Supporting Information

Engaging Dual Donor Sites within an *N*-Heterocyclic Olefin Phosphine Ligand

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Contents

1. Single-crystal X-ray structure determinations

X-ray Crystallography. Crystals for X-ray diffraction studies were removed from a vial and immediately coated with thin a layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to -100 °C. The data was corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using intrinsic phasing SHELXT[1] (compound **4** and **6**), or Patterson/structure expansion[2] (compounds **2** and **3**) and refined using full-matrix least-squares on F^2. The assignment of hydrogen atoms positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Special refinement conditions:

[(IPrCH)PPh$_2$(AuCl)$_2$] (2). The following pairs of distances were constrained to be equal (within 0.03 Å) during refinement: d(Au2A–P1A) = d(Au2B–P1B); d(P1A–C4A) = d(P1B–C4B); d(C1–C4A) = d(C1–C4B). The ring carbons of the disordered phenyl groups C61A–C62A–C63A–C64A–C65A–C66A and C61B–C62B–C63B–C64B–C65B–C66B were refined as idealized regular hexagons, with C–C distances of 1.390 Å and C–C–C bond angles of 120.0°.

Table S1. Crystallographic data for compounds **2**, **3**, **4**, and **6**.

Compound	**2**•CH_2Cl_2	**3**•0.5C_7H_8	**4**	**6**•0.5C_6H_{14}
formula	$C_{41}H_{49}Au_2Cl_4N_2P$	$C_{43.5}H_{51}ClCuN_2P$	$C_{47}H_{55}CuIN_2$	$C_{43}H_{54}AuIN_2P$
formula weight	1136.52	731.82	869.34	953.72
cryst. dimens. (mm) 0.05	0.46 ´ 0.06 ´ 0.05	0.42 ´ 0.09 ´ 0.09	0.17 x 0.14 x 0.05	0.12 ´ 0.08 ´
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	*Ia*	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	18.6168 (5)	9.82456 (15)	10.1058 (2)	10.3405 (4)
b (Å)	13.3772 (3)	20.1043 (3)	13.4540 (3)	18.0429 (7)
c (Å)	19.0712 (5)	20.4797 (3)	16.1604 (3)	21.9333 (8)
a (deg)			79.2065 (8)	
β (deg)	115.6488 (11)	99.4697 (7)	79.8317 (10)	97.4577 (19)
g (deg)			80.8758 (9)	
V (Å^3)	4281.51 (19)	3989.94 (10)	2106.48 (7)	4057.5 (3)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.763	1.218	1.371	1.561
μ (mm^{-1})	15.57	1.993	7.088	13.38
temperature (°C)	–100	–100	–100	–100
$2\theta_{max}$ (deg)	148.03	148.18	148.08	140.51
total data	14947	28198	15212	27037
unique data (R_{int}) (0.0215)	8539 (0.0233)	7929 (0.0222)	8243 (0.0146)	7725
obs [I > 2σ(I)]	8201	7415	7894	7414
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] [a]	0.0262	0.0330	0.0282	0.0293
wR_2 [all data]	0.0677	0.0921	0.0728	0.0638
max / min Δ*r* (e Å^{-3})	1.316/ –1.035	0.581/ –0.622	0.715/–0.970	0.983/–0.612

[a] $R1 = S||F_o| - |F_c||/S|F_o|$; $wR2 = [Sw(F_o^2 - F_c^2)^2/Sw(F_o^4)]^{1/2}$.

2. DFT Computations

All DFT computations were carried out using the Gaussian 09 software package (Rev. E. 01)[3] with the hybrid density functional B3LYP[4-6] in combination with the LANL2DZ[7] basis set for gold, copper and iodide and 6-31(d,p)[8] for all other atoms. Input geometries were generated from the xyz atomic coordinates determined in the solid-state X-ray crystal structures of the molecules being studied and fully optimized in the gas phase without symmetry constraints. The obtained optimized geometries were confirmed to be local energy minimum structures by performing the harmonic vibrational frequency analysis.

Coordinates for [(IPr=CH)PPh$_2$(AuCl)] (1)

	x	y	z
Au	-2.637981	0.462968	-0.696750
Cl	-4.811804	-0.138253	-1.433663
P	-0.564878	1.276686	-0.042166
N	0.597694	-2.105102	0.649613
N	2.626161	-1.401672	0.160288
C	1.298724	-0.976243	0.253987
C	1.481843	-3.188034	0.783224
H	1.116801	-4.159128	1.072342
C	2.720883	-2.757327	0.486239
H	3.667610	-3.271256	0.467393
C	0.937507	0.337068	-0.009424
H	1.788475	0.954686	-0.278117
C	-0.827561	-2.303803	0.765750
C	-1.516707	-2.862392	-0.332227
C	-2.876401	-3.150703	-0.165180
H	-3.441941	-3.559993	-0.995365
C	-3.521420	-2.898096	1.040212
H	-4.580956	-3.111477	1.139986
C	-2.816267	-2.359013	2.113068
H	-3.334224	-2.172981	3.047546
C	-1.454100	-2.055651	2.006379
C	-0.833113	-3.191922	-1.657275
H	0.192899	-2.815311	-1.613404
C	-1.516345	-2.511878	-2.858129
H	-1.548633	-1.426292	-2.731932
H	-0.967920	-2.738788	-3.779419

H	-2.547317	-2.853355	-2.990204
C	-0.750668	-4.718054	-1.866112
H	-0.215962	-5.209185	-1.046345
H	-1.749337	-5.163649	-1.926039
H	-0.225293	-4.949537	-2.799118
C	-0.676022	-1.537081	3.213894
H	0.178426	-0.964658	2.837751
C	-1.498640	-0.592614	4.106648
H	-0.850277	-0.139715	4.863258
H	-1.955251	0.213610	3.527269
H	-2.293437	-1.124790	4.640251
C	-0.119861	-2.710082	4.049714
H	0.440791	-2.334088	4.912861
H	-0.935521	-3.337770	4.425283
H	0.551383	-3.345476	3.464605
C	3.743563	-0.597918	-0.252602
C	4.019016	-0.465774	-1.630933
C	5.144554	0.280479	-2.001033
H	5.382293	0.396785	-3.054000
C	5.966443	0.868512	-1.044115
H	6.837367	1.439122	-1.354096
C	5.673838	0.727581	0.309591
H	6.322660	1.190000	1.047083
C	4.556261	-0.000532	0.735436
C	3.158922	-1.123542	-2.704904
H	2.289713	-1.568047	-2.213575
C	2.627909	-0.102561	-3.728636
H	1.970691	-0.601404	-4.448824
H	2.053786	0.689281	-3.239778
H	3.440026	0.366060	-4.295077
C	3.927261	-2.262679	-3.404548
H	4.267255	-3.016197	-2.686795
H	3.285906	-2.759965	-4.139855
H	4.808809	-1.882876	-3.932627
C	4.266931	-0.154322	2.225384
H	3.263051	-0.576775	2.327101
C	4.276545	1.195255	2.967379
H	3.601269	1.916591	2.497378
H	3.958897	1.055402	4.006160
H	5.276279	1.641300	2.991092
C	5.253548	-1.141670	2.881494
H	5.022254	-1.267939	3.944646
H	5.209827	-2.127294	2.407874
H	6.284326	-0.779125	2.801866
C	-0.101036	2.639484	-1.202534
C	0.673722	3.729162	-0.779119

H	0.969292	3.814794	0.261922
C	1.057349	4.718452	-1.686472
H	1.653424	5.559792	-1.344212
C	0.670030	4.632237	-3.024464
H	0.963426	5.406225	-3.727940
C	-0.104552	3.552485	-3.453653
H	-0.418911	3.483502	-4.491030
C	-0.490044	2.562846	-2.548662
H	-1.106064	1.733445	-2.883668
C	-0.744303	2.165458	1.574193
C	0.299793	2.195996	2.506472
H	1.215518	1.653740	2.291021
C	0.161486	2.903604	3.703076
H	0.979123	2.920094	4.418610
C	-1.025646	3.583339	3.979561
H	-1.136520	4.129819	4.911853
C	-2.074944	3.552663	3.057029
H	-3.004049	4.073323	3.270377
C	-1.937256	2.846610	1.861725
H	-2.760060	2.816437	1.152032

Coordinates for [(IPrCH)PPh$_2$(AuCl)$_2$] (2)

	x	y	z
Au	2.317388	-0.353195	1.123661
Au	-3.018548	0.383505	0.214271
Cl	4.361965	-0.989300	2.140860
Cl	-5.017560	1.138357	-0.817723
P	-1.030829	-0.343596	1.168008
N	0.414111	-0.508532	-2.168701
N	0.730861	1.621868	-1.794816
C	0.511756	0.421808	-1.170342
C	0.561189	0.123141	-3.401241
H	0.509633	-0.436876	-4.318577
C	0.762993	1.438221	-3.169389
H	0.925870	2.263730	-3.841080
C	0.483513	0.299241	0.298094
H	0.472711	1.333894	0.659227
C	0.308601	-1.963642	-2.107007
C	1.505950	-2.713390	-2.029025
C	1.385991	-4.108278	-2.040315
H	2.280835	-4.715804	-1.967302
C	0.146374	-4.727778	-2.160830
H	0.080677	-5.812042	-2.165980
C	-1.004996	-3.962793	-2.302714
H	-1.961519	-4.457164	-2.428178
C	-0.956860	-2.562440	-2.296307

C	2.897918	-2.082446	-2.045392
H	2.820302	-1.067426	-1.643940
C	3.924601	-2.827404	-1.174966
H	4.848194	-2.244990	-1.119395
H	3.574138	-2.960875	-0.149679
H	4.179636	-3.807025	-1.593856
C	3.420237	-1.984219	-3.496497
H	4.410707	-1.517398	-3.509547
H	3.511571	-2.980754	-3.942040
H	2.762039	-1.391016	-4.137812
C	-2.231609	-1.771278	-2.580223
H	-2.108015	-0.759605	-2.179109
C	-3.484409	-2.376511	-1.920107
H	-4.311784	-1.664953	-1.984933
H	-3.797293	-3.299431	-2.420718
H	-3.316339	-2.603522	-0.864416
C	-2.469856	-1.644179	-4.101475
H	-1.642867	-1.146598	-4.615780
H	-2.598985	-2.632281	-4.556676
H	-3.377901	-1.062403	-4.288523
C	1.022803	2.910926	-1.183427
C	2.376638	3.244412	-0.954648
C	2.639226	4.511584	-0.420006
H	3.665841	4.800538	-0.223917
C	1.610467	5.404787	-0.139982
H	1.840222	6.381302	0.276567
C	0.289147	5.055506	-0.399332
H	-0.501948	5.765412	-0.186238
C	-0.041887	3.803525	-0.933104
C	3.540240	2.328593	-1.327267
H	3.155861	1.308997	-1.427545
C	4.644645	2.283926	-0.256176
H	4.246840	2.014566	0.724899
H	5.386497	1.526082	-0.524217
H	5.170701	3.240936	-0.171584
C	4.133731	2.743458	-2.691434
H	3.386994	2.719841	-3.491430
H	4.539794	3.759801	-2.646143
H	4.948681	2.067943	-2.971791
C	-1.493095	3.475628	-1.268540
H	-1.607843	2.385974	-1.263815
C	-2.493444	4.036738	-0.243168
H	-3.486147	3.622949	-0.438145
H	-2.210027	3.770658	0.779906
H	-2.567216	5.128181	-0.300717
C	-1.858963	3.970060	-2.684537

H	-2.892303	3.695874	-2.917982
H	-1.769114	5.060057	-2.750310
H	-1.212810	3.535025	-3.453447
C	-0.824748	0.369990	2.850740
C	0.064158	-0.198277	3.777072
H	0.626625	-1.090340	3.523351
C	0.230330	0.381650	5.034413
H	0.925157	-0.063128	5.740160
C	-0.490410	1.526673	5.380933
H	-0.359439	1.974605	6.361741
C	-1.384743	2.089526	4.469550
H	-1.956259	2.973259	4.737359
C	-1.555065	1.512736	3.209838
H	-2.265607	1.942494	2.509929
C	-1.047413	-2.161605	1.434886
C	0.075937	-2.992863	1.347188
H	1.035415	-2.587130	1.044657
C	-0.028844	-4.351302	1.654378
H	0.851605	-4.982389	1.580714
C	-1.250260	-4.891829	2.055258
H	-1.326439	-5.948186	2.296499
C	-2.376463	-4.070218	2.143861
H	-3.332603	-4.481849	2.453133
C	-2.278359	-2.715570	1.831622
H	-3.159832	-2.083505	1.898883

Coordinates for [(IPr=CH)PPh$_2$(CuCl)] (3)

	x	y	z
Cu	2.911583	0.616027	0.775275
Cl	4.907211	0.656870	1.665354
P	0.943269	1.237184	-0.152762
N	-0.245041	-2.121522	0.078292
N	-2.306734	-1.354800	0.176231
C	-0.978329	-0.943660	0.046690
C	-1.109445	-3.215690	0.243128
H	-0.720590	-4.217923	0.309138
C	-2.369305	-2.746661	0.299065
H	-3.312091	-3.254358	0.418456
C	-0.618278	0.385490	-0.091583
H	-1.470607	1.057285	-0.109726
C	1.186089	-2.276204	0.052173
C	1.837452	-2.404786	-1.194566
C	3.222305	-2.611243	-1.181062
H	3.757664	-2.705368	-2.119511
C	3.927636	-2.694067	0.016602
H	5.004233	-2.830547	0.005017

C	3.259612	-2.585717	1.232475
H	3.825676	-2.640122	2.155641
C	1.874972	-2.379240	1.280586
C	1.066934	-2.382485	-2.512954
H	0.158385	-1.791925	-2.355756
C	1.845223	-1.724643	-3.665351
H	1.190002	-1.608971	-4.534700
H	2.218110	-0.734812	-3.391274
H	2.696168	-2.336190	-3.984442
C	0.633807	-3.809639	-2.913075
H	0.071408	-3.790240	-3.853226
H	1.508940	-4.452899	-3.057469
H	-0.001472	-4.271462	-2.151880
C	1.162146	-2.318365	2.629740
H	0.116174	-2.055543	2.447196
C	1.746066	-1.242487	3.563313
H	1.710340	-0.252802	3.098388
H	1.171646	-1.202920	4.495517
H	2.790445	-1.441246	3.820571
C	1.175329	-3.700921	3.313693
H	0.712594	-4.467108	2.682950
H	2.198911	-4.023249	3.532214
H	0.626150	-3.665474	4.260846
C	-3.451714	-0.489375	0.231518
C	-4.167417	-0.229957	-0.957709
C	-5.313958	0.568523	-0.869181
H	-5.890631	0.777087	-1.765021
C	-5.727089	1.099821	0.349766
H	-6.618883	1.718459	0.397001
C	-4.998523	0.841853	1.507082
H	-5.328618	1.263266	2.451892
C	-3.848535	0.043007	1.476938
C	-3.741818	-0.814881	-2.300978
H	-2.726932	-1.206469	-2.185009
C	-3.699447	0.245614	-3.416653
H	-3.283360	-0.188090	-4.332087
H	-4.697664	0.623847	-3.661231
H	-3.079803	1.101354	-3.131832
C	-4.650503	-1.994002	-2.703651
H	-4.320510	-2.427416	-3.653932
H	-4.636421	-2.786300	-1.948858
H	-5.689053	-1.666995	-2.825034
C	-3.085967	-0.236491	2.767583
H	-2.205245	-0.832537	2.514302
C	-2.582627	1.060749	3.428661
H	-1.943226	1.630183	2.748613

H	-3.411860	1.706818	3.737282
H	-1.998353	0.824560	4.324473
C	-3.937695	-1.067133	3.747953
H	-4.262676	-2.010196	3.296633
H	-3.360800	-1.303496	4.648402
H	-4.834171	-0.521108	4.061116
C	1.253346	1.725760	-1.915557
C	0.280343	1.578040	-2.911782
H	-0.678390	1.137926	-2.653132
C	0.543717	1.973971	-4.225323
H	-0.220279	1.855611	-4.989103
C	1.786925	2.514916	-4.557020
H	1.994484	2.818208	-5.579318
C	2.767882	2.656210	-3.571679
H	3.740737	3.067614	-3.825299
C	2.504385	2.262109	-2.259534
H	3.276247	2.366481	-1.500118
C	0.494661	2.858600	0.619828
C	0.975437	3.166003	1.901208
H	1.643444	2.473943	2.407117
C	0.616451	4.361667	2.526734
H	1.001743	4.587087	3.516960
C	-0.223516	5.266612	1.876473
H	-0.498444	6.199777	2.359921
C	-0.700494	4.973901	0.596620
H	-1.346325	5.679638	0.081466
C	-0.342299	3.779769	-0.029401
H	-0.704761	3.571701	-1.031974

Coordinates for [(IPr=CH)PPh$_2$(CuI)] (4)

	x	y	z
I	-5.001258	0.769020	0.532868
Cu	-2.558216	0.384457	0.049106
P	-0.509214	0.703178	-0.911566
N	0.962765	-1.798512	1.157697
N	2.896982	-0.756417	1.006717
C	1.570765	-0.696105	0.573023
C	1.895562	-2.496116	1.942109
H	1.603985	-3.375169	2.491981
C	3.077785	-1.861069	1.845804
H	4.036151	-2.073863	2.289741
C	1.101270	0.296170	-0.269214
H	1.869503	1.001824	-0.568214
C	-0.429233	-2.161198	1.115563
C	-0.880887	-3.024855	0.093326
C	-2.231040	-3.396374	0.111681

H	-2.615959	-4.051961	-0.661638
C	-3.093446	-2.932446	1.101417
H	-4.142253	-3.210699	1.082412
C	-2.619524	-2.097186	2.109427
H	-3.306161	-1.739497	2.868925
C	-1.276666	-1.699296	2.146375
C	0.066358	-3.583339	-0.966412
H	0.877143	-2.859038	-1.098341
C	-0.598848	-3.779513	-2.339545
H	0.160167	-4.045859	-3.082057
H	-1.332051	-4.593165	-2.324524
H	-1.100461	-2.871251	-2.682011
C	0.695202	-4.910738	-0.489807
H	1.379226	-5.304598	-1.249650
H	1.261307	-4.785249	0.437408
H	-0.080207	-5.664071	-0.311944
C	-0.772208	-0.836410	3.300494
H	0.266978	-0.567051	3.092404
C	-1.562354	0.476256	3.449007
H	-1.534082	1.061616	2.524722
H	-2.614465	0.299330	3.690901
H	-1.132164	1.086088	4.251094
C	-0.783147	-1.634250	4.620652
H	-0.182269	-2.546417	4.544415
H	-0.376503	-1.028447	5.437629
H	-1.801403	-1.927972	4.896840
C	3.924438	0.198883	0.697642
C	4.794208	-0.060912	-0.383988
C	5.818841	0.859846	-0.633858
H	6.509017	0.680952	-1.452563
C	5.966419	2.001198	0.149937
H	6.766472	2.704778	-0.062446
C	5.090495	2.242535	1.204124
H	5.213139	3.136154	1.808709
C	4.054288	1.349594	1.504493
C	4.661564	-1.312676	-1.245459
H	3.693176	-1.768861	-1.020371
C	4.679604	-0.994434	-2.751991
H	4.471822	-1.900743	-3.330587
H	3.926931	-0.243697	-3.011399
H	5.653974	-0.616555	-3.079198
C	5.752838	-2.343650	-0.892396
H	5.633442	-3.252317	-1.492306
H	6.752737	-1.940369	-1.087006
H	5.708241	-2.628436	0.163391
C	3.127256	1.634901	2.681442

H	2.383782	0.834771	2.724598
C	2.362750	2.959844	2.498403
H	1.675608	3.117933	3.336598
H	3.043613	3.817328	2.463783
H	1.775934	2.954056	1.575934
C	3.898695	1.617007	4.016031
H	3.212048	1.772797	4.854868
H	4.410482	0.661466	4.169800
H	4.654128	2.409341	4.053733
C	-0.341803	2.533666	-1.135427
C	-1.022765	3.399163	-0.266669
H	-1.679514	2.991951	0.497560
C	-0.879771	4.782922	-0.386800
H	-1.419136	5.439562	0.289703
C	-0.058481	5.317930	-1.380081
H	0.047563	6.394583	-1.478393
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H	1.251111	4.875839	-3.036306
C	0.475845	3.082021	-2.135930
H	0.993154	2.429057	-2.832730
C	-0.591546	0.110335	-2.667629
C	-1.821589	0.164740	-3.342366
H	-2.707575	0.528698	-2.826381
C	-1.917213	-0.250155	-4.671071
H	-2.874965	-0.204688	-5.181592
C	-0.787239	-0.728872	-5.339715
H	-0.863864	-1.055724	-6.372892
C	0.437286	-0.794827	-4.673015
H	1.317671	-1.171972	-5.186549
C	0.533299	-0.379972	-3.342468
H	1.480303	-0.444778	-2.814296

Coordinates for (IPr=CH)PPh_2

	x	y	z
P	-1.535817	1.121822	-0.280899
N	-0.213052	-1.880588	0.797827
N	1.851780	-1.192229	0.430670
C	0.514858	-0.777737	0.345332
C	0.664243	-2.921556	1.144392
H	0.285880	-3.856623	1.522169
C	1.921896	-2.502229	0.919567
H	2.869081	-2.997255	1.055656
C	0.127619	0.471256	-0.087143
H	0.963027	1.112640	-0.356261
C	-1.641336	-2.035610	0.857065
C	-2.320606	-1.661018	2.034812

C	-3.701175	-1.879843	2.088913
H	-4.251778	-1.600673	2.981524
C	-4.380983	-2.451609	1.017481
H	-5.453743	-2.611554	1.079470
C	-3.688135	-2.825978	-0.129503
H	-4.227540	-3.282247	-0.953924
C	-2.306270	-2.629448	-0.236025
C	-1.586035	-1.077832	3.237821
H	-0.597606	-0.757106	2.896537
C	-2.287126	0.157583	3.829177
H	-1.675913	0.583955	4.631724
H	-2.440014	0.931730	3.073138
H	-3.261114	-0.092864	4.263085
C	-1.375468	-2.156713	4.319981
H	-0.817161	-1.747081	5.168960
H	-2.335484	-2.527401	4.696301
H	-0.816228	-3.013025	3.930200
C	-1.564045	-3.095371	-1.485605
H	-0.552113	-2.682590	-1.445427
C	-2.207653	-2.587663	-2.787811
H	-2.278655	-1.497281	-2.799221
H	-1.603828	-2.896151	-3.648113
H	-3.213353	-2.996446	-2.933958
C	-1.437174	-4.632355	-1.503614
H	-0.919742	-5.003566	-0.613599
H	-2.423278	-5.108641	-1.538443
H	-0.873903	-4.961754	-2.383602
C	2.989116	-0.428236	0.006191
C	3.671636	0.367101	0.952333
C	4.810204	1.060690	0.526041
H	5.359389	1.673193	1.234291
C	5.250536	0.977734	-0.791903
H	6.136120	1.524635	-1.103065
C	4.557356	0.196597	-1.711161
H	4.908934	0.139283	-2.737063
C	3.415702	-0.522085	-1.335833
C	3.219876	0.451720	2.406712
H	2.207165	0.042450	2.460257
C	3.157018	1.900098	2.923597
H	2.730633	1.919626	3.932213
H	4.150082	2.357777	2.983331
H	2.535006	2.527137	2.278584
C	4.118501	-0.414316	3.312363
H	3.771403	-0.375148	4.350589
H	4.115251	-1.461733	2.995157
H	5.155606	-0.061581	3.290426

C	2.691104	-1.383917	-2.364463
H	1.811773	-1.814524	-1.878789
C	2.189969	-0.552693	-3.559724
H	1.518462	0.245486	-3.232599
H	3.019261	-0.097710	-4.112456
H	1.639515	-1.191238	-4.259019
C	3.577263	-2.555164	-2.831949
H	3.895069	-3.177005	-1.988860
H	3.029133	-3.191503	-3.534930
H	4.479223	-2.197646	-3.340487
C	-1.422413	2.767254	0.585090
C	-0.569848	2.959409	1.682047
H	0.103816	2.158354	1.971112
C	-0.570446	4.161644	2.393489
H	0.104006	4.288199	3.236619
C	-1.426827	5.197812	2.022011
H	-1.426350	6.134739	2.571823
C	-2.287149	5.018335	0.935925
H	-2.959249	5.818322	0.636623
C	-2.288198	3.816430	0.229770
H	-2.961270	3.696592	-0.614872
C	-1.558570	1.721089	-2.049250
C	-2.648154	1.360348	-2.854200
H	-3.446633	0.760290	-2.425352
C	-2.722463	1.763815	-4.191328
H	-3.576389	1.474034	-4.797731
C	-1.703150	2.538092	-4.742534
H	-1.756352	2.853559	-5.780794
C	-0.612560	2.911669	-3.950834
H	0.180985	3.522503	-4.373204
C	-0.543851	2.509143	-2.617913
H	0.301454	2.819558	-2.009908

Coordinates for [(IPr=CH)PPh$_2$(AuI)] (6)

Au	-2.316944	0.489148	-0.263480
I	-4.904138	0.020558	-0.837590
P	-0.135940	1.237548	0.184396
N	1.161194	-2.148931	0.511332
N	3.104823	-1.367432	-0.167115
C	1.788721	-0.983542	0.100126
C	2.075604	-3.214702	0.480316
H	1.765713	-4.210047	0.750876
C	3.263007	-2.736051	0.067805
H	4.210882	-3.223436	-0.089010
C	1.367433	0.328835	-0.054613
H	2.163037	0.981821	-0.398674

C	-0.240249	-2.388472	0.759280
C	-1.036515	-2.861990	-0.305590
C	-2.365619	-3.197296	-0.021710
H	-3.011702	-3.544202	-0.821262
C	-2.877753	-3.075432	1.265574
H	-3.915673	-3.327351	1.459126
C	-2.068185	-2.618318	2.301839
H	-2.482766	-2.531287	3.300149
C	-0.731484	-2.269177	2.077240
C	-0.493457	-3.053922	-1.719456
H	0.530560	-2.670613	-1.743956
C	-1.298400	-2.267925	-2.770600
H	-1.311763	-1.199252	-2.539316
H	-0.852821	-2.402436	-3.762738
H	-2.338689	-2.603063	-2.823428
C	-0.429874	-4.551078	-2.084965
H	0.182648	-5.114327	-1.373326
H	-1.428771	-5.000132	-2.092571
H	0.002791	-4.683462	-3.082630
C	0.162766	-1.839566	3.238006
H	0.975159	-1.232280	2.825218
C	-0.568268	-0.975154	4.279710
H	0.151497	-0.574494	5.000453
H	-1.084156	-0.131597	3.814745
H	-1.303847	-1.555265	4.847149
C	0.799800	-3.069083	3.920693
H	1.448816	-2.756669	4.746454
H	0.025866	-3.727248	4.330765
H	1.404628	-3.655301	3.222644
C	4.151977	-0.509867	-0.649742
C	4.277715	-0.298838	-2.039735
C	5.336576	0.503393	-2.483208
H	5.459062	0.681961	-3.547228
C	6.236895	1.069107	-1.585530
H	7.053867	1.684352	-1.951883
C	6.092842	0.848315	-0.218363
H	6.802844	1.293575	0.471687
C	5.047794	0.061859	0.280536
C	3.326766	-0.926075	-3.053828
H	2.544602	-1.451495	-2.500086
C	2.629761	0.135929	-3.924947
H	1.921782	-0.345221	-4.608043
H	2.075207	0.850609	-3.310775
H	3.347091	0.695735	-4.534812
C	4.055927	-1.969354	-3.923795
H	4.510501	-2.754231	-3.310652

H	3.354512	-2.444793	-4.617638
H	4.851929	-1.508074	-4.518243
C	4.923036	-0.183978	1.781073
H	3.935646	-0.617621	1.965851
C	5.014982	1.115987	2.601471
H	4.294622	1.862208	2.253055
H	4.809846	0.909058	3.657218
H	6.012453	1.564644	2.547741
C	5.974254	-1.204958	2.262744
H	5.858485	-1.399854	3.334368
H	5.879569	-2.158858	1.734852
H	6.990305	-0.830620	2.096085
C	0.170600	2.689858	-0.918576
C	0.992580	3.752419	-0.515428
H	1.418528	3.762460	0.483057
C	1.257674	4.810479	-1.386807
H	1.892407	5.629542	-1.060389
C	0.703604	4.820865	-2.667686
H	0.905576	5.647998	-3.342278
C	-0.119088	3.768952	-3.075648
H	-0.562530	3.774663	-4.067111
C	-0.386541	2.710615	-2.206407
H	-1.040509	1.903412	-2.523212
C	-0.113753	1.998842	1.873662
C	1.030390	1.955073	2.679968
H	1.911534	1.431149	2.321764
C	1.036597	2.568667	3.935183
H	1.930770	2.528236	4.551305
C	-0.103241	3.228410	4.396760
H	-0.100654	3.702447	5.374188
C	-1.251318	3.270877	3.600923
H	-2.144152	3.776140	3.957773
C	-1.258850	2.657634	2.348135
H	-2.158130	2.684261	1.737987

Table S2. Computed energies of each complex:

Complex	Energy of complex (au)	Energy of complex (kcal/mol)
[(IPrCH)$PPh_2(AuCl)_2$]	-3194.942959	-2004855.462
[(IPr=CH)PPh_2(AuCl)]	-2599.200027	-1631021.41
[(IPr=CH)PPh_2(AuI)]	-2150.403208	-1349397.367
[(IPr=CH)PPh_2(CuCl)]	-2659.895537	-1669108.389
[(IPr=CH)PPh_2(CuI)]	-2211.09358	-1387481.121
(IPr=CH)PPh_2	-2003.48171	-1257202.805

Table S3. TD-B3LYP/6-31G(d,p) transition energies of each complex:

Complex	S_1 (eV)	S_2 (eV)	S_3 (eV)
[(IPrCH)$PPh_2(AuCl)_2$]	4.11	4.17	4.31
[(IPr=CH)PPh_2(AuCl)]	3.45	3.51	3.70
[(IPr=CH)PPh_2(AuI)]	3.43	3.51	3.70
[(IPr=CH)PPh_2(CuCl)]	3.40	3.42	3.56
[(IPr=CH)PPh_2(CuI)]	3.42	3.50	3.65
(IPr=CH)PPh_2	3.23	3.42	3.47

Complex	T_1 (eV)	T_2 (eV)	T_3 (eV)
[(IPrCH)$PPh_2(AuCl)_2$]	3.63	3.65	3.66
[(IPr=CH)PPh_2(AuCl)]	3.32	3.37	3.43
[(IPr=CH)PPh_2(AuI)]	3.30	3.36	3.42
[(IPr=CH)PPh_2(CuCl)]	3.23	3.26	3.35
[(IPr=CH)PPh_2(CuI)]	3.30	3.33	3.37
(IPr=CH)PPh_2	4.25	4.45	4.61

Computed absorptions for [(IPr=CH)PPh_2] with their associated oscillator strengths (f):

S0 to Excited State S1: Singlet-A 3.2257 eV f = 0.0003
HOMO -> LUMO 0.70537
S0 to Excited State S2: Singlet-A 3.4228 eV f = 0.0059
HOMO ->LUMO+1 0.69972
S0 to Excited State S3: Singlet-A 3.4683 eV f = 0.0013
HOMO ->LUMO + 2 0.64887
HOMO ->LUMO + 3 0.26629

Computed absorptions for [(IPr=CH)PPh_2(CuI)] with their associated oscillator strengths (f):

S0 to Excited State S1: Singlet-A 3.4223 eV f = 0.0027
HOMO -> LUMO 0.53138
HOMO -> LUMO +1 0.45778

Excited State S2: Singlet-A 3.4988 eV f = 0.0094
HOMO -> LUMO 0.46012
HOMO -> LUMO +1 0.52441

Excited State S3: Singlet-A 3.6506 eV f = 0.0178
HOMO -> LUMO +2 0.68428
HOMO -> LUMO +3 0.13302

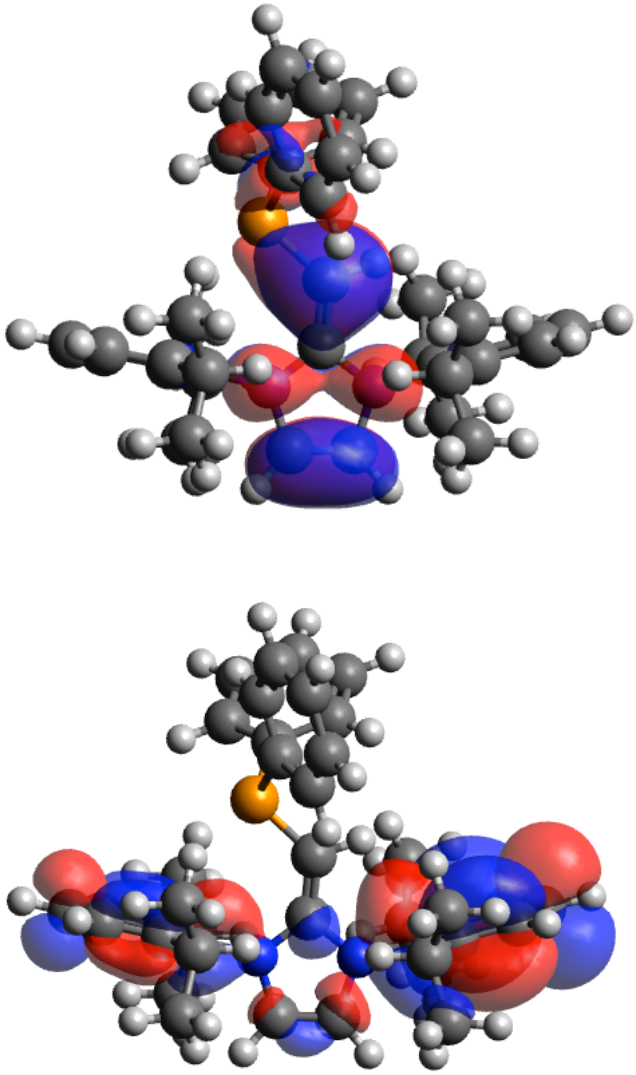

Figure S1. Computed HOMO (top) and LUMO (bottom) for (IPr=CH)PPh_2.

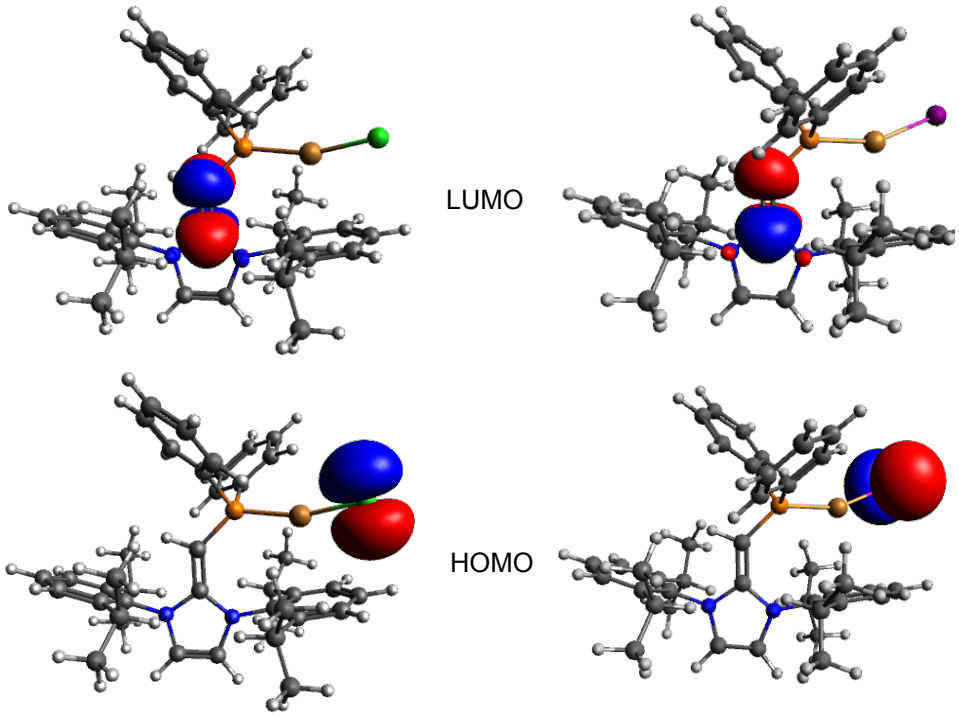

Figure S2. Computed HOMO and LUMO for [(IPr=CH)PPh_2(CuCl)] **3** (left) and [(IPr=CH)PPh_2(CuI)] **4** (right).

3. Ultraviolet–visible spectroscopy (UV/Vis) measurements

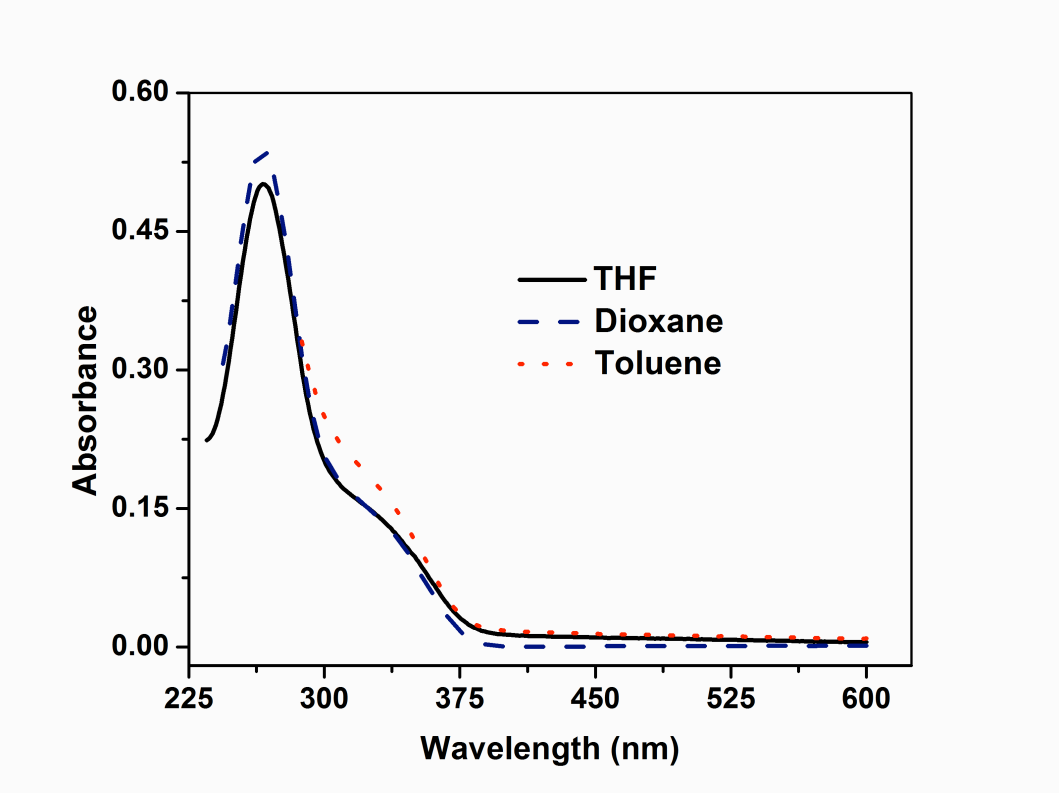

Figure S3. UV/Vis absorption spectra of $(IPr{=}CH)PPh_2$ in different solutions (THF, dioxane, and toluene) under N_2; $[(IPr{=}CH)PPh_2] = 2.2 \times 10^{-5}$ M.

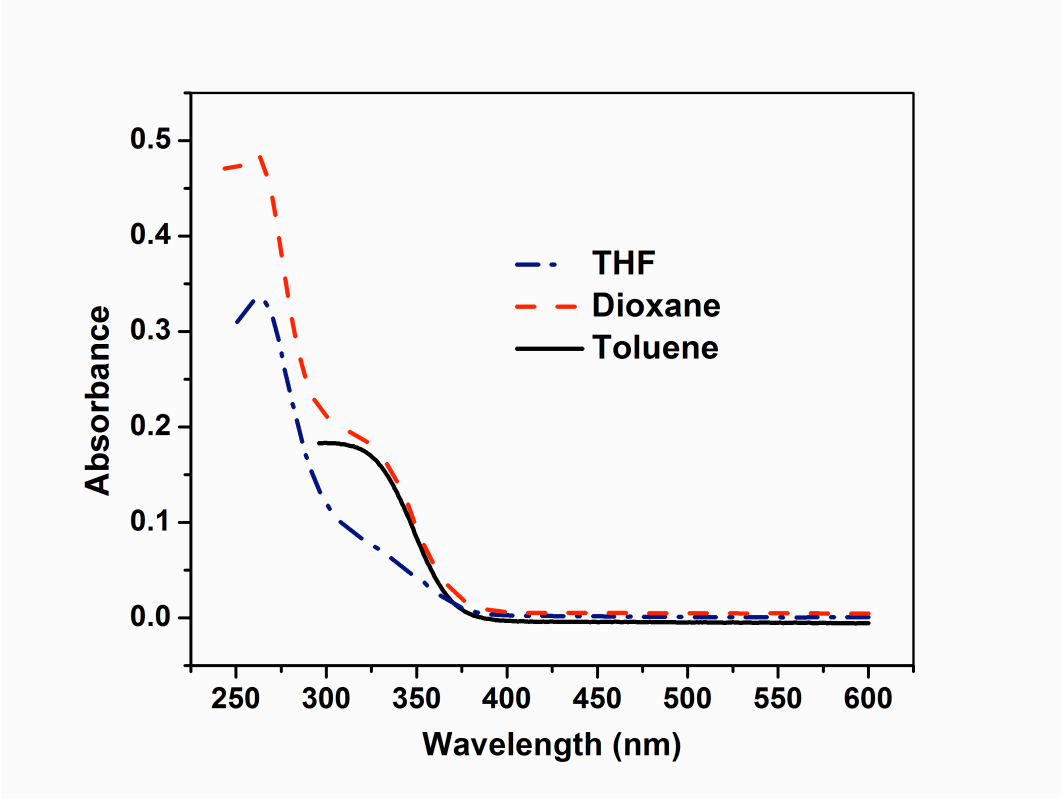

Figure S4. UV/Vis absorption spectra of [(IPr=CH)PPh_2(CuI)] **4** in different solutions (THF, dioxane, and toluene) under N_2; [{(IPr=CH)PPh_2(CuI)}] = 2.2×10^{-5} M.

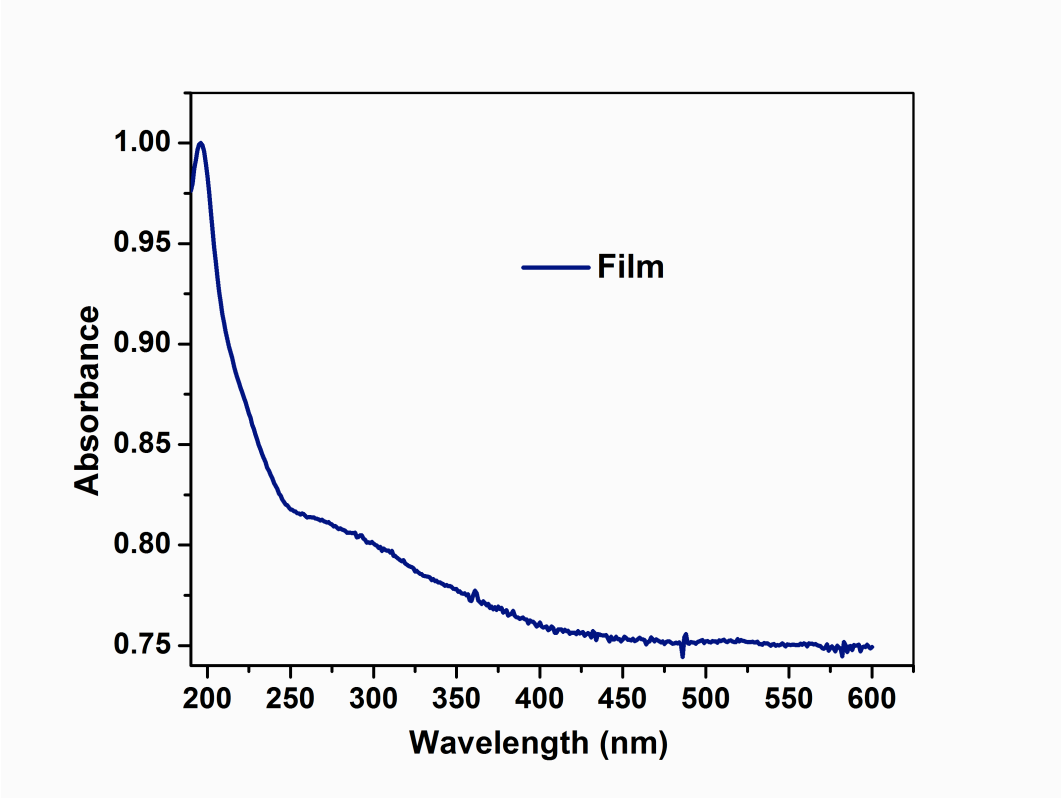

Figure S5. UV/Vis absorption spectra of [(IPr=CH)PPh_2(CuI)] **4** in the film state under air.*

*Solid [(IPr=CH)PPh_2(CuI)] was exposed to air for 12 hours and monitored by multinuclear NMR spectroscopy (^{1}H and ^{13}C{^{1}H}). Spectra were recorded before and after exposure, and they did not show any sign of decomposition. The UV/Vis measurements were done in triplicate. Films were prepared inside of the glovebox: 180 µL of 2.2 × 10^{-3} M solution (in toluene) drop-casted on the quartz slide (prior dried in the oven for 10 hours) and the solvent was left to evaporate over 8 hours. Then each film was taken outside one by one for immediate measurements.

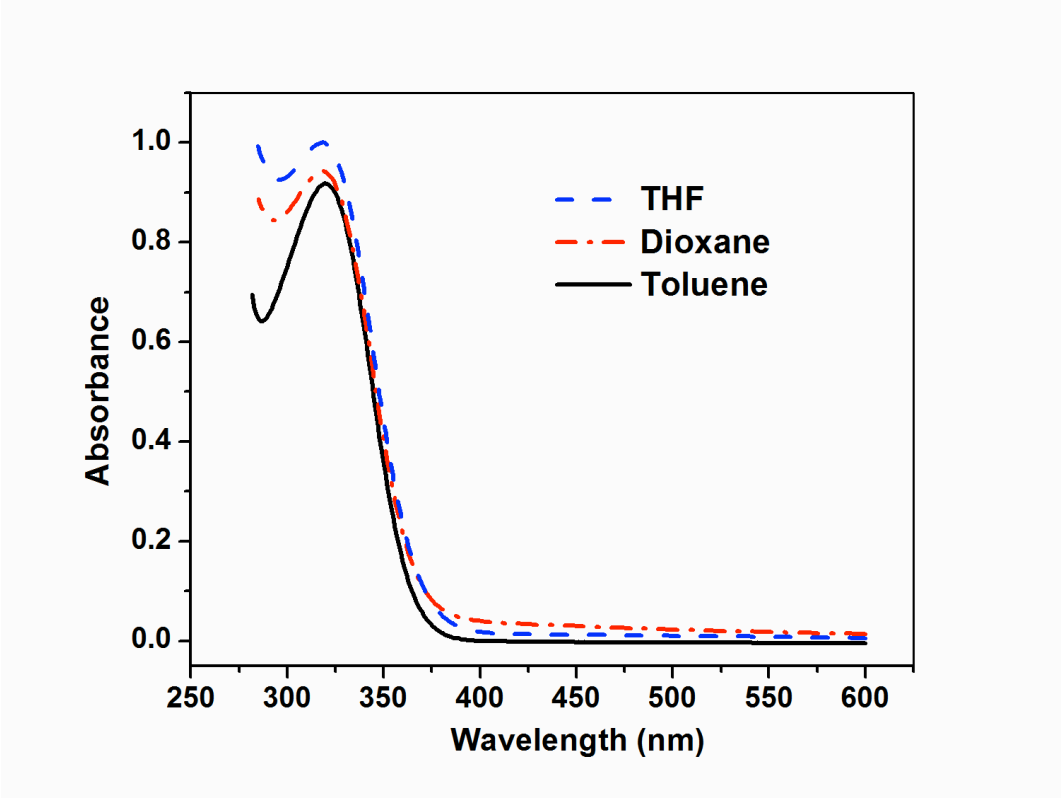

Figure S6. Normalized UV/Vis absorption spectra of [(IPr=CH)PPh_2(AuI)] **6** in different solutions (THF, dioxane, and toluene) under N_2; [{(IPr=CH)PPh_2(AuI)}] = 2.2×10^{-5} M.

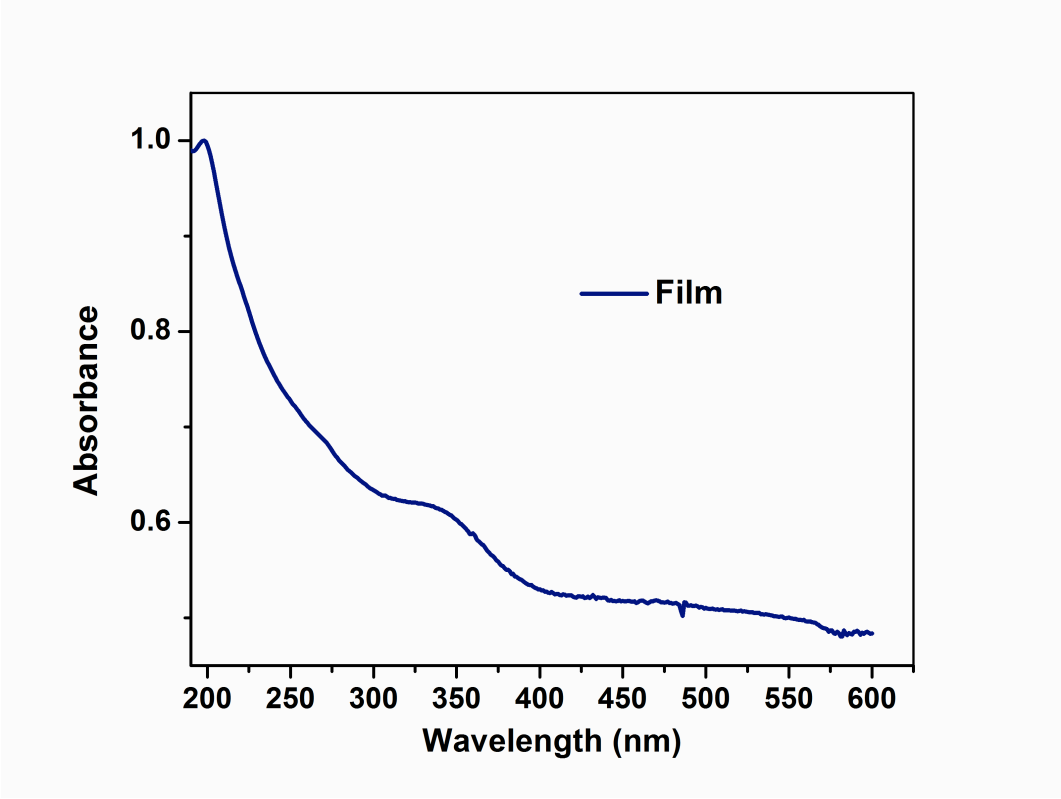

Figure S7. UV/Vis absorption spectra of [(IPr=CH)PPh_2(AuI)] **6** in film state under air. †

†Solid [(IPr=CH)PPh_2(AuI)] was exposed to air for 12 hours and monitored by multinuclear NMR spectroscopy (^{1}H and ^{13}C{^{1}H}). Spectra were recorded before and after exposure and they did not show any sign of decomposition. The UV/Vis measurements were done in triplicate. Films were prepared inside of the glovebox: 180 µL of 2.2 × 10^{-3} M solution (in toluene) drop-casted on the quartz slide (prior dried in the oven for 10 hours) and the solvent was left to evaporate over 8 hours. Then each film was taken outside one by one for immediate measurements.

4. NMR Spectra

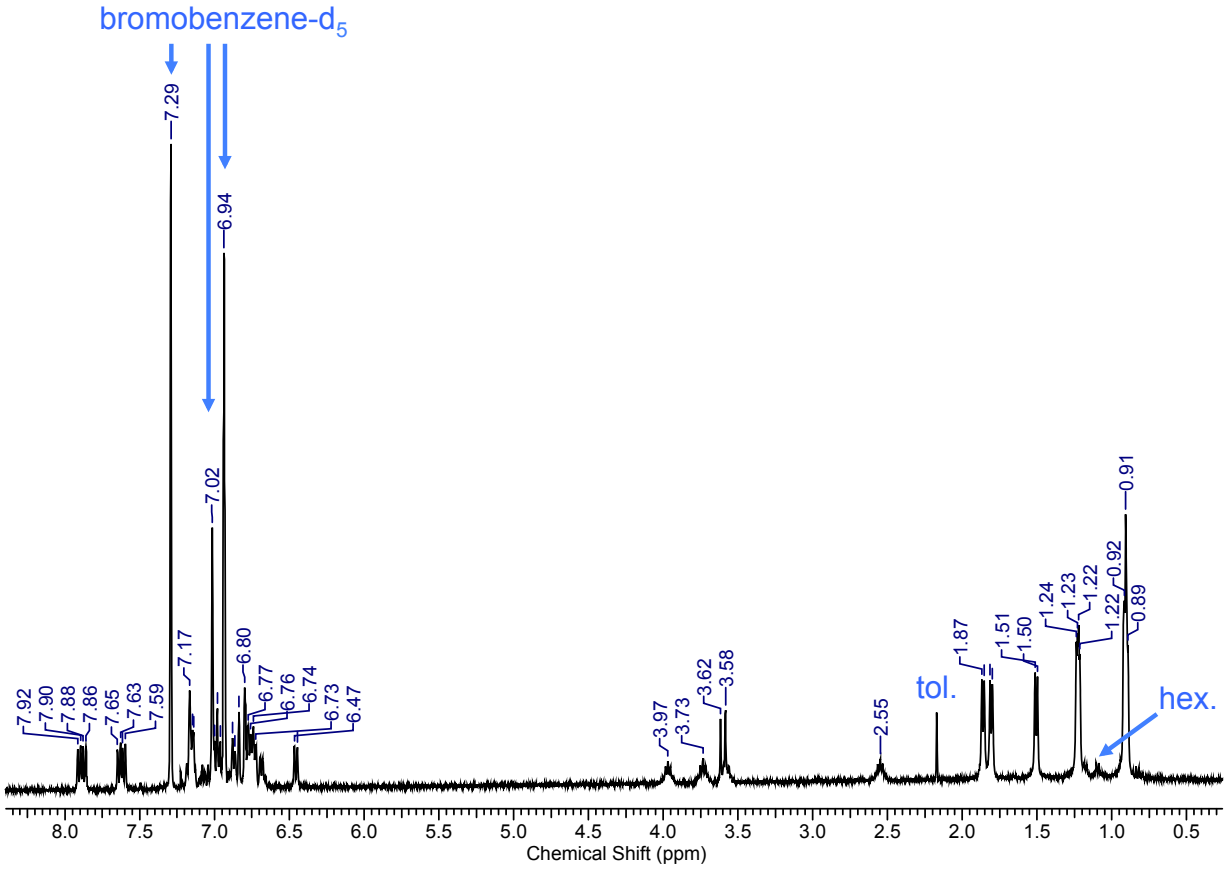

Figure S8. ^{1}H NMR (400 MHz, BrC_6D_5, -10 °C) of compound **2** in bromobenzene-d_5.

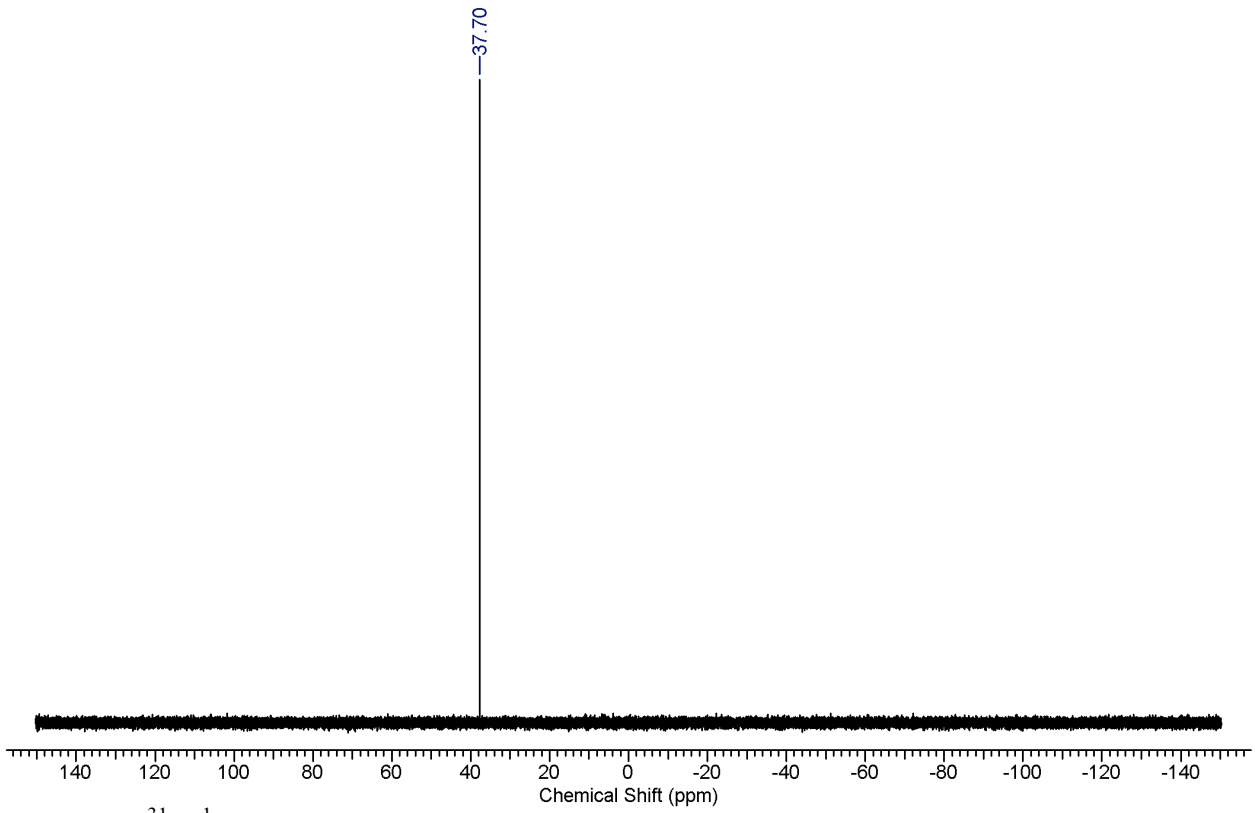

Figure S9. $^{31}P\{^{1}H\}$ NMR **(**400 MHz, BrC_6D_5) of compound **2** in bromobenzene-d_5.

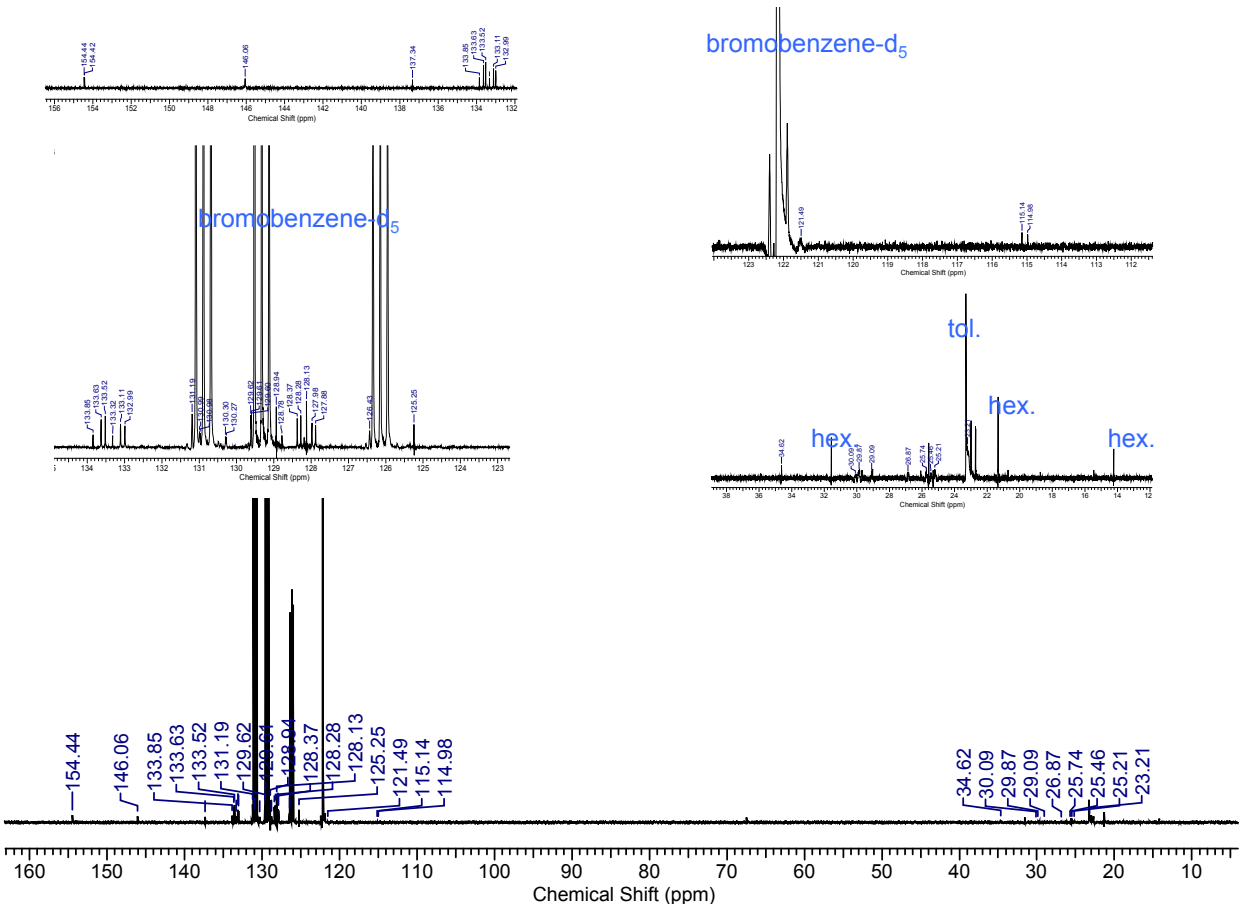

Figure S10. $^{13}C\{^{1}H\}$ NMR (126 MHz, BrC_6D_5) of compound **2** in bromobenzene-d_5.

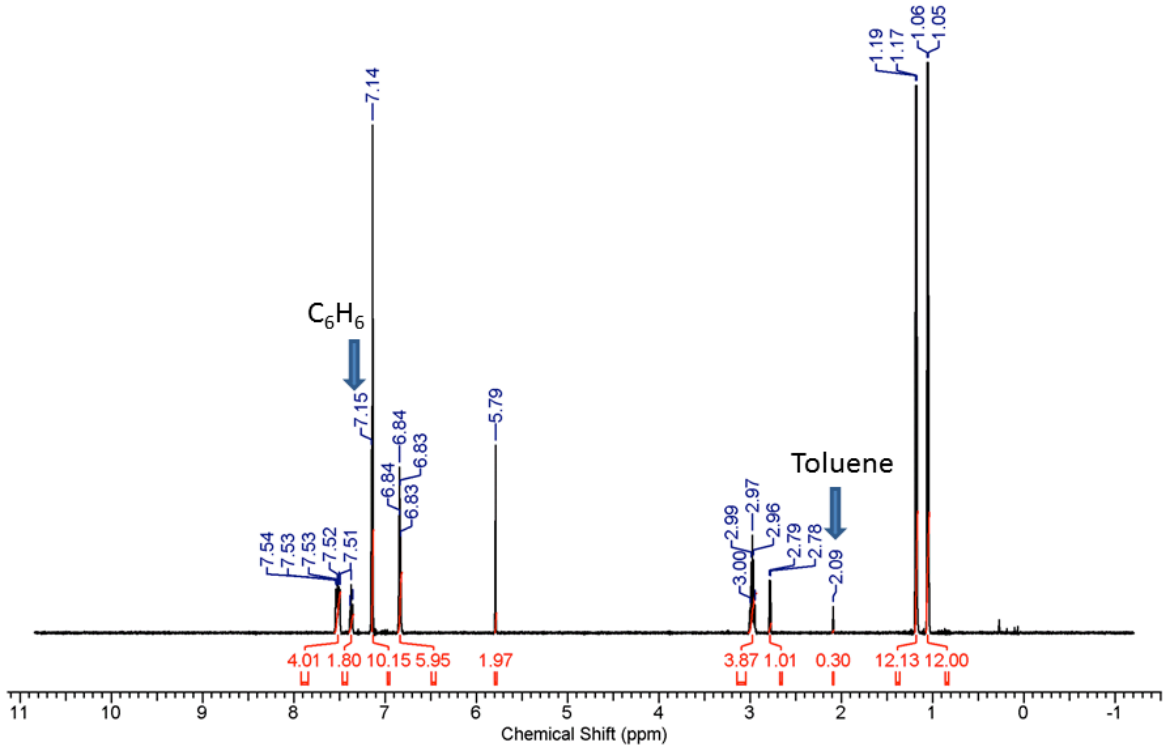

Figure S11. ^{1}H NMR (400 MHz, C_6D_6) of compound **6** in benzene-d_6.

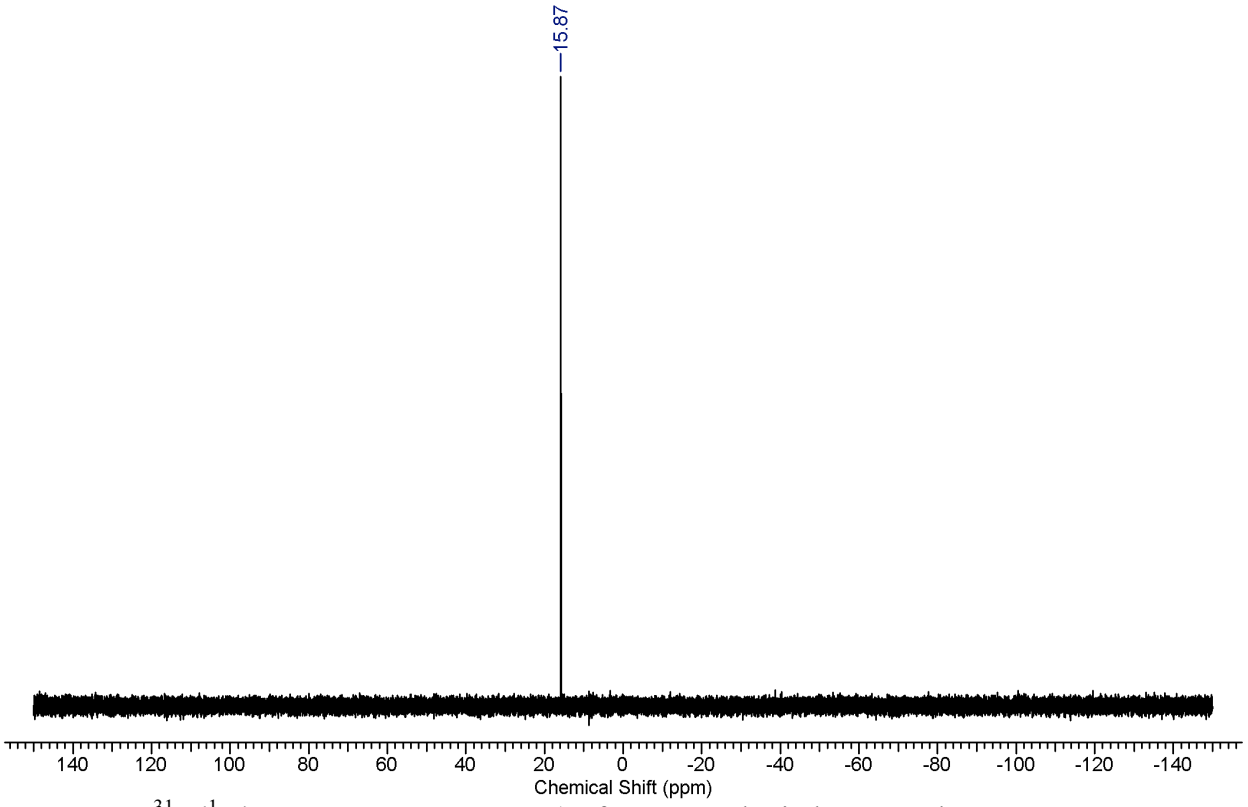

Figure S12. $^{31}P\{^{1}H\}$ NMR **(**400 MHz, C_6D_6) of compound **6** in benzene-d_6.

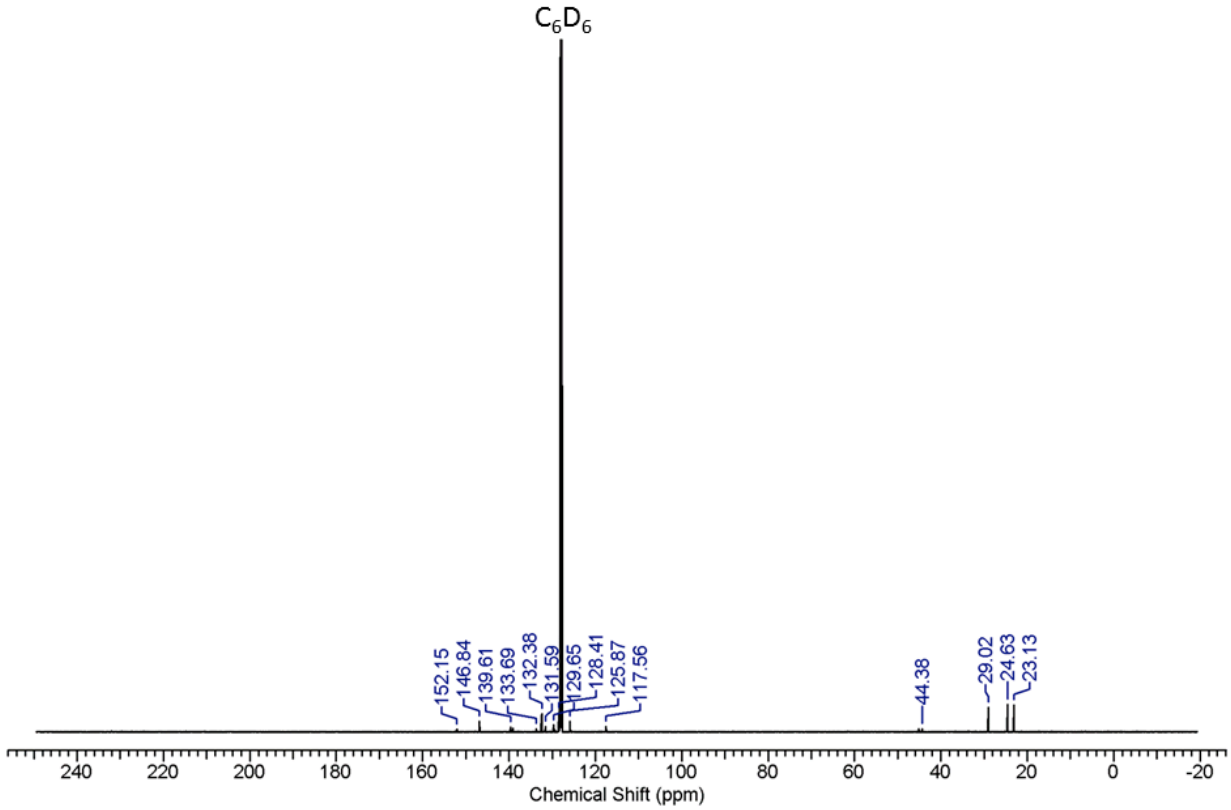

Figure S13. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6) of compound **6** in benzene-d_6.

5. Lifetime measurements

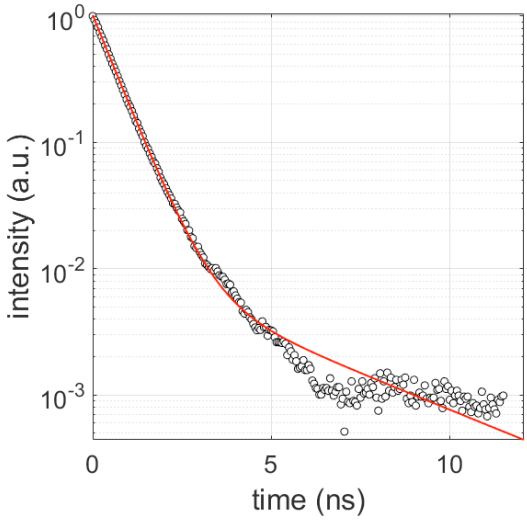

Figure S14. Lifetime of $(IPr{=}CH)PPh_2$ in THF solution (under N_2). A mode-locked, frequency-doubled Ti:sapphire laser (Spectra-Physics Tsunami, 385 nm) operated at 80 MHz with ~2 ps pulses was used as the excitation source. τ = ~ 0.62 ns, R = 0.9998.

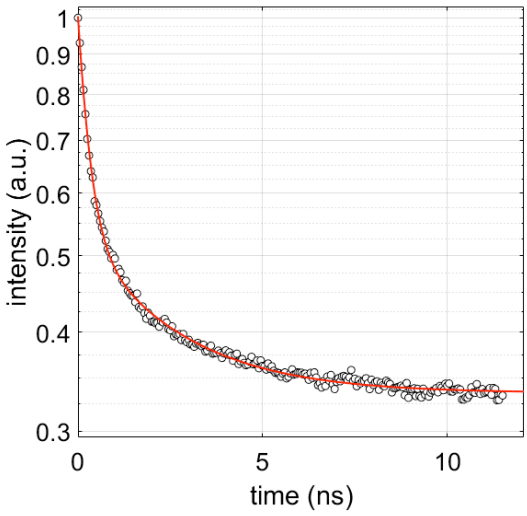

Figure S15. Lifetime of $[(IPr{=}CH)PPh_2(AuI)]$ **6** in the film state. A mode-locked, frequency-doubled Ti:sapphire laser (Spectra-Physics Tsunami, 385 nm) operated at 80 MHz with ~2 ps pulses was used as the excitation source. τ = ~ 0.29 ns, R = 0.9974.

6. Image of Compounds 1-4, 6 and (IPr=CH)PPh_2

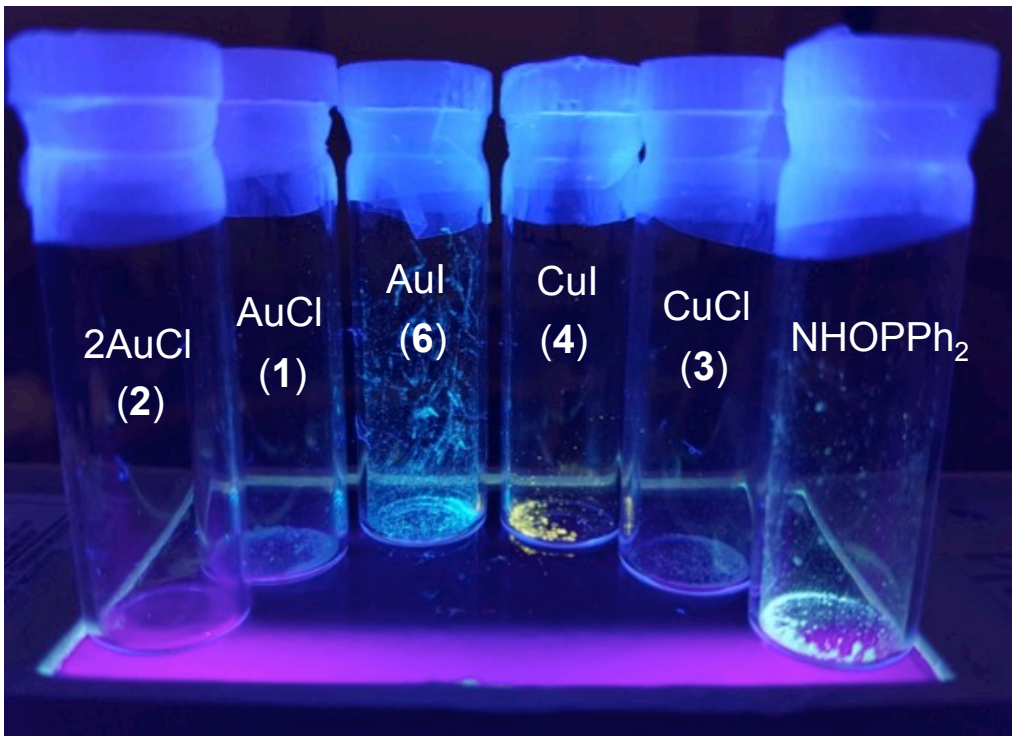

Figure S16. Compounds **1-4**, **6** and **(IPr=CH)PPh_2** in the solid state under UV light (λ_{ex} = 365 nm) in an N_2 atmosphere.

References

[1] M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

[2] P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. O. Gould, *DIRDIF-2008 Program*. Crystallographic Laboratory, Radboud University, Nijmegen, The Netherlands.

[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc.: Wallingford CT, 2010.

[4] A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

[5] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.

[6] S.H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys*. 1980, **58**, 1200.

[7] (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys*. 1985, **82**, 270; (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys*. 1985, **82**, 284; (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys*. 1985, **82**, 299.

[8] V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, and L. A. Curtiss, *J. Comp. Chem*. 2001, **22**, 976 and references therein.