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Intermolecular C-H Activation with an Ir-METAMORPhos Piano-Stool Complex – Multiple reaction steps at a reactive ligand

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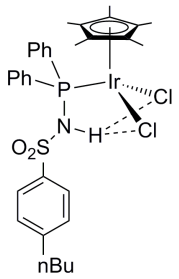
Table of contents

General procedures and Materials

All reactions were carried out in dry glassware under nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. THF, toluene and pentane were distilled from sodium under dinitrogen, CH_2Cl_2 was collected from an MB SPS-800. Deuterated solvents were degassed by four freeze-pump-thaw cycles and dried over molecular sieves (4Å). NMR spectra were measured on a Bruker AMX 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz and ^{31}P: 162.0 MHz) or on a Varian Mercury 300 (^{1}H: 300.1 MHz) spectrometer. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. High resolution mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV mass spectrometer. All reagents were purchased from commercial suppliers and used without further purification: Chlorodiphenylphosphine (Sigma Aldrich), trichlorophosphine (Sigma Aldrich), 4-butylbenzene-1-sulfonamide (ABCR GmbH), $[IrCl(Cp^*)(\mu\text{-}Cl)]_2$ (Strem Chemicals) and $[Cp^*RhCl_2]_2$ (Strem Chemicals), Phenylacetylene (Sigma Aldrich). Triethylamine (Sigma Aldrich) was freshly distilled and stored over molecular sieves (4 Å). Ligand $\mathbf{1^H}$ was prepared according to a literature procedure.[S1]

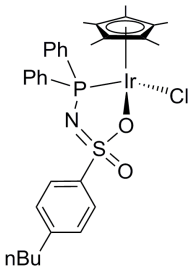
Synthetic Procedures, Characterization Data and NMR Spectra

Complex 2



Ligand **1** (190.6 mg) was dissolved in CH_2Cl_2 (2.0 mL) and $[Cp^*IrCl_2]_2$ (191.0 mg, 0.5 equivalent) was added. The formed suspension was stirred for 1 hour and a clear deep orange solution was obtained. The reaction mixture was concentrated to approximately 0.5 mL and pentane was added until an orange precipitate was formed. The suspension was carefully concentrated under high vacuum and **2a** was obtained quantitatively. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, ppm): δ 37.57 (s); **^{1}H NMR** (400 MHz, CD_2Cl_2, ppm): δ 7.87 (dt, *J* = 12.4, 7.4 Hz, 4H), 7.48-7.43 (m, 2H), 7.41 - 7.36 (m, 5H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.57-1.48 (m, 2H), 1.35 – 1.28 (m, 2H), 1.31 (d, *J* = 2.4 Hz, 15H), 0.94 (t, *J* = 7.8 Hz, 3H); **^{1}H{^{31}P} NMR** (400 MHz, CD_2Cl_2, ppm): δ 7.87 (d, *J* = 7.4 Hz, 4H), 7.48-7.43 (m, 2H), 7.41 – 7.36 (m, 5H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.57-1.48 (m, 2H), 1.35 – 1.28 (m, 2H), 1.31 (s, 15H), 0.94 (t, *J* = 7.8 Hz, 3H); **^{13}C NMR** (101 MHz, CD_2Cl_2, ppm): δ 147.71 (s, C_{quat}), 138.94 (s, C_{quat}), 134.10 (d, *J* = 11.8 Hz, CH), 132.00 (d, *J* = 2.2 Hz, CH), 128.38 (s, CH), 128.38 (d, *J* = 63.0 Hz C_{quat}), 127.90 (d, *J* = 11.4 Hz, CH), 126.35 (s, CH), 93.33 (d, *J* = 3.5 Hz, C_{quat}), 35.48 (s, CH_2), 33.41 (s, CH_2), 22.39 (s, CH_2), 13.89 (s, CH_3), 8.19 (s, CH_3); **HR-MS** (FAB^+): *m*/*z* calcd. for $C_{32}H_{39}Cl_2IrNO_2PS$ $[M]^+$: 795.1432, observed: 795.1443.

Complex 3



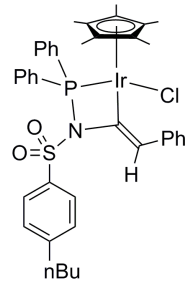
To a solution of **2** (350 mg) in CH_2Cl_2 (3 mL) was added sodium acetate (10-15 equivalents) and the suspension was stirred for 24 hours at room temperature. A slight color change from deep orange to orange was observed. The reaction mixture was filtered and concentrated to approximately 0.5 mL and pentane (5 mL) was added under vigorous stirring. The formed precipitate was filtered, washed with pentane (3 × 5 mL) and collected as yellow/orange solid (287 mg, yield 86 %).

*Note: Care should be taken in using $CHCl_3$ as solvent, because reprotonation of **3** occurs, probably due to trace amount of HCl in solution (although direct reaction with the solvent can not be excluded), which regenerates **2**.*

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, ppm): δ 48.80 (s), (δ 45.71 in THF-d_8); **^1H NMR** (400 MHz, CD_2Cl_2, ppm): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.60 (br. m, 2H), 7.60 – 7.38 (br. m, 8H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.51 (d, *J* = 2.1 Hz, 15H), 1.40 – 1.29 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **$^1H\{^{31}P\}$ NMR** (400 MHz, CD_2Cl_2, ppm): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.68 (br. s, 2H), 7.58 – 7.40 (m, 8H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.51 (s, 15H), 1.40 – 1.29 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_2Cl_2, ppm): δ 147.18 (s, C_{quat}), 138.80 (d, *J* = 60 Hz, C_{quat}), 137.86 (s, C_{quat}), 133.24 (s, C_{quat}), 132.41 (d, *J* = 11.4 Hz, CH), 132.11 (d, *J* = 11.2 Hz, CH), 130.68 (d, *J* = 25.7 Hz, CH), 128.55 (s, CH), 128.40 – 127.92 (m, CHs), 91.80 (d, *J* = 2.8 Hz, C_{quat}), 35.68 (s, CH_2), 33.66 (s, CH_2), 22.58 (s, CH_2), 13.99 (s, CH_3), 9.02 (s, CH_3); **HR-MS** (FAB^+): *m/z* calcd. for $C_{32}H_{39}ClIrNO_2PS$ $[M+H]^+$: 760.1749, observed: 760.1751 **Anal. Calcd.** for $C_{32}H_{38}ClIrNO_2PS$: C, 50.61; H, 5.04; N, 1.84, found: C, 50.73; H, 4.99, N, 1.89.

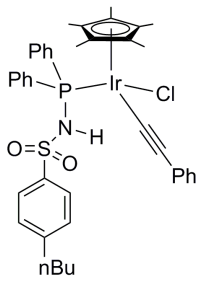
Note: From the broadness of the aromatic signals in the ^1H-NMR originating from -PPh_2 groups, the phenyl groups appear to have limited freedom in rotation due to steric hindrance from the Cp group. This is in line with the X-ray crystal structure obtained for complex **3**.*

Complex 4



Complex **3** (50 mg, 0.066 mmol) was dissolved in THF (2 mL) and phenylacetylene was added (7.2 µL, 0.066 mmol) and the reaction mixture was stirred at 50 °C for 3 hours. The reaction mixture was allowed to cool to room temperature and thereafter concentrated under vacuum. To the obtained yellow solid was added 0.2 mL CH_2Cl_2 followed by 5 mL pentane under stirring. The formed suspension was stirred for 15 minutes and then filtered. The yellow residue was washed with pentane (2 ×3 mL) and dried under vacuum. Complex **6a** was obtained as yellow solid (yield 76%). **$^{31}P\{^1H\}$ NMR** (162 MHz, THF-d_8, ppm): δ 30.98 (s); **^1H NMR** (400 MHz, THF-d_8, ppm): δ 8.45 – 8.33 (m, 2H), 7.62 – 7.53 (m, 2H), 7.54 – 7.47 (m, 6H), 7.47 – 7.39 (m, 4H), 7.10 – 7.01 (m, 4H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 4.4 Hz, 1H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.53 – 1.40 (m, 2H), 1.28 (d, *J* = 2.6 Hz, 15H), 1.28 – 1.17

(m, 2H), 0.84 (t, J = 7.3 Hz, 3H); **^{1}H{^{31}P} NMR** (400 MHz, THF-d_8, ppm): δ 8.45 – 8.33 (dd, J = 8.2, 1.4 Hz, 2H), 7.62 – 7.53 (m, 2H), 7.54 – 7.47 (m, 6H), 7.47 – 7.39 (m, 4H), 7.10 – 7.01 (m, 4H), 6.94 (t, J = 7.3 Hz, 1H), 6.88 (s, 1H), 2.50 (t, J = 7.6 Hz, 2H), 1.53 – 1.40 (m, 2H), 1.28 (s, 15H), 1.28 – 1.17 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8, ppm): δ 149.28 (s, C_{quat}), 143.23 (s, C_{quat}), 139.83 (d, J = 14.7 Hz, CH), 139.09 (s, C_{quat}), 134.42 (d, J = 63.5 Hz, C_{quat}) 134.13 (d, J = 2.6 Hz, CH), 133.45 (d, J = 11.5 Hz, CH), 132.83 (d, J = 2.7 Hz, CH), 130.77 (s, CH), 129.74 (s, CH), 129.58 (d, J = 11.6 Hz, CH), 129.08 (s, CH), 128.92 (s, CH), 128.82 (s, CH), 128.73 (s, CH), 128.08 (d, J = 48.3 Hz, C_{quat}), 125.53 (s, CH), 114.06 (d, J = 11.7 Hz, CH), 95.46 (d, J = 3.5 Hz, C_{quat}), 36.13 (s, CH_2), 33.60 (s, CH_2), 23.01 (s, CH_2), 14.01 (s, CH_3), 8.55 (s, CH_3); **HR-MS** (FD^+): *m/z* calcd. for $C_{40}H_{44}ClIrNO_2P_1S_1$ $[M]^+$: 859.21248 observed: 859.21648; **Anal. Calcd.** for $C_{40}H_{44}ClIrNO_2P_1S_1 \cdot 0.7$pentane: C, 57.29; H, 5.79; N, 1.54 found: C, 57.58; H, 5.45, N, 1.71.



Complex 5

Complex **3** (25 mg, 0.033 mmol) was dissolved in THF-d_8 (0.7 mL) and phenylacetylene was added (3.6 µL, 0.033 mmol) at 0 °C. In situ NMR spectra were obtained at 0 °C after 3 hours of reaction. **^{31}P{^{1}H} NMR** (162 MHz, THF-d_8, ppm): δ 33.14 (s); **^{1}H NMR** (400 MHz, THF-d_8, ppm): δ 8.04 – 7.96 (m, 2H), 7.93 (dd, J = 11.8, 7.8 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.45 – 7.36 (m, 5H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 – 7.10 (m, 3H), 7.09 – 7.02 (m, 2H), 6.82 (t, J = 7.1 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 1.66 – 1.50 (m, 2H), 1.47 (d, J = 1.8 Hz, 15H), 1.33 – 1.22 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8, ppm): δ 147.31 (s, C_{quat}), 142.37 (s, C_{quat}), 138.94 (s, CH), 135.76 (d, J = 15.0 Hz, CH), 133.91 (s, CH), 132.72 – 132.53 (m), 132.29 (s, CH), 131.55 (s, CH), 128.62 (s), 128.39 – 127.82 (m), 127.04 (s), 125.25 (s), 124.87 – 124.76 (m), 124.70 (s, C_{quat}), 102.70 (d, J = 6.4 Hz, C_{quat}), 95.74 (d, J = 3.4 Hz, C_{quat}), 94.86 (s, C_{quat}), 35,87 (s, CH_2), 33.98 (s, CH_2), 22.93 (s, CH_2), 14.05 (s, CH_3), 8.26 (s, CH_3).

Computational details

Geometry optimizations were carried out with the Turbomole program package,[S2] coupled to the PQS Baker optimizer[S3] via the BOpt package,[S4] at the spin unrestricted ri-DFT level using the BP86 functional, the resolution-of-identity (ri) method, and the def2-TZVP basis set for the geometry optimizations.

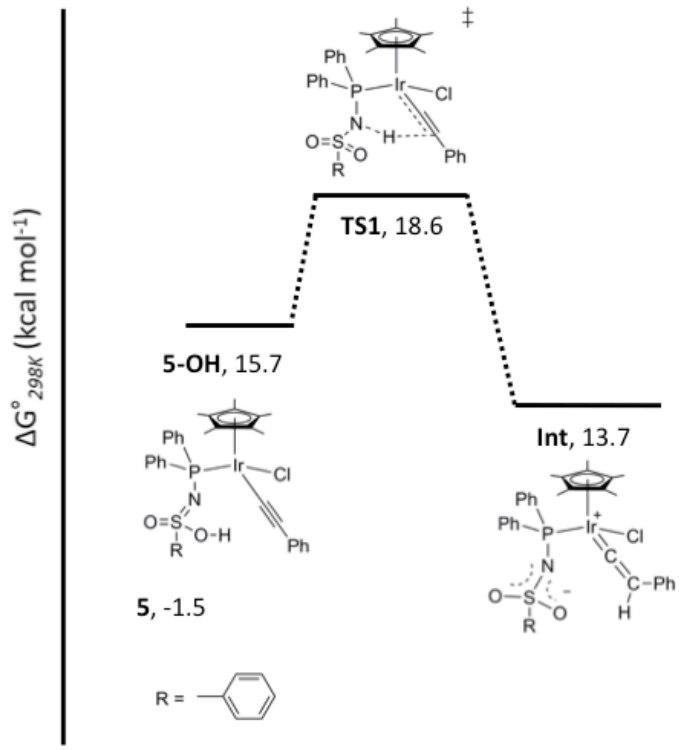


Figure S1. *Potential energy diagram (DFT, BP86, def2-TZVP) for the formation of* ***Int*** *from* ***5a-OH*** *via protonation with the sulfone group;* ΔG^{o}_{298K} *is in kcal mol*$^{-1}$ *complex* ***3a*** *+ phenylacetylene are used as reference point.*

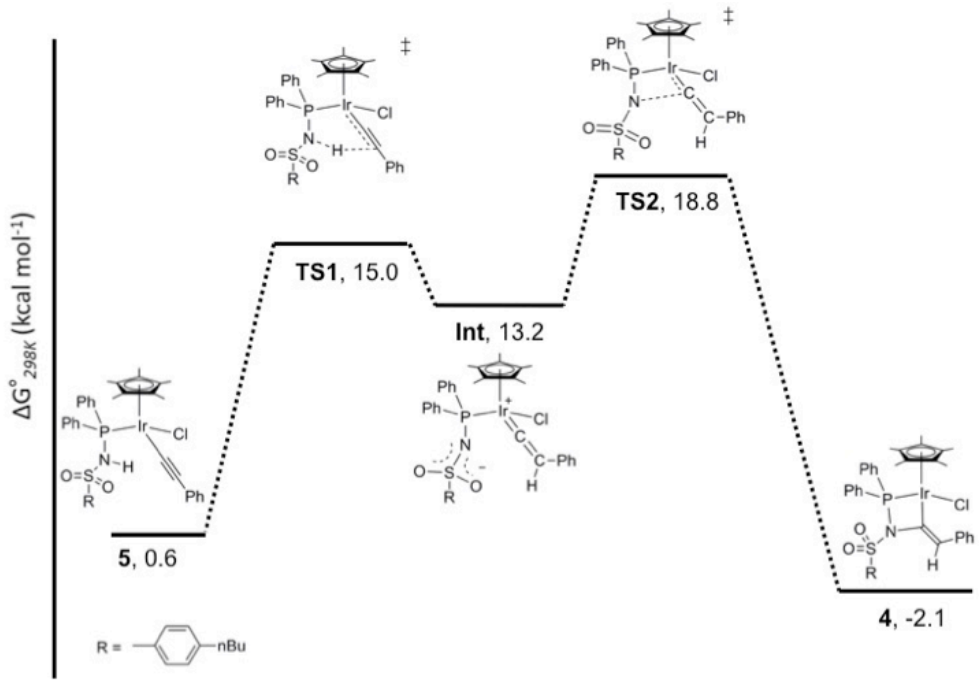


Figure S2. *Potential energy diagram (DFT, BP86, def2-TZVP) with COSMO solvent correction, dielectric constant 7.58,* ΔG^{o}_{298K} *is in kcal mol*$^{-1}$ *complex* ***3a*** *+ phenylacetylene are used as reference point.*

Energies and imaginairy frequencies of calculated structures

Structure	SCF	imaginairy frequencies
3	-2595.34263	
5	-2903.87957	
TS1	-2903.84688	-1059.23999
Int	-2903.85509	
TS2	-2903.85259	-251.80999
4	-2903.89349	
5_OH	-2903.85477	
TS1_OH	-2903.84744	-734.07007

Cartesian Coordinates for Optimized Structures

Complex **3**

X	Y	Z
0.657	3.997	10.337
-1.193	3.371	8.933
2.564	1.907	8.812
1.857	4.551	8.425
1.438	2.040	9.847
3.841	1.520	9.405
2.617	3.174	7.890
2.040	0.555	7.762
0.720	0.512	7.301
0.333	-0.537	6.467
1.253	-1.524	6.097
2.568	-1.469	6.568
2.968	-0.427	7.409
0.959	5.212	6.972
-0.130	6.081	7.124
-0.756	6.627	6.001
-0.305	6.299	4.720
0.770	5.421	4.563
1.404	4.879	5.683
3.222	5.770	8.623
3.082	7.122	8.276
4.142	8.013	8.462
5.354	7.562	8.991
5.505	6.212	9.326
4.447	5.319	9.142
-0.658	4.124	12.188
-0.356	5.431	11.589
1.079	5.641	11.697
1.672	4.431	12.229
0.575	3.513	12.547
-2.033	3.557	12.325
-1.387	6.443	11.198
1.786	6.937	11.471
3.105	4.223	12.607
0.772	2.149	13.125
0.010	1.285	7.605
-0.696	-0.585	6.106
3.286	-2.240	6.284
3.985	-0.368	7.797
-0.508	6.301	8.123
-1.609	7.295	6.128
-0.800	6.719	3.843

1.117	5.153	3.564
2.236	4.184	5.568
2.147	7.479	7.841
4.024	9.061	8.180
6.184	8.256	9.128
6.456	5.849	9.718
4.577	4.260	9.371
-2.013	2.543	12.743
-2.531	3.509	11.345
-2.643	4.188	12.990
-0.953	7.239	10.579
-1.825	6.917	12.092
-2.200	5.975	10.628
1.762	7.525	12.403
1.308	7.535	10.687
2.835	6.793	11.191
3.771	4.862	12.015
3.413	3.181	12.447
3.266	4.463	13.672
-0.152	1.559	13.098
1.102	2.225	14.174
1.541	1.597	12.569
0.943	-2.341	5.443

Complex **4**

X	Y	Z
8.211	4.091	3.432
6.221	4.129	4.825
6.864	0.055	2.030
7.168	3.120	1.661
6.111	0.238	0.798
7.998	-0.856	2.035
7.370	1.608	2.473
5.750	-0.444	3.338
5.711	-1.801	3.674
4.792	-2.236	4.630
3.936	-1.319	5.248
3.997	0.036	4.912
4.903	0.484	3.950
5.448	3.497	1.158
4.833	2.851	0.068
3.539	3.204	-0.312
2.850	4.208	0.376
3.460	4.862	1.448
4.755	4.511	1.840

8.045	2.971	0.061
7.789	3.892	-0.970
8.502	3.826	-2.169
9.471	2.836	-2.355
9.727	1.916	-1.335
9.027	1.986	-0.129
10.178	4.832	2.755
9.223	5.924	2.553
8.701	6.294	3.822
9.374	5.485	4.844
10.302	4.620	4.187
11.113	4.286	1.721
8.945	6.598	1.246
7.705	7.369	4.123
9.178	5.674	6.313
11.321	3.733	4.828
8.535	0.038	4.189
6.399	-2.498	3.196
4.753	-3.292	4.899
3.346	0.756	5.409
4.970	1.545	3.709
5.361	2.065	-0.468
3.066	2.689	-1.149
1.836	4.480	0.075
2.929	5.646	1.989
5.224	5.000	2.693
7.015	4.651	-0.844
8.289	4.542	-2.964
10.018	2.776	-3.297
10.472	1.132	-1.479
9.231	1.258	0.657
10.653	4.258	0.726
11.432	3.266	1.970
12.019	4.912	1.653
7.946	7.052	1.224
9.021	5.901	0.402
9.681	7.400	1.075
8.190	8.221	4.626
6.913	6.993	4.787
7.230	7.748	3.209
9.705	4.909	6.894
8.111	5.628	6.575
9.557	6.662	6.622
12.303	4.234	4.818
11.425	2.783	4.289
11.067	3.497	5.867

8.129	2.016	3.648
8.602	1.083	4.508
9.200	1.258	5.834
10.311	1.434	8.435
8.733	2.214	6.759
10.215	0.373	6.260
10.769	0.465	7.536
9.284	2.298	8.039
7.906	2.864	6.469
10.571	-0.394	5.568
11.559	-0.227	7.834
8.891	3.033	8.745
10.734	1.500	9.438
3.227	-1.661	6.003

TS 1

X	Y	Z
1.244	8.913	12.778
1.313	10.041	10.642
4.930	12.077	13.630
3.566	9.499	13.131
4.380	13.251	14.308
6.040	11.382	14.289
3.690	11.122	13.264
0.884	10.587	13.538
0.971	11.801	13.956
0.264	12.988	14.389
0.993	14.140	14.747
0.324	15.290	15.167
-1.072	15.313	15.240
-1.802	14.172	14.885
-1.144	13.020	14.462
5.553	12.657	12.043
6.885	13.081	11.976
7.381	13.596	10.777
6.554	13.682	9.653
5.227	13.250	9.729
4.718	12.737	10.925
0.855	7.121	14.086
1.391	6.562	12.844
0.521	6.918	11.781
-0.589	7.693	12.330
-0.398	7.769	13.760
1.332	6.793	15.465
2.571	5.646	12.757
0.651	6.553	10.338

-1.763	8.174	11.538
-1.369	8.323	14.756
4.166	8.745	14.702
4.945	7.579	14.750
5.360	7.052	15.978
5.000	7.684	17.170
4.226	8.848	17.130
3.812	9.375	15.907
4.707	8.826	11.854
4.238	8.227	10.677
5.137	7.750	9.719
6.512	7.871	9.926
6.988	8.483	11.090
6.096	8.961	12.051
2.142	11.802	13.823
2.083	14.118	14.689
0.900	16.175	15.440
-1.591	16.214	15.570
-2.892	14.183	14.936
-1.716	12.135	14.179
7.521	12.995	12.858
8.420	13.927	10.720
4.580	13.307	8.851
3.689	12.384	10.990
1.020	7.553	16.191
2.425	6.716	15.514
0.912	5.826	15.789
2.239	4.603	12.892
3.305	5.860	13.542
3.078	5.713	11.787
0.611	7.453	9.705
-0.177	5.893	10.037
1.592	6.028	10.135
-2.405	7.329	11.241
-1.434	8.689	10.625
-2.378	8.876	12.115
-2.019	9.086	14.310
-0.858	8.773	15.615
-2.014	7.514	15.135
5.262	7.094	13.826
5.980	6.154	15.999
5.333	7.280	18.127
3.957	9.359	18.055
3.231	10.297	15.882
3.165	8.177	10.491
4.758	7.295	8.802
7.214	7.502	9.176

8.061	8.597	11.250
6.473	9.454	12.948
6.946	14.080	8.716
Int		
X	Y	Z
1.486	8.926	12.919
1.543	9.696	10.653
5.234	11.587	13.803
3.884	9.145	12.890
4.449	11.998	14.985
6.571	11.066	14.098
4.407	10.665	12.808
1.467	10.636	13.592
1.440	11.855	14.078
0.539	12.964	13.744
0.595	14.147	14.505
-0.259	15.214	14.225
-1.184	15.123	13.181
-1.238	13.955	12.411
-0.387	12.887	12.684
5.451	13.069	12.809
6.505	13.921	13.158
6.682	15.115	12.458
5.815	15.454	11.415
4.768	14.594	11.071
4.580	13.397	11.767
0.895	7.383	14.453
1.177	6.565	13.279
0.286	6.955	12.247
-0.600	7.994	12.763
-0.255	8.218	14.141
1.441	7.135	15.823
2.138	5.420	13.258
0.194	6.403	10.862
-1.737	8.592	11.996
-1.003	9.066	15.122
4.576	8.246	14.346
5.240	7.017	14.206
5.775	6.368	15.324
5.661	6.944	16.591
5.011	8.174	16.736
4.464	8.818	15.626
4.667	8.302	11.458
4.029	7.335	10.675
4.711	6.711	9.627
6.038	7.053	9.355
6.678	8.025	10.130

5.998	8.653	11.175
2.265	12.044	14.790
1.320	14.225	15.317
-0.198	16.124	14.824
-1.850	15.958	12.962
-1.945	13.881	11.582
-0.411	11.993	12.059
7.183	13.635	13.963
7.505	15.780	12.725
4.094	14.852	10.253
3.778	12.709	11.502
1.361	8.026	16.457
2.496	6.838	15.797
0.874	6.324	16.310
1.678	4.544	13.745
3.060	5.650	13.807
2.414	5.128	12.238
0.337	7.201	10.116
-0.800	5.962	10.692
0.943	5.623	10.682
-2.544	7.856	11.858
-1.406	8.921	11.001
-2.160	9.460	12.516
-1.544	9.881	14.628
-0.331	9.516	15.863
-1.738	8.449	15.663
5.366	6.574	13.218
6.297	5.418	15.198
6.091	6.445	17.461
4.938	8.643	17.718
3.991	9.793	15.750
2.983	7.094	10.864
4.199	5.971	9.010
6.568	6.572	8.532
7.711	8.304	9.917
6.490	9.422	11.772
5.958	16.387	10.867

TS2

X	Y	Z
1.531	9.063	12.841
1.671	10.032	10.642
5.275	11.766	13.749
3.872	9.248	13.042
4.712	12.667	14.763
6.486	11.028	14.127

4.080	10.854	13.210
1.645	10.792	13.556
1.521	11.993	14.083
0.285	12.794	14.114
0.122	13.772	15.114
-1.037	14.546	15.168
-2.054	14.365	14.227
-1.893	13.409	13.218
-0.735	12.634	13.156
5.710	12.802	12.345
6.927	13.493	12.402
7.280	14.346	11.356
6.424	14.507	10.260
5.215	13.809	10.211
4.850	12.953	11.255
0.830	7.500	14.302
1.127	6.757	13.080
0.276	7.238	12.051
-0.600	8.263	12.615
-0.280	8.390	14.010
1.335	7.160	15.669
2.078	5.605	12.990
0.211	6.775	10.631
-1.705	8.936	11.865
-1.013	9.214	15.022
4.493	8.373	14.537
5.076	7.097	14.467
5.518	6.457	15.629
5.388	7.086	16.869
4.818	8.361	16.944
4.369	9.000	15.788
4.884	8.526	11.690
4.309	7.800	10.638
5.112	7.273	9.623
6.493	7.475	9.648
7.072	8.208	10.688
6.277	8.732	11.709
2.433	12.418	14.532
0.915	13.921	15.849
-1.143	15.301	15.949
-2.956	14.976	14.267
-2.667	13.282	12.459
-0.588	11.927	12.338
7.589	13.350	13.256
8.228	14.885	11.394
4.548	13.926	9.355

3.914	12.394	11.224
1.275	8.021	16.346
2.379	6.824	15.649
0.728	6.348	16.104
1.569	4.678	13.302
2.943	5.740	13.652
2.450	5.455	11.969
0.336	7.623	9.939
-0.767	6.313	10.424
0.987	6.033	10.409
-2.526	8.229	11.664
-1.348	9.320	10.899
-2.122	9.778	12.432
-1.497	10.086	14.568
-0.342	9.577	15.810
-1.794	8.602	15.503
5.218	6.615	13.499
5.981	5.471	15.560
5.744	6.592	17.774
4.734	8.868	17.906
3.950	10.005	15.850
3.226	7.683	10.595
4.653	6.716	8.804
7.119	7.069	8.851
8.149	8.380	10.705
6.730	9.311	12.516
6.705	15.172	9.442

Complex **5**

X	Y	Z
8.432	4.472	3.747
6.845	3.977	5.537
7.223	-0.277	3.323
7.599	2.696	2.542
7.094	-0.544	1.900
8.125	-1.070	4.141
7.692	1.303	3.540
5.593	-0.390	4.055
4.750	-1.406	3.589
3.512	-1.595	4.205
3.125	-0.776	5.269
3.973	0.240	5.717
5.217	0.440	5.114
5.864	2.788	1.956
5.372	1.937	0.949

4.040	2.030	0.544
3.185	2.964	1.136
3.664	3.801	2.146
4.996	3.716	2.556
8.593	2.298	1.053
8.240	2.746	-0.230
9.082	2.505	-1.321
10.285	1.820	-1.140
10.646	1.378	0.137
9.810	1.618	1.227
9.590	5.800	2.415
8.187	6.194	2.273
7.716	6.632	3.544
8.835	6.569	4.492
9.986	6.102	3.782
10.523	5.450	1.297
7.434	6.250	0.980
6.361	7.166	3.880
8.759	7.007	5.919
11.374	5.977	4.323
8.325	1.447	4.343
5.062	-2.031	2.753
2.849	-2.385	3.849
3.668	0.889	6.539
5.870	1.247	5.448
6.023	1.190	0.499
3.668	1.363	-0.236
2.144	3.032	0.816
2.998	4.520	2.625
5.366	4.342	3.368
7.295	3.266	-0.389
8.789	2.848	-2.314
10.937	1.625	-1.992
11.582	0.839	0.286
10.103	1.277	2.221
10.020	4.870	0.513
11.370	4.855	1.658
10.928	6.364	0.831
6.359	6.081	1.121
7.805	5.506	0.264
7.561	7.243	0.517
6.413	8.249	4.079
5.961	6.678	4.781
5.649	7.010	3.060
9.655	6.712	6.478
7.890	6.556	6.419

8.663	8.103	5.985
11.957	6.875	4.062
11.889	5.102	3.908
11.374	5.876	5.414
9.683	3.164	4.565
10.486	2.385	5.084
11.452	1.529	5.688
13.389	-0.156	6.872
12.615	2.064	6.289
11.283	0.125	5.700
12.242	-0.700	6.285
13.568	1.231	6.871
12.756	3.146	6.293
10.392	-0.311	5.246
12.089	-1.781	6.283
14.458	1.667	7.329
14.135	-0.807	7.329
2.156	-0.927	5.748

Complex **5_OH**

X	Y	Z
1.606	8.779	12.770
1.790	9.645	10.509
4.925	11.648	13.619
3.911	8.942	12.886
3.744	12.007	14.645
6.130	11.642	14.430
4.557	10.470	12.734
1.380	10.659	13.334
1.042	11.807	13.649
0.507	13.112	13.889
0.796	13.831	15.069
0.252	15.097	15.282
-0.594	15.675	14.331
-0.887	14.975	13.156
-0.344	13.712	12.932
4.977	13.040	12.507
5.798	14.121	12.844
5.831	15.231	11.999
5.052	15.254	10.839
4.238	14.164	10.515
4.194	13.044	11.348
0.860	7.378	14.335
1.248	6.545	13.199
0.445	6.920	12.081

-0.491	7.959	12.513
-0.256	8.203	13.906
1.293	7.170	15.752
2.203	5.395	13.274
0.448	6.323	10.710
-1.548	8.565	11.646
-1.054	9.101	14.795
4.622	8.182	14.414
5.346	6.979	14.378
5.852	6.419	15.555
5.651	7.057	16.781
4.932	8.256	16.825
4.413	8.809	15.655
4.844	8.093	11.546
4.223	7.196	10.671
4.963	6.546	9.679
6.331	6.794	9.551
6.957	7.700	10.414
6.219	8.349	11.404
2.839	11.778	14.219
1.457	13.388	15.815
0.492	15.637	16.200
-1.018	16.665	14.502
-1.543	15.419	12.405
-0.563	13.169	12.012
6.405	14.076	13.747
6.471	16.079	12.248
3.635	14.179	9.607
3.573	12.181	11.105
1.174	8.083	16.347
2.345	6.867	15.817
0.687	6.379	16.226
1.684	4.508	13.674
3.047	5.608	13.941
2.608	5.128	12.290
0.595	7.102	9.946
-0.515	5.829	10.508
1.238	5.570	10.593
-2.354	7.840	11.446
-1.126	8.880	10.681
-1.997	9.446	12.120
-1.515	9.923	14.235
-0.433	9.546	15.582
-1.858	8.523	15.280
5.533	6.484	13.426
6.417	5.487	15.508

6.056	6.626	17.697
4.777	8.766	17.776
3.854	9.743	15.708
3.148	7.039	10.746
4.464	5.860	8.993
6.908	6.292	8.772
8.023	7.908	10.311
6.706	9.068	12.064
5.083	16.124	10.181

TS1_OH

X	Y	Z
1.514	8.798	12.762
1.638	9.618	10.494
4.908	11.671	13.697
3.844	9.042	12.858
3.801	12.141	14.662
6.131	11.418	14.449
4.398	10.584	12.726
1.384	10.614	13.346
1.353	11.806	13.773
0.599	13.039	13.891
1.074	14.111	14.673
0.336	15.289	14.788
-0.889	15.425	14.129
-1.368	14.370	13.344
-0.635	13.192	13.222
5.195	13.065	12.610
6.172	13.993	12.983
6.388	15.112	12.177
5.635	15.296	11.013
4.664	14.357	10.650
4.437	13.233	11.447
0.827	7.361	14.341
1.203	6.521	13.207
0.375	6.868	12.105
-0.565	7.901	12.540
-0.309	8.166	13.927
1.284	7.164	15.752
2.188	5.397	13.276
0.371	6.267	10.735
-1.652	8.470	11.684
-1.109	9.054	14.828
4.540	8.266	14.382
5.298	7.084	14.335

5.808	6.522	15.509
5.578	7.137	16.741
4.829	8.317	16.795
4.306	8.872	15.628
4.765	8.205	11.505
4.171	7.249	10.675
4.917	6.616	9.676
6.264	6.940	9.499
6.861	7.903	10.318
6.117	8.537	11.314
2.624	11.892	14.215
2.032	14.012	15.186
0.722	16.107	15.398
-1.465	16.347	14.221
-2.319	14.469	12.817
-1.000	12.379	12.593
6.757	13.824	13.886
7.152	15.839	12.457
4.081	14.495	9.739
3.695	12.484	11.171
1.161	8.077	16.347
2.340	6.875	15.803
0.693	6.367	16.235
1.712	4.516	13.738
3.060	5.655	13.890
2.547	5.100	12.283
0.499	7.046	9.968
-0.588	5.760	10.545
1.169	5.526	10.612
-2.427	7.713	11.481
-1.251	8.813	10.720
-2.139	9.324	12.170
-1.634	9.836	14.268
-0.475	9.548	15.573
-1.863	8.457	15.365
5.509	6.610	13.377
6.401	5.607	15.455
5.988	6.706	17.655
4.655	8.812	17.751
3.731	9.797	15.687
3.110	7.029	10.788
4.439	5.883	9.024
6.845	6.452	8.714
7.910	8.170	10.176
6.578	9.301	11.940
5.810	16.170	10.384

Comparison between DFT and X-ray Crystallographic Metric Parameters

Complex **3**	X-ray	DFT
Ir1–P1	2,297	2,324
Ir1-O1	2,163	2,163
Ir1-Cl1	2,398	2,405
P1-N1	1,654	1,661
N1-S1	1,546	1,568
S1-O1	1,510	1,525
S1-O2	1,445	1,460
P_1-Ir_1-O_1	80,41	80,96

Table S2

Complex **4**	X-ray	DFT
Ir1–P1	2,232	2,273
Ir1-C1	2,077	2,088
Ir1-Cl1	2,408	2,429
P1-N1	1,717	1,728
N1-C1	1,468	1,457
N1-S1	1,653	1,692
S1-O1	1,436	1,455
S1-O2	1,430	1,455
C1-C2	1,338	1,354
P1-Ir1-C1	69,21	68,78
Ir1-P1-N1	88,48	87,37
P1-N1-C1	100,26	101,23
N1-C1-Ir1	101,91	102,43

Table S3

X-ray Crystallographic Details

X-ray crystal structure determination of complex ***2***

$C_{32}H_{39}Cl_2IrNO_2PS$, Fw = 795.77, orange needle, 0.63 × 0.33 × 0.16 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 10.16597(16), b = 10.5116(3), c = 15.5310(3) Å, α = 76.518(1), β = 78.361(1), γ = 80.796 °, V = 1569.58(6) $Å^3$, Z = 2, D_x = 1.684 g/cm^3, μ = 4.57 mm^{-1}. 22217 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. The intensities were integrated with the Eval15 software.[S5] An analytical absorption correction and scaling was performed with SADABS[S6] (correction range 0.15-0.69). 7214 Reflections were unique (R_{int} = 0.012), of which 7109 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.[S7] Least-squares refinement was performed with SHELXL-97[S8] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. The N-H hydrogen atom was refined freely with an isotropic displacement parameter; all other hydrogen atoms were refined with a riding model. 371 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0117 / 0.0297. R1/wR2 [all refl.]: 0.0120 / 0.0298. S = 1.091. Residual electron density between -0.68 and 0.81 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[S9]

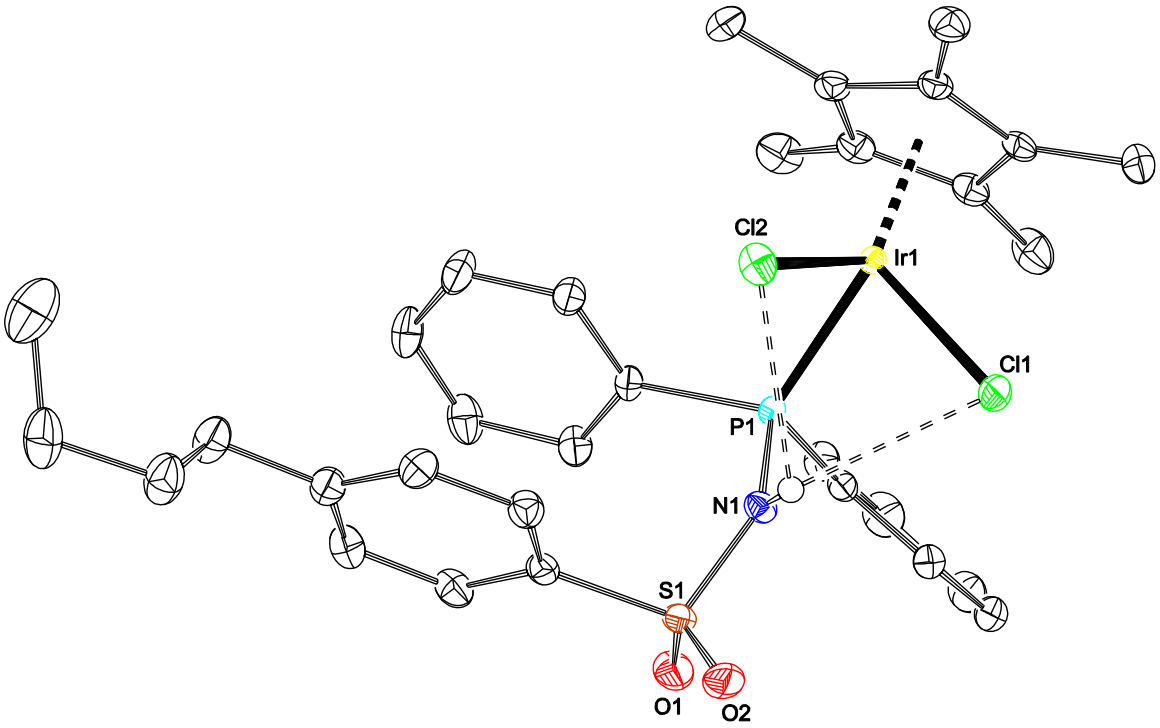


Figure S3. *Displacement ellipsoid plot of complex* ***2*** *in the crystal (50% probability level). C-H hydrogen atoms are omitted for clarity. Intramolecular N-H…Cl hydrogen bonds are drawn as dashed lines.*

Table S1. *Hydrogen bond geometries in complex **2**.*

	D-H [Å]	H…A [Å]	D….A [Å]	D-H…A [°]
N1-H1N…Cl1	0.81(2)	2.67(2)	3.1451(13)	119.8(19)
N1-H1N…Cl2	0.81(2)	2.82(2)	3.2529(14)	115.9(19)

*X-ray crystal structure determination of complex **3***

$C_{32}H_{38}ClIrNO_2PS$, Fw = 759.31, orange block, 0.46 × 0.28 × 0.14 mm^3, monoclinic, $P2_1/n$ (no. 14), a = 14.3385(17), b = 14.6511(17), c = 15.2223(18) Å, β = 107.9132(17) °, V = 3042.8(6) $Å^3$, Z = 4, D_x = 1.658 g/cm^3, μ = 4.63 mm^{-1}. 45334 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. The intensities were integrated with the Saint software.[S10] Multi-scan absorption correction and scaling was performed with SADABS[S6] (correction range 0.28-0.43). 7021 Reflections were unique (R_{int} = 0.013), of which 6806 were observed [I>2σ(I)]. The initial structural model was taken from the isostructural Rh-complex. Least-squares refinement was performed with SHELXL-2013[S11] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 358 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0118 / 0.0293. R1/wR2 [all refl.]: 0.0126 / 0.0296. S = 1.083. Residual electron density between -0.36 and 0.92 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[S9]

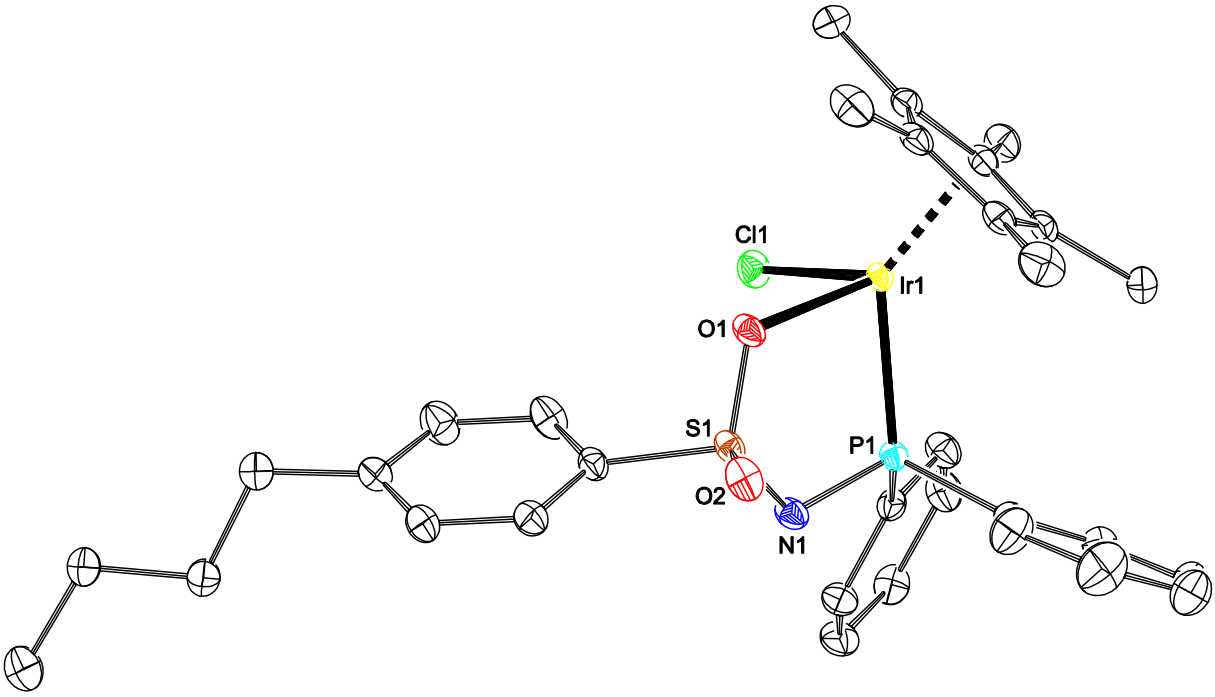


Figure S4. *Displacement ellipsoid plot of complex **3** in the crystal (50% probability level). Hydrogen atoms are omitted for clarity.*

*X-ray determination of complex **4***

X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.[S12] Absorption correction and scaling was performed with SADABS.[S13] The structures were solved with the program SHELXTL.[S12] Least-squares refinement was performed with SHELXL-2013[S14] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atoms. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[S9]

$C_{40}H_{44}ClIrNO_2PS$, Fw = 861.44, light-yellow blocks, 0.24×0.24×0.10 mm, monoclinic, *C2/c*, a = 22.7439(8), b = 18.8669(7), c = 17.5730(6) Å, β = 106.1060(15), V = 7244.7(4) $Å^3$, Z = 8, D_x = 1.580 g/cm^3, μ = 3.897 mm^{-1}. 40820 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.59 $Å^{-1}$. 6384 Reflections were unique (R_{int} = 0.0389), of which 5662 were observed [I>2σ(I)]. 430 Parameters were refined with 0 restraints. R1/wR2 [I > 2σ(I)]: 0.0226 / 0.0642. R1/wR2 [all refl.]: 0.0292 / 0.0707. S = 1.073. Residual electron density between -1.14 and 1.12 e/$Å^3$.

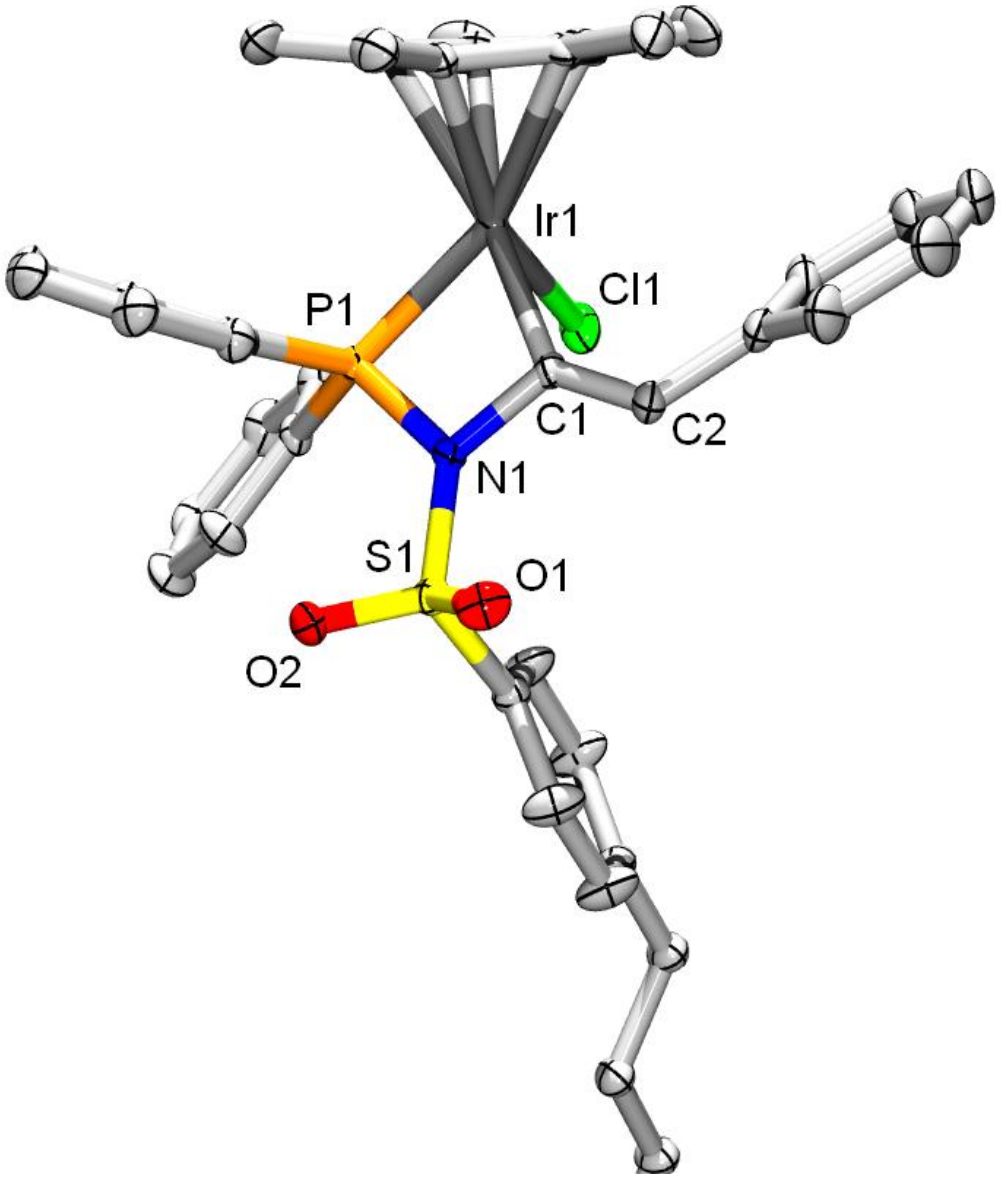
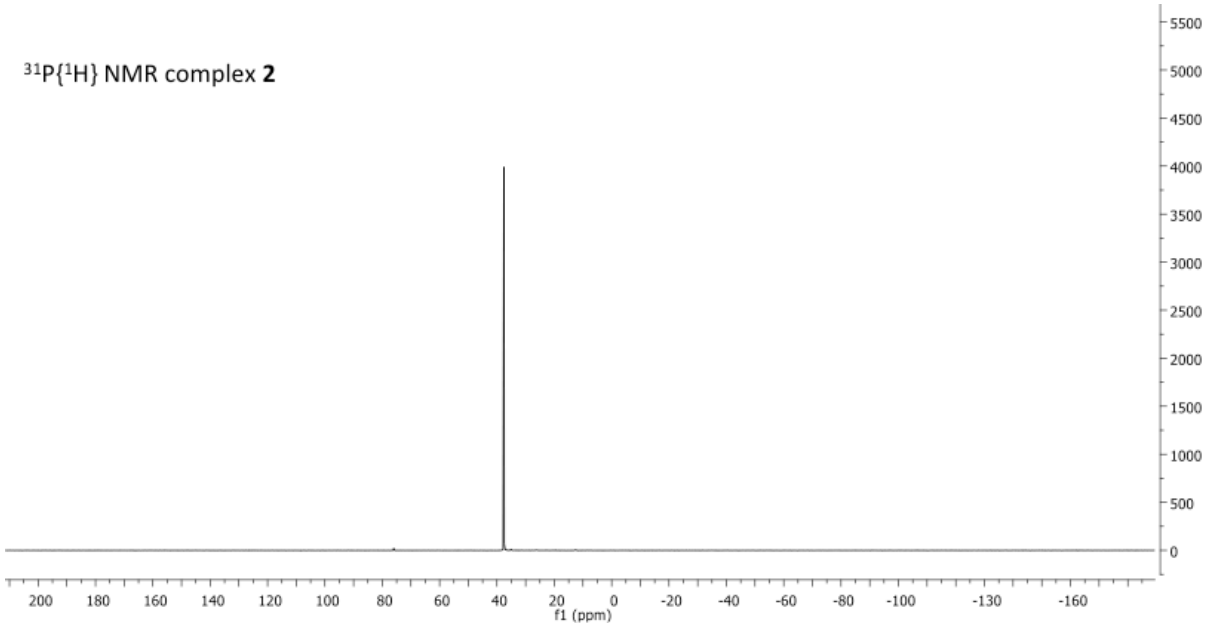
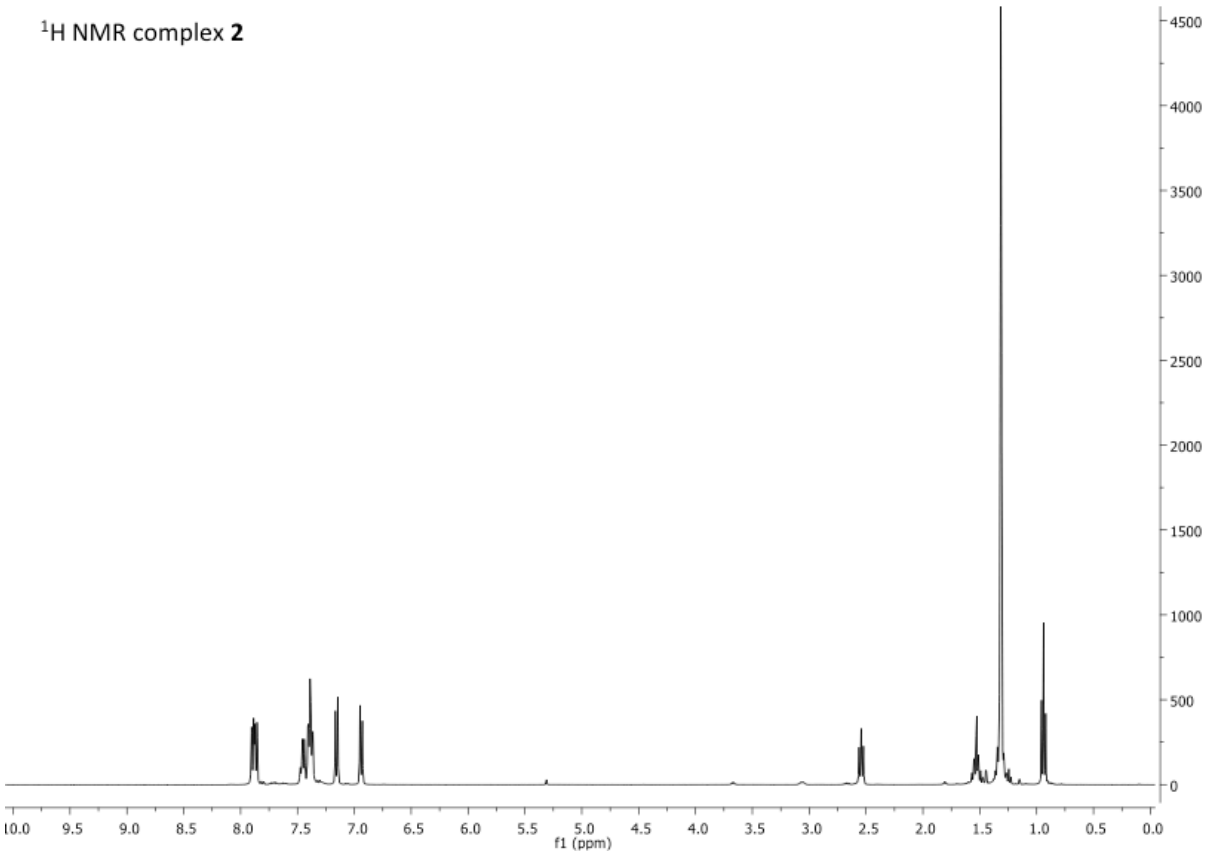


Figure S5. *Displacement ellipsoid plot of complex **4** in the crystal (50% probability level). Hydrogen atoms are omitted for clarity.*

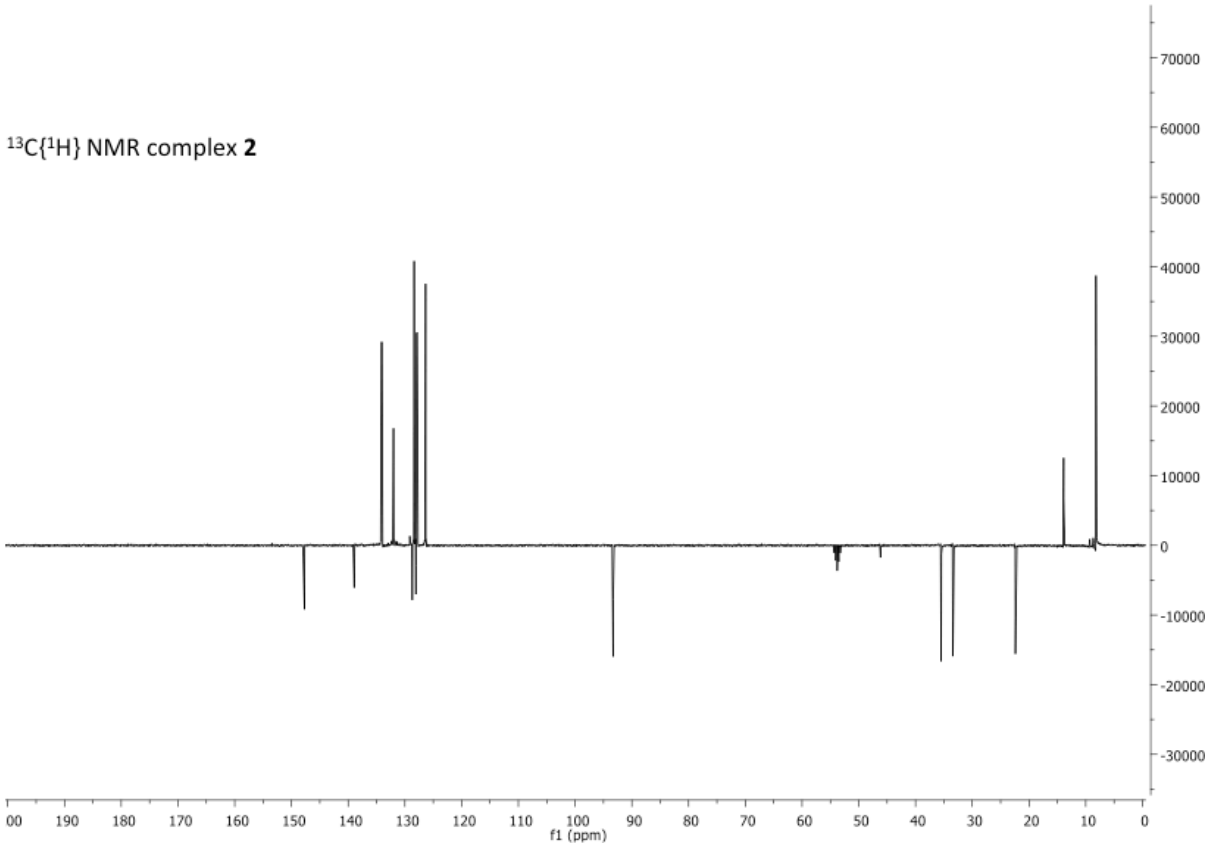
CCDC 1410768 (complex **2**), 1410769 (complex **3**) and 1412995 (complex **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

NMR Spectra

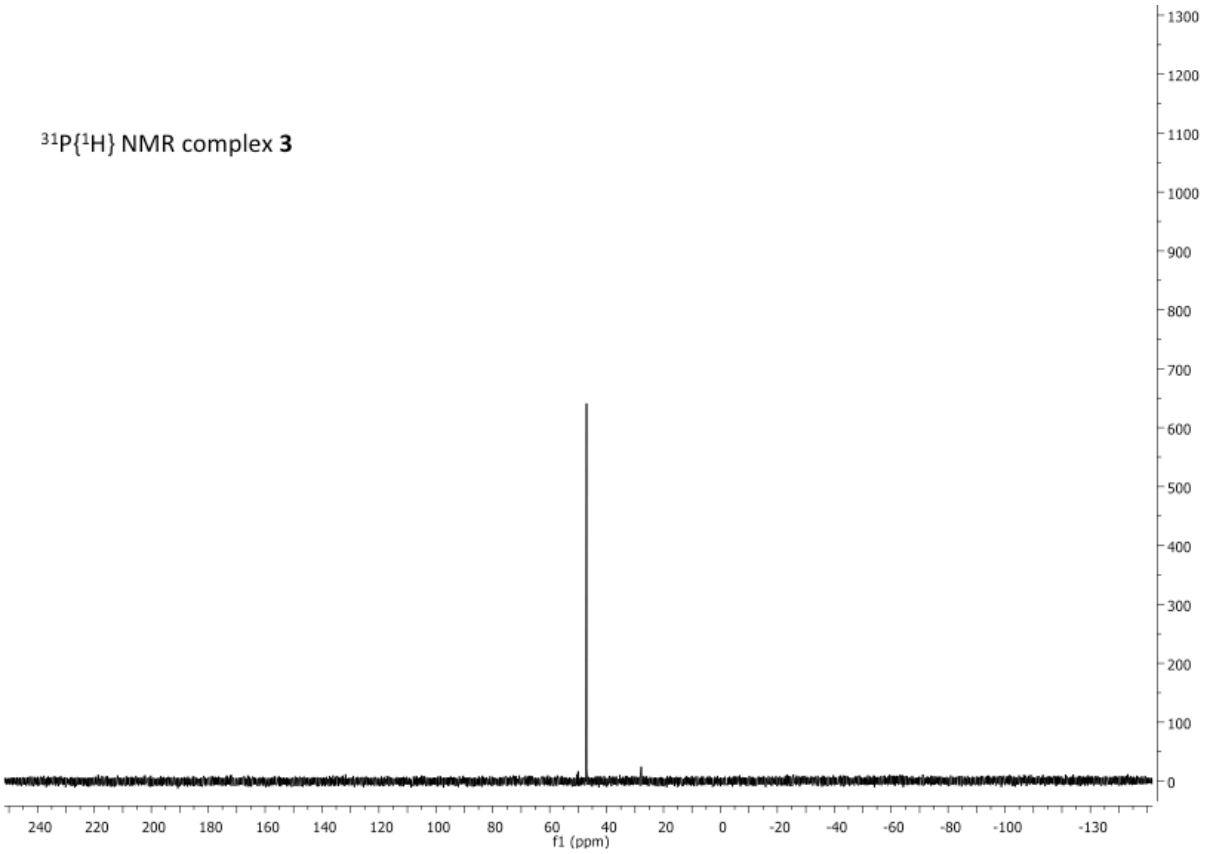




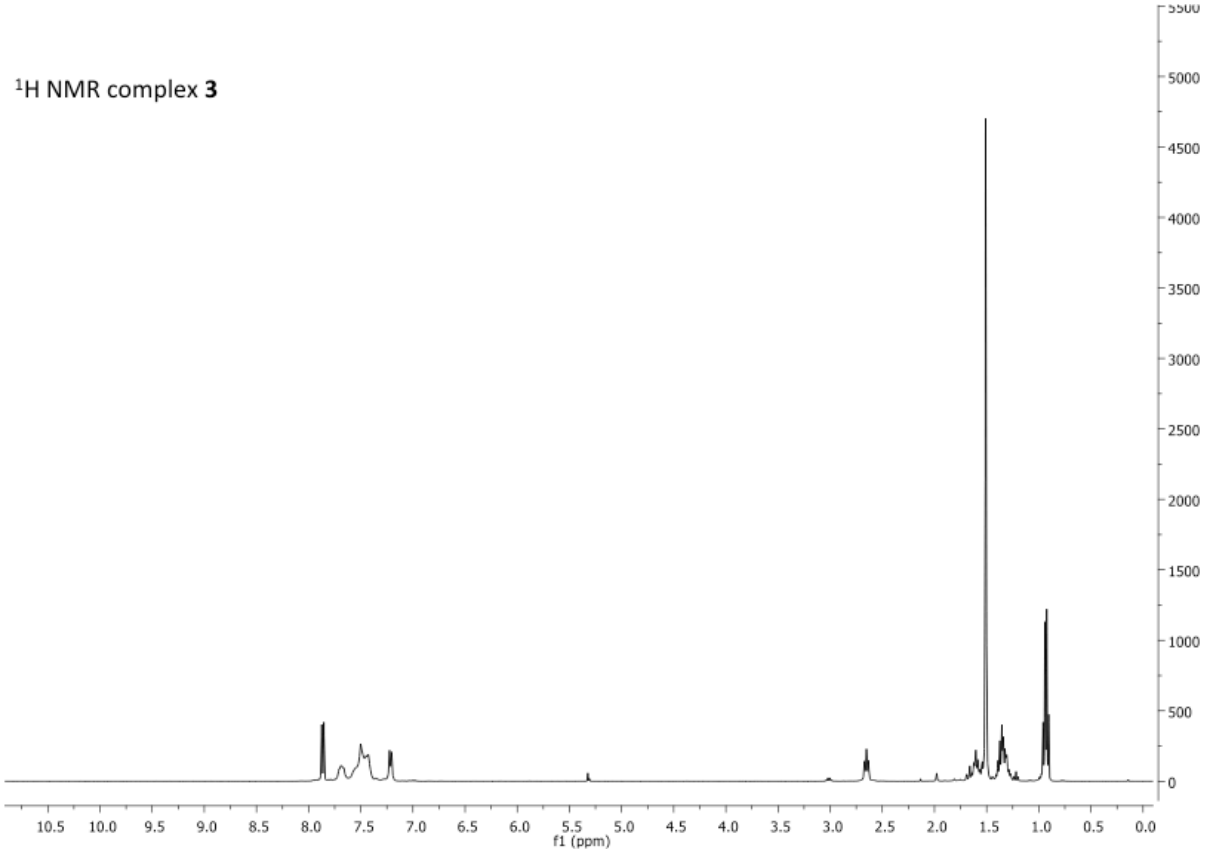
$^{13}C\{^{1}H\}$ NMR complex **2**



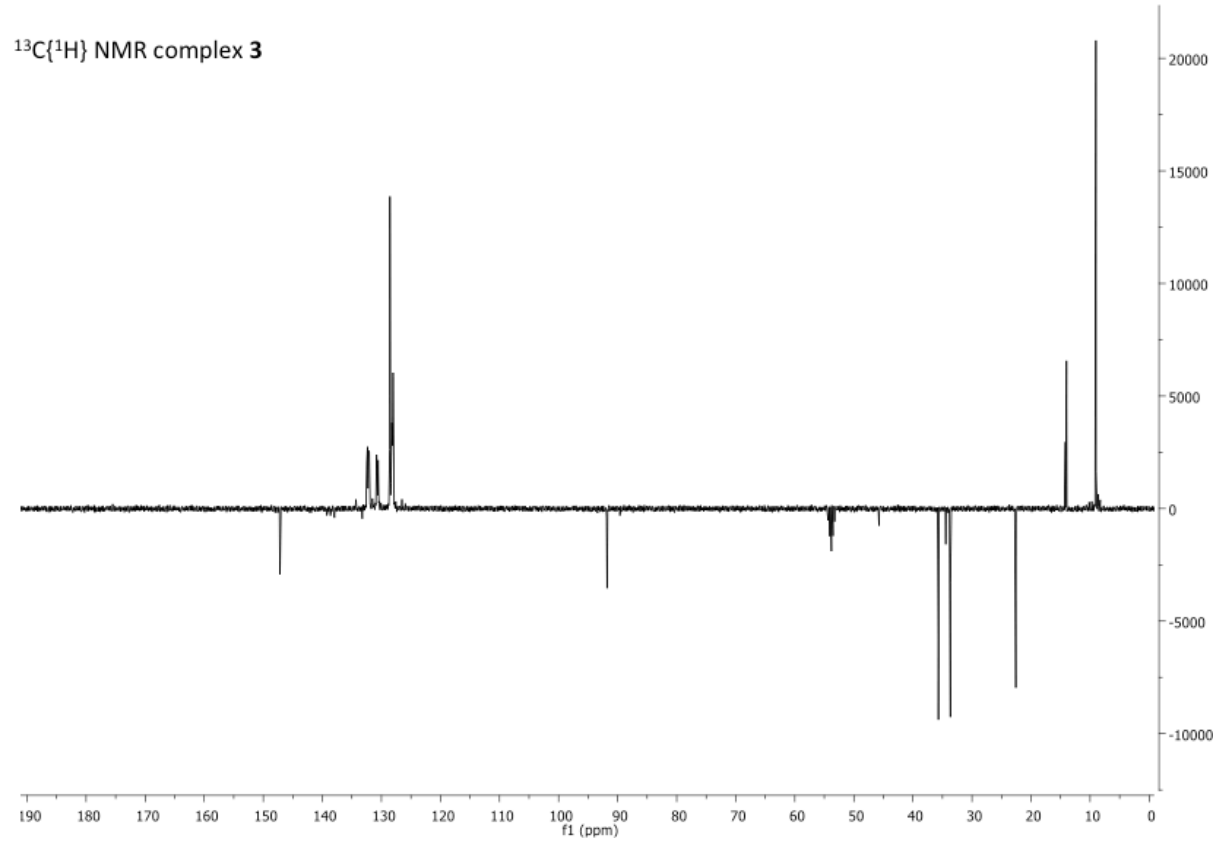
$^{31}P\{^{1}H\}$ NMR complex **3**



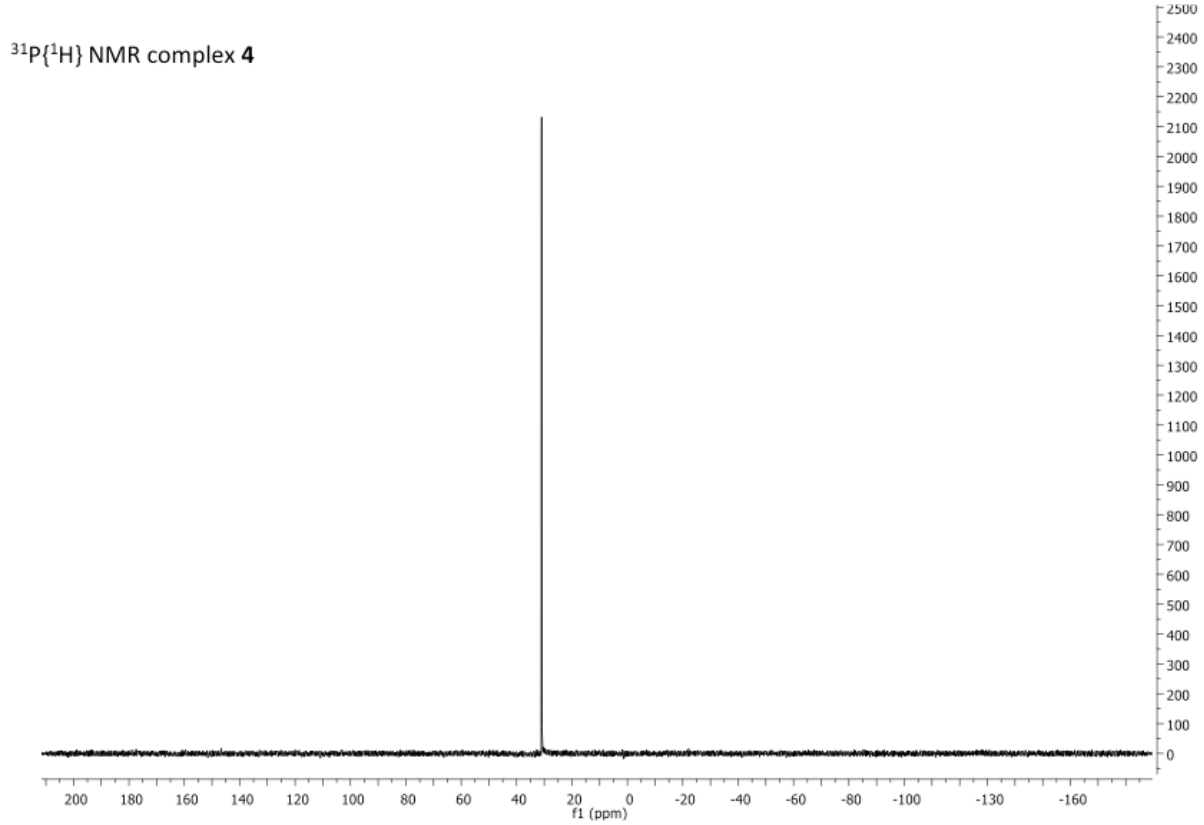
^{1}H NMR complex **3**



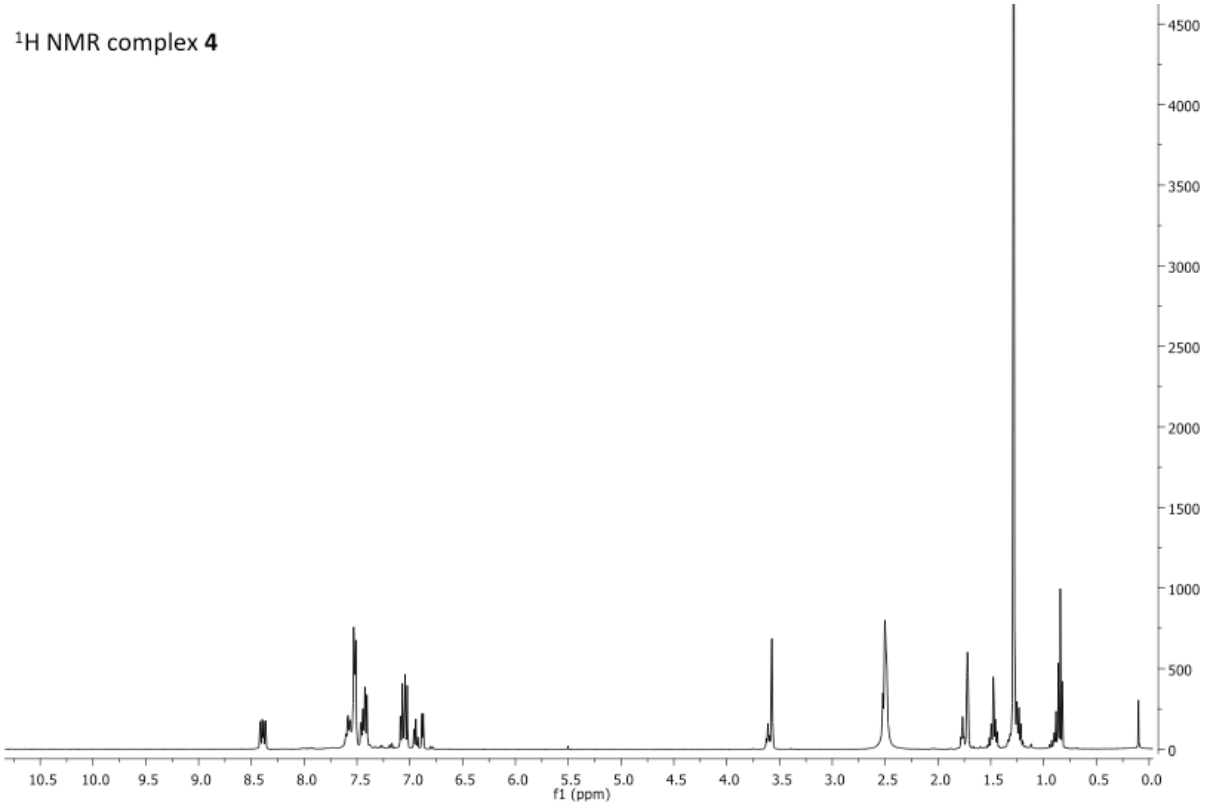
^{13}C{^{1}H} NMR complex **3**



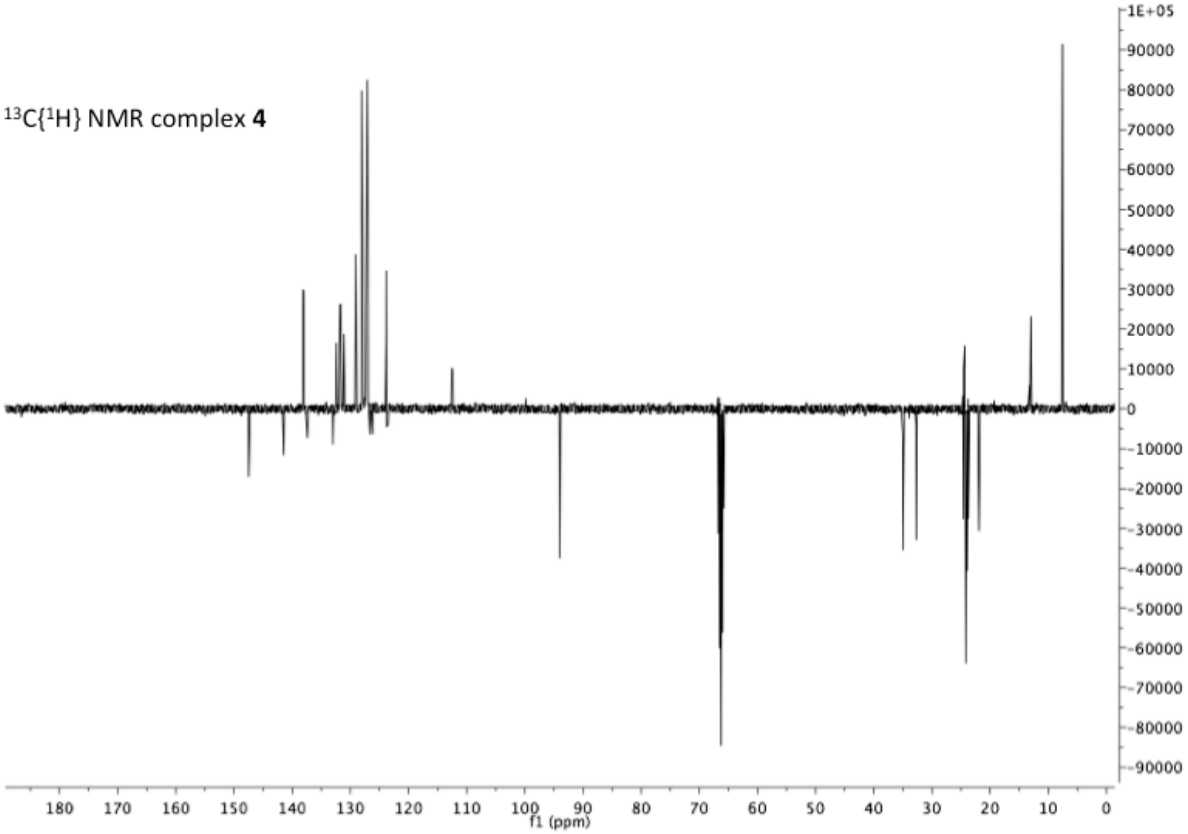
$^{31}P\{^{1}H\}$ NMR complex **4**



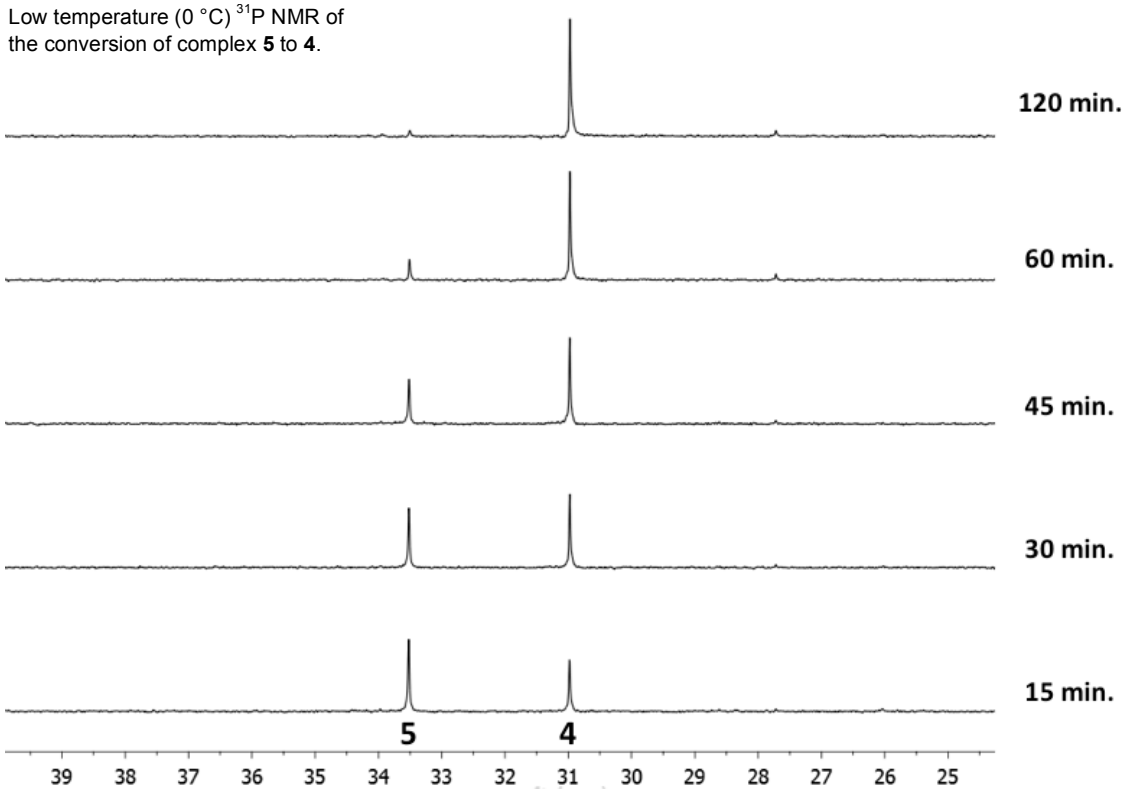
^{1}H NMR complex **4**



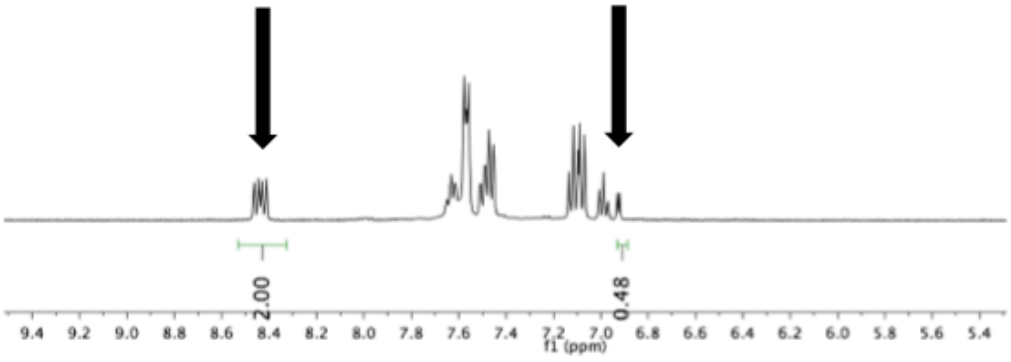
$^{13}C\{^{1}H\}$ NMR complex **4**



Low temperature (0 °C) ^{31}P NMR of the conversion of complex **5** to **4**.



^{1}H NMR complex **4** formed with D-phenylacetylene
Shows the decrease in intensity of vinylidene proton



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