C	0.267766	2.198443	0.117009
Si	1.084649	-6.104160	-0.308778
C	1.202633	-6.934537	1.383652
H	2.116005	-6.686867	1.923313
H	1.185149	-8.019812	1.264896
H	0.356130	-6.665333	2.017153
C	-0.324126	-6.952184	-1.233777
H	-0.488478	-6.513816	-2.218952
H	-1.270876	-6.907969	-0.695416
H	-0.080402	-8.006821	-1.380477
C	2.668559	-6.378011	-1.294969
H	2.708209	-5.733565	-2.173826

H	2.706982	-7.411967	-1.644267
H	3.573950	-6.198095	-0.715954
Si	-2.896249	-1.482849	-0.490592
C	-4.012737	-2.768080	0.321801
H	-4.052045	-3.705826	-0.232214
H	-5.032268	-2.380564	0.381708
H	-3.692196	-3.002601	1.337733
C	-3.524326	-1.230970	-2.253221
H	-3.327610	-2.110628	-2.867957
H	-3.074879	-0.370682	-2.748096
H	-4.604524	-1.072306	-2.248836
C	-3.034196	0.112479	0.505823
H	-2.473805	0.049915	1.439336
H	-4.080084	0.292553	0.763449
H	-2.677473	0.990007	-0.032534
H	-0.774580	-0.101007	-2.700497
H	2.128326	-1.175175	-0.211009
H	5.919024	-3.115104	-1.225022
H	6.709502	-4.312605	0.800482
H	0.596689	2.814441	0.946778
H	-0.924748	2.366187	-3.029924
H	-0.243994	3.862557	-1.140418
H	5.018828	-4.968623	2.527816
H	2.621329	-4.432058	2.102491

### TMS-PyrrEt-Py-PP<sup>+</sup> (18)

Total SCF Energy = -1922.09799051

Total thermal Energy = -1921.56994329

Total Enthalpy = -1921.56899908

Total Free Energy = -1921.65973251

Lowest frequency: 16.21 cm<sup>-1</sup>

Second lowest frequency: 28.13 cm<sup>-1</sup>

C	-1.136793	-2.165985	-0.658118
C	0.005074	-1.369186	-0.570781
P	-1.045152	-3.902922	-0.653939
C	0.640867	-4.275541	-0.468268
C	1.577462	-3.248660	-0.327287
C	1.283146	-1.893797	-0.372207
C	-0.061273	0.112916	-0.668980
C	3.001752	-3.576730	-0.071776
N	3.887364	-3.599762	-1.088200
C	3.451406	-3.835498	1.214545
C	4.782863	-4.114191	1.450164
C	5.187929	-3.869418	-0.875040
C	5.669842	-4.130764	0.380613
N	0.492246	0.794986	0.326898
C	-0.625772	0.727151	-1.780774
C	-0.658737	2.111664	-1.826264
C	-0.128023	2.825701	-0.765278
C	0.445969	2.117383	0.281334
Si	0.997917	-6.146605	-0.336483
C	0.984267	-6.630812	1.481260
H	1.800681	-6.181087	2.047930
H	1.078468	-7.712673	1.590418
H	0.050334	-6.336562	1.961601
C	-0.350404	-7.067941	-1.259558
H	-0.414115	-6.768366	-2.306416
H	-1.336771	-6.923756	-0.819434
H	-0.142751	-8.139615	-1.240448
C	2.664853	-6.621906	-1.091428
H	2.801319	-6.239536	-2.104619
H	2.700053	-7.710581	-1.169733
H	3.526598	-6.335271	-0.487564
Si	-2.941121	-1.502485	-0.593907
C	-3.978863	-2.864302	0.188763
H	-4.045573	-3.764191	-0.422493
H	-4.998086	-2.497207	0.328565
H	-3.606852	-3.157961	1.171307
C	-3.616849	-1.182288	-2.321939
H	-3.437106	-2.030585	-2.983859
H	-3.204420	-0.293176	-2.797377
H	-4.698093	-1.041041	-2.270337

C	-3.040738	0.016057	0.511901
H	-2.436044	-0.100716	1.412277
H	-4.074426	0.153493	0.835537
H	-2.731371	0.938409	0.023309
C	3.469675	-3.337910	-2.486655
C	3.759063	-1.912518	-2.912871
H	2.410938	-3.567826	-2.566356
H	4.004829	-4.053781	-3.109343
H	3.182078	-1.193573	-2.334954
H	3.480145	-1.795147	-3.958813
H	4.815994	-1.661881	-2.824506
H	-1.015803	0.133057	-2.595750
H	2.087546	-1.181351	-0.227062
H	2.731464	-3.803700	2.019494
H	5.130498	-4.313347	2.454715
H	5.825111	-3.874043	-1.747794
H	6.719607	-4.346017	0.513113
H	0.892599	2.641003	1.118669
H	-1.089689	2.622863	-2.676794
H	-0.141382	3.906406	-0.750945

### TMS-PyrrEt<sub>2</sub>-PP<sup>2+</sup> (19)

Total SCF Energy = -2000.87505001

Total thermal Energy = -2000.24915632

Total Enthalpy = -2000.24821211

Total Free Energy = -2000.34424795

Lowest frequency: 16.22 cm<sup>-1</sup>

Second lowest frequency: 28.83 cm<sup>-1</sup>

C	-1.120253	-2.166147	-0.465049
C	0.030728	-1.373741	-0.459671
P	-1.025934	-3.895675	-0.369873
C	0.663559	-4.250138	-0.199686
C	1.613335	-3.229859	-0.096527
C	1.308439	-1.881754	-0.252118
C	-0.055793	0.093788	-0.686103
C	3.037159	-3.544920	0.191323
N	3.940667	-3.157685	-0.701651
C	3.384771	-4.185651	1.377488
C	4.717796	-4.473195	1.613883
C	5.212880	-3.439778	-0.468716
C	5.657157	-4.105510	0.664163
N	0.346896	0.889198	0.297761
C	-0.506294	0.584762	-1.908652
C	-0.580385	1.954835	-2.090045
C	-0.198361	2.786193	-1.049571
C	0.267766	2.198443	0.117009
Si	1.084649	-6.104160	-0.308778
C	1.202633	-6.934537	1.383652
H	2.116005	-6.686867	1.923313
H	1.185149	-8.019812	1.264896
H	0.356130	-6.665333	2.017153
C	-0.324126	-6.952184	-1.233777
H	-0.488478	-6.513816	-2.218952
H	-1.270876	-6.907969	-0.695416
H	-0.080402	-8.006821	-1.380477
C	2.668559	-6.378011	-1.294969
H	2.708209	-5.733565	-2.173826
H	2.706982	-7.411967	-1.644267
H	3.573950	-6.198095	-0.715954
Si	-2.896249	-1.482849	-0.490592
C	-4.012737	-2.768080	0.321801
H	-4.052045	-3.705826	-0.232214
H	-5.032268	-2.380564	0.381708
H	-3.692196	-3.002601	1.337733
C	-3.524326	-1.230970	-2.253221
H	-3.327610	-2.110628	-2.867957
H	-3.074879	-0.370682	-2.748096
H	-4.604524	-1.072306	-2.248836
C	-3.034196	0.112479	0.505823
H	-2.473805	0.049915	1.439336
H	-4.080084	0.292553	0.763449
H	-2.677473	0.990007	-0.032534
H	-0.774580	-0.101007	-2.700497

H	2.128326	-1.175175	-0.211009
H	5.919024	-3.115104	-1.225022
H	6.709502	-4.312605	0.800482
H	0.596689	2.814441	0.946778
H	-0.924748	2.366187	-3.029924
H	-0.243994	3.862557	-1.140418
H	5.018828	-4.968623	2.527816
H	2.621329	-4.432058	2.102491

### 1.3. FMOs energy calculation of phosphinines and pyridinium salts

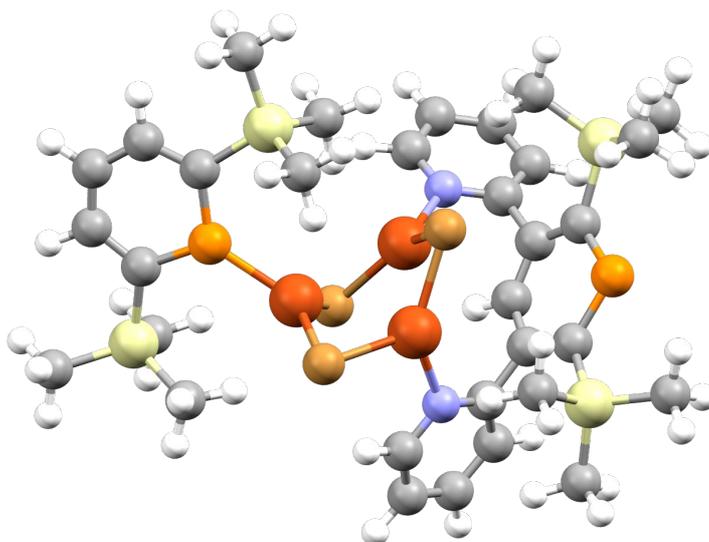
**Table S1:** Calculated FMO energies [eV] for the H-substituted phosphinine (**5**), TMS-pyridyl phosphinine (**8**), the mono- (**18**) and bis-ethyl pyridinium (**19**) phosphinine salts.

	H-Py-PP	TMS-Py-PP	TMS-PyrrEt-Py-PP <sup>+</sup>	TMS-PyrrEt2-PP <sup>2+</sup>
LUMO+3	-0.831	-0.846	-1.902	-2.549
LUMO+2	-0.919	-0.916	-2.039	-2.800
LUMO+1	-1.703	-1.569	-2.199	-3.233
LUMO	-1.785	-1.605	-2.894	-3.257
HOMO	-6.614	-6.536	-7.108	-7.790
HOMO-1	-6.641	-6.772	-7.347	-8.085
HOMO-2	-7.193	-7.037	-7.521	-8.363
HOMO-3	-7.261	-7.301	-7.744	-8.419

### 1.4. Computational details for QTAIM analysis of **14**

DFT calculations were performed using Gaussian 09 revision D01.<sup>[10]</sup> Geometry optimizations and vibrational frequency calculations were carried out with the M06 functional<sup>[11]</sup> with the def2-TZVP basis set.<sup>[9,12]</sup> Geometry optimisations were followed by frequency calculations to ascertain the nature of the stationary points; minima gave no imaginary frequencies. QTAIM analyses were undertaken using the AIMAll program.<sup>[13]</sup>

## 1.5. Computed Cartesian coordinated (A) and energies (E<sub>H</sub>)



**Figure S2:** Calculated structure of TMS-Py-PP-Cu<sub>3</sub>Br<sub>3</sub>-TMS-PP used for QTAIM analysis.

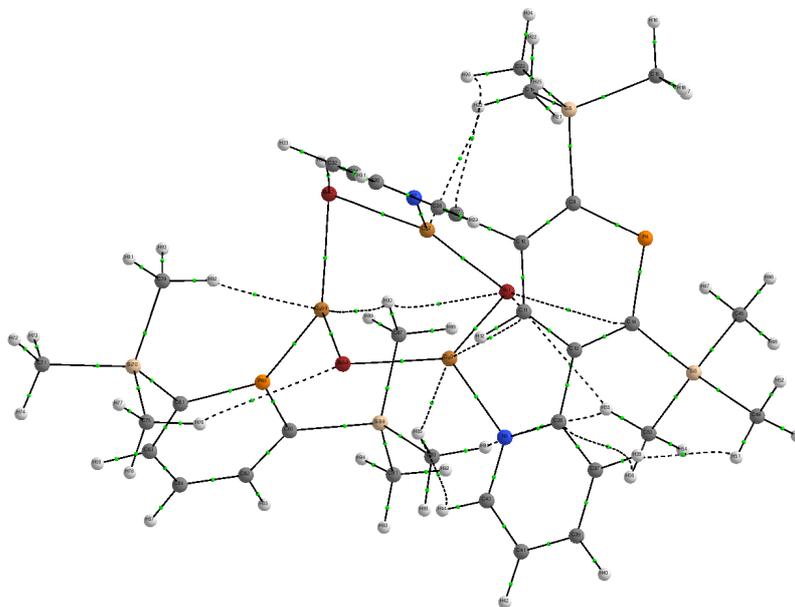
### TMS-Py-PP-Cu<sub>3</sub>Br<sub>3</sub>-TMS-PP

Total SCF Energy = -15842.074932 E<sub>H</sub>

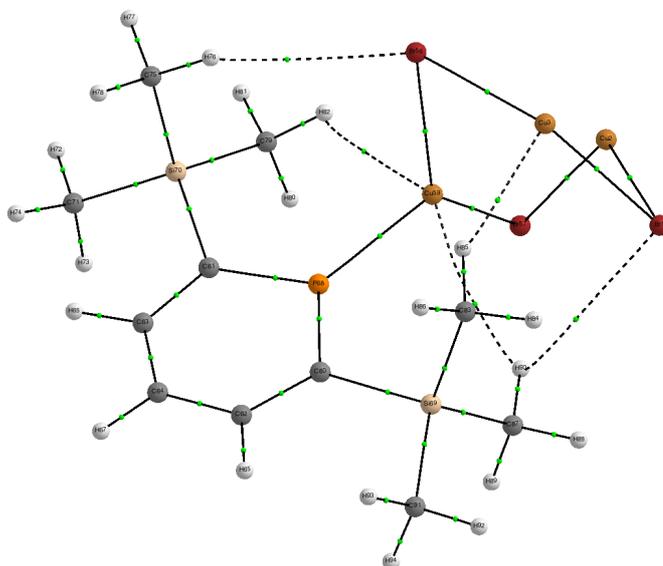
Br	1.107140168883	0.794829215603	1.732068272904
Cu	0.458543811719	-1.401732736660	0.993339860199
Cu	0.320500644895	0.758628400199	-0.523164572882
P	4.828410830065	-0.104892665723	0.608200934181
Si	4.278963727541	-3.021595940486	1.282404189816
Si	4.653396763107	2.914227300833	0.209344462600
N	1.094435015858	-2.850681055644	-0.328908233677
N	1.239100184448	2.123951900884	-1.873621602356
C	3.961188832788	-1.538601832520	0.140172401428
C	3.005525668435	-1.501628010645	-0.871627607770
C	2.712106990093	-0.365310645282	-1.614275951730
H	1.961583165304	-0.460097893144	-2.395376741516
C	3.223963899334	0.903963381116	-1.359790795275
C	4.176121517743	1.172389959477	-0.379526464583
C	6.024573256935	-2.900750082255	1.941262665727
H	6.235449498849	-3.783826531215	2.550699703217
H	6.171372533794	-2.019026753478	2.567318384075
H	6.760545669439	-2.865437958691	1.134687459681
C	3.077402961129	-2.927498953117	2.707331182664
H	2.042089168975	-3.072956076513	2.383416774418
H	3.136337061650	-1.945573837419	3.184494481483
H	3.306736409624	-3.687591747075	3.458892183634
C	4.124371765858	-4.665545520076	0.399659428606
H	4.513823772442	-5.445909821230	1.059692440758
H	4.710459494838	-4.689272633033	-0.522015647714
H	3.092739155345	-4.925583430210	0.156477421125
C	2.127414860893	-2.666974725196	-1.159659887057
C	2.328122873824	-3.476626085732	-2.265978391345
H	3.169181401640	-3.280481891740	-2.920321759223
C	1.455447355612	-4.520340131400	-2.503041458401
H	1.594028505431	-5.167023703919	-3.361562397062
C	0.404813269429	-4.725227268076	-1.627620363502
H	-0.304224154087	-5.529567931125	-1.773244041466
C	0.256954922081	-3.864633823925	-0.559307123130
H	-0.569956763302	-3.959333580425	0.139998566355
C	2.549784972989	1.991895174613	-2.113104964852
C	3.205418085669	2.798779535944	-3.029577423622
H	4.260100244861	2.639763290406	-3.218538523496
C	2.491626535249	3.779064514021	-3.691984901647
H	2.982552600104	4.419768275235	-4.415193584492

C	1.141522533362	3.923338343373	-3.426833256279
H	0.545536605396	4.676774940274	-3.925070500835
C	0.555112975203	3.066022205066	-2.516017429782
H	-0.506121546372	3.121858222581	-2.290407254895
C	5.362917437589	2.795897760855	1.933024167557
H	6.281757373271	2.208925318332	1.979111429498
H	4.644752798080	2.354513366581	2.628330214730
H	5.591596748473	3.807754815334	2.280432734183
C	5.962686772108	3.679194976899	-0.891294225911
H	6.349720337328	4.587413183564	-0.421510778799
H	5.583510570853	3.953406041138	-1.877154716868
H	6.802018986444	2.992928561449	-1.027382285135
C	3.139745328349	4.009767321094	0.310261914082
H	3.384740565380	4.890603749016	0.910255038005
H	2.322209964635	3.479458013650	0.808168383874
H	2.783672940040	4.357906657841	-0.660779540437
Br	-1.584554850040	-2.239386704970	2.064691633776
Br	-1.204660276276	-0.474261199234	-1.927702076763
Cu	-2.105385116968	-0.621160081709	0.363432682378
C	-4.239703297386	2.205991688603	1.135994318642
C	-5.472938780214	0.213935063273	-0.337466943152
C	-5.467397112039	2.841368869328	1.005183767287
C	-6.556338518777	1.086009519302	-0.296535087696
C	-6.564368964999	2.317856986037	0.336844988687
H	-5.590995192528	3.825113573280	1.455563587720
H	-7.476998692386	0.788689574205	-0.797549891258
H	-7.474908269231	2.906353666457	0.304058213196
P	-4.000584766989	0.641013417074	0.449165501726
Si	-2.773920284100	3.022051642034	2.006289142360
Si	-5.600056455286	-1.383511436406	-1.339254307958
C	-7.380469338203	-1.959158623452	-1.297978071753
H	-7.465438939657	-2.921392610196	-1.809313012266
H	-7.735303893609	-2.092512105689	-0.273611818612
H	-8.053491870270	-1.262018031762	-1.802065620918
C	-5.104734764475	-0.979757964954	-3.092591859922
H	-4.067632882678	-0.634326454696	-3.123451921713
H	-5.191054146495	-1.856569457958	-3.739061783108
H	-5.739140132925	-0.190591957484	-3.503967907950
C	-4.502302767669	-2.720713844620	-0.645691909580
H	-4.662328118671	-2.876603864500	0.423376405680
H	-4.717075032327	-3.661453380064	-1.160684545405
H	-3.439851459756	-2.501538285731	-0.793329588058
C	-1.499730810000	3.402482494996	0.688175722265
H	-0.553938940771	3.738297815286	1.121244371793
H	-1.286364616690	2.506963666723	0.092371234310
H	-1.872722783474	4.178565957303	0.014058037783
C	-2.127413559504	1.878152570485	3.322125191486
H	-1.238137432804	2.300377750478	3.796342242282
H	-2.887558222996	1.724066178177	4.092139993588
H	-1.845792244311	0.899061713185	2.925300754151
C	-3.349826081524	4.623560183844	2.781884663240
H	-2.513136992829	5.098087590764	3.300438542420
H	-3.719646568004	5.332140683330	2.037015367706
H	-4.140351002367	4.455471323586	3.517043498974

## 1.6. QTAIM figures



**Figure S3:** QTAIM analysis depicting the bond critical points between in the model of the metal cluster binding site of compound **14**. Solid lines depict covalent bonding, dotted lines depict electrostatic interactions.



**Figure S4:** QTAIM analysis depicting the bond critical points between the trimethyl silyl groups on the phosphinine with the  $\text{Cu}_3\text{Br}_3$  cluster. Solid lines depict covalent bonding, dotted lines depict electrostatic interactions

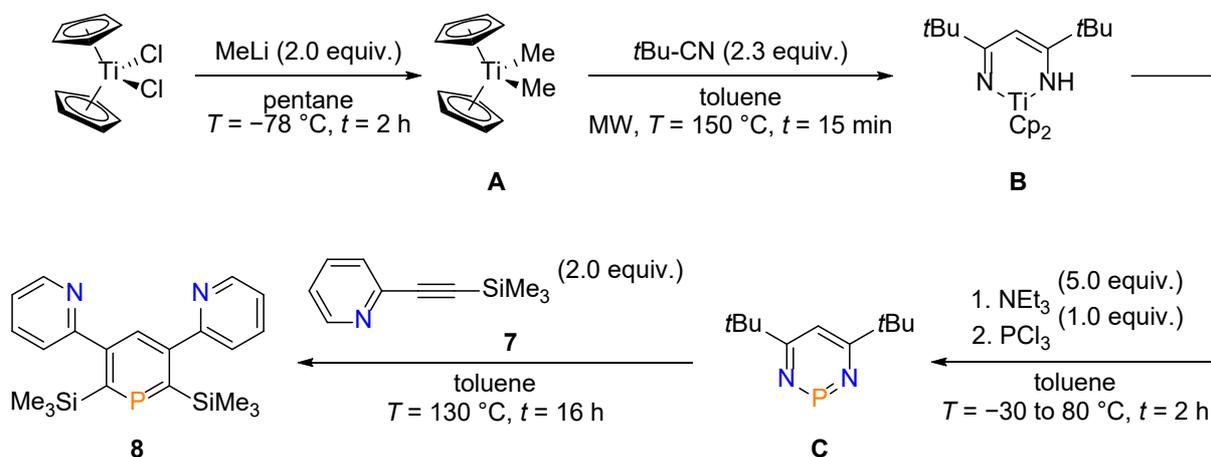
## 2. Experimental procedures

### 2.1. General remarks

Unless otherwise stated, all reactions and workups were performed following standard Schlenk techniques or using an argon filled *Unilab* glovebox by *MBraun* ( $\text{H}_2\text{O} < 0.1 \text{ ppm}$ ,  $\text{O}_2 < 0.1 \text{ ppm}$ ). Room temperature refers to  $T = 23 \text{ }^\circ\text{C}$ , while elevated reaction temperatures are referred to the respective oil bath's temperature. Dry acetonitrile; toluene; dichloromethane and *n*pentane were collected from a solvent purification system, *MB SPS-800* by *MBraun*, and additionally stored over 4 Å molecular sieves prior to use. Solvents and reagents were degassed using the *freeze-pump-thaw* method (three cycles) or by purging with argon.  $\text{CD}_2\text{Cl}_2$ ,  $\text{CD}_3\text{CN}$  and  $\text{CDCl}_3$  were dried over  $\text{CaH}_2$ , distilled, and degassed.  $\text{C}_6\text{D}_6$  was dried over  $\text{NaK}$ , distilled and storage over 4 Å molecular sieves.  $\text{DMSO-d}_6$  was dried over 4 Å molecular sieves for 2 weeks prior to use. 2,2Dimethylpropanenitrile was degassed and stored over 4 Å molecular sieves.  $\text{NEt}_3$  was distilled, degassed, and stored over 4 Å molecular sieves.  $\text{PCl}_3$  was refluxed and distilled prior to use. All other commercially available chemicals were used without further purification. Microwave reactions were conducted using a *Discover 2.0* reactor by *CEM*. The  $^1\text{H}$ ,  $^1\text{H}\{^{31}\text{P}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on *JEOL* (ECX 400, Lambda 400) and *Bruker AVANCE 700* spectrometer, and all chemical shifts are reported relative to the residual resonance in the respective deuterated solvents. Quantitative  $^{31}\text{P}$  NMR spectroscopic measurements were carried out using an internal triphenylphosphine standard. High resolution mass spectrometry (HRMS) was performed on an *Agilent 6210 ESI-TOF*.

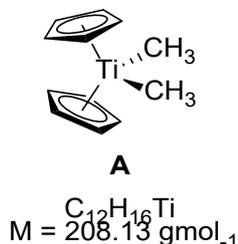
## 2.2. Synthetic Procedures

Phosphinine **8** was synthesized *via* [4+2]-cycloaddition-cycloreversion reactions between 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine **C** and the respective alkyne [2-(trimethylsilyl)ethynyl]pyridine **7**. The starting material were obtained over four-step syntheses, following modified literature procedures.<sup>[14,15]</sup>



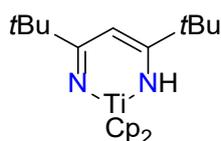
**Scheme S1:** Synthetic pathway to phosphinine **8**.

### Bis( $\eta^5$ -cyclopentadienyl)dimethyltitanium (**A**)

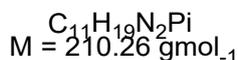


The compound **A** was prepared using a modified literature procedure.<sup>[14]</sup> In a 500 mL dried Schlenk flask,  $Cp_2TiCl_2$  (9.0 g, 36 mmol) was suspended in dried and degassed *n*-pentane (200 mL) and was cooled to  $-78^\circ C$ . Methyl lithium (1.5 M in  $Et_2O$ , 50 mL, 72 mmol, 2.0 equiv.) was added dropwise and the reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The resulting bright orange reaction mixture with a white precipitate was filtered through Celite<sup>®</sup> and the solvent removed *in vacuo*, affording in an orange solid. The residue was dissolved in toluene (100 mL) and stored in the freezer. All steps of the synthetic procedure were carried out under exclusion of light. **A** was obtained as a 0.29 M solution in toluene (6.1 g, 30 mmol, 83%).

## Bis( $\eta^5$ -cyclopentadienyl)N,N-(2,2,6,6-tetramethylheptane-3,5-diimine)titanium (**B**)



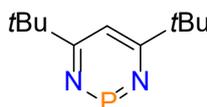
**B**



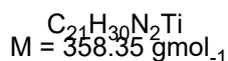
The compound **B** was prepared using a modified literature procedure.<sup>[14]</sup> In a dried 100 mL microwave vial, dried and degassed 2,2-dimethylpropanenitrile (4.2 mL, 38 mmol, 2.3 equiv.) was added to a 0.39 M toluene solution of **A** (42 mL, 16 mmol, 1.0 equiv.). The mixture was placed in a microwave reactor at 150 °C for 15 min, employing 300 W, inducing a color change from deep red to dark brown. After the mixture was cooled down to 50 °C, it was transferred into a dried 250 mL Schlenk flask, and the microwave vial rinsed with dried and degassed toluene (20 mL). The yield was directly calculated from the reaction mixture by quantitative <sup>1</sup>H NMR spectroscopy. Titanocene **B** was obtained as a 0.24 M solution in toluene (5.8 g, 16 mmol, >99%).

The concentrations of **B** were determined after every reaction. The different concentrations are due to different reactions setups and varying initial concentrations of **A**. The spectroscopic data is consistent with the literature.

## 4,6-Di-tert-butyl-1,3,2-diazaphosphinine (**C**)



**C**



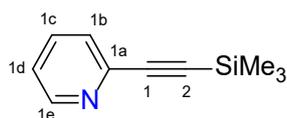
Compound **C** was prepared using a modified literature procedure.<sup>[15]</sup> A 0.15 M toluene solution of **C** (25 mL, 3.7 mmol, 1.0 equiv.) was directly used for the synthesis of **B**. The Schlenk flask was cooled to -78 °C and dried and degassed NEt<sub>3</sub> (2.6 mL, 19 mmol, 5.0 equiv.) was added. The mixture was stirred for 10 min at -30 °C and freshly distilled and degassed PCl<sub>3</sub> (0.32 mL, 3.7 mmol, 1.0 equiv) was added dropwise with vigorous stirring. The mixture was heated to 80 °C and stirred for 2 h, resulting in a brown solution containing a dark green precipitate. The flask was allowed to cool down to r.t. The mixture was filtered, and the residue thoroughly washed with dry toluene (4 x 30 mL). The dark brown filtrates were combined in a dried 250 mL Schlenk flask, and the yield was calculated *via* quantitative <sup>31</sup>P NMR spectroscopy with PPh<sub>3</sub>

as reference. Diazaphosphinine **C** was obtained as a 0.13 M solution in toluene (0.59 g, 2.8 mmol, 77%).

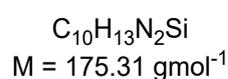
**<sup>31</sup>P NMR (162 MHz):**  $\delta$  = 268.4 ppm.

The spectroscopic data is consistent with the literature.<sup>[15]</sup>

## 2-((trimethylsilyl)ethynyl)pyridine (**7**)



**7**



The procedure was adapted from the literature.<sup>[16]</sup> Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (177 mg, 0.25 mmol, 5 mol%) and CuI (95 mg, 0.50 mmol, 10 mol%) were introduced to a 35 mL Schlenk flask and MeCN (6 mL) was added. The mixture was degassed, NEt<sub>3</sub> (2.6 mL, 26 mmol, 5.1 equiv.), trimethylsilylacetylene (0.71 mL, 5.0 mmol, 1.0 equiv.) and 2-bromopyridine (0.48 mL, 4.9 mmol, 1.0 equiv.) were added. The reaction was performed in the microwave at 300 W for 20 min and 120 °C. After cooling down the reaction mixture, the precipitate was filtered off, and the solvent removed *in vacuo*. The crude product was purified *via* trap-to-trap condensation at high vacuum and acetylene **7** was obtained as colorless crystals suitable for sXRD analysis (0.78 g, 4.4 mmol, 90%).

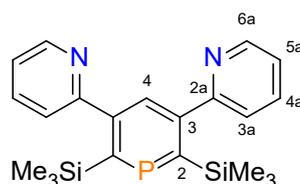
The data obtained was similar with the literature.<sup>[16]</sup>

**<sup>1</sup>H-NMR (400.5 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.57 (ddd, <sup>3</sup>J<sub>H-1e,H-1d</sub> = 4.9 Hz, <sup>4</sup>J<sub>H-1e,H-1c</sub> = 1.8 Hz, <sup>5</sup>J<sub>H-1e,H-1b</sub> = 1.0 Hz, 1H, *H*-1e), 7.63 (ddd, <sup>3</sup>J<sub>H-1c,H-1b</sub> = 7.7 Hz, <sup>3</sup>J<sub>H-1c,1d-H</sub> = 7.7 Hz, <sup>4</sup>J<sub>H-1c,H-1e</sub> = 1.8 Hz, 1H, *H*-1c), 7.45 (ddd, <sup>3</sup>J<sub>H-1b,H-1c</sub> = 7.8 Hz, <sup>4</sup>J<sub>H-1b,H-1d</sub> = 1.0 Hz, <sup>5</sup>J<sub>H-b,H-e</sub> = 1.0 Hz, 1H, *H*-1b), 7.22 (ddd, <sup>3</sup>J<sub>H-1d,H-1c</sub> = 7.6 Hz, <sup>3</sup>J<sub>H-1d,H-1e</sub> = 4.9 Hz, <sup>4</sup>J<sub>H-1d,H-1b</sub> = 1.2 Hz, 1H, *H*-1d), 0.27 (s, 9H, Si-Me<sub>3</sub>)ppm.

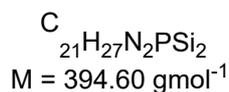
**<sup>13</sup>C{<sup>1</sup>H}-NMR (100.5 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.1 (1C, C-1e), 143.2 (1C, C-1a), 136.2 (1C, C-1d), 127.4 (1C, C-1b), 123.1 (1C, C-1c), 103.8 (1C, C-1), 94.9 (1C, C-2), 0.2 (3C, 1-SiMe<sub>3</sub>)ppm.

**<sup>29</sup>Si-NMR (79.4 MHz, CDCl<sub>3</sub>):**  $\delta$  = -16.7ppm.

## 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine (**8**)



**8**



To a 0.07 M toluene solution of **C** (4.3 mmol, 65 mL) acetylene **7** (1.7 g, 9.7 mmol, 2.3 equiv.) was added and the reaction mixture heated for 14 h at 130 °C. All volatile components were removed *in vacuo* and the crude product purified *via* recrystallization from MeCN. The phosphinine **8** was obtained as a colorless crystalline solid. (1.10 g, 2.78 mmol, 64%). Suitable crystals for sXRD were obtained from a saturated solution in MeCN.

**<sup>1</sup>H NMR (700.23 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ = 8.66 ddd, <sup>3</sup>J<sub>H-6a,H-5a</sub> = 4.9 Hz, <sup>4</sup>J<sub>H-6a,H-4a</sub> = 1.8 Hz, <sup>5</sup>J<sub>H-6a,H-3a</sub> = 1.1 Hz, 2H, *H*-6a), 7.77 (ddd, <sup>3</sup>J<sub>H-4a,H-3a</sub> = 7.7 Hz, <sup>3</sup>J<sub>H-4a,H-5a</sub> = 7.7 Hz, <sup>4</sup>J<sub>H-4a,H-6a</sub> = 1.8 Hz, 2H, *H*-4a), 7.54 (s, 1H, *H*-4), 7.49 (ddd, <sup>3</sup>J<sub>H-3a,H-4a</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-3a,H-4a</sub> = 1.1 Hz, <sup>5</sup>J<sub>H-3a,H-6a</sub> = 1.1 Hz, 2H, *H*-3a), 7.32 (<sup>3</sup>J<sub>H-5a,H-4a</sub> = 7.6 Hz, <sup>3</sup>J<sub>H-5a,H-6a</sub> = 4.9 Hz, <sup>4</sup>J<sub>H-5a,H-3a</sub> = 1.1 Hz, 2H, *H*-5a), 0.16 (d, <sup>4</sup>J<sub>SiMe<sub>3</sub>,P</sub> = 1.7 Hz 18H, SiMe<sub>3</sub>) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.42 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ = 168.1 (d, <sup>1</sup>J<sub>C-2,P</sub> = 90.0 Hz, 2C, C-2), 162.8 (d, <sup>3</sup>J<sub>C-2a,P</sub> = 3.0 Hz, 2C, C-2a), 152.1 (d, <sup>2</sup>J<sub>C-3,P</sub> = 11.2 Hz, 2C, C-3), 149.1 (s, 2C, C-6a) 136.9 (s, 2C, C-4a), 131.0 (d, <sup>3</sup>J<sub>C-4,P</sub> = 21.1 Hz, 1C, C-4), 123.6 (s, 2C, C-3a), 122.9 (s, 2C, C-5a), 2.1 (d, <sup>3</sup>J<sub>SiMe<sub>3</sub>,P</sub> = 10.3 Hz, 6C, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

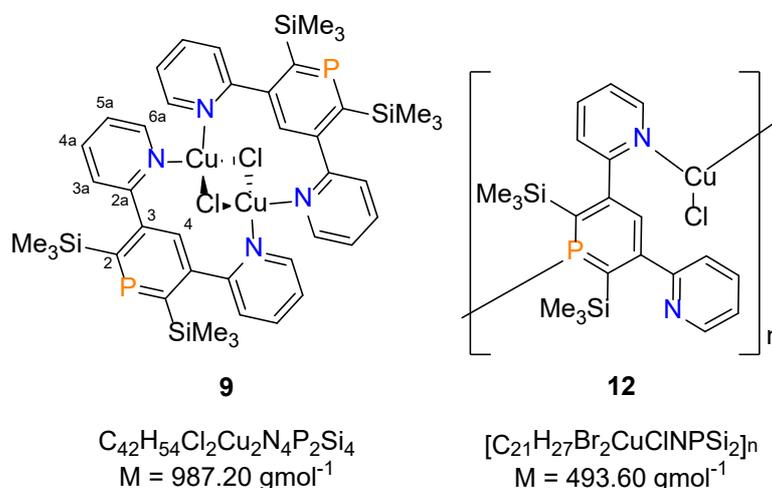
**<sup>31</sup>P NMR (161.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ = 274.0 (m, <sup>4</sup>J<sub>P,Si(CH<sub>3</sub>)<sub>3</sub></sub> = 1.7 Hz, 1P, PP-*P*) ppm.

**<sup>31</sup>P NMR (161.7 MHz, CD<sub>3</sub>CN):** δ = 272.8 (s, 1P, PP-*P*) ppm.

**<sup>29</sup>Si{<sup>1</sup>H} NMR (79.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ = -2.9 (<sup>2</sup>J<sub>Si,P</sub> = 36.2 Hz, 2Si, SiMe<sub>3</sub>) ppm.

**HRMS-ESI:** *m/z* calculated for C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>PSi<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 417.1348. Found: 417.1352

**Synthesis of 2,6-bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine copper(I) chloride complex (9) and 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine copper(I) chloride coordination polymer (12)**



Phosphinine **8** (30 mg, 76  $\mu\text{mol}$ ) was introduced to a J-Young NMR tube and suspended in dry MeCN (0.6 mL). added. Upon addition of  $\text{CuCl}\cdot\text{SMe}_2$  (13 mg, 80  $\mu\text{mol}$ , 1.1 equiv.) at room temperature, the solids dissolved, affording a dark yellow solution. A grey precipitate was filtered off and the product purified due recrystallization at  $-20^\circ\text{C}$ . Suitable thin, off-white, single crystals for scXRD analysis of coordination polymer **12** were directly obtained from the recrystallization. (35 mg, 93%).

**$^1\text{H}$  NMR (399.7 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = 8.65$  (ddd,  $^3J_{\text{H-6a,H-5a}} = 4.8 \text{ Hz}$ ,  $^4J_{\text{H-6a,H-4a}} = 1.8 \text{ Hz}$ ,  $^5J_{\text{H-6a,H-3a}} = 1.0 \text{ Hz}$ , 2H, *H*-6a), 7.85 (ddd,  $^3J_{\text{H-4a,H-3a}} = 7.7 \text{ Hz}$ ,  $^3J_{\text{H-4a,H-5a}} = 7.7 \text{ Hz}$ ,  $^4J_{\text{H-4a,H-6a}} = 1.8 \text{ Hz}$ , 2H, *H*-4a), 7.59 (ddd,  $^3J_{\text{H-3a,H-4a}} = 7.8 \text{ Hz}$ ,  $^4J_{\text{H-3a,H-5a}} = 6.4 \text{ Hz}$ ,  $^5J_{\text{H-3a,H-6a}} = 1.1 \text{ Hz}$ , 2H, *H*-3a), 7.59 (s, 1H, *H*-4), 7.39 (ddd,  $^3J_{\text{H-5a,H-4a}} = 7.5 \text{ Hz}$ ,  $^3J_{\text{H-5a,H-6a}} = 4.8 \text{ Hz}$ ,  $^4J_{\text{H-5a,H-3a}} = 1.1 \text{ Hz}$ , 2H, *H*-5a), 0.15 (d,  $^4J_{\text{SiMe}_3,\text{P}} = 1.3 \text{ Hz}$  18H,  $\text{SiMe}_3$ ) ppm.

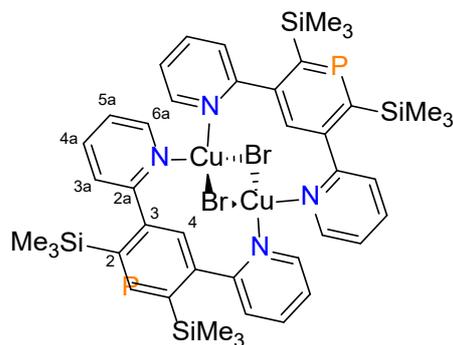
**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = 168.0$  (d,  $^1J_{\text{C-2,P}} = 84.0 \text{ Hz}$ , 2C, *C*-2), 162.7 (d,  $^1J_{\text{C-2a,P}} = 3.6 \text{ Hz}$ , 2C, *C*-2a), 152.9 (d,  $^2J_{\text{C-3,P}} = 11.7 \text{ Hz}$ , 2C, *C*-3), 149.7 (s, 2C, *C*-6a) 138.0 (s, 2C, *C*-4a), 131.5 (d,  $^3J_{\text{C-4,P}} = 22.6 \text{ Hz}$ , 1C, *C*-4), 124.3 (s, 2C, *C*-3a), 123.9 (s, 2C, *C*-5a), 2.3 (d,  $^3J_{\text{SiMe}_3,\text{P}} = 9.9 \text{ Hz}$ , 6C,  $\text{Si}(\text{CH}_3)_3$ ) ppm

**$^{31}\text{P}$  NMR (162.1 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = 264.1$  (s, 1P, *PP-P*) ppm.

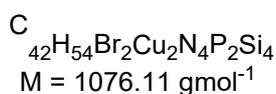
**$^{29}\text{Si}\{^1\text{H}\}$  NMR (79.6 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = -3.2$  ( $^2J_{\text{Si,P}} = 35.5 \text{ Hz}$ , 2Si,  $\text{SiMe}_3$ ) ppm.

**HRMS-ESI<sup>+</sup>:** *m/z* calculated for fragment 1:  $\text{C}_{21}\text{H}_{27}\text{ClCu}_2\text{N}_2\text{PSi}_2^+$ ,  $[\text{PPCu}_2\text{Cl}]^+$ : 554.9725, found 554.9719; *m/z* calculated for fragment 2:  $[\text{C}_{42}\text{H}_{54}\text{CuN}_4\text{P}_2\text{Si}_4]^+$ ,  $[(\text{PP})_2\text{Cu}]^+$ : 851.2191, found 851.2165; *m/z* calculated for fragment 3:  $[\text{C}_{42}\text{H}_{54}\text{Cl}_2\text{Cu}_3\text{N}_4\text{P}_2\text{Si}_4]^+$ ,  $[(\text{PP})_2(\text{CuCl})_2\text{Cu}]^+$ : 1047.0165, found: 1047.0135.

**2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine) copper(I) bromide complex (10)**



**10**



Phosphinine **8** (25 mg, 63  $\mu\text{mol}$ ) and CuBr (9.9 mg, 69  $\mu\text{mol}$ , 1.1 equiv.) were introduced to a J-Young NMR tube and suspended in  $\text{D}_3\text{CCN}$  (0.6 mL). The mixture was heated at 100 °C until the solids were dissolved, resulting in a yellow solution. The solution was then allowed to cool down to room temperature. Suitable yellow crystals for scXRD analysis were obtained from a concentrated solution at room temperature (20 mg, 37  $\mu\text{mol}$ , 59%).

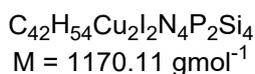
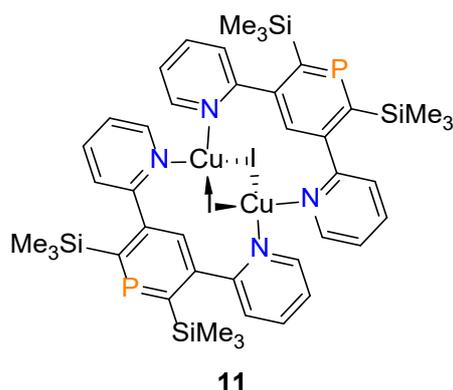
**$^1\text{H}$  NMR (399.7 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = 8.65 (ddd,  $^3J_{\text{H-6a,H-5a}}$  = 4.8 Hz,  $^4J_{\text{H-6a,H-4a}}$  = 1.8 Hz,  $^5J_{\text{H-6a,H-3a}}$  = 1.0 Hz, 2H, *H*-6a), 7.85 (ddd,  $^3J_{\text{H-4a,H-3a}}$  = 7.7 Hz,  $^3J_{\text{H-4a,H-5a}}$  = 7.7 Hz,  $^4J_{\text{H-4a,H-6a}}$  = 1.8 Hz, 2H, *H*-4a), 7.59 (ddd,  $^3J_{\text{H-3a,H-4a}}$  = 7.8 Hz,  $^4J_{\text{H-3a,H-5a}}$  = 6.4 Hz,  $^5J_{\text{H-3a,H-6a}}$  = 1.1 Hz, 2H, *H*-3a), 7.59 (s, 1H, *H*-4), 7.39 (ddd,  $^3J_{\text{H-5a,H-4a}}$  = 7.5 Hz,  $^3J_{\text{H-5a,H-6a}}$  = 4.8 Hz,  $^4J_{\text{H-5a,H-3a}}$  = 1.1 Hz, 2H, *H*-5a), , 0.15 (d,  $^4J_{\text{SiMe}_3,\text{P}}$  = 1.3 Hz 18H,  $\text{SiMe}_3$ ) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = 167.6 (d,  $^1J_{\text{C-2,P}}$  = 85.2 Hz, 2C, *C*-2), 162.7 (s, 2C, *C*-2a), 153.1 (d,  $^2J_{\text{C-3,P}}$  = 11.6 Hz, 2C, *C*-3), 149.8 (s, 2C, *C*-6a) 138.0 (s, 2C, *C*-4a), 131.5 (d,  $^3J_{\text{C-4,P}}$  = 21.8 Hz, 1C, *C*-4), 124.4 (s, 2C, *C*-3a), 123.9 (s, 2C, *C*-5a), 2.3 (d,  $^3J_{\text{SiMe}_3,\text{P}}$  = 10.0 Hz, 6C,  $\text{Si}(\text{CH}_3)_3$ ) ppm

**$^{31}\text{P}$  NMR (162.1 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = 257.1 (s, 1P, PP-*P*) ppm.

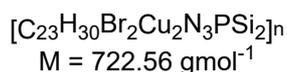
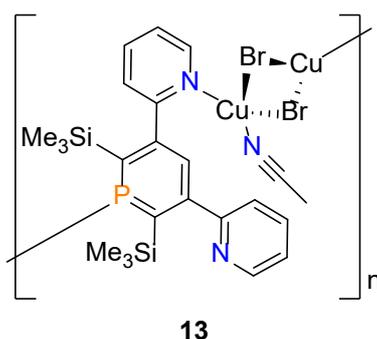
**$^{29}\text{Si}\{^1\text{H}\}$  NMR (79.6 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = -2.8 ( $^2J_{\text{Si,P}}$  = 33.8 Hz, 2Si,  $\text{SiMe}_3$ ) ppm.

## 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine copper(I) iodide complex (11)



Phosphinine **8** (25 mg, 63  $\mu\text{mol}$ ) and CuI (12 mg, 64  $\mu\text{mol}$ , 1.0 equiv.) were introduced to a J-Young NMR tube and MeCN (0.7 mL) added. The mixture was heated at 100 °C until the solids were dissolved, and then the solution was allowed to slowly cool down to room temperature. Suitable yellow crystals for XRD analysis were directly obtained from the reaction mixture (38 mg, 30  $\mu\text{mol}$ , 95%). NMR characterization was not possible due to poor solubility in available deuterated solvents.

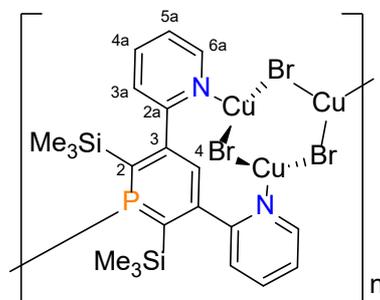
## Synthesis of 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine (copper(I) bromide)<sub>2</sub> coordination polymer with acetonitrile as co-ligand (13)



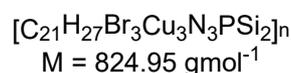
Phosphinine **8** (20 mg, 51  $\mu\text{mol}$ ) and CuBr (20 mg, 140  $\mu\text{mol}$ , 2.7 equiv.) were introduced to a J-Young NMR tube and D<sub>3</sub>CCN (0.6 mL) added. The mixture was heated at 100 °C until the solids were dissolved, resulting in a dark yellow solution. The solution was allowed to cool down slowly to room temperature. Suitable yellow crystals for XRD analysis were obtained directly from the reaction mixture (15 mg, 21  $\mu\text{mol}$ , 40%). Complete NMR characterization was not possible due to poor solubility in deuterated solvents.

$^{31}\text{P}$  NMR (161.8 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = 242.5$  (s, 1P, PP-*P*) ppm.

**Synthesis of 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine (copper(I) bromide)<sub>3</sub> coordination polymer (14)**



**14**



Phosphinine **8** (14 mg, 35  $\mu\text{mol}$ , 0.5 equiv.) and  $\text{CuBr}\cdot\text{SMe}_2$  (15 mg, 72  $\mu\text{mol}$ ) were introduced to a 10 mL Schlenk tube and diglyme (5 mL) added. The mixture was heated to 120°C until the solid was dissolved, obtaining a yellow solution. The solution was allowed to cool down slowly to room temperature. Suitable yellow crystals for XRD were obtained directly from the reaction mixture (9.1 mg, 11  $\mu\text{mol}$ , 46%). The supernatant solution was filtered off and the crystalline solid dried *in vacuo*. For NMR characterization, the solid was heated in  $\text{DMSO}-d_6$  until the solid was entirely dissolved.

The reaction was performed repeatedly with the same quantities of **8** and  $\text{CuBr}\cdot\text{SMe}_2$  in a high pressure Schlenk tube in THF (5 mL). The suspended solids were heated to 120 °C, resulting in a yellow solution and was allowed to cool down slowly to room temperature. Suitable yellow single crystals for XRD were obtained directly from the reaction mixture and confirmed the calculated structure of 14, obtained from the diglyme solution. The supernatant solution was filtered off and the crystalline solid dried *in vacuo*. (8.2 mg, 10  $\mu\text{mol}$ , 42%).

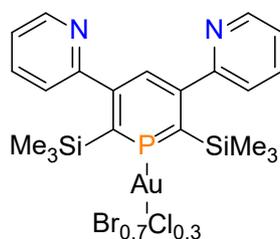
$^1\text{H}$  NMR (399.7 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 8.74$ -8.58 (m, 2H, *H*-6a), 8.08-7.85 (m, 2H, *H*-4a), 7.80-7.63 (m, 2H, *H*-3a), 7.59-7.50 (m, 3H, *H*-4, *H*-5a), 0.16 (s, 18H,  $\text{SiMe}_3$ ) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 160.4$  (s, 2C, C-2a), 159.7 (d,  $^1J_{\text{C-2,P}} = 62.3$  Hz, 2C, C-2), 152.5 (d,  $^2J_{\text{C-3,P}} = 13.0$  Hz, 2C, C-3), 149.1 (s, 2C, C-6a) 137.7 (s, 2C, C-4a), 129.7 (d,  $^3J_{\text{C-4,P}} = 27.7$  Hz, 1C, C-4), 124.2 (s, 2C, C-3a), 123.8 (s, 2C, C-5a), 2.2 (d,  $^3J_{\text{SiMe}_3,\text{P}} = 7.4$  Hz, 6C,  $\text{Si}(\text{CH}_3)_3$ )ppm

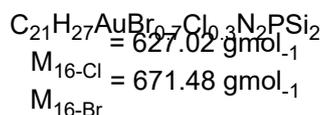
$^{31}\text{P}$  NMR (161.8 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 233.5$  ( $s_{\text{br}}$ , 1P, PP-*P*) ppm.

$^{29}\text{Si}\{^1\text{H}\}$  NMR (79.4 MHz, DMSO- $d_6$ ):  $\delta = -2.4$  ( $^2J_{\text{Si,P}} = 29.8$  Hz, 2Si, SiMe $_3$ ) ppm.

### Synthesis of 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine gold(I) chloride/bromide complex (16)



**16**



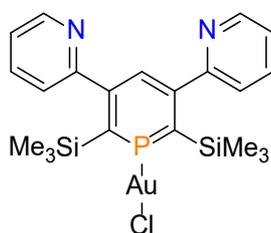
A solution of copper bromide complex **10** was freshly prepared. In a 10 mL Schlenk tube phosphinine **8** (14 mg, 37  $\mu\text{mol}$ ) and CuBr (5.7 mg, 40  $\mu\text{mol}$ , 1.1 equiv.) was introduced and suspended in  $d^3$ -MeCN (0.6 mL) and heated until the solids were dissolved. The obtained yellow solution was filtered and transferred into a J-Young NMR tube and AuCl·SMe $_2$  (11 mg, 37  $\mu\text{mol}$ , 1.0 equiv.) added. A colorless solid formed immediately after adding. The consumption of the copper bromide complex **10** was controlled *via* NMR spectroscopy and the supernatant solution subsequently removed by filtration. The solid was suspended in THF (3 mL) and transferred into a 10 mL Schlenk tube. The mixture was heated to 130  $^\circ\text{C}$ , resulting in a yellow solution with an off-white precipitate. The reaction mixture was allowed to cool down to room temperature and a yellow crystalline solid formed. (14 mg, 21  $\mu\text{mol}$ , 57%) Suitable yellow crystals for XRD were obtained directly from the reaction mixture. NMR characterization was not possible due to poor solubility in deuterated solvents.

For HRMS ESI measurement, the crystalline solid was suspended in MeCN and signals for both compounds **16-Cl** and **16-Br** detected. A quantitative correlation between the intensity of observed signals and the concentration of specific compounds or ions in solution cannot be drawn. Nevertheless, under identical measurement conditions, the same ionization, structural similarity, and comparable reactivity can be inferred. On this behalf, the ESI measurements indicate a relative higher abundance of **16-Br** to **16-Cl**, in which these findings are in agreement to the obtained results of the single crystal XRD analysis.

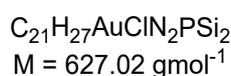
**16-Cl**: HRMS-ESI:  $m/z$  calculated for  $\text{C}_{21}\text{H}_{33}\text{AuClN}_2\text{OPSi}_2^-$ :  $[\text{M}+\text{OH}]^-$ : 643.0837. Found: 643.0976.

**16-Br:** HRMS-ESI:  $m/z$  calculated for  $C_{21}H_{33}AuBrN_2OPSi_2^-$ :  $[M+HO]^-$ : 687.0332. Found: 687.0487.

**Synthesis of 2,6-Bis(trimethylsilyl)-3,5-bis(pyridine-2-yl)-phosphinine gold(I) chloride complex (16a)**



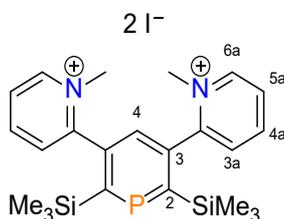
**16a**



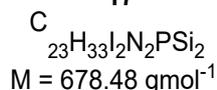
In a 10 mL Schlenk tube phosphinine **8** (36 mg, 90  $\mu\text{mol}$ ) was introduced and dissolved in a mixture of MeCN/CH<sub>2</sub>Cl<sub>2</sub>(1:1) (2.0 mL). The solution was cooled down to  $-20^\circ\text{C}$  and a solution of AuCl·SMe<sub>2</sub> (27 mg, 93  $\mu\text{mol}$ , 1.0 equiv.) in MeCN (1.0 mL) added. The reaction mixture was allowed to warm up to room temperature and resulting in a yellow solution with a black precipitate. The supernatant solution was filtered off, and all volatile compounds were removed *in vacuo*. The remaining brown solid was suspended in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) resulting in a yellow solution and a black precipitate. Complete NMR characterization was not possible due to poor solubility and successive decomposition.

$^{31}\text{P}\{^1\text{H}\}$  NMR (161.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 212.7$  (s<sub>br</sub>, 1P, PP-*P*) ppm.

**2,6-Bis(trimethylsilyl)-3,5-bis(*N*-methyl-pyridinium-2-yl)-phosphinine iodide (17)**



**17**



In a 25 mL Schlenk tube phosphinine **8** (100 mg, 250  $\mu\text{mol}$ ) was suspended in MeCN (10 mL) and MeI (0.1 mL, 1.6 mmol, 6.5 equiv.) added dropwise at room temperature. The solid dissolved and the reactions mixture was obtained as a deep yellow solution. To ensure the

completeness of the alkylation, the mixture was heated for 2 h to 70 °C. The solution was allowed to cool down to room temperature, and all volatile components were removed *in vacuo*. Pyridinium salt **17** was obtained as a yellow crystalline solid (160 mg, 240 μmol, 96%) and suitable crystals for scXRD were obtained from a saturated solution at -20°C.

The reaction to bis-methylpyridinium salt **17** afforded two sets of resonances which could be assigned to rotamers **17a** and **17b** in a ratio of 1:0.7. Both rotamers were able to characterize separately from the same spectra.

### 17a

**<sup>1</sup>H NMR (700.2 MHz, CD<sub>3</sub>CN):** δ = 9.02 (ddd, <sup>3</sup>J<sub>H-6a,H-5a</sub> = 6.2 Hz, <sup>4</sup>J<sub>H-6a,H-4a</sub> = 1.4 Hz, <sup>5</sup>J<sub>H-6a,H-3a</sub> = 0.6 Hz, 2H, *H*-6a), 8.64 (tdd, <sup>3</sup>J<sub>H-4a,H-3a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-4a,H-5a</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-4a,H-6a</sub> = 0.6 Hz, 2H, *H*-4a), 8.16 (ddd, <sup>3</sup>J<sub>H-5a,H-4a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-5a,H-6a</sub> = 6.4 Hz, <sup>4</sup>J<sub>H-5a,H-3a</sub> = 1.3 Hz, 2H, *H*-5a), 8.24 (s, 1H, *H*-4), 8.06 (dd, <sup>3</sup>J<sub>H-3a,H-4a</sub> = 8.0 Hz, <sup>4</sup>J<sub>H-3a,H-4a</sub> = 1.5 Hz, 2H, *H*-3a), 4.21 (s, 6H, CH<sub>3</sub>), 0.15 (s, 18H, SiMe<sub>3</sub>) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR (176.1 MHz, CD<sub>3</sub>CN):** δ = 171.4 (d, <sup>1</sup>J<sub>C-2,P</sub> = 96.0 Hz, 2C, C-2), 156.4 (2C, C-2a), 147.4 (2C, C-6a), 147.0 (2C, C-4a), 141.9 (d, <sup>2</sup>J<sub>C-3,P</sub> = 11.1 Hz, 1C, C-3), 131.0 (2C, C-3a), 131.1 (d, <sup>3</sup>J<sub>C-4,P</sub> = 19.6 Hz, 1C, C-4), 129.0 (2C, C-5a), 49.3 (2C, CH<sub>3</sub>), 1.0 (6C, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

**<sup>31</sup>P NMR (161.7 MHz, CD<sub>3</sub>CN):** δ = 282.1 (s, 1P, PP-*P*) ppm.

**<sup>29</sup>Si{<sup>1</sup>H} NMR (79.4 MHz, CD<sub>3</sub>CN):** -0.75 (d, <sup>2</sup>J<sub>Si-P</sub> =, 2Si, SiMe<sub>3</sub>) ppm.

### 17b

**<sup>1</sup>H NMR (700.2 MHz, CD<sub>3</sub>CN):** δ = 9.01 (ddd, <sup>3</sup>J<sub>H-6a,H-5a</sub> = 6.3 Hz, <sup>4</sup>J<sub>H-6a,H-4a</sub> = 1.4 Hz, <sup>5</sup>J<sub>H-6a,H-3a</sub> = 0.6 Hz, 2H, *H*-6a), 8.67 (tdd, <sup>3</sup>J<sub>H-4a,H-3a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-4a,H-5a</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-4a,H-6a</sub> = 0.6 Hz, 2H, *H*-4a), 8.16 (ddd, <sup>3</sup>J<sub>H-5a,H-4a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-5a,H-6a</sub> = 6.4 Hz, <sup>4</sup>J<sub>H-5a,H-3a</sub> = 1.3 Hz, 2H, *H*-5a), 8.19 (dd, <sup>3</sup>J<sub>H-3a,H-4a</sub> = 8.0 Hz, <sup>4</sup>J<sub>H-3a,H-4a</sub> = 1.6 Hz, 2H, *H*-3a), 8.10 (s, 1H, *H*-4), 4.09 (s, 6H, CH<sub>3</sub>), 0.15 (s, 18H, SiMe<sub>3</sub>) ppm.

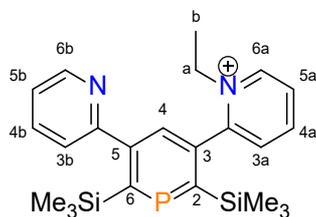
**<sup>13</sup>C{<sup>1</sup>H} NMR (176.1 MHz, CD<sub>3</sub>CN):** δ = 171.7 (d, <sup>1</sup>J<sub>C-2,P</sub> = 95.0 Hz, 2C, C-2), 156.3 (2C, C-2a), 147.4 (2C, C-6a), 147.1 (2C, C-4a), 141.9 (d, <sup>2</sup>J<sub>C-3,P</sub> = 11.9 Hz, 1C, C-3), 131.4 (2C, C-3a), 130.4 (d, <sup>3</sup>J<sub>C-4,P</sub> = 19.9 Hz, 1C, C-4), 129.0 (2C, C-5a), 48.8 (2C, CH<sub>3</sub>), 1.0 (6C, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

**<sup>31</sup>P NMR (161.7 MHz, CD<sub>3</sub>CN):** δ = 281.8 (s, 1P, PP-*P*) ppm.

**<sup>29</sup>Si{<sup>1</sup>H} NMR (79.4 MHz, CD<sub>3</sub>CN):** -0.75 (d, <sup>2</sup>J<sub>Si-P</sub> =, 2Si, SiMe<sub>3</sub>) ppm.

**HRMS-ESI:** *m/z* calculated for C<sub>23</sub>H<sub>33</sub>N<sub>2</sub>PSi<sub>2</sub><sup>2+</sup>: ½ [M]<sup>2+</sup>: 212.0959. Found: 212.0954.

**2,6-Bis(trimethylsilyl)-3-(*N*-ethyl-pyridinium-2-yl)-5-(pyridine-2-yl)-phosphinine hexafluorophosphate (18)**



[PF<sub>6</sub>]<sup>-</sup>

**18**

C<sub>23</sub>H<sub>32</sub>F<sub>6</sub>N<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>

M: 568.63 g/mol

In a 20 mL Schlenk flask phosphinine **8** (220 mg, 560 μmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and cooled down to -40 °C. A solution of [Et<sub>3</sub>O][PF<sub>6</sub>] (14 mg, 560 μmol, 1.0 equiv.) in MeCN (5 mL) was freshly prepared and added dropwise to the phosphinine solution. The reaction mixture was allowed under stirring to warm up to room temperature and subsequently all volatile compounds were removed *in vacuo*. The obtained crude product was suspended in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and the supernatant filtered off. After drying the purified solid *in vacuo*, **18** was obtained as a colorless solid (300 mg, 0.49 mmol, 87%). For scXRD analysis, suitable single crystals were obtained of a saturated solution in MeCN at -20 °C.

**<sup>1</sup>H NMR (400.5 MHz, CD<sub>3</sub>CN):** δ = 8.86 (dd, <sup>3</sup>J<sub>H-6a,H-5a</sub> = 6.4 Hz, <sup>4</sup>J<sub>H-6a,H-4a</sub> = 1.5 Hz, 1H, *H*-6a), 8.68 (ddd, <sup>3</sup>J<sub>H-6b,H-5b</sub> = 4.9 Hz, <sup>4</sup>J<sub>H-6b,H-4b</sub> = 1.9 Hz, <sup>5</sup>J<sub>H-6b,H-3b</sub> = 1.1 Hz, 1H, *H*-6b), 8.59 (ddd, <sup>3</sup>J<sub>H-4a,H-3a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-4a,H-5a</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-4a,H-6a</sub> = 1.4 Hz, 1H, *H*-4a), 8.15 (ddd, <sup>3</sup>J<sub>H-5a,H-4a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-5a,H-6a</sub> = 6.3 Hz, <sup>4</sup>J<sub>H-5a,H-3a</sub> = 1.6 Hz, 1H, *H*-5a), 8.02 (dd, <sup>3</sup>J<sub>H-3a,H-4a</sub> = 8.0 Hz, <sup>4</sup>J<sub>H-3a,H-5a</sub> = 1.7 Hz, 1H, *H*-3a), 7.89 (ddd, <sup>3</sup>J<sub>H-4b,H-3b</sub> = 7.7 Hz, <sup>3</sup>J<sub>H-4b,H-5b</sub> = 7.7 Hz, <sup>4</sup>J<sub>H-4b,H-6b</sub> = 1.8 Hz, 1H, *H*-4b), 7.62 (s, 1H, *H*-4), 7.59 (ddd, <sup>3</sup>J<sub>H-3b,H-4b</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-3b,H-5b</sub> = 1.1 Hz, <sup>5</sup>J<sub>H-3b,H-6b</sub> = 1.1 Hz, 1H, *H*-3b), 7.43 (ddd, <sup>3</sup>J<sub>H-5b,H-4b</sub> = 7.6 Hz, <sup>3</sup>J<sub>H-5b,H-6b</sub> = 4.9 Hz, <sup>4</sup>J<sub>H-5b,H-3b</sub> = 1.0 Hz, 1H, *H*-5b), 4.41 (dq, <sup>2</sup>J<sub>H-a',H-a''</sub> = 14.5 Hz, <sup>3</sup>J<sub>H-a',H-b</sub> = 7.3 Hz, 1H, *CH*-a'), 4.25 (dq, <sup>2</sup>J<sub>H-a'',H-a'</sub> = 14.3 Hz, <sup>3</sup>J<sub>H-a'',H-b</sub> = 7.1 Hz, 1H, *CH*-a''), 1.44 (t, <sup>3</sup>J<sub>H-b,H-a''/H-a'</sub> = 7.2 Hz, 3H, *CH*<sub>3</sub>-b), 0.19 (s, 9H, *SiMe*<sub>3</sub>-6), 0.11 (s, 9H, *SiMe*<sub>3</sub>-2) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, CD<sub>3</sub>CN):** δ = 173.6 (d, <sup>1</sup>J<sub>C-6,P</sub> = 92.5 Hz, 1C, C-6), 167.4 (d, <sup>1</sup>J<sub>C-2,P</sub> = 93.6 Hz, 1C, C-2), 161.3 (1C, C-2b), 157.8 (1C, C-2a), 152.2 (d, <sup>2</sup>J<sub>C-5,P</sub> = 10.6 Hz, 1C, C-5), 149.9 (1C, C-6b), 146.9 (1C, C-4a), 145.5 (1C, C-6a), 142.0 (d, <sup>2</sup>J<sub>C-3,P</sub> = 11.2 Hz, 1C, C-3), 138.3 (1C, C-4b), 131.6 (1C, C-3a), 130.3 (d, <sup>3</sup>J<sub>C-4,P</sub> = 20.7 Hz, 1C, C-4), 129.3 (1C, C-5a),

124.4 (1C, C-5b), 124.1 (1C, C-3b), 55.3 (1C, C-a), 16.3 (1C, C-b), 2.4 (d,  $^3J_{C-SiMe_3-6,P} = 10.4$  Hz, 3C, Si(CH<sub>3</sub>)<sub>3</sub>-6), 1.3 (d,  $^3J_{C-SiMe_3-2,P} = 9.9$  Hz, 3C, Si(CH<sub>3</sub>)<sub>3</sub>-2) ppm.

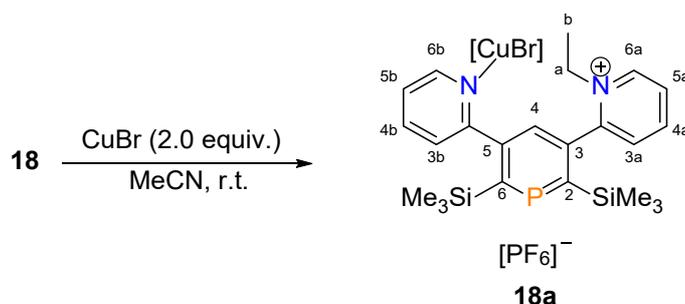
**<sup>31</sup>P NMR (162.1 MHz, CD<sub>3</sub>CN):**  $\delta = 278.1$  (s, 1P, PP-P),  $-144.6$  (hept,  $^1J_{P,F} = 707.1$  Hz, 1P, PF<sub>6</sub>) ppm.

**<sup>29</sup>Si{<sup>1</sup>H} NMR (79.6 MHz, CD<sub>3</sub>CN):**  $\delta = -1.7$  (d,  $^2J_{Si-6,P} = 33.3$  Hz, 1Si, SiMe<sub>3</sub>-6),  $-2.5$  (d,  $^2J_{Si-2,P} = 36.4$  Hz, 1Si, SiMe<sub>3</sub>-2).

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.9 MHz, CD<sub>3</sub>CN):**  $\delta = -72.6$  (d,  $^1J_{P,F} = 707.1$  Hz, 6F, PF<sub>6</sub>) ppm.

**HRMS-ESI<sup>+</sup>:** *m/z* calculated for C<sub>23</sub>H<sub>32</sub>N<sub>2</sub>PSi<sub>2</sub><sup>+</sup>: [M]<sup>+</sup>: 423.1841. Found: 423.1893.

### 2,6-Bis(trimethylsilyl)-3-(*N*-ethyl-pyridinium-2-yl)-5-(pyridine-2-yl)-phosphinine hexafluorophosphate copper(I) bromide complex (18a)



In a J-Young NMR tube pyridinium phosphinine salt **18** (20 mg, 36  $\mu$ mol) was dissolved in d<sup>3</sup>-MeCN (0.5 mL) and CuBr (11 mg, 72  $\mu$ mol, 2.0 equiv.) added. The CuBr dissolved immediately, resulting in a deep yellow solution. The solution gradually darkened and after several days the formation of a brown precipitate was observed. All attempts to obtain suitable crystals for scXRD analysis failed, and only NMR characterization was performed.

**<sup>1</sup>H NMR (400.5 MHz, CD<sub>3</sub>CN):**  $\delta = 8.86$  (ddd,  $^3J_{H-6a,H-5a} = 6.3$  Hz,  $^4J_{H-6a,H-4a} = 1.5$  Hz,  $^5J_{H-6a,H-3a} = 0.6$  Hz, 1H, H-6a),  $8.69$  (ddd,  $^3J_{H-6b,H-5b} = 5.1$  Hz,  $^4J_{H-6b,H-4b} = 1.6$  Hz,  $^5J_{H-6b,H-3b} = 1.1$  Hz, 1H, H-6b),  $8.57$  (ddd,  $^3J_{H-4a,H-3a} = 7.9$  Hz,  $^3J_{H-4a,H-5a} = 7.9$  Hz,  $^4J_{H-4a,H-6a} = 1.5$  Hz, 1H, H-4a),  $8.14$  (ddd,  $^3J_{H-5a,H-4a} = 7.9$  Hz,  $^3J_{H-5a,H-6a} = 6.3$  Hz,  $^4J_{H-5a,H-3a} = 1.6$  Hz, 1H, H-5a),  $8.03$  (ddd,  $^3J_{H-3a,H-4a} = 7.9$  Hz,  $^5J_{H-3a,H-6a} = 0.6$  Hz, 1H, H-3a),  $7.91$  (ddd,  $^3J_{H-4b,H-3b} = 7.6$  Hz,  $^3J_{H-4b,H-5b} = 7.6$  Hz,  $^4J_{H-4b,H-6b} = 1.8$  Hz, 1H, H-4b),  $7.58$  (d,  $^4J_{H-4,P} = 0.7$  Hz, 1H, H-4),  $7.58$  (ddd,  $^3J_{H-3b,H-4b} = 7.9$  Hz,  $^4J_{H-3b,H-5b} = 1.1$  Hz,  $^5J_{H-3b,H-6b} = 1.1$  Hz, 1H, H-3b),  $7.46$  (ddd,  $^3J_{H-5b,H-4b} = 7.6$  Hz,  $^3J_{H-5b,H-6b} = 4.9$  Hz,  $^4J_{H-5b,H-3b} = 1.2$  Hz, 1H, H-5b),  $4.42$  (dq,  $^2J_{H-a',H-a''} = 14.6$  Hz,  $^3J_{H-a',H-b} = 7.4$  Hz, 1H, CH-a'),  $4.28$  (dq,  $^2J_{H-a'',H-a'} = 14.4$  Hz,  $^3J_{H-a'',H-b} = 7.2$  Hz, 1H, CH-a''),  $1.44$  (t,  $^3J_{H-b,H-a''/H-a'} = 7.2$  Hz, 3H, CH<sub>3</sub>-b),  $0.20$  (d,  $^4J_{SiMe_3-6,P} = 1.5$  Hz, 9H, SiMe<sub>3</sub>-6),  $0.13$  (d,  $^4J_{SiMe_3-2,P} = 1.5$  Hz 9H, -2) ppm.



${}^4J_{\text{H-4b,H-5b}} = 7.8 \text{ Hz}$ ,  ${}^4J_{\text{H-4b,H-6b}} = 1.8 \text{ Hz}$ , 1H, *H-4b*), 7.64 (d,  ${}^4J_{\text{H-4,P}} = 4.0 \text{ Hz}$ , 1H, *H-4*), 7.60 (ddd,  ${}^3J_{\text{H-3b,H-4b}} = 7.9 \text{ Hz}$ ,  ${}^4J_{\text{H-3b,H-5b}} = 1.1 \text{ Hz}$ ,  ${}^5J_{\text{H-3b,H-6b}} = 1.1 \text{ Hz}$ , 1H, *H-3b*), 7.48 (ddd,  ${}^3J_{\text{H-5b,H-4b}} = 7.6 \text{ Hz}$ ,  ${}^3J_{\text{H-5b,H-6b}} = 4.9 \text{ Hz}$ ,  ${}^4J_{\text{H-5b,H-3b}} = 1.1 \text{ Hz}$ , 1H, *H-5b*), 4.48 (dq,  ${}^2J_{\text{H-a',H-a''}} = 14.6 \text{ Hz}$ ,  ${}^3J_{\text{H-a',H-b}} = 7.3 \text{ Hz}$ , 1H, *CH-a'*), 4.33 (dq,  ${}^2J_{\text{H-a'',H-a'}}$  = 14.2 Hz,  ${}^3J_{\text{H-a'',H-b}} = 7.2 \text{ Hz}$ , 1H, *CH-a''*), 1.44 (t,  ${}^3J_{\text{H-b,H-a''/H-a'}}$  = 7.2 Hz, 3H, *CH<sub>3</sub>-b*), 0.32 (d,  ${}^4J_{\text{SiMe}_3,\text{P}} = 0.8 \text{ Hz}$ , 9H, *SiMe<sub>3</sub>-6*), 0.29 (d,  ${}^4J_{\text{SiMe}_3,\text{P}} = 0.7 \text{ Hz}$ , 9H, *SiMe<sub>3</sub>-2*) ppm.

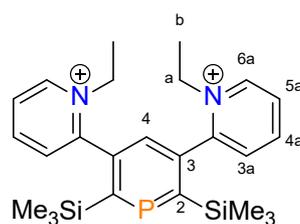
**${}^{13}\text{C}\{^1\text{H}\}$  NMR (100.7 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = 162.7$  (d,  ${}^1J_{\text{C-2,P}} = 20.0 \text{ Hz}$ , 1C, *C-2*), 160.6 (d,  ${}^3J_{\text{C-2b,P}} = 13.5 \text{ Hz}$ , 1C, *C-2b*), 158.0 (d,  ${}^1J_{\text{C-6,P}} = 16.9 \text{ Hz}$ , 1C, *C-6*), 155.9 (d,  ${}^3J_{\text{C-2a,P}} = 20.0 \text{ Hz}$ , 1C, *C-2a*), 152.5 (d,  ${}^2J_{\text{C-5,P}} = 11.7 \text{ Hz}$ , 1C, *C-5*), 150.4 (1C, *C-6b*), 147.2 (1C, *C-4a*), 145.8 (1C, *C-6a*), 145.3 (d,  ${}^2J_{\text{C-3,P}} = 15.9 \text{ Hz}$ , 1C, *C-3*), 138.6 (1C, *C-4b*), 131.8 (1C, *C-3a*), 130.9 (d,  ${}^3J_{\text{C-4,P}} = 42.5 \text{ Hz}$ , 1C, *C-4*), 129.8 (1C, *C-5a*), 125.1 (1C, *C-5b*), 124.31 (1C, *C-3b*), 55.6 (1C, *CH<sub>2</sub>-a*), 16.2 (1C, *CH<sub>3</sub>-b*), 3.2 (d,  ${}^3J_{\text{SiMe}_3,\text{P}} = 5.9 \text{ Hz}$ , 3C, *Si(CH<sub>3</sub>)<sub>3</sub>-2*), 2.5 (d,  ${}^3J_{\text{SiMe}_3,\text{P}} = 5.4 \text{ Hz}$ , 3C, *Si(CH<sub>3</sub>)<sub>3</sub>-6*) ppm.

**${}^{31}\text{P}$  NMR (162.1 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = 219.5$  (s<sub>br</sub>, 1P, *PP-P*),  $-144.6$  (hept,  ${}^1J_{\text{P,F}} = 706.5 \text{ Hz}$ , 1P, *PF<sub>6</sub>*) ppm.

**${}^{29}\text{Si}\{^1\text{H}\}$  NMR (79.6 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = 0.9$  (d,  ${}^2J_{\text{Si-2,P}} = 17.8 \text{ Hz}$ , 1Si, *SiMe<sub>3</sub>-2*), 0.3 (d,  ${}^2J_{\text{Si-6,P}} = 19.5 \text{ Hz}$ , 1Si, *SiMe<sub>3</sub>-6*).

**${}^{19}\text{F}\{^1\text{H}\}$  NMR (376.9 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta = -72.8$  (d,  ${}^1J_{\text{P,F}} = 706.4 \text{ Hz}$ , 6F, *PF<sub>6</sub>*) ppm.

## 2,6-Bis(trimethylsilyl)-3,5-bis(*N*-ethyl-pyridinium-2-yl)-phosphinine hexafluorophosphate (19)



2 [PF<sub>6</sub>]<sup>-</sup>

**19**

C  
 ${}_{25}\text{H}_{37}\text{F}_{12}\text{N}_2\text{P}_3\text{Si}_2$   
 M: 742.66 g/mol

In a 20 mL Schlenk tube phosphinine **8** (143 mg, 0.36 mmol) was introduced and dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL) and cooled down to  $-40 \text{ }^\circ\text{C}$ . Then, a solution of  $[\text{Et}_3\text{O}][\text{PF}_6]$  (150 mg, 0.73 mmol, 2.03 equiv.) in MeCN (5 mL) was added dropwise to reaction mixture. The mixture was allowed to warm up to room temperature and stirred for 3 h. The completeness of the reaction was

controlled *via* NMR spectroscopy and all volatile compounds removed *in vacuo*. The crude product was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the supernatant filtered off. The purified solid was dried *in vacuo* and the bis-pyridinium salt **19** obtained as a colorless solid (246 mg, 0.33 mmol, 92%). Crystals suitable for scXRD were obtained from saturated solution in MeCN/CH<sub>2</sub>Cl<sub>2</sub> of 1:2 at -20 °C.

**<sup>1</sup>H NMR (700.23 MHz, CD<sub>3</sub>CN):** δ = 8.86 (dd, <sup>3</sup>J<sub>H-6a,H-5a</sub> = 6.3 Hz, <sup>4</sup>J<sub>H-6a,H-4a</sub> = 1.4 Hz, 2H, *H*-6a), 8.60 (ddd, <sup>3</sup>J<sub>H-4a,H-3a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-4a,H-5a</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-4a,H-6a</sub> = 1.4 Hz, 2H, *H*-4a), 8.17 (ddd, <sup>3</sup>J<sub>H-5a,H-4a</sub> = 7.8 Hz, <sup>3</sup>J<sub>H-5a,H-6a</sub> = 6.3 Hz, <sup>4</sup>J<sub>H-5a,H-3a</sub> = 1.4 Hz, 2H, *H*-5a), 7.91 (dd, <sup>3</sup>J<sub>H-3a,H-4a</sub> = 8.0 Hz, <sup>4</sup>J<sub>H-3a,H-4a</sub> = 1.6 Hz, 2H, *H*-3a), 7.46 (d, <sup>4</sup>J<sub>H-4,P</sub> = 3.4 Hz, 1H, *H*-4), 4.43 (dq, <sup>2</sup>J<sub>H-a',H-a''</sub> = 13.6 Hz, <sup>3</sup>J<sub>H-a',H-b</sub> = 7.3 Hz, 2H, *CH*-a'), 4.34 (dq, <sup>2</sup>J<sub>H-a'',H-a'</sub> = 14.1 Hz, <sup>3</sup>J<sub>H-a'',H-b</sub> = 7.3 Hz, 2H, *CH*-a''), 1.44 (t, <sup>3</sup>J<sub>H-b,H-a'/H-a''</sub> = 7.3 Hz, 6H, *CH*<sub>3</sub>-b), 0.1 (s, 18H, SiMe<sub>3</sub>) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.71 MHz, CD<sub>3</sub>CN):** δ = 172.5 (d, <sup>1</sup>J<sub>C-2,P</sub> = 96.1 Hz, 2C, C-2), 156.4 (2C, C-2a), 147.2 (2C, C-4a), 145.7 (2C, C-6a), 141.7 (d, <sup>2</sup>J<sub>C-3,P</sub> = 11.2 Hz, 1C, C-3), 131.7 (2C, C-3a), 129.8 (2C, C-5a), 129.2 (d, <sup>3</sup>J<sub>C-4,P</sub> = 20.8 Hz, 1C, C-4), 55.3 (2C, C-a), 16.3 (2C, C-b), 1.0 (d, <sup>3</sup>J<sub>C-SiMe<sub>3</sub>,2-P</sub> = 9.7 Hz, 6C, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

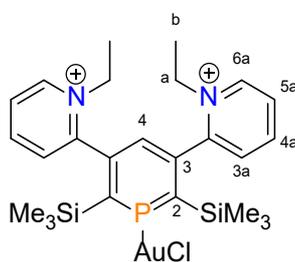
**<sup>31</sup>P NMR (162.14 MHz, CD<sub>3</sub>CN):** δ = 284.3 (s, 1P, PP-*P*), -144.7 (hept, <sup>1</sup>J<sub>P,F</sub> = 706.7 Hz, 2P, PF<sub>6</sub>) ppm.

**<sup>29</sup>Si{<sup>1</sup>H} NMR (79.57 MHz, CD<sub>3</sub>CN):** -0.5 (d, <sup>2</sup>J<sub>Si-6,P</sub> =, 2Si, SiMe<sub>3</sub>) ppm

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.88 MHz, CD<sub>3</sub>CN):** -72.9 (d, <sup>1</sup>J<sub>F,P</sub> = 706.7 Hz, 12F, PF<sub>6</sub>) ppm.

**HRMS-ESI:** *m/z* calculated for C<sub>25</sub>H<sub>37</sub>N<sub>2</sub>PSi<sub>2</sub><sup>2+</sup>: ½ ([M]<sup>2+</sup>): 226.1116. Found: 226.1149.

**2,6-Bis(trimethylsilyl)-3,5-bis(*N*-ethyl-pyridinium-2-yl)-phosphinine hexafluorophosphate gold(I) chloride complex (**21**)**



2 [PF<sub>6</sub>]<sup>-</sup>

**21**

C<sub>25</sub>H<sub>37</sub>F<sub>12</sub>AuClN<sub>2</sub>P<sub>3</sub>Si<sub>2</sub>  
M: 975.07 g/mol

Pyridinium salt **19** (25 mg, 34  $\mu\text{mol}$ ) was introduced in a 10 mL Schlenk tube and dissolved in MeCN (2 mL). To this solution AuCl·SMe<sub>2</sub> (9.9 mg, 34  $\mu\text{mol}$ , 1.0 equiv.) was added. The supernatant light-yellow solution was filter off from a fine grey precipitate, all volatile components were removed *in vacuo* and the product obtain as a light-yellow solid (31 mg, 32  $\mu\text{mol}$ , 92%). For NMR analysis the reaction was carried out directly in CD<sub>3</sub>CN (0.6 mL) following the same procedures. Colorless light sensitive crystals suitable for scXRD were obtain from saturated solution in MeCN/DCM (1:2) at -20 °C.

**<sup>1</sup>H NMR (399.7 MHz, CD<sub>3</sub>CN):**  $\delta$  = 8.87 (dd, <sup>3</sup>J<sub>H-6a,H-5a</sub> = 6.4 Hz, <sup>4</sup>J<sub>H-6a,H-4a</sub> = 1.4 Hz, 2H, H-6a), 8.61 (ddd, <sup>3</sup>J<sub>H-4a,H-3a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-4a,H-5a</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-4a,H-6a</sub> = 1.5 Hz, 2H, H-4a), 8.19 (ddd, <sup>3</sup>J<sub>H-5a,H-4a</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-5a,H-6a</sub> = 6.4 Hz, <sup>4</sup>J<sub>H-5a,H-3a</sub> = 1.7 Hz, 2H, H-5a), 8.01 (dd, <sup>3</sup>J<sub>H-3a,H-4a</sub> = 8.0 Hz, <sup>4</sup>J<sub>H-3a,H-5a</sub> = 1.6 Hz, 2H, H-3a), 4.49 (dq, <sup>2</sup>J<sub>H-a',H-a''</sub> = 14.6 Hz, <sup>3</sup>J<sub>H-a',H-b</sub> = 7.3 Hz, 1H, CH-a'), 4.30 (dq, <sup>2</sup>J<sub>H-a'',H-a'</sub> = 14.1 Hz, <sup>3</sup>J<sub>H-a'',H-b</sub> = 7.1 Hz, 1H, CH-a''), 1.42 (t, <sup>3</sup>J<sub>H-b,H-a'/H-a''</sub> = 7.3 Hz, 3H, CH<sub>3</sub>-b), 0.29 (18H, SiMe<sub>3</sub>) ppm.

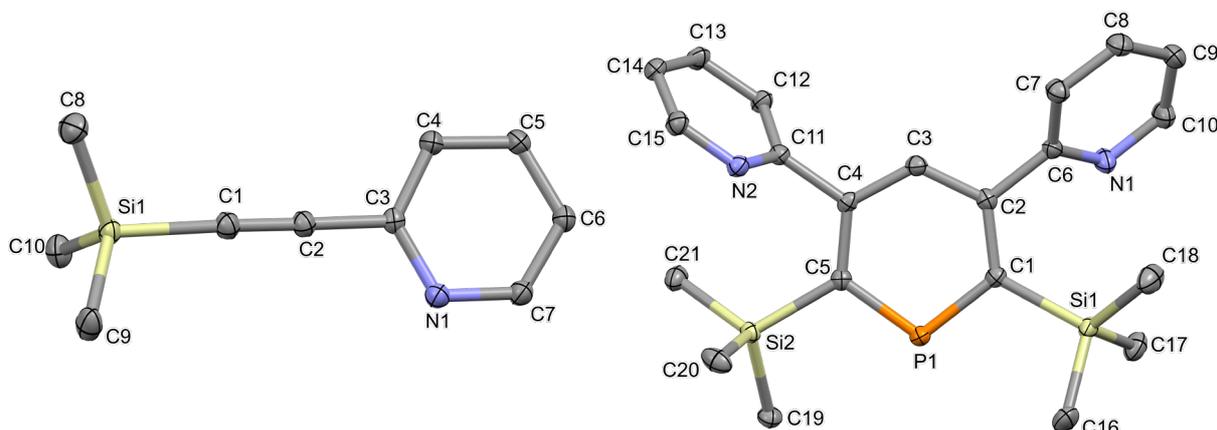
**<sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, CD<sub>3</sub>CN):**  $\delta$  = 162.1 (d, <sup>1</sup>J<sub>C-2,P</sub> = 25.0 Hz, 2C, C-2), 154.6 (d, <sup>2</sup>J<sub>C-3,P</sub> = 16.9 Hz, 2C, C-3), 153.2 (d, <sup>3</sup>J<sub>C-2a,P</sub> = 11.3 Hz, 2C, C-2a), 147.6 (2C, C-4a), 146.0 (2C, C-6a), 131.8 (1C, C-3a), 130.4 (2C, C-5a), 129.9 (d, <sup>2</sup>J<sub>C-3,P</sub> = 42.5 Hz, 1C, C-4), 55.5 (2C, CH<sub>2</sub>-a), 16.2 (2C, CH<sub>3</sub>-b), 2.3 (d, <sup>3</sup>J<sub>SiMe<sub>3</sub>-P</sub> = 5.2 Hz, 6C, Si(CH<sub>3</sub>)<sub>3</sub>-2) ppm.

**<sup>31</sup>P{<sup>1</sup>H} NMR (162.1 MHz, CD<sub>3</sub>CN):**  $\delta$  = 227.9 (s<sub>br</sub>, 1P, PP-P), -144.6 (hept, <sup>1</sup>J<sub>P,F</sub> = 706.5 Hz, 1P, PF<sub>6</sub>) ppm.

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.9 MHz, CD<sub>3</sub>CN):**  $\delta$  = - 72.8 (d, <sup>1</sup>J<sub>P,F</sub> = 706.4 Hz, 6F, PF<sub>6</sub>) ppm.

### 3. Crystallographic Data

Single crystal x-ray diffraction data was collected on a Bruker D8 Venture fitted with a Photon II CMOS Detector with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) from an  $I\mu S$  micro-source, performing  $\varphi$ - and  $\omega$ -scans. Data collection and processing was handled using the *Bruker APEX3* software package. Structures were solved within Olex2<sup>[17]</sup> by dual space iterative methods (SHELXT)<sup>[18]</sup> and all non-hydrogen atoms refined by full-matrix least-squares on all unique  $F^2$  values with anisotropic displacement parameters (SHELXL).<sup>[19]</sup> All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. Structures were checked with checkCIF.<sup>[20]</sup> Selected crystallographic data can be found below in **Table S2** to **Table S6**. The CCDC entries contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures)

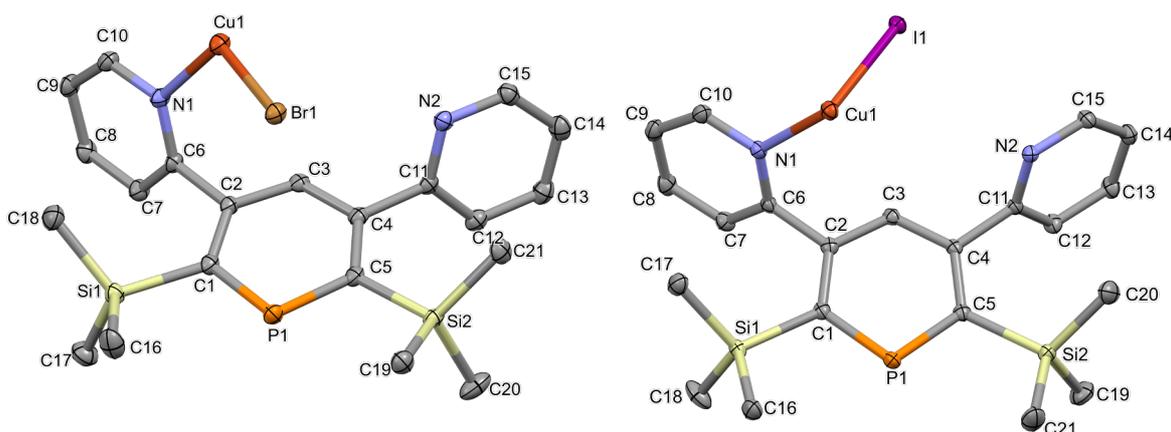


**Figure S5:** Solid state structures of acetylene **7** and phosphinine **8**.

**Table S2:** Structural details of acetylene **7** and phosphinine **8**.

	TMS-CC-Py	TMS-Py-PP
Compound number	<b>7</b>	<b>8</b>
Empirical formula	C <sub>10</sub> H <sub>13</sub> NSi	C <sub>21</sub> H <sub>27</sub> N <sub>2</sub> PSi <sub>2</sub>
Formula weight	175.30	394.59
Temperature [K]	100.00	100.0
Crystal system	tetragonal	monoclinic
Space group	I4 <sub>1</sub> /a	P2 <sub>1</sub>
a [Å]	14.0895(3)	9.6561(3)
b [Å]	14.0895(3)	11.9401(4)
c [Å]	21.3068(6)	9.8357(3)
$\alpha$ [°]	90	90
$\beta$ [°]	90	103.1930(10)
$\gamma$ [°]	90	90
Volume [Å <sup>3</sup> ]	4229.7(2)	1104.07(6)

Z	16	2
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.101	1.187
$\mu / \text{mm}$	0.171	0.240
F(000)	1504.0	420.0
Crystal size/ $\text{mm}^3$	0.431 × 0.376 × 0.222	0.214 × 0.115 × 0.033
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	5.782 to 66.33	4.254 to 61.114
Index ranges	-21 ≤ h ≤ 21, -21 ≤ k ≤ 18, -32 ≤ l ≤ 32	-13 ≤ h ≤ 13, -16 ≤ k ≤ 17, -14 ≤ l ≤ 13
Reflections collected	31858	36361
Independent reflections	4043 [ $R_{\text{int}} = 0.0231$ , $R_{\text{sigma}} = 0.0132$ ]	6709 [ $R_{\text{int}} = 0.0525$ , $R_{\text{sigma}} = 0.0408$ ]
Data/restraints/parameters	4043/0/112	6709/1/241
Goodness-of-fit on $F^2$	1.060	1.084
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0305$ , $wR_2 = 0.0837$	$R_1 = 0.0320$ , $wR_2 = 0.0652$
Final R indexes [all data]	$R_1 = 0.0330$ , $wR_2 = 0.0853$	$R_1 = 0.0468$ , $wR_2 = 0.0739$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.49/-0.24	0.24/-0.30
Diffractometer	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector
CCDC access code	2502839	2502835

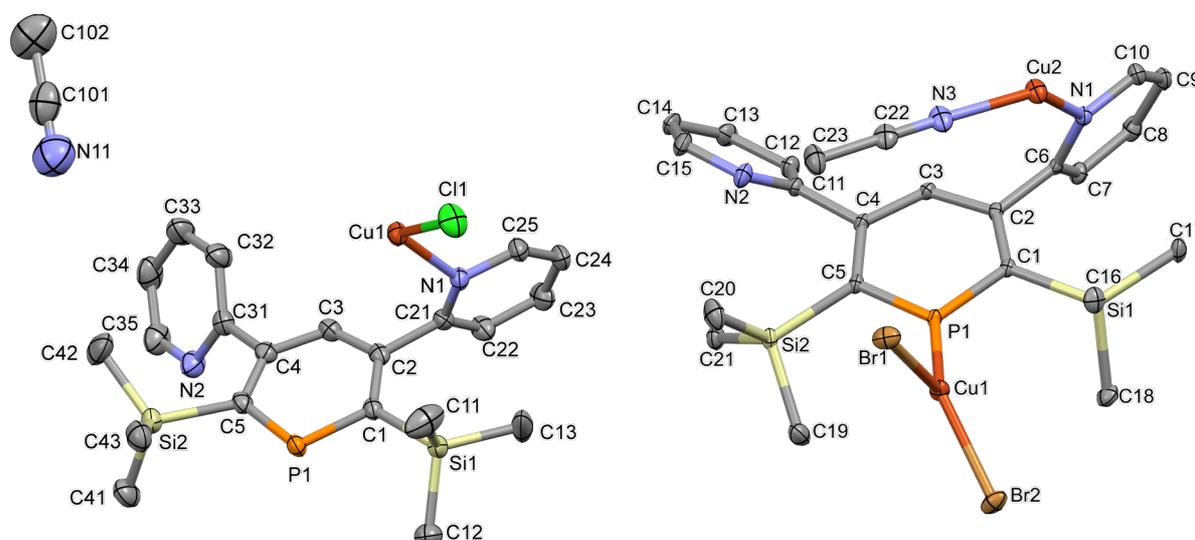


**Figure S6:** Solid state structures of the asymmetric unit of Cu(I)Br complex **10** and Cu(I) complex **11** of phosphinine **8**.

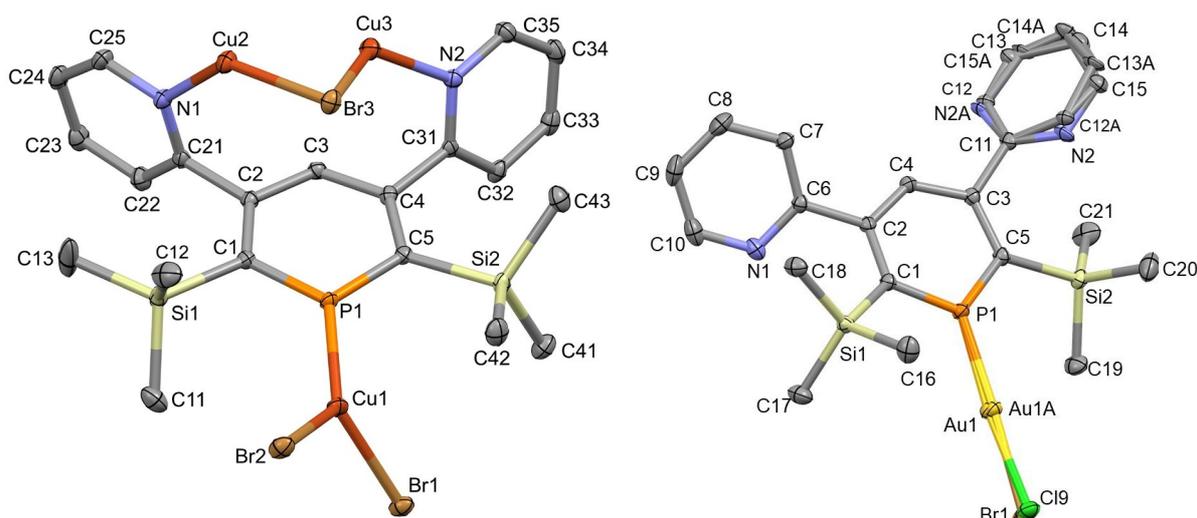
**Table S3:** Structural details of Copper(I) complexes **10**, **11** and coordination polymer **12**.

	$[\text{PP}_2(\text{CuBr})_2]$	$[\text{PP}_2(\text{CuI})_2]$	$[\text{PP}(\text{CuCl})_n]$
Compound number	<b>10</b>	<b>11</b>	<b>12</b>
Empirical formula	$\text{C}_{21}\text{H}_{27}\text{BrCuN}_2\text{PSi}_2$	$\text{C}_{42}\text{H}_{54}\text{Cu}_2\text{I}_2\text{N}_4\text{P}_2\text{S}_4$	$\text{C}_{23}\text{H}_{30}\text{ClCuN}_3\text{PSi}_2$
Formula weight	538.04	1170.07	534.64
Temperature [K]	100.0	100.0	150.00
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [ $\text{\AA}$ ]	9.9940(3)	10.2249(3)	11.9412(3)
b [ $\text{\AA}$ ]	18.2047(6)	18.1799(5)	20.8529(6)
c [ $\text{\AA}$ ]	13.0124(4)	13.0915(4)	10.5592(3)

$\alpha$ [°]	90	90	90
$\beta$ [°]	94.1464(12)	94.3915(11)	94.5610(10)
$\gamma$ [°]	90	90	90
Volume [Å <sup>3</sup> ]	2361.25(13)	2426.40(12)	2621.01(12)
Z	4	2	4
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.514	1.602	1.355
$\mu$ /mm <sup>-1</sup>	2.796	2.347	1.103
F(000)	1096.0	1168.0	1112.0
Crystal size/mm <sup>3</sup>	0.45 × 0.21 × 0.19	0.29 × 0.2 × 0.14	0.415 × 0.072 × 0.051
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	4.658 to 61.122	4.878 to 61.102	4.334 to 50.762
Index ranges	-14 ≤ h ≤ 14, -25 ≤ k ≤ 25, -18 ≤ l ≤ 18	-14 ≤ h ≤ 14, -25 ≤ k ≤ 23, -18 ≤ l ≤ 18	-14 ≤ h ≤ 13, -25 ≤ k ≤ 25, -12 ≤ l ≤ 12
Reflections collected	68374	85829	40713
Independent reflections	7202 [R <sub>int</sub> = 0.0445, R <sub>sigma</sub> = 0.0243]	7425 [R <sub>int</sub> = 0.0622, R <sub>sigma</sub> = 0.0272]	4801 [R <sub>int</sub> = 0.0442, R <sub>sigma</sub> = 0.0253]
Data/restraints/parameters	7202/0/259	7425/0/259	4801/0/287
Goodness-of-fit on F <sup>2</sup>	1.070	1.098	1.117
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0301, wR <sub>2</sub> = 0.0654	R <sub>1</sub> = 0.0244, wR <sub>2</sub> = 0.0537	R <sub>1</sub> = 0.0274, wR <sub>2</sub> = 0.0673
Final R indexes [all data]	R <sub>1</sub> = 0.0464, wR <sub>2</sub> = 0.0771	R <sub>1</sub> = 0.0327, wR <sub>2</sub> = 0.0570	R <sub>1</sub> = 0.0300, wR <sub>2</sub> = 0.0687
Largest diff. peak/hole / e Å <sup>-3</sup>	0.77/-0.75	0.88/-0.94	0.29/-0.30
Diffractometer	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector
CCDC access code	2502836	2502837	2502845



**Figure S7:** Solid state structures of the asymmetric units of Cu(I)Cl (**12**) and (Cu(I)Br)<sub>2</sub>·MeCN (**13**) coordination polymers of phosphinine **8**.

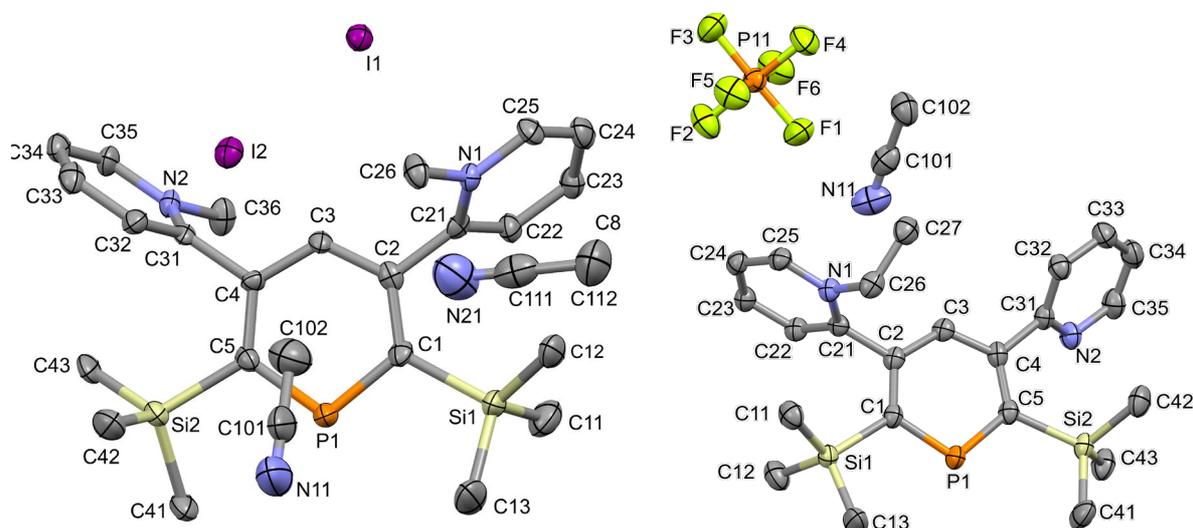


**Figure S8:** Solid state structures of the asymmetric unit of (Cu(I)Br)<sub>3</sub> coordination polymer **14** and Au(I) phosphinine complex (**16**) with mixed halogen counter anion.

**Table S4:** Structural details of coordination polymers **13** and **14**, and gold-complex **16**.

	[PP(CuBr) <sub>2</sub> MeCN] <sub>n</sub>	[PP(CuBr) <sub>3</sub> ] <sub>n</sub>	PP-AuCl/Br
Compound number	<b>13</b>	<b>14</b>	<b>16</b>
Empirical formula	C <sub>23</sub> H <sub>30</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>3</sub> PSi <sub>2</sub>	C <sub>21</sub> H <sub>27</sub> Br <sub>3</sub> Cu <sub>3</sub> N <sub>2</sub> PSi <sub>2</sub>	C <sub>21</sub> H <sub>27</sub> AuBr <sub>0.7</sub> Cl <sub>0.29</sub> N <sub>2</sub> PSi <sub>2</sub>
Formula weight	722.55	824.94	658.36
Temperature [K]	119.0	100.00	100.00
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P-1
a [Å]	12.2352(7)	13.5374(4)	9.6410(4)
b [Å]	18.7065(9)	10.5021(3)	11.0679(5)
c [Å]	13.3799(7)	19.5350(6)	12.7090(5)
α [°]	90	90	100.019(2)
β [°]	103.583(2)	90.2760(10)	107.6930(10)
γ [°]	90	90	106.5960(10)
Volume [Å <sup>3</sup> ]	2976.7(3)	2777.28(14)	1186.57(9)
Z	4	4	2
ρ <sub>calc</sub> /g cm <sup>-3</sup>	1.612	1.973	1.843
μ/mm <sup>-1</sup>	4.264	6.750	7.598
F(000)	1440.0	1608.0	637.0
Crystal size/mm <sup>3</sup>	0.62 × 0.51 × 0.28	0.196 × 0.194 × 0.162	0.15 × 0.123 × 0.106
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.156 to 61.104	4.404 to 59.162	4.992 to 59.172
Index ranges	-17 ≤ h ≤ 17, -26 ≤ k ≤ 26, -19 ≤ l ≤ 19	-18 ≤ h ≤ 18, -14 ≤ k ≤ 14, -27 ≤ l ≤ 27	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	91727	68630	43810

Independent reflections	9108 [ $R_{\text{int}} = 0.0520$ , $R_{\text{sigma}} = 0.0257$ ]	7792 [ $R_{\text{int}} = 0.0392$ , $R_{\text{sigma}} = 0.0243$ ]	6657 [ $R_{\text{int}} = 0.0400$ , $R_{\text{sigma}} = 0.0259$ ]
Data/restraints/parameters	9108/0/305	7792/0/295	6657/15/288
Goodness-of-fit on $F^2$	1.025	1.030	1.100
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0256$ , $wR_2 = 0.0619$	$R_1 = 0.0192$ , $wR_2 = 0.0427$	$R_1 = 0.0167$ , $wR_2 = 0.0387$
Final R indexes [all data]	$R_1 = 0.0313$ , $wR_2 = 0.0649$	$R_1 = 0.0241$ , $wR_2 = 0.0452$	$R_1 = 0.0184$ , $wR_2 = 0.0401$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.70/-0.91	0.45/-0.52	0.52/-0.91
Diffractometer	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector
CCDC access code	2502838	2502844	2502843

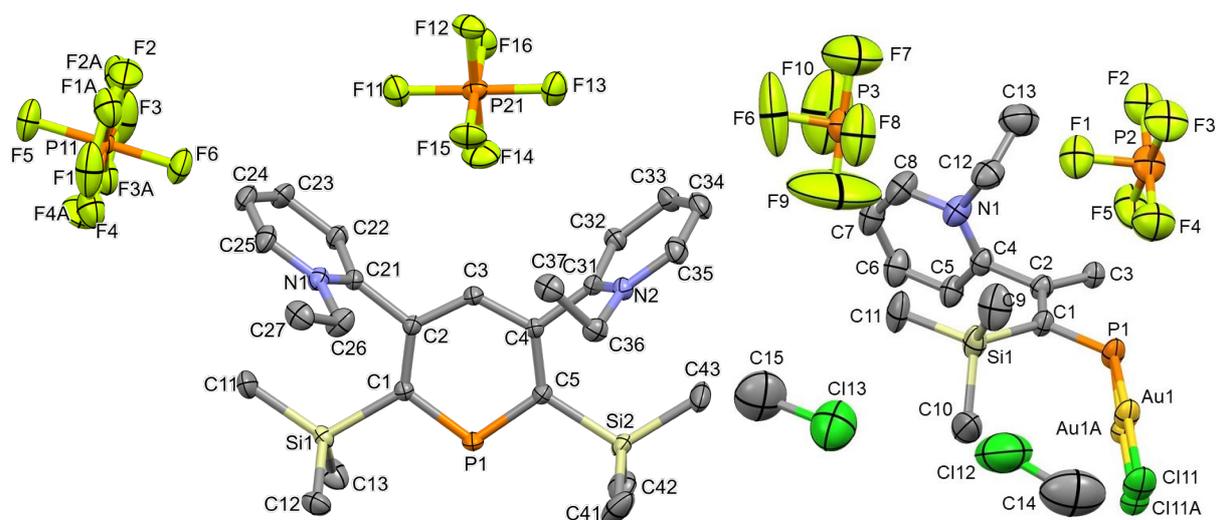


**Figure S9:** Solid state structures of the bis-methyl pyridinium salt TMS-PyrrMe<sub>2</sub>-PP-I<sub>2</sub> **17** and TMS-PyrrEtPy-PP-PF<sub>6</sub> salt **18**.

**Table S5:** Structural details of pyridinium salts **17** and **18**.

	TMS-PyrrMe <sub>2</sub> PP I <sub>2</sub>	TMS-PyrrEtPyPP [PF <sub>6</sub> ]
Compound number	<b>17</b>	<b>18</b>
Empirical formula	C <sub>27</sub> H <sub>39</sub> I <sub>2</sub> N <sub>4</sub> PSi <sub>2</sub>	C <sub>25</sub> H <sub>35</sub> F <sub>6</sub> N <sub>3</sub> P <sub>2</sub> Si <sub>2</sub>
Formula weight	760.57	609.68
Temperature [K]	100.00	150.00
Crystal system	monoclinic	triclinic
Space group	P2 <sub>1</sub> /c	P-1
a [Å]	16.3574(6)	6.5266(3)
b [Å]	12.6752(5)	12.3570(5)
c [Å]	16.8576(7)	19.5307(8)
α [°]	90	90.607(2)
β [°]	96.159(2)	95.550(2)
γ [°]	90	102.463(2)
Volume [Å <sup>3</sup> ]	3475.0(2)	1530.01(11)

Z	4	2
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.454	1.323
$\mu / \text{mm}^{-1}$	1.946	0.277
F(000)	1512.0	636.0
Crystal size/ $\text{mm}^3$	0.1 × 0.06 × 0.039	0.205 × 0.132 × 0.09
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	4.028 to 50.742	5.298 to 51.414
Index ranges	-19 ≤ h ≤ 19, -15 ≤ k ≤ 15, -19 ≤ l ≤ 20	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	50387	29371
Independent reflections	6379 [ $R_{\text{int}} = 0.0938$ , $R_{\text{sigma}} = 0.0502$ ]	5792 [ $R_{\text{int}} = 0.0416$ , $R_{\text{sigma}} = 0.0298$ ]
Data/restraints/parameters	6379/0/335	5792/0/351
Goodness-of-fit on $F^2$	1.166	1.051
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0574$ , $wR_2 = 0.0887$	$R_1 = 0.0454$ , $wR_2 = 0.0952$
Final R indexes [all data]	$R_1 = 0.0767$ , $wR_2 = 0.0959$	$R_1 = 0.0552$ , $wR_2 = 0.1017$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.28/-0.63	0.33/-0.30
Diffractometer	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector
CCDC access code	2502842	2502846



**Figure S10:** Solid state structures of the bis-ethyl pyridinium phosphinine salt (**19**) and asymmetric unit of its AuCl complex (**21**).

**Table S6:** Structural details of pyridinium salts **19** and its Au(I) complex **21**.

	TMS-PyrrEt <sub>2</sub> PP [PF <sub>6</sub> ] <sub>2</sub>	TMS-PyrrEt <sub>2</sub> PP-AuCl [PF <sub>6</sub> ] <sub>2</sub>
Compound number	<b>19</b>	<b>21</b>
Empirical formula	C <sub>25</sub> H <sub>37</sub> F <sub>12</sub> N <sub>2</sub> P <sub>3</sub> Si <sub>2</sub>	C <sub>27</sub> H <sub>37</sub> AuCl <sub>5</sub> F <sub>12</sub> N <sub>2</sub> P <sub>3</sub> Si <sub>2</sub>
Formula weight	742.65	1140.89
Temperature [K]	150.00	273.15
Crystal system	monoclinic	orthorhombic
Space group	P2 <sub>1</sub> /n	Pnma
a [Å]	13.0384(6)	9.1844(4)

b [Å]	9.1095(5)	13.2583(5)
c [Å]	28.3352(15)	34.4803(14)
$\alpha$ [°]	90	90
$\beta$ [°]	102.279(2)	90
$\gamma$ [°]	90	90
Volume [Å <sup>3</sup> ]	3288.5(3)	4198.7(3)
Z	4	4
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.500	1.805
$\mu$ /mm <sup>-1</sup>	0.343	4.071
F(000)	1528.0	2232.0
Crystal size/mm <sup>3</sup>	0.4 × 0.24 × 0.11	0.259 × 0.245 × 0.142
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	3.792 to 61.14	4.59 to 52.816
Index ranges	-16 ≤ h ≤ 18, -13 ≤ k ≤ 13, -40 ≤ l ≤ 40	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -43 ≤ l ≤ 42
Reflections collected	104946	74106
Independent reflections	10050 [R <sub>int</sub> = 0.0330, R <sub>sigma</sub> = 0.0157]	4500 [R <sub>int</sub> = 0.0352, R <sub>sigma</sub> = 0.0138]
Data/restraints/parameters	10050/4/424	4500/22/233
Goodness-of-fit on F <sup>2</sup>	1.065	1.066
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0380, wR <sub>2</sub> = 0.0933	R <sub>1</sub> = 0.0488, wR <sub>2</sub> = 0.1295
Final R indexes [all data]	R <sub>1</sub> = 0.0424, wR <sub>2</sub> = 0.0962	R <sub>1</sub> = 0.0513, wR <sub>2</sub> = 0.1315
Largest diff. peak/hole / e Å <sup>-3</sup>	0.67/-0.35	1.64/-2.37
Diffractometer	Bruker D8 Venture, Photon II CMOS Detector	Bruker D8 Venture, Photon II CMOS Detector
CCDC access code	2502840	2502841

**Table S7:** Bond length (Å) for acetylene 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C1	1.8493(8)	C1	C2	1.2127(10)
Si1	C8	1.8604(9)	C2	C3	1.4417(9)
Si1	C9	1.8629(8)	C3	C4	1.3978(10)
Si1	C10	1.8625(9)	C4	C5	1.3896(10)
N1	C3	1.3502(9)	C5	C6	1.3869(10)
N1	C7	1.3394(9)	C6	C7	1.3914(10)

**Table S8:** Bond angles (°) for acetylene 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Si1	C8	108.44(4)	C1	C2	C3	177.95(8)
C1	Si1	C9	107.54(4)	N1	C3	C2	116.76(6)
C1	Si1	C10	106.96(4)	N1	C3	C4	123.21(6)
C8	Si1	C9	111.57(4)	C4	C3	C2	120.02(6)
C8	Si1	C10	111.89(4)	C5	C4	C3	118.67(6)
C10	Si1	C9	110.22(4)	C6	C5	C4	118.83(7)
C7	N1	C3	116.72(6)	C5	C6	C7	118.37(6)
C2	C1	Si1	176.41(7)	N1	C7	C6	124.20(7)

**Table S9:** Bond length (Å) for TMS-Py-PP (**8**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.735(2)	C1	C2	1.407(3)
P1	C5	1.743(2)	C2	C3	1.401(3)
Si1	C1	1.906(2)	C2	C6	1.495(3)
Si1	C16	1.878(3)	C3	C4	1.396(3)
Si1	C17	1.867(3)	C4	C5	1.407(3)
Si1	C18	1.869(2)	C4	C11	1.502(3)
Si2	C5	1.898(2)	C6	C7	1.394(3)
Si2	C19	1.874(2)	C7	C8	1.389(3)
Si2	C20	1.857(3)	C8	C9	1.385(4)
Si2	C21	1.872(2)	C9	C10	1.387(4)
N1	C6	1.346(3)	C11	C12	1.392(3)
N1	C10	1.338(3)	C12	C13	1.391(3)
N2	C11	1.341(3)	C13	C14	1.382(3)
N2	C15	1.343(3)	C14	C15	1.383(3)

**Table S10:** Bond angles (°) for TMS-Py-PP (**8**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C5	106.03(10)	C4	C3	C2	125.5(2)
C16	Si1	C1	106.47(11)	C3	C4	C5	123.39(19)
C17	Si1	C1	111.90(11)	C3	C4	C11	116.02(19)
C17	Si1	C16	108.38(13)	C5	C4	C11	120.59(18)
C17	Si1	C18	112.85(12)	P1	C5	Si2	113.71(11)
C18	Si1	C1	111.66(10)	C4	C5	P1	120.60(15)
C18	Si1	C16	105.08(14)	C4	C5	Si2	125.59(15)
C19	Si2	C5	107.54(10)	N1	C6	C2	116.17(19)
C20	Si2	C5	109.04(11)	N1	C6	C7	122.4(2)
C20	Si2	C19	109.78(12)	C7	C6	C2	121.5(2)
C20	Si2	C21	110.38(12)	C8	C7	C6	119.1(2)
C21	Si2	C5	113.02(11)	C9	C8	C7	119.2(2)
C21	Si2	C19	107.00(11)	C8	C9	C10	117.6(2)
C10	N1	C6	117.3(2)	N1	C10	C9	124.5(2)
C11	N2	C15	116.8(2)	N2	C11	C4	116.09(19)
P1	C1	Si1	113.62(12)	N2	C11	C12	123.00(19)
C2	C1	P1	121.24(16)	C12	C11	C4	120.91(19)
C2	C1	Si1	125.11(16)	C13	C12	C11	119.0(2)
C1	C2	C6	121.35(19)	C14	C13	C12	118.6(2)
C3	C2	C1	122.8(2)	C13	C14	C15	118.4(2)
C3	C2	C6	115.89(19)	N2	C15	C14	124.3(2)

**Table S11:** Bond length (Å) for phosphinine copper(I) bromide complex [(TMS-Py-PP)CuBr]<sub>2</sub> **10**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu1	2.4922(3)	N2	C11	1.355(3)

Br1	Cu1 <sup>1</sup>	2.5211(4)	N2	C15	1.346(3)
Cu1	Cu1 <sup>1</sup>	2.8778(5)	C1	C2	1.400(3)
Cu1	N1	2.0942(17)	C2	C3	1.398(3)
Cu1	N2 <sup>1</sup>	2.1124(18)	C2	C6	1.496(3)
P1	C1	1.744(2)	C3	C4	1.399(3)
P1	C5	1.742(2)	C4	C5	1.407(3)
Si1	C1	1.903(2)	C4	C11	1.492(3)
Si1	C16	1.868(2)	C6	C7	1.395(3)
Si1	C17	1.872(2)	C7	C8	1.388(3)
Si1	C18	1.871(2)	C8	C9	1.385(3)
Si2	C5	1.902(2)	C9	C10	1.389(3)
Si2	C19	1.872(2)	C11	C12	1.395(3)
Si2	C20	1.868(2)	C12	C13	1.391(3)
Si2	C21	1.870(2)	C13	C14	1.389(3)
N1	C6	1.356(2)	C14	C15	1.386(3)
N1	C10	1.346(2)			

**Table S12:** Bond angles (°) for phosphinine copper(I) bromide complex  $[(\text{TMS-Py-PP})\text{CuBr}]_2$  **10**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu1	Br1	Cu1 <sup>1</sup>	70.062(11)	C15	N2	C11	117.11(18)
Br1	Cu1	Br1 <sup>1</sup>	109.938(11)	P1	C1	Si1	114.53(11)
Br1 <sup>1</sup>	Cu1	Cu1 <sup>1</sup>	54.498(10)	C2	C1	P1	120.75(15)
Br1	Cu1	Cu1 <sup>1</sup>	55.440(10)	C2	C1	Si1	124.61(14)
N1	Cu1	Br1	118.48(5)	C1	C2	C6	120.00(17)
N1	Cu1	Br1 <sup>1</sup>	101.23(5)	C3	C2	C1	124.26(17)
N1	Cu1	Cu1 <sup>1</sup>	125.70(5)	C3	C2	C6	115.73(17)
N1	Cu1	N2 <sup>1</sup>	105.25(7)	C2	C3	C4	124.44(18)
N2 <sup>1</sup>	Cu1	Br1	102.89(5)	C3	C4	C5	123.77(19)
N2 <sup>1</sup>	Cu1	Br1 <sup>1</sup>	119.92(5)	C3	C4	C11	116.15(17)
N2 <sup>1</sup>	Cu1	Cu1 <sup>1</sup>	129.06(5)	C5	C4	C11	120.08(17)
C5	P1	C1	105.77(10)	P1	C5	Si2	114.65(11)
C16	Si1	C1	107.76(10)	C4	C5	P1	120.96(15)
C16	Si1	C17	108.75(12)	C4	C5	Si2	124.23(15)
C16	Si1	C18	106.05(12)	N1	C6	C2	117.53(16)
C17	Si1	C1	110.65(10)	N1	C6	C7	122.29(17)
C18	Si1	C1	111.98(10)	C7	C6	C2	120.18(17)
C18	Si1	C17	111.44(11)	C8	C7	C6	119.57(19)
C19	Si2	C5	108.67(9)	C9	C8	C7	118.64(18)
C20	Si2	C5	110.55(10)	C8	C9	C10	118.36(18)
C20	Si2	C19	108.16(11)	N1	C10	C9	124.20(19)
C20	Si2	C21	110.74(12)	N2	C11	C4	117.18(17)
C21	Si2	C5	112.07(9)	N2	C11	C12	122.37(19)
C21	Si2	C19	106.47(10)	C12	C11	C4	120.45(18)
C6	N1	Cu1	125.98(13)	C13	C12	C11	119.4(2)
C10	N1	Cu1	116.69(13)	C14	C13	C12	118.4(2)
C10	N1	C6	116.87(17)	C15	C14	C13	118.6(2)
C11	N2	Cu1 <sup>1</sup>	124.79(14)	N2	C15	C14	123.9(2)

C15 N2 Cu1<sup>1</sup> 117.88(14)<sup>1</sup>2-X,-Y,1-Z**Table S13:** Bond length (Å) for phosphinine copper(I) iodide complex  $[(\text{TMS-Py-PP})\text{CuI}]_2$  **11**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	Cu1	2.6385(2)	N2	C11	1.352(2)
I1	Cu1 <sup>1</sup>	2.6699(2)	N2	C15	1.348(2)
Cu1	Cu1 <sup>1</sup>	2.7710(4)	C1	C2	1.404(2)
Cu1	N1	2.1445(14)	C2	C3	1.395(2)
Cu1	N2 <sup>1</sup>	2.1190(14)	C2	C6	1.498(2)
P1	C1	1.7436(16)	C3	C4	1.397(2)
P1	C5	1.7445(16)	C4	C5	1.403(2)
Si1	C1	1.9047(17)	C4	C11	1.496(2)
Si1	C16	1.8723(18)	C6	C7	1.393(2)
Si1	C17	1.8738(18)	C7	C8	1.388(2)
Si1	C18	1.8636(19)	C8	C9	1.385(3)
Si2	C5	1.9048(16)	C9	C10	1.387(2)
Si2	C19	1.870(2)	C11	C12	1.395(2)
Si2	C20	1.8720(19)	C12	C13	1.387(2)
Si2	C21	1.870(2)	C13	C14	1.387(2)
N1	C6	1.353(2)	C14	C15	1.388(2)
N1	C10	1.350(2)			

<sup>1</sup>1-X,-Y,-Z**Table S14:** Bond angles (°) for phosphinine copper(I) iodide complex  $[(\text{TMS-Py-PP})\text{CuI}]_2$  **11**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu1	I1	Cu1 <sup>1</sup>	62.930(8)	C15	N2	C11	117.14(14)
I1	Cu1	I1 <sup>1</sup>	117.072(8)	P1	C1	Si1	114.64(9)
I1	Cu1	Cu1 <sup>1</sup>	59.089(8)	C2	C1	P1	120.77(12)
I1 <sup>1</sup>	Cu1	Cu1 <sup>1</sup>	57.983(8)	C2	C1	Si1	124.38(12)
N1	Cu1	I1	101.56(4)	C1	C2	C6	120.31(14)
N1	Cu1	I1 <sup>1</sup>	118.38(4)	C3	C2	C1	124.07(15)
N1	Cu1	Cu1 <sup>1</sup>	130.46(4)	C3	C2	C6	115.62(14)
N2 <sup>1</sup>	Cu1	I1 <sup>1</sup>	100.02(4)	C2	C3	C4	124.59(15)
N2 <sup>1</sup>	Cu1	I1	115.54(4)	C3	C4	C5	124.00(14)
N2 <sup>1</sup>	Cu1	Cu1 <sup>1</sup>	125.32(4)	C3	C4	C11	115.99(14)
N2 <sup>1</sup>	Cu1	N1	104.22(5)	C5	C4	C11	120.00(14)
C1	P1	C5	105.77(8)	P1	C5	Si2	114.92(9)
C16	Si1	C1	109.13(8)	C4	C5	P1	120.76(12)
C16	Si1	C17	105.96(8)	C4	C5	Si2	124.16(12)
C17	Si1	C1	112.31(8)	N1	C6	C2	117.10(14)
C18	Si1	C1	110.47(8)	N1	C6	C7	122.41(15)
C18	Si1	C16	108.06(9)	C7	C6	C2	120.49(15)
C18	Si1	C17	110.72(10)	C8	C7	C6	119.58(16)
C19	Si2	C5	110.72(8)	C9	C8	C7	118.33(16)
C19	Si2	C20	110.81(10)	C8	C9	C10	118.88(16)

C19	Si2	C21	108.97(10)	N1	C10	C9	123.60(16)
C20	Si2	C5	112.13(8)	N2	C11	C4	117.95(13)
C21	Si2	C5	107.60(8)	N2	C11	C12	122.30(14)
C21	Si2	C20	106.42(10)	C12	C11	C4	119.75(14)
C6	N1	Cu1	125.32(11)	C13	C12	C11	119.51(15)
C10	N1	Cu1	117.34(11)	C12	C13	C14	118.67(15)
C10	N1	C6	117.04(14)	C13	C14	C15	118.43(16)
C11	N2	Cu1 <sup>1</sup>	126.88(11)	N2	C15	C14	123.88(16)
C15	N2	Cu1 <sup>1</sup>	115.43(11)				

<sup>1</sup>1-X,-Y,-Z

**Table S15:** Bond length (Å) for phosphinine copper(I) chloride coordination polymer [(TMS-Py-PP)CuCl]<sub>n</sub> **12**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.2266(6)	C1	C2	1.404(3)
Cu1	P1 <sup>1</sup>	2.1685(5)	C2	C3	1.392(3)
Cu1	N1	2.0371(16)	C2	C21	1.503(3)
P1	C1	1.7396(18)	C3	C4	1.399(3)
P1	C5	1.730(2)	C4	C5	1.411(3)
Si1	C1	1.907(2)	C4	C31	1.496(3)
Si1	C11	1.855(3)	C21	C22	1.385(3)
Si1	C12	1.855(2)	C22	C23	1.387(3)
Si1	C13	1.859(3)	C23	C24	1.373(3)
Si2	C5	1.9143(19)	C24	C25	1.377(3)
Si2	C41	1.856(2)	C31	C32	1.385(3)
Si2	C42	1.868(2)	C32	C33	1.380(3)
Si2	C43	1.874(2)	C33	C34	1.375(4)
N1	C21	1.347(2)	C34	C35	1.372(4)
N1	C25	1.355(2)	N11	C101	1.137(4)
N2	C31	1.340(3)	C101	C102	1.449(5)
N2	C35	1.341(3)			

<sup>1</sup>+X,1/2-Y,-1/2+Z

**Table S16:** Bond angles (°) for phosphinine copper(I) chloride coordination polymer [(TMS-Py-PP)CuCl]<sub>n</sub> **12**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1 <sup>1</sup>	Cu1	Cl1	125.56(2)	C1	C2	C21	120.80(17)
N1	Cu1	Cl1	105.85(5)	C3	C2	C1	124.10(17)
N1	Cu1	P1 <sup>1</sup>	125.97(5)	C3	C2	C21	115.02(17)
C1	P1	Cu1 <sup>2</sup>	127.24(7)	C2	C3	C4	125.83(18)
C5	P1	Cu1 <sup>2</sup>	124.08(7)	C3	C4	C5	123.41(18)
C5	P1	C1	108.64(9)	C3	C4	C31	115.85(17)
C11	Si1	C1	109.23(10)	C5	C4	C31	120.67(17)
C11	Si1	C12	109.28(13)	P1	C5	Si2	116.84(11)

C11	Si1	C13	109.80(17)	C4	C5	P1	118.77(14)
C12	Si1	C1	107.14(10)	C4	C5	Si2	124.06(15)
C12	Si1	C13	107.78(12)	N1	C21	C2	117.48(16)
C13	Si1	C1	113.50(12)	N1	C21	C22	122.10(17)
C41	Si2	C5	110.78(10)	C22	C21	C2	120.39(17)
C41	Si2	C42	111.66(13)	C21	C22	C23	119.4(2)
C41	Si2	C43	109.52(11)	C24	C23	C22	118.82(19)
C42	Si2	C5	111.57(10)	C23	C24	C25	119.04(19)
C42	Si2	C43	105.46(12)	N1	C25	C24	123.04(19)
C43	Si2	C5	107.63(10)	N2	C31	C4	115.29(18)
C21	N1	Cu1	126.75(12)	N2	C31	C32	122.79(19)
C21	N1	C25	117.47(16)	C32	C31	C4	121.87(18)
C25	N1	Cu1	112.84(13)	C33	C32	C31	119.1(2)
C31	N2	C35	116.91(19)	C34	C33	C32	118.6(2)
P1	C1	Si1	114.37(11)	C35	C34	C33	118.9(2)
C2	C1	P1	118.54(14)	N2	C35	C34	123.8(2)
C2	C1	Si1	127.04(14)	N11	C101	C102	179.2(4)

<sup>1</sup>+X,1/2-Y,-1/2+Z; <sup>2</sup>+X,1/2-Y,1/2+Z

**Table S17:** Bond length (Å) for phosphinine copper(I) bromide coordination polymer [(TMS-Py-PP)(CuBr)<sub>2</sub>(MeCN)]<sub>n</sub> **13**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu1	2.3902(3)	N1	C10	1.347(2)
Br1	Cu2 <sup>1</sup>	2.6868(3)	N2	C11	1.341(2)
Br2	Cu1	2.3652(3)	N2	C15	1.346(2)
Br2	Cu2 <sup>1</sup>	2.4953(3)	N3	C22	1.139(2)
Cu1	Cu2 <sup>1</sup>	2.8255(3)	C1	C2	1.402(2)
Cu1	P1	2.1766(4)	C2	C3	1.399(2)
Cu2	N1	2.0113(13)	C2	C6	1.496(2)
Cu2	N3	1.9350(16)	C3	C4	1.395(2)
P1	C1	1.7335(15)	C4	C5	1.410(2)
P1	C5	1.7303(15)	C4	C11	1.491(2)
Si1	C1	1.9111(15)	C6	C7	1.396(2)
Si1	C16	1.8692(17)	C7	C8	1.386(2)
Si1	C17	1.8677(17)	C8	C9	1.388(3)
Si1	C18	1.8657(17)	C9	C10	1.384(2)
Si2	C5	1.9130(16)	C11	C12	1.397(2)
Si2	C19	1.8760(19)	C12	C13	1.387(2)
Si2	C20	1.8649(19)	C13	C14	1.381(3)
Si2	C21	1.8732(17)	C14	C15	1.378(3)
N1	C6	1.346(2)	C22	C23	1.457(3)

<sup>1</sup>-1/2+X,1/2-Y,-1/2+Z

**Table S18:** Bond angles (°) for phosphinine copper(I) bromide coordination polymer [(TMS-Py-PP)(CuBr)<sub>2</sub>(MeCN)]<sub>n</sub> **13**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu1	Br1	Cu2 <sup>1</sup>	67.338(8)	C6	N1	Cu2	122.06(10)
Cu1	Br2	Cu2 <sup>1</sup>	71.030(9)	C6	N1	C10	117.77(14)
Br1	Cu1	Cu2 <sup>1</sup>	61.344(8)	C10	N1	Cu2	119.32(11)
Br2	Cu1	Br1	111.993(10)	C11	N2	C15	116.90(16)
Br2	Cu1	Cu2 <sup>1</sup>	56.633(8)	C22	N3	Cu2	178.22(18)
P1	Cu1	Br1	111.608(15)	P1	C1	Si1	112.97(8)
P1	Cu1	Br2	136.092(15)	C2	C1	P1	118.53(11)
P1	Cu1	Cu2 <sup>1</sup>	159.797(14)	C2	C1	Si1	128.40(11)
Br1 <sup>2</sup>	Cu2	Cu1 <sup>2</sup>	51.319(7)	C1	C2	C6	122.35(13)
Br2 <sup>2</sup>	Cu2	Br1 <sup>2</sup>	98.992(9)	C3	C2	C1	123.73(14)
Br2 <sup>2</sup>	Cu2	Cu1 <sup>2</sup>	52.337(7)	C3	C2	C6	113.89(13)
N1	Cu2	Br1 <sup>2</sup>	97.54(4)	C4	C3	C2	125.93(14)
N1	Cu2	Br2 <sup>2</sup>	112.13(4)	C3	C4	C5	124.05(14)
N1	Cu2	Cu1 <sup>2</sup>	130.48(4)	C3	C4	C11	115.75(14)
N3	Cu2	Br1 <sup>2</sup>	105.51(5)	C5	C4	C11	120.19(14)
N3	Cu2	Br2 <sup>2</sup>	110.29(5)	P1	C5	Si2	117.13(8)
N3	Cu2	Cu1 <sup>2</sup>	100.30(5)	C4	C5	P1	118.10(11)
N3	Cu2	N1	127.14(6)	C4	C5	Si2	124.14(11)
C1	P1	Cu1	122.39(5)	N1	C6	C2	117.11(13)
C5	P1	Cu1	125.43(5)	N1	C6	C7	122.29(14)
C5	P1	C1	109.42(7)	C7	C6	C2	120.46(14)
C16	Si1	C1	109.31(7)	C8	C7	C6	119.03(15)
C17	Si1	C1	115.03(7)	C7	C8	C9	118.94(15)
C17	Si1	C16	107.51(8)	C10	C9	C8	118.59(15)
C18	Si1	C1	106.29(7)	N1	C10	C9	123.30(16)
C18	Si1	C16	110.40(8)	N2	C11	C4	115.75(14)
C18	Si1	C17	108.28(8)	N2	C11	C12	123.25(15)
C19	Si2	C5	106.28(7)	C12	C11	C4	121.00(14)
C20	Si2	C5	114.52(8)	C13	C12	C11	118.47(16)
C20	Si2	C19	107.81(9)	C14	C13	C12	118.70(17)
C20	Si2	C21	111.95(9)	C15	C14	C13	119.01(16)
C21	Si2	C5	110.60(7)	N2	C15	C14	123.63(17)
C21	Si2	C19	105.02(8)	N3	C22	C23	179.6(2)

<sup>1</sup>-1/2+X, 1/2-Y, -1/2+Z; <sup>2</sup>1/2+X, 1/2-Y, 1/2+Z

**Table S19:** Bond length (Å) for phosphinine copper(I) bromide coordination polymer [(TMS-Py-PP)(CuBr)<sub>3</sub>]<sub>n</sub> **14**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu1	2.3862(3)	Si2	C43	1.8685(19)
Br1	Cu2 <sup>1</sup>	2.4568(3)	N1	C21	1.349(2)
Br2	Cu1	2.3882(3)	N1	C25	1.349(2)
Br2	Cu3 <sup>1</sup>	2.4144(3)	N2	C31	1.349(2)
Br3	Cu2	2.3778(3)	N2	C35	1.351(2)
Br3	Cu3	2.3543(3)	C1	C2	1.402(2)
Cu1	P1	2.1843(5)	C2	C3	1.400(2)

Cu2	Cu3	2.6893(3)	C2	C21	1.496(2)
Cu2	N1	1.9956(14)	C3	C4	1.399(2)
Cu3	N2	2.0108(14)	C4	C5	1.403(2)
P1	C1	1.7383(17)	C4	C31	1.496(2)
P1	C5	1.7300(16)	C21	C22	1.388(2)
Si1	C1	1.9072(17)	C22	C23	1.389(2)
Si1	C11	1.870(2)	C23	C24	1.381(3)
Si1	C12	1.867(2)	C24	C25	1.387(3)
Si1	C13	1.862(2)	C31	C32	1.392(2)
Si2	C5	1.9137(16)	C32	C33	1.391(2)
Si2	C41	1.8658(18)	C33	C34	1.384(3)
Si2	C42	1.8668(18)	C34	C35	1.382(3)

<sup>1</sup>+X,3/2-Y,-1/2+Z

**Table S20:** Bond angles (°) for phosphinine copper(I) bromide coordination polymer  $[[(\text{TMS-Py-PP})(\text{CuBr})_3]_n$  **14**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu1	Br1	Cu2 <sup>1</sup>	88.979(9)	C21	N1	Cu2	122.95(11)
Cu1	Br2	Cu3 <sup>1</sup>	116.635(10)	C25	N1	Cu2	118.90(12)
Cu3	Br3	Cu2	69.262(9)	C25	N1	C21	117.93(15)
Br1	Cu1	Br2	111.258(10)	C31	N2	Cu3	117.22(11)
P1	Cu1	Br1	118.061(15)	C31	N2	C35	118.12(15)
P1	Cu1	Br2	130.375(15)	C35	N2	Cu3	124.24(12)
Br1 <sup>2</sup>	Cu2	Cu3	119.203(10)	P1	C1	Si1	114.50(9)
Br3	Cu2	Br1 <sup>2</sup>	112.416(10)	C2	C1	P1	118.90(12)
Br3	Cu2	Cu3	54.958(8)	C2	C1	Si1	126.39(12)
N1	Cu2	Br1 <sup>2</sup>	107.99(4)	C1	C2	C21	122.03(14)
N1	Cu2	Br3	138.60(4)	C3	C2	C1	123.84(15)
N1	Cu2	Cu3	111.10(4)	C3	C2	C21	114.04(14)
Br2 <sup>2</sup>	Cu3	Cu2	78.607(9)	C4	C3	C2	125.35(15)
Br3	Cu3	Br2 <sup>2</sup>	126.086(11)	C3	C4	C5	124.53(15)
Br3	Cu3	Cu2	55.780(8)	C3	C4	C31	113.50(14)
N2	Cu3	Br2 <sup>2</sup>	103.46(4)	C5	C4	C31	121.77(14)
N2	Cu3	Br3	130.45(4)	P1	C5	Si2	117.53(9)
N2	Cu3	Cu2	148.63(4)	C4	C5	P1	118.42(12)
C1	P1	Cu1	125.52(6)	C4	C5	Si2	123.80(12)
C5	P1	Cu1	124.37(6)	N1	C21	C2	115.64(14)
C5	P1	C1	108.93(8)	N1	C21	C22	122.07(15)
C11	Si1	C1	107.68(8)	C22	C21	C2	122.24(15)
C12	Si1	C1	106.42(9)	C21	C22	C23	119.44(17)
C12	Si1	C11	112.85(9)	C24	C23	C22	118.72(17)
C13	Si1	C1	115.31(9)	C23	C24	C25	118.87(16)
C13	Si1	C11	106.76(12)	N1	C25	C24	122.94(17)
C13	Si1	C12	107.99(12)	N2	C31	C4	114.45(14)
C41	Si2	C5	109.55(8)	N2	C31	C32	122.22(15)
C41	Si2	C42	109.65(9)	C32	C31	C4	123.25(15)
C41	Si2	C43	104.85(9)	C33	C32	C31	118.84(16)
C42	Si2	C5	109.55(8)	C34	C33	C32	119.11(16)
C42	Si2	C43	113.21(9)	C35	C34	C33	118.88(16)

C43	Si2	C5	109.90(8)	N2	C35	C34	122.78(17)
				<sup>1</sup> +X, <sub>3/2</sub> -Y,-1/2+Z; <sup>2</sup> +X, <sub>3/2</sub> -Y,1/2+Z			

**Table S21:** Bond lengths (Å) for gold (I) phosphinine complex TMS-Py-PP-AuClBr **16**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.2270(15)	C6	C7	1.387(3)
Au1	Br1	2.3741(19)	C4	C11	1.494(2)
P1	C1	1.7199(19)	C4	C11A	1.494(2)
P1	C5	1.7213(19)	C12	C13	1.375(14)
P1	Au1A	2.200(4)	C12	C11	1.397(11)
Si1	C1	1.9136(19)	C13	C14	1.383(12)
Si1	C16	1.869(2)	C7	C8	1.389(3)
Si1	C18	1.867(2)	N2	C11	1.327(6)
Si1	C17	1.856(2)	N2	C15	1.333(9)
Si2	C5	1.9116(19)	C8	C9	1.384(3)
Si2	C19	1.864(2)	C14	C15	1.377(11)
Si2	C20	1.863(2)	C9	C10	1.381(4)
Si2	C21	1.866(2)	C19	Au1A	2.355(9)
C1	C2	1.415(3)	C12A	C13A	1.372(10)
C3	C2	1.399(2)	C12A	C11A	1.425(8)
C3	C4	1.398(2)	C13A	C14A	1.385(12)
N1	C6	1.349(2)	N2A	C11A	1.337(10)
N1	C10	1.342(3)	N2A	C15A	1.340(14)
C5	C4	1.406(3)	C14A	C15A	1.390(13)
C2	C6	1.488(2)			

**Table S22:** Bond angles (Å) for gold (I) phosphinine complex TMS-Py-PP-AuClBr **16**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Au1	Br1	176.69(7)	N1	C6	C2	115.77(16)
C1	P1	Au1	122.83(8)	N1	C6	C7	123.18(17)
C1	P1	C5	111.51(9)	C7	C6	C2	121.04(16)
C1	P1	Au1A	121.33(12)	C3	C4	C5	123.81(16)
C5	P1	Au1	125.62(8)	C3	C4	C11	115.10(16)
C5	P1	Au1A	126.84(12)	C3	C4	C11A	115.10(16)
C16	Si1	C1	107.32(9)	C5	C4	C11	121.08(16)
C18	Si1	C1	110.61(9)	C5	C4	C11A	121.08(16)
C18	Si1	C16	103.48(10)	C13	C12	C11	118.0(8)
C17	Si1	C1	111.77(9)	C12	C13	C14	118.1(9)
C17	Si1	C16	109.59(11)	C6	C7	C8	118.31(18)
C17	Si1	C18	113.57(10)	C11	N2	C15	114.7(5)
C19	Si2	C5	109.29(9)	C12	C11	C4	122.8(5)
C19	Si2	C21	105.87(11)	N2	C11	C4	111.9(3)
C20	Si2	C5	111.25(10)	N2	C11	C12	125.2(4)
C20	Si2	C19	108.05(11)	C9	C8	C7	119.1(2)
C20	Si2	C21	112.31(13)	C15	C14	C13	118.7(8)
C21	Si2	C5	109.88(10)	C10	C9	C8	118.7(2)

P1	C1	Si1	118.51(10)	N2	C15	C14	125.2(8)
C2	C1	P1	116.54(13)	N1	C10	C9	123.4(2)
C2	C1	Si1	124.63(13)	P1	Au1A	Ci9	171.2(2)
C4	C3	C2	126.17(17)	C13A	C12A	C11A	120.2(6)
C10	N1	C6	117.26(18)	C12A	C13A	C14A	118.1(8)
P1	C5	Si2	120.47(10)	C11A	N2A	C15A	117.5(8)
C4	C5	P1	116.45(13)	C12A	C11A	C4	122.8(4)
C4	C5	Si2	122.92(13)	N2A	C11A	C4	115.5(5)
C1	C2	C6	120.52(16)	N2A	C11A	C12A	121.3(4)
C3	C2	C1	123.04(16)	C13A	C14A	C15A	118.6(9)
C3	C2	C6	116.45(16)	N2A	C15A	C14A	124.2(10)

**Table S23:** Bond lengths (Å) for bis-methyl pyridinium salt TMS-PyrrMe<sub>2</sub>-PP-I 17.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.740(6)	C2	C3	1.399(8)
P1	C5	1.739(6)	C2	C21	1.501(8)
Si1	C1	1.917(6)	C3	C4	1.397(8)
Si1	C11	1.861(8)	C4	C5	1.391(8)
Si1	C12	1.861(7)	C4	C31	1.497(8)
Si1	C13	1.863(8)	C21	C22	1.385(9)
Si2	C5	1.907(6)	C22	C23	1.369(9)
Si2	C41	1.870(7)	C23	C24	1.387(9)
Si2	C42	1.863(8)	C24	C25	1.349(9)
Si2	C43	1.866(7)	C31	C32	1.387(9)
N1	C21	1.361(8)	C32	C33	1.383(9)
N1	C25	1.356(8)	C33	C34	1.364(9)
N1	C26	1.461(8)	C34	C35	1.369(9)
N2	C31	1.356(8)	N21	C111	1.134(11)
N2	C35	1.346(8)	C111	C112	1.444(13)
N2	C36	1.483(8)	N11	C101	1.148(12)
C1	C2	1.392(9)	C101	C102	1.454(13)

**Table S24:** Bond angles (°) for bis-methyl pyridinium salt TMS-PyrrMe<sub>2</sub>-PP-I 17

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	P1	C1	105.3(3)	C3	C2	C21	116.7(5)
C11	Si1	C1	110.0(3)	C4	C3	C2	123.8(5)
C11	Si1	C12	112.0(4)	C3	C4	C31	115.5(5)
C11	Si1	C13	108.2(4)	C5	C4	C3	124.6(5)
C12	Si1	C1	110.6(3)	C5	C4	C31	119.9(5)
C12	Si1	C13	108.8(4)	P1	C5	Si2	113.8(3)
C13	Si1	C1	107.0(3)	C4	C5	P1	120.9(5)
C41	Si2	C5	106.9(3)	C4	C5	Si2	125.3(5)
C42	Si2	C5	108.0(3)	N1	C21	C26	121.1(5)
C42	Si2	C41	110.7(3)	N1	C21	C22	118.6(6)
C42	Si2	C43	108.8(3)	C22	C21	C2	120.4(6)
C43	Si2	C5	114.1(3)	C23	C22	C21	120.9(6)

C43	Si2	C41	108.4(3)	C22	C23	C24	119.2(6)
C21	N1	C26	121.0(5)	C25	C24	C23	118.9(6)
C25	N1	C21	120.3(5)	C24	C25	N1	122.0(6)
C25	N1	C26	118.7(5)	N2	C31	C4	119.5(5)
C31	N2	C36	119.6(5)	N2	C31	C32	119.2(5)
C35	N2	C31	121.3(5)	C32	C31	C4	121.3(6)
C35	N2	C36	119.0(5)	C33	C32	C31	119.5(6)
P1	C1	Si1	112.5(3)	C34	C33	C32	119.7(6)
C2	C1	P1	121.4(5)	C33	C34	C35	120.0(6)
C2	C1	Si1	126.1(5)	N2	C35	C34	120.3(6)
C1	C2	C3	123.8(6)	N21	C111	C112	179.2(12)
C1	C2	C21	119.4(5)	N11	C101	C102	178.2(12)

**Table S25:** Bond lengths (Å) for mono-ethyl pyridinium salt TMS-PyrrEt-Py-PP-PF<sub>6</sub> **18**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.747(2)	C4	C5	1.400(3)
P1	C5	1.741(2)	C4	C31	1.500(3)
Si1	C1	1.908(2)	C21	C22	1.381(3)
Si1	C11	1.860(3)	C22	C23	1.380(3)
Si1	C12	1.859(3)	C23	C24	1.384(3)
Si1	C13	1.856(3)	C24	C25	1.365(3)
Si2	C5	1.913(2)	C26	C27	1.507(4)
Si2	C41	1.868(3)	C31	C32	1.385(3)
Si2	C42	1.864(3)	C32	C33	1.388(3)
Si2	C43	1.861(3)	C33	C34	1.381(4)
N1	C21	1.358(3)	C34	C35	1.376(4)
N1	C25	1.355(3)	P11	F1	1.5953(17)
N1	C26	1.491(3)	P11	F2	1.5988(16)
N2	C31	1.344(3)	P11	F3	1.5832(17)
N2	C35	1.346(3)	P11	F4	1.5921(16)
C1	C2	1.397(3)	P11	F5	1.5899(17)
C2	C3	1.396(3)	P11	F6	1.5914(17)
C2	C21	1.505(3)	N11	C101	1.136(4)
C3	C4	1.402(3)	C101	C102	1.456(4)

**Table S26:** Bond angles (°) for mono-ethyl pyridinium salt TMS-PyrrEt-Py-PP-PF<sub>6</sub> **18**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	P1	C1	105.60(11)	N1	C21	C22	118.6(2)
C11	Si1	C1	111.06(11)	C22	C21	C2	121.26(19)
C12	Si1	C1	110.13(12)	C23	C22	C21	120.6(2)
C12	Si1	C11	111.73(13)	C22	C23	C24	119.5(2)
C13	Si1	C1	108.27(11)	C25	C24	C23	118.9(2)
C13	Si1	C11	106.10(14)	N1	C25	C24	121.2(2)
C13	Si1	C12	109.41(14)	N1	C26	C27	111.81(19)
C41	Si2	C5	108.31(11)	N2	C31	C4	115.0(2)
C42	Si2	C5	109.36(11)	N2	C31	C32	122.7(2)

C42	Si2	C41	106.89(14)	C32	C31	C4	122.3(2)
C43	Si2	C5	113.64(11)	C31	C32	C33	119.2(2)
C43	Si2	C41	105.81(14)	C34	C33	C32	118.5(2)
C43	Si2	C42	112.48(13)	C35	C34	C33	118.6(2)
C21	N1	C26	122.01(19)	N2	C35	C34	123.9(2)
C25	N1	C21	121.23(19)	F1	P11	F2	89.50(10)
C25	N1	C26	116.73(18)	F3	P11	F1	178.65(11)
C31	N2	C35	117.0(2)	F3	P11	F2	91.78(10)
P1	C1	Si1	113.69(12)	F3	P11	F4	89.63(10)
C2	C1	P1	120.60(17)	F3	P11	F5	89.53(10)
C2	C1	Si1	125.65(16)	F3	P11	F6	90.19(10)
C1	C2	C21	119.00(19)	F4	P11	F1	89.09(10)
C3	C2	C1	124.3(2)	F4	P11	F2	178.57(10)
C3	C2	C21	116.54(19)	F5	P11	F1	90.07(10)
C2	C3	C4	124.8(2)	F5	P11	F2	89.39(9)
C3	C4	C31	116.6(2)	F5	P11	F4	90.86(10)
C5	C4	C3	123.2(2)	F5	P11	F6	179.17(11)
C5	C4	C31	120.20(19)	F6	P11	F1	90.24(10)
P1	C5	Si2	113.61(12)	F6	P11	F2	89.83(9)
C4	C5	P1	121.52(17)	F6	P11	F4	89.92(10)
C4	C5	Si2	124.62(17)	N11	C101	C102	179.2(3)
N1	C21	C2	120.11(19)				

**Table S27:** Bond lengths (Å) for pyridinium salt TMS-PyrrEt<sub>2</sub>-PP-PF<sub>6</sub> **19**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.7423(12)	C23	C24	1.379(2)
P1	C5	1.7421(13)	C24	C25	1.370(2)
Si1	C1	1.9098(12)	C26	C27	1.505(2)
Si1	C11	1.8627(16)	C31	C32	1.3837(18)
Si1	C12	1.8602(16)	C32	C33	1.3850(19)
Si1	C13	1.8661(16)	C33	C34	1.383(2)
Si2	C5	1.9085(12)	C34	C35	1.368(2)
Si2	C41	1.8638(18)	C36	C37	1.514(2)
Si2	C42	1.8616(17)	P11	F5	1.5840(10)
Si2	C43	1.8637(16)	P11	F6	1.6018(10)
N1	C21	1.3598(17)	P11	F1	1.5793(13)
N1	C25	1.3490(17)	P11	F2	1.5710(15)
N1	C26	1.5043(19)	P11	F3	1.5820(15)
N2	C31	1.3555(16)	P11	F4	1.5769(15)
N2	C35	1.3559(17)	P11	F1A	1.588(9)
N2	C36	1.4920(18)	P11	F2A	1.546(10)
C1	C2	1.3977(17)	P11	F3A	1.545(9)
C2	C3	1.3970(16)	P11	F4A	1.535(9)
C2	C21	1.4967(16)	P21	F11	1.5978(10)
C3	C4	1.3966(16)	P21	F12	1.5994(10)
C4	C5	1.4001(16)	P21	F13	1.6056(10)
C4	C31	1.4969(16)	P21	F14	1.5953(11)
C21	C22	1.3786(18)	P21	F15	1.6017(10)

C22      C23      1.3889(19)      P21      F16      1.6004(10)

**Table S28** Bond angles (°) for pyridinium salt TMS-PyrrEt<sub>2</sub>-PP-PF<sub>6</sub> **19**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	P1	C1	106.26(6)	N2	C35	C34	121.00(14)
C11	Si1	C1	114.79(6)	N2	C36	C37	109.20(12)
C11	Si1	C13	107.76(9)	F5	P11	F6	179.49(7)
C12	Si1	C1	106.79(7)	F5	P11	F1A	88.7(3)
C12	Si1	C11	110.43(8)	F1	P11	F5	89.15(7)
C12	Si1	C13	109.92(8)	F1	P11	F6	90.36(7)
C13	Si1	C1	107.04(7)	F1	P11	F3	178.59(12)
C41	Si2	C5	106.89(7)	F2	P11	F5	91.89(8)
C42	Si2	C5	107.71(7)	F2	P11	F6	88.25(8)
C42	Si2	C41	110.06(10)	F2	P11	F1	90.84(13)
C42	Si2	C43	107.49(8)	F2	P11	F3	90.33(15)
C43	Si2	C5	115.04(7)	F2	P11	F4	179.41(12)
C43	Si2	C41	109.60(10)	F3	P11	F5	91.61(8)
C21	N1	C26	118.73(11)	F3	P11	F6	88.88(8)
C25	N1	C21	120.28(12)	F4	P11	F5	88.57(9)
C25	N1	C26	120.98(12)	F4	P11	F6	91.29(8)
C31	N2	C35	121.04(12)	F4	P11	F1	89.55(12)
C31	N2	C36	121.23(11)	F4	P11	F3	89.28(13)
C35	N2	C36	117.48(12)	F1A	P11	F6	91.1(3)
P1	C1	Si1	111.10(6)	F2A	P11	F5	83.7(3)
C2	C1	P1	120.41(9)	F2A	P11	F6	96.7(3)
C2	C1	Si1	128.49(9)	F2A	P11	F1A	88.9(6)
C1	C2	C21	121.29(10)	F3A	P11	F5	93.6(3)
C3	C2	C1	124.40(11)	F3A	P11	F6	86.7(3)
C3	C2	C21	114.22(11)	F3A	P11	F1A	176.9(5)
C4	C3	C2	124.18(11)	F3A	P11	F2A	89.3(6)
C3	C4	C5	124.50(11)	F4A	P11	F5	96.7(3)
C3	C4	C31	113.83(10)	F4A	P11	F6	82.9(3)
C5	C4	C31	121.62(10)	F4A	P11	F1A	88.8(6)
P1	C5	Si2	110.90(7)	F4A	P11	F2A	177.6(6)
C4	C5	P1	120.23(9)	F4A	P11	F3A	92.9(6)
C4	C5	Si2	128.84(9)	F11	P21	F12	90.10(6)
N1	C21	C2	119.73(11)	F11	P21	F13	179.23(6)
N1	C21	C22	119.48(11)	F11	P21	F15	90.11(6)
C22	C21	C2	120.76(11)	F11	P21	F16	89.93(6)
C21	C22	C23	120.57(13)	F12	P21	F13	89.61(6)
C24	C23	C22	118.58(14)	F12	P21	F15	89.16(6)
C25	C24	C23	119.55(13)	F12	P21	F16	90.18(6)
N1	C25	C24	121.45(14)	F14	P21	F11	90.26(6)
N1	C26	C27	114.59(13)	F14	P21	F12	179.11(7)
N2	C31	C4	119.85(11)	F14	P21	F13	90.04(6)
N2	C31	C32	119.01(11)	F14	P21	F15	90.03(6)
C32	C31	C4	121.07(11)	F14	P21	F16	90.64(6)
C31	C32	C33	120.45(13)	F15	P21	F13	90.60(6)

C34	C33	C32	119.13(14)	F16	P21	F13	89.35(5)
C35	C34	C33	119.29(13)	F16	P21	F15	179.33(6)

**Table S 29:** Bond lengths (Å) for gold complex TMS-PyrrEt<sub>2</sub>-PP-AuCl **21**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.207(2)	C3	C2	1.399(7)
Au1	Cl1	2.279(4)	N1	C4	1.325(8)
P1	C1 <sup>1</sup>	1.718(6)	N1	C8	1.385(9)
P1	C1	1.718(6)	N1	C12	1.487(9)
P1	Au1A	2.225(7)	C1	C2	1.407(8)
Si1	C1	1.939(6)	C2	C4	1.503(8)
Si1	C9	1.873(10)	C5	C4	1.390(9)
Si1	C11	1.861(7)	C5	C6	1.378(9)
Si1	C10	1.858(8)	C8	C7	1.333(11)
P2	F1 <sup>1</sup>	1.593(5)	C7	C6	1.386(11)
P2	F1	1.594(5)	C12	C13	1.474(12)
P2	F2	1.601(8)	P3	F8	1.580(9)
P2	F4	1.547(9)	P3	F6 <sup>2</sup>	1.538(8)
P2	F3	1.604(6)	P3	F6	1.538(8)
P2	F5	1.595(7)	P3	F10	1.510(10)
Cl3	C15	1.777(11)	P3	F7	1.583(13)
Cl2	C14	1.753(13)	P3	F9	1.412(14)
C3	C2 <sup>1</sup>	1.399(7)	Au1A	Cl1A	2.277(14)

<sup>1</sup>+X,1/2-Y,+Z; <sup>2</sup>+X,3/2-Y,+Z

**Table S 30:** Bond angles (°) for gold complex TMS-PyrrEt<sub>2</sub>-PP-AuCl **21**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Au1	Cl1	175.8(2)	C2	C1	P1	116.1(4)
C1	P1	Au1	123.70(19)	C2	C1	Si1	128.7(4)
C1 <sup>1</sup>	P1	Au1	123.70(19)	C3	C2	C1	125.2(5)
C1 <sup>1</sup>	P1	C1	112.5(4)	C3	C2	C4	114.4(5)
C1 <sup>1</sup>	P1	Au1A	122.5(2)	C1	C2	C4	120.3(5)
C1	P1	Au1A	122.5(2)	C6	C5	C4	120.5(7)
C9	Si1	C1	106.4(3)	N1	C4	C2	121.1(5)
C11	Si1	C1	114.4(3)	N1	C4	C5	119.2(6)
C11	Si1	C9	108.8(4)	C5	C4	C2	119.7(5)
C10	Si1	C1	108.6(4)	C7	C8	N1	121.0(7)
C10	Si1	C9	111.8(5)	C8	C7	C6	119.9(7)
C10	Si1	C11	106.9(5)	C13	C12	N1	110.0(7)
F1 <sup>1</sup>	P2	F1	178.3(5)	C5	C6	C7	118.7(7)
F1 <sup>1</sup>	P2	F2	89.2(2)	Cl3 <sup>2</sup>	C15	Cl3	111.7(10)
F1	P2	F2	89.2(2)	Cl2	C14	Cl2 <sup>1</sup>	109.6(12)
F1	P2	F3	89.9(2)	F8	P3	F7	82.3(8)
F1 <sup>1</sup>	P2	F3	89.9(2)	F6	P3	F8	88.5(3)
F1 <sup>1</sup>	P2	F5	90.1(2)	F6 <sup>2</sup>	P3	F8	88.5(3)
F1	P2	F5	90.1(2)	F6 <sup>2</sup>	P3	F6	170.9(10)

F2	P2	F3	89.3(4)	F6	P3	F7	85.5(5)
F4	P2	F1 <sup>1</sup>	90.8(2)	F6 <sup>2</sup>	P3	F7	85.5(5)
F4	P2	F1	90.8(2)	F10	P3	F8	176.5(10)
F4	P2	F2	179.9(5)	F10	P3	F6 <sup>2</sup>	91.3(3)
F4	P2	F3	90.6(5)	F10	P3	F6	91.3(3)
F4	P2	F5	90.4(5)	F10	P3	F7	94.2(11)
F5	P2	F2	89.8(5)	F9	P3	F8	91.0(11)
F5	P2	F3	179.1(5)	F9	P3	F6	94.3(5)
C2	C3	C2 <sup>1</sup>	125.0(7)	F9	P3	F6 <sup>2</sup>	94.3(5)
C4	N1	C8	120.7(6)	F9	P3	F10	92.6(13)
C4	N1	C12	122.9(6)	F9	P3	F7	173.3(13)
C8	N1	C12	116.3(6)	P1	Au1A	Cl1A	173.5(8)
P1	C1	Si1	115.2(3)				

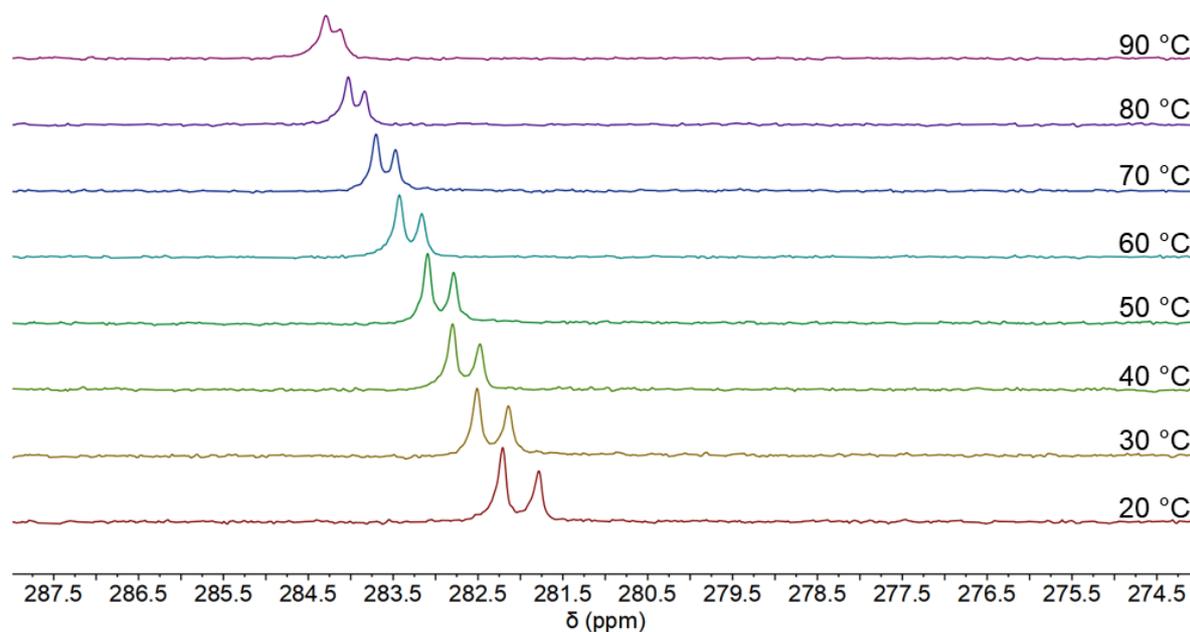
<sup>1</sup>+X,1/2-Y,+Z; <sup>2</sup>+X,3/2-Y,+Z

## 4. Spectroscopic Data

### 4.1. Additional NMR spectroscopic measurements

#### High temperature measurement of bis-methyl-pyridinium salt **17**

To confirm the hypothesis that the two resonances from the reaction of MeI and phosphinine **8** at  $\sigma$  (ppm) = 281.8 and 282.1 can assigned to two different rotamers of the same compound, a temperature depending <sup>31</sup>P NMR study was conducted.<sup>[21]</sup> By increasing temperature within intervals of  $\Delta T = 10$  °C a sample of **17** in CD<sub>3</sub>CN was spectroscopically monitored.

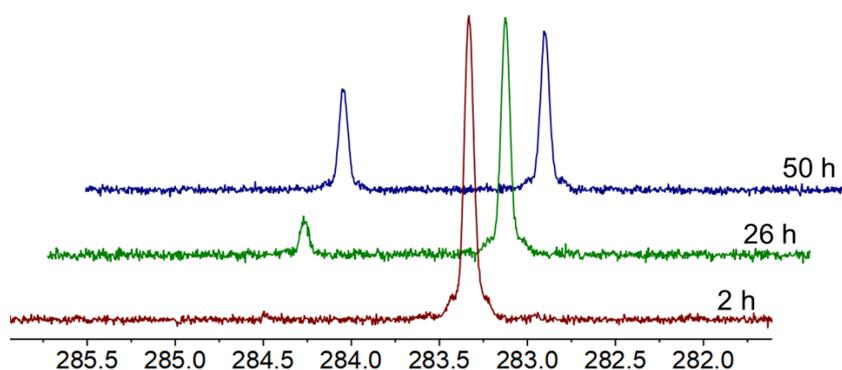


**Figure S11:** Temperature depending <sup>31</sup>P NMR study of a solution of **176** in CD<sub>3</sub>CN.

From  $T = 70\text{ }^{\circ}\text{C}$ , a clear convergence of the resonances can be observed. Unfortunately, it was not possible to determine the temperature which the two resonances coalesced. MeCN is the only suitable solvent to dissolve pyridinium salt **17**. Attempts to dissolve in higher boiling solvents, as diglyme or *o*-difluoro benzene failed. Since the convergence point is higher as the boiling point of  $T = 82\text{ }^{\circ}\text{C}$  it was only possible to detect a resonance at  $T = 90\text{ }^{\circ}\text{C}$ . Nevertheless, the emerging coalescence is evidencing the detected resonances can be assigned to two coexisting rotational isomers.

### **$^{31}\text{P}$ NMR monitoring solution of bis-ethyl-pyridinium salt **19****

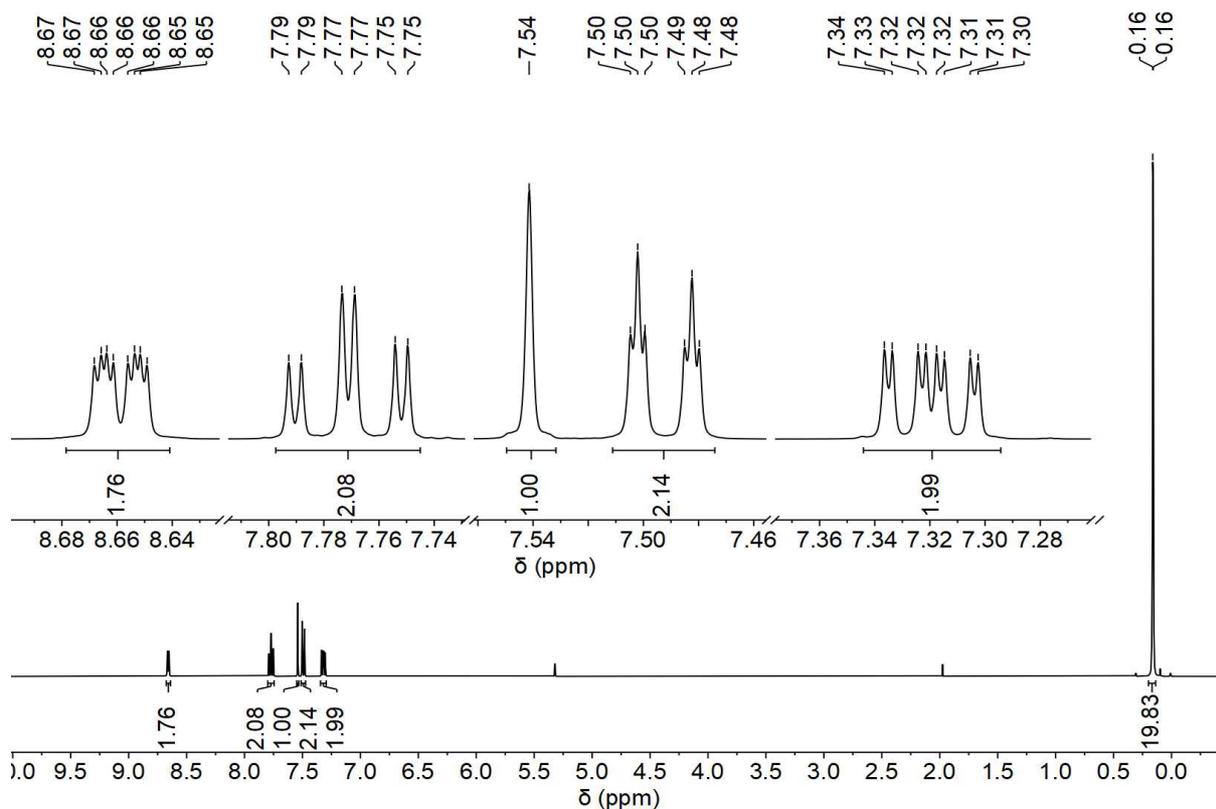
Obtained single crystals of bis-ethyl-pyridinium-salt **19** were dissolved in freshly added  $\text{CD}_3\text{CN}$  and the solution spectroscopically monitored. In the solid state one conformation of the ethyl-pyridinium moieties appears to be favored. The forming of a second resonance at room temperature indicates a slow conversion of a single rotational isomer into a second one.



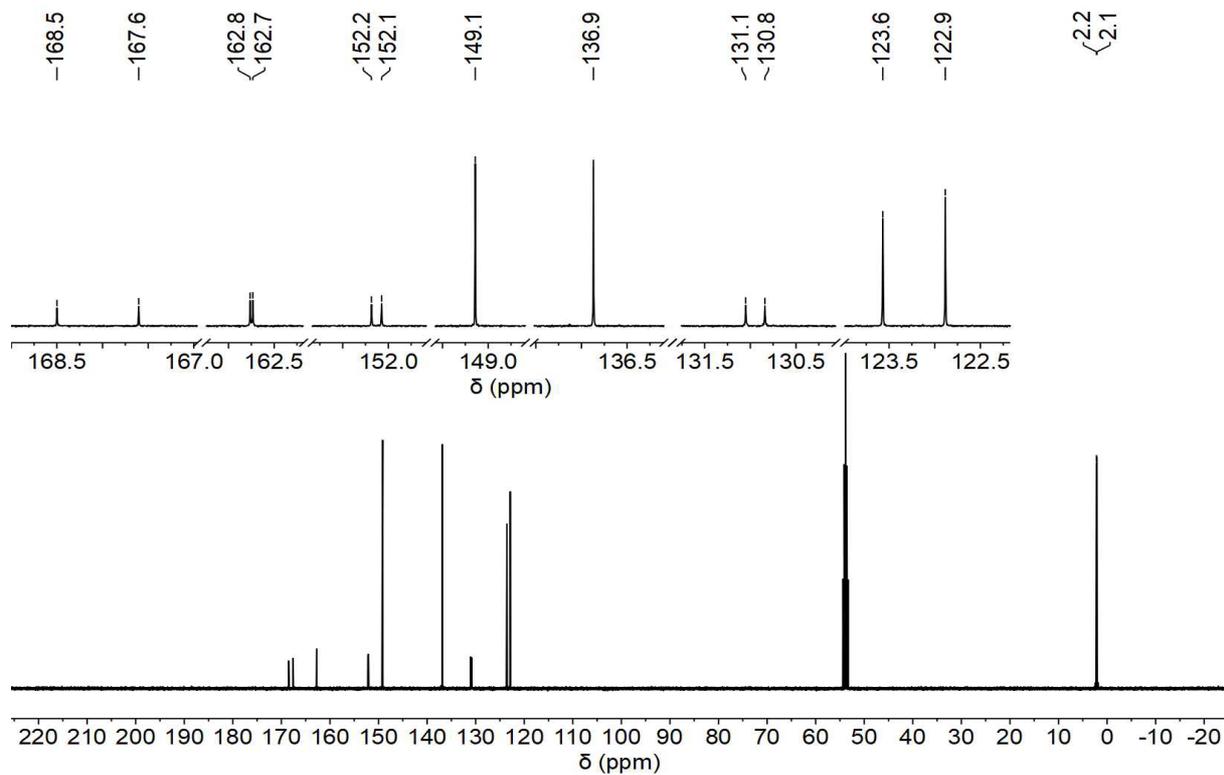
**Figure S12:**  $^{31}\text{P}$  NMR spectroscopic monitoring of a solution in  $\text{CD}_3\text{CN}$  of dissolved single crystals of pyridinium salt **19**.

## 4.2. NMR spectral data

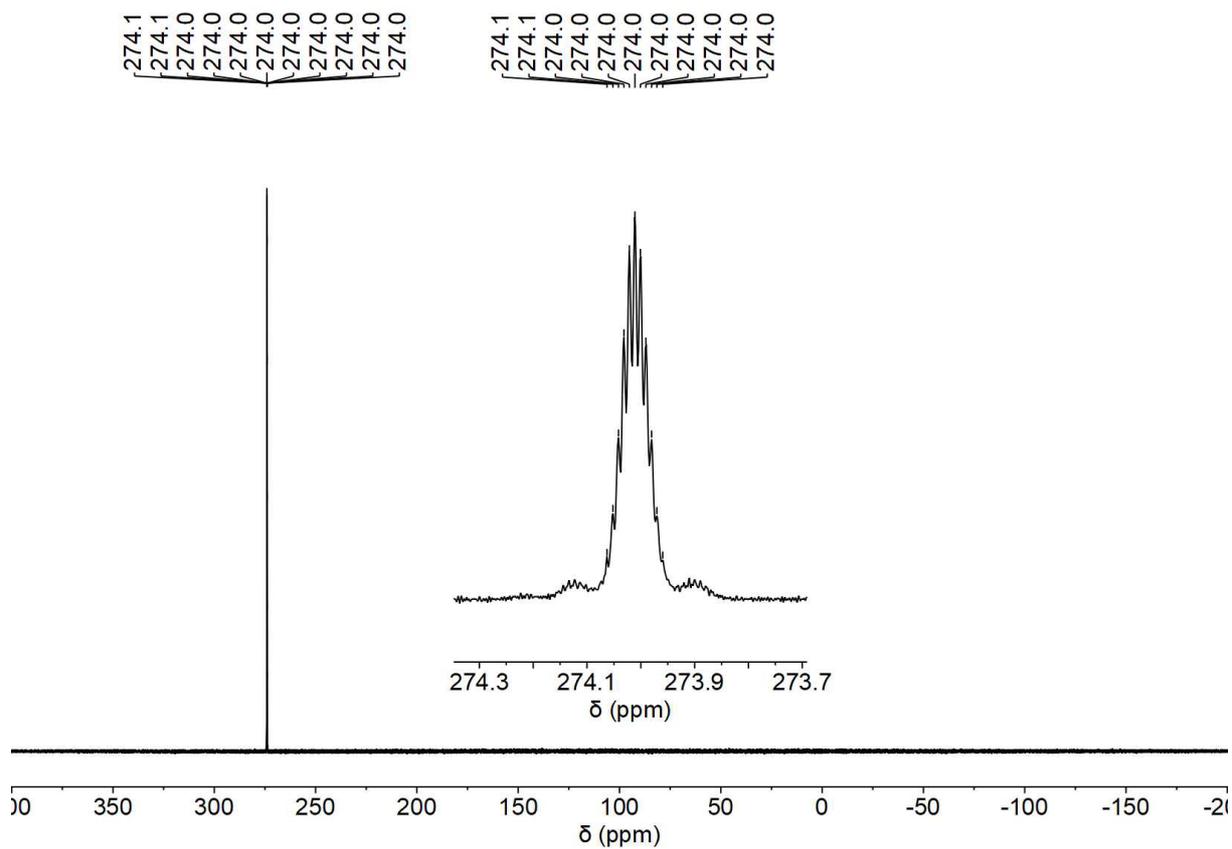
### TMS-Py-PP (8)



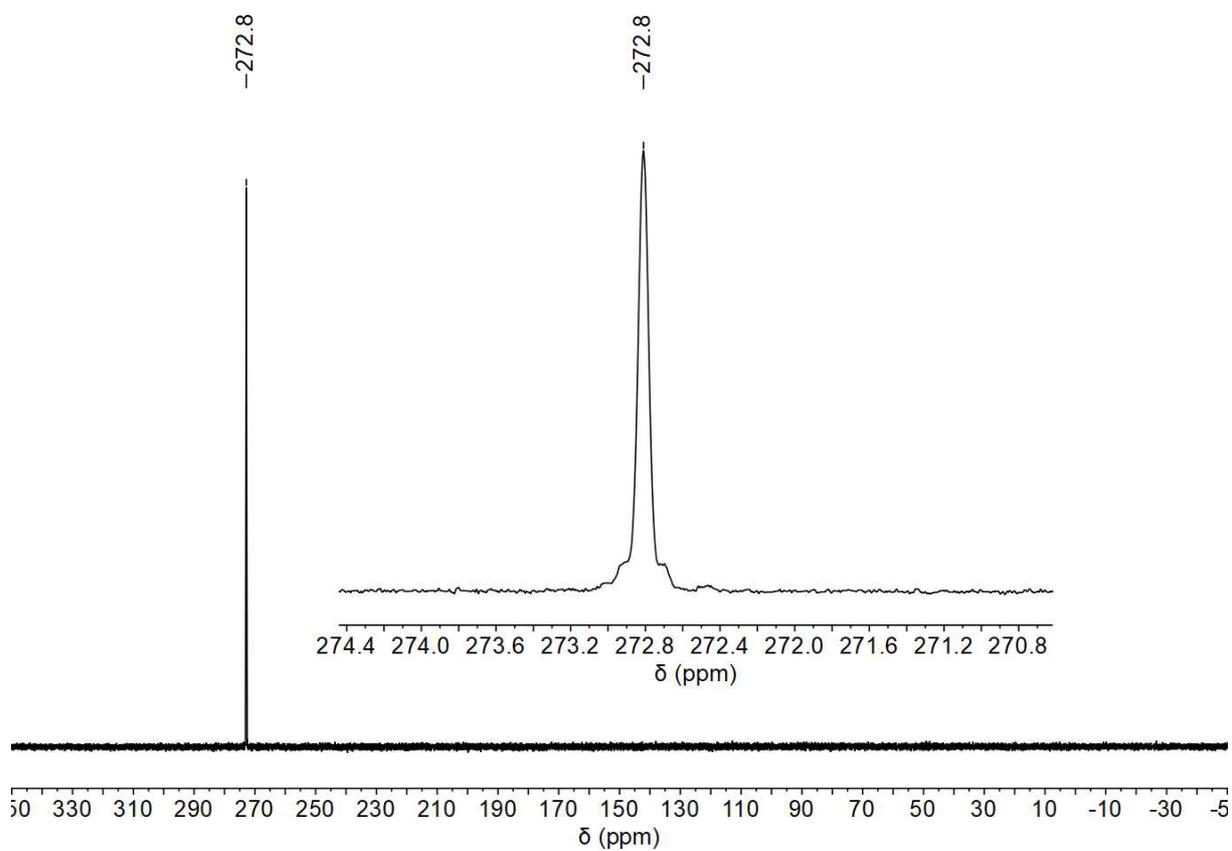
**Figure S13:** <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) of 8.



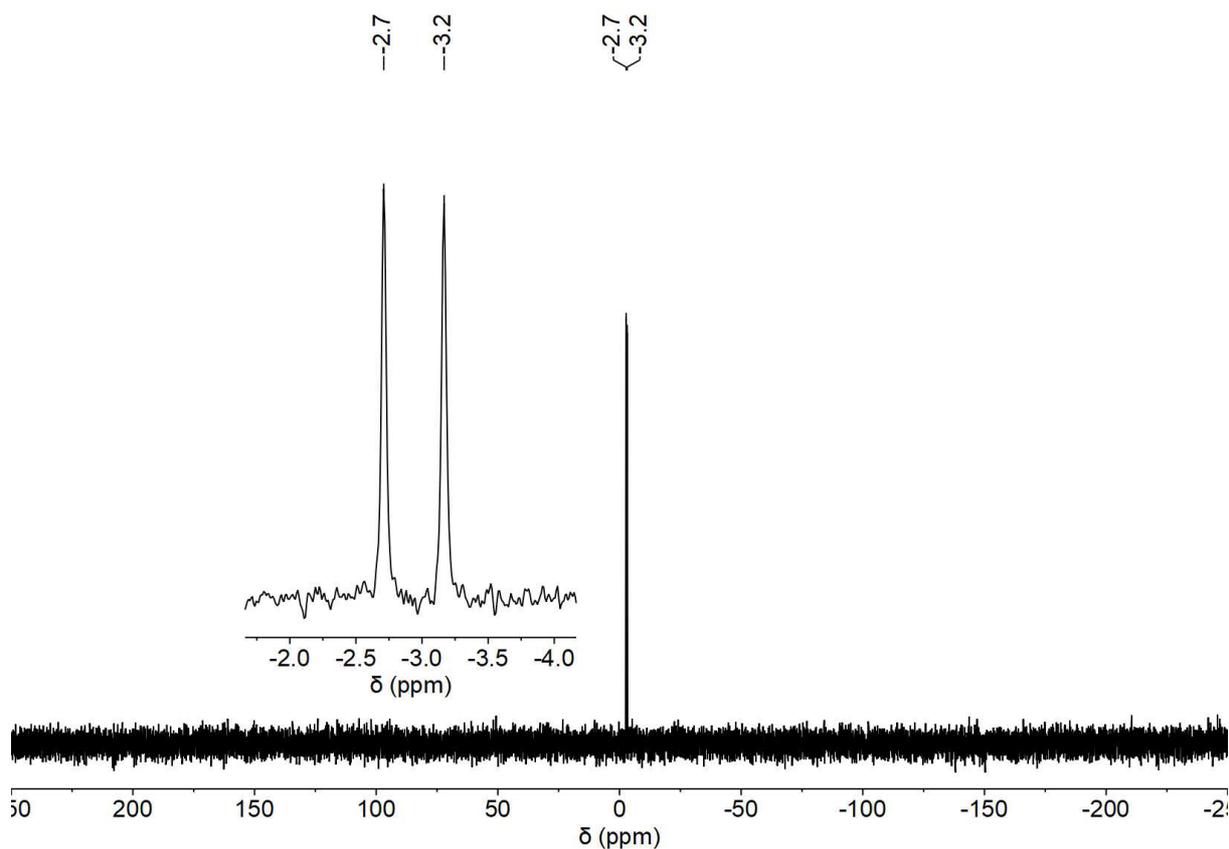
**Figure S14:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) of 8.



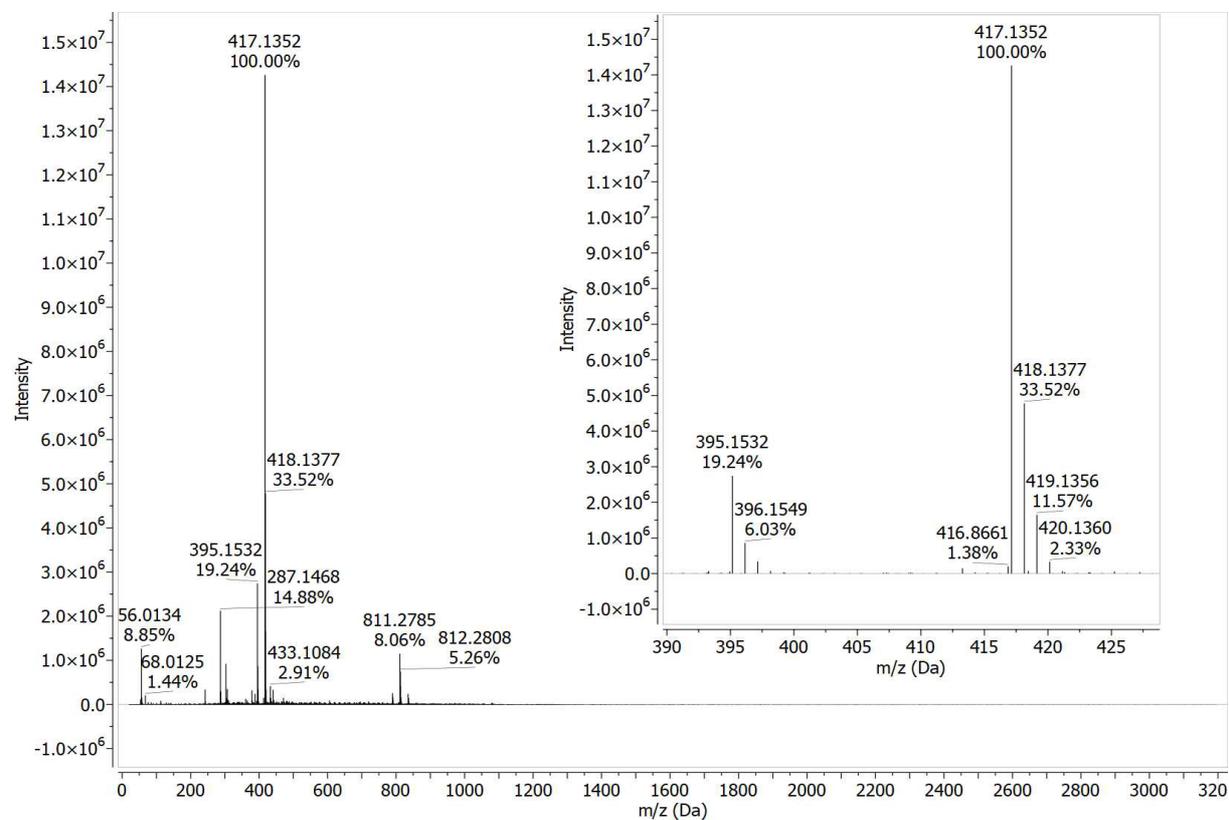
**Figure S15:** <sup>31</sup>P NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) of **8**.



**Figure S16:** <sup>31</sup>P NMR spectrum (CD<sub>3</sub>CN) of **8**

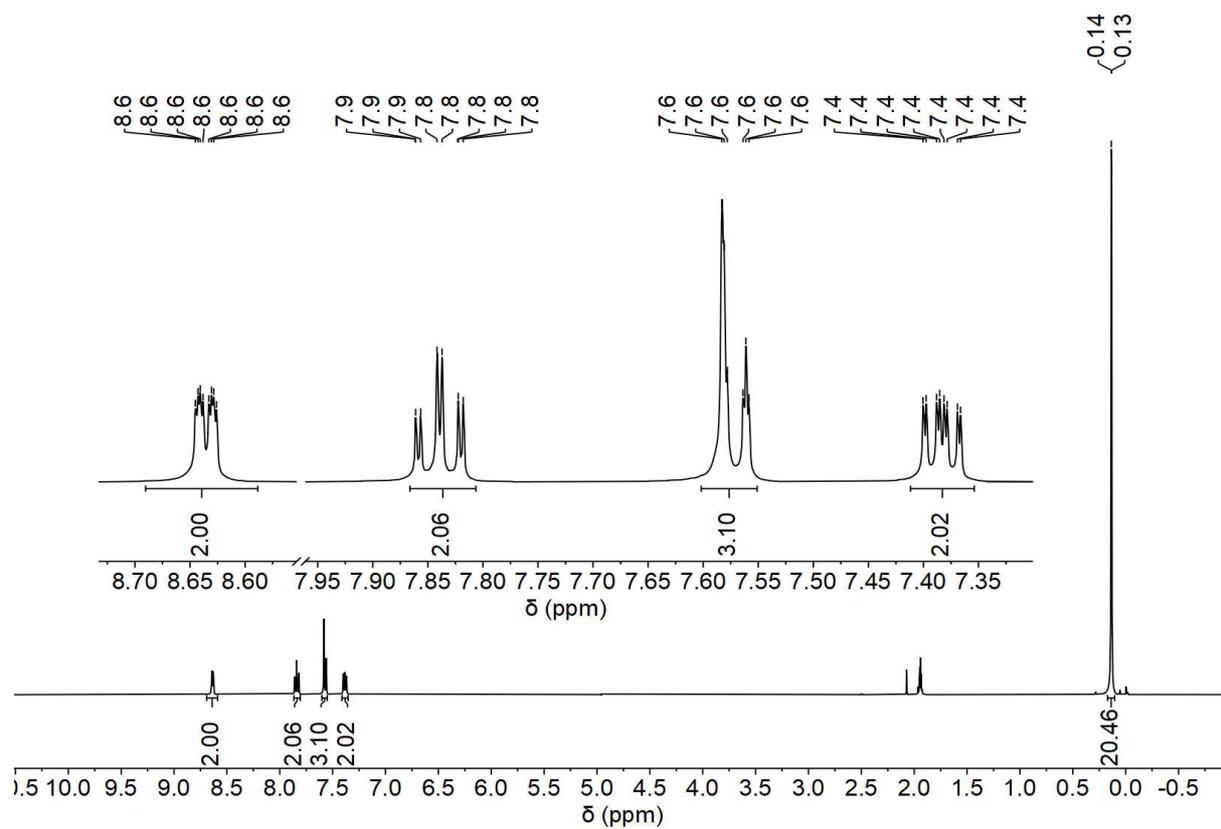


**Figure S17:**  $^{29}\text{Si}\{^1\text{H}\}$ -DEPT NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ) of **8**.

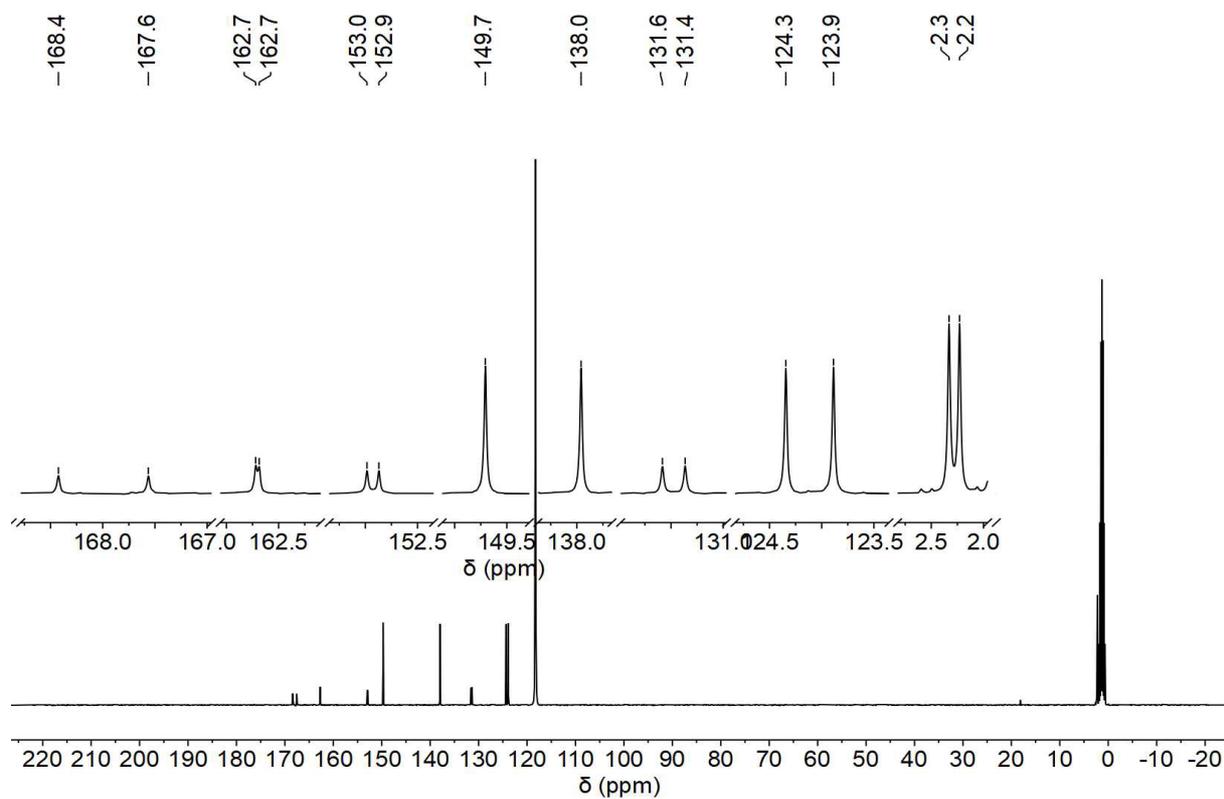


**Figure S18:** HRMS-ESI<sup>+</sup> for **8**  $[\text{M}+\text{H}]^+$   $[\text{C}_{21}\text{H}_{27}\text{N}_2\text{PSi}_2-\text{H}]^+$ .

**[(TMS-Py-PP)(CuCl)]<sub>2</sub> (9)**



**Figure S19:** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) of **9**.



**Figure S20:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>3</sub>CN) of **9**.

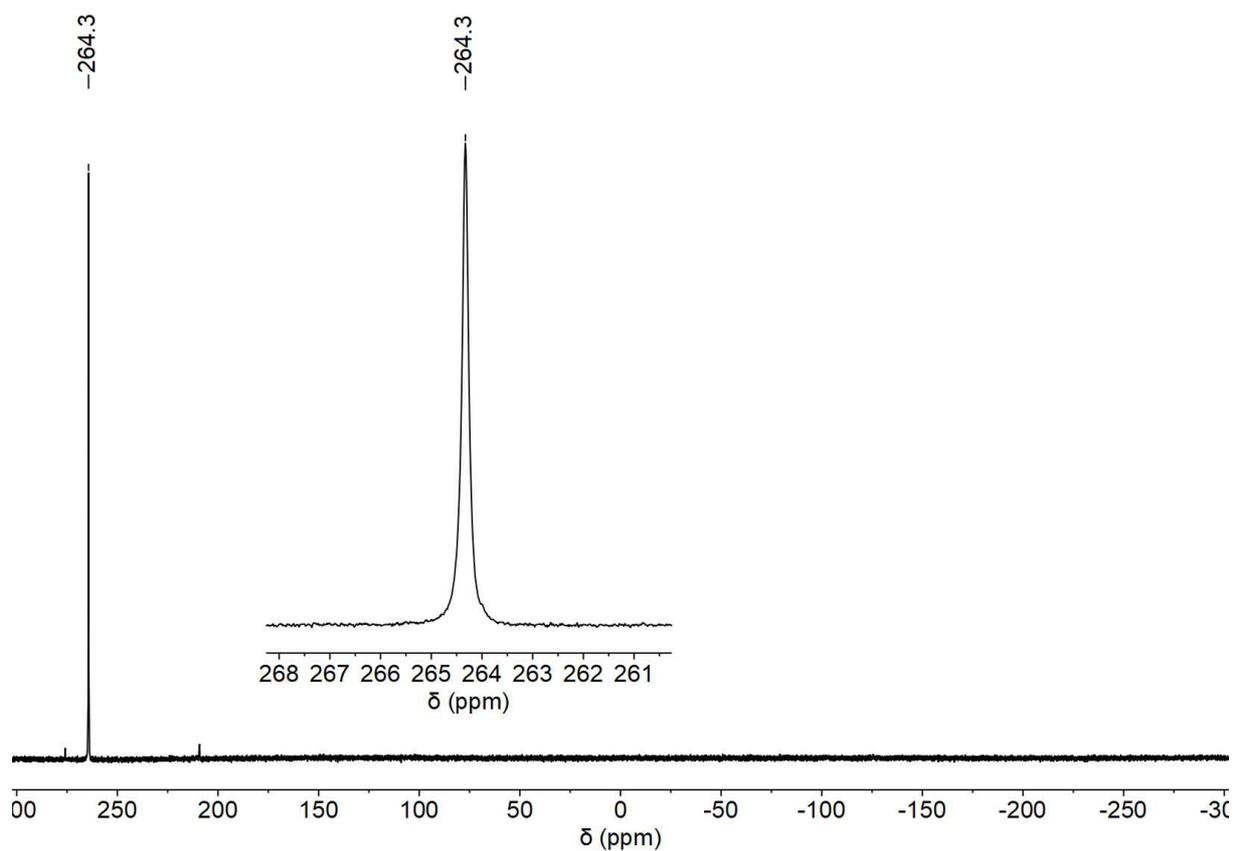


Figure S21:  $^{31}\text{P}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of **9**.

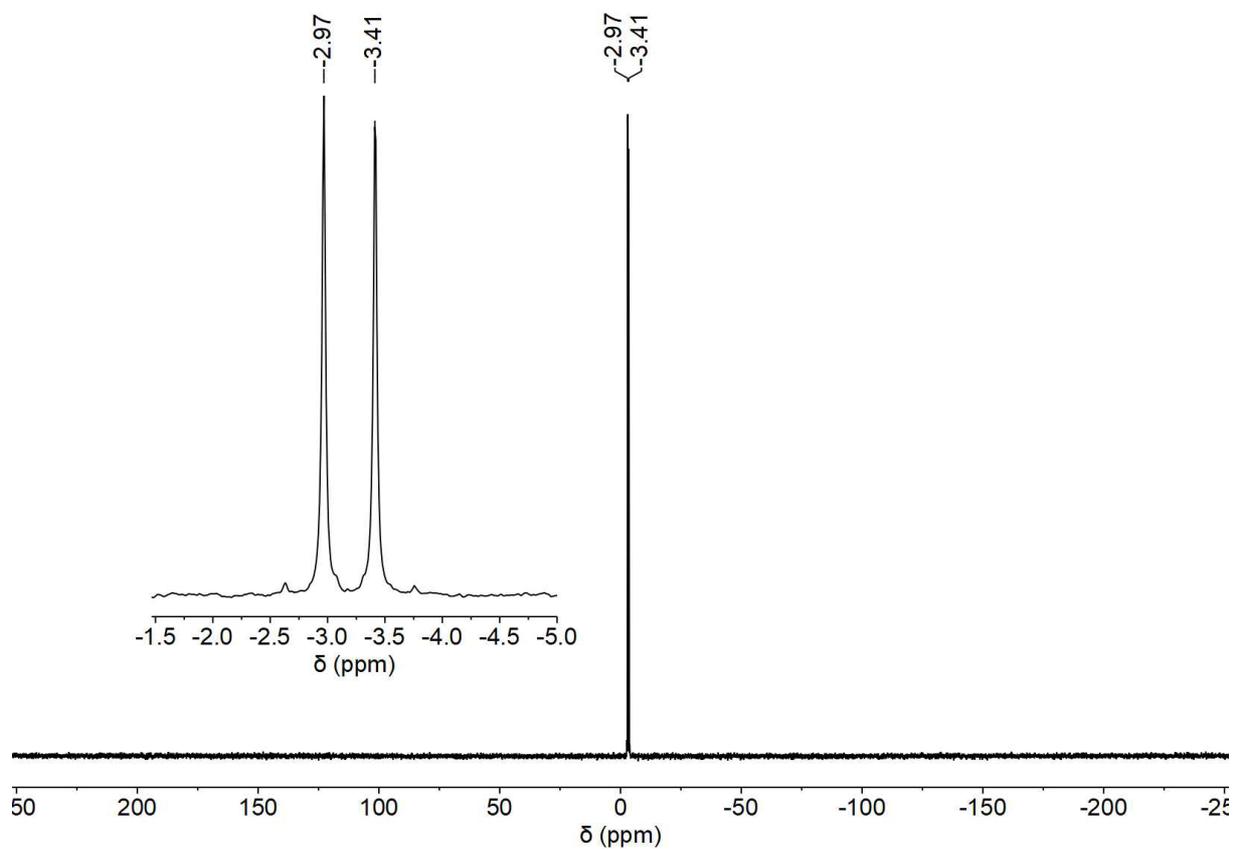


Figure S22:  $^{29}\text{Si}\{^1\text{H}\}$ -DEPT NMR spectrum ( $\text{CD}_3\text{CN}$ ) of **9**.

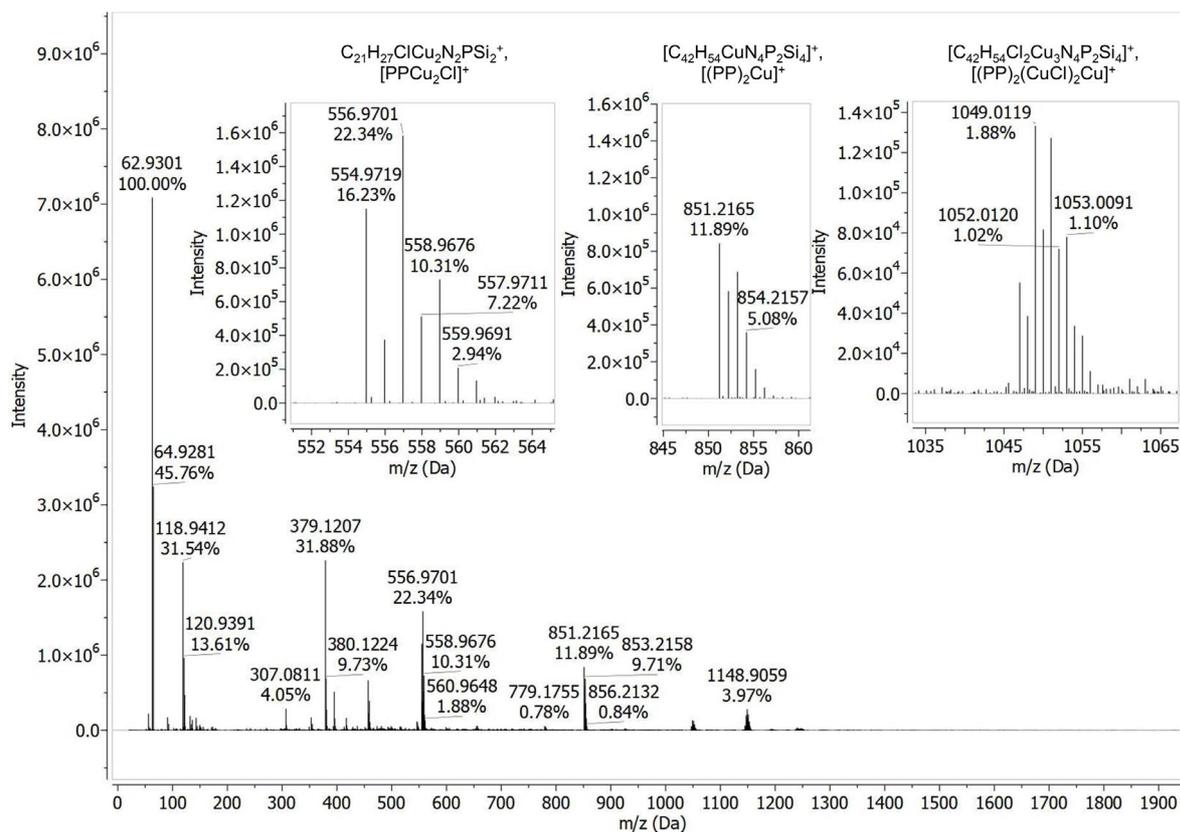


Figure S23: HRMS-ESI<sup>+</sup> for **9**, different fragments indicating dimeric structure in solution:

**[(TMS-Py-PP)(CuBr)<sub>2</sub> (10)**

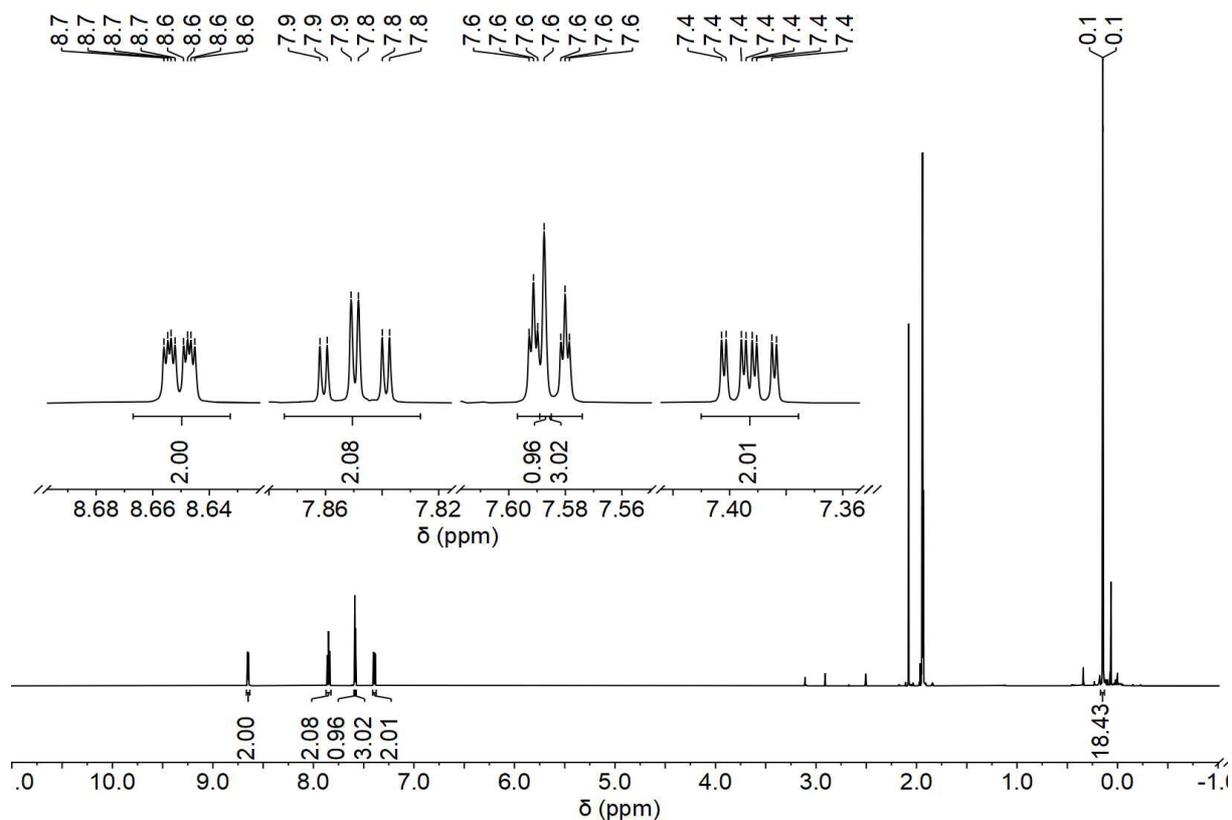
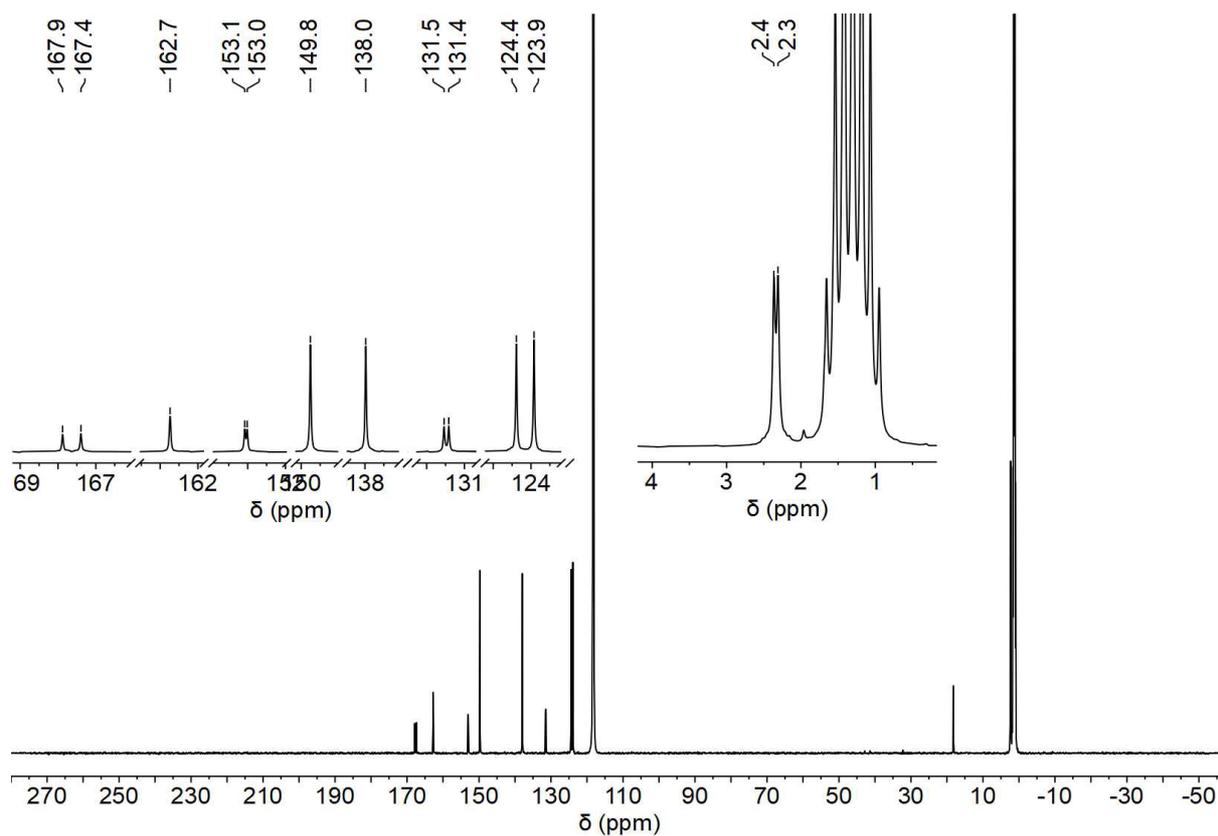
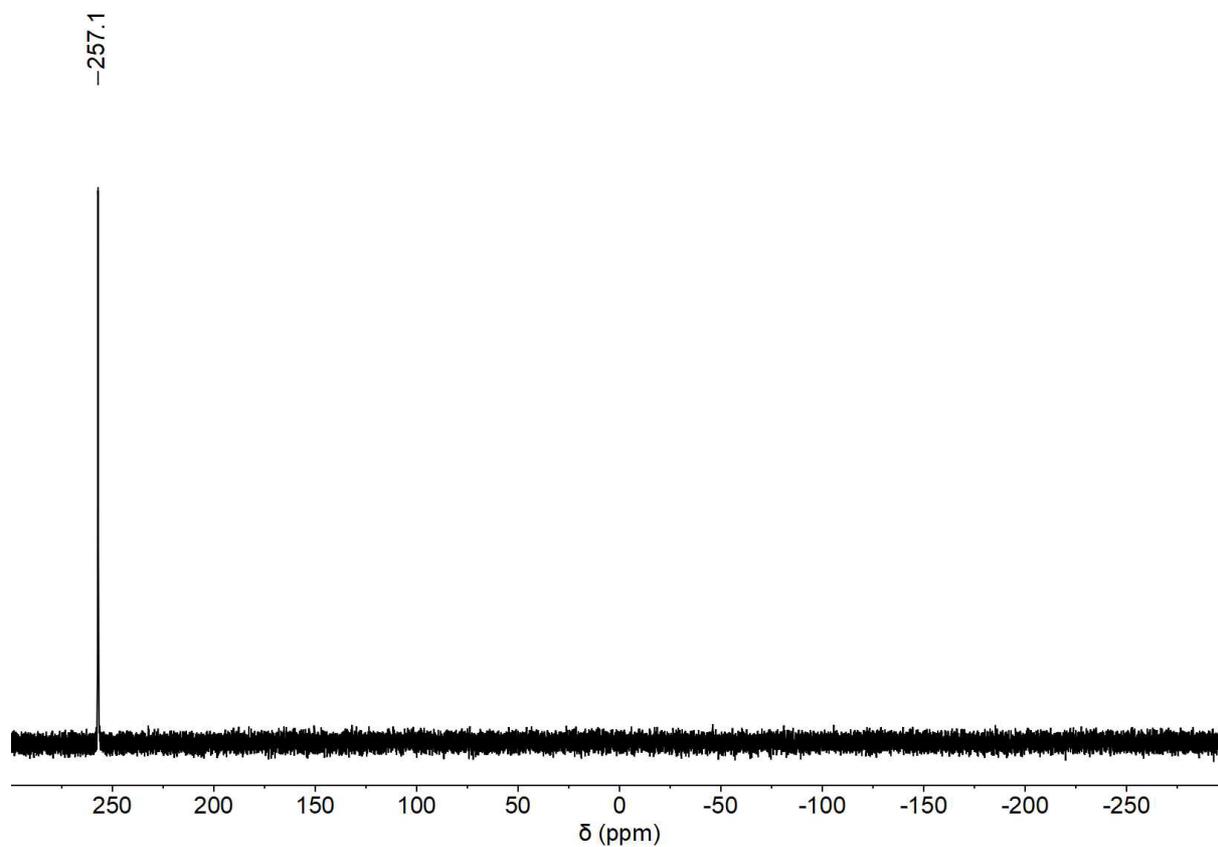


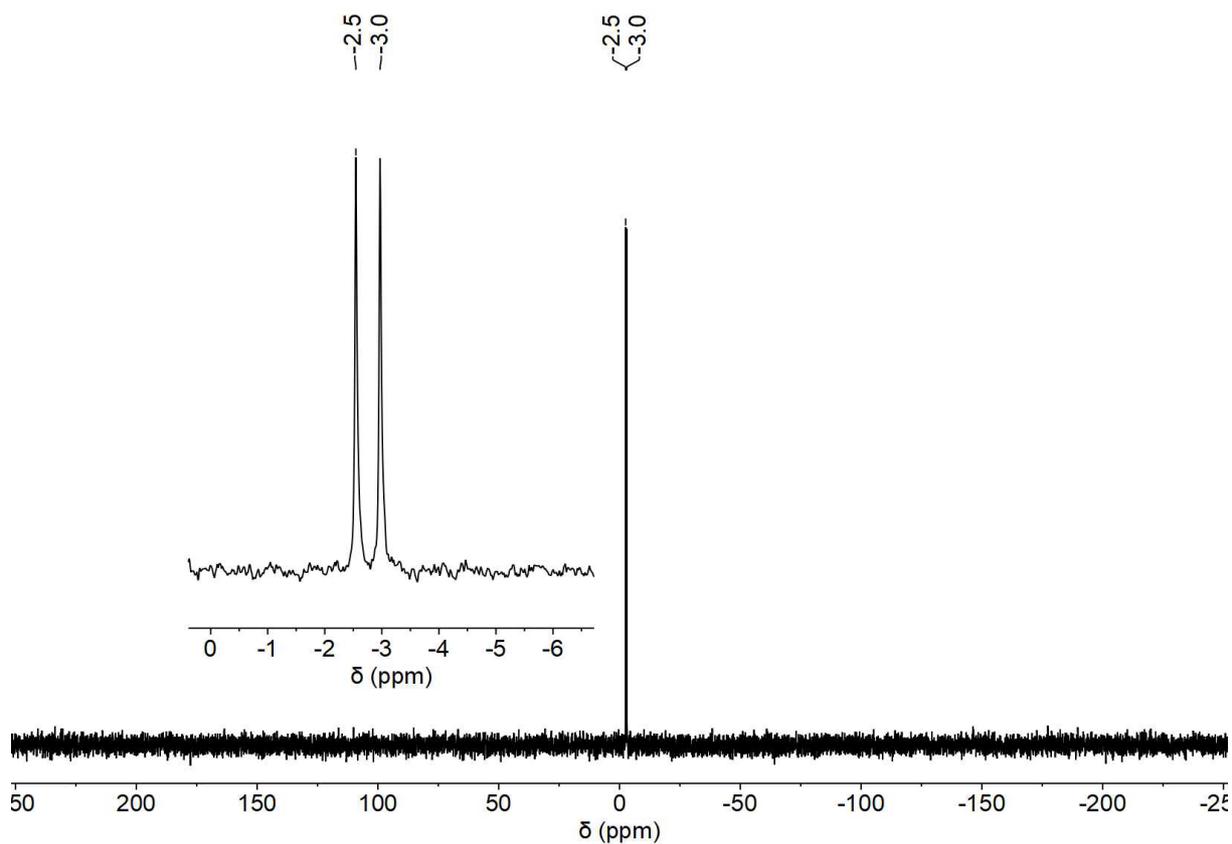
Figure S 24: <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) of **10**.



**Figure S 25:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of **10**.

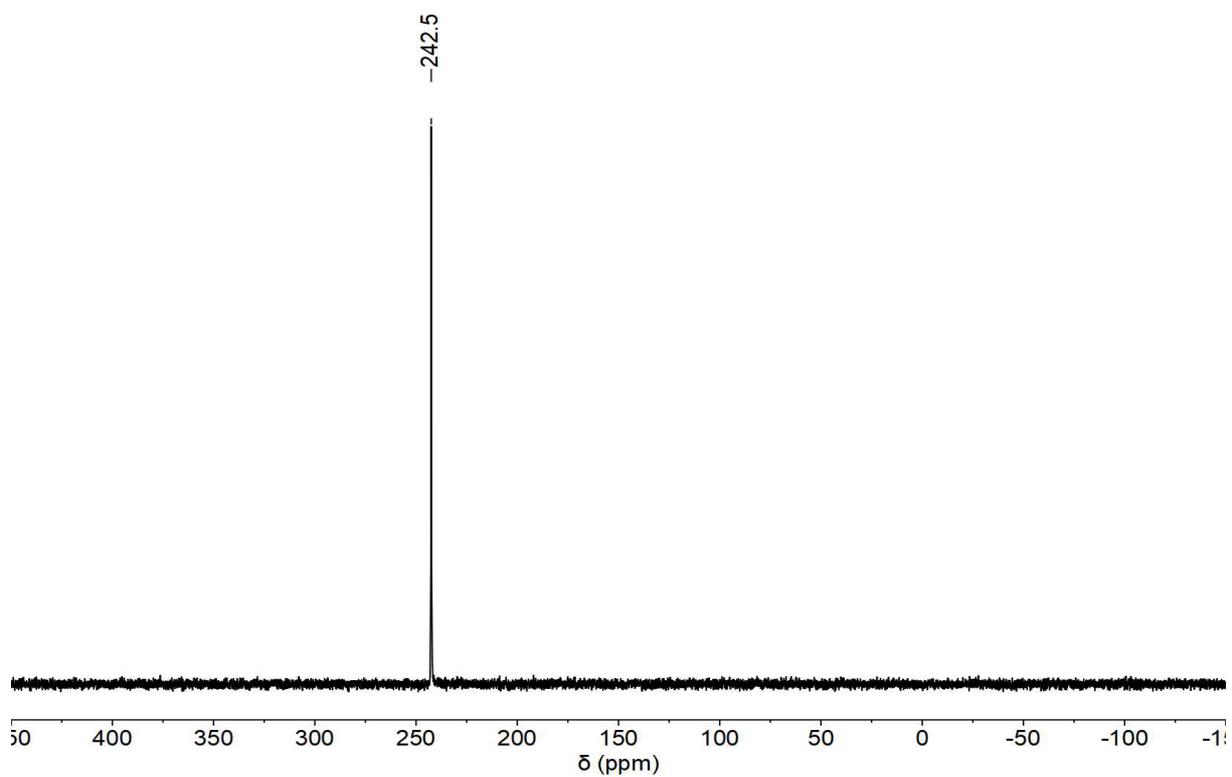


**Figure S26:**  $^{31}\text{P}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of **10**.



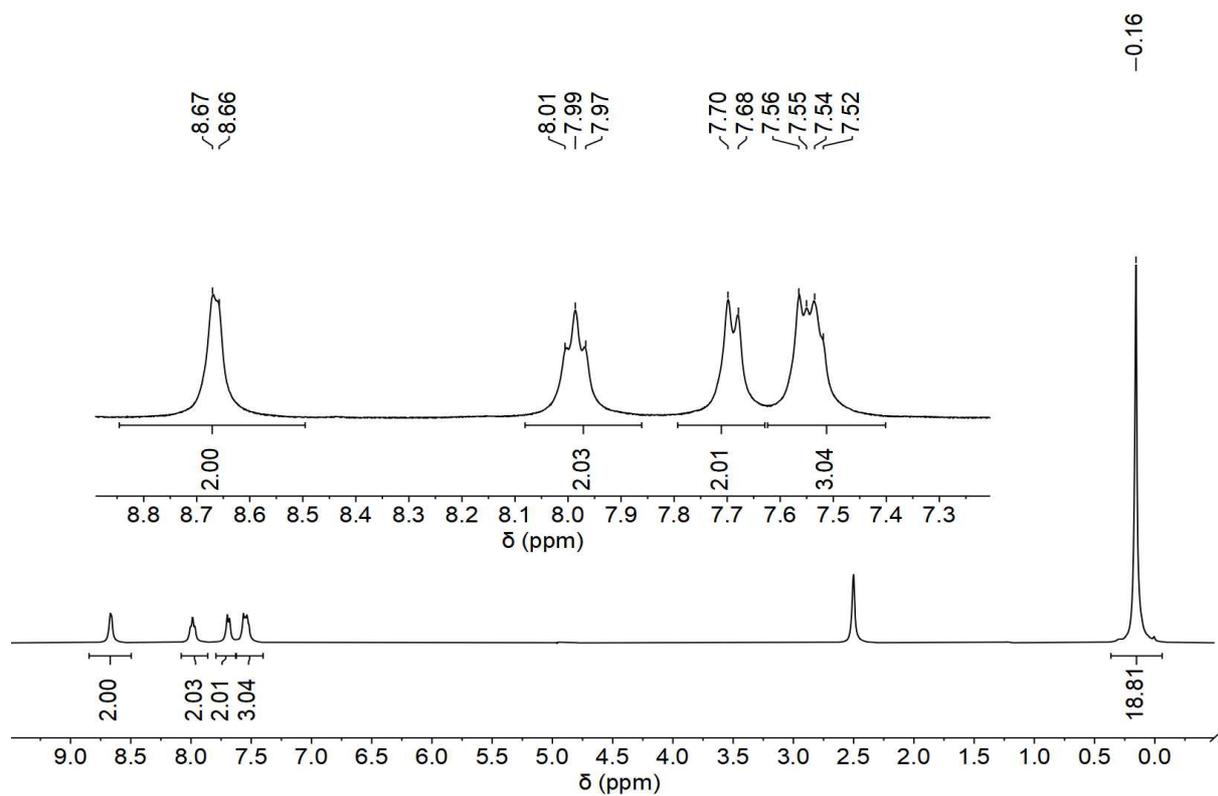
**Figure S27:**  $^{29}\text{Si}\{^1\text{H}\}$ -DEPT NMR spectrum ( $\text{CD}_3\text{CN}$ ) of **10**.

**$[(\text{TMS-Py-PP})(\text{CuBr})_2\text{MeCN}]_n$  (**13**)**

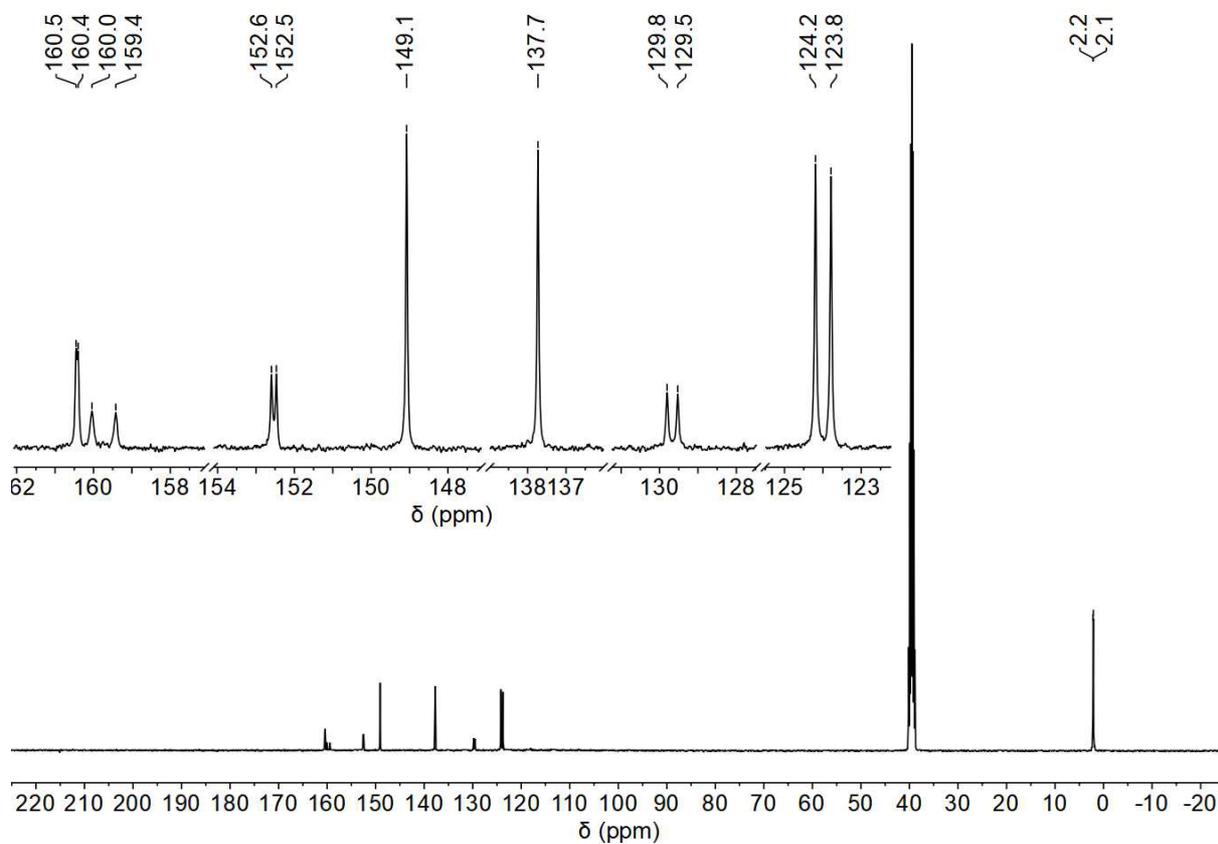


**Figure S 28:**  $^{31}\text{P}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of the crude solution of **13**.

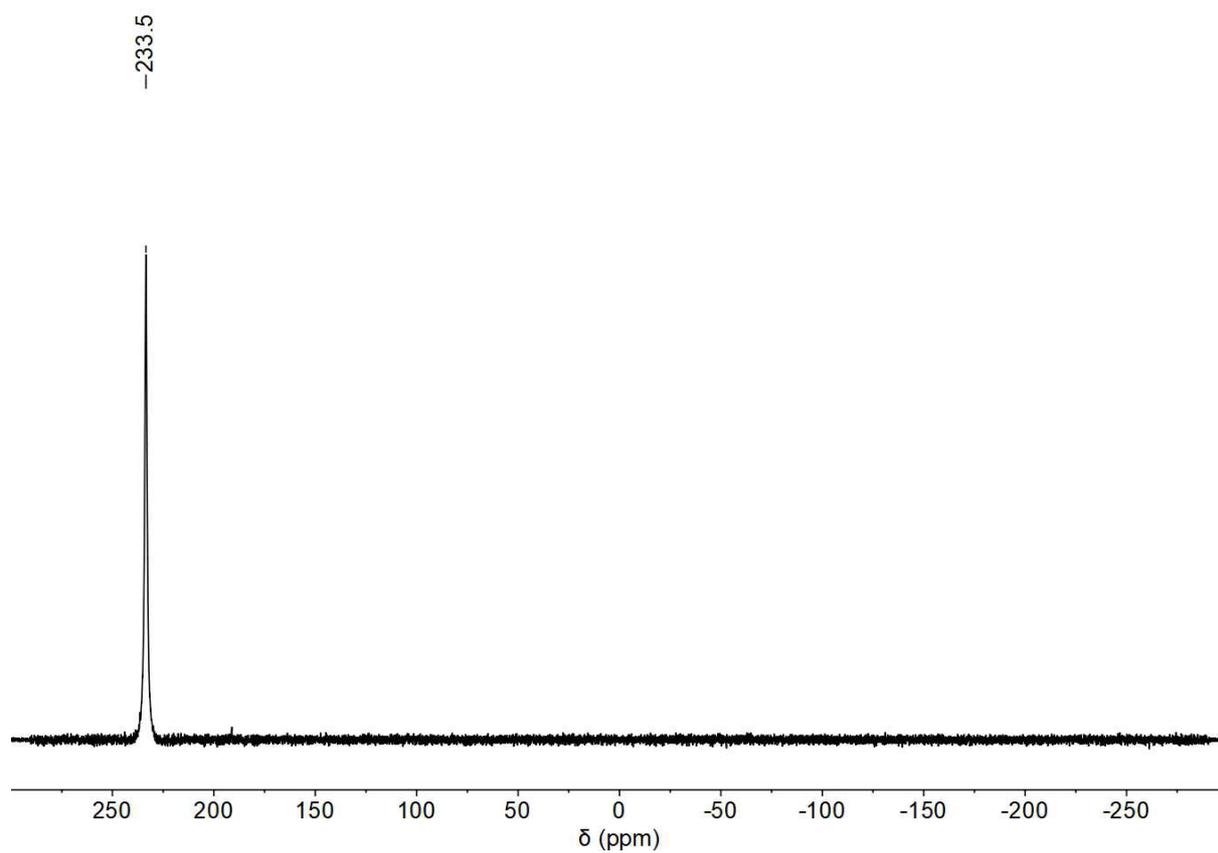
**[(TMS-Py-PP)(CuBr)<sub>3</sub>]<sub>n</sub> (14)**



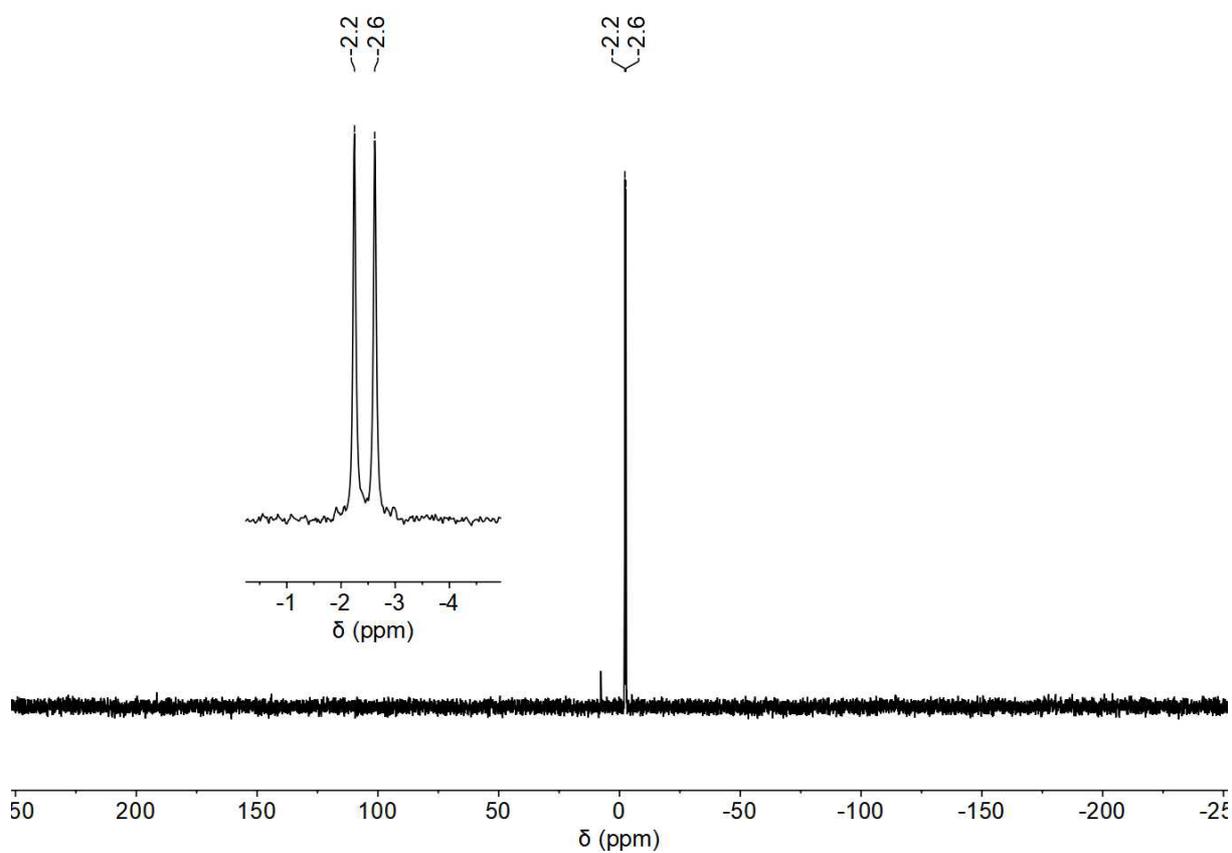
**Figure S29:** <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>) of 14.



**Figure S30:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (DMSO-d<sub>6</sub>) of 14.



**Figure S31:** <sup>31</sup>P NMR spectrum (DMSO-d<sub>6</sub>) of **14**.



**Figure S32:** <sup>29</sup>Si{<sup>1</sup>H}-DEPT NMR spectrum (DMSO-d<sub>6</sub>) of **14**.

### TMS-Py-PP-AuCl<sub>0.3</sub>Br<sub>0.7</sub> (16)

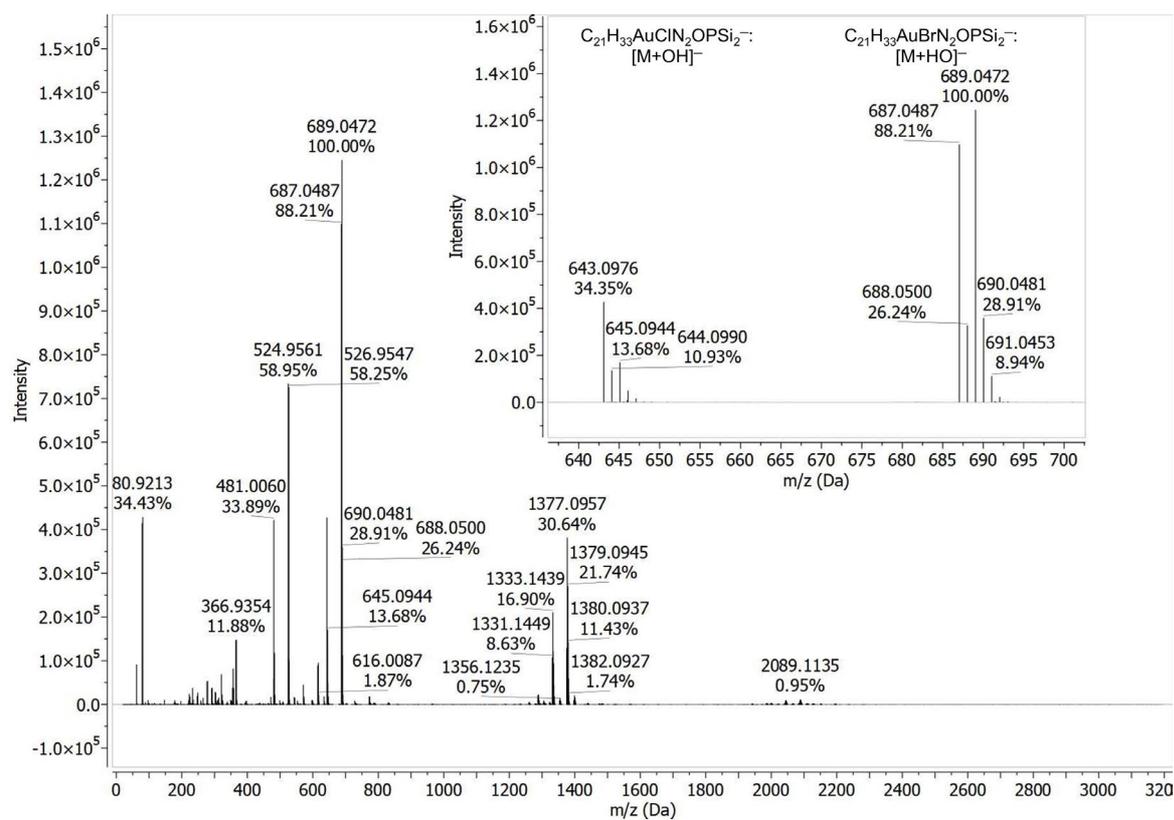


Figure S 33: HRMS-ESI<sup>-</sup> for supernatant solution of **16**. [M+OH]<sup>-</sup>: [C<sub>21</sub>H<sub>33</sub>AuXN<sub>2</sub>OPSi<sub>2</sub>]<sup>-</sup>.

### TMS-Py-PP-AuCl (16a)

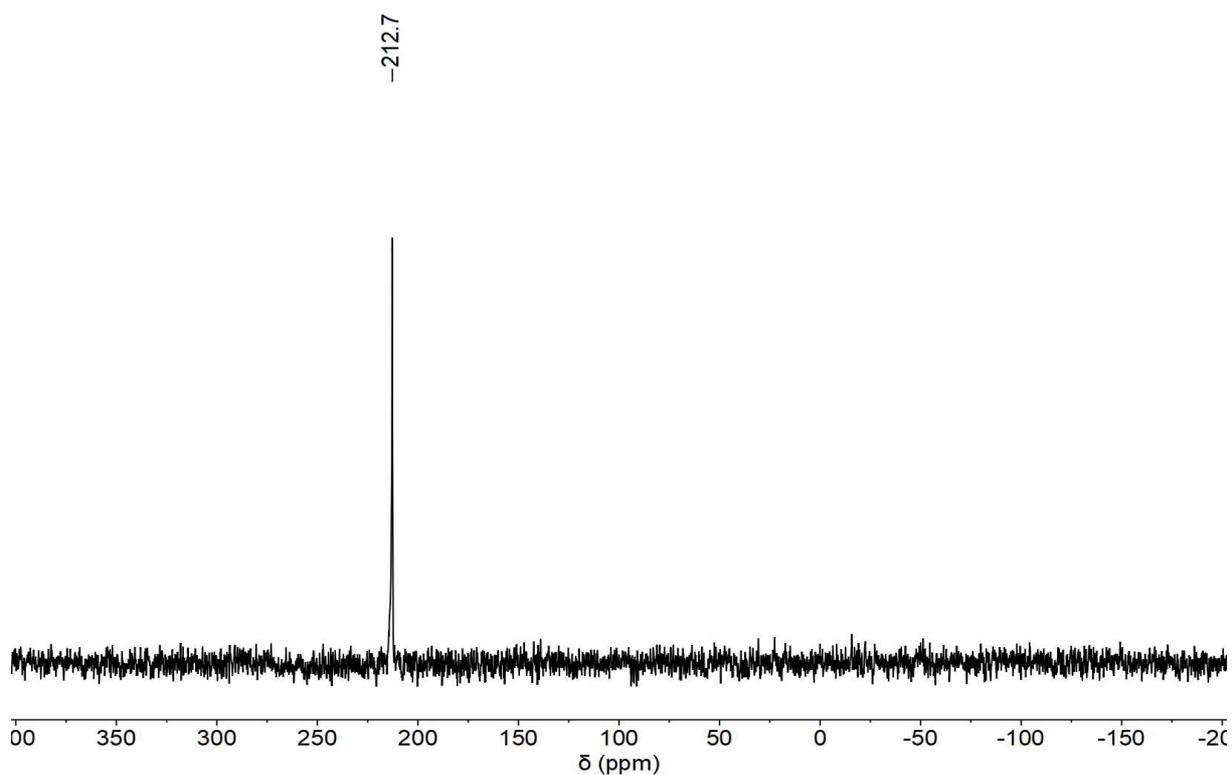
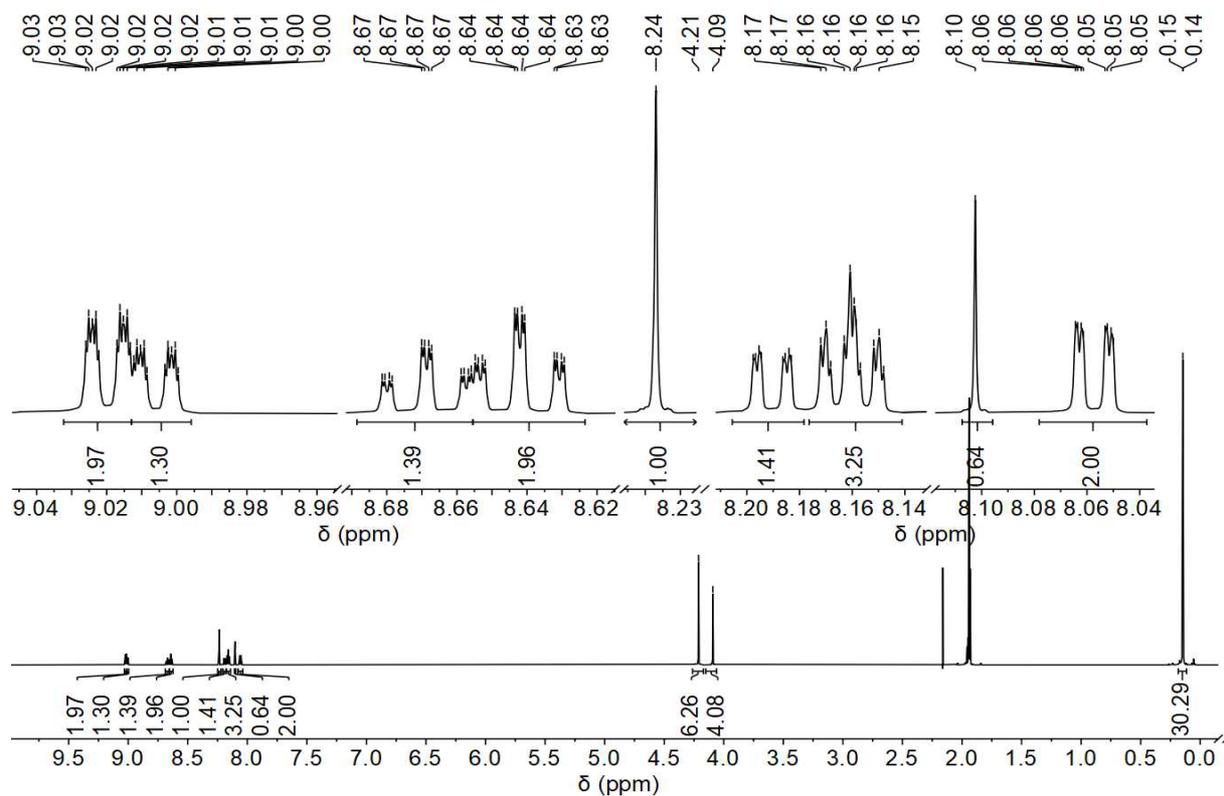
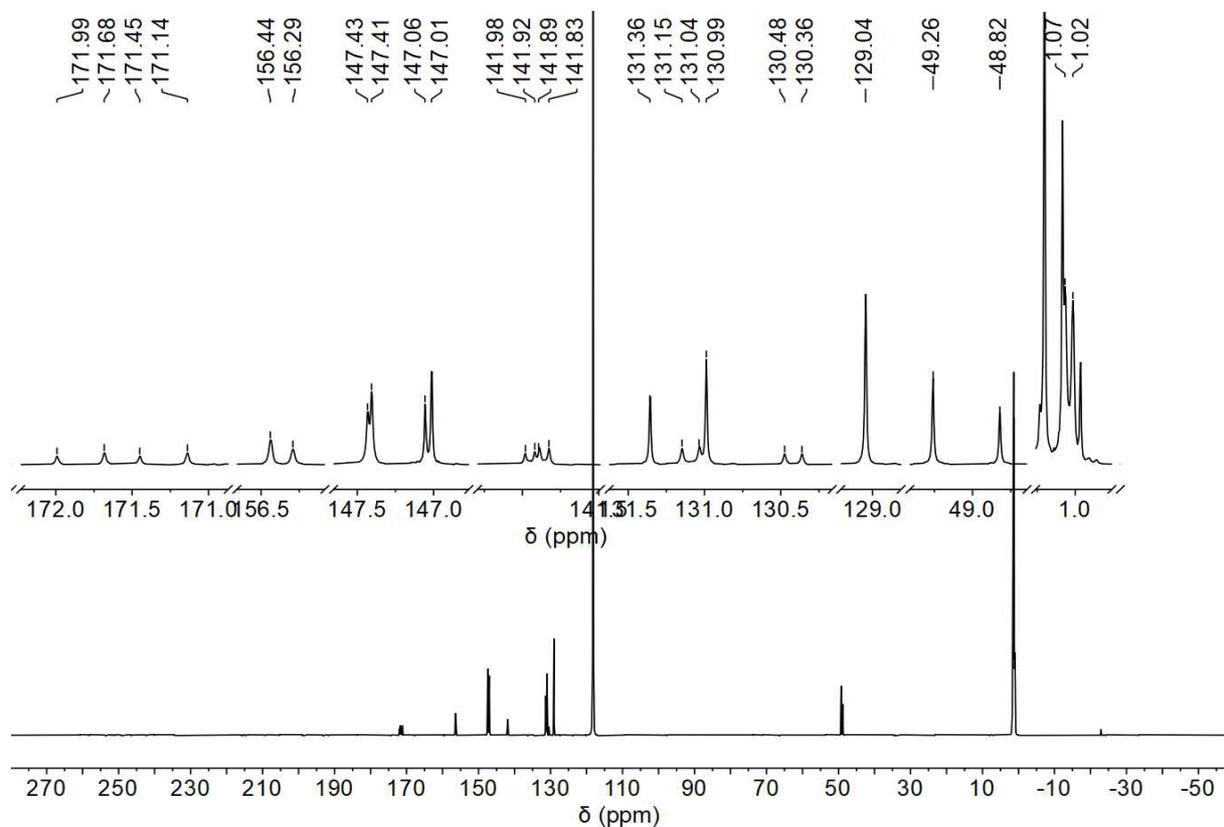


Figure S34: <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) of **16a**.

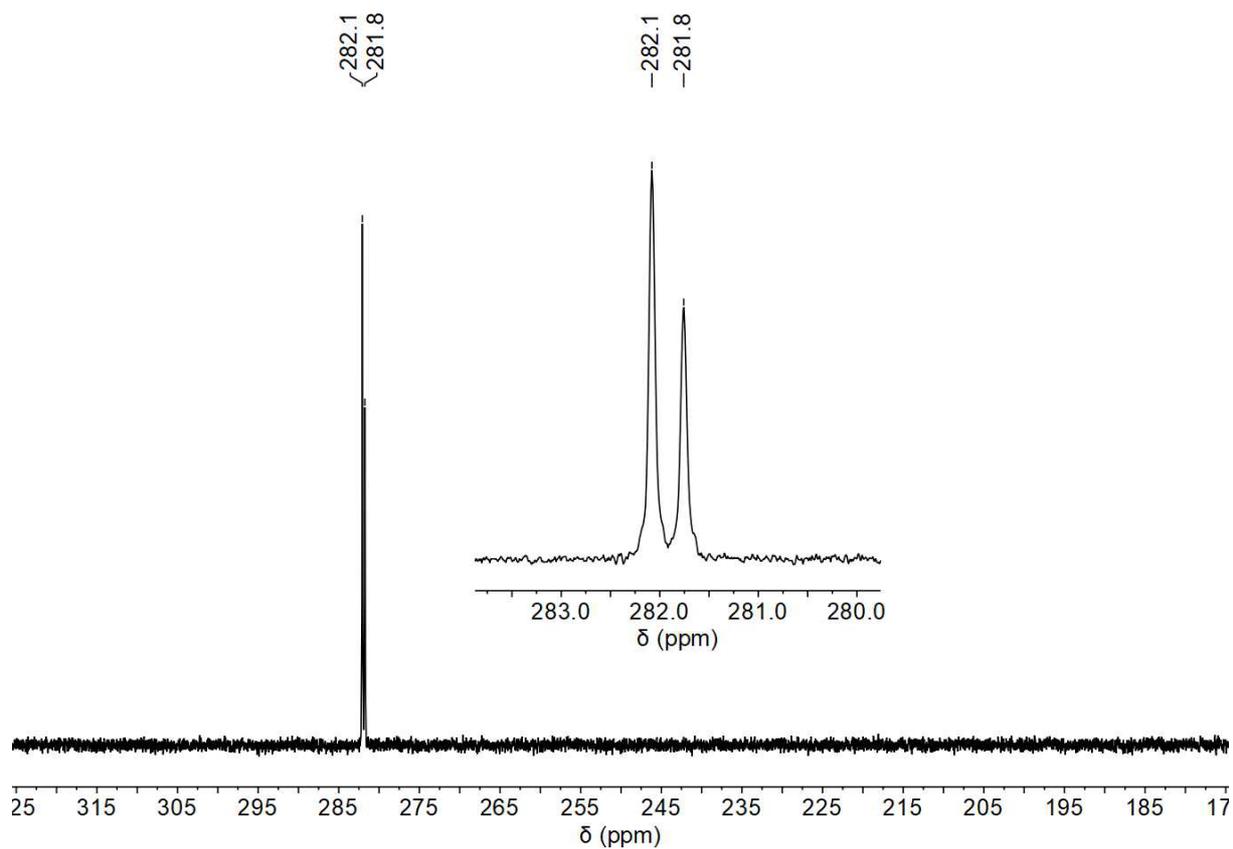
**TMS-PyrrMe<sub>2</sub>-PPI<sub>2</sub> (17)**



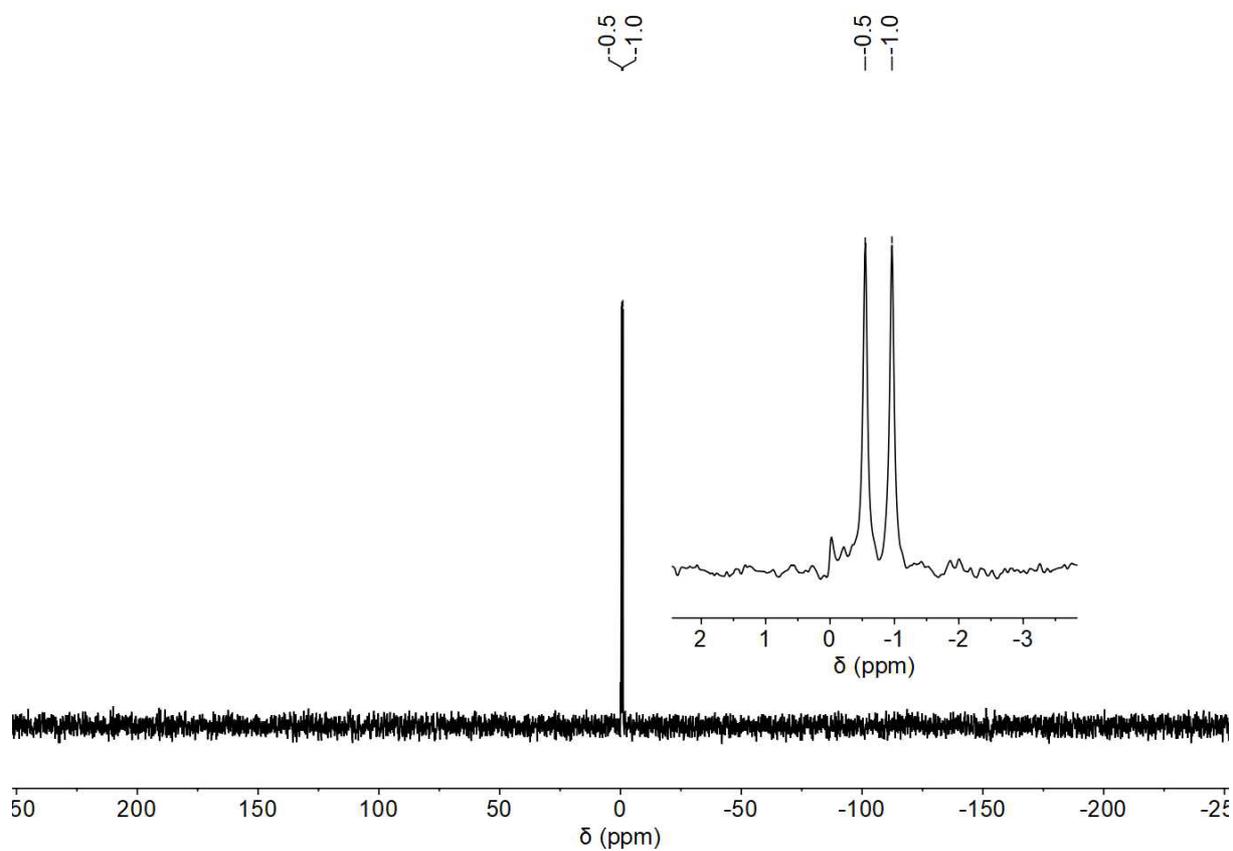
**Figure S35:** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) of bis-methyl pyridinium salt **17**.



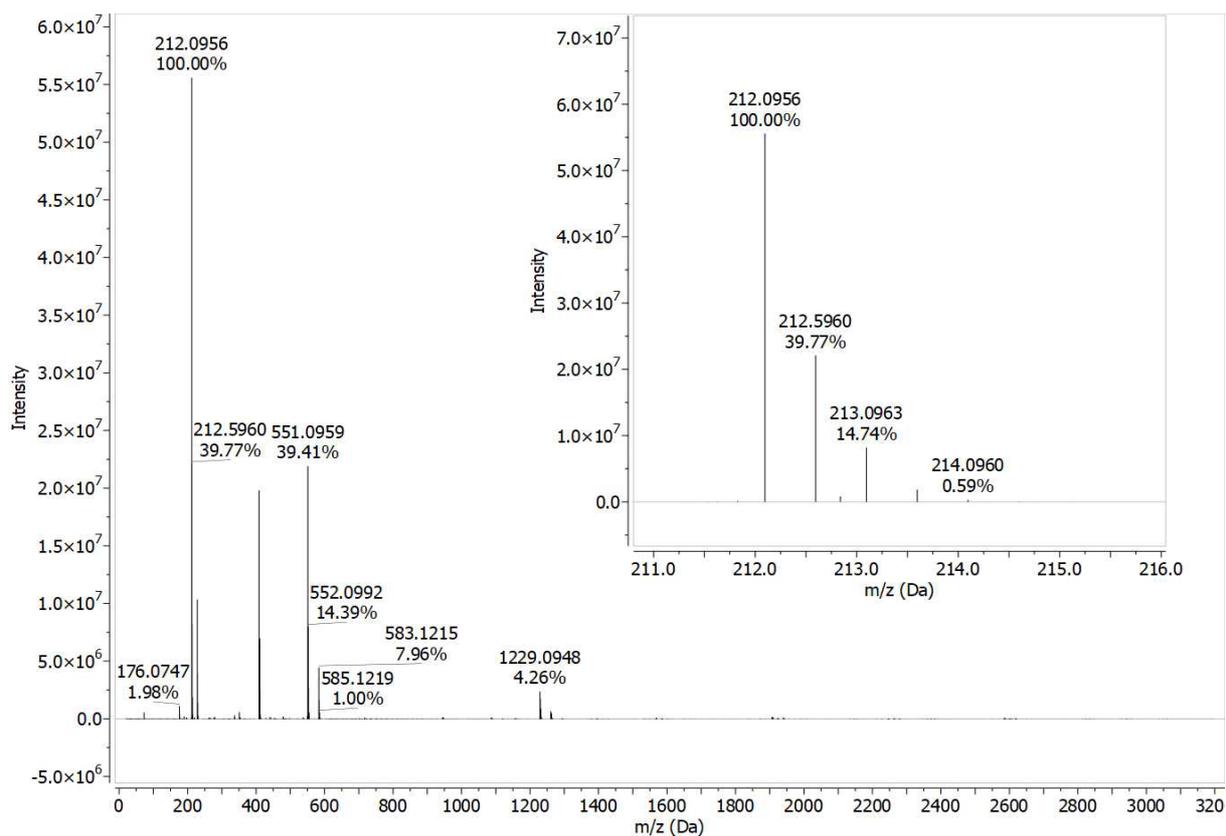
**Figure S36:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>3</sub>CN) of bis-methyl pyridinium salt **17**.



**Figure S37:** <sup>31</sup>P NMR spectrum (CD<sub>3</sub>CN) of bis-methyl pyridinium salt **17**.

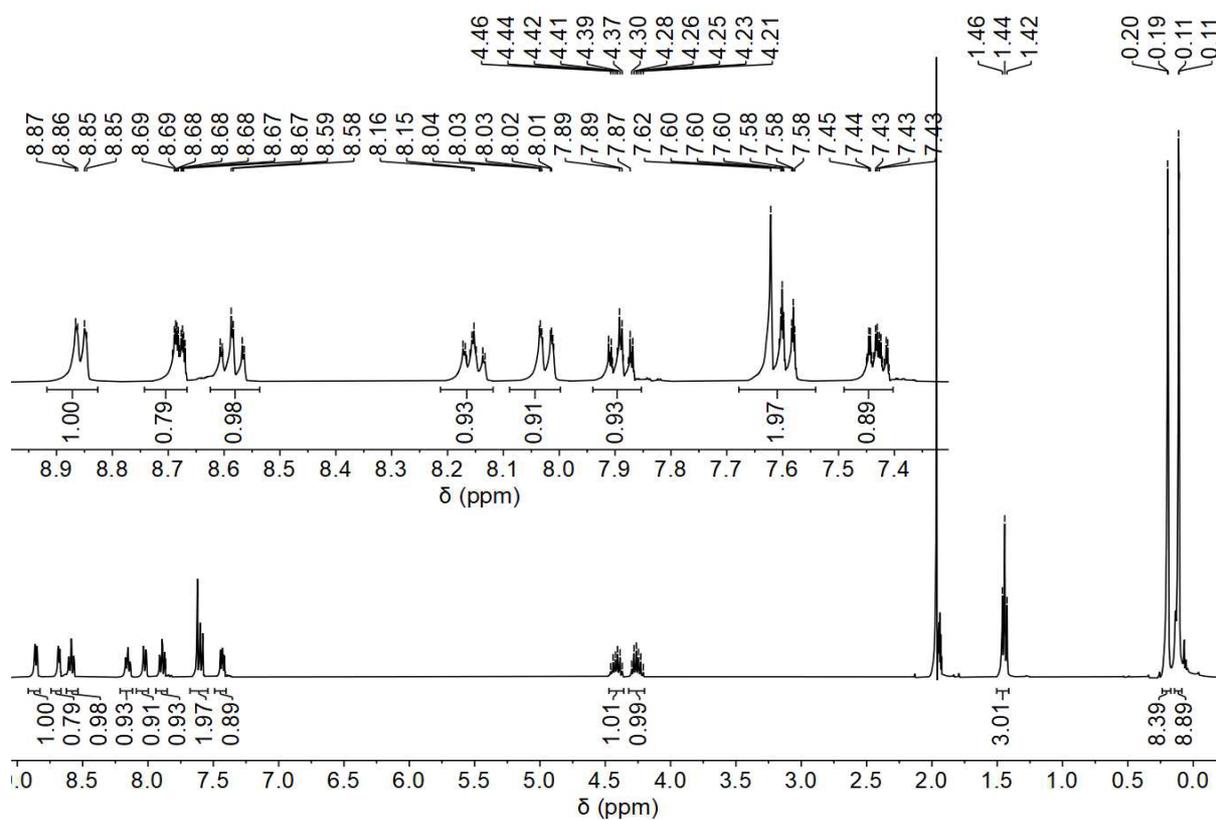


**Figure S38:** <sup>29</sup>Si{<sup>1</sup>H}-DEPT NMR spectrum (CD<sub>3</sub>CN) of bis-methyl pyridinium salt **17**.

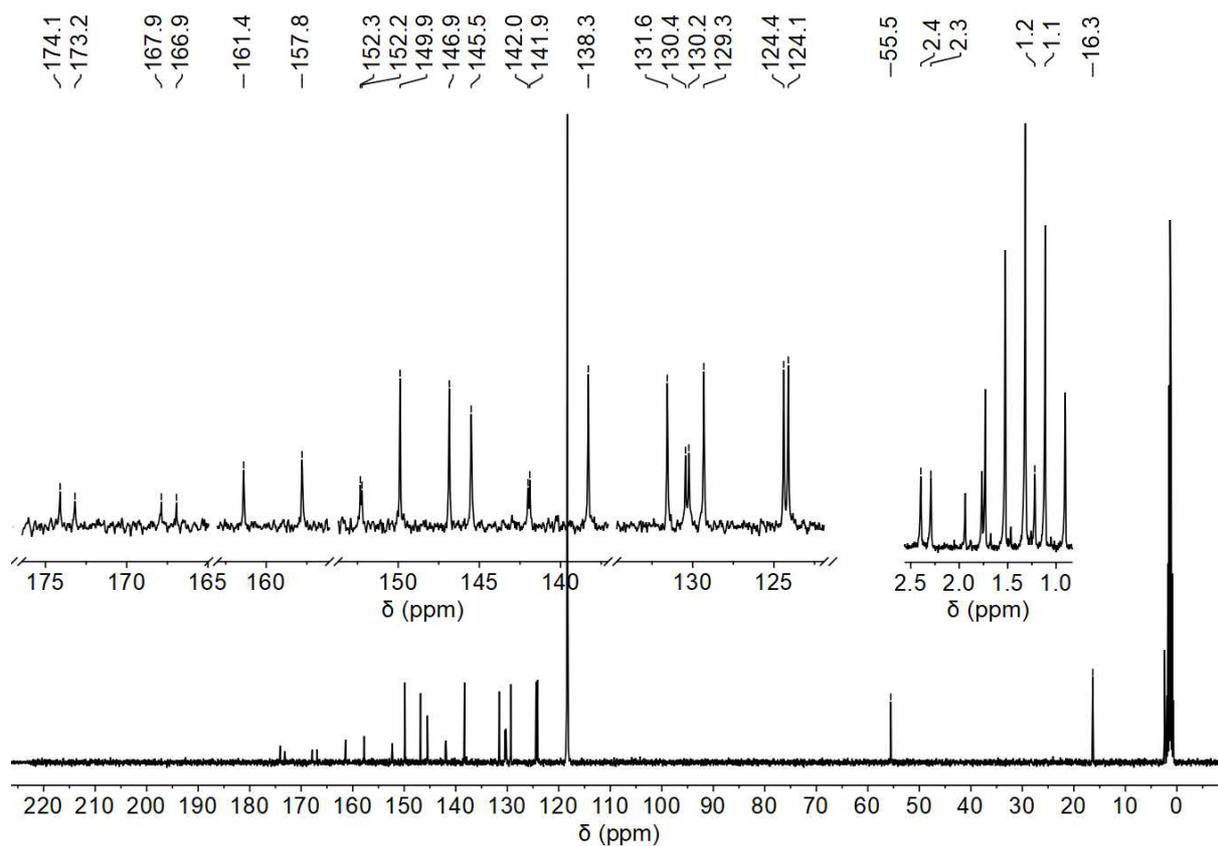


**Figure S39:** HRMS-ESI<sup>+</sup> for of bis-methyl pyridinium salt **17**.  $[M]^{2+} [C_{23}H_{33}N_2PSi_2]^{2+}$ .

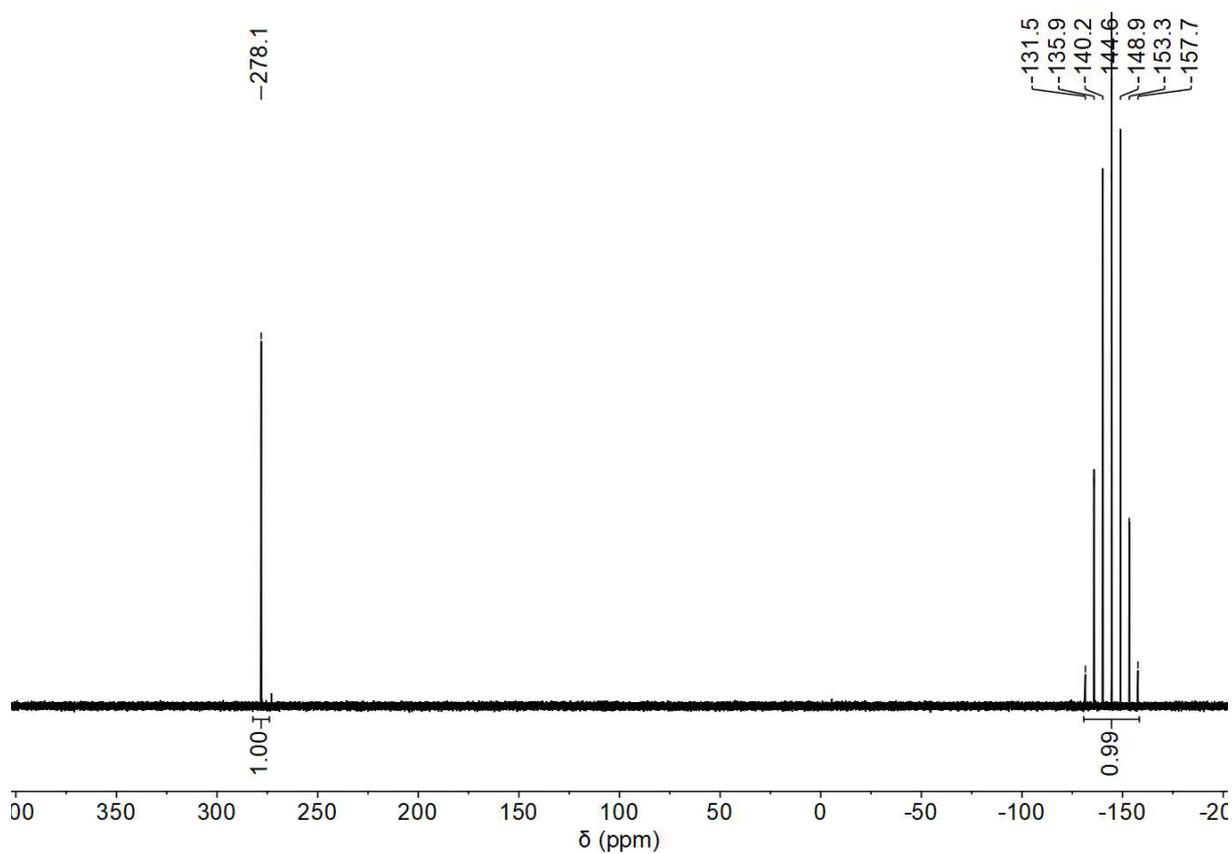
**TMS-PyrrEt-Py-PP[PF<sub>6</sub>] (**18**)**



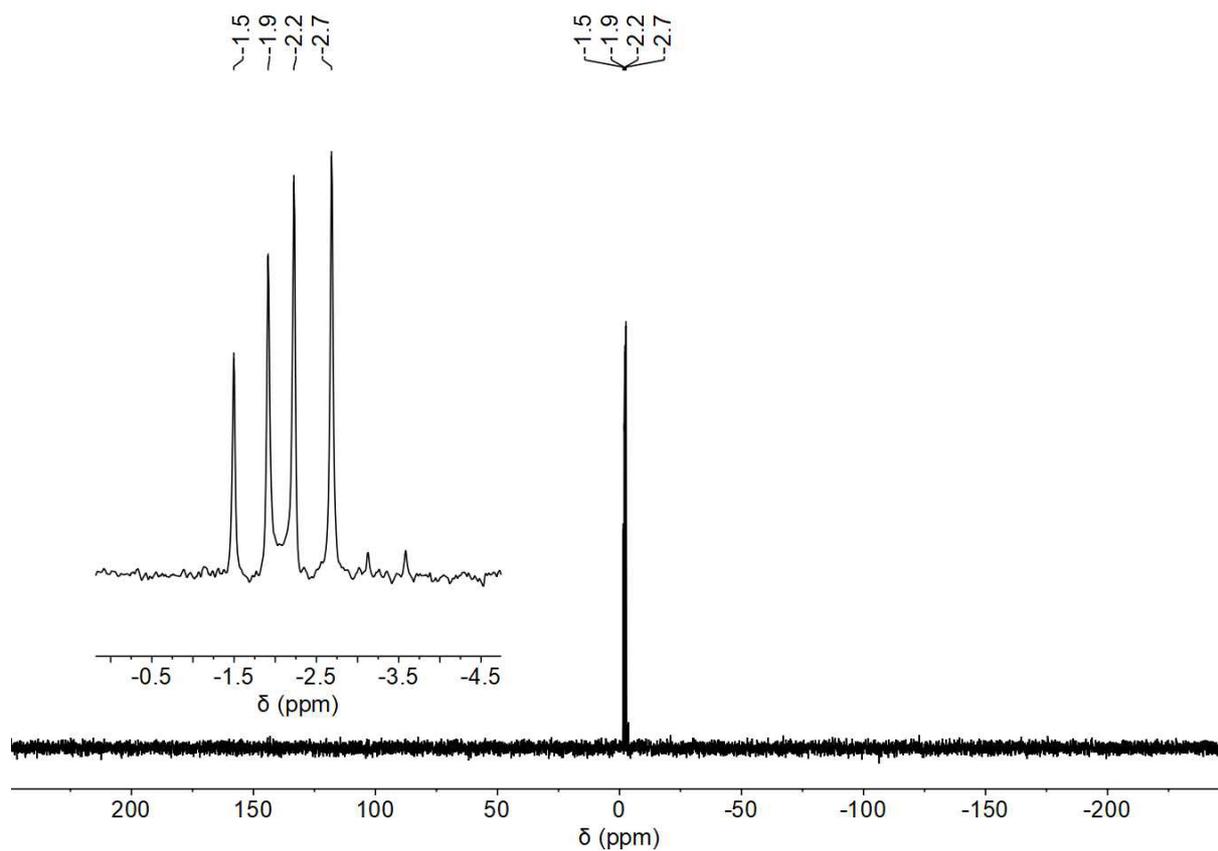
**Figure S40:** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) of mono-ethyl pyridinium salt **18**.



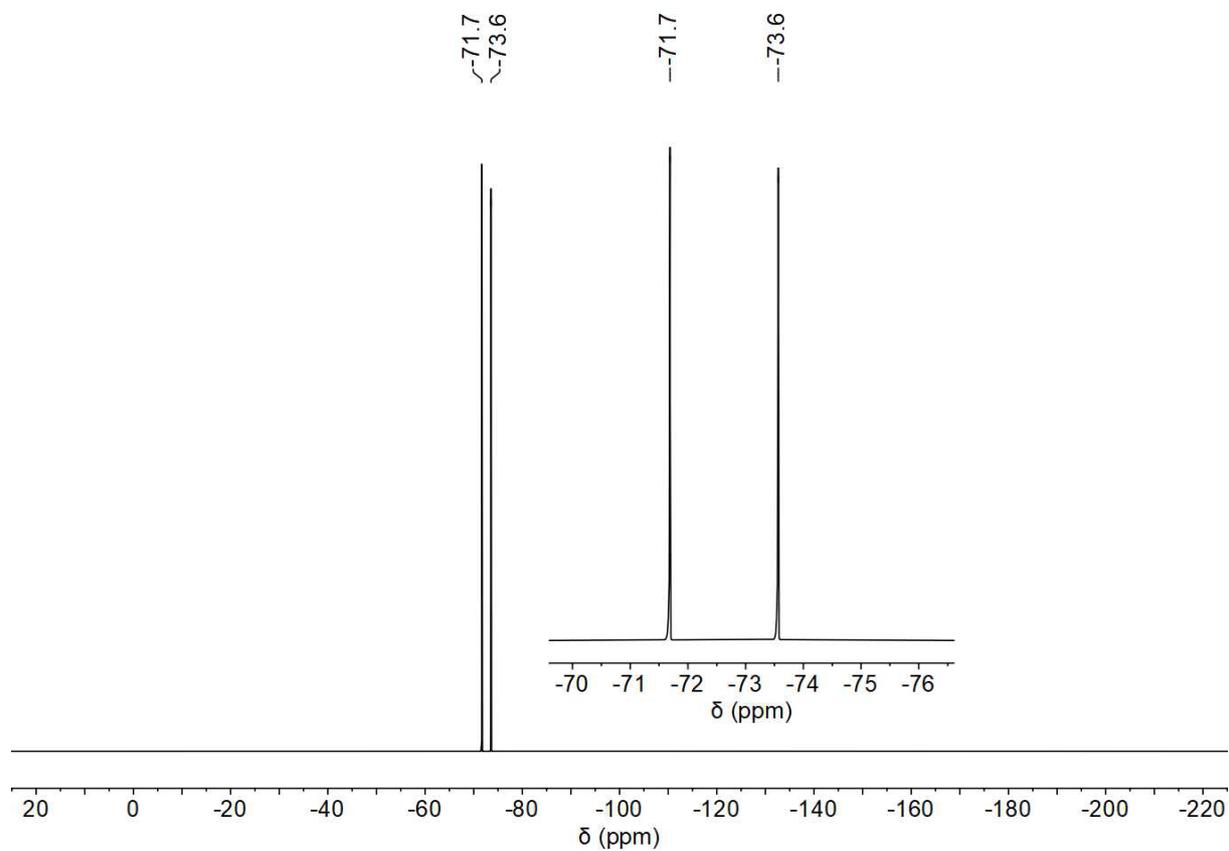
**Figure S41:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of mono-ethyl pyridinium salt **18**.



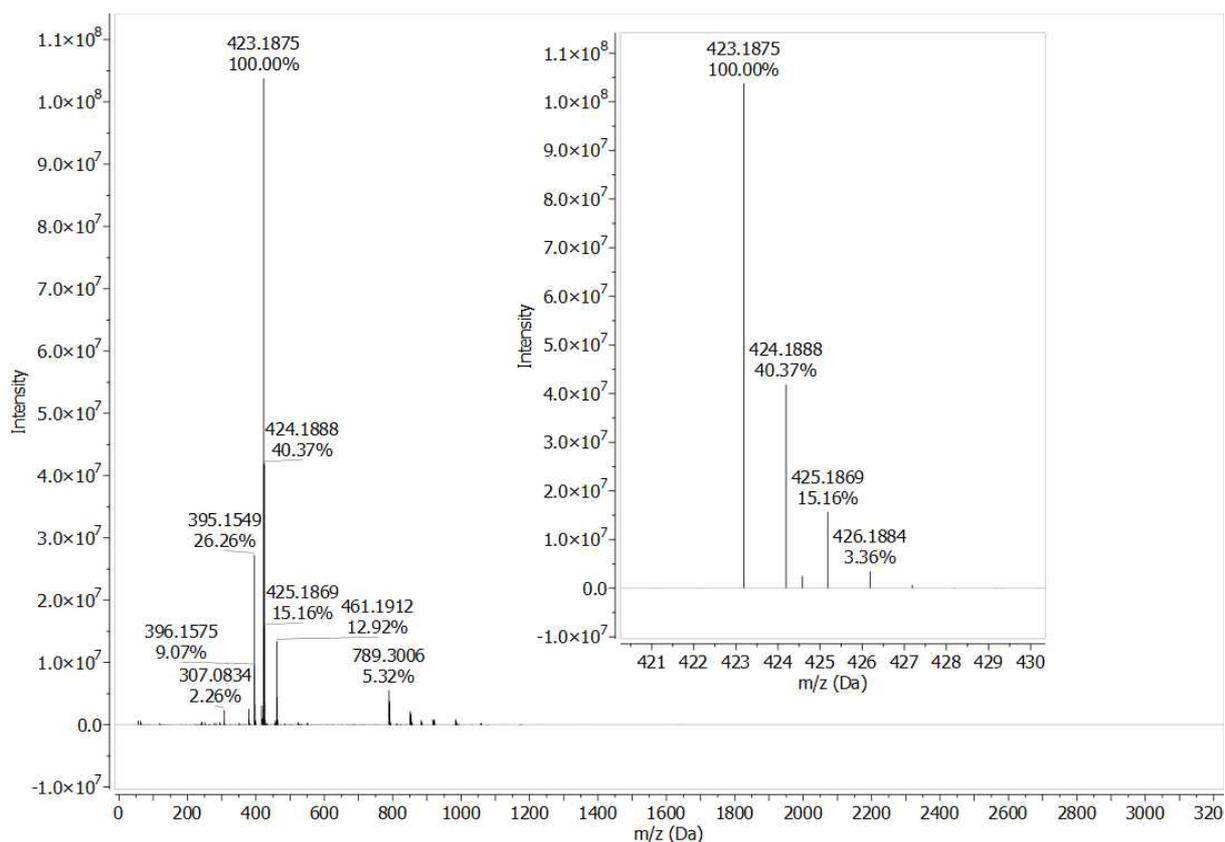
**Figure S42:**  $^{31}\text{P}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of mono-ethyl pyridinium salt **18**.



**Figure S43:**  $^{29}\text{Si}\{^1\text{H}\}$ -DEPT NMR spectrum ( $\text{CD}_3\text{CN}$ ) of mono-ethyl pyridinium salt **18**.

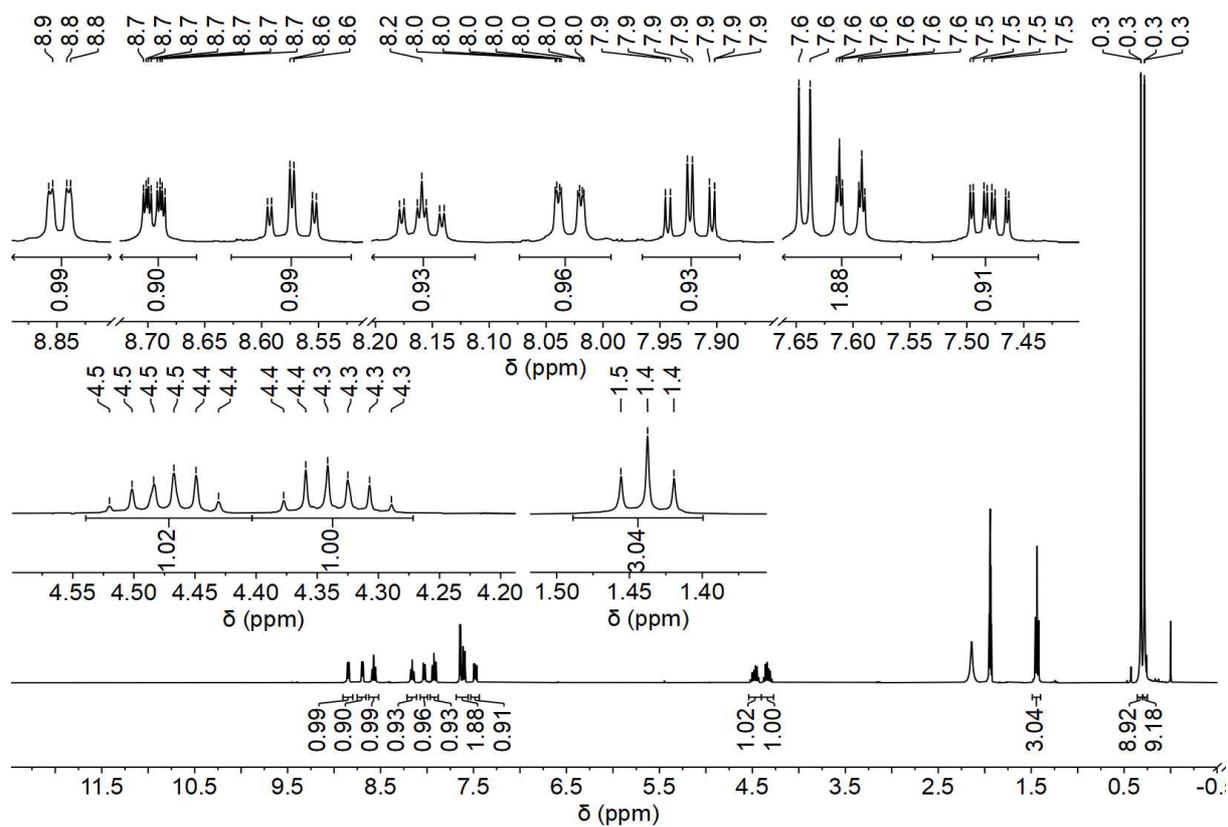


**Figure S44:**  $^{19}\text{F}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of mono-ethyl pyridinium salt **18**.

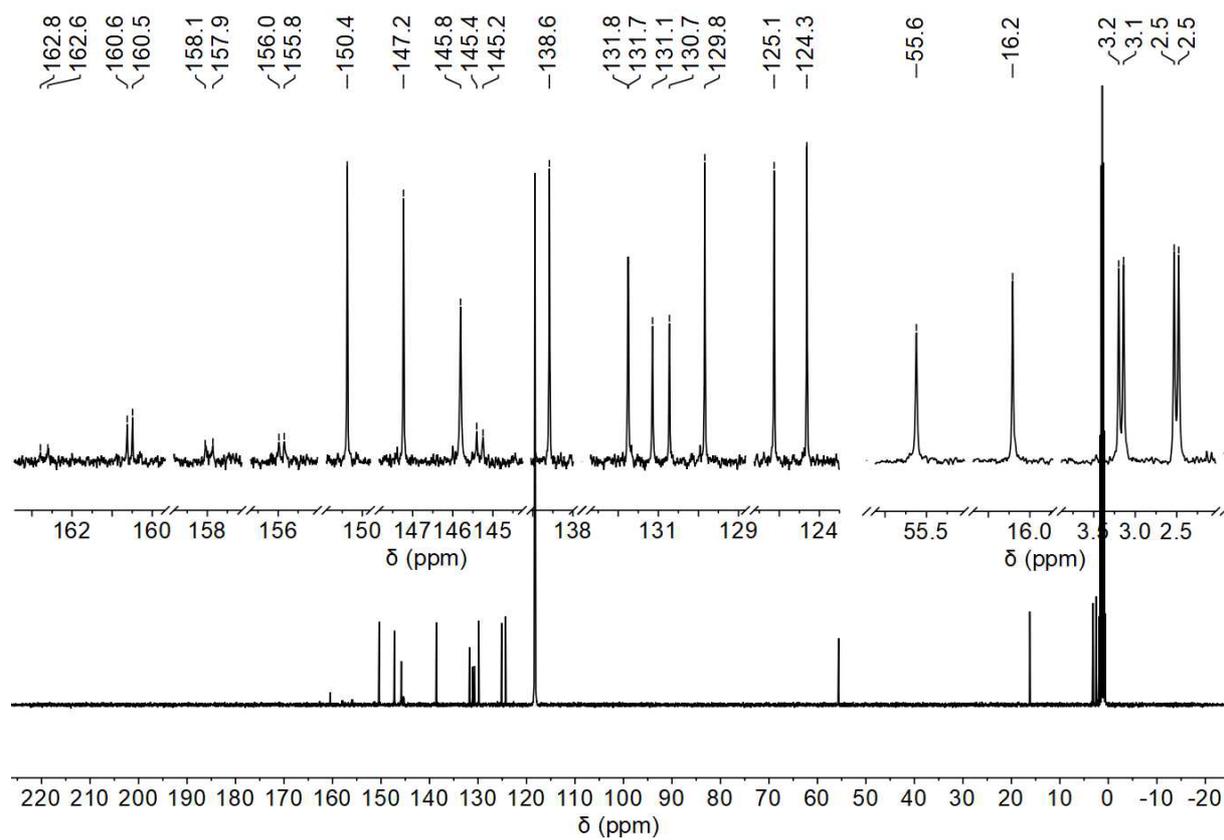


**Figure S45:** HRMS-ESI<sup>+</sup> for mono-ethyl pyridinium salt **18**. [M+H]<sup>+</sup> [C<sub>23</sub>H<sub>32</sub>N<sub>2</sub>PSi<sub>2</sub>]<sup>+</sup>.

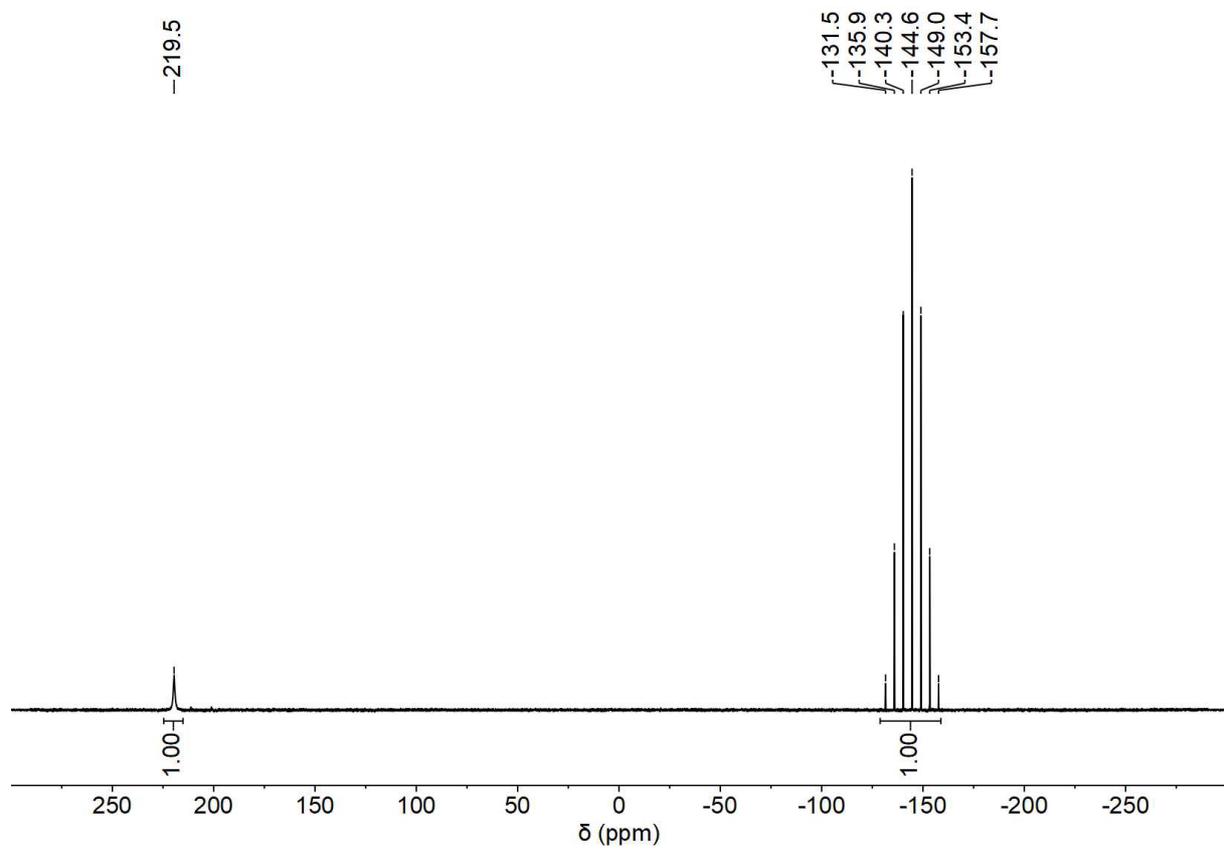
**TMS-PyrrEt-Py-PP-AuCl[PF<sub>6</sub>] (**20**)**



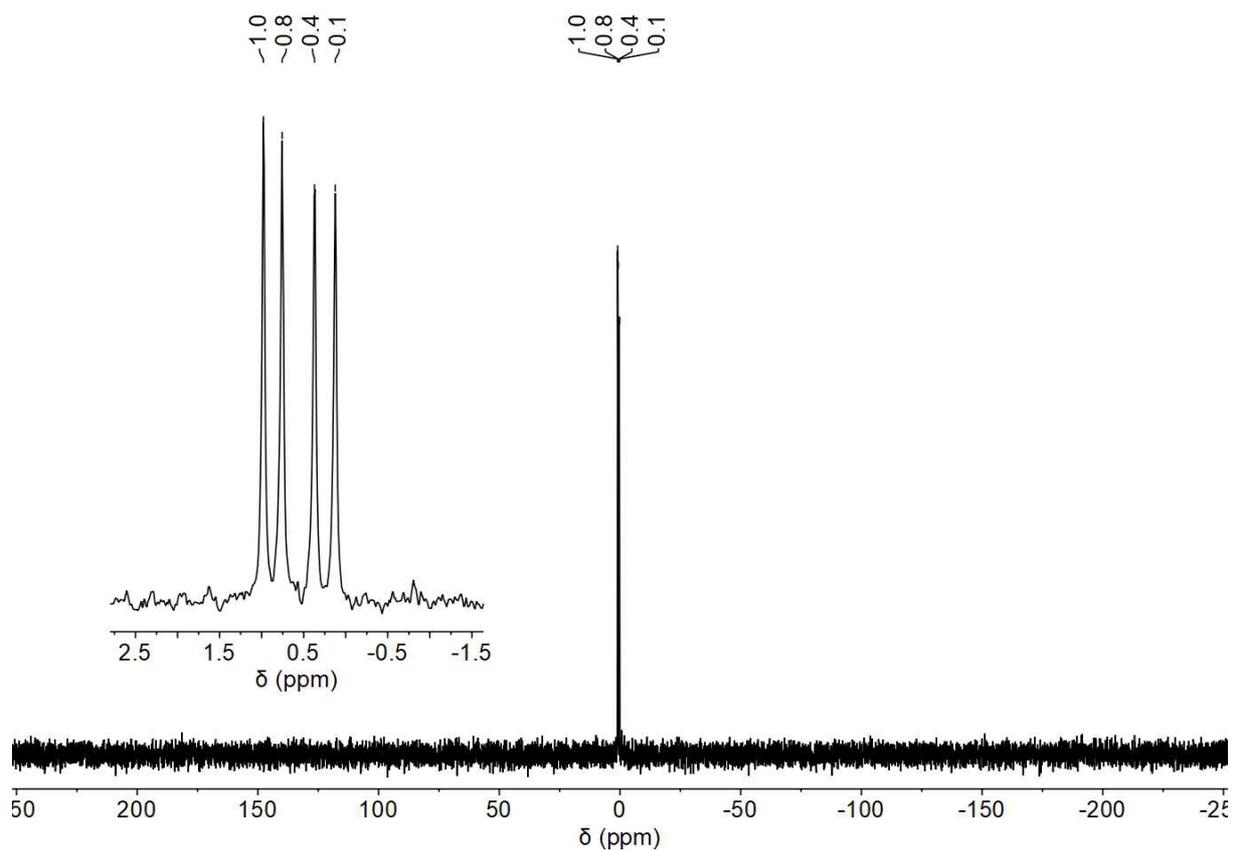
**Figure S46:** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) of gold complex **20**.



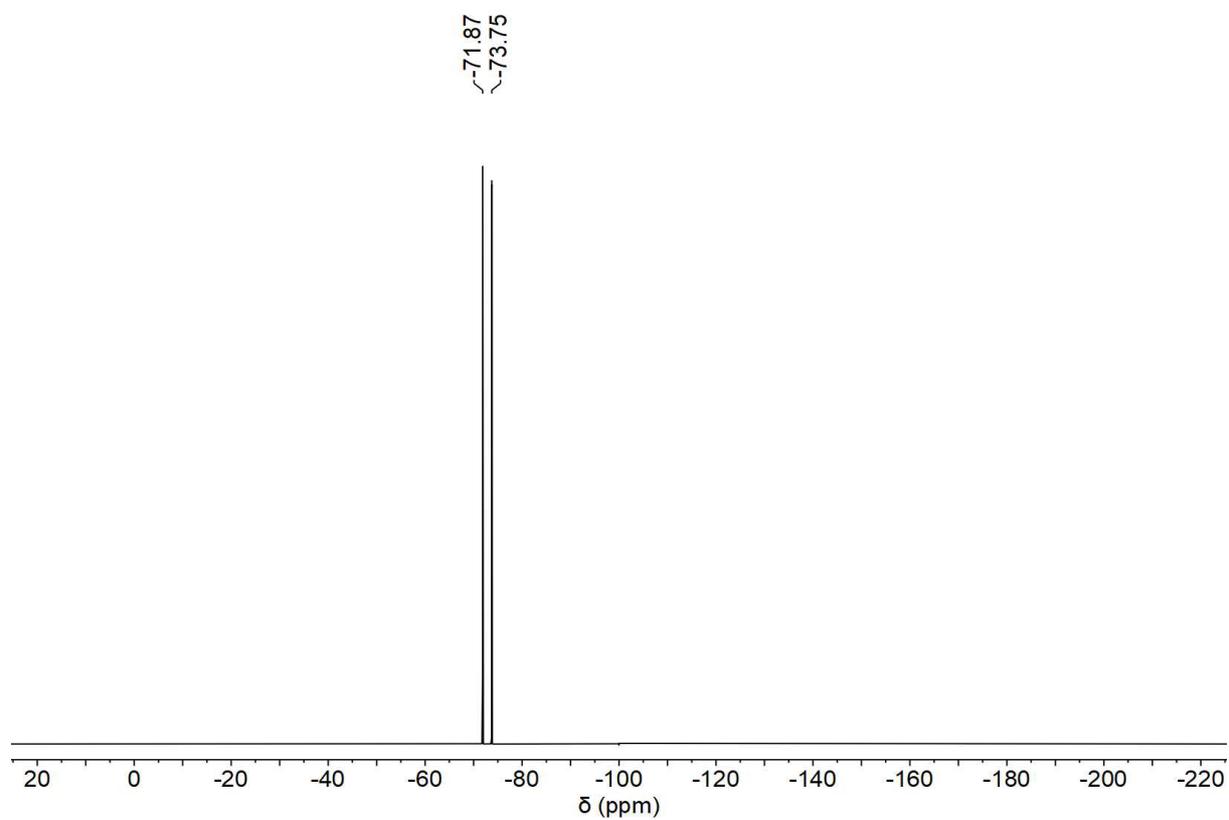
**Figure S47:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of gold complex **20**.



**Figure S48:**  $^{31}\text{P}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of gold complex **20**.

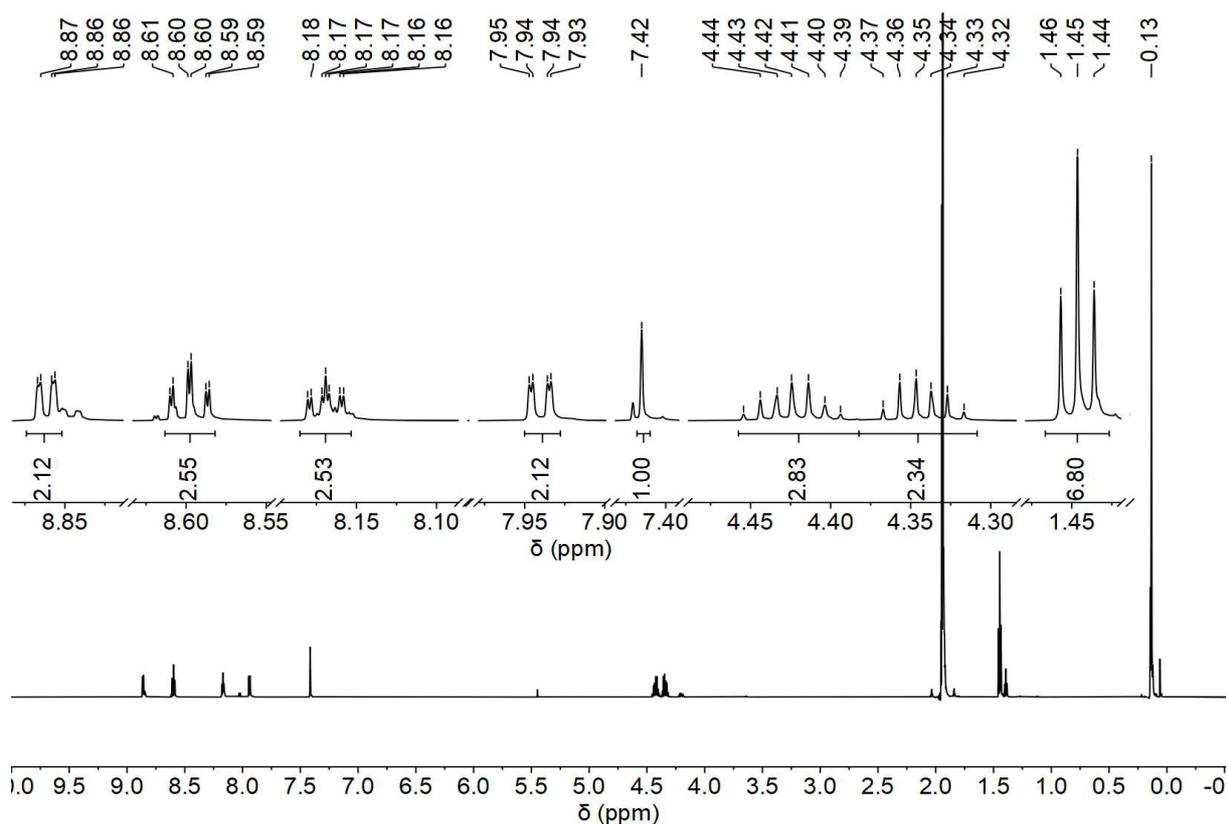


**Figure S49:**  $^{29}\text{Si}\{^1\text{H}\}$ -DEPT NMR spectrum ( $\text{CD}_3\text{CN}$ ) of gold complex **20**.

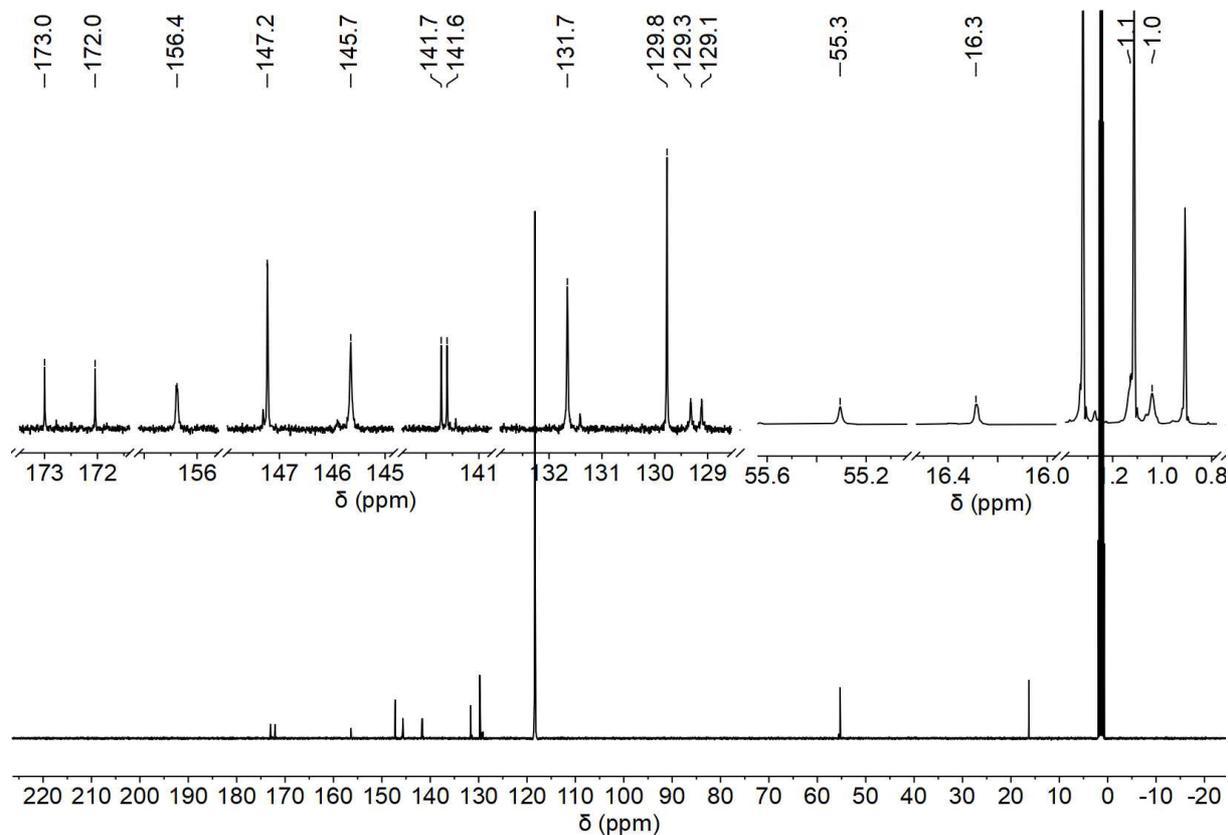


**Figure S50:**  $^{19}\text{F}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of gold complex **20**.

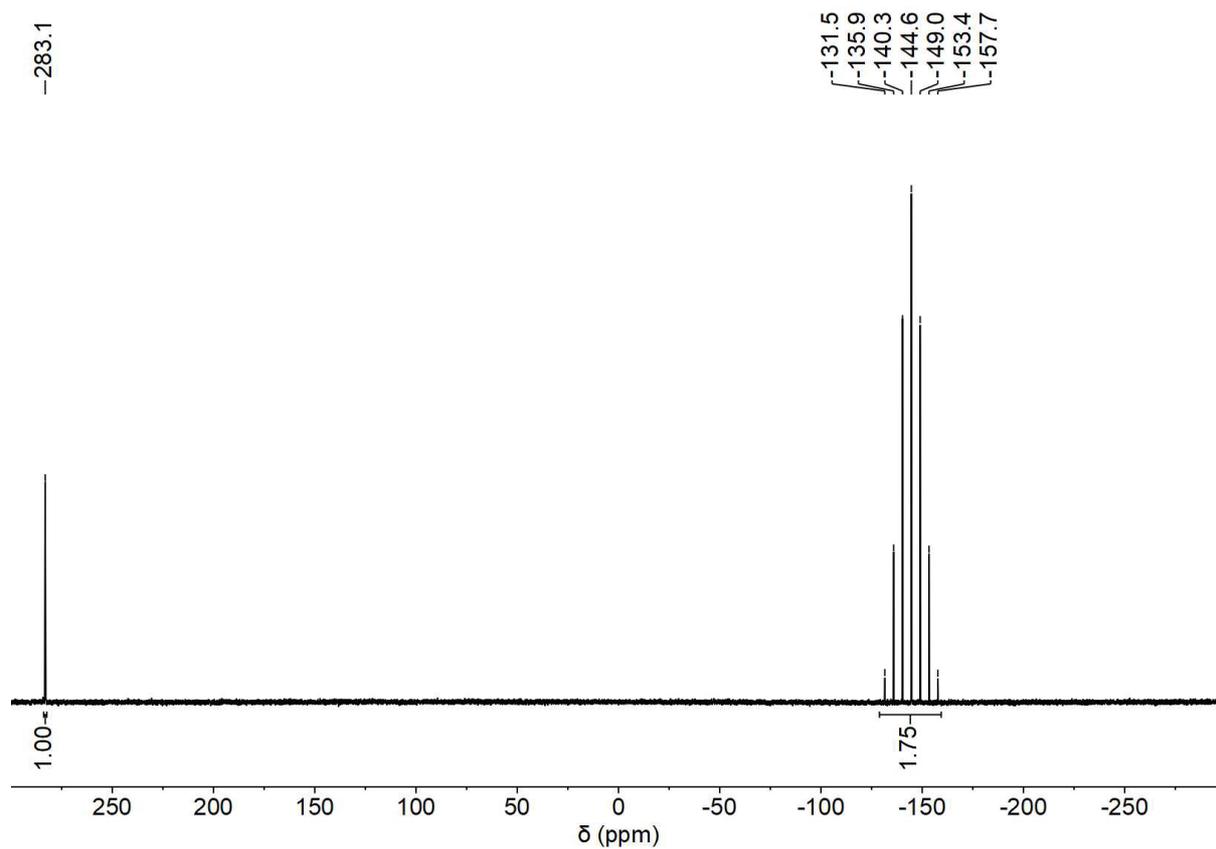
**TMS-PyrrEt<sub>2</sub>-PP[PF<sub>6</sub>]<sub>2</sub> (19)**



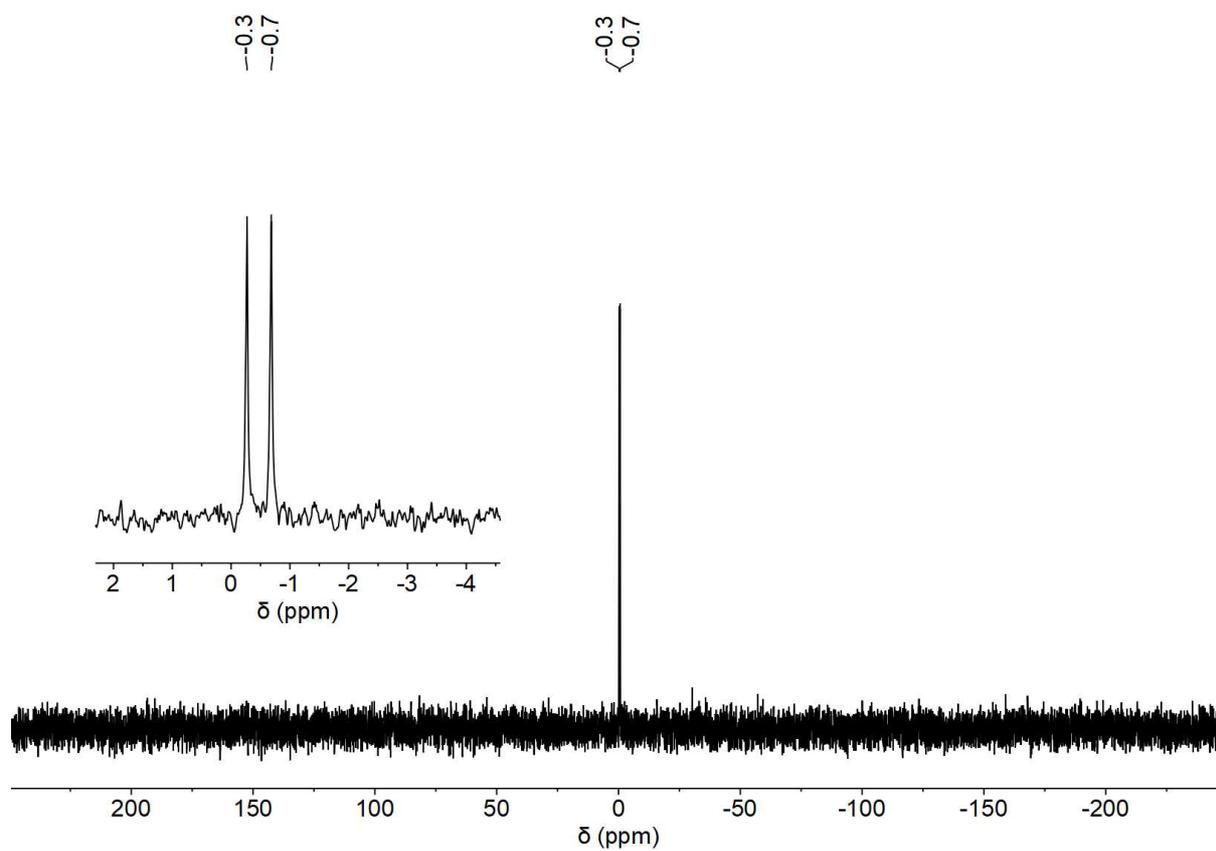
**Figure S51:** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) of bis-ethyl pyridinium salt **19**.



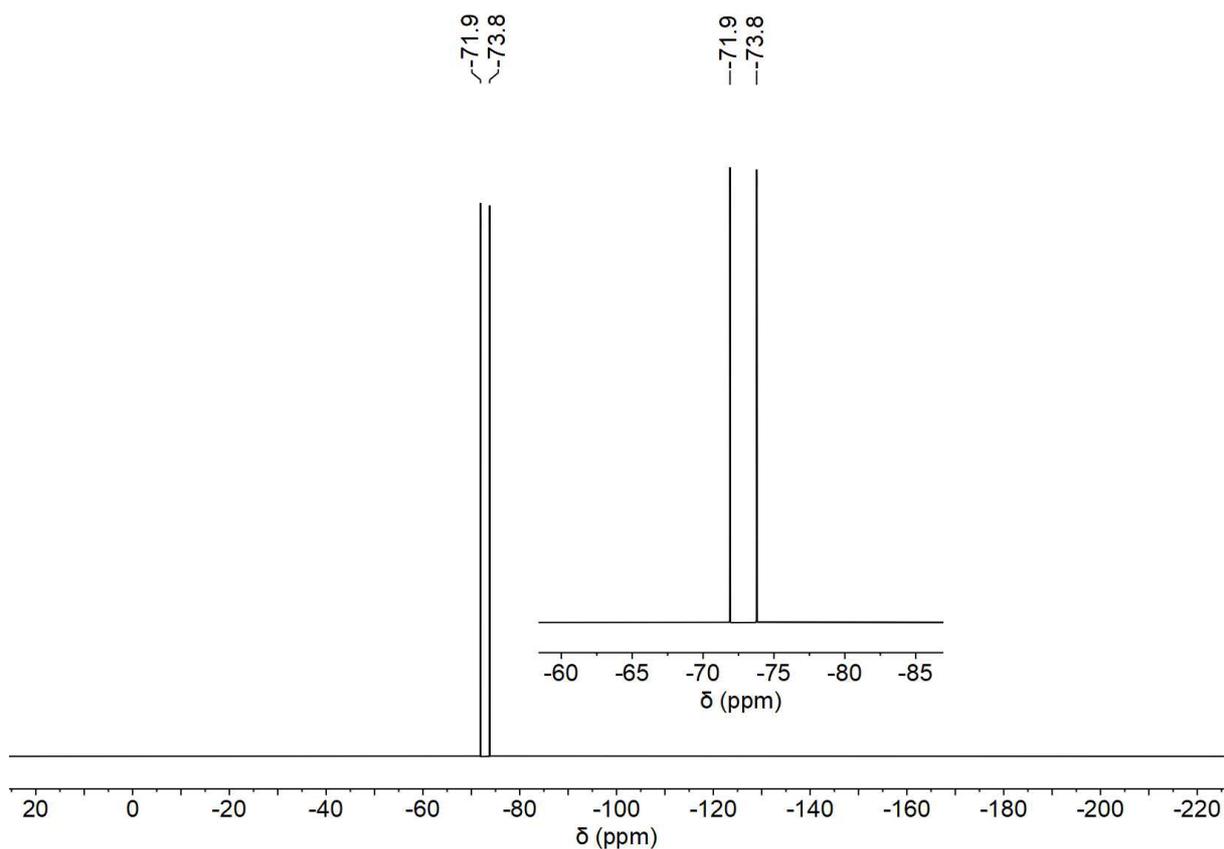
**Figure S52:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>3</sub>CN) of bis-ethyl pyridinium salt **19**.



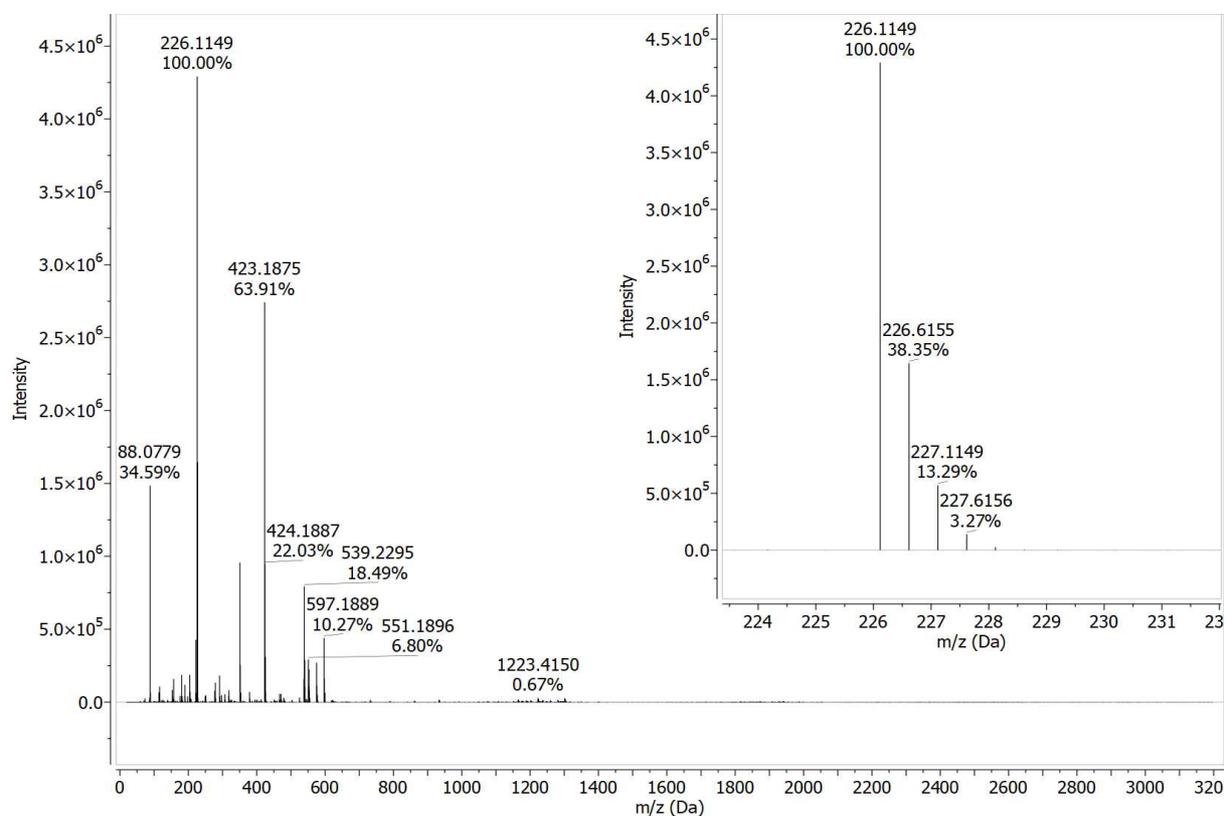
**Figure S53:** <sup>31</sup>P NMR spectrum (CD<sub>3</sub>CN) of bis-ethyl pyridinium salt **19**.



**Figure S54:** <sup>29</sup>Si{<sup>1</sup>H}-DEPT NMR spectrum (CD<sub>3</sub>CN) of bis-ethyl pyridinium salt **19**.

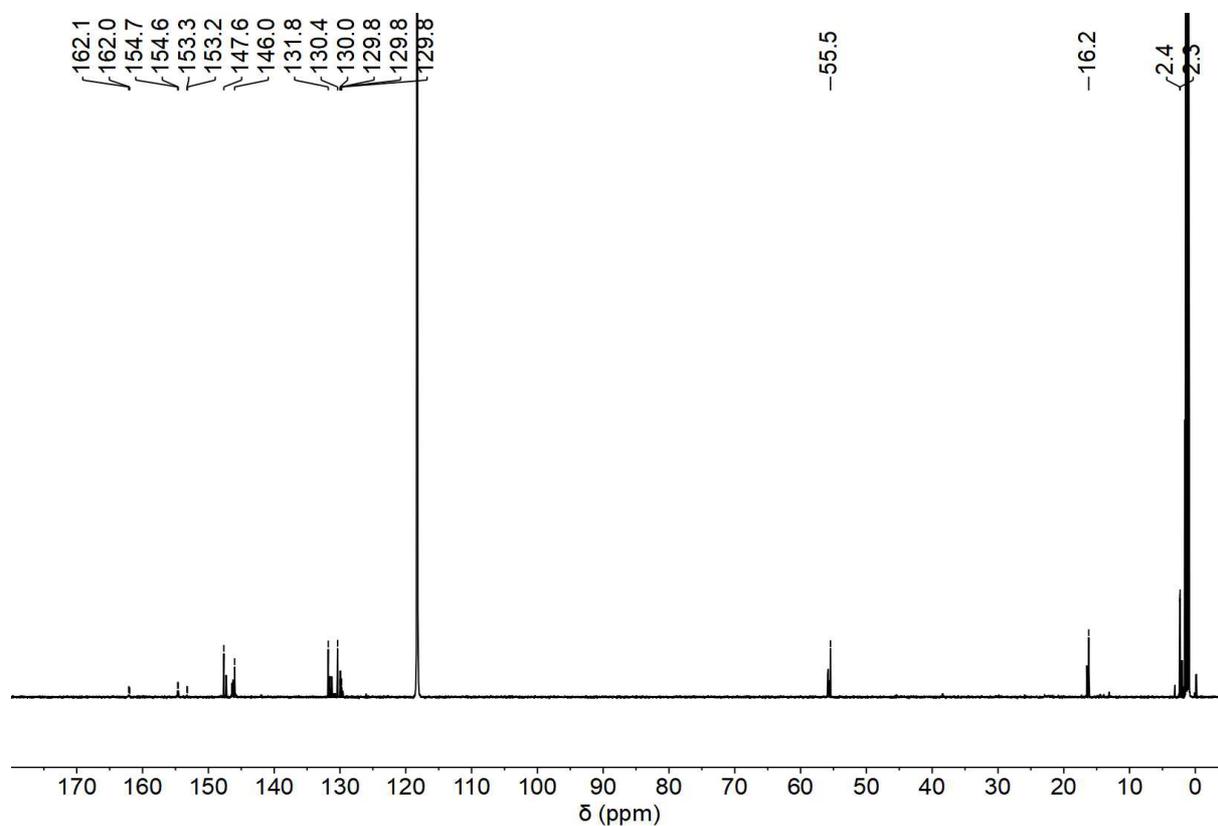
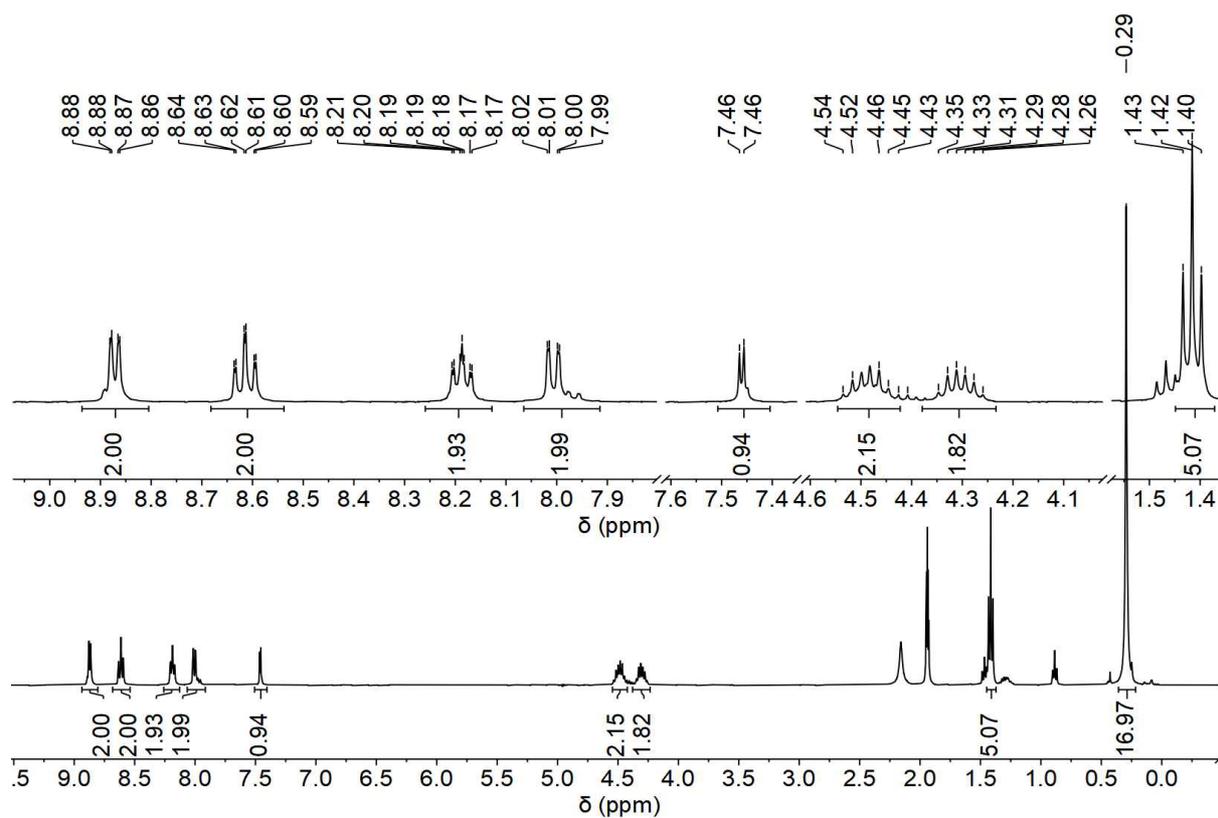


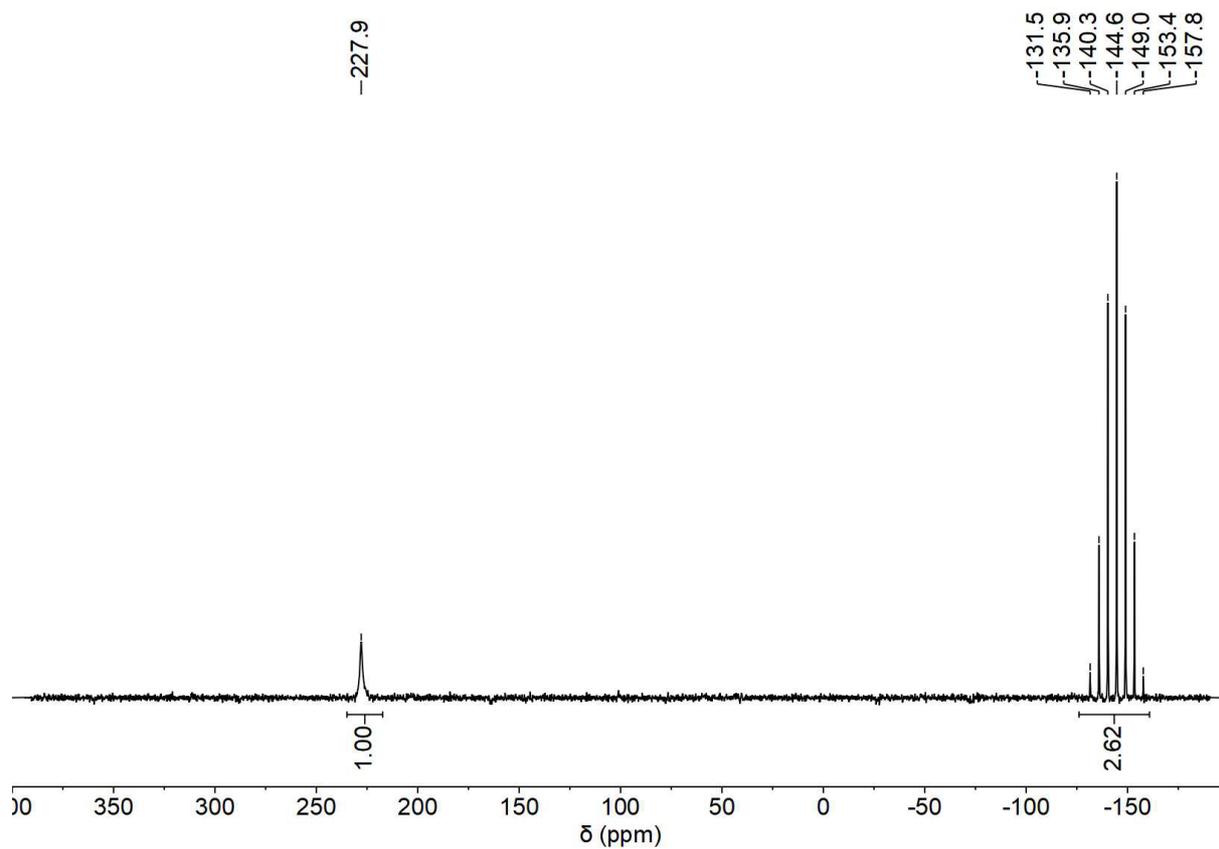
**Figure S55:**  $^{19}\text{F}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of bis-ethyl pyridinium salt **19**.



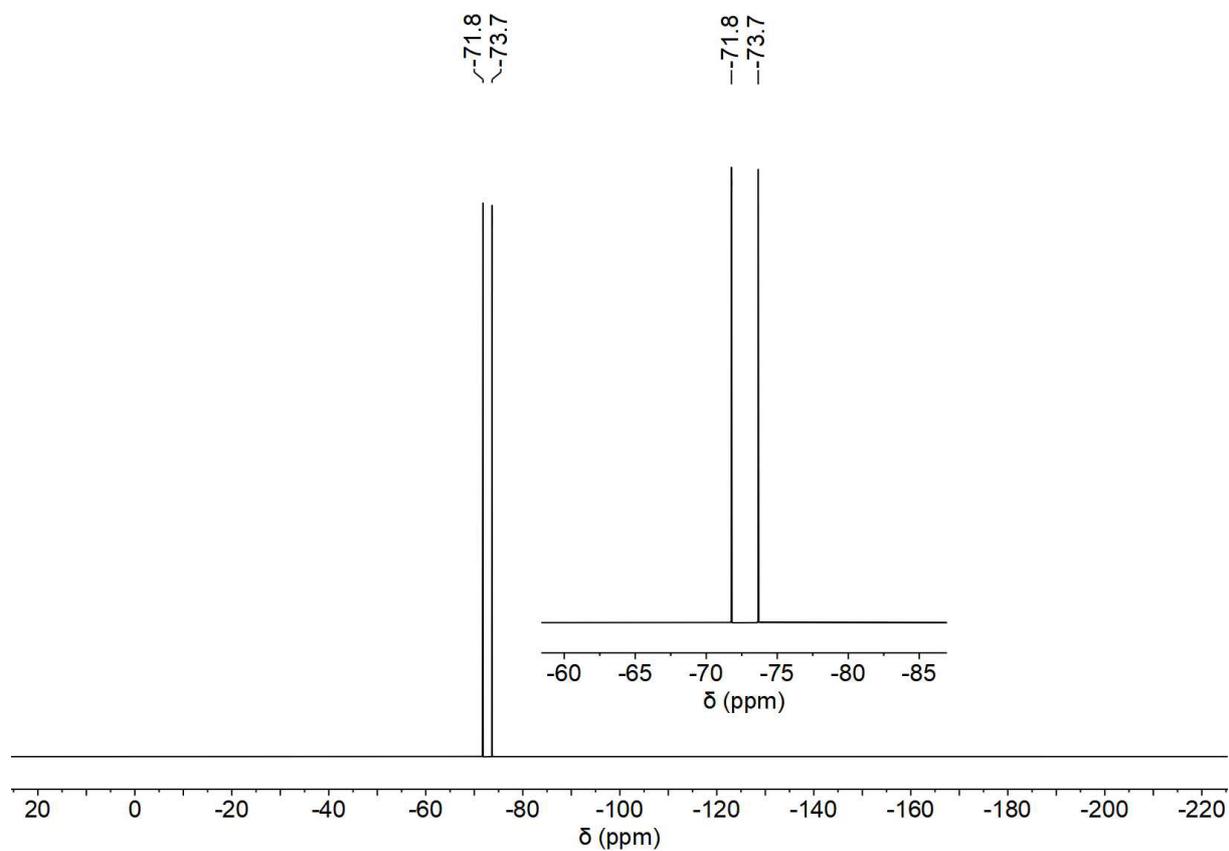
**Figure S56:** HRMS-ESI<sup>+</sup> for bis-ethyl pyridinium salt **19**  $[\text{M}]^{2+} [\text{C}_{25}\text{H}_{37}\text{N}_2\text{PSi}_2]^{2+}$ .

**TMS-PyrrEt<sub>2</sub>-PP-AuCl[PF<sub>6</sub>]<sub>2</sub> (21)**





**Figure S59:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of gold complex **21**.



**Figure S60:**  $^{19}\text{F}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) of gold complex **21**.

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