Mechanistic Studies on Direct Arylation of Pyridine *N*-Oxide: Evidence for Cooperative Catalysis between Two Distinct Palladium Centers

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Supporting Information

Table of Contents

General Experimental Information

All manipulations were conducted under an inert atmosphere using a nitrogen-filled glovebox (Innovative Technologies, Newburyport, Massachusetts) equipped with an oxygen sensor (working oxygen level <6.0 ppm) and low-temperature refrigeration unit (–25 °C). All reactions were conducted in flame- or oven-dried J-Young NMR tubes or 4-mL vials fitted with a Teflon-lined screw cap under an atmosphere of nitrogen, unless otherwise stated.

All GC analyses were conducted with an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. The temperature for each run was held at 100 ºC for 1.5 min, ramped from 100 ºC to 300 ºC at 40 ºC/min, and held at 300 ºC for 3 min. GC calibration curves for quantifying the amount the biaryl products versus dodecane internal standard (Aldrich, anhydrous) were conducted in triplicate using three calibration points.

All NMR spectroscopy was conducted with Varian 400 MHz and 500 MHz Unity and Inova instruments. NMR spectra were processed with either NutsPro (Acorn NMR) or MestReNova 5.0 (Metrelab Research S.L). Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H, 77 ppm for ^{13}C, C_6H_6 in C_6D_6: 7.15 ppm for ^1H, 128 ppm for ^{13}C). Coupling constants are reported in Hertz.

All reactions of isolated complexes with PyO were run with degassed and anhydrous solvents. Benzene and pentane were degassed with argon and passed through a column of activated alumina in a solvent purification system from Innovative Technologies.

P*t*Bu_3 ligand was purchased from Strem. K_2CO_3 was purchased from Aldrich (98%, reagent grade) and dried at 120 ºC in a vacuum oven for 12 h before use. All other reagents were purchased from Sigma-Aldrich unless otherwise stated.

Synthesis of (P*t*Bu_3)Pd(Ar)(OAc) (1)

To a mixture of Pd(P*t*Bu_3)$_2$ (0.11 g, 0.20 mmol) AgOAc (0.033 g, 0.20 mmol) and 3-fluoromethyl phenyl iodide (0.50 mL) was added toluene (1.5 mL). The reaction mixture was sonicated at room temperature for 5 hours. The resulting mixture was filtered through Celite and concentrated under vacuum until the volume of the solution did not change. Recrystallization from pentane at -25 ºC gave 0.054 g (57% yield) of complex **1**.

^1H NMR (500 MHz, C_6D_6) δ 7.57 (s, 1H), 7.47 (d, J = 7.5, 1H), 6.82 (t, J = 7.5, 1H), 6.75 (d, J = 7.4, 1H), 4.94 (d, J = 48.3, 2H), 1.87 (s, 3H), 1.21 (d, J = 12.6, 27H). ^{13}C NMR (126 MHz, C_6D_6)

δ188.58, 142.98 (t, *J* = 2.5), 136.30 (t, *J* = 2.5), 135.20 (m), 135.11 (d, *J* = 1.2), 126.88, 123.42 (d, *J* = 6.3), 84.60 (d, *J* = 167.6), 40.40 (d, *J* = 12.6), 32.19, 28.84. ^{31}P NMR (202 MHz, C_6D_6) δ 78.37. ^{19}F NMR (C_6D_6, 470 MHz) δ -200.82 (t, *J* = 48.9) Anal. Calcd for $C_{21}H_{36}FO_2PPd$: C, 52.89; H, 7.61. Found: C, 52.92; H, 7.80.

Procedures for the Reactions of Complex 1 with Heteroarenes

Reactions of complex 1 with PyO

Complex **1** (4.3 mg, 0.0090 mmol), K_2CO_3 (3.1 mg, 0.023 mmol), and P*t*Bu$_3$ (1.8 mg, 0.0090 mmol) were weighed in a 4-mL vial. To this vial was added 0.30 mL toluene solution of PyO (17 mg, 0.018 mmol) that had been heated at 50 ºC to ensure that all the PyO was fully dissolved. The reaction mixture was then heated at 120 °C with stirring until >99% of the complex was consumed, as judged by ^{31}P NMR spectroscopy (~2 h). The yields of the biaryl products were determined by GC/MS using dodecane as internal standard.

Reactions of complex 1 with Benzothiophene

Complex **1** (4.3 mg, 0.0090 mmol), K_2CO_3 (3.1 mg, 0.023 mmol), P*t*Bu$_3$ (1.8 mg, 0.0090 mmol) and benzothiophene (24 mg, 0.018 mmol) were weighed in a 4-mL vial. To this vial was added 0.30 mL of DMA. The reaction mixture was then heated at 120 °C with stirring until >99% of the complex was consumed, as judged by ^{31}P NMR spectroscopy (~2 h). The yields of the biaryl products were determined by GC/MS using dodecane as internal standard.

Procedures for Kinetics Studies

General procedure for kinetic experiments. The amounts and reagents used to prepare each sample are described below. The sample solutions were transferred to a J-Young NMR tube. A sealed capillary tube with a toluene solution of fluorooctane was placed inside the NMR tube as an external standard for calculation of yields and conversions. Before inserting the sample into the NMR probe, the temperature was adjusted. Once the temperature was stable, the tube with the sample was inserted into the NMR probe, and ^{19}F NMR spectra were acquired at fixed time intervals throughout the length of the experiment, with the aid of an automated data collection program.

Representative procedure for the reaction of 1 with PyO. Complex **1** (4.3 mg, 0.0090 mmol), K_2CO_3 (3.1 mg, 0.023 mmol), and P*t*Bu$_3$ (1.8 mg, 0.0090 mmol) were weighed in a 4-mL vial. To this vial was

added 0.30 mL of a toluene solution of PyO (17 mg, 0.018 mmol) that had been heated at 50 ºC to ensure that all the PyO was fully dissolved. The mixture was stirred at room temperature to facilitate dissolution of **1** and immediately transferred to a J-Young NMR tube. The reaction was performed at 60 °C.

Representative procedure for the reaction of 1 and PyO with addition of complex 2. Complex **1** (4.3 mg, 0.0090 mmol), complex **2** (3.3 mg, 0.0045 mmol), K_2CO_3 (3.1 mg, 0.023 mmol), and P*t*Bu_3 (1.8 mg, 0.0090 mmol) were weighed in a 4-mL vial. To this vial was added 0.30 mL of a toluene solution of PyO (17 mg, 0.018 mmol) that had been heated at 50 ºC to ensure that all the PyO was fully dissolved. The mixture was stirred at room temperature to facilitate dissolution of **1** and immediately transferred to a J-Young NMR tube. The reaction was performed at 60 °C.

Representative procedure for the reaction of 1 with Benzothiophene. Complex **1** (4.3 mg, 0.0090 mmol), K_2CO_3 (3.1 mg, 0.023 mmol), P*t*Bu_3 (1.8 mg, 0.0090 mmol) and benzothiophene (24 mg, 0.018 mmol) were weighed in a 4-mL vial. To this vial was added 0.30 mL of DMA. The mixture was stirred at room temperature to facilitate dissolution of **1** and immediately transferred to a J-Young NMR tube. The reaction was performed at 50 °C.

Procedures for Reactions with Varied Amounts of Pd Catalysts

Reactions with varied concentrations of Pd catalyst were assembled side by side in the drybox and were run side by side in a pre-heated heating block. A stock solution was prepared by adding 3-bromotoluene (51 mg, 0.30 mmol), PyO (114 mg, 0.060 mmol), Pd(P*t*Bu_3)$_2$ (7.6 mg, 0.015 mmol), and 3.0 mL of toluene into a 4-mL vial. After all the reagents dissolved, the stock solution was divided into three 4-mL vials. K_2CO_3 (34 mg, 0.25 mmol) was added to each of the three vials, and toluene solution (0.5 M) of complex **2** (10 μl, 5.0 μl and 2.0 μl, respectively) and anhydrous HOAc (1.0 μl) were added each of the three vials. The reaction mixtures were then heated at 120 °C with stirring. The reactions were monitored by GC until > 99 % of the 4-bromotoluene was consumed. The yields of the arylated products were determined by GC with dodecane as internal standard. Reactions with varied concentrations of Pd(P*t*Bu_3)$_2$ were set up by preparing the stock solution of 3-bromotoluene (51 mg, 0.30 mmol), PyO (114 mg, 0.060 mmol), complex **2** (7.1 mg, 0.015 mmol), in 3.0 mL of toluene, and adding toluene solution (0.5 M) of Pd(P*t*Bu_3)$_2$ (10 μl, 5.0 μl and 2.0 μl, respectively) and anhydrous HOAc (1.0 μl) to each of the three vials.

Synthesis of Complex 4

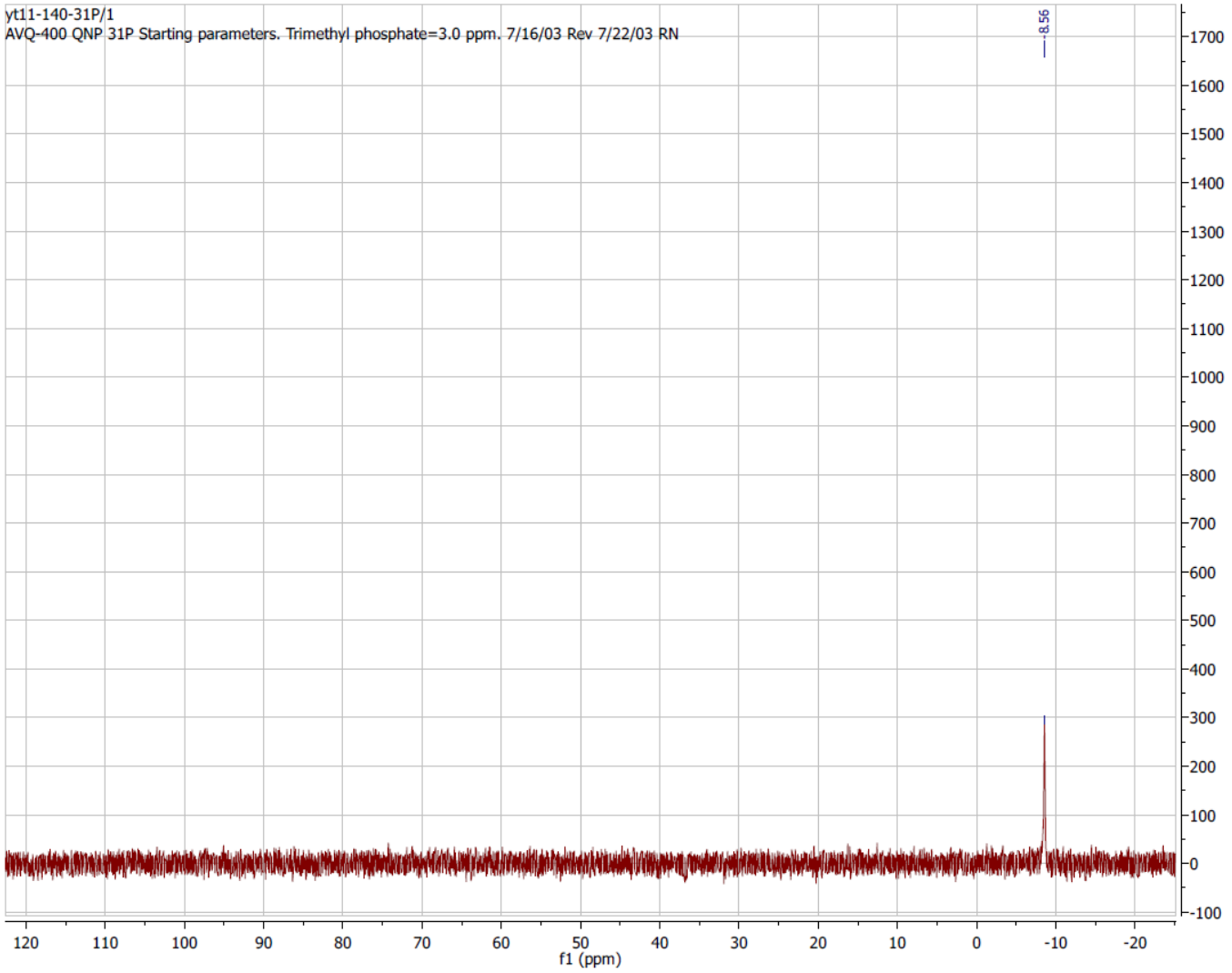
To a solution of benzothiophene (13 mg, 0.10 mmol) in THF (1.2 mL) was added n-BuLi (1.6 M solution in hexane, 67 μL, 1.1 equiv) at room temperature. The resulting solution was stirred for 10 min. Complex **3** (31 mg, 0.080 mmol), Ag_2CO_3 (44 mg, 0.16 mmol) and PEt_3 (9.5 mg, 0.080 mmol) were weighed in a 4-mL vial, and 1.2 mL of THF was then added. The mixture was stirred at room temperature inside the drybox, and the solution of Ar-Li in THF was added dropwise. The reaction was stirred for 30 minutes. The resulting mixture was filtered through Celite, and all solvent was removed under vacuum. Pentane (1.2 mL) was added, and the resulting solution was filtered through Celite again to give a light yellow solution. The solvent was removed under vacuum, and recrystallization from pentane at -30 ^{o}C gave 0.024 g (54% yield) of complex **4**.

^{1}H NMR (600 MHz, d^8-THF) δ 7.57 (d, J = 7.8, 1H), 7.41 (d, J = 7.8, 1H), 6.98-6.95 (m, 1H), 6.96 (s, 1H), 6.81-6.79 (m, 1H), 1.53 (d, J = 12.6, 6H), 1.53-1.48 (m, 6H), 1.44 (d, J = 16.2, 18H), 1.11-1.06 (m, 9H), 0.45-0.43 (m, 2H). ^{13}C NMR (100 MHz, d^8-THF) δ 168.68 (d, J = 18), 146.91, 144.17, 128.01, 122.33, 120.97, 120.04, 119.20, 52.98 (d, J = 18), 38.28 (d, J = 7), 34.48, 32.60 (d, J = 3), 16.13(d, J = 31), 15.58 (d, J = 22), 8.66. ^{31}P NMR (162 MHz, d^8-THF) δ 18.08 (d, J = 420), 5.07 (d, J = 420).

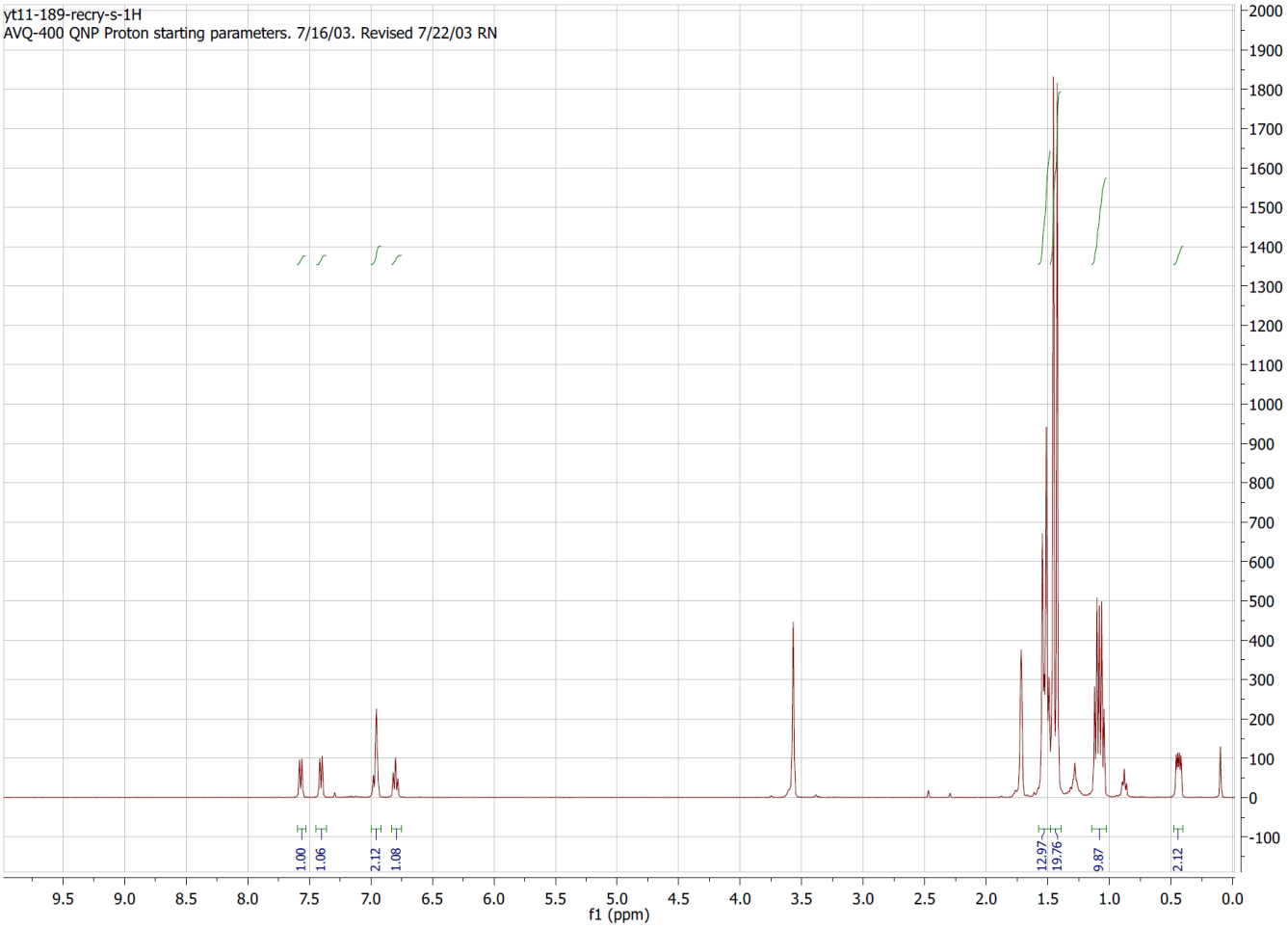
Procedures for Reaction of Complex 4 with 1.

Complex **1** (2.4 mg, 0.0050 mmol) and complex **4** (5.6 mg, 0.010 mmol) were weighed in a 4-mL vial. To this vial was added 0.50 mL of DMA. The reaction mixture was then heated at 50 °C until >99% of the complex **1** was consumed, as judged by ^{31}P NMR spectroscopy. The yield of arylated benzothiophene product was determined by GC/MS with dodecane as internal standard.

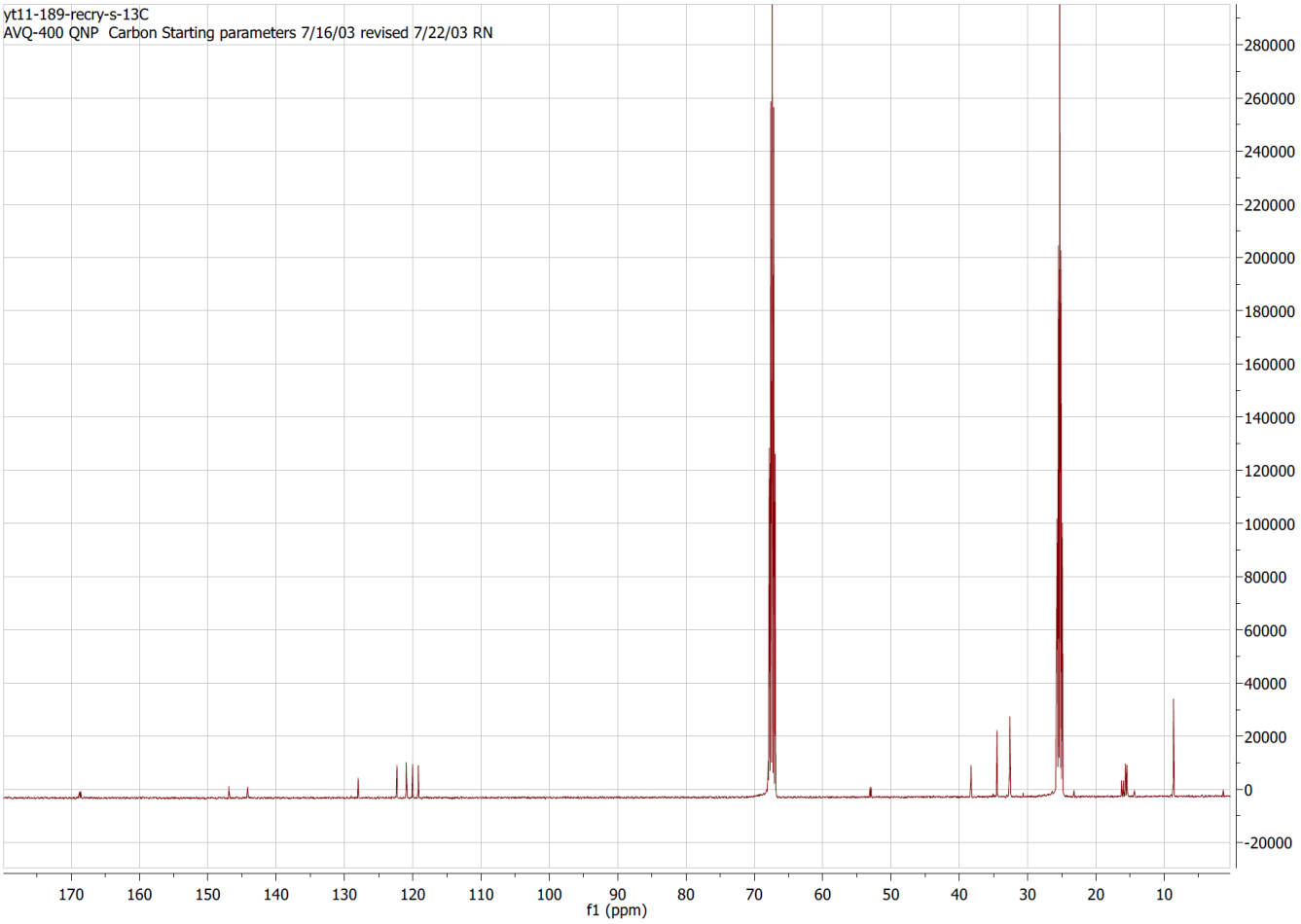
^{31}P NMR spectrum of catalyst's resting state in the catalytic reaction of Ar-Br and PyO.



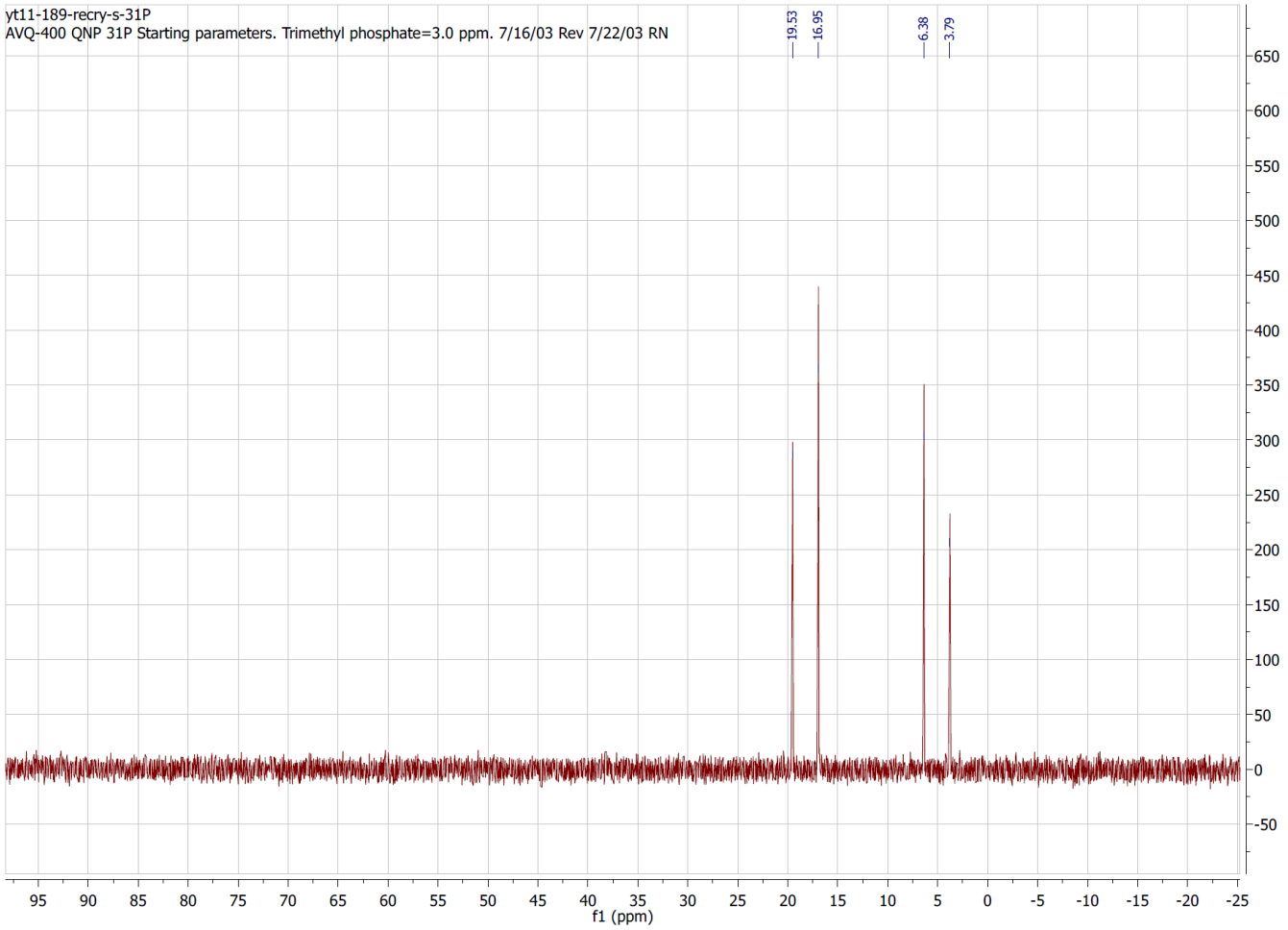
^{1}H NMR spectrum of complex **4**



^{13}C NMR spectrum of complex **4**



^{31}P NMR spectrum of complex **4**



DFT Calculations

All DFT calculations were performed using a hybrid functional [the three-parameter exchange functional of Becke (B3)[1] and the correlation functional of Lee, Yang, and Parr (LYP)[2]] (B3LYP) as implemented in Gaussian 09.[3] A mixed basis set (DZVP[4] on Pd and TZVP[5] on all other atoms) was used for this calculation. Unless otherwise noted, all geometries are fully optimized and confirmed as minima or n-order saddle points by analytical frequency calculations at the same level.

Table S1. B3LYP computed energies in Hartrees

Complex	**G**
PyO	-323.496921
(P*t*Bu$_3$)Pd(Ph)(OAc)	-6214.647913
(P*t*Bu$_3$)Pd(Ph)(OAc)(PyO)-TS	-6538.092856
Pd(OAc)(*t*Bu$_2$PCMe$_2$CH$_2$)	-5982.419081
Pd(OAc)(*t*Bu$_2$PCMe$_2$CH$_2$)(PyO)-TS	-6305.873807

Table S2. Energy-minimized geometries computed with DFT

PyO

N	-4.228134	0.592731	1.146640
C	-5.492541	0.187626	0.805190
C	-6.564392	0.401928	1.644825
C	-6.389330	1.039585	2.869027
C	-5.102850	1.447451	3.207471
C	-4.046689	1.221915	2.351060
H	-5.549156	-0.298129	-0.156406
H	-7.540979	0.061762	1.325952
H	-7.223741	1.211956	3.534122
H	-4.903594	1.948438	4.145779
H	-3.024382	1.508058	2.542999
O	-3.243108	0.388949	0.361691

(P*t*Bu$_3$)Pd(Ph)(OAc)

Pd	-0.911061	0.693901	-0.023375
C	-1.988980	-1.002346	-0.022999
C	-2.437679	-1.546007	1.178399
C	-3.386241	-2.568575	1.174484
C	-3.892955	-3.052676	-0.027292
C	-3.456678	-2.498648	-1.226566
C	-2.507936	-1.476209	-1.226533
O	-0.653617	2.981951	-0.002963
C	-1.917672	3.080300	0.008489
O	-2.649610	2.044447	0.002889
C	-2.564287	4.443015	-0.001992
H	-2.068063	-1.173445	2.126164
H	-3.730231	-2.982432	2.115717
H	-4.629469	-3.846978	-0.028711
H	-3.855936	-2.857353	-2.168570
H	-2.190385	-1.050009	-2.170779
H	-1.956808	5.153896	0.557050
H	-3.571854	4.392824	0.407222
H	-2.628367	4.793874	-1.035122
P	1.297226	-0.261579	0.001389
C	2.326138	1.022497	-1.075043
C	1.629058	-2.055648	-0.710530
C	1.917984	-0.183692	1.846873
C	3.729329	0.544052	-1.485322
C	2.483909	2.360486	-0.325195
C	1.508105	1.337326	-2.346849

C	0.627125	-3.072644	-0.129016
C	3.045147	-2.595383	-0.437657
C	1.375385	-2.023638	-2.229143
C	1.286810	1.056581	2.512761
C	3.446696	-0.128370	2.014961
C	1.392249	-1.406776	2.620158
H	3.709336	-0.313699	-2.154007
H	4.358553	0.301764	-0.630006
H	4.219306	1.359006	-2.026632
H	1.529400	2.779306	-0.016391
H	2.939519	3.071831	-1.021017
H	3.148754	2.289699	0.533030
H	0.555726	1.804943	-2.098103
H	1.314616	0.465811	-2.966283
H	2.077881	2.050409	-2.950478
H	0.827215	-4.039023	-0.602020
H	-0.401284	-2.803862	-0.344106
H	0.725320	-3.212820	0.942644
H	3.151179	-3.551345	-0.959952
H	3.208334	-2.795280	0.620724
H	3.840656	-1.944534	-0.789351
H	0.398356	-1.600422	-2.463901
H	1.384309	-3.052064	-2.600491
H	2.135875	-1.474702	-2.779600
H	0.197913	0.991823	2.522393
H	1.555390	1.993088	2.034441
H	1.629205	1.099981	3.551370

H	3.951015	-0.982334	1.566667
H	3.677427	-0.140229	3.084821
H	3.884081	0.779349	1.605584
H	1.918539	-2.324184	2.363404
H	0.324033	-1.561525	2.469952
H	1.553670	-1.230152	3.687430

(P*t*Bu$_3$)Pd(Ph)(OAc)(PyO)-TS

Pd	-0.484541	0.398664	-0.226538
C	-1.166604	-1.508213	-0.264470
O	-2.065742	3.246513	-0.592373
O	0.044548	2.581509	-0.300554
P	1.978356	-0.220591	0.043613
C	-0.822672	3.474597	-0.452415
C	-0.396133	4.925967	-0.448761
C	-2.761871	0.790084	-0.187100
N	-3.199704	0.668588	1.124175
C	-4.450295	0.190223	1.400085
C	-5.298539	-0.215926	0.396062
C	-4.898805	-0.129828	-0.936573
C	-3.640368	0.382085	-1.197034
O	-2.429467	0.989618	2.096175
H	-4.683363	0.150082	2.453114
H	-6.273536	-0.599855	0.667419
H	-5.556669	-0.441401	-1.736713
H	-3.303408	0.498498	-2.219922
H	-2.253247	1.995100	-0.412076
C	-1.344280	-2.161950	-1.484561
C	-1.882181	-3.447037	-1.528310
C	-2.253061	-4.092947	-0.352318
C	-2.099942	-3.435214	0.863960
C	-1.565175	-2.146901	0.908303
C	2.631595	0.936532	1.504054
C	2.919441	0.238594	-1.606647

C	2.478267	-2.064386	0.526030
C	2.698732	-0.870660	-2.651357
C	4.433724	0.464875	-1.453350
C	2.283115	1.513746	-2.190930
C	2.810870	2.393448	1.035825
C	3.969704	0.511110	2.134664
C	1.532988	0.945910	2.587713
C	3.988980	-2.359901	0.440675
C	1.770491	-3.095730	-0.374821
C	1.988111	-2.351876	1.958857
H	3.265593	-1.773817	-2.435800
H	3.041785	-0.498202	-3.621075
H	1.645541	-1.133851	-2.755442
H	4.667139	1.323426	-0.828059
H	4.854050	0.666133	-2.444016
H	4.953599	-0.400597	-1.050389
H	2.788918	1.747475	-3.133076
H	2.368998	2.376642	-1.538790
H	1.223943	1.367792	-2.402404
H	3.658425	2.517826	0.364168
H	3.019070	2.998484	1.923926
H	1.915433	2.786049	0.565923
H	4.221878	1.245877	2.905580
H	4.788657	0.509906	1.415409
H	3.936677	-0.459363	2.622275
H	0.591298	1.343005	2.208972
H	1.862190	1.592197	3.407433

H	1.334686	-0.037167	3.008092
H	4.611691	-1.665967	0.996800
H	4.340048	-2.388483	-0.589922
H	4.159342	-3.357232	0.858429
H	2.119326	-4.088327	-0.073192
H	1.997198	-2.982710	-1.429891
H	0.694917	-3.074857	-0.254155
H	0.925814	-2.143462	2.073804
H	2.535133	-1.804253	2.721263
H	2.132816	-3.417715	2.158675
H	-1.062352	-1.678729	-2.413126
H	-2.006726	-3.943835	-2.484132
H	-2.665976	-5.093966	-0.385075
H	-2.400300	-3.921131	1.785689
H	-1.479721	-1.637100	1.861280
H	0.661935	5.020899	-0.683595
H	-0.572324	5.332321	0.550130
H	-0.998274	5.499790	-1.151669

Pd(OAc)(*t*Bu$_2$PCMe$_2$CH$_2$)

Pd	-1.234640	-0.350982	-0.038365
P	1.018069	0.081078	-0.004288
O	-2.792920	1.282359	0.187122
O	-3.403380	-0.826097	-0.053414
C	1.244633	-1.642756	-0.828455
C	1.668167	0.098173	1.819301
C	1.743866	1.543841	-1.043940
C	-3.697410	0.400729	0.094629
C	-5.150033	0.813313	0.131192
C	0.845411	1.743668	-2.280326
C	3.193429	1.277670	-1.483725
C	1.691583	2.856002	-0.243456
C	2.439790	-2.517849	-0.442214
C	1.182378	-1.577234	-2.362244
C	-0.138108	-2.101308	-0.321382
C	1.024241	1.289257	2.561540
C	3.199360	0.182948	1.917845
C	1.174607	-1.163089	2.554566
H	1.181117	2.641952	-2.807038
H	-0.197688	1.888522	-1.997128
H	0.898177	0.917700	-2.983639
H	3.874942	1.190055	-0.637505
H	3.538778	2.116983	-2.095598
H	3.287307	0.375803	-2.085201
H	0.691678	3.061952	0.139617
H	1.962583	3.674775	-0.916186

H	2.400849	2.873621	0.581955
H	2.557064	-2.645132	0.630593
H	3.375093	-2.114521	-0.839271
H	2.301703	-3.514253	-0.874086
H	2.070075	-1.133932	-2.812467
H	0.298810	-1.046068	-2.712129
H	1.107685	-2.604327	-2.731074
H	-0.109559	-2.637004	0.624719
H	-0.706731	-2.663493	-1.063416
H	-0.061860	1.281443	2.462577
H	1.390257	2.255354	2.228625
H	1.265503	1.200093	3.624987
H	3.493606	0.132263	2.969817
H	3.586683	1.121938	1.522542
H	3.695886	-0.636463	1.396460
H	0.087738	-1.237943	2.529750
H	1.479166	-1.081529	3.601755
H	1.592540	-2.089294	2.169488
H	-5.463340	1.085376	-0.881134
H	-5.279261	1.686556	0.771415
H	-5.774408	-0.013133	0.473490

Pd(OAc)(*t*Bu$_2$PCMe$_2$CH$_2$)(PyO)-TS

Pd	-0.491994	0.231087	-0.224967
P	1.766605	-0.265072	-0.019382
O	-0.489161	2.465344	-0.125439
O	-2.724044	2.483455	-0.066237
C	1.308083	-2.001422	-0.702815
C	2.213008	-0.336691	1.862896
C	3.126306	0.643667	-1.056395
C	-1.577827	3.065219	-0.050212
C	-1.601412	4.568679	0.083798
C	2.479931	1.102658	-2.377830
C	4.341048	-0.254748	-1.343965
C	3.602542	1.915319	-0.334015
C	2.018878	-3.239134	-0.147663
C	1.382407	-2.065678	-2.237199
C	-0.179181	-1.841372	-0.316179
C	2.078134	1.084277	2.451151
C	3.623386	-0.885668	2.125526
C	1.172340	-1.195931	2.608603
H	3.212579	1.695595	-2.933799
H	1.606629	1.728836	-2.192138
H	2.180743	0.275029	-3.014432
H	4.855757	-0.560731	-0.433744
H	5.059703	0.303587	-1.953854
H	4.073191	-1.152898	-1.897723
H	2.771580	2.567994	-0.065784
H	4.252407	2.469637	-1.017845

H	4.187692	1.699132	0.558220
H	2.002718	-3.297689	0.937397
H	3.061682	-3.281298	-0.473462
H	1.518406	-4.135202	-0.529088
H	2.401422	-2.049643	-2.622205
H	0.810376	-1.266435	-2.706538
H	0.930325	-3.012009	-2.548099
H	-0.427570	-2.241356	0.663653
H	-0.849615	-2.249118	-1.072369
H	1.104744	1.517245	2.221966
H	2.848100	1.768404	2.108346
H	2.166343	1.011989	3.539002
H	3.794131	-0.928706	3.205593
H	4.399524	-0.248580	1.702342
H	3.757264	-1.893675	1.731989
H	0.156782	-0.822643	2.471241
H	1.403954	-1.142455	3.676352
H	1.194259	-2.246255	2.329387
H	-1.909269	4.826606	1.099417
H	-2.335626	4.997504	-0.598891
H	-0.614600	4.981791	-0.109471
C	-2.753591	-0.121655	-0.243000
C	-3.420722	-0.530805	-1.399432
C	-4.409143	-1.505578	-1.400069
C	-4.762081	-2.064254	-0.174388
C	-4.128161	-1.656434	0.978008
N	-3.135508	-0.715450	0.950250

O	-2.546990	-0.402826	2.048942
H	-2.599891	1.357447	-0.122612
H	-4.902021	-1.808897	-2.314301
H	-5.533556	-2.819970	-0.100160
H	-4.345762	-2.038929	1.963865
H	-3.140569	-0.047649	-2.328549

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