

# Supporting Information

## Attempted synthesis of *ortho*-phenylene phosphino-tritylium cations

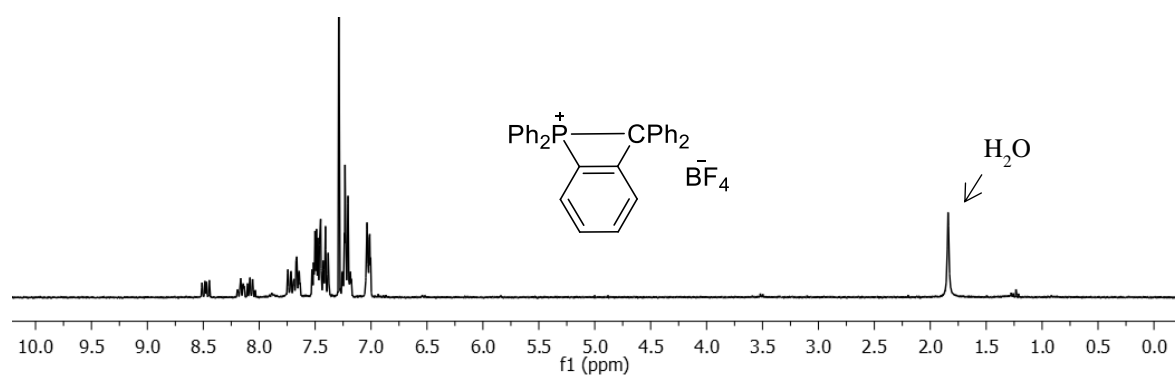
Kantapat Chansaenpak, Mengxi Yang, and François P. Gabbaï

Philosophical Transactions A

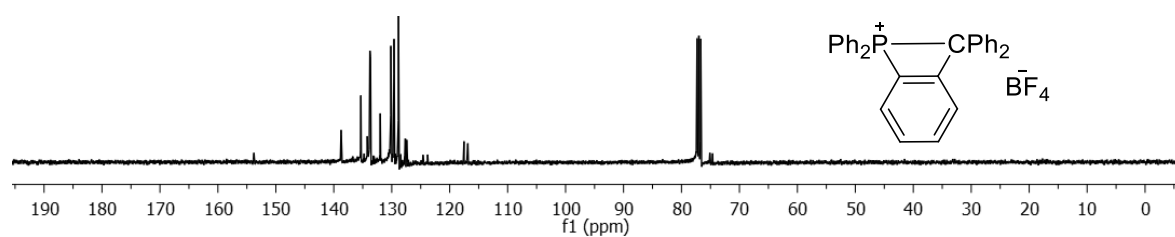
DOI: 10.1098/rsta.2017.0007

**Figure S1.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of **3** $[\text{BF}_4]$ .

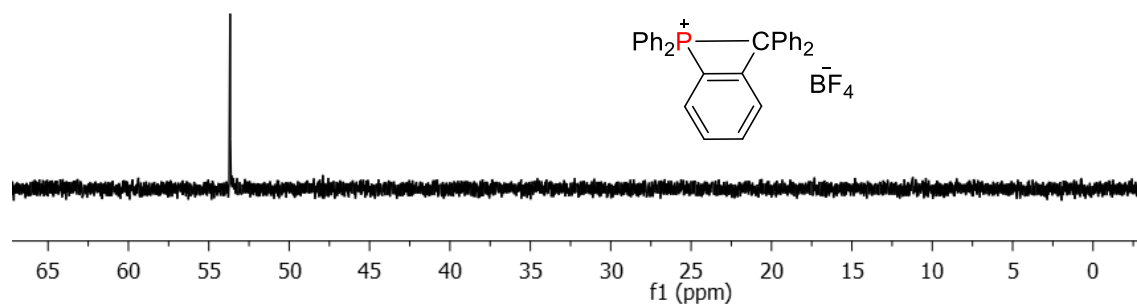
$^1\text{H}$  NMR



$^{13}\text{C}$  NMR

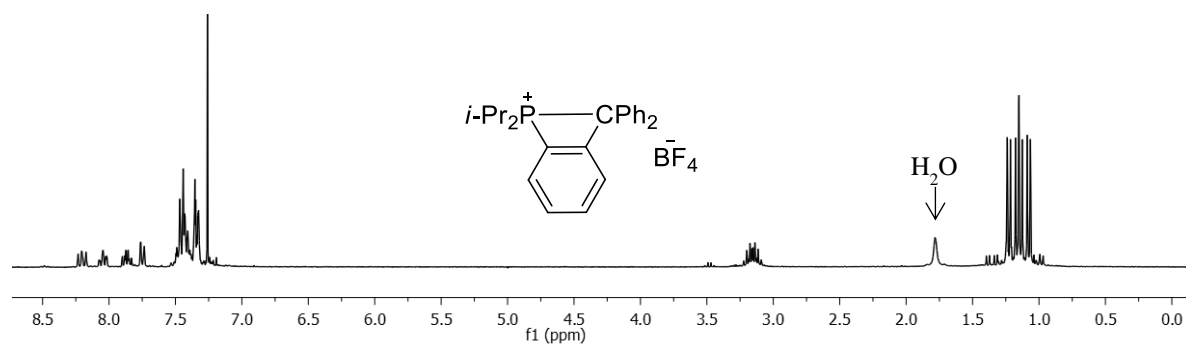


$^{31}\text{P}$  NMR

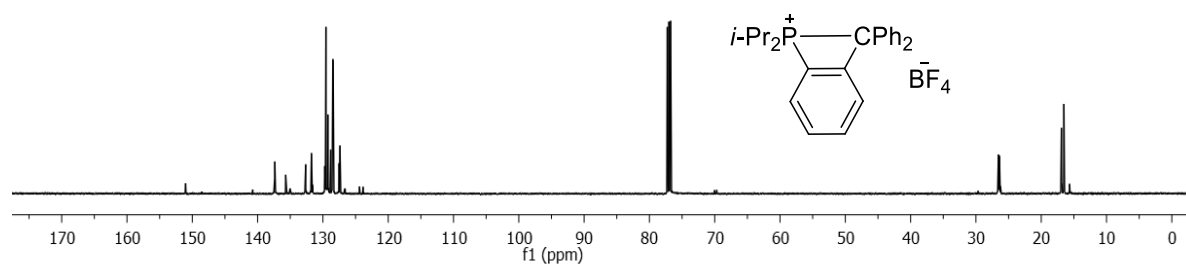


**Figure S2.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of **4** $[\text{BF}_4]$ .

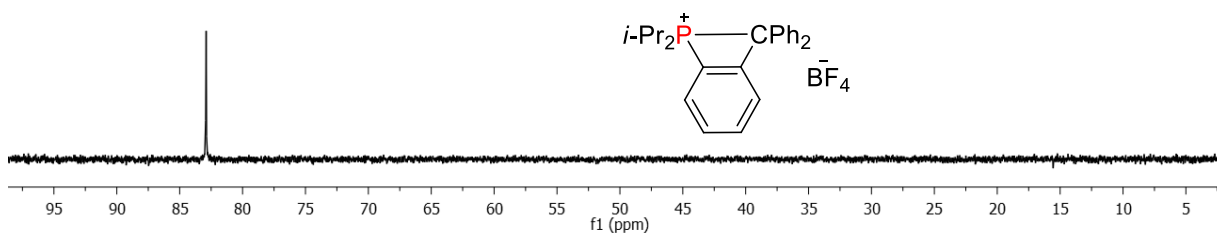
$^1\text{H}$  NMR



$^{13}\text{C}$  NMR

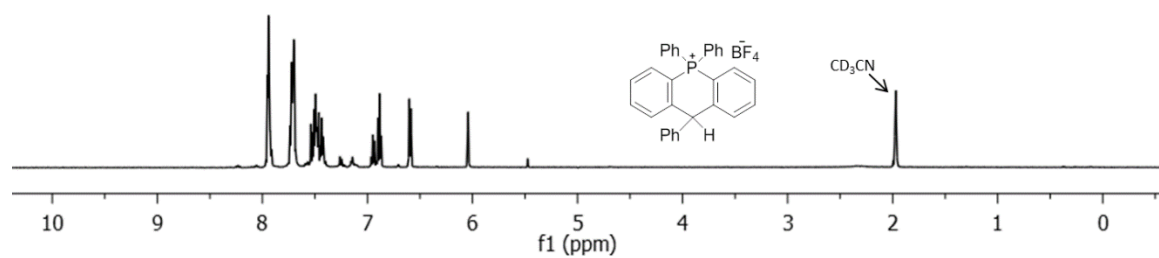


$^{31}\text{P}$  NMR

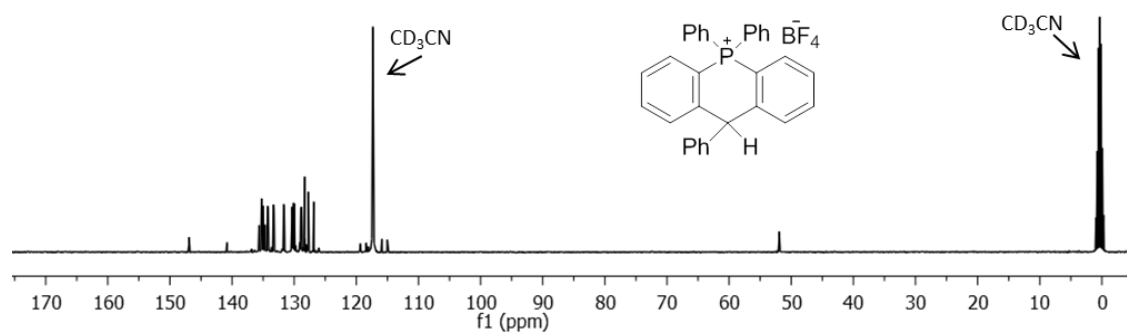


**Figure S3.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of **5**[ $\text{BF}_4$ ].

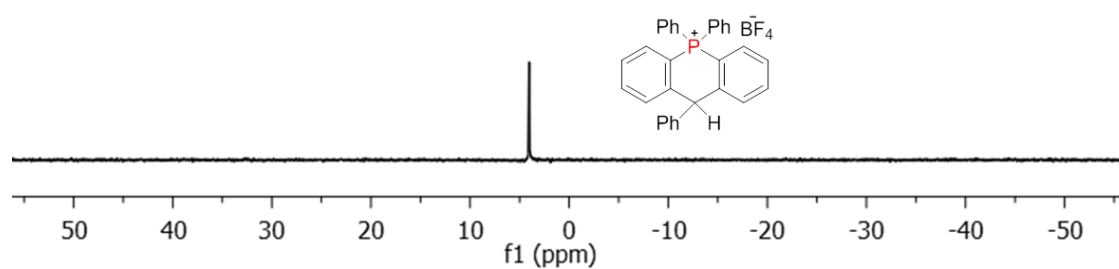
$^1\text{H}$  NMR



$^{13}\text{C}$  NMR

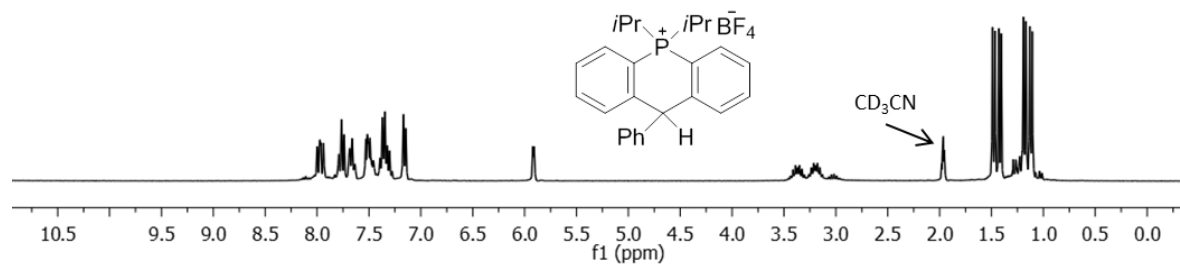


$^{31}\text{P}$  NMR

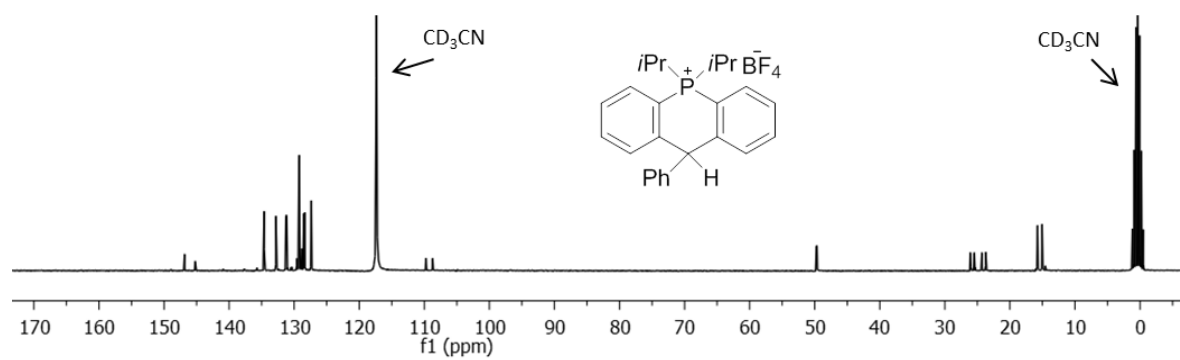


**Figure S4.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of **6** $[\text{BF}_4]$ .

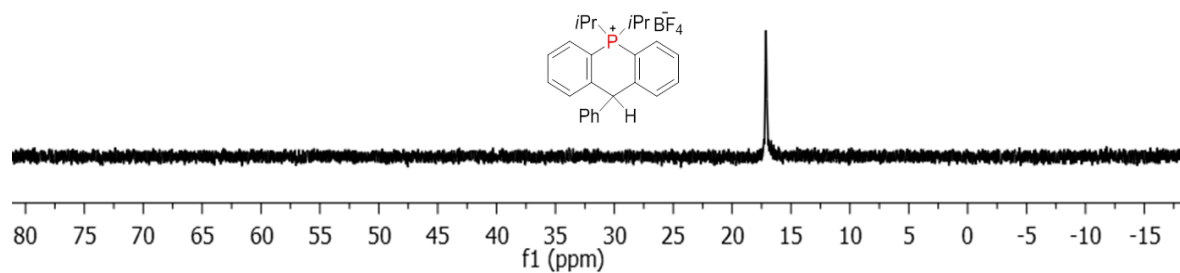
$^1\text{H}$  NMR



$^{13}\text{C}$  NMR



$^{31}\text{P}$  NMR



**Table S1.** Crystal data, data collection, and structure refinement for **3[BF<sub>4</sub>]**

Empirical formula	C <sub>31</sub> H <sub>24</sub> B F <sub>4</sub> P
Formula weight	514.28
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 1 2 <sub>1</sub> 1
Unit cell dimensions	<i>a</i> = 8.858(4) Å <i>b</i> = 16.639(7) Å <i>c</i> = 9.682(4) Å $\alpha$ = 90°. $\beta$ = 115.031(4)°. $\gamma$ = 90°.
Volume	1293.0(9) Å <sup>3</sup>
Z	2
Density (calculated)	1.321 Mg/m <sup>3</sup>
Absorption coefficient	0.154 mm <sup>-1</sup>
F(000)	532
Crystal size	0.5 x 0.3 x 0.25 mm <sup>3</sup>
Theta range for data collection	2.322 to 25.999°.
Index ranges	-10 ≤ <i>h</i> ≤ 10, -20 ≤ <i>k</i> ≤ 20, -11 ≤ <i>l</i> ≤ 10
Reflections collected	11486
Independent reflections	5028 [R(int) = 0.0333]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6239
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	5028 / 4 / 341
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.067
Final R indices [I > 2σ(I)]	R1 <sup>a</sup> = 0.0486, wR2 <sup>b</sup> = 0.0997
R indices (all data)	R1 = 0.0637, wR2 = 0.1059
Absolute structure parameter	0.07(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.314 and -0.303 e.Å <sup>-3</sup>

<sup>a</sup> $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> $wR2 = ([\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2])^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2) / 3$  with  $a = 0.03500$  and  $b = 0.66200$ .

**Table S2.** Crystal data, data collection, and structure refinement for **4[BF<sub>4</sub>]**

Empirical formula	C <sub>25</sub> H <sub>28</sub> B F <sub>4</sub> P
Formula weight	446.25
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 1 2 <sub>1</sub> / <i>c</i> 1
Unit cell dimensions	<i>a</i> = 8.1220(8) Å <i>b</i> = 13.5733(14) Å <i>c</i> = 20.319(2) Å $\alpha$ = 90°. $\beta$ = 91.8340(10)°. $\gamma$ = 90°.
Volume	2238.9(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.324 Mg/m <sup>3</sup>
Absorption coefficient	0.166 mm <sup>-1</sup>
F(000)	936
Crystal size	0.7 x 0.45 x 0.2 mm <sup>3</sup>
Theta range for data collection	1.805 to 28.261°.
Index ranges	-10 ≤ <i>h</i> ≤ 10, -18 ≤ <i>k</i> ≤ 18, -27 ≤ <i>l</i> ≤ 26
Reflections collected	25603
Independent reflections	5390 [R(int) = 0.0277]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7017
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	5390 / 3 / 308
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.042
Final R indices [I > 2σ(I)]	R1 <sup>a</sup> = 0.0374, wR2 <sup>b</sup> = 0.0940
R indices (all data)	R1 = 0.0461, wR2 = 0.0999
Extinction coefficient	n/a
Largest diff. peak and hole	0.390 and -0.260 e.Å <sup>-3</sup>

<sup>a</sup>*RI* =  $\sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>*wR2* =  $([\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2])^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2) / 3$  with  $a = 0.04540$  and  $b = 0.96990$ .

**Table S3.** Crystal data, data collection, and structure refinement for **5[BF<sub>4</sub>]**

Empirical formula	C <sub>31</sub> H <sub>24</sub> B F <sub>4</sub> P
Formula weight	514.28
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 1 2 <sub>1</sub> / <i>n</i> 1
Unit cell dimensions	<i>a</i> = 10.748(7) Å <i>b</i> = 17.213(11) Å <i>c</i> = 13.441(9) Å $\alpha$ = 90°. $\beta$ = 94.818(8)°. $\gamma$ = 90°.
Volume	2478(3) Å <sup>3</sup>
Z	4
Density (calculated)	1.378 Mg/m <sup>3</sup>
Absorption coefficient	0.160 mm <sup>-1</sup>
F(000)	1064
Crystal size	0.52 x 0.48 x 0.35 mm <sup>3</sup>
Theta range for data collection	1.926 to 28.445°.
Index ranges	-14 ≤ <i>h</i> ≤ 14, -22 ≤ <i>k</i> ≤ 23, -17 ≤ <i>l</i> ≤ 17
Reflections collected	29443
Independent reflections	6165 [R(int) = 0.0603]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6369
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	6165 / 0 / 334
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.031
Final R indices [I > 2σ(I)]	R1 <sup>a</sup> = 0.0421, wR2 <sup>b</sup> = 0.0956
R indices (all data)	R1 = 0.0643, wR2 = 0.1061
Extinction coefficient	n/a
Largest diff. peak and hole	0.311 and -0.351 e.Å <sup>-3</sup>

<sup>a</sup>*RI* =  $\sum||F_o| - |F_c|| / \sum|F_o|$ . <sup>b</sup>*wR2* =  $([\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2])^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2) / 3$  with  $a = 0.04010$  and  $b = 0.69770$ .

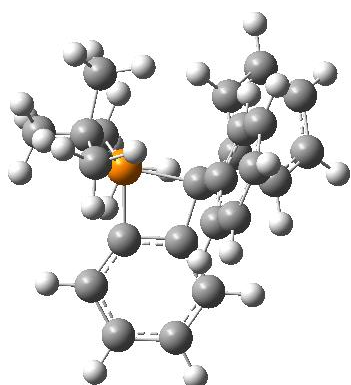
**Table S4.** Crystal data, data collection, and structure refinement for **6[BF<sub>4</sub>]**

Empirical formula	C <sub>25</sub> H <sub>28</sub> B F <sub>4</sub> P
Formula weight	446.25
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 2 <sub>1</sub> /c 1
Unit cell dimensions	a = 9.807(5) Å b = 15.502(11) Å c = 14.979(7) Å α = 90°. β = 101.83(6)°. γ = 90°.
Volume	2229(2) Å <sup>3</sup>
Z	4
Density (calculated)	1.330 Mg/m <sup>3</sup>
Absorption coefficient	0.166 mm <sup>-1</sup>
F(000)	936
Crystal size	0.3 x 0.3 x 0.12 mm <sup>3</sup>
Theta range for data collection	2.496 to 29.204°.
Index ranges	-13 ≤ h ≤ 12, -20 ≤ k ≤ 20, -19 ≤ l ≤ 20
Reflections collected	26706
Independent reflections	5759 [R(int) = 0.1069]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6390
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5759 / 12 / 315
Goodness-of-fit on F <sup>2</sup>	1.010
Final R indices [I > 2σ(I)]	R1 <sup>a</sup> = 0.0761, wR2 <sup>b</sup> = 0.1875
R indices (all data)	R1 = 0.1703, wR2 = 0.2318
Extinction coefficient	0.038(4)
Largest diff. peak and hole	0.381 and -0.531 e.Å <sup>-3</sup>

<sup>a</sup>R1 =  $\sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>wR2 =  $(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2)/3$  with  $a = 0.10780$  and  $b = 0.0000$ .

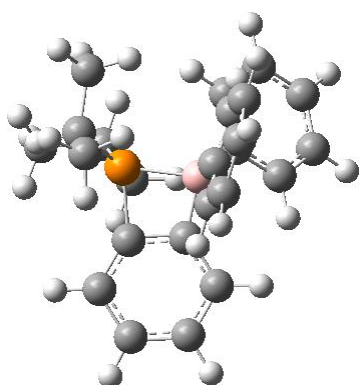


**Table S5.** XYZ coordinates of the optimized geometry of **4<sup>+</sup>**.



P	-0.351092	0.916331	-0.932679	H	-0.719675	-1.914814	-1.653516
C	0.838023	1.276527	-2.276538	C	-2.043552	0.786334	-1.647701
H	0.406460	2.180940	-2.730195	H	-2.063869	-0.145160	-2.226336
C	0.088547	-0.335624	0.428561	C	-2.559170	-3.758910	0.525818
C	-0.384146	1.944490	0.522577	H	-3.225382	-4.616849	0.548346
C	-0.844346	-1.533721	0.471231	C	3.383697	-2.143907	-0.344142
C	-0.238436	1.015291	2.753246	H	3.710577	-3.014162	-0.907461
H	-0.054187	0.197460	3.444712	C	3.872896	-0.260409	1.071822
C	-0.208202	0.844655	1.369138	H	4.583705	0.354181	1.618156
C	1.574521	-0.717487	0.426613	C	2.515432	0.058333	1.115357
C	-0.652729	3.399433	2.371394	H	2.204418	0.929906	1.684535
H	-0.821997	4.386097	2.793956	C	-3.110774	0.721820	-0.547187
C	2.026203	-1.834778	-0.289047	H	-4.088334	0.584150	-1.022000
H	1.320876	-2.485983	-0.797250	H	-3.142312	1.656397	0.024949
C	2.259830	1.605389	-1.804985	H	-2.955451	-0.108182	0.148658
H	2.792280	2.085206	-2.633808	C	-2.001597	-3.335670	-0.680647
H	2.809318	0.700733	-1.527380	H	-2.228476	-3.862459	-1.603921
H	2.271276	2.293180	-0.951965	C	4.314713	-1.355008	0.332478
C	-2.252857	-3.076650	1.701870	H	5.372420	-1.601412	0.294649
H	-2.678104	-3.402105	2.647630	C	0.822340	0.137127	-3.306258
C	-1.401187	-1.971751	1.675188	H	1.470479	0.408480	-4.147006
H	-1.182832	-1.451936	2.602809	H	-0.176858	-0.063515	-3.710426
C	-0.611395	3.237993	0.988011	H	1.221081	-0.786821	-2.869552
H	-0.746378	4.083245	0.318148	C	-2.293951	1.978285	-2.585901
C	-0.470552	2.305621	3.233022	H	-3.338839	1.949921	-2.914212
H	-0.497887	2.473269	4.306798	H	-1.667549	1.958139	-3.483207
C	-1.150911	-2.232348	-0.702769	H	-2.142768	2.936911	-2.071820

**Table S6.** XYZ coordinates of the optimized geometry of *o*-<sup>i</sup>Pr<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)BPh<sub>2</sub>.



P	0.221205	-1.026599	-0.861091	H	0.948664	1.821517	-1.818220
C	-1.021098	-1.688452	-2.052633	C	1.884293	-1.280058	-1.643482
H	-0.718335	-2.719470	-2.283468	H	1.973833	-0.479623	-2.392188
B	-0.073339	0.555378	0.497254	C	3.130957	3.600140	0.084014
C	0.215424	-1.844945	0.741889	H	3.920758	4.341650	-0.011713
C	1.079705	1.656655	0.331986	C	-3.298416	2.485448	-0.649708
C	0.214815	-0.840193	2.927133	H	-3.556900	3.254949	-1.374834
H	0.152715	0.021636	3.590357	C	-3.940175	0.947243	1.087703
C	0.147854	-0.684932	1.535528	H	-4.701982	0.504687	1.726721
C	-1.593556	1.079812	0.402962	C	-2.610285	0.537135	1.204878
C	0.392379	-3.259196	2.654039	H	-2.362916	-0.236893	1.930938
H	0.482542	-4.243385	3.107831	C	2.996931	-1.094695	-0.603555
C	-1.972504	2.075843	-0.513466	H	3.971241	-1.143898	-1.105394
H	-1.211735	2.546898	-1.135245	H	2.961165	-1.892169	0.148865
C	-2.427885	-1.711116	-1.445760	H	2.927698	-0.132518	-0.086189
H	-3.107814	-2.235021	-2.129728	C	2.458160	3.138245	-1.047948
H	-2.812325	-0.696365	-1.293027	H	2.722868	3.518687	-2.032708
H	-2.450354	-2.227869	-0.479020	C	-4.292239	1.917236	0.150548
C	2.782926	3.096910	1.337433	H	-5.327405	2.236037	0.050067
H	3.302645	3.445908	2.227621	C	-0.985415	-0.841139	-3.330390
C	1.773950	2.138662	1.452136	H	-1.721342	-1.217357	-4.051576
H	1.529248	1.748928	2.439879	H	-0.002709	-0.851953	-3.817788
C	0.332737	-3.133164	1.267240	H	-1.244580	0.201472	-3.102388
H	0.374049	-4.012796	0.626828	C	2.013158	-2.641892	-2.333865
C	0.338853	-2.120038	3.470830	H	3.031622	-2.762331	-2.724250
H	0.386677	-2.242683	4.551209	H	1.320943	-2.762435	-3.174447
C	1.450228	2.182439	-0.916882	H	1.835565	-3.459189	-1.621819