An unusually unstable *ortho*-phopshinophenol and its use to prepare benzoxaphospholes having enhanced air-stability

Shanshan Wu, Nihal Deligonal and John D. Protasiewicz

Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106

Supplementary Information:

1. Experimental Section
2. Crystallography Study
3. Computational Study
4. Air-stability Study
5. ^{1}H NMR and ^{13}C NMR of Compounds

Experimental Section

All air-sensitive operations were performed under nitrogen atmosphere, using Schelenk line or in Vacuum Atmospheres MBraun glove box unless otherwise stated. Tetrahydrofuran, hexanes and toluene were dried by distillation from sodium benzophenone ketyl. Dichloromethane was dried by distillation from CaH_2 prior to use for UV-vis and fluorescence measurements. Benzimidoyl chlorides were prepared according to literature procedure. [1] 2-Bromo-3,5-di-*tert*-butylphenol was prepared by the reaction of 3,5-di-*tert*-butylphenol with Br_2. [2] ^1H, $^{13}C\{^1H\}$ and ^{31}P NMR spectra were recorded on a Varian INOVA AS-400 or 600 spectrometers, and all chemical shifts are referred to residual $CHCl_3$ signals (for ^1H NMR spectra) or to an external sample of 85% H_3PO_4 (for ^{31}P NMR spectra). Melting points were measured on a Mel-temp melting point apparatus. Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ). High resolution mass spectrometry was performed by the University of Michigan Mass Spectrometry facility using a VG (Micrimass) 70-250-S magnetic sector spectrometer. UV-Vis and fluorescence data were recorded using a Cary 50 Bio UV-Visible spectrophotometer and a Cary Eclipse spectrometer, respectively. Anthracene in ethanol was used as the quantum yield standard. [3]

Diethyl (2-bromo-3,5-di-*tert*-butylphenyl)phosphate (2):

To a suspension of NaH (60% in mineral oil, 1.47 g, 36.8 mmol) in THF (50 mL) was slowly added a solution of 2-bromo-3,5-di-*tert*-butylphenol (10.0 g, 35.1 mmol) in THF (50 mL) at 0°C. The yellow mixture was stirred at 0°C for 30 min, and then diethylchlorophosphate (5.40 mL, 36.8 mmol) was added. The mixture was stirred at room temperature for 1 hour to yield a brown solution. To the reaction mixture was slowly added saturated NH_4Cl solution (~ 5 mL), followed by the addition of 100 mL of diethylether, then by addition of 100 mL of a saturated brine solution. The organic layer was separated and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to yield a brown oil. Yield: 13.9 g (94.0 %). ^1H NMR (399.7 Hz): δ 7.34 (m, 1H), 7.27 (m, 1H), 4.27 (m, 4H), 1.52 (s, 9H), 1.35 (td, 6H, $^4J_{PH} = 1.2$ Hz, $^3J_{HH} = 7.2$ Hz), 1.29 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ

-6.3 (s). $^{13}C\{^{1}H\}$ NMR (100.5 Hz): δ 150.7, 148.8, 148.2 (d, J_{pc} = 5.6 Hz), 121.1, 115.7 (d, J_{pc} = 2.1 Hz), 112.0 (d, J_{pc} = 7.9 Hz), 64.6 (d, J_{pc} = 6.3 Hz), 37.3, 34.7, 31.0, 29.7, 16.0 (d, J_{pc} = 6.8 Hz). HRMS ($[M+H]^{+}$): *m*/*z* 421.1138 (calc 421.1138).

Diethyl (2-hydroxy-4,6-di-*tert*-butylphenyl)phosphonate (3):

To a solution of diethyl (2-bromo-3,5-di-*tert*-butylphenyl)phosphate (2.53 g, 6.01 mmol) in THF (75 mL) was added 3.40 ml *n*-BuLi (2.5M in hexane, 8.41 mmol) at -78°C. The mixture was stirred at -78°C for 30 minutes, and then was poured into a room temperature mixture of saturated NH_4Cl solution (50 ml) and diethylether (50 ml). The organic layer was separated and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to yield a yellow oil. The material was further purified by distillation using Buchi glass oven (B-585 kugelrohr, 190°C, 0.05 mm Hg) to initially afford a colorless oil, which after cooling to room temperature, yielded a colorless crystalline solid. Yield: 1.55 g (75.2 %). mp: 39-40°C. ^{1}H NMR (399.7 Hz): δ 11.9 (br s, 1H, $^{4}J_{PH}$ = 0.8), 7.14 (dd, 1H, $^{4}J_{HH}$ = 2.0 Hz, $^{4}J_{PH}$ = 6.0 Hz), 6.85 (dd, 1H, $^{4}J_{HH}$ = 2.0 Hz, $^{4}J_{PH}$ = 4.8 Hz), 4.19 (m, 4H), 1.46 (s, 9H), 1.35 (td, 6H, $^{4}J_{PH}$ = 0.4 Hz, $^{4}J_{HH}$=6.8 Hz), 1.28 (s, 9H). $^{31}P\{^{1}H\}$ NMR (161.8 Hz): δ -27.6 (s). $^{13}C\{^{1}H\}$ NMR (100.5 Hz): δ 164.6 (d, J_{pc} = 7.9 Hz), 157.1 (d, J_{pc} = 2.8 Hz), 154.3 (d, J_{pc} = 8.2 Hz), 117.1 (d, J_{pc} = 14.2 Hz), 114.0 (d, J_{pc} = 12.1 Hz), 103.6 (d, J_{pc} = 177.1 Hz), 62.4 (d, J_{pc} = 5.8 Hz), 38.2 (d, J_{pc} = 3.1 Hz), 35.0, 32.6, 30.7, 16.1 (d, J_{pc} = 6.9 Hz). Elemental Analyses Calc. for $C_{18}H_{31}O_4P$, C 63.14%, H 9.13 %; found: C 63.02%, H 8.88 %.

3,5-Di-*tert*-butyl-2-phosphinophenol (4):

To a solution of $LiAlH_4$ (1.03 g, 27.0 mmol) in 150 mL THF was slowly added a solution of diethyl (2-hydroxy-4,6-di-*tert*-butylphenyl)phosphonate (3.70 g, 10.8 mmol) in 50 mL THF at 0°C. The mixture was stirred at room temperature overnight. To the reaction mixture was slowly added a degassed saturated NH_4Cl solution (~5 mL). The mixture was then extracted with degassed diethylether (~100 ml) and the organic layer was separated and dried over $MgSO_4$. The solvent was removed in *vacuo* to yield a colorless oil. Yield: 1.42 g (55.3 %). ^{1}H NMR (399.7 Hz): δ 7.11 (m, 1H), 6.86 (d, 1H, $^{4}J_{HH}$ = 1.6 Hz), 5.53 (br s, 1H), 3.68 (d, 2H, $^{1}J_{PH}$ = 198.4 Hz), 1.55 (s, 9H), 1.30 (s, 9H). $^{31}P\{^{1}H\}$ NMR (161.8 Hz): δ -169.7

(s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 158.2, 155.6 (d, J_{pc} = 16.7 Hz), 153.1, 116.0 (d, J_{pc} = 6.3 Hz), 109.8, 107.4 (d, J_{pc} = 22.2 Hz), 37.3, 34.8, 31.7 (d, J_{pc} = 11.9 Hz), 31.1. HRMS (EI, 70 eV): *m*/*z* 238.1487 (calc 238.1487).

4,6-Di-*tert*-butyl-2-(4-methylphenyl)-1,3-benzoxaphosphole (5a):

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (0.562 g, 2.36 mmol) in 10 mL THF was added a solution of 4-methyl-N-phenylbenzimidoyl chloride (1.08 g, 4.68 mmol) in 20 mL THF. The reaction was refluxed for 96 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, the mixture was filtered to remove a white precipitate. The solvent was removed under vacuum from the filtrate to yield a yellow solid. The solid was extracted with hexanes and filtered through Celite, and then passed through basic alumina to yield a colorless solution. The solvent was removed in *vacuo* to yield a colorless crystalline solid. Yield: 0.167 g (20.9 %). mp: 92-94°C. ^1H NMR (399.7 Hz): δ 7.92 (m, 2H), 7.62 (m, 1H), 7.31 (m, 1H), 7.23 (d, 2H, $^3J_{HH}$ = 8 Hz), 2.39 (s, 3H), 1.59 (s, 9H), 1.41 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 85.8 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 193.9 (d, J_{pc} = 54.1 Hz), 161.2 (d, J_{pc} = 4.0 Hz), 151.1 (d, J_{pc} = 9.7 Hz), 150.7 (d, J_{pc} = 3.1 Hz), 139.6 (d, J_{pc} = 4.7 Hz), 132.0 (d, J_{pc} = 13.6 Hz), 130.6 (d, J_{pc} = 44.3 Hz), 129.5, 124.6 (d, J_{pc} = 14.2 Hz), 117.2 (d, J_{pc} = 7.5 Hz), 108.0, 36.9 (d, J_{pc} = 2.3 Hz), 35.2, 31.5, 31.0 (d, J_{pc} = 8.8 Hz), 21.5. HRMS (EI, 70 eV): *m*/*z* 338.1806 (calc 338.1800). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} • cm^{-1}) 348 (23650). Fluorescence (CH_2Cl_2): λ_{ex}, 430 nm. Quantum Yield (CH_2Cl_2): Φ 0.13.

4,6-Di-*tert*-butyl-2-(4-methoxyphenyl)-1,3-benzoxaphosphole (5b):

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (0.458 g, 1.92 mmol) in 10 mL THF was added a solution of 4-methoxy-N-phenylbenzimidoyl chloride (0.519 g, 2.11 mmol) in 20 mL THF. The reaction was refluxed for 38 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, the mixture was filtered to remove a white precipitate. The solvent was removed by vacuum to yield a yellow solid. The solid was extracted with hexanes and filtered through Celite and then passed through basic alumina to give a yellow solution. The solvent was removed in *vacuo* to yield a yellow solid.

Recrystallization from toluene afforded a yellow crystalline. Yield: 0.250 g (36.8 %). mp: 99-100°C. ^{1}H NMR (399.7 Hz): δ 7.96 (m, 2H), 7.59 (m, 1H), 7.29 (m, 1H), 6.94 (m, 2H), 3.87 (s, 3H), 1.59 (s, 9H), 1.40 (s, 9H). ^{31}P{^{1}H} NMR (161.8 Hz): δ 80.9 (s). ^{13}C{^{1}H} NMR (150.0 Hz): δ 193.8 (d, J_{pc} = 54 Hz), 161.1 (d, J_{pc} = 3.8 Hz) , 160.7 (d, J_{pc} = 4.5 Hz), 151.0 (d, J_{pc} = 9.8 Hz), 150.5 (d, J_{pc} = 3.0 Hz), 130.6 (d, J_{pc} = 44.1 Hz), 127.8 (d, J_{pc} = 13.4 Hz), 126.2 (d, J_{pc} = 14.0 Hz), 117.1 (d, J_{pc} = 7.4 Hz), 114.1, 107.9, 55.4, 36.9 (d, J_{PC} = 2.1 Hz), 35.2, 31.5, 31.0 (d, J_{PC} = 8.9 Hz). HRMS (EI, 70 eV): *m*/*z* 354.1735 (calc 354.1749). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} • cm^{-1}) 354 (12190). Fluorescence (CH_2Cl_2): λ_{ex}, 438 nm. Quantum Yield (CH_2Cl_2): Φ 0.12.

4,6-Di-*tert*-butyl-2-phenyl-1,3-benzoxaphosphole (5c):

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.00 g, 4.21 mmol) in 20 mL THF was added a solution of N-phenyl-benzimidoyl chloride (0.998 g, 4.63 mmol) in 20 mL THF. The reaction was refluxed for 13 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, a white precipitate was removed by filtration, and the solvent was removed by vacuum to yield a yellow solid. The solid was extracted with hexanes and filtered through Celite and then passed through basic alumina to yield a colorless solution. The solvent was removed in *vacuo* to yield a colorless crystalline solid. Yield: 0.630 g (46.2 %). ^{1}H NMR (399.7 Hz): δ 8.03 (m, 2H), 7.63 (m, 1H), 7.43 (m, 2H), 7.38 (m, 1H), 7.32 (m, 1H), 1.60 (s, 9H), 1.41 (s, 9H). ^{31}P{^{1}H} NMR (161.8 Hz): δ 89.4 (s). ^{13}C{^{1}H} NMR (100.5 Hz): δ 193.5 (d, J_{pc} = 54.0 Hz), 161.4 (d, J_{pc} = 4.0 Hz), 151.3 (d, J_{pc} = 9.8 Hz), 150.9 (d, J_{pc} = 3.0 Hz), 134.7 (d, J_{pc} = 13.2 Hz), 130.6 (d, J_{pc} = 44.5 Hz), 129.3 (d, J_{pc} = 4.6 Hz), 128.7, 124.6 (d, J_{pc} = 14.4 Hz), 117.2 (d, J_{pc} = 7.6 Hz), 108.1, 36.9 (d, J_{pc} = 2.1Hz), 35.2, 31.5, 31.0 (d, J_{pc} = 8.8 Hz). HRMS (EI, 70 eV): *m*/*z* 324.1644 (calc 324.1643). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} • cm^{-1}) 345 (12110). Fluorescence (CH_2Cl_2): λ_{ex}, 425 nm. Quantum Yield (CH_2Cl_2): Φ 0.12.

4,6-Di-*tert*-butyl-2-(4-bromophenyl)-1,3-benzoxaphosphole (5d):

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.00 g, 4.20 mmol) in 20 mL THF was added a solution of 4-bromo-N-phenyl-benzimidoyl chloride (1.36 g, 4.62 mmol) in 20 mL

THF. The reaction was refluxed for 13 hours to produce a yellow cloudy solution. After the reaction was cooled down to room temperature a white precipitate was removed by filtration, and the solvent was removed under vacuum to yield a yellow solid. The solid was extracted with hexanes and the solution was filtered through Celite and then passed through basic alumina to yield a yellow solution. The solvent was removed in *vacuo* to yield a yellow solid. Recrystallization from hexanes provided a yellow crystalline solid. Yield: 0.730 g (43.1 %). mp: 102-103°C. ^{1}H NMR (399.7 Hz): δ 7.88 (m, 2H), 7.61 (m, 1H), 7.54 (m, 2H), 7.32 (m, 1H), 1.59 (s, 9H), 1.40 (s, 9H). ^{31}P{^{1}H} NMR (161.8 Hz): δ 92.2 (s). ^{13}C{^{1}H} NMR (150.0 Hz): δ 191.8 (d, J_{pc} = 53.3 Hz), 161.4 (d, J_{pc} = 4.1 Hz), 151.5, 151.4 (d, J_{pc} = 2.3 Hz), 133.6 (d, J_{pc} = 13.4 Hz), 131.9 (d, J_{pc} = 1.1 Hz),130.4 (d, J_{PC} = 44.3 Hz), 126.0 (d, J_{pc} = 14.4 Hz), 123.2 (d, J_{pc} = 5.9 Hz), 117.4 (d, J_{pc} = 7.8 Hz), 108.1, 36.9 (d, J_{pc} = 2.1 Hz), 35.2, 31.5, 31.1 (d, J_{pc} = 8.7 Hz). HRMS (EI, 70 eV): *m*/*z* 402.0741 (calc 402.0748). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} • cm^{-1}) 353 (21680). Fluorescence (CH_2Cl_2): λ_{ex}, 427 nm. Quantum Yield (CH_2Cl_2): Φ 0.07.

4,6-Di-*tert*-butyl-2-adamantyl-1,3-benzoxaphosphole (5e):

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.04 g, 4.37 mmol) in 20 mL THF was added a solution of 1-adamantane-benzimidoyl chloride (1.32 g, 4.82 mmol) in 20 mL THF. The reaction was refluxed for 17 hours to produce a yellow cloudy solution. After the reaction was cooled down to room temperature a white precipitate was removed by filtration, and the solvent was removed under vacuum to yield a yellow solid. The solid was extracted with hexanes and the solution was filtered through Celite and then passed through basic alumina to give a colorless solution. The solvent was removed in *vacuo* to yield a white solid. Yield: 0.776 g (46.4 %). mp: 103-104°C. ^{1}H NMR (399.7 Hz): δ 7.54 (m, 1H), 7.27 (m, 1H), 2.11 (m, 3H), 2.09 (m, 6H), 1.80 (m, 6H), 1.56 (s, 9H), 1.38 (s, 9H). ^{31}P{^{1}H} NMR (161.8 Hz): δ 77.2 (s). ^{13}C{^{1}H} NMR (100.5 Hz): δ 210.8 (d, J_{pc} = 61.3 Hz), 161.4 (d, J_{pc} = 3.1 Hz), 151.2 (d, J_{pc} = 9.7 Hz), 149.9 (d, J_{pc} = 2.5 Hz), 129.5 (d, J_{pc} = 45.1 Hz), 116.7 (d, J_{pc} = 6.9 Hz), 107.8, 42.0 (d, J_{pc} = 9.3 Hz), 39.6 (d, J_{pc} = 10.8 Hz), 36.9 (d, J_{pc} = 2.4 Hz), 36.7, 35.1, 31.5, 31.0 (d, J_{pc} = 9.0 Hz), 28.4. HRMS (EI, 70 eV): *m*/*z* 382.2422 (calc 383.2455).

UV(CH_2Cl_2): λ_{max}, nm (ε, $M^{-1} \bullet cm^{-1}$) 289 (14440). Fluorescence (CH_2Cl_2): λ_{ex}, 424 nm. Quantum Yield (CH_2Cl_2): Φ 0.04.

Air-stability Studies

Air-stability tests were performed in NMR tubes with deuterated solvent and opened to air at room temperature. As $CDCl_3$ evaporated, more $CDCl_3$ was added to replenish the solution. Samples were monitored by ^{1}H NMR and ^{31}P NMR spectroscopy.

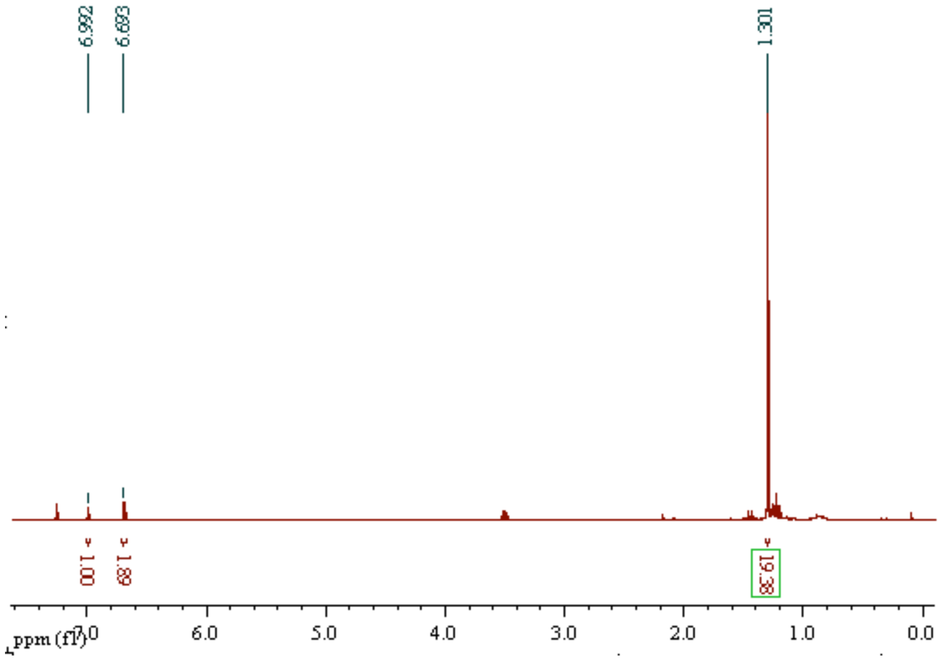


Figure S1. ^{1}H NMR spectrum of solution of compound **4** after addition of 5% HCl in ether in $CDCl_3$, showing selective formation of 3,5-di-*tert*-butyl-phenol.

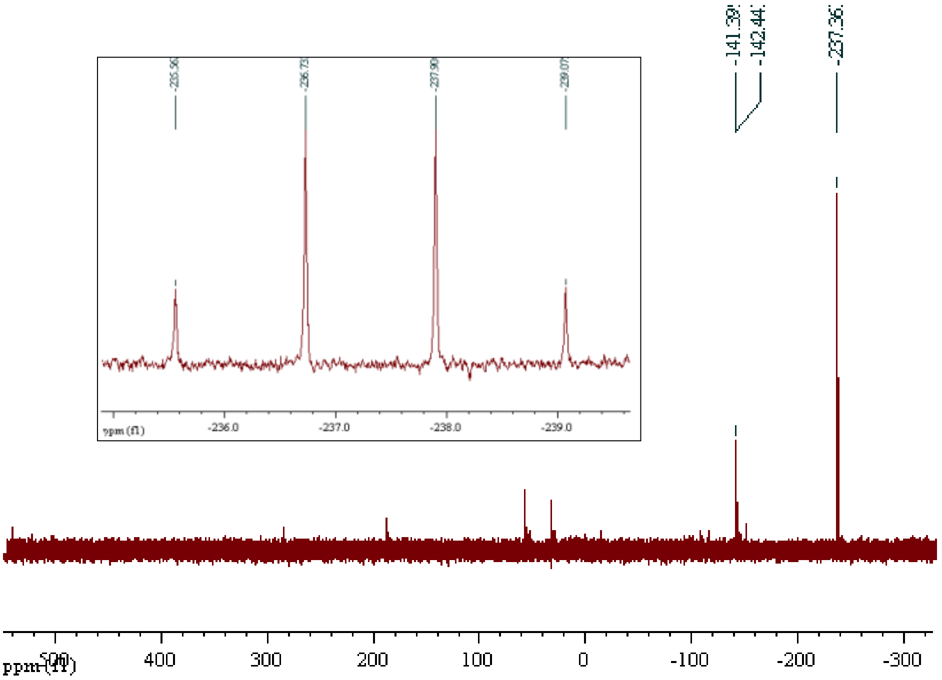


Figure S2. ^{31}P NMR spectrum of solution of compound **4** after addition of 5% HCl in ether in $CDCl_3$, recorded immediately after mixing, showing major product is PH_3.

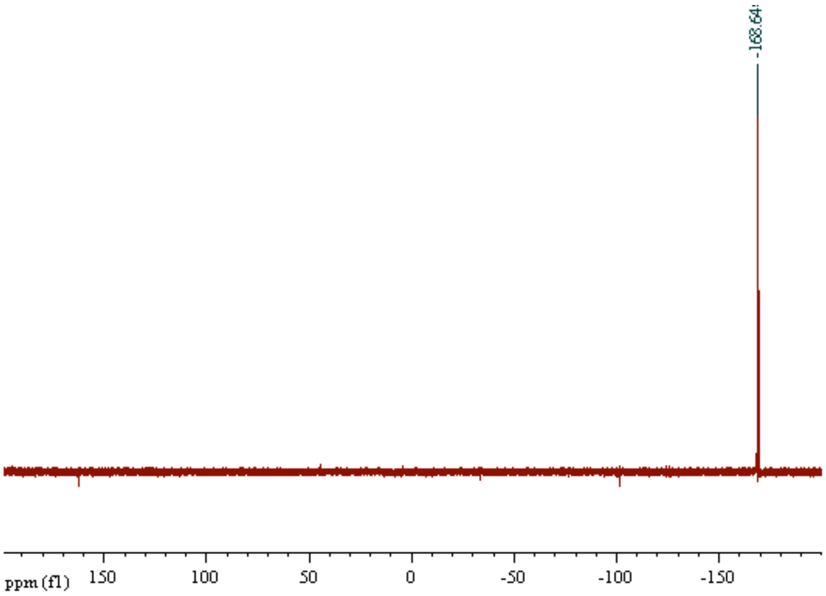


Figure S3. ^{31}P{1H} NMR of mixture solution of compound **4** in $CDCl_3$ and 5% by mol. TSOH in Et_2O recorded immediately after mixing, showing only compound **4**.

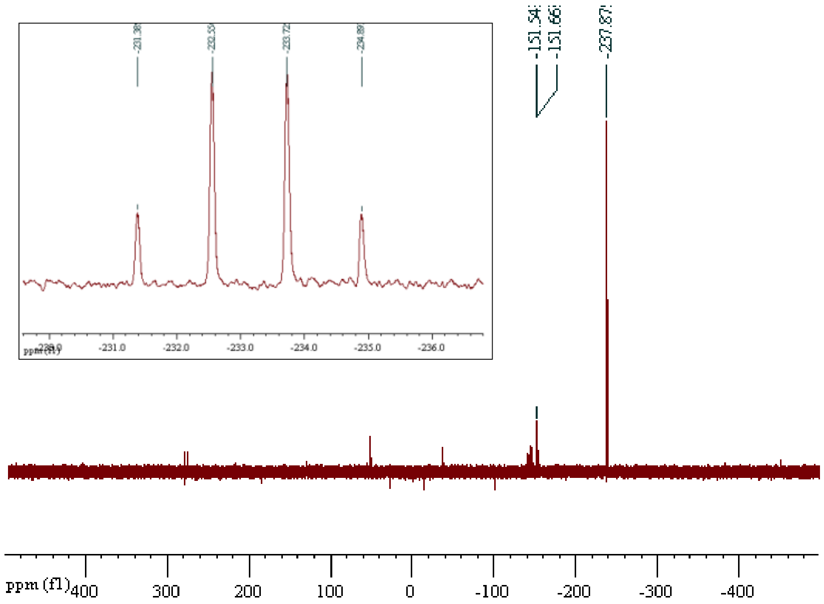


Figure S4. ^{31}P NMR of mixture solution of compound **4** in $CDCl_3$ and 5% by mol. TSOH in Et_2O recorded 5 days after mixing, showing major compound is PH_3.

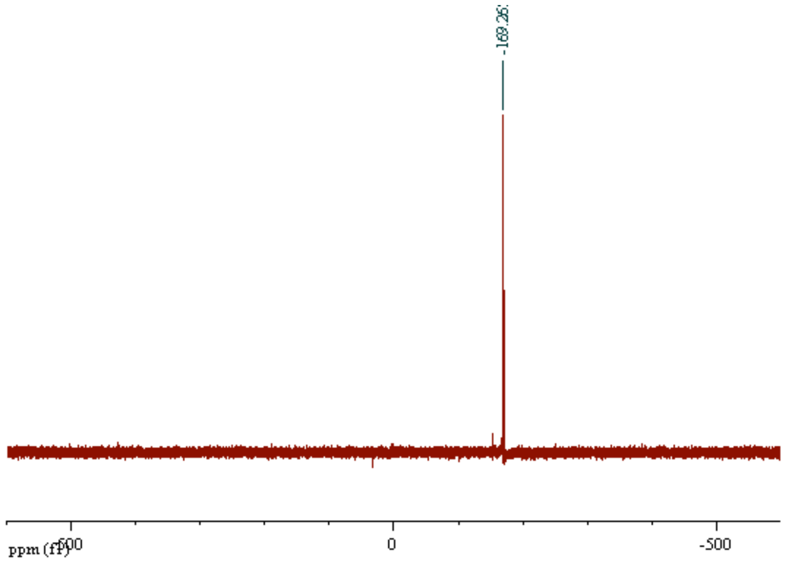


Figure S5. **Figure S3.** ^{31}P{1H} NMR of mixture solution of compound **4** in $CDCl_3$ and 1 equiv. TSOH in Et_2O recorded immediately after mixing, showing only compound **4**.

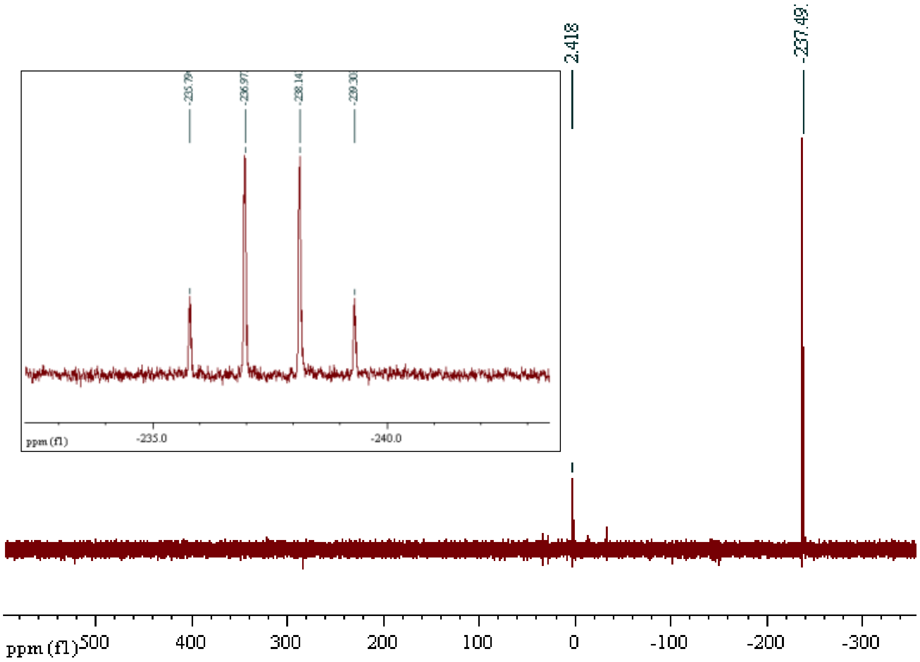


Figure S6. ^{31}P NMR spectrum (proton coupled) of solution of compound **4** and 1eq. TSOH in $CDCl_3$ (5 hours). Inset represents ^{31}P NMR spectrum highlighting PH coupling.

Crystallography

The X-ray intensity data were measured at 100 K on a Bruker AXS SMART APEX II CCD-based X-ray diffractometers system within monochromatic Mo Ka radiation with the omega scan technique. The unit cell was determined using SMART[a] and SAINT+.[b] The structures were solved by direct method and refined by full matrix least-squares against with F^2 with all reflections using SHELXTL.[c] Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in standard calculated positions and all hydrogen atoms were refined with an isotropic displacement parameter 1.2 times that of the adjacent carbon. For further details see table **S1**.

[a] Bruker Advanced X-ray Solutions. SMART for WNT/2000 (Version 5.628); Briker ACS Inc.: Madison, WI, 1997-2002

[b] Bruker Advanced X-ray Solutions. SAINT (Version 6.45); Bruker AXS Inc.: Madison, WI, 1997-2003

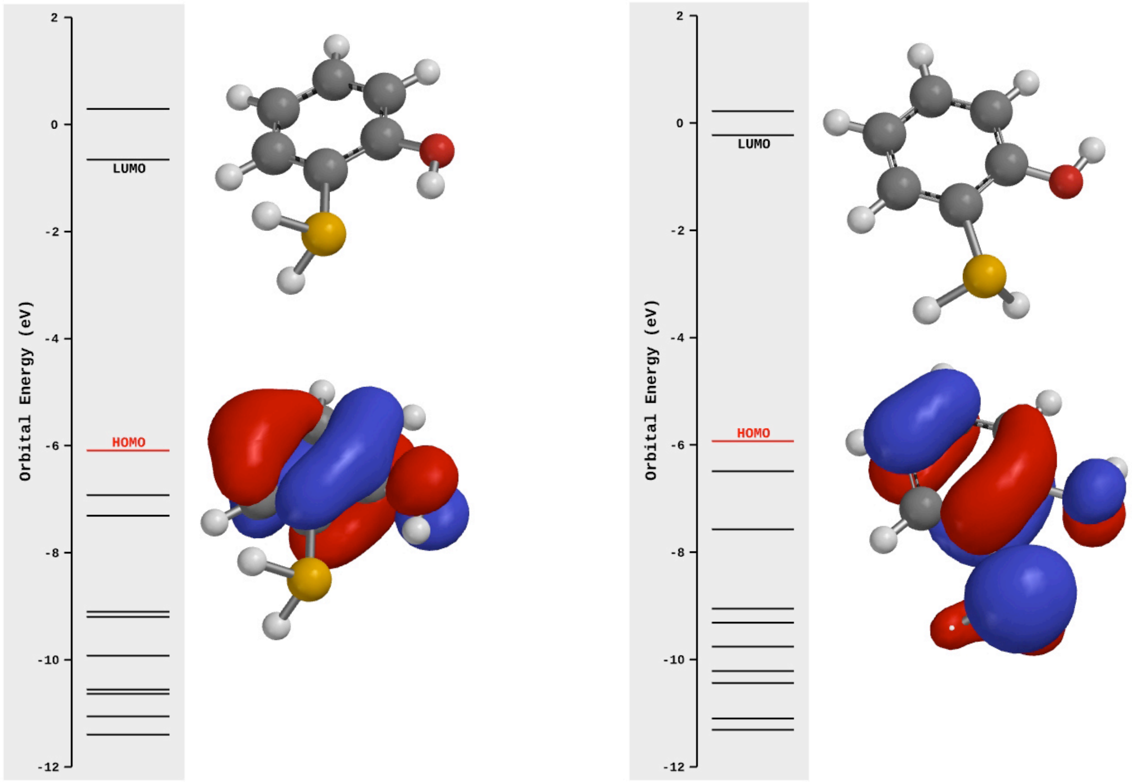
[c] Bruker Advanced X-ray Solutions. SHELXTL (Version 6.10); Bruker AXS Inc.: Madison, WI, 2000.

Table S1 Crystal data and structure refinement for **5a** and **5c**

	5a	**5c**
Empirical formula	$C_{22}H_{27}OP$	$C_{21}H_{25}OP$
Formula weight	338.41	324.38
Temperature	160 (2) K	180 (2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/n	Pbca
Unit cell dimensions	a=7.7787(8) Å α=90° b=26.404(3)Å β=93.7840(10)° c=9.4840(10) Å γ=90°	a=10.5448(9) Å α=90° b=10.0465(8) Å β=90° c=35.559(3) Å γ=90°
Volume	1943.6 (3) $Å^3$	3767.1 (5) $Å^3$
Z	4	8
Calculated density	1.156 Mg/m^3	1.144 Mg/m^3
Absorption coefficient	0.147 mm^{-1}	0.149 mm^{-1}
F(000)	728	1392
Crystal size	0.33×0.10×0.09 mm	0.30×0.25×0.04 mm
θ range for data collection	2.29 to 28.41 °	1.15 to 27.50 °
Limiting indices	-10<=h<=10, -35<=k<=35, -12<=l<=12	-13<=h<=13, -13<=k<=13, -46<=l<=45
Reflections collected / unique	24183/4812 [R(int)=0.0304]	40817/4307 [R(int)=0.0609]
Completeness to θ = 27.50	98.3 %	99.7 %
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.9868 and 0.9528	0.9945 and 0.9575
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4812/0/224	4307/0/214
Goodness-of-fit on F^2	1.024	1.036
Final R indices [I>2σ (I)]	R1=0.0382, wR2=0.1022	R1=0.0412, wR2=0.0983
R indices (all data)	R1=0.0459, wR2=0.1084	R1=0.0658, wR2=0.1139
Largest diff. peak and hole	0.278 and -0.251 e.A^{-3}	0.228 and -0.231 e.A^{-3}

Computational Studies

Calculations were undertaken using DFT (6-31G*) as implemented in the program SPARTAN '10 (Wavefunction, Inc., Irvine, CA) and as described in B. Stewart, A. Harriman and L. J. Higham, *Organometallics*, 2011, **30**, 5338-5343.



Lowest Energy
-649.409924 au -6.1 eV
Δ E = 1.0 kcal/mol

2nd Lowest Energy
-649.408292 au -5.9 eV

Figure S7. Calculational results for two lowest energy isomers of *ortho*-phosphinophenol. Upper structure in each panel displays lowest energy conformation and lower structure shows HOMO orbital.

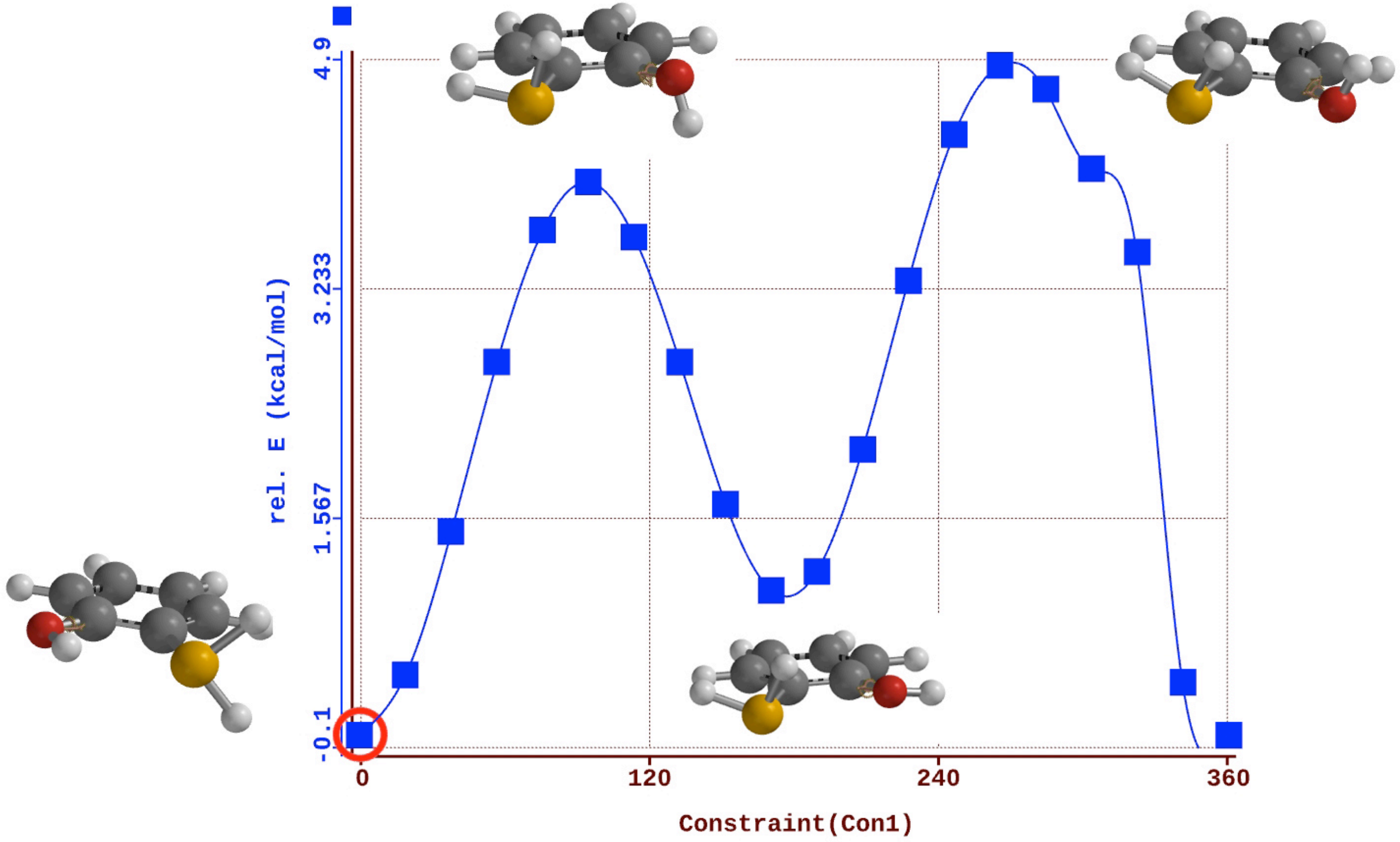
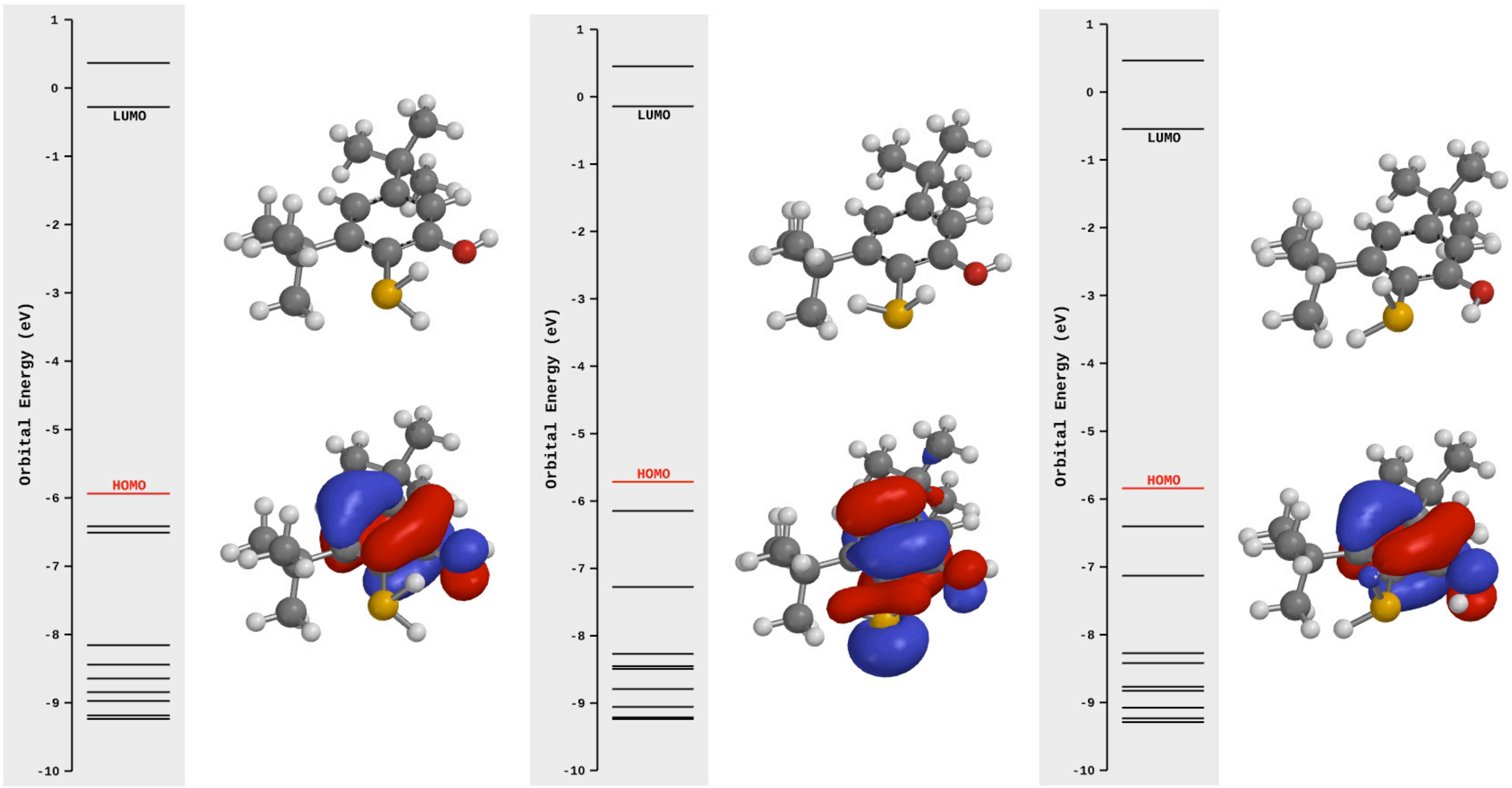
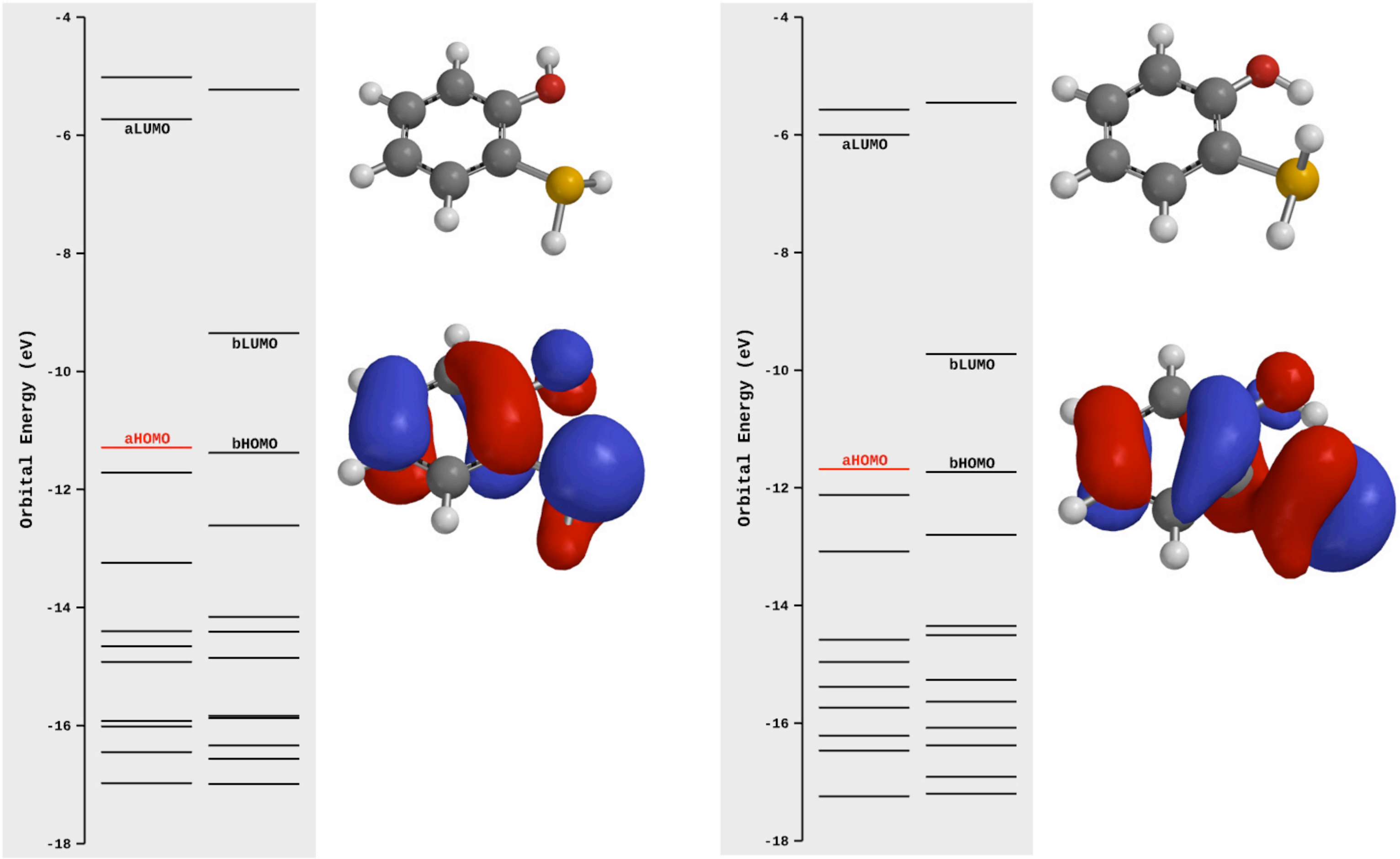


Figure S8. Energy profile analysis for rotation about the C-OH bond in *ortho*-phosphinophenol (DFT B3LYP/6-31G*) showing lowest and highest energy conformations.



Lowest Energy	2nd Lowest Energy	3rd Lowest Energy
-963.906500 au -5.9 eV	-963.905092 au -5.7 eV	-963.904387 au -5.8 eV
Δ E = 0	0.88	1.3 kcal/mol

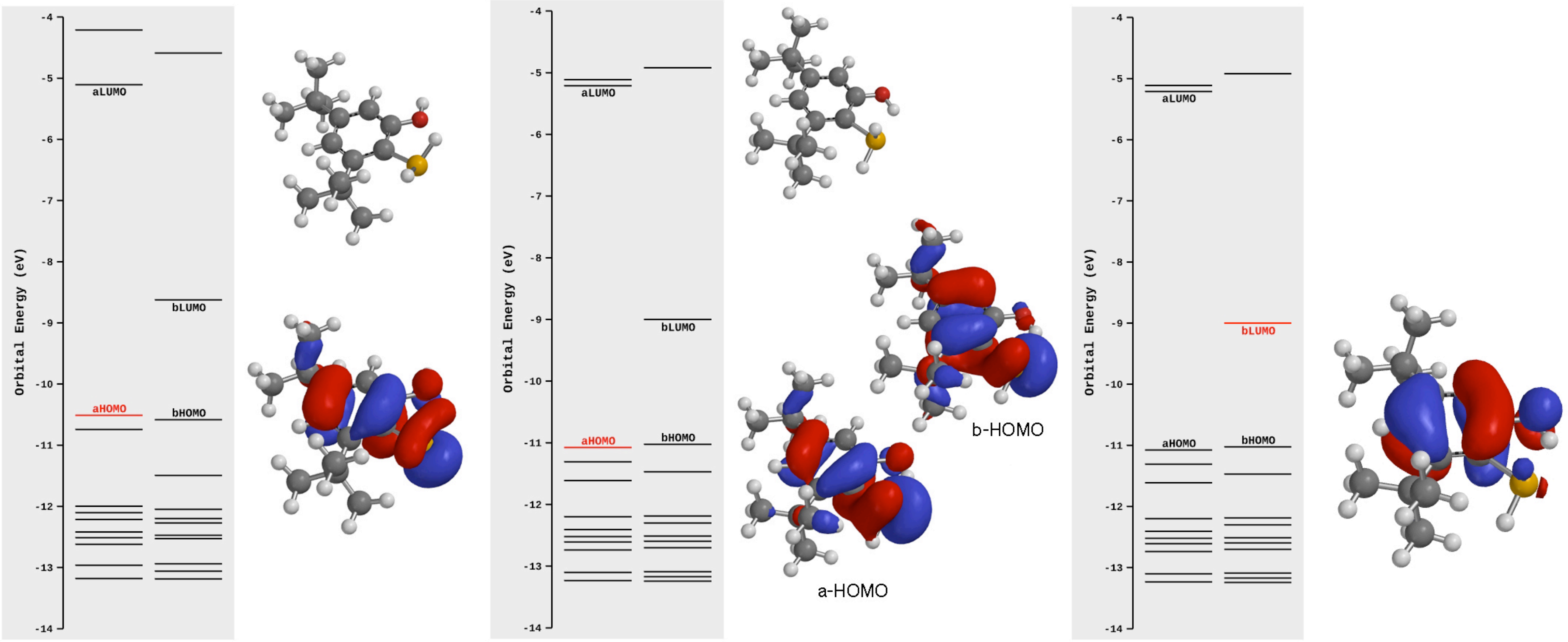
Figure S9. Calculational results for three lowest energy isomers of compound **4**. Upper structure in each panel displays lowest energy conformation and lower structure shows HOMO orbital.



Lowest Energy
-649.126308 au -11.3 eV
Δ E = 5.5 kcal/mol

2nd Lowest Energy
-649.117533 au -11.7 eV

Figure S10. Calculational results for three lowest energy isomers of the radical cation of *ortho*-phosphinophenol. Upper structure in each panel displays lowest energy conformation and lower structure shows SOMO orbital.



Lowest Energy

-963.640404 au   -10.5 eV

Δ E = 5.8 kcal/mol

2nd Lowest Energy,
[note similarity of aHOMO/bHOMO
neither of which match bLUMO]
-963.631165 au   -11.1, -11.0 eV

2nd Lowest Energy, bLUMO

Figure S11. Calculational results for three lowest energy isomers of the radical cation of **4**. Upper structure in each panel displays lowest energy conformation and lower structure shows SOMO orbital.

References

1. van den Nieuwendijk, A.M.C.H., et al., *Synthesis and Biological Evaluation of 2,3,5-Substituted [1,2,4]Thiadiazoles as Allosteric Modulators of Adenosine Receptors.* Journal of Medicinal Chemistry, 2004. **47**(3): p. 663-672.
2. Huichang Zhang, F.Y.K., Yuan Tian and Kin Shing Chan, *Base and cation effects on the suzuki cross-coupling of bulky aryboronic acid with halopyridines: synthesis of pyridylphenols.* J. Org. Chem., 1998. **63**.
3. Crosby, J.N.D.a.G.A., *The Measurement of Photoluminescence Quantum Yields A Review.* The Jornal of Physical Chemistry, 1971. **75**(8).