Supporting Information

Simple synthetic access to [Au(IBiox)Cl] complexes

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Abstract:

A sustainable entryway into chiral and achiral gold-IBiox complexes is reported. The gold complexes were synthesized using a simple, air-tolerant weak base protocol carried out in a green solvent. Their catalytic activity was examined in the hydroamination of alkynes. The steric protection afforded the gold center by these ligands was quantified using the %Vbur model and compared with the most commonly encountered NHCs.

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Computational details

Geometries were optimized with the Gaussian09[1] package using the PBE0 functional.[2] The electronic configuration of the system was described with the triple-ζ TZVP basis set [3] for main group atoms (C, H, N, Cl and O) and the relativistic Stuttgart-Dresden effective core potential with the associated valence triple-ζ basis set for Au.[4] All geometries were confirmed as minimum or transition state through frequency calculations.

Cartesian coordinates of species reported in the context with solvent energies (in a.u.).

[Au(IBiox^{i}Pr)Cl] (3a)

E= -1362.56772834 A.U.

Au	0.000297	1.635964	0.000076
Cl	0.000948	3.932254	-0.000029
O	-1.640575	-3.366408	0.530034
O	1.639469	-3.366827	-0.529838
N	-0.986909	-1.202427	0.353010
N	0.986347	-1.202682	-0.352736
C	-0.000155	-0.352515	0.000135
C	-2.382016	-1.079301	0.746459
H	-2.454305	-0.416898	1.611930
C	-2.640309	-2.544420	1.175424
H	-2.531156	-2.660173	2.256672
H	-3.616271	-2.914682	0.867106
C	-0.637159	-2.531417	0.220672
C	0.636195	-2.531602	-0.220511
C	2.638934	-2.545080	-1.175919
H	2.528804	-2.660496	-2.257116
H	3.615017	-2.915737	-0.868495
C	2.381428	-1.079987	-0.746477
H	2.453796	-0.417359	-1.611767
C	-3.271673	-0.534330	-0.374655
H	-2.847055	0.443552	-0.630912
C	-3.256765	-1.404238	-1.623608
H	-2.244151	-1.545366	-2.008376
H	-3.844886	-0.933457	-2.414167
H	-3.689279	-2.392064	-1.437915
C	-4.686788	-0.312137	0.143025
H	-5.174319	-1.255080	0.411234
H	-5.301193	0.160859	-0.625517
H	-4.697563	0.337864	1.022016
C	3.271522	-0.535693	0.374617
H	2.847254	0.442243	0.631262
C	3.256592	-1.405993	1.623286
H	2.244062	-1.546456	2.008515
H	3.845481	-0.935907	2.413687
H	3.688244	-2.394097	1.437078
C	4.686582	-0.313793	-0.143335
H	5.173777	-1.256813	-0.411903
H	5.301316	0.158824	0.625178
H	4.697335	0.336417	-1.022162

[Au(IBiox^{t}Bu)Cl] (3b)

E= -1441.11477991 A.U.

Au	-0.000548	1.670160	0.000052
Cl	-0.001377	3.968662	0.000240
O	-1.595110	-3.345812	0.632843
O	1.596843	-3.345252	-0.631797
N	-0.995273	-1.175450	0.344919
N	0.996027	-1.175066	-0.344426
C	0.000128	-0.324219	-0.000037
C	-2.380903	-1.088058	0.811395
H	-2.442851	-0.340198	1.604824
C	-2.497547	-2.514051	1.395990
H	-2.181017	-2.532288	2.443010
H	-3.490958	-2.944161	1.306297
C	-0.631249	-2.505600	0.229612
C	0.632641	-2.505378	-0.228654
C	2.498490	-2.513318	-1.395677
H	2.181445	-2.532044	-2.442536

H	3.492149	-2.942923	-1.306338
C	2.381438	-1.087179	-0.811507
H	2.442689	-0.339558	-1.605215
C	-3.435620	-0.756941	-0.272679
C	-3.176683	0.621946	-0.872986
H	-3.129057	1.399190	-0.105840
H	-3.986980	0.878039	-1.560906
H	-2.241250	0.656641	-1.433373
C	-4.802780	-0.724757	0.417370
H	-5.097097	-1.694932	0.825585
H	-5.568936	-0.434305	-0.304930
H	-4.821100	0.008573	1.228988
C	-3.442585	-1.799426	-1.389584
H	-2.476881	-1.844326	-1.899586
H	-4.194343	-1.529821	-2.135367
H	-3.680212	-2.802350	-1.026926
C	3.436416	-0.755193	0.272033
C	3.176901	0.623716	0.872047
H	3.128488	1.400687	0.104665
H	3.987333	0.880525	1.559542
H	2.241682	0.658038	1.432817
C	3.444416	-1.797394	1.389186
H	2.478941	-1.842771	1.899577
H	4.196305	-1.527149	2.134595
H	3.682503	-2.800251	1.026656
C	4.803309	-0.722375	-0.418522
H	5.098061	-1.692475	-0.826591
H	5.569546	-0.431280	0.303435
H	4.820891	0.010753	-1.230333

[Au(IBioxMe$_4$)Cl] (3c)

E= -1284.02164462 A.U.

Au	1.519071	-0.000151	-0.000001
Cl	3.816569	-0.000431	0.000004
O	-3.487427	1.723022	0.008863
O	-3.488011	-1.722028	-0.008948
N	-1.321200	1.048061	0.057068
N	-1.321531	-1.047844	-0.057196
C	-0.473110	-0.000010	-0.000052
C	-1.210175	2.511998	-0.003871
C	-2.670794	2.849580	0.390508
H	-2.752088	2.985704	1.473551
H	-3.055225	3.727643	-0.125400
C	-2.650025	0.673243	0.025080
C	-2.650223	-0.672562	-0.025152
C	-2.671757	-2.848945	-0.390416
H	-2.753124	-2.985234	-1.473432
H	-3.056502	-3.726763	0.125655
C	-1.211026	-2.511840	0.003865
C	-0.213214	3.058109	0.999422
H	-0.432698	2.700191	2.007053
H	-0.249897	4.150105	0.999198
H	0.801288	2.749665	0.739319
C	-0.884230	2.945650	-1.427083
H	0.091960	2.557070	-1.723150
H	-0.854893	4.035910	-1.488150
H	-1.635232	2.578520	-2.130393
C	-0.885269	-2.945540	1.427118
H	0.091483	-2.558166	1.722918
H	-0.857368	-4.035826	1.488441
H	-1.635644	-2.577270	2.130496
C	-0.214138	-3.058244	-0.999321
H	-0.434090	-2.701243	-2.007172
H	-0.250097	-4.150242	-0.998208
H	0.800267	-2.748955	-0.739740

[Au(IBiox6)Cl] (3d)

E= -1517.29310671 A.U.

Au	0.000078	1.529728	0.000022
Cl	0.000277	3.829042	0.000082

N	-1.045088	-1.312157	0.107991
N	1.044966	-1.312250	-0.107911
O	-1.717414	-3.478849	0.090642
O	1.717156	-3.478977	-0.090330
C	-0.000031	-0.464388	-0.000025
C	-0.671017	-2.639241	0.058193
C	0.670806	-2.639294	-0.057938
C	-2.508016	-1.196442	0.127347
C	-2.837196	-2.666720	0.501951
H	-2.957562	-2.767123	1.585526
H	-3.720265	-3.052023	-0.003314
C	2.836908	-2.666972	-0.501958
H	2.957006	-2.767450	-1.585561
H	3.720056	-3.052306	0.003133
C	4.511548	-0.064643	-1.153618
C	2.993882	-0.209508	-1.181114
C	2.507897	-1.196641	-0.127396
C	3.018202	-0.809335	1.263178
C	4.531599	-0.625971	1.291577
C	4.996377	0.358918	0.226806
H	2.531383	0.762255	-0.976067
H	2.641841	-0.526982	-2.167258
H	4.987303	-1.013164	-1.435656
H	4.815438	0.665584	-1.907977
H	2.528377	0.130161	1.540118
H	2.701723	-1.564625	1.989892
H	4.832363	-0.287161	2.286630
H	5.031632	-1.590517	1.137082
H	4.599970	1.354991	0.455351
H	6.086714	0.442409	0.238416
C	-4.511678	-0.064324	1.153385
C	-2.994019	-0.209225	1.180993
C	-3.018210	-0.809112	-1.263259
C	-4.531614	-0.625856	-1.291754
C	-4.996498	0.359093	-0.227078
H	-2.531447	0.762499	0.975942
H	-2.642091	-0.526679	2.167185
H	-4.987447	-1.012814	1.435517
H	-4.815598	0.665979	1.907660
H	-2.528426	0.130435	-1.540096
H	-2.701603	-1.564331	-1.989994
H	-4.832366	-0.287169	-2.286851
H	-5.031577	-1.590424	-1.137171
H	-4.600186	1.355180	-0.455717
H	-6.086845	0.442484	-0.23869

The DFT optimized structure of Au-IBiox complexes 3a-d shows linear geometry in all complexes and the bond lengths are similar compared with X-ray molecular structure for 3a-3d with Au-C_{NHC} bonds of 1.99 Å and Au-Cl bonds of 2.30 Å. The Au-C_{NHC} and Au-Cl bond lengths in the optimized 3d-DFT geometry are found the same as in 3b-DFT. In case of complex 3d the largest deviation between X-ray data and optimized geometries was noticed.

Table S1. Selected bond lengths (Å) and angles (°) for each complex from DFT optimized structures.

Complex	C_{NHC}-Au	Au-Cl	C_{NHC}-Au-Cl
3a-DFT	1.988	2.296	180.0
3b-DFT	1.994	2.299	180.0
3c-DFT	1.992	2.298	180.0
3d-DFT	1.994	2.299	180.0

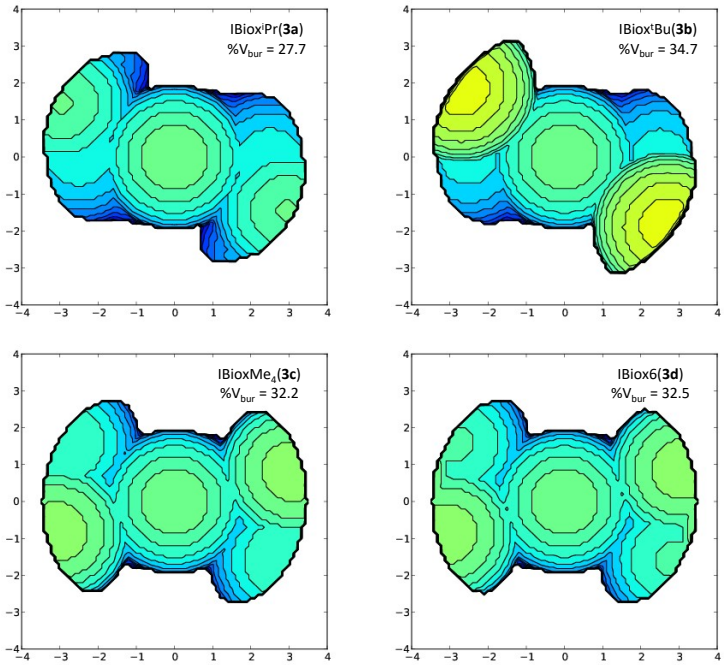
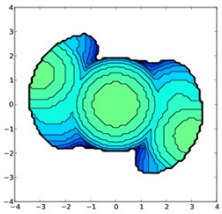


Figure S1. Steric maps and buried volumes of IBiox ligands in [Au(IBiox)Cl] complexes from DFT optimized geometries.

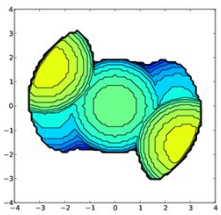
X-ray Crystallography

Crystals that were of suitable quality for single crystal X-ray diffraction analysis were obtained in all cases by slow vapor diffusion of the antisolvent (pentane) into saturated solutions of the complexes (in dichloromethane) at 4 °C. 2238228-2238230, 2253267 **3a-d** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

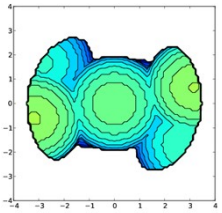
FigureS2. X-ray molecular structures of complexes **3a-d** are presented (2238228-2238230, 2253267) showing thermal displacement ellipsoids at the 30% probability level (**3a**) and at the 60% probability level (**3b-d**), hydrogen atoms are omitted for clarity.



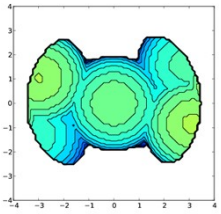
IBiox^{i}Pr (**3a**)
$\%V_{bur}$ = 28.4



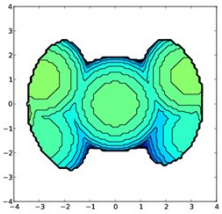
IBiox^{t}Bu (**3b**)
$\%V_{bur}$ = 35.3



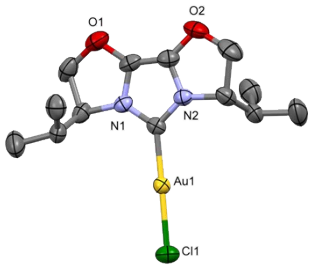
IBioxMe$_4$ (**3c**)
$\%V_{bur}$ = 31.8



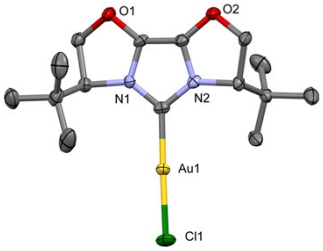
IBiox6 (**3d-1**)
$\%V_{bur}$ = 32.7



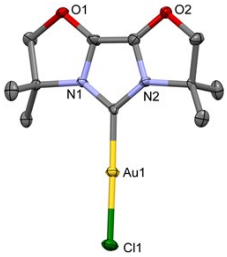
IBiox6 (**3d-2**)
$\%V_{bur}$ = 32.6



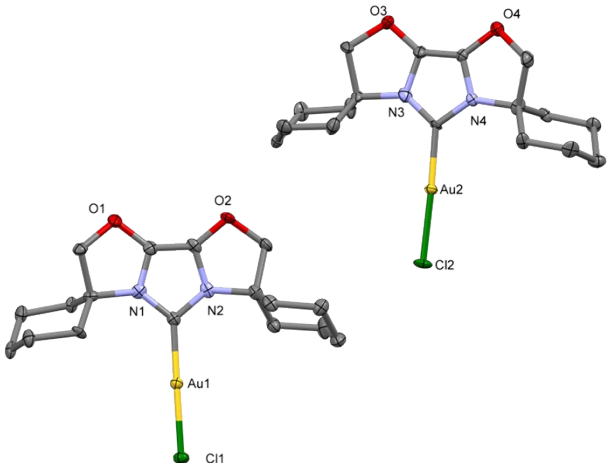
3a



3b



3c



3d

Figure S3. Steric maps and buried volumes of IBiox ligands (including two non-equivalent molecules in unit cell for the complex 3d) [Au(IBiox)Cl] complexes: NHC structures were extracted from crystal structures (r = 3.5 Å, d = 2.0 Å, Bondi radii scaled by 1.17) to perform the calculations.

References

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3 F. Weigend, F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2003, **119**, 12753–12762.

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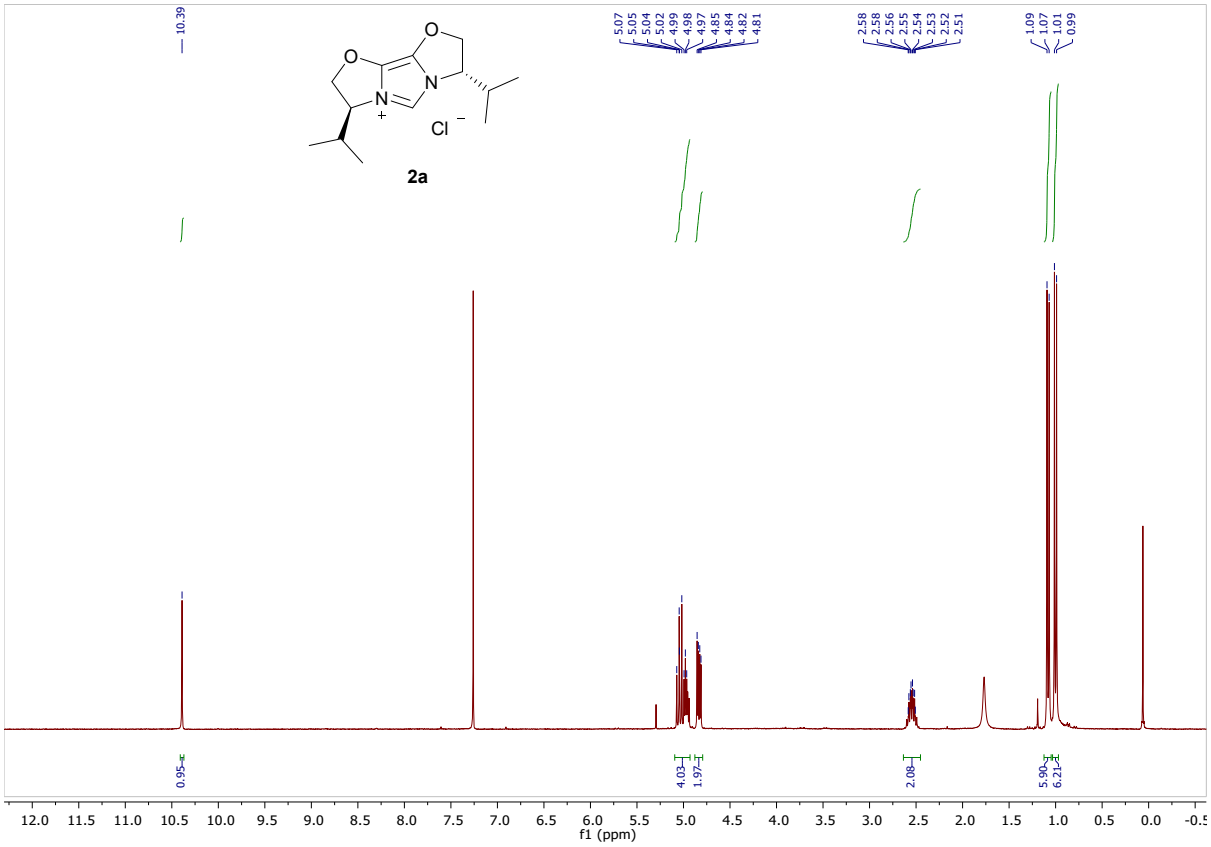
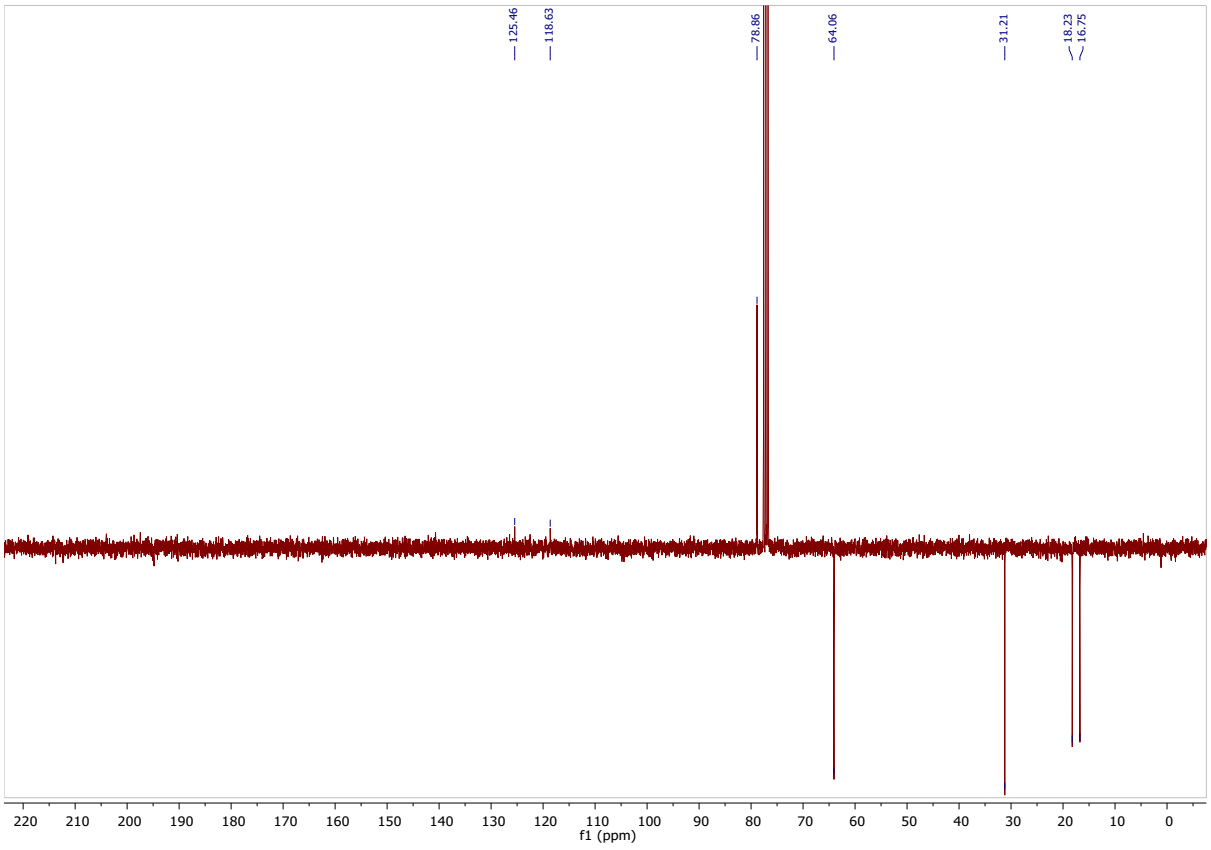
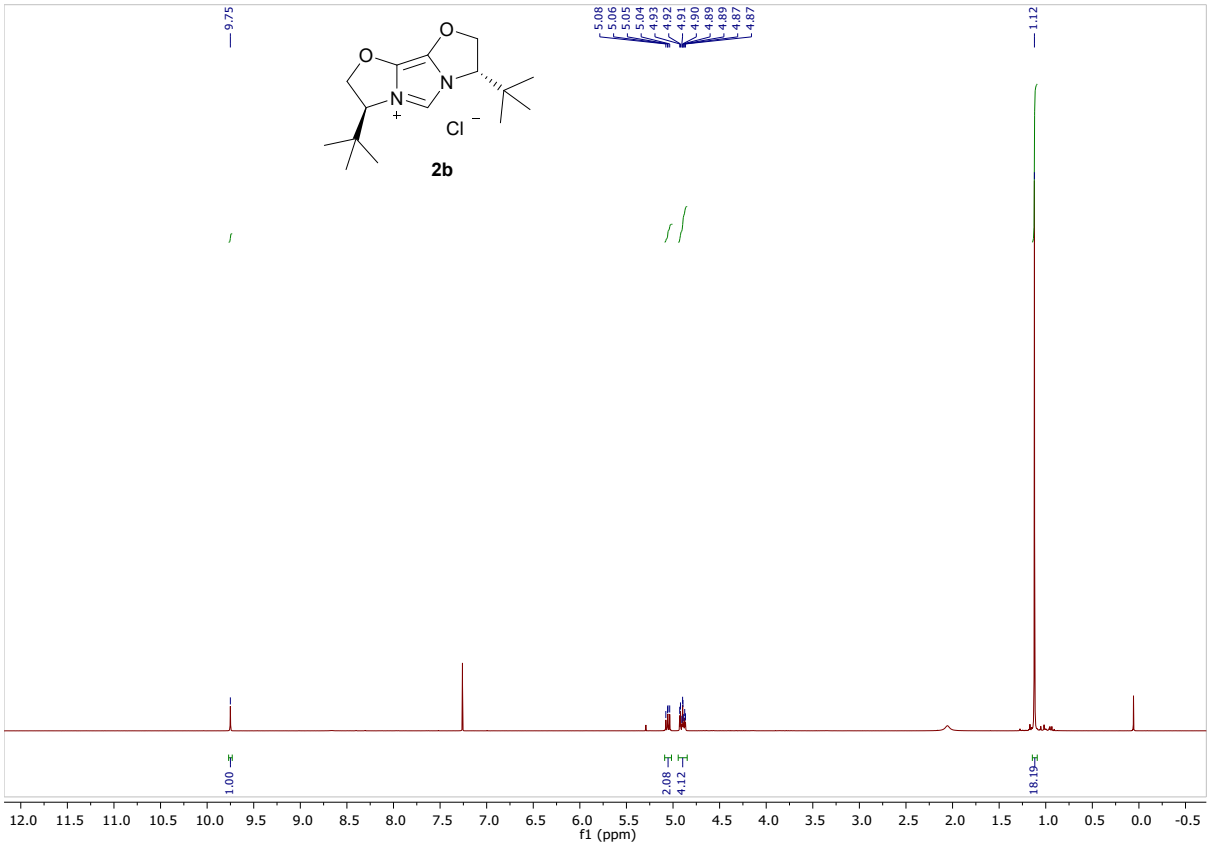
NMR Spectra

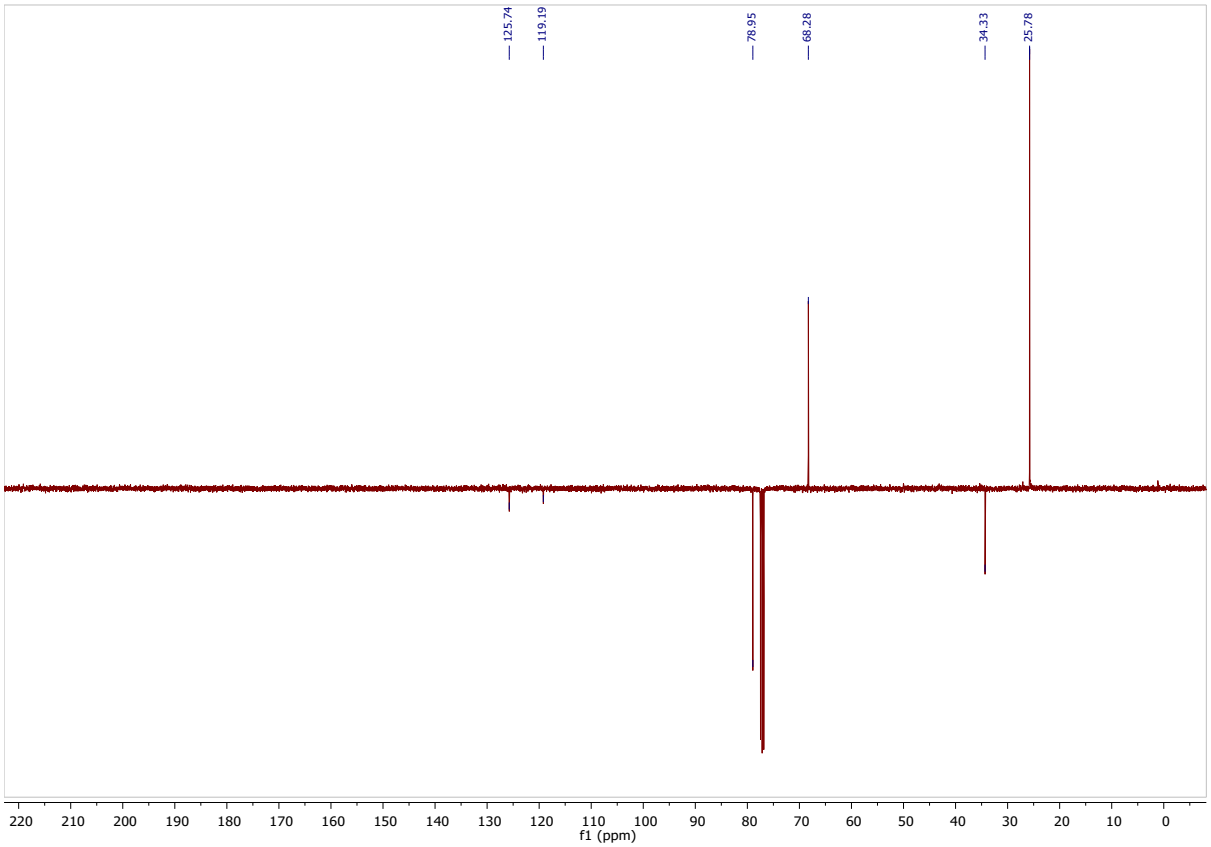
^{1}H NMR and ^{13}C {^{1}H} NMR for **(3S,7S)-3,7-diisopropyl-2,3,7,8-tetrahydroimidazo[4,3-b:5,1-b']bis(oxazole)-4-ium chloride (2a):**



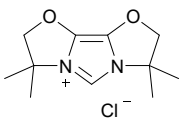


***[1]H NMR and [13]C {[1]H} NMR for* (3S,7S)-3,7-di-tert-butyl-2,3,7,8-tetrahydroimidazo[4,3-b:5,1-b']bis(oxazole)-4-ium chloride (2b):**

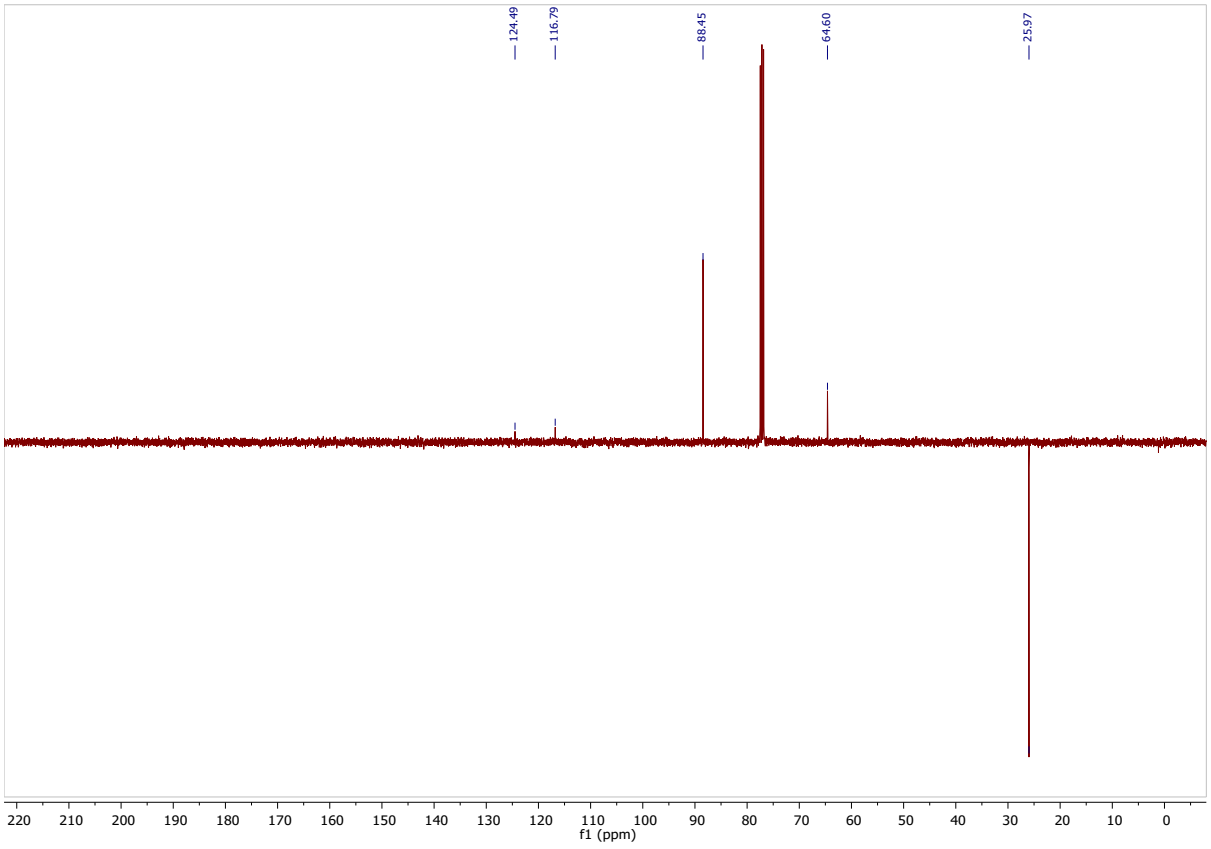




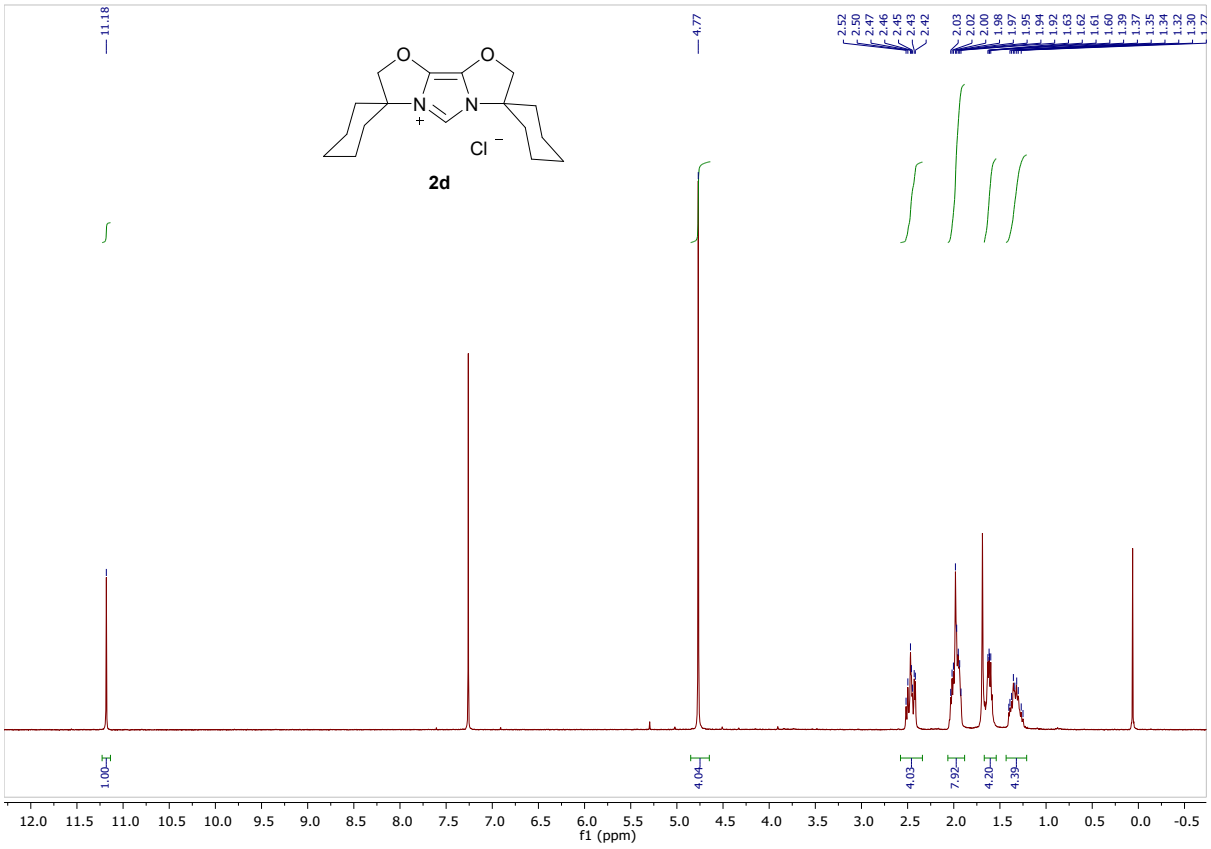
^{1}H NMR and ^{13}C {^{1}H} NMR for **3,3,7,7-tetramethyl-2,3,7,8-tetrahydroimidazo[4,3-b:5,1-b']bis(oxazole)-4-ium chloride (2c):**



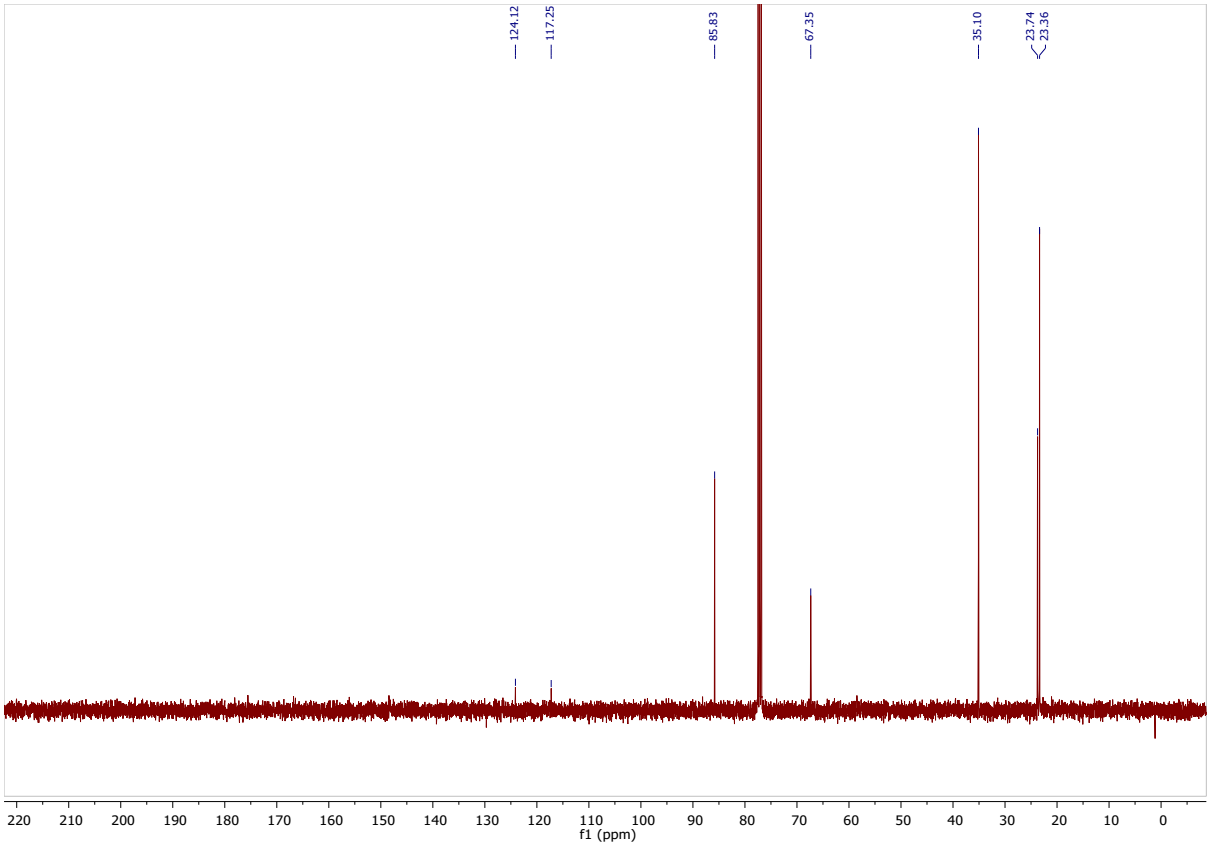
2c



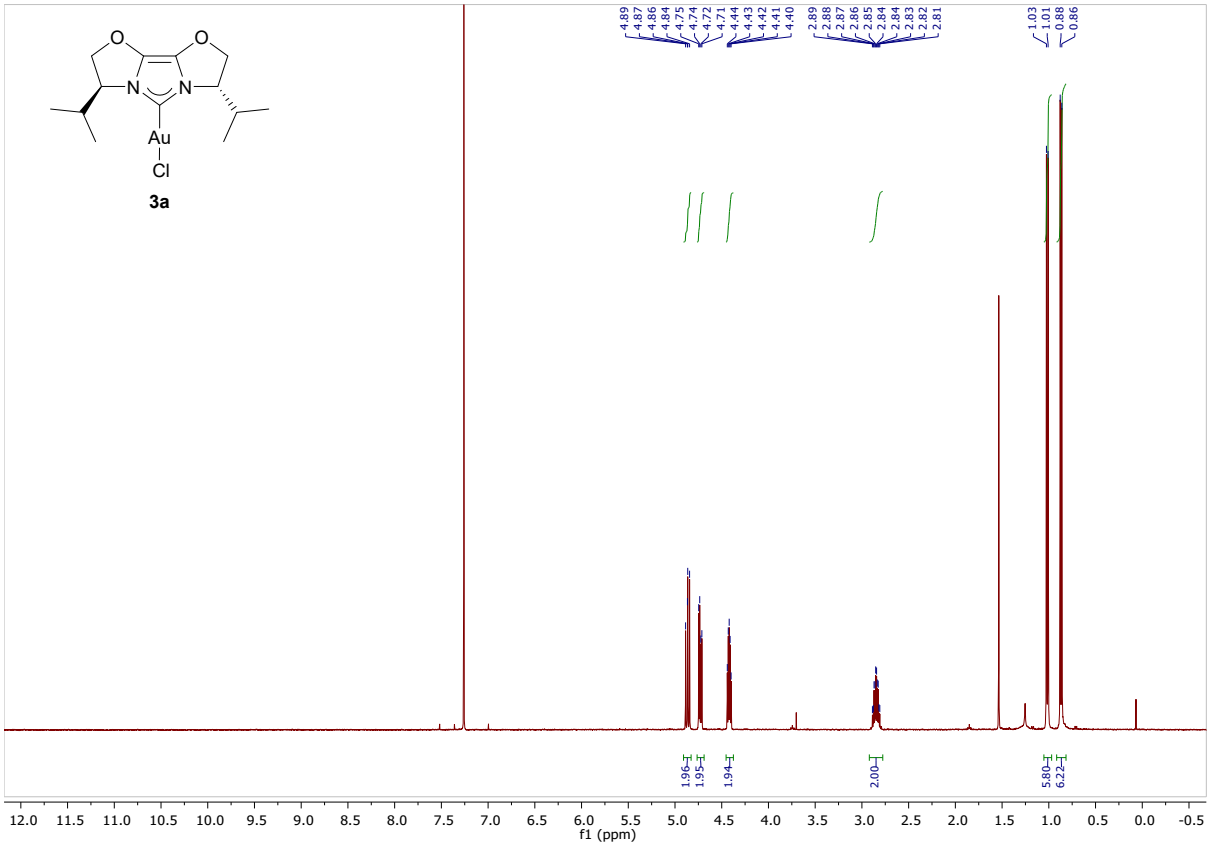
***^{1}H NMR and ^{13}C {^{1}H} NMR for* 2'H,8'H-dispiro[cyclohexane-1,3'-imidazo[4,3-b:5,1-b']bis(oxazole)-7',1''-cyclohexan]-4'-ium chloride (2d):**

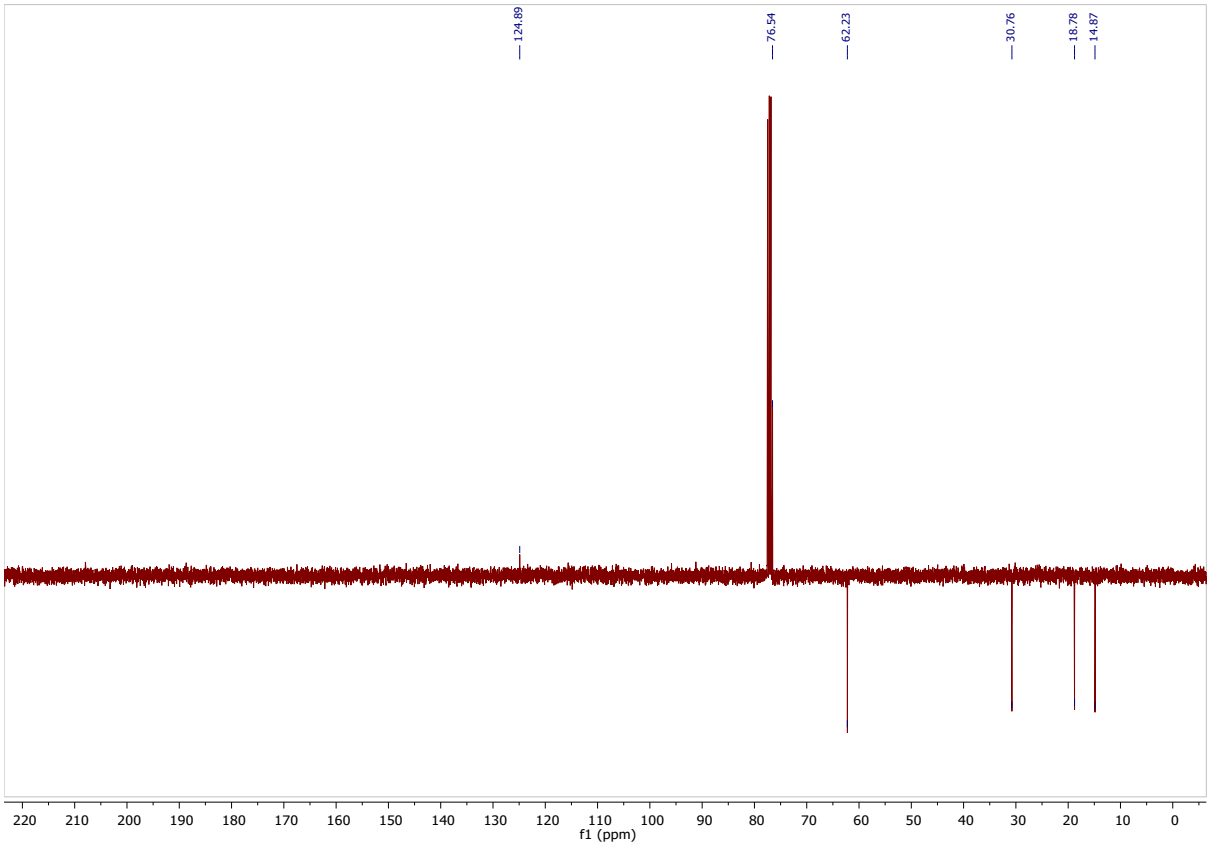


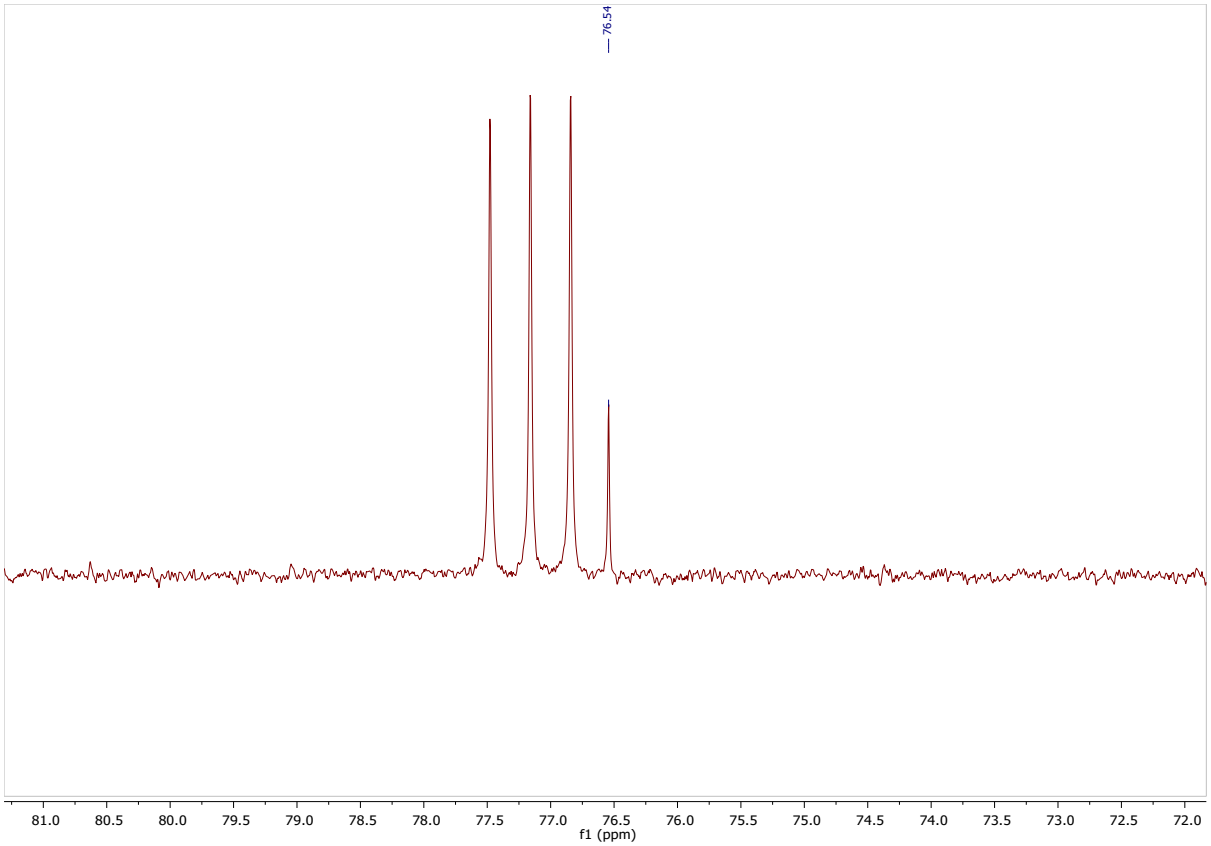
2d



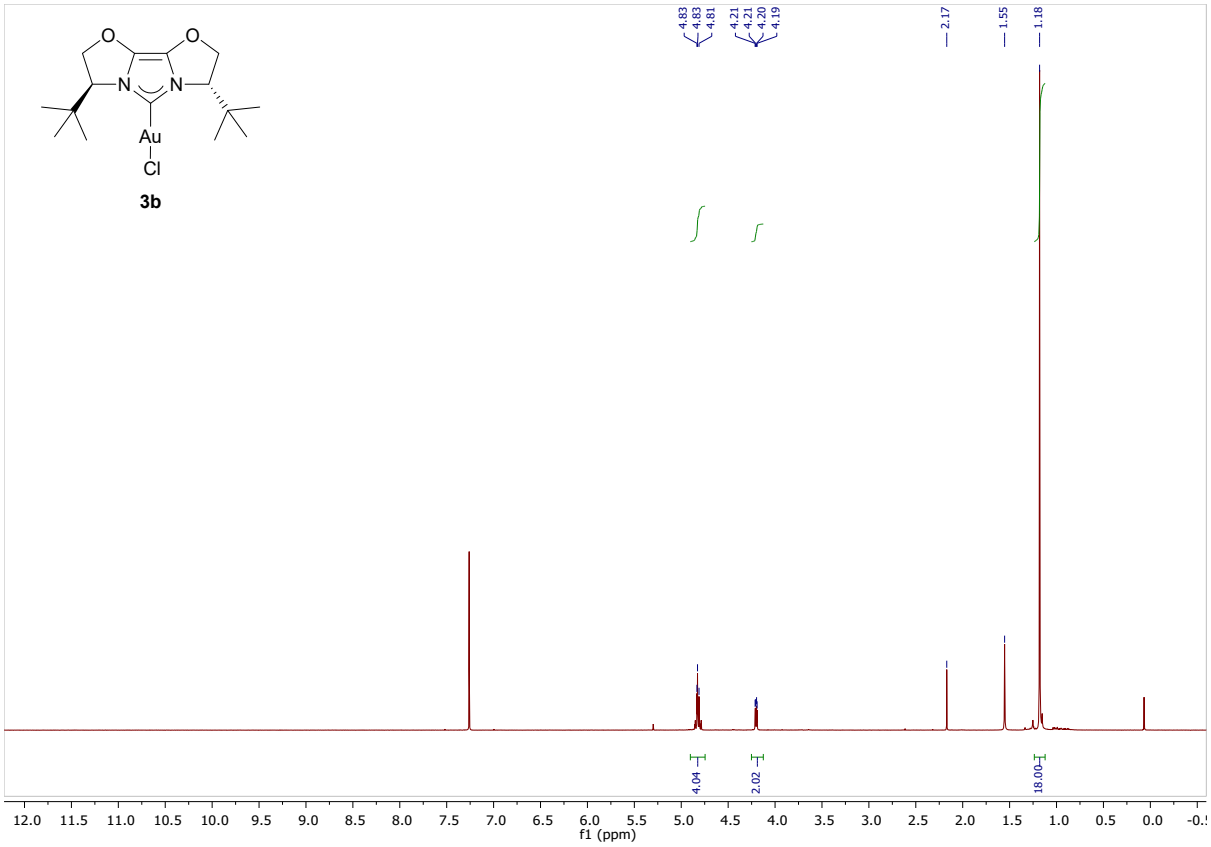
***^{1}H NMR and ^{13}C {^{1}H} NMR for* [Au(IBiox^{i}Pr)Cl] (3a):**

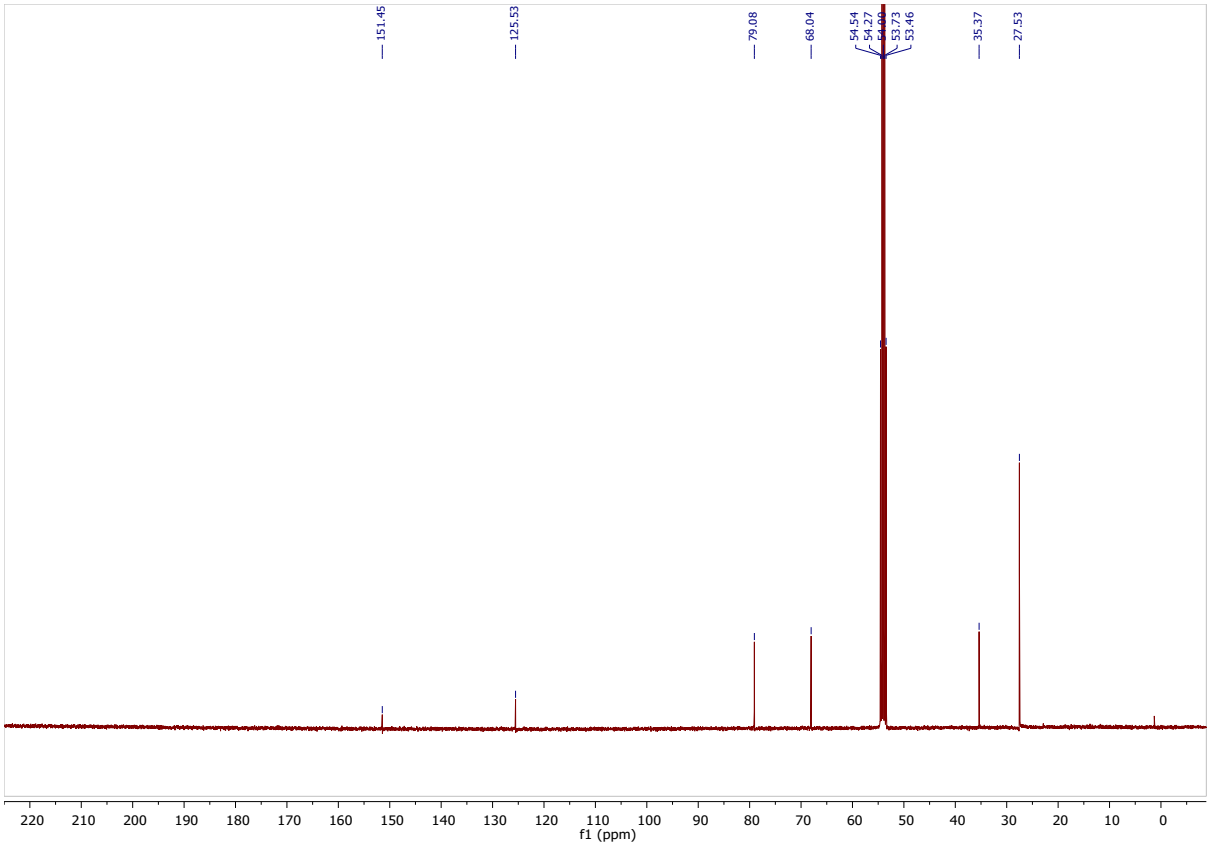




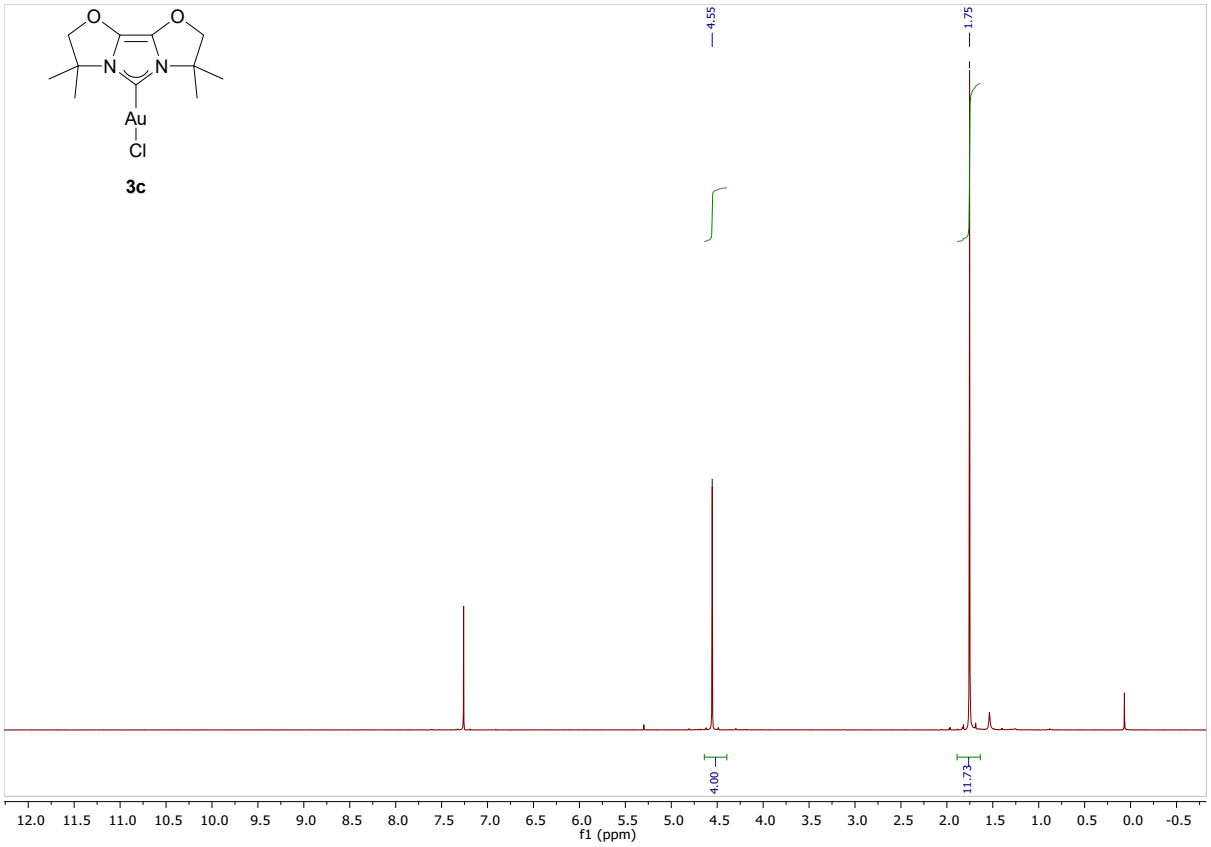


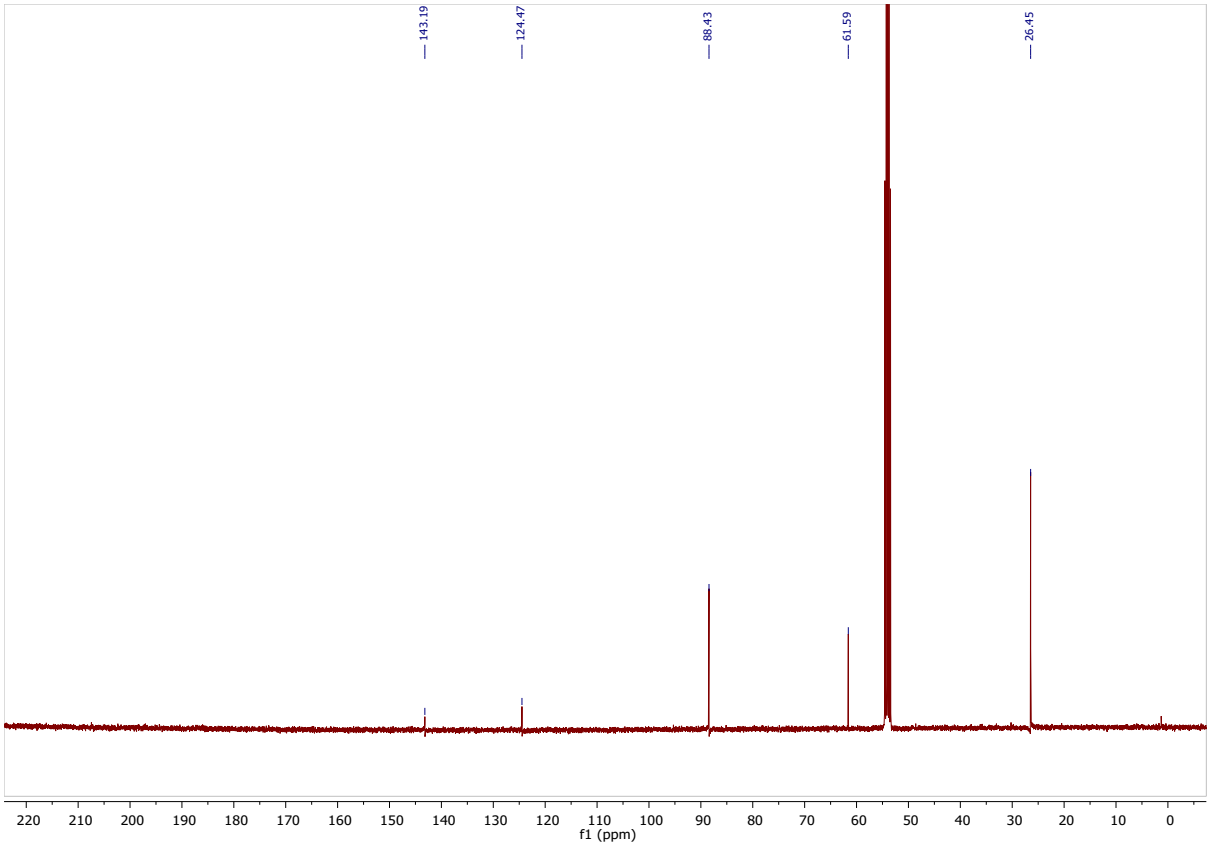
***^{1}H NMR and ^{13}C {^{1}H} NMR for* [Au(IBiox^{t}Bu)Cl] (3b):**



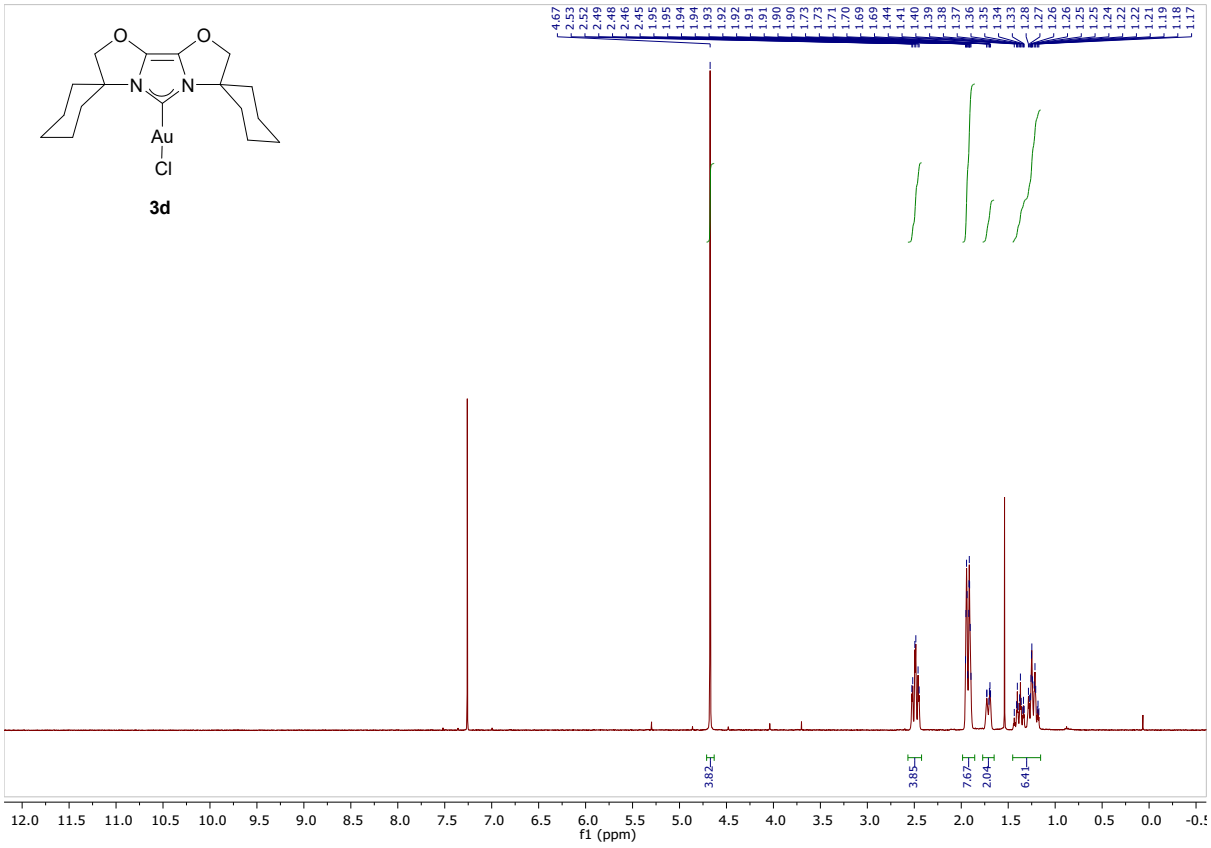


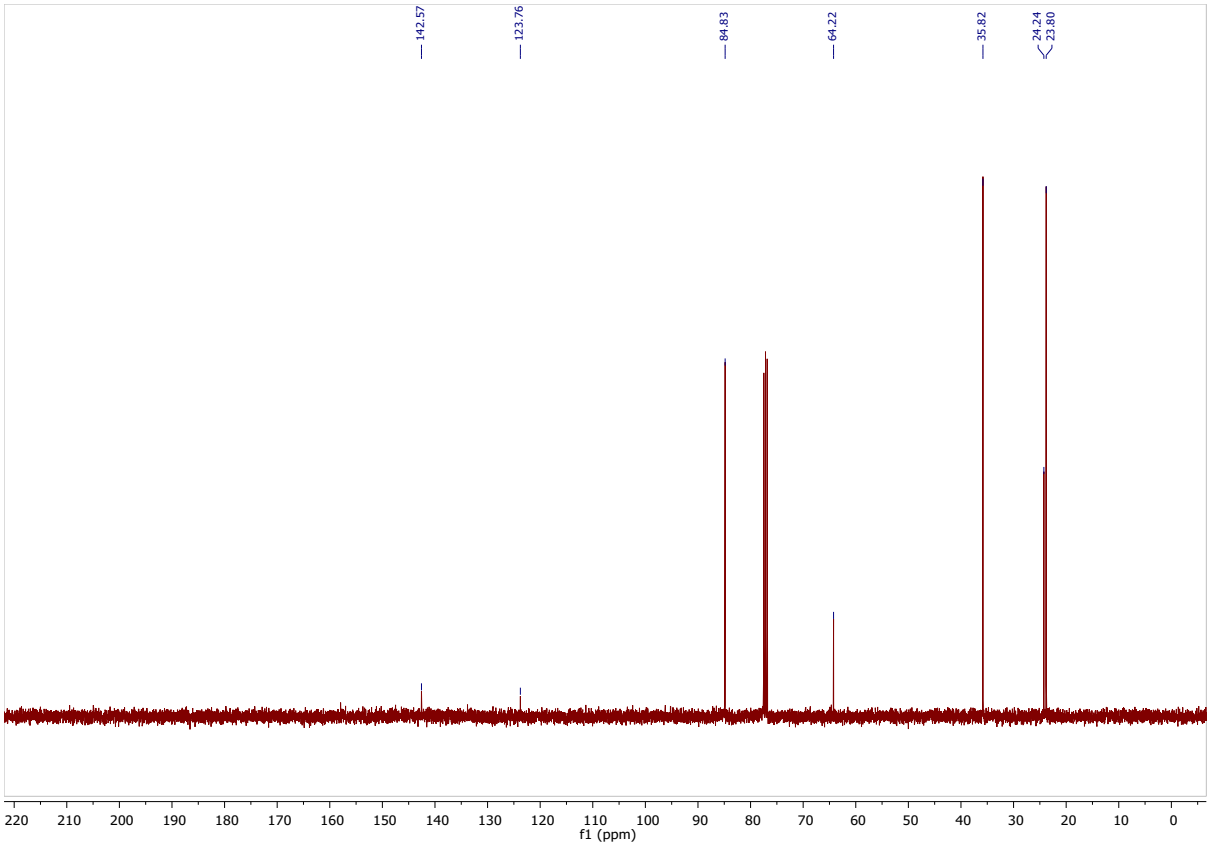
***^{1}H NMR and ^{13}C {^{1}H} NMR for* [Au(IBioxMe$_4$)Cl] (3c):**





***^{1}H NMR and ^{13}C {^{1}H} NMR for* [Au(IBiox6)Cl] (3d):**




142.57
123.76
84.83
64.22
35.82
24.24
23.80
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)