Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Metallo-Wittig Chemistry of an Alkylidene to Form a Terminal Titanium Oxo Complex

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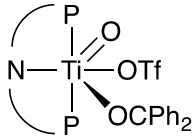
NMR Spectroscopic Data of 2 and 3



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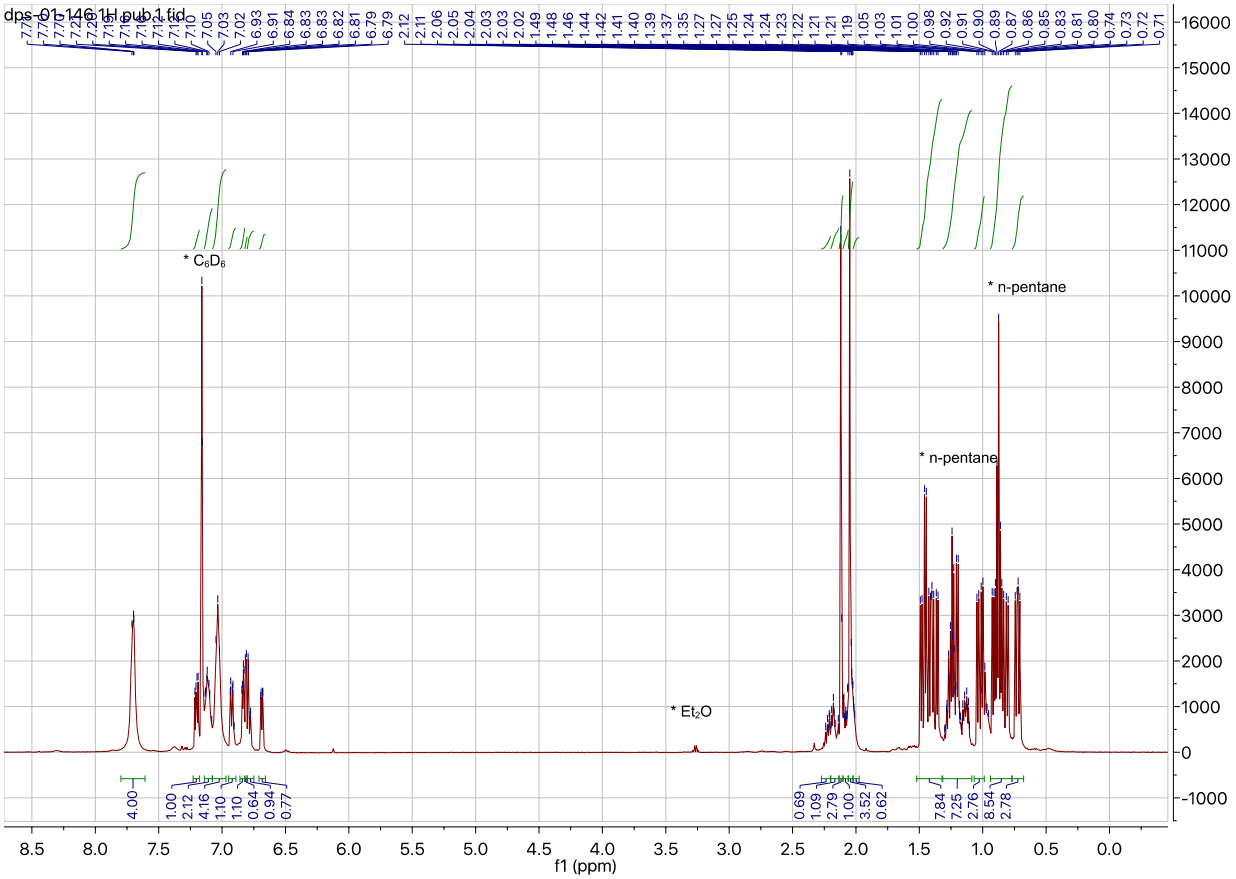


Figure S1. ^{1}H NMR spectrum of **2** recorded in C_6D_6 (500.39 MHz, 23 °C)

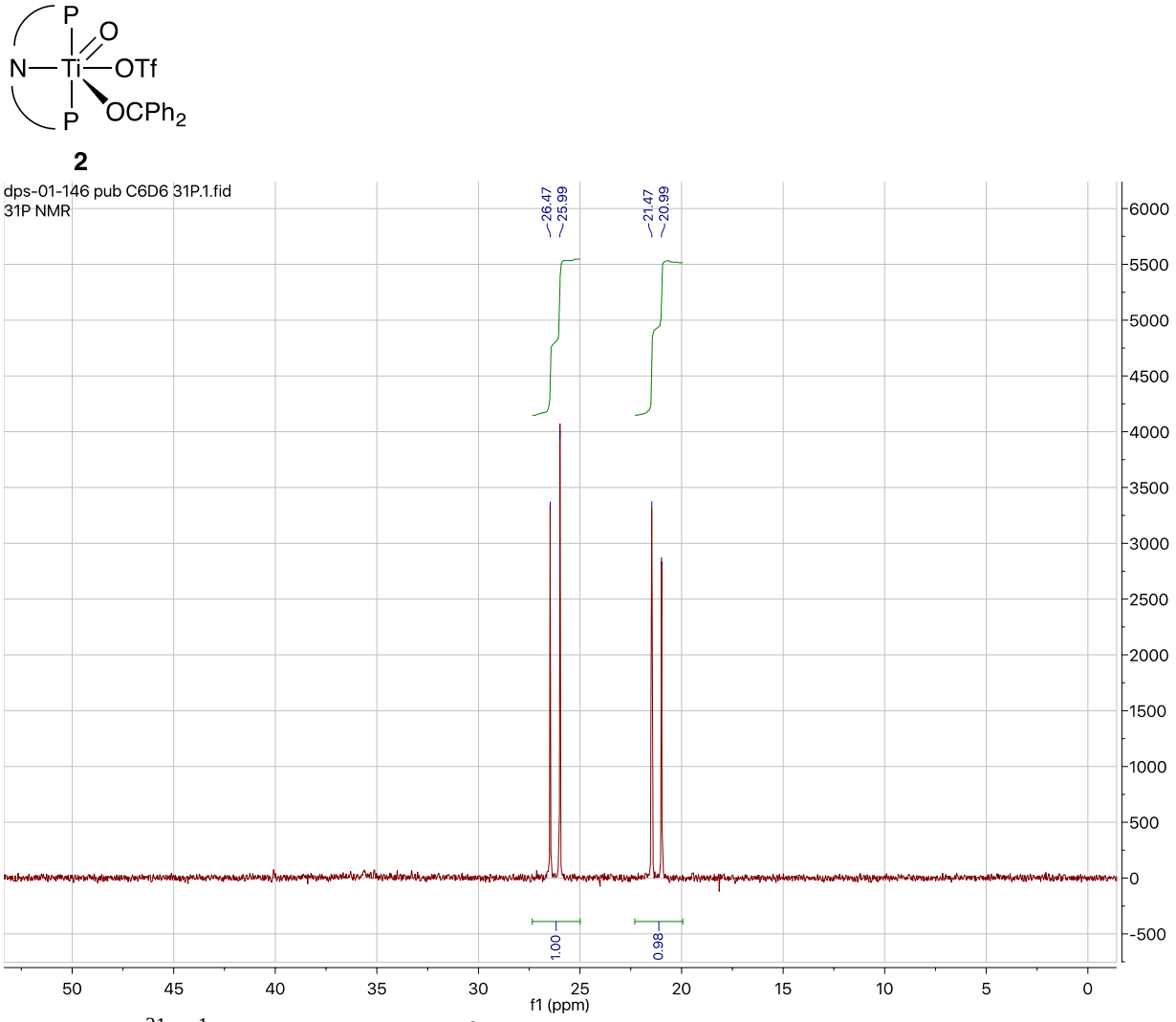
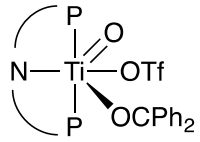


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **2** recorded in C_6D_6 (145.78 MHz, 23 °C)



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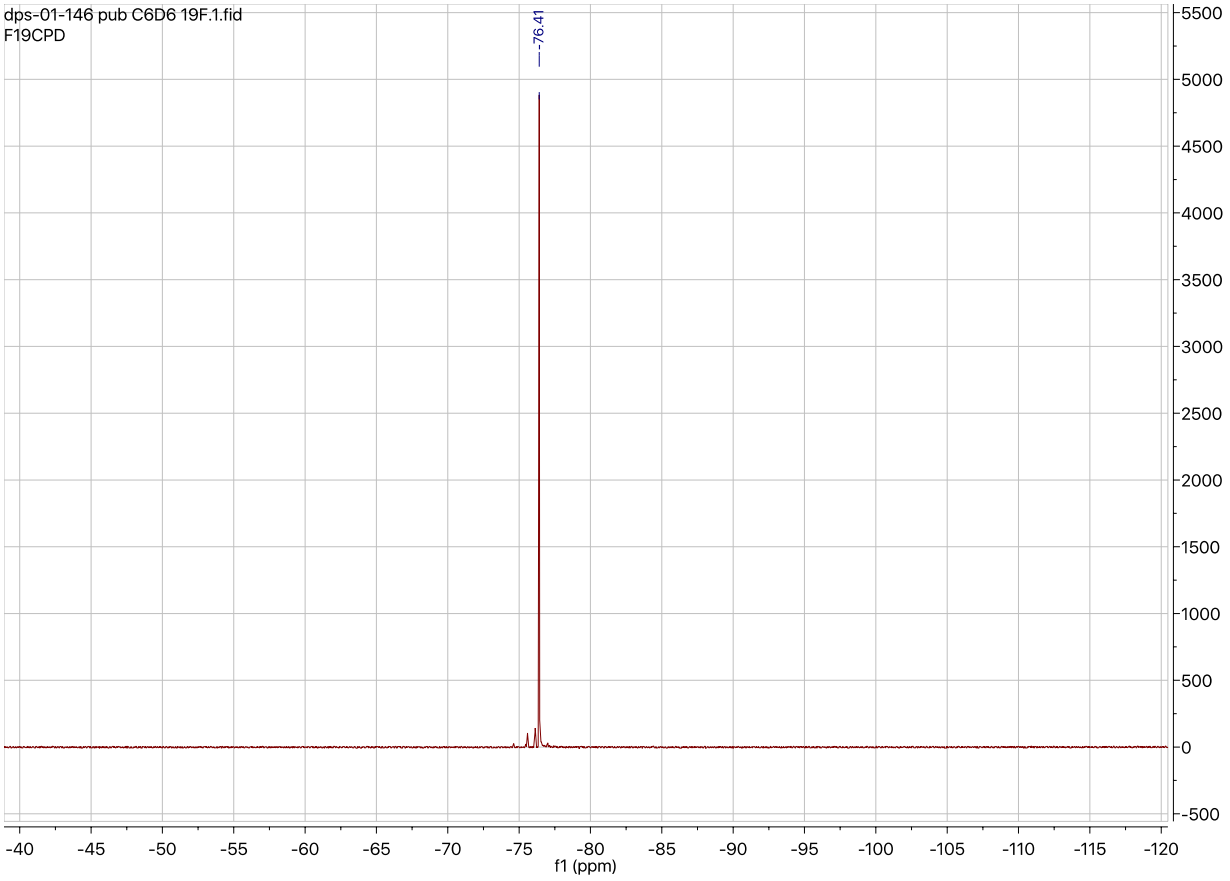


Figure S3. $^{19}F\{^{1}H\}$ NMR spectrum of **2** recorded in C_6D_6 (338.86 MHz, 23 °C)

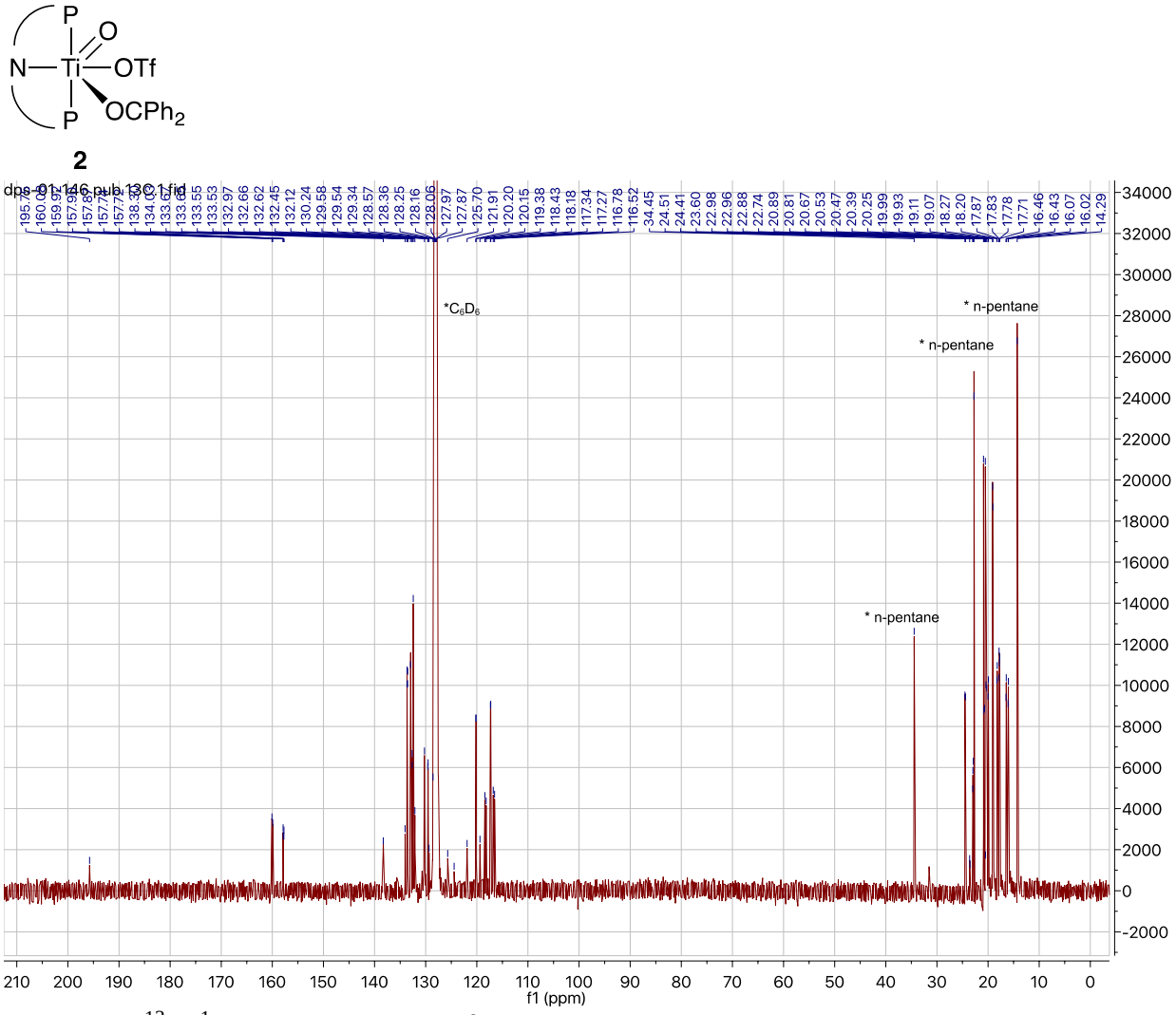


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** recorded in C_6D_6 (125.82 MHz, 23 °C)

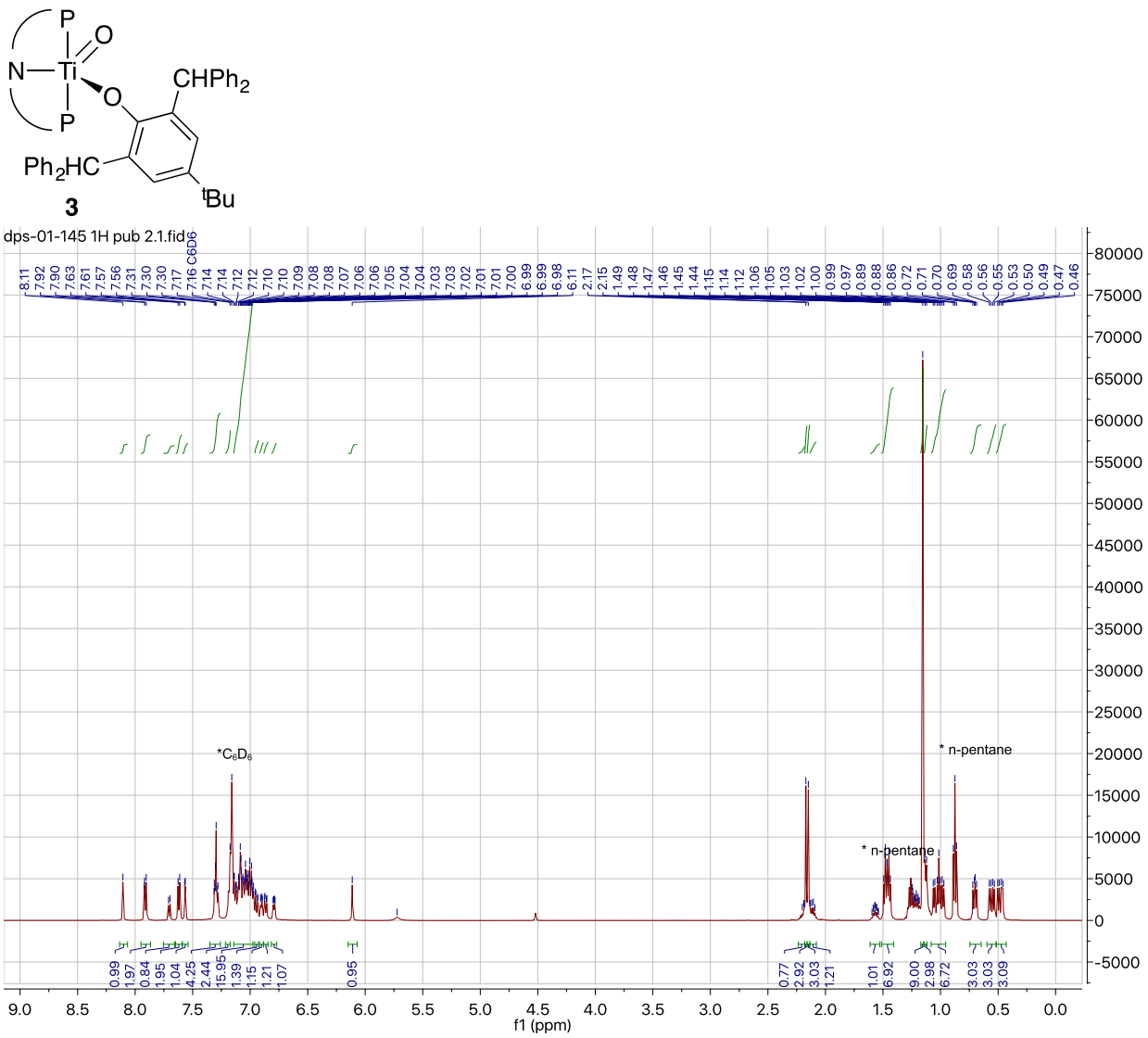


Figure S5. ^{1}H NMR spectrum of **3** recorded in C_6D_6 (500.39 MHz, 23 °C)

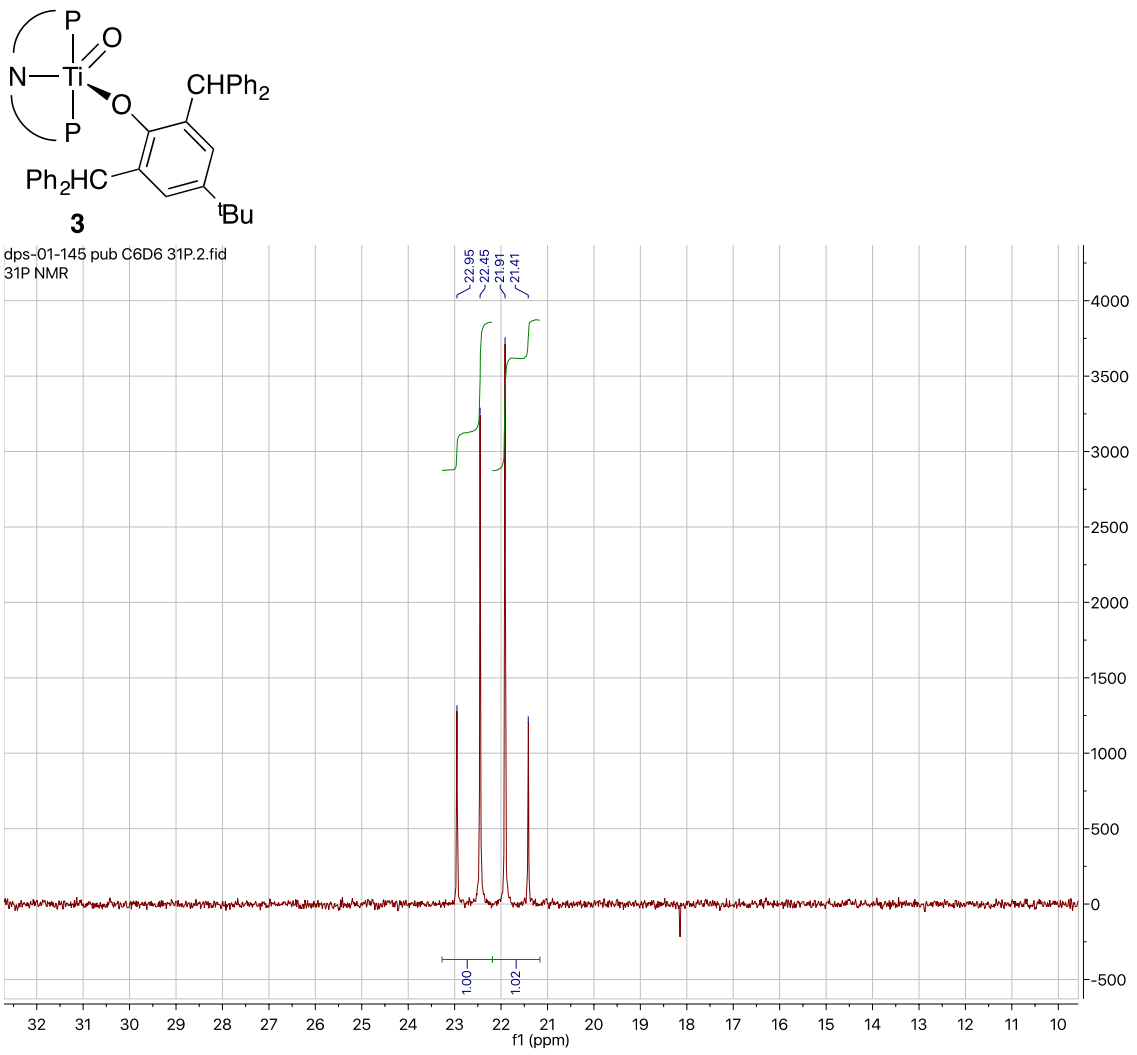


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **3** recorded in C_6D_6 (145.78 MHz, 23 °C)

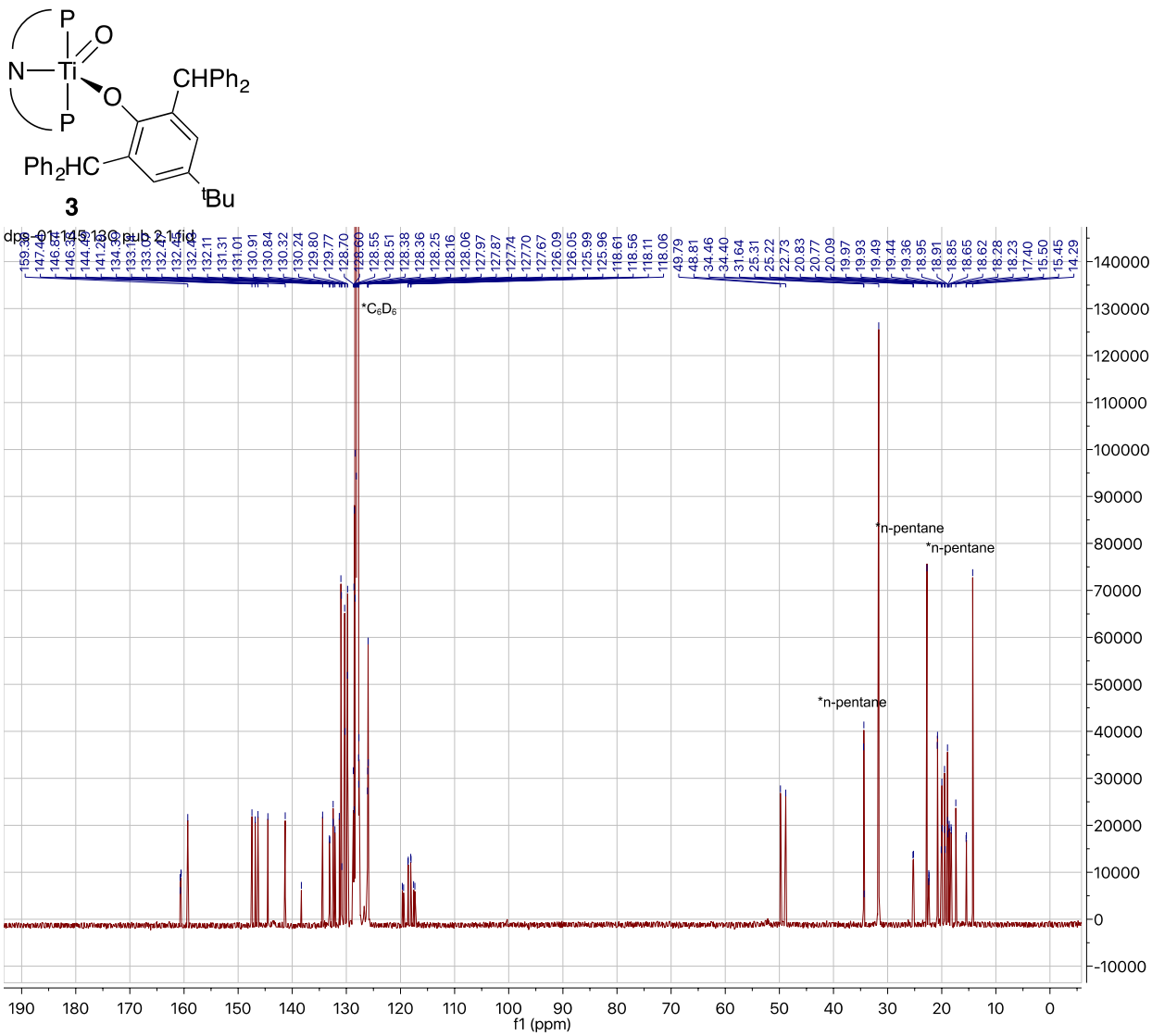
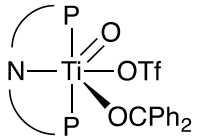


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **3** recorded in C_6D_6 (125.82 MHz, 23 °C)

UV-Vis Spectroscopic Data of 2 and 3



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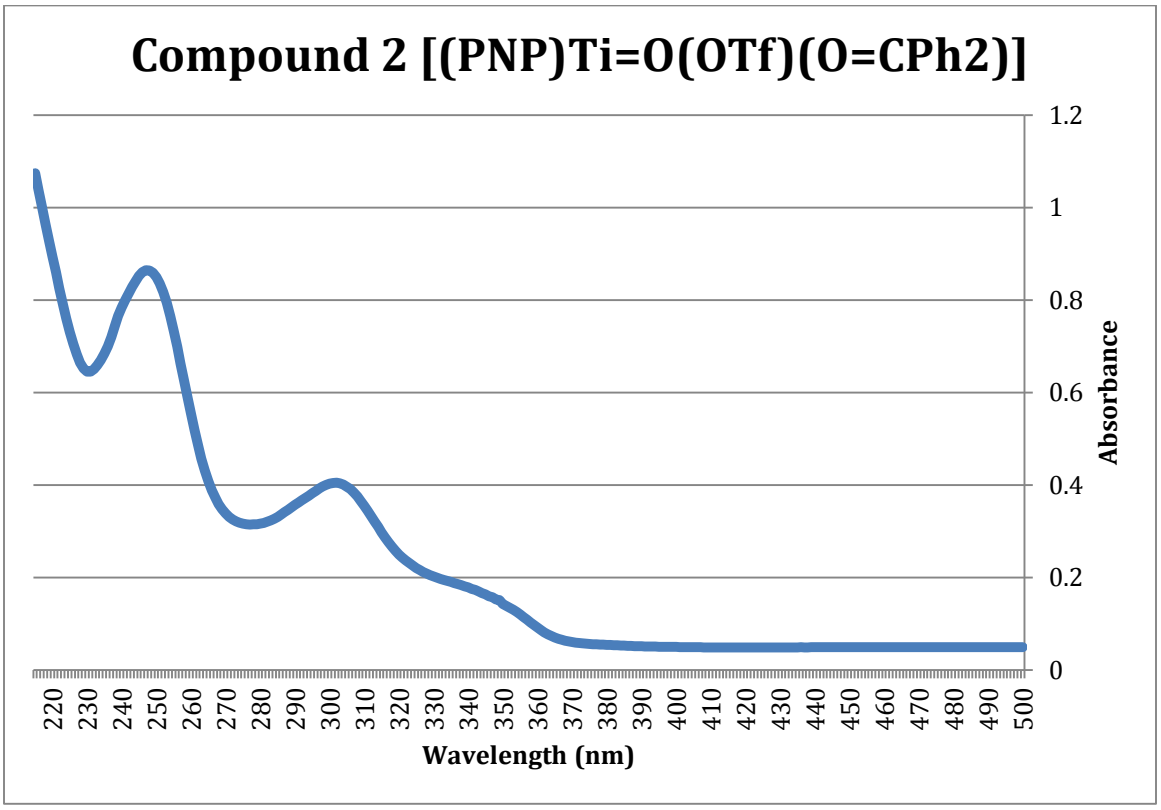
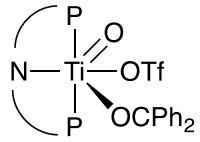


Figure S8. UV-Vis-NIR absorption spectrum of Compound **2** in hexanes solution (0.0526 mM).

$$\varepsilon_{\lambda=274} = 15494 \frac{L}{mol(cm)}$$

$$\varepsilon_{\lambda=302} = 6762 \frac{L}{mol(cm)}$$



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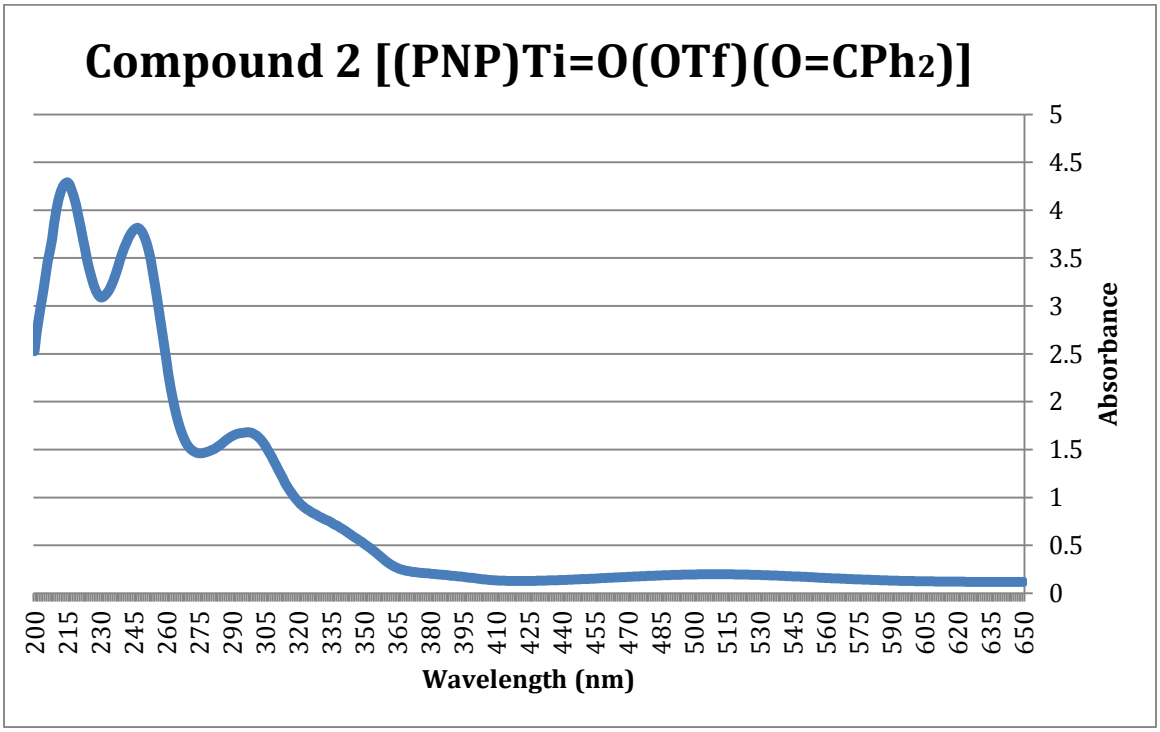
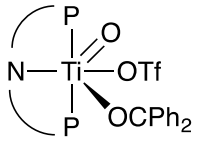


Figure S9. UV-Vis-NIR absorption spectrum of Compound **2** in hexanes solution (0.259 mM)



2

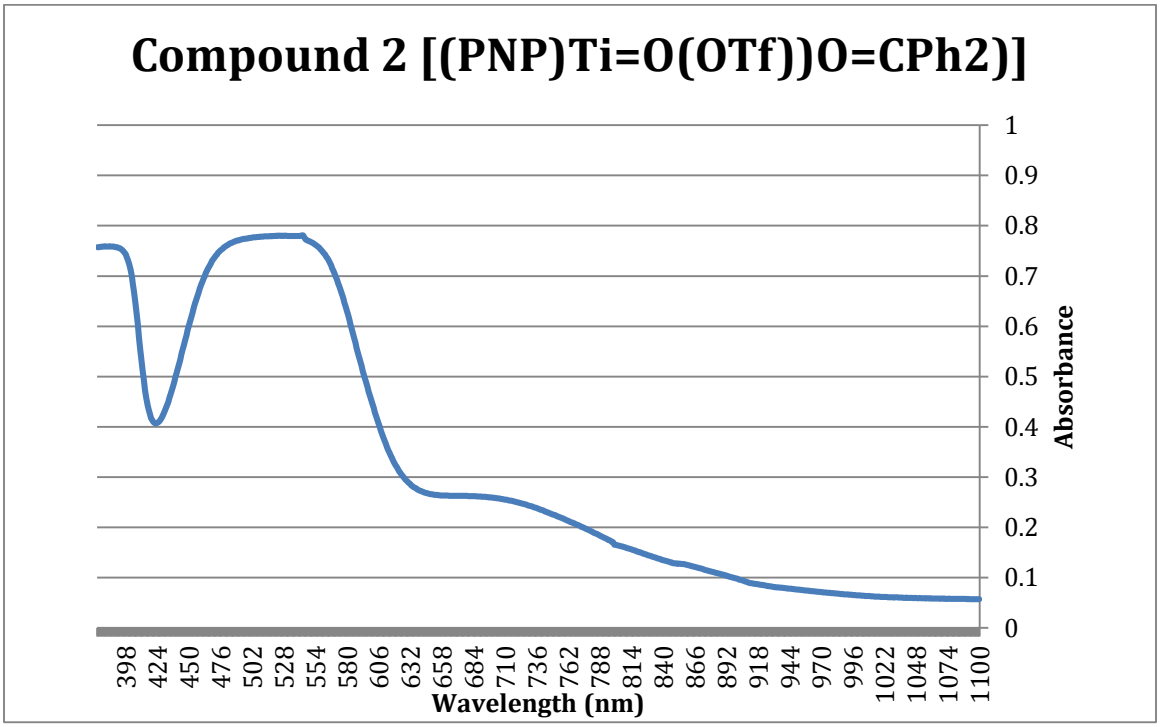
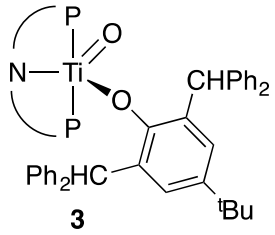


Figure S10. UV-Vis-NIR absorption spectrum of Compound **2** in hexanes solution (1.178 mM)

$\varepsilon_{\lambda=511} = 661 \frac{L}{mol(cm)}$



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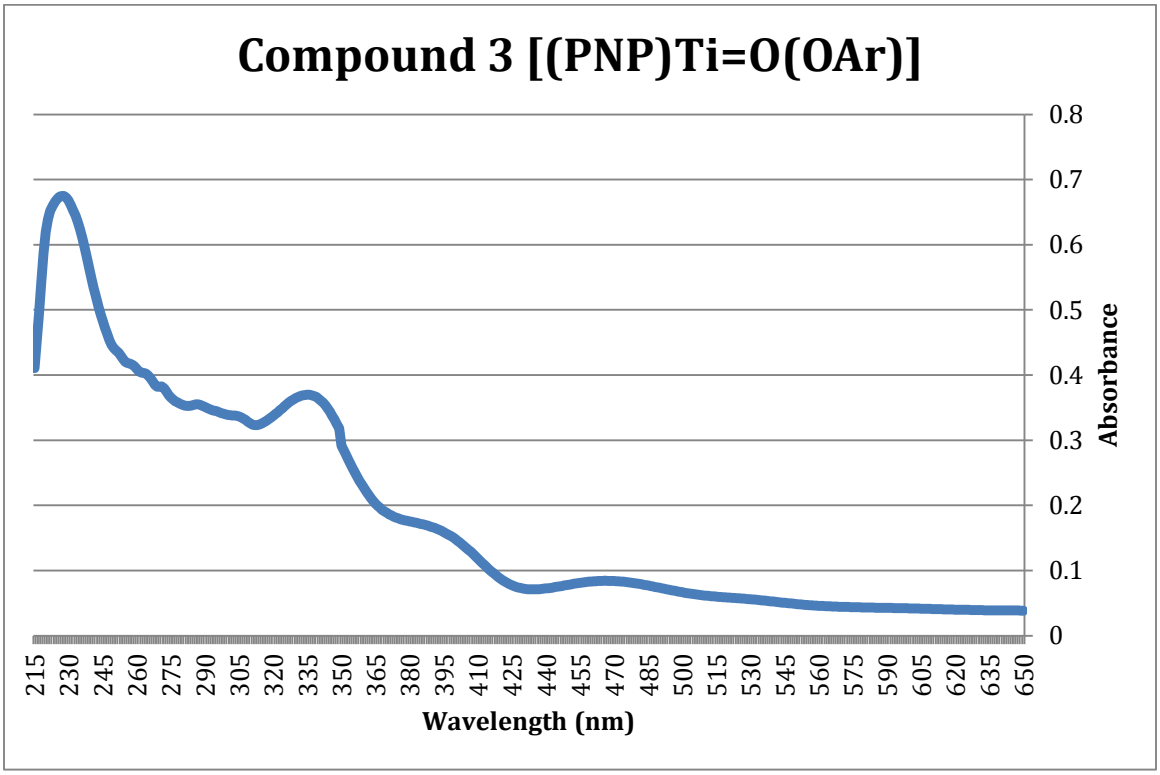

Figure S11. UV-Vis-NIR absorption spectrum of Compound **3** in hexanes solution (0.0513 mM)

$$\varepsilon_{\lambda=227} = 13156 \frac{L}{mol(cm)}$$

$$\varepsilon_{\lambda=335} = 7210 \frac{L}{mol(cm)}$$

$$\varepsilon_{\lambda=466} = 1643 \frac{L}{mol(cm)}$$

Computational Data for 2 and 3

Table S1. Cartesian coordinates of B3LYP optimized geometry of **2** (singlet).

0 1

Ti	0.283813	0.434270	-0.985170
S	-2.362127	0.976797	-2.765526
P	0.680572	-2.041884	-1.797297
P	0.946508	2.564609	0.437742
F	-4.047691	-1.010397	-2.284776
F	-4.588132	0.870811	-1.328783
F	-4.870453	0.618493	-3.472355
O	0.889162	1.230782	-2.264294
O	-0.892275	-0.429670	1.025971
O	-1.689130	0.463705	-1.490230
O	-1.919672	0.282009	-3.955648
O	-2.501618	2.418706	-2.767349
N	2.028936	-0.162325	-0.015967
C	2.264654	-1.484523	0.390607
C	3.018636	-1.814617	1.538441
H	3.451205	-1.016311	2.133107
C	3.208515	-3.138621	1.922181
H	3.794204	-3.348034	2.815598
C	2.655191	-4.204669	1.196973
C	1.890316	-3.881320	0.069844
H	1.439845	-4.690746	-0.500101
C	1.691764	-2.558629	-0.343155
C	2.898573	-5.641442	1.598477
H	3.863978	-6.007951	1.223192
H	2.123592	-6.305863	1.200979
H	2.915547	-5.759601	2.688543
C	-0.661270	-3.353181	-2.009366
H	-0.156353	-4.328117	-1.983986
C	-1.670194	-3.292992	-0.852388
H	-2.228392	-2.352569	-0.871444
H	-1.186850	-3.387713	0.123931
H	-2.391591	-4.114102	-0.954001
C	-1.368975	-3.205901	-3.368214
H	-2.171845	-3.950686	-3.437806
H	-0.692345	-3.373487	-4.212231
H	-1.817209	-2.215255	-3.487582
C	1.796856	-2.234729	-3.316214
H	1.145304	-1.923344	-4.142953
C	2.983620	-1.261422	-3.255749
H	3.655634	-1.508050	-2.425994
H	2.651713	-0.227135	-3.137812
H	3.561512	-1.337378	-4.185621
C	2.268449	-3.676360	-3.556055

H	2.876683	-3.716306	-4.468380
H	1.438375	-4.378857	-3.685413
H	2.892773	-4.031392	-2.728033
C	3.058901	0.787941	0.113642
C	4.427450	0.454086	0.001568
H	4.707635	-0.580328	-0.167157
C	5.418433	1.423126	0.082394
H	6.458919	1.120217	-0.020796
C	5.111943	2.780089	0.270724
C	3.760691	3.118580	0.374044
H	3.497572	4.165731	0.505844
C	2.740566	2.158730	0.306422
C	6.200107	3.825364	0.346991
H	5.780828	4.828236	0.479762
H	6.809573	3.840144	-0.565722
H	6.883700	3.638227	1.185288
C	0.649738	2.830867	2.299635
H	-0.442631	2.826669	2.396046
C	1.191013	4.155941	2.856976
H	0.996251	4.207145	3.936106
H	0.719761	5.030622	2.398422
H	2.275327	4.234659	2.716054
C	1.208710	1.644866	3.102923
H	2.303992	1.651737	3.093512
H	0.879580	0.681406	2.706329
H	0.880957	1.718168	4.147592
C	0.696812	4.265865	-0.344359
H	1.293079	4.971126	0.248931
C	-0.787117	4.663576	-0.239431
H	-0.919628	5.684981	-0.617638
H	-1.159640	4.641076	0.791167
H	-1.412258	4.002268	-0.849298
C	1.176141	4.323895	-1.802556
H	0.601672	3.644979	-2.436424
H	2.231799	4.054550	-1.898134
H	1.047006	5.347371	-2.178100
C	-1.649631	-0.502764	2.002911
C	-1.708225	-1.763666	2.797918
C	-0.567696	-2.583073	2.859602
H	0.341441	-2.268516	2.359086
C	-0.603414	-3.779780	3.570512
H	0.288715	-4.396680	3.624945
C	-1.782419	-4.186471	4.202935
H	-1.809908	-5.125099	4.749992
C	-2.926666	-3.389066	4.128415
H	-3.848100	-3.709537	4.606233

C	-2.889267	-2.177941	3.438472
H	-3.782592	-1.565332	3.374210
C	-2.492383	0.661132	2.402643
C	-2.970876	1.531597	1.408765
H	-2.762074	1.310838	0.369834
C	-3.728695	2.646812	1.760307
H	-4.112872	3.299642	0.981992
C	-3.988505	2.923189	3.106119
H	-4.572095	3.798542	3.378462
C	-3.499357	2.073413	4.102017
H	-3.691439	2.291618	5.148816
C	-2.765730	0.939899	3.754218
H	-2.382449	0.285491	4.530467
C	-4.066953	0.325736	-2.443681

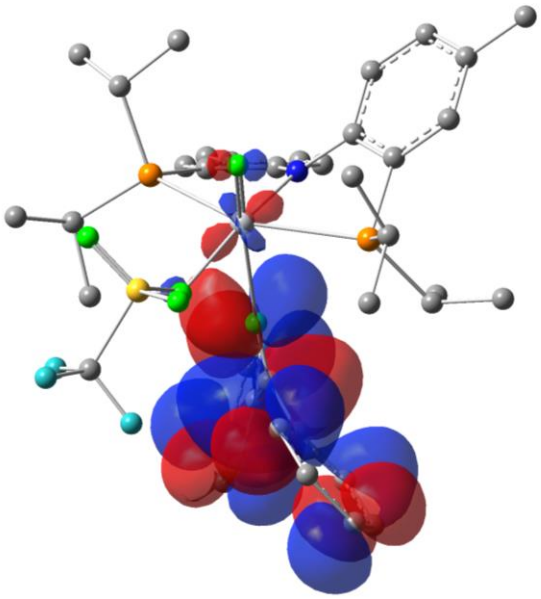

Figure S12. Computed Molecular Orbital 197 (LUMO) of Compound **2**.

Table S2. Selected Calculated Absorptions of **2** in n-hexane solution at the TD-DFT-B3LYP level.

Orbital Transition	**CI Coef.**	**Transition Energy (eV)**	**Oscillator Strength**
196 (HOMO) → 197 (LUMO)	0.70466	1.9133 (648.02 nm)	0.0002

196 (HOMO) → 198 (LUMO+1)	0.69861	2.4127 (513.88 nm)	0.0341

Table S3. Cartesian coordinates of B3LYP optimized geometry of **3** (singlet).

0 1

Ti	1.122162	-0.927504	0.377287
P	1.683998	-0.061007	2.813660
P	1.884965	-1.408001	-2.123359
O	1.021747	-2.534631	0.753996
O	-0.527646	-0.114609	0.075381
N	3.100795	-0.223348	0.279755
C	3.520370	0.905113	1.019691
C	4.463727	1.833967	0.528717
H	4.901225	1.675016	-0.451819
C	4.837005	2.944871	1.276539
H	5.565074	3.638531	0.859435
C	4.291819	3.199772	2.544868
C	3.342953	2.292564	3.025662
H	2.896368	2.477405	3.999586
C	2.954280	1.163187	2.294036
C	4.723115	4.398660	3.357859
H	4.689010	5.322732	2.767461
H	5.753523	4.290894	3.722319
H	4.079377	4.539185	4.232504
C	2.573908	-1.312584	3.928902
H	1.764510	-1.975985	4.261329
C	3.574715	-2.160709	3.129697
H	4.391065	-1.546735	2.733922
H	3.091652	-2.674579	2.294432
H	4.017931	-2.915988	3.791617
C	3.238350	-0.669756	5.154705
H	3.716942	-1.446090	5.764793
H	2.525091	-0.141835	5.796829
H	4.015950	0.040854	4.852639
C	0.504335	0.851063	3.969421
H	1.120229	1.382203	4.706982
C	-0.398868	-0.137137	4.726309
H	-1.112723	0.421521	5.344243
H	0.165413	-0.795881	5.393730
H	-0.980489	-0.764308	4.042532
C	-0.325162	1.882121	3.189993
H	-0.972532	1.395785	2.453457
H	0.300752	2.603723	2.657904
H	-0.965013	2.440867	3.884626
C	4.056999	-0.914922	-0.498107
C	5.413178	-1.029555	-0.117555
H	5.750243	-0.549435	0.795287

C	6.319854	-1.752235	-0.882255
H	7.352643	-1.821618	-0.545196
C	5.936799	-2.406278	-2.064023
C	4.596678	-2.299442	-2.442786
H	4.271024	-2.803987	-3.349751
C	3.662459	-1.573032	-1.690462
C	6.929588	-3.205264	-2.875686
H	7.279634	-4.090731	-2.328691
H	7.817916	-2.612047	-3.126417
H	6.487432	-3.553698	-3.815103
C	1.378530	-3.020020	-2.957999
H	2.005518	-3.124119	-3.853411
C	1.625145	-4.227976	-2.041223
H	1.075904	-4.129062	-1.101737
H	2.686071	-4.341661	-1.798394
H	1.291495	-5.141575	-2.549958
C	-0.093450	-2.934819	-3.398867
H	-0.378625	-3.859855	-3.914015
H	-0.275320	-2.103102	-4.089732
H	-0.760717	-2.820326	-2.538549
C	1.825700	-0.096985	-3.497420
H	0.755790	0.109548	-3.624887
C	2.506734	1.196660	-3.023684
H	3.590370	1.059470	-2.939576
H	2.138302	1.524952	-2.047635
H	2.319407	2.001010	-3.744696
C	2.405940	-0.545585	-4.846260
H	2.335453	0.278933	-5.567079
H	1.871118	-1.399679	-5.273571
H	3.465202	-0.811991	-4.754194
C	-1.815337	0.243097	-0.146550
C	-2.888340	-0.582503	0.276807
C	-4.197484	-0.144122	0.059389
H	-5.002266	-0.771728	0.431204
C	-4.508882	1.052171	-0.600366
C	-3.430271	1.825225	-1.037908
H	-3.609688	2.744075	-1.584675
C	-2.097271	1.459604	-0.812344
C	-2.637268	-1.936529	0.940211
H	-1.611689	-1.919859	1.325329
C	-2.684883	-3.108886	-0.049991
C	-1.775917	-4.167028	0.105091
H	-0.994994	-4.089319	0.855784
C	-1.844179	-5.297288	-0.712695
H	-1.128827	-6.103818	-0.572718
C	-2.816219	-5.386875	-1.711064

H	-2.870683	-6.266107	-2.348121
C	-3.712889	-4.331657	-1.888488
H	-4.469905	-4.383526	-2.667274
C	-3.647233	-3.204883	-1.065294
H	-4.351830	-2.394005	-1.218835
C	-3.550826	-2.160163	2.163376
C	-4.234772	-3.360616	2.391557
H	-4.163112	-4.166981	1.670153
C	-5.011605	-3.539911	3.540919
H	-5.533011	-4.482176	3.690450
C	-5.120862	-2.522647	4.487085
H	-5.725139	-2.662683	5.379572
C	-4.446825	-1.317619	4.271449
H	-4.524663	-0.510767	4.996199
C	-3.676287	-1.141034	3.123277
H	-3.174781	-0.191687	2.957844
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H	-6.693356	-0.603178	-1.113380
H	-6.241019	0.230765	-2.609386
C	-6.671343	1.617791	0.562334
H	-7.726114	1.890552	0.431040
H	-6.188499	2.404364	1.154036
H	-6.634809	0.692456	1.146762
C	-6.112882	2.790061	-1.576008
H	-5.659078	2.737323	-2.572163
H	-5.647467	3.621067	-1.033420
H	-7.173167	3.035376	-1.707160
C	-0.962265	2.365338	-1.288032
H	-0.075221	1.726623	-1.354097
C	-1.209021	2.898188	-2.711415
C	-1.489670	1.980522	-3.739367
H	-1.581677	0.924593	-3.496769
C	-1.677123	2.403028	-5.053999
H	-1.894338	1.672091	-5.829046
C	-1.594561	3.761866	-5.373314
H	-1.743270	4.095245	-6.396981
C	-1.325378	4.683074	-4.363231
H	-1.263755	5.743546	-4.594693
C	-1.132928	4.255104	-3.044934
H	-0.920986	4.987875	-2.273754
C	-0.604917	3.468672	-0.285369
C	0.740564	3.818217	-0.099497
H	1.513945	3.279822	-0.641251
C	1.109305	4.845328	0.771673

H	2.161032	5.084690	0.901714
C	0.131029	5.548412	1.477438
H	0.412410	6.348694	2.156986
C	-1.212527	5.209425	1.305528
H	-1.983925	5.745745	1.852665
C	-1.575484	4.179190	0.435161
H	-2.623324	3.918888	0.324826

Table S4. Selected Calculated Absorptions of **3** in n-hexane solution at the TD-DFT-B3LYP level.

Orbital Transition	**CI Coef.**	**Transition Energy (eV)**	**Oscillator Strength**
245 (HOMO) → 246 (LUMO)	0.70254	2.5384 (488.44 nm)	0.0808

Crystallographic Data

For description of solid-state structure analysis and refinement for **2** and **3**, refer to Experimental Procedure.

For compound **2**, A total of 85632 reflections were measured over the ranges $1.489 \leq \theta \leq 27.00°$, $-21 \leq h \leq 21$, $-15 \leq k \leq 15$, $-35 \leq l \leq 35$ yielding 12515 unique reflections (Rint = 0.0471). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[1] (minimum and maximum transmission 0.6834, 0.7456). The structure was solved by direct methods (SHELXS-97[2]). Refinement was by full-matrix least squares based on F^2 using SHELXL-2014. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0927P)^2 + 2.8904P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0539 and wR2=0.1519 for 9264 observed reflections for which $F > 4\sigma(F)$ and R1=0.0758 and wR2=0.1618 and GOF =1.051 for all 12515 unique, non-zero reflections and 536 variables.[3] The maximum □□□ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +1.400 and -0.779 e/Å^3.

For compound **3**, A total of 135355 reflections were measured over the ranges $1.271 \leq \theta \leq 27.498°$, $-14 \leq h \leq 14$, $-28 \leq k \leq 28$, $-31 \leq l \leq 31$ yielding 13521 unique reflections (R_{int} = 0.0792). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS (minimum and maximum transmission 0.7205, 0.7456). The structure was solved by direct methods SHELXS-97. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0837P)^2 + 4.9007P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0595 and wR2=0.1466 for 9482 observed reflections for which $F > 4\sigma(F)$ and R1=0.0958 and wR2=0.1704 and GOF =1.064 for all 13521 unique, non-zero reflections and 721 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +1.162 and -0.544 e/Å^3.

These results were checked using the IUCR's CheckCIF routine. Any Level A, B, or C alerts in the output are related to disordered tert-butyl and isopropyl groups, as well as the presence of disordered, co-crystallized solvent molecules.

Table S5: Summary of Structure Determinations for Compounds **2** and **3**

	Compound **2**	Compound **3**
Empirical formula	$C_{50}H_{75}NP_2SO_{7.5}F_3Ti$	$C_{69}H_{81}NO_2P_2Ti$
Formula weight	1009.01	1066.18
Temperature	100(1) K	100(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell constants:		
a	16.5327(12) Å	11.4489(3)Å
b	12.0477(8) Å	21.9022(6)Å
c	27.564(2) Å	23.9798(6)Å
β	97.271(4)°	101.442(2)°
Volume	5446.2(7) $Å^3$	5893.6(3)$Å^3$
Z	4	4
Density	1.231 g/cm^3	1.202 g/cm^3
Absorption coefficient	0.312 mm^{-1}	0.245 mm^{-1}
F(000)	2148	2280
Crystal size	0.48 x 0.33 x 0.13 mm^3	0.15 × 0.08 × 0.06 mm^3
Theta range for data collection	1.489 to 27.500°	1.271 – 27.498°
Index ranges	$-21 \le h \le 21$, $-15 \le k \le 15$, $-35 \le l \le 35$	$-14 \le h \le 14$, $-28 \le k \le 28$, $-31 \le l \le 31$
Reflections collected	85632	135355
Independent reflections	12515 [R(int) = 0.0471]	13521[R(int) = 0.0792]
Completeness to theta = 27.52°	100%	100%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6834	0.7456 and 0.7205
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	12515/0/536	13521/45/721
Goodness-of-fit on F2	1.051	1.064
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0539$, $wR_2 = 0.1519$	$R_1 = 0.0595$, $wR_2 = 0.1466$
R indices (all data)	$R_1 = 0.0758$, $wR_2 = 0.1618$	$R_1 = 0.0958$, $wR_2 = 0.1704$
Largest diff. peak and hole	1.400/-0.779 $eÅ^{-3}$	1.162/-0.544 $eÅ^{-3}$

References

1) G. M. Sheldrick, SADABS. University of Gottingen, Germany, 2007.
2) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
3) $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$
where n = the number of reflections and p = the number of parameters refined